



Supplementary Materials for
**Catalyst-controlled doubly enantioconvergent coupling of
racemic alkyl nucleophiles and electrophiles**

Haohua Huo, Bradley J. Gorsline, Gregory C. Fu*

*Corresponding author. Email: gcfu@caltech.edu

Published 31 January 2020, *Science* **367**, 559 (2020)
DOI: 10.1126/science.aaz3855

This PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 and S2
Tables S1 to S5
Spectral Data
References

Table of Contents

I.	General Information	S-2
II.	Preparation of Chiral Ligands	S-3
III.	Preparation of Electrophiles	S-5
IV.	Preparation of Nucleophiles	S-14
V.	Enantioconvergent Couplings	S-28
VI.	Effect of Reaction Parameters	S-70
VII.	Functional-Group Compatibility	S-73
VIII.	Derivatization of Coupling Products	S-74
IX.	Assignment of Absolute Configuration	S-83
X.	^1H -NMR and ^{13}C -NMR Spectra; Stereoselectivity Analysis	S-88
XI.	References	S-251

I. General Information

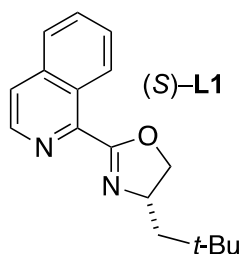
All reactions were performed under an atmosphere of dry nitrogen or argon. CH_2Cl_2 and THF were purified and dried using a solvent-purification system that contained activated alumina under argon; THF was further dried using freshly activated 4Å MS. $\text{NiCl}_2\cdot\text{glyme}$ (>97%, Strem), $\text{NiBr}_2\cdot\text{glyme}$ (>97%, Strem), zinc powder (~100 mesh, 99.9% metals basis, Alfa Aesar), 1,5-bis(diphenylphosphino)pentane (97%, Sigma-Aldrich), LiCl (anhydrous, beads, -10 mesh, 99.998% trace metals basis, Sigma-Aldrich), and all commercially available alkyl iodides (Acros, Alfa Aesar, Oakwood, and Sigma-Aldrich) were used as received.

^1H and ^{13}C NMR data were collected on a Bruker 400 MHz, a Varian 500 MHz, or a Varian 300 MHz spectrometer at ambient temperature. ^{19}F NMR data were collected on a Varian 300 MHz spectrometer at ambient temperature. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). SFC analyses were carried out on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). FT-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. HRMS were acquired using an Agilent 6220 TOF-LCMS system. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm and at 22–24 °C, using a 100 mm path-length cell in the solvent and at the concentration indicated. GC analyses were obtained on an Agilent 6890N GC. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 μm, Silicycle).

II. Preparation of Chiral Ligands

The yields have not been optimized.

General Procedure 1 (GP-1) (22). In an oven-dried round-bottom flask equipped with a stir bar, ZnCl₂ (0.20 equiv) was melted by a propane flame under high vacuum and cooled under nitrogen. Chlorobenzene (7 mL/mmol of isoquinoline-1-carbonitrile) was added, followed by isoquinoline-1-carbonitrile (1.0 equiv, as a solid under a positive flow of nitrogen) and the aminoalcohol (1.2 equiv, dissolved in chlorobenzene (1.0 mL/mmol of aminoalcohol)). The resulting mixture was heated at 140 °C for 48 h. Next, the mixture was allowed to cool to room temperature, and it was concentrated under reduced pressure. The residue was added to CH₂Cl₂/H₂O (3/2; for H₂O: 4.0 mL/mmol of isoquinoline-1-carbonitrile), and the mixture was filtered through a sintered funnel that contained celite. The resulting solution was extracted three times with CH₂Cl₂ (4.0 mL/mmol of isoquinoline-1-carbonitrile), and the combined organic layers were washed with brine, dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to provide the pure product.



(S)-2-(Isoquinolin-1-yl)-4-neopentyl-4,5-dihydrooxazole. The title compound was synthesized according to GP-1 from isoquinoline-1-carbonitrile (4.19 g, 27.2 mmol) and (S)-2-amino-4,4-dimethylpentan-1-ol (34) (4.27 g, 32.6 mmol). The product was purified by flash chromatography on silica gel (1:10 → 1:4 EtOAc/hexanes) to afford the product as a pale-yellow solid (5.20 g, 71%), which was recrystallized in hexanes to provide the ligand as colorless needles (3.88 g, 53%, >99% ee).

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (10.0% 2-PrOH in hexanes, 1.0 mL/min with t_r = 10.2 min ((R)-L1), t_r = 9.4 min ((S)-L1).

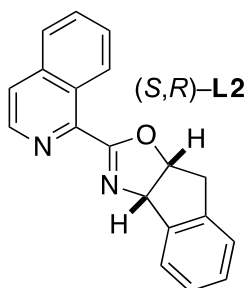
¹H NMR (400 MHz, CDCl₃) δ 9.37 – 9.23 (m, 1H), 8.65 (d, J = 5.5 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.77 (dd, J = 5.6, 0.9 Hz, 1H), 7.76 – 7.66 (m, 2H), 4.71 (dd, J = 9.6, 8.0 Hz, 1H), 4.64 – 4.53 (m, 1H), 4.11 (t, J = 8.4 Hz, 1H), 2.05 (dd, J = 13.9, 5.0 Hz, 1H), 1.59 (dd, J = 14.0, 7.6 Hz, 1H), 1.08 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 161.3, 146.4, 141.7, 136.7, 130.3, 128.4, 127.5, 127.3, 127.0, 123.2, 73.7, 65.2, 50.7, 30.4, 30.0.

FT-IR (film): 2952, 2900, 2865, 1363, 1131, 998, 830, 751 cm⁻¹.

HRMS (ESI-MS) m/z [M+H]⁺ calcd for C₁₇H₂₁N₂O: 269.1648, found: 269.1650.

[α]_D²⁴ = -32.7 (c 1.0, CHCl₃).



(3a*S*,8a*R*)-2-(Isoquinolin-1-yl)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole. The title compound was synthesized according to **GP-1** from isoquinoline-1-carbonitrile (5.00 g, 32.5 mmol) and (1*S*,2*R*)-1-amino-2,3-dihydro-1*H*-inden-2-ol (5.82 g, 39.0 mmol). The product was purified by flash chromatography on silica gel (1:10 → 1:1 EtOAc/hexanes) to afford the product as a black solid (6.00 g, 65%), which was recrystallized in EtOAc/hexanes to provide the ligand as white needles (2.33 g, 25%, >99% ee).

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in supercritical CO₂, 2.5 mL/min) with *t_r* = 15.6 min ((*S,R*)-L2), *t_r* = 16.3 min ((*R,S*)-L2).

¹H NMR (400 MHz, CDCl₃) δ 9.21 (dq, *J* = 8.3, 1.0 Hz, 1H), 8.64 (d, *J* = 5.5 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.78 – 7.60 (m, 4H), 7.38 – 7.27 (m, 3H), 5.99 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.63 (ddd, *J* = 8.2, 4.9, 3.5 Hz, 1H), 3.66 – 3.51 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.4, 146.2, 141.7, 141.6, 139.9, 136.6, 130.3, 128.6, 128.4, 127.5, 127.4, 127.3, 126.9, 125.5, 125.4, 123.3, 82.7, 77.8, 39.7.

FT-IR (film): 3052, 2982, 2917, 1615, 1130, 1020, 1003, 832, 749, 644 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₁₉H₁₄N₂ONa: 309.0998, found: 309.1001.

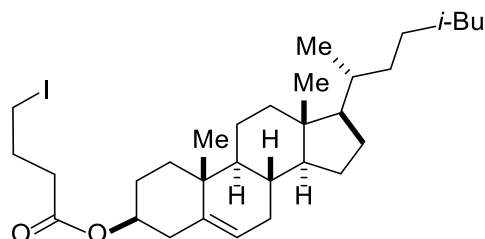
[α]_D²² = -47.7 (*c* 1.0, CHCl₃).

III. Preparation of Electrophiles

The yields have not been optimized.

General Procedure 2 (GP-2): Preparation of an alkyl iodide from the corresponding alkyl bromide. To a solution of NaI (2.5 equiv) in acetone (HPLC grade, 0.5 M in NaI) was added the alkyl bromide (1.0 equiv). The reaction mixture was refluxed at 85 °C for 2 h. Next, the mixture was allowed to cool to room temperature, it was filtered through a sintered glass funnel, and then the solvent was evaporated in vacuo. The resulting paste was diluted with Et₂O (~5 times the volume of original acetone), and the solution was washed with aqueous Na₂S₂O₃ (0.1 M). The organic layer was dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the pure product.

General Procedure 3 (GP-3): Preparation of a propargylic bromide from the corresponding alcohol. Imidazole (1.2 equiv) and PPh₃ (1.2 equiv) were dissolved in CH₂Cl₂ (0.2 M in imidazole), and the resulting solution was cooled to 0 °C. At this temperature, bromine (1.2 equiv) was added slowly in portions over 10 min, and the resulting mixture was stirred for 10 min. Next, the propargylic alcohol (25) (1.0 equiv) was added, and the resulting mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction mixture was added to hexanes/Et₂O (5/1; for hexanes: 10 mL/mmol of propargylic alcohol), stirred for 15 min, then filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the pure product.



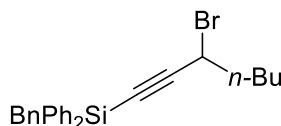
(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-iodobutanoate. The title compound was synthesized according to GP-2 from the corresponding alkyl bromide (35) (7.17 g, 13.4 mmol). The product was purified by column chromatography on silica gel (1:10 hexanes/EtOAc). 7.33 g (12.6 mmol, 94% yield). White solid.

¹H NMR (400 MHz, CDCl₃) δ 5.39 (dd, *J* = 5.1, 1.8 Hz, 1H), 4.73 – 4.56 (m, 1H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.39 – 2.29 (m, 2H), 2.14 (p, *J* = 7.0 Hz, 2H), 2.08 – 1.94 (m, 2H), 1.93 – 1.79 (m, 3H), 1.68 – 1.44 (m, 7H), 1.43 – 1.24 (m, 4H), 1.24 – 1.06 (m, 7H), 1.04 (s, 3H), 1.04 – 0.96 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 1.9 Hz, 3H), 0.88 (d, *J* = 1.9 Hz, 3H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.7, 139.5, 122.7, 74.2, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 36.9, 36.5, 36.1, 35.8, 35.1, 31.9, 31.8, 28.5, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8, 5.5.

FT-IR (film): 2932, 2865, 1728, 1466, 1438, 1374, 1189, 1012 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{31}\text{H}_{55}\text{IO}_2\text{N}$: 600.3272, found: 600.3260.



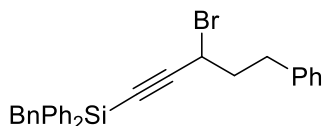
Benzyl(3-bromohept-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzylidiphenylsilyl)hept-1-yn-3-ol (9.52 g, 24.8 mmol) and purified by flash chromatography on silica gel (0 \rightarrow 1% EtOAc/hexanes). 6.32 g (14.2 mmol, 57% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.52 (m, 4H), 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 4H), 7.20 – 7.10 (m, 2H), 7.10 – 7.06 (m, 1H), 7.06 – 6.98 (m, 2H), 4.57 (t, J = 6.8 Hz, 1H), 2.71 (s, 2H), 2.09 – 1.98 (m, 2H), 1.58 – 1.45 (m, 2H), 1.44 – 1.30 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 134.9, 132.98, 132.97, 129.9, 129.0, 128.0, 127.9, 124.6, 108.6, 86.8, 39.1, 36.7, 29.4, 24.2, 21.9, 13.9.

FT-IR (film): 3067, 3024, 2956, 2930, 3173, 1428, 1115, 734, 700 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{26}\text{H}_{31}\text{BrSiN}$: 464.1404, found: 464.1402.



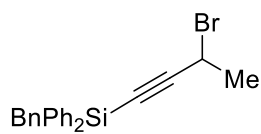
Benzyl(3-bromo-5-phenylpent-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzylidiphenylsilyl)-5-methylhex-1-yn-3-ol (4.56 g, 10.6 mmol) and purified by flash chromatography on silica gel (0 \rightarrow 1% EtOAc/hexanes). 4.17 g (8.4 mmol, 80% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.44 (m, 4H), 7.37 – 7.30 (m, 2H), 7.30 – 7.24 (m, 4H), 7.24 – 7.18 (m, 2H), 7.16 – 7.11 (m, 1H), 7.10 – 7.02 (m, 4H), 7.00 – 6.89 (m, 3H), 4.41 (t, J = 6.8 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.63 (s, 2H), 2.31 – 2.17 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 137.2, 134.9, 132.9, 130.0, 129.0, 128.6, 128.0, 127.9, 126.3, 124.7, 108.1, 87.4, 40.9, 35.8, 33.3, 24.2.

FT-IR (film): 3066, 3025, 2926, 2171, 1493, 1428, 1112, 769, 734, 697 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{30}\text{H}_{31}\text{BrSiN}$: 512.1404, found: 512.1393.



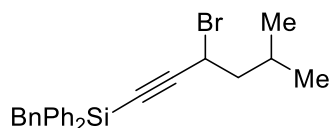
Benzyl(3-bromobut-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 4-(benzyl-diphenylsilyl)but-3-yn-2-ol (3.84 g, 11.2 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 3.81 g (9.4 mmol, 84% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.42 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.21 (m, 4H), 7.09 – 7.01 (m, 2H), 7.01 – 6.88 (m, 3H), 4.54 (q, $J = 6.9$ Hz, 1H), 2.61 (s, 2H), 1.82 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 134.9, 132.8, 129.9, 129.0, 128.0, 127.9, 124.6, 109.5, 86.1, 30.6, 27.0, 24.2.

FT-IR (film): 3068, 3050, 3024, 2169, 1428, 1111, 908, 768, 733, 699 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{23}\text{H}_{25}\text{BrSiN}$: 422.0934, found: 422.0938.



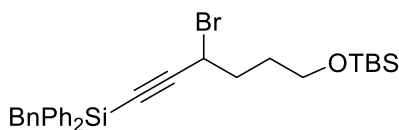
Benzyl(3-bromo-5-methylhex-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyl-diphenylsilyl)-5-methylhex-1-yn-3-ol (4.83 g, 12.6 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 4.71 g (10.6 mmol, 84% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.56 (m, 4H), 7.49 – 7.34 (m, 6H), 7.22 – 7.15 (m, 2H), 7.14 – 7.09 (m, 1H), 7.09 – 7.02 (m, 2H), 4.62 (t, $J = 7.5$ Hz, 1H), 2.75 (s, 2H), 2.04 – 1.86 (m, 3H), 0.98 (d, $J = 6.4$ Hz, 3H), 0.97 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 134.9, 133.0, 129.9, 129.0, 128.0, 127.9, 124.6, 108.7, 86.7, 48.3, 35.2, 26.8, 24.2, 21.9, 21.8.

FT-IR (film): 3068, 3052, 3024, 2957, 2931, 2173, 1428, 1113, 770, 734, 701 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{26}\text{H}_{31}\text{BrSiN}$: 464.1404, found: 464.1399.



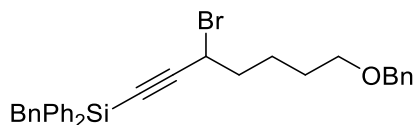
Benzyl(3-bromo-6-((tert-butyl)dimethylsilyloxy)hex-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyl-diphenylsilyl)-6-((tert-butyl)dimethylsilyloxy)hex-1-yn-3-ol (4.20 g, 8.4 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 1.00 g (1.8 mmol, 21% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.52 (m, 4H), 7.48 – 7.38 (m, 2H), 7.38 – 7.29 (m, 4H), 7.18 – 7.11 (m, 2H), 7.10 – 7.04 (m, 1H), 7.04 – 6.98 (m, 2H), 4.64 (t, J = 6.7 Hz, 1H), 3.66 (t, J = 6.1 Hz, 2H), 2.71 (s, 2H), 2.18 – 2.07 (m, 2H), 1.81 – 1.69 (m, 2H), 0.91 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 134.9, 132.9, 129.9, 129.0, 128.0, 127.9, 124.6, 108.4, 86.9, 62.1, 36.6, 36.3, 30.4, 25.9, 24.2, 18.3, -5.3.

FT-IR (film): 2952, 2928, 2857, 2173, 1429, 1255, 1108, 835, 772, 698 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{31}\text{H}_{43}\text{BrOSi}_2\text{N}$: 580.2061, found: 580.2058.



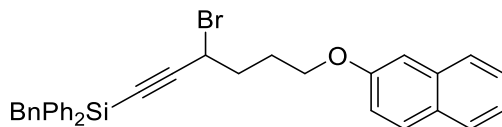
Benzyl(7-(benzyloxy)-3-bromohept-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzylidiphenylsilyl)-7-(benzyloxy)hept-1-yn-3-ol (6.23 g, 12.7 mmol) and purified by flash chromatography on silica gel (0 \rightarrow 1% EtOAc/hexanes). 4.50 g (8.2 mmol, 64% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.54 (m, 4H), 7.46 – 7.27 (m, 11H), 7.19 – 7.11 (m, 2H), 7.10 – 6.99 (m, 3H), 4.58 (t, J = 6.7 Hz, 1H), 4.52 (s, 2H), 3.49 (t, J = 6.0 Hz, 2H), 2.72 (s, 2H), 2.07 (q, J = 7.0 Hz, 2H), 1.75 – 1.59 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 138.5, 137.3, 134.9, 132.9, 129.9, 129.0, 128.4, 128.0, 127.9, 127.6, 127.5, 124.6, 108.4, 87.0, 72.9, 69.9, 39.1, 36.5, 28.8, 24.2, 24.1.

FT-IR (film): 3053, 3024, 2941, 2856, 2172, 1428, 1110, 767, 734, 702 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{33}\text{H}_{37}\text{BrOSiN}$: 570.1822, found: 570.1828.



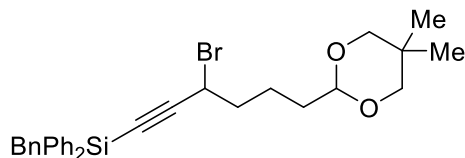
Benzyl(3-bromo-6-(naphthalen-2-yloxy)hex-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzylidiphenylsilyl)-6-(naphthalen-2-yloxy)hex-1-yn-3-ol (4.58 g, 8.9 mmol) and purified by flash chromatography on silica gel (0 \rightarrow 1% EtOAc/hexanes). 4.39 g (7.6 mmol, 85% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.71 (m, 3H), 7.66 – 7.56 (m, 4H), 7.51 – 7.41 (m, 3H), 7.41 – 7.33 (m, 5H), 7.22 – 7.13 (m, 4H), 7.13 – 7.02 (m, 3H), 4.73 (t, J = 6.6 Hz, 1H), 4.13 (t, J = 6.0 Hz, 2H), 2.75 (s, 2H), 2.37 – 2.26 (m, 2H), 2.19 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 137.3, 134.9, 134.5, 132.9, 130.0, 129.4, 129.05, 128.95, 128.0, 127.9, 127.6, 126.7, 126.3, 124.7, 123.6, 118.8, 108.1, 106.5, 87.4, 66.7, 36.21, 36.20, 27.1, 24.2.

FT-IR (film): 3056, 3024, 2927, 2174, 1628, 1601, 1258, 1216, 1181, 1115, 837, 742, 699 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{35}\text{H}_{35}\text{BrOSiN}$: 592.1666, found: 592.1661.



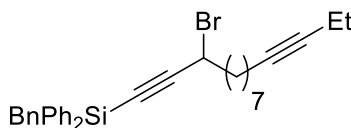
Benzyl(3-bromo-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyldiphenylsilyl)-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-yn-3-ol (3.51 g, 7.2 mmol) and purified by flash chromatography on silica gel (0 → 2% EtOAc/hexanes). 3.57 g (6.5 mmol, 90% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.53 (m, 4H), 7.47 – 7.40 (m, 2H), 7.40 – 7.31 (m, 4H), 7.21 – 7.12 (m, 2H), 7.12 – 7.06 (m, 1H), 7.06 – 7.00 (m, 2H), 4.58 (t, $J = 6.8$ Hz, 1H), 4.49 – 4.40 (m, 1H), 3.67 – 3.58 (m, 2H), 3.48 – 3.39 (m, 2H), 2.72 (s, 2H), 2.14 – 2.02 (m, 2H), 1.76 – 1.64 (m, 4H), 1.21 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 134.9, 132.9, 129.9, 129.0, 128.0, 127.9, 124.6, 108.4, 101.7, 86.9, 77.2, 39.2, 36.4, 33.7, 30.1, 24.2, 23.0, 22.0, 21.8.

FT-IR (film): 3024, 2953, 2849, 2171, 1429, 1115, 697 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{31}\text{H}_{39}\text{BrO}_2\text{SiN}$: 564.1928, found: 564.1929.



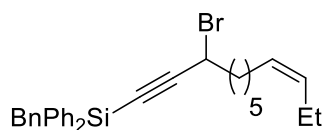
Benzyl(3-bromotetradeca-1,11-diyn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyldiphenylsilyl)tetradeca-1,11-diyn-3-ol (4.62 g, 9.7 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 4.14 g (7.7 mmol, 79% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.53 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.34 (m, 4H), 7.21 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 7.06 – 6.99 (m, 2H), 4.58 (t, $J = 6.7$ Hz, 1H), 2.72 (s, 2H), 2.24 – 2.11 (m, 4H), 2.09 – 1.98 (m, 2H), 1.61 – 1.44 (m, 4H), 1.44 – 1.27 (m, 6H), 1.14 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 134.9, 133.0, 129.9, 129.0, 128.0, 127.9, 124.6, 108.5, 86.9, 81.7, 79.4, 39.4, 36.7, 29.1, 28.9, 28.7, 28.6, 27.2, 24.2, 18.7, 14.4, 12.4.

FT-IR (film): 2930, 2856, 2173, 1429, 1110, 698 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{33}\text{H}_{41}\text{BrSiN}$: 558.2186, found: 558.2177.



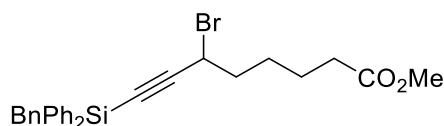
(Z)-Benzyl(3-bromododec-9-en-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from (Z)-1-(benzyl-diphenylsilyl)dodec-9-en-1-yn-3-ol (5.44 g, 12.0 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 5.50 g (10.7 mmol, 89% yield). Pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.57 (m, 4H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 4H), 7.24 – 7.16 (m, 2H), 7.16 – 7.09 (m, 1H), 7.09 – 7.02 (m, 2H), 5.52 – 5.32 (m, 2H), 4.61 (t, $J = 6.7$ Hz, 1H), 2.76 (s, 2H), 2.18 – 1.99 (m, 6H), 1.65 – 1.52 (m, 2H), 1.49 – 1.33 (m, 4H), 1.02 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 134.9, 133.0, 131.8, 129.9, 129.0, 128.8, 127.95, 127.87, 124.6, 108.5, 86.9, 39.3, 36.7, 29.5, 28.3, 27.2, 26.9, 24.2, 20.5, 14.4.

FT-IR (film): 3004, 2931, 2172, 1429, 1113, 763, 733, 701 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{31}\text{H}_{39}\text{BrSiN}$: 532.2030, found: 532.2027.



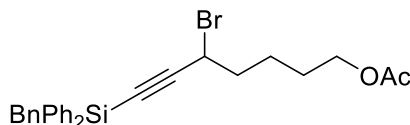
Methyl 8-(benzyl-diphenylsilyl)-6-bromo-oct-7-ynoate. The title compound was synthesized according to **GP-3** from methyl 8-(benzyl-diphenylsilyl)-6-hydroxy-oct-7-ynoate (4.46 g, 10.1 mmol) and purified by flash chromatography on silica gel (0 → 2% EtOAc/hexanes). 4.20 g (8.3 mmol, 83% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.53 (m, 4H), 7.47 – 7.40 (m, 2H), 7.40 – 7.33 (m, 4H), 7.20 – 7.12 (m, 2H), 7.12 – 7.05 (m, 1H), 7.02 (d, $J = 7.5$ Hz, 2H), 4.58 (t, $J = 6.6$ Hz, 1H), 3.67 (s, 3H), 2.72 (s, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 2.05 (q, $J = 7.0$ Hz, 2H), 1.75 – 1.64 (m, 2H), 1.57 (tt, $J = 10.0, 5.7$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.7, 137.2, 134.9, 132.9, 129.9, 129.0, 128.0, 127.9, 124.6, 108.2, 87.1, 51.5, 38.9, 36.2, 33.7, 26.8, 24.2, 24.0.

FT-IR (film): 3024, 2171, 1737, 1429, 1208, 1114, 770, 735, 698 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{28}\text{H}_{33}\text{BrO}_2\text{SiN}$: 522.1458, found: 522.1460.



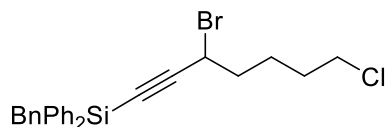
7-(benzyl-diphenylsilyl)-5-bromohept-6-yn-1-yl acetate. The title compound was synthesized according to **GP-3** from 7-(benzyl-diphenylsilyl)-5-hydroxyhept-6-yn-1-yl acetate (3.90 g, 8.8 mmol) and purified by flash chromatography on silica gel (0 → 2% EtOAc/hexanes). 3.75 g (7.4 mmol, 84% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.52 (m, 4H), 7.47 – 7.40 (m, 2H), 7.40 – 7.32 (m, 4H), 7.21 – 7.13 (m, 2H), 7.13 – 7.04 (m, 1H), 7.04 – 6.98 (m, 2H), 4.59 (t, J = 6.6 Hz, 1H), 4.07 (t, J = 6.3 Hz, 2H), 2.72 (s, 2H), 2.11 – 2.03 (m, 2H), 2.02 (s, 3H), 1.73 – 1.57 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 137.2, 134.9, 132.9, 130.0, 129.0, 128.0, 127.9, 124.6, 108.1, 87.2, 64.0, 38.8, 36.2, 27.7, 24.2, 23.8, 20.9.

FT-IR (film): 3067, 3024, 2954, 2172, 1736, 1240, 1113, 768, 735, 698 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{28}\text{H}_{33}\text{BrO}_2\text{SiN}$: 522.1458, found: 522.1462.



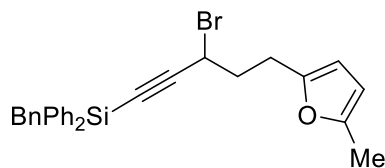
Benzyl(3-bromo-7-chlorohept-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyl(diphenylsilyl)-7-chlorohept-1-yn-3-ol (4.65 g, 11.1 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 4.62 g (9.6 mmol, 86% yield). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.58 (ddt, J = 6.6, 2.8, 1.5 Hz, 4H), 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 4H), 7.21 – 7.12 (m, 2H), 7.12 – 7.06 (m, 1H), 7.06 – 6.99 (m, 2H), 4.59 (t, J = 6.6 Hz, 1H), 3.53 (t, J = 6.5 Hz, 2H), 2.73 (s, 2H), 2.12 – 2.00 (m, 2H), 1.89 – 1.77 (m, 2H), 1.77 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 134.9, 132.8, 130.0, 129.0, 128.0, 127.9, 124.6, 108.0, 87.3, 44.5, 38.5, 36.1, 31.6, 24.6, 24.2.

FT-IR (film): 3067, 3053, 3024, 2954, 2170, 1600, 1428, 1112, 762, 736, 703 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{BrClSiN}$: 498.1014, found: 498.1011.



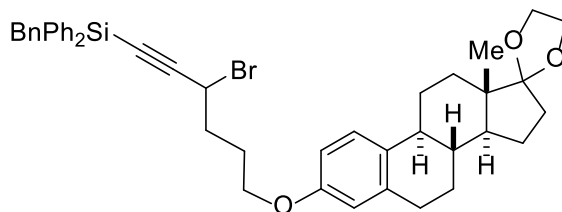
Benzyl(3-bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to **GP-3** from 1-(benzyl(diphenylsilyl)-5-(5-methylfuran-2-yl)pent-1-yn-3-ol (6.71 g, 15.4 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 5.54 g (11.1 mmol, 72% yield). Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.57 (m, 4H), 7.48 – 7.42 (m, 2H), 7.42 – 7.35 (m, 4H), 7.22 – 7.13 (m, 2H), 7.13 – 7.01 (m, 3H), 5.96 – 5.86 (m, 2H), 4.59 (t, J = 6.8 Hz, 1H), 2.85 (t, J = 7.4 Hz, 2H), 2.75 (s, 2H), 2.37 (dt, J = 8.1, 7.0 Hz, 2H), 2.30 (d, J = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.6, 150.9, 137.2, 134.9, 132.9, 130.0, 129.0, 128.0, 127.9, 124.7, 108.0, 106.5, 105.9, 87.4, 37.8, 35.7, 25.9, 24.2, 13.5.

FT-IR (film): 3068, 3024, 2920, 2175, 1428, 1208, 1110, 769, 701 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{29}\text{H}_{31}\text{BrOSiN}$: 516.1353, found: 516.1334.



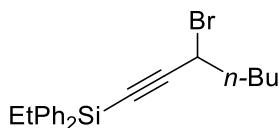
Benzyl(3-bromo-6-(((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)hex-1-yn-1-yl)diphenylsilane. The title compound was synthesized according to GP-3 from 1-(benzyl(diphenyl)silyl)-6-(((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)hex-1-yn-3-ol (4.15 g, 6.1 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 2.71 g (3.6 mmol, 60% yield). Colorless sticky oil.

¹H NMR (400 MHz, CDCl₃, mixture of diastereoisomers) δ 7.64 – 7.55 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.34 (m, 4H), 7.23 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.06 (m, 1H), 7.06 – 7.02 (m, 2H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 4.68 (t, *J* = 6.6 Hz, 1H), 4.05 – 3.86 (m, 6H), 2.96 – 2.79 (m, 2H), 2.74 (s, 2H), 2.40 – 2.32 (m, 1H), 2.31 – 2.20 (m, 3H), 2.13 – 1.97 (m, 3H), 1.96 – 1.75 (m, 4H), 1.74 – 1.62 (m, 1H), 1.62 – 1.54 (m, 1H), 1.53 – 1.31 (m, 4H), 0.92 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, mixture of diastereoisomers) δ 156.6, 138.0, 137.2, 134.9, 132.85, 132.79, 129.9, 129.0, 128.0, 127.9, 126.3, 124.6, 119.4, 114.4, 111.9, 108.1, 87.2, 66.6, 65.2, 64.5, 49.3, 46.1, 43.6, 39.0, 36.24, 36.19, 34.2, 30.7, 29.8, 27.1, 27.0, 26.1, 24.2, 22.3, 14.3.

FT-IR (film): 2933, 2873, 2171, 1605, 1494, 1254, 1107, 1043, 762, 734, 701 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+NH₄]⁺ calcd for C₄₅H₅₃BrO₃SiN: 762.2973, found: 762.2967.



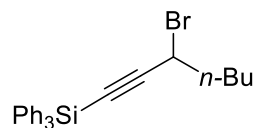
(3-Bromohept-1-yn-1-yl)(ethyl)diphenylsilane. The title compound was synthesized according to GP-3 from 1-(ethyl(diphenyl)silyl)hept-1-yn-3-ol (2.21 g, 6.9 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 1.80 g (4.7 mmol, 68% yield). Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.62 (m, 4H), 7.48 – 7.34 (m, 6H), 4.63 (t, *J* = 6.8 Hz, 1H), 2.15 – 2.05 (m, 2H), 1.66 – 1.53 (m, 2H), 1.47 – 1.33 (m, 2H), 1.22 – 1.08 (m, 5H), 0.95 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 134.7, 133.9, 129.7, 127.9, 107.7, 87.3, 39.3, 36.9, 29.5, 21.8, 13.9, 7.4, 6.1.

FT-IR (film): 3068, 2958, 2933, 2173, 1428, 1114, 717, 704 cm⁻¹.

HRMS (ESI-MS) m/z $[M+NH_4]^+$ calcd for $C_{21}H_{29}BrSiN$: 402.1247, found: 402.1236.



(3-Bromohept-1-yn-1-yl)triphenylsilane. The title compound was synthesized according to **GP-3** from 1-(triphenylsilyl)hept-1-yn-3-ol (5.95 g, 16.1 mmol) and purified by flash chromatography on silica gel (0 → 1% EtOAc/hexanes). 2.40 g (5.6 mmol, 35% yield). White solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 6H), 7.52 – 7.36 (m, 9H), 4.65 (t, J = 6.8 Hz, 1H), 2.17 – 2.07 (m, 2H), 1.67 – 1.54 (m, 2H), 1.47 – 1.33 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 133.1, 130.0, 128.0, 108.5, 87.0, 39.2, 36.8, 29.5, 21.8, 13.9.

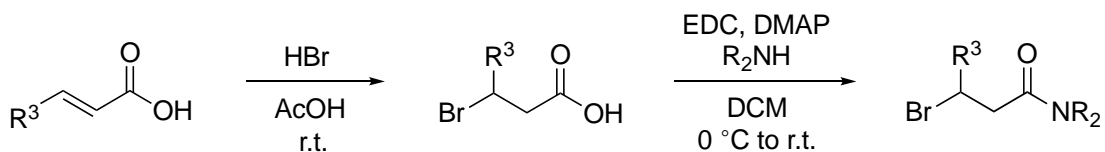
FT-IR (film): 3050, 3067, 2956, 2932, 2171, 1428, 1113, 710, 698 cm^{-1} .

HRMS (ESI-MS) m/z $[M+NH_4]^+$ calcd for $C_{25}H_{29}BrSiN$: 450.1247, found: 450.1242.

IV. Preparation of Nucleophiles

The yields have not been optimized.

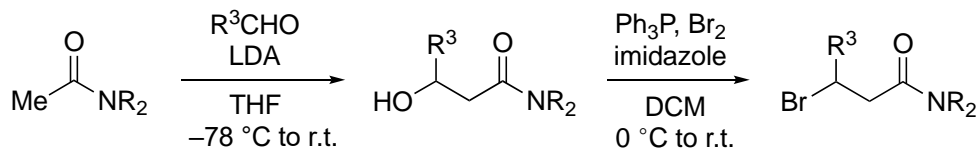
General Procedure 4 (GP-4): Preparation of β -bromo amides from α,β -unsaturated carboxylic acids.



A solution of the carboxylic acid and HBr (33% in AcOH, 1 mL/mmol of the carboxylic acid) was stirred at room temperature for 6 h. The AcOH was then removed via rotary evaporation in a fume hood (any remaining AcOH can be removed by vigorously flushing the flask with air overnight). The product was used in the next step without further purification.

EDC·HCl (1.1 equiv) and DMAP (0.05 equiv) were added in turn as solids to a solution of the unpurified β -bromo carboxylic acid (1.0 equiv) in CH_2Cl_2 (0.4 M) at 0 °C. This solution was stirred at 0 °C for 5 min, and then the secondary amine (1.1 equiv) was added in one portion. The reaction mixture was stirred at 0 °C for 5 h, and then it was allowed to warm to room temperature for 1 h. Next, the mixture was transferred to a separatory funnel, and Et_2O (~4 times the volume of CH_2Cl_2) was added. This mixture was washed with aqueous HCl (2 M) and then brine, dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography on silica gel, which afforded the pure β -bromo amide.

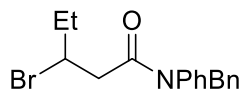
General Procedure 5 (GP-5): Preparation of β -bromo amides via aldol reactions.



A solution of LDA (1.1 equiv, 3 M in THF, freshly prepared) was added dropwise to a solution of acetamide (1.0 equiv, 0.4 M) in THF at -78°C . The resulting mixture was stirred at -78°C for 1 h, and then the aldehyde (1.1 equiv) was added dropwise. The reaction mixture was stirred at -78°C for 1 h, and then it was allowed to slowly warm to room temperature overnight. Next, the reaction was quenched with aqueous saturated NH_4Cl , and the mixture was extracted with Et_2O (3 mL/mmol of acetamide \times 3). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was passed through a short column of silica gel (EtOAc /hexanes) to afford the aldol adduct (>80% purity), which was used in the next step without further purification.

Imidazole (1.2 equiv) and PPh_3 (1.2 equiv) were dissolved in CH_2Cl_2 (0.2 M), and the resulting solution was cooled to 0 °C. Bromine (1.2 equiv, neat) was added dropwise, and the resulting mixture was stirred at 0 °C for 10 min. Next, the unpurified alcohol (1.0 equiv, dissolved in CH_2Cl_2 (3.0 mL/mmol of alcohol)) was added, and the resulting mixture was

allowed to slowly warm to room temperature overnight. Then, the reaction mixture was added to hexanes/Et₂O (5/1, for hexanes: 10 mL/mmol of alcohol), stirred for 15 min, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel, which afforded the pure β -bromo amide.



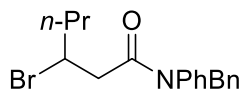
N-Benzyl-3-bromo-N-phenylbutanamide. The title compound was synthesized according to **GP-4** from trans-pent-2-enoic acid (5.1 mL, 50.0 mmol) and *N*-benzylaniline (10.1 g, 55.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 10.52 g (30.5 mmol, 61% yield over 2 steps). White solid.

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.16 (m, 8H), 7.02 (d, *J* = 6.8 Hz, 2H), 5.00 (d, *J* = 14.3 Hz, 1H), 4.88 (d, *J* = 14.3 Hz, 1H), 4.53 (tt, *J* = 9.6, 4.9 Hz, 1H), 2.74 (dd, *J* = 16.0, 8.6 Hz, 1H), 2.61 (dd, *J* = 16.0, 5.1 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.79 – 1.67 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.6, 141.7, 137.2, 129.7, 128.8, 128.6, 128.4, 128.3, 127.4, 54.0, 53.2, 43.2, 31.9, 12.2.

FT-IR (film): 2963, 1647, 1496, 1001, 773, 705 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₈H₂₁BrNO: 346.0801, found: 346.0792.



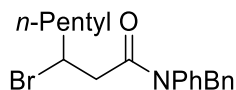
N-Benzyl-3-bromo-N-phenylhexanamide. The title compound was synthesized according to **GP-5** from *N*-benzyl-*N*-phenylacetamide (6.75 g, 30.0 mmol) and butyraldehyde (3.31 g, 33.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 9.20 g (25.6 mmol, 85% yield over 2 steps). Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.33 (m, 3H), 7.32 – 7.19 (m, 5H), 7.06 – 6.97 (m, 2H), 5.00 (d, *J* = 14.2 Hz, 1H), 4.88 (d, *J* = 14.3 Hz, 1H), 4.67 – 4.48 (m, 1H), 2.74 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.60 (dd, *J* = 16.0, 5.0 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.61 – 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.5, 141.7, 137.2, 129.6, 128.8, 128.6, 128.3, 128.2, 127.4, 53.1, 51.9, 43.6, 40.7, 20.8, 13.3.

FT-IR (film): 2958, 2930, 2872, 1655, 1594, 1494, 1401, 772 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₉H₂₃BrNO: 360.0958, found: 360.0968.



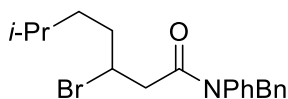
N-Benzyl-3-bromo-N-phenyloctanamide. The title compound was synthesized according to **GP-4** from *trans*-2-octenoic acid (5.69 g, 40.0 mmol) and *N*-benzylaniline (8.1 g, 44.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 10.10 g (26.1 mmol, 65% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.33 (m, 3H), 7.30 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.01 (dd, $J = 7.5, 2.2$ Hz, 2H), 4.99 (d, $J = 14.3$ Hz, 1H), 4.88 (d, $J = 14.3$ Hz, 1H), 4.56 (tt, $J = 8.6, 5.1$ Hz, 1H), 2.73 (dd, $J = 15.9, 8.7$ Hz, 1H), 2.60 (dd, $J = 15.9, 5.1$ Hz, 1H), 1.81 – 1.67 (m, 2H), 1.53 – 1.19 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 141.7, 137.2, 129.6, 128.8, 128.6, 128.4, 128.2, 127.4, 53.2, 52.3, 43.6, 38.7, 31.0, 27.2, 22.4, 14.0.

FT-IR (film): 2954, 2928, 2857, 1655, 1594, 1494, 1401, 772, 728 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{BrNO}$: 388.1271, found: 388.1277.



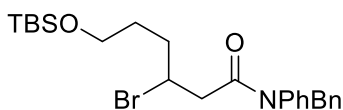
N-Benzyl-3-bromo-6-methyl-N-phenylheptanamide. The title compound was synthesized according to **GP-5** from *N*-benzyl-*N*-phenylacetamide (6.12 g, 27.2 mmol) and 4-methylpentanal (3.00 g, 29.9 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 4.42 g (11.4 mmol, 42% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.32 (m, 3H), 7.31 – 7.21 (m, 5H), 7.02 (dd, $J = 7.4, 2.2$ Hz, 2H), 4.98 (d, $J = 14.3$ Hz, 1H), 4.90 (d, $J = 14.3$ Hz, 1H), 4.54 (tt, $J = 8.6, 4.9$ Hz, 1H), 2.74 (dd, $J = 16.0, 8.7$ Hz, 1H), 2.61 (dd, $J = 16.0, 5.1$ Hz, 1H), 1.86 – 1.66 (m, 2H), 1.61 – 1.48 (m, 1H), 1.45 – 1.19 (m, 2H), 0.89 (d, $J = 5.1$ Hz, 3H), 0.87 (d, $J = 5.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 141.7, 137.2, 129.6, 128.8, 128.6, 128.4, 128.2, 127.4, 53.2, 52.5, 43.6, 36.7, 36.6, 27.5, 22.7, 22.3.

FT-IR (film): 2953, 2927, 2868, 1655, 1594, 1494, 1401, 1254, 1208, 1165, 772, 731 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{BrNO}$: 388.1271, found: 388.1276.



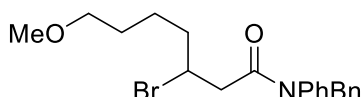
N-Benzyl-3-bromo-6-((*tert*-butyldimethylsilyloxy)-*N*-phenylhexanamide. The title compound was synthesized according to **GP-5** from *N*-benzyl-*N*-phenylacetamide (5.16 g, 23.0 mmol) and 4-((*tert*-butyldimethylsilyloxy)butanal (5.10 g, 25.2 mmol). The product was purified by column chromatography on silica gel (1:30 EtOAc/hexanes). 4.70 g (9.6 mmol, 42% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 3H), 7.28 – 7.20 (m, 3H), 7.20 – 7.14 (m, 2H), 6.96 (dd, $J = 7.4, 2.2$ Hz, 2H), 4.95 (d, $J = 14.3$ Hz, 1H), 4.82 (d, $J = 14.3$ Hz, 1H), 4.53 (tt, $J = 9.0, 4.6$ Hz, 1H), 3.57 (t, $J = 6.2$ Hz, 2H), 2.70 (dd, $J = 16.0, 8.9$ Hz, 1H), 2.55 (dd, $J = 16.0, 4.8$ Hz, 1H), 1.90 – 1.78 (m, 1H), 1.77 – 1.61 (m, 2H), 1.61 – 1.47 (m, 1H), 0.84 (s, 9H), -0.00 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 141.7, 137.2, 129.6, 128.8, 128.6, 128.3, 128.2, 127.4, 62.2, 53.2, 52.0, 43.6, 35.3, 30.8, 25.9, 18.3, -5.3.

FT-IR (film): 2951, 2927, 2854, 1655, 1594, 1402, 1252, 1072, 834, 774 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}-\text{TBS}+2\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{BrNO}_2$: 376.0907, found: 376.0909.



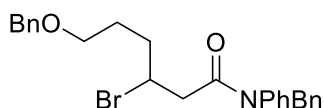
N-Benzyl-3-bromo-7-methoxy-N-phenylheptanamide. The title compound was synthesized according to GP-5 from *N*-benzyl-*N*-phenylacetamide (5.56 g, 24.7 mmol) and 5-methoxypentanal (3.15 g, 27.2 mmol). The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). 4.38 g (10.9 mmol, 44% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.33 (m, 3H), 7.32 – 7.25 (m, 3H), 7.25 – 7.19 (m, 2H), 7.01 (dd, $J = 7.5, 2.2$ Hz, 2H), 4.99 (d, $J = 14.3$ Hz, 1H), 4.88 (d, $J = 14.3$ Hz, 1H), 4.56 (tt, $J = 8.6, 4.9$ Hz, 1H), 3.37 (t, $J = 6.2$ Hz, 2H), 3.33 (s, 3H), 2.73 (dd, $J = 16.0, 8.7$ Hz, 1H), 2.60 (dd, $J = 16.0, 5.0$ Hz, 1H), 1.89 – 1.72 (m, 2H), 1.66 – 1.40 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 141.7, 137.2, 129.6, 128.8, 128.6, 128.3, 128.2, 127.4, 72.4, 58.5, 53.2, 51.9, 43.5, 38.5, 28.8, 24.3.

FT-IR (film): 2924, 2863, 1655, 1594, 1494, 1401, 1116, 772, 733 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{BrNO}_2$: 404.1220, found: 404.1219.



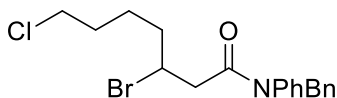
N-Benzyl-6-(benzyloxy)-3-bromo-N-phenylhexanamide. The title compound was synthesized according to GP-5 from *N*-benzyl-*N*-phenylacetamide (3.33 g, 14.8 mmol) and 4-(benzyloxy)butanal (2.90 g, 16.3 mmol). The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). 2.62 g (5.6 mmol, 38% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.19 (m, 7H), 7.18 – 7.08 (m, 6H), 6.94 – 6.82 (m, 2H), 4.87 (d, $J = 14.2$ Hz, 1H), 4.75 (d, $J = 14.3$ Hz, 1H), 4.47 (tt, $J = 8.8, 4.6$ Hz, 1H), 4.37 (s, 2H), 3.36 (t, $J = 6.0$ Hz, 2H), 2.63 (dd, $J = 16.0, 8.8$ Hz, 1H), 2.48 (dd, $J = 16.0, 4.8$ Hz, 1H), 1.87 – 1.76 (m, 1H), 1.76 – 1.65 (m, 2H), 1.65 – 1.55 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 141.7, 138.4, 137.1, 129.6, 128.8, 128.6, 128.3, 128.2, 127.6, 127.5, 127.4, 72.9, 69.3, 53.2, 51.8, 43.5, 35.5, 27.8.

FT-IR (film): 2924, 2856, 1650, 1594, 1494, 1402, 735 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{26}H_{29}BrNO_2$: 466.1376, found: 466.1381.



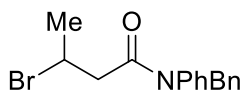
N-Benzyl-3-bromo-7-chloro-N-phenylheptanamide. The title compound was synthesized according to **GP-5** from *N*-benzyl-*N*-phenylacetamide (8.48 g, 37.7 mmol) and 5-chloropentanal (5.00 g, 41.5 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 9.61 g (23.6 mmol, 63% yield over 2 steps). Colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 3H), 7.32 – 7.18 (m, 5H), 7.01 (dd, J = 7.5, 2.1 Hz, 2H), 4.98 (d, J = 14.3 Hz, 1H), 4.87 (d, J = 14.3 Hz, 1H), 4.55 (tt, J = 9.0, 4.8 Hz, 1H), 3.51 (td, J = 6.5, 2.3 Hz, 2H), 2.75 (dd, J = 16.0, 8.3 Hz, 1H), 2.61 (dd, J = 16.1, 5.4 Hz, 1H), 1.90 – 1.69 (m, 4H), 1.69 – 1.61 (m, 1H), 1.61 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 141.5, 137.0, 129.5, 128.6, 128.3, 128.2, 128.1, 127.2, 53.0, 51.3, 51.2, 44.4, 43.4, 37.6, 31.5, 24.7.

FT-IR (film): 2936, 1651, 1594, 1494, 1401, 773, 731 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{20}H_{24}BrClNO$: 408.0724, found: 408.0737.



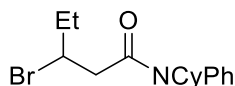
N-Benzyl-3-bromo-N-phenylbutanamide. The title compound was synthesized according to **GP-4** from crotonic acid (4.30 g, 50.0 mmol) and *N*-benzylaniline (10.1 g, 55.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 9.06 g (27.4 mmol, 55% yield over 2 steps). Colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 3H), 7.33 – 7.25 (m, 3H), 7.25 – 7.17 (m, 2H), 7.01 (dd, J = 7.4, 2.2 Hz, 2H), 4.98 (d, J = 14.3 Hz, 1H), 4.88 (d, J = 14.3 Hz, 1H), 4.68 (dq, J = 8.3, 6.7, 5.5 Hz, 1H), 2.75 (dd, J = 16.0, 8.3 Hz, 1H), 2.56 (dd, J = 16.0, 5.5 Hz, 1H), 1.69 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 141.6, 137.1, 129.7, 128.8, 128.5, 128.4, 128.2, 127.4, 53.1, 45.5, 45.2, 26.2.

FT-IR (film): 3062, 3029, 2922, 1651, 1494, 1400, 772, 731 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{18}H_{19}BrNO$: 332.0645, found: 332.0653.



3-Bromo-N-cyclohexyl-N-phenylpentanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (8.37 g, 38.6 mmol) and

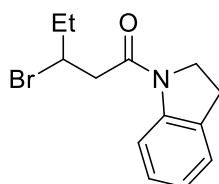
propionaldehyde (2.69 g, 46.3 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 6.44 g (19.1 mmol, 49% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.31 (m, 3H), 7.16 (d, $J = 7.4$ Hz, 1H), 7.10 – 6.93 (m, 1H), 4.61 (tt, $J = 12.1, 3.6$ Hz, 1H), 4.43 (tdd, $J = 8.4, 5.5, 4.3$ Hz, 1H), 2.49 (dd, $J = 16.0, 8.3$ Hz, 1H), 2.40 (dd, $J = 16.0, 5.5$ Hz, 1H), 1.90 – 1.60 (m, 6H), 1.60 – 1.50 (m, 1H), 1.46 – 1.29 (m, 2H), 1.11 – 0.97 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H), 0.92 – 0.82 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 138.6, 130.7, 130.1, 129.3, 129.1, 128.3, 54.3, 54.1, 43.8, 31.8, 31.5, 25.70, 25.68, 25.3, 12.1.

FT-IR (film): 2932, 2856, 1651, 1401, 707 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{BrNO}$: 338.1114, found: 338.1135.



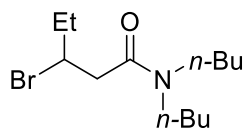
3-Bromo-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to GP-4 from 2-pentenoic acid (3.00 g, 30.0 mmol) and indoline (3.93 g, 33.0 mmol). The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). 5.31 g (18.9 mmol, 63% yield over 2 steps). White solid.

^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.1$ Hz, 1H), 7.27 – 7.18 (m, 2H), 7.05 (td, $J = 7.4, 1.1$ Hz, 1H), 4.66 – 4.51 (m, 1H), 4.28 – 4.12 (m, 1H), 4.12 – 3.98 (m, 1H), 3.30 – 3.18 (m, 2H), 3.13 (dd, $J = 16.0, 7.8$ Hz, 1H), 2.97 (dd, $J = 16.1, 5.7$ Hz, 1H), 2.05 (dtd, $J = 14.5, 7.2, 4.1$ Hz, 1H), 1.91 (ddq, $J = 14.4, 8.6, 7.2$ Hz, 1H), 1.13 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.8, 142.6, 131.2, 127.5, 124.5, 123.9, 117.2, 53.0, 48.1, 44.9, 32.1, 27.9, 12.2.

FT-IR (film): 2976, 1656, 1596, 1479, 1461, 1412, 1394, 773 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{BrNO}$: 282.0488, found: 282.0493.



3-Bromo-N,N-dibutylpentanamide. The title compound was synthesized according to GP-5 from N,N-dibutylacetamide (8.07 g, 47.2 mmol) and propionaldehyde (3.01 g, 51.9 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 7.88 g (27.1 mmol, 57% yield over 2 steps). Colorless oil.

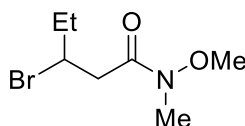
^1H NMR (400 MHz, CDCl_3) δ 4.50 (dddd, $J = 8.7, 7.9, 5.7, 4.1$ Hz, 1H), 3.44 – 3.34 (m, 1H), 3.33 – 3.23 (m, 2H), 3.19 (ddd, $J = 15.1, 9.5, 6.0$ Hz, 1H), 3.00 (dd, $J = 15.6, 7.9$ Hz, 1H), 2.76 (dd, $J = 15.6,$

5.7 Hz, 1H), 1.96 (dq, $J = 14.4, 7.3, 4.1$ Hz, 1H), 1.91 – 1.76 (m, 1H), 1.64 – 1.46 (m, 4H), 1.40 – 1.24 (m, 4H), 1.08 (t, $J = 7.2$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.1, 54.3, 47.8, 46.0, 42.1, 32.1, 31.3, 29.8, 20.2, 20.0, 13.82, 13.77, 12.2.

FT-IR (film): 2957, 2929, 2872, 1639, 1454, 1427, 730 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{27}\text{BrNO}$: 292.1271, found: 292.1272.



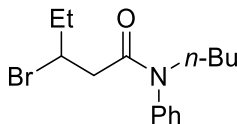
3-Bromo-N-methoxy-N-methylpentanamide. The title compound was synthesized according to **GP-4** from 2-pentenoic acid (4.00 g, 40.0 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (4.29 g, 44.0 mmol). The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). 4.25 g (19.1 mmol, 48% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 4.46 (tdd, $J = 8.5, 5.4, 4.4$ Hz, 1H), 3.74 (s, 3H), 3.23 (s, 3H), 3.22 – 3.13 (m, 1H), 2.90 (dd, $J = 16.3, 5.4$ Hz, 1H), 2.02 – 1.91 (m, 1H), 1.91 – 1.81 (m, 1H), 1.10 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 61.4, 52.7, 41.1, 32.0 (2C), 12.1.

FT-IR (film): 2965, 2937, 1658, 1443, 1415, 1386, 1011, 990, 788 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_{15}\text{BrNO}_2$: 224.0281, found: 224.0283.



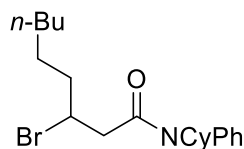
3-Bromo-N-butyl-N-phenylpentanamide. The title compound was synthesized according to **GP-5** from *N*-butyl-*N*-phenylacetamide (9.28 g, 48.6 mmol) and propionaldehyde (3.11 g, 53.5 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 10.3 g (33.1 mmol, 68% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.43 (m, 2H), 7.43 – 7.34 (m, 1H), 7.25 – 7.14 (m, 2H), 4.47 (tdd, $J = 8.5, 5.4, 4.4$ Hz, 1H), 3.85 – 3.64 (m, 2H), 2.68 (dd, $J = 15.9, 8.5$ Hz, 1H), 2.53 (dd, $J = 15.9, 5.3$ Hz, 1H), 1.89 – 1.77 (m, 1H), 1.77 (ddt, $J = 14.5, 8.6, 7.3$ Hz, 1H), 1.58 – 1.46 (m, 2H), 1.41 – 1.29 (m, 2H), 0.99 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 142.1, 129.8, 128.5, 128.1, 54.1, 49.2, 43.3, 31.9, 29.7, 20.0, 13.8, 12.1.

FT-IR (film): 2960, 2931, 2872, 1650, 1594, 1493, 1403, 773, 732 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{23}\text{BrNO}$: 312.0958, found: 312.0967.



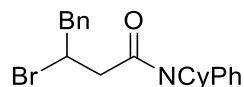
3-Bromo-N-cyclohexyl-N-phenylnonanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and heptanal (3.42 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 5.64 g (14.4 mmol, 58% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.30 (m, 3H), 7.16 (d, J = 8.1 Hz, 1H), 7.09 – 6.90 (m, 1H), 4.60 (tt, J = 12.1, 3.6 Hz, 1H), 4.46 (tt, J = 8.5, 5.0 Hz, 1H), 2.49 (dd, J = 16.0, 8.3 Hz, 1H), 2.40 (dd, J = 16.0, 5.4 Hz, 1H), 1.90 – 1.75 (m, 2H), 1.75 – 1.50 (m, 5H), 1.49 – 1.13 (m, 10H), 1.10 – 0.95 (m, 2H), 0.95 – 0.86 (m, 1H), 0.84 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 138.6, 130.7, 130.1, 129.3, 129.1, 128.3, 54.2, 52.4, 44.2, 38.7, 31.54, 31.48, 28.4, 27.5, 25.69, 25.67, 25.3, 22.5, 14.0.

FT-IR (film): 2928, 2856, 1659, 1650, 1401, 708 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{33}\text{BrNO}$: 394.1740, found: 394.1754.



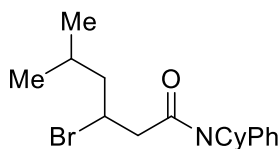
3-Bromo-N-cyclohexyl-N,4-diphenylbutanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 2-phenylacetaldehyde (3.60 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 3.81 g (9.5 mmol, 38% yield over 2 steps). White solid.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.38 (m, 3H), 7.35 – 7.22 (m, 3H), 7.22 – 7.13 (m, 3H), 7.06 – 6.96 (m, 1H), 4.77 – 4.58 (m, 2H), 3.15 (dd, J = 14.2, 6.3 Hz, 1H), 3.07 (dd, J = 14.2, 7.9 Hz, 1H), 2.51 (dd, J = 16.1, 7.7 Hz, 1H), 2.47 (dd, J = 16.1, 5.8 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H), 1.65 – 1.53 (m, 1H), 1.42 (qq, J = 13.3, 3.4 Hz, 2H), 1.15 – 0.99 (m, 2H), 0.93 (qt, J = 13.1, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 138.5, 138.0, 130.6, 130.1, 129.3, 129.13, 129.10, 128.34, 128.28, 126.7, 54.3, 51.2, 44.8, 43.2, 31.5, 25.68, 25.66, 25.3.

FT-IR (film): 2929, 2856, 1644, 1492, 1407, 710 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{27}\text{BrNO}$: 400.1271, found: 400.1280.



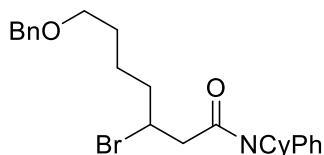
3-Bromo-N-cyclohexyl-5-methyl-N-phenylhexanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 3-methylbutanal (2.58 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 5.42 g (14.8 mmol, 59% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.31 (m, 3H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.10 – 6.95 (m, 1H), 4.62 (tt, $J = 12.1, 3.6$ Hz, 1H), 4.57 – 4.47 (m, 1H), 2.50 (dd, $J = 16.0, 8.3$ Hz, 1H), 2.40 (dd, $J = 16.0, 5.3$ Hz, 1H), 1.92 – 1.76 (m, 3H), 1.76 – 1.67 (m, 2H), 1.67 – 1.52 (m, 2H), 1.51 – 1.30 (m, 3H), 1.13 – 0.97 (m, 2H), 0.97 – 0.89 (m, 1H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.87 (d, $J = 6.7$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.9, 131.6, 123.8, 123.2, 122.3, 122.1, 121.4, 47.3, 43.8, 40.7, 37.6, 24.54, 24.51, 19.4, 18.74, 18.72, 18.3, 15.9, 13.9.

FT-IR (film): 2931, 2856, 1651, 1401, 1263, 708 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{BrNO}$: 366.1427, found: 366.1479.



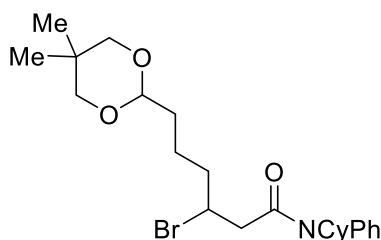
7-(Benzyloxy)-3-bromo-N-cyclohexyl-N-phenylheptanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 5-(benzyloxy)pentanal (5.76 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 8.02 g (17.0 mmol, 68% yield over 2 steps). Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.28 (m, 3H), 7.27 – 7.17 (m, 5H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.03 – 6.86 (m, 1H), 4.55 (tt, $J = 12.2, 3.6$ Hz, 1H), 4.41 (s, 3H), 3.37 (t, $J = 6.1$ Hz, 2H), 2.43 (dd, $J = 16.0, 8.3$ Hz, 1H), 2.34 (dd, $J = 16.0, 5.4$ Hz, 1H), 1.84 – 1.58 (m, 6H), 1.58 – 1.43 (m, 4H), 1.42 – 1.25 (m, 3H), 1.07 – 0.76 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 138.6, 138.5, 130.8, 130.1, 129.4, 129.2, 128.4, 128.3, 127.6, 127.5, 72.9, 70.0, 54.3, 52.2, 44.2, 38.5, 31.5, 29.0, 25.8, 25.7, 25.3, 24.3.

FT-IR (film): 3033, 2931, 2856, 1651, 1400, 1101, 734, 708 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{35}\text{BrNO}_2$: 472.1846, found: 472.1850.



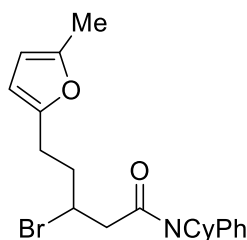
3-Bromo-*N*-cyclohexyl-6-(5,5-dimethyl-1,3-dioxan-2-yl)-*N*-phenylhexanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)butanal (5.59 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 4.62 g (9.9 mmol, 40% yield over 2 steps). White solid.

^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.34 (m, 3H), 7.16 (d, J = 6.9 Hz, 1H), 7.08 – 6.97 (m, 1H), 4.60 (tt, J = 12.1, 3.6 Hz, 1H), 4.46 (tt, J = 8.4, 5.1 Hz, 1H), 4.36 (t, J = 4.6 Hz, 1H), 3.56 (dt, J = 11.1, 1.4 Hz, 2H), 3.38 (d, J = 10.6 Hz, 2H), 2.48 (dd, J = 16.0, 8.4 Hz, 1H), 2.41 (dd, J = 16.0, 5.3 Hz, 1H), 1.91 – 1.65 (m, 6H), 1.65 – 1.50 (m, 4H), 1.50 – 1.30 (m, 3H), 1.15 (s, 3H), 1.10 – 0.94 (m, 2H), 0.94 – 0.81 (m, 1H), 0.69 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 138.6, 130.7, 130.1, 129.3, 129.1, 128.3, 101.8, 77.1, 54.2, 52.1, 44.1, 38.6, 34.0, 31.5, 30.1, 25.71, 25.69, 25.3, 22.9, 22.2, 21.8.

FT-IR (film): 2929, 2854, 1651, 1401, 1133, 708 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{37}\text{BrNO}_3$: 466.1951, found: 466.1962.



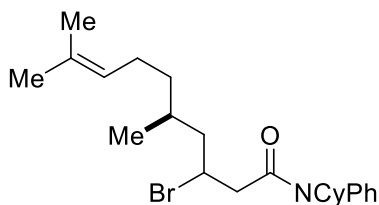
3-Bromo-*N*-cyclohexyl-5-(5-methylfuran-2-yl)-*N*-phenylpentanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 3-(5-methylfuran-2-yl)propanal (4.14 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 6.47 g (15.5 mmol, 62% yield over 2 steps). White solid.

^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.29 (m, 3H), 7.15 (d, J = 7.3 Hz, 1H), 7.10 – 6.92 (m, 1H), 5.85 (d, J = 3.0 Hz, 1H), 5.80 (d, J = 3.0 Hz, 1H), 4.61 (tt, J = 12.1, 3.7 Hz, 1H), 4.54 – 4.43 (m, 1H), 2.81 – 2.60 (m, 2H), 2.54 (dd, J = 16.0, 8.4 Hz, 1H), 2.42 (dd, J = 16.0, 5.3 Hz, 1H), 2.21 (s, 3H), 2.14 – 2.00 (m, 1H), 1.99 – 1.76 (m, 3H), 1.76 – 1.66 (m, 2H), 1.61 – 1.52 (m, 1H), 1.47 – 1.30 (m, 2H), 1.14 – 0.81 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 152.4, 150.4, 138.5, 130.7, 130.1, 129.3, 129.1, 128.4, 106.0, 105.8, 54.3, 51.3, 44.1, 37.0, 31.51, 31.47, 26.2, 25.71, 25.69, 25.3, 13.4.

FT-IR (film): 2924, 2858, 1642, 1400, 782, 713 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{22}H_{29}BrNO_2$: 418.1376, found: 418.1374.



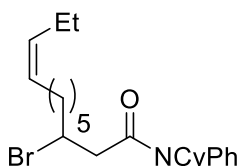
(5S)-3-Bromo-N-cyclohexyl-5,9-dimethyl-N-phenyldec-8-enamide. The title compound was synthesized according to GP-5 from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and (*S*)-3,7-dimethyloct-6-enal (4.63 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 4.63 g (10.7 mmol, 43% yield over 2 steps). Colorless oil.

1H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers) δ 7.48 – 7.36 (m, 3H), 7.18 (d, J = 7.4 Hz, 1H), 7.10 – 6.95 (m, 1H), 5.06 (q, J = 6.3 Hz, 1H), 4.68 – 4.48 (m, 2H), 2.59 – 2.33 (m, 2H), 2.01 – 1.77 (m, 4H), 1.75 – 1.64 (m, 6H), 1.62 – 1.53 (m, 5H), 1.46 – 1.32 (m, 3H), 1.29 – 1.13 (m, 1H), 1.13 – 0.77 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereoisomers) δ 168.9, 168.8, 138.7, 138.6, 131.3, 131.2, 130.80, 130.75, 130.2, 129.3, 129.1, 128.4, 128.3, 124.5, 54.3, 50.9, 50.5, 46.4, 45.8, 44.9, 44.3, 37.4, 35.4, 31.54, 31.51, 30.9, 30.8, 25.74, 25.72, 25.67, 25.66, 25.4, 25.3, 25.1, 19.6, 18.3, 17.6.

FT-IR (film): 2928, 2855, 2359, 1651, 1397, 707 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{24}H_{37}BrNO$: 434.2053, found: 434.2062.



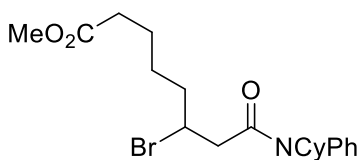
(Z)-3-Bromo-N-cyclohexyl-N-phenyl-dodec-9-enamide. The title compound was synthesized according to GP-5 from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and (*Z*)-dec-7-enal (4.62 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 6.87 g (15.9 mmol, 64% yield over 2 steps). Colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 3H), 7.16 (d, J = 8.0 Hz, 1H), 7.08 – 6.92 (m, 1H), 5.40 – 5.21 (m, 2H), 4.61 (tt, J = 12.1, 3.6 Hz, 1H), 4.47 (tt, J = 8.6, 5.0 Hz, 1H), 2.49 (dd, J = 16.0, 8.3 Hz, 1H), 2.40 (dd, J = 16.0, 5.5 Hz, 1H), 2.07 – 1.91 (m, 4H), 1.90 – 1.76 (m, 2H), 1.76 – 1.59 (m, 4H), 1.55 (dt, J = 13.1, 3.4 Hz, 1H), 1.50 – 1.17 (m, 8H), 1.11 – 0.97 (m, 2H), 0.97 – 0.82 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 138.6, 131.6, 130.7, 130.1, 129.3, 129.1, 128.9, 128.3, 54.3, 52.4, 44.2, 38.7, 31.5, 29.4, 28.4, 27.4, 26.9, 25.71, 25.69, 25.3, 20.4, 14.3.

FT-IR (film): 3003, 2931, 2855, 1652, 1595, 1401, 1262, 1072, 706 cm^{-1} .

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{24}H_{37}BrNO$: 434.2053, found: 434.2072.



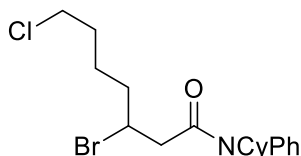
Methyl 6-bromo-8-(cyclohexyl(phenyl)amino)-8-oxooctanoate. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and methyl 6-oxohexanoate (4.32 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 4.31 g (11.9 mmol, 48% yield over 2 steps). Pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.32 (m, 3H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.11 – 6.95 (m, 1H), 4.60 (tt, $J = 12.1, 3.7$ Hz, 1H), 4.45 (tt, $J = 9.1, 4.9$ Hz, 1H), 3.64 (s, 3H), 2.50 (dd, $J = 16.0, 8.1$ Hz, 1H), 2.39 (dd, $J = 16.0, 5.6$ Hz, 1H), 2.28 (t, $J = 7.4$ Hz, 2H), 1.89 – 1.48 (m, 10H), 1.45 – 1.32 (m, 3H), 1.12 – 0.95 (m, 2H), 0.95 – 0.86 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.8, 168.7, 138.6, 130.7, 130.1, 129.4, 129.2, 128.4, 54.3, 51.9, 51.5, 44.2, 38.3, 33.8, 31.5, 27.1, 25.73, 25.71, 25.3, 24.1.

FT-IR (film): 2932, 2857, 1737, 1658, 1650, 1402, 708 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{31}\text{BrNO}_3$: 424.1482, found: 424.1470.



3-Bromo-7-chloro-*N*-cyclohexyl-*N*-phenylheptanamide. The title compound was synthesized according to **GP-5** from *N*-cyclohexyl-*N*-phenylacetamide (5.43 g, 25.0 mmol) and 5-chloropentanal (3.60 g, 30.0 mmol). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). 4.80 g (12.0 mmol, 48% yield over 2 steps). White solid.

^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.32 (m, 3H), 7.15 (d, $J = 7.3$ Hz, 1H), 7.09 – 6.96 (m, 1H), 4.60 (tt, $J = 12.1, 3.6$ Hz, 1H), 4.46 (dddd, $J = 9.0, 7.9, 5.8, 4.1$ Hz, 1H), 3.50 (t, $J = 6.6$ Hz, 2H), 2.52 (dd, $J = 16.0, 7.9$ Hz, 1H), 2.41 (dd, $J = 16.0, 5.8$ Hz, 1H), 1.91 – 1.67 (m, 8H), 1.67 – 1.45 (m, 3H), 1.45 – 1.31 (m, 2H), 1.11 – 0.96 (m, 2H), 0.90 (qt, $J = 13.1, 3.8$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 138.5, 130.7, 130.1, 129.4, 129.2, 128.4, 54.3, 51.6, 44.6, 44.2, 37.8, 31.7, 31.5, 25.72, 25.70, 25.3, 24.9.

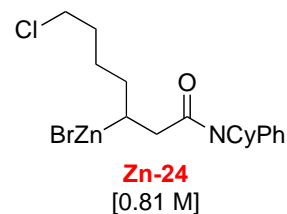
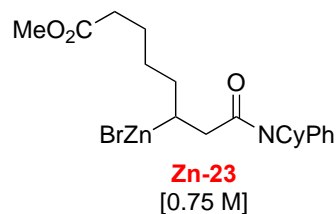
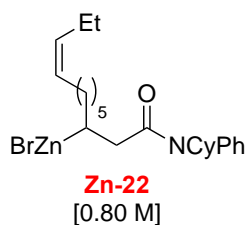
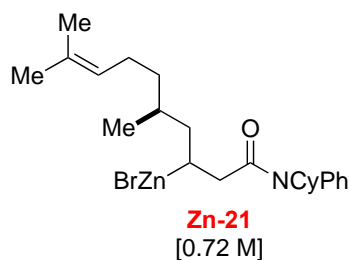
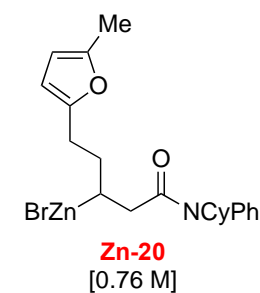
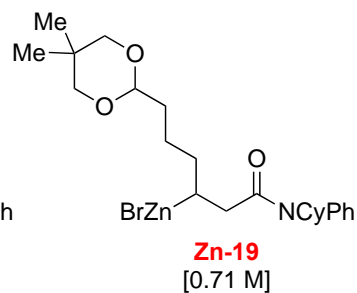
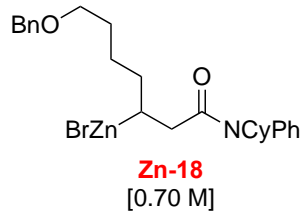
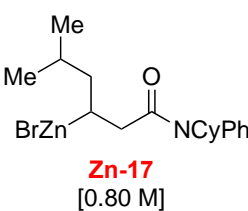
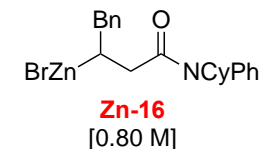
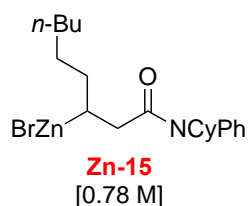
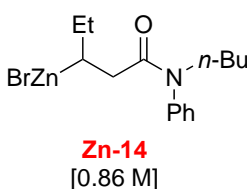
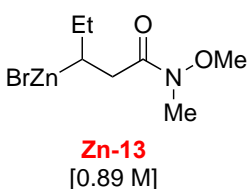
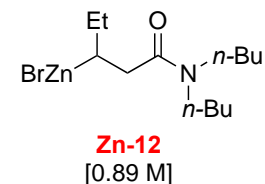
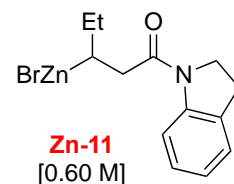
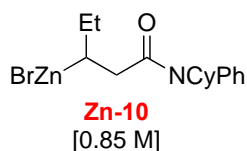
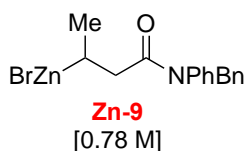
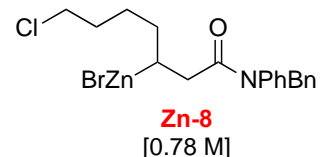
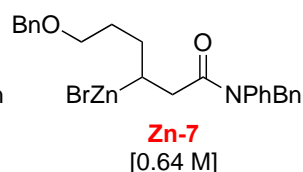
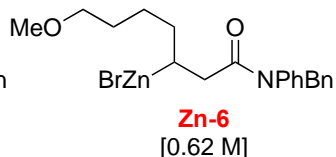
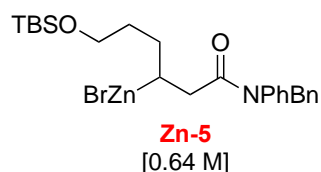
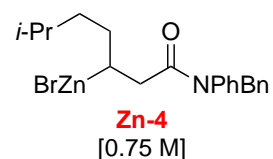
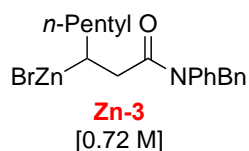
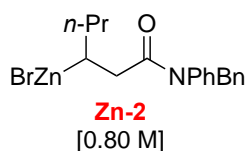
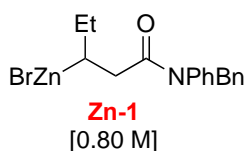
FT-IR (film): 2932, 2855, 1656, 1648, 1400, 1261, 707 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{28}\text{BrClNO}$: 400.1037, found: 400.1069.

General Procedure 6 (GP-6): Preparation of β -zincated amide reagents. In the air, an oven-dried 100-mL Schlenk tube was charged with zinc powder (1.5 equiv, ~100 mesh, Alfa,

99.9%) and a stir bar. The tube was heated with a heat gun (~250 °C) under high vacuum (~200 mtorr) for 10 min. The Schlenk tube was then evacuated and back-filled with nitrogen (three cycles). The Schlenk tube was allowed to cool to room temperature, the cap was removed, and then THF (0.3 mL/mmol of alkyl bromide) was added via syringe under a positive flow of nitrogen to the un-capped (open) Schlenk tube. Iodine (0.05 equiv) was added in one portion, leading initially to a red color that faded after ~5 sec of vigorous stirring (1500 rpm). A solution of the alkyl bromide (1.0 equiv) in THF (0.3 mL/mmol of alkyl bromide), prepared in a 20-mL vial equipped with a nitrogen balloon, was added via syringe in one portion to the gray suspension of zinc powder. The vial that contained residual alkyl bromide was rinsed with THF (0.1 mL/mmol of bromide), and the solution was transferred via syringe to the Schlenk tube. Then, the Schlenk tube was capped tightly under a nitrogen atmosphere and transferred to an oil bath. The reaction mixture was stirred vigorously at 85 °C for 14 h (the disappearance of the alkyl iodide and the formation of the alkylzinc reagent can readily be monitored via GC analysis of the quenched alkylzinc reagent; a small amount of the β,α -unsaturated amide can also be observed via GC analysis). After the alkyl bromide had been consumed, the gray mixture was filtered through a syringe filter (PTFE, 0.45 μ M) to afford a colorless-to-slightly-yellow solution, which can be stored in a freezer at -35 °C for several weeks without deterioration.

The alkylzinc solution was titrated by the method of Knochel, using iodine in THF (0.6–0.9 M) (36).



V. Enantioconvergent Couplings

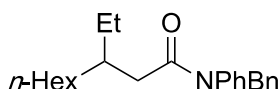
Note: To ensure reproducible results, the couplings should be set up using standard Schlenk techniques, as described below.

General Procedure 7 (GP-7): Enantioconvergent couplings with primary alkyl iodides (Fig. 2). In the air, NiCl₂·glyme (13.2 mg, 0.060 mmol, 10%), chiral ligand **L1** (19.3 mg, 0.072 mmol, 12%), 1,5-bis(diphenylphosphino)pentane (26.4 mg, 0.060 mmol, 10%), and an oven-dried cross-type stir bar were added sequentially to an oven-dried 40-mL vial. The vial was closed with a PTFE septum cap and wrapped with electrical tape. Next, the vial was evacuated and back-filled with nitrogen on a Schlenk line (four cycles), and an argon-filled balloon was attached. Then, anhydrous THF (6.0 mL) was added via syringe, and the reaction mixture was allowed to stir at room temperature for 45 min, after which it turned to a pale-pink suspension. Next, the solution of the alkylzinc bromide (0.90 mmol, 1.5 equiv) was added dropwise via syringe; the reaction mixture was stirred for 10 min, at which time it became dark-red and homogeneous. Then, the reaction mixture was cooled to -5 °C and stirred at that temperature for 10 min. Next, the alkyl iodide (0.6 mmol) was added dropwise via microsyringe (if the iodide is a solid, it was dissolved in THF (0.5 mL) in a 4-mL vial under an argon atmosphere and transferred into the vial via syringe; the vial was rinsed with THF (0.3 mL), and the residual iodide was also transferred via syringe). The argon balloon was removed, and then vacuum grease was liberally applied to cover the punctures in the septum cap. The reaction mixture was stirred at -5 °C for 72 h, and then the reaction was quenched by the addition of MeOH (0.5 mL). The resulting mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography.

General Procedure 8 (GP-8): Enantioconvergent couplings with achiral secondary alkyl iodides (Fig. 2). The procedure is the same as GP-7, except for changes in the following quantities: NiCl₂·glyme (15.8 mg, 0.072 mmol, 12%), chiral ligand **L1** (24.1 mg, 0.090 mmol, 15%) and 1,5-bis(diphenylphosphino)pentane (23.8 mg, 0.054 mmol, 9%).

General Procedure 9 (GP-9): Doubly enantioconvergent couplings with racemic propargylic bromides (Fig. 3). In the air, NiBr₂·glyme (15.4 mg, 0.050 mmol, 10%), anhydrous LiCl (25.4 mg, 0.60 mmol; because LiCl is hygroscopic, it is recommended that it be stored and weighed in a glovebox, and then transferred out of the glovebox), and an oven-dried cross-type stir bar were added sequentially to an oven-dried 40-mL vial. Next, the vial was capped with a PTFE septum cap and wrapped with electrical tape. The vial was evacuated and back-filled with nitrogen on a Schlenk line (four cycles), and then an argon-filled balloon was attached. Next, anhydrous THF (4.0 mL) was added via syringe, and the reaction mixture was allowed to stir for 15 min, during which it turned to a blue, homogeneous solution. Next, chiral ligand **L2** (18.6 mg, 0.065 mmol, 13%) was dissolved in anhydrous THF (1.0 mL) in a 4-mL vial under an argon atmosphere. The solution of the ligand was added via syringe into the reaction vial, and the resulting mixture was allowed to stir for 40 min, after which it was a cloudy yellow suspension. Next, the propargylic bromide (0.50 mmol, sticky colorless oil or solid, dissolved

in THF (0.5 mL) in a 4-mL vial under an argon atmosphere) was added via syringe, the 4-mL vial was rinsed with THF (0.3 mL), and the rinse was also added to the reaction vial. Next, the solution of the alkylzinc bromide (0.50 mmol) was added quickly (within 5 sec) as a stream, leading to a dark-red reaction mixture. The argon balloon was removed, and then vacuum grease was liberally applied to cover the punctures in the septum cap. The reaction mixture was stirred (~800 rpm) at room temperature for 20 h. The reaction mixture was then passed through a short pad of silica gel, with Et₂O as the eluent (~30 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography on silica gel.



N-Benzyl-3-ethyl-N-phenylnonanamide (Fig. 2, entry 1). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 201 mg, 95% yield, 90% ee; (*S*)-**L1**: 198 mg, 94% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD column (5.0% 2-PrOH in supercritical CO₂, 3.5 mL/min); retention times for compound obtained using (*R*)-**L1**: 10.7 min (major), 12.3 min (minor).

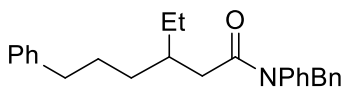
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 2H), 6.97 (dd, *J* = 7.8, 1.9 Hz, 2H), 4.94 (d, *J* = 14.2 Hz, 1H), 4.89 (d, *J* = 14.3 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.95 – 1.83 (m, 1H), 1.37 – 1.09 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 38.6, 36.5, 33.3, 31.8, 29.6, 26.5, 26.2, 22.6, 14.1, 10.8.

FT-IR (film): 2956, 2923, 2854, 1655, 1595, 1494, 1392, 726 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₄H₃₄NO: 352.2635, found: 352.2633.

[α]_D²⁴ = -13.9 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-3-ethyl-N,6-diphenylhexanamide (Fig. 2, entry 2). The title compound was synthesized according to **GP-7** from (3-iodopropyl)benzene and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 → 1:6 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 189 mg, 82% yield, 91% ee; (*S*)-**L1**: 186 mg, 81% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AS-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 10.6 min (major), 12.5 min (minor).

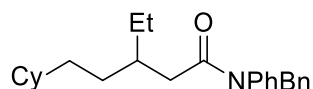
^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.25 (m, 8H), 7.25 – 7.19 (m, 3H), 7.19 – 7.14 (m, 2H), 7.03 – 6.86 (m, 2H), 4.94 (d, $J = 14.3$ Hz, 1H), 4.89 (d, $J = 14.3$ Hz, 1H), 2.57 (t, $J = 7.7$ Hz, 2H), 2.15 – 1.86 (m, 3H), 1.61 – 1.45 (m, 2H), 1.40 – 1.11 (m, 4H), 0.76 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.6, 142.6, 142.5, 137.7, 129.4, 128.8, 128.5, 128.33, 128.28, 128.2, 127.8, 127.2, 125.5, 53.0, 38.5, 36.4, 36.1, 33.0, 28.5, 26.1, 10.8.

FT-IR (film): 2928, 2855, 1652, 1594, 1494, 1393, 746 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{32}\text{NO}$: 386.2478, found: 386.2477.

$[\alpha]_D^{25} = -17.7$ (c 1.0, CHCl_3); 91% ee from (S)-L1.



N-Benzyl-5-cyclohexyl-3-ethyl-N-phenylpentanamide (Fig. 2, entry 3). The title compound was synthesized according to GP-7 from (2-iodoethyl)cyclohexane and zinc nucleophile Zn-1. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(R)-L1: 222 mg, 98% yield, 90% ee; (S)-L1: 219 mg, 97% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (R)-L1: 11.2 min (minor), 12.5 min (major).

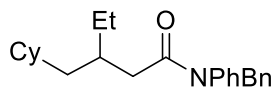
^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.21 (m, 3H), 7.20 – 7.15 (m, 3H), 7.14 – 7.10 (m, 2H), 6.93 – 6.83 (m, 2H), 4.86 (d, $J = 14.3$ Hz, 1H), 4.77 (d, $J = 14.2$ Hz, 1H), 1.98 – 1.87 (m, 2H), 1.77 (hept, $J = 6.4$ Hz, 1H), 1.65 – 1.50 (m, 5H), 1.23 – 0.99 (m, 8H), 0.98 – 0.88 (m, 2H), 0.82 – 0.70 (m, 2H), 0.66 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 38.6, 37.9, 36.7, 34.2, 33.4, 30.4, 26.7, 26.4, 26.1, 10.8.

FT-IR (film): 2919, 2849, 1653, 1594, 1494, 1393, 728 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{36}\text{NO}$: 378.2791, found: 378.2790.

$[\alpha]_D^{25} = -16.2$ (c 1.0, CHCl_3); 91% ee from (S)-L1.



N-Benzyl-3-(cyclohexylmethyl)-N-phenylpentanamide (Fig. 2, entry 4). The title compound was synthesized according to GP-7 from (iodomethyl)cyclohexane and zinc nucleophile Zn-1. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(R)-L1: 211 mg, 97% yield, 91% ee; (S)-L1: 213 mg, 98% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AS-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-L1: 8.6 min (major), 12.5 min (minor).

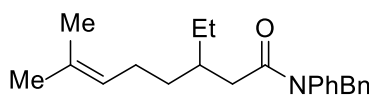
¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.20 (m, 2H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.91 (s, 2H), 2.06 – 1.90 (m, 3H), 1.74 – 1.55 (m, 5H), 1.33 – 1.22 (m, 2H), 1.21 – 1.09 (m, 4H), 1.09 – 0.94 (m, 2H), 0.91 – 0.78 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.6, 128.3, 127.7, 127.2, 53.0, 41.6, 38.9, 34.8, 33.54, 33.45, 26.7, 26.44, 26.36, 10.6.

FT-IR (film): 2918, 2848, 1654, 1594, 1494, 1392, 729 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₅H₃₄NO: 364.2635, found: 364.2634.

[α]_D²⁴ = -23.2 (*c* 1.0, CHCl₃); 91% ee from (*S*)-L1.



***N*-Benzyl-3-ethyl-7-methyl-*N*-phenyloct-6-enamide (Fig. 2, entry 5).** The title compound was synthesized according to GP-7 from 5-iodo-2-methylpent-2-ene and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:20 → 1:15 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 172 mg, 82% yield, 92% ee; (*S*)-L1: 170 mg, 81% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-L1: 14.0 min (minor), 15.2 min (major).

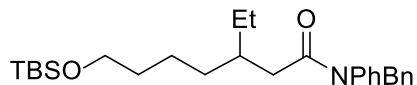
¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 2H), 6.97 (dd, *J* = 7.7, 1.9 Hz, 2H), 5.07 (tt, *J* = 7.1, 1.3 Hz, 1H), 4.91 (s, 2H), 2.10 – 1.98 (m, 2H), 1.97 – 1.79 (m, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.58 (d, *J* = 1.3 Hz, 3H), 1.37 – 1.17 (m, 4H), 0.77 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 142.6, 137.8, 131.1, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 124.6, 53.0, 38.5, 36.2, 33.4, 26.0, 25.7, 25.2, 17.6, 10.7.

FT-IR (film): 2960, 2921, 2854, 1653, 1594, 1494, 1393, 728 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₄H₃₁NONa: 372.2298, found: 372.2298.

[α]_D²⁴ = -29.1 (*c* 1.0, CHCl₃); 92% ee from (*S*)-L1.



***N*-Benzyl-7-((*tert*-butyldimethylsilyloxy)-3-ethyl-*N*-phenylheptanamide (Fig. 2, entry 6).** The title compound was synthesized according to GP-7 from *tert*-butyl(4-iodobutoxy)dimethylsilane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 245 mg, 90% yield, 91% ee; (*S*)-L1: 257 mg, 94% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (0.5% 2-PrOH in hexanes, 0.5 mL/min); retention times for compound obtained using (*R*)-L1: 42.8 min (minor), 44.0 min (major).

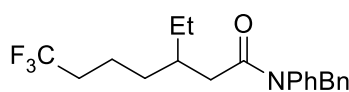
¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 3H), 7.24 – 7.19 (m, 3H), 7.18 – 7.14 (m, 2H), 6.96 – 6.87 (m, 2H), 4.85 (s, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.91 – 1.75 (m, 1H), 1.50 – 1.32 (m, 2H), 1.28 – 1.07 (m, 6H), 0.85 (s, 9H), 0.71 (t, *J* = 7.4 Hz, 3H), 0.00 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 63.1, 53.0, 38.5, 36.5, 33.10, 33.07, 26.1, 26.0, 22.7, 18.3, 10.8, -5.3.

FT-IR (film): 2927, 2855, 1656, 1595, 1494, 1391, 1094, 833, 773 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₈H₄₄NO₂Si: 454.3136, found: 454.3141.

[α]_D²⁴ = -13.7 (*c* 1.0, CHCl₃); 90% ee from (*S*)-L1.



N-Benzyl-3-ethyl-7,7,7-trifluoro-N-phenylheptanamide (Fig. 2, entry 7). The title compound was synthesized according to GP-7 from 1,1,1-trifluoro-4-iodobutane and zinc nucleophile Zn-1. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 172 mg, 76% yield, 90% ee; (*S*)-L1: 176 mg, 78% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-L1: 14.2 min (major), 16.3 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.31 (m, 3H), 7.31 – 7.25 (m, 3H), 7.25 – 7.18 (m, 2H), 6.97 (dd, *J* = 7.7, 2.0 Hz, 2H), 4.91 (s, 2H), 2.15 – 1.85 (m, 5H), 1.53 – 1.38 (m, 2H), 1.37 – 1.18 (m, 4H), 0.77 (t, *J* = 7.4 Hz, 3H).

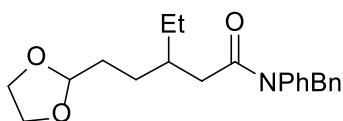
¹³C NMR (101 MHz, CDCl₃) δ 172.3, 142.4, 137.6, 129.5, 128.8, 128.5, 128.3, 127.9, 127.3, 127.1 (q, *J* = 276.8 Hz), 53.0, 38.3, 36.1, 33.9 (q, *J* = 28.1 Hz), 32.4, 26.0, 19.0 (q, *J* = 2.9 Hz), 10.8.

¹⁹F NMR (282 MHz, CDCl₃) δ -66.37 (t, *J* = 10.9 Hz, 3F).

FT-IR (film): 2960, 2935, 1652, 1495, 1393, 1252, 1147, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₂H₂₆F₃NONa: 400.1859, found: 400.1863.

[α]_D²⁴ = +1.4 (*c* 1.0, CHCl₃); 89% ee from (*S*)-L1.



N-Benzyl-5-(1,3-dioxolan-2-yl)-3-ethyl-N-phenylpentanamide (Fig. 2, entry 8). The title compound was synthesized according to GP-7 from 2-(2-iodoethyl)-1,3-dioxolane and zinc

nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:10 → 1:2 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 179 mg, 81% yield, 91% ee; (*S*)-**L1**: 189 mg, 86% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 22.8 min (minor), 26.1 min (major).

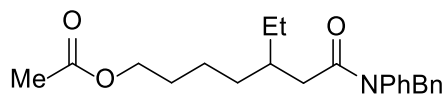
¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 6.97 (dd, *J* = 7.7, 1.9 Hz, 2H), 4.91 (s, 2H), 4.80 (t, *J* = 4.8 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.89 – 3.79 (m, 2H), 2.09 – 1.89 (m, 3H), 1.62 – 1.46 (m, 2H), 1.44 – 1.19 (m, 4H), 0.78 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.4, 142.4, 137.7, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 104.7, 64.8, 53.0, 38.4, 36.2, 30.9, 27.3, 26.0, 10.7.

FT-IR (film): 2957, 2926, 2874, 1652, 1594, 1494, 1394, 766 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₃H₃₀NO₃: 368.2220, found: 368.2220.

[α]_D²⁴ = -18.2 (c 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



7-(Benzyl(phenyl)amino)-5-ethyl-7-oxoheptyl acetate (Fig. 2, entry 9). The title compound was synthesized according to **GP-7** from 4-iodobutyl acetate and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 → 1:5 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 216 mg, 94% yield, 90% ee; (*S*)-**L1**: 214 mg, 93% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 21.0 min (minor), 23.8 min (major).

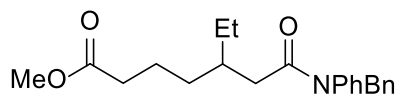
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 6.97 (dd, *J* = 7.9, 1.8 Hz, 2H), 4.92 (d, *J* = 14.2 Hz, 1H), 4.88 (d, *J* = 14.2 Hz, 1H), 4.03 (t, *J* = 6.7 Hz, 2H), 2.05 (s, 3H), 2.04 – 1.95 (m, 2H), 1.95 – 1.83 (m, 1H), 1.66 – 1.48 (m, 2H), 1.32 – 1.17 (m, 6H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 171.2, 142.5, 137.7, 129.4, 128.8, 128.5, 128.3, 127.8, 127.3, 64.5, 53.0, 38.5, 36.4, 32.9, 28.8, 26.1, 23.0, 21.0, 10.8.

FT-IR (film): 2957, 2932, 1734, 1652, 1594, 1494, 1393, 1237, 1030, 729 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₄H₃₂NO₃: 382.2377, found: 382.2377.

[α]_D²⁴ = -13.4 (c 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



Methyl 7-(benzyl(phenyl)amino)-5-ethyl-7-oxoheptanoate (Fig. 2, entry 10). The title compound was synthesized according to **GP-7** from methyl 4-iodobutanoate and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 → 1:5 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 206 mg, 94% yield, 90% ee; (*S*)-**L1**: 208 mg, 95% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AS-H column (10.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 11.8 min (major), 12.8 min (minor).

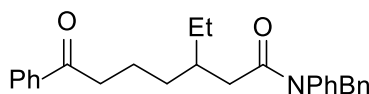
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.17 (m, 2H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.90 (s, 2H), 3.67 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.12 – 1.84 (m, 3H), 1.60 – 1.43 (m, 2H), 1.35 – 1.14 (m, 4H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.1, 172.4, 142.4, 137.7, 129.5, 128.8, 128.5, 128.3, 127.8, 127.2, 53.0, 51.4, 38.4, 36.1, 34.2, 32.7, 26.0, 22.0, 10.7.

FT-IR (film): 2955, 2926, 1735, 1651, 1494, 1393, 1194, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₃H₃₀NO₃: 368.2220, found: 368.2223.

[α]_D²⁴ = -11.8 (c 1.0, CHCl₃); 91% ee from (*S*)-**L1**.



N-Benzyl-3-ethyl-7-oxo-N,7-diphenylheptanamide (Fig. 2, entry 11). The title compound was synthesized according to **GP-7** from 4-iodo-1-phenylbutan-1-one and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:10 → 1:5 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 221 mg, 89% yield, 91% ee; (*S*)-**L1**: 212 mg, 85% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (10.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 16.6 min (minor), 18.1 min (major).

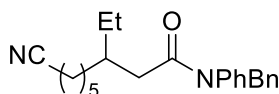
¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.91 (m, 2H), 7.64 – 7.54 (m, 1H), 7.53 – 7.43 (m, 2H), 7.36 – 7.24 (m, 6H), 7.24 – 7.18 (m, 2H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.90 (s, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.13 – 1.91 (m, 3H), 1.64 (dt, *J* = 14.9, 7.5 Hz, 2H), 1.41 – 1.19 (m, 4H), 0.77 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 200.3, 172.5, 142.4, 137.7, 137.0, 132.8, 129.5, 128.8, 128.50, 128.49, 128.3, 128.0, 127.8, 127.2, 53.0, 38.7, 38.4, 36.2, 32.9, 26.1, 21.2, 10.8.

FT-IR (film): 2957, 2927, 1682, 1650, 1594, 1494, 1393, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₈H₃₂NO₂: 414.2428, found: 414.2432.

[α]_D²⁴ = -25.4 (c 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-8-cyano-3-ethyl-N-phenyloctanamide (Fig. 2, entry 12). The title compound was synthesized according to **GP-7** from 6-iodohexanenitrile and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:10 → 1:2 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 204 mg, 94% yield, 88% ee; (*S*)-**L1**: 202 mg, 93% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (10.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 19.1 min (minor), 21.1 min (major).

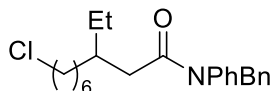
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.31 (m, 3H), 7.31 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.93 (d, *J* = 14.2 Hz, 1H), 4.88 (s, *J* = 14.4 Hz, 1H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.01 (qd, *J* = 15.0, 6.8 Hz, 2H), 1.94 – 1.82 (m, 1H), 1.68 – 1.56 (m, 2H), 1.46 – 1.33 (m, 2H), 1.33 – 1.12 (m, 6H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 142.5, 137.7, 129.5, 128.8, 128.5, 128.3, 127.8, 127.3, 119.8, 53.0, 38.5, 36.4, 33.0, 28.8, 26.1, 25.8, 25.3, 17.1, 10.8.

FT-IR (film): 2929, 2856, 2220, 1652, 1594, 1494, 1394, 728 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₄H₃₁N₂O: 363.2431, found: 363.2432.

[α]_D²⁴ = –12.1 (*c* 1.0, CHCl₃); 89% ee from (*S*)-**L1**.



N-Benzyl-9-chloro-3-ethyl-N-phenylnonanamide (Fig. 2, entry 13). The title compound was synthesized according to **GP-7** from 1-chloro-6-iodohexane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 189 mg, 82% yield, 91% ee; (*S*)-**L1**: 215 mg, 93% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (0.5% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 23.0 min (major), 26.4 min (minor).

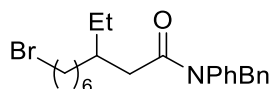
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.16 (m, 2H), 7.03 – 6.92 (m, 2H), 4.93 (d, *J* = 14.2 Hz, 1H), 4.89 (d, *J* = 14.2 Hz, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.11 – 1.95 (m, 2H), 1.95 – 1.82 (m, 1H), 1.82 – 1.70 (m, 2H), 1.45 – 1.34 (m, 2H), 1.33 – 1.07 (m, 8H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 142.6, 137.7, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 53.0, 45.2, 38.5, 36.5, 33.2, 32.6, 29.1, 26.8, 26.4, 26.2, 10.8.

FT-IR (film): 2957, 2927, 2855, 1651, 1594, 1494, 1392, 726 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₄H₃₃ClNO: 386.2245, found: 386.2246.

[α]_D²⁴ = –13.7 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-9-bromo-3-ethyl-N-phenylnonanamide (Fig. 2, entry 14). The title compound was synthesized according to **GP-7** from 1-bromo-6-iodohexane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 170 mg, 66% yield, 91% ee; (*S*)-**L1**: 178 mg, 69% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 11.7 min (major), 13.1 min (minor).

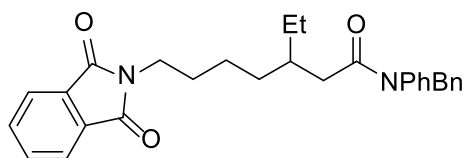
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 7.03 – 6.92 (m, 2H), 4.93 (d, *J* = 14.2 Hz, 1H), 4.89 (d, *J* = 14.2 Hz, 1H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.11 – 1.95 (m, 2H), 1.95 – 1.78 (m, 3H), 1.48 – 1.34 (m, 2H), 1.34 – 1.11 (m, 8H), 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 142.6, 137.7, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 53.0, 38.5, 36.5, 34.0, 33.2, 32.8, 29.0, 28.1, 26.4, 26.2, 10.8.

FT-IR (film): 2926, 2854, 1651, 1594, 1494, 1392, 726 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₄H₃₃BrNO: 430.1740, found: 430.1756.

[α]_D²⁴ = –13.5 (c 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-7-(1,3-dioxisoindolin-2-yl)-3-ethyl-N-phenylheptanamide (Fig. 2, entry 15). The title compound was synthesized according to **GP-7** from 2-(4-iodobutyl)isoindoline-1,3-dione and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:10 → 1:2 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 263 mg, 94% yield, 92% ee; (*S*)-**L1**: 266 mg, 95% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OJ-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 43.3 min (minor), 47.5 min (major).

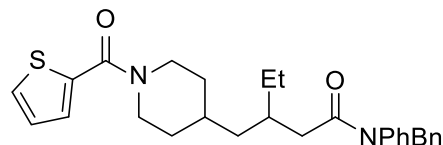
¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.81 (m, 2H), 7.77 – 7.68 (m, 2H), 7.36 – 7.17 (m, 8H), 7.03 – 6.90 (m, 2H), 4.92 (d, *J* = 14.3 Hz, 1H), 4.87 (d, *J* = 14.3 Hz, 1H), 3.64 (t, *J* = 7.4 Hz, 2H), 2.10 – 1.94 (m, 2H), 1.93 – 1.80 (m, *J* = 6.0 Hz, 1H), 1.69 – 1.53 (m, 2H), 1.37 – 1.12 (m, 6H), 0.75 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 168.3, 142.5, 137.7, 133.8, 132.1, 129.4, 128.8, 128.5, 128.2, 127.8, 127.2, 123.1, 53.0, 38.4, 37.9, 36.4, 32.9, 28.8, 26.1, 23.9, 10.8.

FT-IR (film): 2930, 2858, 1770, 1707, 1650, 1393, 718 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_3$: 469.2486, found: 469.2489.

$[\alpha]_D^{24} = -12.8$ (c 1.0, CHCl_3); 92% ee from (*S*)-**L1**.



N-Benzyl-N-phenyl-3-((1-(thiophene-2-carbonyl)piperidin-4-yl)methyl)pentanamide (Fig. 2, entry 16). The title compound was synthesized according to **GP-7** from (4-(iodomethyl)piperidin-1-yl)(thiophen-2-yl)methanone and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:10 \rightarrow 1:2 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 252 mg, 89% yield, 90% ee; (*S*)-**L1**: 246 mg, 86% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (30.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 12.4 min (minor), 14.3 min (major).

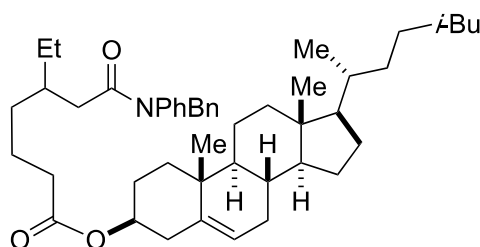
^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.39 – 7.31 (m, 3H), 7.31 – 7.24 (m, 4H), 7.24 – 7.18 (m, 2H), 7.05 (dd, $J = 5.0, 3.6$ Hz, 1H), 6.97 (dd, $J = 7.8, 1.8$ Hz, 2H), 4.90 (s, 2H), 4.40 (br s, 2H), 2.88 (br s, 2H), 2.14 – 1.88 (m, 3H), 1.79 – 1.58 (m, 2H), 1.55 – 1.40 (m, 1H), 1.36 – 1.23 (m, 2H), 1.23 – 1.04 (m, 4H), 0.77 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 163.4, 142.5, 137.61, 137.57, 129.5, 128.9, 128.5, 128.3, 128.1, 127.9, 127.3, 126.5, 53.1, 40.6, 38.8, 33.5, 33.3, 32.6, 26.5, 10.6.

FT-IR (film): 2918, 2849, 1647, 1612, 1594, 1436, 1394, 1269, 734 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_2\text{SNa}$: 497.2233, found: 497.2240.

$[\alpha]_D^{24} = -33.4$ (c 1.0, CHCl_3); 91% ee from (*S*)-**L1**.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 7-(benzyl(phenyl)amino)-5-ethyl-7-oxoheptanoate (Fig. 2, entry 17). The title compound was synthesized according to **GP-7** from the alkyl iodide and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Sticky colorless oil.

(*R*)-**L1**: 355 mg, 82% yield, 4:96 dr; (*S*)-**L1**: 370 mg, 85% yield, 95:5 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 13.3 min (minor), 14.3 min (major).

The ¹H NMR data for the product from (*S*)-**L1** and (*R*)-**L1** (identical for both diastereomers):

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.17 (m, 2H), 6.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 5.45 – 5.32 (m, 1H), 4.90 (s, 2H), 4.68 – 4.53 (m, 1H), 2.37 – 2.28 (m, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 2.09 – 1.81 (m, 8H), 1.65 – 1.44 (m, 9H), 1.43 – 1.33 (m, 3H), 1.32 – 1.06 (m, 13H), 1.04 (s, 3H), 1.03 – 0.96 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 1.9 Hz, 3H), 0.88 (d, *J* = 1.9 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H), 0.70 (s, 3H).

The ¹³C NMR data for the product from (*R*)-**L1**:

¹³C NMR (101 MHz, CDCl₃) δ 173.1, 172.5, 142.5, 139.7, 137.7, 129.5, 128.8, 128.5, 128.3, 127.8, 127.2, 122.6, 73.7, 56.6, 56.1, 53.0, 50.0, 42.3, 39.7, 39.5, 38.4, 38.1, 37.0, 36.6, 36.2, 36.1, 35.8, 34.8, 32.7, 31.9, 31.8, 28.2, 28.0, 27.8, 26.0, 24.3, 23.8, 22.8, 22.5, 22.1, 21.0, 19.3, 18.7, 11.8, 10.8.

The ¹³C NMR data for the product from (*S*)-**L1**:

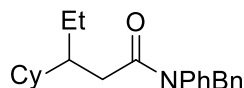
¹³C NMR (101 MHz, CDCl₃) δ 173.1, 172.5, 142.5, 139.7, 137.7, 129.5, 128.9, 128.6, 128.3, 127.9, 127.3, 122.6, 73.7, 56.7, 56.1, 53.0, 50.0, 42.3, 39.7, 39.5, 38.5, 38.2, 37.0, 36.6, 36.3, 36.2, 35.8, 34.9, 32.7, 31.9, 31.8, 28.3, 28.0, 27.8, 26.1, 24.3, 23.8, 22.9, 22.6, 22.1, 21.0, 19.4, 18.7, 11.9, 10.8.

FT-IR (film): 2933, 2866, 1733, 1653, 1495, 1169, 754 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₉H₇₂NO₃: 722.5507, found: 722.5511.

[α]_D²⁴ = -30.5 (*c* 1.0, CHCl₃); 95:5 dr from (*S*)-**L1**.

[α]_D²⁴ = -10.2 (*c* 1.0, CHCl₃); 4:96 dr from (*R*)-**L1**.



N-Benzyl-3-cyclohexyl-N-phenylpentanamide (Fig. 2, entry 18). The title compound was synthesized according to **GP-8** from iodocyclohexane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless viscous oil.

(*R*)-**L1**: 181 mg, 87% yield, 92% ee; (*S*)-**L1**: 180 mg, 86% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 13.6 min (minor), 16.1 min (major).

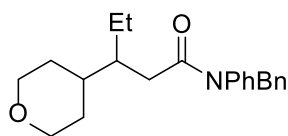
¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.12 (m, 8H), 7.11 – 6.76 (m, 2H), 4.89 (s, 2H), 2.19 – 1.87 (m, 2H), 1.85 – 1.72 (m, 1H), 1.71 – 1.53 (m, 3H), 1.51 – 1.01 (m, 8H), 0.93 – 0.63 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 173.4, 142.7, 137.9, 129.5, 129.0, 128.7, 128.4, 127.9, 127.4, 53.2, 42.3, 39.9, 35.8, 29.64, 29.60, 26.91, 26.86, 23.4, 11.9.

FT-IR (film): 2921, 2850, 1653, 1595, 1494, 1392, 1196, 1079, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₄H₃₁NONa: 372.2298, found: 372.2302.

[α]_D²² = +1.9 (*c* 0.50, CHCl₃); 92% ee from (*S*)-**L1**.



N-Benzyl-N-phenyl-3-(tetrahydro-2H-pyran-4-yl)pentanamide (Fig. 2, entry 19). The title compound was synthesized according to **GP-8** from 4-iodotetrahydro-2H-pyran and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Colorless viscous oil.

(*R*)-**L1**: 197 mg, 93% yield, 91% ee; (*S*)-**L1**: 187 mg, 89% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 20.2 min (minor), 22.9 min (major).

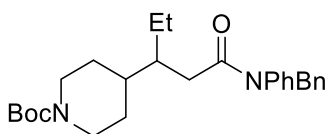
¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 3H), 7.26 – 7.16 (m, 5H), 7.07 – 6.80 (m, 2H), 4.90 (d, *J* = 14.2 Hz, 1H), 4.86 (d, *J* = 14.2 Hz, 1H), 4.00 – 3.81 (m, 2H), 3.29 (td, *J* = 11.4, 2.7 Hz, 2H), 2.09 (dd, *J* = 15.3, 6.0 Hz, 1H), 1.95 (dd, *J* = 15.3, 7.0 Hz, 1H), 1.89 – 1.74 (m, 1H), 1.62 – 1.46 (m, 1H), 1.36 – 1.15 (m, 6H), 0.78 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 172.8, 142.6, 137.8, 129.6, 129.0, 128.6, 128.4, 128.0, 127.4, 68.5, 53.2, 41.4, 37.2, 35.3, 29.8, 29.5, 23.1, 11.5.

FT-IR (ATR) 2932, 2840, 1651, 1494, 1393, 1094, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₃H₂₉NO₂Na: 374.2095, found: 374.2091.

[α]_D²⁵ = -3.8 (*c* 0.49, CHCl₃); 92% ee from (*S*)-**L1**.



tert-Butyl 4-(1-(benzyl(phenyl)amino)-1-oxopentan-3-yl)piperidine-1-carboxylate (Fig. 2, entry 20). The title compound was synthesized according to **GP-8** from *tert*-butyl 4-iodopiperidine-1-carboxylate and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Colorless viscous oil.

(*R*)-**L1**: 247 mg, 91% yield, 91% ee; (*S*)-**L1**: 243 mg, 90% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 19.0 min (minor), 26.5 min (major).

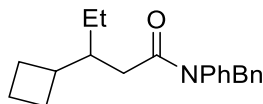
¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.10 (m, 8H), 6.99 – 6.84 (m, 2H), 4.87 (s, 2H), 4.05 (d, 2H), 2.71 – 2.40 (m, 2H), 2.11 – 1.89 (m, 2H), 1.83 (q, *J* = 5.8 Hz, 1H), 1.43 (s, 9H), 1.37 – 1.11 (m, 5H), 1.10 – 0.92 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 172.6, 154.7, 142.4, 137.6, 129.5, 128.8, 128.4, 128.3, 127.9, 127.3, 79.1, 53.1, 44.24, 44.22, 41.2, 38.2, 35.4, 28.55, 28.49, 28.4, 23.2, 11.6.

FT-IR (film) 2930, 1688, 1652, 1392, 1234, 1166, 1141, 768 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{O}_3$: 451.2955, found: 451.2943.

$[\alpha]_{\text{D}}^{22} = -15.4$ ($c = 0.62$, CHCl_3); 92% ee from (S)-L1.



N-Benzyl-3-cyclobutyl-N-phenylpentanamide (Fig. 2, entry 21). The title compound was synthesized according to GP-8 from iodocyclobutane and zinc nucleophile **Zn-1**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless viscous oil.

(R)-L1: 142 mg, 88% yield, 90% ee; (S)-L1: 122 mg, 76% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (R)-L1: 14.8 min (minor), 17.8 min (major).

