Electronic Supplementary Material (ESI) for ChemComm.

Synthetic Studies on Daphniglaucins

Yuanyou Qiu, Jiaxin Zhong, Shan Du, Shuanhu Gao*

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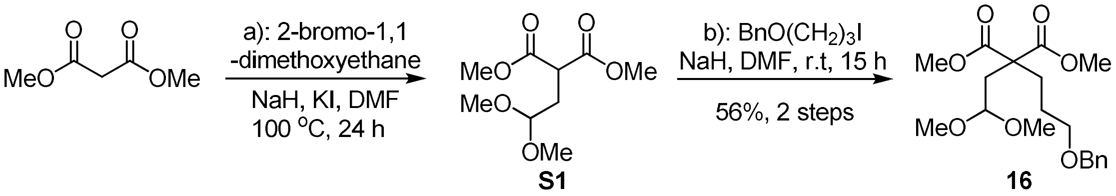
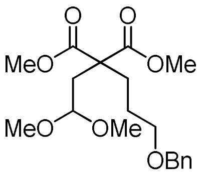
I. Experimental Procedures

General Information:

Oxygen- and moisture-sensitive reactions were carried out under a nitrogen atmosphere. Solvents were purified and dried by standard. All reactions were monitored by thin-layer chromatography with Huang Hai silica gel HSGF254 pre-coated plates (0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh) purchased from Qingdao Haiyang. All commercially available reagents and catalysts were purchased from Sigma-Aldrich, TCI, Alfa Aesar, Strem Chemicals and J&K Chemicals. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-500, 400 spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent (^{1}H, δ 7.26 for $CDCl_3$; ^{13}C, δ 77.00 for $CDCl_3$ ppm; the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were acquired on Waters Micromass GCT Premier or Bruker Daltonics Inc. APEXIII 7.0 TESLA FTMS. Mass spectra were acquired on Agilent 5975C. Specific rotation was performed on Rudolph Research Analytical Autopol VI Polarimeter (λ = 589 nm, T = 20 °C). Melting point was performed on SGW-X4 melting point apparatus. Photochemistry experiments were performed using a BILON-GHX-V 1000 W high pressure mercury lamp housed in quartz immersion.

Experimental Procedures and Compound Characterization:





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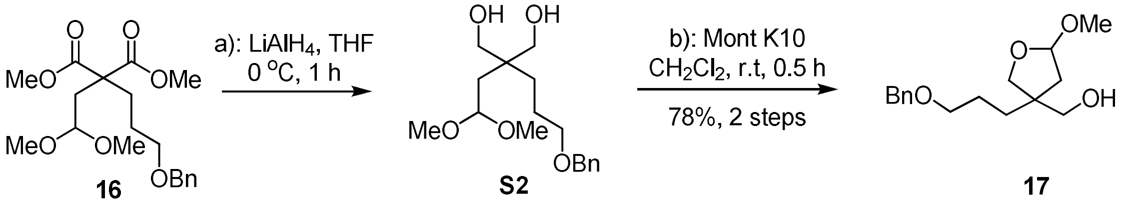
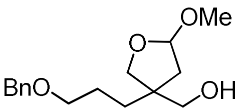
To a suspension of NaH (36.5 g，913.7 mmol, 1.8 equiv., 60%) in DMF (450 mL) was added dimethyl malonate (86.7 mL, 761.46 mmol, 1.50 equiv.) dropwise at 0 °C during 30 mins. After heated to 60 °C, KI (8.4 g, 101.53 mmol, 0.20 equiv.) was added, followed by addition of 2-bromo-1,1-dimethoxyethane (60.0 mL, 507.64 mmol, 1.0 equiv.). The mixture was stirred at 100 °C for 24 h. After cooling to rt, the reaction mixture was poured into pre-ice cold saturated NH_4Cl and extracted with EtOAc (4×850 mL). The combined organic layer was washed with brine (4×850 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was distilled to remove the by-product (bp: 40 °C - 60 °C, 1.0

mmHg) and the residue was mainly the product **S1**[1] and used directly for next step without purification. R_f = 0.35 (20% ethyl acetate-petroleum ether). To a suspension of NaH (16.9 g, 421,19 mmol, 1.30 equiv., 60%) in DMF (300 mL) was added a solution of **S1** (71.4 g, 323.99 mmol, 1.0 equiv.) in DMF (50 mL) dropwise at 0 °C during 1 h. After stirring at 0 °C for 30 mins, a solution of BnO(CH$_2$)$_3$I (134.2 g, 485.99 mmol, 1.50 equiv.) in DMF (50 mL) was added and moved to stir at rt for 15 h. The reaction mixture was quenched with pre-ice cold saturated NH$_4$Cl and extracted with EtOAc (4×550 mL). The combined organic layer was washed with brine (4×550 mL), dried over Na$_2$SO$_4$, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (5% to 20% ethyl acetate-petroleum ether) to give product **16** as colorless oil (100.3 g, 56% over 2 steps). R_f = 0.31 (20% ethyl acetate-petroleum ether) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.27 (m, 5H), 4.50 (s, 2H), 4.44 (t, J = 5.5 Hz, 1H), 3.71 (s, 6H), 3.48 (t, J = 6.4 Hz, 2H), 3.27 (s, 6H), 2.25 (d, J = 5.5 Hz, 2H), 2.03– 2.00 (m, 2H), 1.52 – 1.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.7, 138.4, 128.3, 127.6, 101.9, 72.8, 70.0, 55.1, 53.6, 52.4, 36.1, 30.0, 24.6 ppm. IR ν_{max} 3030, 2952, 1732, 1454, 1365, 1193, 1175, 698 cm^{-1}. HRMS (m/z): ESI [M+Na] calcd for C$_{19}$H$_{28}$NaO$_7$ [M+Na]$^+$: 391.1727: found [M+Na]$^+$: 391.1732.





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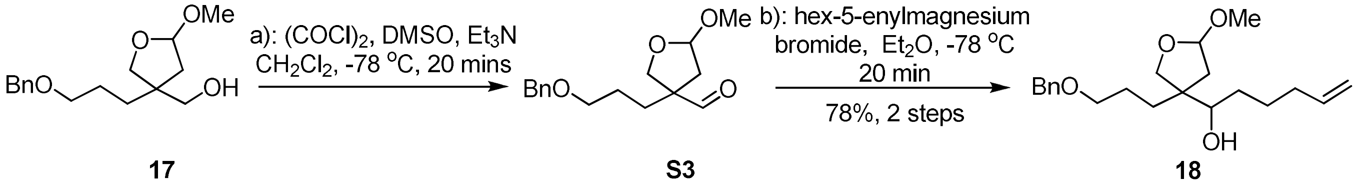
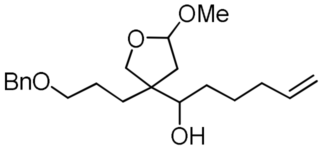
To a stirred solution of **16** (29.0 g, 78.71 mmol, 1.0 equiv.) in THF (350 mL) was added a solution of LiAlH$_4$ (63.0 mL, 157.43 mmol, 2.0 equiv., 2.4 M in THF) dropwise at 0 °C. After stirred at rt for 1 h, the reaction mixture was carefully quenched with EtOAc (50 mL), H$_2$O (6 mL), 15% aq. NaOH (18 mL) and H$_2$O (18 mL) in sequence at 0 °C, followed by addition of MgSO$_4$ and celite. The resulting mixture was filtered and the filtrate was concentrated under vacuum to afford the crude product **S2** as a slight yellow oil (24.0 g). R_f=0.47 (20% ethyl acetate-petroleum ether). The crude product of **S2** was dissolved in CH$_2$Cl$_2$ (350 mL), then Mont K10 (2.4 g) was added and stirred at rt for 1.5 h. The reaction mixture was filtered and the filtrate was concentrated under vacuum to afford the crude product, which was purified by silica gel column chromatography (10% to 30% ethyl acetate-petroleum ether) to give product **17** as colorless oil (16.7 g, 78% over 2 steps). R_f = 0.29 (40% ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.27 (m, 5H), 5.00 (dd, J = 5.2, 0.8 Hz, 1H), 4.50 (s, 2H), 3.89 (d, J = 8.7 Hz, 1H), 3.64 (d, J = 8.7 Hz, 1H), 3.62 – 3.51 (m, 2H), 3.46 (t, J = 5.9 Hz, 2H), 3.33 (s, 3H), 2.84 (s, 1H), 1.93 – 1.75 (m, 2H), 1.64 – 1.47 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.3, 128.4, 127.7, 105.3, 74.0, 73.0, 70.6, 67.2, 54.4, 46.7, 41.9, 33.4, 25.1 ppm. IR ν_{max} 3087, 2940, 2861, 1738, 1453, 1361, 1107, 1028, 698 cm^{-1}. HRMS (m/z): ESI [M+Na] calcd for $C_{16}H_{24}NaO_4$ [M+Na]$^+$: 303.1567: found [M+Na]$^+$: 303.1575.





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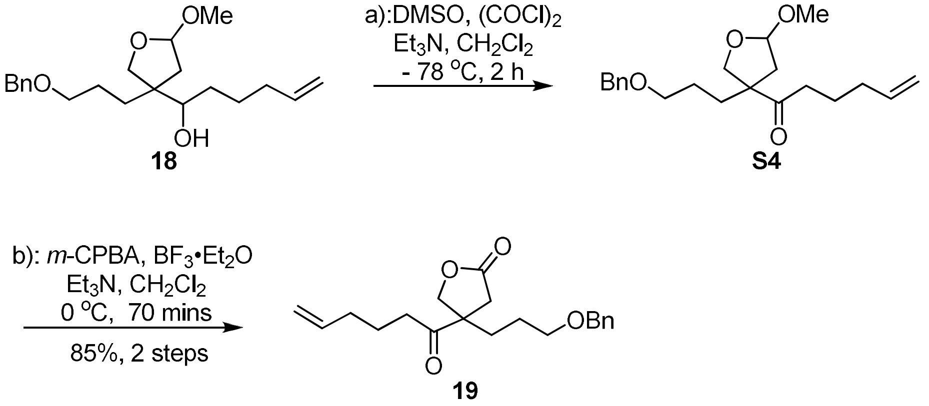
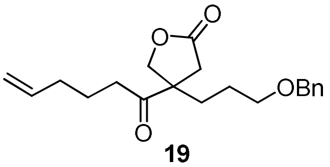
To a stirred solution of oxalyl chloride (9.2 mL, 107.01 mmol, 2.0 equiv.) in CH_2Cl_2 (300 mL) was added a solution of DMSO (15.2 mL, 214.01 mmol, 4.0 equiv.) in CH_2Cl_2 (50 mL) dropwise at -78 °C within 20 mins. After stirring at -78 °C for 20 mins, a solution of **17** (15.0 g, 53.50 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) was added and stirred at -78 °C for 1 h. Then Et_3N (44.8 mL, 321.02 mmol, 6.0 equiv.) was added, stirred at -78 °C for 30 mins and at rt for another 30 mins. The reaction was quenched with sat. NH_4Cl (100 mL), washed with H_2O (2×150 mL) and brine (3×150 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product of **S3** (14.9 g), which was used directly for next step without purification. To a stirred solution of crude **S3** (14.9 g) in Et_2O (250 mL) was added a freshly prepared solution of pent-4-enylmagnesium bromide (80.2 mL, 80.24 mmol, 1.5 equiv., 1.0 M) in Et_2O at -78 °C within 15 mins. The mixture was stirred at -78 °C for 20 mins, and then quenched with MeOH (5 mL) and sat. NH_4Cl (100 mL). The resulting mixture was diluted with EtOAc (250 mL), washed with H_2O (2×100 mL), brine (2×100 mL) and the organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (5% to 10% ethyl acetate-petroleum ether) to give product **18** as colorless oil (14.5 g, 78% over 2 steps). $R_f = 0.48$ (30% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.86 – 5.79 (m, 1H), 5.06 – 4.96 (m, 3H), 4.52 – 4.51 (m, 2H), 4.00 – 3.83 (m, 1H), 3.72 – 3.45 (m, 4H), 3.35 – 3.33 (m, 3H), 2.24 – 1.81 (m, 4H), 1.76 – 1.36 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.4, 128.4, 127.6, 114.7, 106.1, 105.4, 105.0, 75.2, 74.4, 74.0, 73.4, 73.0, 72.7, 72.5, 70.8, 54.8, 54.2, 49.8, 42.7, 41.1, 40.3, 39.9, 33.7, 33.4, 32.7, 32.4, 32.0, 31.4, 31.0, 26.1, 25.9, 25.8, 25.4, 25.2, 24.8 ppm. IR ν_{max} 3064, 3030, 2943, 2862, 1454, 1100, 1042, 790, 698 cm^{-1}. HRMS (m/z): ESI [M+Na] calcd for $C_{21}H_{32}NaO_4$ [M+Na]$^+$: 371.2193; found [M+Na]$^+$: 371.2166.

