Supplementary data for the article:

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Supporting information for the paper under the title:

Gold(I)-catalyzed domino cyclizations of diynes for the synthesis of functionalized cyclohexenone derivatives. Total synthesis of (–)-gabosine H and (–)-6-epi-gabosine H.

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1 General information

All chromatographic separations[1] were performed on Silica, 10-18, 60Å, ICN Biomedicals. Standard techniques were used for the purification of reagents and solvents, and for gabosine synthesis 1,2-dichloroethane was additionally degassed before use (three freeze-pump-thaw cycles).[2] NMR spectra were recorded on a Varian Gemini 200, (^{1}H NMR at 200 MHz, ^{13}C NMR at 50 MHz), and on Bruker Avance III 500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz). Chemical shifts are expressed in ppm (δ) using tetramethylsilane as internal standard, coupling constants (*J*) are in Hz. IR spectra were recorded on a Nicolet 6700 FT instrument, and are expressed in cm^{-1}. Mass spectra were obtained on Agilent technologies 6210 TOF LC/MS instrument (LC: series 1200) and LTQ Orbitrap XL hybrid FTMS (Thermo Scientific). Optical rotation was measured on Rudolph Research Analytical AUTOPOL IV Automatic Polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

[1] For description of the technique of dry-flash chromatography, see: a) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25; b) *Vogel's Textbook of Practical Organic Chemistry*, Longman Scientific&Technical, 5th edition, London, 1989, p. 220; c) For an account which includes some improvements of the separation technique, see: Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431-2434.

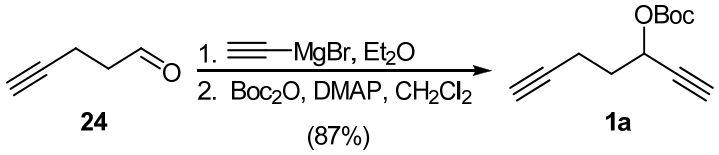
[2] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th edition, Elsevier, Oxford, 2009.

2 Experimental

2.1 Methodology (as described in Table 1)

2.1.1 Entry 1

2.1.1.1 tert-Butyl hepta-1,6-diyn-3-yl carbonate (1a)



A solution of ethynylmagnesium bromide (0.5 M in THF, 34 mL, 17.1 mmol) was added to a solution of pent-4-ynal **24**[3] (1.0 g, 12.2 mmol) in Et_2O (90 mL), at 0 °C, under an argon atmosphere. After 10 min, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl, and the mixture was extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was used immediately in the next step, without further purification.

To a solution of crude propargyl alcohol (1.32 g, 12.2 mmol) in CH_2Cl_2 (100 mL) were added di-*tert*-butyl dicarbonate (3.20 g, 14.7 mmol) and DMAP (149 mg, 1.22 mmol) at room temperature. After 30 min of stirring, the reaction was quenched with H_2O, the organic layer was dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 9:1) to give **1a** (2.2 g, 87%) as a colorless oil.

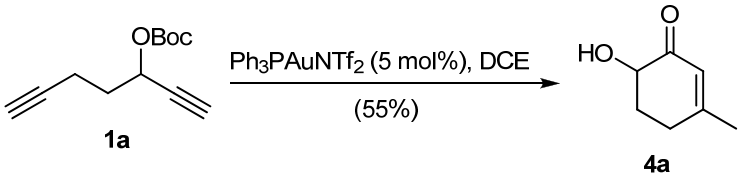
^{1}H NMR (200 MHz, $CDCl_3$): δ 5.30 (td, J^1 = 6.6, J^2 = 2.1, 1H), 2.53 (d, J = 2.1 Hz, 1H), 2.40 (td, J^1 = 7.3, J^2 = 2.6 Hz, 2H), 2.15-2.03 (m, 2H), 2.03-1.97 (m, 1H), 1.51 (s, 9H).

^{13}C NMR (50 MHz, $CDCl_3$): δ 152.4, 83.1, 82.3, 80.0, 74.7, 69.3, 65.3, 33.4, 27.7, 14.3.

IR_{film}: 3296, 2982, 1745, 1276, 1159, 1097, 633.

HRMS (ESI): calcd. for $C_{12}H_{16}O_3Na$ $[M+Na]^+$: 231.0992, found: 231.0987.

2.1.1.2 6-Hydroxy-3-methylcyclohex-2-enone (4a)[4]



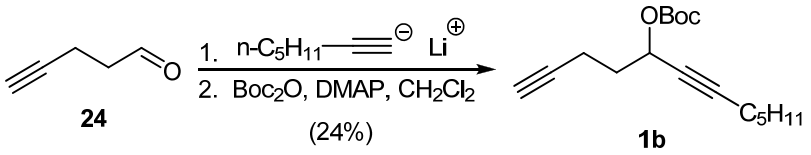
[3] Desrat, S.; Remeur, C.; Roussi F. *Org. Biomol. Chem*. **2015**, *13*, 5520-5531.
[4] Lin, J.; Nikaido, M. M.; Clark, G. *J. Org. Chem*. **1987**, *52*, 3745-3752.

$Ph_3PAuNTf_2$ (5.6 mg, 7.5 μmol) was added to a solution of diyne **1a** (18.5 mg, 0.088 mmol) in dry 1,2-dichloroethane (1.9 mL), at room temperature and under an argon atmosphere. After 5 minutes, the stirring was continued at 55 °C for 4 h. The solvent was removed on rotovap and the residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 4:1) to give 6-hydroxy-3-methylcyclohex-2-enone **4a** (6.1 mg, 55%), as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (dq, J = 2.6, 1.3 Hz, 1H), 4.11 (ddd, J^1 = 13.5, J^2 = 5.5, J^3 = 1.4 Hz, 1H), 3.74 (d, J = 1.6 Hz, 1H), 2.59-2.48 (m, 1H), 2.43-2.33 (m, 2H), 1.99 (s, 3H), 1.91-1.80 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 164.5, 123.6, 72.0, 30.9, 30.6, 24.4.
HRMS (ESI): calcd. for $C_7H_{11}O_2$ $[M+H]^+$: 127.0754 found: 127.0756.

2.1.2 Entry 2

2.1.2.1 tert-Butyl dodeca-1,6-diyn-5-yl carbonate (1b)



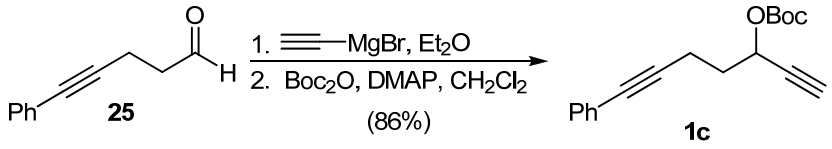
n-Butyl lithium (0.72 mL, 1.15 mmol, c 1.6M) was added to a cold (0 °C) solution of hept-1-yne (0.15 mL, 1.15 mmol) in dry diethyl ether (15 mL), and the mixture was stirred under an argon atmosphere, for 10 minutes, when a solution of pent-4-ynal **24** (90 mg, 1.1 mmol) in dry diethyl ether (2 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature, diluted HCl (4.3 %) was added, and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.

A solution of previously obtained crude propargyl alcohol, di-*tert*-butyl dicarbonate (252 mg, 1.16 mmol) and DMAP (13 mg, 0.11 mmol) in CH_2Cl_2 (3 mL) was stirred for 1 h, at rt. The reaction was quenched with H_2O, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 96:4) to give **1b** (65 mg, 24%), as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.26 (tt, J^1 = 6.5, J^2 = 1.9 Hz, 1H), 2.35 (dt, J^1 = 7.3, J^2 = 2.6 Hz, 2H), 2.18 (dt, J^1 = 7.2, J^2 = 2.4 Hz, 2H), 1.92-2.05 (m, 3H), 1,45-1,51 (m, 11H), 1.25-1.37 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 87.5, 82.8, 82.5, 76.4, 68.9, 66.2, 34.0, 30.9, 28.0, 27.7, 22.1, 18.6, 14.4, 13.9.

2.1.3 Entry 3

2.1.3.1 tert-Butyl 7-phenylhepta-1,6-diyn-3-yl carbonate (1c)



A solution of ethynylmagnesium bromide (0.5 M in THF, 3 mL, 1.52 mmol) was added to a solution of aldehyde **25**[5] (200 mg, 1.26 mmol) in Et_2O (10 mL), at 0 °C, under an argon atmosphere. After 5 min, diluted HCl (4.3 %) was added, and the mixture was extracted with EtOAc (2 x 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.

A solution of previously obtained crude propargyl alcohol, di-*tert*-butyl dicarbonate (304 mg, 1.39 mmol) and DMAP (15.4 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h, at rt. The reaction was quenched with H_2O, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to give **1c** (310 mg, 86%) as a colorless oil.

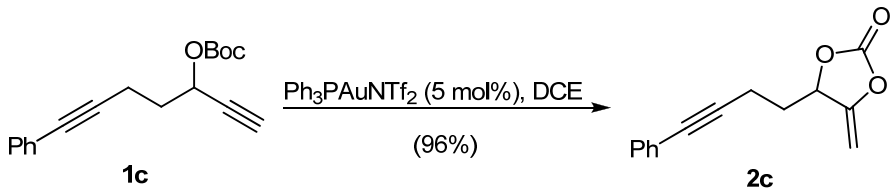
IR_{film}: 3290, 2980, 1745, 1276, 1255, 1160, 1096, 758.

HRMS (ESI): calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found: 285.1485.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.42 (m, 2H), 7.24-7.30 (m, 3H), 5.36 (dt, J^1 = 6.6, J^2 = 2.2 Hz, 1H), 2.61 (t, J = 7.4 Hz, 2H), 2.53 (d, J = 2.1 Hz, 1H), 2.06-2.19 (m, 2H), 1.50 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 131.5, 128.1, 127.7, 123.5, 87.8, 82.9, 81.4, 80.2, 74.6, 65.4, 33.6, 27.7, 15.3.

2.1.3.2 4-Methylene-5-(4-phenylbut-3-ynyl)-1,3-dioxolan-2-one (2c)



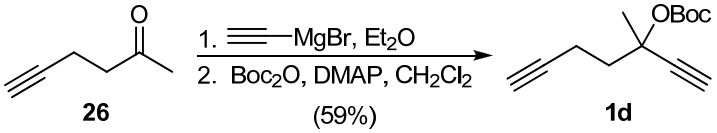
$Ph_3PAuNTf_2$ (3.9 mg, 5.3 μmol) was added to a solution of diyne **1c** (30 mg, 0.106 mmol) in dry 1,2-dichloroethane (1 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 5 minutes, filtered through a short plug of celite, and the celite was washed with CH_2Cl_2. After concentration on rotovap, the residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 7:1) to give enol carbonate **2c** (23 mg, 96%), as a colorless oil.

[5] Bouvet, S.; Moreau, X.; Coeffard, V.; Greck, C. *J. Org. Chem.* **2013**, *78*, 427-437.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.41 (m, 2H), 7.27-7.31 (m, 3H), 5.37-5.41 (m, 1H), 4.91 (dd, J^1 = 4.0, J^2 = 2.5 Hz, 1H), 4.43 (dd, J^1 = 4.0, J^2 = 2.3 Hz, 1H), 2.66 (dt, J^1 = 6.8, J^2 = 1.6 Hz, 2H), 2.08-2.13 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 151.8, 131.6, 128.3, 128.0, 123.1, 87.3, 86.6, 82.3, 78.2, 33.8, 14.9.

2.1.4 Entry 4

2.1.4.1 tert-Butyl (3-methylhepta-1,6-diyn-3-yl) carbonate (1d)

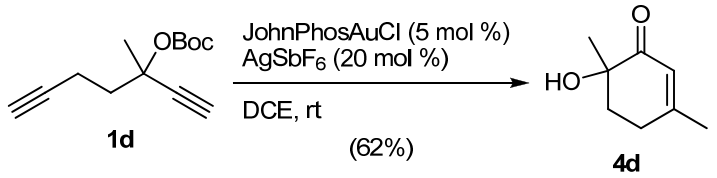


A solution of ethynylmagnesium bromide (0.5 M in THF, 5 mL, 2.5 mmol) was added to a solution of **26**[6] (200 mg, 2.1 mmol) in Et_2O (20 mL), at 0 °C, under an argon atmosphere. After 10 min, diluted HCl (4.3 %) was added, and the mixture was extracted with EtOAc (3 x 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.

A solution of previously obtained crude propargyl alcohol (110 mg, 0.9 mmol), di-*tert*-butyl dicarbonate (216 mg, 1.0 mmol) and DMAP (11 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was stirred for 16 h, at rt. The reaction was quenched with H_2O, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 9:1) to give **1d** (118 mg, 59%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.60 (s, 1H), 2.47-2.41 (m, 2H), 2.27-2.20 (m, 1H), 2.11-2.04 (m, 1H), 1.95 (t, J = 2.7 Hz, 1H), 1.72 (s, 3H), 1.49 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 151.2, 83.3, 82.5, 82.4, 74.9, 74.2, 68.5, 40.3, 27.8, 26.3, 13.8.
IR_{film}: 3294, 2982, 2939, 1749, 1458, 1393, 1372, 1283, 1257, 1158, 1092, 853.
HRMS (ESI): calcd. for $C_{13}H_{18}O_3Na$ $[M+Na]^+$: 245.1148, found: 245.1145.

2.1.4.2 6-Hydroxy-3,6-dimethylcyclohex-2-enone 4d



JohnPhosAuCl (3.6 mg, 6.75 μmol) and $AgSbF_6$ (9.3 mg, 27 μmol) were added to a solution of diyne **1d** (30 mg, 0.135 mmol) in dry 1,2-dichloroethane (1.5 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 24 h, filtered through a short plug of celite and the celite was washed with CH_2Cl_2. The organic extract was washed with H_2O, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified

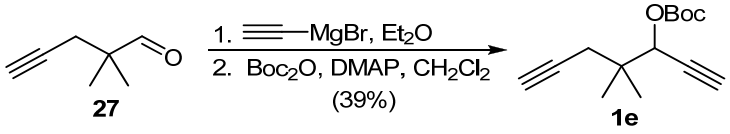
[6] Boaventura, M. A.; Drouin, J. *J. Bull. Soc. Chim. Fr.* **1987**, *6*, 1015-1026.

by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 4:1) to give 6-hydroxy-3,6-dimethylcyclohex-2-enone **4d** (11.7 mg, 62%), as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (s, 1H), 3.68 (s, 1H), 2.52-2.31 (m, 2H), 2.10 (ddd, J^1 = 13.2 Hz, J^2 = 5.2 Hz, J^3 = 2.3 Hz, 1H), 2.06-2.01 (m, 1H), 1.98 (s, 3H), 1.31 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 163.2, 123.1, 72.3, 35.4, 30.3, 24.2 (two carbons).
IR_{film}: 3475, 2974, 2931, 1673, 1438, 1377, 1264, 1217, 1163, 1115, 1026, 977.
HRMS (ESI): calcd. for $C_8H_{13}O_2$ $[M+H]^+$: 141.0910 found: 141.0904.

2.1.5 Entry 5

2.1.5.1 tert-Butyl (4,4-dimethylhepta-1,6-diyn-3-yl) carbonate (1e)

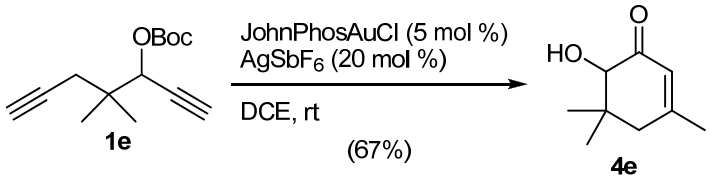


A solution of ethynylmagnesium bromide (0.5 M in THF, 5.45 mL, 2.72 mmol) was added to a solution of aldehyde **27**[7] (300 mg, 2.72 mmol) in Et_2O (15 mL), at 0 °C, under an argon atmosphere. After 10 min, saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O (2 x 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.
A solution of the previously obtained crude propargyl alcohol (370 mg, 2.72 mmol), di-*tert*-butyl dicarbonate (652 mg, 2.99 mmol) and DMAP (33 mg, 0.27 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 2 h at rt and the reaction quenched with H_2O, the organic extract was dried over anh. $MgSO_4$ and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to give **1e** (250 mg, 39%) as a viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.13 (d, J = 2.2 Hz, 1H), 2.50 (d, J = 2.2 Hz, 1H), 2.30 (d, J = 2.7 Hz, 2H), 2.02 (t, J = 2.7 Hz, 1H), 1.50 (s, 9H), 1.13 (d, J = 2.2 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 82.7, 80.7, 79.0, 75.2, 72.7, 70.8, 37.9, 28.1, 27.7, 22.7, 22.3.
IR_{film}: 3294, 2979, 2937, 1748, 1464, 1371, 1280, 1256, 1164, 1086, 1034, 951, 851.
HRMS (ESI): calcd. for $C_{14}H_{20}O_3Na$ $[M+Na]^+$: 259.1307, found: 259.1305.

[7] Rigby, J. H.; Laxmisha, M. S.; Hudson, A. R.; Heap, C. H.; Heeg M. J. *J. Org. Chem*. **2004**, *69*, 6751-6760.

2.1.5.2 6-Hydroxy-3,5,5-trimethylcyclohex-2-enone (4e)

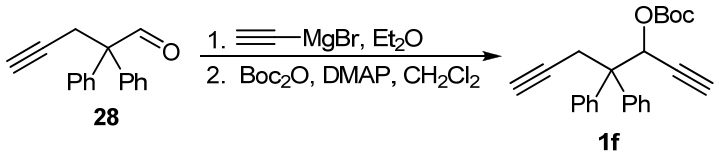


added JohnPhosAuCl (11.2 mg, 21 μmol) and $AgSbF_6$ (29.1 mg, 85 μmol) were added to a solution of diyne **1e** (100 mg, 0.423 mmol) in dry 1,2-dichloroethane (4 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 16 h and evaporated to dryness. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 5:1) to give 6-hydroxy-3,5,5-trimethylcyclohex-2-enone **4e** (44 mg, 67%), as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.94 (dq, *J* = 2.7, 1.3 Hz, 1H), 3.93 (bs, 1H), 3.71 (s, 1H), 2.44 (d, *J* = 18.0 Hz, 1H), 2.13 (d, *J* = 18.5 Hz, 1H), 1.94 (s, 3H), 1.17 (s, 3H), 0.80 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 161.7, 123.0, 79.7, 45.9, 39.4, 27.6, 24.5, 18.0.
IR_{film}: 3474, 2970, 2872, 1673, 1437, 1380, 1243, 1148, 1098, 947, 892.
HRMS (ESI): calcd. for $C_9H_{15}O_2$ $[M+H]^+$: 155.1067, found: 155.1063.

2.1.6 Entry 6

2.1.6.1 tert-Butyl (4,4-diphenylhepta-1,6-diyn-3-yl) carbonate (1f)



A solution of ethynylmagnesium bromide (0.5 M in THF, 3.3 mL, 1.64 mmol) was added to a solution of aldehyde **28**[8] (350 mg, 1.49 mmol) in Et_2O (15 mL), at 0 °C, under an argon atmosphere. After 10 min, a diluted HCl (4.3%) was added, and the mixture was extracted with EtOAc (2 x 30 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.
A solution of previously obtained crude propargyl alcohol (389 mg, 1.49 mmol), di-*tert*-butyl dicarbonate (359 mg, 1.64 mmol) and DMAP (18.3 mg, 0.15 mmol) in dry CH_2Cl_2 (15 mL) was stirred for 10 min at rt and the reaction mixture was quenched with H_2O, the organic layer was dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 9:1) to give **1f** (474 mg, 88%) as a white solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.51-7.17 (m, 10H), 6.16 (d, *J* = 2.0 Hz, 1H), 3.17 (d, *J* = 2.4 Hz, 2H), 2.47 (d, *J* = 1.9 Hz, 1H), 1.97 (t, *J* = 2.2 Hz, 1H), 1.44 (s, 9H).

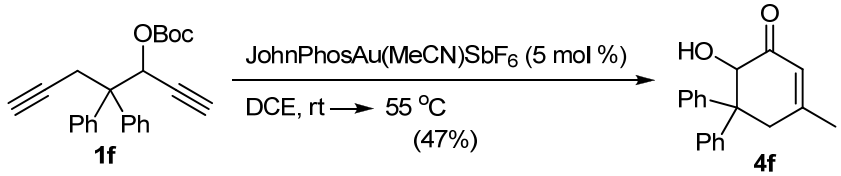
[8] Nakamura, I.; Chan, C. S.; Araki T.; Terada, M.; Yamamoto, Y. *Org. Lett*. **2008**, *10*, 309-312.

^{13}C NMR (50 MHz, $CDCl_3$): δ 152.6, 142.2, 141.9, 129.4, 129.1, 127.6, 127.5, 127.1, 126.9, 82.9, 80.2, 79.0, 76.4, 72.4, 70.2, 53.8, 29.2, 27.6.

IR_{film}: 3286, 3023, 2979, 2932, 1754, 1498, 1448, 1393, 1368, 1297, 1270, 1251, 1157, 1091, 1042, 954, 863, 791, 704, 634.

HRMS (ESI): calcd. for $C_{24}H_{28}O_3N$ $[M+NH_4]^+$: 378.2064, found: 378.2063.

2.1.6.2 6-Hydroxy-3-methyl-5,5-diphenylcyclohex-2-enone (4f)



To a solution of diyne **1f** (55 mg, 0.153 mmol) in dry 1,2-dichloroethane (2 mL) was added commercial JohnPhosAu(MeCN)SbF_6 (5.9 mg, 7.63 μmol), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 3 days at room temperature and additional 24 h at 55 °C. The reaction mixture was evaporated to dryness and purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 6:1) to give 6-hydroxy-3-methyl-5,5-diphenylcyclohex-2-enone **4f** (20 mg, 47%), as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37-7.22 (m, 10H), 6.01 (s, 1H), 5.10 (d, J = 2.9 Hz, 1H), 4.00 (d, J = 2.9 Hz, 1H), 3.13 (d, J = 18.7 Hz, 1H), 2.92 (d, J = 18.8 Hz, 1H), 2.11 (s, 3H).

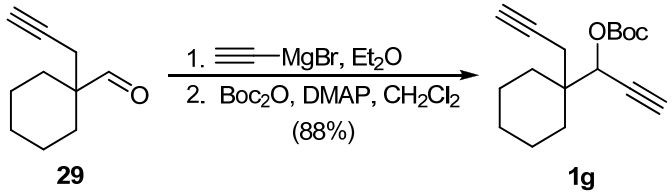
^{13}C NMR (50 MHz, $CDCl_3$): δ 197.8, 161.3, 146.8, 140.1, 129.8, 128.4, 127.6, 127.2, 126.9, 126.5, 124.4, 77.2, 55.4, 46.1, 24.1.

IR_{film}: 3449, 3057, 2928, 2852, 1833, 1677, 1495, 1443, 1379, 1266, 1124, 1056, 759, 737, 701.

HRMS (ESI): calcd. for $C_{19}H_{18}O_2Na$ $[M+Na]^+$: 301.1205, found: 301.1186.

2.1.7 Entry 7

2.1.7.1 tert-Butyl (1-(1-(prop-2-yn-1-yl)cyclohexyl)prop-2-yn-1-yl) carbonate (1g)



A solution of ethynylmagnesium bromide (0.5 M in THF, 5.27 mL, 2.64 mmol) was added to a solution of aldehyde **29**[9] (330 mg, 2.20 mmol) in Et_2O (15 mL), at 0 °C, under an argon atmosphere. After 10 min, a diluted HCl (4.3 %) was added, and the mixture was extracted with EtOAc (2 x 25 mL). The combined organic extracts were washed

[9] Chen, Y.; Chulbom, L. *J. Am. Chem. Soc.* **2006**, *128*, 15598-15599.

with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification.

A solution of previously obtained crude propargyl alcohol, di-*tert*-butyl dicarbonate (527 mg, 2.42 mmol) and DMAP (27 mg, 0.22 mmol) in CH_2Cl_2 (20 mL) was stirred for 2 h at rt The reaction was quenched with H_2O, the organic layer was dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to give **1g** (535 mg, 88%) as a white solid.

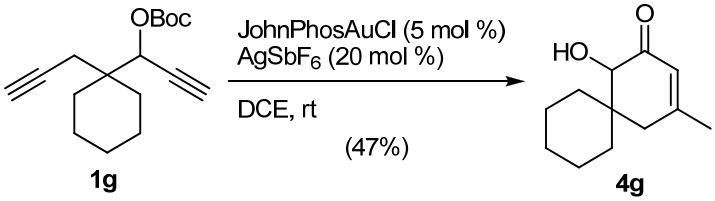
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.39 (d, J = 2.2 Hz, 1H), 2.50 (d, J = 2.2 Hz, 1H), 2.47 (dd, J^1 = 6.6, J^2 = 2.7 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.72-1.61 (m, 3H), 1.60-1.51 (m, 4H), 1.50 (s, 9H), 1.47-1.29 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 82.6, 80.7, 79.0, 75.7, 71.2, 71.0, 40.2, 29.9, 29.1, 27.7, 25.5, 23.0, 21.2, 21.1.

IR_{film}: 3287, 2986, 2936, 2869, 1733, 1460, 1391, 1370, 1338, 1285, 1259, 1151, 1112, 1083, 1036, 1005, 957, 866.

HRMS (ESI): calcd. for $C_{17}H_{28}O_3N$ $[M+NH_4]^+$: 294.2064, found: 294.2063.

2.1.7.2 1-Hydroxy-4-methylspiro[5.5]undec-3-en-2-one (4g)



JohnPhosAuCl (2.9 mg, 5.4 μmol) and $AgSbF_6$ (7.5 mg, 22 μmol) were added to a solution of diyne **1g** (30 mg, 0.109 mmol) in dry 1,2-dichloroethane (1 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 24 h and evaporated to dryness. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 7:1) to give 1-hydroxy-4-methylspiro[5.5]undec-3-en-2-one **4g** (10 mg, 47%), as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.96 (dq, J^1 = 2.6 Hz, J^2 = 1.3 Hz, 1H), 3.90 (d, J = 1.7 Hz, 1H), 3.70 (d, J = 2.3 Hz, 1H), 2.74 (d, J = 18.6 Hz, 1H), 2.15-2.09 (m, 1H),), 1.98 (s, 3H), 1.91 (td, J^1 = 13.4, J^2 = 3.8 Hz, 1H), 1.67-1.59 (m, 3H), 1.59-1.52 (m, 1H), 1.47-1.10 (m, 5H).

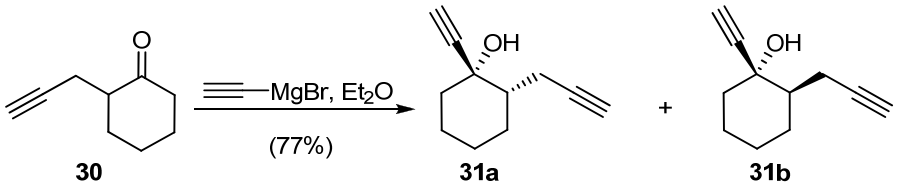
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.6, 161.3, 123.0, 79.9, 42.4, 39.4, 35.4, 25.8, 24.8, 23.8, 21.7, 21.3.

IR_{film}: 3475, 2933, 2858, 2667, 2566, 1761, 1674, 1450, 1378, 1261, 1239, 1116, 1091, 927.

HRMS (ESI): calcd. for $C_{12}H_{18}O_2Na$ $[M+Na]^+$: 217.1205 found: 217.1191.

2.1.8 Entries 8 and 9

2.1.8.1 rel-(1S,2S)-1-Ethynyl-2-(prop-2-yn-1-yl)cyclohexan-1-ol (31a) and rel-(1S,2R)-1-ethynyl-2-(prop-2-yn-1-yl)cyclohexan-1-ol (31b)



Ketone **30**[10] (360 mg, 2.64 mmol) was added to a solution of ethynylmagnesium bromide (5.82 mL, 2.91 mmol) in dry Et_2O (25 mL), at 0 °C, under an argon atmosphere. After 2 h, the reaction was quenched with saturated aqueous solution of NH_4Cl and extracted with diethyl ether. The organic extract was dried over $MgSO_4$, filtered and concentrated on rotovap. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to give: **31a** (167 mg, 39%) and **31b** (162 mg, 38%), both as colorless liquids.

*Physical data for **31a:***

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.67 (td, J^1 = 16.9, J^2 = 6.2 Hz, 1H), 2.48 (s, 1H), 2.39 (ddd, J^1 = 16.9, J^2 = 9.4, J^3 = 2.7 Hz, 1H), 2.19 (s, 1H), 2.04-1.97 (m, 2H), 1.88-1.81 (m, 1H), 1.78-1.46 (m, 6H), 1.35-1.25 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 87.6, 83.5, 71.9, 69.9, 69.3, 44.7, 39.6, 25.6, 24.8, 20.7, 20.2.

IR_{film}: 3526, 3296, 2936, 2859, 2115, 1701, 1650, 1558, 1449, 1367, 1303, 1274, 1192, 1142, 1055, 975, 952, 634.

HRMS (ESI): calcd. for $C_{11}H_{18}ON$ $[M+NH_4]^+$: 180.1383, found: 180.1382.

*Physical data for **31b:***

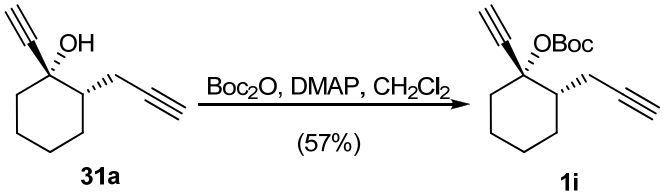
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.80 (s, 1H), 2.72 (ddd, J^1 = 16.9, J^2 = 5.6, J^3 = 2.7 Hz, 1H), 2.53 (s, 1H), 2.14 (ddd, J^1 = 16.9, J^2 = 8.9, J^3 = 2.7 Hz, 1H), 2.06-2.01 (m, 2H), 1.99-1.93 (m, 1H), 1.75-1.66 (m, 3H), 1.60-1.49 (m, 2H), 1.28-1.17 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 84.0, 83.8, 74.8, 72.5, 69.6, 46.8, 40.8, 29.3, 25.2, 23.7, 20.3.

IR_{film}: 3397, 3297, 2935, 2859, 2115, 1448, 1324, 1127, 1055, 1032, 950, 633.

HRMS (ESI): calcd. for $C_{11}H_{13}$ $[M+H-H_2O]^+$: 145.1012, found: 145.1011.

2.1.8.2 rel-tert-Butyl ((1S,2S)-1-ethynyl-2-(prop-2-yn-1-yl)cyclohexyl) carbonate (1i)



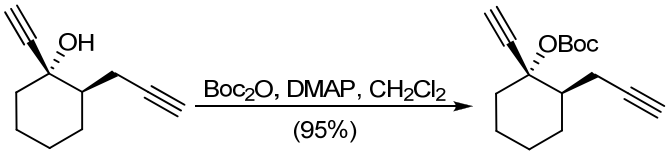
A solution of **31a** (140 mg, 0.86 mmol), di-*tert*-butyl dicarbonate (248 mg, 1.14 mmol) and DMAP (210 mg, 1.72 mmol) in CH_2Cl_2 (10 mL) was stirred for 4 days, at rt. The reaction was quenched with H_2O, the organic extract was

[10] Harrison, T. J.; Kozak, J. A.; Corbella-Pane, M.; Dake, G. R. *J. Org. Chem.* **2006**, *71*, 4524-4529.

dried over anh. $MgSO_4$, filtered and concentrated on rotovap. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to afford **1i** (130 mg, 57%, 88% brsm) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.84 – 2.72 (m, 2H), 2.60 (s, 1H), 2.24 (ddd, J^1 = 16.8, J^2 = 11.4, J^3 = 2.6 Hz, 1H), 2.07-1.99 (m, 1H), 1.95 (t, J = 2.7 Hz, 1H), 1.94-1.88 (m, 1H), 1.71 (m 1H), 1.67-1.53 (m, 3H), 1.51-1.46 (m, 9H), 1.44-1.31 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 151.3, 83.4, 83.2, 82.1, 76.6, 74.2, 69.0, 45.8, 34.6, 27.8, 25.6, 24.2, 20.8, 19.9.
IR_{film}: 3291, 3268, 2981, 2938, 2856, 2116, 1451, 1392, 1369, 1254, 1162, 1145, 1096, 971, 920, 871, 852, 789.
HRMS (ESI): calcd. for $C_{16}H_{22}O_3Na$ $[M+Na]^+$: 285.1461, found: 285.1456.

2.1.8.3 rel-tert-Butyl ((1S,2R)-1-ethynyl-2-(prop-2-yn-1-yl)cyclohexyl) carbonate (1h)

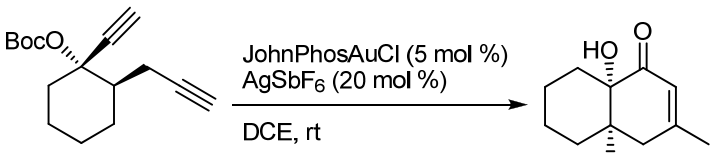


31b **1h**

A solution of **31b** (140 mg, 0.86 mmol), di-*tert*-butyl dicarbonate (248 mg, 1.14 mmol) and DMAP (210 mg, 1.72 mmol) in CH_2Cl_2 (10 mL) was stirred for 4 days, at rt. The reaction was quenched with H_2O, the organic extract was dried over anh. $MgSO_4$, filtered and concentrated on rotovap. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to afford **1h** (216 mg, 95%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.78-2.67 (m, 2H), 2.64 (s, 1H), 2.19-2.08 (m, 2H), 1.93-1.86 (m, 2H), 1.74-1.65 (m, 2H), 1.63-1.49 (m, 2H), 1.46 (s, 9H), 1.37-1.17 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 83.0, 82.2, 80.0, 79.7, 77.2, 69.1, 45.4, 35.9, 28.0, 27.8, 27.8, 24.8, 23.4, 19.9.
IR_{film}: 3750, 3281, 2982, 2936, 2864, 1735, 1452, 1392, 1368, 1282, 1251, 1157, 1128, 1082, 1055, 966, 928, 861, 821, 789.
HRMS (ESI): calcd. for $C_{16}H_{22}O_3Na$ $[M+Na]^+$: 285.1461, found: 285.1468.

2.1.8.4 rel-(4aR,8aS)-8a-Hydroxy-3-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4H)-one (4h)



1h **4h**

JohnPhosAuCl (4.6 mg, 8.6 mmol) and $AgSbF_6$ (11.8 mg, 34 μmol) were added to a solution of diyne **1h** (45 mg, 0.172 mmol) in dry 1,2-dichloroethane (3.5 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 24 h and evaporated to dryness. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 8:1) to give bicyclic enone **4h** (21 mg, 68%), as a yellowish oil.

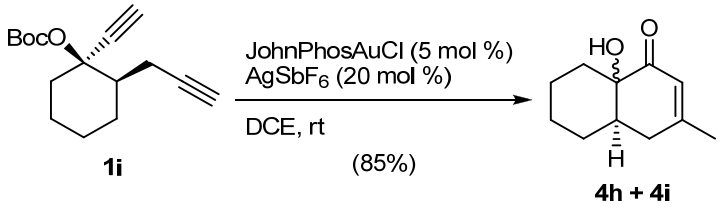
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (s, 1H), 3.48 (s, 1H), 2.57 (dd, J^1 = 18.5, J^2 = 11.4 Hz, 1H), 2.23-2.13 (m, 2H), 1.97 (d, J = 1.2 Hz, 3H), 1.95-1.89 (m, 1H), 1.81-1.72 (m, 2H), 1.62-1.47 (m, 3H), 1.42-1.36 (m, 1H), 1.30-1.23 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7, 163.1, 123.0, 73.9, 38.7, 34.3, 31.0, 25.2, 24.4, 19.9, 19.8.

IR_{film}: 3474, 2923, 2873, 1821, 1664, 1439, 1381, 1353, 1247, 1171, 1137, 1042, 1012, 927, 869.

HRMS (ESI): calcd. for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223, found: 181.1229.

2.1.8.5 rel-(4aR,8aS)-8a-hydroxy-3-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4H)-one (4h) and (4aR,8aR)-8a-hydroxy-3-methyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4H)-one (4i)



1i → **4h + 4i**

trans/*cis*=1:1.8

JohnPhosAuCl (5.6 mg, 10.5 mmol) and $AgSbF_6$ (14.4 mg, 42 μmol) were added to a solution of diyne **1i** (55 mg, 0.21 mmol) in dry 1,2-dichloroethane (3.5 mL), at room temperature, under an argon atmosphere. The resulting mixture was stirred for 7 days and evaporated to dryness. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 8:1) to give bicyclic enone **4h** (21 mg, 56%) and enone **4i** (11 mg, 29%), both as yellowish oils.

*Physical data for isomer **4i**:*

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (s, 1H), 2.37 (ddd, J^1 = 18.4, J^2 = 10.7, J^3 = 2.4 Hz, 1H), 2.09 (ddd, J^1 = 14.4, J^2 = 4.7, J^3 = 3.2 Hz, 1H), 2.01 (dd, J^1 = 18.5, J^2 = 4.5 Hz, 1H), 1.96 (s, 3H), 1.87-1.79 (m, 1H), 1.78-1.58 (m, 4H), 1.54-1.48 (m, 1H), 1.35-1.21 (m, 2H).

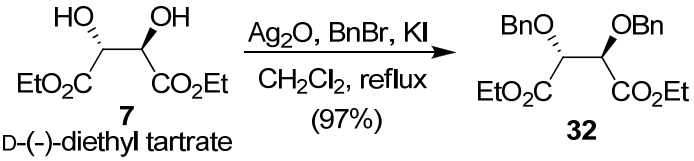
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0, 162.3, 123.8, 71.2, 41.7, 34.8, 31.4, 27.3, 25.4, 24.3, 20.9.

IR_{film}: 3420, 3039, 2976, 2932, 2858, 1821, 1647, 1435, 1381, 1312, 1251, 1208, 1141, 1108, 1064, 949, 869.

HRMS (ESI): calcd. for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223, found: 181.1230.

2.2 Synthesis of (–)-*epi*-gabosine H (5) and (–)-gabosine H (*epi*-5) (as described in Schemes 3, 4 and 5)

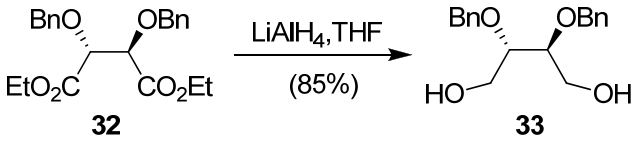
2.2.1.1 Diethyl (2R,3R)-2,3-bis(benzyloxy)succinate (32)[11]



To a solution of D-(–)-diethyl tartrate **7** (4.3 mL, 0.03 mol) in dry CH_2Cl_2 (50 mL), BnBr (8.9 mL, 75 mmol), Ag_2O (12.4 g, 53 mmol), and KI (0.8 g, 5 mmol) were added. The reaction mixture was refluxed under an argon atmosphere for 1 h and filtered through a short pad of celite. The filtrate was washed with water, dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residual oil was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 9:1 → 5:1), to give **32** (9.5 g, 97%), as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.22 (m, 10H), 4.87 (d, *J* = 12.0 Hz, 2H), 4.45 (d, *J* = 12.0 Hz, 2H), 4.40 (s, 2H), 4.24-4.15 (m, 2H), 4.11-4.01 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 136.9, 128.4, 128.3, 128.2, 128.2, 127.8, 78.3, 73.1, 61.2, 14.0.
IR_{film}: 3474, 2923, 2873, 1821, 1664, 1439, 1381, 1353, 1247, 1171, 1137, 1042, 1012, 927, 869.
HRMS (ESI): calcd. for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223, found: 181.1229.
$[\alpha]_D^{25}$ -120.4 (*c* 0.8, $CHCl_3$).

2.2.1.2 (2S,3S)-2,3-bis(Benzyloxy)butane-1,4-diol (33)[12]



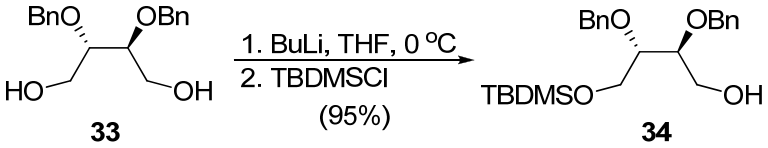
A suspension of lithium aluminum hydride (3.57 g, 94 mmol) in dry Et_2O (60 mL) was added dropwise over 1 h to a cold (0 °C) solution of **32** (11.00 g, 28.5 mmol) in dry Et_2O (60 mL), under an argon atmosphere. The reaction mixture was then refluxed for 4 h. The excess of LAH was destroyed by sequential addition of H_2O (4.5 mL), 15% NaOH (4.5 mL) and H_2O (4.5 mL) at 0 °C. The reaction mixture was filtered through a celite, and the celite pad was washed with Et_2O. After solvent removal, the residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 1:1), to yield diol **33** (11.2 g, 85 %) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.26 (m, 10H), 4.63 (d, *J* = 1.7 Hz, 4H), 3.79 (d, *J* = 11.5 Hz, 2H), 3.73-3.63 (m, 2H), 2.61 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 128.5, 127.9, 78.9, 72.5, 60.7.

[11] Ahn, M.; Pietersma, A. L.; Schofield, L. R.; Parker, E. J. *J. Org. Biomol. Chem*. **2005**, *3*, 4046-4049.
[12] Wu, S.-F.; Ruan, Y.-P.; Zheng, X.; Huang, P.-Q. *Tetrahedron*, **2010**, *66*, 1653-1660.

$[\alpha]_D^{25}$ -10.9 (*c* 0.8, $CHCl_3$).

2.2.1.3 (2S,3S)-2,3-bis(Benzyloxy)-4-((tert-butyldimethylsilyl)oxy)butan-1-ol (34)[13]



33 **34**

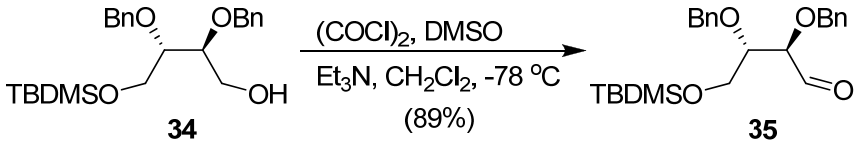
n-Butyllithium (2.15 M in hexane, 10.3 mL, 22,2 mmol) was added dropwise (20 min) to a solution of diol **33** (6.40 g, 21.2 mmol) in THF (125 mL), at 0 °C, under an argon atmosphere. The resulting solution was stirred at 0 °C for 45 min, whereupon *tert*-butylchlorodimethylsilane (3.51 g, 23.3 mmol) in THF (35 mL) was added. After being stirred at 0 °C for 1 h, the reaction was quenched with saturated aqueous solution of $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extract was dried over anh. $MgSO_4$ and concentrated. The crude material was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 4:1) to give alcohol **34** (8.38 g, 95%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.26 (m, 10H), 4.76-4.63 (m, 3H), 3.87-3.73 (m, 3H), 3.73-3.63 (m, 3H), 2.48-2.44 (m, 1H), 0.92 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4, 138.3, 128.4, 128.3, 127.9, 127.9, 127.7, 127.7, 80.2, 79.3, 73.0, 72.8, 62.3, 61.5, 25.8, 18.2, -5.5.

$[\alpha]_D^{25}$ -12.5 (*c* 0.95, $CHCl_3$).

