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Supporting Information

Total Synthesis of (+)-Asteriscanolide: Further Exploration of the Rhodium(I)-Catalyzed [(5+2)+1] Reaction of Ene-Vinylcyclopropanes and CO

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Contents

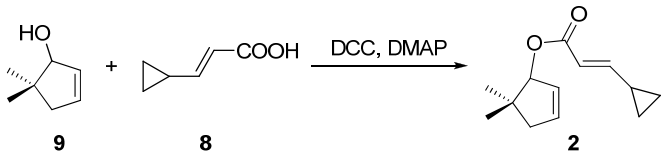
1. General Methods

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, diethyl ether, dioxane, benzene, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane was distilled from CaH_2 prior to use. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC. The diastereomeric ratio and the regioisomeric ratio were determined by ^{1}H NMR of crude reaction mixtures. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR spectra are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm).

Abbreviations:

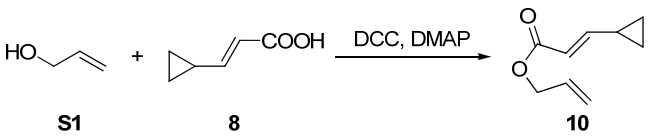
Ac = acetyl
acac = acetylacetonyl
AIBN = 2,2'-azo *bis*isobutyronitrile
brsm = based on recovered starting material
DCC = dicyclohexylcarbodiimide
DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIBAl-H = diisobutylaluminum hydride
DMAP = *N,N*-4-dimethylaminopyridine
DMF = *N,N*-dimethylformamide
DMP = Dess-Martin periodinane
LDA = lithium diisopropylamide
*m*CPBA = *m*-chloroperbenzoic acid
PE = petroleum ether
PMB = *p*-methoxybenzyl
Py = pyridine
Red-Al = sodium *bis*(2-methoxyethoxy) aluminum hydride
TBAF = tetrabutylammonium fluoride
TBS = *tert*-butyldimethylsilyl
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TMS = trimethylsilyl
Ts = *p*-toluenesulfonyl

2. Experimental Procedures and Characterization Data



To a mixture of acid **8**[1] (150 mg, 1.34 mmol), alcohol **9**[2] (167 mg, 1.49 mmol), and DMAP (68 mg, 0.56 mmol) in anhydrous CH_2Cl_2 (5 mL) at room temperature, was added DCC (305 mg, 1.48 mmol) in anhydrous CH_2Cl_2 (5 mL). After stirred for 21 hours, the reaction mixture was filtered and concentrated. The residue was purified by flash column chromatography to give ester **2** (175 mg, 63%).

2: colorless oil; R_f = 0.11 (PE/AcOEt = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62−0.65 (m, 2H), 0.91−0.97 (m, 2H), 1.04 (s, 3H), 1.13 (s, 3H), 1.53−1.60 (m, 1H), 2.13 (dm, J = 16.7 Hz, 1H), 2.33 (ddd, J = 16.7, 4.4, 2.0 Hz, 1H), 5.33−5.35 (m, 1H), 5.68−5.71 (m, 1H), 5.90 (d, J = 15.3 Hz, 1H), 5.99−6.02 (m, 1H), 6.41 (dd, J = 15.3, 9.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 8.6, 14.3, 22.9, 28.6, 40.9, 46.9, 85.5, 118.3, 128.8, 136.3, 153.9, 166.6. IR ν (cm^{-1}): 1270, 1386, 1475, 1646, 1713, 2969. HRMS (ESI): calcd for $C_{13}H_{18}NaO_2$: 229.1199; found: 229.1193.



To a mixture of acid **8**[1] (83 mg, 0.74 mmol), alcohol **S1** (52 mg, 0.90 mmol), and DMAP (35 mg, 0.29 mmol) in anhydrous CH_2Cl_2 (4 mL) at room temperature, was added DCC (227 mg, 1.10 mmol) in anhydrous CH_2Cl_2 (2.5 mL). After stirred for 5 hours, the reaction mixture was filtered and concentrated. The residue was purified by flash column chromatography to give ester **10** (86 mg, 77%).

10: colorless oil; R_f = 0.29 (PE/AcOEt = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62−0.66 (m, 2H), 0.93−0.98 (m, 2H), 1.54−1.62 (m, 1H), 4.62 (d, J = 6.0 Hz, 2H), 5.23 (d, J = 10.4 Hz, 1H), 5.32 (d, J = 17.1 Hz, 1H), 5.89−5.99 (m, 1H), 5.92 (d, J = 15.7 Hz, 1H), 6.45 (dd, J = 15.7, 9.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 8.6, 14.3, 64.7, 117.7, 117.8, 132.4, 154.4, 166.2. IR ν (cm^{-1}): 1266, 1311, 1389, 1456, 1646, 1713, 3013. HRMS (ESI): calcd for $C_9H_{12}NaO_2$: 175.0730; found: 175.0727.

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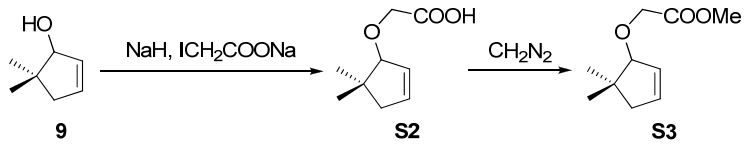
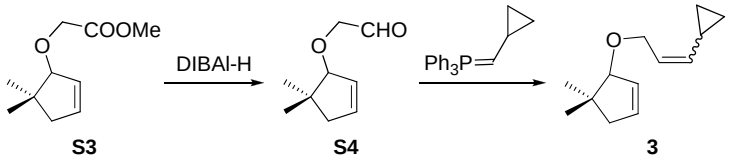
[1] (a) De Boeck, B.; Herbert, N. M. A.; Harrington-Frost, N. M.; Pattenden, G. *Org. Biomol. Chem.* **2005**, *3*, 328. (b) Ma, Z.; Wang, S.; Cooper, C. S.; Fung, A. K. L.; Lynch, J. K.; Plagge, F.; Chu, D. T. W. *Tetrahedron: Asymmetry* **1997**, *8*, 883.
[2] Limanto, J.; Snapper, M. L. *J. Am. Chem. Soc.* **2000**, *122*, 8071.



To a suspension of NaH (1.00 g, 41.7 mmol) in 10 mL anhydrous THF was added alcohol **9** (1.00 g, 8.93 mmol) in THF (15 mL). After stirred at 60 ºC for 15 minutes, ICH_2COONa (2.00 g, 9.62 mmol) was added, and the reaction mixture was stirred at 60 ºC for 13 hours. The resulting mixture was quenched and diluted by water and washed with CH_2Cl_2. The separated aqueous layer was acidified with 1 M HCl and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated to give the crude acid **S2**, which was used in the next step without further purification.

To a solution of crude acid **S2** in 10 mL diethyl ether at room temperature was added excess CH_2N_2[3] in diethyl ether. After stirred for 30 minutes, the solution was concentrated and then submitted to flash column chromatography on silica gel to afford ester **S3** (0.80 g, 49% over two steps).

S3: colorless oil; R_f = 0.15 (PE/AcOEt = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 3H), 1.11 (s, 3H), 2.07 (dm, J = 16.7 Hz, 1H), 2.28 (ddd, J = 16.7, 4.2, 1.9 Hz, 1H), 3.76 (s, 3H), 3.98−3.99 (m, 1H), 4.11 (d, J = 16.3 Hz, 1H), 4.18 (d, J = 16.3 Hz, 1H), 5.80−5.83 (m, 1H), 5.93−5.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.7, 29.1, 41.7, 46.9, 51.7, 67.2, 92.7, 129.4, 135.2, 171.3. IR ν (cm^{-1}): 1214, 1441, 1762, 2961. HRMS (ESI): calcd for $C_{10}H_{16}NaO_3$: 207.0992; found: 207.0989.



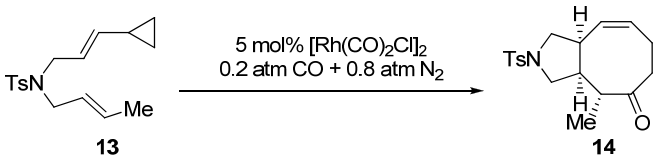
To a solution of ester **S3** (270 mg, 1.47 mmol) in 10 mL anhydrous CH_2Cl_2 at −78 ºC was added DIBAl-H (1.0 M in hexane, 1.5 mL, 1.5 mmol). After stirred at −78 ºC for 2 hours, the reaction mixture was quenched by methanol at −78 ºC, warmed to room temperature, diluted with diethyl ether, and washed with saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated to give the crude aldehyde **S4**, which was used in the next step without further purification.

To a suspension of cyclopropylmethyltriphenylphosphonium bromide (875 mg, 2.20 mmol) in 10 mL anhydrous THF at 0 ºC was added *n*-BuLi (1.6 M in hexane, 1.3 mL, 2.1 mmol). After stirred for 10 minutes, the crude aldehyde **S4** in THF (5 mL) was

[3] de Boer, T. J.; Backer, H. J. *Org. Synth.* **1956**, *36*, 16.

added. The resulting mixture was stirred at 0 ºC for 1 hour before it was quenched with saturated NH_4Cl solution and extracted with diethyl ether. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue, which was purified by flash column chromatography to give substrate **3** (156 mg, 55% over two steps, *E*:*Z* = 14:86). The *E*:*Z*-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons: a triplet at 4.90 ppm for *Z* isomer and a doublet of doublets at 5.21 ppm for *E* isomer.

3: colorless oil; R_f = 0.14 (PE/AcOEt = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer): δ 0.34−0.39 (m, 2H), 0.74−0.78 (m, 2H), 1.09 (s, 3H), 1.11 (s, 3H), 1.53−1.62 (m, 1H), 2.05 (d, J = 16.5 Hz, 1H), 2.25 (dm, J = 16.5 Hz, 1H), 3.97−4.00 (m, 1H), 4.21 (d, J = 6.8 Hz, 2H), 4.90 (t, J = 10.5 Hz, 1H), 5.48 (dt, J = 10.5, 6.8 Hz, 1H), 5.77−5.82 (m, 1H), 5.85−5.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, *Z* isomer): δ 7.1, 10.0, 22.9, 29.2, 41.7, 47.1, 66.2, 91.1, 125.0, 130.7, 133.7, 137.0. IR ν (cm^{-1}): 1270, 1352, 1471, 1657, 2961. HRMS (ESI): calcd for $C_{13}H_{21}O$: 193.1587; found: 193.1584.

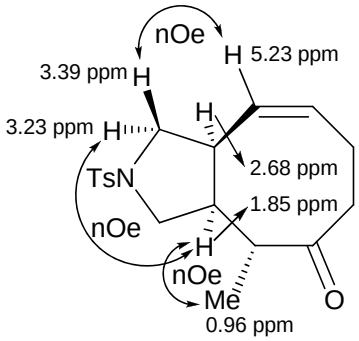


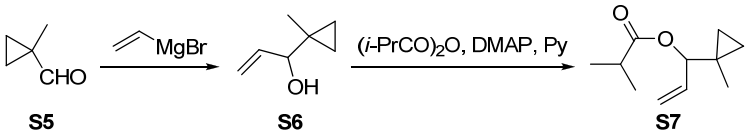
A solution of substrate **13**[4] (50 mg, 0.16 mmol) and $[Rh(CO)_2Cl]_2$ (3.2 mg, 0.008 mmol) in 11 mL anhydrous dioxane was degassed by bubbling CO/N_2 (balloon pressured mixed gas of CO and N_2, 1:4 V/V) for 5 minutes. Then the reaction mixture was immersed in a 90 ºC oil bath and stirred under the above atmosphere for 90 hours. The reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the [(5+2)+1] cycloadduct **14** (22 mg, 40%).

14: colorless oil; R_f = 0.31 (PE/AcOEt = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.96 (d, J = 6.0 Hz, 3H), 1.82−1.88 (m, 1H), 2.06−2.13 (m, 1H), 2.26−2.32 (m, 1H), 2.37−2.41 (m, 1H), 2.46 (s, 3H), 2.46−2.54 (m, 2H), 2.66−2.70 (m, 1H), 2.83 (t, J = 10.2 Hz, 1H), 3.23 (dd, J = 10.2, 5.4 Hz, 1H), 3.39 (d, J = 10.2 Hz, 1H), 3.45 (dd, J = 10.0, 8.1 Hz, 1H), 5.20−5.25 (m, 1H), 5.89−5.95 (m, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 15.4, 21.5, 23.8, 38.8, 45.0, 45.7, 45.8, 50.1, 53.4, 127.3, 129.7, 130.1, 130.4, 133.9, 143.6, 215.4. IR ν (cm^{-1}): 1348, 1456, 1605,

[4] Wang, Y.; Wang, J.; Su, J.; Huang, F.; Jiao, L.; Liang, Y.; Yang, D.; Zhang, S.; Wender, P. A.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007**, *129*, 10060. **13**: colorless oil; R_f = 0.28 (PE/AcOEt = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25−0.33 (m, 2H), 0.63−0.71 (m, 2H), 1.24−1.34 (m, 1H), 1.63 (d, J = 6.4 Hz, 3H), 2.42 (s, 3H), 3.72 (d, J = 6.8 Hz, 4H), 5.03 (dd, J = 15.2, 9.2 Hz, 1H), 5.19−5.30 (m, 2H), 5.49−5.58 (m, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 6.6, 13.2, 17.6, 21.4, 48.2, 48.3, 121.4, 125.5, 127.2, 129.5. 130.1, 137.7, 139.3, 142.9. IR ν (cm^{-1}): 1341, 1441, 1497, 1602, 1669, 2928. HRMS (ESI): calcd for $C_{17}H_{23}NNaO_2S$: 328.1342; found: 328.1341.

1706, 2935. HRMS (ESI): calcd for $C_{18}H_{24}NO_3S$: 334.1471; found: 334.1470.





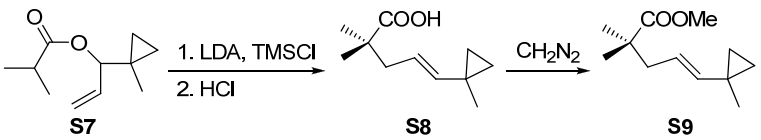
S5 **S6** **S7**

To a solution of vinylmagnesium bromide (0.7 M in THF, 74 mL, 52 mmol) at 0 ºC was added aldehyde **S5**[5] (2.18 g, 26.0 mmol) in 30 mL anhydrous diethyl ether. After stirred for 100 minutes, the reaction mixture was diluted with diethyl ether and washed with 1 M HCl and brine. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated to give the crude alcohol **S6**, which was used in the next step without further purification.

To a mixture of the crude alcohol **S6**, DMAP (1.10 g, 9.0 mmol), and pyridine (14.0 g, 177 mmol) was added $(i\text{-PrCO})_2O$ (5.96 g, 37.7 mmol). After stirred at 30 ºC for 13 hours, the reaction mixture was diluted with diethyl ether and washed sequentially with water, 1 M HCl, water, saturated $NaHCO_3$ solution, and brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by flash column chromatography to give ester **S7** (3.80 g, 80% over two steps).

S7: pale yellow oil; R_f = 0.47 (PE/AcOEt = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.30−0.36 (m, 2H), 0.47−0.60 (m, 2H), 1.06 (s, 3H), 1.19 (d, J = 7.0 Hz, 3H), 1.20 (d, J = 7.0 Hz, 3H), 2.60 (heptet, J = 7.0 Hz, 1H), 4.76 (dt, J = 5.6, 1.6 Hz, 1H), 5.17 (dt, J = 10.4, 1.6 Hz, 1H), 5.21 (dt, J = 17.2, 1.6 Hz, 1H), 5.82 (ddd, J = 17.2, 10.4, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 10.5, 11.8, 18.6, 18.7, 18.9, 19.1, 34.3, 79.5, 116.3, 134.8, 176.2. IR ν (cm^{-1}): 1263, 1393, 1475, 1736, 2976. HRMS (ESI): calcd for $C_{11}H_{18}NaO_2$: 205.1199; found: 205.1198.

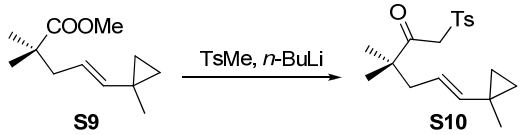
[5] Larock, R. C.; Yum, E. K. *Tetrahedron* **1996**, *52*, 2743.



To a solution of $(i\text{-Pr})_2NH$ (1.30 g, 12.9 mmol) in 20 mL anhydrous THF at 0 ºC was added *n*-BuLi (1.6 M in hexane, 7.5 mL, 12.0 mmol). After stirred for 10 minutes, the resulting mixture was cooled to −78 ºC, and then ester **S7** (1.10 g, 6.0 mmol) in THF (20 mL) was added via syringe. After stirred at −78 ºC for 10 minutes, TMSCl (1.33 g, 12.3 mmol) was added. The reaction mixture was maintained at −78 ºC for 30 minutes and at room temperature for another 1 hour and then diluted with diethyl ether. To the solution was added 1 M HCl. After stirred at room temperature for 30 minutes, the organic layer was separated, washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the crude acid **S8**, which was used in the next step without further purification.

To a solution of crude acid **S8** in diethyl ether at room temperature was added excess CH_2N_2[3] in diethyl ether. After stirred for 30 minutes, the solution was concentrated and then submitted to flash column chromatography on silica gel to afford ester **S9** (0.94 g, 80% over two steps).

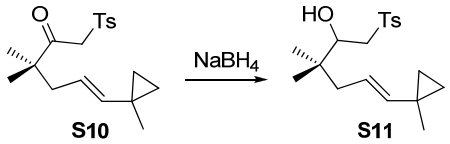
S9: colorless oil; R_f = 0.35 (PE/AcOEt = 30:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50 (s, 4H), 1.13 (s, 3H), 1.15 (s, 6H), 2.21 (d, J = 7.2 Hz, 2H), 3.66 (s, 3H), 5.09 (d, J = 15.6 Hz, 1H), 5.26 (dt, J = 15.6, 7.2 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.8, 17.0, 21.6, 24.7, 42.8, 43.5, 51.5, 120.8, 141.4, 178.2. IR ν (cm^{-1}): 1259, 1475, 1732, 2976. HRMS (ESI): calcd for $C_{12}H_{20}NaO_2$: 219.1356; found: 219.1355.



To a solution of TsMe (0.43 g, 2.5 mmol) in 15 mL anhydrous THF at 0 ºC was added *n*-BuLi (2.0 M in hexane, 2.5 mL, 5.0 mmol). After stirred for 30 minutes, ester **S9** (0.37 g, 1.9 mmol) in THF (6 mL) was added. The reaction mixture was maintained at 0 ºC for 30 minutes and at room temperature for another 30 minutes and then quenched with saturated NH_4Cl solution. After extracted with diethyl ether, the organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give ketone **S10** (0.52 g, 84%).

S10: white solid, mp 68−69 ºC; R_f = 0.54 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.46−0.52 (m, 4H), 1.07 (s, 3H), 1.08 (s, 6H), 2.14 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H), 4.28 (s, 2H),5.03−5.12 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.9, 17.0, 21.4, 21.7, 23.3, 42.2, 49.0, 61.4, 119.4, 128.7, 129.6, 136.5, 142.4, 145.0, 203.1. IR ν (cm^{-1}): 1326, 1471, 1602, 1717,

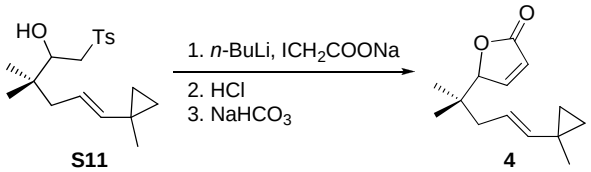
2972. HRMS (ESI): calcd for $C_{19}H_{26}NaO_3S$: 357.1495; found: 357.1495.



S10 **S11**

To a solution of ketone **S10** (480 mg, 1.44 mmol) in 15 mL anhydrous methanol at 0 ºC was added $NaBH_4$ (170 mg, 4.47 mmol). After stirred for 90 minutes, most methanol was removed by evaporation, and the residue was dissolved in CH_2Cl_2 and washed with 1 M HCl. After the aqueous layer was extracted with CH_2Cl_2, the combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give alcohol **S11** (470 mg, 97%).

S11: colorless oil; R_f = 0.53 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.45−0.52 (m, 4H), 0.76 (s, 3H), 0.84 (s, 3H),1.08 (s, 3H), 1.82 (dd, J = 14.0, 7.2 Hz, 1H), 2.04 (dd, J = 14.0, 7.2 Hz, 1H), 2.46 (s, 3H), 3.12 (dd, J = 14.4, 10.0 Hz, 1H), 3.22 (d, J = 2.0 Hz, 1H), 3.25 (d, J = 14.4 Hz, 1H), 3.79 (dd, J = 10.0, 2.0 Hz, 1H), 5.03 (d, J = 15.6 Hz, 1H), 5.18 (dt, J = 15.6, 7.2 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.8, 17.0, 21.5, 21.6, 22.4, 22.7, 37.9, 41.7, 58.5, 71.5, 120.5, 127.9, 130.0, 136.1, 141.3, 145.0. IR ν (cm^{-1}): 1304, 1389, 1471, 1602, 2965, 3531. HRMS (ESI): calcd for $C_{19}H_{28}NaO_3S$: 359.1651; found: 359.1651.

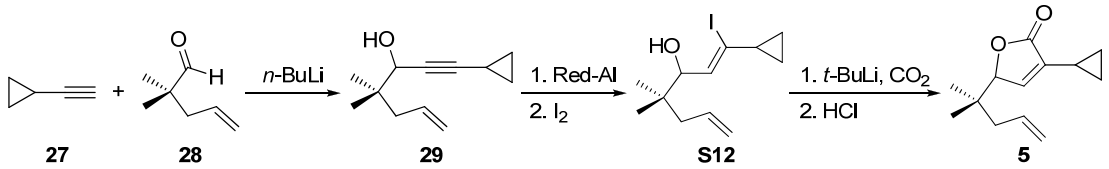


S11 **4**

To a solution of **S11** (370 mg, 1.10 mmol) in 12 mL anhydrous THF at −78 ºC was added *n*-BuLi (1.6 M in hexane, 1.8 mL, 2.9 mmol). After stirred at 0 ºC for 1 hour, the resulting mixture was cooled to −78 ºC, and then ICH_2COONa (282 mg, 1.36 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 18 hours. Then the mixture was quenched and diluted with brine and washed with diethyl ether. The separated aqueous layer was acidified with 1 M HCl and extracted with diethyl ether. The combined organic extracts were washed with saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give substrate **4** (65 mg, 27%).

4: colorless oil; R_f = 0.54 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.51−0.56 (m, 4H), 0.89 (s, 3H), 0.94 (s, 3H),1.16 (s, 3H), 2.00 (dd, J = 13.8, 7.2 Hz,

1H), 2.15 (dd, J = 13.8, 7.2 Hz, 1H), 4.82 (t, J = 1.6 Hz, 1H), 5.15 (d, J = 15.3 Hz, 1H), 5.35 (dd, J = 15.3, 7.2 Hz, 1H), 6.15 (dd, J = 5.6, 1.6 Hz, 1H), 7.47 (dd, J = 5.6, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.9, 17.1, 21.6, 22.5, 22.6, 38.0, 42.2, 89.4, 120.0, 122.5, 142.4, 154.4, 173.2. IR ν (cm^{-1}): 1322, 1471, 1602, 1665, 1758, 2969. HRMS (ESI): calcd for $C_{14}H_{20}NaO_2$: 243.1356; found: 243.1358.



27 28 29 S12 5

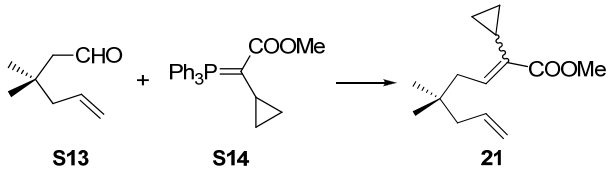
To a solution of alkyne **27** (300 mg, 4.55 mmol) in 3 mL anhydrous THF at −78 ºC was added *n*-BuLi (1.6 M in hexane, 2.8 mL, 4.5 mmol). After stirred at −78 ºC for 30 minutes, aldehyde **28** (460 mg, 4.11 mmol) in THF (5 mL) was added. Then the reaction mixture was allowed to warm up to room temperature and stirred overnight. After the reaction mixture was diluted with diethyl ether and washed with brine, the organic layer was separated, dried over $MgSO_4$, filtered, and concentrated to give the crude alcohol **29**, which was used in the next step without further purification.

To a solution of the crude alcohol **29** in 15 mL anhydrous THF at −78 ºC was added Red-Al (3.5 M in toluene, 3.0 mL, 10.5 mmol). Then the reaction mixture was allowed to warm up to room temperature. After stirred at 45 ºC for 20 hours, the mixture was cooled to −78 ºC, quenched with I_2 (3.00 g, 11.8 mmol) in THF (15 mL), and then warmed up to room temperature. After stirred for 2 hours, to the mixture was added saturated potassium sodium tartrate solution and diethyl ether. The separated aqueous layer was extracted with diethyl ether. Then the combined organic extracts were washed with saturated $Na_2S_2O_3$ solution and brine, dried over $MgSO_4$, filtered, and concentrated. The resulting oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude iodide **S12**, which was used in the next step without further purification.

To a solution of the crude iodide **S12** in 30 mL anhydrous diethyl ether at −78 ºC was added *t*-BuLi (1.5 M in pentane, 8.0 mL, 12.0 mmol). After stirred at −78 ºC for 70 minutes, the reaction mixture was bubbled with CO_2 gas and slowly warmed to room temperature. Then the mixture was quenched with 1 M HCl at 0 ºC and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by flash column chromatography to give substrate **5** (220 mg, 26% over three steps).

5: pale yellow oil; R_f = 0.33 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73−0.79 (m, 2H), 0.88 (s, 3H), 0.89−0.95 (m, 2H), 0.92 (s, 3H), 1.62−1.71 (m, 1H), 2.02 (dd, J = 13.6, 7.6 Hz, 1H), 2.15 (dd, J = 13.6, 7.6 Hz, 1H), 4.63 (d, J = 0.8 Hz, 1H), 5.05−5.14 (m, 2H), 5.76−5.86 (m, 1H), 6.79 (d, J = 0.8 Hz, 1H). ^{13}C NMR (101 MHz,

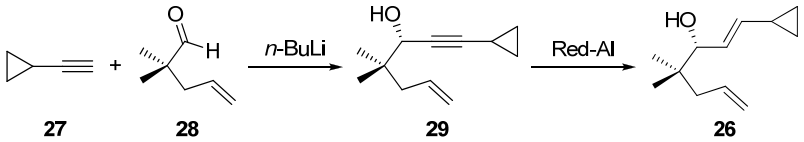
$CDCl_3$): δ 7.1, 7.8, 7.9, 22.3, 22.6, 37.7, 43.2, 87.0, 118.5, 133.6, 137.6, 141.6, 173.0. IR v (cm^{-1}): 1319, 1471, 1643, 1754, 2969. HRMS (ESI): calcd for $C_{13}H_{18}NaO_2$: 229.1199; found: 229.1193.



S13 **S14** **21**

A solution of aldehyde **S13**[6] (253 mg, 2.01 mmol) and ylide **S14**[7] (1.50 g, 4.01 mmol) in 10 mL anhydrous benzene was heated to reflux for 24 hours. Additional **S14** (0.75 g, 2.01 mmol) was added at room temperature, and the reaction mixture continued to reflux for 40 hours. Purification by flash column chromatography gave substrate **21** (409 mg, 92%, *Z*:*E* = 12:88).[8] The *Z*:*E*-ratio was determined using ^{1}H-NMR by integration of the methyl group of the ester: a singlet at 3.71 ppm for *E* isomer and a singlet at 3.75 ppm for *Z* isomer.

21: colorless oil; R_f = 0.20 (PE/AcOEt = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$, *E* isomer): δ 0.56−0.61 (m, 2H), 0.75−0.81 (m, 2H), 0.94 (s, 6H), 1.38−1.47 (m, 1H), 2.01 (d, J = 7.4 Hz, 2H), 2.26 (dd, J = 7.7, 1.0 Hz, 2H), 3.71 (s, 3H), 4.99−5.08 (m, 2H), 5.76−5.88 (m, 1H), 6.82 (td, J = 7.7, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, *E* isomer): δ 6.6, 9.0, 26.9, 34.3, 40.2, 46.5, 51.4, 117.3, 133.8, 135.1, 141.5, 168.4. IR v (cm^{-1}): 1199, 1248, 1438, 1639, 1717, 2961. HRMS (ESI): calcd for $C_{14}H_{22}NaO_2$: 245.1512; found: 245.1506.



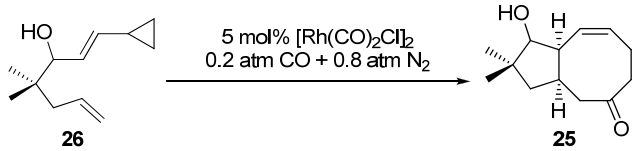
27 **28** **29** **26**

To a solution of alkyne **27** (4.40 g, 66.7 mmol) in 25 mL anhydrous THF at −78 ºC was added *n*-BuLi (2.2 M in hexane, 30 mL, 66 mmol). After stirred at −78 ºC for 30 minutes, aldehyde **28** (6.53 g, 58.3 mmol) in THF (50 mL) was added. Then the reaction mixture was allowed to warm up to room temperature and stirred overnight. After the reaction mixture was diluted with diethyl ether and washed with brine, the organic layer was separated, dried over $MgSO_4$, filtered, and concentrated to give the crude alcohol **29**, which was used in the next step without further purification.

[6] Jiao, L.; Yuan, C.; Yu, Z.-X. *J. Am. Chem. Soc.* **2008**, *130*, 4421.
[7] Maercher, A. *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 557.
[8] Sternbach, D. D.; Ensinger, C. L. *J. Org. Chem.* **1990**, *55*, 2725.

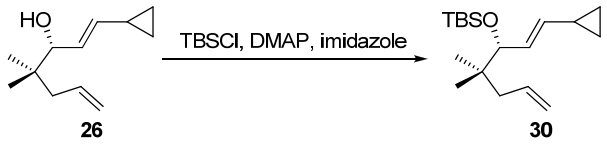
To a solution of the crude alcohol **29** in 90 mL anhydrous THF at −78 ºC was added Red-Al (3.5 M in toluene, 42 mL, 147 mmol). Then the reaction mixture was allowed to warm up to room temperature. After stirred at 40 ºC for 24 hours, the mixture was cooled to 0 ºC, slowly quenched with 10 mL saturated potassium sodium tartrate solution, and diluted with another 190 mL saturated potassium sodium tartrate solution. After stirred at room temperature overnight, the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting oil was purified by flash column chromatography to give alcohol **26** (9.75 g, 93% over two steps).

26: colorless oil; R_f = 0.33 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35−0.39 (m, 2H), 0.69−0.74 (m, 2H), 0.85 (s, 3H), 0.89 (s, 3H), 1.35−1.45 (m, 1H), 1.49 (br, 1H), 1.98 (dd, J = 13.5, 7.5 Hz, 1H), 2.10 (dd, J = 13.5, 7.5 Hz, 1H), 3.74 (dd, J = 7.7, 3.7 Hz, 1H), 5.00−5.07 (m, 2H), 5.16 (dd, J = 15.5, 8.8 Hz, 1H), 5.60 (dd, J = 15.5, 7.7 Hz, 1H), 5.79−5.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 6.69, 6.74, 13.5, 22.6, 22.9, 37.7, 43.4, 79.6, 117.1, 126.8, 135.5, 137.6. IR ν (cm^{-1}): 1371, 1389, 1475, 1643, 1669, 2969, 3393. HRMS (ESI): calcd for $C_{12}H_{20}NaO$: 203.1406; found: 203.1405. $[\alpha]^{20}_D$: +30.1 (c 0.98, $CHCl_3$).



A solution of substrate **26** (180 mg, 1.00 mmol) and $[Rh(CO)_2Cl]_2$ (20 mg, 0.05 mmol) in 20 mL anhydrous dioxane was degassed by bubbling CO/N_2 (balloon pressured mixed gas of CO and N_2, 1:4 V/V) for 5 minutes. Then the reaction mixture was immersed in a 90 ºC oil bath and stirred under the above atmosphere for 14 hours. The reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the [(5+2)+1] cycloadduct **25** (62 mg, 30%).

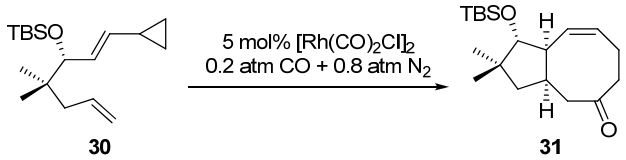
25: pale yellow oil; R_f = 0.26 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (s), 1.07 (s), 1.14 (t, J = 12.4 Hz), 1.26 (t, J = 12.4 Hz), 1.60 (dd, J = 12.4, 6.0 Hz), 1.69 (dd, J = 12.4, 6.0 Hz), 2.05−2.30 (m), 2.36−2.62 (m), 2.73−2.81 (m), 2.97−3.05 (m), 3.65 (d, J = 6.0 Hz), 3.89 (d, J = 6.5 Hz), 5.55 (dd, J = 10.8, 6.6 Hz), 5.81 (t, J = 9.8 Hz), 5.90−5.97 (m), 6.02−6.09 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.8, 23.4, 23.7, 25.2, 27.7, 30.8, 34.7, 35.9, 39.9, 40.6, 43.9, 44.3, 44.8, 45.9, 46.1, 46.5, 46.75, 46.78, 81.6, 88.1, 127.8, 130.7, 130.8, 133.1, 213.7, 213.8. IR ν (cm^{-1}): 1337, 1464, 1695, 2928, 3445. HRMS (ESI): calcd for $C_{13}H_{20}NaO_2$: 231.1356; found: 231.1353.



26 **30**

To a solution of allylic alcohol **26** (1.80 g, 10.0 mmol) in 40 mL anhydrous DMF was added imidazole (1.20 g, 17.6 mmol), DMAP (0.35 g, 2.9 mmol), and TBSCl (2.17 g, 14.4 mmol). After stirred at 40 ºC for 48 hours, the reaction mixture was poured into 150 mL water and extracted with diethyl ether. The combined organic extracts were washed with brine and dried over $MgSO_4$. The filtrate was evaporated and purified by flash column chromatography on silica gel to afford compound **30** (2.83 g, 96%).

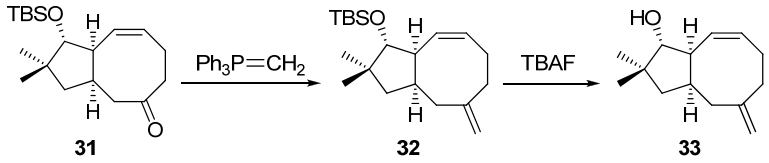
30: colorless oil; R_f = 0.61 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.01 (s, 3H), 0.01 (s, 3H), 0.30−0.38 (m, 2H), 0.65−0.72 (m, 2H), 0.79 (s, 3H), 0.83 (s, 3H), 0.89 (s, 9H), 1.32−1.42 (m, 1H), 1.94 (dd, J = 13.5, 7.7 Hz, 1H), 2.06 (dd, J = 13.5, 7.7 Hz, 1H), 3.66 (d, J = 8.0 Hz, 1H), 4.96−5.09 (m, 3H), 5.46 (dd, J = 15.4, 8.0 Hz, 1H), 5.77−5.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.9, −3.5, 6.3, 6.4, 13.2, 18.2, 22.92, 22.94, 26.0, 38.5, 43.2, 80.8, 116.6, 127.9, 135.9, 136.2. IR ν (cm^{-1}): 1255, 1367, 1389, 1475, 1643, 1669, 2961. HRMS (ESI): calcd for $C_{18}H_{34}NaOSi$: 317.2271; found: 317.2278. $[\alpha]^{20}_D$: +10.6 (c 1.78, $CHCl_3$).



30 **31**

A solution of substrate **30** (1.50 g, 5.1 mmol) and $[Rh(CO)_2Cl]_2$ (100 mg, 0.26 mmol) in 310 mL anhydrous toluene was degassed by bubbling CO/N_2 (balloon pressured mixed gas of CO and N_2, 1:4 V/V) for 5 minutes. Then the reaction mixture was immersed in a 90 ºC oil bath and stirred under the above atmosphere for 50 hours. The reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the [(5+2)+1] cycloadduct **31** (1.15 g, 70%).

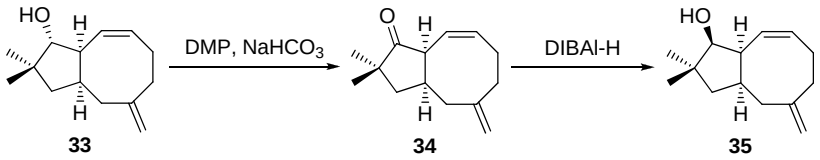
31: pale yellow oil; R_f = 0.19 (PE/AcOEt = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 0.93 (s, 3H), 1.01 (s, 3H), 1.10 (t, J = 12.4 Hz, 1H), 1.54−1.63 (m, 1H), 2.01−2.30 (m, 3H), 2.34−2.56 (m, 4H), 2.61−2.70 (m, 1H), 3.63 (d, J = 4.4 Hz, 1H), 5.44−5.51 (m, 1H), 5.87−5.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.9, −4.2, 18.0, 22.0, 23.8, 25.8, 28.4, 36.9, 41.7, 44.6, 44.7, 46.7, 47.8, 89.2, 130.0, 133.9, 213.9. IR ν (cm^{-1}): 1255, 1367, 1464, 1706, 2957. HRMS (ESI): calcd for $C_{19}H_{34}NaO_2Si$: 345.2220; found: 345.2221. $[\alpha]^{20}_D$: −45.3 (c 1.18, $CHCl_3$).