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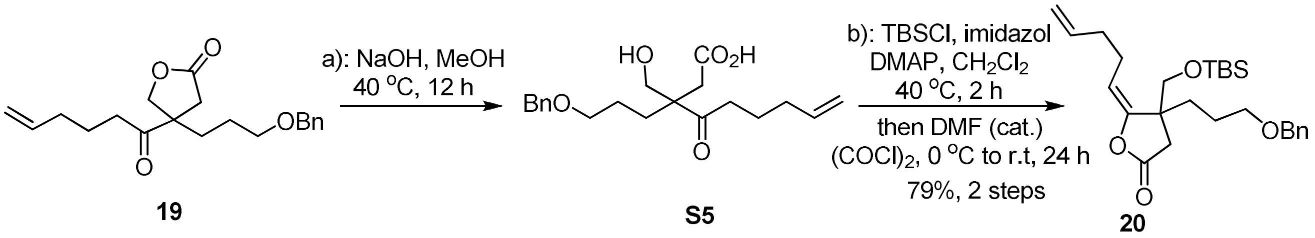
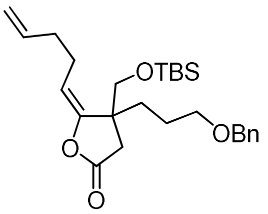
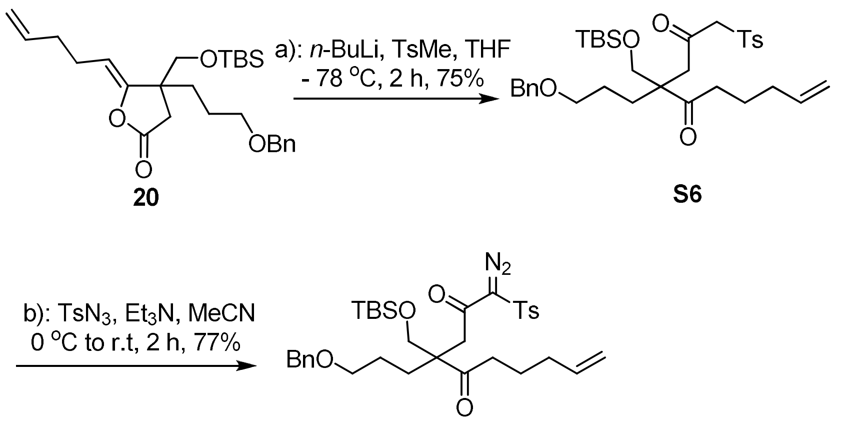
To a stirred solution of oxalyl chloride (356 uL, 4.15 mmol, 2.0 equiv.) in CH_2Cl_2 (30 mL) was added a solution of DMSO (590 uL, 8.30 mmol, 4.0 equiv.) in CH_2Cl_2 (5 mL) dropwise at -78 °C. After stirring at -78 °C for 20 mins, a solution of **18** (723 mg, 2.07 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was added and stirred at -78 °C for 1 h. Then Et_3N (2.3 mL, 16.60 mmol, 8.0 equiv.) was added, stirred at -78 °C for 30 mins and moved to stir at rt for another 30 mins. The reaction was quenched with sat. NH_4Cl (10 mL), washed with H_2O (2×15 mL) and brine (3×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product **S4** (723 mg), which was used directly for next step without purification. To a stirred solution of crude **S4** (723 mg) in CH_2Cl_2 (20 mL) was added $BF_3•Et_2O$ (339 uL, 2.70 mmol, 1.3 equiv.) quickly at 0 °C, followed by dropwise addition of *m*-CPBA (716 mg, 3.11 mmol, 1.5 equiv., 75%) in CH_2Cl_2 (10 mL). The mixture was stirred at 0 °C for 10 mins and moved to stir at rt for 30 mins. Then Et_3N (1.45 mL, 10.38 mmol, 5.0 equiv.) was added and stirred at 0 °C for 30 mins. The resulting mixture was washed with H_2O (2×15 mL) and brine (3×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (10% ethyl acetate-petroleum ether) to give 584 mg of the product **19** (85%, 2 steps) as brown oil. $R_f = 0.35$ (20% ethyl acetate-petroleum ether).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.75 – 5.70 (m, 1H), 5.02 – 4.97 (m, 2H), 4.50 – 4.47 (m, 3H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.44 (t, *J* = 5.9 Hz, 2H), 2.97 (d, *J* = 17.6 Hz, 1H), 2.46 (td, *J* = 7.1, 1.8 Hz, 2H), 2.41 (d, *J* = 17.6 Hz, 1H), 2.04 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.96 – 1.84 (m, 2H), 1.73 – 1.66 (m, 3H), 1.50 – 1.40 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 175.0, 138.1, 137.6, 128.5, 127.7, 115.7, 73.1, 72.9, 69.2, 56.0, 36.8, 35.9, 32.9, 25.2, 22.4 ppm. IR ν_{max} 3065, 3030, 2933, 2861, 1783, 1708, 1454, 1175, 1101, 699 cm^{-1}. HRMS (m/z): ESI [M+ Na] calcd for $C_{20}H_{26}NaO_4$ $[M+ Na]^+$: 353.1723, found $[M+ Na]^+$: 353.1736.

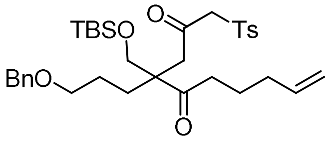




20

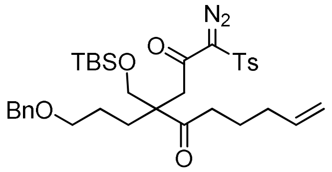
To a stirred solution of **19** (18.0 g, 54.48 mmol, 1.0 equiv.) in MeOH (300 mL) was added aq. NaOH (109.0 mL, 109.0 mmol, 2.0 equiv., 1.0 N) at rt and the mixture was stirred at 40 °C for 10 h. After removing the solvent, the residue was dissolved in CH_2Cl_2 (50 mL), adjusted with aq. HCl (1N) to pH=6 and extracted with EtOAc (3×150 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product of **S5** (19.0 g), which was used directly for next step without purification. To a stirred solution of crude **S5** (19.0 g) in CH_2Cl_2 (400 mL) was added imidazole (18.6 g, 272.65 mmol, 6.25 equiv.), DMAP (666 mg, 5.45 mmol, 0.1 equiv.) and TBSCl (16.4 g, 109.06 mmol, 2.5 equiv.) successively at 0 °C. The mixture was stirred at 40 °C for 2 h. After cooling to 0 °C, DMF (484 uL, 5.45 mmol, 0.1 equiv.) was added, followed by dropwise addition of oxalyl chloride (13.8 mL, 161.39 mmol, 3.0 equiv.) at 0 °C within 2 h. The mixture was stirred at rt for 24 h, and then quenched with ice solid $NaHCO_3$ carefully. The resulting mixture was extracted with EtOAc (3×550 mL), and the combined organic layer was washed with brine (2×550 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (2% to 5% ethyl acetate-petroleum ether) to give 19.1 g of the product **20** (79%, 2 steps) as colorless oil. R_f = 0.78 (20% ethyl acetate-petroleum ether). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.83 – 5.75 (m, 1H), 5.03 – 4.95 (m, 2H), 4.52 – 4.43 (m, 4H), 3.53 – 3.47 (m, 2H), 3.49 – 3.41 (m, 2H), 2.62 (d, J = 18.0 Hz, 1H), 2.46 (d, J = 18.0 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.14 – 2.10 (m, 2H), 1.67 – 1.58 (m, 3H), 1.54 – 1.51 (m, 1H), 0.86 (s, 9H), 0.02 – 0.01 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ173.7, 154.2, 138.4, 138.0, 128.4, 127.6, 115.0, 102.7, 72.9, 70.1, 69.9, 47.7, 35.9, 33.7, 31.5, 30.2, 29.7, 25.7, 24.7, 24.5, 18.1, -5.60 ppm. IR ν_{max} 3065, 3030, 2954, 2928, 2856, 1804, 1701, 1100, 837, 777, 697 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{26}H_{40}NaO_4Si$ $[M+Na]^+$: 467.2588; Found $[M+Na]^+$: 467.2590.





S6

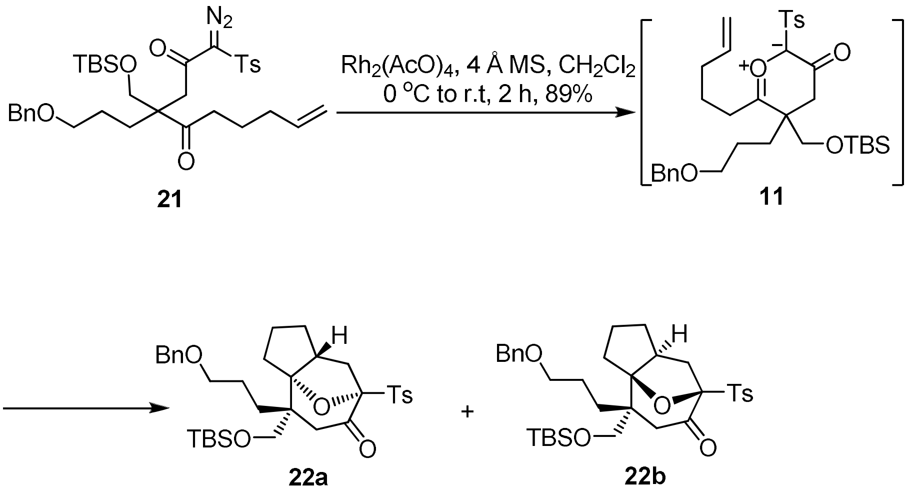
To a stirred solution of TsMe (1.4 g, 8.10 mmol, 2.0 equiv.) in anhydrous THF (40 mL) was added a solution *n*-BuLi (8.9 mL, 14.17 mmol, 3.5 equiv., 1.6 M in hexane) dropwise at -78 ºC under nitrogen atmosphere. [2] After stirring at -78 ºC for 20 mins, a solution of **20** (1.8 g, 4.05 mmol, 1.0 equiv.) in THF (10 mL) was added carefully and stirred at -78 ºC for 2 h. Then the reaction mixture was quenched with sat. NH_4Cl (15 mL), extracted with EtOAc (3×55 mL), and the combined organic layer was washed with brine (2×55 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (3% to 5% to 20% ethyl acetate-petroleum ether) to give 1.86 g of the product **S6** (75%) as yellow oil. R_f = 0.57 (20% ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 7H), 5.78 – 5.70 (m, 1H), 5.01 – 4.93 (m, 2H), 4.48 (s, 2H), 4.14 (q, *J* = 13.3 Hz, 2H), 3.70 (s, 2H), 3.42 (t, *J* = 6.2 Hz, 2H), 3.07 – 2.91 (m, 2H), 2.47 – 2.42 (m, 5H), 2.04 – 1.97 (m, 2H), 1.78 – 1.73 (m, 2H), 1.62 – 1.57 (m, 2H), 1.50 – 1.43 (m, 2H), 0.85 (s, 9H), 0.004 – -0.003 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 196.9, 145.3, 138.5, 138.2, 135.9, 129.9, 128.3, 127.6, 114.9, 72.9, 70.2, 67.8, 65.1, 55.8, 45.8, 37.6, 33.0, 28.9, 25.8, 24.3, 22.4, 18.1, -5.7 ppm. IR ν_{max} 2953, 2928, 2111, 1661, 1340, 1154, 1098, 836, 667 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{50}NaO_6SSi$ [M+Na]$^+$: 637.2990; Found [M+Na]$^+$:637.3015.



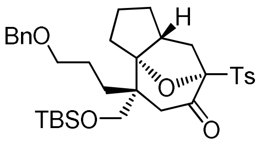
21

To a stirred solution of **20** (1.8 g, 2.93 mmol, 1.0 equiv.) and TsN_3 (1.2 g, 5.85 mmol, 2.0 equiv.) in MeCN (15 mL) was added Et_3N (1.2 mL, 8.78 mmol, 3.0 equiv.) dropwise at 0 ºC. After stirring at rt for 2 h, the reaction mixture was quenched with $NaHCO_3$(15 mL), extracted with EtOAc (3×35 mL), and the combined organic layer was washed with brine (2×35 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (3% to 7% ethyl acetate-petroleum ether) to give 1.50 g of the product **21** (77%). R_f = 0.71 (20% ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d,

J = 8.3 Hz, 2H), 7.36– 7.26 (m, 7H), 5.79 – 5.69 (m, 1H), 5.01 – 4.93 (m, 2H), 4.45 (s, 2H), 3.70 (q, J = 10.0 Hz, 2H), 3.38 (t, J = 6.3 Hz, 2H), 2.95 (d, J = 17.5 Hz, 1H), 2.78 (d, J = 17.5 Hz, 1H), 2.43 – 2.40 (m, 5H), 1.99 (dd, J = 13.9, 6.4 Hz, 2H), 1.75 – 1.69 (m, 2H), 1.38 – 1.32 (m, 2H), 0.81 (s, 9H), -0.04 – -0.05 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 186.8, 145.3, 139.2, 138.4, 130.03 (s), 128.4, 127.5, 114.9, 72.8, 70.2, 64.9, 55.1, 40.6, 37.5, 33.0, 28.9, 25.7, 24.3, 22.4, 18.1, -5.8 ppm. IR ν_{max}3063, 3031, 2919, 2850, 2114, 1779, 1708, 1178, 1151, 1086, 815 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{48}O_6NaSSiN_2$ [M+Na]$^+$: 663.2895; Found [M+Na]$^+$: 663.2919.

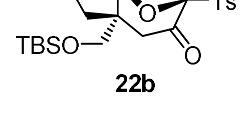


To a solution of **21** (1.45 g, 2.26 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (200 mL) was added activated 4Å MS (1.45 g) and $Rh_2(OAc)_4$ (5.0 mg, 11.31 umol, 0.005 equiv.) at 0 ºC. The mixture was stirred at rt for 8 h, and then filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (7% to 20% ethyl acetate-petroleum ether) to give **22a** (965 mg, 70%) as light yellow oil, R_f = 0.29 (20% ethyl acetate-petroleum ether) and **22b** (268 mg, 19%) as light brown oil, R_f = 0.33 (20% ethyl acetate-petroleum ether).