2.2.1.4 (2R,3S)-2,3-bis(Benzyloxy)-4-((tert-butyldimethylsilyl)oxy)butanal (35)[14]



34 **35**

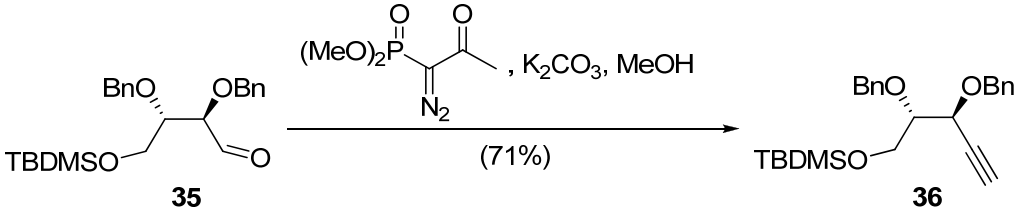
DMSO (146 mg, 0.15 mL, 1.87 mmol) was added dropwise over 10 min to a stirred solution of oxalyl chloride (128 mg, 90 μL, 1.01 mmol) in dry CH_2Cl_2 (5 mL), at -78 °C, under an argon atmosphere. After 20 min, a solution of alcohol **34** (300 mg, 0.72 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise. After stirring at -78 °C for 1 h, Et_3N (423 mg, 0.58 mL, 4.18 mmol) was added dropwise over 15 min and stirring was continued for 1 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with 4.3 % $HCl_{(aq)}$, saturated aqueous solution of $NaHCO_3$, and brine, dried over anh. $MgSO_4$ and concentrated. Purification by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 7:1) afforded aldehyde **35** (265 mg, 89%), as a viscous oil.

[13] Fourriere, G.; Leclerc, E.; Quirion, J.-C.; Pannecoucke, X. *J. Fluor. Chem*. **2012**, *134*, 172-179.
[14] Dorfmueller, H. C.; Borodkin, V. S.; Schimpl, M.; Shepherd, S. M.; Shpiro, N. A.; van Aalten, D. M. F. *J. Am. Chem. Soc.* **2006**, *128*, 16484-16485.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (d, J = 1.1 Hz, 1H), 7.38-7.21 (m, 10H), 4.74 (d, J = 11.9 Hz, 1H), 4.63-4.53 (m, 3H), 3.97 (dd, J^1 = 3.8, J^2 = 1.1 Hz, 1H), 3.85-3.70 (m, 3H), 0.97-0.83 (m, 9H), 0.09 – -0.06 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9, 137.8, 137.3, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 82.8, 79.8, 73.5, 73.0, 60.9, 25.8, 18.2, -5.5, -5.6.

$[\alpha]_D^{25}$ -8.9 (*c* 1.23, $CHCl_3$).

2.2.1.5 (((2S,3S)-2,3-bis(Benzyloxy)pent-4-yn-1-yl)oxy)(tert-butyl)dimethylsilane (36)[13]

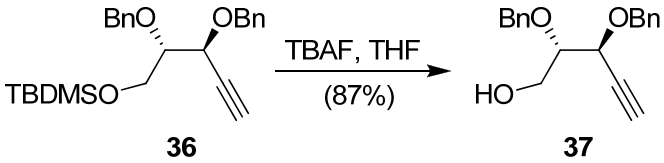


Bestmann-Ohira reagent (0.74 g, 3.6 mmol) was added to a solution of aldehyde **35** (1.00 g, 2.41 mmol) in MeOH (25 mL), followed by the addition of solid K_2CO_3 (0.40 g, 2.89 mmol) in one portion. The resulting suspension was stirred at room temperature for 4 h, and the reaction was quenched with saturated aqueous solution of NH_4Cl. The mixture was extracted with Et_2O (2x50 mL), the organic extract was washed with water and brine, dried over anh. $MgSO_4$ and evaporated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to afford acetylene **36** (705 mg, 71%), as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.26 (m, 10H), 4.84 (d, J = 11.9 Hz, 1H), 4.78 (q, J = 11.9 Hz, 2H), 4.55 (d, J = 11.9 Hz, 1H), 4.29 (dd, J^1 = 5.1, J^2 = 2.2 Hz, 1H), 3.90 (dd, J^1 = 10.7, J^2 = 4.3 Hz, 1H), 3.78 (dd, J^1 = 10.7, J^2 = 6.2 Hz, 1H), 3.68-3.64 (m, 1H), 2.50 (d, J = 2.2 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6, 137.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 81.3, 80.6, 75.2, 73.7, 71.0, 68.7, 63.0, 25.9, 18.2, -5.4, -5.5.

$[\alpha]_D^{25}$ - 42.6 (*c* 0.51, $CHCl_3$).

2.2.1.6 (2R,3R)-2,3-bis(Benzyloxy)pent-4-yn-1-ol (37)[13]

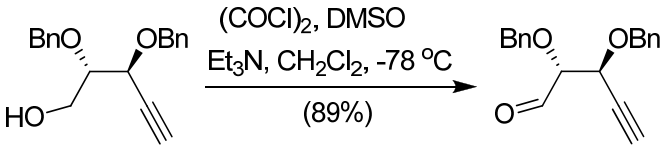


A solution of TBAF·$3H_2O$ (2.28 g, 7.23 mmol) in THF (10 mL) was added to a solution of acetylene **36** (2.70 g, 6.58 mmol) in THF (50 mL), at 0 °C, and the mixture was stirred for 4 h. The reaction mixture was diluted with water and product was extracted with Et_2O (2 x 70 mL). The combined layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude material was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 7:1 → 4:1) to give alcohol **37** (1.69 g, 87%), as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.26 (m, 10H), 4.84 (dd, J^1 = 13.9 Hz, J^2 = 11.7 Hz, 2H), 4.65 (d, J = 11.6 Hz, 1H), 4.56-4.52 (m, 1H), 4.32 (dd, J^1 = 6.1 Hz, J^2 = 2.2 Hz, 1H), 3.88 (dd, J^1 = 11.6 Hz, J^2 = 4.1 Hz, 1H), 3.77 (dd, J^1 = 11.6 Hz, J^2 = 6.0 Hz, 1H), 3.71 (m, 1H), 2.56 (d, J = 2.2 Hz, 1H), 2.04 (s, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 137.2, 128.5, 128.4, 128.0, 127.9, 127.8, 80.3, 79.6, 76.2, 73.6, 71.1, 69.8, 62.2.

$[\alpha]_D^{25}$ -47.0 (*c* 1.25, $CHCl_3$).

2.2.1.7 (2S,3R)-2,3-bis(Benzyloxy)pent-4-ynal (8)[13]

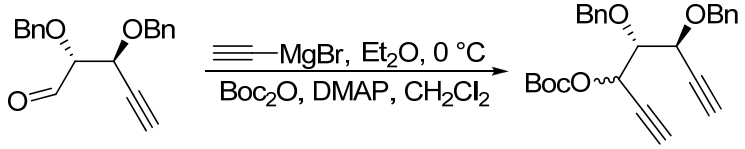


37 **8**

DMSO (137 mg, 0.14 mL, 1.76 mmol) was added dropwise over 10 min to a stirred solution of oxalyl chloride (120 mg, 0.08 mL, 0.95 mmol) in dry CH_2Cl_2 (5 mL), at -78 °C, under an argon atmosphere. After 20 min, a solution of alcohol **37** (200 mg, 0.68 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise. After stirring at -78 °C for 1 h, Et_3N (396 mg, 0.55 mL, 3.91 mmol) was added dropwise over 15 min and the mixture was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with 4.3 % $HCl_{(aq)}$, saturated aqueous solution of $NaHCO_3$, and brine, dried over anh. $MgSO_4$ and concentrated. Purification by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 5:1) afforded aldehyde **8** (265 mg, 89%), as a viscous oil in a mixture with 5% of isomerized aldehyde.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.68 (d, J = 1.4 Hz, 1H), 7.39-7.26 (m, 10H), 4.85-4.74 (m, 4H), 4.54 (dd, J^1 = 11.9, J^2 = 5.6 Hz, 1H), 4.44 (dd, J^1 = 4.4, J^2 = 2.2 Hz, 1H), 3.93 (dd, J^1 = 4.4, J^2 = 1.4 Hz, 1H), 2.62 (d, J = 2.2 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 136.8, 136.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 83.5, 78.5, 77.0, 73.6, 70.9, 68.1.

2.2.1.8 (3R,4R,5S)-4,5-bis(Benzyloxy)hepta-1,6-diyn-3-yl tert-butyl carbonate (10a) and (3S,4R,5S)-4,5-bis(benzyloxy)hepta-1,6-diyn-3-yl tert-butyl carbonate (10b)



8 **10a,b**

A solution of ethynylmagnesium bromide (0.5 M in THF, 19.0 mL, 9.51 mmol) was added to a solution of aldehyde **8** (2.0 g, 6.79 mmol) in Et_2O (70 mL), at 0 °C, under an argon atmosphere. After 10 min, the reaction was quenched

by the addition of saturated aqueous solution of NH_4Cl and the mixture was extracted with Et_2O (2 x 50 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was immediately used in the next step without further purification and the yield was considered as a quantitative.

To a solution of previously obtained crude propargyl alcohol (2.18 g, 6.79 mmol) in CH_2Cl_2 (65 mL) were added di-*tert*-butyl dicarbonate (1.86 g, 8.51 mmol) and DMAP (83 mg, 0.68 mmol) at room temperature. The reaction mixture was stirred for 2 h and quenched by the addition of water, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95:5) to give a mixture of inseparable products **10a** and **10b** (2.7 g, 94%), as a viscous oil (ca. 1:1 ratio).

*Physical data for the mixture of **10a** and **10b***

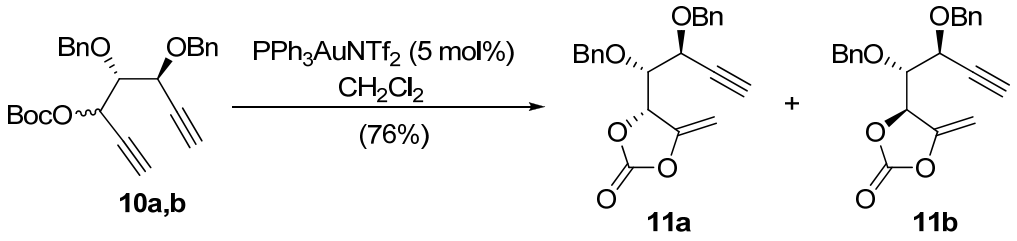
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.41 (m, 20H), 5.61 (dd, J^1 = 5.0, J^2 = 2.2 Hz, 1H), 5.59 (dd, J^1 = 6.6, J^2 = 2.3 Hz, 1H), 4.73-4.93 (m, 6H), 4.55 (d, J = 3.6 Hz, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.49 (dd, J^1 = 4.1, J^2 = 2.3 Hz, 1H), 4.34 (dd, J^1 = 6.0, J^2 = 2.4 Hz, 1H), 3.92 (dd, J^1 = 6.0, J^2 = 4.9 Hz, 1H), 3.86 (dd, J^1 = 6.7, J^2 = 4.2 Hz, 1H), 2.58 (d, J = 2.1 Hz, 1H), 2.55 (d, J = 2.4 Hz, 1H), 2.51 (d, J = 2.4 Hz, 1H), 2.38 (d, J = 2.4 Hz, 1H), 1.46 (s, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 152.3, 152.0, 137.8, 137.7, 137.3, 137.0, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 83.0, 82.8, 82.1, 80.8, 79.5, 79.2, 78.3, 78.2, 76.7, 76.1, 75.8, 75.7, 75.6, 75.2, 71.1, 71.1, 69.4, 68.7, 67.0, 66.6, 27.6.

IR_{film}: 3284, 2980, 1747, 1275, 1256, 1159, 1089, 697.

HRMS (ESI): calcd. for $C_{26}H_{32}NO_5$ $[M+NH_4]^+$: 438.2275, found: 438.2265.

2.2.1.9 (S)-4-((1S,2R)-1,2-bis(Benzyloxy)but-3-yn-1-yl)-5-methylene-1,3-dioxolan-2-one (11a) and (R)-4-((1S,2R)-1,2-bis(benzyloxy)but-3-yn-1-yl)-5-methylene-1,3-dioxolan-2-one (11b)



$Ph_3PAuNTf_2$ (119 mg, 0.161 mmol) was added to a solution of **10a,b** (2.7 g, 6.42 mmol) in CH_2Cl_2 (25 mL), under an argon atmosphere. After 80 min, the reaction mixture was concentrated and the residue was purified by flash chromatography (Biotage SP1, SiO_2, 40+M, 132 mL CV; eluent: petroleum ether/ethyl acetate 100:0 → 9:1). After two purifications, both diastereisomers were separated: **11a** (950 mg, 41%) was obtained as viscous oil and **11b** (820 mg, 35%) as a yellowish solid.

*Physical data for **11a**:*

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.28 (m, 10H), 5.52 (dt, J^1 = 3.7, J^2 = 1.8 Hz, 1H), 4.92 (d, J = 11.0 Hz, 1H), 4.91 (dd, J^1 = 3.7, J^2 = 2.2 Hz, 1H), 4.88 (d, J = 11.4 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 4.57 (d, J = 11.4 Hz, 1H), 4.54 (dd, J^1 = 3.8, J^2 = 1.7 Hz, 1H), 4.37 (dd, J^1 = 7.0, J^2 = 2.2 Hz, 1H), 3.97 (dd, J^1 = 7.0, J^2 = 3.8 Hz, 1H), 2.73 (d, J = 2.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 149.6, 136.9, 136.8, 128.5, 128.4, 128.0, 89.2, 80.6, 78.6, 78.4, 78.4, 76.0, 71.5, 69.1.

IR_{film}: 3285, 3064, 3032, 2871, 1837, 1690, 1455, 1320, 1147, 1103, 1057, 860, 803, 740.

HRMS (ESI): calcd. for $C_{22}H_{20}O_5Na$ $[M+Na]^+$: 387.1203, found: 387.1198.

$[\alpha]_D^{25}$ -119.5 (*c* 1.28, $CHCl_3$).

*Physical data for **11b**:*

mp 74-76 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.14 (m, 10H), 5.45 (dd, J^1 = 4.3, J^2 = 2.4 Hz, 1H), 4.84 (d, J = 10.9, 1H), 4.78 (d, J = 10.9 Hz, 1H), 4.72 (dd, J^1 = 4.2, J^2 = 1.8 Hz, 1H), 4.58 (d, J = 10.9 Hz, 1H), 4.49 (d, J = 10.9 Hz, 1H), 4.36 (dd, J^1 = 8.6, J^2 = 2.4 Hz, 1H), 4.21 (dd, J^1 = 4.8, J^2 = 2.4 Hz, 1H), 3.68 (dd, J^1 = 5.2, J^2 = 1.8 Hz, 1H), 2.60 (d, J = 2.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 150.9, 137.1, 137.0, 128.5, 128.3, 128.1, 128.0, 127.9, 87.2, 81.4, 78.9, 78.8, 77.7, 75.9, 71.8, 70.4.

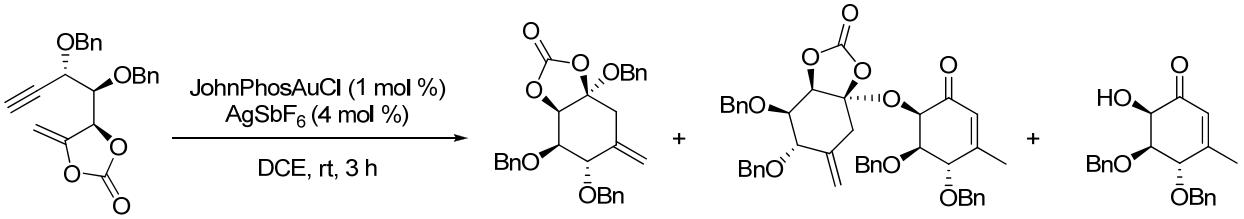
IR_{film}: 3231, 3117, 3032, 3013, 2937, 2873, 1822, 1690, 1453, 1349, 1273, 1145, 1061, 1022, 859, 752, 698.

HRMS (ESI): calcd. for $C_{22}H_{20}O_5Na$ $[M+Na]^+$: 387.1203, found: 387.1190.

$[\alpha]_D^{25}$ -35.0 (*c* 0.53, $CHCl_3$).

2.2.2 Synthesis of 6-*epi*-gabosine H (*epi*-5)

2.2.2.1 Cyclization of enol carbonate 11a in the absence of an external nucleophile



A flame dried Schlenk tube was charged with $AgSbF_6$ (1.2 mg, 3.5 μmol), JohnPhosAuCl (2.4 mg, 0.9 μmol) and dry 1,2-dichloroethane (3.2 mL), under an argon atmosphere. AgCl precipitate (suspension) formed immediately;

the Schlenk tube was protected from light using aluminum foil. A solution of enol carbonate **11a** (32.0 mg, 0.088 mmol) in dry 1,2-dichloroethane (0.9 mL) was added dropwise. After 3 h of stirring at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (2 mL), SiO_2 (120 mg) was added and the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 975:25) afforded 5.7 mg (11%) of **12** (colorless oil), 4.5 mg (18%) of dimer **13** (colorless oil) and 4.1 mg (15%) of enone **14** (colorless oil).

*Physical data for **12**:*

R_f=0.53 (benzene/ethyl acetate=975/25).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.22 (m, 15H), 5.32 (s, 1H), 5.20 (s, 1H), 4.79 (d, *J* = 4.4 Hz, 1H), 4.76 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.31 (d, *J* = 11.8 Hz, 1H), 4.03 (d, *J* = 4.6 Hz, 1H), 3.99 (t, *J* = 4.5 Hz, 1H), 3.07 (d, *J* = 14.9 Hz, 1H), 2.79 (dt, J^1 = 14.9, J^2 = 1.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 137.3, 137.2, 136.4, 136.1, 128.6, 128.5, 128.4, 128.1, 127.9, 127.9, 127.7, 127.6, 119.8, 106.4, 79.5, 78.7, 74.7, 73.7, 70.0, 65.0, 35.1.

IR_{ATR}: 3063, 3032, 2880, 1813, 1695, 1497, 1455, 1324, 1290, 1206, 1153, 1093, 1040, 938, 739, 700.

HRMS (ESI): calcd. for $C_{29}H_{32}NO_6$ $[M+NH4]^+$: 490.2224, found 490.2221, $C_{29}H_{28}O_6Na$ $[M+Na]^+$: 495.1778, found 495.1767, $C_{29}H_{28}O_6K$ $[M+K]^+$: 511.1518, found 511.1520.

$[\alpha]_D^{25}$ -47.3 (*c* 0.6, $CHCl_3$).

*Physical data for **13**:*

R_f=0.38 (benzene/ethyl acetate=975/25).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.27 (m, 20H), 5.88 (q, *J* = 1.4 Hz, 1H), 5.26 (s, 1H), 5.15 (s, 1H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.90 (bs, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 11.1 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.25 (*d*, *J* = 11.8 Hz, 1H), 4.13 (bs, 1H), 4.04 (t, *J* = 4.6 Hz, 1H), 3.99 (d, *J* = 4.5 Hz, 1H), 3.81 (bs, 1H), 3.04 (d, *J* = 15.0 Hz, 1H), 2.87 (d, *J* = 15.2 Hz, 1H), 1.88 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 153.8 (2xC), 137.6, 137.2, 137.2, 136.8, 135.9, 128.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 126.8, 119.6, 106.9, 79.7, 78.4 (2xCH), 77.5, 74.4, 74.0, 73.9 (CH and CH_2), 73.8, 70.0, 34.0, 21.6.

IR_{ATR}: 3062, 3031, 2919, 1815, 1699, 1496, 1454, 1206, 1150, 1093, 930, 739, 700.

HRMS (ESI): calcd. for $C_{43}H_{43}O_9$ $[M+H]^+$: 703.2902, found 703.2902, $C_{43}H_{42}O_9Na$ $[M+Na]^+$: 725.2721, found 725.2710, $C_{43}H_{42}O_9K$ $[M+K]^+$: 741.2460, found 741.2460.

$[\alpha]_D^{25}$ -80.9 (*c* 0.5, $CHCl_3$).

*Physical data for **14**:*

R_f=0.18 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.14 (m, 10H), 5.87 (q, *J* = 1.4 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.58 (t, *J* = 3.3 Hz 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 12.4 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.14 (t, *J* = 2.9 Hz, 1H), 3.76 (d, *J* = 2.8 Hz, 1H), 3.43 (d, *J* = 3.6 Hz, 1H), 1.79 (d, *J* = 1.4 Hz, 4H)

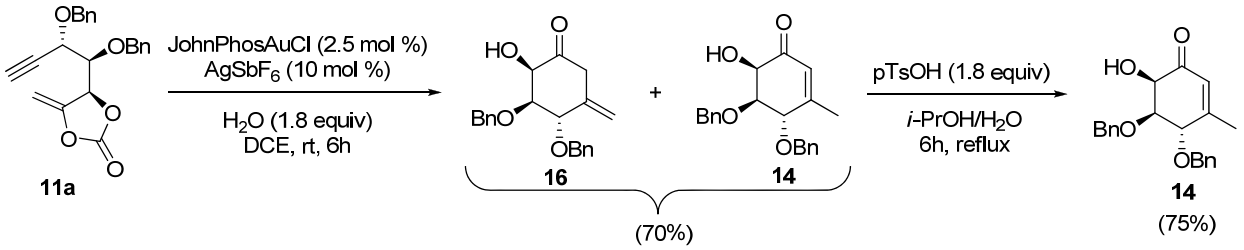
^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3, 155.7, 138.0, 136.9, 128.6, 128.5, 128.4, 127.9, 127.9, 125.0, 77.6, 77.1, 73.9, 73.6, 72.6, 21.8.

IR_{ATR}: 3472, 3062, 3030, 2870, 1818, 1729, 1691, 1455, 1375, 1234, 1212, 1119, 1092, 1067, 1021, 751, 700.

HRMS (ESI): calcd. for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found 339.1585, $C_{21}H_{22}O_4Na$ $[M+Na]^+$: 361.1410, found 356.1408.

$[\alpha]_D^{25}$ -92.8 (*c* 1.1, $CHCl_3$).

2.2.2.2 Cyclization of enol carbonate 11a in presence of water: preparation of (4S,5S,6R)-4,5-bis(benzyloxy)-6-hydroxy-3-methylcyclohex-2-enone (14)



A flame dried Schlenk tube was charged with $AgSbF_6$ (3.0 mg, 8.7 μmol), JohnPhosAuCl (1.2 mg, 2.2 μmol) and dry 1,2-dichloroethane (3 mL) under an argon atmosphere. AgCl precipitate (suspension) formed immediately; the Schlenk tube was protected from light using aluminum foil. To this mixture, a solution of enol carbonate **11a** (32.8 mg, 0.090 mmol) and water (3 μL, 3.0 mg, 0.167 mmol) in dry 1,2-dichloroethane (2.1 mL) was added. After 6 h of stirring at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (1 mL), SiO_2 (130 mg) was added and the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 95:5) afforded 20.8 mg (70%) of a mixture of ketones **14** and **16** (approximately 1:1 relative ratio).

A solution of *p*TsOH (20.8 mg, 0.109 mmol) in water (1 mL) and isopropanol (2 mL) was added to the above mixture of ketones **14** and **16** (20.0 mg, 0.059 mmol) and the reaction mixture was heated to reflux for 6h, when TLC indicated a complete isomerization. The reaction mixture was cooled to rt, diluted with diethyl ether (50 mL), washed with saturated sodium bicarbonate (10 mL), brine (10 mL), dried over $MgSO_4$ (anh.) and concentrated under reduced pressure. Purification of the residue afforded 15.1 mg (75%) of the cyclohexenone **14**, as a pale yellow oil.

*Physical data for **16**:*

R_f=0.26 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.20 (m, 10H), 5.20 (d, J = 2.5 Hz, 1H), 5.09 (d, J = 2.1 Hz, 1H), 4.78 (dd, J^1 = 5.7, J^2 = 3.6 Hz, 1H), 4.65 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.1 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.18 (t, J = 3.7 Hz, 1H), 4.08 (d, J = 3.0 Hz, 1H), 3.39 (dt, J^1 = 4.1, J^2 = 2.5 Hz, 1H), 3.30 (d, J = 6.3 Hz, 1H), 3.17 (dd, J^1 = 15.2, J^2 = 1.2 Hz, 1H).

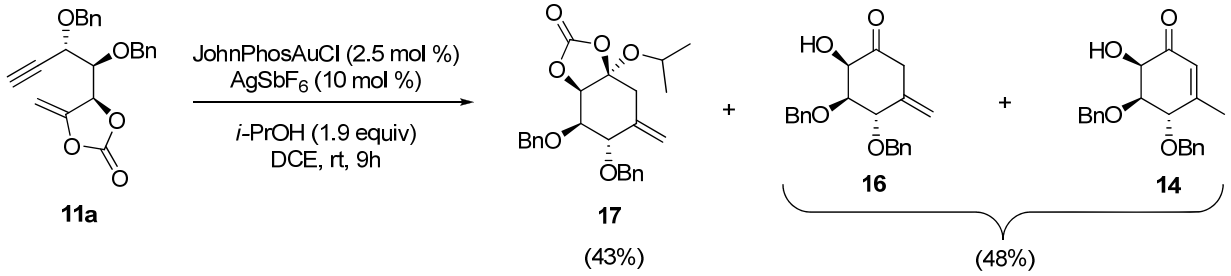
^{13}C NMR (125 MHz, $CDCl_3$): δ 206.1, 139.3, 137.8, 137.5, 128.5, 128.3, 127.8, 127.7, 127.6, 127.5, 118.5, 80.4, 79.4, 74.8, 73.2, 70.1, 44.9.

IR_{ATR}: 3496, 3063, 3031, 2922, 1814, 1729, 1656, 1496, 1455, 1393, 1338, 1206, 1119, 1087, 1028, 913, 736, 699.

HRMS (ESI): calcd. for $C_{21}H_{26}NO_4$ $[M+NH4]^+$: 356.1856, found 356.1844, $C_{21}H_{22}O_4Na$ $[M+Na]^+$: 361.1410, found 356.1402, $C_{21}H_{22}O_4K$ $[M+K]^+$: 377.1150, found 356.1144.

$[\alpha]_D^{25}$ -8.9 (c 0.3 $CHCl_3$).

2.2.2.3 Cyclization of enol carbonate 11a in the presence of isopropanol



A flame dried Schlenk tube was charged with $AgSbF_6$ (6.1 mg, 17.8 μmol), JohnPhosAuCl (2.4 mg, 4.5 μmol) and dry 1,2-dichloroethane (6.4 mL) under an argon atmosphere. AgCl precipitate (suspension) formed immediately; the Schlenk tube was protected from light using aluminum foil. A solution of enol carbonate **11a** (62.5 mg, 0.172 mmol) and isopropanol (25 μL, 19.6 mg, 0.326 mmol)[NOTE 1] in dry 1,2-dichloroethane (2.1 mL) was added to the reaction mixture. After 9 h of stirring at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (2 mL), SiO_2 (250 mg) was added and the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 95:5) afforded 31.5 mg (43%) of **17** and 27.6 mg (48%) of a mixture of unconjugated ketone **16** and conjugated ketone **14** (in 1:1 relative ratio)[NOTE 2, 3].

NOTE 1: When a larger excess of isopropanol (5.5 equiv) was used, AgCl precipitate (highly dispersed) changed to more globular form (particles). In this case, there was no desired reaction – the starting material was isolated in 70% yield.

NOTE 2: The products ratio was variable. For example, in another experiment 63% of isopropyl carbonate **17** and 20% of a mixture of **16** and **14** was isolated (in 2.5:1 relative ratio).

NOTE 3: Unconjugated ketone **16** isomerizes to enone **14** during chromatographic purification (on SiO_2). Longer column durations and the use of more active silica gels resulted in a higher level of isomerization. During reaction

only traces of enone **14** were observed (TLC), but the amount increases significantly after chromatographic purification.

*Physical data for **17***:

R_f=0.55 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.25 (m, 10H), 5.31 (s, 1H), 5.20 (s, 1H), 4.74 (d, J = 12.1 Hz, 1H), 4.63 (t, J = 4.1 Hz, 1H), 4.62 (d, J = 11.9 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.35 (d, J = 11.8 Hz, 1H), 4.18 (hept, J = 6.1 Hz, 1H), 4.04 (d, J = 4.9 Hz, 1H), 3.95 (dd, J^1 = 4.9 Hz, J^2 = 4.1 Hz, 1H), 2.97 (d, J = 14.6 Hz, 1H), 2.68 (dt, J^1 = 14.6, J^2 = 1.7 Hz, 1H), 1.23 (d, J = 6.1 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H).

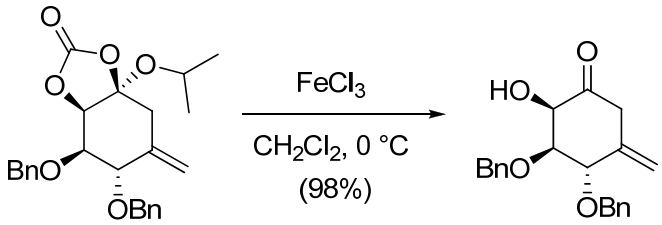
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 137.4, 137.3, 136.4, 128.5, 128.4, 127.9, 127.8, 127.8, 127.6, 119.8, 106.4, 80.0, 78.9, 75.4, 73.4, 70.1, 67.4, 35.6, 24.2, 23.9.

IR_{ATR}: 3063, 3031, 2978, 2929, 2873, 1812, 1697, 1496, 1455, 1371, 1325, 1290, 1208, 1154, 1094, 1033, 938, 739, 700.

HRMS (ESI): calcd. for $C_{25}H_{29}O_6$ $[M+H]^+$: 425.1959, found 425.1948, $C_{25}H_{28}O_6Na$ $[M+Na]^+$: 447.1778, found 447.1768, $C_{25}H_{28}O_6K$ $[M+K]^+$: 463.1517, found 463.1509.

$[\alpha]_D^{25}$ -36.2 (*c* 1.0, $CHCl_3$).

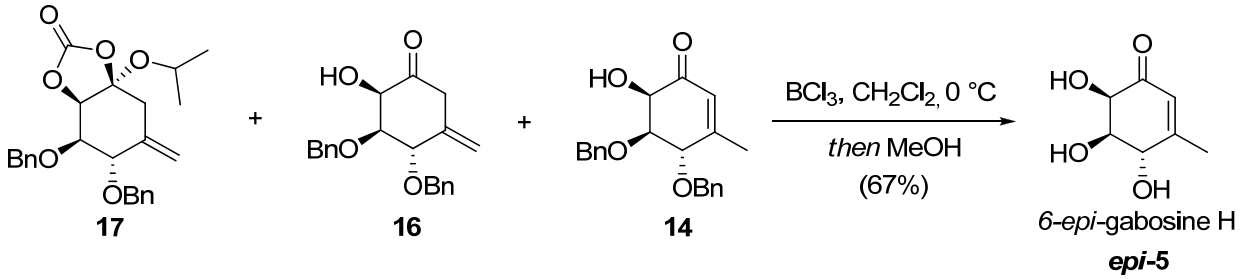
2.2.2.4 Selective deprotection of acetal 17: preparation of (2R,3S,4S)-3,4-bis(benzyloxy)-2-hydroxy-5-methylenecyclohexanone (16)



17 **16**

[$FeCl_3$ (38 mg) was stirred with dry dichloromethane (3 mL) at rt for 5 min, which resulted in incomplete dissolution, and the clear yellow supernatant was used as a reagent for deprotection.] A solution of $FeCl_3$ in dry dichloromethane (1.2 mL) was added dropwise to a cold (0 °C) solution of **17** (5.0 mg, 1.2 μmol) in dry dichloromethane (0.25 mL), under an argon atmosphere. After 15 min the reaction mixture was diluted with ethyl acetate (1.5 mL), filtered through short pad of silica (approx. 500 mg) to remove inorganics, and the silica was washed with ethyl acetate (5 x 1 mL). The combined fractions were concentrated under reduced pressure, affording 3.9 mg (98%) of unconjugated ketone **16**, as a pale yellow oil. Under acidic conditions (prolonged standing on silica gel, for example), the product isomerizes to a more stable (conjugated) enone **14**.

2.2.2.5 (4S,5R,6R)-4,5,6-Trihydroxy-3-methylcyclohex-2-enone (6-epi-gabosine H) (epi-5)[15]



A solution of BCl_3 (0.650 mL, 1M in heptane, 0.650 mmol) was added to a cold (0 °C) solution of a mixture of isopropyl carbonate **17** (31.5 mg, 0.074 mmol) and ketones **16** and **14** (27.6 mg, 0.082 mmol) in dry dichloromethane (3.9 mL), under an argon atmosphere. After 15 min the reaction was quenched by addition of methanol (3.9 mL), the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2: chloroform/methanol 9:1), to afford 16.4 mg (67%) of 6-*epi*-gabosine H (***epi*-5**) as a yellowish oil.

*Physical data for **epi**-5*:

R_f=0.29 (dichloromethane/methanol=9/1).

^{1}H NMR (500 MHz, CD_3OD): δ 5.88 (q, *J* = 1.4 Hz, 1H), 4.50 (d, *J* = 2.6 Hz, 1H), 4.20-4.15 (m, 2H), 2.08 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (125 MHz, CD_3OD): δ 200.6, 160.5, 126.5, 77.2, 74.3, 74.2, 22.7.

IR_{ATR}: 3401, 2981, 2913, 1682, 1437, 1378, 1228, 1158, 1119, 1083, 1033, 982, 868, 821, 728.

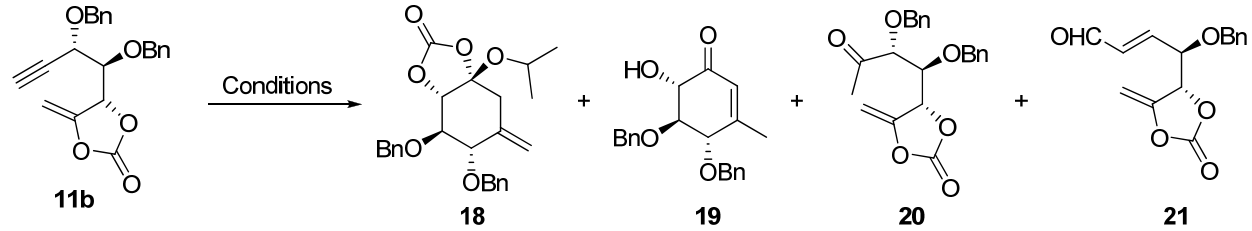
HRMS (ESI): calcd. for $C_7H_{11}O_4$ $[M+H]^+$: 159.0652, found 159.0651.

$[\alpha]_D^{25}$ -112.2 (*c* 0.5, MeOH).

[15] Kumar, V.; Das, P.; Ghosal, P.; Shaw, A. K. *Tetrahedron*, **2011**, *67*, 4539.

2.2.3 Synthesis of gabosine H (5)

2.2.3.1 Cyclizations of enol carbonate 11b in the presence of isopropanol



11b **18** **19** **20** **21**

Conditions:

1	JohnPhosAu(MeCN)SbF_6 (7 mol %) *i*-PrOH (1.9 equiv), DCE, rt, overnight	(34%)	(0%)	(30%)	(30%)
2	JohnPhosAuCl (2.5 mol %), $AgSbF_6$ (10 mol %) *i*-PrOH (1.8 equiv), DCE, rt, 5 day	*traces*	(25%)	(14%)	(9%)
3	JohnPhosAuCl (8 mol %), $AgSbF_6$ (32 mol %) *i*-PrOH (1.9 equiv), DCE, rt, 24 h	(24%)	(10%)	(35%)	(25%)

Conditions 1

A solution of enol carbonate **11b** (75.0 mg, 0.172 mmol) and isopropanol (25 µL, 19.6 mg, 0.326 mmol) in dry 1,2-dichloroethane (4.5 mL) was added dropwise to a solution of JohnPhosAu(MeCN)SbF_6 (10.8 mg, 14.0 µmol) in dry 1,2-dichloroethane (6.0 mL), under an argon atmosphere, in a flame dried Schlenk tube. After stirring overnight at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (2 mL), SiO_2 (450 mg) was added and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 95:5) afforded 30.1 mg (34%) of isopropyl carbonate **18**, as a colorless oil.

Conditions 2

A flame dried Schlenk tube was charged with $AgSbF_6$ (1.6 mg, 3.0 µmol), JohnPhosAuCl (4.1 mg, 12.0 µmol) and dry 1,2-dichloroethane (3.6 mL), under an argon atmosphere. AgCl precipitate (suspension) formed immediately; the Schlenk tube was protected from light using aluminum foil. A solution of enol carbonate **11b** (44.4 mg, 0.122 mmol) and isopropanol (17 µL, 13.3 mg, 0.222 mmol) in dry 1,2-dichloroethane (2.4 mL) was added to the reaction mixture. After five days of stirring at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (3 mL), SiO_2 (150 mg) was added and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 95:5) afforded 10.7 mg (25%) of enone **19**, as a white solid.

Conditions 3

A flame dried Schlenk tube was charged with $AgSbF_6$ (7.5 mg, 21 μmol), JohnPhosAuCl (3.3 mg, 6.2 μmol) and dry 1,2-dichloroethane (2 mL), under an argon atmosphere. AgCl precipitate (suspension) formed immediately; the Schlenk tube was protected from light using aluminum foil. A solution of enol carbonate **11b** (25 mg, 0.069 mmol) and isopropanol (10 μL, 7.9 mg, 0.13 mmol) in dry 1,2-dichloroethane (1.5 mL) was added to the reaction mixture. After 24 h of stirring at rt, TLC indicated a complete consumption of the starting material. The reaction mixture was diluted with dry chloroform (3 mL), SiO_2 (150 mg) was added and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2; eluent: benzene/ethyl acetate 95:5) afforded isopropyl carbonate **18** (7 mg, 24%), enone **19** (2.5 mg, 10%), ketone **20** (9.2 mg, 35%) and enal **21** (5 mg, 26%).

*Physical data for **18**:*

R_f=0.60 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.27 (m, 10H), 5.31 (d, J = 1.2 Hz, 1H), 5.24 (s, 1H), 4.72 (s, 2H), 4.67 (d, J = 12.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 5.4 Hz, 1H), 4.17 (hept, J = 6.1 Hz, 1H), 4.00 (d, J = 7.0 Hz, 1H), 3.68 (dd, J^1 = 7.0, J^2 = 5.5 Hz, 1H), 3.09 (d, J = 15.1 Hz, 1H), 2.63 (d, J = 15.1 Hz, 1H), 1.23 (t, J = 6.4 Hz, 3H), 1.21 (t, J = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 137.6, 137.4, 136.4, 128.4, 128.0, 127.9, 127.8, 116.9, 106.3, 84.4, 80.7, 78.3, 73.7, 71.6, 67.5, 36.4, 24.3, 24.0.

IR_{ATR}: 3063, 3032, 2978, 2931, 2873, 1814, 1496, 1455, 1364, 1305, 1107, 1208, 1075, 1036, 930, 737, 700.

HRMS (ESI): calcd. for $C_{25}H_{32}O_6N$ $[M+NH4]^+$: 442.2224, found 442.2217, $C_{25}H_{28}O_6Na$ $[M+Na]^+$: 447.1778, found 447.1774, $C_{25}H_{28}O_6K$ $[M+K]^+$: 463.1518, found 463.1518.

$[\alpha]_D^{25}$ +26.3 (*c* 0.7, $CHCl_3$).

*Physical data for **19**:*

mp 71-72 °C

R_f=0.20 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.27 (m, 10H), 6.01 (dt, J^1 = 2.3, J^2 = 1.3 Hz, 1H), 5.09 (d, J = 11.1 Hz, 1H), 4.97 (d, J = 11.0 Hz, 1H), 4.80 (d, J = 11.1 Hz, 1H), 4.75 (d, J = 11.0 Hz, 1H), 4.29 (ddd, J^1 = 8.4, J^2 = 2.2, J^3 = 1.2 Hz, 1H), 4.24 (d, J = 10.5 Hz, 1H), 3.83 (dd, J^1 = 10.5, J^2 = 8.4 Hz, 1H), 3.70 (bs, 1H), 2.04 (t, J = 1.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 163.5, 138.2, 137.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 124.0, 86.2, 80.4, 78.0, 75.8, 75.0, 25.6.

IR_{ATR}: 3431, 3088, 3062, 3034, 2921, 2879, 1685, 1631, 1455, 1359, 1326, 1139, 1109, 1067, 1027, 742, 697.

HRMS (ESI): calcd. for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found 339.1593, $C_{21}H_{22}O_4Na$ $[M+Na]^+$: 361.1410, found 356.1408.

$[\alpha]_D^{25}$ -95.0 (*c* 0.2, $CHCl_3$).

*Physical data for **20**:*

R_f=0.33 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.22 (m, 10H), 5.32 (dd, J^1 = 4.0, J^2 = 2.0 Hz, 1H), 4.80 (dd, J^1 = 4.0, J^2 = 2.2 Hz, 1H), 4.75 (d, J = 11.3 Hz, 1H), 4.72 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 11.3 Hz, 1H), 4.57 (d, J = 11.5 Hz, 1H), 4.24 (dd, J^1 = 4.0, J^2 = 1.8 Hz, 1H), 4.09 (d, J = 6.5 Hz, 1H), 3.80 (dd, J^1 = 6.5, J^2 = 2.2 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.8, 151.8, 150.9, 136.7, 136.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 87.6, 81.5, 80.1, 78.2, 75.4, 74.1, 28.0.

HRMS (ESI): calcd. for $C_{22}H_{26}O_6N$ $[M+NH4]^+$: 400.1755, found 400.1748, $C_{22}H_{22}O_6Na$ $[M+Na]^+$: 405.1309, found 405.1310, $C_{22}H_{22}O_6K$ $[M+K]^+$: 421.1048, found 421.1046.

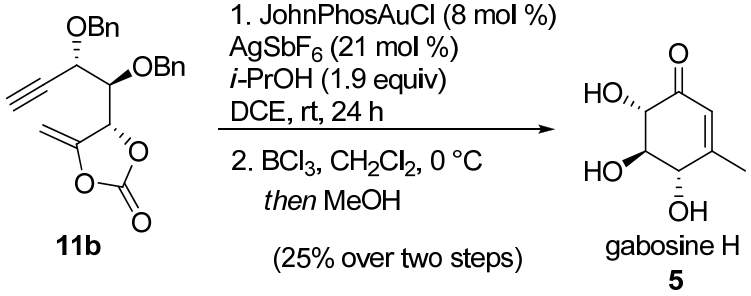
*Physical data for **21**:*

R_f=0.20 (benzene/ethyl acetate=95/5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (d, J = 7.6 Hz, 1H), 7.43-7.29 (m, 5H), 6.72 (dd, J^1 = 15.9, J^2 = 6.7 Hz, 1H), 6.38 (ddd, J^1 = 15.9, J^2 = 7.6, J^3 = 1.0 Hz, 1H), 5.17 (dd, J^1 = 4.8, J^2 = 2.0 Hz, 1H), 4.95 (dd, J^1 = 4.0, J^2 = 2.2 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 11.3 Hz, 2H), 4.46 (dd, J^1 = 15.9, J^2 = 6.7 Hz, 1H), 4.29-4.27 (m, 1H).

HRMS (ESI): calcd. for $C_{15}H_{18}O_5N$ $[M+NH4]^+$: 292.1180, found 292.1180.