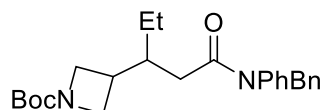
^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.33 (m, 3H), 7.33 – 7.27 (m, 3H), 7.27 – 7.20 (m, 2H), 7.08 – 6.93 (m, 2H), 4.94 (s, 2H), 2.14 – 1.90 (m, 5H), 1.90 – 1.81 (m, 1H), 1.80 – 1.64 (m, 3H), 1.64 – 1.52 (m, 1H), 1.44 – 1.31 (m, 1H), 1.31 – 1.18 (m, 1H), 0.79 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.8, 142.6, 137.7, 129.4, 128.9, 128.5, 128.2, 127.7, 127.2, 53.0, 42.8, 40.1, 35.7, 27.5, 27.0, 24.0, 17.7, 10.6.

FT-IR (ATR) 2958, 2929, 1652, 1494, 1393, 1260, 766, 749 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{28}\text{NO}$: 322.2165, found: 322.2166.

$[\alpha]_{\text{D}}^{22} = -24.2$ ($c 0.62$, CHCl_3); 87% ee from (S)-L1.



tert-Butyl 3-(1-(benzyl(phenyl)amino)-1-oxopentan-3-yl)azetidine-1-carboxylate (Fig. 2, entry 22). The title compound was synthesized according to GP-8 from *tert*-butyl 3-iodoazetidine-1-carboxylate (0.50 mmol) and zinc nucleophile **Zn-1** (0.75 mmol). The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Colorless viscous oil.

(R)-L1: 202 mg, 96% yield, 87% ee; (S)-L1: 190 mg, 90% yield, 89% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-3 column (20.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (R)-L1: 3.4 min (minor), 3.9 min (major).

^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.28 (m, 3H), 7.26 – 7.16 (m, 5H), 7.30 – 7.25 (m, 3H), 7.24 – 7.16 (m, 2H), 7.03 – 6.88 (m, 2H), 4.91 (d, $J = 14.2$ Hz, 1H), 4.88 (d, $J = 14.1$ Hz, 1H), 3.87 (t, $J = 8.4$ Hz, 1H), 3.82 (t, $J = 8.4$ Hz, 1H), 3.59 (dd, $J = 8.5, 6.3$ Hz, 1H), 3.51 (dd, $J = 8.4, 6.4$ Hz, 1H), 2.47 –

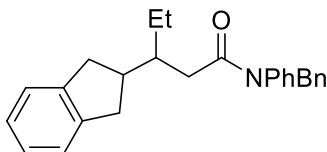
2.32 (m, 1H), 2.19 – 2.09 (m, 1H), 2.01 (dd, $J = 15.2, 7.5$ Hz, 1H), 1.92 (dd, $J = 15.2, 5.4$ Hz, 1H), 1.44 (s, 9H), 1.39 – 1.21 (m, 2H), 0.75 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.7, 156.2, 142.2, 137.4, 129.6, 128.9, 128.4, 128.3, 128.0, 127.4, 79.1, 53.1, 40.0, 35.5, 32.7, 28.4, 24.1, 10.6.

FT-IR (film) 2961, 2919, 1697, 1652, 1395, 1364, 1131, 767, 749 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_3\text{Na}$: 445.2462, found: 445.2466.

$[\alpha]^{25}_{\text{D}} = -27.6$ (c 0.66, CHCl_3); 89% ee from (S)-L1.



N-Benzyl-3-(2,3-dihydro-1H-inden-2-yl)-N-phenylpentanamide (Fig. 2, entry 23). The title compound was synthesized according to GP-8 from 2-iodo-2,3-dihydro-1H-indene (0.50 mmol) and zinc nucleophile Zn-1 (0.75 mmol). The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). White solid.

(R)-L1: 133 mg, 69% yield, 94% ee; (S)-L1 130 mg, 68% yield, 94% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-3 column (25.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (R)-L1: 5.1 min (minor), 6.7 min (major).

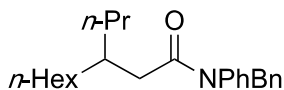
^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.19 (m, 9H), 7.18 – 7.13 (m, 1H), 7.13 – 7.08 (m, 2H), 7.04 – 6.90 (m, 2H), 4.95 (d, $J = 14.2$ Hz, 1H), 4.90 (d, $J = 14.0$ Hz, 1H), 2.90 (dd, $J = 15.5, 7.9$ Hz, 1H), 2.82 (dd, $J = 15.3, 7.8$ Hz, 1H), 2.54 (ddd, $J = 34.8, 15.4, 9.5$ Hz, 2H), 2.45 – 2.33 (m, 1H), 2.23 – 2.04 (m, 3H), 1.57 – 1.44 (m, 1H), 1.44 – 1.31 (m, 1H), 0.84 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.5, 143.4, 143.3, 142.5, 137.6, 129.5, 128.9, 128.5, 128.3, 127.9, 127.3, 126.0, 125.9, 124.2, 124.1, 109.9, 53.1, 43.0, 40.8, 36.8, 36.7, 36.5, 24.5, 10.4.

FT-IR (ATR) 2966, 2925, 1643, 1596, 1494, 1398, 765, 747 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{29}\text{NONa}$: 406.2141, found: 406.2145.

$[\alpha]^{25}_{\text{D}} = -34.8$ ($c = 1.0$, CHCl_3); 94% ee from (S)-L1.



N-Benzyl-N-phenyl-3-propylnonanamide (Fig. 2, entry 24). The title compound was synthesized according to GP-7 from 1-iodohexane and zinc nucleophile Zn-2. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(R)-L1: 205 mg, 94% yield, 90% ee; (S)-L1: 201 mg, 92% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (0.5% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-L1: 10.2 min (major), 11.1 min (minor).

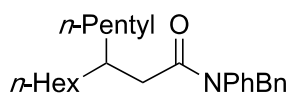
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 2H), 6.96 (dd, $J = 7.8, 1.9$ Hz, 2H), 4.94 (d, $J = 14.2$ Hz, 1H), 4.89 (d, $J = 14.3$ Hz, 1H), 2.08 – 2.00 (m, 2H), 2.00 – 1.87 (m, 1H), 1.33 – 1.12 (m, 14H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.87 – 0.81 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 39.0, 36.2, 35.0, 33.8, 31.9, 29.6, 26.5, 22.6, 19.7, 14.3, 14.1.

FT-IR (film): 2954, 2924, 2854, 1655, 1595, 1494, 1392, 727 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{36}\text{NO}$: 366.2719, found: 366.2791.

$[\alpha]^{24}_{\text{D}} = -5.4$ (c 1.0, CHCl_3); 90% ee from (*S*)-L1.



N-Benzyl-3-pentyl-N-phenylnonanamide (Fig. 2, entry 25). The title compound was synthesized according to GP-7 from 1-iodohexane and zinc nucleophile Zn-3. The product was purified by column chromatography on silica gel (1:15 \rightarrow 1:6 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 187 mg, 79% yield, 90% ee; (*S*)-L1: 203 mg, 86% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (1.0% 2-PrOH in hexanes, 0.6 mL/min); retention times for compound obtained using (*R*)-L1: 17.4 min (major), 18.3 min (minor).

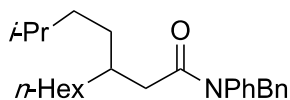
^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.20 (m, 3H), 7.20 – 7.15 (m, 3H), 7.14 – 7.10 (m, 2H), 6.87 (dd, $J = 7.8, 1.9$ Hz, 2H), 4.81 (s, 2H), 1.93 (d, $J = 6.8$ Hz, 2H), 1.89 – 1.77 (m, 1H), 1.22 – 1.03 (m, 18H), 0.84 – 0.74 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 39.0, 35.2, 33.9, 33.8, 32.1, 31.9, 29.6, 26.5, 26.2, 22.6, 14.10, 14.08.

FT-IR (film): 2923, 2853, 1655, 1595, 1494, 1392, 725 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{40}\text{NO}$: 394.3104, found: 394.3110.

$[\alpha]^{24}_{\text{D}} = -1.8$ (c 1.0, CHCl_3); 90% ee from (*S*)-L1.



N-Benzyl-3-isopentyl-N-phenylnonanamide (Fig. 2, entry 26). The title compound was synthesized according to GP-7 from 1-iodohexane and zinc nucleophile Zn-4. The product was purified by column chromatography on silica gel (1:15 \rightarrow 1:6 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 219 mg, 92% yield, 89% ee; (*S*)-L1: 221 mg, 93% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-L1: 18.3 min (major), 20.0 min (minor).

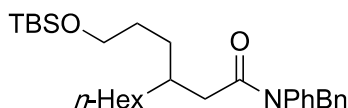
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.25 (m, 3H), 7.24 – 7.19 (m, 2H), 6.96 (dd, $J = 7.8, 1.9$ Hz, 2H), 4.94 (d, $J = 14.2$ Hz, 1H), 4.88 (d, $J = 14.3$ Hz, 1H), 2.02 (d, $J = 6.8$ Hz, 2H), 1.97 – 1.86 (m, 1H), 1.52 – 1.39 (m, 1H), 1.34 – 1.13 (m, 12H), 1.09 – 1.00 (m, 2H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.85 (dd, $J = 6.6, 0.8$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 39.0, 35.7, 35.4, 33.9, 31.9, 31.5, 29.6, 28.2, 26.5, 22.63, 22.60, 14.1.

FT-IR (film): 2923, 2853, 1655, 1595, 1494, 1392, 726 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{40}\text{NO}$: 394.3104, found: 394.3105.

$[\alpha]^{25}_{\text{D}} = -5.2$ (c 1.0, CHCl_3); 89% ee from (*S*)-L1.



N-Benzyl-3-(3-((tert-butyldimethylsilyl)oxy)propyl)-N-phenylnonanamide (Fig. 2, entry 27). The title compound was synthesized according to GP-7 from 1-iodohexane and zinc nucleophile Zn-5. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-L1: 282 mg, 95% yield, 88% ee; (*S*)-L1: 274 mg, 92% yield, 87% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IE column (10.0% 2-PrOH in supercritical CO_2 , 2.5 ml/min); retention times for compound obtained using (*R*)-L*: 10.9 min (minor), 11.6 min (major).

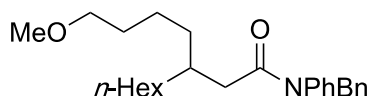
^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.25 (m, 3H), 7.25 – 7.19 (m, 3H), 7.19 – 7.12 (m, 2H), 6.91 (dd, $J = 7.7, 1.9$ Hz, 2H), 4.89 (d, $J = 14.3$ Hz, 1H), 4.82 (d, $J = 14.3$ Hz, 1H), 3.50 (td, $J = 6.6, 1.2$ Hz, 2H), 1.97 (d, $J = 7.4$ Hz, 2H), 1.95 – 1.84 (m, 1H), 1.41 – 1.29 (m, 2H), 1.29 – 1.06 (m, 12H), 0.85 (s, 12H), 0.00 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.6, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 63.5, 53.0, 39.0, 34.9, 33.7, 31.8, 29.8, 29.7, 29.6, 26.5, 26.0, 22.6, 18.3, 14.1, -5.3.

FT-IR (film): 2925, 2854, 1653, 1495, 1393, 1253, 1095, 833, 773 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{49}\text{NO}_2\text{SiNa}$: 518.3425, found: 518.3434.

$[\alpha]^{25}_{\text{D}} = +0.6$ (c 1.0, CHCl_3); 87% ee from (*S*)-L1.



N-Benzyl-3-(4-methoxybutyl)-N-phenylnonanamide (Fig. 2, entry 28). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-6**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 182 mg, 74% yield, 90% ee; (*S*)-**L1**: 171 mg, 70% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 46.8 min (minor), 48.6 min (major).

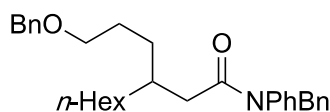
¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 6.96 (dd, *J* = 7.8, 1.9 Hz, 2H), 4.90 (s, 2H), 3.34 (t, *J* = 6.6 Hz, 2H), 3.33 (s, 3H), 2.02 (d, *J* = 7.8 Hz, 2H), 1.98 – 1.86 (m, 1H), 1.60 – 1.44 (m, 2H), 1.32 – 1.10 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 72.8, 58.5, 53.0, 38.9, 35.2, 33.8, 33.7, 31.8, 29.9, 29.6, 26.5, 23.1, 22.6, 14.1.

FT-IR (film): 2922, 2853, 1655, 1595, 1494, 1392, 1116, 727 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₇H₃₉NO₂Na: 432.2873, found: 432.2882.

[α]_D²⁴ = -1.0 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-3-(3-(benzyloxy)propyl)-N-phenylnonanamide (Fig. 2, entry 29). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-7**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 169 mg, 60% yield, 85% ee; (*S*)-**L1**: 168 mg, 60% yield, 84% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 22.2 min (major), 24.9 min (minor).

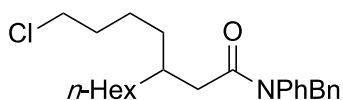
¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.25 (m, 8H), 7.24 – 7.20 (m, 3H), 7.19 – 7.15 (m, 2H), 6.91 (dd, *J* = 7.5, 2.2 Hz, 2H), 4.89 (d, *J* = 14.2 Hz, 1H), 4.83 (d, *J* = 14.2 Hz, 1H), 4.46 (s, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.05 – 1.87 (m, 3H), 1.53 – 1.39 (m, 2H), 1.30 – 1.06 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 142.5, 138.6, 137.7, 129.4, 128.8, 128.5, 128.29, 128.26, 127.8, 127.6, 127.4, 127.2, 72.8, 70.7, 53.0, 38.9, 34.9, 33.8, 31.8, 30.2, 29.6, 26.8, 26.5, 22.6, 14.1.

FT-IR (film): 2923, 2852, 1655, 1594, 1494, 1392, 733 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₃₂H₄₁NO₂Na: 494.3030, found: 494.3034.

[α]_D²⁴ = +2.9 (*c* 1.0, CHCl₃); 84% ee from (*S*)-**L1**.



N-Benzyl-3-(4-chlorobutyl)-N-phenylnonanamide (Fig. 2, entry 30). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-8**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 232 mg, 94% yield, 90% ee; (*S*)-**L1**: 232 mg, 94% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 17.1 min (minor), 18.3 min (major).

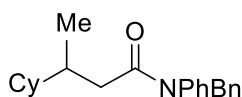
^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.22 (m, 3H), 7.21 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.87 (dd, $J = 7.7, 1.9$ Hz, 2H), 4.83 (d, $J = 14.4$ Hz, 1H), 4.79 (d, $J = 14.4$ Hz, 1H), 3.42 (t, $J = 6.7$ Hz, 2H), 2.00 – 1.81 (m, 3H), 1.68 – 1.58 (m, 2H), 1.27 – 0.98 (m, 14H), 0.80 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 142.5, 137.7, 129.5, 128.8, 128.5, 128.3, 127.8, 127.3, 53.0, 45.1, 38.9, 34.9, 33.8, 33.0, 32.7, 31.8, 29.5, 26.5, 23.8, 22.6, 14.1.

FT-IR (film): 2924, 2854, 1653, 1594, 1494, 1394, 727 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{36}\text{ClNO}$: 436.2378, found: 436.2378.

$[\alpha]_{\text{D}}^{25} = -4.1$ (c 1.0, CHCl_3); 90% ee from (*S*)-**L1**.



N-Benzyl-3-cyclohexyl-N-phenylbutanamide (Fig. 2, entry 31). The title compound was synthesized according to **GP-8** from iodocyclohexane and zinc nucleophile **Zn-9**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 171 mg, 86% yield, 89% ee; (*S*)-**L1**: 183 mg, 91% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (3.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 14.6 min (minor), 18.0 min (major).

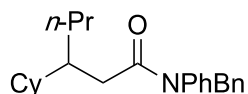
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 3H), 7.29 – 7.24 (m, 3H), 7.24 – 7.19 (m, 2H), 6.96 (dd, $J = 7.7, 1.9$ Hz, 2H), 4.92 (d, $J = 14.3$ Hz, 1H), 4.90 (d, $J = 14.3$ Hz, 1H), 2.18 (dd, $J = 14.4, 5.0$ Hz, 1H), 2.03 – 1.92 (m, 1H), 1.87 (dd, $J = 14.4, 8.7$ Hz, 1H), 1.73 – 1.56 (m, 3H), 1.52 (d, $J = 12.7$ Hz, 1H), 1.39 (d, $J = 12.4$ Hz, 1H), 1.23 – 1.02 (m, 4H), 0.96 – 0.74 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.8, 127.2, 53.0, 42.3, 38.7, 35.5, 30.4, 28.7, 26.7, 26.6, 26.5, 16.4.

FT-IR (film): 2921, 2849, 1651, 1594, 1494, 1392, 732 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{30}\text{NO}$: 336.2322, found: 336.2322.

$[\alpha]_{\text{D}}^{25} = -22.6$ (c 1.0, CHCl_3); 89% ee from (*S*)-**L1**.



N-Benzyl-3-cyclohexyl-N-phenylhexanamide (Fig. 2, entry 32). The title compound was synthesized according to **GP-8** from iodocyclohexane and zinc nucleophile **Zn-2**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 156 mg, 72% yield, 91% ee; (*S*)-**L1**: 153 mg, 70% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (3.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 12.1 min (minor), 12.9 min (major).

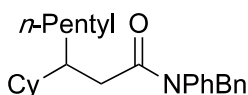
¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.21 (m, 3H), 7.21 – 7.15 (m, 3H), 7.15 – 7.10 (m, 2H), 6.87 (dd, *J* = 7.9, 1.9 Hz, 2H), 4.81 (s, 2H), 2.00 (dd, *J* = 14.8, 6.7 Hz, 1H), 1.86 (dd, *J* = 14.9, 6.9 Hz, 1H), 1.82 – 1.72 (m, 1H), 1.62 – 1.49 (m, 3H), 1.38 (d, *J* = 12.0 Hz, 1H), 1.27 (d, *J* = 12.2 Hz, 1H), 1.22 – 0.92 (m, 8H), 0.84 – 0.67 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 173.2, 142.6, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 40.3, 40.2, 36.1, 33.1, 29.5, 29.4, 26.8, 26.7, 20.5, 14.4.

FT-IR (film): 2921, 2850, 1653, 1594, 1494, 1448, 1391, 732 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₅H₃₄NO: 364.2635, found: 364.2634.

[α]_D²⁴ = +6.9 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Benzyl-3-cyclohexyl-N-phenyloctanamide (Fig. 2, entry 33). The title compound was synthesized according to **GP-8** from iodocyclohexane and zinc nucleophile **Zn-3**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 146 mg, 62% yield, 90% ee; (*S*)-**L1**: 145 mg, 62% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 13.5 min (minor), 14.9 min (major).

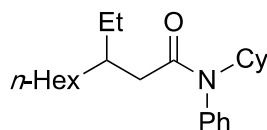
¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (m, 3H), 7.21 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.87 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.83 (d, *J* = 14.2 Hz, 1H), 4.79 (d, *J* = 14.2 Hz, 1H), 2.00 (dd, *J* = 14.9, 6.7 Hz, 1H), 1.87 (dd, *J* = 14.9, 6.9 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.65 – 1.47 (m, 3H), 1.44 – 1.24 (m, 2H), 1.23 – 0.89 (m, 12H), 0.86 – 0.66 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 173.2, 142.7, 137.8, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 53.0, 40.6, 40.2, 36.1, 32.2, 30.7, 29.5, 29.4, 27.0, 26.8, 26.7, 22.7, 14.1.

FT-IR (film): 2921, 2850, 1655, 1595, 1494, 1391, 727 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₇H₃₈NO: 392.2948, found: 392.2947.

[α]_D²⁴ = +11.3 (*c* 1.0, CHCl₃); 91% ee from (*S*)-**L1**.



N-Cyclohexyl-3-ethyl-N-phenylnonanamide (Fig. 2, entry 34). The title compound was synthesized according to **GP-7** from 1-iodohexane (0.50 mmol) and zinc nucleophile **Zn-10** (0.75 mmol). The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 151 mg, 88% yield, 90% ee; (*S*)-**L1**: 155 mg, 90% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 10.9 min (major), 12.6 min (minor).

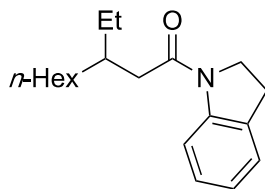
¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.25 (m, 3H), 7.06 – 6.93 (m, 2H), 4.56 (tt, *J* = 12.1, 3.6 Hz, 1H), 1.80 – 1.70 (m, 5H), 1.64 (dt, *J* = 13.7, 3.5 Hz, 2H), 1.56 – 1.42 (m, 1H), 1.32 (qt, *J* = 13.2, 3.5 Hz, 2H), 1.25 – 1.01 (m, 12H), 1.01 – 0.82 (m, 3H), 0.79 (t, *J* = 7.0 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.1, 139.5, 130.4, 128.9, 127.9, 53.9, 39.3, 36.4, 33.3, 31.8, 31.7, 29.5, 26.5, 26.2, 25.8, 25.4, 22.6, 14.1, 10.8.

FT-IR (film): 2927, 2854, 1652, 1595, 1493, 1391, 1262, 1072, 705 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₃H₃₇NONa: 366.2767, found: 366.2773.

[α]_D²⁵ = -13.2 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



3-Ethyl-1-(indolin-1-yl)nonan-1-one (Fig. 2, entry 35). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-11**. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). White solid.

(*R*)-**L1**: 157 mg, 91% yield, 90% ee; (*S*)-**L1**: 149 mg, 87% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 10.4 min (major), 13.1 min (minor).

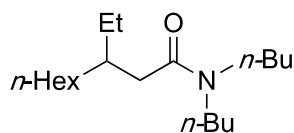
¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.06 (m, 2H), 6.93 (td, *J* = 7.4, 1.1 Hz, 1H), 4.00 (t, *J* = 8.5 Hz, 2H), 3.12 (t, *J* = 8.5 Hz, 2H), 2.26 (d, *J* = 6.8 Hz, 2H), 1.94 (hept, *J* = 6.5 Hz, 1H), 1.39 – 1.31 (m, 2H), 1.29 – 1.13 (m, 10H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.3, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.1, 40.4, 35.7, 33.4, 31.9, 29.6, 28.0, 26.7, 26.3, 22.7, 14.1, 10.9.

FT-IR (film): 2959, 2922, 2853, 1647, 1599, 1480, 1462, 1415, 753, 745 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₉H₃₀NO: 288.2322, found: 288.2320.

[α]_D²⁵ = +4.4 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



***N,N*-Dibutyl-3-ethylnonanamide (Fig. 2, entry 36).** The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-12**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 175 mg, 98% yield, 85% ee; (*S*)-**L1**: 178 mg, 99% yield, 85% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (0.5% 2-PrOH in hexanes, 0.5 mL/min); retention times for compound obtained using (*R*)-**L1**: 13.7 min (major), 15.0 min (minor).

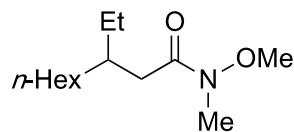
¹H NMR (400 MHz, CDCl₃) δ 3.31 – 3.19 (m, 2H), 3.19 – 3.04 (m, 2H), 2.12 (d, *J* = 6.9 Hz, 2H), 1.90 – 1.74 (m, *J* = 5.7 Hz, 1H), 1.53 – 1.37 (m, 4H), 1.32 – 1.12 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 6.9 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 172.4, 47.8, 45.7, 37.5, 36.4, 33.5, 31.9, 31.3, 29.9, 29.7, 26.7, 26.3, 22.6, 20.3, 20.1, 14.1, 13.9, 13.8, 10.9.

FT-IR (film): 2956, 2925, 2872, 1640, 1456, 1419, 1377, 730 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₉H₄₀NO: 298.3104, found: 298.3109.

[α]_D²⁴ = -0.6 (c 1.0, CHCl₃); 85% ee from (*S*)-**L1**.



3-Ethyl-*N*-methoxy-*N*-methylnonanamide (Fig. 2, entry 37). The title compound was synthesized according to **GP-7** from 1-iodohexane and zinc nucleophile **Zn-13**. The product was purified by column chromatography on silica gel (1:10 → 1:6 EtOAc/hexanes). Colorless oil.

(*R*)-**L1**: 124 mg, 90% yield, 88% ee; (*S*)-**L1**: 129 mg, 94% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (0.7% 2-PrOH in hexanes, 0.5 mL/min); retention times for compound obtained using (*R*)-**L1**: 31.9 min (minor), 33.4 min (major).

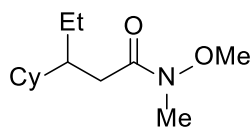
¹H NMR (400 MHz, CDCl₃) δ 3.69 (s, 3H), 3.19 (s, 3H), 2.43 – 2.24 (m, 2H), 1.97 – 1.83 (m, 1H), 1.42 – 1.20 (m, 12H), 0.93 – 0.81 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 174.6, 61.1, 36.2, 35.7, 33.5, 32.1, 31.9, 29.6, 26.6, 26.4, 22.6, 14.1, 10.8.

FT-IR (film): 2957, 2924, 2855, 1662, 1457, 1379, 1006, 749 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₃H₂₈NO₂: 230.2115, found: 230.2118.

[α]_D²⁴ = -2.3 (c 1.0, CHCl₃); 88% ee from (*S*)-**L1**.



3-Cyclohexyl-*N*-methoxy-*N*-methylpentanamide (Fig. 2, entry 38). The title compound was synthesized according to **GP-8** from iodocyclohexane and zinc nucleophile **Zn-13**. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Pale-yellow oil.

(*R*)-**L1**: 122 mg, 90% yield, 88% ee; (*S*)-**L1**: 124 mg, 91% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 6.6 min (minor), 7.7 min (major).

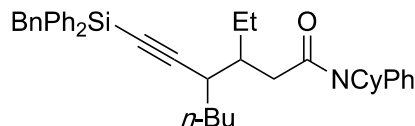
¹H NMR (400 MHz, CDCl₃) δ 3.70 (s, 3H), 3.20 (s, 3H), 2.42 (dd, *J* = 15.3, 5.9 Hz, 1H), 2.28 (dd, *J* = 15.3, 7.6 Hz, 1H), 1.85 – 1.71 (m, 3H), 1.70 – 1.58 (m, 3H), 1.47 – 1.33 (m, 2H), 1.32 – 1.15 (m, 3H), 1.15 – 0.94 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 61.1, 41.1, 40.0, 33.2, 32.2, 30.0, 29.2, 26.83, 26.79, 26.78, 23.8, 11.8.

FT-IR (film): 2921, 2850, 1662, 1447, 1380, 1008, 749 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₃H₂₆NO₂: 228.1958, found: 228.1961.

[α]_D²⁴ = -9.1 (*c* 1.0, CHCl₃); 88% ee from (*S*)-**L1**.



4-((Benzylidiphenylsilyl)ethynyl)-*N*-cyclohexyl-3-ethyl-*N*-phenyloctanamide (Fig. 3, entry 1). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 228 mg, 73% yield, 92% ee, 98:2 dr;

(*S,R*)-**L2**: 232 mg, 74% yield, 92% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 8.8 min (major), 9.6 min (minor).

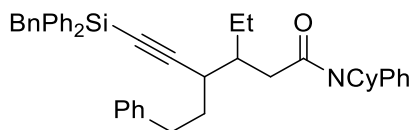
¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.38 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.18 (m, 5H), 7.12 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.01 – 6.82 (m, 6H), 6.82 – 6.73 (m, 2H), 4.53 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.61 – 2.55 (m, 1H), 2.53 (d, *J* = 14.0 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.02 – 1.83 (m, 3H), 1.80 – 1.58 (m, 4H), 1.52 – 1.20 (m, 10H), 1.03 – 0.74 (m, 7H), 0.68 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 139.1, 137.8, 134.9, 134.8, 134.4, 134.3, 130.5, 130.1, 129.51, 129.48, 129.2, 129.0, 128.9, 128.0, 127.8, 127.71, 127.67, 124.3, 114.6, 80.6, 54.0, 39.8, 37.5, 36.7, 32.6, 31.7, 31.6, 30.2, 25.80, 25.78, 25.4, 24.6, 22.6, 22.3, 14.0, 11.9.

FT-IR (film): 3024, 2931, 2858, 2162, 1651, 1596, 1395, 1111, 769, 733, 697 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{52}\text{NOSi}$: 626.3813, found: 626.3813.

$[\alpha]_D^{25} = +20.1$ (c 1.0, CHCl_3); 92% ee, 98:2 dr from (*S,R*)-**L2**.



6-(Benzylidiphenylsilyl)-N-cyclohexyl-3-ethyl-4-phenethyl-N-phenylhex-5-ynamide (Fig. 3, entry 2). The title compound was synthesized according to **GP-9** from benzyl(3-bromo-5-phenylpent-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). White foamy solid.

(*R,S*)-**L2**: 252 mg, 75% yield, 89% ee, 98:2 dr;

(*S,R*)-**L2**: 251 mg, 75% yield, 90% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 12.6 min (major), 18.5 min (minor).

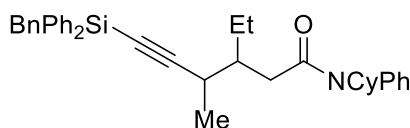
^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.41 (m, 4H), 7.36 – 7.29 (m, 2H), 7.28 – 7.16 (m, 7H), 7.15 – 7.05 (m, 4H), 7.01 – 6.88 (m, 5H), 6.87 – 6.75 (m, 3H), 4.50 (tt, $J = 12.1, 3.5$ Hz, 1H), 2.77 (ddd, $J = 13.7, 10.1, 5.0$ Hz, 1H), 2.68 – 2.40 (m, 4H), 2.01 – 1.86 (m, 3H), 1.76 – 1.59 (m, 6H), 1.52 – 1.43 (m, 1H), 1.41 – 1.23 (m, 3H), 1.02 – 0.77 (m, 4H), 0.66 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 142.1, 139.0, 137.8, 134.9, 134.8, 134.3, 134.2, 130.4, 130.0, 129.60, 129.57, 129.3, 129.0, 128.9, 128.5, 128.3, 128.0, 127.83, 127.78, 127.7, 125.7, 124.4, 113.9, 81.4, 54.1, 40.1, 37.5, 36.5, 35.0, 34.3, 31.65, 31.55, 25.8, 25.4, 24.6, 22.5, 11.9.

FT-IR (film): 3061, 3026, 2927, 2856, 2164, 1651, 1596, 1493, 1395, 1113, 745 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{47}\text{H}_{52}\text{NOSi}$: 674.3813, found: 674.3822.

$[\alpha]_D^{25} = +9.4$ (c 1.0, CHCl_3); 90% ee, 98:2 dr from (*S,R*)-**L2**.



6-(Benzylidiphenylsilyl)-N-cyclohexyl-3-ethyl-4-methyl-N-phenylhex-5-ynamide (Fig. 3, entry 3). The title compound was synthesized according to **GP-9** from benzyl(3-bromobut-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 223 mg, 77% yield, 90% ee, >98:2 dr;

(*S,R*)-**L2**: 228 mg, 78% yield, 90% ee, >98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK AD-3 column (15.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 8.1 min (major), 9.6 min (minor).

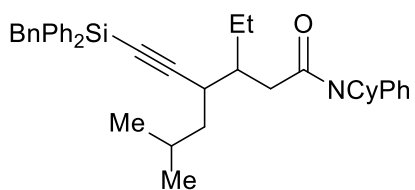
¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.48 (m, 4H), 7.46 – 7.30 (m, 7H), 7.25 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.13 – 6.94 (m, 6H), 6.93 – 6.84 (m, 2H), 4.64 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.82 (qd, *J* = 7.1, 3.6 Hz, 1H), 2.64 (d, *J* = 13.9 Hz, 1H), 2.60 (d, *J* = 13.9 Hz, 1H), 2.17 – 1.91 (m, 3H), 1.91 – 1.70 (m, 4H), 1.65 – 1.54 (m, 1H), 1.53 – 1.34 (m, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.15 – 0.86 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 139.1, 137.8, 134.89, 134.85, 134.24, 134.21, 130.5, 130.1, 129.54, 129.51, 129.2, 129.0, 128.9, 128.0, 127.8, 127.73, 127.69, 124.3, 115.4, 79.8, 54.1, 41.1, 37.4, 31.7, 31.6, 30.3, 25.81, 25.79, 25.4, 24.6, 22.1, 18.6, 11.9.

FT-IR (film): 3050, 3024, 2932, 2344, 2166, 1646, 1394, 1110, 737, 702 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₀H₄₆NOSi: 584.3343, found: 584.3343.

[α]_D²⁵ = +33.1 (*c* 1.0, CHCl₃); 90% ee, >98:2 dr from (*S,R*)-**L2**.



4-((Benzoyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-ethyl-6-methyl-N-phenylheptanamide (Fig. 3, entry 4). The title compound was synthesized according to **GP-9** from benzyl(3-bromo-5-methylhex-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 190 mg, 61% yield, 95% ee, >99:1 dr;

(*S,R*)-**L2**: 197 mg, 63% yield, 95% ee, >99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IC-3 column (15.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 5.2 min (major), 5.8 min (minor).

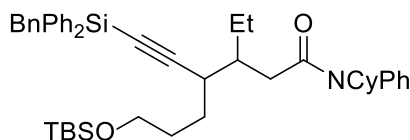
¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.37 (m, 4H), 7.35 – 7.19 (m, 7H), 7.12 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.02 – 6.82 (m, 6H), 6.83 – 6.72 (m, 2H), 4.53 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.67 (ddd, *J* = 10.1, 5.4, 3.4 Hz, 1H), 2.53 (d, *J* = 13.9 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.04 – 1.80 (m, 3H), 1.80 – 1.58 (m, 5H), 1.53 – 1.43 (m, 1H), 1.43 – 1.23 (m, 4H), 1.11 (ddd, *J* = 13.1, 8.7, 5.4 Hz, 1H), 1.03 – 0.74 (m, 10H), 0.68 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 139.1, 137.8, 134.9, 134.8, 134.4, 134.3, 130.5, 130.1, 129.51, 129.48, 129.2, 129.0, 128.9, 128.0, 127.8, 127.72, 127.68, 124.3, 114.6, 80.5, 53.9, 41.7, 39.9, 37.6, 34.5, 31.7, 31.6, 26.1, 25.79, 25.77, 25.4, 24.6, 23.2, 22.3, 21.9, 12.0.

FT-IR (film): 3067, 2929, 2857, 2163, 1651, 1393, 1112, 769, 734, 703 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₃H₅₂NOSi: 626.3813, found: 626.3848.

$[\alpha]_D^{25} = -24.8$ (c 1.0, CHCl_3); 95% ee, >99:1 dr from (*S,R*)-L2.



4-((Benzoyldiphenylsilyl)ethynyl)-7-((*tert*-butyldimethylsilyloxy)-*N*-cyclohexyl-3-ethyl-*N*-phenylheptanamide (Fig. 3, entry 5). The title compound was synthesized according to GP-9 from benzyl(3-bromo-6-((*tert*-butyldimethylsilyloxy)hex-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-L2: 248 mg, 67% yield, 90% ee, 99:1 dr;

(*S,R*)-L2: 248 mg, 67% yield, 91% ee, 99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IF-3 column (15.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (*R,S*)-L2: 9.8 min (major), 11.1 min (minor).

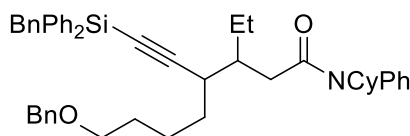
^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.43 (m, 4H), 7.38 – 7.23 (m, 7H), 7.17 (tt, $J = 7.4, 1.0$ Hz, 1H), 7.05 – 6.92 (m, 5H), 6.92 – 6.85 (m, 1H), 6.85 – 6.78 (m, 2H), 4.56 (tt, $J = 12.1, 3.6$ Hz, 1H), 3.64 – 3.51 (m, 2H), 2.62 (td, $J = 7.6, 2.9$ Hz, 1H), 2.57 (d, $J = 13.9$ Hz, 1H), 2.52 (d, $J = 13.9$ Hz, 1H), 2.07 – 1.86 (m, 3H), 1.83 – 1.63 (m, 5H), 1.60 – 1.43 (m, 4H), 1.43 – 1.25 (m, 3H), 1.09 – 0.90 (m, 3H), 0.89 – 0.81 (m, 10H), 0.72 (t, $J = 7.4$ Hz, 3H), 0.00 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 139.1, 137.8, 134.9, 134.8, 134.3, 134.2, 130.5, 130.1, 129.52, 129.48, 129.2, 129.0, 128.9, 128.0, 127.8, 127.72, 127.68, 124.3, 114.3, 80.8, 63.0, 54.0, 39.8, 37.5, 36.4, 31.7, 31.6, 31.2, 29.1, 26.0, 25.80, 25.78, 25.4, 24.6, 22.3, 18.3, 11.9, -5.3.

FT-IR (film): 3050, 3024, 2932, 2857, 2164, 1651, 1394, 1253, 1110, 767, 704 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{48}\text{H}_{63}\text{NO}_2\text{Si}_2\text{Na}$: 764.4290, found: 764.4287.

$[\alpha]_D^{25} = +15.4$ (c 1.0, CHCl_3); 91% ee, 99:1 dr from (*S,R*)-L2.



4-((Benzoyldiphenylsilyl)ethynyl)-8-(benzyloxy)-*N*-cyclohexyl-3-ethyl-*N*-phenyloctanamide (Fig. 3, entry 6). The title compound was synthesized according to GP-9 from benzyl(7-(benzyloxy)-3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Pale-yellow oil.

(*R,S*)-L2: 285 mg, 78% yield, 92% ee, 98:2 dr;

(*S,R*)-L2: 265 mg, 73% yield, 92% ee, 99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-L2: 15.1 min (major), 16.7 min (minor).

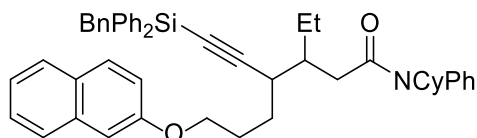
¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.36 (m, 4H), 7.34 – 7.16 (m, 12H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.81 (m, 6H), 6.81 – 6.71 (m, 2H), 4.52 (tt, *J* = 12.1, 3.6 Hz, 1H), 4.41 (s, 2H), 3.37 (t, *J* = 6.5 Hz, 2H), 2.58 (dt, *J* = 9.0, 4.1 Hz, 1H), 2.52 (d, *J* = 13.9 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.03 – 1.82 (m, 3H), 1.78 – 1.60 (m, 4H), 1.58 – 1.27 (m, 10H), 1.01 – 0.73 (m, 4H), 0.67 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.5, 139.0, 138.6, 137.8, 134.9, 134.8, 134.32, 134.26, 130.5, 130.1, 129.53, 129.50, 129.2, 129.0, 128.9, 128.3, 128.0, 127.8, 127.72, 127.68, 127.59, 127.4, 124.3, 114.3, 80.8, 72.8, 70.4, 54.0, 39.8, 37.5, 36.7, 32.7, 31.7, 31.6, 29.6, 25.79, 25.78, 25.4, 24.62, 24.61, 22.3, 11.9.

FT-IR (film): 3062, 3025, 2933, 2857, 2163, 1651, 1594, 1395, 1111, 735, 700 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₅₀H₅₇NO₂SiNa: 754.4051, found: 754.4059.

[α]_D²² = +13.6 (*c* 1.0, CHCl₃); 92% ee, 99:1 dr from (*S,R*)-L2.



4-((Benzyldiphenylsilyl)ethynyl)-*N*-cyclohexyl-3-ethyl-7-(naphthalen-2-yloxy)-*N*-phenylheptanamide (Fig. 3, entry 7). The title compound was synthesized according to GP-9 from benzyl(3-bromo-6-(naphthalen-2-yloxy)hex-1-yn-1-yl)diphenylsilane and zinc nucleophile Zn-10. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). White foamy solid.

(*R,S*)-L2: 298 mg, 79% yield, 91% ee, >99:1 dr;

(*S,R*)-L2: 314 mg, 83% yield, 91% ee, >99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (4.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-L2: 17.8 min (major), 19.7 min (minor).

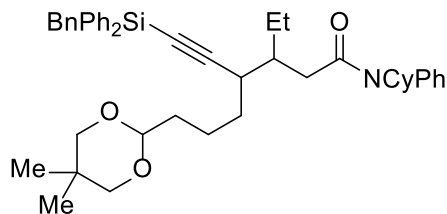
¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.63 (m, 3H), 7.58 – 7.47 (m, 4H), 7.42 – 7.24 (m, 9H), 7.20 – 7.07 (m, 3H), 7.07 – 6.89 (m, 6H), 6.86 (d, *J* = 7.2 Hz, 2H), 4.57 (tt, *J* = 12.1, 3.7 Hz, 1H), 4.12 – 3.97 (m, 2H), 2.83 – 2.66 (m, 1H), 2.59 (d, *J* = 13.9 Hz, 1H), 2.55 (d, *J* = 13.9 Hz, 1H), 2.16 – 1.83 (m, 5H), 1.83 – 1.61 (m, 6H), 1.57 – 1.28 (m, 4H), 1.11 – 0.82 (m, 4H), 0.75 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 157.0, 139.0, 137.8, 134.83, 134.79, 134.6, 134.19, 134.16, 130.4, 130.0, 129.55, 129.53, 129.24, 129.21, 128.93, 128.87, 128.83, 128.0, 127.8, 127.74, 127.71, 127.5, 126.7, 126.2, 124.4, 123.4, 119.0, 113.9, 106.5, 81.2, 67.6, 54.0, 39.9, 37.4, 36.5, 31.6, 31.5, 29.5, 27.7, 25.7, 25.3, 24.5, 22.3, 11.9.

FT-IR (film): 3056, 3023, 2931, 2858, 2165, 1649, 1633, 1598, 1391, 1112, 733, 702 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₅₂H₅₆NO₂Si: 754.4075, found: 754.4079.

[α]_D²² = +11.4 (*c* 1.0, CHCl₃); 91% ee, >99:1 dr from (*S,R*)-L2.



4-((Benzyldiphenylsilyl)ethynyl)-N-cyclohexyl-7-(5,5-dimethyl-1,3-dioxan-2-yl)-3-ethyl-N-phenylheptanamide (Fig. 3, entry 8). The title compound was synthesized according to GP-9 from benzyl(3-bromo-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 266 mg, 73% yield, 88% ee, 98:2 dr;

(*S,R*)-**L2**: 265 mg, 73% yield, 89% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (4.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 9.0 min (minor), 10.9 min (major).

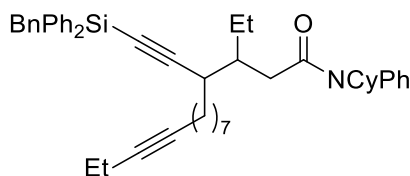
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.35 (m, 4H), 7.34 – 7.20 (m, 7H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.87 (m, 5H), 6.87 – 6.81 (m, 1H), 6.79 (d, *J* = 6.9 Hz, 2H), 4.51 (tt, *J* = 12.1, 3.6 Hz, 1H), 4.30 (t, *J* = 4.7 Hz, 1H), 3.51 (dt, *J* = 11.1, 2.6 Hz, 2H), 3.32 (dd, *J* = 11.1, 5.3 Hz, 2H), 2.61 – 2.55 (m, 1H), 2.53 (d, *J* = 13.9 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.01 – 1.85 (m, 3H), 1.77 – 1.56 (m, 6H), 1.55 – 1.44 (m, 2H), 1.44 – 1.24 (m, 6H), 1.11 (s, 3H), 1.00 – 0.77 (m, 4H), 0.67 (t, *J* = 7.4 Hz, 3H), 0.63 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.5, 139.0, 137.8, 134.9, 134.8, 134.32, 134.26, 130.5, 130.0, 129.49, 129.45, 129.2, 128.9, 128.8, 128.0, 127.8, 127.70, 127.66, 124.3, 114.2, 102.1, 80.8, 77.2, 54.0, 39.7, 37.5, 36.7, 34.7, 32.6, 31.64, 31.57, 30.1, 25.8, 25.4, 24.6, 23.0, 22.6, 22.3, 21.8, 11.9.

FT-IR (film): 3049, 2935, 2858, 2162, 1651, 1392, 1116, 749 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₈H₆₀NO₃Si: 726.4337, found: 726.4339.

[α]_D²⁵ = +8.3 (*c* 1.0, CHCl₃); 89% ee, 98:2 dr from (*S,R*)-**L2**.



4-((Benzyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-ethyl-N-phenylpentadec-12-ynamide (Fig. 3, entry 9). The title compound was synthesized according to GP-9 from benzyl(3-bromotetradeca-1,11-diyn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 283 mg, 79% yield, 90% ee, 99:1 dr;

(*S,R*)-**L2**: 273 mg, 76% yield, 91% ee, >98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 7.8 min (major), 8.9 min (minor).

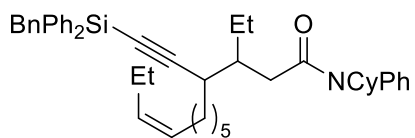
¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.35 (m, 4H), 7.35 – 7.20 (m, 7H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.82 (m, 6H), 6.82 – 6.73 (m, 2H), 4.53 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.65 – 2.37 (m, 3H), 2.16 – 2.01 (m, 4H), 2.01 – 1.81 (m, 3H), 1.79 – 1.57 (m, 4H), 1.52 – 1.17 (m, 16H), 1.04 (t, *J* = 7.3 Hz, 3H), 1.01 – 0.75 (m, 4H), 0.68 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 139.1, 137.8, 134.9, 134.8, 134.4, 134.3, 130.5, 130.1, 129.52, 129.49, 129.2, 129.0, 128.9, 128.0, 127.8, 127.72, 127.67, 124.3, 114.6, 81.6, 80.6, 79.6, 54.0, 39.9, 37.5, 36.8, 32.9, 31.7, 31.6, 29.4, 29.2, 29.1, 28.9, 28.0, 25.8, 25.4, 24.6, 22.3, 18.7, 14.4, 12.4, 11.9.

FT-IR (film): 3049, 2932, 2857, 2163, 1651, 1394, 1112, 765, 733, 702 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₅₀H₆₁NOSiNa: 742.4415, found: 742.4415.

[α]_D²⁵ = +12.9 (*c* 1.0, CHCl₃); 91% ee, >98:2 dr from (*S,R*)-**L2**.



(*Z*)-4-((Benzylidiphenylsilyl)ethynyl)-*N*-cyclohexyl-3-ethyl-*N*-phenyltridec-10-enamide (Fig. 3, entry 10). The title compound was synthesized according to **GP-9** from (*Z*)-benzyl(3-bromododec-9-en-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 260 mg, 75% yield, 90% ee, 98:2 dr;

(*S,R*)-**L2**: 266 mg, 77% yield, 92% ee, 98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IE-3 column (20.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 5.8 min (major), 6.4 min (minor).

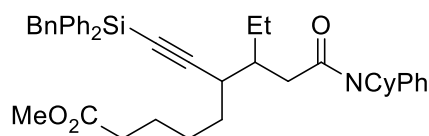
¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.37 (m, 4H), 7.35 – 7.18 (m, 7H), 7.13 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.03 – 6.83 (m, 6H), 6.83 – 6.72 (m, 2H), 5.38 – 5.17 (m, 2H), 4.52 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.63 – 2.42 (m, 3H), 2.07 – 1.83 (m, 7H), 1.83 – 1.56 (m, 4H), 1.52 – 1.19 (m, 12H), 1.02 – 0.75 (m, 7H), 0.68 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.6, 139.1, 137.8, 134.9, 134.8, 134.4, 134.3, 131.5, 130.5, 130.1, 129.52, 129.48, 129.2, 129.0, 128.9, 128.0, 127.8, 127.72, 127.67, 124.3, 114.6, 80.6, 54.0, 39.8, 37.5, 36.8, 32.9, 31.7, 31.6, 29.7, 29.2, 27.9, 27.1, 25.80, 25.79, 25.4, 24.6, 22.3, 20.5, 14.4, 11.9.

FT-IR (film): 3001, 2926, 2858, 2163, 1651, 1595, 1393, 1110, 768, 734, 704 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₈H₆₀NOSi: 694.4439, found: 694.4441.

[α]_D²⁵ = +13.8 (*c* 1.0, CHCl₃); 92% ee, 98:2 dr from (*S,R*)-**L2**.



Methyl 6-((benzyldiphenylsilyl)ethynyl)-9-(cyclohexyl(phenyl)amino)-7-ethyl-9-oxononanoate (Fig. 3, entry 11). The title compound was synthesized according to **GP-9** from methyl 8-(benzyldiphenylsilyl)-6-bromooct-7-ynoate and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:10 → 1:5 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 249 mg, 73% yield, 93% ee, >99:1 dr;

(*S,R*)-**L2**: 250 mg, 73% yield, 93% ee, >99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 22.2 min (major), 25.7 min (minor).

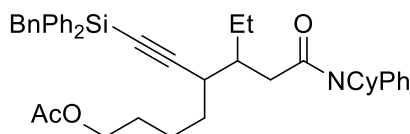
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.40 (m, 4H), 7.34 – 7.21 (m, 7H), 7.16 – 7.10 (m, 1H), 7.00 – 6.89 (m, 5H), 6.88 – 6.81 (m, 1H), 6.81 – 6.73 (m, 2H), 4.52 (tt, *J* = 12.1, 3.6 Hz, 1H), 3.56 (s, 3H), 2.63 – 2.55 (m, 1H), 2.53 (d, *J* = 13.9 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.27 – 2.13 (m, 2H), 2.01 – 1.84 (m, 3H), 1.79 – 1.60 (m, 4H), 1.57 – 1.25 (m, 10H), 1.01 – 0.74 (m, 4H), 0.67 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.1, 171.5, 139.0, 137.8, 134.84, 134.80, 134.3, 134.2, 130.5, 130.0, 129.6, 129.5, 129.3, 128.94, 128.88, 128.0, 127.8, 127.74, 127.70, 124.4, 114.1, 80.9, 54.0, 51.4, 39.8, 37.4, 36.6, 34.0, 32.5, 31.7, 31.6, 27.6, 25.79, 25.77, 25.4, 24.8, 24.6, 22.2, 11.9.

FT-IR (film): 3024, 2929, 2857, 2163, 1732, 1651, 1595, 1395, 1110, 769, 735, 708 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₅H₅₄NO₃Si: 684.3867, found: 684.3859.

[α]_D²² = +13.4 (*c* 1.0, CHCl₃); 93% ee, >99:1 dr from (*S,R*)-**L2**.



5-((Benzyldiphenylsilyl)ethynyl)-8-(cyclohexyl(phenyl)amino)-6-ethyl-8-oxooctyl acetate (Fig. 3, entry 12). The title compound was synthesized according to **GP-9** from 7-(benzyldiphenylsilyl)-5-bromohept-6-yn-1-yl acetate and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:15 → 1:5 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 265 mg, 78% yield, 92% ee, 99:1 dr;

(*S,R*)-**L2**: 246 mg, 72% yield, 92% ee, 99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (4.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 15.4 min (major), 19.1 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.38 (m, 4H), 7.32 – 7.27 (m, 2H), 7.27 – 7.19 (m, 5H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.83 (m, 6H), 6.83 – 6.72 (m, 2H), 4.52 (tt, *J* = 12.1, 3.6 Hz, 1H), 3.96 (t, *J* =

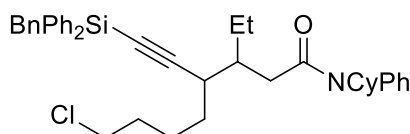
6.3 Hz, 2H), 2.60 (td, $J = 8.4, 4.1$ Hz, 1H), 2.53 (d, $J = 13.8$ Hz, 1H), 2.48 (d, $J = 13.9$ Hz, 1H), 2.00 – 1.84 (m, 6H), 1.78 – 1.60 (m, 4H), 1.59 – 1.42 (m, 5H), 1.40 – 1.25 (m, 5H), 0.99 – 0.74 (m, 4H), 0.67 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 171.1, 139.0, 137.7, 134.80, 134.76, 134.22, 134.16, 130.4, 130.0, 129.55, 129.52, 129.2, 128.91, 128.86, 128.0, 127.74, 127.72, 127.68, 124.3, 114.0, 81.0, 64.4, 54.0, 39.8, 37.4, 36.6, 32.5, 31.6, 31.5, 28.4, 25.8, 25.7, 25.3, 24.5, 24.4, 22.2, 20.9, 11.9.

FT-IR (film): 3048, 3024, 2931, 2858, 2165, 1737, 1651, 1240, 1112, 706, 699 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{45}\text{H}_{54}\text{NO}_3\text{Si}$: 684.3867, found: 684.3871.

$[\alpha]_D^{25} = +14.3$ (c 1.0, CHCl_3); 92% ee, 99:1 dr from (*S,R*)-L2.



4-((Benzyldiphenylsilyl)ethynyl)-8-chloro-N-cyclohexyl-3-ethyl-N-phenyloctanamide (Fig. 3, entry 13). The title compound was synthesized according to GP-9 from benzyl(3-bromo-7-chlorohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-L2: 230 mg, 70% yield, 92% ee, >99:1 dr;

(*S,R*)-L2: 234 mg, 71% yield, 93% ee, >99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK AD-3 column (20.0% 2-PrOH in supercritical CO_2 , 2.5 ml/min); retention times for compound obtained using (*R,S*)-L2*: 5.4 min (major), 5.8 min (minor).

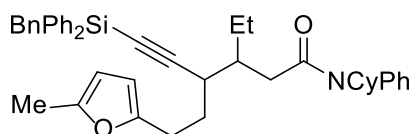
^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.47 (m, 4H), 7.45 – 7.29 (m, 7H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.12 – 6.99 (m, 5H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.92 – 6.84 (m, 2H), 4.62 (tt, $J = 12.1, 3.6$ Hz, 1H), 3.51 (t, $J = 6.7$ Hz, 2H), 2.74 – 2.67 (m, 1H), 2.64 (d, $J = 13.9$ Hz, 1H), 2.59 (d, $J = 13.9$ Hz, 1H), 2.13 – 1.91 (m, 3H), 1.87 – 1.70 (m, 6H), 1.65 – 1.34 (m, 8H), 1.11 – 0.88 (m, 4H), 0.78 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.4, 139.0, 137.8, 134.82, 134.78, 134.2, 134.1, 130.4, 130.0, 129.55, 129.52, 129.2, 128.92, 128.87, 128.0, 127.74, 127.72, 127.68, 124.3, 113.9, 81.1, 54.0, 44.8, 39.8, 37.4, 36.5, 32.4, 32.1, 31.6, 31.5, 25.8, 25.3, 24.5, 22.2, 11.9.

FT-IR (film): 3049, 2929, 2857, 2164, 1645, 1595, 1394, 1111, 760, 734, 707 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{51}\text{ClNOSi}$: 660.3423, found: 660.3418.

$[\alpha]_D^{25} = +13.8$ (c 1.0, CHCl_3); 93% ee, >99:1 dr from (*S,R*)-L2.



6-((Benzyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-ethyl-4-(2-(5-methylfuran-2-yl)ethyl)-N-phenylhex-5-ynamide (Fig. 3, entry 14). The title compound was synthesized according to

GP-9 from benzyl(3-bromo-5-(5-methylfuran-2-yl)pent-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 286 mg, 84% yield, 88% ee, 98:2 dr;

(*S,R*)-**L2**: 272 mg, 80% yield, 90% ee, 98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IE-3 column (20.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 6.4 min (major), 7.5 min (minor).

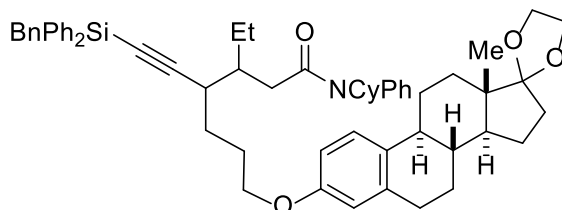
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.40 (m, 4H), 7.35 – 7.28 (m, 2H), 7.28 – 7.19 (m, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.88 (m, 5H), 6.88 – 6.75 (m, 3H), 5.80 – 5.71 (m, 2H), 4.51 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.79 – 2.66 (m, 1H), 2.66 – 2.42 (m, 4H), 2.18 (s, 3H), 2.03 – 1.85 (m, 3H), 1.78 – 1.59 (m, 6H), 1.53 – 1.43 (m, 1H), 1.39 – 1.23 (m, 3H), 1.06 – 0.79 (m, 4H), 0.68 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 153.8, 150.2, 139.0, 137.8, 134.9, 134.8, 134.22, 134.17, 130.4, 130.1, 129.6, 129.5, 129.2, 128.94, 128.87, 128.0, 127.82, 127.75, 127.7, 124.4, 113.6, 105.7, 105.5, 81.4, 54.1, 40.0, 37.5, 36.3, 31.65, 31.57, 31.4, 26.6, 25.80, 25.78, 25.4, 24.6, 22.5, 13.5, 11.9.

FT-IR (film): 3048, 3025, 2933, 2857, 2164, 1650, 1394, 1112, 759, 741, 710 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₄₆H₅₁NO₂SiNa: 700.3581, found: 700.3582.

[α]_D²² = +7.4 (*c* 1.0, CHCl₃); 90% ee, 98:2 dr from (*S,R*)-**L2**.



4-((Benzyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-ethyl-7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)-N-phenylheptanamide (Fig. 3, entry 15). The title compound was synthesized according to **GP-9** from benzyl(3-bromo-6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)hex-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). White solid.

(*R,S*)-**L2**: 345 mg, 75% yield, 6:94 dr;

(*S,R*)-**L2**: 321 mg, 69% yield, 94:6 dr.

SFC analysis: The dr was determined via SFC on a CHIRALPAK AD-3 column (30.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 7.8 min (major), 10.0 min (minor).

NMR data for the product from (*R,S*)-**L2**:

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.39 (m, 4H), 7.33 – 7.27 (m, 2H), 7.27 – 7.20 (m, 5H), 7.15 – 7.06 (m, 2H), 7.00 – 6.88 (m, 5H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.81 – 6.73 (m, 2H), 6.61 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 4.51 (tt, *J* = 12.1, 3.6 Hz, 1H), 3.90 – 3.79 (m, 6H), 2.84 – 2.67 (m,

2H), 2.67 – 2.57 (m, 1H), 2.53 (d, $J = 13.8$ Hz, 1H), 2.48 (d, $J = 13.9$ Hz, 1H), 2.23 (dq, $J = 12.6, 3.6$ Hz, 1H), 2.15 (td, $J = 10.6, 4.1$ Hz, 1H), 2.02 – 1.84 (m, 5H), 1.84 – 1.66 (m, 7H), 1.62 – 1.43 (m, 7H), 1.41 – 1.23 (m, 7H), 1.03 – 0.84 (m, 3H), 0.80 (s, 4H), 0.67 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 156.9, 139.0, 137.9, 137.8, 134.84, 134.80, 134.23, 134.19, 132.5, 130.4, 130.0, 129.53, 129.51, 129.2, 128.94, 128.87, 128.0, 127.8, 127.74, 127.71, 126.2, 124.3, 119.4, 114.4, 113.9, 112.0, 81.1, 67.5, 65.2, 64.5, 54.0, 49.3, 46.1, 43.6, 39.9, 39.0, 37.4, 36.5, 34.2, 31.64, 31.56, 30.7, 29.8, 29.4, 27.8, 27.0, 26.1, 25.78, 25.77, 25.3, 24.6, 22.3, 14.3, 11.9.

NMR data for the product from (*S,R*)-**L2**:

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.39 (m, 4H), 7.35 – 7.18 (m, 7H), 7.16 – 7.07 (m, 2H), 7.03 – 6.82 (m, 6H), 6.82 – 6.73 (m, 2H), 6.61 (dd, $J = 8.6, 2.7$ Hz, 1H), 6.54 (d, $J = 2.7$ Hz, 1H), 4.51 (tt, $J = 12.1, 3.6$ Hz, 1H), 3.96 – 3.73 (m, 6H), 2.85 – 2.67 (m, 2H), 2.67 – 2.58 (m, 1H), 2.53 (d, $J = 13.9$ Hz, 1H), 2.48 (d, $J = 13.9$ Hz, 1H), 2.29 – 2.10 (m, 2H), 2.03 – 1.84 (m, 5H), 1.82 – 1.59 (m, 9H), 1.58 – 1.43 (m, 5H), 1.41 – 1.24 (m, 7H), 1.03 – 0.85 (m, 3H), 0.80 (s, 4H), 0.67 (t, $J = 7.4$ Hz, 3H).

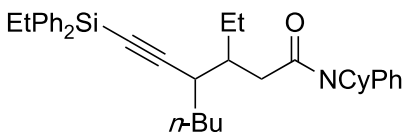
^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 156.9, 139.0, 137.9, 137.8, 134.85, 134.81, 134.24, 134.19, 132.5, 130.4, 130.0, 129.54, 129.52, 129.2, 128.95, 128.88, 128.0, 127.80, 127.75, 127.71, 126.2, 124.4, 119.4, 114.5, 113.9, 112.0, 81.1, 67.5, 65.2, 64.5, 54.0, 49.3, 46.1, 43.6, 39.9, 39.1, 37.4, 36.5, 34.2, 31.65, 31.57, 30.7, 29.8, 29.5, 27.8, 27.0, 26.1, 25.79, 25.78, 25.4, 24.6, 22.3, 14.3, 11.9.

FT-IR (film): 2927, 2165, 1644, 1493, 1241, 1110, 732, 703 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{62}\text{H}_{74}\text{NO}_4\text{Si}$: 924.5382, found: 924.5379.

$[\alpha]_D^{25} = +0.8$ (c 1.0, CHCl_3); 94:6 dr from (*R,S*)-**L2**.

$[\alpha]_D^{25} = +20.3$ (c 1.0, CHCl_3); 6:94 dr from (*S,R*)-**L2**.



N-Cyclohexyl-3-ethyl-4-((ethyldiphenylsilyl)ethynyl)-N-phenyloctanamide (Fig. 3, entry 16). The title compound was synthesized according to **GP-9** from (3-bromohept-1-yn-1-yl)(ethyl)diphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 180 mg, 64% yield, 91% ee, 99:1 dr;

(*S,R*)-**L2**: 176 mg, 63% yield, 91% ee, 99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 6.1 min (major), 6.6 min (minor).

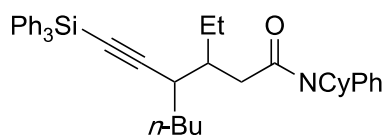
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 4H), 7.37 – 7.18 (m, 7H), 7.18 – 7.11 (m, 1H), 7.03 – 6.82 (m, 3H), 4.53 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.69 – 2.55 (m, 1H), 2.08 – 1.86 (m, 3H), 1.80 – 1.68 (m, 2H), 1.68 – 1.55 (m, 2H), 1.53 – 1.21 (m, 10H), 1.17 – 1.06 (m, 1H), 1.01 – 0.87 (m, 7H), 0.87 – 0.77 (m, 4H), 0.72 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 139.0, 135.3, 135.1, 134.7, 134.6, 130.5, 130.1, 129.31, 129.28, 129.2, 128.9, 127.9, 127.7, 113.5, 81.0, 54.0, 39.7, 37.7, 36.7, 32.7, 31.63, 31.59, 30.2, 25.8, 25.4, 22.6, 22.5, 14.0, 12.0, 7.5, 6.4.

FT-IR (film): 3067, 3048, 2929, 2858, 2162, 1658, 1651, 1595, 1393, 1111, 704, 696 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{38}\text{H}_{49}\text{NOSiNa}$: 586.3476, found: 586.3480.

$[\alpha]_D^{25} = +18.7$ (c 1.0, CHCl_3); 91% ee, 99:1 dr from (*S,R*)-**L2**.



***N*-Cyclohexyl-3-ethyl-*N*-phenyl-4-((triphenylsilyl)ethynyl)octanamide (Fig. 3, entry 17).**

The title compound was synthesized according to **GP-9** from (3-bromohept-1-yn-1-yl)triphenylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 221 mg, 72% yield, 91% ee, 99:1 dr;

(*S,R*)-**L2**: 221 mg, 72% yield, 90% ee, 99:1 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 6.1 min (major), 7.4 min (minor).

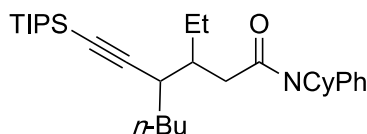
^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.42 (m, 6H), 7.37 – 7.29 (m, 3H), 7.29 – 7.17 (m, 7H), 7.13 – 7.04 (m, 1H), 6.93 (d, $J = 7.9$ Hz, 1H), 6.89 – 6.74 (m, 2H), 4.52 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.73 – 2.61 (m, 1H), 2.08 – 1.85 (m, 3H), 1.80 – 1.57 (m, 4H), 1.55 – 1.21 (m, 10H), 1.19 – 1.03 (m, 1H), 0.98 – 0.85 (m, 2H), 0.85 – 0.76 (m, 4H), 0.70 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 139.0, 135.4, 134.3, 130.5, 130.0, 129.6, 129.2, 128.8, 127.9, 127.7, 114.6, 81.0, 54.0, 39.7, 37.6, 36.6, 32.6, 31.63, 31.58, 30.2, 25.78, 25.77, 25.4, 22.6, 22.5, 14.0, 11.9.

FT-IR (film): 3067, 3048, 2932, 2857, 2162, 1651, 1594, 1394, 1112, 704 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{42}\text{H}_{50}\text{NOSi}$: 612.3656, found: 612.3660.

$[\alpha]_D^{25} = +12.0$ (c 1.0, CHCl_3); 90% ee, 99:1 dr from (*S,R*)-**L2**.



***N*-Cyclohexyl-3-ethyl-*N*-phenyl-4-((triisopropylsilyl)ethynyl)octanamide (Fig. 3, entry 18).**

The title compound was synthesized according to **GP-9** from (3-bromohept-1-yn-1-yl)triisopropylsilane and zinc nucleophile **Zn-10**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 105 mg, 41% yield, 91% ee, >99:1 dr;

(*S,R*)-**L2**: 105 mg, 41% yield, 90% ee, >99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK AD-3 column (5.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 5.1 min (major), 5.6 min (minor).

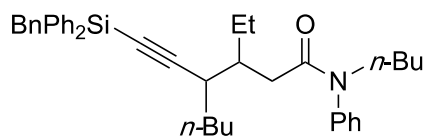
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.22 (m, 3H), 7.08 – 6.92 (m, 2H), 4.54 (tt, *J* = 12.1, 3.7 Hz, 1H), 2.50 – 2.37 (m, 1H), 2.05 – 1.80 (m, 3H), 1.74 (t, *J* = 12.4 Hz, 2H), 1.64 (d, *J* = 13.4 Hz, 2H), 1.49 (d, *J* = 13.4 Hz, 1H), 1.44 – 1.17 (m, 9H), 1.14 – 1.04 (m, 1H), 0.98 – 0.84 (m, 23H), 0.84 – 0.76 (m, 4H), 0.71 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.7, 139.2, 130.5, 130.2, 129.2, 129.0, 128.0, 110.8, 81.5, 54.0, 39.7, 38.1, 36.8, 33.0, 31.6, 30.2, 25.8, 25.4, 22.6, 22.5, 18.7, 18.6, 14.0, 12.0, 11.2.

FT-IR (film): 2931, 2663, 2161, 1652, 1595, 1461, 1393, 1072, 883, 703, 681 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₃₃H₅₅NOSiNa: 532.3945, found: 532.3950.

[α]_D²⁵ = +13.9 (*c* 1.0, CHCl₃); 91% ee, >99:1 dr from (*S,R*)-**L2**.



4-((Benzylidiphenylsilyl)ethynyl)-*N*-butyl-3-ethyl-*N*-phenyloctanamide (Fig. 3, entry 19).

The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-14**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 218 mg, 73% yield, 90% ee, >98:2 dr;

(*S,R*)-**L2**: 226 mg, 76% yield, 90% ee, >98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK AD-3 column (15.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 4.1 min (major), 4.4 min (minor).

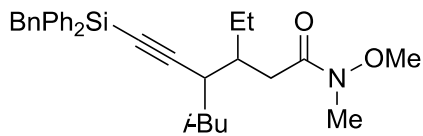
¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.48 (m, 4H), 7.45 – 7.38 (m, 2H), 7.38 – 7.30 (m, 4H), 7.25 – 7.14 (m, 3H), 7.12 – 6.99 (m, 5H), 6.96 – 6.83 (m, 2H), 3.81 – 3.60 (m, 2H), 2.77 – 2.50 (m, 3H), 2.20 (dd, *J* = 16.1, 8.8 Hz, 1H), 2.12 (dd, *J* = 16.1, 4.7 Hz, 1H), 2.08 – 1.92 (m, 1H), 1.60 – 1.28 (m, 11H), 1.09 (ddq, *J* = 14.3, 9.3, 7.3 Hz, 1H), 1.00 – 0.86 (m, 6H), 0.80 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.9, 142.6, 137.8, 134.9, 134.8, 134.4, 134.3, 129.6, 129.52, 129.49, 129.0, 128.3, 127.8, 127.72, 127.68, 127.65, 124.3, 114.5, 80.7, 49.1, 39.9, 36.9, 36.6, 32.6, 30.2, 29.9, 24.6, 22.5, 22.3, 20.1, 14.0, 13.8, 11.9.

FT-IR (film): 3023, 2957, 2932, 2343, 2163, 1653, 1595, 1494, 1402, 1112, 767, 733, 695 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₄₁H₄₉NOSiNa: 622.3476, found: 622.3484.

[α]_D²⁵ = +22.3 (*c* 1.0, CHCl₃); 90% ee, >98:2 dr from (*S,R*)-**L2**.



4-((Benzyl(diphenyl)silyl)ethynyl)-3-ethyl-N-methoxy-N,6-dimethylheptanamide (Fig. 3, entry 20). The title compound was synthesized according to **GP-9** from benzyl(3-bromo-5-methylhex-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-13**. The product was purified by column chromatography on silica gel (1:20 → 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 146 mg, 58% yield, 85% ee, 95:5 dr;

(*S,R*)-**L2**: 147 mg, 57% yield, 85% ee, 95:5 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK OD-H column (0.5% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 14.1 min (minor), 15.3 min (major).

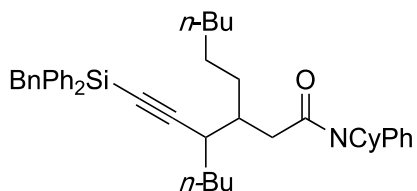
¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.46 (m, 4H), 7.32 – 7.21 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 6.99 – 6.93 (m, 1H), 6.93 – 6.85 (m, 2H), 3.34 (s, 3H), 3.05 (s, 3H), 2.70 (ddd, *J* = 10.5, 5.2, 3.4 Hz, 1H), 2.57 (s, 3H), 2.43 – 2.24 (m, 1H), 1.98 – 1.83 (m, 1H), 1.82 – 1.66 (m, 1H), 1.55 – 1.42 (m, 2H), 1.33 – 1.13 (m, 2H), 0.89 – 0.81 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 173.9, 137.8, 135.89, 135.86, 134.85, 134.84, 134.2, 129.6, 129.2, 129.0, 127.8, 127.72, 127.70, 124.4, 114.6, 80.9, 61.0, 41.3, 39.0, 34.4, 34.2, 32.2, 26.1, 24.5, 23.2, 22.5, 21.8, 12.0.

FT-IR (film): 3024, 2954, 2934, 2163, 1667, 1456, 1428, 1385, 1113, 769, 733, 703 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₃₃H₄₂NO₂Si: 512.2979, found: 512.2984.

[α]_D²⁵ = +24.2 (*c* 1.0, CHCl₃); 85% ee, 95:5 dr from (*S,R*)-**L2**.



3-(1-(Benzyl(diphenyl)silyl)hept-1-yn-3-yl)-N-cyclohexyl-N-phenylnonanamide (Fig. 3, entry 21). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-15**. The product was purified by column chromatography on silica gel (1:50 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 245 mg, 72% yield, 92% ee, >98:2 dr;

(*S,R*)-**L2**: 244 mg, 72% yield, 91% ee, >98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK AD-3 column (30.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 8.0 min (minor), 9.0 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.49 (m, 4H), 7.46 – 7.39 (m, 2H), 7.39 – 7.29 (m, 5H), 7.23 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.13 – 6.94 (m, 6H), 6.94 – 6.86 (m, 2H), 4.64 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.73 –

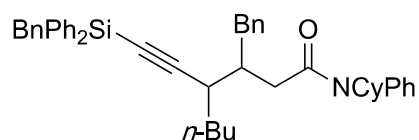
2.66 (m, 1H), 2.64 (d, $J = 13.7$ Hz, 1H), 2.59 (d, $J = 13.9$ Hz, 1H), 2.17 – 1.92 (m, 3H), 1.91 – 1.67 (m, 4H), 1.66 – 1.33 (m, 10H), 1.33 – 0.98 (m, 11H), 0.91 (dt, $J = 16.9, 7.1$ Hz, 7H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 139.1, 137.8, 134.89, 134.85, 134.4, 134.3, 130.5, 130.1, 129.51, 129.48, 129.2, 129.0, 128.9, 128.0, 127.8, 127.7, 127.6, 124.4, 114.7, 80.6, 54.0, 38.2, 38.1, 36.9, 32.7, 31.8, 31.7, 31.6, 30.2, 29.6, 29.5, 27.3, 25.80, 25.79, 25.4, 24.7, 22.64, 22.58, 14.09, 14.06.

FT-IR (film): 3049, 3024, 2929, 2857, 2162, 1651, 1595, 1393, 1112, 701 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{47}\text{H}_{60}\text{NOSi}$: 682.4439, found: 682.4453.

$[\alpha]_D^{25} = +17.9$ (c 1.0, CHCl_3); 91% ee, >98:2 dr from (*S,R*)-L2.



3-Benzyl-4-((benzyl-diphenylsilyl)ethynyl)-N-cyclohexyl-N-phenyloctanamide (Fig. 3, entry 22). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-16**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-L2: 207 mg, 60% yield, 95% ee, 97:3 dr;

(*S,R*)-L2: 203 mg, 59% yield, 95% ee, 99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK OJ-3 column (10.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (*R,S*)-L2: 4.0 min (minor), 5.4 min (major).

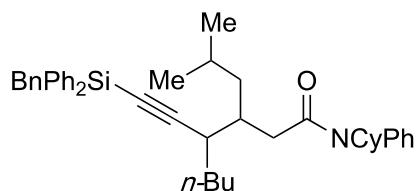
^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.40 (m, 4H), 7.35 – 7.29 (m, 2H), 7.29 – 7.21 (m, 4H), 7.21 – 7.04 (m, 5H), 7.01 – 6.92 (m, 3H), 6.92 – 6.82 (m, 5H), 6.82 – 6.64 (m, 2H), 4.45 (tt, $J = 12.1, 3.5$ Hz, 1H), 2.76 – 2.70 (m, 1H), 2.67 (dd, $J = 13.7, 4.6$ Hz, 1H), 2.55 (s, 2H), 2.43 – 2.26 (m, 1H), 2.16 (dd, $J = 13.8, 10.3$ Hz, 1H), 1.96 (dd, $J = 16.6, 9.2$ Hz, 1H), 1.75 (dd, $J = 16.6, 3.9$ Hz, 1H), 1.72 – 1.54 (m, 4H), 1.50 – 1.38 (m, 4H), 1.36 – 1.20 (m, 5H), 0.95 – 0.71 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.2, 140.5, 138.8, 137.8, 134.90, 134.86, 134.3, 134.2, 130.3, 130.1, 129.59, 129.56, 129.23, 129.16, 129.0, 128.8, 128.1, 127.9, 127.85, 127.75, 127.72, 125.7, 124.4, 114.3, 81.3, 53.9, 39.8, 37.2, 36.5, 35.8, 32.7, 31.6, 31.5, 30.2, 25.8, 25.7, 25.3, 24.6, 22.6, 14.1.

FT-IR (film): 3059, 3024, 2930, 2858, 2163, 1651, 1595, 1394, 1111, 763, 694 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{48}\text{H}_{54}\text{NOSi}$: 688.3969, found: 688.3987.

$[\alpha]_D^{25} = +60.6$ (c 1.0, CHCl_3); 95% ee, 99:1 dr from (*S,R*)-L2.



4-((Benzoyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-isobutyl-N-phenyloctanamide (Fig. 3, entry 23). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-17**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 207 mg, 63% yield, 92% ee, 98:2 dr;

(*S,R*)-**L2**: 217 mg, 66% yield, 92% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 5.6 min (major), 6.3 min (minor).

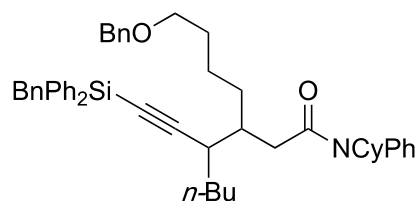
¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.50 (m, 4H), 7.46 – 7.39 (m, 2H), 7.39 – 7.30 (m, 5H), 7.26 – 7.17 (m, 1H), 7.12 – 6.93 (m, 6H), 6.93 – 6.86 (m, 2H), 4.64 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.64 (d, *J* = 13.8 Hz, 1H), 2.60 (d, *J* = 13.8 Hz, 1H), 2.23 – 2.04 (m, 2H), 1.96 (dd, *J* = 15.8, 3.4 Hz, 1H), 1.89 – 1.68 (m, 4H), 1.66 – 1.49 (m, 3H), 1.49 – 1.32 (m, 7H), 1.13 (ddd, *J* = 13.3, 9.5, 3.5 Hz, 1H), 1.09 – 0.97 (m, 3H), 0.97 – 0.89 (m, 4H), 0.84 (t, *J* = 6.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 171.5, 139.0, 137.8, 134.90, 134.86, 134.4, 134.3, 130.5, 130.0, 129.51, 129.47, 129.2, 129.0, 128.8, 128.0, 127.8, 127.7, 127.6, 124.4, 114.7, 80.6, 54.0, 38.9, 38.3, 36.9, 35.8, 32.7, 31.7, 31.6, 30.2, 25.80, 25.78, 25.4, 25.3, 24.7, 23.8, 22.6, 21.9, 14.1.

FT-IR (film): 3049, 2999, 2930, 2858, 2161, 1651, 1596, 1392, 1108, 702 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₄₅H₅₆NOSi: 654.4126, found: 654.4142.

[α]_D²² = +18.4 (*c* 1.0, CHCl₃); 92% ee, 98:2 dr from (*S,R*)-**L2**.



4-((Benzoyldiphenylsilyl)ethynyl)-3-(4-(benzyloxy)butyl)-N-cyclohexyl-N-phenyloctanamide (Fig. 3, entry 24). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-18**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 239 mg, 63% yield, 90% ee, 99:1 dr;

(*S,R*)-**L2**: 231 mg, 61% yield, 91% ee, 99:1 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IF-3 column (25.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 9.2 min (major), 11.0 min (minor).

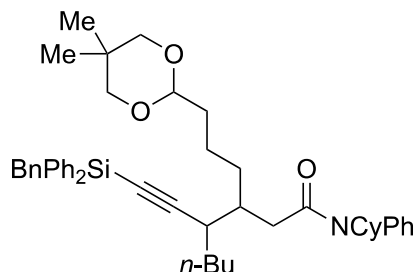
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.35 (m, 4H), 7.33 – 7.15 (m, 12H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.99 – 6.81 (m, 6H), 6.78 (d, *J* = 7.0 Hz, 2H), 4.51 (tt, *J* = 12.1, 3.7 Hz, 1H), 4.37 (s, 2H), 3.30 (t, *J* = 6.5 Hz, 2H), 2.61 – 2.54 (m, 1H), 2.52 (d, *J* = 13.9 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.08 – 1.81 (m, 3H), 1.79 – 1.57 (m, 4H), 1.50 – 1.11 (m, 14H), 1.00 – 0.77 (m, 7H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 139.0, 138.6, 137.8, 134.84, 134.80, 134.28, 130.2, 130.0, 129.50, 129.46, 129.2, 128.92, 128.85, 128.3, 128.0, 127.73, 127.68, 127.6, 127.5, 127.4, 124.3, 114.5, 80.7, 72.8, 70.3, 54.0, 38.1, 38.0, 36.8, 32.7, 31.6, 31.5, 30.1, 29.9, 29.4, 25.8, 25.7, 25.3, 24.6, 24.0, 22.5, 14.0.

FT-IR (film): 3059, 3049, 2923, 2860, 2162, 1651, 1644, 1595, 1492, 1451, 1110, 767, 735 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₅₂H₆₂NO₂Si: 760.4544, found: 760.4550.

[α]_D²⁵ = +19.4 (*c* 1.0, CHCl₃); 91% ee, 99:1 dr from (*S,R*)-**L2**.



4-((Benzyldiphenylsilyl)ethynyl)-*N*-cyclohexyl-3-(3-(5,5-dimethyl-1,3-dioxan-2-yl)propyl)-*N*-phenyloctanamide (Fig. 3, entry 25). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-19**. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 241 mg, 64% yield, 91% ee, 99:1 dr;

(*S,R*)-**L2**: 234 mg, 62% yield, 91% ee, 99:1 dr.

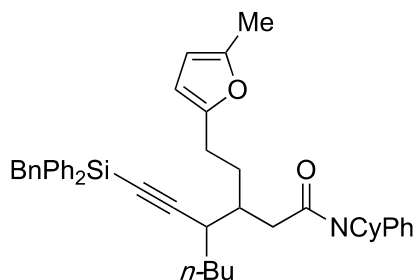
HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 10.6 min (minor), 20.0 min (major).

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.37 (m, 4H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 5H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.00 – 6.82 (m, 6H), 6.78 (d, *J* = 6.9 Hz, 2H), 4.51 (tt, *J* = 12.1, 3.6 Hz, 1H), 4.23 (t, *J* = 5.0 Hz, 1H), 3.48 (d, *J* = 11.0 Hz, 2H), 3.27 (dd, *J* = 11.2, 3.2 Hz, 2H), 2.62 – 2.54 (m, 1H), 2.52 (d, *J* = 13.7 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.05 – 1.82 (m, 3H), 1.80 – 1.57 (m, 4H), 1.54 – 1.36 (m, 5H), 1.36 – 1.13 (m, 9H), 1.09 (s, 3H), 1.01 – 0.85 (m, 3H), 0.82 (t, *J* = 7.0 Hz, 4H), 0.61 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 139.0, 137.8, 134.84, 134.80, 134.29, 134.26, 130.4, 130.1, 129.49, 129.46, 129.2, 128.91, 128.85, 127.9, 127.8, 127.7, 127.6, 124.4, 114.5, 102.0, 80.7, 77.1, 54.0, 38.2, 38.1, 36.8, 35.0, 32.7, 31.6, 31.5, 30.12, 30.06, 29.4, 25.8, 25.3, 24.6, 23.0, 22.5, 21.84, 21.79, 14.0.

FT-IR (film): 3053, 2936, 2855, 2163, 1650, 1594, 1395, 1112, 760, 701 cm⁻¹.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{50}H_{64}NO_3Si$: 754.4650, found: 754.4650.
 $[\alpha]_D^{22} = +24.5$ (c 1.0, $CHCl_3$); 91% ee, 99:1 dr from (*S,R*)-L2.



4-((Benzyldiphenylsilyl)ethynyl)-N-cyclohexyl-3-(2-(5-methylfuran-2-yl)ethyl)-N-phenyloctanamide (Fig. 3, entry 26). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-20**. The product was purified by column chromatography on silica gel (1:30 → 1:15 EtOAc/hexanes). Colorless oil.

(*R,S*)-L2: 216 mg, 61% yield, 90% ee, >98:2 dr;

(*S,R*)-L2: 210 mg, 60% yield, 92% ee, >98:2 dr.

SFC analysis: The ee and dr were determined via SFC on a CHIRALPAK IE-3 column (20.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (*R,S*)-L2: 6.4 min (major), 7.2 min (minor).

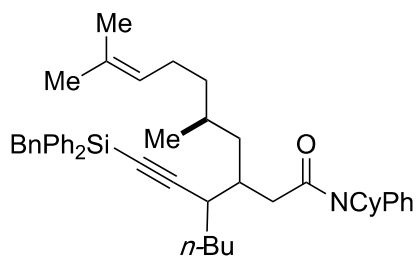
1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 4H), 7.35 – 7.27 (m, 2H), 7.27 – 7.18 (m, 5H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.02 – 6.81 (m, 6H), 6.79 (d, $J = 7.0$ Hz, 2H), 5.73 (d, $J = 3.2$ Hz, 1H), 5.68 (d, $J = 3.0$ Hz, 1H), 4.52 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.66 – 2.56 (m, 1H), 2.53 (d, $J = 13.8$ Hz, 1H), 2.48 (d, $J = 13.8$ Hz, 1H), 2.41 (ddd, $J = 15.3, 9.9, 5.3$ Hz, 1H), 2.30 (ddd, $J = 15.6, 9.7, 6.6$ Hz, 1H), 2.14 (s, 3H), 2.09 – 1.96 (m, 2H), 1.96 – 1.84 (m, 1H), 1.80 – 1.57 (m, 5H), 1.51 – 1.20 (m, 10H), 0.98 – 0.76 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 154.1, 150.0, 138.9, 137.8, 134.9, 134.8, 134.3, 134.2, 130.4, 130.1, 129.53, 129.50, 129.2, 128.9, 128.0, 127.8, 127.72, 127.67, 124.4, 114.2, 105.8, 105.3, 80.9, 54.0, 38.0, 37.6, 36.8, 32.7, 31.65, 31.57, 30.1, 28.0, 26.0, 25.78, 25.77, 25.4, 24.6, 22.6, 14.0, 13.5.

FT-IR (film): 3048, 2923, 2859, 2162, 1651, 1397, 1110, 760, 736 cm^{-1} .

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{48}H_{55}NO_2SiNa$: 728.3894, found: 728.3896.

$[\alpha]_D^{22} = +14.5$ (c 1.0, $CHCl_3$); 92% ee, >98:2 dr from (*S,R*)-L2.



(5S)-3-(1-(Benzyl(diphenyl)silyl)hept-1-yn-3-yl)-N-cyclohexyl-5,9-dimethyl-N-phenyldec-8-enamide (Fig. 3, entry 27). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-21**. The product was purified by column chromatography on silica gel (1:25 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 203 mg, 56% yield, 96:4 dr;

(*S,R*)-**L2**: 199 mg, 55% yield, 3:97 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 0.6 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 8.2 min (major), 9.2 min (minor).

NMR data for the product from (*R,S*)-**L2**:

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.36 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.18 (m, 5H), 7.10 (t, $J = 7.3$ Hz, 1H), 7.00 – 6.74 (m, 8H), 5.00 (t, $J = 7.1$ Hz, 1H), 4.53 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.65 – 2.56 (m, 1H), 2.53 (d, $J = 13.9$ Hz, 1H), 2.49 (d, $J = 13.9$ Hz, 1H), 2.14 – 1.96 (m, 2H), 1.96 – 1.64 (m, 6H), 1.64 – 1.58 (m, 4H), 1.51 (s, 3H), 1.49 – 1.10 (m, 12H), 1.01 – 0.77 (m, 8H), 0.72 (d, $J = 5.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.4, 139.0, 137.8, 134.90, 134.86, 134.34, 134.30, 130.9, 130.5, 130.0, 129.51, 129.48, 129.2, 129.0, 128.8, 128.0, 127.8, 127.7, 127.6, 124.9, 124.4, 114.7, 80.7, 53.9, 38.4, 37.3, 36.7, 36.1, 35.7, 32.4, 31.7, 31.6, 30.2, 30.0, 25.8, 25.7, 25.4, 25.2, 24.7, 22.6, 20.5, 17.7, 14.1.

NMR data for the product from (*S,R*)-**L2**:

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.37 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.18 (m, 5H), 7.15 – 7.04 (m, 1H), 7.02 – 6.90 (m, 4H), 6.90 – 6.73 (m, 4H), 4.93 (tt, $J = 7.1, 1.3$ Hz, 1H), 4.52 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.68 – 2.56 (m, 1H), 2.52 (d, $J = 13.9$ Hz, 1H), 2.49 (d, $J = 13.9$ Hz, 1H), 2.13 – 1.92 (m, 2H), 1.90 – 1.60 (m, 7H), 1.58 (s, 3H), 1.55 – 1.42 (m, 3H), 1.41 (s, 3H), 1.38 – 1.21 (m, 6H), 1.14 – 0.94 (m, 5H), 0.94 – 0.78 (m, 6H), 0.73 (d, $J = 5.9$ Hz, 3H).

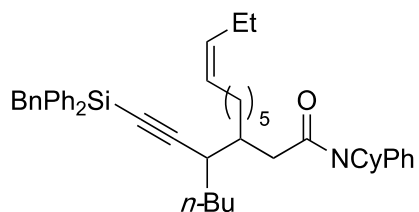
^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 139.0, 137.8, 134.9, 134.8, 134.3, 130.9, 130.5, 130.0, 129.50, 129.47, 129.3, 129.0, 128.8, 128.0, 127.8, 127.7, 127.6, 124.8, 124.4, 114.6, 80.7, 54.0, 38.2, 38.1, 36.94, 36.90, 35.6, 32.8, 31.7, 31.6, 30.2, 29.6, 25.80, 25.78, 25.7, 25.5, 25.4, 24.7, 22.6, 19.4, 17.6, 14.1.

FT-IR (film): 3058, 3024, 2927, 2857, 2163, 1651, 1595, 1394, 1113, 706, 700 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{50}\text{H}_{63}\text{NOSiNa}$: 744.4571, found: 744.4573.

$[\alpha]_D^{25} = -18.7$ (c 1.0, CHCl_3); 96:4 dr from (*R,S*)-**L2**.

$[\alpha]_D^{25} = +38.8$ (c 1.0, CHCl_3); 3:97 dr from (*S,R*)-**L2**.



(Z)-3-(1-(Benzyldiphenylsilyl)hept-1-yn-3-yl)-N-cyclohexyl-N-phenyldodec-9-enamide (Fig. 3, entry 28). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-22**. The product was purified by column chromatography on silica gel (1:30 → 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 232 mg, 65% yield, 94% ee, 98:2 dr;

(*S,R*)-**L2**: 233 mg, 64% yield, 93% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 0.6 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 16.5 min (major), 18.6 min (minor).

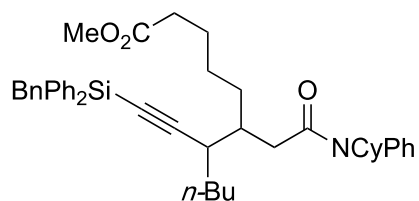
¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.38 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.19 (m, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.82 (m, 6H), 6.82 – 6.74 (m, 2H), 5.40 – 5.11 (m, 2H), 4.52 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.53 (d, *J* = 13.8 Hz, 1H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.07 – 1.79 (m, 7H), 1.78 – 1.59 (m, 4H), 1.53 – 1.02 (m, 16H), 1.00 – 0.77 (m, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 171.5, 139.0, 137.8, 134.9, 134.8, 134.34, 134.31, 131.5, 130.5, 130.0, 129.51, 129.47, 129.25, 129.21, 129.0, 128.8, 128.0, 127.8, 127.7, 127.6, 124.3, 114.6, 80.6, 54.0, 38.2, 38.1, 36.8, 32.7, 31.7, 31.6, 30.2, 29.7, 29.6, 29.5, 27.3, 27.0, 25.8, 25.4, 24.7, 22.6, 20.5, 14.4, 14.1.

FT-IR (film): 3023, 3001, 2932, 2857, 2162, 1659, 1650, 1393, 1113, 707, 699 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₅₀H₆₄NOSi: 722.4752, found: 722.4748.

[α]_D²⁵ = +21.4 (c 1.0, CHCl₃); 93% ee, 98:2 dr from (*S,R*)-**L2**.



Methyl 7-((benzyldiphenylsilyl)ethynyl)-6-(2-(cyclohexyl(phenyl)amino)-2-oxoethyl)undecanoate (Fig. 3, entry 29). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-23**. The product was purified by column chromatography on silica gel (1:30 → 1:5 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 227 mg, 64% yield, 90% ee, 98:2 dr;

(*S,R*)-**L2**: 228 mg, 64% yield, 90% ee, 98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (5.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 10.0 min (minor), 13.0 min (major).

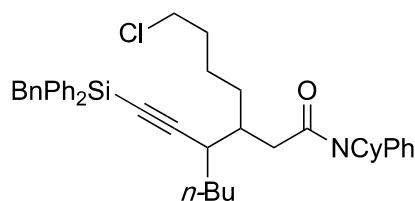
^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.35 (m, 4H), 7.34 – 7.28 (m, 2H), 7.28 – 7.19 (m, 5H), 7.12 (t, J = 7.4 Hz, 1H), 7.01 – 6.82 (m, 6H), 6.81 – 6.71 (m, 2H), 4.51 (tt, J = 12.1, 3.6 Hz, 1H), 3.56 (s, 3H), 2.62 – 2.43 (m, 3H), 2.13 (t, J = 7.5 Hz, 2H), 2.05 – 1.78 (m, 3H), 1.77 – 1.57 (m, 4H), 1.53 – 1.20 (m, 12H), 1.14 – 0.74 (m, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.0, 171.3, 139.0, 137.8, 134.84, 134.80, 134.3, 134.2, 130.4, 130.0, 129.52, 129.49, 129.2, 128.93, 128.88, 128.0, 127.74, 127.69, 127.65, 124.3, 114.4, 80.8, 54.0, 51.4, 38.0, 36.8, 34.0, 32.6, 31.62, 31.55, 30.1, 29.3, 26.9, 25.8, 25.7, 25.3, 25.1, 24.6, 22.5, 14.0.

FT-IR (film): 3066, 3052, 2926, 2858, 2162, 1738, 1651, 1594, 1493, 1393, 1112, 740, 704 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{47}\text{H}_{58}\text{NO}_3\text{Si}$: 712.4180, found: 712.4181.

$[\alpha]_D^{25} = +19.9$ (c 1.0, CHCl_3); 90% ee, 98:2 dr from (*S,R*)-**L2**.



4-((Benzylidiphenylsilyl)ethynyl)-3-(4-chlorobutyl)-N-cyclohexyl-N-phenyloctanamide (Fig. 3, entry 30). The title compound was synthesized according to **GP-9** from benzyl(3-bromohept-1-yn-1-yl)diphenylsilane and zinc nucleophile **Zn-24**. The product was purified by column chromatography on silica gel (1:30 \rightarrow 1:10 EtOAc/hexanes). Colorless oil.

(*R,S*)-**L2**: 230 mg, 67% yield, 92% ee, >98:2 dr;

(*S,R*)-**L2**: 233 mg, 68% yield, 92% ee, >98:2 dr.

HPLC analysis: The ee and dr were determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 12.9 min (minor), 17.5 min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.48 (m, 4H), 7.46 – 7.30 (m, 7H), 7.28 – 7.21 (m, 1H), 7.12 – 7.00 (m, 5H), 6.97 (d, J = 8.0 Hz, 1H), 6.93 – 6.83 (m, 2H), 4.63 (tt, J = 12.1, 3.6 Hz, 1H), 3.45 (t, J = 6.7 Hz, 2H), 2.70 – 2.56 (m, 3H), 2.19 – 1.92 (m, 3H), 1.90 – 1.27 (m, 18H), 1.15 – 0.98 (m, 3H), 0.98 – 0.84 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 139.0, 137.8, 134.9, 134.8, 134.3, 134.2, 130.4, 130.1, 129.6, 129.5, 129.3, 129.0, 128.1, 127.8, 127.72, 127.68, 124.4, 114.3, 80.9, 54.1, 44.9, 38.03, 37.99, 36.9, 32.69, 32.65, 31.64, 31.58, 30.1, 28.9, 25.78, 25.77, 25.4, 24.6, 24.5, 22.5, 14.0.

FT-IR (film): 3048, 3024, 2920, 2858, 2163, 1651, 1595, 1394, 1111, 762, 733, 706 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{45}\text{H}_{55}\text{ClNOSi}$: 688.3736, found: 688.3758.

$[\alpha]_D^{25} = +21.8$ (c 1.0, CHCl_3); 92% ee, >98:2 dr from (*S,R*)-**L2**.

VI. Effect of Reaction Parameters

General Procedure 10 (GP-10): In a glovebox, NiCl₂·glyme (2.2 mg, 0.010 mmol), chiral ligand **L1** (3.2 mg, 0.012 mmol), 1,5-bis(diphenylphosphino)pentane (4.4 mg, 0.010 mmol), and THF (1.0 mL) were added sequentially to a 4-mL vial equipped with a stir bar. The mixture was stirred at room temperature for 30 min (pink suspension), and then a solution of the alkylzinc nucleophile (0.15 mmol) was added dropwise via a 0.25 mL syringe (for the additive studies, the additive was added before the alkylzinc reagent). The vial was sealed with a septum cap and wrapped with electrical tape. The reaction mixture was stirred at room temperature for 10 min, at which time it had become a dark-red homogeneous solution. Next, the vial was transferred out of the glovebox and cooled to -5 °C. After the reaction mixture had stirred at -5 °C for 10 min, 1-iodohexane (0.10 mmol, 0.015 mL) was added via a microsyringe in one portion. The punctures in the septum cap were covered with grease, and then the reaction mixture was stirred at -5 °C for 72 h. Next, the reaction was quenched by the addition of MeOH (0.1 mL). The resulting mixture was allowed to warm to room temperature, and then dodecane (22 μL, 0.10 mmol) was added as an internal standard. The mixture was filtered through a small plug of silica gel, which was flushed with Et₂O (20 mL). A portion of the filtrate (0.1 mL) was diluted with acetone (total volume: 1 mL) and analyzed via GC, and the remainder of the filtrate was concentrated via rotary evaporation, and the pure product was isolated by preparative TLC on silica gel (1:5 EtOAc/hexanes).

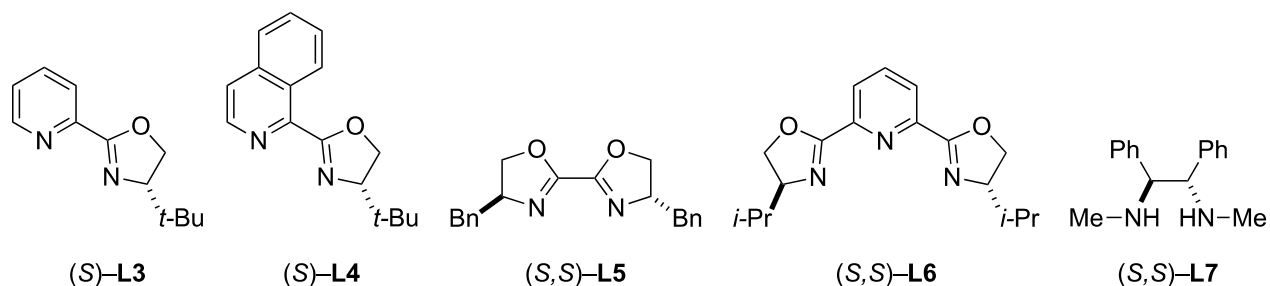
GP-10 was followed, using 1-iodohexane (0.10 mmol) and **Zn-1** (0.15 mmol). The yield and conversion were determined via GC analysis with dodecane as an internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

Table S-1.

entry	variation from the "standard conditions"	yield (%) ^a	ee (%) ^b
1	none	96	90
2	no NiCl ₂ ·glyme	<2	NA
3	no (S)-L1	4	NA
4	no phosphine	5	<2
5	1.1 equiv of alkylzinc reagent	85	88
6	5% NiCl ₂ ·glyme, 6% (S)-L1, 5% Ph ₂ P(CH ₂) ₅ PPh ₂	55	92
7	r.t., instead of -5 °C	79	86
8	10% H ₂ O added	96	90
9	0.5 mL of air added by syringe	85	87
10	(S,R)-L2, instead of (S)-L1	94	84
11	(S)-L3, instead of (S)-L1	18	7
12	(S)-L4, instead of (S)-L1	33	85
13	(S,S)-L5, instead of (S)-L1	7	12
14	(S,S)-L6, instead of (S)-L1	<2	NA
15	(S,S)-L7, instead of (S)-L1	4	35

All data are the average of two experiments. ^a Determined via GC analysis versus a calibrated standard.

^b Determined via HPLC analysis.

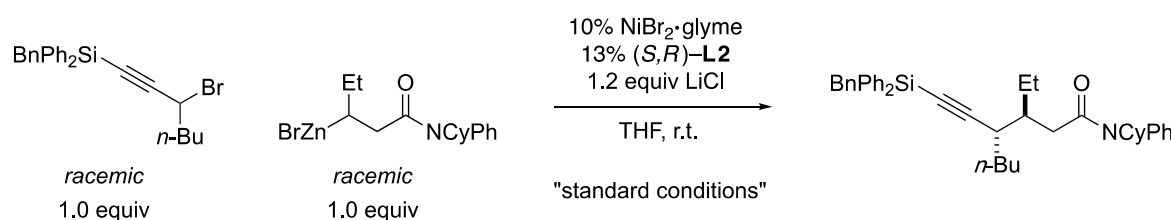


The role of the phosphine has not yet been elucidated. The presence of the phosphine leads to a homogeneous, rather than a heterogeneous, reaction mixture. ³¹P NMR spectroscopic studies establish that the resonance for the free phosphine is altered in the presence of the alkylzinc nucleophile, as well as under the coupling conditions.

General Procedure 11 (GP-11): In a glovebox, NiBr₂·glyme (3.1 mg, 0.010 mmol, 10%), chiral ligand **L2** (3.7 mg, 0.013 mmol, 13%), anhydrous LiCl (5.1 mg, 0.12 mmol), and THF (1.0 mL) were added sequentially to a 4-mL vial equipped with a stir bar. The mixture was allowed to stir for 40 min, after which it was a cloudy, yellow suspension. Then, a solution of the propargylic bromide (100 μL, 0.10 mmol, 1.0 M in THF) was added via microsyringe. Next, a solution of the alkylzinc nucleophile (0.10 mmol) was added in one portion, leading to a dark-red reaction mixture. The reaction mixture was transferred out of the glovebox and stirred (~800 rpm) at room temperature for 20 h. The reaction mixture was then passed through a short pad of silica gel, with Et₂O as the eluent (~10 mL). The resulting mixture was concentrated, and the residue was purified by preparative TLC on silica gel (1:5 EtOAc/hexanes).

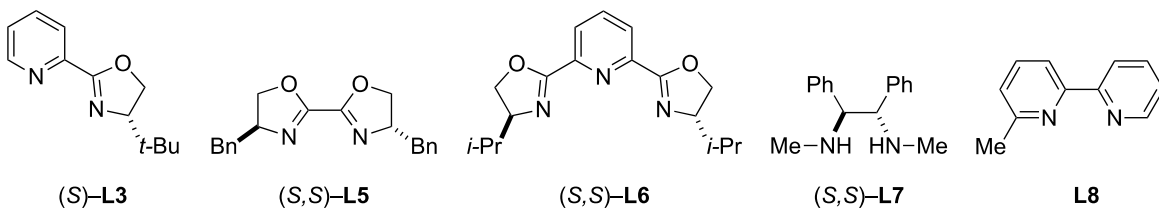
Benzyl(3-bromohept-1-yn-1-yl)diphenylsilane (0.10 mmol) was reacted with zinc nucleophile **Zn-10** (0.10 mmol) according to **GP-11**. The yield was determined after purification by preparative thin-layer chromatography. The ee and dr values were determined via HPLC analysis.

Table S-2.



entry	variation from the "standard conditions"	yield (%) ^a	ee (%) ^b	dr (%) ^b
1	none	75	92	98:2
2	no NiBr ₂ ·glyme	<2	NA	NA
3	no (S,R)- L2	<2	NA	NA
4	no LiCl	47	65	95:5
5	0 °C, instead of r.t.	77	81	97:3
6	(S)- L1 , instead of (S)- L2	11	46	99:1
7	(S)- L3 , instead of (S)- L2	15	63	81:19
8	(S,S)- L5 , instead of (S)- L2	8	17	86:14
9	(S,S)- L6 , instead of (S)- L2	10	<5	65:35
10	(S,S)- L7 , instead of (S)- L2	<2	NA	NA
11	L8 , instead of (S)- L2	16	–	60:40

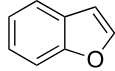

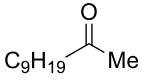
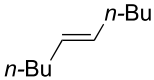
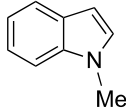


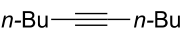
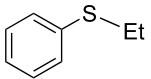
All data are the average of two experiments. ^a Purified product. ^b Determined via HPLC analysis.



VII. Functional-Group Compatibility

GP-10 was followed, using 1-iodohexane (0.10 mmol) and **Zn-1** (0.15 mmol), in the presence of 1.0 equiv of the additives shown below. The yield and conversion were determined via GC analysis with dodecane as an internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

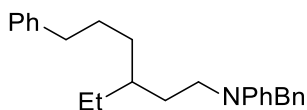
Table S-3.

entry	additive	recovery of additive (%) ^a	yield, ^a ee (%) ^b
1	none	NA	96, 90
2	Cy-Br	99	97, 90
3		99	95, 90
4		99	95, 90
5		99	95, 90
6	Ph-Cl	98	95, 90
7		95	86, 90
8		94	94, 90
9		94	90, 90
10	Ph-CN	94	76, 90
11	NCy ₂ Me	92	95, 90
12	Ph-Br	91	98, 90
13		90	94, 90
14	Ph-I	88	33, 91
15		82	25, 91
16		79	88, 90

All data are the average of two experiments. ^a Determined via GC analysis versus a calibrated standard.

^b Determined via HPLC analysis.

VIII. Derivatization of Coupling Products



N-Benzyl-N-(3-ethyl-6-phenylhexyl)aniline (top of Fig. 4). Borane-SMe₂ (0.24 mL, 2.0 M in THF, 1.2 equiv) was added dropwise to a solution of *N*-benzyl-3-ethyl-*N*,6-diphenylhexanamide (154 mg, 0.40 mmol, 1.0 equiv) in THF (4.0 mL) at 0 °C in a 25-mL Schlenk tube. Next, the reaction mixture was allowed to warm to room temperature, and then it was heated to 85 °C. After being stirred at 85 °C in the sealed Schlenk tube for 8 h, the reaction was quenched with aqueous NaOH (1 M, 1.0 mL), and the reaction mixture was extracted with Et₂O (3 × 20 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:20 EtOAc/hexanes) to afford the pure product. Colorless oil.

(*R*)-**L1**: 133 mg, 90% yield, 90% ee; (*S*)-**L1**: 126 mg, 85% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK OD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 12.7 min (minor), 13.6 min (major).

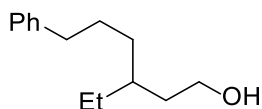
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.31 (m, 3H), 7.31 – 7.25 (m, 4H), 7.25 – 7.17 (m, 5H), 6.75 – 6.65 (m, 3H), 4.54 (s, 2H), 3.48 – 3.33 (m, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.71 – 1.58 (m, 4H), 1.45 – 1.28 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.5, 142.6, 139.1, 129.2, 128.5, 128.3, 128.2, 126.7, 126.5, 125.6, 115.9, 112.0, 54.3, 49.2, 37.1, 36.3, 32.8, 30.0, 28.6, 25.9, 10.9.

FT-IR (film): 3024, 2928, 2856, 1596, 1504, 1451, 1354, 744, 726 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₂₇H₃₄N: 372.2686, found: 372.2678.

[α]_D²⁵ = -4.2 (*c* 1.0, CHCl₃); 91% ee from (*S*)-**L1**.



3-Ethyl-6-phenylhexan-1-ol (top of Fig. 4). Lithium aluminum hydride (0.98 mL, 1.0 M in Et₂O, 2.0 equiv) was added dropwise to a solution of *N*-benzyl-3-ethyl-*N*,6-diphenylhexanamide (188 mg, 0.49 mmol, 1.0 equiv) in THF (5.0 mL) at 0 °C in a 25-mL Schlenk tube. Next, the reaction mixture was allowed to warm to room temperature, and then it was heated to 85 °C. After being stirred at 85 °C in the sealed Schlenk tube overnight, the reaction mixture was diluted with Et₂O (20 mL) and cooled to 0 °C. The reaction was then quenched in turn with H₂O (38 μL), 15% aqueous NaOH (38 μL), and H₂O (114 μL). Next, the suspension was filtered through a sintered funnel to remove the white solid. The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by

flash chromatography on silica gel (1:10 EtOAc/hexanes) to afford the pure product. Colorless oil.

(*R*)-**L1**: 88 mg, 87% yield, 90% ee; (*S*)-**L1**: 86 mg, 85% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (1.0% EtOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*)-**L1**: 17.5 min (minor), 18.9 min (major).

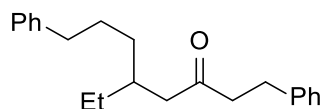
¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 3.67 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.59 – 1.52 (m, 2H), 1.52 – 1.40 (m, 1H), 1.40 – 1.26 (m, 5H), 0.88 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 142.7, 128.3, 128.2, 125.6, 61.2, 36.4, 36.3, 35.4, 32.8, 28.5, 25.9, 10.7.

FT-IR (film): 3336, 2958, 2928, 2857, 1495, 1452, 1057, 1029, 745 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+H]⁺ calcd for C₁₄H₂₃O: 207.1743, found: 207.1737.

[α]_D²⁴ = +2.2 (*c* 1.0, CHCl₃); 91% ee from (*S*)-**L1**.



5-Ethyl-1,8-diphenyloctan-3-one (top of Fig. 4). Trifluoromethanesulfonic anhydride (40 μL, 0.24 mmol, 1.2 equiv) was added dropwise to a mixture of *N*-benzyl-3-ethyl-*N*,6-diphenylhexanamide (77.0 mg, 0.20 mmol, 1.0 equiv) and DTBMP (49.2 mg, 0.24 mmol, 1.2 equiv) in CH₂Cl₂ (2.0 mL) at –78 °C in a 40-mL vial. The reaction mixture was allowed to stir at –78 °C for 3 h. Next, phenethylmagnesium chloride (0.22 mL, 1.0 M in THF, 1.2 equiv) was added dropwise to this mixture at –78 °C, and the mixture was stirred at –78 °C for 5 h. Next, the reaction was quenched with aqueous saturated NH₄Cl (2.0 mL), and the reaction mixture was extracted with Et₂O (3 × 20 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel (1:30 EtOAc/hexanes) to afford the pure product. Colorless oil.

(*R*)-**L1**: 43 mg, 69% yield, 90% ee; (*S*)-**L1**: 45 mg, 73% yield, 90% ee.

SFC analysis: The ee was determined via SFC on a CHIRALPAK IC-3 column (5.0% 2-PrOH in supercritical CO₂, 2.5 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.5 min (major), 9.2 min (minor).

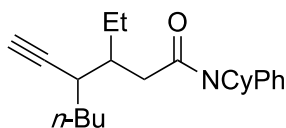
¹H NMR (400 MHz,) δ 7.23 – 7.15 (m, 4H), 7.13 – 7.06 (m, 6H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.9 Hz, 2H), 2.23 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.20 (dd, *J* = 16.1, 6.6 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.54 – 1.41 (m, 2H), 1.31 – 1.07 (m, 4H), 0.73 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 210.2, 142.5, 141.1, 128.4, 128.31, 128.30, 128.2, 126.0, 125.6, 47.5, 44.8, 36.1, 35.0, 33.1, 29.7, 28.5, 26.3, 10.8.