22a

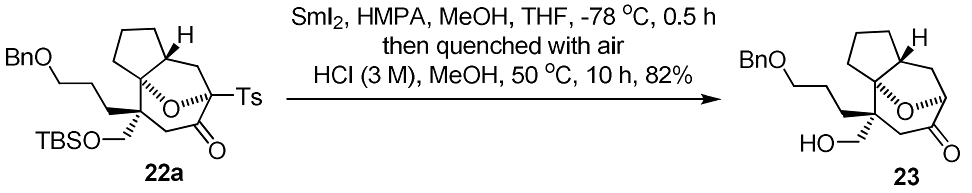
22a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.36 – 7.26 (m, 7H), 4.46 (d, J = 1.9 Hz, 2H), 3.56 (d, J = 10.0 Hz, 1H), 3.44 – 3.37 (m, 2H), 3.26 (d, J = 10.0 Hz, 1H), 2.86 – 2.81 (m, 1H), 2.54 – 2.49 (m 1H), 2.42 (s, 3H), 2.39 – 2.34 (m, 1H), 2.13 (s, 2H), 1.94 – 1.90 (m, 1H), 1.75 – 1.38 (m, 9H), 0.82 (s, 9H), -0.06 (s, 3H), -0.12 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 144.9, 138.5, 133.6, 130.6, 129.0, 128.4, 127.6, 101.5, 99.4, 72.9, 70.6, 64.5, 47.1, 44.4, 42.5, 38.8, 33.5, 32.8, 28.9, 25.8, 24.7, 23.8, 18.1, -5.9 ppm. IR ν_{max} 3446, 3066, 3031, 2953, 2928, 2856, 1730, 1326, 1159, 1094, 853, 836, 776, 660 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{48}NaO_6SSi$ [M+Na]$^+$: 635.2833, found [M+Na]$^+$: 635.2866.



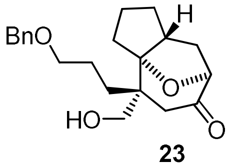
22b

22b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.37 – 7.25 (m, 7H), 4.43 (s, 2H), 3.33 – 3.29 (m, 4H), 3.05 – 3.03 (m, 1H), 2.51 – 2.47 (m, 1H), 2.38

(s, 3H), 2.22 – 2.13 (m, 3H), 1.92 – 1.89 (m, 1H), 1.78 – 1.44 (m, 8H), 0.85 (s, 9H), 0.003 – 0.000 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 145.0, 138.5, 133.4, 130.5, 129.1, 128.4, 127.6, 101.9, 99.4, 728, 70.7, 65.9, 46.2, 43.3, 41.8, 39.2, 33.6, 33.4, 30.5, 29.7, 25.8, 24.6, 23.9, 18.1, -5.8 ppm. IR ν_{max} 3066, 3031, 2953, 2928, 2858, 1730, 1323, 1184, 1094, 837, 776, 664 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{34}H_{48}NaO_6SSi$ $[M+Na]^+$: 635.2833, found $[M+Na]^+$: 635.2866.

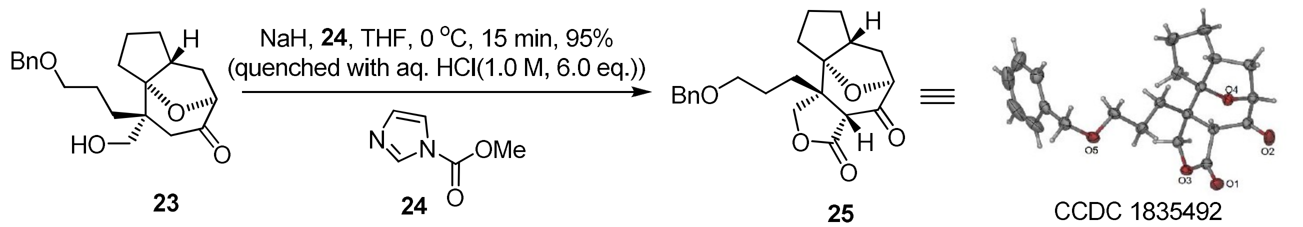


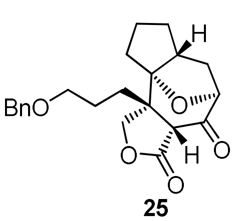
General procedure for preparation of SmI_2: [3] An oven-dried flask charged with samarium metal powder (5.13 g, 34.09 mmol, 1.1 equiv.) was flame-dried and cooled. After cooling to rt under N_2, degassed anhydrous THF (310 mL) was added and then cooled to 0 °C, followed by addition of CH_2I_2 (2.5 mL, 30.99 mmol, 1.0 equiv.). The mixture was stirred at 0 °C for 15 mins and then at rt for 2 h. The resulting SmI_2 solution was deep blue-green.



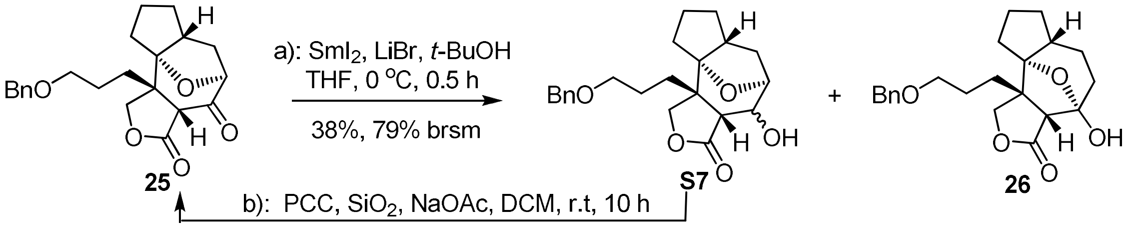
23

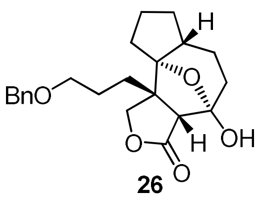
To an oven-dried flask charged with **22a** (6.6 g, 10.77 mmol, 1.0 equiv.), HMPA (9.40 mL, 54.83 mmol, 5.0 equiv.) and MeOH (2.20 mL, 54.83 mmol, 5.0 equiv.), was added a freshly prepared SmI_2 solution (323 mL, 32.31 mmol, 3.0 equiv., 0.1 M) in THF under nitrogen atmosphere at - 78 °C. The mixture was stirred at - 78 °C for 30 mins and quenched with the air at rt. Then aq. HCl (72.1 mL, 216.26 mmol, 20.0 equiv., 3 M) and (8.8 mL, 216.26 mmol, 20.0 equiv.) was added and stirred at 50 °C for 10 h. After cooling to rt, the reaction mixture was quenched with ice-cold sat. $NaHCO_3$ carefully and the solvent was removed under vacuum. The residue was dissolved in EtOAc (550 mL), washed with $Na_2S_2O_3$ (1×150 mL), H_2O (2×250 mL) and brine (2×250 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (20% ethyl acetate-petroleum ether) to give 3.05 g of the product **23** (82%) as colorless oil. R_f = 0.10 (20% ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 4.49 (s, 2H), 4.33 (d, *J* = 7.6 Hz, 1H), 3.80 (d, *J* = 11.6 Hz, 1H), 3.60 (t, *J* = 10.4 Hz, 1H), 3.44 (td, *J* = 6.1, 2.0 Hz, 2H), 3.34 (d, *J* = 9.7 Hz, 1H), 2.75 (d, *J* = 8.7 Hz, 1H), 2.45 (dd, *J* = 17.5, 1.4 Hz, 1H), 2.26 – 2.13 (m, 2H), 1.97 – 1.52 (m, 10H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 138.3, 128.4, 127.7, 100.4, 83.6, 73.0, 70.4, 68.4, 44.6, 42.9, 42.3, 38.7), 33.9, 31.7, 29.6, 24.4, 23.4 ppm. IR ν_{max} 2920, 2851, 1722, 1384, 1040, 839, 776, 698 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{21}H_{28}NaO_4$ $[M+Na]^+$: 367.1880, found $[M+Na]^+$: 367.1891.



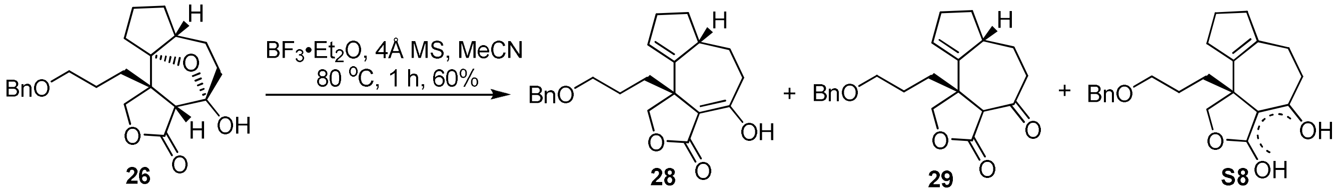

25

To a stirred suspension of NaH (770 mg, 19.25 mmol, 3.0 equiv., 60%) in anhydrous THF (25 mL) was added a solution of **23** (2.21 g, 6.42 mmol, 1.0 equiv.) in THF (20 mL) carefully at 0 °C under nitrogen atmosphere. After stirring at 0 °C for 5 mins, a solution of **24**[4] (1.62 g, 12.83 mmol, 2.0 equiv.) in THF (20 mL) was added carefully and stirred at 0 °C for 15 mins. Then the reaction mixture was poured into aq. HCl (38.25 mL, 38.25 mmol, 6.0 equiv., 1 N) carefully at rt and extracted with EtOAc (3×100 mL). The combined organic layer was washed with brine (2×250 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (20% ethyl acetate-petroleum ether) to give 2.25 g of the product **25** (95%) as colorless oil. R_f = 0.33 (30% ethyl acetate-petroleum ether)。 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 4.69 (d, *J* = 9.1 Hz, 1H), 4.49 – 4.45 (m, 3H), 4.17 (d, *J* = 9.1 Hz, 1H), 3.48 (t, *J* = 4.9 Hz, 2H), 3.12 (s, 1H), 2.62 – 2.57 (m, 1H), 2.25 – 2.21 (m, 1H), 1.89 – 1.50 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 170.0, 138.2, 128.5, 127.7, 96.5, 82.5, 73.9, 73.1, 69.7, 56.2, 48.1, 42.2, 38.4, 33.6, 32.3, 31.9, 24.3, 24.0 ppm. IR ν_{max} 2954, 2866, 1790, 1725, 1453, 1170, 1030, 699 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{22}H_{26}NaO_5$ $[M+Na]^+$: 393.1672, found $[M+Na]^+$: 393.1647. Conditions for culturing single crystal: CH_2Cl_2:Hexane=1:4, Static mixing, volatilization and crystallization at room temperature, CCDC 1835492.

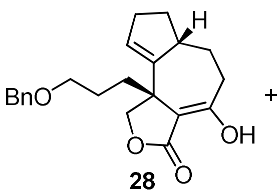



26

An oven-dried flask charged with LiBr (4.0 mg, 45.55 mmol, 7.5 equiv.) was flame-dried and cooled. A freshly prepared solution of SmI_2 (303.7 mL, 30.37 mmol, 5.0 equiv., 0.1 M) in THF was added and stirred at rt for 20 mins. Then the above solution was transferred to another oven-dried flask charged with **25** (2.25 g, 6.07 mmol, 1.0 equiv.) and *t*-BuOH (2.8 mL, 30.37 mmol, 5.0 equiv.) at 0 °C via syringe. The mixture was stirred at 0 °C for 1 h and quenched with the air at rt. After removing the solvent, the residue was dissolved EtOAc (500 mL), washed with $Na_2S_2O_3$ (1×150 mL), H_2O (2×250 mL) and brine (2×250 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product **S7** and **26**. To the crude product in CH_2Cl_2 (100 mL) was added SiO_2 (2.25 g), NaOAc (1.49 g, 18.12 mmol, 3.0 equiv.) and PCC (3,91 g, 18.12 mmol, 3.0 equiv.) successively at rt. After stirring at rt for 8 h, the reaction mixture was filtered and the filtrate was washed with 1 N aq. HCl (2×55 mL), H_2O (2×55 mL) and brine (2×55 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (20% to 40% ethyl acetate-petroleum ether) to give 850 mg of **26** (38%, 79% brsm), R_f = 0.36 (40% ethyl acetate-petroleum ether) and 1.18 g of **25** recovered. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 4.50 (s, 2H), 4.36 (d, *J* = 9.1 Hz, 1H), 4.14 (d, *J* = 9.1 Hz, 1H), 3.92 – 3.90 (m, 1H), 3.51 – 3.48 (m, 2H), 2.77 (s, 1H), 1.82 – 1.55 (m, 15H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 138.2, 128.5, 127.7, 103.1, 93.1, 7 74.6, 73.1, 69.9, 56.0, 54.8, 37.4, 32.7, 30.4, 28.7, 28.1, 25.5, 21.0, 20.5 ppm. IR ν_{max} 3062, 3030, 2952, 2864, 1769, 1454, 1175, 1098, 1027, 698 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{22}H_{28}NaO_5$ $[M+Na]^+$: 395.1829, found $[M+Na]^+$: 395.1848.

