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SUPPLEMENTARY INFORMATION

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Catalytic enantioconvergent coupling of secondary and tertiary electrophiles with olefins

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Supplementary Information for

Catalytic Enantioconvergent Alkyl-Alkyl Couplings of Secondary and Tertiary Electrophiles with Olefins

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I. General Information

Unless otherwise noted, reagents received from commercial suppliers were used as received. All reactions were performed under an atmosphere of dry nitrogen. Anhydrous 2-methyltetrahydrofuran was purchased from Sigma-Aldrich and stored under nitrogen; other solvents were purified by passage through activated aluminum oxide in a solvent-purification system. NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (400 MHz for ^{1}H and 101 MHz for ^{13}C); chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm, using a 100 mm path-length cell in the solvent and at the concentration indicated. Mass spectra were obtained on an Agilent 7890A GC-MS system with an Agilent 5975C detector or on an Agilent 1290 UHPLC-LCMS system with an Agilent 6140 detector. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm). IR spectra of organic compounds were recorded on a Thermo Scientific Nicolet iS5 (iD5 ATR) spectrometer by attenuated total reflection (ATR). IR spectra of nickel complexes were collected in a nitrogen-filled glovebox on a Bruker ALPHA FT-IR spectrometer by attenuated total reflection (ATR). Electronic absorption spectra were collected on a Cary 50 UV-vis spectrometer using a 10 mm path length quartz cuvette with a Unisoku CoolSpek cryostat for variable-temperature measurements. X-band continuous-wave EPR measurements were conducted on a Bruker EMX spectrometer with the sample in a frozen solvent glass at 77 K. Elemental analyses were carried out at the Beckman Institute at Caltech with a PerkinElmer 2400 Series II CHN Elemental Analyzer or at Midwest Microlab.

The ligand (*R*,*R*)-**L*** and (*S*,*S*)-**L*** were prepared according to a literature procedure, and all analytical data matched the report[1].

II. Catalytic Enantioconvergent Couplings

General Procedure 1 (GP-1): 2-Methyl-THF as the solvent.

Preparation of a solution of the catalyst: In the air, an oven-dried 20 mL vial that contained a magnetic stir bar was charged with $NiBr_2$·glyme (25 mg, 0.080 mmol, 0.10 equiv) and ligand **L*** (61 mg, 0.096 mmol, 0.12 equiv). The vial was capped with a PTFE septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). Next, 2-methyl-THF (4.0 mL) was added via syringe, and the mixture was stirred at room temperature for 30 min.

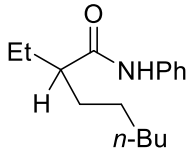
Cross-coupling: In the air, a separate oven-dried 20 mL vial was charged with the racemic electrophile (0.80 mmol, 1.0 equiv) and K_3PO_4·H_2O (553 mg, 2.4 mmol, 3.0 equiv) (if the olefin is a solid, it was also added at this time). The vial was capped with a PTFE septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). Next, the solution of the catalyst (see above) was added in one portion via syringe, followed by the olefin (1.6 mmol, 2.0 equiv). The vial was then placed in an *i*-PrOH cooling bath at –5 °C, and a nitrogen-filled balloon was attached to the vial. The reaction mixture was stirred at –5 °C for 10 min, and then $HSi(OEt)_3$ (0.443 mL, 2.4 mmol, 3.0 equiv) was added dropwise via syringe over one min. Next, the balloon was removed, and all of the puncture holes in the septum cap were covered with grease. The reaction mixture was stirred at –5 °C for 40 h.

Work-up: The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography.

General Procedure 2 (GP-2): Toluene as the solvent.

Preparation of a solution of the catalyst: In the air, an oven-dried 20 mL vial that contained a magnetic stir bar was charged with $NiBr_2$·glyme (25 mg, 0.080 mmol, 0.10 equiv) and ligand **L*** (61 mg, 0.096 mmol, 0.12 equiv). The vial was capped with a PTFE septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). Next, toluene (4.0 mL) was added via syringe, and the mixture was stirred at room temperature for 60 min.

Cross-coupling and workup: Same as **GP-1**.



2-Ethyl-*N*-phenyloctanamide (Figure 2a, entry 1). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 166 mg, 84% yield, 94% ee; (*S*,*S*)-**L***: 167 mg, 84% yield, 94% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.9 min (major), 8.0 min (minor).

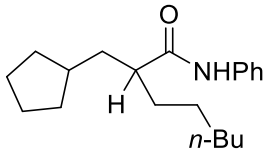
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 2H), 7.43 – 7.33 (m, 2H), 7.31 (s, 1H), 7.17 – 7.08 (m, 1H), 2.20 – 2.07 (m, 1H), 1.79 – 1.68 (m, 2H), 1.64 – 1.45 (m, 2H), 1.40 – 1.24 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 137.9, 128.9, 124.2, 119.9, 50.9, 32.9, 31.7, 29.4, 27.7, 26.3, 22.6, 14.1, 12.2.

FT-IR (film) 3292, 2957, 1657, 1500, 1442, 1310, 1200, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{26}NO$: 248.2014, found: 248.2009.

$[\alpha]^{24}_D$ = −10.4 (*c* 1.0, $CHCl_3$); 94% ee, from (*R,R*)-**L***.



2-(Cyclopentylmethyl)-*N*-phenyloctanamide (Figure 2a, entry 2). The title compound was prepared according to **GP-1** from 2-bromo-3-cyclopentyl-*N*-phenylpropanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 230 mg, 95% yield, 93% ee; (*S,S*)-**L***: 238 mg, 98% yield, 90% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 5.9 min (major), 7.4 min (minor).

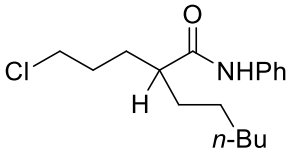
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 2H), 7.38 – 7.30 (m, 2H), 7.21 (s, 1H), 7.16 – 7.08 (m, 1H), 2.30 – 2.17 (m, 1H), 1.92 – 1.75 (m, 4H), 1.72 – 1.57 (m, 3H), 1.56 – 1.40 (m, 4H), 1.37 – 1.24 (m, 8H), 1.19 – 1.04 (m, 2H), 0.94 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 137.9, 128.9, 124.1, 119.8, 48.5, 39.6, 38.1, 33.7, 33.1, 32.6, 31.7, 29.4, 27.7, 25.1, 25.0, 22.6, 14.1.

FT-IR (film) 3293, 2926, 1654, 1529, 1442, 1311, 1255, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{32}NO$: 302.2484, found: 302.2477.

$[\alpha]^{24}_D$ = +11.6 (*c* 1.0, $CHCl_3$); 93% ee, from (*R,R*)-**L***.



2-(3-Chloropropyl)-*N*-phenyloctanamide (Figure 2a, entry 3). The title compound was prepared according to **GP-1** from 2-bromo-5-chloro-*N*-phenylpentanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 178 mg, 75% yield, 95% ee; (*S,S*)-**L***: 188 mg, 79% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 9.3 min (minor), 11.6 min (major).

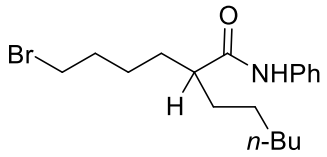
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.41 – 7.33 (m, 2H), 7.32 (s, 1H), 7.17 – 7.09 (m, 1H), 3.65 – 3.46 (m, 2H), 2.32 – 2.17 (m, 1H), 1.93 – 1.79 (m, 3H), 1.78 – 1.68 (m, 2H), 1.60 – 1.45 (m, 1H), 1.40 – 1.24 (m, 8H), 0.96 – 0.80 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 137.7, 129.0, 124.4, 119.9, 48.4, 44.9, 33.2, 31.7, 30.4, 30.3, 29.3, 27.5, 22.6, 14.0.

FT-IR (film) 3296, 2927, 1654, 1529, 1441, 1312, 1250, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{27}ClNO$: 296.1781, found: 296.1775.

$[\alpha]^{24}_D$ = −1.6 (*c* 1.0, $CHCl_3$); 95% ee, from (*R*,*R*)-**L***.



2-(4-Bromobutyl)-*N*-phenyloctanamide (Figure 2a, entry 4). The title compound was prepared according to **GP-1** from 2,6-dibromo-*N*-phenylhexanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 206 mg, 73% yield, 94% ee; (*S*,*S*)-**L***: 195 mg, 69% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.3 min (minor), 11.3 min (major).

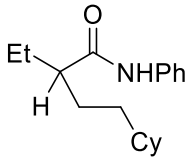
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.40 – 7.31 (m, 2H), 7.23 (s, 1H), 7.16 – 7.10 (m, 1H), 3.49 – 3.34 (m, 2H), 2.25 – 2.13 (m, 1H), 1.94 – 1.85 (m, 2H), 1.81 – 1.68 (m, 2H), 1.60 – 1.46 (m, 4H), 1.38 – 1.26 (m, 8H), 0.94 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 137.7, 129.0, 124.3, 119.9, 49.1, 33.6, 33.3, 32.7, 32.2, 31.7, 29.4, 27.6, 26.2, 22.6, 14.1.

FT-IR (film) 3291, 2925, 1654, 1529, 1442, 1311, 1256, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{29}BrNO$: 354.1433, found: 354.1430.

$[\alpha]^{24}_D$ = +12.4 (*c* 1.0, $CHCl_3$); 94% ee, from (*R*,*R*)-**L***.



4-Cyclohexyl-2-ethyl-*N*-phenylbutanamide (Figure 2a, entry 5). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and vinylcyclohexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 201 mg, 92% yield, 97% ee; (*S*,*S*)-**L***: 192 mg, 88% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.1 min (major), 8.4 min (minor).

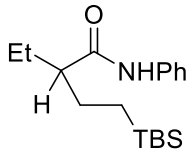
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.40 – 7.30 (m, 2H), 7.23 – 7.07 (m, 2H), 2.13 – 2.01 (m, 1H), 1.79 – 1.63 (m, 7H), 1.61 – 1.50 (m, 2H), 1.29 – 1.13 (m, 6H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 – 0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 137.9, 128.9, 124.2, 119.8, 51.2, 37.8, 35.4, 33.4, 33.2, 30.2, 26.6, 26.4, 26.3, 26.2, 12.2.

FT-IR (film) 3250, 2923, 1652, 1540, 1442, 1074, 750 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO$: 274.2171, found: 274.2168.

$[\alpha]^{24}_D$ = −14.5 (*c* 1.0, $CHCl_3$); 97% ee, from (*R,R*)-**L***.



4-(*tert*-Butyldimethylsilyl)-2-ethyl-*N*-phenylbutanamide (Figure 2a, entry 6). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and *tert*-butyldimethyl(vinyl)silane. Purification by flash column chromatography on silica gel: 10% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 217 mg, 89% yield, 93% ee; (*S,S*)-**L***: 215 mg, 88% yield, 91% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 13.1 min (minor), 14.0 min (major).

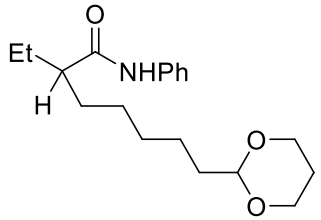
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.38 – 7.31 (m, 2H), 7.23 (s, 1H), 7.17 – 7.09 (m, 1H), 2.13 – 1.97 (m, 1H), 1.80 – 1.67 (m, 2H), 1.65 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.87 (s, 9H), 0.66 – 0.47 (m, 2H), –0.04 (s, 3H), –0.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 137.9, 129.0, 124.2, 119.9, 54.4, 27.7, 26.6, 25.8, 16.6, 12.2, 10.5, –6.3, –6.4.

FT-IR (film) 3293, 2928, 1658, 1542, 1442, 1310, 1250, 828, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{32}NOSi$: 306.2253, found: 306.2247.

$[\alpha]^{24}_D$ = −11.2 (*c* 1.0, $CHCl_3$); 93% ee, from (*R,R*)-**L***.



7-(1,3-Dioxan-2-yl)-2-ethyl-*N*-phenylheptanamide (Figure 2a, entry 7). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and 2-(pent-4-en-1-yl)-1,3-dioxane. Purification by flash column chromatography on silica gel: 15→25% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 200 mg, 78% yield, 94% ee; (*S,S*)-**L***: 211 mg, 82% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 8.2 min (minor), 11.2 min (major).

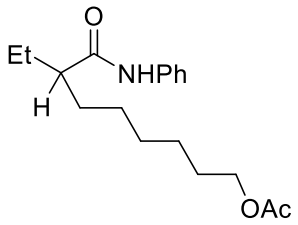
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.38 – 7.30 (m, 2H), 7.25 (s, 1H), 7.15 – 7.08 (m, 1H), 4.51 (t, *J* = 5.2 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.81 – 3.71 (m, 2H), 2.18 – 1.99 (m, 2H), 1.78 – 1.68 (m, 2H), 1.62 – 1.47 (m, 4H), 1.43 – 1.30 (m, 7H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 137.9, 128.9, 124.2, 119.8, 102.4, 66.9, 50.8, 35.1, 32.8, 29.5, 27.5, 26.2, 25.8, 23.8, 12.2.

FT-IR (film) 3282, 2925, 1654, 1530, 1442, 1147, 1004, 751 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{30}NO_3$: 320.2226, found: 320.2223.

$[\alpha]^{24}_D$ = −13.8 (*c* 1.0, $CHCl_3$); 94% ee, from (*R,R*)-**L***.



7-(Phenylcarbamoyl)nonyl acetate (Figure 2a, entry 8). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and hex-5-en-1-yl acetate. Purification by flash column chromatography on silica gel: Et_2O/CH_2Cl_2/hexanes = 1:1:2, white solid.

(*R,R*)-**L***: 221 mg, 90% yield, 95% ee; (*S,S*)-**L***: 225 mg, 92% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 10.9 min (major), 13.2 min (minor).

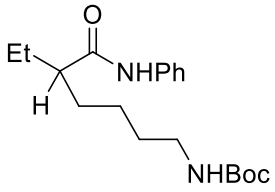
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.42 – 7.29 (m, 3H), 7.17 – 7.07 (m, 1H), 4.06 (t, *J* = 6.7 Hz, 2H), 2.16 – 2.07 (m, 1H), 2.06 (s, 3H), 1.82 – 1.70 (m, 2H), 1.67 – 1.44 (m, 4H), 1.35 (s, 6H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 171.3, 137.9, 128.9, 124.2, 119.8, 64.5, 50.8, 32.7, 29.3, 28.5, 27.5, 26.3, 25.7, 21.1, 12.1.

FT-IR (film) 3297, 2933, 1737, 1660, 1539, 1442, 1247, 1041, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO_3$: 306.2069, found: 306.2070.

$[\alpha]^{23}_D$ = –10.1 (*c* 1.0, $CHCl_3$); 95% ee, from (*R,R*)-**L***.



***tert*-Butyl (5-(phenylcarbamoyl)heptyl)carbamate (Figure 2a, entry 9).** The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and *tert*-butyl but-3-en-1-ylcarbamate. Purification by flash column chromatography on silica gel: 15→25% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 152 mg, 57% yield, 93% ee; (*S*,*S*)-**L***: 163 mg, 61% yield, 92% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.9 min (minor), 6.7 min (major).

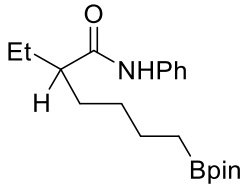
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.54 (s, 1H), 7.36 – 7.30 (m, 2H), 7.19 – 7.05 (m, 1H), 4.60 (s, 1H), 3.23 – 2.99 (m, 2H), 2.24 – 2.03 (m, 1H), 1.79 – 1.70 (m, 2H), 1.63 – 1.48 (m, 4H), 1.44 (s, 9H), 1.42 – 1.34 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 156.1, 138.0, 128.9, 124.1, 119.9, 79.2, 50.4, 40.2, 32.3, 29.9, 28.4, 26.1, 24.7, 12.1.

FT-IR (film) 3309, 2933, 1684, 1539, 1442, 1172, 755 cm^{-1}.

HRMS (ESI) m/z [M+H]$^+$ calcd for $C_{19}H_{31}N_2O_3$: 335.2335, found: 335.2329.

$[\alpha]^{24}_D$ = −28.1 (*c* 1.0, $CHCl_3$); 93% ee, from (*R*,*R*)-**L***.



2-Ethyl-*N*-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (Figure 2a, entry 10). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and 2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 178 mg, 64% yield, 94% ee; (*S*,*S*)-**L***: 177 mg, 64% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 19.7 min (major), 20.7 min (minor).

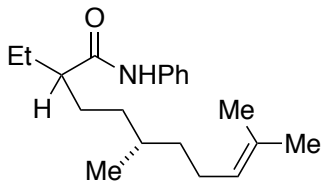
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.37 – 7.30 (m, 2H), 7.19 (s, 1H), 7.14 – 7.07 (m, 1H), 2.17 – 2.06 (m, 1H), 1.78 – 1.69 (m, 2H), 1.64 – 1.49 (m, 2H), 1.49 – 1.33 (m, 4H), 1.23 (s, 12H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 137.9, 128.9, 124.1, 119.8, 82.9, 50.6, 32.7, 30.3, 26.1, 24.8, 24.0, 12.1.

FT-IR (film) 3299, 2932, 1660, 1601, 1541, 1442, 1379, 1312, 1145, 968, 755 cm^{-1}.

HRMS (ESI) m/z [M+H]$^+$ calcd for $C_{20}H_{33}BNO_3$: 346.2553, found: 346.2556.

$[\alpha]^{23}_D$ = −13.2 (*c* 1.0, $CHCl_3$); 94% ee, from (*R*,*R*)-**L***.



(5*S*)-2-Ethyl-5,9-dimethyl-*N*-phenyldec-8-enamide (Figure 2a, entries 11 and 12). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and (*S*)-3,7-

dimethylocta-1,6-diene. Purification by flash column chromatography on silica gel: 10% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 187 mg, 78% yield, 26:1 d.r.; (*S*,*S*)-**L***: 170 mg, 70% yield, 1:>30 d.r.

HPLC analysis: The d.r. was determined on a CHIRALCEL AS-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.1 min (minor), 10.4 min (major).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.40 – 7.30 (m, 2H), 7.25 (s, 1H), 7.16 – 7.09 (m, 1H), 5.18 – 5.04 (m, 1H), 2.16 – 2.03 (m, 1H), 2.04 – 1.87 (m, 2H), 1.83 – 1.67 (m, 2H), 1.70 (s, 3H), 1.64 – 1.49 (m, 2H), 1.60 (s, 3H), 1.47 – 1.29 (m, 3H), 1.23 – 1.08 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 137.9, 131.1, 128.9, 124.8, 124.2, 119.9, 51.2, 36.9, 34.9, 32.5, 30.3, 26.2, 25.7, 25.5, 19.5, 17.7, 12.2.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 7.42 – 7.30 (m, 2H), 7.20 (s, 1H), 7.16 – 7.06 (m, 1H), 5.10 (dddd, *J* = 7.1, 5.6, 2.9, 1.4 Hz, 1H), 2.15 – 2.04 (m, 1H), 2.04 – 1.86 (m, 2H), 1.83 – 1.71 (m, 2H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.60 (d, *J* = 1.3 Hz, 3H), 1.59 – 1.38 (m, 3H), 1.38 – 1.25 (m, 2H), 1.25 – 1.10 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H).

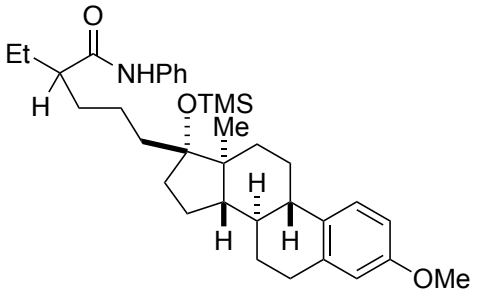
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 137.9, 131.2, 128.9, 124.8, 124.2, 119.9, 51.2, 36.9, 34.8, 32.6, 30.4, 26.3, 25.8, 25.5, 19.4, 17.7, 12.2.

FT-IR (film) 3294, 2927, 1659, 1541, 1442, 1309, 1250, 753 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{32}NO$: 302.2484, found: 302.2480.

$[\alpha]^{24}_D$ = −6.0 (*c* 1.0, $CHCl_3$); 26:1 d.r., from (*R*,*R*)-**L***.

$[\alpha]^{24}_D$ = +24.1 (*c* 1.0, $CHCl_3$); 1:>30 d.r., from (*S*,*S*)-**L***.



2-Ethyl-5-((8*R*,9*S*,13*S*,14*S*,17*S*)-3-methoxy-13-methyl-17-((trimethylsilyl)oxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)-*N*-phenylpentanamide (Figure 2a, entries 13 and 14). The title compound was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and (((8*R*,9*S*,13*S*,14*S*,17*R*)-17-allyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)oxy)trimethylsilane. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 357 mg, 79% yield, >30:1 d.r.; (*S*,*S*)-**L***: 346 mg, 77% yield, 1:26 d.r.

HPLC analysis: The d.r. was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.2 min (minor), 7.7 min (major).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.41 – 7.32 (m, 2H), 7.32 (s, 1H), 7.22 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.17 – 7.07 (m, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 3.81 (s, 3H), 2.96 – 2.79 (m, 2H), 2.38 – 2.24 (m, 1H), 2.24 – 2.09 (m, 2H), 1.93 – 1.74 (m, 5H), 1.70 – 1.43 (m, 10H), 1.42 – 1.26 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.82 (s, 3H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 154.9, 135.6, 135.5, 130.4, 126.5, 123.9, 121.7, 117.4, 111.3, 108.9, 84.4, 52.8, 48.7, 46.2, 45.2, 41.4, 37.3, 35.9, 32.7, 31.4, 29.6, 27.5, 25.1, 24.0, 23.8, 21.0, 20.6, 12.8, 9.8, 0.3.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.49 (m, 2H), 7.40 – 7.30 (m, 2H), 7.26 – 7.16 (m, 2H), 7.16 – 7.09 (m, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 2.96 – 2.77 (m, 2H), 2.37 – 2.22 (m, 1H), 2.21 – 2.04 (m, 2H), 1.96 – 1.70 (m, 5H), 1.68 – 1.43 (m, 10H), 1.42 – 1.24 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.82 (s, 3H), 0.09 (s, 9H).

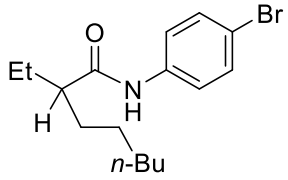
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 157.4, 138.0, 137.9, 132.9, 128.9, 126.3, 124.2, 119.8, 113.7, 111.4, 86.8, 55.2, 51.3, 48.6, 47.7, 43.8, 39.8, 38.4, 35.1, 33.8, 32.0, 29.9, 27.6, 26.5, 26.4, 23.4, 23.2, 15.3, 12.2, 2.8.

FT-IR (film) 3303, 2935, 1662, 1540, 1499, 1441, 1252, 1040, 755 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{35}H_{55}N_2O_3Si$: 579.3982, found: 579.3960.

$[\alpha]^{24}_D$ = +16.5 (*c* 1.0, $CHCl_3$); >30:1 d.r., from (*R*,*R*)-**L***.

$[\alpha]^{24}_D$ = +33.5 (*c* 1.0, $CHCl_3$); 1:26 d.r., from (*S*,*S*)-**L***.



2-Ethyl-*N*-(4-bromophenyl)octanamide (Figure 2a, entry 15). The title compound was prepared according to **GP-1** from 2-bromo-*N*-(4-bromophenyl)butanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, pale-yellow solid.

(*R*,*R*)-**L***: 156 mg, 60% yield, 90% ee; (*S*,*S*)-**L***: 161 mg, 62% yield, 94% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.1 min (minor), 10.5 min (major).

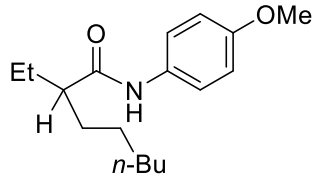
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.39 (m, 4H), 7.29 (s, 1H), 2.17 – 2.03 (m, 1H), 1.77 – 1.66 (m, 2H), 1.63 – 1.47 (m, 2H), 1.37 – 1.24 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 136.9, 131.9, 121.4, 116.7, 50.8, 32.8, 31.7, 29.4, 27.6, 26.1, 22.6, 14.0, 12.1.

FT-IR (film) 3288, 2926, 1660, 1521, 1398, 1300, 1073, 819 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{25}BrNO$: 326.1120, found: 326.1112.

$[\alpha]^{24}_D$ = −12.9 (*c* 1.0, $CHCl_3$); 90% ee, from (*R*,*R*)-**L***.



2-Ethyl-*N*-(4-methoxyphenyl)octanamide (Figure 2a, entry 16). The title compound was prepared according to **GP-1** from 2-bromo-*N*-(4-methoxyphenyl)butanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 214 mg, 96% yield, 95% ee; (*S*,*S*)-**L***: 210 mg, 95% yield, 98% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.9 min (major), 12.5 min (minor).

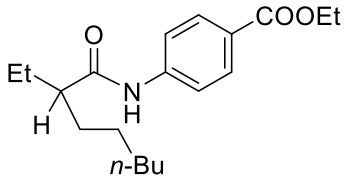
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.24 (s, 1H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 2.16 – 2.02 (m, 1H), 1.77 – 1.67 (m, 2H), 1.60 – 1.44 (m, 2H), 1.37 – 1.22 (m, 8H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 156.3, 131.0, 121.8, 114.0, 55.5, 50.6, 32.9, 31.7, 29.4, 27.7, 26.2, 22.6, 14.1, 12.1.

FT-IR (film) 3282, 2923, 1650, 1514, 1248, 1035, 827 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{28}NO_2$: 278.2120, found: 278.2119.

$[\alpha]^{24}_D$ = +12.8 (*c* 1.0, $CHCl_3$); 95% ee, from (*R*,*R*)-**L***.



Ethyl 4-(2-ethyloctanamido)benzoate (Figure 2a, entry 17). The title compound was prepared according to **GP-1** from ethyl 4-(2-bromobutanamido)benzoate and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 236 mg, 92% yield, 92% ee; (*S*,*S*)-**L***: 234 mg, 92% yield, 92% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.8 min (minor), 8.0 min (major).

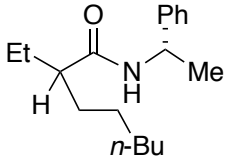
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.96 (m, 2H), 7.75 (s, 1H), 7.75 – 7.59 (m, 2H), 4.37 (q, *J* = 7.0 Hz, 2H), 2.23 – 2.11 (m, 1H), 1.78 – 1.66 (m, 2H), 1.64 – 1.47 (m, 2H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.34 – 1.23 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.91 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 166.2, 142.1, 130.7, 125.7, 118.8, 60.8, 50.8, 32.8, 31.7, 29.4, 27.6, 26.1, 22.6, 14.3, 14.0, 12.1.

FT-IR (film) 3313, 2930, 1718, 1669, 1597, 1529, 1409, 1276, 1173, 1106, 770 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{30}NO_3$: 320.2226, found: 320.2223.

$[\alpha]^{24}_D$ = −4.7 (*c* 1.0, $CHCl_3$); 92% ee, from (*R*,*R*)-**L***.



2-Ethyl-*N*-((*S*)-1-phenylethyl)octanamide (Figure 2a, entries 18 and 19). The title compound was prepared according to **GP-1** from 2-bromo-*N*-((*S*)-1-phenylethyl)butanamide and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 195 mg, 71% yield, 24:1 d.r.; (*S*,*S*)-**L***: 190 mg, 69% yield, 1:19 d.r.

HPLC analysis: The d.r. was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.4 min (minor), 13.2 min (major).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.69 (d, *J* = 8.1 Hz, 1H), 5.28 – 5.14 (m, 1H), 1.92 (ddd, *J* = 9.3, 5.0, 4.2 Hz, 1H), 1.62 (dddd, *J* = 12.2, 9.1, 4.7, 3.0 Hz, 2H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.50 – 1.40 (m, 2H), 1.37 – 1.25 (m, 8H), 0.93 – 0.88 (m, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 143.3, 128.6, 127.3, 126.2, 49.9, 48.3, 32.9, 31.8, 29.4, 27.7, 26.2, 22.6, 21.6, 14.1, 12.2.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.31 – 7.28 (m, 1H), 5.67 (d, *J* = 8.1 Hz, 1H), 5.22 (dq, *J* = 8.2, 6.9 Hz, 1H), 1.92 (tt, *J* = 9.3, 5.0 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.50 – 1.34 (m, 2H), 1.29 – 1.17 (m, 8H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H).

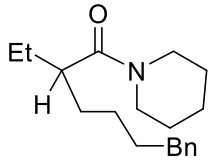
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 143.3, 128.6, 127.3, 126.2, 49.9, 48.4, 32.9, 31.8, 29.3, 27.6, 26.2, 22.6, 21.6, 14.1, 12.2.

FT-IR (film) 3293, 2923, 1638, 1547, 1448, 1233, 1130, 751, 697 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{30}NO$: 276.2327, found: 276.2319.

$[\alpha]^{24}_D$ = –72.1 (*c* 1.0, $CHCl_3$); 24:1 d.r., from (*R*,*R*)-**L***.

$[\alpha]^{24}_D$ = –77.7 (*c* 0.50, $CHCl_3$); 1:19 d.r., from (*S*,*S*)-**L***.



2-Ethyl-6-phenyl-1-(piperidin-1-yl)hexan-1-one (Figure 2a, entry 20). The title compound was prepared according to **GP-1** from 2-bromo-1-(piperidin-1-yl)butan-1-one and 4-phenyl-1-butene. Purification by flash column chromatography on silica gel: Et_2O/CH_2Cl_2/hexanes = 1:1:2, colorless oil.

(*R*,*R*)-**L***: 207 mg, 89% yield, 97% ee; (*S*,*S*)-**L***: 215 mg, 93% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 15.0 min (minor), 19.0 min (major).

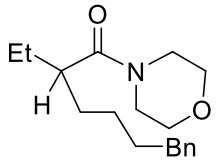
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 3.62 (t, *J* = 5.5 Hz, 2H), 3.48 (t, *J* = 5.5 Hz, 2H), 2.69 – 2.53 (m, 3H), 1.75 – 1.59 (m, 6H), 1.59 – 1.51 (m, 4H), 1.51 – 1.41 (m, 2H), 1.38 – 1.23 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 142.7, 128.4, 128.2, 125.6, 46.7, 42.9, 42.2, 35.9, 32.7, 31.7, 27.4, 26.9, 26.1, 25.9, 24.7, 12.1.

FT-IR (film) 2932, 1635, 1442, 1222, 1134, 1012, 699 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{30}NO$: 288.2327, found: 288.2328.

$[\alpha]^{24}_D$ = −6.0 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.



2-Ethyl-1-morpholino-6-phenylhexan-1-one (Figure 2a, entry 21). The title compound was prepared according to **GP-1** from 2-bromo-1-morpholinobutan-1-one and 4-phenyl-1-butene. Purification by flash column chromatography on silica gel: 15→25% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 150 mg, 65% yield, 96% ee; (*S*,*S*)-**L***: 144 mg, 62% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 18.1 min (minor), 22.6 min (major).

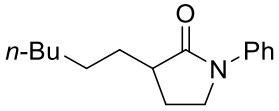
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.24 – 7.14 (m, 3H), 3.75 – 3.61 (m, 6H), 3.58 – 3.50 (m, 2H), 2.68 – 2.58 (m, 2H), 2.58 – 2.50 (m, 1H), 1.81 – 1.61 (m, 4H), 1.53 – 1.43 (m, 2H), 1.35 – 1.25 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 142.5, 128.4, 128.3, 125.7, 67.2, 66.9, 46.2, 42.2, 42.1, 35.8, 32.5, 31.6, 27.3, 26.0, 12.1.

FT-IR (film) 2928, 1643, 1454, 1226, 1116, 1032, 700 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO_2$: 290.2120, found: 290.2119.

$[\alpha]^{24}_D$ = −6.4 (*c* 1.0, $CHCl_3$); 96% ee, from (*R*,*R*)-**L***.



3-Hexyl-1-phenylpyrrolidin-2-one (Figure 2a, entry 22). The title compound was prepared according to **GP-1** from 3-iodo-1-phenylpyrrolidin-2-one and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 167 mg, 85% yield, 88% ee; (*S*,*S*)-**L***: 171 mg, 87% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.7 min (minor), 10.8 min (major).

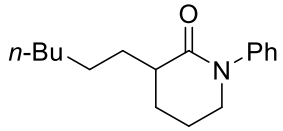
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 2H), 7.43 – 7.34 (m, 2H), 7.19 – 7.12 (m, 1H), 3.86 – 3.75 (m, 2H), 2.70 – 2.53 (m, 1H), 2.42 – 2.27 (m, 1H), 2.09 – 1.93 (m, 1H), 1.89 – 1.76 (m, 1H), 1.57 – 1.29 (m, 9H), 0.97 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 139.7, 128.8, 124.3, 119.7, 46.8, 43.5, 31.8, 31.2, 29.3, 27.2, 24.8, 22.6, 14.1.

FT-IR (film) 2923, 1684, 1501, 1394, 1225, 1114, 752 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO$: 246.1858, found: 246.1854.

$[\alpha]^{24}_D$ = −7.9 (*c* 1.0, $CHCl_3$); 88% ee, from (*R,R*)-**L***.



3-Hexyl-1-phenylpiperidin-2-one (Figure 2a, entry 23). The title compound was prepared according to **GP-1** from 3-iodo-1-phenylpiperidin-2-one and 1-hexene. Purification by flash column chromatography on silica gel: 15→25% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 200 mg, 96% yield, 98% ee; (*S,S*)-**L***: 192 mg, 92% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 8.5 min (minor), 9.4 min (major).

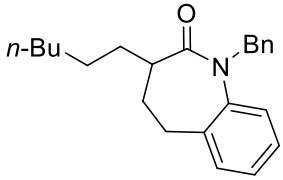
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.28 – 7.23 (m, 3H), 3.71 – 3.60 (m, 2H), 2.57 – 2.39 (m, 1H), 2.15 – 1.88 (m, 4H), 1.77 – 1.66 (m, 1H), 1.61 – 1.51 (m, 1H), 1.44 – 1.28 (m, 8H), 0.96 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 143.7, 129.0, 126.4, 126.2, 51.6, 41.9, 31.9, 31.8, 29.4, 27.1, 26.5, 22.7, 22.2, 14.1.

FT-IR (film) 2926, 1652, 1495, 1302, 1184, 760, 695 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{26}NO$: 260.2014, found: 260.2012.

$[\alpha]^{23}_D$ = −34.3 (*c* 0.50, $CHCl_3$); 98% ee, from (*R,R*)-**L***.



1-Benzyl-3-hexyl-1,3,4,5-tetrahydro-2*H*-benzo[*b*]azepin-2-one (Figure 2a, entry 24). The title compound was prepared according to **GP-1** from 1-benzyl-3-iodo-1,3,4,5-tetrahydro-2*H*-benzo[b]azepin-2-one and 1-hexene. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 225 mg, 84% yield, 97% ee; (*S,S*)-**L***: 214 mg, 80% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 6.4 min (minor), 7.2 min (major).

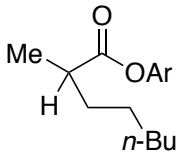
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 6H), 7.22 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 5.16 (d, *J* = 14.7 Hz, 1H), 4.93 (d, *J* = 14.7 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.46 – 2.31 (m, 2H), 2.14 – 2.00 (m, 1H), 1.97 – 1.79 (m, 2H), 1.34 – 1.22 (m, 8H), 1.20 – 1.08 (m, 1H), 0.90 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 142.3, 138.1, 136.5, 129.0, 128.4, 128.1, 127.4, 127.2, 126.2, 122.9, 51.7, 41.6, 37.0, 31.8, 30.9, 29.9, 29.5, 27.8, 22.6, 14.1.

FT-IR (film) 2928, 1665, 1490, 1454, 1395, 1260, 1181, 700 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{30}NO$: 336.2327, found: 336.2321.

$[\alpha]^{24}_D$ = +186 (*c* 0.50, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.



Ar = 2,6-di-*t*-butyl-4-methylphenyl

2,6-Di-*tert*-butyl-4-methylphenyl-2-methyloctanoate (Figure 2a, entry 25). The title compound was prepared according to **GP-2** from 2,6-di-*tert*-butyl-4-methylphenyl 2-bromopropanoate and 1-hexene at room temperature for 40 h. Purification by flash column chromatography on silica gel: 20→33% CH_2Cl_2 in hexanes, colorless oil.

(*R*,*R*)-**L***: 254 mg, 88% yield, 98% ee; (*S*,*S*)-**L***: 249 mg, 86% yield, 96% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.3 min (major), 9.0 min (minor).

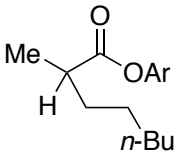
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 0.8 Hz, 2H), 2.83 – 2.65 (m, 1H), 2.35 (d, *J* = 0.6 Hz, 3H), 2.12 – 1.98 (m, 1H), 1.62 – 1.49 (m, 2H), 1.42 – 1.31 (m, 7H), 1.40 (d, *J* = 8.0 Hz, 3H), 1.36 (s, 9H), 1.35 (s, 9H), 0.99 – 0.89 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 146.5, 142.01, 141.98, 134.3, 127.01, 127.00, 40.2, 35.3, 35.2, 32.6, 31.8, 31.5, 31.4, 29.2, 27.2, 22.6, 21.5, 15.8, 14.1.

FT-IR (film) 2958, 1753, 1420, 1363, 1183, 1106, 859 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{24}H_{44}NO_2$: 378.3372, found: 378.3364.

$[\alpha]^{24}_D$ = −4.3 (*c* 1.0, $CHCl_3$); 98% ee, from (*R*,*R*)-**L***.



Ar = 2,6-di-*t*-butyl-4-methoxyphenyl

2,6-Di-*tert*-butyl-4-methoxyphenyl-2-methyloctanoate (Figure 2a, entry 26). The title compound was prepared according to **GP-2** from 2,6-di-*tert*-butyl-4-methoxyphenyl 2-bromopropanoate and 1-hexene at room temperature for 40 h. Purification by flash column chromatography on silica gel: 25→50% CH_2Cl_2 in hexanes, colorless oil.

(*R*,*R*)-**L***: 262 mg, 87% yield, 98% ee; (*S*,*S*)-**L***: 249 mg, 86% yield, 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 3.82 (s, 3H), 2.82 – 2.64 (m, 1H), 2.11 – 1.98 (m, 1H), 1.59 – 1.47 (m, 2H), 1.43 – 1.31 (m, 7H), 1.39 (d, *J* = 8.0 Hz, 3 H), 1.35 (s, 9H), 1.34 (s, 9H), 0.96 – 0.89 (m, 3H).

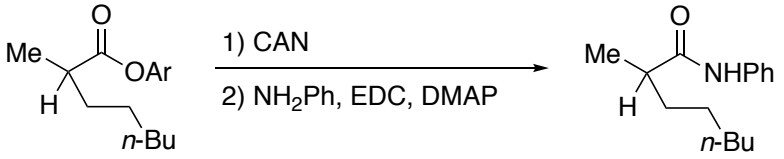
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 156.1, 143.5, 143.4, 142.3, 111.6, 55.2, 40.2, 35.7, 35.6, 32.6, 31.7, 31.3, 31.2, 29.2, 27.1, 22.6, 15.8, 14.1.

FT-IR (film) 2958, 1752, 1594, 1456, 1417, 1303, 1171, 1104, 867 cm^{-1}.

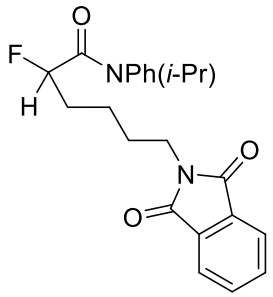
HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{24}H_{44}NO_3$: 394.3321, found: 394.3317.

$[\alpha]^{24}_D$ = −2.5 (*c* 1.0, $CHCl_3$); 98% ee, from (*R,R*)-**L***.

Determination of the ee: see Derivatization of the Coupling Products for additional details.



HPLC analysis: The ee was determined on a CHIRALPAK IC column (5% *i*-PrOH in hexane, 1 mL/min); retention times for compound obtained using (*R,R*)-**L***: 12.4 min (major), 13.3 min (minor).



6-(1,3-Dioxoisoindolin-2-yl)-2-fluoro-*N*-isopropyl-*N*-phenylhexanamide (Figure 2c, entry 32). The title compound was prepared according to **GP-1** from 2-bromo-2-fluoro-*N*-isopropyl-*N*-phenylacetamide and 2-(but-3-en-1-yl)isoindoline-1,3-dione. Purification by flash column chromatography on silica gel: 20→33% EtOAc in hexanes, white solid.

(*R,R*)-**L***: 234 mg, 74% yield, 90% ee; (*S,S*)-**L***: 225 mg, 71% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 10.3 min (major), 12.4 min (minor).

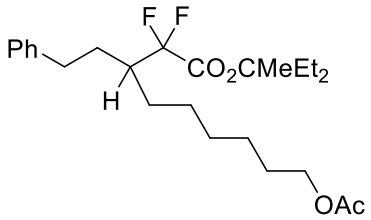
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.78 – 7.67 (m, 2H), 7.53 – 7.39 (m, 3H), 7.21 – 7.10 (m, 2H), 5.05 - 4.95 (m, 1H), 4.55 (ddd, *J* = 49.3, 8.3, 4.3 Hz, 1H), 3.61 (t, *J* = 7.1 Hz, 2H), 1.94 – 1.80 (m, 1H), 1.79 – 1.69 (m, 1H), 1.62 – 1.49 (m, 2H), 1.44 – 1.30 (m, 1H), 1.29 – 1.20 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 168.1 (d, *J* = 21 Hz), 136.8, 133.9, 132.1, 130.4 (d, *J* = 19 Hz), 129.4 (d, *J* = 34 Hz), 128.8, 123.2, 87.8 (d, *J* = 174 Hz), 46.7, 37.6, 31.7 (d, *J* = 23 Hz), 28.0, 21.8 (d, *J* = 5 Hz), 21.0, 20.4.

FT-IR (film) 2975, 1714, 1669, 1397, 1368, 1248, 1118, 720 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{26}FN_2O_3$: 397.1927, found: 397.1926.

$[\alpha]^{23}_D$ = +3.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*R,R*)-**L***.



3-Methylpentan-3-yl 9-acetoxy-2,2-difluoro-3-phenethylnonanoate (Figure 2c, entry 33). The title compound was prepared according to **GP-2** from 3-methylpentan-3-yl 3-bromo-2,2-difluoro-5-phenylpentanoate and hex-5-en-1-yl acetate. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 209 mg, 59% yield, 89% ee; (*S*,*S*)-**L***: 206 mg, 58% yield, 89% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.7 min (minor), 9.6 min (major).

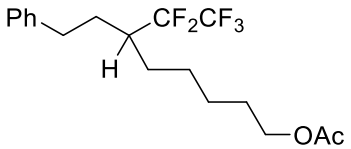
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.26 – 7.15 (m, 3H), 4.07 (t, *J* = 6.8 Hz, 2H), 2.81 – 2.61 (m, 2H), 2.23 – 2.09 (m, 1H), 2.07 (s, 3H), 2.00 – 1.88 (m, 3H), 1.88 – 1.75 (m, 2H), 1.72 – 1.56 (m, 4H), 1.48 (s, 3H), 1.47 – 1.26 (m, 7H), 0.91 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 163.2 (t, *J* = 32 Hz), 141.8, 128.4, 128.3, 126.0, 118.1 (t, *J* = 252 Hz), 89.8, 64.5, 41.8 (t, *J* = 21 Hz), 33.5, 30.3, 29.5, 29.4, 28.6, 27.6 (t, *J* = 4 Hz), 27.0, 25.8, 22.5, 21.0, 7.9.

FT-IR (film) 2941, 1742, 1458, 1240, 1126, 1057, 842, 750, 700 cm^{-1}.

HRMS (FAB) m/z $[M+H]^+$ calcd for $C_{25}H_{39}F_2O_4$: 441.2816, found: 441.2841.

$[\alpha]^{23}_D$ = −3.2 (*c* 1.0, $CHCl_3$); 89% ee, from (*R*,*R*)-**L***.



7,7,8,8,8-Pentafluoro-6-phenethyloctyl acetate (Figure 2c, entry 34). The title compound was prepared according to **GP-2** from (3-bromo-4,4,5,5,5-pentafluoropentyl)benzene and pent-4-en-1-yl acetate for 60 h. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 230 mg, 78% yield, 90% ee; (*S*,*S*)-**L***: 236 mg, 80% yield, 89% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.9 min (minor), 8.2 min (major).

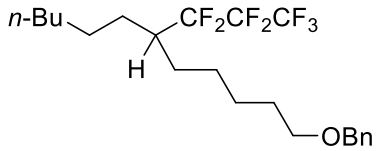
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.80 – 2.62 (m, 2H), 2.24 – 2.09 (m, 1H), 2.08 (s, 3H), 2.07 – 1.97 (m, 1H), 1.87 – 1.61 (m, 4H), 1.59 – 1.42 (m, 2H), 1.42 – 1.29 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 141.1, 128.5, 128.3, 126.2, 128.6 – 114.5 (m, 2 carbons), 64.4, 39.9 (t, *J* = 20 Hz), 33.1, 28.7, 28.4, 26.7, 26.4, 26.1, 21.0.

FT-IR (film) 2953, 1741, 1456, 1366, 1243, 1202, 1081, 753, 700 cm^{-1}.

HRMS (FAB) m/z $[M+H]^+$ calcd for $C_{18}H_{24}F_5O_2$: 367.1696, found: 367.1686.

$[\alpha]^{23}_D$ = −5.8 (*c* 1.0, $CHCl_3$); 90% ee, from (*R*,*R*)-**L***.



(((6-(Perfluoropropyl)dodecyl)oxy)methyl)benzene (Figure 2c, entry 35). The title compound was prepared according to **GP-2** from 4-bromo-1,1,1,2,2,3,3-heptafluorodecane and ((pent-4-en-1-yloxy)methyl)benzene for 60 h. Purification by flash column chromatography on silica gel: 5→10% CH_2Cl_2 in hexanes, colorless oil.

(*R*,*R*)-**L***: 245 mg, 69% yield, 90% ee; (*S*,*S*)-**L***: 264 mg, 74% yield, 89% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (hexanes, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 14.6 min (minor), 16.7 min (major).

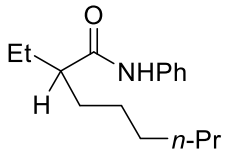
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 4H), 7.25 – 7.16 (m, 1H), 4.43 (s, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 2.10 – 2.00 (m, 1H), 1.69 – 1.50 (m, 4H), 1.45 – 1.15 (m, 14H), 0.89 – 0.73 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 128.4, 127.6, 127.5, 128.5 – 109.7 (m, 3 carbons), 72.9, 70.2, 40.8 (t, *J* = 20 Hz), 31.6, 29.6, 29.4, 26.8, 26.74, 26.69, 26.6 (q, *J* = 2 Hz), 26.4, 22.6, 14.1.

FT-IR (film) 2932, 2859, 1455, 1350, 1227, 1174, 1104, 937, 733 cm^{-1}.

HRMS (FAB) m/z [M+H-H_2]$^+$ calcd for $C_{22}H_{30}F_7O$: 443.2185, found: 443.2213.

$[\alpha]^{24}_D$ = −1.8 (*c* = 1.0, $CHCl_3$); 90% ee, from (*R*,*R*)-**L***.

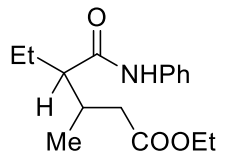


2-Ethyl-*N*-phenyloctanamide (Figure 2d, entry 36). The title compound was prepared according to **GP-2** from 2-bromo-*N*-phenylbutanamide and *cis*-2-hexene with 2.0 equiv NaI as an additive. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 132 mg, 67% yield, 90% ee; (*S*,*S*)-**L***: 131 mg, 66% yield, 90% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.8 min (major), 7.9 min (minor).

The characterization data match that for Figure 2a, entry 1.



Ethyl 3-methyl-4-(phenylcarbamoyl)hexanoate (Figure 2d, entry 37). The title compound

was prepared according to **GP-1** from 2-bromo-*N*-phenylbutanamide and ethyl but-3-enoate with 0.5 equiv $(n\text{-Bu})_4NI$ as an additive. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, white solid as a mixture of diastereomers.

(*R*,*R*)-**L***: 155 mg, 70% yield, 86% ee/ 93% ee, 2:1 diastereoselectivity, 7:1 regioselectivity; (*S*,*S*)-**L***: 160 mg, 72% yield, 87% ee / 93% ee, 2:1 diastereoselectivity, 6:1 regioselectivity.

The diastereoselectivity was determined via ^1H NMR analysis of the unpurified reaction mixture. The regioselectivity was determined via GC analysis of the unpurified reaction mixture.

The diastereomers were separated via HPLC: Agilent XDB-C18 (internal diameter 9.4 mm, column length 250 mm, particle size 5 μm), 45% CH_3CN in H_2O, 4.5 mL/min.

Characterization data of the major diastereomer:

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 17.4 min (major), 20.5 min (minor).

^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.58 – 7.45 (m, 2H), 7.31 – 7.20 (m, 2H), 7.08 – 6.96 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.37 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.25 (dd, *J* = 14.1, 5.9 Hz, 1H), 2.22 – 2.07 (m, 2H), 1.90 – 1.72 (m, 1H), 1.52 – 1.34 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 172.0, 138.0, 128.9, 124.1, 119.8, 60.7, 53.0, 39.8, 33.7, 23.2, 17.0, 14.3, 12.4.

FT-IR (film) 3291, 2965, 1727, 1654, 1532, 1442, 1379, 1309, 1174, 1032, 752 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO_3$: 278.1756, found: 278.1755.

$[\alpha]^{24}_D$ = +61.0 (*c* = 0.80, $CHCl_3$); 86% ee, from (*R*,*R*)-**L***.

Charaterization data of the minor diastereomer:

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 13.3 min (major), 15.6 min (minor).

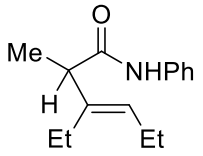
^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.56 – 7.43 (m, 2H), 7.29 – 7.21 (m, 2H), 7.09 – 6.97 (m, 1H), 4.08 (qd, *J* = 7.2, 2.4 Hz, 2H), 2.39 (dd, *J* = 15.1, 4.8 Hz, 1H), 2.25 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.21 – 2.06 (m, 2H), 1.71 – 1.63 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.3, 137.9, 128.9, 124.1, 119.8, 60.5, 54.2, 39.0, 33.1, 22.3, 17.2, 14.2, 12.4.

FT-IR (film) 3291, 2959, 1727, 1654, 1534, 1440, 1376, 1309, 1200, 1175, 1030, 752 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO_3$: 278.1756, found: 278.1755.

$[\alpha]^{24}_D$ = −52.3 (*c* = 1.0, $CHCl_3$); 93% ee, from (*R*,*R*)-**L***.



(*E*)-3-Ethyl-2-methyl-*N*-phenylhex-3-enamide (Figure 2e, entry 38). The title compound was prepared according to **GP-2** from 2-bromo-*N*-phenylpropanamide and 3-hexyne. Purification by flash column chromatography on silica gel: 15% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 148 mg, 80% yield, 98% ee, *E:Z* >15:1; (*S*,*S*)-**L***: 156 mg, 84% yield, 98% ee, *E:Z* >15:1.

The *E*/*Z* ratio was determined via GC analysis of the unpurified product.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.2 min (minor), 8.2 min (major).

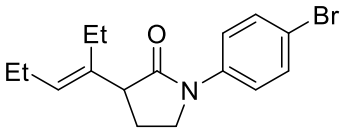
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.48 (s, 1H), 7.37 – 7.30 (m, 2H), 7.16 – 7.05 (m, 1H), 5.50 (t, *J* = 7.2 Hz, 1H), 3.26 – 3.09 (m, 1H), 2.28 – 2.14 (m, 3H), 2.13 – 2.04 (m, 1H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 141.0, 137.9, 130.5, 128.9, 124.0, 119.4, 49.6, 22.7, 21.1, 15.9, 14.5, 13.9.

FT-IR (film) 3248, 2964, 1653, 1544, 1443, 1245, 1190, 761 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{22}NO$: 232.1701, found: 232.1694.

$[\alpha]^{24}_D$ = −37.2 (*c* = 1.0, $CHCl_3$); 98% ee, from (*R*,*R*)-**L***.



(*E*)-1-(4-Bromophenyl)-3-(hex-3-en-3-yl)pyrrolidin-2-one (Figure 2e, entry 39). The title compound was prepared according to **GP-2** from 3-bromo-1-(4-bromophenyl)pyrrolidin-2-one and 3-hexyne. Purification by flash column chromatography on silica gel: 10→15% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 195 mg, 76% yield, 98% ee, *E:Z* >15:1; (*S*,*S*)-**L***: 207 mg, 80% yield, 98% ee, *E:Z* > 15:1.

The *E*/*Z* ratio was determined via GC analysis of the unpurified product.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 15.0 min (minor), 16.3 min (major).

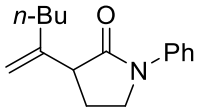
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 2H), 7.53 – 7.42 (m, 2H), 5.30 (td, *J* = 6.9, 0.8 Hz, 1H), 3.90 – 3.68 (m, 2H), 3.27 (ddd, *J* = 9.0, 8.3, 0.7 Hz, 1H), 2.38 – 2.30 (m, 1H), 2.30 – 2.20 (m, 1H), 2.17 – 2.06 (m, 4H), 1.06 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 138.7, 137.2, 131.7, 130.3, 121.1, 117.0, 50.9, 46.5, 24.9, 22.7, 21.1, 14.4, 13.8.

FT-IR (film) 2961, 2872, 1697, 1492, 1386, 1316, 1221, 1074, 826 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{21}BrNO$: 322.0807, found: 322.0798.

$[\alpha]^{23}_D$ = −21.2 (*c* = 1.0, $CHCl_3$); 98% ee, from (*R*,*R*)-**L***.



3-(Hex-1-en-2-yl)-1-phenylpyrrolidin-2-one (Figure 2e, entry 40). The title compound was prepared according to **GP-2** from 3-bromo-1-phenylpyrrolidin-2-one and 1-hexyne for 60 h. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, pale-yellow oil as a mixture of regioisomers.

(*R*,*R*)-**L***: 130 mg, 67% yield, 96% ee, 5:1 regioselectivity; (*S*,*S*)-**L***: 121 mg, 62% yield, 96% ee, 5:1 regioselectivity.

The regioselectivity was determined via GC analysis of the unpurified reaction mixture.

SFC analysis: The ee was determined on a CHIRALCEL OD-H column (15% *i*-PrOH in CO_2, 3.5 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 3.2 min (minor), 5.0 min (major).

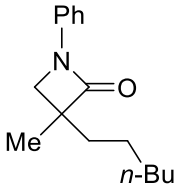
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.34 – 7.27 (m, 2H), 7.11 – 7.04 (m, 1H), 5.03 – 4.76 (m, 2H), 3.84 – 3.69 (m, 2H), 3.25 (ddd, *J* = 8.9, 7.8, 1.0 Hz, 1H), 2.38 – 2.18 (m, 1H), 2.16 – 1.96 (m, 3H), 1.49 – 1.36 (m, 2H), 1.33 – 1.25 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 146.7, 139.5, 128.8, 124.5, 119.8, 111.6, 50.4, 46.8, 34.0, 29.8, 24.7, 22.6, 14.1.

FT-IR (film) 2955, 2871, 1698, 1498, 1392, 1302, 1225, 893, 758 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{22}NO$: 244.1701, found: 244.1699.

$[\alpha]^{24}_D$ = −20.5 (*c* = 1.0, $CHCl_3$); 96% ee, from (*R*,*R*)-**L***.



3-Hexyl-3-methyl-1-phenylazetidin-2-one (Figure 3a, entry 41). The title compound was prepared according to **GP-1** from 3-bromo-3-methyl-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 183 mg, 93% yield, 99% ee; (*S*,*S*)-**L***: 172 mg, 88% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.5 min (major), 6.4 min (minor).

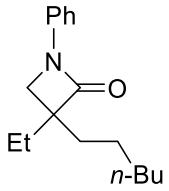
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 4H), 7.17 – 7.04 (m, 1H), 3.52 (d, *J* = 5.5 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 1.80 – 1.66 (m, 2H), 1.56 – 1.44 (m, 1H), 1.41 (s, 3H), 1.39 – 1.26 (m, 7H), 0.98 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 138.6, 129.1, 123.6, 116.3, 53.7, 51.1, 34.9, 31.7, 29.6, 24.7, 22.6, 19.6, 14.1.

FT-IR (film): 2929, 1750, 1600, 1503, 1388, 1150, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO$: 246.1858, found: 246.1854.

$[\alpha]^{23}_D$ = −15.9 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



3-Ethyl-3-hexyl-1-phenylazetidin-2-one (Figure 3a, entry 42). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 190 mg, 92% yield, 99% ee; (*S*,*S*)-**L***: 198 mg, 95% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.9 min (major), 6.8 min (major).

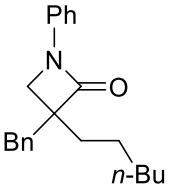
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.13 – 7.07 (m, 1H), 3.43 (s, 2H), 1.84 – 1.76 (m, 2H), 1.76 – 1.67 (m, 2H), 1.55 – 1.41 (m, 1H), 1.41 – 1.27 (m, 7H), 1.03 (t, *J* = 7.6 Hz, 3H), 0.95 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 138.5, 129.1, 123.6, 116.3, 58.2, 48.2, 32.8, 31.7, 29.7, 25.9, 24.4, 22.6, 14.1, 8.9.

FT-IR (film): 2929, 1748, 1600, 1503, 1381, 1150, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{26}NO$: 260.2014, found: 260.2009.

$[\alpha]^{23}_D$ = +3.3 (*c* = 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



3-Benzyl-3-hexyl-1-phenylazetidin-2-one (Figure 3a, entry 43). The title compound was prepared according to **GP-1** from 3-benzyl-3-bromo-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 227 mg, 88% yield, 99% ee; (*S*,*S*)-**L***: 210 mg, 82% yield, 98% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.4 min (major), 8.2 min (minor).

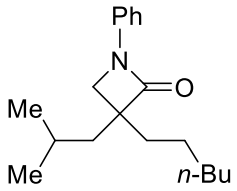
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 8H), 7.25 – 7.19 (m, 1H), 7.11 – 7.04 (m, 1H), 3.47 (d, *J* = 5.7 Hz, 1H), 3.40 (d, *J* = 5.7 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 1.87 – 1.66 (m, 2H), 1.59 – 1.40 (m, 2H), 1.38 – 1.26 (m, 6H), 0.94 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 138.1, 136.8, 129.9, 129.0, 128.4, 126.7, 123.7, 116.3, 58.4, 47.4, 39.3, 33.7, 31.7, 29.6, 24.5, 22.6, 14.1.

FT-IR (film): 2929, 1747, 1600, 1501, 1385, 1153, 755 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{28}NO$: 322.2171, found: 322.2171.

$[\alpha]^{23}_D$ = +66.8 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



3-Hexyl-3-isobutyl-1-phenylazetidin-2-one (Figure 3a, entry 44). The title compound was prepared according to **GP-1** from 3-bromo-3-isobutyl-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 195 mg, 85% yield, 97% ee; (*S*,*S*)-**L***: 184 mg, 80% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 4.1 min (major), 4.9 min (minor).

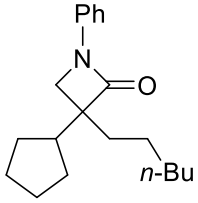
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 4H), 7.18 – 7.02 (m, 1H), 3.51 (d, *J* = 5.7 Hz, 1H), 3.46 (d, *J* = 5.7 Hz, 1H), 1.96 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H), 1.61 – 1.44 (m, 2H), 1.43 – 1.21 (m, 7H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.92 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 138.5, 129.1, 123.6, 116.3, 57.1, 50.1, 41.6, 32.9, 31.7, 29.8, 24.8, 24.4, 24.3, 22.8, 22.6, 14.1.

FT-IR (film): 2929, 1748, 1599, 1502, 1383, 1151, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{30}NO$: 288.2327, found: 288.2329.

$[\alpha]^{23}_D$ = +2.2 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.



3-Cyclopentyl-3-hexyl-1-phenylazetidin-2-one (Figure 3a, entry 45). The title compound was prepared according to **GP-1** from 3-bromo-3-cyclopentyl-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 193 mg, 80% yield, 97% ee; (*S*,*S*)-**L***: 181 mg, 76% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.7 min (major), 8.7 min (minor).

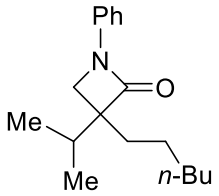
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 4H), 7.17 – 7.05 (m, 1H), 3.50 – 3.32 (m, 2H), 2.25 (tt, *J* = 9.9, 7.9 Hz, 1H), 1.90 – 1.73 (m, 4H), 1.71 – 1.64 (m, 2H), 1.64 – 1.53 (m, 2H), 1.53 – 1.38 (m, 3H), 1.37 – 1.25 (m, 7H), 0.98 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 138.3, 129.1, 123.6, 116.3, 60.6, 46.6, 42.2, 33.4, 31.7, 29.8, 28.1, 27.7, 25.5, 25.4, 24.6, 22.6, 14.1.

FT-IR (film): 2953, 1747, 1599, 1501, 1382, 1149, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{30}NO$: 300.2327, found: 300.2325.

$[\alpha]^{23}_D$ = +11.1 (*c* 1.0, $CHCl_3$); 97% ee, from (*R,R*)-**L***.



3-Hexyl-3-isopropyl-1-phenylazetidin-2-one (Figure 3a, entry 46). The title compound was prepared according to **GP-1** from 3-bromo-3-isopropyl-1-phenylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless oil.

(*R,R*)-**L***: 161 mg, 74% yield, 98% ee; (*S,S*)-**L***: 170 mg, 78% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 6.4 min (major), 7.2 min (minor).

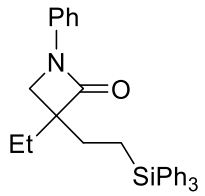
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 4H), 7.15 – 7.06 (m, 1H), 3.45 (d, *J* = 5.8 Hz, 1H), 3.35 (d, *J* = 5.8 Hz, 1H), 2.17 – 2.02 (m, 1H), 1.79 – 1.67 (m, 2H), 1.49 – 1.37 (m, 2H), 1.36 – 1.26 (m, 6H), 1.08 – 0.99 (m, 6H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 138.3, 129.1, 123.6, 116.2, 61.8, 45.9, 31.7, 30.8, 30.4, 29.8, 24.4, 22.6, 18.2, 17.6, 14.1.

FT-IR (film): 2931, 1744, 1600, 1502, 1382, 1151, 754 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO$: 274.2171, found: 274.2165.

$[\alpha]^{23}_D$ = +31.6 (*c* 1.0, $CHCl_3$); 98% ee, from (*R,R*)-**L***.



3-Ethyl-1-phenyl-3-(2-(triphenylsilyl)ethyl)azetidin-2-one (Figure 3a, entry 47). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and triphenyl(vinyl)silane at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, colorless viscous oil.

(*R,R*)-**L***: 283 mg, 77% yield, 95% ee; (*S,S*)-**L***: 293 mg, 79% yield, 94% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 5.8 min (major), 7.4 min (minor).

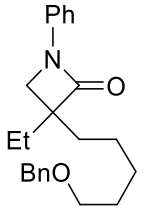
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 6H), 7.45 – 7.35 (m, 13H), 7.16 – 7.07 (m, 1H), 3.46 – 3.37 (m, 2H), 2.00 – 1.86 (m, 2H), 1.86 – 1.76 (m, 2H), 1.59 – 1.49 (m, 1H), 1.49 – 1.36 (m, 1H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 138.4, 135.6, 134.4, 129.6, 129.1, 128.0, 123.6, 116.3, 59.6, 47.8, 27.2, 25.3, 8.8, 7.6.

FT-IR (film) 3068, 2925, 1740, 1599, 1502, 1382, 1150, 1111, 756, 701 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{31}H_{35}N_2OSi$: 479.2519, found: 479.2510.

$[\alpha]^{23}_D$ = –5.6 (*c* 1.0, $CHCl_3$); 95% ee, from (*R,R*)-**L***.



3-(5-(Benzyloxy)pentyl)-3-ethyl-1-phenylazetidin-2-one (Figure 3a, entry 48). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and ((pent-4-en-1-yloxy)methyl)benzene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R,R*)-**L***: 246 mg, 87% yield, 99% ee; (*S,S*)-**L***: 234 mg, 83% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,R*)-**L***: 9.5 min (major), 10.7 min (minor).

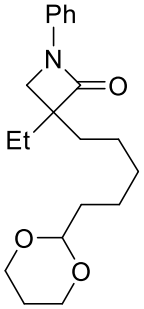
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 8H), 7.34 – 7.29 (m, 1H), 7.14 – 7.08 (m, 1H), 4.52 (s, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 3.46 – 3.38 (m, 2H), 1.86 – 1.71 (m, 4H), 1.70 – 1.59 (m, 2H), 1.57 – 1.36 (m, 4H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 138.6, 138.4, 129.1, 128.4, 127.6, 127.5, 123.6, 116.3, 72.9, 70.2, 58.1, 48.2, 32.8, 29.6, 26.7, 25.9, 24.3, 8.9.

FT-IR (film): 2935, 2858, 1744, 1599, 1502, 1383, 1151, 1105, 755 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{23}H_{33}N_2O_2$: 369.2542, found: 369.2542.

$[\alpha]^{23}_D$ = +2.1 (*c* 1.0, $CHCl_3$); 99% ee, from (*R,R*)-**L***.



3-(5-(1,3-Dioxan-2-yl)pentyl)-3-ethyl-1-phenylazetidin-2-one (Figure 3a, entry 49). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and

2-(pent-4-en-1-yl)-1,3-dioxane at 0 °C. Purification by flash column chromatography on silica gel: Et_2O/CH_2Cl_2/hexanes = 1:2:5→1:1:3, colorless oil.

(*R*,*R*)-**L***: 249 mg, 94% yield, 99% ee; (*S*,*S*)-**L***: 253 mg, 95% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.5 min (minor), 8.4 min (major).

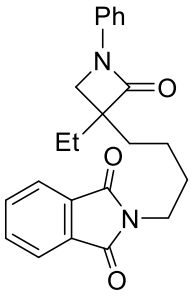
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.03 – 6.97 (m, 1H), 4.42 (t, *J* = 5.1 Hz, 1H), 4.07 – 3.95 (m, 2H), 3.73 – 3.61 (m, 2H), 3.32 (s, 2H), 2.08 – 1.91 (m, 1H), 1.72 – 1.61 (m, 4H), 1.54 – 1.47 (m, 2H), 1.41 – 1.19 (m, 7H), 0.93 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 138.4, 129.1, 123.6, 116.3, 102.3, 66.9, 58.2, 48.2, 35.1, 32.6, 29.8, 25.9, 25.8, 24.4, 23.8, 8.9.

FT-IR (film): 2931, 1746, 1599, 1502, 1382, 1146, 1090, 756 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{20}H_{33}N_2O_3$: 349.2491, found: 349.2494.

$[\alpha]^{23}_D$ = +11.9 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



2-(4-(3-Ethyl-2-oxo-1-phenylazetidin-3-yl)butyl)isoindoline-1,3-dione (Figure 3a, entry 50). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and 2-(but-3-en-1-yl)isoindoline-1,3-dione at 0 °C. Purification by flash column chromatography on silica gel: 20→33% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 273 mg, 91% yield, 99% ee; (*S*,*S*)-**L***: 280 mg, 93% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 17.0 min (major), 20.5 min (minor).

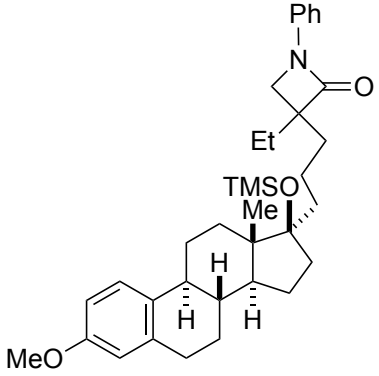
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.18 – 7.05 (m, 1H), 3.76 – 3.64 (m, 2H), 3.47 – 3.39 (m, 2H), 1.86 – 1.69 (m, 6H), 1.62 – 1.51 (m, 1H), 1.51 – 1.40 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.4, 138.4, 133.9, 132.1, 129.1, 123.7, 123.2, 116.3, 58.0, 48.2, 37.6, 32.3, 28.9, 25.7, 21.8, 8.8.

FT-IR (film): 2939, 1742, 1717, 1598, 1502, 1396, 1152, 721 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3$: 377.1865, found: 377.1864.

$[\alpha]^{23}_D$ = −3.5 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



3-Ethyl-3-(3-((8*R*,9*S*,13*S*,14*S*,17*S*)-3-methoxy-13-methyl-17-((trimethylsilyl)oxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)propyl)-1-phenylazetidin-2-one (Figure 3a, entries 51 and 52). The title compound was prepared according to **GP-1** from 3-bromo-3-ethyl-1-phenylazetidin-2-one and (((8*R*,9*S*,13*S*,14*S*,17*R*)-17-allyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)oxy)trimethylsilane at 0 °C. Purification by flash column chromatography on silica gel: 5→10% EtOAc in hexanes, white solid.

(*R*,*R*)-**L***: 387 mg, 84% yield, >30:1 d.r.; (*S*,*S*)-**L***: 401 mg, 87% yield, 1:>30 d.r.

HPLC analysis: The d.r. was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.9 min (minor), 11.7 min (major).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 4H), 7.13 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.07 – 6.95 (m, 1H), 6.64 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 3.70 (s, 3H), 3.46 – 3.24 (m, 2H), 2.82 – 2.72 (m, 2H), 2.28 – 2.18 (m, 1H), 2.10 – 2.00 (m, 1H), 1.83 – 1.70 (m, 5H), 1.69 – 1.50 (m, 6H), 1.45 – 1.19 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.73 (s, 3H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.9, 136.1, 135.6, 130.4, 126.6, 123.9, 121.1, 113.8, 111.3, 108.9, 84.4, 55.9, 52.8, 46.2, 45.9, 45.3, 41.4, 37.3, 36.2, 32.8, 31.1, 29.6, 27.5, 25.1, 24.0, 23.4, 21.0, 17.4, 12.8, 6.5, 0.3.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.19 – 7.14 (m, 1H), 7.04 (tt, *J* = 6.8, 1.4 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 3.74 (s, 3H), 3.41 (q, *J* = 5.7 Hz, 2H), 2.84 – 2.76 (m, 2H), 2.31 – 2.22 (m, 1H), 2.10 (q, *J* = 5.6 Hz, 1H), 1.85 – 1.72 (m, 5H), 1.72 – 1.52 (m, 6H), 1.48 – 1.25 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.77 (s, 3H), 0.00 (s, 9H).

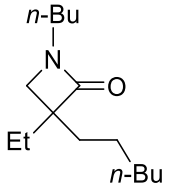
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 154.9, 136.0, 135.6, 130.4, 126.6, 123.9, 121.2, 113.8, 111.3, 108.9, 84.4, 55.9, 52.8, 46.1, 45.6, 45.2, 41.4, 37.3, 35.9, 32.4, 30.9, 29.5, 27.5, 25.1, 24.1, 23.9, 21.0, 17.4, 12.8, 6.5, 0.3.

FT-IR (film) 2951, 2878, 1748, 1599, 1502, 1381, 1250, 1150, 839, 754 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{36}H_{55}N_2O_3Si$: 591.3982, found: 591.3959.

$[\alpha]^{23}_D$ = +20.3 (*c* 1.0, $CHCl_3$); >30:1 d.r., from (*R*,*R*)-**L***.

$[\alpha]^{23}_D$ = +22.8 (*c* 1.0, $CHCl_3$); 1:>30 d.r., from (*S*,*S*)-**L***.



1-Butyl-3-ethyl-3-hexylazetidin-2-one (Figure 3a, entry 53). The title compound was prepared according to **GP-1** from 3-bromo-1-butyl-3-ethylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 183 mg, 95% yield, 99% ee; (*S*,*S*)-**L***: 173 mg, 90% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.8 min (minor), 10.2 min (major).

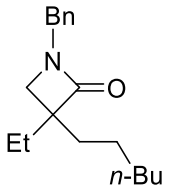
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (td, *J* = 7.1, 1.4 Hz, 2H), 3.07 – 2.98 (m, 2H), 1.66 (q, *J* = 7.5 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.55 – 1.46 (m, 2H), 1.42 – 1.24 (m, 10H), 1.00 – 0.92 (m, 6H), 0.91 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 58.7, 48.9, 40.9, 32.7, 31.7, 29.8, 29.7, 25.7, 24.5, 22.6, 20.2, 14.1, 13.7, 8.9.

FT-IR (film): 1748, 1459, 1404, 1379, 1174, 732 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{30}NO$: 240.2327, found: 240.2324.

$[\alpha]^{23}_D$ = +3.8 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



1-Benzyl-3-ethyl-3-hexylazetidin-2-one (Figure 3a, entry 54). The title compound was prepared according to **GP-1** from 1-benzyl-3-bromo-3-ethylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 205 mg, 94% yield, 99% ee; (*S*,*S*)-**L***: 210 mg, 96% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.5 min (minor), 7.2 min (major).

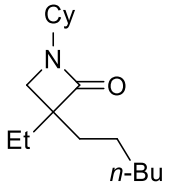
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 4.38 (s, 2H), 2.91 (s, 2H), 1.71 – 1.64 (m, 2H), 1.64 – 1.55 (m, 2H), 1.38 – 1.24 (m, 8H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.92 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 136.0, 128.7, 128.3, 127.6, 59.3, 48.6, 45.6, 32.7, 31.7, 29.7, 25.8, 24.5, 22.6, 14.1, 8.9.

FT-IR (film): 2929, 1747, 1456, 1400, 1353, 1171, 700 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO$: 274.2171, found: 274.2170.

$[\alpha]^{23}_D$ = +20.4 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



1-Cyclohexyl-3-ethyl-3-hexylazetidin-2-one (Figure 3a, entry 55). The title compound was prepared according to **GP-1** from 3-bromo-1-cyclohexyl-3-ethylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 201 mg, 95% yield, 99% ee; (*S*,*S*)-**L***: 198 mg, 93% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.0 min (minor), 8.7 min (major).

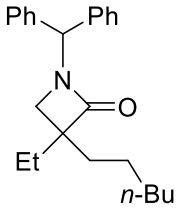
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 – 3.42 (m, 1H), 3.00 – 2.83 (m, 2H), 1.77 – 1.65 (m, 4H), 1.61 – 1.43 (m, 5H), 1.33 – 1.16 (m, 12H), 1.12 – 1.00 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H), 0.84 – 0.74 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 57.2, 49.9, 45.7, 32.9, 31.7, 30.85, 30.81, 29.7, 25.8, 25.3, 24.9, 24.4, 22.6, 14.1, 8.8.

FT-IR (film): 1744, 1453, 1397, 1365, 1171, 999, 891 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{32}NO$: 266.2484, found: 266.2480.

$[\alpha]^{23}_D$ = +3.6 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



1-Benzhydryl-3-ethyl-3-hexylazetidin-2-one (Figure 3a, entry 56). The title compound was prepared according to **GP-1** from 1-benzhydryl-3-bromo-3-ethylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 249 mg, 89% yield, 99% ee; (*S*,*S*)-**L***: 243 mg, 87% yield, 99% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.4 min (minor), 7.4 min (major).

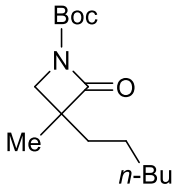
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 6H), 7.27 – 7.19 (m, 4H), 6.23 (s, 1H), 2.99 (s, 2H), 1.67 (td, *J* = 7.4, 1.9 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.34 – 1.23 (m, 8H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 139.14, 139.09, 128.6, 128.23, 128.21, 127.6, 58.4, 58.3, 48.0, 32.9, 31.7, 29.7, 26.0, 24.6, 22.6, 14.1, 9.0.

FT-IR (film): 2929, 1747, 1494, 1454, 1379, 1177, 700 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{32}NO$: 350.2484, found: 350.2489.

$[\alpha]^{23}_D$ = +17.9 (*c* 1.0, $CHCl_3$); 99% ee, from (*R*,*R*)-**L***.



***tert*-Butyl 3-hexyl-3-methyl-2-oxoazetidine-1-carboxylate (Figure 3a, entry 57).** The title compound was prepared according to **GP-1** from *tert*-butyl 3-bromo-3-methyl-2-oxoazetidine-1-carboxylate and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 178 mg, 82% yield, 97% ee; (*S*,*S*)-**L***: 190 mg, 88% yield, 96% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.0 min (major), 9.1 min (minor).

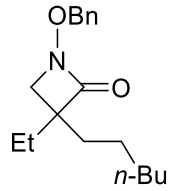
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (d, *J* = 6.7 Hz, 1H), 3.28 (d, *J* = 6.7 Hz, 1H), 1.67 – 1.62 (m, 2H), 1.54 (s, 9H), 1.50 – 1.41 (m, 1H), 1.34 (s, 3H), 1.33 – 1.25 (m, 7H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 148.6, 83.1, 53.9, 50.8, 34.6, 31.6, 29.5, 28.0, 24.5, 22.6, 19.2, 14.1.

FT-IR (film): 1802, 1723, 1458, 1369, 1343, 1160, 1127, 992, 773 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{15}H_{31}N_2O_3$: 287.2335, found: 287.2334.

$[\alpha]^{23}_D$ = −16.0 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.



1-(Benzyloxy)-3-ethyl-3-hexylazetidin-2-one (Figure 3a, entry 58). The title compound was prepared according to **GP-1** from 1-(benzyloxy)-3-bromo-3-ethylazetidin-2-one and 1-hexene at 0 °C. Purification by flash column chromatography on silica gel: 10→20% EtOAc in hexanes, colorless oil.

(*R*,*R*)-**L***: 133 mg, 57% yield, 97% ee; (*S*,*S*)-**L***: 138 mg, 60% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.3 min (major), 11.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.32 (m, 5H), 4.96 (s, 2H), 3.20 – 2.95 (m, 2H), 1.60 (q, *J* = 7.4 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.35 – 1.16 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 135.4, 129.2, 128.9, 128.6, 77.7, 55.3, 54.6, 32.3, 31.6, 29.6, 25.4, 24.4, 22.6, 14.1, 8.9.

FT-IR (film): 2930, 1770, 1456, 1379, 1166, 987, 689 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{18}H_{31}N_2O_2$: 307.2386, found: 307.2380.

$[\alpha]^{23}_D$ = +17.1 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.

III. Effect of Reaction Parameters

General Procedure 3 (GP-3).

Preparation of a solution of the catalyst: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a magnetic stir bar was charged with $NiBr_2$·glyme (6.2 mg, 0.020 mmol, 0.10 equiv) and ligand **L*** (15.4 mg, 0.024 mmol, 0.12 equiv). Next, 2-methyl-THF (1.0 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min.

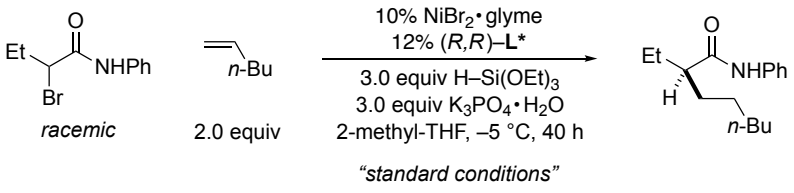
Cross-coupling: In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with the racemic electrophile (0.20 mmol, 1.0 equiv) and K_3PO_4·H_2O (138 mg, 0.60 mmol, 3.0 equiv). Next, the solution of the catalyst (see above) was added in one portion via syringe, followed by the olefin (0.40 mmol, 2.0 equiv). The vial was capped with a PTFE septum cap, taken out of the glovebox, and placed in an *i*-PrOH cooling bath at –5 °C, and a nitrogen-filled balloon was attached to the vial. The reaction mixture was stirred at –5 °C for 10 min, and then $HSi(OEt)_3$ (110 μL, 0.60 mmol, 3.0 equiv) was added dropwise via syringe over one min. Next, the balloon was removed, and all of the puncture holes in the septum cap were covered with grease. The reaction mixture was stirred at –5 °C for 40 h.

Work-up: *n*-Dodecane (46 μL, 0.20 mmol, 1.0 equiv) was added via syringe. The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The solvent was removed under reduced pressure, and the residue was purified by chromatography.

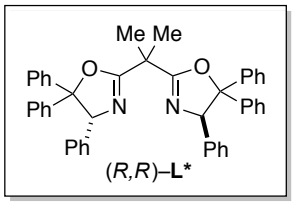
2-Bromo-*N*-phenylbutanamide was reacted with 1-hexene according to **GP-3**.

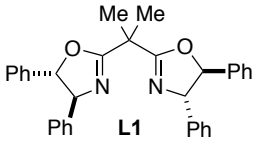
The yields were determined via GC analysis with *n*-dodecane as the internal standard. The ee's were determined via HPLC analysis after purification by preparative thin-layer chromatography; a negative ee value indicates that the opposite enantiomer (*S*) of product was formed predominantly. All data are the average of two experiments.

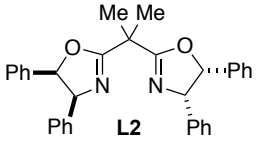
Table S-1. Effect of Reaction Parameters.

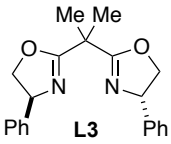


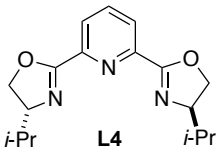
Entry	Variation from the "standard conditions"	ee (%)	Yield (%)
1	none	94	84
2	no $NiBr_2$•glyme	–	<1
3	no (*R,R*)–**L***	–	<1
4	no K_3PO_4•H_2O	–	<1
5	**L1**, instead of (*R,R*)–**L***	–92	84
6	**L2**, instead of (*R,R*)–**L***	–69	26
7	**L3**, instead of (*R,R*)–**L***	–49	33
8	**L4**, instead of (*R,R*)–**L***	–	12
9	H–SiMe$(OEt)_2$, instead of H–Si$(OEt)_3$	94	72
10	5% $NiBr_2$•glyme, 6% (*R,R*)–L*	94	75
11	1.5 equiv 1-hexene	94	70
12	2.0 equiv H–Si$(OEt)_3$, 2.0 equiv K_3PO_4•H_2O	94	76
13	r.t., instead of –5 °C	89	74
14	24 h, instead of 40 h	95	62
15	THF, instead of 2-methyl-THF	94	70
16	toluene, instead of 2-methyl-THF	92	82
17	1.0 equiv H_2O added	95	78
18	under air (balloon)	94	66









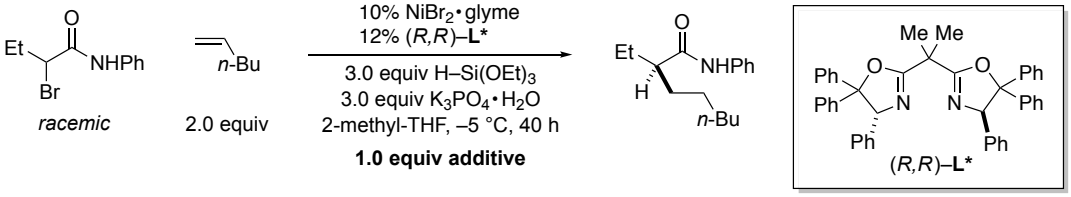


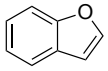
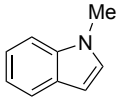
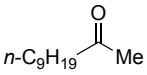
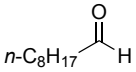
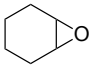
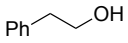
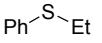
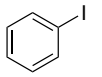
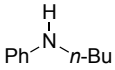
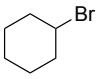
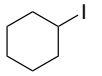
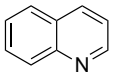
IV. Functional-Group Compatibility

2-Bromo-*N*-phenylbutanamide was reacted with 1-hexene according to **GP-3**, in the presence of 1.0 equiv of the additives shown below. The additive was added after the addition of 1-hexene.

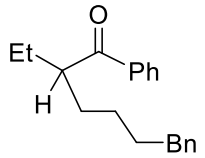
The yields were determined via GC analysis with *n*-dodecane as the internal standard. The ee's were determined via HPLC analysis after purification by preparative thin-layer chromatography. All data are the average of two experiments.

Table S-2. Functional-Group Compatibility.



Entry	Additive	Recovery of additive (%)	Yield (%)	ee (%)
1	none	–	86	94
2		>95	86	94
3		92	86	94
4		>95	88	95
5		92	86	95
6		>95	84	94
7		>95	85	94
8		>95	84	95
9		94	85	94
10		84	86	95
11		88	83	94
12		77	82	95
13	Ph–CN	>95	75	90
14		82	24	64

V. Derivatization of the Coupling Products



2-Ethyl-1,6-diphenylhexan-1-one (Figure 2b, entry 27). A solution of PhLi (1.9 M in Et_2O; 0.46 mL, 0.87 mmol, 3.0 equiv) was added dropwise via syringe over 30 seconds to a solution of 2-ethyl-1-morpholino-6-phenylhexan-1-one (75 mg, 0.29 mmol, 1.0 equiv) in THF (2 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, and then it was allowed to warm to room temperature. Next, the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (5 mL), and the reaction mixture was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (5→10% Et_2O in hexanes) provided the desired product as a pale-yellow oil.

(*R*,*R*)-**L***: 52 mg, 64% yield, 95% ee (starting material: 96% ee); (*S*,*S*)-**L***: 56 mg, 69% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 9.7 min (major), 11.5 min (minor).

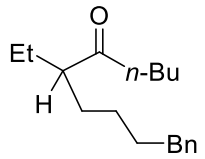
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.87 (m, 2H), 7.69 – 7.56 (m, 1H), 7.55 – 7.44 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.12 (m, 2H), 3.47 – 3.32 (m, 1H), 2.70 – 2.44 (m, 2H), 1.93 – 1.71 (m, 2H), 1.66 – 1.50 (m, 4H), 1.41 – 1.29 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 142.6, 137.7, 132.8, 128.6, 128.4, 128.2, 128.1, 125.6, 47.6, 35.7, 31.8, 31.7, 27.3, 25.4, 11.9.

FT-IR (film) 2932, 1680, 1596, 1448, 1381, 1218, 1001, 699 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{25}O$: 281.1905, found: 281.1903.

$[\alpha]^{24}_D$ = −6.4 (*c* 1.0, $CHCl_3$); 95% ee, from (*R*,*R*)-**L***.



6-Ethyl-10-phenyldecan-5-one (Figure 2b, entry 28). A solution of *n*-BuLi (2.5 M in hexane; 0.36 mL, 0.90 mmol, 3.0 equiv) was added dropwise via syringe over 30 seconds to a solution of 2-ethyl-1-morpholino-6-phenylhexan-1-one (87 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h, and then it was allowed to warm to room temperature. Next, the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (5 mL), and the reaction mixture was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (5→10% Et_2O in hexanes) provided the desired product as a pale-yellow oil.

(*R*,*R*)-**L***: 55 mg, 70% yield, 93% ee (starting material: 96% ee); (*S*,*S*)-**L***: 53 mg, 68% yield, 92% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 4.5 min (major), 4.8 min (minor).

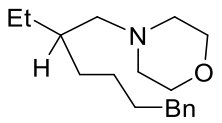
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.12 (m, 3H), 2.61 (td, *J* = 7.4, 1.2 Hz, 2H), 2.46 – 2.34 (m, 3H), 1.73 – 1.59 (m, 4H), 1.58 – 1.51 (m, 2H), 1.50 – 1.38 (m, 2H), 1.37 – 1.24 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 142.5, 128.3, 128.2, 125.6, 53.8, 42.2, 35.8, 31.6, 31.2, 27.2, 25.6, 24.8, 22.4, 13.9, 11.9.

FT-IR (film) 2933, 1711, 1496, 1455, 1380, 1043, 699 cm^{-1}.

HRMS (ESI) m/z $[M+NH_4]^+$ calcd for $C_{18}H_{32}NO$: 278.2484, found: 278.2473.

$[\alpha]^{24}_D$ = −7.6 (*c* 1.0, $CHCl_3$); 93% ee, from (*R*,*R*)-**L***.



4-(2-Ethyl-6-phenylhexyl)morpholine (Figure 2b, entry 29). A solution of BH_3·THF (1.0 M; 2.0 mL, 2.0 mmol, 5.0 equiv) was added by syringe to a solution of 2-ethyl-1-morpholino-6-phenylhexan-1-one (116 mg, 0.40 mmol, 1.0 equiv) in THF (4 mL), and then the reaction mixture was refluxed for 12 h. Next, the mixture was cooled to 0 °C, and the reaction was quenched by the addition of MeOH (1.0 mL). The solvent was evaporated, an aqueous solution of HCl (2 N; 4 mL) was added to the residue, and the mixture was refluxed for 1 h. The reaction mixture was made basic through the addition of K_2CO_3 and extracted with $CHCl_3$ (10 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (25% EtOAc in hexanes) provided the desired product as a colorless oil.

(*R*,*R*)-**L***: 94 mg, 85% yield, 96% ee (starting material: 96% ee); (*S*,*S*)-**L***: 96 mg, 87% yield, 95% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (1% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 13.2 min (minor), 14.2 min (major).

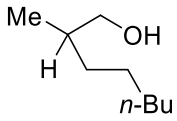
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.14 – 7.07 (m, 3H), 3.69 – 3.55 (m, 4H), 2.54 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.29 (dd, *J* = 4.2, 2.4 Hz, 4H), 2.17 – 1.97 (m, 2H), 1.60 – 1.46 (m, 2H), 1.45 – 1.35 (m, 1H), 1.33 – 1.17 (m, 6H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.4, 128.2, 125.6, 67.2, 63.4, 54.2, 35.9, 35.7, 31.9, 31.5, 26.3, 24.6, 10.8.

FT-IR (film) 2930, 1455, 1272, 1119, 1016, 866, 698 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{30}NO$: 276.2327, found: 276.2328.

$[\alpha]^{23}_D$ = +1.8 (*c* 1.0, $CHCl_3$); 96% ee, from (*R*,*R*)-**L***.



2-Methyloctan-1-ol (Figure 2b, entry 30) [818-81-5]. Under an atmosphere of nitrogen, a solution of $LiAlH_4$ (1.0 M in Et_2O; 0.44 mL, 0.44 mmol, 1.1 equiv) was added dropwise via syringe over 60 seconds to a stirred solution of 2,6-di-*tert*-butyl-4-methylphenyl 2-methyloctanoate (144 mg, 0.40 mmol, 1.0 equiv) in Et_2O (4 mL) at 0 °C. The reaction mixture was stirred at 40 °C for 2 h, and then it was cooled to 0 °C, and the reaction was quenched by the addition of a saturated aqueous solution of potassium sodium tartrate (3 mL) (*caution: exothermic; gas evolution*). Next, the biphasic mixture was stirred at 40 °C for 30 min. The layers were separated, and the aqueous layer was extracted with Et_2O (10 mL x 2). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (25% Et_2O in hexanes) to provide the desired product as a colorless oil.

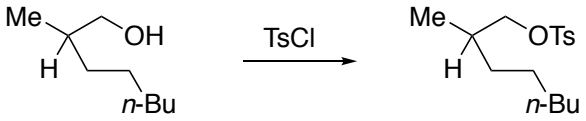
(*R*,*R*)-**L***: 50 mg, 87% yield, 97% ee (starting material: 98% ee); (*S*,*S*)-**L***: 48 mg, 83% yield, 96% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (dd, *J* = 10.5, 5.8 Hz, 1H), 3.44 (dd, *J* = 10.5, 6.5 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.42 – 1.26 (m, 9H), 1.20 – 1.06 (m, 1H), 0.99 – 0.84 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 68.5, 35.8, 33.2, 31.9, 29.6, 26.9, 22.7, 16.6, 14.1.

$[\alpha]^{24}_D$ = −12.8 (*c* 1.0, EtOH); 97% ee, from (*R*,*R*)-**L***.

Determination of the ee:



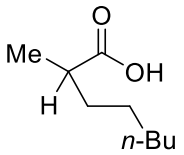
2-Methyloctyl 4-methylbenzenesulfonate [254435-67-1; 117555-29-0]. NEt_3 (17 μL, 0.12 mmol, 1.2 equiv), TsCl (23 mg, 0.12 mmol, 1.2 equiv), and DMAP (2 mg, 0.02 mmol, 0.2 equiv) were added to a stirred solution of 2-methyloctan-1-ol (14 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 3 h, and then it was concentrated and purified by chromatography on silica gel (25% Et_2O in hexanes), which provided the desired product as a colorless oil.

(*R*,*R*)-**L***: 97% ee; (*S*,*S*)-**L***: 96% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.3 min (minor), 6.8 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.43 – 7.32 (m, 2H), 3.90 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.82 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.47 (s, 3H), 1.85 – 1.71 (m, 1H), 1.35 – 1.08 (m, 10H), 0.93 – 0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 133.1, 129.8, 127.9, 75.2, 32.8, 32.7, 31.7, 29.4, 26.5, 22.6, 21.7, 16.5, 14.1.



2-Methyloctanoic acid (Figure 2b, entry 31) [3004-93-1]. A solution of cerium ammonium nitrate (548 mg, 1.0 mmol, 2.5 equiv) in H_2O (1 mL) was added to a vigorously stirred solution of 2,6-di-*tert*-butyl-4-methoxyphenyl 2-methyloctanoate (151 mg, 0.40 mmol, 1.0 equiv) in CH_3CN (3 mL) at room temperature. The reaction mixture was stirred vigorously at room temperature for 6 h. Next, mannitol (290 mg) was added, and the mixture was stirred for 30 min. Then, the mixture was poured into water (20 mL), acidified with 4 N HCl, and extracted with Et_2O (25 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (10→25% EtOAc in hexanes), which provided the desired product as a colorless oil.

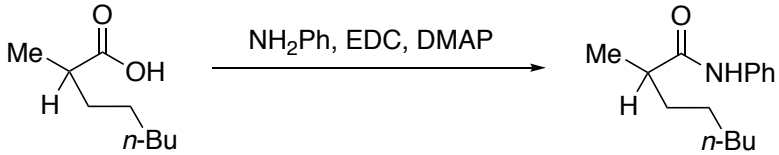
(*R*,*R*)-**L***: 59 mg, 93% yield, 98% ee (starting material: 98% ee); (*S*,*S*)-**L***: 60 mg, 95% yield, 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 – 2.42 (m, 1H), 1.77 – 1.64 (m, 1H), 1.53 – 1.40 (m, 1H), 1.37 – 1.27 (m, 8H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.95 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.0, 39.3, 33.6, 31.7, 29.2, 27.1, 22.6, 16.8, 14.1.

$[\alpha]^{24}_D$ = +17.0 (*c* 1.0, MeOH); 98% ee, from (*R*,*R*)-**L***.

Determination of the ee:



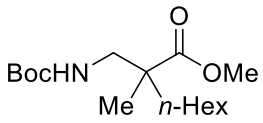
2-Methyl-*N*-phenyloctanamide. NH_2Ph (14 μL, 0.15 mmol, 1.5 equiv), EDC (23 mg, 0.15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (2 mg, 0.02 mmol, 0.2 equiv) were added to a stirred solution of 2-methyloctanoic acid (16 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 h. Next, the mixture was concentrated and purified by chromatography on silica gel (10→20% EtOAc in hexanes), which provided the desired product as a white solid.

(*R*,*R*)-**L***: 98% ee (starting material: 98% ee); (*S*,*S*)-**L***: 98% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 12.4 min (major), 6.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.41 – 7.30 (m, 2H), 7.17 (s, 1H), 7.15 – 7.09 (m, 1H), 2.43 – 2.27 (m, 1H), 1.85 – 1.68 (m, 1H), 1.54 – 1.42 (m, 1H), 1.40 – 1.24 (m, 11H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 138.0, 129.0, 124.1, 119.8, 42.8, 34.5, 31.7, 29.4, 27.5, 22.6, 17.9, 14.1.



Methyl 2-(((*tert*-butoxycarbonyl)amino)methyl)-2-methyloctanoate (Figure 3b, entry 59). KCN (2.6 mg, 0.040 mmol, 0.10 equiv) was added to a solution of *tert*-butyl 3-hexyl-3-methyl-2-oxoazetidine-1-carboxylate (108 mg, 0.40 mmol, 1.0 equiv) in MeOH (4 mL) at room temperature. The reaction mixture was stirred at room temperature for 24 h. Next, the MeOH was removed under reduced pressure, and a saturated solution of $NaHCO_3$ (4 mL) and Et_2O (6 mL) were added. The aqueous solution was extracted with Et_2O (6 mL x 2), and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. Chromatography on silica gel (5→10% EtOAc in hexanes) provided the desired product as a colorless oil.

(*R*,*R*)-**L***: 93 mg, 77% yield, 97% ee (starting material: 97% ee); (*S*,*S*)-**L***: 90 mg, 75% yield, 97% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 – 4.80 (m, 1H), 3.70 (s, 3H), 3.33 (dd, *J* = 13.8, 5.9 Hz, 1H), 3.23 (dd, *J* = 13.8, 7.3 Hz, 1H), 1.61 – 1.48 (m, 2H), 1.45 (s, 9H), 1.35 – 1.21 (m, 8H), 1.17 (s, 3H), 0.92 – 0.84 (m, 3H).

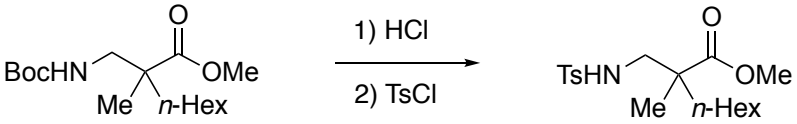
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 156.1, 79.2, 51.9, 47.2, 46.9, 37.1, 31.6, 29.7, 28.4, 24.2, 22.6, 20.3, 14.1.

FT-IR (film): 3387, 2932, 1722, 1506, 1463, 1366, 1249, 1173, 778 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{32}NO_4$: 302.2331, found: 302.2329.

$[\alpha]^{23}_D$ = −6.2 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.

Determination of the ee:



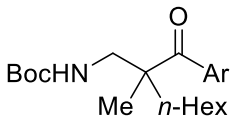
Methyl 2-methyl-2-(((4-methylphenyl)sulfonamido)methyl)octanoate. At room temperature, a solution of HCl in anhydrous dioxane (4 M; 1.0 mL) was added to an oven-dried 4 mL vial charged with a magnetic stirrer and methyl 2-(((*tert*-butoxycarbonyl)amino)methyl)-2-methyloctanoate (30 mg, 0.10 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 1 h, and then the solvent was removed under vacuum. The residue was dissolved in anhydrous CH_2Cl_2 (1 mL) and diisopropylethylamine (0.5 mL), and then tosyl chloride (23 mg, 0.12 mmol, 1.2 equiv) was added. The reaction mixture was stirred at room temperature for 2 h. Next, the mixture was diluted with Et_2O (10 mL), washed with 2 N aqueous HCl (5 mL x 2), dried over anhydrous Na_2SO_4, and concentrated under vacuum. Chromatography on silica gel (15% EtOAc in hexanes) provided the desired product as a colorless oil.

(*R*,*R*)-**L***: 30 mg, 84% yield, 97% ee; (*S*,*S*)-**L***: 28 mg, 79% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 12.2 min (minor), 13.8 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.21 (m, 2H), 4.93 (t, *J* = 7.0 Hz, 1H), 3.58 (s, 3H), 3.01 (dd, *J* = 12.6, 6.5 Hz, 1H), 2.78 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.36 (s, 3H), 1.50 – 1.39 (m, 2H), 1.24 – 0.99 (m, 8H), 1.10 (s, 3H), 0.79 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 143.3, 137.0, 129.7, 127.0, 52.1, 49.2, 46.4, 36.9, 31.6, 29.6, 23.9, 22.6, 21.5, 20.8, 14.1.



Ar = *p*-anisyl

***tert*-Butyl (2-(4-methoxybenzoyl)-2-methyloctyl)carbamate (Figure 3b, entry 60).** Under an atmosphere of nitrogen, a solution of (4-methoxyphenyl)magnesium bromide solution (0.94 M in THF; 0.56 mL, 0.53 mmol, 1.2 equiv) was added dropwise via syringe over 60 seconds to a stirred solution of *tert*-butyl 3-hexyl-3-methyl-2-oxoazetidine-1-carboxylate (118 mg, 0.44 mmol, 1.0 equiv) in anhydrous THF (4 mL) at –40 °C. The solution was stirred at –40 °C for 2 h, and then the reaction was quenched through the addition of a saturated aqueous solution of $NHCl_4$ (2 mL), and the resulting mixture was extracted with Et_2O (5 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. Chromatography on silica gel (10→20% EtOAc in hexanes) provided the desired product as a colorless oil.

(*R*,*R*)-**L***: 154 mg, 93% yield, 97% ee (starting material: 97% ee); (*S*,*S*)-**L***: 150 mg, 90% yield, 97% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AS-H column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 6.4 min (minor), 7.6 min (major).

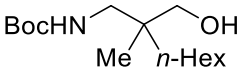
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.79 (m, 2H), 7.00 – 6.87 (m, 2H), 5.15 – 4.93 (m, 1H), 3.89 (s, 3H), 3.52 (dd, *J* = 13.6, 5.3 Hz, 1H), 3.34 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.99 – 1.73 (m, 2H), 1.44 (s, 9H), 1.40 (s, 3H), 1.34 – 1.14 (m, 8H), 0.85 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 162.5, 156.4, 130.9, 129.8, 113.4, 78.9, 55.4, 52.3, 47.9, 38.1, 31.4, 29.9, 28.4, 24.3, 22.5, 22.0, 14.0.

FT-IR (film) 3465, 2931, 1715, 1659, 1601, 1508, 1256, 1170, 1033, 769 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{36}NO_4$: 378.2644, found: 378.2643.

$[\alpha]^{23}_D$ = −2.6 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.



***tert*-Butyl (2-(hydroxymethyl)-2-methyloctyl)carbamate (Figure 3b, entry 61).** Under an atmosphere of nitrogen, a solution of $LiAlH_4$ (1.0 M in Et_2O; 1.2 mL, 1.2 mmol, 3.0 equiv) was added dropwise via syringe over 60 seconds to a stirred solution of *tert*-butyl 3-hexyl-3-methyl-2-oxoazetidine-1-carboxylate (108 mg, 0.40 mmol, 1.0 equiv) in anhydrous THF (4 mL) at 0 °C. The solution was stirred at 0 °C for 2 h. The reaction was then quenched by the addition of a saturated aqueous solution of $NHCl_4$ (2 mL), and the resulting mixture was extracted with Et_2O (5 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. Chromatography on silica gel (10→25% EtOAc in hexanes) provided the desired product as a white solid.

(*R*,*R*)-**L***: 75 mg, 68% yield, 97% ee (starting material: 97% ee); (*S*,*S*)-**L***: 79 mg, 72% yield, 97% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (t, *J* = 6.8 Hz, 1H), 3.66 (t, *J* = 7.3 Hz, 1H), 3.23 – 3.04 (m, 2H), 3.03 – 2.79 (m, 2H), 1.38 (s, 9H), 1.25 – 1.06 (m, 10H), 0.84 – 0.79 (m, 3H), 0.72 (s, 3H).

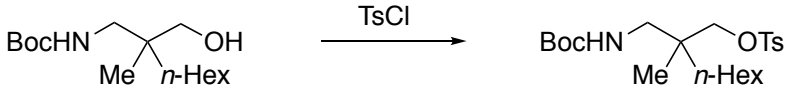
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 80.0, 66.7, 45.8, 39.4, 35.0, 31.9, 30.2, 28.3, 23.2, 22.7, 19.2, 14.1.

FT-IR (film): 3336, 2930, 1684, 1540, 1366, 1281, 1174, 1044, 899 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{32}NO_3$: 274.2382, found: 274.2376.

$[\alpha]^{23}_D$ = −18.6 (*c* 1.0, $CHCl_3$); 97% ee, from (*R*,*R*)-**L***.

Determination of the ee:



2-(((*tert*-Butoxycarbonyl)amino)methyl)-2-methyloctyl 4-methylbenzenesulfonate. At room temperature, anhydrous pyridine (1.0 mL) and then tosyl chloride (23 mg, 0.12 mmol, 1.2 equiv) were added to an oven-dried 4 mL vial charged with a magnetic stirrer and *tert*-butyl (2-(hydroxymethyl)-2-methyloctyl)carbamate (27 mg, 0.10 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 12 h. Next, the mixture was diluted with Et_2O (10 mL), washed with 2 N aqueous HCl (5 mL x 2), dried over anhydrous Na_2SO_4, and concentrated under vacuum. Chromatography on silica gel (10% EtOAc in hexanes) provided the desired product as a colorless oil.

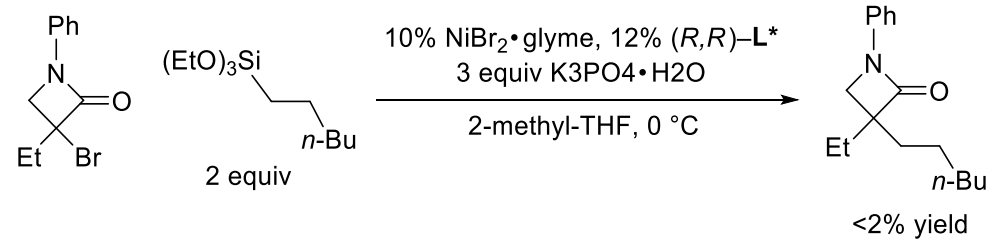
(*R*,*R*)-**L***: 40 mg, 94% yield, 97% ee; (*S*,*S*)-**L***: 38 mg, 89% yield, 97% ee.

SFC analysis: The ee was determined on a CHIRALCEL OJ-H column (2% *i*-PrOH in CO_2, 3.5 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 5.1 min (major), 7.3 min (minor).

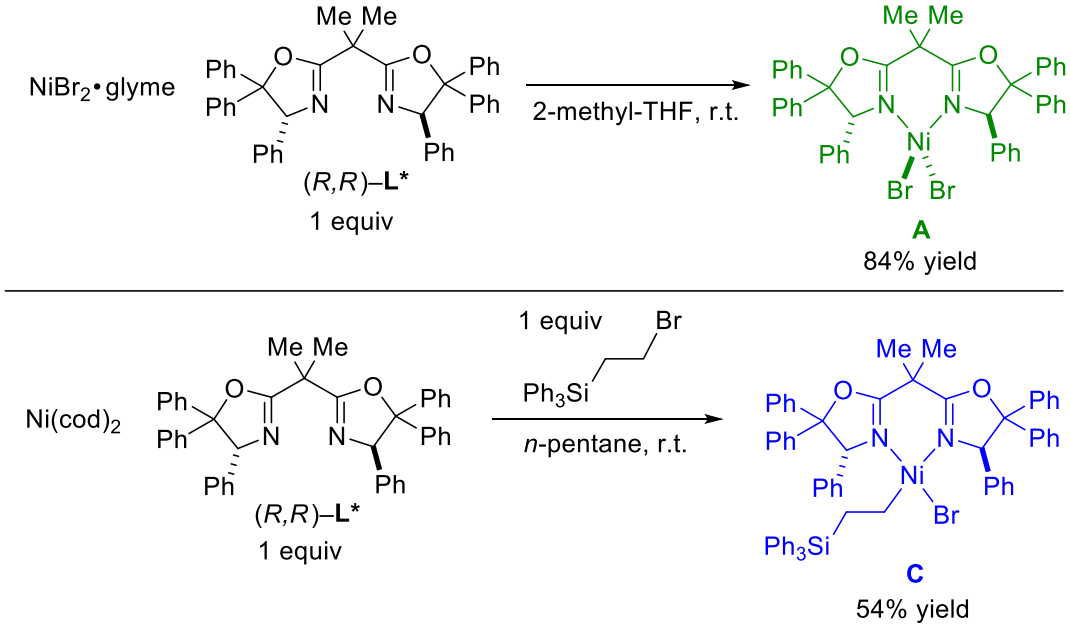
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.33 (m, 2H), 4.62 (t, *J* = 6.7 Hz, 1H), 3.86 – 3.65 (m, 2H), 3.04 (dd, *J* = 6.9, 2.9 Hz, 2H), 2.48 (s, 3H), 1.44 (s, 9H), 1.31 – 1.15 (m, 9H), 1.14 – 1.01 (m, 1H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 144.9, 132.7, 129.9, 127.9, 79.2, 74.4, 45.6, 38.4, 34.6, 31.7, 29.9, 28.4, 22.9, 22.6, 21.7, 19.1, 14.1.

VI. Mechanistic Studies



Evidence against a conventional cross-coupling mechanism (Figure 4a). The reaction was set up according to **GP-3**, except that the olefin and $HSi(OEt)_3$ were omitted, and triethoxy(hexyl)silane was added at the very end, to the reaction mixture at 0 °C. The yield was determined via GC analysis with *n*-dodecane as the internal standard.



Synthesis of proposed intermediates A and C (Figure 4c).

The yields have not been optimized.

Complex A. In a nitrogen-filled glovebox, 2-methyl-THF (7.0 mL) was added to a 20 mL vial that contained (*R*,*R*)-**L*** (128 mg, 0.20 mmol) and $NiBr_2$·glyme (62 mg, 0.20 mmol), resulting in the immediate formation of a magenta solution. The mixture was stirred for 16 h at room temperature, and then it was filtered through an Acrodisc filter. The filtrate was layered with *n*-pentane (10 mL), and the resulting solution was allowed to sit at room temperature, resulting in the formation of magenta crystals over 1 day. The crystals were collected on a medium porosity fritted filter, washed with *n*-pentane (3.0 mL x 3), and dried under reduced pressure: 144 mg, 84% yield.

This complex is not sensitive to dry air, but it degrades slowly in the presence of moisture.

Crystals suitable for X-ray crystallography were obtained by vapor diffusion (2-methyl-THF/*n*-pentane) at room temperature.

^{1}H NMR (400 MHz, THF-d_8) δ 14.14 (br, 4H), 9.06 (br, 4H), 8.80 (br, 4H), 8.46 (br, 2H), 8.38 (br, 4H), 6.70 – 6.30 (m, 12H), 6.24 (br, 2H), 1.19 (br, 6H). This is a high spin Ni(II) complex.

^{13}C NMR (101 MHz, THF-d_8) δ 185.0, 150.9, 148.5, 147.3, 138.1, 133.1, 131.2, 130.3, 129.2, 126.3, 125.2, 125.0, 123.0, 75.6, 34.0, 26.7, 21.3, –46.2.

FT-IR (film) 3062, 3032, 1665, 1471, 1370, 1146, 972, 695 cm^{-1}.

Elemental analysis calculated for $C_{45}H_{38}Br_2N_2NiO_2$: C, 63.05; H, 4.47; N, 3.27. Found: C, 62.81; H, 4.51; N, 3.26.

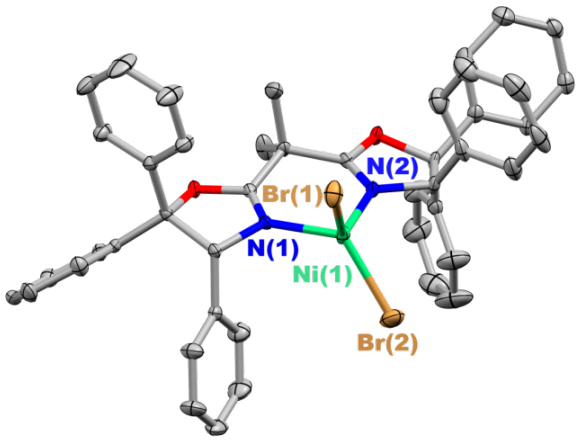


Figure S-1. Thermal ellipsoids plot at the 30% probability level of complex A·2-methyl-THF. Interstitial solvent molecules and hydrogen atoms are omitted for clarity.

X-ray quality crystals were obtained by slow crystallization from *n*-pentane and 2-methyl-THF. A suitable crystal was selected and structurally characterized. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Mo–Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization.

Table S-3. Crystal Data and Structure Refinement for Nickel Complex A.

Identification code	P17524
Empirical formula	$C_{25}H_{24}BrNNi_{0.5}O_{1.5}$
Formula weight	471.72
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.8229(6)
b/Å	16.0087(10)
c/Å	12.7174(7)
α/°	90.00
β/°	93.918(2)
γ/°	90.00

Volume/Å^3	2198.3(2)
Z	4
ρ_{calc}g/cm^3	1.425
μ/mm^{-1}	2.303
F(000)	968.0
Crystal size/mm^3	0.244 × 0.174 × 0.068
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.56 to 55.06
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -16 ≤ l ≤ 16
Reflections collected	98740
Independent reflections	10088 [R_{int} = 0.0581, R_{sigma} = 0.0339]
Data/restraints/parameters	10088/1/583
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0215, wR_2 = 0.0525
Final R indexes [all data]	R_1 = 0.0255, wR_2 = 0.0534
Largest diff. peak/hole / e Å^{-3}	0.36/-0.37
Flack parameter	0.000(4)

Table S-4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Nickel Complex A.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	4926.0(2)	7515.73(13)	3640.20(16)	32.35(6)
Br2	6136.14(18)	5233.78(14)	2532.35(15)	28.22(5)
Ni1	4697.3(2)	6074.48(15)	3350.88(16)	16.66(6)
O1	3065.1(11)	5235.2(9)	6016.3(8)	17.2(3)
O2	1325.4(11)	4917.4(8)	2532.2(8)	14.3(3)
N1	4176.6(14)	5757.4(10)	4755.6(11)	15.0(3)
N2	3139.5(13)	5591.0(9)	2698.1(10)	12.8(3)
C1	4865.8(17)	6025.4(13)	5749.0(12)	18.4(4)
C2	6104.3(18)	5571.8(14)	5879.2(13)	22.6(4)
C3	6214(2)	4728.6(16)	5676.5(17)	31.8(5)
C4	7352(2)	4323.9(18)	5819.9(18)	38.1(6)
C5	8391(2)	4779(2)	6145.7(18)	39.9(6)
C6	8303(2)	5626.3(19)	6314.8(18)	39.4(7)
C7	7154(2)	6022.2(17)	6198.3(14)	30.8(5)
C8	3896.9(17)	5853.2(12)	6587.7(13)	16.5(4)

C9	4396.5(16)	5445.1(12)	7599.2(13)	16.9(4)
C10	4611(2)	4586.0(13)	7659.0(15)	26.4(5)
C11	5116(2)	4225.3(15)	8578.8(16)	30.6(5)
C12	5404.1(19)	4710.8(14)	9458.2(15)	24.2(4)
C13	5189.3(18)	5553.7(14)	9413.5(14)	22.2(4)
C14	4700.2(16)	5928.3(12)	8492.3(12)	17.9(4)
C15	3062.4(18)	6607.7(13)	6778.0(13)	20.0(4)
C16	1945(2)	6454.3(15)	7225.8(18)	32.9(5)
C17	1148(2)	7089.7(17)	7430(2)	41.6(6)
C18	1458(3)	7908.9(18)	7183(2)	46.1(7)
C19	2562(3)	8069.5(17)	6772(2)	52.2(8)
C20	3355(2)	7419.6(16)	6562.7(19)	40.3(6)
C21	3250.1(16)	5324.7(12)	4990.6(12)	14.6(4)
C22	2332.0(16)	4858.1(12)	4262.1(13)	15.2(4)
C23	1041.1(18)	4904.5(15)	4678.1(14)	26.1(5)
C24	2779(2)	3939.8(13)	4220.6(15)	28.1(5)
C25	2314.2(15)	5179.9(12)	3144.0(12)	13.2(3)
C26	1702.1(16)	4993.6(11)	1433.9(12)	12.5(4)
C27	593.7(15)	5220.7(12)	714.0(12)	14.1(3)
C28	-563.8(17)	5379.4(12)	1072.3(13)	16.9(4)
C29	-1573.4(18)	5518.2(12)	362.1(15)	21.0(4)
C30	-1427.7(18)	5502.2(12)	-716.8(15)	21.5(4)
C31	-270.6(18)	5362.6(14)	-1075.0(14)	23.8(4)
C32	735.6(17)	5217.5(14)	-364.3(13)	21.1(4)
C33	2175.1(17)	4120.8(11)	1185.1(13)	15.0(4)
C34	1312.9(19)	3498.9(13)	901.1(16)	23.6(4)
C35	1678(2)	2692.5(14)	727(2)	36.0(6)
C36	2927(2)	2490.5(16)	833(2)	46.0(6)
C37	3795(2)	3096.4(15)	1119(2)	38.9(6)
C38	3425.5(18)	3908.2(13)	1298.6(16)	23.7(4)
C39	2730.6(16)	5673.8(11)	1562.2(12)	12.9(3)
C40	2370.0(17)	6566.6(11)	1299.4(13)	14.7(4)
C41	1846(2)	7083.3(14)	2025.7(17)	26.4(4)
C42	1547(2)	7898.9(14)	1771.1(19)	32.7(5)
C43	1763(2)	8210.0(14)	784.2(19)	32.6(5)
C44	2289(2)	7705.6(14)	60.2(18)	32.8(5)
C45	2587(2)	6882.5(13)	314.5(15)	24.7(4)
O3	754(6)	3214(4)	6294(4)	30.6(13)
C46	561(6)	2439(4)	5734(5)	35.1(15)

C47	1202(12)	1760(8)	6397(6)	53(3)
C48	1661(6)	2208(4)	7422(5)	24.9(13)
C49	1764(5)	3097(3)	7060(4)	26.3(13)
C50	1719(5)	3760(3)	7916(4)	29.5(13)
O00{	899(8)	3347(5)	6679(5)	45.1(17)
C0AA	1666(8)	3272(7)	7644(9)	70(4)
C1AA	1822(12)	2345(8)	7869(8)	70(3)
C01N	1081(8)	2593(5)	6085(6)	47(2)
C2AA	1242(9)	1896(6)	6834(11)	56(4)
C3AA	19(10)	2509(5)	5300(6)	67(2)

Table S-5. Anisotropic Displacement Parameters ($Å^2×10^3$) for Nickel Complex A.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	45.37(14)	19.30(11)	32.6(1)	3.89(9)	4.34(9)	-7.22(10)
Br2	18.72(10)	37.55(13)	28.45(10)	-9.22(9)	2.07(7)	-1.87(9)
Ni1	15.69(12)	21.60(13)	12.57(9)	1.17(9)	0.16(8)	-7.38(10)
O1	18.6(6)	21.2(7)	11.6(5)	-1.6(5)	0.2(4)	-10.0(6)
O2	12.8(6)	19.4(7)	10.4(5)	-0.2(5)	-1.1(5)	-3.0(5)
N1	15.2(8)	17.3(8)	12.1(6)	0.7(6)	-1.6(5)	-4.9(6)
N2	13.5(7)	14.6(8)	10.2(6)	1.6(5)	-0.8(5)	0.1(6)
C1	20.8(9)	21.1(10)	12.8(7)	-2.3(8)	-1.6(6)	-10.4(8)
C2	15.0(9)	38.8(13)	13.4(8)	4.5(8)	-3.1(7)	-6.9(8)
C3	21.3(11)	39.6(14)	33.7(11)	-3.4(10)	-3.1(9)	1.9(10)
C4	31.8(14)	47.2(16)	35.3(12)	5.4(11)	2.9(10)	10.2(11)
C5	19.6(12)	68(2)	32.3(11)	20.0(12)	5.6(9)	3.8(12)
C6	16.5(11)	70(2)	30.7(11)	21.5(12)	-6.9(9)	-12.2(12)
C7	25.4(11)	43.4(14)	22.6(9)	11.6(10)	-6.2(8)	-14.2(11)
C8	17.4(9)	17.9(10)	14.0(7)	-4.5(7)	-1.8(6)	-8.4(7)
C9	15.9(9)	22.0(11)	12.9(7)	0.1(7)	2.4(6)	-4.8(8)
C10	32.4(12)	24.2(11)	21.7(9)	-4.0(8)	-4.8(8)	-1.6(9)
C11	33.8(13)	24.5(12)	32.6(11)	4.5(9)	-5.1(9)	3.4(10)
C12	20.7(10)	31.2(12)	20.1(9)	6.0(8)	-3.9(8)	-3.6(9)
C13	17.2(10)	32.9(12)	16.4(8)	-1.8(8)	0.5(7)	-3.4(8)
C14	15.8(9)	22.0(11)	15.8(7)	-2.8(7)	0.3(7)	-3.6(8)
C15	22.9(10)	22.4(11)	14.0(8)	-0.1(7)	-3.0(7)	-3.0(8)

C16	30.7(12)	24.5(12)	44.3(13)	-2.7(10)	8.9(10)	-3.9(10)
C17	33.2(14)	35.6(15)	56.9(16)	-3.6(12)	9.6(12)	0.5(11)
C18	55.3(18)	39.9(16)	43.6(13)	2.9(12)	7.8(13)	20.8(14)
C19	76(2)	24.1(14)	59.3(16)	14.1(12)	25.7(15)	1.1(14)
C20	50.1(15)	24.1(13)	49.3(13)	7.3(11)	22.7(12)	0.2(12)
C21	18.3(9)	16.2(10)	9.0(7)	1.1(7)	-1.4(6)	-0.1(8)
C22	16.4(9)	16.9(9)	11.9(7)	2.5(7)	-0.8(6)	-6.3(7)
C23	16.2(10)	45.9(14)	16.4(8)	4.5(9)	2.1(7)	-10.1(9)
C24	45.8(14)	17.5(11)	19.5(9)	2.5(8)	-7.8(9)	-4.4(10)
C25	14.1(8)	12.4(9)	12.6(7)	-0.4(7)	-2.3(6)	0.7(8)
C26	15.4(9)	12.4(9)	9.7(7)	2.6(6)	0.9(6)	0.1(7)
C27	16.1(8)	9.4(8)	16.1(7)	-0.5(7)	-4.1(6)	-2.1(8)
C28	18.3(9)	15.8(10)	16.4(7)	-4.9(7)	-0.6(6)	3.6(8)
C29	17.3(10)	18.2(10)	26.9(9)	-4.2(8)	-3.0(8)	4.2(8)
C30	23.3(10)	15(1)	24.4(9)	6.3(7)	-10.6(8)	-2.9(8)
C31	25.5(10)	29.5(12)	15.7(8)	6.4(8)	-4.6(7)	-6.3(9)
C32	17.5(9)	27.8(10)	17.8(8)	3.5(8)	0.9(7)	-3.1(9)
C33	19.0(9)	11.8(9)	14.2(8)	0.0(7)	-0.1(7)	1.0(7)
C34	18.1(10)	17.4(11)	34.5(10)	-1.6(8)	-3.2(8)	-0.8(8)
C35	26.1(12)	17.1(12)	63.9(15)	-6.2(10)	-2.6(11)	-5.7(9)
C36	32.7(13)	16.1(11)	88.9(19)	-15.3(13)	2.2(13)	5.0(11)
C37	19.3(11)	20.7(12)	75.8(17)	-2.2(12)	-2.1(11)	3.4(9)
C38	18.8(10)	15.5(10)	36.4(11)	-1.7(8)	-1.4(8)	-0.7(8)
C39	15.0(9)	14.2(9)	9.1(7)	0.5(6)	-1.0(6)	0.3(7)
C40	13.5(9)	14(1)	16.3(8)	0.3(7)	-2.2(7)	-1.8(7)
C41	28.5(11)	21.8(11)	29(1)	-2.5(9)	3.9(8)	4.5(9)
C42	33.7(13)	20.9(12)	43.3(12)	-9.6(10)	0.4(10)	6.8(10)
C43	28.2(12)	15.8(11)	51.8(13)	5.1(10)	-11.7(10)	3.8(9)
C44	42.1(14)	21.5(13)	34.3(11)	13.6(9)	-1.2(10)	1.6(10)
C45	34.2(12)	17.5(11)	22.8(9)	4.8(8)	4.3(8)	4.1(9)
O3	34(2)	34(3)	23(2)	6(2)	-4(2)	6.5(18)
C46	45(4)	36(3)	23(3)	7(2)	-7(2)	-13(3)
C47	68(5)	54(5)	38(4)	-15(4)	1(4)	12(3)
C48	33(3)	20(3)	23(3)	4(3)	6(3)	6(2)
C49	26(3)	29(3)	25(2)	5(2)	5(2)	5.1(19)
C50	28(3)	21(3)	40(3)	-3(2)	10.7(19)	-7(2)
O00{	70(4)	30(3)	34(4)	10(3)	-7(4)	7(3)
C0AA	43(5)	85(9)	77(7)	43(8)	-34(5)	-31(6)
C1AA	81(7)	80(8)	51(6)	27(6)	28(6)	36(6)

C01N	60(5)	36(5)	48(5)	9(3)	26(4)	-1(4)
C2AA	40(5)	34(7)	97(11)	37(7)	27(7)	21(5)
C3AA	106(7)	47(4)	43(4)	7(4)	-19(4)	-20(5)

Table S-6. Bond Lengths for Nickel Complex A.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3468(3)	C22	C24	1.550(3)
Br2	Ni1	2.3540(3)	C22	C25	1.511(2)
Ni1	N1	1.9759(14)	C26	C27	1.503(2)
Ni1	N2	1.9848(14)	C26	C33	1.529(3)
O1	C8	1.493(2)	C26	C39	1.558(2)
O1	C21	1.3409(18)	C27	C28	1.385(2)
O2	C25	1.347(2)	C27	C32	1.390(2)
O2	C26	1.4865(19)	C28	C29	1.387(2)
N1	C1	1.486(2)	C29	C30	1.392(3)
N1	C21	1.271(2)	C30	C31	1.380(3)
N2	C25	1.273(2)	C31	C32	1.387(3)
N2	C39	1.488(2)	C33	C34	1.395(3)
C1	C2	1.524(3)	C33	C38	1.393(3)
C1	C8	1.570(2)	C34	C35	1.373(3)
C2	C3	1.381(3)	C35	C36	1.387(3)
C2	C7	1.382(3)	C36	C37	1.382(3)
C3	C4	1.393(3)	C37	C38	1.383(3)
C4	C5	1.379(4)	C39	C40	1.513(3)
C5	C6	1.378(4)	C40	C41	1.390(3)
C6	C7	1.395(3)	C40	C45	1.386(3)
C8	C9	1.510(2)	C41	C42	1.378(3)
C8	C15	1.537(3)	C42	C43	1.385(3)
C9	C10	1.396(3)	C43	C44	1.377(3)
C9	C14	1.395(2)	C44	C45	1.390(3)
C10	C11	1.383(3)	O3	C46	1.438(8)
C11	C12	1.380(3)	O3	C49	1.426(7)
C12	C13	1.370(3)	C46	C47	1.514(14)
C13	C14	1.388(2)	C47	C48	1.540(8)
C15	C16	1.393(3)	C48	C49	1.503(8)
C15	C20	1.370(3)	C49	C50	1.523(7)
C16	C17	1.370(3)	O00{	C0AA	1.439(9)
C17	C18	1.395(4)	O00{	C01N	1.444(10)

C18	C19	1.361(4)	C0AA	C1AA	1.517(16)
C19	C20	1.386(4)	C1AA	C2AA	1.591(14)
C21	C22	1.509(2)	C01N	C2AA	1.470(12)
C22	C23	1.529(3)	C01N	C3AA	1.476(12)

Table S-7. Bond Angles for Nickel Complex A.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Ni1	Br2	124.441(13)	C23	C22	C24	110.65(17)
N1	Ni1	Br1	98.30(5)	C25	C22	C23	110.84(15)
N1	Ni1	Br2	119.41(5)	C25	C22	C24	105.98(15)
N1	Ni1	N2	89.50(6)	O2	C25	C22	113.31(14)
N2	Ni1	Br1	121.76(4)	N2	C25	O2	117.26(14)
N2	Ni1	Br2	99.25(4)	N2	C25	C22	129.12(15)
C21	O1	C8	106.12(13)	O2	C26	C27	109.48(13)
C25	O2	C26	105.02(12)	O2	C26	C33	103.69(13)
C1	N1	Ni1	122.47(11)	O2	C26	C39	101.47(12)
C21	N1	Ni1	129.12(11)	C27	C26	C33	111.08(14)
C21	N1	C1	108.40(14)	C27	C26	C39	115.43(14)
C25	N2	Ni1	128.09(11)	C33	C26	C39	114.43(15)
C25	N2	C39	107.89(14)	C28	C27	C26	123.09(15)
C39	N2	Ni1	124.01(11)	C28	C27	C32	119.24(15)
N1	C1	C2	109.98(15)	C32	C27	C26	117.55(16)
N1	C1	C8	101.95(13)	C27	C28	C29	120.33(16)
C2	C1	C8	117.77(15)	C28	C29	C30	120.10(18)
C3	C2	C1	122.14(18)	C31	C30	C29	119.67(17)
C3	C2	C7	119.0(2)	C30	C31	C32	120.14(17)
C7	C2	C1	118.8(2)	C31	C32	C27	120.50(17)
C2	C3	C4	121.1(2)	C34	C33	C26	118.57(16)
C5	C4	C3	119.3(3)	C38	C33	C26	122.57(17)
C6	C5	C4	120.2(2)	C38	C33	C34	118.71(17)
C5	C6	C7	120.1(2)	C35	C34	C33	121.20(19)
C2	C7	C6	120.2(2)	C34	C35	C36	119.5(2)
O1	C8	C1	101.20(12)	C37	C36	C35	120.2(2)
O1	C8	C9	107.28(14)	C36	C37	C38	120.3(2)
O1	C8	C15	104.84(14)	C37	C38	C33	120.14(19)
C9	C8	C1	115.96(15)	N2	C39	C26	101.68(13)
C9	C8	C15	112.70(15)	N2	C39	C40	110.72(14)
C15	C8	C1	113.32(15)	C40	C39	C26	117.74(14)

C10	C9	C8	121.42(16)	C41	C40	C39	121.77(16)
C14	C9	C8	120.31(17)	C45	C40	C39	119.17(17)
C14	C9	C10	118.23(16)	C45	C40	C41	119.06(19)
C11	C10	C9	120.79(19)	C42	C41	C40	120.5(2)
C12	C11	C10	120.3(2)	C41	C42	C43	120.1(2)
C13	C12	C11	119.52(19)	C44	C43	C42	119.9(2)
C12	C13	C14	120.96(18)	C43	C44	C45	120.0(2)
C13	C14	C9	120.17(18)	C40	C45	C44	120.4(2)
C16	C15	C8	117.49(18)	C49	O3	C46	107.7(5)
C20	C15	C8	124.60(19)	O3	C46	C47	107.4(6)
C20	C15	C16	117.9(2)	C46	C47	C48	104.3(8)
C17	C16	C15	121.5(2)	C49	C48	C47	101.9(7)
C16	C17	C18	119.4(2)	O3	C49	C48	105.3(5)
C19	C18	C17	119.7(2)	O3	C49	C50	109.6(5)
C18	C19	C20	120.2(2)	C48	C49	C50	115.7(4)
C15	C20	C19	121.3(2)	C0AA	O00{	C01N	106.6(8)
O1	C21	C22	114.11(15)	O00{	C0AA	C1AA	107.0(9)
N1	C21	O1	117.36(14)	C0AA	C1AA	C2AA	104.7(8)
N1	C21	C22	128.48(15)	O00{	C01N	C2AA	108.1(7)
C21	C22	C23	110.02(15)	O00{	C01N	C3AA	107.6(7)
C21	C22	C24	107.25(15)	C2AA	C01N	C3AA	114.9(8)
C21	C22	C25	111.98(14)	C01N	C2AA	C1AA	102.4(8)

Table S-8. Torsion Angles for Nickel Complex A.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	Ni1	N1	C1	-50.04(15)	C15	C16	C17	C18	0.2(4)
Br1	Ni1	N1	C21	129.11(17)	C16	C15	C20	C19	-0.6(4)
Br1	Ni1	N2	C25	-105.89(16)	C16	C17	C18	C19	-2.0(4)
Br1	Ni1	N2	C39	72.79(14)	C17	C18	C19	C20	2.4(4)
Br2	Ni1	N1	C1	87.55(15)	C18	C19	C20	C15	-1.1(4)
Br2	Ni1	N1	C21	-93.30(17)	C20	C15	C16	C17	1.1(3)
Br2	Ni1	N2	C25	113.33(16)	C21	O1	C8	C1	-20.20(18)
Br2	Ni1	N2	C39	-68.00(13)	C21	O1	C8	C9	-142.13(15)
Ni1	N1	C1	C2	-70.41(19)	C21	O1	C8	C15	97.83(16)
Ni1	N1	C1	C8	163.89(12)	C21	N1	C1	C2	110.29(18)
Ni1	N1	C21	O1	-176.56(12)	C21	N1	C1	C8	-15.4(2)
Ni1	N1	C21	C22	6.1(3)	C21	C22	C25	O2	-165.60(15)
Ni1	N2	C25	O2	179.63(11)	C21	C22	C25	N2	21.1(3)

Ni1	N2	C25	C22	-7.3(3)	C23	C22	C25	O2	-42.3(2)
Ni1	N2	C39	C26	164.86(11)	C23	C22	C25	N2	144.4(2)
Ni1	N2	C39	C40	-69.23(18)	C24	C22	C25	O2	77.77(19)
O1	C8	C9	C10	32.3(2)	C24	C22	C25	N2	-95.5(2)
O1	C8	C9	C14	-150.13(16)	C25	O2	C26	C27	-146.54(15)
O1	C8	C15	C16	50.3(2)	C25	O2	C26	C33	94.85(16)
O1	C8	C15	C20	-131.4(2)	C25	O2	C26	C39	-24.08(16)
O1	C21	C22	C23	38.4(2)	C25	N2	C39	C26	-16.23(18)
O1	C21	C22	C24	-81.98(19)	C25	N2	C39	C40	109.67(17)
O1	C21	C22	C25	162.16(15)	C26	O2	C25	N2	16.0(2)
O2	C26	C27	C28	3.7(2)	C26	O2	C25	C22	-158.07(14)
O2	C26	C27	C32	-172.19(16)	C26	C27	C28	C29	-174.66(18)
O2	C26	C33	C34	79.87(18)	C26	C27	C32	C31	175.38(19)
O2	C26	C33	C38	-95.74(19)	C26	C33	C34	C35	-176.26(19)
O2	C26	C39	N2	23.89(15)	C26	C33	C38	C37	176.3(2)
O2	C26	C39	C40	-97.24(15)	C26	C39	C40	C41	83.8(2)
N1	Ni1	N2	C25	-6.42(17)	C26	C39	C40	C45	-97.3(2)
N1	Ni1	N2	C39	172.25(14)	C27	C26	C33	C34	-37.6(2)
N1	C1	C2	C3	-43.4(2)	C27	C26	C33	C38	146.75(17)
N1	C1	C2	C7	135.77(17)	C27	C26	C39	N2	142.14(14)
N1	C1	C8	O1	20.90(17)	C27	C26	C39	C40	21.0(2)
N1	C1	C8	C9	136.56(16)	C27	C28	C29	C30	-0.3(3)
N1	C1	C8	C15	-90.80(17)	C28	C27	C32	C31	-0.7(3)
N1	C21	C22	C23	-144.1(2)	C28	C29	C30	C31	-1.2(3)
N1	C21	C22	C24	95.5(2)	C29	C30	C31	C32	1.7(3)
N1	C21	C22	C25	-20.4(3)	C30	C31	C32	C27	-0.7(3)
N2	Ni1	N1	C1	-172.10(15)	C32	C27	C28	C29	1.2(3)
N2	Ni1	N1	C21	7.05(18)	C33	C26	C27	C28	117.62(19)
N2	C39	C40	C41	-32.5(2)	C33	C26	C27	C32	-58.3(2)
N2	C39	C40	C45	146.41(17)	C33	C26	C39	N2	-87.06(16)
C1	N1	C21	O1	2.7(2)	C33	C26	C39	C40	151.81(14)
C1	N1	C21	C22	-174.70(18)	C33	C34	C35	C36	-0.1(4)
C1	C2	C3	C4	-178.79(18)	C34	C33	C38	C37	0.7(3)
C1	C2	C7	C6	-179.38(17)	C34	C35	C36	C37	0.5(4)
C1	C8	C9	C10	-79.9(2)	C35	C36	C37	C38	-0.2(4)
C1	C8	C9	C14	97.7(2)	C36	C37	C38	C33	-0.4(4)
C1	C8	C15	C16	159.77(16)	C38	C33	C34	C35	-0.5(3)
C1	C8	C15	C20	-21.9(3)	C39	N2	C25	O2	0.8(2)
C2	C1	C8	O1	-99.51(17)	C39	N2	C25	C22	173.81(18)

C2	C1	C8	C9	16.2(2)	C39	C26	C27	C28	-109.99(19)
C2	C1	C8	C15	148.79(16)	C39	C26	C27	C32	74.1(2)
C2	C3	C4	C5	-1.6(3)	C39	C26	C33	C34	-170.53(15)
C3	C2	C7	C6	-0.2(3)	C39	C26	C33	C38	13.9(2)
C3	C4	C5	C6	-0.8(3)	C39	C40	C41	C42	178.79(19)
C4	C5	C6	C7	2.6(3)	C39	C40	C45	C44	-178.66(19)
C5	C6	C7	C2	-2.1(3)	C40	C41	C42	C43	0.3(3)
C7	C2	C3	C4	2.0(3)	C41	C40	C45	C44	0.3(3)
C8	O1	C21	N1	12.3(2)	C41	C42	C43	C44	-0.7(4)
C8	O1	C21	C22	-169.94(15)	C42	C43	C44	C45	0.8(4)
C8	C1	C2	C3	72.7(2)	C43	C44	C45	C40	-0.6(3)
C8	C1	C2	C7	-108.1(2)	C45	C40	C41	C42	-0.1(3)
C8	C9	C10	C11	177.36(19)	O3	C46	C47	C48	5.3(9)
C8	C9	C14	C13	-178.34(17)	C46	O3	C49	C48	-34.6(6)
C8	C15	C16	C17	179.5(2)	C46	O3	C49	C50	-159.7(4)
C8	C15	C20	C19	-178.9(2)	C46	C47	C48	C49	-24.7(9)
C9	C8	C15	C16	-66.0(2)	C47	C48	C49	O3	36.3(7)
C9	C8	C15	C20	112.3(2)	C47	C48	C49	C50	157.6(6)
C9	C10	C11	C12	0.7(3)	C49	O3	C46	C47	17.9(8)
C10	C9	C14	C13	-0.7(3)	O00{	C0AA	C1AA	C2AA	8.8(11)
C10	C11	C12	C13	-0.2(3)	O00{	C01N	C2AA	C1AA	-28.4(10)
C11	C12	C13	C14	-0.8(3)	C0AA	O00{	C01N	C2AA	35.7(10)
C12	C13	C14	C9	1.2(3)	C0AA	O00{	C01N	C3AA	160.3(7)
C14	C9	C10	C11	-0.3(3)	C0AA	C1AA	C2AA	C01N	11.6(11)
C15	C8	C9	C10	147.16(18)	C01N	O00{	C0AA	C1AA	-26.7(10)
C15	C8	C9	C14	-35.2(2)	C3AA	C01N	C2AA	C1AA	-148.5(8)

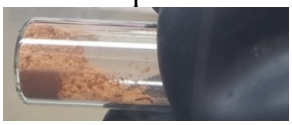
Table S-9. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Nickel Complex A.