FT-IR (film): 3061, 3027, 2931, 2366, 1712, 1457, 748, 735, 698 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₂H₂₈ONa: 331.2032, found: 331.2041.

[α]_D²² = +4.5 (*c* 1.0, CHCl₃); 90% ee from (*S*)-**L1**.



N-Cyclohexyl-3-ethyl-4-ethynyl-N-phenyloctanamide. To a solution of 4-((benzyldiphenylsilyl)ethynyl)-*N*-cyclohexyl-3-ethyl-*N*-phenyloctanamide (1.450 g, 2.32 mmol, 1.0 equiv) in anhydrous THF (11.6 mL) at room temperature was added TBAF (4.6 mL, 1.0 M in THF, 2.0 equiv) dropwise. The reaction mixture was allowed to stir at room temperature for 36 h. Next, the reaction was quenched with aqueous saturated NH_4Cl (2.0 mL) and extracted with Et_2O (3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:20 EtOAc /hexanes) to afford the pure product. Colorless oil.

(*R,S*)-**L2**: 747 mg, 93% yield, 90% ee, >99:1 dr;

(*S,R*)-**L2**: 719 mg, 89% yield, 91% ee, 98:2 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (1.0% 2- PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 9.4 min (minor), 10.9 min (major).

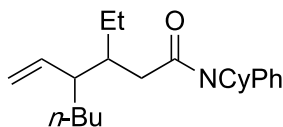
^1H NMR (500 MHz, CDCl_3) δ 7.47 – 7.38 (m, 3H), 7.18 (d, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 4.66 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.60 – 2.52 (m, 1H), 2.11 – 1.95 (m, 3H), 1.91 (d, $J = 2.4$ Hz, 1H), 1.89 – 1.81 (m, 2H), 1.76 (dt, $J = 13.5, 3.4$ Hz, 2H), 1.60 (dt, $J = 13.2, 3.3$ Hz, 1H), 1.57 – 1.28 (m, 9H), 1.23 – 1.12 (m, 1H), 1.07 (q, $J = 12.5, 3.6$ Hz, 2H), 1.00 – 0.87 (m, 4H), 0.81 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.7, 139.1, 130.7, 130.2, 129.0, 128.9, 128.0, 86.2, 69.9, 53.9, 39.7, 37.1, 34.9, 32.1, 31.62, 31.56, 30.1, 25.7, 25.3, 22.5, 22.1, 14.0, 11.8.

FT-IR (film): 3306, 3243, 2930, 2857, 1651, 1595, 1394, 1072, 705 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{35}\text{NONa}$: 376.2611, found: 376.2615.

$[\alpha]_D^{25} = +37.8$ (c 1.0, CHCl_3); 91% ee, 98:2 dr from (*S,R*)-**L2**.



N-Cyclohexyl-3-ethyl-N-phenyl-4-vinyloctanamide (Fig. 4, reaction a). A 40-mL vial equipped with a stir bar was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (70.6 mg, 0.20 mmol, 1.0 equiv), 5 wt.% Pd/CaCO_3 (21.2 mg, 0.010 mmol, 0.050 equiv) and quinoline (36.0 mg, 0.28 mmol, 1.4 equiv). The vial was evacuated and backfilled with nitrogen on Schlenk line for three times. Next, a hydrogen-filled balloon was attached, and hexane (2.0 mL) was added via syringe. The reaction mixture was allowed to stir at room temperature for 3 h, and then it was passed through a short pad of silica gel, with Et_2O as the eluent (~20 mL). The

resulting mixture was concentrated, and the residue was purified by preparative TLC on silica gel (1:6 EtOAc/hexanes) to afford the pure product. Colorless oil.

(*R,S*)-**L2**: 66 mg, 93% yield, 90% ee, 98:2 dr;

(*S,R*)-**L2**: 70 mg, 98% yield, 90% ee, 99:1 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 7.6 min (major), 10.7 min (minor).

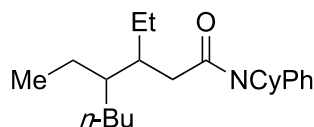
¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.23 (m, 3H), 6.99 (d, *J* = 7.0 Hz, 2H), 5.40 – 5.22 (m, 1H), 4.90 – 4.73 (m, 2H), 4.55 (tt, *J* = 12.1, 3.6 Hz, 1H), 1.93 (tt, *J* = 8.2, 3.8 Hz, 1H), 1.86 – 1.69 (m, 5H), 1.69 – 1.58 (m, 2H), 1.54 – 1.42 (m, 1H), 1.40 – 1.25 (m, 3H), 1.25 – 1.03 (m, 6H), 1.02 – 0.80 (m, 4H), 0.78 (t, *J* = 6.9 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.1, 140.6, 139.3, 130.3, 128.9, 127.9, 115.4, 53.9, 46.6, 40.6, 37.0, 31.7, 31.6, 31.4, 29.9, 25.8, 25.3, 22.8, 22.4, 14.0, 11.9.

FT-IR (film): 3065, 2932, 2857, 1659, 1650, 1595, 1493, 1453, 1393, 1072, 910, 706 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₂₄H₃₇NONa: 378.2767, found: 378.2772.

[α]_D²⁵ = +13.1 (c 1.0, CHCl₃); 90% ee, 99:1 dr from (*S,R*)-**L2**.



N-Cyclohexyl-3,4-diethyl-N-phenyloctanamide (Fig. 4, reaction b). A 40-mL vial equipped with a stir bar was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (70.6 mg, 0.20 mmol, 1.0 equiv), 5 wt.% Pd/C (43.1 mg, 0.020 mmol, 0.10 equiv). The vial was evacuated and backfilled with nitrogen on Schlenk line for three times. Next, a hydrogen-filled balloon was attached, and EtOAc (2.0 mL) was added via syringe. The reaction mixture was allowed to stir at room temperature for 18 h, and then it was passed through a short pad of silica gel, with Et₂O as the eluent (~20 mL). The resulting mixture was concentrated, and the residue was purified by preparative TLC on silica gel (1:6 EtOAc/hexanes) to afford the pure product. Colorless oil.

(*R,S*)-**L2**: 67 mg, 94% yield, 90% ee, 98:2 dr;

(*S,R*)-**L2**: 72 mg, 100% yield, 91% ee, 98:2 dr.

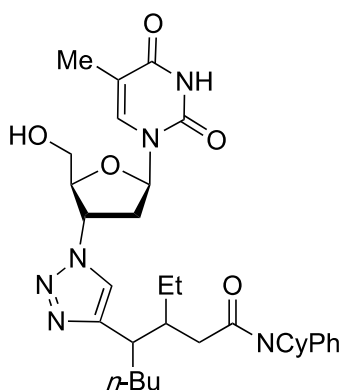
HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L2**: 7.0 min (major), 7.6 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.24 (m, 3H), 7.05 – 6.93 (m, 2H), 4.56 (tt, *J* = 12.1, 3.6 Hz, 1H), 1.90 – 1.59 (m, 7H), 1.53 – 1.44 (m, 1H), 1.32 (qt, *J* = 13.1, 3.6 Hz, 2H), 1.13 (tt, *J* = 11.9, 6.9 Hz, 6H), 1.05 – 0.71 (m, 14H), 0.68 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 139.5, 130.42, 130.36, 128.9, 127.9, 53.9, 41.3, 38.3, 36.2, 31.64, 31.62, 30.1, 29.7, 25.8, 25.4, 23.2, 23.1, 23.0, 14.1, 12.4, 12.1.

FT-IR (film): 2956, 2933, 2858, 2356, 1652, 1595, 1493, 1455, 1391, 1073, 705 cm⁻¹.

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{24}H_{39}NONa$: 380.2924, found: 380.2931.
 $[\alpha]_D^{25} = -6.1$ (c 1.0, $CHCl_3$); 91% ee, 98:2 dr from (*S,R*)-L2.



***N*-Cyclohexyl-3-ethyl-4-(1-((2*S*,3*S*,5*R*)-2-(hydroxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)tetrahydrofuran-3-yl)-1*H*-1,2,3-triazol-4-yl)-*N*-phenyloctanamide (Fig. 4, reaction c).** A 4-mL vial was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (71.0 mg, 0.20 mmol, 1.0 equiv). The vial was loosely capped and transferred into glovebox. Then, CuTC (3.8 mg, 0.020 mmol, 0.10 equiv), toluene (2.0 mL), and a stir bar were added sequentially. Next, Zidovudine (59.0 mg, 0.22 mmol, 1.1 equiv) was added slowly. The vial was then capped and transferred out of glovebox. The reaction was stirred at 50 °C for 20 h, and then quenched with aqueous saturated NH_4Cl (2.0 mL) and extracted with Et_2OAc (3×20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (2:1 $EtOAc/CH_2Cl_2$) to afford the pure product. White solid.

(*R,S*)-L2: 116 mg, 94% yield, 97:3 dr;

(*S,R*)-L2: 120 mg, 97% yield, 3:97 dr.

SFC analysis: The dr was determined via SFC on a CHIRALPAK AD-3 column (30.0% 2-PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (*R,S*)-L2: 3.2 min (major), 3.9 min (minor).

NMR data for the product from (*R,S*)-L2:

1H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.57 (s, 1H), 7.45 (s, 1H), 7.39 – 7.26 (m, 3H), 7.03 (dd, $J = 31.9, 7.3$ Hz, 2H), 6.26 (t, $J = 6.5$ Hz, 1H), 5.33 (dt, $J = 10.3, 5.5$ Hz, 1H), 4.50 (tt, $J = 12.1, 3.6$ Hz, 1H), 4.37 – 4.25 (m, 1H), 4.17 (s, 1H), 4.01 – 3.85 (m, 1H), 3.75 (d, $J = 12.1$ Hz, 1H), 3.04 – 2.69 (m, 3H), 2.04 – 1.90 (m, 1H), 1.90 – 1.79 (m, 4H), 1.79 – 1.69 (m, 3H), 1.69 – 1.53 (m, 3H), 1.53 – 1.40 (m, 2H), 1.38 – 1.23 (m, 3H), 1.22 – 1.13 (m, 2H), 1.13 – 1.03 (m, 2H), 1.03 – 0.89 (m, 2H), 0.89 – 0.65 (m, 5H), 0.55 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 164.0, 150.5, 150.0, 139.0, 137.5, 130.5, 130.2, 129.1, 128.9, 128.1, 121.8, 111.0, 87.8, 85.4, 61.5, 59.0, 54.1, 41.1, 38.8, 37.6, 36.7, 31.7, 31.4, 30.6, 30.1, 25.7, 25.3, 23.3, 22.6, 13.9, 12.4, 11.6.

NMR data for the product from (*S,R*)-L2:

^1H NMR (400 MHz, CDCl_3) δ 9.61 (s, 1H), 7.58 (s, 1H), 7.47 (s, 1H), 7.40 – 7.25 (m, 3H), 7.02 (dd, $J = 18.6, 7.2$ Hz, 2H), 6.28 (t, $J = 6.5$ Hz, 1H), 5.35 (dt, $J = 9.8, 5.4$ Hz, 1H), 4.51 (tt, $J = 12.1, 3.6$ Hz, 1H), 4.36 – 4.26 (m, 1H), 4.21 (s, 1H), 3.94 (d, $J = 12.1$ Hz, 1H), 3.73 (d, $J = 12.1$ Hz, 1H), 3.02 – 2.69 (m, 3H), 2.01 – 1.80 (m, 5H), 1.79 – 1.53 (m, 6H), 1.53 – 1.41 (m, 2H), 1.39 – 1.24 (m, 3H), 1.23 – 1.12 (m, 2H), 1.12 – 1.02 (m, 2H), 1.02 – 0.80 (m, 3H), 0.75 (t, $J = 7.2$ Hz, 4H), 0.53 (t, $J = 7.3$ Hz, 3H).

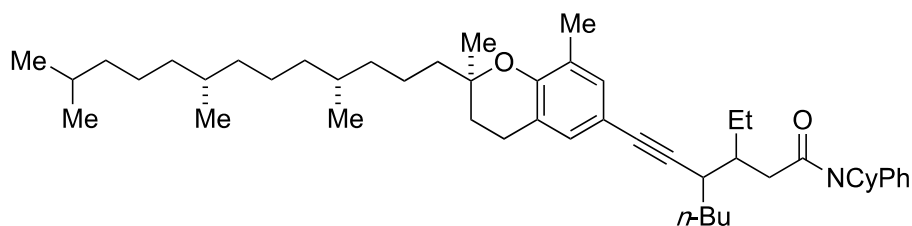
^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 164.1, 150.5, 149.9, 139.0, 137.5, 130.5, 130.2, 129.1, 128.9, 128.1, 121.8, 111.0, 87.7, 85.4, 61.5, 59.1, 54.1, 41.1, 38.8, 37.6, 36.7, 31.7, 31.4, 30.8, 30.1, 25.7, 25.3, 23.1, 22.6, 13.9, 12.4, 11.6.

FT-IR (film): 3192, 2931, 2858, 1697, 1403, 1276, 1104, 735 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{49}\text{N}_6\text{O}_5$: 621.3759, found: 621.3759.

$[\alpha]_D^{25} = +19.7$ (c 1.0, CHCl_3); 97:3 dr from (*R,S*)-L2.

$[\alpha]_D^{25} = -33.1$ (c 1.0, CHCl_3); 3:97 dr from (*S,R*)-L2.



***N*-Cyclohexyl-4-(((*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)ethynyl)-3-ethyl-*N*-phenyloctanamide (Fig. 4, reaction d).** A 4-mL vial was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (71.0 mg, 0.20 mmol, 1.0 equiv) and (*R*)-6-iodo-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane (133.0 mg, 0.26 mmol, 1.3 equiv). The vial was loosely capped and transferred into glovebox. Next, $\text{Pd}(\text{PPh}_3)_2\text{Cl}$ (5.6 mg, 0.0080 mmol, 0.040 equiv), CuI (7.6 mg, 0.040 mmol, 0.20 equiv), toluene (2.0 mL), TMG (76.0 μL , 0.60 mmol, 3.0 equiv) and a stir bar were added sequentially. Then, the vial was capped and transferred out of glovebox. After being stirred at 80 $^\circ\text{C}$ for 12 h, the reaction was quenched with aqueous saturated NH_4Cl (2.0 mL) and extracted with Et_2O (3×20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:20 EtOAc /hexanes) to afford the pure product. Colorless oil.

(*R,S*)-L2: 135 mg, 92% yield, 97:3 dr;

(*S,R*)-L2: 135 mg, 92% yield, 3:97 dr.

SFC analysis: The ee was determined via SFC on a CHIRALPAK AD-3 column (15.0% 2- PrOH in supercritical CO_2 , 2.5 mL/min); retention times for compound obtained using (*R,S*)-L2: 6.5 min (major), 8.3 min (minor).

NMR data for the product from (*R,S*)-L2:

^1H NMR (500 MHz, CDCl_3) δ 7.43 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 1H), 7.33 – 7.27 (m, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.11 (s, 1H), 6.95 – 6.87 (m, 2H), 4.69 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.82 – 2.68 (m, 3H), 2.21 (s, 3H), 2.17 – 2.01 (m, 3H), 1.96 – 1.73 (m, 6H), 1.70 – 1.52 (m, 7H), 1.52 – 1.29 (m, 20H), 1.29 – 1.02 (m, 11H), 0.99 – 0.90 (m, 15H), 0.86 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.9, 151.7, 139.2, 131.5, 130.8, 130.20, 130.15, 129.1, 128.8, 127.8, 126.1, 120.2, 114.2, 89.2, 82.7, 76.3, 53.9, 40.3, 39.9, 39.3, 37.5, 37.4, 37.2, 35.8, 32.8, 32.7, 32.6, 31.7, 31.6, 31.2, 30.3, 27.9, 25.8, 25.4, 24.8, 24.4, 24.2, 22.70, 22.67, 22.61, 22.2, 22.0, 20.9, 19.7, 19.6, 15.8, 14.1, 11.9.

NMR data for the product from (*S,R*)-**L2**:

^1H NMR (500 MHz, CDCl_3) δ 7.43 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 1H), 7.30 (t, $J = 8.2$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.12 (d, $J = 7.7$ Hz, 1H), 6.96 – 6.83 (m, 2H), 4.69 (tt, $J = 12.1, 3.6$ Hz, 1H), 2.82 – 2.67 (m, 3H), 2.24 (d, $J = 3.8$ Hz, 3H), 2.17 – 2.03 (m, 3H), 1.93 – 1.74 (m, 6H), 1.70 – 1.28 (m, 27H), 1.28 – 1.02 (m, 11H), 1.01 – 0.90 (m, 15H), 0.86 (t, $J = 7.4$ Hz, 3H).

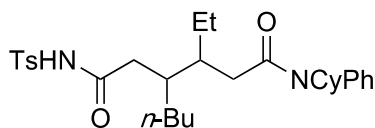
^{13}C NMR (126 MHz, CDCl_3) δ 171.9, 151.7, 139.2, 131.5, 130.8, 130.20, 130.15, 129.1, 128.8, 127.8, 126.1, 120.2, 114.2, 89.2, 82.7, 76.3, 53.9, 40.3, 40.0, 39.3, 37.5, 37.4, 37.2, 35.8, 32.8, 32.7, 32.6, 31.7, 31.6, 31.2, 30.3, 28.0, 25.8, 25.4, 24.8, 24.4, 24.2, 22.70, 22.67, 22.61, 22.2, 22.0, 20.9, 19.7, 19.6, 15.8, 14.1, 11.9.

FT-IR (film): 2933, 2858, 2365, 1651, 1464, 1393, 1378, 1242, 704 cm^{-1} .

HRMS (ESI-MS) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{51}\text{H}_{80}\text{NO}_2$: 738.6184, found: 738.6164.

$[\alpha]_D^{25} = +1.2$ (c 1.0, CHCl_3); 97:3 dr from (*R,S*)-**L2**.

$[\alpha]_D^{25} = +16.9$ (c 1.0, CHCl_3); 3:97 dr from (*S,R*)-**L2**.



3-Butyl-*N*⁶-cyclohexyl-4-ethyl-*N*⁶-phenyl-*N*¹-tosylhexanediamide (Fig. 4, reaction e). A 4-mL vial was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (71.0 mg, 0.20 mmol, 1.0 equiv), TsN_3 (47.3 mg, 0.24 mmol, 1.2 equiv), CuI (3.8 mg, 0.020 mmol, 0.10 equiv), and a stir bar. The vial was evacuated and backfilled with nitrogen on Schlenk line for three times. Then, CHCl_3 (0.40 mL, 0.5 M), H_2O (9.0 μL , 0.50 mmol, 2.5 equiv) and NEt_3 (34.0 μL , 0.24 mmol, 1.2 equiv) were added sequentially under nitrogen atmosphere. After stirring the reaction at room temperature for 12 h, it was quenched with aqueous saturated NH_4Cl (1.0 mL) and diluted with CH_2Cl_2 (2.0 mL). The mixture was allowed to stir for additional 30 min, and then extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:2 EtOAc/hexanes) to afford the pure product. White foamy solid.

(*R,S*)-**L2**: 84 mg, 78% yield, 91% ee, >98:2 dr;

(*S,R*)-**L2**: 86 mg, 80% yield, 92% ee, 99:1 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-L2: 8.7 min (minor), 10.3 min (major).

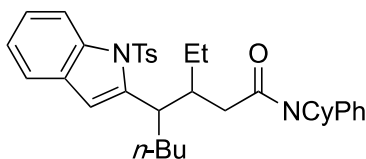
¹H NMR (400 MHz, CDCl₃) δ 10.96 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.93 (m, 2H), 4.64 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.34 (s, 3H), 2.22 (dd, *J* = 12.8, 5.0 Hz, 1H), 2.09 (dd, *J* = 14.3, 4.1 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.77 – 1.64 (m, 5H), 1.63 – 1.51 (m, 2H), 1.50 – 1.34 (m, 3H), 1.15 – 0.86 (m, 10H), 0.72 (t, *J* = 6.9 Hz, 3H), 0.65 – 0.50 (m, 1H), 0.30 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.1, 172.1, 144.1, 138.5, 136.7, 130.0, 129.9, 129.3, 129.1, 128.9, 128.6, 128.3, 54.6, 39.02, 38.97, 38.4, 36.8, 31.9, 31.2, 30.9, 29.4, 25.7, 25.6, 25.2, 22.9, 22.5, 21.5, 13.8, 11.6.

FT-IR (film): 3068, 2932, 2858, 1717, 1618, 1592, 1451, 1345, 1086, 860, 706 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₃₁H₄₄N₂O₄SNa: 563.2914, found: 563.2914.

[α]_D²⁵ = -13.6 (*c* 1.0, CHCl₃); 92% ee, 99:1 dr from (*S,R*)-L2.



***N*-Cyclohexyl-3-ethyl-*N*-phenyl-4-(1-tosyl-1*H*-indol-2-yl)octanamide (Fig. 4, reaction f, X = NTs).** A 4-mL vial was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (70.6 mg, 0.20 mmol, 1.0 equiv) and *N*-tosyl-2-iodoaniline (74.6 mg, 0.20 mmol, 1.0 equiv). The vial was loosely capped and transferred into glovebox. Next, Pd(PPh₃)₂Cl (5.6 mg, 0.0080 mmol, 0.040 equiv), CuI (7.6 mg, 0.040 mmol, 0.20 equiv), toluene (2.0 mL), TMG (76.0 μL, 0.60 mmol, 3.0 equiv) and a stir bar were added sequentially. Then, the vial was capped and transferred out of glovebox. The reaction was stirred at 80 °C for 13 h, and then was quenched with aqueous saturated NH₄Cl (2.0 mL) and extracted with Et₂O (3 × 20 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:2 CH₂Cl₂/hexanes) to afford the pure product. White foamy solid.

(*R,S*)-L2: 115 mg, 96% yield, 94% ee, >99:1 dr;

(*S,R*)-L2: 116 mg, 97% yield, 94% ee, >99:1 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (10.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-L2: 12.5 min (major), 14.0 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.10 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.93 – 6.85 (m, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.03 (s, 1H), 4.42 (tt, *J* = 12.1, 3.5 Hz, 1H), 3.36 (dt, *J* = 11.1, 3.6 Hz, 1H), 2.21 (s, 3H), 2.16 – 2.02 (m, 1H), 1.95 (dd, *J* = 14.2, 4.8 Hz, 1H), 1.76 – 1.48 (m,

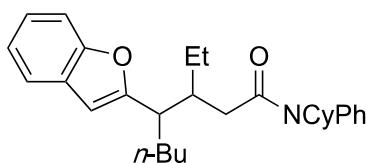
5H), 1.48 – 1.12 (m, 7H), 1.08 – 0.96 (m, 2H), 0.95 – 0.84 (m, 4H), 0.83 – 0.68 (m, 3H), 0.66 – 0.51 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 172.0, 144.4, 144.1, 138.5, 137.6, 136.6, 130.3, 129.9, 129.5, 128.7, 128.2, 127.7, 126.1, 123.6, 123.3, 119.9, 115.5, 109.3, 53.8, 40.2, 39.8, 36.2, 31.5, 31.3, 29.8, 27.9, 25.71, 25.70, 25.3, 24.8, 22.8, 21.4, 13.9, 11.9.

FT-IR (film): 2931, 2856, 1647, 1594, 1368, 1172, 712 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₃₇H₄₆N₂O₃SNa: 621.3121, found: 621.3119.

[α]_D²⁵ = +164.4 (c 1.0, CHCl₃); 94% ee, >99:1 dr from (*S,R*)-L2.



4-(Benzofuran-2-yl)-N-cyclohexyl-3-ethyl-N-phenyloctanamide (Fig. 4, reaction f, X = O).

A 4-mL vial was charged with *N*-cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide (70.6 mg, 0.20 mmol, 1.0 equiv) and 2-iodophenol (44.0 mg, 0.20 mmol, 1.0 equiv). The vial was loosely capped and transferred into glovebox. Next, Pd(PPh₃)₂Cl (5.6 mg, 0.0080 mmol, 0.040 equiv), CuI (7.6 mg, 0.040 mmol, 0.20 equiv), toluene (2.0 mL), TMG (76.0 μL, 0.60 mmol, 3.0 equiv) and a stir bar were added sequentially. Then, the vial was capped and transferred out of glovebox. The reaction was stirred at 80 °C for 13 h, and then was quenched with aqueous saturated NH₄Cl (2.0 mL) and extracted with Et₂O (3 × 20 mL). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:2 CH₂Cl₂/hexanes) to afford the pure product. Colorless oil.

(*R,S*)-L2: 77 mg, 87% yield, 94% ee, >98:2 dr;

(*S,R*)-L2: 80 mg, 90% yield, 94% ee, >98:2 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R,S*)-L2: 9.2 min (major), 14.2 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.33 (m, 1H), 7.32 – 7.21 (m, 2H), 7.20 – 7.13 (m, 2H), 7.13 – 7.04 (m, 2H), 7.02 – 6.85 (m, 2H), 6.21 (d, *J* = 0.8 Hz, 1H), 4.55 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.88 (dt, *J* = 9.8, 4.7 Hz, 1H), 2.18 – 2.04 (m, 1H), 1.91 – 1.80 (m, 2H), 1.80 – 1.69 (m, 2H), 1.69 – 1.54 (m, 3H), 1.52 – 1.25 (m, 5H), 1.24 – 1.08 (m, 4H), 1.05 – 0.79 (m, 4H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.66 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.8, 161.1, 154.4, 139.1, 130.4, 130.2, 128.9, 128.7, 127.9, 122.8, 122.2, 120.0, 110.7, 103.2, 54.0, 41.9, 40.6, 36.9, 31.7, 31.6, 30.3, 30.1, 25.80, 25.79, 25.4, 23.1, 22.7, 14.0, 11.9.

FT-IR (film): 2926, 2856, 1658, 1649, 1595, 1493, 1454, 1392, 1254, 1072, 751, 708 cm⁻¹.

HRMS (ESI-MS) *m/z* [M+Na]⁺ calcd for C₃₀H₃₉NO₂Na: 468.2873, found: 468.2877.

[α]_D²⁵ = –26.3 (c 1.0, CHCl₃); 94% ee, >98:2 dr from (*S,R*)-L2.

IX. Assignment of Absolute Configuration

The configuration of the coupling product illustrated in Fig. 2, entry 35, using (*R*)-L1, was determined via X-ray crystallography.

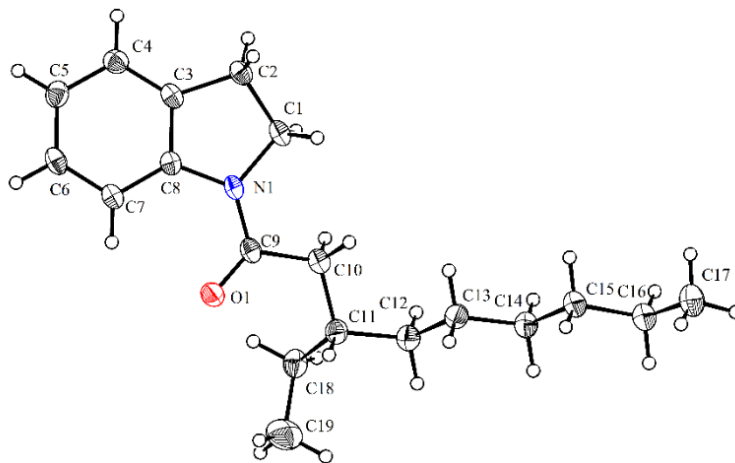
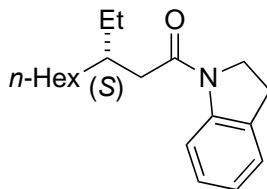


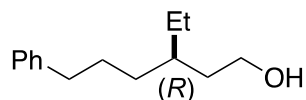
Figure S-1. Thermal ellipsoid plot at the 50% probability level.



(*S*)-3-Ethyl-1-(indolin-1-yl)nonan-1-one. X-ray quality crystals were obtained by slow evaporation of a saturated solution in hexane of a sample synthesized using (*R*)-L1. A crystal of $C_{19}H_{29}NO$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a 'Bruker APEX-II CCD' diffractometer with filtered $Cu-K\alpha$ radiation at a temperature of 100 K. Using Olex2 (37), the structure was solved with the XT (38) structure solution program using direct methods and refined with the ShelXL (39) refinement package using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-4. Crystal data and structure refinement for the product in Fig. 2, entry 35.

Identification code	v18075	
Empirical formula	C ₁₉ H ₂₉ N O	
Formula weight	287.43	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.1922(11) Å	α = 90 °
	b = 9.4775(15) Å	β = 92.783(7) °
	c = 35.588(4) Å	γ = 90 °
Volume	3433.6(8) Å ³	
Z	8	
Density (calculated)	1.112 g/cm ³	
Absorption coefficient	0.514 mm ⁻¹	
F(000)	1264	
Crystal size	0.17 x 0.15 x 0.01 mm ³	
Theta range for data collection	3.730 to 79.874 °	
Index ranges	-12 ≤ h ≤ 12, -10 ≤ k ≤ 11, -44 ≤ l ≤ 43	
Reflections collected	53983	
Independent reflections	13680 [R(int) = 0.0515]	
Completeness to theta = 67.679 °	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8279	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13680 / 46 / 782	
Goodness-of-fit on F ²	1.065	
Final R indices [I > 2σ(I)]	R1 = 0.0487, wR2 = 0.1153	
R indices (all data)	R1 = 0.0537, wR2 = 0.1179	
Absolute structure parameter [Flack]	0.11(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.525 and -0.221 e.Å ⁻³	



(R)-3-Ethyl-6-phenylhexan-1-ol. The stereochemistry of this compound has been established in the literature (40). It was synthesized via the reduction of the coupling product of Fig. 2, entry 2, obtained with (S)-L1. The (R) configuration was assigned by comparison with the published optical rotation and chiral HPLC data:

Optical rotation:

$[\alpha]_D^{25} = +2.2$ (*c* 1.0, CHCl₃); 91% ee from (S)-L1.

Lit. (40): $[\alpha]_D^{25} = +1.39$ (*c* 1.1, CHCl₃); 92% ee for (R) configuration.

HPLC (CHIRALPAK AD-H column, 1.0% EtOH in hexanes, 1.0 mL/min):

17.2 min (major), 18.8 min (minor); 91% ee from (S)-L1.

Lit. (40): 19.8 min (major), 22.4 min (minor); 92% ee (R) configuration.

The configuration of the desilylated terminal alkyne derived from the coupling product illustrated in Fig. 3, entry 1 (generated using (*R,S*)-L2) was determined via X-ray crystallography.

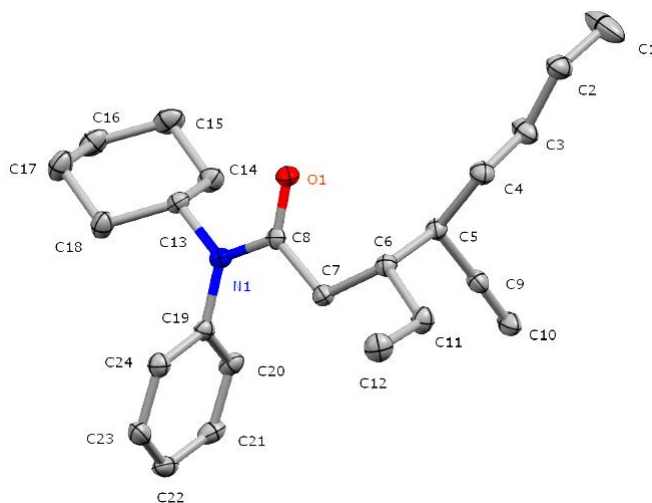
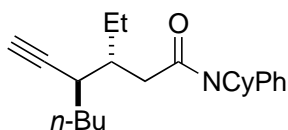


Figure S-2. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



(3*R*,4*R*)-*N*-Cyclohexyl-3-ethyl-4-ethynyl-*N*-phenyloctanamide. X-ray quality crystals were obtained by slow evaporation of a saturated solution in pentane of a sample synthesized with (*R,S*)-L2. A crystal of C₂₄H₃₅NO was selected and mounted in a nylon loop in immersion oil. All measurements were made on a 'Bruker APEX-II CCD' diffractometer with filtered Cu-K α radiation at a temperature of 100 K. Using Olex2 (37), the structure was solved with the XT (38) structure solution program using direct methods and refined with the ShelXL (39) refinement package using least squares minimisation. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-5. Crystal data and structure refinement for the alkyne in the center of Fig. 4.

Identification code	v19168
Empirical formula	C ₂₄ H ₃₅ NO
Formula weight	353.53
Temperature/K	100
Crystal system	orthorhombic
Space group	P212121
a/Å	8.0453(6)
b/Å	11.7790(13)
c/Å	22.674(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2148.8(4)
Z	4
ρ _{calc} /cm ³	1.093
μ/mm ⁻¹	0.495
F(000)	776.0
Crystal size/mm ³	0.29 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.798 to 144.662
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -28 ≤ l ≤ 27
Reflections collected	49459
Independent reflections	4245 [R _{int} = 0.0417, R _{sigma} = 0.0153]
Data/restraints/parameters	4245/0/238
Goodness-of-fit on F ²	1.045
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0266, wR ₂ = 0.0692
Final R indexes [all data]	R ₁ = 0.0272, wR ₂ = 0.0697
Largest diff. peak/hole / e Å ⁻³	0.18/-0.14
Flack parameter	0.06(4)

X. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ Spectra; Stereoselectivity Analysis

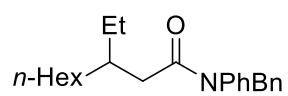
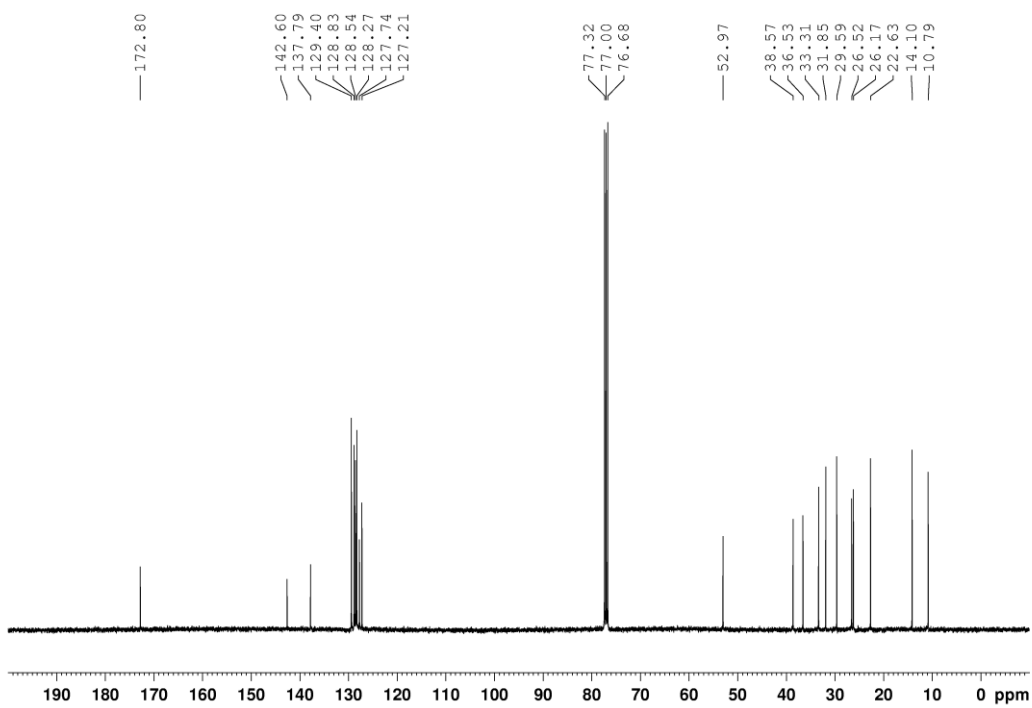
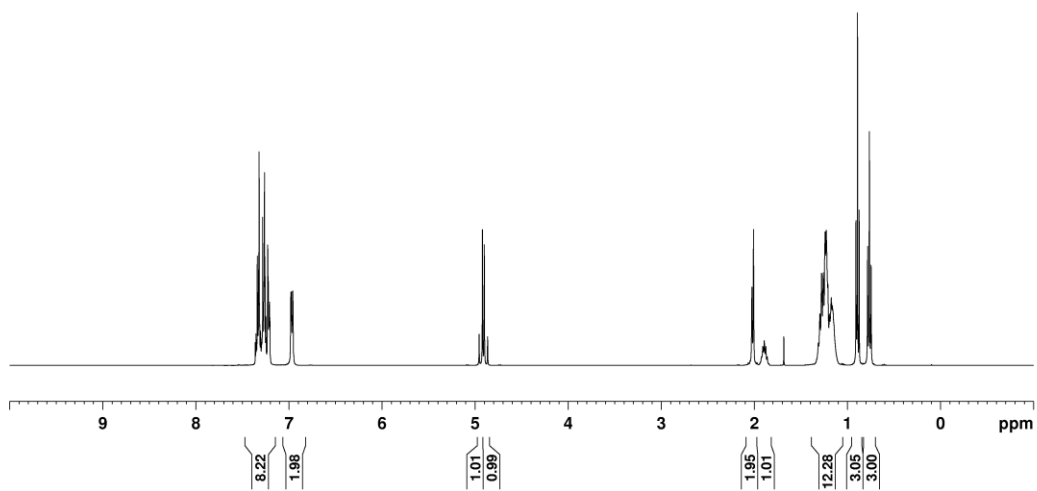


Fig. 2, entry 1



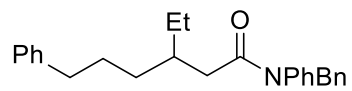
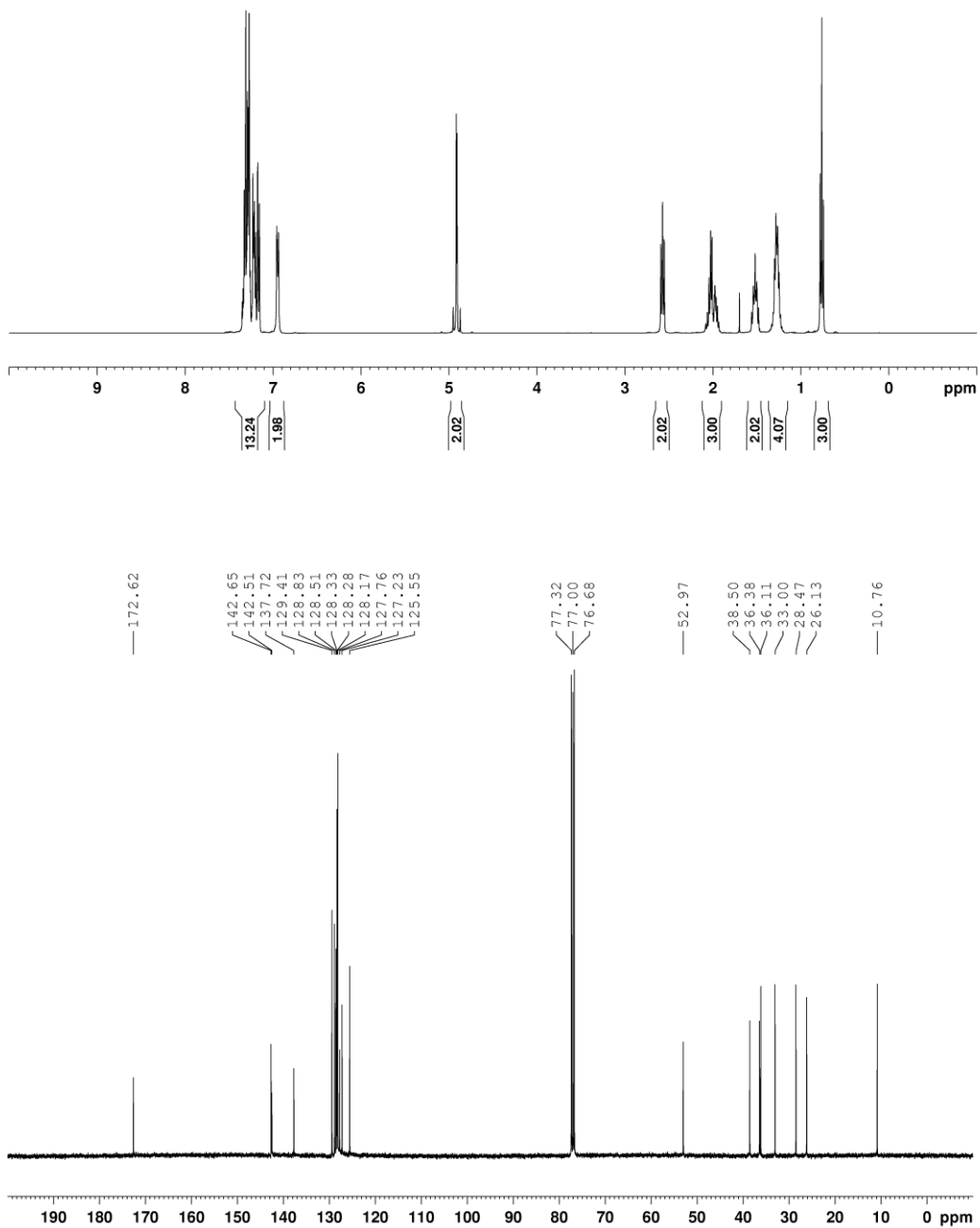


Fig. 2, entry 2



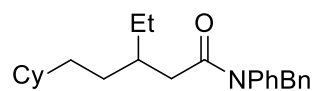
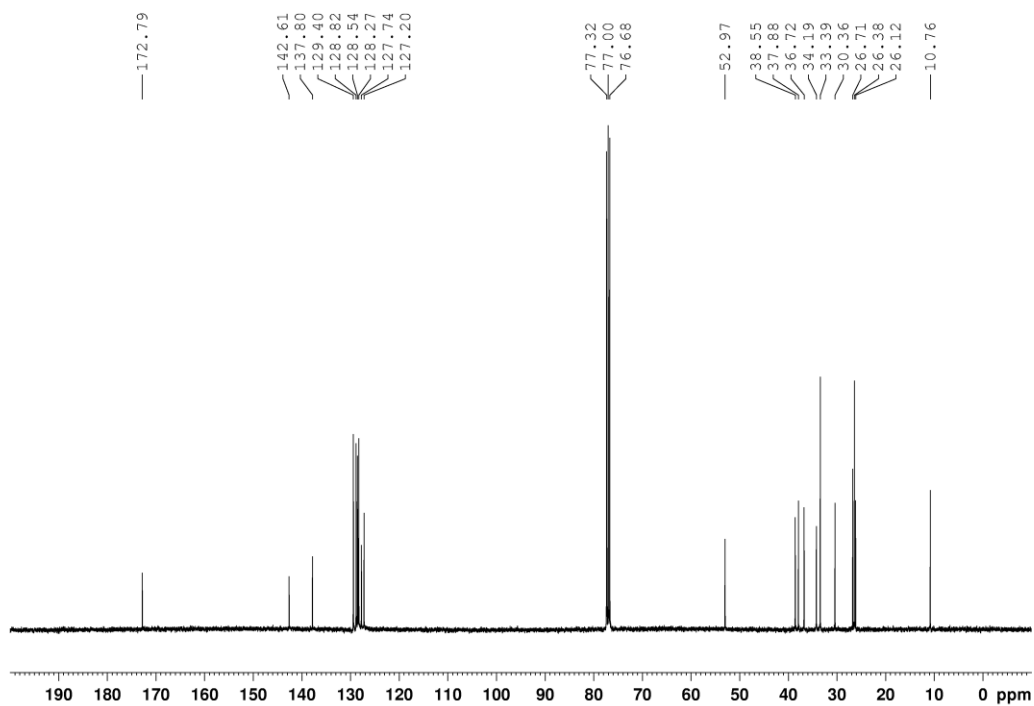
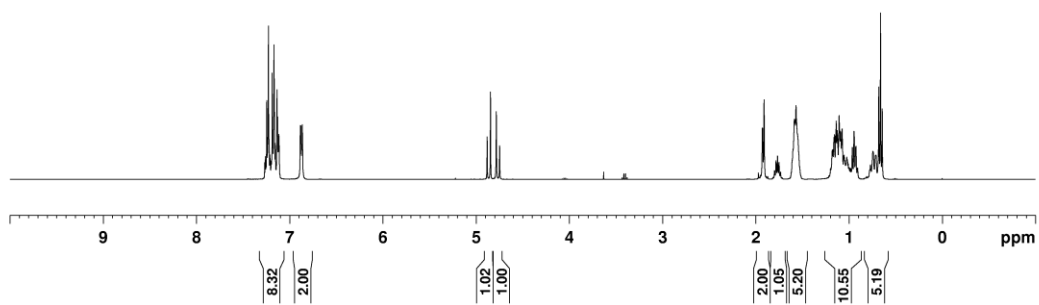


Fig. 2, entry 3



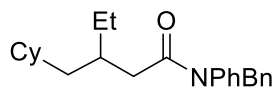
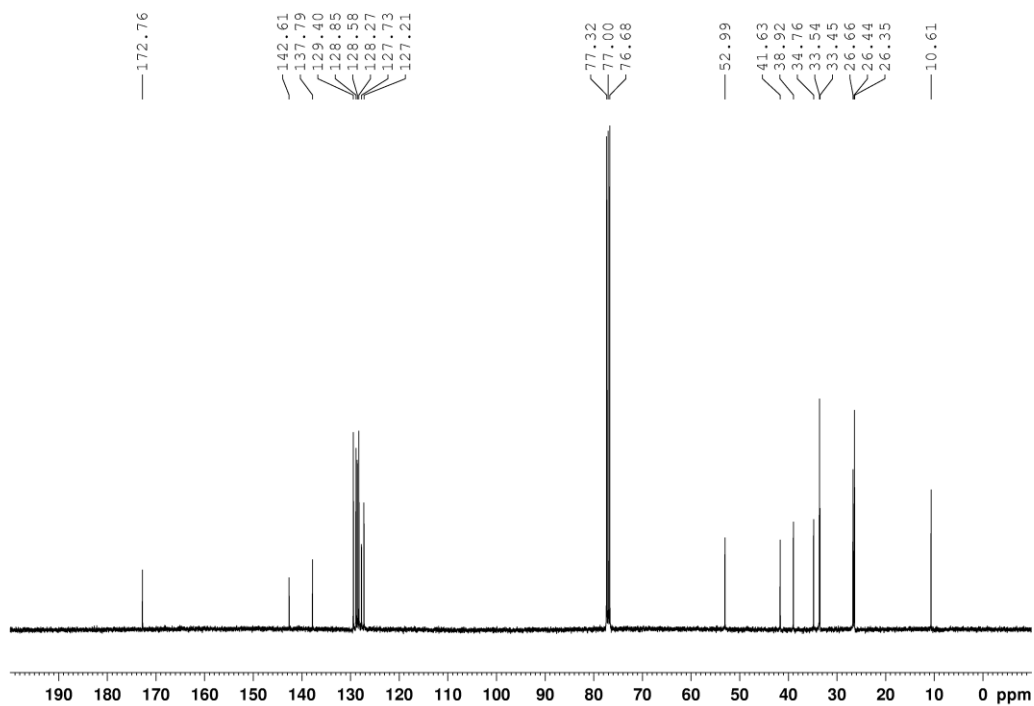
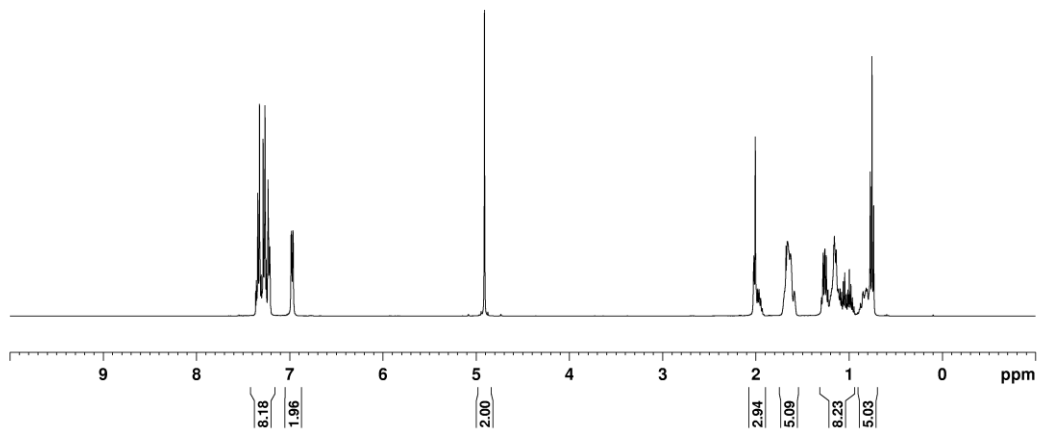


Fig. 2, entry 4



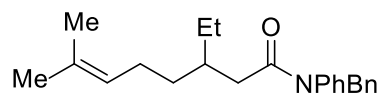
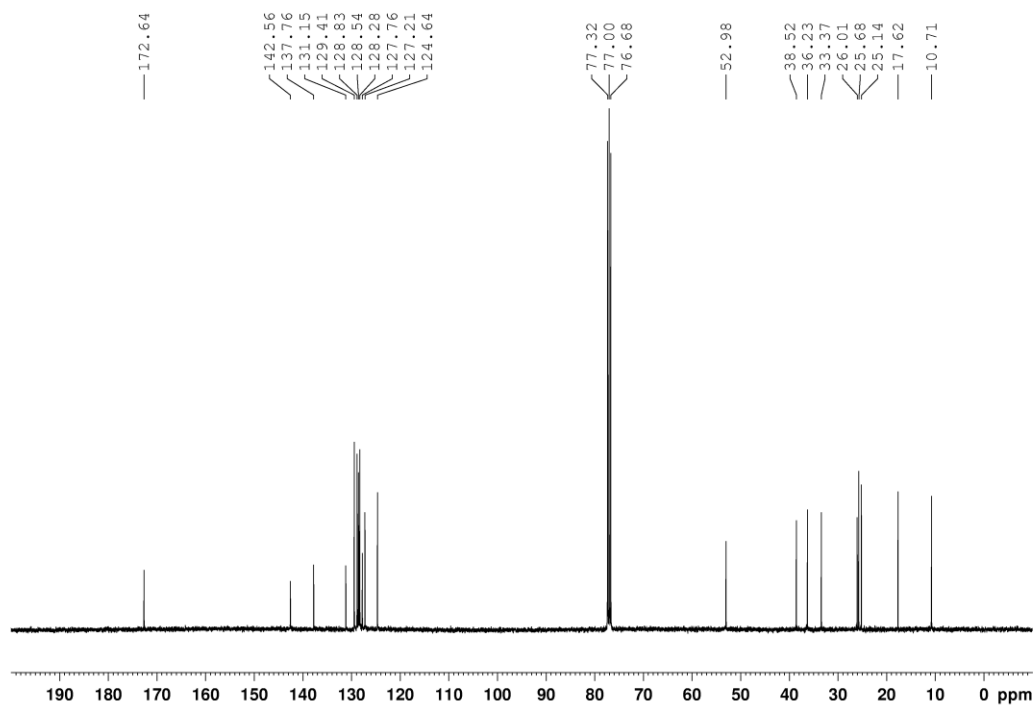
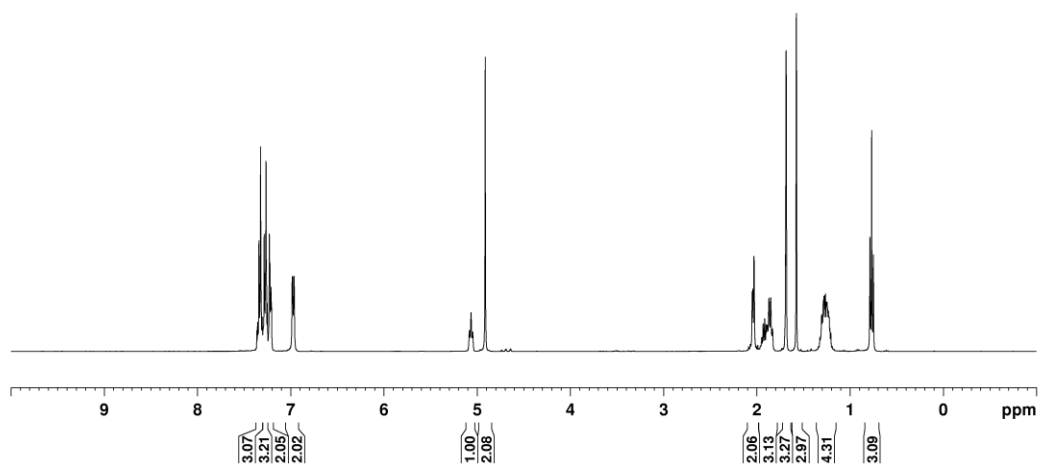


Fig. 2, entry 5



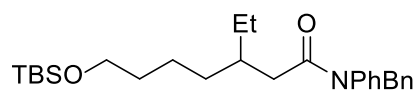
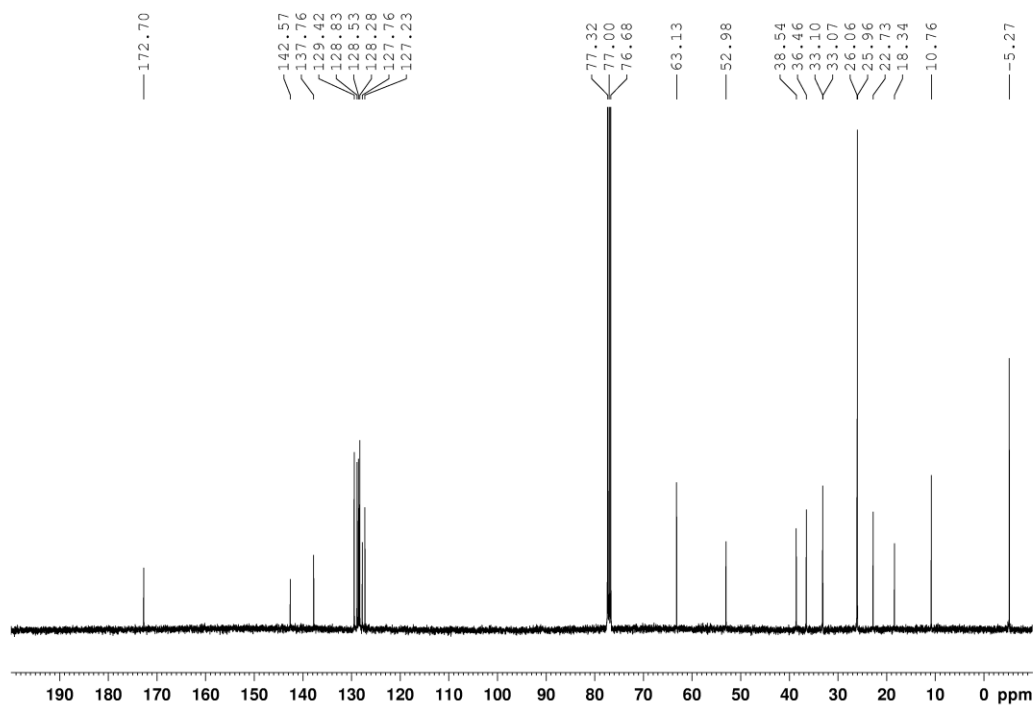
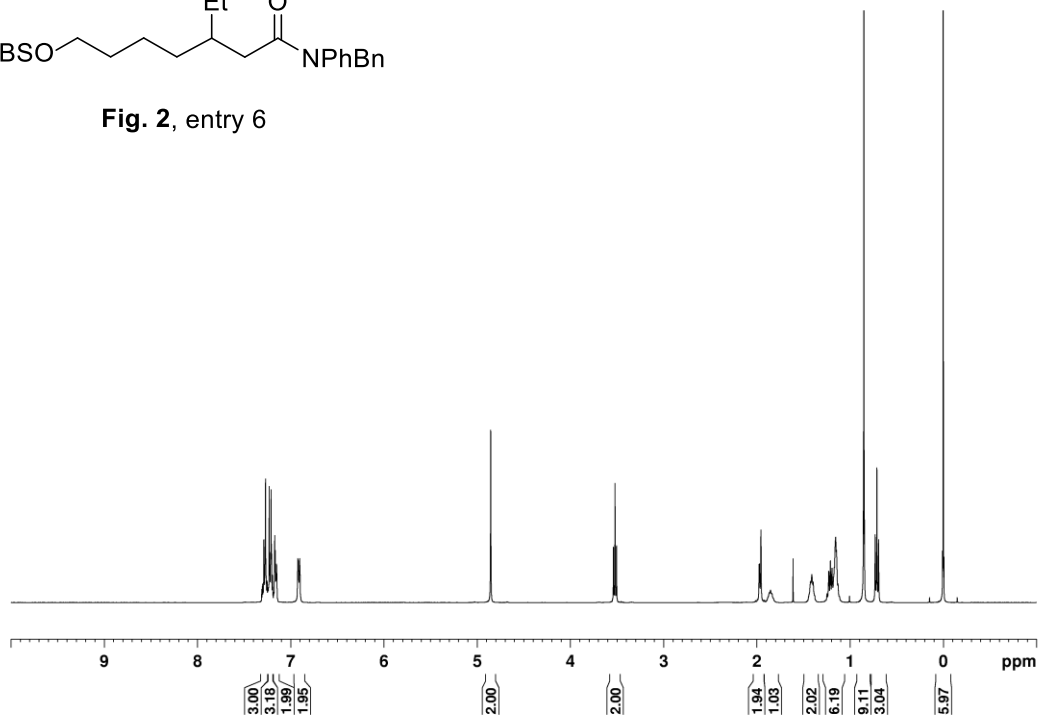


Fig. 2, entry 6



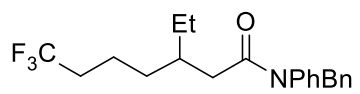
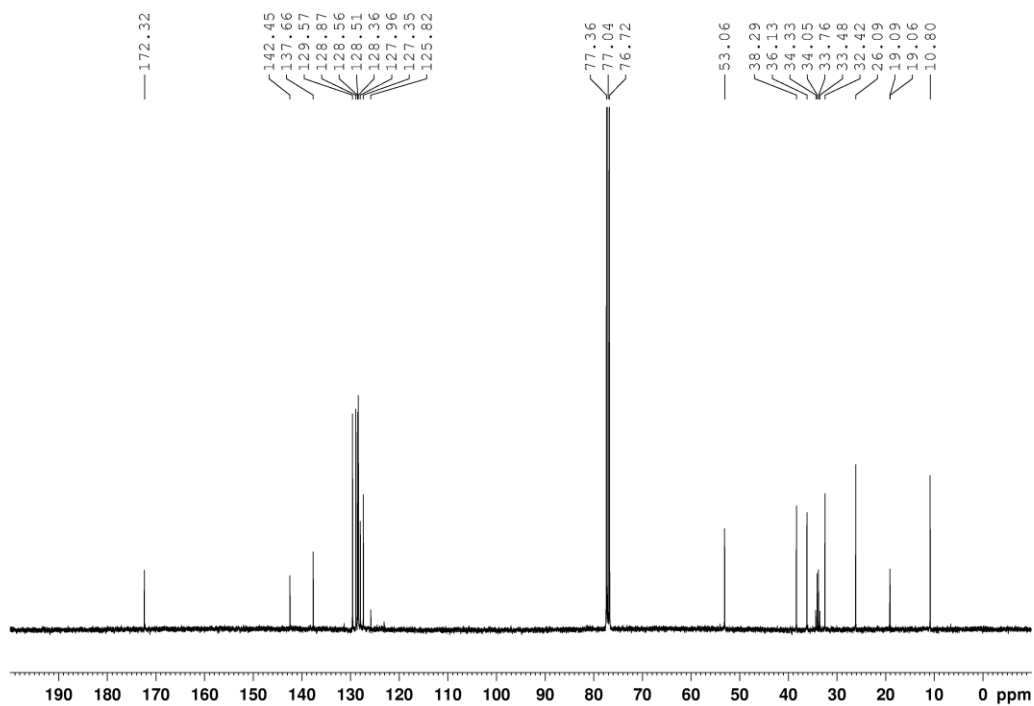
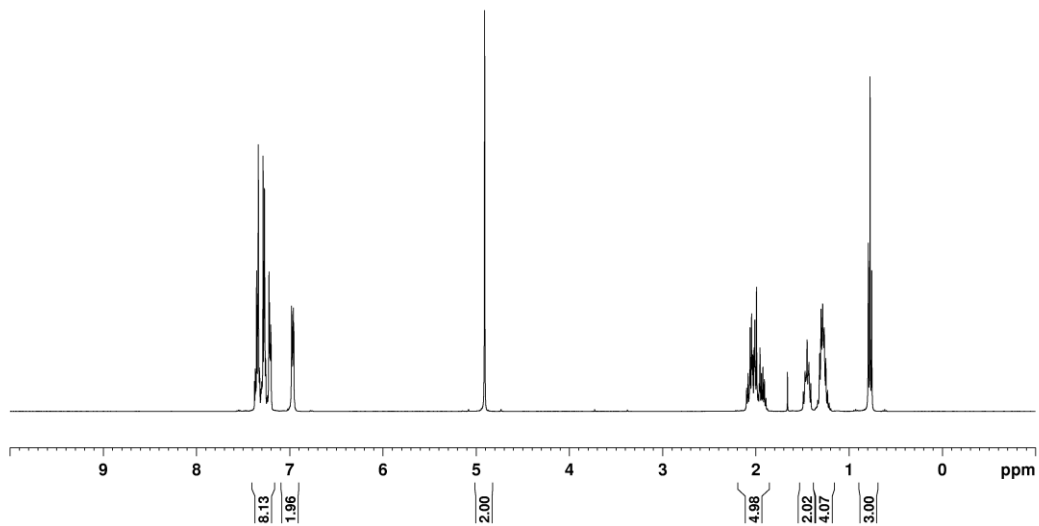


Fig. 2, entry 7



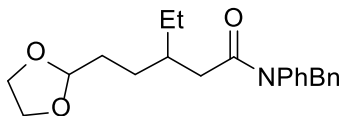
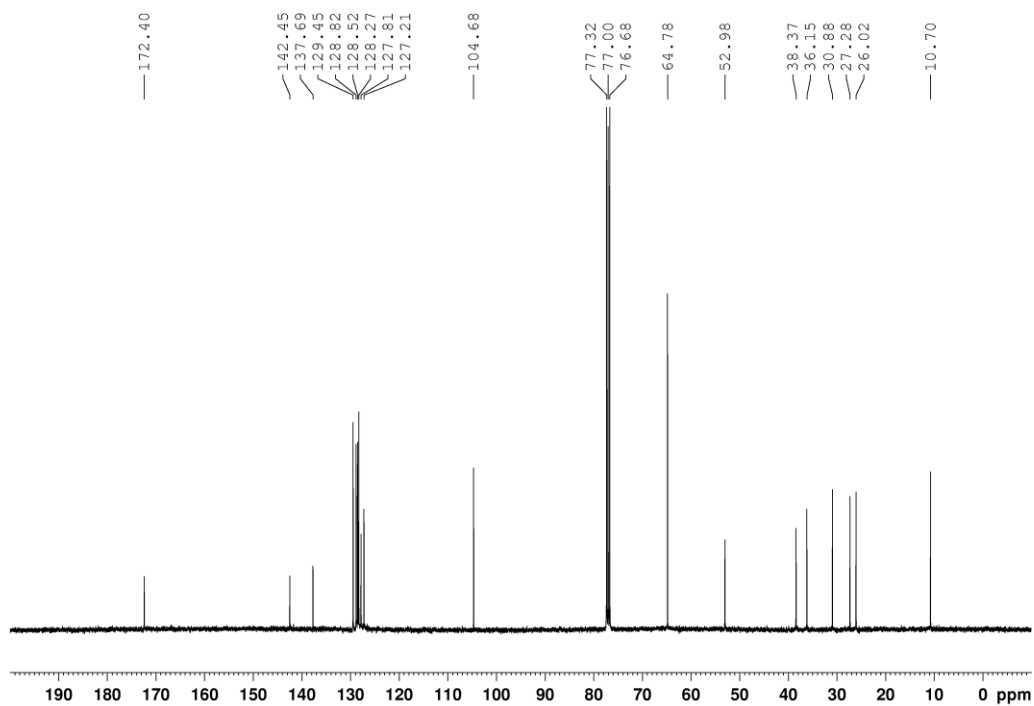
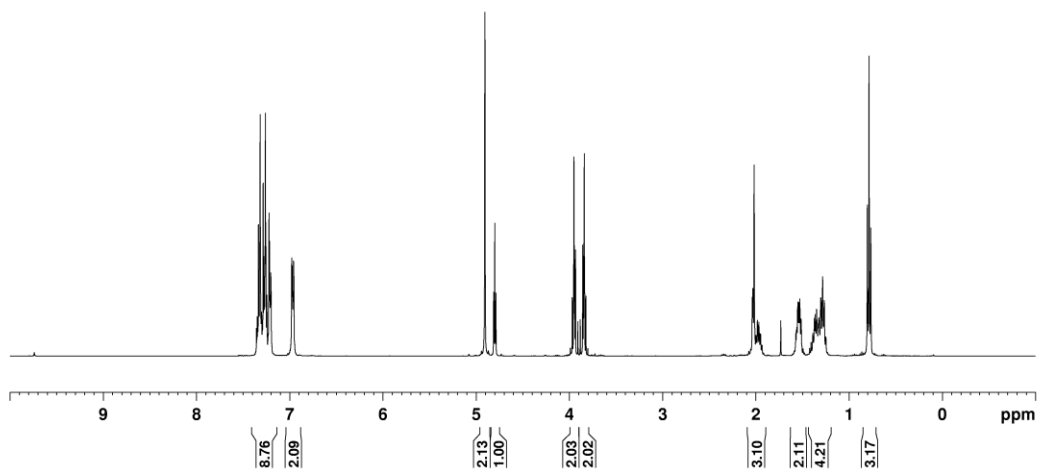


Fig. 2, entry 8



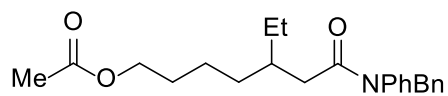
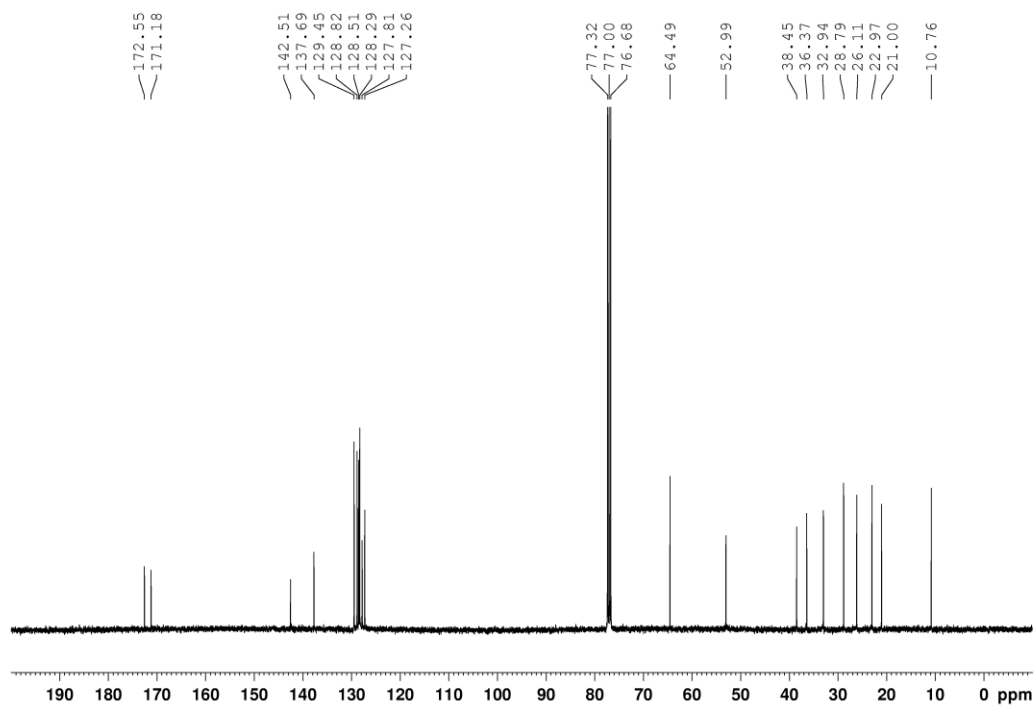
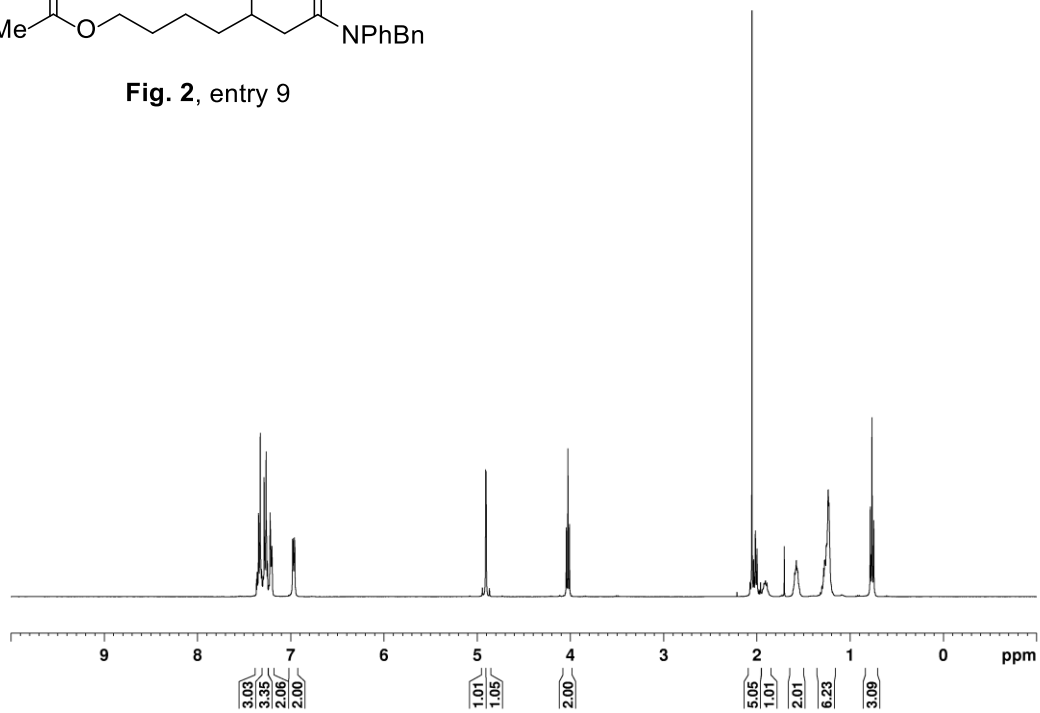


Fig. 2, entry 9



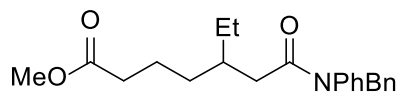
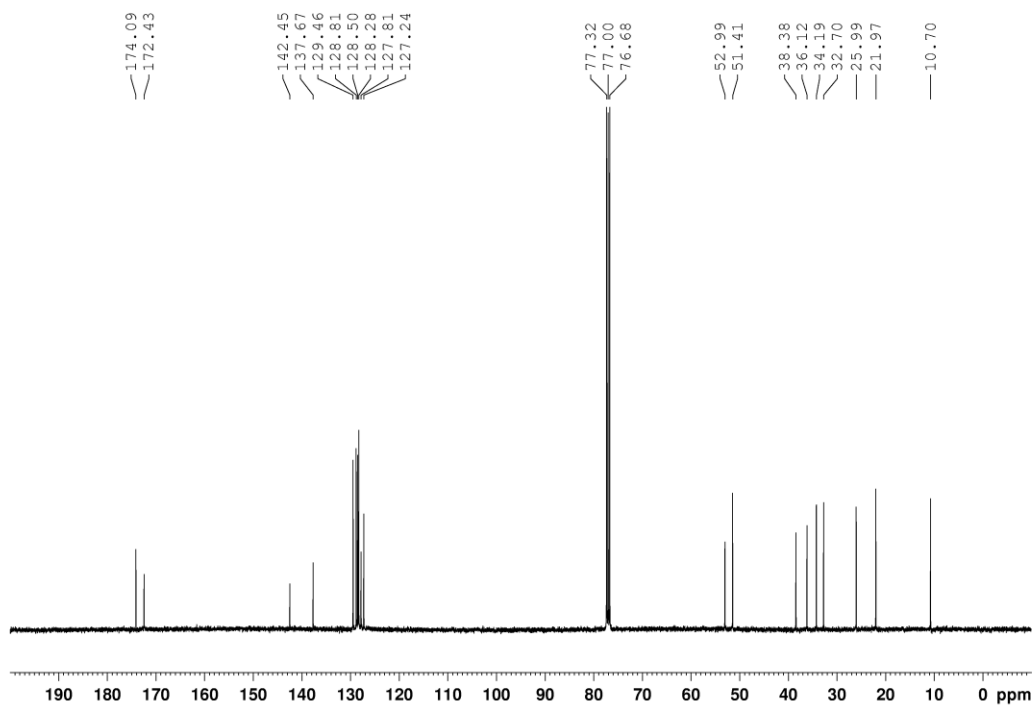
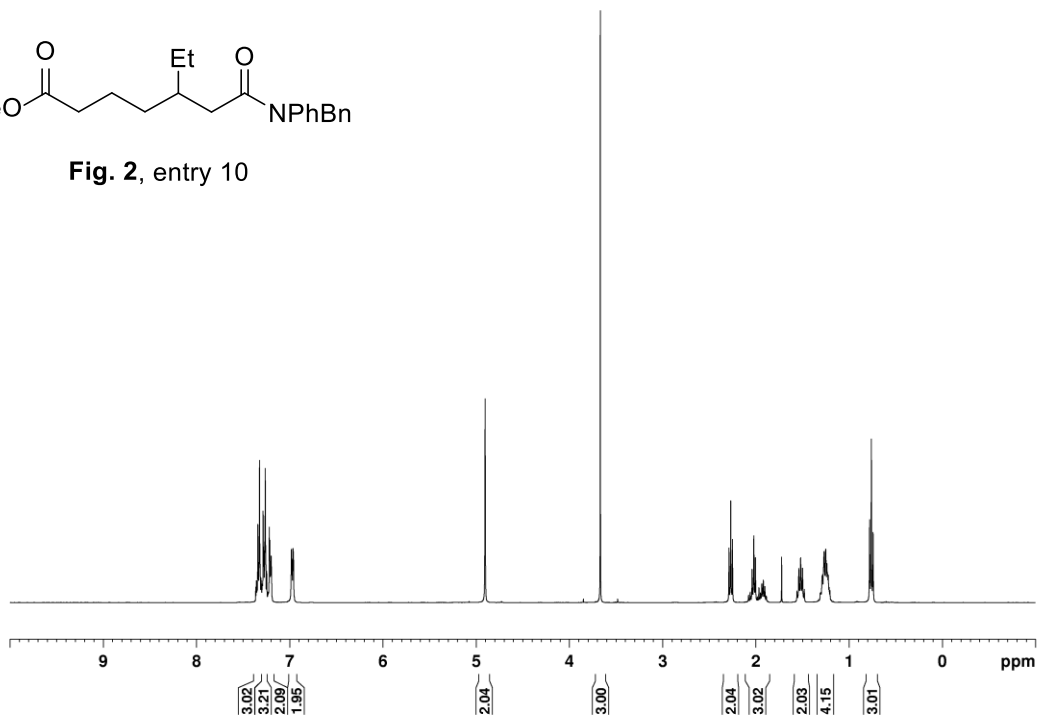


Fig. 2, entry 10



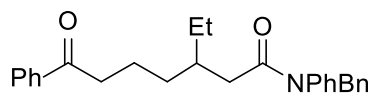
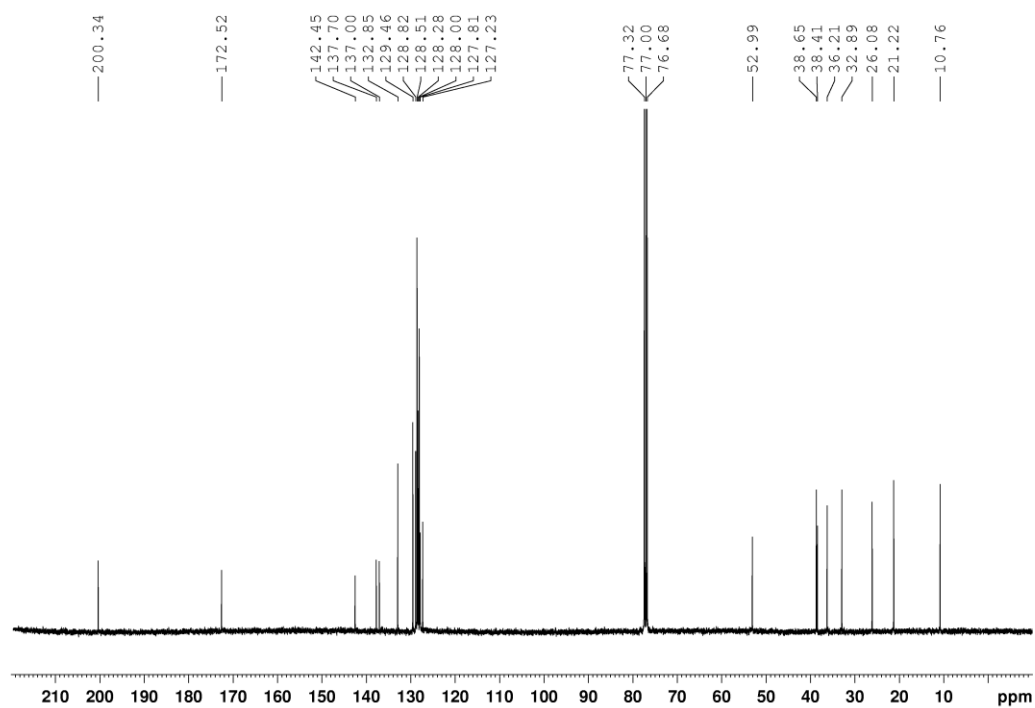
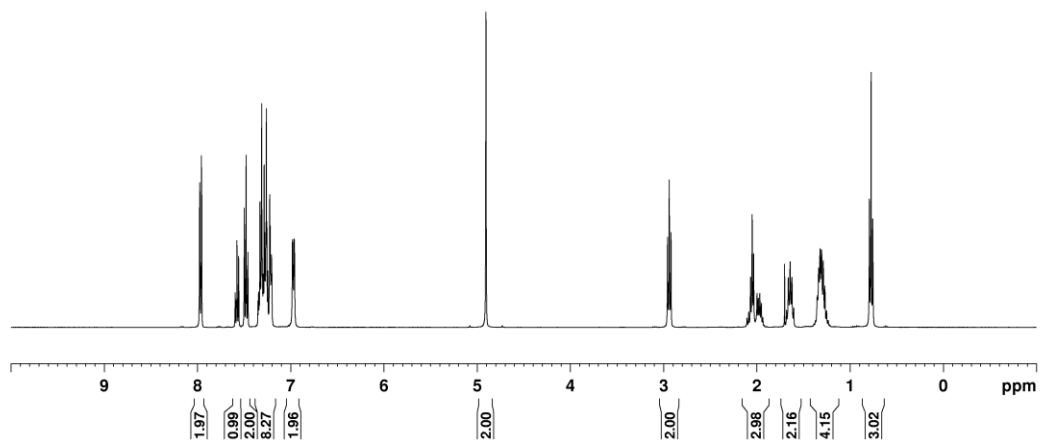


Fig. 2, entry 11



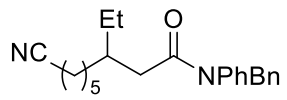
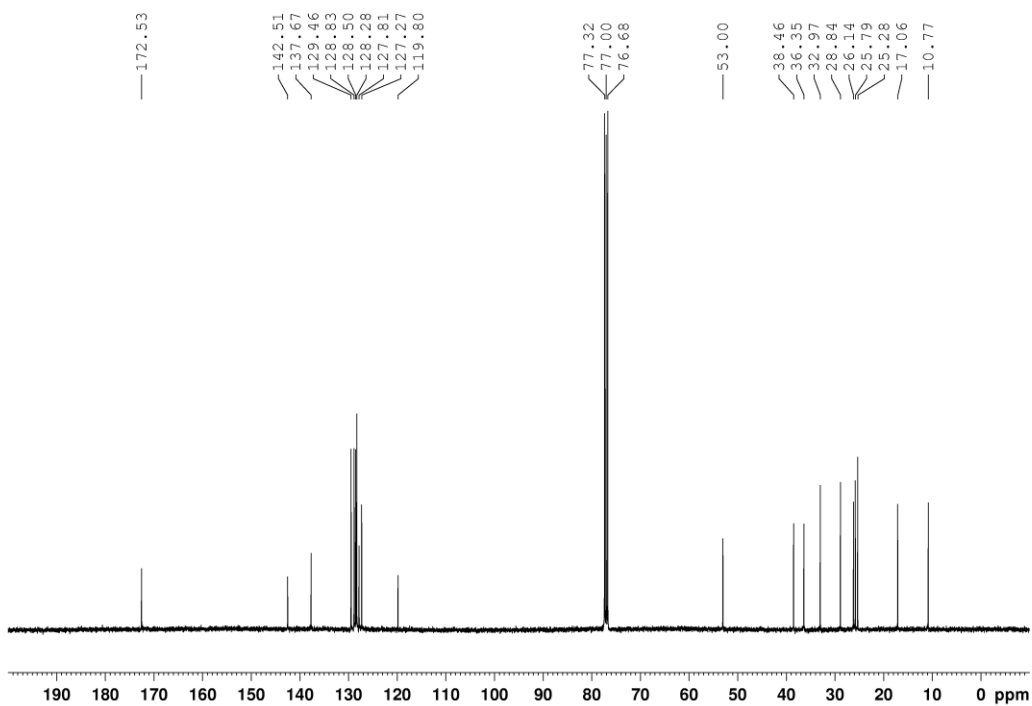
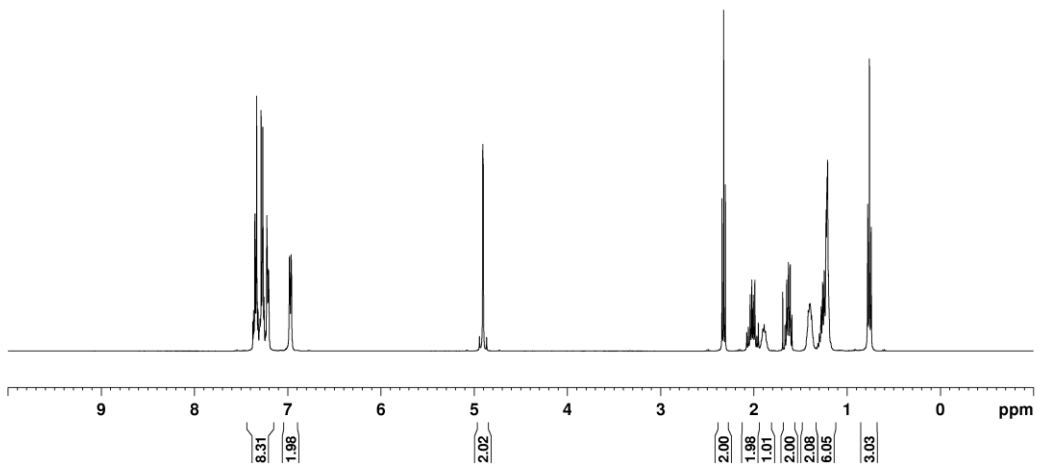


Fig. 2, entry 12



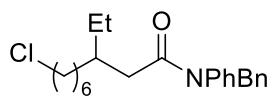
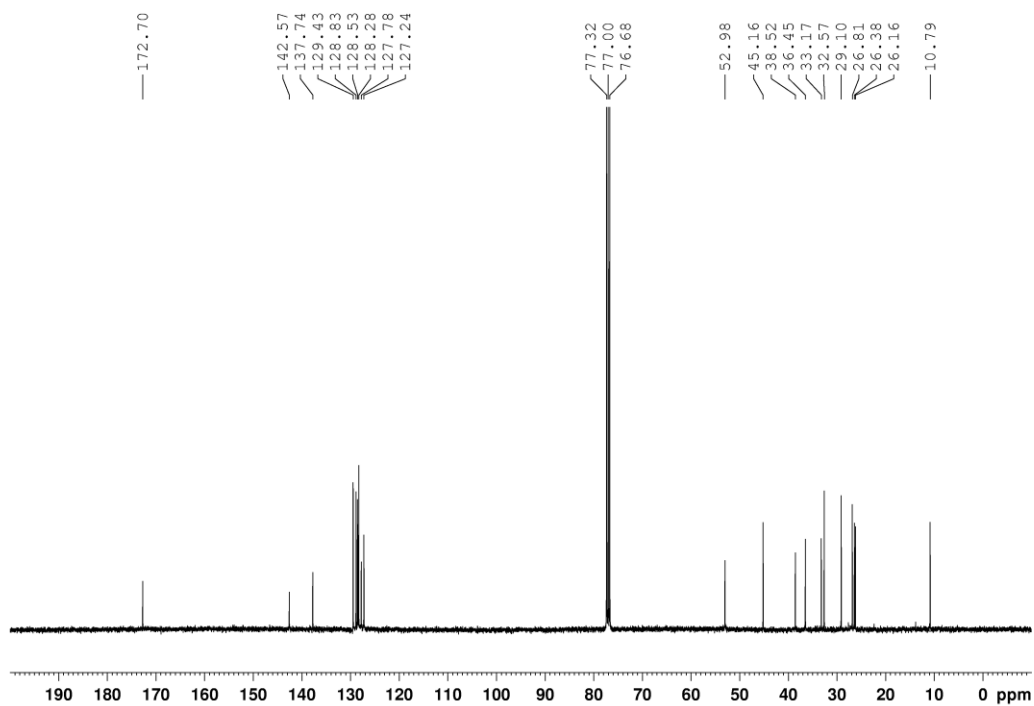
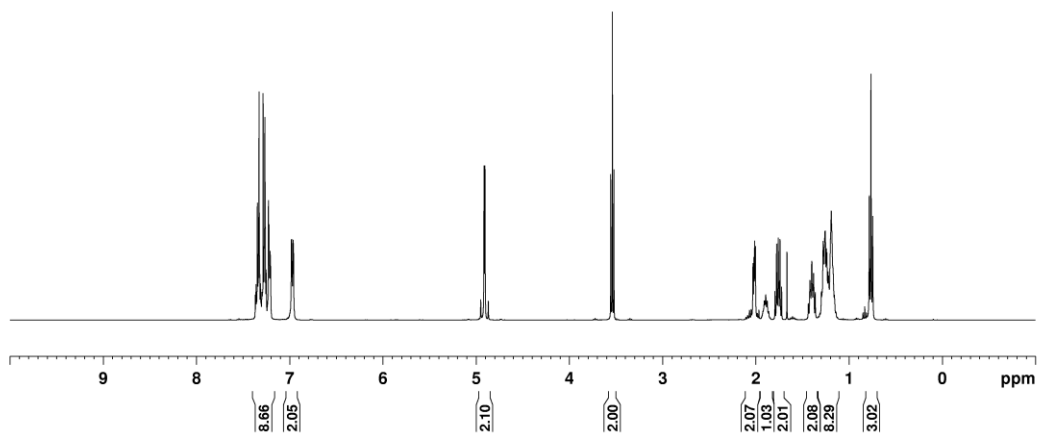


Fig. 2, entry 13



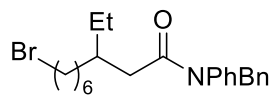
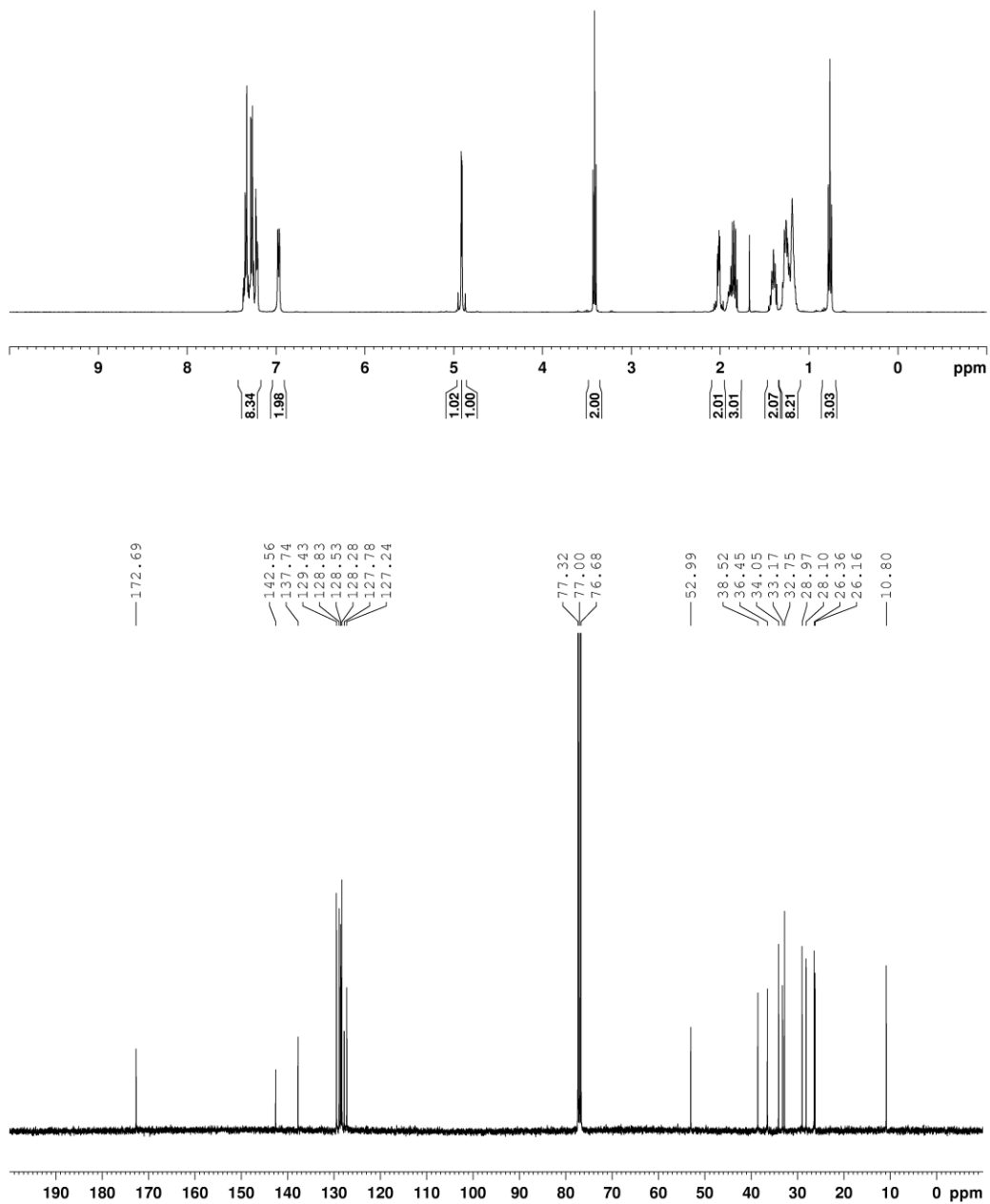


Fig. 2, entry 14



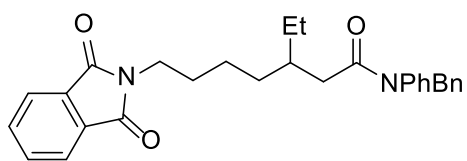
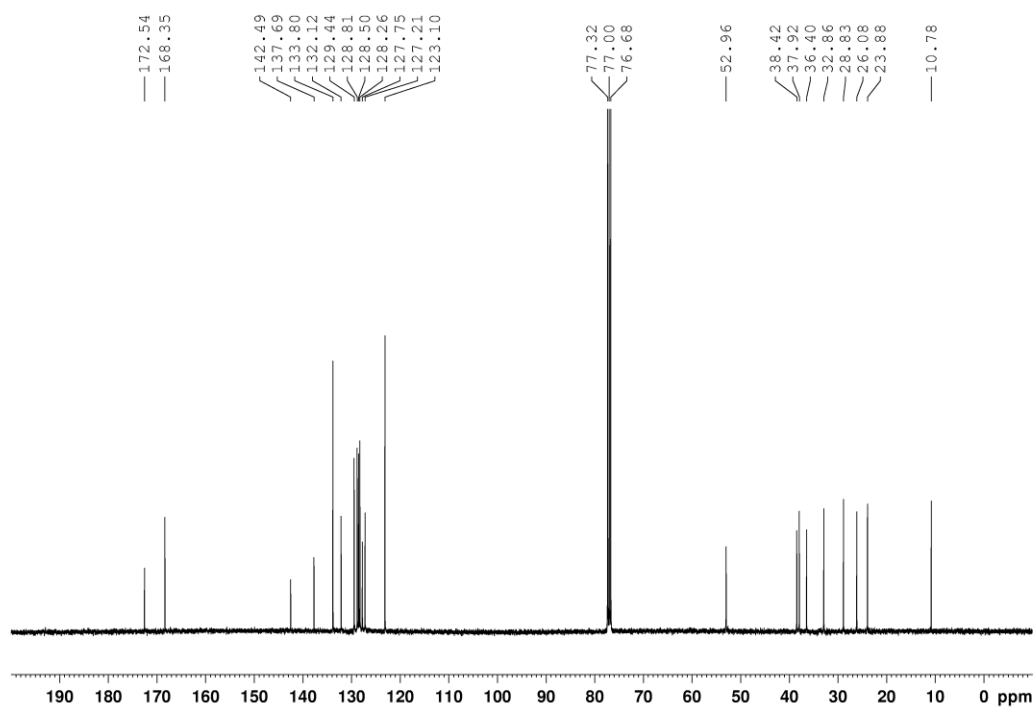
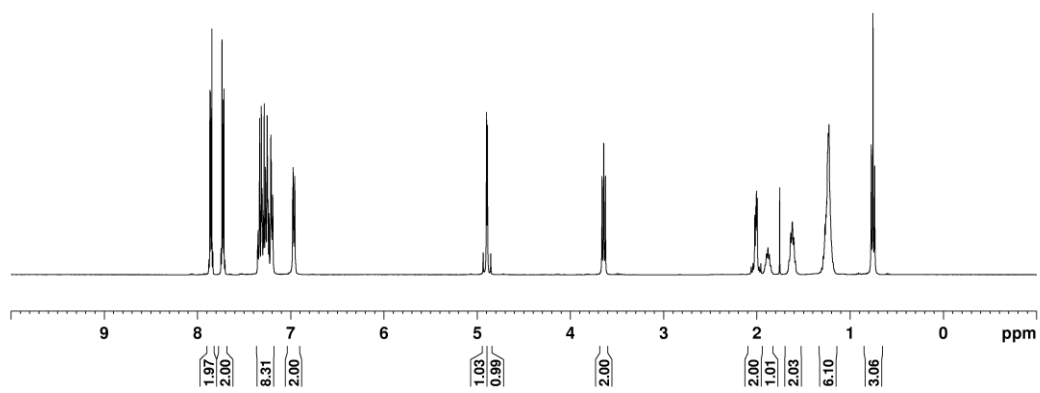


Fig. 2, entry 15



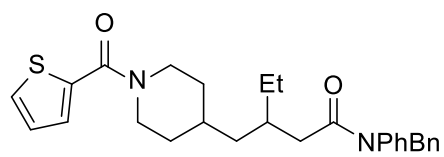
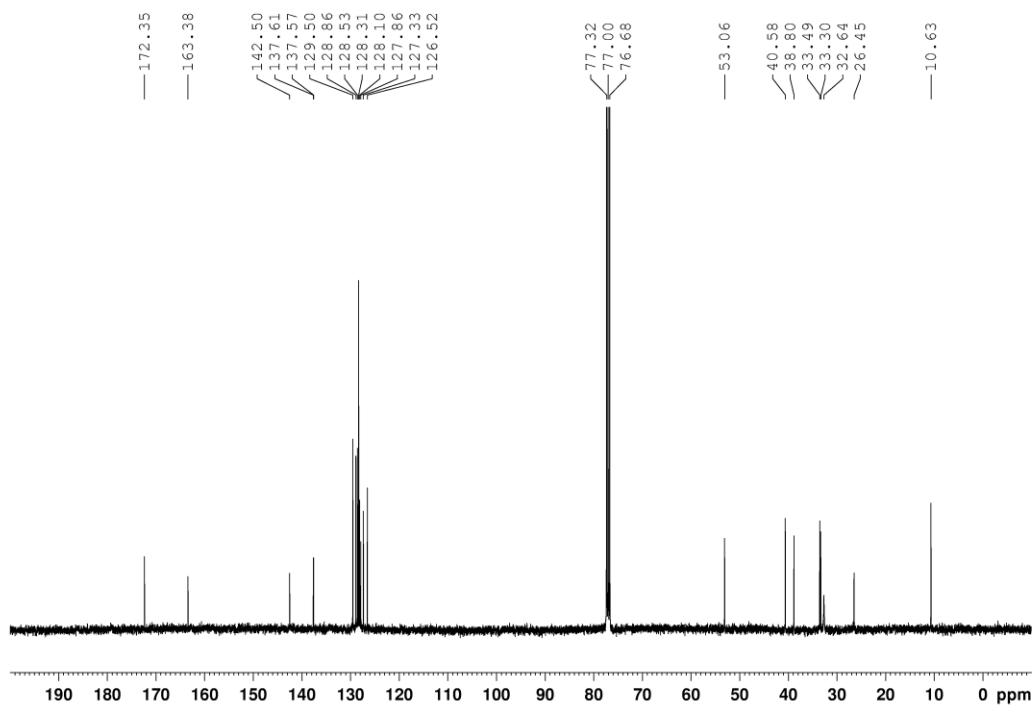
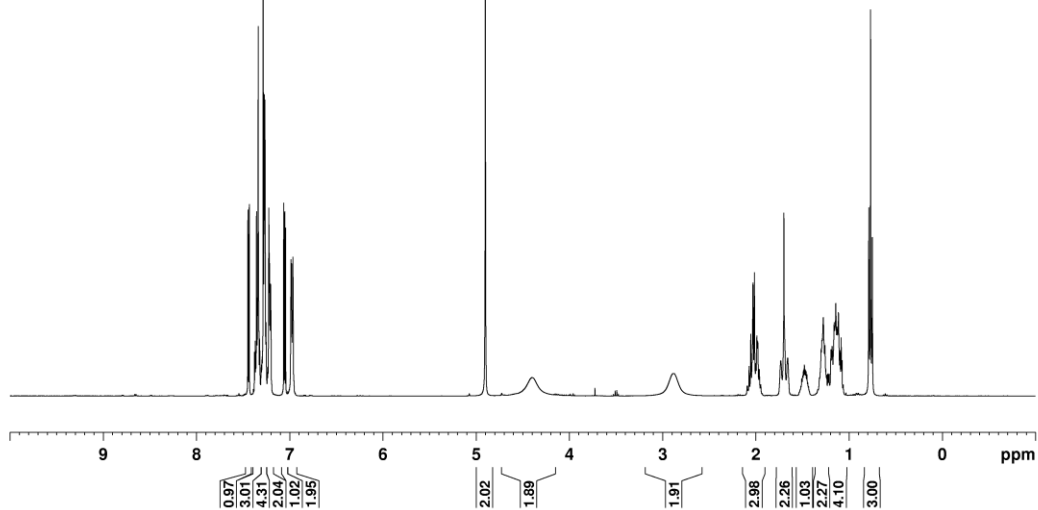


Fig. 2, entry 16



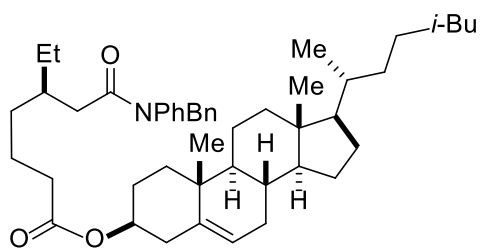
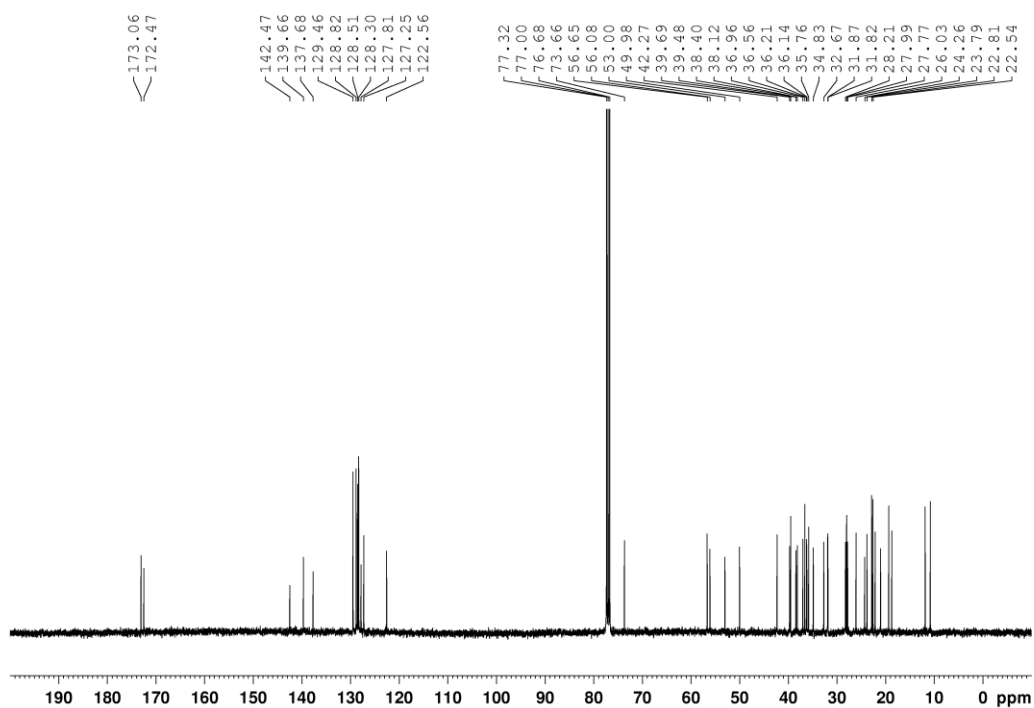
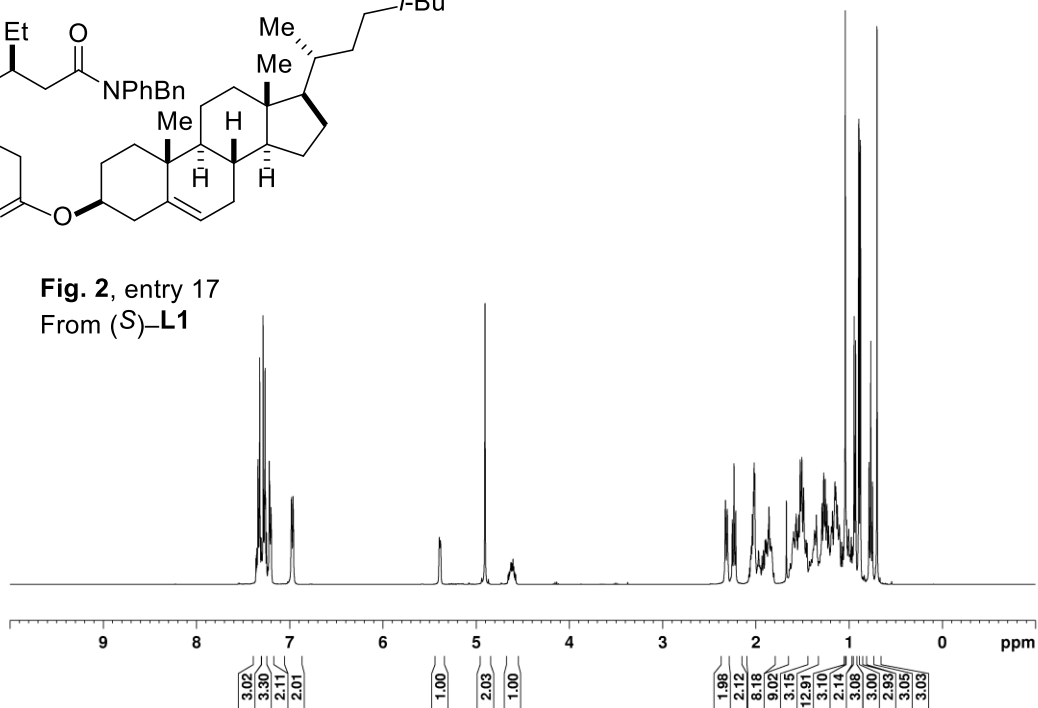


Fig. 2, entry 17
From (S)-L1



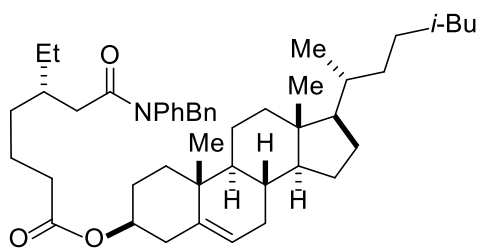
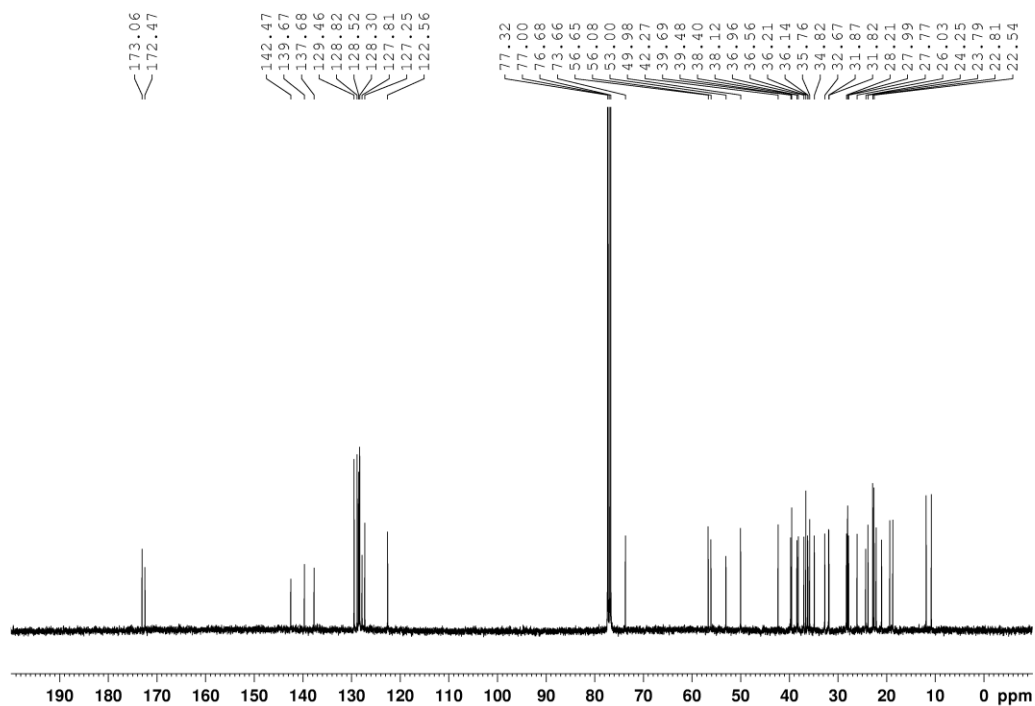
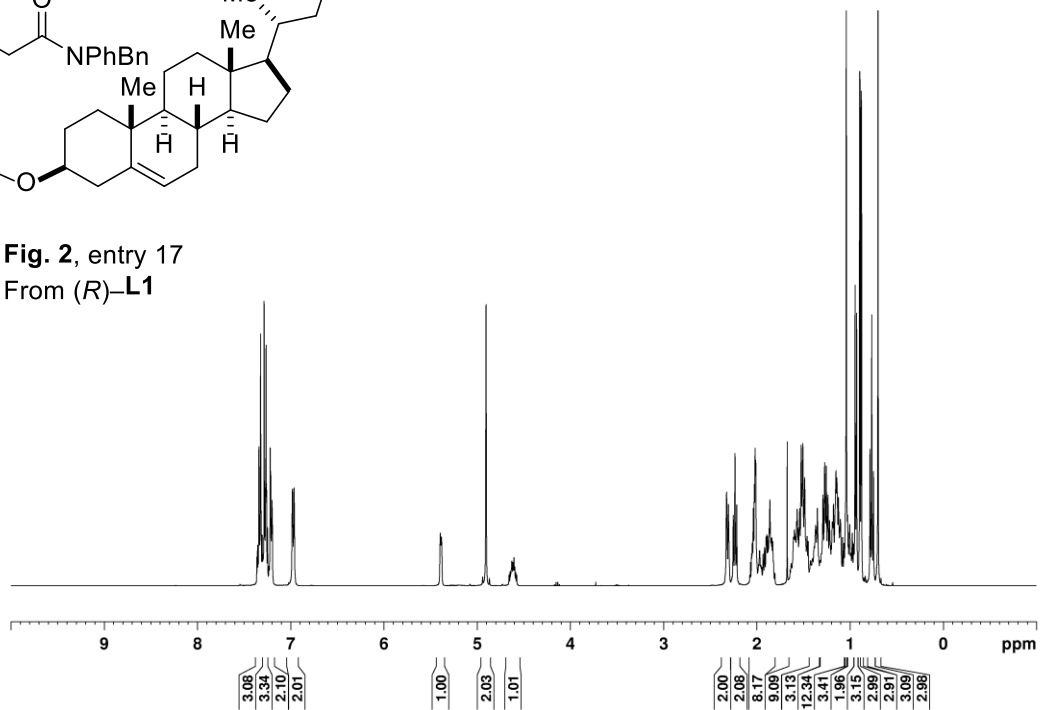


Fig. 2, entry 17
From *(R)*-L1



PROTON01
BJG-2-199-1

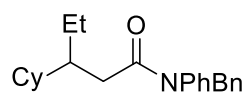
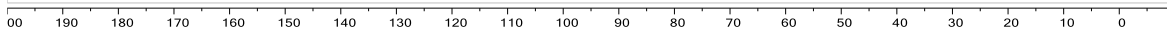
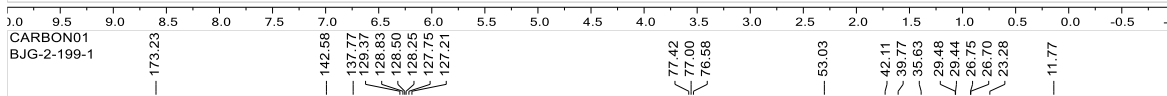
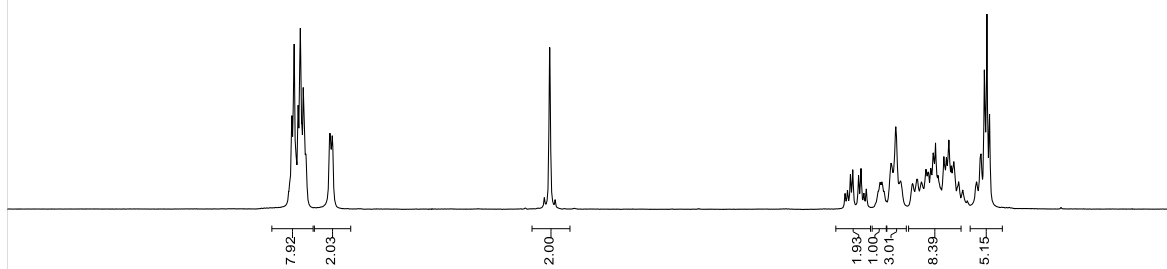