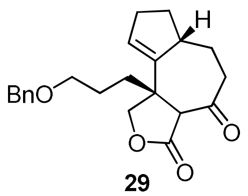


To an oven-dried flask charged with **26** (30.0 mg, 80.55 umol, 1.0 equiv.), 4Å MS (30.0 mg) and anhydrous MeCN (5 mL) was added BF_3•OEt_2 (79.5 uL, 644.37 umol, 8.0 equiv.) at rt. The mixture was stirred at 80 °C for 1 h. After cooling to rt, the reaction mixture was quenched with sat. $NaHCO_3$ (5 mL) and extracted with EtOAc (3×15 mL). The combined organic layer was washed with brine (2×15 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by preparative thin layer chromatography, (20% ethyl acetate-petroleum ether) to give 12.2 mg of the mixture of **28** and **29** (43%) as colorless oil. R_f = 0.86 (40% ethyl acetate-petroleum ether), and 4.9 mg of the mixture of **S8** as colorless oil. R_f = 0.87 (40% ethyl acetate-petroleum ether).



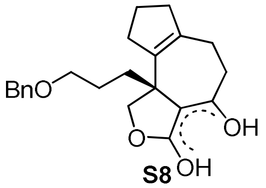
28

+



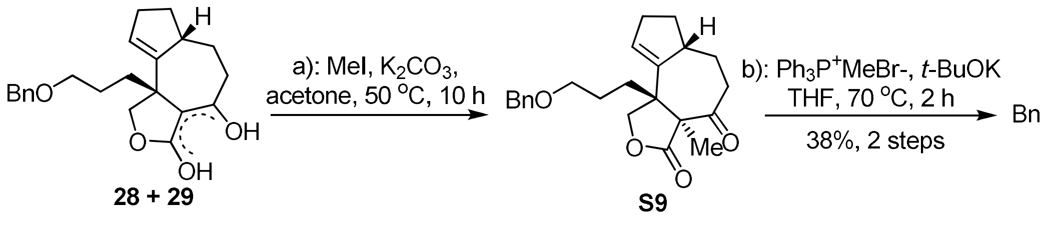
29

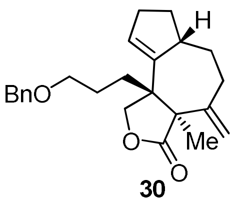
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.26 (s, 0.49 H), 7.38 – 7.26 (m, 5H), 5.37 (dd, *J* = 4.3, 2.1 Hz, 0.44 H), 5.27 (d, *J* = 1.8 Hz, 0.49 H), 4.49 (dd, *J* = 8.5, 3.5 Hz, 2H), 4.40 – 4.20 (m, 2H), 3.81 (s, 0.44 H), 3.44 (dtd, *J* = 10.2, 6.3, 1.3 Hz, 2H), 3.04 – 2.96 (m, 0.44 H), 2.81 – 2.72 (m, 0.49 H), 2.69 – 2.03 (m, 6H), 1.95 – 1.35 (m, 8H). ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 176.1, 173.8, 173.3, 144.5, 143.1, 138.2, 130.5, 128.5, 128.4, 127.8, 127.7, 127.6, 124.8, 103.0, 74.8, 73.1, 72.9, 70.0, 69.7, 62.8, 47.9, 46.5, 45.8, 43.5, 38.8, 34.0, 33.6, 32.7, 32.0, 31.6, 31.1, 30.2, 29.8, 26.5, 25.0, 24.7 ppm. IR ν_{max}3087, 3031, 2940, 2853, 1784, 1703, 1454, 1361, 1200, 1171, 1101, 1031, 818, 698 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{22}H_{26}NaO_4$ [M+Na]$^+$: 377.1723, found [M+Na]$^+$: 377.1736.



S8

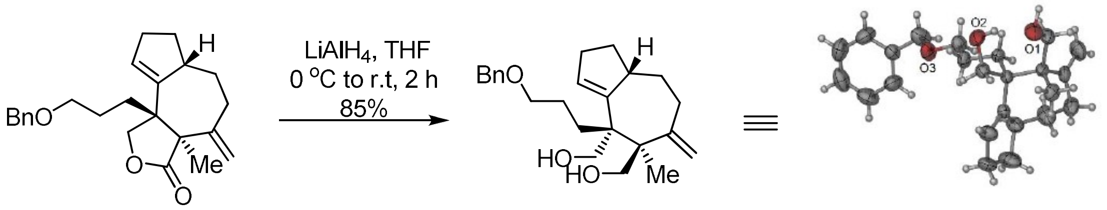
^{1}H NMR (500 MHz, CDCl$_3$) δ 11.45 (s, 0.10H), 10.96 (s, 0.63H), 7.39 – 7.26 (m, 5H), 4.53 – 4.44 (m, 2H), 4.21 – 4.02 (m, 2H), 3.45 (dt, *J* = 10.2, 6.3 Hz, 2H), 2.83 – 2.58 (m, 2H), 2.48 – 2.02 (m, 6H), 1.88 – 1.53 (m, 8H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 204.2, 175.9, 172.6, 138.4, 136.5, 133.5, 128.4, 127.7, 101.5, 77.9, 75.9, 73.1, 70.3, 69.8, 59.9, 49.7, 45.7, 44.4, 39.5, 38.2, 36.3, 34.1, 33.9, 32.8, 30.7, 26.1, 25.5, 24.8, 21.9, 21.3 ppm. IR ν_{max}3030, 2921, 2850, 1786, 1702, 1202, 1172, 1029, 812, 698 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{22}H_{26}NaO_4$ [M+Na]$^+$: 377.1723, found [M+Na]$^+$: 377.1736.



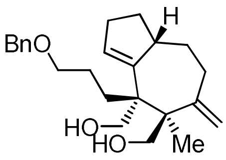


30

To a solution of **28** and **29** (20.0 mg, 56.43 umol, 1.0 equiv.) in anhydrous acetone (3 mL) was added K_2CO_3 (39.0 mg, 284.14 umol, 5.0 equiv.) and MeI (17.6 uL, 284.14 umol, 5.0 equiv.) at rt. The mixture was stirred at 50 °C for 5 h. After removing the solvent, the residue was dissolved in EtOAc (30 mL), washed with $Na_2S_2O_3$ (1×10 mL), H_2O (2×10 mL) and brine (2×10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give 10.0 mg of crude product **S8**, which was used directly for next step without purification. To an oven-dried flask charged with PPh_3MeBr (53.3 mg, 149.27 umol, 5.5 equiv.) and *t*-BuOK (15.2 mg, 135.70 umol, 5.0 equiv.) was added anhydrous THF (3 mL) at rt under nitrogen atmosphere. After stirring at rt for 10 mins, the suspention was transferred to another oven-dried flask charged with crude **S9** via syringe. The mixture was stirred at rt for 10 mins and then moved to stir at 70 °C for 4 h. After cooling to rt, the reaction mixture was quenched with sat. NH_4Cl (3 mL), extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (2×10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by preparative thin layer chromatography (10% ethyl acetate-petroleum ether) to give 7.8 mg of the product **30** (38%, 2 steps) as colorless oil. R$_f$ = 0.51 (10% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.28 (m, 5H), 5.70 (s, 1H), 5.41 (d, *J* = 2.1 Hz, 1H), 5.11 (s, 1H), 4.50 – 4.45 (m, 2H), 4.22 (dd, $J = 9.1, 1.6$ Hz, 1H), 4.08 (d, $J = 9.1$ Hz, 1H), 3.48 – 3.34 (m, 2H), 2.76 – 2.64 (m, 1H), 2.58 – 2.50 (m, 1H), 2.49 – 2.42 (m, 1H), 2.40 – 2.33 (m, 1H), 2.28 – 2.19 (m, 1H), 2.13 – 2.05 (m, 1H), 1.86 – 1.73 (m, 2H), 1.70 – 1.60 (m, 1H), 1.53 – 1.33 (m, 4H), 1.31 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 144.1, 143.9, 128.4, 127.6, 115.1, 72.9, 70.2, 68.4, 53.2, 50.9, 45.7, 32.8, 32.2, 30.9, 29.1, 25.5, 22.1 ppm. IR ν_{max} 3055, 2995, 2924, 2853, 1437, 1182, 1120, 882, 743, 694 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{24}H_{30}NaO_3$ [M+Na]$^+$: 389.2087, found [M+Na]$^+$: 389.2102.

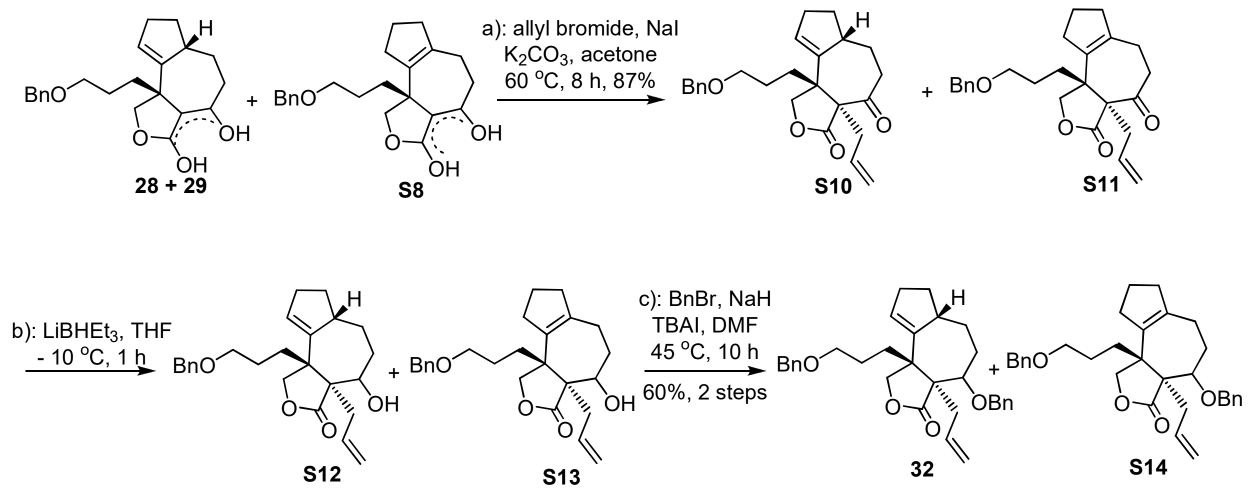


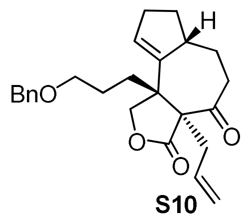
30 **31** CCDC 1835496



31

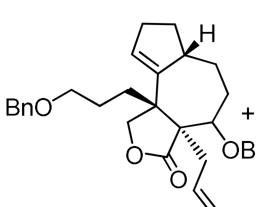
To a solution of **30** (80 mg, 218.20 umol, 1.0 equiv.) in anhydrous THF (5 mL) was added a solution of $LiAlH_4$ (364 uL, 873.15 umol, 4.0 equiv., 2.5 M in THF) at 0 °C. After stirring at rt for 2 h, the reaction mixture was quenched with EtOAc (5 mL) and 1N aq. HCl (5 mL), extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (2×10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (20% ethyl acetate-petroleum ether) to give 69.0 mg of **31** (85%) as thick solid, $R_f = 0.12$ (20% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.31 (d, J = 1.2 Hz, 0.36 H), 5.01 (s, 0.73H), 4.93 (s, 0.36H), 4.84 (s, 0.73H), 4.64 (d, J = 1.0 Hz, 0.36H), 4.51 – 4.49 (m, 2H), 4.12 – 3.80 (m, 3H), 3.70 (d, $J = 12.2$ Hz, 1H), 3.55 – 3.34 (m, 3H), 2.66 – 1.79 (m, 10H), 1.78 – 1.34 (m, 7H), 1.14 – 1.07 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 138.7, 137.9, 137.4, 128.5, 127.9, 112.8, 112.4, 73.2, 71.3, 71.1, 68.5, 66.9, 62.4, 49.3, 48.0, 47.7, 44.3, 40.0, 37.4, 34.8, 33.5, 32.8, 30.4, 29.4, 24.9, 24.2, 22.0, 19.6, 18.3 ppm. IR ν_{max} 3424, 2960, 2943, 2874, 1464, 1383, 1108, 1052, 887cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{24}H_{34}NaO_3$ [M+Na]$^+$: 393.2400, found [M+Na]$^+$: 393.2417. Conditions for culturing single crystal: CH_2Cl_2:Hexane=1:4, Static mixing, volatilization and crystallization at room temperature, CCDC 1835496.





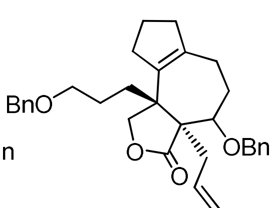
S10

To a solution of a mixture of **28**, **29** and **S8** (620 mg, 1.75 umol, 1.0 equiv.) in anhydrous acetone (35 mL) was added K_2CO_3 (2.44 g, 17.49 mmol, 10.0 equiv.), NaI (2.60 g, 17.49 mmol, 10.0 equiv.) and allyl bromide (1.20 mL, 13.99 mmol, 8.0 equiv.) at rt under nitrogen atmosphere. After stirring at 60 ºC for 10 h, the solvent was removed and the residue was dissolved in EtOAc (50 mL), washed with $Na_2S_2O_3$ (1×15 mL), H_2O (2×15 mL) and brine (2×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (10% ethyl acetate-petroleum ether) to give a mixture of **S10** and **S11** (602 mg, 87%) as colorless oil, R_f = 0.34 (20% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 5.77 – 5.69 (m, 1H), 5.02 – 4.97 (m, 2H), 4.50 – 4.47 (m, 3H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.44 (t, *J* = 5.9 Hz, 2H), 2.97 (d, *J* = 17.6 Hz, 1H), 2.48 – 2.39 (m, 3H), 2.04 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.97 – 1.84 (m, 2H), 1.73 – 1.66 (m, 2H), 1.50 – 1.40 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 175.0, 138.1, 137.6, 128.5, 127.7, 115.7, 73.1, 72.9, 69.2, 55.9, 36.8, 35.9, 32.9, 25.2, 22.4 ppm. IR ν_{max} 2927, 2856, 1786, 1702, 1454, 1102, 1022, 699 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{25}H_{30}NaO_4$ [M+Na]$^+$: 417.2036, found [M+Na]$^+$: 417.2020.