Atom	*x*	*y*	*z*	U(eq)
H1	5022	6640	5715	22
H3	5501	4419	5435	38
H4	7413	3741	5695	46
H5	9170	4507	6254	48
H6	9026	5941	6511	47
H7	7092	6603	6339	37
H10	4407	4245	7061	32
H11	5265	3641	8605	37

H12	5749	4462	10090	29
H13	5378	5887	10022	27
H14	4572	6515	8470	21
H16	1731	5897	7393	39
H17	392	6973	7738	50
H18	901	8353	7301	55
H19	2790	8629	6628	63
H20	4116	7540	6264	48
H23A	1064	4665	5388	39
H23B	455	4589	4210	39
H23C	777	5489	4703	39
H24A	3613	3924	3966	42
H24B	2211	3620	3741	42
H24C	2795	3696	4928	42
H28	-667	5393	1808	20
H29	-2366	5624	612	25
H30	-2121	5587	-1204	26
H31	-163	5366	-1810	29
H32	1528	5115	-616	25
H34	457	3636	827	28
H35	1080	2276	536	43
H36	3186	1934	708	55
H37	4649	2955	1193	47
H38	4026	4322	1500	28
H39	3431	5509	1132	15
H41	1692	6873	2703	32
H42	1193	8249	2274	39
H43	1549	8771	607	39
H44	2447	7920	-614	39
H45	2942	6535	-190	30
H46A	914	2472	5038	42
H46B	-335	2319	5624	42
H47A	1904	1522	6037	64
H47B	616	1306	6543	64
H48A	1058	2154	7970	30
H48B	2474	1987	7701	30
H49	2556	3162	6706	32
H50A	1761	4316	7598	44
H50B	2422	3684	8434	44

H50C	944	3706	8266	44
H0AA	1268	3550	8228	84
H0AB	2482	3536	7568	84
H1AA	1377	2182	8491	84
H1AB	2709	2200	7999	84
H01N	1855	2654	5705	57
H2AA	1811	1468	6580	67
H2AB	439	1630	6959	67
H3AA	-751	2488	5662	100
H3AB	107	1994	4895	100
H3AC	-2	2990	4821	100

Complex C (Figure 4c). In a nitrogen-filled glovebox, *n*-pentane (20 mL) was added to a 20 mL vial that contained (*R*,*R*)-**L*** (128 mg, 0.20 mmol) and $Ni(cod)_2$ (55 mg, 0.20 mmol). The resulting yellow solution was stirred at room temperature for 10 min, and then the reaction mixture was filtered through an Acrodisc filter into a 20 mL vial that contained $Ph_3SiCH_2CH_2Br$ (73 mg, 0.20 mmol). The mixture was stirred for 30 min, resulting in the precipitation of an orange solid. The orange solid was collected on a medium porosity fritted filter, washed with *n*-pentane (3.0 mL x 3), and dried under reduced pressure: 115 mg, 54% yield.

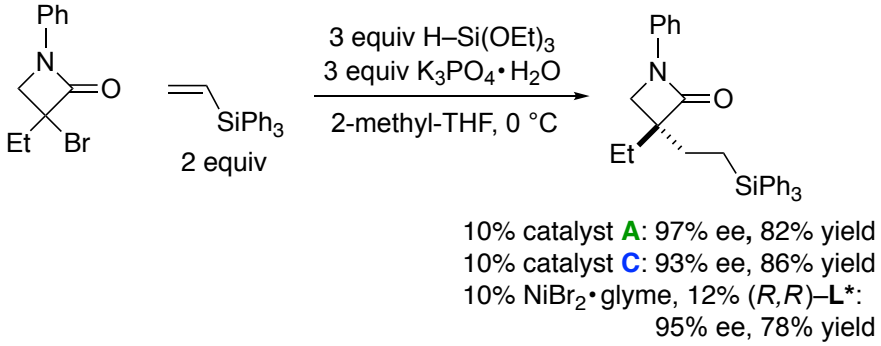


This complex is sensitive to air and moisture in the solid state and is unstable in solution at ambient temperature.

FT-IR (solid) 3055, 3025, 1653, 1445, 1362, 1127, 1108, 967, 744, 694 cm^{-1}.

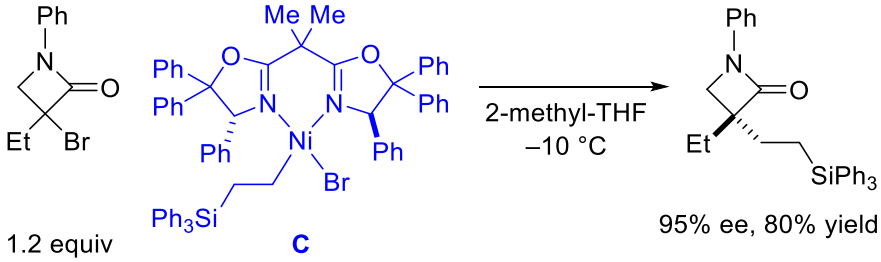
Elemental analysis calculated for $C_{65}H_{57}BrN_2NiO_2Si$: C, 73.32; H, 5.40; N, 2.63. Found: C, 73.11; H, 5.58; N, 2.36.

Protonation of complex C: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with complex **C** (11 mg, 0.010 mmol) and a stir bar. Then, the vial was capped with a PTFE septum cap, removed from the glovebox and cooled to −78 °C in a dry ice/acetone bath. While complex **C** was stirred, EtOH (0.10 mL) was added dropwise via syringe over 30 seconds, followed by Et_2O (2.0 mL). The mixture was stirred at −78 °C for 10 min, and then it was allowed to warm to room temperature over 30 min. Next, the reaction mixture was filtered through a short pad of silica gel, with Et_2O as the eluent. After removal of the volatiles, the yield of ethyltriphenylsilane was determined to be 94% via ^1H NMR analysis with CH_2Br_2 as internal standard.

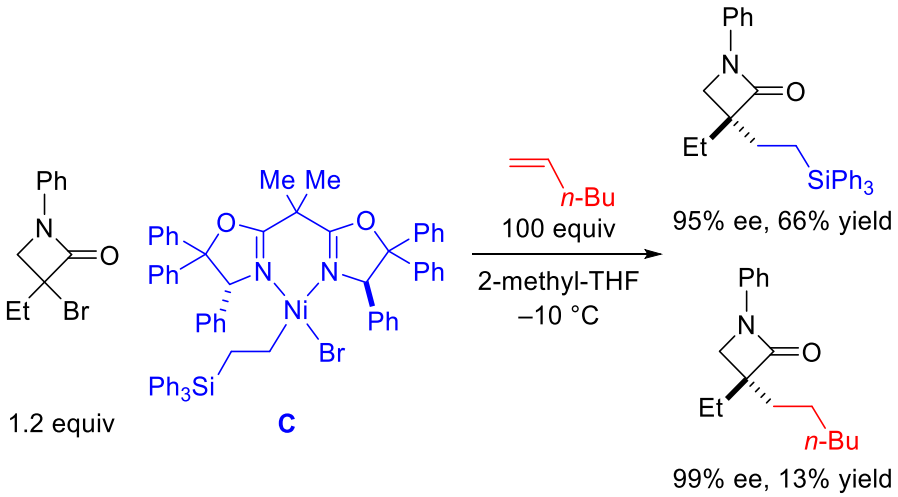


Competence of complex A as a catalyst (Figure 4d). Following **GP-3**, the reaction was run on a 0.10 mmol scale, based on the electrophile. The yield was determined via GC analysis with *n*-dodecane as the internal standard. The ee was determined via HPLC analysis after purification by preparative thin-layer chromatography.

Competence of complex C as a catalyst (Figure 4d). Due to the instability of complex **C**, the reaction was set up using a variant of **GP-3**. In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a magnetic stir bar was charged with the racemic electrophile (25 mg, 0.10 mmol, 1.0 equiv), $K_3PO_4 \cdot H_2O$ (69 mg, 0.30 mmol, 3.0 equiv), triphenyl(vinyl)silane (57 mg, 0.20 mmol, 2.0 equiv), $HSi(OEt)_3$ (55 μL, 0.30 mmol, 3.0 equiv), and 2-methyl-THF (0.5 mL). Next, the vial was capped and cooled in the cold well of a glovebox with stirring (internal temperature maintained at –10 °C). After 30 min, complex **C** (11 mg, 0.010 mmol, 10%) was added quickly as a solid to the reaction mixture. The vial was capped, taken out of the glovebox, placed in a cooling bath at 0 °C, and stirred for 40 h. Next, *n*-dodecane (23 μL, 0.10 mmol, 1.0 equiv) was added via syringe. The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The yield was determined via GC analysis, and the ee was determined via HPLC analysis after purification by preparative thin-layer chromatography



Chemical competence of complex C (Figure 4e). In a nitrogen-filled glovebox, a 4 mL vial that contained complex **C** (11 mg, 0.010 mmol) was cooled in the cold well of a glovebox (internal temperature kept at −10 °C). 2-Methyl-THF (1.0 mL; pre-cooled to −10 °C) was added to the solids (stirred), followed by the dropwise addition via syringe over 30 seconds of a solution of the electrophile (3.0 mg, 0.012 mmol) in 2-methyl-THF (0.1 mL). The resulting orange mixture was stirred at −10 °C for 4 h, resulting in a gradual color change to magenta. The reaction mixture was filtered through a short plug of silica gel, with Et_2O as the eluent. The yield was determined via GC analysis with *n*-dodecane as the internal standard. The ee was determined via HPLC analysis after purification by preparative thin-layer chromatography.



Support for *β*–migratory insertion (B ⇌ C; Figure 4f). In a nitrogen-filled glovebox, a 4 mL vial that contained complex **C** (11 mg, 0.010 mmol) was cooled in the cold well of a glovebox (internal temperature kept at −10 °C). A solution of 1-hexene (84 mg, 1.0 mmol, 100 equiv) in 2-methyl-THF (1.0 mL; pre-cooled to −10 °C) was added to the solids (stirred), followed by the dropwise addition via syringe over 30 seconds of a solution of the electrophile (3.0 mg, 0.012 mmol) in 2-methyl-THF (0.1 mL). The resulting orange mixture was stirred at −10 °C for 4 h, resulting in a gradual color change to magenta. The reaction mixture was filtered through a short plug of silica gel, with Et_2O as the eluent. The yield was determined via GC analysis with *n*-dodecane as internal standard. The ee was determined via HPLC analysis after purification by preparative thin-layer chromatography.

Identification and quantification of the likely resting state (Figure 4g). Following **GP-3**, the reaction was run on a 0.10 mmol scale, based on the electrophile. The reaction mixture was stirred vigorously at 0 °C for 6 h. For UV-vis analysis, the mixture was diluted 8-fold with cold 2-methyl-THF at 0 °C. The conversion of the electrophile was determined via GC analysis with *n*-dodecane as the internal standard. The ee of the coupling product was determined via HPLC analysis to be 96%.

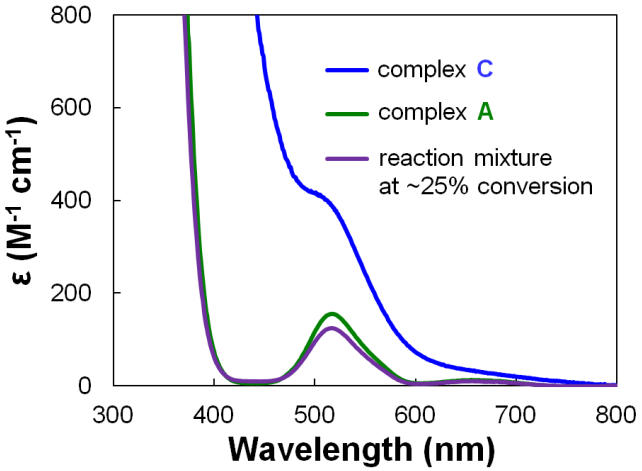


Figure S-2. Identification and quantification of the likely resting state via UV-vis spectroscopy.

VII. Assignment of Absolute Configuration

For entries 1–19 and 36, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

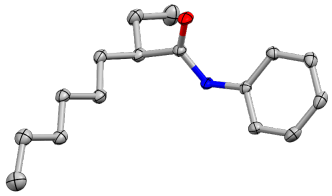
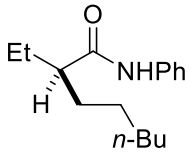


Figure S-3. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



(*R*)-2-Ethyl-*N*-phenyloctanamide. X-ray quality crystals were obtained by slow evaporation of a saturated solution in Et_2O/hexanes of a sample synthesized with (*R,R*)-**L***. A crystal of $C_{16}H_{25}NO$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu−Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-10. Crystal Data and Structure Refinement for cu_p17072_0m.

Identification code	cu_p17072_0m
Empirical formula	$C_{16}H_{25}NO$
Formula weight	247.37
Temperature/K	100(2)
Crystal system	tetragonal
Space group	$P4_1$
a/Å	17.8738(6)
b/Å	17.874
c/Å	5.0353(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1608.64(11)
Z	4

ϱ_{calc}g/cm^3	1.021
μ/mm^{-1}	0.480
F(000)	544.0
Crystal size/mm^3	0.23 × 0.22 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.94 to 158.24
Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -6 ≤ l ≤ 6
Reflections collected	44662
Independent reflections	3462 [R_{int} = 0.0352, R_{sigma} = 0.0151]
Data/restraints/parameters	3462/1/166
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0694
Final R indexes [all data]	R_1 = 0.0276, wR_2 = 0.0699
Largest diff. peak/hole / e Å^{-3}	0.13/-0.18
Flack parameter	0.00(18)

Table S-11. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_p17072_0m.

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(1)	2012.5(4)	3562.8(4)	2034.3(13)	26.36(16)
N(1)	2327.3(4)	3476.2(4)	6394.5(15)	17.95(15)
C(1)	3116.7(4)	3393.0(5)	6110.9(17)	16.21(17)
C(2)	3433.0(5)	2956.1(5)	4122.3(18)	20.15(18)
C(3)	4209.2(5)	2886.3(5)	3992.1(19)	24.5(2)
C(4)	4663.3(5)	3249.6(6)	5819(2)	26.6(2)
C(5)	4343.5(5)	3684.6(6)	7796.4(19)	25.0(2)
C(6)	3570.7(5)	3755.5(5)	7951.3(19)	20.31(17)
C(7)	1833.7(5)	3569.7(5)	4393.8(18)	18.85(18)
C(8)	1025.0(5)	3704.7(5)	5244.9(19)	21.64(19)
C(9)	518.5(5)	3107.0(6)	3998(2)	27.7(2)
C(10)	684.9(6)	2314.6(6)	4934(3)	36.5(3)
C(11)	791.5(5)	4492.5(5)	4362(2)	23.15(19)
C(12)	1218.3(5)	5120.0(5)	5757(2)	23.47(19)
C(13)	1021.2(5)	5895.9(5)	4721.9(19)	23.88(19)
C(14)	1397.0(5)	6524.6(6)	6275.5(19)	23.96(19)
C(15)	1211.8(6)	7303.5(6)	5250(2)	28.3(2)
C(16)	1480.7(6)	7922.8(6)	7107(2)	34.7(2)

Table S-12. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_p17072_0m.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	23.4(3)	43.6(4)	12.0(3)	0.3(3)	0.2(3)	5.8(3)
N(1)	16.0(3)	26.9(4)	10.9(3)	0.7(3)	1.5(3)	2.4(3)
C(1)	16.7(4)	17.7(4)	14.2(4)	4.6(3)	0.0(3)	1.5(3)
C(2)	22.0(4)	21.9(4)	16.5(4)	1.0(3)	1.6(3)	3.3(3)
C(3)	23.9(4)	31.0(5)	18.6(5)	4.1(4)	4.2(4)	8.6(4)
C(4)	17.1(4)	39.5(5)	23.0(5)	10.3(4)	0.5(4)	4.2(4)
C(5)	21.8(4)	31.5(5)	21.7(5)	5.4(4)	-5.5(4)	-3.7(3)
C(6)	22.2(4)	22.6(4)	16.0(4)	0.2(3)	-1.7(3)	1.7(3)
C(7)	18.9(4)	24.3(4)	13.3(4)	0.7(3)	0.2(3)	2.8(3)
C(8)	16.8(4)	32.4(5)	15.7(4)	1.8(4)	0.0(3)	2.4(3)
C(9)	20.5(4)	34.8(5)	27.7(5)	1.6(4)	-3.0(4)	-1.4(4)
C(10)	29.9(5)	33.6(5)	46.0(7)	4.1(5)	-2.2(5)	-1.8(4)
C(11)	17.3(4)	33.6(5)	18.7(4)	2.1(4)	-0.8(3)	3.9(3)
C(12)	19.3(4)	33.3(5)	17.8(4)	1.1(4)	-0.3(3)	3.1(3)
C(13)	20.9(4)	33.8(5)	16.9(4)	2.1(4)	0.1(3)	3.4(3)
C(14)	20.2(4)	33.8(5)	17.8(4)	3.4(4)	1.7(3)	0.6(3)
C(15)	28.2(5)	33.5(5)	23.2(5)	7.0(4)	2.7(4)	-0.3(4)
C(16)	39.5(6)	31.6(5)	32.9(6)	6.3(5)	1.6(5)	-5.0(4)

Table S-13. Bond Lengths for cu_p17072_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(7)	1.2304(11)	C(7)	C(8)	1.5269(11)
N(1)	C(1)	1.4259(10)	C(8)	C(9)	1.5347(13)
N(1)	C(7)	1.3495(11)	C(8)	C(11)	1.5345(13)
C(1)	C(2)	1.3899(12)	C(9)	C(10)	1.5220(15)
C(1)	C(6)	1.3918(12)	C(11)	C(12)	1.5275(13)
C(2)	C(3)	1.3947(13)	C(12)	C(13)	1.5229(13)
C(3)	C(4)	1.3879(15)	C(13)	C(14)	1.5251(14)
C(4)	C(5)	1.3867(15)	C(14)	C(15)	1.5212(13)
C(5)	C(6)	1.3892(13)	C(15)	C(16)	1.5267(16)

Table S-14. Bond Angles for cu_p17072_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(7)	N(1)	C(1)	125.80(7)	N(1)	C(7)	C(8)	115.40(8)
C(2)	C(1)	N(1)	122.22(8)	C(7)	C(8)	C(9)	109.49(8)
C(2)	C(1)	C(6)	120.27(8)	C(7)	C(8)	C(11)	108.73(7)
C(6)	C(1)	N(1)	117.50(8)	C(11)	C(8)	C(9)	111.09(8)
C(1)	C(2)	C(3)	119.26(9)	C(10)	C(9)	C(8)	113.94(8)
C(4)	C(3)	C(2)	120.58(9)	C(12)	C(11)	C(8)	113.87(8)
C(5)	C(4)	C(3)	119.81(8)	C(13)	C(12)	C(11)	113.31(8)
C(4)	C(5)	C(6)	120.09(9)	C(12)	C(13)	C(14)	113.18(8)
C(5)	C(6)	C(1)	119.99(9)	C(15)	C(14)	C(13)	113.85(8)
O(1)	C(7)	N(1)	123.35(8)	C(14)	C(15)	C(16)	112.78(9)
O(1)	C(7)	C(8)	121.23(8)				

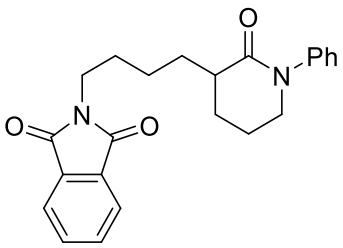
Table S-15. Torsion Angles for cu_p17072_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O(1)	C(7)	C(8)	C(9)	58.44(12)	C(4)	C(5)	C(6)	C(1)	-0.35(14)
O(1)	C(7)	C(8)	C(11)	-63.10(11)	C(6)	C(1)	C(2)	C(3)	-0.07(13)
N(1)	C(1)	C(2)	C(3)	-178.67(8)	C(7)	N(1)	C(1)	C(2)	-41.44(12)
N(1)	C(1)	C(6)	C(5)	179.00(8)	C(7)	N(1)	C(1)	C(6)	139.92(9)
N(1)	C(7)	C(8)	C(9)	-122.84(9)	C(7)	C(8)	C(9)	C(10)	63.80(11)
N(1)	C(7)	C(8)	C(11)	115.63(9)	C(7)	C(8)	C(11)	C(12)	-65.61(10)
C(1)	N(1)	C(7)	O(1)	3.14(14)	C(8)	C(11)	C(12)	C(13)	175.88(8)
C(1)	N(1)	C(7)	C(8)	-175.55(8)	C(9)	C(8)	C(11)	C(12)	173.84(8)
C(1)	C(2)	C(3)	C(4)	-0.19(14)	C(11)	C(8)	C(9)	C(10)	-176.10(9)
C(2)	C(1)	C(6)	C(5)	0.33(13)	C(11)	C(12)	C(13)	C(14)	175.05(8)
C(2)	C(3)	C(4)	C(5)	0.17(14)	C(12)	C(13)	C(14)	C(15)	179.45(8)
C(3)	C(4)	C(5)	C(6)	0.10(14)	C(13)	C(14)	C(15)	C(16)	170.03(8)

Table S-16. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for cu_p17072_0m.

Atom	*x*	*y*	*z*	U(eq)
H(1)	2146	3466	8019	22
H(2)	3124	2708	2866	24
H(3)	4429	2587	2641	29
H(4)	5192	3200	5714	32
H(5)	4653	3934	9047	30
H(6)	3352	4051	9313	24
H(8)	990	3670	7223	26
H(9A)	-9	3228	4422	33
H(9B)	575	3127	2043	33
H(10A)	329	1967	4118	55
H(10B)	638	2290	6871	55
H(10C)	1195	2177	4415	55
H(11A)	871	4538	2423	28
H(11B)	250	4557	4707	28
H(12A)	1109	5099	7683	28
H(12B)	1762	5036	5523	28
H(13A)	472	5963	4809	29
H(13B)	1172	5932	2834	29
H(14A)	1242	6490	8159	29
H(14B)	1946	6453	6204	29
H(15A)	663	7347	5023	34
H(15B)	1446	7372	3486	34
H(16A)	1338	8411	6377	52
H(16B)	2026	7897	7278	52
H(16C)	1251	7858	8859	52

For entries 20–24, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:



2-(4-(2-Oxo-1-phenylpiperidin-3-yl)butyl)isoindoline-1,3-dione. The title compound was prepared according to **GP-1** from 3-iodo-1-phenylpiperidin-2-one and 2-(but-3-en-1-yl)isoindoline-1,3-dione. Purification by flash column chromatography on silica gel: 20% EtOAc in CH_2Cl_2, white solid.

(*R*,*R*)-**L***: 216 mg, 72% yield, 98% ee; (*S*,*S*)-**L***: 221 mg, 73% yield, 98% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 24.3 min (major), 30.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.33 – 7.25 (m, 2H), 7.18 – 7.11 (m, 3H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.56 (dddd, *J* = 12.0, 10.8, 7.1, 4.6 Hz, 2H), 2.44 – 2.29 (m, 1H), 2.05 – 1.90 (m, 3H), 1.89 – 1.76 (m, 1H), 1.71 – 1.53 (m, 4H), 1.46 – 1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 168.5, 143.6, 133.7, 132.2, 129.0, 126.5, 126.2, 123.2, 51.5, 41.8, 37.9, 31.5, 28.8, 26.6, 24.6, 22.2.

FT-IR (film) 2940, 1770, 1711, 1650, 1493, 1396, 1303, 1187, 1071, 759, 720 cm^{-1}.

HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3$: 377.1865, found: 377.1868.

$[\alpha]^{23}_D$ = −39.2 (*c* 1.0, $CHCl_3$); 98% ee, from (*R*,*R*)-**L***.

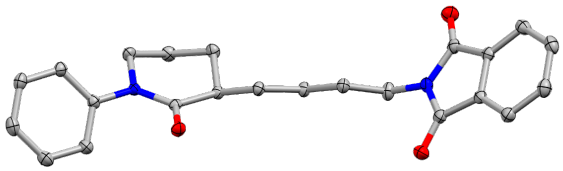
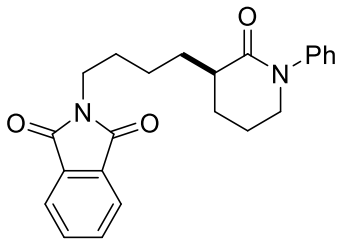


Figure S-4. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



(*R*)-2-(4-(2-Oxo-1-phenylpiperidin-3-yl)butyl)isoindoline-1,3-dione. X-ray quality crystals were obtained by slow evaporation of a saturated solution in Et_2O/hexanes of a sample

synthesized with (*R,R*)-**L***. A crystal of $C_{23}H_{24}N_2O_3$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu−Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-17. Crystal Data and Structure Refinement for p17590.

Identification code	p17590
Empirical formula	$C_{23}H_{24}N_2O_3$
Formula weight	376.44
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.3179(5)
b/Å	9.0668(5)
c/Å	16.8138(14)
α/°	90.00
β/°	99.051(7)
γ/°	90.00
Volume/Å^3	951.15(12)
Z	2
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.703
F(000)	400.0
Crystal size/mm^3	0.25 × 0.24 × 0.17
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.32 to 159.16
Index ranges	$-8 \le h \le 7$, $-11 \le k \le 11$, $-21 \le l \le 21$
Reflections collected	60027
Independent reflections	4082 [R_{int} = 0.0365, R_{sigma} = 0.0125]
Data/restraints/parameters	4082/1/254
Goodness-of-fit on F^2	1.126
Final R indexes [I>=2σ (I)]	R_1 = 0.0274, wR_2 = 0.0700
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0701
Largest diff. peak/hole / e Å^{-3}	0.17/-0.28
Flack parameter	0.00(14)

Table S-18. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p17590.

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(1)	5121.8(12)	4810.2(9)	4000.6(5)	19.70(16)
O(2)	-758.8(13)	5373.4(11)	7375.7(5)	26.38(19)
O(3)	5279.2(13)	4858.6(10)	9251.4(5)	26.25(18)
N(1)	8275.9(14)	3722.3(10)	3846.4(5)	15.03(17)
N(2)	2466.2(14)	4870.2(11)	8187.1(5)	18.47(19)
C(1)	8201.5(17)	4304.7(12)	3047.1(6)	16.5(2)
C(2)	6319.3(18)	4215.5(13)	2485.9(7)	20.1(2)
C(3)	6294.2(19)	4741.5(14)	1706.0(7)	23.1(2)
C(4)	8122(2)	5350.0(14)	1474.2(7)	23.1(2)
C(5)	9988.6(18)	5427.1(13)	2030.4(7)	21.7(2)
C(6)	10043.2(17)	4904.2(12)	2813.7(6)	18.3(2)
C(7)	6652.0(16)	4035.6(12)	4278.9(6)	14.6(2)
C(8)	6726.9(16)	3333.9(11)	5113.3(6)	14.7(2)
C(9)	8953.1(17)	2816.9(12)	5506.1(6)	17.6(2)
C(10)	10035.5(18)	1995.7(12)	4892.8(7)	18.5(2)
C(11)	10308.3(17)	3003.6(13)	4196.0(6)	18.4(2)
C(12)	5677.8(16)	4358.7(12)	5665.0(6)	16.0(2)
C(13)	5136.3(17)	3599.5(12)	6418.0(6)	17.5(2)
C(14)	4088.3(17)	4663.4(12)	6940.5(6)	17.2(2)
C(15)	3349.6(19)	3862.6(13)	7643.6(7)	21.4(2)
C(16)	458.5(17)	5540.3(12)	8000.6(6)	18.6(2)
C(17)	196.5(17)	6448.4(12)	8716.1(7)	17.0(2)
C(18)	-1523.7(18)	7274.4(13)	8876.1(7)	21.0(2)
C(19)	-1306(2)	7996.6(13)	9618.4(7)	24.0(2)
C(20)	585(2)	7910.5(14)	10167.0(7)	24.2(2)
C(21)	2311.0(19)	7062.3(13)	10004.3(7)	21.9(2)
C(22)	2059.4(17)	6327.7(12)	9274.5(6)	17.2(2)
C(23)	3534.7(17)	5292.1(13)	8942.2(6)	18.5(2)

Table S-19. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for p17590.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	15.6(3)	23.7(4)	19.9(4)	2.9(3)	3.1(3)	4.4(3)
O(2)	21.5(4)	36.3(5)	20.3(4)	-6.0(4)	0.3(3)	-1.4(4)
O(3)	22.1(4)	30.0(4)	25.8(4)	5.2(4)	1.1(3)	5.1(3)
N(1)	13.7(4)	17.9(4)	13.5(4)	-0.1(3)	2.2(3)	1.6(3)
N(2)	19.7(4)	20.9(4)	15.6(4)	0.1(4)	5.1(3)	2.2(4)
C(1)	18.0(5)	16.1(5)	15.5(5)	-1.4(4)	3.2(4)	1.6(4)
C(2)	19.8(5)	23.0(5)	17.4(5)	-0.9(4)	2.2(4)	-1.4(4)
C(3)	25.4(5)	24.7(6)	18.1(5)	1.0(5)	-0.4(4)	0.5(5)
C(4)	32.5(6)	20.9(5)	17.1(5)	1.6(4)	7.5(4)	4.2(5)
C(5)	23.8(5)	20.5(5)	22.9(5)	0.3(5)	10.4(4)	2.2(4)
C(6)	17.7(5)	18.7(5)	19.1(5)	-2.8(4)	4.6(4)	1.1(4)
C(7)	13.3(4)	13.6(5)	16.6(5)	-1.7(4)	1.6(4)	-1.7(4)
C(8)	15.2(5)	13.9(5)	15.4(5)	-0.4(4)	3.4(4)	-0.1(4)
C(9)	19.4(5)	17.2(5)	16.1(5)	1.4(4)	2.2(4)	3.7(4)
C(10)	18.7(5)	16.1(5)	20.7(5)	-0.3(4)	2.5(4)	4.8(4)
C(11)	14.8(5)	22.1(5)	18.3(5)	-1.4(4)	2.8(4)	4.8(4)
C(12)	16.7(5)	14.8(5)	17.0(5)	-0.1(4)	4.3(4)	0.2(4)
C(13)	19.5(5)	15.9(5)	18.1(5)	0.3(4)	6.2(4)	-0.7(4)
C(14)	18.4(5)	17.3(5)	16.9(5)	0.2(4)	5.5(4)	-0.2(4)
C(15)	26.7(6)	18.4(5)	21.0(5)	0.9(4)	10.2(4)	2.8(4)
C(16)	18.3(5)	20.0(5)	18.4(5)	0.9(4)	5.3(4)	-2.0(4)
C(17)	18.5(5)	16.9(5)	15.9(5)	0.8(4)	4.0(4)	-3.1(4)
C(18)	20.0(5)	21.9(6)	21.4(5)	0.7(4)	4.4(4)	0.1(4)
C(19)	28.1(6)	21.1(5)	24.7(6)	-0.4(5)	10.2(4)	2.6(5)
C(20)	35.3(6)	19.9(5)	18.1(5)	-1.5(4)	6.3(4)	-1.5(5)
C(21)	26.5(6)	20.9(5)	17.6(5)	1.0(4)	1.3(4)	-2.7(4)
C(22)	19.4(5)	16.0(5)	16.7(5)	3.4(4)	3.9(4)	-1.9(4)
C(23)	19.7(5)	18.8(5)	17.8(5)	4.2(4)	5.1(4)	-2.0(4)

Table S-20. Bond Lengths for p17590.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(7)	1.2266(13)	C(8)	C(9)	1.5303(14)
O(2)	C(16)	1.2100(14)	C(8)	C(12)	1.5351(13)

O(3)	C(23)	1.2080(14)	C(9)	C(10)	1.5190(14)
N(1)	C(1)	1.4378(13)	C(10)	C(11)	1.5170(15)
N(1)	C(7)	1.3772(13)	C(12)	C(13)	1.5265(14)
N(1)	C(11)	1.4770(13)	C(13)	C(14)	1.5244(14)
N(2)	C(15)	1.4634(14)	C(14)	C(15)	1.5218(15)
N(2)	C(16)	1.3969(14)	C(16)	C(17)	1.4882(15)
N(2)	C(23)	1.3944(14)	C(17)	C(18)	1.3808(16)
C(1)	C(2)	1.3993(14)	C(17)	C(22)	1.3896(15)
C(1)	C(6)	1.3954(15)	C(18)	C(19)	1.3969(16)
C(2)	C(3)	1.3930(16)	C(19)	C(20)	1.3921(18)
C(3)	C(4)	1.3900(17)	C(20)	C(21)	1.3961(17)
C(4)	C(5)	1.3866(16)	C(21)	C(22)	1.3832(16)
C(5)	C(6)	1.3950(16)	C(22)	C(23)	1.4921(15)
C(7)	C(8)	1.5344(14)			

Table S-21. Bond Angles for p17590.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C(1)	N(1)	C(11)	115.63(8)	N(1)	C(11)	C(10)	112.08(9)
C(7)	N(1)	C(1)	120.02(9)	C(13)	C(12)	C(8)	113.74(9)
C(7)	N(1)	C(11)	123.65(8)	C(14)	C(13)	C(12)	111.53(9)
C(16)	N(2)	C(15)	123.60(9)	C(15)	C(14)	C(13)	111.09(9)
C(23)	N(2)	C(15)	124.21(9)	N(2)	C(15)	C(14)	112.39(9)
C(23)	N(2)	C(16)	112.18(9)	O(2)	C(16)	N(2)	124.83(10)
C(2)	C(1)	N(1)	120.56(9)	O(2)	C(16)	C(17)	129.40(10)
C(6)	C(1)	N(1)	119.99(9)	N(2)	C(16)	C(17)	105.77(9)
C(6)	C(1)	C(2)	119.38(10)	C(18)	C(17)	C(16)	130.44(10)
C(3)	C(2)	C(1)	119.84(10)	C(18)	C(17)	C(22)	121.33(10)
C(4)	C(3)	C(2)	120.86(10)	C(22)	C(17)	C(16)	108.21(9)
C(5)	C(4)	C(3)	119.13(10)	C(17)	C(18)	C(19)	117.29(10)
C(4)	C(5)	C(6)	120.78(10)	C(20)	C(19)	C(18)	121.29(11)
C(5)	C(6)	C(1)	120.00(10)	C(19)	C(20)	C(21)	121.10(11)
O(1)	C(7)	N(1)	121.64(9)	C(22)	C(21)	C(20)	117.05(11)
O(1)	C(7)	C(8)	119.68(9)	C(17)	C(22)	C(23)	108.01(9)
N(1)	C(7)	C(8)	118.61(9)	C(21)	C(22)	C(17)	121.90(10)
C(7)	C(8)	C(12)	110.33(8)	C(21)	C(22)	C(23)	130.07(10)
C(9)	C(8)	C(7)	114.56(8)	O(3)	C(23)	N(2)	125.51(11)
C(9)	C(8)	C(12)	112.30(9)	O(3)	C(23)	C(22)	128.68(11)
C(10)	C(9)	C(8)	109.79(9)	N(2)	C(23)	C(22)	105.79(9)

C(11) C(10) C(9) 110.31(9)

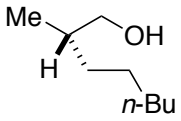
Table S-22. Torsion Angles for p17590.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O(1)	C(7)	C(8)	C(9)	-161.63(10)	C(11)	N(1)	C(7)	O(1)	169.78(10)
O(1)	C(7)	C(8)	C(12)	-33.74(13)	C(11)	N(1)	C(7)	C(8)	-13.04(15)
O(2)	C(16)	C(17)	C(18)	3.7(2)	C(12)	C(8)	C(9)	C(10)	-171.83(8)
O(2)	C(16)	C(17)	C(22)	-177.98(12)	C(12)	C(13)	C(14)	C(15)	174.21(9)
N(1)	C(1)	C(2)	C(3)	-177.90(10)	C(13)	C(14)	C(15)	N(2)	176.16(9)
N(1)	C(1)	C(6)	C(5)	177.99(10)	C(15)	N(2)	C(16)	O(2)	-0.40(17)
N(1)	C(7)	C(8)	C(9)	21.13(13)	C(15)	N(2)	C(16)	C(17)	179.38(9)
N(1)	C(7)	C(8)	C(12)	149.03(9)	C(15)	N(2)	C(23)	O(3)	-2.03(17)
N(2)	C(16)	C(17)	C(18)	-176.03(11)	C(15)	N(2)	C(23)	C(22)	179.40(9)
N(2)	C(16)	C(17)	C(22)	2.26(11)	C(16)	N(2)	C(15)	C(14)	73.86(13)
C(1)	N(1)	C(7)	O(1)	-0.15(16)	C(16)	N(2)	C(23)	O(3)	178.95(11)
C(1)	N(1)	C(7)	C(8)	177.02(9)	C(16)	N(2)	C(23)	C(22)	0.38(12)
C(1)	N(1)	C(11)	C(10)	-160.93(9)	C(16)	C(17)	C(18)	C(19)	178.78(11)
C(1)	C(2)	C(3)	C(4)	0.33(17)	C(16)	C(17)	C(22)	C(21)	179.42(10)
C(2)	C(1)	C(6)	C(5)	0.92(16)	C(16)	C(17)	C(22)	C(23)	-2.05(11)
C(2)	C(3)	C(4)	C(5)	0.12(18)	C(17)	C(18)	C(19)	C(20)	1.29(17)
C(3)	C(4)	C(5)	C(6)	-0.04(18)	C(17)	C(22)	C(23)	O(3)	-177.42(11)
C(4)	C(5)	C(6)	C(1)	-0.48(17)	C(17)	C(22)	C(23)	N(2)	1.09(11)
C(6)	C(1)	C(2)	C(3)	-0.84(16)	C(18)	C(17)	C(22)	C(21)	-2.10(16)
C(7)	N(1)	C(1)	C(2)	-46.74(14)	C(18)	C(17)	C(22)	C(23)	176.43(10)
C(7)	N(1)	C(1)	C(6)	136.23(10)	C(18)	C(19)	C(20)	C(21)	-1.93(18)
C(7)	N(1)	C(11)	C(10)	28.74(14)	C(19)	C(20)	C(21)	C(22)	0.53(17)
C(7)	C(8)	C(9)	C(10)	-44.94(12)	C(20)	C(21)	C(22)	C(17)	1.44(16)
C(7)	C(8)	C(12)	C(13)	164.41(9)	C(20)	C(21)	C(22)	C(23)	-176.73(11)
C(8)	C(9)	C(10)	C(11)	61.06(12)	C(21)	C(22)	C(23)	O(3)	0.95(19)
C(8)	C(12)	C(13)	C(14)	-179.66(8)	C(21)	C(22)	C(23)	N(2)	179.46(11)
C(9)	C(8)	C(12)	C(13)	-66.46(11)	C(22)	C(17)	C(18)	C(19)	0.68(17)
C(9)	C(10)	C(11)	N(1)	-52.20(12)	C(23)	N(2)	C(15)	C(14)	-105.05(12)
C(11)	N(1)	C(1)	C(2)	142.55(10)	C(23)	N(2)	C(16)	O(2)	178.63(11)
C(11)	N(1)	C(1)	C(6)	-34.49(14)	C(23)	N(2)	C(16)	C(17)	-1.60(12)

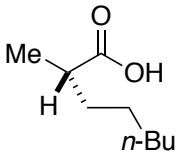
Table S-23. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for p17590.

Atom	*x*	*y*	*z*	U(eq)
H(2)	5062	3797	2636	24
H(3)	5011	4684	1328	28
H(4)	8094	5708	942	28
H(5)	11245	5841	1876	26
H(6)	11334	4956	3188	22
H(8)	5809	2431	5033	18
H(9A)	9833	3679	5713	21
H(9B)	8822	2160	5966	21
H(10A)	11456	1635	5153	22
H(10B)	9157	1131	4689	22
H(11A)	11385	3771	4387	22
H(11B)	10855	2422	3773	22
H(12A)	6659	5193	5831	19
H(12B)	4345	4769	5356	19
H(13A)	4152	2764	6257	21
H(13B)	6464	3198	6735	21
H(14A)	5126	5443	7149	21
H(14B)	2843	5143	6609	21
H(15A)	2244	3128	7432	26
H(15B)	4579	3325	7950	26
H(18)	-2803	7349	8497	25
H(19)	-2472	8557	9751	29
H(20)	703	8438	10660	29
H(21)	3601	6993	10378	26

For entries 25 and 26, the absolute configuration of the cross-coupling product is assigned on the basis of comparison with two independent literature reports:



(*S*)-2-Methyloctan-1-ol. The title compound was prepared from 2,6-di-*tert*-butyl-4-methylphenyl (*S*)-2-methyloctanoate (from (*R*,*R*)-**L***) (see procedure for Figure 2b, entry 30, above). The title compound has $[\alpha]^{24}_{D}$: –12.8 (c 1.0, EtOH). The absolute configuration was assigned by comparing with a literature report: $[\alpha]^{25}_{D}$: –13.1 (c 1.63, EtOH) for the *S* enantiomer[5].



(*S*)-2-Methyloctanoic acid. The title compound was prepared from 2,6-di-*tert*-butyl-4-methoxyphenyl (*S*)-2-methyloctanoate (from (*R*,*R*)-**L***) (see procedure for Figure 2b, entry 31, above). The title compound has $[\alpha]^{24}_{D}$: +17.0 (c 1.0, MeOH). The absolute configuration was assigned by comparing with a literature report: $[\alpha]^{25}_{D}$: +16.2 (c 1.1, MeOH) for the *S* enantiomer[6].

For entry 32, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

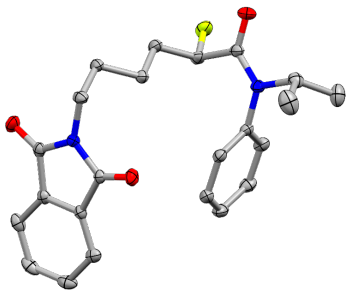
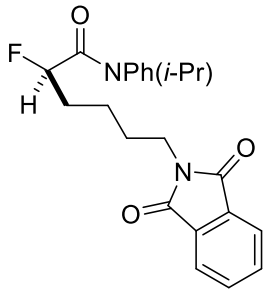


Figure S-5. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



(*R*)-6-(1,3-Dioxoisoindolin-2-yl)-2-fluoro-*N*-isopropyl-*N*-phenylhexanamide. A sample synthesized with (*R,R*)-**L*** was crystallized once from CH_2Cl_2/hexanes to give product with >99% ee. Then, X-ray quality crystals were obtained by slow evaporation of a saturated solution in CH_2Cl_2/hexanes. A crystal of $C_{23}H_{25}FN_2O_3$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu−Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-24. Crystal Data and Structure Refinement for p17415.

Identification code	p17415
Empirical formula	$C_{23}H_{25}FN_2O_3$
Formula weight	396.45
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	14.8771(11)
b/Å	17.9770(13)
c/Å	7.8036(6)

α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2087.0(3)
Z	4
ρ_{calc}g/cm^3	1.262
μ/mm^{-1}	0.736
F(000)	840.0
Crystal size/mm^3	0.3 × 0.25 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.72 to 159.12
Index ranges	-19 ≤ h ≤ 17, -22 ≤ k ≤ 22, -9 ≤ l ≤ 9
Reflections collected	19351
Independent reflections	4445 [R_{int} = 0.0372, R_{sigma} = 0.0254]
Data/restraints/parameters	4445/0/265
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0304, wR_2 = 0.0772
Largest diff. peak/hole / e Å^{-3}	0.17/-0.26
Flack parameter	0.00(11)

Table S-25. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for p17415.

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F(1)	4147.0(5)	4547.2(4)	3212.6(11)	29.65(18)
O(1)	3882.3(6)	4086.0(6)	6471.6(14)	35.4(2)
O(2)	5628.3(6)	875.2(5)	3909.7(11)	24.27(19)
O(3)	3976.5(6)	1074.0(5)	-1012.9(12)	27.10(19)
N(1)	5298.2(6)	3606.3(6)	6413.6(13)	19.5(2)
N(2)	4600.9(6)	980.6(5)	1693.9(13)	17.75(19)
C(1)	6069.5(7)	3384.1(6)	5410.1(14)	18.0(2)
C(2)	6639.0(7)	3927.2(7)	4738.9(16)	21.1(2)
C(3)	7338.8(8)	3717.7(7)	3661.3(16)	25.0(3)
C(4)	7483.3(8)	2971.6(8)	3286.9(17)	25.7(3)
C(5)	6932.3(7)	2429.3(7)	3999.8(16)	23.2(2)
C(6)	6223.4(7)	2634.7(7)	5065.0(15)	19.6(2)
C(7)	5368.6(8)	3614.4(7)	8316.0(16)	24.1(2)

C(8)	6080.3(11)	4163.2(8)	8901.3(18)	35.0(3)
C(9)	5531.2(13)	2841.2(8)	9025.8(19)	40.9(4)
C(10)	4532.6(7)	3859.6(6)	5664.1(16)	21.2(2)
C(11)	4476.9(8)	3846.6(6)	3701.1(16)	21.0(2)
C(12)	3821.6(7)	3264.8(6)	3058.2(17)	22.4(2)
C(13)	4121.8(7)	2462.9(6)	3365.0(15)	19.4(2)
C(14)	3468.7(7)	1914.7(7)	2544.8(16)	21.1(2)
C(15)	3782.5(8)	1111.1(7)	2683.2(16)	22.1(2)
C(16)	4619.6(8)	973.5(6)	-98.5(15)	19.0(2)
C(17)	5454.2(7)	880.5(6)	2394.9(14)	16.4(2)
C(18)	6073.7(7)	784.9(6)	915.0(14)	16.7(2)
C(19)	5572.7(8)	830.6(6)	-579.9(14)	18.0(2)
C(20)	5955.9(9)	746.9(7)	-2180.0(15)	24.7(3)
C(21)	6880.1(9)	609.7(7)	-2223.3(17)	28.2(3)
C(22)	7382.6(8)	563.9(7)	-728.8(18)	26.4(3)
C(23)	6991.1(7)	655.3(6)	882.2(16)	20.6(2)

Table S-26. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for p17415.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	26.8(3)	16.9(3)	45.3(4)	0.3(3)	-12.0(3)	2.4(3)
O(1)	20.6(4)	44.9(6)	40.6(6)	-13.9(5)	2.7(4)	10.0(4)
O(2)	27.4(4)	31.6(5)	13.9(4)	-0.3(3)	-1.3(3)	-2.2(4)
O(3)	27.1(4)	25.5(4)	28.7(4)	-2.0(3)	-12.7(4)	3.9(4)
N(1)	15.6(4)	21.3(5)	21.4(5)	-0.2(4)	2.5(3)	0.1(4)
N(2)	16.4(4)	17.9(4)	19.0(4)	-2.4(4)	0.0(4)	0.9(3)
C(1)	12.9(4)	22.0(5)	19.0(5)	1.6(4)	-1.5(4)	0.6(4)
C(2)	17.4(5)	20.5(5)	25.5(6)	3.4(4)	-1.1(4)	-0.3(4)
C(3)	18.4(5)	30.9(6)	25.9(6)	5.5(5)	1.6(4)	-2.7(5)
C(4)	16.7(5)	36.5(7)	23.9(6)	-2.6(5)	2.0(4)	2.7(5)
C(5)	18.8(5)	25.7(6)	25.0(6)	-6.3(5)	-2.8(4)	2.9(4)
C(6)	15.9(5)	20.8(5)	22.2(5)	-0.1(4)	-2.5(4)	-1.7(4)
C(7)	25.2(5)	26.6(6)	20.7(5)	-1.3(5)	3.8(5)	-1.4(5)
C(8)	44.9(7)	36.2(7)	24.0(6)	-1.7(5)	-3.4(6)	-10.7(6)
C(9)	64.9(10)	31.8(7)	25.9(7)	6.9(6)	5.1(7)	-5.5(7)
C(10)	15.8(5)	17.8(5)	30.0(6)	-4.9(5)	1.3(4)	-0.3(4)
C(11)	17.6(5)	16.7(5)	28.8(6)	-1.1(4)	-3.9(4)	3.3(4)

C(12)	16.7(5)	20.1(6)	30.3(6)	-3.4(5)	-4.0(4)	1.4(4)
C(13)	16.2(5)	17.4(5)	24.6(5)	-3.4(4)	-0.1(4)	-0.1(4)
C(14)	15.2(5)	20.3(5)	27.7(6)	-5.6(5)	0.1(4)	-0.1(4)
C(15)	16.0(5)	19.7(5)	30.5(6)	-3.9(5)	4.8(4)	-2.4(4)
C(16)	23.5(5)	13.0(5)	20.4(5)	-1.8(4)	-3.9(4)	-0.3(4)
C(17)	17.7(5)	14.0(5)	17.4(5)	-0.5(4)	-0.3(4)	-1.4(4)
C(18)	20.3(5)	13.8(5)	16.0(5)	0.1(4)	0.9(4)	-1.2(4)
C(19)	22.5(5)	14.2(5)	17.4(5)	0.4(4)	-1.0(4)	0.3(4)
C(20)	38.6(6)	19.7(5)	15.8(5)	1.0(4)	3.3(5)	-1.1(5)
C(21)	38.5(7)	21.4(6)	24.7(6)	-0.2(5)	16.0(5)	-1.8(5)
C(22)	23.7(5)	19.2(5)	36.4(7)	2.8(5)	11.6(5)	-0.2(4)
C(23)	18.8(5)	16.4(5)	26.6(6)	2.1(5)	1.1(4)	-0.4(4)

Table S-27. Bond Lengths for p17415.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(1)	C(11)	1.4044(13)	C(7)	C(8)	1.5175(18)
O(1)	C(10)	1.2242(15)	C(7)	C(9)	1.5158(19)
O(2)	C(17)	1.2102(14)	C(10)	C(11)	1.5343(17)
O(3)	C(16)	1.2073(14)	C(11)	C(12)	1.5152(16)
N(1)	C(1)	1.4456(14)	C(12)	C(13)	1.5280(15)
N(1)	C(7)	1.4883(15)	C(13)	C(14)	1.5248(15)
N(1)	C(10)	1.3589(15)	C(14)	C(15)	1.5220(16)
N(2)	C(15)	1.4606(14)	C(16)	C(19)	1.4891(16)
N(2)	C(16)	1.3990(15)	C(17)	C(18)	1.4875(15)
N(2)	C(17)	1.3940(14)	C(18)	C(19)	1.3868(15)
C(1)	C(2)	1.3947(16)	C(18)	C(23)	1.3848(15)
C(1)	C(6)	1.3927(16)	C(19)	C(20)	1.3809(16)
C(2)	C(3)	1.3903(17)	C(20)	C(21)	1.397(2)
C(3)	C(4)	1.3894(19)	C(21)	C(22)	1.388(2)
C(4)	C(5)	1.3899(18)	C(22)	C(23)	1.3952(18)
C(5)	C(6)	1.3927(16)			

Table S-28. Bond Angles for p17415.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1)	N(1)	C(7)	119.16(9)	C(12)	C(11)	C(10)	112.08(10)
C(10)	N(1)	C(1)	121.65(10)	C(11)	C(12)	C(13)	114.28(9)
C(10)	N(1)	C(7)	119.02(10)	C(14)	C(13)	C(12)	110.96(9)
C(16)	N(2)	C(15)	123.13(10)	C(15)	C(14)	C(13)	112.84(10)
C(17)	N(2)	C(15)	124.92(9)	N(2)	C(15)	C(14)	111.75(9)
C(17)	N(2)	C(16)	111.90(9)	O(3)	C(16)	N(2)	125.01(11)
C(2)	C(1)	N(1)	119.49(10)	O(3)	C(16)	C(19)	129.15(11)
C(6)	C(1)	N(1)	120.17(10)	N(2)	C(16)	C(19)	105.83(9)
C(6)	C(1)	C(2)	120.31(10)	O(2)	C(17)	N(2)	125.40(10)
C(3)	C(2)	C(1)	119.50(11)	O(2)	C(17)	C(18)	128.67(10)
C(4)	C(3)	C(2)	120.29(11)	N(2)	C(17)	C(18)	105.93(9)
C(5)	C(4)	C(3)	120.12(11)	C(19)	C(18)	C(17)	108.26(9)
C(4)	C(5)	C(6)	119.96(12)	C(23)	C(18)	C(17)	130.13(10)
C(1)	C(6)	C(5)	119.76(11)	C(23)	C(18)	C(19)	121.61(11)
N(1)	C(7)	C(8)	110.84(10)	C(18)	C(19)	C(16)	108.04(10)
N(1)	C(7)	C(9)	111.51(11)	C(20)	C(19)	C(16)	129.79(11)
C(9)	C(7)	C(8)	112.01(12)	C(20)	C(19)	C(18)	122.17(11)
O(1)	C(10)	N(1)	123.52(12)	C(19)	C(20)	C(21)	116.57(11)
O(1)	C(10)	C(11)	118.44(11)	C(22)	C(21)	C(20)	121.35(11)
N(1)	C(10)	C(11)	118.03(10)	C(21)	C(22)	C(23)	121.69(11)
F(1)	C(11)	C(10)	106.03(9)	C(18)	C(23)	C(22)	116.61(11)
F(1)	C(11)	C(12)	107.72(9)				

Table S-29. Torsion Angles for p17415.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F(1)	C(11)	C(12)	C(13)	175.44(10)	C(10)	N(1)	C(1)	C(2)	78.68(14)
O(1)	C(10)	C(11)	F(1)	47.94(14)	C(10)	N(1)	C(1)	C(6)	-98.99(13)
O(1)	C(10)	C(11)	C(12)	-69.33(14)	C(10)	N(1)	C(7)	C(8)	-113.34(13)
O(2)	C(17)	C(18)	C(19)	179.88(11)	C(10)	N(1)	C(7)	C(9)	121.12(13)
O(2)	C(17)	C(18)	C(23)	1.2(2)	C(10)	C(11)	C(12)	C(13)	-68.29(13)
O(3)	C(16)	C(19)	C(18)	177.30(12)	C(11)	C(12)	C(13)	C(14)	-175.00(10)
O(3)	C(16)	C(19)	C(20)	-3.0(2)	C(12)	C(13)	C(14)	C(15)	175.02(10)
N(1)	C(1)	C(2)	C(3)	-174.89(10)	C(13)	C(14)	C(15)	N(2)	-65.91(13)
N(1)	C(1)	C(6)	C(5)	175.59(10)	C(15)	N(2)	C(16)	O(3)	0.20(18)
N(1)	C(10)	C(11)	F(1)	-133.17(10)	C(15)	N(2)	C(16)	C(19)	179.47(9)

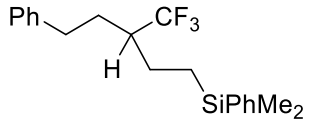
N(1)	C(10)	C(11)	C(12)	109.55(11)	C(15)	N(2)	C(17)	O(2)	1.37(17)
N(2)	C(16)	C(19)	C(18)	-1.93(12)	C(15)	N(2)	C(17)	C(18)	-178.70(10)
N(2)	C(16)	C(19)	C(20)	177.82(12)	C(16)	N(2)	C(15)	C(14)	-70.58(14)
N(2)	C(17)	C(18)	C(19)	-0.05(11)	C(16)	N(2)	C(17)	O(2)	178.82(11)
N(2)	C(17)	C(18)	C(23)	-178.76(11)	C(16)	N(2)	C(17)	C(18)	-1.25(12)
C(1)	N(1)	C(7)	C(8)	61.89(14)	C(16)	C(19)	C(20)	C(21)	-179.47(12)
C(1)	N(1)	C(7)	C(9)	-63.64(15)	C(17)	N(2)	C(15)	C(14)	106.61(12)
C(1)	N(1)	C(10)	O(1)	-176.38(11)	C(17)	N(2)	C(16)	O(3)	-177.31(11)
C(1)	N(1)	C(10)	C(11)	4.80(16)	C(17)	N(2)	C(16)	C(19)	1.96(12)
C(1)	C(2)	C(3)	C(4)	-1.50(18)	C(17)	C(18)	C(19)	C(16)	1.21(12)
C(2)	C(1)	C(6)	C(5)	-2.06(17)	C(17)	C(18)	C(19)	C(20)	-178.56(11)
C(2)	C(3)	C(4)	C(5)	-0.51(19)	C(17)	C(18)	C(23)	C(22)	177.79(11)
C(3)	C(4)	C(5)	C(6)	1.24(18)	C(18)	C(19)	C(20)	C(21)	0.25(17)
C(4)	C(5)	C(6)	C(1)	0.04(17)	C(19)	C(18)	C(23)	C(22)	-0.78(16)
C(6)	C(1)	C(2)	C(3)	2.79(17)	C(19)	C(20)	C(21)	C(22)	-0.27(18)
C(7)	N(1)	C(1)	C(2)	-96.43(13)	C(20)	C(21)	C(22)	C(23)	-0.26(19)
C(7)	N(1)	C(1)	C(6)	85.90(13)	C(21)	C(22)	C(23)	C(18)	0.77(17)
C(7)	N(1)	C(10)	O(1)	-1.27(18)	C(23)	C(18)	C(19)	C(16)	-179.94(10)
C(7)	N(1)	C(10)	C(11)	179.91(10)	C(23)	C(18)	C(19)	C(20)	0.29(17)

Table S-30. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for p17415.

Atom	*x*	*y*	*z*	U(eq)
H(2)	6549	4436	5016	25
H(3)	7720	4086	3179	30
H(4)	7959	2832	2542	31
H(5)	7039	1919	3761	28
H(6)	5846	2265	5554	24
H(7)	4778	3790	8776	29
H(8A)	6674	3991	8528	53
H(8B)	6069	4201	10154	53
H(8C)	5958	4652	8400	53
H(9A)	5050	2508	8644	61
H(9B)	5538	2861	10281	61
H(9C)	6111	2655	8612	61
H(11)	5086	3761	3196	25
H(12A)	3730	3339	1813	27
H(12B)	3235	3343	3630	27

H(13A)	4729	2389	2876	23
H(13B)	4156	2367	4613	23
H(14A)	2875	1963	3106	25
H(14B)	3393	2044	1320	25
H(15A)	3896	990	3902	26
H(15B)	3301	777	2262	26
H(20)	5609	781	-3199	30
H(21)	7170	546	-3298	34
H(22)	8009	468	-804	32
H(23)	7336	630	1905	25

For entries 33–35, the absolute configuration of the cross-coupling product is assigned on the basis of comparison with an independent literature report:



Dimethyl(phenyl)(5-phenyl-3-(trifluoromethyl)pentyl)silane. The title compound was prepared according to **GP-2** from (3-bromo-4,4,4-trifluorobutyl)benzene and dimethyl(phenyl)(vinyl)silane. Purification by flash column chromatography on silica gel: 20% CH_2Cl_2 in hexanes, colorless oil.

(*R*,*R*)-**L***: 136 mg, 48% yield, 72% ee; (*S*,*S*)-**L***: 128 mg, 46% yield, 72% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 8.2 min (major), 9.6 min (minor).

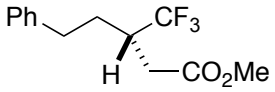
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 6.1, 2.9, 1.7 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.19 – 7.12 (m, 2H), 7.10 – 7.04 (m, 1H), 7.03 – 6.97 (m, 2H), 2.49 (t, *J* = 8.1 Hz, 2H), 1.89 (ddd, *J* = 9.5, 6.3, 5.1 Hz, 1H), 1.83 – 1.70 (m, 1H), 1.70 – 1.57 (m, 1H), 1.55 – 1.46 (m, 1H), 1.40 – 1.31 (m, 1H), 0.77 – 0.54 (m, 2H), 0.15 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 138.5, 133.5, 129.1, 128.6 (q, *J* = 279 Hz), 128.5, 128.4, 127.8, 126.1, 44.3 (q, *J* = 24 Hz), 32.9, 28.8 (q, *J* = 2 Hz), 21.8 (q, *J* = 2 Hz), 12.3, –3.3.

FT-IR (film) 3027, 2953, 1260, 1183, 1150, 1113, 838, 699 cm^{-1}.

HRMS (EI) m/z $[M-H]^+$ calcd for $C_{20}H_{24}F_3Si$: 349.1599, found: 349.1603.

$[\alpha]^{23}_D$ = +1.2 (*c* 1.0, $CHCl_3$); 72% ee, from (*R*,*R*)-**L***.



Methyl (*S*)-5-phenyl-3-(trifluoromethyl)pentanoate [1779534-14-3; 1779534-31-4]. The title compound was prepared from (*S*)-dimethyl(phenyl)(5-phenyl-3-(trifluoromethyl)pentyl)silane (from (*R*,*R*)-**L***; 70 mg, 0.20 mmol, 1.0 equiv) via two literature procedures[7,8]: 27 mg, 52% yield (over 2 steps).

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*R*)-**L***: 7.6 min (major), 13.6 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 7.17 – 7.12 (m, 1H), 7.12 – 7.09 (m, 2H), 3.63 (s, 3H), 2.74 – 2.54 (m, 4H), 2.37 (dd, *J* = 16.4, 7.5 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.78 – 1.58 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 140.8, 130.5 (q, *J* = 278 Hz), 128.6, 128.3, 126.3, 52.1, 39.4 (q, *J* = 26 Hz), 33.2 (q, *J* = 3 Hz), 32.9, 30.2 (q, *J* = 2 Hz).

HPLC analysis: With a CHIRALCEL OD-H column (1% *i*-PrOH in hexane, flow rate 1 mL/min), the title compound has the following retention times: 7.6 min (major) and 13.6 (minor). The absolute configuration was assigned by comparing with the reported retention times, under the same conditions, in a literature report: 6.7 min (minor) and 10.6 min (major)[9].

For entry 37, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

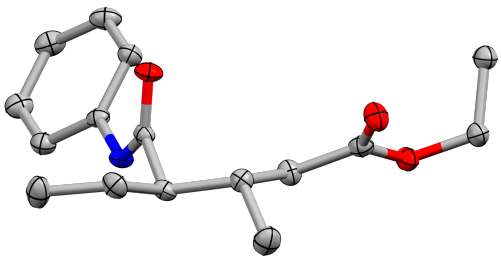
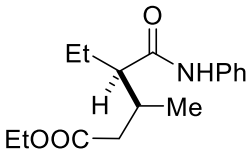


Figure S-6. Thermal ellipsoid plot at the 50% probability level. Hydrogen atoms are omitted for clarity.



Ethyl (*3S,4R*)-3-methyl-4-(phenylcarbamoyl)hexanoate. X-ray quality crystals were obtained by slow evaporation of a saturated solution in Et_2O/*n*-pentane of a sample (the *minor* diastereomer) synthesized with (*R,R*)-**L***. A crystal of $C_{16}H_{23}NO_3$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu−Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-31. Crystal Data and Structure Refinement for cu_v18380_0m.

Identification code	cu_v18380_0m
Empirical formula	$C_8H_{11.5}N_{0.5}O_{1.5}$
Formula weight	138.68
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.0392(2)
b/Å	13.4868(6)
c/Å	11.2913(5)
α/°	90.00
β/°	92.322(2)
γ/°	90.00
Volume/Å^3	766.76(6)

Z	4
ρ_{calc}g/cm^3	1.201
μ/mm^{-1}	0.662
F(000)	300.0
Crystal size/mm^3	0.28 × 0.21 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.84 to 161.28
Index ranges	-6 ≤ h ≤ 6, -17 ≤ k ≤ 15, -14 ≤ l ≤ 14
Reflections collected	18030
Independent reflections	3163 [R_{int} = 0.0526, R_{sigma} = 0.0298]
Data/restraints/parameters	3163/1/185
Goodness-of-fit on F^2	1.153
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1110
Largest diff. peak/hole / e Å^{-3}	0.22/-0.34
Flack parameter	0.0(2)

Table S-32. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_v18380_0m.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5223(2)	5681.8(10)	5307.3(12)	22.2(3)
O2	3711(3)	4388.5(11)	1531.6(13)	25.7(3)
O3	6765(3)	3189.4(10)	1801.8(13)	22.2(3)
N1	9642(3)	5470.5(11)	5724.5(13)	17.3(3)
C1	9527(3)	4972.3(13)	6829.1(16)	17.2(4)
C2	11501(4)	5180.2(14)	7687.0(18)	22.2(4)
C3	11504(4)	4700.8(16)	8784.0(19)	25.7(4)
C4	9561(4)	4008.8(16)	9008.2(19)	26.6(4)
C5	7623(4)	3794.0(16)	8143(2)	26.4(4)
C6	7578(4)	4273.8(14)	7048.8(17)	20.9(4)
C7	7555(3)	5796.4(13)	5042.3(16)	17.0(3)
C8	8257(4)	6328.1(13)	3907.7(17)	18.3(4)
C9	7336(4)	7409.3(14)	3991.7(19)	24.3(4)
C10	8488(5)	7952.7(16)	5075(2)	31.4(5)
C11	6960(3)	5789.0(14)	2822.8(16)	19.3(4)
C12	7912(5)	6215.8(16)	1659.7(19)	29.6(5)

C13	7498(4)	4672.7(14)	2866.0(17)	21.5(4)
C14	5758(4)	4097.8(14)	1990.2(17)	20.1(4)
C15	5231(4)	2550.2(15)	998.9(18)	23.0(4)
C16	2973(4)	2050.6(16)	1605.7(18)	25.2(4)

Table S-33. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_v18380_0m.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	13.6(6)	25.8(7)	27.3(7)	4.7(6)	1.4(5)	-0.6(5)
O2	24.2(7)	23.3(7)	29.0(7)	-1.6(5)	-6.5(6)	3.2(6)
O3	19.7(6)	18.9(6)	27.9(7)	-2.3(5)	1.5(5)	0.0(5)
N1	13.0(6)	18.1(7)	21.1(8)	2.8(6)	2.4(6)	-0.4(5)
C1	16.0(8)	16.1(8)	19.9(9)	1.4(6)	4.4(7)	2.4(7)
C2	18.8(9)	23.4(10)	24.6(10)	0.8(7)	1.5(7)	0.2(7)
C3	21.6(9)	30.2(11)	25(1)	2.9(8)	-0.6(7)	3.4(8)
C4	26.1(10)	28(1)	26(1)	7.9(8)	3.7(8)	6.1(8)
C5	21.8(9)	26.2(11)	31.5(11)	9.9(8)	4.9(8)	1.5(8)
C6	20.1(8)	20.2(9)	22.3(9)	1.5(7)	0.6(7)	-0.9(7)
C7	15.1(7)	14.0(8)	22.0(9)	-1.2(7)	0.8(6)	-0.4(6)
C8	14.5(7)	17.3(8)	23.0(9)	2.4(7)	-0.4(7)	-1.5(6)
C9	27.1(10)	16.4(9)	29.1(10)	3.4(7)	-0.4(8)	-0.8(7)
C10	47.9(13)	20.9(10)	25.5(10)	-1.1(8)	1.7(9)	-4.3(9)
C11	18.9(8)	18.4(9)	20.6(9)	1.4(7)	-0.4(7)	2.1(7)
C12	39.1(12)	25.5(10)	24.5(11)	2.9(8)	4.3(9)	-0.6(9)
C13	20.9(9)	20.7(9)	22.7(9)	1.0(7)	-3.3(7)	2.3(7)
C14	19.7(8)	18.2(9)	22.6(9)	3.2(7)	3.9(7)	1.1(7)
C15	23.9(9)	20.0(9)	25.4(10)	-2.7(7)	3.2(7)	-2.2(7)
C16	23.6(10)	22.7(9)	29.6(10)	-3.6(8)	4.3(8)	-1.4(8)

Table S-34. Bond Lengths for cu_v18380_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.234(2)	C4	C5	1.383(3)
O2	C14	1.201(2)	C5	C6	1.395(3)
O3	C14	1.346(2)	C7	C8	1.522(3)
O3	C15	1.451(2)	C8	C9	1.534(3)

N1	C1	1.420(2)	C8	C11	1.546(3)
N1	C7	1.352(2)	C9	C10	1.521(3)
C1	C2	1.389(3)	C11	C12	1.529(3)
C1	C6	1.391(3)	C11	C13	1.530(3)
C2	C3	1.397(3)	C13	C14	1.509(3)
C3	C4	1.383(3)	C15	C16	1.510(3)

Table S-35. Bond Angles for cu_v18380_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O3	C15	116.41(15)	C7	C8	C9	108.34(15)
C7	N1	C1	126.58(15)	C7	C8	C11	109.88(14)
C2	C1	N1	117.62(16)	C9	C8	C11	112.13(15)
C2	C1	C6	120.24(17)	C10	C9	C8	113.65(17)
C6	C1	N1	122.11(17)	C12	C11	C8	111.48(16)
C1	C2	C3	119.99(18)	C12	C11	C13	109.66(16)
C4	C3	C2	119.96(19)	C13	C11	C8	111.63(15)
C5	C4	C3	119.78(19)	C14	C13	C11	112.77(15)
C4	C5	C6	120.94(19)	O2	C14	O3	123.47(18)
C1	C6	C5	119.09(18)	O2	C14	C13	125.51(17)
O1	C7	N1	123.21(17)	O3	C14	C13	111.00(15)
O1	C7	C8	121.26(16)	O3	C15	C16	111.94(16)
N1	C7	C8	115.53(15)				

Table S-36. Torsion Angles for cu_v18380_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C7	C8	C9	64.3(2)	C7	N1	C1	C6	38.3(3)
O1	C7	C8	C11	-58.6(2)	C7	C8	C9	C10	56.3(2)
N1	C1	C2	C3	-179.14(17)	C7	C8	C11	C12	-172.43(16)
N1	C1	C6	C5	178.37(17)	C7	C8	C11	C13	-49.41(19)
N1	C7	C8	C9	-115.48(17)	C8	C11	C13	C14	166.54(15)
N1	C7	C8	C11	121.72(17)	C9	C8	C11	C12	67.0(2)
C1	N1	C7	O1	-1.0(3)	C9	C8	C11	C13	-169.95(15)
C1	N1	C7	C8	178.77(17)	C11	C8	C9	C10	177.76(17)
C1	C2	C3	C4	0.9(3)	C11	C13	C14	O2	-19.5(3)
C2	C1	C6	C5	0.6(3)	C11	C13	C14	O3	162.08(16)

C2	C3	C4	C5	0.0(3)	C12	C11	C13	C14	-69.4(2)
C3	C4	C5	C6	-0.7(3)	C14	O3	C15	C16	-81.2(2)
C4	C5	C6	C1	0.4(3)	C15	O3	C14	O2	-0.2(3)
C6	C1	C2	C3	-1.2(3)	C15	O3	C14	C13	178.33(15)
C7	N1	C1	C2	-143.84(19)					

Table S-37. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²× 10³) for cu_v18380_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	11233	5578	5457	21
H2	12850	5648	7528	27
H3	12838	4850	9375	31
H4	9558	3682	9754	32
H5	6304	3313	8298	32
H6	6234	4126	6461	25
H8	10229	6317	3840	22
H9A	7850	7767	3270	29
H9B	5374	7422	4011	29
H10A	10432	7922	5080	47
H10B	7861	7639	5795	47
H10C	7915	8647	5049	47
H11	4996	5891	2838	23
H12A	7484	6924	1617	44
H12B	7024	5870	991	44
H12C	9837	6127	1626	44
H13A	9383	4552	2698	26
H13B	7198	4426	3676	26
H15A	6413	2038	679	28
H15B	4505	2949	324	28
H16A	2162	1550	1076	38
H16B	1638	2547	1799	38
H16C	3655	1731	2336	38

For entry 38, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

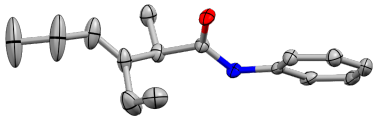
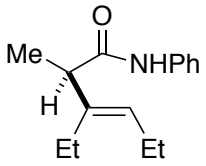


Figure S-7. Thermal ellipsoid plot at the 50% probability level. Only one of the four molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.



(*R,E*)-3-Ethyl-2-methyl-*N*-phenylhex-3-enamide. X-ray quality crystals were obtained by slow evaporation of a saturated solution in Et_2O/hexanes of a sample synthesized with (*R,R*)-**L***. A crystal of $C_{15}H_{21}NO$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu−Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-38. Crystal Data and Structure refinement for cu_P17241_0m.

Identification code	cu_P17241_0m
Empirical formula	$C_{15}H_{21}NO$
Formula weight	462.66
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	17.078(4)
b/Å	9.4728(17)
c/Å	18.746(4)
α/°	90.00
β/°	112.816(16)
γ/°	90.00
Volume/Å^3	2795.4(10)
Z	8
ρ_{calc}g/cm^3	1.099

μ/mm^{-1}	0.526
F(000)	1008.0
Crystal size/mm^3	0.27 × 0.25 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.12 to 158.68
Index ranges	-21 ≤ h ≤ 21, -11 ≤ k ≤ 9, -23 ≤ l ≤ 23
Reflections collected	71007
Independent reflections	11434 [R_{int} = 0.0529, R_{sigma} = 0.0308]
Data/restraints/parameters	11434/1/626
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0541, wR_2 = 0.1337
Largest diff. peak/hole / e $Å^{-3}$	0.76/-0.32
Flack parameter	0.0(2)

Table S-39. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å²×10^3) for cu_P17241_0m.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*Z*	U(eq)
O(1)	5048.7(9)	6500.1(15)	7341.1(10)	43.0(4)
N(1)	5530.7(9)	8743.8(15)	7556.4(8)	20.9(3)
C(1)	6416.1(10)	8471.8(19)	7889.8(9)	20.4(3)
C(2)	6751.9(11)	7215(2)	8275.4(10)	24.0(4)
C(3)	7626.1(12)	7004(2)	8571.9(11)	28.4(4)
C(4)	8167.5(12)	8035(2)	8499.6(11)	30.7(4)
C(5)	7832.8(12)	9291(2)	8127.7(10)	29.0(4)
C(6)	6958.4(12)	9514(2)	7820.9(10)	24.6(4)
C(7)	4907.7(11)	7763.5(19)	7299.7(10)	24.2(4)
C(8)	4002.3(11)	8352(2)	6984.5(10)	25.7(4)
C(9)	3693.0(14)	8335(3)	7650.0(12)	40.4(5)
C(10)	3450.2(11)	7537(2)	6264.1(10)	24.5(4)
C(11)	3411.4(13)	8165(2)	5511.2(11)	33.7(4)
C(12)	2666.1(15)	9178(3)	5166.2(14)	45.6(6)
C(13)	3028.5(12)	6373(2)	6291.0(11)	29.1(4)
C(14)	2476.3(13)	5489(2)	5605.1(12)	34.7(5)
C(15)	2271.8(13)	4055(2)	5846.2(13)	35.9(5)
O(3)	253.7(8)	6270.6(15)	2253.2(9)	37.5(4)

N(3)	599.3(9)	8557.7(15)	2567.4(8)	22.1(3)
C(31)	1495.3(10)	8390.9(19)	2870.3(9)	21.1(3)
C(32)	1886.2(11)	7165(2)	3268.4(10)	24.6(4)
C(33)	2763.2(12)	7054(2)	3548.8(11)	31.0(4)
C(34)	3258.4(12)	8149(3)	3458.2(12)	34.8(5)
C(35)	2869.5(13)	9364(2)	3074.0(11)	32.5(4)
C(36)	1988.5(12)	9489(2)	2777.7(10)	26.1(4)
C(37)	33.7(11)	7493.2(19)	2293.3(10)	24.4(4)
C(38)	-895.3(11)	7871(2)	2088(1)	25.5(4)
C(39)	-1085.1(14)	7462(3)	2802.5(11)	37.7(5)
C(40)	-1457.0(11)	7157(2)	1337.9(10)	23.4(4)
C(41)	-1484.8(11)	7896(2)	613.1(11)	27.7(4)
C(42)	-2230.5(13)	8928(2)	298.3(12)	35.7(5)
C(43)	-1900.1(11)	5999(2)	1318.8(10)	26.4(4)
C(44)	-2453.7(13)	5200(2)	601.8(11)	31.8(4)
C(45)	-2701.8(13)	3749(2)	798.9(12)	35.7(5)
O(2)	5002.8(9)	1510.1(14)	7018.9(7)	29.0(3)
N(2)	4671.9(9)	3800.3(16)	6664.3(9)	22.4(3)
C(16)	4446.2(10)	3640.5(19)	5854.3(10)	22.1(4)
C(17)	4647.0(11)	4745(2)	5460.0(11)	27.8(4)
C(18)	4438.9(12)	4638(3)	4667.3(12)	35.2(5)
C(19)	4024.6(13)	3456(3)	4264.3(12)	36.5(5)
C(20)	3815.2(13)	2368(2)	4659.2(11)	33.3(4)
C(21)	4025.5(11)	2454(2)	5449.9(11)	26.9(4)
C(22)	4952.7(11)	2752.9(19)	7196(1)	22.9(4)
C(23)	5232.5(12)	3222(2)	8038.8(10)	26.0(4)
C(24)	6207.2(13)	3182(2)	8409.6(11)	35.1(5)
C(25)	4782.3(12)	2345(2)	8443.1(11)	28.9(4)
C(26)	3817.4(14)	2494(3)	8091.5(13)	39.2(5)
C(27)	3516.7(16)	3879(3)	8313.7(17)	55.3(7)
C(28)	5198.3(14)	1561(2)	9065.8(11)	35.3(5)
C(29)	4830.6(19)	713(3)	9536.5(14)	48.4(6)
C(30)	4936.1(18)	1412(3)	10299.7(13)	52.4(7)
O(4)	108.2(9)	1309.5(14)	2033.1(7)	27.8(3)
N(4)	-222.1(9)	3585.7(15)	1655.2(8)	20.9(3)
C(46)	-497.4(10)	3407.4(19)	841.1(10)	20.6(3)
C(47)	-918.1(11)	2198(2)	462.7(10)	25.5(4)
C(48)	-1200.3(13)	2116(2)	-340.6(11)	32.5(4)
C(49)	-1058.4(13)	3205(2)	-763.7(11)	34.5(5)

C(50)	-637.6(12)	4412(2)	-383.1(12)	32.6(5)
C(51)	-356.9(11)	4520(2)	417.3(11)	25.8(4)
C(52)	69.0(11)	2562.0(19)	2193.2(10)	21.9(4)
C(53)	373.0(12)	3070(2)	3037.6(10)	26.7(4)
C(54)	1344.9(12)	3033(2)	3395.2(11)	34.1(5)
C(55)	-65.7(14)	2226(3)	3459.0(11)	37.9(5)
C(56)	-1023.5(16)	2507(4)	3167.2(15)	52.5(7)
C(57)	-1560.1(16)	1459(3)	2582.8(16)	53.2(6)
C(58)	346.0(18)	1340(3)	4031.9(12)	52.5(7)
C(59)	-28(3)	453(4)	4485.5(16)	93.3(16)
C(60)	306(3)	850(5)	5322.0(17)	110.8(19)

Table S-40. Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_P17241_0m.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	32.9(7)	13.2(7)	57.4(9)	-1.7(6)	-10.3(7)	-2.2(6)
N(1)	21.3(7)	12.6(7)	23.9(7)	0.2(5)	3.4(6)	1.0(5)
C(1)	21.3(8)	18.0(9)	17.4(8)	-3.5(6)	2.6(6)	-1.3(6)
C(2)	24.1(8)	19.4(9)	23.1(8)	0.4(7)	3.2(7)	0.3(7)
C(3)	24.8(9)	27.7(10)	27.2(9)	-2.0(7)	4.0(7)	5.0(7)
C(4)	21.4(8)	42.7(13)	24.7(9)	-6.9(8)	5.2(7)	-0.8(8)
C(5)	27.1(9)	36.3(12)	23.4(9)	-8.9(8)	9.5(7)	-10.0(8)
C(6)	30.1(9)	21.3(9)	19.7(8)	-4.3(6)	6.9(7)	-6.3(7)
C(7)	25.2(8)	16.2(9)	22.7(8)	0.2(6)	-0.2(7)	-3.2(7)
C(8)	24.5(8)	21.5(9)	28.2(9)	-2.6(7)	7.1(7)	-4.0(7)
C(9)	40.5(11)	46.7(14)	35.6(11)	-15.9(10)	16.7(9)	-14.1(10)
C(10)	20.5(8)	26.1(10)	23.9(8)	-2.2(7)	5.5(6)	0.2(7)
C(11)	32.8(10)	38.7(12)	28.1(10)	0.0(8)	10.2(8)	-7.4(8)
C(12)	46.1(13)	41.8(14)	37.0(12)	11.5(10)	3.1(10)	-4.3(10)
C(13)	29.9(9)	30.9(11)	23.1(9)	-2.1(7)	6.4(7)	-4.8(8)
C(14)	33.3(10)	38.6(13)	25.7(10)	-4.1(8)	4.2(8)	-12.5(9)
C(15)	34.5(10)	36.1(13)	36.8(11)	-9.2(9)	13.7(9)	-9.7(9)
O(3)	26.5(7)	14.7(7)	52.9(9)	-7.4(6)	-4.6(6)	0.7(5)
N(3)	23.5(7)	11.8(7)	24.4(7)	-1.6(5)	2.2(6)	0.3(5)
C(31)	22.2(8)	18.8(9)	17.1(7)	-4.1(6)	1.9(6)	-2.1(6)
C(32)	24.9(8)	21.9(10)	20.9(8)	-0.6(7)	2.1(7)	0.3(7)

C(33)	26.1(9)	32.7(11)	26.6(9)	-6.6(8)	1.9(7)	4.9(8)
C(34)	22.3(9)	48.5(14)	30.6(10)	-12.1(9)	7.1(7)	-4.0(8)
C(35)	32.2(10)	40.1(12)	27.5(9)	-10.5(8)	13.8(8)	-14.3(8)
C(36)	33.2(9)	22.3(10)	20.6(8)	-3.9(7)	8.1(7)	-5.3(7)
C(37)	23.3(8)	16.5(10)	24.0(8)	-2.9(6)	-1.1(6)	-1.0(7)
C(38)	24.5(8)	21.8(10)	24.4(9)	-1.4(7)	3.1(7)	-0.1(7)
C(39)	42.1(11)	41.3(13)	27.2(10)	-6.7(9)	10.8(8)	-3.4(9)
C(40)	18.6(8)	25(1)	23.3(8)	-1.9(7)	4.6(6)	1.6(6)
C(41)	24.8(8)	30.4(11)	25.4(9)	0.6(7)	6.9(7)	-2.9(7)
C(42)	37.2(10)	30.9(12)	33.1(11)	6.6(8)	7.2(8)	1.6(8)
C(43)	22.8(8)	30.3(11)	22.0(8)	1.3(7)	4.3(7)	-1.8(7)
C(44)	27.1(9)	36.9(12)	25.6(9)	-2.2(8)	3.7(7)	-10.0(8)
C(45)	33(1)	39.3(13)	33.9(10)	-5.9(9)	11.9(8)	-11.7(9)
O(2)	40.6(7)	14.5(7)	25.4(6)	0.9(5)	5.5(5)	1.2(5)
N(2)	26.3(7)	13.1(7)	26.2(8)	0.9(5)	8.2(6)	0.4(5)
C(16)	18.6(7)	21.1(10)	24.8(9)	5.6(7)	6.6(6)	5.6(6)
C(17)	21.0(8)	24.1(10)	35.2(10)	11.0(7)	7.4(7)	6.3(7)
C(18)	25.5(9)	43.7(13)	36.4(11)	22.0(9)	12.2(8)	11.9(8)
C(19)	34.7(10)	48.0(14)	24.8(9)	10.6(9)	9.2(8)	14.5(9)
C(20)	34.2(10)	32.9(12)	28.4(10)	-1.6(8)	7.2(8)	6.8(8)
C(21)	28.5(9)	23.6(10)	26.6(9)	2.5(7)	8.5(7)	2.7(7)
C(22)	24.9(8)	16.8(9)	23.7(8)	0.8(7)	5.8(7)	-2.0(6)
C(23)	32.3(9)	19.7(9)	24.3(9)	-1.9(7)	8.9(7)	-4.1(7)
C(24)	32.7(10)	41.2(13)	28.5(10)	-6.8(8)	8.8(8)	-13.6(9)
C(25)	34.6(10)	24.4(10)	25.3(9)	-4.0(7)	9.0(7)	-9.3(8)
C(26)	34.8(11)	45.6(14)	37.5(11)	-4.0(9)	14.3(9)	-7.6(9)
C(27)	38.2(12)	58.0(18)	64.3(17)	-1.3(13)	13.9(12)	6.4(11)
C(28)	45.5(12)	25.3(11)	29.6(10)	-1.3(8)	8.6(9)	-12.5(9)
C(29)	72.9(17)	36.2(14)	33.4(12)	1.4(9)	17.8(11)	-19.9(12)
C(30)	71.3(17)	48.1(16)	31.3(11)	1.8(10)	12.9(11)	-20.1(13)
O(4)	40.1(7)	14.4(7)	24.0(6)	0.7(5)	6.9(5)	3.2(5)
N(4)	26.0(7)	12.9(8)	21.4(7)	-0.6(5)	6.5(6)	-1.4(5)
C(46)	18.8(7)	19.3(9)	22.1(8)	3.0(6)	6.3(6)	4.9(6)
C(47)	29.6(9)	20.8(10)	23.7(9)	-1.3(7)	7.5(7)	-0.5(7)
C(48)	34.3(10)	32.8(12)	26.1(9)	-4.3(8)	7.0(8)	2.3(8)
C(49)	35.9(10)	44.8(13)	20.7(9)	5.7(8)	8.8(8)	10.6(9)
C(50)	28.9(9)	36.5(12)	34.2(10)	17.7(9)	14.0(8)	12.1(8)
C(51)	23.1(8)	20.6(10)	31.7(10)	6.9(7)	8.4(7)	4.0(7)
C(52)	26.0(8)	17.9(9)	19.8(8)	-0.7(6)	6.7(6)	-1.0(6)

C(53)	34.9(10)	21.4(10)	21.1(8)	-3.0(7)	8.1(7)	-4.5(7)
C(54)	32.3(10)	41.0(13)	25.0(9)	-6.1(8)	6.7(8)	-10.8(8)
C(55)	42.9(11)	48.7(14)	20.7(9)	-6.5(8)	10.6(8)	-17.5(10)
C(56)	42.6(13)	74(2)	47.9(14)	-16.0(13)	24.8(11)	-12.8(12)
C(57)	47.4(14)	49.5(16)	62.0(16)	0.5(12)	20.5(12)	3.6(12)
C(58)	66.7(16)	54.1(17)	26.9(11)	1.8(10)	7.5(10)	-30.5(13)
C(59)	141(3)	100(3)	28.0(13)	-3.2(14)	20.8(16)	-82(3)
C(60)	178(4)	123(4)	33.3(15)	-15.9(18)	43(2)	-93(3)

Table S-41. Bond Lengths for cu_P17241_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(7)	1.217(2)	O(2)	C(22)	1.235(2)
N(1)	C(1)	1.418(2)	N(2)	C(16)	1.422(2)
N(1)	C(7)	1.352(2)	N(2)	C(22)	1.355(2)
C(1)	C(2)	1.396(2)	C(16)	C(17)	1.398(3)
C(1)	C(6)	1.394(2)	C(16)	C(21)	1.390(3)
C(2)	C(3)	1.391(3)	C(17)	C(18)	1.391(3)
C(3)	C(4)	1.387(3)	C(18)	C(19)	1.382(3)
C(4)	C(5)	1.386(3)	C(19)	C(20)	1.394(3)
C(5)	C(6)	1.393(3)	C(20)	C(21)	1.386(3)
C(7)	C(8)	1.530(2)	C(22)	C(23)	1.528(2)
C(8)	C(9)	1.532(3)	C(23)	C(24)	1.536(3)
C(8)	C(10)	1.524(2)	C(23)	C(25)	1.519(3)
C(10)	C(11)	1.509(3)	C(25)	C(26)	1.526(3)
C(10)	C(13)	1.328(3)	C(25)	C(28)	1.333(3)
C(11)	C(12)	1.524(3)	C(26)	C(27)	1.525(4)
C(13)	C(14)	1.518(3)	C(28)	C(29)	1.499(3)
C(14)	C(15)	1.515(3)	C(29)	C(30)	1.522(3)
O(3)	C(37)	1.229(2)	O(4)	C(52)	1.232(2)
N(3)	C(31)	1.419(2)	N(4)	C(46)	1.422(2)
N(3)	C(37)	1.352(2)	N(4)	C(52)	1.347(2)
C(31)	C(32)	1.401(2)	C(46)	C(47)	1.391(3)
C(31)	C(36)	1.391(3)	C(46)	C(51)	1.396(2)
C(32)	C(33)	1.386(3)	C(47)	C(48)	1.394(3)
C(33)	C(34)	1.390(3)	C(48)	C(49)	1.379(3)
C(34)	C(35)	1.384(3)	C(49)	C(50)	1.391(3)
C(35)	C(36)	1.392(3)	C(50)	C(51)	1.391(3)
C(37)	C(38)	1.523(2)	C(52)	C(53)	1.539(2)

C(38)	C(39)	1.545(3)	C(53)	C(54)	1.531(3)
C(38)	C(40)	1.520(2)	C(53)	C(55)	1.511(3)
C(40)	C(41)	1.513(3)	C(55)	C(56)	1.534(3)
C(40)	C(43)	1.325(3)	C(55)	C(58)	1.329(4)
C(41)	C(42)	1.531(3)	C(56)	C(57)	1.499(4)
C(43)	C(44)	1.513(3)	C(58)	C(59)	1.503(4)
C(44)	C(45)	1.525(3)	C(59)	C(60)	1.494(4)

Table S-42. Bond Angles for cu_P17241_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(7)	N(1)	C(1)	126.12(15)	C(22)	N(2)	C(16)	125.40(16)
C(2)	C(1)	N(1)	122.48(16)	C(17)	C(16)	N(2)	117.66(17)
C(6)	C(1)	N(1)	117.63(16)	C(21)	C(16)	N(2)	122.48(16)
C(6)	C(1)	C(2)	119.89(16)	C(21)	C(16)	C(17)	119.84(17)
C(3)	C(2)	C(1)	119.41(17)	C(18)	C(17)	C(16)	119.78(19)
C(4)	C(3)	C(2)	120.88(18)	C(19)	C(18)	C(17)	120.51(19)
C(5)	C(4)	C(3)	119.54(17)	C(18)	C(19)	C(20)	119.40(19)
C(4)	C(5)	C(6)	120.35(18)	C(21)	C(20)	C(19)	120.8(2)
C(5)	C(6)	C(1)	119.91(18)	C(20)	C(21)	C(16)	119.70(18)
O(1)	C(7)	N(1)	122.92(17)	O(2)	C(22)	N(2)	122.80(16)
O(1)	C(7)	C(8)	121.88(17)	O(2)	C(22)	C(23)	121.90(16)
N(1)	C(7)	C(8)	115.15(16)	N(2)	C(22)	C(23)	115.27(16)
C(7)	C(8)	C(9)	107.31(16)	C(22)	C(23)	C(24)	108.08(15)
C(10)	C(8)	C(7)	110.04(15)	C(25)	C(23)	C(22)	109.91(15)
C(10)	C(8)	C(9)	115.23(16)	C(25)	C(23)	C(24)	115.47(16)
C(11)	C(10)	C(8)	114.63(17)	C(23)	C(25)	C(26)	113.86(17)
C(13)	C(10)	C(8)	123.05(17)	C(28)	C(25)	C(23)	122.74(18)
C(13)	C(10)	C(11)	122.32(17)	C(28)	C(25)	C(26)	123.35(19)
C(10)	C(11)	C(12)	111.83(18)	C(27)	C(26)	C(25)	112.55(19)
C(10)	C(13)	C(14)	126.41(18)	C(25)	C(28)	C(29)	127.7(2)
C(15)	C(14)	C(13)	112.42(17)	C(28)	C(29)	C(30)	113.3(2)
C(37)	N(3)	C(31)	124.70(15)	C(52)	N(4)	C(46)	126.18(15)
C(32)	C(31)	N(3)	121.49(16)	C(47)	C(46)	N(4)	122.37(16)
C(36)	C(31)	N(3)	118.54(16)	C(47)	C(46)	C(51)	120.02(16)
C(36)	C(31)	C(32)	119.96(16)	C(51)	C(46)	N(4)	117.58(16)
C(33)	C(32)	C(31)	119.13(18)	C(46)	C(47)	C(48)	119.39(18)
C(32)	C(33)	C(34)	121.08(19)	C(49)	C(48)	C(47)	121.00(19)
C(35)	C(34)	C(33)	119.52(18)	C(48)	C(49)	C(50)	119.41(18)

C(34)	C(35)	C(36)	120.30(19)	C(51)	C(50)	C(49)	120.48(18)
C(31)	C(36)	C(35)	119.99(18)	C(50)	C(51)	C(46)	119.68(18)
O(3)	C(37)	N(3)	122.39(16)	O(4)	C(52)	N(4)	123.36(16)
O(3)	C(37)	C(38)	121.29(16)	O(4)	C(52)	C(53)	121.54(16)
N(3)	C(37)	C(38)	116.18(16)	N(4)	C(52)	C(53)	115.09(16)
C(37)	C(38)	C(39)	105.68(15)	C(54)	C(53)	C(52)	108.62(15)
C(40)	C(38)	C(37)	110.55(15)	C(55)	C(53)	C(52)	109.52(15)
C(40)	C(38)	C(39)	114.91(16)	C(55)	C(53)	C(54)	115.61(16)
C(41)	C(40)	C(38)	114.45(16)	C(53)	C(55)	C(56)	113.5(2)
C(43)	C(40)	C(38)	122.86(17)	C(58)	C(55)	C(53)	122.8(2)
C(43)	C(40)	C(41)	122.68(17)	C(58)	C(55)	C(56)	123.7(2)
C(40)	C(41)	C(42)	111.92(16)	C(57)	C(56)	C(55)	114.3(2)
C(40)	C(43)	C(44)	126.30(18)	C(55)	C(58)	C(59)	127.0(3)
C(43)	C(44)	C(45)	111.86(17)	C(60)	C(59)	C(58)	112.3(2)

Table S-43. Torsion Angles for cu_P17241_0m.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O(1)	C(7)	C(8)	C(9)	83.1(2)	O(2)	C(22)	C(23)	C(24)	72.6(2)
O(1)	C(7)	C(8)	C(10)	-43.0(3)	O(2)	C(22)	C(23)	C(25)	-54.3(2)
N(1)	C(1)	C(2)	C(3)	178.42(16)	N(2)	C(16)	C(17)	C(18)	-179.99(16)
N(1)	C(1)	C(6)	C(5)	-179.01(15)	N(2)	C(16)	C(21)	C(20)	179.31(16)
N(1)	C(7)	C(8)	C(9)	-94.19(19)	N(2)	C(22)	C(23)	C(24)	-105.57(18)
N(1)	C(7)	C(8)	C(10)	139.74(17)	N(2)	C(22)	C(23)	C(25)	127.60(17)
C(1)	N(1)	C(7)	O(1)	1.2(3)	C(16)	N(2)	C(22)	O(2)	-3.6(3)
C(1)	N(1)	C(7)	C(8)	178.47(15)	C(16)	N(2)	C(22)	C(23)	174.49(15)
C(1)	C(2)	C(3)	C(4)	1.0(3)	C(16)	C(17)	C(18)	C(19)	0.9(3)
C(2)	C(1)	C(6)	C(5)	0.9(3)	C(17)	C(16)	C(21)	C(20)	0.6(3)
C(2)	C(3)	C(4)	C(5)	0.1(3)	C(17)	C(18)	C(19)	C(20)	0.1(3)
C(3)	C(4)	C(5)	C(6)	-0.7(3)	C(18)	C(19)	C(20)	C(21)	-0.7(3)
C(4)	C(5)	C(6)	C(1)	0.2(3)	C(19)	C(20)	C(21)	C(16)	0.3(3)
C(6)	C(1)	C(2)	C(3)	-1.5(3)	C(21)	C(16)	C(17)	C(18)	-1.2(3)
C(7)	N(1)	C(1)	C(2)	-26.6(3)	C(22)	N(2)	C(16)	C(17)	-143.21(17)
C(7)	N(1)	C(1)	C(6)	153.34(17)	C(22)	N(2)	C(16)	C(21)	38.1(2)
C(7)	C(8)	C(10)	C(11)	-92.2(2)	C(22)	C(23)	C(25)	C(26)	-61.5(2)
C(7)	C(8)	C(10)	C(13)	88.4(2)	C(22)	C(23)	C(25)	C(28)	120.9(2)
C(8)	C(10)	C(11)	C(12)	-92.0(2)	C(23)	C(25)	C(26)	C(27)	-76.3(2)
C(8)	C(10)	C(13)	C(14)	-179.14(19)	C(23)	C(25)	C(28)	C(29)	176.7(2)
C(9)	C(8)	C(10)	C(11)	146.31(19)	C(24)	C(23)	C(25)	C(26)	175.90(17)

C(9)	C(8)	C(10)	C(13)	-33.1(3)	C(24)	C(23)	C(25)	C(28)	-1.7(3)
C(10)	C(13)	C(14)	C(15)	165.5(2)	C(25)	C(28)	C(29)	C(30)	-103.3(3)
C(11)	C(10)	C(13)	C(14)	1.5(3)	C(26)	C(25)	C(28)	C(29)	-0.7(4)
C(13)	C(10)	C(11)	C(12)	87.4(2)	C(28)	C(25)	C(26)	C(27)	101.3(3)
O(3)	C(37)	C(38)	C(39)	79.4(2)	O(4)	C(52)	C(53)	C(54)	73.1(2)
O(3)	C(37)	C(38)	C(40)	-45.6(2)	O(4)	C(52)	C(53)	C(55)	-54.0(2)
N(3)	C(31)	C(32)	C(33)	179.66(16)	N(4)	C(46)	C(47)	C(48)	177.48(16)
N(3)	C(31)	C(36)	C(35)	179.43(16)	N(4)	C(46)	C(51)	C(50)	-178.09(16)
N(3)	C(37)	C(38)	C(39)	-96.48(19)	N(4)	C(52)	C(53)	C(54)	-105.64(18)
N(3)	C(37)	C(38)	C(40)	138.60(17)	N(4)	C(52)	C(53)	C(55)	127.25(18)
C(31)	N(3)	C(37)	O(3)	-3.1(3)	C(46)	N(4)	C(52)	O(4)	-2.1(3)
C(31)	N(3)	C(37)	C(38)	172.65(15)	C(46)	N(4)	C(52)	C(53)	176.59(15)
C(31)	C(32)	C(33)	C(34)	1.7(3)	C(46)	C(47)	C(48)	C(49)	0.9(3)
C(32)	C(31)	C(36)	C(35)	0.6(3)	C(47)	C(46)	C(51)	C(50)	-0.1(3)
C(32)	C(33)	C(34)	C(35)	-0.8(3)	C(47)	C(48)	C(49)	C(50)	-0.9(3)
C(33)	C(34)	C(35)	C(36)	-0.2(3)	C(48)	C(49)	C(50)	C(51)	0.4(3)
C(34)	C(35)	C(36)	C(31)	0.3(3)	C(49)	C(50)	C(51)	C(46)	0.1(3)
C(36)	C(31)	C(32)	C(33)	-1.6(3)	C(51)	C(46)	C(47)	C(48)	-0.4(3)
C(37)	N(3)	C(31)	C(32)	-32.7(3)	C(52)	N(4)	C(46)	C(47)	34.9(3)
C(37)	N(3)	C(31)	C(36)	148.52(18)	C(52)	N(4)	C(46)	C(51)	-147.19(17)
C(37)	C(38)	C(40)	C(41)	-80.36(19)	C(52)	C(53)	C(55)	C(56)	-67.3(2)
C(37)	C(38)	C(40)	C(43)	101.0(2)	C(52)	C(53)	C(55)	C(58)	113.4(2)
C(38)	C(40)	C(41)	C(42)	-93.40(19)	C(53)	C(55)	C(56)	C(57)	96.3(3)
C(38)	C(40)	C(43)	C(44)	-178.20(18)	C(53)	C(55)	C(58)	C(59)	-179.9(3)
C(39)	C(38)	C(40)	C(41)	160.16(17)	C(54)	C(53)	C(55)	C(56)	169.61(18)
C(39)	C(38)	C(40)	C(43)	-18.5(3)	C(54)	C(53)	C(55)	C(58)	-9.7(3)
C(40)	C(43)	C(44)	C(45)	166.81(19)	C(55)	C(58)	C(59)	C(60)	-116.4(4)
C(41)	C(40)	C(43)	C(44)	3.2(3)	C(56)	C(55)	C(58)	C(59)	0.9(4)
C(43)	C(40)	C(41)	C(42)	85.3(2)	C(58)	C(55)	C(56)	C(57)	-84.4(3)

Table S-44. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for cu_P17241_0m.

Atom	*x*	*y*	*z*	U(eq)
H(1)	5375	9614	7513	25
H(2A)	6394	6524	8334	29
H(3A)	7851	6162	8822	34
H(4A)	8751	7884	8699	37
H(5)	8194	9989	8083	35
H(6)	6737	10358	7570	29

H(8)	4026	9337	6835	31
H(9A)	3691	7382	7823	61
H(9B)	3128	8715	7474	61
H(9C)	4066	8898	8070	61
H(11A)	3358	7411	5145	40
H(11B)	3937	8665	5600	40
H(12A)	2692	9623	4716	68
H(12B)	2694	9886	5542	68
H(12C)	2143	8665	5024	68
H(13)	3076	6070	6778	35
H(14B)	1950	5991	5327	42
H(14A)	2767	5363	5256	42
H(15A)	1895	3557	5398	54
H(15B)	2004	4174	6207	54
H(15C)	2787	3525	6086	54
H(3)	402	9396	2558	26
H(32)	1561	6437	3344	30
H(33)	3025	6233	3802	37
H(34)	3847	8066	3655	42
H(35)	3198	10101	3013	39
H(36)	1730	10306	2518	31
H(38)	-959	8896	2017	31
H(39A)	-1674	7632	2696	57
H(39B)	-739	8020	3238	57
H(39C)	-960	6480	2917	57
H(41A)	-1534	7196	220	33
H(41B)	-957	8406	727	33
H(42A)	-2223	9383	-156	54
H(42B)	-2182	9625	685	54
H(42C)	-2755	8422	169	54
H(43)	-1867	5643	1792	32
H(44A)	-2151	5087	262	38
H(44B)	-2964	5743	327	38
H(45A)	-3062	3283	332	54
H(45B)	-3001	3856	1136	54
H(45C)	-2199	3195	1052	54
H(2)	4626	4630	6830	27
H(17)	4919	5549	5727	33
H(18)	4580	5367	4407	42

H(19)	3887	3387	3734	44
H(20)	3531	1576	4389	40
H(21)	3886	1720	5709	32
H(23)	5055	4206	8039	31
H(24A)	6398	2225	8425	53
H(24B)	6399	3551	8926	53
H(24C)	6434	3746	8109	53
H(26A)	3620	2441	7532	47
H(26B)	3567	1713	8264	47
H(27A)	2907	3914	8091	83
H(27B)	3741	4657	8124	83
H(27C)	3713	3940	8867	83
H(28)	5786	1536	9228	42
H(29A)	5103	-205	9643	58
H(29B)	4230	564	9235	58
H(30A)	4579	2231	10200	79
H(30B)	5518	1687	10569	79
H(30C)	4778	758	10612	79
H(4)	-243	4426	1820	25
H(47)	-1010	1452	743	31
H(48)	-1489	1314	-595	39
H(49)	-1242	3134	-1299	41
H(50)	-543	5152	-666	39
H(51)	-77	5330	669	31
H(53)	197	4057	3029	32
H(54A)	1536	2079	3401	51
H(54B)	1544	3389	3915	51
H(54C)	1564	3609	3094	51
H(56A)	-1190	2503	3606	63
H(56B)	-1138	3442	2939	63
H(57A)	-1402	1455	2144	80
H(57B)	-2148	1714	2419	80
H(57C)	-1474	535	2811	80
H(58)	929	1261	4167	63
H(59A)	-641	561	4267	112
H(59B)	100	-532	4439	112
H(60A)	901	1059	5497	166
H(60B)	223	79	5618	166
H(60C)	8	1666	5389	166

For entries 39 and 40, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

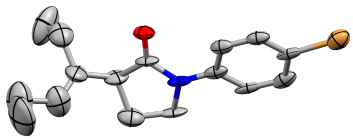
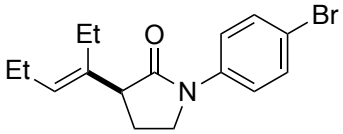


Figure S-8. Thermal ellipsoid plot at the 50% probability level. Only one of the two molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.



(*S,E*)-1-(4-Bromophenyl)-3-(hex-3-en-3-yl)pyrrolidin-2-one. X-ray quality crystals were obtained by slow evaporation of a saturated solution in *n*-pentane of a sample synthesized with (*R,R*)-**L***. A crystal of $C_{16}H_{20}BrNO$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu–Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-45. Crystal data and structure refinement for cu_v18037_0m.

Identification code	cu_v18037_0m
Empirical formula	$C_{16}H_{20}NOBr$
Formula weight	322.24
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.3158(4)
b/Å	10.5058(4)
c/Å	34.6465(16)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	3026.9(2)
Z	8
ρ_{calc}g/cm^3	1.414

μ/mm^{-1}	3.628
F(000)	1328.0
Crystal size/mm^3	0.281 × 0.233 × 0.042
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	5.1 to 164.28
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -44 ≤ l ≤ 43
Reflections collected	38919
Independent reflections	6440 [R_{int} = 0.0630, R_{sigma} = 0.0355]
Data/restraints/parameters	6440/0/358
Goodness-of-fit on F^2	1.190
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1579
Final R indexes [all data]	R_1 = 0.0740, wR_2 = 0.1592
Largest diff. peak/hole / e Å	1.01/-0.81
Flack parameter	0.21(4)

Table S-46. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_v18037_0m.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	115.3(10)	7478.2(8)	1361.0(2)	52.9(2)
O1	2607(5)	6069(4)	3236.8(14)	41.4(11)
N1	1213(6)	7908(5)	3098.0(16)	35.4(11)
C17	1024(7)	7785(5)	2693.0(18)	31.2(13)
C18	73(8)	8685(5)	2497(2)	36.1(13)
C19	-199(7)	8606(5)	2105(2)	35.8(14)
C20	533(7)	7633(6)	1899.6(19)	34.3(13)
C21	1548(7)	6773(6)	2081(2)	35.9(14)
C22	1798(7)	6840(5)	2473.2(19)	33.2(13)
C23	590(8)	9002(5)	3311(2)	37.7(15)
C24	940(9)	8733(8)	3729(2)	48.5(18)
C25	2270(8)	7712(6)	3724.5(18)	42.5(16)
C26	2078(8)	7099(6)	3332.5(18)	36.5(14)
C27	2272(10)	6800(8)	4060(2)	51.9(19)
C28	920(11)	5859(8)	4086(3)	64(2)
C29	-294(17)	6154(14)	4409(3)	115(5)
C30	3485(14)	6874(11)	4316(3)	94(4)
C31	3780(20)	6047(16)	4645(4)	133(7)

C5BA	5320(30)	5950(30)	4765(8)	109(11)
C32	4470(50)	6560(40)	4946(8)	98(14)
Br2	3034.1(10)	2058.3(8)	1428.0(3)	59.2(2)
O2	3932(6)	615(4)	3365.7(15)	47.0(12)
N2	4439(6)	2630(5)	3143.2(18)	40.0(13)
C2	4585(7)	3393(6)	2483(3)	42.7(18)
C3	4295(8)	3302(7)	2093(3)	50(2)
C4	3409(7)	2267(6)	1961(2)	42.8(17)
C5	2835(8)	1377(6)	2220(2)	42.0(16)
C6	3126(8)	1484(6)	2608(2)	41.0(15)
C1	4077(7)	2504(6)	2751(2)	39.9(14)
C7	5206(10)	3809(6)	3297(3)	54(2)
C8	5010(12)	3628(7)	3726(3)	65(2)
C9	5161(11)	2203(6)	3781(2)	53.2(19)
C10	4433(8)	1704(5)	3416(2)	41.8(17)
C11	4465(14)	1625(8)	4150(3)	70(3)
C12	4954(14)	310(9)	4224(3)	80(3)
C13	6651(16)	249(15)	4397(4)	127(6)
C14	3404(13)	2216(15)	4370(3)	95(4)
C15	2584(18)	1733(18)	4729(4)	126(6)
C16	860(20)	1900(20)	4699(4)	165(8)

Table S-47. Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_v18037_0m.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	56.1(4)	50.7(4)	52.0(4)	8.0(4)	-5.1(4)	-0.5(4)
O1	39(3)	25(2)	60(3)	-1(2)	-6(2)	3.2(19)
N1	33(3)	19(2)	53(3)	2(2)	4(2)	-4(2)
C17	20(2)	18(3)	55(3)	3(2)	1(2)	-9(2)
C18	27(3)	25(3)	56(4)	1(3)	6(3)	-7(3)
C19	20(3)	17(3)	70(4)	9(3)	-1(3)	-3(2)
C20	30(3)	16(3)	57(3)	6(3)	-1(2)	-11(2)
C21	24(3)	25(3)	58(4)	8(3)	4(3)	2(2)
C22	24(3)	13(3)	62(4)	5(2)	4(3)	-6(2)
C23	33(3)	12(3)	67(4)	-4(3)	12(3)	-2(2)
C24	38(4)	52(4)	56(4)	-8(4)	9(3)	1(3)

C25	39(3)	38(4)	50(3)	-2(3)	1(3)	-18(3)
C26	29(3)	31(3)	50(3)	2(3)	-5(3)	-15(3)
C27	57(5)	51(5)	48(4)	0(3)	-6(3)	-10(4)
C28	66(6)	51(5)	75(6)	22(4)	-9(5)	-8(4)
C29	105(10)	144(12)	95(8)	38(8)	10(8)	-50(10)
C30	105(9)	83(7)	93(7)	35(6)	-41(6)	-56(7)
C31	160(15)	146(13)	93(9)	52(9)	-82(10)	-53(11)
C5BA	120(20)	120(20)	78(16)	24(14)	4(14)	59(17)
C32	130(30)	110(30)	54(15)	15(16)	10(16)	-20(20)
Br2	48.0(4)	55.8(5)	73.7(5)	11.0(4)	0.6(4)	8.0(4)
O2	54(3)	25(2)	63(3)	-5(2)	8(2)	0(2)
N2	30(3)	14(2)	77(4)	-3(3)	5(2)	0(2)
C2	16(3)	15(3)	97(6)	2(3)	1(3)	3(2)
C3	30(3)	40(4)	82(6)	19(4)	15(4)	9(3)
C4	23(3)	16(3)	89(5)	7(3)	11(3)	4(2)
C5	25(3)	26(3)	75(5)	-1(3)	6(3)	1(3)
C6	26(3)	29(3)	68(5)	0(3)	11(3)	1(3)
C1	19(2)	26(3)	75(4)	2(3)	7(3)	3(3)
C7	46(4)	11(3)	103(6)	-8(3)	-3(4)	-2(3)
C8	59(5)	48(4)	89(6)	-19(4)	-6(5)	-9(4)
C9	60(5)	23(3)	77(5)	-7(3)	-9(4)	-12(3)
C10	37(3)	13(3)	75(5)	-6(3)	5(3)	-3(2)
C11	110(8)	40(4)	58(5)	-21(4)	-10(5)	-5(5)
C12	91(8)	69(6)	80(6)	-9(5)	0(6)	-27(6)
C13	113(11)	152(13)	117(10)	59(10)	-67(9)	-44(10)
C14	71(7)	134(12)	82(7)	-1(8)	-6(5)	4(8)
C15	101(11)	182(17)	95(9)	17(10)	10(8)	-16(11)
C16	147(15)	250(20)	94(9)	3(13)	60(10)	32(16)

Table S-48. Bond Lengths for cu_v18037_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C20	1.905(6)	Br2	C4	1.887(8)
O1	C26	1.214(8)	O2	C10	1.230(7)
N1	C17	1.418(8)	N2	C1	1.399(9)
N1	C23	1.459(8)	N2	C7	1.491(8)
N1	C26	1.379(8)	N2	C10	1.357(9)
C17	C18	1.407(9)	C2	C3	1.376(11)
C17	C22	1.407(8)	C2	C1	1.384(9)

C18	C19	1.378(10)	C3	C4	1.390(10)
C19	C20	1.387(9)	C4	C5	1.380(9)
C20	C21	1.388(8)	C5	C6	1.372(10)
C21	C22	1.375(9)	C6	C1	1.421(9)
C23	C24	1.505(10)	C7	C8	1.510(12)
C24	C25	1.541(10)	C8	C9	1.514(10)
C25	C26	1.512(9)	C9	C10	1.495(10)
C25	C27	1.507(10)	C9	C11	1.530(12)
C27	C28	1.499(11)	C11	C12	1.462(13)
C27	C30	1.344(12)	C11	C14	1.321(14)
C28	C29	1.539(15)	C12	C13	1.535(16)
C30	C31	1.455(15)	C14	C15	1.508(16)
C31	C5BA	1.35(3)	C15	C16	1.45(2)
C31	C32	1.31(3)			

Table S-49. Bond Angles for cu_v18037_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	N1	C23	122.1(5)	C32	C31	C5BA	50.8(17)
C26	N1	C17	125.8(5)	C1	N2	C7	121.2(6)
C26	N1	C23	111.9(5)	C10	N2	C1	127.5(6)
C18	C17	N1	118.6(5)	C10	N2	C7	110.4(6)
C18	C17	C22	118.0(6)	C3	C2	C1	124.0(6)
C22	C17	N1	123.3(5)	C2	C3	C4	117.9(7)
C19	C18	C17	121.8(6)	C3	C4	Br2	119.9(5)
C18	C19	C20	118.6(6)	C5	C4	Br2	120.0(5)
C19	C20	Br1	119.1(5)	C5	C4	C3	120.1(8)
C19	C20	C21	120.9(6)	C6	C5	C4	121.4(7)
C21	C20	Br1	120.0(5)	C5	C6	C1	120.0(6)
C22	C21	C20	120.4(6)	N2	C1	C6	122.0(6)
C21	C22	C17	120.1(6)	C2	C1	N2	121.5(6)
N1	C23	C24	105.6(5)	C2	C1	C6	116.5(7)
C23	C24	C25	105.1(5)	N2	C7	C8	101.6(6)
C26	C25	C24	103.3(5)	C7	C8	C9	103.8(6)
C27	C25	C24	115.8(6)	C8	C9	C11	117.7(7)
C27	C25	C26	115.0(6)	C10	C9	C8	102.0(6)
O1	C26	N1	125.3(6)	C10	C9	C11	114.4(6)
O1	C26	C25	125.9(6)	O2	C10	N2	124.7(7)
N1	C26	C25	108.8(6)	O2	C10	C9	125.7(7)

C28	C27	C25	117.6(7)	N2	C10	C9	109.6(5)
C30	C27	C25	118.2(7)	C12	C11	C9	114.6(8)
C30	C27	C28	124.2(8)	C14	C11	C9	123.2(10)
C27	C28	C29	113.7(9)	C14	C11	C12	122.0(11)
C27	C30	C31	127.4(10)	C11	C12	C13	111.3(10)
C5BA	C31	C30	116.5(17)	C11	C14	C15	128.3(14)
C32	C31	C30	117.0(19)	C16	C15	C14	110.3(13)

Table S-50. Torsion Angles for cu_v18037_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C20	C21	C22	-177.0(4)	Br2	C4	C5	C6	178.1(5)
N1	C17	C18	C19	-178.3(5)	N2	C7	C8	C9	33.9(9)
N1	C17	C22	C21	179.5(5)	C2	C3	C4	Br2	-177.9(5)
N1	C23	C24	C25	19.3(7)	C2	C3	C4	C5	0.6(9)
C17	N1	C23	C24	176.5(5)	C3	C2	C1	N2	178.4(6)
C17	N1	C26	O1	-11.4(10)	C3	C2	C1	C6	-3.7(9)
C17	N1	C26	C25	168.1(5)	C3	C4	C5	C6	-0.3(9)
C17	C18	C19	C20	-2.1(9)	C4	C5	C6	C1	-2.0(10)
C18	C17	C22	C21	-3.5(8)	C5	C6	C1	N2	-178.3(6)
C18	C19	C20	Br1	178.0(4)	C5	C6	C1	C2	3.8(9)
C18	C19	C20	C21	-1.5(8)	C1	N2	C7	C8	167.8(6)
C19	C20	C21	C22	2.6(8)	C1	N2	C10	O2	-8.2(11)
C20	C21	C22	C17	0.0(8)	C1	N2	C10	C9	170.4(6)
C22	C17	C18	C19	4.5(8)	C1	C2	C3	C4	1.5(9)
C23	N1	C17	C18	-6.2(8)	C7	N2	C1	C2	7.8(9)
C23	N1	C17	C22	170.8(5)	C7	N2	C1	C6	-169.9(6)
C23	N1	C26	O1	173.3(6)	C7	N2	C10	O2	-177.1(7)
C23	N1	C26	C25	-7.2(7)	C7	N2	C10	C9	1.5(8)
C23	C24	C25	C26	-22.9(7)	C7	C8	C9	C10	-33.3(9)
C23	C24	C25	C27	-149.6(6)	C7	C8	C9	C11	-159.4(8)
C24	C25	C26	O1	-161.7(6)	C8	C9	C10	O2	-161.3(7)
C24	C25	C26	N1	18.8(7)	C8	C9	C10	N2	20.1(9)
C24	C25	C27	C28	69.3(9)	C8	C9	C11	C12	-167.3(9)
C24	C25	C27	C30	-111.2(10)	C8	C9	C11	C14	18.0(14)
C25	C27	C28	C29	-107.7(10)	C9	C11	C12	C13	79.4(11)
C25	C27	C30	C31	-176.1(14)	C9	C11	C14	C15	177.4(11)
C26	N1	C17	C18	178.9(5)	C10	N2	C1	C2	-159.9(6)
C26	N1	C17	C22	-4.1(9)	C10	N2	C1	C6	22.3(9)

C26	N1	C23	C24	-7.9(7)	C10	N2	C7	C8	-22.5(8)
C26	C25	C27	C28	-51.2(10)	C10	C9	C11	C12	72.9(11)
C26	C25	C27	C30	128.4(9)	C10	C9	C11	C14	-101.7(10)
C27	C25	C26	O1	-34.5(9)	C11	C9	C10	O2	-33.1(11)
C27	C25	C26	N1	146.0(6)	C11	C9	C10	N2	148.4(7)
C27	C30	C31	C5BA	154(2)	C11	C14	C15	C16	-128.6(17)
C27	C30	C31	C32	-149(3)	C12	C11	C14	C15	3.1(19)
C28	C27	C30	C31	3(2)	C14	C11	C12	C13	-105.8(13)
C30	C27	C28	C29	72.8(13)					

Table S-51. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for cu_v18037_0m.