Fig. 2, entry 18



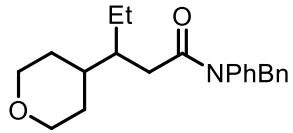
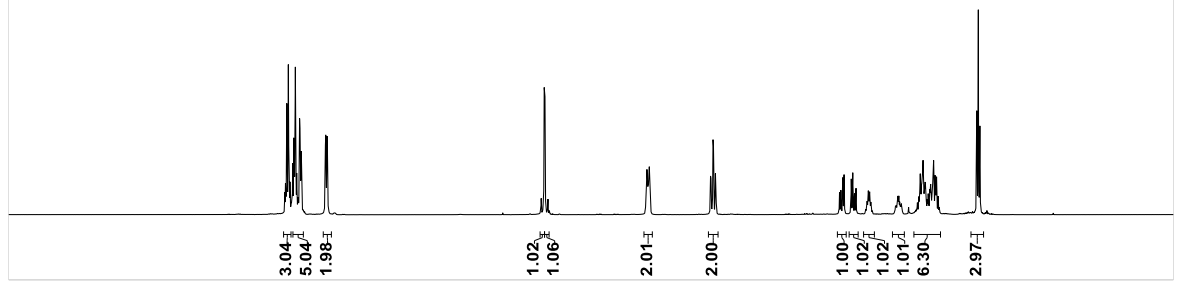
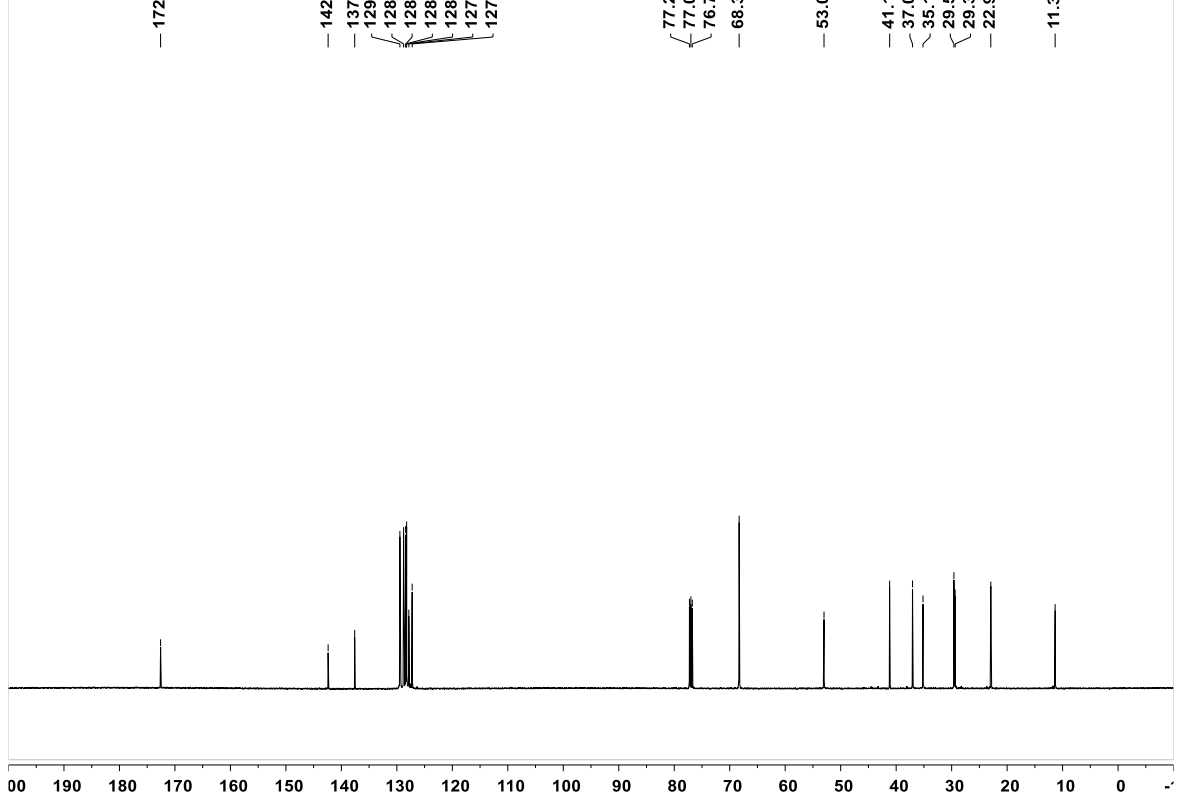


Fig. 2, entry 19



hh-bjg2-199-3/CARBON01.fid/fid



PROTON01
BJG-2-211-4

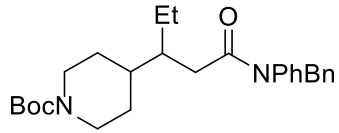
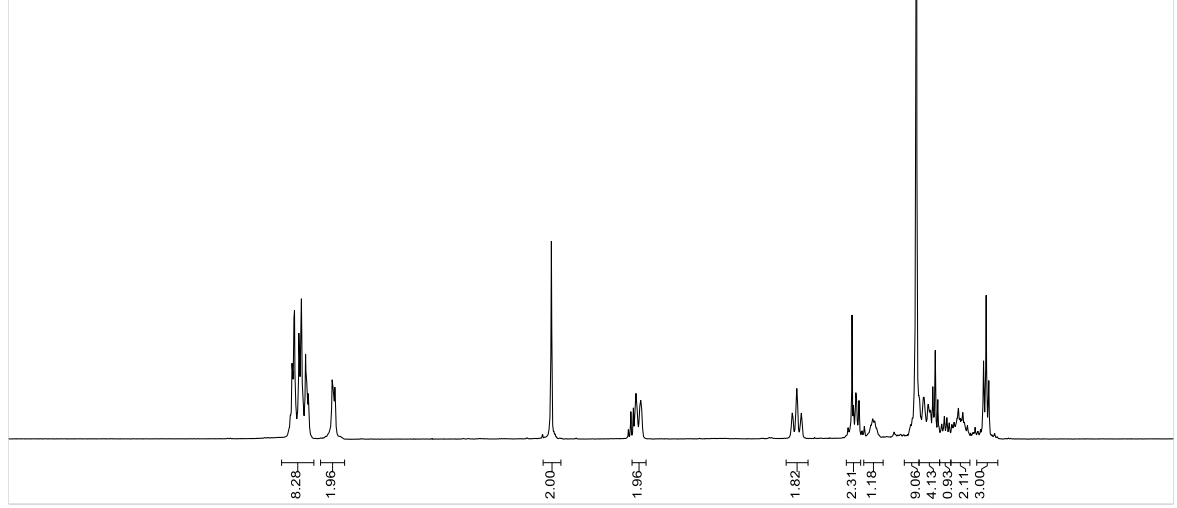
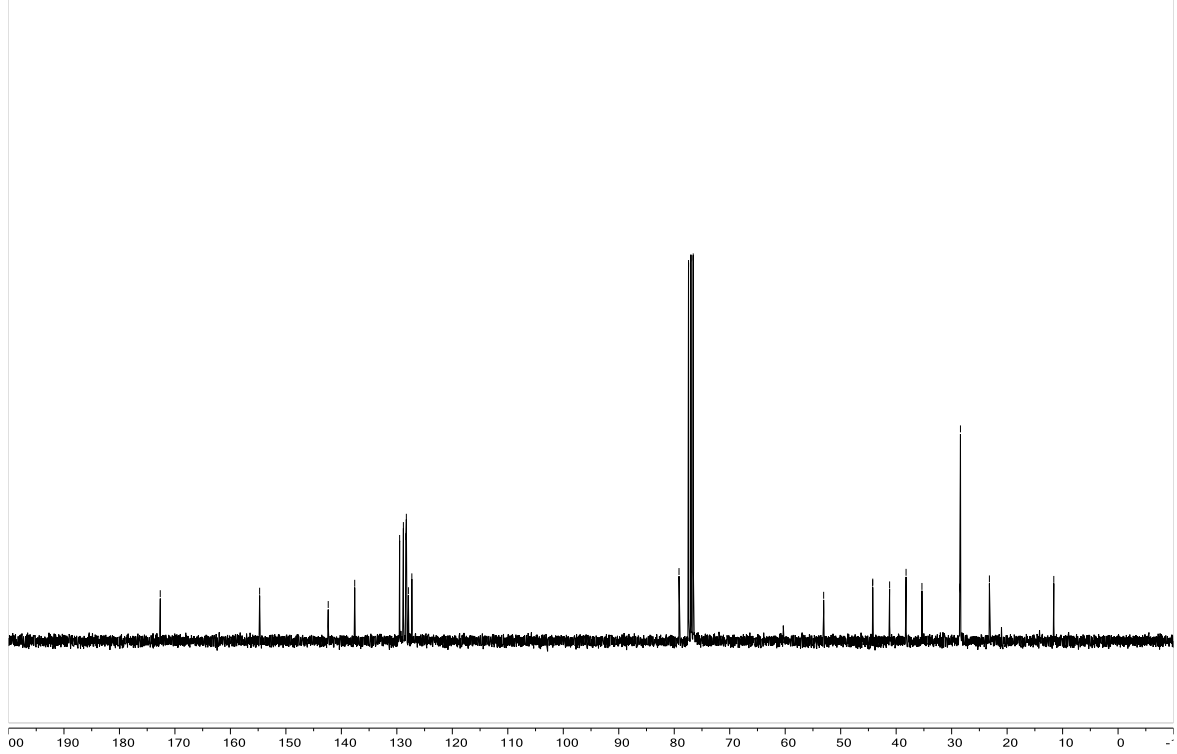


Fig. 2, entry 20



CARBON01
BJG-2-211-4

172.65, 154.73, 142.37, 137.59, 136.56, 128.82, 128.39, 128.29, 127.92, 127.30, 79.14, 77.42, 77.00, 76.58, 53.07, 44.24, 44.22, 41.16, 38.22, 35.55, 28.55, 28.49, 28.41, 23.19, 11.59



PROTON01
BJG-2-222-1

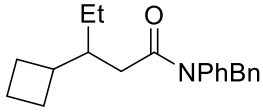
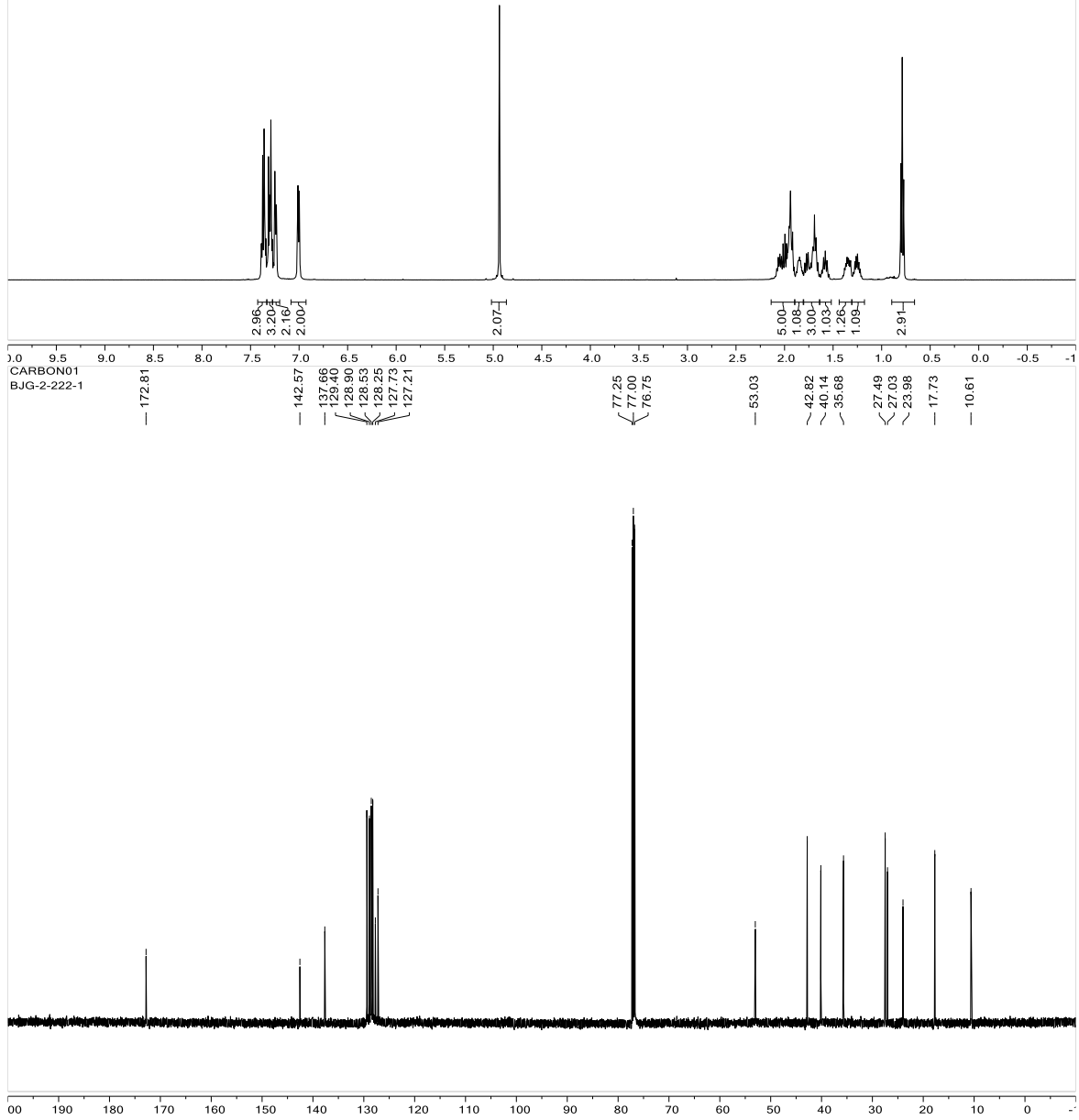


Fig. 2, entry 21



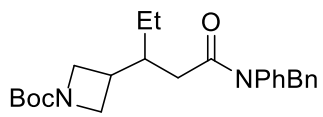
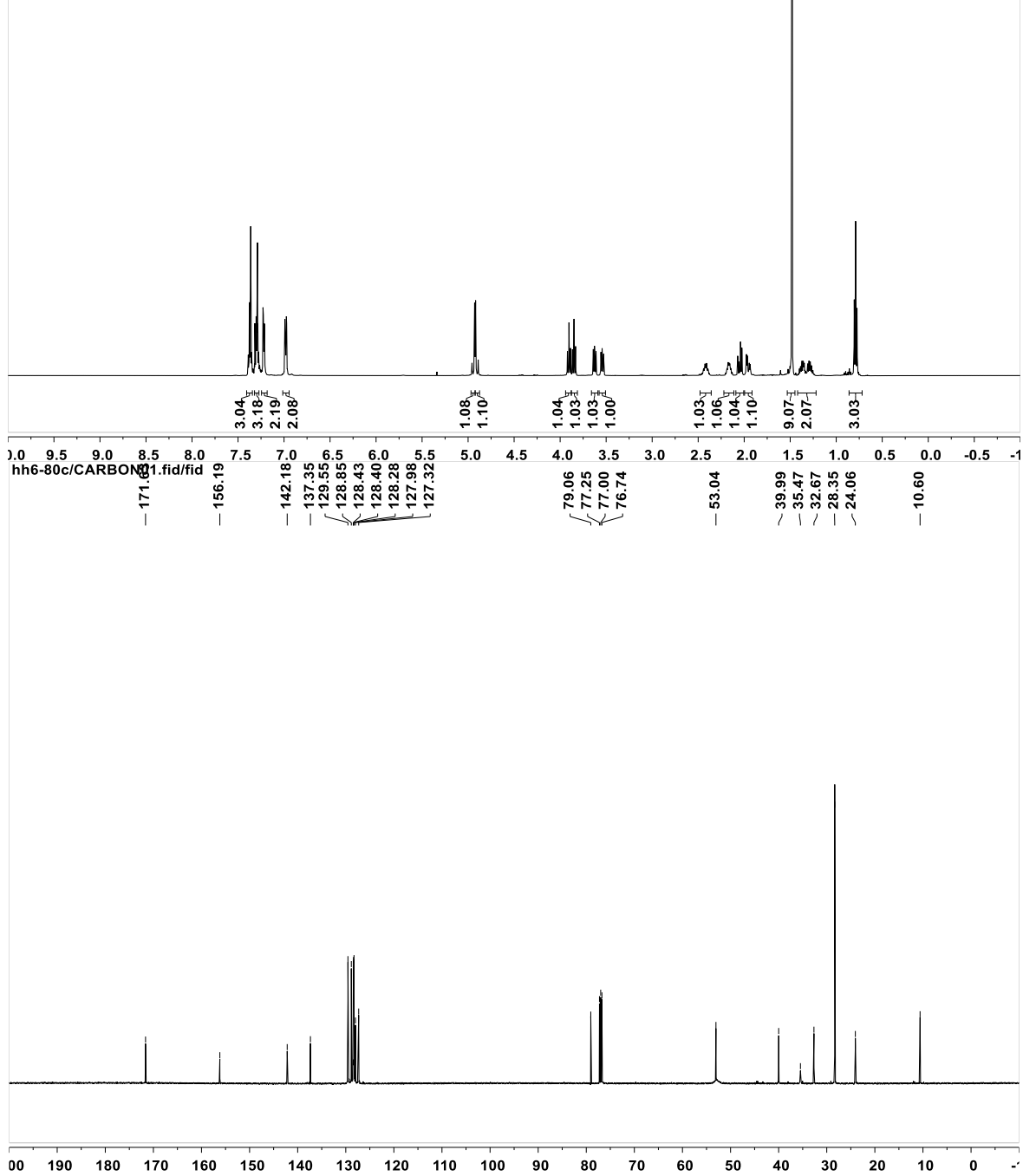


Fig. 2, entry 22



PROTON01
BJG-2-275-3

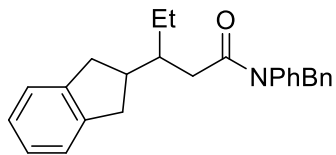
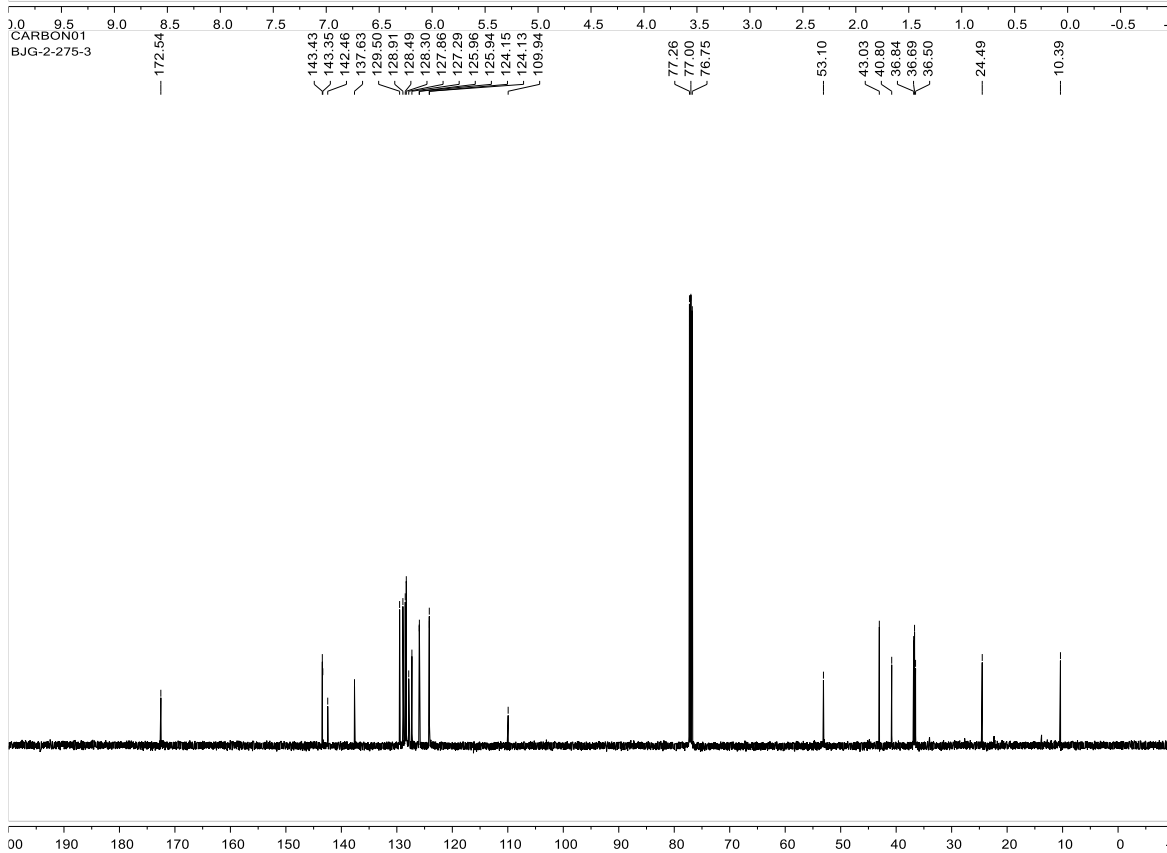
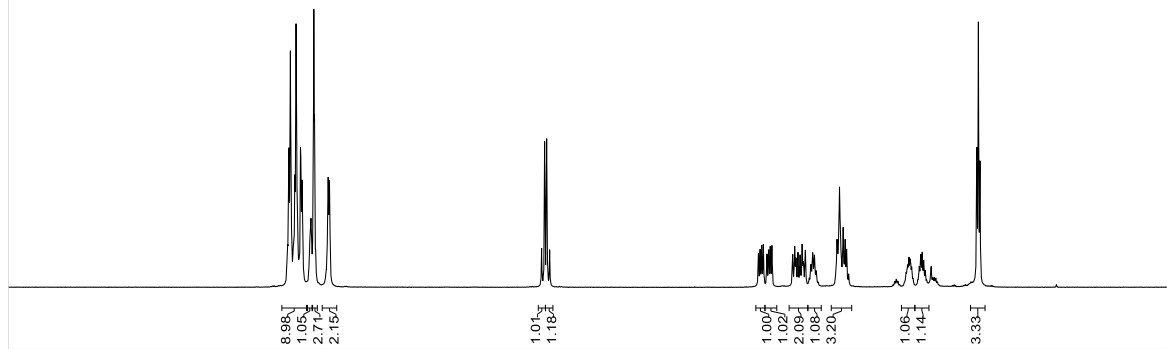


Fig. 2, entry 23



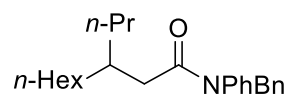
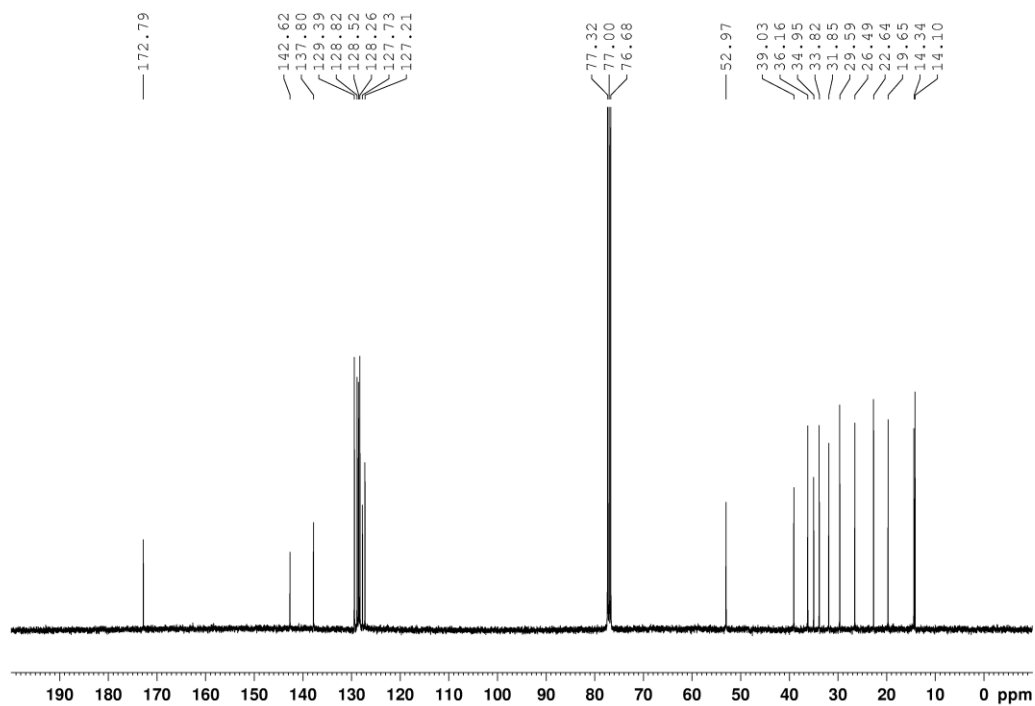
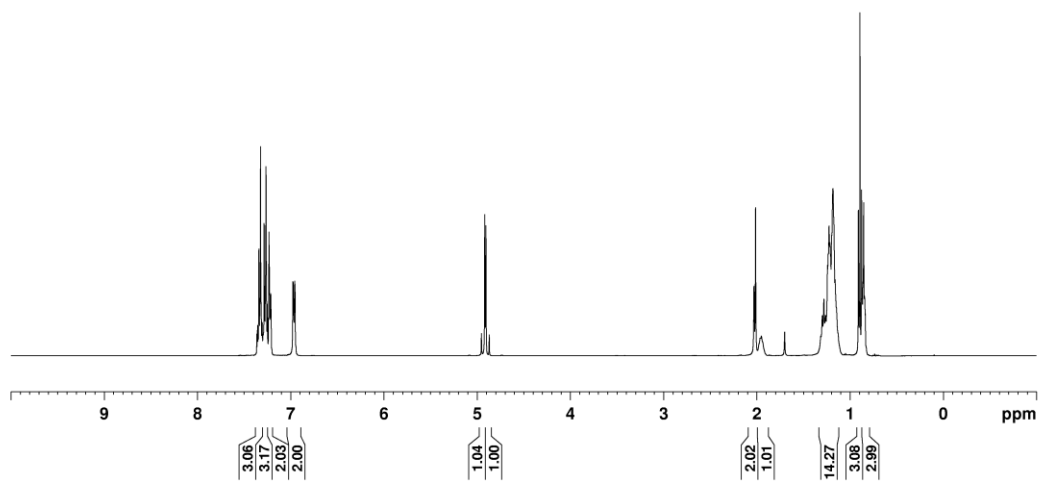


Fig. 2, entry 24



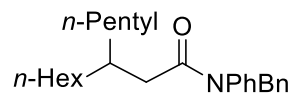
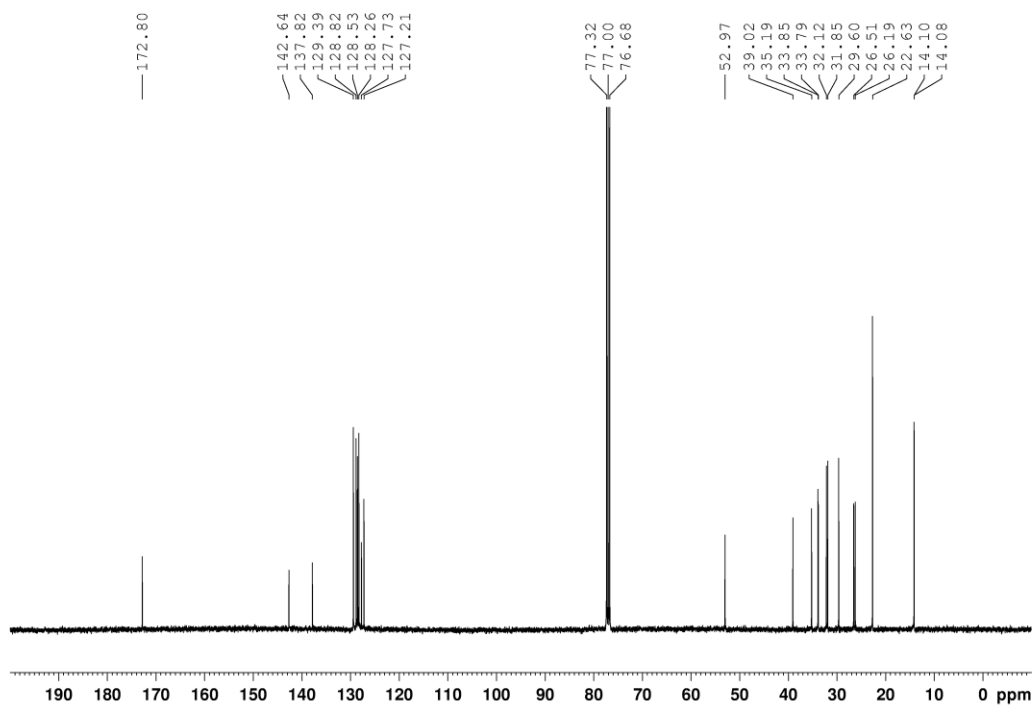
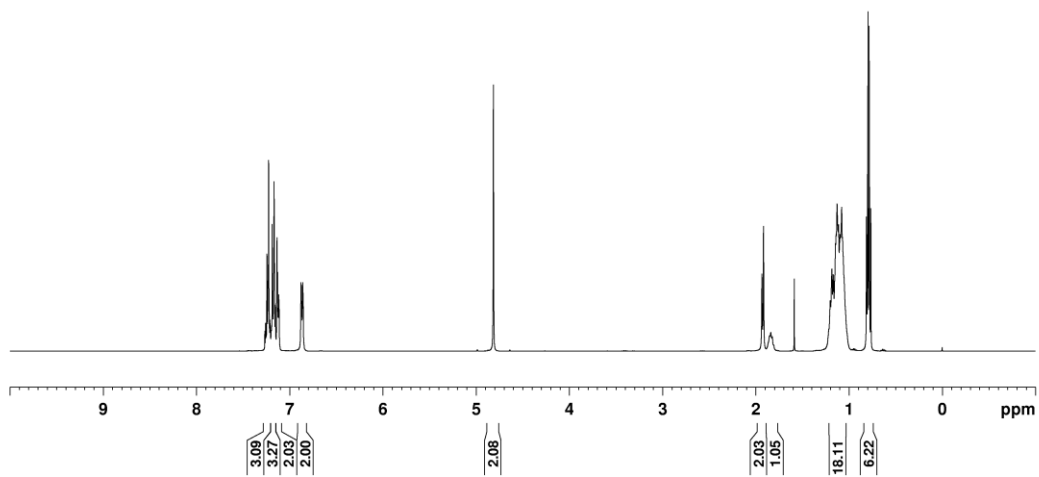


Fig. 2, entry 25



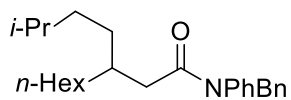
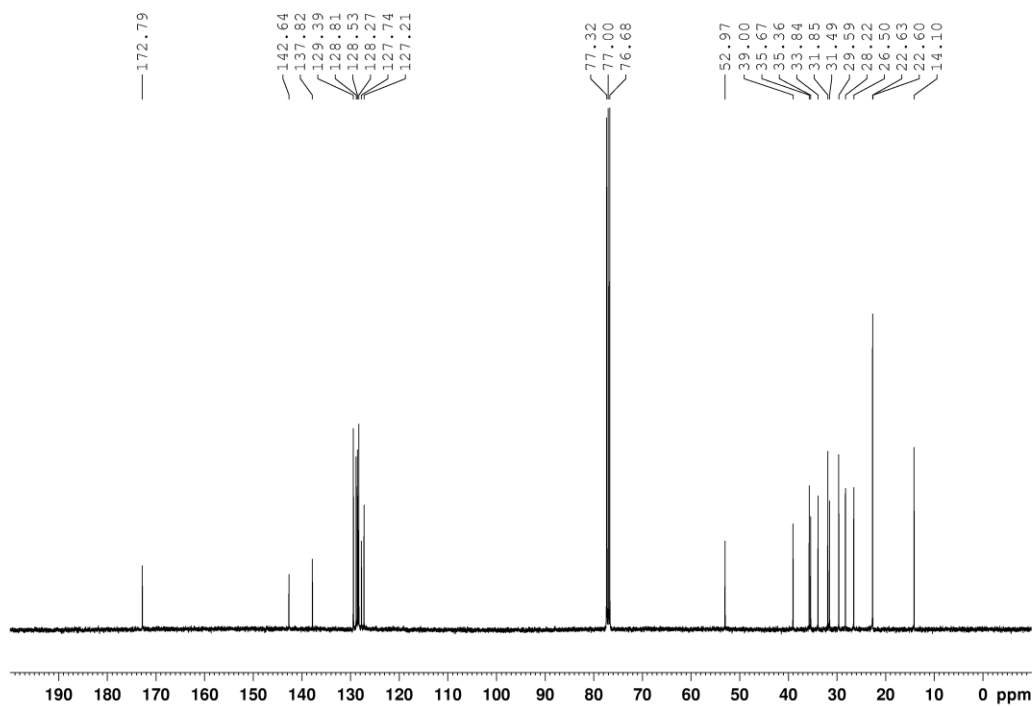
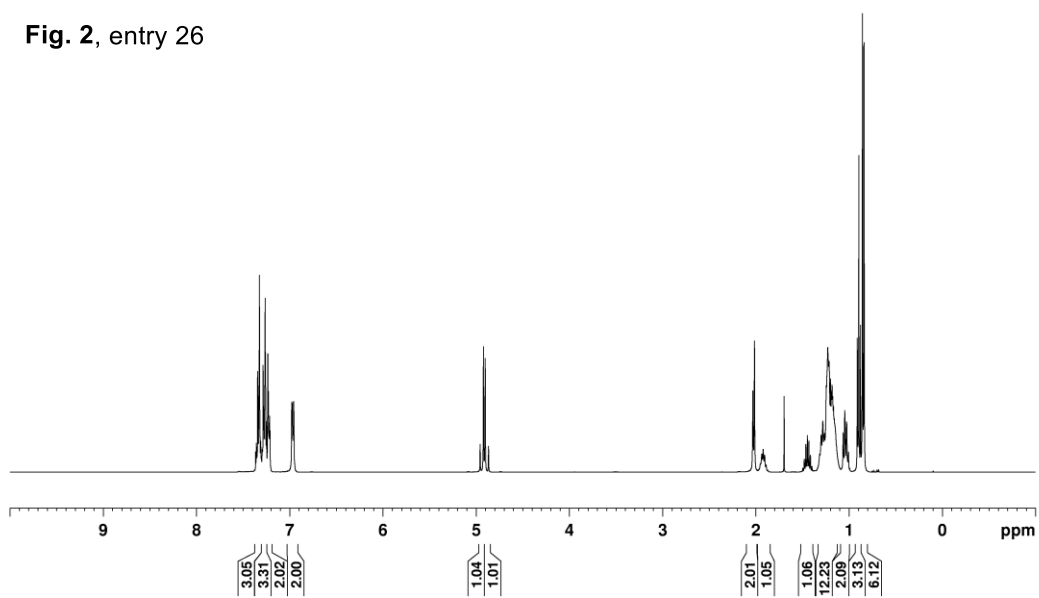


Fig. 2, entry 26



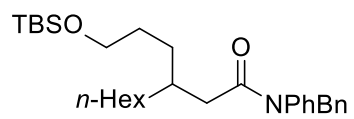
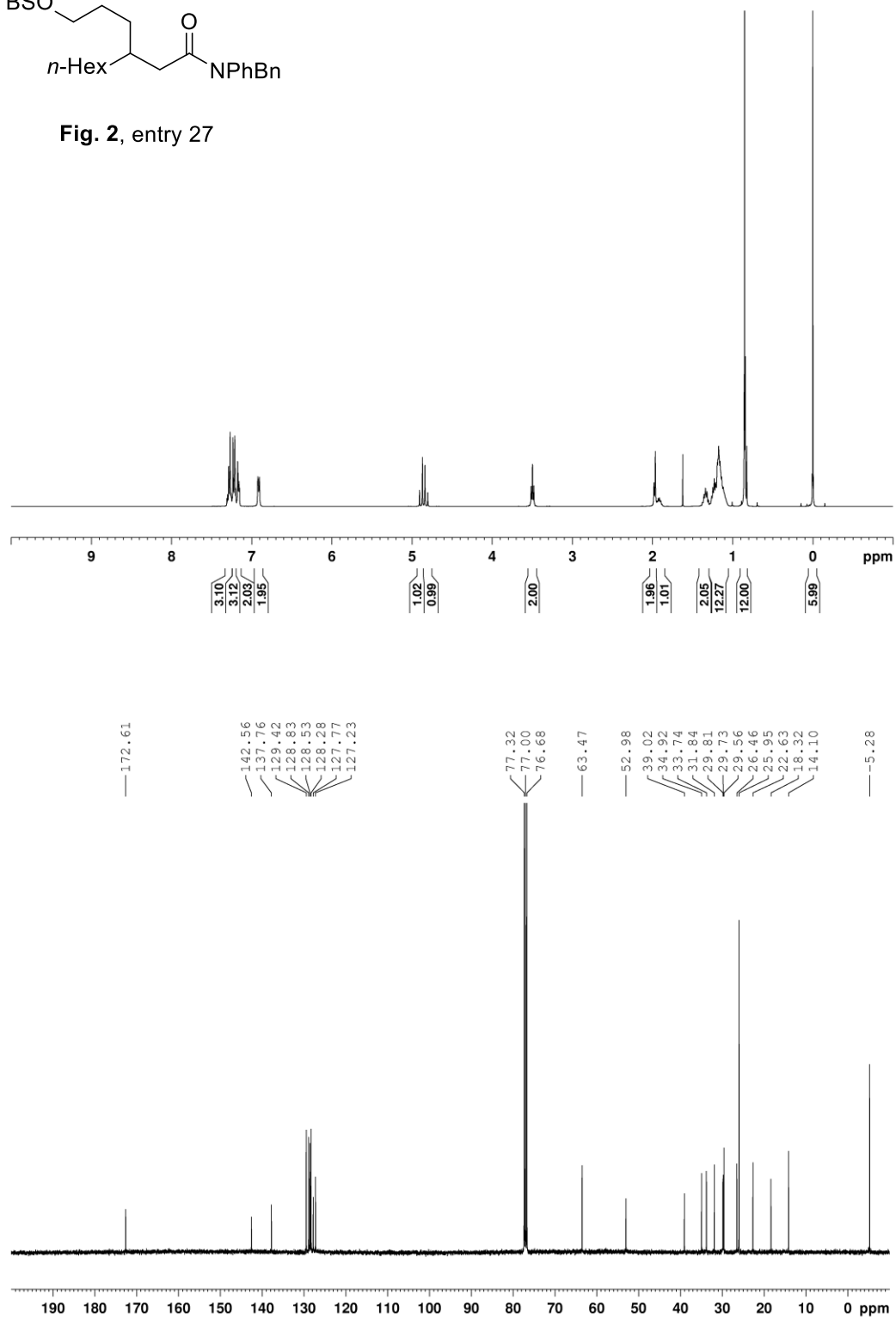


Fig. 2, entry 27



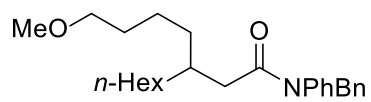
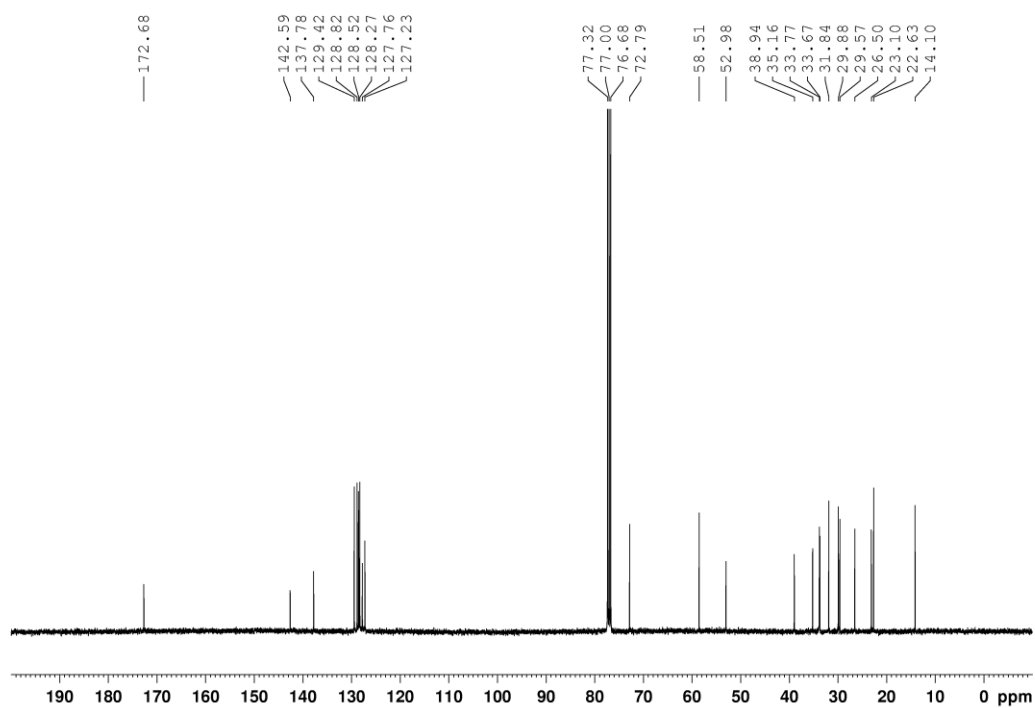
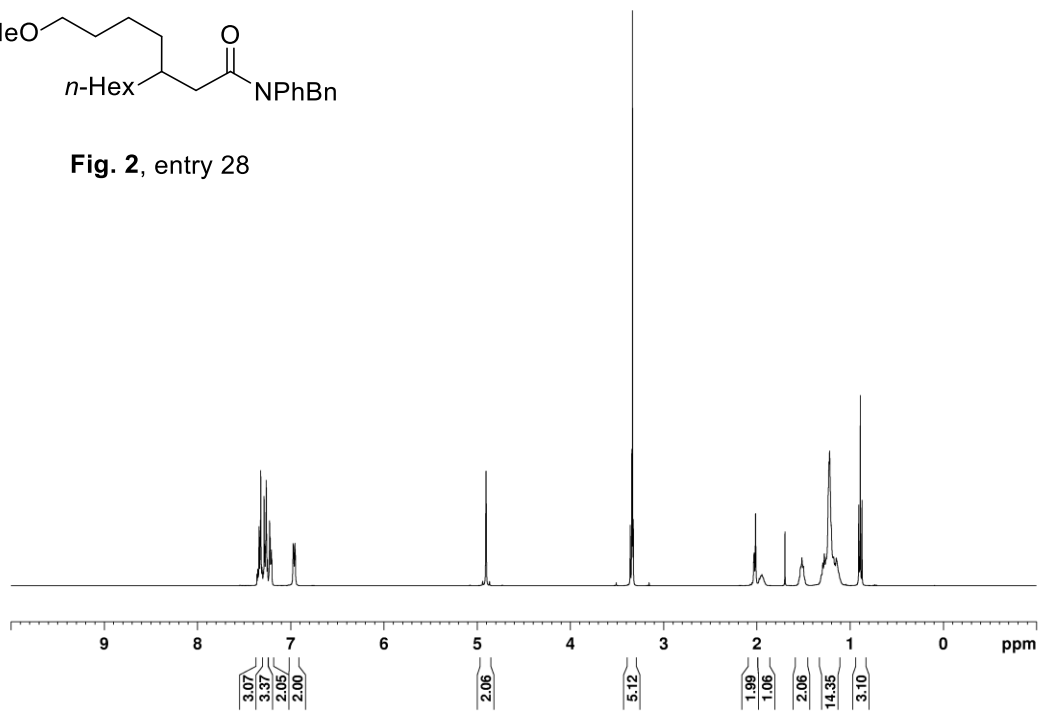


Fig. 2, entry 28



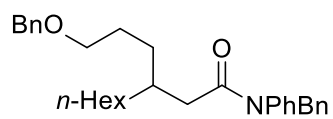
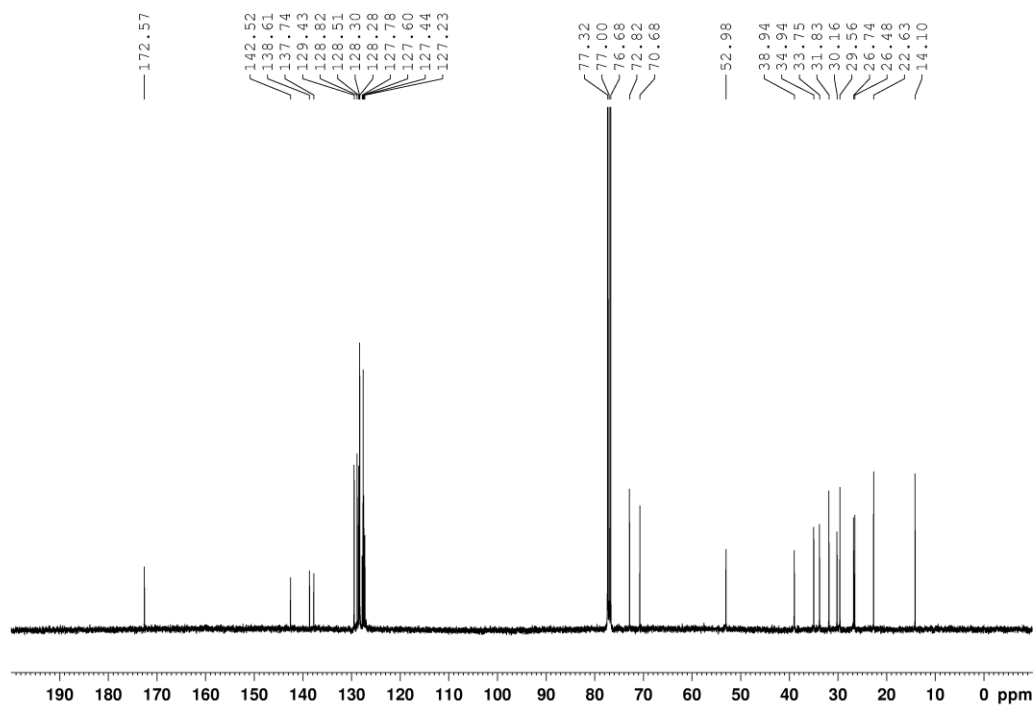
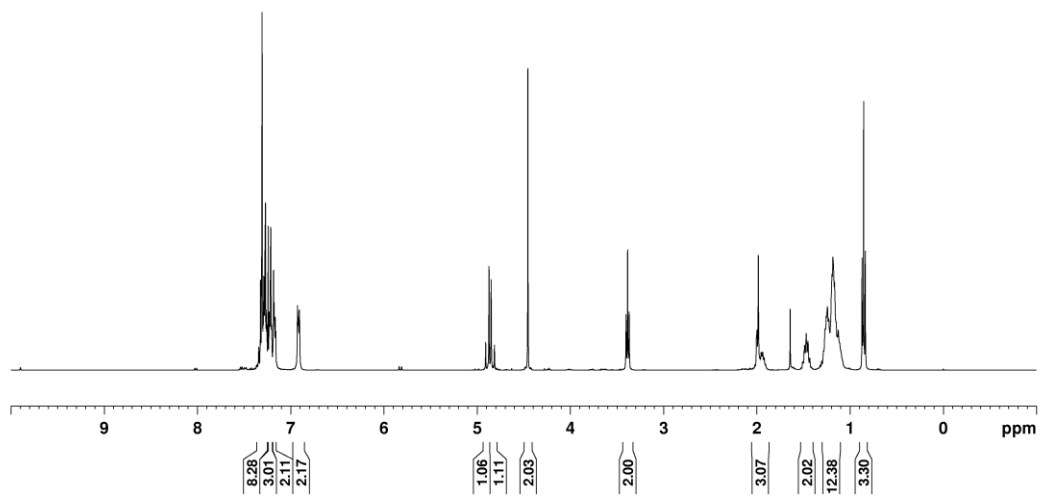


Fig. 2, entry 29



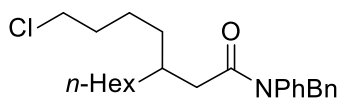
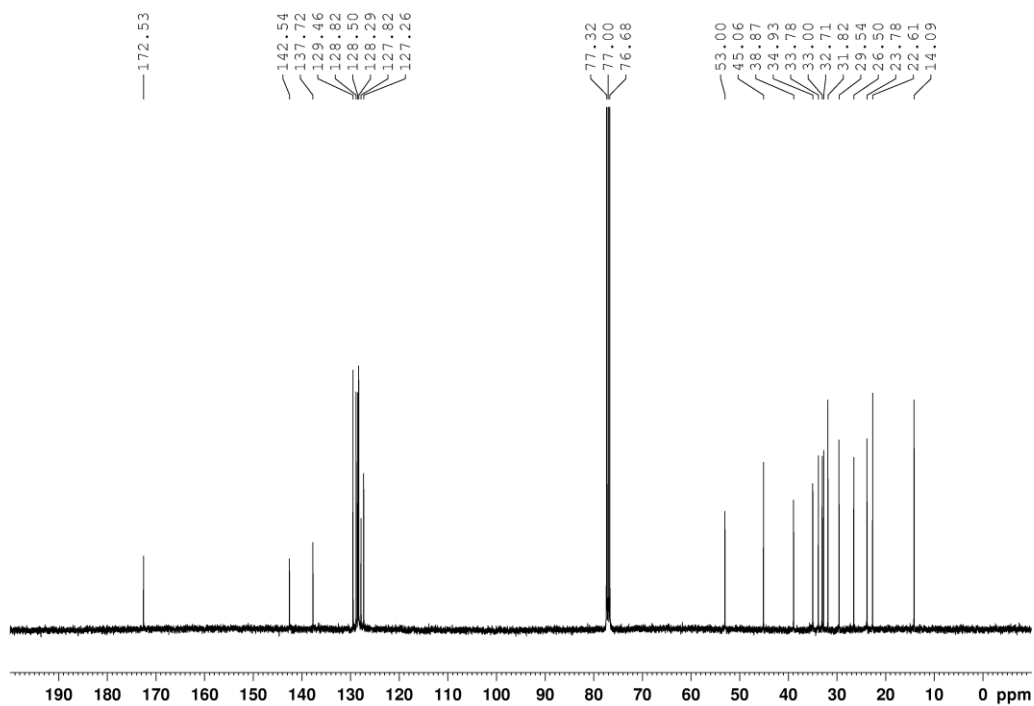
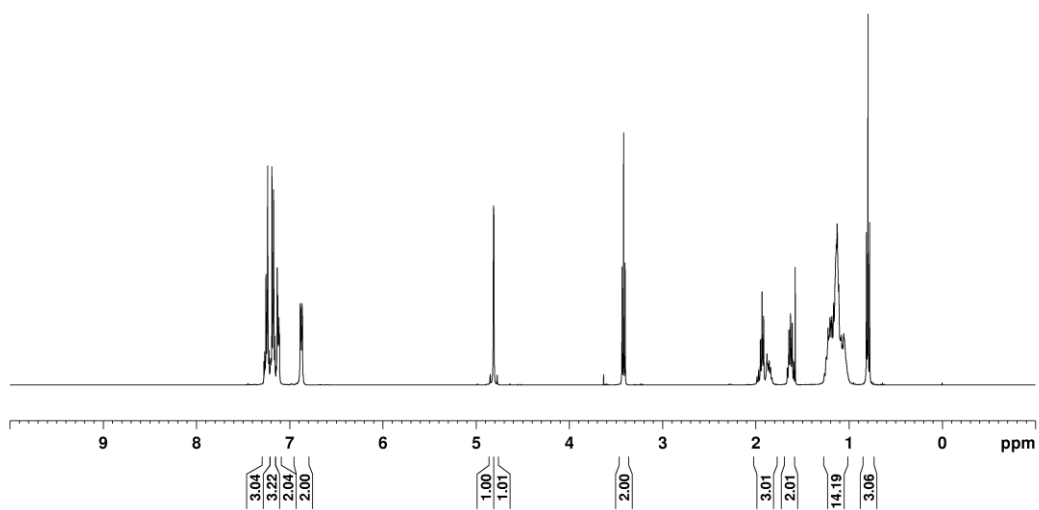


Fig. 2, entry 30



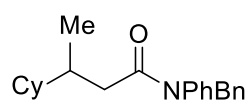
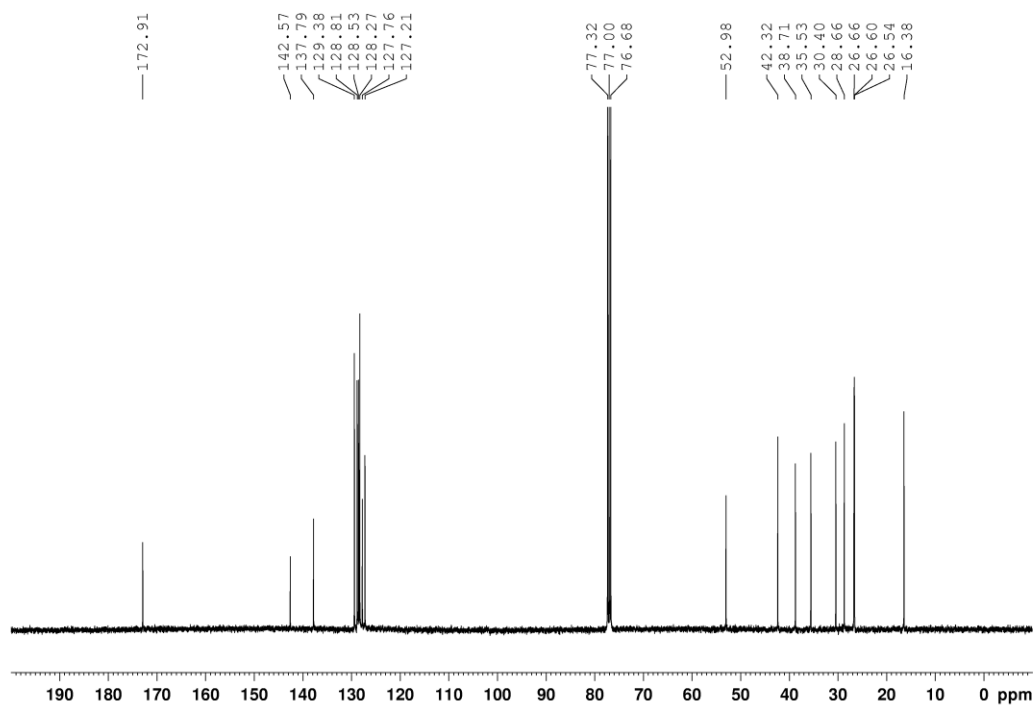
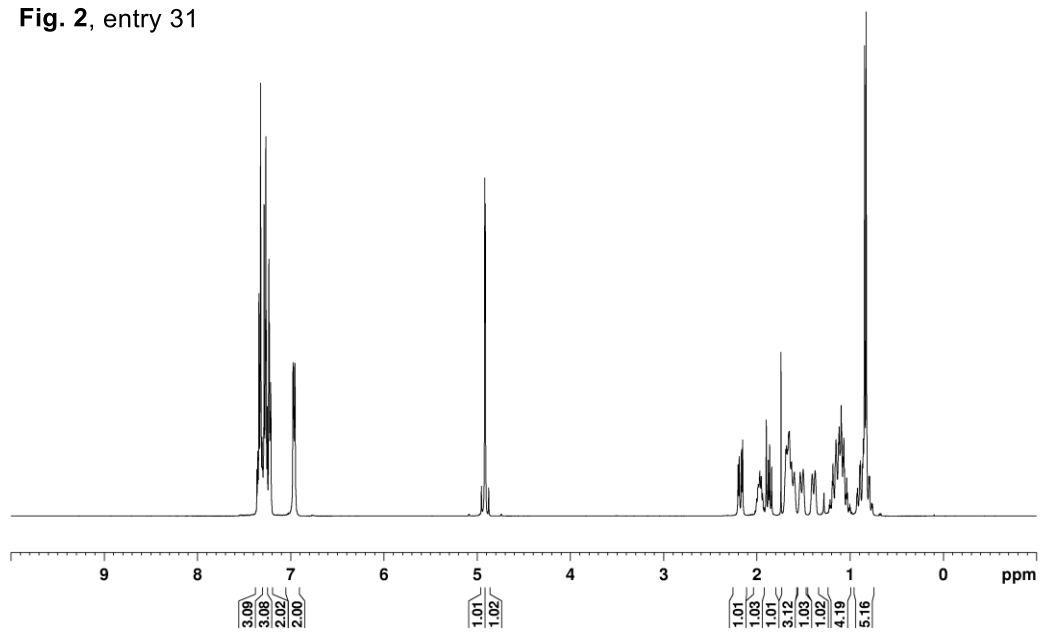


Fig. 2, entry 31



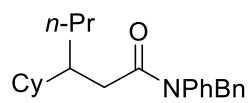
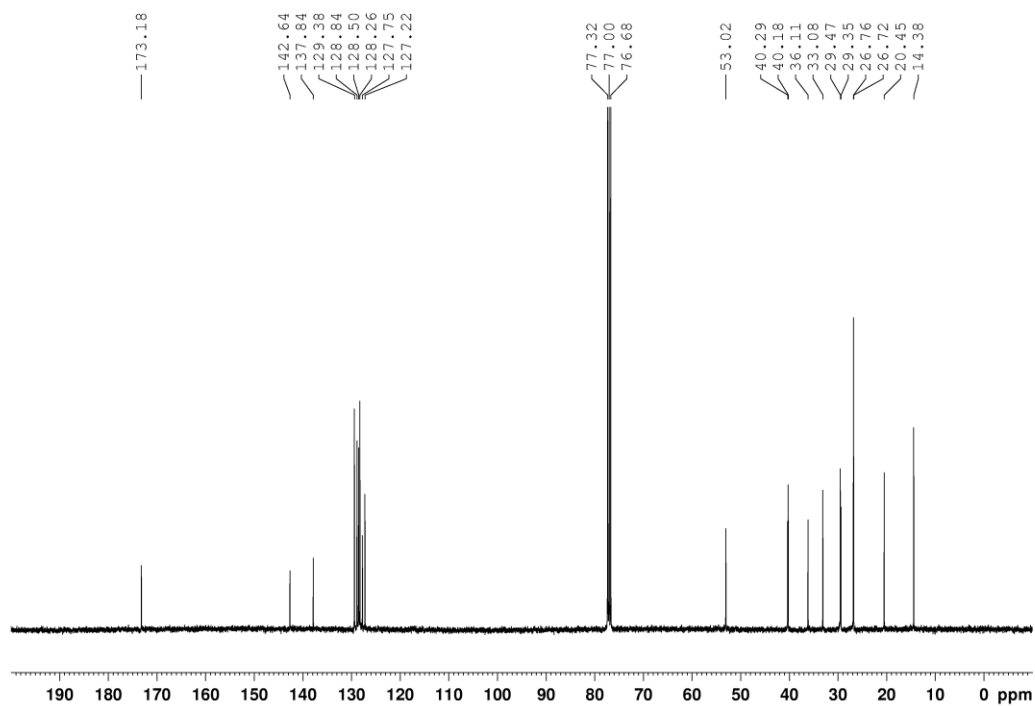
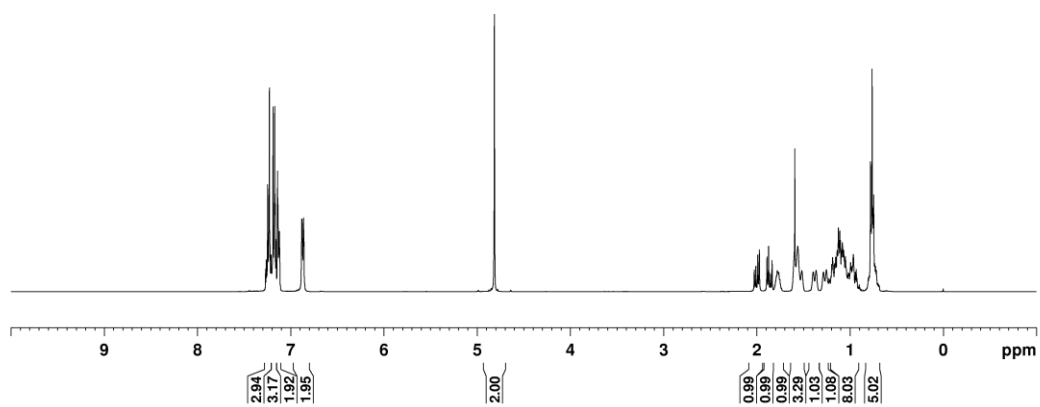


Fig. 2, entry 32



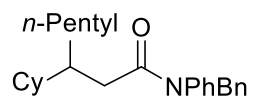
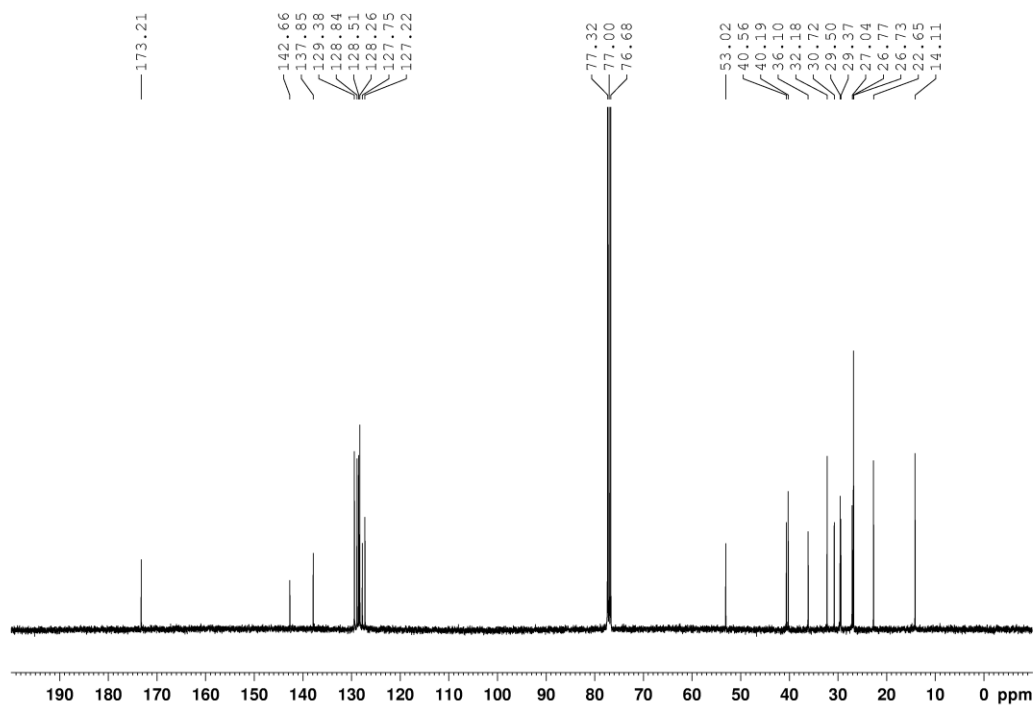
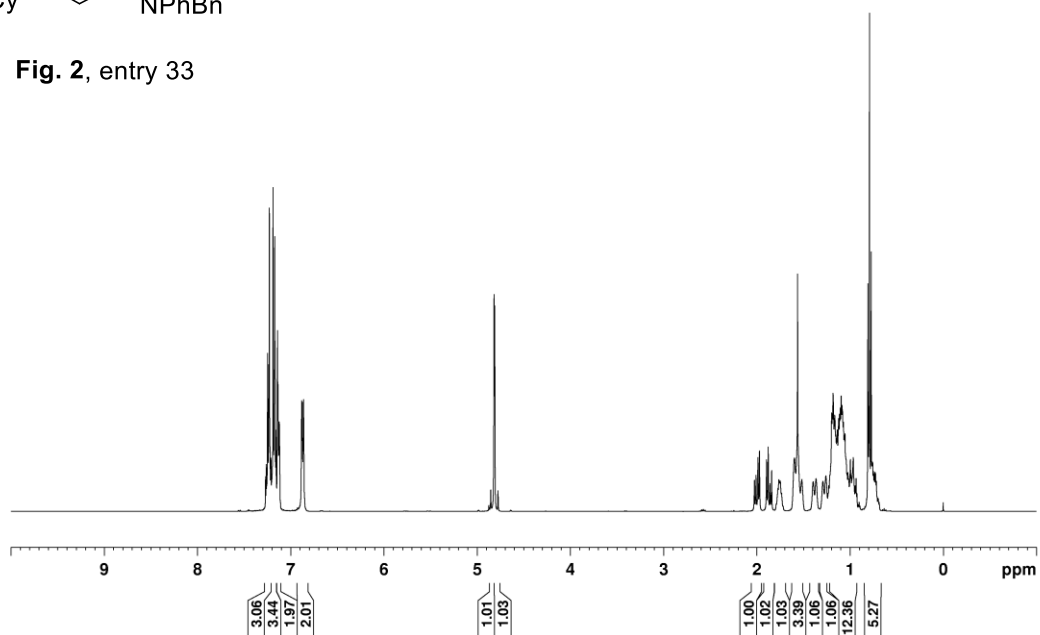


Fig. 2, entry 33



hh6-51a/1/fid

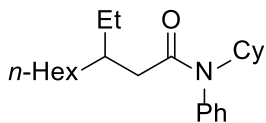
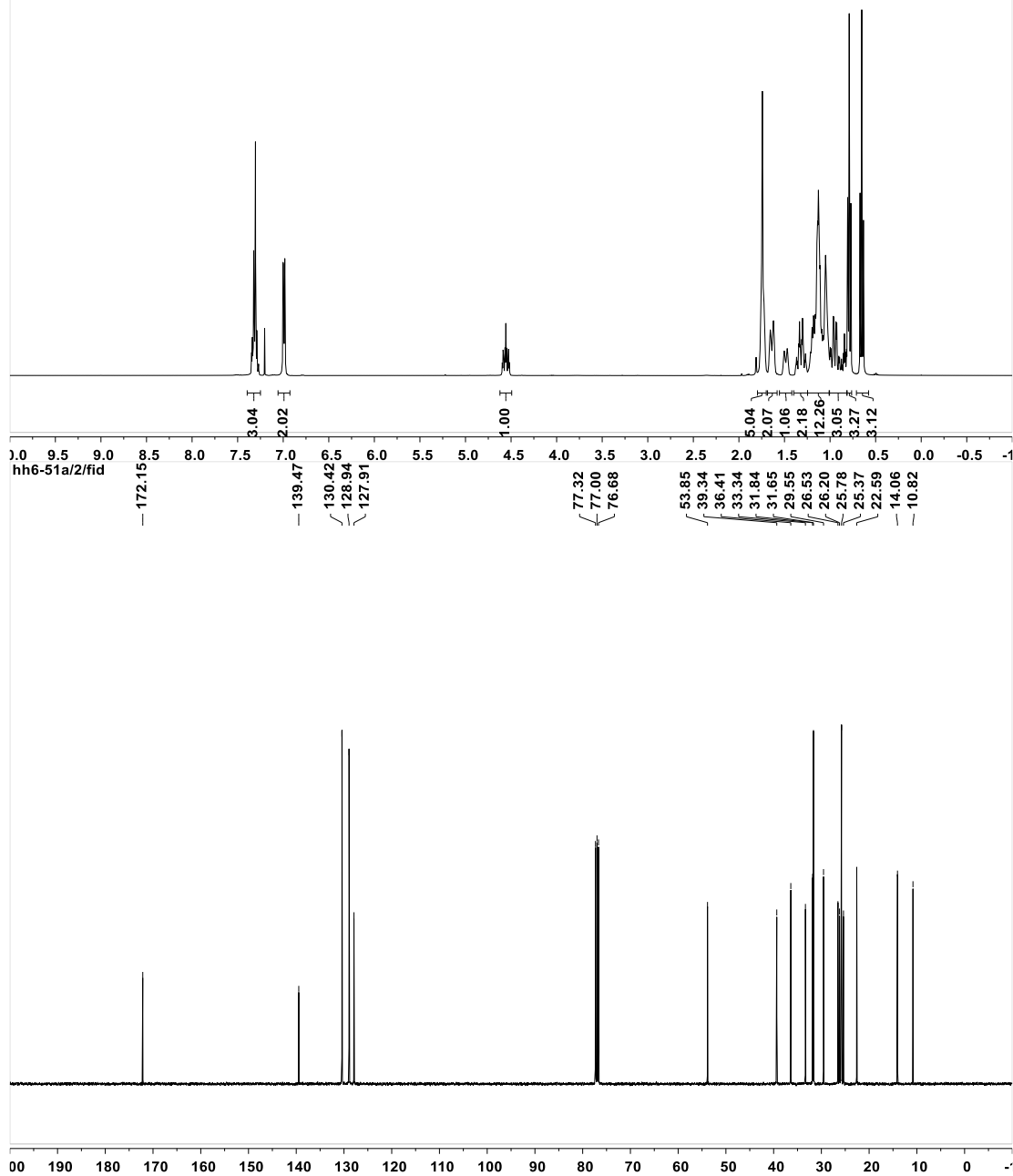


Fig. 2, entry 34



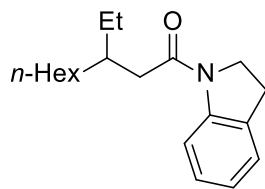
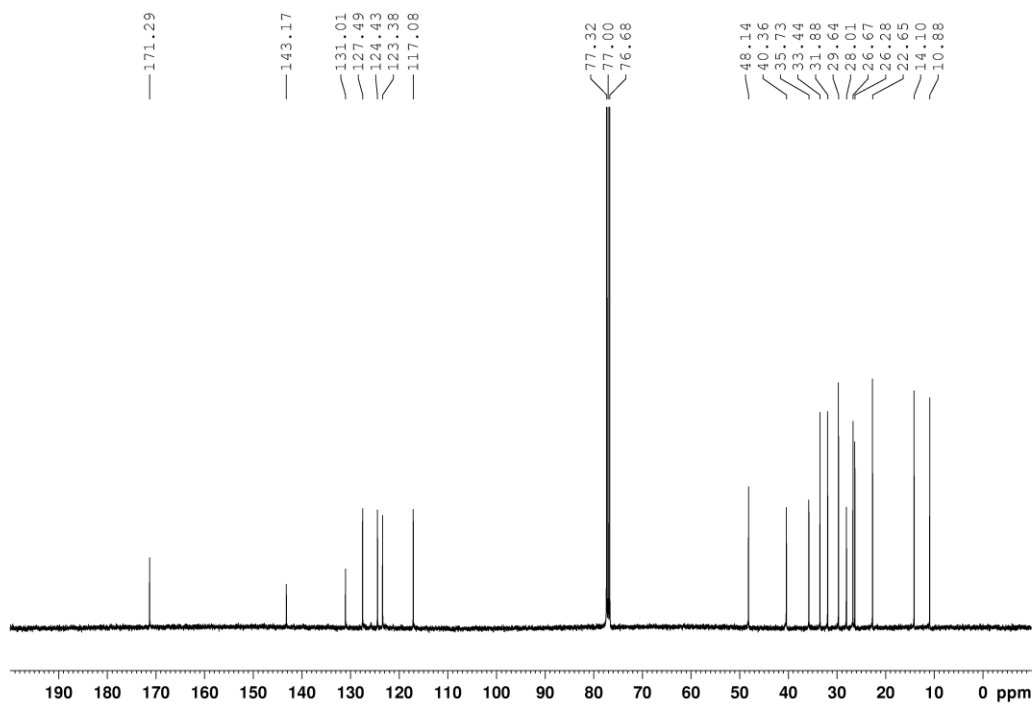
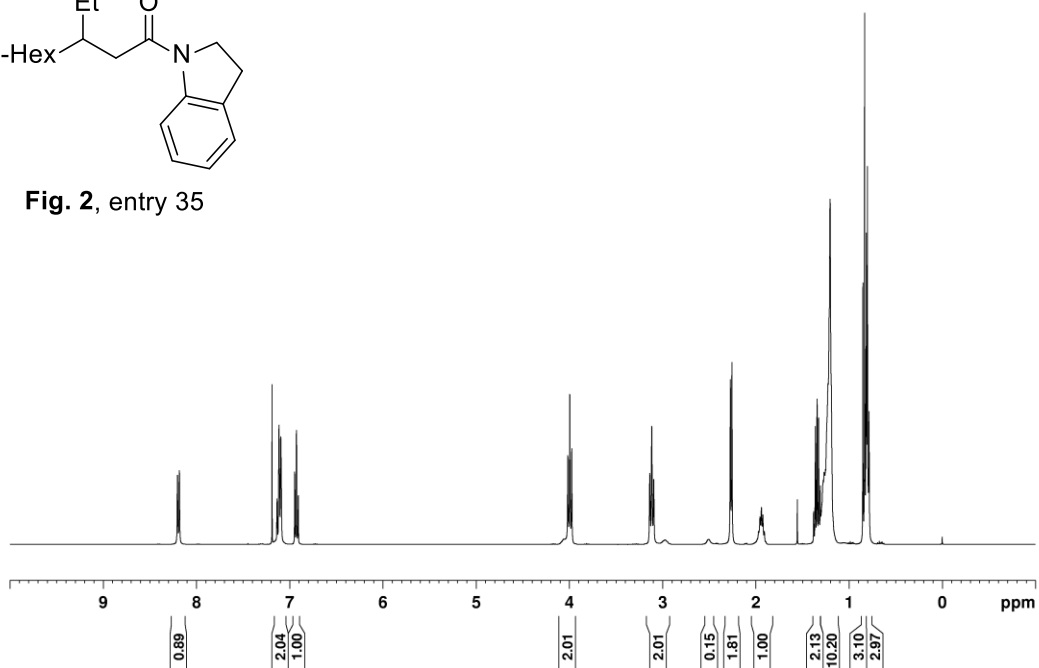


Fig. 2, entry 35



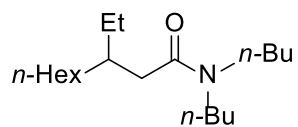
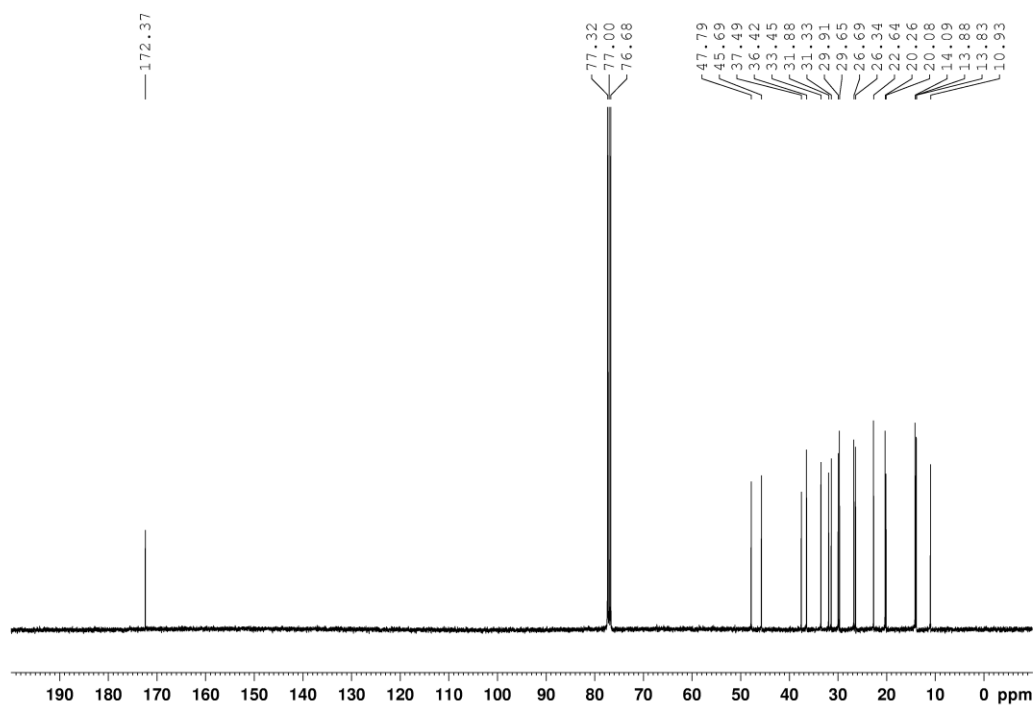
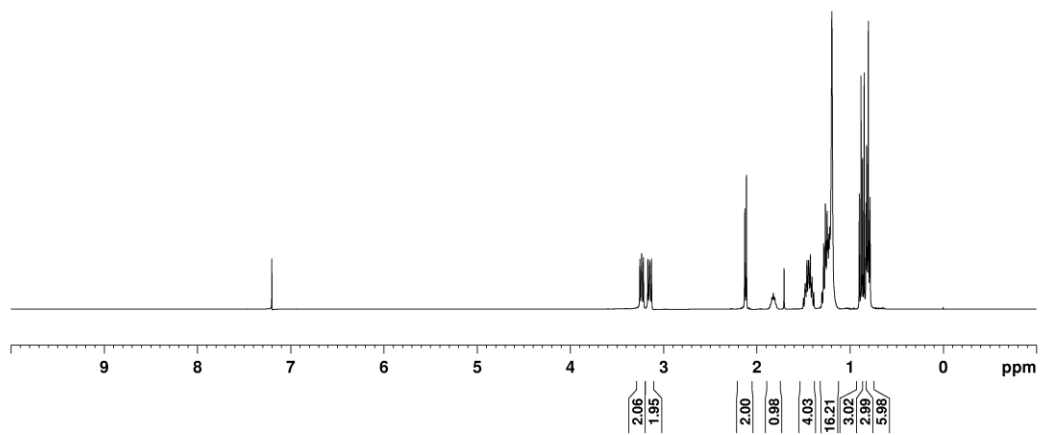


Fig. 2, entry 36



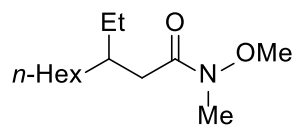
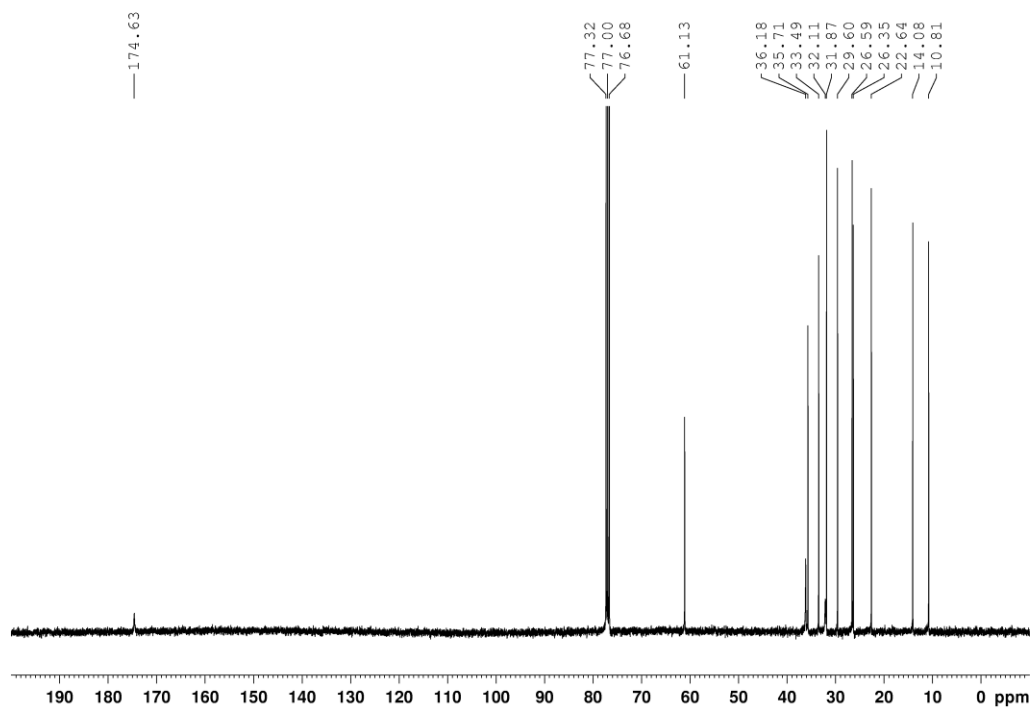
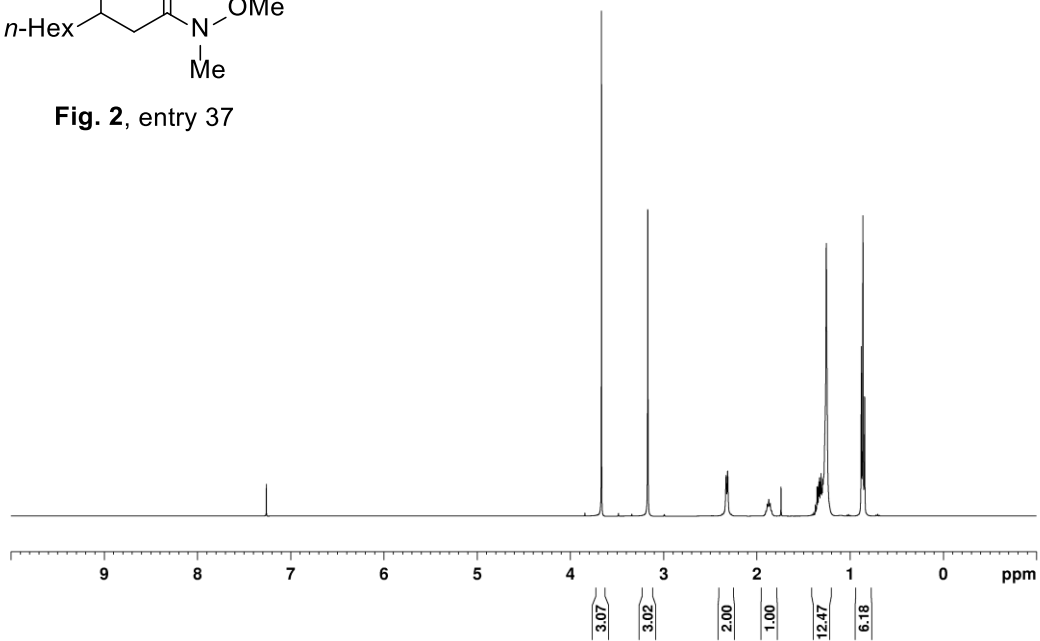


Fig. 2, entry 37



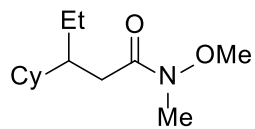
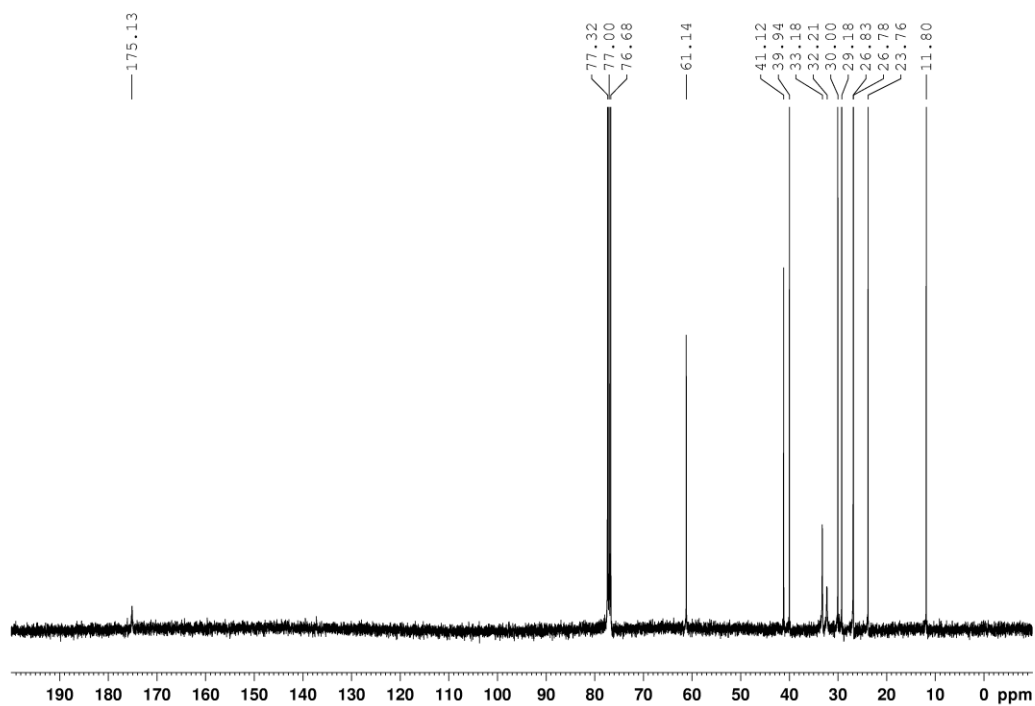
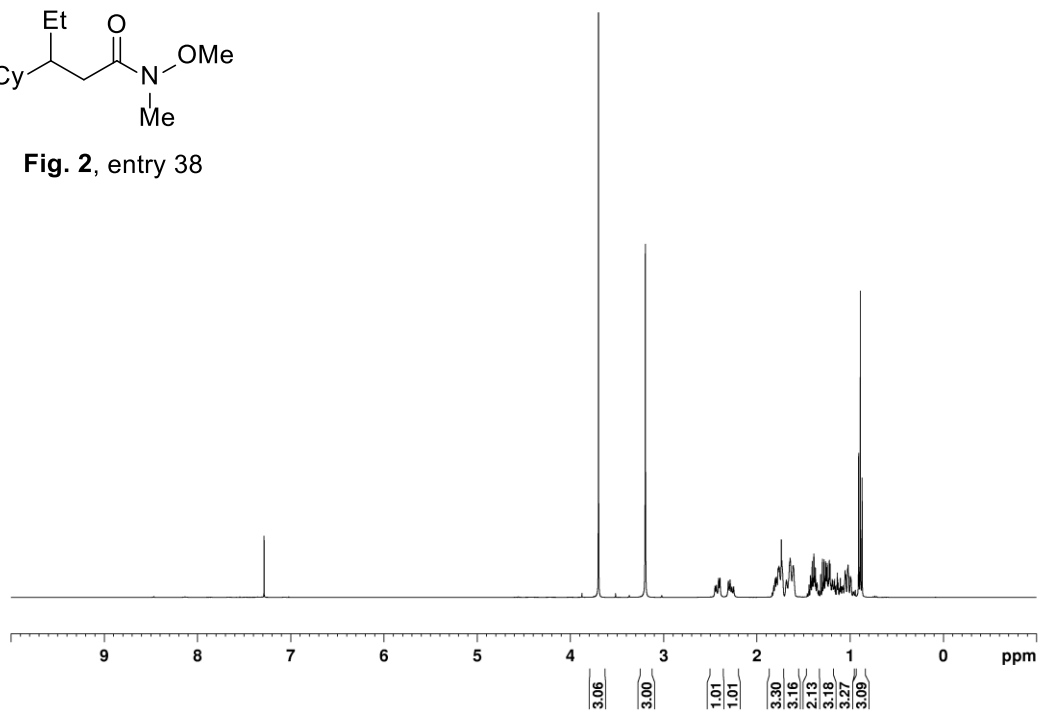


Fig. 2, entry 38



hh5-254a/1/fid

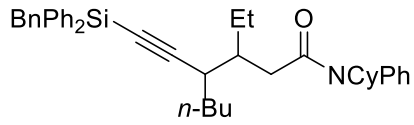
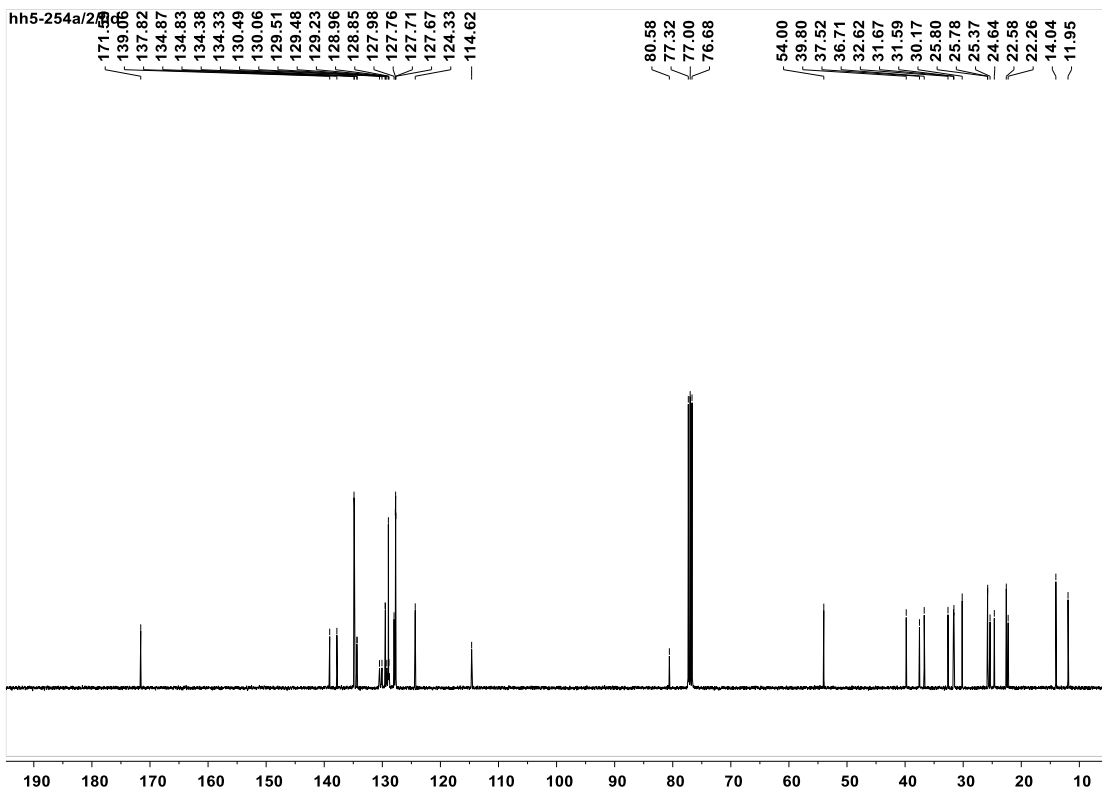
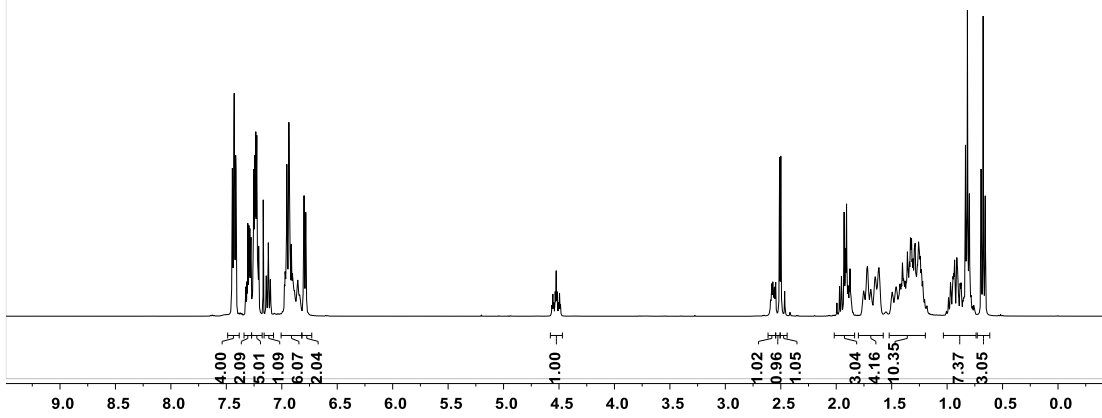


Fig. 3, entry 1



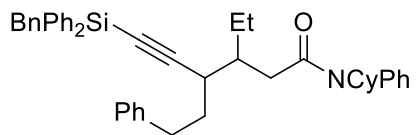
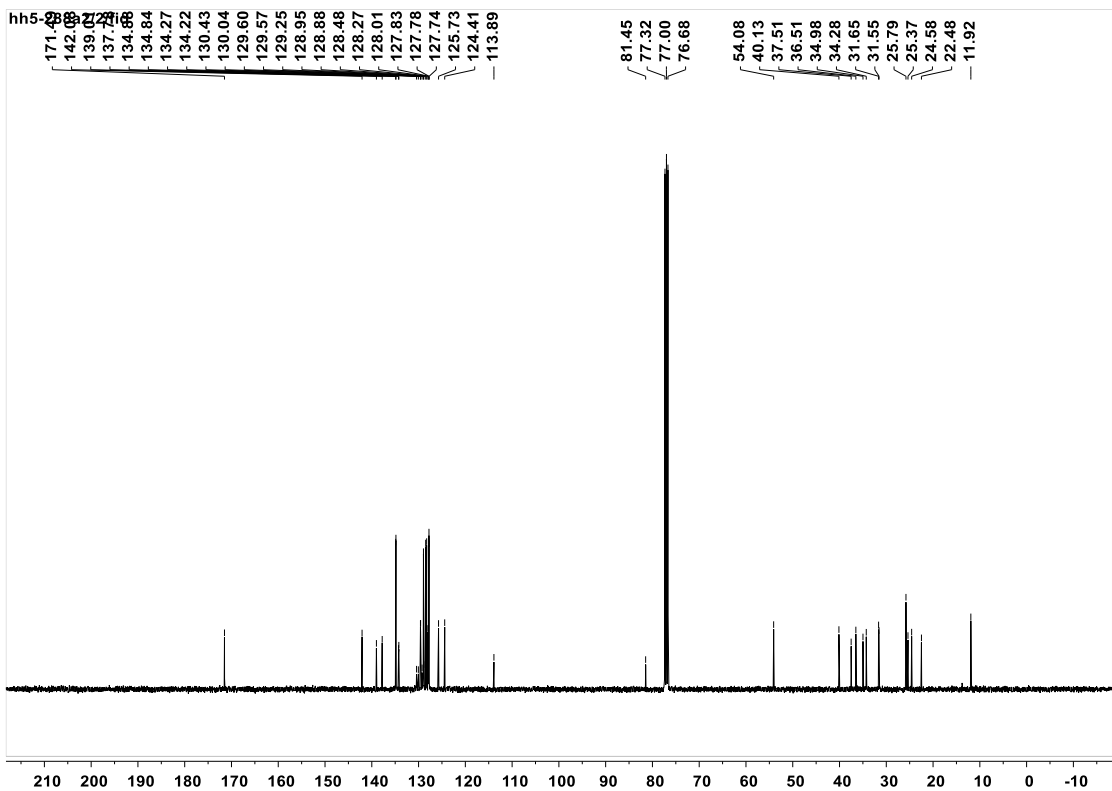
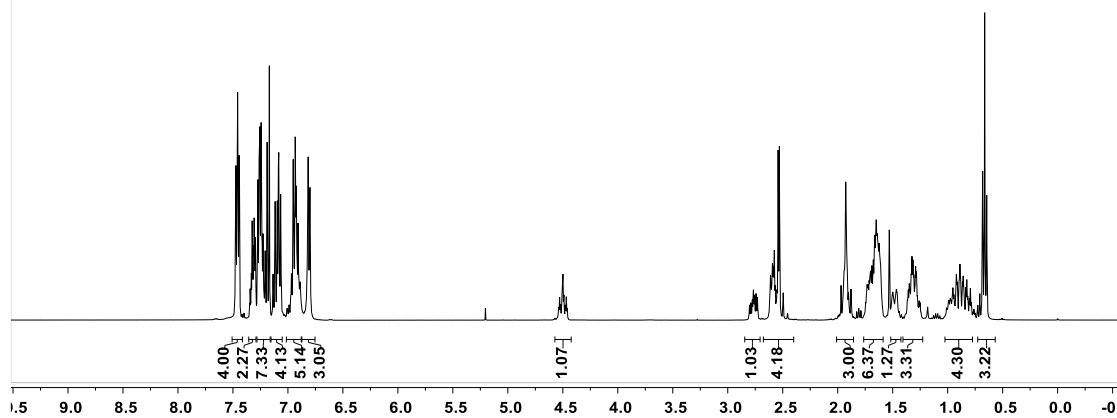


Fig. 3, entry 2



hh5-260a/1/fid

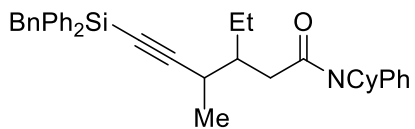
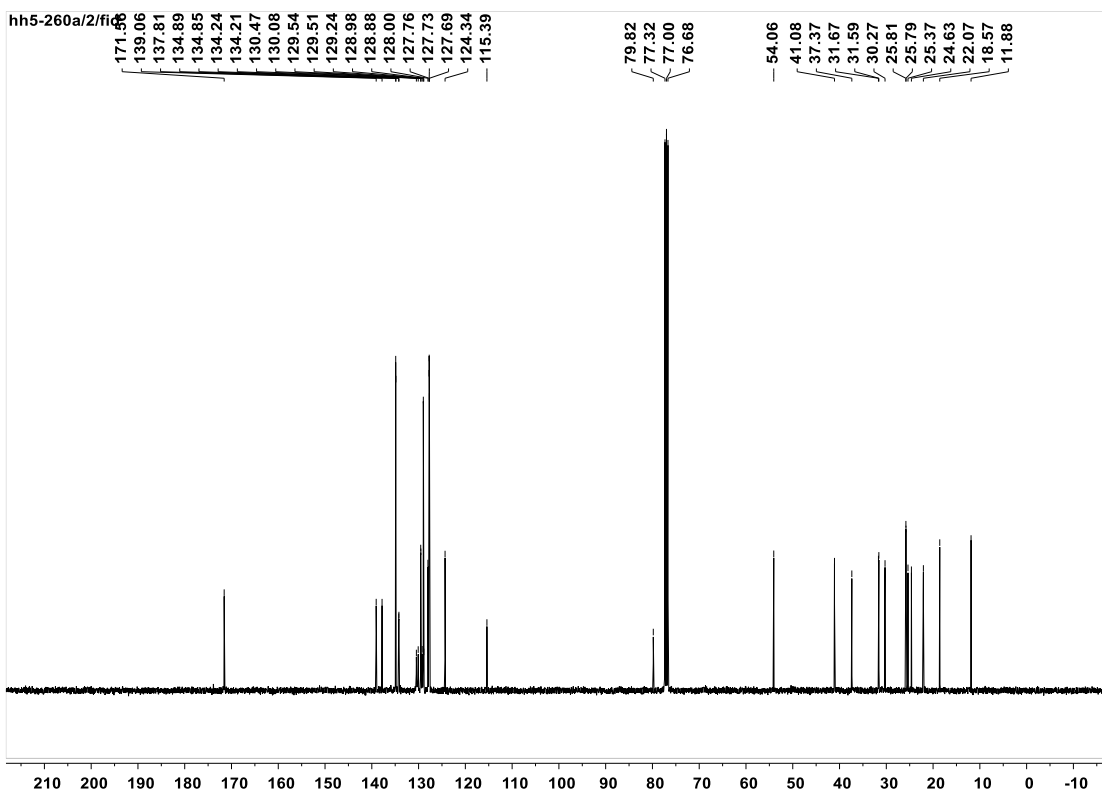
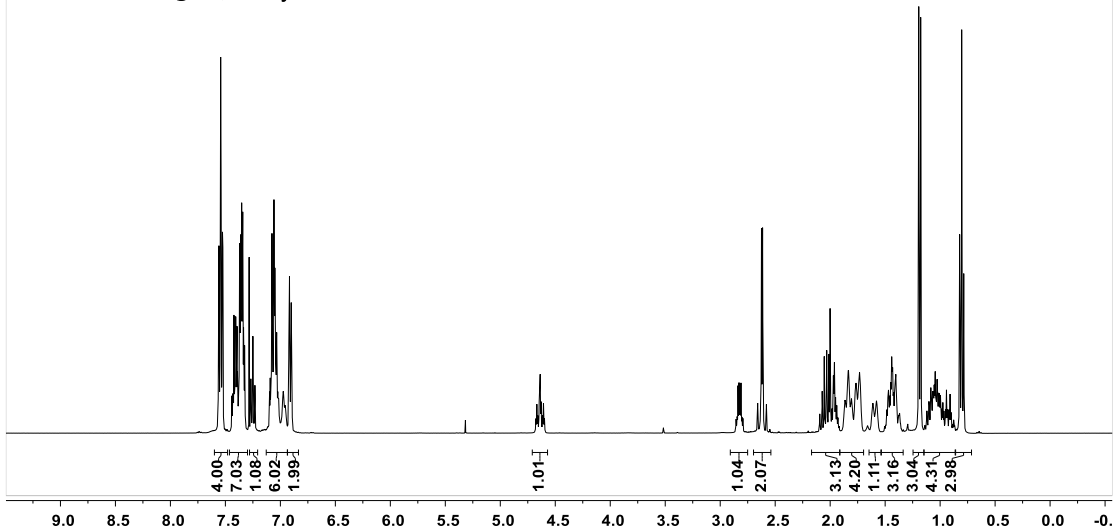


Fig. 3, entry 3



hh5-261a/1/fid

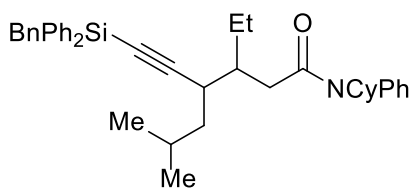
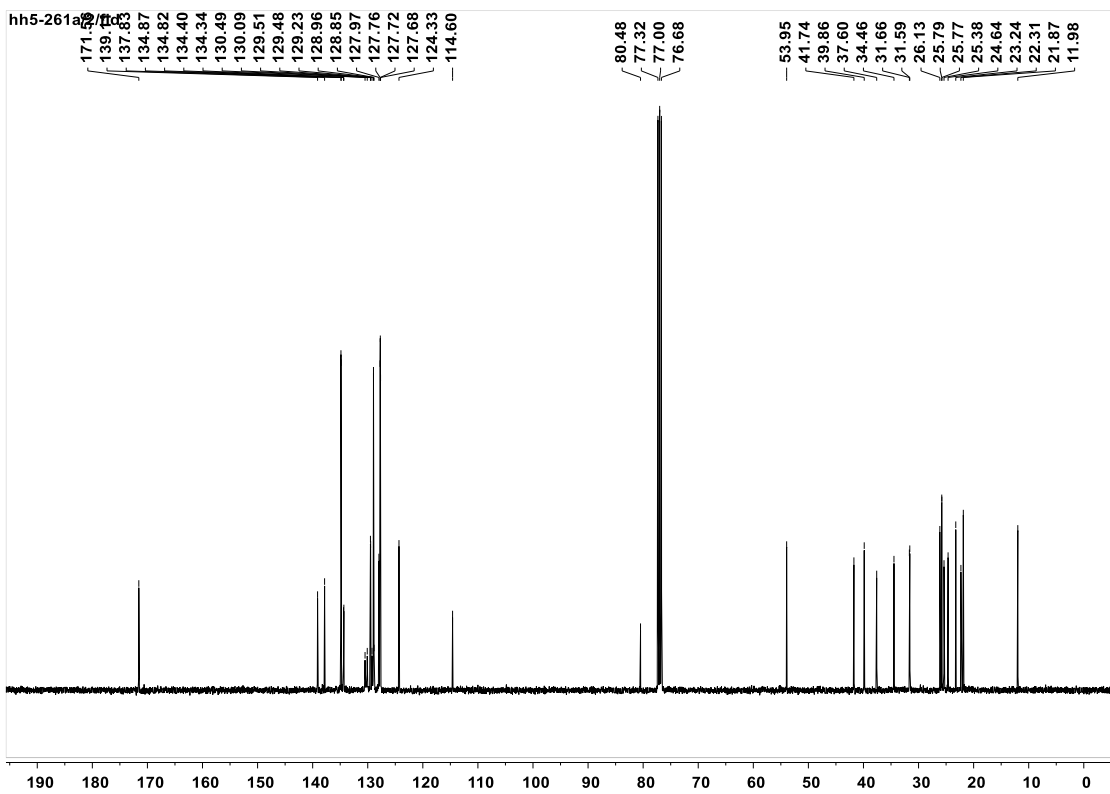
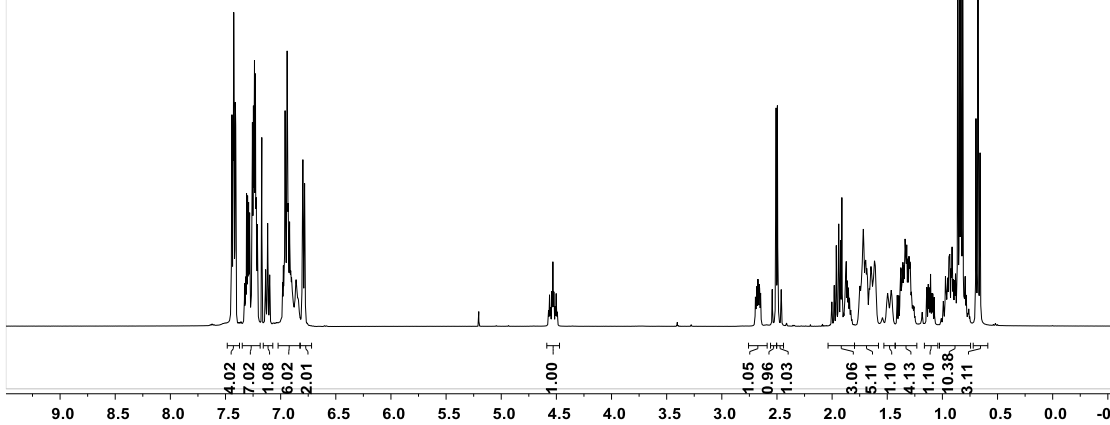
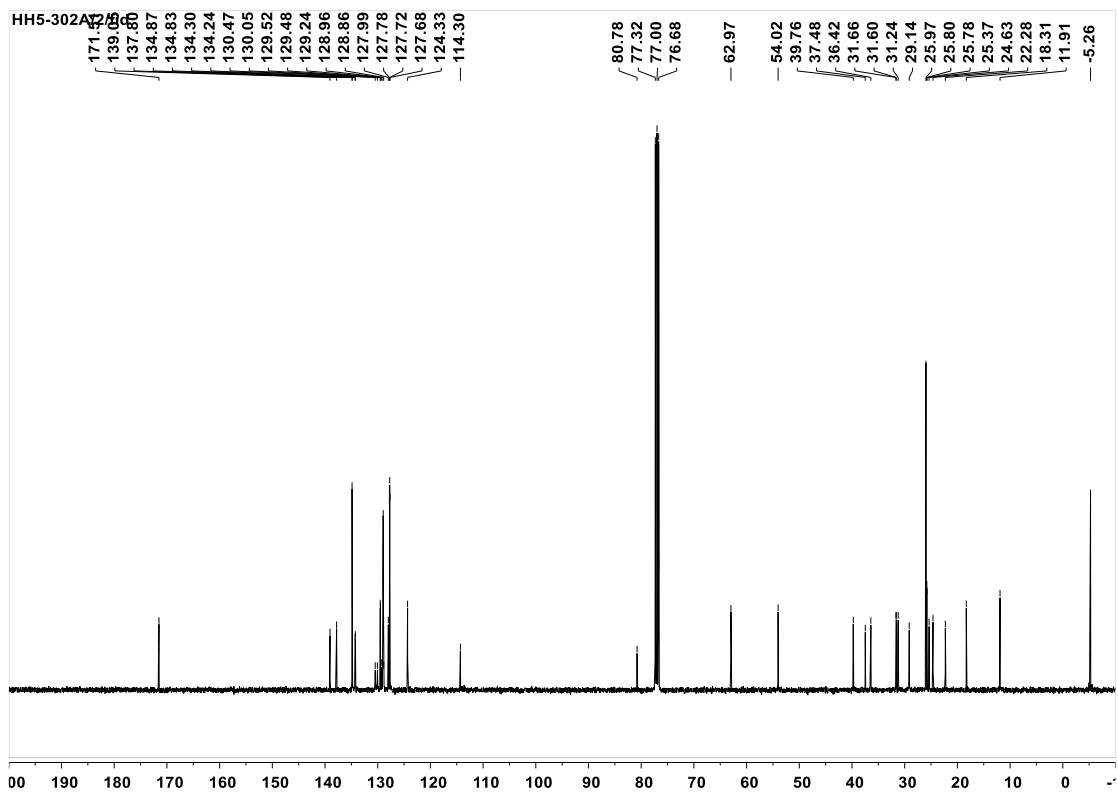
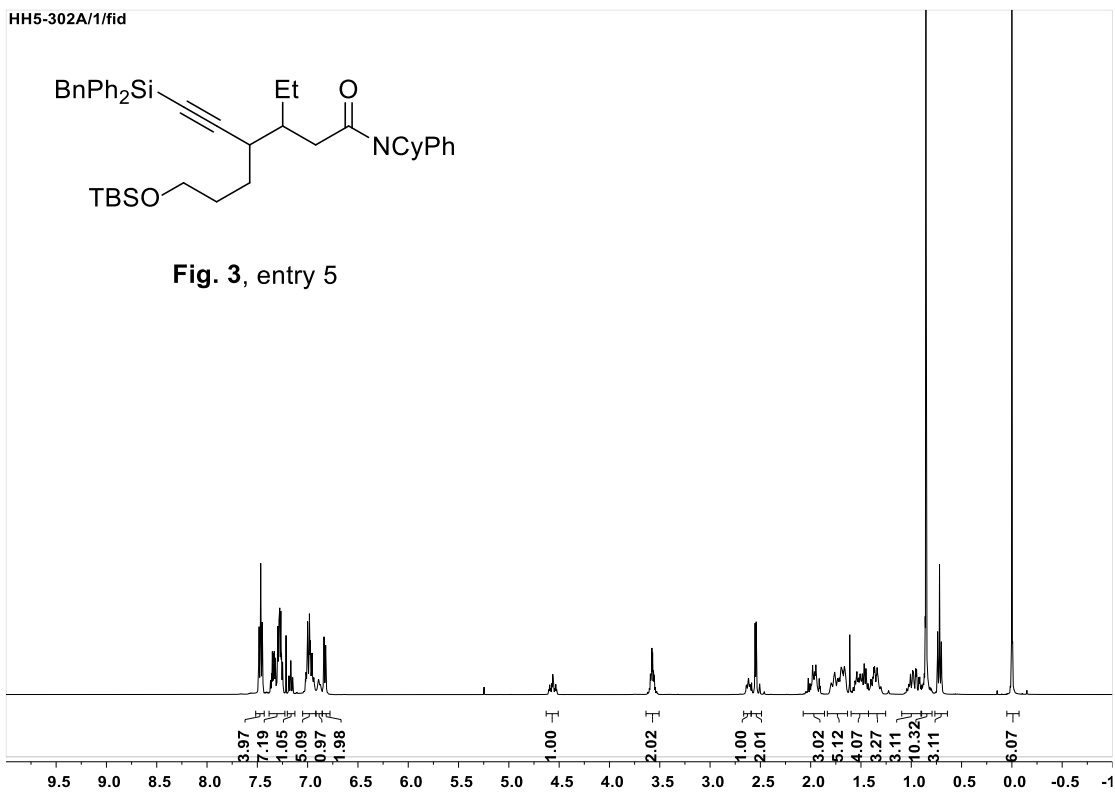
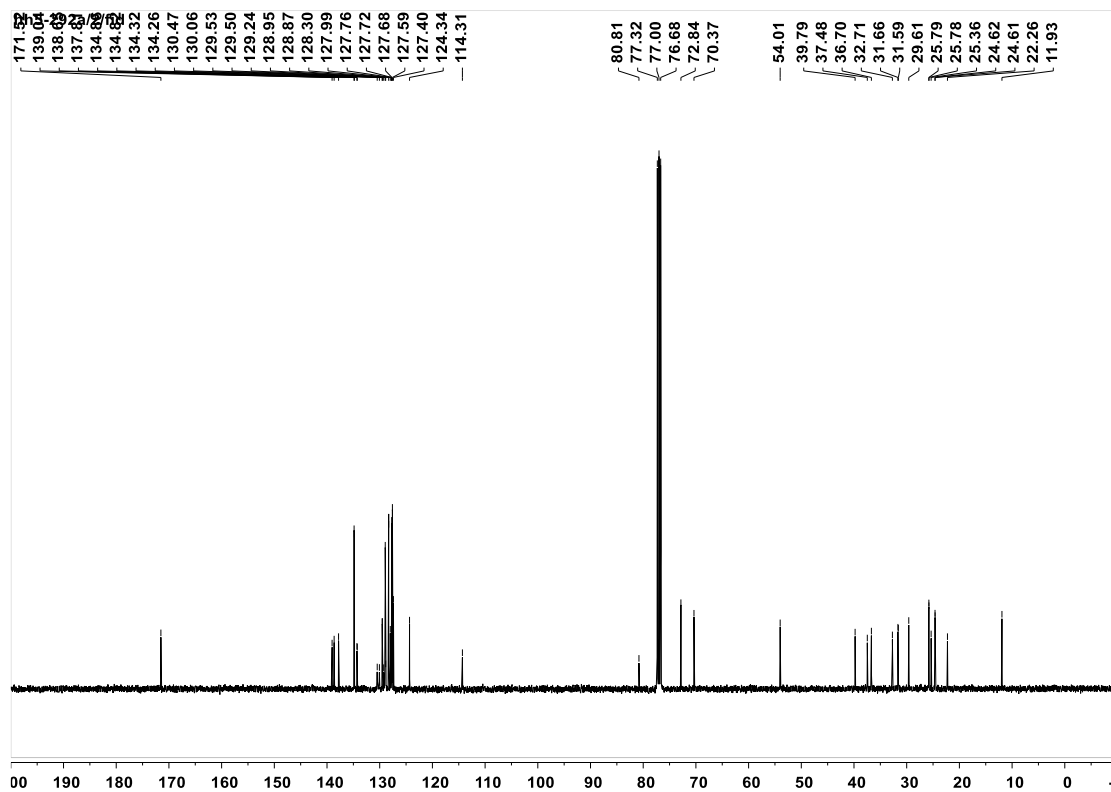
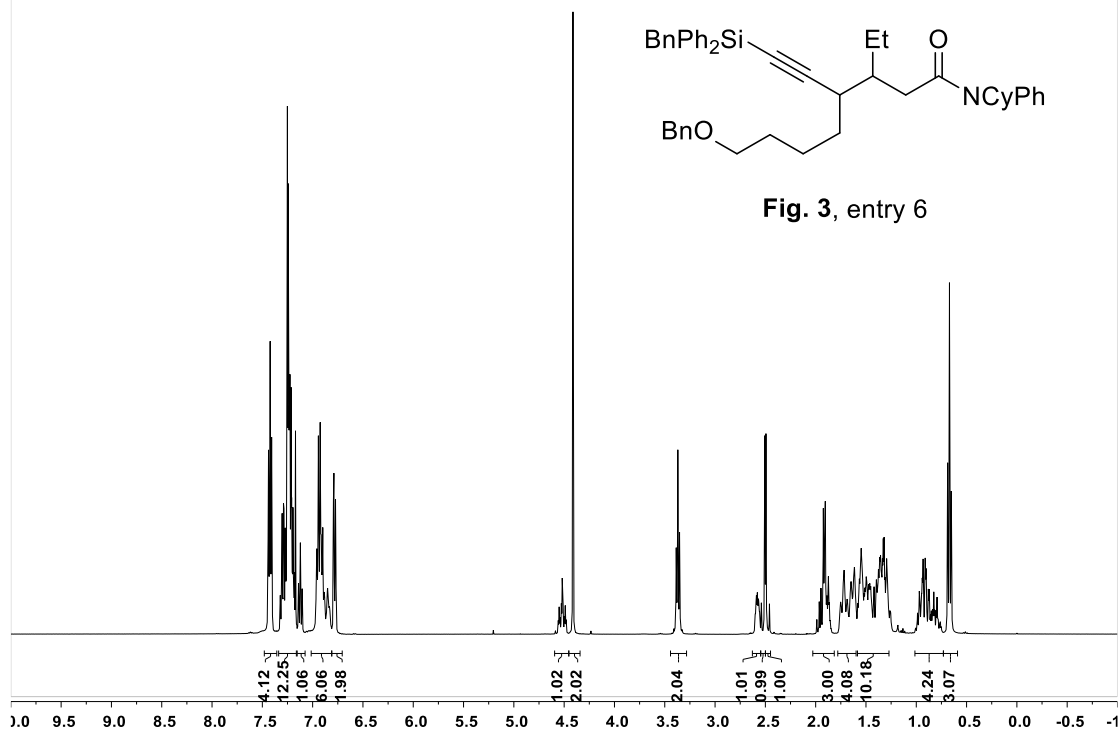