32

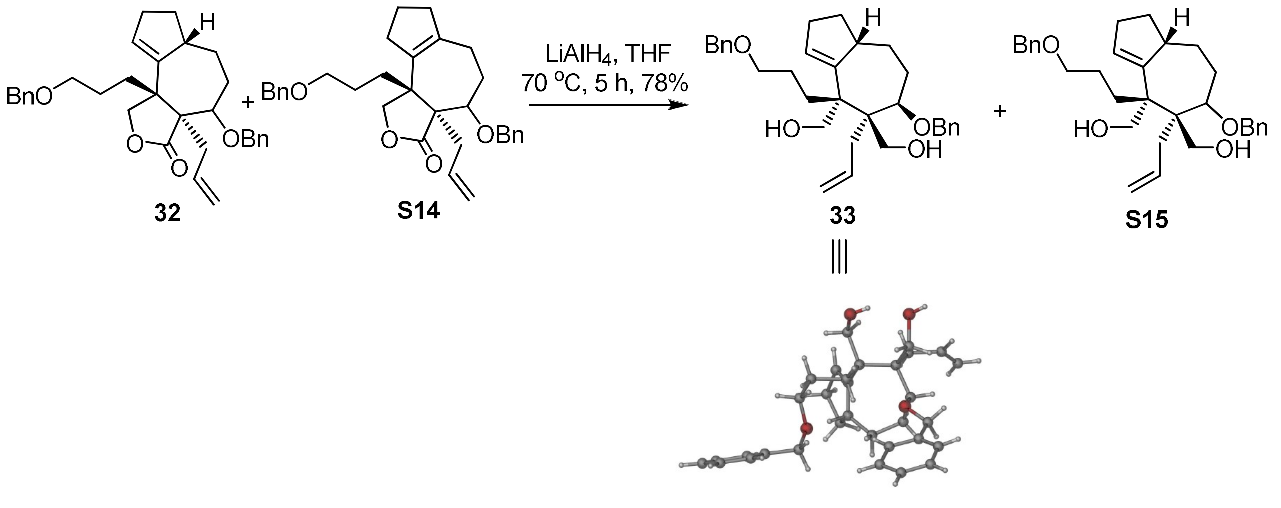
+



S14

To a solution of a mixture of **S10** and **S11** (602 mg, 1.53 mmol, 1.0 equiv.) in anhydrous THF (35 mL) was added a solution of $LiBHEt_3$ (7.6 mL, 7.63 mmol, 5.0 equiv., 1.0 M in THF) at -10 ºC and stirred at that temperature for 1 h. After quenched with MeOH (1 mL) and 1 N aq. HCl (10 mL), the mixture was extracted with EtOAc (3×30 mL). The combined organic layer was washed with brine (2×30 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give 605 mg of the crude mixture of **S12** and **S13**, which was used directly for next step without purification. To a crude mixture of **S12** and **S13** in anhydrous DMF (20 mL) was added TBAI (559.0 mg, 1.51 mmol, 1.0 equiv.) and NaH (605.0 mg, 15.13 mmol, 10.0 equiv.) at rt. After stirring at rt for 10 mins, BnBr (1.6 mL, 15.13

mmol, 10.0 equiv.) was added at rt and stirred at 45 ºC for 10 h. After cooling to rt, the reaction mixture was quenched with sat. NH_4Cl (35 mL), extracted with EtOAc (2×55 mL). The combined organic layer was washed with brine (2×35 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (5% ethyl acetate-petroleum ether) to give a mixture of **32** and **S14** (440 mg, 60%, 2 steps) as colorless oil, R_f = 0.72 (20% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 10H), 5.89 – 5.80 (m, 1H), 5.39 (d, *J* = 2.1 Hz, 1H), 5.18 – 5.07 (m, 2H), 4.73 – 4.68 (m, 1H), 4.59 – 4.56 (m, 1H), 4.48 – 4.36 (m, 2H), 4.31 – 4.26 (m, 1H), 4.20 – 4.03 (m, 2H), 3.46 – 3.30 (m, 2H), 2.83 – 2.66 (m, 2H), 2.53 – 2.26 (m, 3H), 2.19 – 1.65 (m, 6H), 1.55 – 1.29 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 176.5, 144.3, 139.3, 138.5, 137.9, 135.5, 132.9, 132.3, 128.3, 128.1, 127.4, 118.9, 118.8, 78.9, 73.2, 73.1, 70.9, 70.6, 69.9, 56.2, 54.4, 52.6, 50.9, 46.2, 39.1, 37.3, 36.5, 35.3, 32.5, 30.9, 29.6, 27.0, 26.2, 25.9, 23.4, 22.7 ppm. IR ν_{max} 3063, 3029, 2925, 2853, 1774, 1496, 1454, 1103, 1012, 697 cm^{-1}. HRMS (m/z): ESI $[M+N_a]^+$ calcd for $C_{32}H_{38}NaO_4$ $[M+N_a]^+$: 509.2668, found $[M+N_a]^+$: 509.2620.



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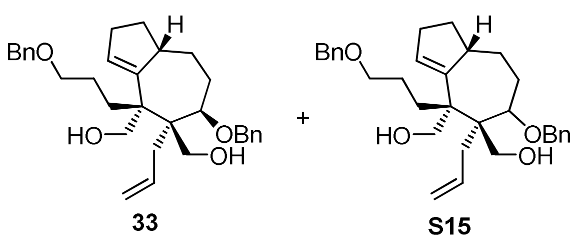
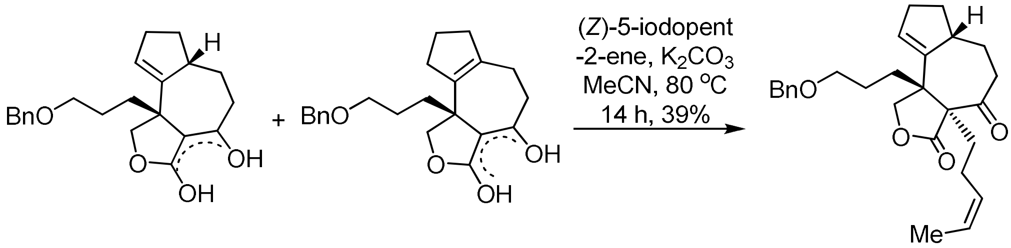
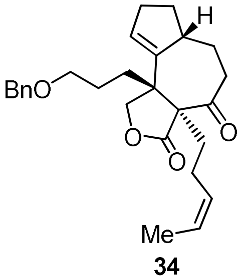


To a solution of **30** (30.0 mg, 71.33 umol, 1.0 equiv.) in anhydrous THF (5 mL) was added a solution of $LiAlH_4$ (570.6 uL, 1.43 mmol, 20.0 equiv., 2.5 M in TH F) at 0 ºC. After stirring at rt for 5 h, the reaction mixture was quenched with EtOAc (5 mL) and 1N aq. HCl (5 mL), extracted with EtOAc (3×15 mL). The combined organic layer was washed with brine (2×15 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (20% ethyl acetate-petroleum ether) to give 23.6 mg of a mixture of **33** and **S15** (78%) as thick solid, R_f = 0.23 (20% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 10H), 5.93 – 5.86 (m, 1H), 5.30 (d, *J* = 2.2 Hz, 0.69H), 5.09 – 5.03 (m, 2H), 4.63 – 4.15 (m, 7H), 4.01 – 3.71 (m, 2H), 3.61 – 3.37 (m, 5H), 2.87 – 2.84 (m, 1H), 2.69 – 2.47 (m, 2H), 2.39 – 1.15 (m, 15H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.2, 139.1, 138.2, 137.8, 136.4, 135.5, 129.5, 128.5, 128.4, 128.3, 128.2, 127.8, 127.2, 126.9, 117.5, 117.4, 87.3, 84.6, 73.4, 73.2, 72.0, 71.6, 71.4, 63.9, 63.3, 49.7, 49.3, 45.4, 39.5, 37.1, 34.6, 34.4, 32.5, 30.8, 25.1, 24.9, 24.4, 23.5, 22.9, 22.2, 21.2 ppm. IR ν_{max} 3420, 3064, 3029, 2930, 2855, 1454, 1094, 1052, 910, 696 cm^{-1}. HRMS (m/z): ESI [M+N$_a$]$^+$ calcd for $C_{32}H_{42}NaO_4$ [M+N$_a$]$^+$: 513.2975, found [M+N$_a$]$^+$: 513.2962. Conditions for culturing single crystal: CH_2Cl_2:Hexane=1:4, Static mixing, volatilization and crystallization at room temperature, CCDC 1835500.

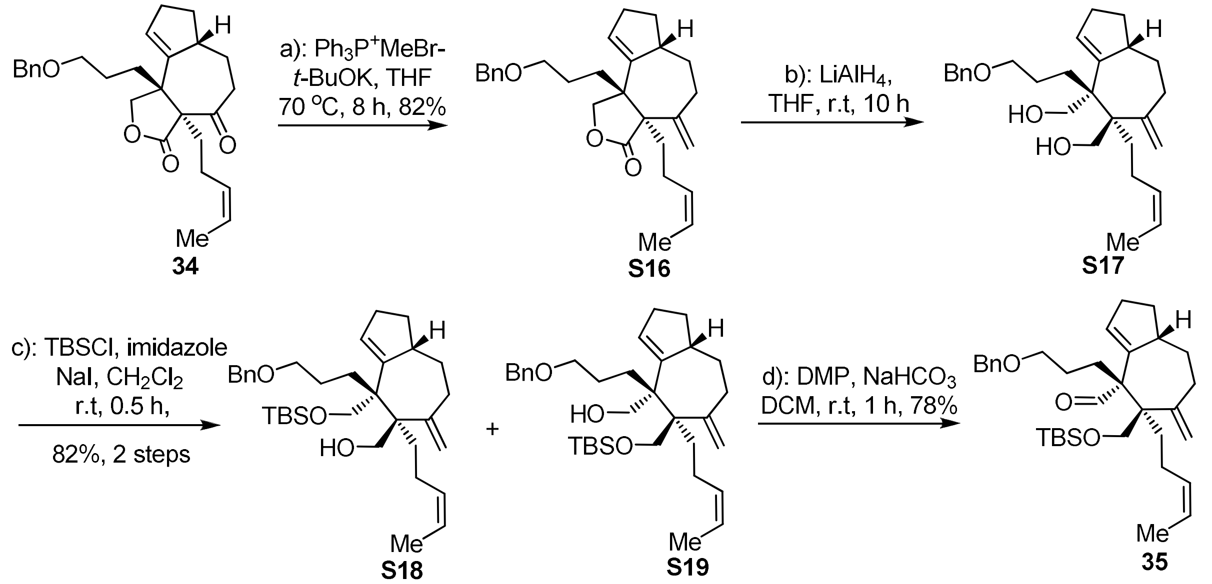


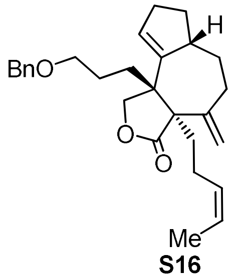
28 + 29 **S8** **34**



34

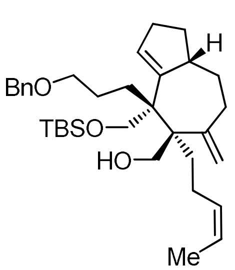
To a solution of a mixture of **28**, **29** and **S8** (98.6 mg, 278.19 umol, 1.0 equiv.) in anhydrous MeCN (8 mL) was added K_2CO_3 (115.3 mg, 834.56 umol, 2.0 equiv.) and (Z)-5-iodopent-2-ene (272.7 mg, 1.39 mmol, 5.0 equiv.) at rt under nitrogen atmosphere. After stirring at 80 °C for 14 h, the solvent was removed and the residue was dissolved in EtOAc (50 mL), washed with $Na_2S_2O_3$ (1×15 mL), H_2O (2×15 mL) and brine (2×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (10% ethyl acetate-petroleum ether) to give **34** (45.3 mg, 39%) as colorless oil, R_f = 0.50 (25% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.27 (m, 5H), 5.54 – 5.39 (m, 2H), 5.34 – 5.23 (m, 1H), 4.44 (s, 2H), 4.23 – 4.11 (m, 2H), 3.45 – 3.29 (m, 2H), 2.83 – 2.09 (m, 10H), 1.92 – 1.77 (m, 3H), 1.56 (d, J = 3.9 Hz, 3H), 1.53 – 1.41 (m, 4H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 203.5, 172.3, 142.2, 138.2, 129.8, 128.9, 128.4, 127.9, 127.7, 126.8, 125.9, 73.2,69.6, 68.3, 64.1, 50.0, 45.3, 42.5, 31.1, 30.1, 29.6, 27.3, 24.7.21.8, 17.9, 12.8 ppm. IR ν_{max} 2920, 2850, 1786, 1697, 1384, 1099, 1024, 698 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{27}H_{34}NaO_4$ [M+Na]$^+$: 445.2355, found [M+Na]$^+$: 445.2364.