Atom	*x*	*y*	*z*	U(eq)
H18	-385	9351	2635	43
H19	-858	9193	1982	43
H21	2062	6147	1937	43
H22	2481	6261	2593	40
H23A	-558	9093	3269	45
H23B	1121	9778	3228	45
H24A	-13	8419	3859	58
H24B	1307	9497	3859	58
H25	3306	8157	3726	51
H28A	1367	5018	4129	77
H28B	356	5843	3841	77
H29A	-975	6845	4330	172
H29B	275	6387	4639	172
H29C	-939	5414	4458	172
H30	4222	7528	4277	112
H31	2945	5611	4767	159
H31A	3482	5194	4642	159
H5BA	5909	5430	4587	163
H5BB	5341	5560	5016	163
H5BC	5790	6779	4778	163
H32A	5029	7317	4870	147
H32B	5221	5965	5055	147
H32C	3669	6769	5136	147
H2	5156	4096	2571	51
H3	4681	3913	1922	61

H5	2238	691	2129	50
H6	2700	887	2779	49
H7A	4654	4567	3208	64
H7B	6332	3859	3224	64
H8A	3968	3929	3812	78
H8B	5844	4076	3867	78
H9	6310	1995	3775	64
H12A	4931	-166	3984	96
H12B	4197	-83	4400	96
H13A	6641	-286	4622	191
H13B	6992	1090	4468	191
H13C	7382	-95	4210	191
H14	3128	3036	4293	114
H15A	2832	838	4765	151
H15B	2980	2195	4952	151
H16A	502	1580	4453	248
H16B	602	2784	4720	248
H16C	340	1434	4902	248

Table S-52. Atomic Occupancy for cu_v18037_0m.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H31	0.58(4)	H31A	0.42(4)	C5BA	0.58(4)
H5BA	0.58(4)	H5BB	0.58(4)	H5BC	0.58(4)
C32	0.42(4)	H32A	0.42(4)	H32B	0.42(4)
H32C	0.42(4)				

For entries 41–58, the absolute configuration of the cross-coupling product is assigned on the basis of an X-ray crystal structure:

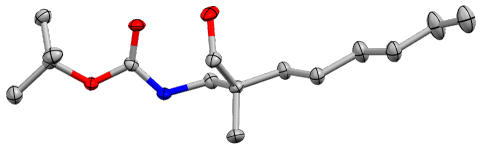
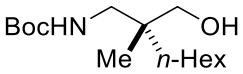


Figure S-9. Thermal ellipsoid plot at the 50% probability level. Only one of the three molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.



tert*-Butyl (*R*)-(2-(hydroxymethyl)-2-methyloctyl)carbamate.** X-ray quality crystals were obtained by slow evaporation of a saturated solution in CH_2Cl_2/hexanes of a sample synthesized with (*R,R*)-**L. A crystal of $C_{15}H_{31}NO_3$ was selected and mounted in a nylon loop in Paratone oil. All measurements were made on a Bruker APEX-II CCD diffractometer with filtered Cu–Kα radiation at a temperature of 100 K. Using Olex 2[2], the structure was solved with the XT structure solution program[3] using Direct Methods and refined with the ShelXL refinement package[4] using Least Square minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S-53. Crystal Data and Structure Refinement for cu_p17578_0m_a.

Identification code	cu_p17578_0m_a
Empirical formula	$C_{45}H_{88}N_3O_9$
Formula weight	815.18
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	15.4919(8)
b/Å	9.0297(6)
c/Å	18.2616(13)
α/°	90.00
β/°	98.637(7)
γ/°	90.00
Volume/Å^3	2525.6(3)
Z	2
ρ_{calc}g/cm^3	1.072
μ/mm^{-1}	0.583
F(000)	902.0

Crystal size/mm^3	0.24 × 0.18 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.9 to 159.58
Index ranges	-19 ≤ h ≤ 19, -11 ≤ k ≤ 9, -22 ≤ l ≤ 23
Reflections collected	67414
Independent reflections	10338 [R_{int} = 0.0570, R_{sigma} = 0.0320]
Data/restraints/parameters	10338/1/533
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0600, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.0695, wR_2 = 0.1782
Largest diff. peak/hole / e Å^{-3}	0.62/-0.40
Flack parameter	0.00(19)

Table S-54. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_p17578_0m_a.

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(1)	2081.6(10)	5261(2)	10667.6(8)	33.1(5)
O(2)	796.7(10)	6179.7(18)	9608.4(8)	24.7(3)
O(3)	235.3(9)	5410.8(17)	8445.6(7)	19.9(3)
N(1)	1667.3(11)	5551(2)	8755.5(9)	21.1(4)
C(1)	6910.6(18)	4365(3)	12759.8(16)	45.0(7)
C(2)	6404.4(19)	5227(3)	12137.8(16)	46.2(7)
C(3)	5724.8(15)	4342(3)	11638.4(13)	31.4(5)
C(4)	5130.5(16)	5258(3)	11086.4(14)	33.3(5)
C(5)	4421.6(13)	4412(3)	10592.3(12)	24.5(4)
C(6)	3798.2(13)	5445(2)	10110.0(12)	23.9(4)
C(7)	2966.5(13)	4748(2)	9679.6(11)	19.2(4)
C(8)	3187.0(15)	3473(3)	9190.1(13)	29.5(5)
C(9)	2374.5(13)	4148(3)	10213.0(11)	23.4(5)
C(10)	2491.2(13)	5990(2)	9196.2(11)	22.0(4)
C(11)	894.7(13)	5742(2)	8990.7(10)	18.6(4)
C(12)	-659.5(13)	5221(2)	8612.6(11)	21.9(4)
C(13)	-1162.3(15)	4838(3)	7858.0(13)	30.4(5)
C(14)	-1000.4(15)	6667(3)	8895.0(13)	28.2(5)
C(15)	-676.9(16)	3950(3)	9156.2(13)	30.0(5)
O(7)	2098.7(10)	4952(2)	4006.2(8)	31.2(4)
O(8)	857.5(10)	6120.0(18)	2988.4(8)	24.7(3)

O(9)	322.9(9)	5447.4(17)	1805.9(7)	21.7(3)
N(3)	1750.8(12)	5672(2)	2130.2(9)	26.3(4)
C(31)	6326(3)	4781(4)	6124.0(18)	63.1(9)
C(32)	6582.1(19)	4368(5)	5410.1(17)	56.7(8)
C(33)	5844.8(18)	3775(4)	4843.8(17)	49.6(7)
C(34)	5178.1(15)	4913(3)	4487.2(14)	33.7(6)
C(35)	4468.3(14)	4219(3)	3929.4(13)	27.8(5)
C(36)	3835.7(14)	5350(2)	3524.0(12)	25.2(4)
C(37)	3029.1(13)	4724(2)	3033.7(11)	20.1(4)
C(38)	3274.3(15)	3587(3)	2479.1(12)	31.9(5)
C(39)	2418.8(13)	3972(2)	3507.4(11)	23.0(4)
C(40)	2556.8(14)	6045(3)	2605.2(11)	24.5(4)
C(41)	969.3(13)	5770(2)	2360.8(10)	20.4(4)
C(42)	-574.7(13)	5226(2)	1963.8(11)	22.2(4)
C(43)	-1065.3(15)	4858(3)	1197.6(13)	31.7(5)
C(44)	-932.9(15)	6645(3)	2252.7(13)	27.2(5)
C(45)	-597.2(16)	3930(3)	2493.9(13)	29.7(5)
O(4)	2067.5(10)	5013(2)	7332.8(8)	30.4(4)
O(5)	808.8(9)	6024.0(17)	6279.1(7)	23.1(3)
O(6)	255.2(8)	5261.2(16)	5113.3(7)	18.1(3)
N(2)	1686.5(11)	5364(2)	5436.3(9)	20.7(4)
C(16)	6858.4(17)	4512(3)	9540.2(15)	42.9(6)
C(17)	6326.6(18)	5330(3)	8909.8(17)	47.2(7)
C(18)	5678.6(15)	4361(3)	8417.8(13)	31.7(5)
C(19)	5085.3(15)	5228(3)	7836.1(14)	32.3(5)
C(20)	4404.4(14)	4326(3)	7338.0(12)	24.4(4)
C(21)	3788.0(13)	5311(2)	6818.4(12)	23.1(4)
C(22)	2987.5(12)	4583(2)	6366.6(10)	18.2(4)
C(23)	3249.0(15)	3330(3)	5879.5(12)	29.7(5)
C(24)	2382.5(13)	3934(2)	6873.9(11)	21.8(4)
C(25)	2505.2(13)	5819(2)	5878.1(11)	21.5(4)
C(26)	911.5(13)	5583(2)	5660.2(10)	17.5(4)
C(27)	-645.9(12)	5115(2)	5270.8(11)	18.4(4)
C(28)	-1141.7(14)	4735(3)	4510.0(12)	27.2(5)
C(29)	-972.5(15)	6583(3)	5543.4(13)	27.1(5)
C(30)	-697.4(14)	3863(3)	5818.0(12)	25.7(4)

Table S-55. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_p17578_0m_a.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	28.1(8)	57.4(13)	14.5(7)	1.0(7)	6.2(6)	14.9(8)
O(2)	27.0(7)	30.7(9)	16.7(7)	-5.3(6)	4.3(5)	8.0(6)
O(3)	19.0(7)	26.3(8)	14.9(6)	-1.3(5)	3.7(5)	0.4(6)
N(1)	19.8(8)	30.3(10)	13.8(7)	-3.8(6)	4.5(6)	0.4(7)
C(1)	41.7(14)	38.2(15)	50.1(15)	9.8(12)	-9.5(12)	-11.1(12)
C(2)	45.2(15)	31.8(15)	54.4(16)	8.0(12)	-16.5(12)	-11.9(12)
C(3)	26.5(11)	26.9(12)	38.7(12)	0.4(10)	-2.4(9)	-3.8(9)
C(4)	29.2(11)	30.1(13)	37.1(13)	0(1)	-6.0(9)	-4.5(10)
C(5)	21.4(10)	24.8(12)	26.5(10)	-0.3(8)	0.5(8)	-1.9(8)
C(6)	21(1)	23.8(11)	25.6(10)	-0.4(8)	-0.4(8)	-4.3(8)
C(7)	18.7(9)	21.9(11)	17.8(9)	-0.3(7)	5.2(7)	-1.3(8)
C(8)	26.5(11)	34.1(13)	28.5(11)	-10.4(9)	6.7(9)	4.5(9)
C(9)	21.6(10)	30.4(13)	18.8(9)	4.0(8)	5.1(7)	0.7(8)
C(10)	22.2(10)	24.9(11)	18.8(9)	1.8(8)	2.7(7)	-3.9(8)
C(11)	21.3(9)	19.7(10)	14.1(8)	1.9(7)	0.6(7)	1.0(7)
C(12)	19.2(9)	23.3(11)	23.8(10)	0.1(8)	5.1(7)	0.7(8)
C(13)	24.7(11)	34.9(14)	30.6(11)	-1.2(9)	0.4(9)	-1.9(9)
C(14)	25.3(11)	26.0(12)	34.3(12)	-1.4(9)	7.3(9)	4.2(9)
C(15)	34.3(12)	28.3(13)	29.9(11)	2.2(9)	12.7(9)	-0.2(9)
O(7)	28.6(8)	52.0(12)	14.2(7)	2.4(6)	6.9(6)	11.8(7)
O(8)	26.6(7)	30.8(9)	17.5(7)	-3.2(6)	6.1(6)	8.4(6)
O(9)	19.5(7)	30.7(9)	15.4(6)	0.0(6)	3.7(5)	5.1(6)
N(3)	24.7(9)	40.7(13)	14.1(8)	2.4(7)	5.4(6)	7.9(8)
C(31)	87(3)	44.2(19)	55.3(19)	-5.4(14)	3.2(17)	-5.6(17)
C(32)	41.1(15)	78(2)	49.7(16)	8.3(16)	1.5(13)	-5.6(16)
C(33)	35.9(14)	62(2)	46.7(15)	8.6(14)	-6.5(12)	-1.1(13)
C(34)	24.7(11)	38.3(15)	37.3(13)	-2.3(10)	2.2(9)	-5.0(9)
C(35)	24.8(10)	26.7(12)	30.2(11)	-1.3(9)	-0.9(8)	0.1(8)
C(36)	25.1(10)	19.7(10)	30.9(11)	-0.5(8)	4.6(8)	-1.6(8)
C(37)	20.9(9)	22.9(11)	17.2(9)	1.1(7)	5.1(7)	2.7(8)
C(38)	29.5(11)	40.6(15)	25.6(11)	-10.5(9)	4.7(9)	10.4(10)
C(39)	23(1)	22.7(11)	24.2(10)	2.0(8)	6.0(8)	-1.8(8)
C(40)	23.9(10)	26.8(12)	23.3(10)	3.7(8)	5.0(8)	-0.4(8)
C(41)	25(1)	20.1(11)	16.5(9)	0.8(7)	3.8(7)	4.0(8)

C(42)	20.3(10)	23.9(11)	23(1)	-0.4(8)	5.7(7)	4.2(8)
C(43)	29.1(11)	36.1(14)	29.0(11)	-3.7(9)	0.8(9)	1.4(10)
C(44)	24.5(11)	23.9(11)	33.8(12)	-2.2(8)	6.8(9)	5.5(8)
C(45)	34.5(12)	25.3(12)	31.4(11)	2.0(9)	12.0(9)	3.3(9)
O(4)	28.2(8)	49.9(11)	14.2(7)	0.6(6)	6.5(6)	12.1(7)
O(5)	25.8(7)	27.7(9)	16.2(6)	-5.5(6)	4.3(5)	6.6(6)
O(6)	16.4(6)	24.5(8)	13.2(6)	-0.8(5)	1.9(5)	0.9(5)
N(2)	19.6(8)	30.6(11)	12.0(7)	-2.9(6)	3.4(6)	-1.6(7)
C(16)	38.4(13)	37.1(15)	48.9(15)	5.7(12)	-7.5(11)	-7.5(12)
C(17)	41.2(15)	35.4(15)	57.1(17)	11.0(13)	-18.3(12)	-12.0(12)
C(18)	26.1(10)	27.6(12)	39.0(12)	2.7(10)	-2.6(9)	-1.9(9)
C(19)	27.0(11)	28.8(13)	37.5(12)	3.3(10)	-7.3(9)	-5.6(9)
C(20)	22.6(10)	22.0(11)	28(1)	-0.1(8)	1.5(8)	-1.3(8)
C(21)	21.5(10)	21.0(11)	25.3(10)	1.7(8)	-1.1(8)	-4.9(8)
C(22)	18.9(9)	19.2(11)	17.0(8)	-1.2(7)	4.5(7)	-3.2(7)
C(23)	28.6(11)	33.8(13)	27.3(11)	-9.9(9)	5.8(9)	5.4(9)
C(24)	22.0(9)	21.8(11)	22.5(9)	3.7(7)	6.7(7)	-1.4(8)
C(25)	19.7(9)	26.4(12)	18.1(9)	2.1(8)	2.5(7)	-2.9(8)
C(26)	21.3(9)	16.3(10)	14.2(8)	0.1(7)	0.3(7)	0.4(7)
C(27)	16.9(9)	18.3(10)	20.3(9)	0.8(7)	4.1(7)	0.3(7)
C(28)	24.1(10)	32.8(13)	23.5(10)	-1.4(9)	0.2(8)	-1.5(9)
C(29)	24.1(10)	23.8(12)	34.3(12)	-1.6(8)	7.6(9)	6.3(8)
C(30)	29.1(11)	23.7(11)	25.6(10)	4.4(8)	8.2(8)	-0.5(9)

Table S-56. Bond Lengths for cu_p17578_0m_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(9)	1.421(3)	C(34)	C(35)	1.517(3)
O(2)	C(11)	1.226(2)	C(35)	C(36)	1.527(3)
O(3)	C(11)	1.348(2)	C(36)	C(37)	1.532(3)
O(3)	C(12)	1.473(2)	C(37)	C(38)	1.529(3)
N(1)	C(10)	1.458(2)	C(37)	C(39)	1.532(3)
N(1)	C(11)	1.342(3)	C(37)	C(40)	1.549(3)
C(1)	C(2)	1.498(4)	C(42)	C(43)	1.525(3)
C(2)	C(3)	1.513(3)	C(42)	C(44)	1.521(3)
C(3)	C(4)	1.506(3)	C(42)	C(45)	1.523(3)
C(4)	C(5)	1.518(3)	O(4)	C(24)	1.418(3)
C(5)	C(6)	1.524(3)	O(5)	C(26)	1.231(2)
C(6)	C(7)	1.539(3)	O(6)	C(26)	1.346(2)

C(7)	C(8)	1.527(3)	O(6)	C(27)	1.473(2)
C(7)	C(9)	1.533(3)	N(2)	C(25)	1.456(2)
C(7)	C(10)	1.544(3)	N(2)	C(26)	1.340(3)
C(12)	C(13)	1.518(3)	C(16)	C(17)	1.505(4)
C(12)	C(14)	1.527(3)	C(17)	C(18)	1.520(3)
C(12)	C(15)	1.520(3)	C(18)	C(19)	1.514(3)
O(7)	C(39)	1.412(3)	C(19)	C(20)	1.522(3)
O(8)	C(41)	1.226(2)	C(20)	C(21)	1.527(3)
O(9)	C(41)	1.345(2)	C(21)	C(22)	1.531(3)
O(9)	C(42)	1.475(2)	C(22)	C(23)	1.531(3)
N(3)	C(40)	1.449(3)	C(22)	C(24)	1.530(3)
N(3)	C(41)	1.343(3)	C(22)	C(25)	1.549(3)
C(31)	C(32)	1.467(4)	C(27)	C(28)	1.522(3)
C(32)	C(33)	1.518(4)	C(27)	C(29)	1.529(3)
C(33)	C(34)	1.531(4)	C(27)	C(30)	1.519(3)

Table S-57. Bond Angles for cu_p17578_0m_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(11)	O(3)	C(12)	120.33(15)	C(39)	C(37)	C(40)	109.97(16)
C(11)	N(1)	C(10)	122.52(16)	O(7)	C(39)	C(37)	113.16(18)
C(1)	C(2)	C(3)	114.9(2)	N(3)	C(40)	C(37)	114.99(18)
C(4)	C(3)	C(2)	114.4(2)	O(8)	C(41)	O(9)	124.49(18)
C(3)	C(4)	C(5)	115.9(2)	O(8)	C(41)	N(3)	124.78(19)
C(4)	C(5)	C(6)	112.03(19)	N(3)	C(41)	O(9)	110.72(16)
C(5)	C(6)	C(7)	117.03(18)	O(9)	C(42)	C(43)	101.81(16)
C(6)	C(7)	C(10)	106.60(17)	O(9)	C(42)	C(44)	110.94(18)
C(8)	C(7)	C(6)	111.30(17)	O(9)	C(42)	C(45)	109.91(17)
C(8)	C(7)	C(9)	108.27(18)	C(44)	C(42)	C(43)	110.14(18)
C(8)	C(7)	C(10)	110.01(17)	C(44)	C(42)	C(45)	112.48(17)
C(9)	C(7)	C(6)	110.77(16)	C(45)	C(42)	C(43)	111.1(2)
C(9)	C(7)	C(10)	109.90(16)	C(26)	O(6)	C(27)	120.48(14)
O(1)	C(9)	C(7)	113.29(18)	C(26)	N(2)	C(25)	122.37(16)
N(1)	C(10)	C(7)	114.88(17)	C(16)	C(17)	C(18)	114.0(2)
O(2)	C(11)	O(3)	124.46(18)	C(19)	C(18)	C(17)	113.2(2)
O(2)	C(11)	N(1)	125.13(18)	C(18)	C(19)	C(20)	115.8(2)
N(1)	C(11)	O(3)	110.41(16)	C(19)	C(20)	C(21)	111.83(18)
O(3)	C(12)	C(13)	102.06(16)	C(20)	C(21)	C(22)	117.69(18)
O(3)	C(12)	C(14)	110.75(17)	C(21)	C(22)	C(25)	106.40(16)

O(3)	C(12)	C(15)	109.41(17)	C(23)	C(22)	C(21)	111.54(17)
C(13)	C(12)	C(14)	110.21(18)	C(23)	C(22)	C(25)	110.17(16)
C(13)	C(12)	C(15)	111.32(19)	C(24)	C(22)	C(21)	111.00(16)
C(15)	C(12)	C(14)	112.60(17)	C(24)	C(22)	C(23)	107.97(17)
C(41)	O(9)	C(42)	119.93(15)	C(24)	C(22)	C(25)	109.77(16)
C(41)	N(3)	C(40)	122.23(17)	O(4)	C(24)	C(22)	113.04(18)
C(31)	C(32)	C(33)	114.7(3)	N(2)	C(25)	C(22)	114.88(17)
C(32)	C(33)	C(34)	116.3(3)	O(5)	C(26)	O(6)	124.32(18)
C(35)	C(34)	C(33)	112.5(2)	O(5)	C(26)	N(2)	124.97(18)
C(34)	C(35)	C(36)	113.4(2)	N(2)	C(26)	O(6)	110.71(16)
C(35)	C(36)	C(37)	116.39(18)	O(6)	C(27)	C(28)	101.84(15)
C(36)	C(37)	C(39)	110.59(16)	O(6)	C(27)	C(29)	110.82(16)
C(36)	C(37)	C(40)	107.03(17)	O(6)	C(27)	C(30)	109.89(16)
C(38)	C(37)	C(36)	111.89(17)	C(28)	C(27)	C(29)	110.27(18)
C(38)	C(37)	C(39)	108.21(19)	C(30)	C(27)	C(28)	111.31(18)
C(38)	C(37)	C(40)	109.14(17)	C(30)	C(27)	C(29)	112.25(17)

Table S-58. Torsion Angles for cu_p17578_0m_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(1)	C(2)	C(3)	C(4)	171.4(3)	C(39)	C(37)	C(40)	N(3)	-57.4(2)
C(2)	C(3)	C(4)	C(5)	-178.1(2)	C(40)	N(3)	C(41)	O(8)	-2.9(3)
C(3)	C(4)	C(5)	C(6)	174.1(2)	C(40)	N(3)	C(41)	O(9)	176.40(19)
C(4)	C(5)	C(6)	C(7)	-170.22(19)	C(40)	C(37)	C(39)	O(7)	-56.6(2)
C(5)	C(6)	C(7)	C(8)	-55.9(2)	C(41)	O(9)	C(42)	C(43)	-178.66(18)
C(5)	C(6)	C(7)	C(9)	64.6(2)	C(41)	O(9)	C(42)	C(44)	64.2(2)
C(5)	C(6)	C(7)	C(10)	-175.83(18)	C(41)	O(9)	C(42)	C(45)	-60.9(2)
C(6)	C(7)	C(9)	O(1)	61.4(2)	C(41)	N(3)	C(40)	C(37)	93.5(2)
C(6)	C(7)	C(10)	N(1)	-178.56(16)	C(42)	O(9)	C(41)	O(8)	-11.5(3)
C(8)	C(7)	C(9)	O(1)	-176.33(17)	C(42)	O(9)	C(41)	N(3)	169.19(18)
C(8)	C(7)	C(10)	N(1)	60.7(2)	C(16)	C(17)	C(18)	C(19)	174.0(2)
C(9)	C(7)	C(10)	N(1)	-58.5(2)	C(17)	C(18)	C(19)	C(20)	-178.4(2)
C(10)	N(1)	C(11)	O(2)	-6.2(3)	C(18)	C(19)	C(20)	C(21)	174.9(2)
C(10)	N(1)	C(11)	O(3)	172.60(18)	C(19)	C(20)	C(21)	C(22)	-171.07(19)
C(10)	C(7)	C(9)	O(1)	-56.1(2)	C(20)	C(21)	C(22)	C(23)	-58.1(2)
C(11)	O(3)	C(12)	C(13)	-178.84(18)	C(20)	C(21)	C(22)	C(24)	62.4(2)
C(11)	O(3)	C(12)	C(14)	63.9(2)	C(20)	C(21)	C(22)	C(25)	-178.23(17)
C(11)	O(3)	C(12)	C(15)	-60.8(2)	C(21)	C(22)	C(24)	O(4)	59.9(2)
C(11)	N(1)	C(10)	C(7)	94.2(2)	C(21)	C(22)	C(25)	N(2)	-176.26(16)

C(12)	O(3)	C(11)	O(2)	-14.5(3)	C(23)	C(22)	C(24)	O(4)	-177.57(16)
C(12)	O(3)	C(11)	N(1)	166.71(17)	C(23)	C(22)	C(25)	N(2)	62.7(2)
C(31)	C(32)	C(33)	C(34)	73.3(4)	C(24)	C(22)	C(25)	N(2)	-56.1(2)
C(32)	C(33)	C(34)	C(35)	179.9(2)	C(25)	N(2)	C(26)	O(5)	-8.4(3)
C(33)	C(34)	C(35)	C(36)	-175.6(2)	C(25)	N(2)	C(26)	O(6)	171.26(17)
C(34)	C(35)	C(36)	C(37)	-171.66(19)	C(25)	C(22)	C(24)	O(4)	-57.5(2)
C(35)	C(36)	C(37)	C(38)	-53.2(3)	C(26)	O(6)	C(27)	C(28)	-179.17(17)
C(35)	C(36)	C(37)	C(39)	67.5(2)	C(26)	O(6)	C(27)	C(29)	63.5(2)
C(35)	C(36)	C(37)	C(40)	-172.68(18)	C(26)	O(6)	C(27)	C(30)	-61.1(2)
C(36)	C(37)	C(39)	O(7)	61.4(2)	C(26)	N(2)	C(25)	C(22)	96.1(2)
C(36)	C(37)	C(40)	N(3)	-177.61(17)	C(27)	O(6)	C(26)	O(5)	-13.2(3)
C(38)	C(37)	C(39)	O(7)	-175.71(17)	C(27)	O(6)	C(26)	N(2)	167.18(16)
C(38)	C(37)	C(40)	N(3)	61.1(2)					

Table S-59. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for cu_p17578_0m_a.

Atom	*x*	*y*	*z*	U(eq)
H(1)	1722	5789	10416	50
H(1A)	1677	5155	8329	25
H(1B)	7203	3553	12562	68
H(1C)	6519	3990	13076	68
H(1D)	7335	4999	13040	68
H(2A)	6811	5644	11839	55
H(2B)	6116	6045	12346	55
H(3A)	6020	3620	11371	38
H(3B)	5371	3803	11944	38
H(4A)	5486	5773	10773	40
H(4B)	4854	6003	11355	40
H(5A)	4094	3821	10898	29
H(5B)	4690	3744	10277	29
H(6A)	4118	5913	9755	29
H(6B)	3623	6221	10424	29
H(8A)	2664	3136	8887	44
H(8B)	3440	2674	9496	44
H(8C)	3596	3809	8880	44
H(9A)	1871	3674	9928	28
H(9B)	2691	3400	10527	28
H(10A)	2380	6803	9516	26

H(10B)	2877	6355	8865	26
H(13A)	-1157	5671	7532	46
H(13B)	-1754	4597	7908	46
H(13C)	-894	4003	7657	46
H(14A)	-710	6858	9388	42
H(14B)	-1618	6587	8899	42
H(14C)	-888	7466	8575	42
H(15A)	-432	3081	8965	45
H(15B)	-1269	3754	9223	45
H(15C)	-341	4212	9623	45
H(7)	1719	5480	3779	47
H(3)	1774	5378	1686	32
H(31A)	5942	5621	6057	95
H(31B)	6837	5029	6468	95
H(31C)	6031	3964	6314	95
H(32A)	7036	3621	5496	68
H(32B)	6830	5230	5203	68
H(33A)	5536	3025	5082	60
H(33B)	6100	3291	4453	60
H(34A)	4911	5396	4872	40
H(34B)	5478	5665	4241	40
H(35A)	4142	3521	4184	33
H(35B)	4739	3670	3568	33
H(36A)	4154	5957	3217	30
H(36B)	3639	5995	3890	30
H(38A)	2760	3299	2149	48
H(38B)	3528	2733	2741	48
H(38C)	3689	4017	2200	48
H(39)	2274	2973	3470	28
H(40A)	2430	6782	2961	29
H(40B)	2951	6494	2304	29
H(43A)	-1011	5667	866	48
H(43B)	-1671	4695	1230	48
H(43C)	-822	3979	1014	48
H(44A)	-646	6832	2747	41
H(44B)	-1549	6540	2255	41
H(44C)	-830	7457	1938	41
H(45A)	-335	3078	2303	45
H(45B)	-1192	3710	2543	45

H(45C)	-279	4185	2970	45
H(4)	1679	5497	7088	46
H(2)	1701	4941	5017	25
H(16A)	7174	3724	9347	64
H(16B)	6477	4108	9858	64
H(16C)	7263	5184	9818	64
H(17A)	6720	5780	8608	57
H(17B)	6010	6121	9111	57
H(18A)	5998	3634	8173	38
H(18B)	5323	3829	8725	38
H(19A)	5445	5741	7526	39
H(19B)	4785	5976	8085	39
H(20A)	4068	3748	7642	29
H(20B)	4697	3643	7047	29
H(21A)	4125	5775	6474	28
H(21B)	3584	6096	7112	28
H(23A)	2742	2982	5558	45
H(23B)	3499	2531	6188	45
H(23C)	3670	3691	5587	45
H(24)	2236	2936	6881	26
H(25A)	2387	6631	6196	26
H(25B)	2890	6189	5547	26
H(28A)	-1085	5533	4173	41
H(28B)	-1747	4586	4546	41
H(28C)	-905	3846	4331	41
H(29A)	-685	6775	6038	41
H(29B)	-1592	6528	5542	41
H(29C)	-846	7369	5222	41
H(30A)	-462	2976	5636	39
H(30B)	-1296	3700	5875	39
H(30C)	-367	4122	6288	39

VIII. References

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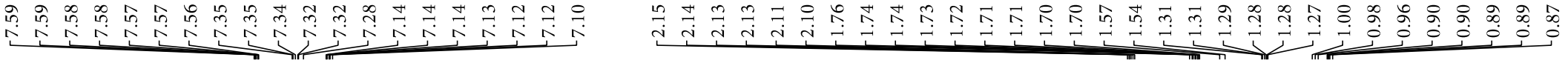

IX. ^{1}H NMR and ^{13}C NMR Spectra; ee Analysis

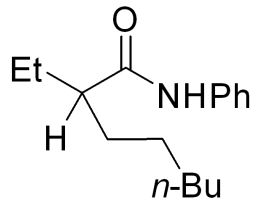

Fig. 2A, Entry 1
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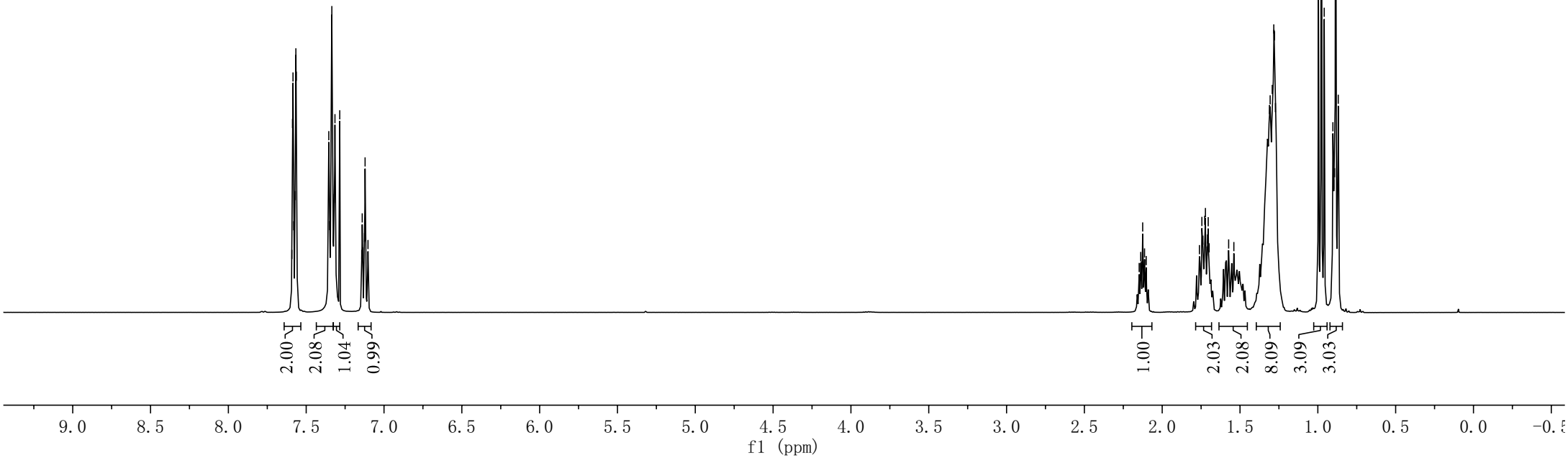

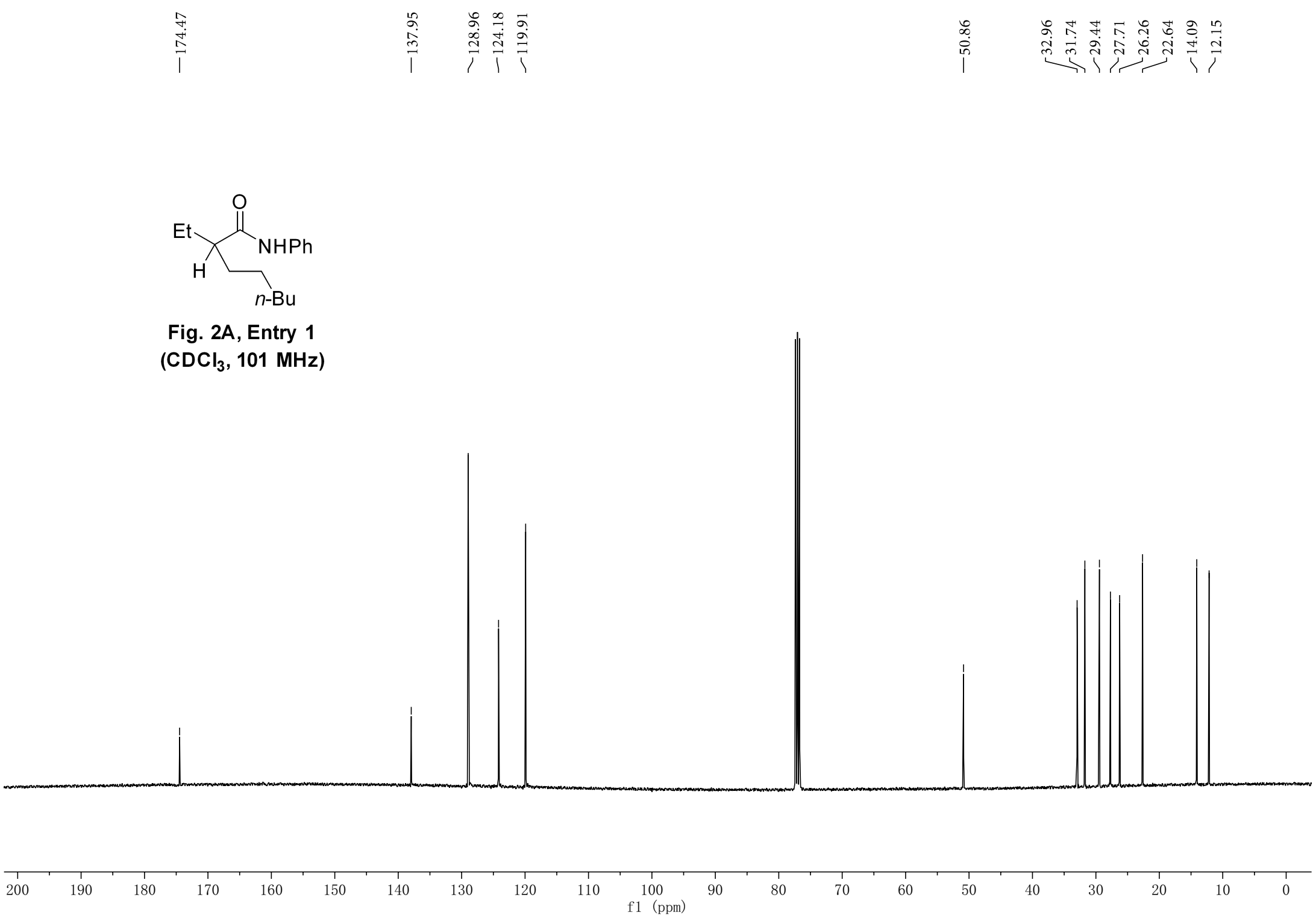

Fig. 2A, Entry 1
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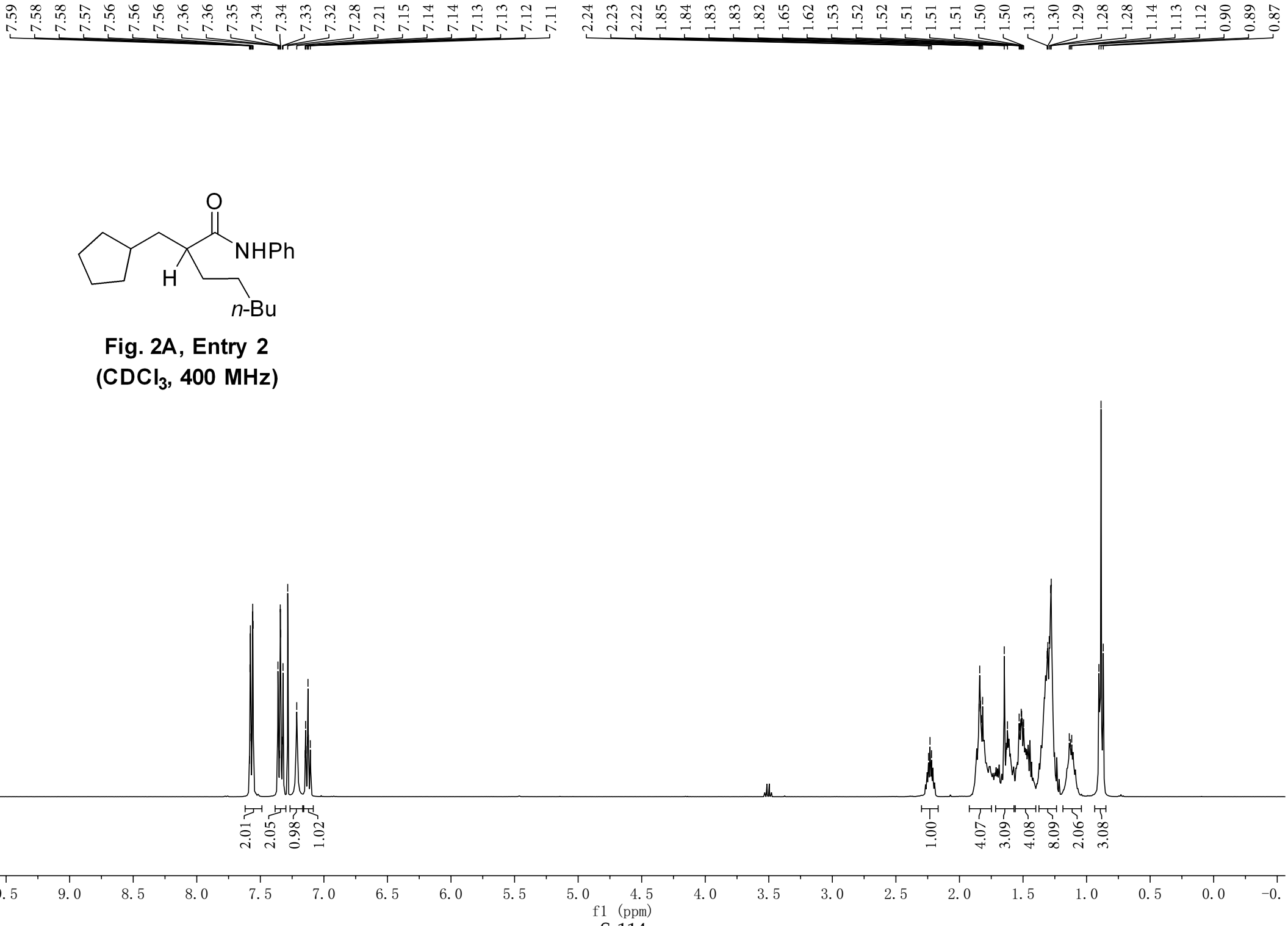

Fig. 2A, Entry 2
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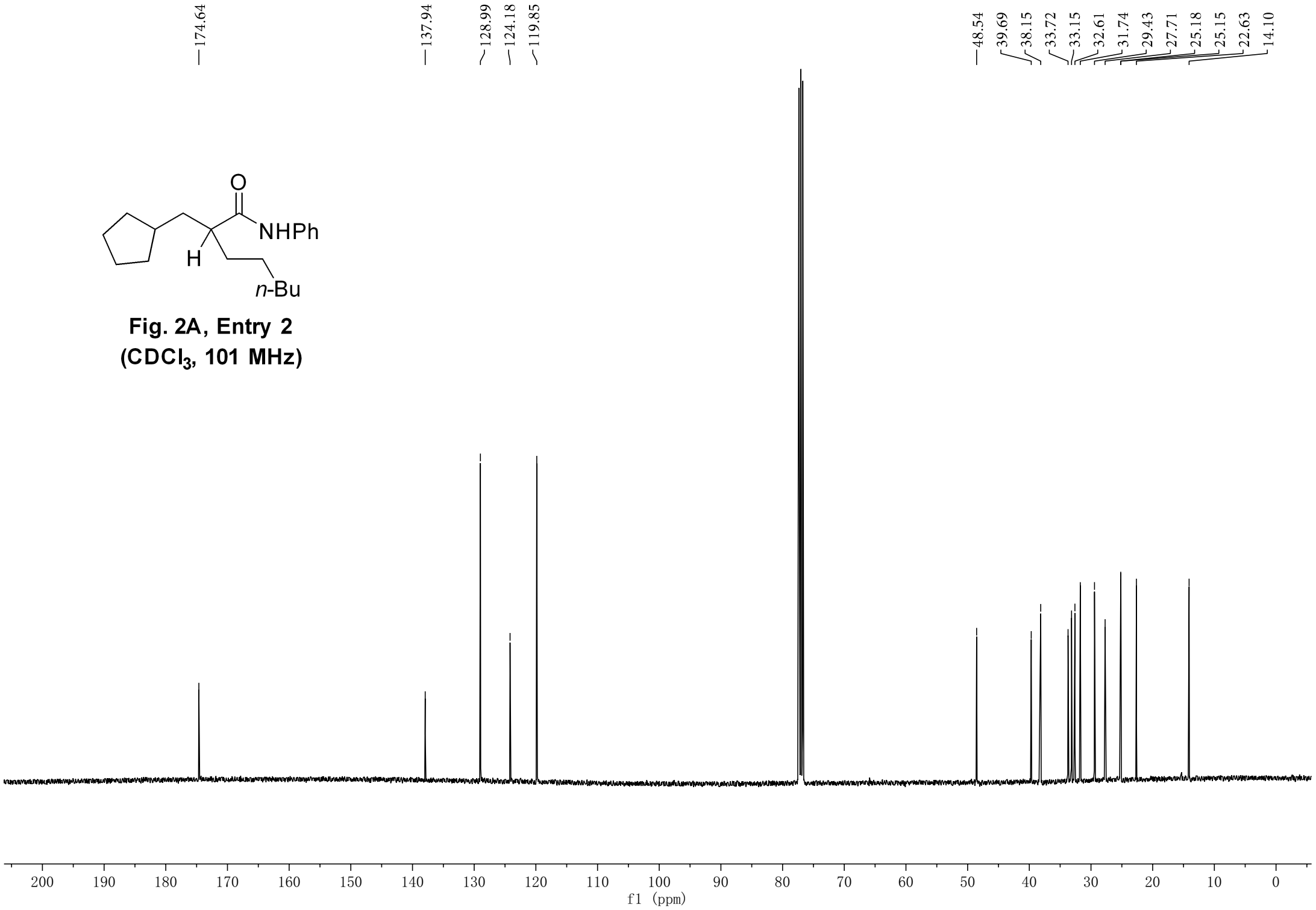

Fig. 2A, Entry 2
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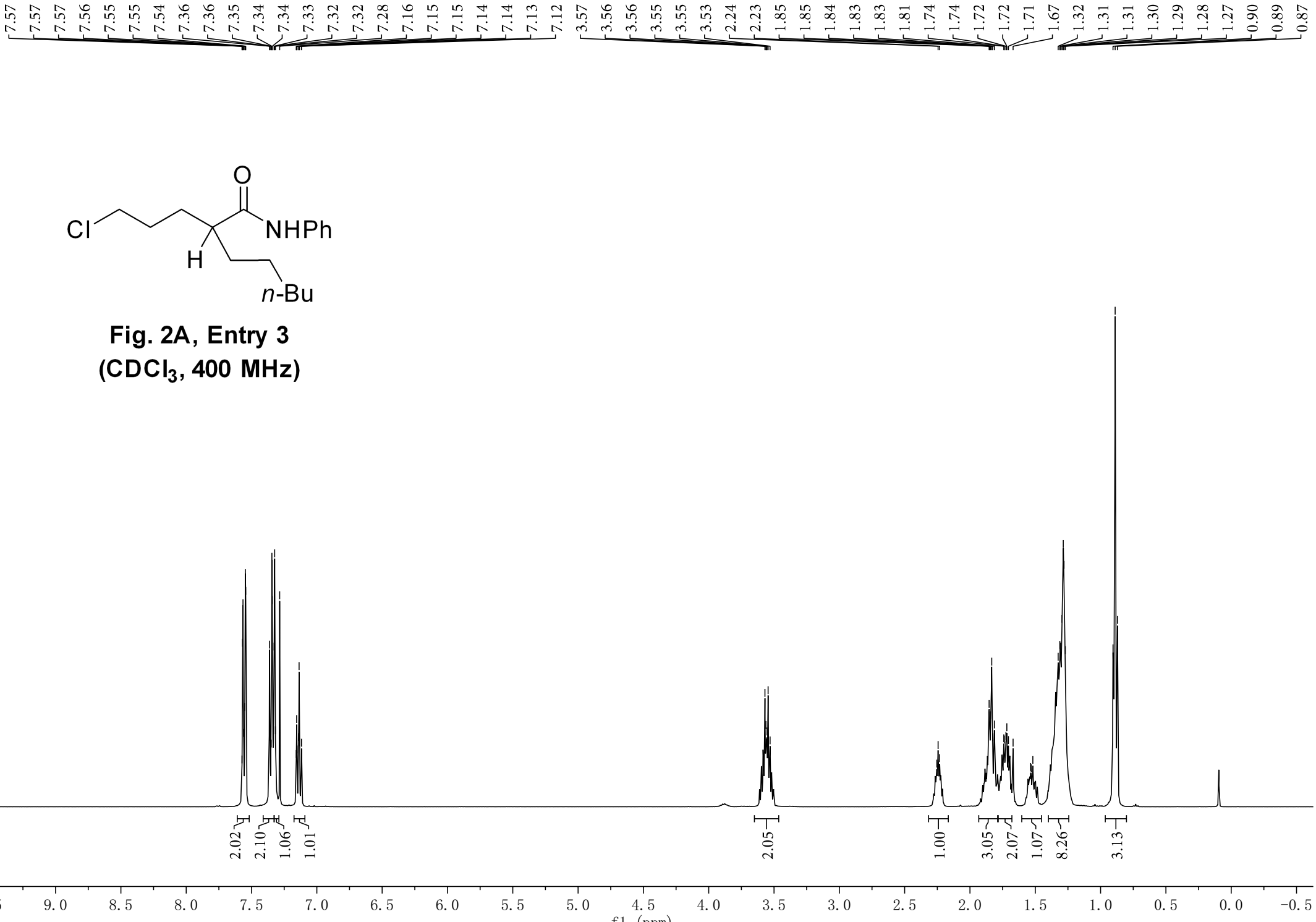

Fig. 2A, Entry 3
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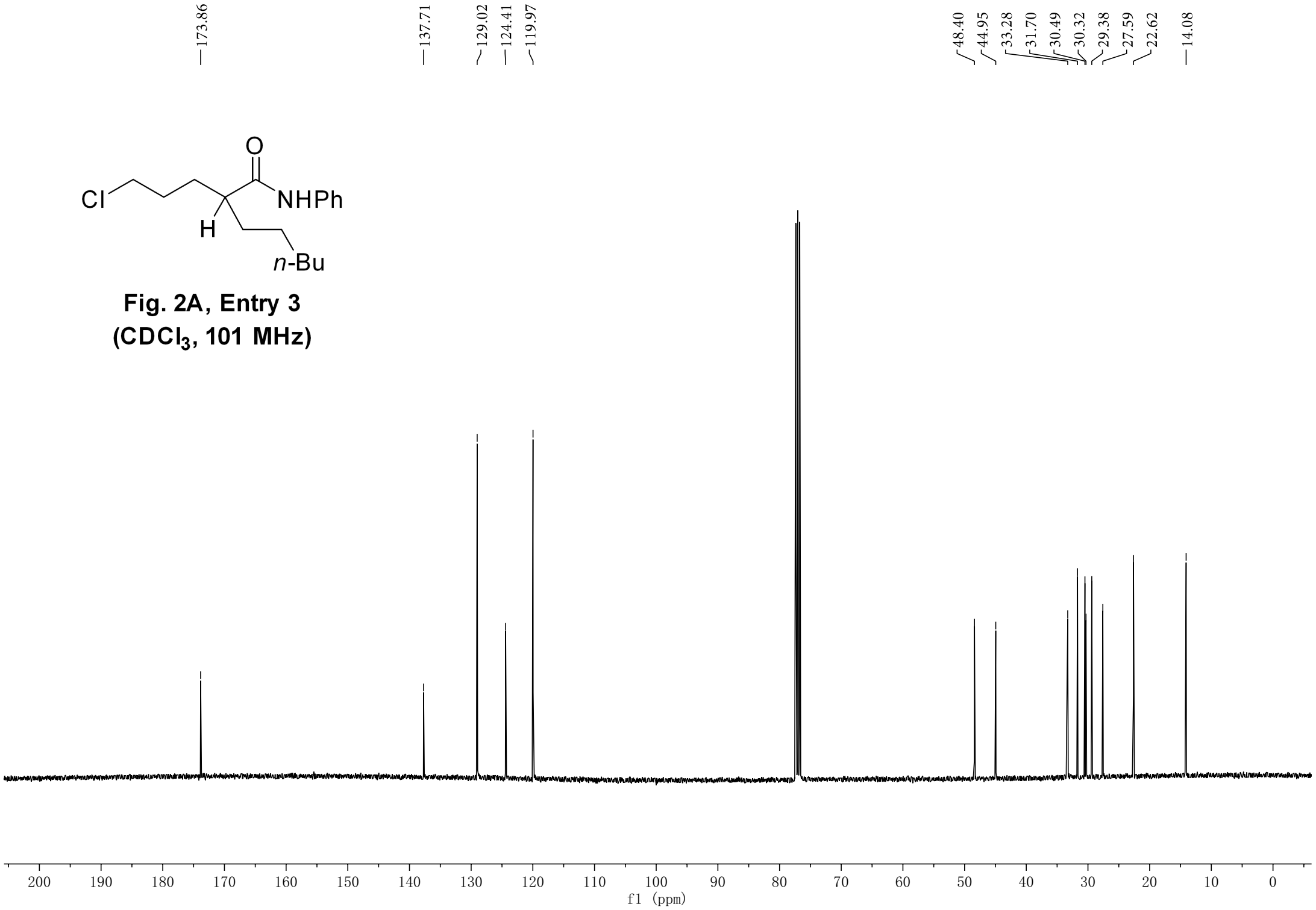

Fig. 2A, Entry 3
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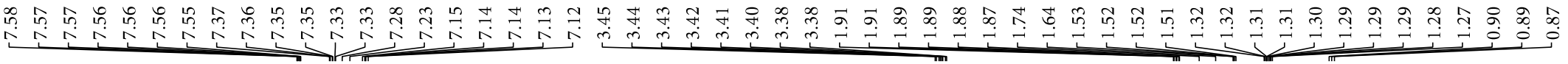

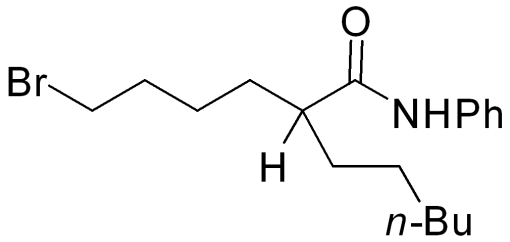

Fig. 2A, Entry 4
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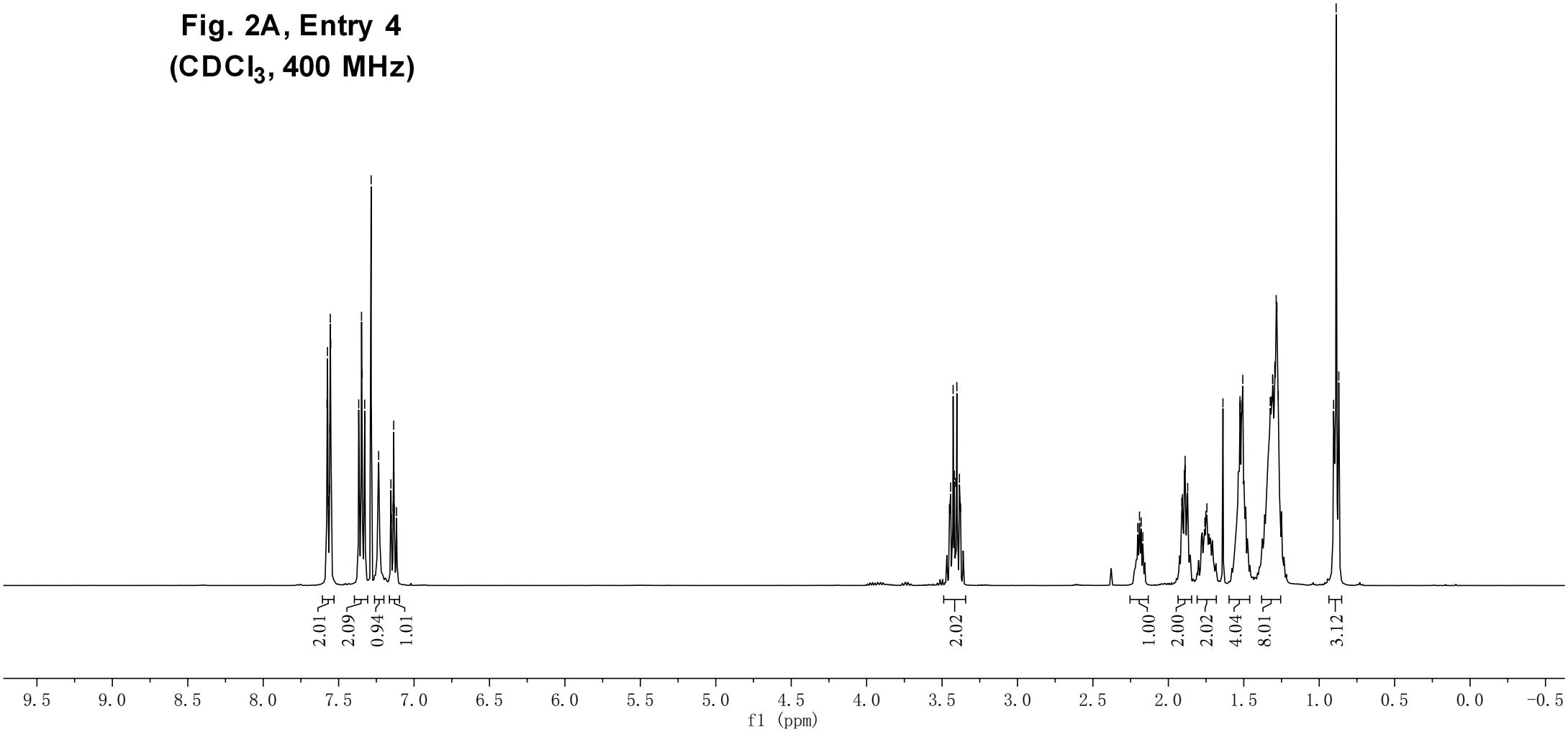

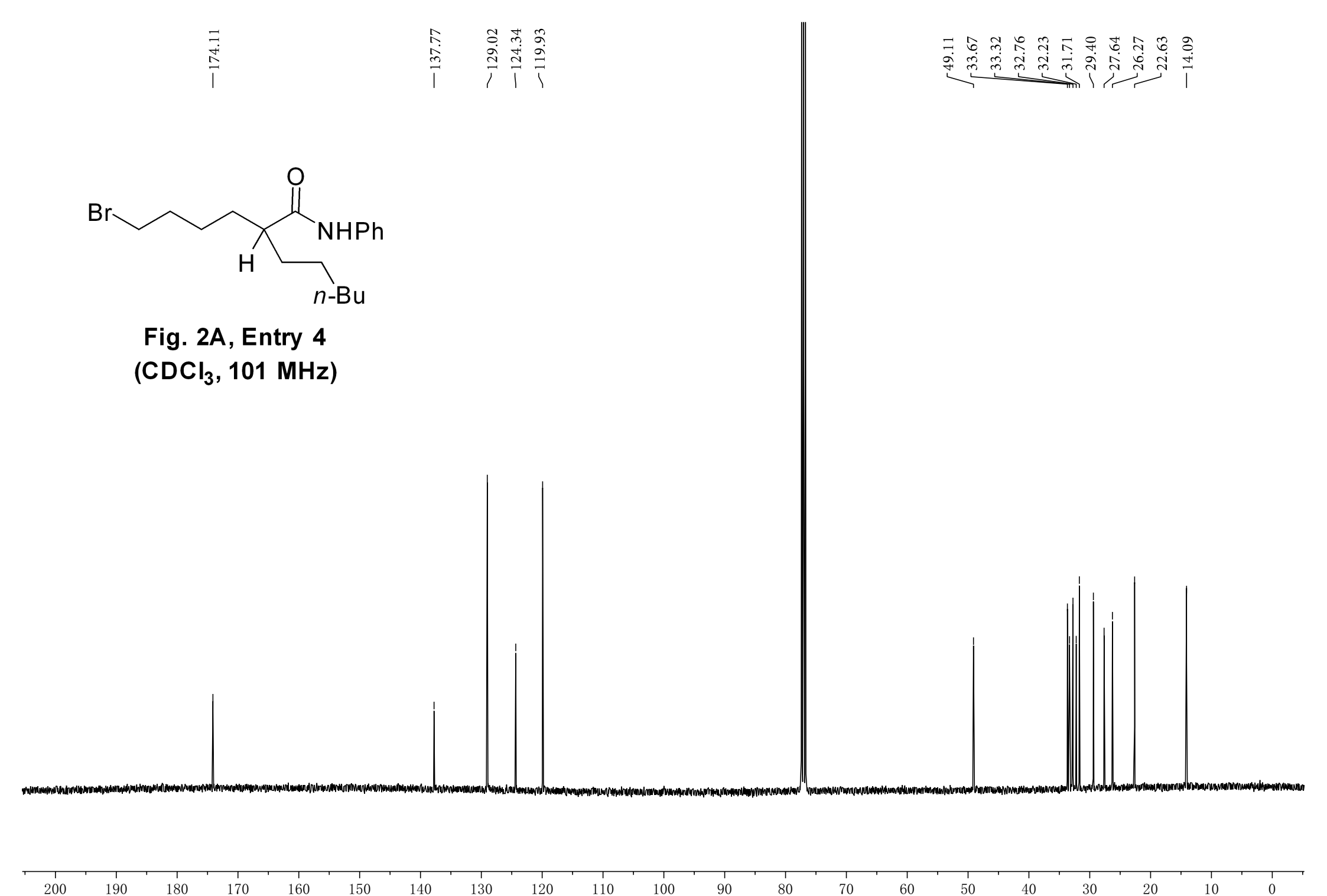

Fig. 2A, Entry 4
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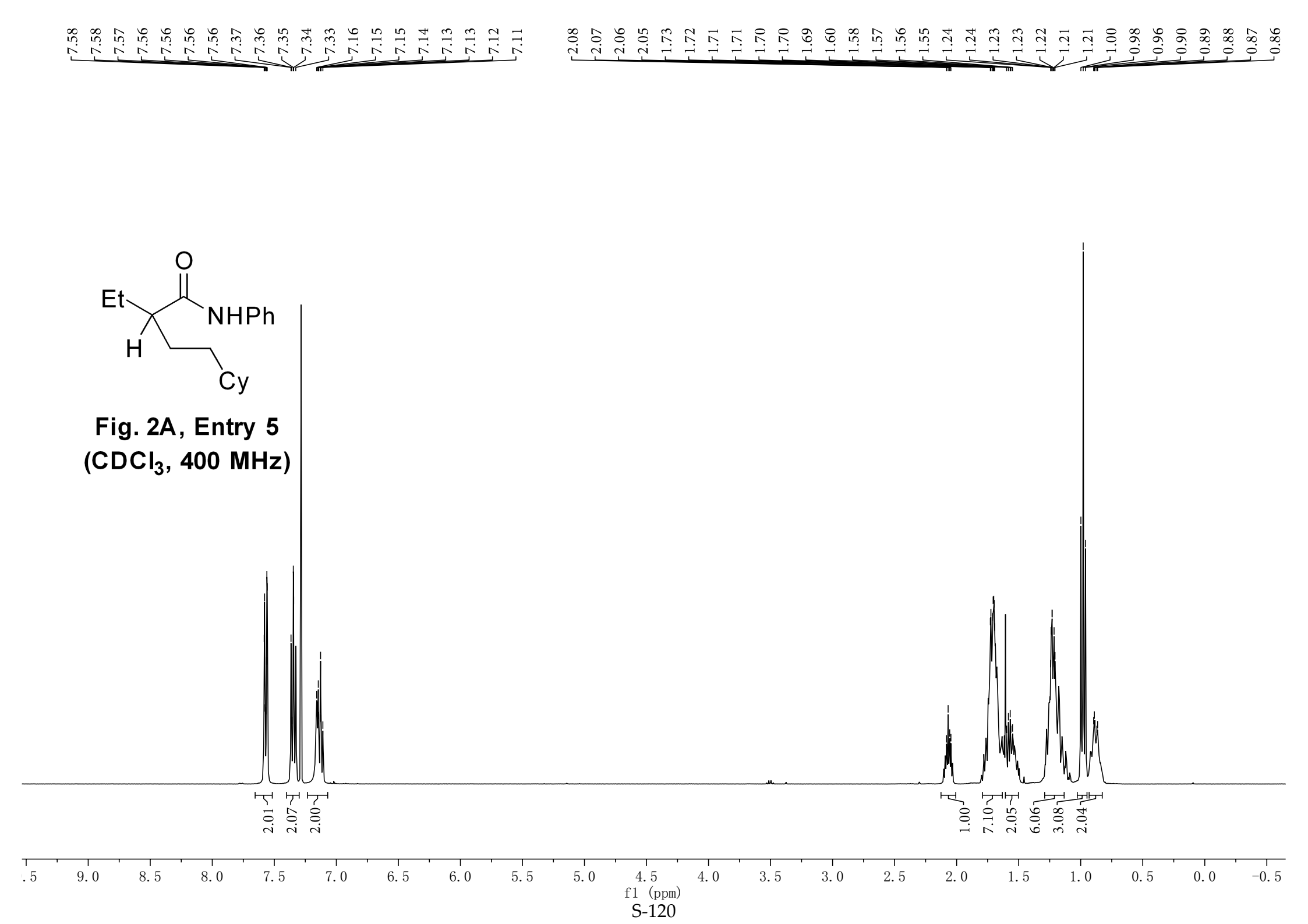

Fig. 2A, Entry 5
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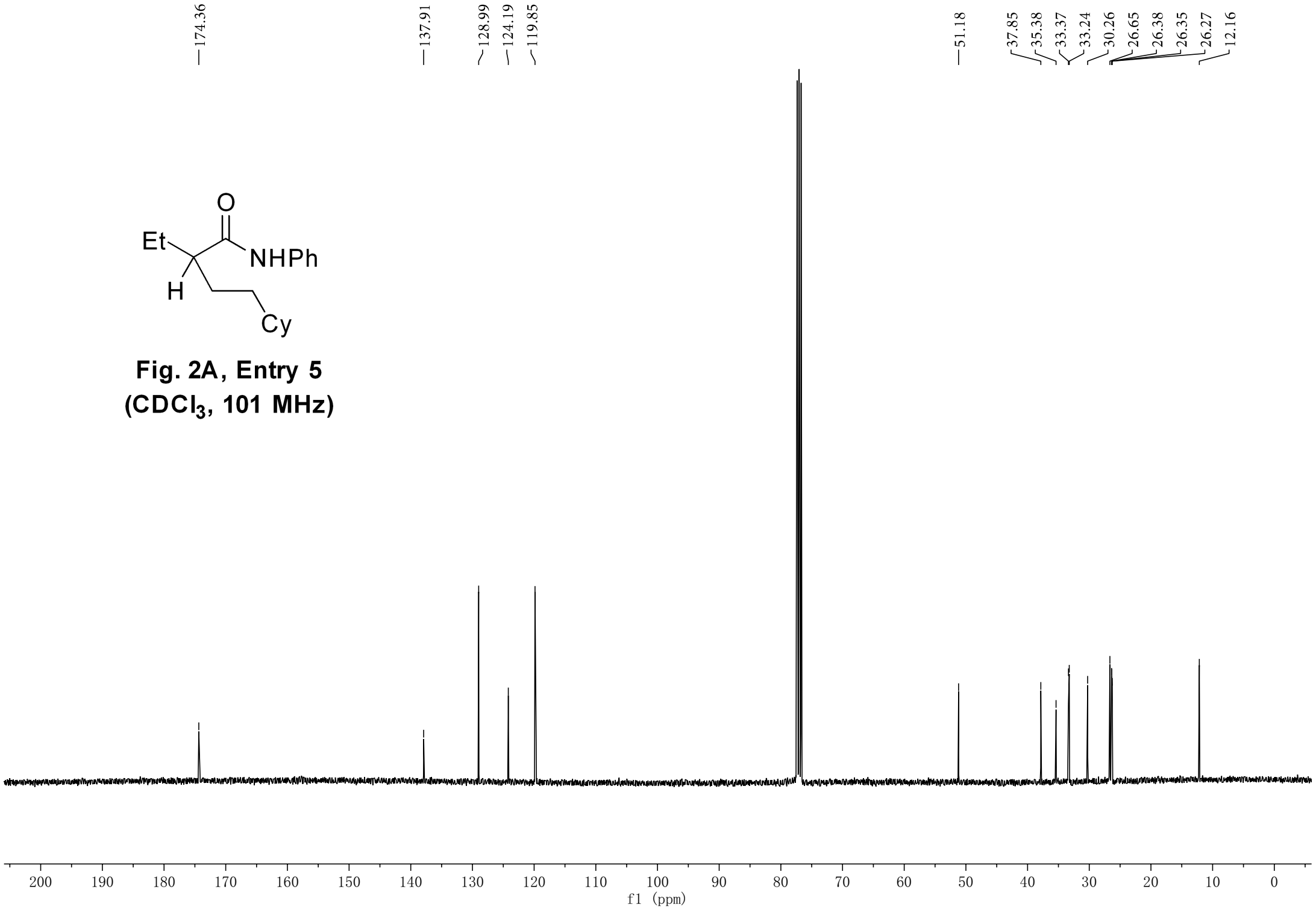

Fig. 2A, Entry 5
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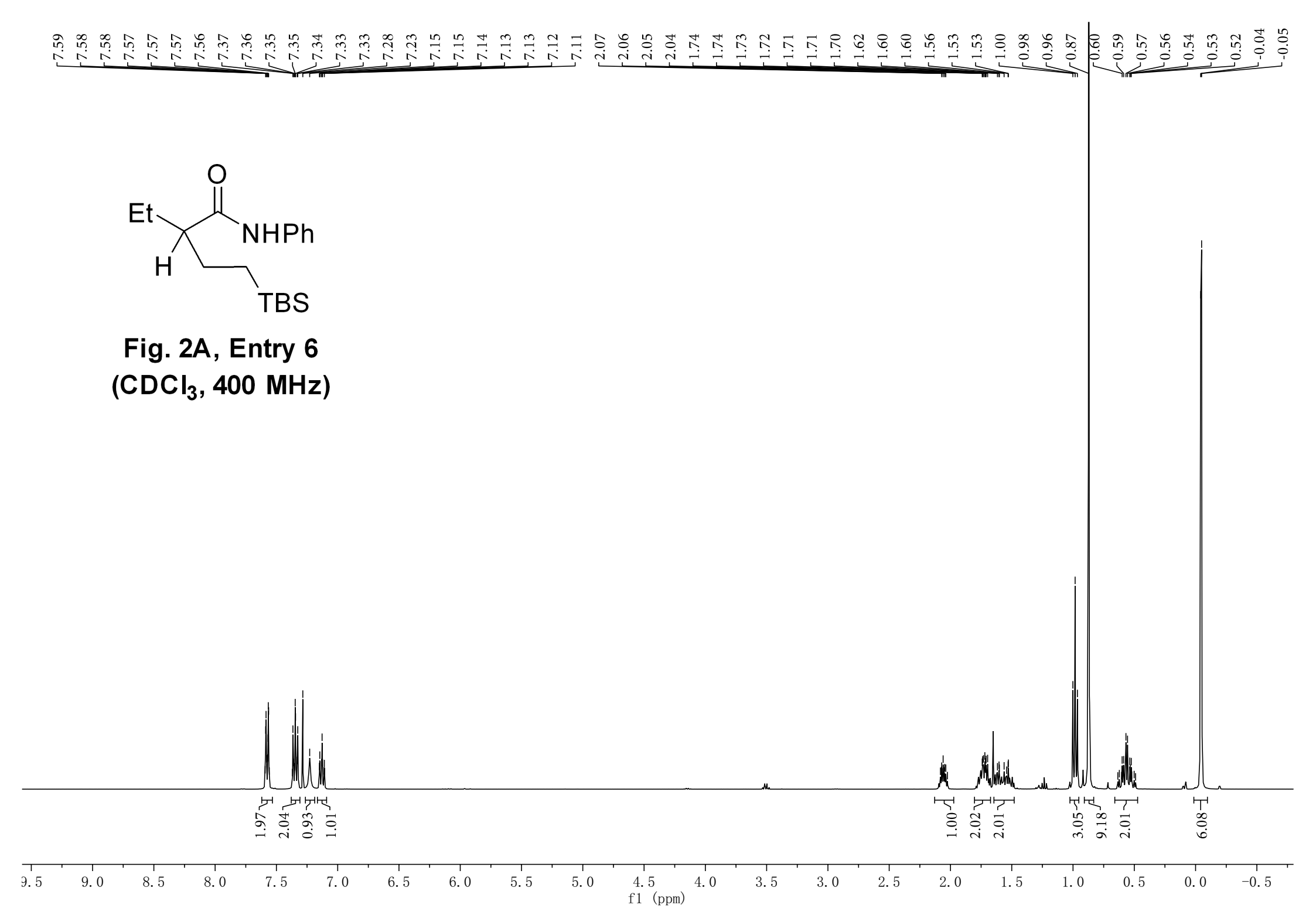

Fig. 2A, Entry 6
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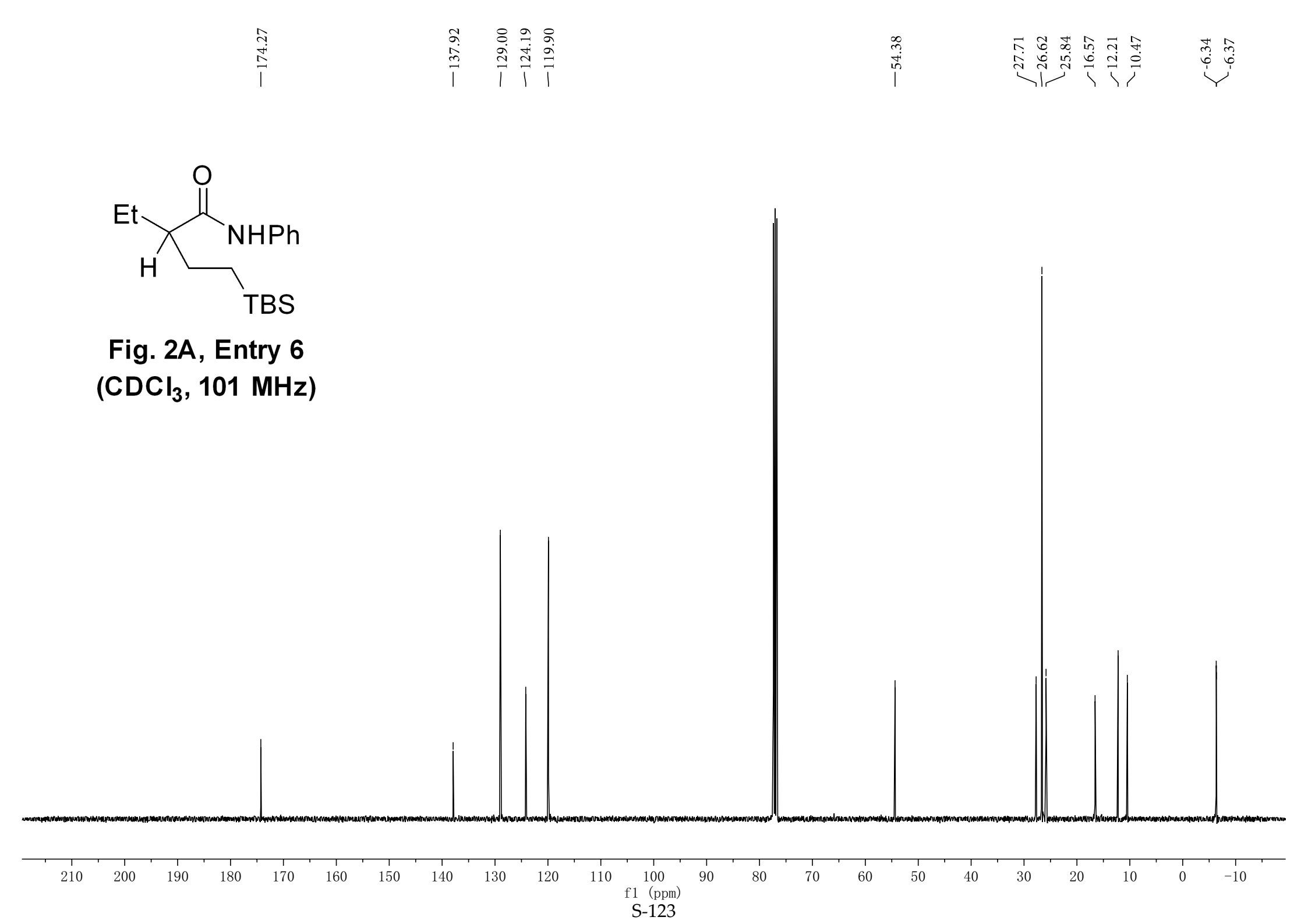

Fig. 2A, Entry 6
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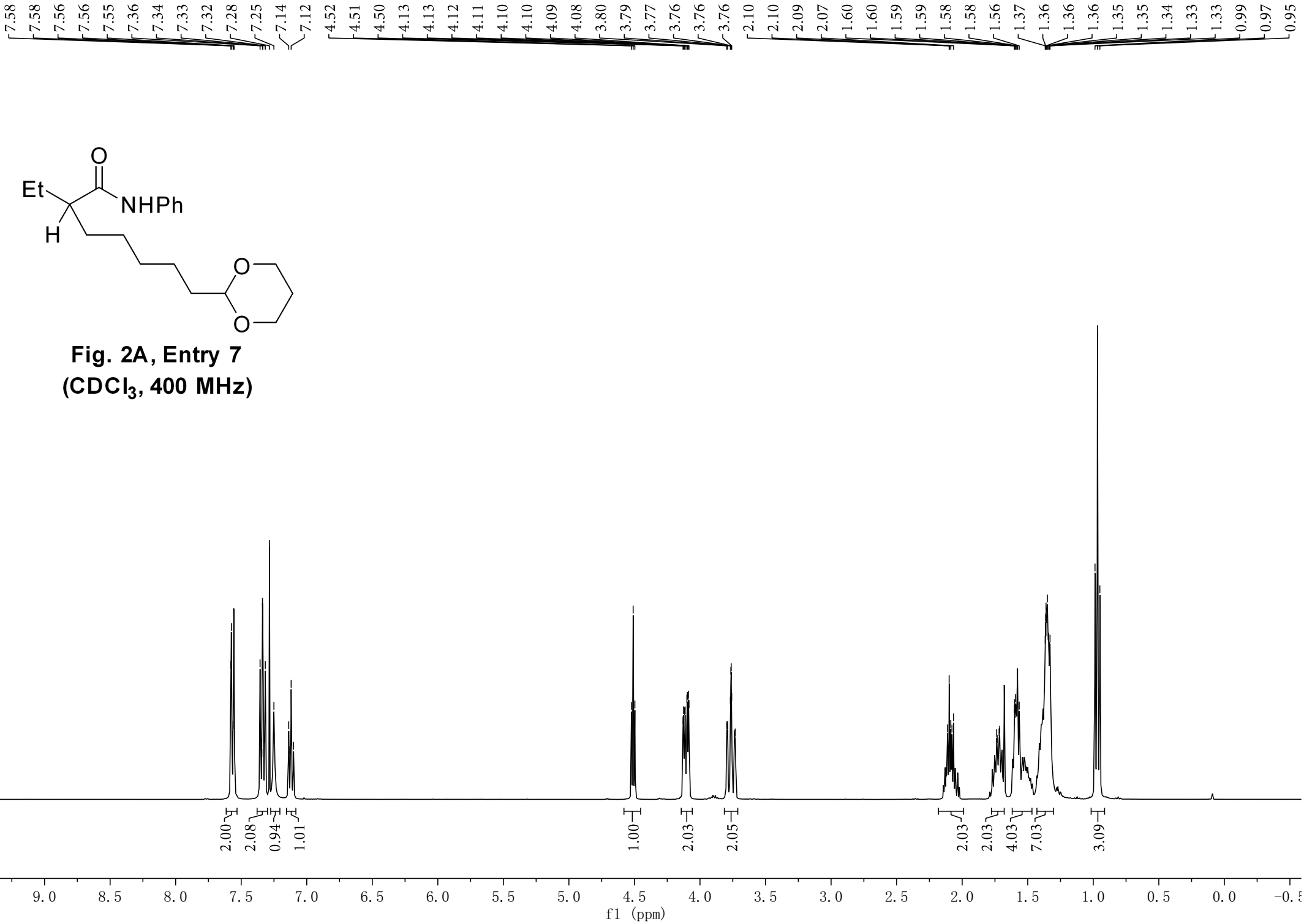

Fig. 2A, Entry 7
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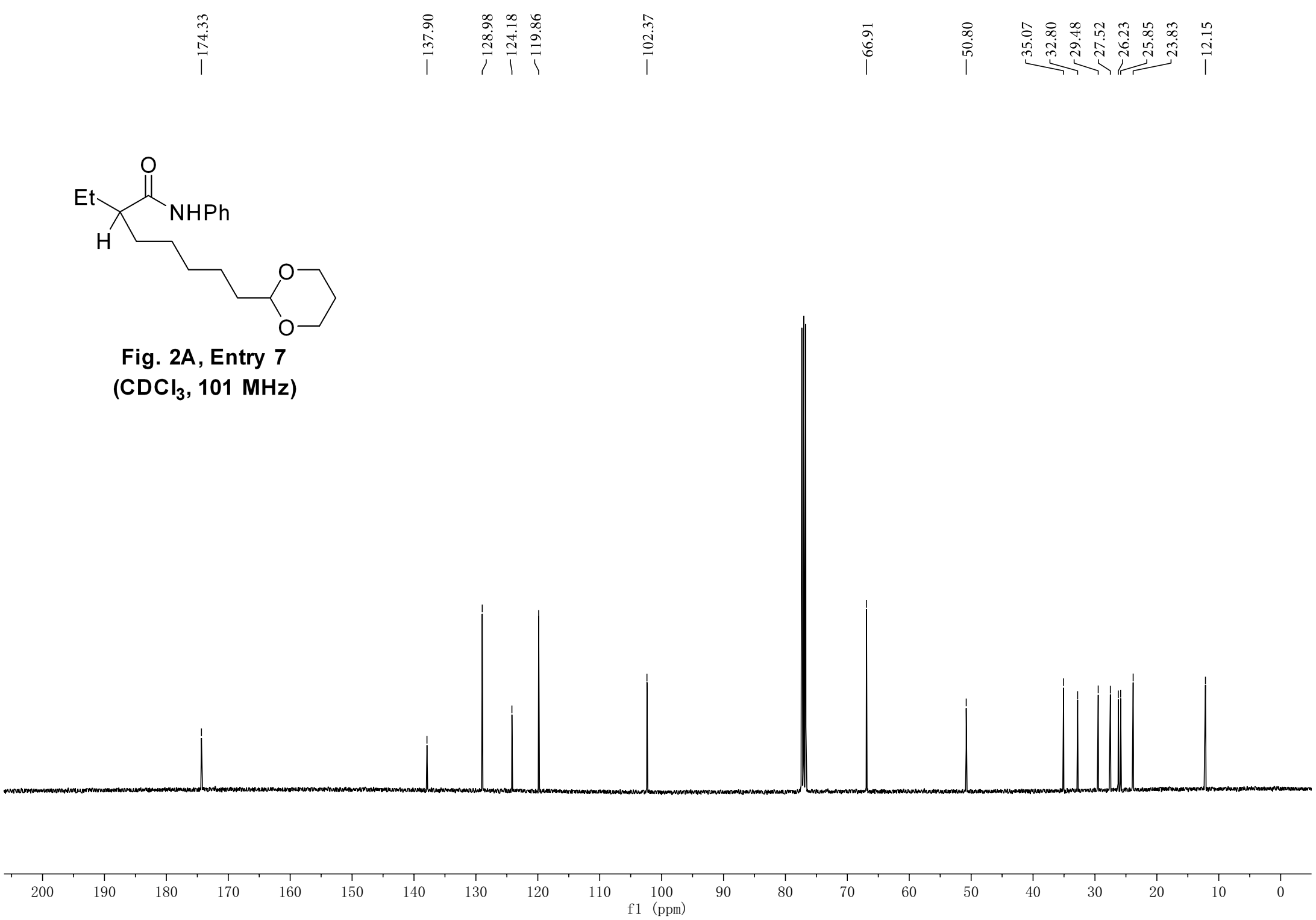

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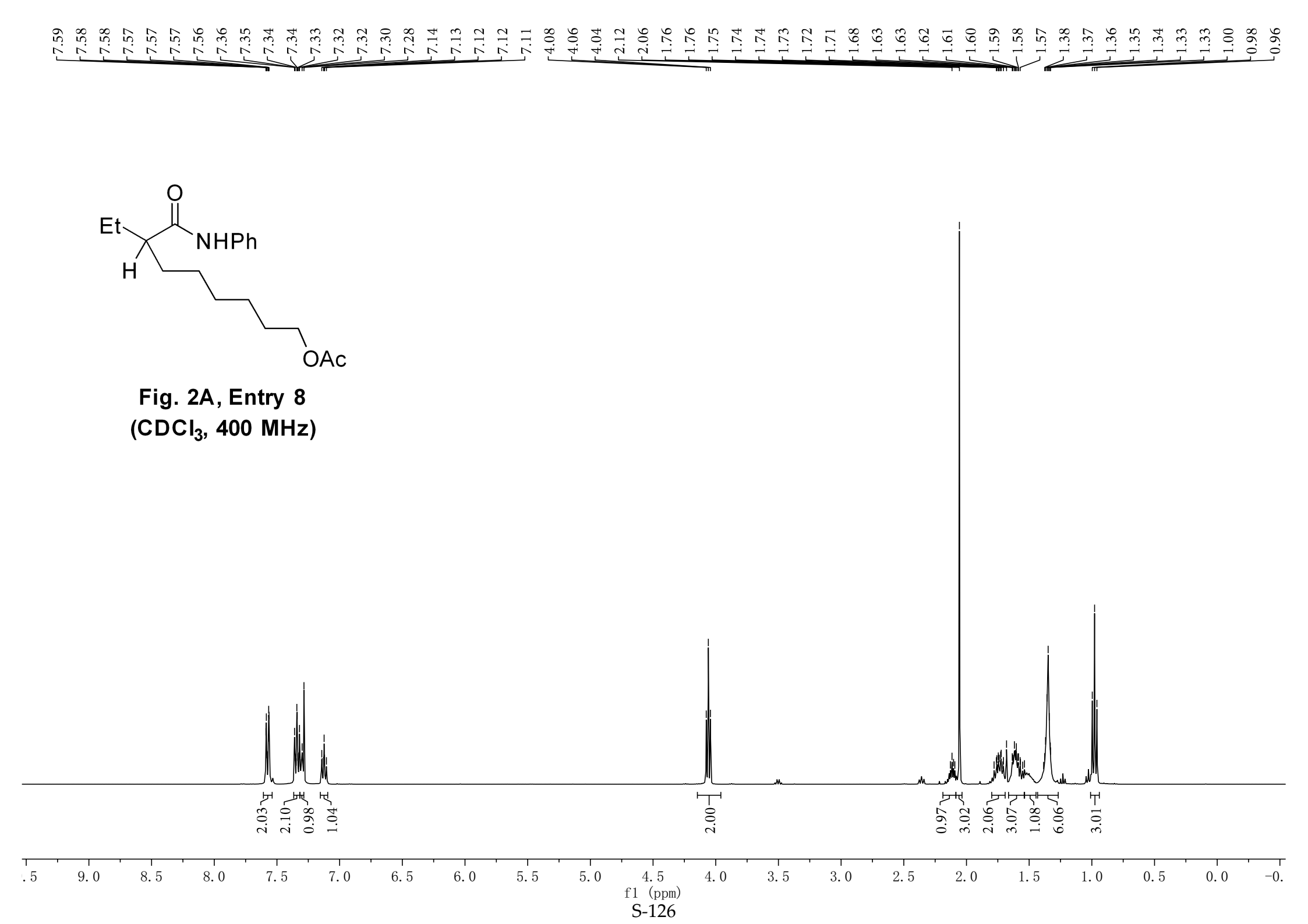

Fig. 2A, Entry 8
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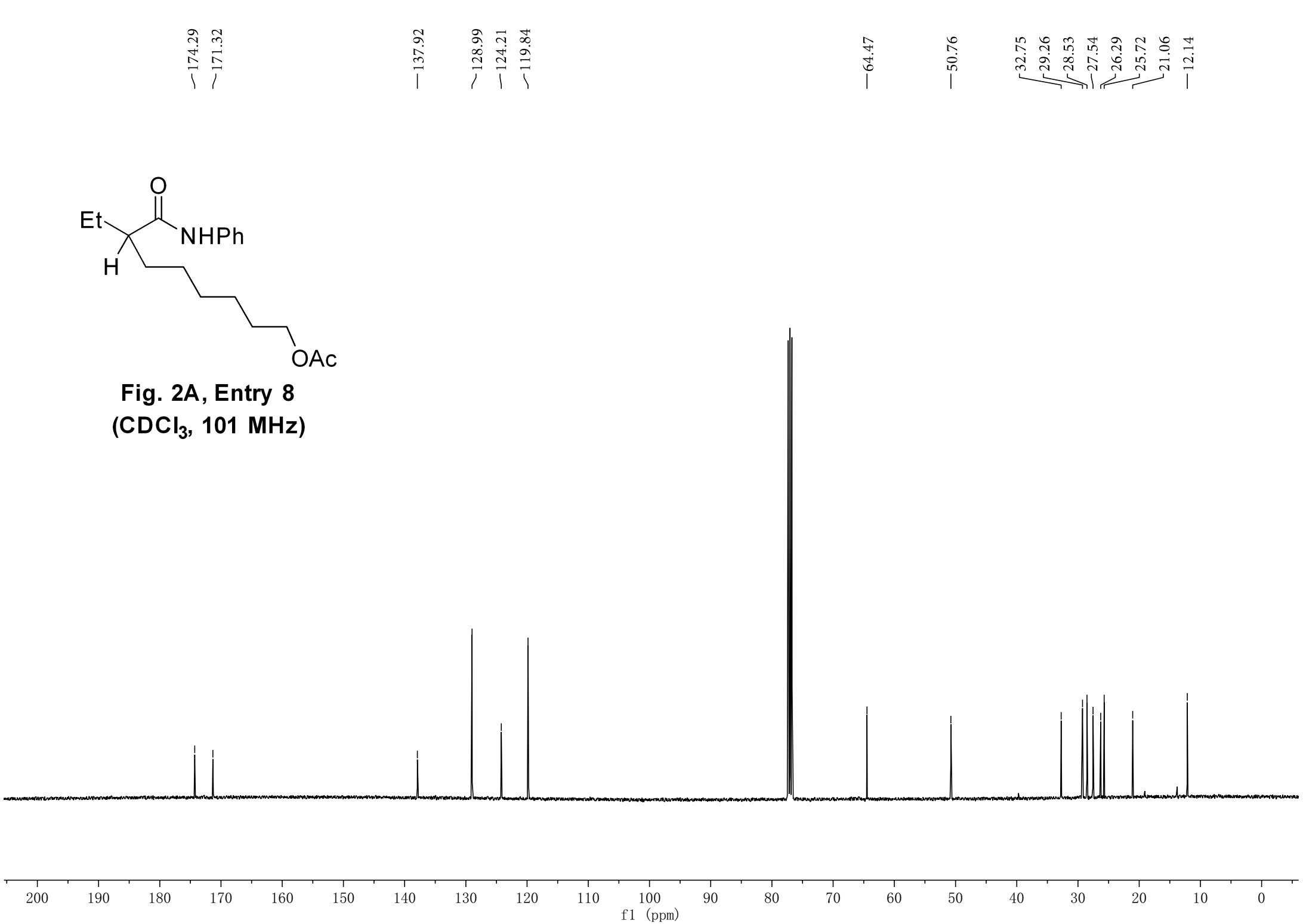

Fig. 2A, Entry 8
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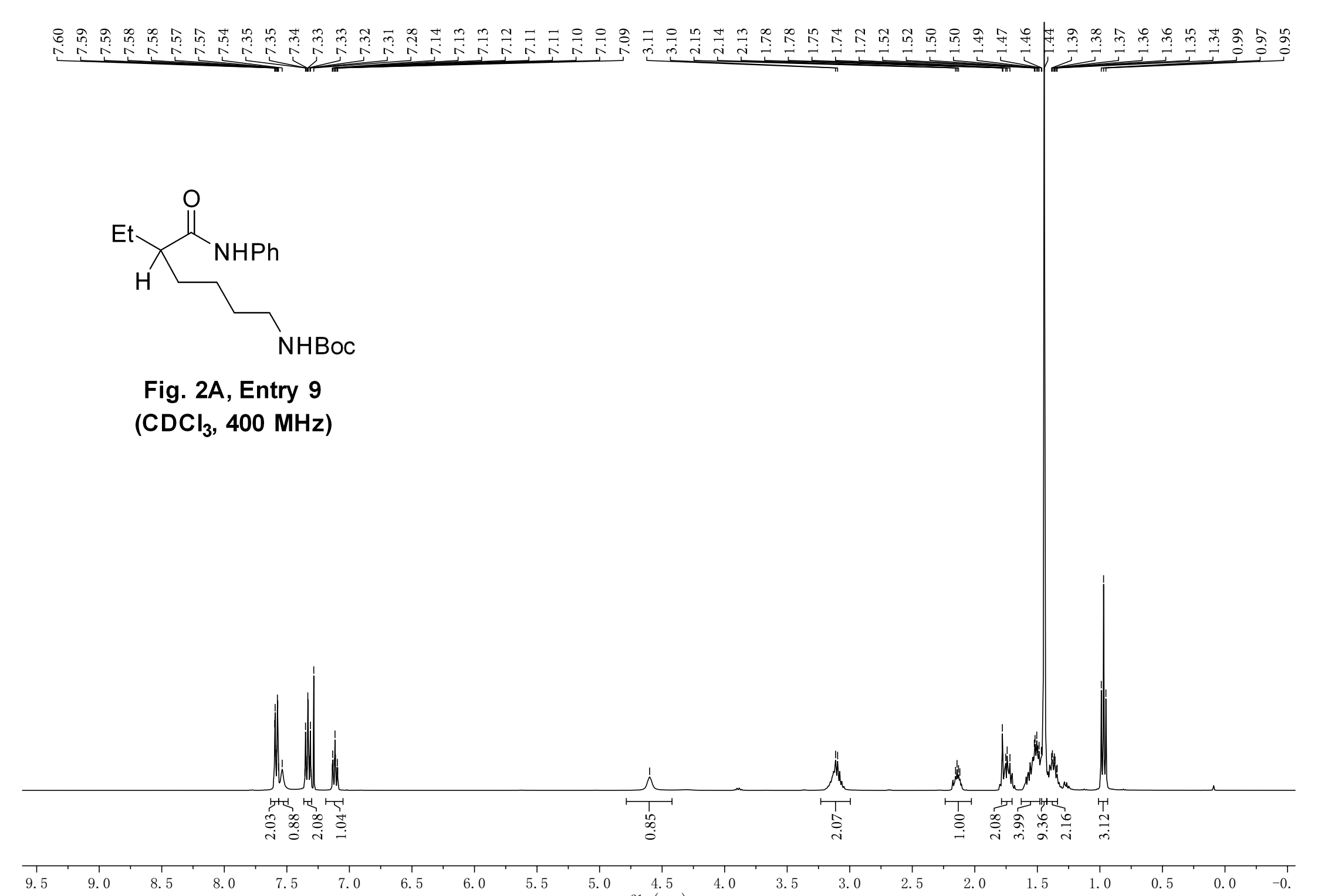


Fig. 2A, Entry 9
($CDCl_3$, 400 MHz)

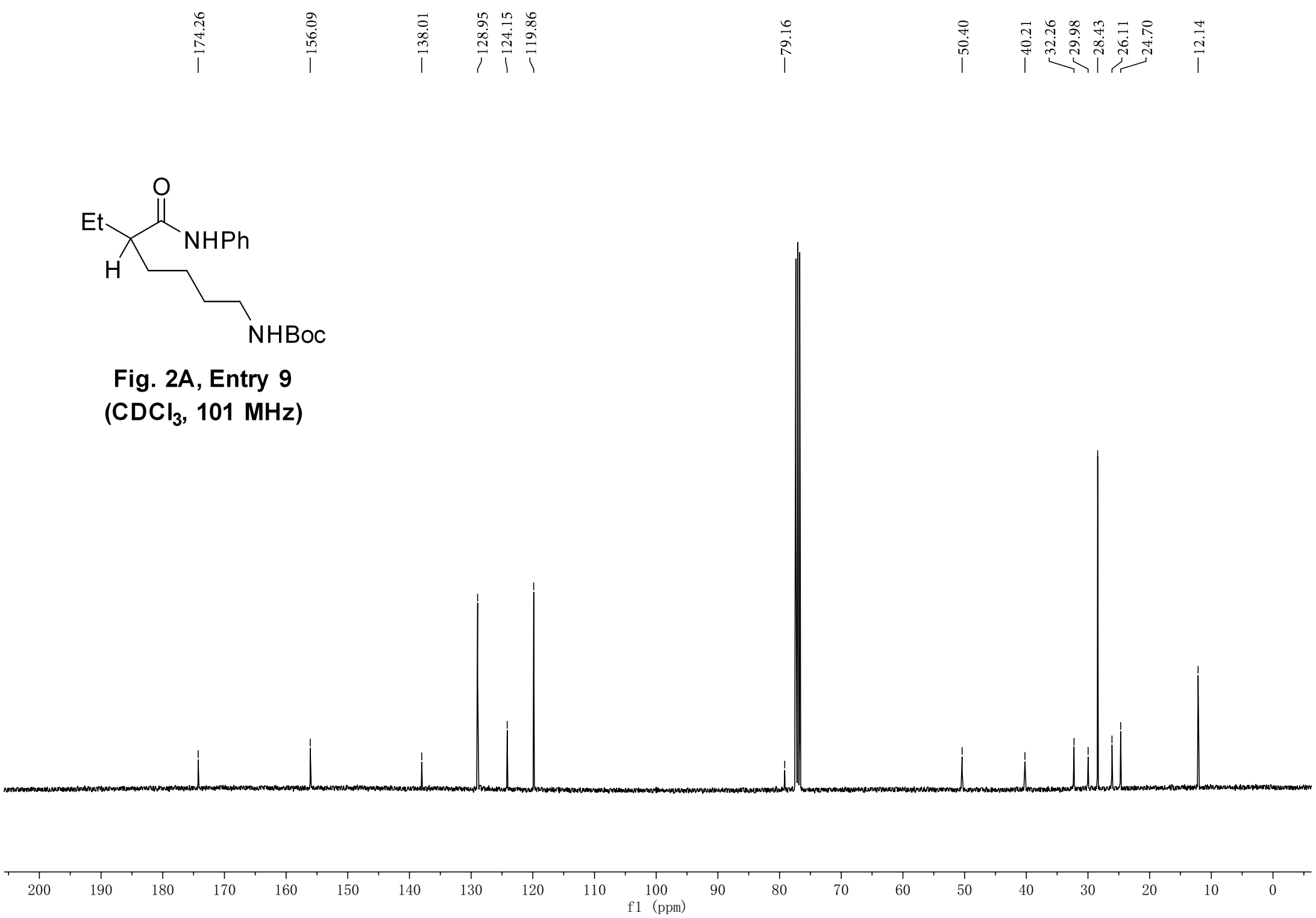


Fig. 2A, Entry 9
($CDCl_3$, 101 MHz)

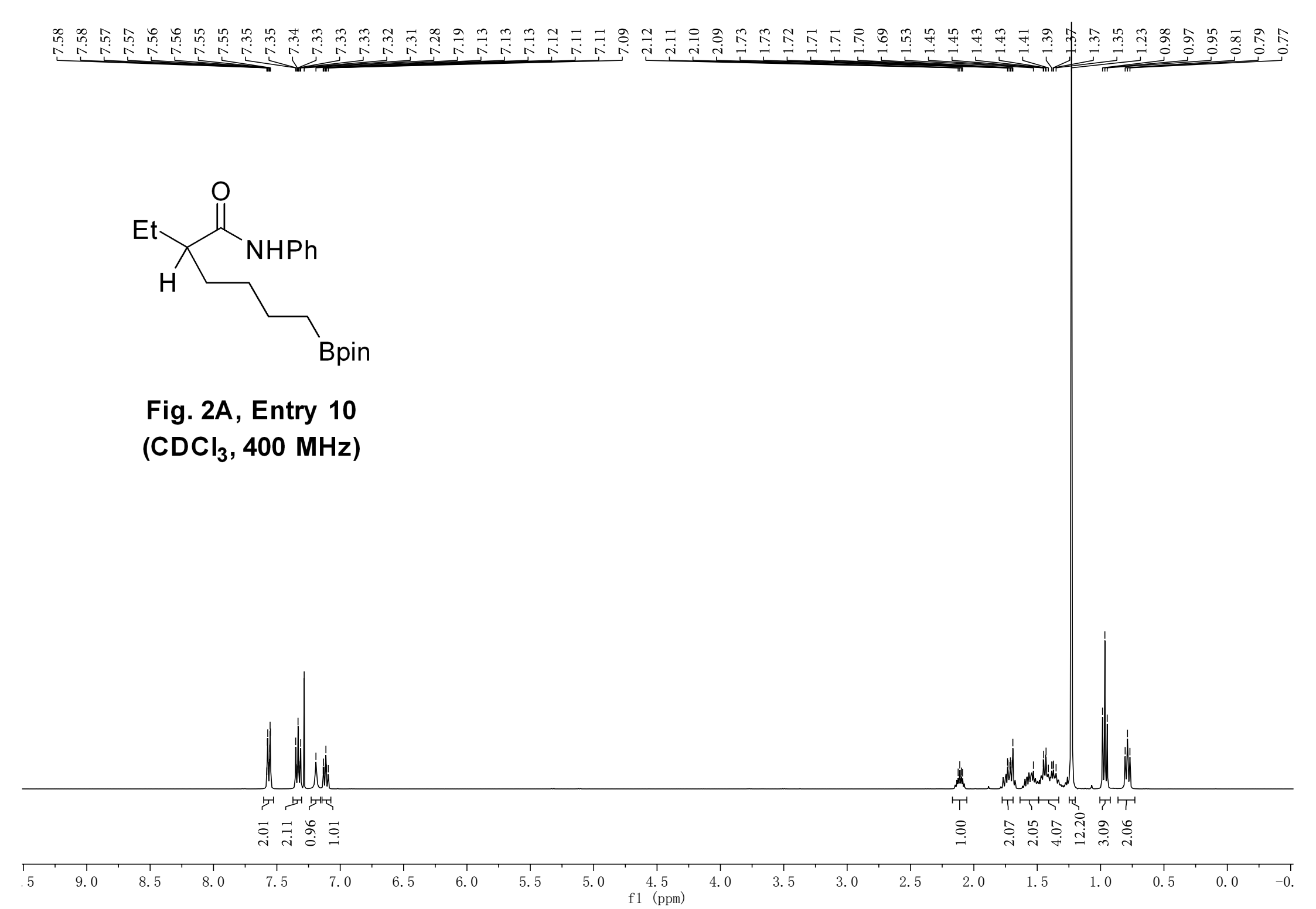


Fig. 2A, Entry 10
($CDCl_3$, 400 MHz)

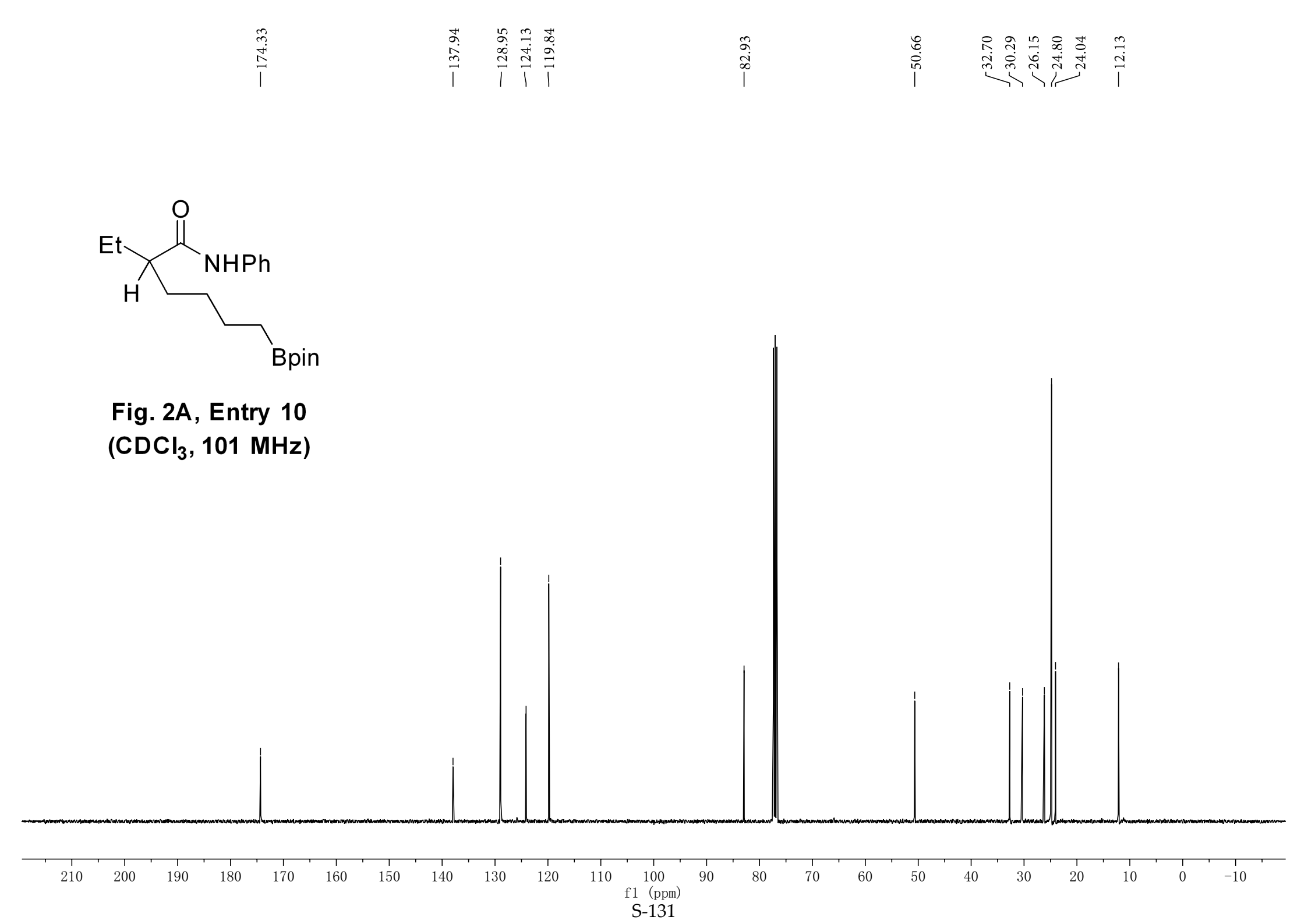
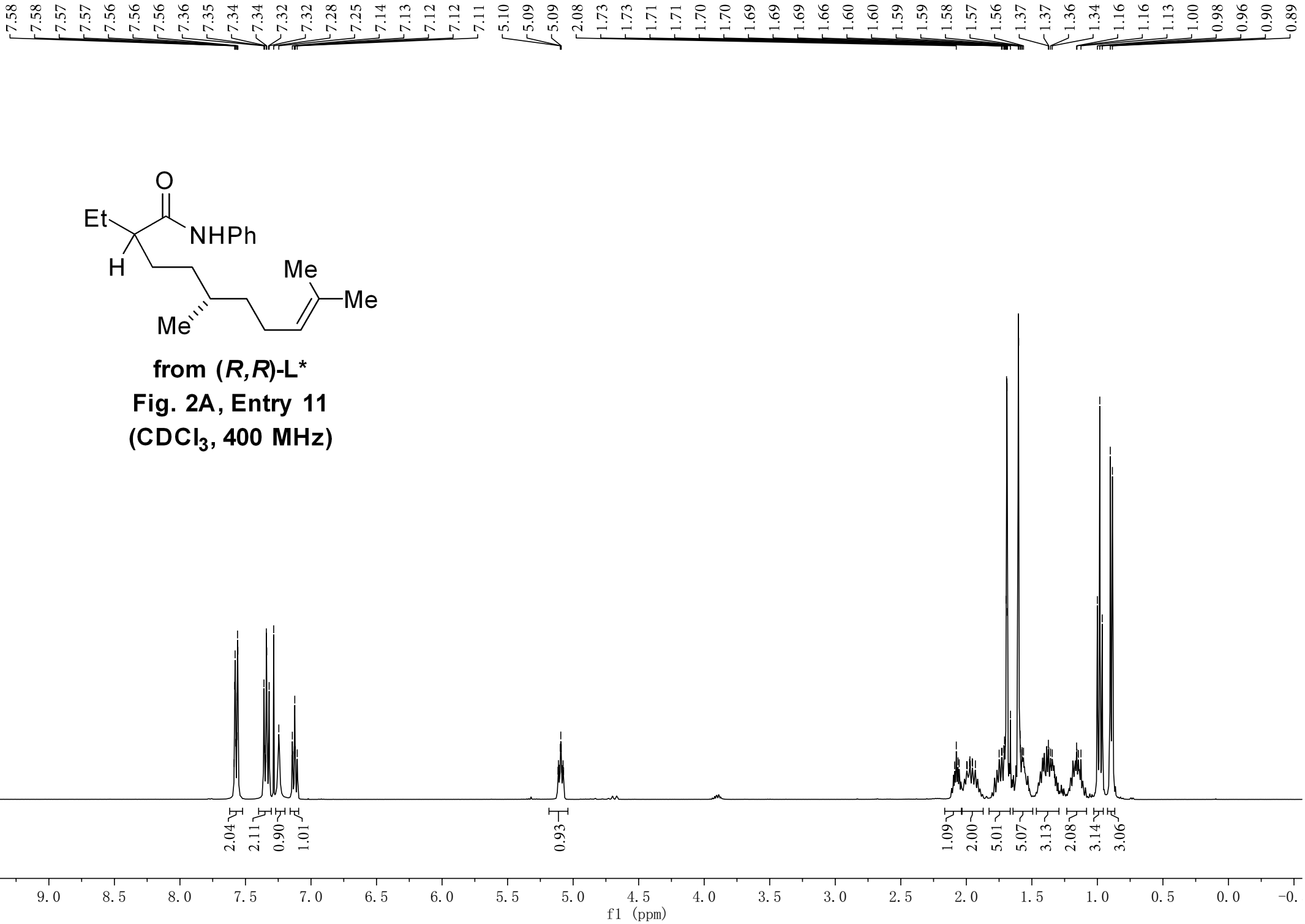
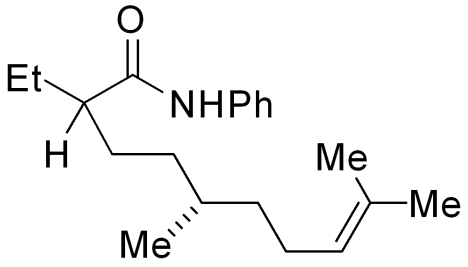
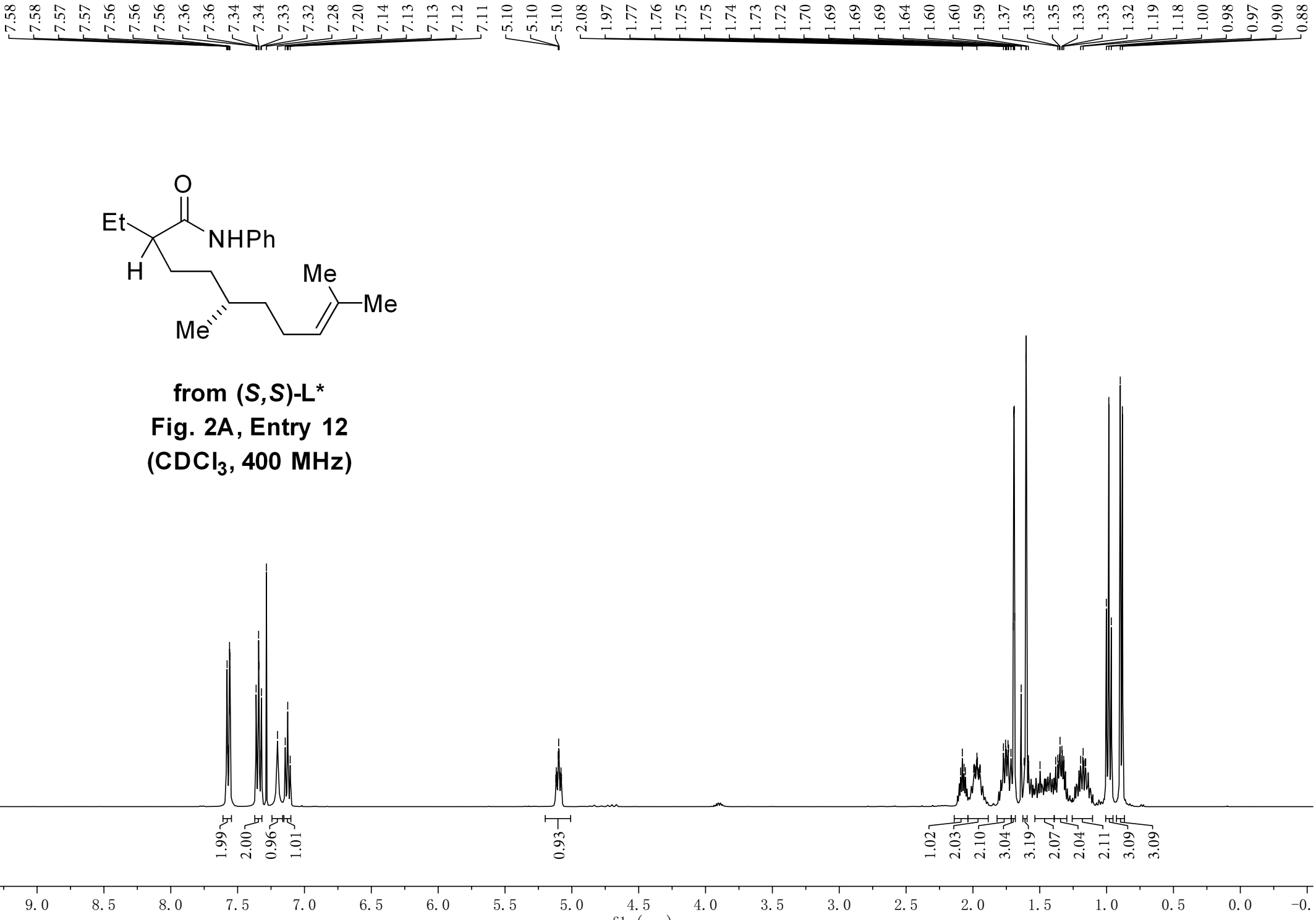


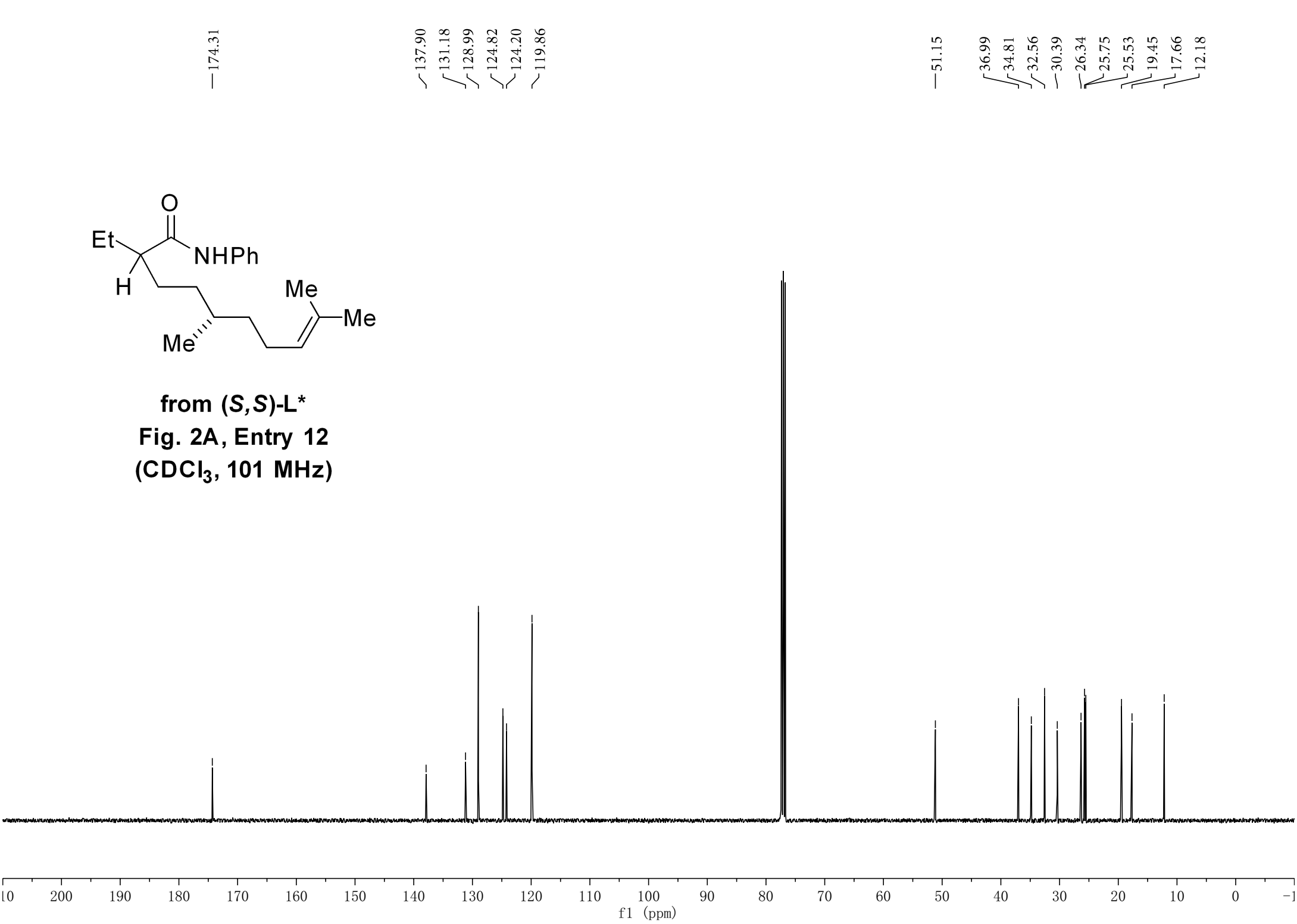
Fig. 2A, Entry 10
($CDCl_3$, 101 MHz)

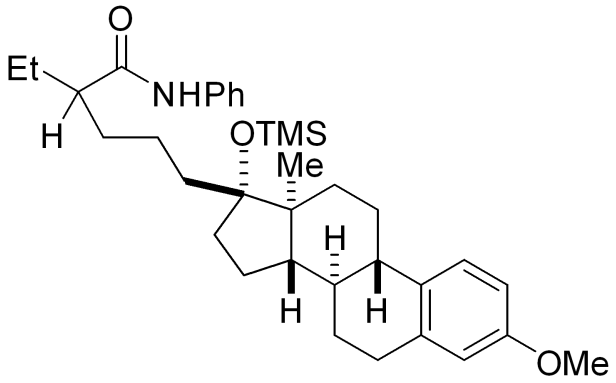

7.58 7.58 7.57 7.57 7.56 7.56 7.56 7.36 7.35 7.34 7.34 7.32 7.32 7.28 7.25 7.14 7.13 7.12 7.12 7.11
5.10 5.09 5.09
2.08 1.73 1.73 1.71 1.71 1.70 1.70 1.69 1.69 1.69 1.66 1.60 1.60 1.59 1.59 1.58 1.57 1.56 1.37 1.37 1.36 1.34 1.16 1.16 1.13 1.00 0.98 0.96 0.90 0.89
O
Et
NHPh
H
Me
Me
Me
from (R,R)-L*
Fig. 2A, Entry 11
(CDCl3, 400 MHz)
2.04 2.11 0.90 1.01
0.93
1.09 2.00 5.01 5.07 3.13 2.08 3.14 3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



from (*R,R*)-L*
Fig. 2A, Entry 11
($CDCl_3$, 101 MHz)


7.58 7.58 7.57 7.57 7.56 7.56 7.56 7.36 7.36 7.34 7.34 7.33 7.32 7.28 7.20 7.14 7.13 7.13 7.12 7.11
5.10 5.10 5.10
2.08 1.97 1.77 1.76 1.75 1.75 1.74 1.73 1.72 1.70 1.69 1.69 1.69 1.64 1.60 1.60 1.59 1.37 1.35 1.35 1.33 1.33 1.32 1.19 1.18 1.00 0.98 0.97 0.90 0.88
O
Et
NHPh
H
Me
Me
Me
from (S,S)-L*
Fig. 2A, Entry 12
(CDCl3, 400 MHz)
1.99 2.00 0.96 1.01
0.93
1.02 2.03 2.10 3.04 3.19 2.07 2.04 2.11 3.09 3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