To a suspension of *t*-BuOK (1.04 g, 9.3 mmol) in 40 mL anhydrous benzene was added methyltriphenylphosphonium bromide (3.45 g, 9.7 mmol). After stirred at 40 ºC for 10 minutes, ketone **31** (0.49 g, 1.5 mmol) in benzene (25 mL) was added. The resulting mixture was stirred at 40 ºC for 40 minutes, cooled to room temperature, and then filtered through a pad of silica gel. The filtrate was concentrated to give the crude compound **32**, which was used in the next step without further purification.

To a solution of the crude compound **32** in 12 mL anhydrous THF was added TBAF (1.14 g, 4.3 mmol). After stirred at 40 ºC for 23 hours, the reaction mixture was quenched with 50 mL saturated NH_4Cl solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to give alcohol **33** (0.24 g, 77%).

33: colorless oil; R_f = 0.23 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (s, 3H), 1.06 (s, 3H), 1.14 (t, J = 12.6 Hz, 1H), 1.62 (dd, J = 12.6, 6.5 Hz, 1H), 1.81 (s, 1H), 1.88−2.08 (m, 4H), 2.11−2.33 (m, 2H), 2.35−2.42 (m, 1H), 2.71−2.79 (m, 1H), 3.61 (d, J = 5.5 Hz, 1H), 4.67 (s, 1H), 4.72 (s, 1H), 5.40 (dd, J = 10.7, 6.9 Hz, 1H), 5.78−5.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.3, 28.2, 28.4, 37.0, 37.4, 40.7, 43.8, 47.1, 47.3, 88.6, 112.0, 131.9, 132.2, 152.9. IR ν (cm^{-1}): 1222, 1456, 1643, 2939, 3360. HRMS (ESI): calcd for $C_{14}H_{22}NaO$: 229.1563; found: 229.1563.

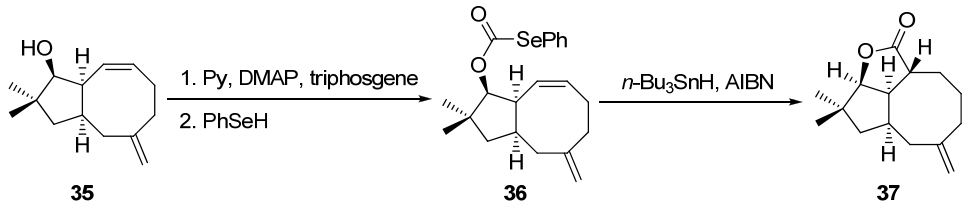


To a mixture of alcohol **33** (170 mg, 0.83 mmol) and $NaHCO_3$ (0.38 g, 4.5 mmol) in 15 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (0.84 g, 2.0 mmol). After stirred for 3.5 hours, the reaction mixture was quenched with 40 mL saturated $NaHCO_3$ solution and 40 mL saturated $Na_2S_2O_3$ solution and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$ twice, filtered, and used directly in the next step.

To the solution of ketone **34** at −78 ºC was added DIBAl-H (1.0 M in hexane, 14 mL, 14 mmol). After stirred at −78 ºC for 2 hours, the reaction mixture was allowed to warm up to 0 ºC and quenched with saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product

was purified by flash column chromatography on silica gel to afford alcohol **35** (149 mg, 88% over two steps).

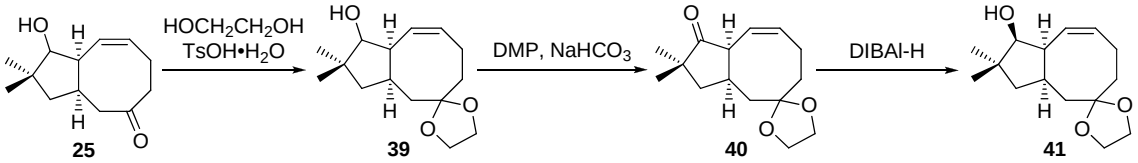
35: white solid, mp 52−53 °C; R_f = 0.23 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.07 (s, 3H), 1.21 (t, J = 12.7 Hz, 1H), 1.53 (dd, J = 12.7, 6.6 Hz, 1H), 1.57−1.67 (m, 2H), 1.88−2.26 (m, 5H), 2.34−2.41 (m, 1H), 3.13 (dd, J = 14.9, 7.2 Hz, 1H), 3.88 (t, J = 6.5 Hz, 1H), 4.71 (s, 1H), 4.81 (s, 1H), 5.64 (t, J = 9.7 Hz, 1H), 5.97 (q, J = 9.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.5, 28.2, 31.5, 37.2, 39.1, 39.7, 41.9, 45.8, 46.6, 82.1, 112.1, 126.3, 133.0, 151.6. IR ν (cm^{-1}): 1371, 1460, 1646, 2935, 3375. HRMS (ESI): calcd for $C_{14}H_{22}NaO$: 229.1563; found: 229.1564.



To a mixture of alcohol **35** (172 mg, 0.83 mmol), DMAP (41 mg, 0.34 mmol), and pyridine (1.69 g, 21.4 mmol) in 10 mL anhydrous THF was added a solution of triphosgene (373 mg, 1.26 mmol) in 15 mL anhydrous benzene. After stirred at room temperature for 3 hours, freshly distilled PhSeH (720 mg, 4.58 mmol) was added, and the reaction mixture was stirred at 40 ºC for 3 hours before 100 mL water and 100 mL diethyl ether were added. The aqueous layer was separated and extracted with diethyl ether. The combined organic phase was washed sequentially with 1M HCl, water, and saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude selenocarbonate **36**, which was used in the next step without further purification.

To a solution of the crude selenocarbonate **36** and AIBN (27 mg, 0.17 mmol) in 100 mL anhydrous benzene was added n-Bu_3SnH (730 mg, 2.50 mmol). The resulting mixture was heated in a 90 °C oil bath to reflux for 2 hours. The solvent was removed by evaporation, and the residue was submitted to flash column chromatography on silica gel to afford the tricyclic compound **37** (153 mg, 78% over two steps).

37: colorless oil; R_f = 0.17 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 3H), 1.07 (s, 3H), 1.35−1.54 (m, 3H), 1.60−1.69 (m, 1H), 1.76−1.88 (m, 1H), 2.10−2.20 (m, 2H), 2.27−2.40 (m, 4H), 2.70 (ddd, J = 11.9, 9.4, 4.1 Hz, 1H), 2.79−2.86 (m, 1H), 4.32 (d, J = 7.7 Hz, 1H), 4.71 (s, 1H), 4.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.7, 24.3, 29.0, 30.4, 34.5, 36.1, 37.6, 38.5, 40.4, 44.4, 48.2, 90.1, 113.5, 147.3, 180.0. IR ν (cm^{-1}): 1374, 1471, 1635, 1773, 2931. HRMS (ESI): calcd for $C_{15}H_{22}NaO_2$: 257.1512; found: 257.1510.

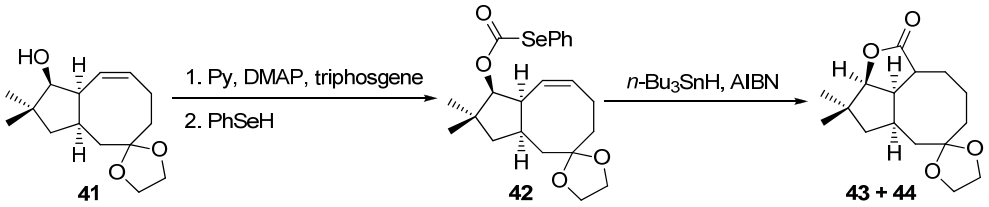


A solution of compound **25** (403 mg, 1.94 mmol), $HOCH_2CH_2OH$ (1.07 g, 17.3 mmol), and $TsOH{\cdot}H_2O$ (36 mg, 0.19 mmol) in 40 mL benzene was refluxed under a Dean-Stark trap for 4 hours. The reaction mixture was then cooled to room temperature, diluted with diethyl ether, and washed with saturated $NaHCO_3$ solution and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated. The resulting pale yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude **39**, which was used in the next step without further purification.

To a mixture of crude alcohol **39** and $NaHCO_3$ (0.81 g, 9.6 mmol) in 25 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (1.36 g, 3.21 mmol). After stirred for 2 hours, the reaction mixture was quenched with 50 mL saturated $NaHCO_3$ solution and 50 mL saturated $Na_2S_2O_3$ solution and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$ twice, filtered, and used directly in the next step.

To the solution of ketone **40** at −78 ºC was added DIBAl-H (1.0 M in toluene, 13 mL, 13 mmol). After stirred at −78 ºC for 1 hour, the reaction mixture was quenched with 1 mL saturated potassium sodium tartrate solution at −78 ºC. The reaction mixture was diluted with diethyl ether and allowed to warm up to 0 ºC. Then additional 60 mL saturated potassium sodium tartrate solution was added. After the aqueous layer was separated, the organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford alcohol **41** (282 mg, 58% over three steps).

41: white solid, mp 80−82 °C; R_f = 0.21 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 3H), 1.05 (s, 3H), 1.22 (t, J = 12.6 Hz, 1H), 1.52 (dd, J = 12.6, 7.2 Hz, 1H), 1.58−1.67 (m, 3H), 1.80 (dd, J = 14.4, 11.6 Hz, 1H), 2.03−2.14 (m, 2H), 2.16−2.40 (m, 2H), 3.38 (dd, J = 13.8, 7.0 Hz, 1H), 3.86−3.97 (m, 5H), 5.65 (m, 1H), 5.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.3, 25.0, 30.4, 34.7, 36.6, 39.3, 39.4, 45.3, 47.1, 63.7, 64.6, 82.4, 111.7, 125.0, 132.0. IR ν (cm^{-1}): 1073, 1114, 1281, 1367, 1460, 2935, 3468. HRMS (ESI): calcd for $C_{15}H_{24}NaO_3$: 275.1618; found: 275.1617.

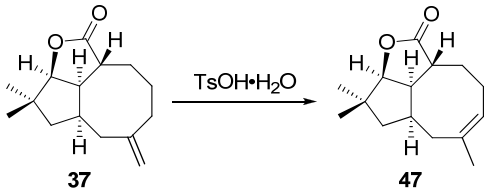


To a mixture of alcohol **41** (280 mg, 1.11 mmol), DMAP (88 mg, 0.72 mmol), and

pyridine (2.57 g, 32.5 mmol) in 26 mL anhydrous THF was added a solution of triphosgene (464 mg, 1.56 mmol) in 25 mL anhydrous benzene. After stirred at room temperature for 3 hours, freshly distilled PhSeH (1.10 g, 7.01 mmol) was added, and the reaction mixture was stirred overnight at room temperature before 200 mL water and 200 mL diethyl ether were added. The aqueous layer was separated and extracted with diethyl ether. The combined organic phase was washed sequentially with saturated NH_4Cl solution, water, and saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude selenocarbonate **42**, which was used in the next step without further purification.

To a solution of the crude selenocarbonate **42** and AIBN (82 mg, 0.50 mmol) in 230 mL anhydrous benzene was added *n*-Bu_3SnH (1.38 g, 4.74 mmol). The resulting mixture was heated in a 90 °C oil bath to reflux for 3 hours. The solvent was removed by evaporation, and the residue was submitted to flash column chromatography on silica gel to afford a mixture of compounds **43** and **44** (211 mg, 68% over two steps). The ratio of **43** and **44** was determined using ^{1}H-NMR by integration of the methine proton at the α-position of the oxygen atom: a doublet at 4.25 ppm (J = 5.2 Hz) for *cis* **44** (minor) and a doublet at 4.34 ppm (J = 8.0 Hz) for *trans* **43** (major).

43 + 44: white solid; R_f = 0.32 (PE/AcOEt = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (s), 1.03 (s), 1.05 (s), 1.14 (s), 1.24−2.20 (m), 2.28−2.55 (m), 2.86 (m), 3.01 (dd, J = 16.4, 8.0 Hz), 3.27 (td, J = 10.0, 5.6 Hz), 3.84−4.02 (m), 4.25 (d, J = 5.2 Hz), 4.34 (d, J = 8.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1, 22.0, 23.0, 23.8, 24.0, 24.4, 28.4, 31.2, 32.5, 33.9, 35.4, 36.5, 37.2, 39.4, 40.4, 40.7, 41.6, 43.2, 43.7, 45.2, 46.1, 47.7, 63.9, 64.6, 64.7, 90.7, 91.9, 111.2, 111.7, 179.25, 179.32. IR ν (cm^{-1}): 1158, 1192, 1266, 1374, 1468, 1765, 2942. HRMS (ESI): calcd for $C_{16}H_{24}NaO_4$: 303.1567; found: 303.1566.

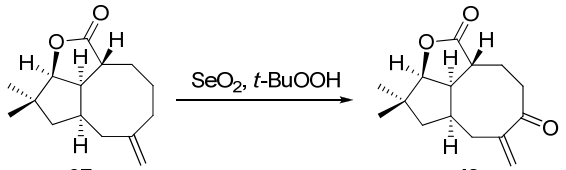


37 **47**

To a solution of compound **37** (70 mg, 0.83 mmol) in 15 mL $CHCl_3$ was added $TsOH{\cdot}H_2O$ (21 mg, 0.12 mmol). After stirred at 45 ºC for 16 hours and at 60 ºC for another 44 hours, the solvent was removed by evaporation, and the residue was purified by flash column chromatography to give compound **47** (61 mg, 87%).

47: white solid, mp 109−110 °C; R_f = 0.22 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 3H), 1.07 (s, 3H), 1.21−1.31 (m, 1H), 1.40 (t, J = 12.8 Hz, 1H), 1.51 (dd, J = 12.8, 5.9 Hz, 1H), 1.75 (s, 3H), 1.94 (dd, J = 12.6, 3.8 Hz, 1H), 2.10−2.35 (m, 4H), 2.37−2.50 (m, 2H), 2.76 (dt, J = 9.4, 7.2 Hz, 1H), 4.26 (d, J = 7.8 Hz, 1H), 5.43 (t,

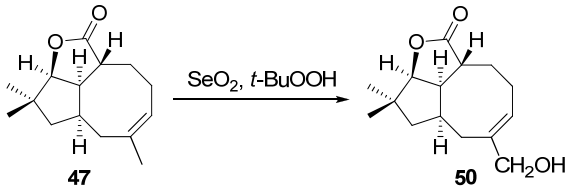
J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.6, 24.7, 26.9, 29.3, 31.5, 33.1, 36.9, 40.9, 42.0, 44.8, 50.2, 88.9, 124.1, 137.5, 179.6. IR ν (cm^{-1}): 1374, 1468, 1773, 2939. HRMS (ESI): calcd for $C_{15}H_{22}NaO_2$: 257.1512; found: 257.1509.



37 **49**

To a solution of compound **37** (27 mg, 0.11 mmol) in 3 mL CH_2Cl_2 was added SeO_2 (15 mg, 0.14 mmol) and *t*-BuOOH (65 wt%, 133 mg, 0.96 mmol). After stirred at 25 ºC for 13 hours, the solvent was removed by evaporation, and the residue was purified by flash column chromatography to give ketone **49** (26 mg, 90%).

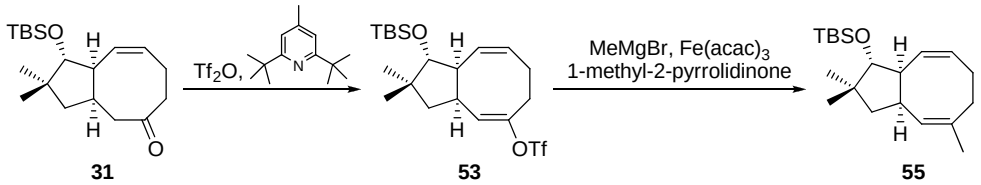
49: white solid, mp 117−118 °C; R_f = 0.26 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 3H), 1.05 (s, 3H), 1.42 (t, J = 13.0 Hz, 1H), 1.56−1.72 (m, 2H), 2.14−2.25 (m, 1H), 2.45−2.59 (m, 5H), 2.64 (dd, J = 14.1, 4.4 Hz, 1H), 2.81−2.89 (m, 1H), 4.30 (d, J = 7.2 Hz, 1H), 5.27 (s, 1H), 5.84 (d, J = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.3, 28.9, 29.8, 34.0, 39.3, 39.8, 41.0, 41.1, 44.8, 48.5, 89.3, 123.3, 148.0, 178.0, 205.4. IR ν (cm^{-1}): 1374, 1464, 1613, 1687. 1762, 2950. HRMS (ESI): calcd for $C_{15}H_{20}NaO_3$: 271.1305; found: 271.1303.



47 **50**

To a solution of compound **47** (44 mg, 0.19 mmol) in 5 mL CH_2Cl_2 was added SeO_2 (24 mg, 0.22 mmol) and *t*-BuOOH (65 wt%, 194 mg, 1.40 mmol). After stirred at 25 ºC for 24 hours, the solvent was removed by evaporation, and the residue was purified by flash column chromatography to give alcohol **50** (36 mg, 78%).

50: colorless oil; R_f = 0.34 (PE/AcOEt = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 3H), 1.06 (s, 3H), 1.25−1.35 (m, 1H), 1.40 (t, J = 12.8 Hz, 1H), 1.54 (dd, J = 12.8, 5.9 Hz, 1H), 1.60 (s, 1H), 2.14−2.24 (m, 3H), 2.27−2.53 (m, 4H), 2.75 (dt, J = 9.4, 7.2 Hz, 1H), 4.07 (d, J = 12.8 Hz, 1H), 4.11 (d, J = 12.8 Hz, 1H), 4.26 (d, J = 7.6 Hz, 1H), 5.73 (t, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.7, 26.6, 29.3 (2 C), 31.0, 37.6, 41.0, 42.0, 45.0, 50.3, 66.9, 88.9, 125.6, 141.1, 179.5. IR ν (cm^{-1}): 1378, 1471, 1758, 2946, 3404. HRMS (ESI): calcd for $C_{15}H_{22}NaO_3$: 273.1461; found: 273.1459.

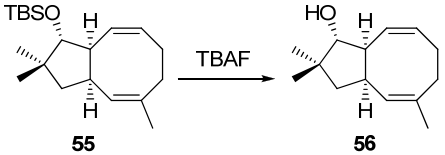


31 **53** **55**

To a solution of 2,6-di-*tert*-butyl-4-methylpyridine (1.16 g, 5.67 mmol) in 30 mL anhydrous CH_2Cl_2 was added sequentially trifluoromethanesulfonic anhydride (1.32 g, 4.68 mmol) and a solution of ketone **31** (890 mg, 2.76 mmol) in 30 mL anhydrous CH_2Cl_2. The reaction mixture was stirred at 25 ºC for 12 hours. After the solvent was removed by evaporation, the residue was dissolved in 150 mL diethyl ether, washed with 1M HCl solution and brine, dried over $MgSO_4$, filtered and concentrated. At this stage, another enol triflate **54** could be detected by ^{1}H-NMR of crude reaction mixture, and the ratio of **53** and **54** was 88:12. The resulting brown oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude enol triflate **53**, which was used in the next step without further purification.

A solution of the crude enol triflate **53** in 35 mL THF was added to a mixture of $Fe(acac)_3$ (199 mg, 0.56 mmol) and 1-methyl-2-pyrrolidinone (3 mL), and the resulting mixture was cooled to −10 ºC. After MeMgBr (3.0 M in ether, 3.5 mL, 10.5 mmol) was added dropwise, the reaction mixture was allowed to warm up to room temperature and stirred overnight. Then, to the reaction mixture was added saturated NH_4Cl solution and diethyl ether, and the aqueous layer was extracted with diethyl ether. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to give compound **55** (515 mg, 58% over two steps).

55: colorless oil; R_f = 0.39 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 3H), 0.05 (s, 3H), 0.89 (s, 9H), 0.92 (s, 3H), 0.98 (s, 3H), 1.24 (t, J = 12.4 Hz, 1H), 1.66 (s, 3H), 1.73 (dd, J = 12.4, 7.6 Hz, 1H), 1.79 (dt, J = 14.1, 6.8 Hz, 1H), 2.02−2.12 (m, 1H), 2.39−2.48 (m, 1H), 2.58−2.66 (m, 1H), 2.84−2.92 (m, 1H), 3.14−3.24 (m, 1H), 3.46 (d, J = 7.7 Hz, 1H), 5.09 (d, J = 4.6 Hz, 1H), 5.41 (ddd, J = 11.0, 5.5, 2.4 Hz, 1H), 5.50−5.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.5, −3.8, 18.2, 21.2, 23.8, 26.0, 26.6, 27.8, 32.0, 38.3, 40.7, 46.0, 50.5, 88.7, 128.6, 128.7, 133.7, 136.4. IR ν (cm^{-1}): 1255, 1363, 1468, 2935. HRMS (ESI): calcd for $C_{20}H_{36}NaOSi$: 343.2428; found: 343.2431. $[\alpha]^{20}_D$: +13.8 (*c* 1.00, $CHCl_3$).

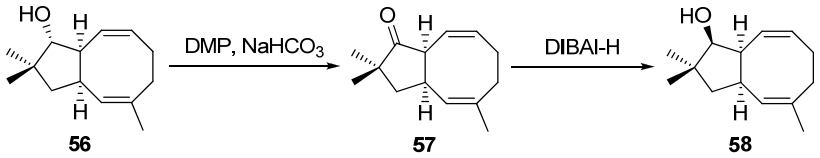


55 **56**

To a solution of compound **55** (150 mg, 0.47 mmol) in 5 mL anhydrous THF was added TBAF (400 mg, 1.53 mmol). After stirred at 40 ºC for 20 hours, the reaction

mixture was quenched with 25 mL saturated NH_4Cl solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to give alcohol **56** (94 mg, 98%).

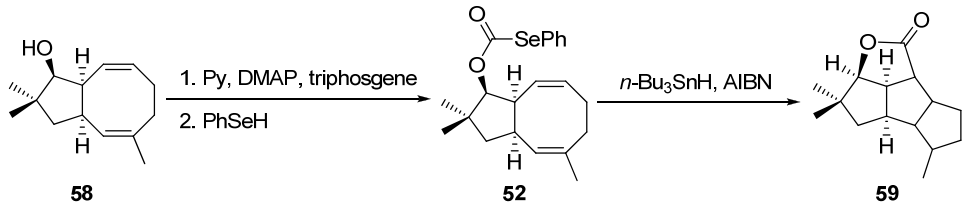
56: white solid, mp 77−78 °C; R_f = 0.11 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 3H), 1.05 (s, 3H), 1.29 (dd, J = 12.9, 9.8 Hz, 1H), 1.67 (s, 3H), 1.76−1.85 (m, 3H), 2.03−2.12 (m, 1H), 2.42−2.52 (m, 1H), 2.55−2.64 (m, 1H), 2.82−2.91 (m, 1H), 3.14−3.25 (m, 1H), 3.43 (d, J = 9.6 Hz, 1H), 5.06 (d, J = 5.9 Hz, 1H), 5.50 (ddd, J = 11.0, 4.2, 2.0 Hz, 1H), 5.56−5.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.7, 24.2, 26.8, 27.4, 32.0, 37.3, 39.7, 46.1, 49.7, 87.2, 128.5, 129.5, 132.2, 136.5. IR ν (cm^{-1}): 1371, 1468, 2931, 3356. HRMS (ESI): calcd for $C_{14}H_{23}O$: 207.1743; found: 207.1743.



To a mixture of alcohol **56** (177 mg, 0.86 mmol) and $NaHCO_3$ (0.60 g, 7.1 mmol) in 20 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (0.84 g, 2.0 mmol). After stirred for 3 hours, the reaction mixture was quenched with 50 mL saturated $NaHCO_3$ solution and 50 mL saturated $Na_2S_2O_3$ solution and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$ twice, filtered, and used directly in the next step.

To the solution of ketone **57** at −78 ºC was added DIBAl-H (1.0 M in hexane, 14 mL, 14 mmol). After stirred at −78 ºC for 2 hours, the reaction mixture was allowed to warm up to 0 ºC and quenched with saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford alcohol **58** (85 mg, 48% over two steps).

58: colorless oil; R_f = 0.21 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 3H), 1.10 (s, 3H), 1.41 (br, 1H), 1.49 (dd, J = 13.1, 6.5 Hz, 1H), 1.66 (s, 3H), 1.80−1.89 (m, 2H), 1.99−2.09 (m, 1H), 2.50−2.64 (m, 2H), 3.23−3.37 (m, 2H), 3.63 (d, J = 4.1 Hz, 1H), 5.07 (d, J = 6.0 Hz, 1H), 5.63−5.70 (m, 1H), 5.75 (dd, J = 11.0, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.0, 26.1, 27.2, 28.6, 32.8, 40.5, 41.9, 47.5, 48.5, 83.6, 128.4, 130.0, 130.1, 135.2. IR ν (cm^{-1}): 1378, 1471, 2939, 3434. HRMS (ESI): calcd for $C_{14}H_{23}O$: 207.1743; found: 207.1742.

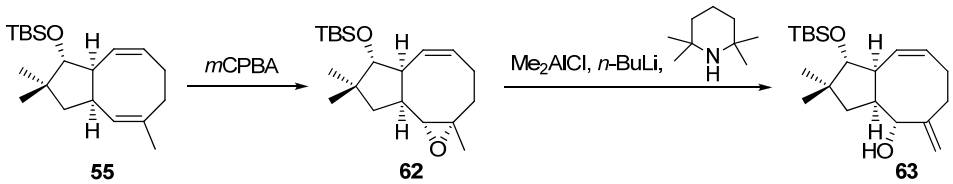


58 **52** **59**

To a mixture of alcohol **58** (25 mg, 0.12 mmol), DMAP (9.0 mg, 0.07 mmol), and pyridine (240 mg, 3.04 mmol) in 4 mL anhydrous THF was added a solution of triphosgene (58 mg, 0.20 mmol) in 3 mL anhydrous benzene. After stirred at 28 ºC for 3 hours, freshly distilled PhSeH (110 mg, 0.70 mmol) was added, and the reaction mixture was stirred at 28 ºC overnight before 30 mL water and 40 mL diethyl ether were added. The aqueous layer was separated and extracted with diethyl ether. The combined organic phase was washed sequentially with 1M HCl, water, and saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude selenocarbonate **52**, which was used in the next step without further purification.

To a solution of the crude selenocarbonate **52** and AIBN (16 mg, 0.10 mmol) in 15 mL anhydrous benzene was added *n*-Bu_3SnH (150 mg, 0.52 mmol). The resulting mixture was heated in a 90 °C oil bath to reflux for 3.5 hours. The solvent was removed by evaporation, and the residue was submitted to flash column chromatography on silica gel to afford the tetracyclic compound **59** (20 mg, 70% over two steps).

59: colorless oil; R_f = 0.13 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s), 0.95 (s), 0.97 (d, J = 6.8 Hz), 0.98 (d, J = 6.4 Hz), 1.09 (s), 1.11 (s), 1.12−1.27 (m), 1.34−1.45 (m), 1.49−1.71 (m), 1.74−2.02 (m), 2.13−2.21 (m), 2.50−2.63 (m), 2.75−2.82 (m), 2.99−3.13 (m), 3.26 (td, J = 9.3, 5.6 Hz), 3.43 (td, J = 9.3, 6.0 Hz), 4.23 (d, J = 5.6 Hz), 4.27 (d, J = 6.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 16.1, 19.2, 22.9, 23.0, 24.4, 24.7, 32.4, 33.1, 34.1, 35.4, 38.1, 42.2, 43.6, 43.8, 45.4, 45.6, 46.0 49.79, 49.85, 50.3, 50.9, 51.2, 53.3, 53.6, 56.2, 59.3, 91.0, 91.2, 180.5, 181.0. IR v (cm^{-1}): 1352, 1468, 1758, 2957. HRMS (ESI): calcd for $C_{15}H_{22}NaO_2$: 257.1512; found: 257.1510.

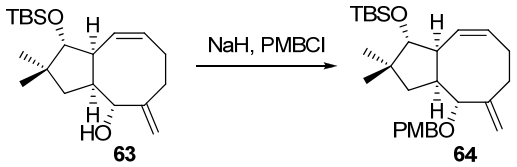


55 **62** **63**

To a solution of compound **55** (200 mg, 0.63 mmol) in 6 mL ethyl acetate at 0 ºC was added *m*CPBA (70 wt%, 195 mg, 0.79 mmol). After stirred at 0 ºC for 2 hours, saturated $NaHCO_3$ solution was added, and the mixture was extracted with diethyl ether. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the crude epoxide **62**, which was used in the next step without further purification.

To a solution of 2,2,6,6-tetramethylpiperidine (520 mg, 3.69 mmol) in 20 mL anhydrous benzene was added *n*-BuLi (1.6 M in hexane, 2.2 mL, 3.5 mmol). To the resulting mixture at 0 ºC was added Me_2AlCl (0.9 M in heptane, 4.0 mL, 3.6 mmol), and the reaction mixture was stirred at 0 ºC for 25 minutes before a solution of the crude epoxide **62** in 15 mL anhydrous benzene was added. After stirred at 0 ºC for 2 hours, the reaction mixture was quenched with 1M HCl and extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give alcohol **63** (180 mg, 86% over two steps).

63: colorless oil; R_f = 0.24 (PE/AcOEt = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ −0.03 (s, 3H), 0.00 (s, 3H), 0.86 (s, 9H), 0.98 (s, 3H), 1.11 (s, 3H), 1.32 (t, J = 12.7 Hz, 1H), 1.39 (d, J = 3.0 Hz, 1H), 1.76−1.80 (m, 1H), 2.00−2.07 (m, 2H), 2.16−2.29 (m, 2H), 2.40−2.46 (m, 1H), 2.60 (t, J = 8.4 Hz, 1H), 3.62 (s, 1H), 3.84 (dd, J = 9.7, 2.4 Hz, 1H), 4.98 (s, 1H), 5.24 (s, 1H), 5.42 (t, J = 9.7 Hz, 1H), 5.71−5.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ −5.1, −4.6, 18.1, 24.3, 25.8, 28.3, 30.2, 37.0, 42.6, 44.7, 49.0, 50.7, 75.7, 88.1, 111.6, 130.1, 132.2, 157.2. IR v (cm^{-1}): 1255, 1367, 1468, 1643, 2935, 3360. HRMS (ESI): calcd for $C_{20}H_{36}NaO_2Si$: 359.2377; found: 359.2377. $[\alpha]^{20}_D$: −7.1 (*c* 1.07, $CHCl_3$).

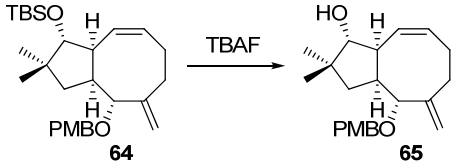


63 **64**

To a solution of alcohol **63** (393 mg, 1.17 mmol) in 6 mL anhydrous DMF was added NaH (206 mg, 8.57 mmol). After stirred at 50 ºC for 50 minutes, freshly distilled PMBCl (658 mg, 4.21 mmol) was added, and the reaction mixture was stirred at 50 ºC for 5 hours before 30 mL water was added. The resulting mixture was extracted with diethyl ether and petroleum ether, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford compound **64** (440 mg, 82%).

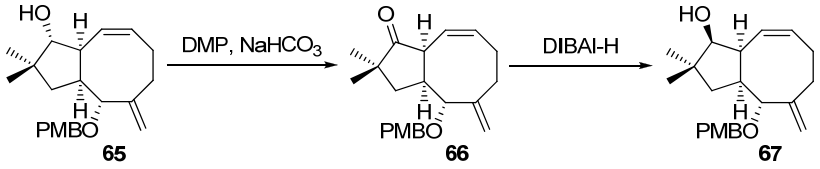
64: colorless oil; R_f = 0.31 (PE/AcOEt = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.04 (s, 3H), −0.02 (s, 3H), 0.85 (s, 9H), 0.95 (s, 3H), 1.09 (s, 3H), 1.23 (t, J = 12.7 Hz, 1H), 1.84−1.92 (m, 2H), 1.96−2.08 (m, 1H), 2.12−2.22 (m, 1H), 2.29−2.41 (m, 1H), 2.49 (ddd, J = 12.5, 5.6, 1.9 Hz, 1H), 2.58 (t, J = 8.4 Hz, 1H), 3.45 (d, J = 9.9 Hz, 1H), 3.60 (d, J = 1.5 Hz, 1H), 3.80 (s, 3H), 4.07 (d, J = 11.3 Hz, 1H), 4.41 (d, J = 11.3 Hz, 1H), 5.07 (s, 1H), 5.28 (d, J = 1.7 Hz, 1H), 5.37−5.43 (m, 1H), 5.66−5.74 (m, 1H), 6.85 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −5.1, −4.7, 18.1, 24.7, 25.8, 28.4, 30.5, 37.8, 42.5, 45.0, 49.0, 50.0, 55.2, 69.5, 82.7, 87.7, 112.5, 113.6, 129.2, 129.8, 131.3, 132.3, 152.9, 158.9. IR v (cm^{-1}): 1255, 1468, 1520, 1620, 2935. HRMS (ESI): calcd for $C_{28}H_{44}NaO_3Si$: 479.2952; found: 479.2954. $[\alpha]^{20}_D$: +39.7 (*c*

2.20, $CHCl_3$).



To a solution of compound **64** (395 mg, 0.87 mmol) in 7 mL anhydrous THF was added TBAF (850 mg, 3.25 mmol). After stirred at 40 ºC for 21 hours, the reaction mixture was quenched with 50 mL saturated NH_4Cl solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give alcohol **65** (266 mg, 90%).

65: colorless oil; R_f = 0.22 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.03 (s, 3H), 1.15 (s, 3H), 1.32 (t, J = 12.6 Hz, 1H), 1.50 (d, J = 4.4 Hz, 1H), 1.87−1.95 (m, 2H), 2.06−2.13 (m, 1H), 2.15−2.21 (m, 1H), 2.32−2.39 (m, 1H), 2.50 (ddd, J = 12.8, 5.5, 2.4 Hz, 1H), 2.68 (t, J = 8.1 Hz, 1H), 3.47 (d, J = 9.7 Hz, 1H), 3.69 (d, J = 2.4 Hz, 1H), 3.80 (s, 3H), 4.07 (d, J = 11.4 Hz, 1H), 4.41 (d, J = 11.4 Hz, 1H), 5.07 (s, 1H), 5.28 (d, J = 1.7 Hz, 1H), 5.41−5.46 (m, 1H), 5.69−5.75 (m, 1H), 6.86 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 9.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 23.7, 28.2, 30.5, 37.5, 41.7, 45.3, 48.6, 49.8, 55.2, 69.5, 82.6, 87.3, 112.9, 113.6, 129.2, 130.3, 131.1, 131.5, 152.4, 158.9. IR ν (cm^{-1}): 1248, 1520, 1620, 2935, 3430. HRMS (ESI): calcd for $C_{22}H_{30}NaO_3$: 365.2087; found: 365.2088. $[\alpha]^{20}_D$: +91.8 (c 1.20, $CHCl_3$).

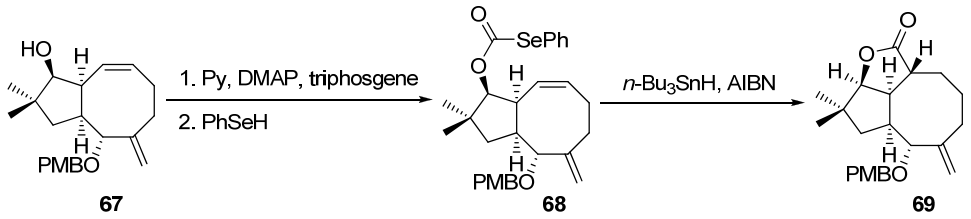


To a mixture of alcohol **65** (106 mg, 0.31 mmol) and $NaHCO_3$ (200 mg, 2.38 mmol) in 7 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (425 mg, 1.00 mmol). After stirred for 90 minutes, the reaction mixture was quenched with 20 mL saturated $NaHCO_3$ solution and 20 mL saturated $Na_2S_2O_3$ solution and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$ twice, filtered, and used directly in the next step.

To the solution of ketone **66** at −78 ºC was added DIBAl-H (1.0 M in hexane, 8.0 mL, 8.0 mmol). After stirred at −78 ºC for 2 hours, the reaction mixture was allowed to warm up to 0 ºC and quenched with saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic phase

was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford alcohol **67** (89 mg, 84% over two steps).