S16

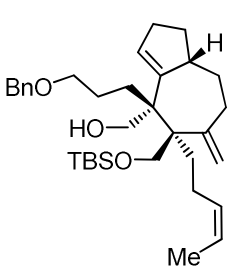
To an oven-dried flask charged with PPh3MeBr (1.26 g, 3.51 mmol, 33.0 equiv.) and *t*-BuOK (358.5 mg, 3.19 mmol, 30.0 equiv.) was added anhydrous THF (10 mL) at rt under nitrogen atmosphere. After stirred at rt for 10 mins, the suspention was transferred to another oven-dried flask charged with crude **34** (45.0 mg, 106.49 umol, 1.0 equiv.) via syringe. The mixture was stirred at rt for 10 mins and at 70 °C for 8 h. After cooling to rt, the reaction mixture was quenched with sat. NH_4Cl (10 mL), extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (2×20 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (5% ethyl acetate-petroleum ether) to give 36.5 mg of the product **S16** (82%) as colorless oil. $R_f = 0.74$ (20% ethyl acetate-petroleum ether). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.70 (s, 1H), 5.46 – 5.39 (m, 2H), 5.34 – 5.24 (m, 1H), 5.22 (s, 1H), 4.51 – 4.43 (m, 2H), 4.27 (dd, J = 9.1, 1.5 Hz, 1H), 4.05 (d, J = 9.1 Hz, 1H), 3.47 – 3.35 (m, 2H), 2.72 (s, 1H), 2.43 – 2.31 (m, 3H), 2.28 – 2.17 (m, 1H), 2.14 – 2.01 (m, 2H), 1.95 – 1.74 (m, 4H), 1.64 – 1.60 (m, 1H), 1.57 – 1.53 (m, 3H), 1.54 – 1.24 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 143.6, 141.3, 138.4, 129.3, 128.9, 128.4, 127.6, 124.8, 117.2, 72.9, 70.2, 68.2, 56.9, 51.4, 45.6, 32.3, 32.2, 31.9, 30.9, 29.6, 25.4, 21.7, 12.8 ppm. IR ν_{max} 2932, 2856, 1786, 1384, 1098, 1026, 697 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{28}H_{36}NaO_3$ $[M+Na]^+$: 443.2557, found $[M+Na]^+$: 443.2572.

To a solution of **S16** (22.0 mg, 52.31 umol, 1.0 equiv.) in anhydrous THF (5 mL) was added a solution of $LiAlH_4$ (418 uL, 1.05 mmol, 20.0 equiv., 2.5 M in THF) at 0 °C. After stirring at rt for 10 h, the reaction mixture was quenched with EtOAc (5 mL) and 1N aq. HCl (5 mL), extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (2×10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude **S17**, which was used directly for next step without purification. To a solution of crude **S17** (22.2 mg) in anhydrous CH_2Cl_2/DMF (5 mL/1mL) was added imidazole (44.5 mg, 653.53 umol, 12.5 equiv.), NaI (78.7 mg, 522.83 umol, 10.0 equiv.) and TBSCl (39.4 mg, 261.41 umol, 5.0 equiv.) successively at rt. The mixture was stirred at 40 ºC for 0.5 h. After cooling to rt, the reaction mixture was diluted with EtOAc (50 mL), washed with $Na_2S_2O_3$ (1×15 mL), H_2O (2×15 mL) and brine (2×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (10% ethyl acetate-petroleum ether) to give **S19** (12.4 mg, 44%) as colorless oil, R_f = 0.40 (5% ethyl acetate-petroleum ether), and **S18** (10.8 mg, 38%) as colorless oil, R_f = 0.60 (5% ethyl acetate-petroleum ether).



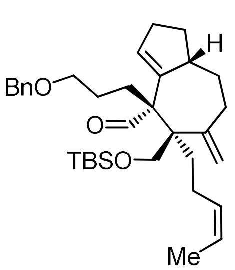
S18

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 5.41 – 5.39 (m, 2H), 5.29 (s, 1H), 5.04 (s, 1H), 4.70 (s, 1H), 4.55 (dd, J = 10.7, 3.3 Hz, 1H), 4.48 (s, 2H), 4.08 (d, J = 10.6 Hz, 1H), 4.03 (dd, J = 12.3, 3.1 Hz, 1H), 3.62 (d, J = 10.7 Hz, 1H), 3.60 – 3.53 (m, 1H), 3.44 – 3.38 (m, 2H), 2.73 – 2.66 (m, 1H), 2.36 – 2.29 (m, 1H), 2.16 – 1.59 (m, 14H), 1.58 (d, J = 4.8 Hz, 3H), 1.47 – 1.40 (m, 3H), 0.93 (s, 9H), 0.14 – 0.12 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 149.4, 138.7, 131.4, 128.6, 128.3, 127.5, 123.4, 114.9, 72.8, 71.1, 64.0, 62.8, 50.7, 48.1, 43.9, 33.8, 33.2, 32.1, 30.4, 29.1, 25.8, 25.1, 24.9, 21.9, 18.2, 12.8, -5.6 ppm. IR ν_{max} 3452, 3087, 3010, 2934, 2857, 1612, 1470, 1266, 1009, 1054, 838, 779, 697 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{54}NaO_3Si$ [M+Na]$^+$: 561.3734, found [M+Na]$^+$: 561.3739.



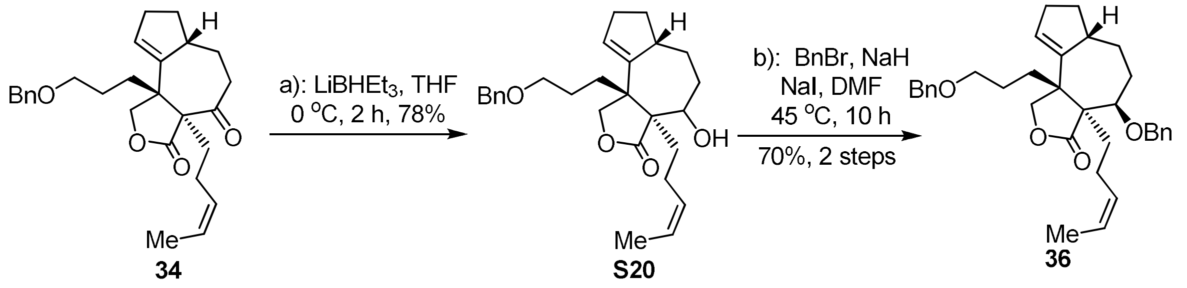
S19

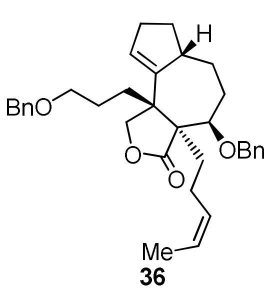
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.42 – 5.39 (m, 2H), 5.35 – 5.31 (m, 1H), 5.01 (s, 1H), 4.65 (dd, J = 11.1, 3.0 Hz, 1H), 4.53 (s, 1H), 4.49 (s, 2H), 4.10 – 4.01 (m, 2H), 3.73 (d, J = 10.7 Hz, 1H), 3.54 – 3.39 (m, 3H), 2.75 (dd, J = 3.6, 1.8 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.16 – 1.66 (m, 11H), 1.60 – 1.48 (m, 6H), 1.40 – 1.38 (m, 1H), 1.28 – 1.24 (m, 1H), 0.94 (s, 9H), 0.16 – 0.14 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 149.3, 138.9, 130.9, 129.9, 128.3, 127.5, 127.3, 123.6, 113.6, 76.8, 72.6, 71.3, 63.3, 50.4, 48.2, 43.9, 33.8, 31.9, 30.5, 28.0, 25.8, 25.3, 25.0, 21.8, 18.2, 12.9, -5.6 ppm. IR ν_{max} 3446, 3011, 2934, 2857, 1470, 1258, 1053, 837, 778, 696 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{54}NaO_3Si$ [M+Na]$^+$: 561.3734, found [M+Na]$^+$: 561.3761.



35

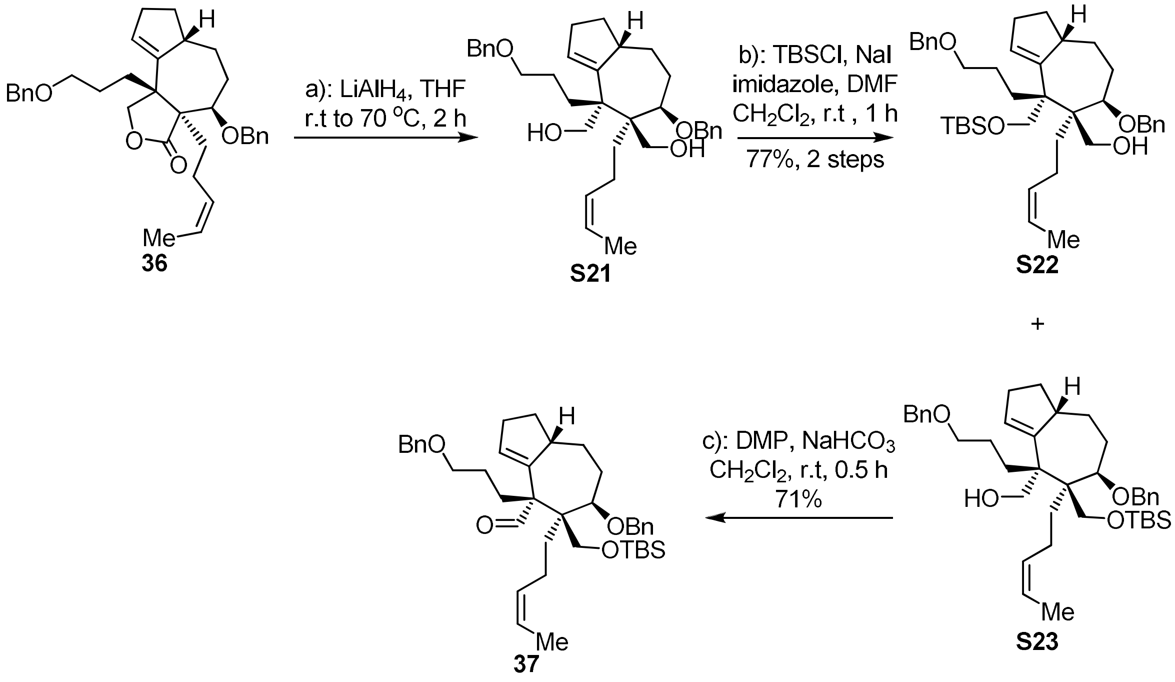
To a solution of **S19** (13.0 mg, 24.12 umol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) was added $NaHCO_3$ (81.1 mg, 964.97 umol, 40.0 equiv.) and DMP (102.3 mg, 241.24 umol, 10.0 equiv.) successively at rt. After stirring at for 1 h, the solvent was removed. The residue was dissolved in EtOAc (30 mL), followed by addition of sat. $Na_2S_2O_3$ (5 mL) and sat. $NaHCO_3$ (5 mL), and then stirred at rt for 20 mins. The resulting mixture was seperated, and the organic layer was washed with H_2O (2×5 mL) and brine (2×5 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (1% ethyl acetate-petroleum ether) to give **35** (10.1 mg, 78%) as colorless oil, R_f = 0.65 (5% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.38 – 7.26 (m, 5H), 5.68 (d, *J* = 1.7 Hz, 1H), 5.44 – 5.35 (m, 2H), 5.05 (s, 1H), 4.54 (s, 1H), 4.50 (s, 2H), 3.89 (d, *J* = 10.4 Hz, 1H), 3.57 (d, *J* = 10.1 Hz, 1H), 3.54 – 3.54 (m, 1H), 3.46 – 3.43 (m, 1H), 2.71 – 2.68 (m, 1H), 2.40 – 2.37 (m, 1H), 2.24 – 2.10 (m, 4H), 1.96 – 1.66 (m, 10H), 1.58 – 1.57 (m, 3H), 1.46 – 1.42 (m, 1H), 1.29 – 1.24 (m, 1H), 0.89 (s, 9H), 0.05 – 0.04 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 150.3, 145.1, 138.9, 130.7, 130.5, 128.3, 127.6, 127.4, 123.7, 114.9, 72.6, 71.3, 62.6, 56.3, 54.1, 45.6, 32.7, 31.5, 30.8, 30.2, 29.7, 28.9, 25.9, 25.5, 22.3, 18.3, 12.8, -5.7, -5.8 ppm. IR ν_{max} 3087, 3011, 2929, 2856, 1720, 1470, 1256, 1096, 837, 770, 696 cm^{-1}. HRMS (m/z): ESI $[M+Na]^+$ calcd for $C_{34}H_{52}NaO_3Si$ $[M+Na]^+$: 559.3578, found $[M+Na]^+$: 559.3591.