2.2.3.2 Synthesis of gabosine H (5)



A solution of BCl_3 (0.25 mL, 1M in heptane, 0.25 mmol) was added to a cold (0 °C) solution of crude products[NOTE 1] from the previous step (20.1 mg) in dry dichloromethane (1.9 mL), under an argon atmosphere. After 15 min the reaction was quenched by the addition of methanol (1.9 mL), the reaction mixture was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2: chloroform/methanol 9:1, then benzene/EtOH 5:1), to afford 2.7 mg (25% over two steps) of gabosine H (**5**), as a white solid.[NOTE 2]

NOTE 1: For this purpose, the gold catalyzed cyclization was conducted on a 25 mg scale, as described under the *Conditions 3*. The reaction mixture was filtered through a plug of silica to remove the catalyst, and the crude product (20.1 mg) was used directly for the deprotection step.

NOTE 2: In a separate experiment, when pure acetal **18** (28 mg) was treated with BCl_3, gabosine H was isolated in 58% yield, indicating that the yield of useful cyclization products (**18**+**19**) in the above procedure is approximately 43%.

Physical data for **5** (gabosine H):

R_f=0.25 (chloroform/methanol=9/1).

mp 119-120 °C (Lit.[16] 118-119 °C, Lit.[17] 123 °C).

^{1}H NMR (500 MHz, CD_3OD): δ 5.92 (dd, J^1 = 2.1, J^2 = 1.4 Hz, 1H), 4.23 (ddd, J^1 = 8.3, J^2 = 2.1, J^3 = 1.1 Hz, 1H), 4.00 (d, J = 10.8 Hz, 1H), 3.56 (dd, J^1 = 10.8, J^2 = 8.4 Hz, 1H), 2.07 (t, J = 1.3 Hz, 3H).

^{13}C NMR (125 MHz, CD_3OD): δ 199.4, 165.7, 125.1, 79.2, 78.1, 75.2, 20.0.

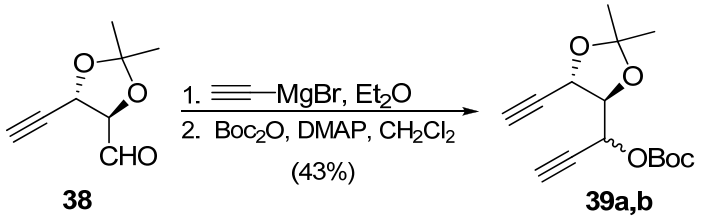
IR_{ATR}: 3434, 2894, 1809, 1657, 1627, 1358, 1286, 1229, 1116, 1089, 1029, 914, 890, 846.

HRMS (ESI): calcd. for $C_7H_{11}O_4$ $[M+H]^+$: 159.0652, found 159.0657.

$[\alpha]_D^{25}$ -59.0 (*c* 0.3, MeOH).

2.3 Cyclization of a dioxolane protected substrate (as described in Scheme 6)

2.3.1.1 tert-Butyl (S)-1-((4R,5S)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-ynyl carbonate (39a) and tert-butyl (R)-1-((4R,5S)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-ynyl carbonate (39b)



38 **39a,b**

Ethynylmagnesium bromide (2.2 mL, 0.5 M solution in THF, 2 mmol) was added dropwise to a cooled (0 °C) solution of aldehyde **38**[18] (80.7 mg, 0.53 mmol) in dry ether (2.4 mL), under an argon atmosphere. The reaction mixture was stirred for 20 minutes and then the reaction was quenched with saturated aqueous solution of NH_4Cl (2.5 mL) and the mixture was extracted with EtOAc (2 x 20 mL). The organic extract was washed with brine, dried over anh. $MgSO_4$, filtered and concentrated on rotovap. The crude product was used in next step without purification.

A solution of propargylic alcohol from the previous step, di-*tert*-butyl dicarbonate (66.0 mg, 0.29 mmol) and DMAP (3 mg) in dichloromethane (1.5 mL) was stirred at room temperature, for 30 minutes. The reaction was quenched with H_2O, extracted with ethyl acetate and the organic extract was dried over anh. $MgSO_4$, filtered and concentrated

[16] Prasad, K. R.; Kumar, S. M. *Synlett* **2011**, *11*, 1602-1604.
[17] Bach, G.; Breiding-Mack, S.; Grabley, S.; Hammann, P.; Hutter, K.; Thiercke, R.; Uhr, H.; Wink, J.; Zeeck, A. *Liebigs Ann. Chem.* **1993**, 241-250.
[18] Sabitha, G.; Bhaskar, V.; Reddy, C. S.; Yadav, J. S. *Synthesis* **2008**, 115-121.

on rotovap. The residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 15:1 + 5% Et_3N), affording a mixture of epimeric **39a,b** (62.5 mg, 81%; 1:1 ratio), as an oil.

Physical data for the epimeric mixture

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.43 (dd, J^1 = 4.0, J^2 = 2.1 Hz, 1H), 5.30 (dd, J^1 = 6.2, J^2 = 2.4 Hz, 1H), 4.76-4.74 (m, 2H), 4.39-4.35 (m, 2H), 2.59-2.56 (m, 4H), 1.54 (s, 3H), 1.53 (s, 3H), 1.52 (s, 9H), 1.50 (s, 9H), 1.46 (s, 3H), 1.45 (s, 3H).

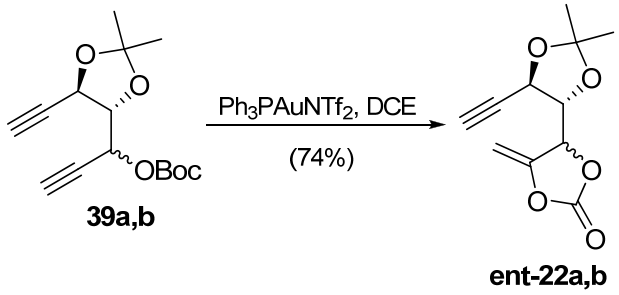
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 152.1, 112.5, 112.1, 83.5, 83.4, 81.9, 81.6, 81.3, 80.8, 76.4, 76.2, 75.1, 74.8, 67.3, 66.8, 66.6, 65.2, 27.7, 26.8, 26.6, 26.3, 26.2.

IR_{film}: 3289, 2922, 1748, 1277, 1255, 1161, 1085.

HRMS (ESI): calcd. for $C_{15}H_{20}O_5NH_4^+$ $[M + NH_4]^+$: 298.1649, found 298.1631.

$[\alpha]_D^{25}$ 39.0 ° (*c* 0.1, $CHCl_3$).

2.3.1.2 (4R,4'R,5'S)-5'-Ethynyl-2',2'-dimethyl-5-methylene-4,4'-bi(1,3-dioxolan)-2-one (ent-22a) and (4S,4'R,5'S)-5'-ethynyl-2',2'-dimethyl-5-methylene-4,4'-bi(1,3-dioxolan)-2-one (ent-22b)



A solution of *tert*-butyl carbonate **39a,b** (24 mg, 0.086 mmol) and $Ph_3PAuNTf_2$ (3.2 mg, 4.3 μmol) in dry 1,2-dichloroethane (0.8 mL) was stirred at rt, for 30 minutes, under an argon atmosphere. The solvent was evaporated on rotovap and the crude product was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 5:1). Two diastereoisomers (**ent-22a,b**) were isolated: less polar compound (5.6 mg, 29%; colorless oil) and more polar compound (8.6 mg, 45%; white solid).

Physical data of the less polar isomer

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.10 (dt, J^1 = 6.3, J^2 = 2.1 Hz, 1H), 5.00 (dd, J^1 = 3.9, J^2 = 2.1 Hz, 1H), 4.69 (dd, J^1 = 5.6, J^2 = 2.2 Hz, 1H), 4.64 (dd, J^1 = 4.1, J^2 = 1.9 Hz, 1H), 4.33 (dd, J^1 = 5.8, J^2 = 5.8 Hz, 1H), 2.60 (d, J = 2.2 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.2, 149.1, 112.7, 90.1, 81.4, 80.1, 77.8, 75.8, 66.9, 26.9, 26.3.

I**R_{film}**: 3281, 2991, 2922, 2852, 1837, 1753, 1690, 1276, 1145, 1056, 848.

HRMS (ESI): calcd. for $C_{11}H_{12}O_5NH_4^+$ $[M + NH_4]^+$ 242.1023, found 242.1018.

$[\alpha]_D^{25}$ -56.0 ° (*c* 0.29, $CHCl_3$).

Physical data of the more polar isomer

mp 117-119 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.21-5.20 (m, 1H), 5.01 (dd, J^1 = 4.2, J^2 = 2.2 Hz, 1H), 4.71 (dd, J^1 = 7.7, J^2 = 2.2 Hz, 1H), 4.54 (dd, J^1 = 4.2, J^2 = 1.8 Hz, 1H), 4.20 (dd, J^1 = 7.7, J^2 = 1.5 Hz, 1H), 2.63 (d, J = 2.1 Hz, 1H), 1.51 (s, 3H), 1.43 (s, 3H).

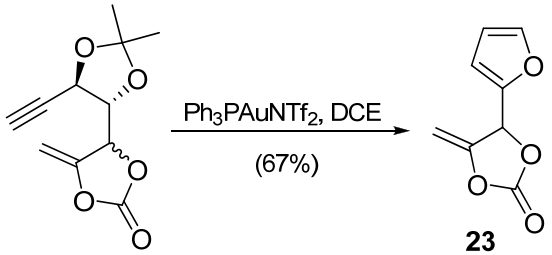
^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 149.7, 112.3, 88.2, 82.2, 78.9, 76.2, 75.7, 66.0, 26.4, 26.0.

IR_{film}: 3280, 2993, 2937, 1821, 2851, 1750, 1695, 1270, 1120, 1045, 861.

HRMS (ESI): calcd. for $C_{11}H_{12}O_5NH_4^+$ $[M + NH_4]^+$ 242.1023, found 242.1021.

$[\alpha]_D^{25}$ 130 ° (*c* 0.32, $CHCl_3$).

2.3.1.3 4-(Furan-2-yl)-5-methylene-1,3-dioxolan-2-one (23)



ent-22a,b **23**

$Ph_3PAuNTf_2$ (1.6 mg, 2.2 μmol%) was added to a solution of diastereomers **ent-22a,b** (10 mg, 0.0446 mmol; 1:1 ratio) in dry 1,2-dichloroethane (0.4 mL) and the reaction mixture was stirred for 3.5 h, at room temperature, under an argon atmosphere. The solvent was evaporated on rotovap and the residue was purified by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 8:2), to afford furan **23** (5 mg, 67%), as a colorless oil.

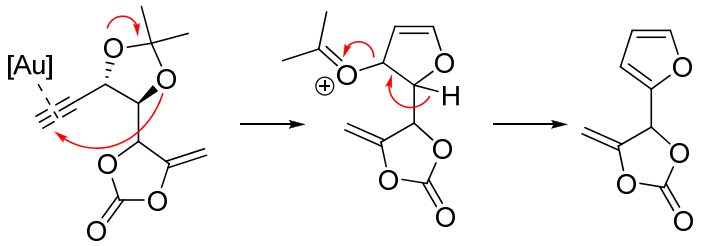
^{1}H NMR (500 MHz, $CDCl_3$): δ δ 7.52 (dd, J^1 = 2.0, J^2 = 1.0 Hz, 1H) 6.62-6.61 (m, 1H), 6.44 (dd, J^1 = 3.0, J^2 = 1.5 Hz, 1H), 6.15 (t, J = 2.5 Hz, 1H), 5.05 (dd, J^1 = 4.0, J^2 = 2.5 Hz, 1H), 4.44 (dd, J^1 = 4.0, J^2 = 2.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6, 150.0, 146.6, 145.1, 112.3, 110.7, 89.5, 73.8.

IR_{film}: 3287, 3120, 2877, 1819, 1685, 1510, 1395, 1120, 1053, 995, 852, 735.

HRMS (ESI): calcd. for $C_8H_6O_4NH_4^+$ $[M + NH_4]^+$ 184.0604, found 184.0598.

Plausible mechanistic explanation for formation of furane 23



3 Computational Details

The calculations using the restricted Kohn–Sham formalism have been performed with the Amsterdam Density Functional (ADF) program package, version 2013.01,[19,20,21] with GGA, hybrid and meta-hybrid exchange-correlation approximations (BLYP[22,23,24], B3LYP[25,26] and M06[27]). Grimme's dispersion (D_3) correction is included for BLYP.[28] MOs were expanded in an uncontracted set of Slater type orbitals (STOs) of triple-ζ quality containing diffuse functions (TZ2P) and two sets of polarization functions. Core electrons (1s for 2nd period, 1s2s2p for 3rd-4th period) were not treated explicitly during the geometry optimizations (frozen core approximation), as it was shown to have a negligible effect on the obtained geometries. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each SCF cycle. Since Scalar relativistic corrections are very important in this type of system, they have been included self-consistently using the zeroth-order regular approximation (ZORA)[29,30,31]. Geometries were optimized with the QUILD[32] program using adapted delocalized coordinates until the maximum gradient component was less than 10^{-4} a.u. Conductor like screening solvation model (COSMO),[33] as implemented in ADF, was included in the density functional theory (DFT) geometry optimizations, with hybrid as a solvent. Numerical harmonic frequencies were calculated and in all cases the nature of the stationary point was confirmed by the presence of ether zero or one imaginary frequency

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modes. Intrinsic reaction coordinate (IRC)[34,35] methodology was use is order to connect the transition states with the appropriate minima structures.

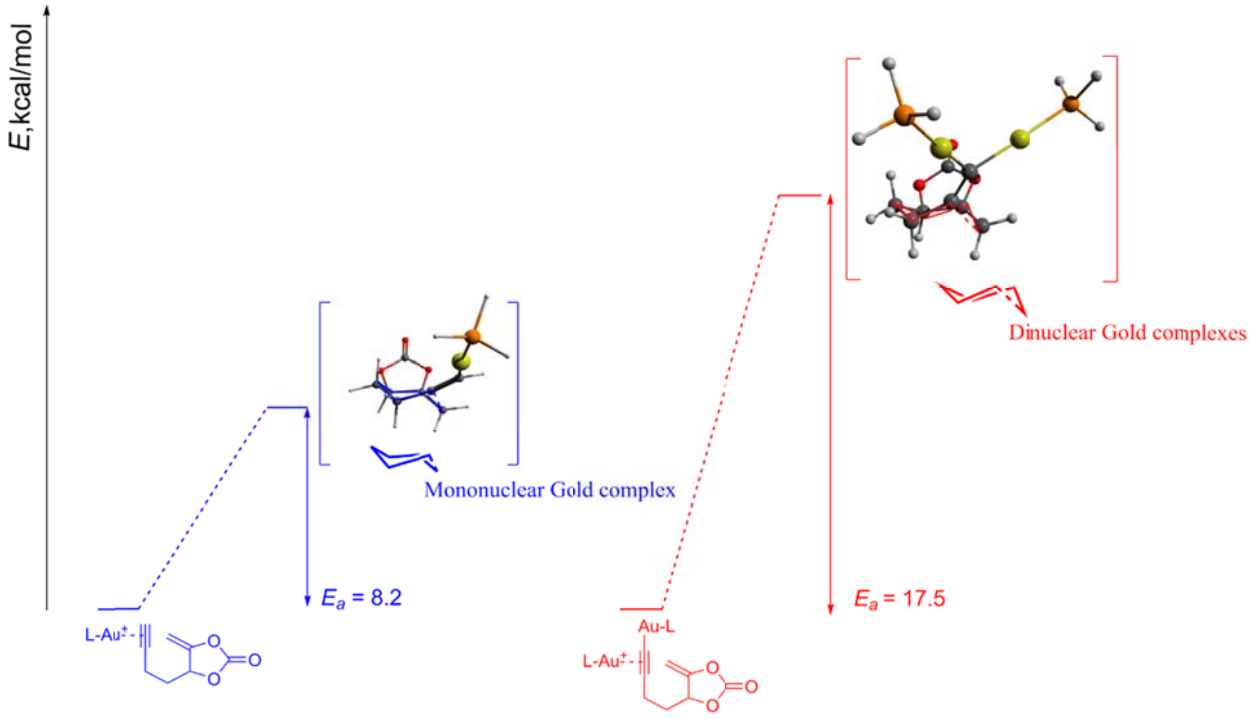

Figure S1. Calculated geometries and transition states for the lowest reaction pathway of the enyne cycloisomerization step for mononuclear and dinuclear gold catalysts. Activation barriers, are given as Gibbs free energies (in kcal/mol), obtained using BLYP-D3/TZ2P level of theory.

Table S1. Calculated geometries and transition states for the enyne cycloisomerization step for mononuclear and dinuclear gold catalysts. Activation barriers, are given as electronic energies and Gibbs free energies (in kcal/mol), obtained using BLYP-D3/TZ2P level of theory and they are labeled the same way as the corresponding TSs and intermediate structures (i.e. $\Delta E^{\ddagger}_1$=E(**TS 1**)-E(**React 1**)).

	$\Delta E^{\ddagger}_1$	$\Delta G^{\ddagger}_1$	$\Delta E^{\ddagger}_2$	$\Delta G^{\ddagger}_2$	$\Delta E^{\ddagger}_3$	$\Delta G^{\ddagger}_3$
Mononuclear Gold complex	7.8	12.0	13.8	8.2	10.1	14.2
Dinuclear Gold complex	16.6	21.6	22.5	17.5	21.7	25.8

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Table S2. Calculated reactants and transition states for the enyne cycloisomerization step. Activation barriers, are given as electronic energies and Gibbs free energies (in kcal/mol), obtained using BLYP-D3/TZ2P, PBE0/TZ2P and M06/TZ2P levels of theory and they are labeled the same way as the corresponding TSs and intermediate structures (i.e. $\Delta E^{\ddagger}_1$=E(**TS 1**)-E(**React 1**)).

XC	$\Delta E^{\ddagger}_1$	$\Delta E^{\ddagger}_2$	$\Delta E^{\ddagger}_3$	$\Delta G^{\ddagger}_1$	$\Delta G^{\ddagger}_2$	$\Delta G^{\ddagger}_3$
M06	12.5	15.9	16.9	12.5	16.7	17.0
PBE0	9.1	10.4	13.9	10.8	11.9	14.2
BLYP-D3	7.8	12.0	13.8	8.2	10.1	14.2

Table S3. Calculated intermediate products the enyne cycloisomerization step. Electronic energies and Gibbs free energies (in kcal/mol) are obtained using BLYP-D3/TZ2P, PBE0/TZ2P and M06/TZ2P levels of theory, and they are given relative to the lowest energy reactant structure.

XC	ΔE_1	ΔE_2	ΔE_3	ΔG_1	ΔG_2	ΔG_3
M06	1.3	4.2	4.2	6.9	8.6	9.0
PBE0	-4.8	-1.5	-1.3	-1.9	-0.1	0.0
BLYP-D3	1.1	5.3	5.4	4.6	9.2	9.3

3.1 Coordinates of optimized structures

3.1.1 Dinuclear Gold complexes

blyp Reaction_path 1 Reactant complex

C	2.52510000	-2.27350000	-1.00120000
C	1.20690000	-2.73880000	-0.30420000
C	0.17130000	-1.69940000	-0.16590000
C	3.71700000	-2.08250000	-0.03800000
H	2.83170000	-3.02270000	-1.73610000
H	2.35610000	-1.33640000	-1.54140000
H	0.75300000	-3.54210000	-0.89680000
H	1.42040000	-3.17130000	0.68100000
H	4.05720000	-3.04110000	0.35810000
C	-0.85610000	-0.99400000	-0.11310000
Au	0.69240000	0.61190000	0.16540000
P	2.00230000	2.47740000	0.41480000
H	2.71740000	2.55610000	1.62480000
H	3.02740000	2.62870000	-0.53820000
H	1.34880000	3.72210000	0.36450000
C	2.94990000	-1.10150000	2.23680000
C	3.56390000	-1.05240000	1.05970000
H	2.43840000	-2.00530000	2.54720000
H	2.93850000	-0.24330000	2.89990000
C	5.03300000	-0.22340000	-0.46400000
O	5.78580000	0.55350000	-0.99900000
O	4.83130000	-1.51270000	-0.82920000
O	4.25040000	0.10190000	0.63040000
Au	-2.76960000	-0.29420000	-0.11970000
P	-4.97670000	0.40210000	-0.13580000
H	-5.84630000	-0.31280000	-0.98180000
H	-5.65630000	0.33750000	1.09640000
H	-5.22070000	1.73240000	-0.53030000

blyp Reaction_path 1 Transition state

C	-1.37660000	-3.56130000	0.02180000
C	-0.32910000	-2.96310000	-0.95230000
C	-0.44410000	-1.46380000	-0.99500000
C	-2.82000000	-3.12200000	-0.35920000
H	-1.32430000	-4.65310000	0.03260000
H	-1.17460000	-3.18820000	1.03270000
H	0.66780000	-3.21780000	-0.58250000
H	-0.43590000	-3.40550000	-1.95010000
H	-3.29300000	-3.83110000	-1.04200000
C	0.10060000	-0.38620000	-0.50970000
Au	2.12540000	-0.48930000	0.06000000
P	4.35760000	-0.56100000	0.69110000
H	4.65190000	-0.27220000	2.03980000
H	5.02040000	-1.79550000	0.52760000
H	5.24140000	0.31230000	0.02330000
C	-2.14060000	-1.21220000	-1.94190000
C	-2.85680000	-1.71640000	-0.87910000
H	-1.94180000	-1.87390000	-2.77930000
H	-2.24190000	-0.15910000	-2.17840000
C	-4.03060000	-1.74730000	1.04990000
O	-4.68730000	-1.30780000	1.95180000
O	-3.66990000	-3.02760000	0.84110000
O	-3.52260000	-0.92820000	0.00300000
Au	-0.72820000	1.48270000	-0.14760000
P	-1.69890000	3.54550000	0.30760000
H	-2.57640000	4.05450000	-0.67280000
H	-2.51470000	3.61400000	1.45660000
H	-0.84650000	4.65040000	0.51050000

blyp Reaction_path 1 Intermediate product

C	-1.37660000	-3.56130000	0.02180000
C	-0.32910000	-2.96310000	-0.95230000
C	-0.44410000	-1.46380000	-0.99500000
C	-2.82000000	-3.12200000	-0.35920000
H	-1.32430000	-4.65310000	0.03260000
H	-1.17460000	-3.18820000	1.03270000
H	0.66780000	-3.21780000	-0.58250000
H	-0.43590000	-3.40550000	-1.95010000
H	-3.29300000	-3.83110000	-1.04200000
C	0.10060000	-0.38620000	-0.50970000
Au	2.12540000	-0.48930000	0.06000000
P	4.35760000	-0.56100000	0.69110000
H	4.65190000	-0.27220000	2.03980000
H	5.02040000	-1.79550000	0.52760000
H	5.24140000	0.31230000	0.02330000
C	-2.14060000	-1.21220000	-1.94190000
C	-2.85680000	-1.71640000	-0.87910000
H	-1.94180000	-1.87390000	-2.77930000
H	-2.24190000	-0.15910000	-2.17840000
C	-4.03060000	-1.74730000	1.04990000
O	-4.68730000	-1.30780000	1.95180000
O	-3.66990000	-3.02760000	0.84110000
O	-3.52260000	-0.92820000	0.00300000
Au	-0.72820000	1.48270000	-0.14760000
P	-1.69890000	3.54550000	0.30760000
H	-2.57640000	4.05450000	-0.67280000
H	-2.51470000	3.61400000	1.45660000
H	-0.84650000	4.65040000	0.51050000

blyp Reaction_path 2 Reactant complex

C	1.33290000	3.42860000	1.59150000
C	0.22170000	2.44720000	2.05250000
C	0.34910000	1.03550000	1.65100000
C	0.50990000	-0.19700000	1.54690000
C	1.35220000	3.81930000	0.10740000
C	1.78840000	2.78430000	-0.91140000
P	-1.77130000	0.30030000	-2.33670000
Au	-0.62820000	0.22100000	-0.34930000
C	2.85710000	1.99960000	-0.95950000
H	3.58320000	2.02270000	-0.15440000
H	3.02090000	1.32490000	-1.79310000

H	1.19910000	4.34940000	2.16780000
H	2.32450000	3.03530000	1.84270000
H	-0.75620000	2.82920000	1.73730000
H	0.21240000	2.45240000	3.15050000
H	1.94950000	4.72930000	-0.01100000
H	-2.22310000	-0.93270000	-2.84280000
H	-2.94450000	1.07620000	-2.32210000
H	-1.06230000	0.84450000	-3.42340000
C	-0.25390000	3.55720000	-1.54700000
O	-1.27400000	3.65120000	-2.19050000
O	0.81640000	2.78070000	-1.93310000
O	-0.01240000	4.16280000	-0.36210000
Au	0.97490000	-2.15590000	1.83320000
P	1.52200000	-4.36370000	2.26040000
H	2.76900000	-4.80740000	1.77770000
H	1.59560000	-4.72650000	3.61940000
H	0.65040000	-5.34460000	1.74730000

blyp Reaction_path 2 Transition state

C	3.79560000	-1.63550000	-1.31670000
C	2.25600000	-1.87700000	-1.32010000
C	1.41430000	-0.63740000	-1.11520000
C	0.34050000	-0.26730000	-0.47350000
C	4.22830000	-0.29420000	-0.71260000
C	3.24080000	0.79110000	-0.97970000
P	-2.57570000	-3.42960000	0.57700000
Au	-1.03450000	-1.78280000	0.02260000
C	2.35030000	0.81610000	-2.03240000
H	2.63800000	0.33050000	-2.96070000
H	1.64900000	1.63740000	-2.11700000
H	4.31770000	-2.44370000	-0.79770000
H	4.17640000	-1.62680000	-2.34350000
H	1.98860000	-2.57190000	-0.51960000
H	1.98150000	-2.35190000	-2.26970000
H	5.23850000	-0.03520000	-1.04540000
H	-3.93400000	-3.05570000	0.64380000
H	-2.64390000	-4.54300000	-0.28650000
H	-2.40300000	-4.06520000	1.82380000
C	3.69820000	0.86620000	1.22100000
O	3.65370000	1.27050000	2.34960000
O	3.10190000	1.56480000	0.13420000
O	4.27540000	-0.26770000	0.77640000
Au	-0.28720000	1.59820000	0.18100000
P	-0.96110000	3.69370000	0.93150000
H	-0.06890000	4.37020000	1.78960000
H	-1.16570000	4.67210000	-0.06390000
H	-2.16570000	3.78790000	1.65800000

blyp Reaction_path 2 Intermediate product

C	3.79560000	-1.63550000	-1.31670000
C	2.25600000	-1.87700000	-1.32010000
C	1.41430000	-0.63740000	-1.11520000
C	0.34050000	-0.26730000	-0.47350000
C	4.22830000	-0.29420000	-0.71260000
C	3.24080000	0.79110000	-0.97970000
P	-2.57570000	-3.42960000	0.57700000
Au	-1.03450000	-1.78280000	0.02260000
C	2.35030000	0.81610000	-2.03240000
H	2.63800000	0.33050000	-2.96070000
H	1.64900000	1.63740000	-2.11700000
H	4.31770000	-2.44370000	-0.79770000
H	4.17640000	-1.62680000	-2.34350000
H	1.98860000	-2.57190000	-0.51960000
H	1.98150000	-2.35190000	-2.26970000
H	5.23850000	-0.03520000	-1.04540000
H	-3.93400000	-3.05570000	0.64380000
H	-2.64390000	-4.54300000	-0.28650000
H	-2.40300000	-4.06520000	1.82380000
C	3.69820000	0.86620000	1.22100000
O	3.65370000	1.27050000	2.34960000
O	3.10190000	1.56480000	0.13420000
O	4.27540000	-0.26770000	0.77640000
Au	-0.28720000	1.59820000	0.18100000
P	-0.96110000	3.69370000	0.93150000
H	-0.06890000	4.37020000	1.78960000
H	-1.16570000	4.67210000	-0.06390000
H	-2.16570000	3.78790000	1.65800000

blyp Reaction_path 3 Reactant complex

C	-2.24950000	3.14110000	0.63420000
C	-1.42290000	2.21000000	1.56200000
C	-0.39310000	1.36420000	0.93330000
C	0.64080000	0.80950000	0.50980000
C	-3.33250000	2.48440000	-0.23200000
C	-2.90340000	1.61020000	-1.39410000
C	-2.04130000	1.82490000	-2.37970000
P	-2.11050000	-2.69090000	-0.32120000
Au	-0.87600000	-0.81750000	0.15370000
H	-2.74990000	3.87010000	1.27940000
H	-1.58920000	3.70580000	-0.03390000
H	-2.10220000	1.58320000	2.15100000
H	-0.89370000	2.84700000	2.28310000
H	-1.52250000	-3.60270000	-1.21850000
H	-2.44290000	-3.51440000	0.77010000
H	-3.36560000	-2.43970000	-0.90650000
H	-1.87440000	1.08040000	-3.15090000
O	-3.63900000	0.41110000	-1.29720000
C	-4.32240000	0.38960000	-0.10100000
O	-4.15410000	1.54950000	0.57510000
H	-4.01980000	3.25950000	-0.58610000
O	-4.96590000	-0.56040000	0.28100000
H	-1.48540000	2.75510000	-2.42130000
Au	2.54370000	0.31010000	-0.00440000
P	4.74700000	-0.18050000	-0.51890000
H	5.65010000	0.89730000	-0.43260000
H	5.37670000	-1.14870000	0.28780000
H	5.00790000	-0.66960000	-1.81410000

blyp Reaction_path 3 Transition state

C	0.94550000	4.03770000	0.82880000
C	-0.18140000	2.97470000	0.98220000
C	0.30550000	1.53960000	0.99550000
C	-0.06740000	0.38680000	0.49750000
C	2.25740000	3.47370000	0.26920000
C	2.51550000	2.08140000	0.73740000
C	2.00010000	1.52590000	1.89800000
P	-4.25390000	-0.09440000	-0.85460000
Au	-2.06800000	0.17200000	-0.10930000
H	0.61810000	4.87310000	0.20450000
H	1.20560000	4.46080000	1.80600000
H	-0.88680000	3.05940000	0.15130000
H	-0.73680000	3.18430000	1.90420000
H	-4.49620000	-1.07740000	-1.83600000
H	-5.22700000	-0.43200000	0.10970000
H	-4.85250000	1.03380000	-1.45530000
H	2.23350000	0.49520000	2.13660000
O	3.01640000	1.34090000	-0.28640000
C	2.79030000	2.06970000	-1.49440000
O	2.27380000	3.27920000	-1.20730000
H	3.09210000	4.14710000	0.48900000
O	3.03530000	1.61400000	-2.57550000
H	1.82910000	2.18490000	2.74490000
Au	1.02260000	-1.34920000	0.15910000
P	2.23900000	-3.29970000	-0.21020000
H	3.27400000	-3.56950000	0.70970000
H	1.53660000	-4.52250000	-0.19500000
H	2.93570000	-3.40140000	-1.43280000

blyp Reaction_path 3 Intermediate product

C	0.94550000	4.03770000	0.82880000
C	-0.18140000	2.97470000	0.98220000
C	0.30550000	1.53960000	0.99550000
C	-0.06740000	0.38680000	0.49750000
C	2.25740000	3.47370000	0.26920000
C	2.51550000	2.08140000	0.73740000
C	2.00010000	1.52590000	1.89800000
P	-4.25390000	-0.09440000	-0.85460000
Au	-2.06800000	0.17200000	-0.10930000
H	0.61810000	4.87310000	0.20450000
H	1.20560000	4.46080000	1.80600000
H	-0.88680000	3.05940000	0.15130000
H	-0.73680000	3.18430000	1.90420000
H	-4.49620000	-1.07740000	-1.83600000
H	-5.22700000	-0.43200000	0.10970000
H	-4.85250000	1.03380000	-1.45530000
H	2.23350000	0.49520000	2.13660000
O	3.01640000	1.34090000	-0.28640000
C	2.79030000	2.06970000	-1.49440000
O	2.27380000	3.27920000	-1.20730000
H	3.09210000	4.14710000	0.48900000
O	3.03530000	1.61400000	-2.57550000
H	1.82910000	2.18490000	2.74490000
Au	1.02260000	-1.34920000	0.15910000
P	2.23900000	-3.29970000	-0.21020000
H	3.27400000	-3.56950000	0.70970000
H	1.53660000	-4.52250000	-0.19500000
H	2.93570000	-3.40140000	-1.43280000

3.1.2 Mononuclear Gold complexes

blyp Reaction_path 1 Reactant complex

C	-1.75830000	1.64830000	-1.24520000
C	-0.84680000	2.73880000	-0.60420000
C	0.53660000	2.33180000	-0.32800000
C	-2.70600000	0.94470000	-0.24770000
H	-2.38900000	2.11630000	-2.00510000
H	-1.14730000	0.89280000	-1.74940000
H	-0.76490000	3.58700000	-1.29500000
H	-1.29050000	3.13250000	0.31810000
H	-3.49690000	1.62230000	0.07910000
C	1.74370000	2.15560000	-0.14370000
H	2.79590000	2.34110000	-0.03240000
Au	1.14770000	0.01150000	0.01710000
P	0.93100000	-2.26900000	0.20830000
H	0.47870000	-2.72230000	1.46080000
H	0.00190000	-2.84220000	-0.67960000
H	2.09780000	-3.02150000	-0.00910000
C	-1.58780000	0.67490000	2.07680000
C	-2.07740000	0.22490000	0.92640000
H	-1.60030000	1.73640000	2.29640000
H	-1.16000000	-0.00300000	2.80740000
C	-2.87960000	-1.35040000	-0.50450000
O	-3.10130000	-2.43900000	-0.97450000
O	-3.34970000	-0.16970000	-0.97620000
O	-2.08780000	-1.14910000	0.61280000

blyp Reaction_path 1 Transition state

C	-2.58690000	1.30160000	-1.25960000
C	-1.37570000	1.74370000	-0.40710000
C	-0.95860000	0.73620000	0.58740000
C	-3.85920000	1.10400000	-0.39230000
H	-2.79440000	2.04420000	-2.03320000
H	-2.35960000	0.34640000	-1.74650000
H	-0.51560000	1.88450000	-1.07450000
H	-1.56250000	2.71050000	0.07530000
H	-4.37950000	2.04560000	-0.20870000
C	-0.10970000	-0.09610000	1.06100000
H	-0.24030000	-0.78810000	1.88660000
Au	1.80200000	-0.12630000	0.15080000
P	3.92200000	-0.28020000	-0.76100000
H	4.33980000	-1.57500000	-1.12550000
H	4.14600000	0.44340000	-1.94890000
H	4.98600000	0.15490000	0.05310000
C	-2.80200000	0.75000000	1.92430000
C	-3.55860000	0.34990000	0.87300000
H	-2.62530000	1.80780000	2.08210000

H	-2.60720000	0.07010000	2.74640000
C	-4.85100000	-0.97810000	-0.42550000
O	-5.46620000	-1.95570000	-0.74830000
O	-4.78920000	0.19990000	-1.08190000
O	-4.07590000	-0.91090000	0.75600000

blyp Reaction_path 1 Intermediate product

C	2.41360000	0.63760000	1.76110000
C	1.28150000	1.48040000	1.11290000
C	1.12120000	1.10100000	-0.34590000
C	3.70130000	0.75680000	0.90240000
H	2.63790000	0.95940000	2.78060000
H	2.12100000	-0.41890000	1.77370000
H	0.35280000	1.28720000	1.65550000
H	1.51400000	2.54980000	1.21160000
H	4.25940000	1.66910000	1.13650000
C	0.11880000	0.42840000	-0.93590000
H	0.27570000	0.13660000	-1.97920000
Au	-1.72820000	-0.05500000	-0.14160000
P	-3.83940000	-0.65940000	0.67390000
H	-4.13080000	-2.03890000	0.72540000
H	-4.17310000	-0.26840000	1.98800000
H	-4.95660000	-0.17890000	-0.04100000
C	2.40090000	1.51230000	-1.19960000
C	3.39020000	0.67600000	-0.55330000
H	2.60670000	2.57450000	-1.02390000
H	2.29930000	1.29960000	-2.26270000
C	4.77790000	-1.05430000	-0.03880000
O	5.41330000	-2.01930000	-0.30080000
O	4.60900000	-0.38480000	1.09530000
O	3.96910000	-0.34620000	-1.10570000

blyp Reaction_path 2 Reactant complex

C	3.01090000	-0.03840000	2.06770000
C	1.56610000	0.15320000	2.60060000
C	0.55590000	-0.80640000	2.14100000
C	-0.28140000	-1.68280000	1.91170000
C	3.26740000	0.32530000	0.59860000
C	2.69070000	-0.57550000	-0.47760000
P	-1.61910000	0.86580000	-1.56690000
Au	-0.80530000	-0.27060000	0.25750000
C	2.76220000	-1.88920000	-0.65020000
H	3.29230000	-2.50300000	0.07000000
H	2.29840000	-2.36920000	-1.50540000
H	-0.86490000	-2.58300000	1.95890000
H	3.65550000	0.59660000	2.68250000
H	3.34300000	-1.07180000	2.21650000
H	1.22210000	1.17230000	2.39210000
H	1.59100000	0.05520000	3.69410000
H	4.34490000	0.44450000	0.44890000
H	-2.95390000	0.58160000	-1.90480000
H	-1.59680000	2.26610000	-1.45120000
H	-0.91920000	0.63230000	-2.76390000
C	1.96530000	1.54150000	-0.88910000
O	1.35790000	2.44160000	-1.42120000
O	2.00800000	0.25790000	-1.38780000
O	2.65840000	1.63590000	0.26960000

blyp Reaction_path 2 Transition state

C	-2.72310000	0.58840000	1.86730000
C	-1.58720000	-0.12470000	1.10420000
C	-1.05800000	0.60740000	-0.07930000
C	-0.01330000	0.85690000	-0.79360000
C	-3.99290000	0.71570000	1.00390000
C	-3.64880000	0.91900000	-0.44150000
P	3.94270000	-0.75140000	0.37060000
Au	1.84720000	0.06750000	-0.18200000
C	-2.68310000	1.75620000	-0.91860000
H	-2.42410000	2.62590000	-0.32330000
H	-2.46980000	1.78190000	-1.98140000
H	0.01860000	1.44590000	-1.70540000
H	-2.97780000	0.03810000	2.77660000
H	-2.41630000	1.59740000	2.16090000
H	-1.92110000	-1.12430000	0.79170000
H	-0.73820000	-0.26940000	1.78300000
H	-4.66550000	1.48480000	1.39290000
H	5.02810000	0.11980000	0.15210000
H	4.13840000	-1.12620000	1.71470000
H	4.35730000	-1.91050000	-0.31430000
C	-4.92070000	-0.94750000	-0.31050000
O	-5.52740000	-1.89950000	-0.70790000
O	-4.23590000	-0.05050000	-1.18450000
O	-4.75560000	-0.54530000	0.96250000

blyp Reaction_path 2 Intermediate product

C	2.87340000	0.32730000	2.14270000
C	1.40980000	-0.16190000	1.87020000
C	1.30380000	-0.99420000	0.60750000
C	0.37780000	-0.90390000	-0.37330000
C	3.83040000	0.08420000	0.95880000
C	3.34490000	-0.95400000	0.01100000
P	-3.44980000	1.26970000	-0.45020000
Au	-1.40730000	0.12240000	-0.35510000
C	2.50200000	-2.04620000	0.41830000
H	2.77560000	-2.48580000	1.37930000
H	2.30100000	-2.79060000	-0.34770000
H	0.58180000	-1.48380000	-1.27950000
H	2.90320000	1.39120000	2.39280000
H	3.29960000	-0.20880000	2.99500000
H	0.73240000	0.69030000	1.78050000
H	1.08060000	-0.75650000	2.73150000
H	4.83270000	-0.17700000	1.31910000
H	-4.61610000	0.50760000	-0.23030000
H	-3.64550000	2.33380000	0.45450000
H	-3.76130000	1.89550000	-1.67500000
C	3.96370000	0.82880000	-1.22670000
O	4.14630000	1.42960000	-2.23740000
O	3.57990000	-0.60100000	-1.23970000