67: white solid, mp 113−114 °C; R_f = 0.26 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.07 (s, 3H), 1.08 (s, 3H), 1.33−1.40 (m, 1H), 1.51 (d, J = 5.0 Hz, 1H), 1.87−1.97 (m, 3H), 2.08−2.16 (m, 1H), 2.18−2.40 (m, 1H), 2.52 (ddd, J = 12.8, 5.4, 2.4 Hz, 1H), 3.02−3.08 (m, 1H), 3.40−3.44 (m, 1H), 3.80 (s, 3H), 3.86 (t, J = 5.5 Hz, 1H), 4.07 (d, J = 11.3 Hz, 1H), 4.40 (d, J = 11.3 Hz, 1H), 5.10 (s, 1H), 5.27 (d, J = 1.7 Hz, 1H), 5.67−5.71 (m, 1H), 5.84−5.90 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 25.8, 28.2, 31.9, 38.1, 39.5, 44.7, 45.2, 46.8, 55.2, 69.6, 81.8, 83.5, 112.6, 113.7, 127.3, 129.3, 131.0, 132.3, 152.3, 159.0. IR v (cm^{-1}): 1251, 1520, 1616, 2928, 3423. HRMS (ESI): calcd for $C_{22}H_{30}NaO_3$: 365.2087; found: 365.2092. $[\alpha]^{20}_D$: +111.5 (c 0.96, $CHCl_3$).



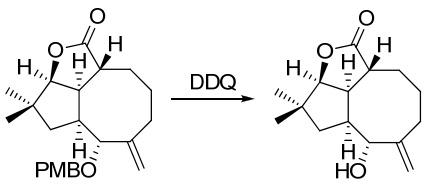
67 68 69

To a mixture of alcohol **67** (101 mg, 0.29 mmol), DMAP (27 mg, 0.22 mmol), and pyridine (0.88 g, 11.1 mmol) in 8 mL anhydrous THF was added a solution of triphosgene (145 mg, 0.49 mmol) in 8 mL anhydrous benzene. After stirred at 30 ºC for 3 hours, freshly distilled PhSeH (387 mg, 2.46 mmol) was added, and the reaction mixture was stirred at 30 ºC for 16 hours before 100 mL water and 100 mL diethyl ether were added. The aqueous layer was separated and extracted with diethyl ether. The combined organic phase was washed sequentially with 1M HCl, water, and saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and concentrated. The resulting yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated to give the crude selenocarbonate **68**, which was used in the next step without further purification.

To a solution of the crude selenocarbonate **68** and AIBN (21 mg, 0.13 mmol) in 60 mL anhydrous benzene was added n-Bu_3SnH (360 mg, 1.20 mmol). The resulting mixture was heated in a 90 °C oil bath to reflux for 3.5 hours. The solvent was removed by evaporation, and the residue was submitted to flash column chromatography on silica gel to afford the tricyclic compound **69** (104 mg, 95% over two steps).

69: colorless oil; R_f = 0.35 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 3H), 1.05 (s, 3H), 1.34−1.45 (m, 2H), 1.69−1.82 (m, 2H), 1.89−2.02 (m, 1H), 2.08−2.25 (m, 2H), 2.39 (dq, J = 12.8, 6.4 Hz, 1H), 2.50−2.63 (m, 2H), 2.77 (dd, J = 15.4, 7.8 Hz, 1H), 3.78 (d, J = 6.9 Hz, 1H), 3.81 (s, 3H), 4.20 (d, J = 11.3 Hz, 1H), 4.30 (d, J = 7.7 Hz, 1H), 4.50 (d, J = 11.3 Hz, 1H), 5.10 (s, 1H), 5.13 (s, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.23

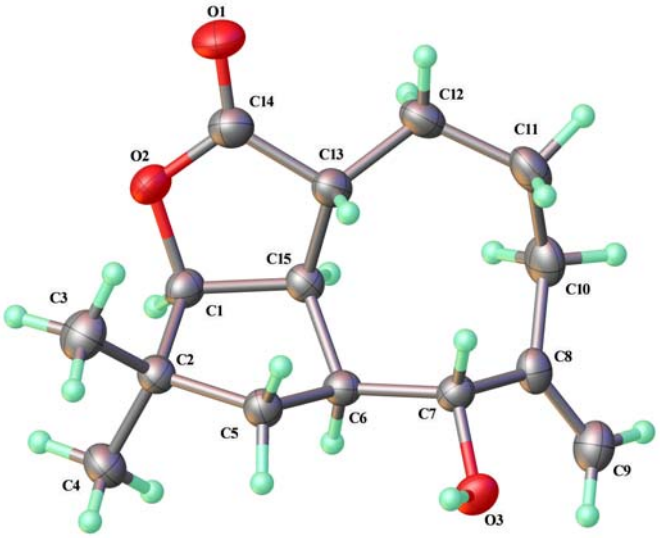
(d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.4, 25.2, 28.8, 29.9, 34.5, 38.1, 40.4, 43.1, 46.0, 46.3, 55.2, 70.4, 81.7, 89.8, 113.8, 113.9, 129.3, 130.3, 148.8, 159.2, 180.0. IR v (cm^{-1}): 1251, 1520, 1620, 1769, 2939. HRMS (ESI): calcd for $C_{23}H_{30}NaO_4$: 393.2036; found: 393.2035. $[\alpha]^{20}_D$: +36.0 (c 0.87, $CHCl_3$).



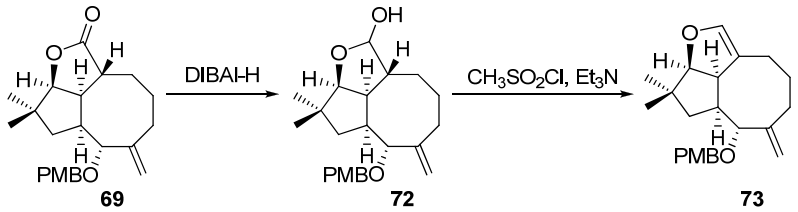
69 **70**

To a solution of compound **69** (46.7 mg, 0.126 mmol) in 4 mL CH_2Cl_2 was added 1 mL H_2O and DDQ (50.5 mg, 0.222 mmol). After stirred at room temperature for 1 hour, the reaction mixture was diluted with diethyl ether and washed with 0.2M NaOH. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was submitted to flash column chromatography on silica gel to afford compound **70** (27.9 mg, 89%).

70: white solid, mp 127−128 °C; R_f = 0.24 (PE/AcOEt = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.08 (s, 3H), 1.41 (m, 1H), 1.50 (t, J = 12.9 Hz, 1H), 1.74−1.82 (m, 2H), 1.88−1.99 (m, 2H), 2.18 (m, 1H), 2.23−2.33 (m, 2H), 2.52 (m, 1H), 2.66 (dq, J = 12.0, 4.4 Hz, 1H), 2.83 (dd, J = 15.3, 7.6 Hz, 1H), 4.19 (d, J = 7.2 Hz, 1H), 4.34 (d, J = 8.0 Hz, 1H), 5.02 (s, 1H), 5.08 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.3, 25.0, 28.7, 30.0, 34.2, 38.2, 40.6, 43.1, 45.8, 47.4, 75.1, 90.0, 112.2, 152.1, 180.0. IR v (cm^{-1}): 1184, 1378, 1464, 1762, 2939, 3434. HRMS (ESI): calcd for $C_{15}H_{23}O_3$: 251.1642; found: 251.1635.



X-ray structure of compound **70**

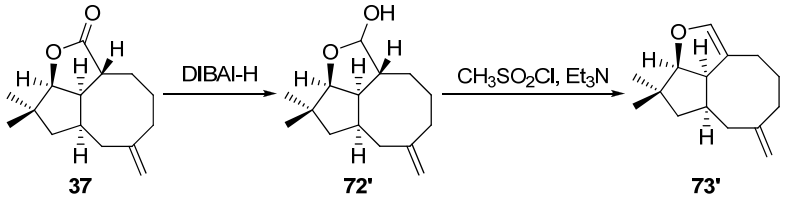


69 **72** **73**

To a solution of compound **69** (104 mg, 0.28 mmol) in 2.5 mL anhydrous CH_2Cl_2 at −78 ºC was added DIBAl-H (1.0 M in hexane, 0.9 mL, 0.9 mmol). After stirred at −78 ºC for 3 hours, the reaction mixture was diluted with 30 mL diethyl ether and quenched with 30 mL saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the crude hemiacetal **72**, which was used in the next step without further purification.

To a solution of the crude hemiacetal **72** and triethylamine (291 mg, 2.88 mmol) in 8 mL anhydrous CH_2Cl_2 was added methanesulfonyl chloride (85 mg, 0.74 mmol). The resulting mixture was stirred at 25 ºC for 2 hours before it was diluted with diethyl ether and washed with saturated $NaHCO_3$ solution and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by flash column chromatography to give enol ether **73** (85 mg, 85% over two steps).

73: colorless oil; R_f = 0.10 (PE/AcOEt = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H), 1.07 (s, 3H), 1.40 (t, J = 12.4 Hz, 1H), 1.57−1.74 (m, 2H), 1.85 (dd, J = 12.4, 5.6 Hz, 1H), 1.95−2.04 (m, 1H), 2.21−2.31 (m, 2H), 2.34−2.52 (m, 2H), 3.17 (t, J = 8.3 Hz, 1H), 3.66 (d, J = 10.2 Hz, 1H), 3.80 (s, 3H), 4.19 (d, J = 11.2 Hz, 1H), 4.37 (d, J = 8.2 Hz, 1H), 4.46 (d, J = 11.2 Hz, 1H), 5.13 (s, 1H), 5.28 (s, 1H), 6.06 (s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.8, 25.4, 26.8, 27.2, 38.9, 42.3, 42.6, 50.1, 50.3, 55.2, 69.8, 79.3, 96.0, 113.2, 113.7, 114.4, 129.2, 131.0, 142.9, 151.0, 159.0. IR v (cm^{-1}): 1251, 1516, 1616, 1654, 2928. HRMS (ESI): calcd for $C_{23}H_{31}O_3$: 355.2268; found: 355.2264. $[\alpha]^{20}_D$: +38.6 (c 0.76, $CHCl_3$).



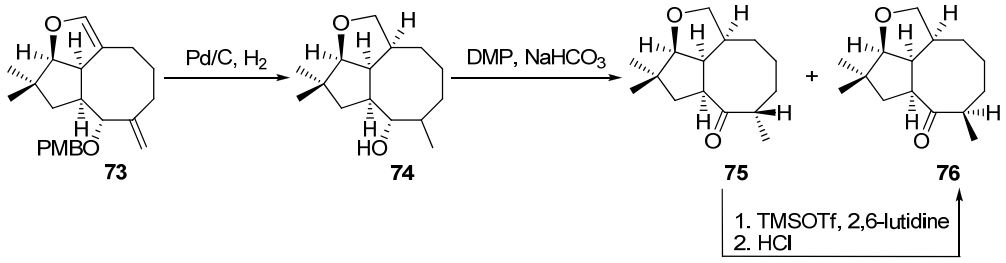
37 **72'** **73'**

To a solution of compound **37** (66 mg, 0.28 mmol) in 2.5 mL anhydrous CH_2Cl_2 at −78 ºC was added DIBAl-H (1.0 M in hexane, 0.9 mL, 0.9 mmol). After stirred at −78 ºC for 3 hours, the reaction mixture was diluted with 30 mL diethyl ether and quenched with 30 mL saturated potassium sodium tartrate solution. The aqueous layer was separated and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the crude hemiacetal

72', which was used in the next step without further purification.

To a solution of the crude hemiacetal **72'** and triethylamine (285 mg, 2.82 mmol) in 8 mL anhydrous CH_2Cl_2 was added methanesulfonyl chloride (70 mg, 0.61 mmol). The resulting mixture was stirred at 25 ºC for 2 hours before it was diluted with diethyl ether and washed with saturated $NaHCO_3$ solution and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated to give a residue, which was purified by flash column chromatography to give enol ether **73'** (47 mg, 76% over two steps).

73': colorless oil; R_f = 0.20 (PE/AcOEt = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H), 1.08 (s, 3H), 1.38 (t, J = 12.3 Hz, 1H), 1.39−1.48 (m, 1H), 1.52 (dd, J = 12.3, 6.3 Hz, 1H), 1.75−1.84 (m, 1H), 1.89−1.98 (m, 1H), 2.02−2.15 (m, 3H), 2.20−2.30 (m, 1H), 2.35 (ddd, J = 14.8, 8.6, 2.1 Hz, 1H), 2.46 (ddd, J = 14.4, 5.7, 2.5 Hz, 1H), 3.13 (t, J = 8.4 Hz, 1H), 4.41 (d, J = 7.4 Hz, 1H), 4.68 (s, 1H), 4.71 (s, 1H), 6.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.3, 26.0, 26.8, 27.2, 35.1, 36.1, 41.7, 43.2, 45.5, 51.1, 98.5, 110.4, 115.5, 142.3, 151.0. IR ν (cm^{-1}): 1259, 1367, 1460, 1654, 2924. HRMS (ESI): calcd for $C_{15}H_{23}O$: 219.1743; found: 219.1743.



To a solution of enol ether **73** (100 mg, 0.28 mmol) in 10 mL ethanol under argon was added Pd/C (10 wt%, 30 mg, 0.028 mmol). Then the argon atmosphere was replaced by hydrogen (1 atm) atmosphere. After stirred at 60 ºC for 20 hours, the reaction mixture was filtered through a pad of silica gel to remove Pd/C, and the filtrate was concentrated to give the crude alcohol **74**, which was used in the next step without further purification.

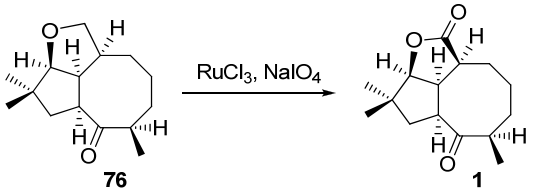
To a mixture of the crude alcohol **74** and $NaHCO_3$ (177 mg, 2.10 mmol) in 5 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (447 mg, 1.06 mmol). After stirred at 25 ºC for 40 minutes, the reaction mixture was quenched with 25 mL saturated $NaHCO_3$ solution and 25 mL saturated $Na_2S_2O_3$ solution and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude mixture was purified by flash column chromatography on silica gel to afford compounds **75** (31 mg, 46%) and **76** (16 mg, 24%).

To a solution of compound **75** (14.1 mg, 0.060 mmol) and 2,6-lutidine (57 mg, 0.53 mmol) in 1 mL anhydrous CH_2Cl_2 at 0 ºC was added TMSOTf (96 mg, 0.43 mmol). After stirred at 0 ºC for 2 hours and at 25 ºC for 20 hours, 2 mL diethyl ether and 1 mL

1M HCl were added, and the resulting mixture was stirred at 25 ºC for 2 hours. Then it was diluted with diethyl ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was submitted to flash column chromatography on silica gel to get the recovered compound **75** (6.4 mg, 45%) and the desired compound **76** (3.7 mg, 48% brsm).

75: white solid, mp 70−71 °C; R_f = 0.22 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (s, 3H), 1.11 (s, 3H), 1.16 (d, J = 7.2 Hz, 3H), 1.24−1.34 (m, 2H), 1.55 (ddd, J = 15.4, 8.5, 4.2 Hz, 1H), 1.62−1.76 (m, 3H), 2.01 (t, J = 12.7 Hz, 1H), 2.12−2.25 (m, 1H), 2.26−2.38 (m, 1H), 2.45−2.56 (m, 1H), 3.15−3.24 (m, 2H), 3.35 (ddd, J = 11.1, 7.4, 5.5 Hz, 1H), 3.88 (t, J = 7.8 Hz, 1H), 3.97 (dd, J = 5.4, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.7, 22.8, 23.1, 25.9, 26.1, 30.5, 40.5, 41.5, 44.0, 46.3, 48.8, 49.2, 74.8, 94.5, 217.9. IR ν (cm^{-1}): 1266, 1371, 1468, 1698, 2935. HRMS (ESI): calcd for $C_{15}H_{24}NaO_2$: 259.1668; found: 259.1667. $[\alpha]^{20}_D$: +39.1 (*c* 1.14, $CHCl_3$).

76: white solid, mp 85−86 °C; R_f = 0.26 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.90 (s, 3H), 1.03−1.11 (m, 1H), 1.12 (s, 3H), 1.13 (d, J = 6.7 Hz, 3H), 1.33 (dd, J = 13.1, 6.6 Hz, 1H), 1.47−1.54 (m, 1H), 1.55−1.66 (m, 1H), 1.75−1.88 (m, 2H), 2.03 (t, J = 12.9 Hz, 1H), 2.28−2.36 (m, 1H), 2.48−2.56 (m, 2H), 3.15 (ddd, J = 12.3, 11.1, 6.6 Hz, 1H), 3.19 (dd, J = 11.5, 7.7 Hz, 1H), 3.39 (ddd, J = 11.0, 7.5, 5.5 Hz, 1H), 3.86 (t, J = 7.9 Hz, 1H), 3.98 (d, J = 5.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.6, 22.3, 23.1, 23.2, 25.9, 28.6, 40.5, 41.8, 44.2, 45.8, 48.7, 50.7, 74.9, 94.4, 215.6. IR ν (cm^{-1}): 1266, 1371, 1468, 1702, 2939. HRMS (ESI): calcd for $C_{15}H_{24}NaO_2$: 259.1668; found: 259.1665. $[\alpha]^{20}_D$: +10.1 (*c* 0.55, $CHCl_3$).



To a mixture of compound **76** (10.5 mg, 0.044 mmol) and sodium periodate (47.0 mg, 0.22 mmol) in 3 mL $CH_3CN/CCl_4/H_2O$ (1:1:1, V/V/V) was added ruthenium trichloride (4.7 mg, 0.023 mmol). After stirred at 25 ºC for 9 hours, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. After solvent evaporation, the residue was subjected to flash column chromatography on silica gel to give natural product **1** (6.6 mg, 59%).

1: white solid, mp 155−156 °C (lit mp 178 °C[9], 156-158 °C[10], 163-165 °C[2], 142-143 °C[11]); R_f = 0.16 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (s,

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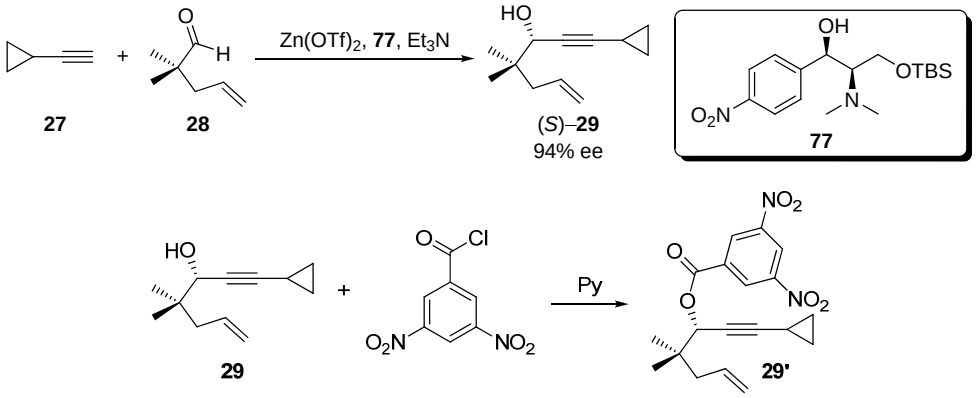
[10] Paquette, L. A.; Tae, J.; Arrington, M. P.; Sadoun, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 2742.
[11] Krafft, M. E.; Cheung, Y. Y.; Abboud, K. A. *J. Org. Chem.* **2001**, *66*, 7443.

3H), 1.13 (d, J = 6.3 Hz, 3H), 1.20 (s, 3H), 1.31−1.44 (m, 2H), 1.51-1.62 (m, 1H), 1.76−1.85 (m, 1H), 1.88−2.01 (m, 2H), 2.19 (t, J = 13.4 Hz, 1H), 2.36−2.57 (m, 2H), 2.72 (ddd, J = 12.3, 9.6, 6.3 Hz, 1H), 3.21 (dt, J = 11.9, 6.8 Hz, 1H), 3.73 (dt, J = 10.5, 5.3 Hz, 1H), 4.27 (d, J = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.2, 22.4, 23.0 (2 C), 24.5, 28.0, 38.4, 40.7, 43.2, 45.66, 45.72, 50.2, 90.9, 177.8, 213.6. IR v (cm^{-1}): 1274, 1475, 1698, 1769, 2928. HRMS (ESI): calcd for $C_{15}H_{22}NaO_3$: 273.1461; found: 273.1463. $[\alpha]^{20}_D$: +11.8 (c 0.28, $CHCl_3$; lit value +12.1[9], +8.5[10], +16.6[2]).

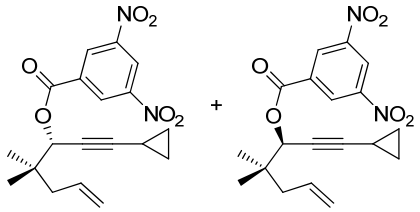


A mixture of $Zn(OTf)_2$ (326 mg, 0.90 mmol), triethylamine (331 mg, 3.28 mmol), and the chiral ligand **77**[12] (402 mg, 1.13 mmol) in 30 mL anhydrous toluene was stirred under argon at 55 ºC until a clear solution was formed, and alkyne **27** (594 mg, 8.99 mmol) was added subsequently. After stirred for 30 minutes, aldehyde **28** (561 mg, 5.00 mmol) was added. The reaction was completed after stirred for 46 hours at 55 ºC. The reaction mixture was diluted with diethyl ether, and then the organic phase was washed with 1M HCl and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford alcohol **29** (804 mg, 90%). 94% ee was determined by HPLC analysis of the 3,5-dinitrobenzoate ester **29'**[13] (Chiralcel OD-H, hexane:isopropanol = 90:10, 1.0 mL/min, 254 nm).

29: colorless oil; R_f = 0.31 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65−0.70 (m, 2H), 0.75−0.80 (m, 2H), 0.93 (s, 3H), 0.94 (s, 3H), 1.22−1.31 (m, 1H), 1.74−1.79 (m, 1H), 2.07 (dd, J = 13.5, 7.5 Hz, 1H), 2.14 (dd, J = 13.5, 7.5 Hz, 1H), 4.02 (dd, J = 6.2, 1.7 Hz, 1H), 5.04 (s, 1H), 5.08 (d, J = 4.9 Hz, 1H), 5.78−5.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −0.6, 8.2, 22.5, 22.6, 38.7, 42.7, 70.4, 74.6, 89.8, 117.4, 135.1. IR ν (cm^{-1}): 1371, 1386, 1475, 1643, 2242, 2972, 3389. HRMS (ESI): calcd for $C_{12}H_{18}NaO$: 201.1250; found: 201.1250. $[\alpha]^{20}_D$: +15.7 (c 1.53, $CHCl_3$).

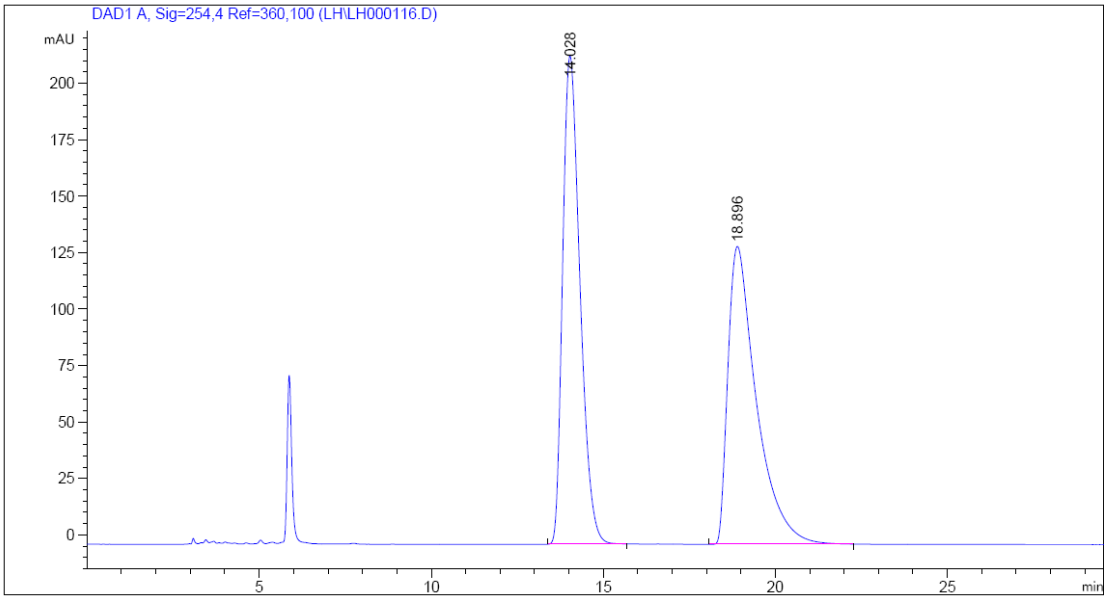
[12] Jiang, B.; Chen, Z.; Tang, X. *Org. Lett.* **2002**, *4*, 3451.

[13] Propargylic alcohol **29** was treated with 3,5-dinitrobenzoyl chloride and pyridine in CH_2Cl_2 at room temperature to give 3,5-dinitrobenzoate ester **29'** quantitatively. **29'**: pale yellow oil; R_f = 0.44 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69−0.74 (m, 2H), 0.79−0.85 (m, 2H), 1.10 (s, 3H), 1.11 (s, 3H), 1.25−1.34 (m, 1H), 2.22 (d, J = 7.4 Hz, 2H), 5.03−5.15 (m, 2H), 5.42 (d, J = 1.9 Hz, 1H), 5.80−5.92 (m, 1H), 9.16 (d, J = 2.0 Hz, 2H), 9.24 (t, J = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ -0.6, 8.3, 23.07, 23.14, 38.4, 43.1, 69.9, 74.1, 91.7, 118.2, 122.3, 129.4, 133.7, 133.9, 148.6, 161.5. IR ν (cm^{-1}): 1266, 1348, 1549, 1631, 1736, 2246, 2980. HRMS (ESI): calcd for $C_{19}H_{20}N_2NaO_6$: 395.1214; found: 395.1213.



(*S*)–**29'** : (*R*)–**29'**

50 : **50**



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峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
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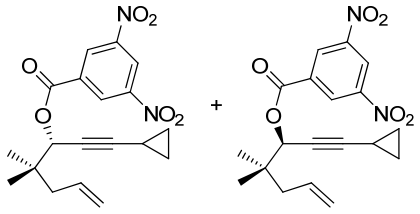
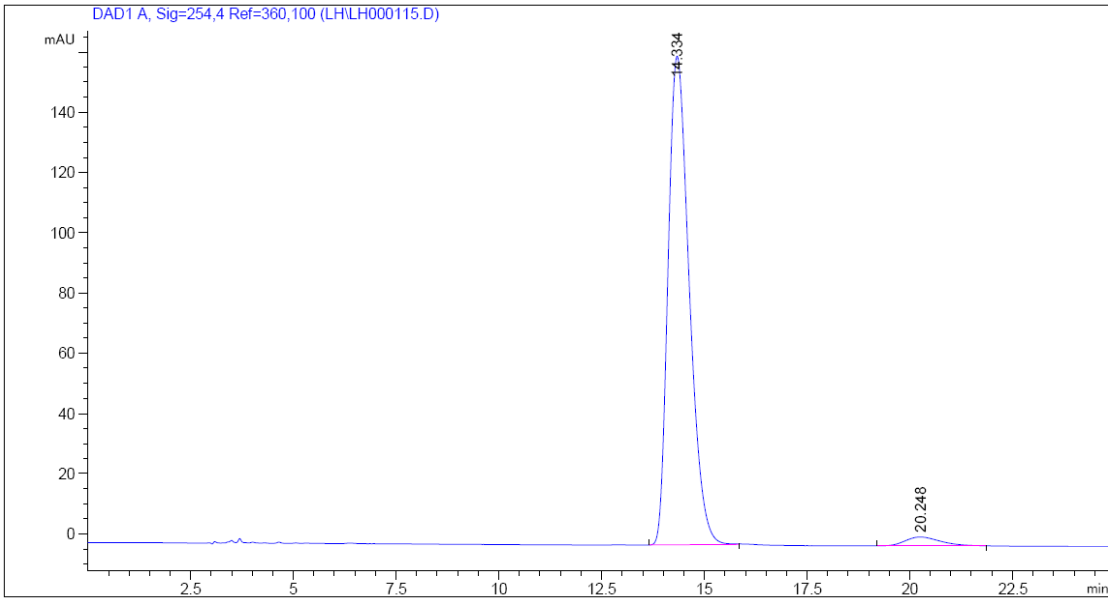
2	18.896	BB	0.8467	7583.31885	131.91266	50.0385



(*S*)–**29'** : (*R*)–**29'**

97 : **3**



Peak RetTime Type Width Area Height Area%

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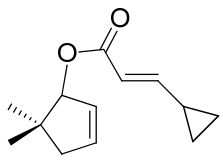
1	14.334	BB	0.5521	5785.60596	162.22356	96.9810
2	20.248	BB	0.9326	180.10561	2.96553	3.0190

3. ^{1}H- and ^{13}C-NMR Spectra



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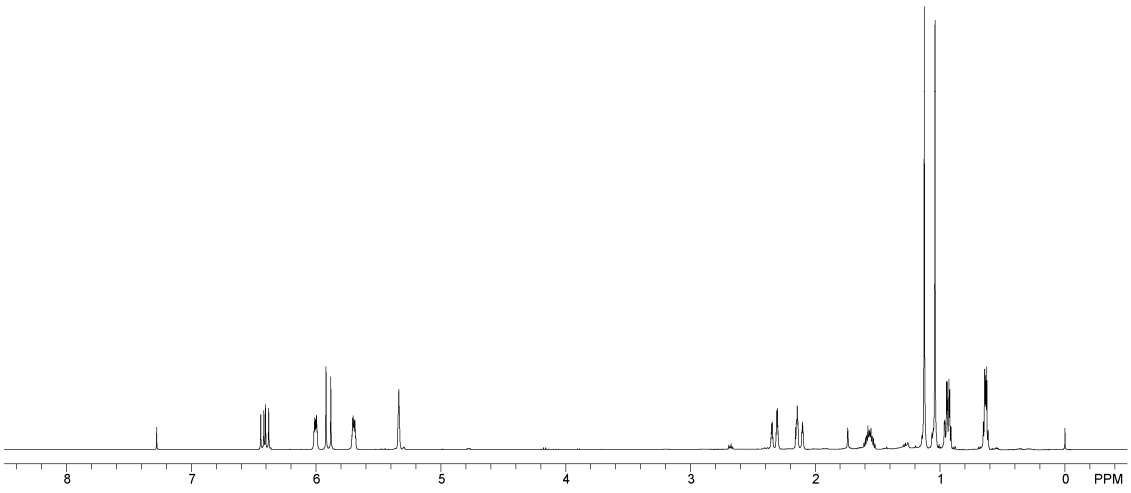

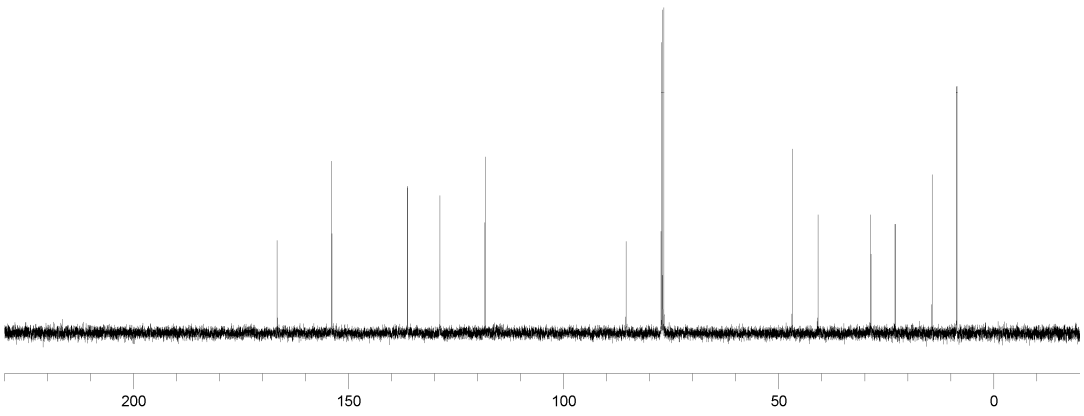

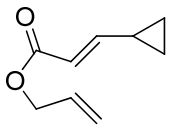

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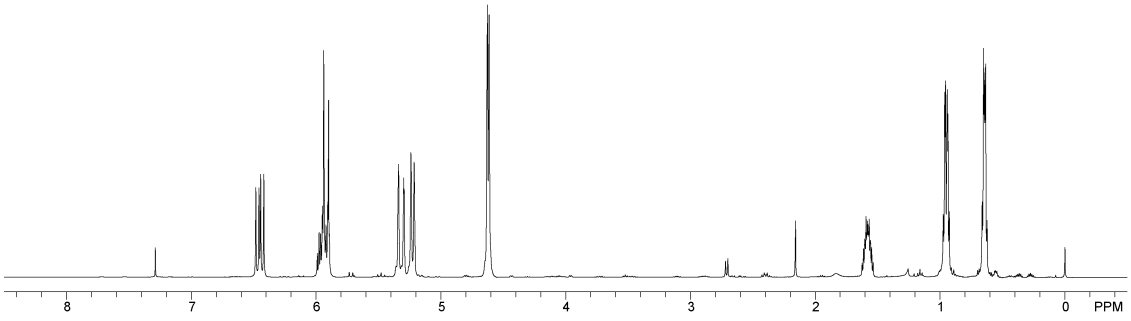

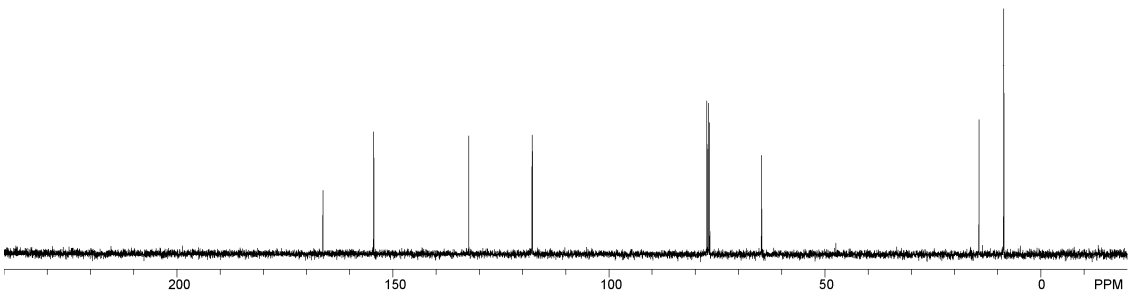

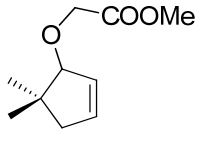

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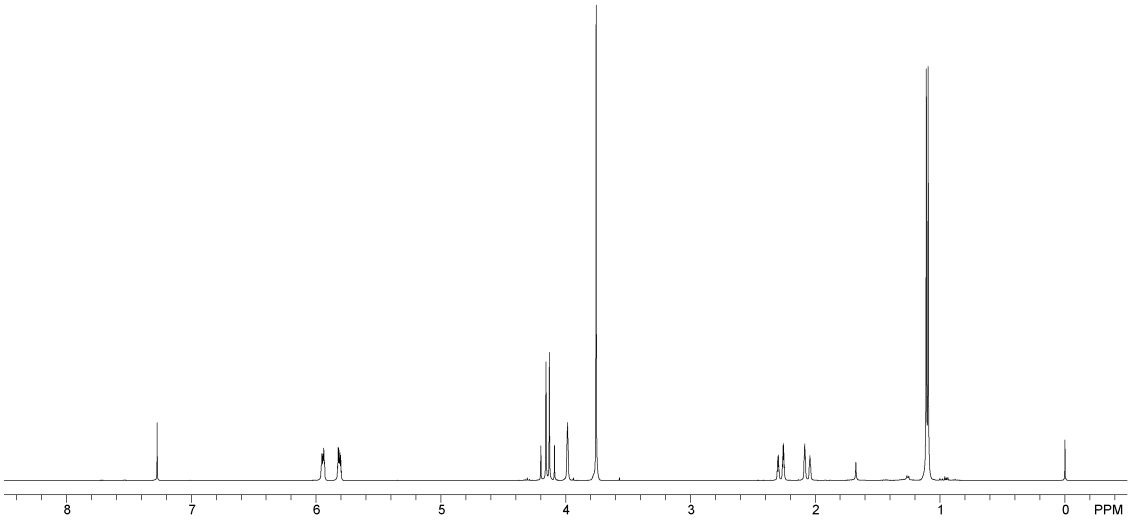