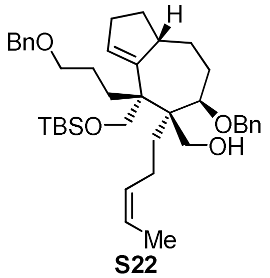


36

To a solution of a mixture of **34** (45.0 mg, 106.49 umol, 1.0 equiv.) in anhydrous THF (10 mL) was added a solution of $LiBHEt_3$ (1.06 mL, 1.06 mmol, 10.0 equiv., 1.0 M) in THF at -10 °C and stirred at that temperature for 2 h. After quenched with MeOH (1 mL) and 1 N aq. HCl (10 mL), the resulting mixture was extracted with EtOAc (3×15 mL). The combined organic layer was washed with brine (2×15 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give 46 mg of the crude **S20**, which was used directly for next step without purification. To a crude **S20** in anhydrous DMF (5 mL) was added NaI (324.8 mg, 2.17 mmol, 20.0 equiv.) and NaH (43.3 mg, 1.07 mmol, 10.0 equiv.) at rt. After stirring at rt for 10 mins, BnBr (226.8 uL, 2.17 mmol, 20.0 equiv.) was added at rt and stirred at 45 °C for 10 h. After cooling to rt, the reaction mixture was quenched with sat. NH_4Cl (15 mL), extracted with EtOAc (2×30 mL). The combined organic layer was washed with brine (3×20 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (5% ethyl acetate-petroleum ether) to give **36** (39.0 mg, 70%, 2 steps) as colorless oil, R_f = 0.62 (20% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 10H), 5.50 – 5.40 (m, 1H), 5.34 – 5.27 (m, 2H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.64 – 4.59 (m, 1H), 4.44 (s, 2H), 4.24 (d, *J* = 8.2 Hz, 1H), 4.11 – 4.08 (m, 2H), 3.45 – 3.33 (m, 2H), 2.78 (s, 1H), 2.45 – 1.62 (m, 11H), 1.60 (d, *J* = 6.1 Hz, 3H), 1.56 – 1.29 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 144.3, 139.3, 138.5, 129.2, 128.3, 128.1, 127.6, 127.5, 127.4, 127.1, 125.1, 73.3, 73.1, 70.7, 69.9, 56.1, 52.9, 46.4, 32.4, 30.9, 29.7, 27.3, 26.8, 25.9, 21.6, 12.8 ppm. IR ν_{max} 3063, 3027, 2925, 2853, 1774, 1496, 1454, 1359, 1103, 1012, 696 cm^{-1}. HRMS (m/z): ESI [M+Na]$^+$ calcd for $C_{34}H_{42}NaO_4$ [M+ Na]$^+$: 537.2975, found [M+ Na]$^+$: 537.2981.

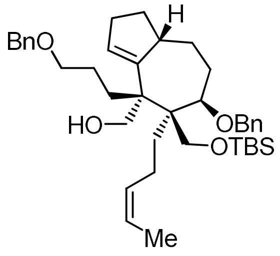


To a solution of **36** (60.0 mg, 116.57 umol, 1.0 equiv.) in anhydrous THF (5 mL) was added a solution of $LiAlH_4$ (1.17 mL, 1.17 mmol, 10.0 equiv., 1.0 M in THF) at rt. After stirring at 70 °C for 5 h, the reaction mixture was quenched with EtOAc (5 mL) and 1N aq. HCl (5 mL), extracted with EtOAc (3×15 mL). The combined organic layer was washed with brine (2×15 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give 60.5 mg of crude **S21**, which was used directly for next step without purification. To a solution of crude **S21** (60.5 mg) in anhydrous CH_2Cl_2/DMF (10 mL/2 mL) was added imidazole (98.4 mg, 1.45 mmol, 12.5 equiv.), NaI (173.4 mg, 1.16 mmol, 10.0 equiv.) and TBSCl (87.2 mg, 578.34 umol, 5.0 equiv.) successively at rt. The mixture was stirred at 40 °C for 0.5 h. After cooling to rt, the reaction mixture was diluted with EtOAc (60 mL), washed with $Na_2S_2O_3$ (1×15 mL), H_2O (2×15 mL) and brine (2×15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by silica gel column chromatography (5% to 10% ethyl acetate-petroleum ether) to give **S22** (35.8 mg, 49%) as colorless oil, R_f = 0.42 (5% ethyl acetate-petroleum ether), and **S23** (20.1 mg, 28%) as colorless oil, R_f = 0.32 (5% ethyl acetate-petroleum ether).



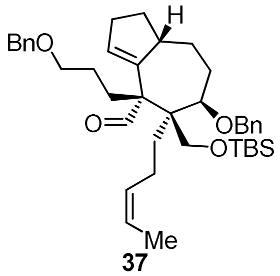
S22

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.21 (m, 10H), 5.43 – 5.28 (m, 3H), 4.61 (dd, *J* = 12.0, 9.7 Hz, 2H), 4.49 (d, *J* = 9.9 Hz, 2H), 4.33 – 4.24 (m, 1H), 4.19 – 4.10 (m, 1H), 3.99 (d, *J* = 11.1 Hz, 1H), 3.59 – 3.26 (m, 5H), 2.93 (d, *J* = 5.8 Hz, 1H), 2.31 – 1.93 (m, 7H), 1.88 – 1.66 (m, 5H), 1.59 (s, 3H), 1.52 – 1.32 (m, 4H), 0.93 – 0.88 (m, 9H), 0.10 – 0.01 (m, 6H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.9, 139.0, 138.8, 131.6, 130.9, 129.7, 128.2, 127.3, 123.7, 83.1, 72.8, 71.7, 70.7, 64.8, 63.5, 50.1, 48.7, 44.7, 32.9, 30.7, 28.5, 26.0, 25.9, 25.8, 25.4, 24.6, 21.7, 21.4, 18.1, 17.9, 12.9, -5.7 ppm. IR ν_{max} 3420, 3064, 3029, 2930, 2855, 1454, 1094, 734, 697 cm^{-1}. HRMS (m/z): ESI [M+N$_a$]$^+$ calcd for $C_{40}H_{60}NaO_4Si$ [M+N$_a$]$^+$: 655.4153, found [M+N$_a$]$^+$: 655.4185.



S23

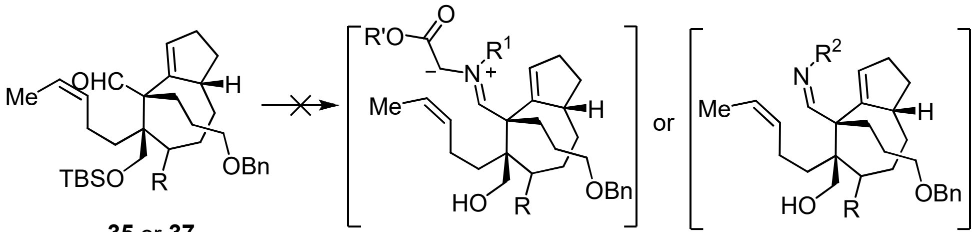
^{1}H NMR (500 MHz, CDCl$_3$) δ 1H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.27 (m, 5H), 5.45 – 5.37 (m, 2H), 5.27 (d, *J* = 2.1 Hz, 1H), 4.57 (dd, *J* = 11.7, 9.3 Hz, 1H), 4.48 (q, *J* = 12.1 Hz, 2H), 4.31 – 4.24 (m, 3H), 4.02 (d, *J* = 10.6 Hz, 1H), 3.63 – 3.41 (m, 6H), 2.94 (s, 1H), 2.35 – 2.31 (m, 2H), 2.20 – 1.76 (m, 10H), 1.62 – 1.57 (m, 3H), 0.94 – 0.87 (m, 9H), 0.16 – 0.04 (m, 6H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.6, 147.3, 132.3, 131.4, 130.9, 128.9, 128.3, 128.2, 127.4, 127.3, 127.1, 126.9, 83.7, 72.9, 71.4, 71.3, 65.6, 64.6, 63.7, 49.4, 49.2, 44.6, 33.0, 31.9, 30.6, 29.4, 27.2, 26.0, 25.4, 22.7, 22.4, 21.5, 12.8, -5.6 ppm. IR ν_{max} 3445, 3063, 3028, 2951, 2929, 2856, 1455, 1361, 1254, 1057, 836, 777, 732, 696 cm^{-1}. HRMS (m/z): ESI [M+N$_a$]$^+$ calcd for $C_{40}H_{60}NaO_4Si$ [M+N$_a$]$^+$: 655.4153, found [M+N$_a$]$^+$: 655.4175.



37

To a solution of **S23**(2.7 mg, 4.27 umol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) was added $NaHCO_3$ (14.3 mg, 170.62 umol, 40.0 equiv.) and DMP (18.1 mg, 42.65 umol, 10.0 equiv.) successively at rt. After stirring at for 0.5 h, the solvent was removed. The residue was dissolved in EtOAc (20 mL), followed by addition of sat. $Na_2S_2O_3$ (5 mL) and sat. $NaHCO_3$ (5 mL), and then stirred at rt for 20 mins. The resulting mixture was seperated, and the organic layer was washed with H_2O (2×5 mL) and brine (2×5 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product, which was purified by preparative thin layer chromatography (3% ethyl acetate-petroleum ether) to give **37** (1.9 mg, 71%) as colorless oil, R_f = 0.74 (5% ethyl acetate-petroleum ether). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1H NMR (500 MHz, CDCl3) δ10.03 – 10.02 (m, 1H), 7.33 – 7.22 (m, 10H), 5.44 – 5.39 (m, 3H), 5.34 (d, *J* = 2.1 Hz, 1H), 4.53 – 4.49 (m, 3H), 4.27 – 4.25 (m, 1H), 3.91 (d, *J* = 6.7 Hz, 1H), 3.86 – 3.84 (m, 1H), 3.51 – 3.43 (m, 3H), 2.95 (s, 1H), 2.62 – 2.55 (m, 1H), 2.43 – 1.75 (m, 10H), 1.68 – 1.58 (m, 4H), 1.55 – 1.34 (m, 5H), 0.92 – 0.82 (m, 9H), 0.05 – 0.00 (m, 6H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 207.8, 146.8, 138.8, 138.7, 130.9, 130.1, 128.3, 127.4, 127.2, 126.9, 124.1, 82.7, 72.9, 71.3, 63.8, 55.9, 51.6, 44.7, 32.9, 30.6, 30.2, 26.2, 25.9, 25.7, 23.9, 23.3, 22.5,18.3, 12.8, -5.7 ppm. IR ν_{max} 3028, 3011, 2927, 2855, 1708, 1454, 1361, 1252, 1091, 837, 777, 733, 696 cm^{-1}. HRMS (m/z): ESI $[M+N_a]^+$ calcd for $C_{40}H_{58}NaO_4Si$ $[M+N_a]^+$: 653.3997, found $[M+N_a]^+$: 653.4042.

Conditions Screening for Cycloaddition



35 or **37** **azomethine ylide** **imine**

Entry	R	Additive	Solvent	Temp.	Time	Yield
1	CH_2 (**35**)	$BnNHCH_2CO_2H$	PhMe	110°C	15 h	decomposed
2	CH_2 (**35**)	$BnNHCH_2CO_2H$	DMF	90 °C to 110 °C	12	NR
3	CH_2 (**35**)	$BnNHCH_2CO_2H$ Et_3N	DMF	110 °C	4 h	decomposed
4	CH_2 (**35**)	$HCl.BnNHCH_2CO_2Et$ Et_3N	PhMe	rt to 110 °C	12.5 h	NR
5	CH_2 (**35**)	$BnNH_2$, $TfOCH_2TMS$ CsF	DCM	rt to 40 °C	28 h	NR
6	CH_2 (**35**)	$BnNHCH_2TMS$ $MgSO_4$	DCE	90 °C	15 h	NR
7	CH_2 (**35**)	NH_3, Ti(Oi-Pr)$_4$ TMSCN	MeOH	0°C to 70°C	22 h	NR
8	CH_2 (**35**)	NH_3, NH_4Cl, TMSCN	MeOH	0°C to 70°C	21 h	NR
9	CH_2 (**35**)	$BnNH_2$, $AlMe_3$ TMSCN	PhMe	0°C to rt	18.5 h	NR
10	OBn (**37**)	$BnNHCH_2TMS$ $MgSO_4$	DCE	90 °C	15 h	NR
11	OBn (**37**)	$BnNHCH_2CO_2H$ Et_3N	DMF	90 °C to 155 °C	23 h	decomposed
12	OBn (**37**)	$BnNHCH_2CO_2H$ 4Å MS, Et_3N	DMF	90 °C to 155 °C	23 h	ND
13	OBn (**37**)	$BnNHCH_2CO_2H$ 4Å MS	DMF	110°C to 155 °C	17 h	decomposed