O 4.02240000 1.23870000 0.04290000

blyp Reaction_path 3 Reactant complex

C -2.05970000 1.12870000 1.44050000
C -1.64710000 2.03850000 0.25400000
C -0.68880000 1.47790000 -0.70390000
C 0.01220000 1.07570000 -1.63540000
C -2.66470000 -0.24000000 1.08930000
C -3.66360000 -0.27260000 -0.05310000
C -4.83260000 0.34170000 -0.19440000
P 2.84050000 -0.73840000 1.35560000
Au 1.24740000 0.28280000 0.05230000
H 0.38880000 0.85850000 -2.61720000
H -1.20160000 0.95280000 2.09840000
H -2.80560000 1.67590000 2.02650000
H -1.23540000 2.97120000 0.65590000
H -2.53390000 2.30790000 -0.33810000
H 2.64780000 -2.11350000 1.58250000
H 4.14690000 -0.67850000 0.83950000
H 2.98430000 -0.21870000 2.65490000
H -5.43230000 0.21600000 -1.08960000
O -3.12960000 -1.11010000 -1.05060000
C -1.91830000 -1.61630000 -0.62790000
O -1.61350000 -1.16190000 0.61200000
H -3.07910000 -0.69060000 1.99480000
O -1.22760000 -2.35310000 -1.28990000
H -5.20290000 0.98310000 0.59870000

blyp Reaction_path 3 Transition state

C 3.00250000 -1.58700000 1.47220000
C 1.57390000 -1.84080000 0.88280000
C 1.25180000 -1.07710000 -0.34140000
C 0.42130000 -0.35510000 -1.00820000
C 3.81450000 -0.50790000 0.74720000
C 3.48420000 -0.38090000 -0.71100000
C 3.14110000 -1.37420000 -1.57070000
P -3.64740000 0.37260000 0.55420000
Au -1.50860000 -0.05870000 -0.22140000
H 0.62690000 0.14240000 -1.95210000
H 2.94440000 -1.31790000 2.52960000
H 3.58400000 -2.51160000 1.41480000
H 0.81120000 -1.54990000 1.61570000
H 1.44460000 -2.91140000 0.69110000
H -3.89800000 1.69570000 0.96830000
H -4.69400000 0.14840000 -0.36150000
H -4.07590000 -0.36730000 1.67420000
H 2.87180000 -1.15050000 -2.59660000
O 3.40640000 0.94830000 -1.03450000
C 3.35540000 1.68900000 0.16960000
O 3.51670000 0.86410000 1.22560000
H 4.88530000 -0.66210000 0.91090000
O 3.17600000 2.87500000 0.19580000
H 3.32280000 -2.40800000 -1.29730000

blyp Reaction_path 3 Intermediate product

C -2.91820000 1.59110000 1.52110000
C -1.48680000 1.75940000 0.91040000
C -1.37780000 1.16880000 -0.48320000
C -0.37600000 0.41240000 -0.98530000
C -3.80530000 0.60560000 0.73580000
C -3.36150000 0.41080000 -0.67030000
C -2.66310000 1.42890000 -1.41020000
P 3.62590000 -0.37240000 0.67740000
Au 1.49290000 0.08180000 -0.18420000
H -0.56800000 -0.05560000 -1.95630000
H -2.87820000 1.26310000 2.56320000
H -3.44980000 2.54690000 1.51250000
H -0.74030000 1.27880000 1.54710000
H -1.25020000 2.83050000 0.87770000
H 3.92290000 -1.72240000 0.95610000
H 4.72490000 -0.01350000 -0.13050000
H 3.97500000 0.24140000 1.89820000
H -2.48470000 1.20420000 -2.45860000
O -3.45980000 -0.85620000 -1.02660000
C -3.69580000 -1.64220000 0.20560000
O -3.80760000 -0.79470000 1.23180000
H -4.85240000 0.92950000 0.75830000
O -3.73860000 -2.83090000 0.18210000
H -3.05030000 2.43720000 -1.25190000

pbe0 Reaction_path 1 Reactant complex

C -2.61400000 0.64890000 -1.25770000
C -1.15340000 1.04170000 -0.98840000
C -0.44660000 0.06610000 -0.16860000
C -3.61360000 1.18210000 -0.24220000
H -2.89450000 1.08040000 -2.21800000
H -2.71080000 -0.43470000 -1.34460000
H -0.63250000 1.11950000 -1.94310000
H -1.08940000 2.02850000 -0.52290000
H -3.48270000 2.25470000 -0.10500000
C -0.03300000 -0.85110000 0.52590000
H 0.07730000 -1.69360000 1.17650000
Au 1.85340000 0.07490000 -0.07540000
P 4.07430000 0.51730000 -0.30340000
H 4.89130000 -0.60760000 -0.13850000
H 4.47510000 1.01570000 -1.54830000
H 4.61440000 1.43780000 0.60170000
C -2.89370000 0.50200000 2.12280000
C -3.69070000 0.46930000 1.07660000
H -2.00980000 1.12260000 2.10580000
H -3.10340000 -0.08170000 3.00730000
C -5.58800000 0.07810000 -0.02170000
O -6.67600000 -0.34950000 -0.25490000
O -4.93630000 0.96800000 -0.76850000
O -4.85070000 -0.28030000 1.04990000

pbe0 Reaction_path 1 Transition state

C	-2.63160000	1.25280000	-1.30810000
C	-1.41850000	1.71880000	-0.51620000
C	-0.94330000	0.74260000	0.45620000
C	-3.86330000	1.09010000	-0.41630000
H	-2.85260000	1.96740000	-2.09770000
H	-2.41550000	0.28740000	-1.76940000
H	-0.58570000	1.86410000	-1.20920000
H	-1.59240000	2.68450000	-0.03710000
H	-4.36380000	2.04020000	-0.24150000
C	-0.11230000	-0.06180000	0.96050000
H	-0.22200000	-0.73360000	1.79900000
Au	1.78860000	-0.07440000	0.09810000
P	3.92430000	-0.28060000	-0.66220000
H	4.32250000	-1.59070000	-0.95970000
H	4.25750000	0.40430000	-1.83820000
H	4.92690000	0.13920000	0.22190000
C	-2.76650000	0.81080000	1.86230000
C	-3.52870000	0.38390000	0.85140000
H	-2.53880000	1.86300000	1.94880000
H	-2.55460000	0.16970000	2.70450000
C	-4.84760000	-0.94450000	-0.33910000
O	-5.47990000	-1.90860000	-0.61930000
O	-4.79670000	0.19100000	-1.02700000
O	-4.06210000	-0.85790000	0.78090000

pbe0 Reaction_path 1 Intermediate product

C	2.33230000	-1.49150000	-1.31700000
C	1.28750000	-2.04620000	-0.33350000
C	1.17600000	-1.09400000	0.82830000
C	3.56660000	-0.99540000	-0.54090000
H	2.63650000	-2.22590000	-2.06600000
H	1.91150000	-0.61880000	-1.82920000
H	0.32450000	-2.12620000	-0.84320000
H	1.57210000	-3.04850000	0.01060000
H	4.32890000	-1.77760000	-0.43900000
C	0.24070000	-0.14510000	1.04310000
H	0.47820000	0.55310000	1.85290000
Au	-1.56540000	0.12560000	0.12040000
P	-3.63630000	0.52020000	-0.86860000
H	-3.93530000	1.87210000	-1.19170000
H	-3.91210000	-0.12850000	-2.10340000
H	-4.78080000	0.16050000	-0.10530000
C	2.42760000	-1.18310000	1.77460000
C	3.20260000	-0.46850000	0.80380000
H	2.73490000	-2.22440000	1.89660000
H	2.30410000	-0.66280000	2.72140000
C	4.19020000	1.17990000	-0.31200000
O	4.61740000	2.27330000	-0.46540000
O	4.18040000	0.15640000	-1.15090000
O	3.58020000	0.77490000	0.91840000

pbe0 Reaction_path 2 Reactant complex

C	2.99890000	1.25890000	-0.80060000
C	1.65400000	1.70140000	-1.37130000
C	0.59860000	1.95890000	-0.40070000
C	-0.23000000	2.37280000	0.39820000
C	3.06780000	-0.13440000	-0.20900000
C	2.39950000	-0.35860000	1.11680000
P	-2.14520000	-1.60100000	0.00510000
Au	-0.97280000	0.34900000	0.02700000
C	2.48890000	0.30770000	2.24700000
H	3.11370000	1.18670000	2.30210000
H	1.95210000	-0.00520000	3.13050000
H	-0.80590000	2.95200000	1.08970000
H	3.71810000	1.31390000	-1.61660000
H	3.33720000	1.95850000	-0.03520000
H	1.30070000	0.98590000	-2.11520000
H	1.80240000	2.64520000	-1.90270000
H	4.11380000	-0.43560000	-0.14860000
H	-3.51440000	-1.45410000	0.25410000
H	-2.11160000	-2.30360000	-1.20480000
H	-1.74460000	-2.55760000	0.94460000
C	1.60930000	-1.87380000	-0.31530000
O	0.95030000	-2.77850000	-0.73110000
O	1.61870000	-1.49100000	0.97750000
O	2.40300000	-1.10060000	-1.05010000

pbe0 Reaction_path 2 Transition state

C	-2.79600000	0.78630000	1.81240000
C	-1.65370000	-0.00860000	1.19960000
C	-1.03580000	0.58700000	0.01090000
C	-0.00970000	0.80460000	-0.70330000
C	-4.01090000	0.79170000	0.90120000
C	-3.59190000	0.87290000	-0.52270000
P	3.91350000	-0.70680000	0.42090000
Au	1.81660000	0.05230000	-0.04280000
C	-2.66780000	1.69910000	-1.03100000
H	-2.41170000	2.58940000	-0.47420000
H	-2.38610000	1.63720000	-2.07070000
H	0.05090000	1.31550000	-1.65320000
H	-3.07550000	0.36060000	2.77370000
H	-2.49840000	1.82070000	1.98560000
H	-1.98410000	-1.02530000	0.96420000
H	-0.84880000	-0.09850000	1.93260000
H	-4.71020000	1.57930000	1.17970000
H	4.95110000	0.17620000	0.09240000
H	4.20940000	-1.02740000	1.75240000
H	4.29520000	-1.87250000	-0.25590000
C	-4.80310000	-0.96820000	-0.29050000
O	-5.36820000	-1.95990000	-0.60910000
O	-4.11810000	-0.17410000	-1.18260000
O	-4.71860000	-0.45860000	0.93160000

pbe0 Reaction_path 2 Intermediate product

C	-2.74810000	-1.54570000	-1.82560000
C	-1.34130000	-1.85690000	-1.25750000
C	-1.29840000	-1.47340000	0.20260000
C	-0.35550000	-0.69920000	0.81890000

C	-3.54170000	-0.70030000	-0.83790000
C	-3.00050000	-0.83630000	0.54450000
P	3.40990000	1.00270000	-0.58930000
Au	1.40580000	0.04310000	0.12120000
C	-2.47850000	-2.04420000	1.08880000
H	-2.88010000	-2.96920000	0.67590000
H	-2.27090000	-2.06850000	2.15340000
H	-0.61610000	-0.42670000	1.84750000
H	-2.70310000	-1.03600000	-2.79100000
H	-3.31820000	-2.46550000	-1.98360000
H	-0.56750000	-1.29160000	-1.78230000
H	-1.11630000	-2.92210000	-1.38190000
H	-4.60830000	-0.95420000	-0.85340000
H	4.53130000	0.81520000	0.26300000
H	3.92780000	0.59080000	-1.84650000
H	3.39560000	2.41670000	-0.73170000
C	-3.30860000	1.31820000	0.18570000
O	-3.31740000	2.48250000	0.43320000
O	-3.12520000	0.34140000	1.17560000
O	-3.44560000	0.73890000	-1.00730000

pbe0 Reaction_path 3 Reactant complex

C	2.15760000	-1.16460000	1.20810000
C	1.52890000	-2.11580000	0.19470000
C	0.48780000	-1.54770000	-0.65000000
C	-0.28540000	-1.16370000	-1.51600000
C	2.86250000	0.05060000	0.63610000
C	3.77550000	-0.21410000	-0.52660000
C	4.86660000	-0.94550000	-0.59950000
P	-2.58500000	0.88590000	1.64520000
Au	-1.20270000	-0.27400000	0.25940000
H	-0.79440000	-0.95230000	-2.43340000
H	1.41000000	-0.81900000	1.92370000
H	2.89480000	-1.73180000	1.77700000
H	1.11510000	-2.97670000	0.72230000
H	2.29230000	-2.50260000	-0.48920000
H	-3.42570000	0.12510000	2.46490000
H	-1.95900000	1.75760000	2.54430000
H	-3.47440000	1.72460000	0.96340000
H	5.41980000	-1.04800000	-1.52110000
O	3.25390000	0.46680000	-1.60730000
C	2.17140000	1.17310000	-1.21890000
O	1.91650000	0.97880000	0.07310000
H	3.38490000	0.57190000	1.43660000
O	1.53400000	1.86860000	-1.94750000
H	5.22430000	-1.45540000	0.28310000

pbe0 Reaction_path 3 Transition state

C	-3.04880000	1.59900000	1.44880000
C	-1.65430000	1.93060000	0.88370000
C	-1.23770000	1.10960000	-0.24460000
C	-0.43600000	0.37660000	-0.89410000
C	-3.76190000	0.47490000	0.73310000
C	-3.43110000	0.39670000	-0.71520000
C	-3.19140000	1.40060000	-1.56300000
P	3.57120000	-0.49490000	0.54700000
Au	1.45550000	0.03970000	-0.09990000
H	-0.62020000	-0.13350000	-1.83030000
H	-2.99160000	1.35370000	2.50720000
H	-3.68560000	2.47940000	1.37010000
H	-0.88900000	1.76310000	1.64630000
H	-1.59540000	2.98410000	0.60790000
H	3.77220000	-1.83860000	0.88940000
H	4.55650000	-0.28730000	-0.42760000
H	4.09980000	0.17990000	1.65490000
H	-2.91560000	1.21610000	-2.59020000
O	-3.27280000	-0.91260000	-1.03580000
C	-3.16260000	-1.62770000	0.12670000
O	-3.35380000	-0.83720000	1.17760000
H	-4.83760000	0.54790000	0.89640000
O	-2.91730000	-2.78900000	0.15370000
H	-3.39290000	2.41620000	-1.25430000

pbe0 Reaction_path 3 Intermediate product

C	-2.90860000	1.56450000	1.50830000
C	-1.55490000	1.91640000	0.84240000
C	-1.46890000	1.23210000	-0.50120000
C	-0.44230000	0.45630000	-0.96230000
C	-3.59320000	0.43670000	0.74700000
C	-3.07800000	0.33730000	-0.64870000
C	-2.71250000	1.45360000	-1.45430000
P	3.49340000	-0.49190000	0.66910000
Au	1.39230000	0.07270000	-0.17060000
H	-0.67170000	-0.05840000	-1.90190000
H	-2.79330000	1.27950000	2.55690000
H	-3.58920000	2.42050000	1.48970000
H	-0.71340000	1.58040000	1.45300000
H	-1.46780000	3.00250000	0.72610000
H	3.54080000	-1.66600000	1.46900000
H	4.50050000	-0.76350000	-0.29580000
H	4.14140000	0.45320000	1.50910000
H	-2.51210000	1.27230000	-2.50510000
O	-3.05820000	-0.95520000	-1.01020000
C	-3.10810000	-1.70960000	0.17060000
O	-3.31360000	-0.90870000	1.21670000
H	-4.68360000	0.55420000	0.74070000
O	-2.96470000	-2.89100000	0.17800000
H	-3.22450000	2.39060000	-1.23700000

m06 Reaction_path 1 Reactant complex

C	1.60370000	-2.01220000	-0.71720000
C	0.48690000	-2.82330000	-0.04680000
C	-0.84860000	-2.25830000	-0.17190000
C	2.51610000	-1.29610000	0.26600000
H	2.23030000	-2.67670000	-1.30750000
H	1.18300000	-1.27830000	-1.40740000
H	0.42300000	-3.81150000	-0.50390000
H	0.70070000	-2.99950000	1.00920000

H	3.06810000	-2.01140000	0.87200000
C	-2.01680000	-1.94760000	-0.32120000
H	-3.07260000	-1.91880000	-0.48280000
Au	-1.16140000	0.09970000	-0.07990000
P	-0.75000000	2.39000000	0.03000000
H	-1.82760000	3.24080000	-0.21630000
H	-0.27610000	2.84490000	1.26430000
H	0.22540000	2.86660000	-0.84990000
C	1.14470000	-0.33170000	2.20360000
C	1.87560000	-0.24160000	1.11330000
H	0.92820000	-1.29890000	2.63150000
H	0.76850000	0.54860000	2.70290000
C	3.19650000	0.77460000	-0.37200000
O	3.73230000	1.65320000	-0.96180000
O	3.45990000	-0.52390000	-0.49500000
O	2.20900000	0.97030000	0.54050000

m06 Reaction_path 1 Transition state

C	-2.58440000	1.07810000	-1.46140000
C	-1.38780000	1.64630000	-0.71460000
C	-0.97500000	0.81300000	0.41890000
C	-3.82570000	1.03220000	-0.57180000
H	-2.79660000	1.67190000	-2.34590000
H	-2.36200000	0.05790000	-1.77850000
H	-0.53300000	1.67770000	-1.39200000
H	-1.56950000	2.67360000	-0.39350000
H	-4.32170000	1.99840000	-0.52030000
C	-0.12520000	0.07290000	1.00070000
H	-0.24830000	-0.48190000	1.91840000
Au	1.78130000	-0.07740000	0.11110000
P	3.93210000	-0.33270000	-0.76240000
H	4.72470000	-1.30670000	-0.14800000
H	4.03270000	-0.70070000	-2.10760000
H	4.77210000	0.78320000	-0.71410000
C	-2.70180000	1.04520000	1.70400000
C	-3.49230000	0.49160000	0.77150000
H	-2.53470000	2.11170000	1.68350000
H	-2.49720000	0.51800000	2.62320000
C	-4.81750000	-0.97450000	-0.23860000
O	-5.45190000	-1.96050000	-0.37780000
O	-4.75340000	0.06120000	-1.06510000
O	-4.01980000	-0.73940000	0.86370000

m06 Reaction_path 1 Intermediate product

C	-2.29085752	1.26206022	-1.42191514
C	-1.26702337	1.90959272	-0.49172790
C	-1.14555709	1.07107168	0.74337444
C	-3.57341436	0.97254576	-0.63847299
H	-2.52670335	1.87939152	-2.28425815
H	-1.89948703	0.30369218	-1.76886121
H	-0.30815949	1.96229772	-1.00259827
H	-1.57070497	2.92909397	-0.24304688
H	-4.22083309	1.84937394	-0.60040874
C	-0.19094779	0.19468590	1.05111853
H	-0.39076988	-0.43047352	1.92048266
Au	1.63033054	-0.08087839	0.10888245
P	3.73680789	-0.47856779	-0.87752193
H	4.32264680	-1.72344457	-0.61954379
H	3.83158513	-0.43439525	-2.27368572
H	4.78534245	0.37838607	-0.52175289
C	-2.42056310	1.18864746	1.64111888
C	-3.27304595	0.49887074	0.72728957
H	-2.69089594	2.23778369	1.74755283
H	-2.32305955	0.69004660	2.59791262
C	-4.42161141	-1.09868415	-0.29961116
O	-4.94785913	-2.14012032	-0.37198197
O	-4.31414927	-0.12817414	-1.17440942
O	-3.74220603	-0.68140831	0.90788559

m06 Reaction_path 2 Reactant complex

C	3.00600000	0.75120000	-1.87090000
C	1.58480000	0.83540000	-2.42050000
C	0.61820000	1.59480000	-1.64010000
C	-0.18620000	2.33490000	-1.10250000
C	3.22670000	-0.14660000	-0.67400000
C	2.68760000	0.31000000	0.64810000
P	-1.50990000	-1.29260000	1.28590000
Au	-0.70170000	0.44110000	-0.03710000
C	2.78650000	1.46270000	1.26890000
H	3.31740000	2.28050000	0.80560000
H	2.35080000	1.61320000	2.24490000
H	-0.78330000	3.16010000	-0.78100000
H	3.63380000	0.38620000	-2.68120000
H	3.37860000	1.74310000	-1.61340000
H	1.19140000	-0.16310000	-2.61440000
H	1.62950000	1.33120000	-3.39190000
H	4.29390000	-0.35050000	-0.58580000
H	-2.78150000	-1.10550000	1.82820000
H	-1.61620000	-2.53370000	0.65600000
H	-0.73200000	-1.58680000	2.40850000
C	1.90580000	-1.74460000	0.25920000
O	1.26860000	-2.73800000	0.41820000
O	2.01780000	-0.77340000	1.19020000
O	2.56610000	-1.41690000	-0.84600000

m06 Reaction_path 2 Transition state

C	-2.75970000	-1.15220000	-1.65350000
C	-1.55130000	-0.37390000	-1.16470000
C	-1.07480000	-0.70980000	0.19240000
C	-0.08360000	-0.72230000	0.99060000
C	-3.97710000	-0.87480000	-0.79450000
C	-3.59400000	-0.75260000	0.63230000
P	3.83240000	0.65260000	-0.60000000
Au	1.75850000	-0.08680000	0.18370000
C	-2.71510000	-1.53890000	1.27800000
H	-2.53380000	-2.53040000	0.88890000
H	-2.46720000	-1.34140000	2.30900000
H	-0.07240000	-0.98850000	2.03630000

H	-2.98740000	-0.89110000	-2.68370000
H	-2.56680000	-2.22430000	-1.62460000
H	-1.76220000	0.69820000	-1.20780000
H	-0.71290000	-0.55840000	-1.83690000
H	-4.74850000	-1.62690000	-0.95320000
H	4.86170000	-0.29250000	-0.64380000
H	3.87280000	1.16740000	-1.89960000
H	4.43260000	1.68530000	0.12680000
C	-4.65320000	1.11120000	0.06820000
O	-5.14670000	2.17300000	0.21380000
O	-4.06290000	0.40640000	1.10460000
O	-4.55280000	0.41440000	-1.05410000

m06 Reaction_path 2 Intermediate product

C	-2.76887444	-1.55537682	-1.80520246
C	-1.34565700	-1.71238477	-1.25417707
C	-1.36358076	-1.34822404	0.20562875
C	-0.41172265	-0.64043624	0.87355151
C	-3.58068156	-0.74228486	-0.82608220
C	-2.99532844	-0.86034695	0.53526332
P	3.49494426	0.85792015	-0.53587399
Au	1.40405858	0.02456176	0.17914079
C	-2.48887089	-2.04665333	1.09515242
H	-2.80248514	-2.98428821	0.65391544
H	-2.26660903	-2.06968419	2.15070863
H	-0.67928473	-0.39358352	1.90065227
H	-2.79270647	-1.10157399	-2.79200531
H	-3.25875287	-2.52426914	-1.89372058
H	-0.64963281	-1.04487265	-1.75939634
H	-0.98596358	-2.73025138	-1.39948702
H	-4.63415545	-1.02036592	-0.82943983
H	4.62753227	0.29384948	0.06054370
H	3.81229185	0.73832397	-1.89286702
H	3.72137232	2.22107068	-0.32033004
C	-3.41680277	1.27168013	0.20046081
O	-3.48268904	2.42490923	0.44241546
O	-3.19758475	0.30982640	1.17704366
O	-3.51609971	0.69043449	-0.99046423

m06 Reaction_path 3 Reactant complex

C	-2.85110000	1.84540000	1.10960000
C	-1.43670000	2.41540000	1.05740000
C	-0.72290000	2.29900000	-0.20630000
C	-0.14180000	2.35740000	-1.27520000
C	-2.99090000	0.33950000	1.10690000
C	-2.69980000	-0.38630000	-0.17230000
C	-3.09790000	-0.16130000	-1.40300000
P	1.72640000	-1.62820000	-0.17920000
Au	0.66640000	0.41020000	-0.53180000
H	0.24210000	2.61560000	-2.23810000
H	-3.30490000	2.22100000	2.02450000
H	-3.45150000	2.23200000	0.28540000
H	-0.82740000	1.99370000	1.85720000
H	-1.49880000	3.48590000	1.26210000
H	0.96900000	-2.75560000	-0.50500000
H	2.90650000	-1.82400000	-0.89760000
H	2.11310000	-1.88850000	1.13660000
H	-2.80630000	-0.81150000	-2.21360000
O	-1.88230000	-1.45180000	0.16310000
C	-1.47700000	-1.32250000	1.44390000
O	-2.06270000	-0.27870000	2.02130000
H	-3.99370000	0.08750000	1.45250000
O	-0.67660000	-2.04050000	1.95600000
H	-3.73410000	0.68380000	-1.61840000

m06 Reaction_path 3 Transition state

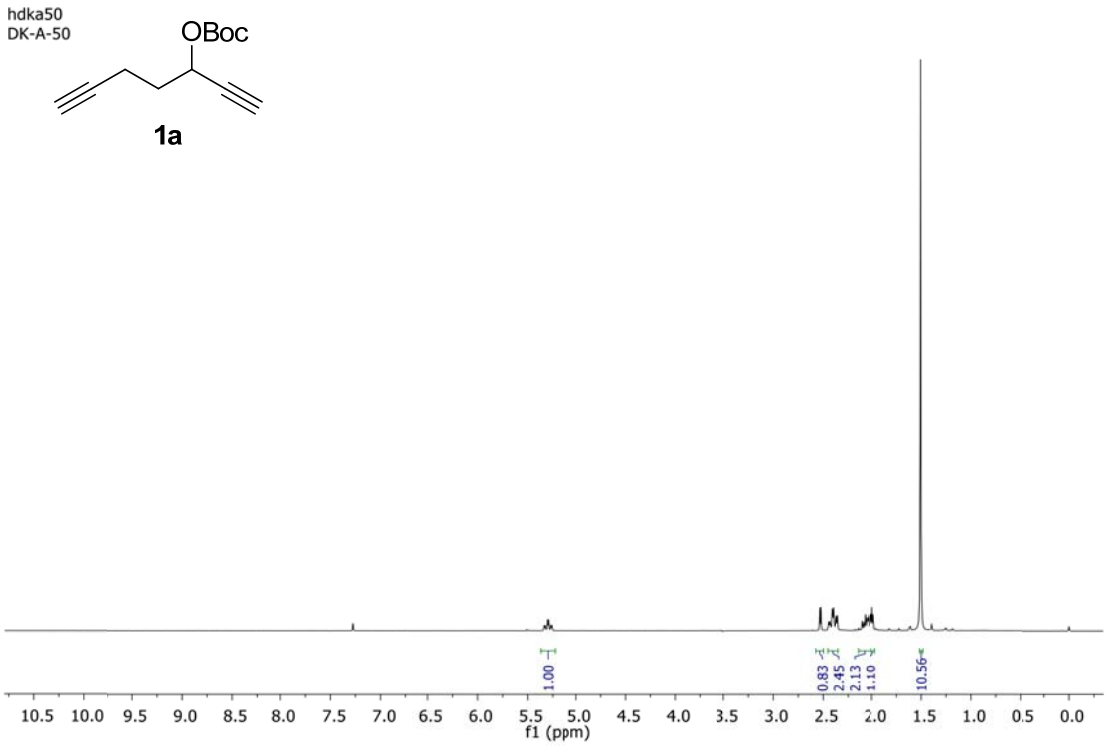
C	-3.01920000	1.56810000	1.43800000
C	-1.58880000	1.72840000	0.90650000
C	-1.30840000	1.03390000	-0.35850000
C	-0.49570000	0.38080000	-1.08680000
C	-3.80750000	0.47350000	0.76440000
C	-3.50040000	0.36940000	-0.68310000
C	-3.16630000	1.36450000	-1.51660000
P	3.58060000	-0.32200000	0.52280000
Au	1.43580000	0.09830000	-0.30060000
H	-0.69810000	-0.06580000	-2.04940000
H	-3.02060000	1.40460000	2.51210000
H	-3.57480000	2.48940000	1.26750000
H	-0.87350000	1.31670000	1.62020000
H	-1.35700000	2.78760000	0.79910000
H	3.81150000	-1.61810000	0.99310000
H	4.64220000	-0.15390000	-0.37070000
H	4.00480000	0.44880000	1.60940000
H	-2.91050000	1.16200000	-2.54490000
O	-3.42820000	-0.93910000	-1.00400000
C	-3.35040000	-1.66670000	0.16400000
O	-3.47190000	-0.85540000	1.20890000
H	-4.87280000	0.61640000	0.94280000
O	-3.18240000	-2.83590000	0.18690000
H	-3.33920000	2.38900000	-1.22160000

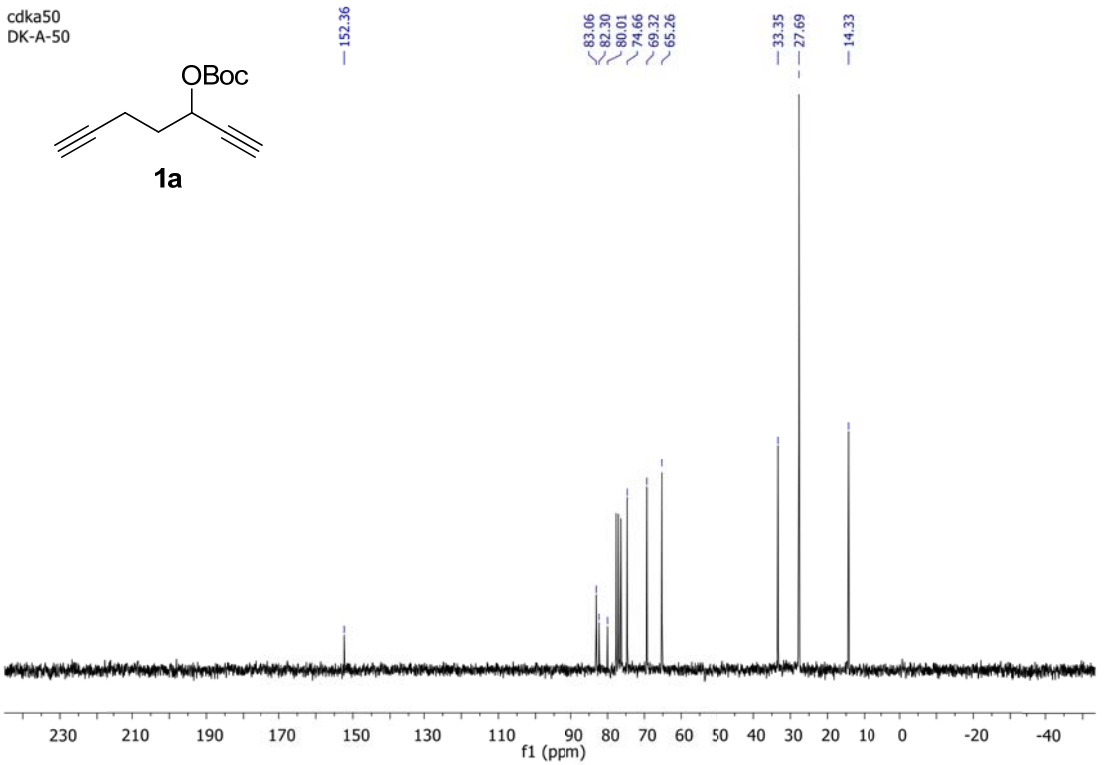
m06 Reaction_path 3 Intermediate product

C	-2.94264567	1.55379881	1.49362183
C	-1.55658070	1.74284738	0.86240598
C	-1.55336700	1.06124592	-0.47898849
C	-0.53063619	0.34522677	-1.02128775
C	-3.67644888	0.47056081	0.74047984
C	-3.12143614	0.34489974	-0.63277798
C	-2.76123048	1.42291846	-1.45911313
P	3.56931800	-0.28562395	0.49060975
Au	1.37616936	0.09873812	-0.29767543
H	-0.78429625	-0.15711749	-1.95437646
H	-2.89497103	1.31580187	2.55261293
H	-3.53692495	2.46174896	1.40292509
H	-0.77812022	1.28904456	1.47327074
H	-1.31865520	2.80121987	0.76359907
H	3.74600235	-1.41917665	1.29068236
H	4.55958432	-0.47759834	-0.47832173

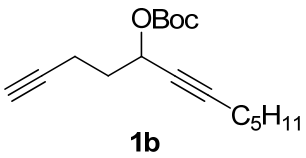
H	4.15566492	0.70325698	1.28736653
H	-2.55642936	1.23428424	-2.50155103
O	-3.20419311	-0.95262330	-0.99708900
C	-3.32378029	-1.69357040	0.16948066
O	-3.46390219	-0.87802518	1.20951451
H	-4.75263771	0.63875557	0.71892963
O	-3.28907050	-2.87312712	0.18406901
H	-3.16812809	2.39776561	-1.22223593

4 Scanned spectra (in numerical order)



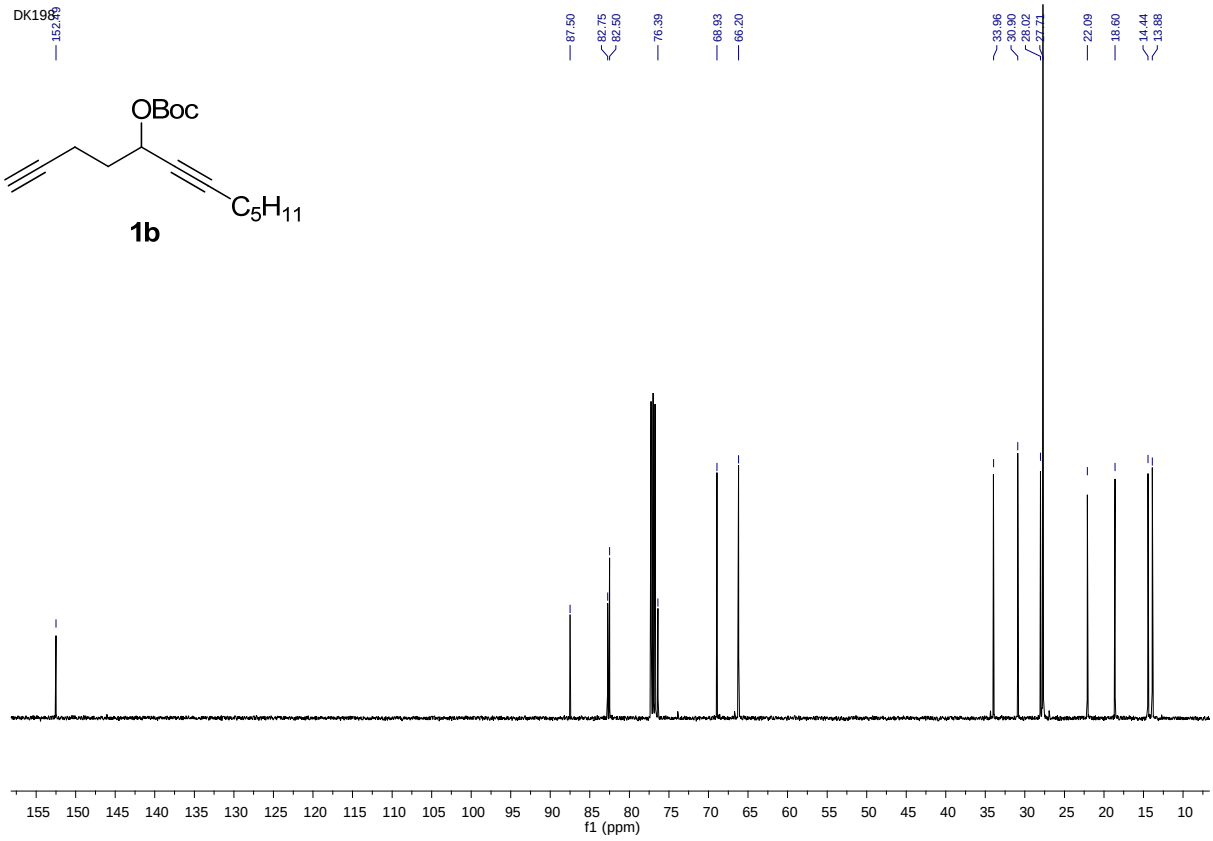


DK198



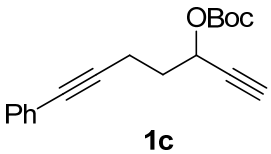
1b

DK198

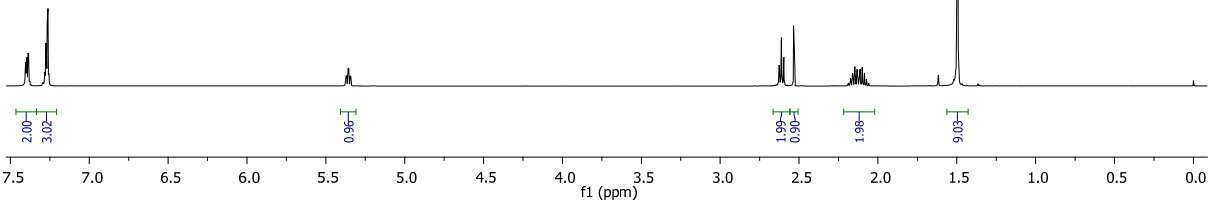


1b

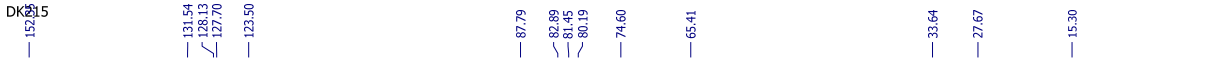
DK215

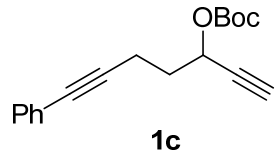


1c

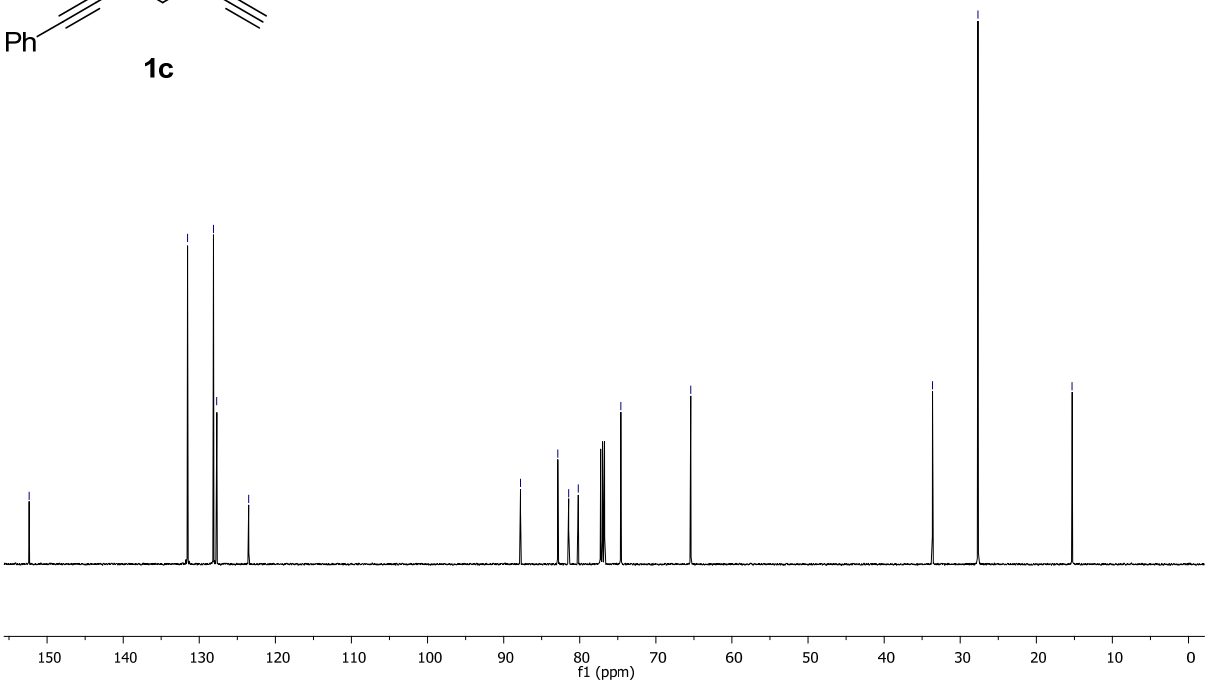


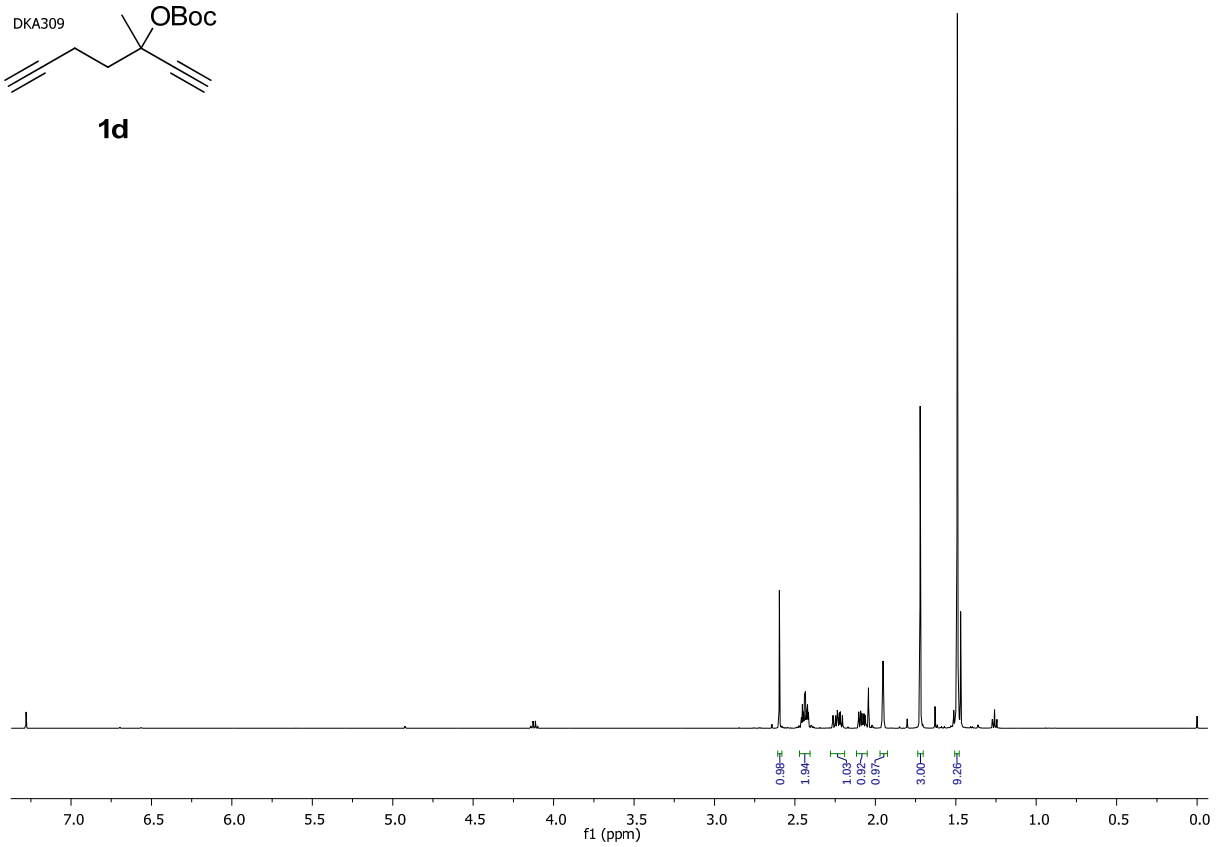
DK215

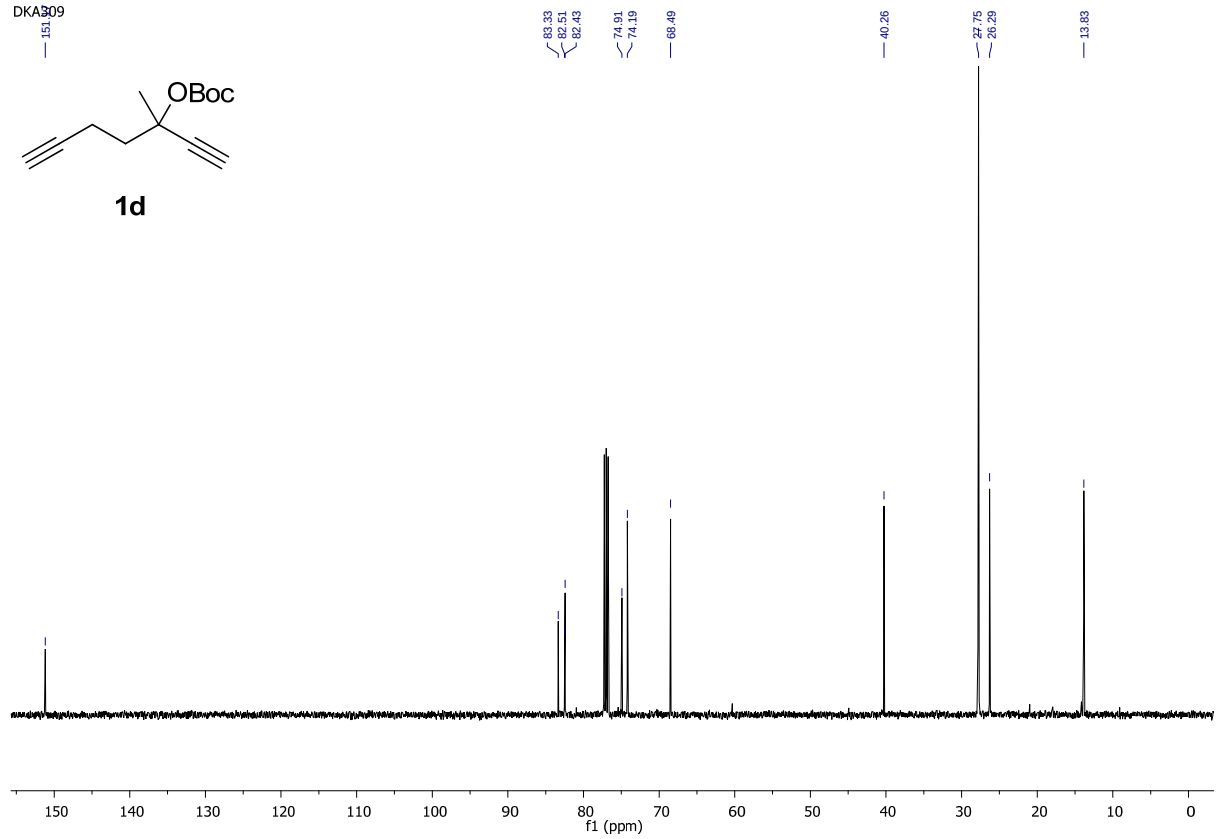




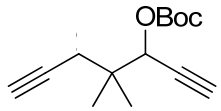
1c



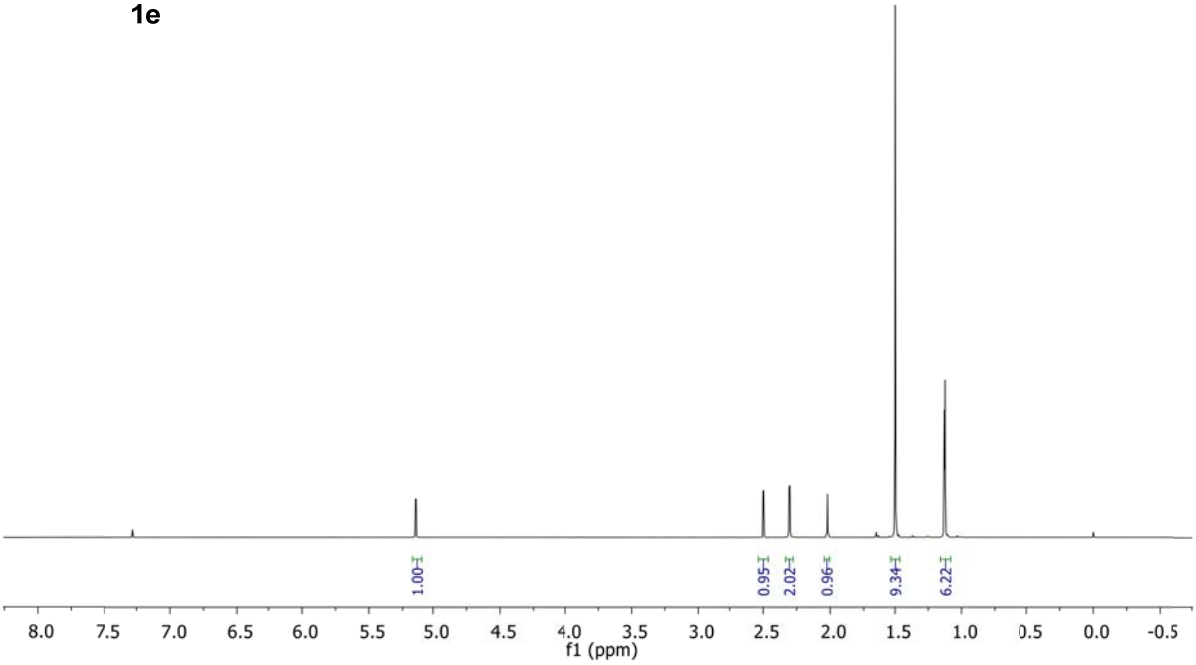

DKA309
OBoc
1d
0.98
1.94
1.03
0.92
0.97
3.00
9.26
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