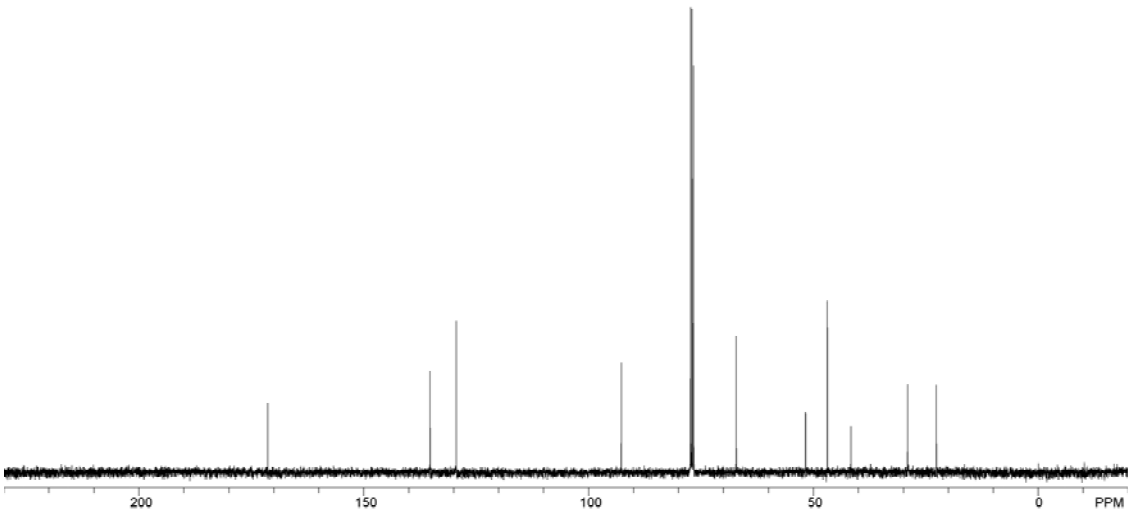

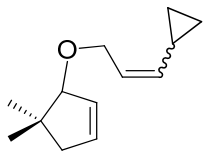

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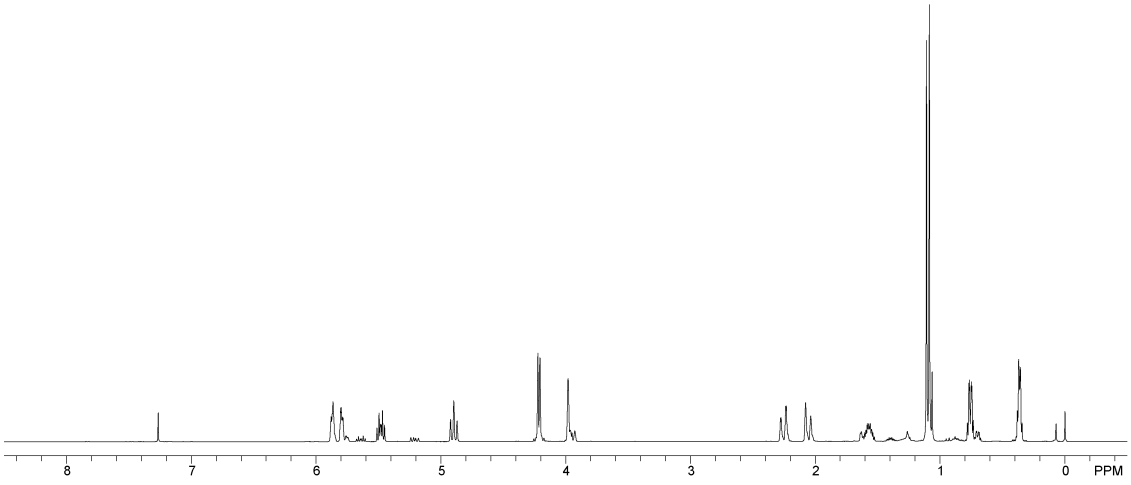

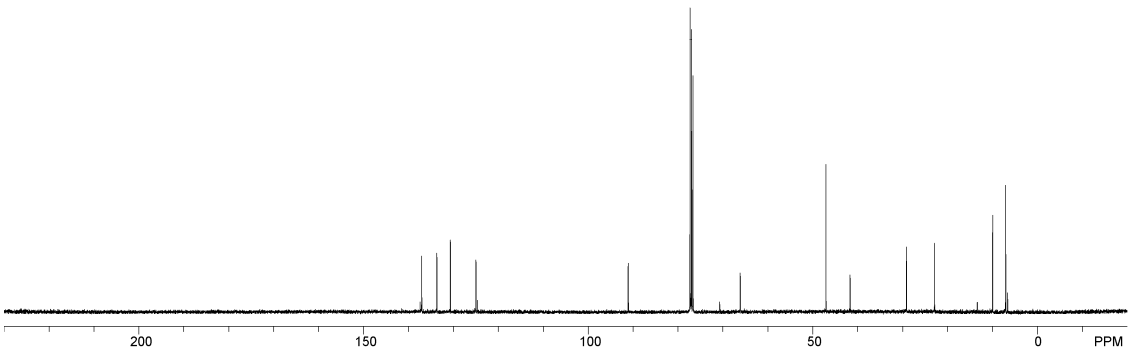

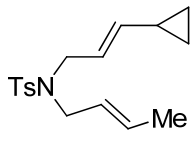

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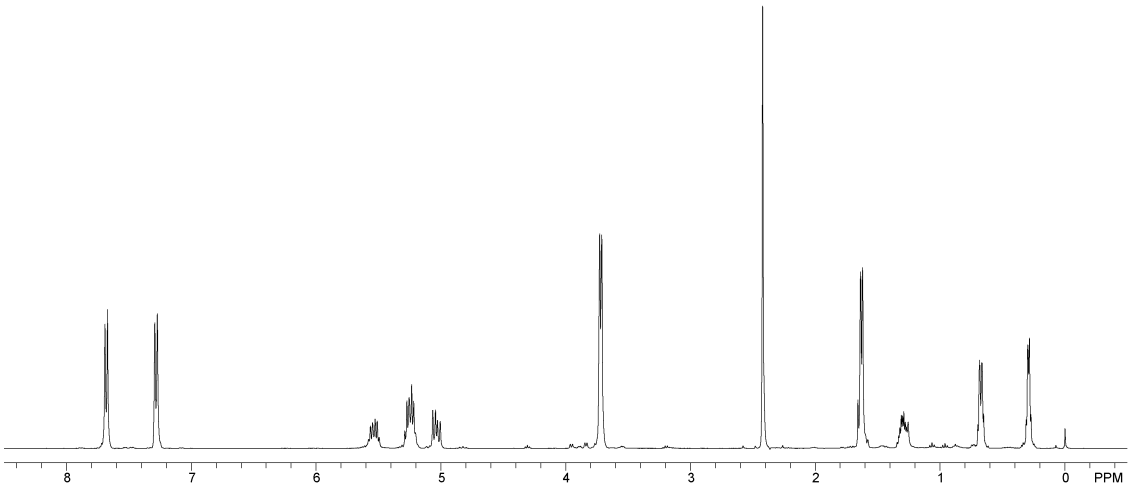

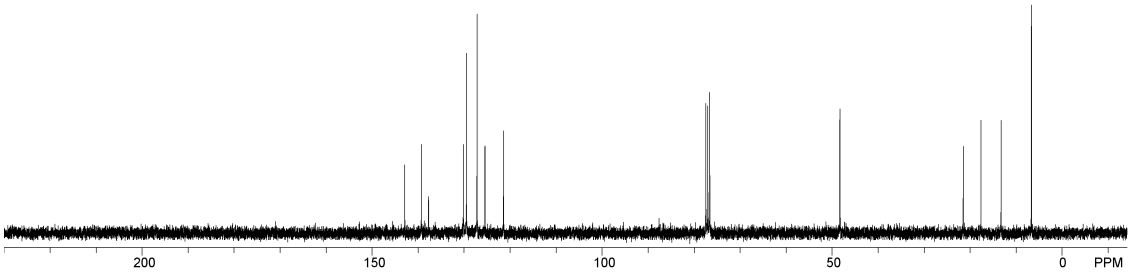

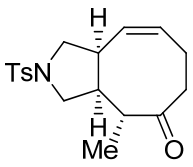

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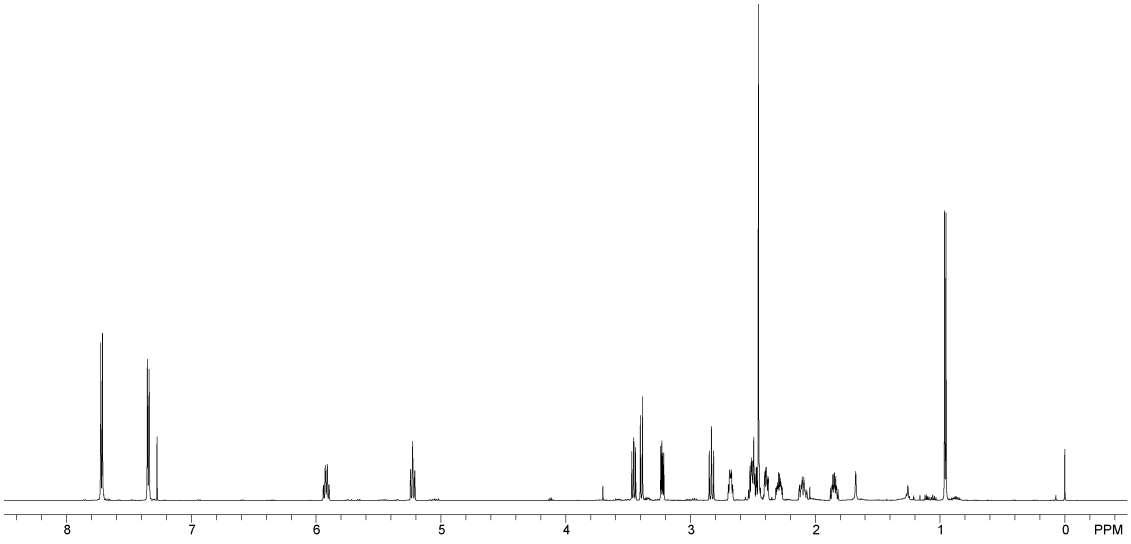

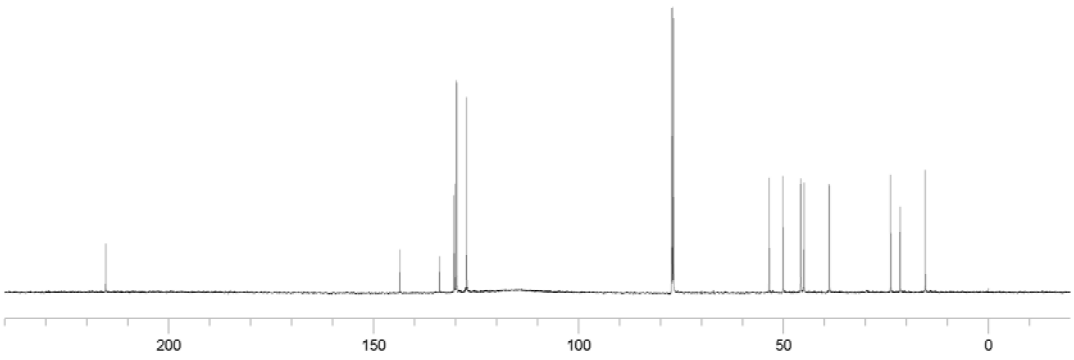

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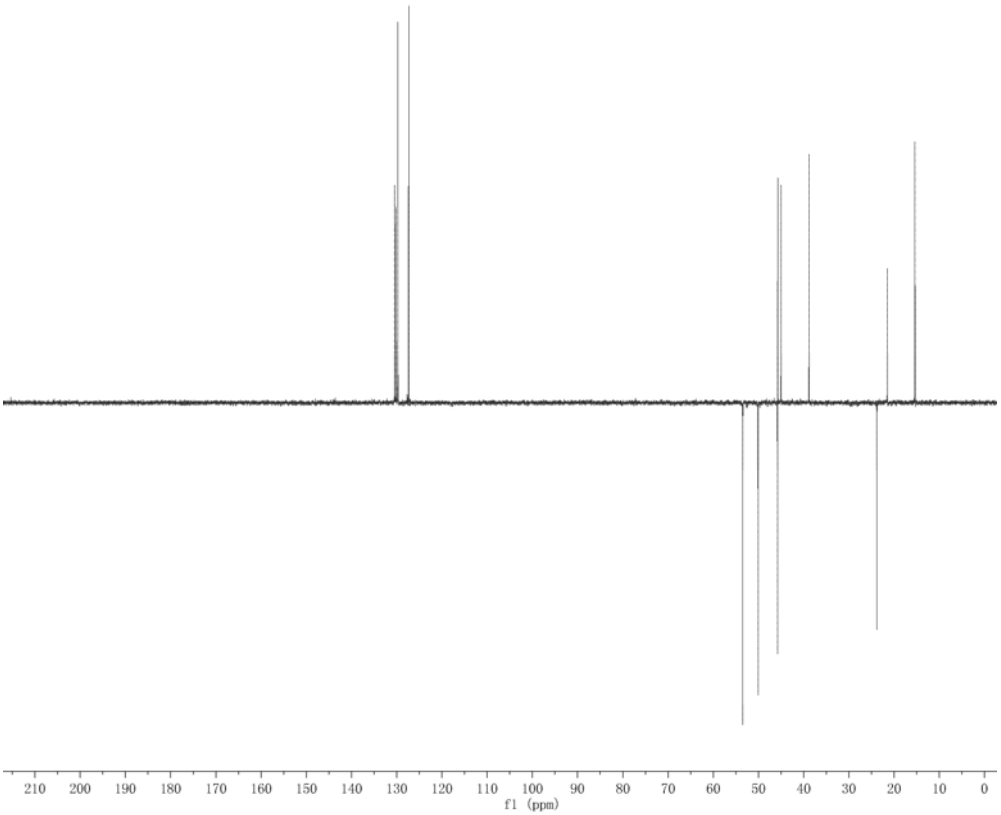

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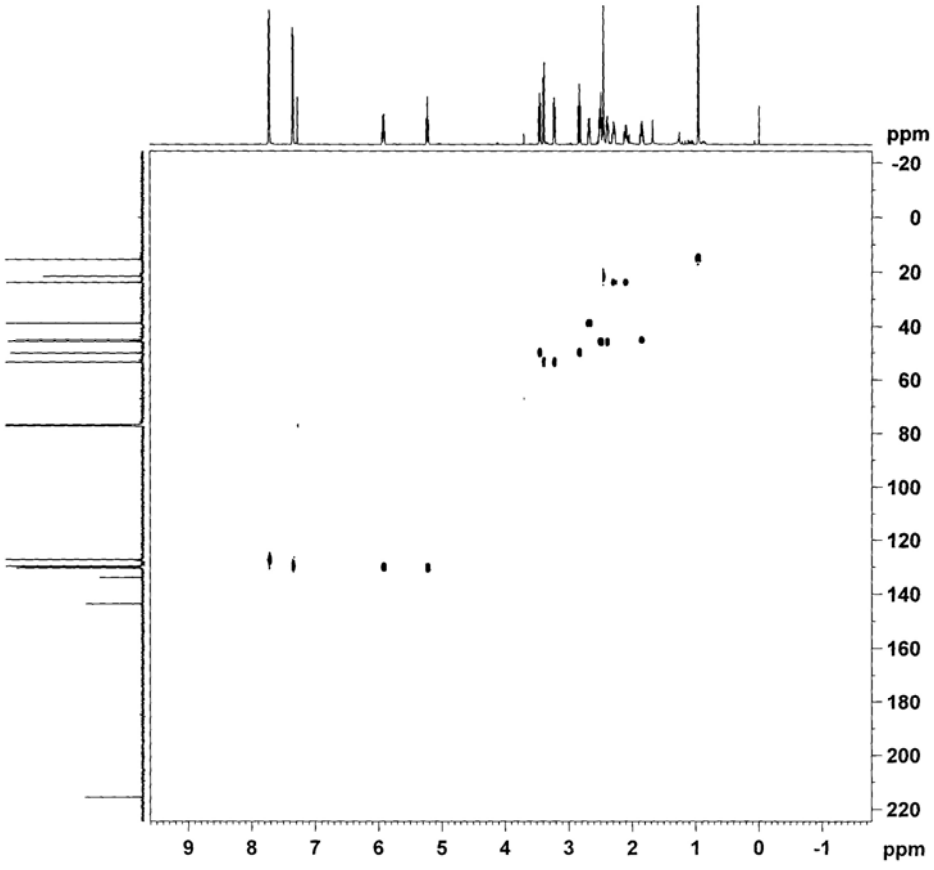

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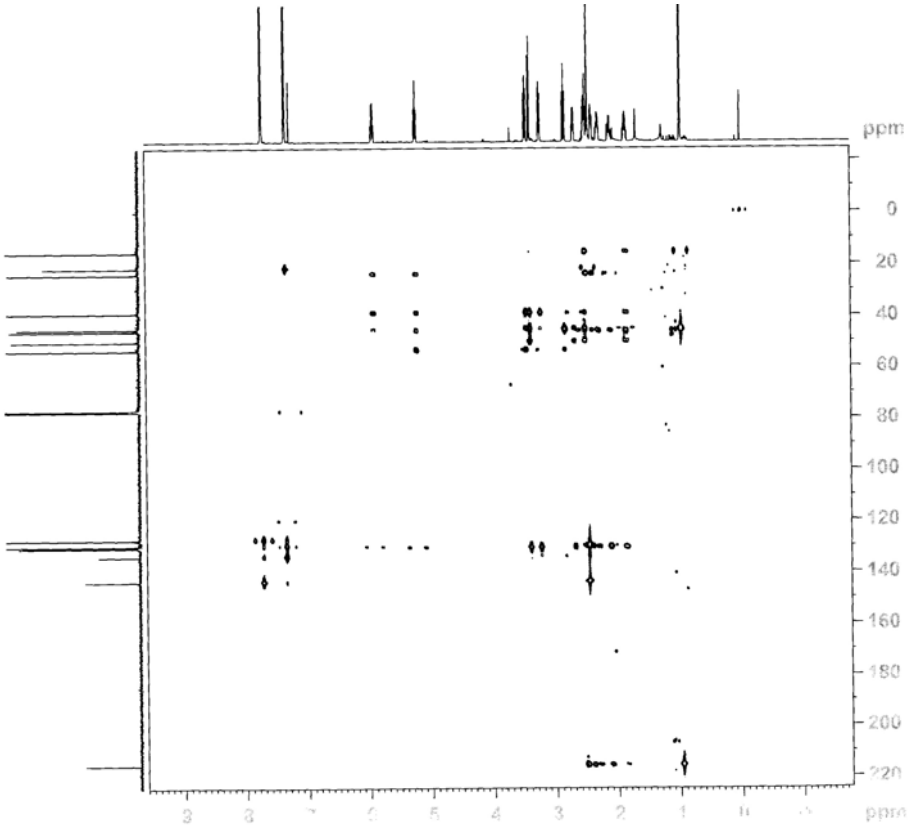
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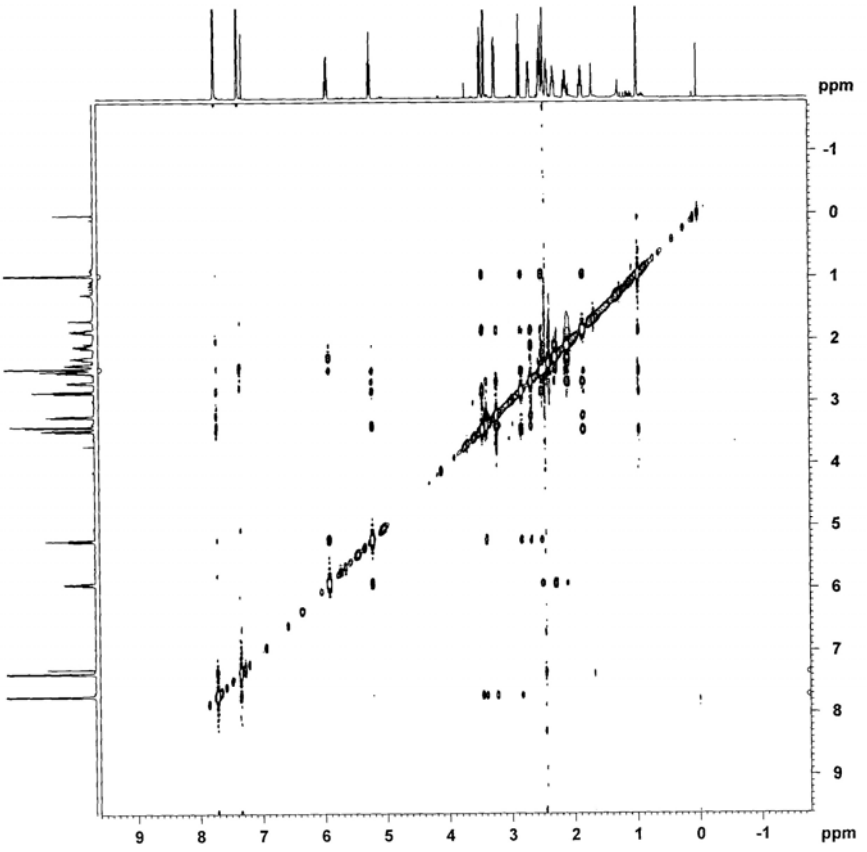
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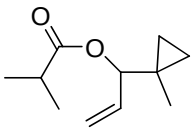

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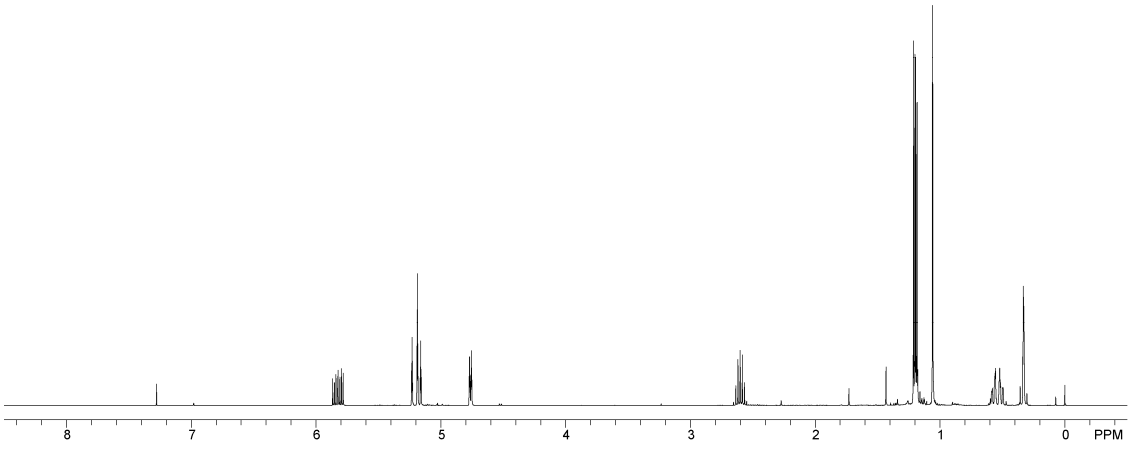

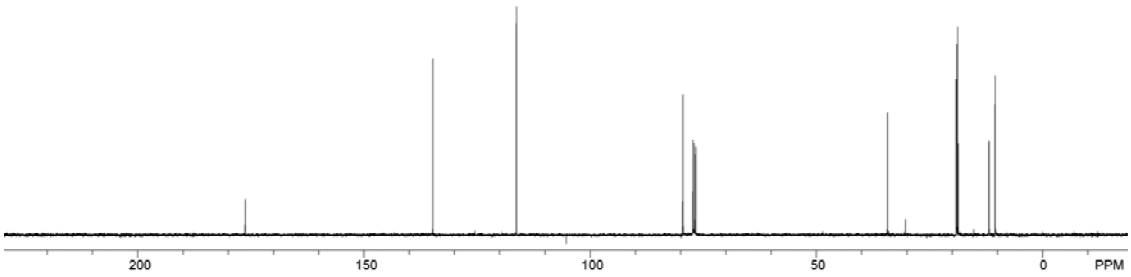

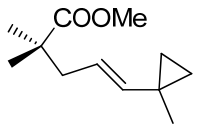

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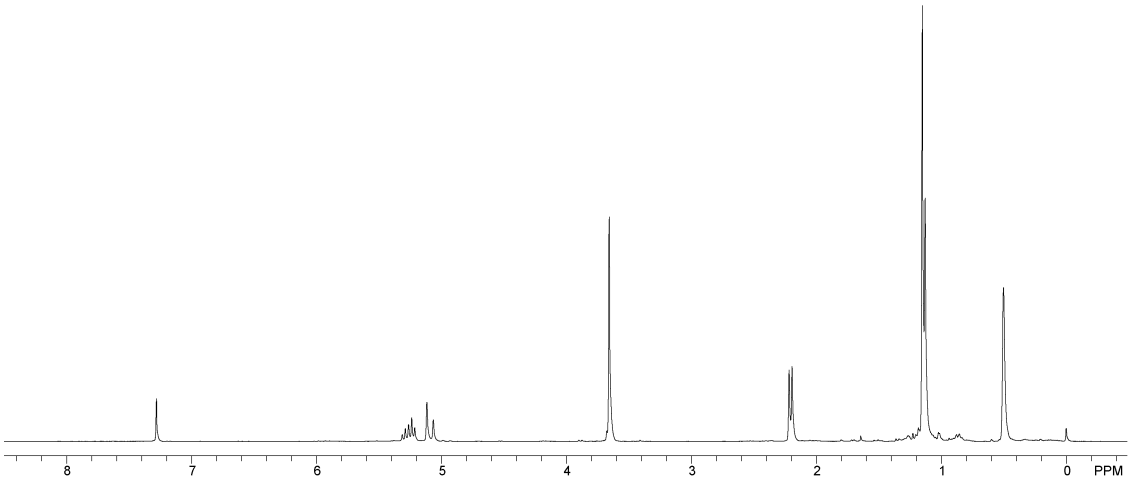

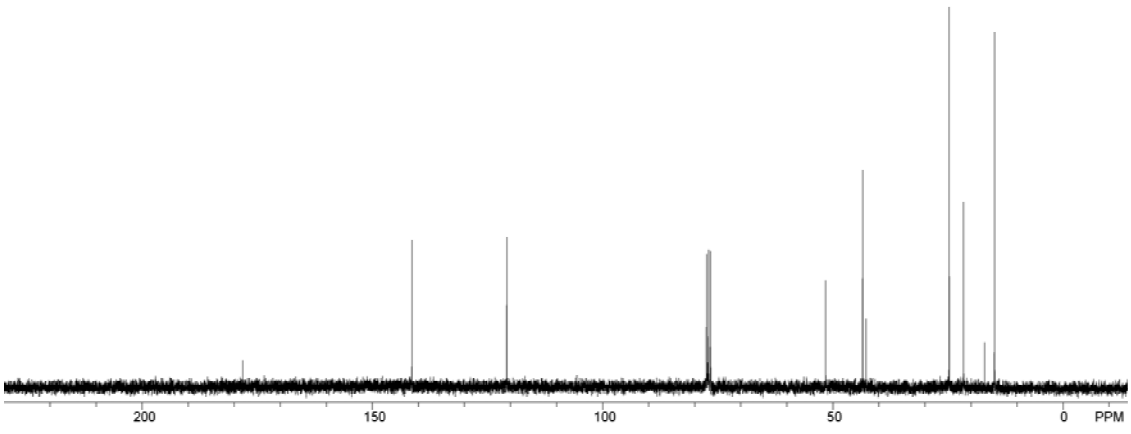

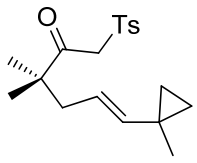

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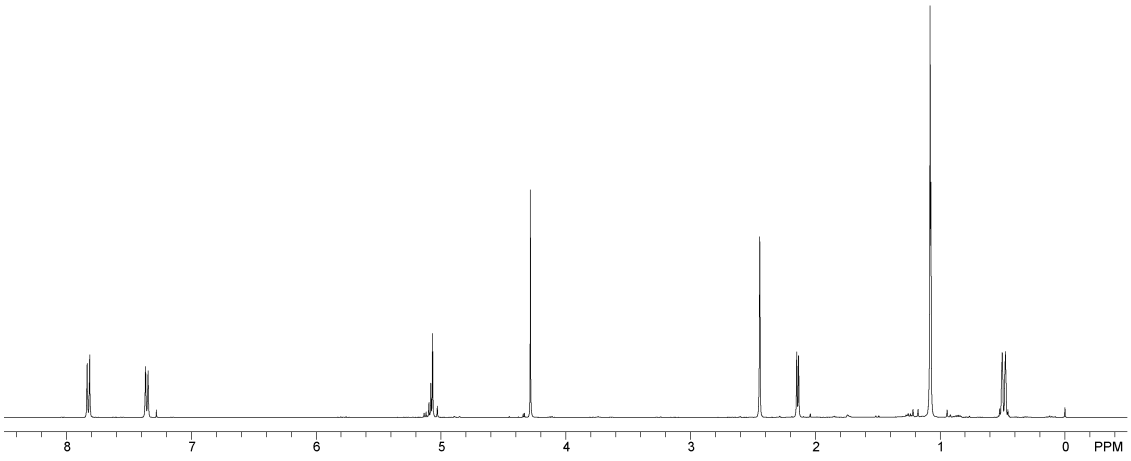

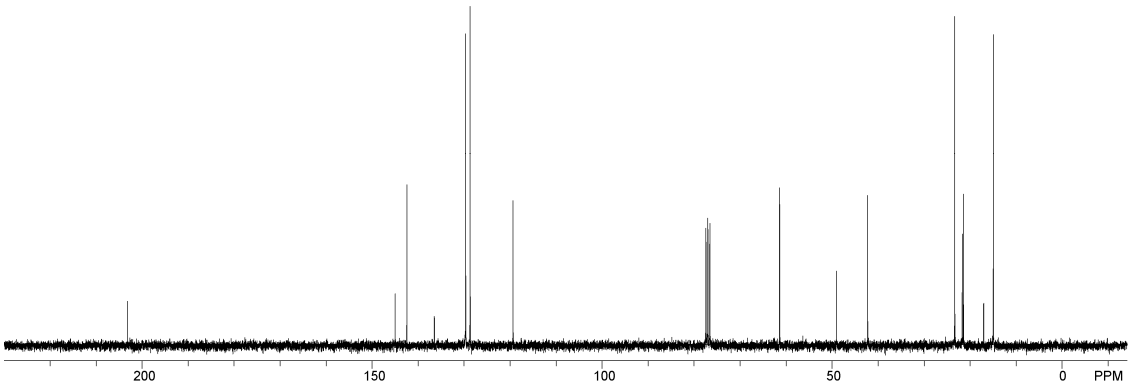

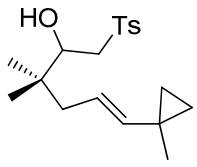

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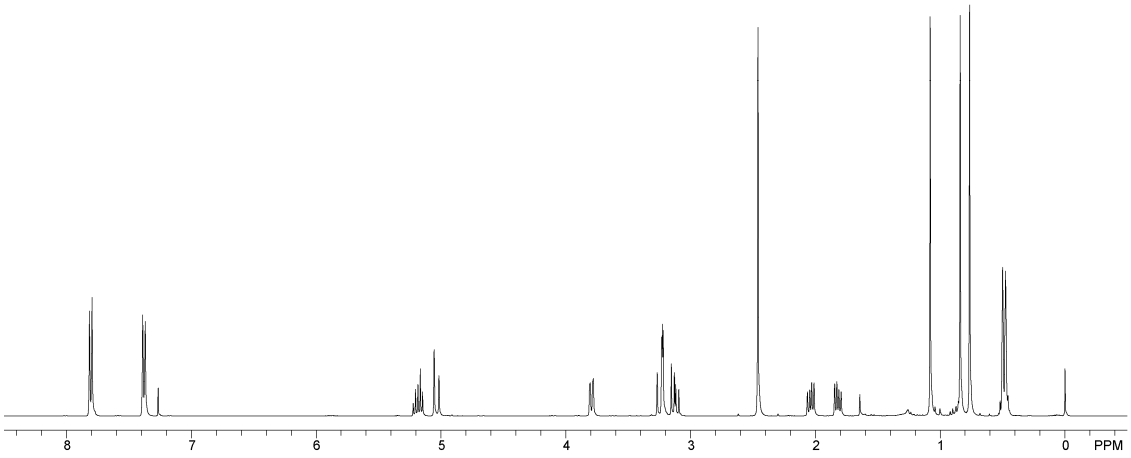

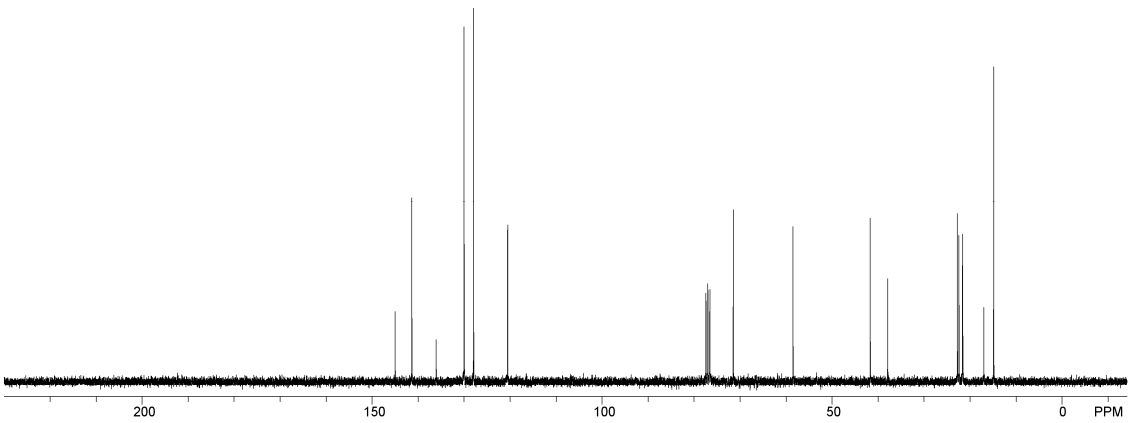

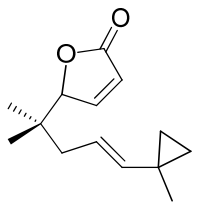

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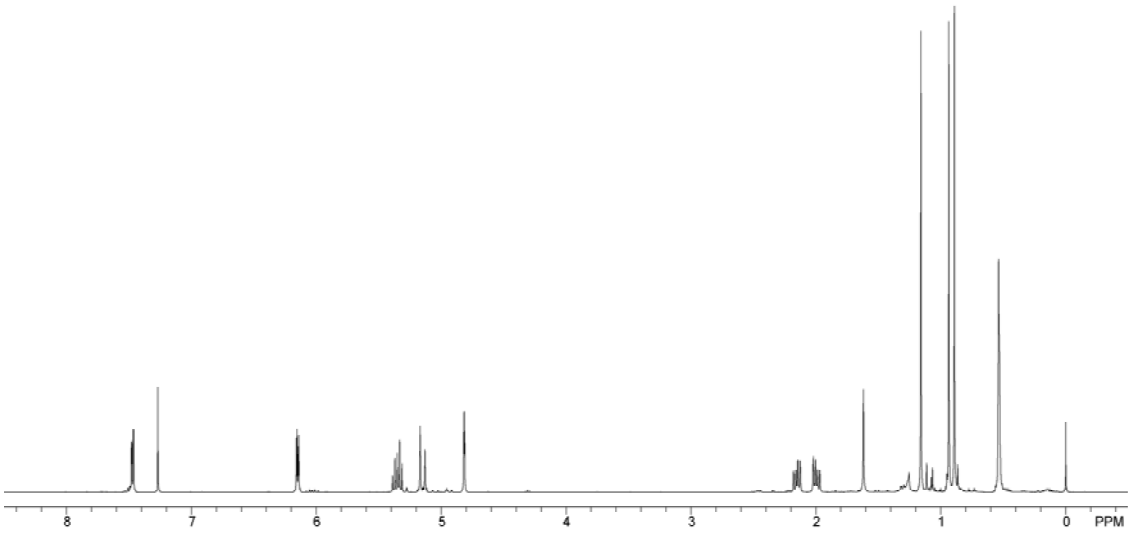