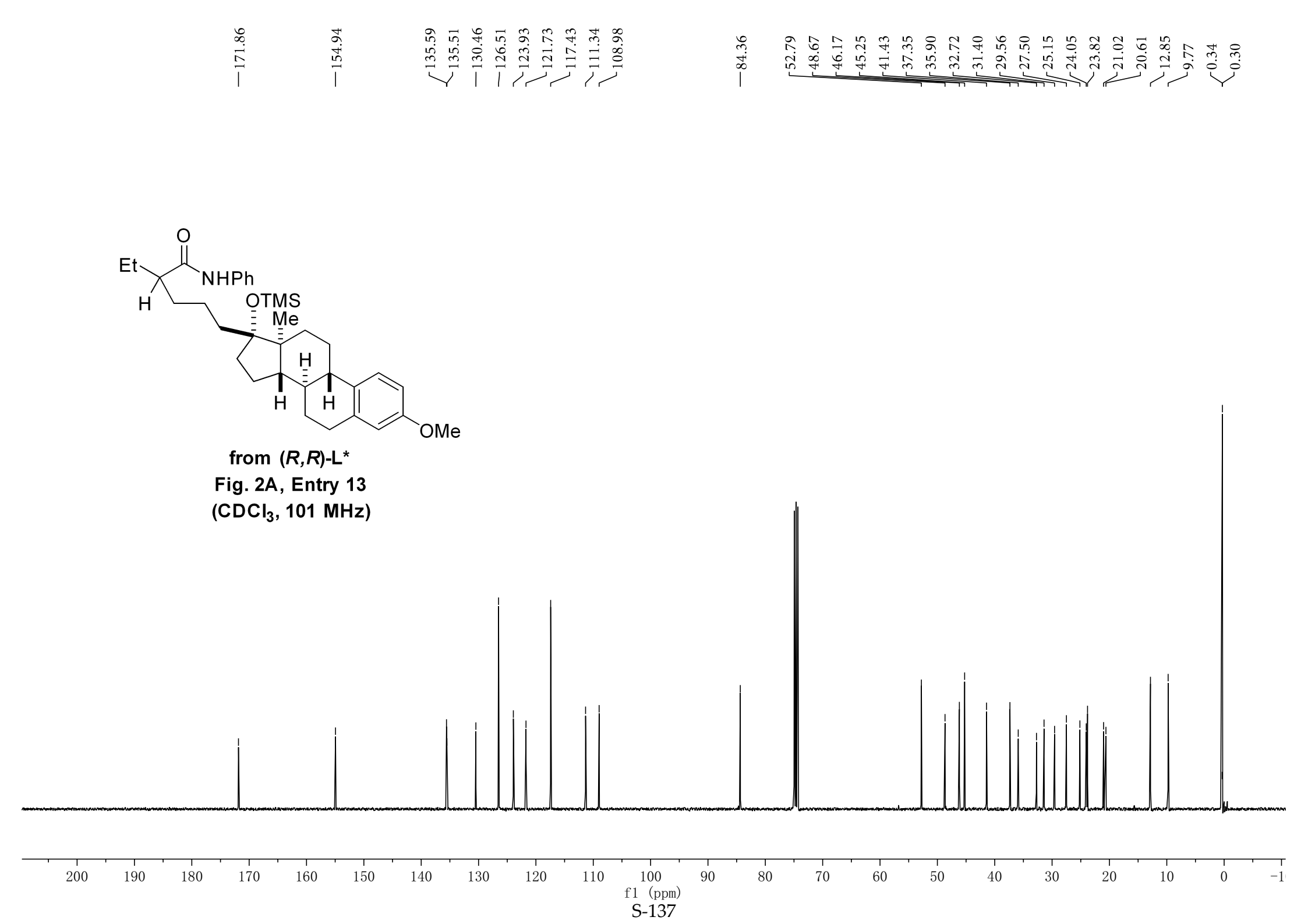

174.31
137.90
131.18
128.99
124.82
124.20
119.86
51.15
36.99
34.81
32.56
30.39
26.34
25.75
25.53
19.45
17.66
12.18
O
Et
NHPh
H
Me
Me
Me
from (S,S)-L*
Fig. 2A, Entry 12
(CDCl3, 101 MHz)
f1 (ppm)



from (*R,R*)-L*

Fig. 2A, Entry 13

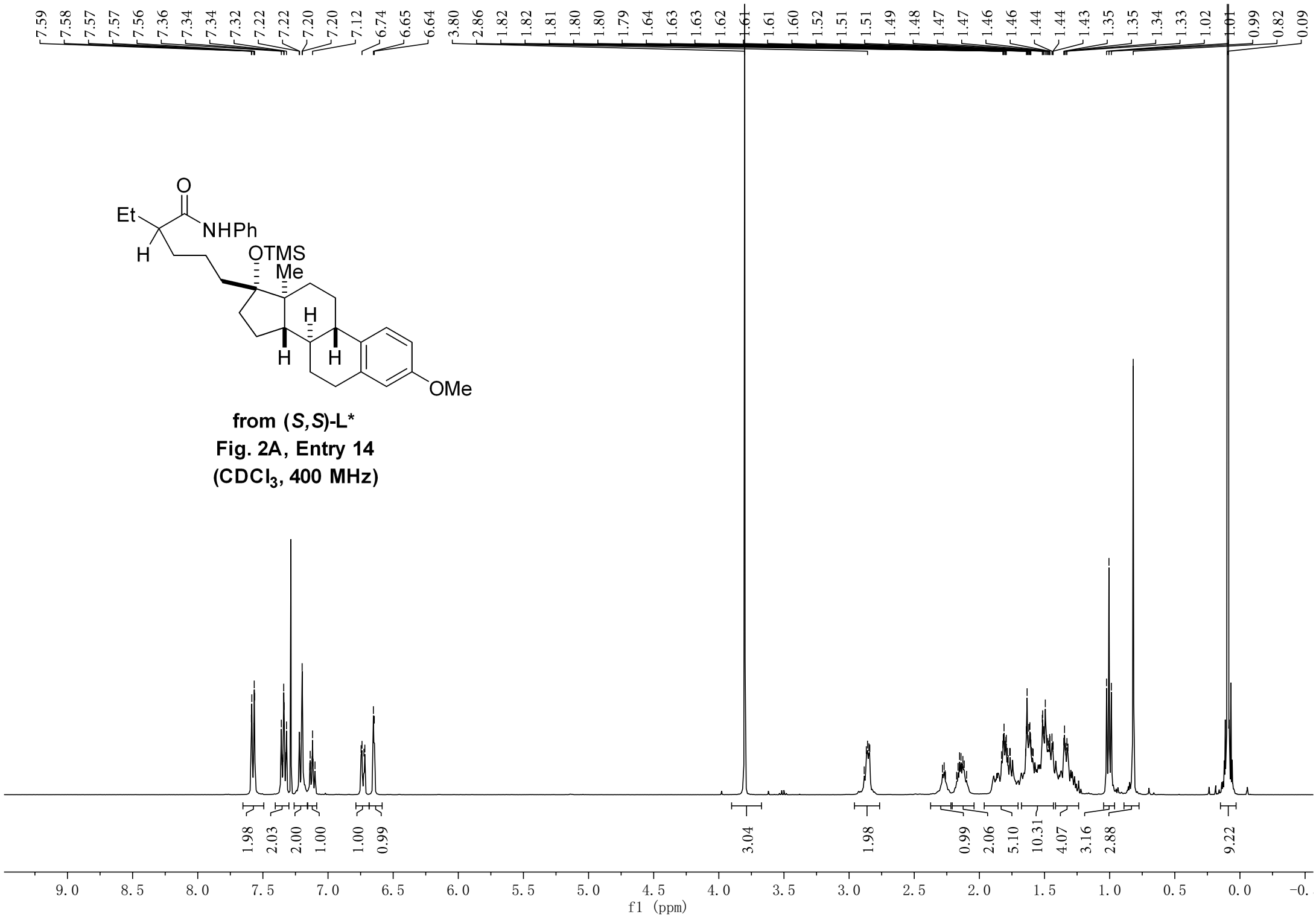
($CDCl_3$, 400 MHz)

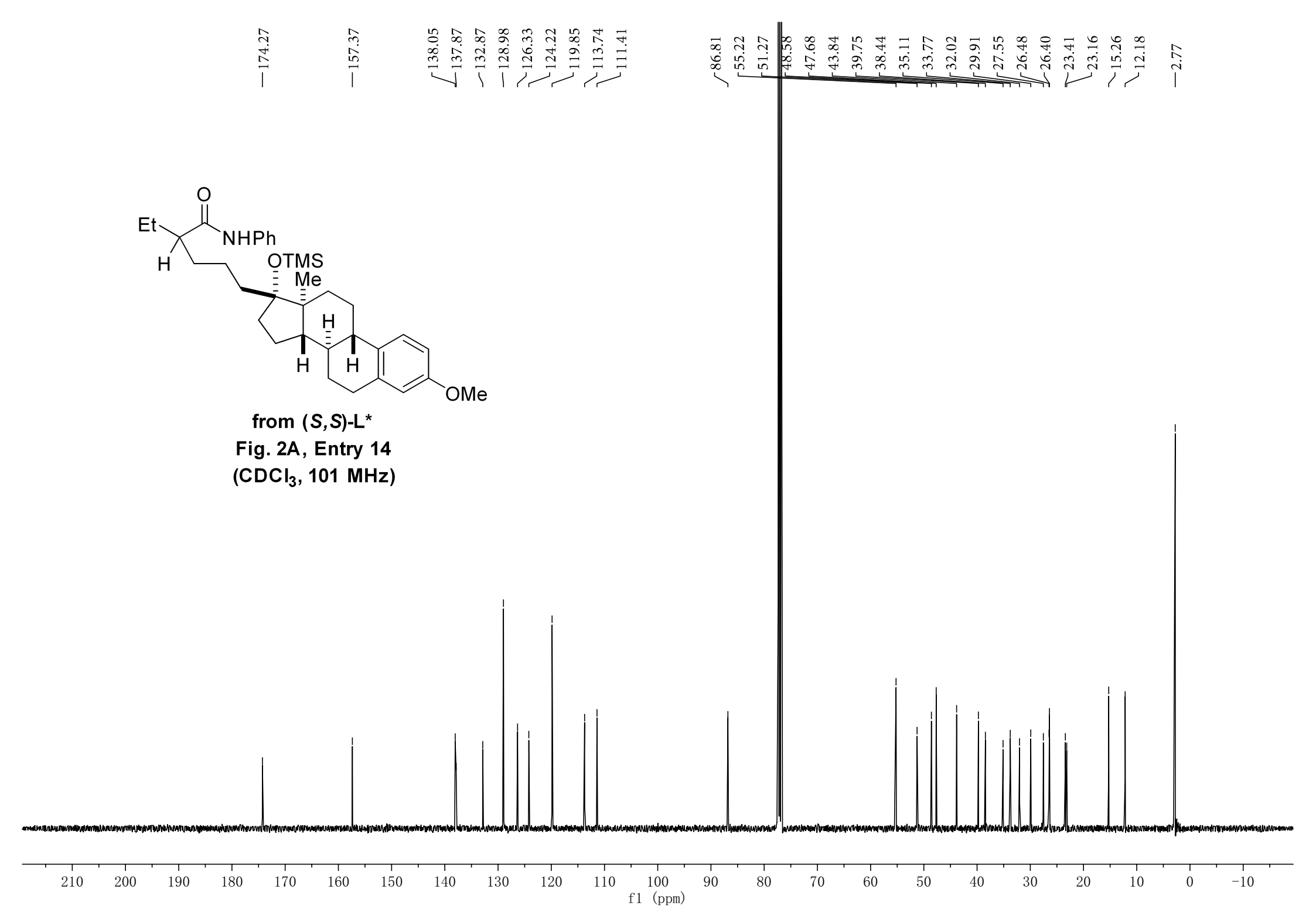


from (*R*,*R*)-L*

Fig. 2A, Entry 13

($CDCl_3$, 101 MHz)


7.59 7.58 7.57 7.57 7.56 7.36 7.34 7.34 7.32 7.22 7.22 7.20 7.20 7.12 6.74 6.65 6.64
3.80 2.86 1.82 1.82 1.81 1.80 1.80 1.79 1.64 1.63 1.63 1.62 1.61 1.61 1.60 1.52 1.51 1.51 1.49 1.48 1.47 1.47 1.46 1.46 1.44 1.44 1.43 1.35 1.35 1.34 1.33 1.02 1.01 0.99 0.82 0.09
O
Et
NHPh
H
OTMS
Me
H
H
H
OMe
from (S,S)-L*
Fig. 2A, Entry 14
(CDCl3, 400 MHz)
1.98 2.03 2.00 1.00 1.00 0.99 3.04 1.98 0.99 2.06 5.10 10.31 4.07 3.16 2.88 9.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.27
157.37
138.05
137.87
132.87
128.98
126.33
124.22
119.85
113.74
111.41
86.81
55.22
51.27
48.58
47.68
43.84
39.75
38.44
35.11
33.77
32.02
29.91
27.55
26.48
26.40
23.41
23.16
15.26
12.18
2.77
O
Et
NHPh
H
OTMS
Me
H
H
H
OMe
from (S,S)-L*
Fig. 2A, Entry 14
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

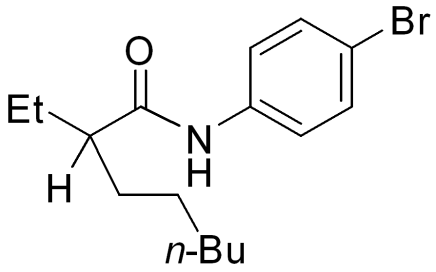


Fig. 2A, Entry 15
($CDCl_3$, 400 MHz)

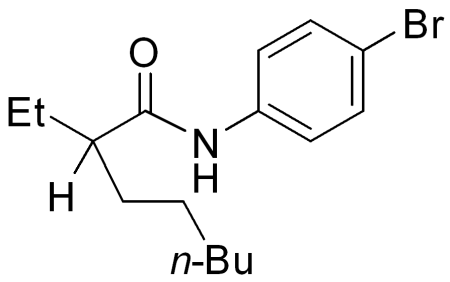


Fig. 2A, Entry 15
($CDCl_3$, 101 MHz)

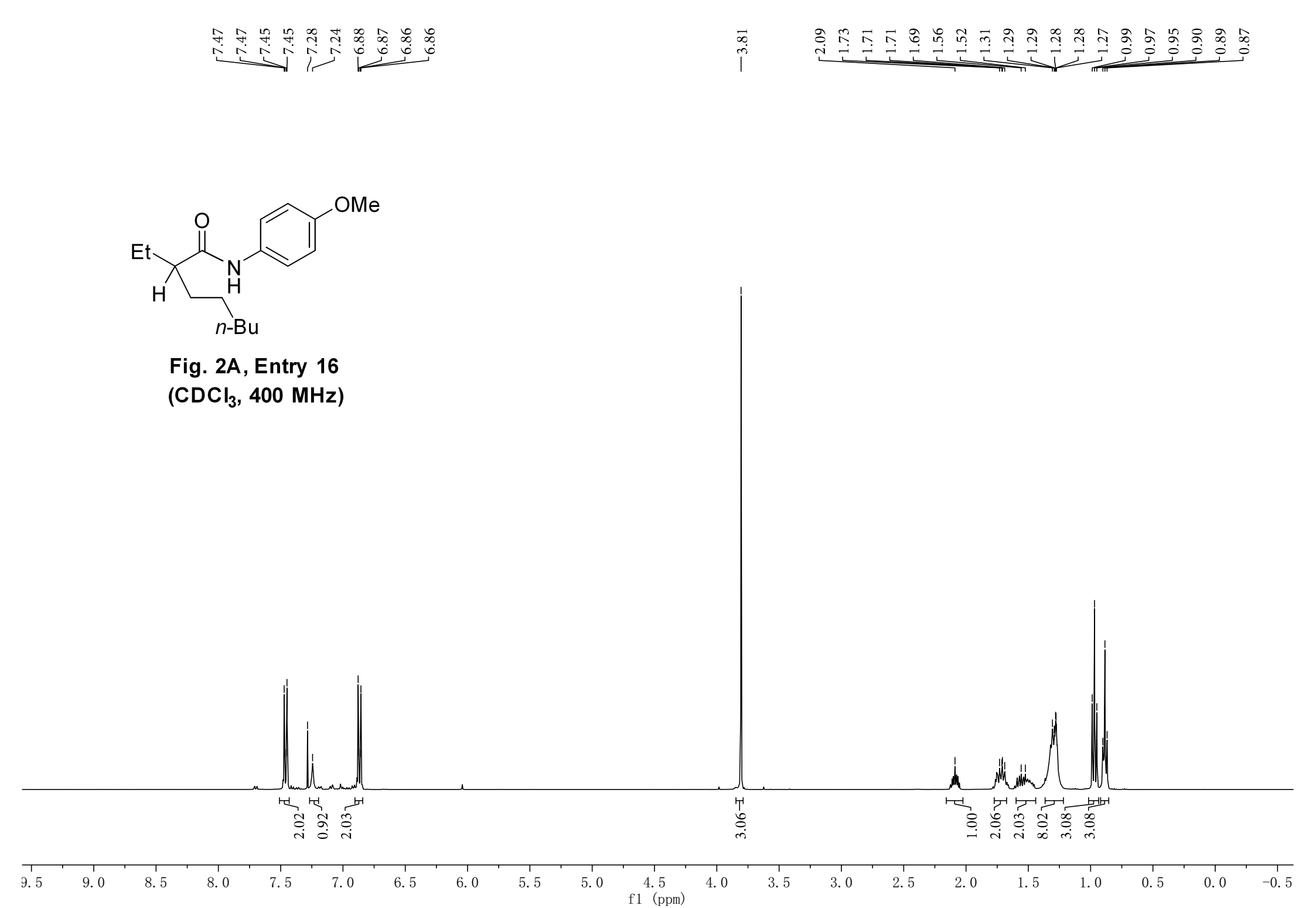


Fig. 2A, Entry 16
($CDCl_3$, 400 MHz)

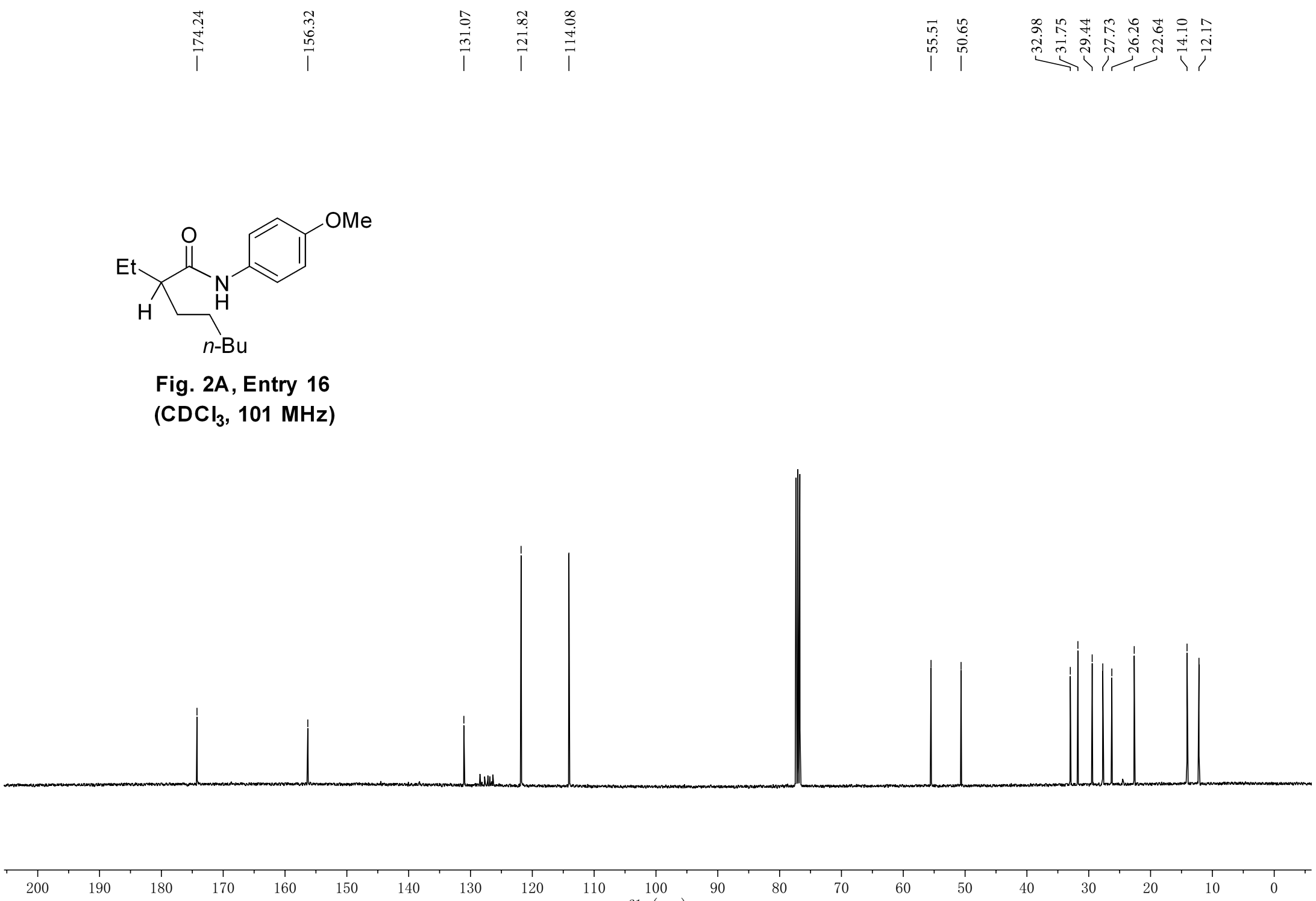


Fig. 2A, Entry 16
($CDCl_3$, 101 MHz)

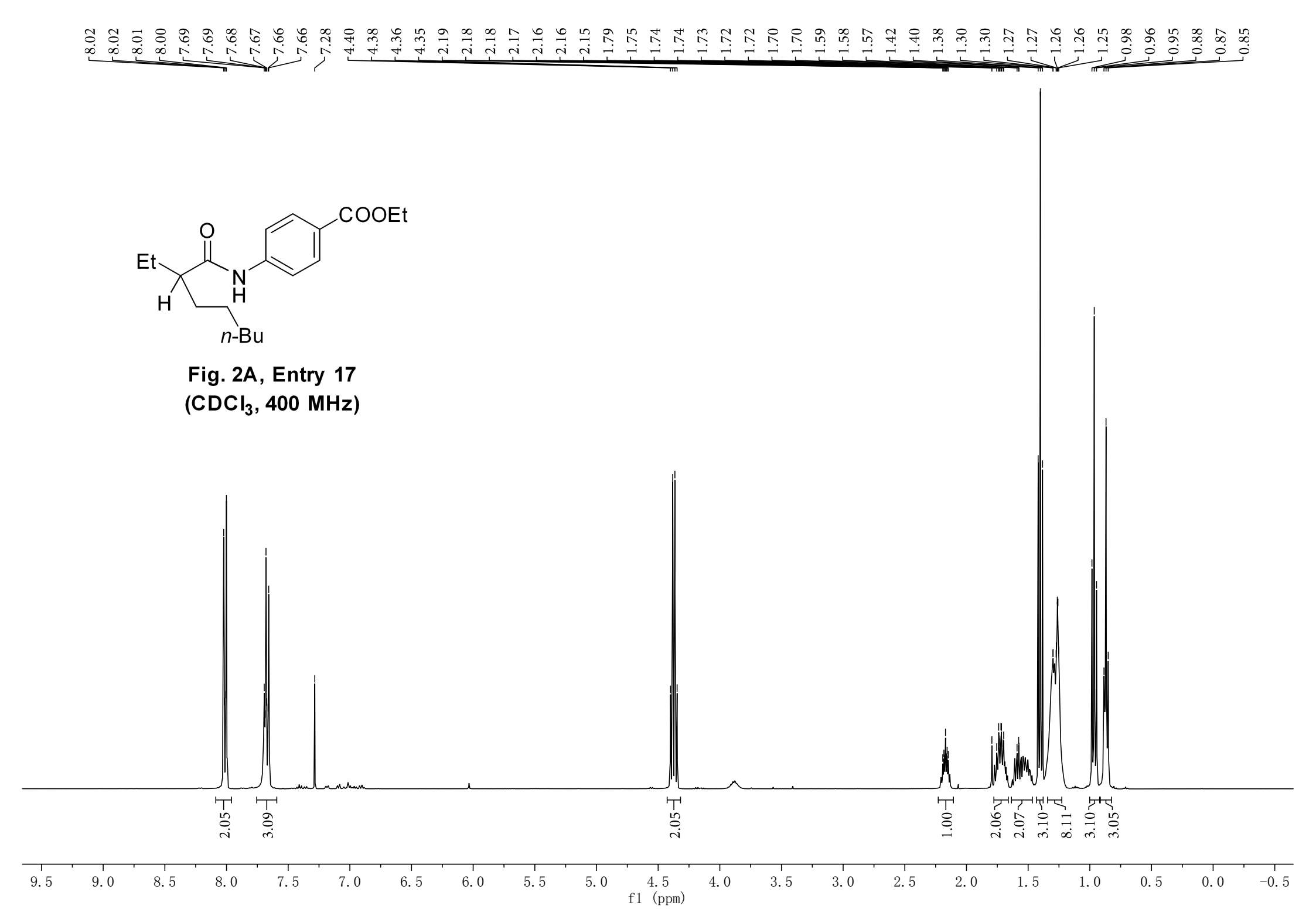


Fig. 2A, Entry 17
($CDCl_3$, 400 MHz)

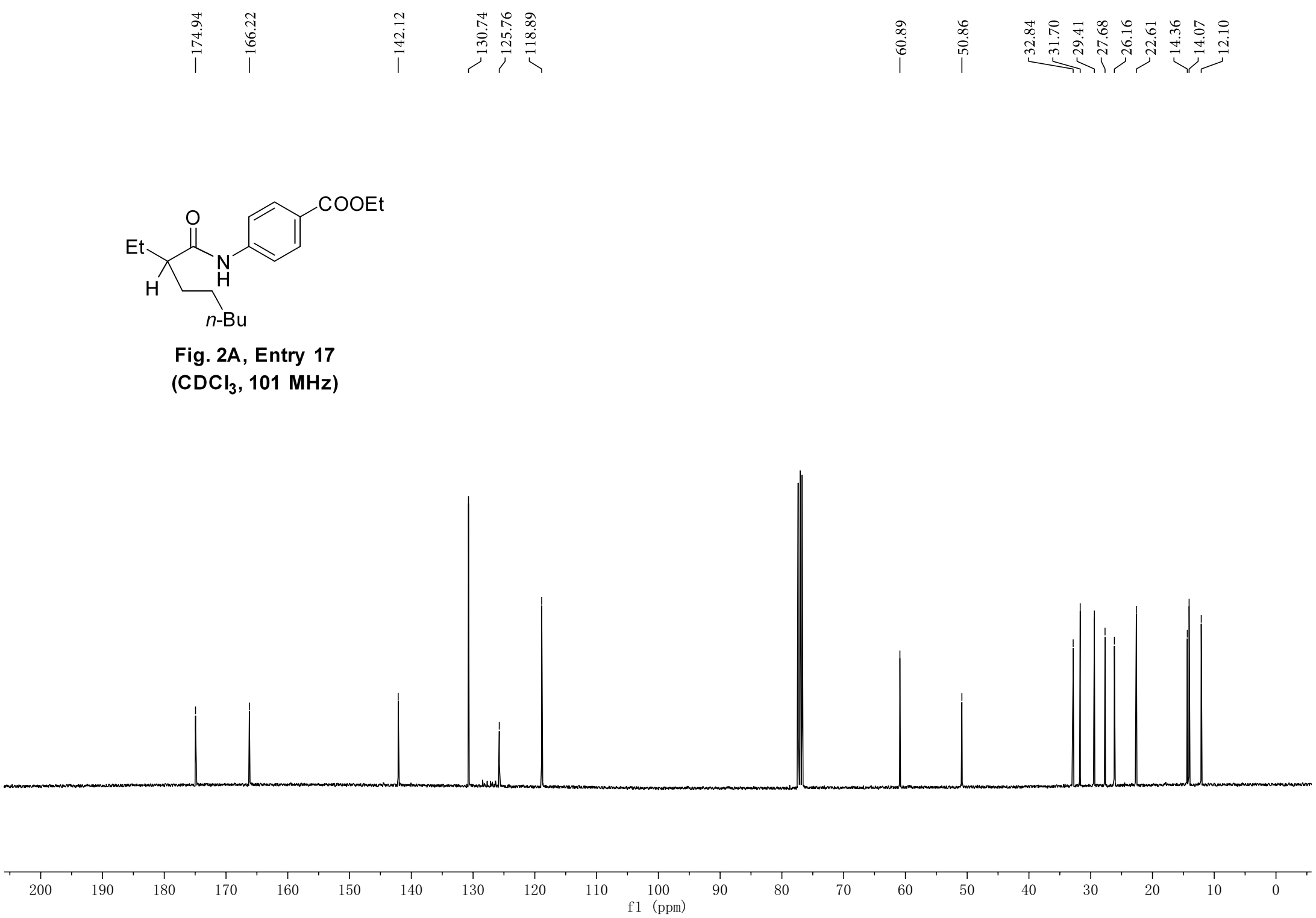
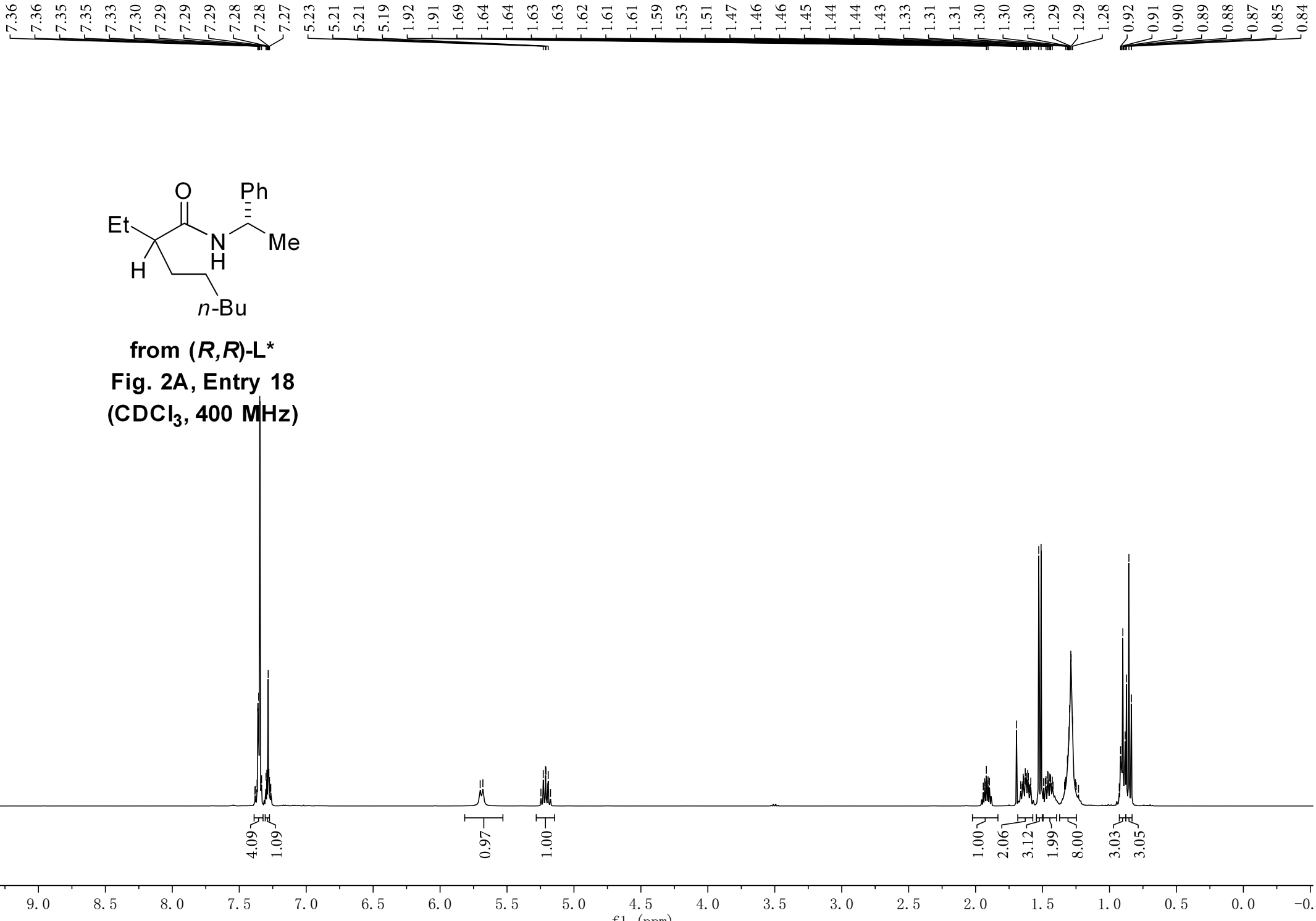
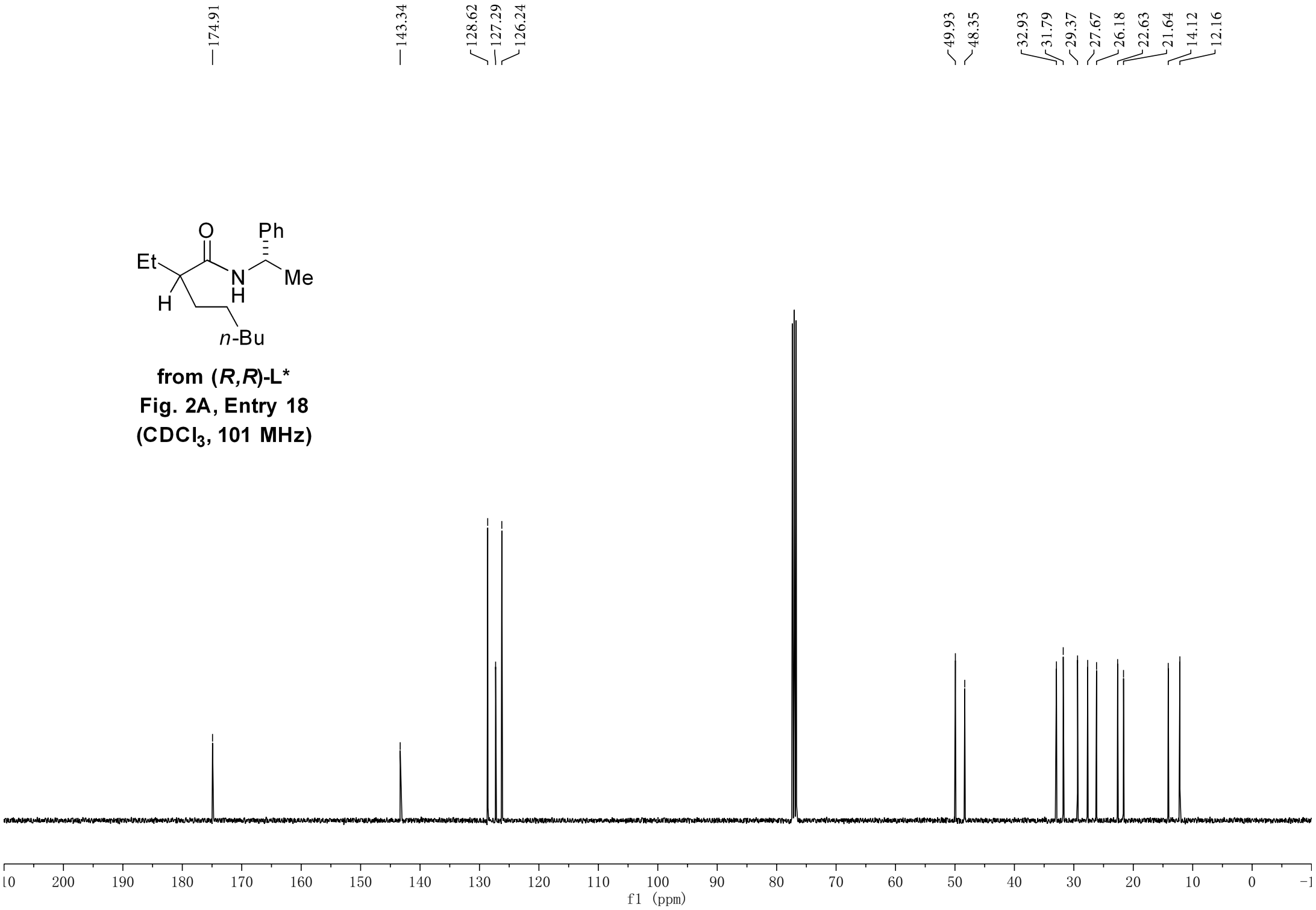
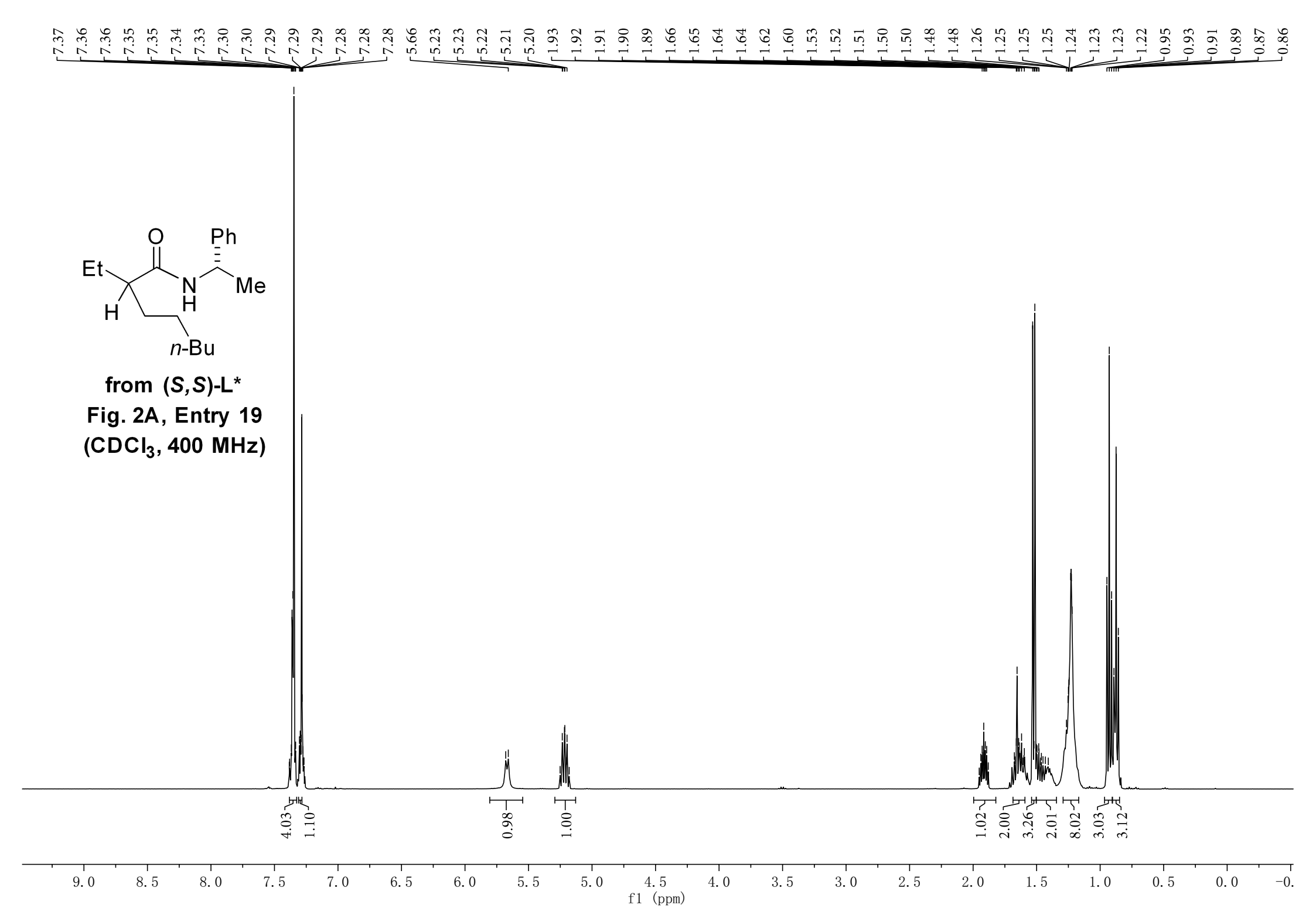
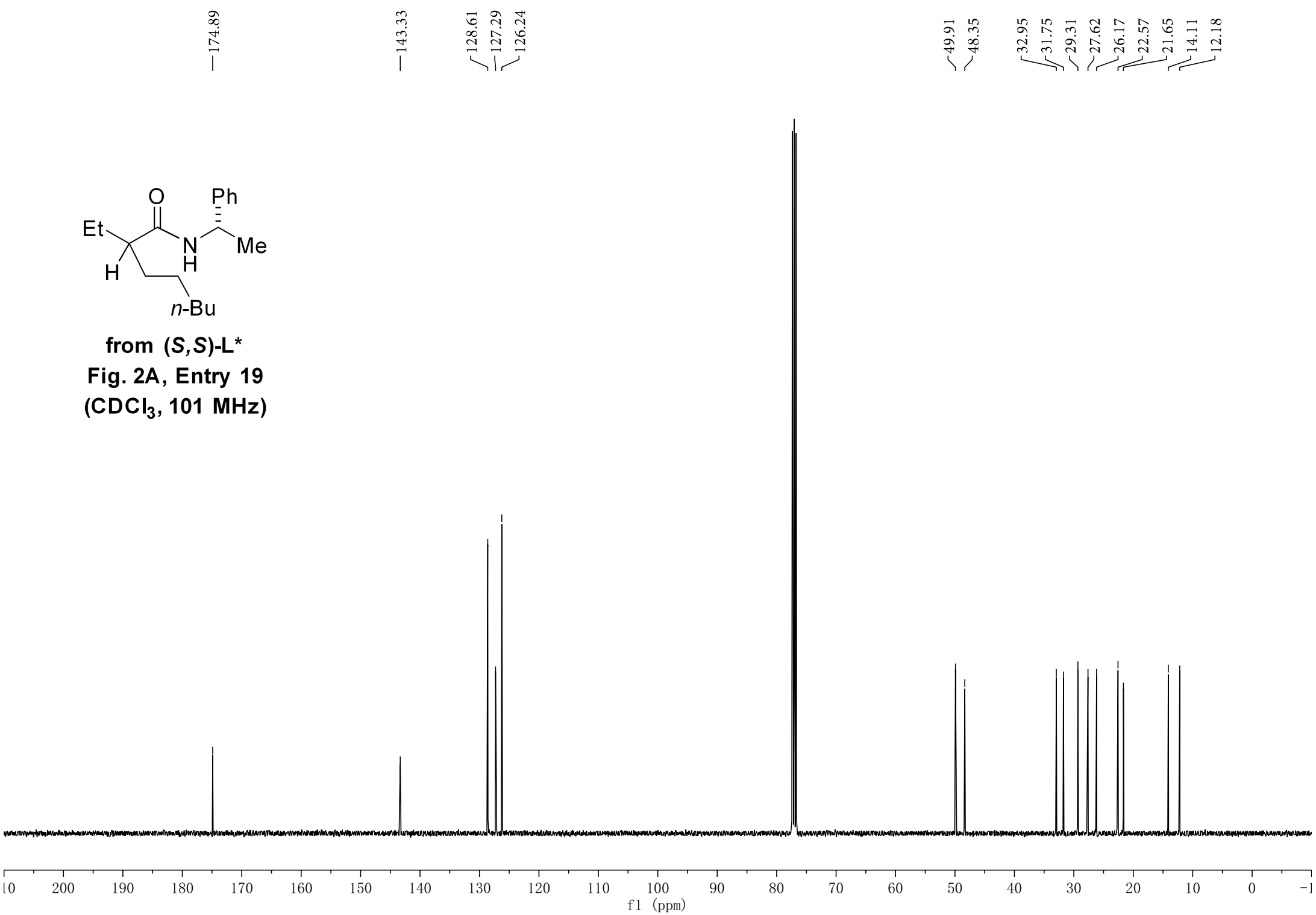


Fig. 2A, Entry 17
($CDCl_3$, 101 MHz)


7.36 7.36 7.35 7.35 7.33 7.30 7.29 7.29 7.29 7.28 7.28 7.27
5.23 5.21 5.21 5.19 1.92 1.91 1.69 1.64 1.64 1.63 1.63 1.62 1.61 1.61 1.59 1.53 1.51 1.47 1.46 1.46 1.45 1.44 1.44 1.43 1.33 1.31 1.31 1.30 1.30 1.30 1.29 1.29 1.28
0.92 0.91 0.90 0.89 0.88 0.87 0.85 0.84
O
Ph
Et
N
Me
H
H
n-Bu
from (R,R)-L*
Fig. 2A, Entry 18
(CDCl3, 400 MHz)
4.09 1.09 0.97 1.00 1.00 2.06 3.12 1.99 8.00 3.03 3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


174.91
143.34
128.62
127.29
126.24
49.93
48.35
32.93
31.79
29.37
27.67
26.18
22.63
21.64
14.12
12.16
O
Ph
Et
N
H
Me
H
n-Bu
from (R,R)-L*
Fig. 2A, Entry 18
(CDCl3, 101 MHz)
f1 (ppm)


7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28
5.66 5.23 5.23 5.22 5.21 5.20 1.93 1.92 1.91 1.90 1.89 1.66 1.65 1.64 1.64 1.62 1.60 1.53 1.52 1.51 1.50 1.50 1.48 1.48 1.26 1.25 1.25 1.25 1.24 1.23 1.23 1.22 0.95 0.93 0.91 0.89 0.87 0.86
O
Ph
Et
N
H
Me
H
n-Bu
from (S,S)-L*
Fig. 2A, Entry 19
(CDCl3, 400 MHz)
4.03 1.10 0.98 1.00 1.02 2.00 3.26 2.01 8.02 3.03 3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


174.89
143.33
128.61
127.29
126.24
49.91
48.35
32.95
31.75
29.31
27.62
26.17
22.57
21.65
14.11
12.18
O
Ph
Et
N
H
Me
H
n-Bu
from (S,S)-L*
Fig. 2A, Entry 19
(CDCl3, 101 MHz)
f1 (ppm)

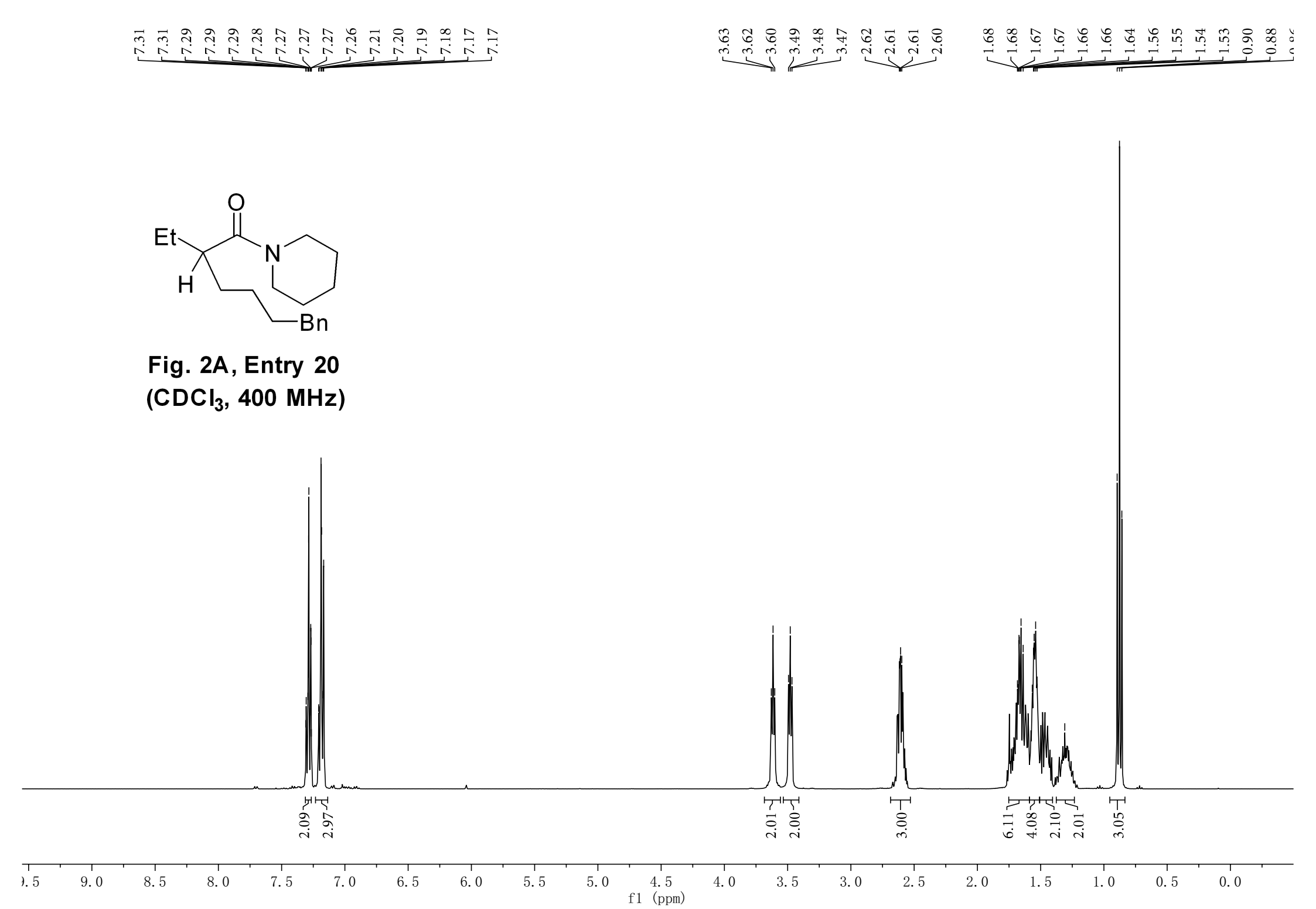


Fig. 2A, Entry 20
($CDCl_3$, 400 MHz)

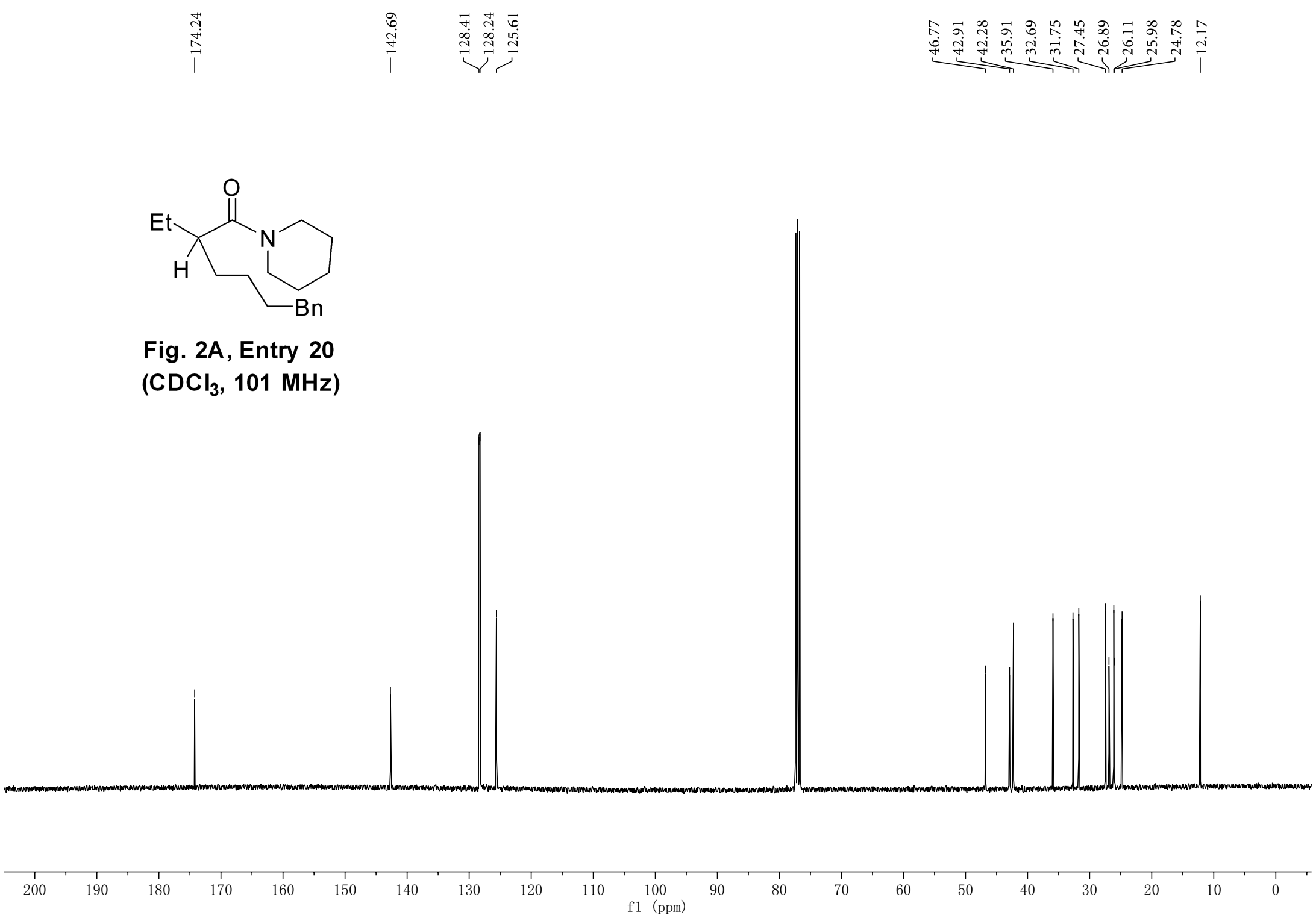


Fig. 2A, Entry 20
($CDCl_3$, 101 MHz)

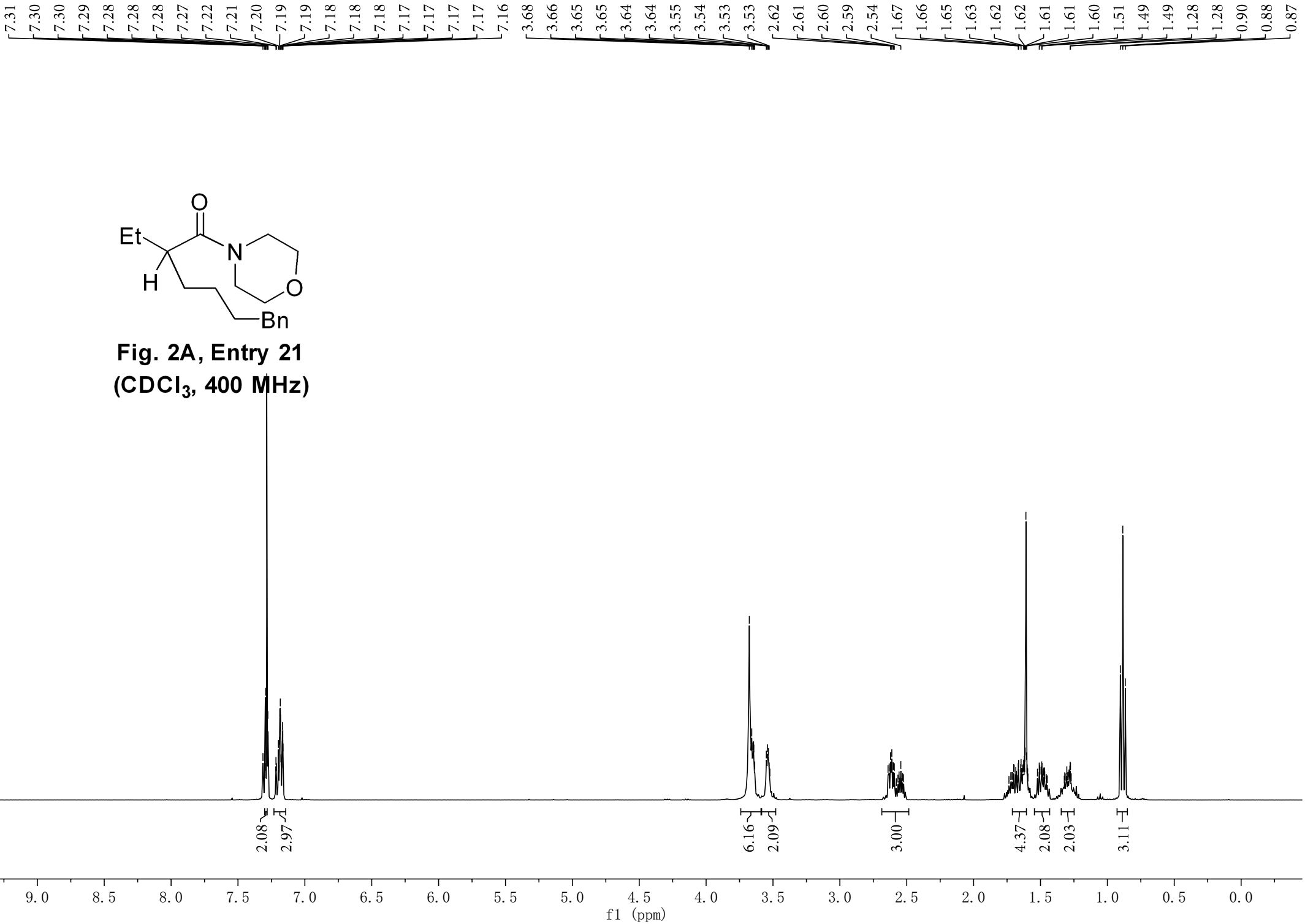


Fig. 2A, Entry 21
($CDCl_3$, 400 MHz)

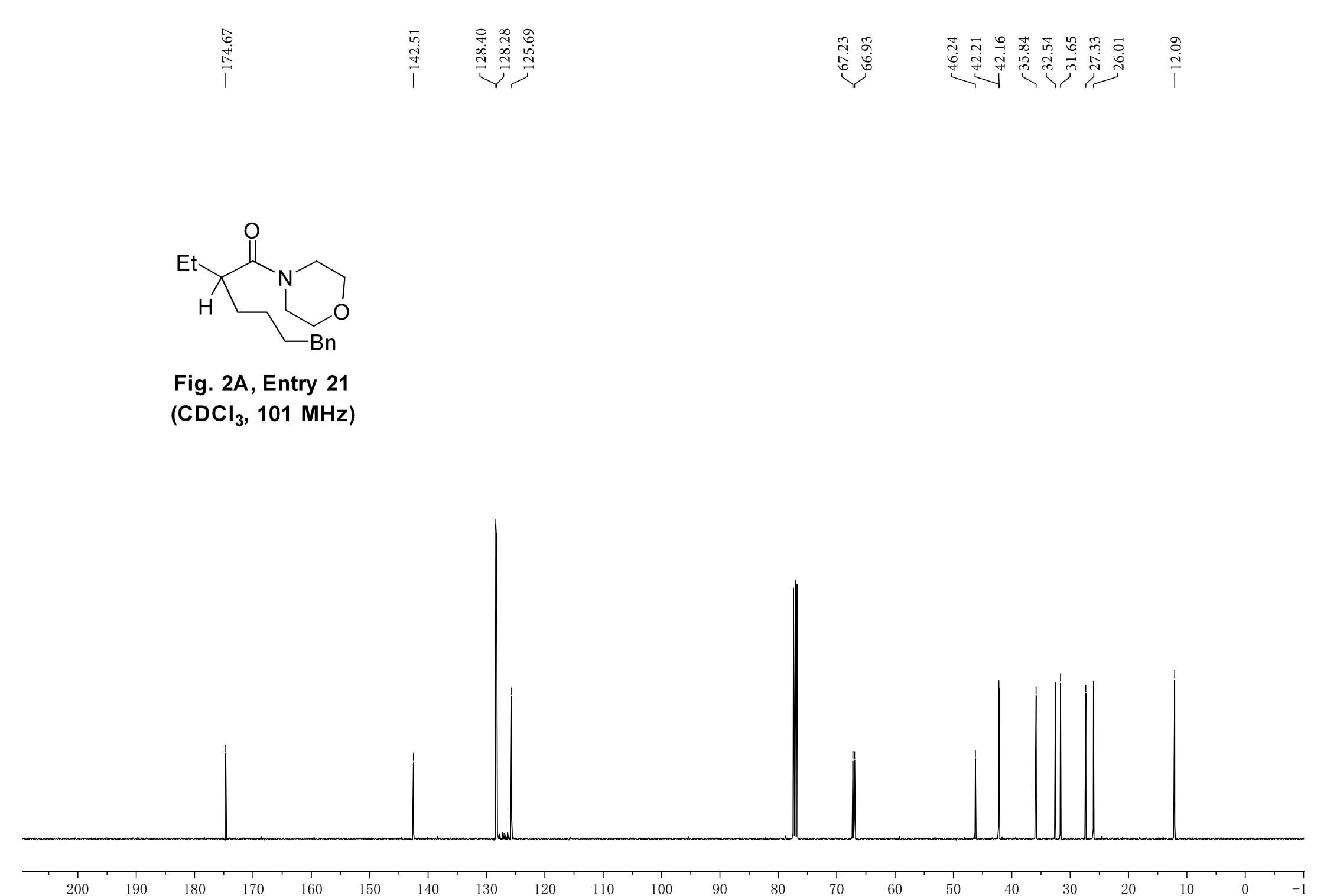


Fig. 2A, Entry 21
($CDCl_3$, 101 MHz)

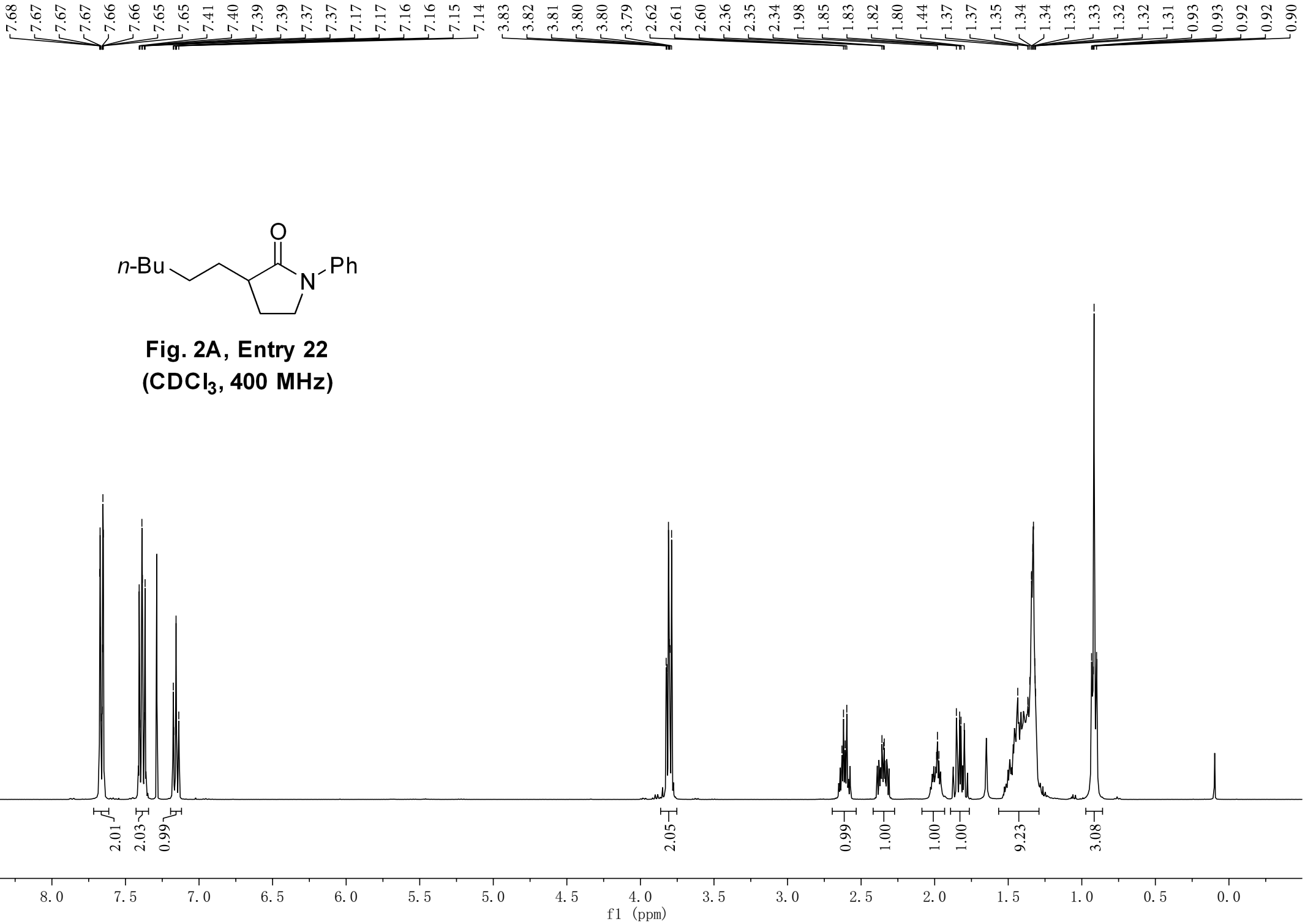


Fig. 2A, Entry 22
($CDCl_3$, 400 MHz)

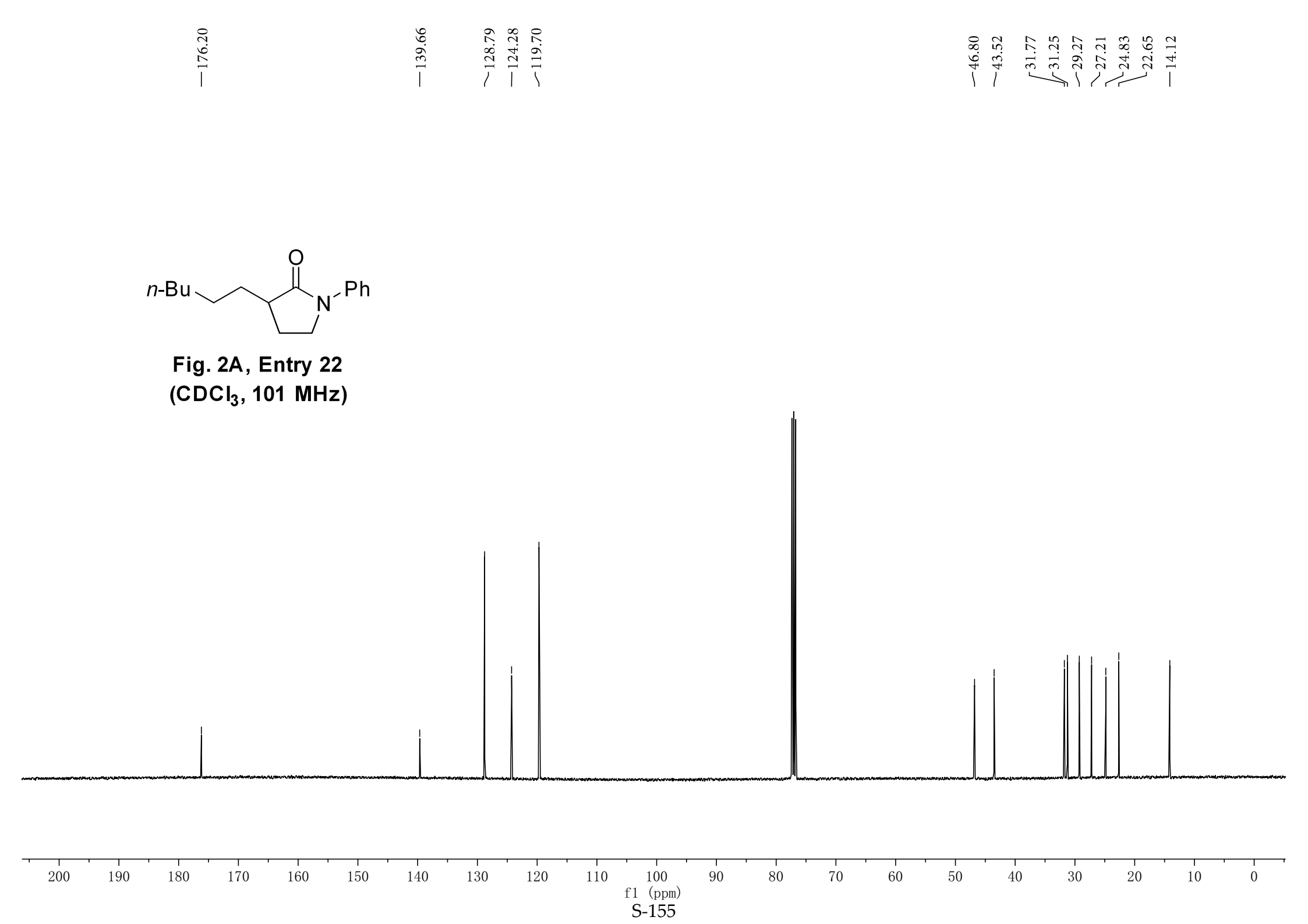


Fig. 2A, Entry 22
($CDCl_3$, 101 MHz)

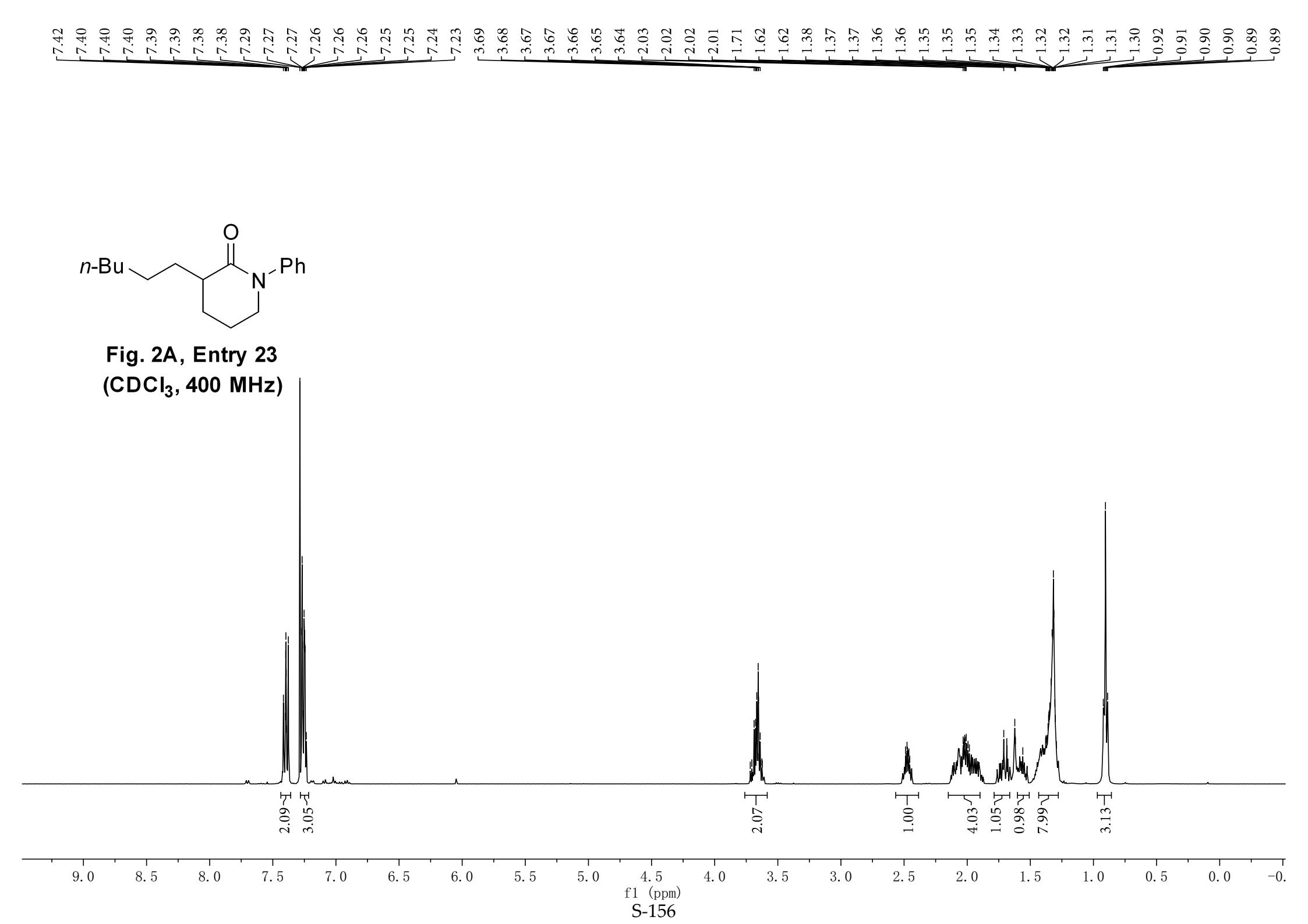


Fig. 2A, Entry 23
($CDCl_3$, 400 MHz)

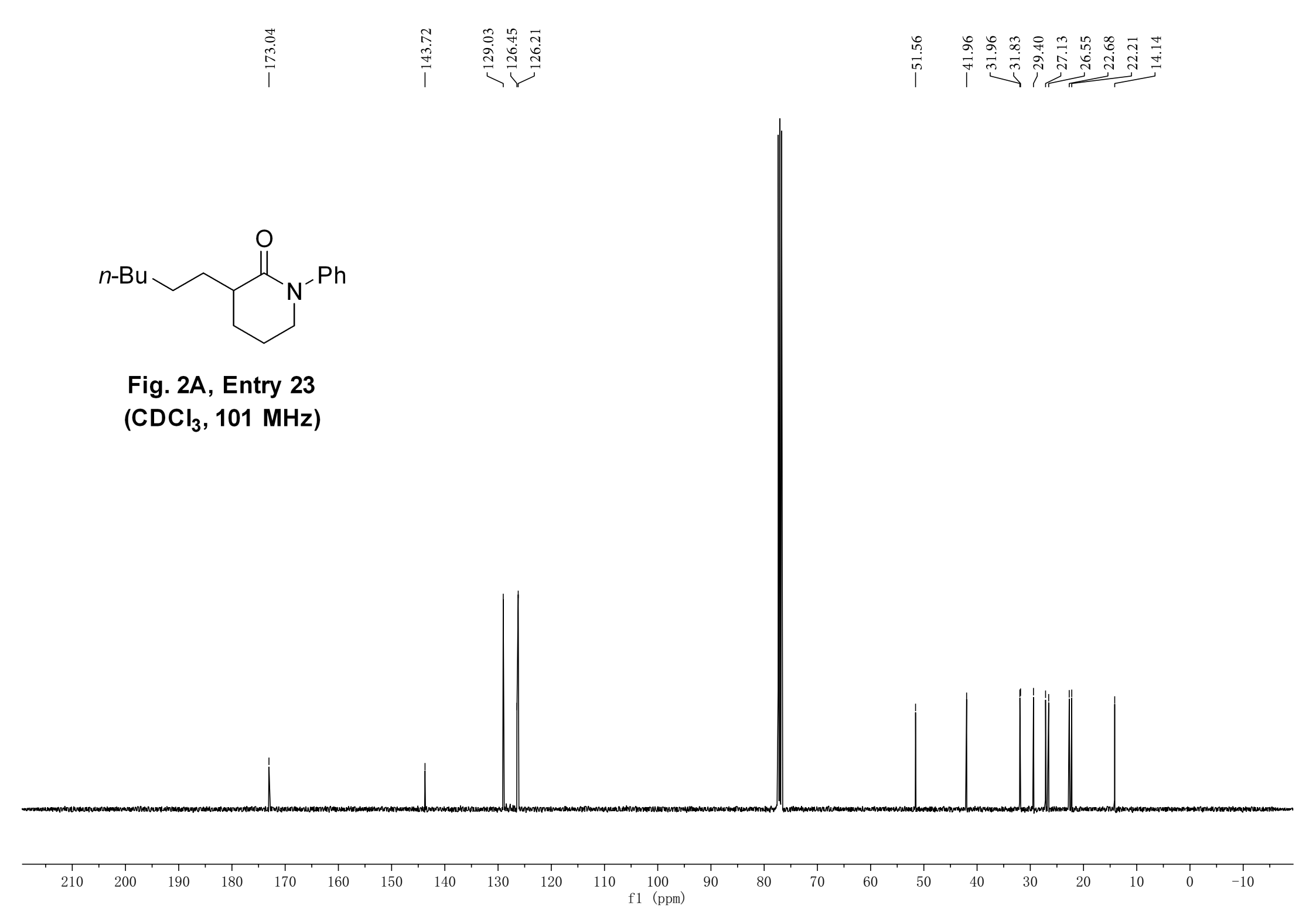
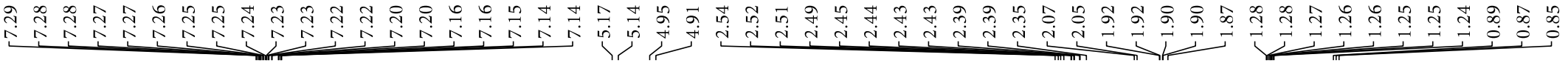


Fig. 2A, Entry 23
($CDCl_3$, 101 MHz)



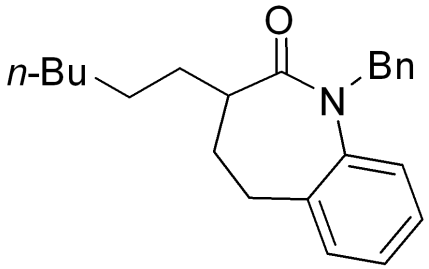
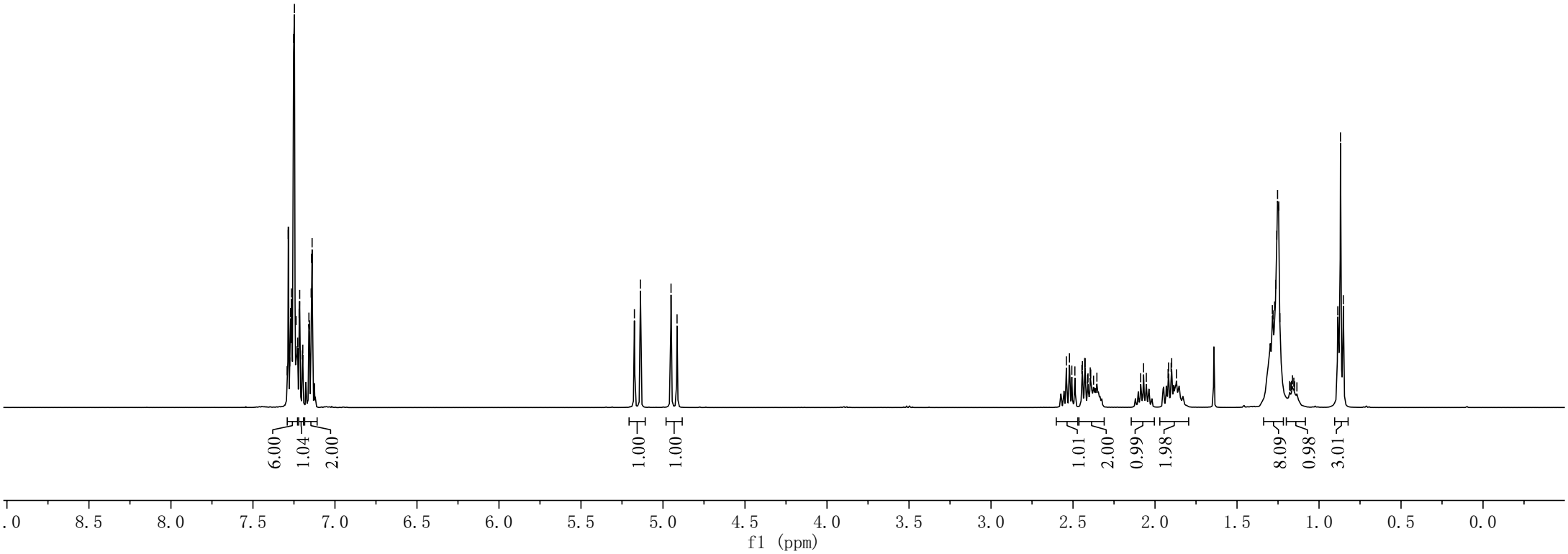


Fig. 2A, Entry 24
($CDCl_3$, 400 MHz)



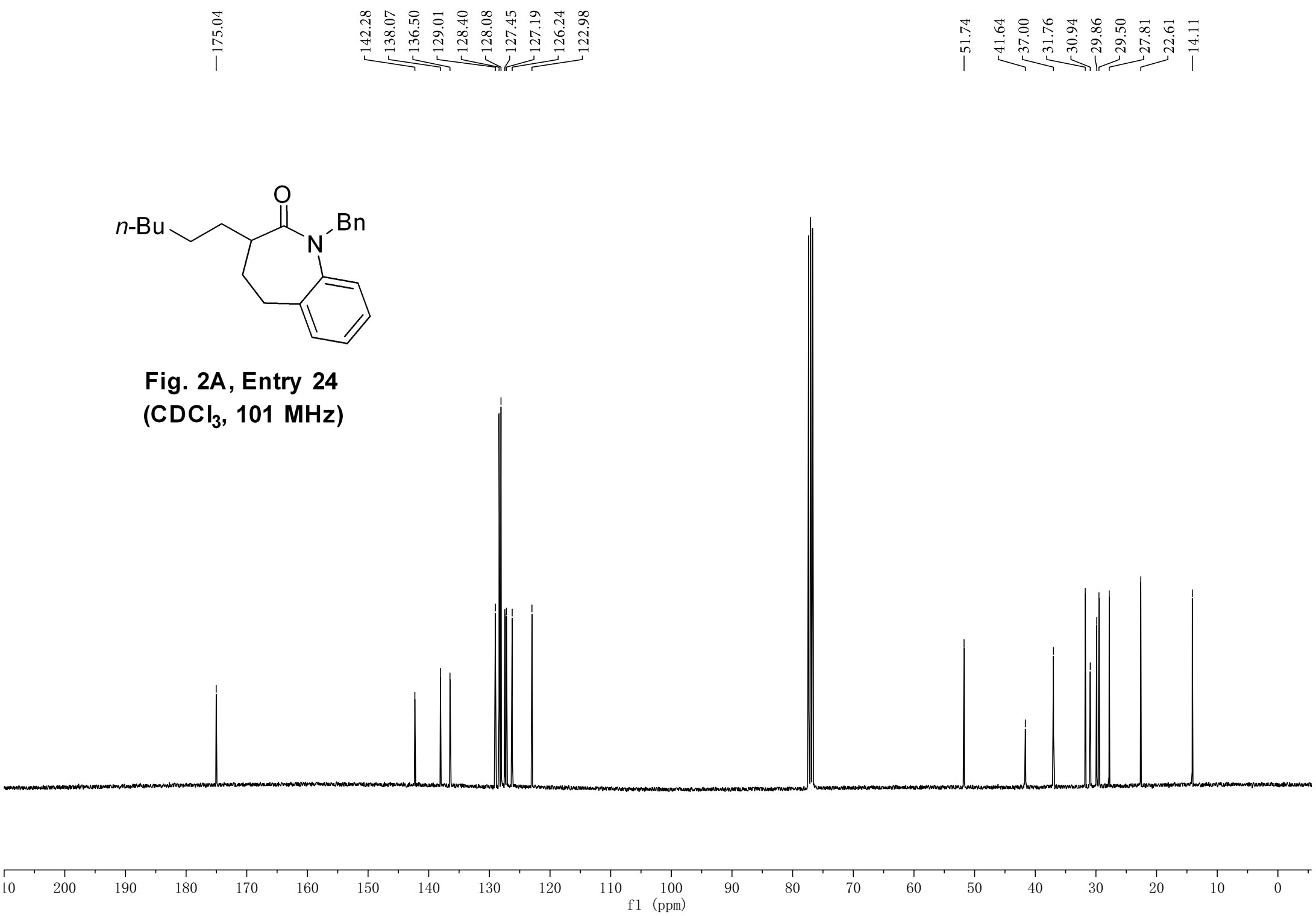


Fig. 2A, Entry 24
($CDCl_3$, 101 MHz)

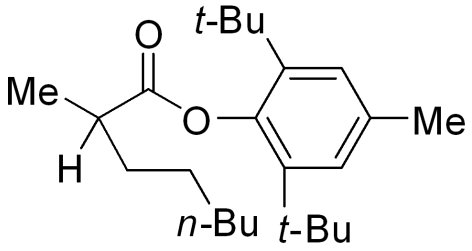


Fig. 2A, Entry 25
($CDCl_3$, 400 MHz)

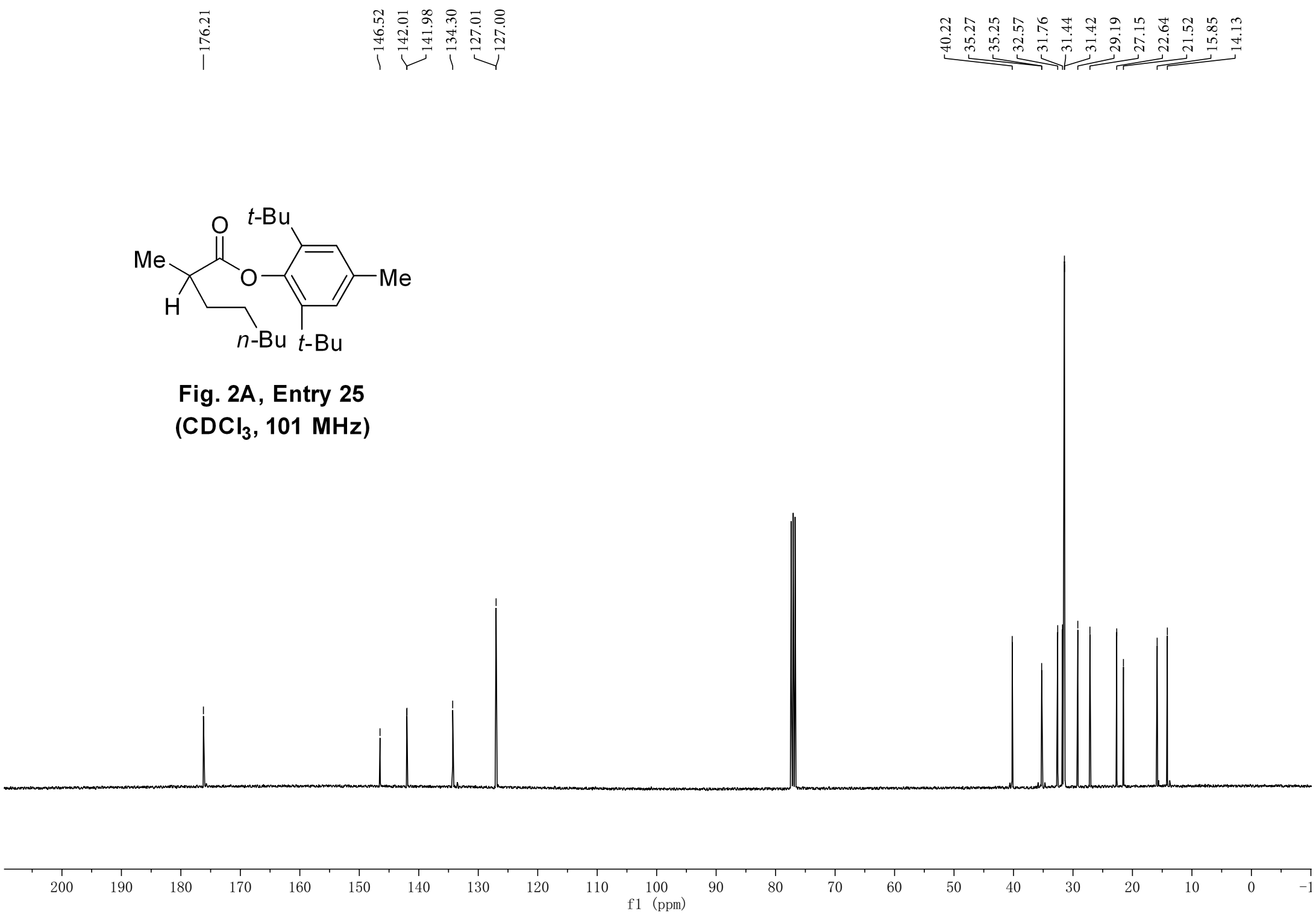


Fig. 2A, Entry 25
($CDCl_3$, 101 MHz)

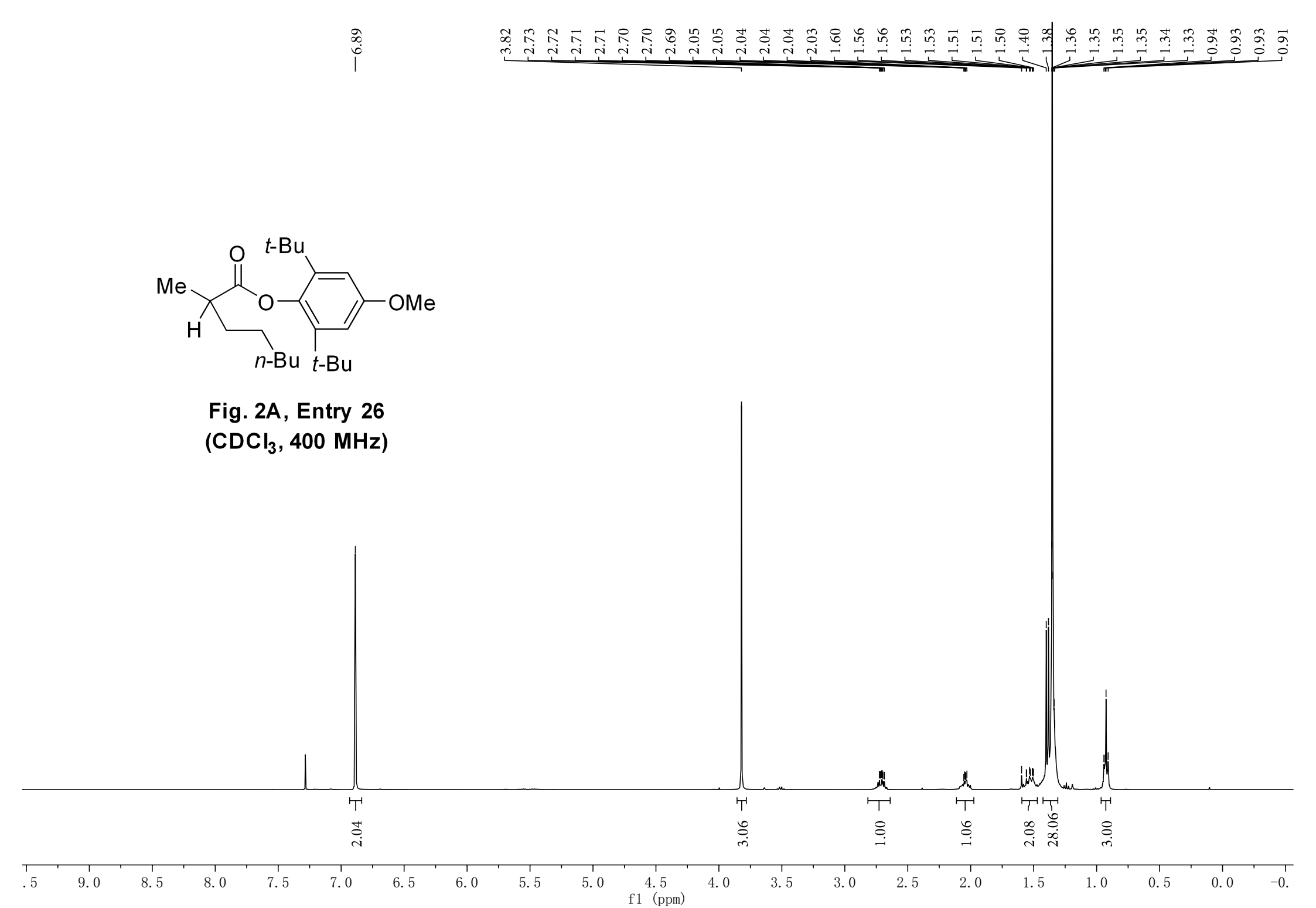


Fig. 2A, Entry 26
($CDCl_3$, 400 MHz)

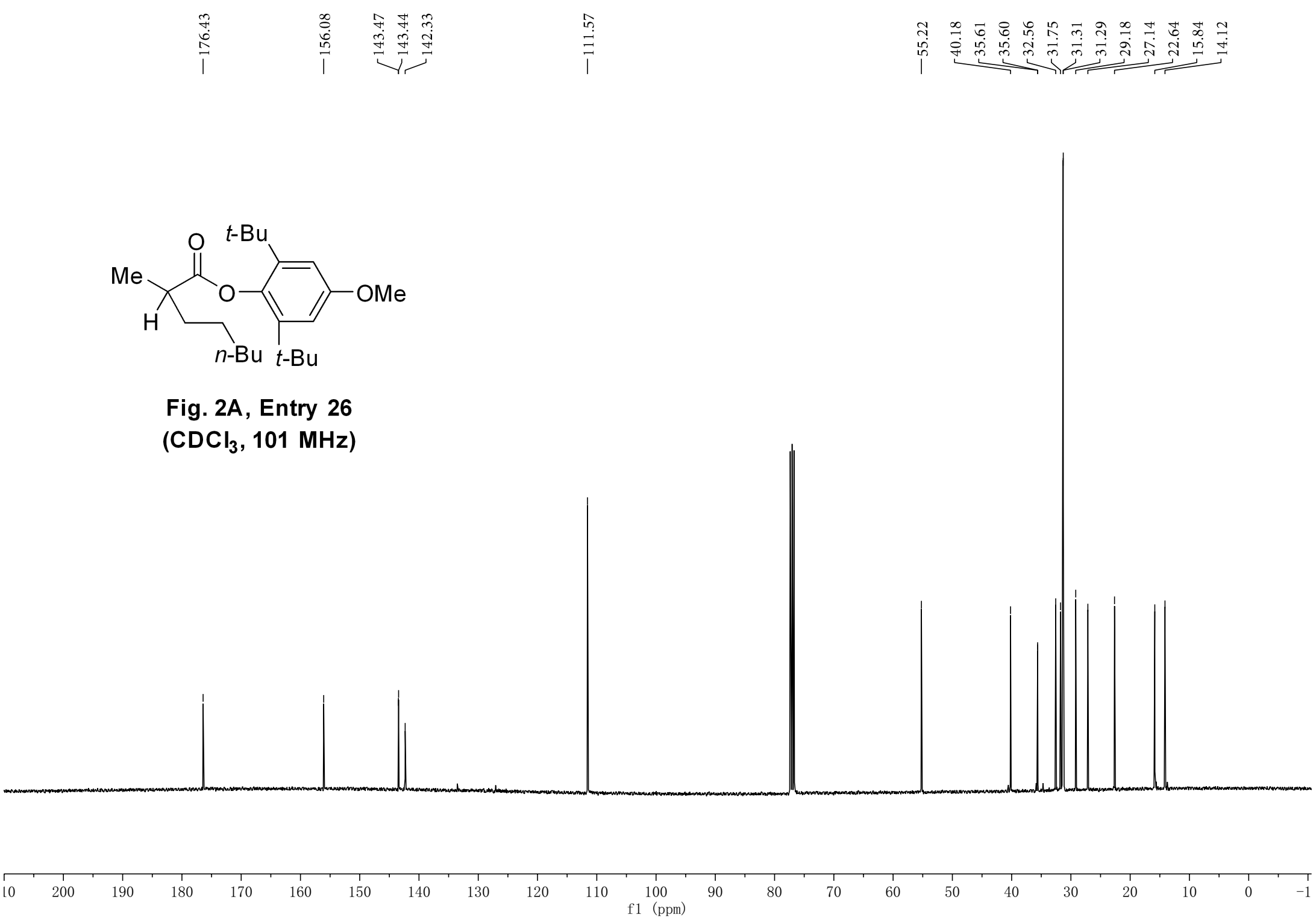


Fig. 2A, Entry 26
($CDCl_3$, 101 MHz)

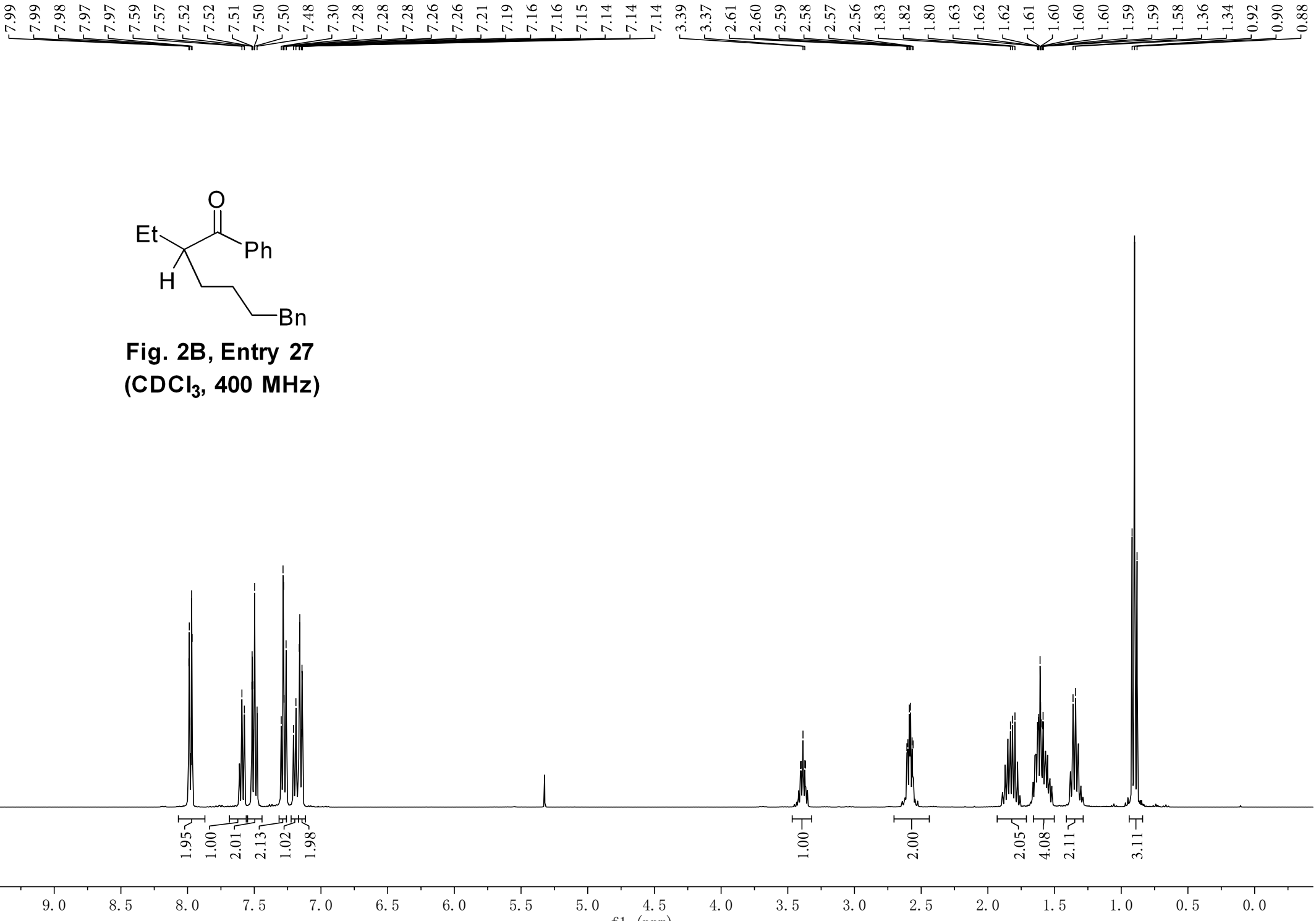


Fig. 2B, Entry 27
($CDCl_3$, 400 MHz)

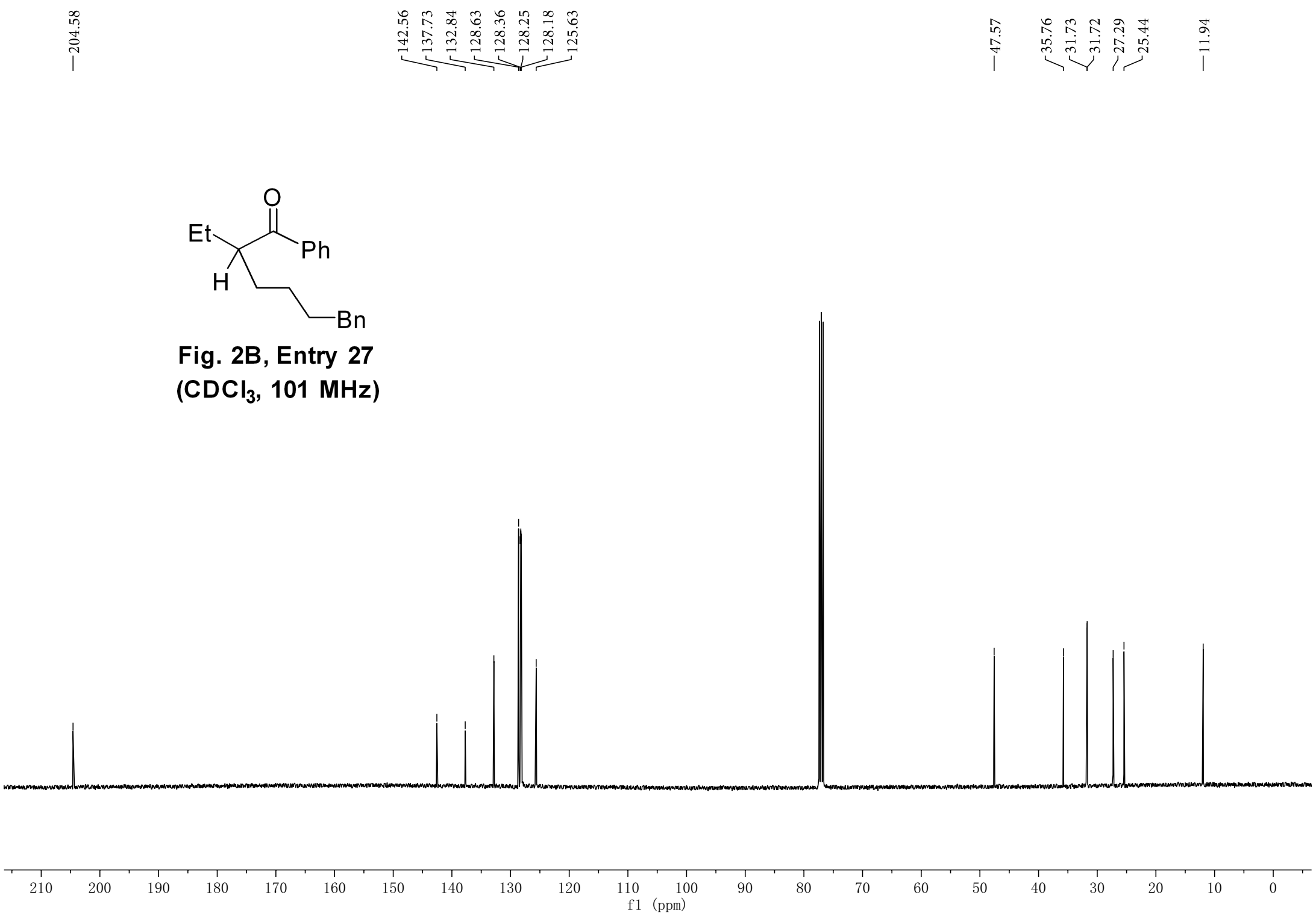


Fig. 2B, Entry 27
($CDCl_3$, 101 MHz)

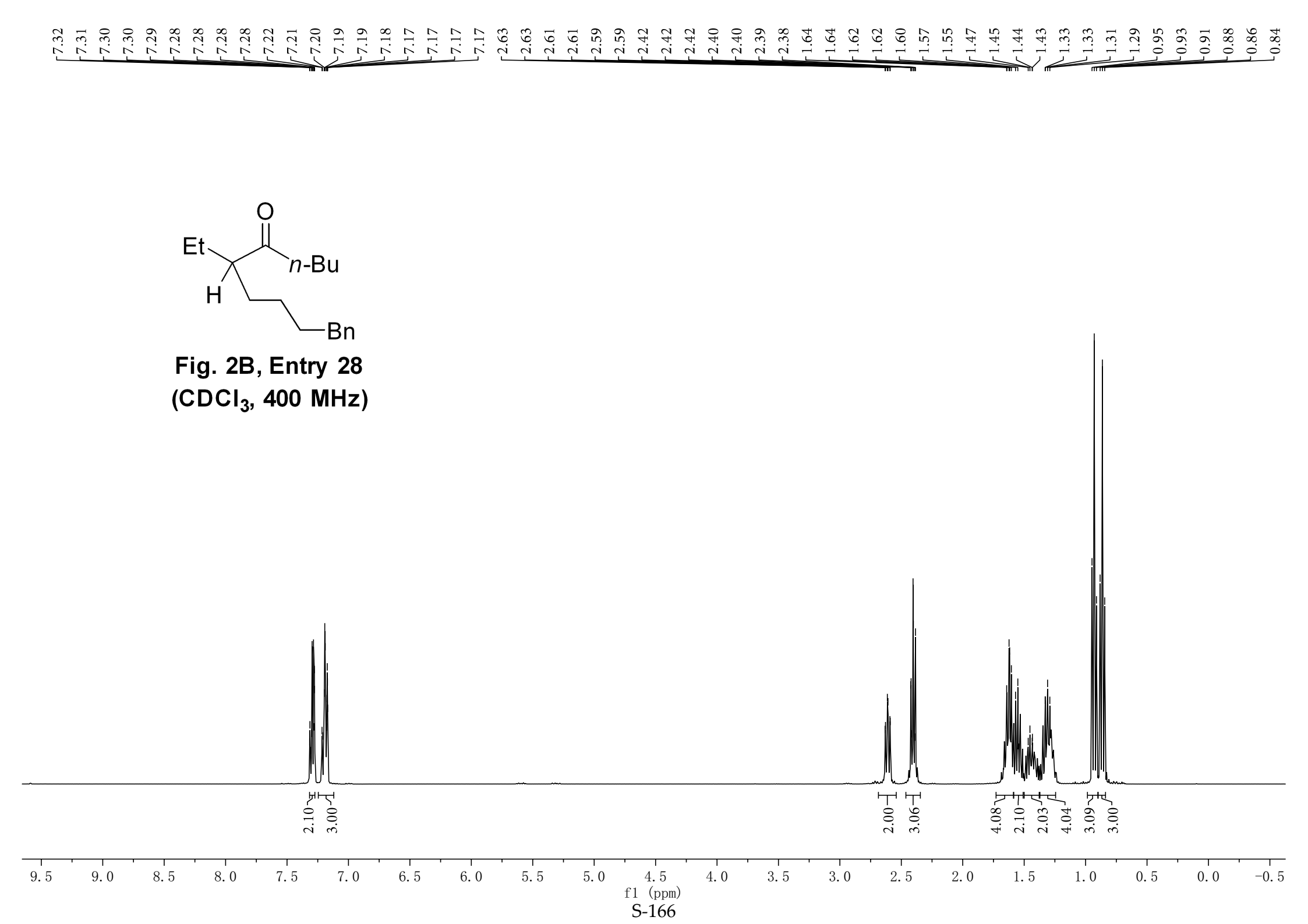


Fig. 2B, Entry 28
($CDCl_3$, 400 MHz)

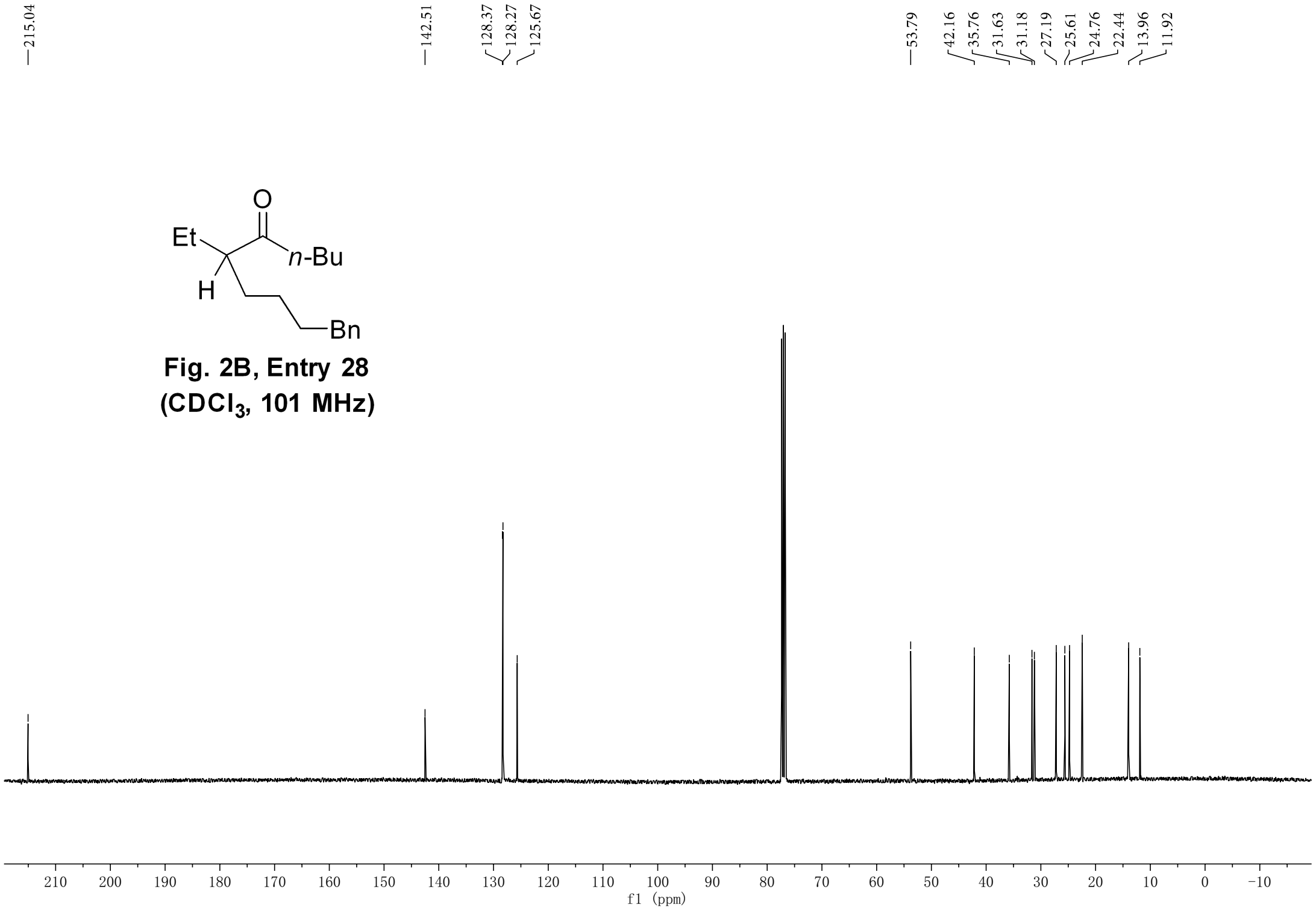


Fig. 2B, Entry 28
($CDCl_3$, 101 MHz)

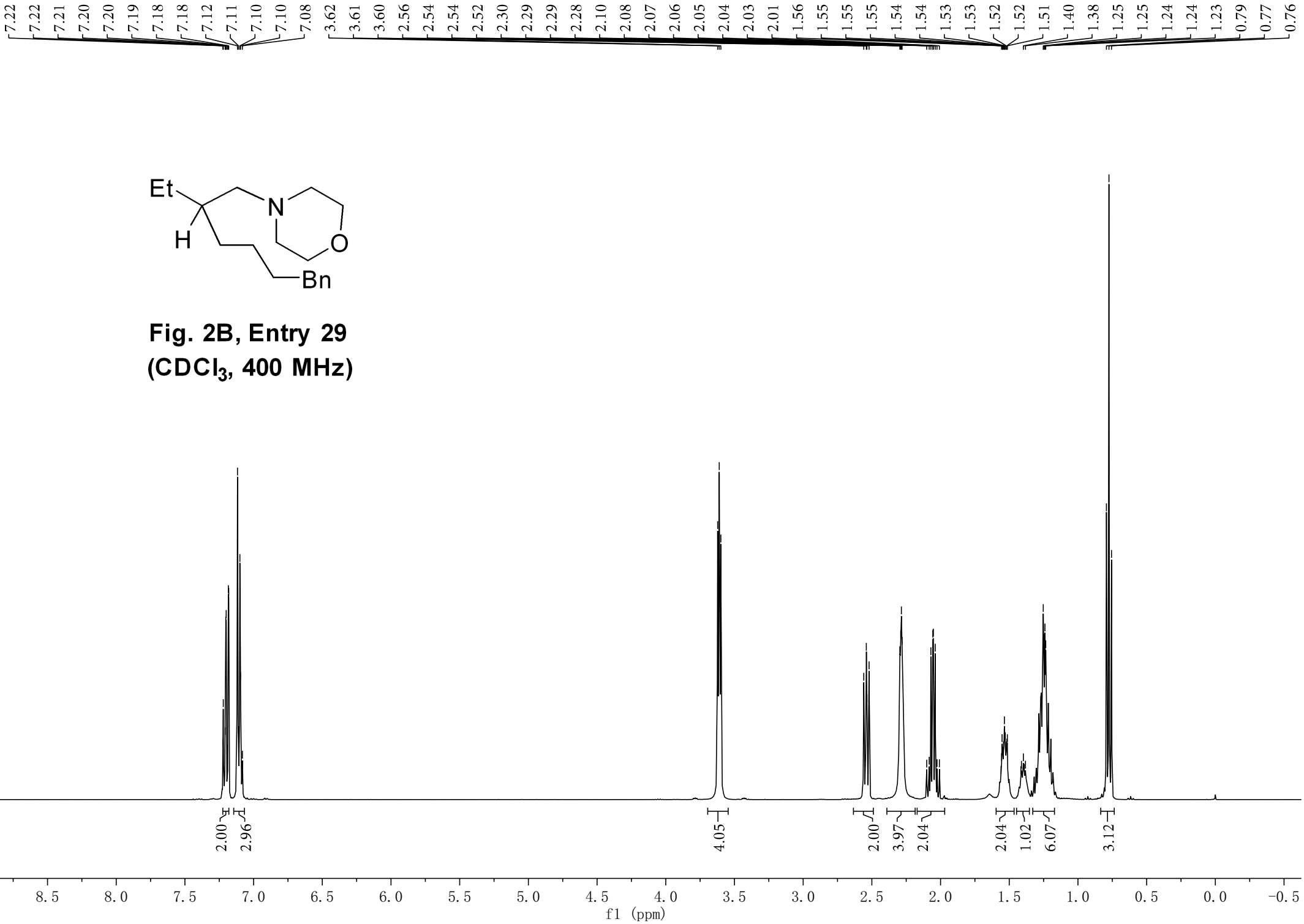


Fig. 2B, Entry 29
($CDCl_3$, 400 MHz)

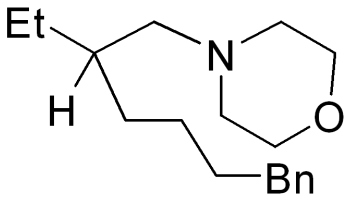


Fig. 2B, Entry 29
($CDCl_3$, 101 MHz)

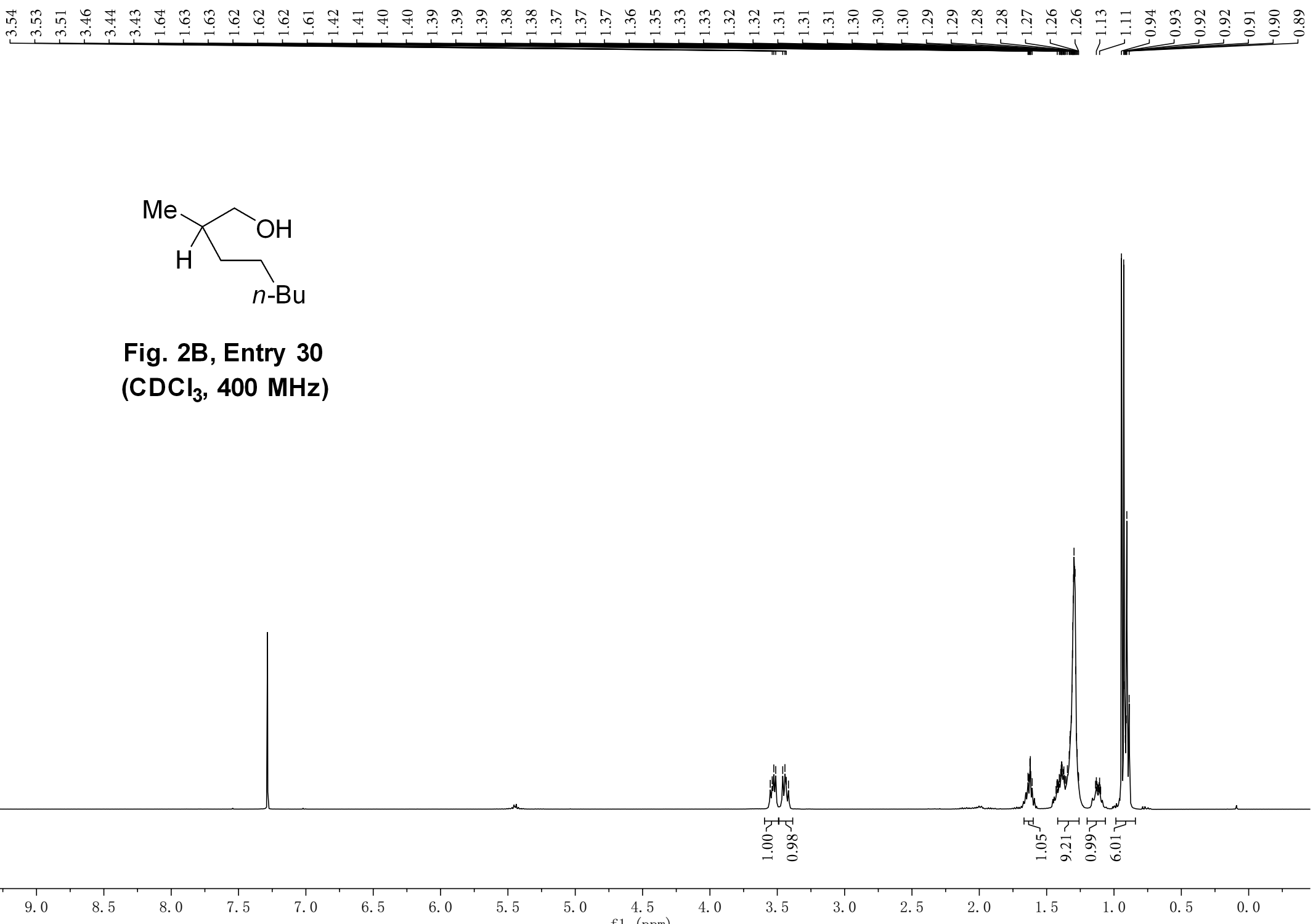


Fig. 2B, Entry 30
($CDCl_3$, 400 MHz)

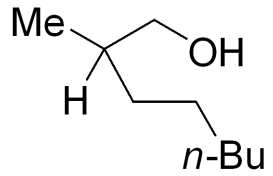
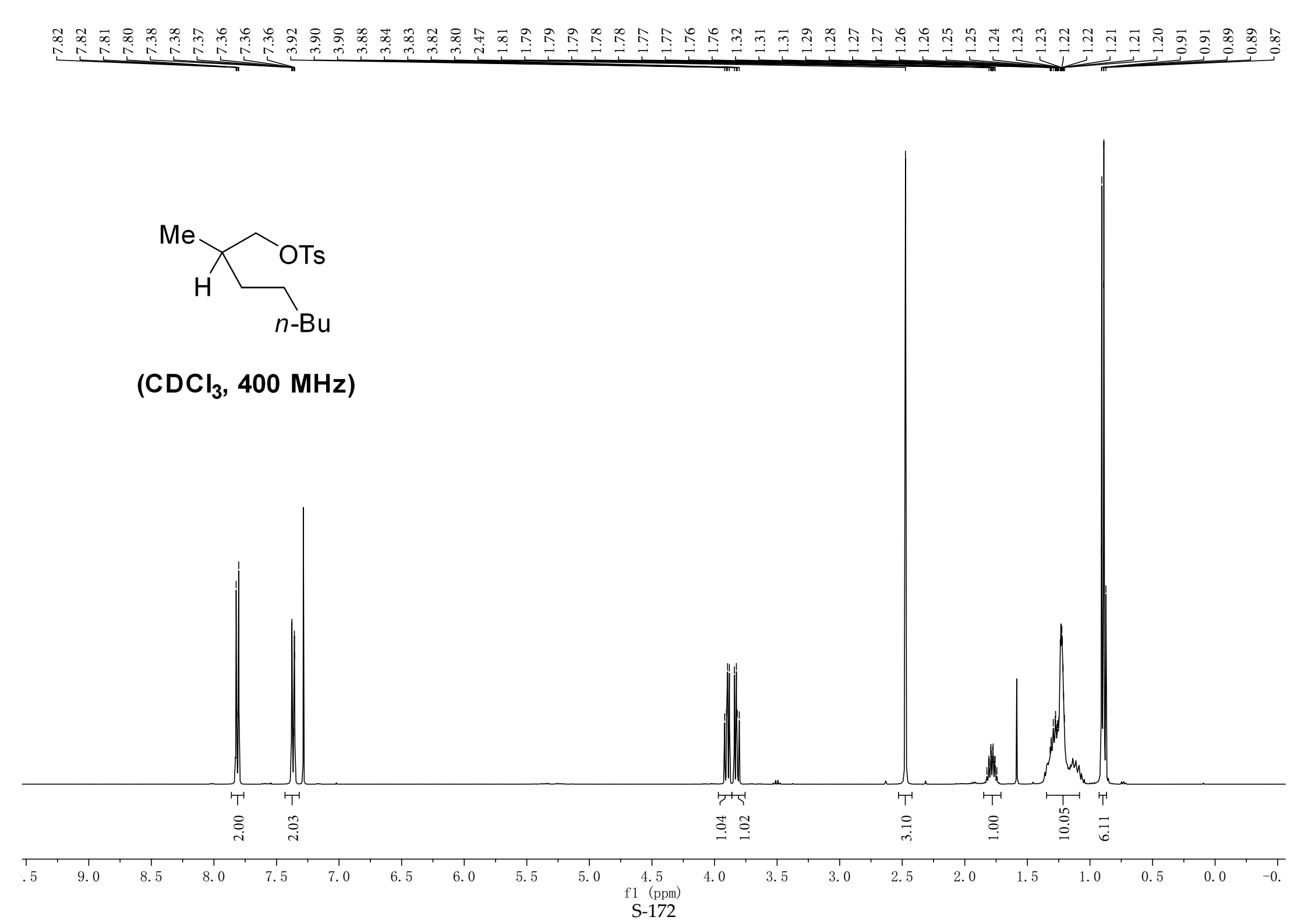
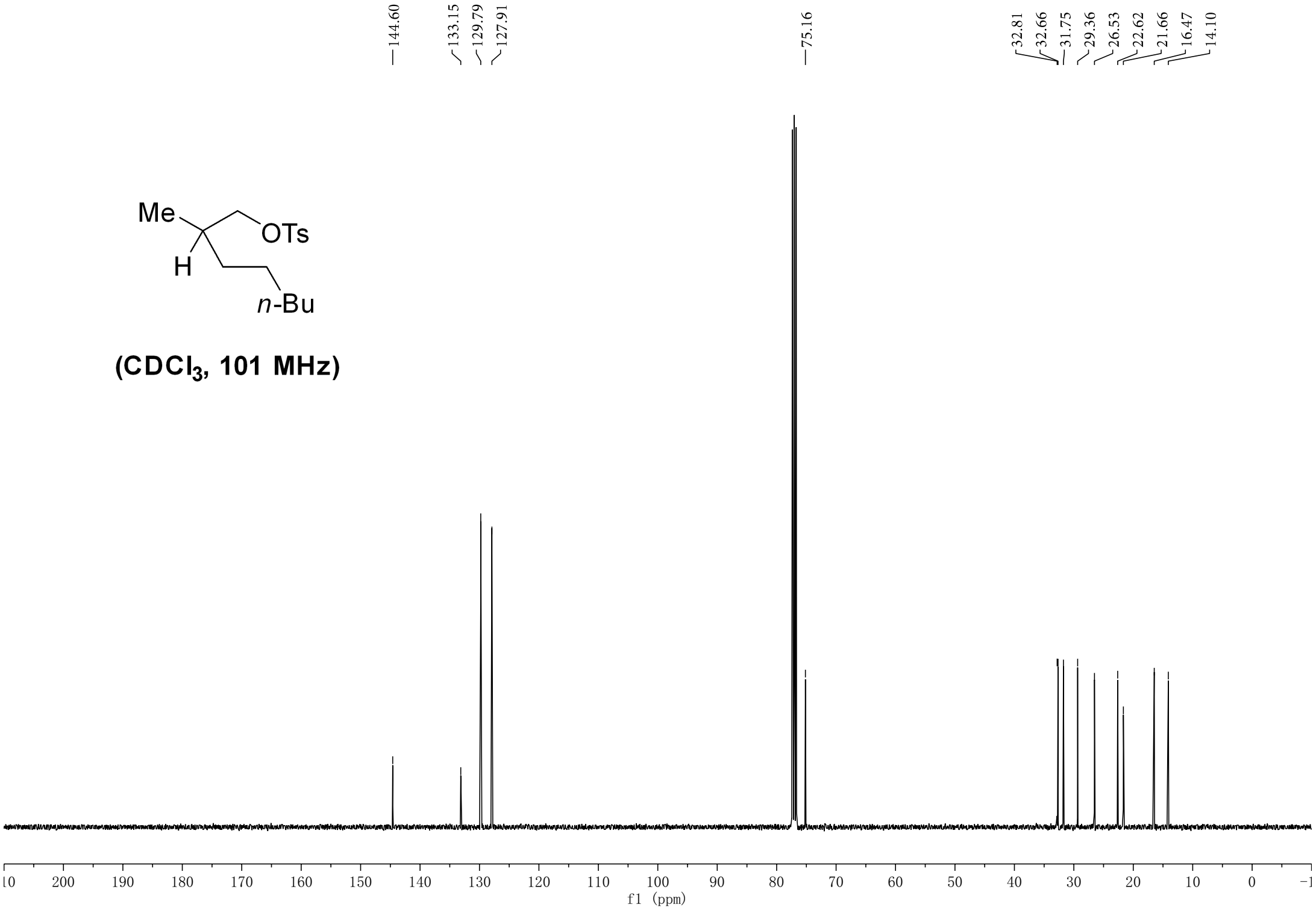


Fig. 2B, Entry 30
($CDCl_3$, 101 MHz)


7.82 7.82 7.81 7.80 7.38 7.38 7.37 7.36 7.36 7.36 3.92 3.90 3.90 3.88 3.84 3.83 3.82 3.80 2.47 1.81 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.32 1.31 1.31 1.29 1.28 1.27 1.27 1.26 1.26 1.25 1.25 1.24 1.23 1.23 1.22 1.22 1.21 1.21 1.20 0.91 0.91 0.89 0.89 0.87
Me
OTs
H
n-Bu
(CDCl3, 400 MHz)
2.00
2.03
1.04
1.02
3.10
1.00
10.05
6.11
f1 (ppm)


144.60
133.15
129.79
127.91
75.16
32.81
32.66
31.75
29.36
26.53
22.62
21.66
16.47
14.10
Me
OTs
H
n-Bu
(CDCl3, 101 MHz)
f1 (ppm)