DKA309
151.93
83.33
82.51
82.43
74.91
74.19
68.49
40.26
27.75
26.29
13.83
OBoc
1d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

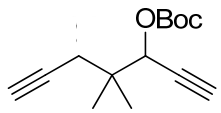
DKA438



1e

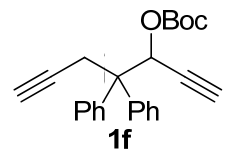


DKA438



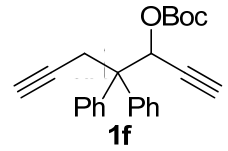
1e

hdka228
DKA228



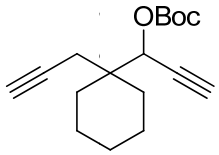
1f

cdka228
DKA 228



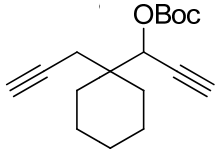
1f

DKA251



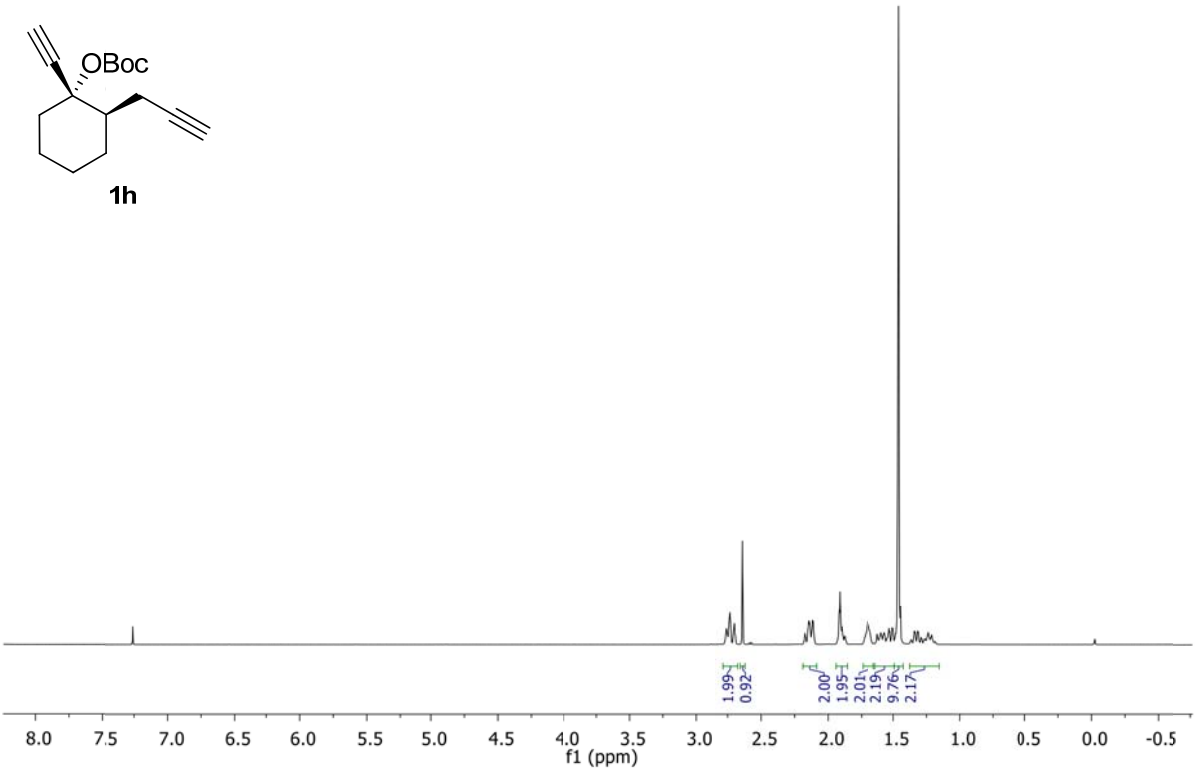
1g

DKA251

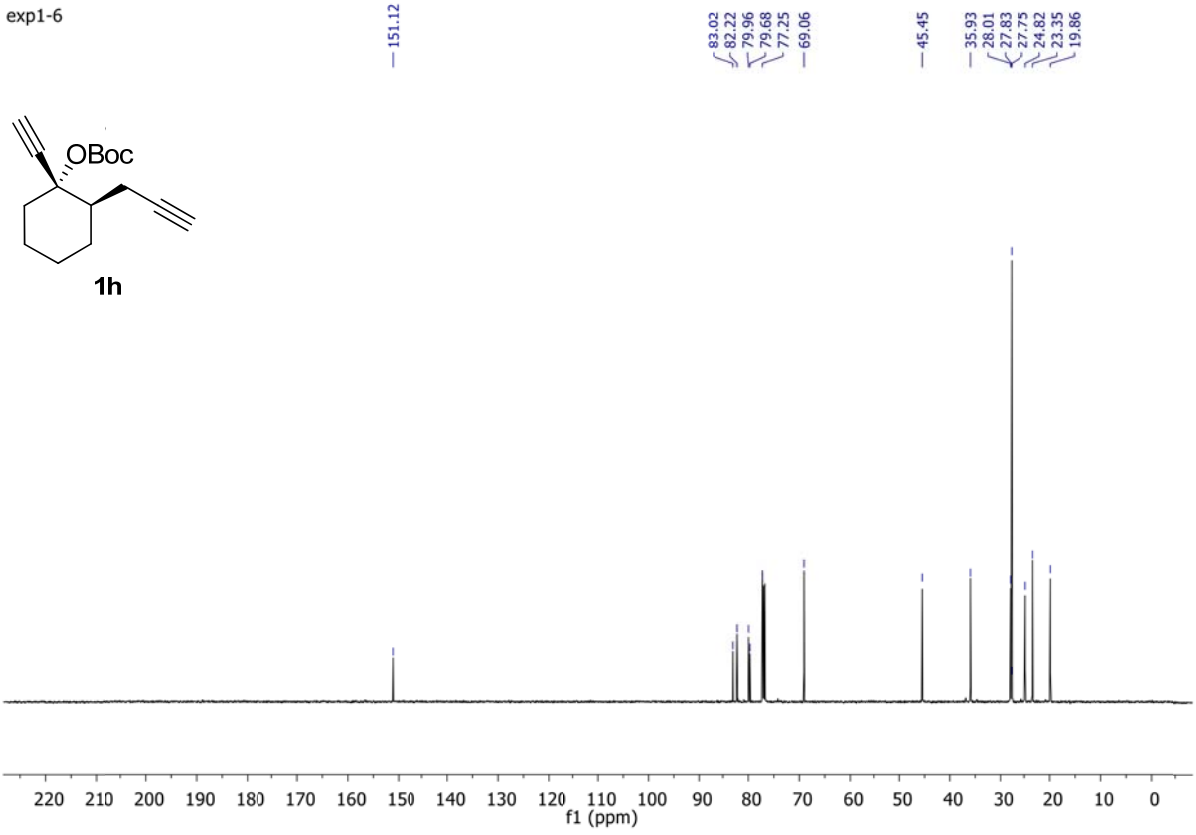


1g

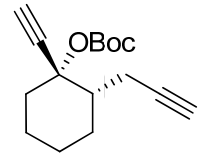
exp1-6
ref. chcl3 = 7.26ppm



exp1-6

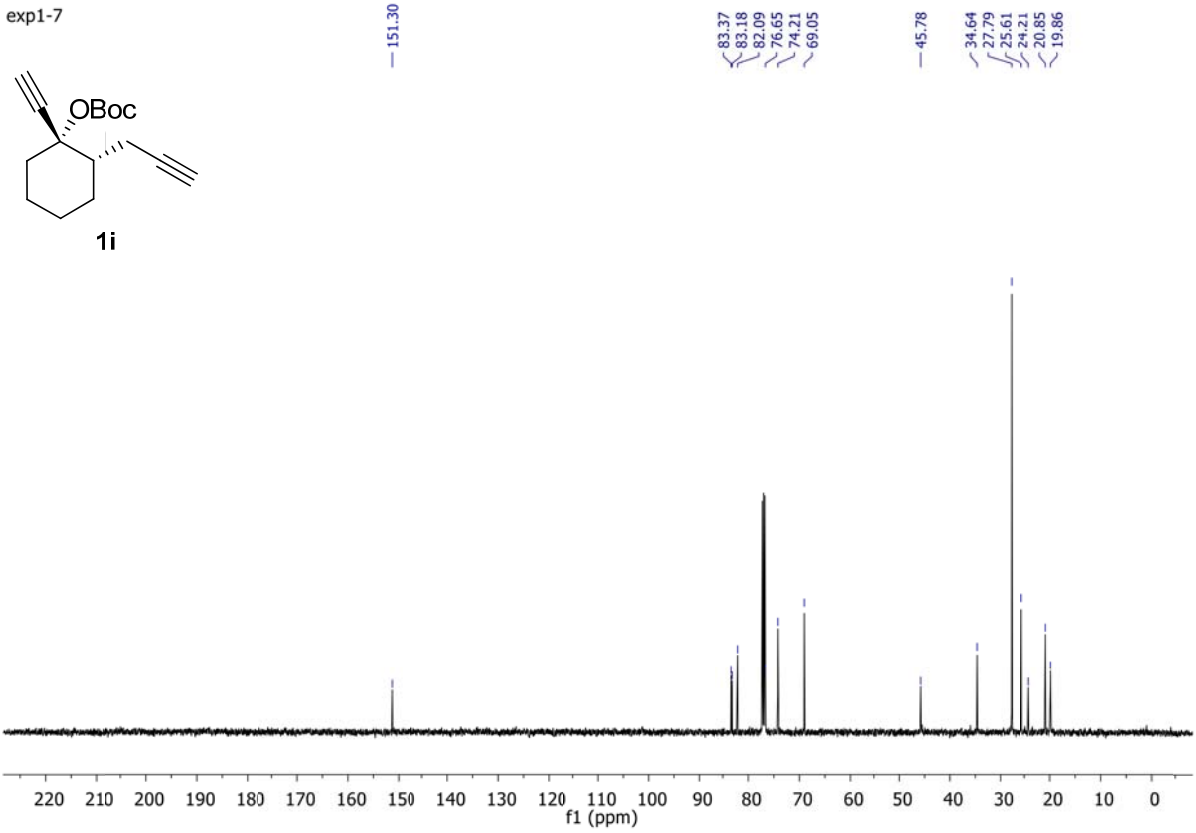


exp1-7



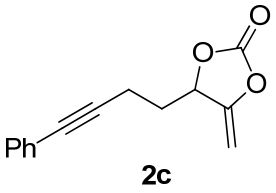
1i

exp1-7



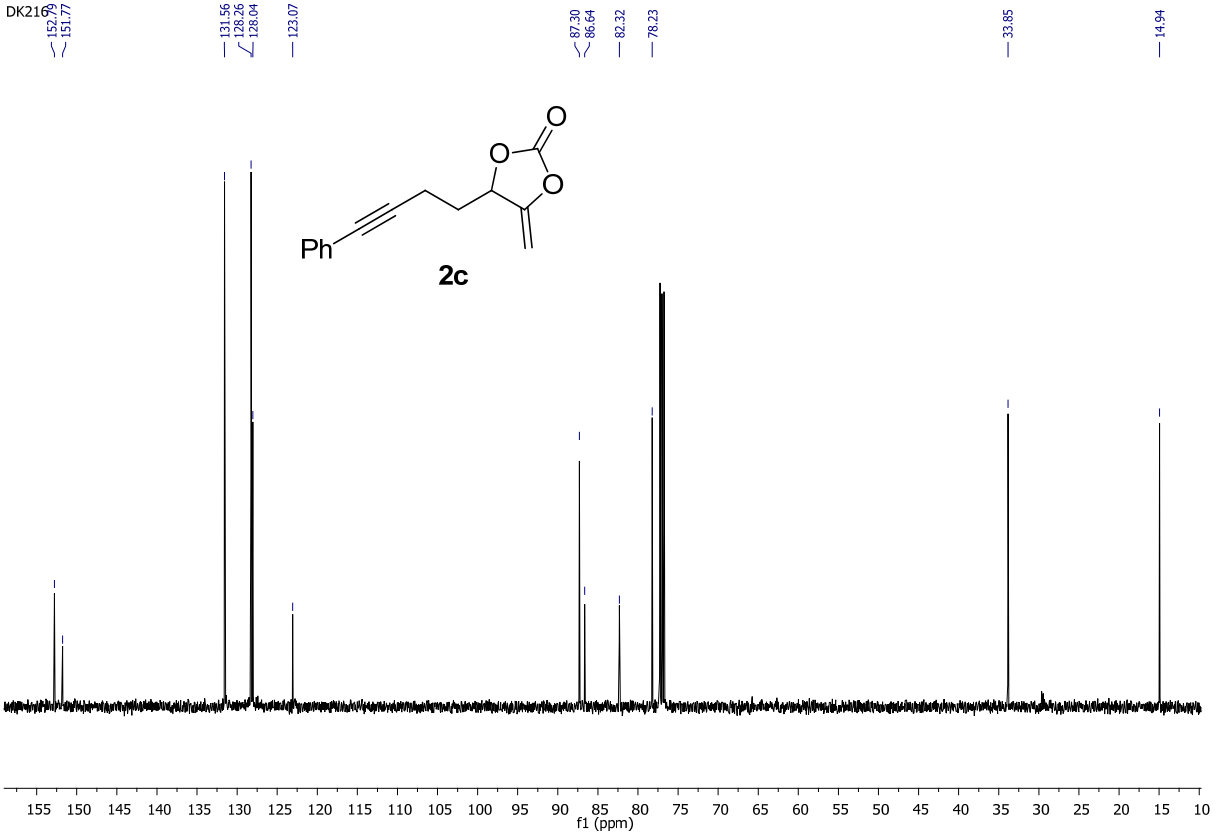
1i

DK216



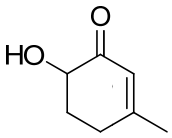
2c

DK216



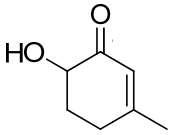
2c

BV-II-435B



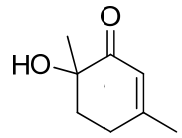
4a

BV-II-435B

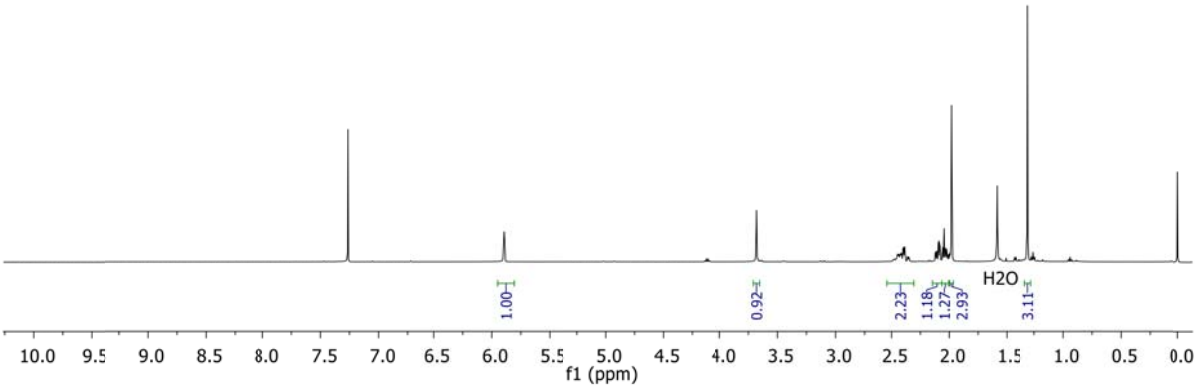


4a

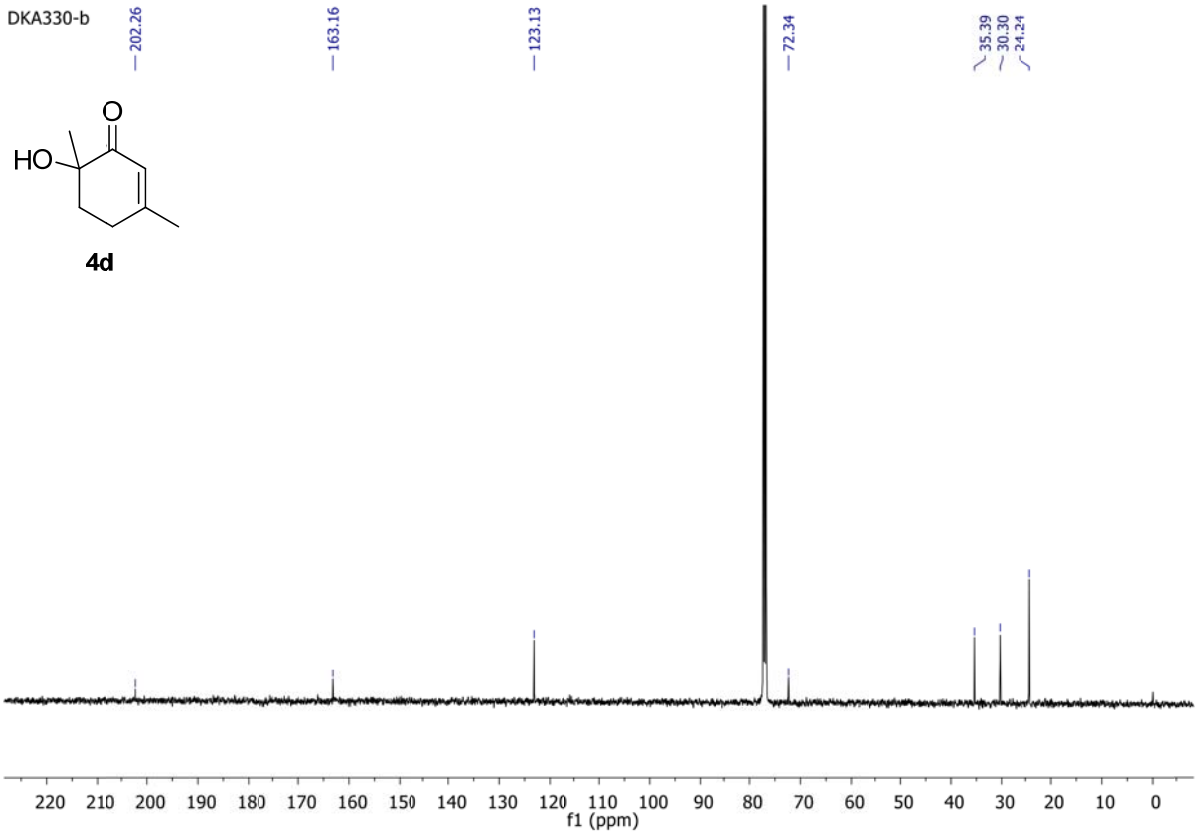
DKA330-b



4d

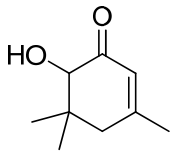


DKA330-b

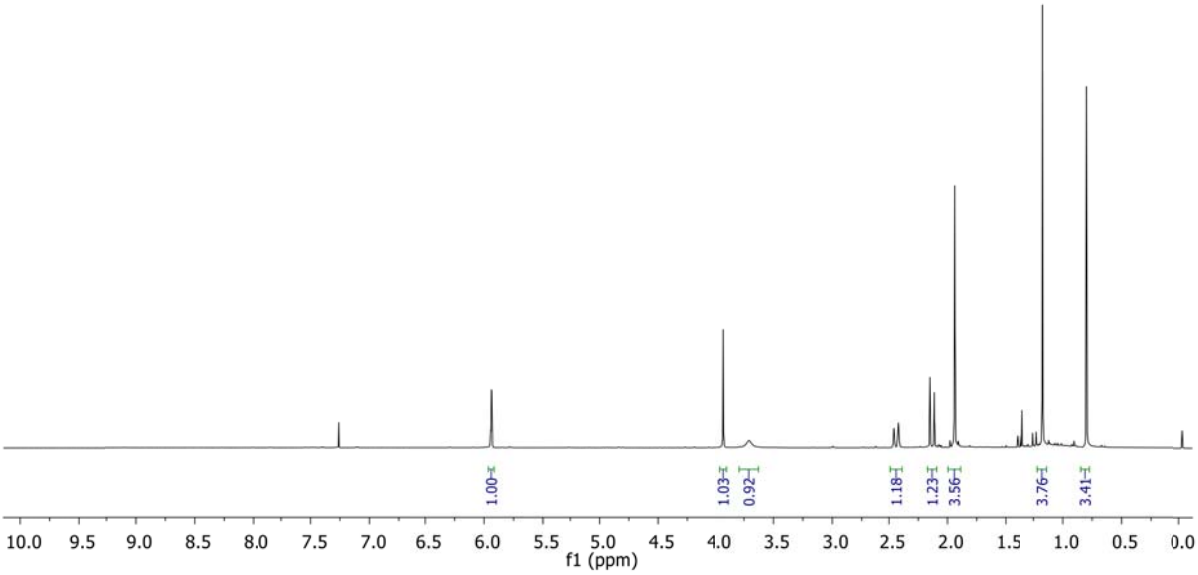


4d

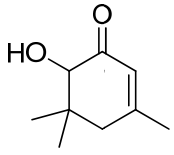
DKA447



4e

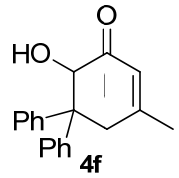


DKA447b

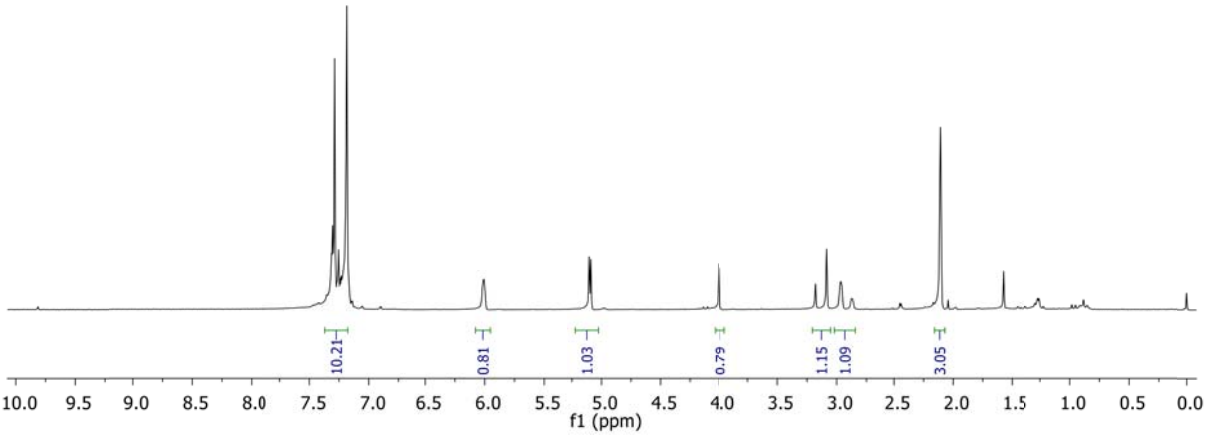


4e

hdka488
DKA 488

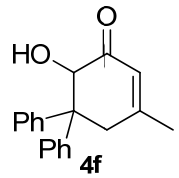


4f

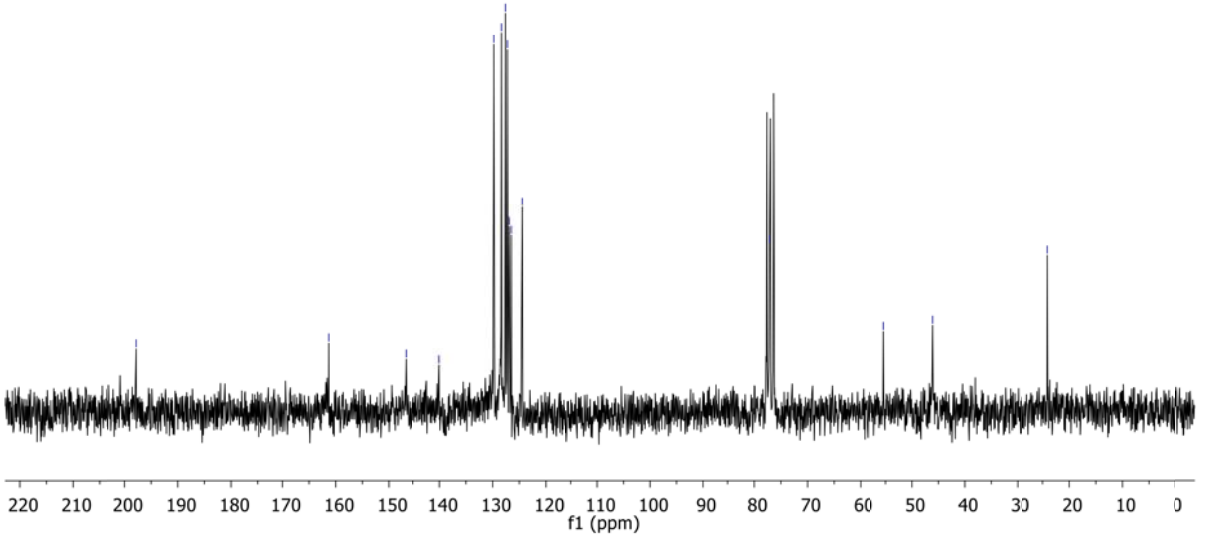


cdka488
DKA488

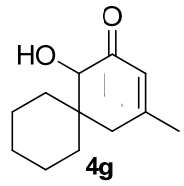
197.81
161.29
146.76
140.08
129.78
128.35
127.59
127.23
126.90
126.50
124.44
77.16
55.41
46.09
24.11



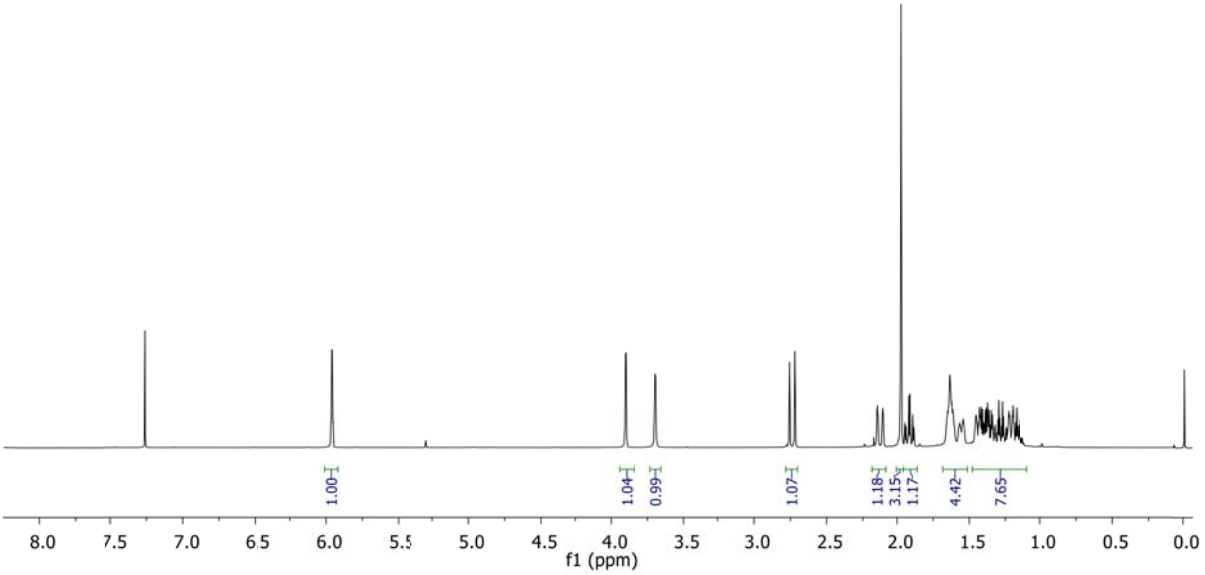
4f



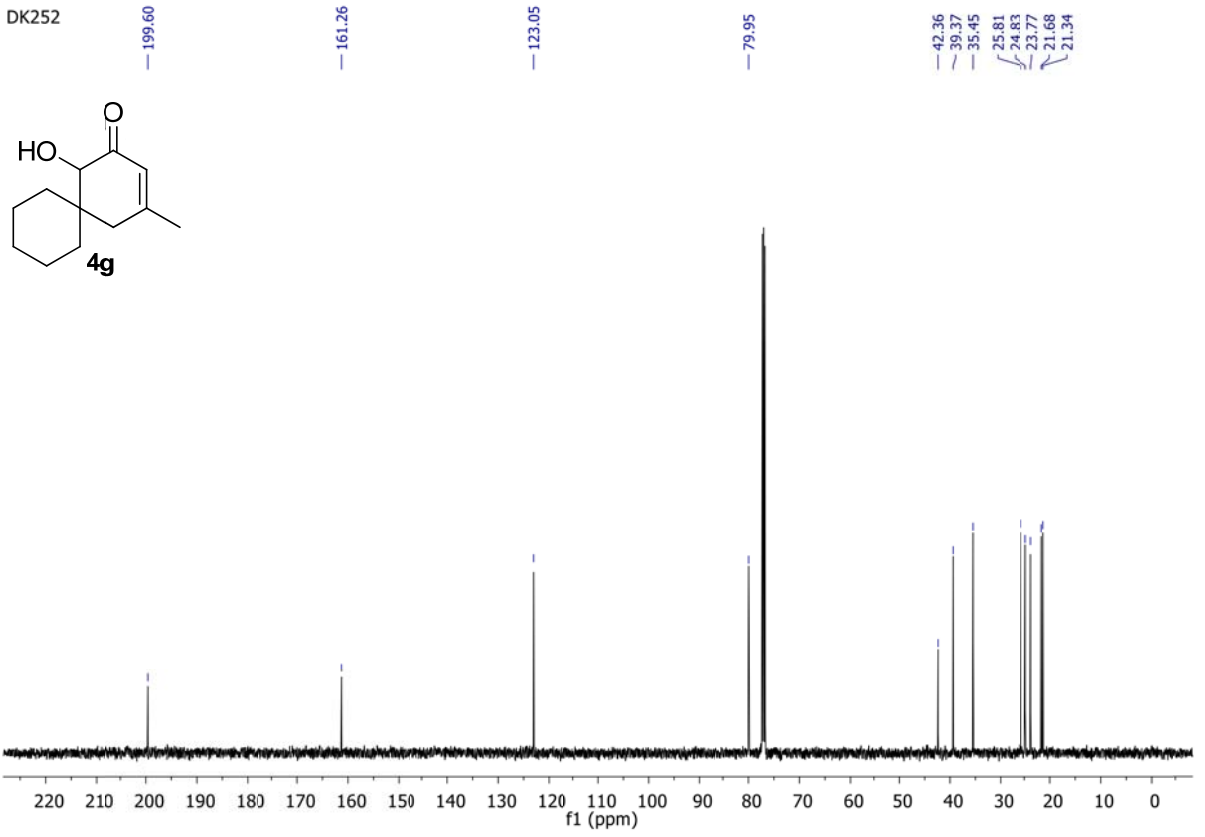
DK252



4g

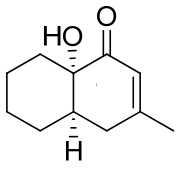


DK252

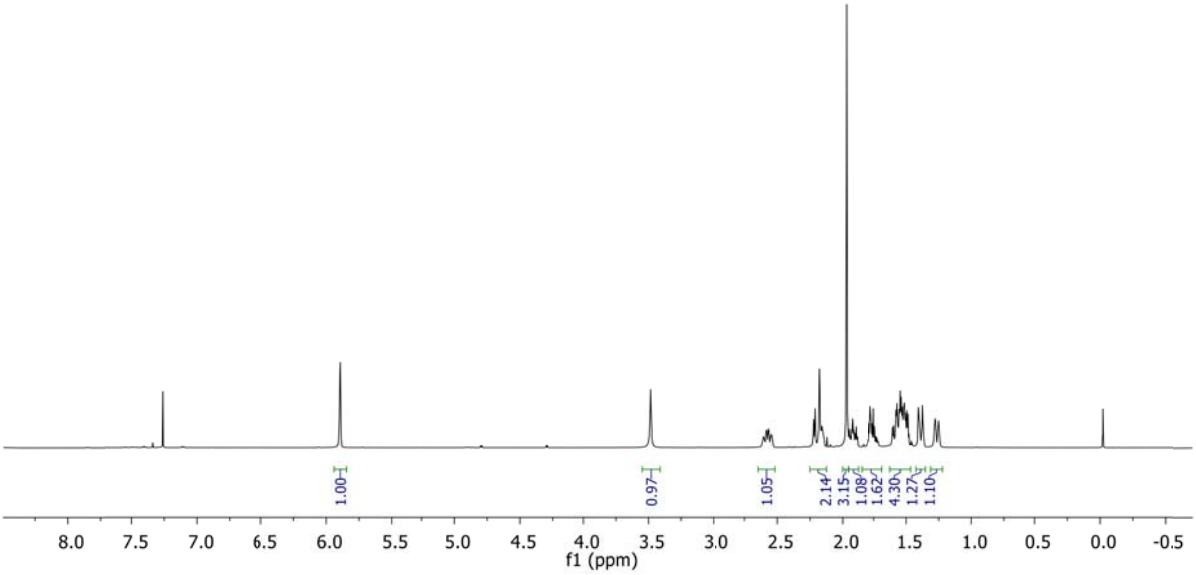


4g

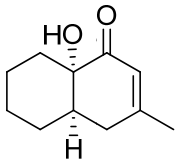
exp1-5



4h

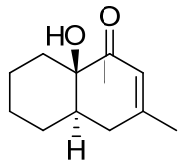


exp1-5

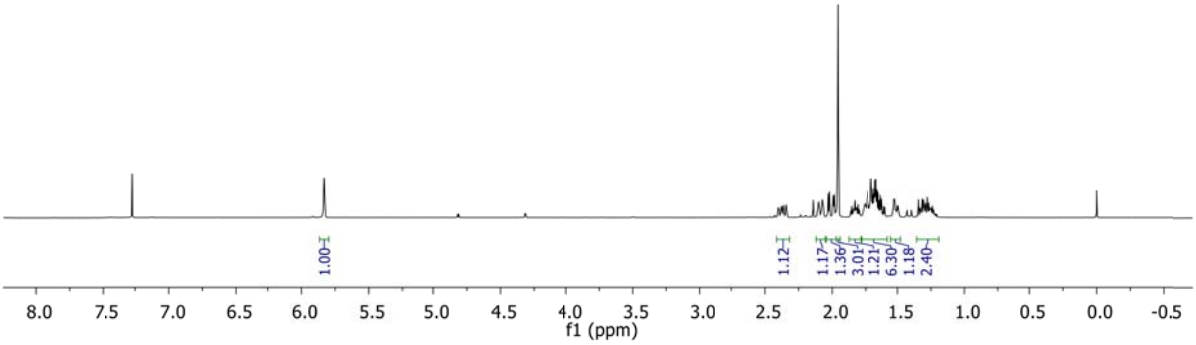


4h

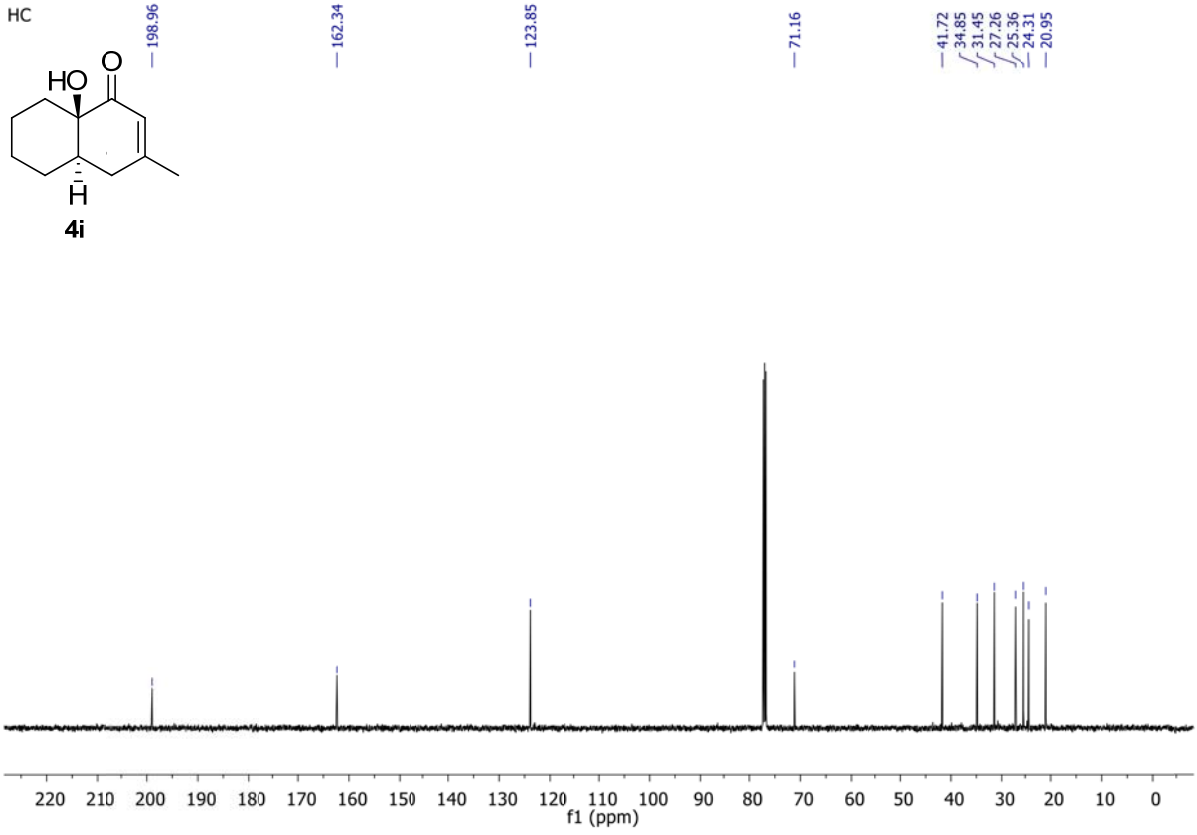
HH


HO
O
H

4i

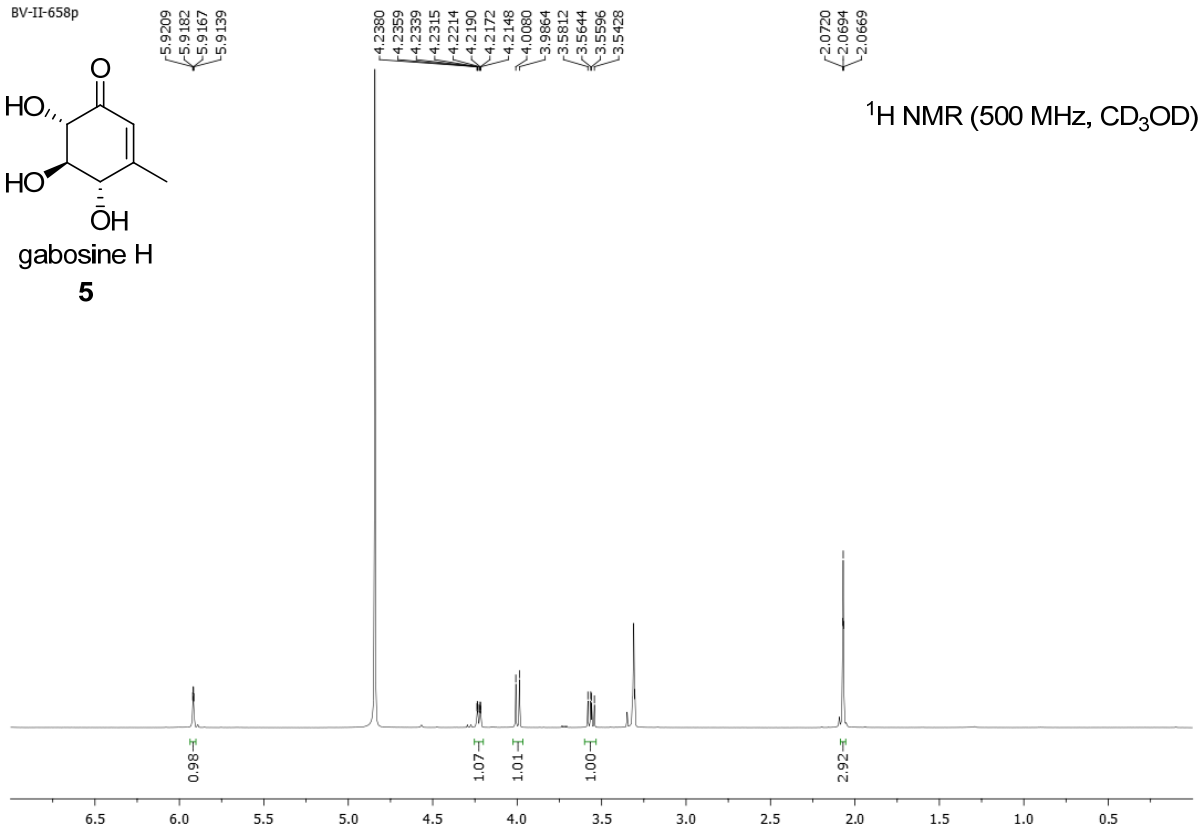

1.00
1.12
1.17
1.36
3.01
1.21
6.30
1.18
2.40
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