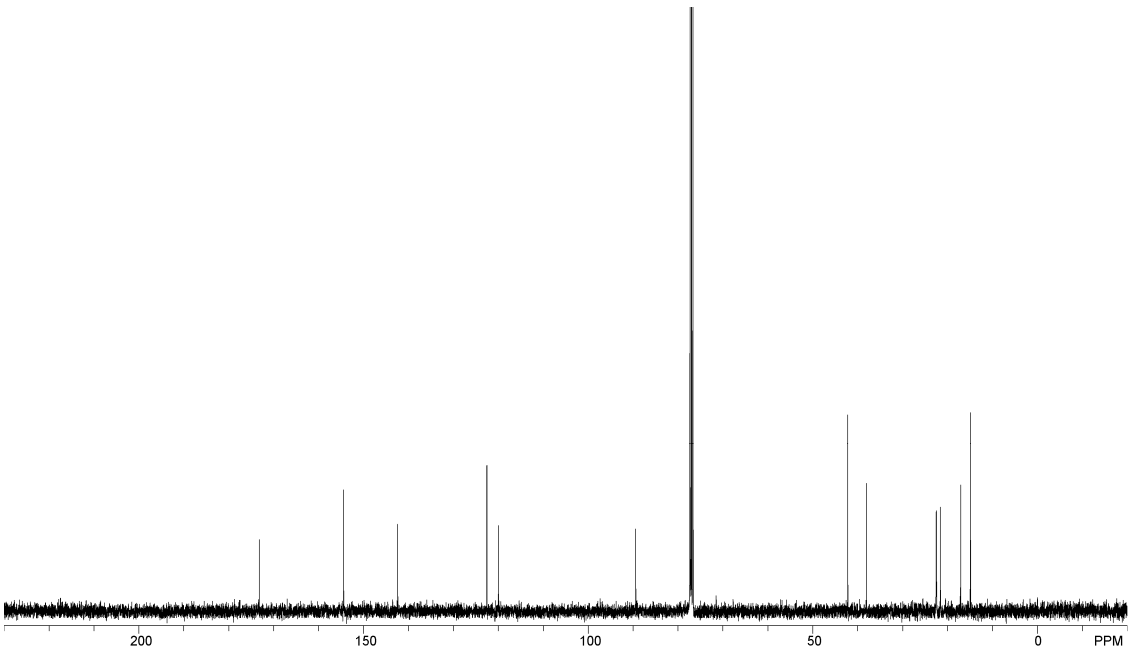

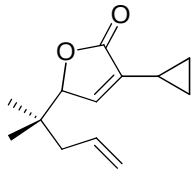

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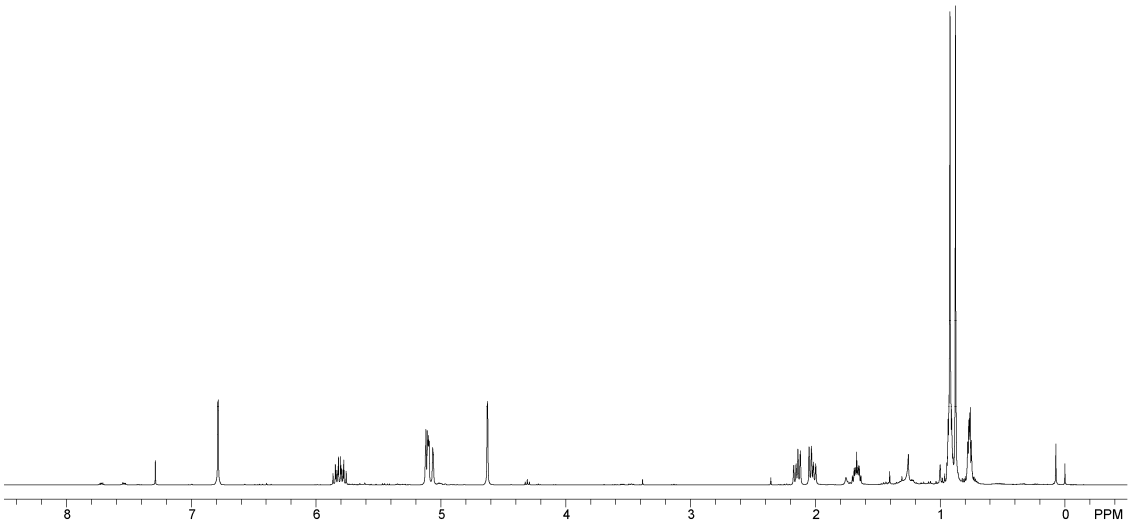

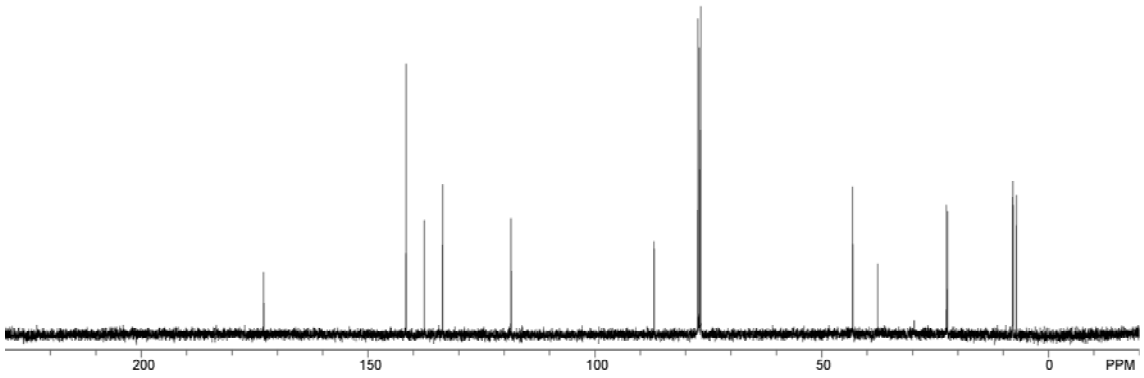

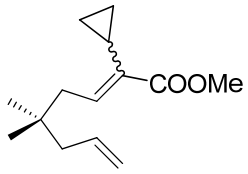

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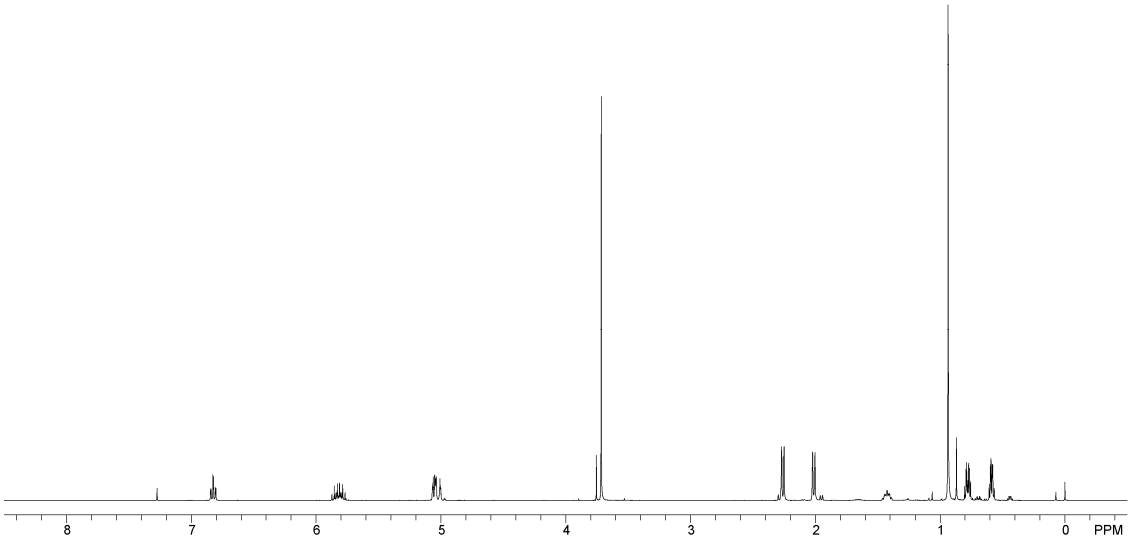

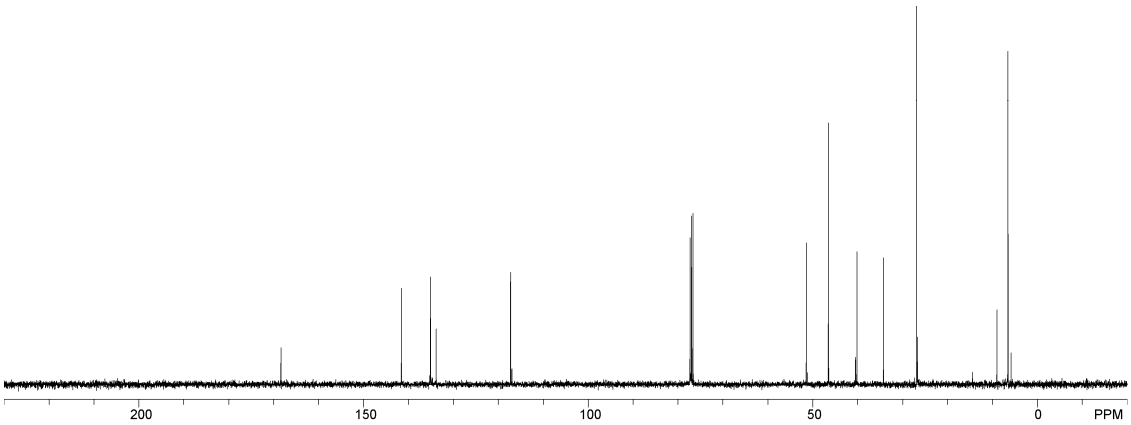

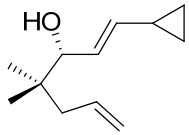

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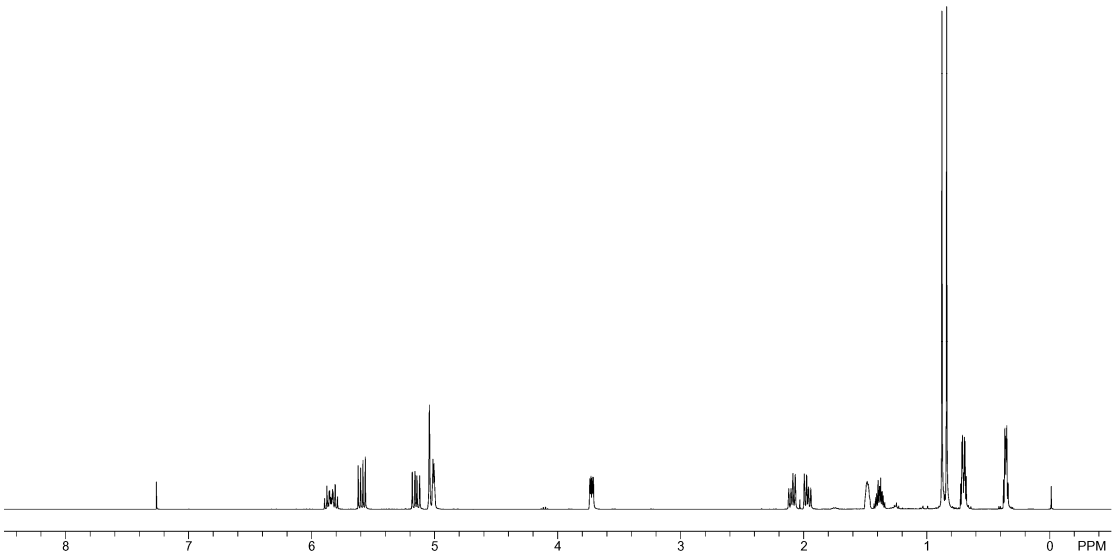

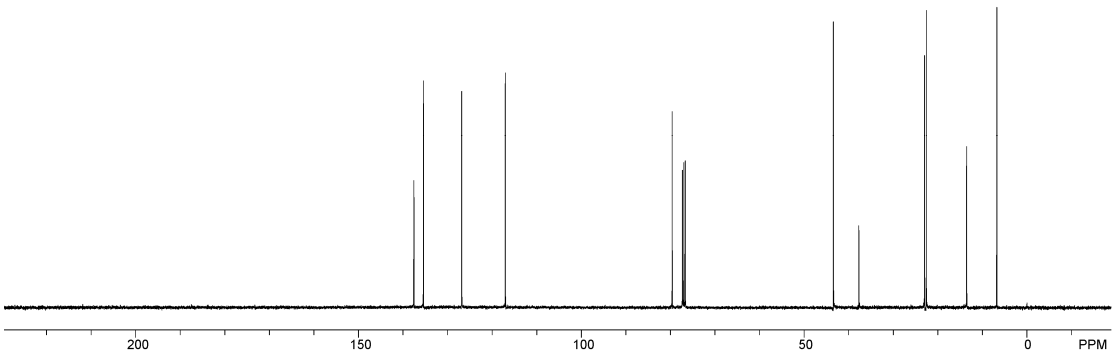

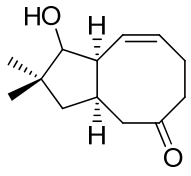

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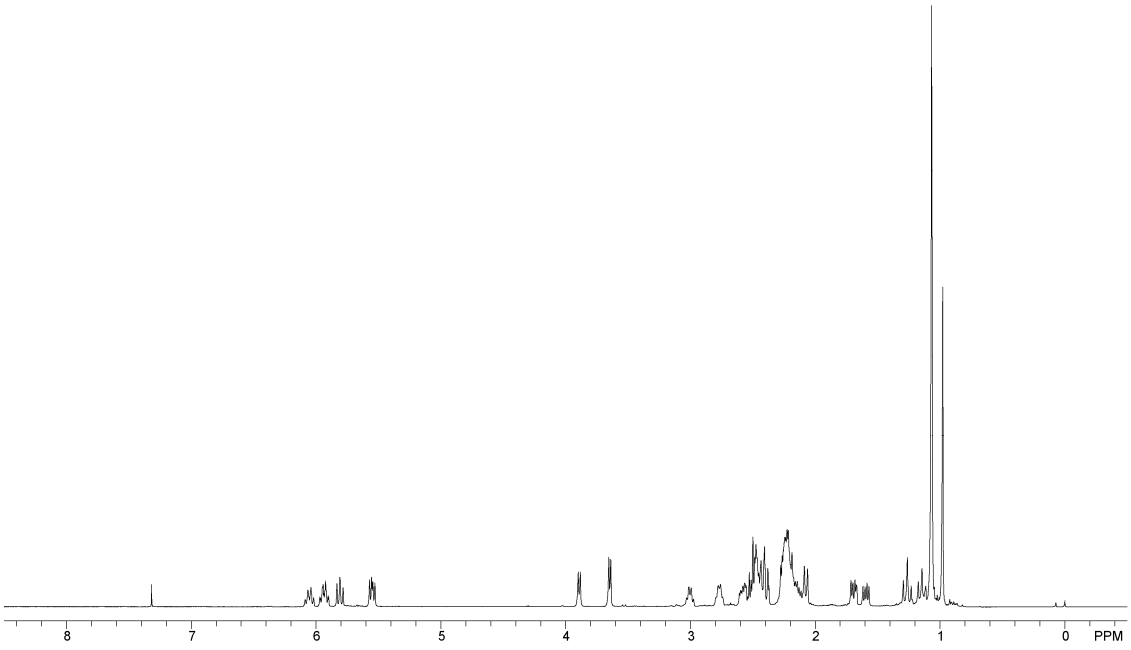

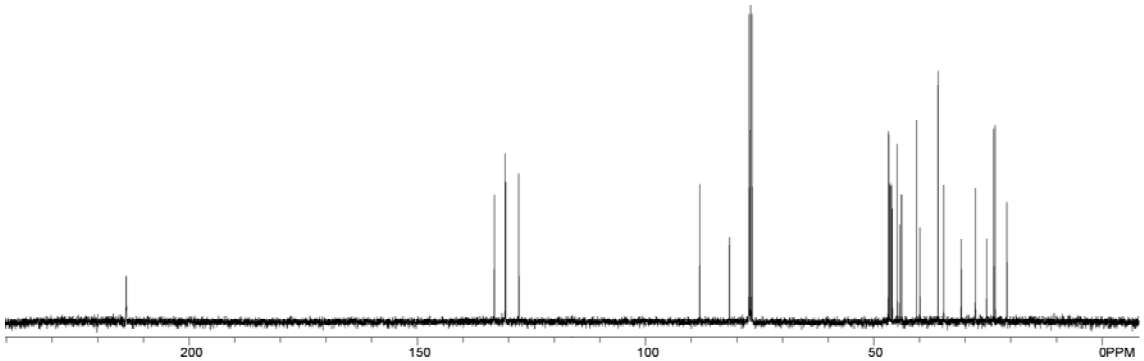

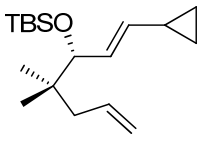

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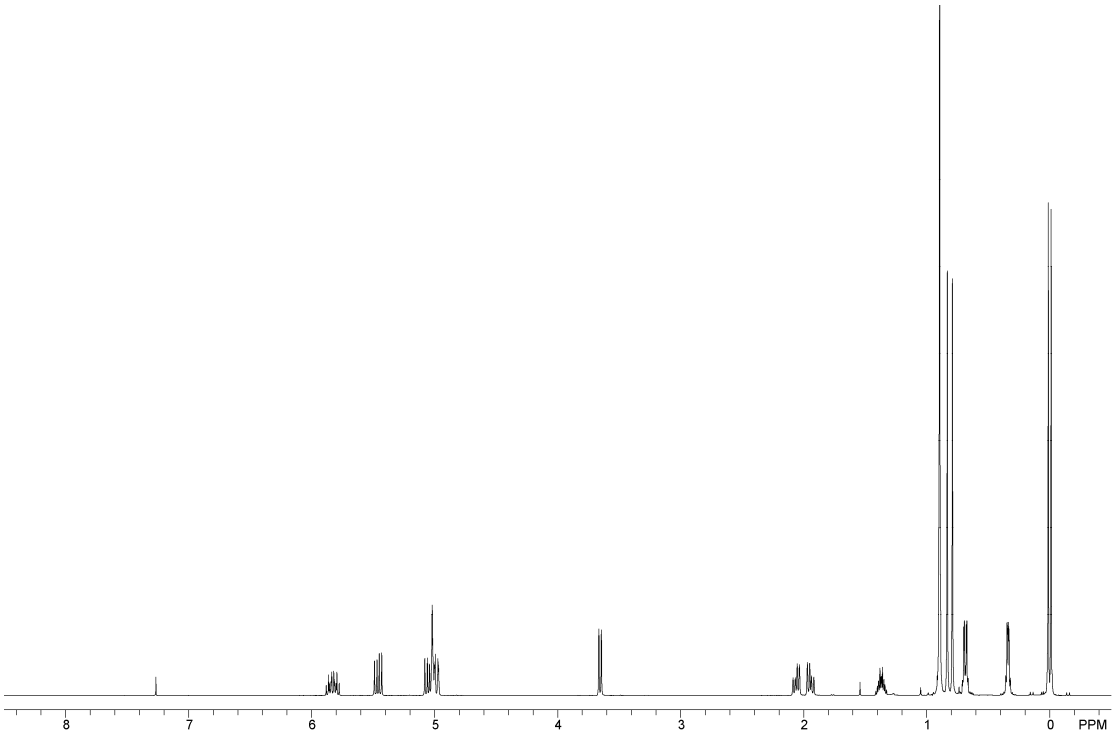

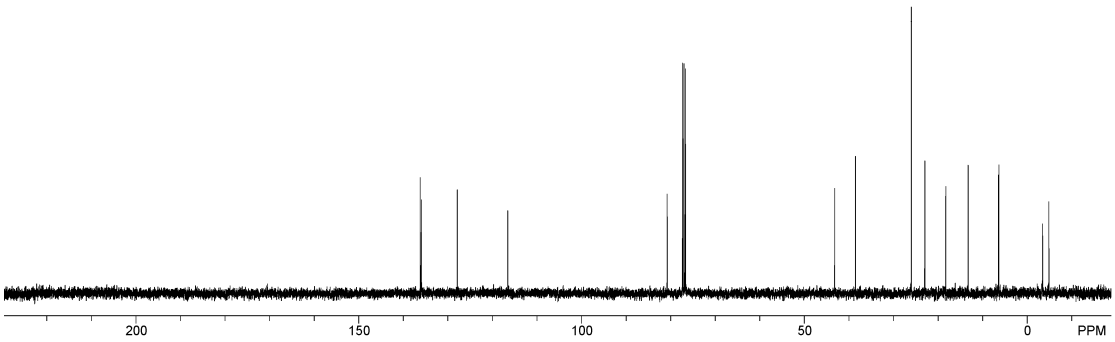

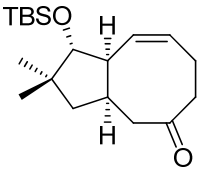

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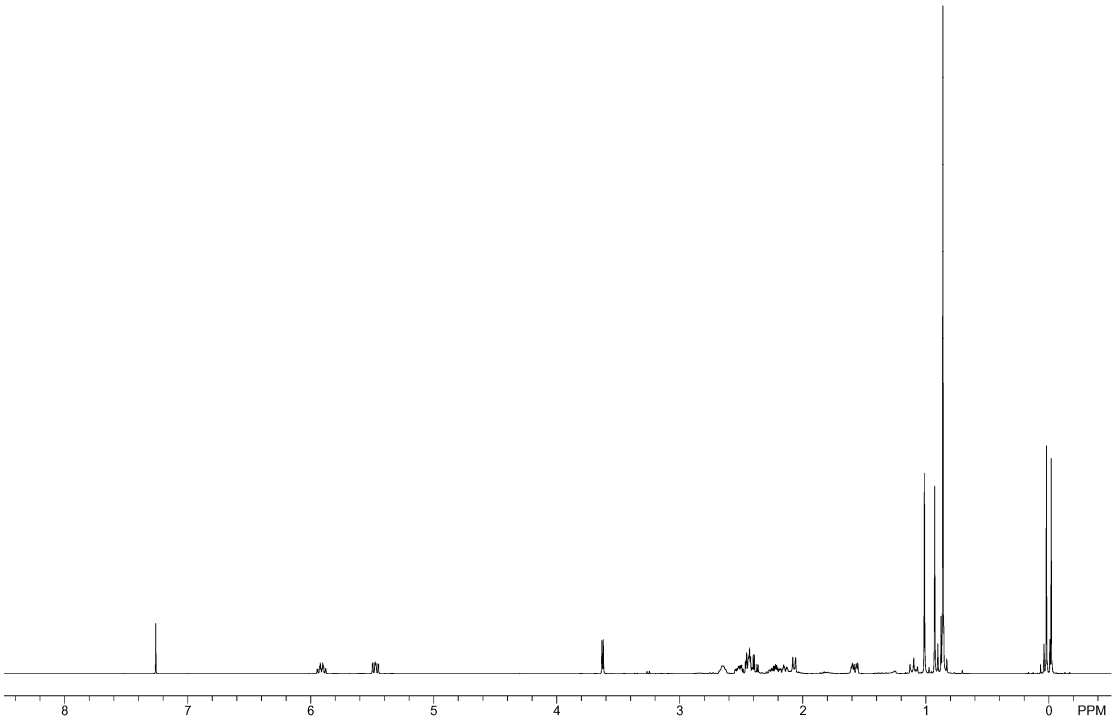

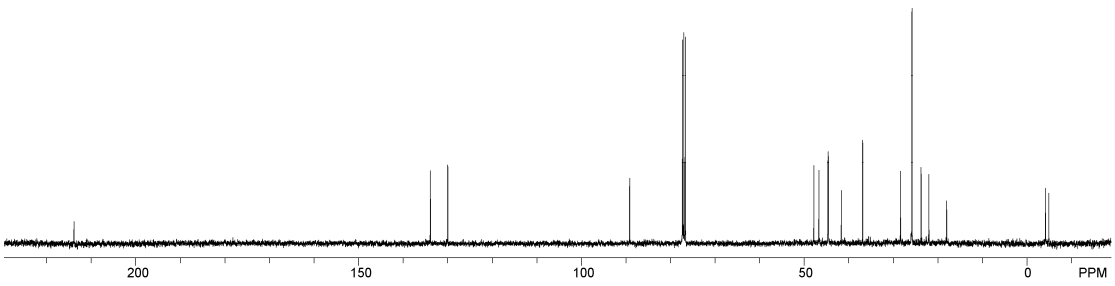

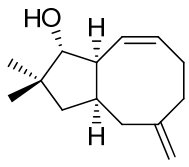

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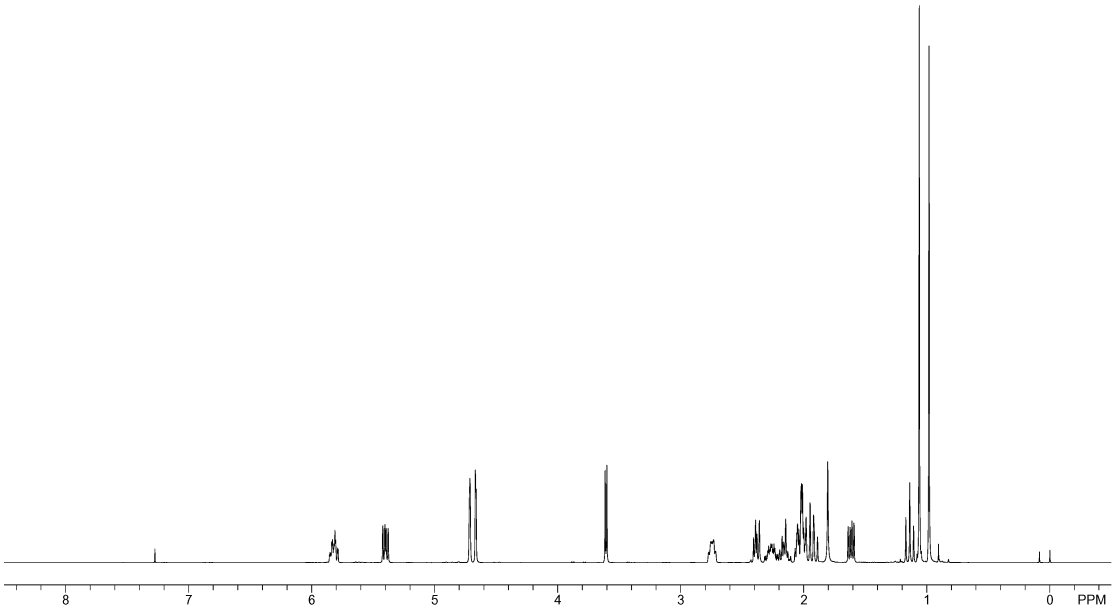

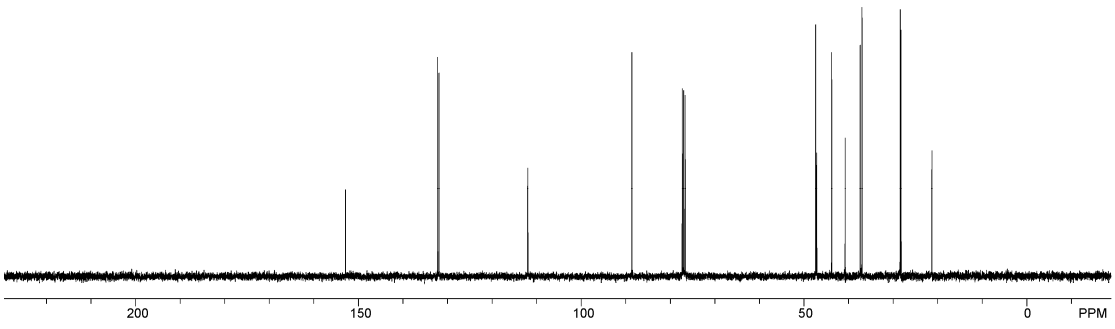

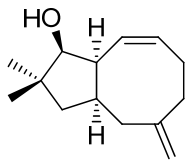

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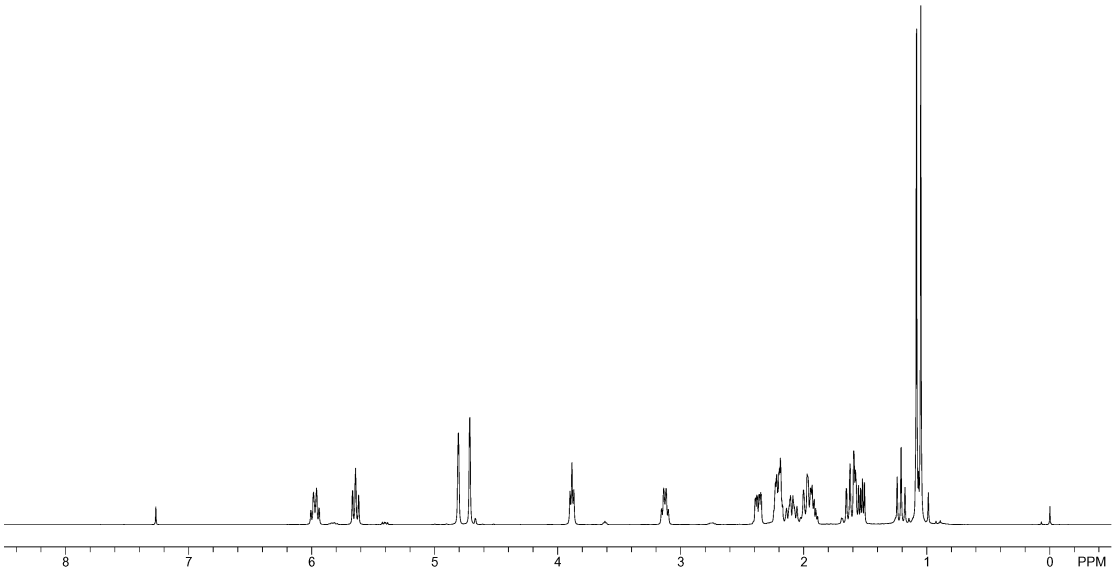

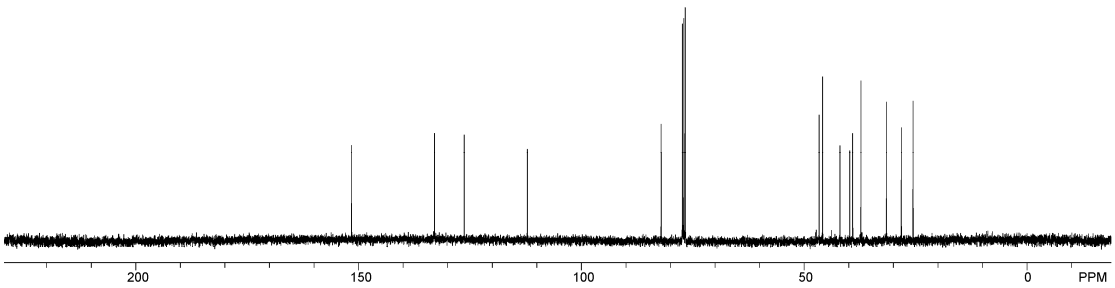

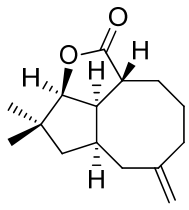

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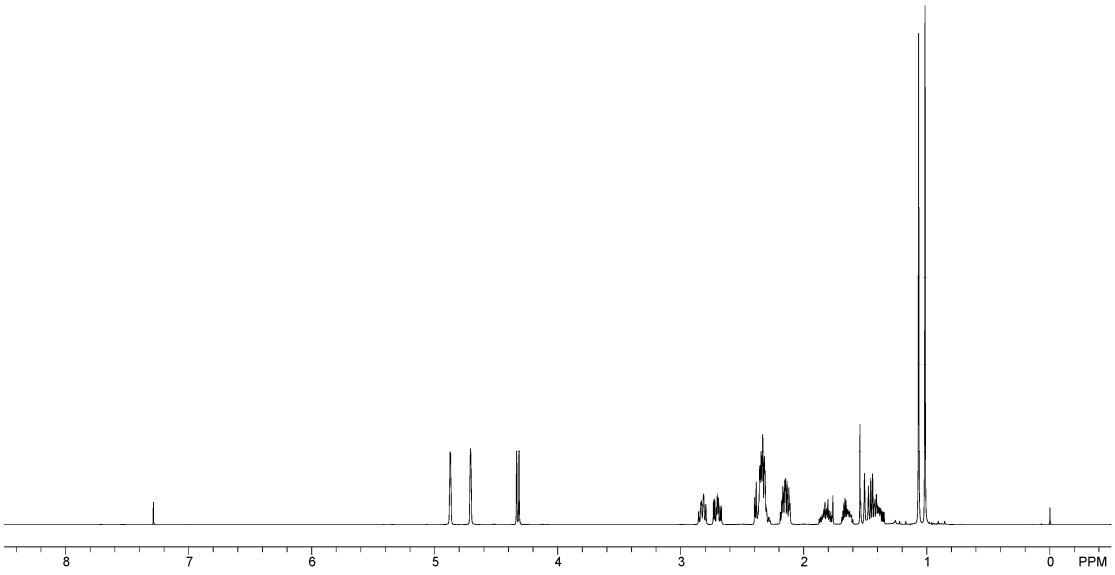

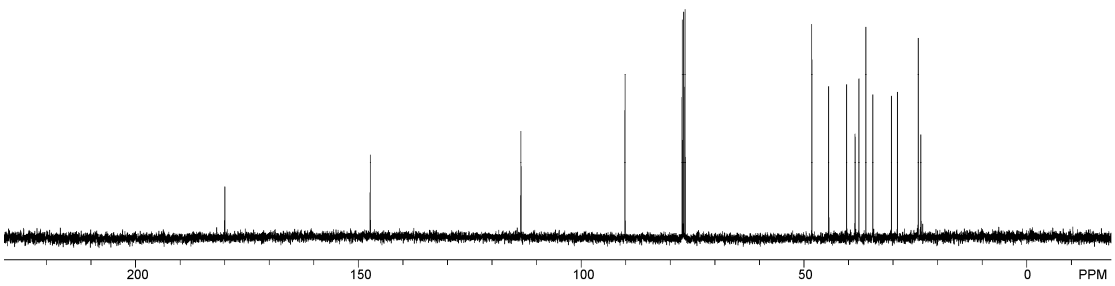

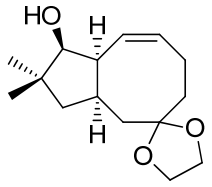
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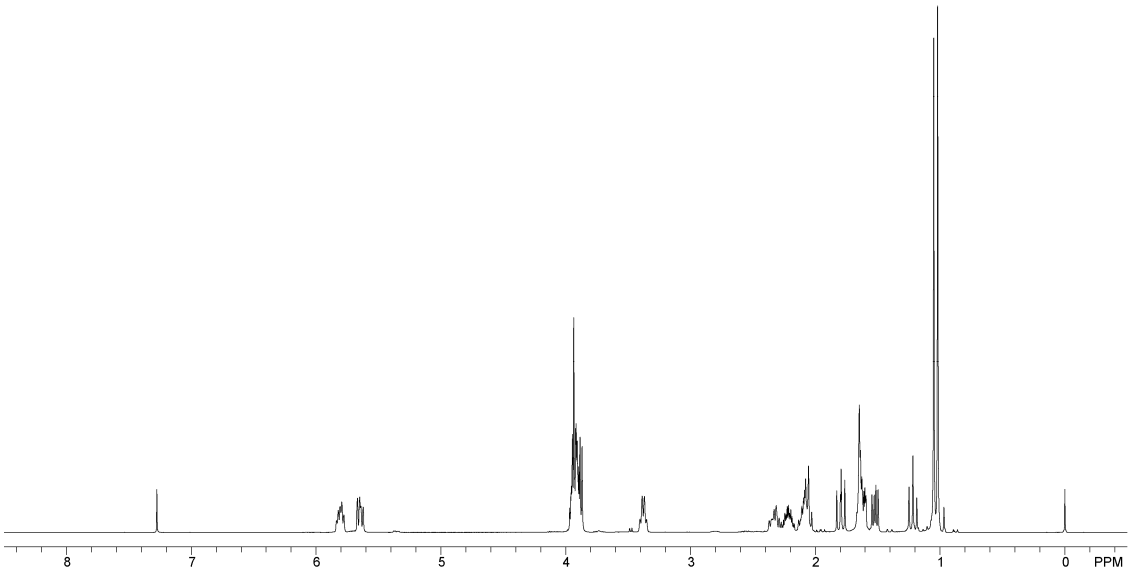
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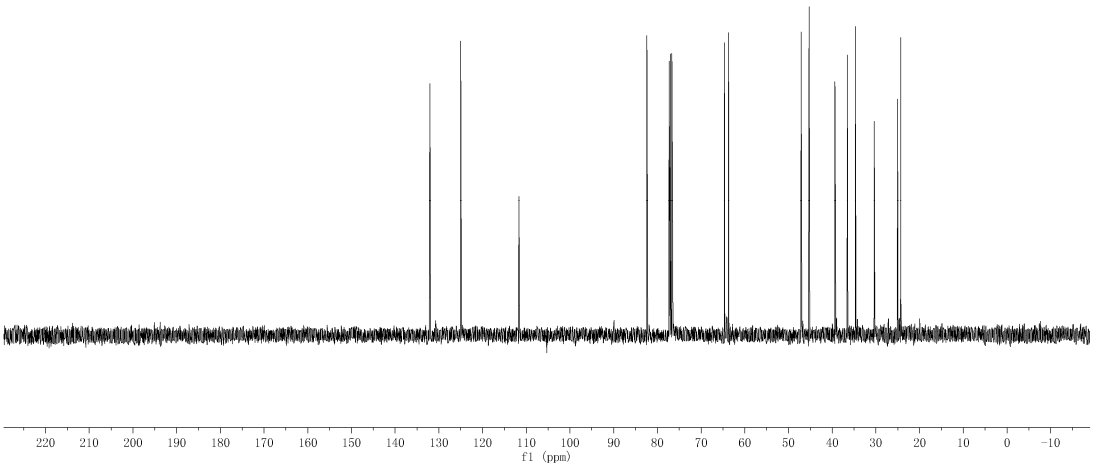
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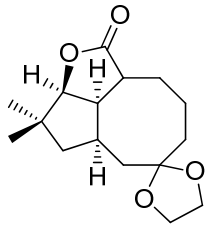