Fig. 3, entry 4





hh5-292a/1/fid



hh5-337a/1/fid

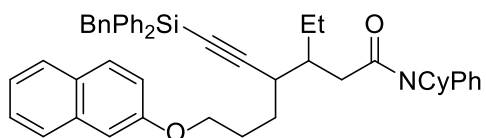
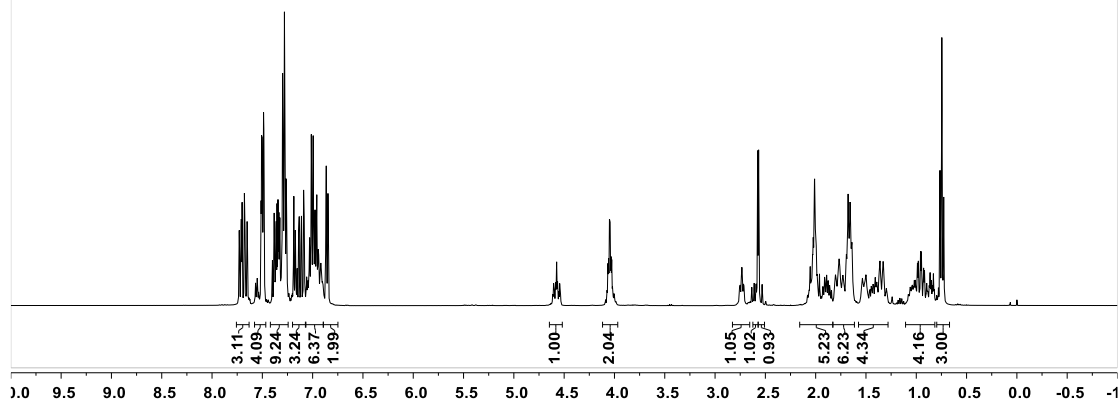
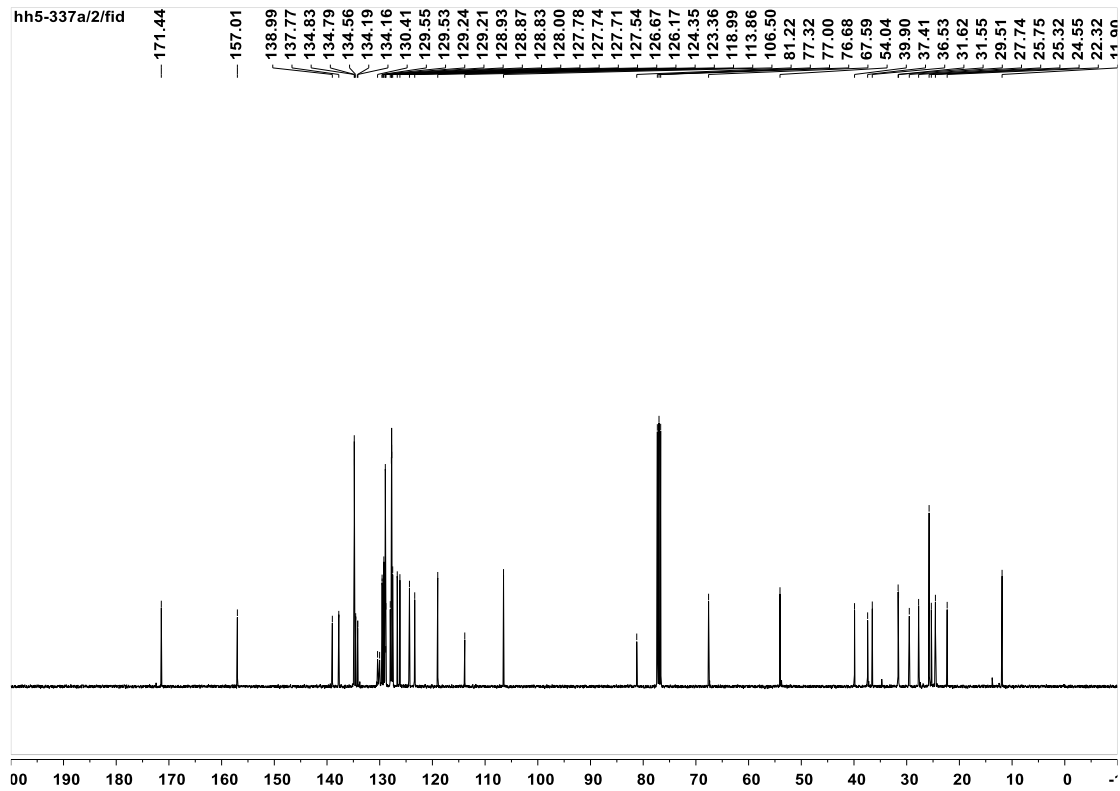


Fig. 3, entry 7



hh5-337a/2/fid



HH5-344/1/fid

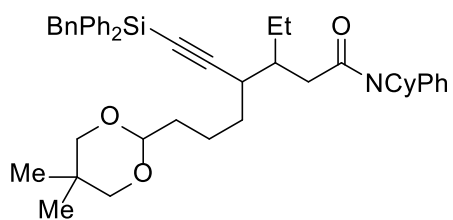
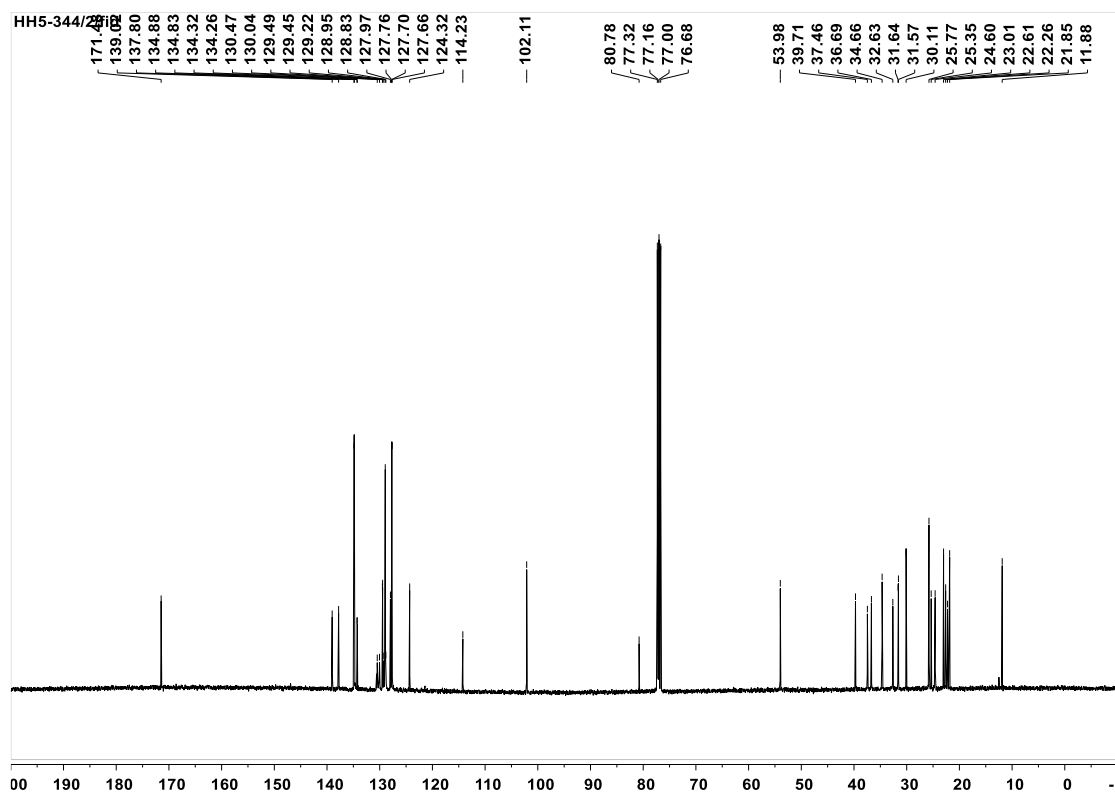
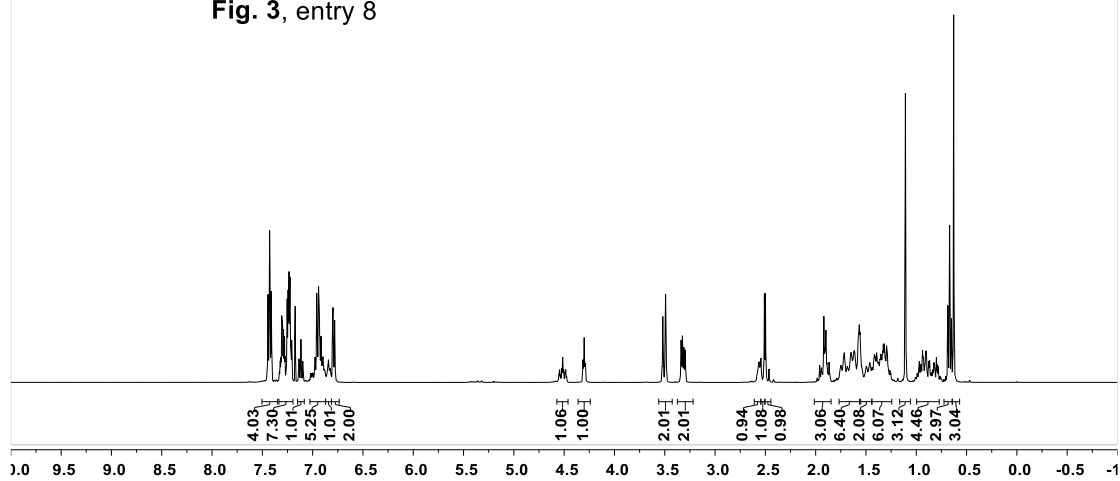


Fig. 3, entry 8



hh5-291a/1/fid

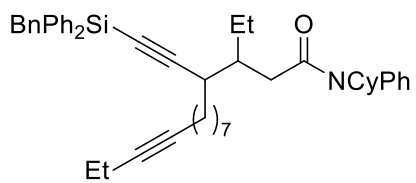
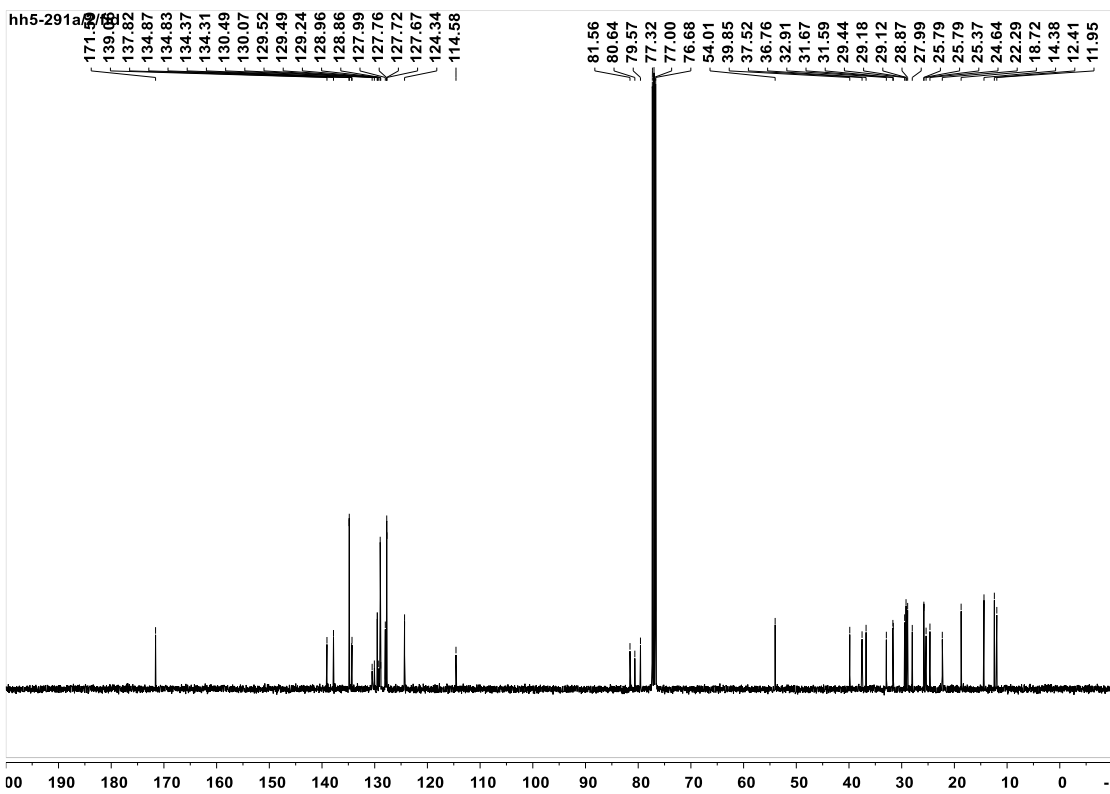
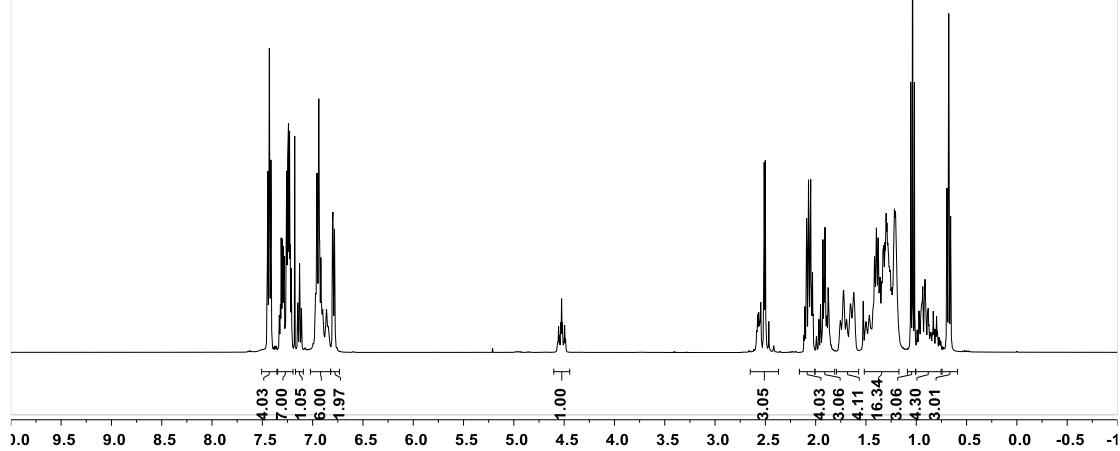


Fig. 3, entry 9



hh5-289a/1/fid

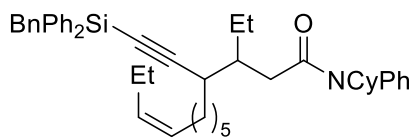
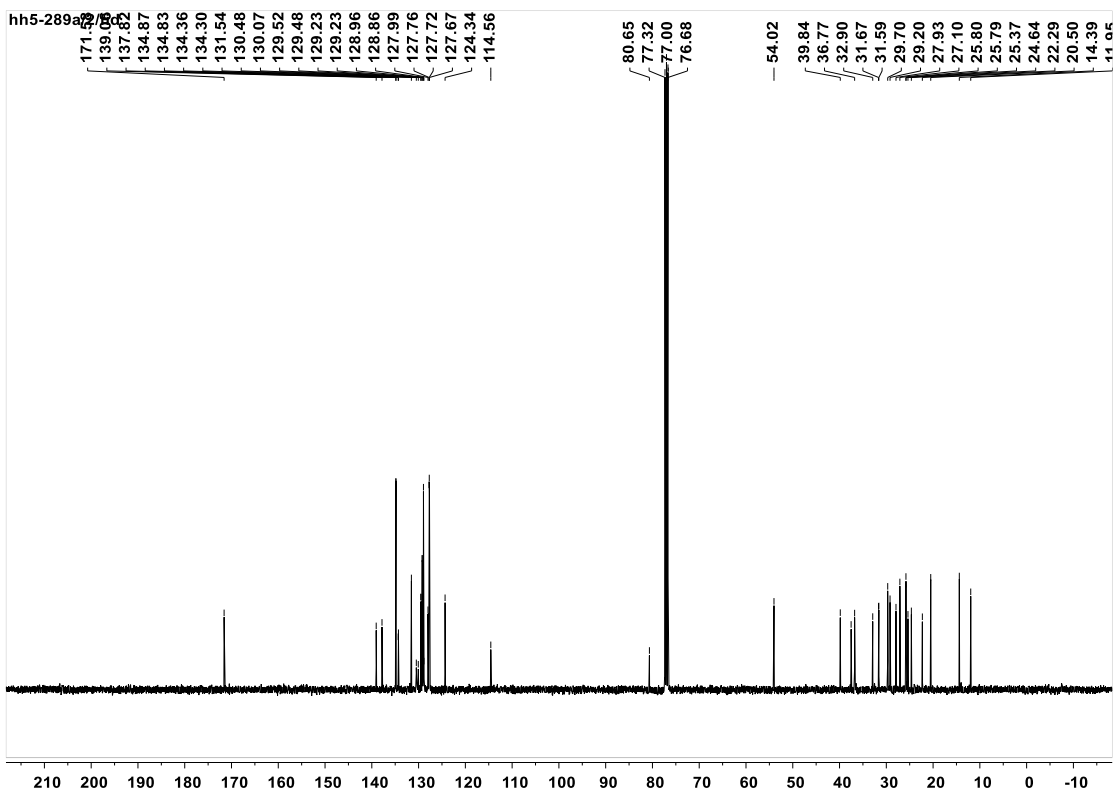
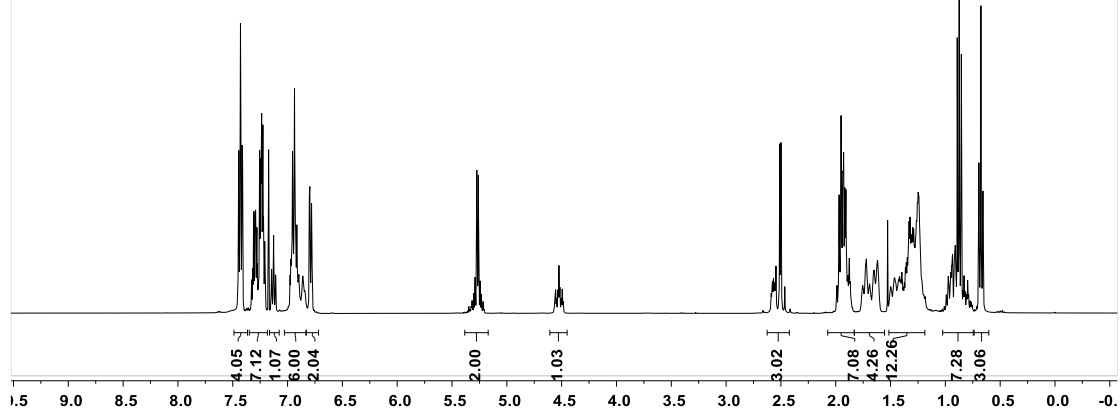


Fig. 3, entry 10



HH5-300D/1/fid

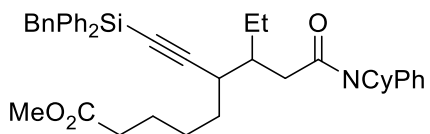
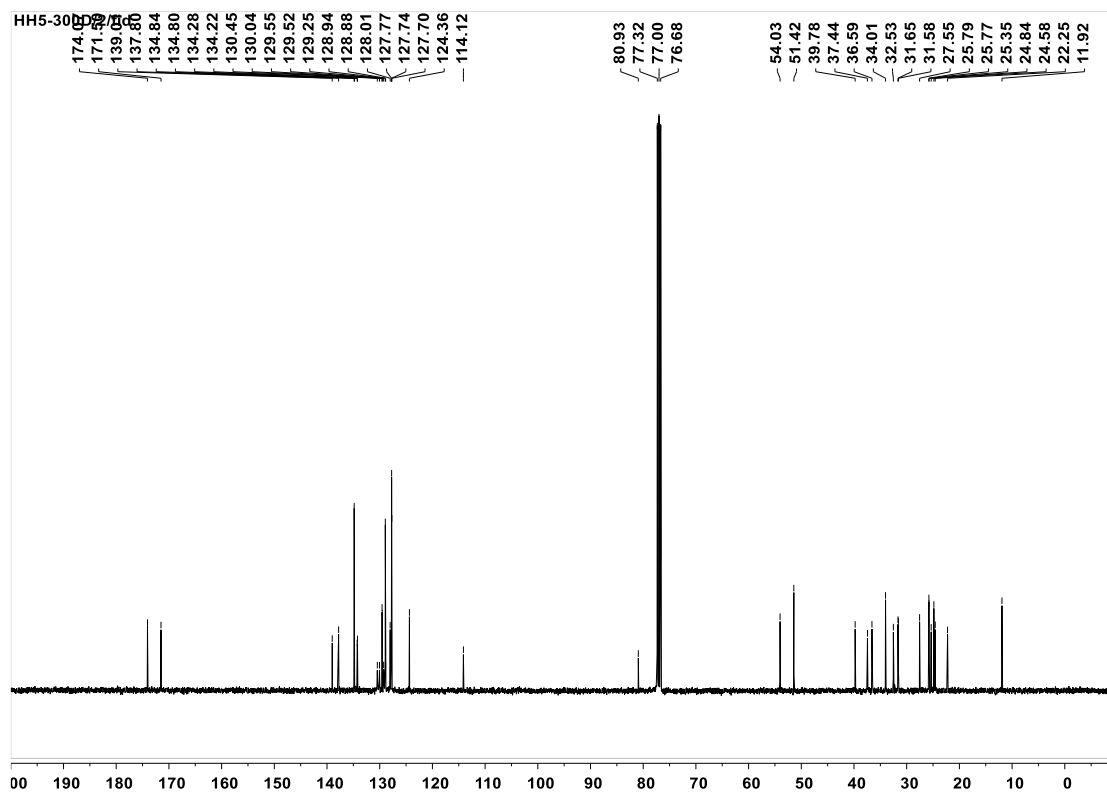
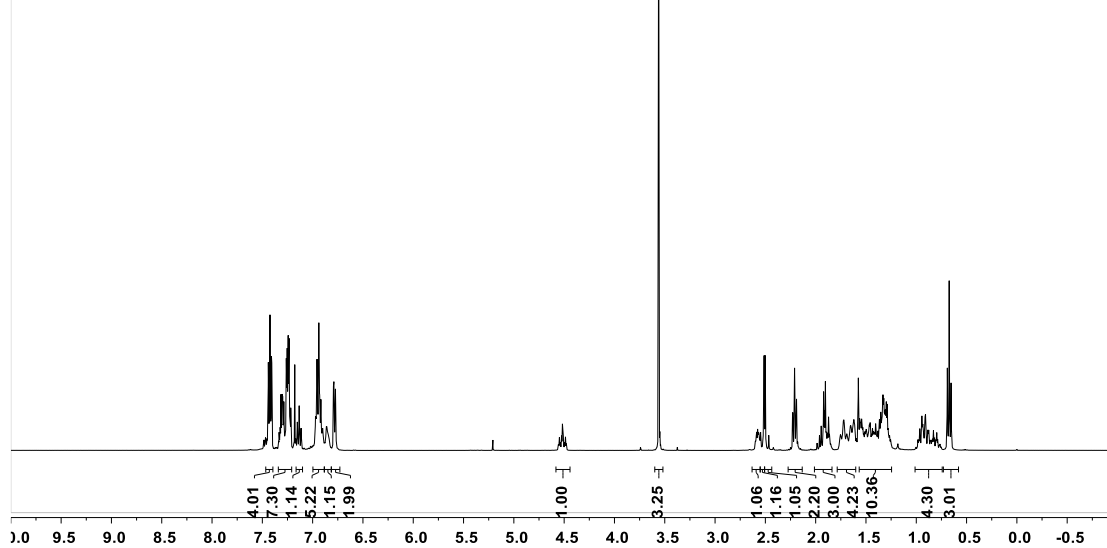


Fig. 3, entry 11



HH5-336/1/fid

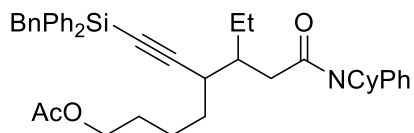
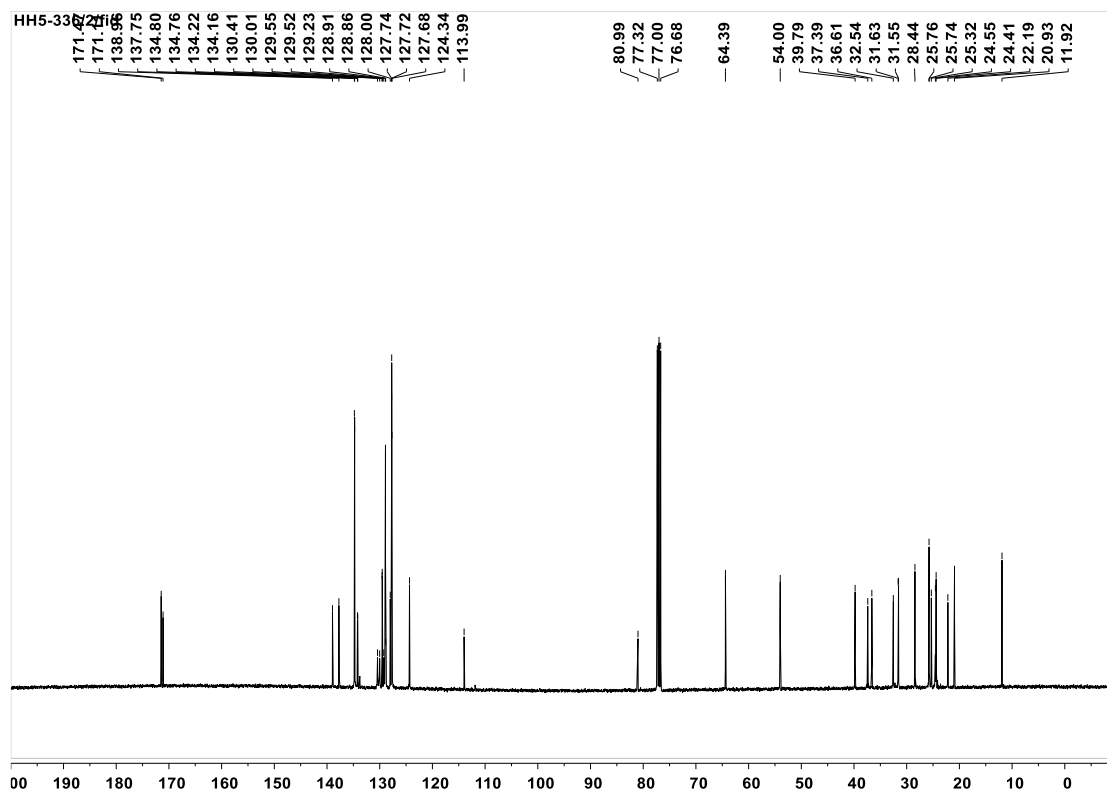
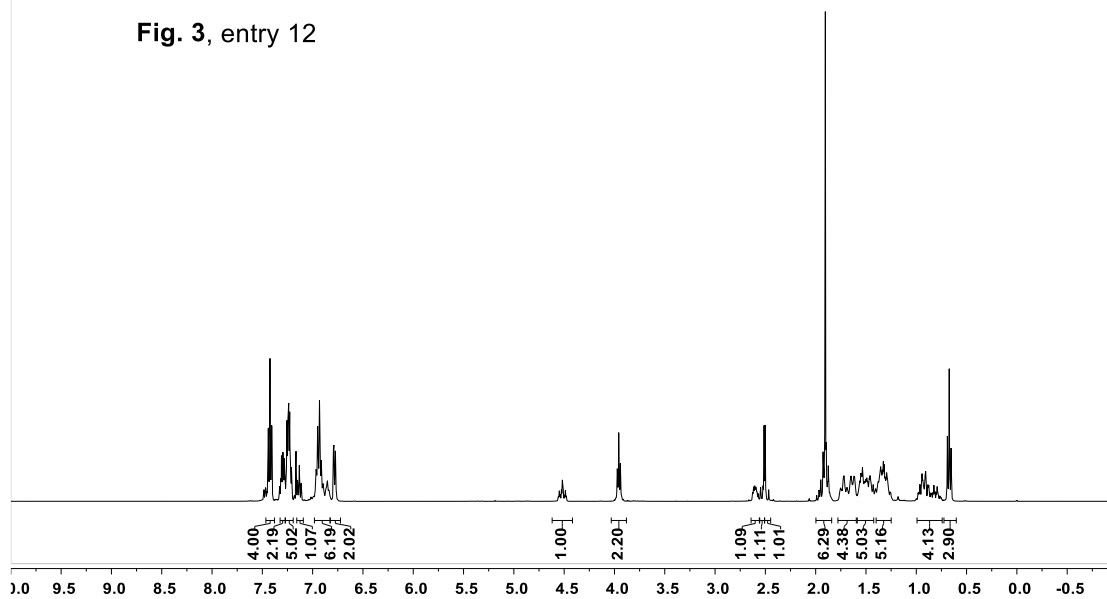


Fig. 3, entry 12



hh5-335a/1/fid

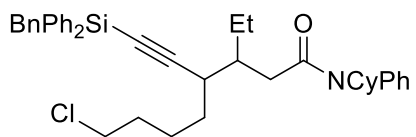
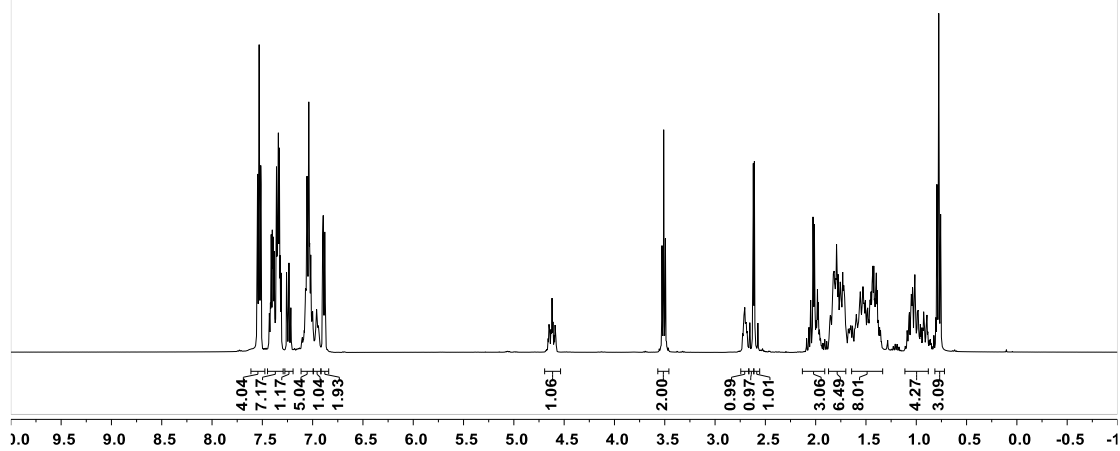
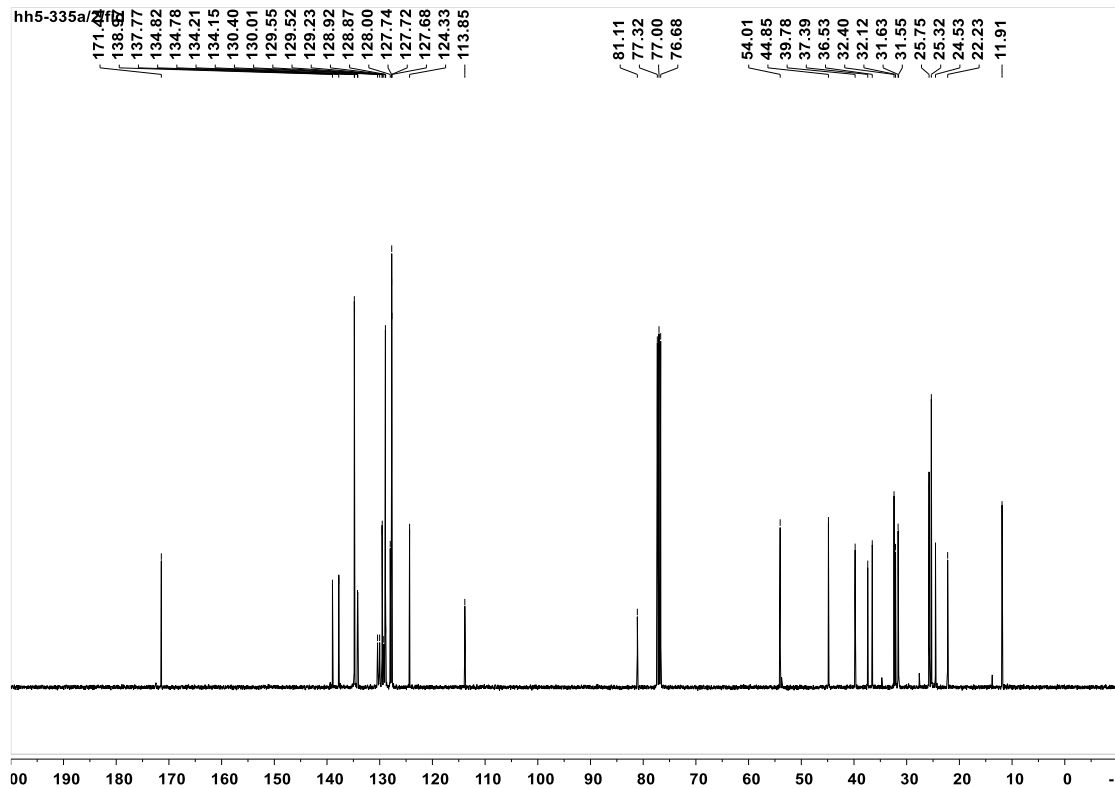


Fig. 3, entry 13



hh5-335a/1/fb



hh5-290a/1/fid

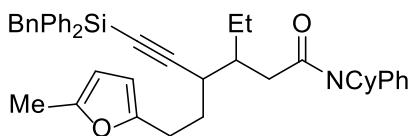
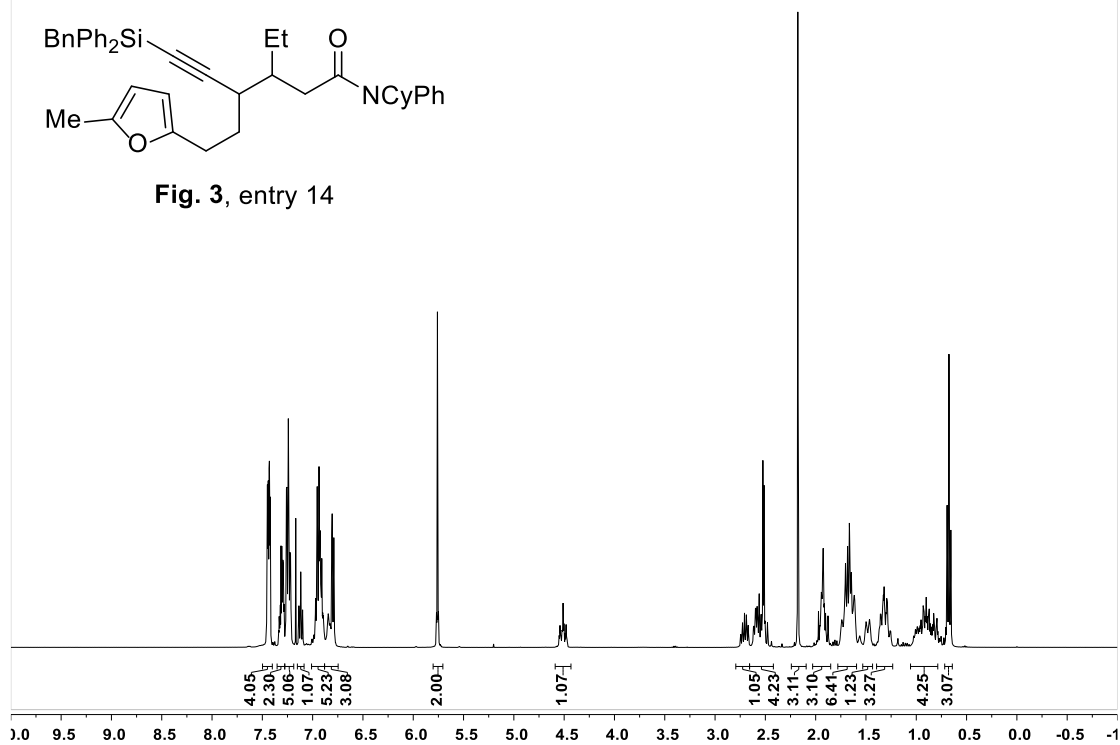
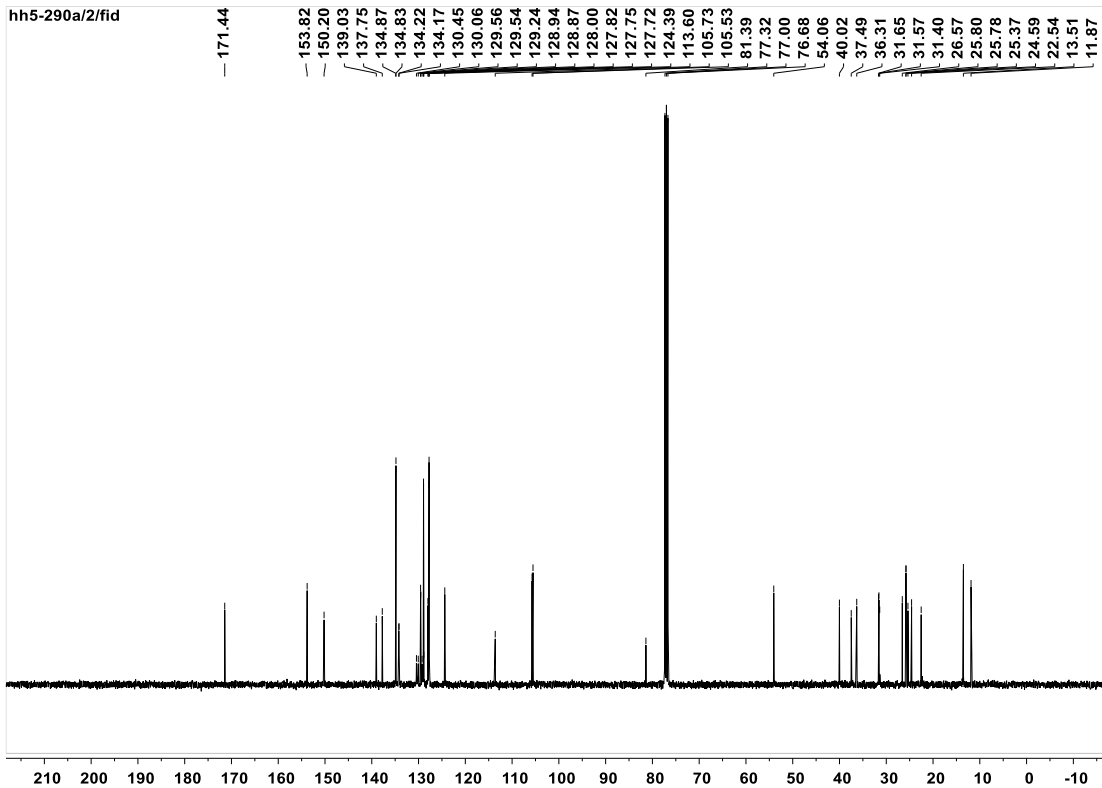


Fig. 3, entry 14



hh5-290a/2/fid



hh6-26/1/fid

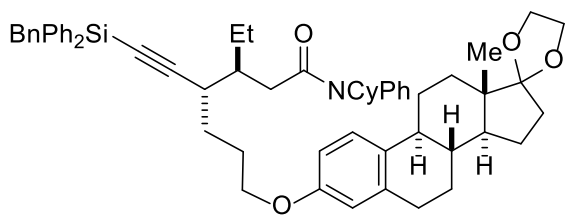
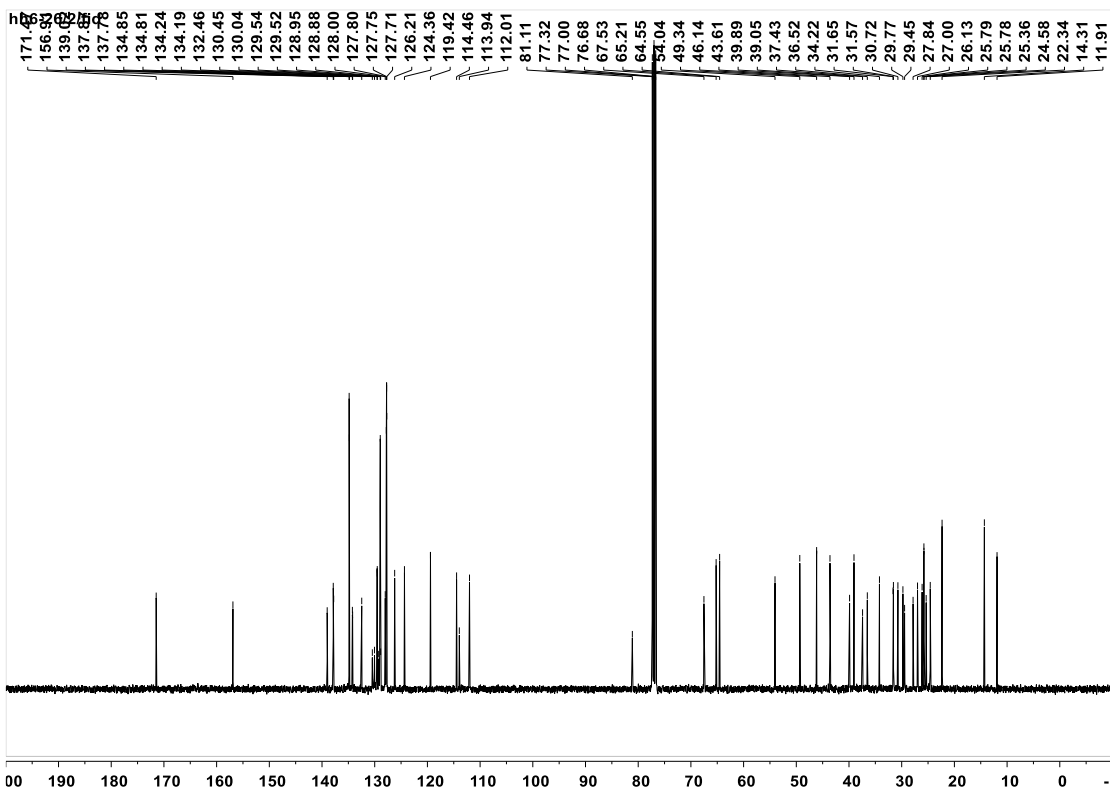
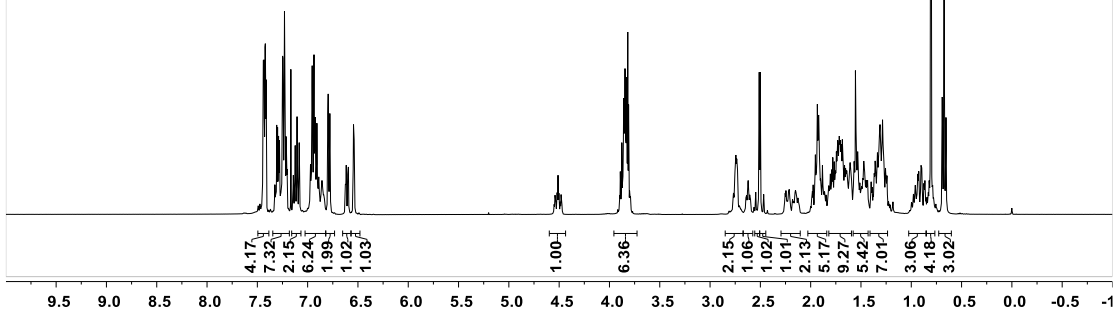


Fig. 3, entry 15
From (S,R)-L2



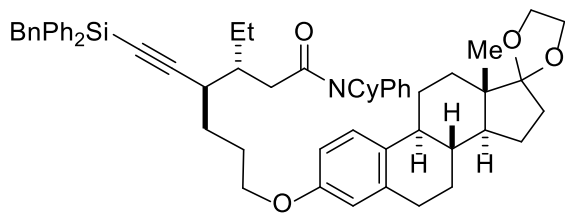
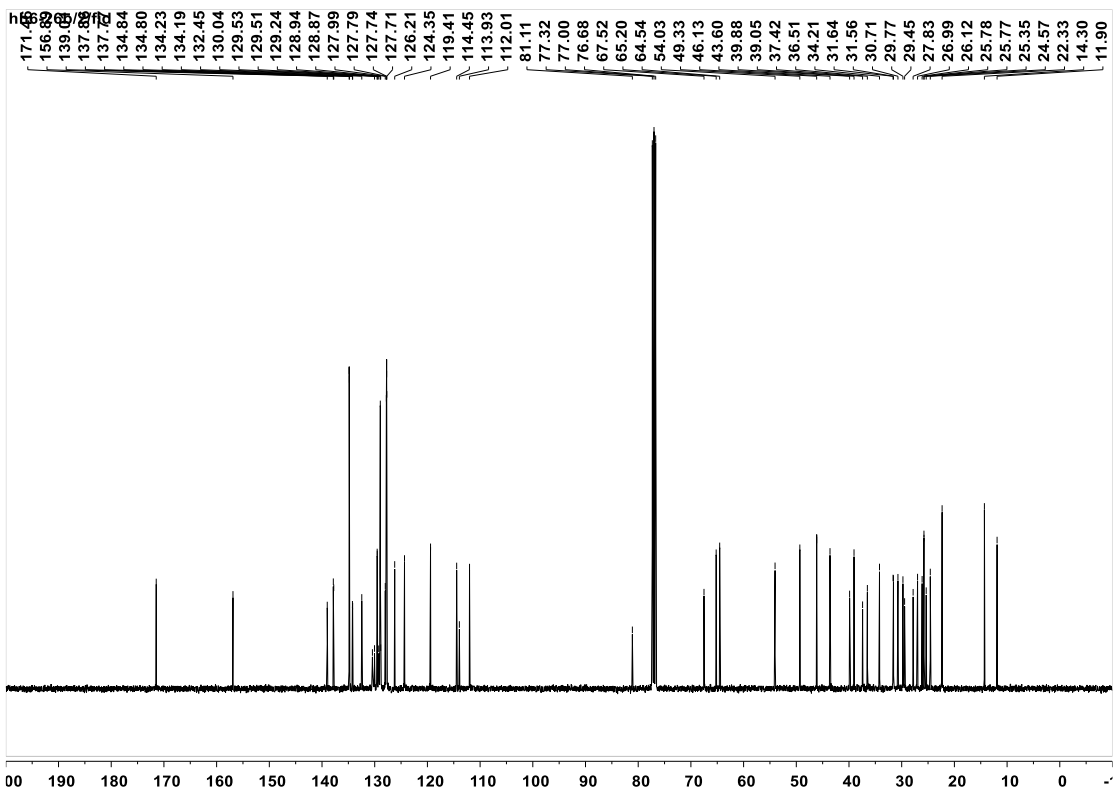
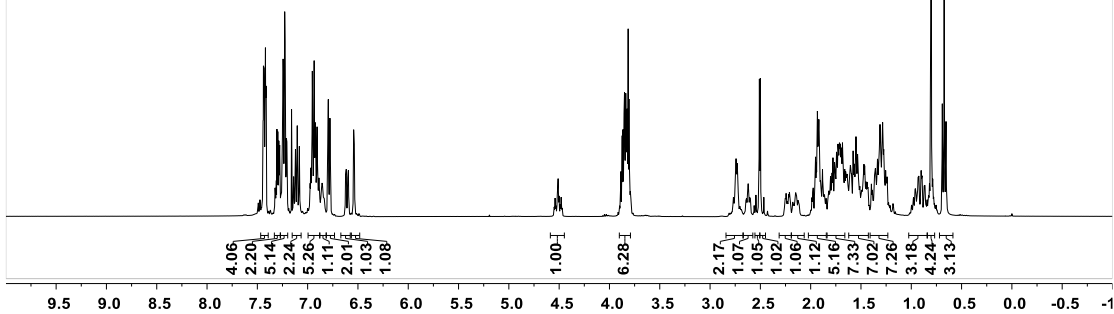


Fig. 3, entry 15
From *(R,S)*-L2



HH5-346/1/fid

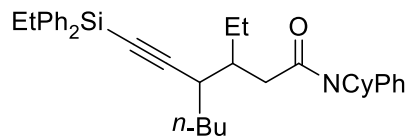
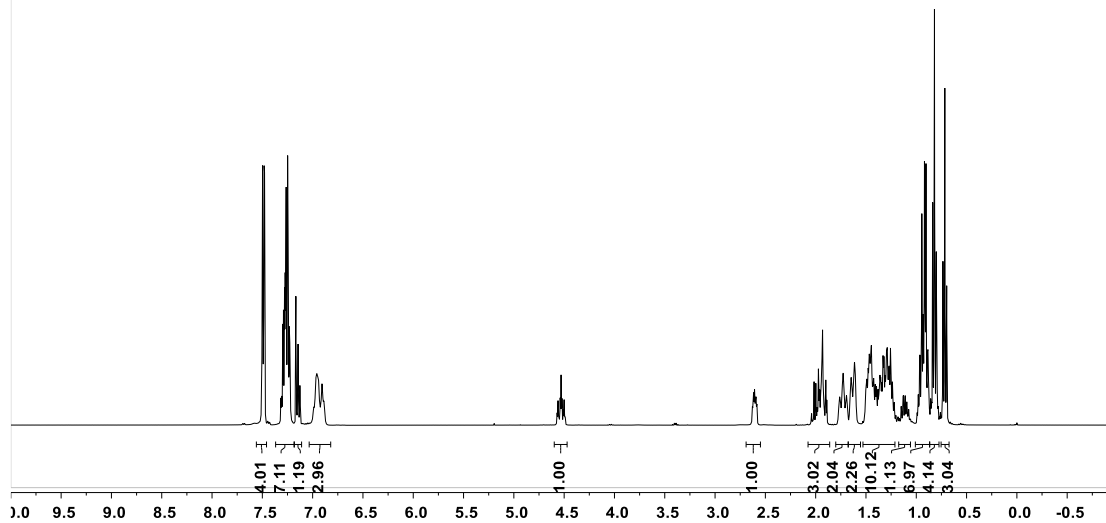
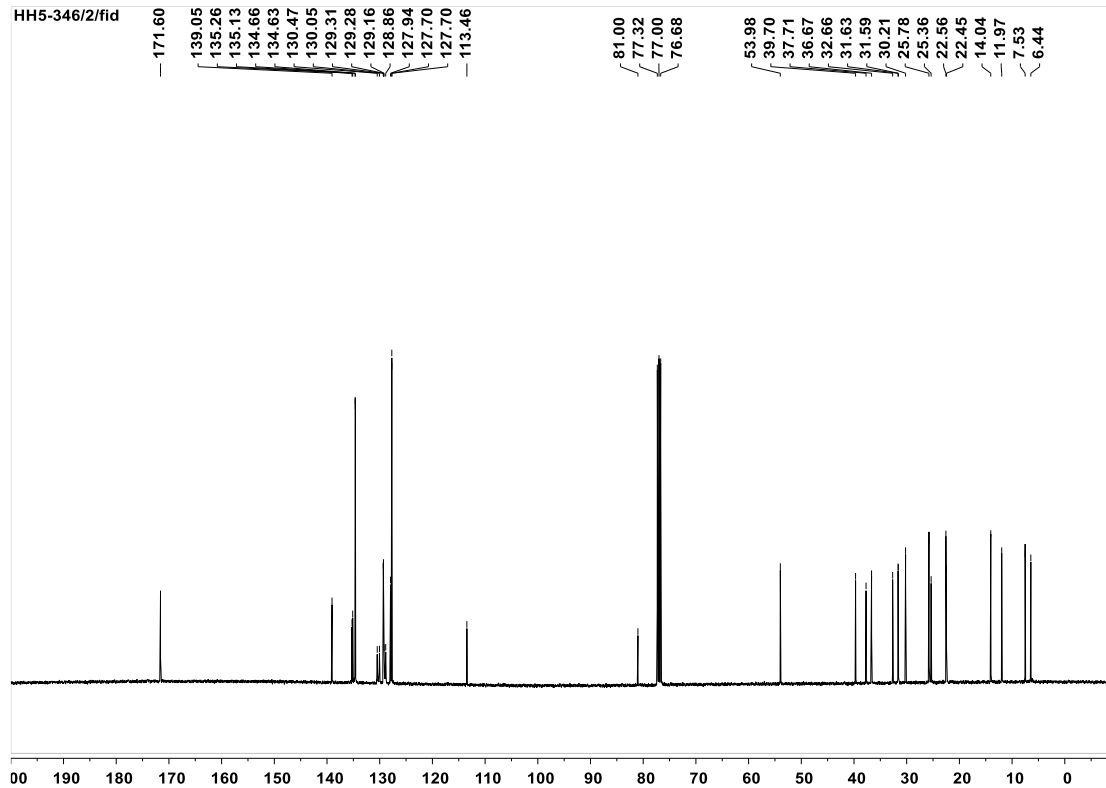


Fig. 3, entry 16



HH5-346/2/fid



HH5-345/1/fid

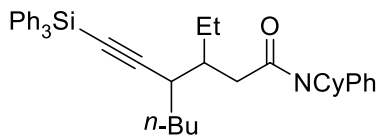
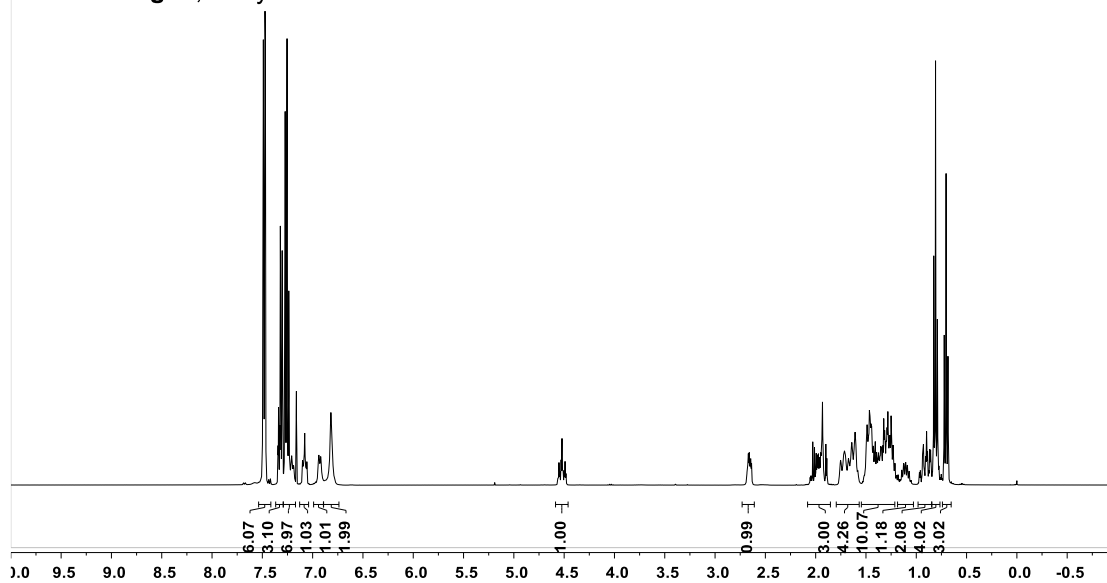
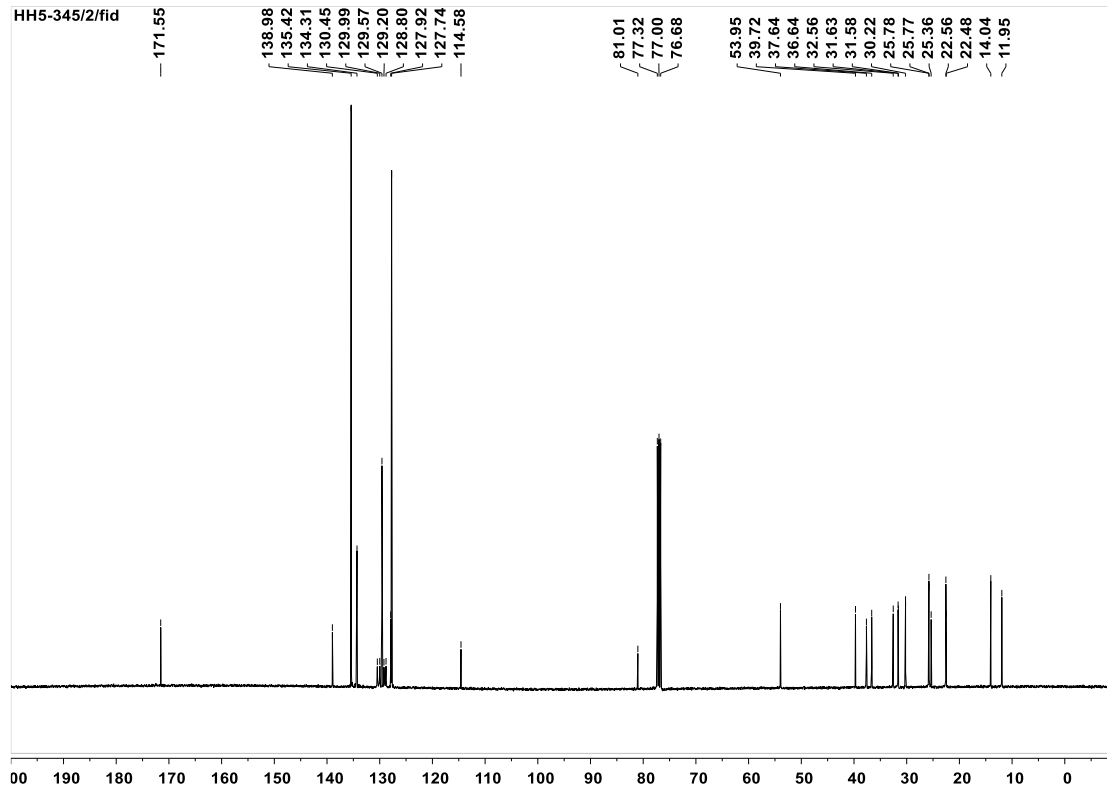


Fig. 3, entry 17



HH5-345/2/fid



hh6-13/1/fid

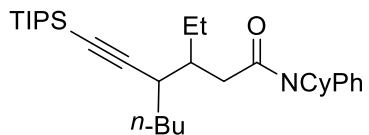
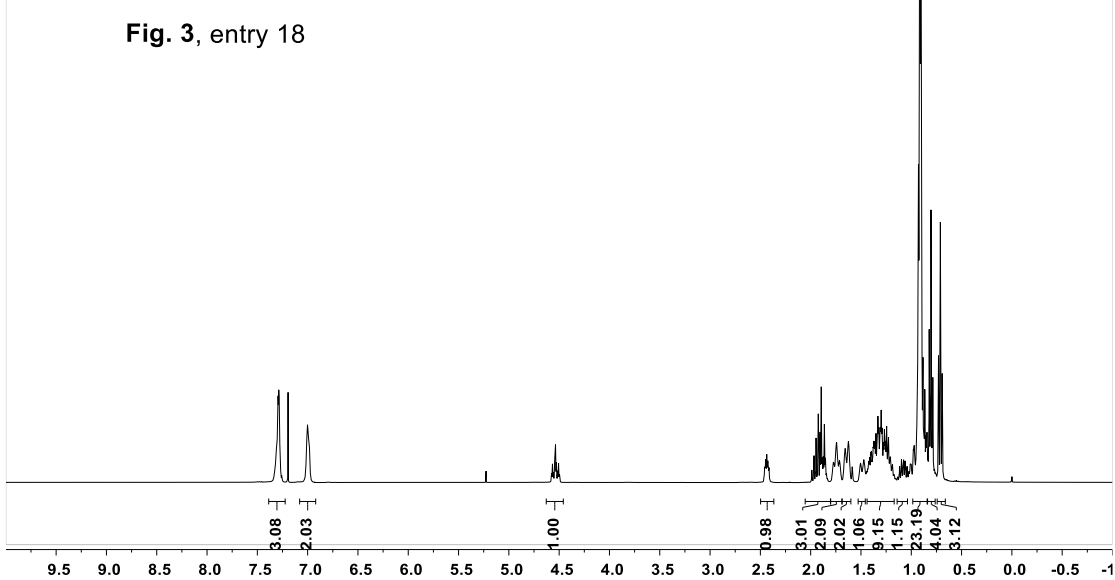
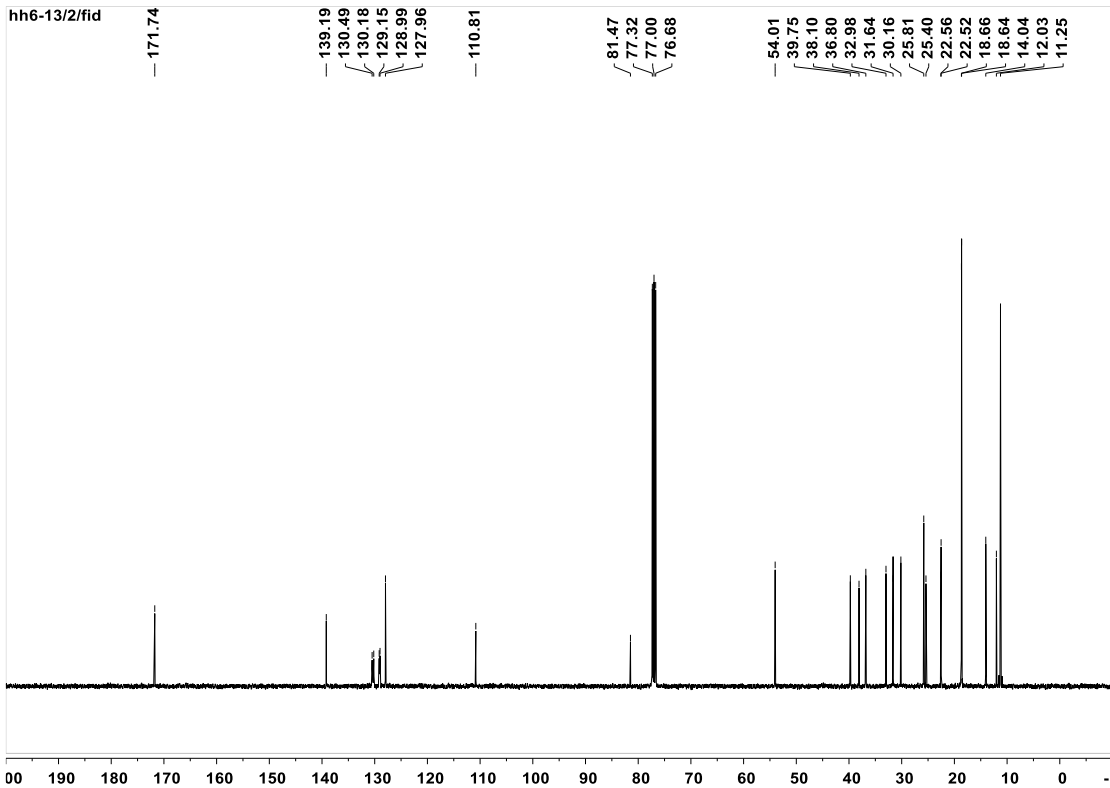


Fig. 3, entry 18



hh6-13/2/fid



hh5-259a/1/fid

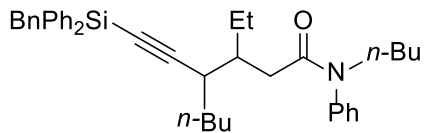
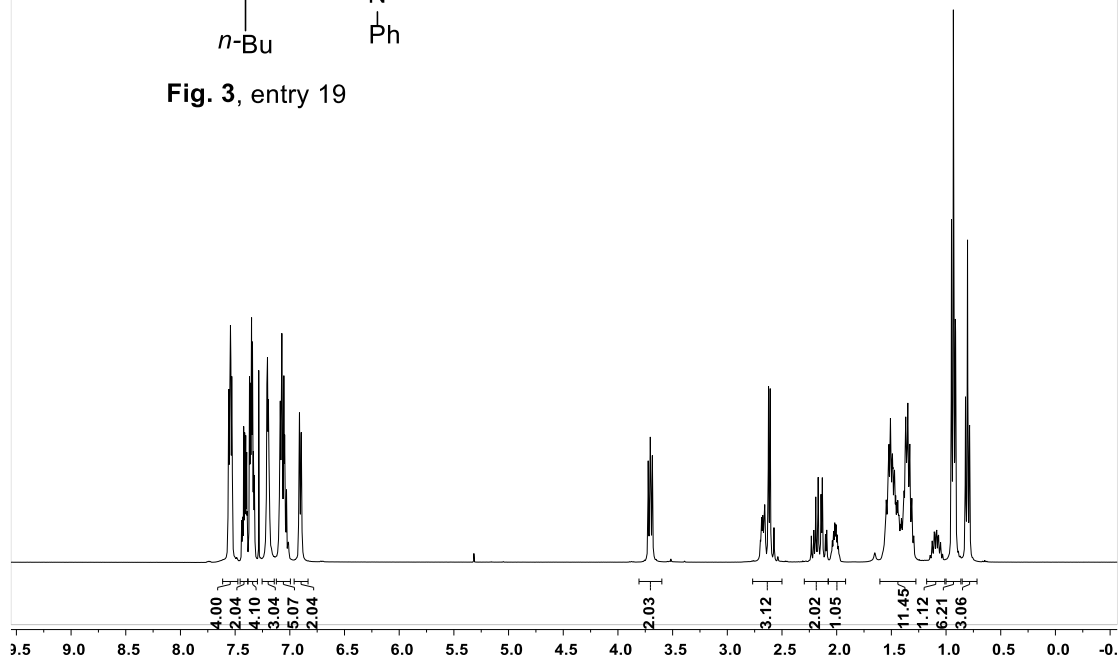
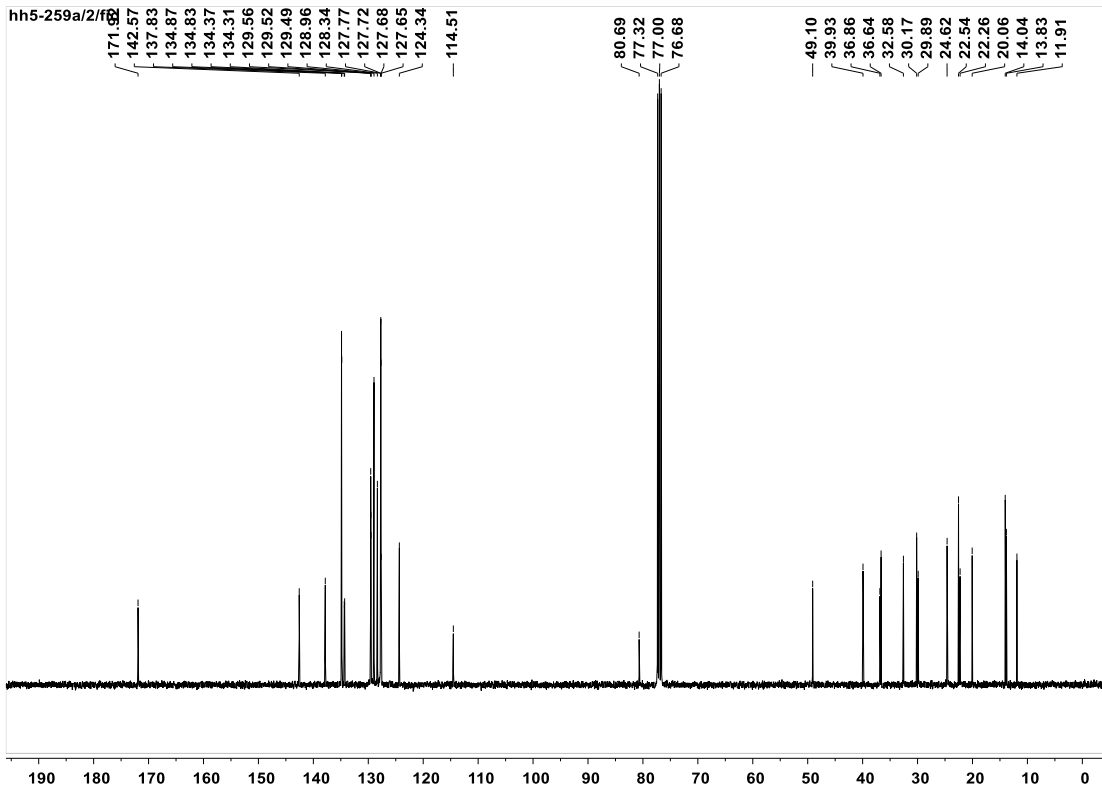


Fig. 3, entry 19



hh5-259a/2/fid



hh6-46a-0501/1/fid

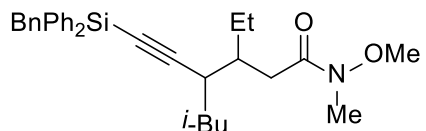
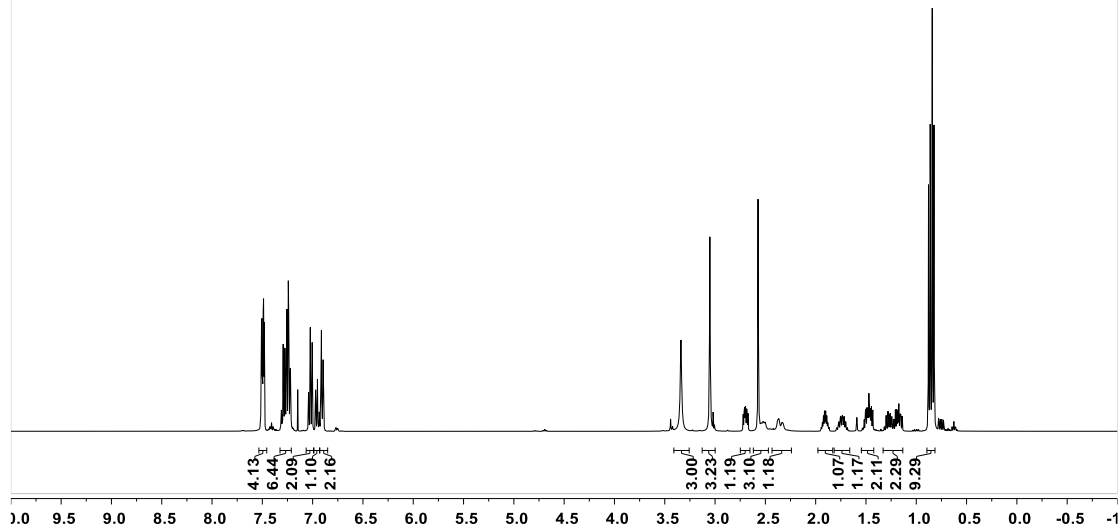
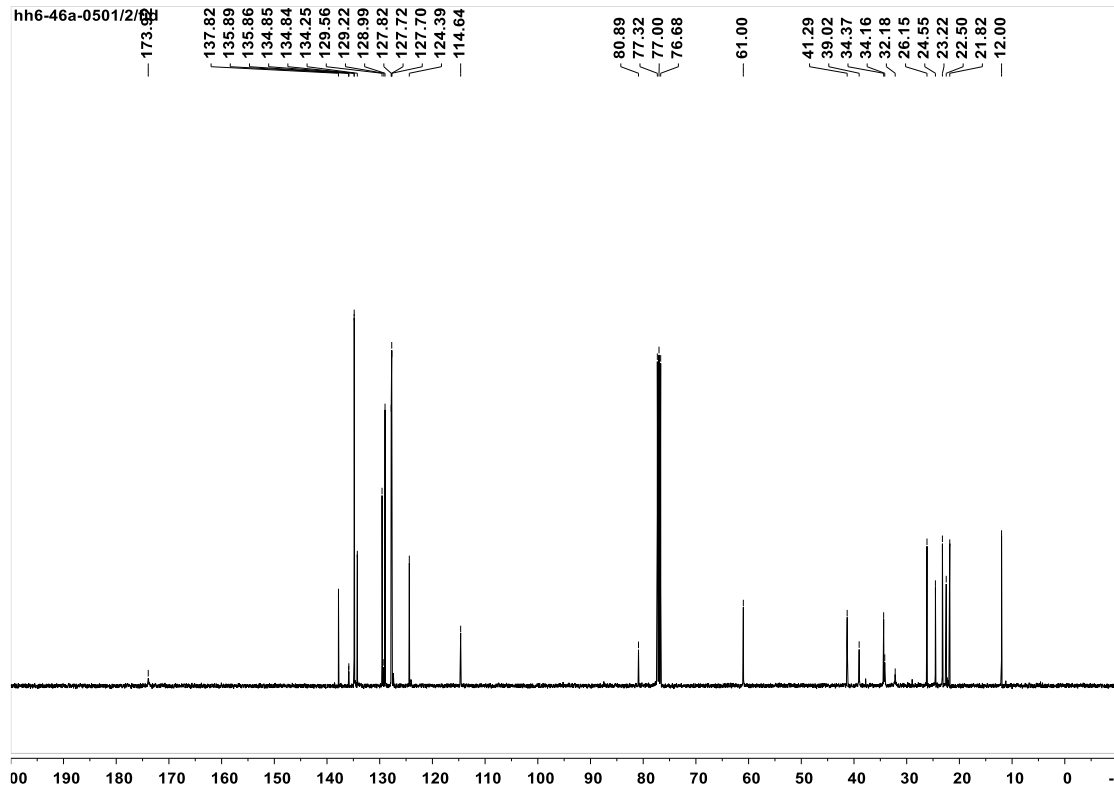


Fig. 3, entry 20



hh6-46a-0501/2/16



hh5-255a/1/fid

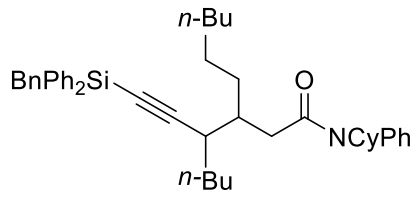
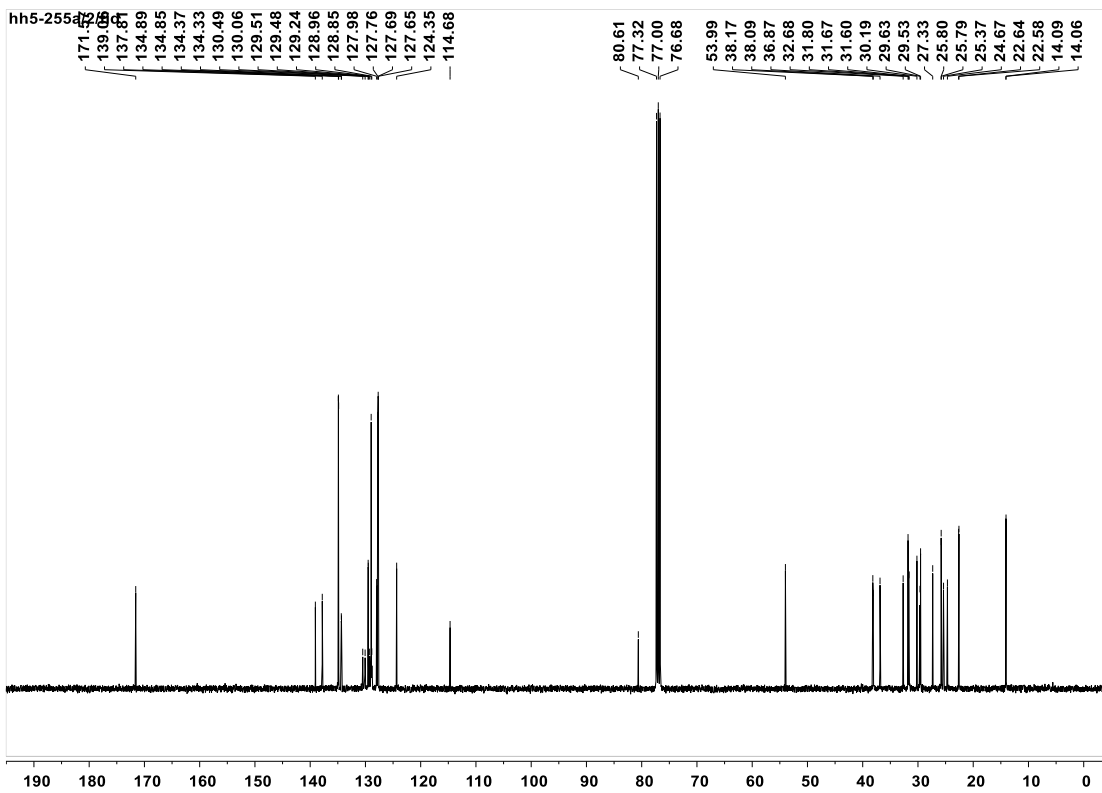
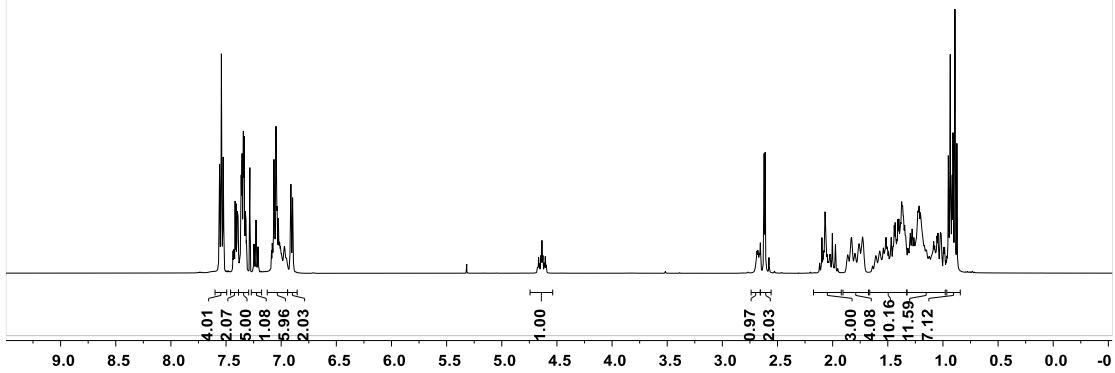


Fig. 3, entry 21



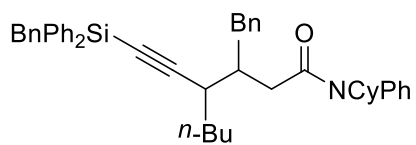
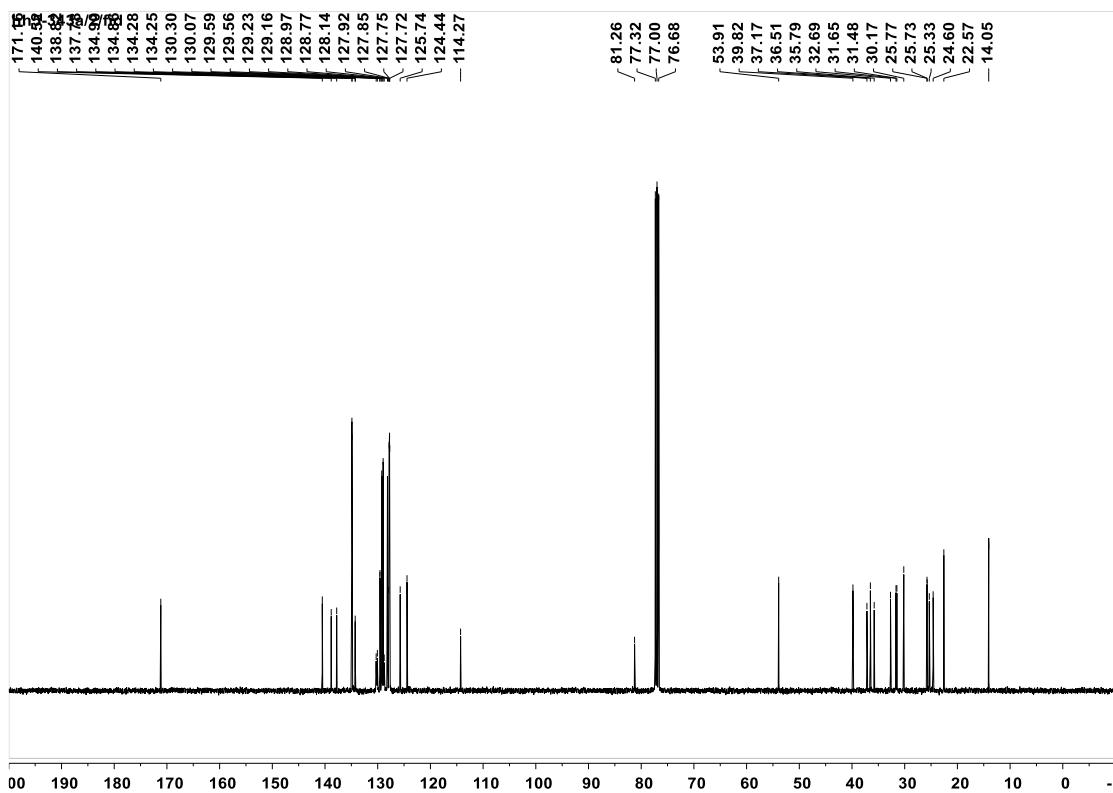
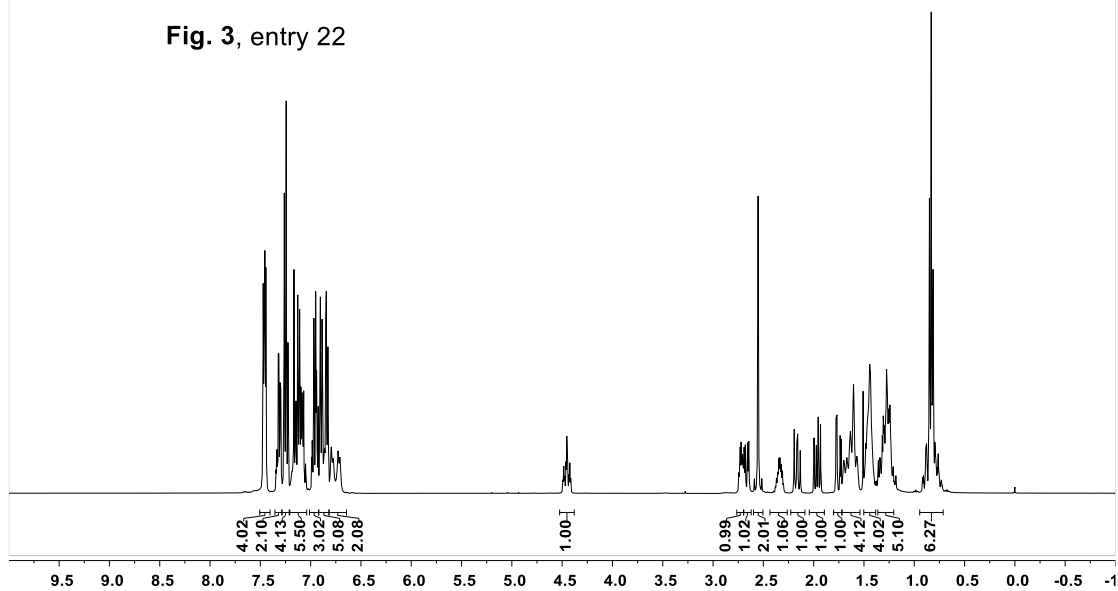


Fig. 3, entry 22



hh5-256a/1/fid

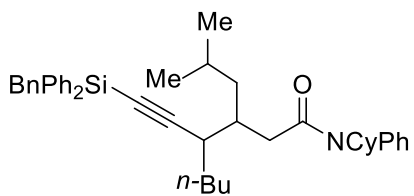
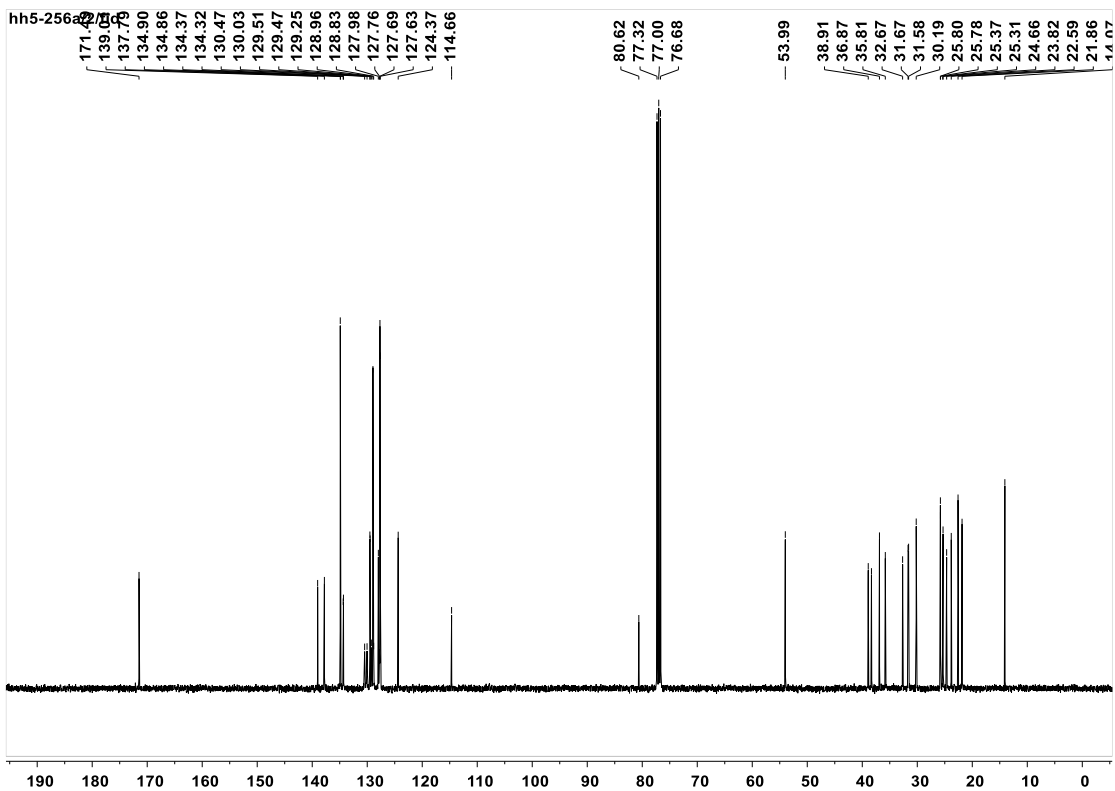
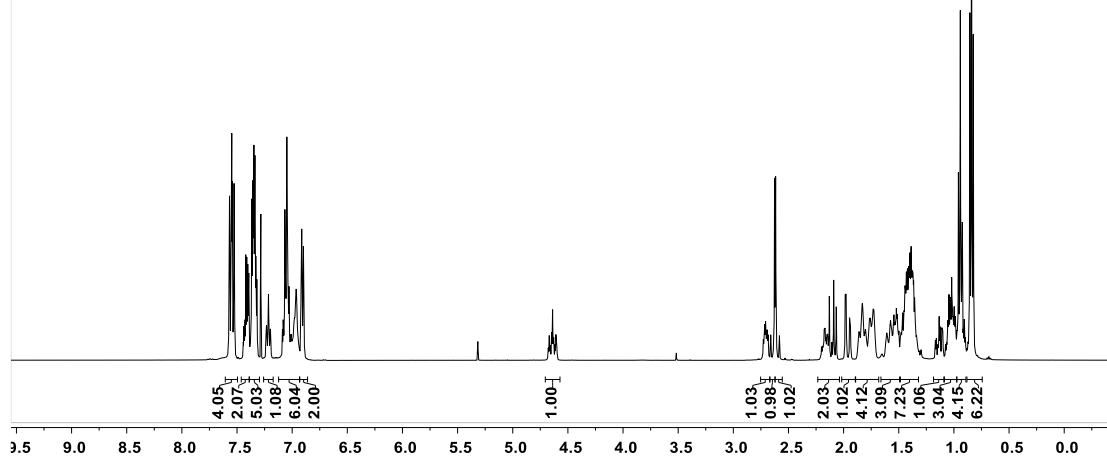


Fig. 3, entry 23



HH5-306A/1/fid

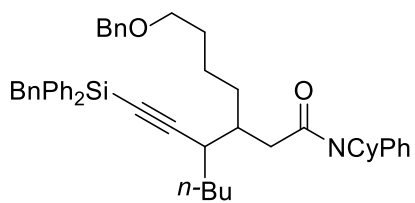
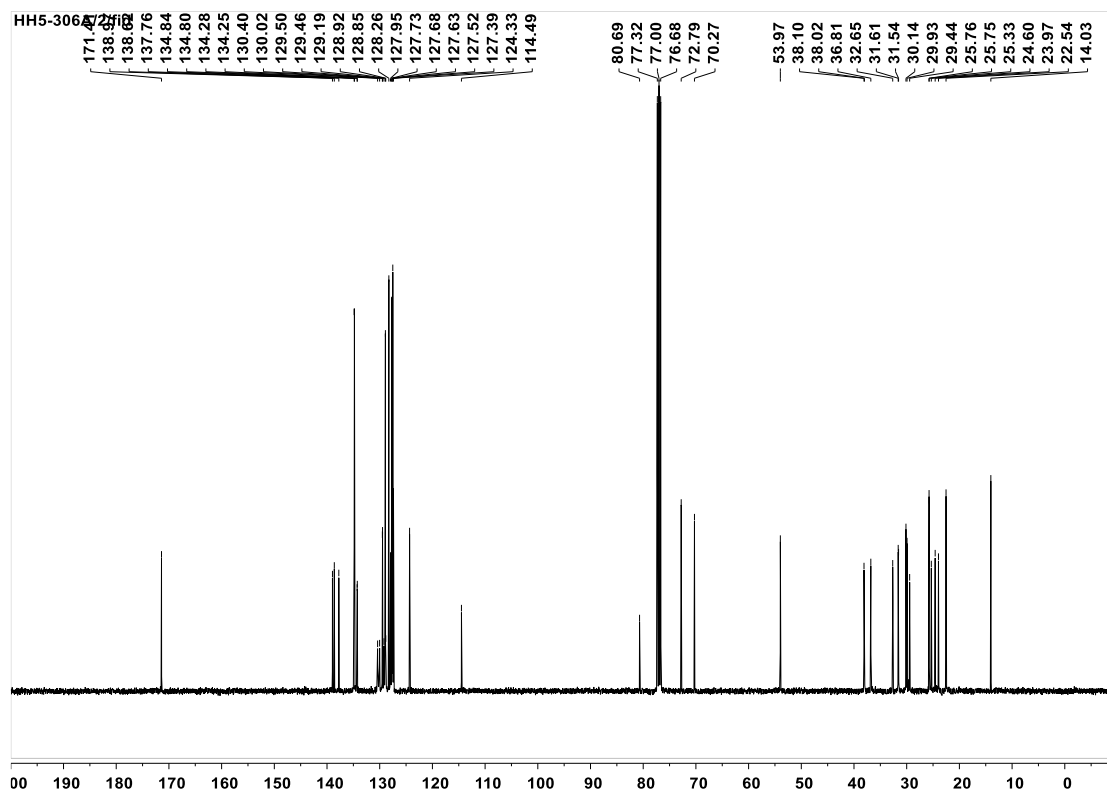
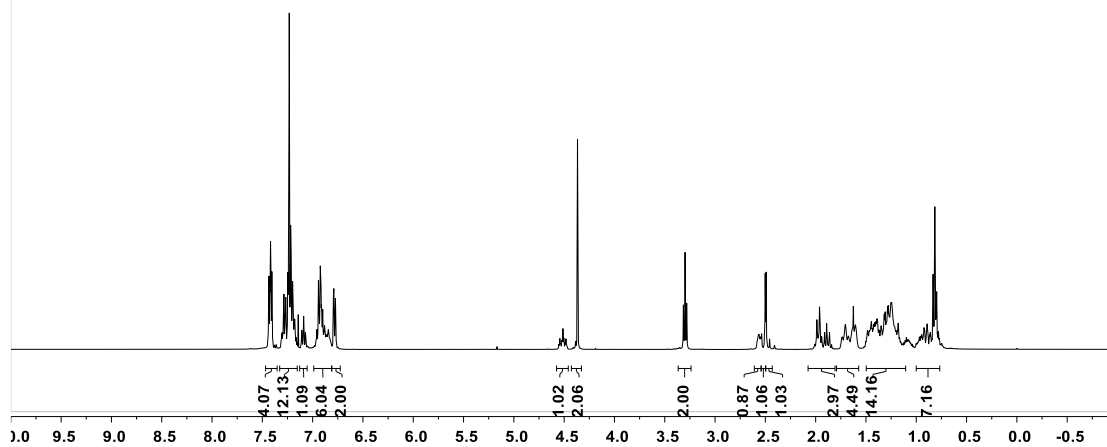


Fig. 3, entry 24



hh6-12/1/fid

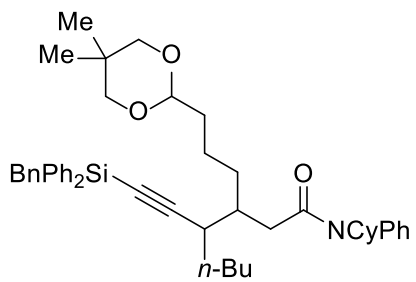
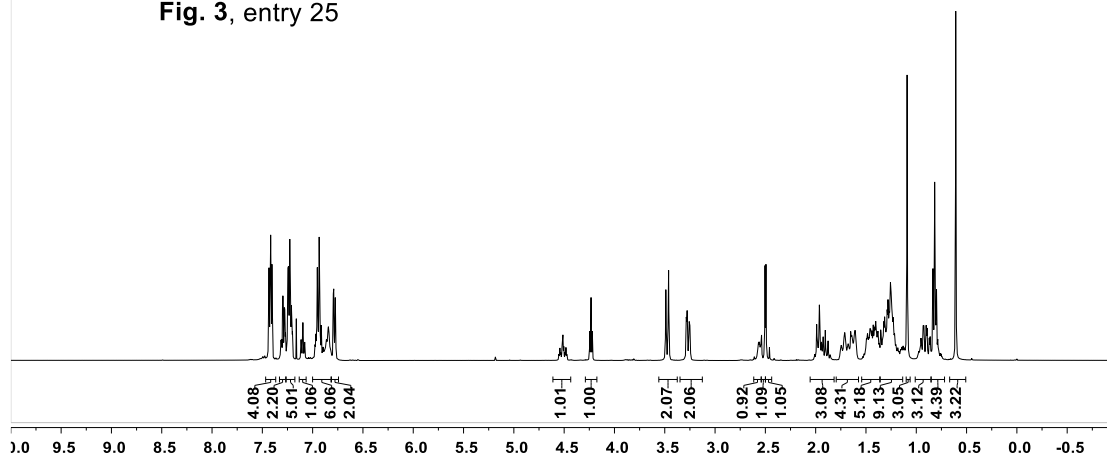
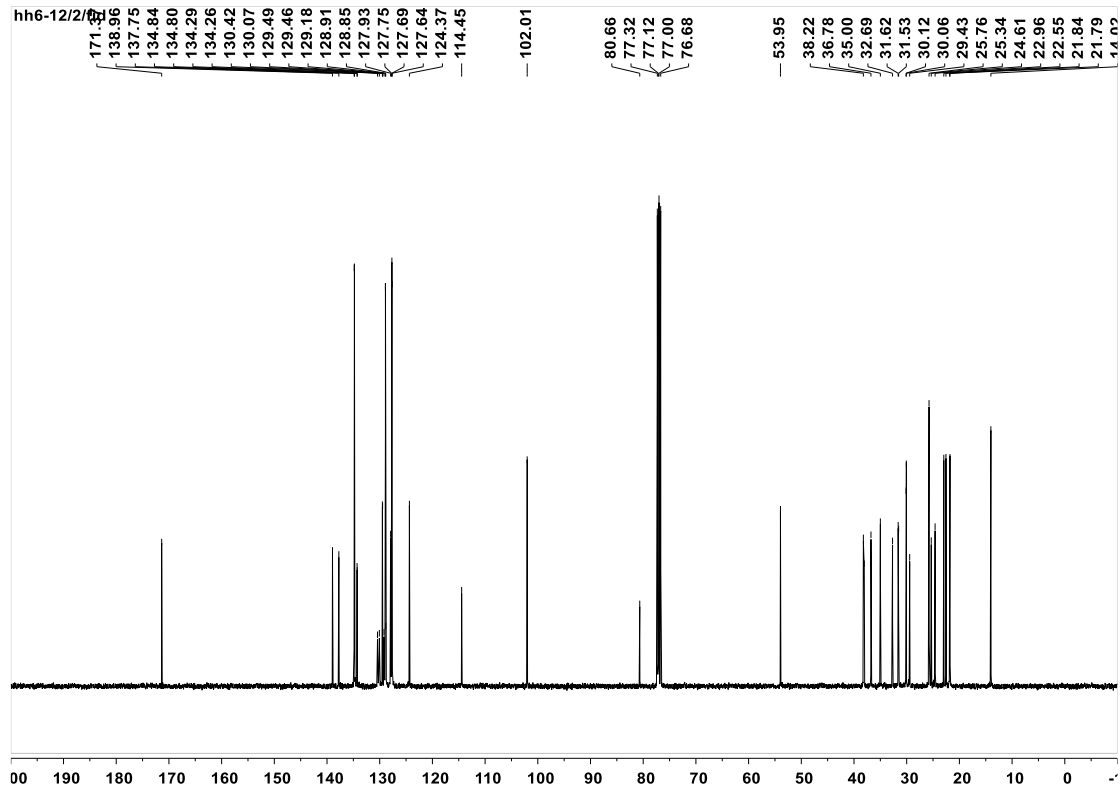


Fig. 3, entry 25



hh6-12/2/fid



HH5-304A/1/fid

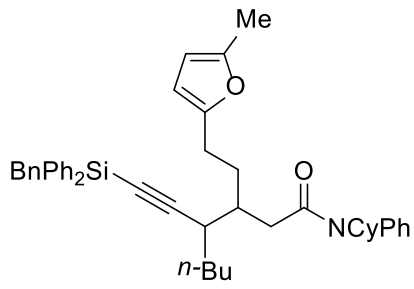
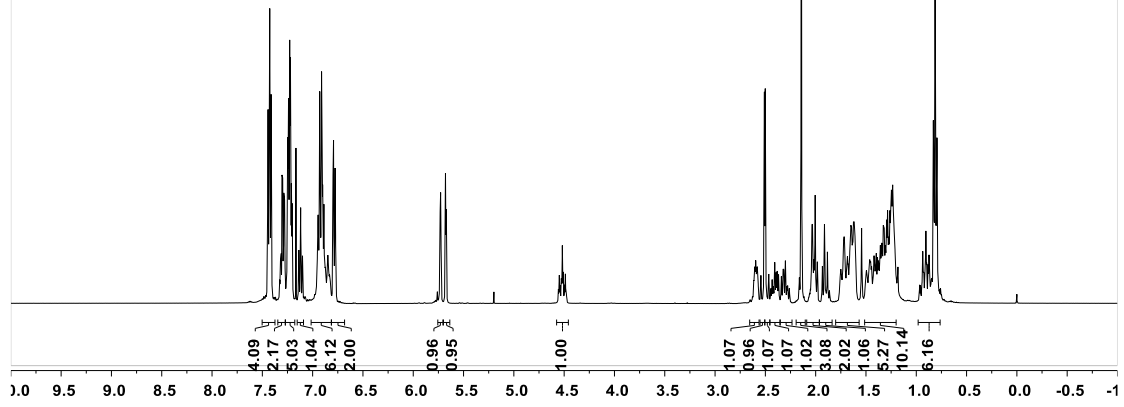
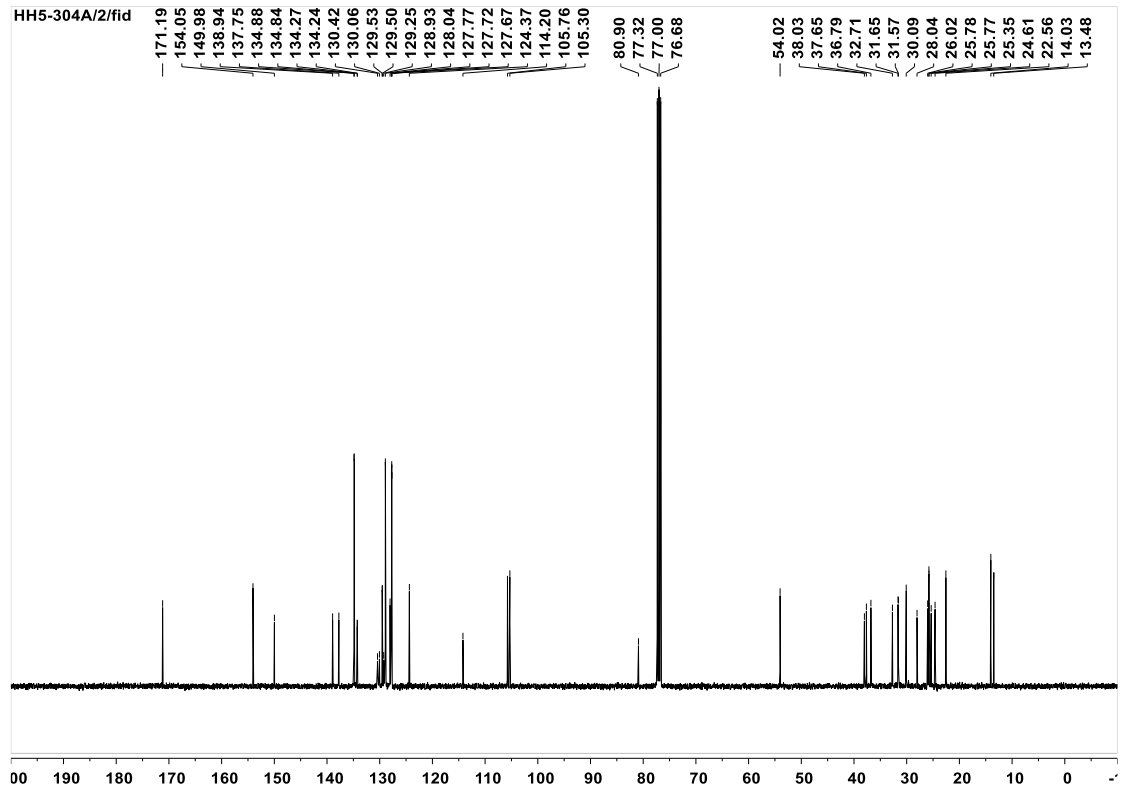


Fig. 3, entry 26



HH5-304A/2/fid



hh5-305a0507/1/fid

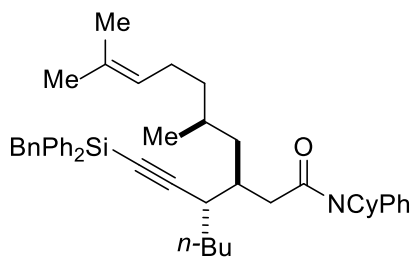
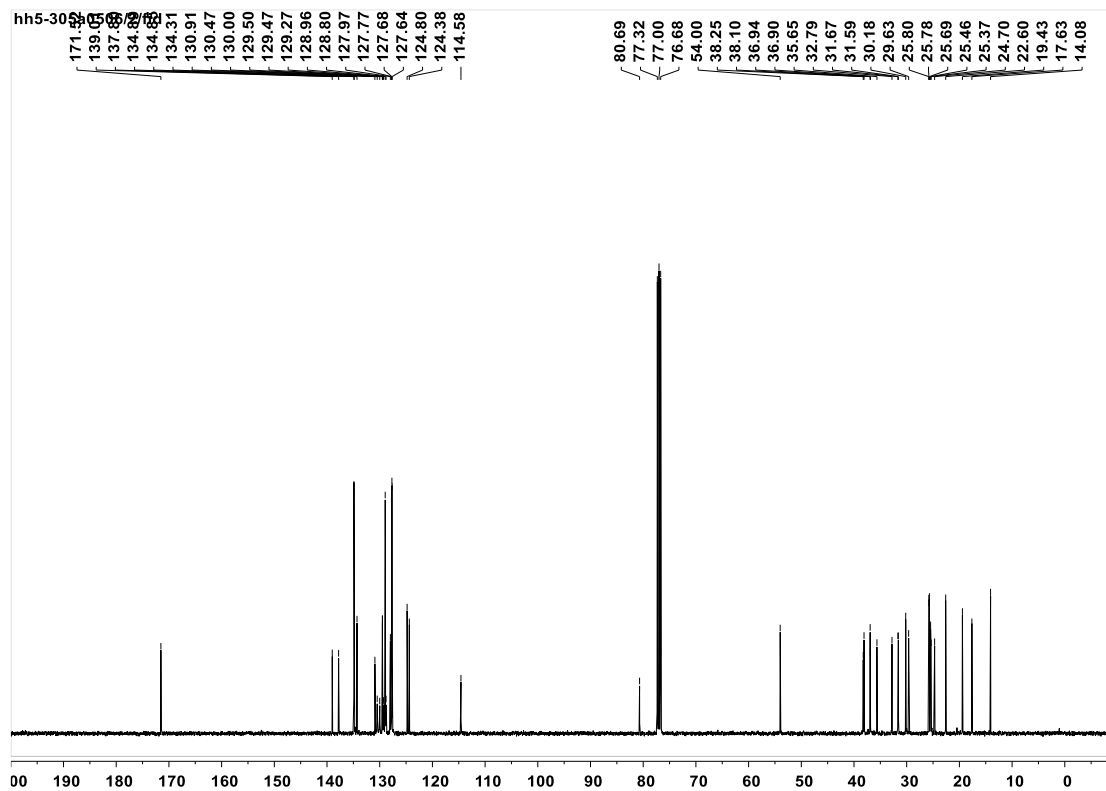
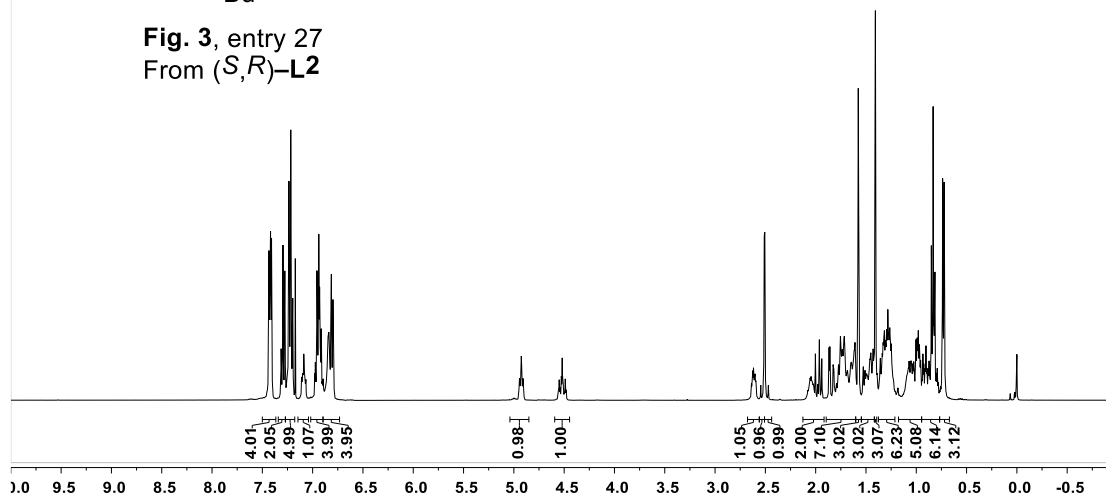