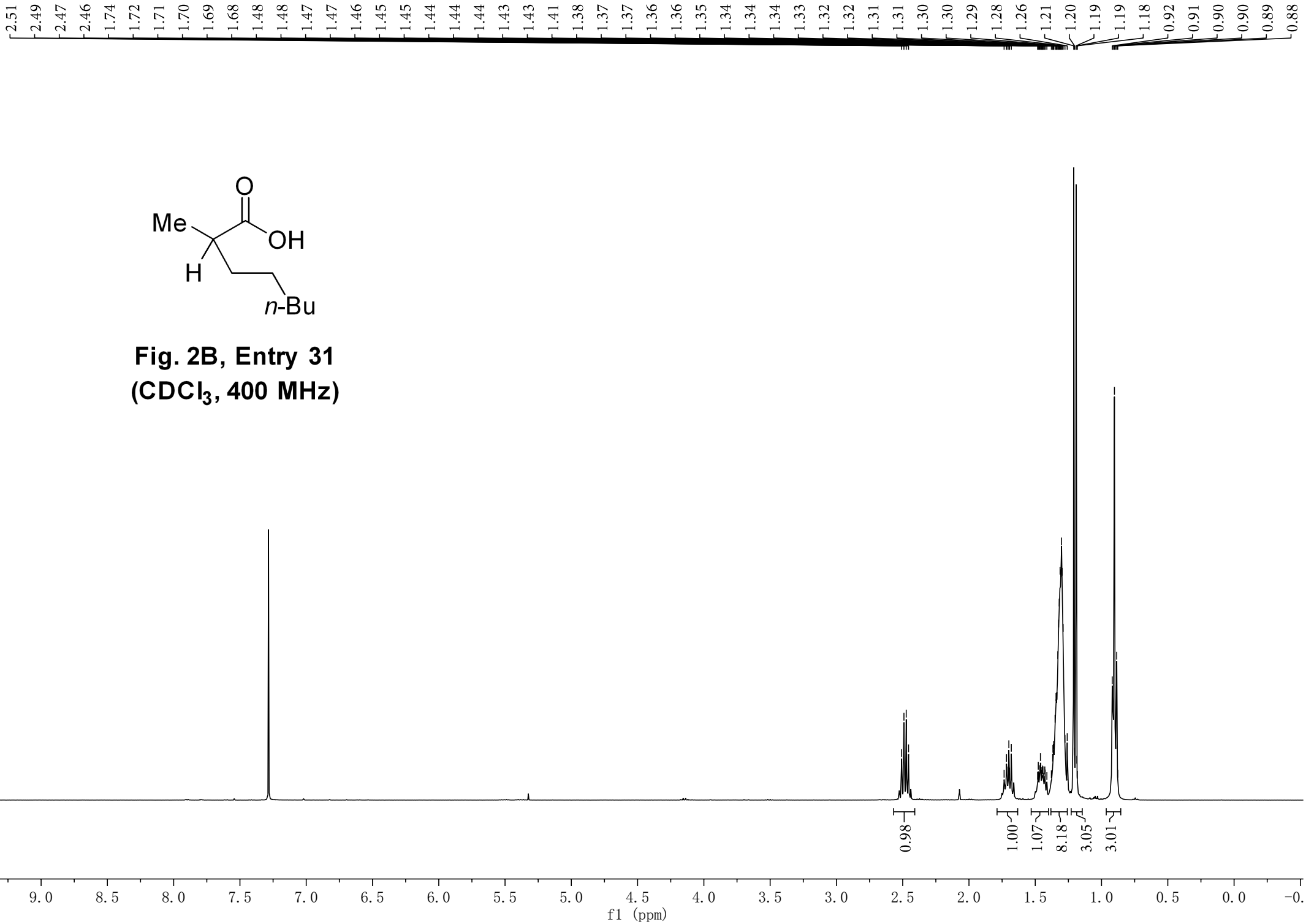


Fig. 2B, Entry 31
($CDCl_3$, 400 MHz)

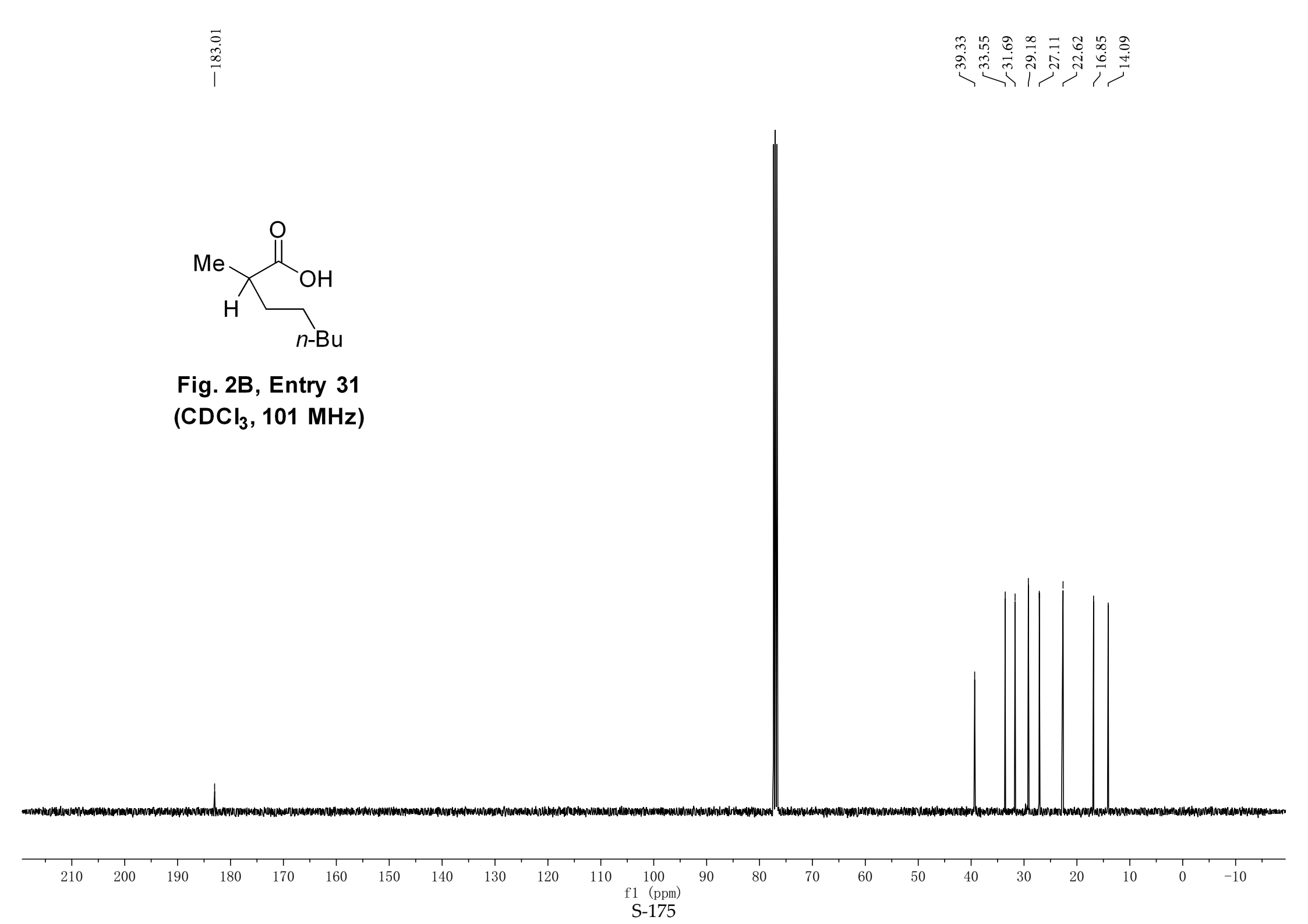
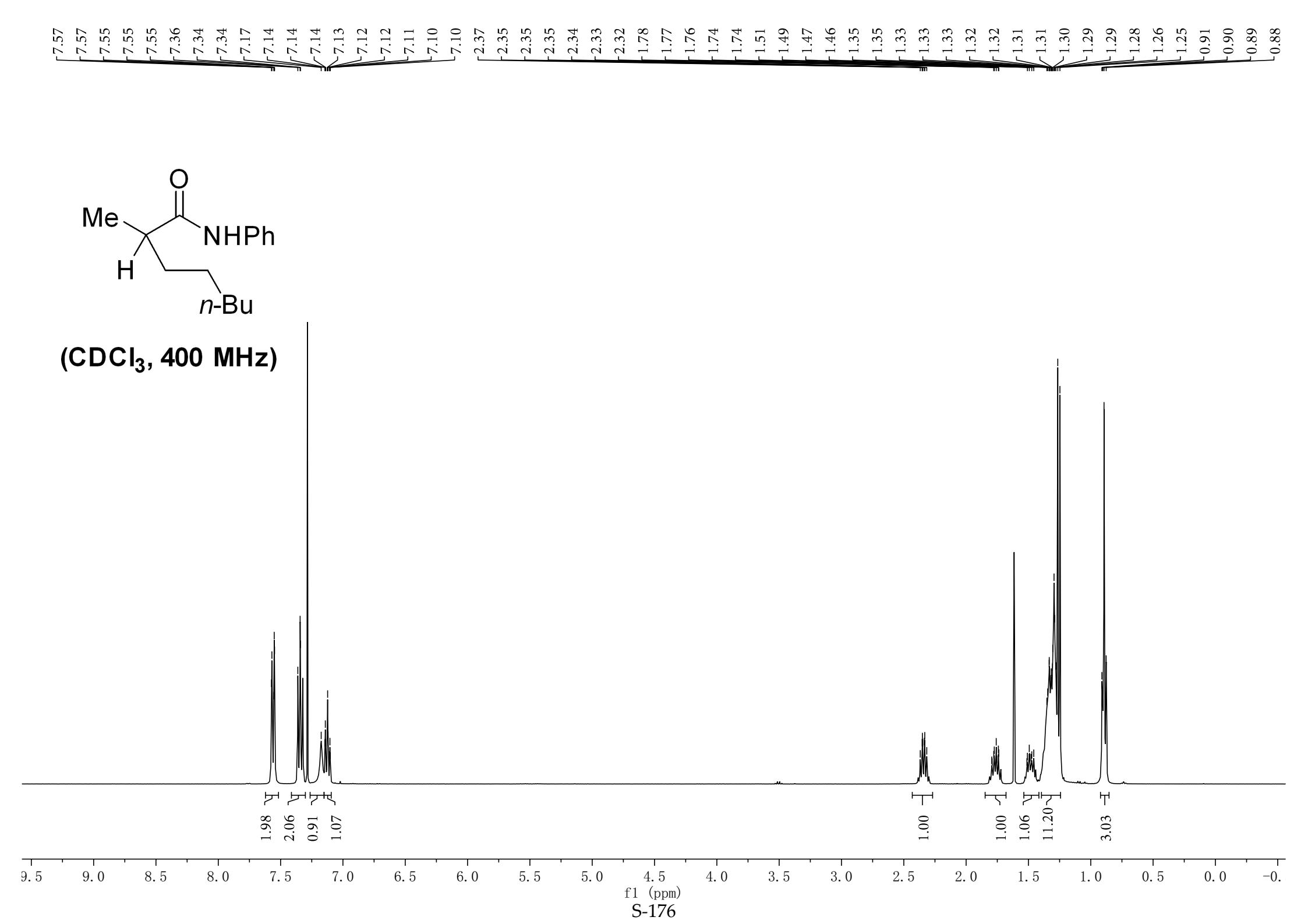
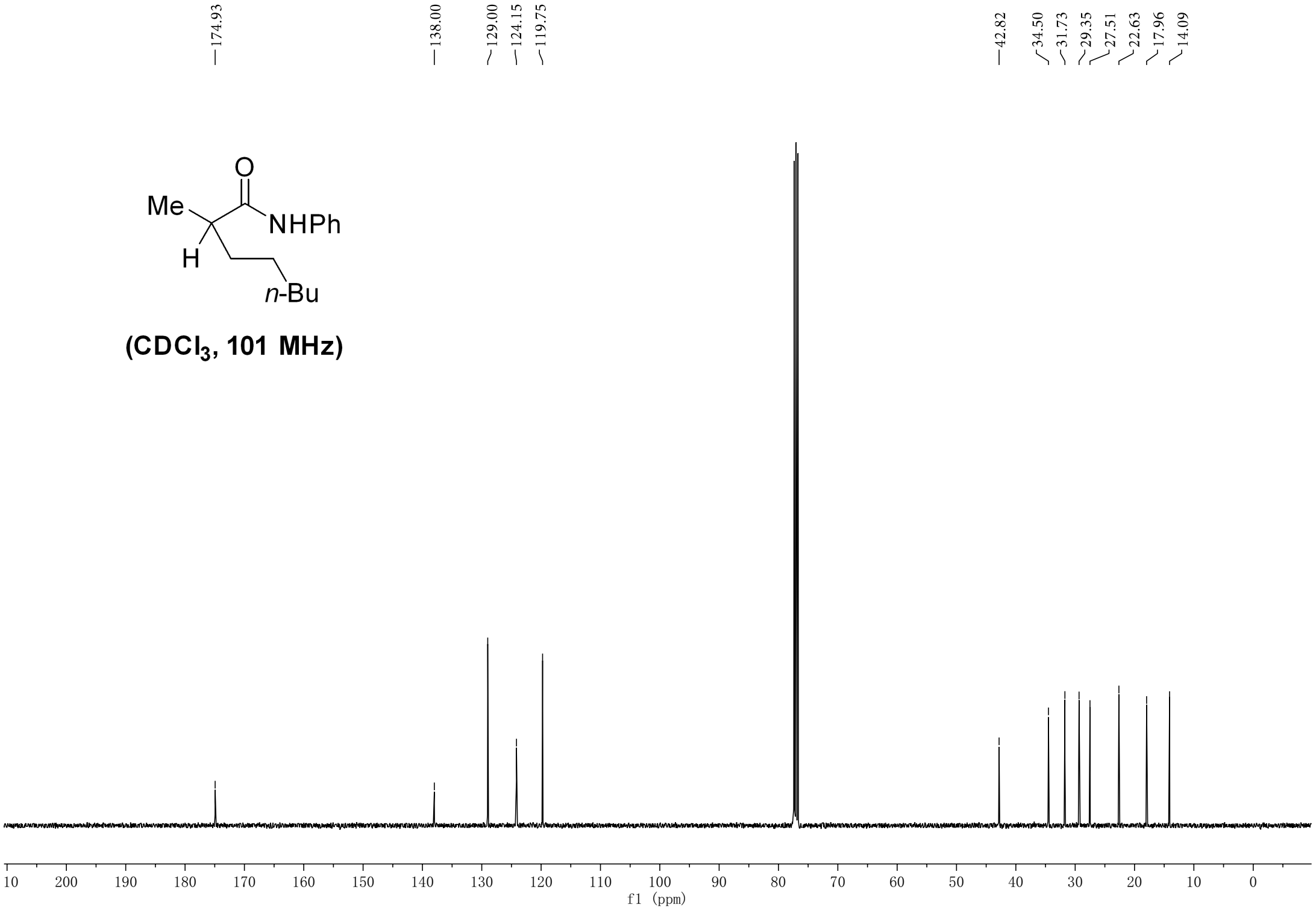


Fig. 2B, Entry 31
($CDCl_3$, 101 MHz)


7.57 7.57 7.55 7.55 7.55 7.36 7.34 7.34 7.17 7.14 7.14 7.14 7.13 7.12 7.12 7.11 7.10 7.10
2.37 2.35 2.35 2.35 2.34 2.33 2.32 1.78 1.77 1.76 1.74 1.74 1.51 1.49 1.47 1.46 1.35 1.35 1.33 1.33 1.33 1.32 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.26 1.25 0.91 0.90 0.89 0.88
O
Me
NHPh
H
n-Bu
(CDCl3, 400 MHz)
1.98
2.06
0.91
1.07
1.00
1.00
1.06
11.20
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


174.93
138.00
129.00
124.15
119.75
42.82
34.50
31.73
29.35
27.51
22.63
17.96
14.09
O
Me
NHPh
H
n-Bu
(CDCl3, 101 MHz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

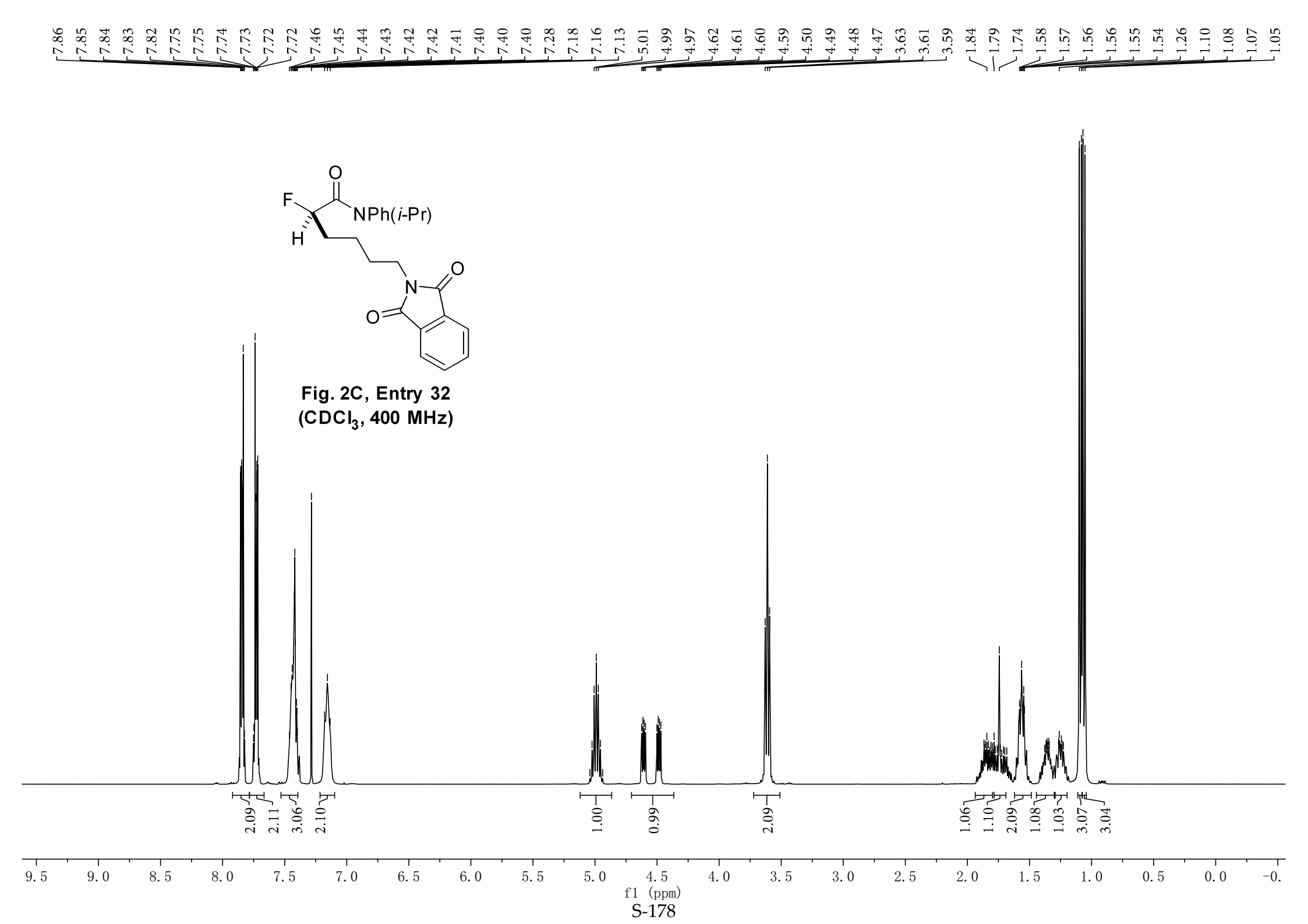


Fig. 2C, Entry 32
($CDCl_3$, 400 MHz)

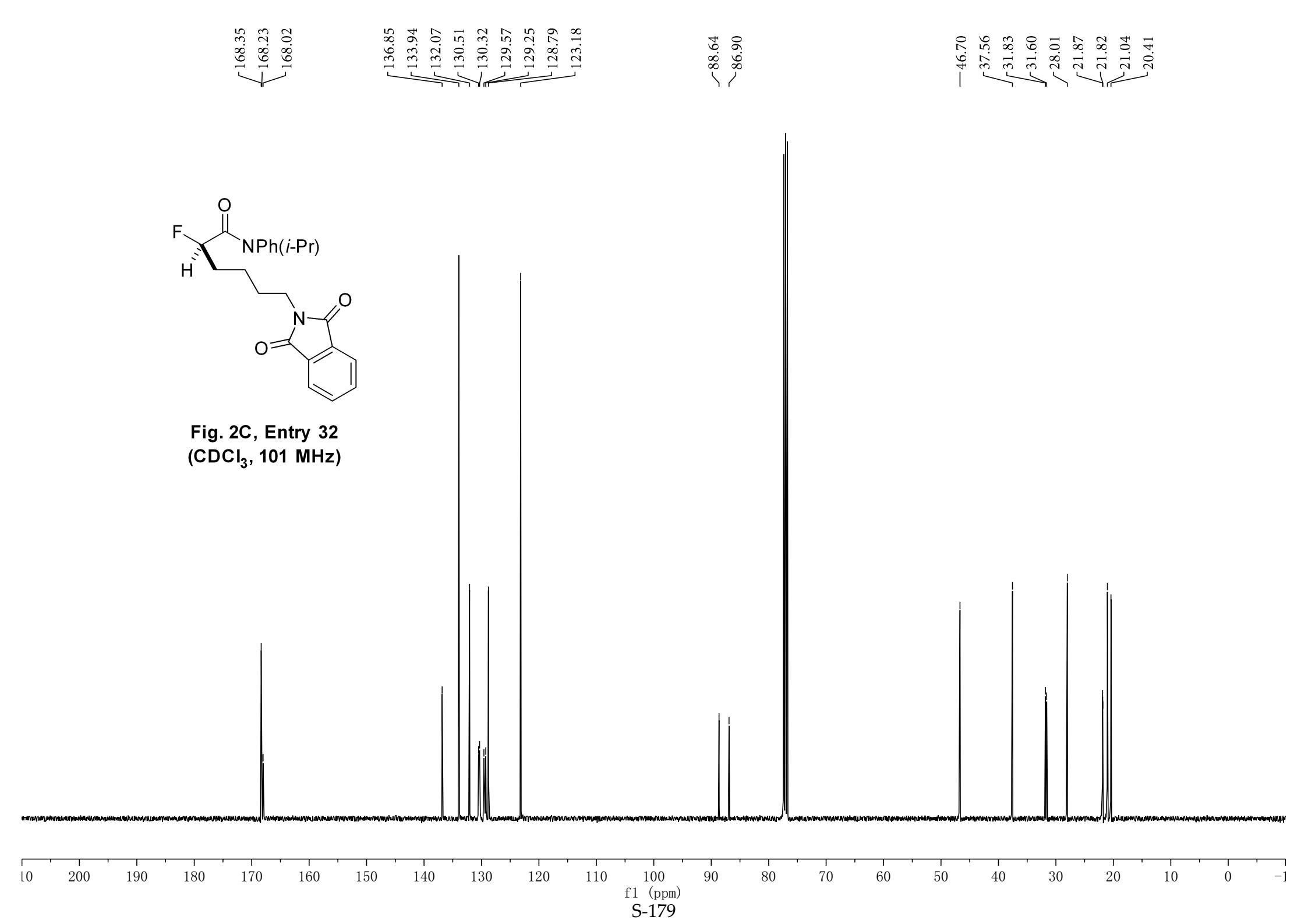


Fig. 2C, Entry 32
($CDCl_3$, 101 MHz)

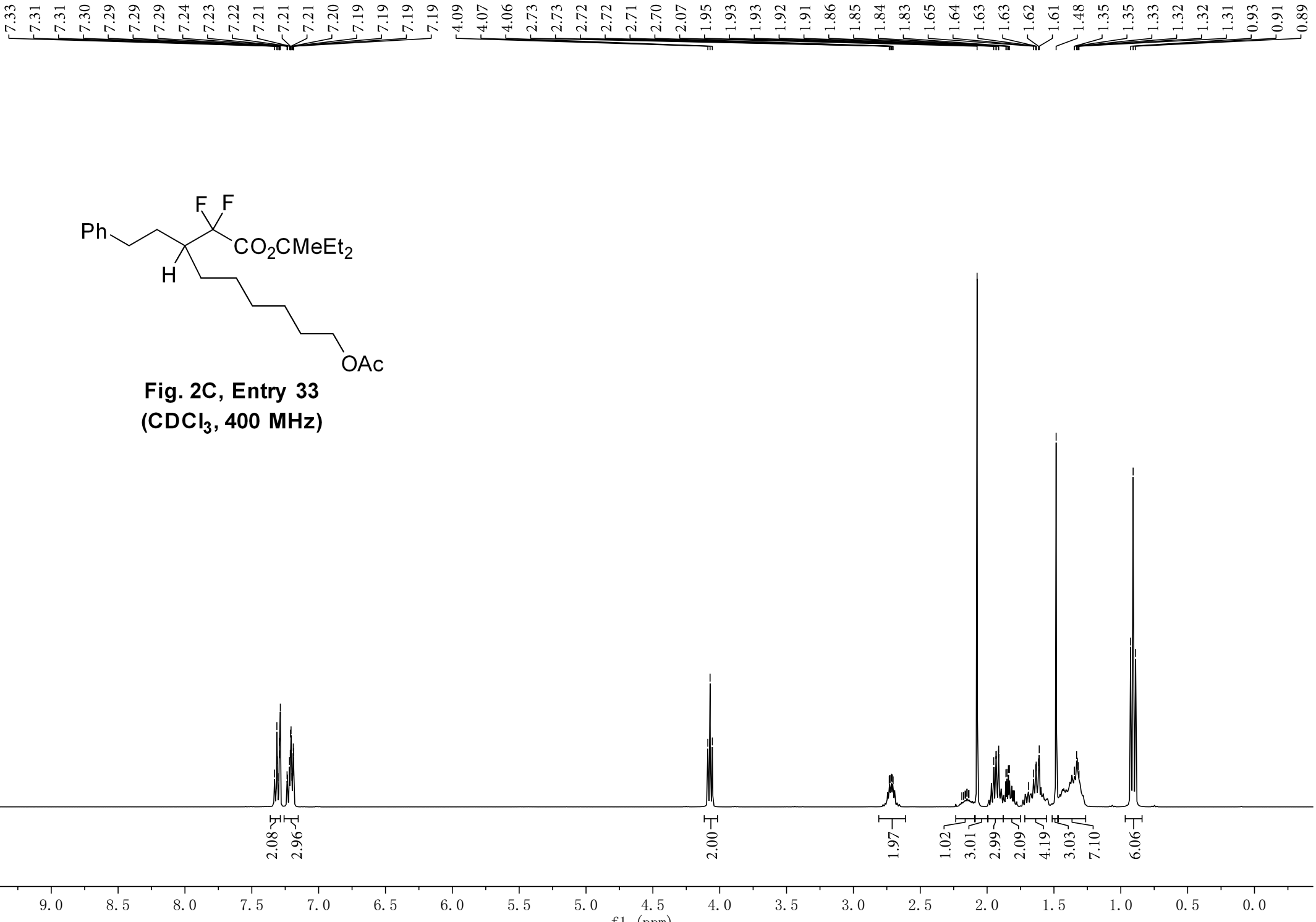


Fig. 2C, Entry 33
($CDCl_3$, 400 MHz)

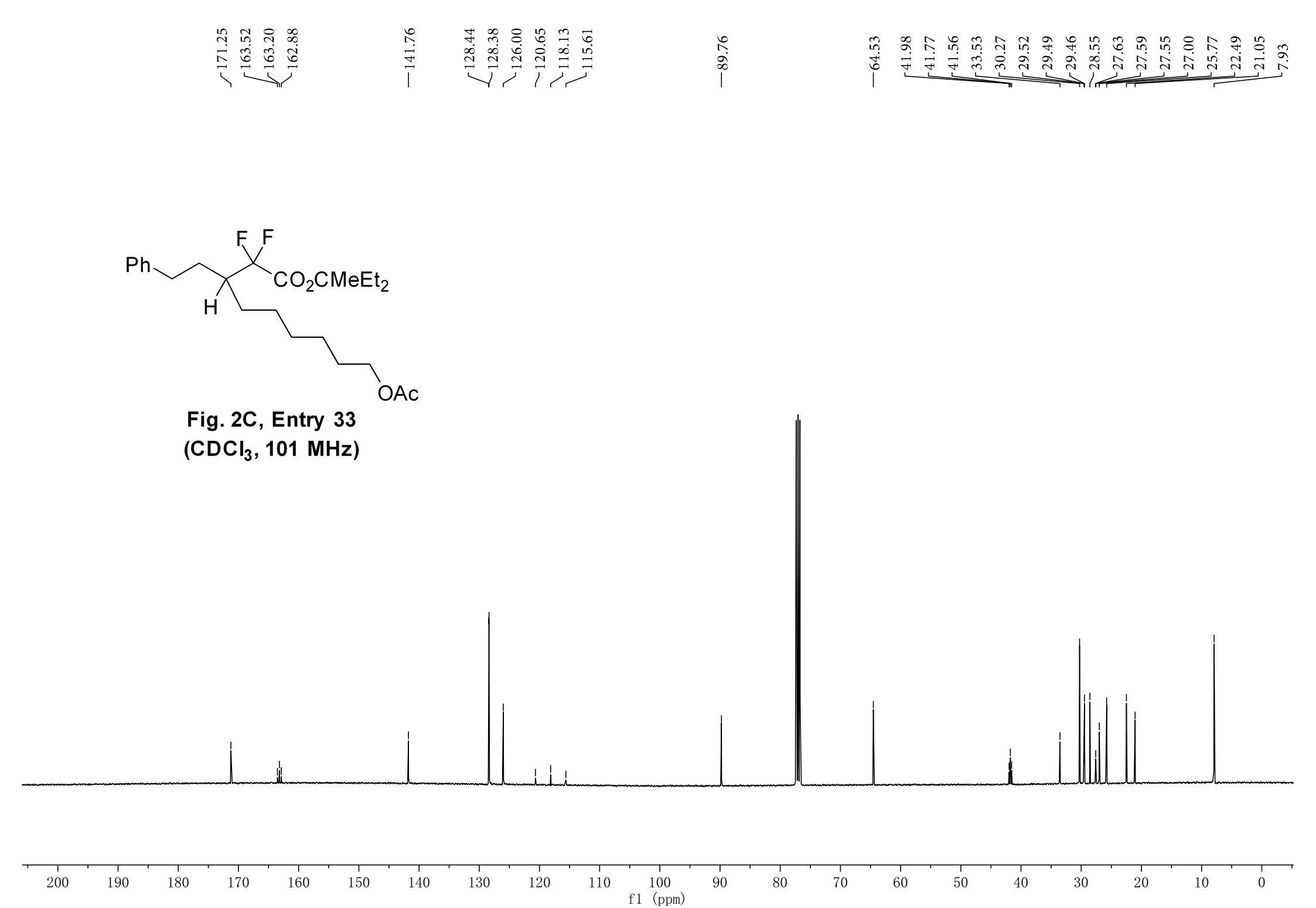


Fig. 2C, Entry 33
($CDCl_3$, 101 MHz)

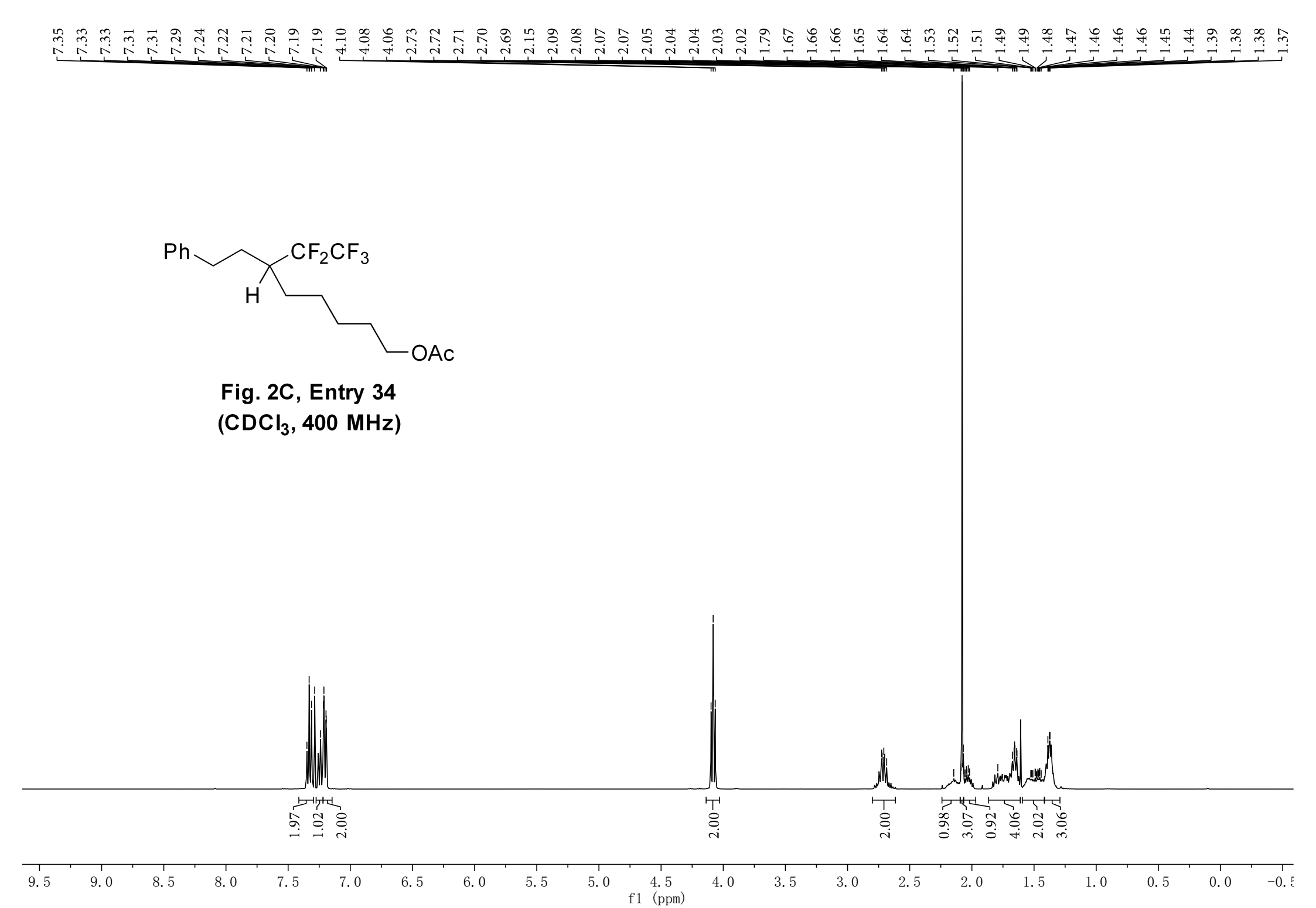


Fig. 2C, Entry 34
($CDCl_3$, 400 MHz)

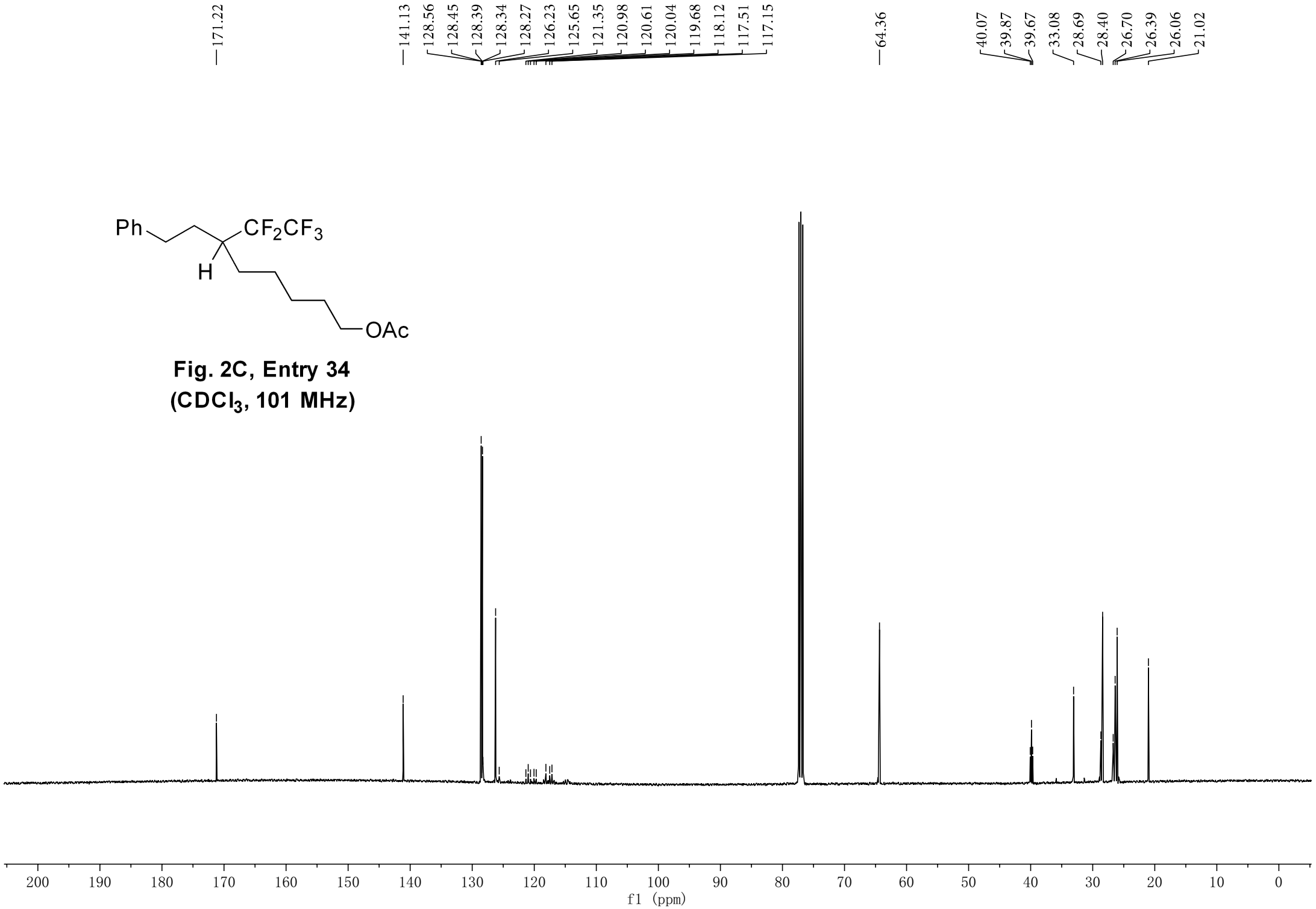


Fig. 2C, Entry 34
($CDCl_3$, 101 MHz)

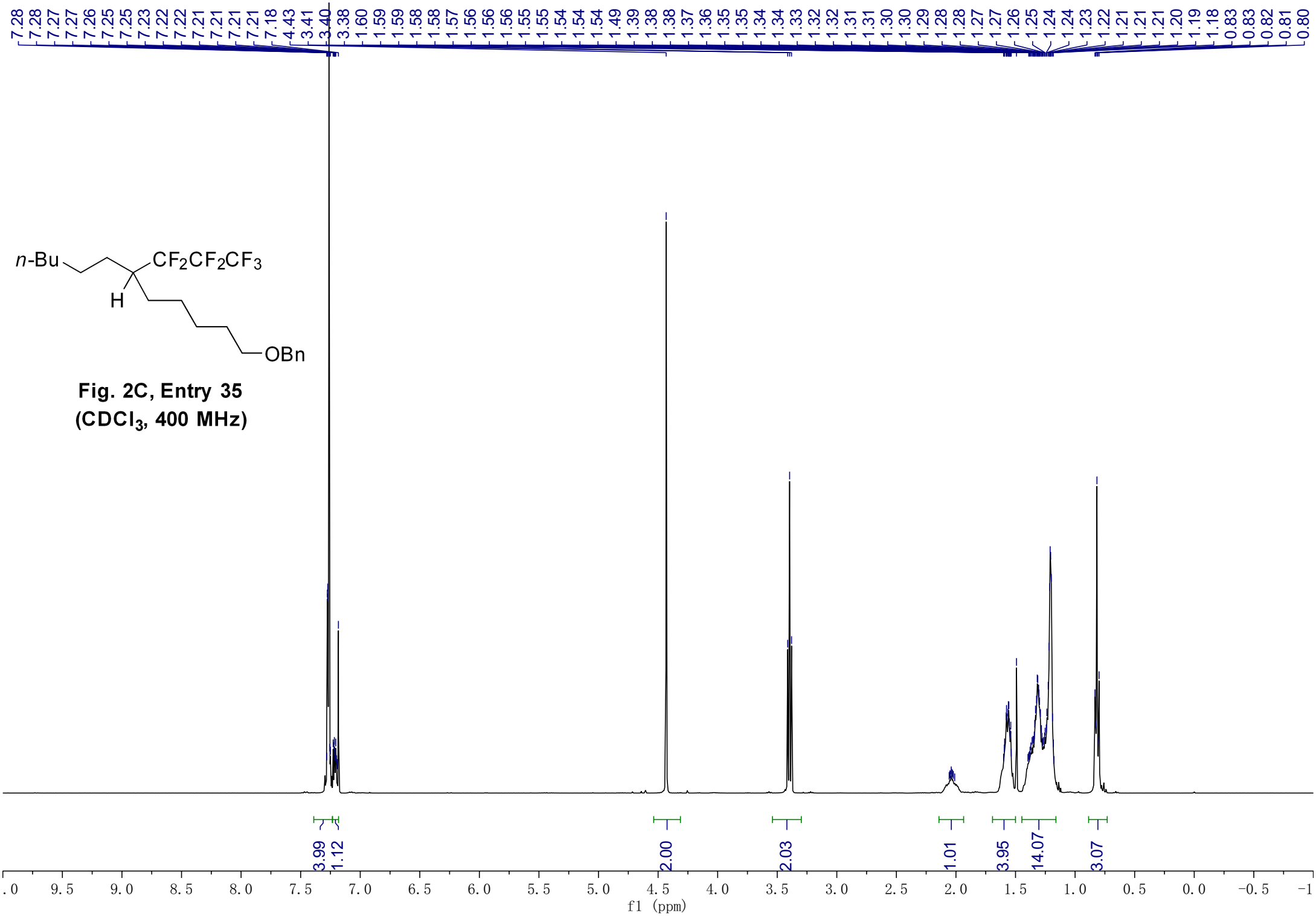


Fig. 2C, Entry 35
($CDCl_3$, 400 MHz)

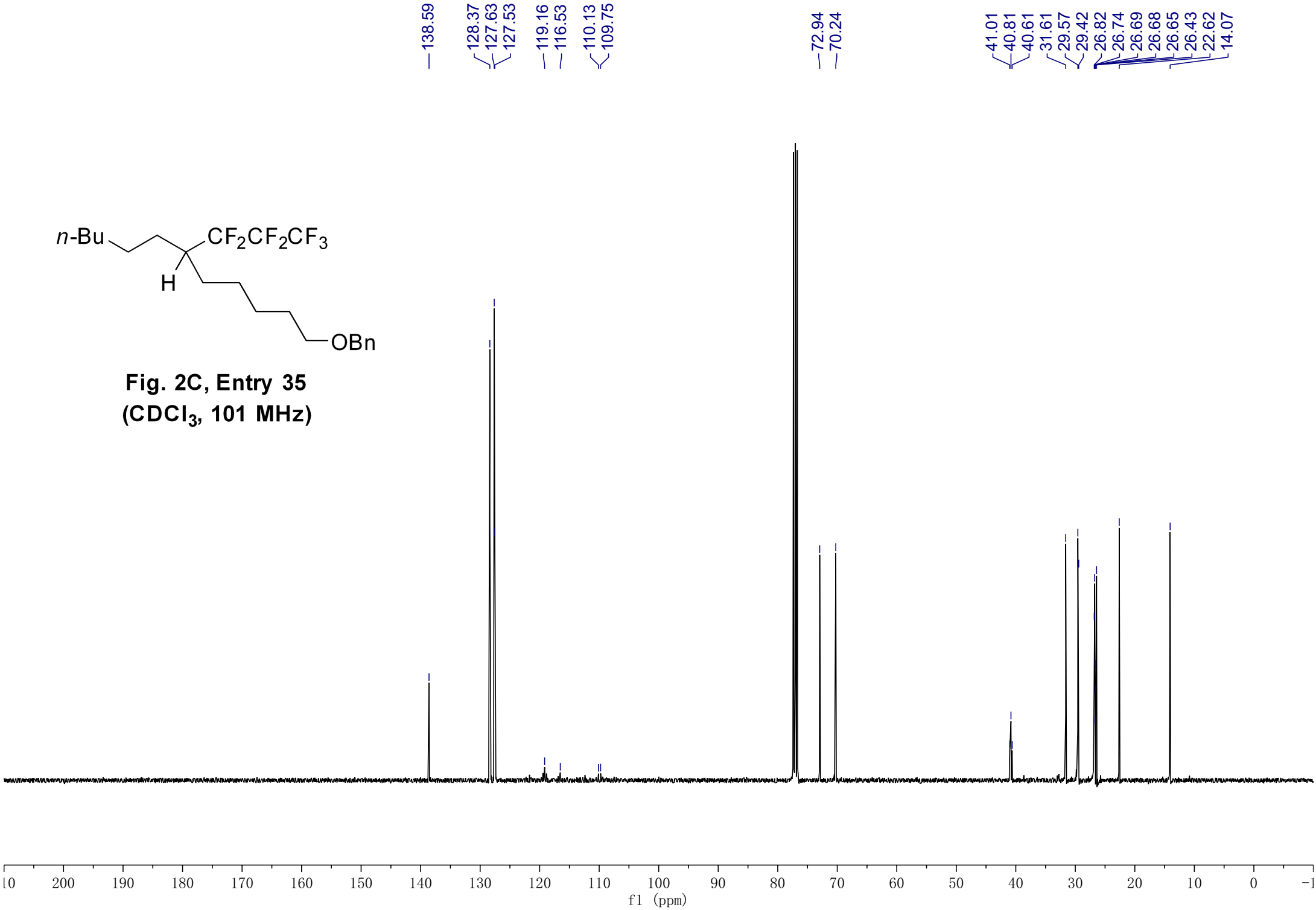


Fig. 2C, Entry 35
($CDCl_3$, 101 MHz)

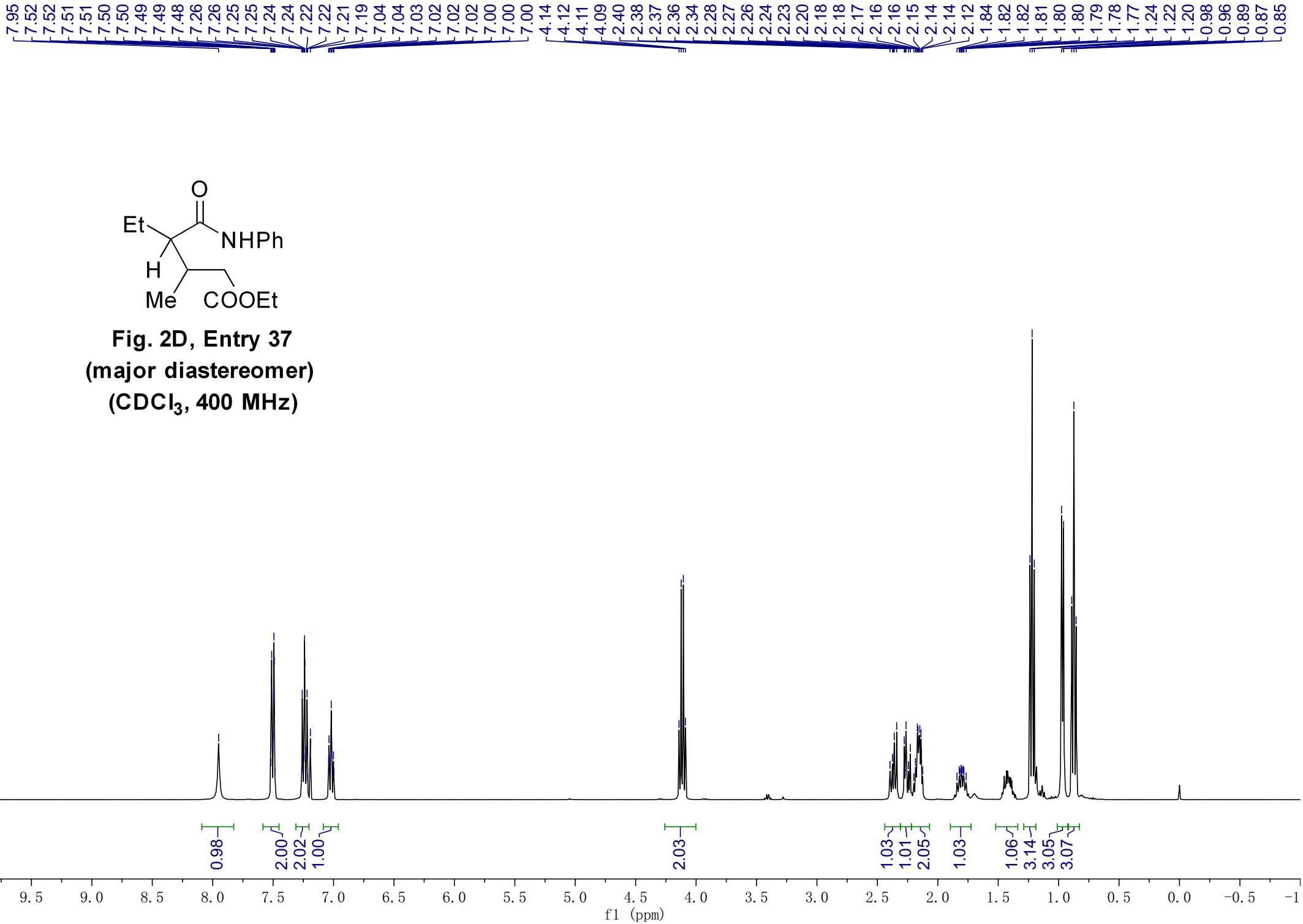


Fig. 2D, Entry 37
(major diastereomer)
($CDCl_3$, 400 MHz)

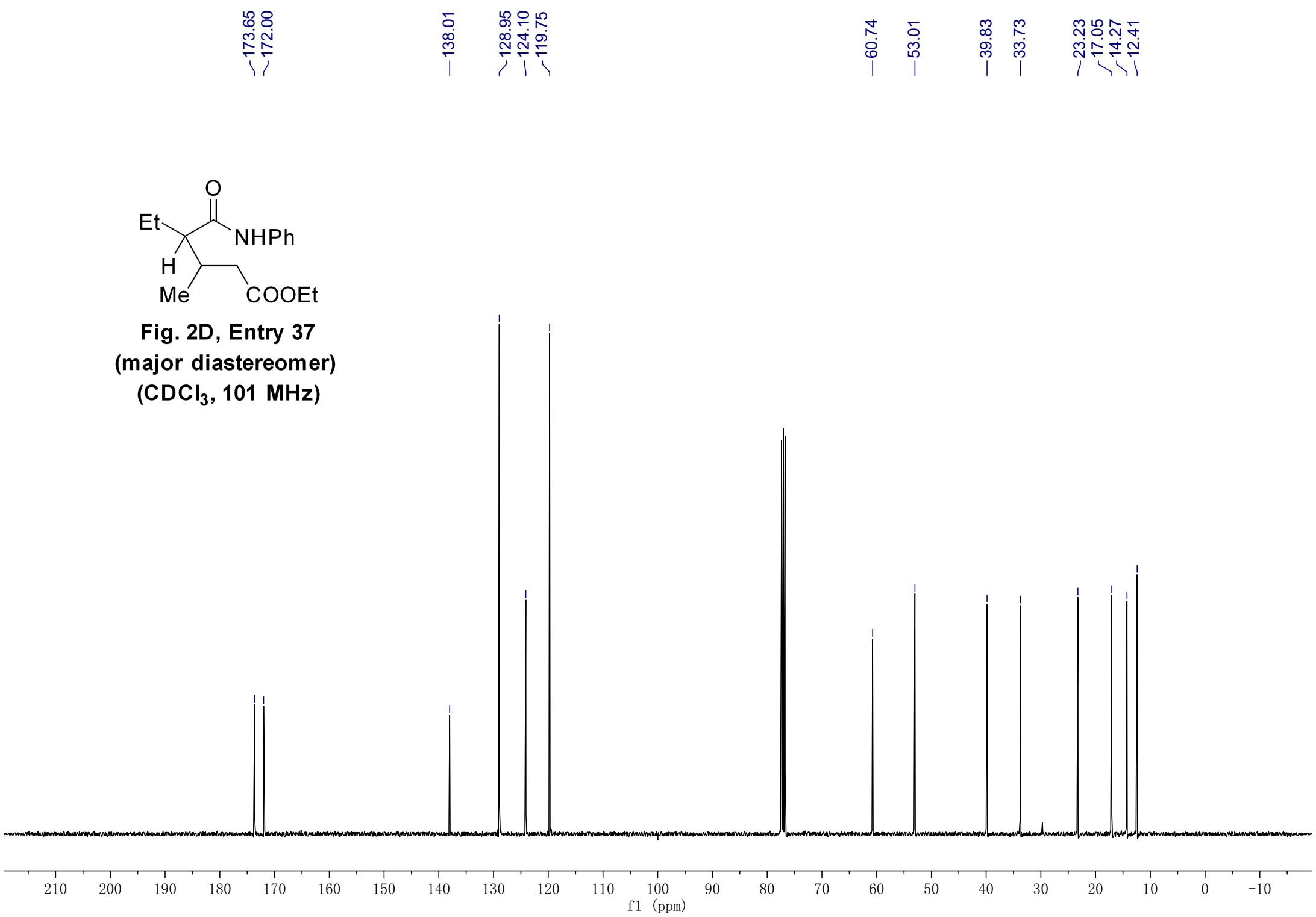


Fig. 2D, Entry 37
(major diastereomer)
($CDCl_3$, 101 MHz)

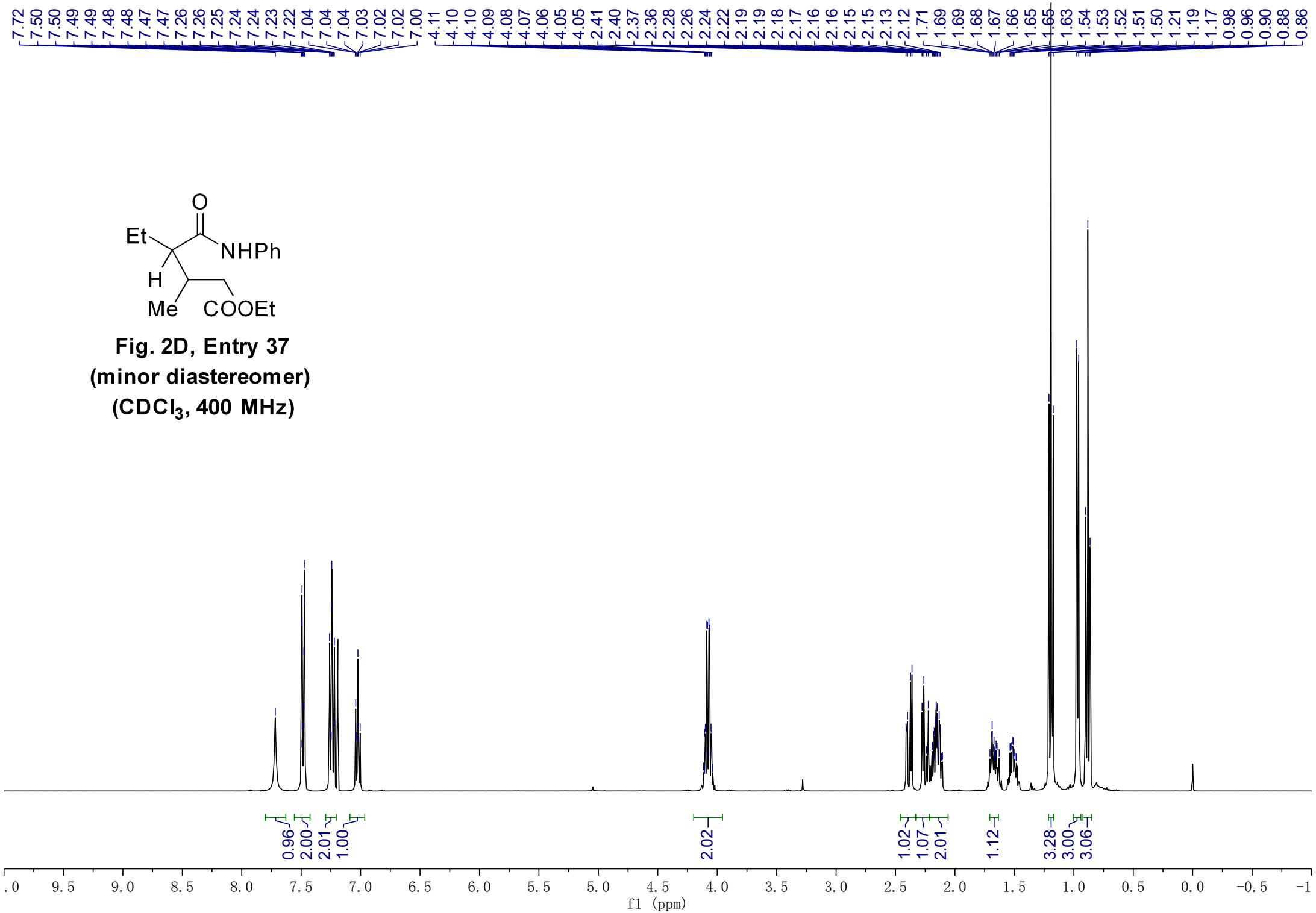


Fig. 2D, Entry 37
(minor diastereomer)
($CDCl_3$, 400 MHz)

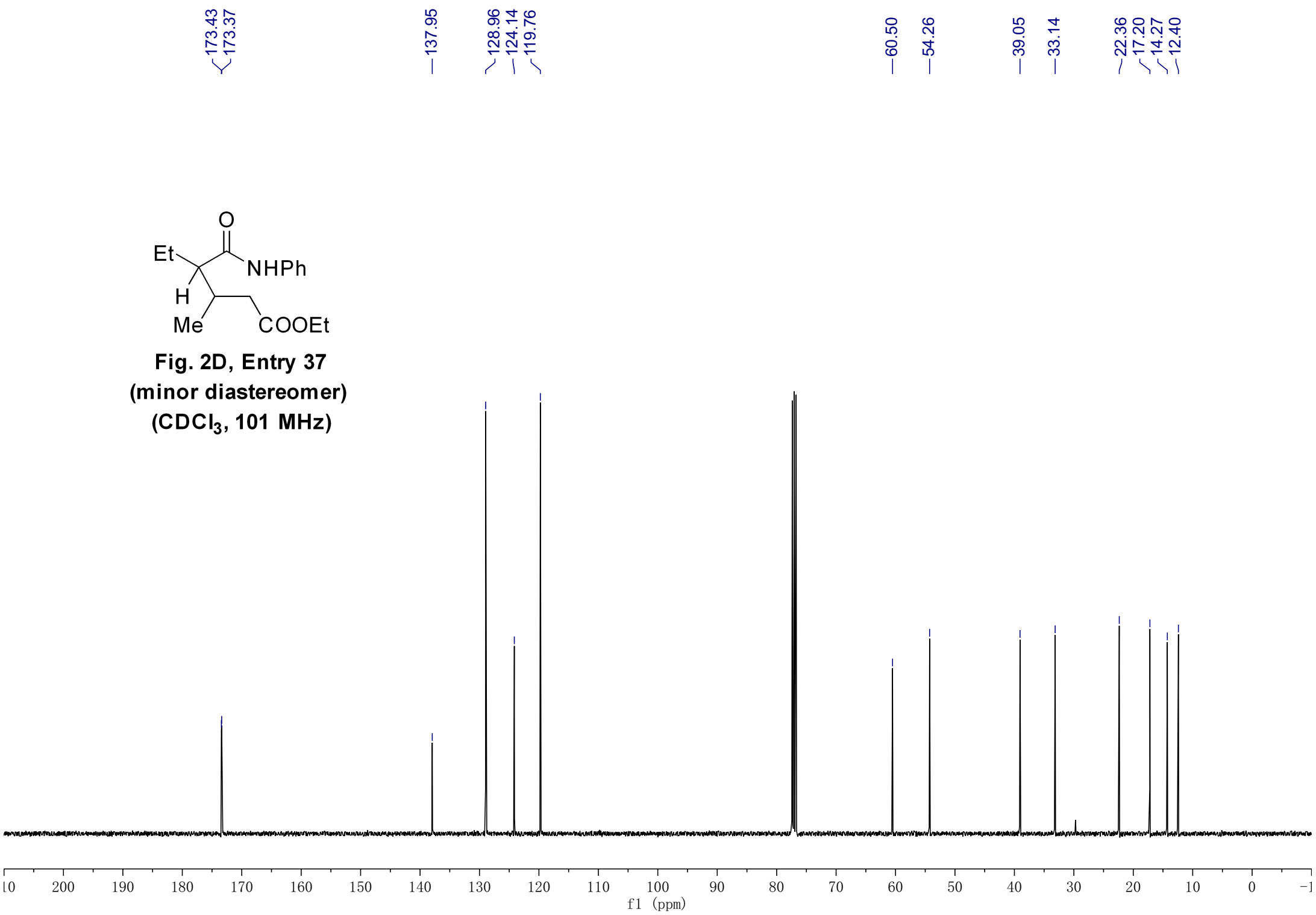


Fig. 2D, Entry 37
(minor diastereomer)
($CDCl_3$, 101 MHz)

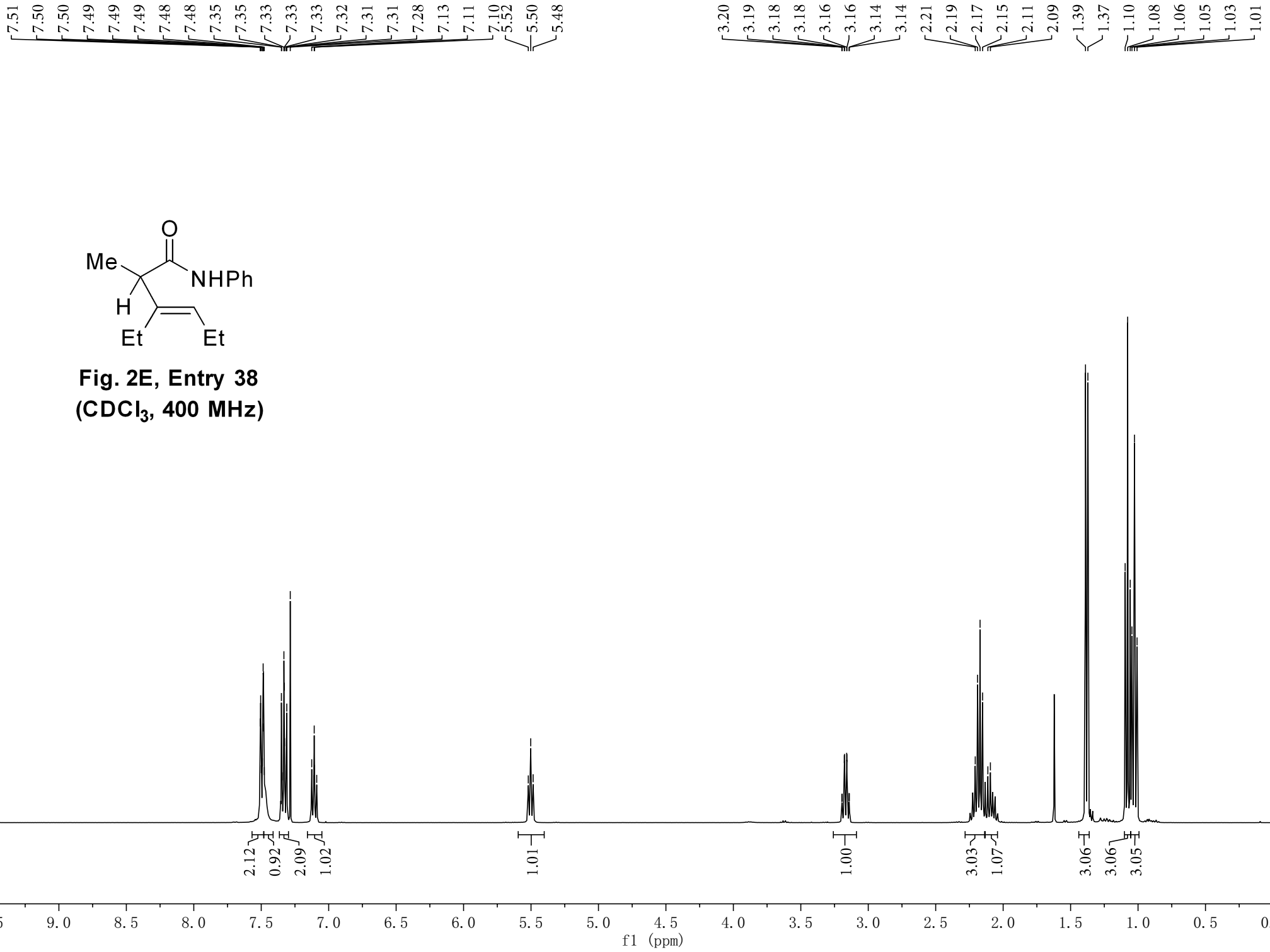


Fig. 2E, Entry 38
($CDCl_3$, 400 MHz)

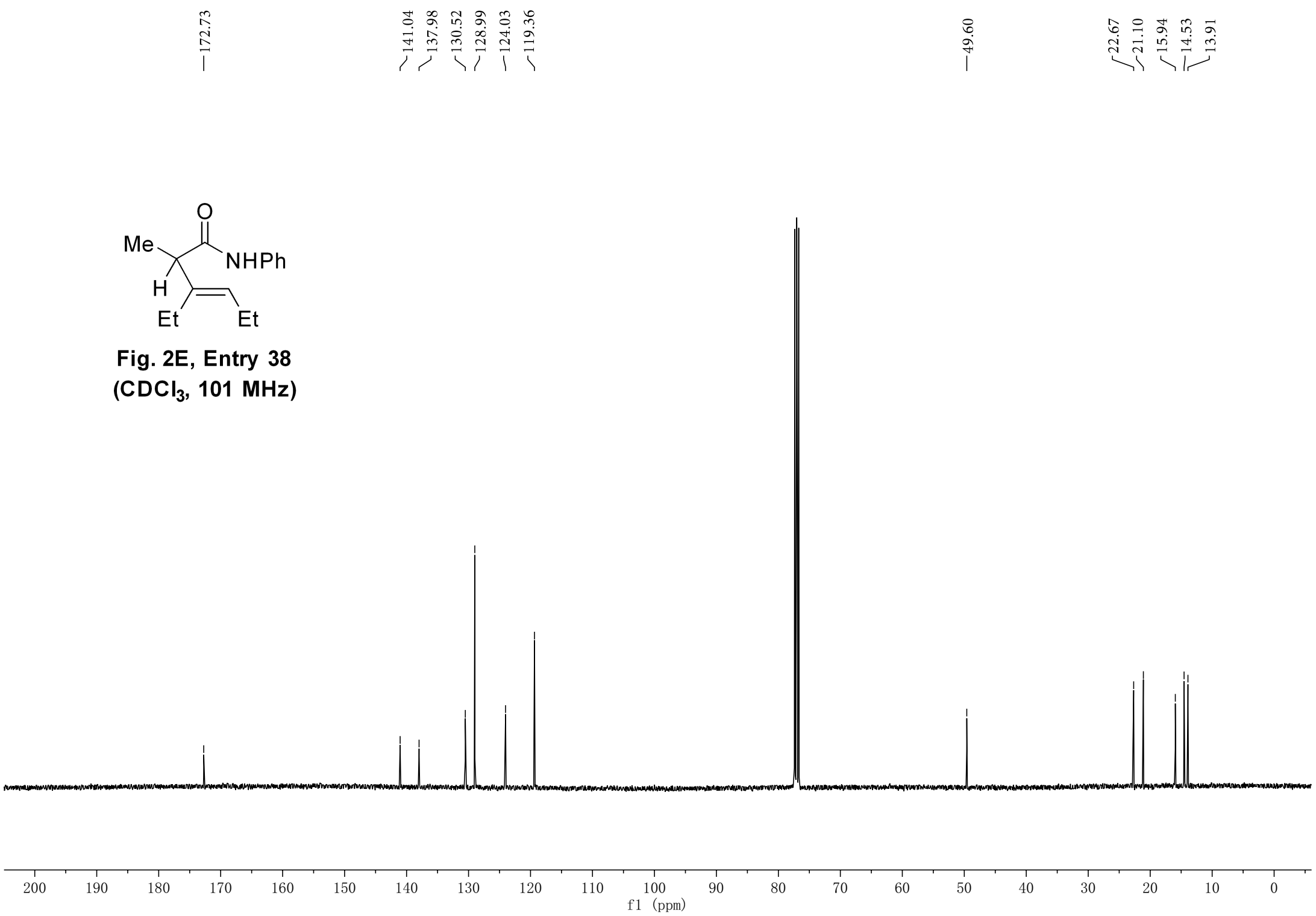


Fig. 2E, Entry 38
($CDCl_3$, 101 MHz)

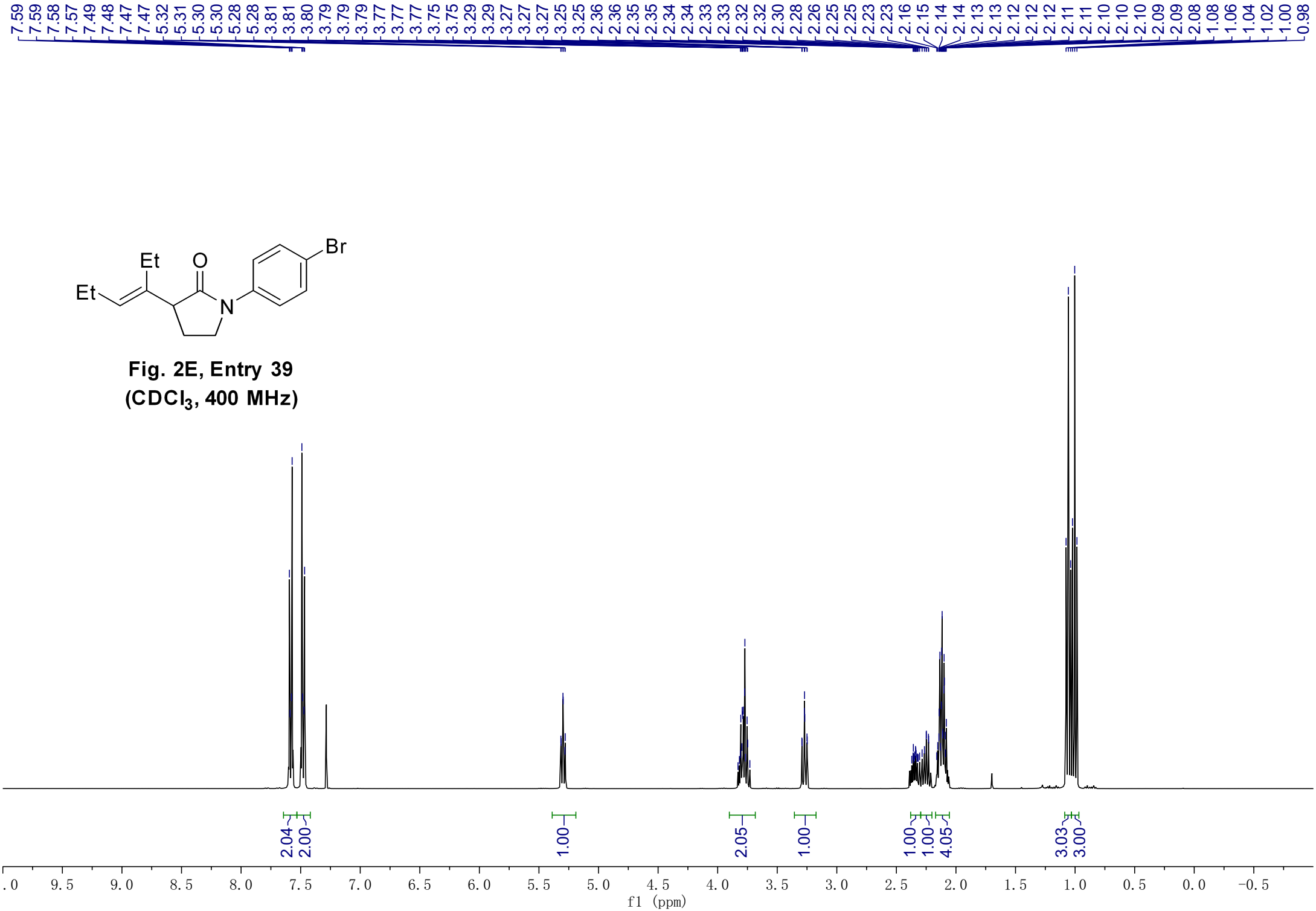


Fig. 2E, Entry 39
($CDCl_3$, 400 MHz)

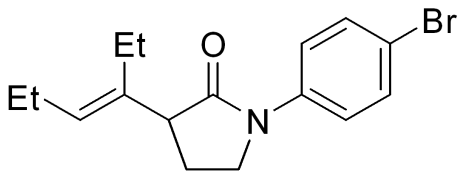


Fig. 2E, Entry 39
($CDCl_3$, 101 MHz)

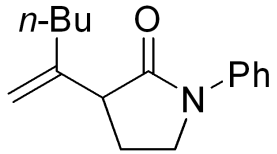


Fig. 2E, Entry 40
($CDCl_3$, 400 MHz)

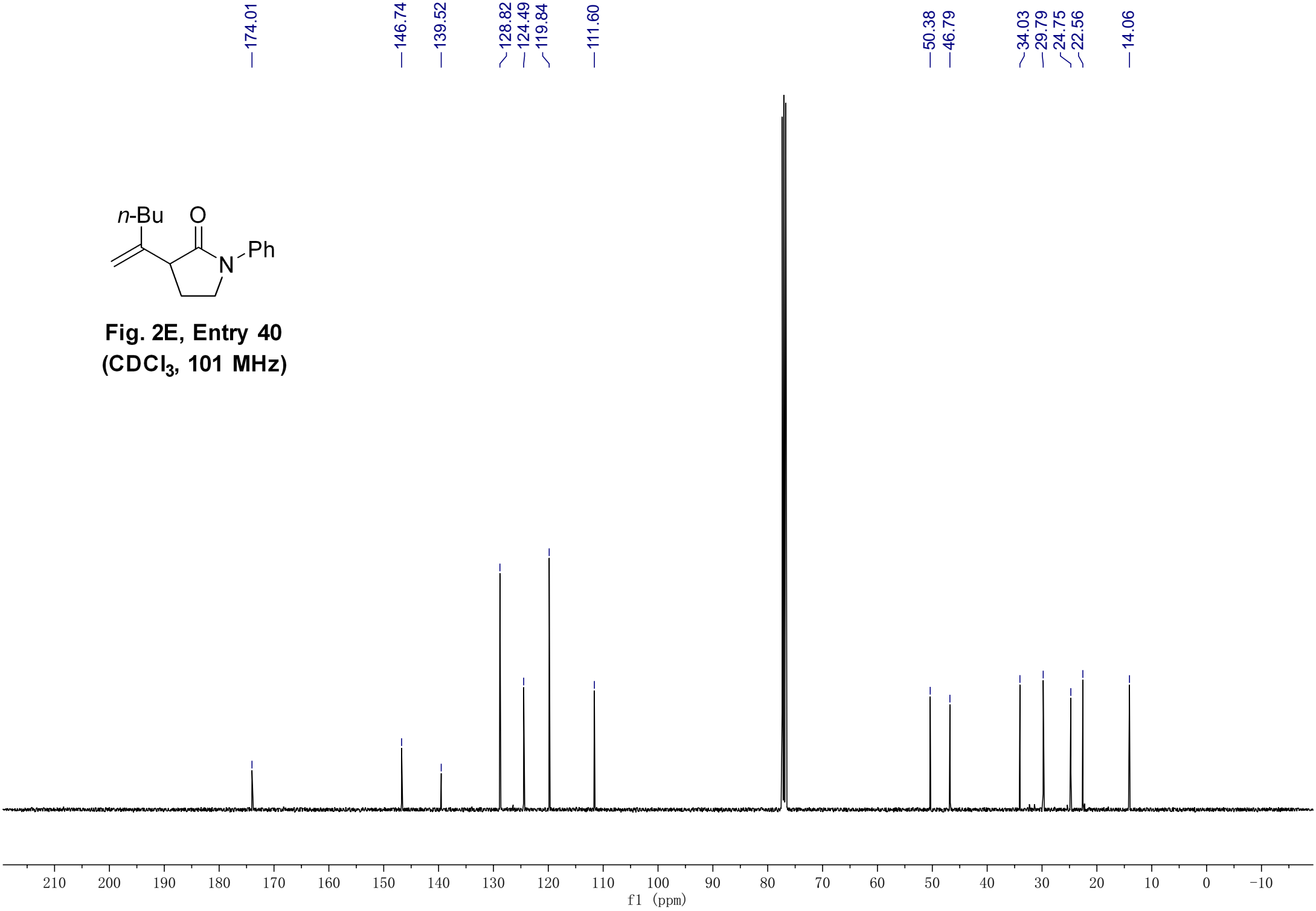
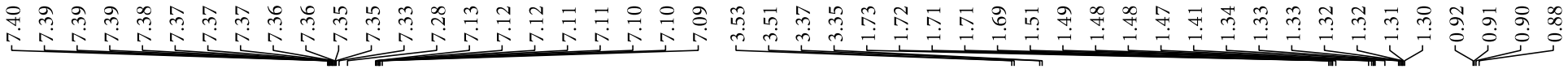


Fig. 2E, Entry 40
($CDCl_3$, 101 MHz)



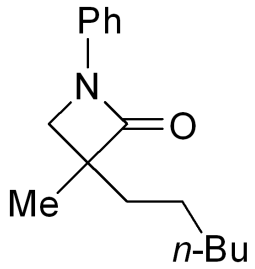


Fig. 3A, Entry 41
($CDCl_3$, 400 MHz)

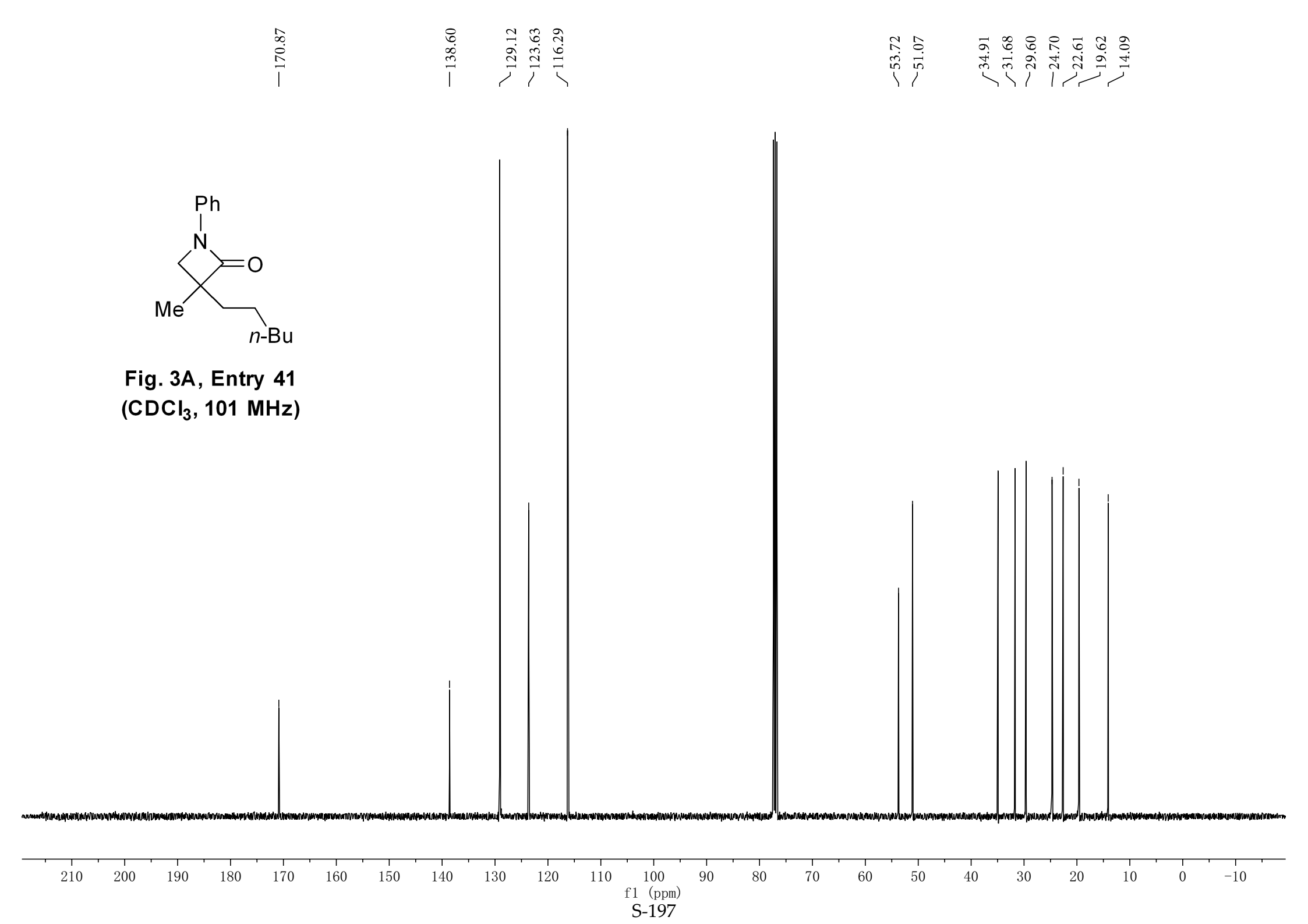


Fig. 3A, Entry 41
($CDCl_3$, 101 MHz)

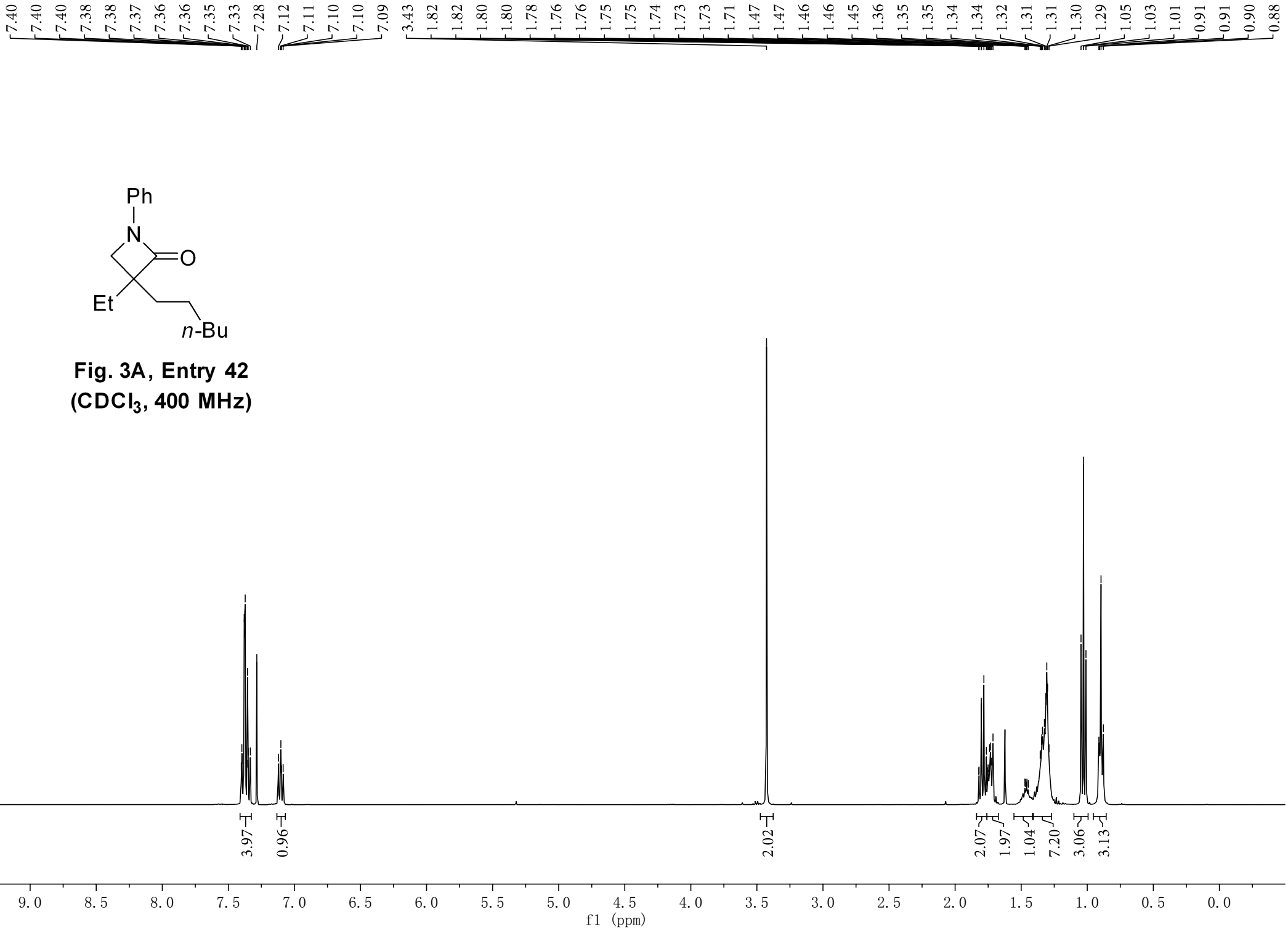


Fig. 3A, Entry 42
($CDCl_3$, 400 MHz)

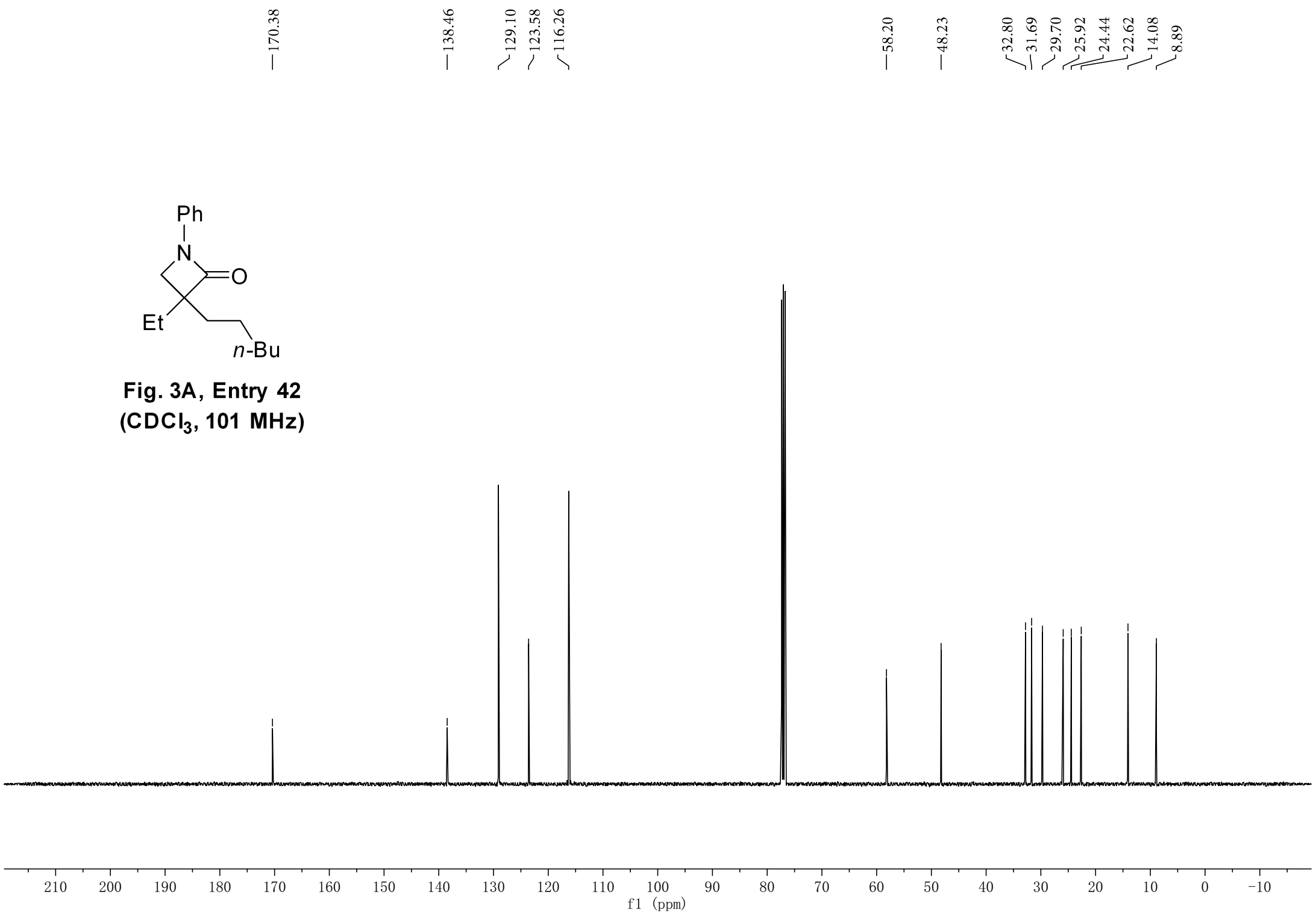


Fig. 3A, Entry 42
($CDCl_3$, 101 MHz)

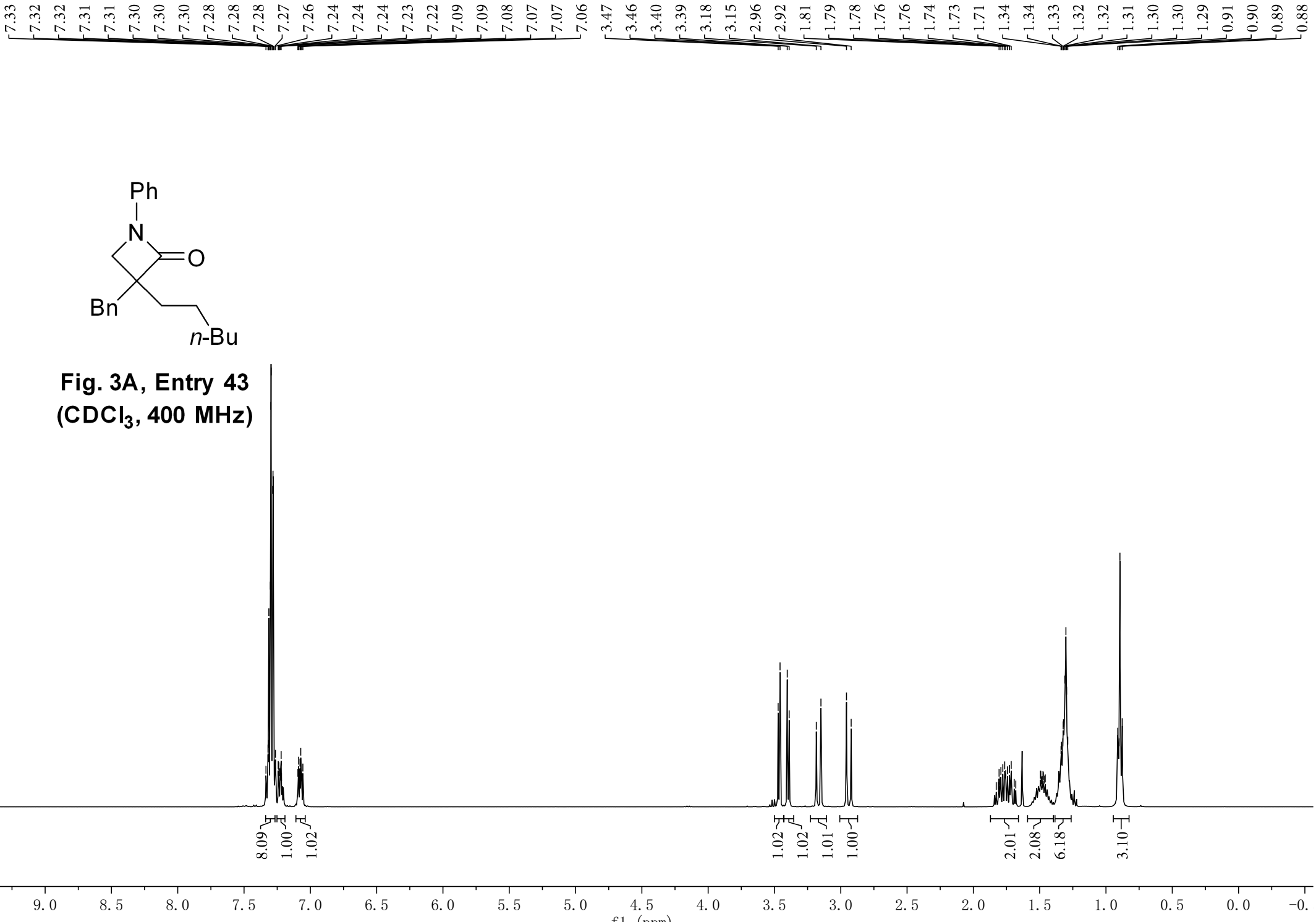


Fig. 3A, Entry 43
($CDCl_3$, 400 MHz)

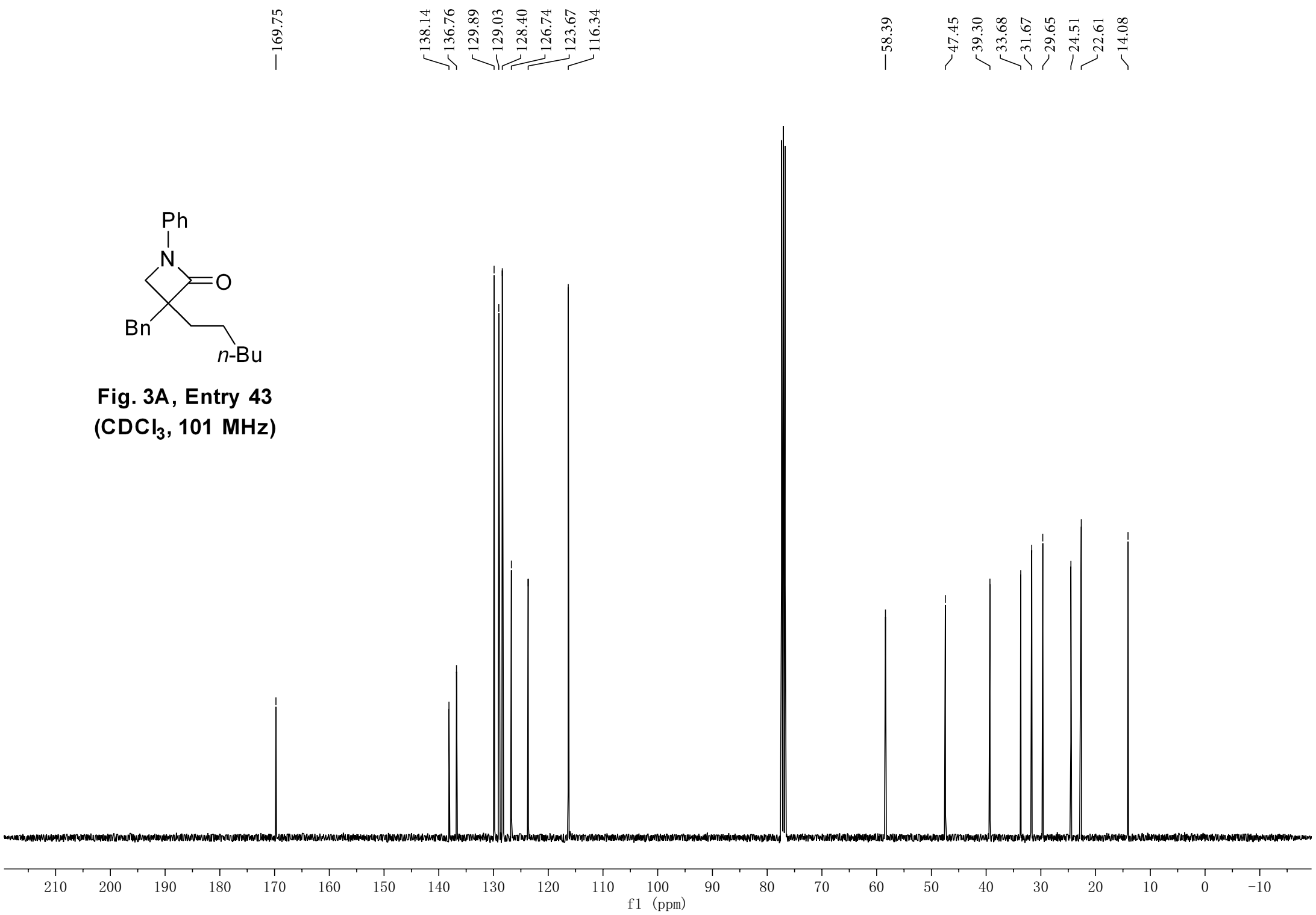


Fig. 3A, Entry 43
($CDCl_3$, 101 MHz)

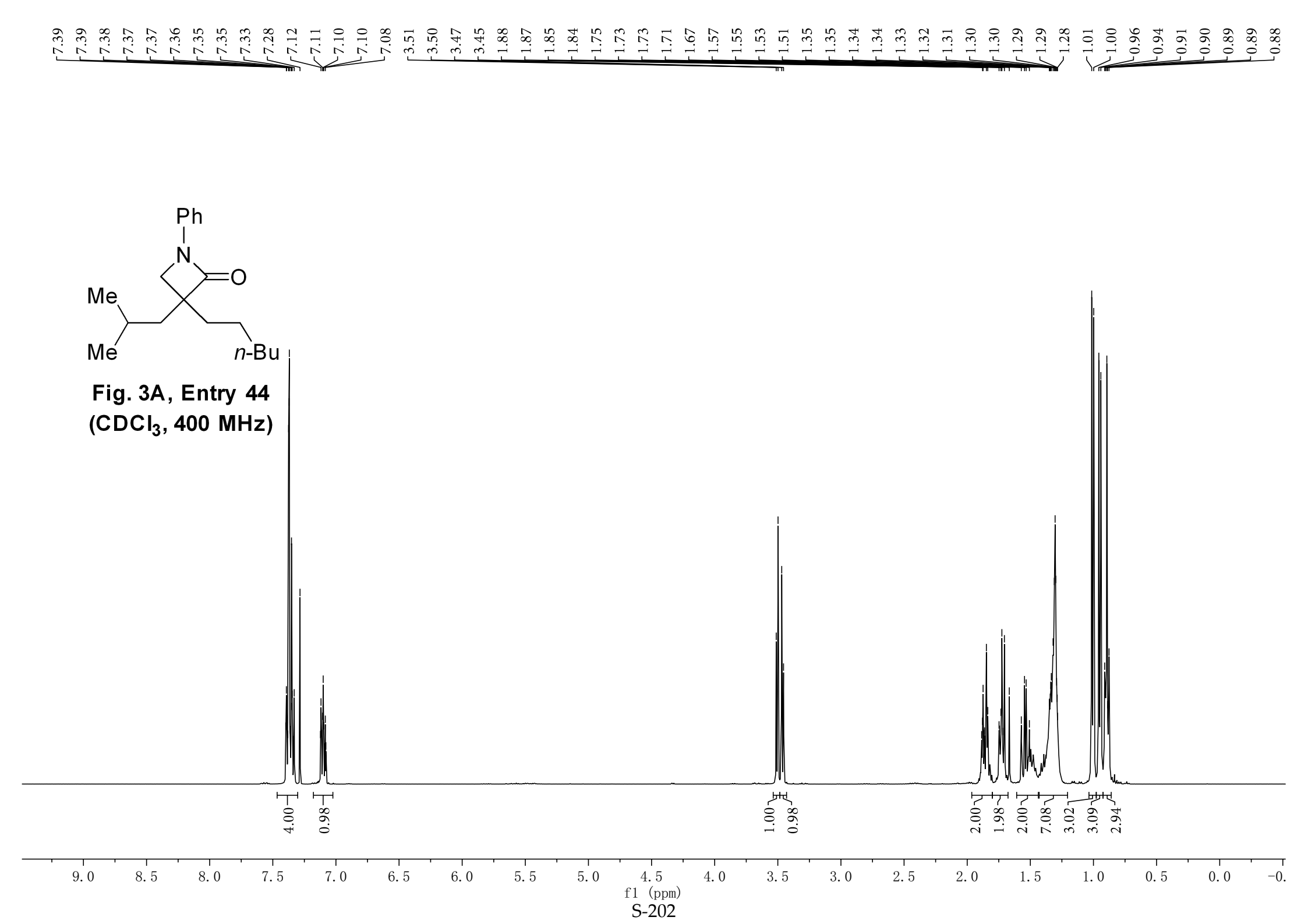


Fig. 3A, Entry 44
($CDCl_3$, 400 MHz)

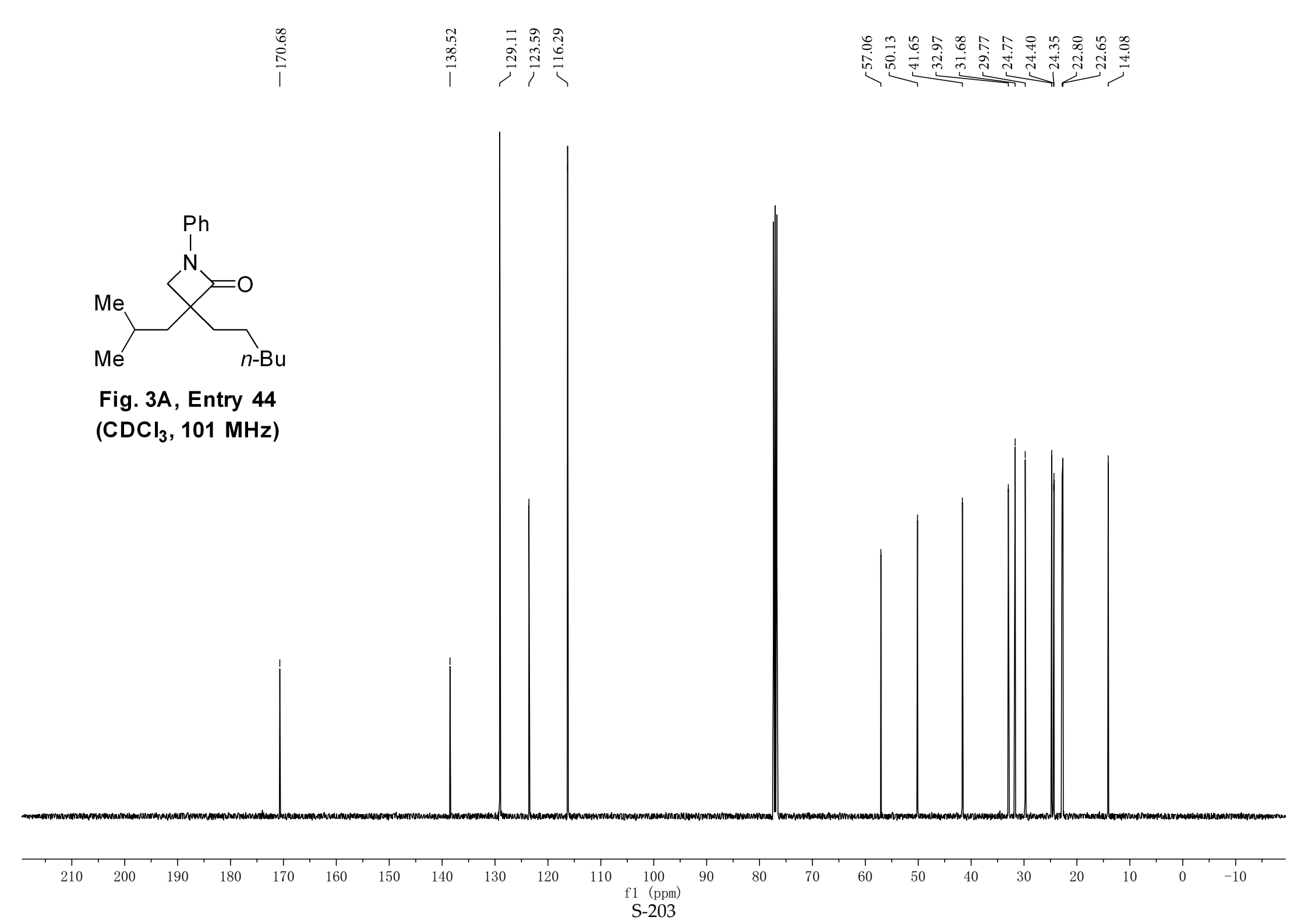


Fig. 3A, Entry 44
($CDCl_3$, 101 MHz)

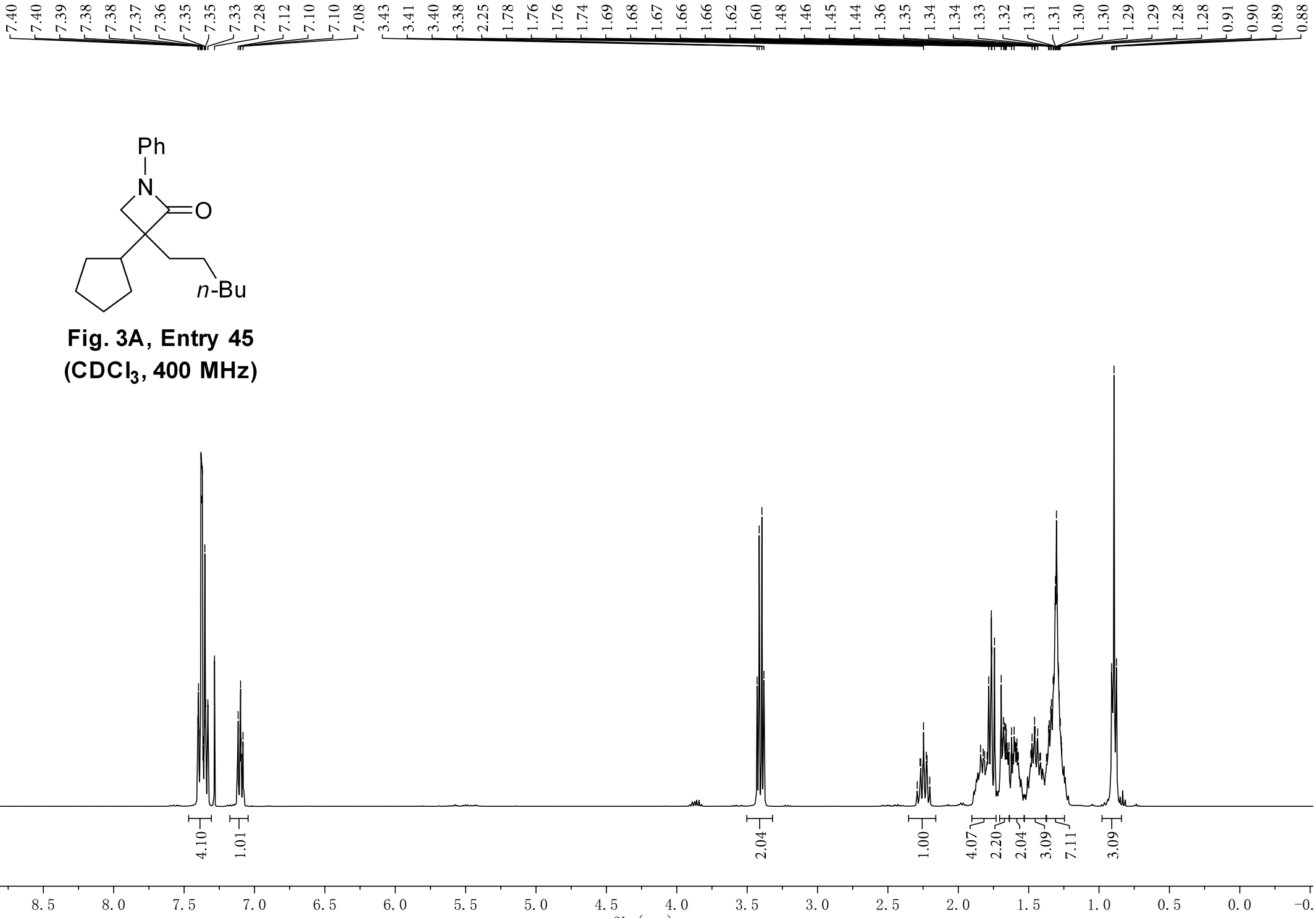


Fig. 3A, Entry 45
($CDCl_3$, 400 MHz)

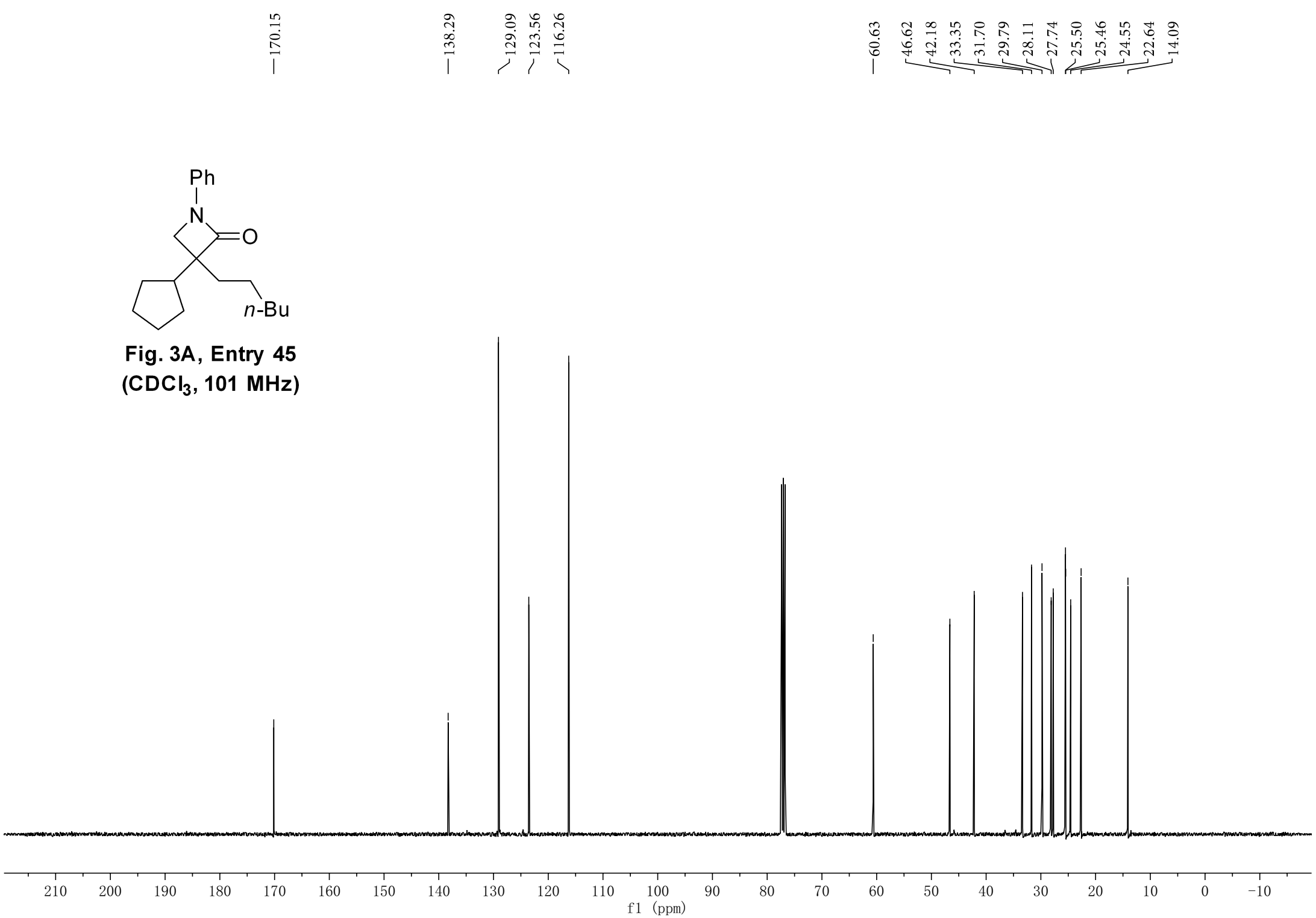


Fig. 3A, Entry 45
($CDCl_3$, 101 MHz)

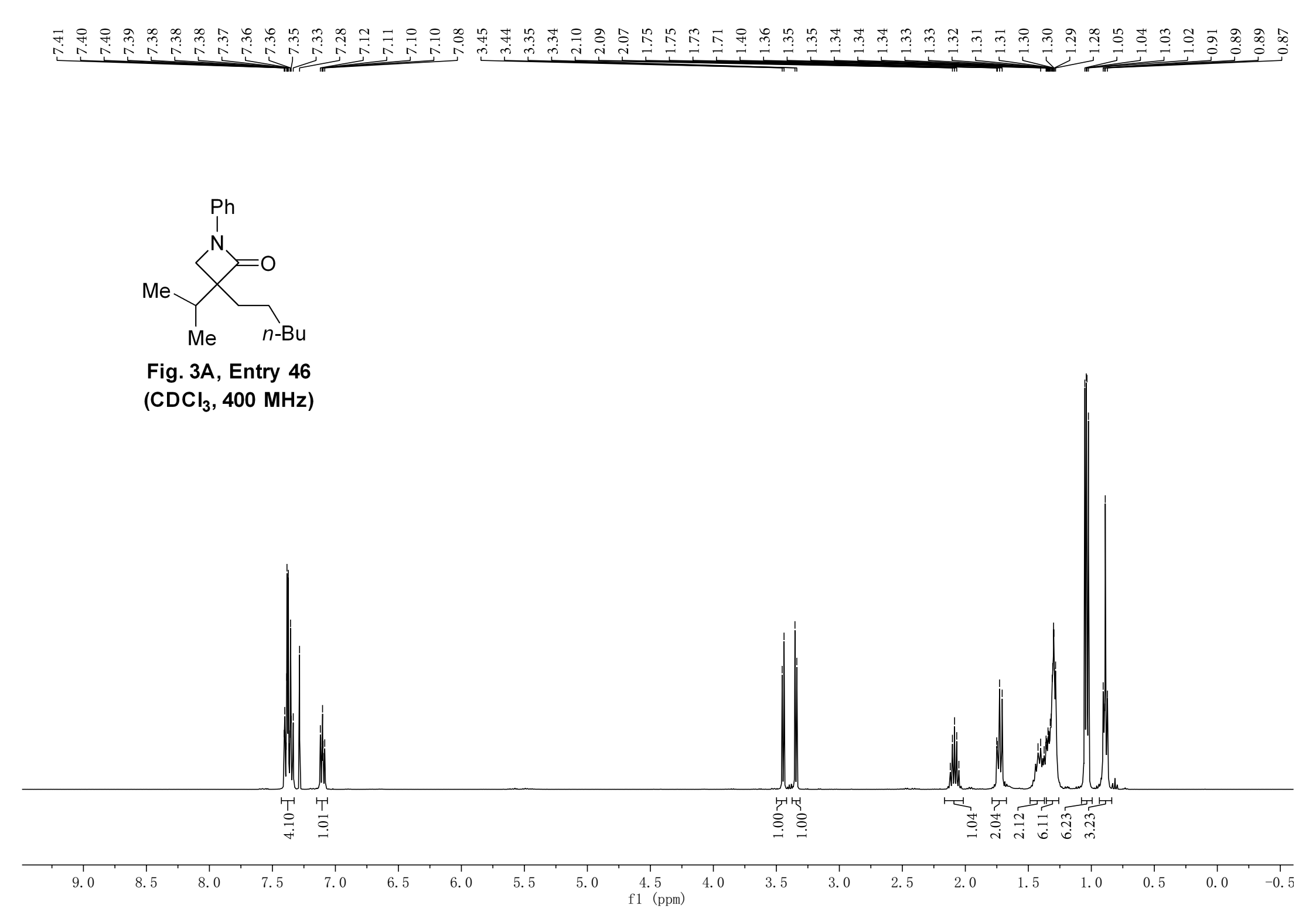


Fig. 3A, Entry 46
($CDCl_3$, 400 MHz)

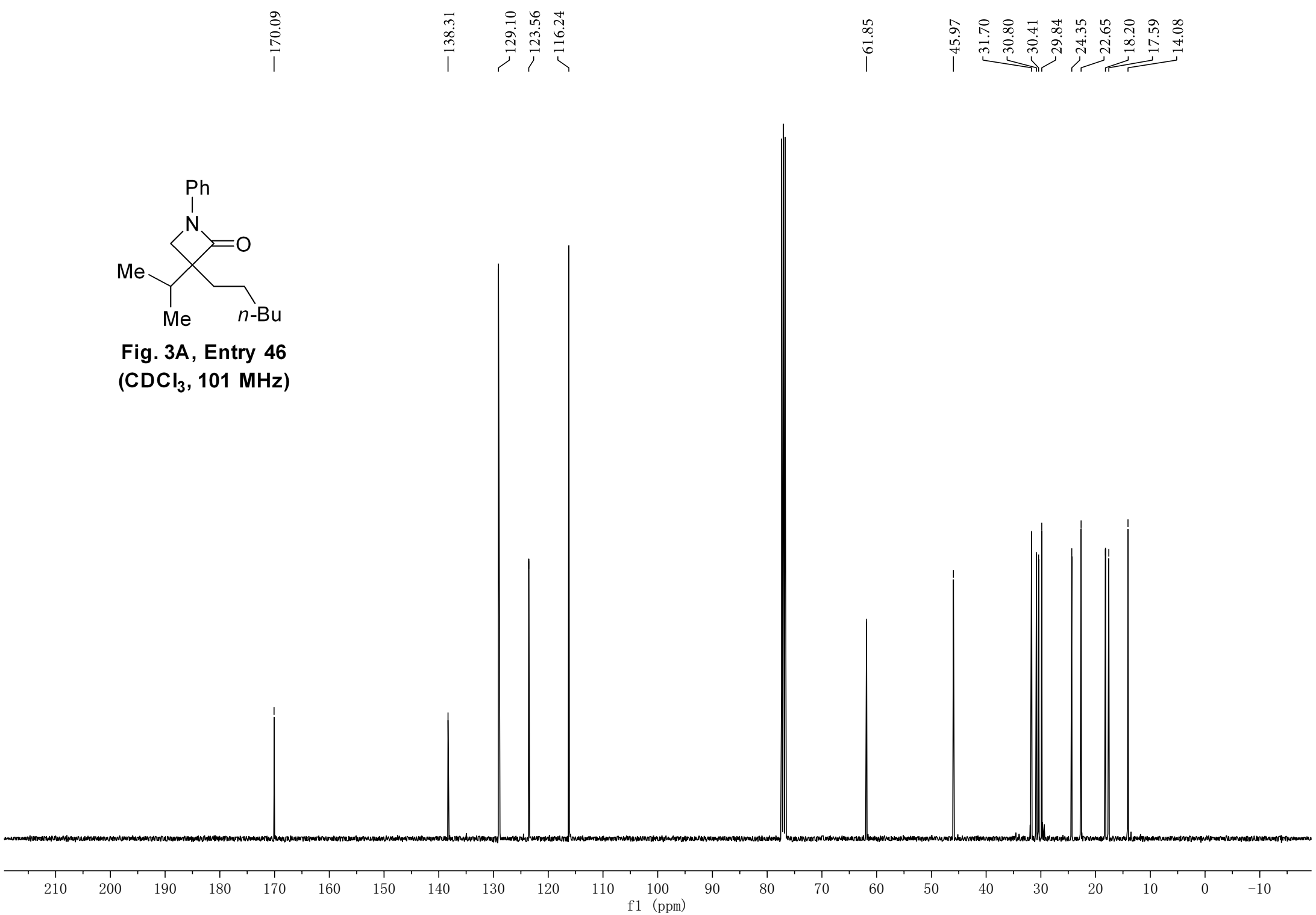
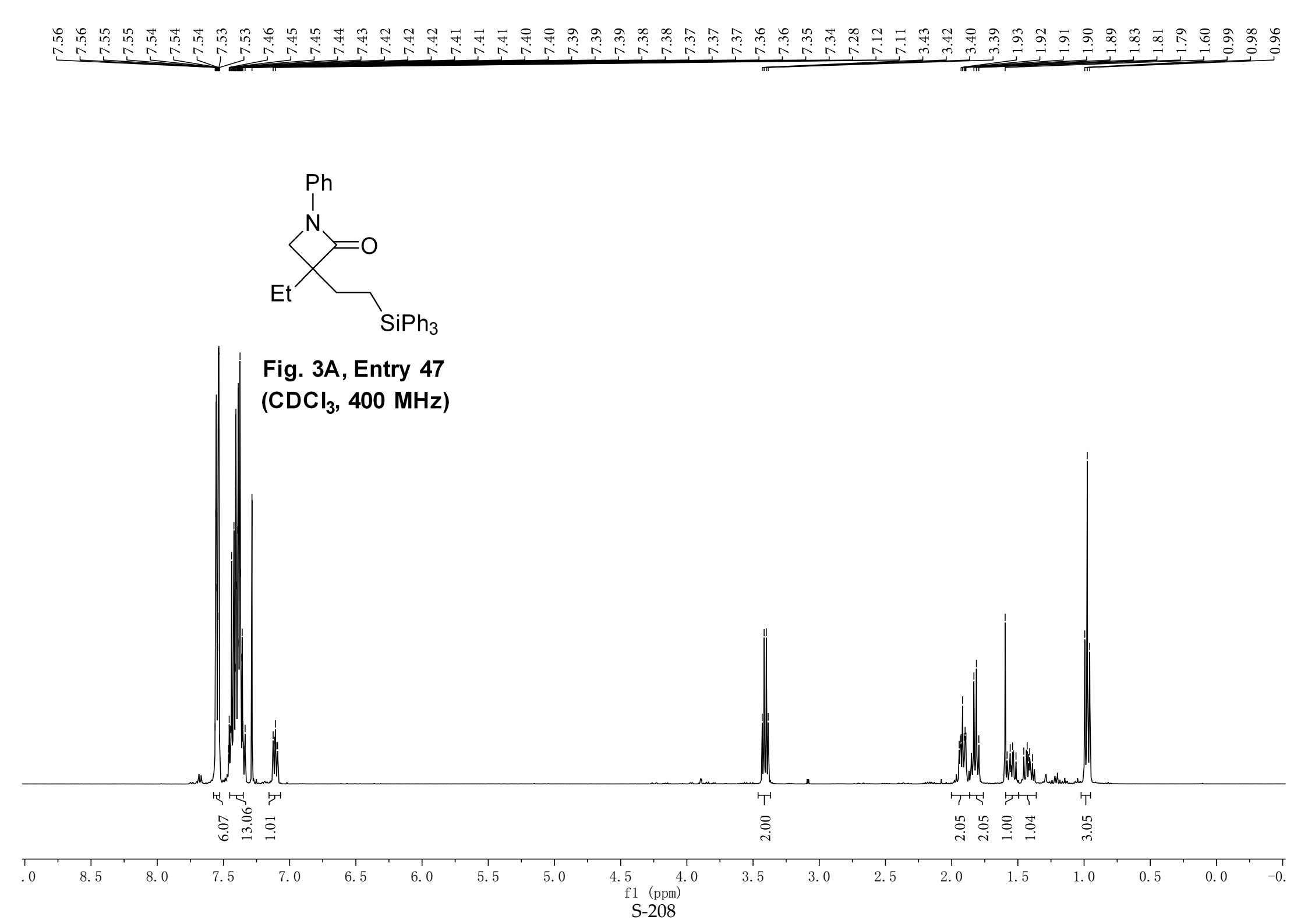


Fig. 3A, Entry 46
($CDCl_3$, 101 MHz)


7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.53 7.53 7.46 7.45 7.45 7.44 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.28 7.12 7.11 3.43 3.42 3.40 3.39 1.93 1.92 1.91 1.90 1.89 1.83 1.81 1.79 1.60 0.99 0.98 0.96
Ph
N
O
Et
SiPh3
Fig. 3A, Entry 47
(CDCl3, 400 MHz)
6.07
13.06
1.01
2.00
2.05
2.05
1.00
1.04
3.05
f1 (ppm)

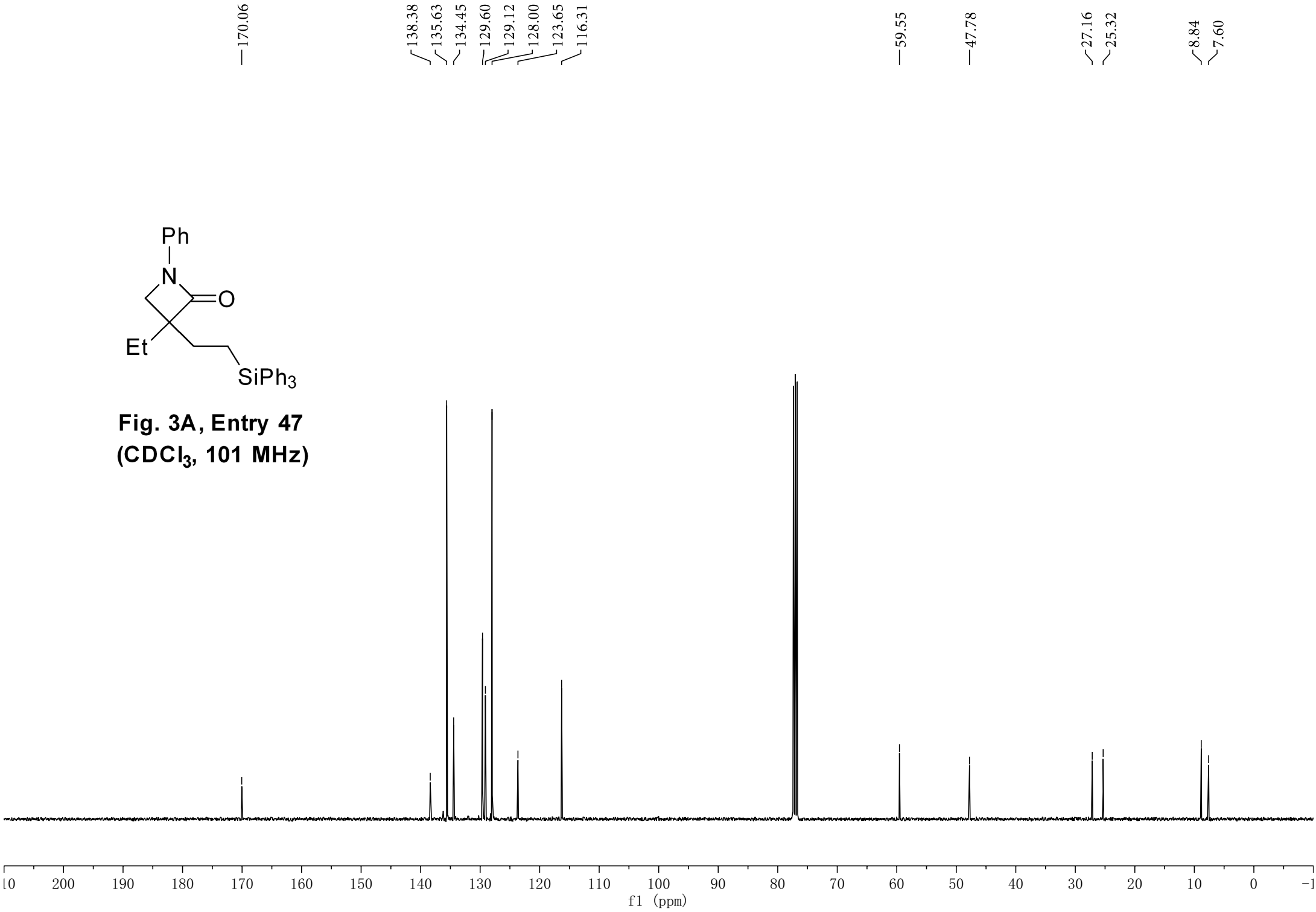
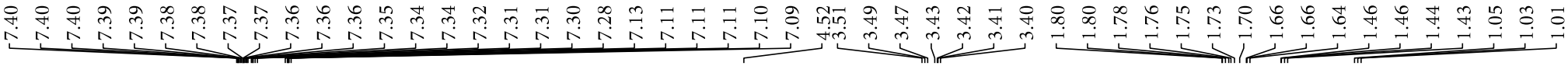