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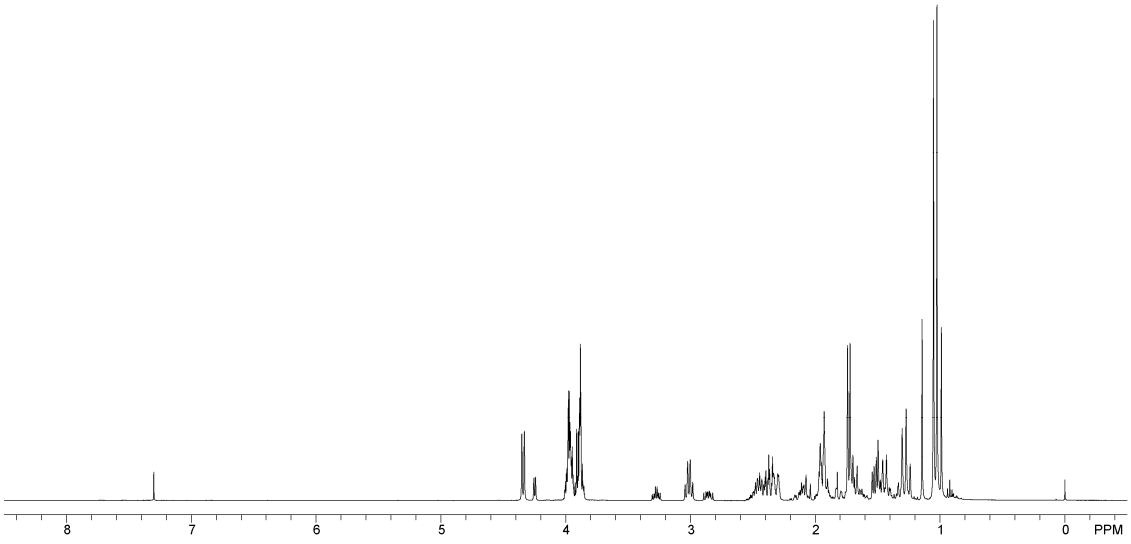
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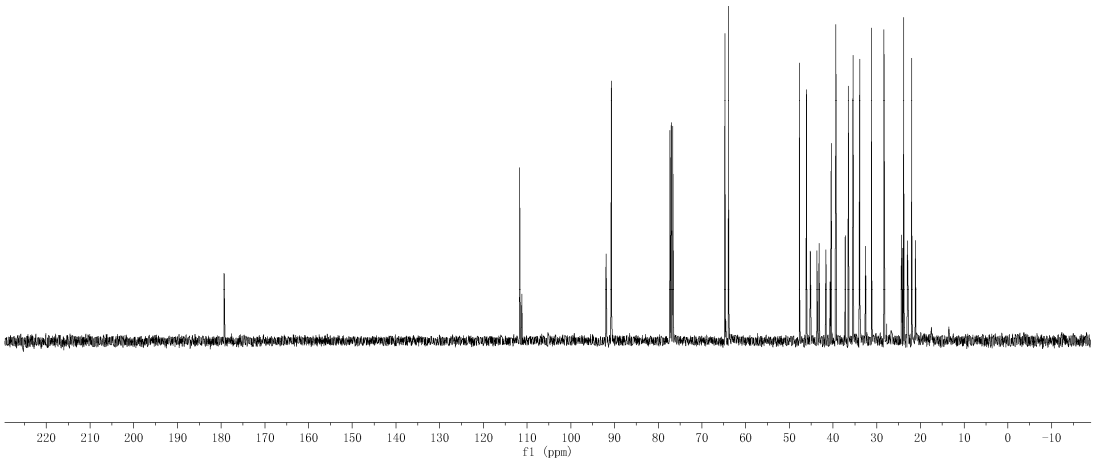
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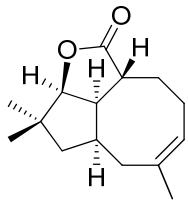

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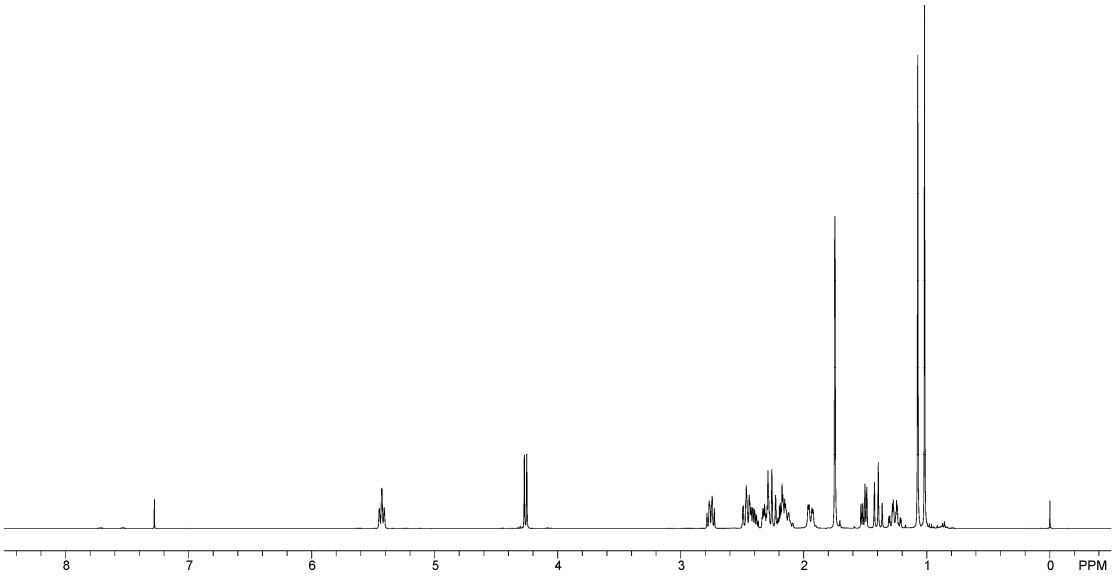

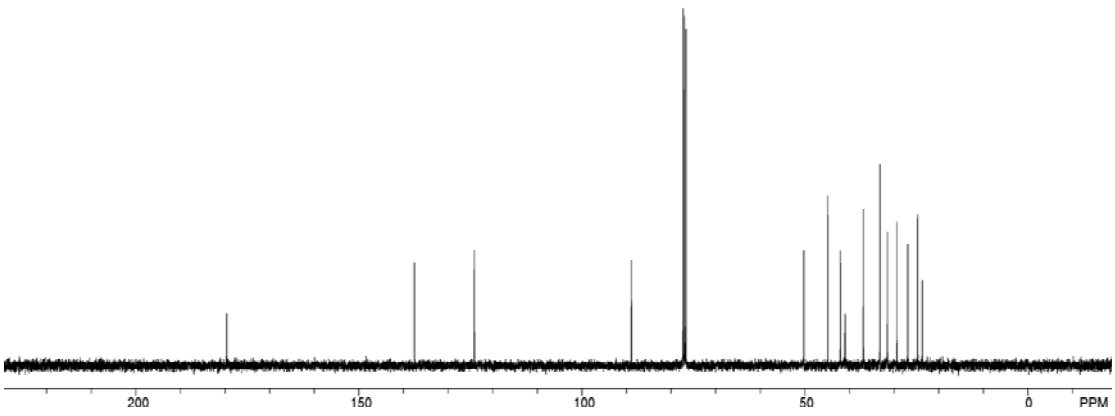

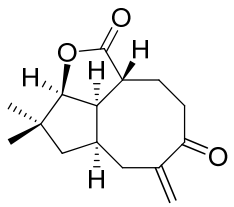

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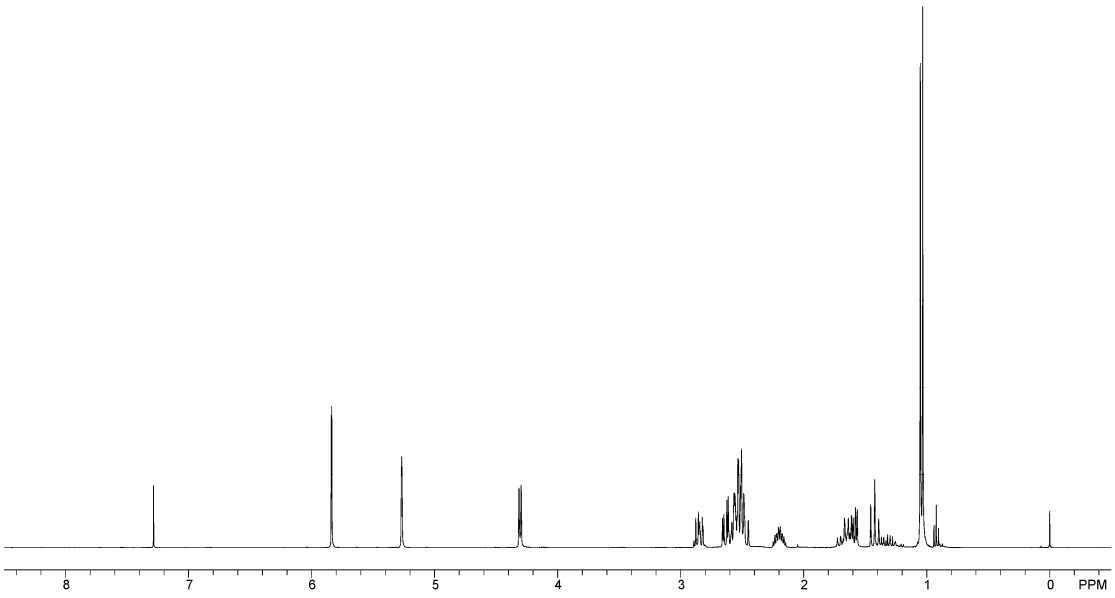

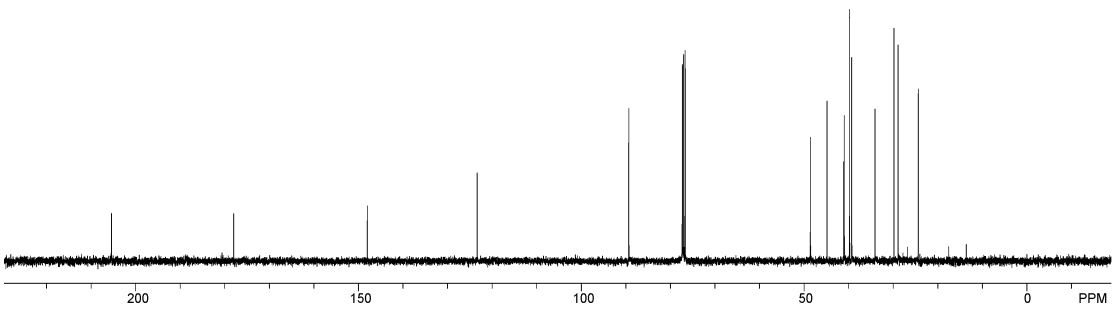

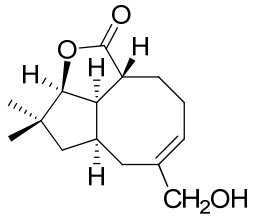

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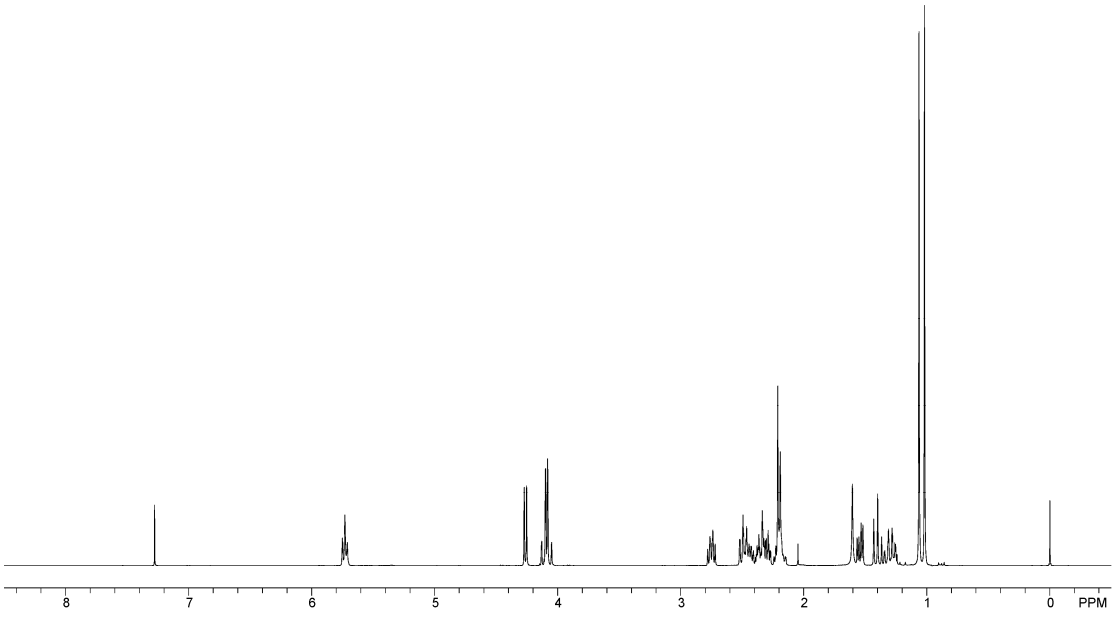

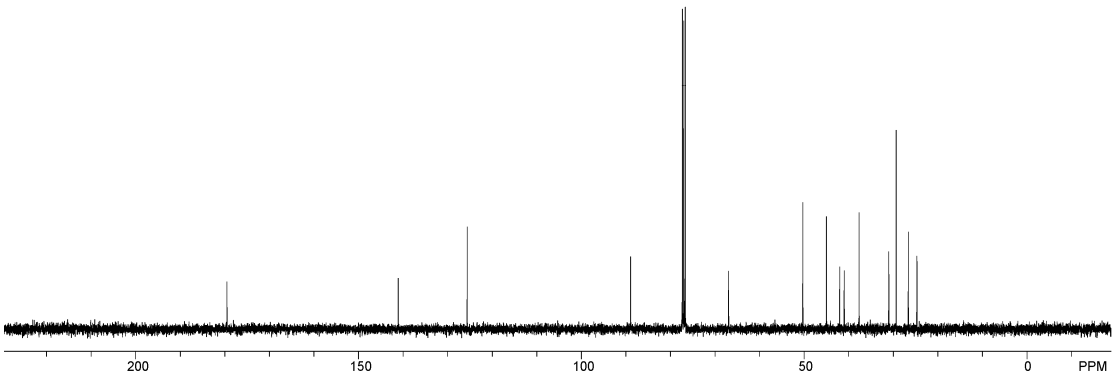

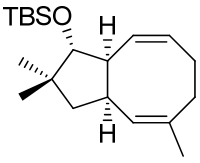

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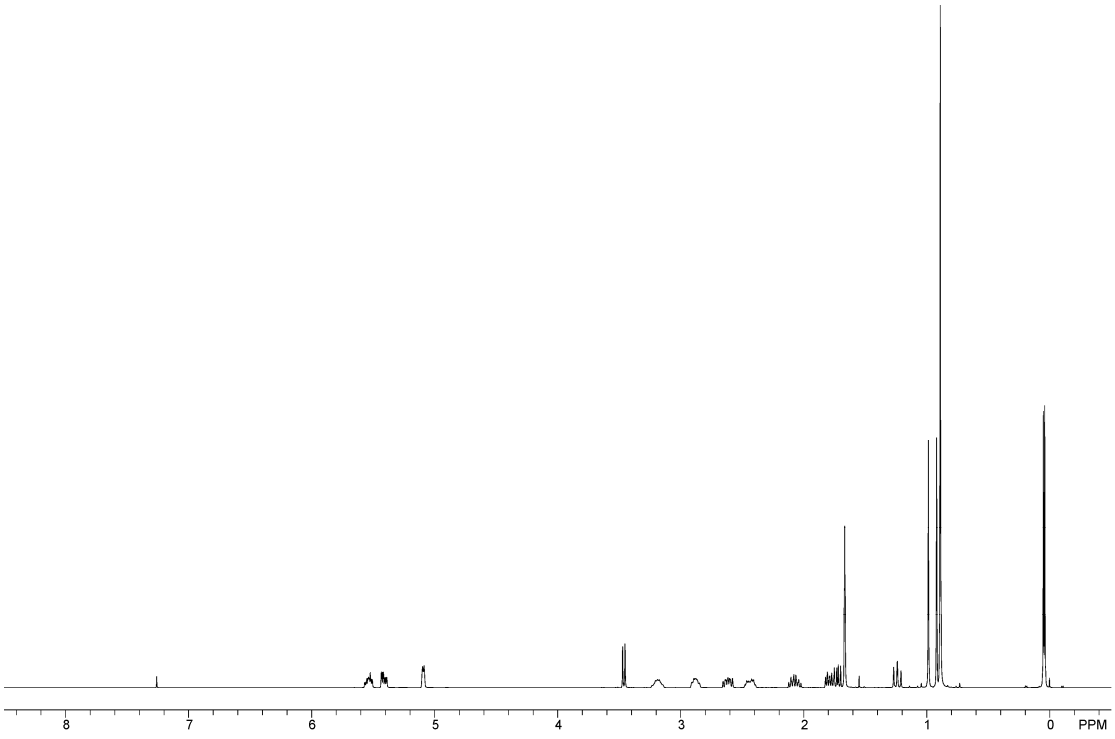

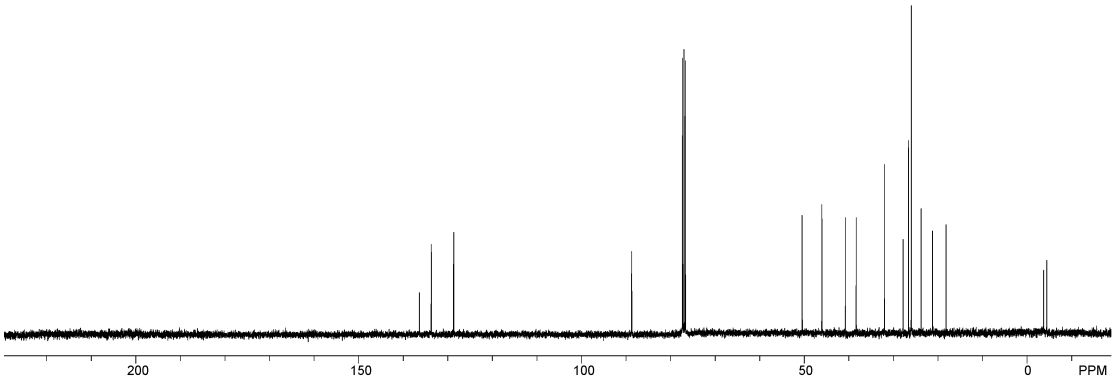

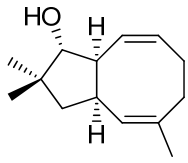

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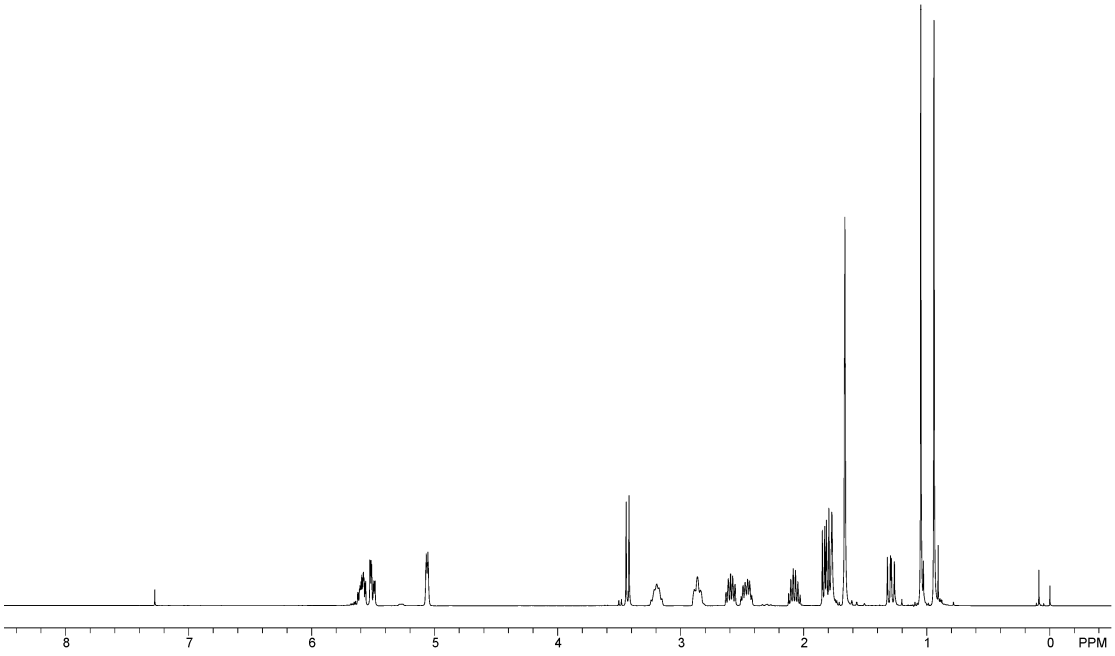

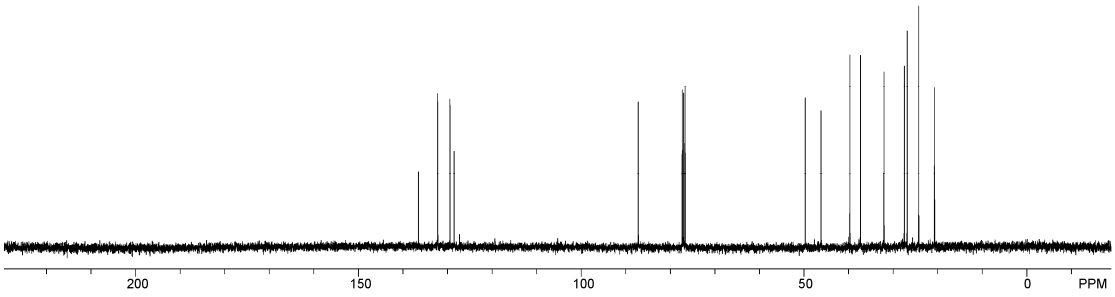

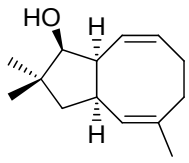

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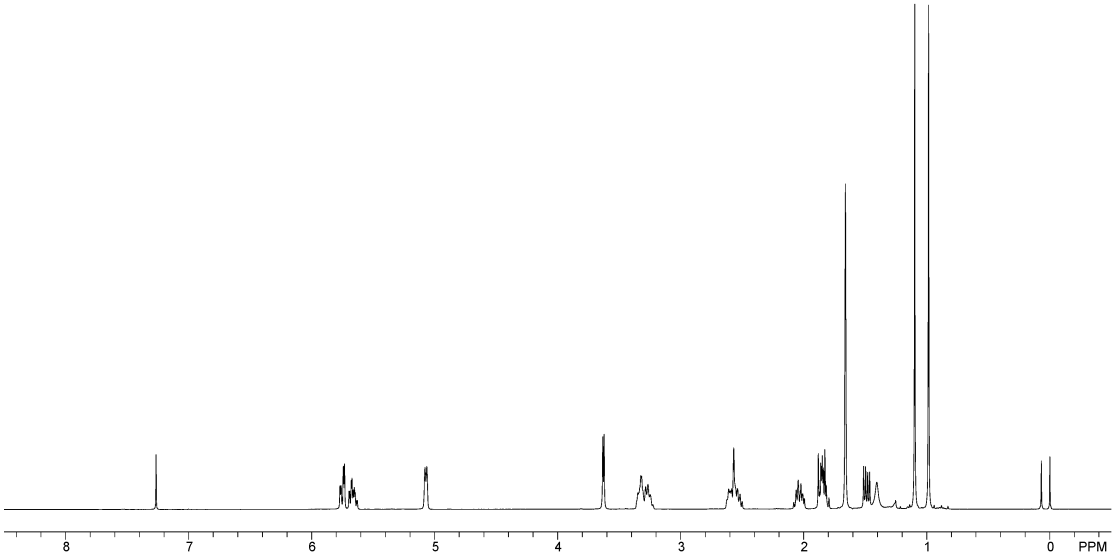

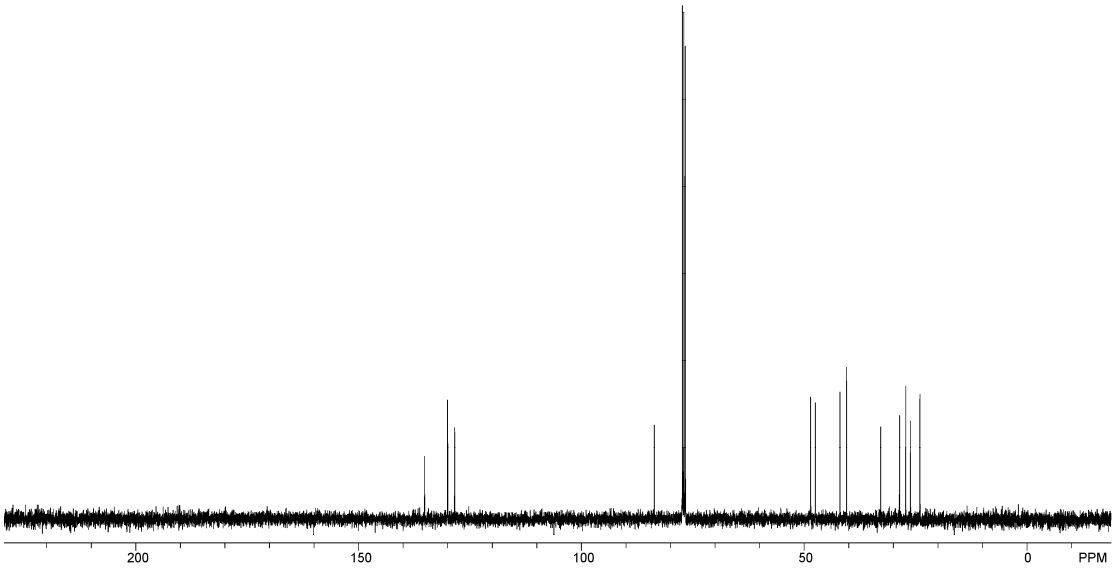

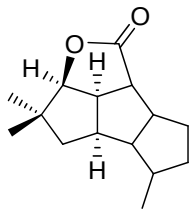

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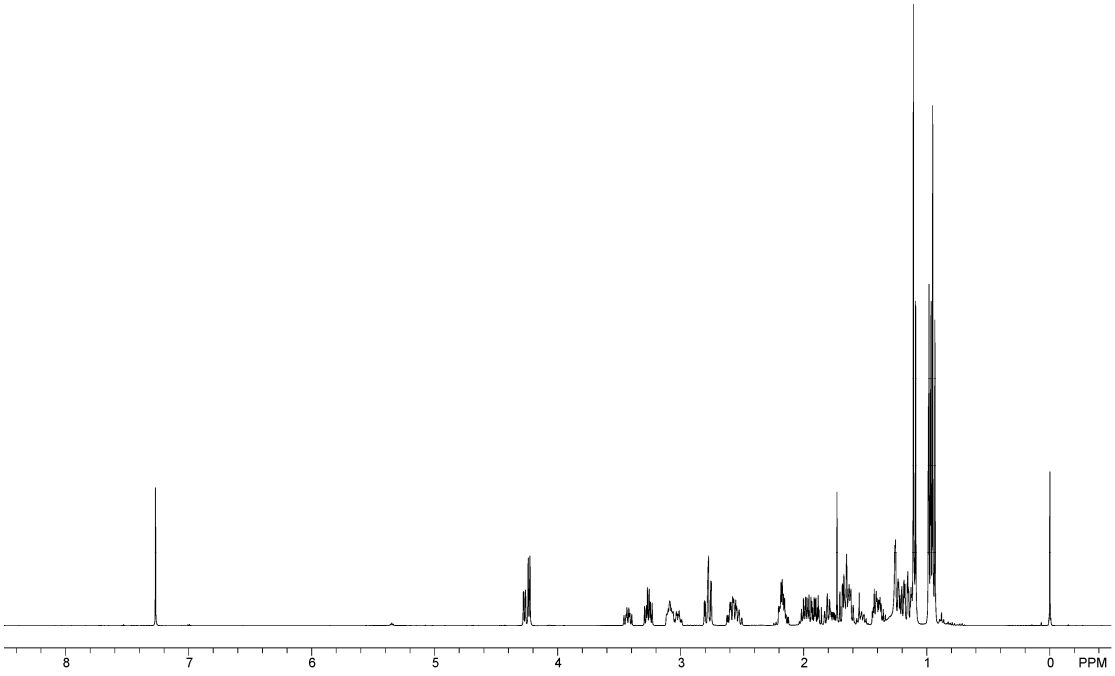

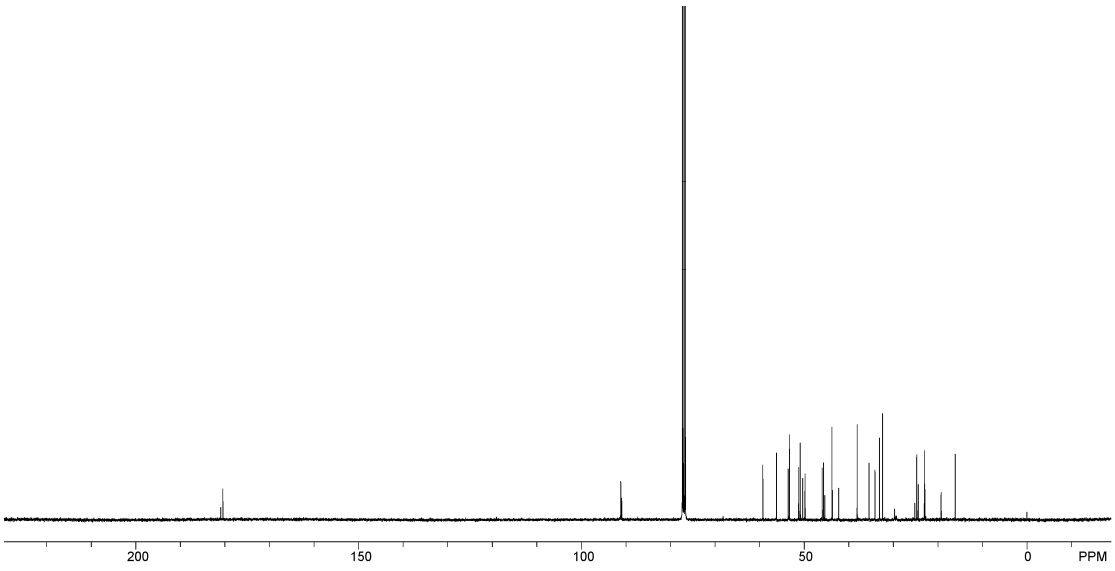

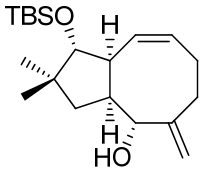

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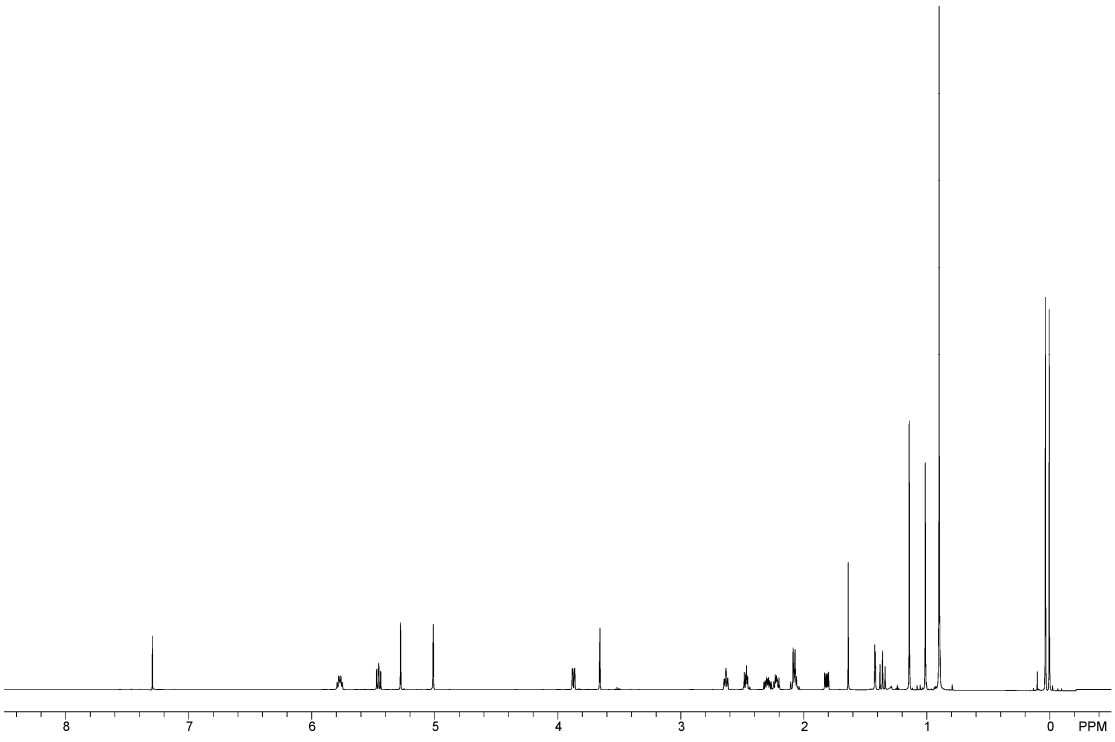

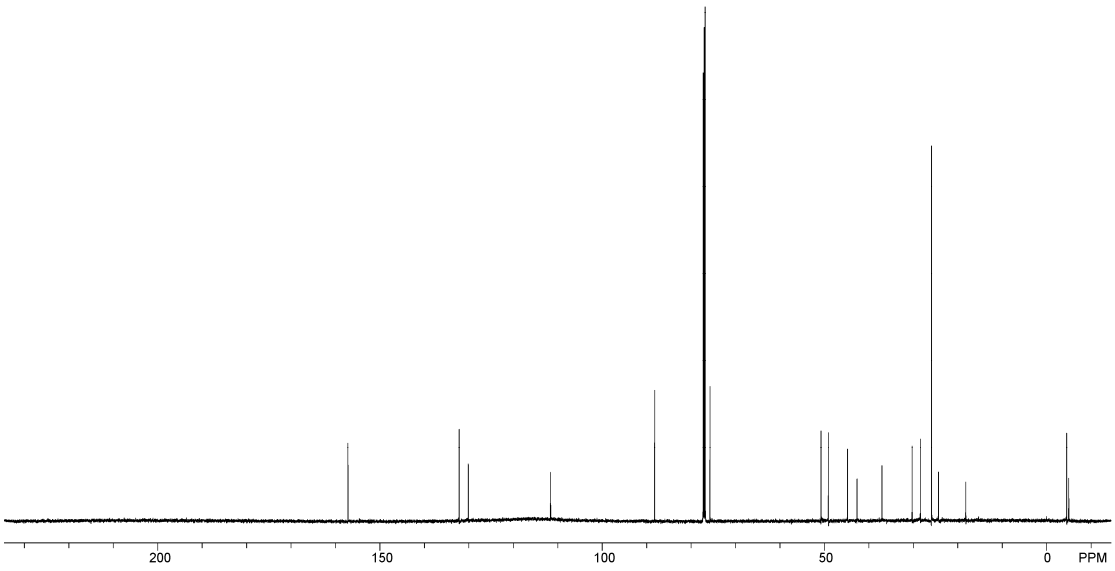

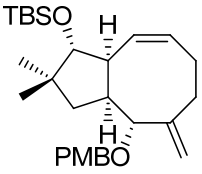

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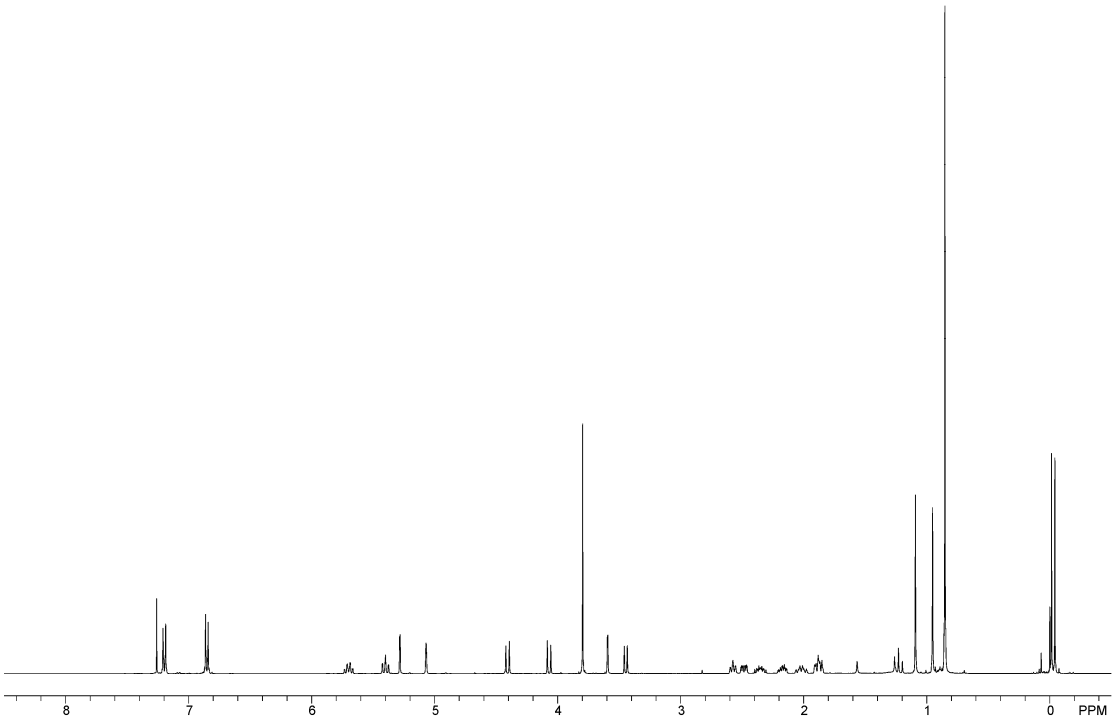