Fig. 3, entry 27
From $(S,R)\text{-L2}$



hh5-305b0507/1/fid

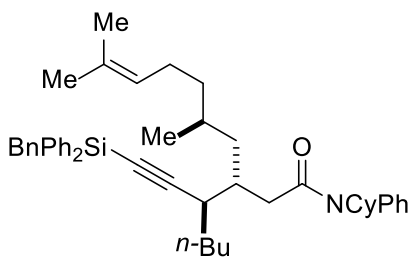
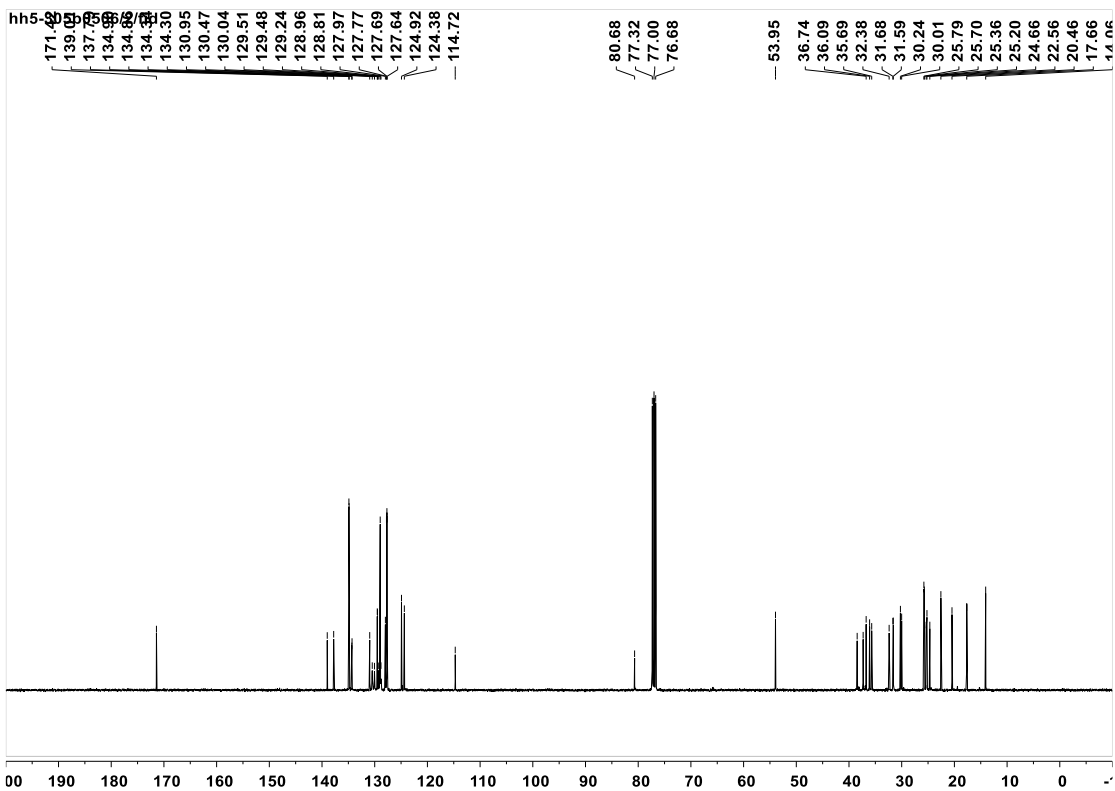
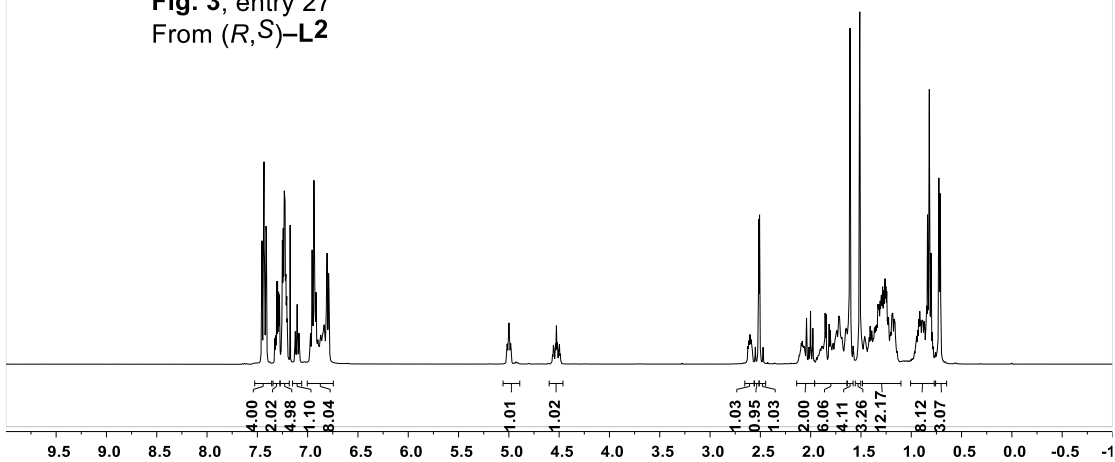


Fig. 3, entry 27
From (*R,S*)-L2



HH5-333/1/fid

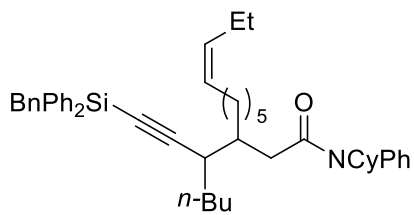
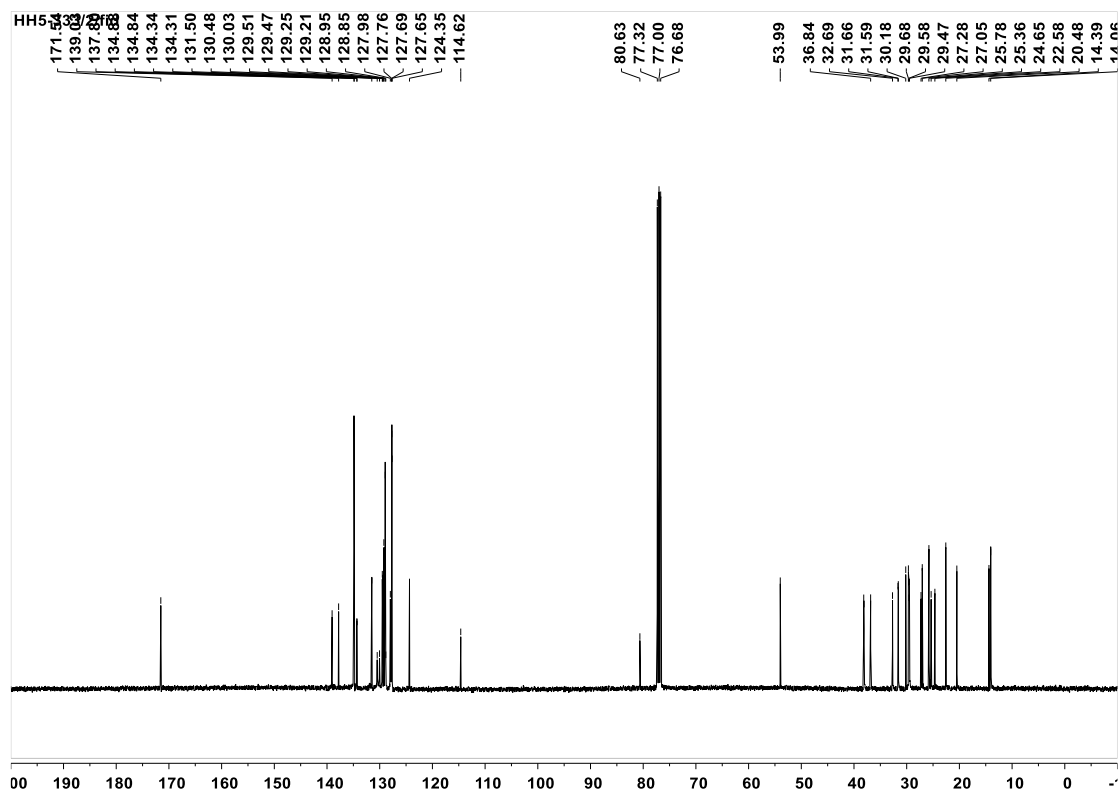
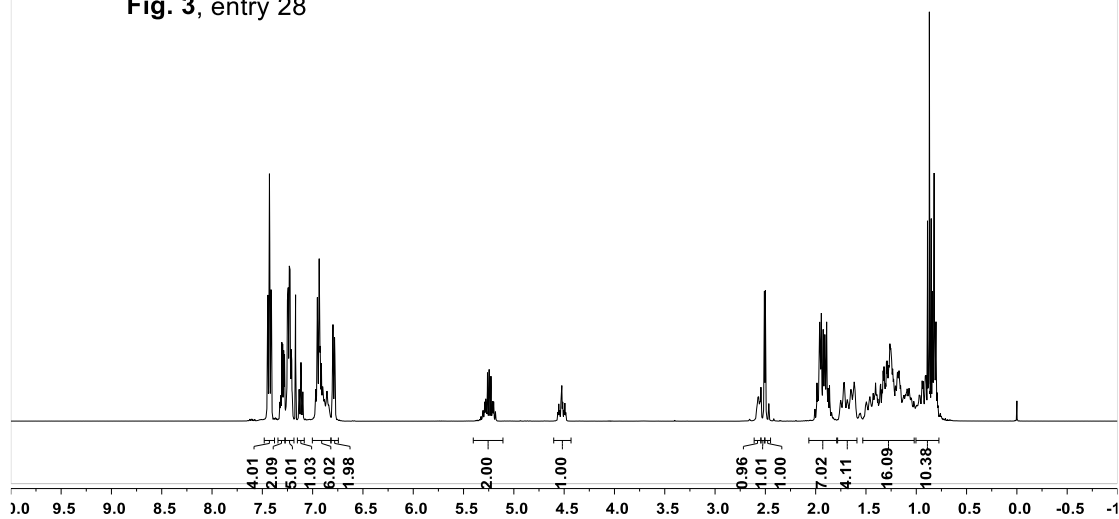


Fig. 3, entry 28



HH5-334/1/fid

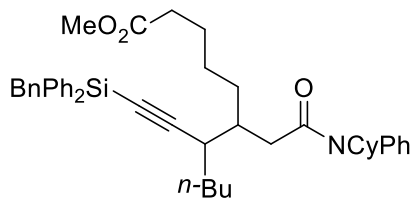
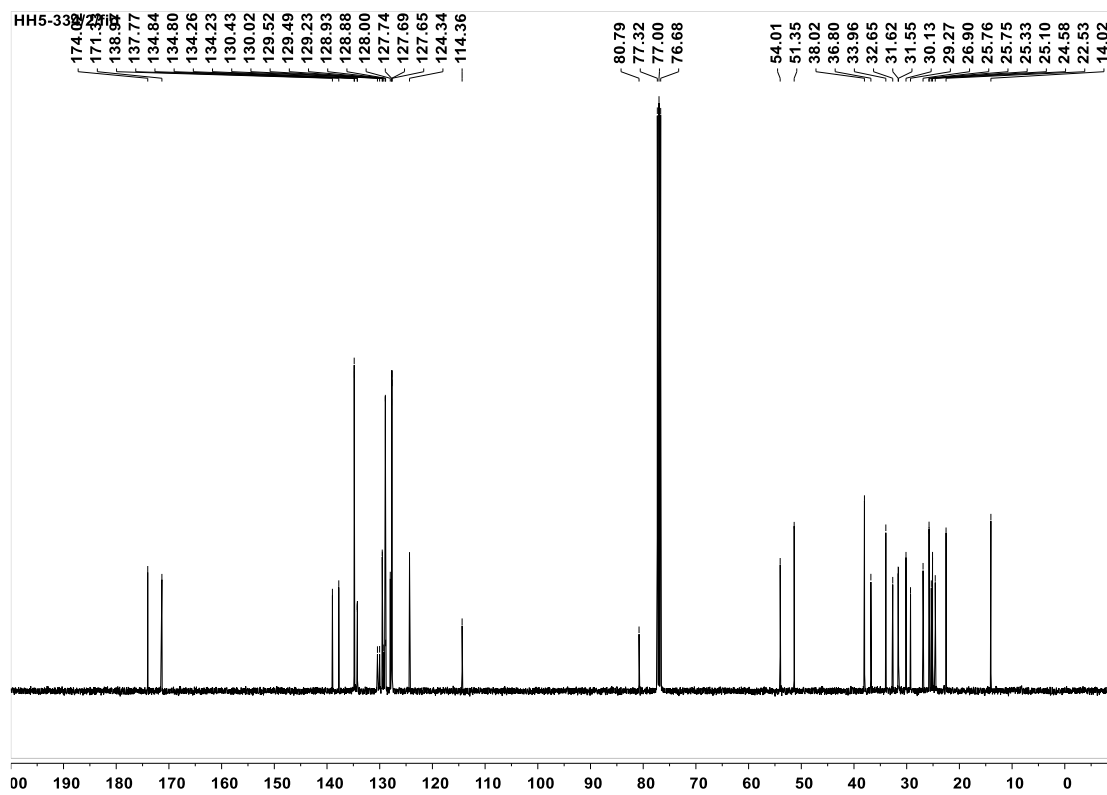
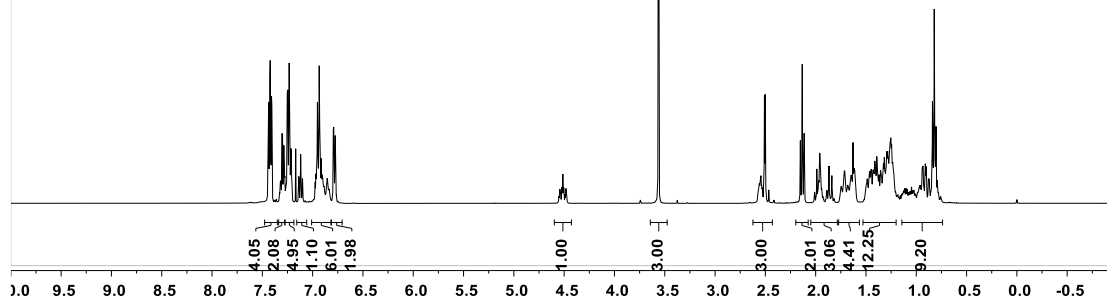


Fig. 3, entry 29



hh5-257a/1/fid

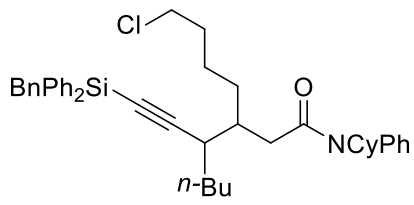
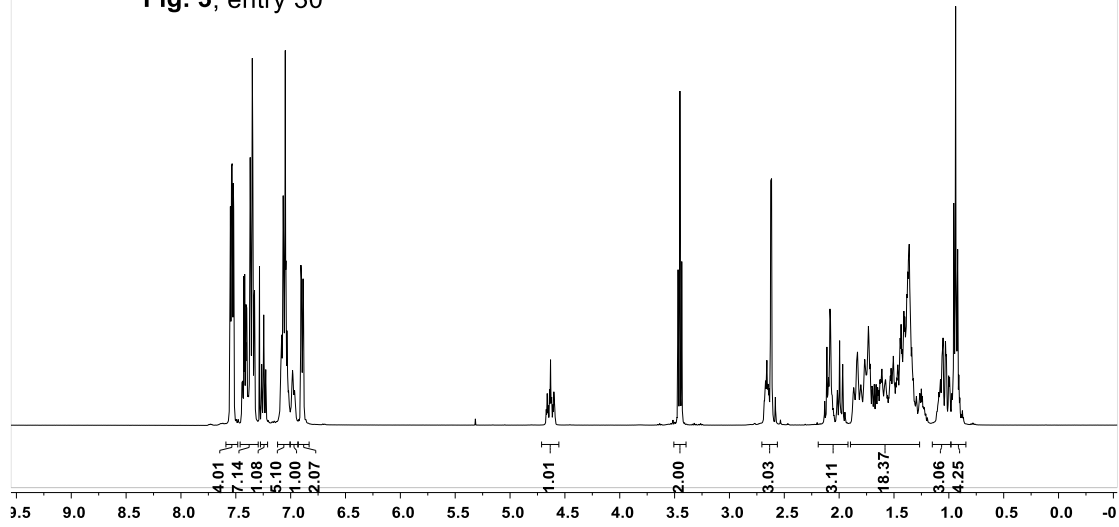
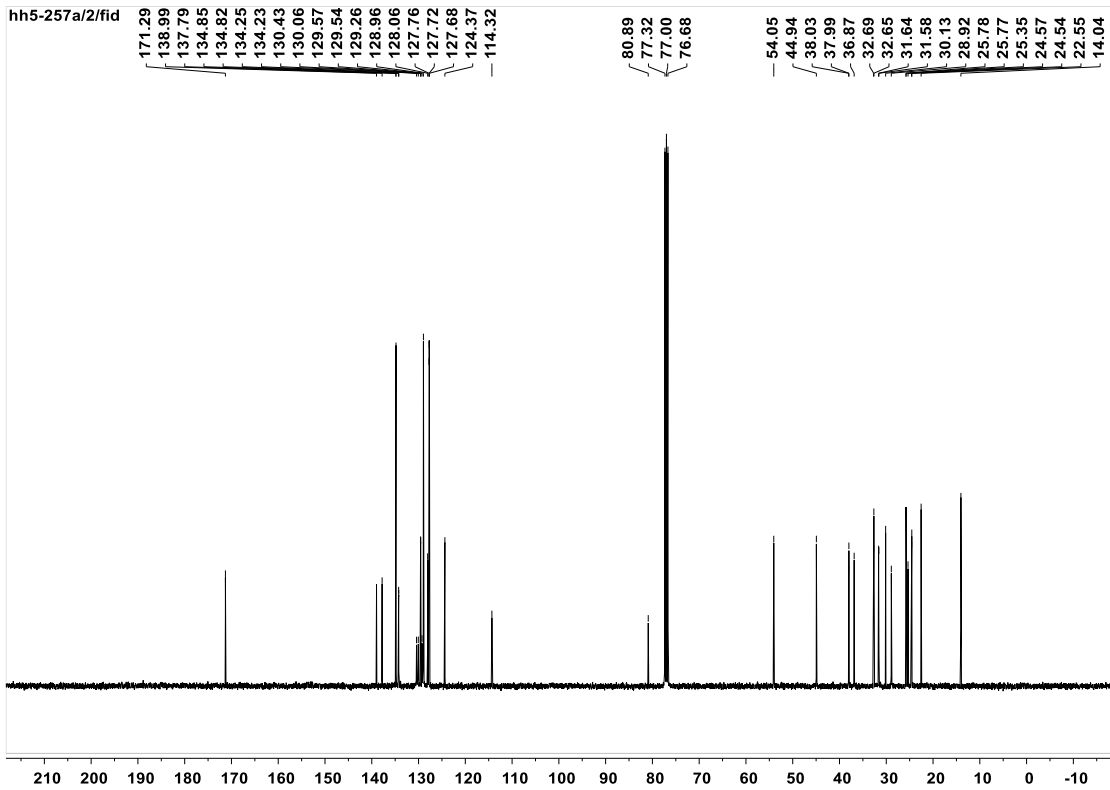
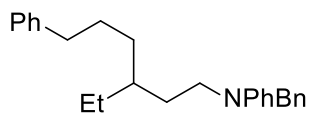


Fig. 3, entry 30

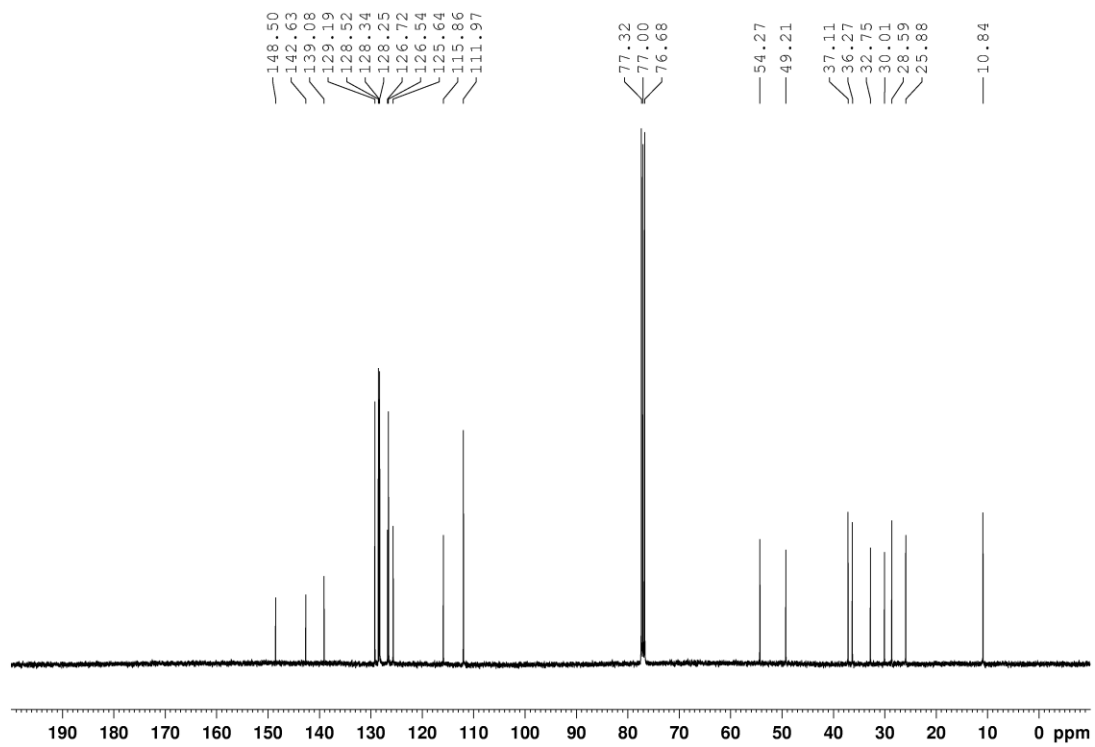
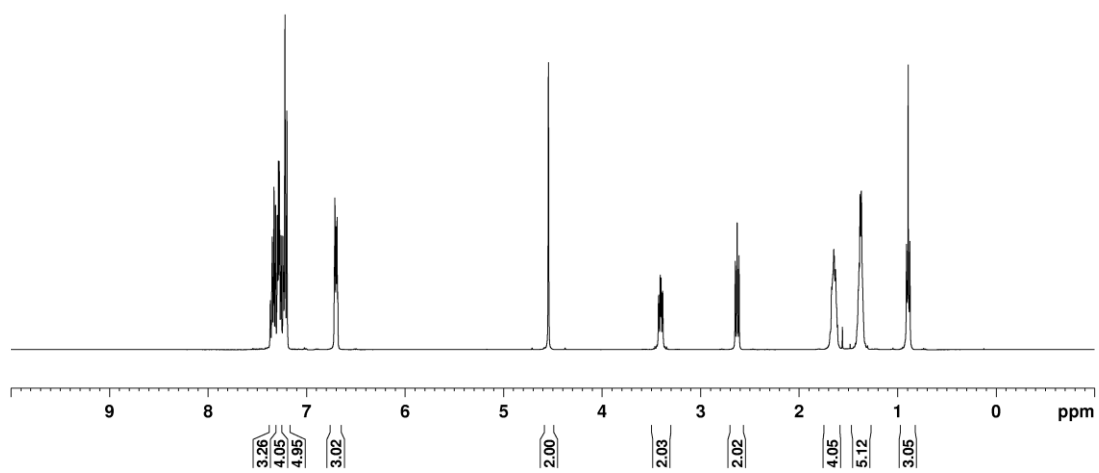


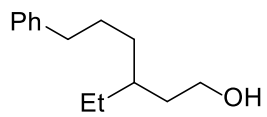
hh5-257a/2/fid



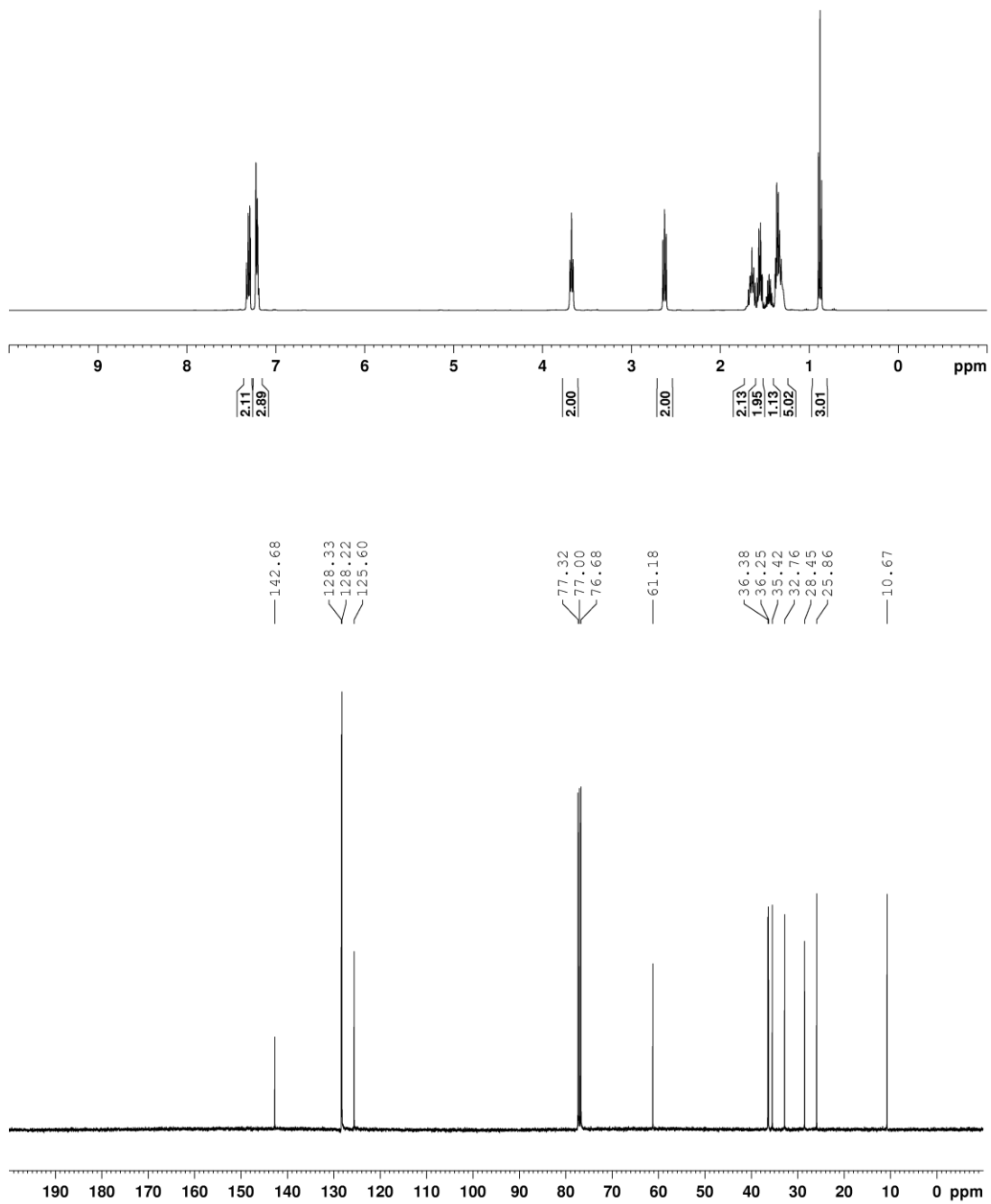


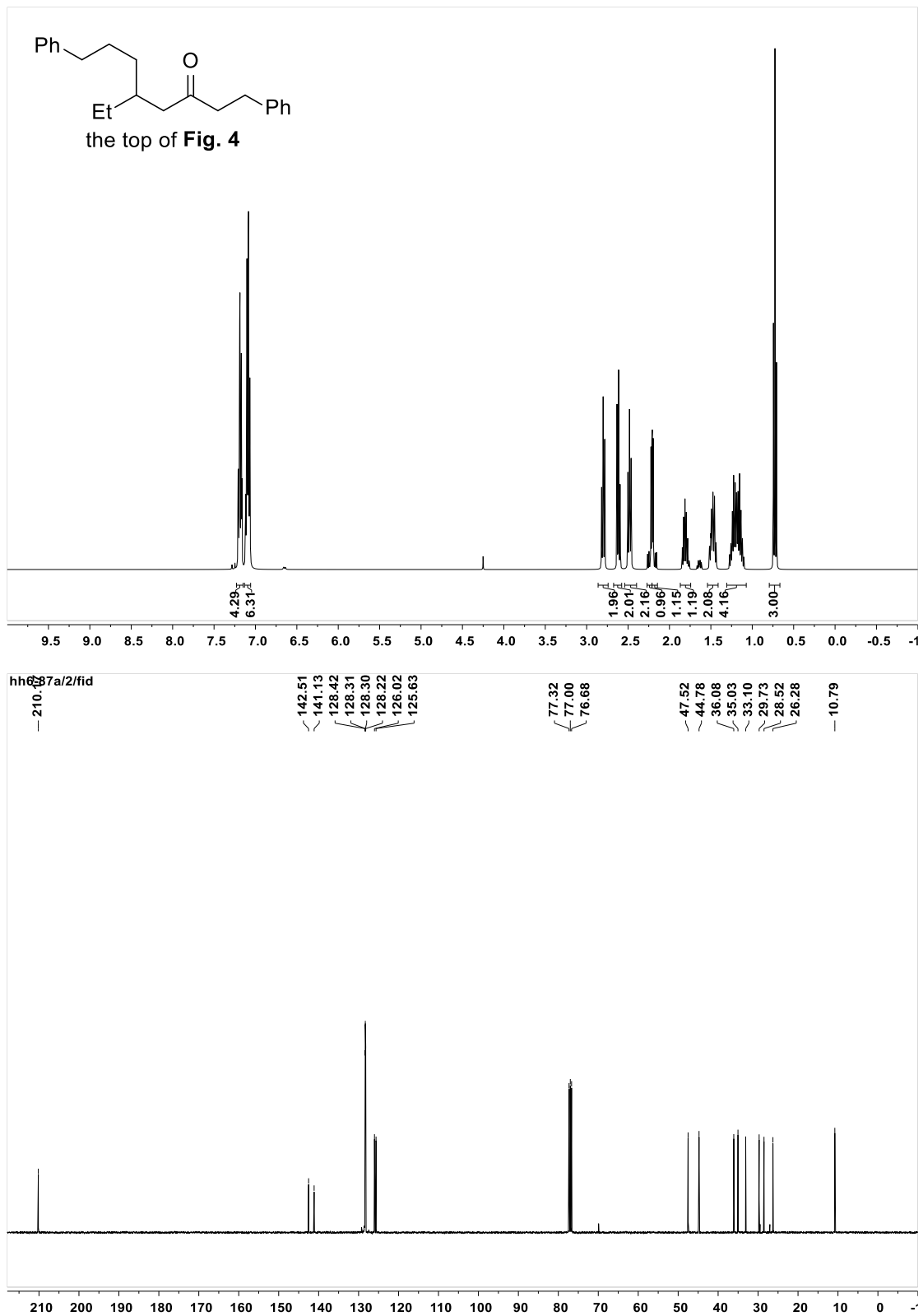
the top of Fig. 4





the top of **Fig. 4**





hh6-33/PROTON01.fid/fid

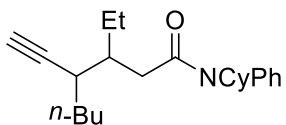
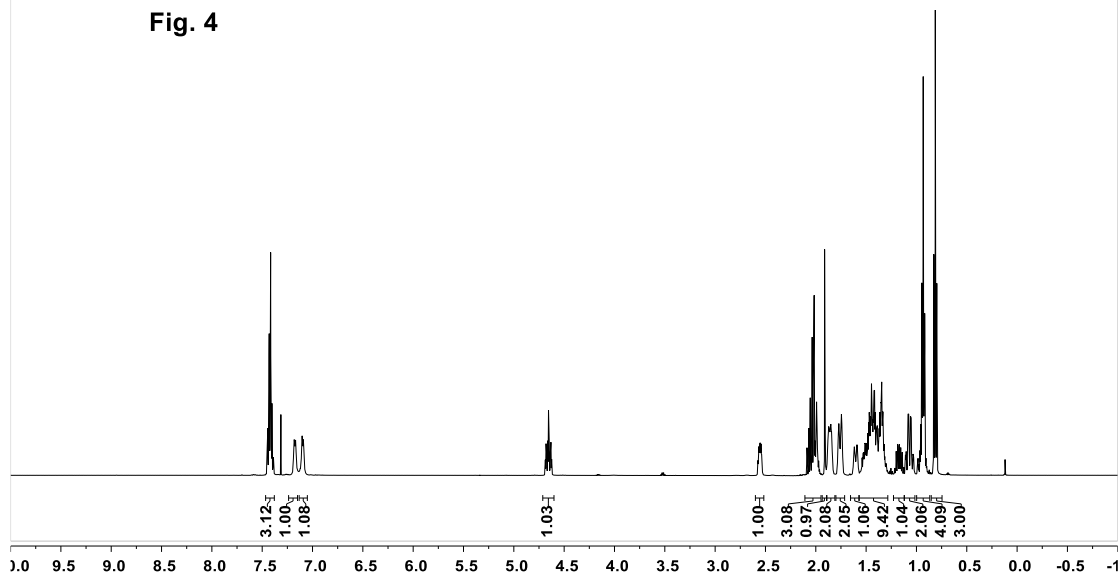
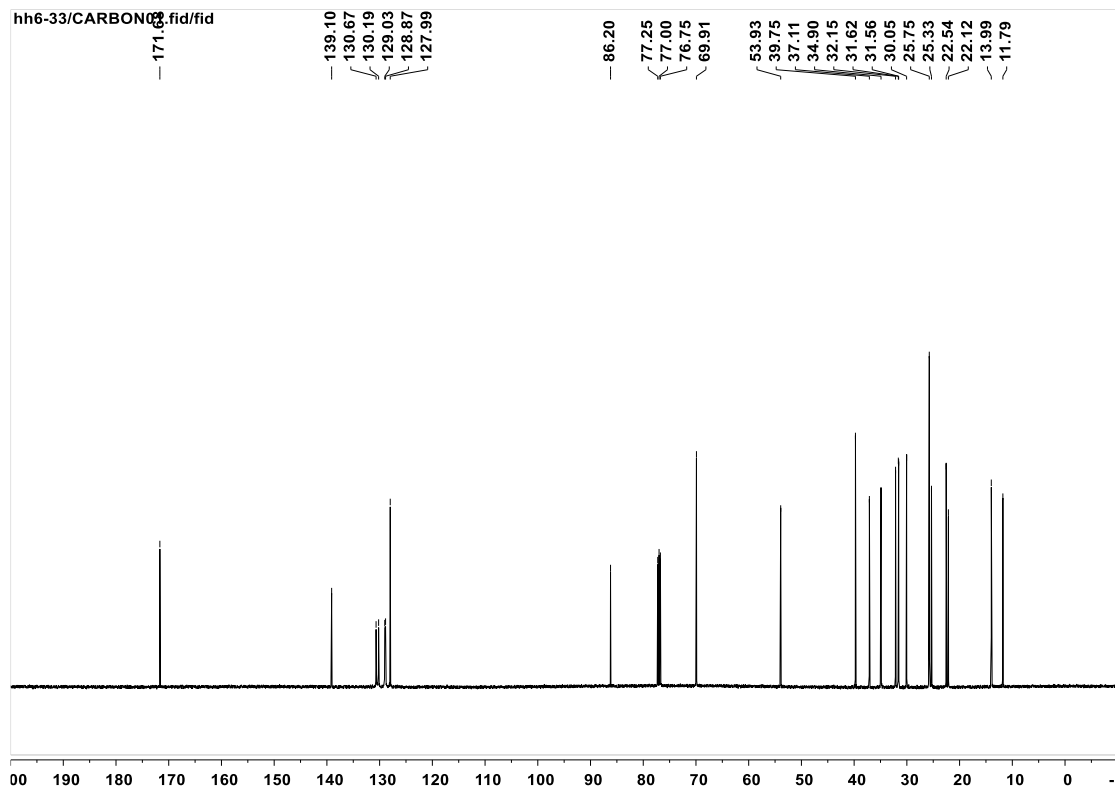


Fig. 4



hh6-33/CARBON01.fid/fid



HH6-37A/1/fid

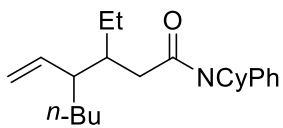
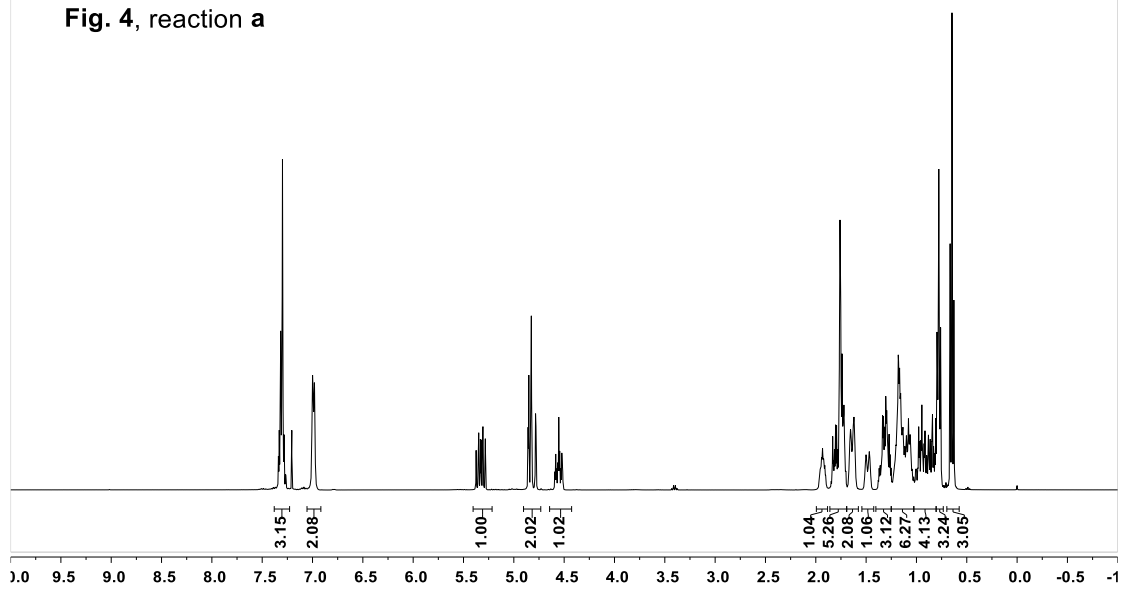
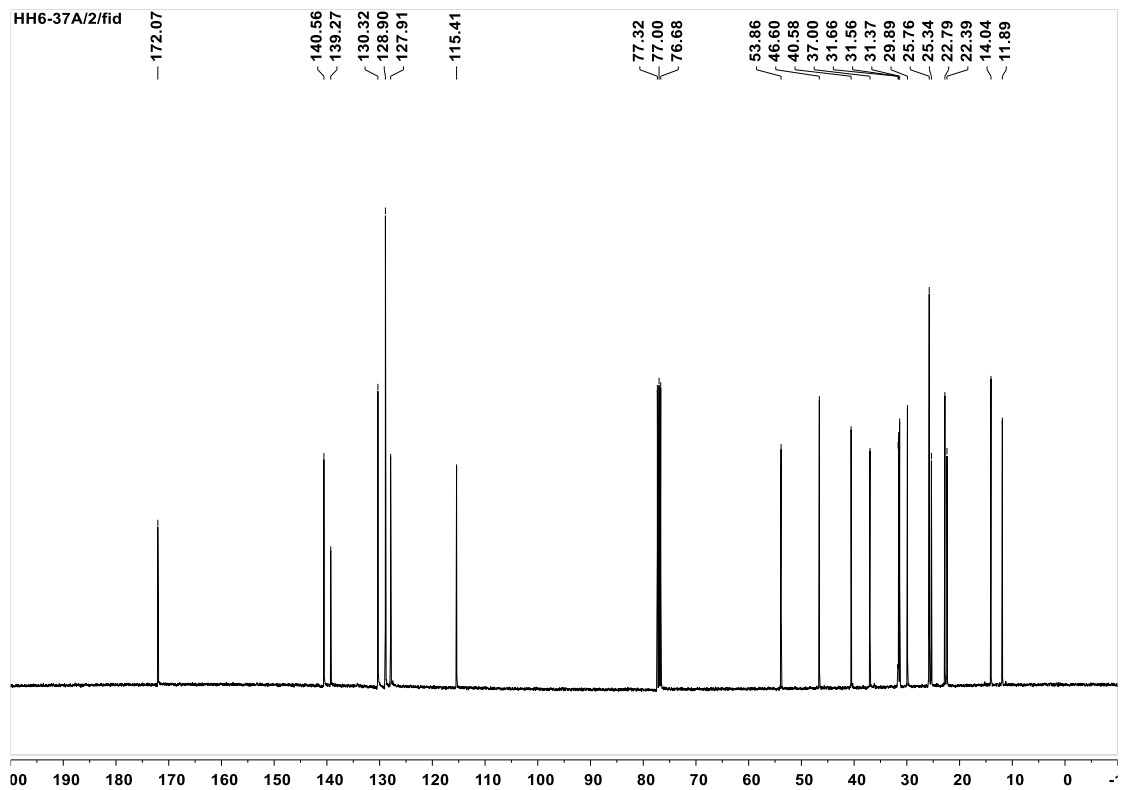


Fig. 4, reaction a



HH6-37A/2/fid



HH6-36A/1/fid

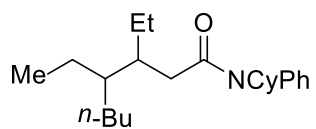
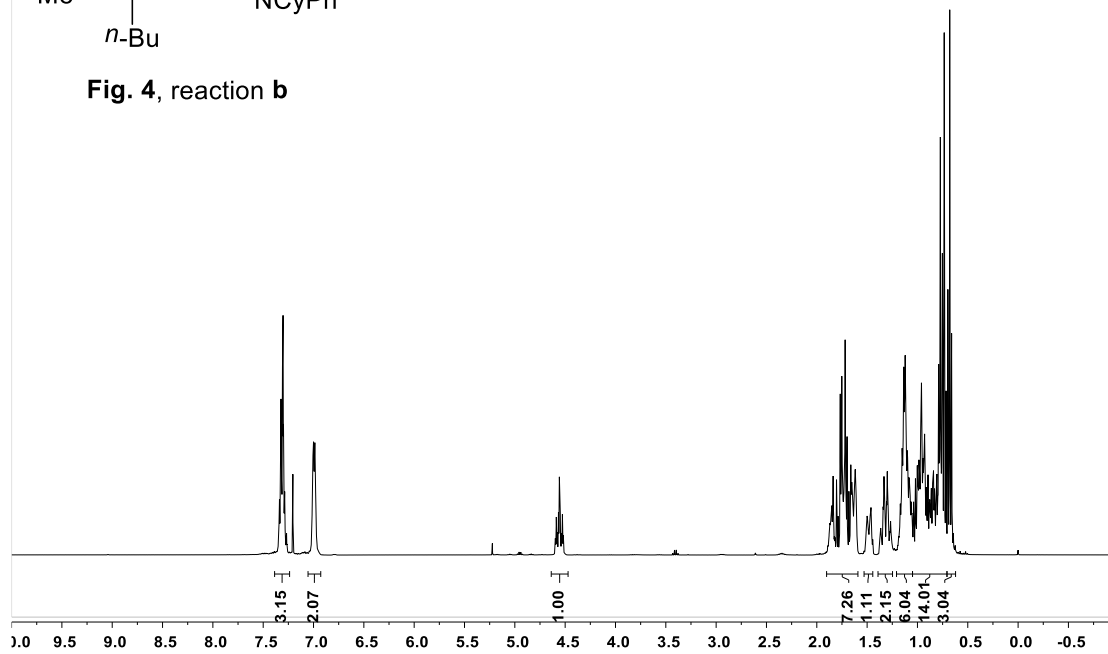
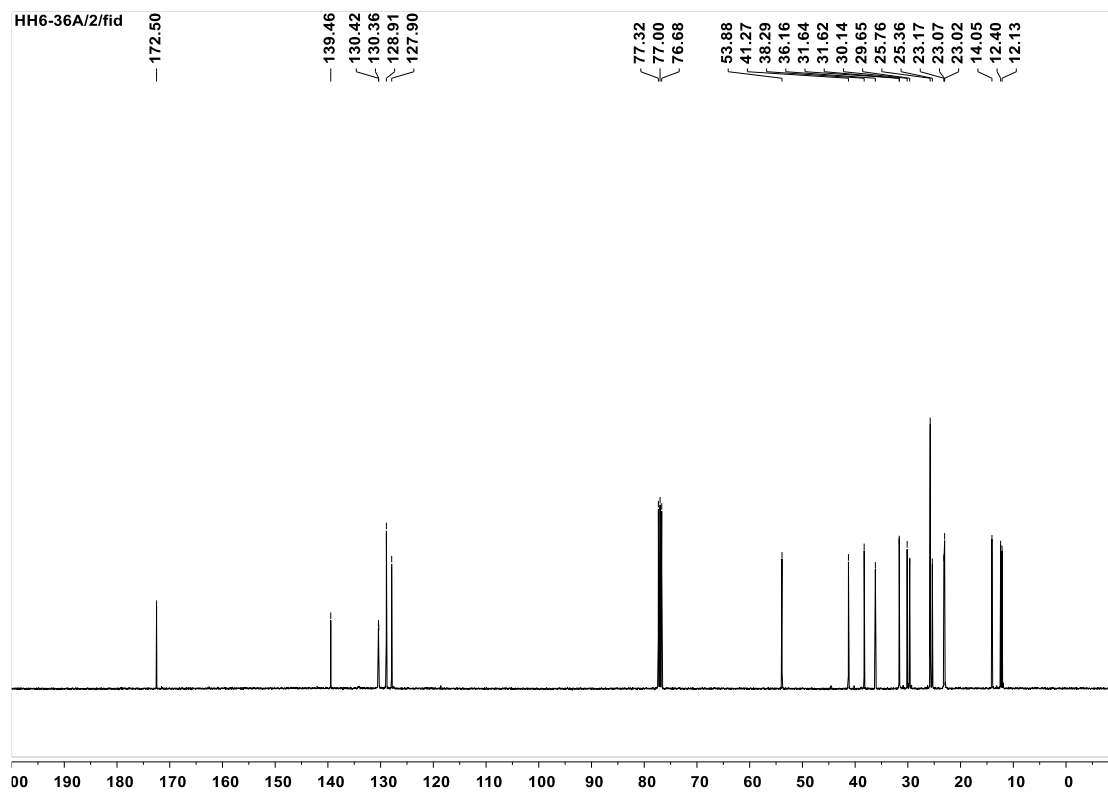


Fig. 4, reaction b



HH6-36A/2/fid



hh6-62a-tm/1/fid

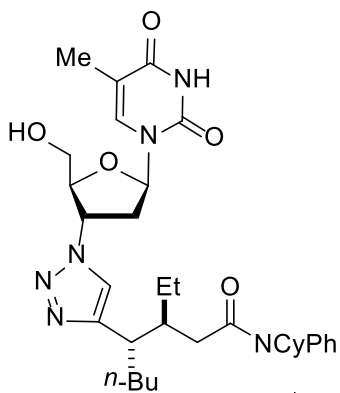
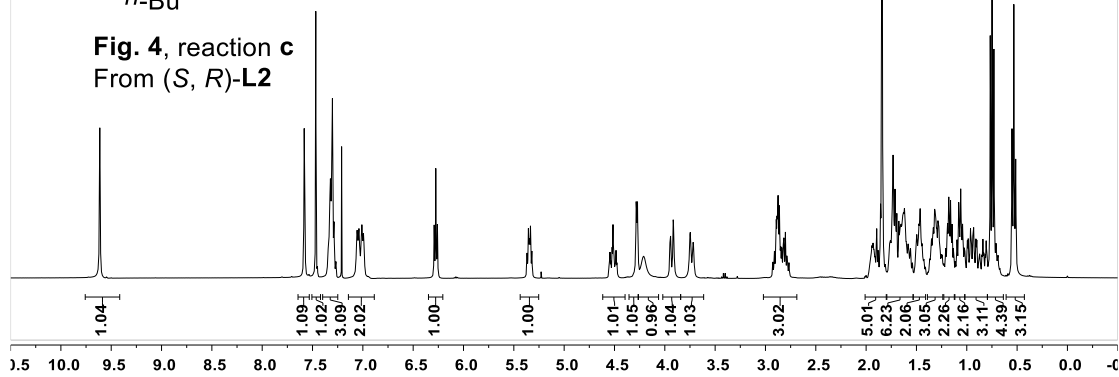
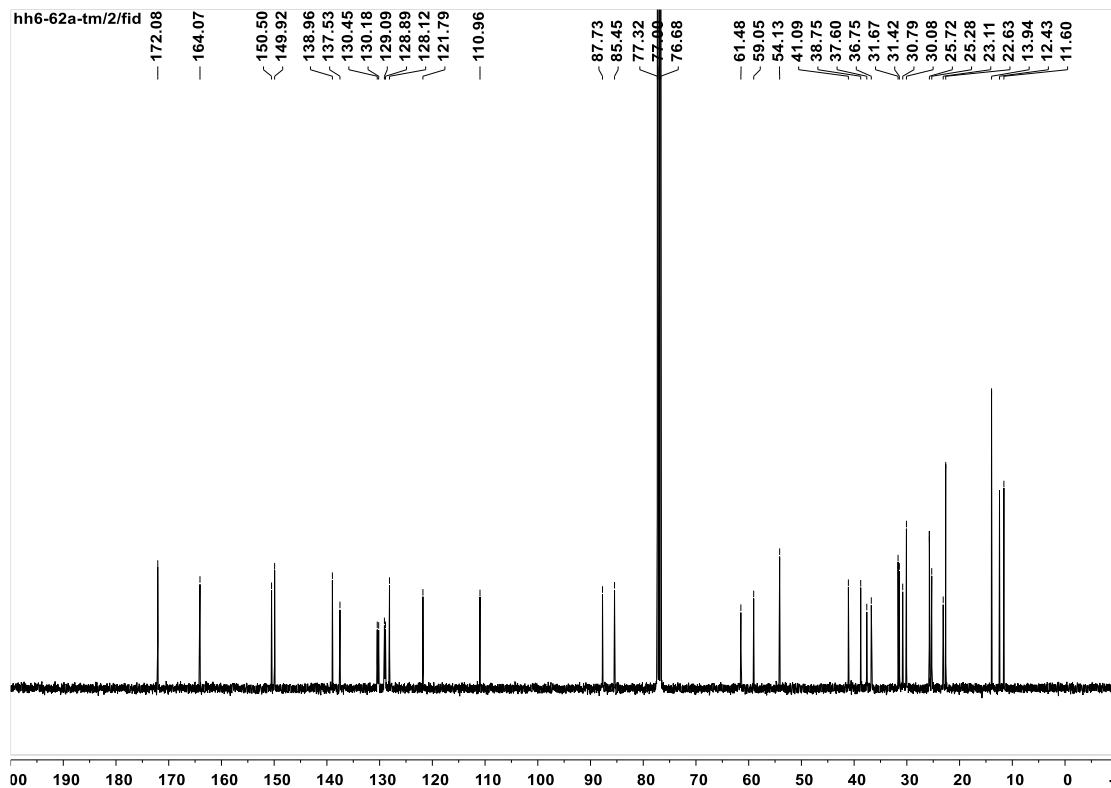
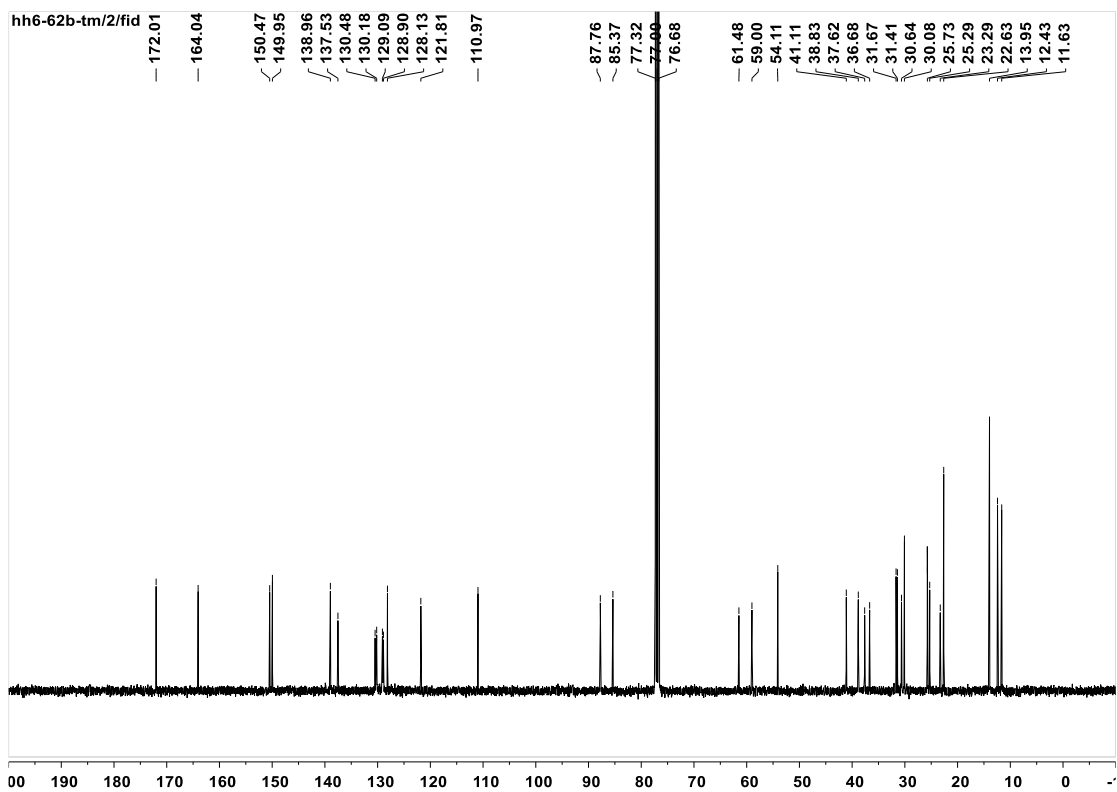
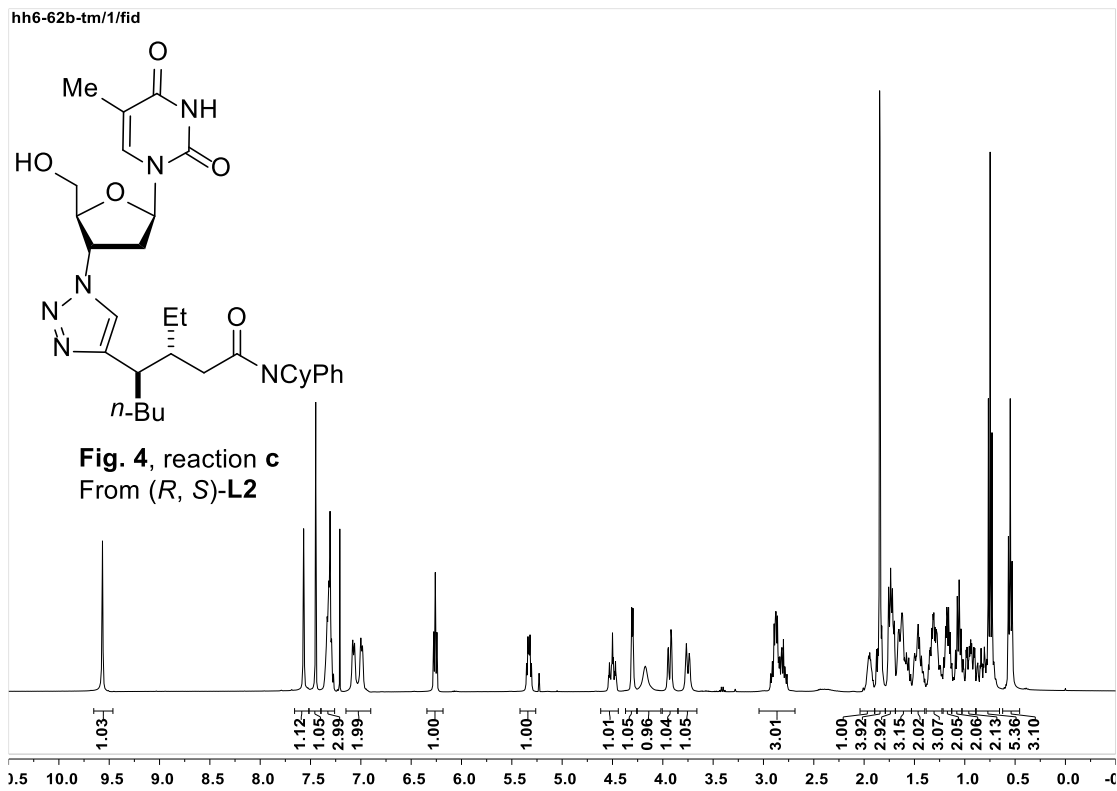


Fig. 4, reaction c
From (S, R)-L2

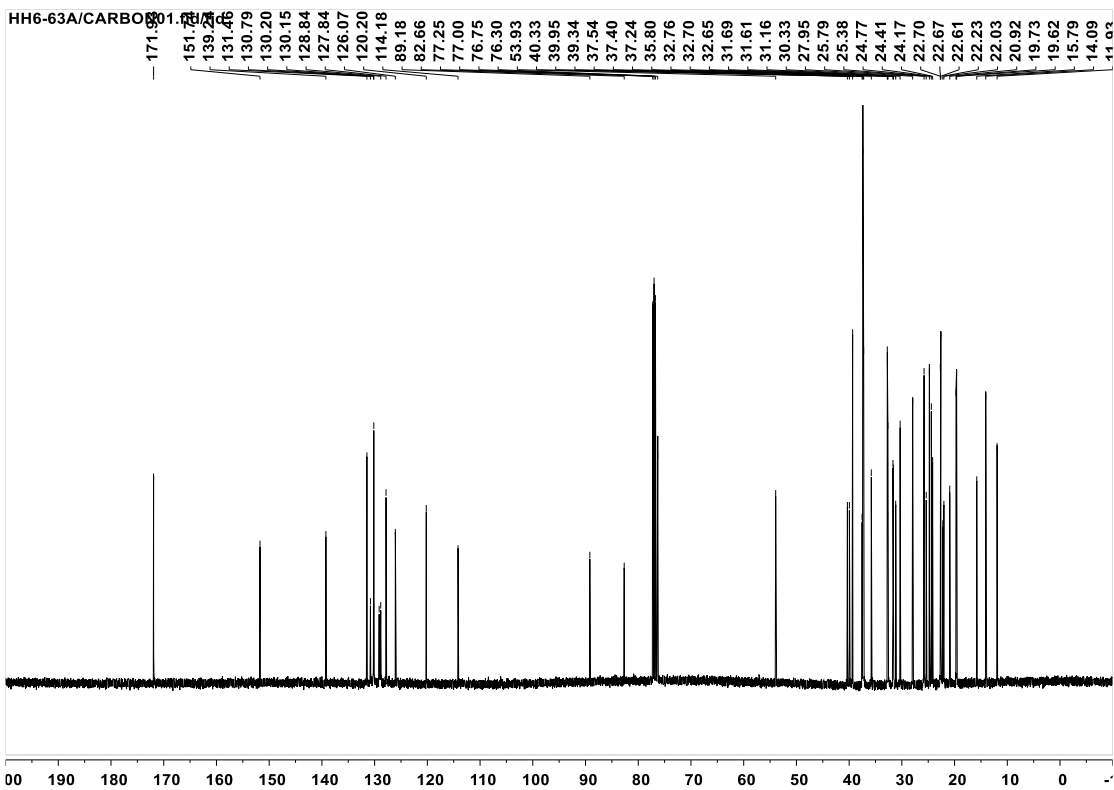
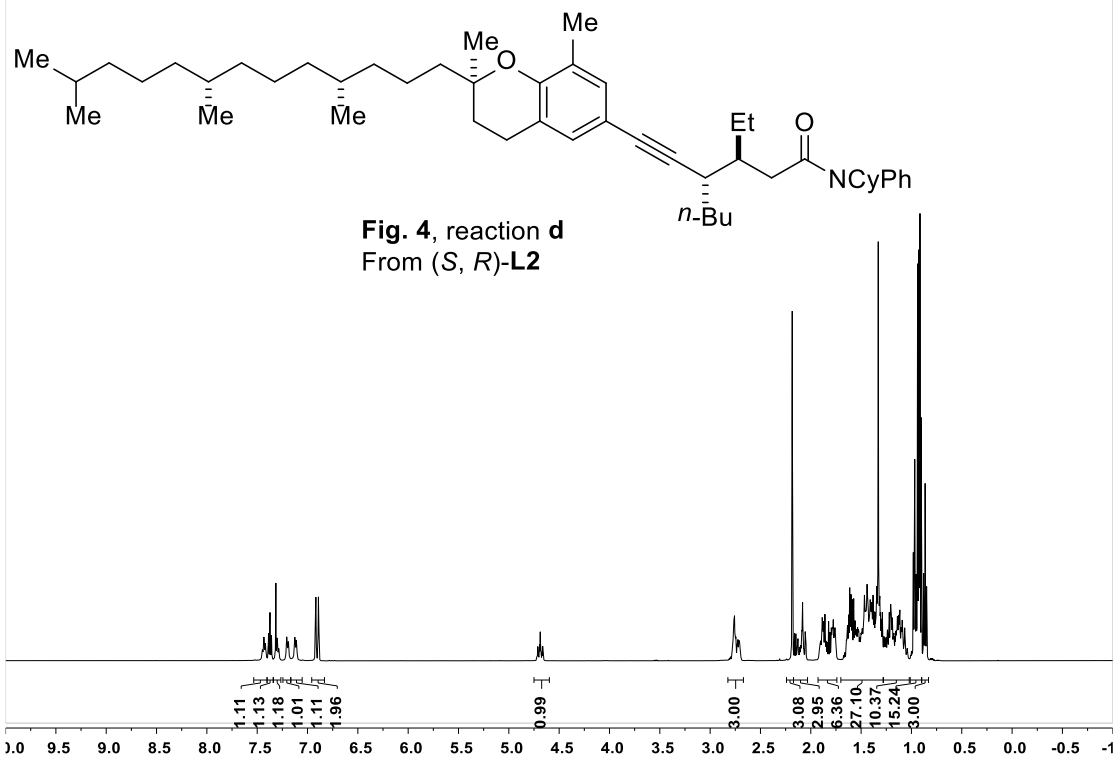


hh6-62a-tm/2/fid

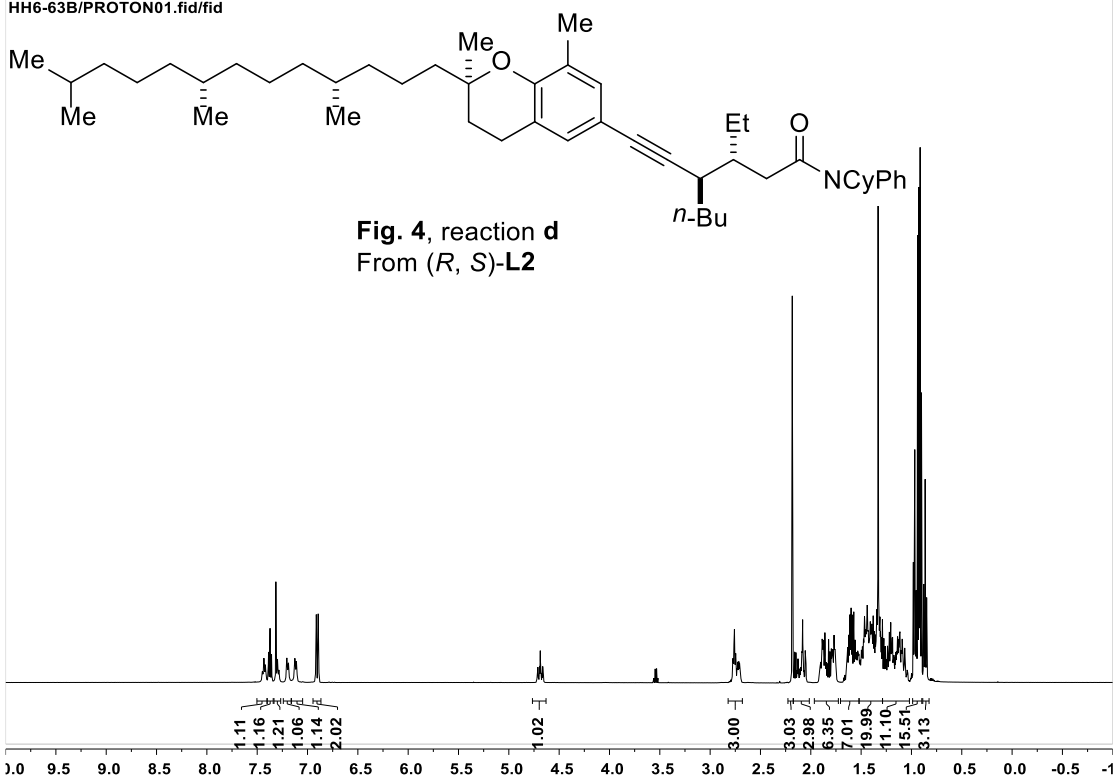




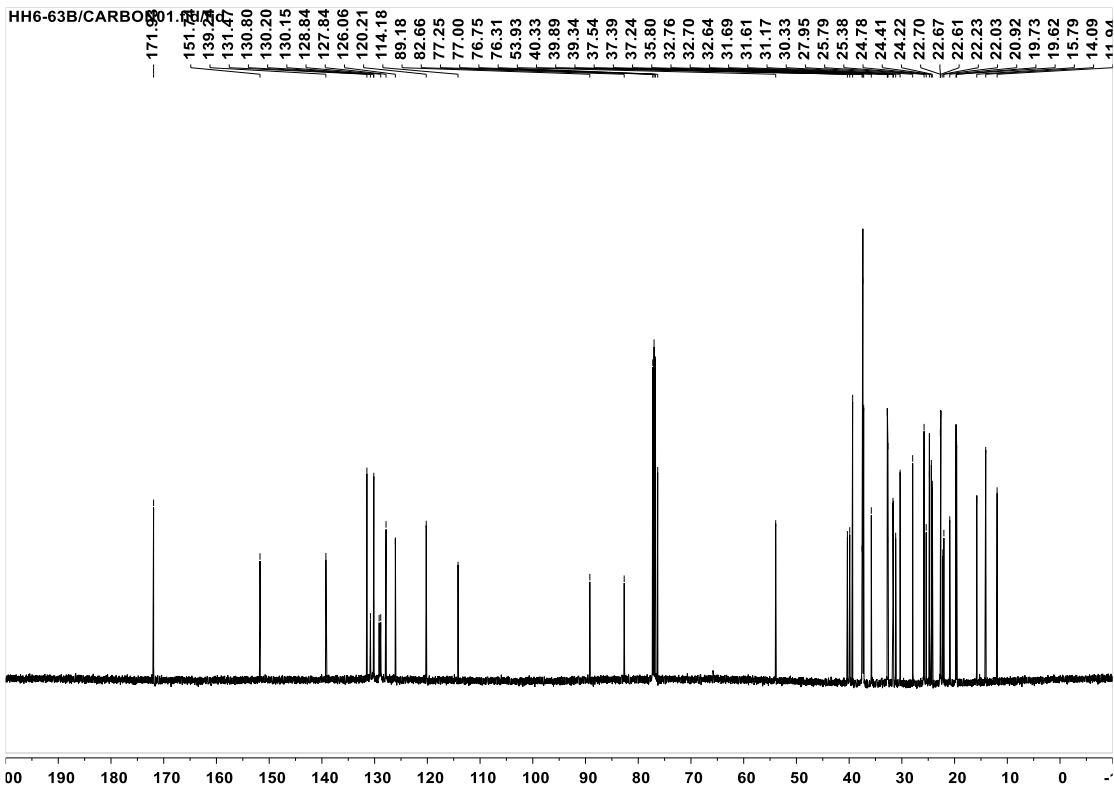
HH6-63A/PROTON01.fid/fid



HH6-63B/PROTON01.fid/fid



HH6-63B/CARBON01.fid



hh6-54a/1/fid

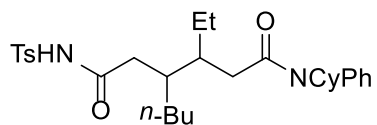
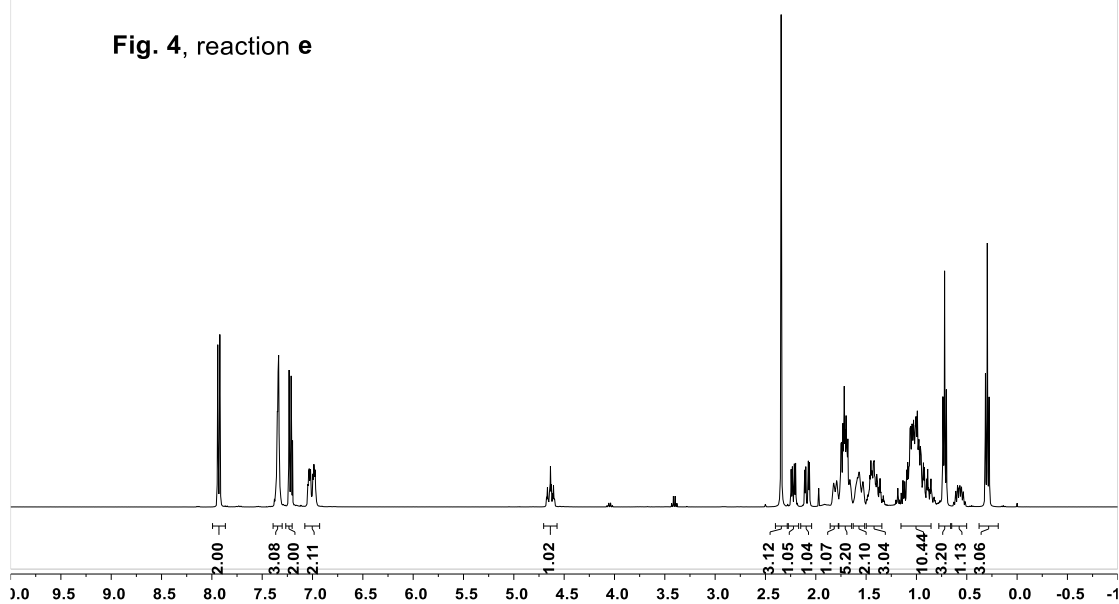
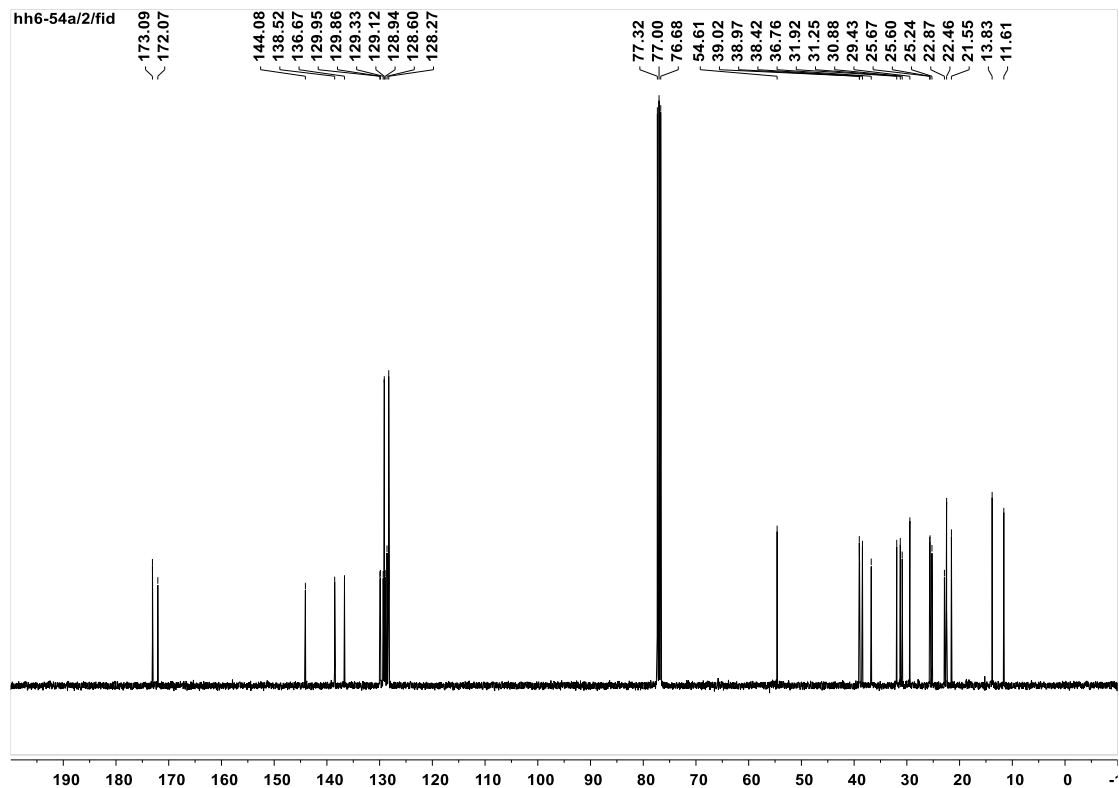


Fig. 4, reaction e



hh6-54a/2/fid



HH6-72A2/1/fid

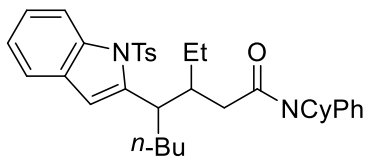
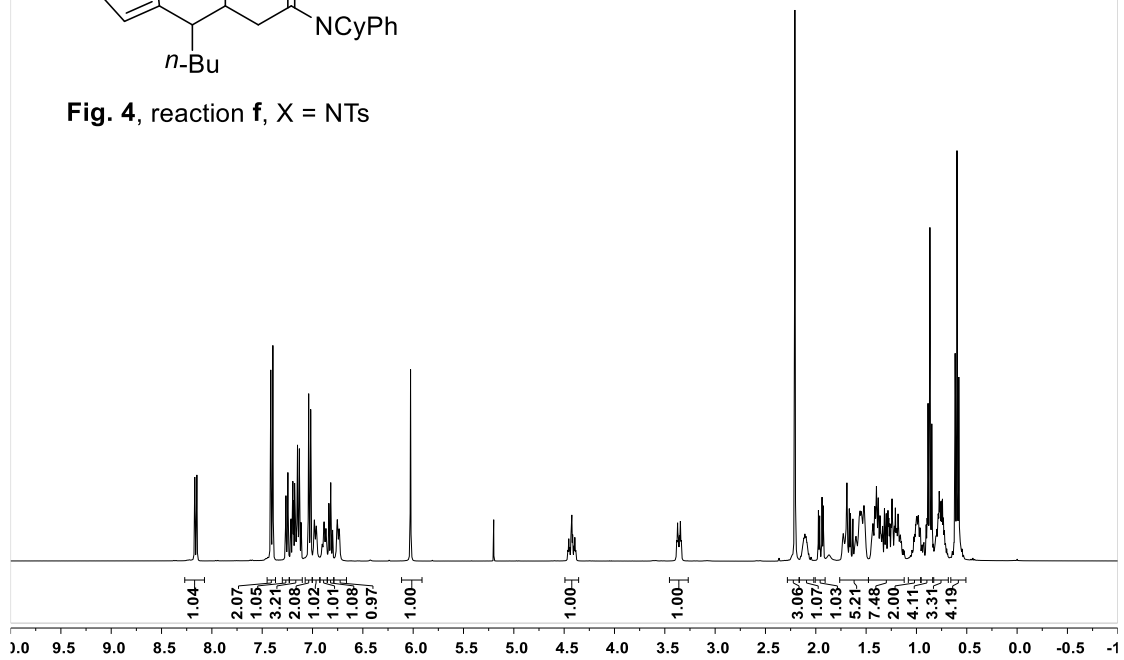
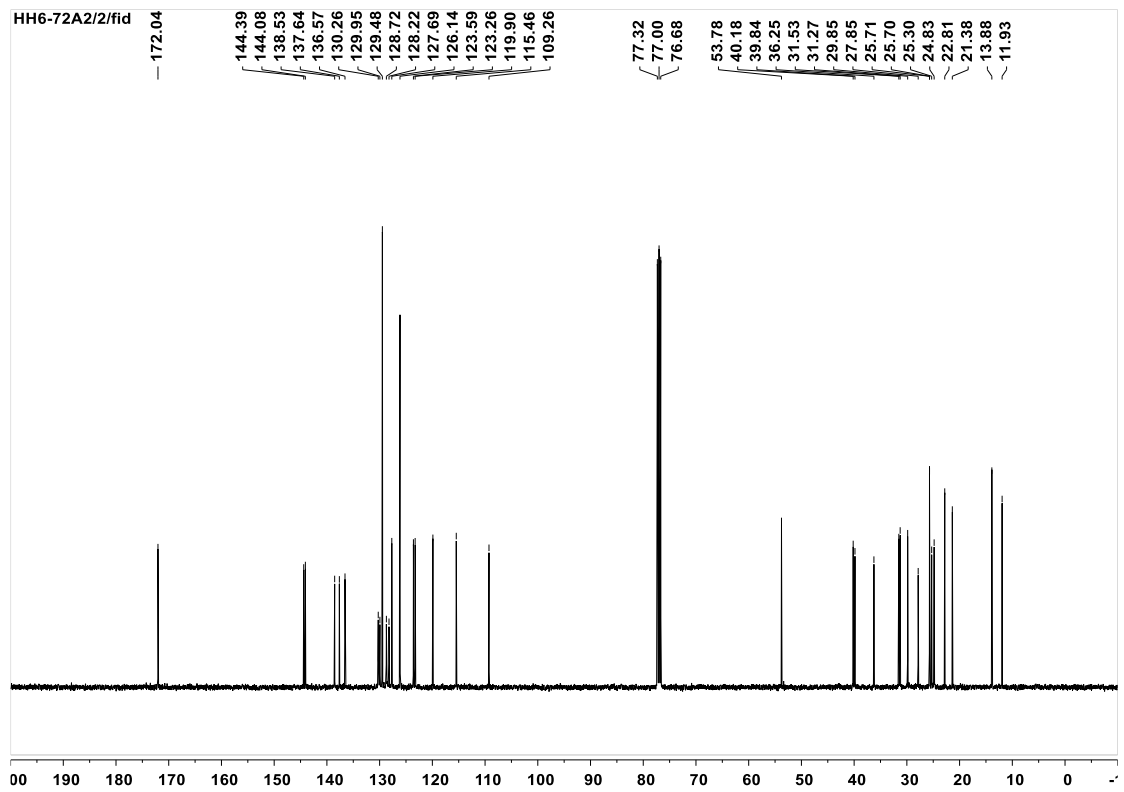


Fig. 4, reaction f, X = NTs



HH6-72A2/2/fid



hh6-73a/1/fid

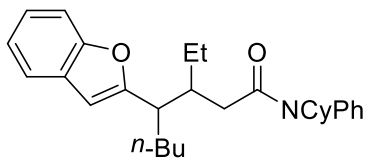
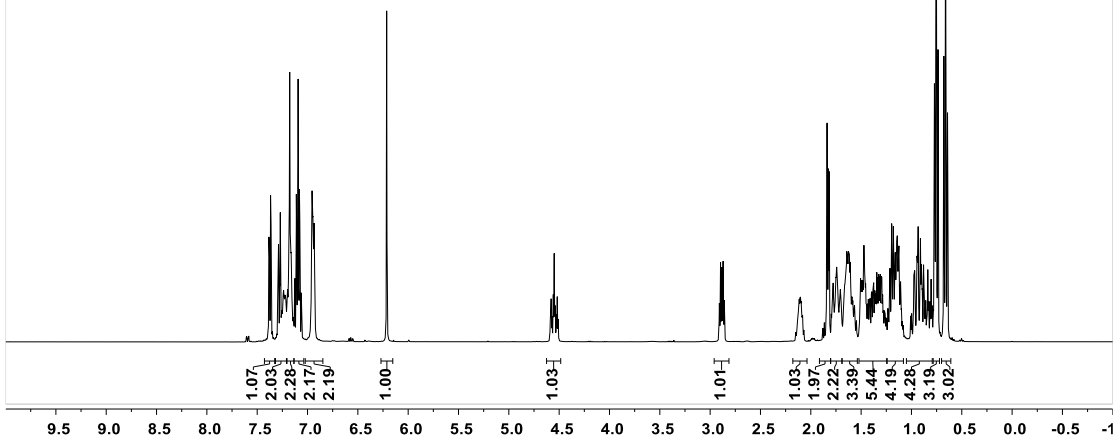
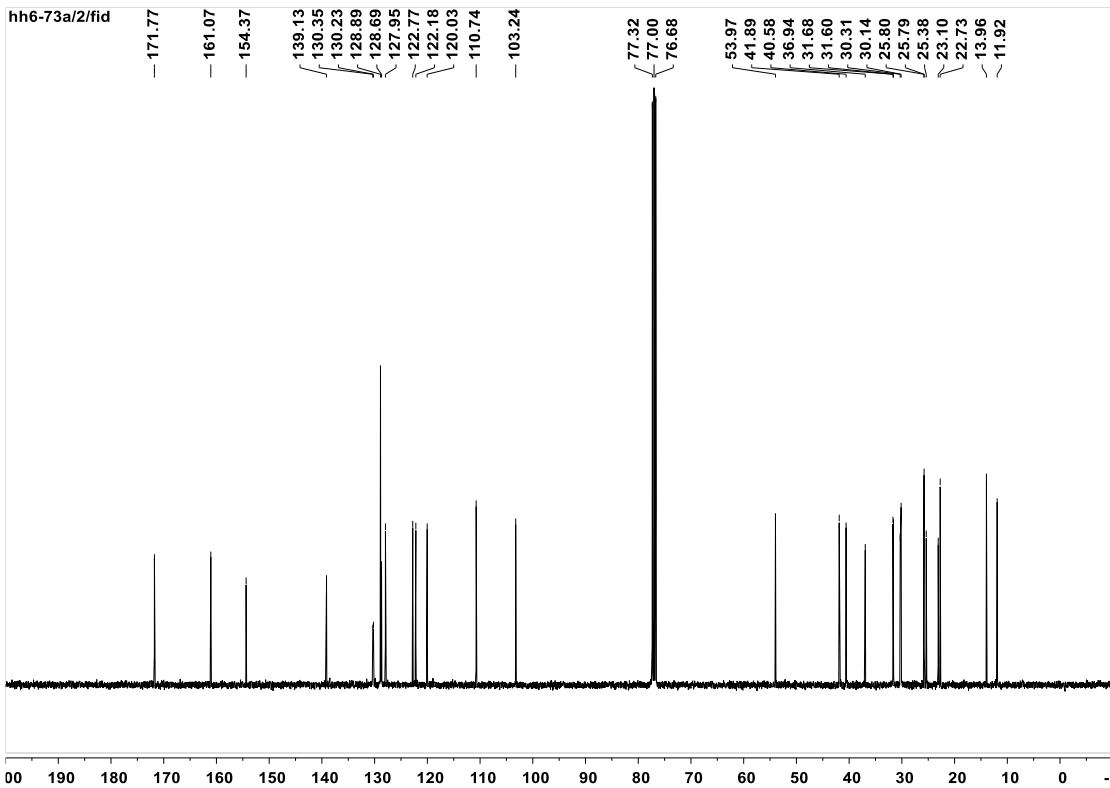


Fig. 4, reaction f, X = O



hh6-73a/2/fid



Stereoselectivity Analysis

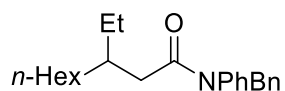
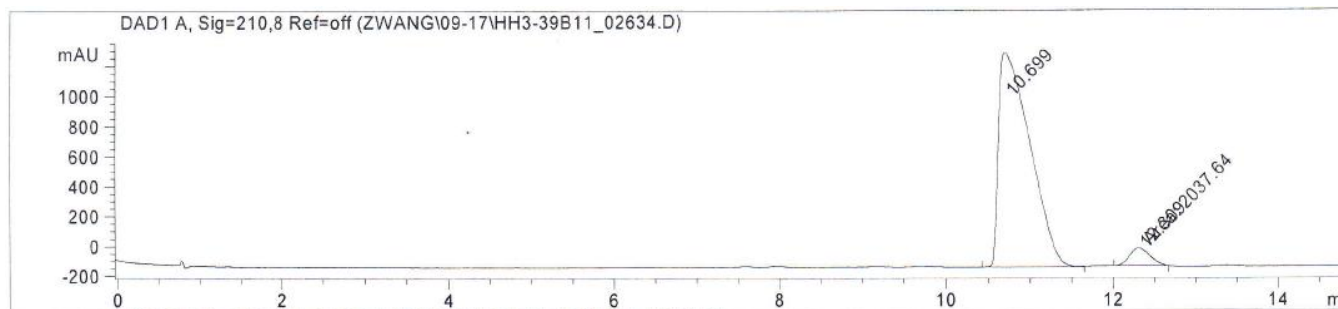
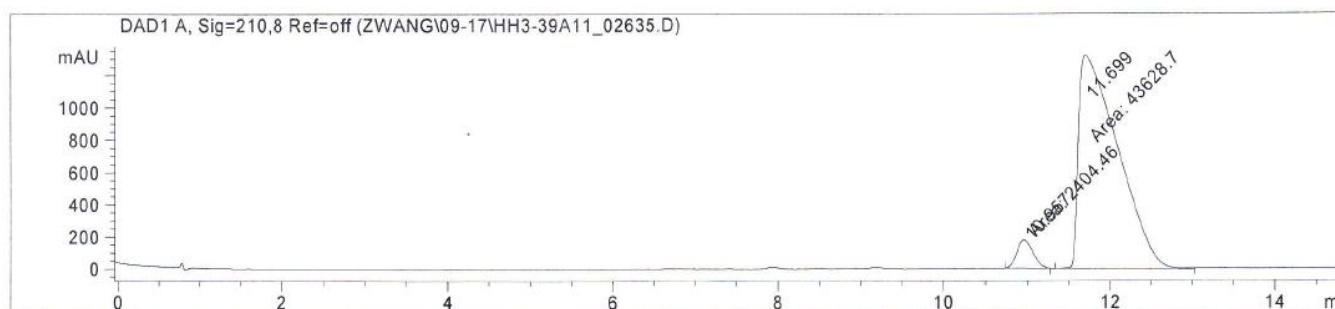


Fig. 2, entry 1

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.699	BB	0.4359	3.74793e4	1420.22412	94.8436
2	12.309	MM	0.2890	2037.64062	117.52613	5.1564



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.957	MM	0.2273	2404.46240	176.29755	5.2233
2	11.699	MM	0.5524	4.36287e4	1316.26416	94.7767

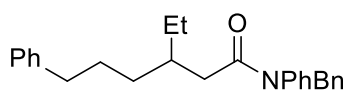
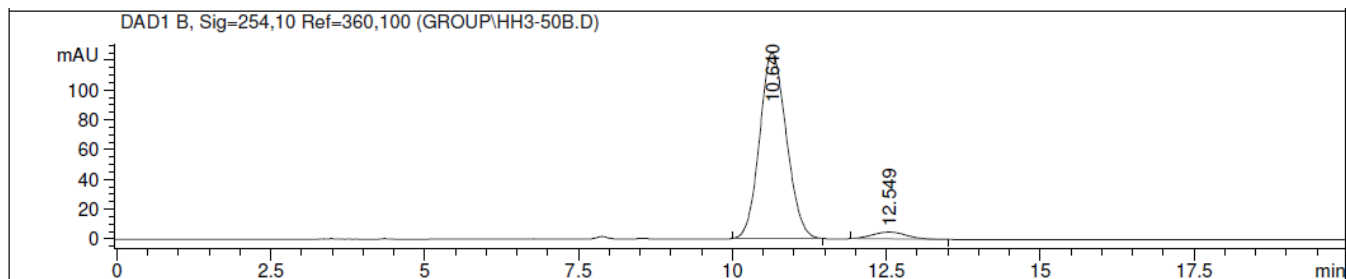
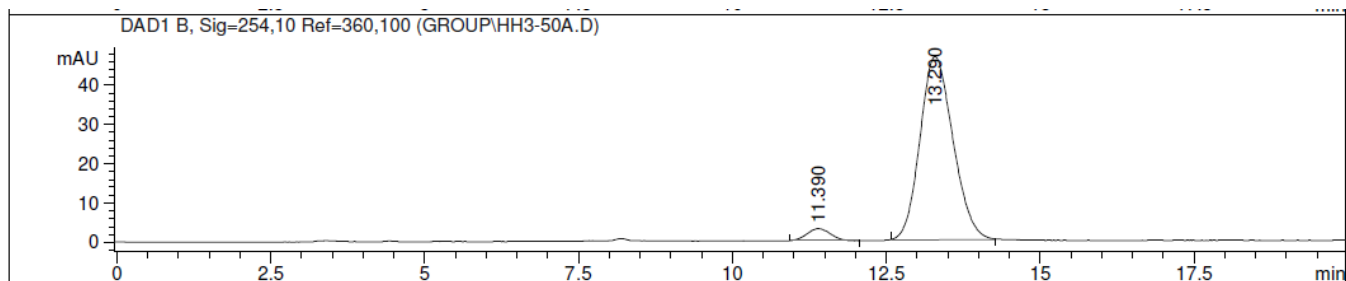


Fig. 2, entry 2
(R)-L1: 91% ee; *(S)*-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.640	BB	0.4704	3791.71973	124.83706	95.5426
2	12.549	BP	0.4563	176.89774	4.64485	4.4574



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.390	BP	0.3350	80.62871	3.04413	4.4228
2	13.290	BB	0.5735	1742.37610	46.67889	95.5772

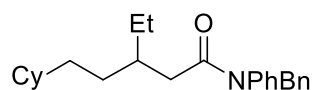
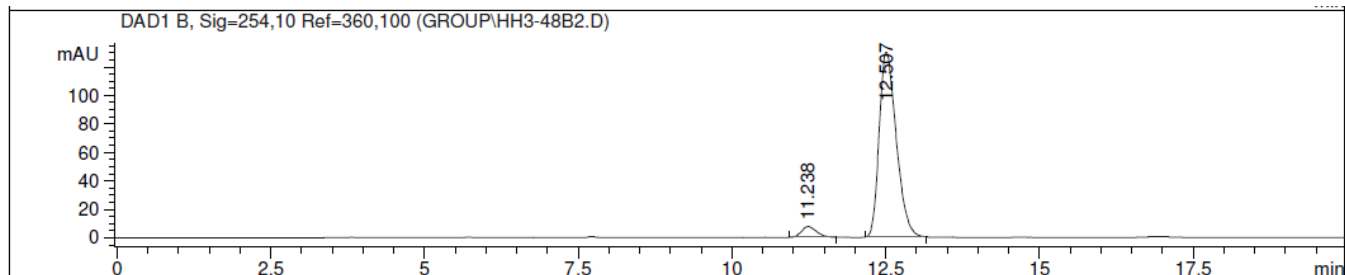
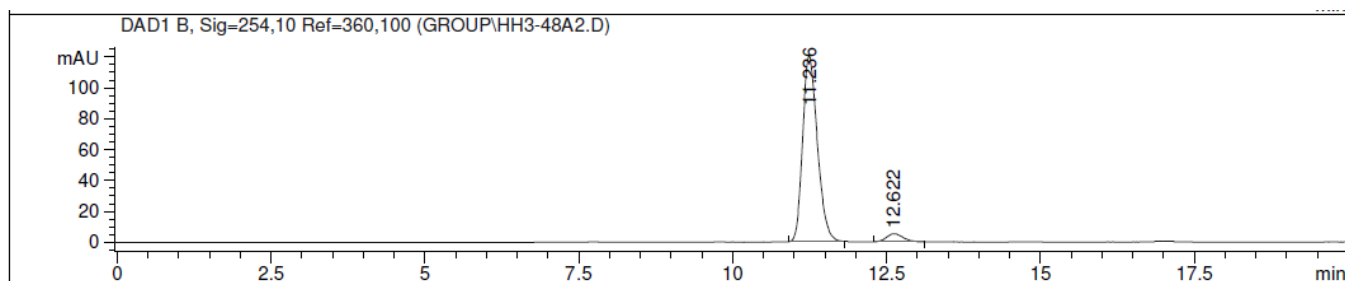


Fig. 2, entry 3

(R)-L1: 90% ee; *(S)*-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.238	BB	0.2613	130.16434	7.54226	4.9078
2	12.507	BB	0.3000	2522.05542	130.17139	95.0922



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.236	BB	0.2590	2007.37134	120.09218	95.2919
2	12.622	BB	0.2920	99.17878	5.25977	4.7081

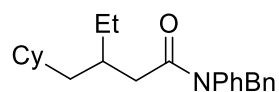
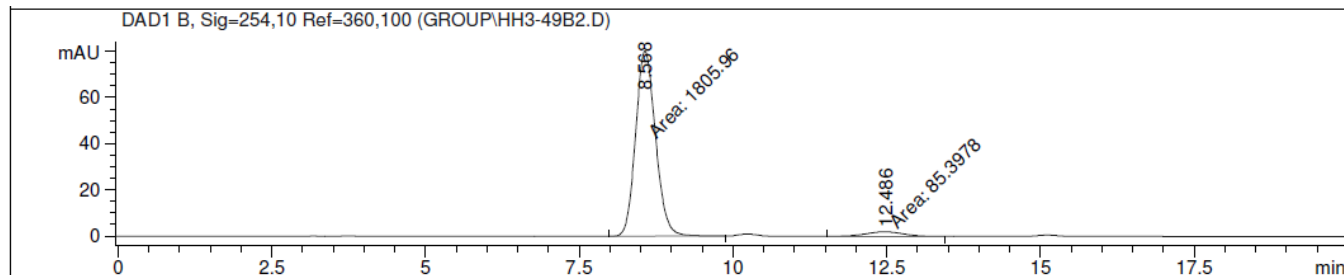
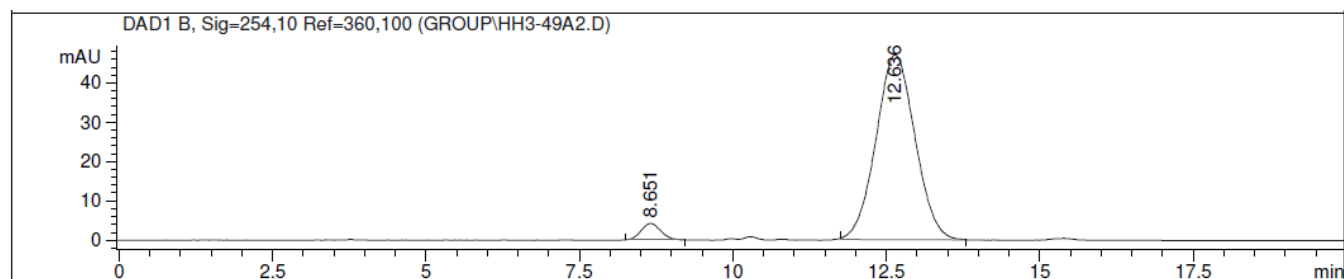


Fig. 2, entry 4

(R)-L1: 91% ee; (S)-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.568	MM	0.3758	1805.9532	80.10318	95.4848
2	12.486	MM	0.7026	85.39780	2.02577	4.5152



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.651	BB	0.3217	93.03956	4.17993	4.2735
2	12.636	BB	0.6809	2084.06689	47.04074	95.7265

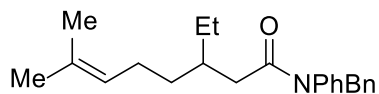
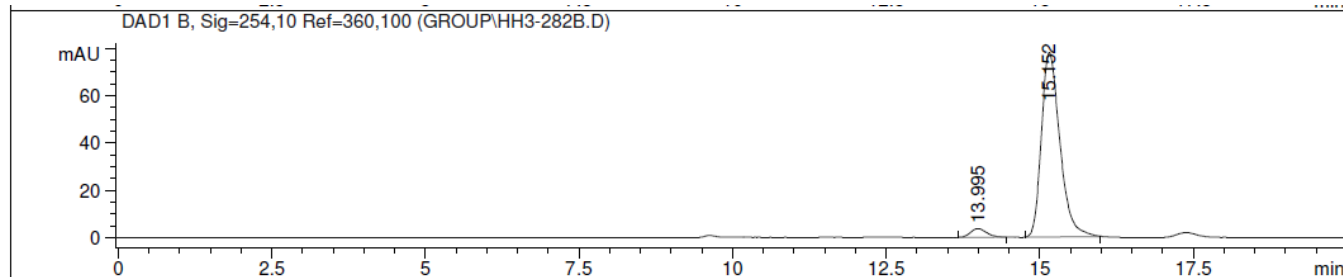
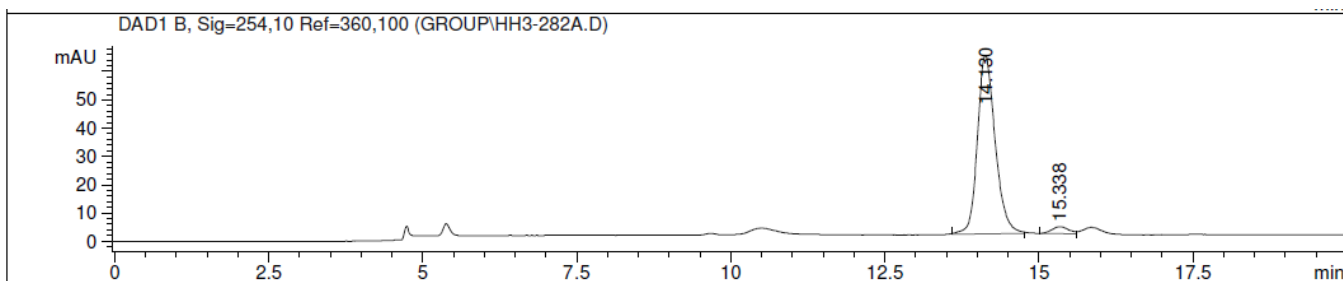


Fig. 2, entry 5

(*R*)-L1: 92% ee; (*S*)-L1: 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.995	BB	0.2747	67.88650	3.72383	3.9755
2	15.152	BB	0.3208	1639.74548	78.13206	96.0245



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.130	BB	0.3060	1267.26636	63.18674	96.4430
2	15.338	PV	0.2803	46.73986	2.43153	3.5570

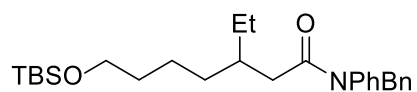
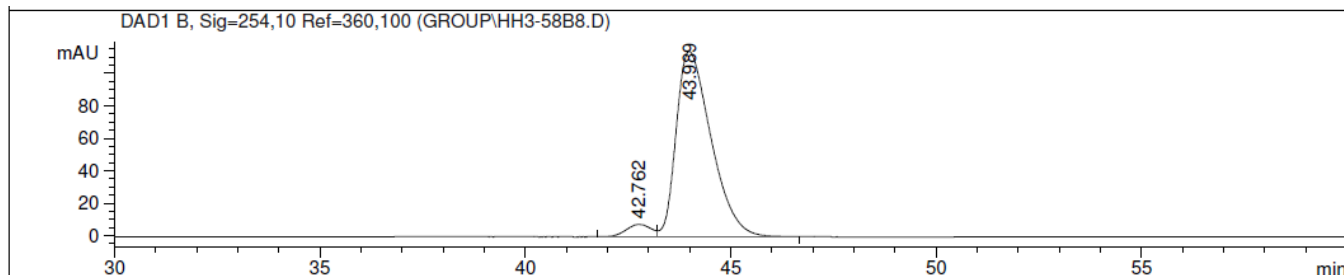
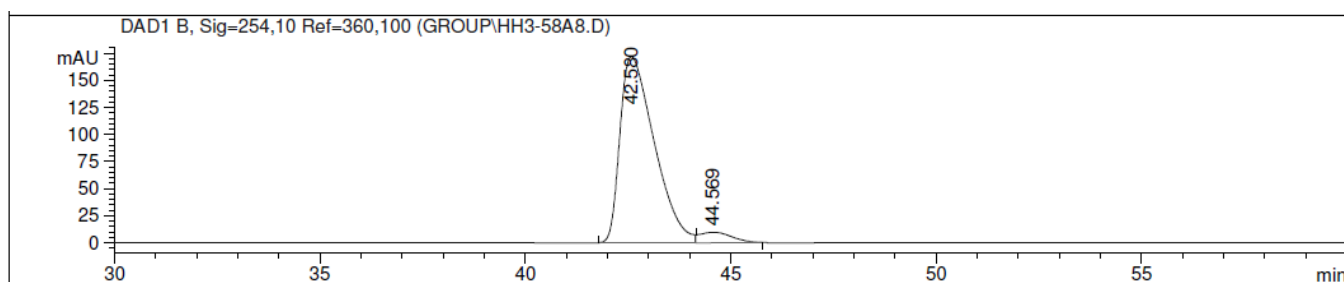


Fig. 2, entry 6

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.762	BV	0.6499	325.73096	7.66400	4.6002
2	43.989	VB	0.9098	6755.11719	114.24879	95.3998



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.580	BB	0.8678	1.00007e4	172.13248	94.9341
2	44.569	BB	0.6467	533.66443	9.84123	5.0659

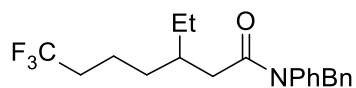
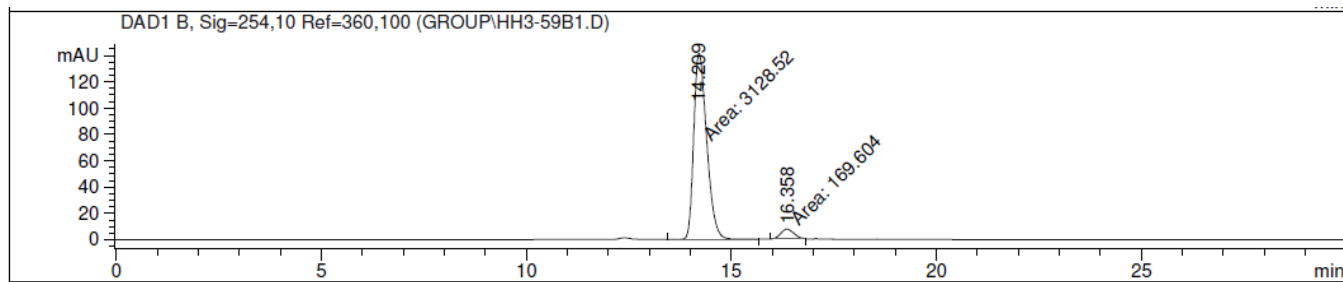
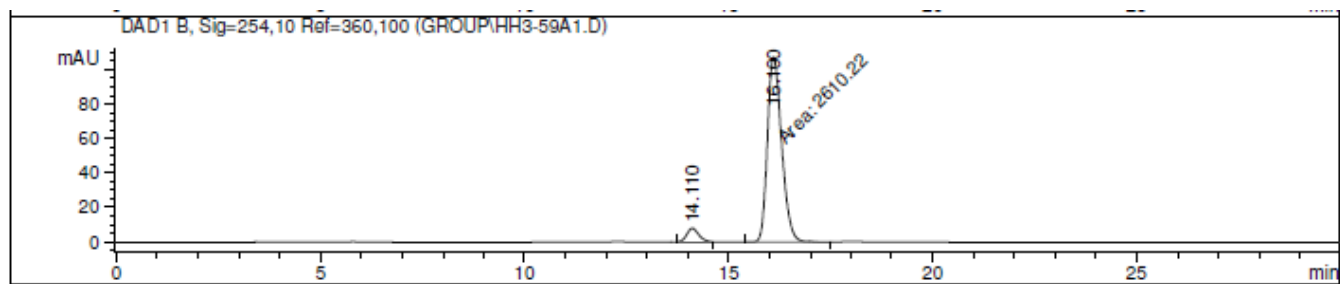


Fig. 2, entry 7

(*R*)-L1: 90% ee; (*S*)-L1: 89% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.209	MM	0.3678	3128.51929	141.76015	94.8576
2	16.358	MF	0.3757	169.60416	7.52336	5.1424



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.110	BB	0.3041	158.78735	7.84528	5.7345
2	16.100	MM	0.4055	2610.21533	107.27811	94.2655

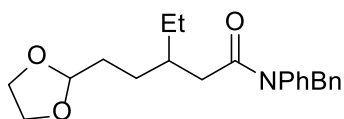
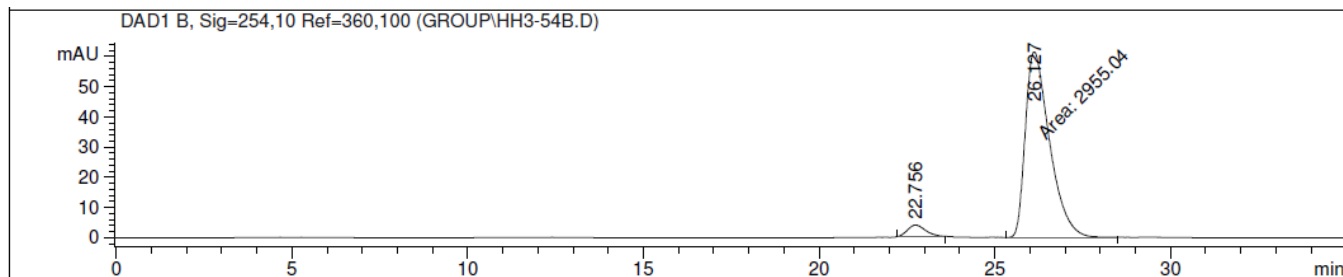
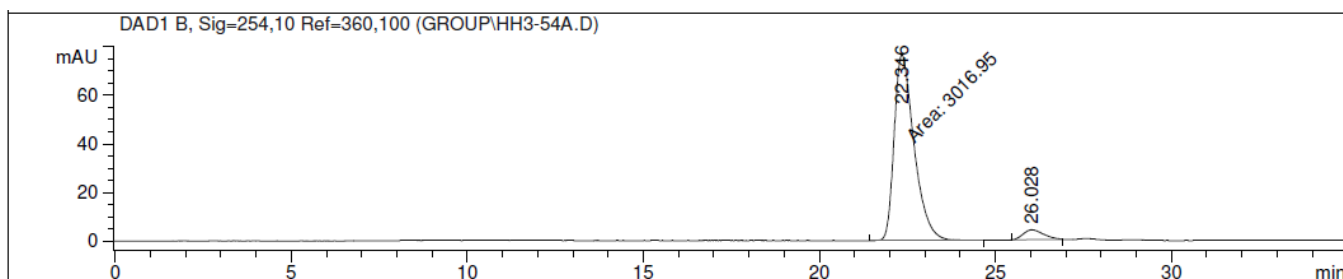


Fig. 2, entry 8

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.756	BB	0.4348	138.65231	3.84390	4.4818
2	26.127	MM	0.8008	2955.03589	61.50257	95.5182



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.346	MM	0.6588	3016.95483	76.32246	94.7819
2	26.028	BB	0.4890	166.09494	4.07953	5.2181

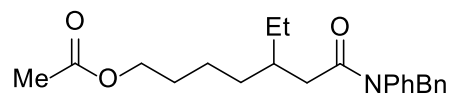
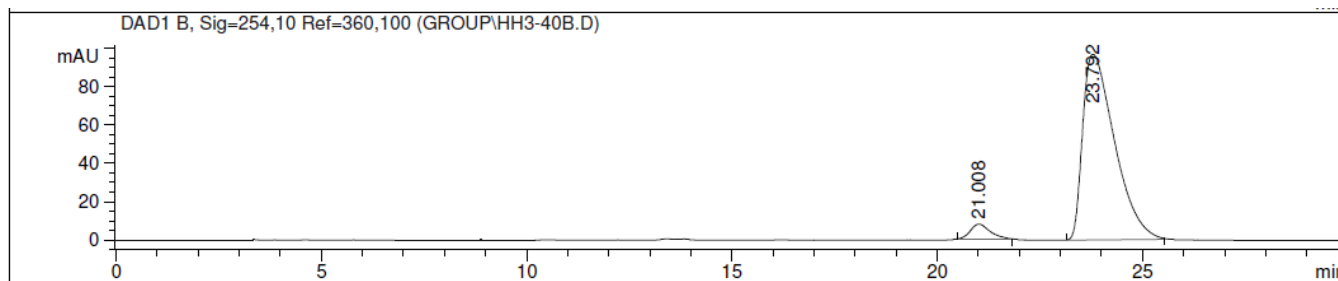
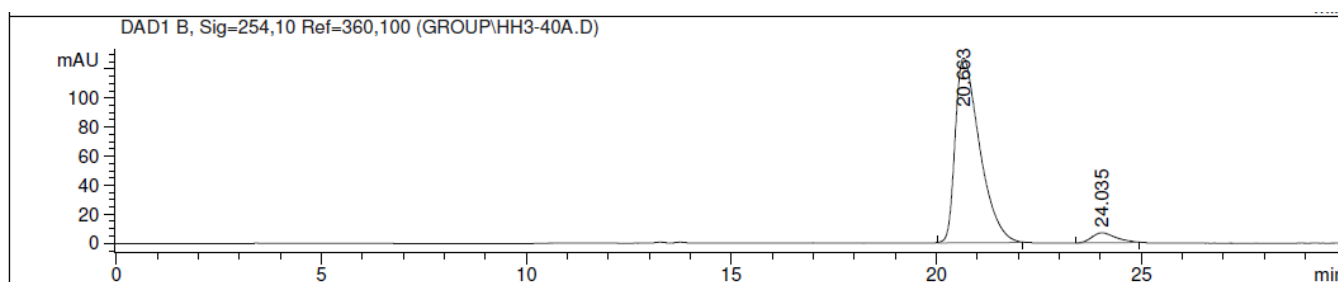