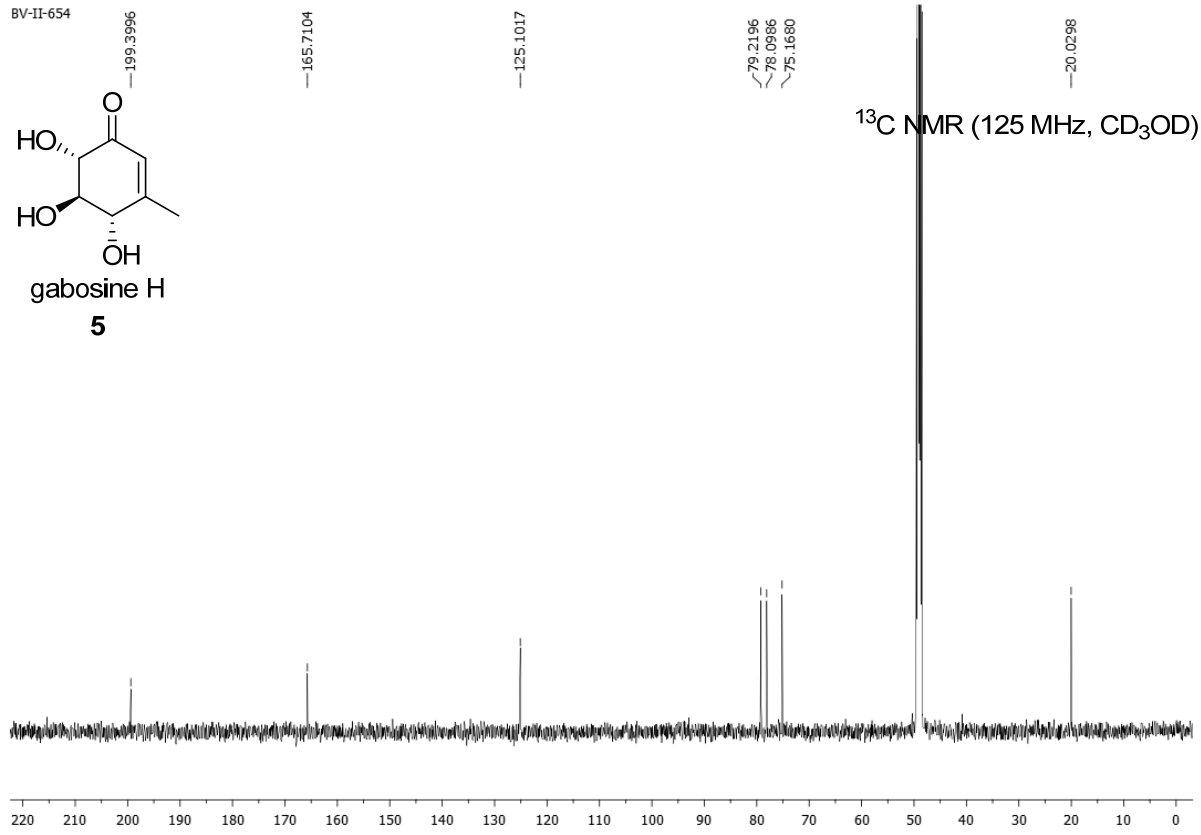
HC

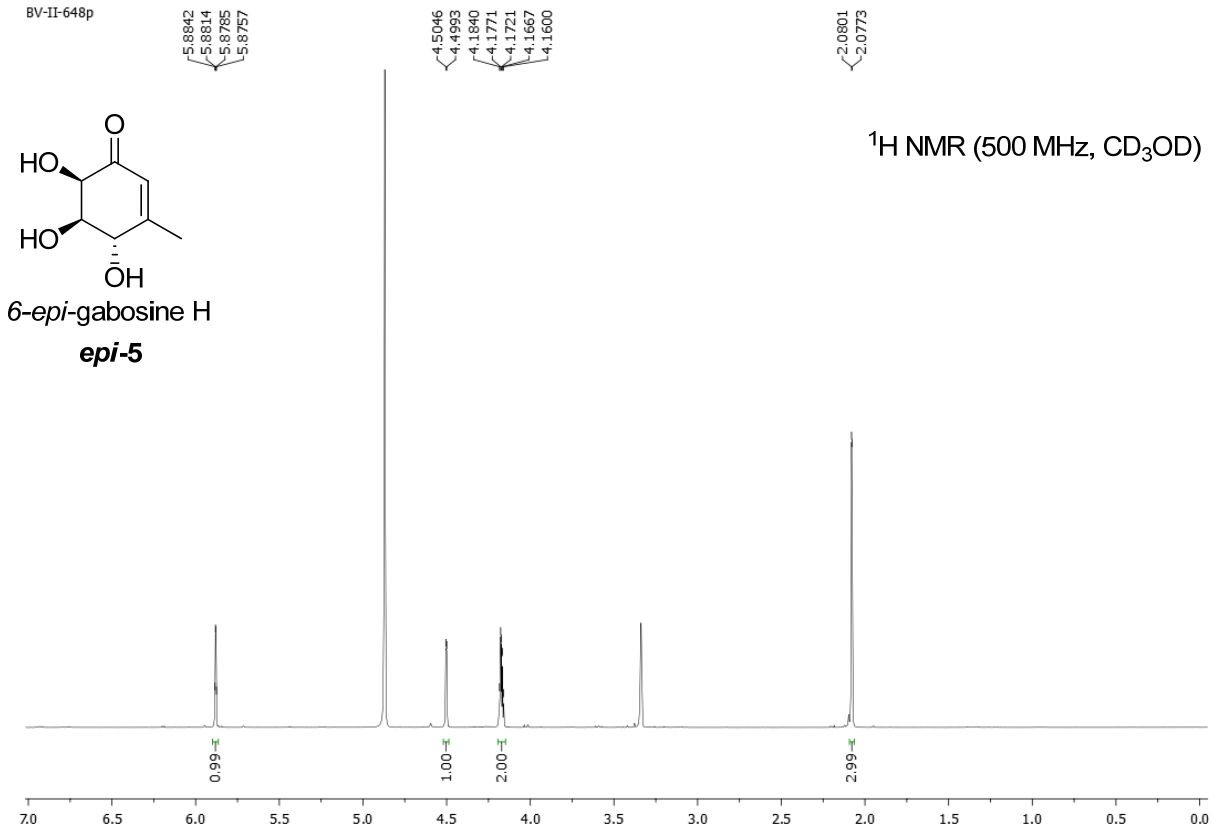

198.96
162.34
123.85
71.16
41.72
34.85
31.45
27.26
25.36
24.31
20.95
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HO
O
H

4i


BV-II-658p
5.9209
5.9182
5.9167
5.9139
4.2380
4.2359
4.2339
4.2315
4.2214
4.2190
4.2172
4.2148
4.0080
3.9864
3.5812
3.5644
3.5596
3.5428
2.0720
2.0694
2.0669
HO
HO
OH
gabosine H
5
^{1}H NMR (500 MHz, CD$_3$OD)
0.98
1.07
1.01
1.00
2.92
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

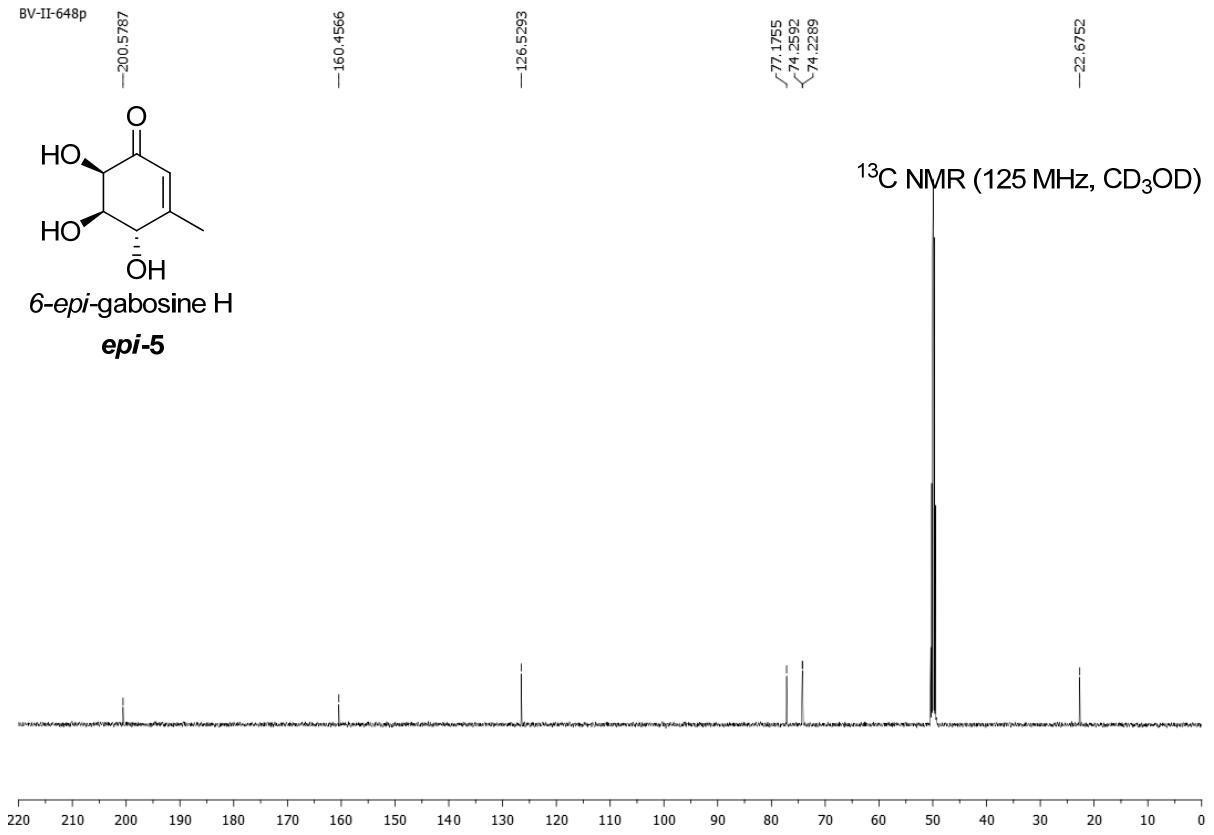

BV-II-654
199.3996
165.7104
125.1017
79.2196
78.0986
75.1680
20.0298
HO
HO
OH
gabosine H
5
^{13}C NMR (125 MHz, CD$_3$OD)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



^{1}H NMR (500 MHz, CD_3OD)

6-epi-gabosine H

***epi*-5**

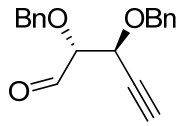


^{13}C NMR (125 MHz, CD_3OD)

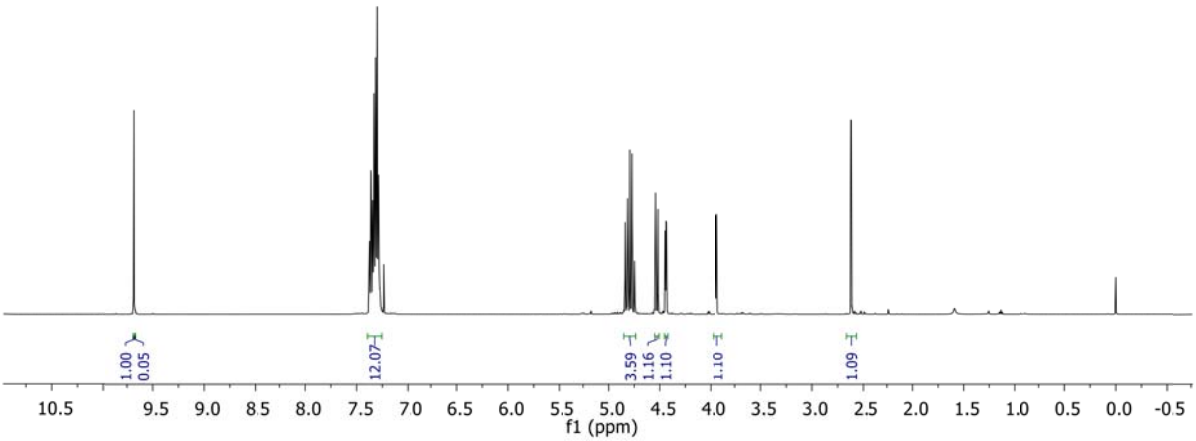
6-epi-gabosine H

***epi*-5**

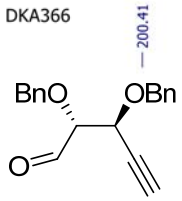
DKA366



8

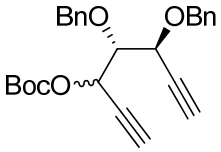


DKA366



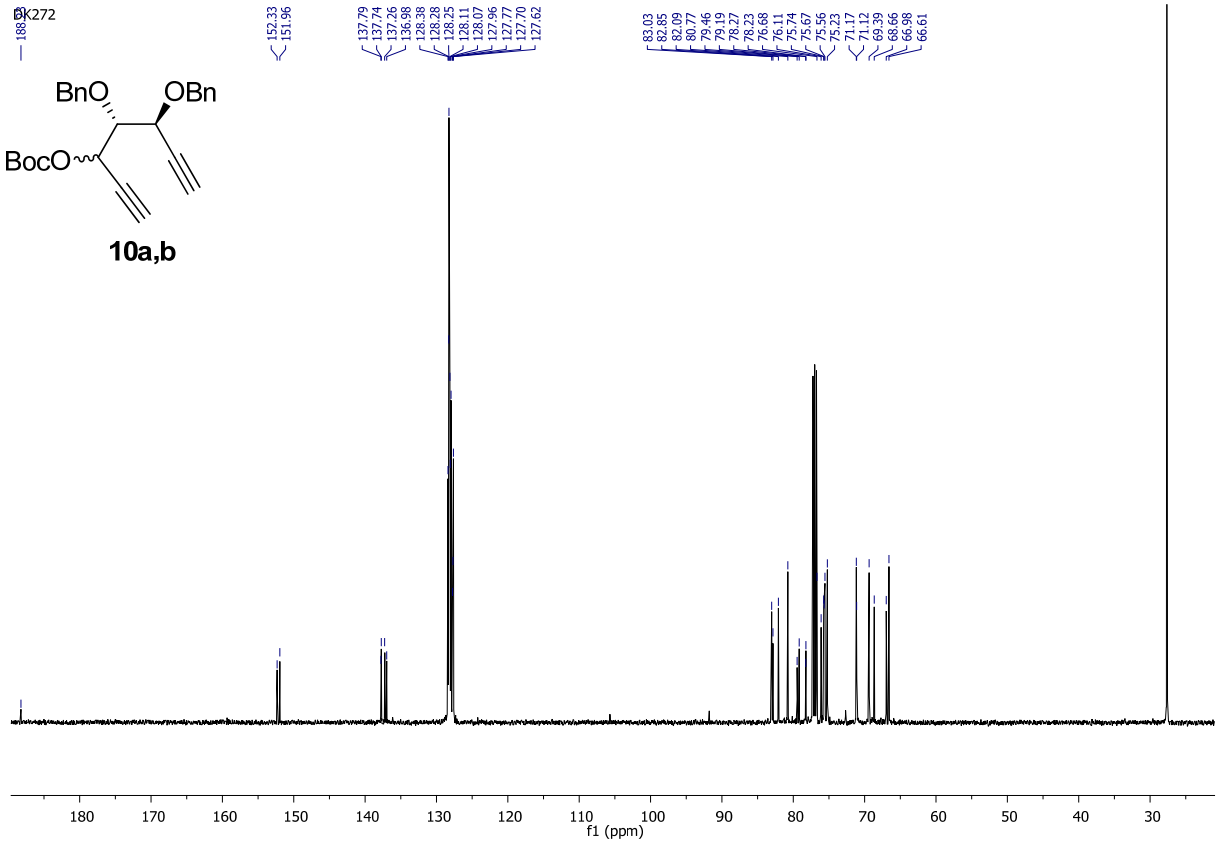
8

DK272

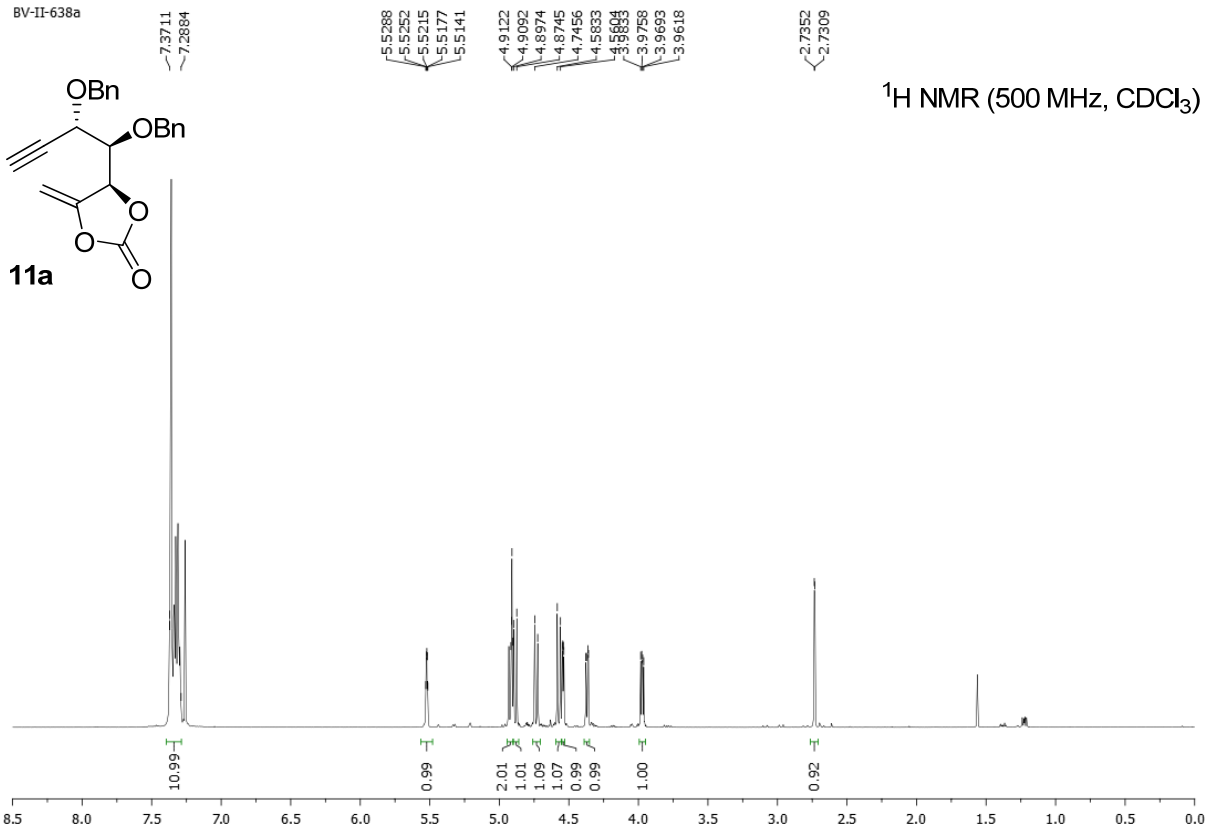


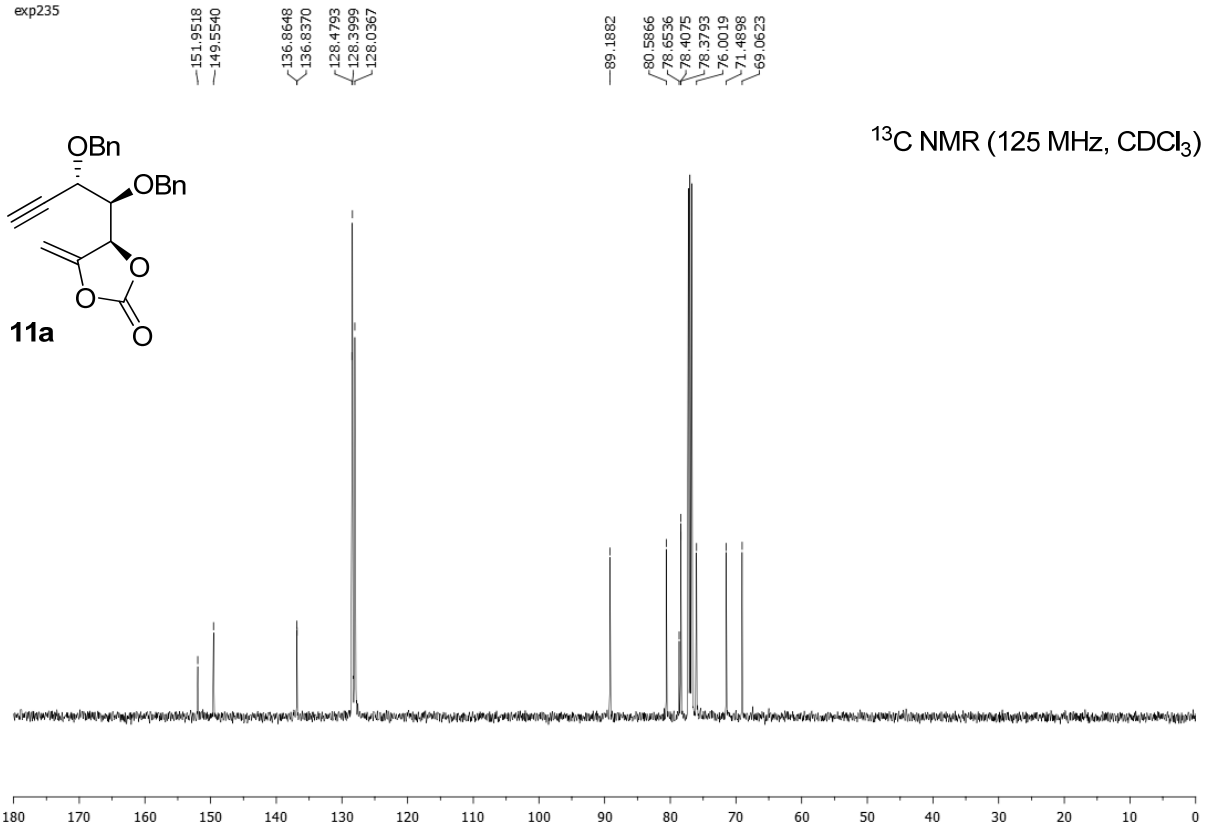
10a,b

DK272

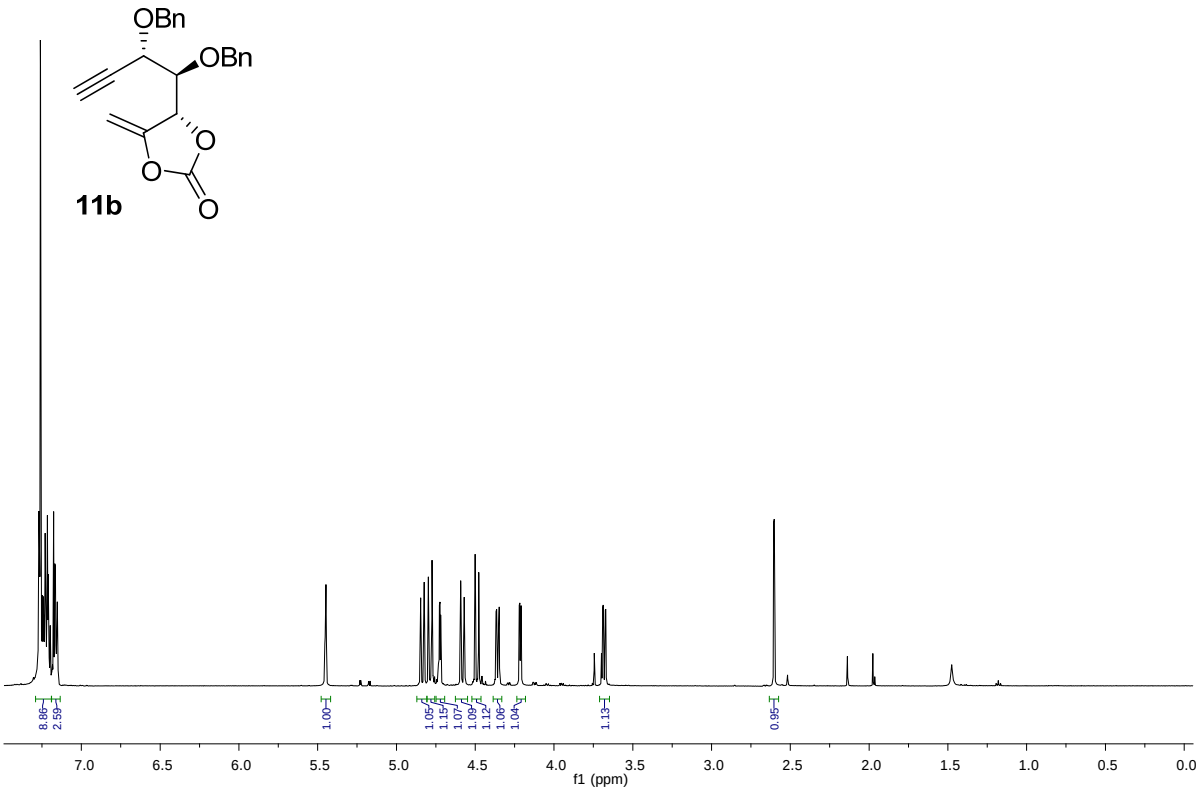


10a,b

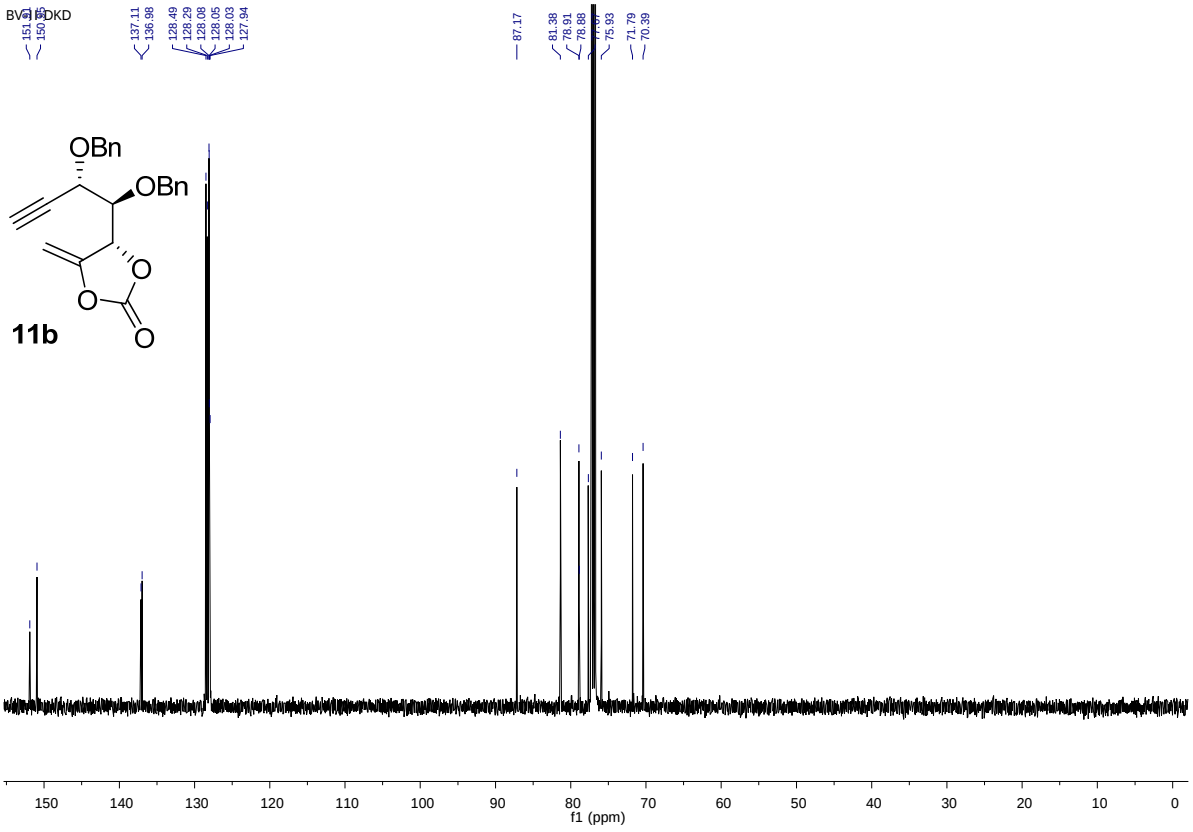

BV-II-638a
7.3711
7.2884
5.5288
5.5252
5.5215
5.5177
5.5141
4.9122
4.9092
4.8974
4.8745
4.7456
4.5833
4.5604
3.9833
3.9758
3.9693
3.9618
2.7352
2.7309
OBn
OBn
O
O
O
11a
^{1}H NMR (500 MHz, CDCl$_3$)
10.99
0.99
2.01
1.01
1.09
1.07
0.99
0.99
1.00
0.92
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

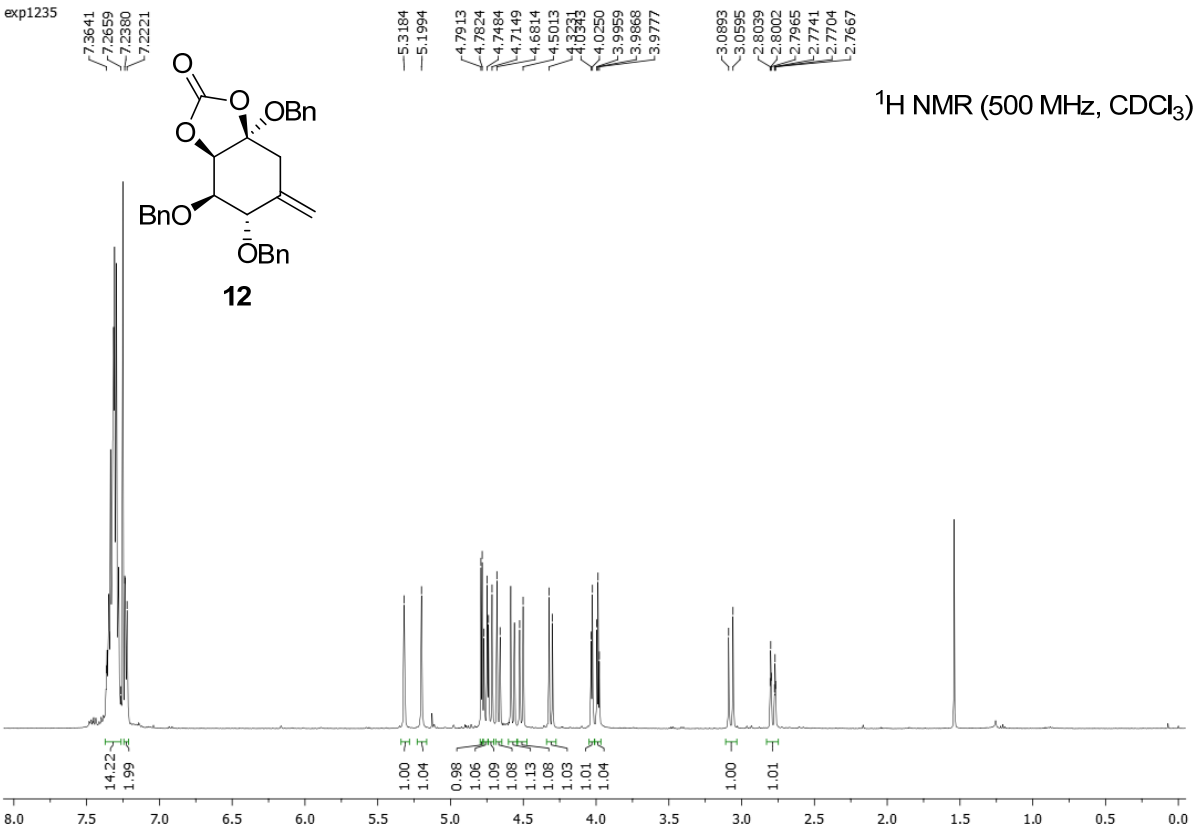

exp235
151.9518
149.5540
136.8648
136.8370
128.4793
128.3999
128.0367
89.1882
80.5866
78.6536
78.4075
78.3793
76.0019
71.4898
69.0623
OBn
OBn
O
O
O
11a
^{13}C NMR (125 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

BV-II-DKD

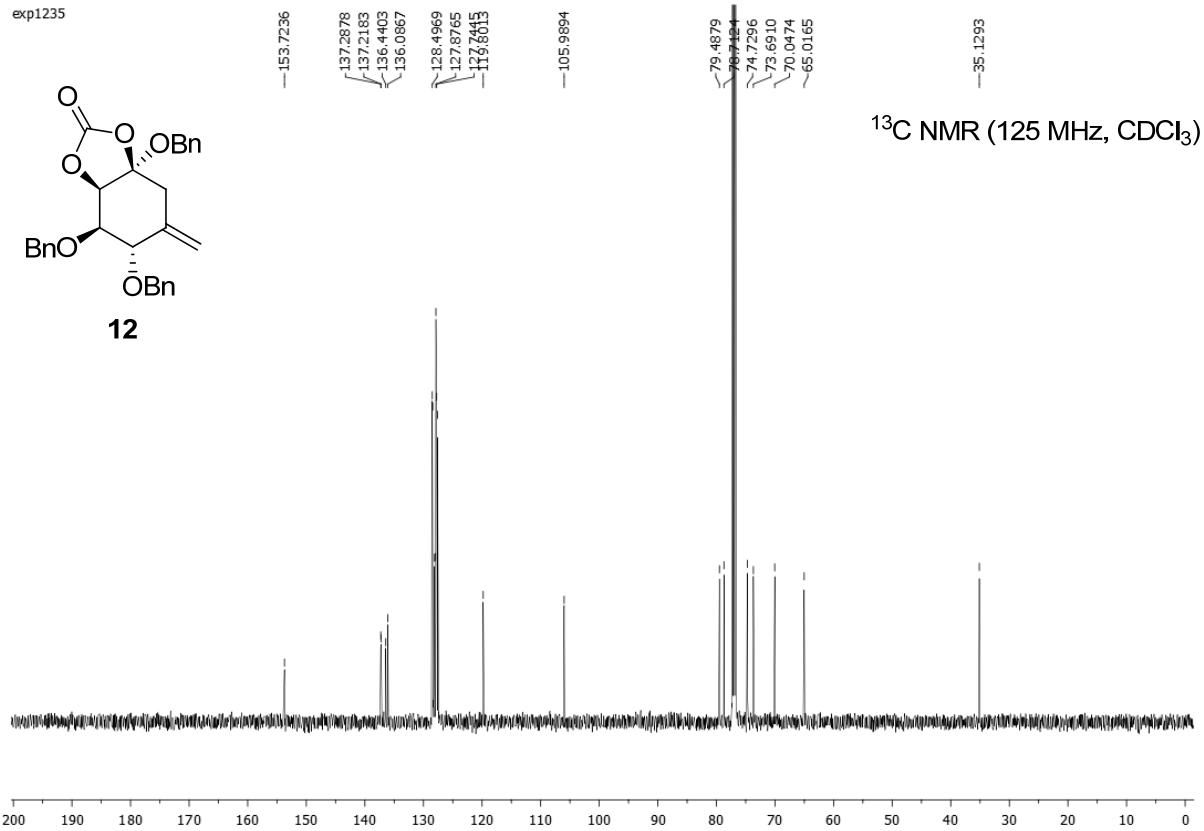


BV-II-DKD

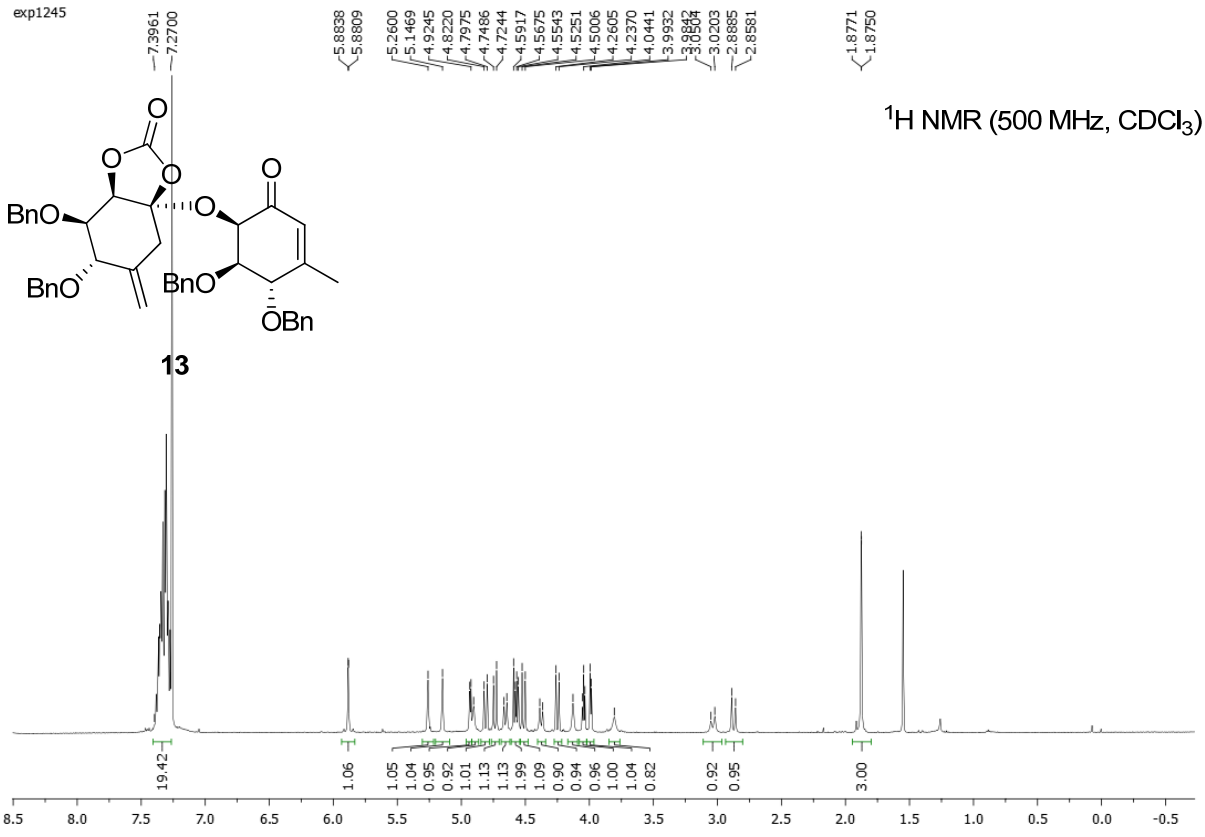




^{1}H NMR (500 MHz, $CDCl_3$)

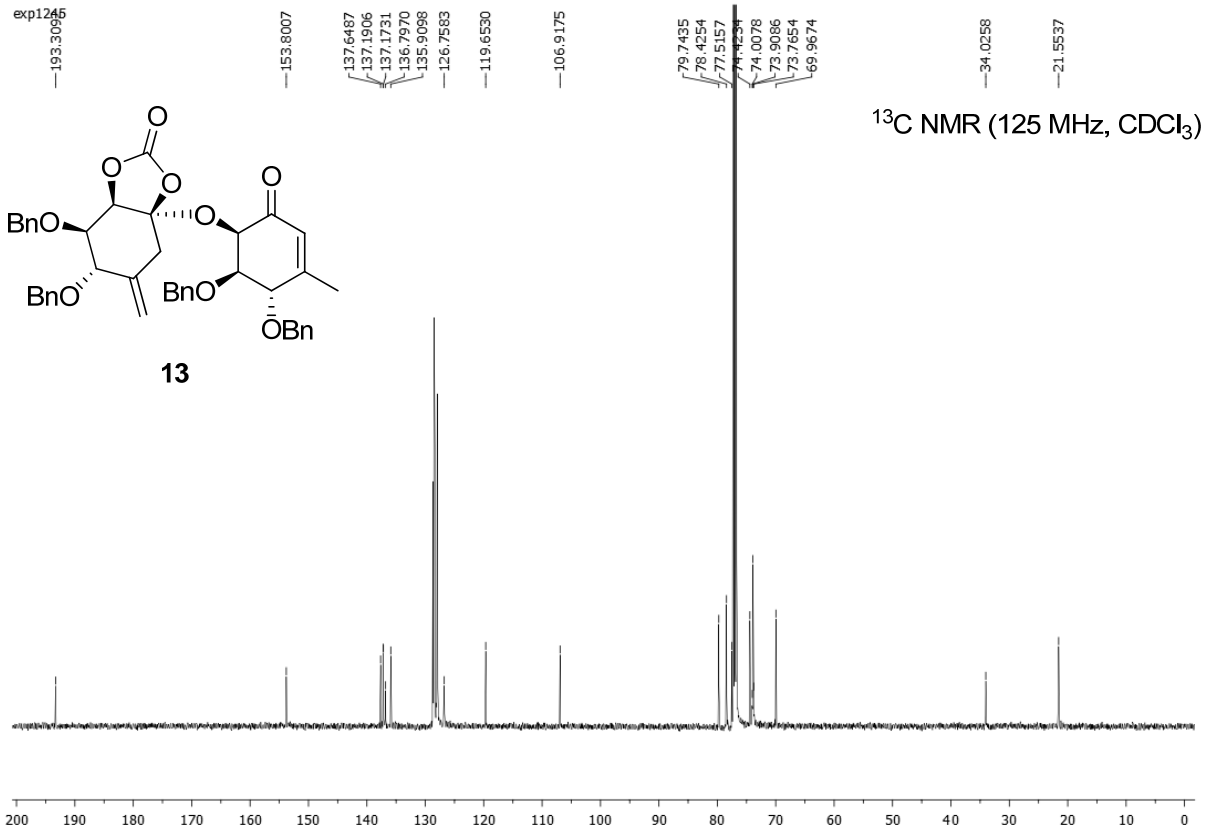


^{13}C NMR (125 MHz, $CDCl_3$)