Fig. 3A, Entry 47
($CDCl_3$, 101 MHz)



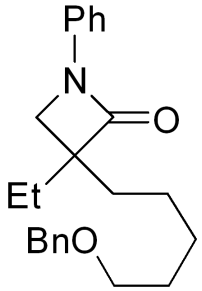
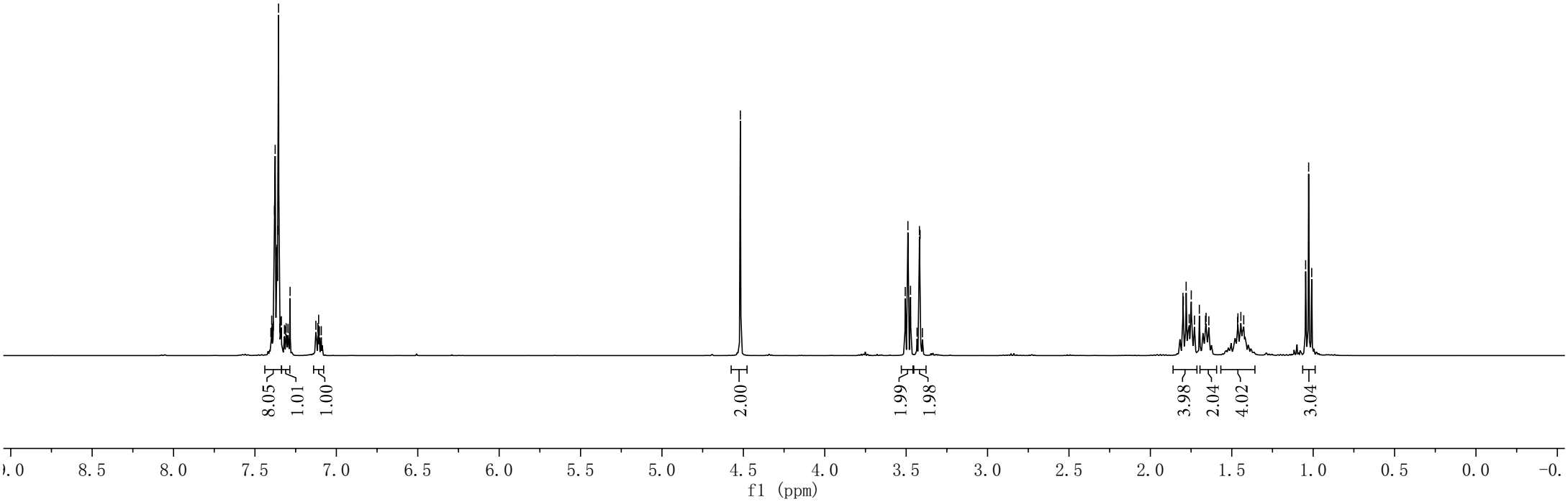


Fig. 3A, Entry 48
($CDCl_3$, 400 MHz)



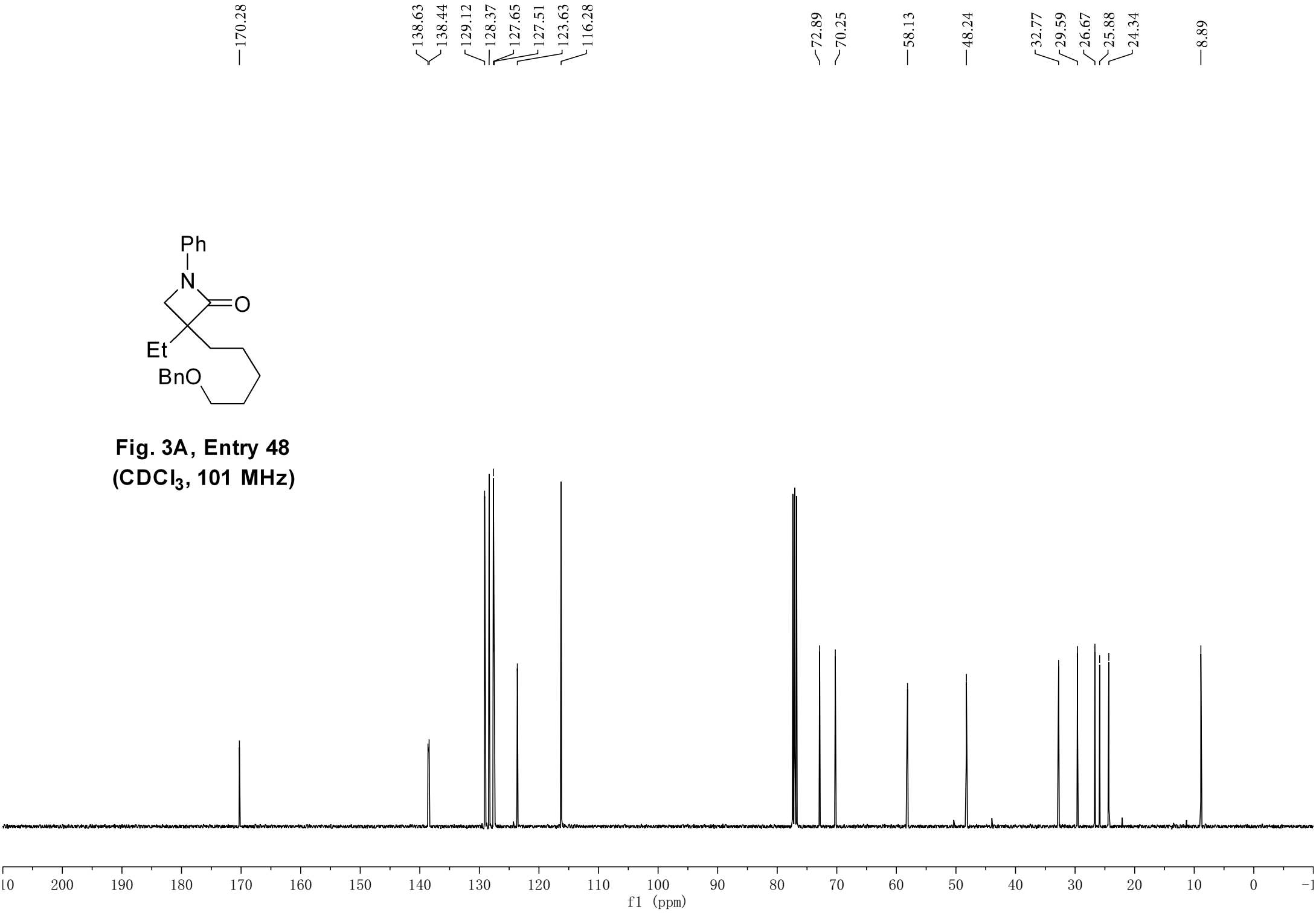


Fig. 3A, Entry 48
($CDCl_3$, 101 MHz)

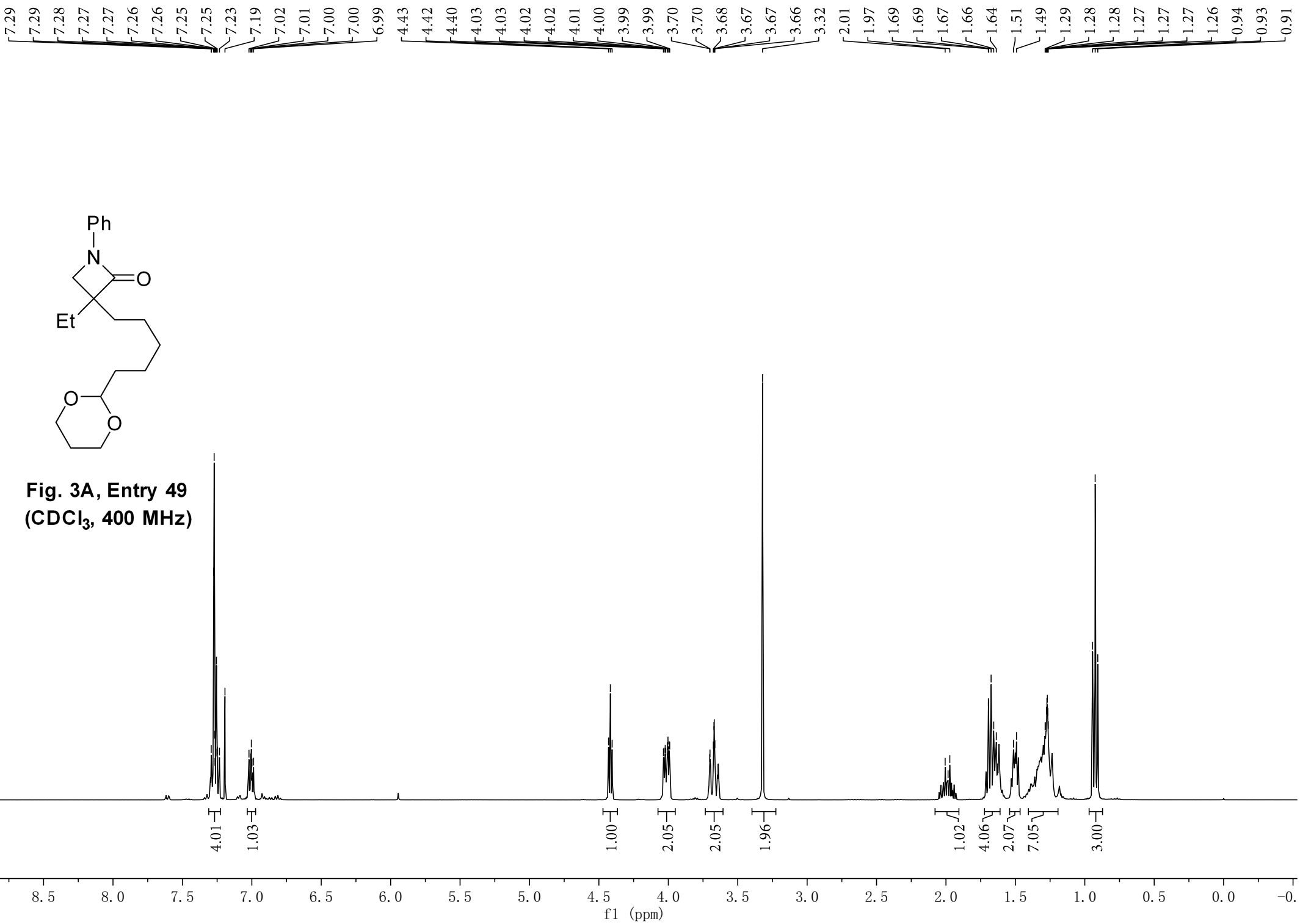


Fig. 3A, Entry 49
($CDCl_3$, 400 MHz)

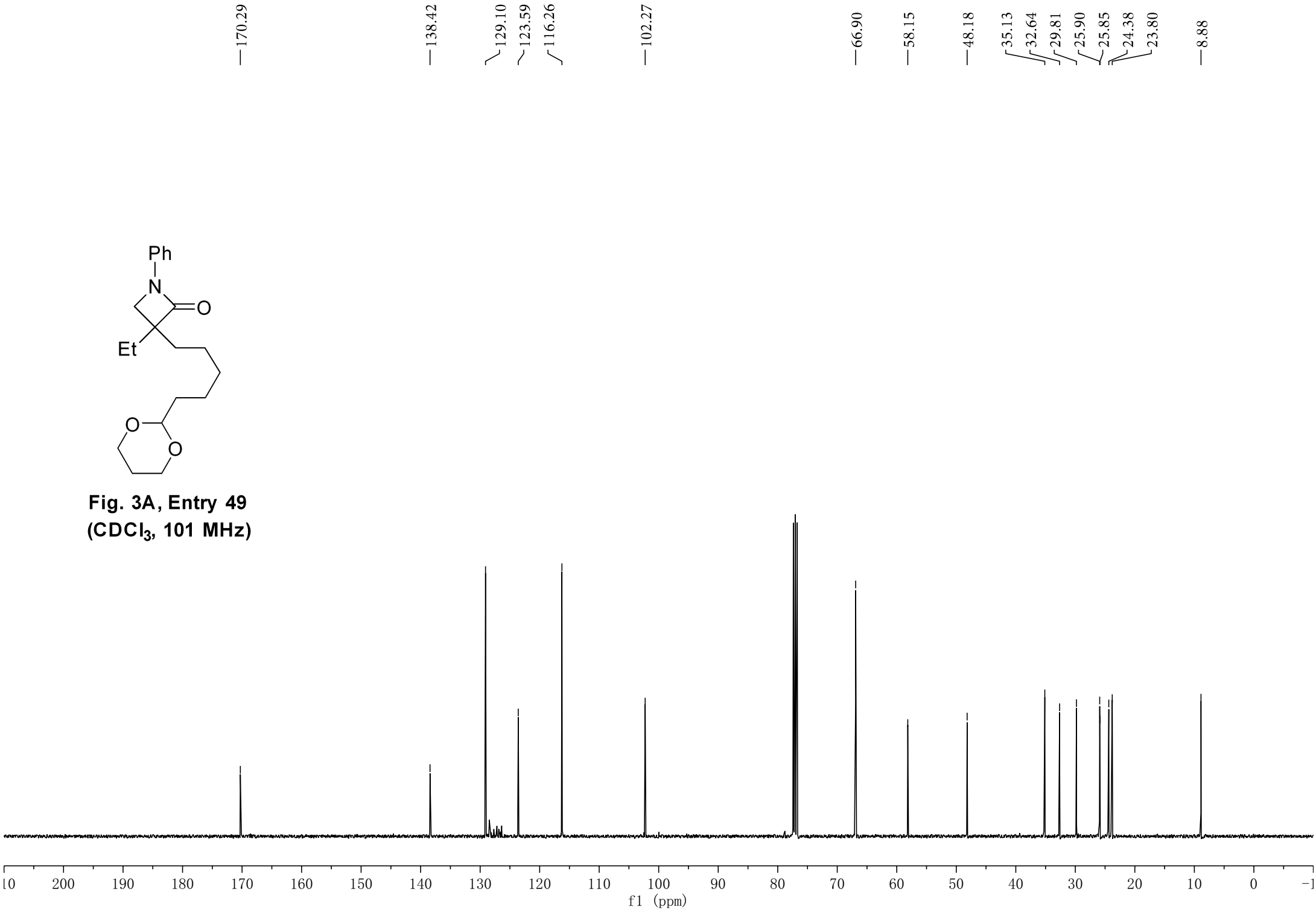


Fig. 3A, Entry 49
($CDCl_3$, 101 MHz)

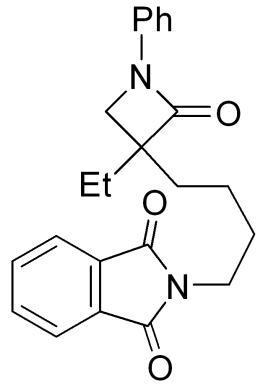
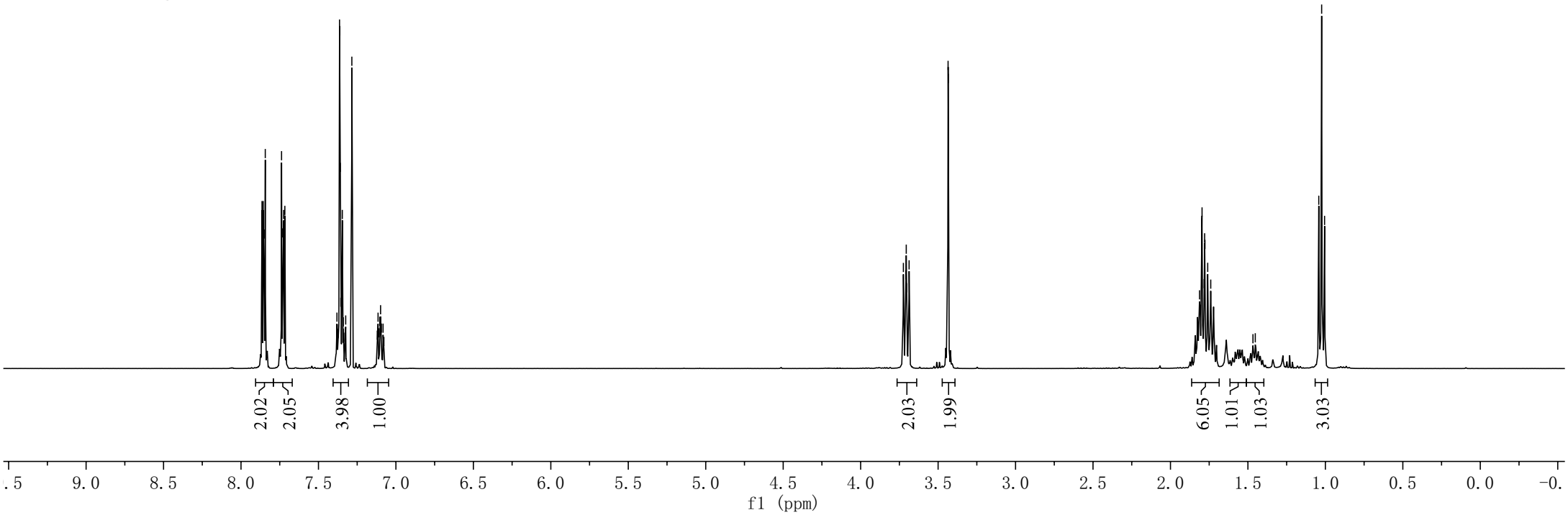


Fig. 3A, Entry 50
($CDCl_3$, 400 MHz)



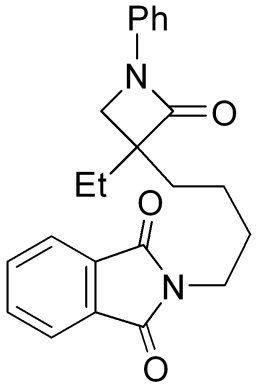
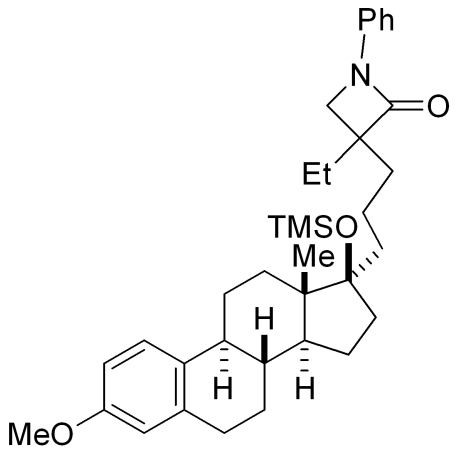


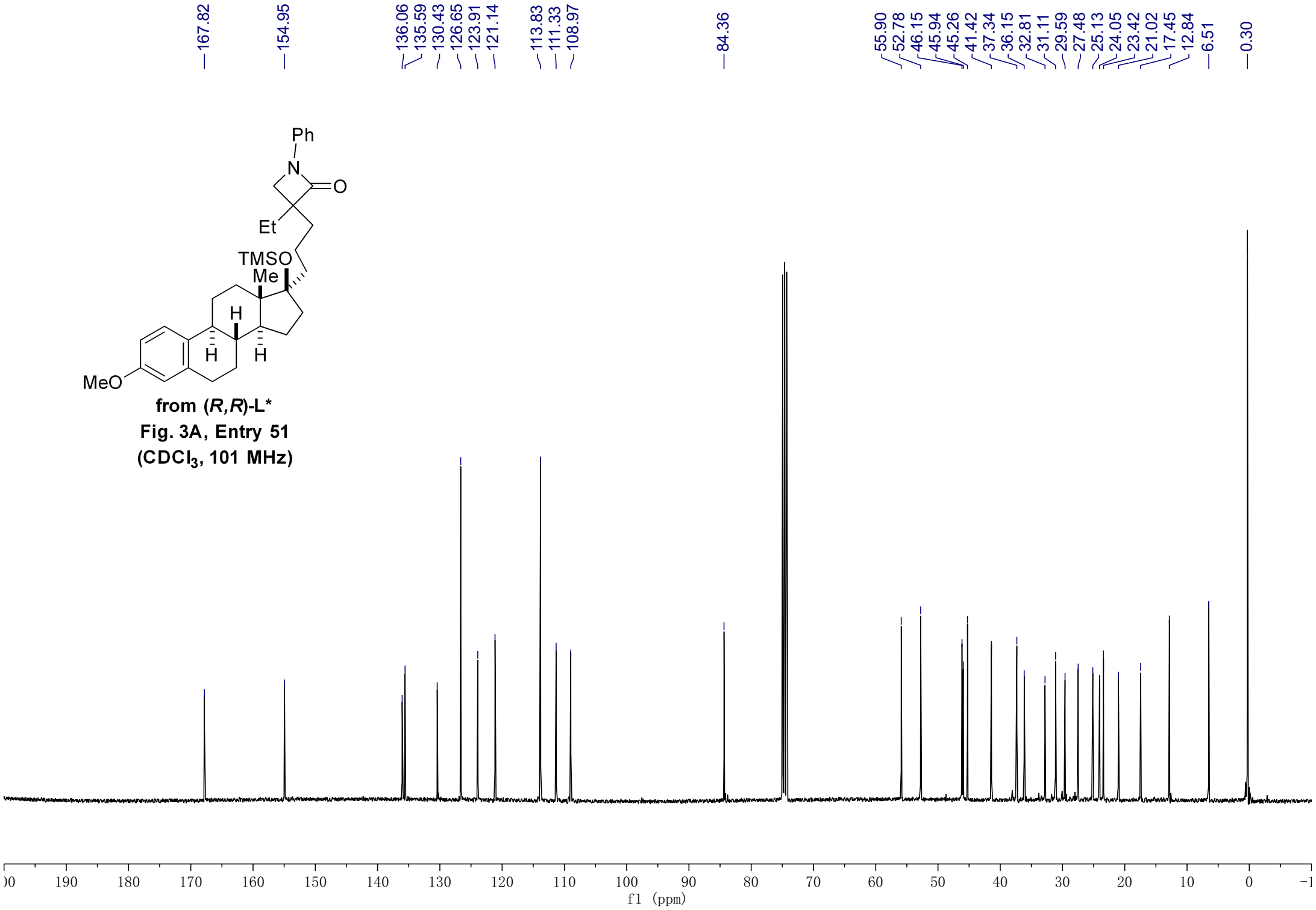
Fig. 3A, Entry 50
($CDCl_3$, 101 MHz)



from (*R*,*R*)-L*

Fig. 3A, Entry 51

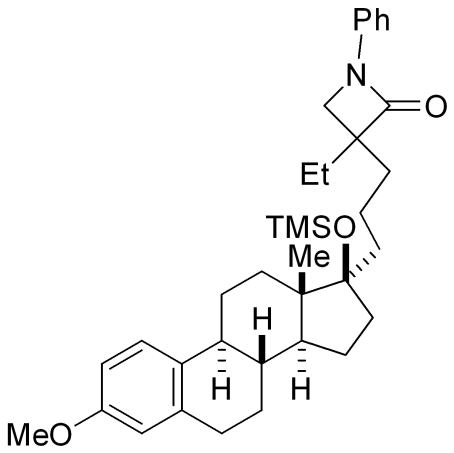
($CDCl_3$, 400 MHz)



from (*R*,*R*)-L*

Fig. 3A, Entry 51

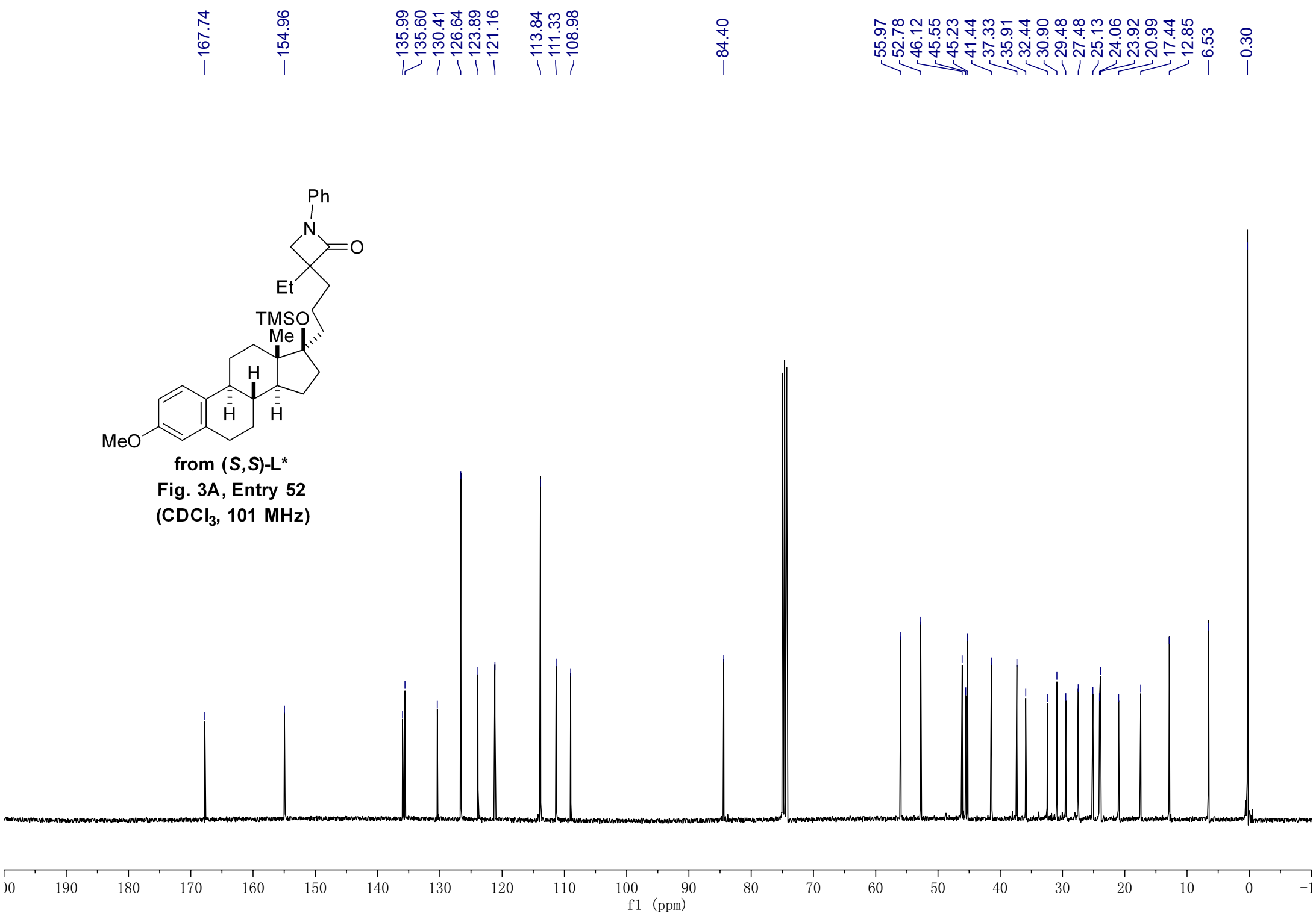
($CDCl_3$, 101 MHz)



from (*S*,*S*)-L*

Fig. 3A, Entry 52

($CDCl_3$, 400 MHz)



from (*S*,*S*)-L*

Fig. 3A, Entry 52

($CDCl_3$, 101 MHz)

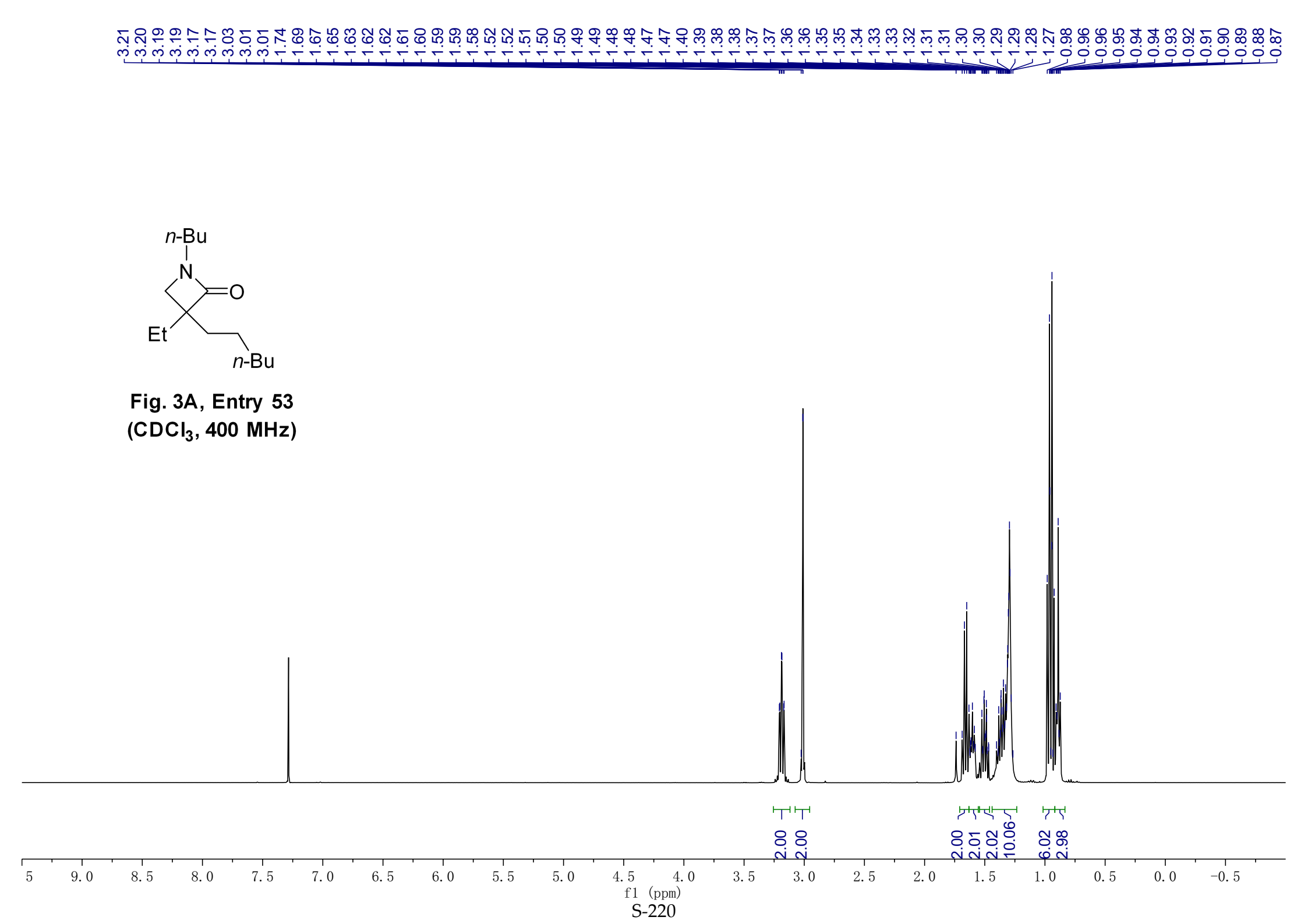


Fig. 3A, Entry 53
($CDCl_3$, 400 MHz)

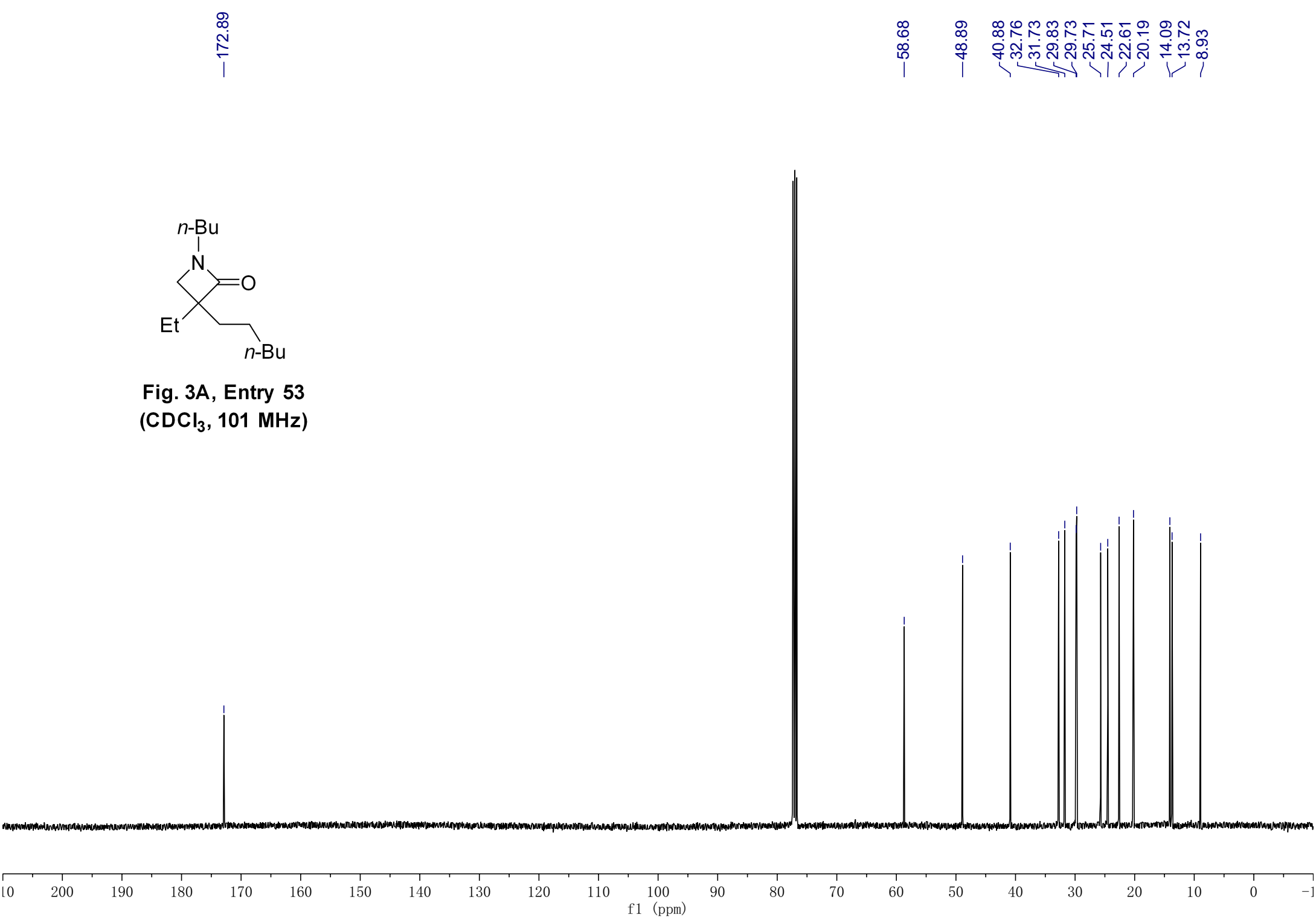


Fig. 3A, Entry 53
($CDCl_3$, 101 MHz)

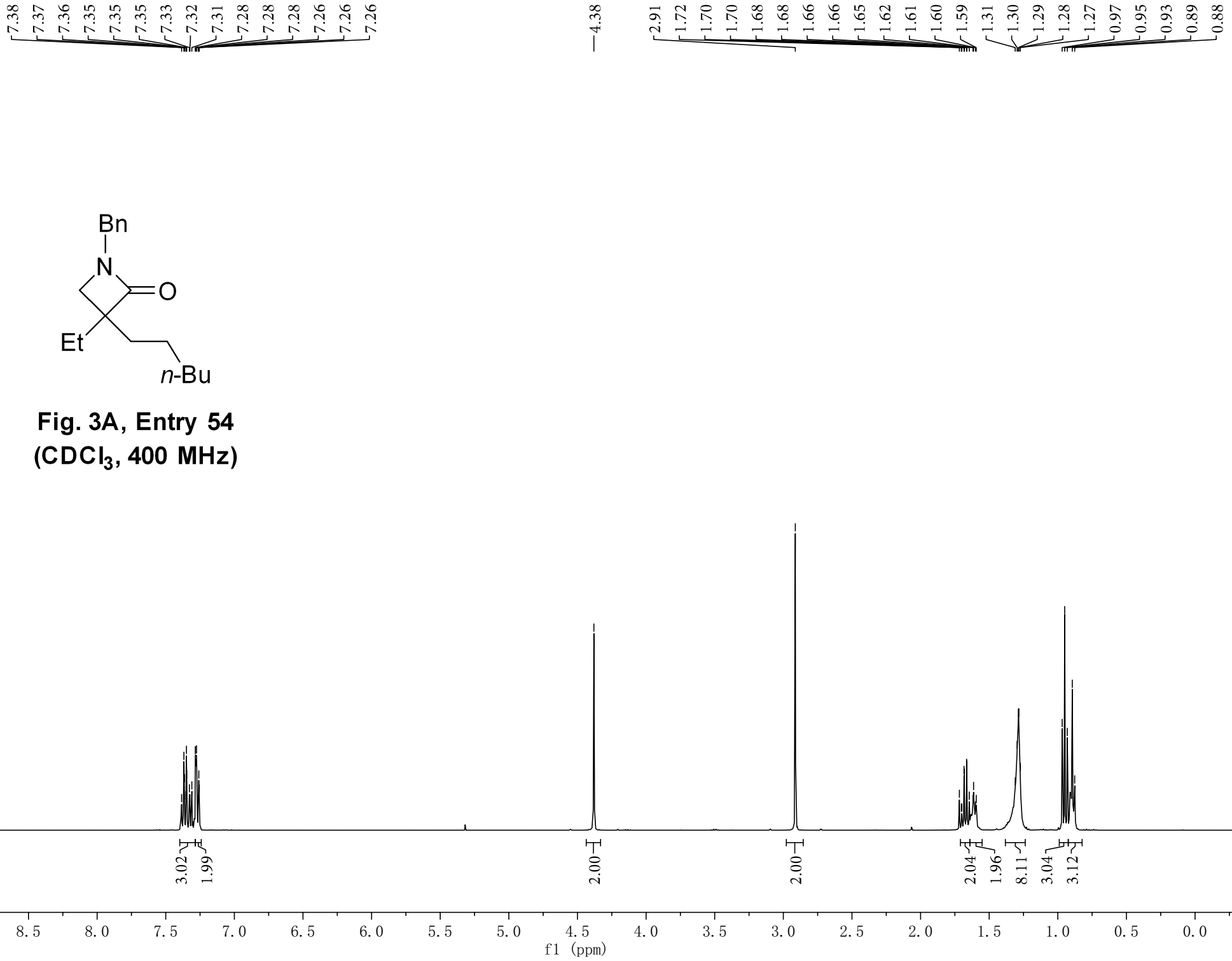


Fig. 3A, Entry 54
($CDCl_3$, 400 MHz)

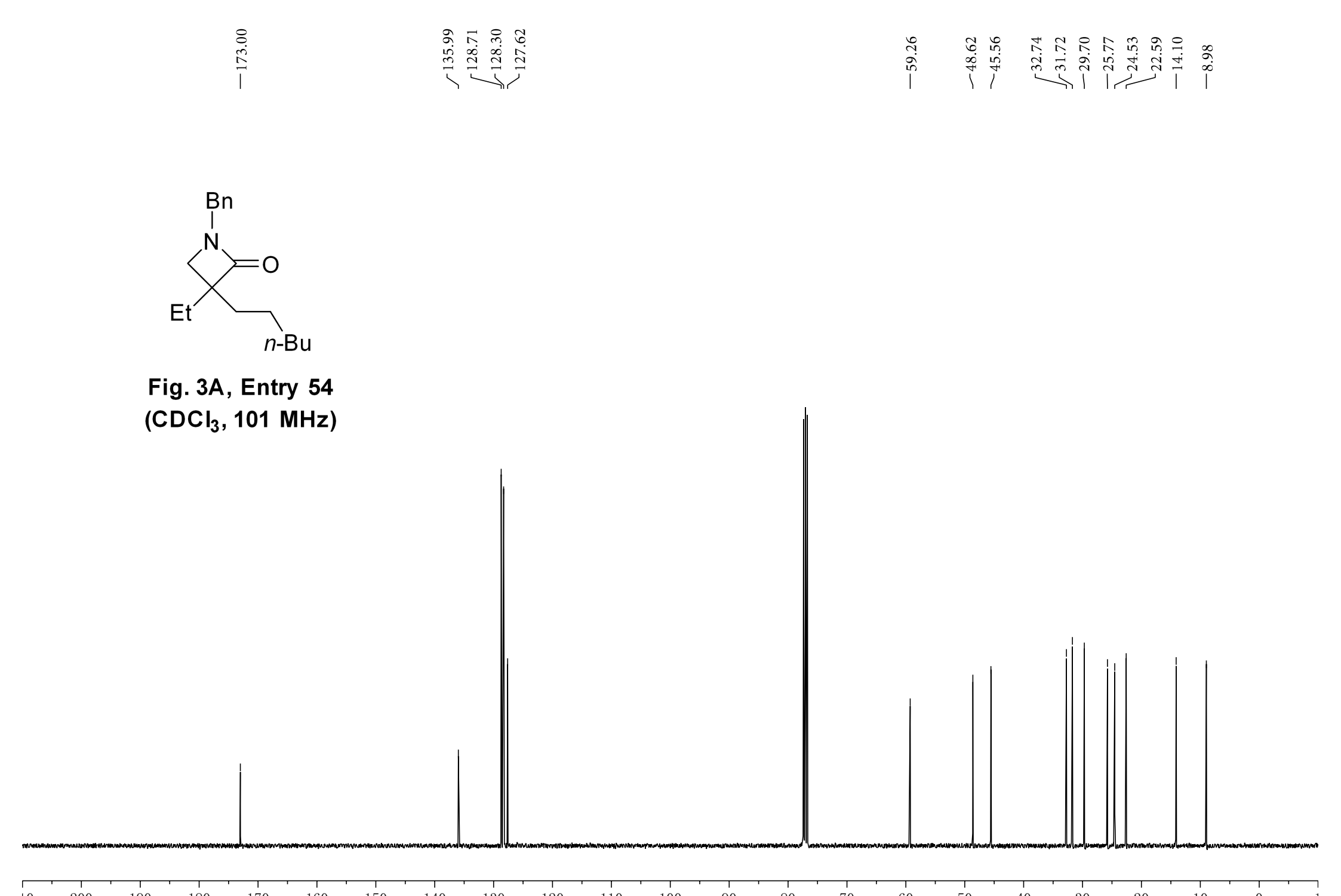


Fig. 3A, Entry 54
($CDCl_3$, 101 MHz)

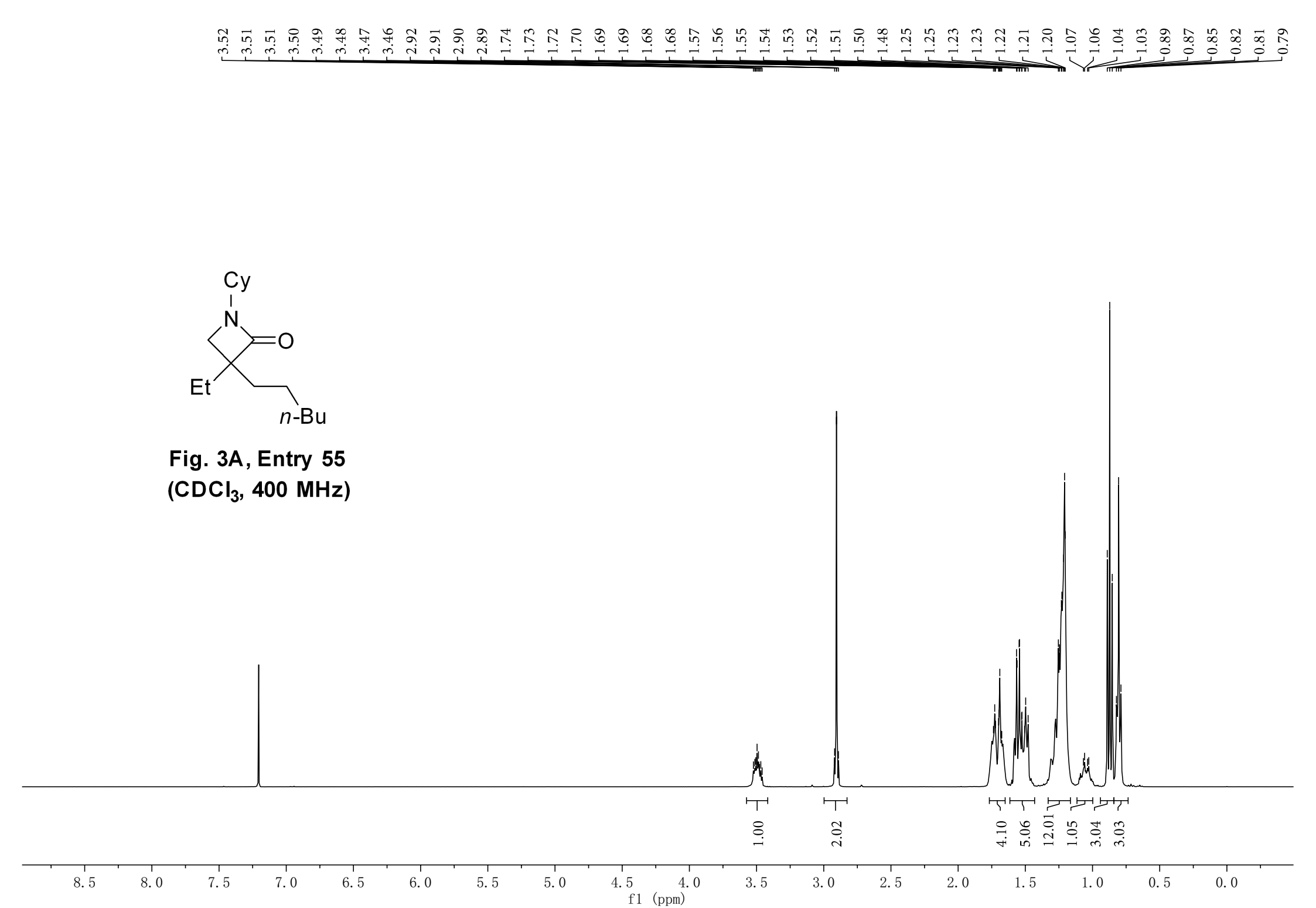


Fig. 3A, Entry 55
($CDCl_3$, 400 MHz)

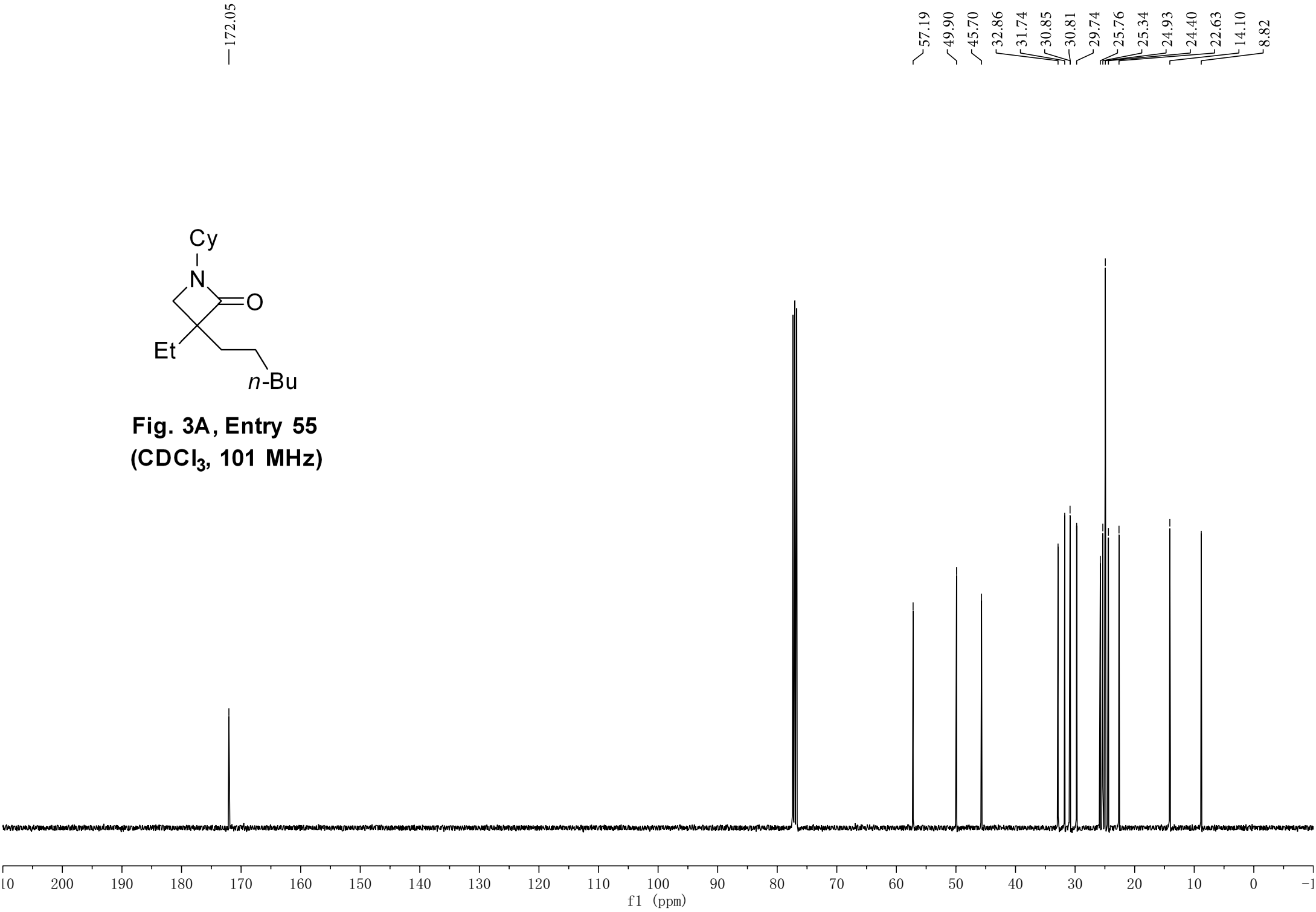


Fig. 3A, Entry 55
($CDCl_3$, 101 MHz)

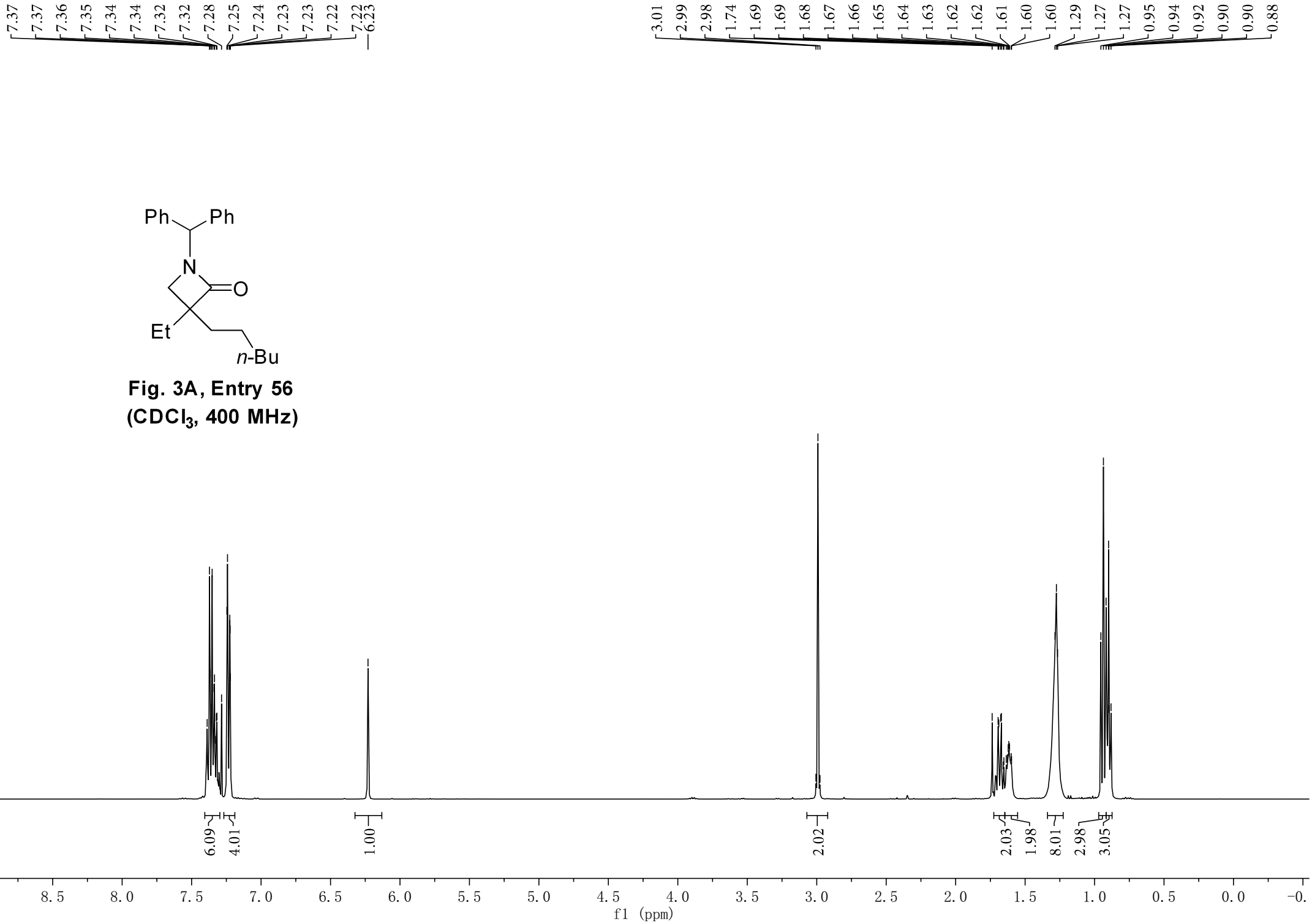


Fig. 3A, Entry 56
($CDCl_3$, 400 MHz)

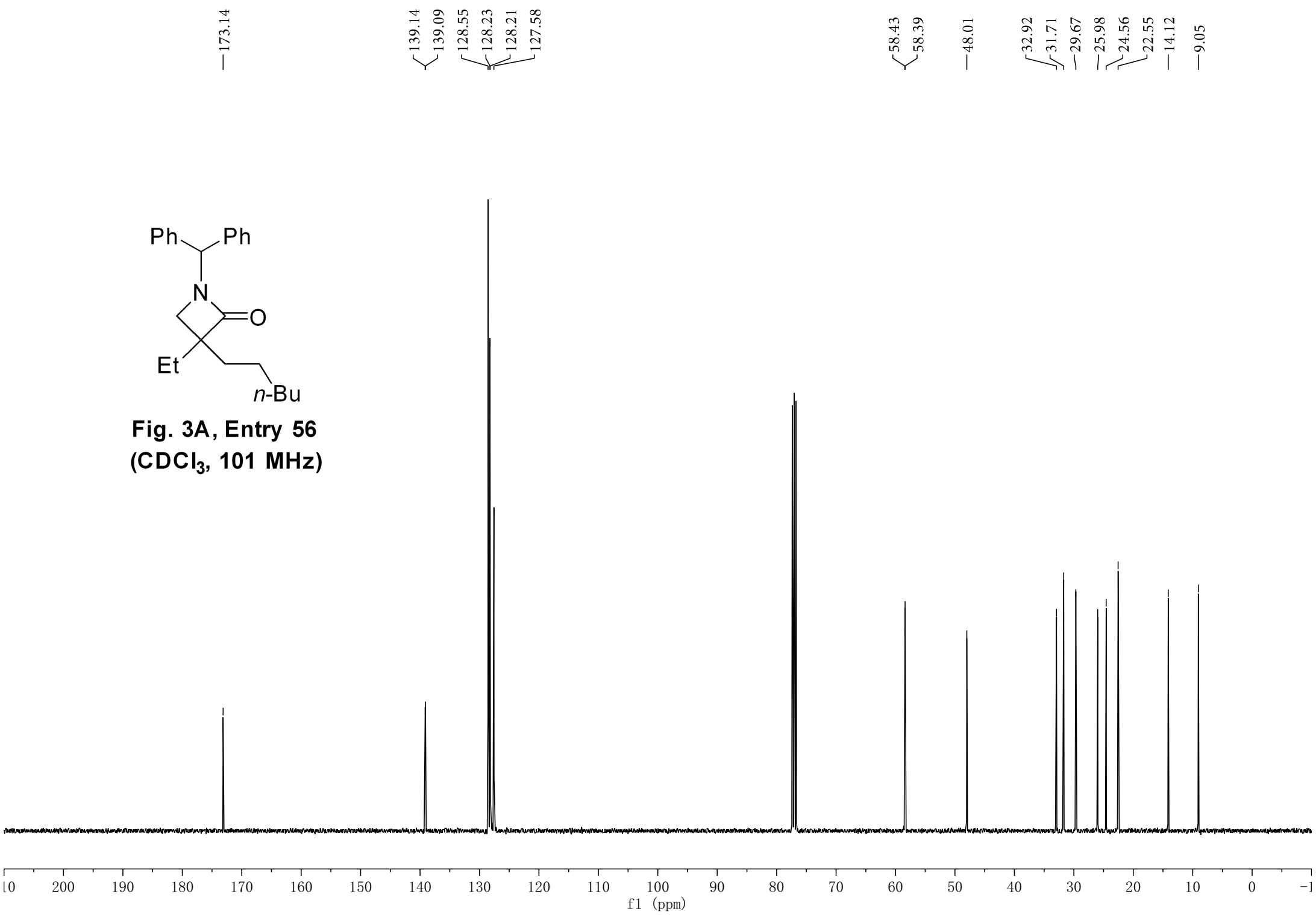


Fig. 3A, Entry 56
($CDCl_3$, 101 MHz)

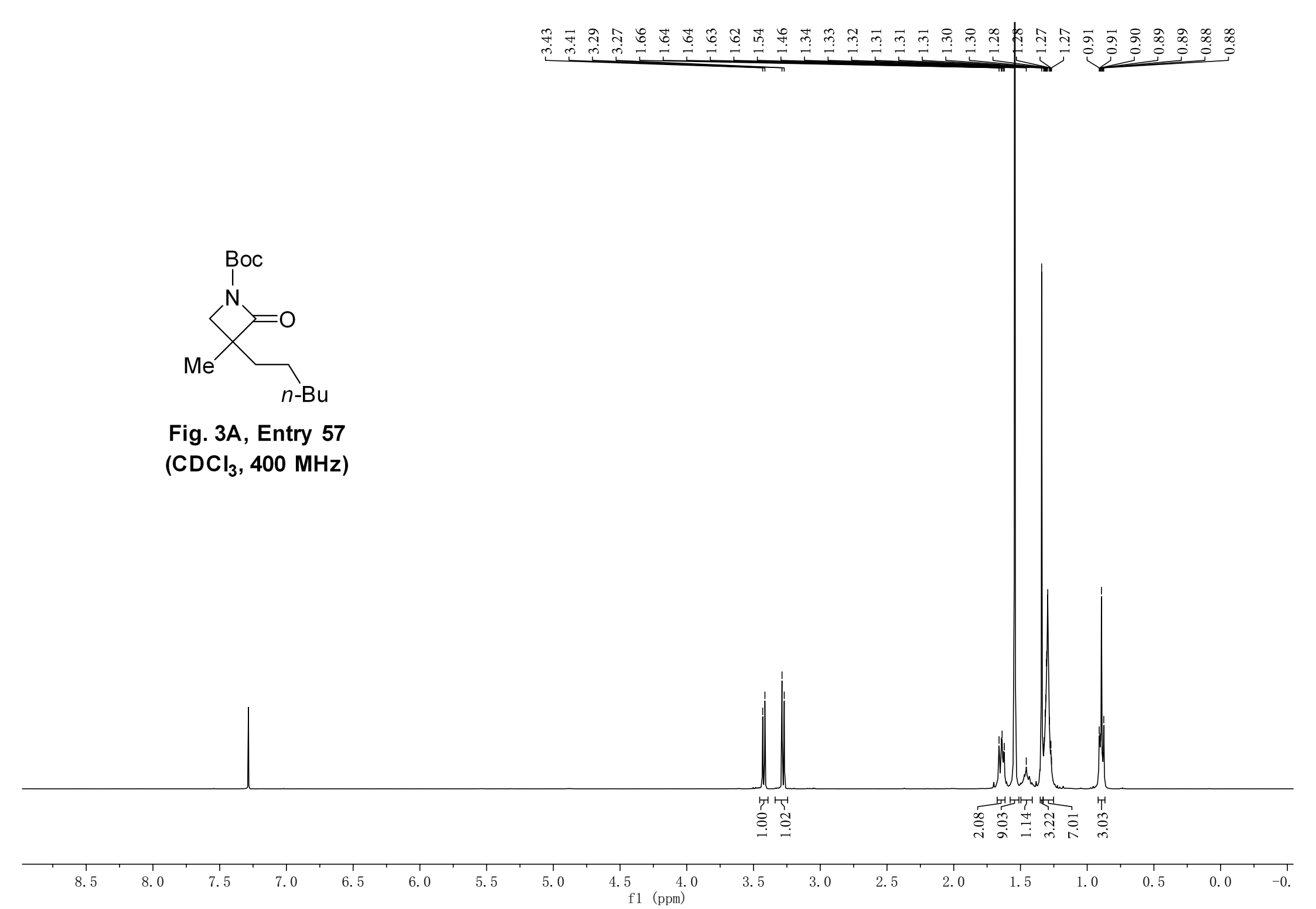


Fig. 3A, Entry 57
($CDCl_3$, 400 MHz)

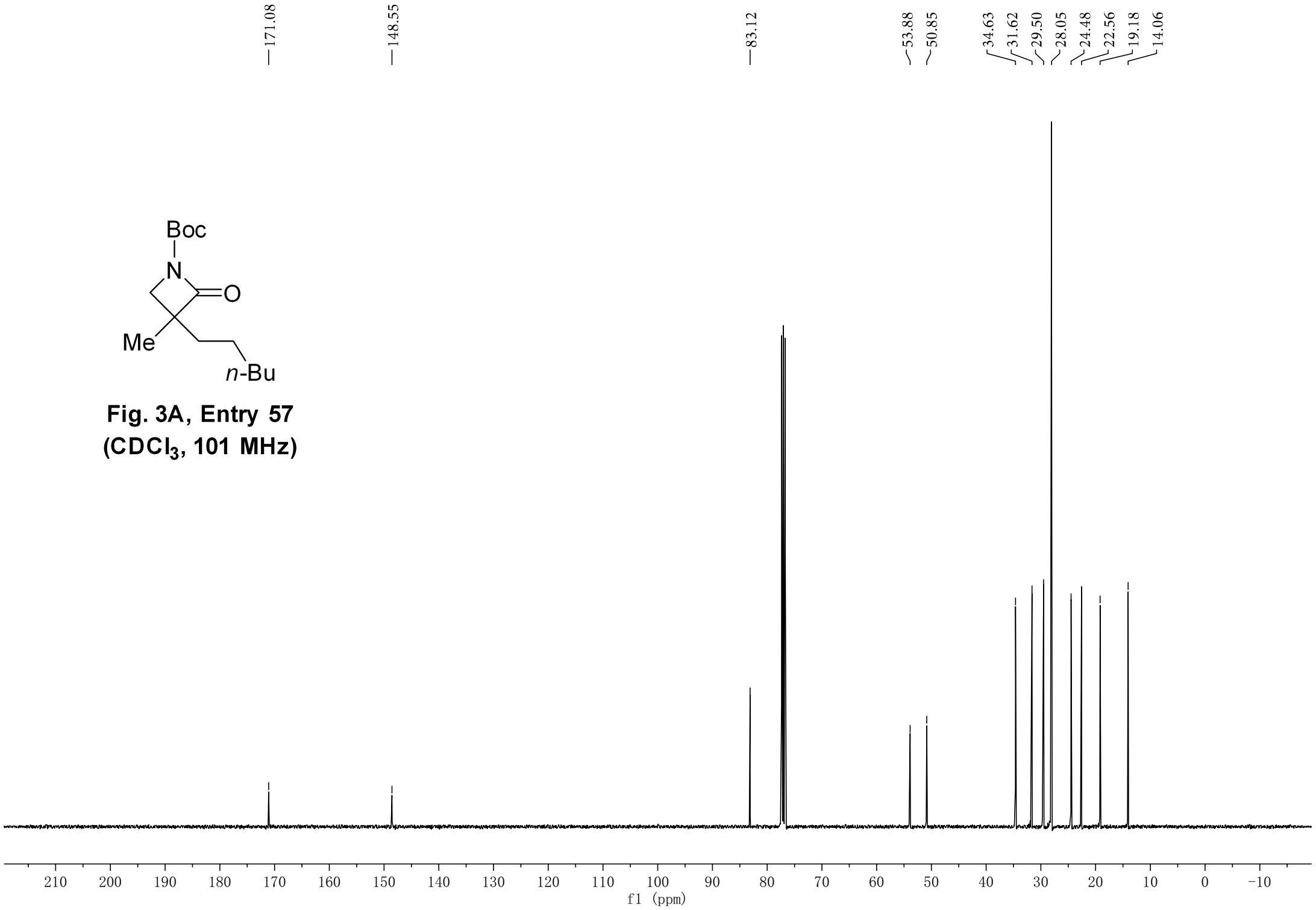


Fig. 3A, Entry 57
($CDCl_3$, 101 MHz)

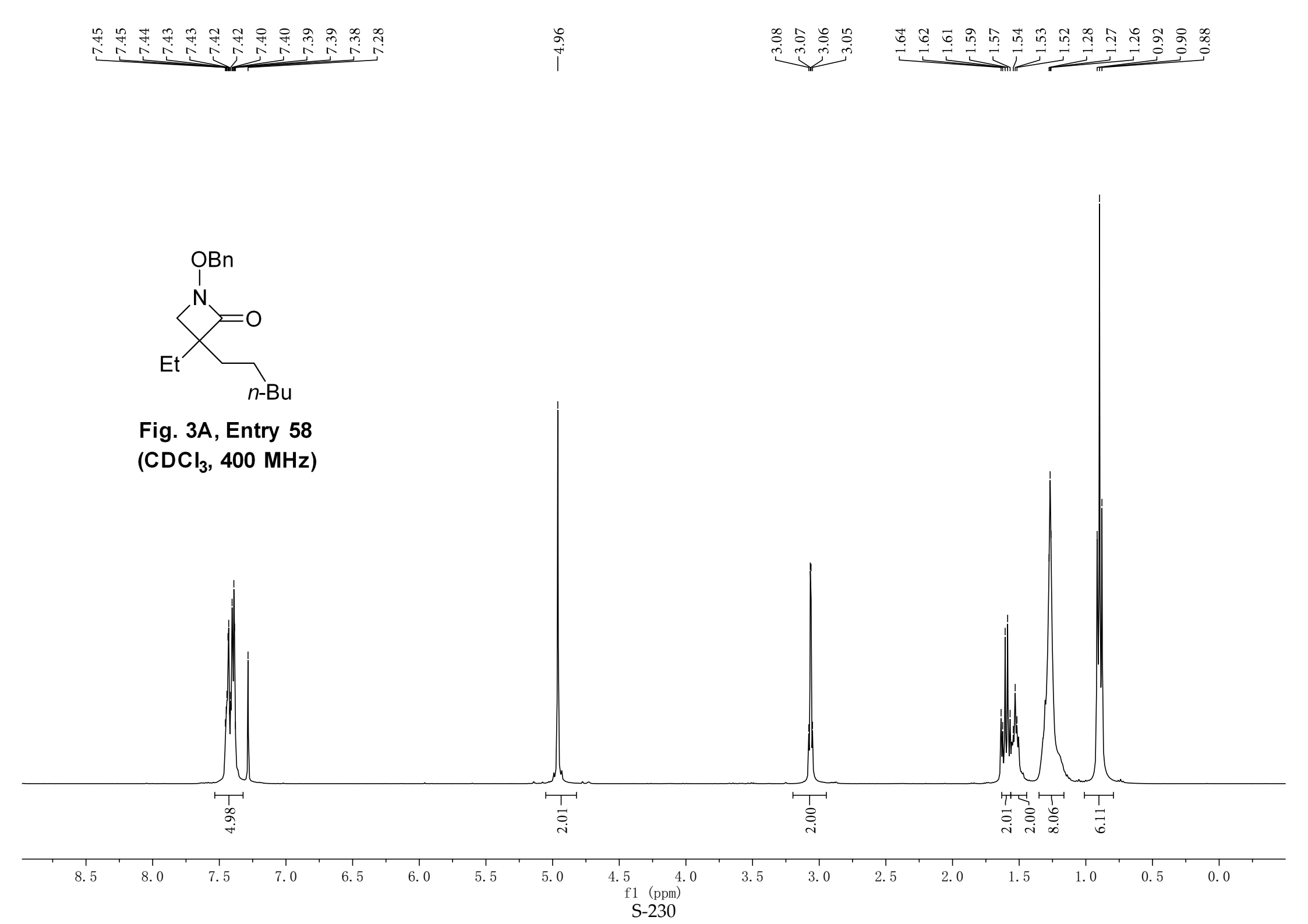


Fig. 3A, Entry 58
($CDCl_3$, 400 MHz)

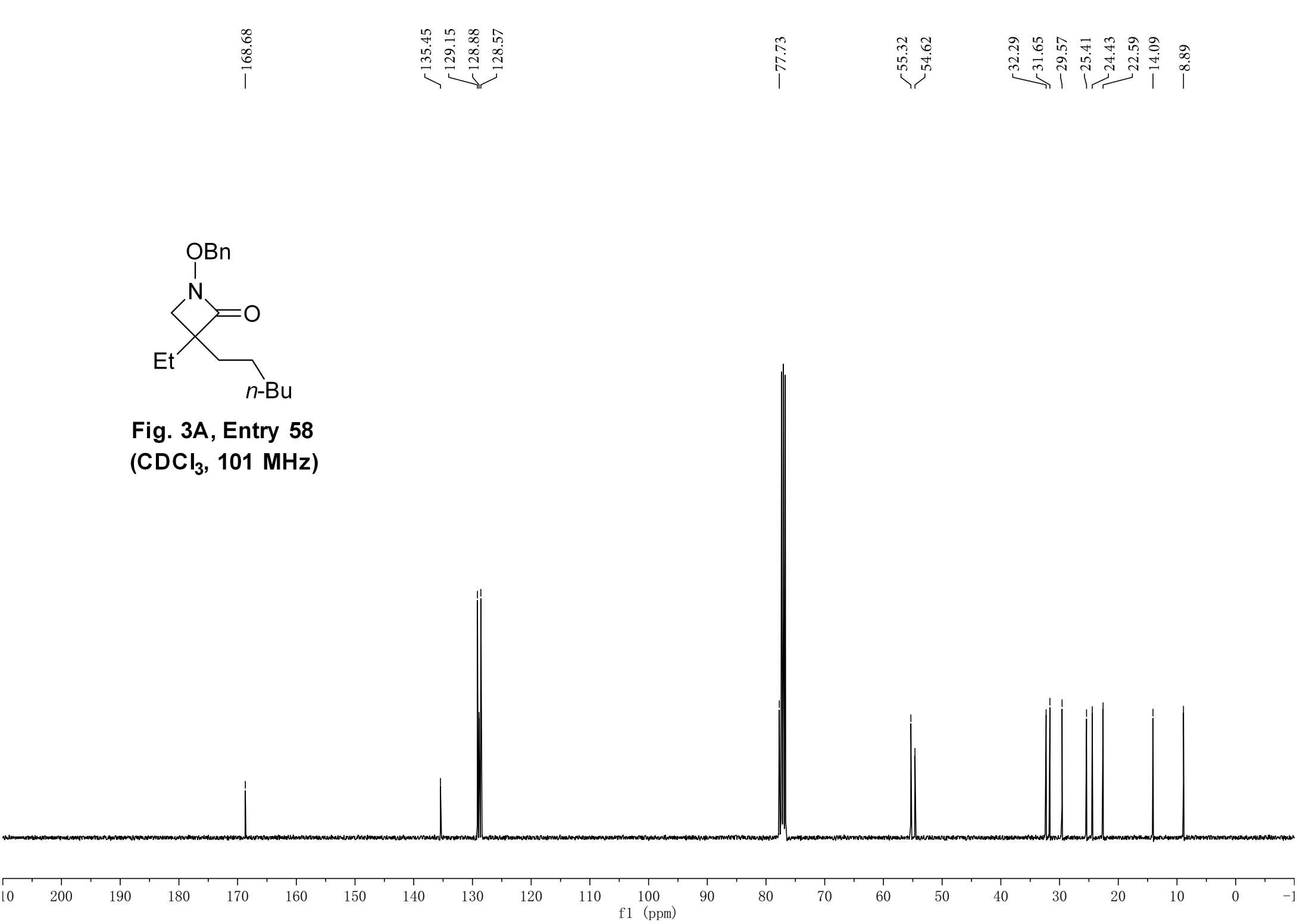


Fig. 3A, Entry 58
($CDCl_3$, 101 MHz)

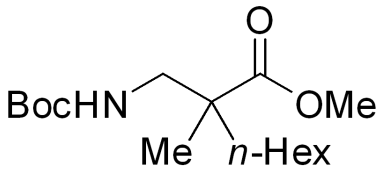


Fig. 3B, Entry 59
($CDCl_3$, 400 MHz)

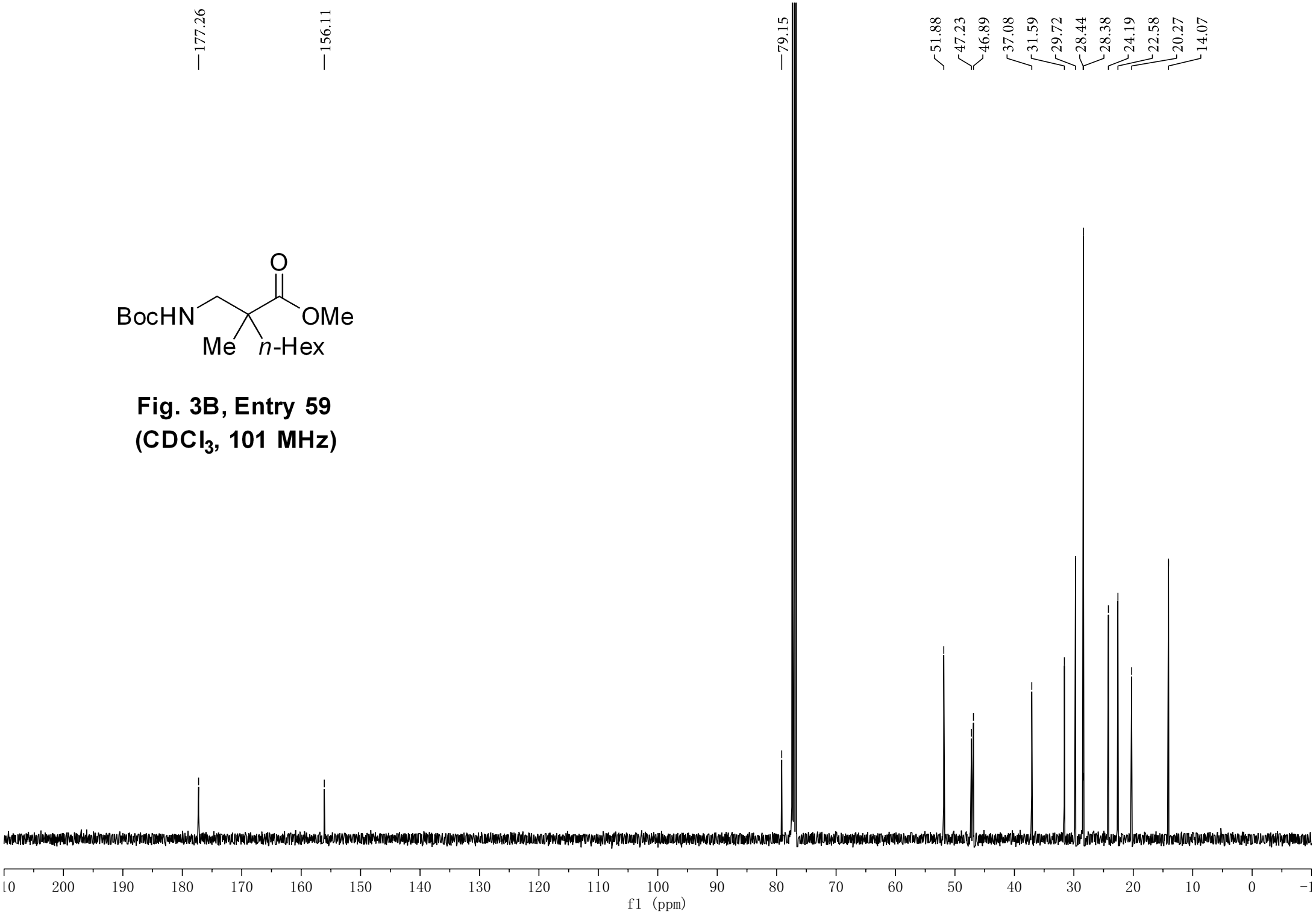
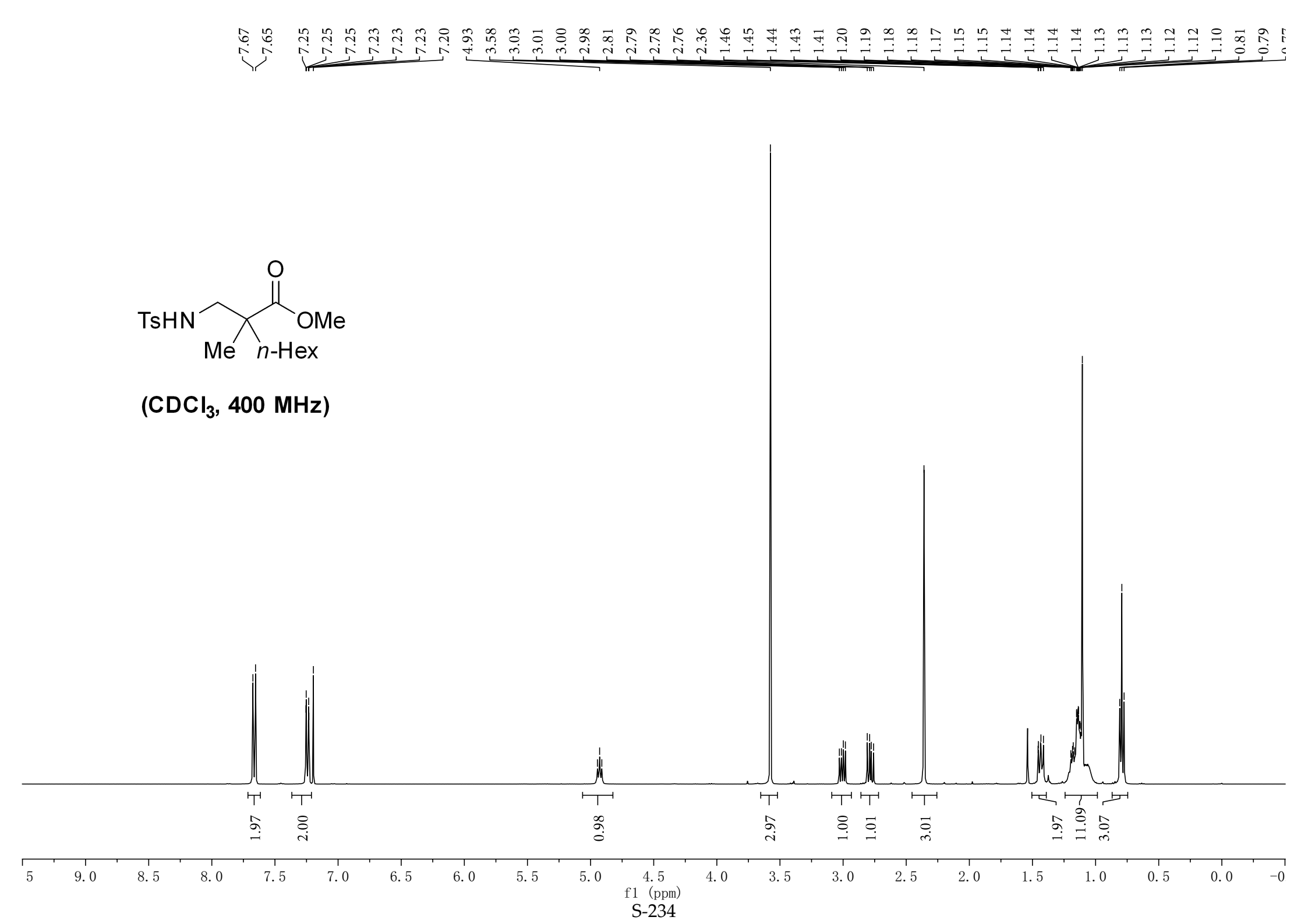
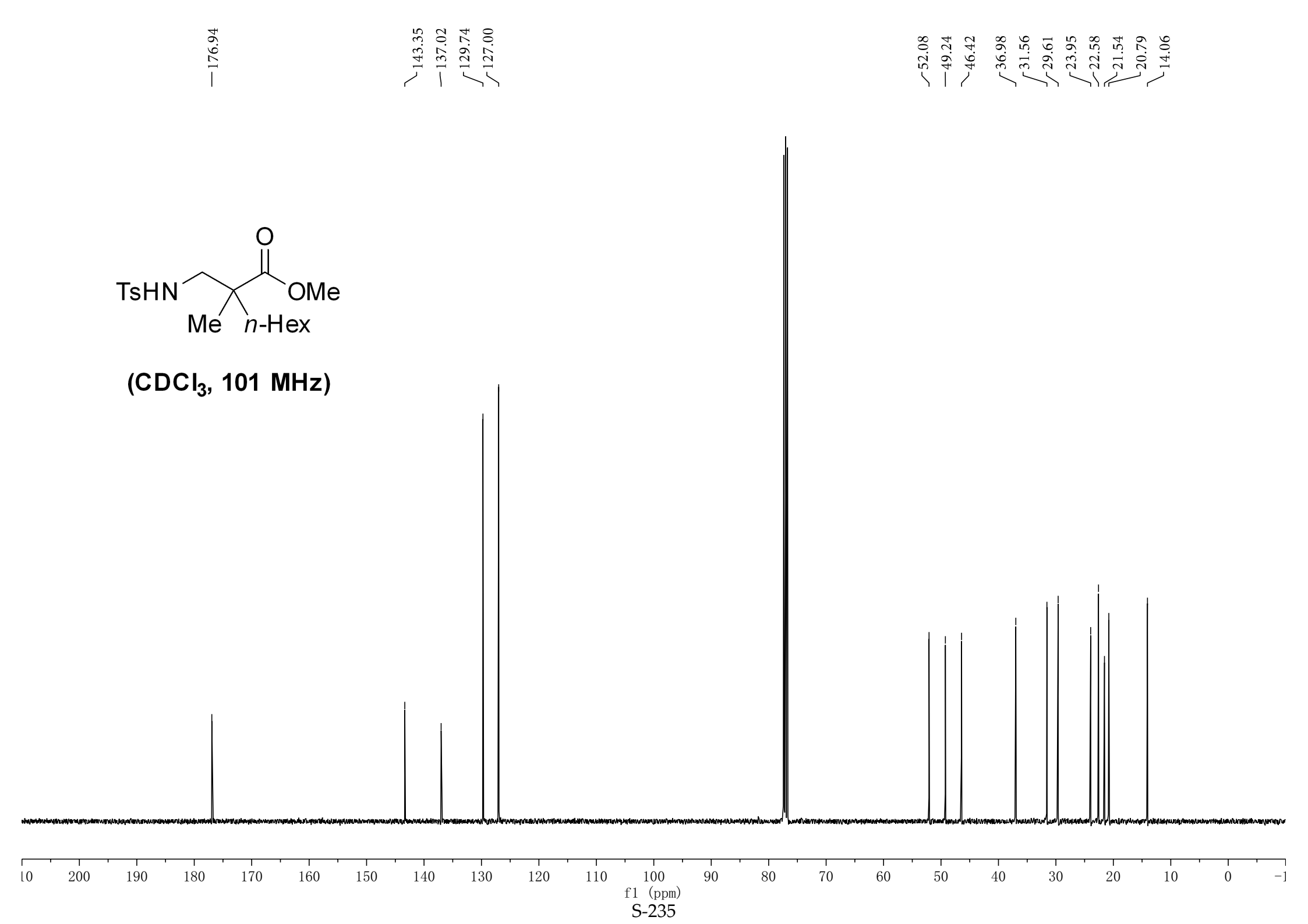
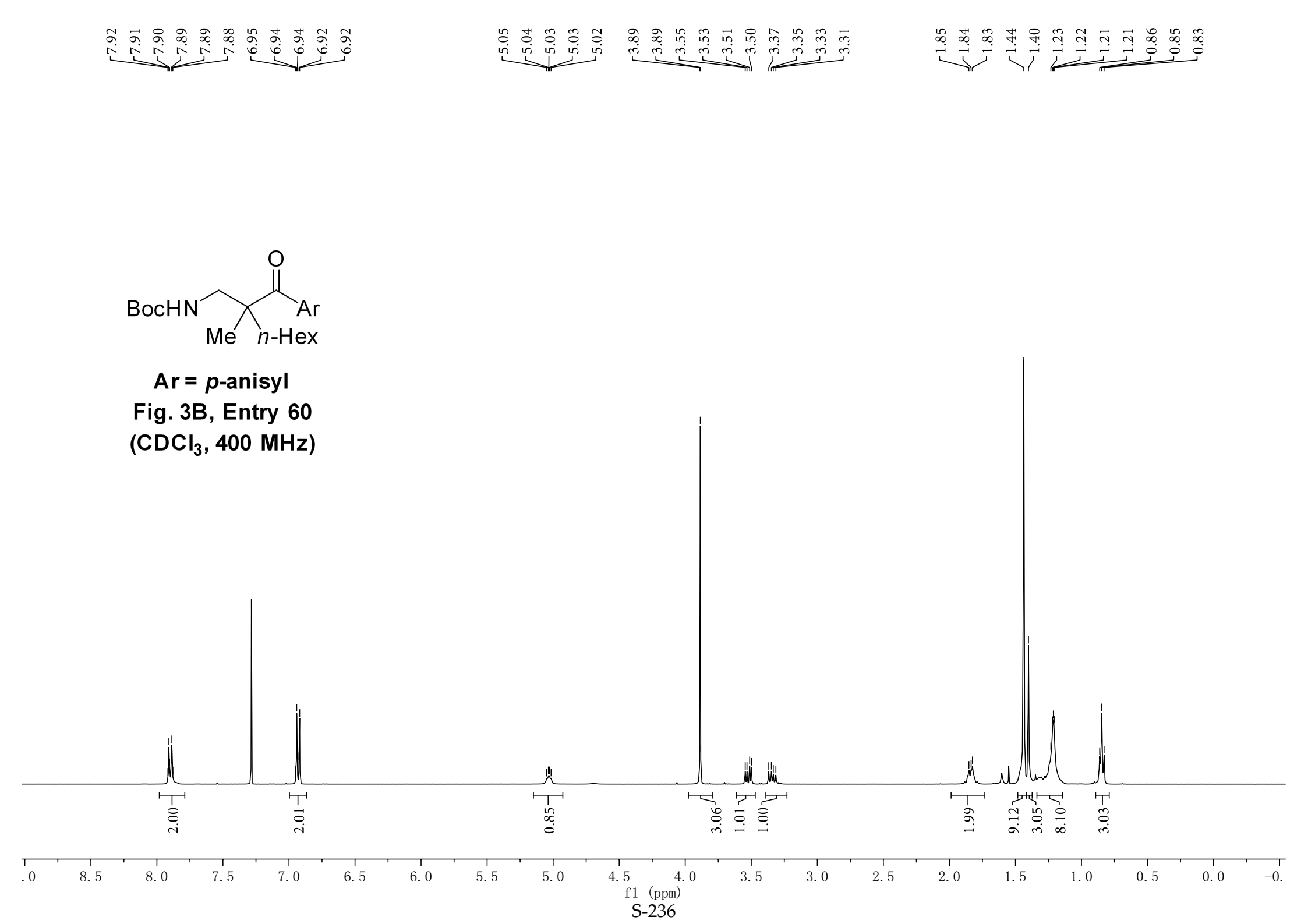
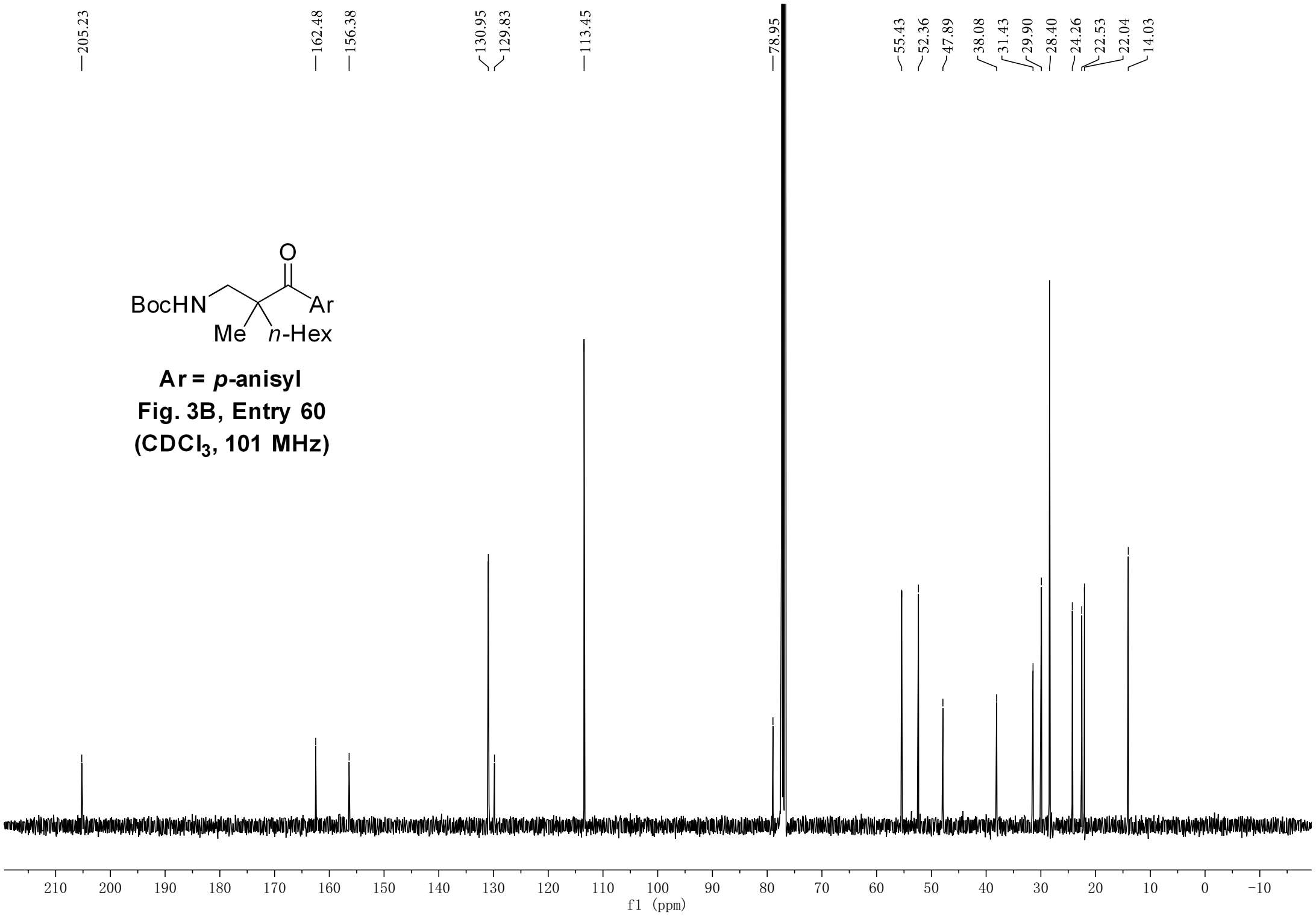


Fig. 3B, Entry 59
($CDCl_3$, 101 MHz)


7.67
7.65
7.25
7.25
7.25
7.23
7.23
7.23
7.20
4.93
3.58
3.03
3.01
3.00
2.98
2.81
2.79
2.78
2.76
2.36
1.46
1.45
1.44
1.43
1.41
1.20
1.19
1.18
1.18
1.17
1.15
1.15
1.14
1.14
1.14
1.14
1.13
1.13
1.13
1.12
1.12
1.10
0.81
0.79
O
TsHN
OMe
Me
n-Hex
(CDCl3, 400 MHz)
1.97
2.00
0.98
2.97
1.00
1.01
3.01
1.97
11.09
3.07
f1 (ppm)


176.94
143.35
137.02
129.74
127.00
52.08
49.24
46.42
36.98
31.56
29.61
23.95
22.58
21.54
20.79
14.06
O
TsHN
OMe
Me
n-Hex
(CDCl3, 101 MHz)
f1 (ppm)


7.92
7.91
7.90
7.89
7.89
7.88
6.95
6.94
6.94
6.92
6.92
5.05
5.04
5.03
5.03
5.02
3.89
3.89
3.55
3.53
3.51
3.50
3.37
3.35
3.33
3.31
1.85
1.84
1.83
1.44
1.40
1.23
1.22
1.21
1.21
0.86
0.85
0.83
O
BocHN
Ar
Me
n-Hex
Ar = p-anisyl
Fig. 3B, Entry 60
(CDCl3, 400 MHz)
2.00
2.01
0.85
3.06
1.01
1.00
1.99
9.12
3.05
8.10
3.03
f1 (ppm)


205.23
162.48
156.38
130.95
129.83
113.45
78.95
55.43
52.36
47.89
38.08
31.43
29.90
28.40
24.26
22.53
22.04
14.03
O
BocHN
Ar
Me
n-Hex
Ar = p-anisyl
Fig. 3B, Entry 60
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

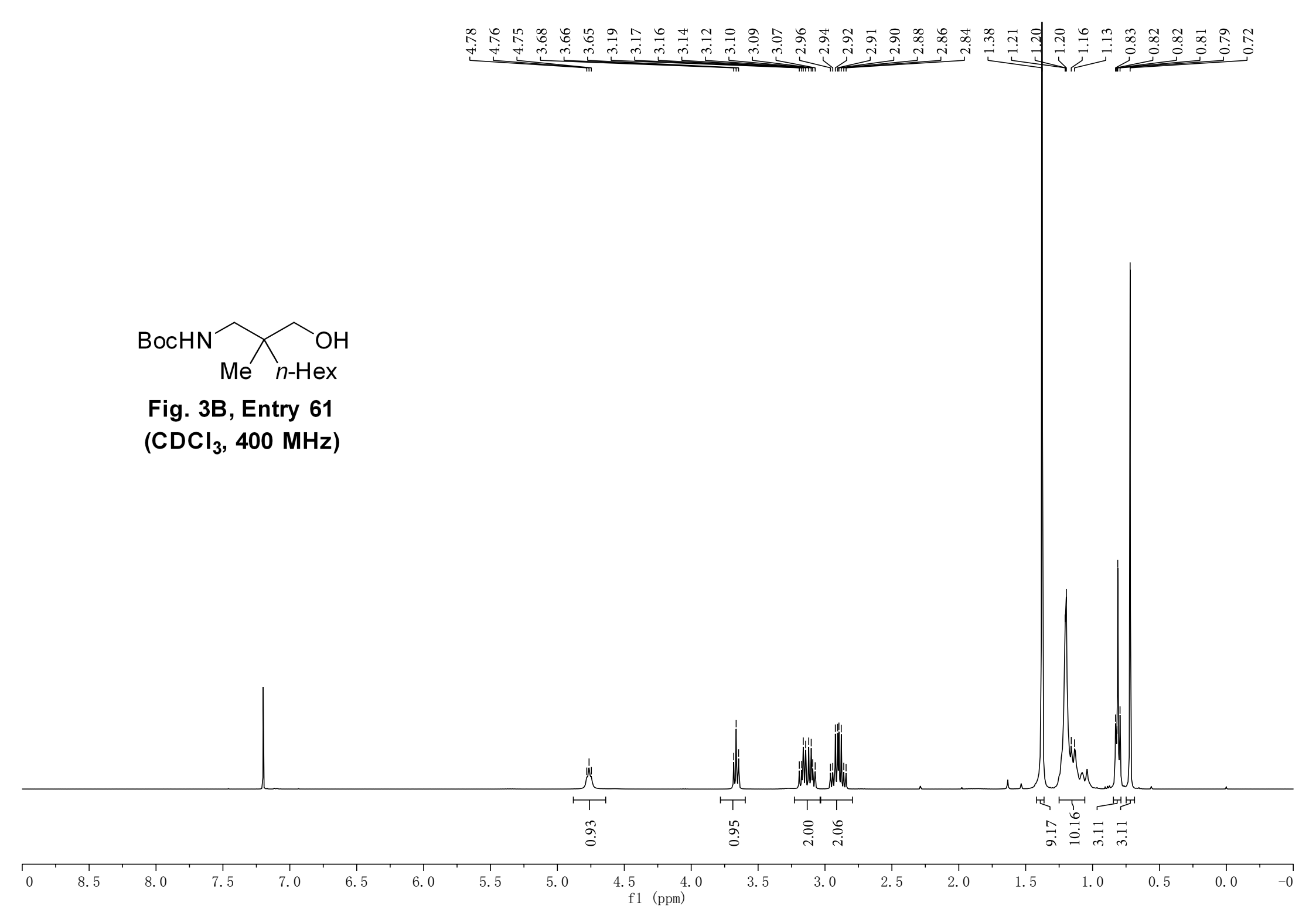


Fig. 3B, Entry 61
($CDCl_3$, 400 MHz)

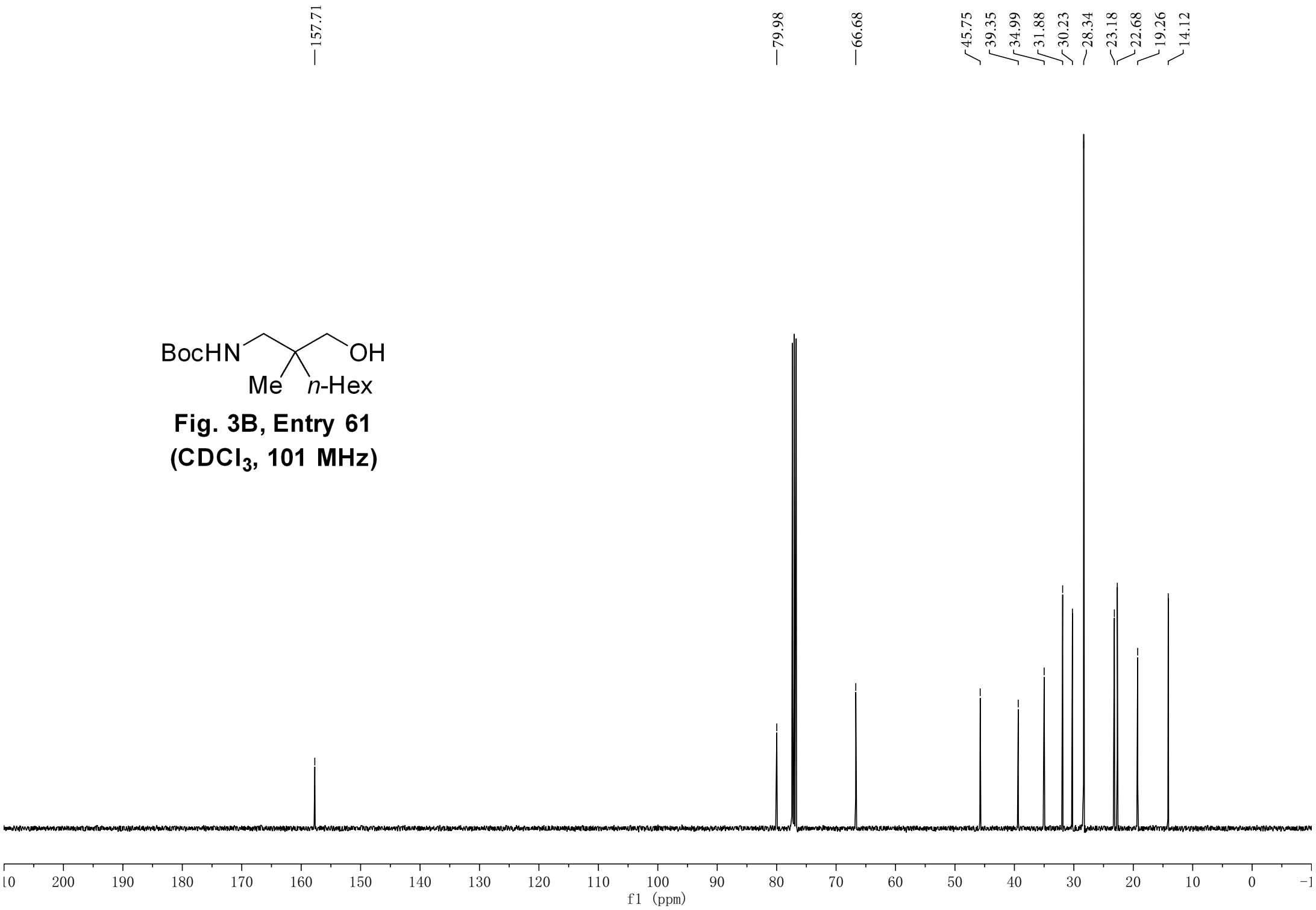
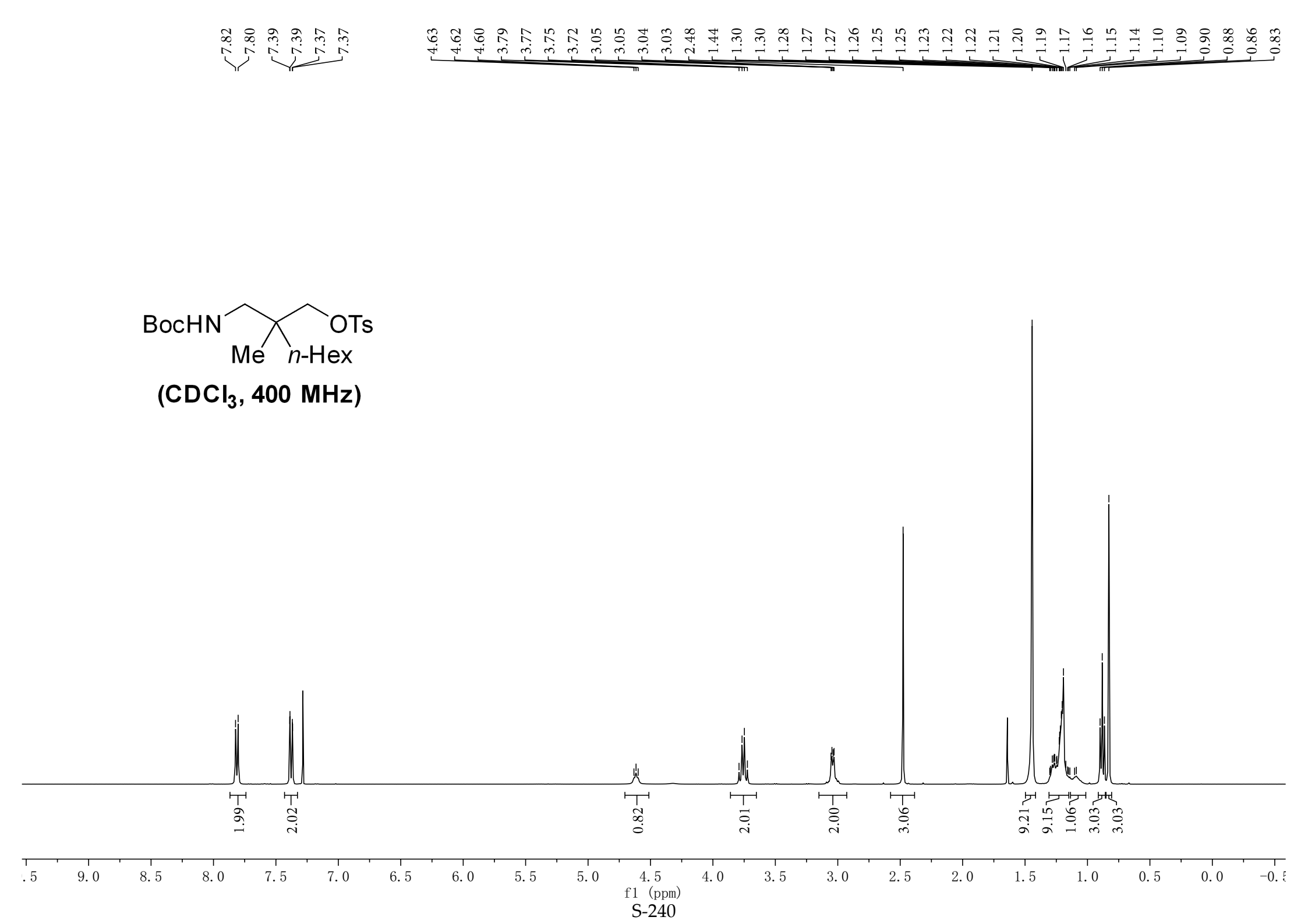
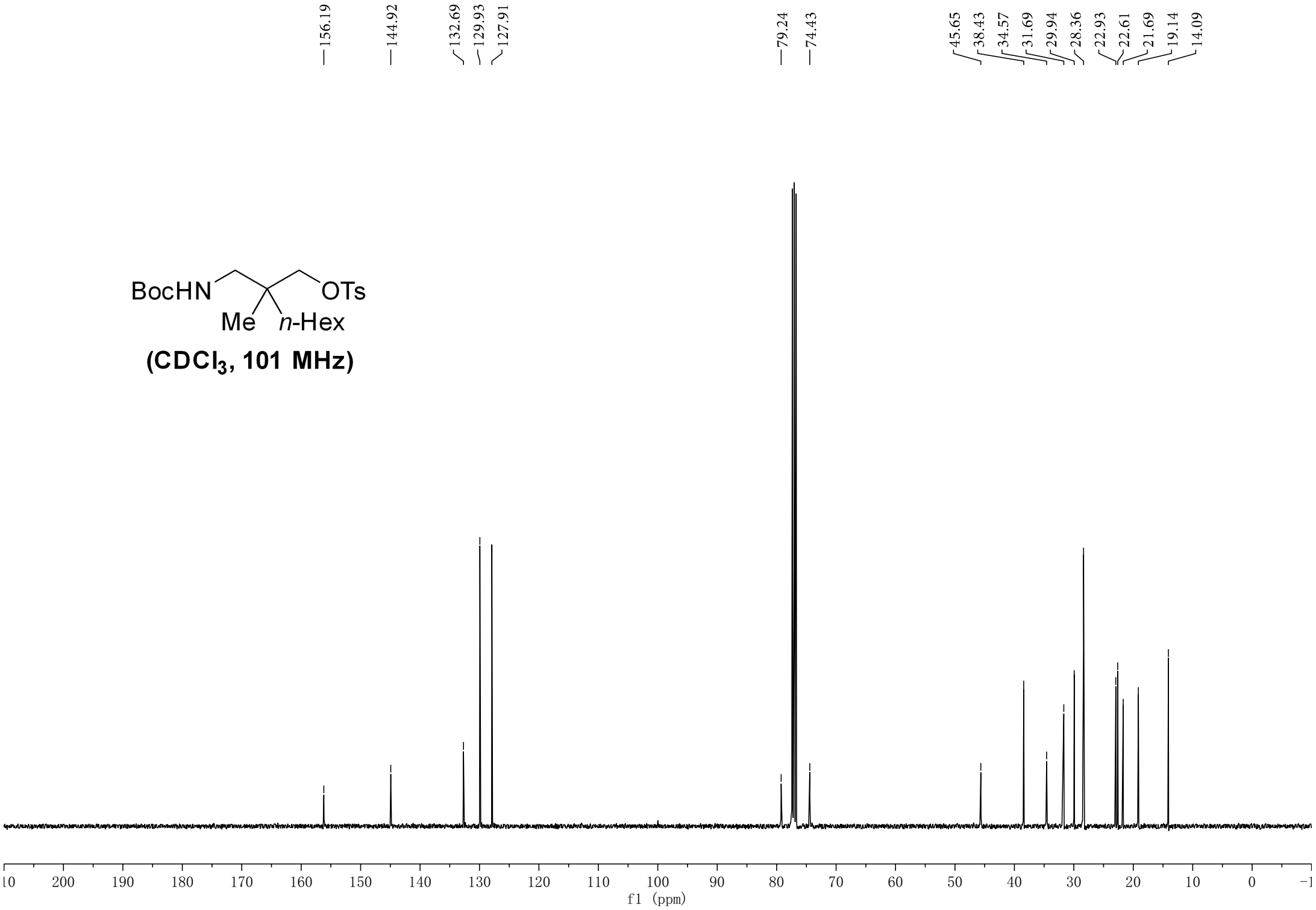
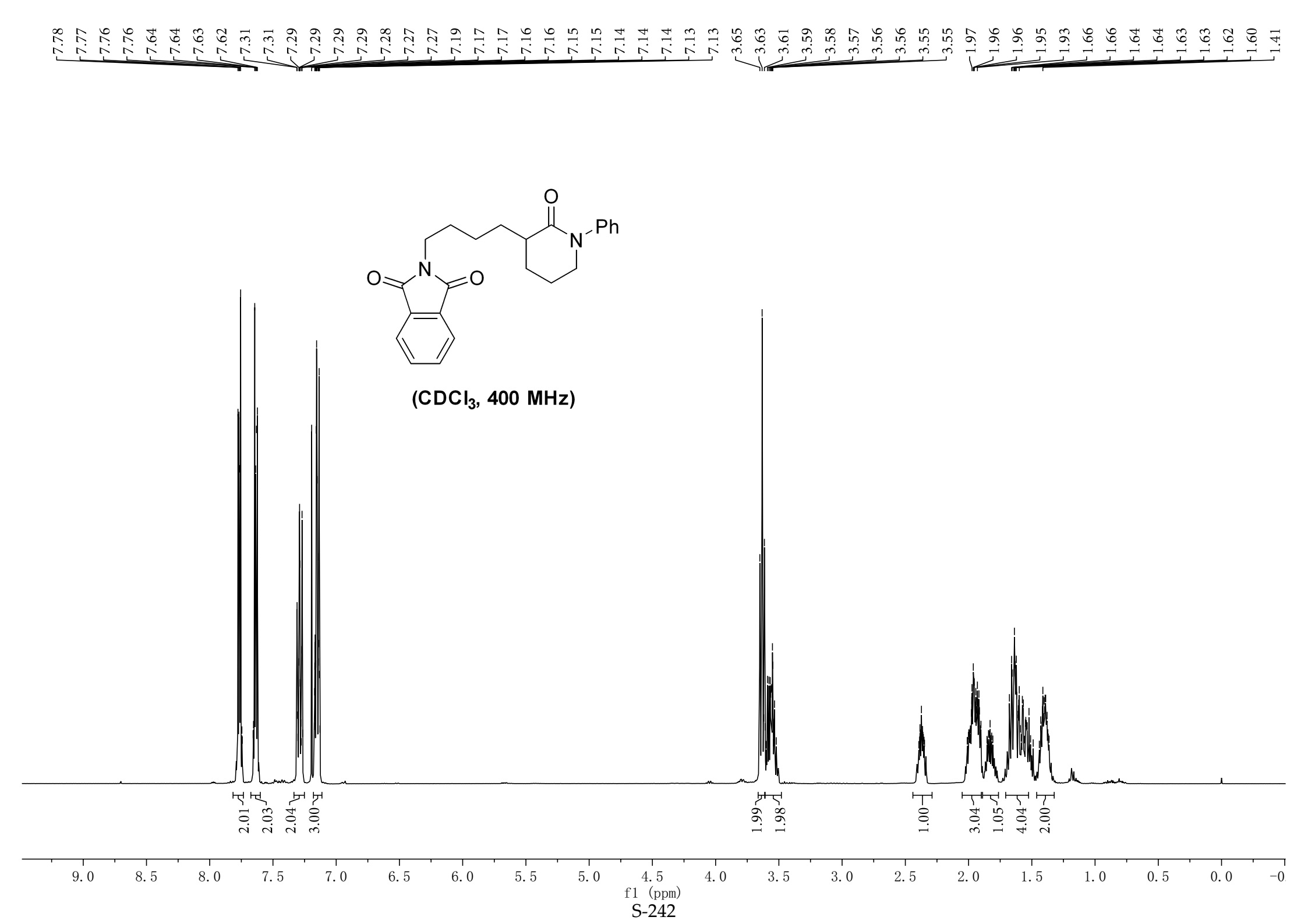
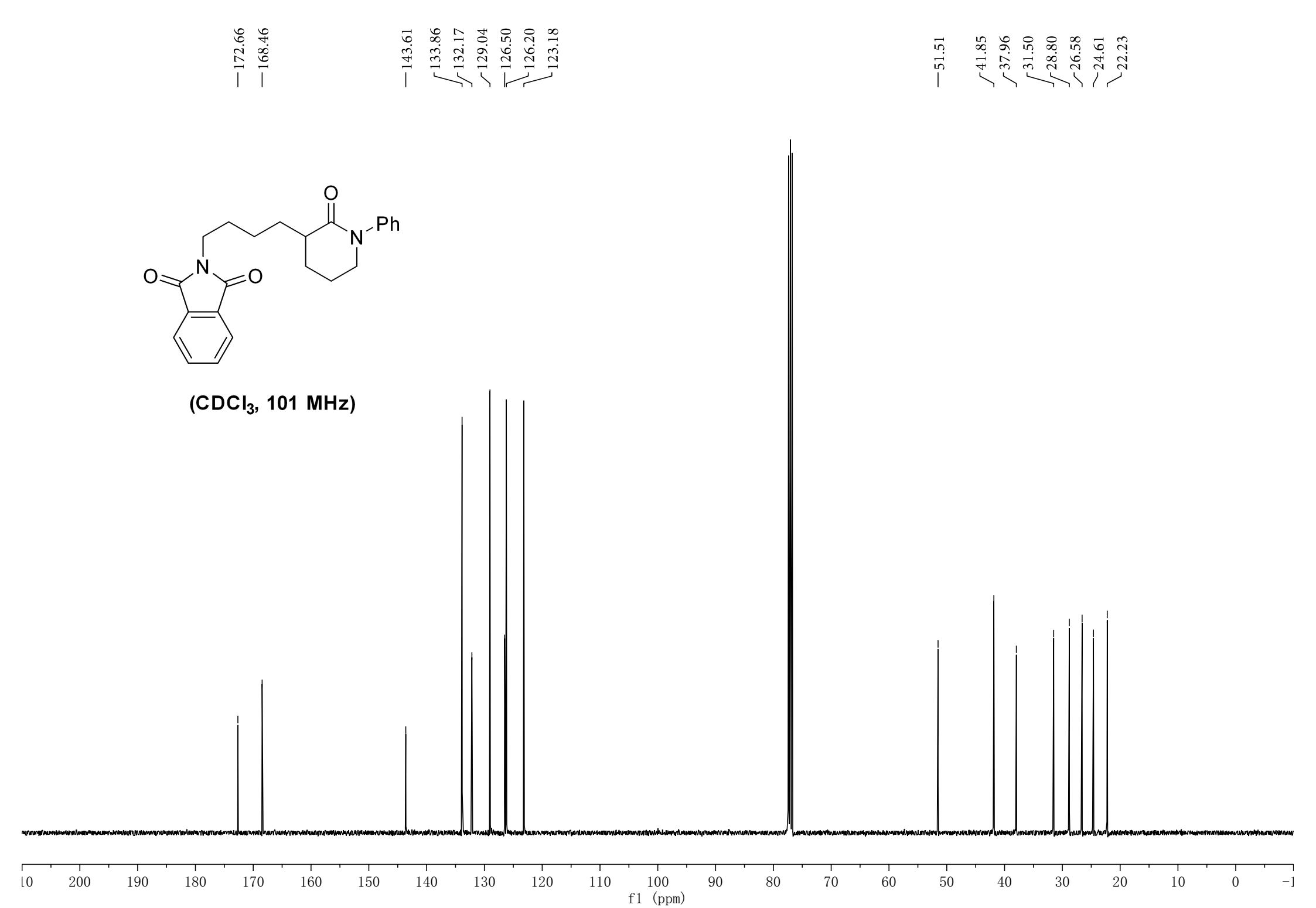


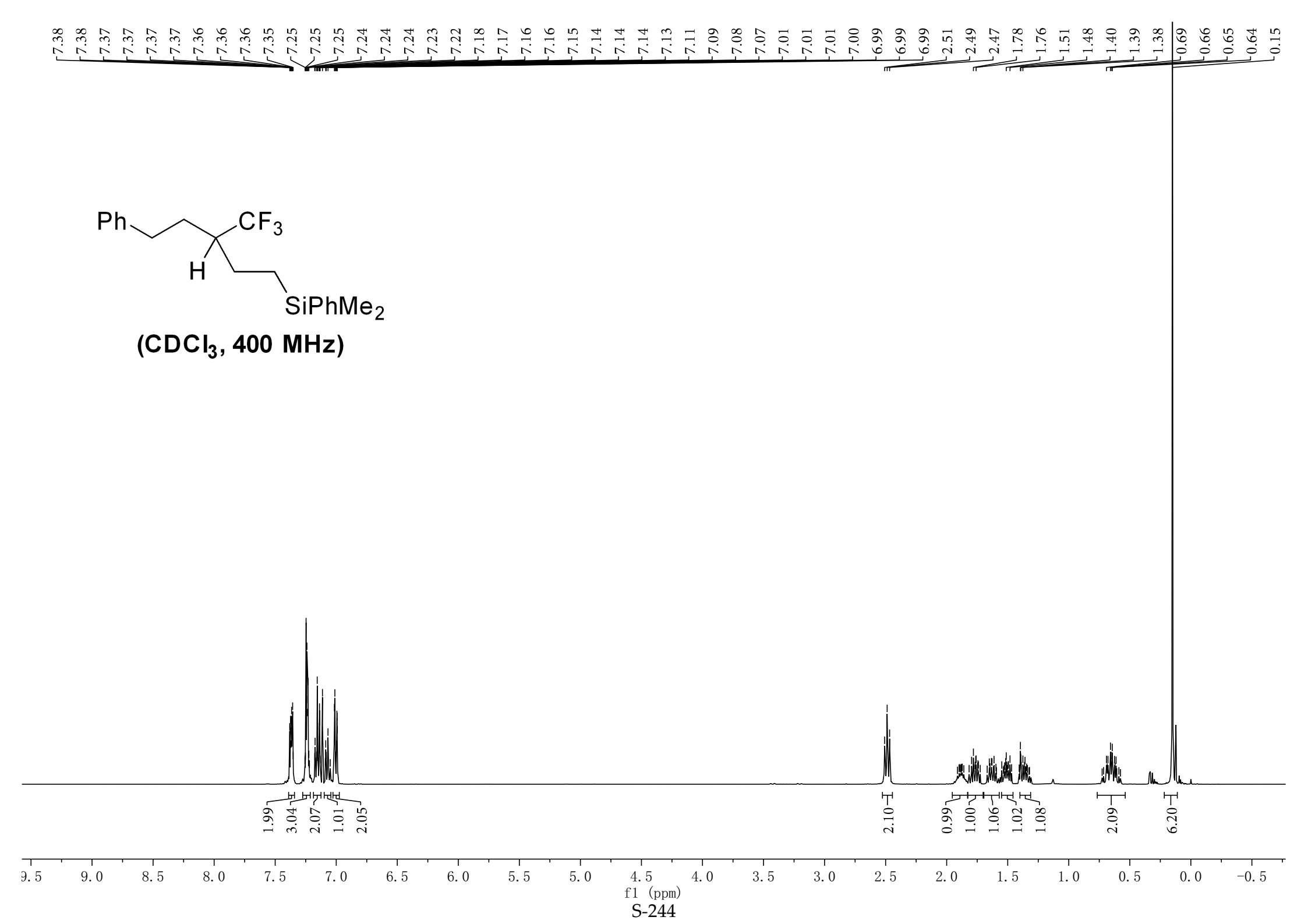
Fig. 3B, Entry 61
($CDCl_3$, 101 MHz)

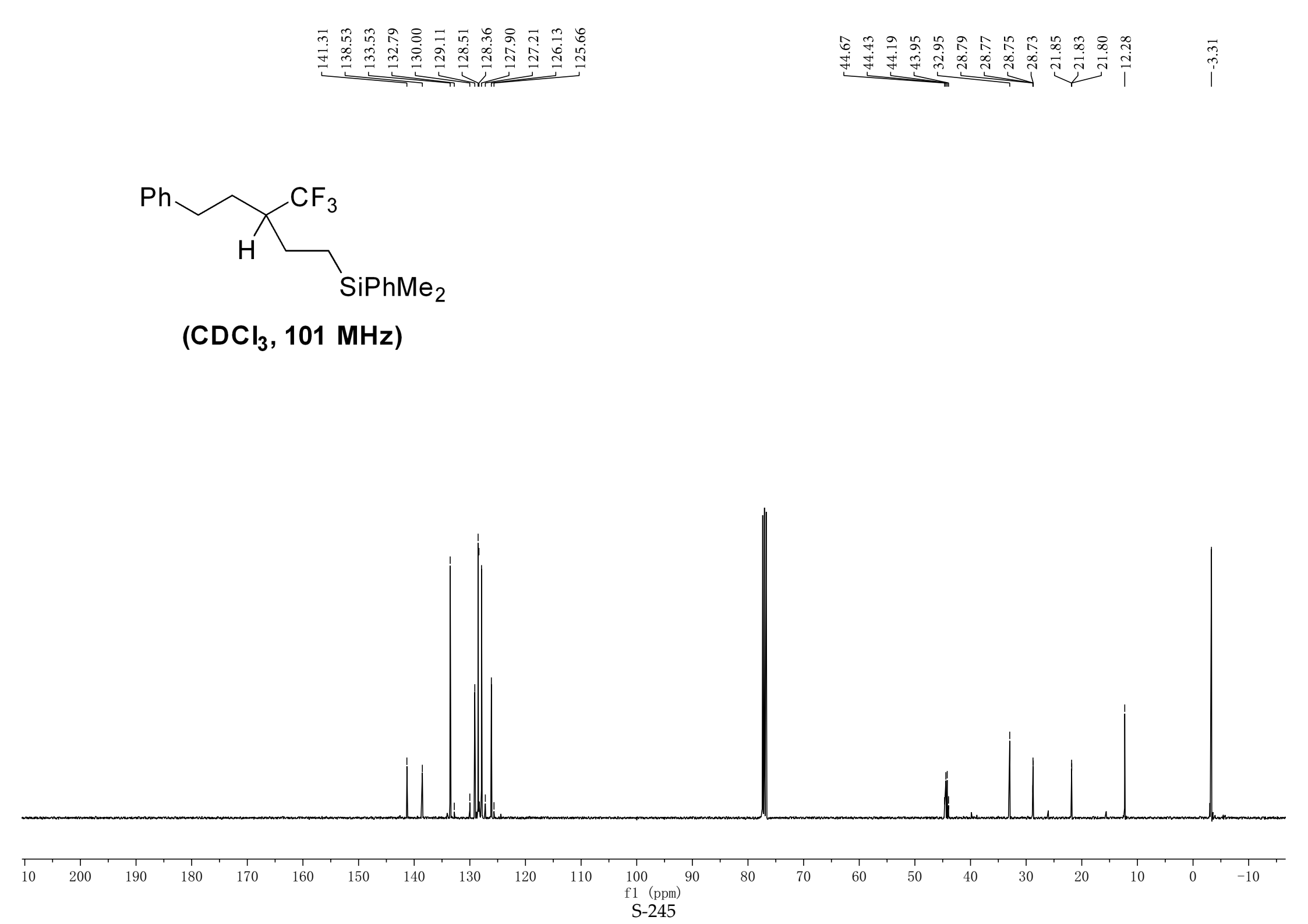

7.82
7.80
7.39
7.39
7.37
7.37
4.63
4.62
4.60
3.79
3.77
3.75
3.72
3.05
3.05
3.04
3.03
2.48
1.44
1.30
1.30
1.28
1.27
1.27
1.26
1.25
1.25
1.23
1.22
1.22
1.21
1.20
1.19
1.17
1.16
1.15
1.14
1.10
1.09
0.90
0.88
0.86
0.83
BocHN
OTs
Me
n-Hex
(CDCl3, 400 MHz)
1.99
2.02
0.82
2.01
2.00
3.06
9.21
9.15
1.06
3.03
3.03
f1 (ppm)

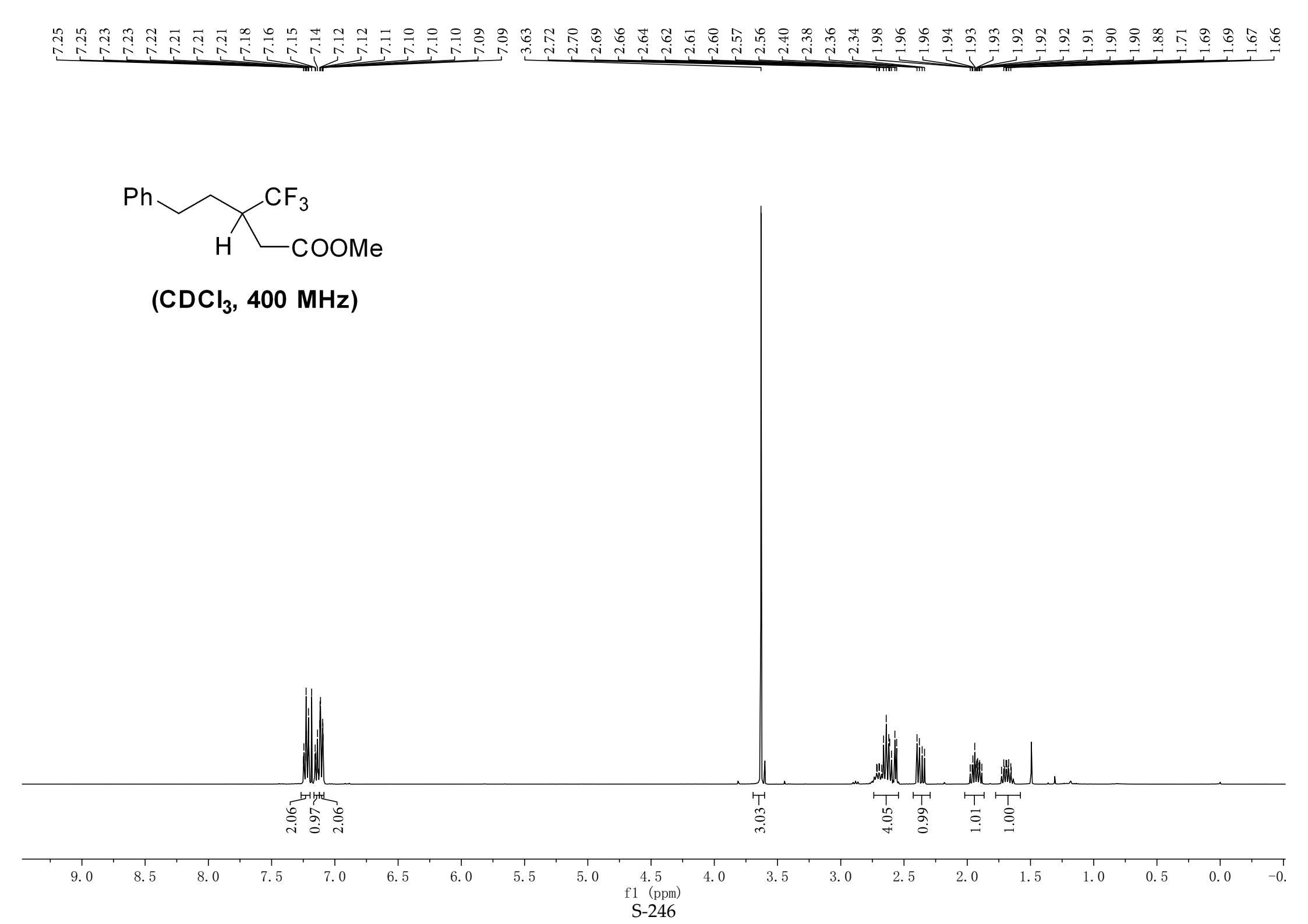

156.19
144.92
132.69
129.93
127.91
79.24
74.43
45.65
38.43
34.57
31.69
29.94
28.36
22.93
22.61
21.69
19.14
14.09
BocHN
OTs
Me
n-Hex
(CDCl3, 101 MHz)
f1 (ppm)

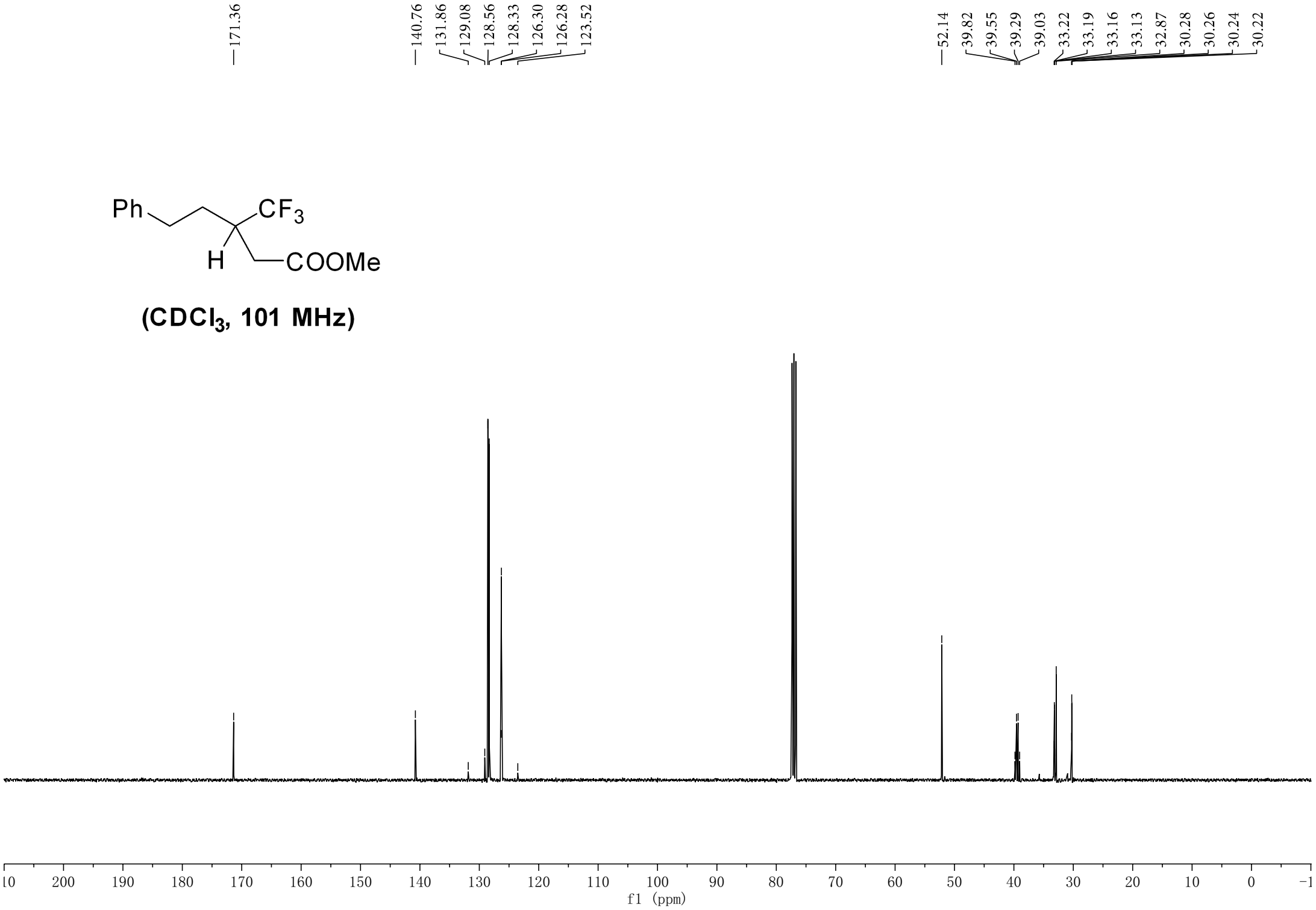

7.78 7.77 7.76 7.76 7.64 7.64 7.63 7.62 7.31 7.31 7.29 7.29 7.29 7.29 7.28 7.27 7.27 7.19 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.14 7.14 7.13 7.13
3.65 3.63 3.61 3.59 3.58 3.57 3.56 3.56 3.55 3.55
1.97 1.96 1.96 1.95 1.93 1.66 1.66 1.64 1.64 1.63 1.63 1.62 1.60 1.41
O
N
Ph
O
N
O
(CDCl3, 400 MHz)
2.01 2.03 2.04 3.00
1.99 1.98 1.00 3.04 1.05 4.04 2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.66
168.46
143.61
133.86
132.17
129.04
126.50
126.20
123.18
51.51
41.85
37.96
31.50
28.80
26.58
24.61
22.23
O
N
Ph
O
N
O
(CDCl3, 101 MHz)
f1 (ppm)

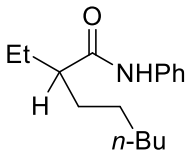

Ph
CF3
H
SiPhMe2
(CDCl3, 400 MHz)
f1 (ppm)


141.31
138.53
133.53
132.79
130.00
129.11
128.51
128.36
127.90
127.21
126.13
125.66
44.67
44.43
44.19
43.95
32.95
28.79
28.77
28.75
28.73
21.85
21.83
21.80
12.28
-3.31
Ph
CF3
H
SiPhMe2
(CDCl3, 101 MHz)
f1 (ppm)


7.25 7.25 7.23 7.23 7.22 7.21 7.21 7.21 7.18 7.16 7.15 7.14 7.12 7.12 7.11 7.10 7.10 7.10 7.09 7.09
3.63 2.72 2.70 2.69 2.66 2.64 2.62 2.61 2.60 2.57 2.56 2.40 2.38 2.36 2.34 1.98 1.96 1.96 1.94 1.93 1.93 1.92 1.92 1.92 1.91 1.90 1.90 1.88 1.71 1.69 1.69 1.67 1.66
Ph
CF3
H
COOMe
(CDCl3, 400 MHz)
2.06
0.97
2.06
3.03
4.05
0.99
1.01
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


171.36
140.76
131.86
129.08
128.56
128.33
126.30
126.28
123.52
52.14
39.82
39.55
39.29
39.03
33.22
33.19
33.16
33.13
32.87
30.28
30.26
30.24
30.22
Ph
CF3
H
COOMe
(CDCl3, 101 MHz)
f1 (ppm)

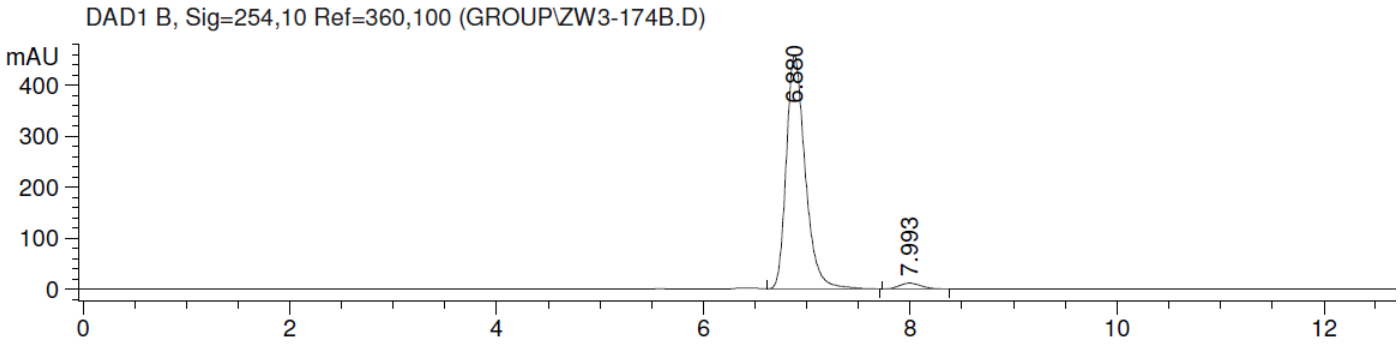
ee Analysis



2-Ethyl-*N*-phenyloctanamide (Fig. 2A, entry 1).