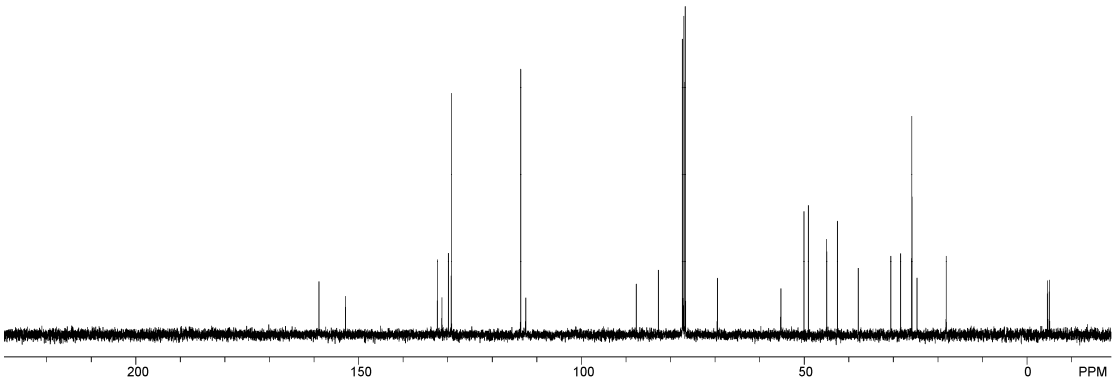

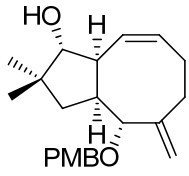

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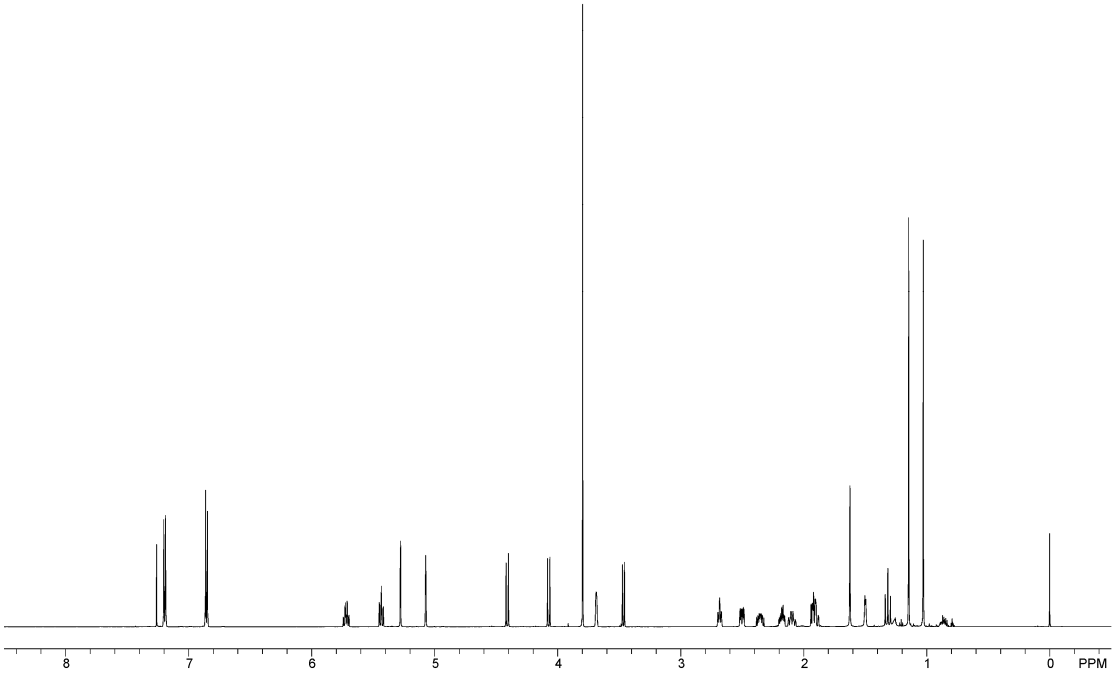

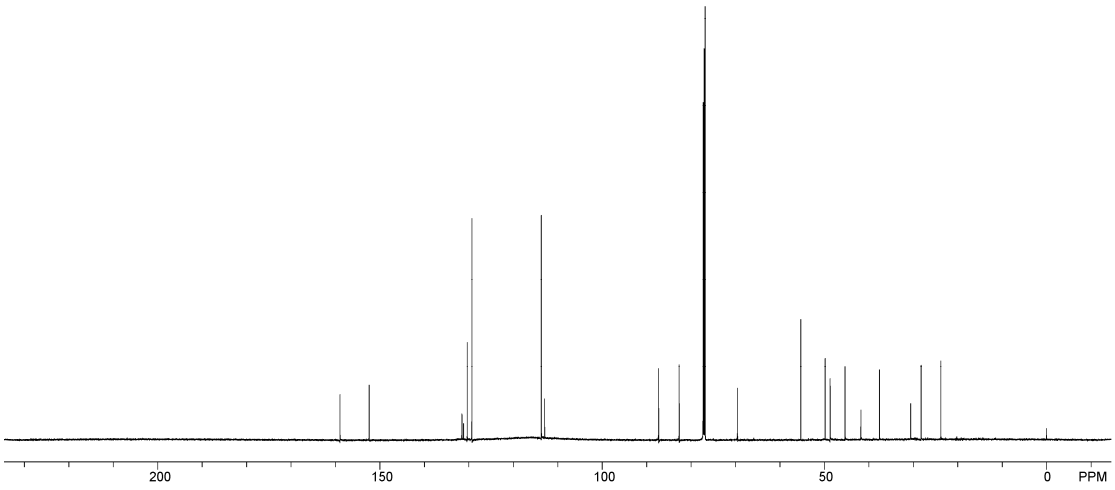

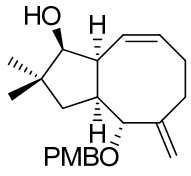

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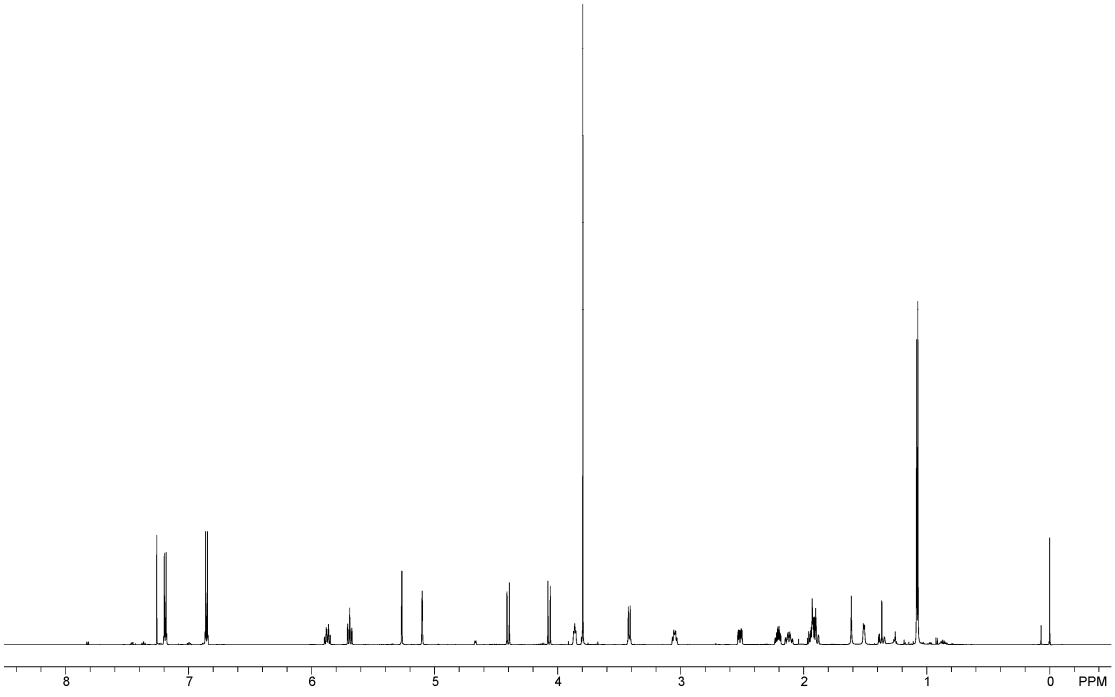

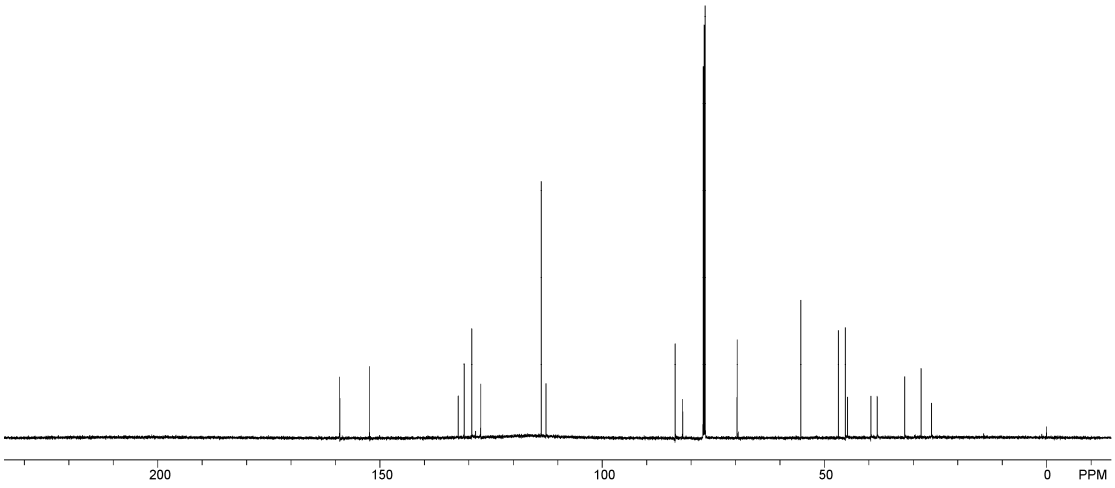

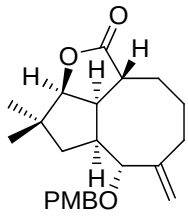

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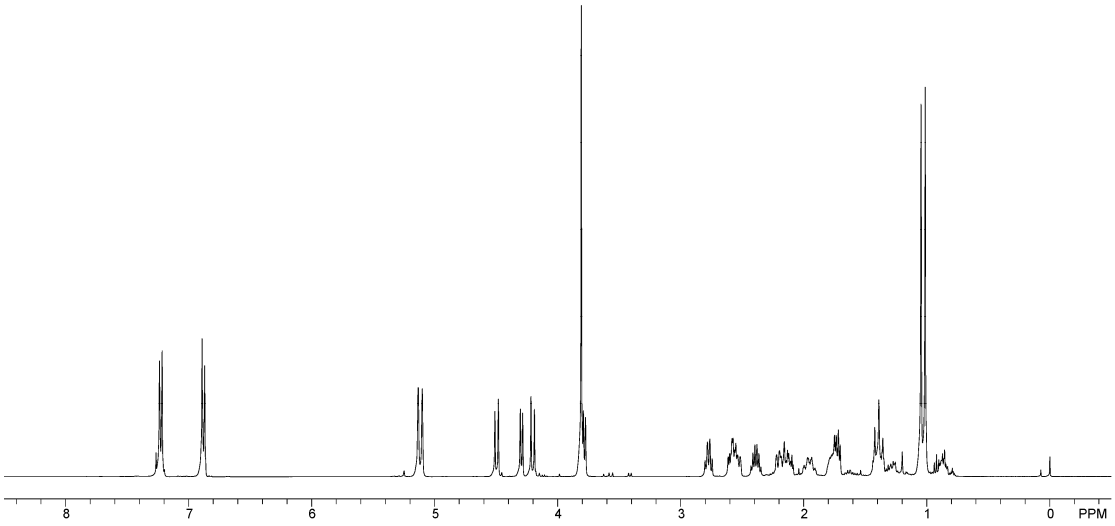

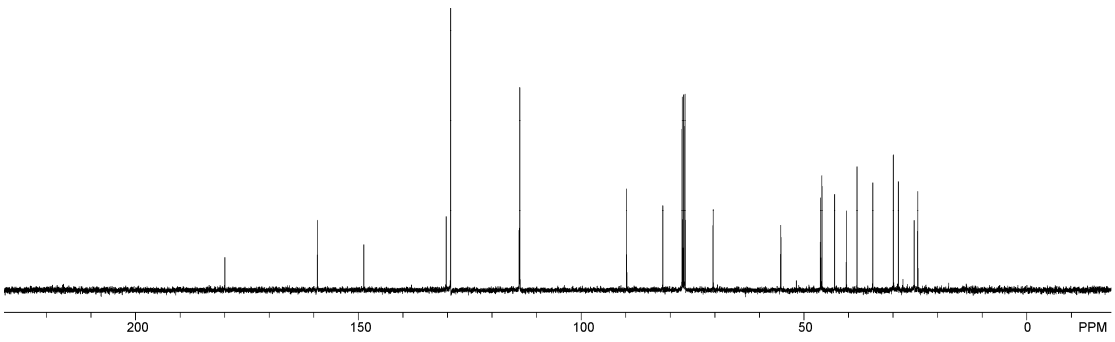

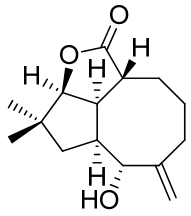
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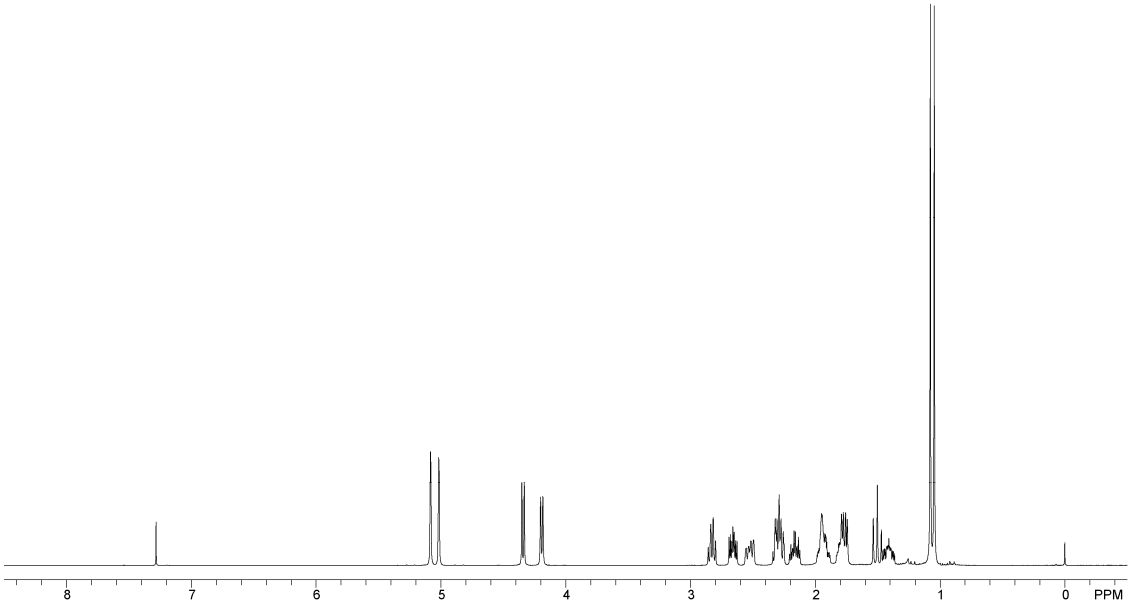
O
H
H
H
H
HO

70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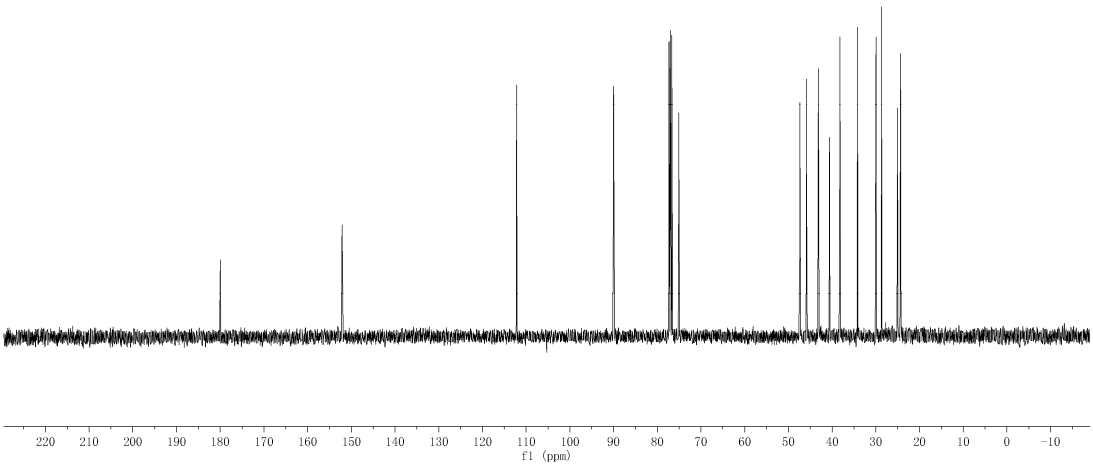
6
5
4
3
2
1
0
PPM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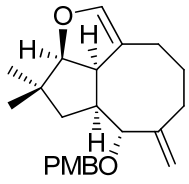
40
30
20
10
0
-10
f1 (ppm)



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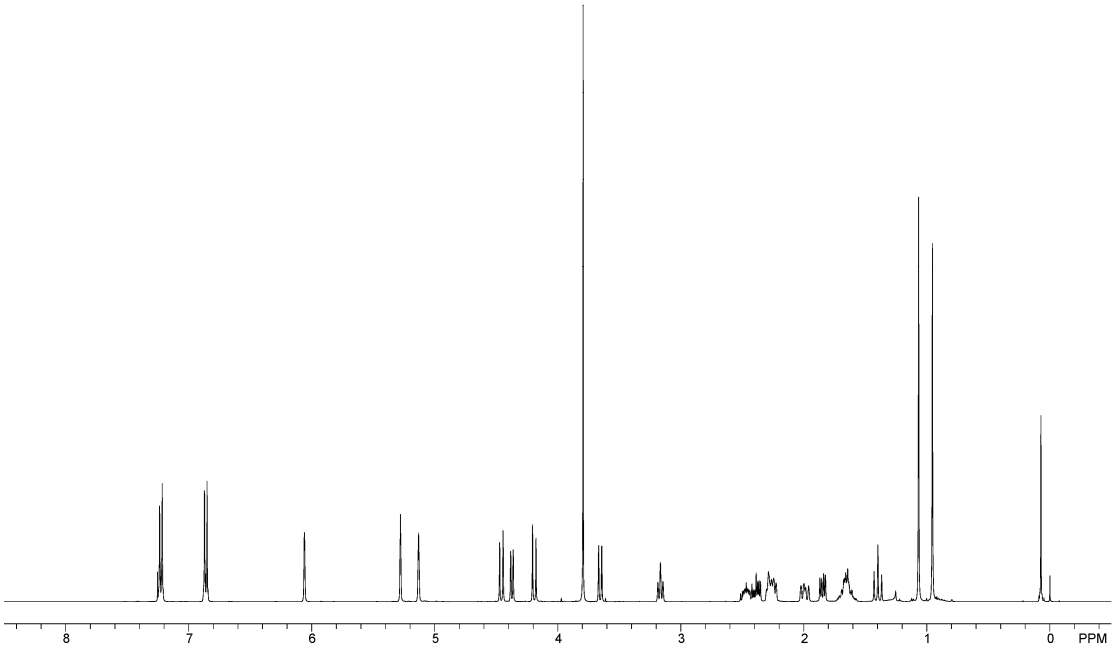

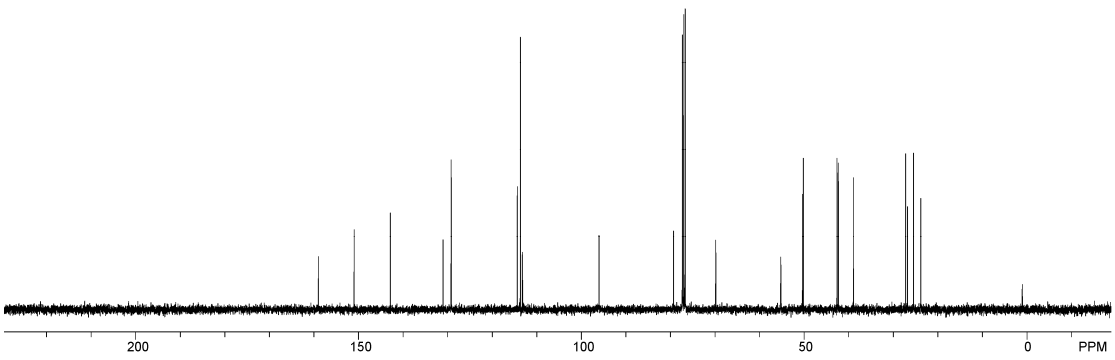

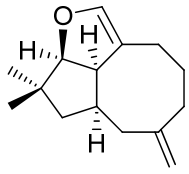

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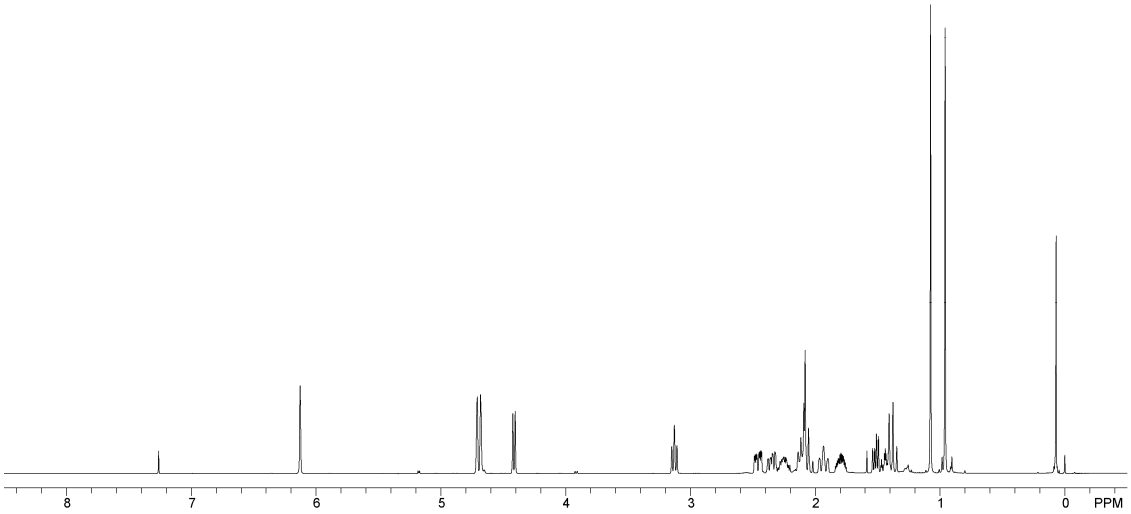

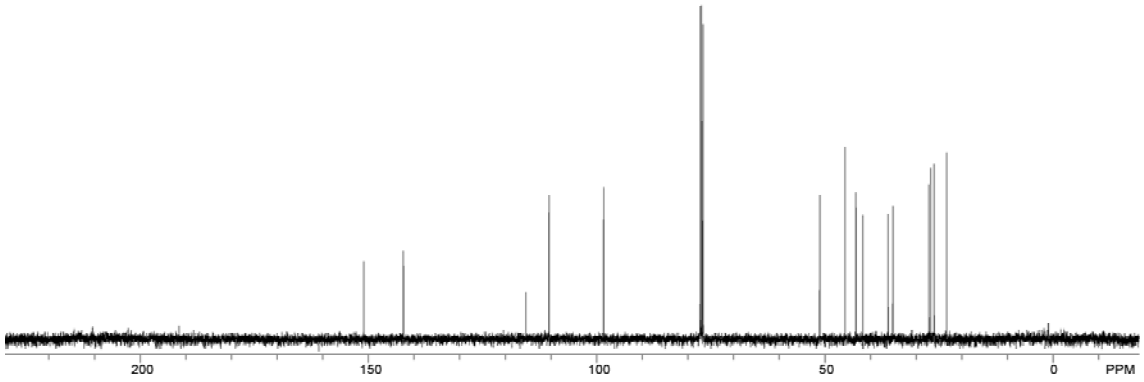

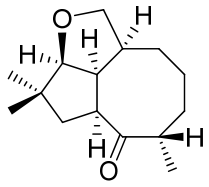

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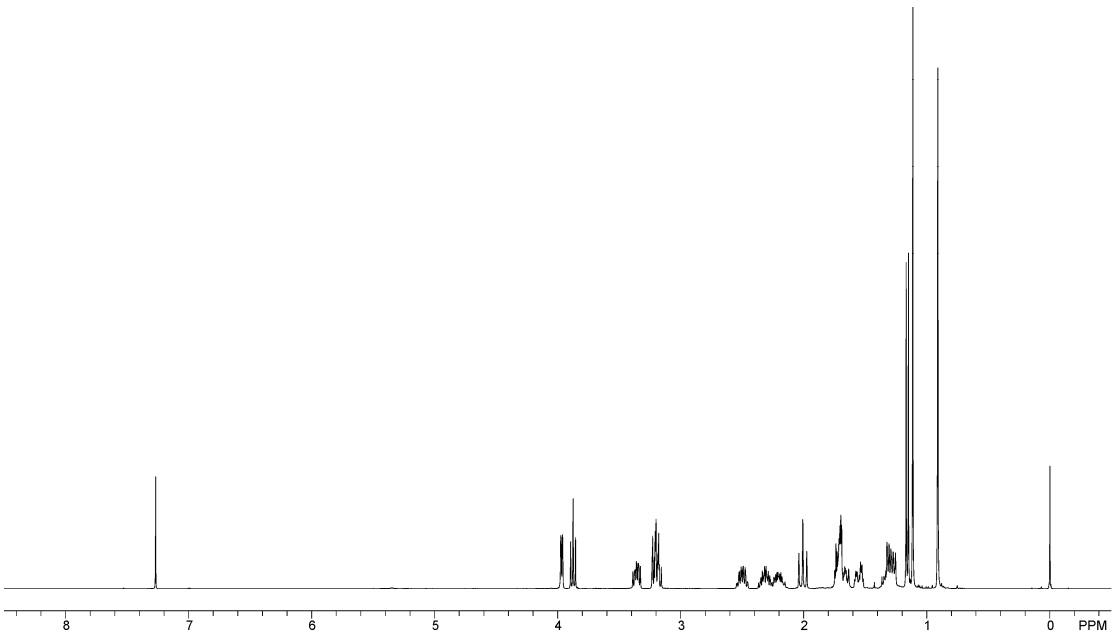

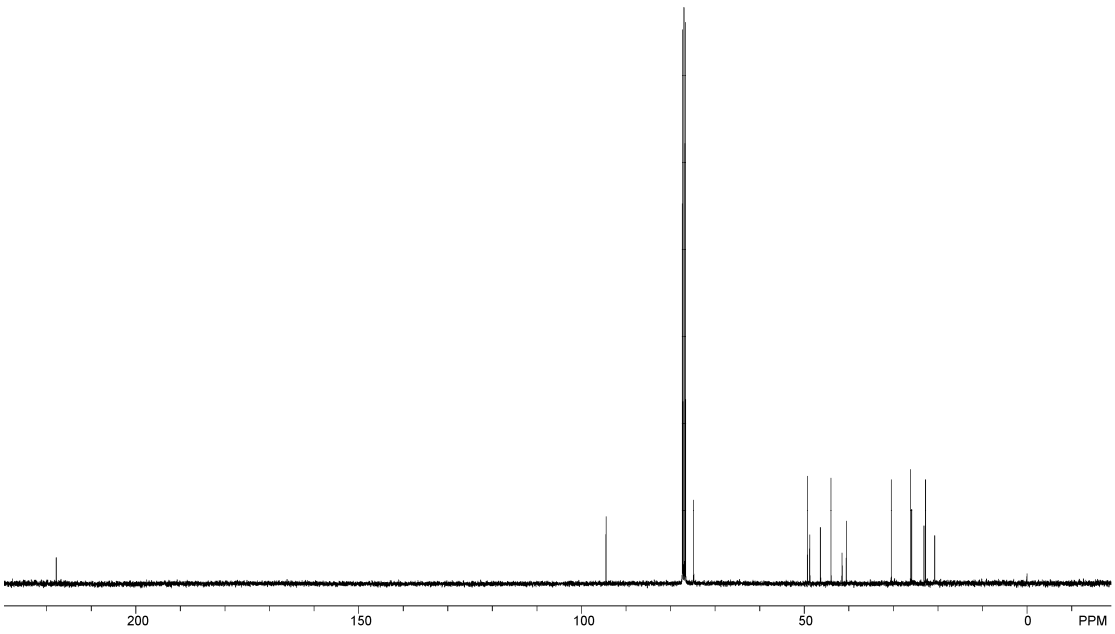

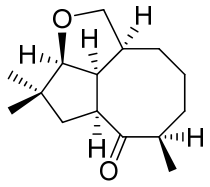

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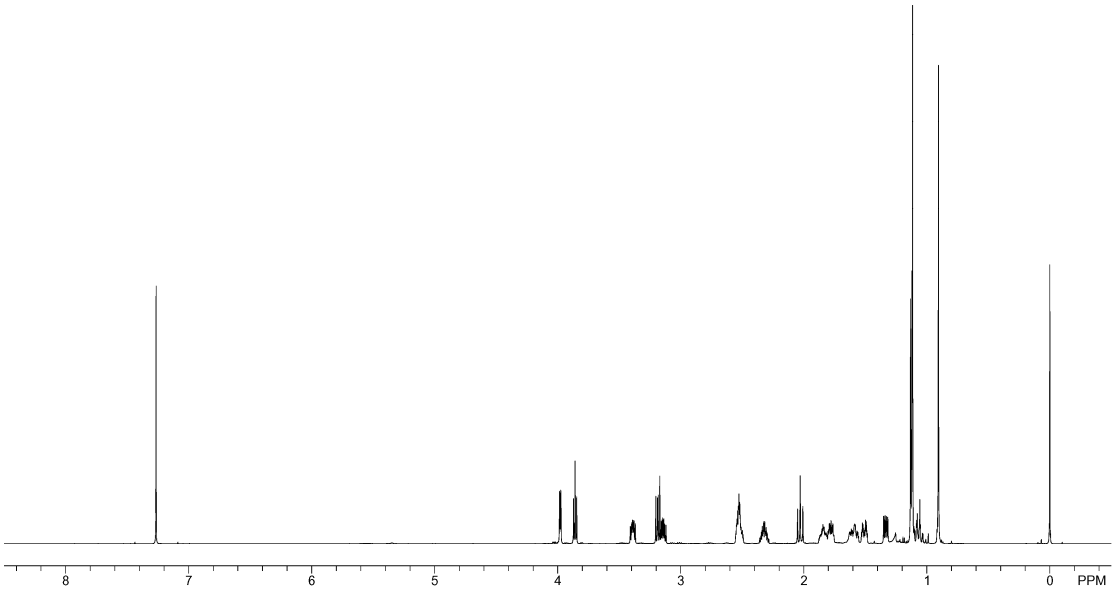

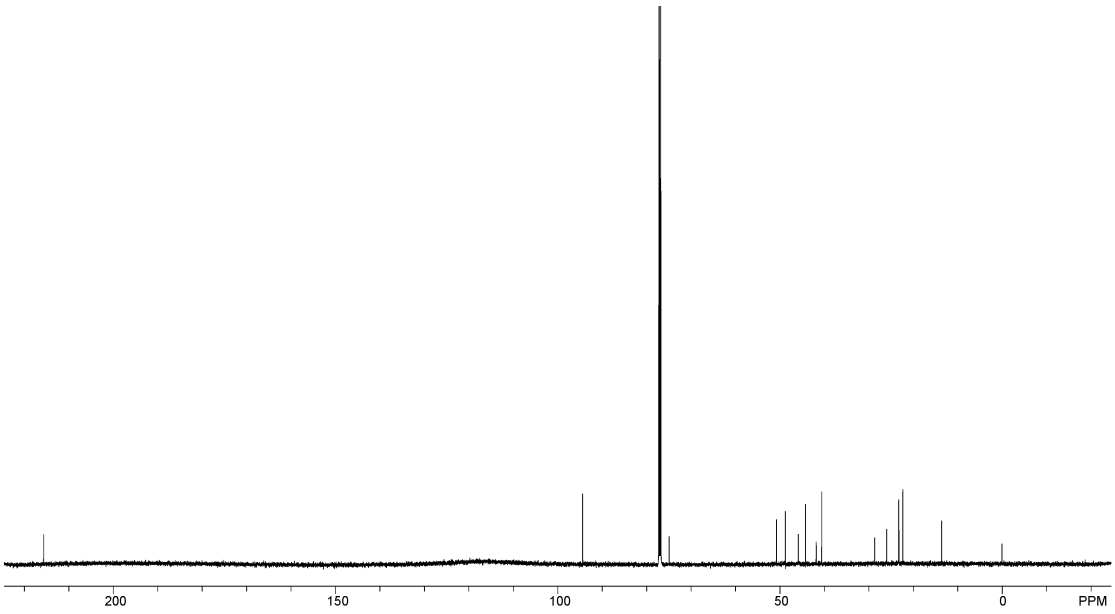

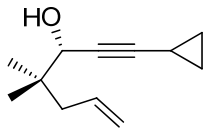

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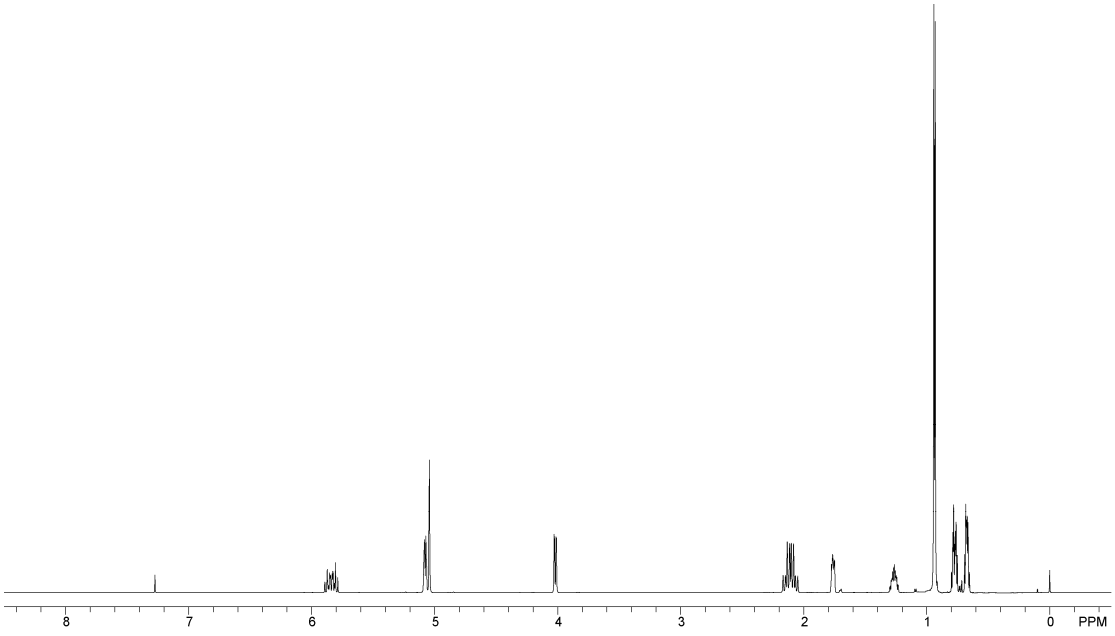

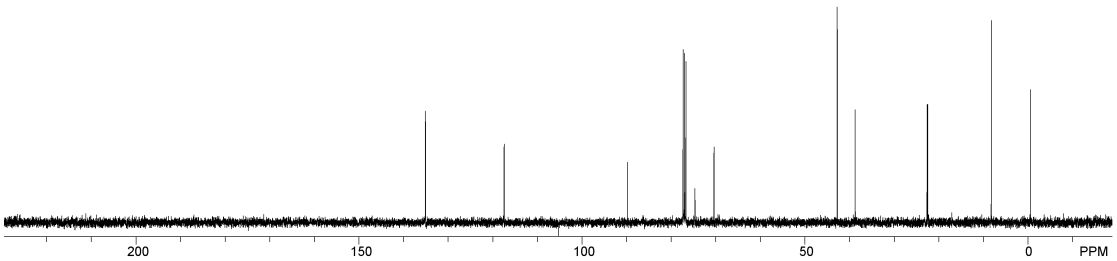

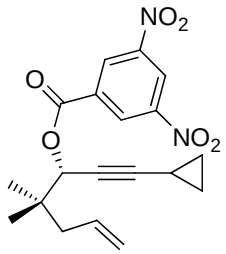

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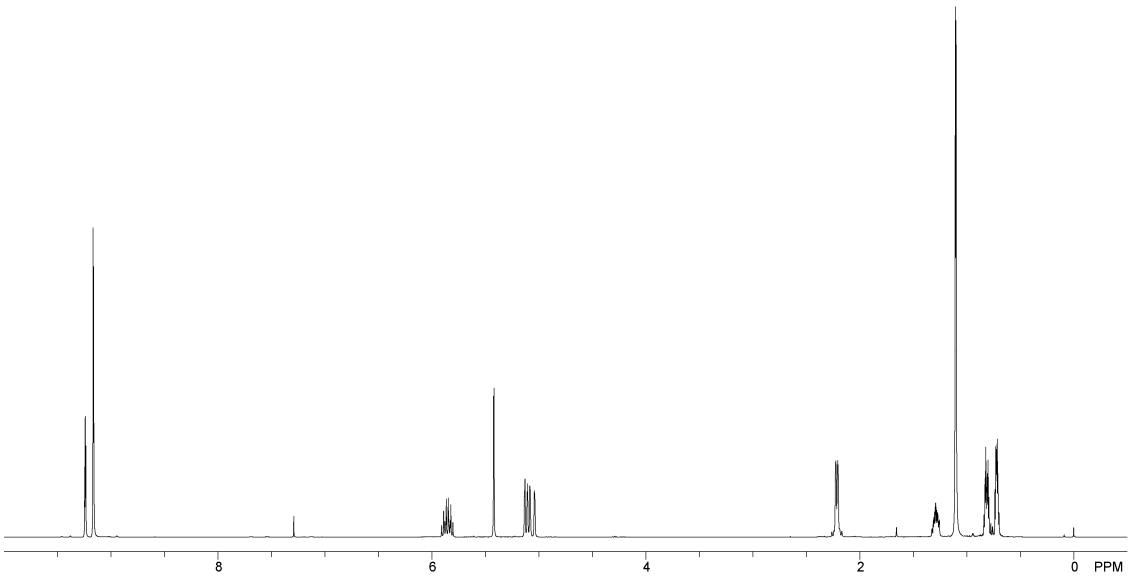