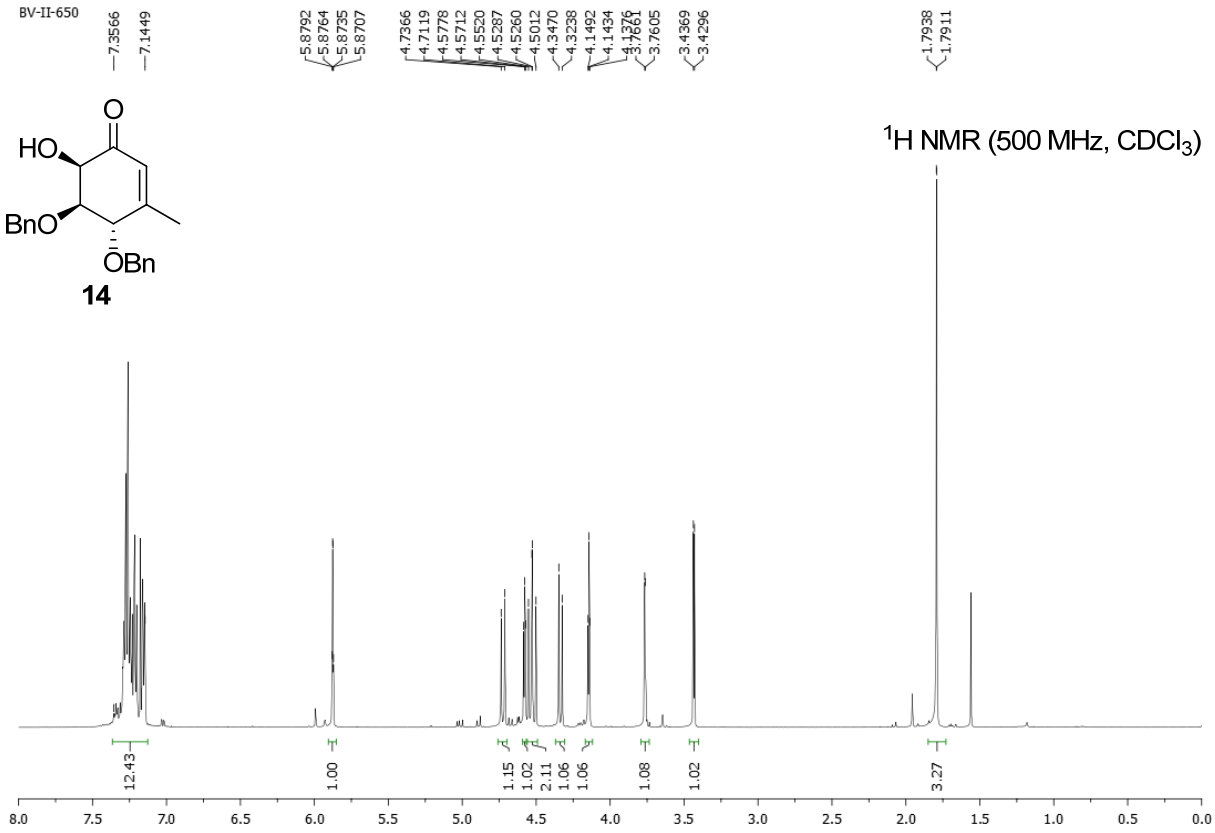
^{1}H NMR (500 MHz, $CDCl_3$)

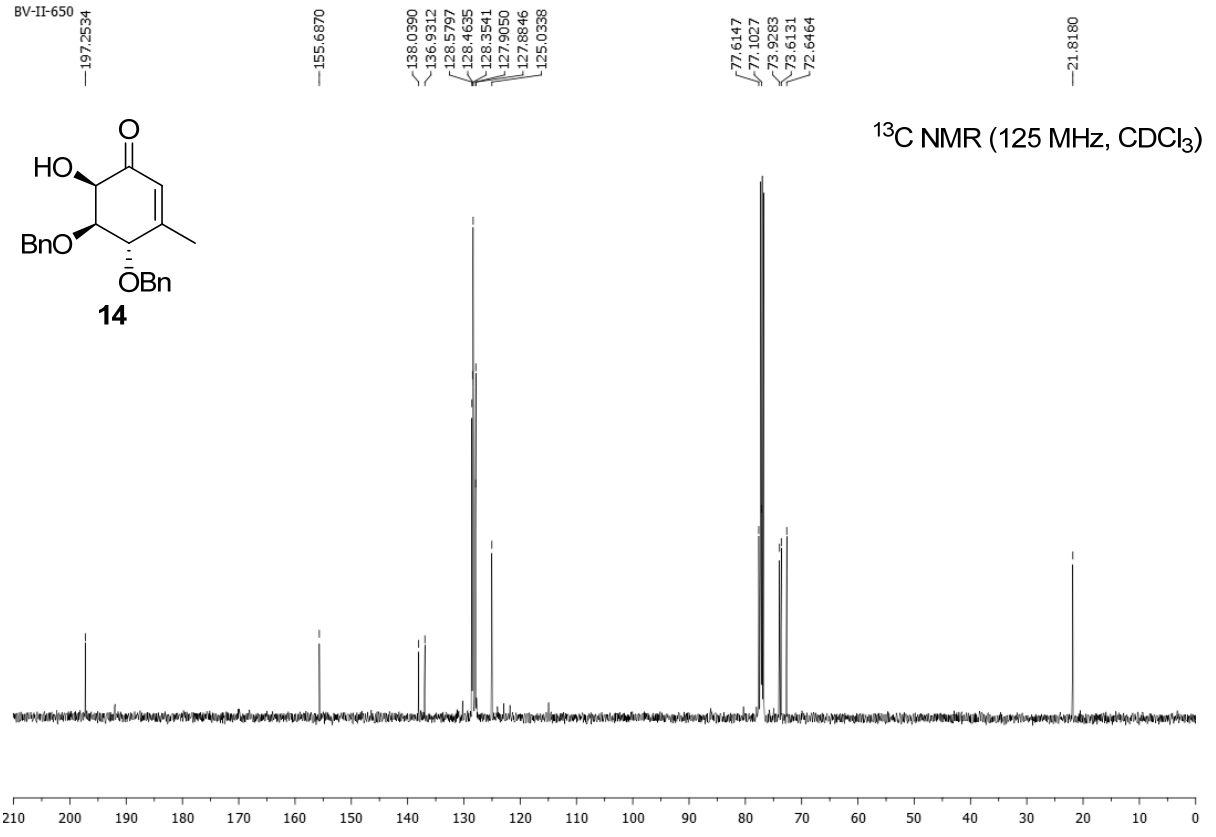
13

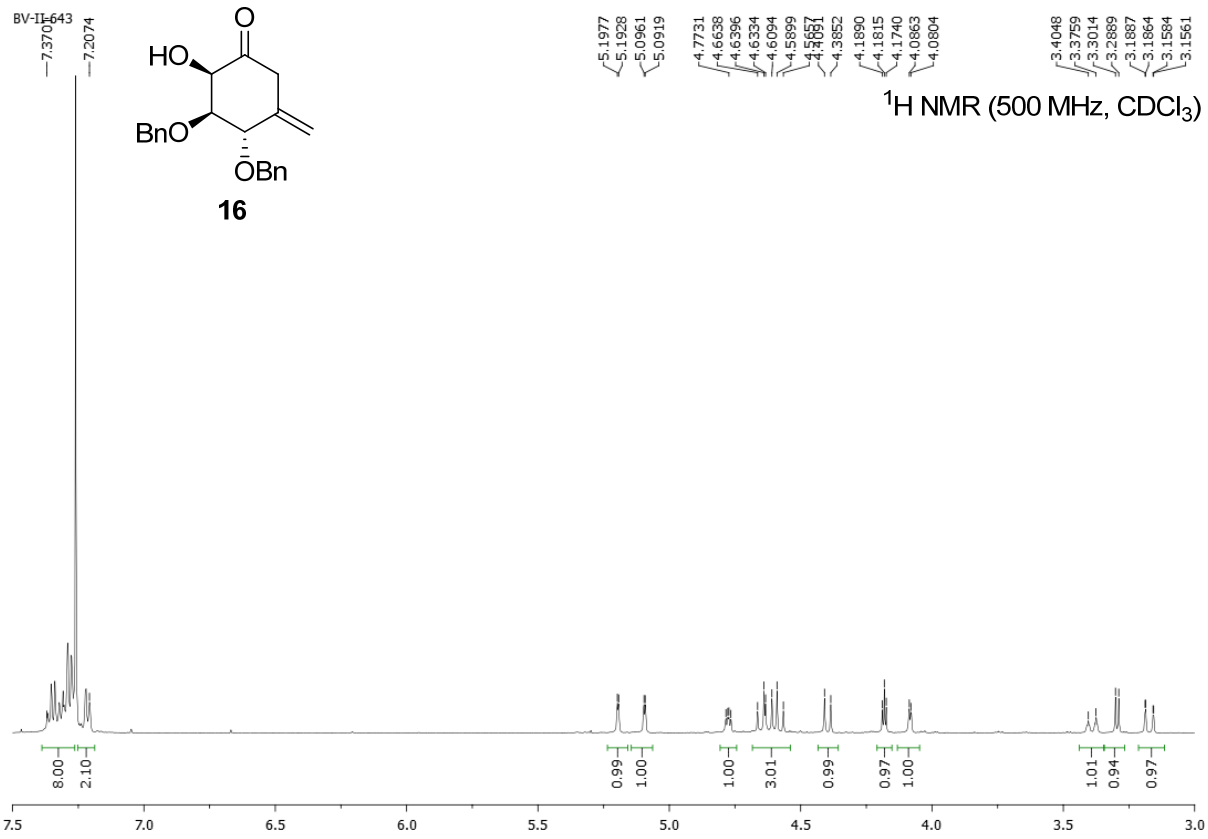


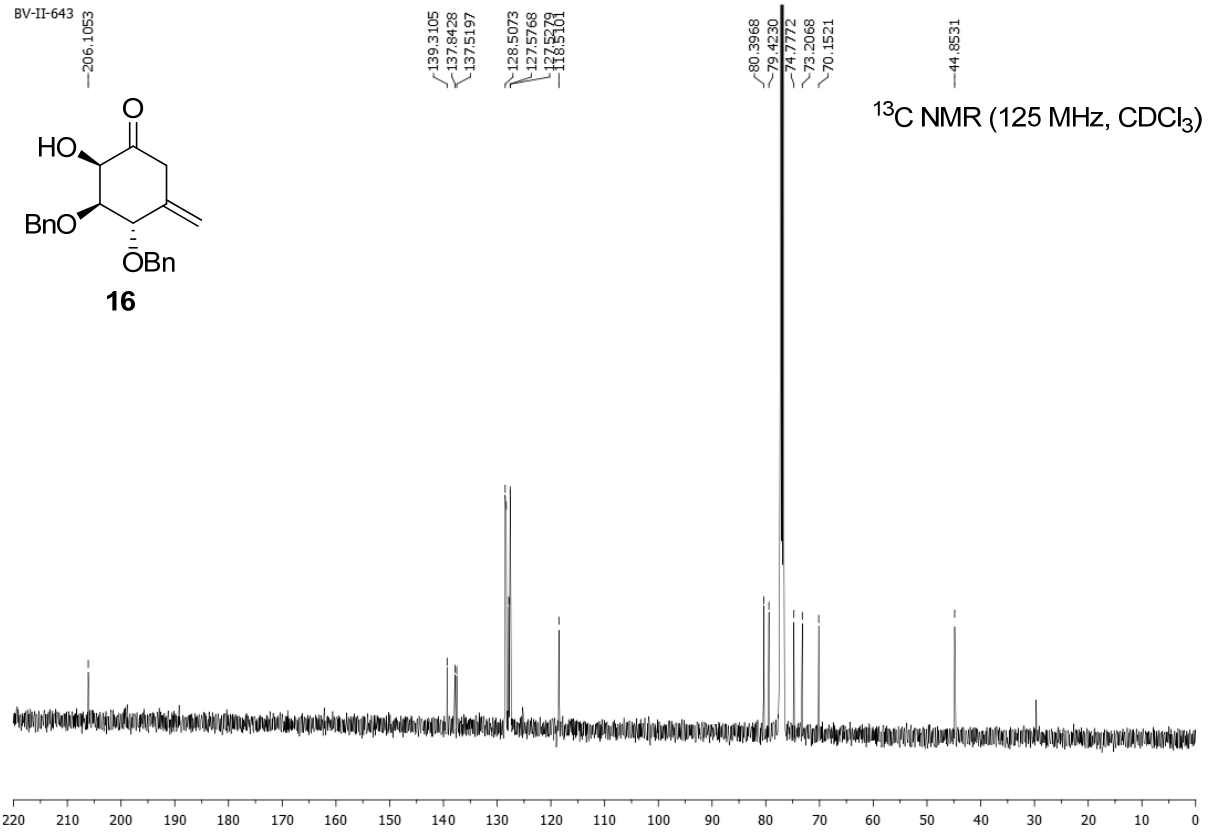
^{13}C NMR (125 MHz, $CDCl_3$)

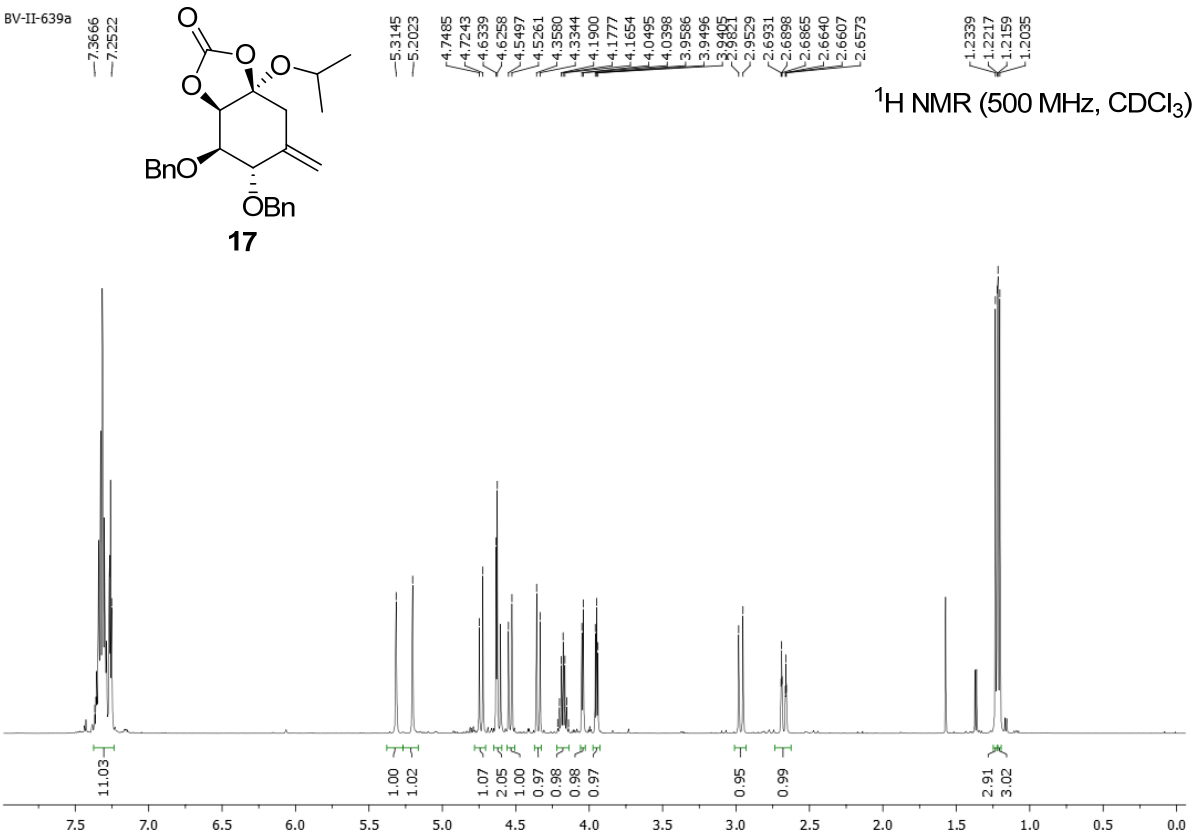
13


BV-II-650
7.3566
7.1449
5.8792
5.8764
5.8735
5.8707
4.7366
4.7119
4.5778
4.5712
4.5520
4.5287
4.5260
4.5012
4.3470
4.3238
4.1492
4.1434
3.7681
3.7605
3.4369
3.4296
1.7938
1.7911
HO
BnO
OBn
14
^{1}H NMR (500 MHz, CDCl$_3$)
12.43
1.00
1.15
1.02
2.11
1.06
1.06
1.08
1.02
3.27
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

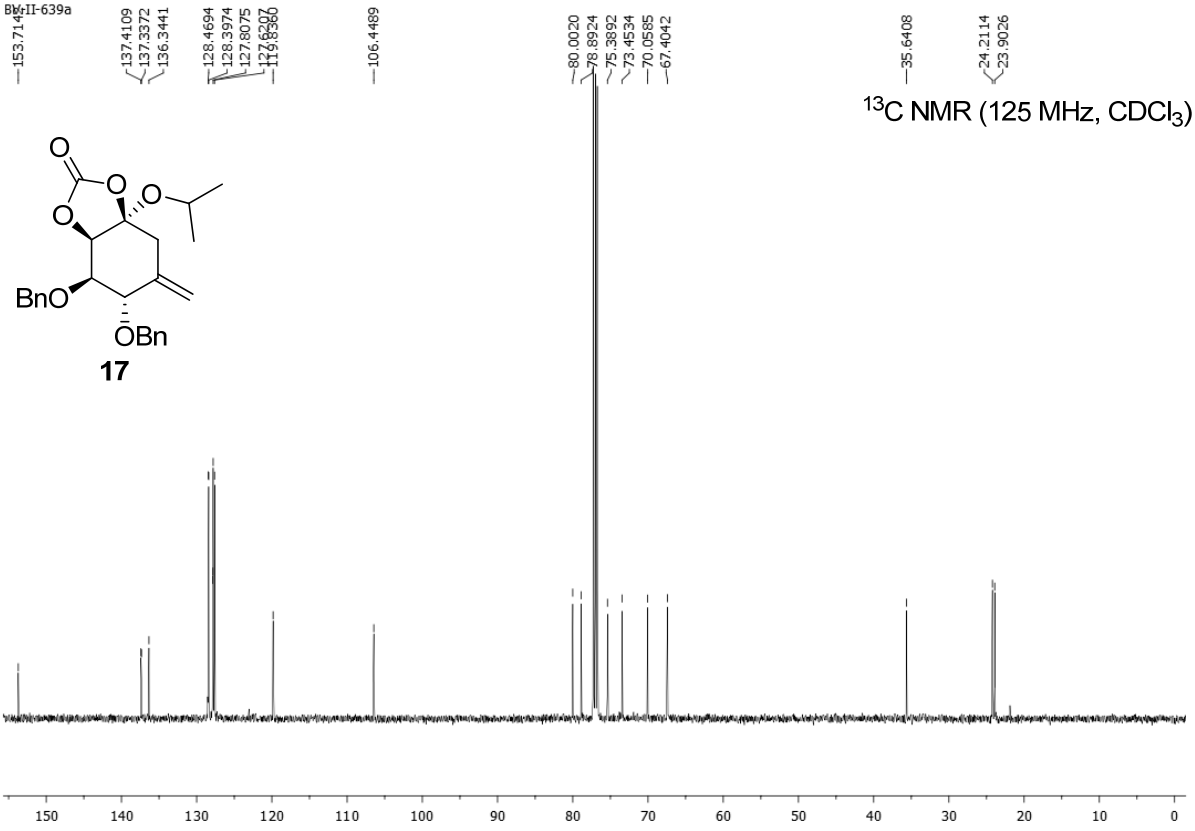

BV-II-650
197.2534
155.6870
138.0390
136.9312
128.5797
128.4635
128.3541
127.9050
127.8846
125.0338
77.6147
77.1027
73.9283
73.6131
72.6464
21.8180
HO
BnO
OBn
14
^{13}C NMR (125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


BV-II-643
7.3705
7.2074
5.1977
5.1928
5.0961
5.0919
4.7731
4.6638
4.6396
4.6334
4.6094
4.5899
4.4057
4.4051
4.3852
4.1890
4.1815
4.1740
4.0863
4.0804
3.4048
3.3759
3.3014
3.2889
3.1887
3.1864
3.1584
3.1561
HO
BnO
OBn
16
^{1}H NMR (500 MHz, $CDCl_3$)
8.00
2.10
0.99
1.00
1.00
3.01
0.99
0.97
1.00
1.01
0.94
0.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

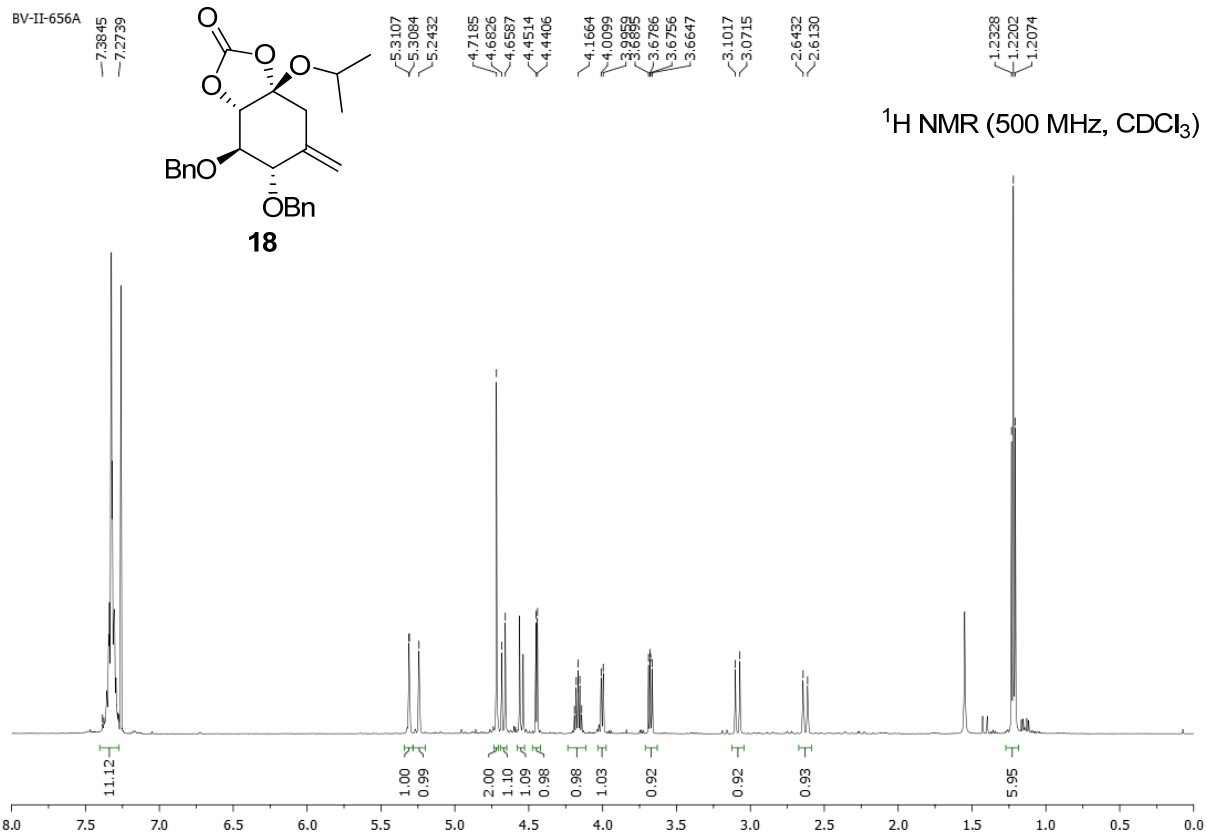

BV-II-643
206.1053
139.3105
137.8428
137.5197
128.5073
127.5768
127.5279
118.5101
80.3968
79.4230
74.7772
73.2068
70.1521
44.8531
HO
BnO
OBn
16
^{13}C NMR (125 MHz, $CDCl_3$)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

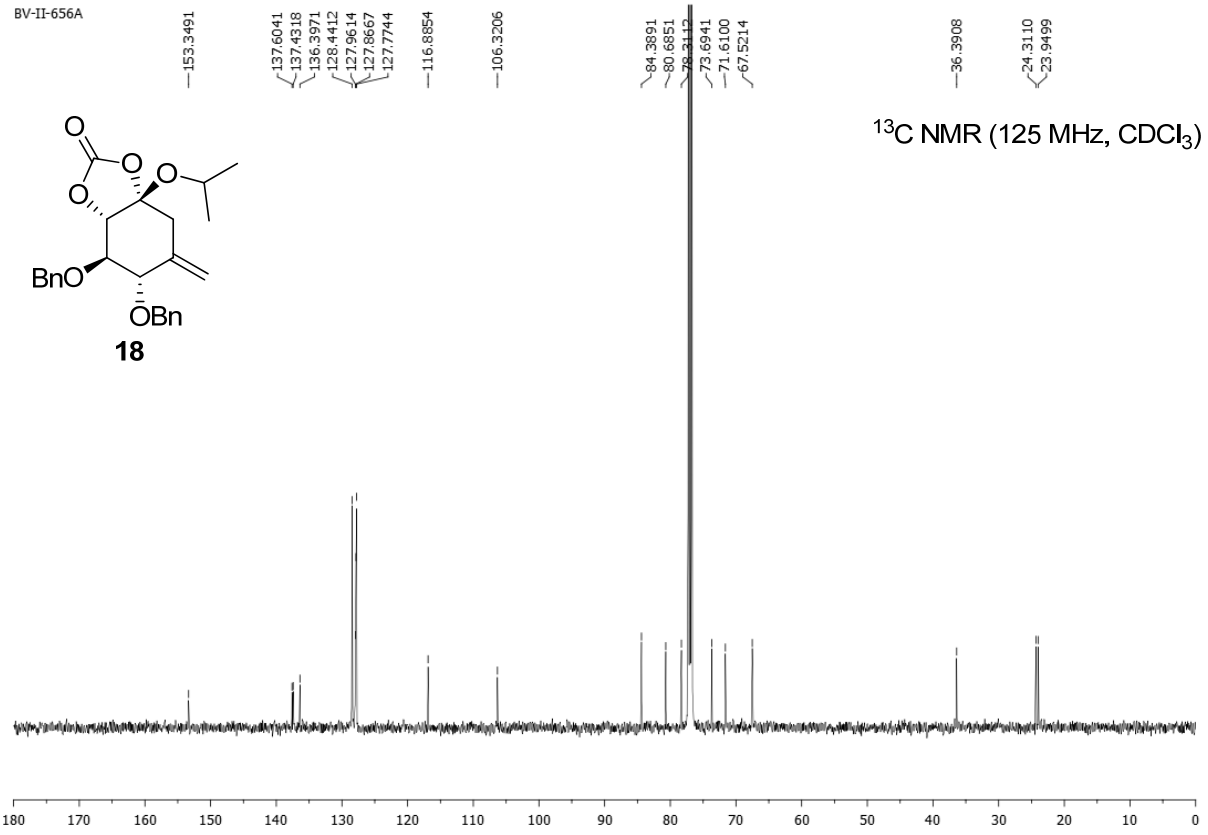


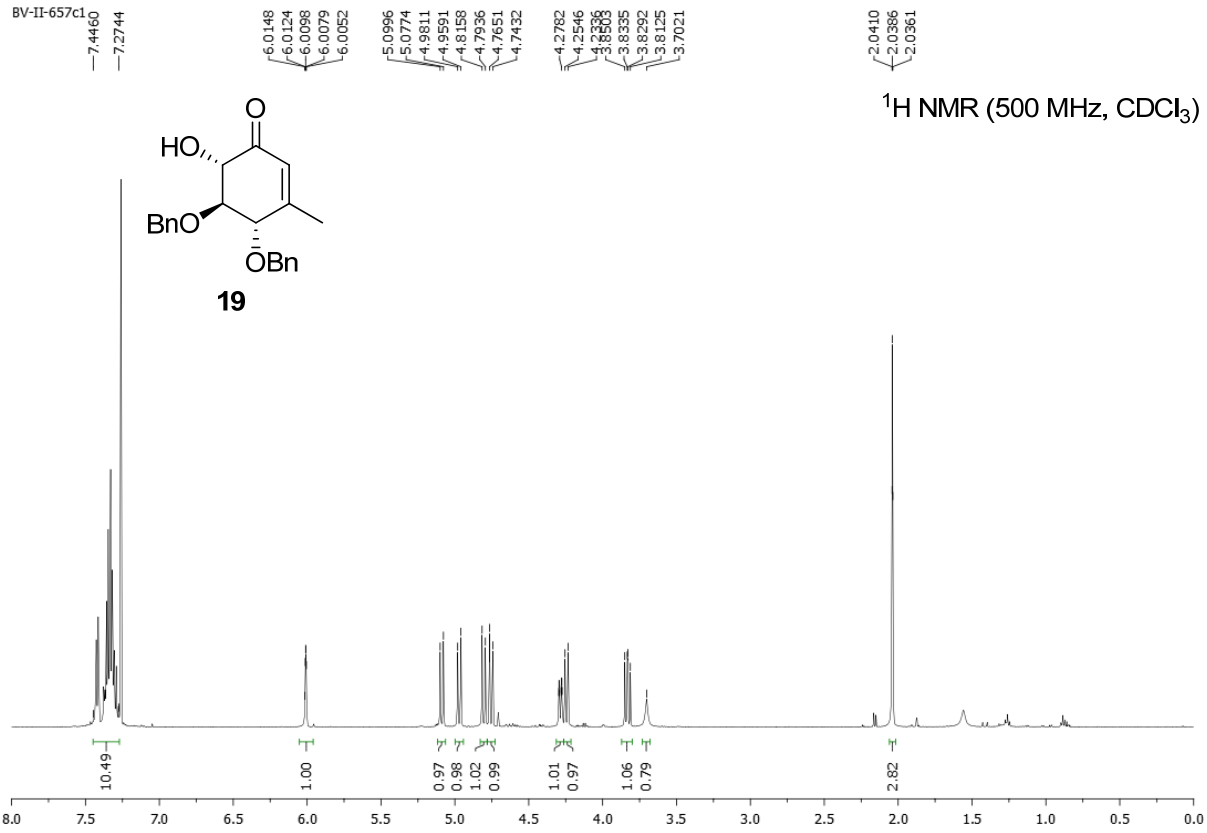
^{1}H NMR (500 MHz, $CDCl_3$)



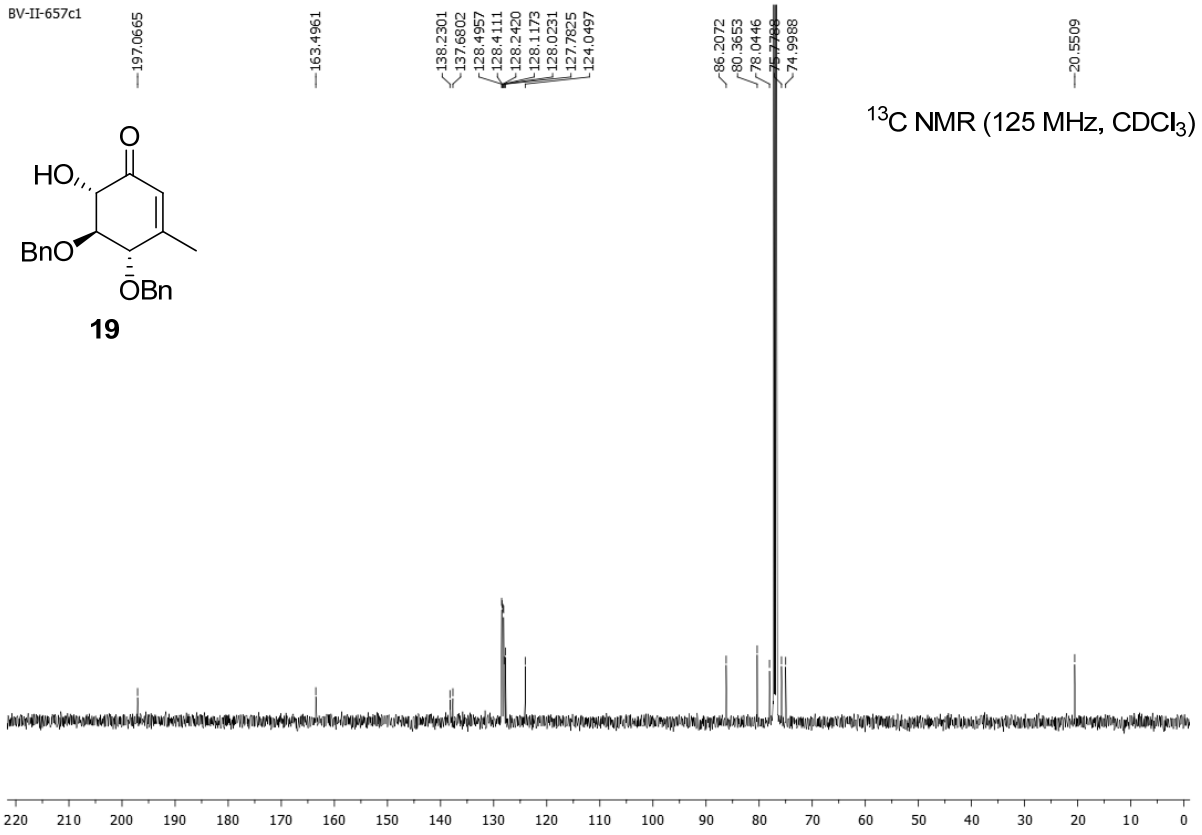
^{13}C NMR (125 MHz, $CDCl_3$)


BV-II-656A
7.3845
7.2739
5.3107
5.3084
5.2432
4.7185
4.6826
4.6587
4.4514
4.4406
4.1664
4.0099
3.8959
3.8895
3.6786
3.6756
3.6647
3.1017
3.0715
2.6432
2.6130
1.2328
1.2202
1.2074
BnO
OBn
18
^{1}H NMR (500 MHz, CDCl$_3$)
11.12
1.00
0.99
2.00
1.10
1.09
0.98
0.98
1.03
0.92
0.92
0.93
5.95
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

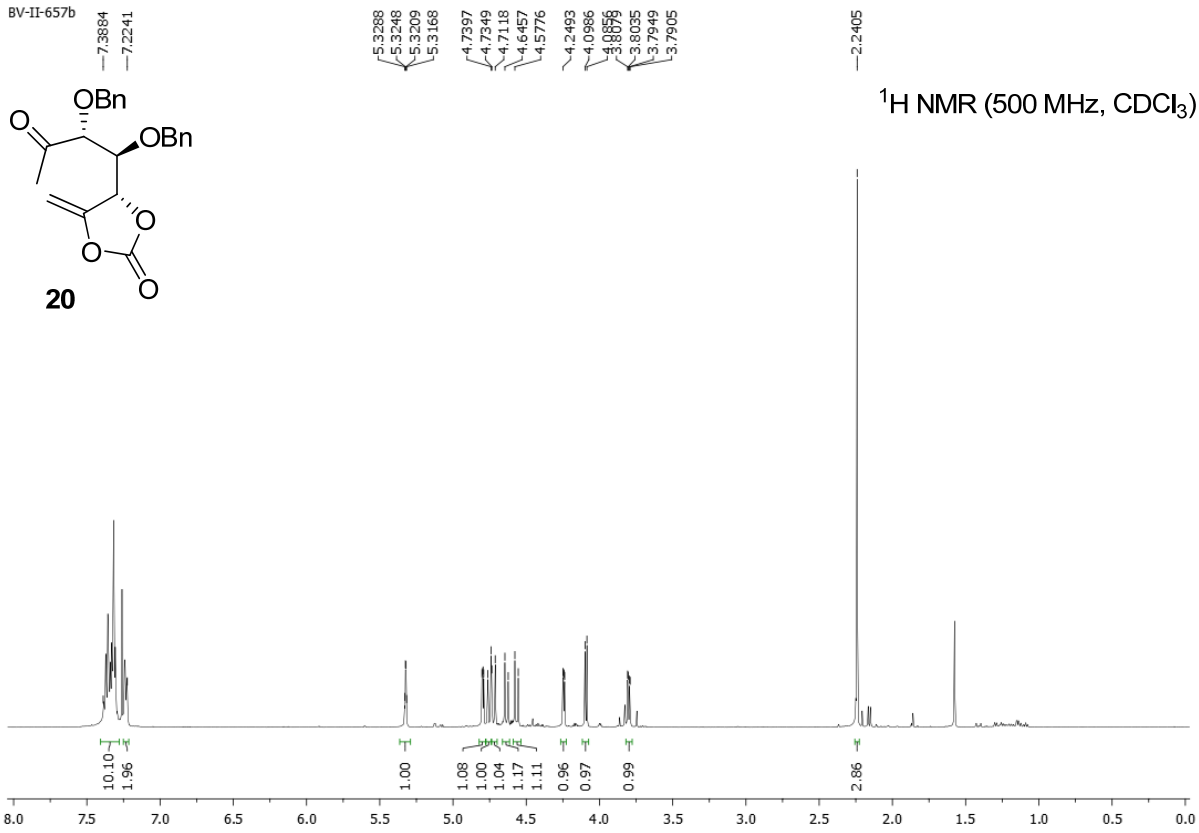

BV-II-656A
153.3491
137.6041
137.4318
136.3971
128.4412
127.9614
127.8667
127.7744
116.8854
106.3206
84.3891
80.6851
78.3112
73.6941
71.6100
67.5214
36.3908
24.3110
23.9499
BnO
OBn
18
^{13}C NMR (125 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

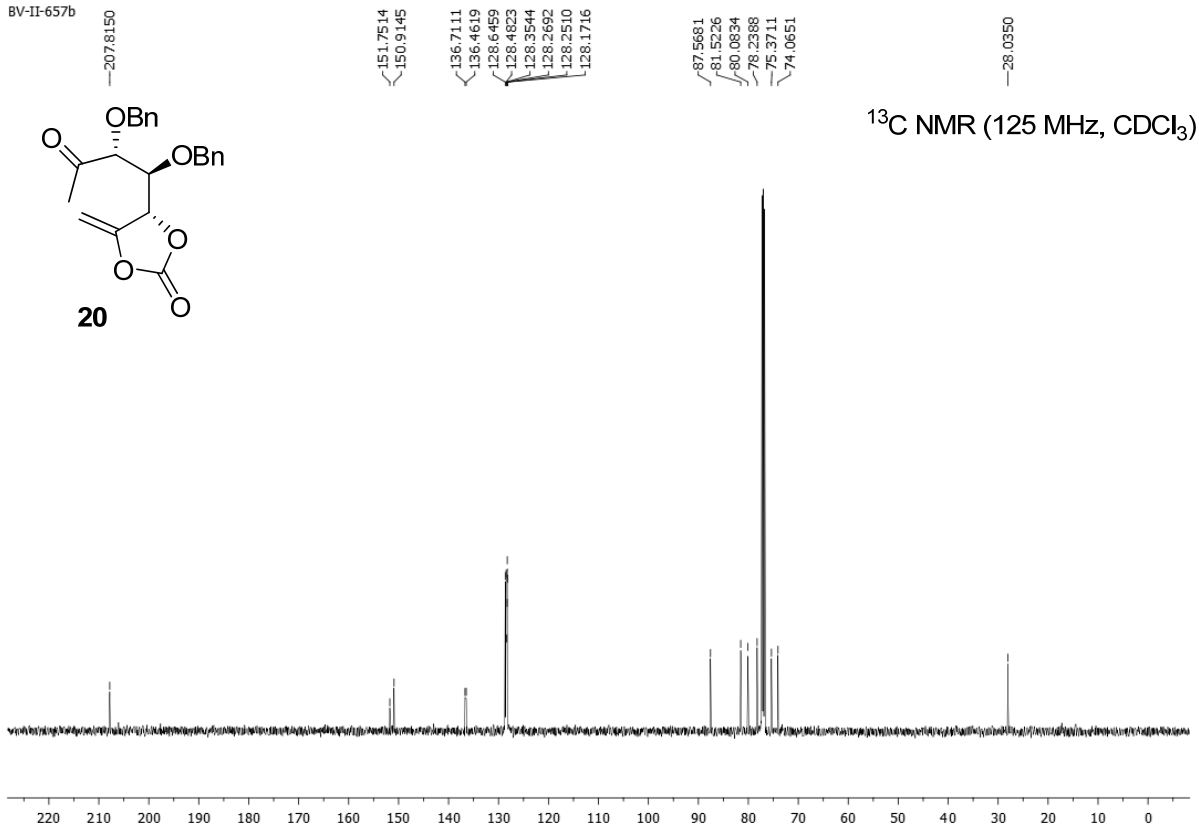


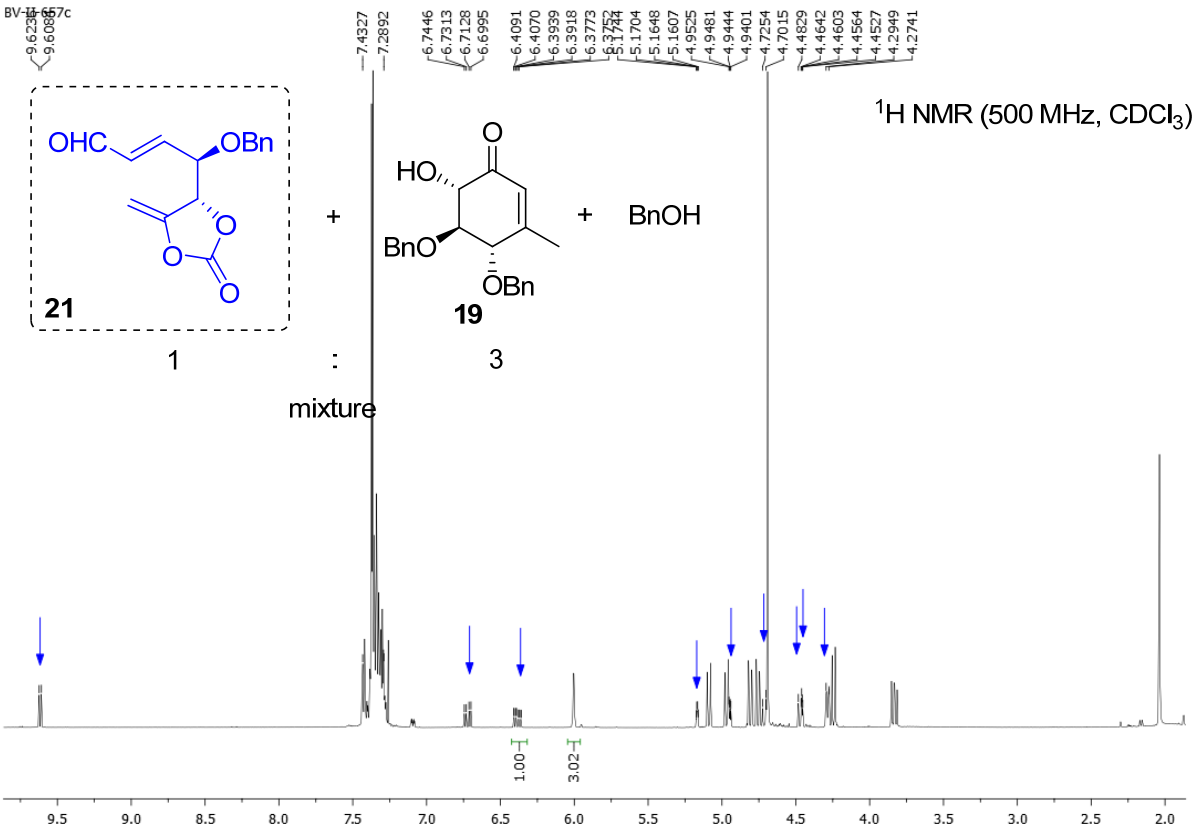
^{1}H NMR (500 MHz, $CDCl_3$)