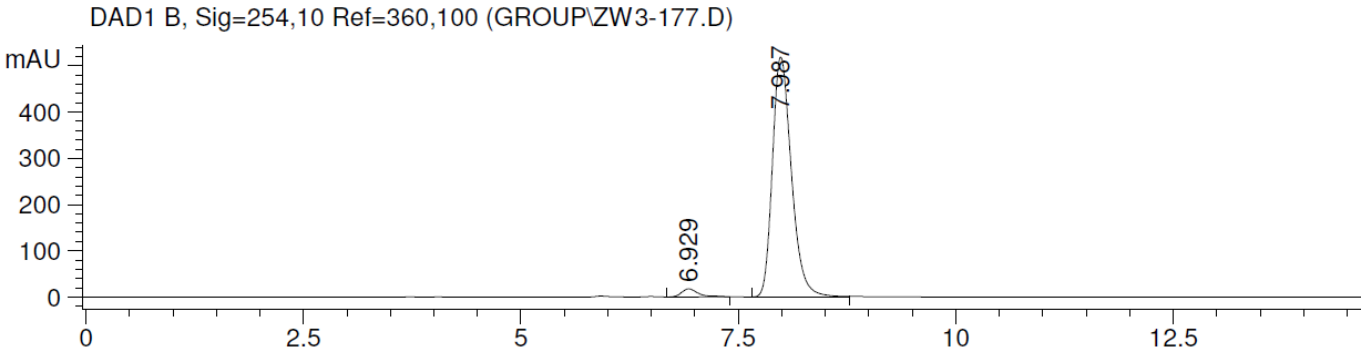
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **1** (Fig. **2A**, entry 1): 94% ee from (*R*,*R*)-**L***

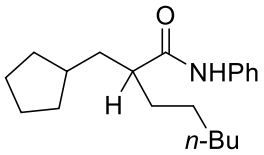


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.880	VB	0.1974	5871.07813	458.45349	96.9895
2	7.993	BB	0.2368	182.23259	11.76130	3.0105

Compound **1** (Fig. **2A**, entry 1): 94% ee from (*S*,*S*)-**L***



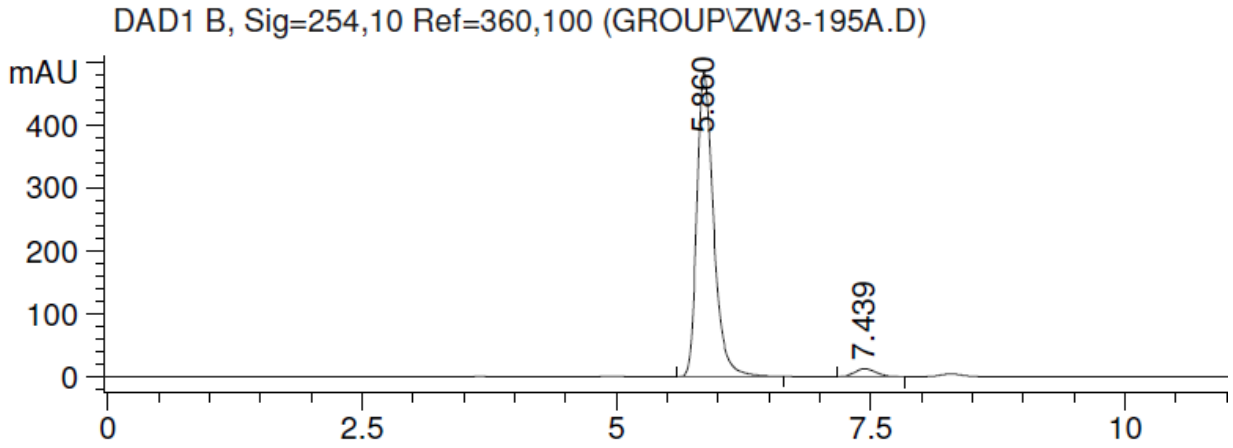
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.929	VB	0.2084	243.66432	17.71763	3.0049
2	7.987	PB	0.2329	7865.26758	518.78076	96.9951



2-(Cyclopentylmethyl)-*N*-phenyloctanamide (Fig. 2A, entry 2).

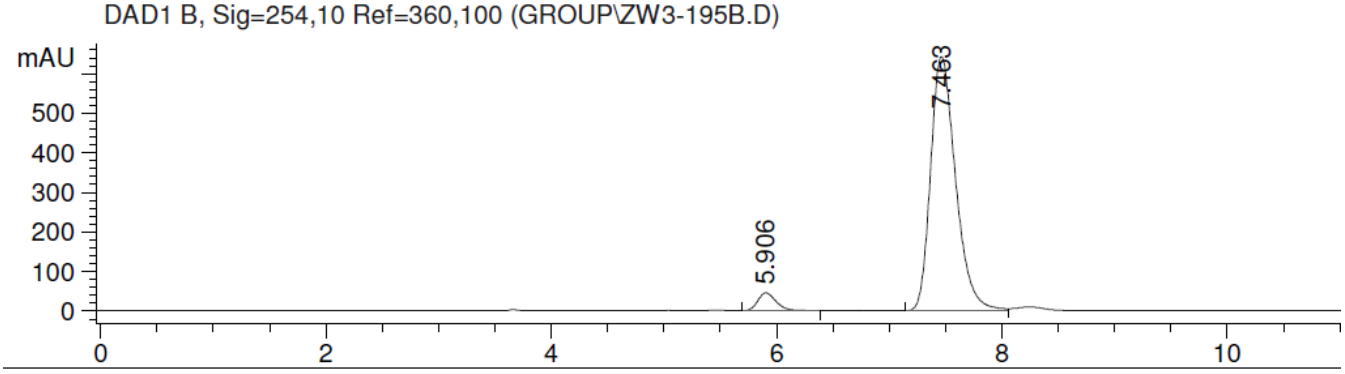
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **2** (Fig. **2A**, entry 2): 93% ee from (*R,R*)-**L***

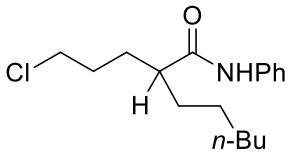


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.860	BB	0.1752	5544.85156	485.56320	96.7896
2	7.439	PB	0.2264	183.91518	12.59103	3.2104

Compound **2** (Fig. **2A**, entry 2): 90% ee from (*S,S*)-**L***



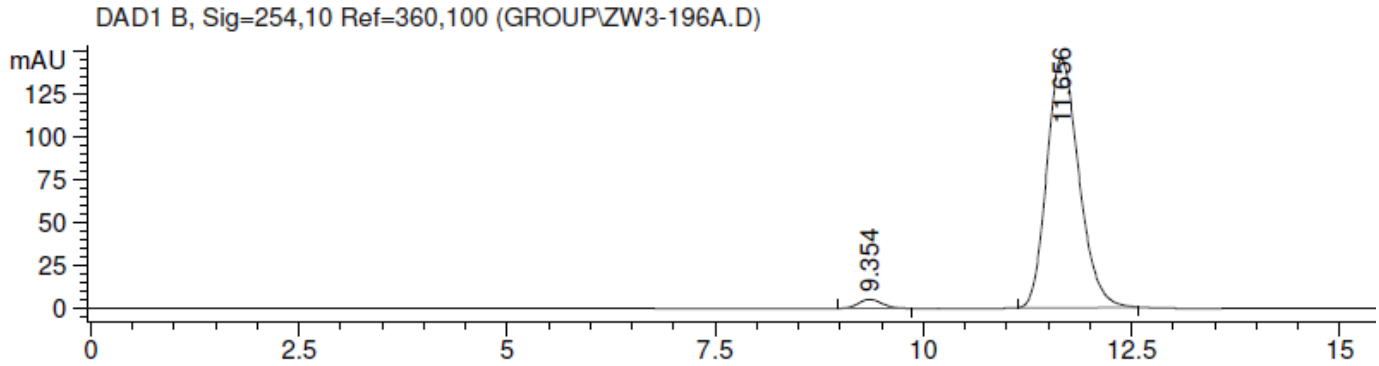
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.906	BB	0.1730	517.29797	45.39297	4.9586
2	7.463	BV	0.2360	9914.98828	642.74005	95.0414



2-(3-Chloropropyl)-*N*-phenyloctanamide (Fig. 2A, entry 3).

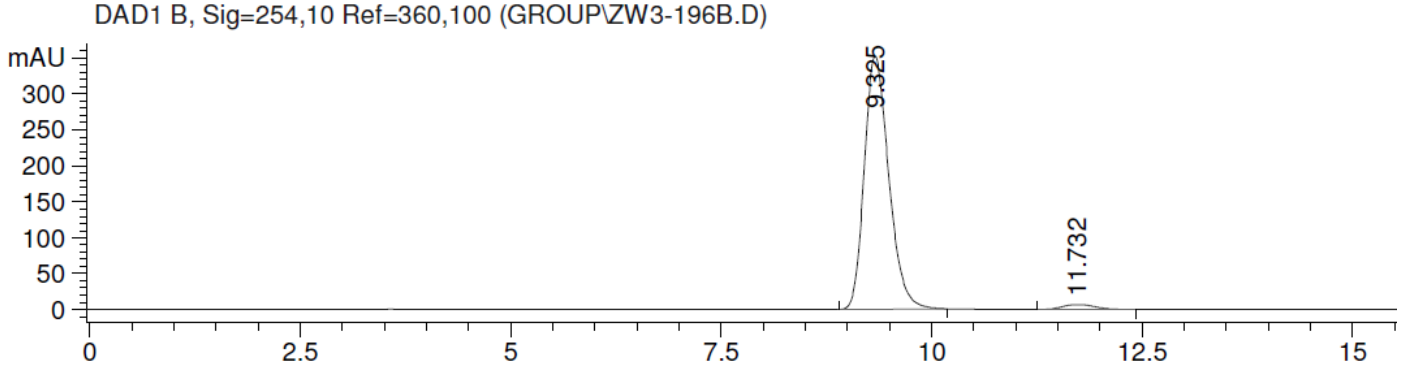
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **3** (Fig. **2A**, entry 3): 95% ee from (*R,R*)-**L***

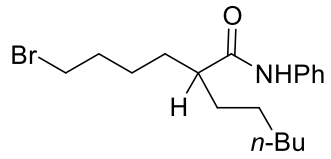


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.354	BB	0.3025	107.47207	5.34636	2.6740
2	11.656	BB	0.4152	3911.66748	145.71103	97.3260

Compound **3** (Fig. **2A**, entry 3): 95% ee from (*S,S*)-**L***



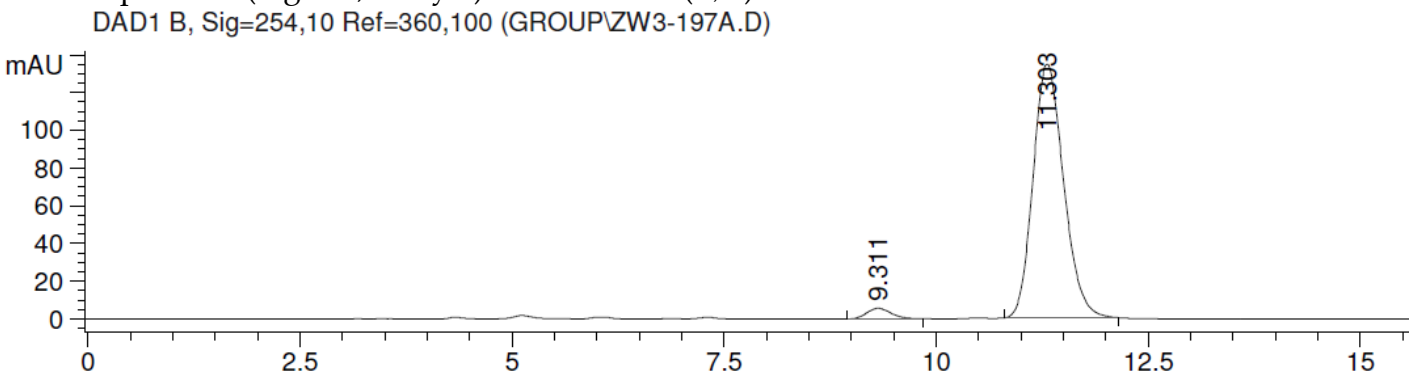
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.325	BB	0.3125	7124.18164	351.50555	97.4289
2	11.732	PB	0.4068	188.00571	7.05801	2.5711



2-(4-Bromobutyl)-N-phenyloctanamide (Fig. 2A, entry 4).

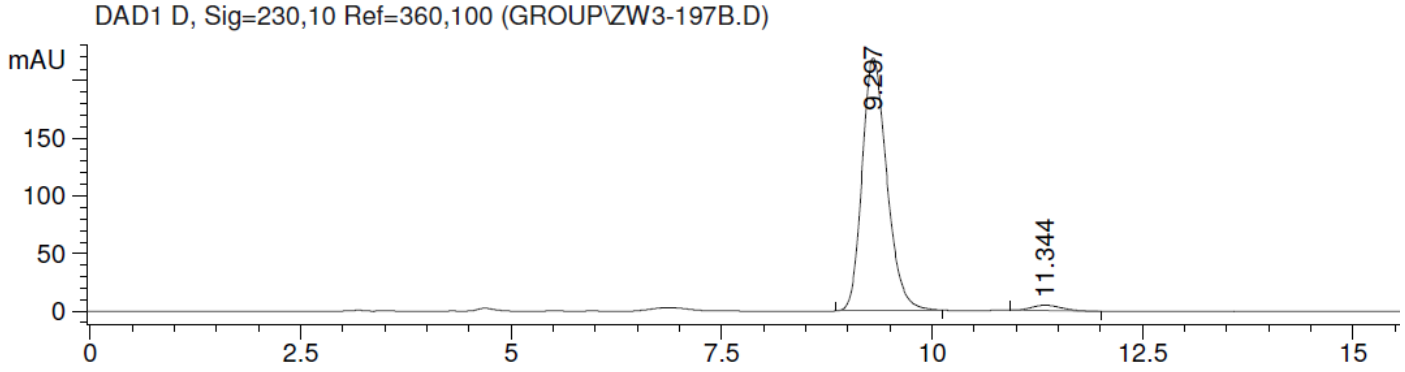
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **4** (Fig. **2A**, entry 4): 94% ee from (*R*,*R*)-**L***

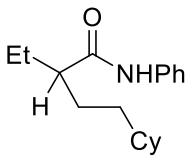


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.311	PB	0.3116	104.40023	5.17066	3.1829
2	11.303	BB	0.3915	3175.61279	126.25076	96.8171

Compound **4** (Fig. **2A**, entry 4): 95% ee from (*S*,*S*)-**L***



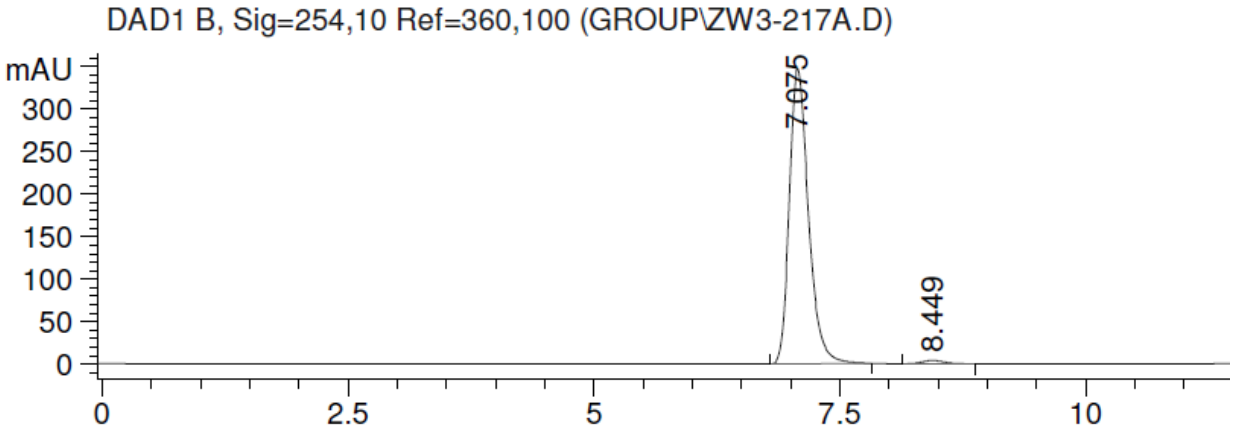
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.297	BB	0.3145	4474.11084	218.86646	97.5540
2	11.344	PP	0.3671	112.17899	4.62355	2.4460



4-Cyclohexyl-2-ethyl-N-phenylbutanamide (Fig. 2A, entry 5).

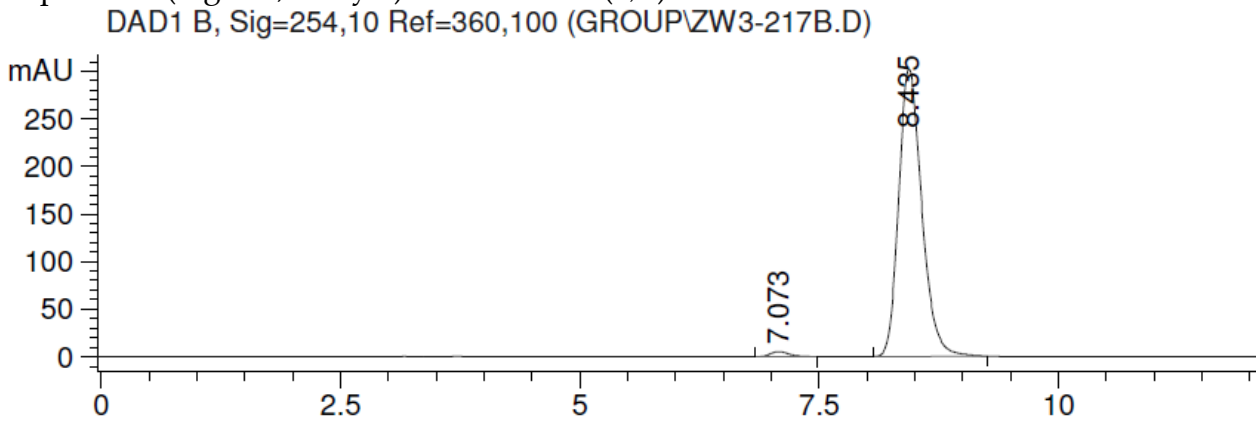
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **5** (Fig. **2A**, entry 5): 97% ee from (*R,R*)-**L***

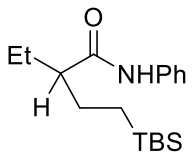


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.075	PB	0.2077	4700.34424	347.62814	98.7064
2	8.449	PB	0.2491	61.59982	3.76113	1.2936

Compound **5** (Fig. **2A**, entry 5): 97% ee from (*S,S*)-**L***



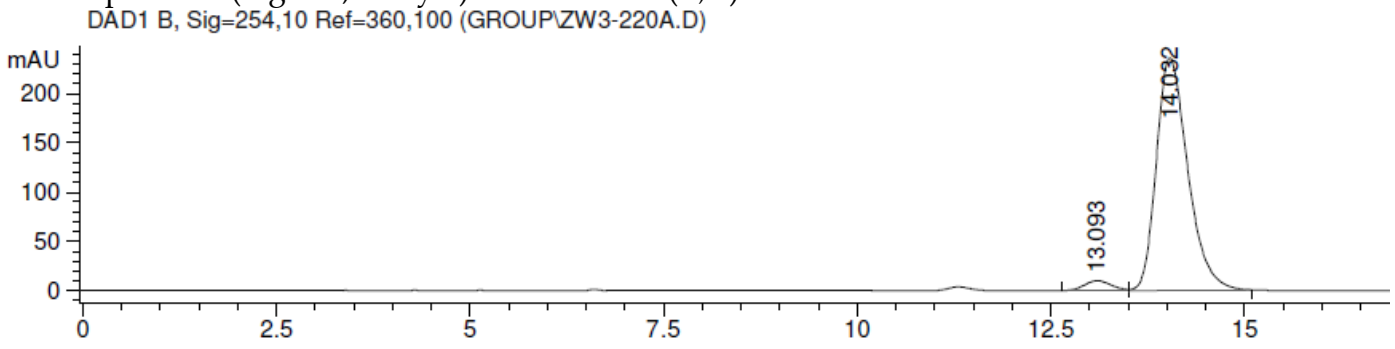
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.073	PB	0.2160	75.32696	5.29341	1.4581
2	8.435	BB	0.2602	5090.78516	302.73892	98.5419



4-(*tert*-Butyldimethylsilyl)-2-ethyl-*N*-phenylbutanamide (Fig. 2A, entry 6).

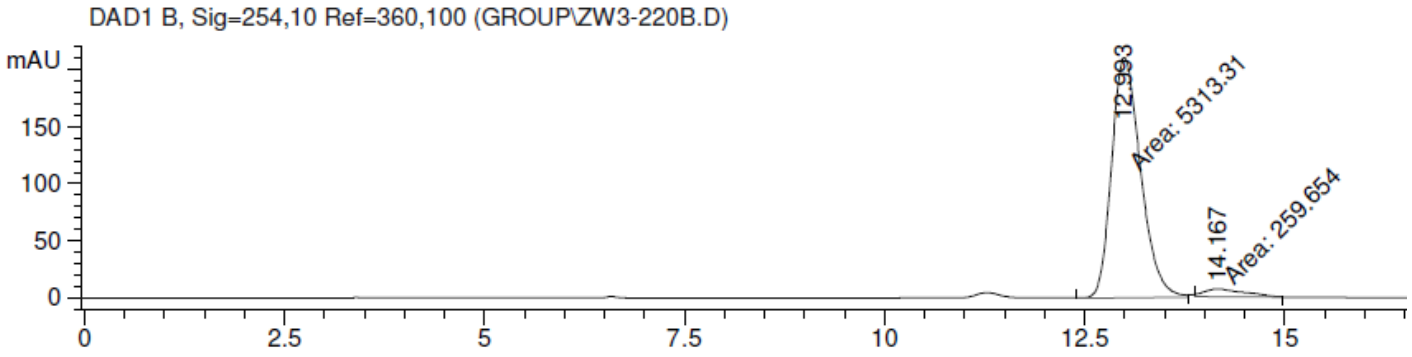
HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

Compound **6** (Fig. **2A**, entry 6): 93% ee from (*R,R*)-**L***

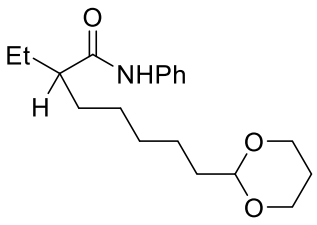


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.093	BV	0.3704	242.78555	10.02962	3.5180
2	14.032	VB	0.4339	6658.41650	235.46095	96.4820

Compound **6** (Fig. **2A**, entry 6): 91% ee from (*S,S*)-**L***



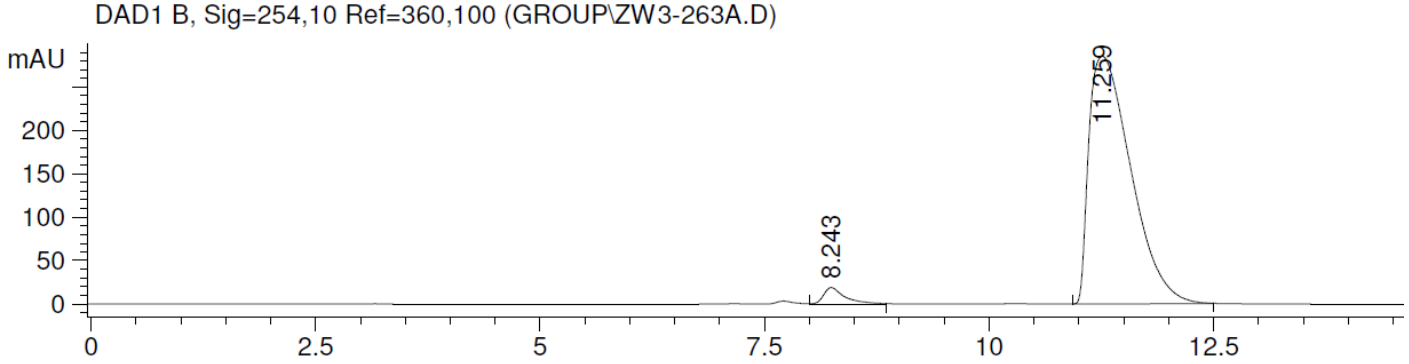
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.993	MM	0.4202	5313.31396	210.73102	95.3408
2	14.167	MM	0.6195	259.65375	6.98586	4.6592



7-(1,3-dioxan-2-yl)-2-ethyl-*N*-phenylheptanamide (Fig. 2A, entry 7).

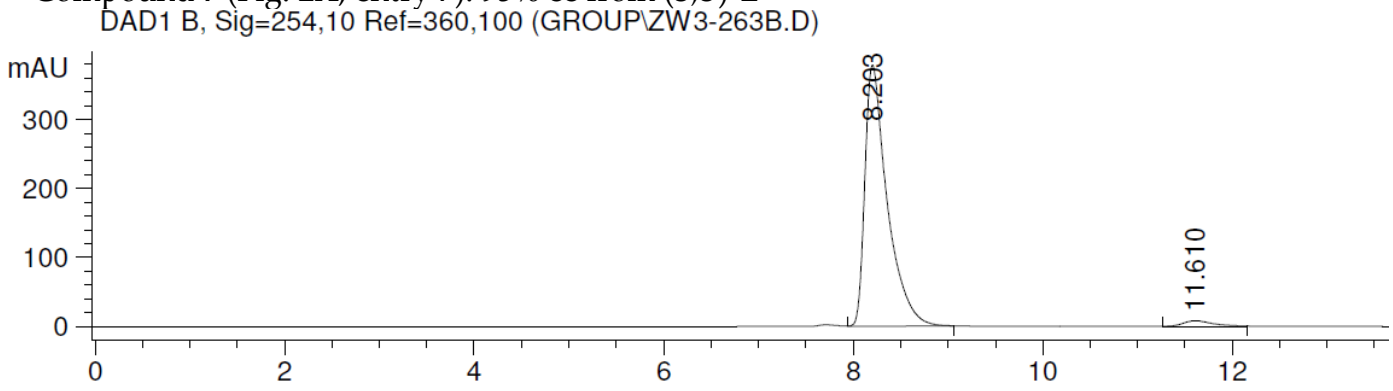
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **7** (Fig. **2A**, entry 7): 94% ee from (*R*,*R*)-**L***

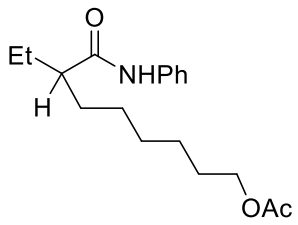


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.243	VB	0.2362	307.93033	18.88757	3.2095
2	11.259	BB	0.5117	9286.54980	285.34528	96.7905

Compound **7** (Fig. **2A**, entry 7): 95% ee from (*S*,*S*)-**L***



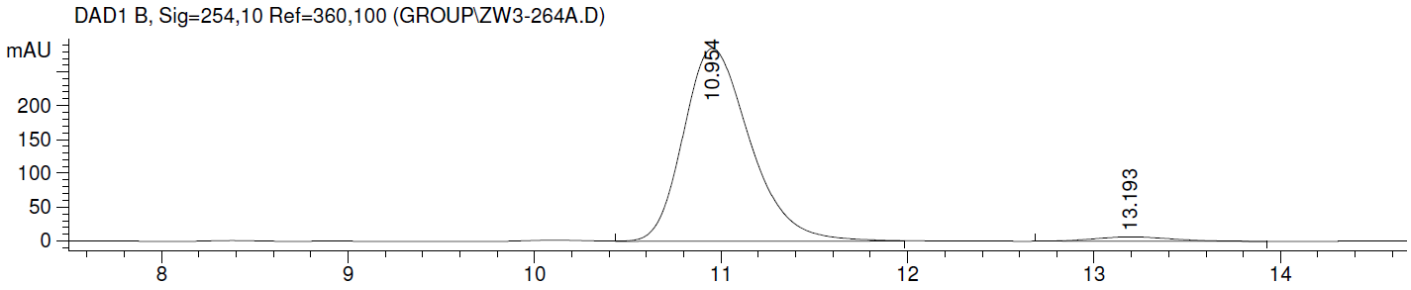
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.203	VB	0.2418	6233.30957	379.16898	97.2938
2	11.610	BB	0.3156	173.37561	8.10349	2.7062



7-(Phenylcarbamoyl)nonyl acetate (Fig. 2A, entry 8).

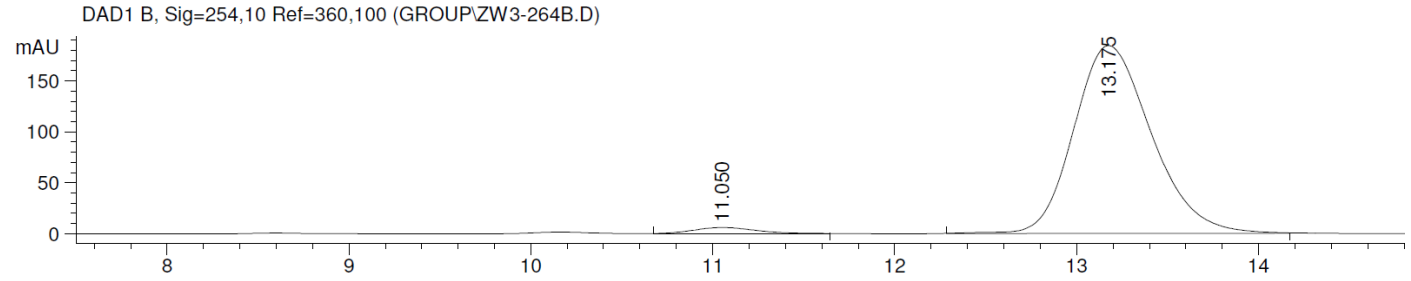
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **8** (Fig. **2A**, entry 8): 95% ee from (*R*,*R*)-**L***

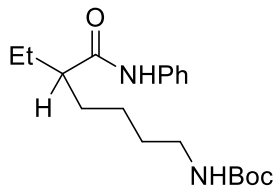


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.954	VB	0.3835	7067.72705	284.83401	97.4715
2	13.193	PB	0.4354	183.34015	6.37695	2.5285

Compound **8** (Fig. **2A**, entry 8): 95% ee from (*S*,*S*)-**L***



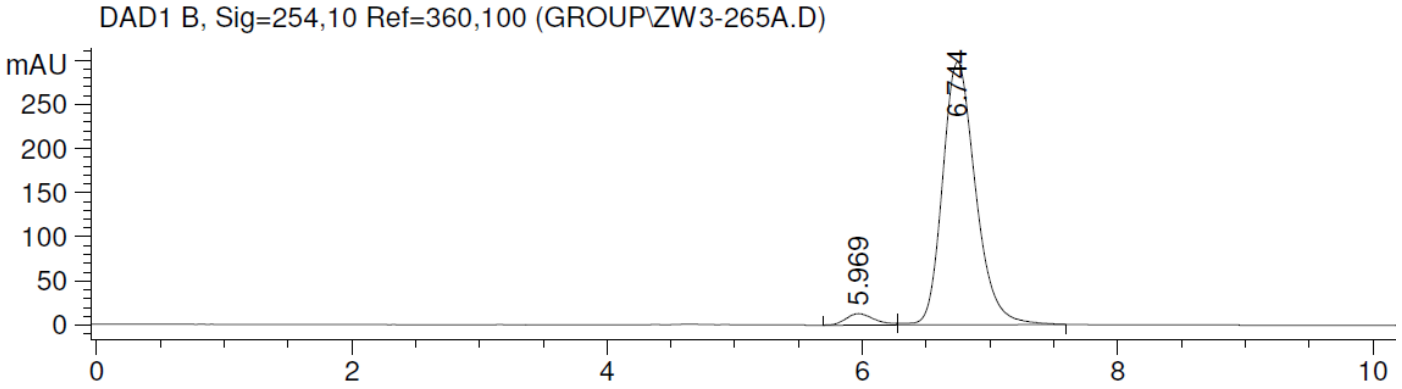
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.050	BB	0.3615	143.31136	5.93885	2.5549
2	13.175	BB	0.4605	5465.99170	184.06102	97.4451



***tert*-Butyl (5-(phenylcarbamoyl)heptyl)carbamate (Fig. 2A, entry 9).**

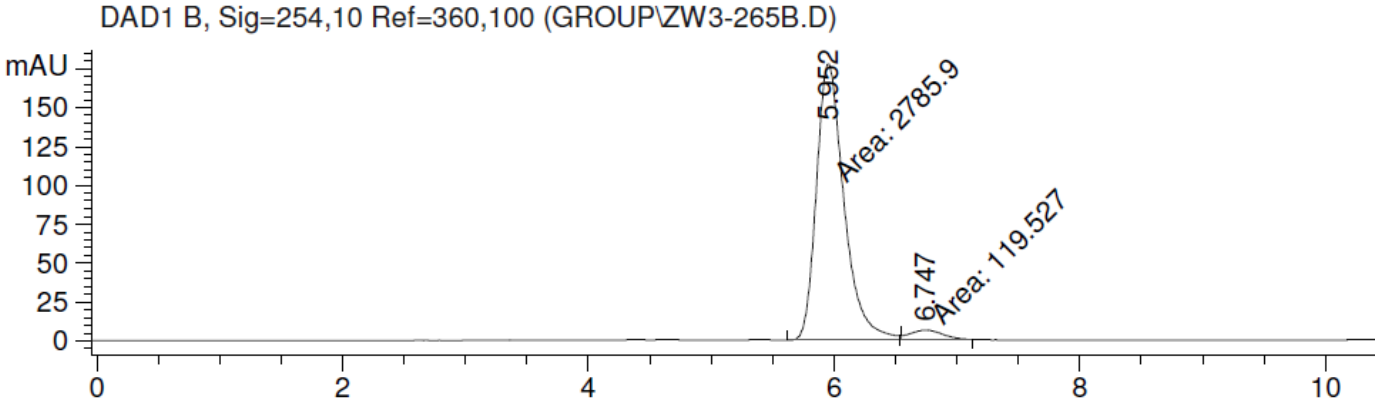
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **9** (Fig. **2A**, entry 9): 93% ee from (*R*,*R*)-**L***

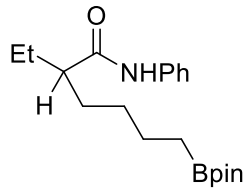


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.969	PV	0.2383	201.17516	12.87653	3.6260
2	6.744	VB	0.2753	5347.02637	298.02200	96.3740

Compound **9** (Fig. **2A**, entry 9): 92% ee from (*S*,*S*)-**L***



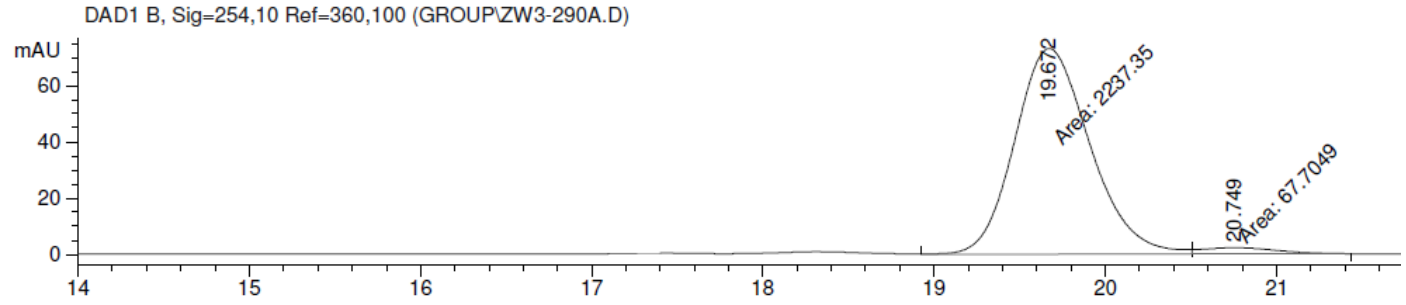
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.952	MM	0.2612	2785.89868	177.77194	95.8861
2	6.747	MM	0.3126	119.52668	6.37322	4.1139



2-Ethyl-*N*-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (Fig. 2A, entry 10).

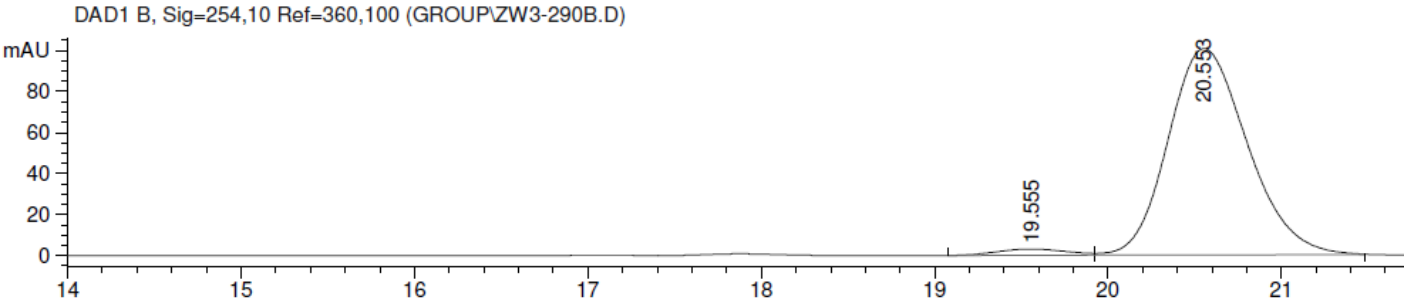
HPLC analysis: CHIRALPAK IC column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **10** (Fig. **2A**, entry 10): 94% ee from (*R,R*)-**L***



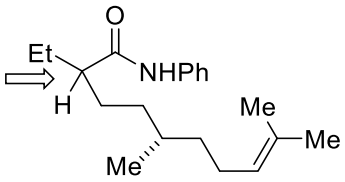
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.672	MF	0.5101	2237.35083	73.09674	97.0628
2	20.749	FM	0.5034	67.70495	2.24150	2.9372

Compound **10** (Fig. **2A**, entry 10): 95% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.555	BV	0.4012	87.73812	3.12882	2.6628
2	20.553	VB	0.4919	3207.25391	100.61310	97.3372

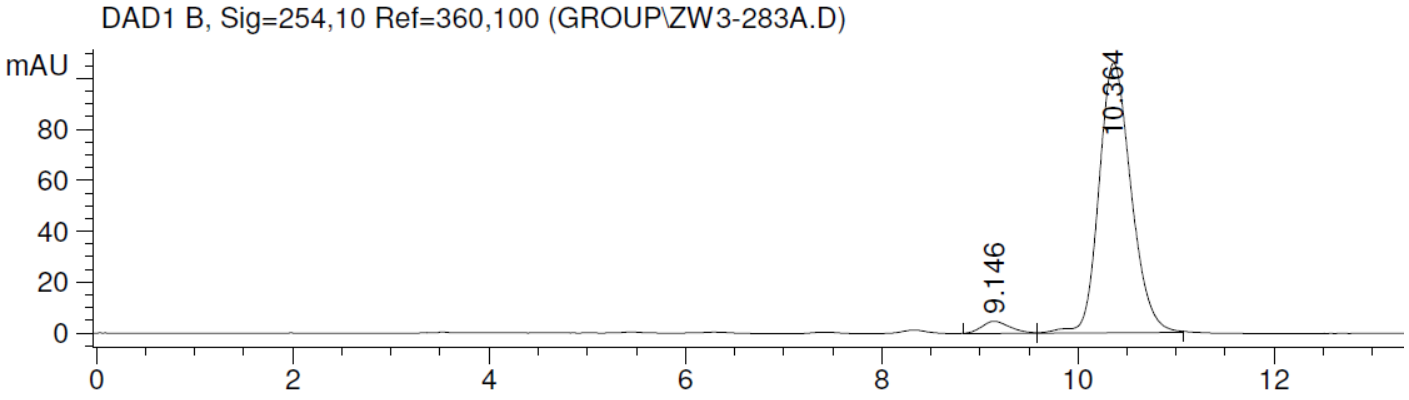
(*R*,*R*)-**L***: **1:26** d.r., 78% yield
(*S*,*S*)-**L***: **>30:1** d.r., 70% yield



(5*S*)-2-Ethyl-5,9-dimethyl-*N*-phenyldec-8-enamide (Fig. 2A, entries 11 and 12).

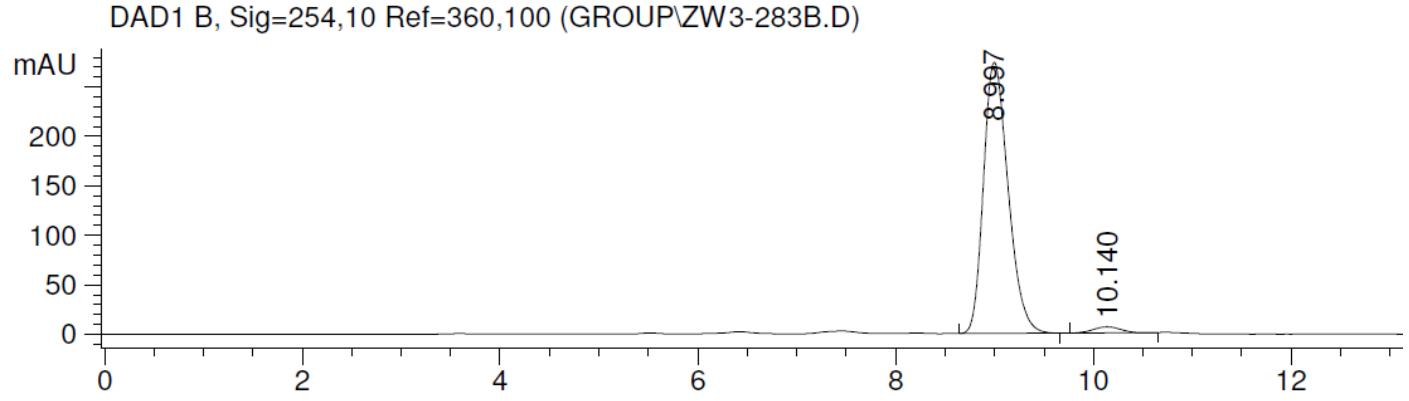
HPLC analysis: CHIRALCEL AS-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

Compound **11** (Fig. **2A**, entry 11): 26:1 d.r. from (*R*,*R*)-**L***



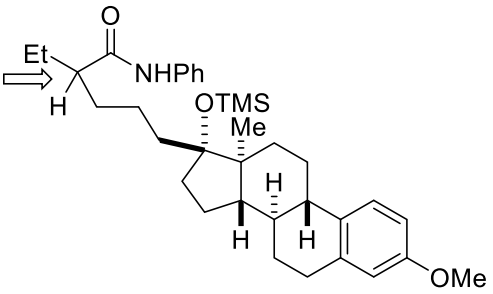
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.146	BV	0.2957	93.05866	4.68654	3.7137
2	10.364	VB	0.3515	2412.76196	106.03738	96.2863

Compound **12** (Fig. **2A**, entry 12): 1:>30 d.r. from (*S*,*S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.997	BP	0.2680	4753.32471	274.55530	97.6457
2	10.140	PP	0.2917	114.60727	6.19805	2.3543

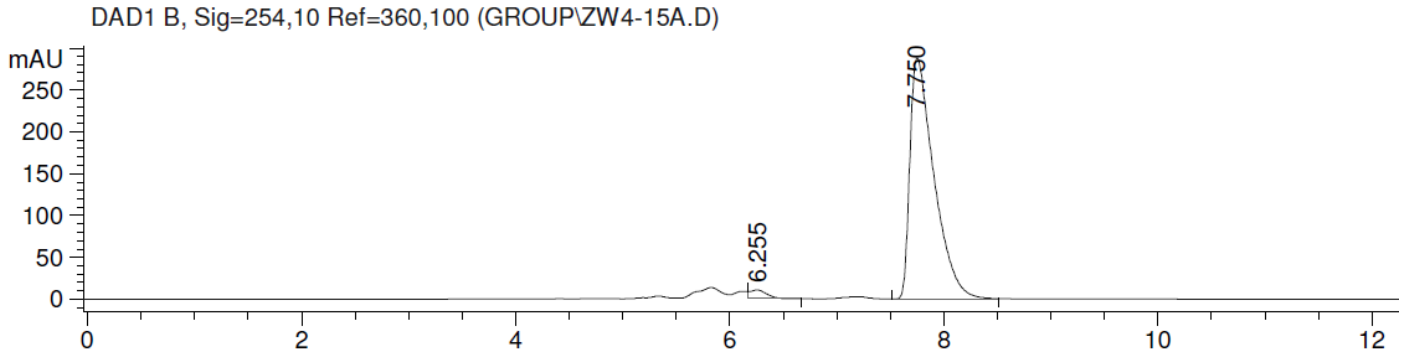
(*R*,*R*)-**L***: **1:>30** d.r., 79% yield
(S,S)-**L***: **26:1** d.r., 77% yield



2-Ethyl-5-((8*R*,9*S*,13*S*,14*S*,17*S*)-3-methoxy-13-methyl-17-((trimethylsilyl)oxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)-*N*-phenylpentanamide (Fig. 2A, entries 13 and 14).

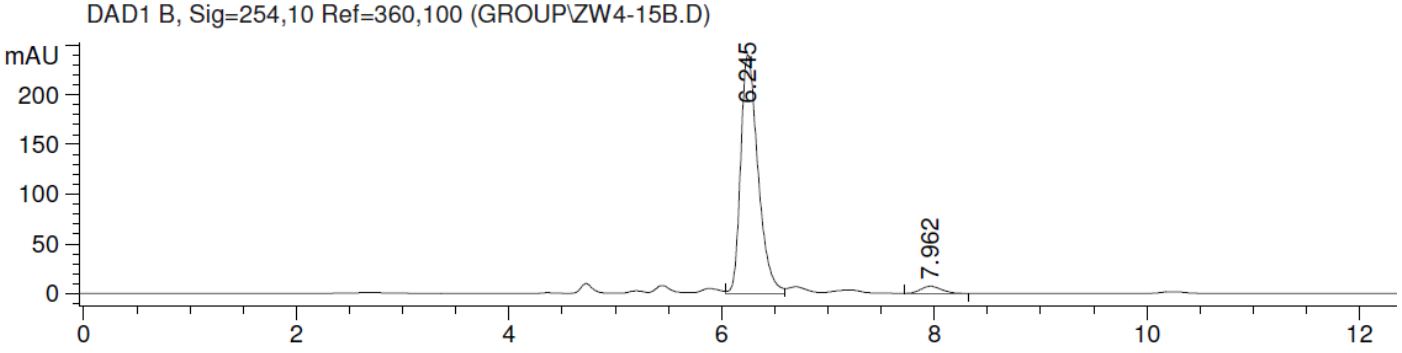
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **13** (Fig. **2A**, entry 13): >30:1 d.r. from (*R*,*R*)-**L***

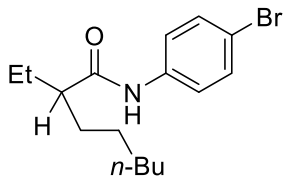


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.255	VB	0.1704	122.82501	10.50197	2.6562
2	7.750	VB	0.2323	4501.17676	288.01712	97.3438

Compound **14** (Fig. **2A**, entry 14): 1:26 d.r. from (*S*,*S*)-**L***



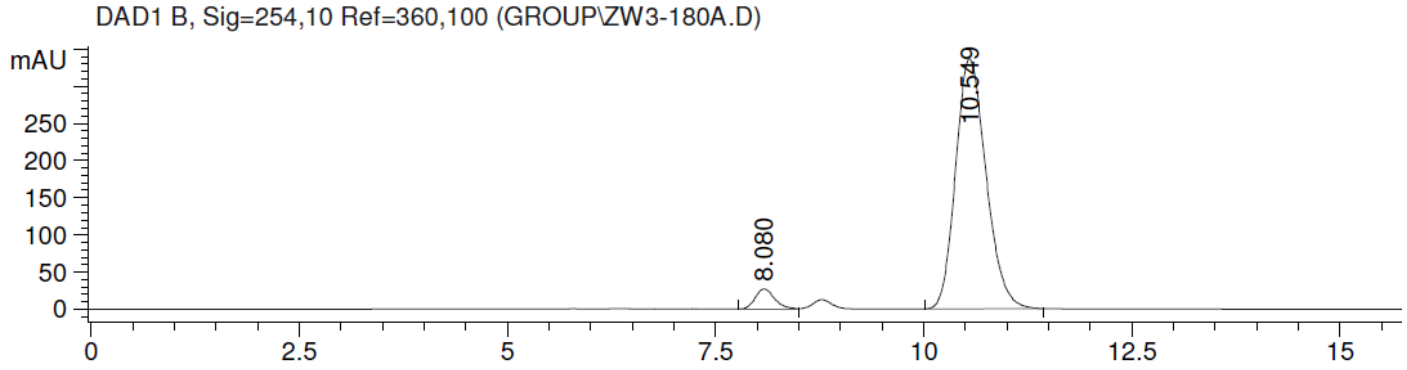
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	VV	0.1723	2726.31909	240.40544	96.4220
2	7.962	BB	0.2170	101.16848	7.24205	3.5780



2-Ethyl-*N*-(4-bromophenyl)octanamide (Fig. 2A, entry 15).

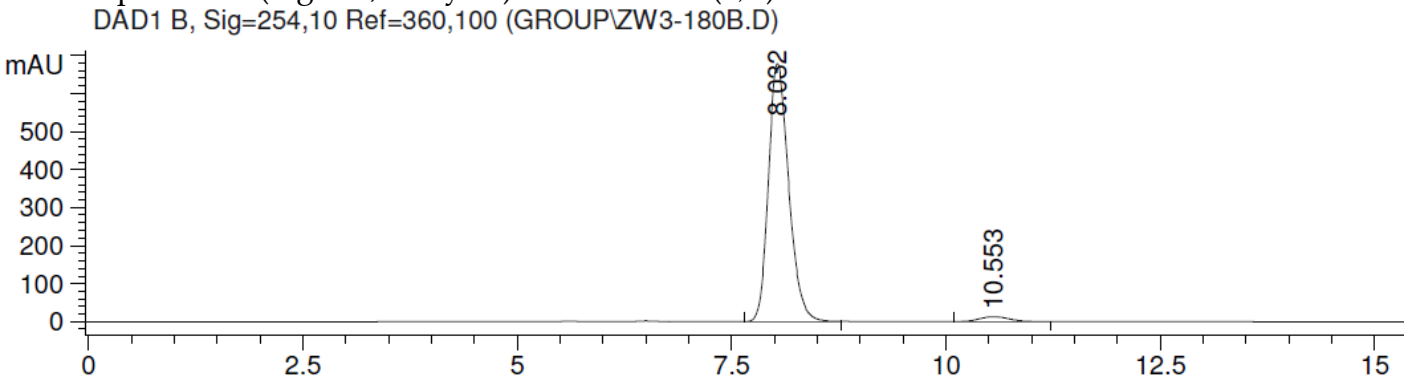
HPLC analysis: CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **15** (Fig. **2A**, entry 15): 90% ee from (*R,R*)-**L***

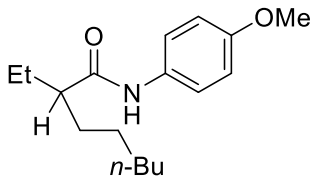


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.080	BV	0.2490	448.35553	27.38617	4.9742
2	10.549	PB	0.3950	8565.21289	336.47855	95.0258

Compound **15** (Fig. **2A**, entry 15): 94% ee from (*S,S*)-**L***



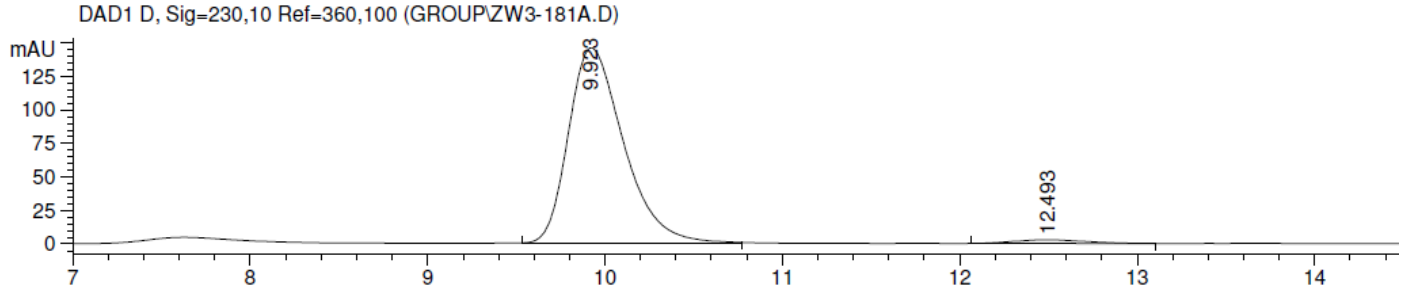
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.032	PB	0.2541	1.11961e4	679.98236	97.0943
2	10.553	BB	0.3955	335.06332	13.14187	2.9057



2-Ethyl-*N*-(4-methoxyphenyl)octanamide (Fig. 2A, entry 16).

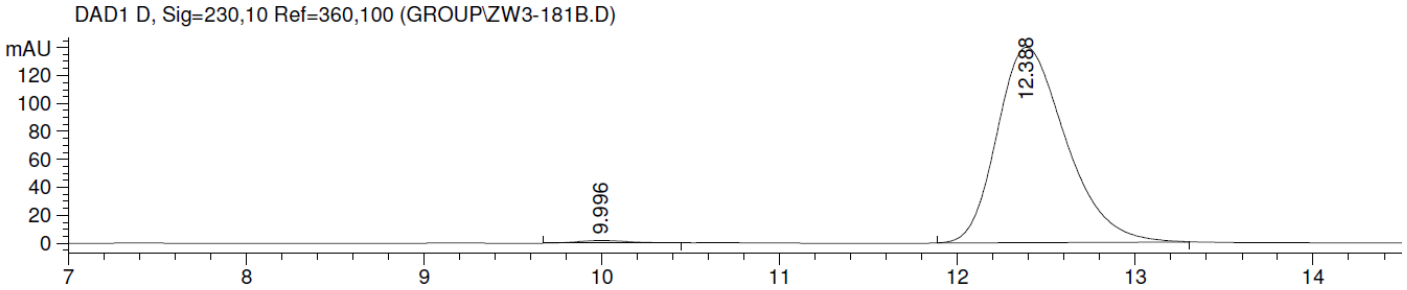
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **16** (Fig. **2A**, entry 16): 95% ee from (*R,R*)-**L***

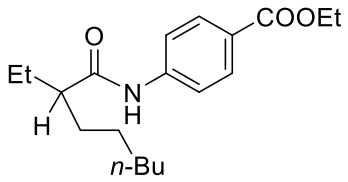


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.923	BB	0.3322	6384.74365	295.39664	97.6672
2	12.495	PB	0.4124	152.49855	5.73138	2.3328

Compound **16** (Fig. **2A**, entry 16): 98% ee from (*S,S*)-**L***



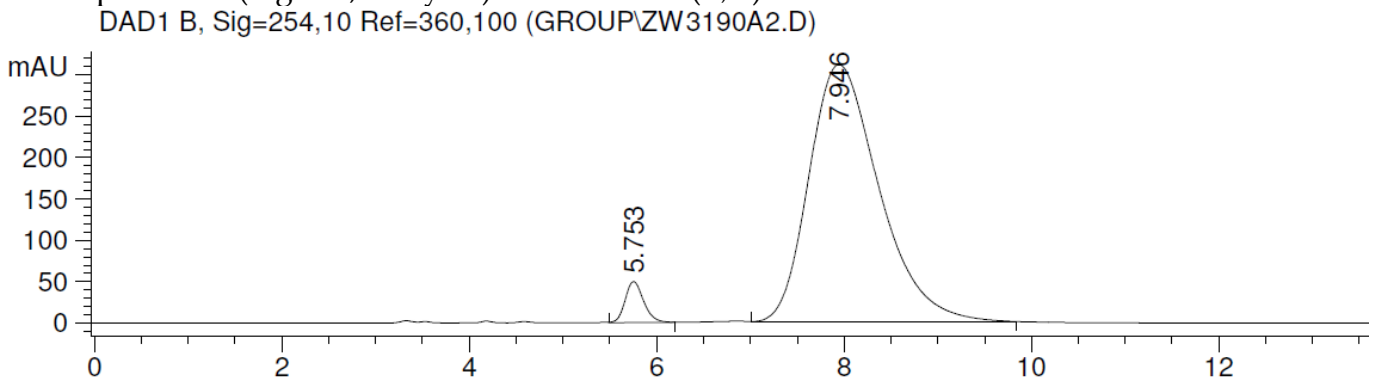
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.996	PB	0.2782	35.50589	1.79956	0.9331
2	12.388	BB	0.4162	3769.74878	139.95982	99.0669



Ethyl 4-(2-ethyloctanamido)benzoate (Fig. 2A, entry 17).

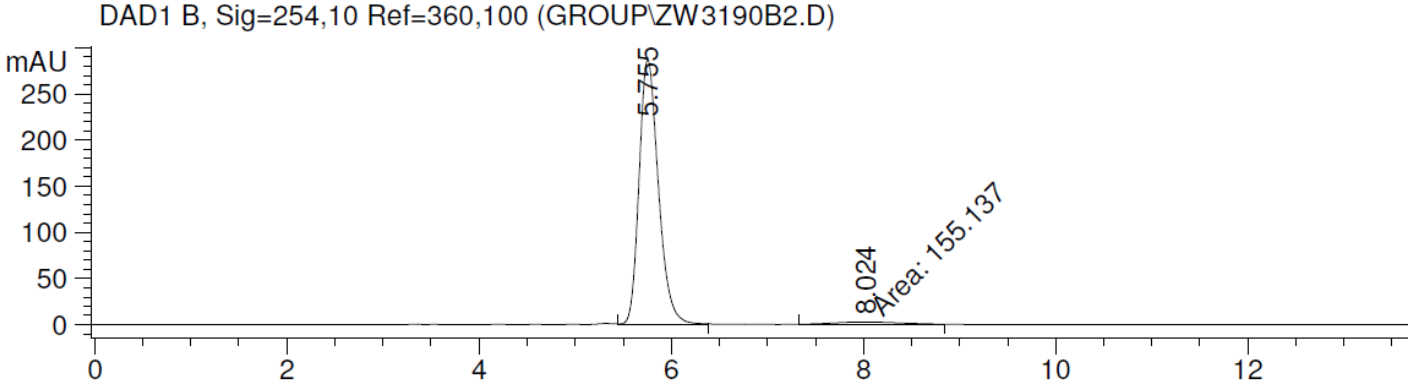
HPLC analysis: CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **17** (Fig. **2A**, entry 17): 92% ee from (*R,R*)-**L***



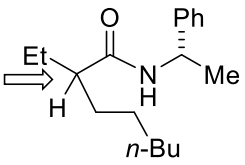
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.753	BB	0.2086	672.65454	49.47715	3.9831
2	7.946	VB	0.8017	1.62149e4	311.31744	96.0169

Compound **17** (Fig. **2A**, entry 17): 92% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.755	VB	0.2141	3986.63184	286.97015	96.2543
2	8.024	MM	0.8809	155.13722	2.93519	3.7457

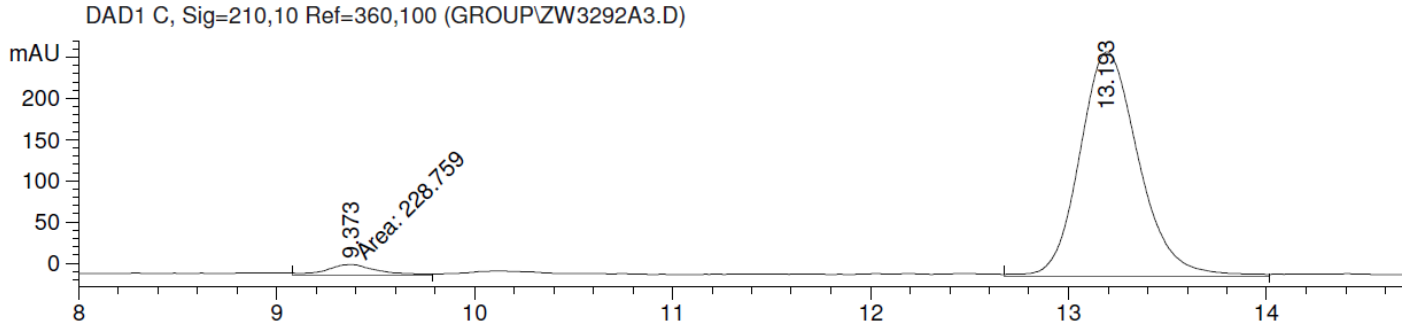
(*R*,*R*)-**L***: **1:24** d.r., 71% yield
(S,S)-**L***: **19:1** d.r., 69% yield



2-Ethyl-*N*-((*S*)-1-phenylethyl)octanamide (Fig. 2A, entries 18 and 19).

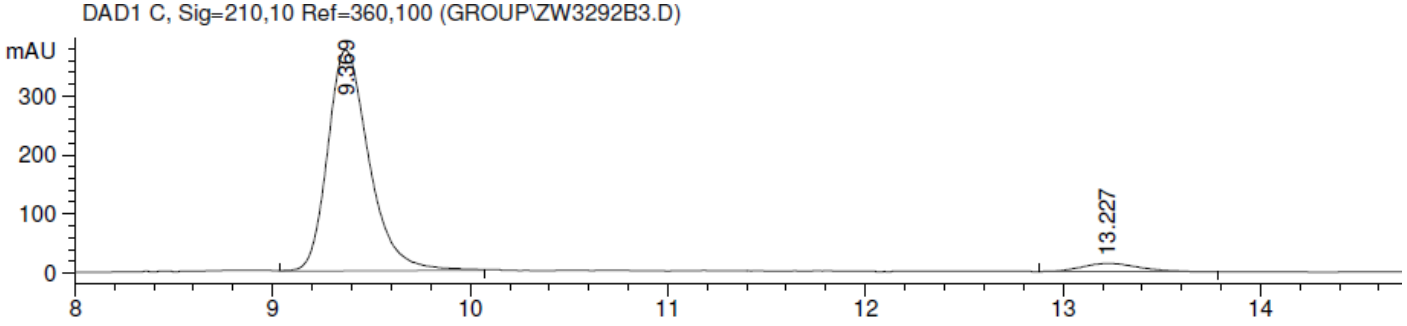
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **18** (Fig. **2A**, entry 18): 24:1 d.r. from (*R*,*R*)-**L***

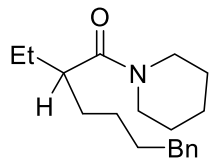


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.373	MM	0.2966	228.75891	12.85584	3.8688
2	13.193	VV	0.3210	5684.11133	272.86096	96.1312

Compound **19** (Fig. **2A**, entry 19): 1:19 d.r. from (*S*,*S*)-**L***



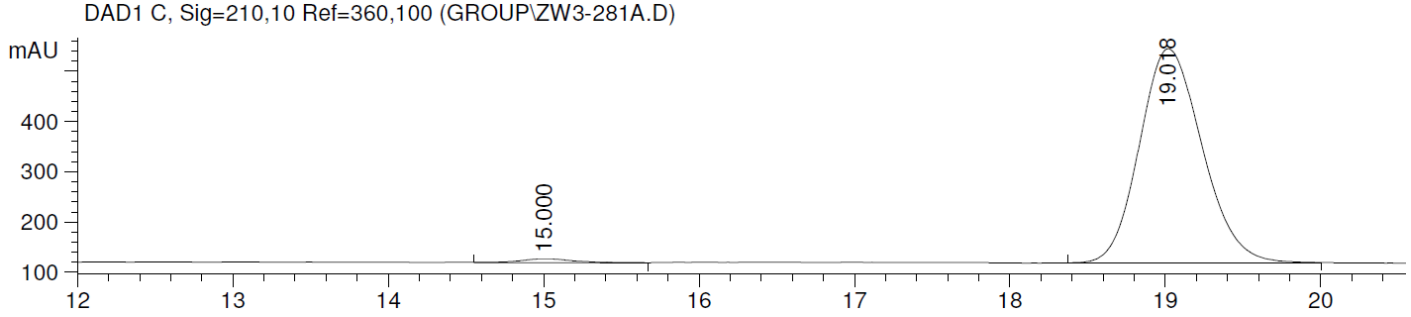
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.369	VB	0.2236	5438.52295	374.18784	94.8564
2	13.227	PP	0.2543	294.90317	14.31831	5.1436



2-Ethyl-6-phenyl-1-(piperidin-1-yl)hexan-1-one (Fig. 2A, entry 20).

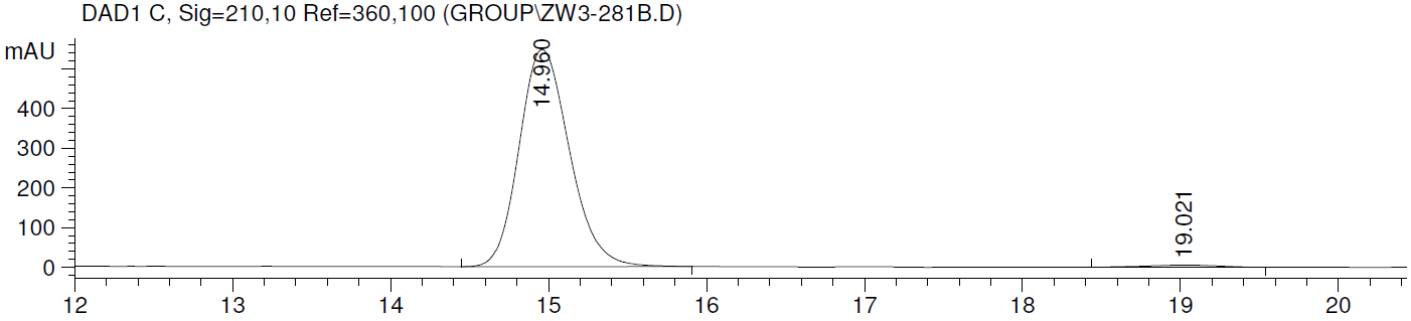
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **20** (Fig. **2A**, entry 20): 97% ee from (*R,R*)-**L***

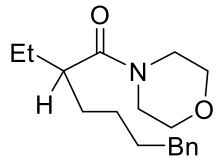


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.000	VP	0.2915	189.59042	7.91347	1.5619
2	19.018	BB	0.4332	1.19486e4	426.02817	98.4381

Compound **20** (Fig. **2A**, entry 20): 97% ee from (*S,S*)-**L***



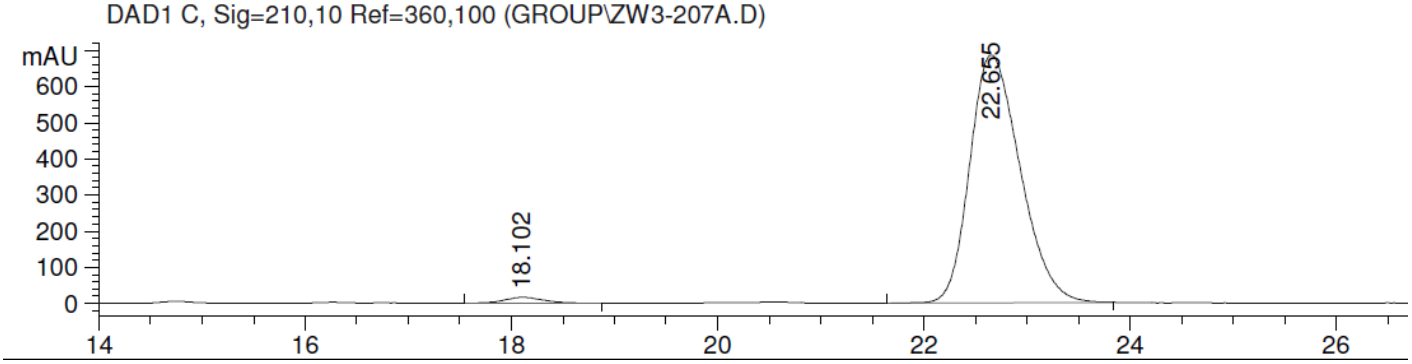
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.960	PB	0.3443	1.21118e4	547.14276	98.5772
2	19.021	PP	0.3605	174.81061	5.85175	1.4228



2-Ethyl-1-morpholino-6-phenylhexan-1-one (Fig. 2A, entry 21).

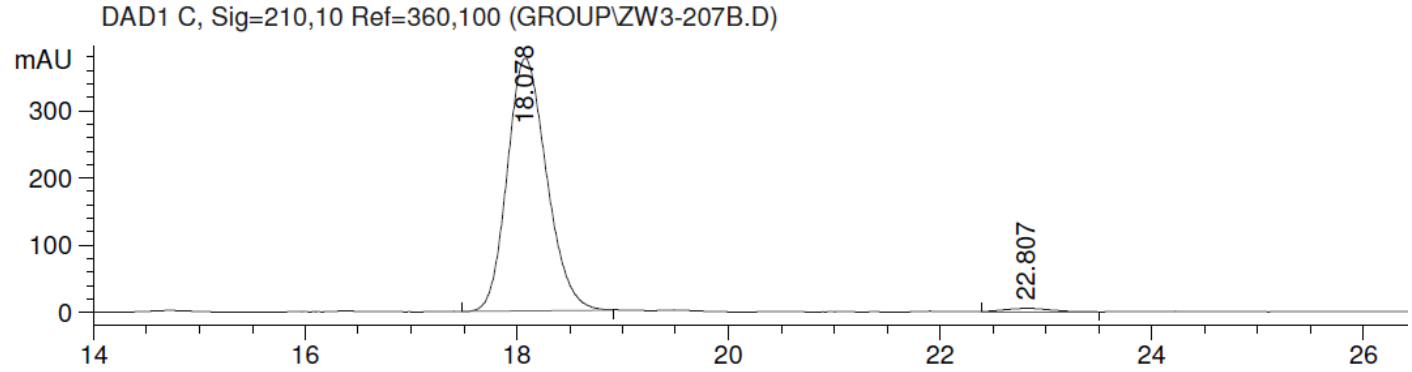
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **21** (Fig. **2A**, entry 21): 96% ee from (*R,R*)-**L***

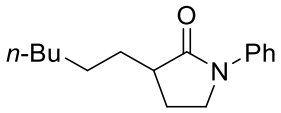


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.102	PB	0.3556	440.59344	16.08162	1.8547
2	22.655	VB	0.5227	2.33152e4	685.75970	98.1453

Compound **21** (Fig. **2A**, entry 21): 97% ee from (*S,S*)-**L***



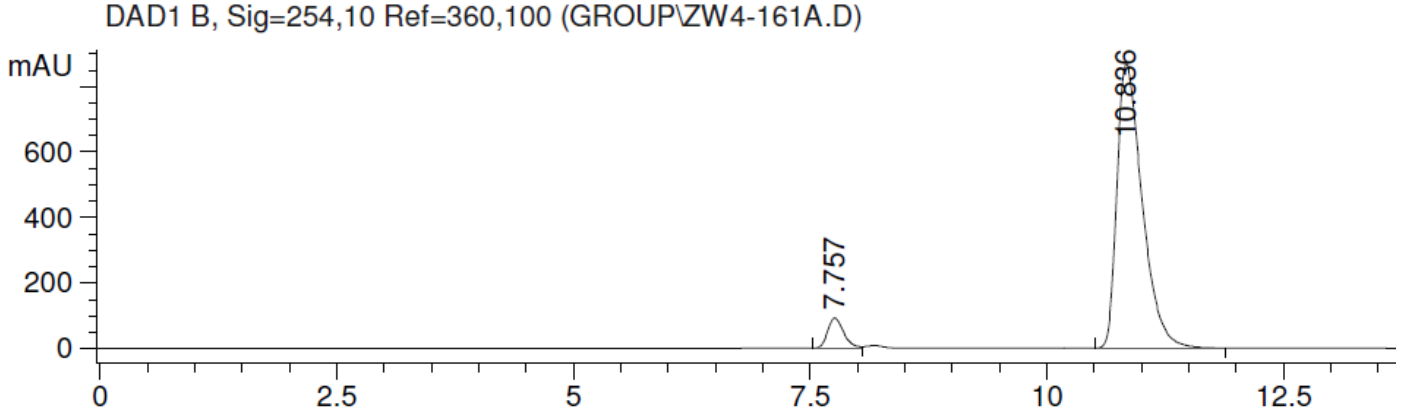
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.078	PB	0.4007	9699.41699	376.37299	98.4582
2	22.807	BP	0.3762	151.88811	4.94705	1.5418



3-Hexyl-1-phenylpyrrolidin-2-one (Fig. 2A, entry 22).

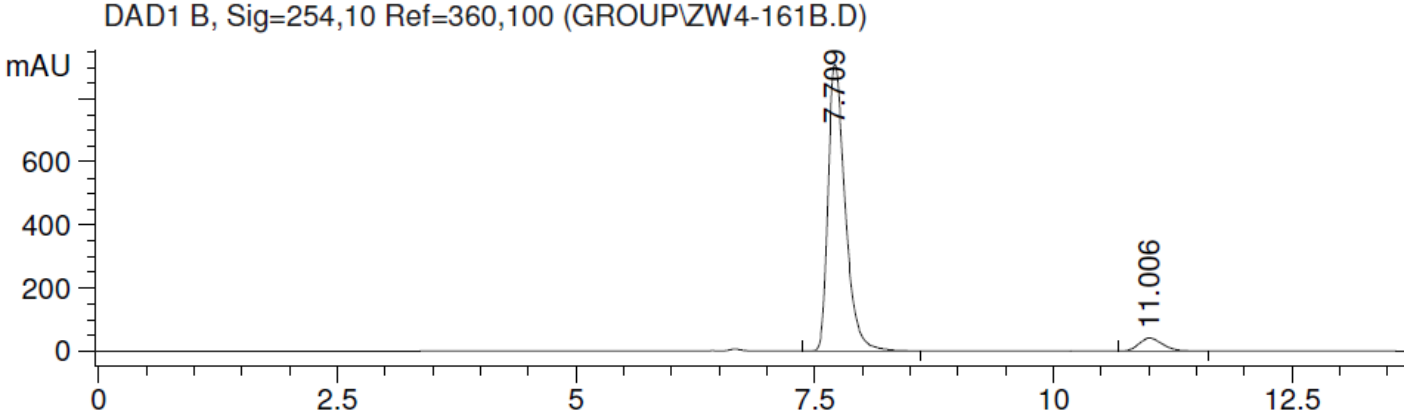
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **22** (Fig. **2A**, entry 22): 88% ee from (*R,R*)-**L***

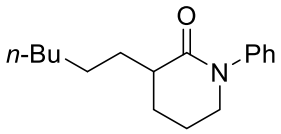


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.757	BV	0.1820	1101.91577	93.19006	6.3757
2	10.836	VB	0.2852	1.61811e4	869.10345	93.6243

Compound **22** (Fig. **2A**, entry 22): 88% ee from (*S,S*)-**L***



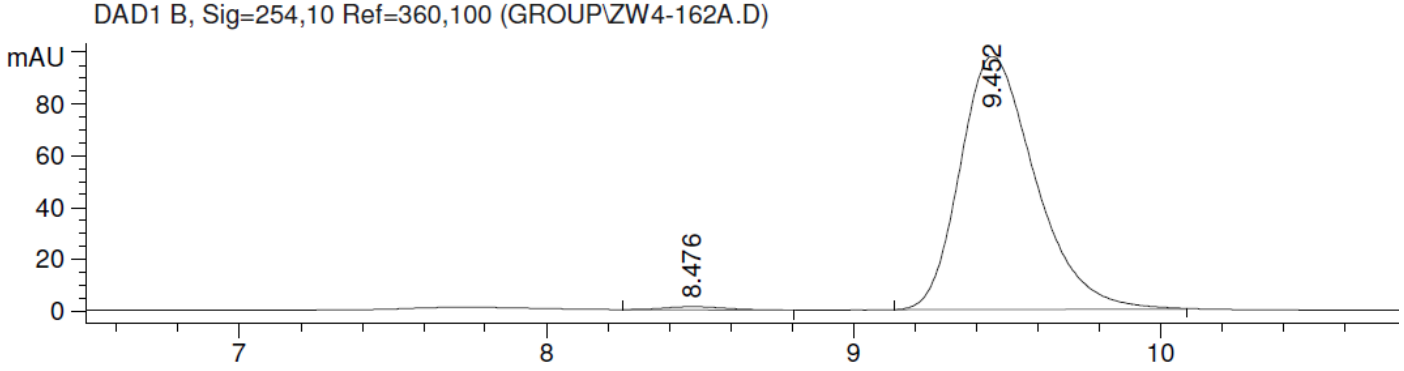
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.709	BB	0.1900	1.14070e4	911.34937	93.9654
2	11.006	PB	0.2717	732.58020	41.54691	6.0346



3-Hexyl-1-phenylpiperidin-2-one (Fig. 2A, entry 23).

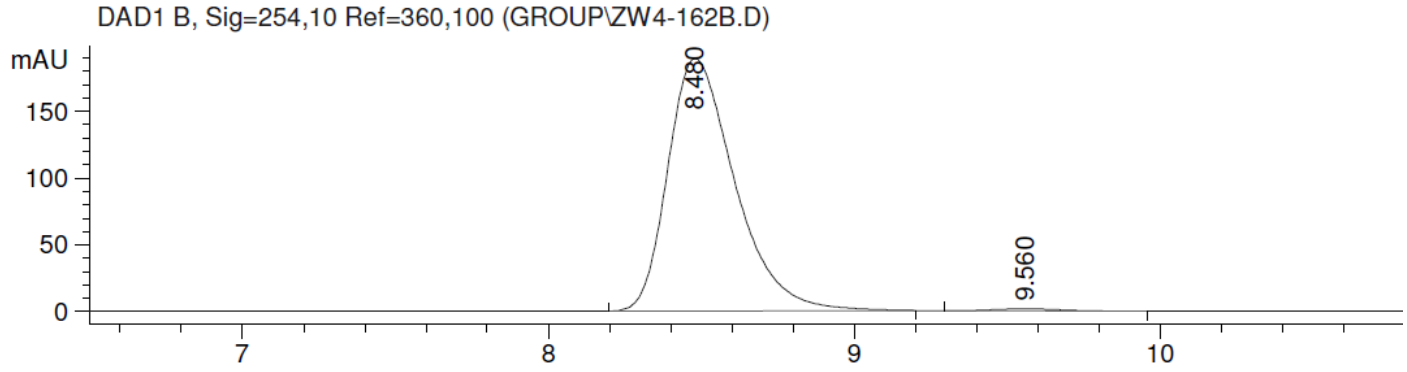
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **23** (Fig. **2A**, entry 23): 98% ee from (*R,R*)-**L***

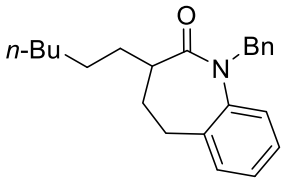


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.476	PP	0.2079	15.77129	1.13665	0.9344
2	9.452	BB	0.2611	1672.12671	97.98386	99.0656

Compound **23** (Fig. **2A**, entry 23): 98% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.480	BB	0.2319	2887.68335	189.37862	99.1595
2	9.560	PP	0.2325	24.47796	1.58208	0.8405

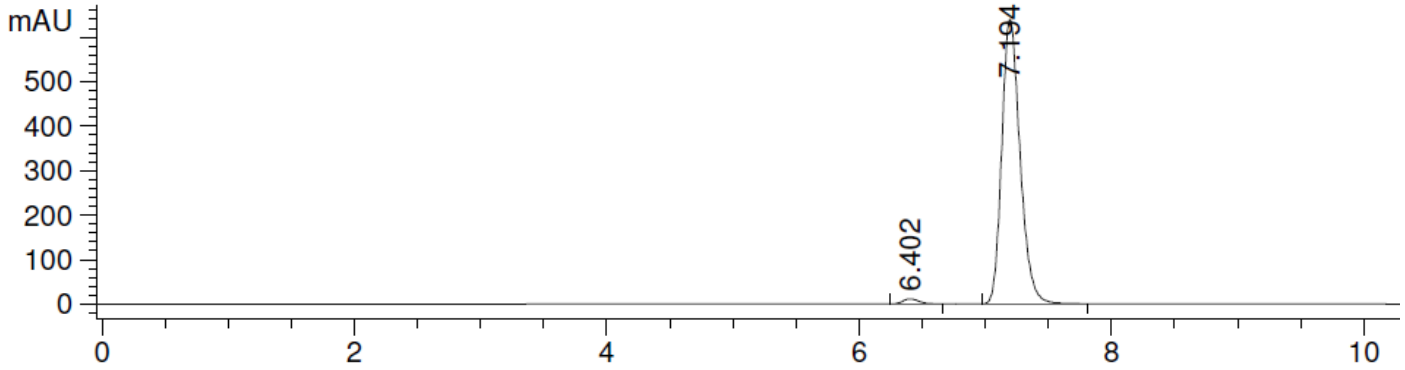


1-Benzyl-3-hexyl-1,3,4,5-tetrahydro-2*H*-benzo[*b*]azepin-2-one (Fig. 2A, entry 24).

HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **24** (Fig. **2A**, entry 24): 97% ee from (*R,R*)-**L***

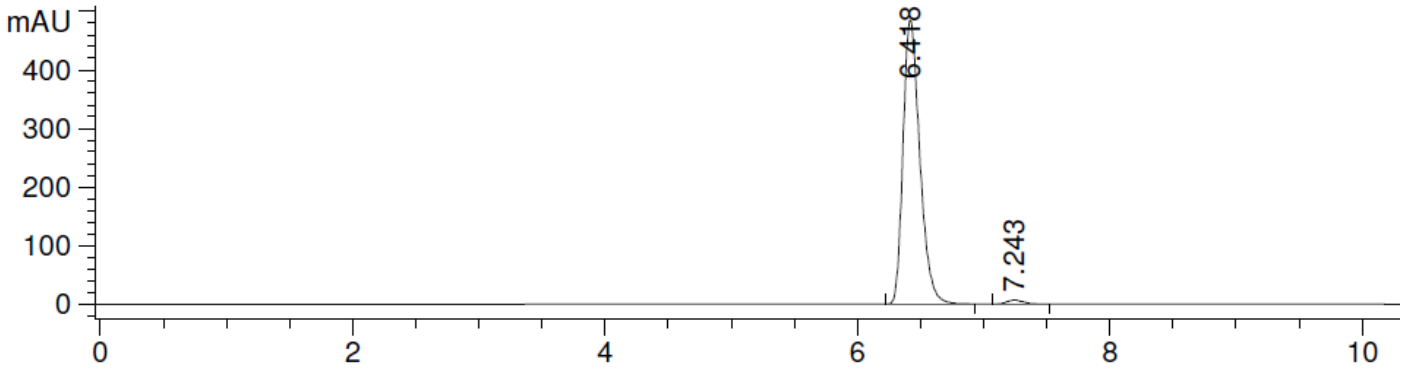
DAD1 B, Sig=254,10 Ref=360,100 (GROUP\ZW4-163A.D)



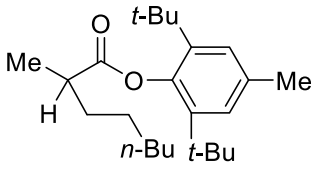
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.402	BB	0.1415	104.12617	11.30160	1.5844
2	7.194	BB	0.1558	6467.87158	640.73206	98.4156

Compound **24** (Fig. **2A**, entry 24): 97% ee from (*S,S*)-**L***

DAD1 B, Sig=254,10 Ref=360,100 (GROUP\ZW4-163B.D)



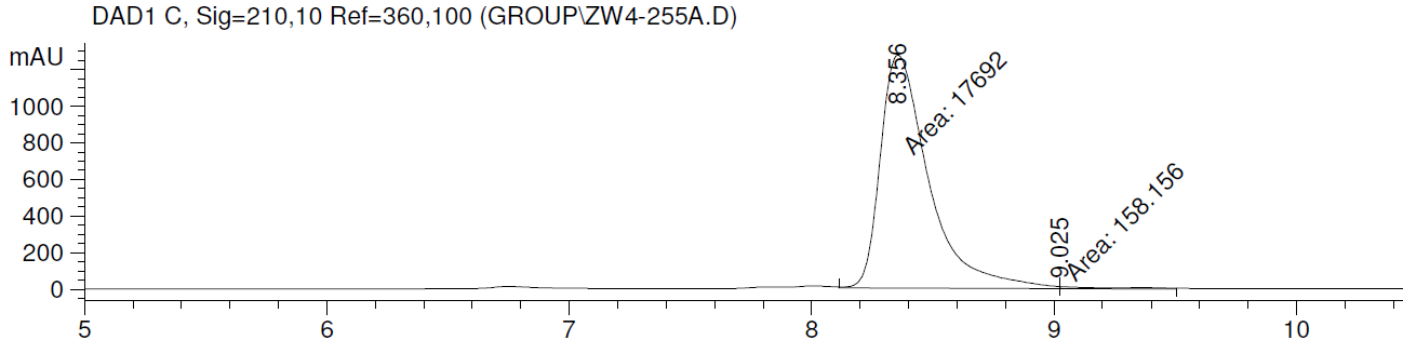
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.418	BB	0.1415	4468.39551	485.01572	98.4137
2	7.243	BB	0.1586	72.02573	6.96507	1.5863



2,6-Di-*tert*-butyl-4-methylphenyl-2-methyloctanoate (Fig. 2A, entry 25).

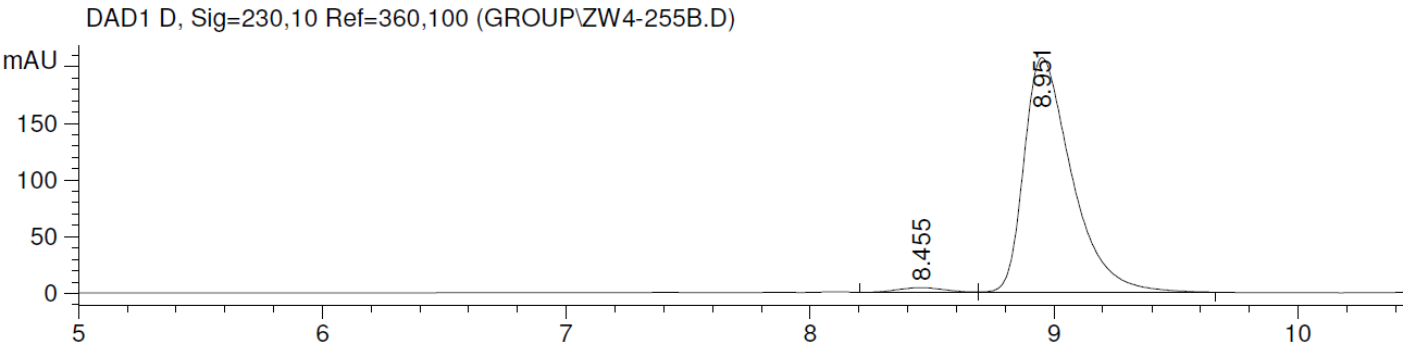
HPLC analysis: CHIRALCEL OD-H column (0.5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **25** (Fig. **2A**, entry 25): 98% ee from (*R,R*)-**L***

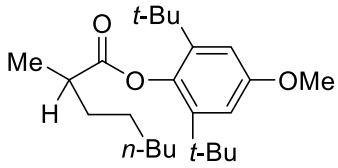


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.356	MF	0.2317	1.76920e4	1272.79797	99.1140
2	9.025	FM	0.2080	158.15578	10.56877	0.8860

Compound **25** (Fig. **2A**, entry 25): 96% ee from (*S,S*)-**L***

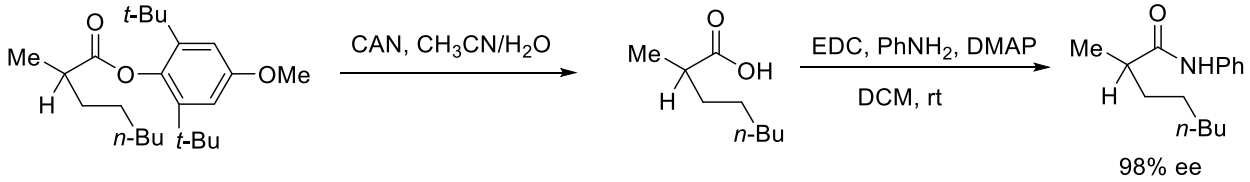


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.455	BV	0.2251	62.93632	4.44780	2.1688
2	8.951	VB	0.2076	2838.91772	207.47882	97.8312



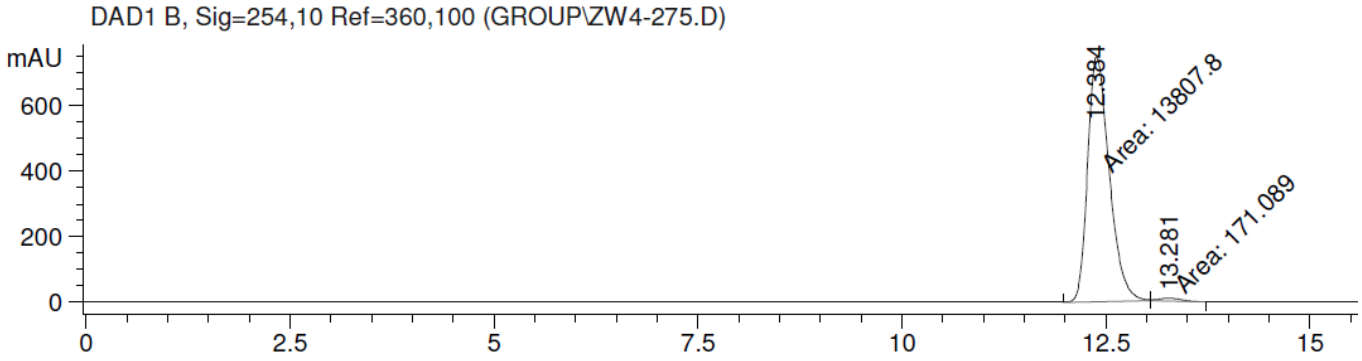
2,6-Di-*tert*-butyl-4-methoxyphenyl-2-methyloctanoate (Fig. 2A, entry 26).

Determination of the ee:



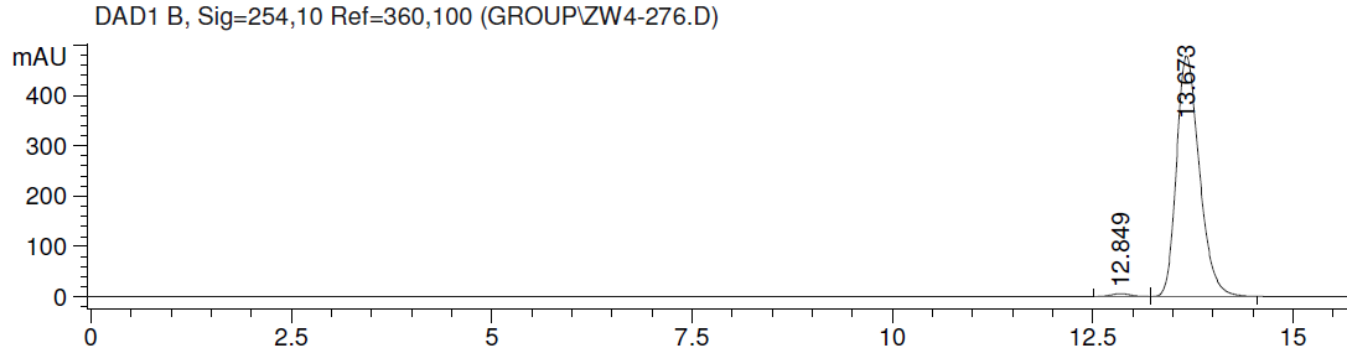
HPLC analysis: CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min).

98% ee from (*R,R*)-**L***

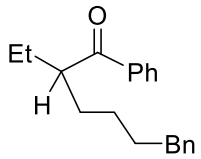


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.384	MM	0.3075	1.38078e4	748.48553	98.7761
2	13.281	MM	0.3344	171.08890	8.52606	1.2239

98% ee from (*S,S*)-**L***



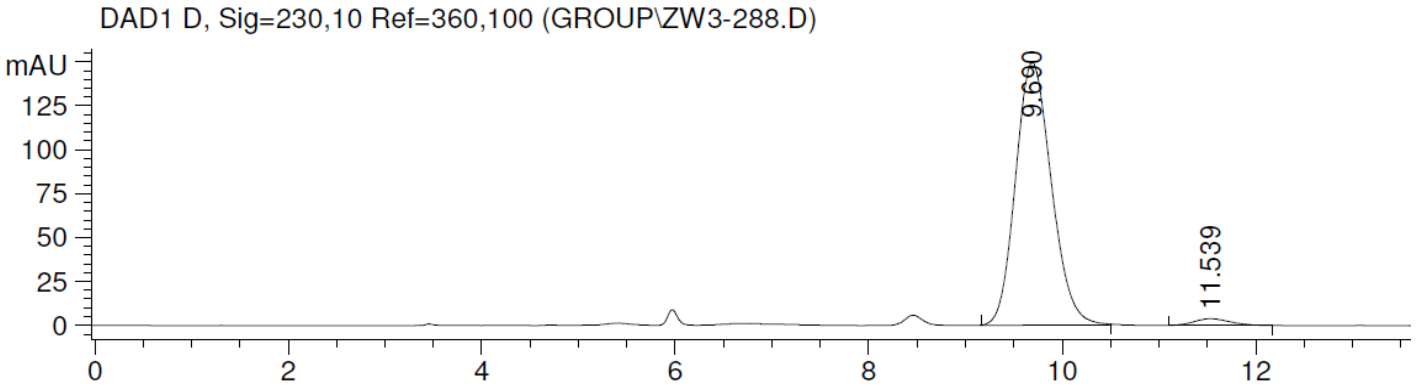
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.849	BV	0.2857	107.46794	5.75981	1.1186
2	13.673	VB	0.3058	9499.71484	478.09290	98.8814



2-Ethyl-1,6-diphenylhexan-1-one (Fig. 2B, entry 27).

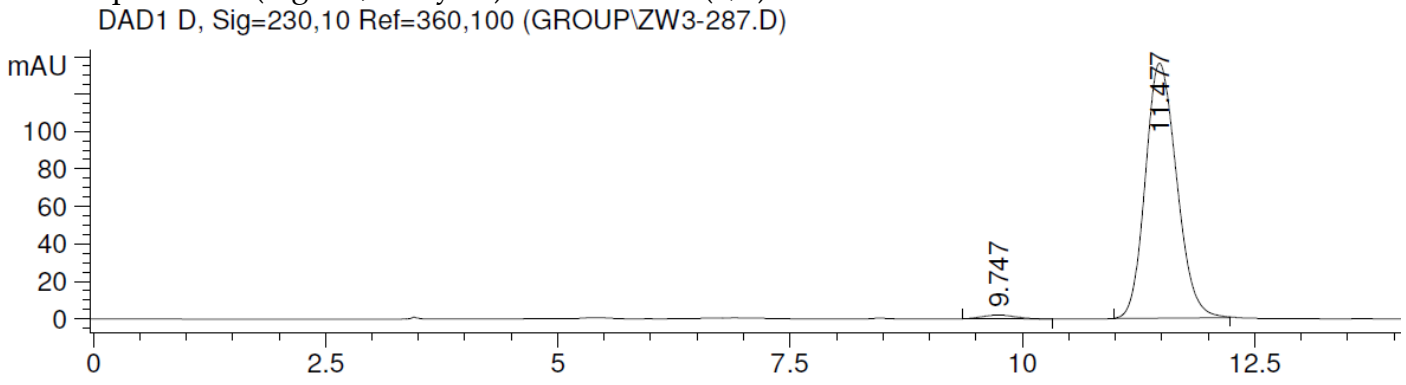
HPLC analysis: CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **27** (Fig. **2B**, entry 27): 95% ee from (*R,R*)-**L***

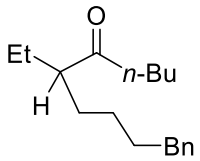


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.690	BB	0.4025	3850.15552	149.45792	97.4488
2	11.539	BB	0.3759	100.79626	3.84399	2.5512

Compound **27** (Fig. **2B**, entry 27): 97% ee from (*S,S*)-**L***



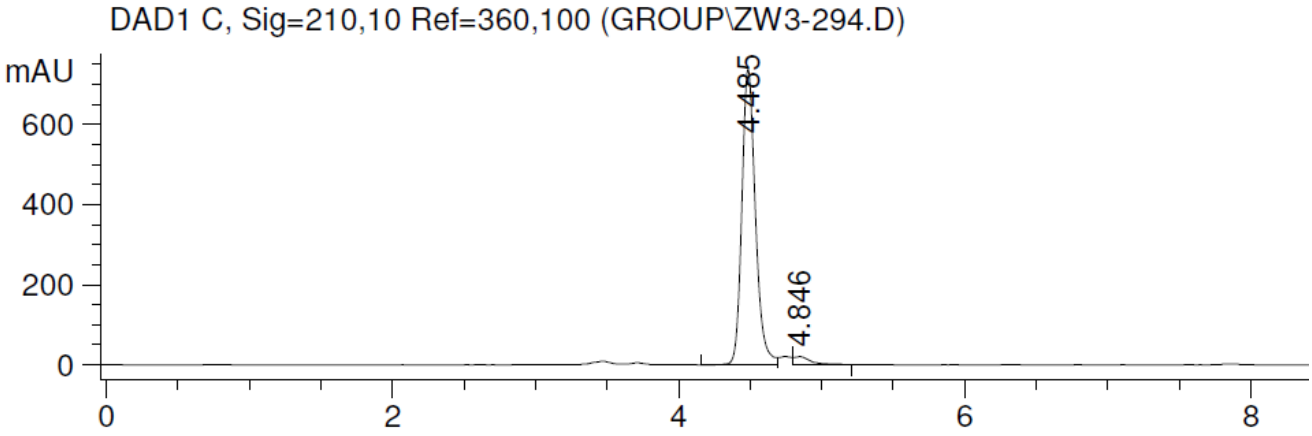
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.747	BP	0.2988	47.16965	1.95992	1.4511
2	11.477	BB	0.3684	3203.42627	136.20999	98.5489



6-Ethyl-10-phenyldecan-5-one (Fig. 2B, entry 28).

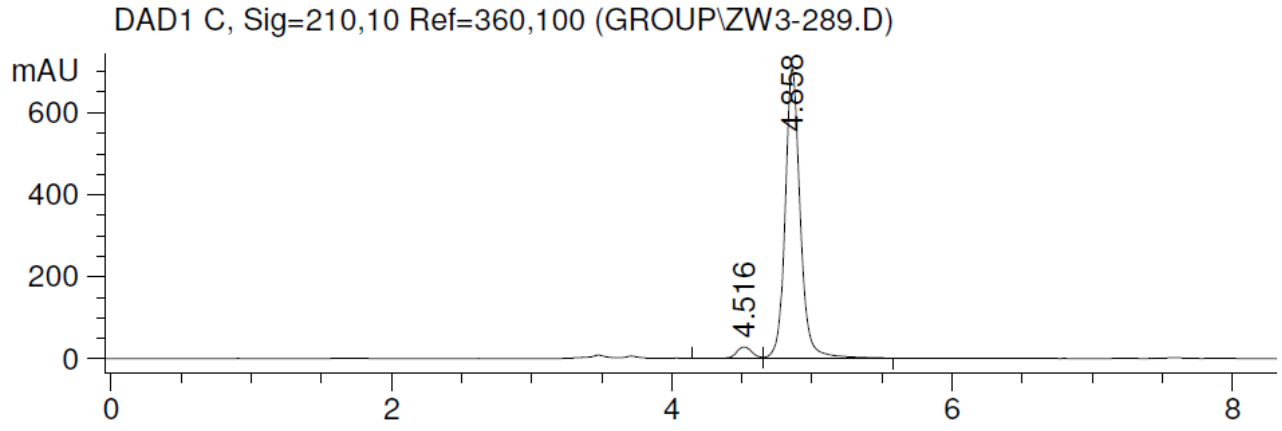
HPLC analysis: CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **28** (Fig. **2B**, entry 28): 93% ee from (*R*,*R*)-**L***

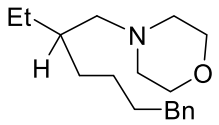


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.485	VV	0.1013	4897.89355	738.96198	96.3925
2	4.846	VB	0.1250	183.30305	20.75433	3.6075

Compound **28** (Fig. **2B**, entry 28): 92% ee from (*S*,*S*)-**L***



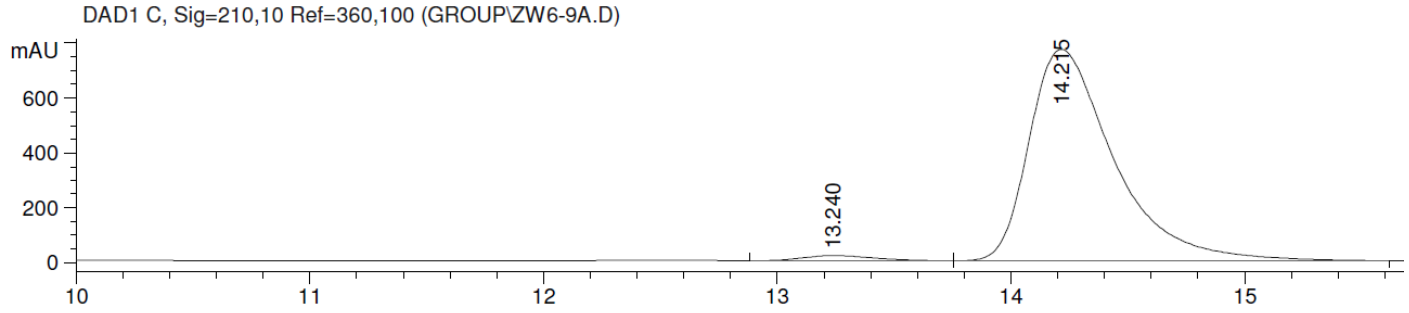
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.516	VV	0.1191	219.53175	28.11463	3.9812
2	4.858	VB	0.1133	5294.64844	707.75702	96.0188



4-(2-Ethyl-6-phenylhexyl)morpholine (Fig. 2B, entry 29).

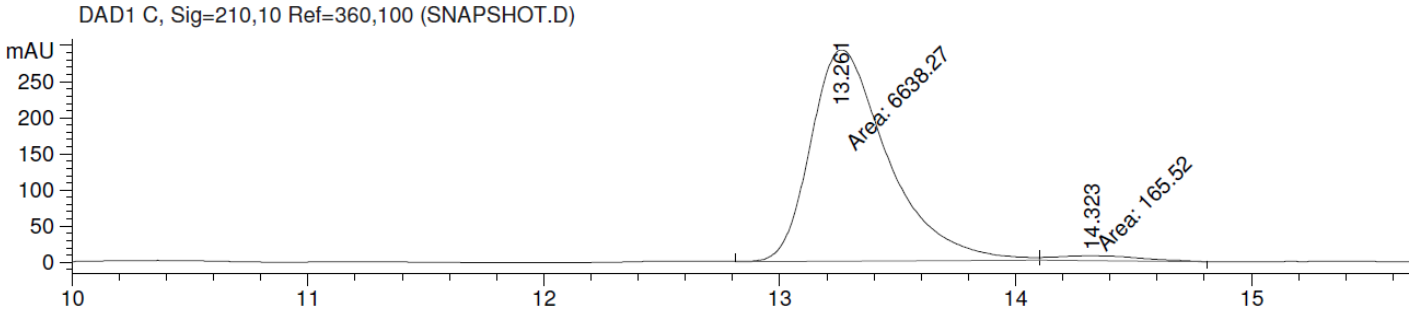
HPLC analysis: CHIRALCEL OJ-H column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **29** (Fig. **2B**, entry 29): 96% ee from (*R,R*)-**L***

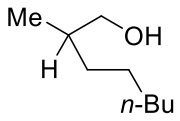


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.240	VV	0.3064	407.36319	19.13231	2.0555
2	14.215	VB	0.3798	1.94113e4	770.69275	97.9445

Compound **29** (Fig. **2B**, entry 29): 95% ee from (*S,S*)-**L***

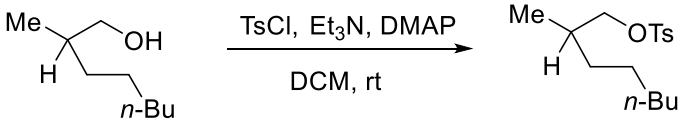


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.261	MM	0.3785	6638.26807	292.26782	97.5672
2	14.323	MM	0.4145	165.51953	6.65531	2.4328



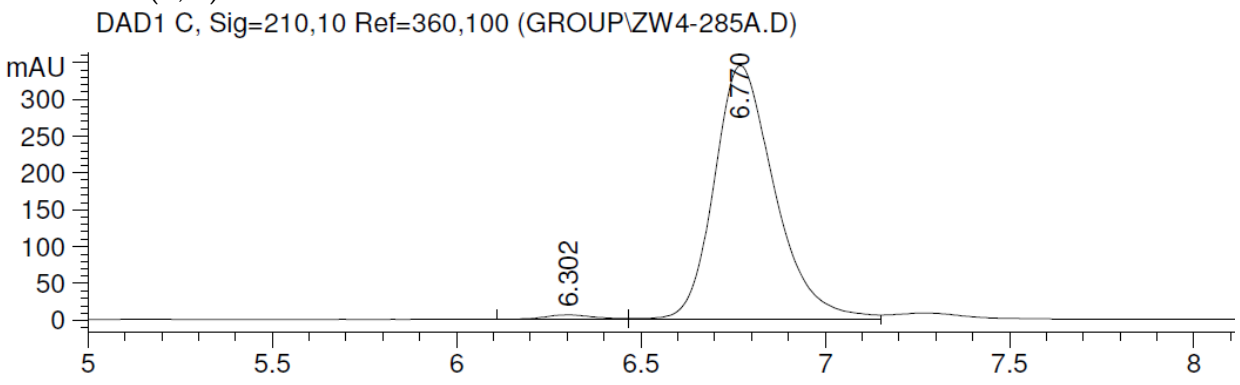
2-Methyloctan-1-ol (Fig. 2B, entry 30).

Determination of the ee:



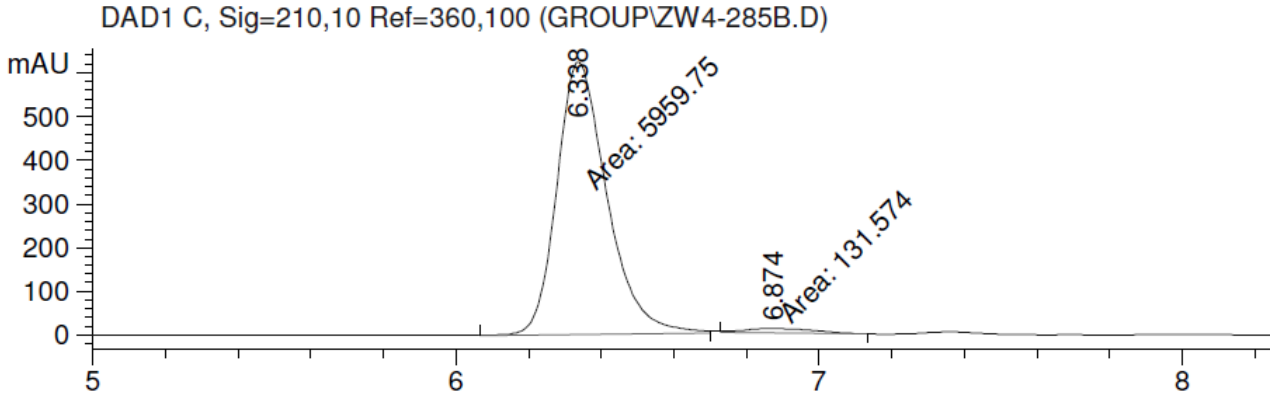
HPLC analysis: CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

97% ee from (*R,R*)-**L***

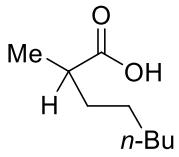


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.302	BV	0.1381	58.28799	6.17543	1.4581
2	6.770	VV	0.1754	3939.32227	344.62769	98.5419

96% ee from (*S,S*)-**L***

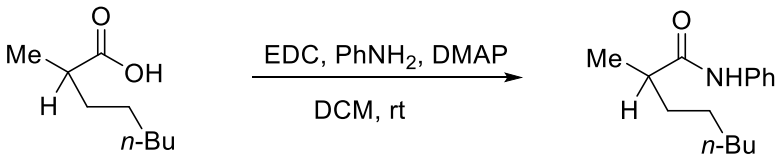


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.338	MM	0.1593	5959.74854	623.39813	97.8400
2	6.874	MM	0.2260	131.57370	9.70198	2.1600



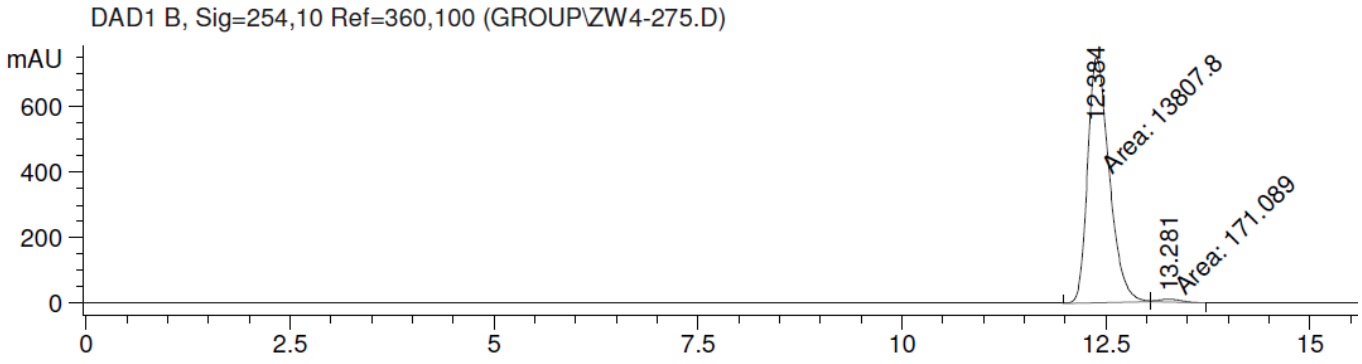
2-Methyloctanoic acid (Fig. 2B, entry 31).

Determination of the ee:



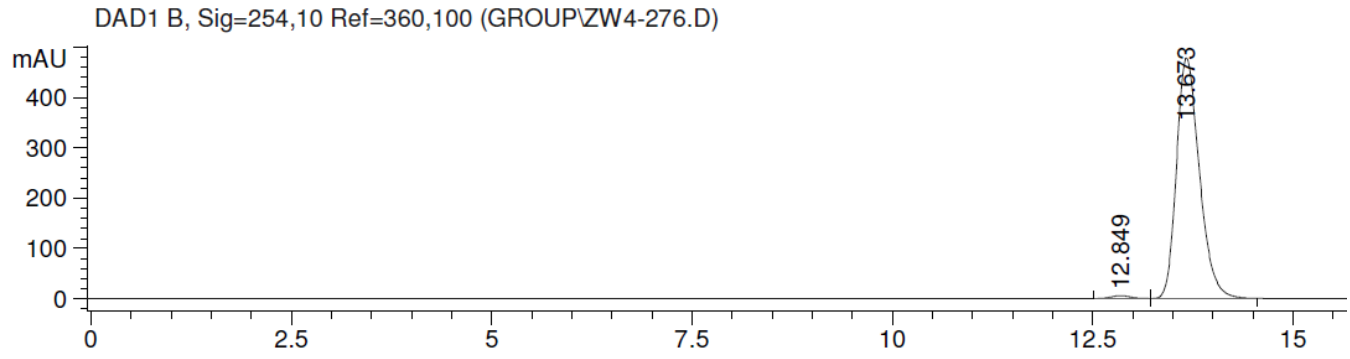
HPLC analysis: CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min).

98% ee from (*R,R*)-**L***

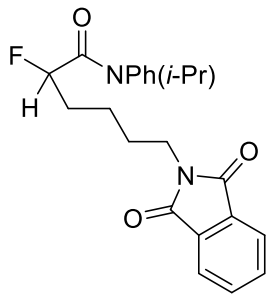


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.384	MM	0.3075	1.38078e4	748.48553	98.7761
2	13.281	MM	0.3344	171.08890	8.52606	1.2239

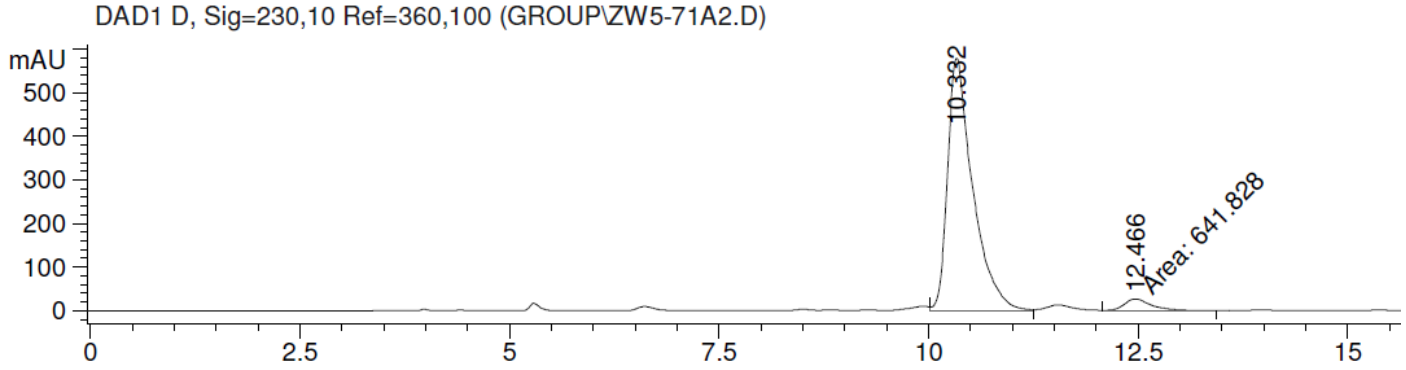
98% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.849	BV	0.2857	107.46794	5.75981	1.1186
2	13.673	VB	0.3058	9499.71484	478.09290	98.8814

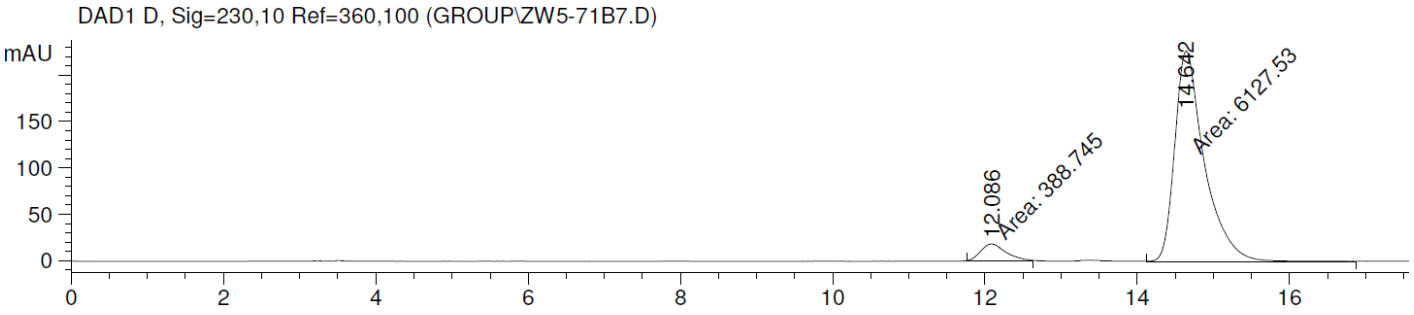


6-(1,3-Dioxoisoindolin-2-yl)-2-fluoro-*N*-isopropyl-*N*-phenylhexanamide (Fig. 2C, entry 32).
HPLC analysis: CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min).
Compound **32** (Fig. **2C**, entry 32): 90% ee from (*R*,*R*)-**L***

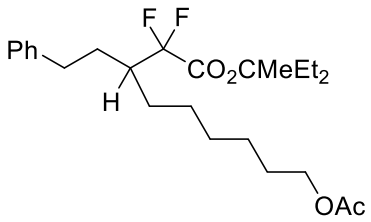


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.332	VV	0.2995	1.20854e4	579.06128	94.9570
2	12.466	MM	0.3918	641.82812	27.30092	5.0430

Compound **32** (Fig. **2C**, entry 32): 88% ee from (S,S)-L*



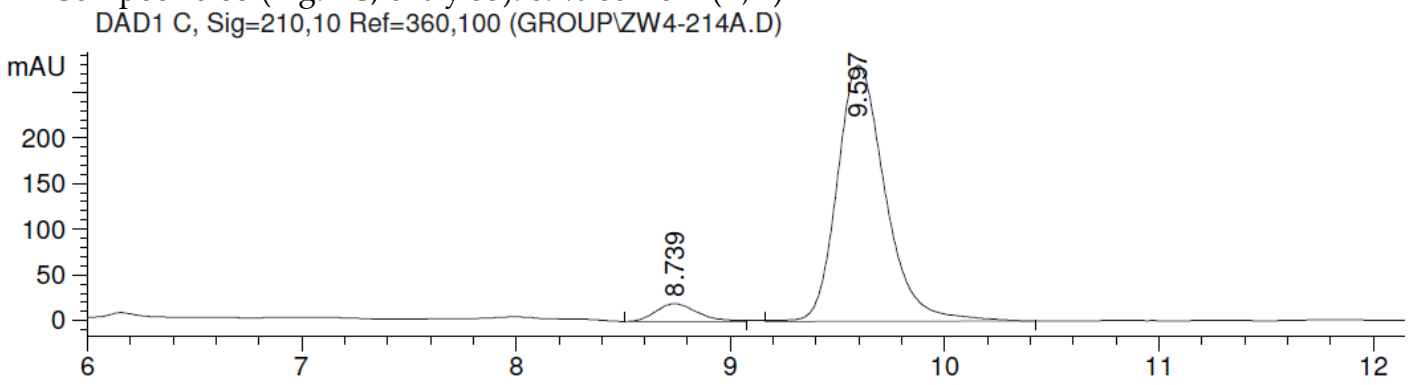
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.086	MM	0.3679	388.74515	17.61034	5.9658
2	14.642	MM	0.4504	6127.53125	226.76492	94.0342



3-Methylpentan-3-yl 9-acetoxy-2,2-difluoro-3-phenethylnonanoate (Fig. 2C, entry 33).