Fig. 2, entry 9

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.008	BB	0.4927	276.49286	7.97150	5.0341
2	23.792	BB	0.8047	5215.94043	96.79768	94.9659



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.663	BB	0.6300	5272.20264	127.07707	94.9241
2	24.035	BB	0.5816	281.91898	6.88690	5.0759

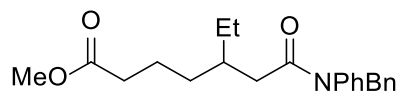
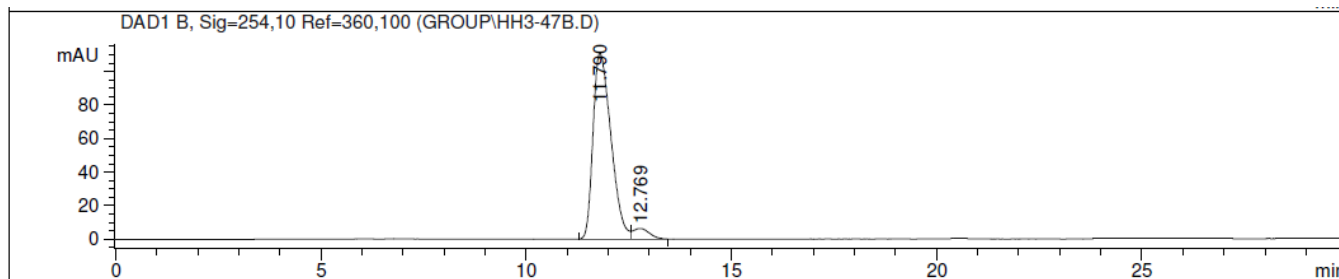
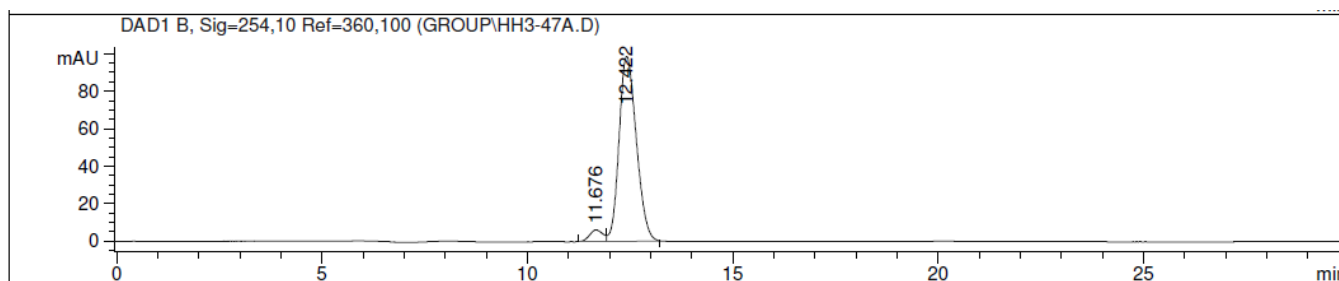


Fig. 2, entry 10

(*R*)-L1: 90% ee; (*S*)-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.790	BV	0.4784	3370.81055	110.95085	94.9468
2	12.769	VB	0.4099	179.39786	6.38272	5.0532



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.676	BV	0.3437	140.58098	6.21916	4.6421
2	12.422	VB	0.4551	2887.79932	98.78307	95.3579

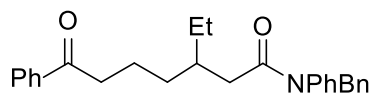
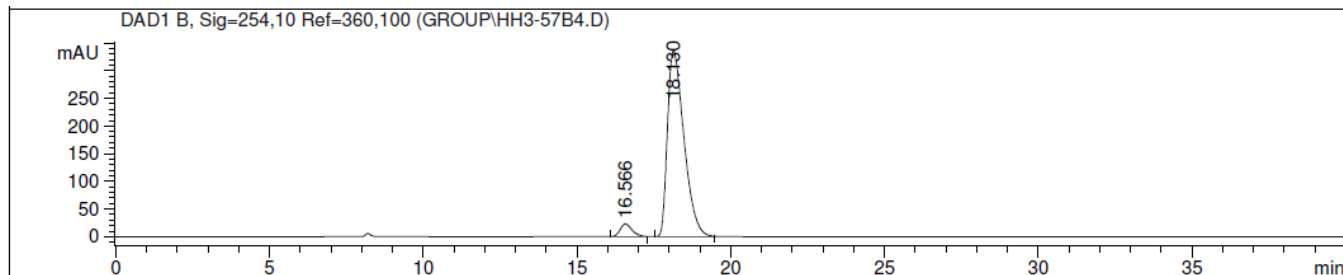
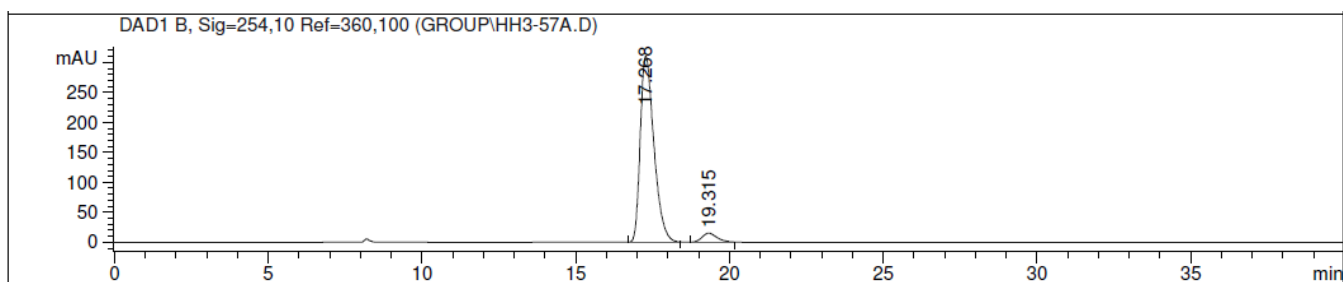


Fig. 2, entry 11

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.566	BB	0.4118	623.82654	23.04549	4.7534
2	18.130	PB	0.5743	1.25001e4	335.75867	95.2466



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.268	BB	0.4719	9588.86719	310.80991	95.0190
2	19.315	PB	0.5003	502.65607	14.94744	4.9810

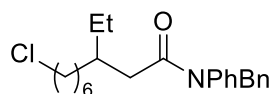
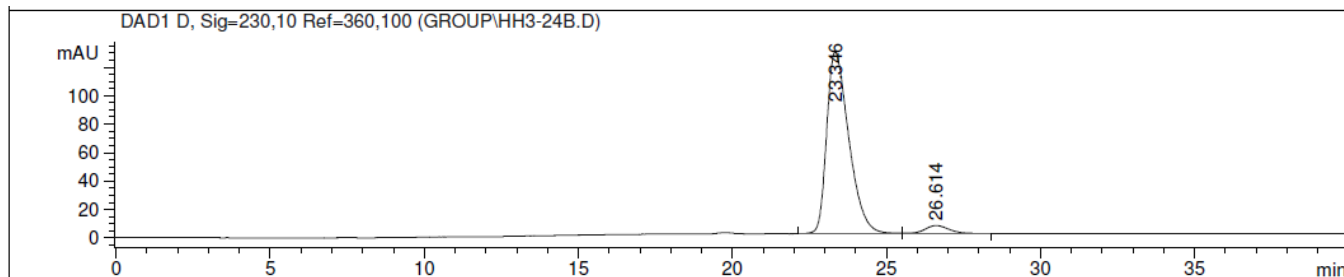
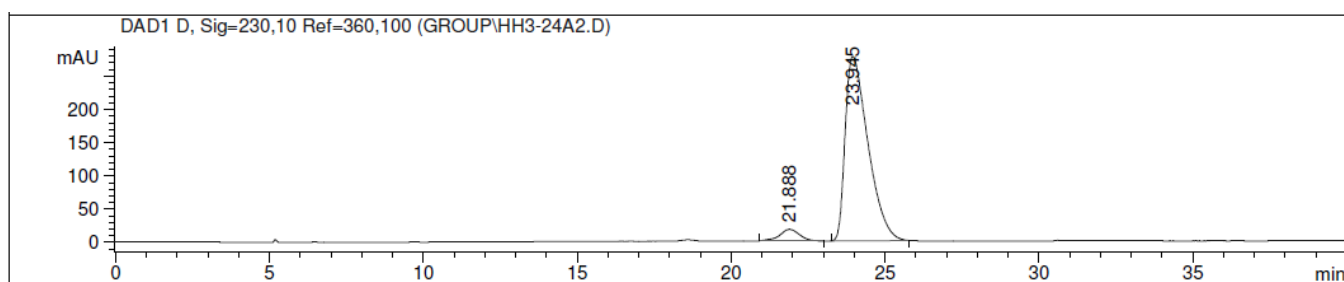


Fig. 2, entry 13

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.346	PB	0.7666	6386.16895	127.87534	95.3341
2	26.614	BB	0.7312	312.55692	5.66923	4.6659



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.888	BP	0.6231	788.36493	17.58369	5.2325
2	23.945	BB	0.7809	1.42784e4	277.23453	94.7675

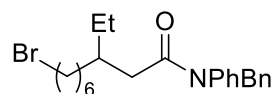
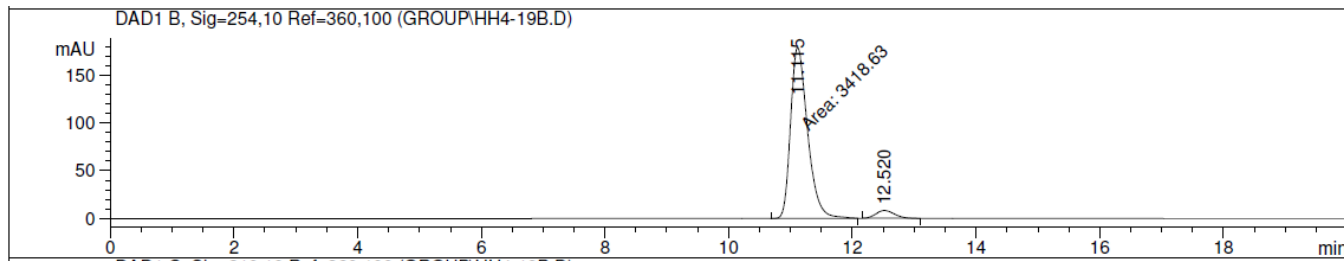
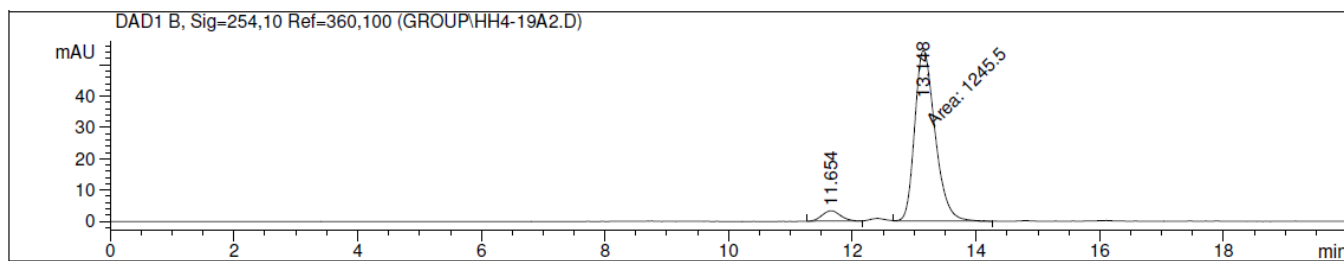


Fig. 2, entry 14

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.115	MM	0.3185	3418.63281	178.90855	95.2905
2	12.520	PB	0.3184	168.95590	8.20031	4.7095



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.654	PP	0.2752	67.11793	3.32905	5.1133
2	13.148	MM	0.3804	1245.49939	54.57257	94.8867

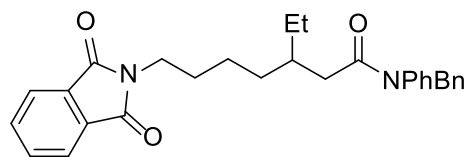
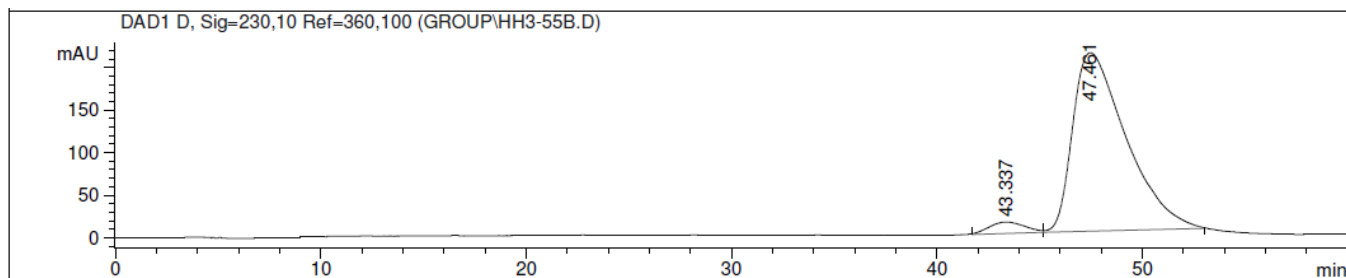
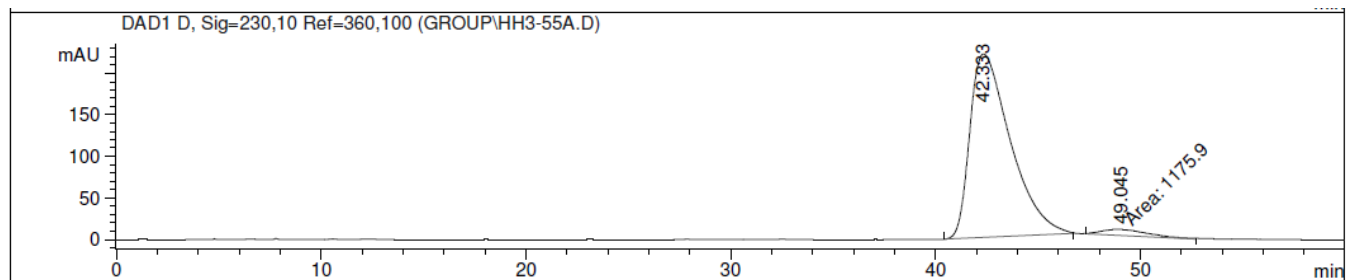


Fig. 2, entry 15

(*R*)-L1: 92% ee; (*S*)-L1: 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.337	BV	1.4135	1618.38000	13.41472	4.0960
2	47.461	VB	2.3621	3.78933e4	209.50900	95.9040



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.333	BB	1.8320	3.04804e4	221.14108	96.2854
2	49.045	MM	2.6686	1175.90454	7.34399	3.7146

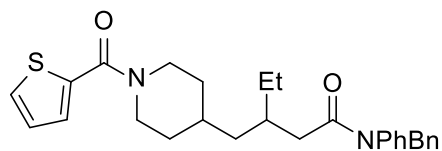
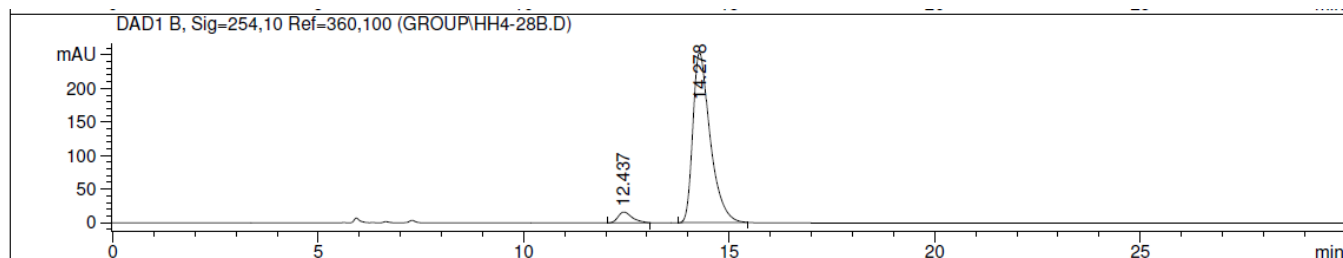
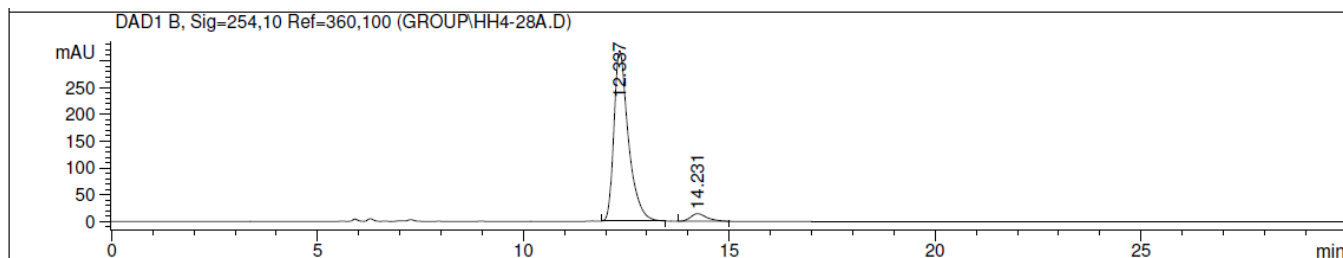


Fig. 2, entry 16

(*R*)-L1: 90% ee; (*S*)-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.437	BB	0.3459	382.41330	16.17101	4.9166
2	14.278	PB	0.4389	7395.54297	253.07199	95.0834



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.337	PB	0.3649	7765.36475	318.03262	95.2846
2	14.231	PB	0.4160	384.28769	14.09872	4.7154

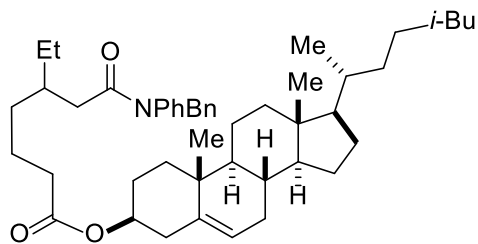
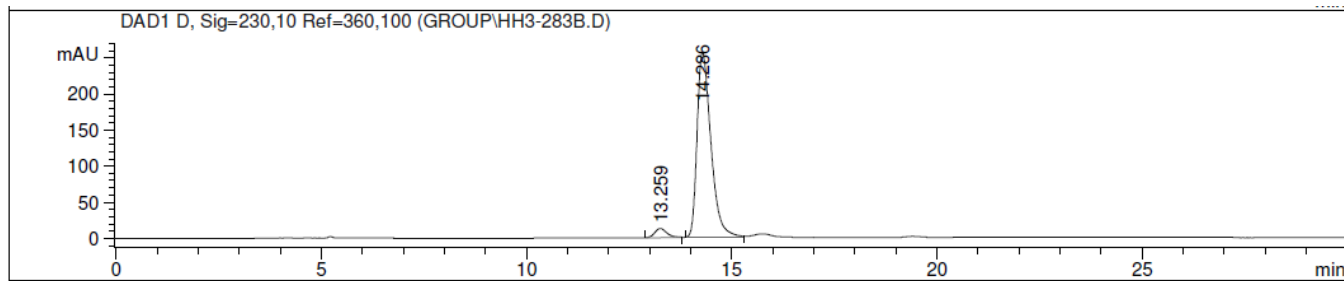
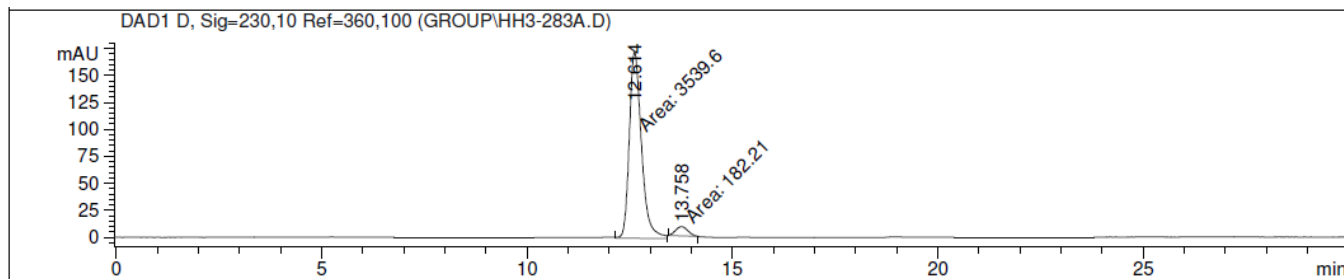


Fig. 2, entry 17

(*R*)-L1: 4:96 dr; (*S*)-L1: 95:5 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.259	BB	0.3081	263.69073	12.81544	4.1904
2	14.286	BB	0.3604	6028.99756	256.33209	95.8096



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.614	MM	0.3425	3539.59814	172.26627	95.1043
2	13.758	MM	0.3525	182.21011	8.61530	4.8957

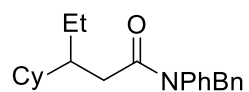
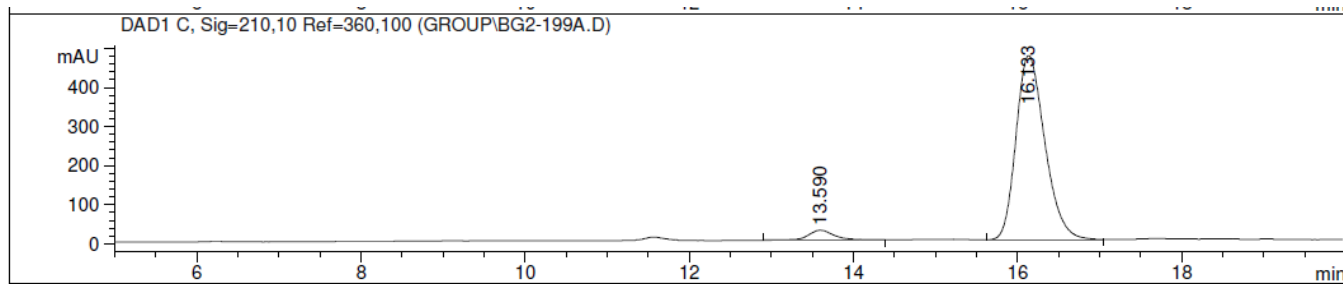
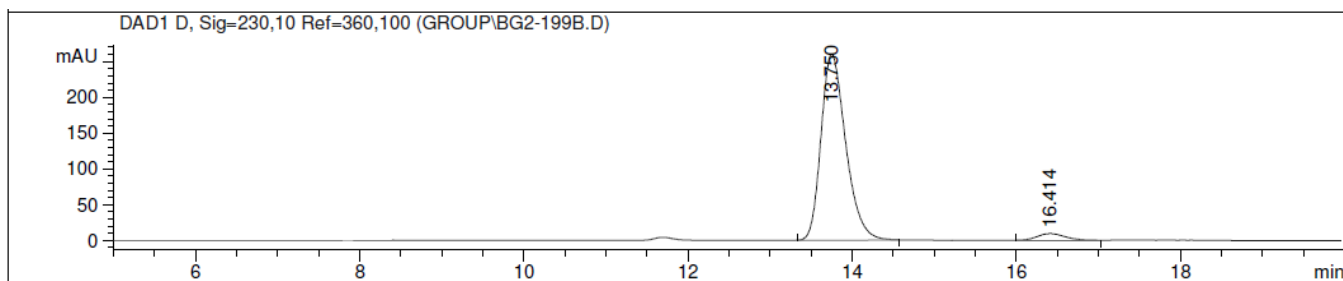


Fig. 2, entry 18

(*R*)-L1: 92% ee; (*S*)-L1: 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.589	BB	0.3028	132.17595	6.68263	3.9168
2	16.133	BB	0.3677	3242.41772	135.23364	96.0832



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.750	BB	0.3220	5433.98340	259.83102	96.1012
2	16.414	BP	0.3436	220.45427	9.40049	3.8988

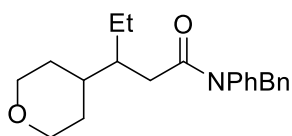
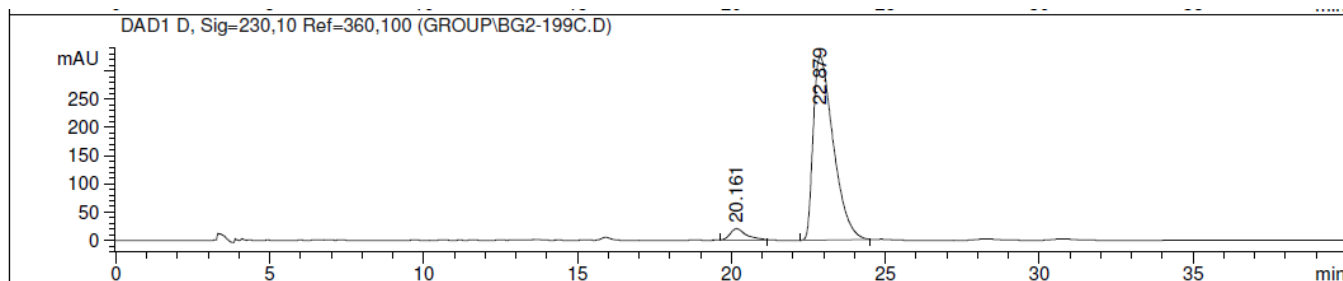
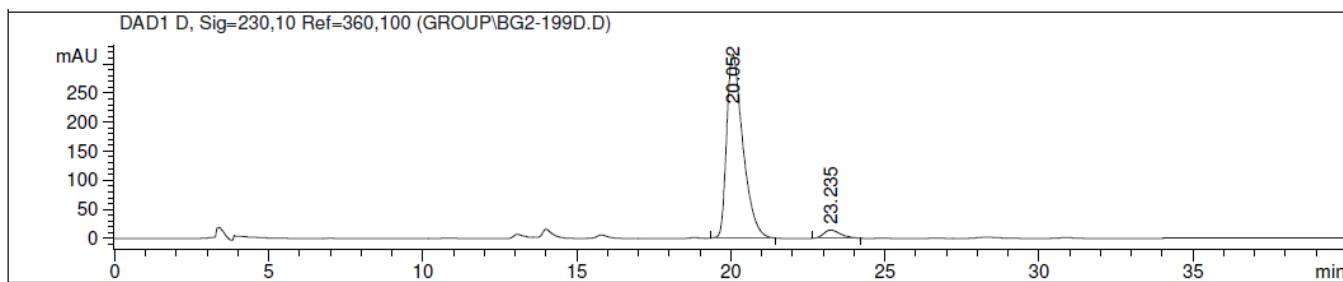


Fig. 2, entry 19

(*R*)-L1: 91% ee; (*S*)-L1: 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.161	BB	0.5231	729.14771	20.20301	4.6996
2	22.879	BB	0.6925	1.47860e4	325.16193	95.3004



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.052	BB	0.5494	1.15335e4	316.28854	95.4898
2	23.235	BB	0.5509	544.75092	14.28348	4.5102

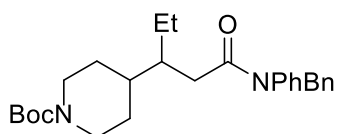
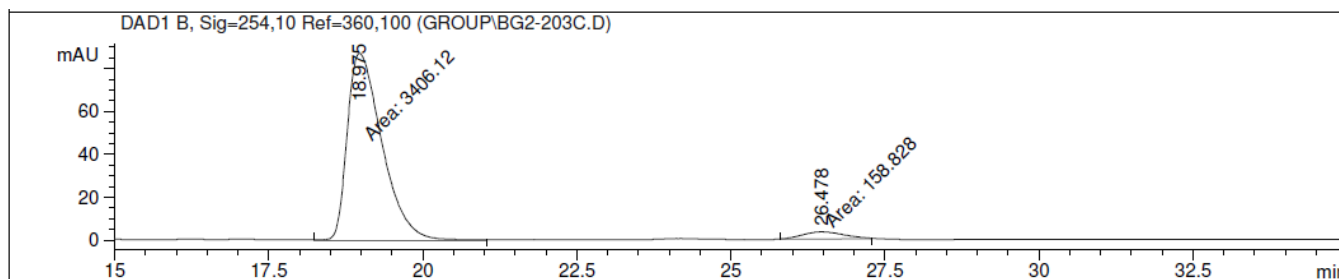
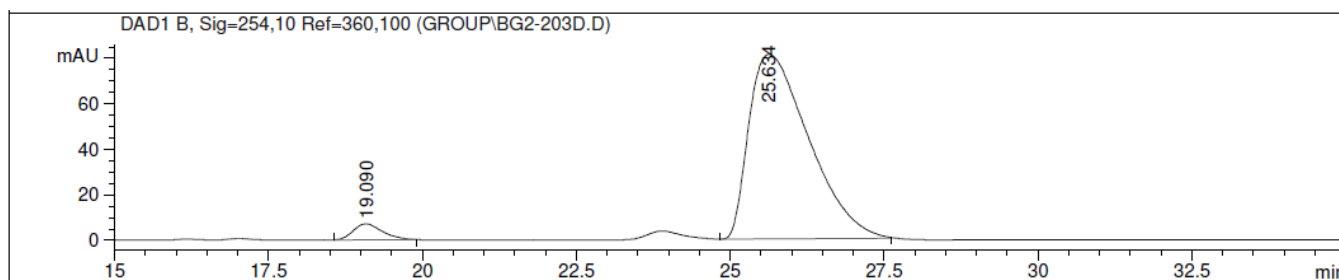


Fig. 2, entry 20

(R)-L1: 91% ee; (S)-L1: 92% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.975	MM	0.6506	3406.12427	87.26006	95.5447
2	26.478	MM	0.7914	158.82787	3.34489	4.4553



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.090	BB	0.4854	233.91611	7.08038	4.0666
2	25.634	PB	0.9972	5518.26611	81.37238	95.9334

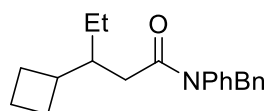
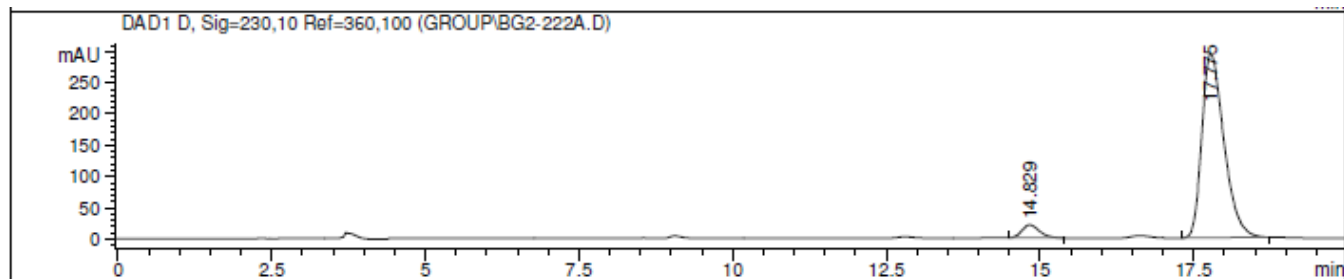
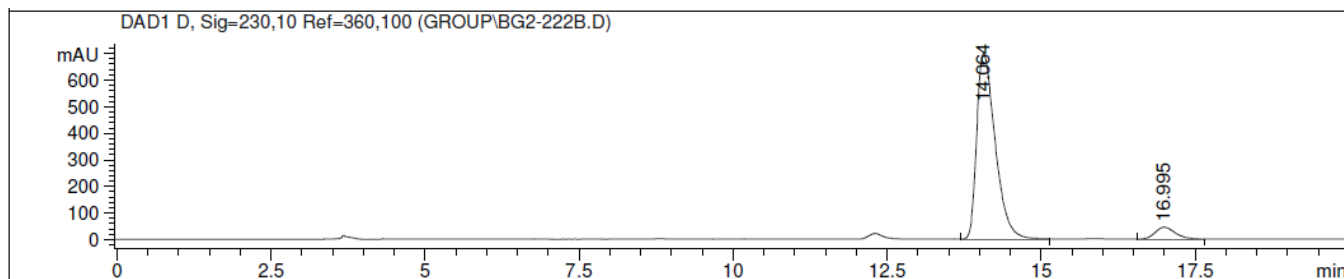


Fig. 2, entry 21

(*R*)-L1: 90% ee; (*S*)-L1: 87% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.829	PB	0.3034	406.00647	20.64421	5.2080
2	17.775	BB	0.3859	7389.77441	295.39236	94.7920



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.064	BB	0.3203	1.45514e4	700.51611	93.4287
2	16.995	BB	0.3558	1023.47461	44.58679	6.5713

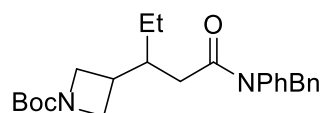
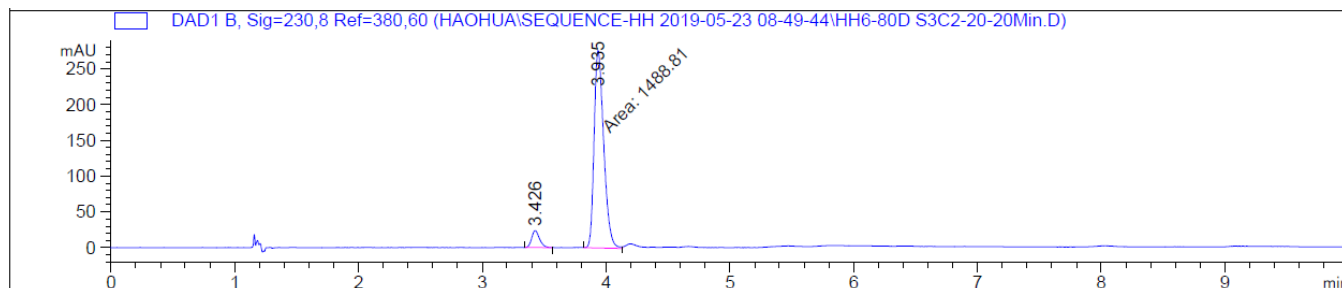
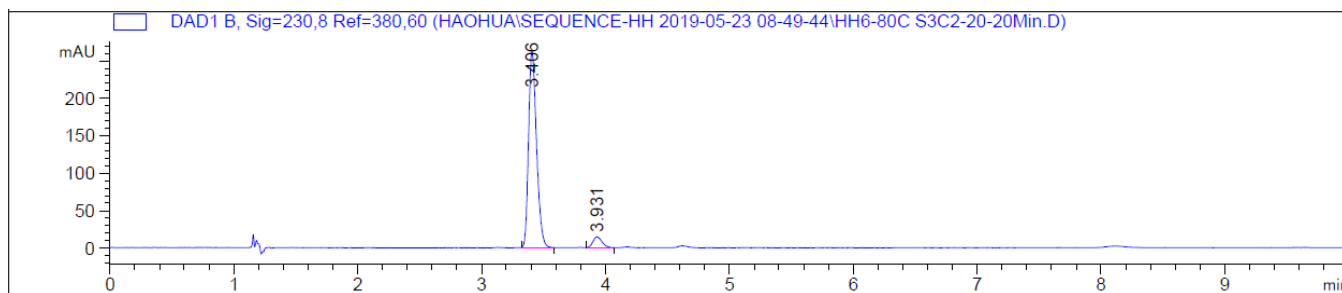


Fig. 2, entry 22

(*R*)-L1: 87% ee; (*S*)-L1: 89% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.426	BB	0.0686	104.71426	23.67196	6.5712
2	3.935	MM	0.0899	1488.80786	275.94672	93.4288



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.406	BB	0.0683	1171.84302	261.43472	94.1373
2	3.931	BB	0.0778	72.98077	14.23569	5.8627

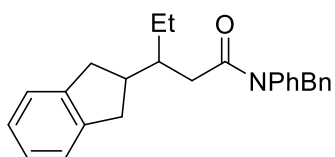
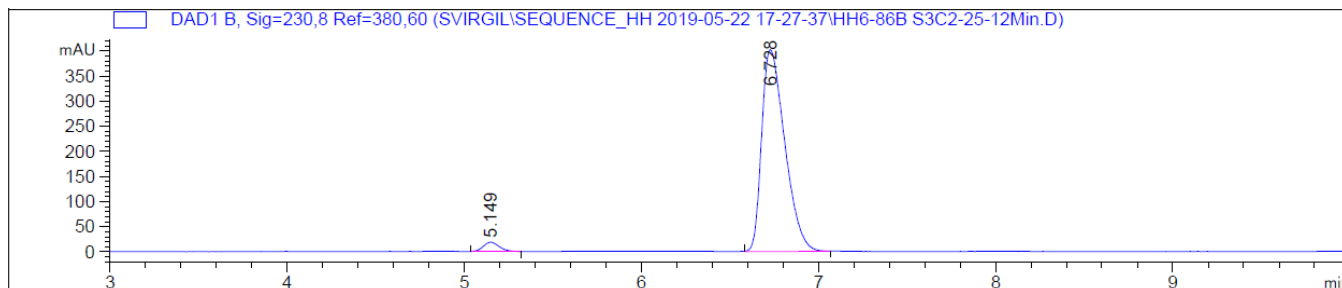
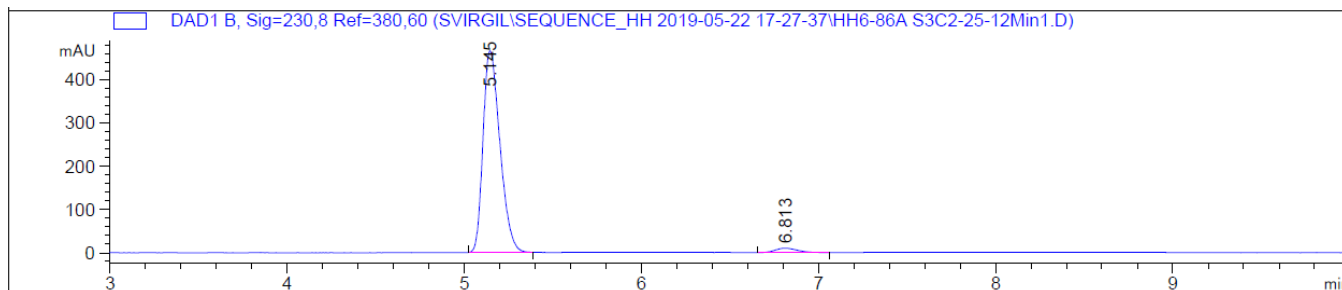


Fig. 2, entry 23

(*R*)-L1: 94% ee; (*S*)-L1: 94% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.149	BB	0.0949	115.49269	18.47967	3.0704
2	6.728	BB	0.1408	3645.94019	402.06918	96.9296



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.145	BB	0.1035	3098.17261	466.38467	97.0955
2	6.813	BB	0.1331	92.67774	10.48592	2.9045

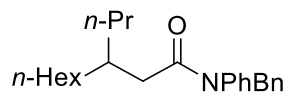
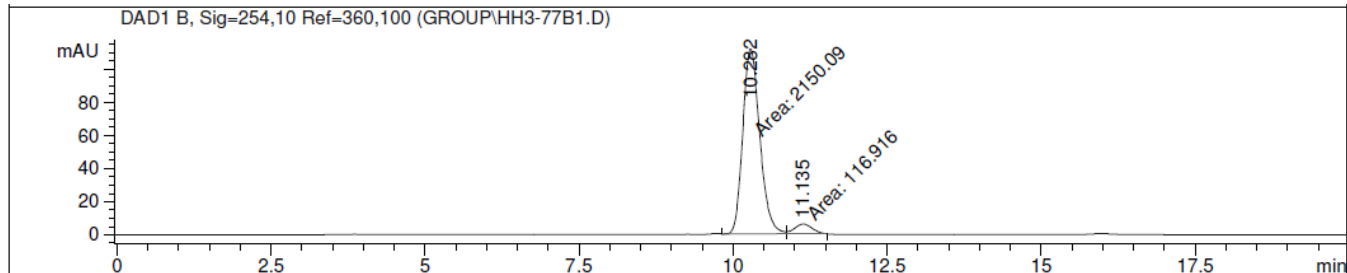
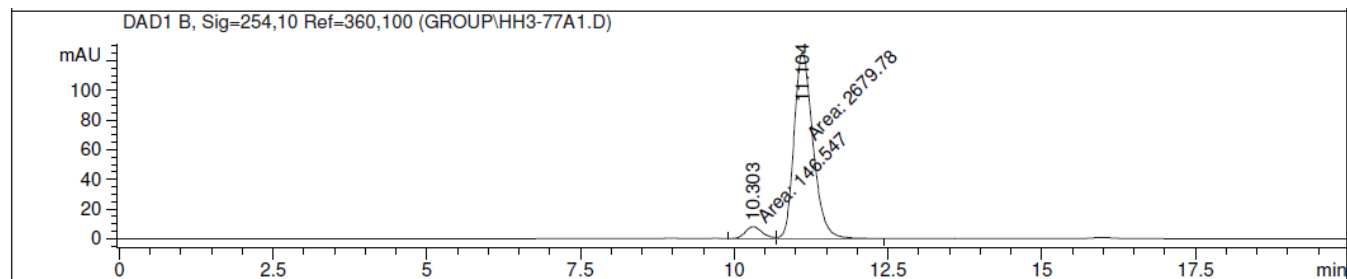


Fig. 2, entry 24

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.282	MF	0.3201	2150.09082	111.95560	94.8427
2	11.135	FM	0.3294	116.91582	5.91481	5.1573



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.303	MM	0.3094	146.54724	7.89325	5.1851
2	11.104	MM	0.3565	2679.77637	125.29027	94.8149

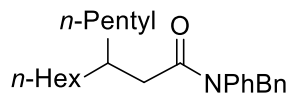
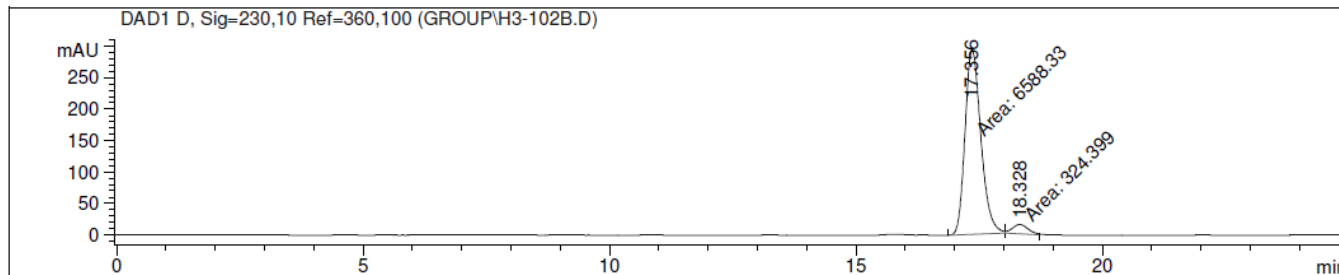
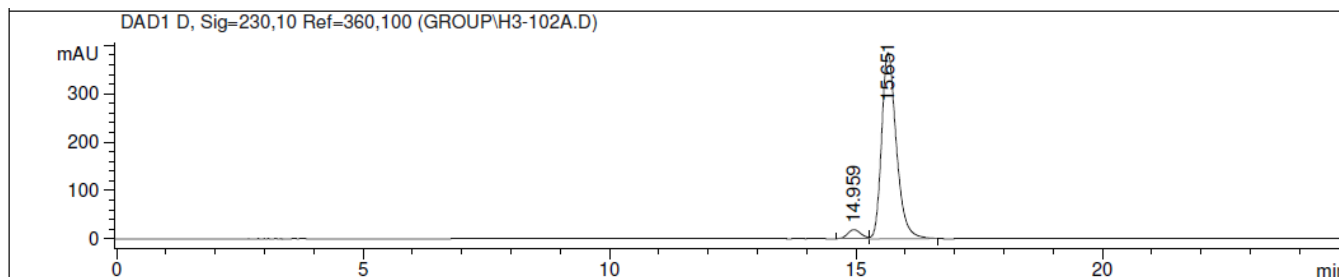


Fig. 2, entry 25
 (R)-L1: 91% ee; (S)-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.356	MM	0.3724	6588.32910	294.88763	95.3072
2	18.328	MM	0.3728	324.39896	14.50153	4.6928



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.959	BV	0.2905	363.76126	19.07212	4.3590
2	15.651	VB	0.3157	7981.31836	385.17725	95.6410

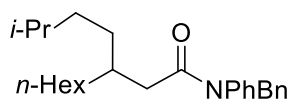
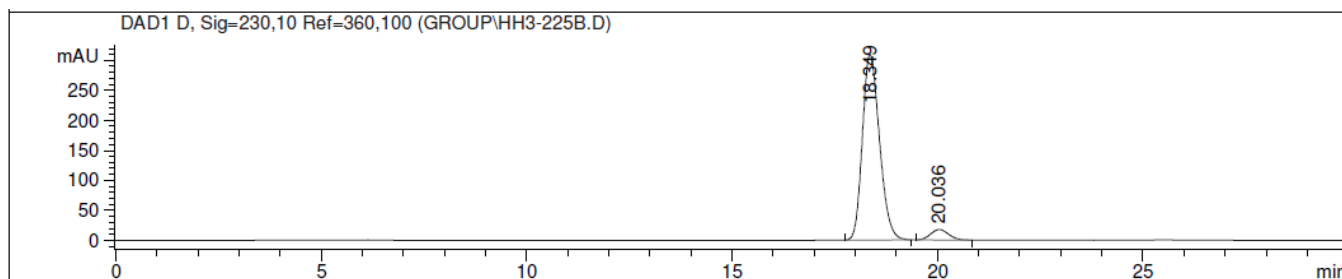
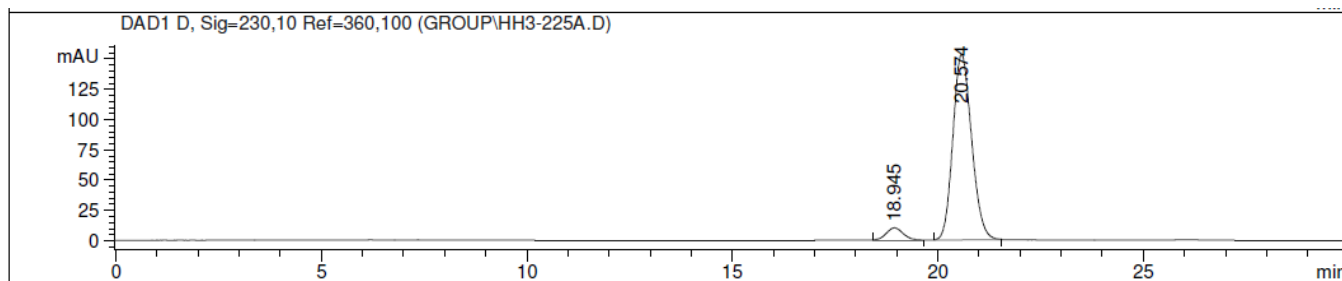


Fig. 2, entry 26

(*R*)-L1: 89% ee; (*S*)-L1: 89% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.349	BB	0.4482	8928.21973	309.78815	94.3658
2	20.036	BB	0.4532	533.07214	17.50949	5.6342



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.945	BB	0.4115	283.94202	10.05333	5.5225
2	20.574	BB	0.4943	4857.60205	153.02626	94.4775

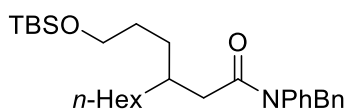
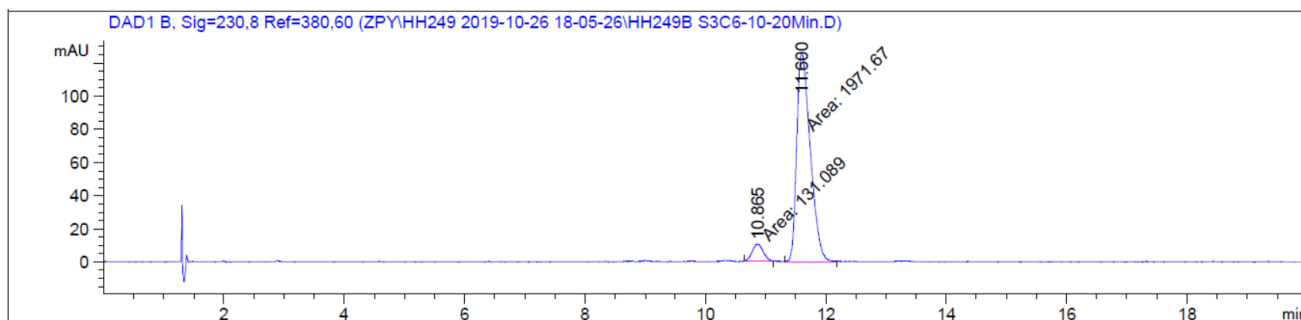
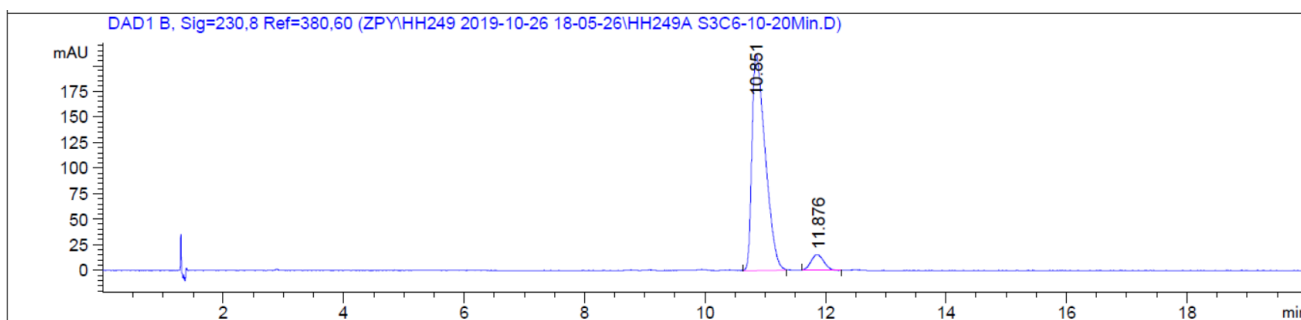


Fig. 2, entry 27

(*R*)-L1: 88% ee; (*S*)-L1: 87% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.865	MM	0.2091	131.08879	10.44822	6.2341
2	11.600	MM	0.2604	1971.66589	126.20064	93.7659



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.851	BB	0.2238	3241.08252	211.49835	93.5457
2	11.876	BB	0.1777	223.62254	15.28757	6.4543

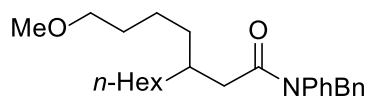
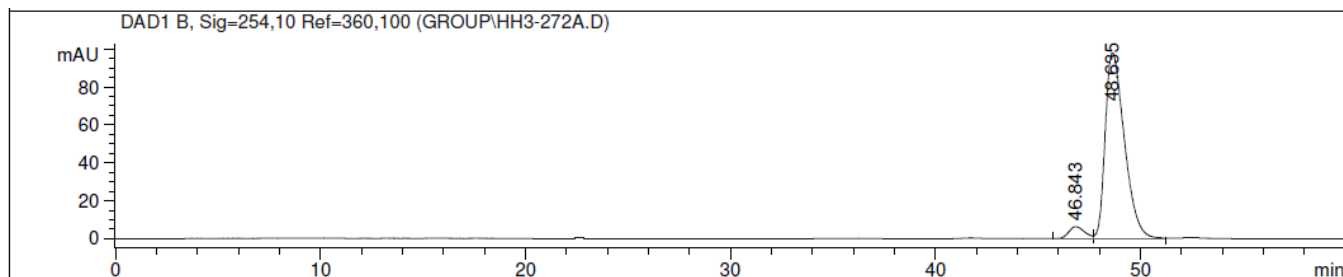
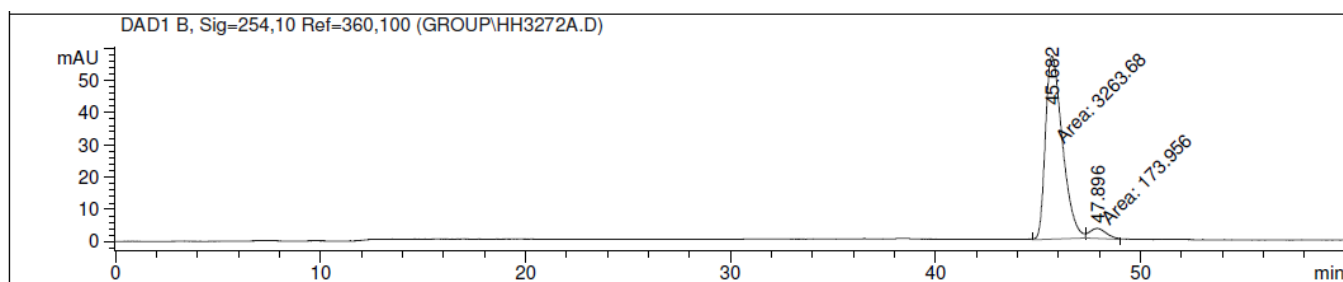


Fig. 2, entry 28

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.843	VV	0.6480	339.81686	6.37371	5.0510
2	48.635	VB	0.9271	6387.88818	98.18021	94.9490



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.682	MM	0.9587	3263.68140	56.74081	94.9397
2	47.896	MM	0.9349	173.95647	3.10102	5.0603

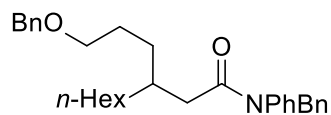
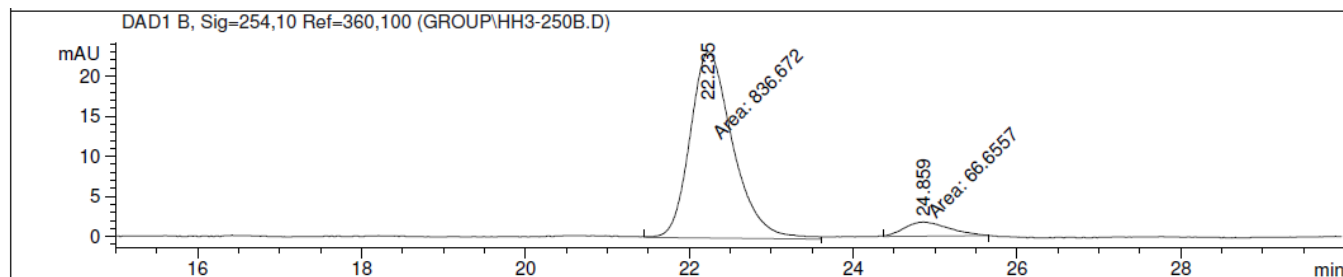
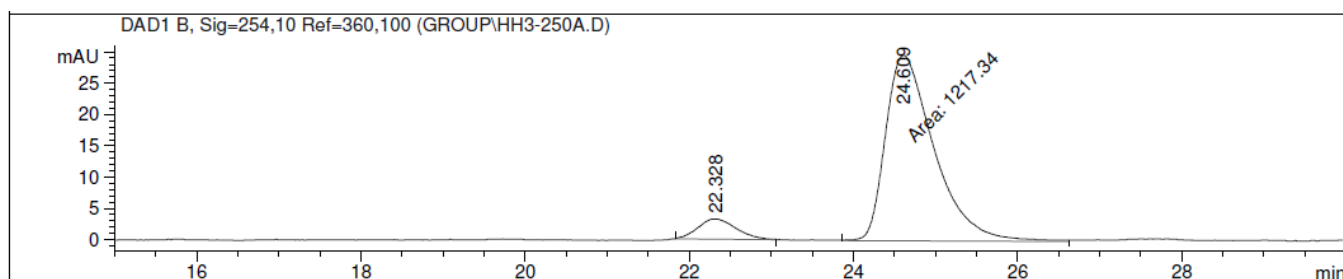


Fig. 2, entry 29

(*R*)-L1: 85% ee; (*S*)-L1: 84% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.235	MM	0.6025	836.67175	23.14291	92.6211
2	24.859	MM	0.6326	66.65566	1.75603	7.3789



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.328	BB	0.3883	103.71006	3.24955	7.8506
2	24.609	MM	0.6843	1217.34448	29.64780	92.1494

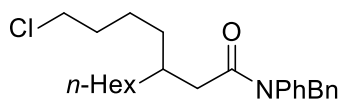
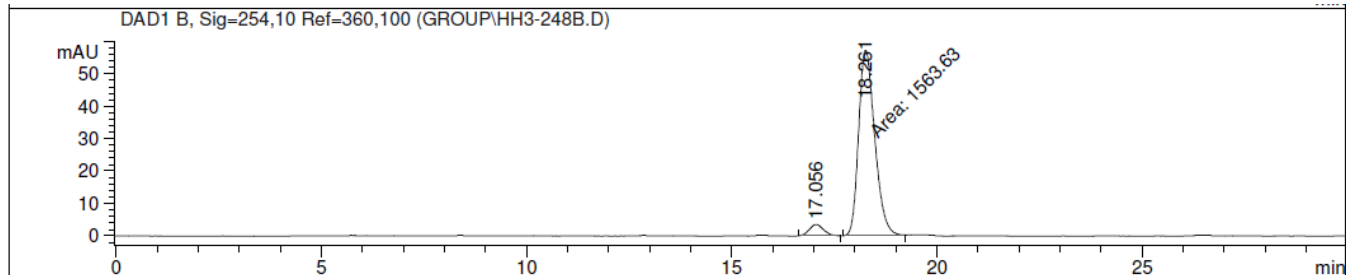
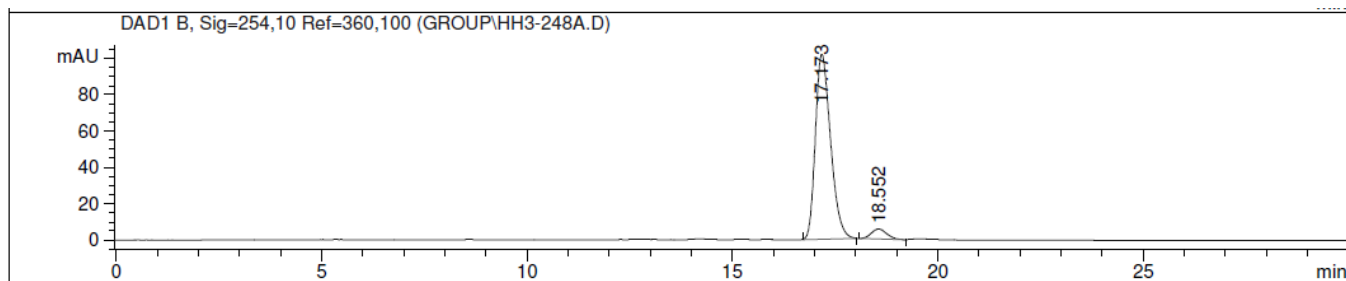


Fig. 2, entry 30

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.056	BP	0.3406	82.13556	3.43915	4.9907
2	18.261	MM	0.4550	1563.63318	57.27143	95.0093



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.173	BB	0.3982	2615.38794	101.65414	94.9140
2	18.552	PP	0.3875	140.14664	5.42257	5.0860

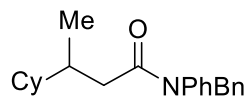
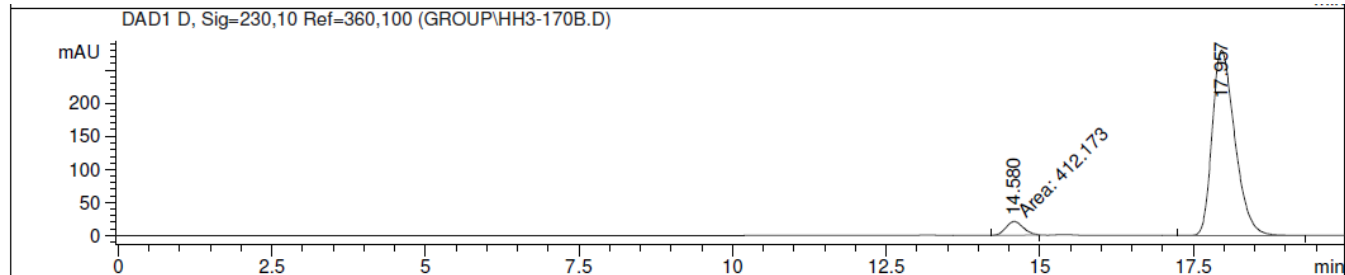
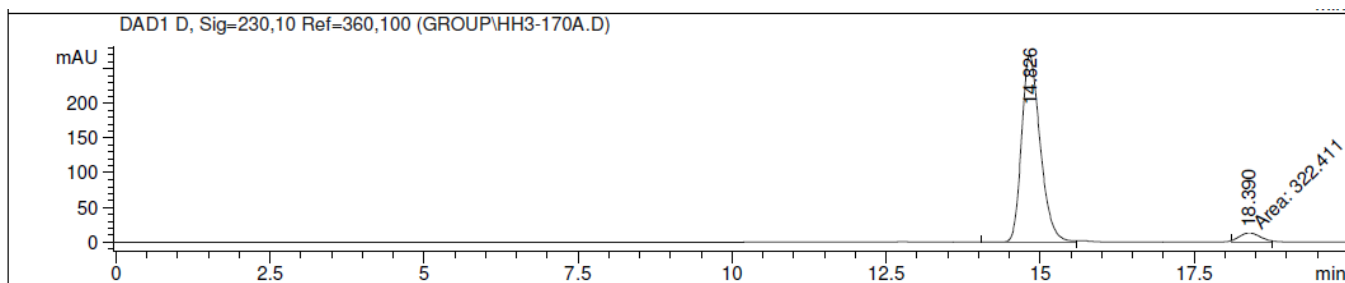


Fig. 2, entry 31

(*R*)-L1: 89% ee; (*S*)-L1: 89% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.580	MM	0.3292	412.17300	20.86625	5.4187
2	17.957	VB	0.3958	7194.34619	279.97937	94.5813



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.826	VV	0.3268	5696.95264	269.27045	94.6438
2	18.390	FM	0.3967	322.41116	13.54651	5.3562

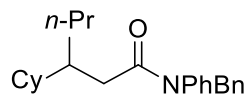
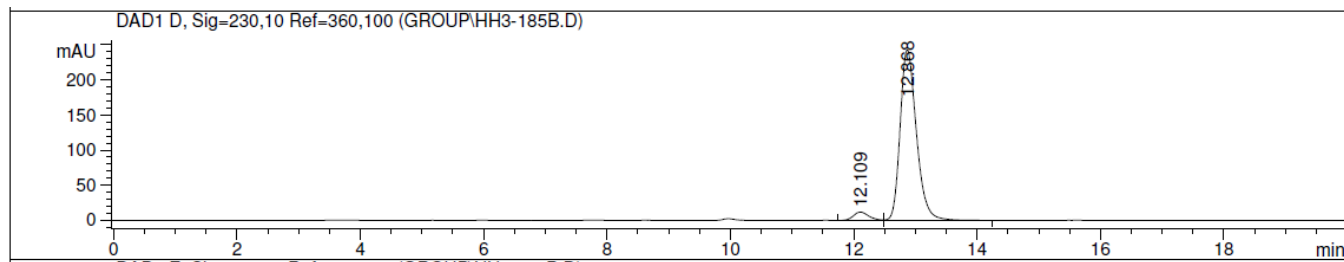
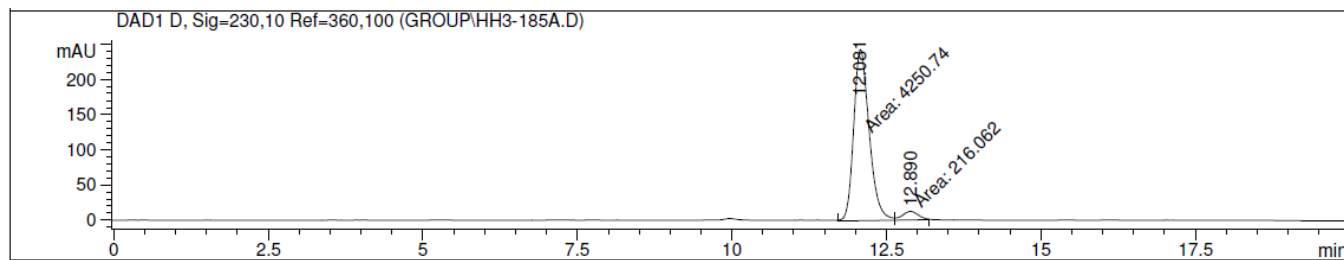


Fig. 2, entry 32

(*R*)-L1: 91% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.109	VV	0.2634	201.82979	11.81022	4.3513
2	12.868	VB	0.2808	4436.58057	243.27858	95.6487



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.081	MF	0.2910	4250.74121	243.41586	95.1629
2	12.890	FM	0.2982	216.06172	12.07667	4.8371

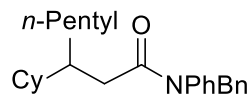
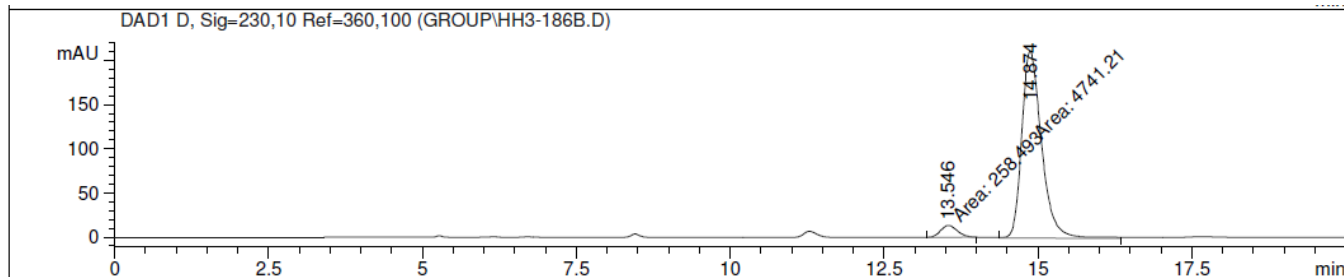
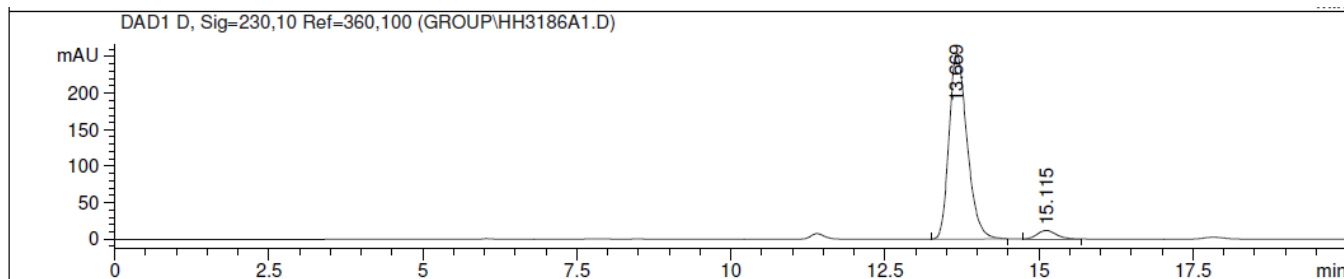


Fig. 2, entry 33

(R)-L1: 90% ee; (S)-L1: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.546	MM	0.3174	258.49350	13.57351	5.1702
2	14.874	MM	0.3738	4741.20850	211.38483	94.8298



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.669	BB	0.3162	5202.97461	254.84381	95.4083
2	15.115	BB	0.3237	250.40001	11.69923	4.5917

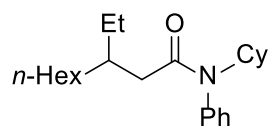
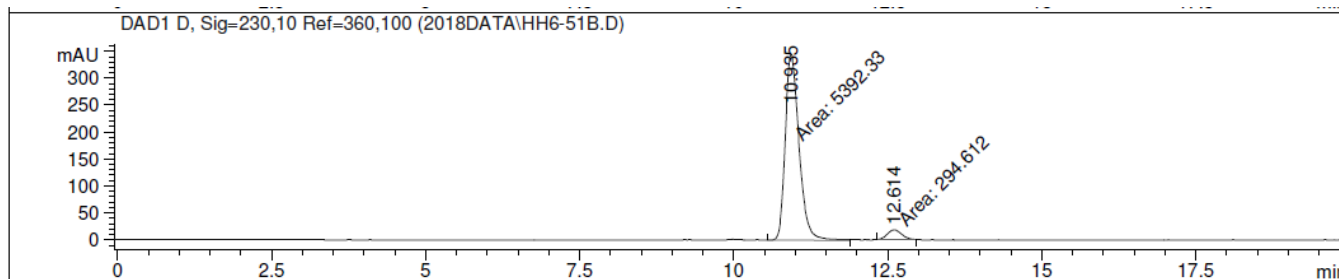
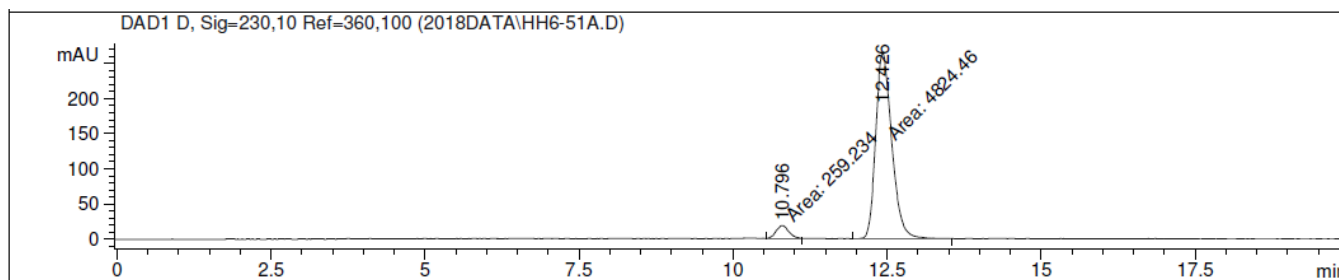


Fig. 2, entry 34

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.935	MM	0.2601	5392.33398	345.48712	94.8195
2	12.614	MM	0.2717	294.61176	18.07255	5.1805



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.796	MM	0.2361	259.23428	18.30230	5.0993
2	12.426	MM	0.3053	4824.46387	263.35114	94.9007

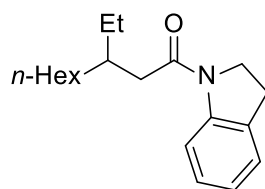
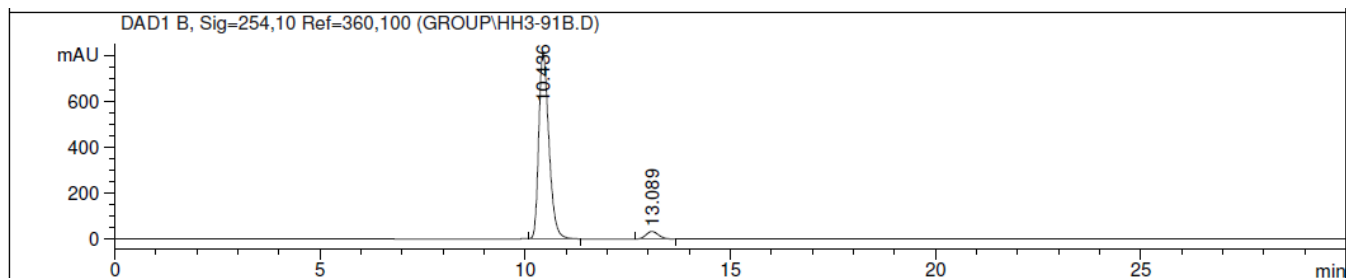
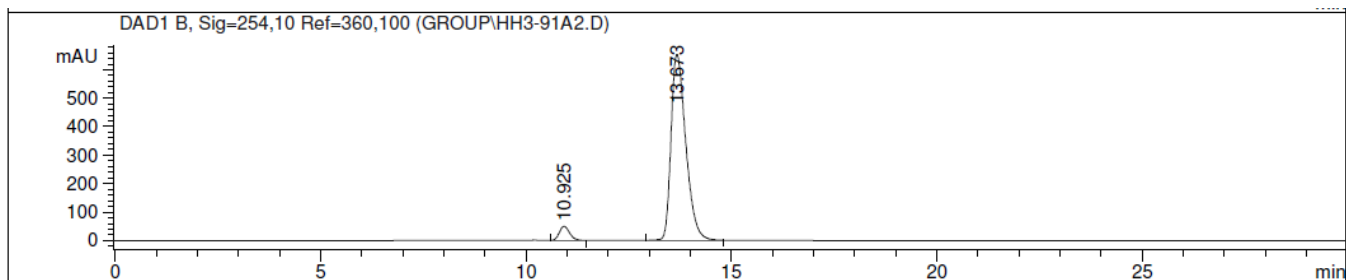


Fig. 2, entry 35

(*R*)-L1: 90% ee; (*S*)-L1: 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.436	VB	0.2654	1.39518e4	808.31647	95.0827
2	13.089	BB	0.3315	721.52942	33.47261	4.9173



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.925	BB	0.2691	873.48633	49.68890	5.0820
2	13.673	BB	0.3811	1.63144e4	653.83630	94.9180

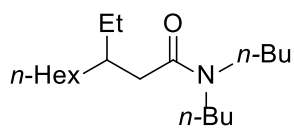
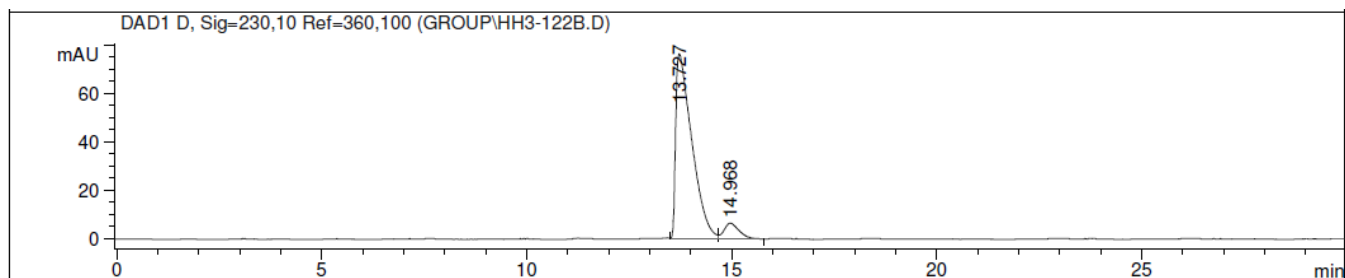
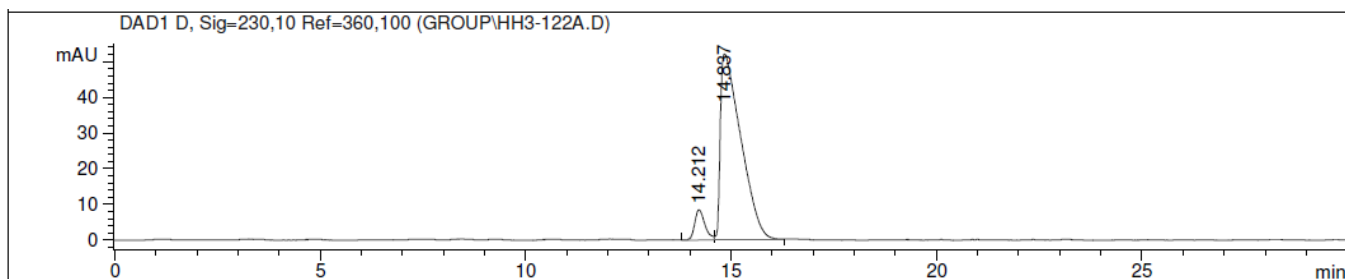


Fig. 2, entry 36

(*R*)-L1: 85% ee; (*S*)-L1: 85% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.727	VV	0.4074	2093.63257	76.47607	92.5393
2	14.968	VB	0.3750	168.79222	6.54172	7.4607



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.212	VV	0.2692	147.81770	8.48485	7.5416
2	14.837	VB	0.5049	1812.22400	52.21329	92.4584

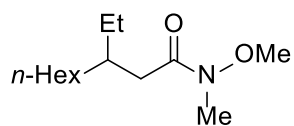
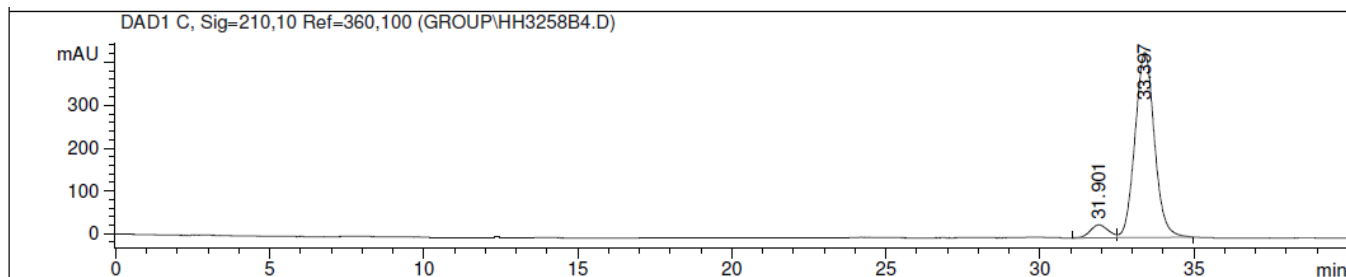
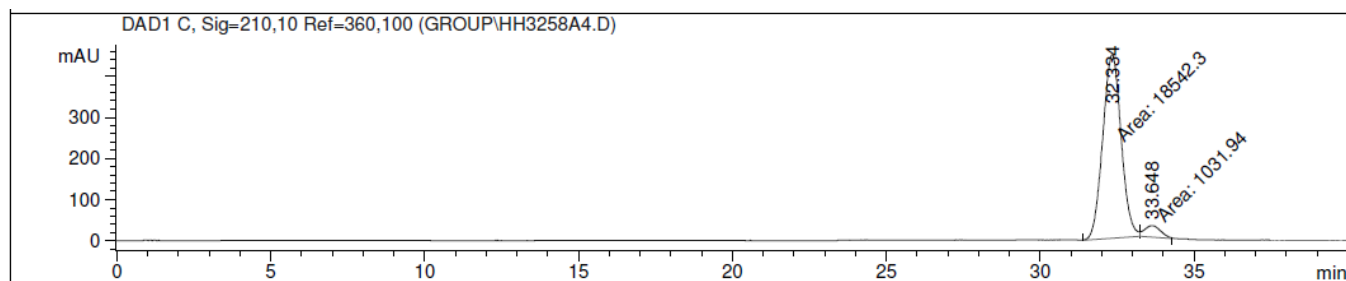


Fig. 2, entry 37

(*R*)-L1: 88% ee; (*S*)-L1: 88% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.901	PV	0.5027	1222.70447	30.17659	6.0528
2	33.397	VB	0.5941	1.89779e4	432.33676	93.9472



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.334	MM	0.6921	1.85423e4	446.53049	94.7281
2	33.648	MM	0.6063	1031.93945	28.36638	5.2719

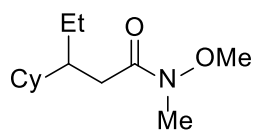
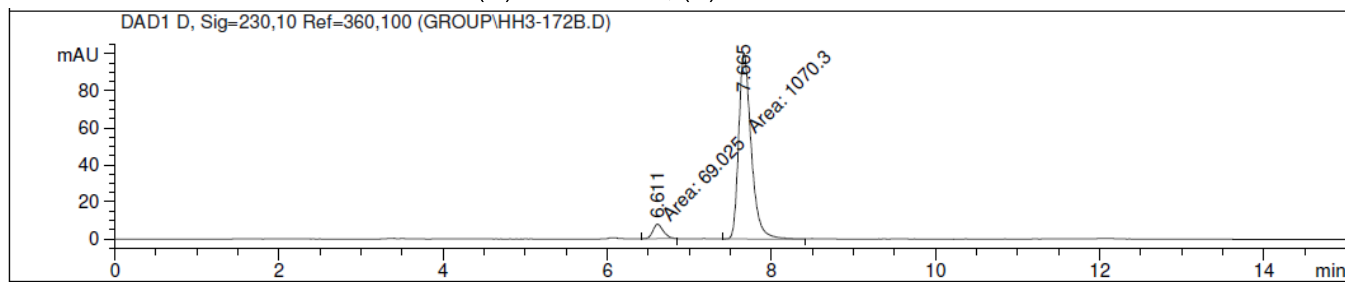
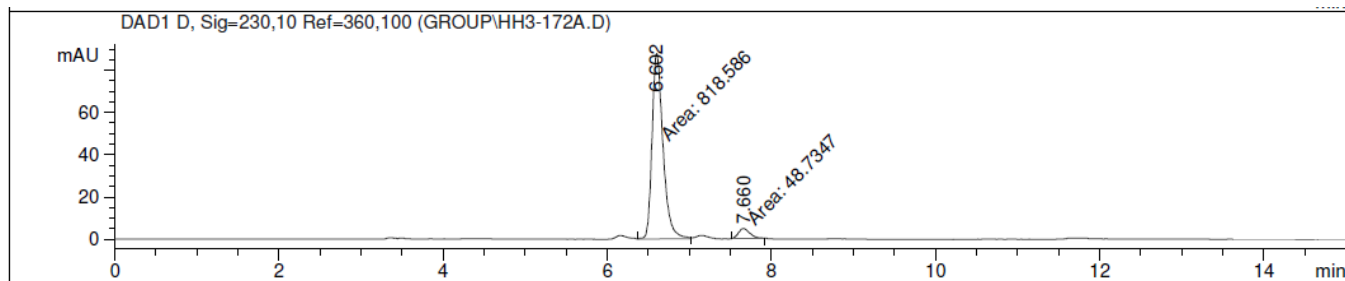


Fig. 2, entry 38

(*R*)-L1: 88% ee; (*S*)-L1: 88% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.611	MM	0.1475	69.02499	7.79848	6.0584
2	7.665	MM	0.1774	1070.29956	100.55565	93.9416



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.602	MM	0.1547	818.58624	88.16462	94.3810
2	7.660	MM	0.1676	48.73470	4.84653	5.6190

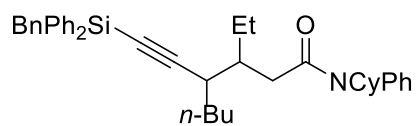
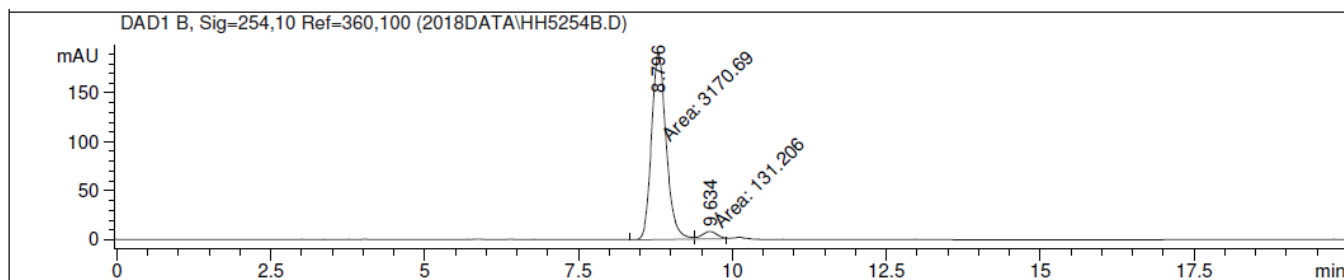


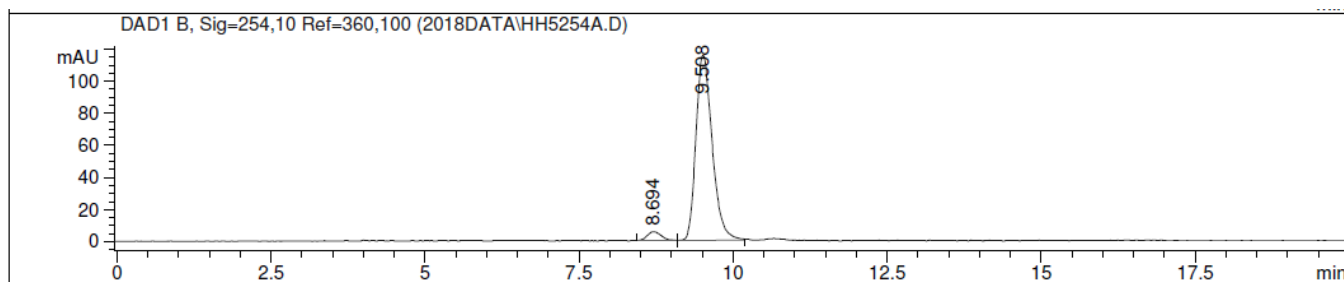
Fig. 3, entry 1

(*R, S*)-**L2**: 92% ee, 98:2 dr

(*S, R*)-**L2**: 92% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.796	MF	0.2780	3170.68555	190.10974	96.0263
2	9.634	FM	0.2859	131.20619	7.64974	3.9737



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.694	BP	0.2119	89.99741	5.52788	4.0812
2	9.508	VB	0.2858	2115.15063	115.40800	95.9188

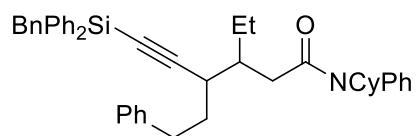
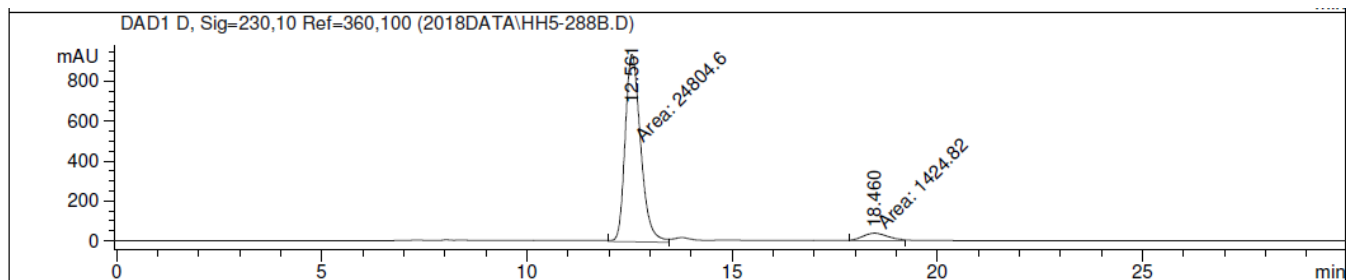


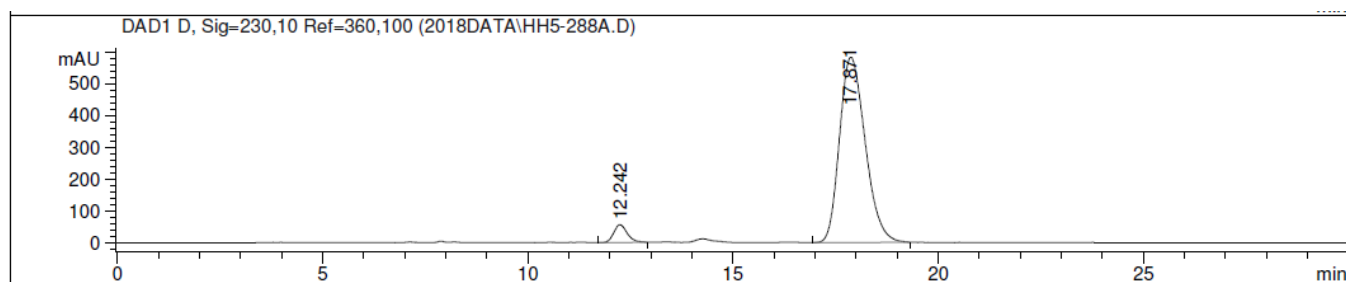
Fig. 3, entry 2

(*R, S*)-L2: 89% ee, 98:2 dr

(*S, R*)-L2: 90% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.561	MM	0.4392	2.48046e4	941.33667	94.5679
2	18.460	MM	0.6745	1424.81592	35.20420	5.4321



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.242	VB	0.3430	1285.55994	56.16482	4.8189
2	17.871	BB	0.6002	2.53916e4	582.85638	95.1811

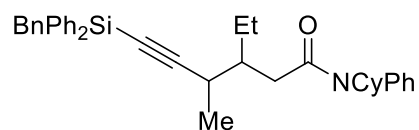
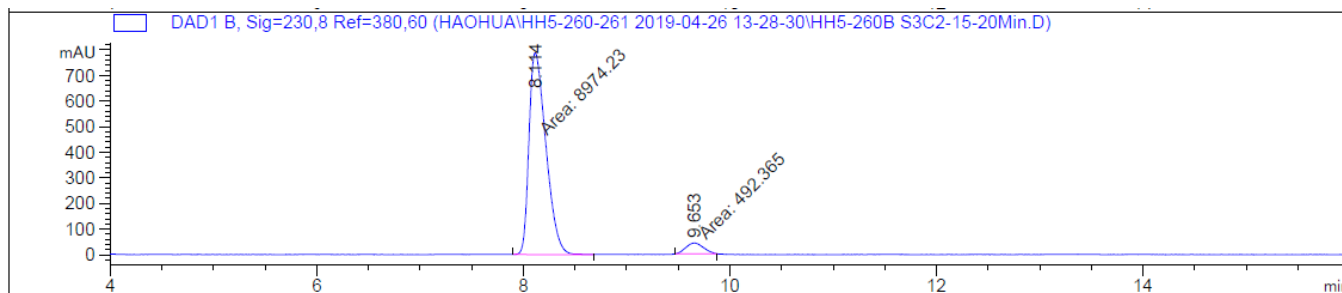


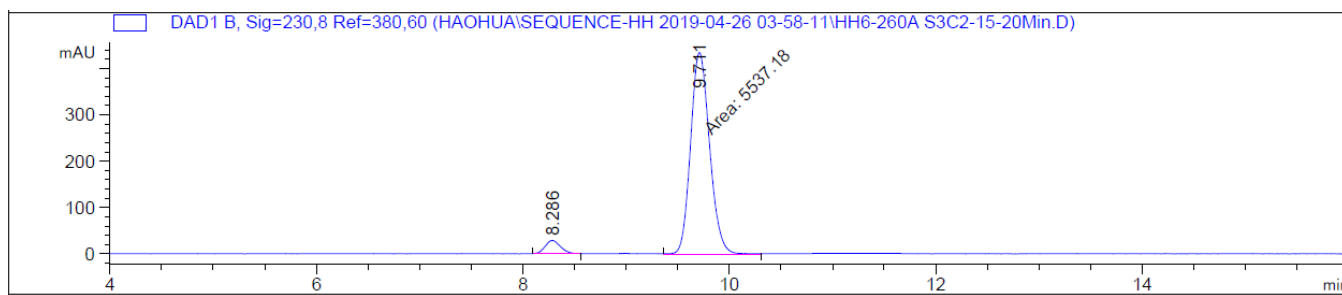
Fig. 3, entry 3

(*R, S*)-L2: 90% ee, > 98:2 dr

(*S, R*)-L2: 90% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.114	MM	0.1898	8974.22656	787.93762	94.7989
2	9.653	MF	0.1967	492.36453	41.70969	5.2011



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.286	BB	0.1562	297.20825	28.60194	5.0941
2	9.711	MM	0.2123	5537.18066	434.64703	94.9059

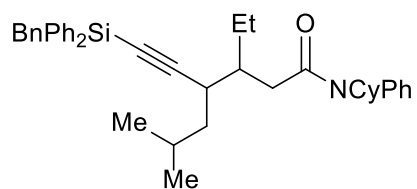
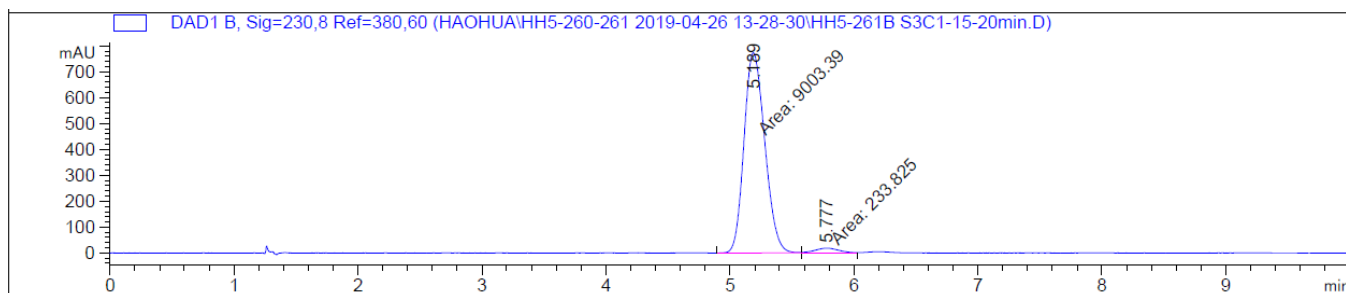


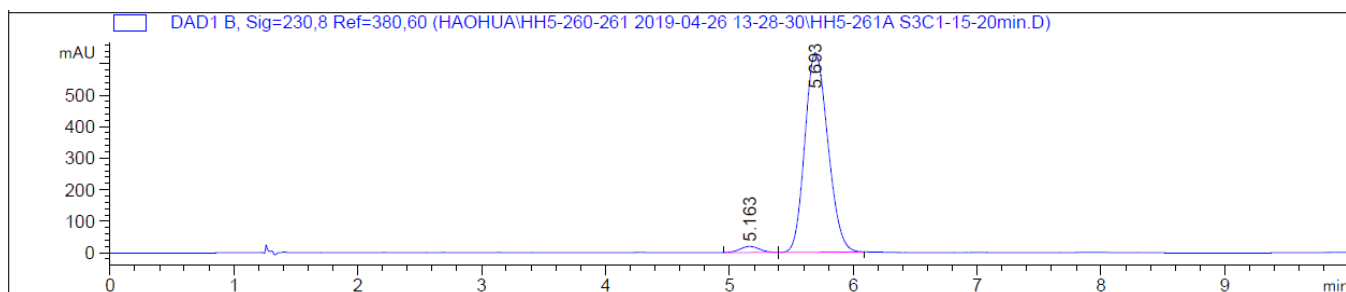
Fig. 3, entry 4

(*R*, *S*)-L2: 95% ee, > 99:1 dr

(*S*, *R*)-L2: 95% ee, > 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.189	MF	0.1942	9003.38574	772.74860	97.4687
2	5.777	FM	0.2158	233.82487	18.06045	2.5313



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.163	BV	0.1452	211.36299	19.39266	2.5154
2	5.693	VB	0.2009	8191.47803	633.12958	97.4846

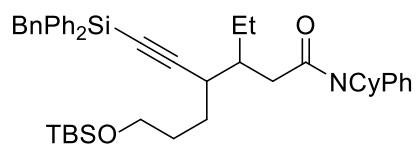
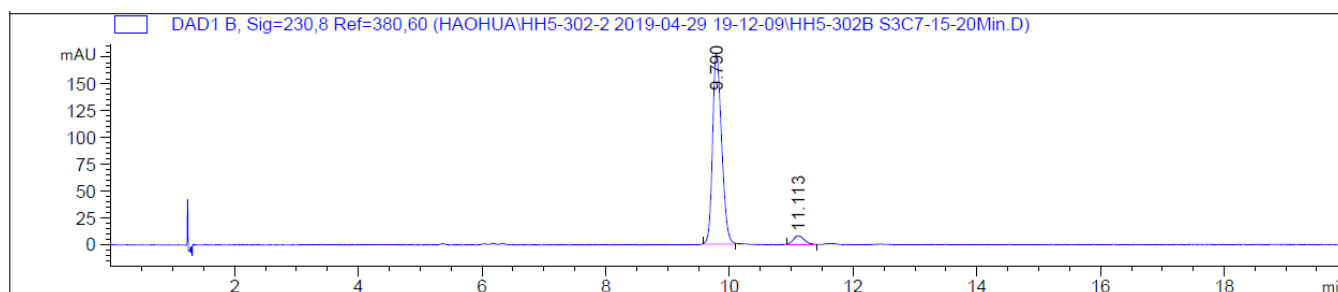


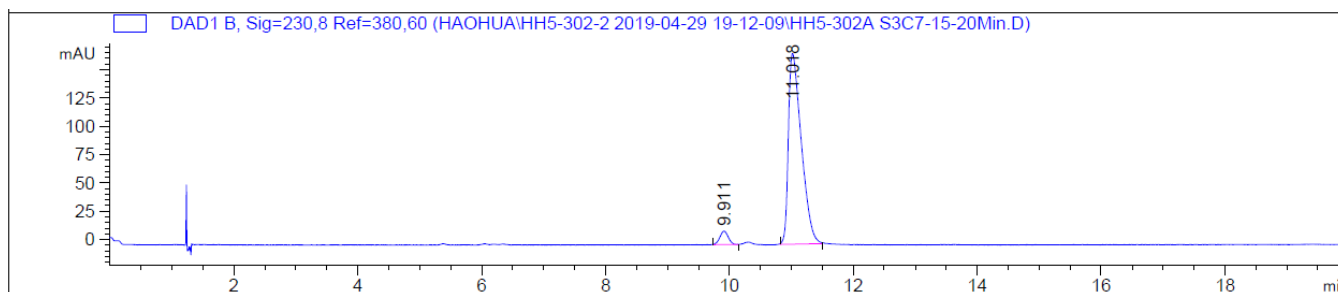
Fig. 3, entry 5

(*R, S*)-L2: 90% ee, 99:1 dr

(*S, R*)-L2: 91% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.790	BB	0.1556	1800.78809	177.11884	94.9238
2	11.113	BB	0.1477	96.30061	8.04014	5.0762



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.911	BB	0.1331	110.49270	11.81952	4.3419
2	11.018	BB	0.2165	2434.31323	168.51039	95.6581

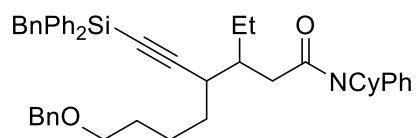
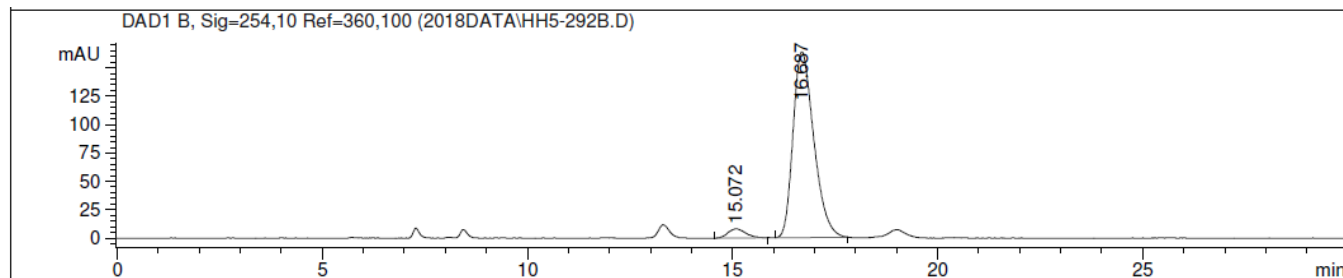


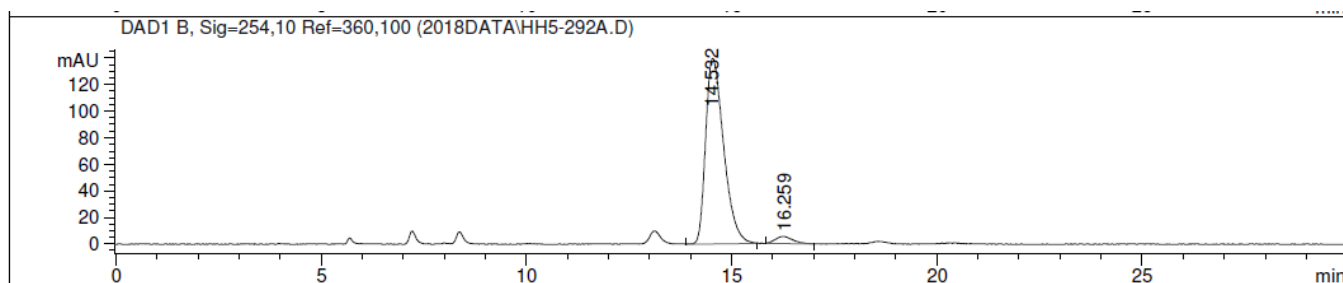
Fig. 3, entry 6

(*R, S*)-**L2**: 92% ee, 98:2 dr

(*S, R*)-**L2**: 92% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.072	BV	0.3758	245.91463	8.01758	4.0745
2	16.687	BB	0.5426	5789.47559	163.70665	95.9255



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.532	VB	0.4658	4261.93945	139.76065	96.3888
2	16.259	BP	0.3549	159.67401	5.43326	3.6112

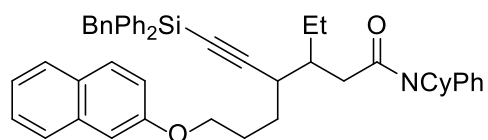
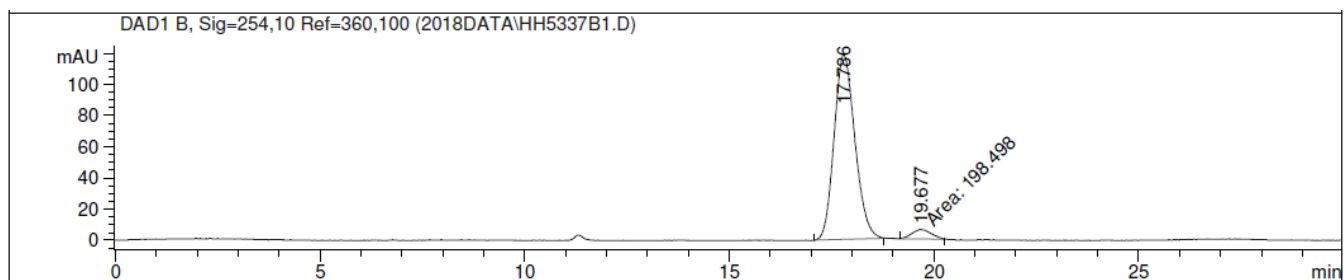


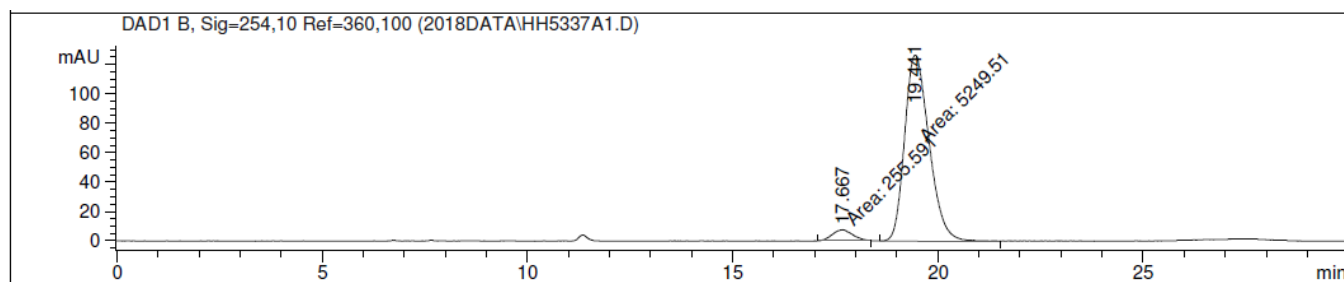
Fig. 3, entry 7

(*R, S*)-L2: 91% ee, > 99:1 dr

(*S, R*)-L2: 91% ee, > 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.786	PB	0.5091	4194.02734	118.44603	95.4810
2	19.677	MM	0.5537	198.49843	5.97478	4.5190



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.667	MM	0.5752	255.59073	7.40575	4.6428
2	19.441	MM	0.6910	5249.51318	126.61031	95.3572

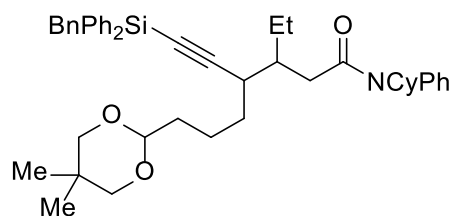
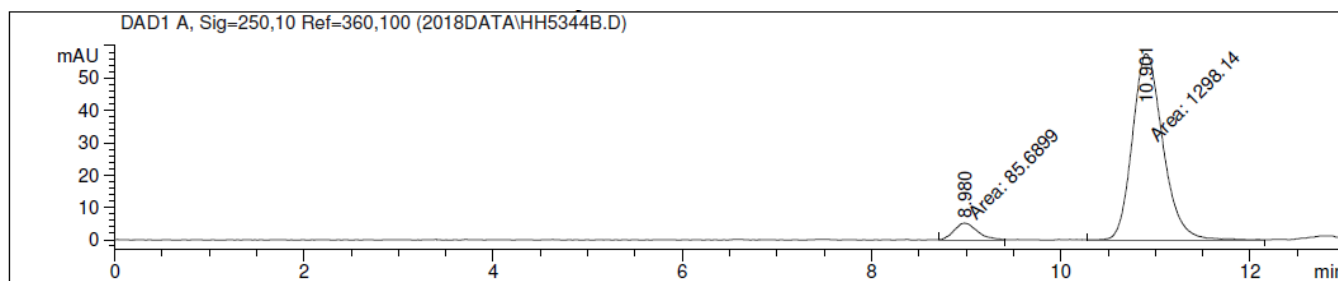


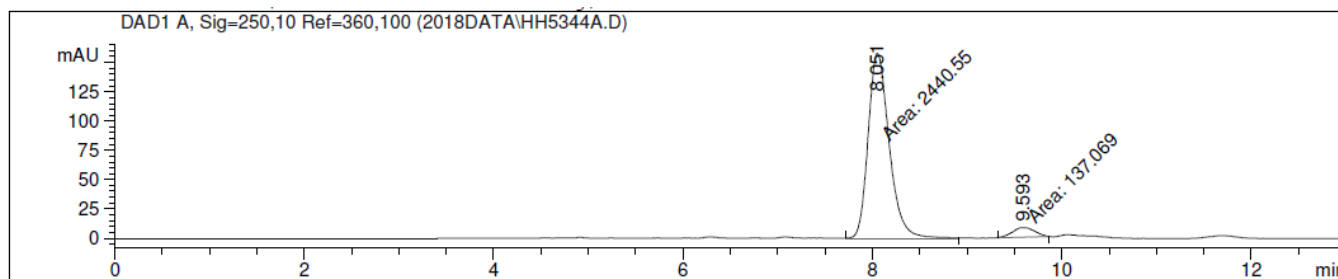
Fig. 3, entry 8

(*R*, *S*)-L2: 88% ee, 98:2 dr

(*S*, *R*)-L2: 89% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.980	MM	0.2804	85.68993	5.09396	6.1922
2	10.901	MM	0.3751	1298.14075	57.68417	93.8078



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.051	MM	0.2575	2440.55347	157.97403	94.6823
2	9.593	MM	0.2741	137.06897	8.33478	5.3177

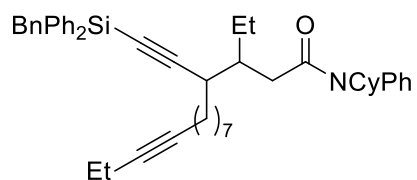
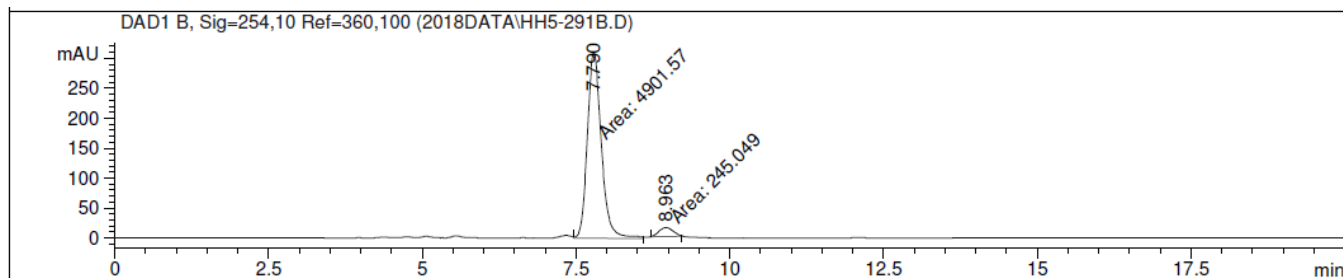


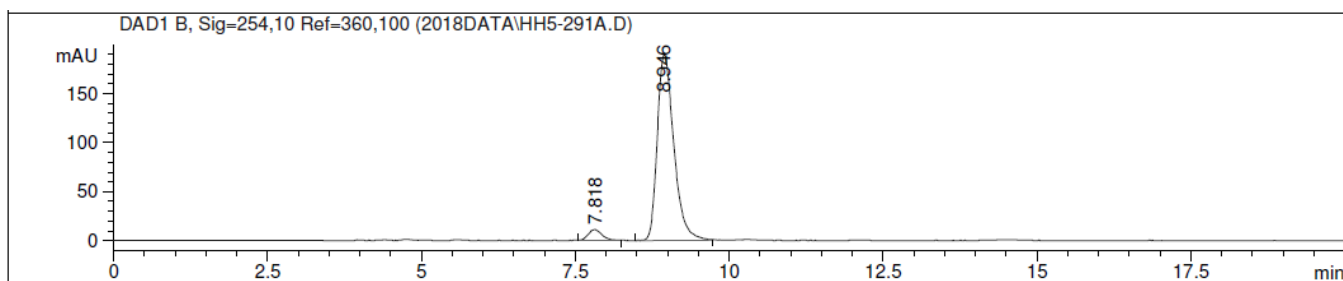
Fig. 3, entry 9

(*R, S*)-L2: 90% ee, 99:1 dr

(*S, R*)-L2: 91% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.790	FM	0.2633	4901.56885	310.24072	95.2386
2	8.963	MM	0.2672	245.04887	15.28270	4.7614



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.818	BB	0.2230	172.03061	11.08746	4.6277
2	8.946	PB	0.2859	3545.36719	189.85799	95.3723