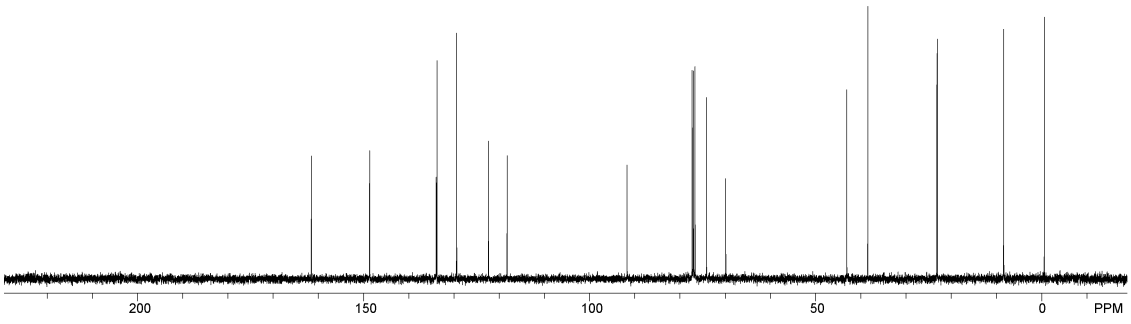

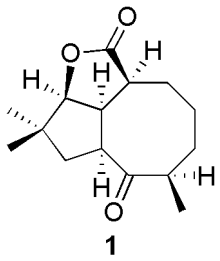

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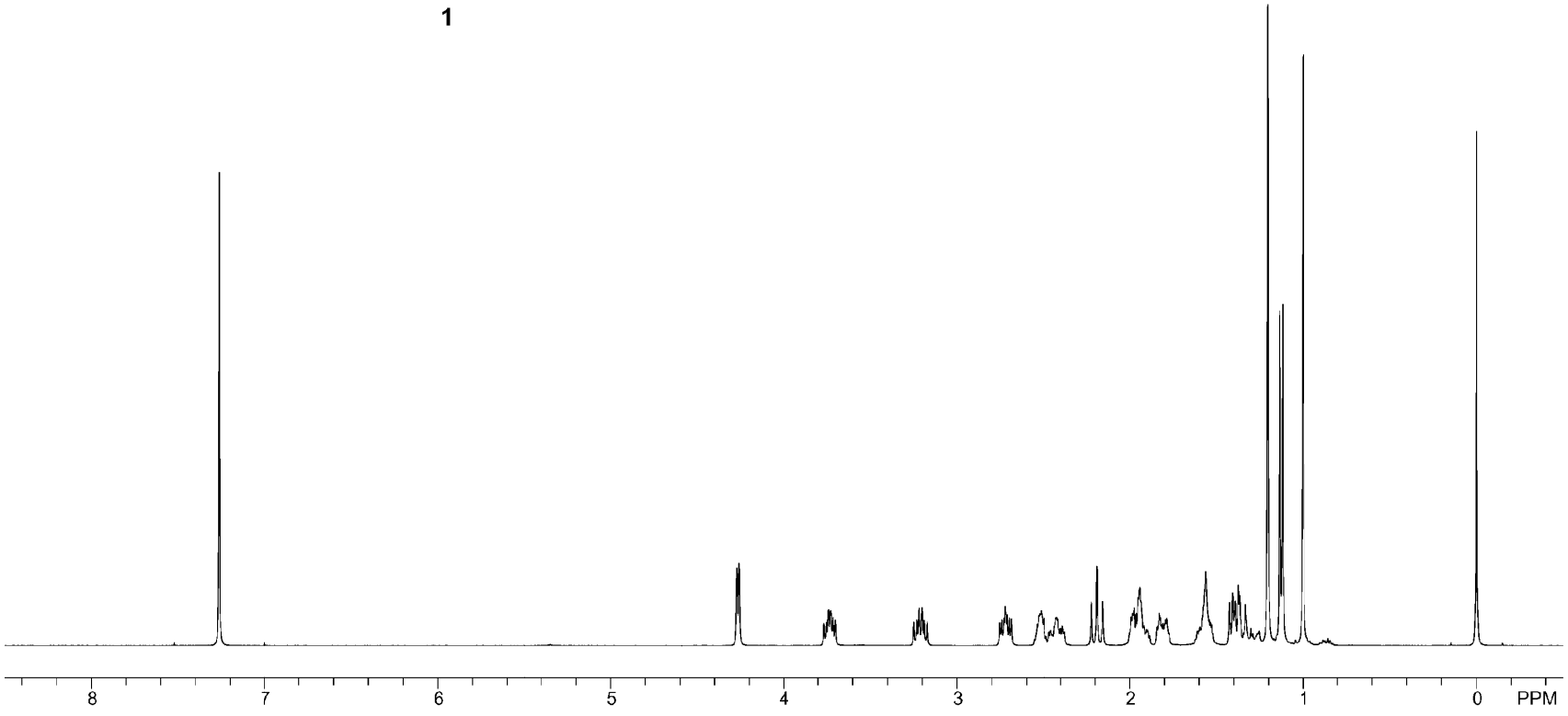

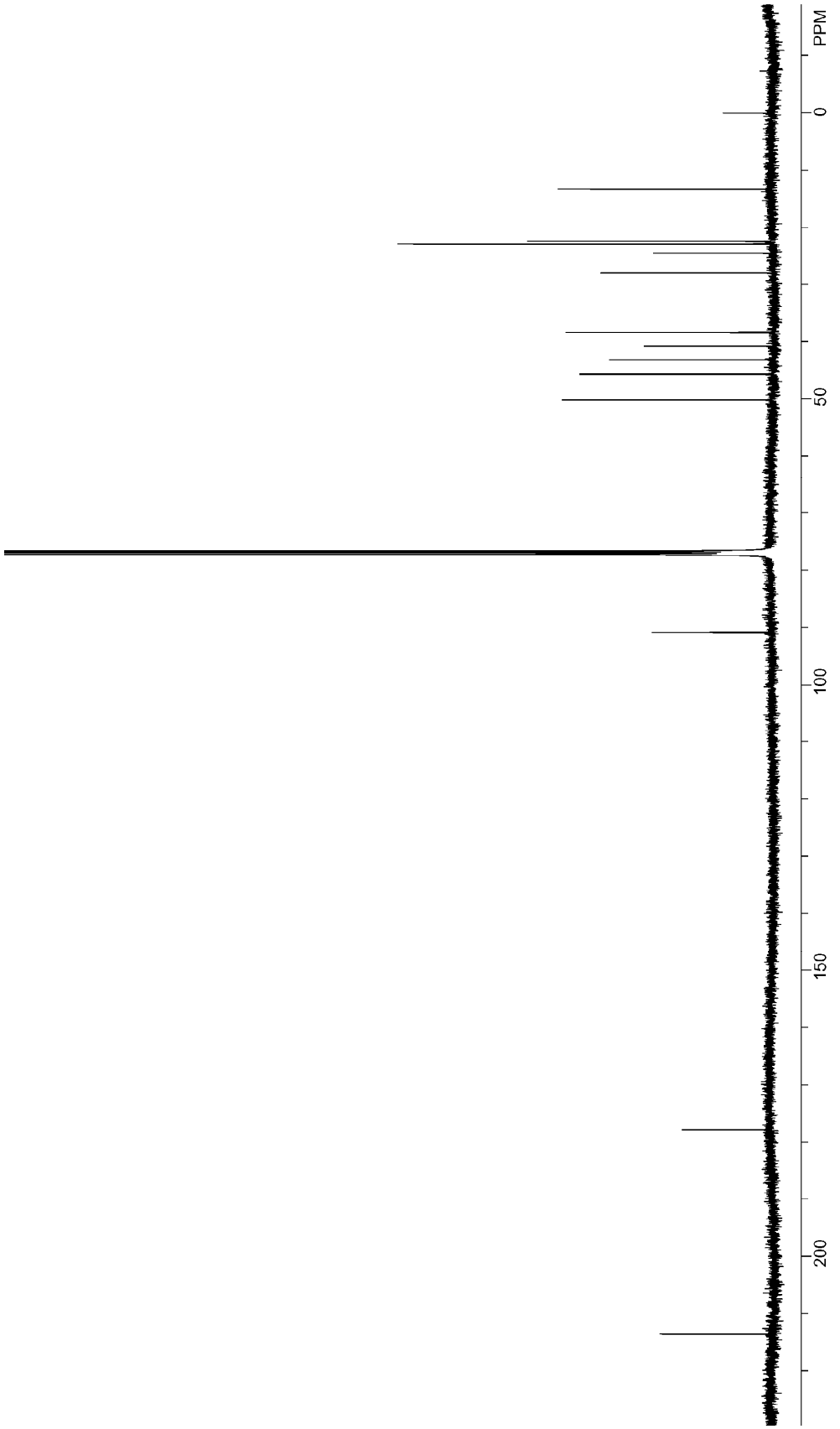
PPM
0
50
100
150
200

4. Computational Details and References

All DFT calculations were performed with the Gaussian 03 program package.[14] The geometry optimization of all the minima and transition states involved were performed at the B3LYP levels of theory (UB3LYP: for radical transition states).[15] The LANL2DZ basis set and pseudopotential were used for rhodium,[16] and the 6-31G(d) basis set for the other atoms.[17] The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibration energy (ZPVE) and thermal corrections at 298 K. Solvent effects were computed at the same level using the gas-phase optimized structures. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the CPCM model,[18] where UAKS radii were used. All computed energies of stationary points are given in Table S1.

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[15] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

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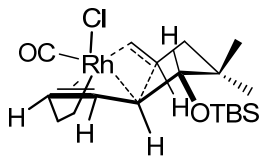
[18] (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669. (c) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70.

5. Coordinates of DFT-Computed Stationary Points

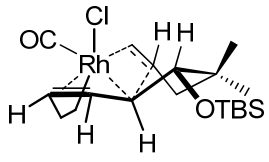


TS-*trans*$_{1,2}$-*cis*$_{2,9}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.340480	-0.781869	0.552236
2	8	0	-5.427411	-1.006624	0.859275
3	45	0	-2.603066	-0.408981	0.078776
4	6	0	-0.268434	0.122032	-0.679941
5	6	0	0.826155	1.036557	-0.079246
6	8	0	2.087305	0.433171	-0.320068
7	6	0	-2.978974	1.384291	-0.835043
8	6	0	-1.542530	1.479859	-1.175988
9	6	0	-0.804252	2.692280	-0.619960
10	6	0	0.711709	2.455064	-0.681881
11	6	0	1.244333	2.509579	-2.126680
12	6	0	-0.424896	-1.115638	0.149621
13	6	0	-0.954517	-2.297369	-0.289958
14	6	0	-1.570433	-2.465752	-1.668945
15	6	0	-2.767036	-1.497496	-1.735118
16	17	0	-2.136670	0.724316	2.271880
17	6	0	1.459393	3.490939	0.170369
18	1	0	-0.951910	-3.143196	0.394533
19	1	0	-2.717409	-0.794543	-2.572866
20	1	0	-0.821995	-2.251874	-2.444771
21	1	0	-3.717268	-2.031355	-1.781328
22	1	0	-1.882645	-3.504780	-1.813161
23	1	0	0.623916	1.112876	0.997415
24	1	0	-1.119183	2.841742	0.419661
25	1	0	-1.099589	3.585093	-1.187483
26	1	0	-1.394976	1.336642	-2.245390
27	1	0	-3.662057	1.261841	-1.675077
28	1	0	-3.333481	2.083691	-0.079363
29	1	0	-0.022045	-0.162496	-1.702727
30	1	0	-0.070065	-1.056117	1.172921
31	1	0	0.746062	1.798120	-2.794895
32	1	0	2.313757	2.281722	-2.151019
33	1	0	1.098366	3.512998	-2.544141

34	1	0	1.295963	4.502917	-0.219469
35	1	0	2.537855	3.303499	0.163229
36	1	0	1.113848	3.473873	1.211154
37	14	0	3.283608	-0.088521	0.751115
38	6	0	4.341255	-1.297487	-0.290656
39	6	0	4.316466	1.376564	1.355566
40	6	0	2.536102	-0.937765	2.267995
41	1	0	3.319125	-1.126169	3.012735
42	1	0	1.777458	-0.312540	2.754517
43	1	0	2.070512	-1.900030	2.028341
44	1	0	5.169385	1.032340	1.953982
45	1	0	4.712589	1.972012	0.525456
46	1	0	3.724383	2.044814	1.991881
47	6	0	5.432322	-1.934772	0.597757
48	6	0	3.448737	-2.415295	-0.871419
49	6	0	5.015283	-0.542183	-1.457043
50	1	0	6.049042	-2.626868	0.006297
51	1	0	6.109025	-1.184667	1.025644
52	1	0	5.003102	-2.510959	1.426708
53	1	0	5.602246	-1.237925	-2.074439
54	1	0	4.275710	-0.063505	-2.109252
55	1	0	5.702914	0.234572	-1.100532
56	1	0	4.053512	-3.117234	-1.464003
57	1	0	2.953764	-2.997654	-0.084274
58	1	0	2.670593	-2.008389	-1.526414



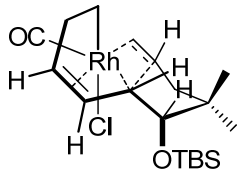
TS-*trans*$_{1,2}$-*trans*$_{2,9}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.418773	-0.865134	0.130406
2	45	0	-2.649897	-0.356549	-0.010176
3	17	0	-2.492666	-0.025489	2.485199
4	8	0	-5.525509	-1.166928	0.227985
5	6	0	-0.325698	0.245968	-0.447805
6	6	0	-0.478571	-1.123119	0.074561
7	6	0	-1.067350	-2.147528	-0.628013
8	6	0	-1.584760	-2.005998	-2.055926

9	6	0	-2.599890	-0.846709	-2.063451
10	6	0	-2.940042	1.685730	-0.317217
11	6	0	-1.513016	1.817237	-0.053740
12	6	0	-0.638862	2.704043	-0.924259
13	6	0	0.854078	2.462219	-0.570300
14	6	0	1.342966	3.515629	0.440359
15	6	0	0.888710	1.033138	0.079672
16	8	0	2.072456	0.325661	-0.242062
17	6	0	1.712987	2.531171	-1.843107
18	1	0	0.786183	1.128139	1.169810
19	1	0	-1.121873	-3.121965	-0.147634
20	1	0	-2.268177	0.030503	-2.628187
21	1	0	-0.749077	-1.849362	-2.753672
22	1	0	-3.576994	-1.153570	-2.439463
23	1	0	-2.064003	-2.944463	-2.350831
24	1	0	-0.922795	3.750637	-0.752558
25	1	0	-0.836468	2.500762	-1.984191
26	1	0	-1.312505	1.905698	1.012905
27	1	0	-3.294331	1.933019	-1.318555
28	1	0	-3.596174	2.007621	0.488441
29	1	0	-0.348848	0.275078	-1.536640
30	1	0	-0.153697	-1.307476	1.093565
31	1	0	1.448915	1.741466	-2.555412
32	1	0	2.777316	2.428683	-1.615300
33	1	0	1.560738	3.497359	-2.339893
34	1	0	1.353673	4.514513	-0.011947
35	1	0	2.360573	3.293527	0.779332
36	1	0	0.695637	3.555670	1.325259
37	14	0	3.272350	-0.274725	0.786653
38	6	0	4.468902	-1.186933	-0.391529
39	6	0	4.124571	1.148117	1.696275
40	6	0	2.539863	-1.443185	2.079896
41	1	0	4.963584	0.778449	2.298602
42	1	0	4.516954	1.902744	1.005721
43	1	0	3.434044	1.651058	2.384106
44	1	0	3.319614	-1.783792	2.772456
45	1	0	1.769824	-0.949413	2.685319
46	1	0	2.088087	-2.332560	1.627146
47	6	0	5.613555	-1.832101	0.421964
48	6	0	3.710260	-2.292951	-1.157431
49	6	0	5.073477	-0.197884	-1.412148
50	1	0	5.760015	-0.724205	-2.091186
51	1	0	4.298283	0.274342	-2.025940
52	1	0	5.649128	0.598059	-0.923181

53	1	0	6.304976	-2.359914	-0.250583
54	1	0	6.202950	-1.086887	0.970611
55	1	0	5.243487	-2.567272	1.147344
56	1	0	4.389690	-2.812211	-1.848782
57	1	0	3.295243	-3.049740	-0.480203
58	1	0	2.883816	-1.880461	-1.746663

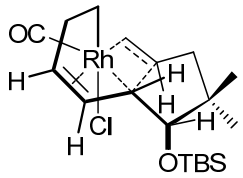


TS-*cis*$_{1,2}$-*cis*$_{2,9}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.854162	-1.392760	-0.584543
2	45	0	-2.389629	-0.431237	-0.040188
3	6	0	-1.520965	-0.705082	2.287717
4	6	0	-2.681487	0.161637	2.756110
5	6	0	-3.483824	0.540107	1.496037
6	8	0	-4.768619	-2.000057	-0.933676
7	17	0	-0.958687	-1.682693	-1.666821
8	6	0	-2.593629	1.113165	-1.374025
9	6	0	-1.465719	1.808661	-0.722047
10	6	0	-0.255236	2.125926	-1.577067
11	6	0	0.887187	2.606348	-0.669078
12	6	0	2.188442	2.751258	-1.469329
13	6	0	-0.575688	-0.285959	1.389068
14	6	0	-0.500822	1.084932	0.817200
15	6	0	0.955539	1.506692	0.431980
16	8	0	1.721646	0.401290	0.010774
17	6	0	0.566184	3.967894	-0.013156
18	1	0	-1.436853	-1.719660	2.671733
19	1	0	-3.496556	1.615478	1.288788
20	1	0	-2.311093	1.041501	3.302414
21	1	0	-4.513680	0.183275	1.543549
22	1	0	-3.295001	-0.406198	3.462271
23	1	0	1.386789	1.941301	1.349287
24	1	0	0.047873	1.221047	-2.117020
25	1	0	-0.522521	2.889238	-2.320524
26	1	0	-1.832151	2.668014	-0.162207

27	1	0	-3.566099	1.594296	-1.275158
28	1	0	-2.395966	0.712842	-2.367163
29	1	0	-0.922829	1.798431	1.524267
30	1	0	0.179034	-0.985148	1.052891
31	1	0	-0.304010	3.939603	0.651996
32	1	0	1.417944	4.314511	0.584139
33	1	0	0.369330	4.727245	-0.779063
34	1	0	2.060516	3.513982	-2.247154
35	1	0	3.020004	3.069862	-0.831538
36	1	0	2.465584	1.812682	-1.954108
37	14	0	3.138082	-0.205119	0.709783
38	6	0	3.679977	-1.638675	-0.428359
39	6	0	4.459039	1.148446	0.820545
40	6	0	2.796750	-0.786245	2.481469
41	1	0	3.726535	-1.125930	2.954962
42	1	0	2.399489	0.027064	3.101976
43	1	0	2.082953	-1.615488	2.524569
44	1	0	5.334394	0.778593	1.368481
45	1	0	4.799872	1.482879	-0.164900
46	1	0	4.090295	2.028751	1.361836
47	6	0	5.066914	-2.149017	0.023358
48	6	0	2.662001	-2.798749	-0.356216
49	6	0	3.768901	-1.147908	-1.890047
50	1	0	4.110828	-1.964462	-2.542137
51	1	0	2.792378	-0.816809	-2.257975
52	1	0	4.480234	-0.319825	-2.006847
53	1	0	2.978653	-3.616109	-1.020301
54	1	0	2.590223	-3.217694	0.655744
55	1	0	1.660504	-2.487804	-0.674760
56	1	0	5.382537	-2.990936	-0.609067
57	1	0	5.840419	-1.374980	-0.055868
58	1	0	5.057571	-2.510321	1.059857



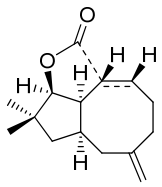
TS-*cis*$_{1,2}$-*trans*$_{2,9}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-3.936488	-1.366038	-0.404403
2	45	0	-2.398442	-0.413488	-0.044987
3	17	0	-1.040324	-2.355309	-0.890771
4	8	0	-4.891975	-1.961848	-0.644396
5	6	0	-0.534079	1.057414	0.584848
6	6	0	-0.773482	-0.017297	1.557904
7	6	0	-1.900493	-0.092098	2.343864
8	6	0	-3.002965	0.964300	2.349606
9	6	0	-3.501633	1.120012	0.899531
10	6	0	-2.188280	0.558675	-1.878557
11	6	0	-0.865200	0.947587	-1.408054
12	6	0	-0.405287	2.385536	-1.565227
13	6	0	0.886568	2.633418	-0.732876
14	6	0	2.123238	2.609526	-1.644539
15	6	0	0.924451	1.490159	0.346455
16	8	0	1.732884	0.396422	-0.021707
17	6	0	0.808640	4.000845	-0.025797
18	1	0	-1.975635	-0.926960	3.037129
19	1	0	-3.249767	2.082386	0.442140
20	1	0	-2.633825	1.906255	2.782621
21	1	0	-4.578979	0.969323	0.814425
22	1	0	-3.811513	0.621138	3.002319
23	1	0	1.277517	1.921155	1.297564
24	1	0	-0.221568	2.571631	-2.631269
25	1	0	-1.212475	3.068314	-1.269064
26	1	0	-0.103107	0.201383	-1.623524
27	1	0	-2.918088	1.352913	-2.039363
28	1	0	-2.210404	-0.236838	-2.619851
29	1	0	-1.129134	1.943311	0.802300
30	1	0	-0.042223	-0.816876	1.604540
31	1	0	-0.018753	4.043746	0.694022
32	1	0	1.736347	4.221830	0.515538
33	1	0	0.650120	4.804376	-0.754778
34	1	0	2.065059	3.432487	-2.367038
35	1	0	3.046107	2.737178	-1.070088
36	1	0	2.199850	1.670039	-2.197615
37	14	0	3.118101	-0.191783	0.757222
38	6	0	3.784679	-1.575424	-0.375724
39	6	0	4.375595	1.208517	0.983681
40	6	0	2.679630	-0.838927	2.481416
41	1	0	5.209485	0.873280	1.612479
42	1	0	4.796295	1.551519	0.031993
43	1	0	3.928049	2.077613	1.482188
44	1	0	3.582775	-1.191122	2.995719

45	1	0	2.237402	-0.055590	3.109807
46	1	0	1.975973	-1.677402	2.443836
47	6	0	5.190778	-1.997062	0.109639
48	6	0	2.845111	-2.801329	-0.334297
49	6	0	3.886114	-1.071030	-1.831545
50	1	0	4.309790	-1.856133	-2.474103
51	1	0	2.901569	-0.810049	-2.233155
52	1	0	4.535371	-0.190532	-1.922702
53	1	0	3.212389	-3.577972	-1.020757
54	1	0	2.805572	-3.249147	0.666279
55	1	0	1.819942	-2.553217	-0.630850
56	1	0	5.573048	-2.816840	-0.514940
57	1	0	5.915792	-1.175904	0.048503
58	1	0	5.180356	-2.360406	1.145381

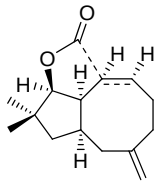


TS-*trans*-37

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.657065	-0.004135	-0.753394
2	6	0	-1.859338	-1.280395	0.154273
3	6	0	-0.404890	-1.837537	0.320281
4	6	0	0.399302	-1.190248	-0.821175
5	6	0	-0.140751	0.260379	-0.818142
6	6	0	1.931829	-1.421379	-0.867759
7	6	0	2.811805	-0.790117	0.199810
8	6	0	3.503995	0.520641	-0.131839
9	6	0	2.548815	1.680955	-0.543644
10	6	0	1.441752	1.797020	0.457844
11	6	0	0.252972	1.131846	0.360540
12	6	0	3.031595	-1.406028	1.367122
13	6	0	-2.744254	-2.295294	-0.594929
14	6	0	-2.509299	-0.960309	1.509679
15	8	0	-2.404735	1.149945	-0.304636
16	6	0	-1.668241	2.242623	-0.017078
17	8	0	-2.100751	3.297484	0.329806
18	1	0	-2.043498	-0.210535	-1.756457

19	1	0	-0.381895	-2.932993	0.279866
20	1	0	0.015131	-1.539593	1.288119
21	1	0	0.031991	-1.638017	-1.758902
22	1	0	0.123224	0.775335	-1.748719
23	1	0	2.282646	-1.091397	-1.855713
24	1	0	2.081641	-2.508624	-0.846752
25	1	0	4.216424	0.355615	-0.955050
26	1	0	4.096474	0.836771	0.734922
27	1	0	2.152814	1.486354	-1.546944
28	1	0	3.135634	2.605381	-0.610919
29	1	0	1.670424	2.309729	1.390876
30	1	0	-0.274630	0.961306	1.297165
31	1	0	3.663440	-0.968415	2.136326
32	1	0	2.594116	-2.375215	1.596181
33	1	0	-2.897411	-3.198417	0.007248
34	1	0	-2.291347	-2.601761	-1.546190
35	1	0	-3.729673	-1.868002	-0.817335
36	1	0	-2.583652	-1.876675	2.107349
37	1	0	-3.517497	-0.553320	1.383916
38	1	0	-1.929828	-0.235099	2.090123

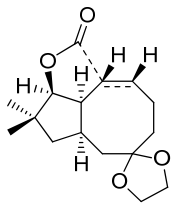


TS-*cis*-38

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.758705	-0.109508	0.437129
2	6	0	1.597662	-1.482861	-0.266848
3	6	0	0.062950	-1.666059	-0.331560
4	6	0	-0.471991	-1.084918	0.989391
5	6	0	0.487571	0.118901	1.329026
6	6	0	-2.017361	-0.897318	1.102430
7	6	0	-2.795030	-0.601819	-0.169030
8	6	0	-2.920436	0.827980	-0.643890
9	6	0	-1.572879	1.579498	-0.792436
10	6	0	-1.006768	2.097667	0.498203
11	6	0	-0.015756	1.556895	1.274852
12	6	0	-3.394030	-1.592934	-0.840075

13	6	0	2.244042	-2.560565	0.630864
14	6	0	2.252372	-1.537029	-1.655244
15	8	0	1.885701	0.943295	-0.546682
16	6	0	1.679330	2.170102	-0.023762
17	8	0	1.878960	3.206873	-0.581585
18	1	0	2.674675	-0.080067	1.037502
19	1	0	-0.221994	-2.715876	-0.469825
20	1	0	-0.339940	-1.119246	-1.190888
21	1	0	-0.241077	-1.826191	1.763626
22	1	0	0.806595	-0.018304	2.367728
23	1	0	-2.222805	-0.123786	1.853384
24	1	0	-2.416636	-1.832570	1.510875
25	1	0	-3.551815	1.390969	0.060478
26	1	0	-3.444227	0.839123	-1.606902
27	1	0	-1.740579	2.441299	-1.450947
28	1	0	-0.849207	0.939678	-1.308617
29	1	0	-1.341450	3.094993	0.781834
30	1	0	0.240031	2.137128	2.158943
31	1	0	-3.953579	-1.410911	-1.754616
32	1	0	-3.350947	-2.624815	-0.498436
33	1	0	2.050645	-3.559863	0.224507
34	1	0	1.862729	-2.541119	1.658137
35	1	0	3.330842	-2.423982	0.680074
36	1	0	2.108632	-2.530811	-2.096392
37	1	0	3.330919	-1.349979	-1.596156
38	1	0	1.821617	-0.795217	-2.332480

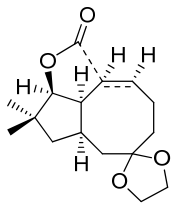


TS-*trans*-43

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.331276	-0.247668	-0.704341
2	6	0	-2.088446	-1.617656	0.040967
3	6	0	-0.530946	-1.773965	0.011186
4	6	0	-0.057105	-0.814219	-1.098814
5	6	0	-0.954572	0.425271	-0.866034

6	6	0	1.460680	-0.655128	-1.344715
7	6	0	2.396919	0.085451	-0.359418
8	6	0	2.555950	1.605678	-0.591565
9	6	0	1.272608	2.467842	-0.696931
10	6	0	0.329196	2.185657	0.431839
11	6	0	-0.663257	1.252923	0.369206
12	6	0	-2.763792	-2.750234	-0.756288
13	6	0	-2.632857	-1.628410	1.478207
14	8	0	-3.292955	0.607124	-0.043753
15	6	0	-2.843089	1.832174	0.300039
16	8	0	-3.495437	2.687126	0.814320
17	1	0	-2.767646	-0.446754	-1.688397
18	1	0	-0.231151	-2.811092	-0.182024
19	1	0	-0.093382	-1.478232	0.969120
20	1	0	-0.415699	-1.246764	-2.047537
21	1	0	-0.948873	1.078710	-1.745818
22	1	0	1.604462	-0.192706	-2.330795
23	1	0	1.871711	-1.667263	-1.435993
24	1	0	3.139963	1.724605	-1.512285
25	1	0	3.177218	1.977142	0.231884
26	1	0	0.791304	2.278666	-1.663286
27	1	0	1.579355	3.521698	-0.705842
28	1	0	0.551150	2.645422	1.392841
29	1	0	-1.009633	0.860309	1.322785
30	1	0	-2.605468	-3.719064	-0.268298
31	1	0	-2.363285	-2.820957	-1.775341
32	1	0	-3.845474	-2.585394	-0.834130
33	1	0	-2.394158	-2.587645	1.953080
34	1	0	-3.719759	-1.500190	1.497767
35	1	0	-2.194065	-0.837781	2.095334
36	8	0	2.054562	-0.166548	1.010386
37	8	0	3.704406	-0.495023	-0.550215
38	6	0	3.015841	-1.063782	1.563068
39	1	0	3.123833	-0.837999	2.627884
40	1	0	2.692126	-2.108568	1.447359
41	6	0	4.257595	-0.769080	0.731133
42	1	0	4.944015	-1.615092	0.635760
43	1	0	4.808159	0.098396	1.124806

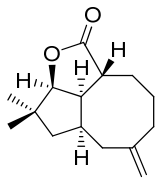


TS-*cis*-44

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.394549	0.499237	0.438813
2	6	0	-1.830345	1.816908	-0.153857
3	6	0	-0.307176	1.549910	-0.210616
4	6	0	0.002899	0.759408	1.076439
5	6	0	-1.265970	-0.144738	1.321234
6	6	0	1.428275	0.179765	1.290298
7	6	0	2.299163	-0.356490	0.130126
8	6	0	1.949437	-1.735523	-0.438908
9	6	0	0.464446	-1.953779	-0.793657
10	6	0	-0.353360	-2.399272	0.383424
11	6	0	-1.198386	-1.657742	1.163441
12	6	0	-2.162661	2.966694	0.822070
13	6	0	-2.410336	2.160358	-1.534311
14	8	0	-2.778953	-0.394764	-0.631204
15	6	0	-2.934843	-1.669104	-0.218692
16	8	0	-3.391710	-2.560704	-0.868940
17	1	0	-3.300853	0.684391	1.026028
18	1	0	0.272834	2.477587	-0.274892
19	1	0	-0.066596	0.974315	-1.107766
20	1	0	-0.068216	1.497910	1.884565
21	1	0	-1.560643	0.007512	2.365356
22	1	0	1.391615	-0.596740	2.064079
23	1	0	2.035546	0.986339	1.716094
24	1	0	2.266054	-2.483900	0.296398
25	1	0	2.573991	-1.871525	-1.328903
26	1	0	0.407232	-2.737539	-1.559551
27	1	0	0.048922	-1.052756	-1.254465
28	1	0	-0.340827	-3.471922	0.574438
29	1	0	-1.672510	-2.202014	1.977390
30	1	0	-1.680685	3.894711	0.493946
31	1	0	-1.831350	2.765783	1.847120
32	1	0	-3.244016	3.145619	0.855837
33	1	0	-1.973855	3.098430	-1.898357

34	1	0	-3.497872	2.292247	-1.490426
35	1	0	-2.198038	1.376620	-2.265632
36	8	0	2.353561	0.581551	-0.953425
37	8	0	3.640434	-0.430324	0.656329
38	6	0	3.578959	1.300646	-0.858382
39	1	0	3.872238	1.613103	-1.864491
40	1	0	3.470062	2.191828	-0.222469
41	6	0	4.509595	0.272826	-0.224029
42	1	0	4.937794	-0.400324	-0.981546
43	1	0	5.321626	0.709629	0.364819



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Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.526405	2.165341	0.343753
2	6	0	0.526519	1.113387	0.013253
3	6	0	-0.168213	0.181588	-0.998484
4	6	0	-1.678175	0.475607	-0.760090
5	8	0	-1.753658	1.738979	-0.066825
6	6	0	-0.030462	-1.339085	-0.754051
7	6	0	-1.025463	-1.593070	0.392776
8	6	0	-2.273237	-0.731231	0.051845
9	6	0	-3.230321	-1.517256	-0.867574
10	6	0	-3.033431	-0.289549	1.310309
11	6	0	1.386049	-1.948808	-0.570546
12	6	0	2.281493	-1.352844	0.505167
13	6	0	2.215548	-1.771962	1.775332
14	6	0	1.849309	1.750977	-0.434529
15	6	0	2.898367	0.747225	-0.929955
16	6	0	3.330153	-0.337158	0.075402
17	8	0	-0.365777	3.223722	0.896472
18	1	0	-2.235622	0.623070	-1.689492
19	1	0	-1.274236	-2.655965	0.499680
20	1	0	-0.592755	-1.270531	1.348176
21	1	0	-0.435538	-1.834496	-1.648605
22	1	0	0.130384	0.458490	-2.016767

23	1	0	1.904759	-1.905372	-1.537176
24	1	0	1.239740	-3.015240	-0.356950
25	1	0	4.153460	-0.898420	-0.394332
26	1	0	3.759406	0.137253	0.967346
27	1	0	2.537785	0.268581	-1.850251
28	1	0	3.795545	1.306586	-1.224774
29	1	0	2.246168	2.338236	0.402157
30	1	0	0.700757	0.573395	0.952001
31	1	0	2.852836	-1.352475	2.550474
32	1	0	1.532232	-2.558746	2.086006
33	1	0	-3.622280	-2.401623	-0.352007
34	1	0	-2.734863	-1.859342	-1.784377
35	1	0	-4.083613	-0.896026	-1.165497
36	1	0	-3.413683	-1.168985	1.844162
37	1	0	-3.886852	0.349792	1.059849
38	1	0	-2.393142	0.271780	1.997276
39	1	0	1.644603	2.469463	-1.239721

6. Energies of DFT-Computed Stationary Points

Table S1. Sum of electronic and thermal enthalpies (*H*, in Hartree), sum of electronic and thermal free energies (*G*, in Hartree), thermal correction to Enthalpy (*TCH*, in Hartree), thermal correction to Gibbs free energy (*TCGFE*, in Hartree), and total free energy in solution (E_S, in Hartree)

Structure	*H*	*G*	*TCH*	*TCGFE*	E_S
TS-*trans*$_{1,2}$-*cis*$_{2,9}$	-1753.671229	-1753.762009	0.527598	0.436818	-1754.188032[a]
TS-*trans*$_{1,2}$-*trans*$_{2,9}$	-1753.666674	-1753.757338	0.52744	0.436776	-1754.183252[a]
TS-*cis*$_{1,2}$-*cis*$_{2,9}$	-1753.663463	-1753.75417	0.527204	0.436496	-1754.180428[a]
TS-*cis*$_{1,2}$-*trans*$_{2,9}$	-1753.664657	-1753.755963	0.526919	0.435613	-1754.180892[a]
TS-*trans*-37	-734.232091	-734.290652	0.347868	0.289307	-734.579392[b]
TS-*cis*-38	-734.229737	-734.288311	0.348632	0.290058	-734.57763[b]
TS-*trans*-43	-923.945404	-924.009822	0.390186	0.325768	-924.336726[b]
TS-*cis*-44	-923.945001	-924.009834	0.390735	0.325902	-924.336818[b]

[a] solvent = toluene
[b] solvent = benzene