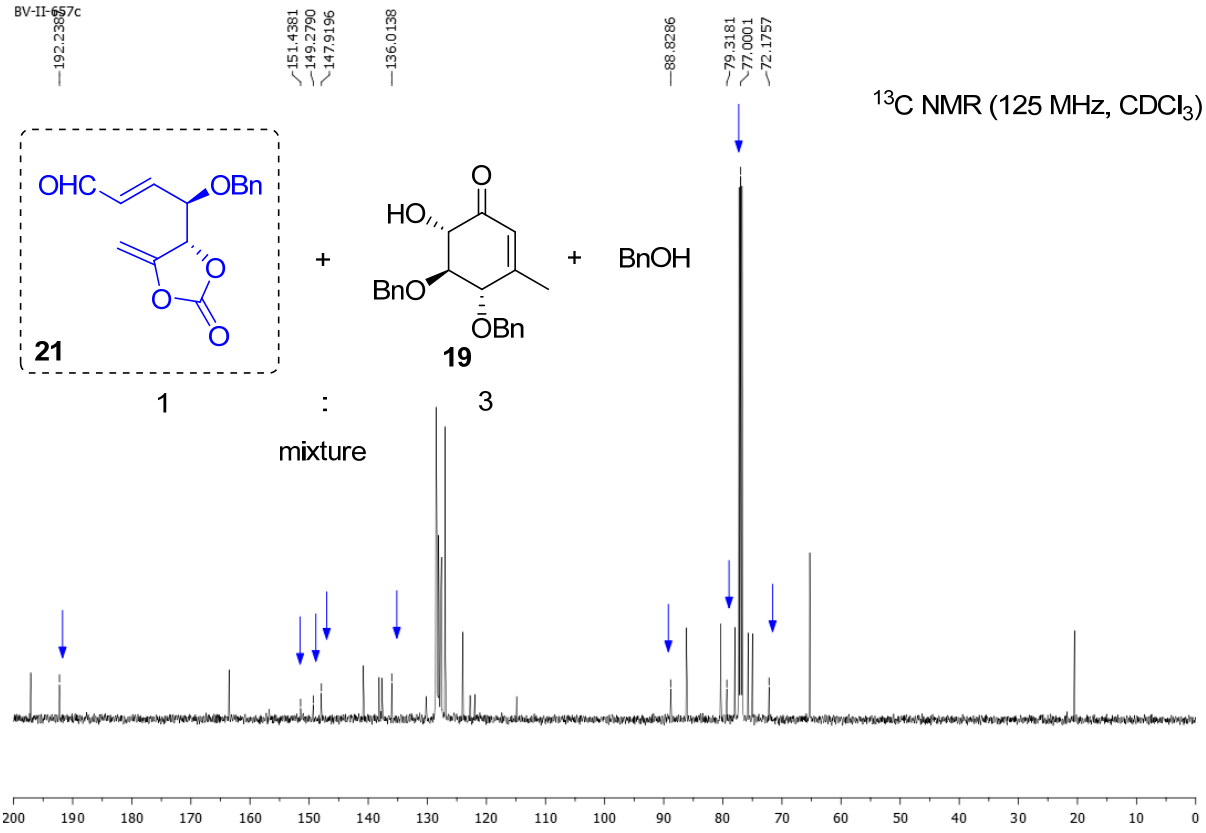


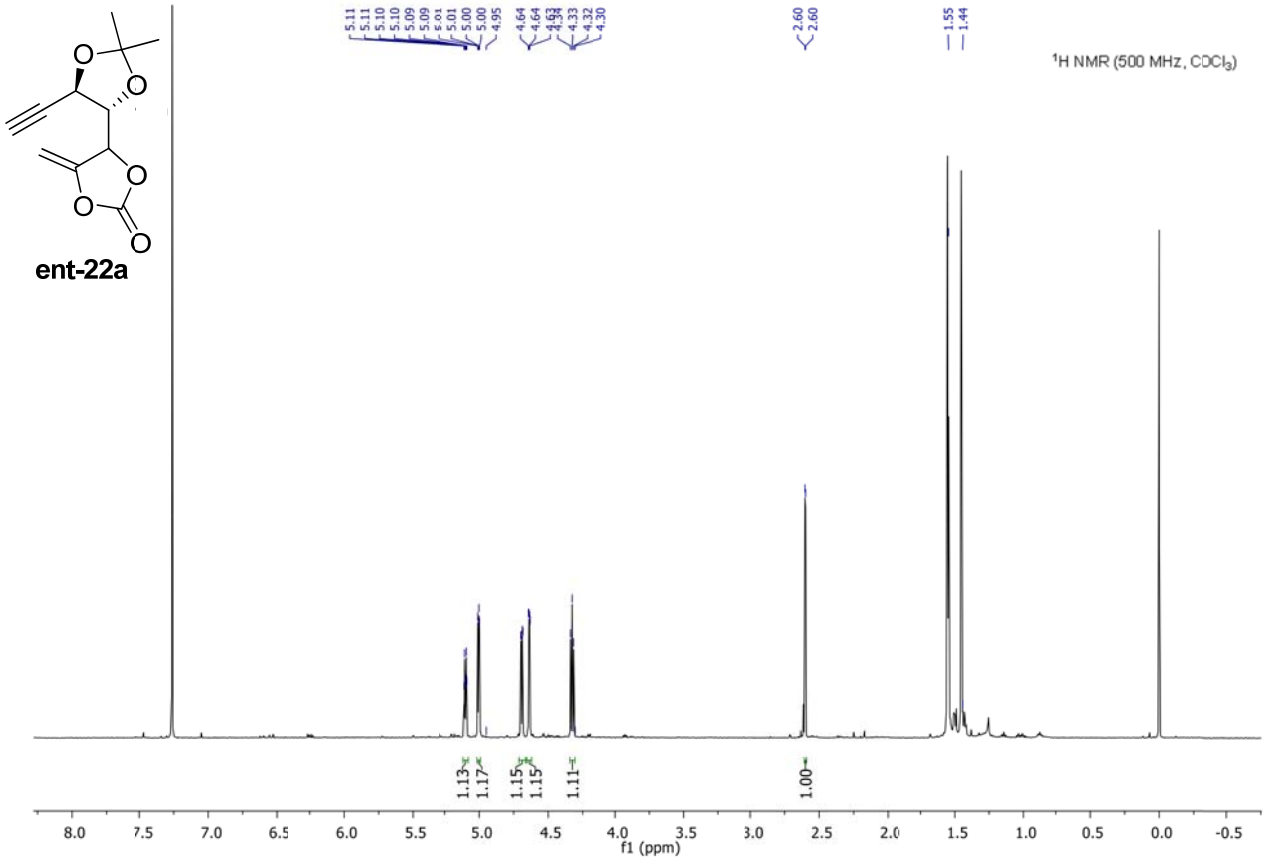
^{13}C NMR (125 MHz, $CDCl_3$)

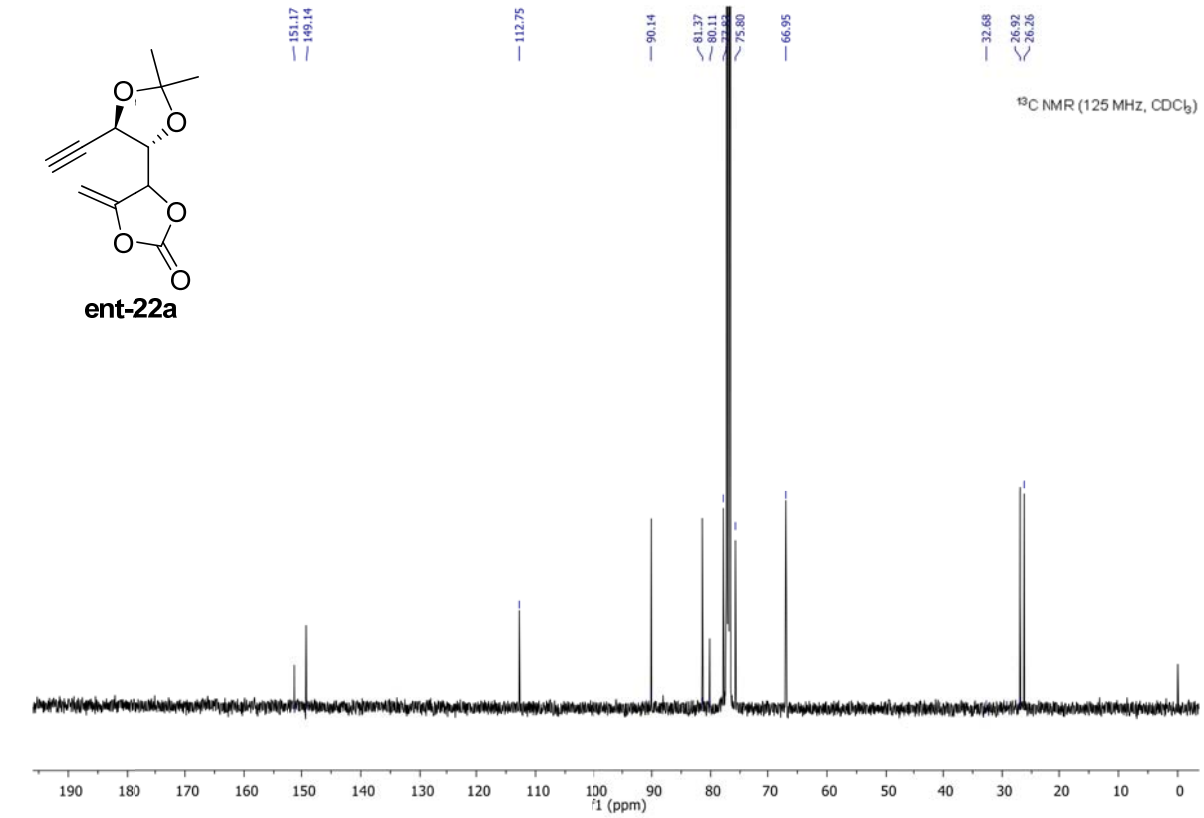

BV-II-657b
7.3884
7.2241
5.3288
5.3248
5.3209
5.3168
4.7397
4.7349
4.7118
4.6457
4.5776
4.2493
4.0986
3.8035
3.7949
3.7905
2.2405
OBn
OBn
O
O
O
O
20
1H NMR (500 MHz, CDCl3)
10.10
1.96
1.00
1.08
1.00
1.04
1.17
1.11
0.96
0.97
0.99
2.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

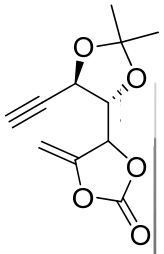

BV-II-657b
207.8150
151.7514
150.9145
136.7111
136.4619
128.6459
128.4823
128.3544
128.2692
128.2510
128.1716
87.5681
81.5226
80.0834
78.2388
75.3711
74.0651
28.0350
OBn
OBn
O
O
O
O
20
13C NMR (125 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BV-II-657c
OHC
OBn
21
+
HO
O
BnO
OBn
19
+ BnOH
1 : 3
mixture
^{1}H NMR (500 MHz, CDCl$_3$)

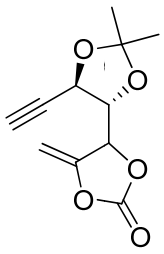

BV-II-657c
OHC
OBn
21
+
HO
O
BnO
OBn
19
+ BnOH
1 : 3
mixture
^{13}C NMR (125 MHz, CDCl$_3$)


ent-22a
5.11
5.11
5.10
5.10
5.09
5.09
5.01
5.01
5.00
5.00
4.95
4.64
4.64
4.33
4.32
4.30
2.60
2.60
1.55
1.44
¹H NMR (500 MHz, CDCl3)
1.13
1.17
1.15
1.15
1.11
1.00
f1 (ppm)

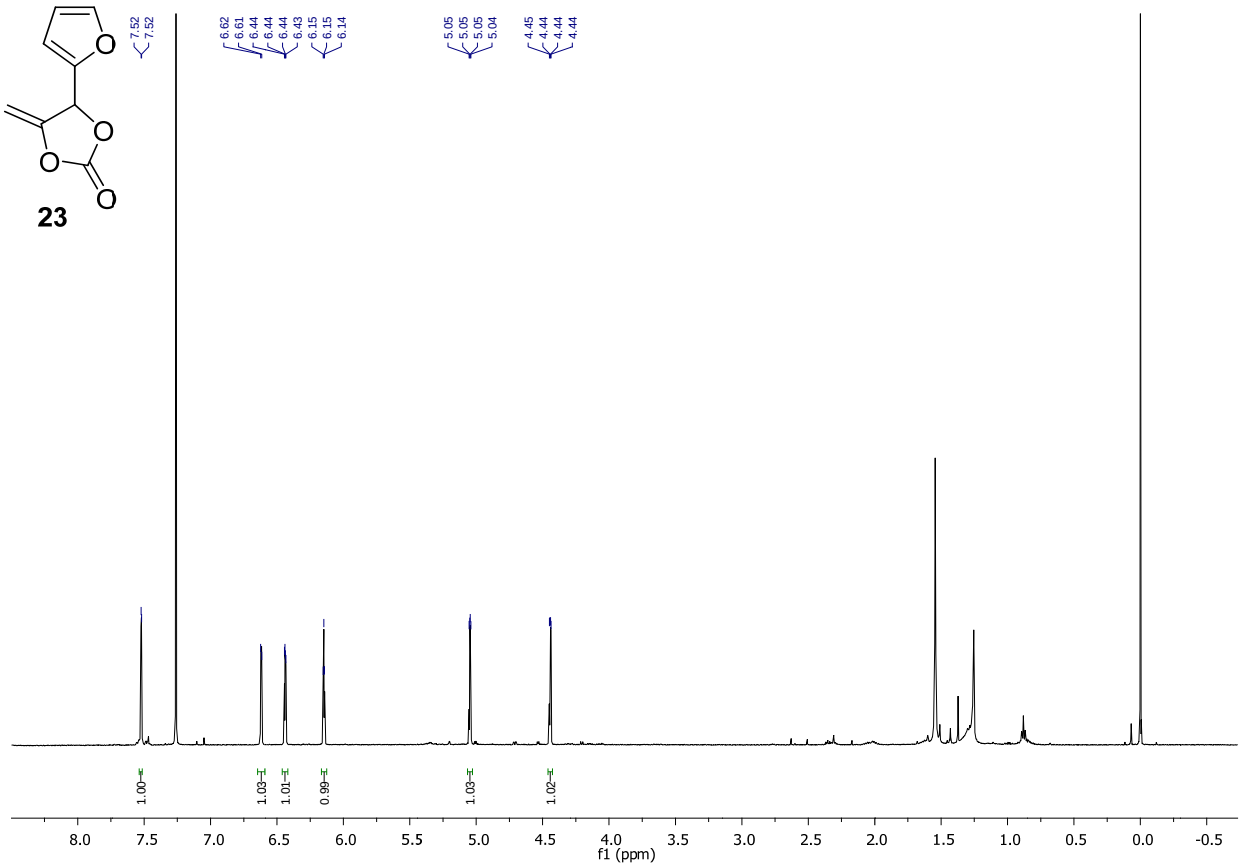

ent-22a
151.17
149.14
112.75
90.14
81.37
80.11
75.80
66.95
32.68
26.92
26.26
¹³C NMR (125 MHz, CDCl3)
f1 (ppm)

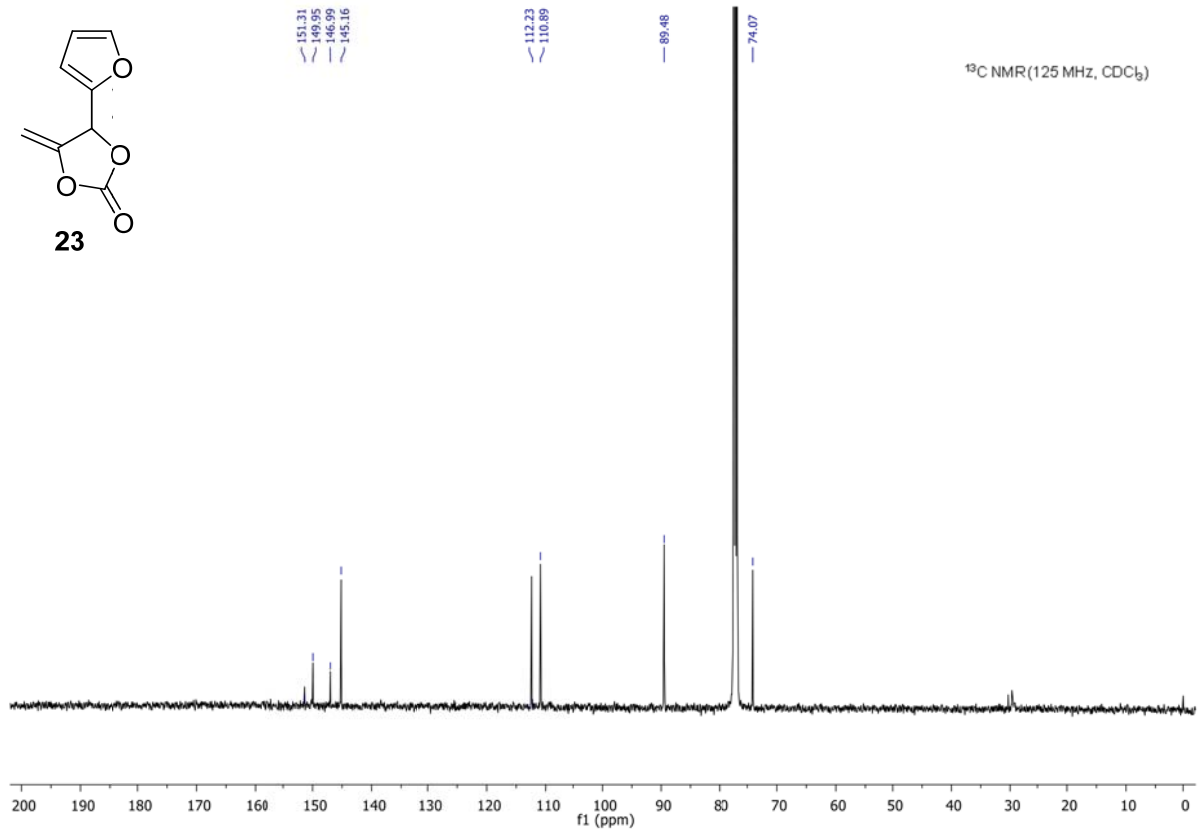


ent-22b

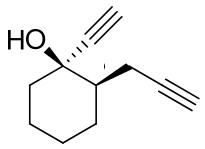


ent-22b

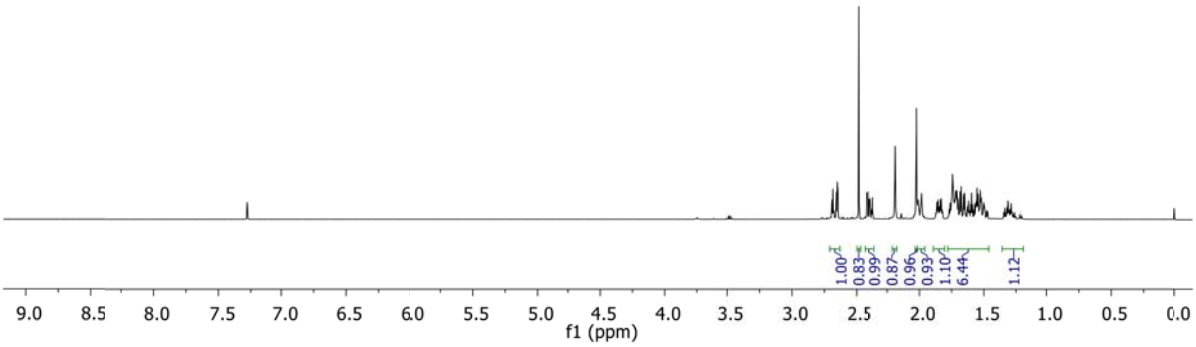

23
7.52
7.52
6.62
6.61
6.44
6.44
6.44
6.43
6.15
6.15
6.14
5.05
5.05
5.05
5.04
4.45
4.44
4.44
4.44
1.00
1.03
1.01
0.99
1.03
1.02
f1 (ppm)


23
151.31
149.95
146.99
145.16
112.23
110.89
89.48
74.07
^{13}C NMR(125 MHz, CDCl$_3$)
f1 (ppm)

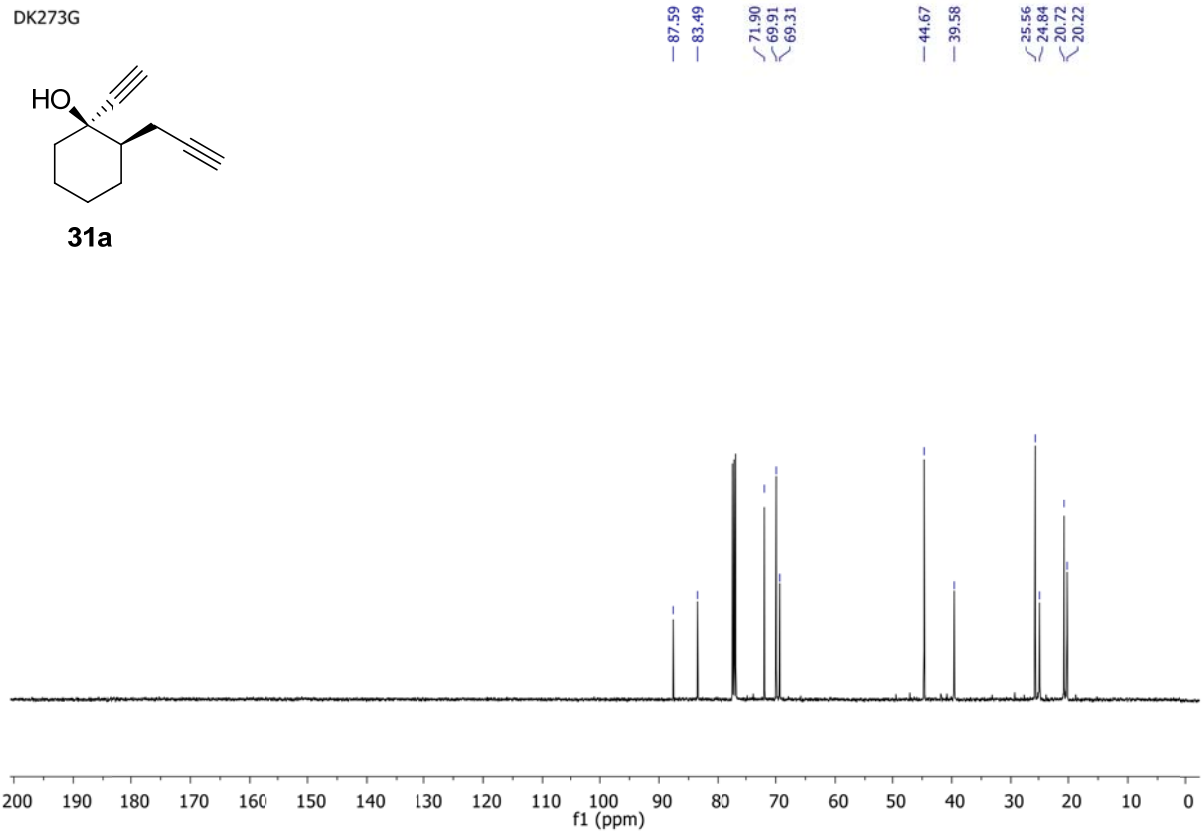
exp1-5



31a

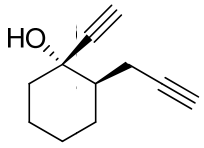


DK273G

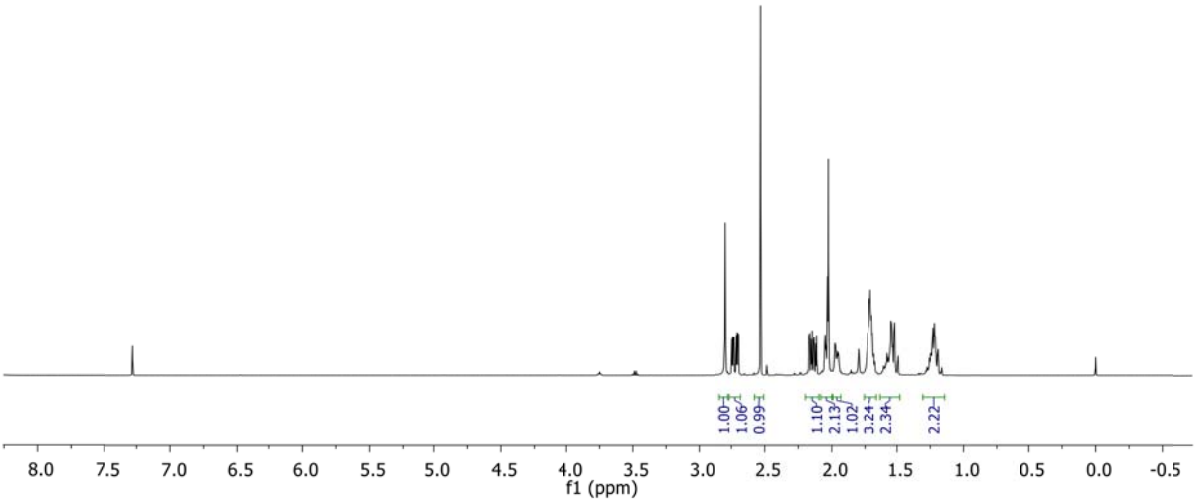


31a

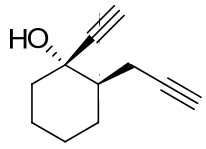
exp1-5



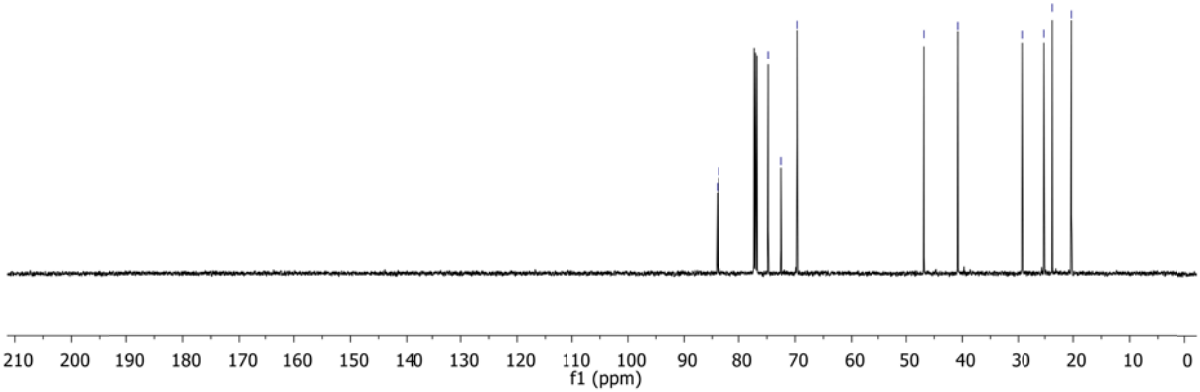
31b



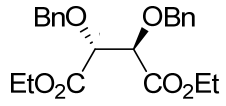
exp1-5



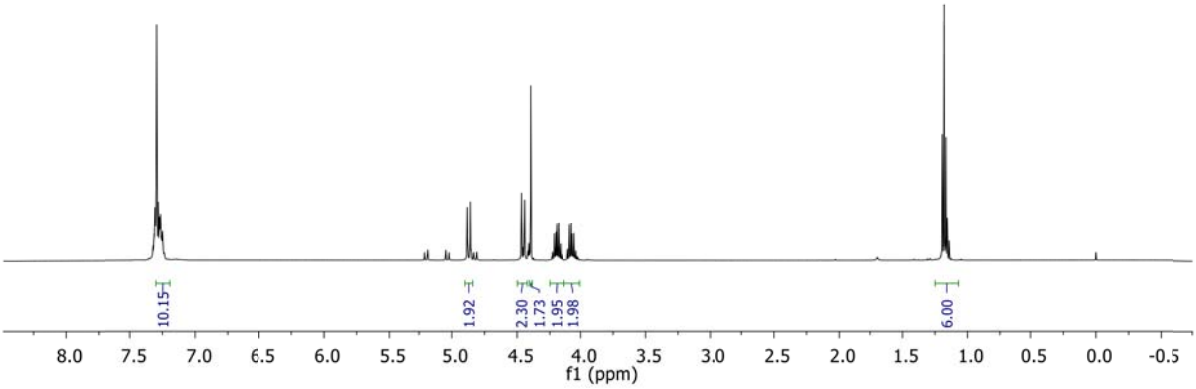
31b



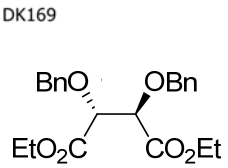
DK169



32



DK169



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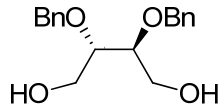
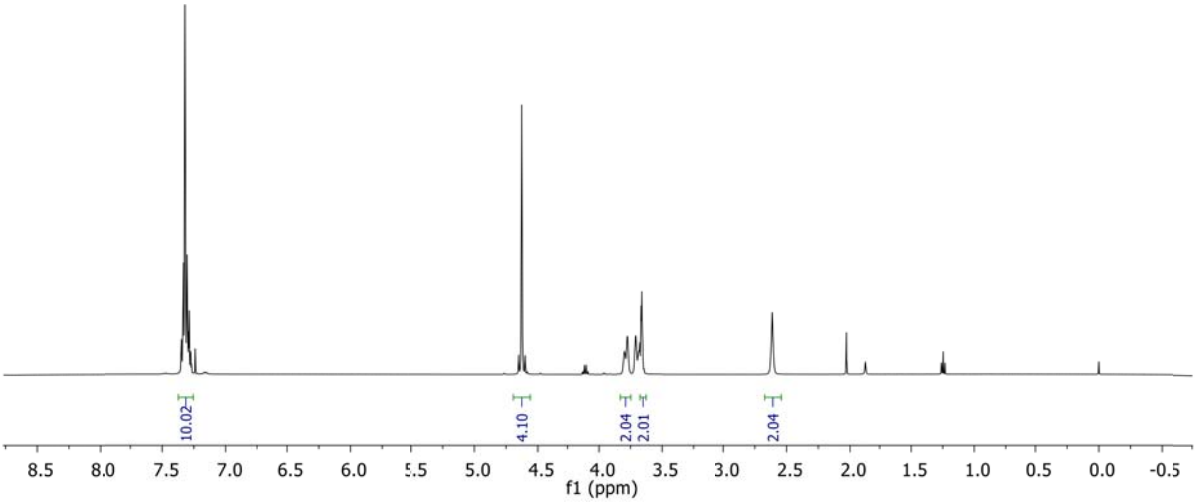
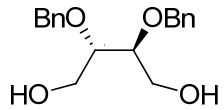


33

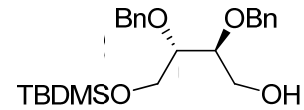


DK170



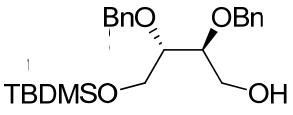
33

DK171



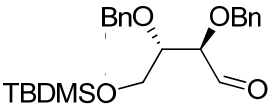
34

DK171



34

DKA178



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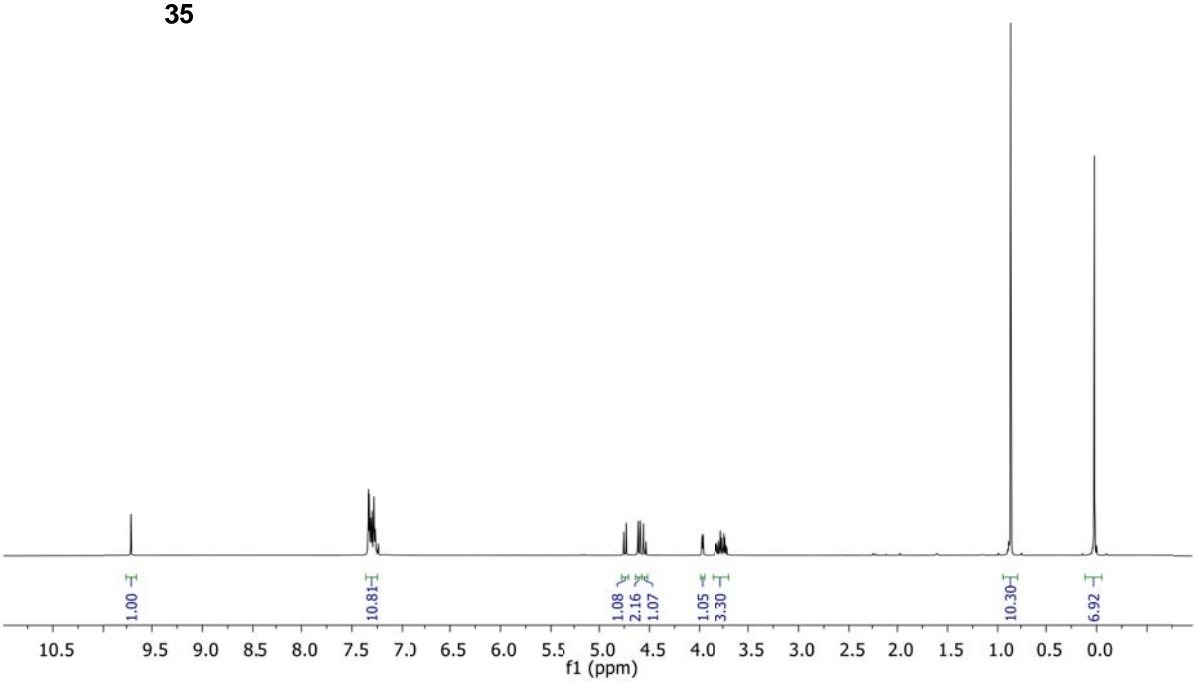
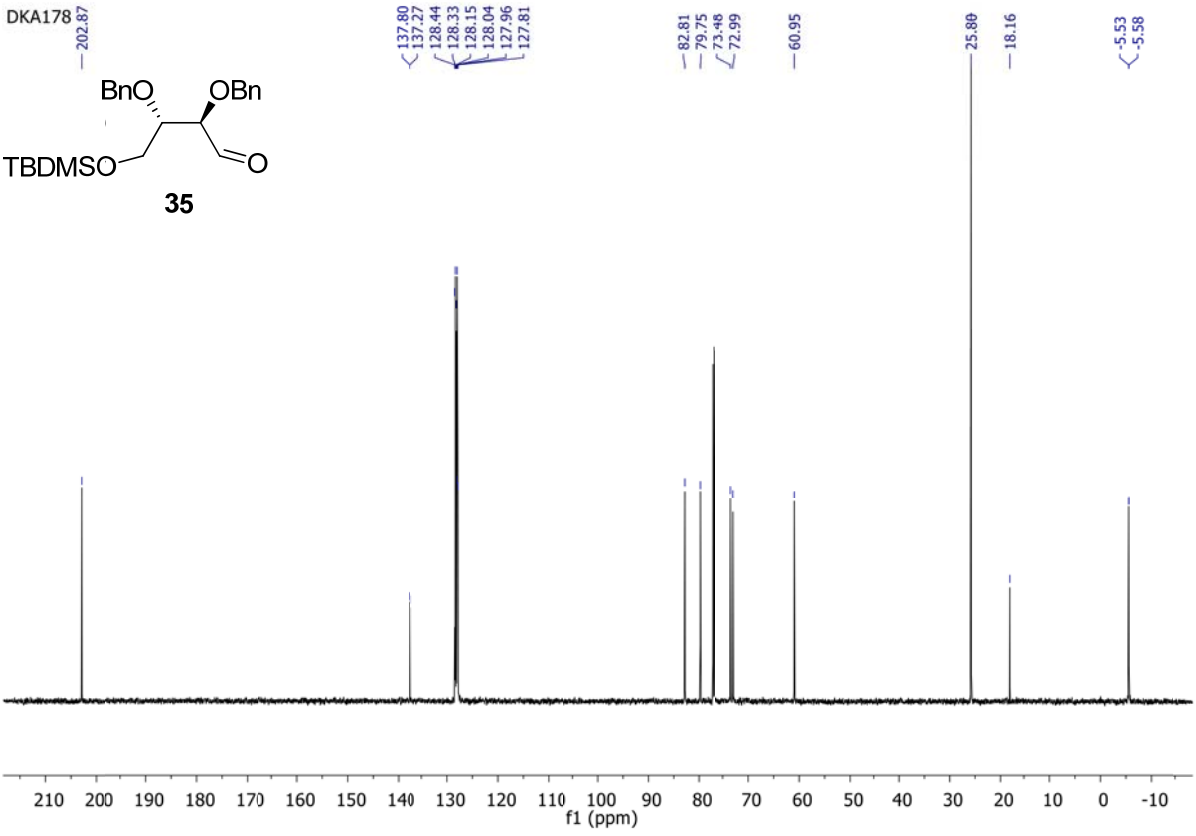


DKA178



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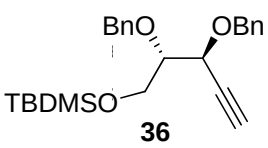
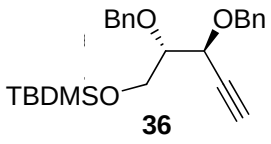
DK264



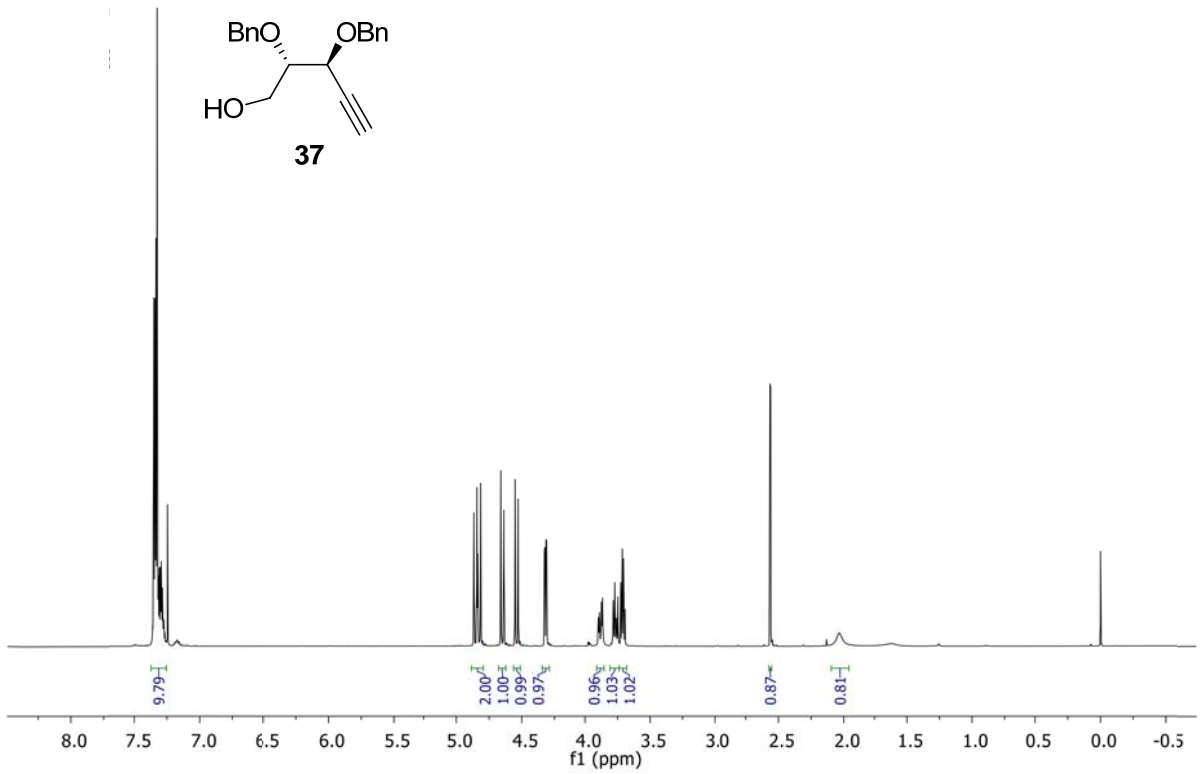
36

DK264

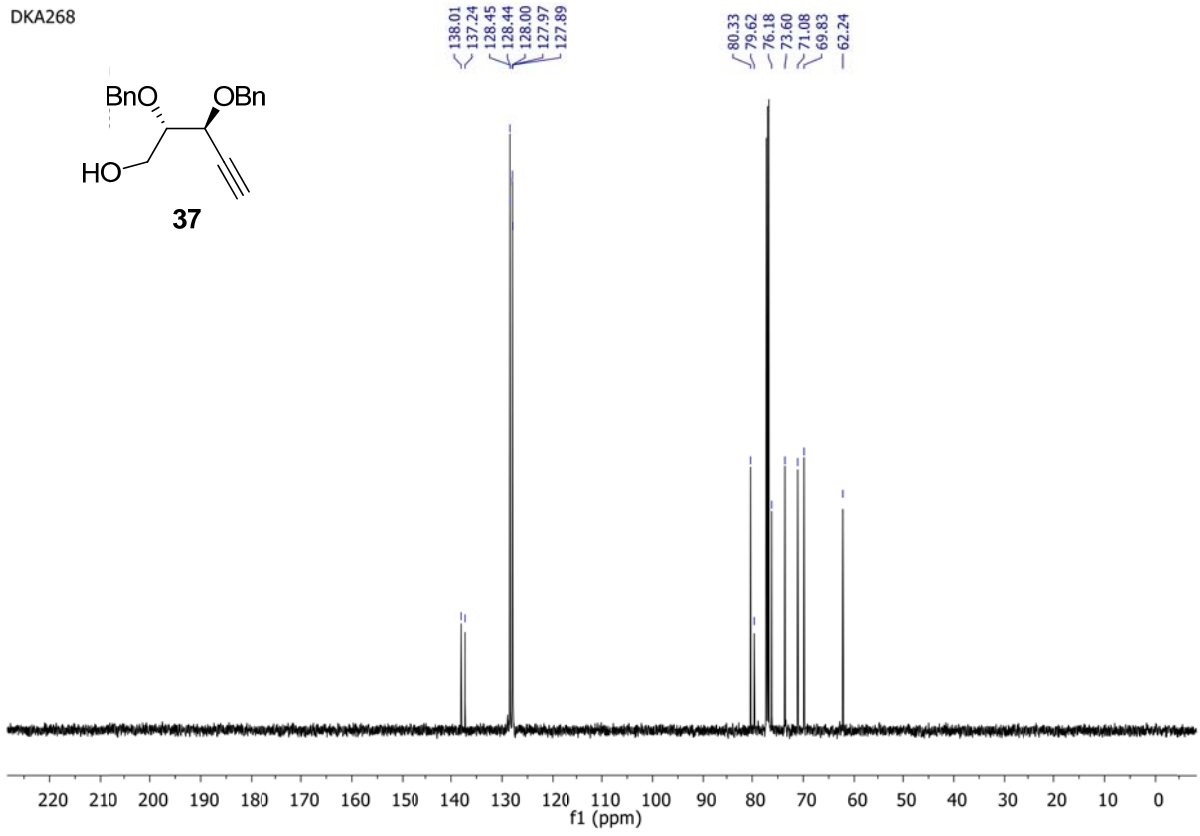


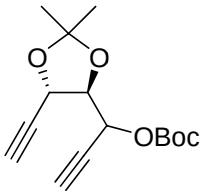
36

DKA268



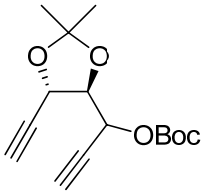
DKA268




OBoc

39a,b

5.43
5.43
5.43
5.42
5.31
5.30
5.30
5.29
4.77
4.74
4.39
4.35
2.59
2.56
1.54
1.53
1.52
1.50
1.46
1.45
1.02
1.00
1.97
2.00
3.27
9.33
3.22
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
-0.5
f1 (ppm)


OBoc

39a,b

152.24
152.12
112.47
112.14
83.50
83.47
81.94
81.58
81.23
80.28
76.42
76.33
75.05
74.60
65.04
27.70
26.78
26.59
26.28
26.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)