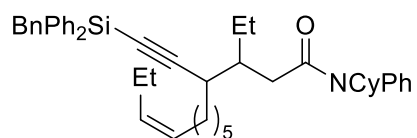
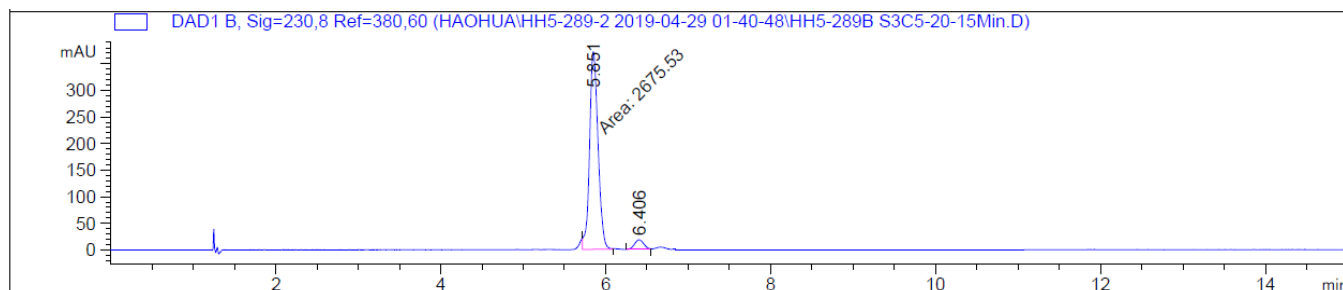


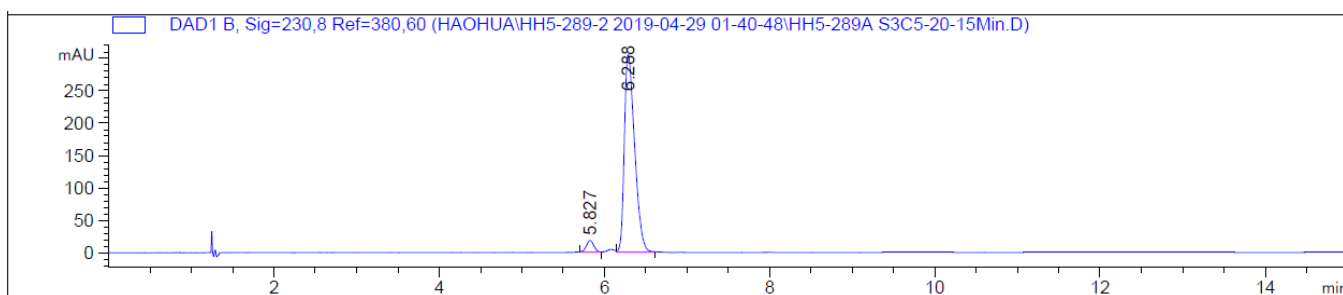
Fig. 3, entry 10

(*R, S*)-**L2**: 90% ee, 98:2 dr

(*S, R*)-**L2**: 92% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.851	FM	0.1200	2675.53271	371.54953	94.9167
2	6.406	BV	0.1237	143.28914	18.02649	5.0833



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.827	BV	0.1000	115.52668	17.95897	4.1899
2	6.288	VB	0.1332	2641.76978	304.43903	95.8101

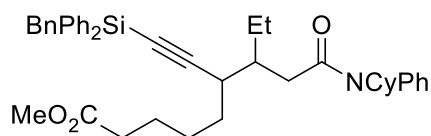
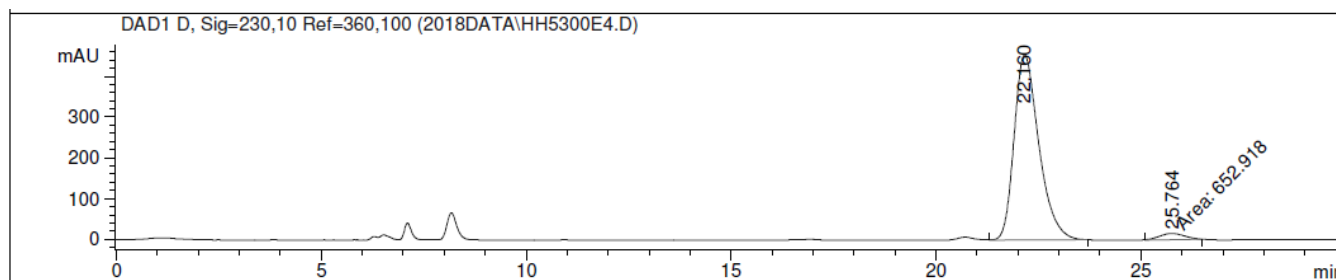


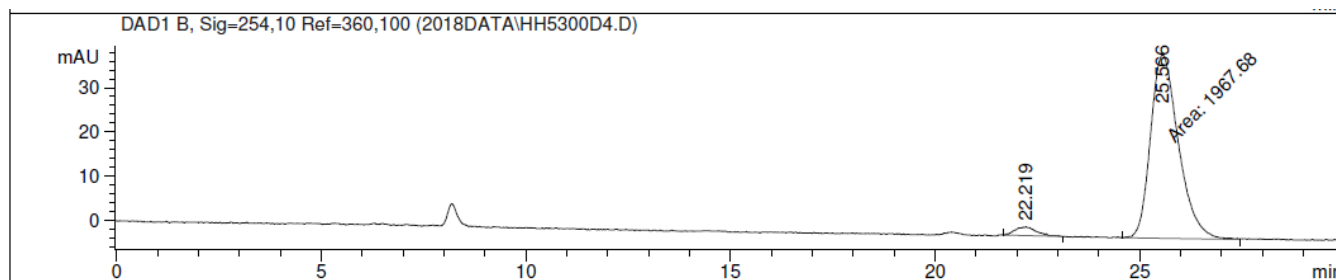
Fig. 3, entry 11

(*R, S*)-**L2**: 93% ee, > 99:1 dr

(*S, R*)-**L2**: 93% ee, > 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.160	VB	0.6207	1.91275e4	454.73895	96.6992
2	25.764	MM	0.7121	652.91833	15.28252	3.3008



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.219	BB	0.4375	74.08813	2.02177	3.6286
2	25.566	MM	0.7905	1967.68433	41.48523	96.3714

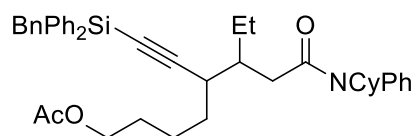
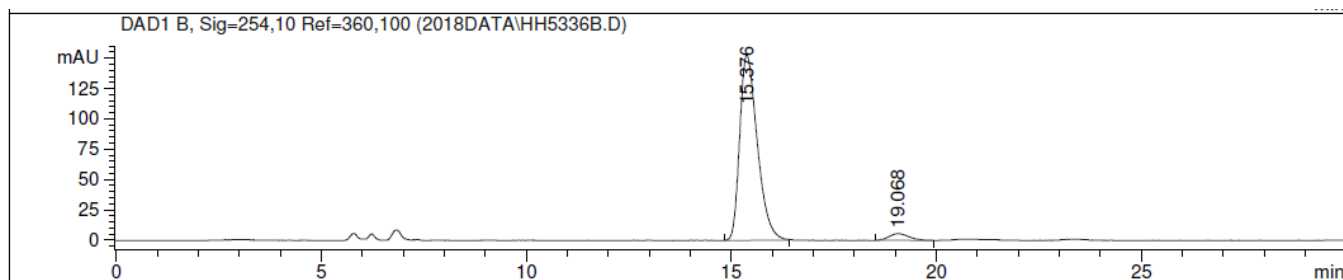


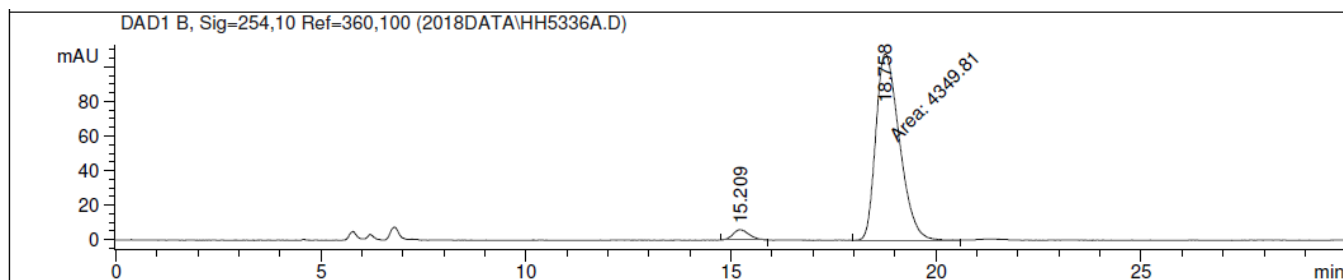
Fig. 3, entry 12

(*R, S*)-L2: 92% ee, 99:1 dr

(*S, R*)-L2: 92% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.376	BB	0.4558	4545.45996	152.45607	96.0171
2	19.068	BP	0.4018	188.55324	5.55843	3.9829



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.209	BB	0.3307	165.24933	6.08727	3.6600
2	18.758	MM	0.6712	4349.81006	108.00600	96.3400

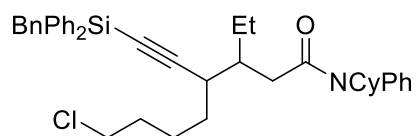
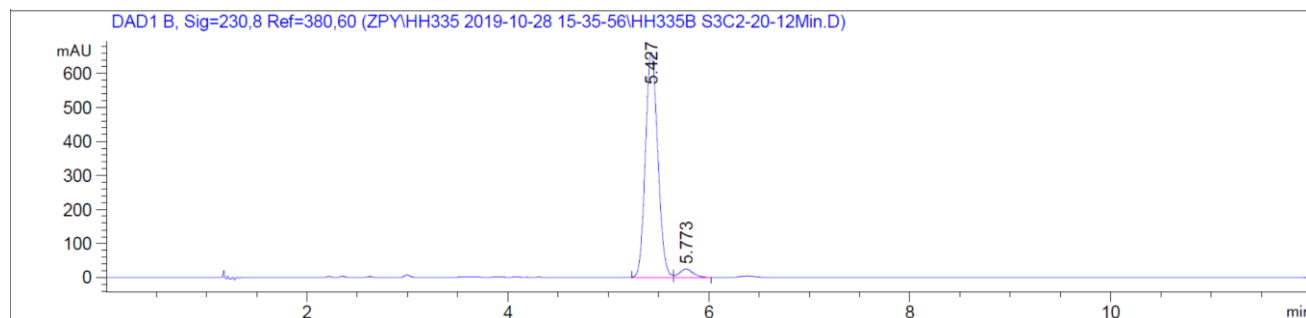
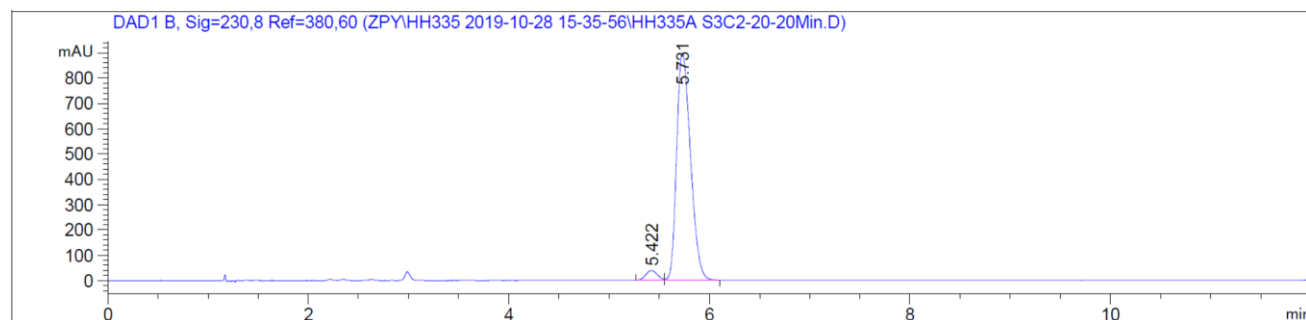


Fig. 3, entry 13

(*R, S*)-L2: 92% ee, > 99:1 dr
 (*S, R*)-L2: 93% ee, > 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.427	BV	0.1338	5655.95801	661.21362	96.0842
2	5.773	VB	0.1464	230.49934	24.58732	3.9158



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.422	BV	0.1262	314.85098	38.97953	3.5197
2	5.731	VB	0.1501	8630.61328	898.28967	96.4803

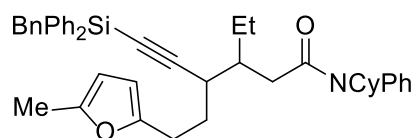
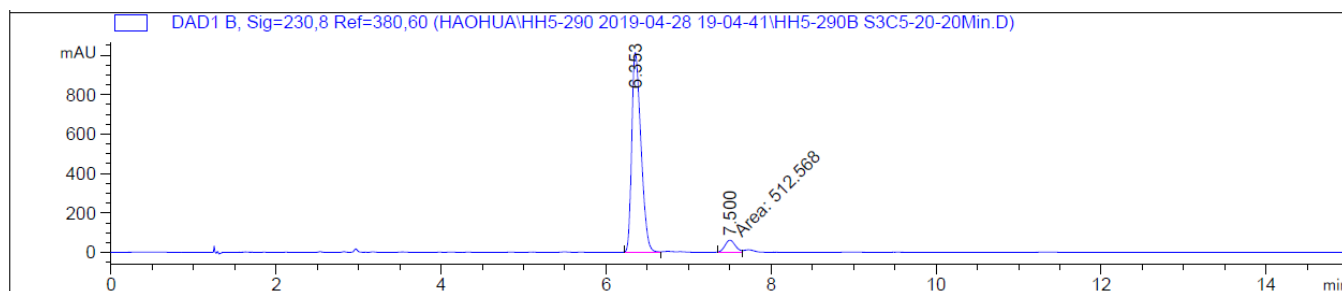


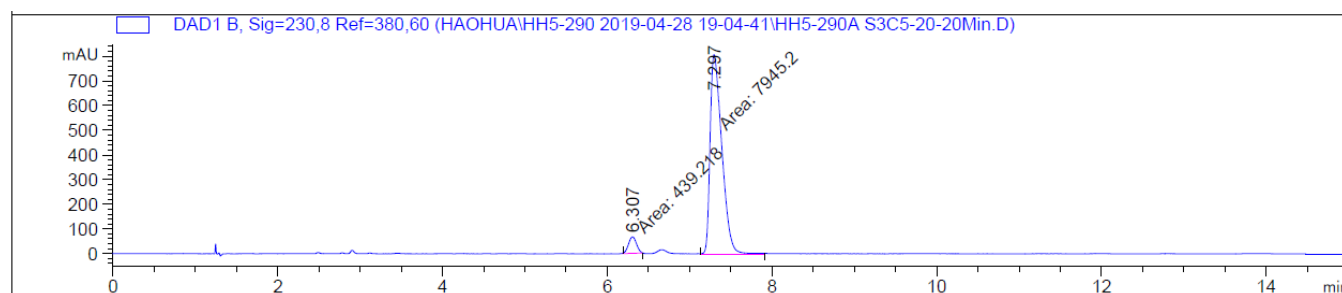
Fig. 3, entry 14

(*R, S*)-**L2**: 88% ee, 98:2 dr

(*S, R*)-**L2**: 90% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.353	BB	0.1226	7953.91162	1013.52124	93.9459
2	7.500	MM	0.1425	512.56824	59.95388	6.0541



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.307	MM	0.1099	439.21790	66.60959	5.2385
2	7.297	MM	0.1641	7945.20410	807.09216	94.7615

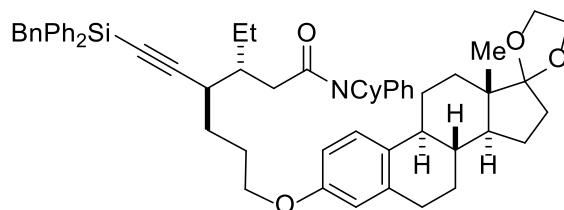
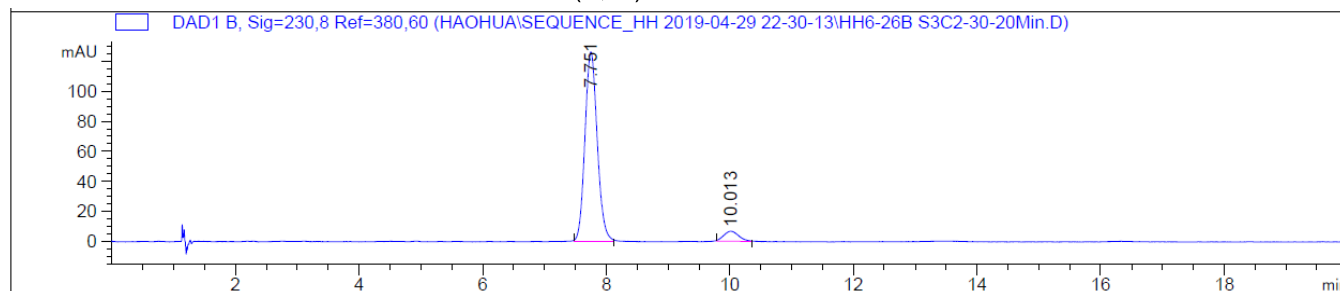


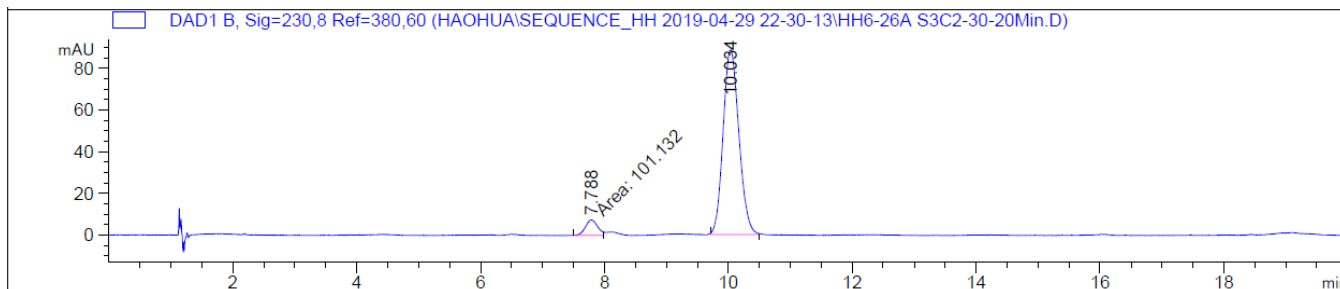
Fig. 3, entry 15

(*R, S*)-L2: 6:94 dr

(*S, R*)-L2: 94:6 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.751	BB	0.2142	4089.90405	295.98825	93.6441
2	10.012	BB	0.2200	277.59174	15.79754	6.3559



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.788	MF	0.2262	101.13154	7.45179	6.0650
2	10.034	BB	0.2666	1566.34094	88.44498	93.9350

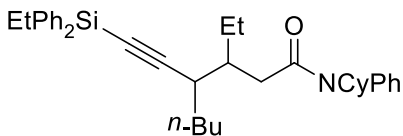
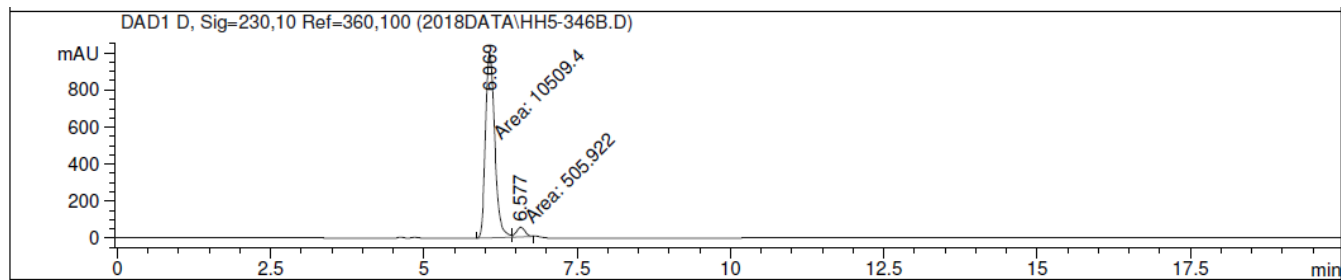


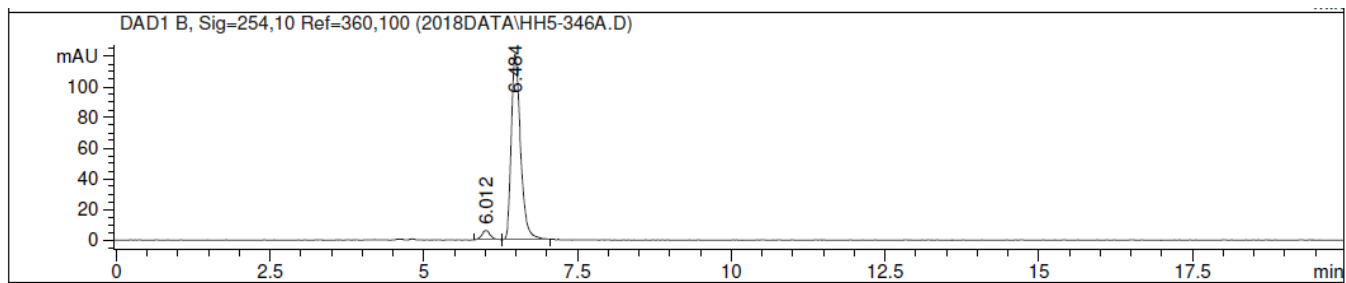
Fig. 3, entry 16

(R, S)-L2: 91% ee, 99:1 dr

(S, R)-L2: 91% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.069	MF	0.1751	1.05094e4	1000.44800	95.4071
2	6.577	FM	0.1632	505.92163	51.65547	4.5929



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.012	BV	0.1435	59.23421	6.08713	4.4310
2	6.484	VB	0.1629	1277.57434	121.31680	95.5690

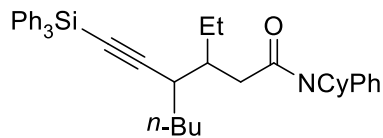
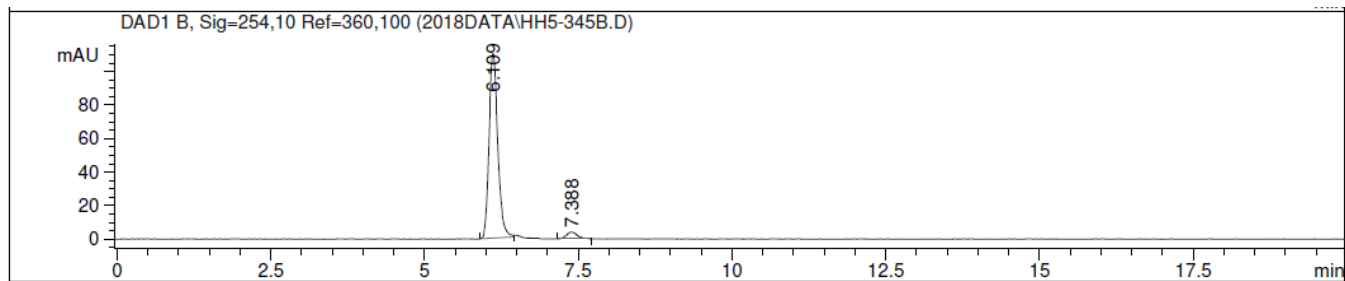


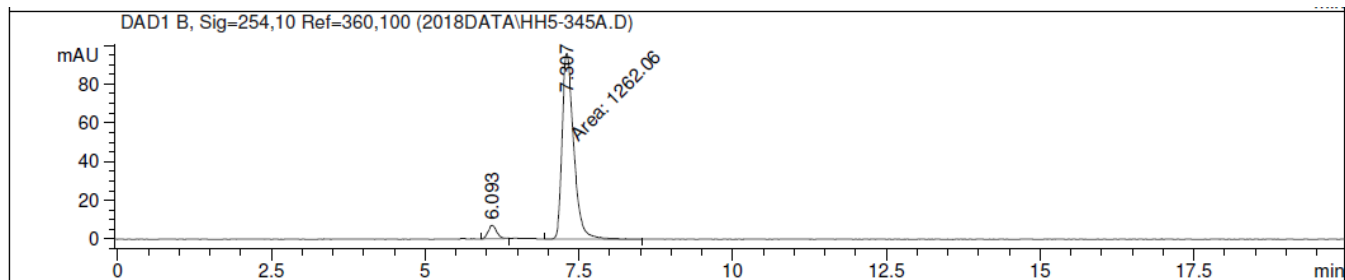
Fig. 3, entry 17

(*R, S*)-L2: 91% ee, 99:1 dr

(*S, R*)-L2: 90% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.109	PB	0.1502	1081.15784	110.45470	95.6782
2	7.388	PB	0.1918	48.83641	3.90664	4.3218



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.093	PB	0.1458	66.29360	6.92073	4.9907
2	7.307	MM	0.2190	1262.05994	96.04848	95.0093

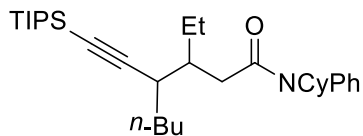
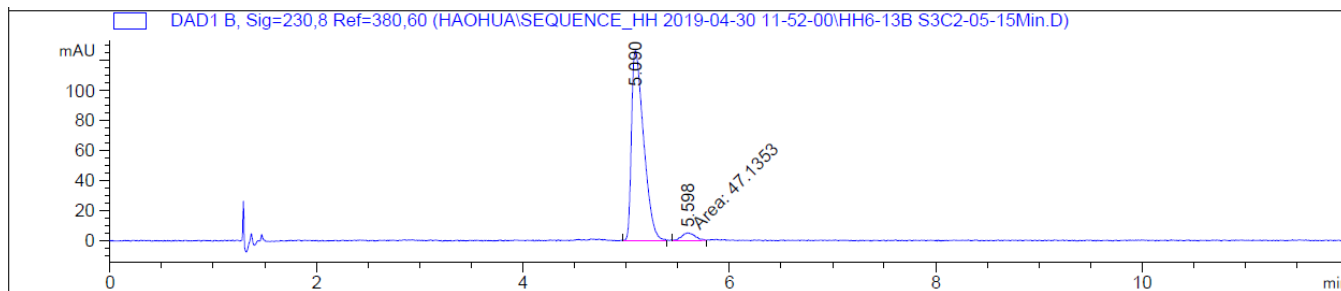


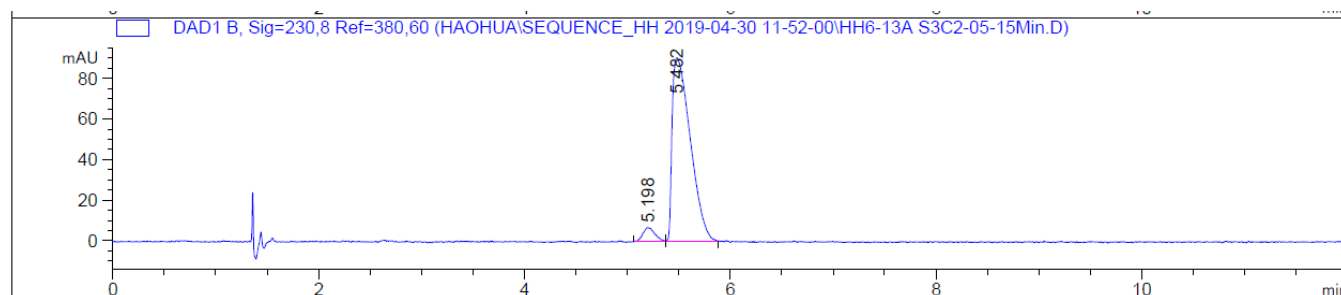
Fig. 3, entry 18

(*R, S*)-L2: 91% ee, > 99:1 dr

(*S, R*)-L2: 90% ee, > 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.090	BB	0.1183	1033.43567	126.45186	95.6379
2	5.598	MM	0.1497	47.13532	5.24899	4.3621



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.198	BV	0.1053	58.68774	6.96459	5.0158
2	5.482	VB	0.1640	1111.36292	90.64331	94.9842

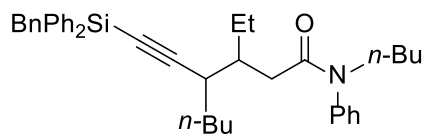
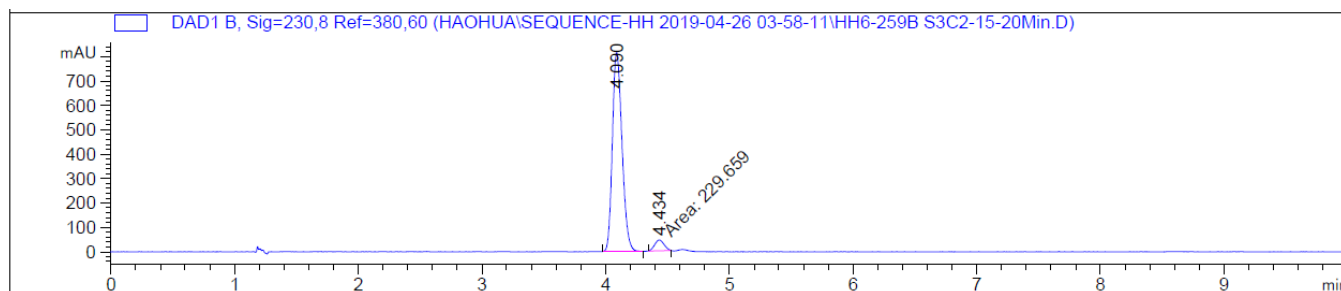


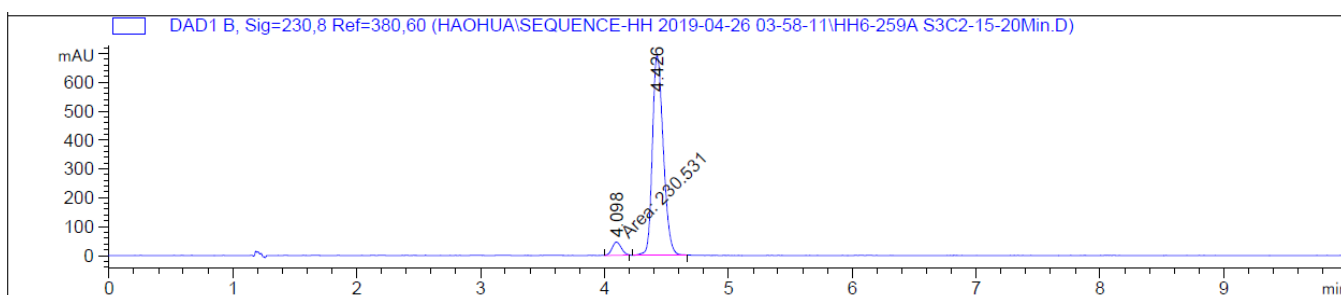
Fig. 3, entry 19

(*R, S*)-L2: 90% ee, > 98:2 dr

(*S, R*)-L2: 90% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.090	BB	0.0833	4427.55664	816.14252	95.0688
2	4.434	MM	0.0874	229.65891	43.80948	4.9312



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.098	MM	0.0846	230.53091	45.41285	5.1543
2	4.426	VB	0.0946	4242.07080	691.33716	94.8457

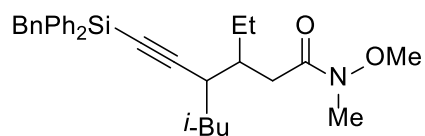
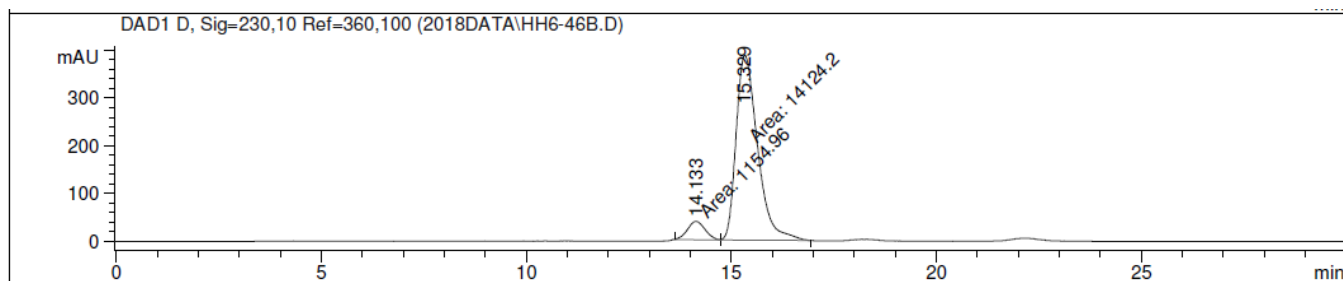


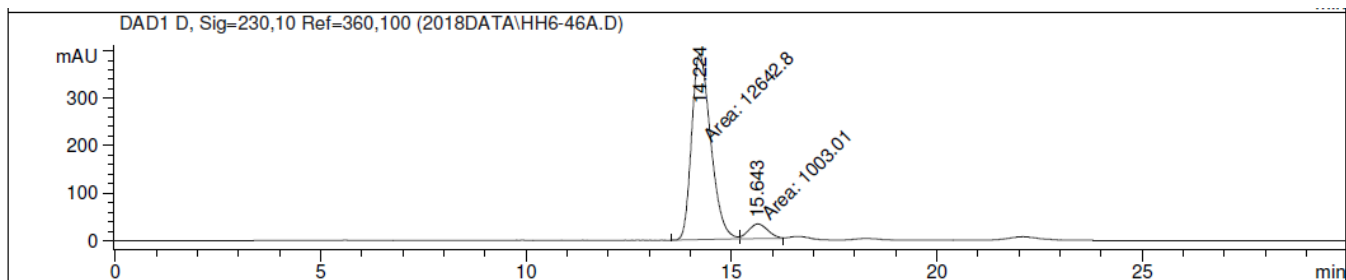
Fig. 3, entry 20

(*R, S*)-**L2**: 85% ee, 95:5 dr

(*S, R*)-**L2**: 85% ee, 95:5 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.133	MF	0.5013	1154.95984	38.39871	7.5591
2	15.329	FM	0.6080	1.41242e4	387.19122	92.4409



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.224	MF	0.5400	1.26428e4	390.19135	92.6497
2	15.643	FM	0.5386	1003.01074	31.03501	7.3503

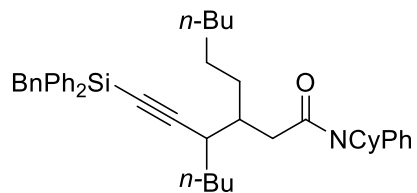
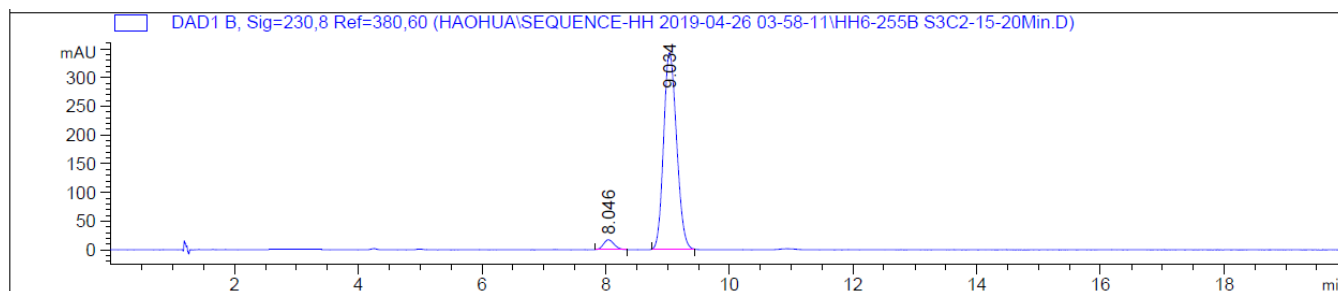


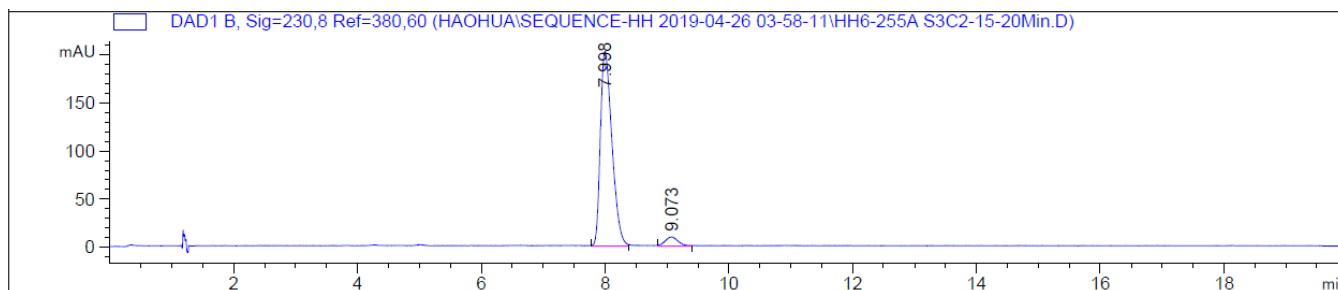
Fig. 3, entry 21

(*R, S*)-L2: 92% ee, > 98:2 dr

(*S, R*)-L2: 91% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.046	BB	0.1538	208.33769	17.38596	3.9758
2	9.034	BB	0.2281	5031.85400	343.08701	96.0242



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.998	BB	0.1957	2609.73853	202.04404	95.5082
2	9.073	BB	0.1630	122.73770	9.00666	4.4918

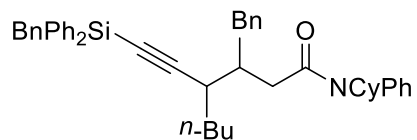
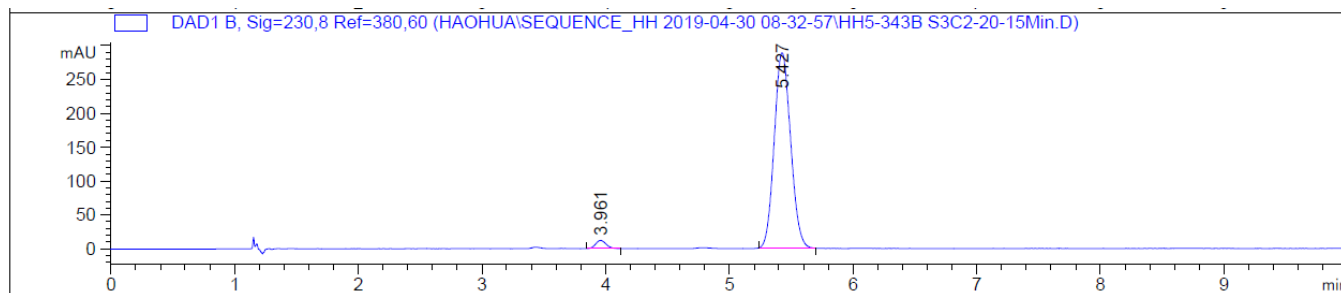


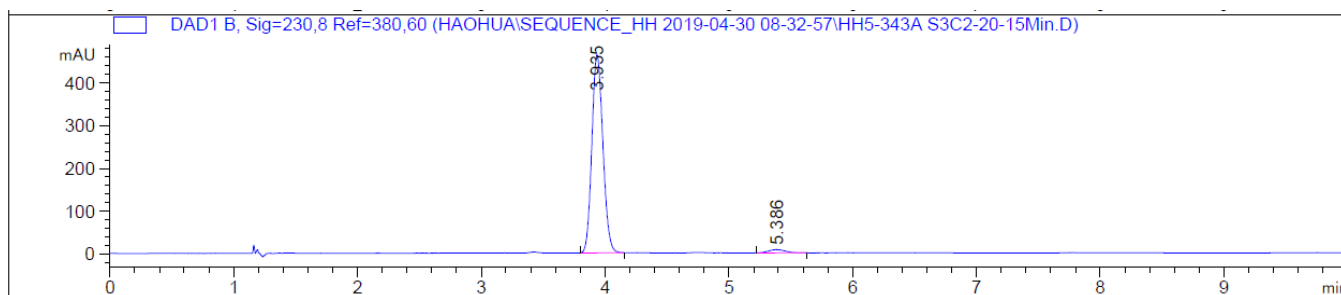
Fig. 3, entry 22

(*R*, *S*)-L2: 95% ee, 97:3 dr

(*S*, *R*)-L2: 95% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.961	BB	0.0911	70.91908	11.97805	2.5924
2	5.427	BB	0.1436	2664.73804	288.94193	97.4076



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.935	BB	0.0976	2880.86914	463.21490	97.5099
2	5.386	BB	0.1412	73.56854	7.71943	2.4901

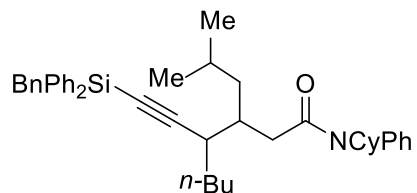
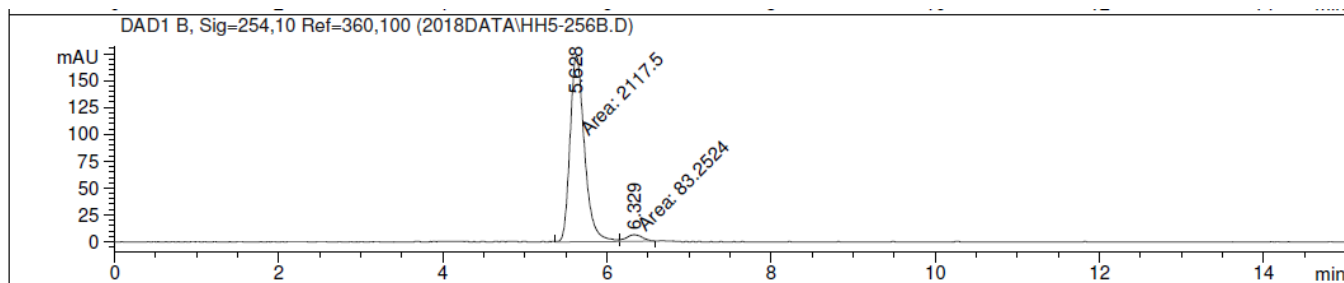


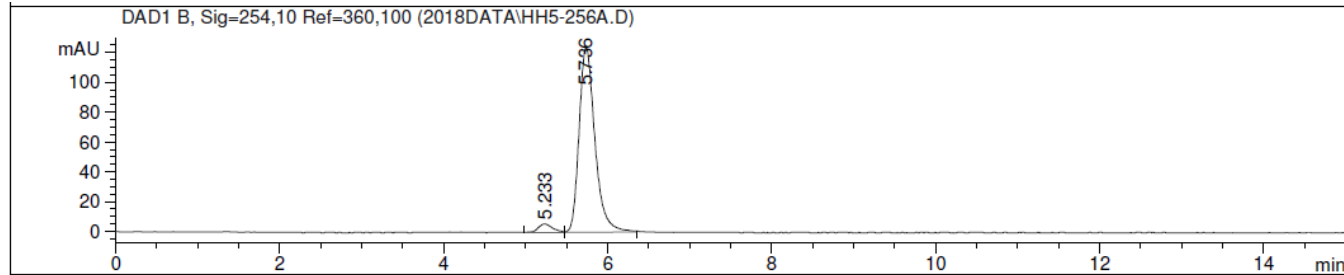
Fig. 3, entry 23

(*R, S*)-**L2**: 92% ee, 98:2 dr

(*S, R*)-**L2**: 92% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.628	MF	0.2039	2117.49951	173.04588	96.2171
2	6.329	FM	0.2249	83.25245	6.16859	3.7829



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.233	PV	0.1844	68.13961	5.58114	3.9524
2	5.736	VB	0.2042	1655.87561	123.70893	96.0476

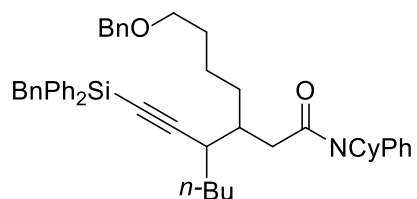
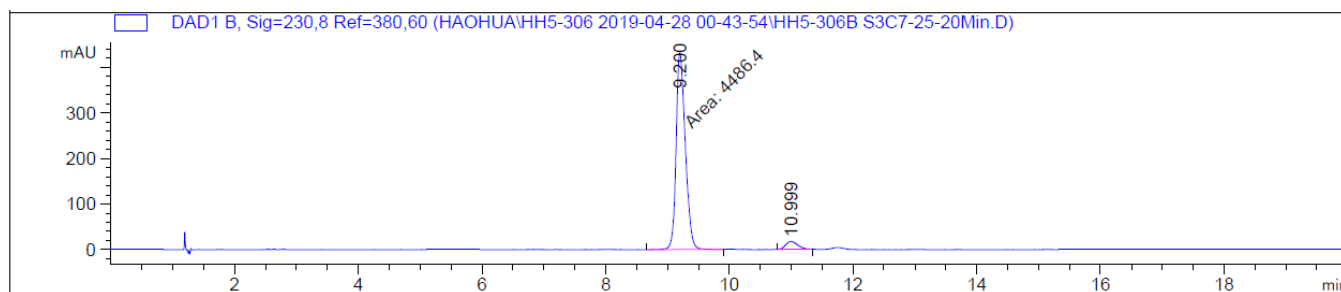


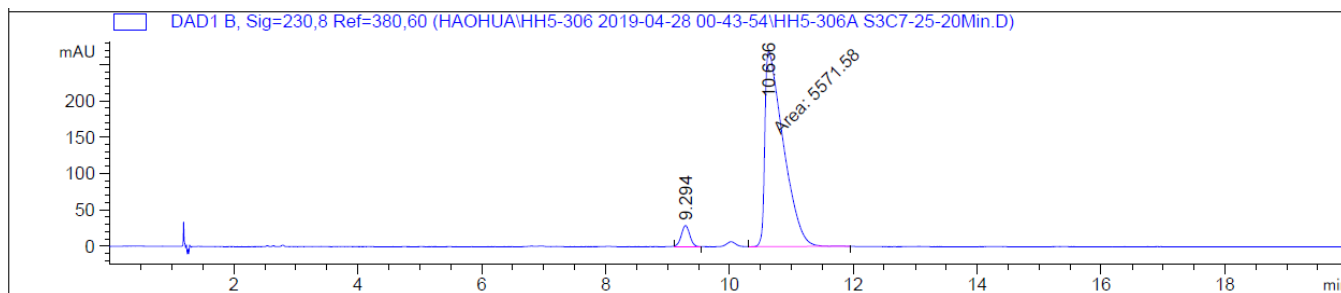
Fig. 3, entry 24

(*R*, *S*)-L2: 90% ee, 99:1 dr

(*S*, *R*)-L2: 91% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.200	MM	0.1729	4486.39844	432.58475	94.8829
2	10.999	BB	0.1864	241.95425	17.37869	5.1171



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.294	BB	0.1471	274.24615	28.80949	4.6913
2	10.636	MM	0.3460	5571.58154	268.35049	95.3087

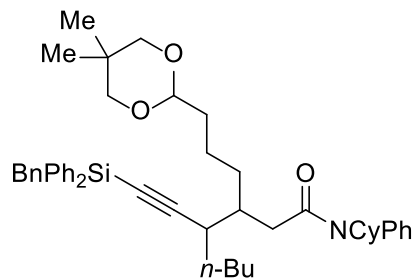
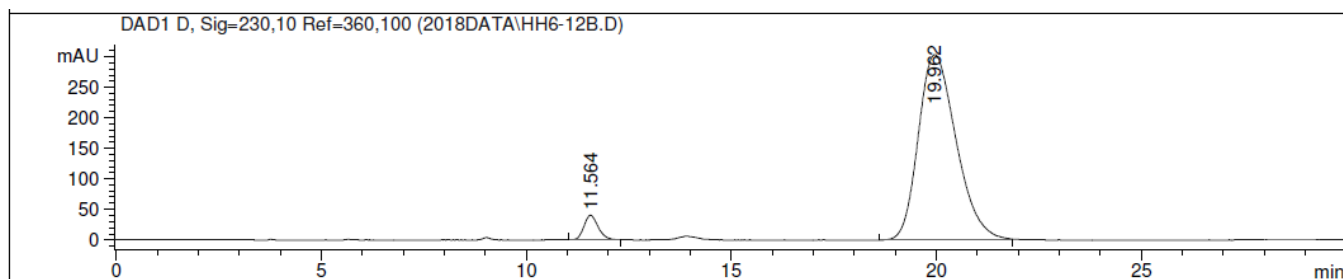


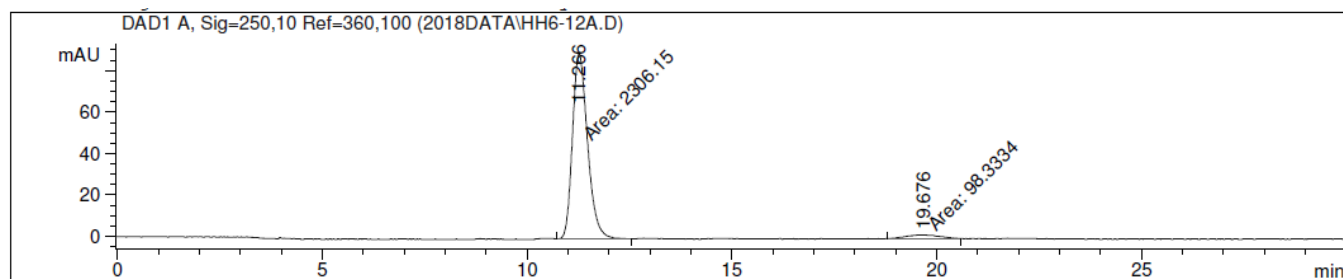
Fig. 3, entry 25

(*R*, *S*)-**L2**: 91% ee, 99:1 dr

(*S*, *R*)-**L2**: 91% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.564	PP	0.3686	969.87494	40.32307	4.7264
2	19.962	VV	0.8158	1.95505e4	303.38251	95.2736



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.266	MM	0.4296	2306.14893	89.46655	95.9104
2	19.676	MM	0.9028	98.33344	1.81536	4.0896

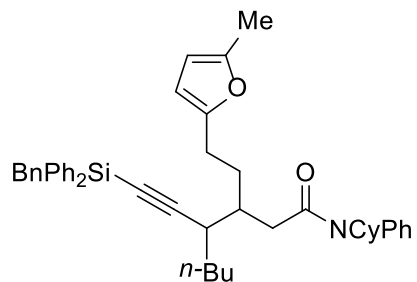
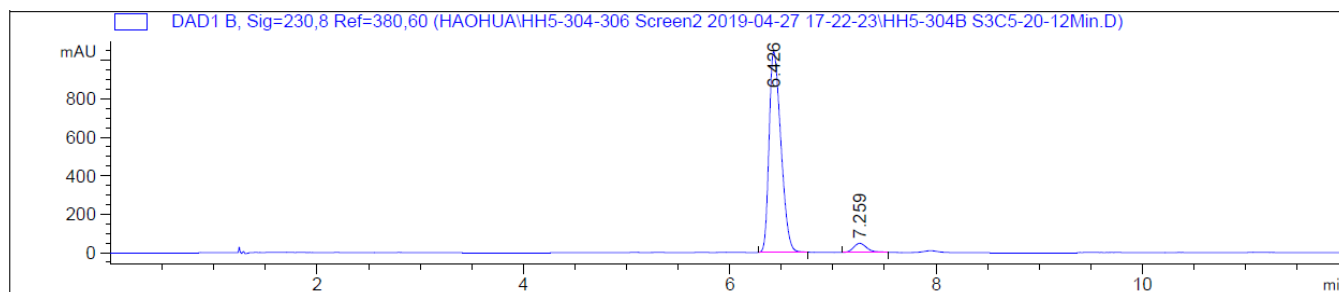


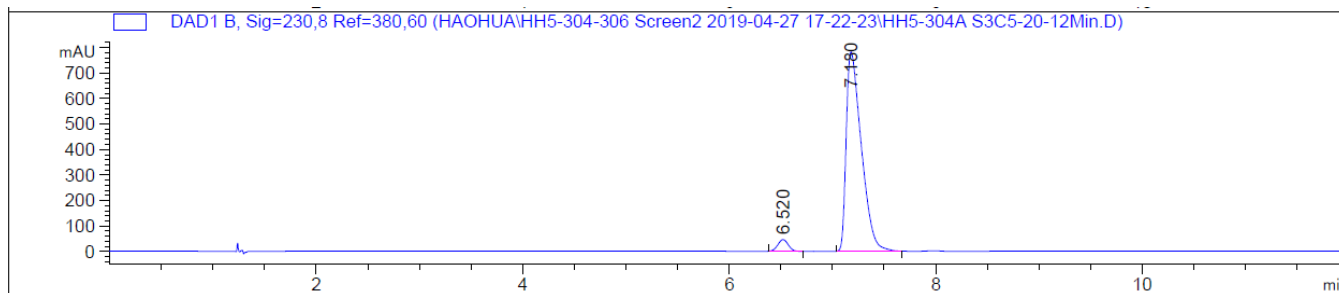
Fig. 3, entry 26

(*R, S*)-L2: 90% ee, > 98:2 dr

(*S, R*)-L2: 92% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.426	BB	0.1238	8314.35547	1044.91443	94.9947
2	7.259	BB	0.1416	438.08731	47.48899	5.0053



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.520	BB	0.1125	331.56189	46.34523	4.0065
2	7.180	BB	0.1534	7944.01123	782.57294	95.9935

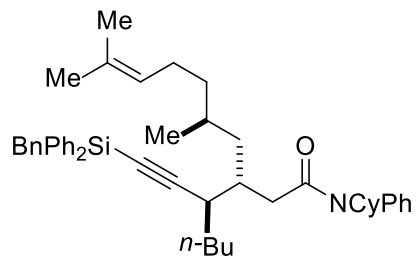
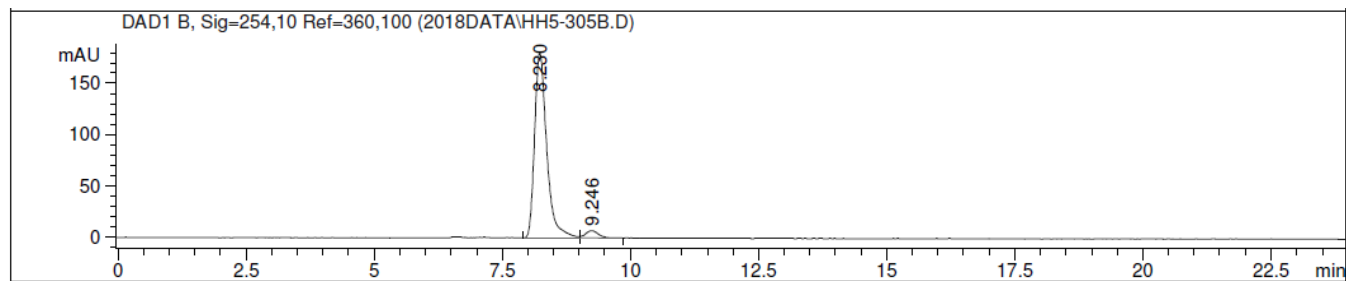


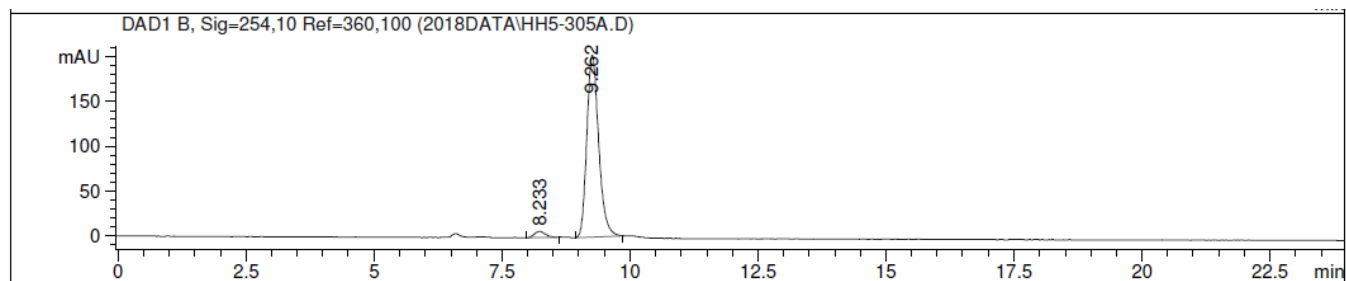
Fig. 3, entry 27

(*R, S*)-L2: 96:4 dr

(*S, R*)-L2: 3:97 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.230	PB	0.2508	2985.13110	180.67819	95.8103
2	9.246	BP	0.2455	130.53818	7.27050	4.1897



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.233	PB	0.1965	100.15603	6.77379	2.9661
2	9.262	PB	0.2497	3276.58105	203.60698	97.0339

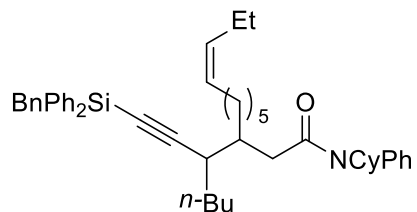
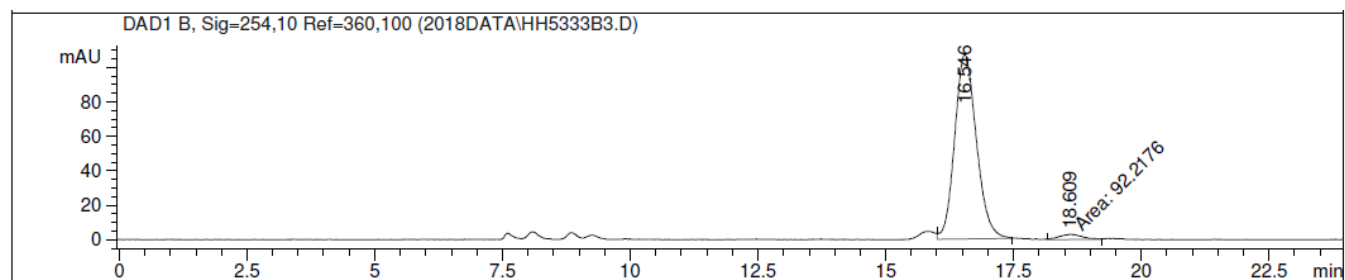


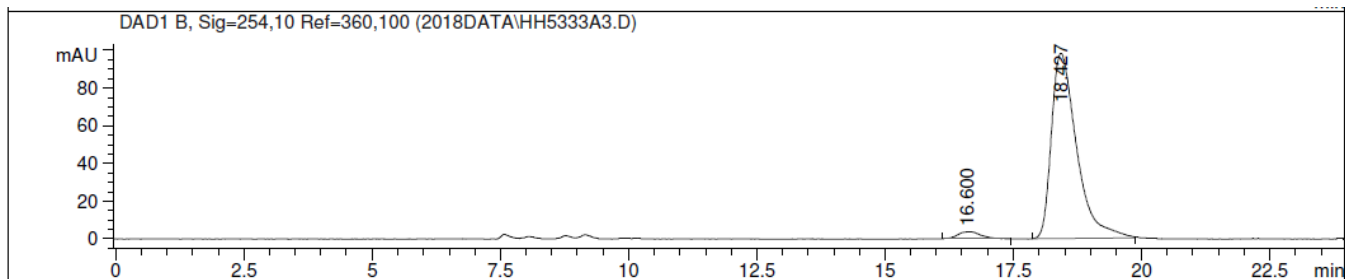
Fig. 3, entry 28

(*R, S*)-**L2**: 94% ee, 98:2 dr

(*S, R*)-**L2**: 93% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.546	VB	0.4538	3173.44067	107.06248	97.1761
2	18.609	MM	0.5317	92.21758	2.89063	2.8239



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.600	PB	0.3725	118.27164	3.80622	3.4041
2	18.427	PB	0.5166	3356.09863	98.23062	96.5959

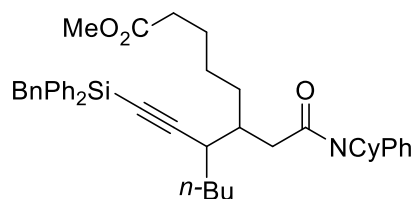
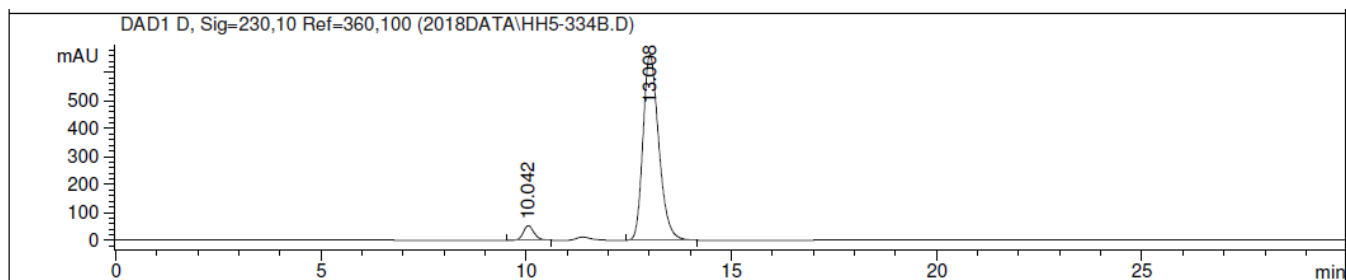


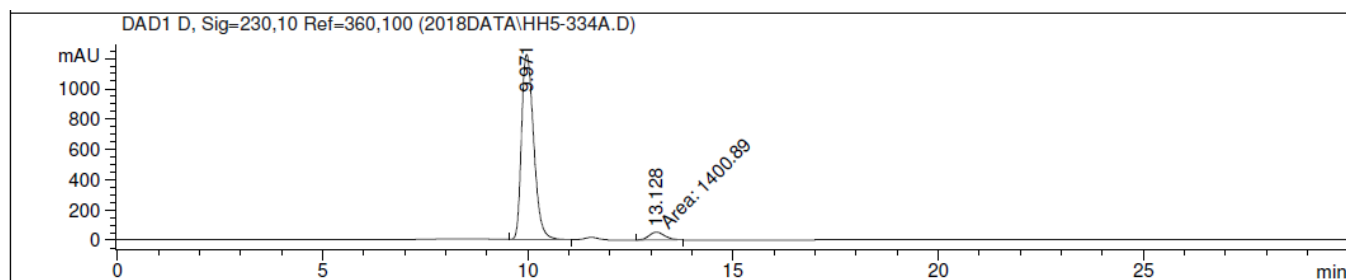
Fig. 3, entry 29

(*R, S*)-L2: 90% ee, 98:2 dr

(*S, R*)-L2: 90% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.042	PB	0.2811	968.60443	52.52682	5.1800
2	13.008	VB	0.4178	1.77305e4	663.40344	94.8200



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.971	VV	0.3317	2.56206e4	1226.38257	94.8156
2	13.128	MM	0.4471	1400.89392	52.22348	5.1844

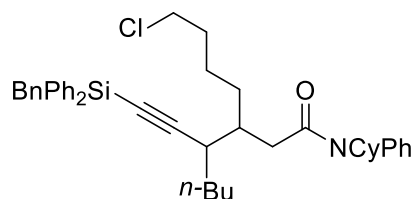
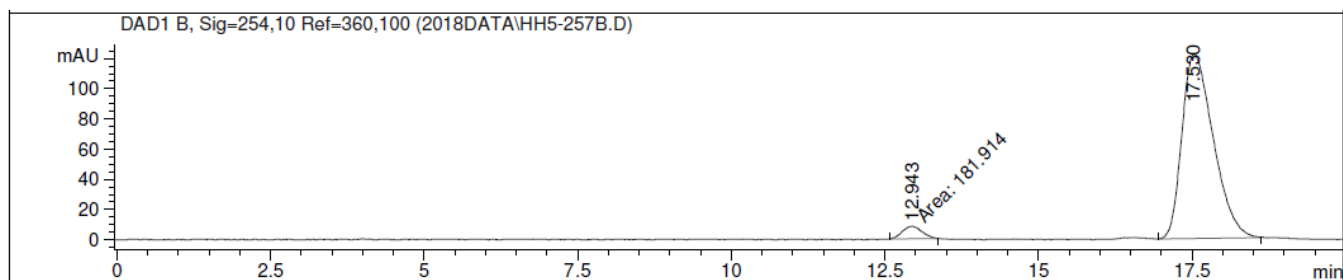


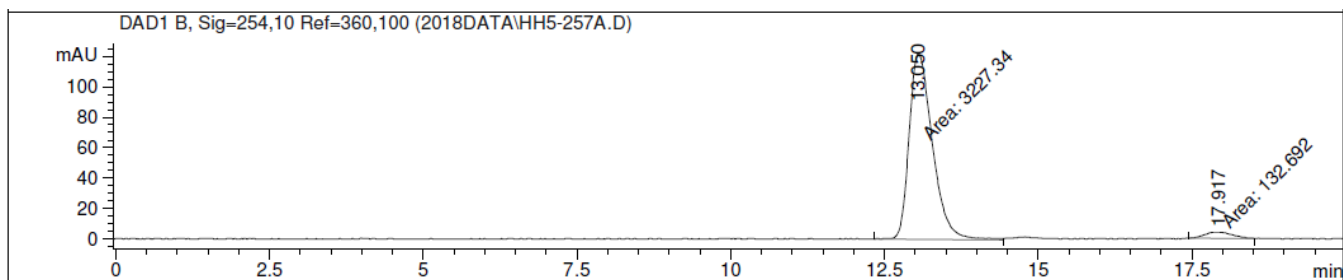
Fig. 3, entry 30

(R, S)-L2: 92% ee, > 98:2 dr

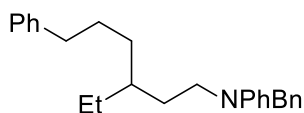
(S, R)-L2: 92% ee, > 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.943	MM	0.3688	181.91414	8.21989	4.0162
2	17.530	BB	0.5226	4347.61865	122.32846	95.9838



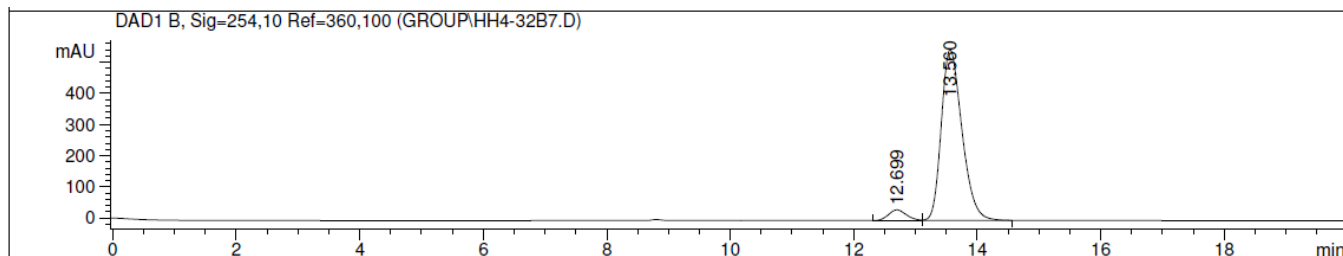
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.050	MM	0.4384	3227.33594	122.69933	96.0509
2	17.917	MM	0.5202	132.69205	4.25145	3.9491



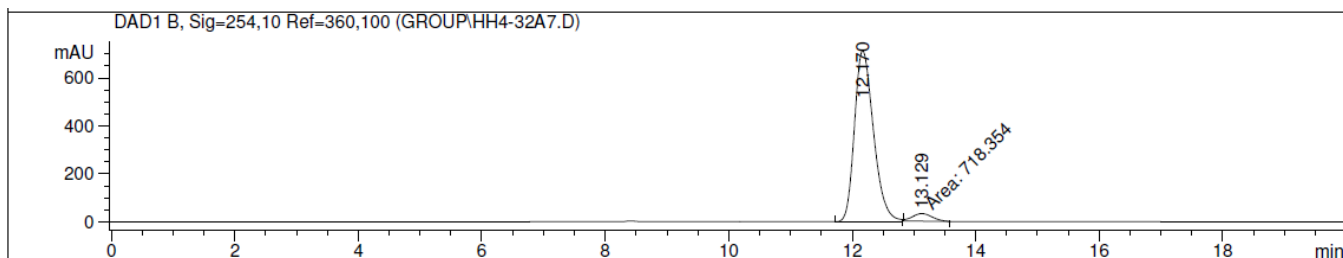
the top of Fig. 4

(*R*)-L1: 90% ee

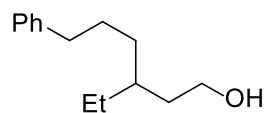
(*S*)-L1: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.699	BV	0.3156	685.78162	33.96115	5.1008
2	13.560	VB	0.3593	1.27589e4	548.72260	94.8992



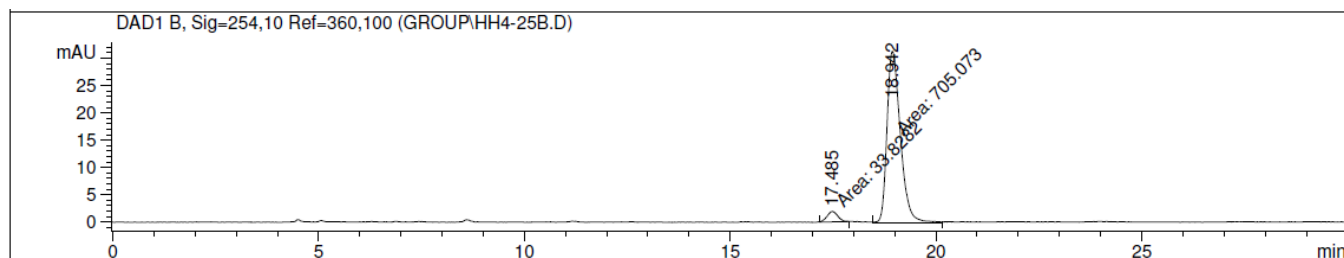
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.170	BV	0.3301	1.53084e4	714.08051	95.5178
2	13.129	MM	0.3724	718.35370	32.15259	4.4822



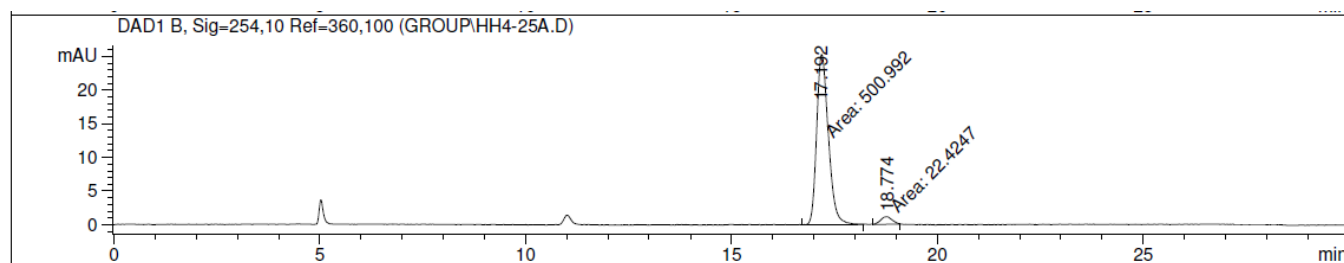
the top of Fig. 4

(*R*)-L1: 91% ee

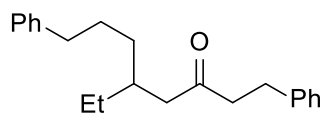
(*S*)-L1: 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.485	MM	0.2987	33.82821	1.88753	4.5782
2	18.942	MM	0.3748	705.07263	31.35424	95.4218



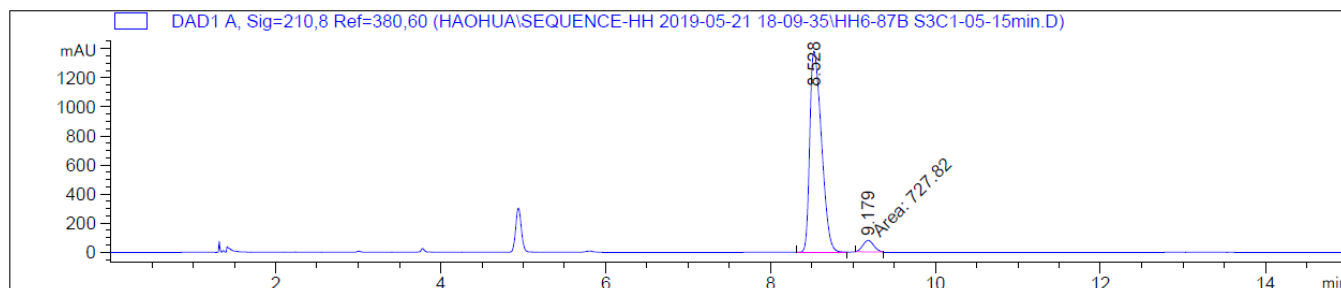
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.192	MM	0.3297	500.99216	25.32614	95.7157
2	18.774	MM	0.3269	22.42470	1.14313	4.2843



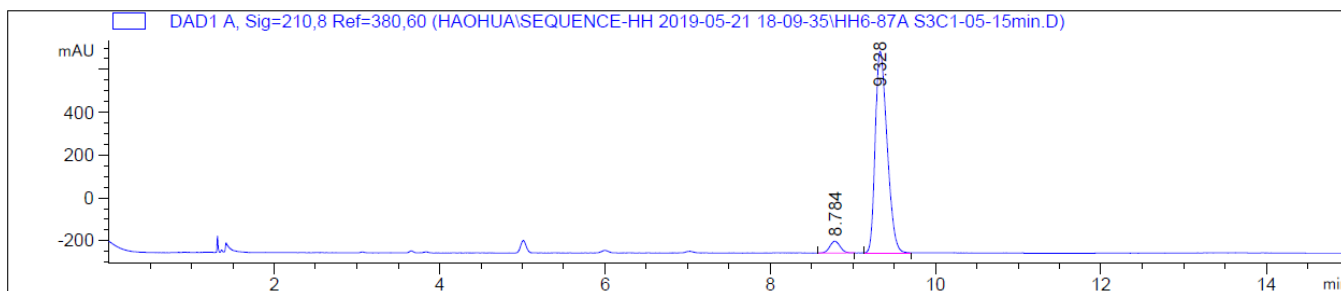
the top of **Fig. 4**

(*R*)-L1: 90% ee

(*S*)-L1: 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.528	BB	0.1540	1.36233e4	1381.92529	94.9285
2	9.179	MM	0.1549	727.81970	78.31062	5.0715



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.784	BB	0.1290	478.48645	55.28483	4.8560
2	9.328	BB	0.1550	9375.10254	942.66882	95.1440

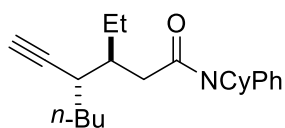
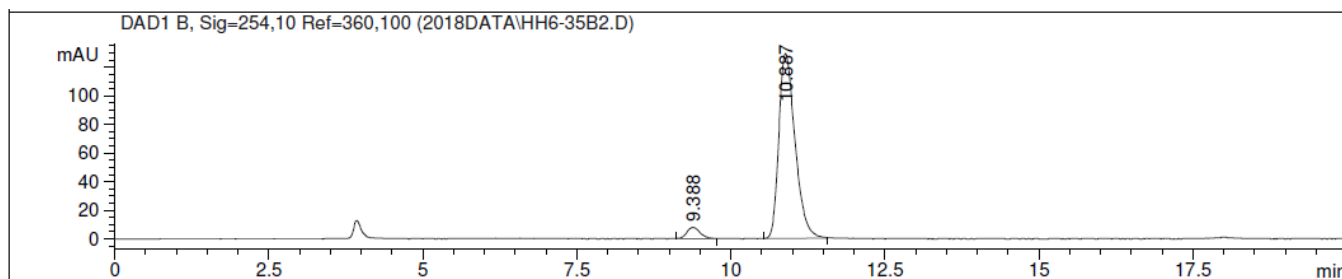


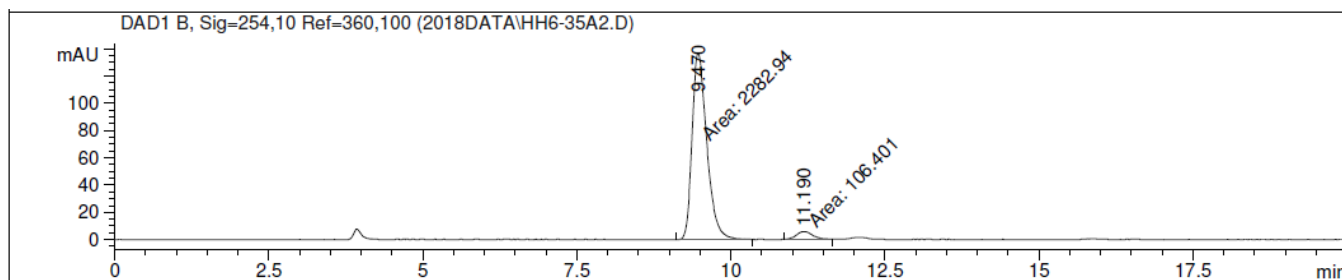
Fig. 4

(*R, S*)-L2: 90% ee, > 99:1 dr

(*S, R*)-L2: 91% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.388	BB	0.2195	119.67050	7.95627	4.8196
2	10.887	PB	0.2771	2363.34204	129.39194	95.1804



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.470	MM	0.2780	2282.94092	136.84560	95.5468
2	11.190	MM	0.3065	106.40149	5.78578	4.4532

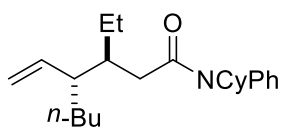
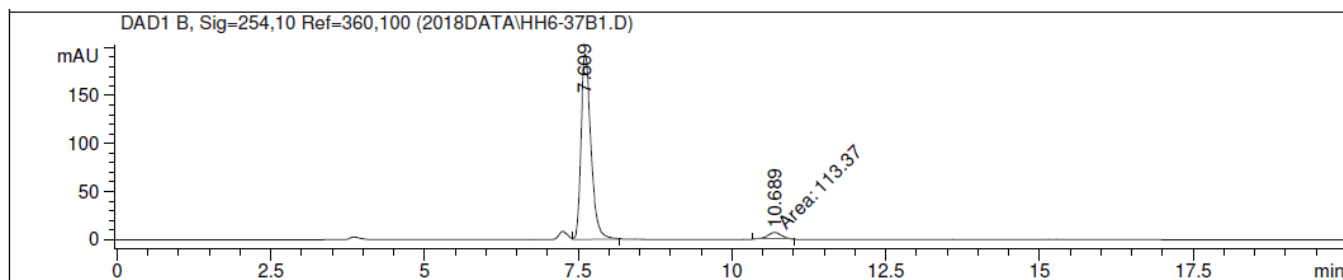


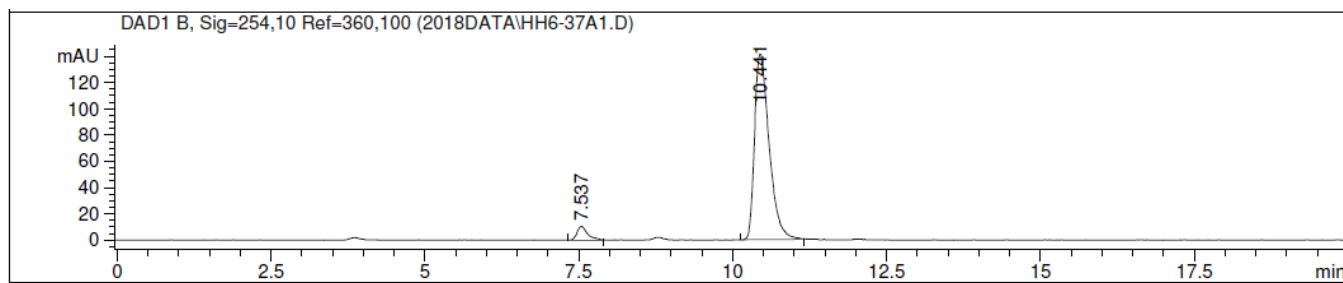
Fig. 4, reaction a

(*R, S*)-L2: 90% ee, 98:2 dr

(*S, R*)-L2: 90% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.609	VB	0.1721	2158.49829	193.56209	95.0098
2	10.689	MM	0.2739	113.37008	6.89898	4.9902



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.537	BB	0.1761	123.91437	10.32085	5.0640
2	10.441	BB	0.2535	2323.04370	141.50923	94.9360

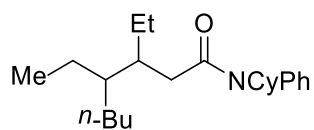
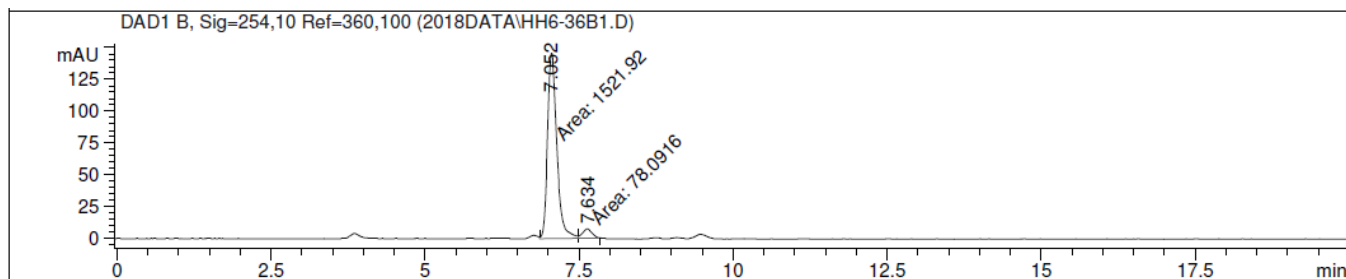


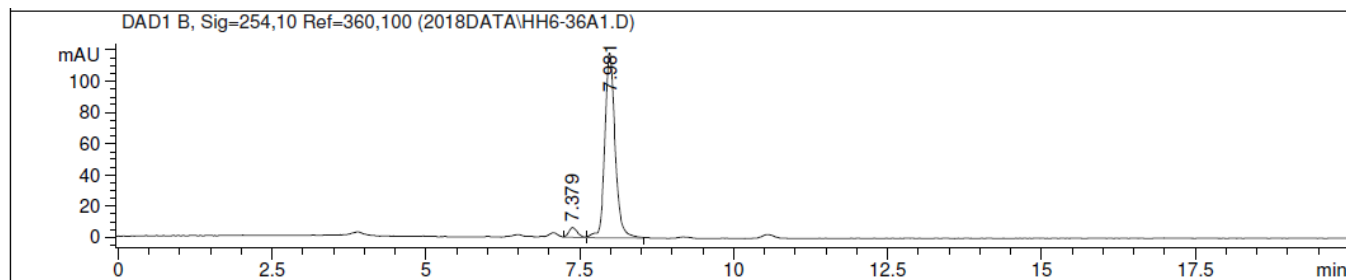
Fig. 4, reaction b

(*R, S*)-L2: 90% ee, 98:2 dr

(*S, R*)-L2: 91% ee, 98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.052	MF	0.1736	1521.92041	146.08575	95.1193
2	7.634	FM	0.1803	78.09162	7.21961	4.8807



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.379	VV	0.1533	62.70704	6.34455	4.3641
2	7.981	VB	0.1773	1374.19019	118.47795	95.6359

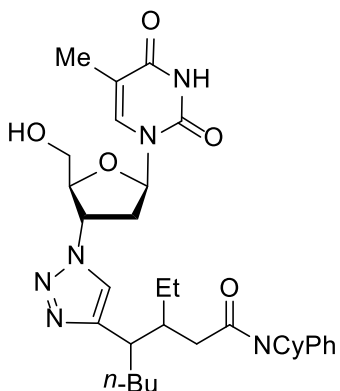
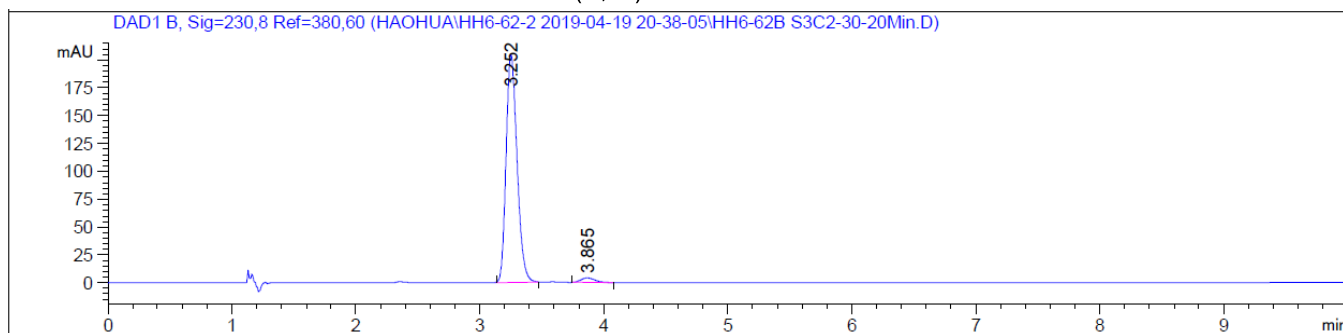


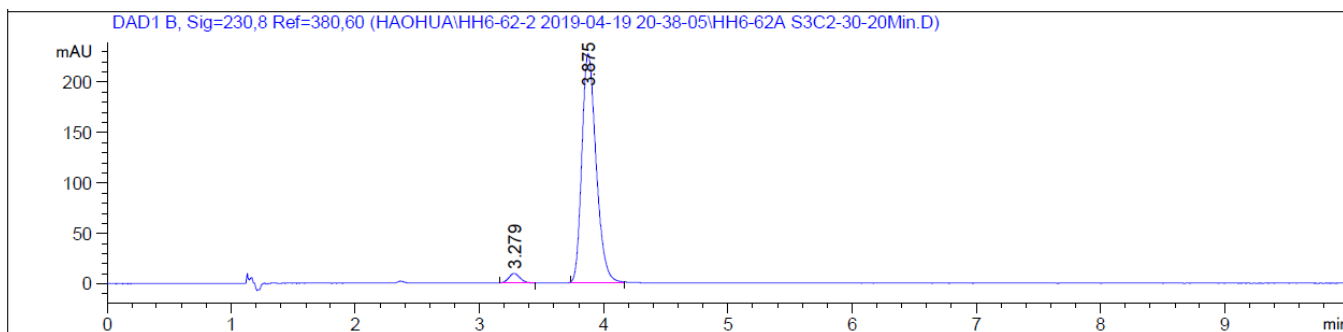
Fig. 4, reaction c

(*R, S*)-L2: 97:3 dr

(*S, R*)-L2: 3:97 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.252	BB	0.0945	1255.18835	204.89052	97.4601
2	3.865	BB	0.1213	32.71146	4.17908	2.5399



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.279	BB	0.0942	59.19547	9.43418	3.1522
2	3.875	BB	0.1234	1818.69006	227.08224	96.8478

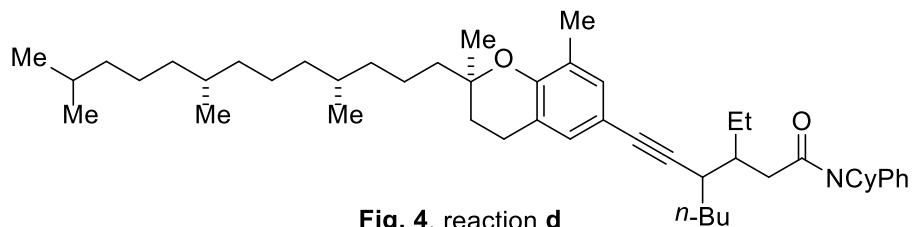
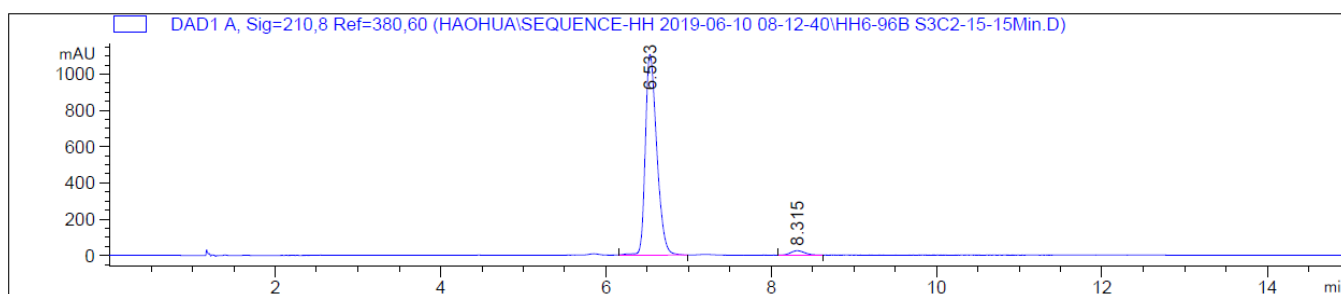


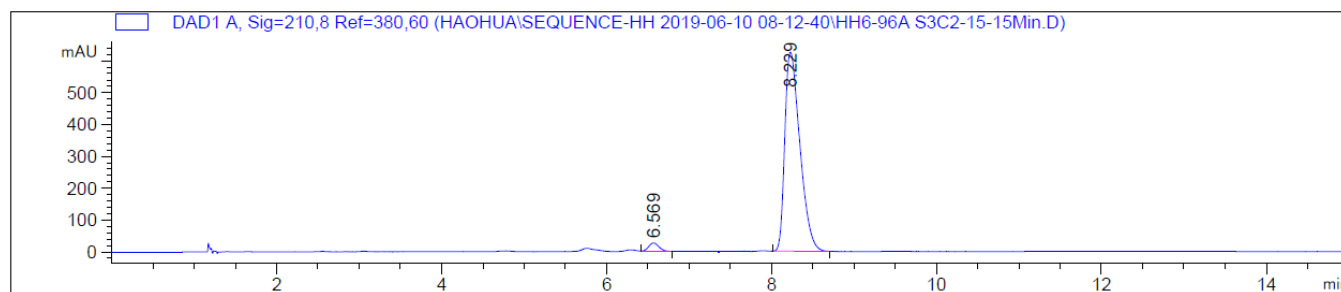
Fig. 4, reaction d

(R, S)-L2: 97:3 dr

(S, R)-L2: 3:97 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.533	BB	0.1510	1.07201e4	1107.05725	97.3615
2	8.315	BB	0.1839	290.50891	24.40571	2.6385



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.569	VB	0.1395	247.40807	27.09835	3.0143
2	8.229	BB	0.1965	7960.49951	625.31360	96.9857

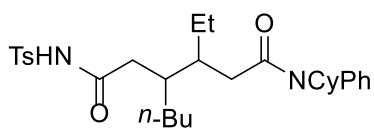
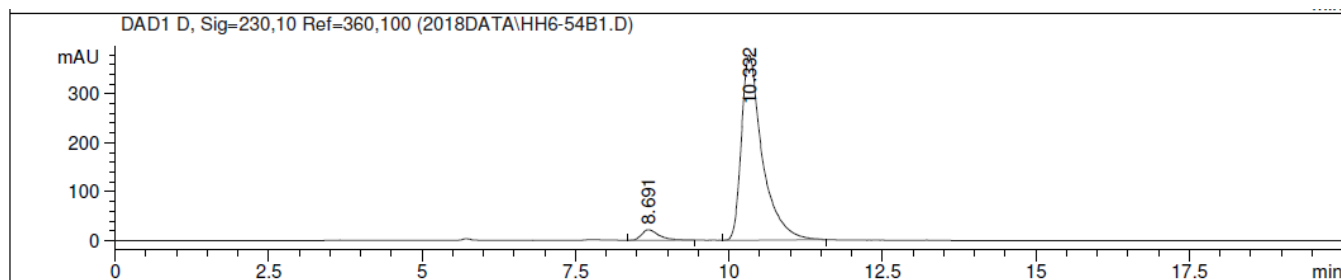


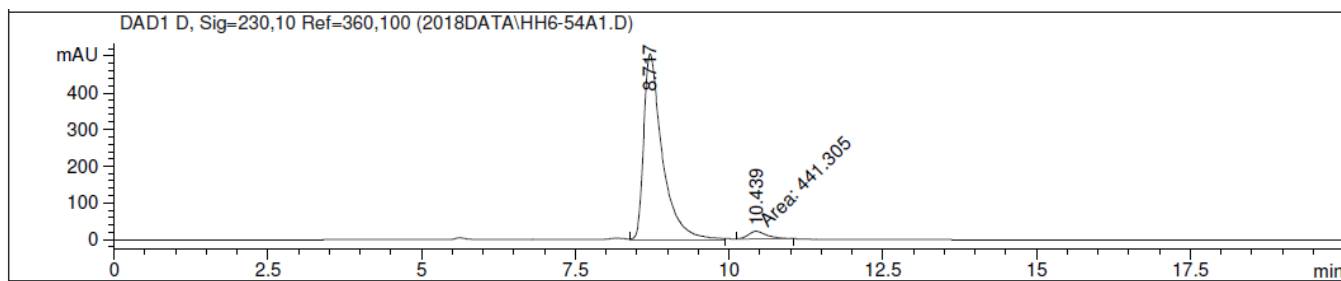
Fig. 4, reaction e

(R, S)-L2: 91% ee, >98:2 dr

(S, R)-L2: 92% ee, 99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.691	VB	0.2806	435.80490	21.67360	4.6324
2	10.332	VB	0.3463	8971.86230	378.82962	95.3676



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.717	VV	0.3069	1.06511e4	507.37802	96.0216
2	10.439	MM	0.3480	441.30493	21.13627	3.9784

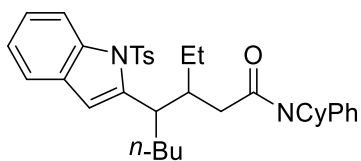
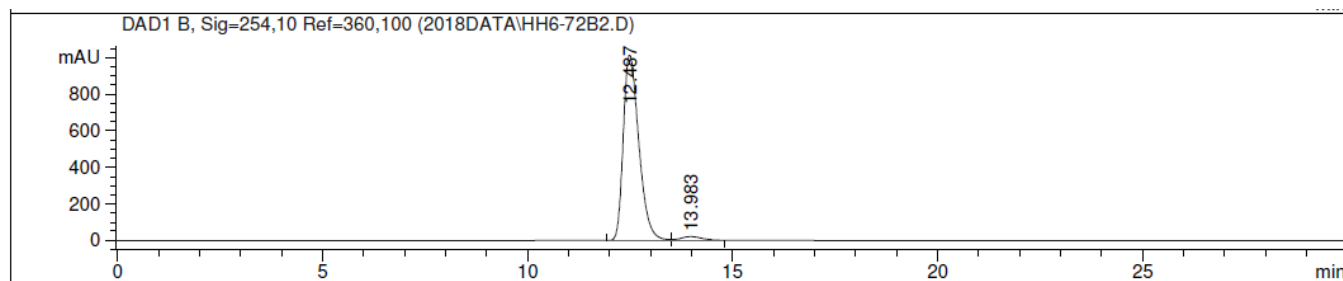


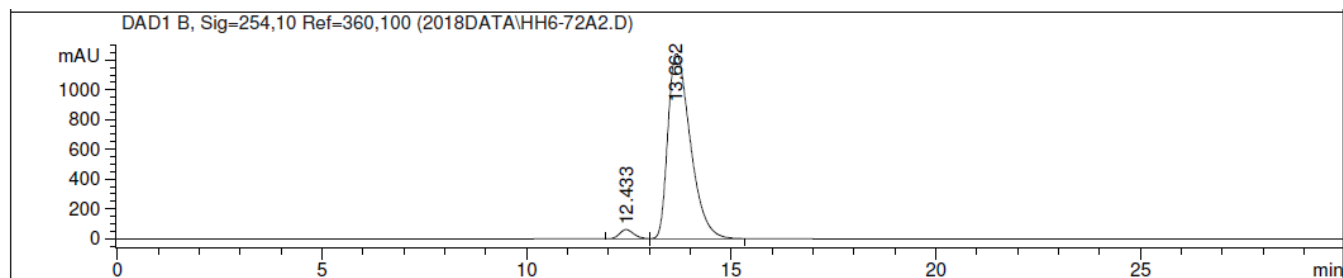
Fig. 4, reaction f, X = NTs

(*R, S*)-L2: 94% ee, >99:1 dr

(*S, R*)-L2: 94% ee, >99:1 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.487	BV	0.4082	2.68207e4	1015.24268	97.1246
2	13.983	VV	0.4963	794.02979	21.33093	2.8754



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.433	BV	0.3722	1502.55554	61.67868	3.0736
2	13.662	VB	0.5595	4.73832e4	1240.82495	96.9264

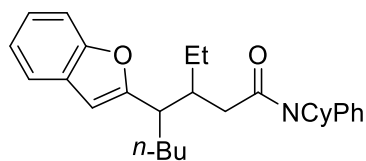
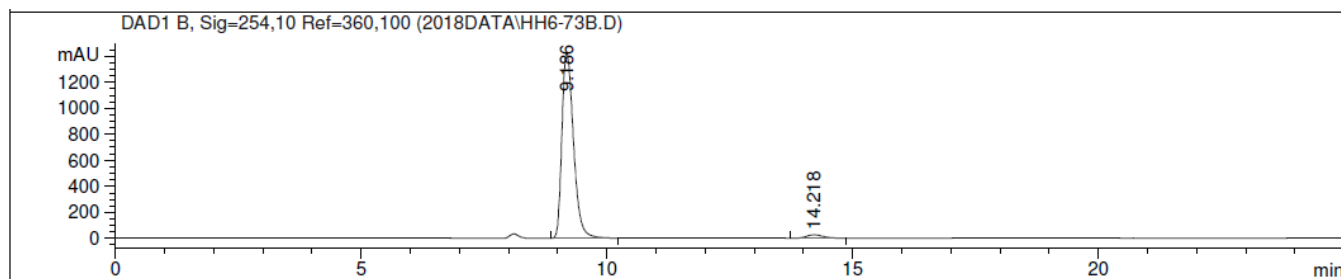


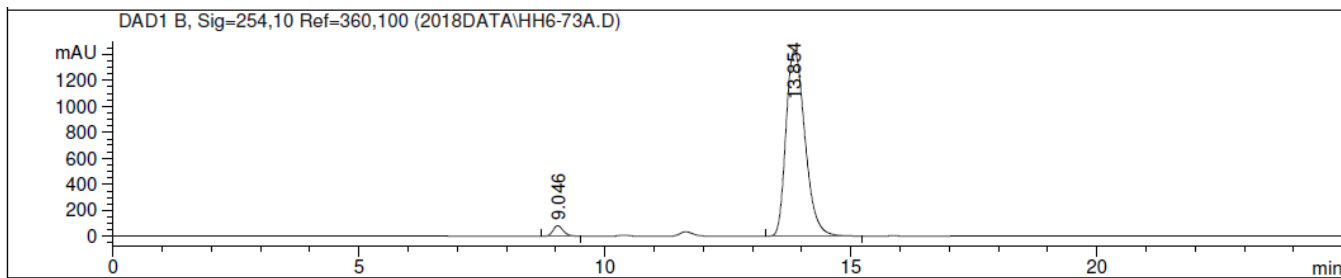
Fig. 4, reaction f, X = O

(*R*, *S*)-L2: 94% ee, >98:2 dr

(*S*, *R*)-L2: 94% ee, >98:2 dr



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.186	PB	0.2553	2.33620e4	1424.55896	97.2335
2	14.218	BB	0.3556	664.69318	27.14959	2.7665



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.046	VB	0.2280	1236.68933	82.93681	3.1207
2	13.854	BB	0.4182	3.83923e4	1425.67969	96.8793

References and Notes

1. A. Suzuki, Cross-coupling reactions of organoboranes: An easy way to construct C-C bonds (Nobel Lecture). *Angew. Chem. Int. Ed.* **50**, 6722–6737 (2011). [doi:10.1002/anie.201101379](https://doi.org/10.1002/anie.201101379) [Medline](#)
2. E. Negishi, Magical power of transition metals: Past, present, and future (Nobel Lecture). *Angew. Chem. Int. Ed.* **50**, 6738–6764 (2011). [doi:10.1002/anie.201101380](https://doi.org/10.1002/anie.201101380) [Medline](#)
3. F. Lovering, J. Bikker, C. Humblet, Escape from flatland: Increasing saturation as an approach to improving clinical success. *J. Med. Chem.* **52**, 6752–6756 (2009). [doi:10.1021/jm901241e](https://doi.org/10.1021/jm901241e) [Medline](#)
4. F. Lovering, Escape from flatland 2: Complexity and promiscuity. *MedChemComm* **4**, 515–519 (2013). [doi:10.1039/c2md20347b](https://doi.org/10.1039/c2md20347b)
5. S. R. Hartshorn, *Aliphatic Nucleophilic Substitution* (Cambridge Univ. Press, 1973).
6. J. Choi, G. C. Fu, Transition metal-catalyzed alkyl-alkyl bond formation: Another dimension in cross-coupling chemistry. *Science* **356**, eaaf7230 (2017). [doi:10.1126/science.aaf7230](https://doi.org/10.1126/science.aaf7230) [Medline](#)
7. G. C. Fu, Transition-metal catalysis of nucleophilic substitution reactions: A radical alternative to S_N1 and S_N2 processes. *ACS Cent. Sci.* **3**, 692–700 (2017). [doi:10.1021/acscentsci.7b00212](https://doi.org/10.1021/acscentsci.7b00212) [Medline](#)
8. A. Kaga, S. Chiba, Engaging radicals in transition metal-catalyzed cross-coupling with alkyl electrophiles: Recent advances. *ACS Catal.* **7**, 4697–4706 (2017). [doi:10.1021/acscatal.7b01405](https://doi.org/10.1021/acscatal.7b01405)
9. T. Iwasaki, N. Kambe, Ni-catalyzed C–C couplings using alkyl electrophiles. *Top. Curr. Chem.* **374**, 66 (2016). [doi:10.1007/s41061-016-0067-6](https://doi.org/10.1007/s41061-016-0067-6) [Medline](#)
10. E. Geist, A. Kirschning, T. Schmidt, sp³-sp³ coupling reactions in the synthesis of natural products and biologically active molecules. *Nat. Prod. Rep.* **31**, 441–448 (2014). [doi:10.1039/c3np70108e](https://doi.org/10.1039/c3np70108e) [Medline](#)
11. S. P. Pitre, N. A. Weires, L. E. Overman, Forging C(sp³)-C(sp³) bonds with carbon-centered radicals in the synthesis of complex molecules. *J. Am. Chem. Soc.* **141**, 2800–2813 (2019). [doi:10.1021/jacs.8b11790](https://doi.org/10.1021/jacs.8b11790) [Medline](#)
12. A. E. Wendlandt, P. Vangal, E. N. Jacobsen, Quaternary stereocentres via an enantioconvergent catalytic S_N1 reaction. *Nature* **556**, 447–451 (2018). [doi:10.1038/s41586-018-0042-1](https://doi.org/10.1038/s41586-018-0042-1) [Medline](#)
13. C. J. Cordier, R. J. Lundgren, G. C. Fu, Enantioconvergent cross-couplings of racemic alkylmetal reagents with unactivated secondary alkyl electrophiles: Catalytic asymmetric Negishi α -alkylations of *N*-Boc-pyrrolidine. *J. Am. Chem. Soc.* **135**, 10946–10949 (2013). [doi:10.1021/ja4054114](https://doi.org/10.1021/ja4054114) [Medline](#)
14. X. Mu, Y. Shibata, Y. Makida, G. C. Fu, Control of vicinal stereocenters through nickel-catalyzed alkyl-alkyl cross-coupling. *Angew. Chem. Int. Ed.* **56**, 5821–5824 (2017). [doi:10.1002/anie.201702402](https://doi.org/10.1002/anie.201702402) [Medline](#)

15. T. Hayashi, M. Tajika, K. Tamao, M. Kumada, High stereoselectivity in asymmetric Grignard cross-coupling catalyzed by nickel complexes of chiral (aminoalkylferrocenyl)phosphines. *J. Am. Chem. Soc.* **98**, 3718–3719 (1976). [doi:10.1021/ja00428a061](https://doi.org/10.1021/ja00428a061)
16. T. Shekh-Ahmad, N. Hen, J. H. McDonough, B. Yagen, M. Bialer, Valnoctamide and *sec*-butyl-propylacetamide (SPD) for acute seizures and status epilepticus. *Epilepsia* **54**, 99–102 (2013). [doi:10.1111/epi.12290](https://doi.org/10.1111/epi.12290) [Medline](#)
17. A. Cordova, Ed., *Catalytic Asymmetric Conjugate Reactions* (Wiley-VCH, 2010).
18. M. Rodríguez-Fernández, X. Yan, J. F. Collados, P. B. White, S. R. Harutyunyan, Lewis acid enabled copper-catalyzed asymmetric synthesis of chiral β -substituted amides. *J. Am. Chem. Soc.* **139**, 14224–14231 (2017). [doi:10.1021/jacs.7b07344](https://doi.org/10.1021/jacs.7b07344) [Medline](#)
19. C. F. Malosh, J. M. Ready, Catalytic cross-coupling of alkylzinc halides with α -chloroketones. *J. Am. Chem. Soc.* **126**, 10240–10241 (2004). [doi:10.1021/ja0467768](https://doi.org/10.1021/ja0467768) [Medline](#)
20. S. W. Smith, G. C. Fu, Nickel-catalyzed Negishi cross-couplings of secondary nucleophiles with secondary propargylic electrophiles at room temperature. *Angew. Chem. Int. Ed.* **47**, 9334–9336 (2008). [doi:10.1002/anie.200802784](https://doi.org/10.1002/anie.200802784) [Medline](#)
21. C.-T. Yang, Z.-Q. Zhang, J. Liang, J.-H. Liu, X.-Y. Lu, H.-H. Chen, L. Liu, Copper-catalyzed cross-coupling of nonactivated secondary alkyl halides and tosylates with secondary alkyl Grignard reagents. *J. Am. Chem. Soc.* **134**, 11124–11127 (2012). [doi:10.1021/ja304848n](https://doi.org/10.1021/ja304848n) [Medline](#)
22. J. T. Binder, C. J. Cordier, G. C. Fu, Catalytic enantioselective cross-couplings of secondary alkyl electrophiles with secondary alkylmetal nucleophiles: Negishi reactions of racemic benzylic bromides with achiral alkylzinc reagents. *J. Am. Chem. Soc.* **134**, 17003–17006 (2012). [doi:10.1021/ja308460z](https://doi.org/10.1021/ja308460z) [Medline](#)
23. U. Kazmaier, Ed., *Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis* (Springer, 2012).
24. S. Balasubramaniam, I. S. Aidhen, The growing synthetic utility of the Weinreb amide. *Synthesis* **23**, 3707–3738 (2008).
25. S. W. Smith, G. C. Fu, Nickel-catalyzed asymmetric cross-couplings of racemic propargylic halides with arylzinc reagents. *J. Am. Chem. Soc.* **130**, 12645–12647 (2008). [doi:10.1021/ja805165y](https://doi.org/10.1021/ja805165y) [Medline](#)
26. N. D. Schley, G. C. Fu, Nickel-catalyzed Negishi arylations of propargylic bromides: A mechanistic investigation. *J. Am. Chem. Soc.* **136**, 16588–16593 (2014). [doi:10.1021/ja508718m](https://doi.org/10.1021/ja508718m) [Medline](#)
27. H. Yin, G. C. Fu, Mechanistic investigation of enantioconvergent Kumada reactions of racemic α -bromoketones catalyzed by a nickel/bis(oxazoline) complex. *J. Am. Chem. Soc.* **141**, 15433–15440 (2019). [doi:10.1021/jacs.9b08185](https://doi.org/10.1021/jacs.9b08185) [Medline](#)
28. P.-Q. Huang, Y. Wang, K.-J. Xiao, Y.-H. Huang, A general method for the direct transformation of common tertiary amides into ketones and amines by addition of Grignard reagents. *Tetrahedron* **71**, 4248–4254 (2015). [doi:10.1016/j.tet.2015.04.074](https://doi.org/10.1016/j.tet.2015.04.074)

29. B. M. Trost, C.-J. Li, Eds., *Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations* (Wiley-VCH, 2015).
30. V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective “ligation” of azides and terminal alkynes. *Angew. Chem. Int. Ed.* **41**, 2596–2599 (2002). [doi:10.1002/1521-3773\(20020715\)41:14<2596:AID-ANIE2596>3.0.CO;2-4](https://doi.org/10.1002/1521-3773(20020715)41:14<2596:AID-ANIE2596>3.0.CO;2-4) [Medline](#)
31. C. W. Tornøe, C. Christensen, M. Meldal, Peptidotriazoles on solid phase: [1,2,3]-Triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J. Org. Chem.* **67**, 3057–3064 (2002). [doi:10.1021/jo011148j](https://doi.org/10.1021/jo011148j) [Medline](#)
32. S. H. Cho, E. J. Yoo, I. Bae, S. Chang, Copper-catalyzed hydrative amide synthesis with terminal alkyne, sulfonyl azide, and water. *J. Am. Chem. Soc.* **127**, 16046–16047 (2005). [doi:10.1021/ja056399e](https://doi.org/10.1021/ja056399e) [Medline](#)
33. R. F. Schumacher, A. Honraedt, C. Bolm, Synthesis of *N*-methyl-2-indolyl- and *N*-methyl-2-benzo[*b*]furyl-substituted sulfoximines by Pd/Cu co-catalyzed domino cross-coupling/cyclization reactions. *Eur. J. Org. Chem.* **2012**, 3737–3741 (2012). [doi:10.1002/ejoc.201200573](https://doi.org/10.1002/ejoc.201200573)
34. M. R. Krout, J. T. Mohr, B. M. Stoltz, Preparation of (*S*)-*tert*-ButylPHOX (Oxazole, 4-(1,1-dimethylethyl)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro- (4*S*)-). *Org. Synth.* **86**, 181–193 (2009). [doi:10.1002/0471264229.os086.19](https://doi.org/10.1002/0471264229.os086.19) [Medline](#)
35. Q. Zhu, D. E. Graff, R. R. Knowles, Intermolecular anti-Markovnikov hydroamination of unactivated alkenes with sulfonamides enabled by proton-coupled electron transfer. *J. Am. Chem. Soc.* **140**, 741–747 (2018). [doi:10.1021/jacs.7b11144](https://doi.org/10.1021/jacs.7b11144) [Medline](#)
36. A. Krasovskiy, P. Knochel, Convenient titration method for organometallic zinc, magnesium, and lanthanide reagents. *Synthesis* 890–891 (2006).
37. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *OLEX2*: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339–341 (2009). [doi:10.1107/S0021889808042726](https://doi.org/10.1107/S0021889808042726)
38. G. M. Sheldrick, *SHELXT* - integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **71**, 3–8 (2015). [doi:10.1107/S2053273314026370](https://doi.org/10.1107/S2053273314026370) [Medline](#)
39. G. M. Sheldrick, Crystal structure refinement with *SHELXL*. *Acta Crystallogr. C* **71**, 3–8 (2015). [doi:10.1107/S2053229614024218](https://doi.org/10.1107/S2053229614024218) [Medline](#)
40. P. Tosatti, A. J. Campbell, D. House, A. Nelson, S. P. Marsden, Catalyst control in sequential asymmetric allylic substitution: Stereodivergent access to *N,N*-diprotected unnatural amino acids. *J. Org. Chem.* **76**, 5495–5501 (2011). [doi:10.1021/jo200720c](https://doi.org/10.1021/jo200720c) [Medline](#)