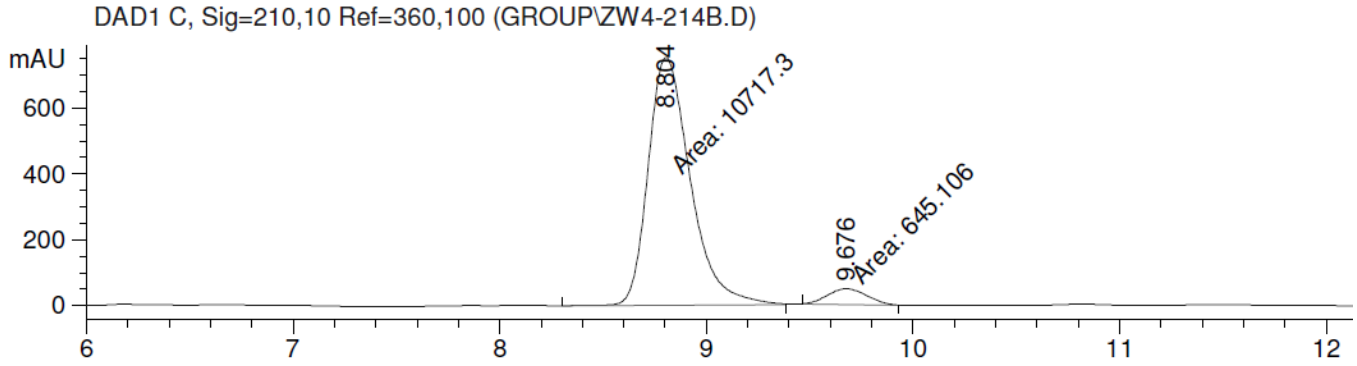
HPLC analysis: CHIRALPAK IC column (2% *i*-PrOH in hexane, 1.0 mL/min).

Compound **33** (Fig. **2C**, entry 33): 89% ee from (*R,R*)-**L***

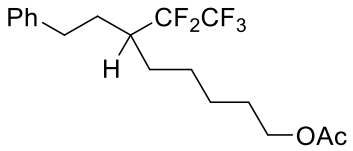


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.739	VB	0.2062	259.23743	19.36241	5.6024
2	9.597	BB	0.2373	4368.03027	281.00635	94.3976

Compound **33** (Fig. **2C**, entry 33): 89% ee from (*S,S*)-**L***



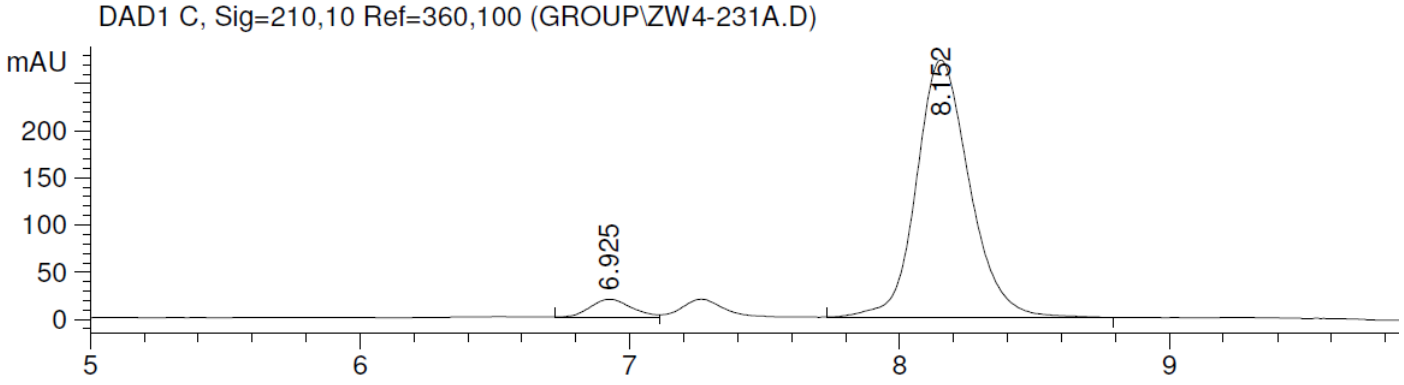
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.804	MM	0.2369	1.07173e4	753.96539	94.3224
2	9.676	MM	0.2232	645.10559	48.16319	5.6776



7,7,8,8,8-Pentafluoro-6-phenethyloctyl acetate (Fig. 2C, entry 34).

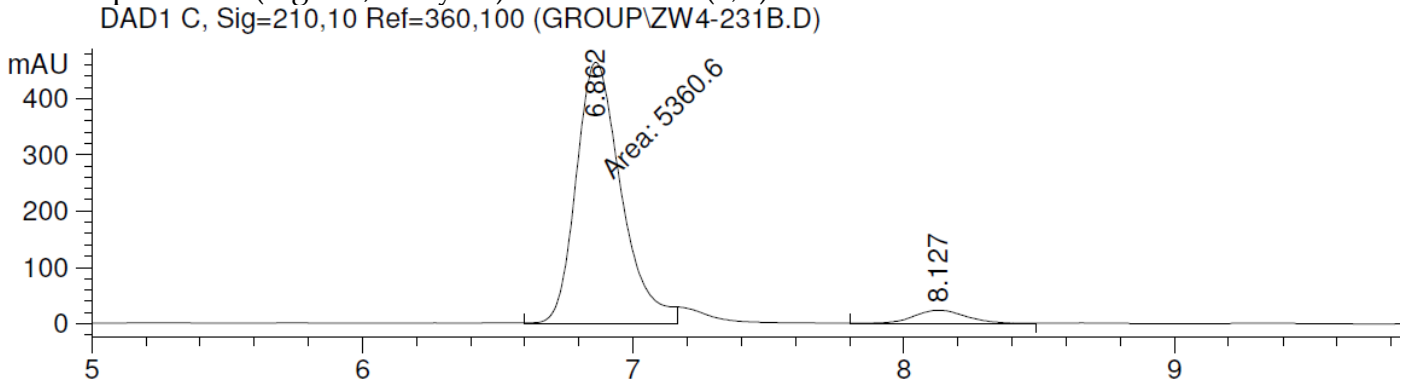
HPLC analysis: CHIRALCEL OD-H column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **34** (Fig. **2C**, entry 34): 90% ee from (*R,R*)-**L***

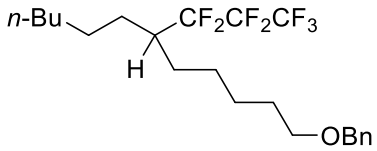


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.925	PV	0.1609	198.65343	18.85288	5.0475
2	8.152	BB	0.2098	3737.02783	272.86371	94.9525

Compound **34** (Fig. **2C**, entry 34): 89% ee from (*S,S*)-**L***



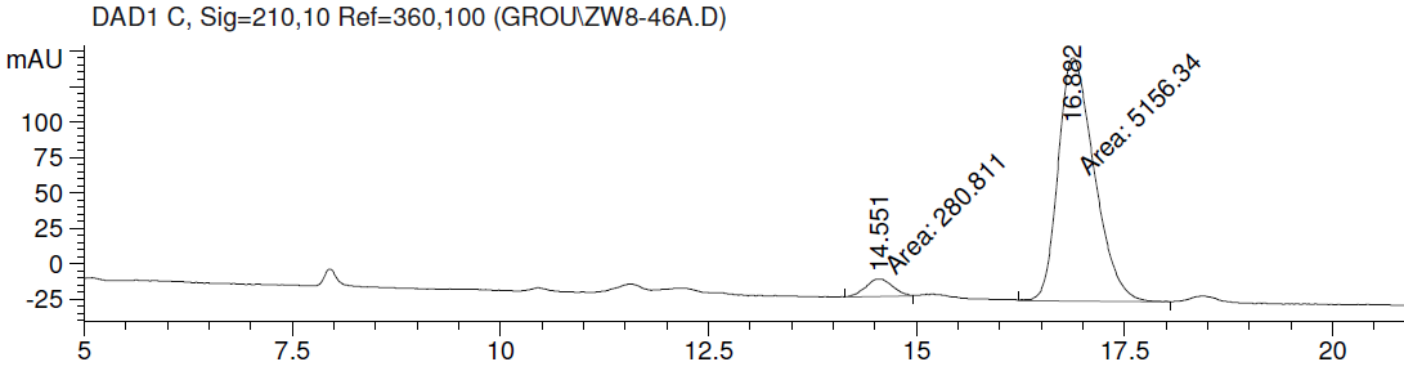
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.862	MF	0.1926	5360.59961	463.76849	94.5458
2	8.127	PV	0.2037	309.24615	23.47125	5.4542



(((6-(Perfluoropropyl)dodecyl)oxy)methyl)benzene (Fig. 2C, entry 35).

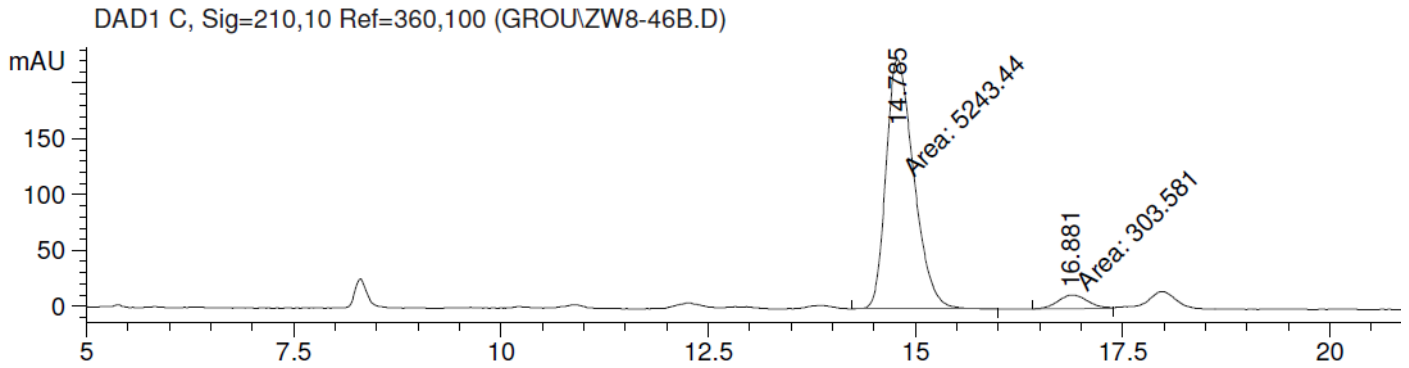
HPLC analysis: CHIRALCEL OD-H column (hexane, 1.0 mL/min).

Compound **35** (Fig. **2C**, entry 35): 90% ee from (*R,R*)-**L***

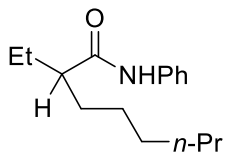


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.551	MM	0.2801	280.81110	12.29627	5.1647
2	16.882	MM	0.5012	5156.33740	171.45676	94.8353

Compound **35** (Fig. **2C**, entry 35): 89% ee from (*S,S*)-**L***



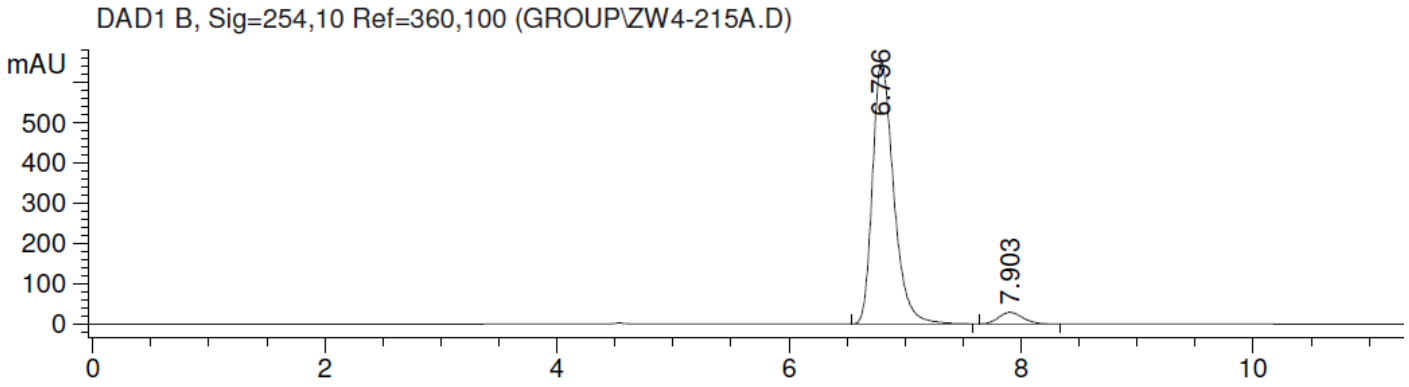
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.785	MM	0.3903	5243.43701	223.88425	94.5271
2	16.881	MM	0.4168	303.58063	12.13845	5.4729



2-Ethyl-*N*-phenyloctanamide (Fig. 2D, entry 36).

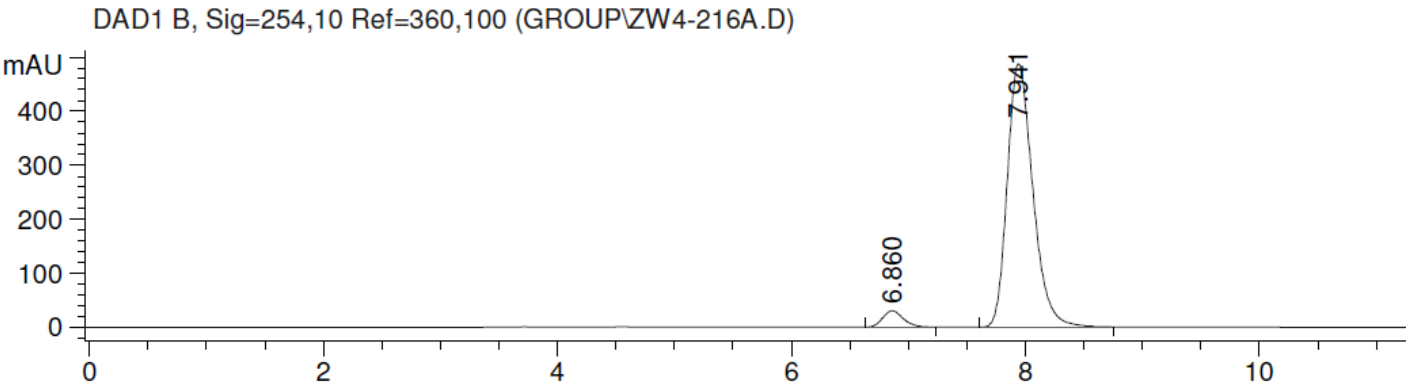
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **36** (Fig. **2D**, entry 36): 90% ee from (*R*,*R*)-**L***

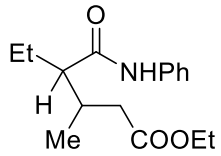


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.796	BB	0.1964	8260.31934	649.20941	95.0119
2	7.903	BB	0.2284	433.66437	29.01053	4.9881

Compound **36** (Fig. **2D**, entry 36): 90% ee from (*S*,*S*)-**L***



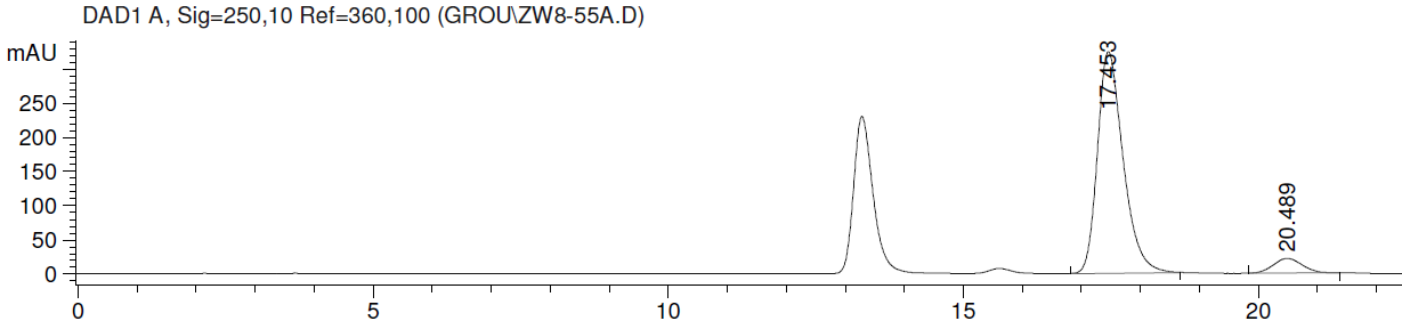
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.860	BB	0.1920	380.23074	30.37713	4.8752
2	7.941	PB	0.2353	7418.98535	488.20984	95.1248



Ethyl 3-methyl-4-(phenylcarbamoyl)hexanoate (Fig. 2D, entry 37).

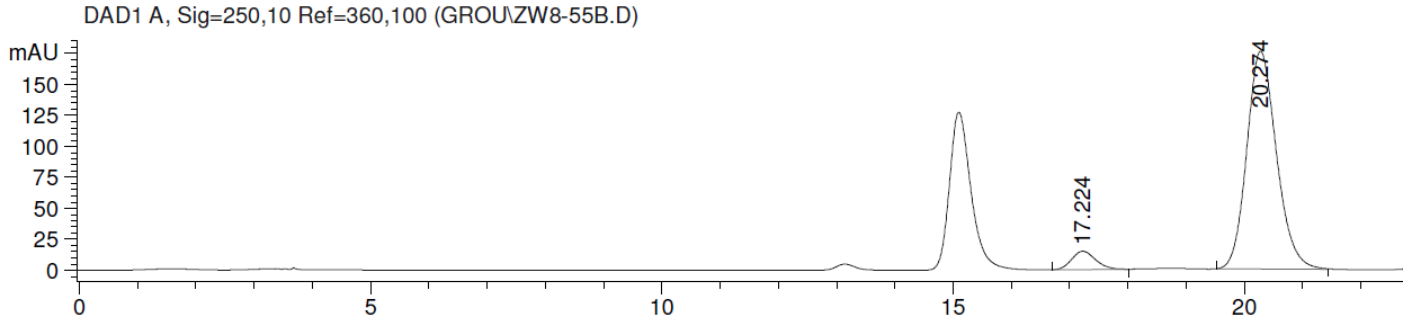
HPLC analysis: CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Major diastereomer: Compound **37** (Fig. **2D**, entry 37): 86% ee from (*R,R*)-**L***



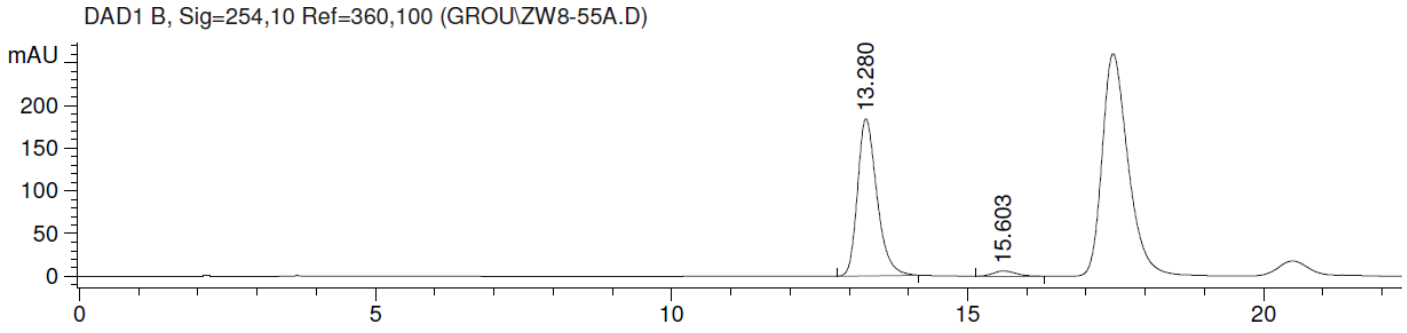
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.453	BB	0.4571	9841.09375	325.19037	93.0900
2	20.489	BB	0.5114	730.49219	21.55390	6.9100

Major diastereomer: Compound **37** (Fig. **2D**, entry 37): 87% ee from (*S,S*)-**L***



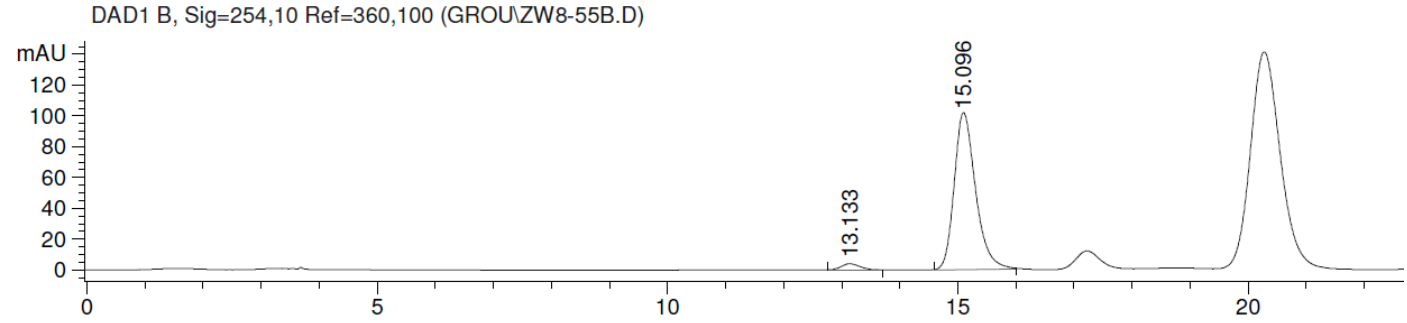
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.224	BP	0.4235	423.57111	14.81783	6.3535
2	20.274	BB	0.5459	6243.12939	175.98491	93.6465

Minor diastereomer: Compound **37** (Fig. **2D**, entry 37): 93% ee from (*R*,*R*)-**L***

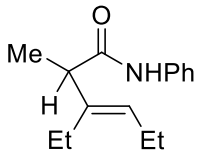


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.280	BB	0.3460	4197.40674	184.11383	96.3202
2	15.603	PB	0.3624	160.35918	6.10673	3.6798

Minor diastereomer: Compound **37** (Fig. **2D**, entry 37): 93% ee from (*S*,*S*)-**L***



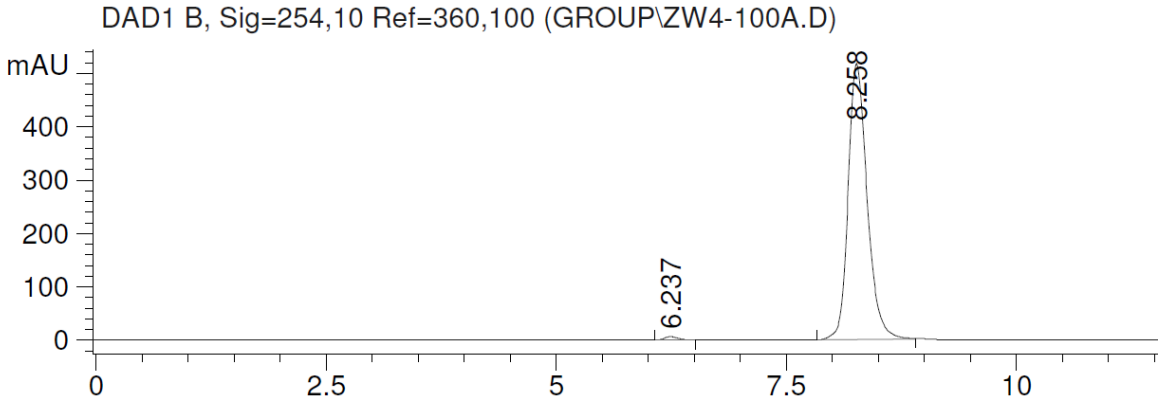
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.133	BB	0.3219	88.92274	3.93047	3.3047
2	15.096	BB	0.3878	2601.89722	101.94774	96.6953



(*E*)-3-Ethyl-2-methyl-N-phenylhex-3-enamide (Fig. 2E, entry 38).

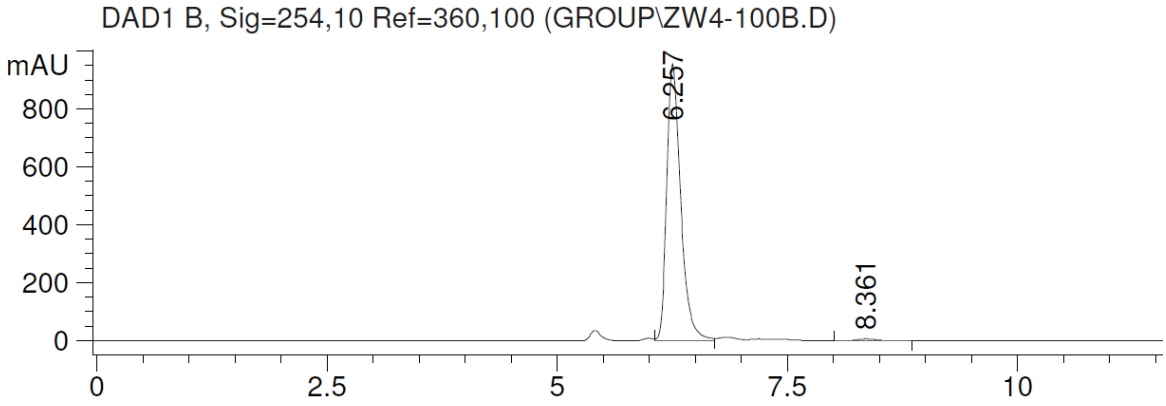
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **38** (Fig. **2E**, entry 38): 98% ee from (*R,R*)-**L***

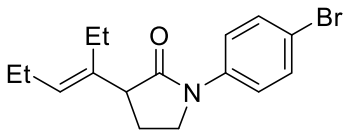


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.237	BB	0.1551	65.32403	6.39919	0.8674
2	8.258	BB	0.2198	7466.01855	519.14435	99.1326

Compound **38** (Fig. **2E**, entry 38): 98% ee from (*S,S*)-**L***



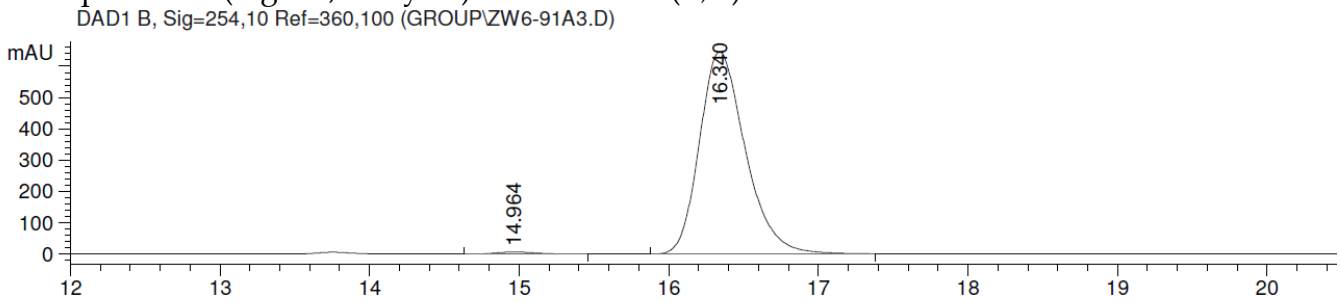
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.257	VV	0.1612	1.01108e4	957.42114	99.0247
2	8.361	BB	0.2310	99.57726	6.41855	0.9753



(*E*)-1-(4-Bromophenyl)-3-(hex-3-en-3-yl)pyrrolidin-2-one (Fig. 2E, entry 39).

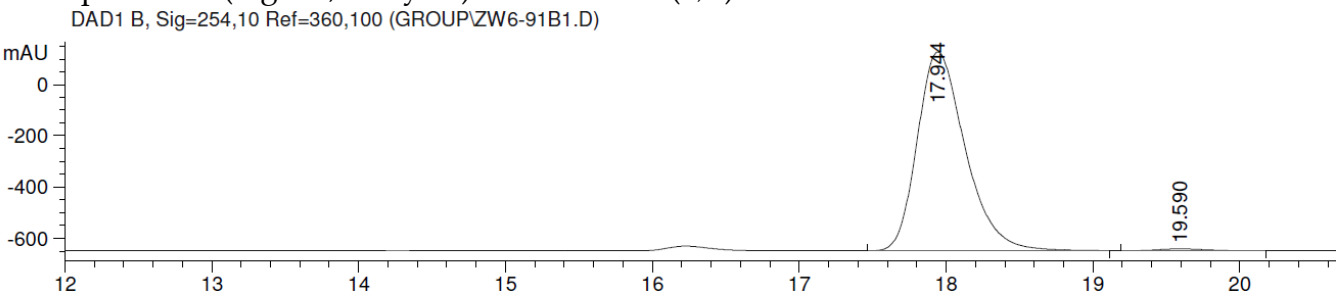
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **39** (Fig. **2E**, entry 39): 98% ee from (*R,R*)-**L***

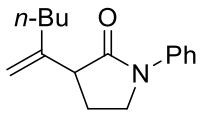


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.964	BB	0.2910	133.26025	6.97130	0.9573
2	16.340	BB	0.3266	1.37865e4	646.90247	99.0427

Compound **39** (Fig. **2E**, entry 39): 98% ee from (*S,S*)-**L***



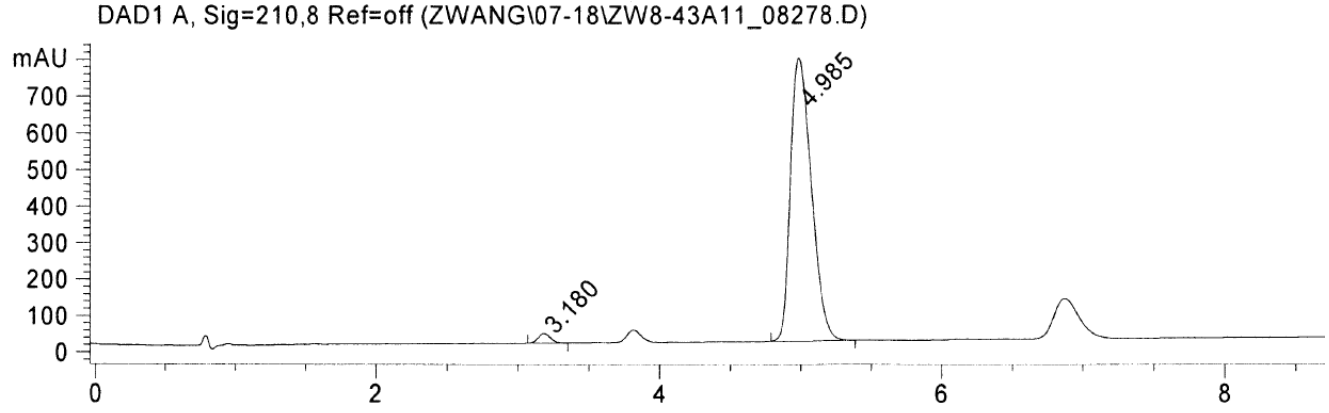
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.944	BB	0.3459	1.77006e4	776.76849	98.9123
2	19.590	BB	0.3657	194.64107	7.89361	1.0877



3-(Hex-1-en-2-yl)-1-phenylpyrrolidin-2-one (Fig. 2E, entry 40).

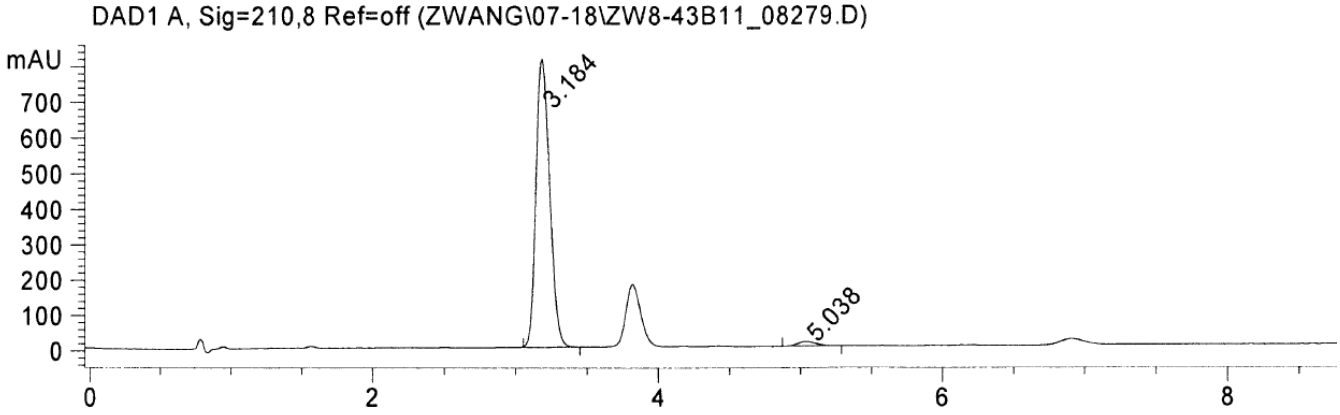
SFC analysis: CHIRALCEL OD-H column (15% *i*-PrOH in CO_2, 3.5 mL/min).

Compound **40** (Fig. **2E**, entry 40): 96% ee from (*R,R*)-**L***

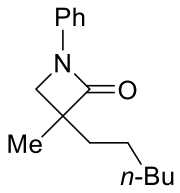


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.180	BB	0.0942	162.17093	26.93568	1.9810
2	4.985	BB	0.1614	8024.03174	771.40991	98.0190

Compound **40** (Fig. **2E**, entry 40): 96% ee from (*S,S*)-**L***



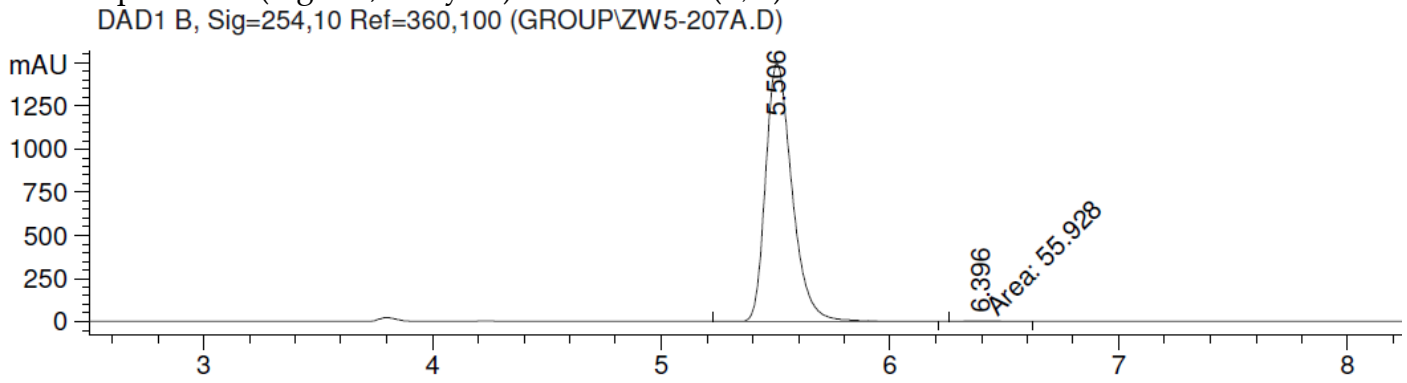
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.184	BB	0.1063	5427.12988	808.39722	97.9505
2	5.038	BB	0.1405	113.55563	12.67169	2.0495



3-Hexyl-3-methyl-1-phenylazetidin-2-one (Fig. 3A, entry 41).

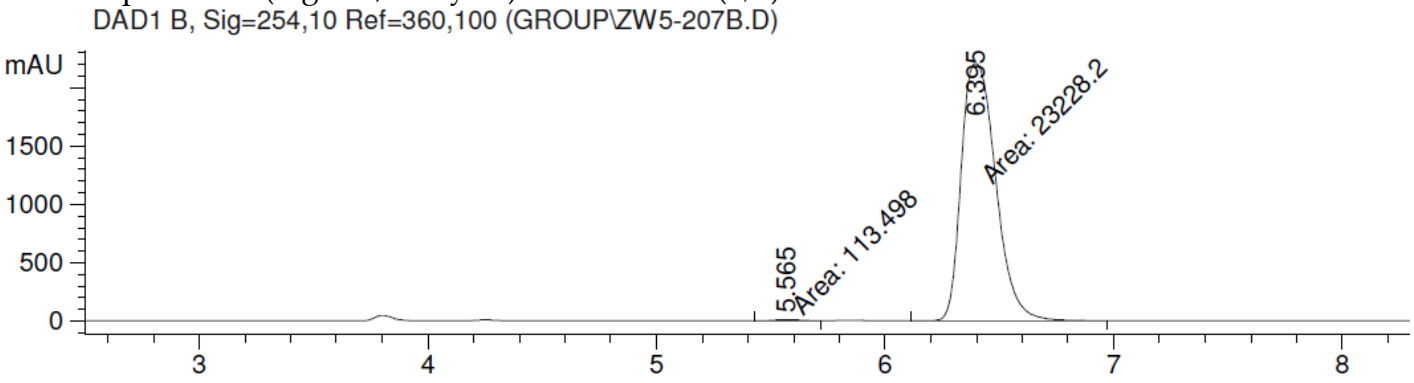
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **41** (Fig. **3A**, entry 41): 99% ee from (*R,R*)-**L***

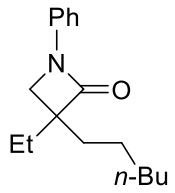


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.506	VV	0.1239	1.20557e4	1497.14978	99.5382
2	6.396	MM	0.1629	55.92803	5.72363	0.4618

Compound **41** (Fig. **3A**, entry 41): 99% ee from (*S,S*)-**L***



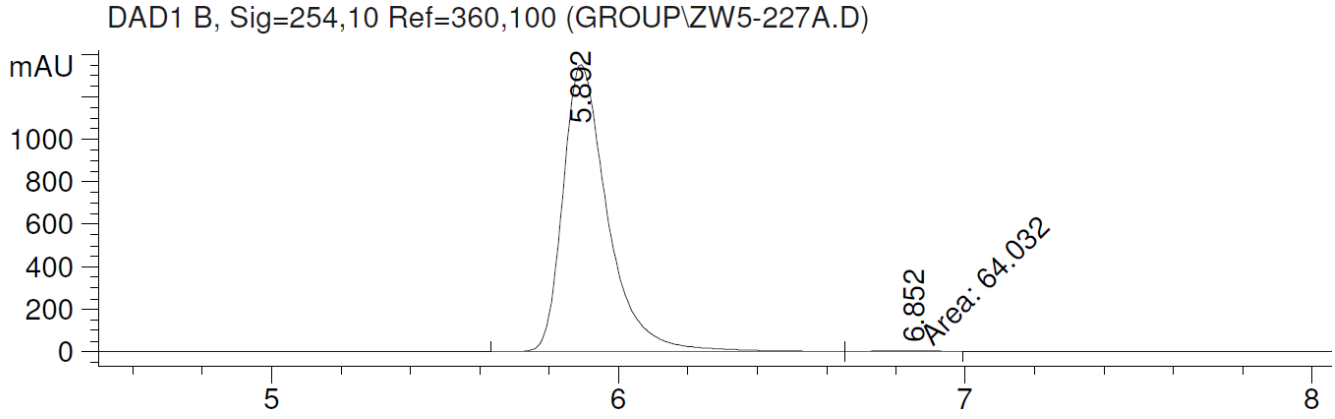
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.565	MM	0.1384	113.49789	13.66634	0.4862
2	6.395	MF	0.1751	2.32282e4	2211.10425	99.5138



3-Ethyl-3-hexyl-1-phenylazetidin-2-one (Fig. 3A, entry 42).

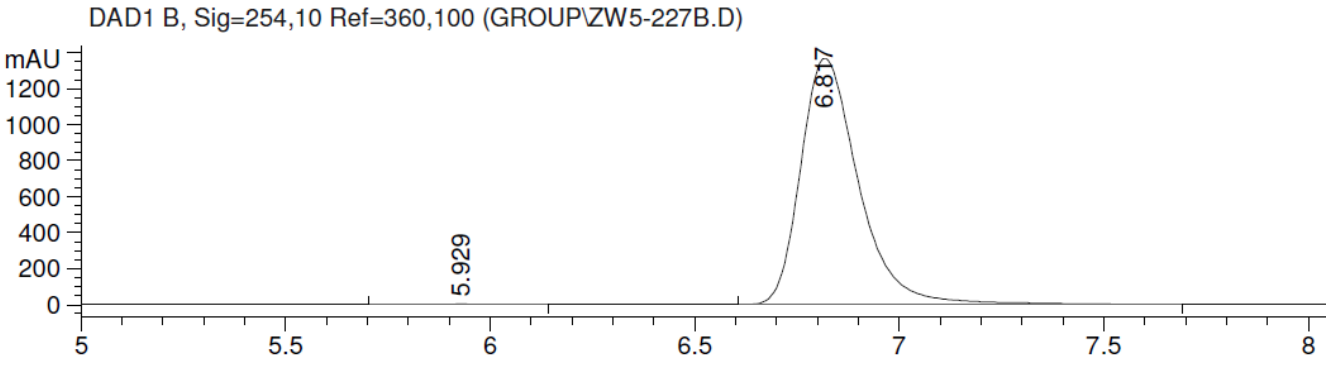
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **42** (Fig. **3A**, entry 42): 99% ee from (*R,R*)-**L***

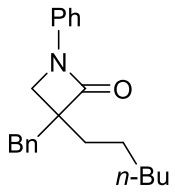


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.892	VV	0.1347	1.21456e4	1353.67139	99.4756
2	6.852	MF	0.2178	64.03198	4.89947	0.5244

Compound **42** (Fig. **3A**, entry 42): 99% ee from (*S,S*)-**L***



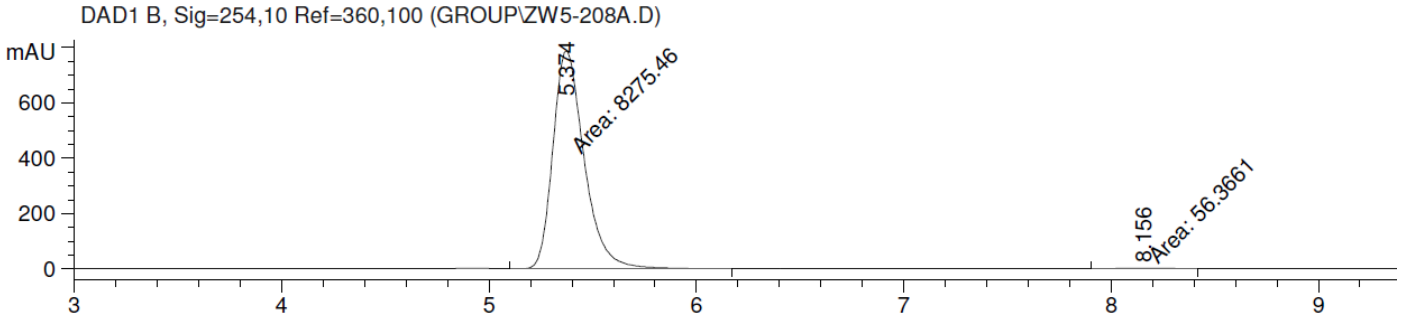
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.929	BV	0.1516	32.16548	3.03603	0.2371
2	6.817	BB	0.1513	1.35367e4	1369.67114	99.7629



3-Benzyl-3-hexyl-1-phenylazetidin-2-one (Fig. 3A, entry 43).

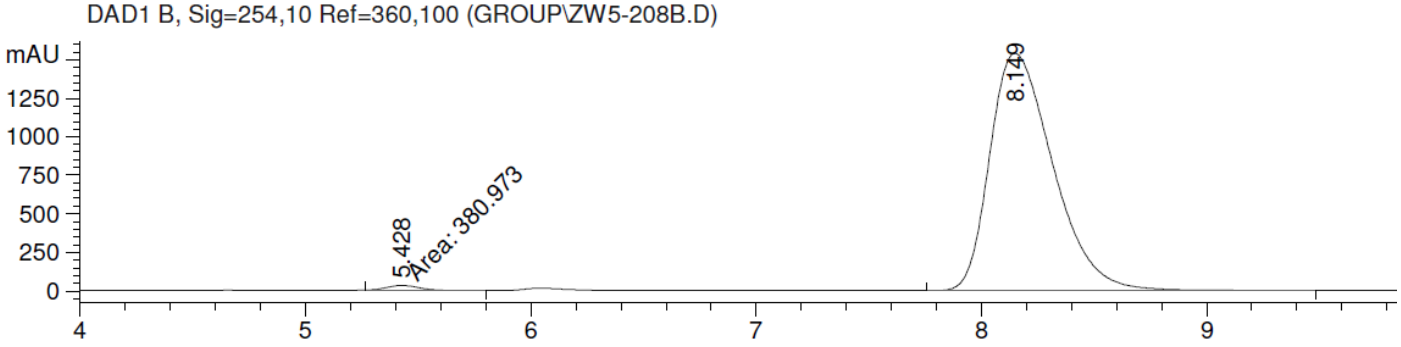
HPLC analysis: CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound 43 (Fig. **3A**, entry 43): 99% ee from (*R,R*)-**L***

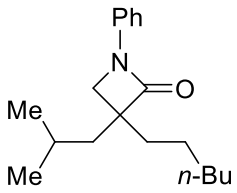


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.374	MM	0.1748	8275.46094	789.03668	99.3235
2	8.156	MM	0.2861	56.36613	3.28383	0.6765

Compound 43 (Fig. **3A**, entry 43): 98% ee from (*S,S*)-**L***



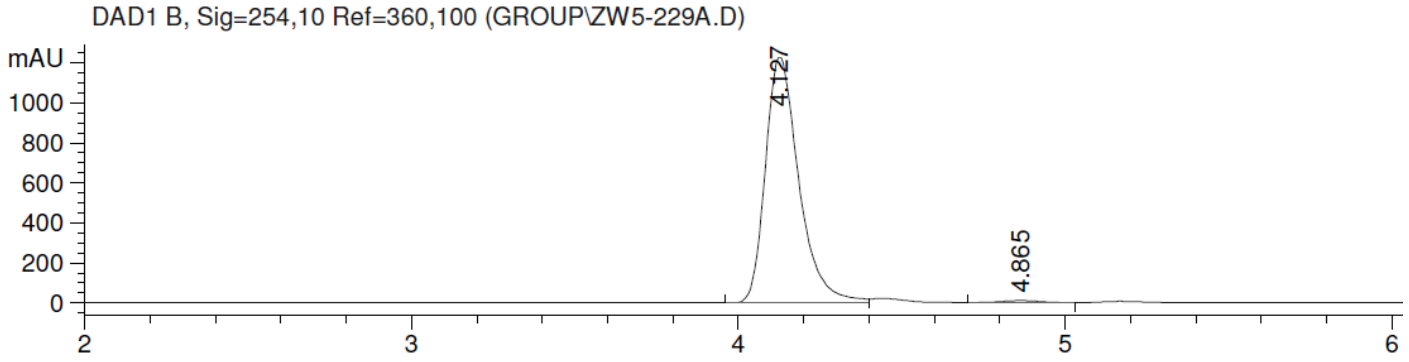
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.428	FM	0.1835	380.97299	34.59313	1.2501
2	8.149	VB	0.3036	3.00938e4	1542.74060	98.7499



3-Hexyl-3-isobutyl-1-phenylazetidin-2-one (Fig. 3A, entry 44).

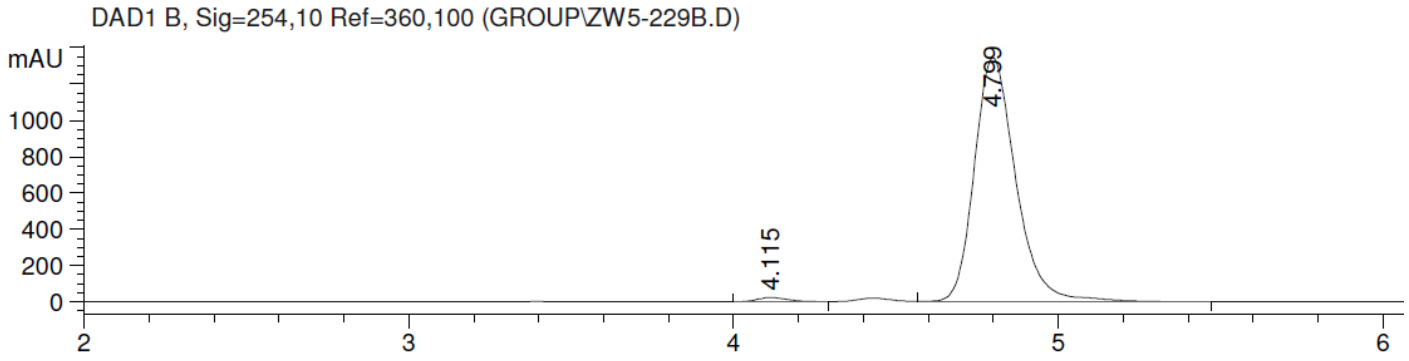
HPLC analysis: CHIRALCEL AS-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **44** (Fig. **3A**, entry 44): 97% ee from (*R,R*)-**L***

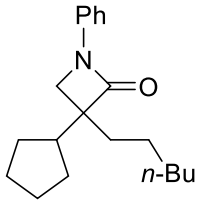


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.127	VV	0.1070	8767.32910	1232.49719	98.6849
2	4.865	VV	0.1466	116.83899	11.89803	1.3151

Compound **44** (Fig. **3A**, entry 44): 97% ee from (*S,S*)-**L***



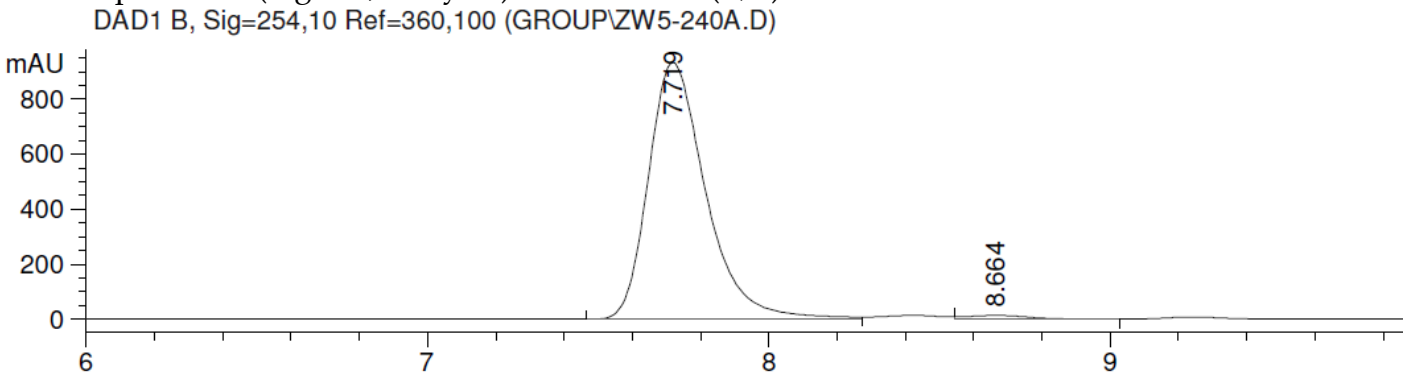
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.115	BV	0.1066	165.90257	23.43388	1.3670
2	4.799	VB	0.1358	1.19700e4	1344.82788	98.6330



3-Cyclopentyl-3-hexyl-1-phenylazetidin-2-one (Fig. 3A, entry 45).

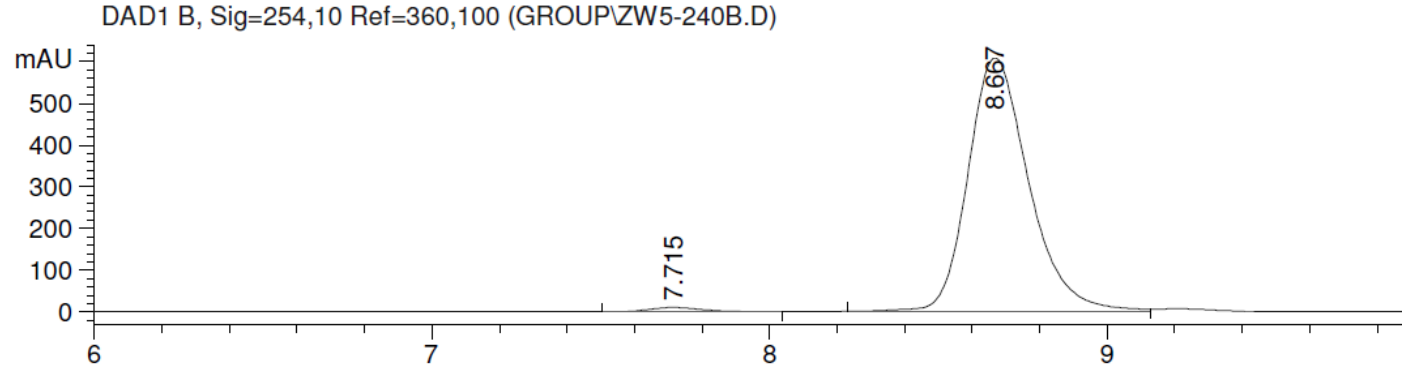
HPLC analysis: CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

Compound **45** (Fig. **3A**, entry 45): 97% ee from (*R,R*)-**L***

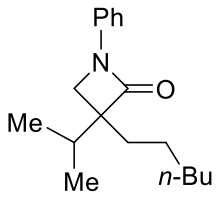


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.719	BV	0.1785	1.09219e4	933.80475	98.3114
2	8.664	VB	0.1995	187.59906	14.07945	1.6886

Compound **45** (Fig. **3A**, entry 45): 97% ee from (*S,S*)-**L***



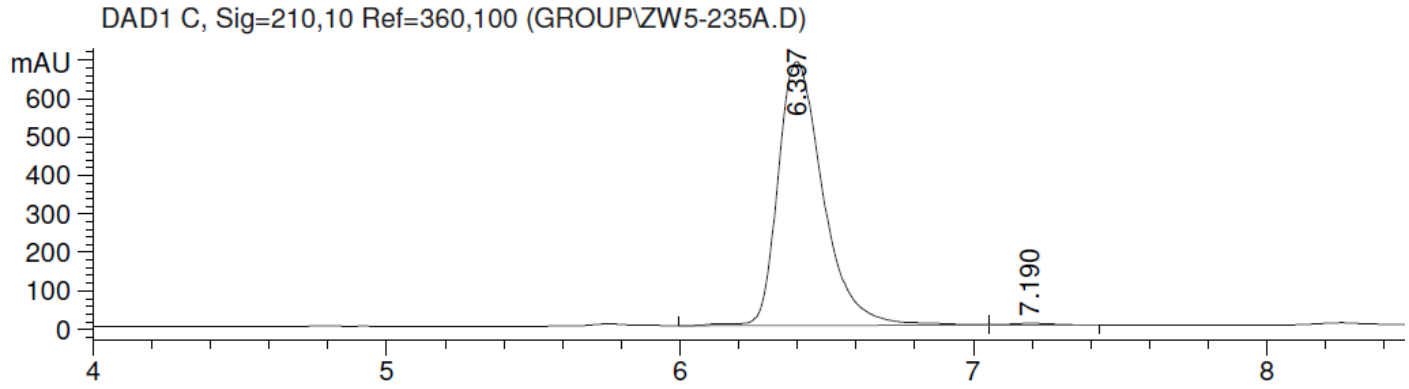
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.715	PB	0.1693	108.72720	9.96261	1.4045
2	8.667	BV	0.1901	7632.45996	609.68506	98.5955



3-Hexyl-3-isopropyl-1-phenylazetidin-2-one (Fig. 3A, entry 46).

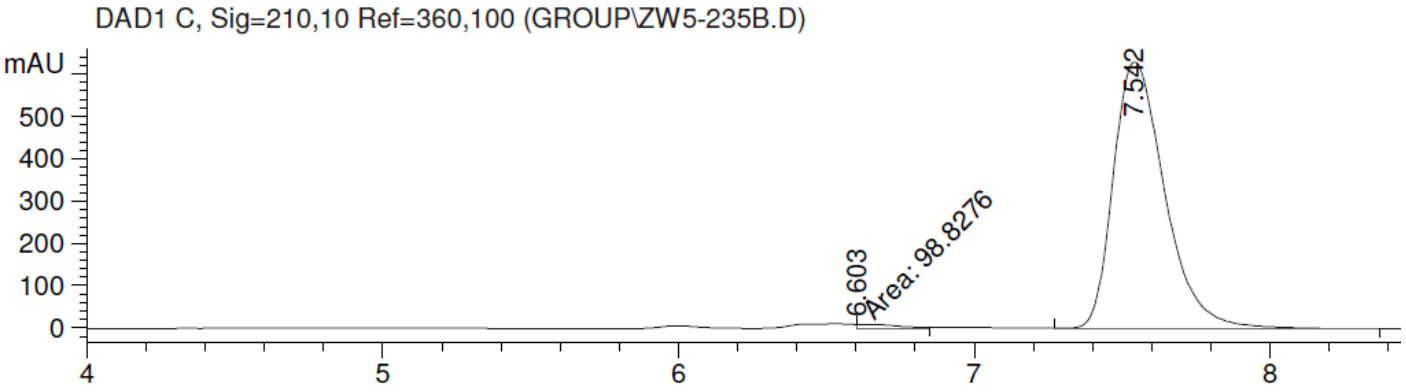
HPLC analysis: CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

Compound **46** (Fig. **3A**, entry 46): 98% ee from (*R,R*)-**L***

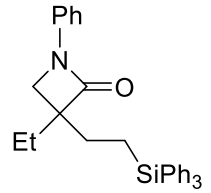


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.397	VB	0.1651	7374.42188	687.81006	99.2672
2	7.190	BV	0.1583	54.44139	4.87570	0.7328

Compound **46** (Fig. **3A**, entry 46): 97% ee from (*S,S*)-**L***



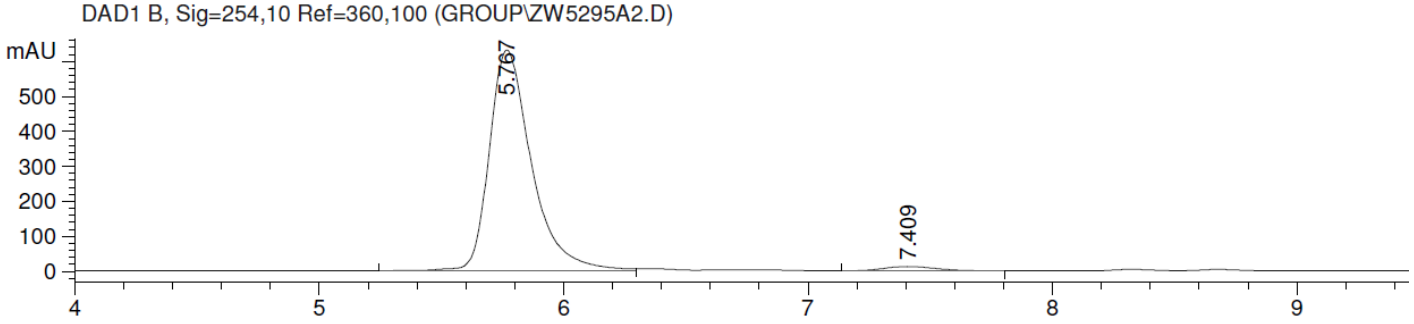
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.603	FM	0.1703	98.82756	9.67447	1.2748
2	7.542	VB	0.1898	7653.60254	629.68274	98.7252



3-Ethyl-1-phenyl-3-(2-(triphenylsilyl)ethyl)azetidin-2-one (Fig. 3A, entry 47).

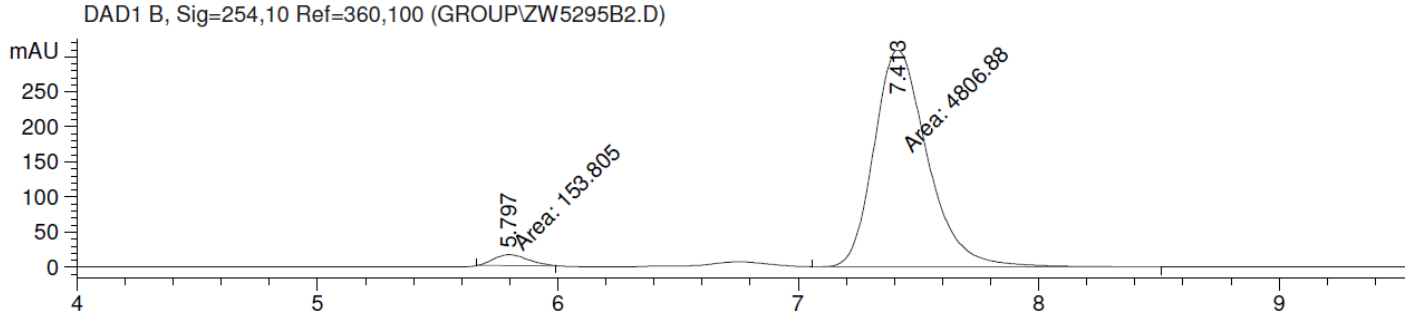
HPLC analysis: CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **47** (Fig. **3A**, entry 47): 95% ee from (*R,R*)-**L***

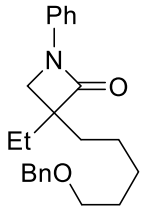


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.767	BV	0.1826	7628.00586	632.86993	97.5100
2	7.409	VB	0.2347	194.78963	12.57373	2.4900

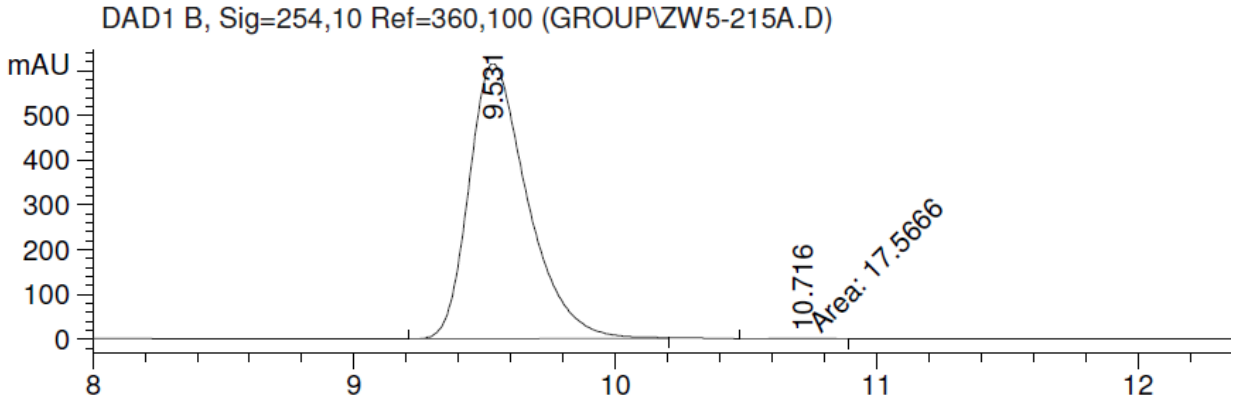
Compound **47** (Fig. **3A**, entry 47): 94% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.797	MM	0.1656	153.80479	15.47956	3.1005
2	7.413	MM	0.2585	4806.88184	309.97131	96.8995

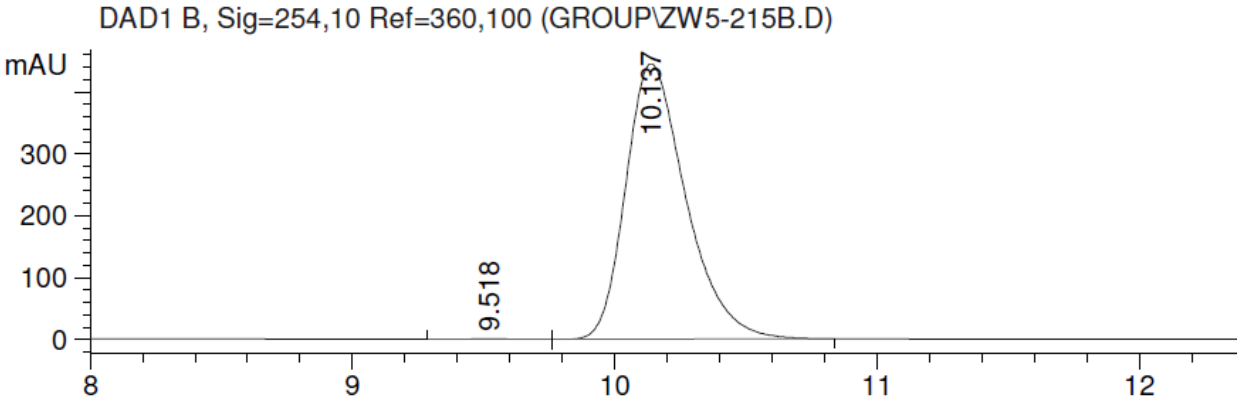


3-(5-(Benzyloxy)pentyl)-3-ethyl-1-phenylazetidin-2-one (Fig. 3A, entry 48).
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).
Compound **48** (Fig. **3A**, entry 48): 99% ee from (*R,R*)-**L***

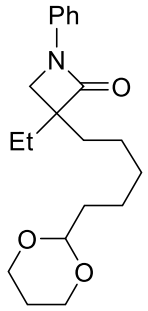


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.531	PB	0.2358	9599.68652	616.17151	99.8173
2	10.716	MF	0.2088	17.56661	1.40245	0.1827

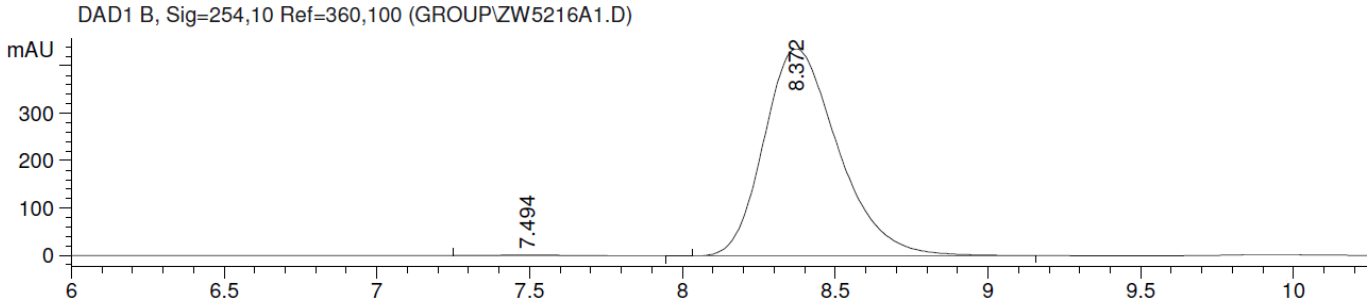
Compound **48** (Fig. **3A**, entry 48): 99% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.518	PP	0.1836	12.99543	1.04126	0.1830
2	10.137	VP	0.2439	7090.17725	445.02518	99.8170

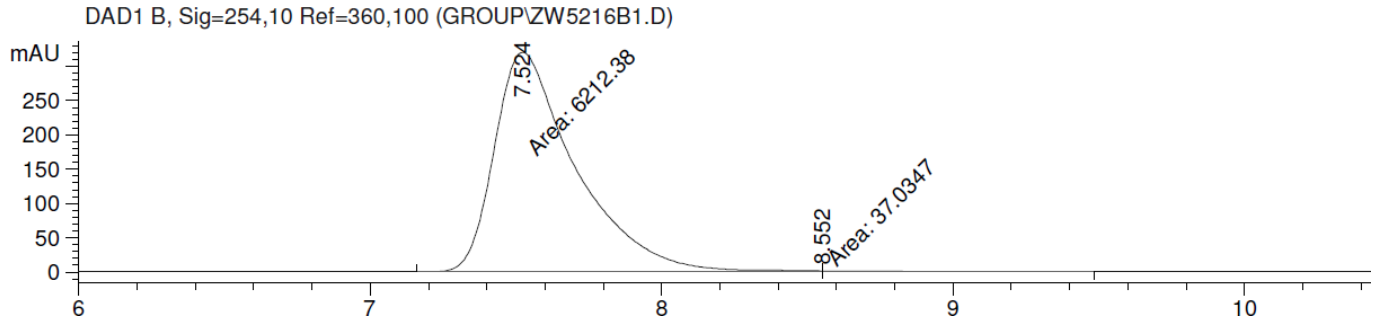


3-(5-(1,3-Dioxan-2-yl)pentyl)-3-ethyl-1-phenylazetidin-2-one (Fig. 3A, entry 49).
HPLC analysis: CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min).
Compound **49** (Fig. **3A**, entry 49): 99% ee from (*R,R*)-**L***

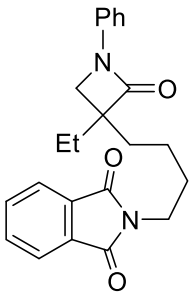


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.494	BP	0.2650	31.81812	1.67994	0.4297
2	8.372	PB	0.2589	7373.30225	436.96918	99.5703

Compound **49** (Fig. **3A**, entry 49): 99% ee from (*S,S*)-**L***



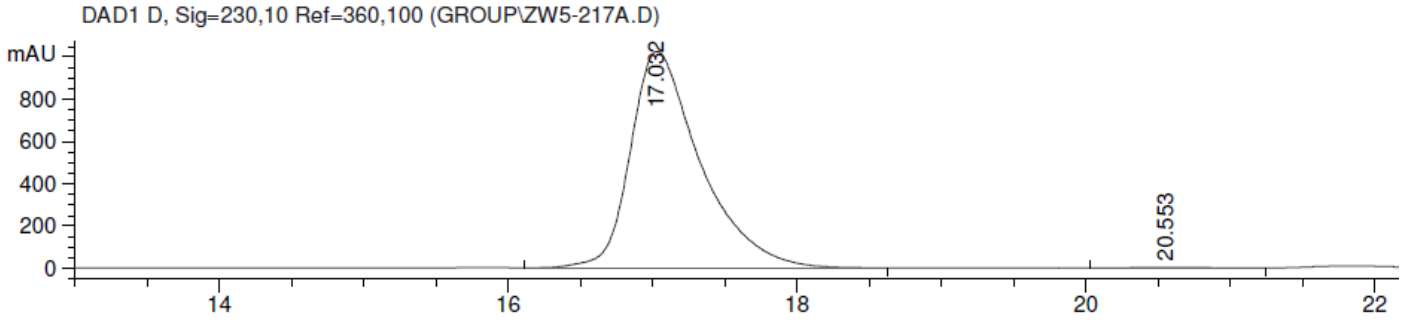
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.524	MF	0.3231	6212.37939	320.45306	99.4074
2	8.552	FM	0.4121	37.03472	1.49798	0.5926



2-(4-(3-Ethyl-2-oxo-1-phenylazetidin-3-yl)butyl)isoindoline-1,3-dione (Fig. 3A, entry 50).

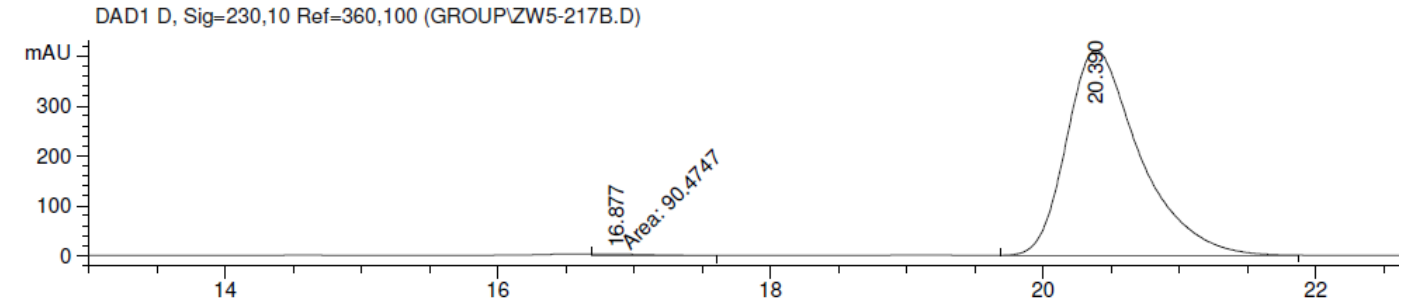
HPLC analysis: CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min).

Compound **50** (Fig. **3A**, entry 50): 99% ee from (*R,R*)-**L***

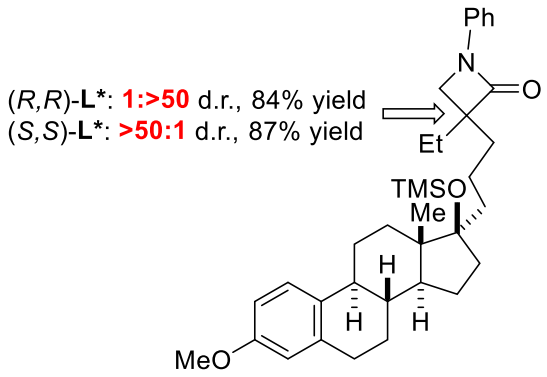


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.032	VB	0.4984	3.46444e4	1024.77966	99.5725
2	20.553	BB	0.4551	148.72627	4.30493	0.4275

Compound **50** (Fig. **3A**, entry 50): 99% ee from (*S,S*)-**L***



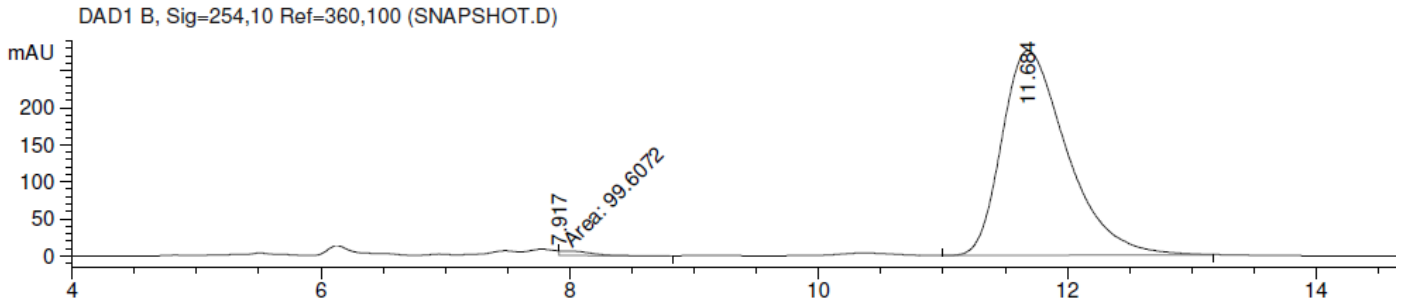
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.877	FM	0.5093	90.47471	2.96052	0.5859
2	20.390	BB	0.5623	1.53514e4	410.49255	99.4141



3-ethyl-3-(3-((8R,9S,13S,14S,17S)-3-methoxy-13-methyl-17-((trimethylsilyl)oxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propyl)-1-phenylazetidin-2-one (Fig. 3A, entries 51 and 52).

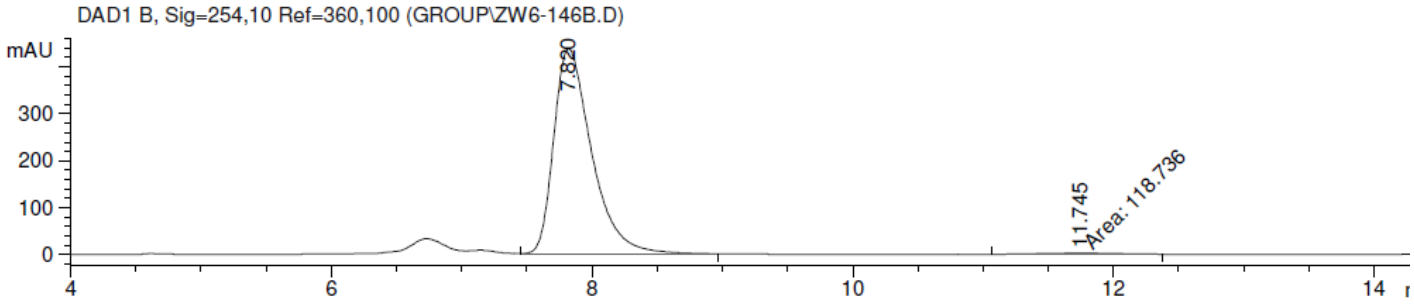
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **51** (Fig. **3A**, entry 51): >50:1 d.r. from (*R,R*)-**L***

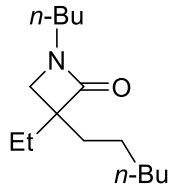


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.917	FM	0.2670	99.60719	6.21658	0.9794
2	11.684	VB	0.5549	1.00702e4	276.50909	99.0206

Compound **52** (Fig. **3A**, entry 52): 1:>50 d.r. from (*S,S*)-**L***



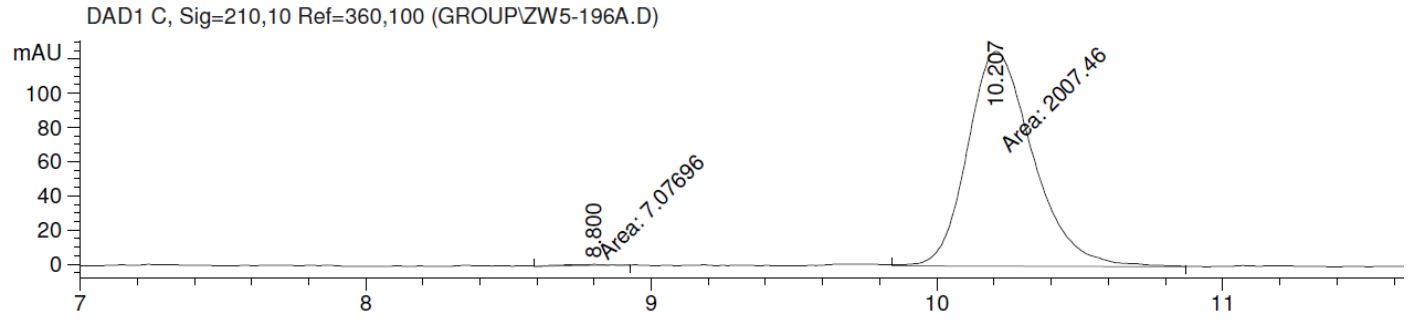
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.820	VB	0.3065	8869.63281	437.61661	98.6790
2	11.745	MM	0.7069	118.73635	2.79959	1.3210



1-Butyl-3-ethyl-3-hexylazetidin-2-one (Fig. 3A, entry 53).

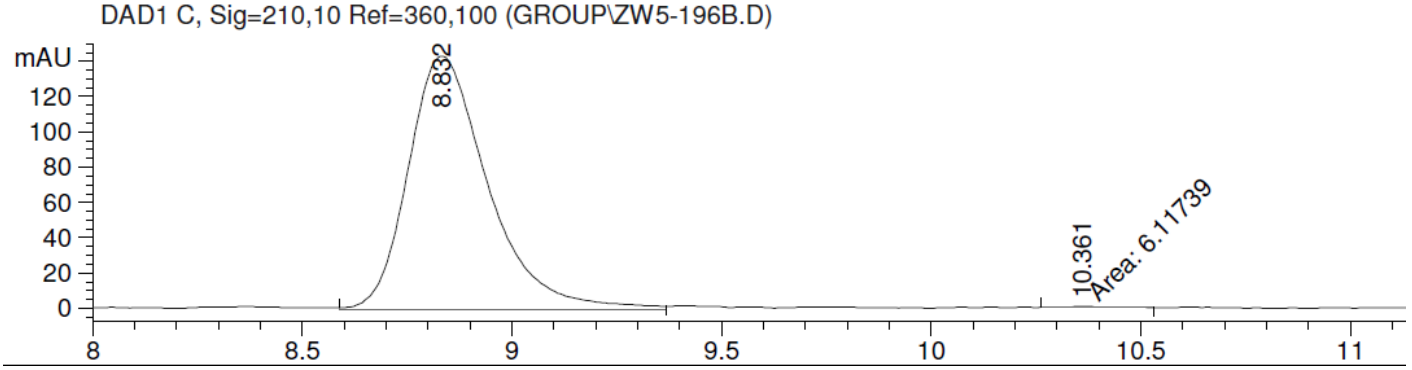
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **53** (Fig. **3A**, entry 53): 99% ee from (*R,R*)-**L***

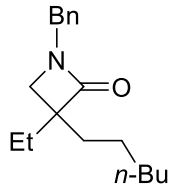


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.800	MM	0.1822	7.07696	6.47491e-1	0.3513
2	10.207	MM	0.2653	2007.46497	126.10775	99.6487

Compound **53** (Fig. **3A**, entry 53): 99% ee from (*S,S*)-**L***



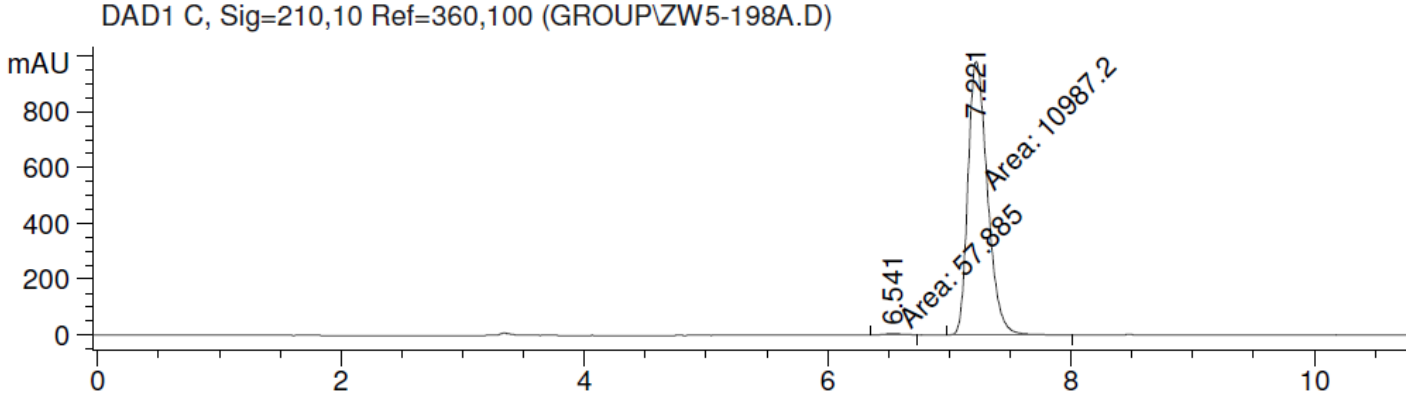
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.832	BV	0.2002	1898.06909	143.57878	99.6787
2	10.361	MM	0.1523	6.11739	6.69362e-1	0.3213



1-Benzyl-3-ethyl-3-hexylazetidin-2-one (Fig. 3A, entry 54).

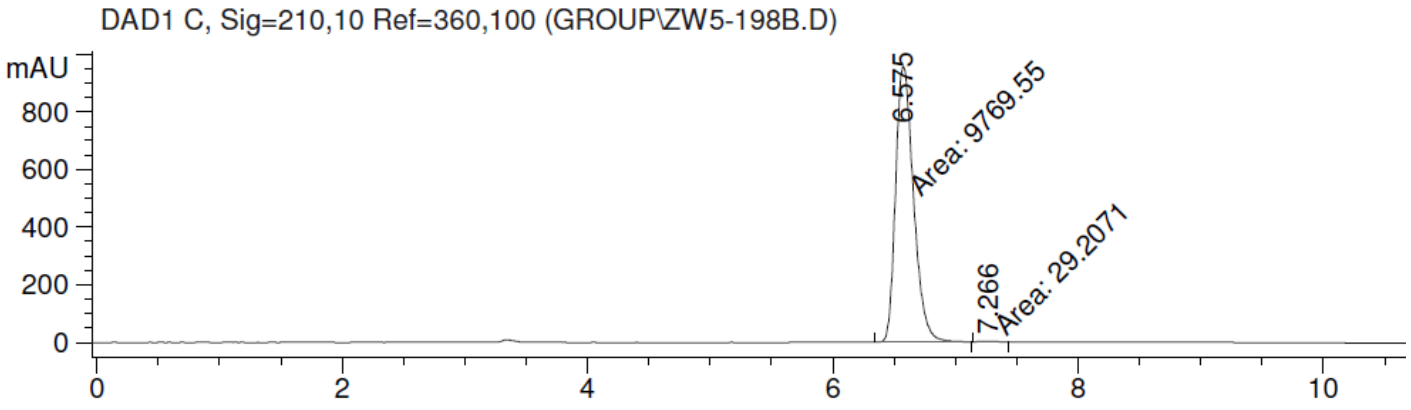
HPLC analysis: CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **54** (Fig. **3A**, entry 54): 99% ee from (*R,R*)-**L***

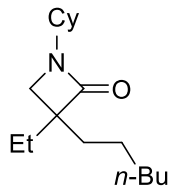


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.541	MM	0.1957	57.88496	4.92893	0.5241
2	7.221	MM	0.1866	1.09872e4	981.20685	99.4759

Compound **54** (Fig. **3A**, entry 54): 99% ee from (*S,S*)-**L***



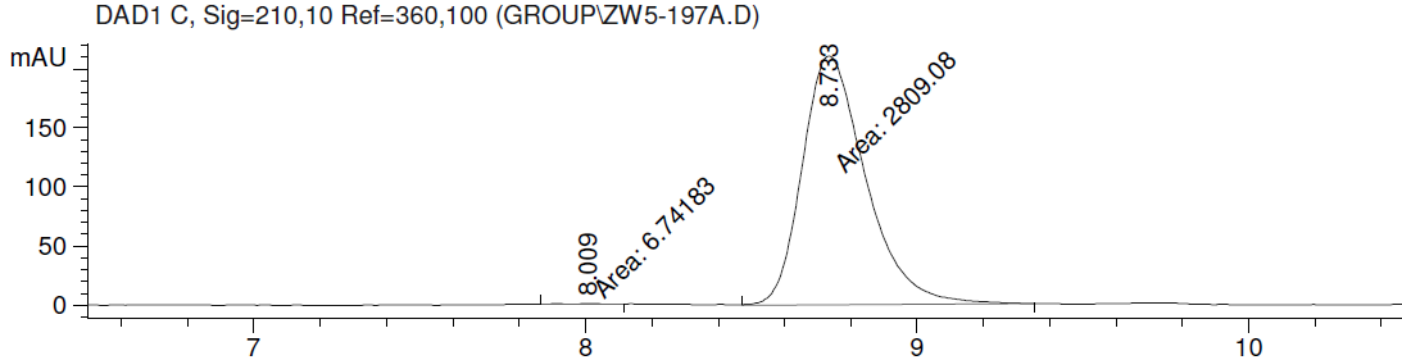
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.575	MM	0.1698	9769.54980	958.73627	99.7019
2	7.266	MM	0.1560	29.20706	3.12058	0.2981



1-Cyclohexyl-3-ethyl-3-hexylazetidin-2-one (Fig. 3A, entry 55).

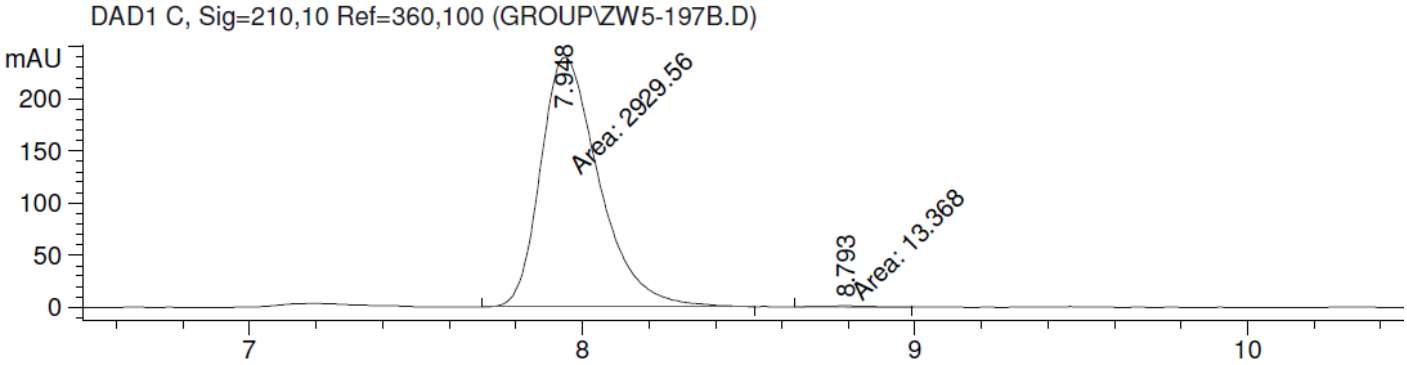
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **55** (Fig. **3A**, entry 55): 99% ee from (*R,R*)-**L***

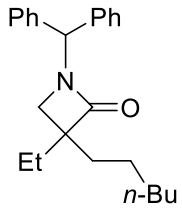


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.009	MM	0.1530	6.74183	7.34430e-1	0.2394
2	8.733	MM	0.2221	2809.08447	210.80296	99.7606

Compound **55** (Fig. **3A**, entry 55): 99% ee from (*S,S*)-**L***



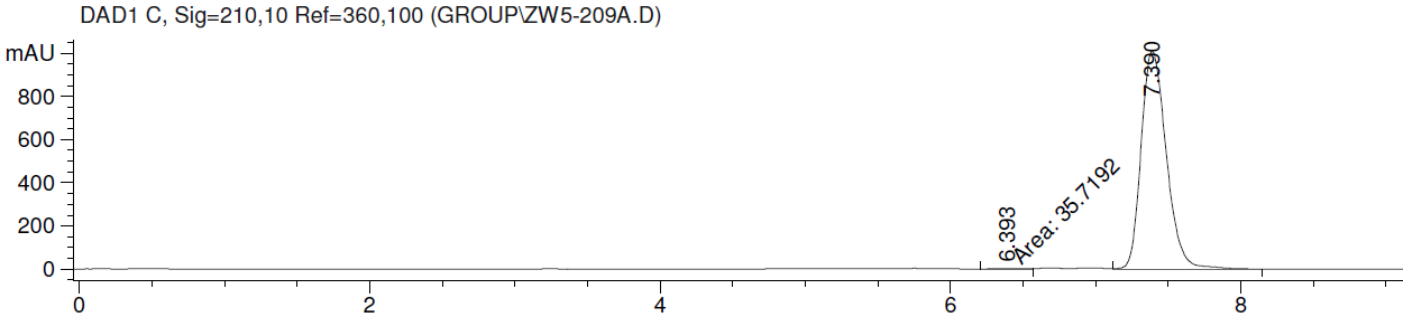
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.948	MM	0.2039	2929.56421	239.51404	99.5458
2	8.793	MM	0.1822	13.36797	1.22267	0.4542



1-Benzhydryl-3-ethyl-3-hexylazetidin-2-one (Fig. 3A, entry 56).

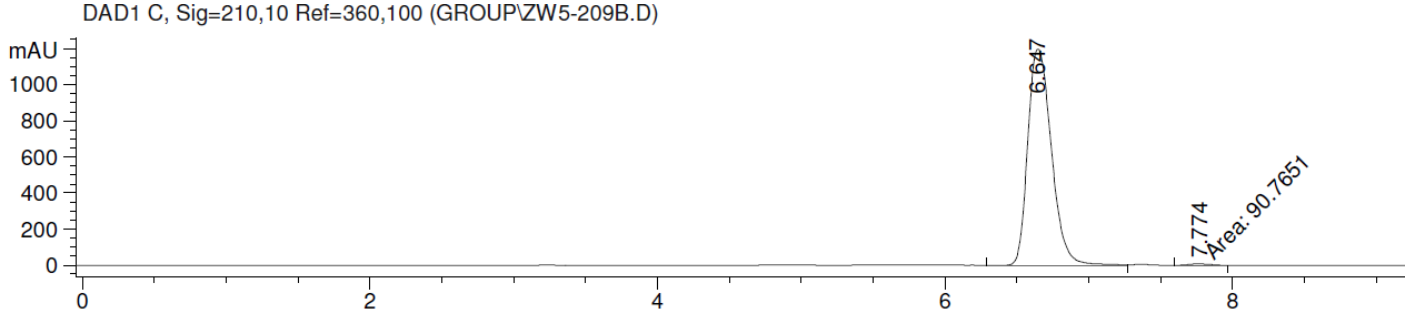
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **56** (Fig. **3A**, entry 53): 99% ee from (*R,R*)-**L***

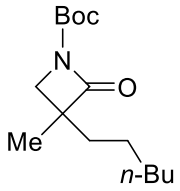


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.393	MM	0.2127	35.71922	2.79923	0.2917
2	7.390	VB	0.1870	1.22076e4	1009.77045	99.7083

Compound **56** (Fig. **3A**, entry 56): 99% ee from (*S,S*)-**L***



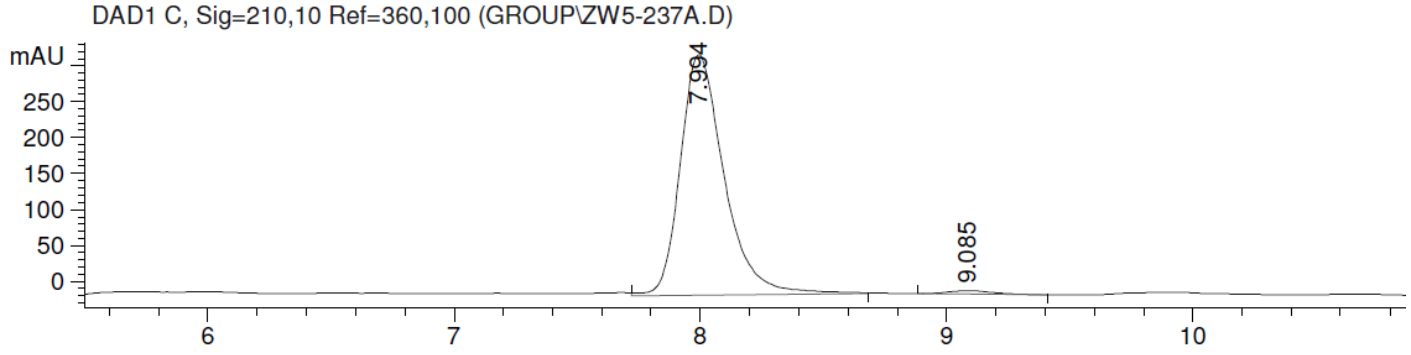
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.647	VV	0.1797	1.37465e4	1199.55225	99.3441
2	7.774	MM	0.1846	90.76510	8.19690	0.6559



***tert*-Butyl 3-hexyl-3-methyl-2-oxoazetidine-1-carboxylate (Fig. 3A, entry 57).**

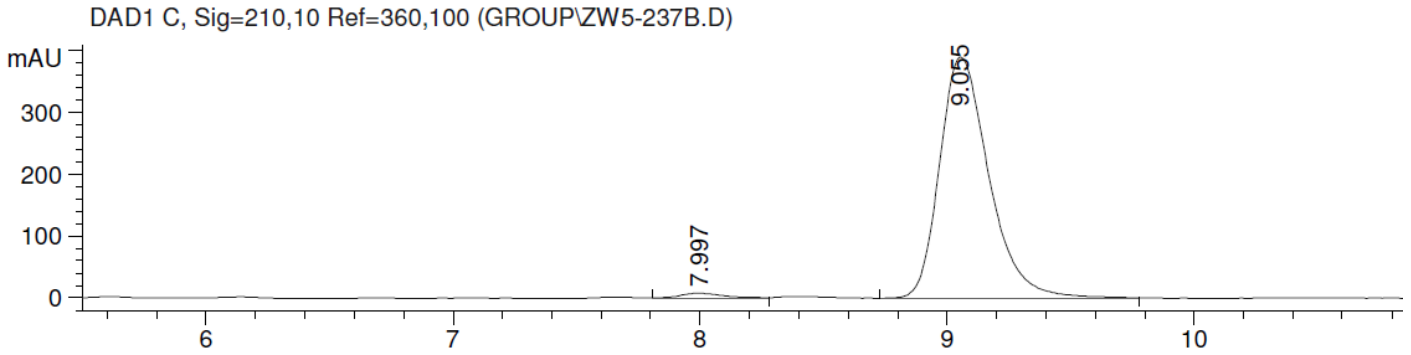
HPLC analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **57** (Fig. **3A**, entry 57): 97% ee from (*R,R*)-**L***

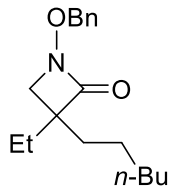


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.994	VB	0.1889	4154.15039	334.52637	98.5607
2	9.085	PP	0.1725	60.66241	4.96642	1.4393

Compound **57** (Fig. **3A**, entry 57): 96% ee from (*S,S*)-**L***



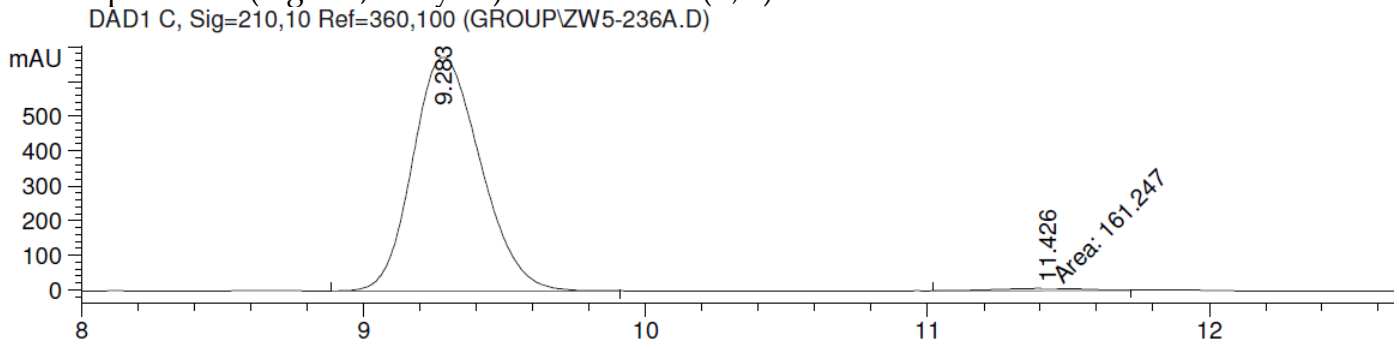
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.997	VV	0.1851	107.36201	8.29059	1.9420
2	9.055	VB	0.2139	5421.09180	390.74713	98.0580



1-(Benzyloxy)-3-ethyl-3-hexylazetidin-2-one (Fig. 3A, entry 58).

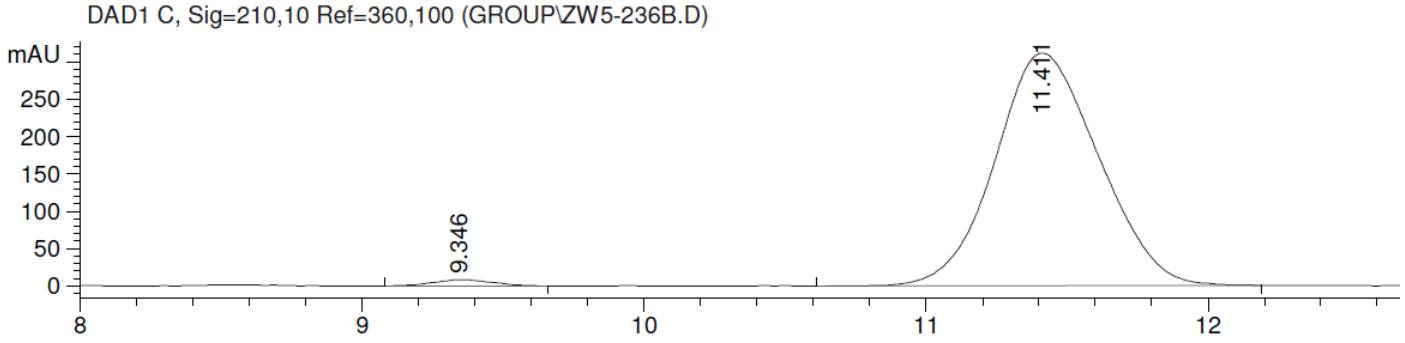
HPLC analysis: CHIRALCEL AS-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **58** (Fig. **3A**, entry 58): 97% ee from (*R,R*)-**L***

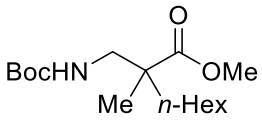


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.283	VB	0.2616	1.12766e4	672.60901	98.5902
2	11.426	MM	0.3976	161.24699	6.75842	1.4098

Compound **58** (Fig. **3A**, entry 58): 97% ee from (*S,S*)-**L***

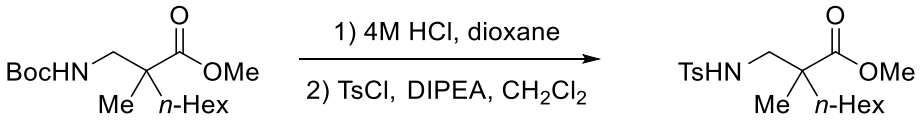


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.346	VP	0.1986	132.88728	8.58467	1.6382
2	11.411	VV	0.3827	7979.09619	311.64389	98.3618



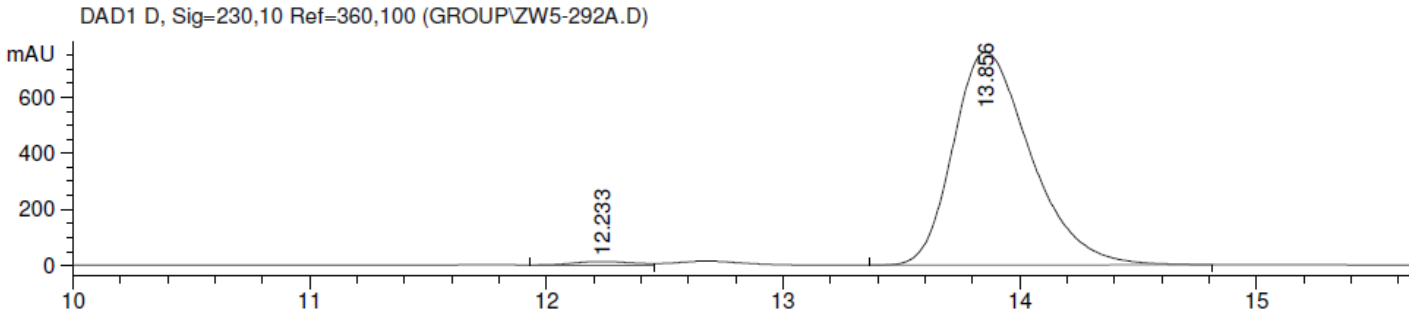
Methyl 2-(((tert-butoxycarbonyl)amino)methyl)-2-methyloctanoate (Fig. 3B, entry 59).

Determination of the ee:



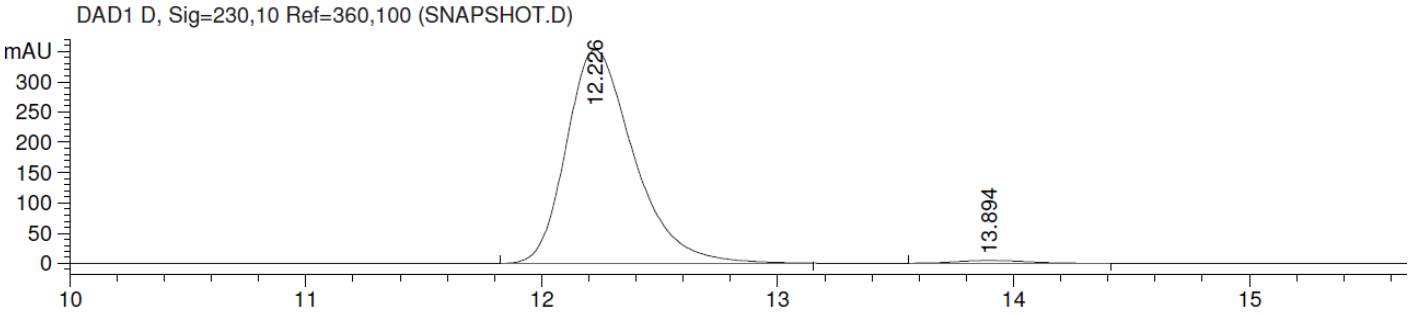
HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

97% ee from (*R,R*)-**L***

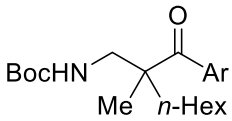


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.233	VV	0.2824	255.46822	13.90359	1.4558
2	13.856	PB	0.3493	1.72932e4	760.60419	98.5442

97% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.226	PB	0.3013	6982.36182	352.19415	98.6534
2	13.894	BB	0.2862	95.30983	4.59102	1.3466

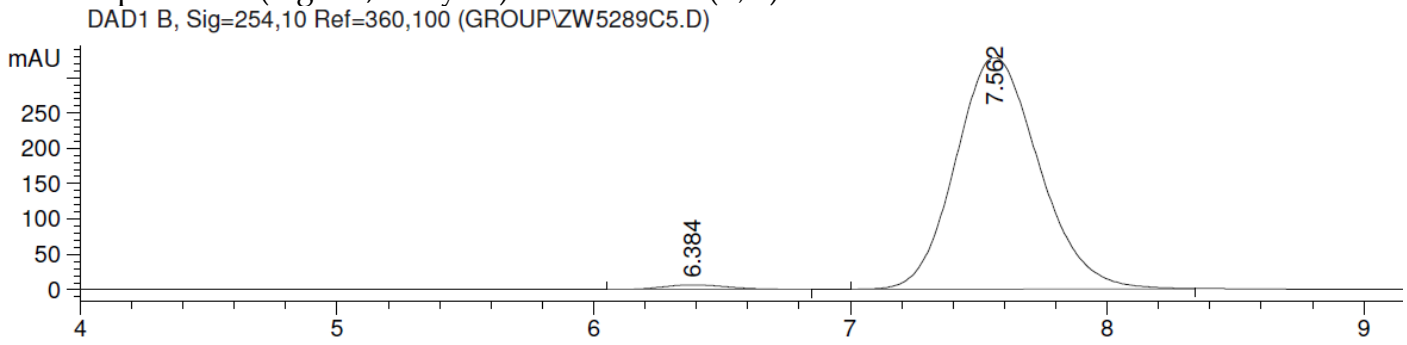


Ar = *p*-anisyl

***tert*-Butyl (2-(4-methoxybenzoyl)-2-methyloctyl)carbamate (Fig. 3B, entry 60).**

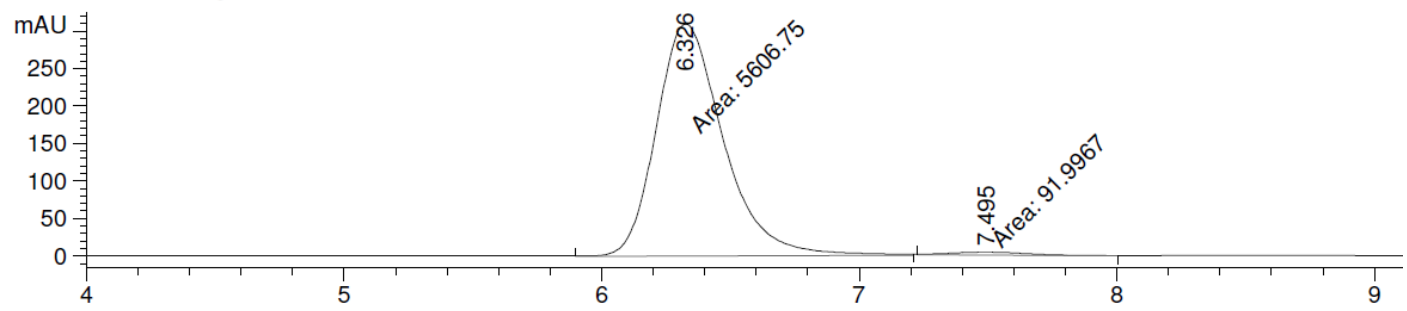
HPLC analysis: CHIRALCEL AS-H column (2% *i*-PrOH in hexane, 1.0 mL/min).

Compound **60** (Fig. **3B**, entry 60): 97% ee from (*R*,*R*)-**L***

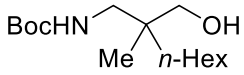


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.384	BP	0.2752	119.34138	6.65689	1.5860
2	7.562	BB	0.3491	7405.22949	328.42874	98.4140

Compound **60** (Fig. **3B**, entry 60): 97% ee from (*S*,*S*)-**L***

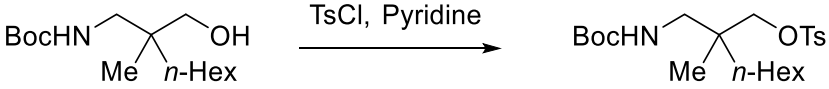


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.326	MM	0.3017	5606.75488	309.76218	98.3857
2	7.495	MM	0.3738	91.99672	4.10197	1.6143



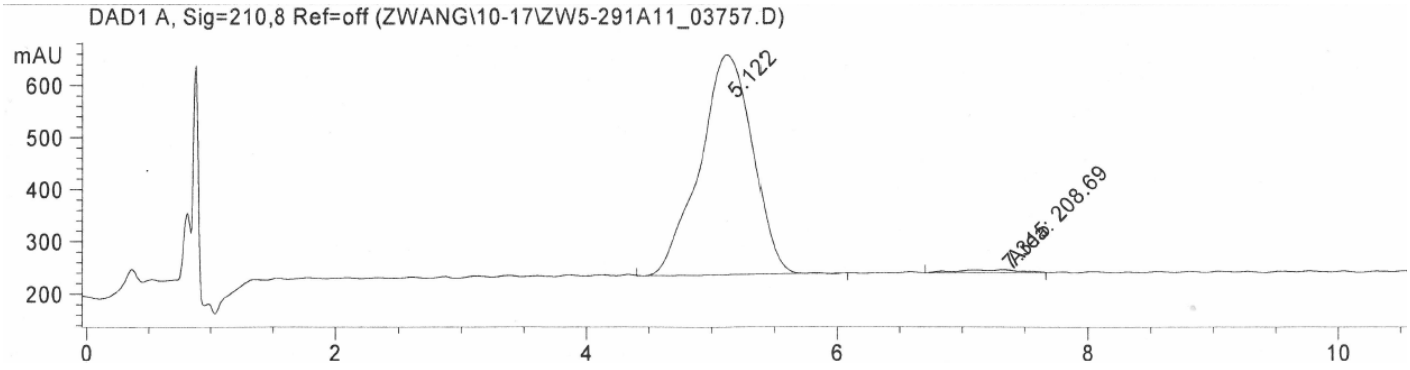
***tert*-Butyl (2-(hydroxymethyl)-2-methyloctyl)carbamate (Fig. 3B, entry 61).**

Determination of the ee:



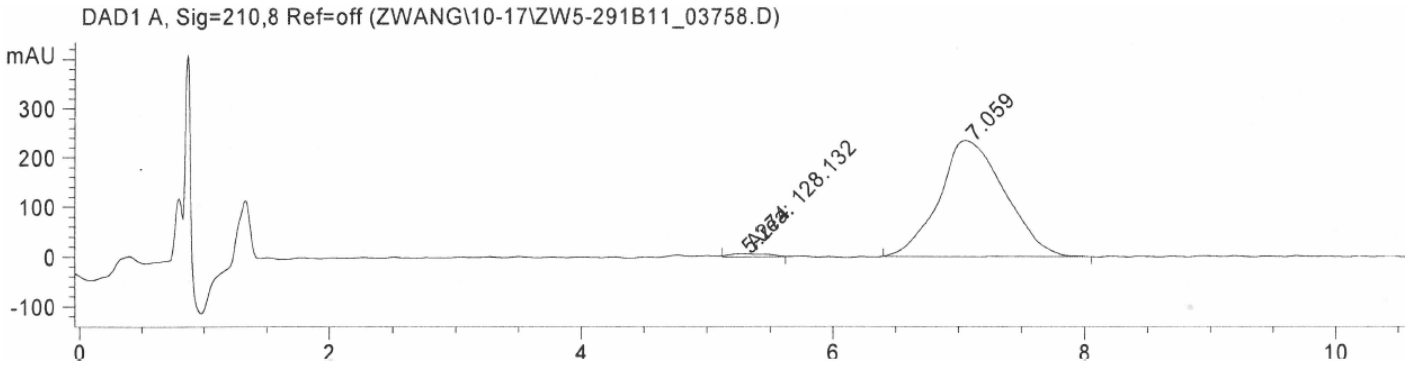
SFC analysis: CHIRALCEL OJ-H column (2% *i*-PrOH in CO_2, 3.5 mL/min).

97% ee from (*R,R*)-**L***

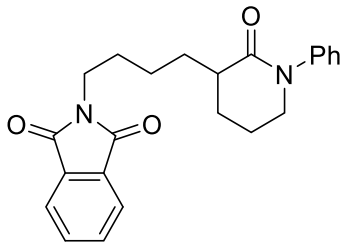


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.122	BB	0.4476	1.24244e4	421.83578	98.3481
2	7.315	MM	0.6036	208.69003	5.76279	1.6519

97% ee from (*S,S*)-**L***



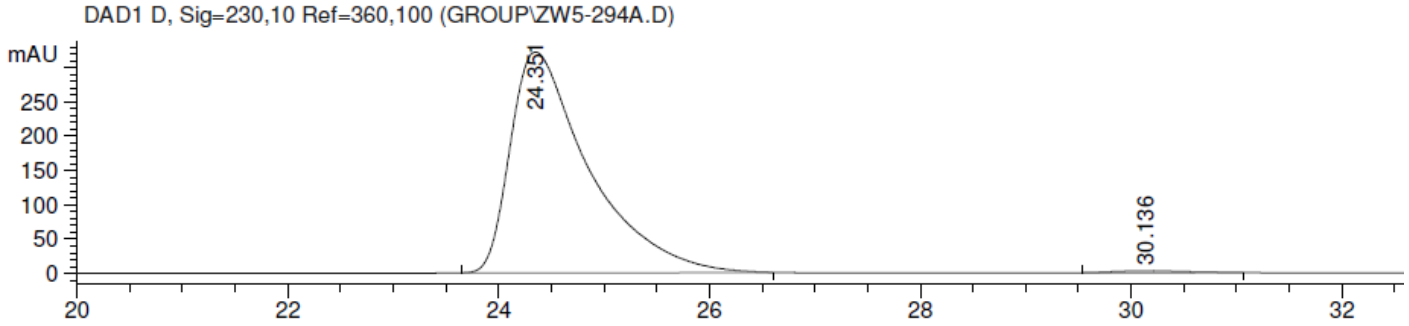
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.274	MM	0.3533	128.13168	6.04371	1.4783
2	7.059	BB	0.5405	8539.40723	234.67041	98.5217



2-(4-(2-Oxo-1-phenylpiperidin-3-yl)butyl)isoindoline-1,3-dione.

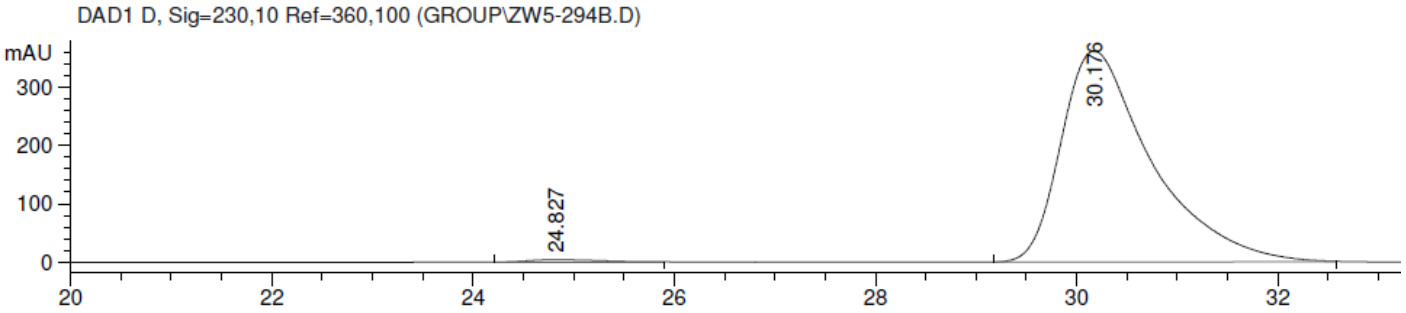
HPLC analysis: CHIRALCEL AD-H column (20% *i*-PrOH in hexane, 1.0 mL/min).

98% ee from (*R,R*)-**L***

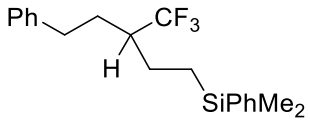


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.351	BB	0.7525	1.67001e4	322.30954	99.1582
2	30.136	BB	0.5924	141.77589	2.88963	0.8418

98% ee from (*S,S*)-**L***



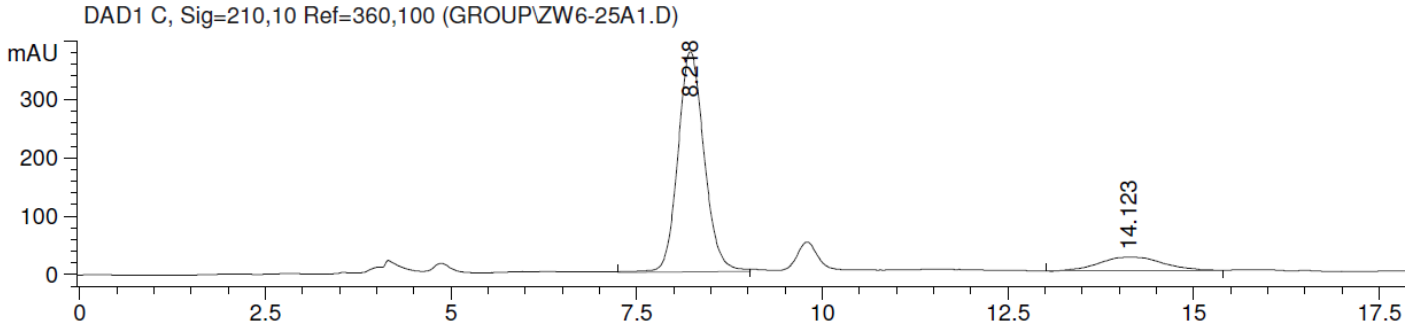
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.827	BB	0.5808	206.77190	4.22624	0.9083
2	30.176	BB	0.9047	2.25579e4	361.17136	99.0917



Dimethyl(phenyl)(5-phenyl-3-(trifluoromethyl)pentyl)silane.

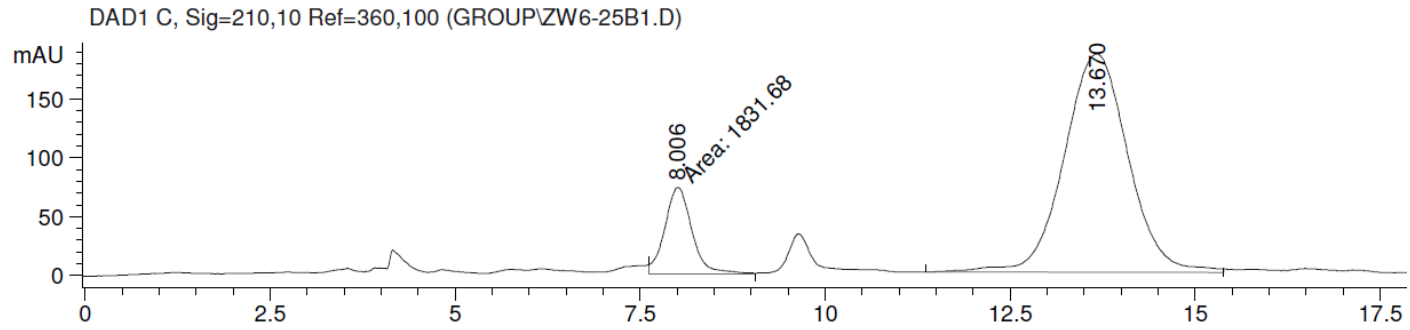
HPLC analysis: CHIRALCEL OJ-H column (1% *i*-PrOH in hexane, 1.0 mL/min).

72% ee from (*R*,*R*)-**L***

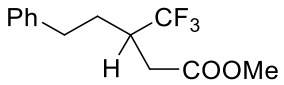


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.218	BB	0.3806	9251.87891	376.66373	86.2344
2	14.123	PV	0.7263	1476.87341	23.92212	13.7656

72% ee from (*S*,*S*)-**L***



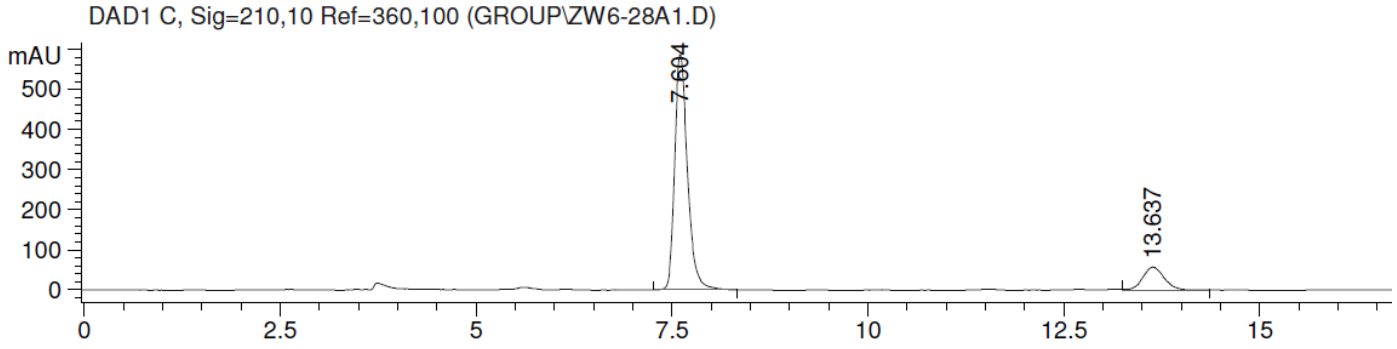
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.006	FM	0.4184	1831.68469	72.97079	14.0761
2	13.670	PB	0.8384	1.11810e4	185.72652	85.9239



Methyl 5-phenyl-3-(trifluoromethyl)pentanoate.

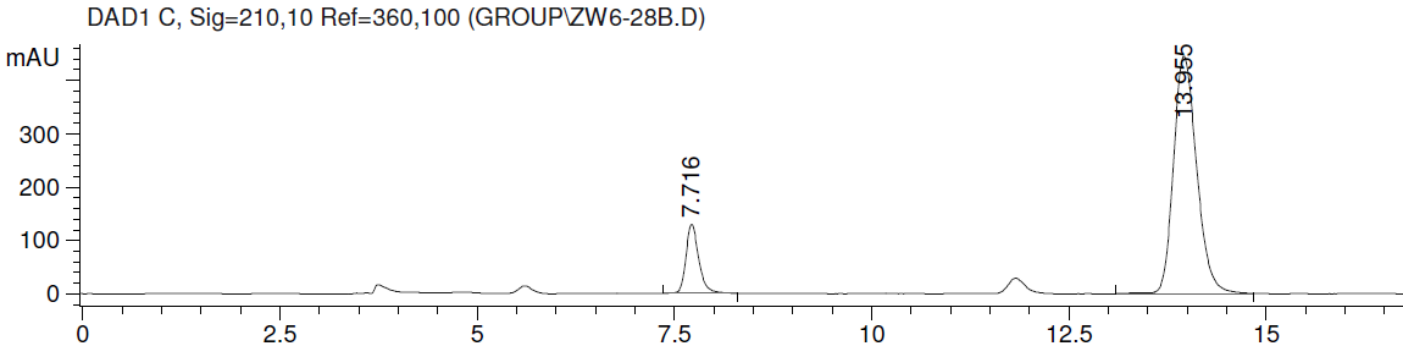
HPLC analysis: CHIRALCEL OD-H column (1% *i*-PrOH in hexane, 1.0 mL/min).

71% ee from (*R,R*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.604	BP	0.1750	6695.55273	587.20502	85.6620
2	13.637	VB	0.3046	1120.69604	57.69826	14.3380

72% ee from (*S,S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.716	VV	0.1722	1468.08228	129.59592	13.7977
2	13.955	BB	0.3178	9171.98242	446.30981	86.2023