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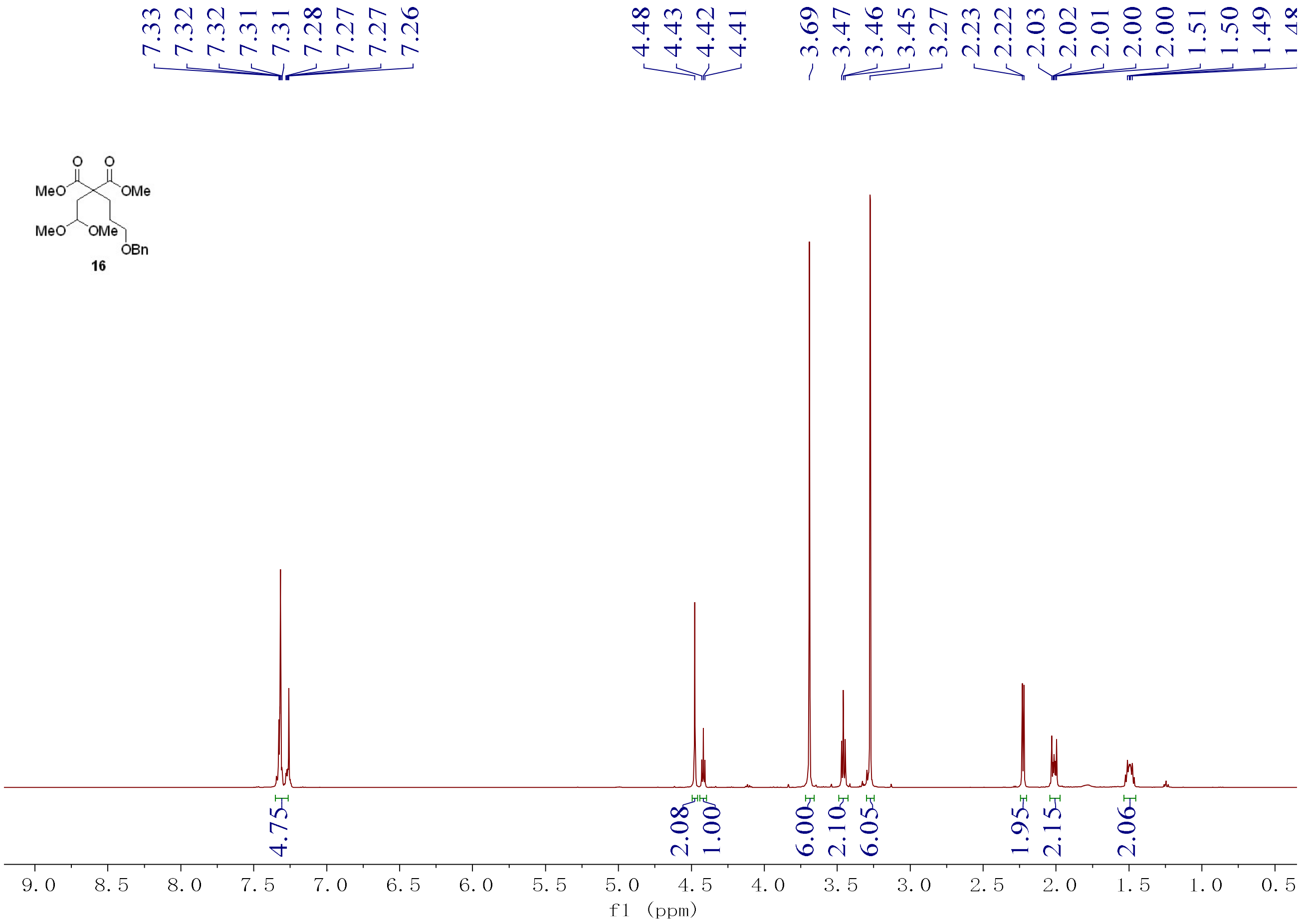
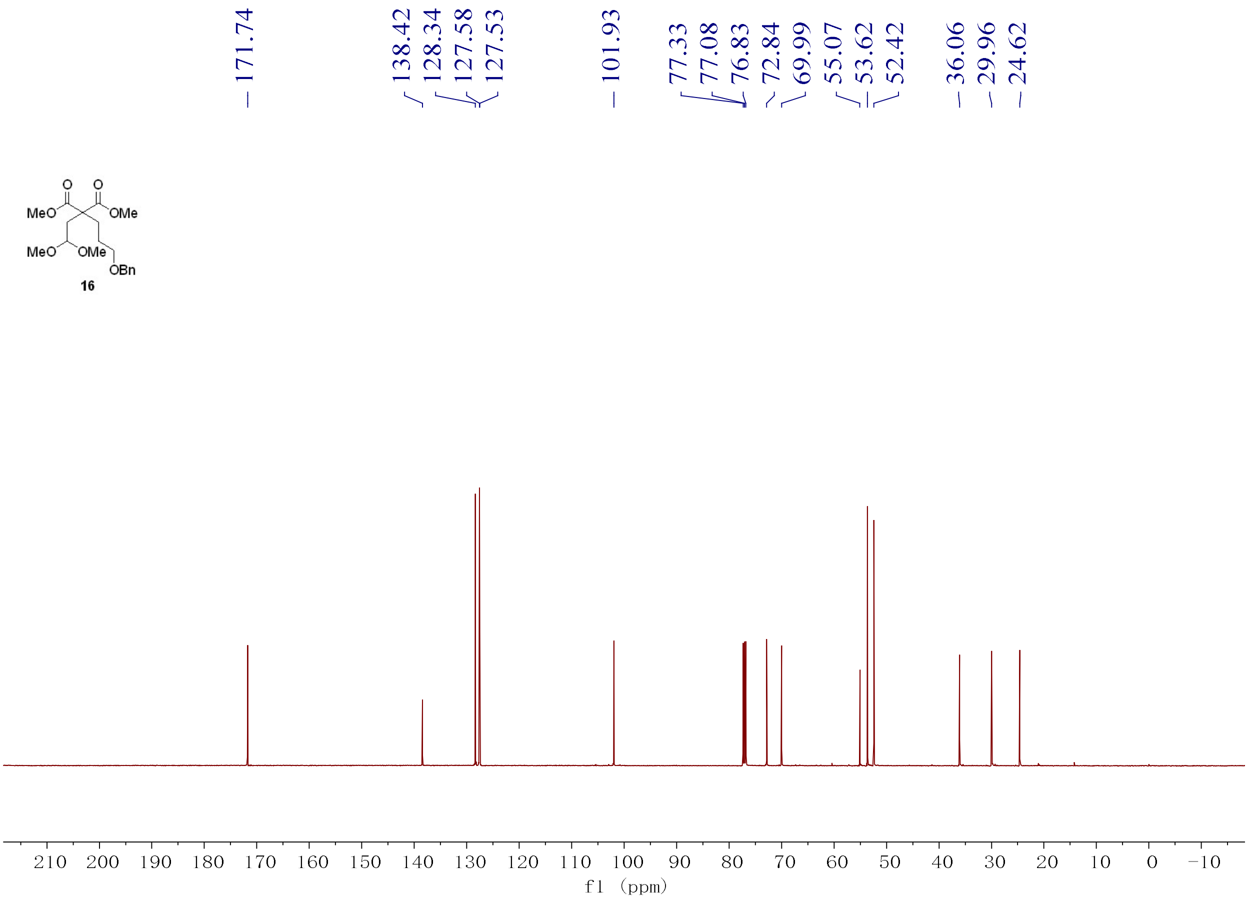
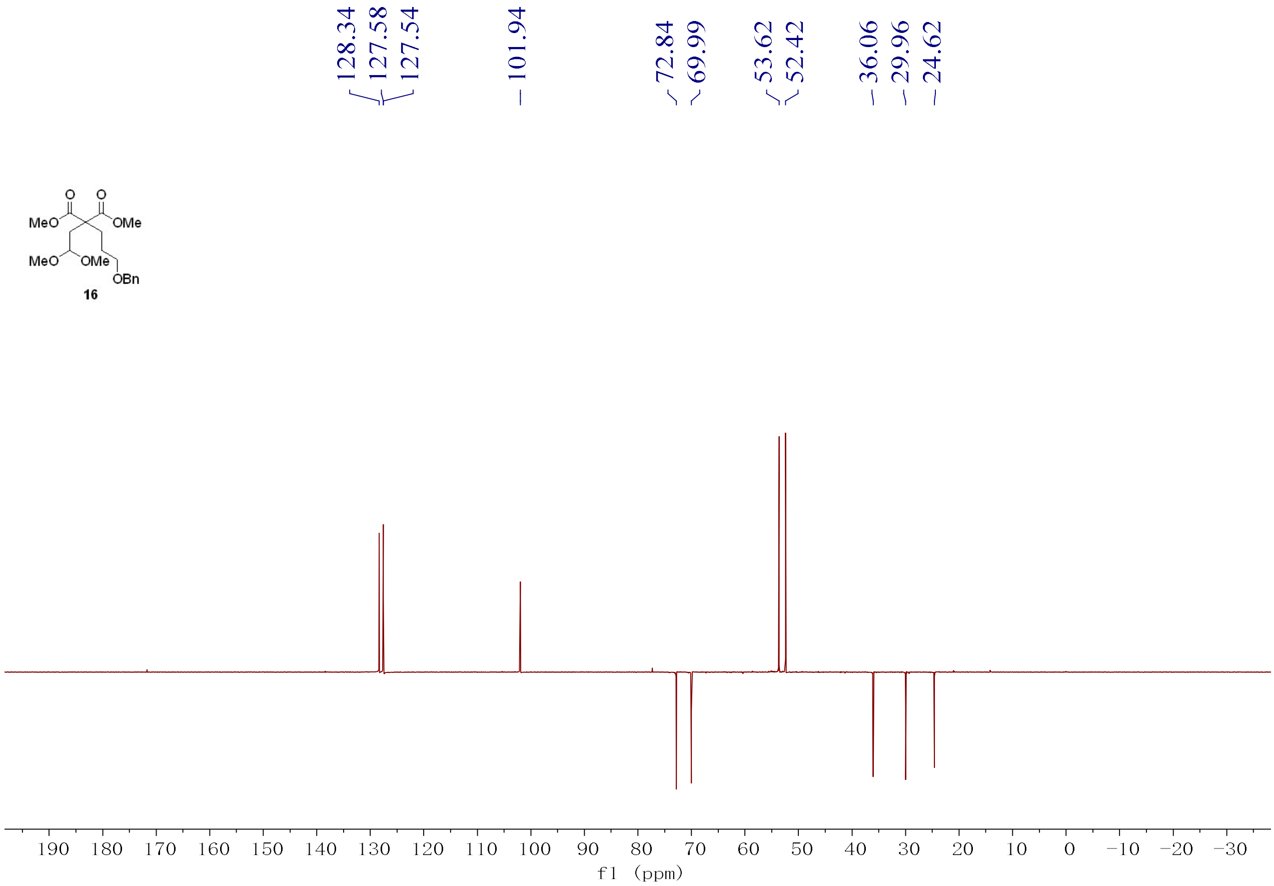
II. ^{1}H and ^{13}C NMR Spectra



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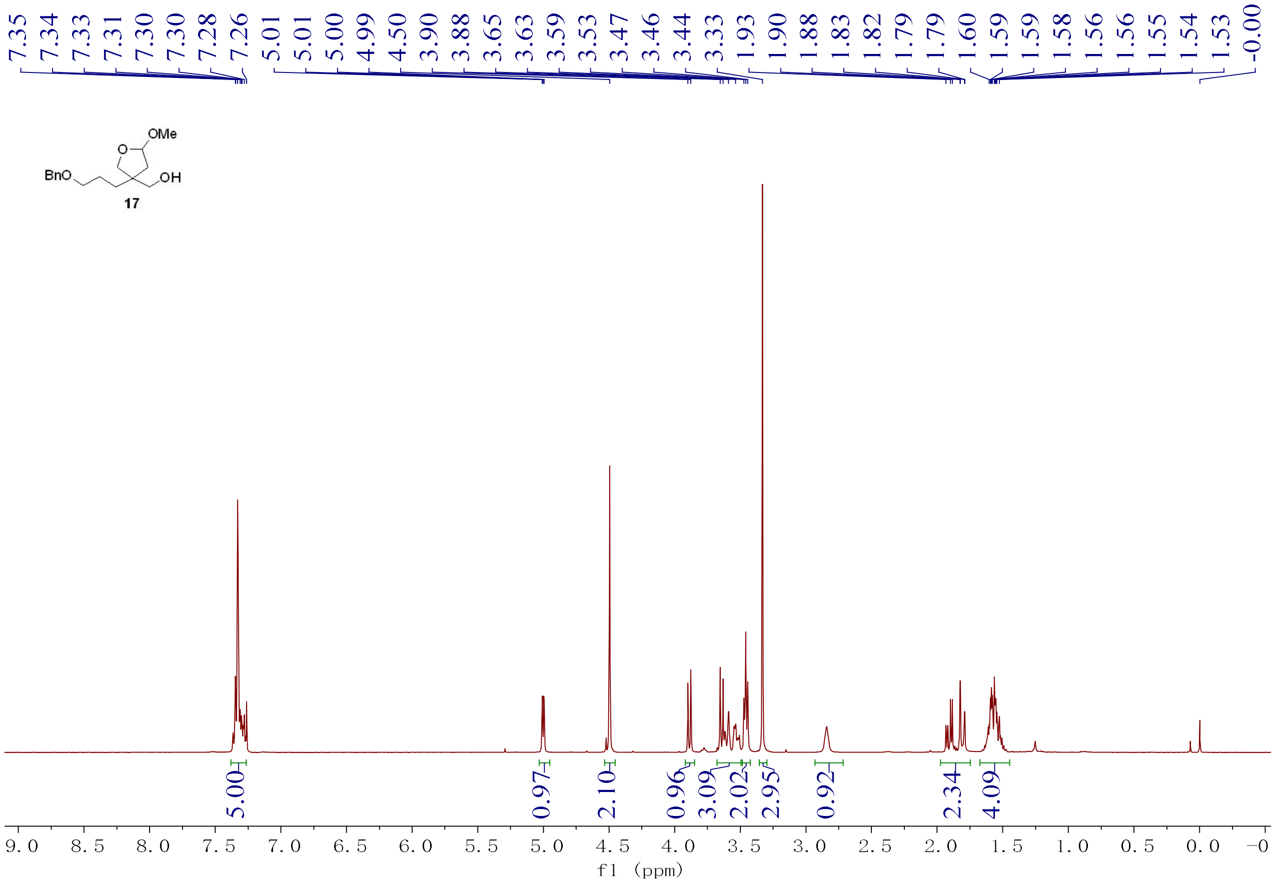
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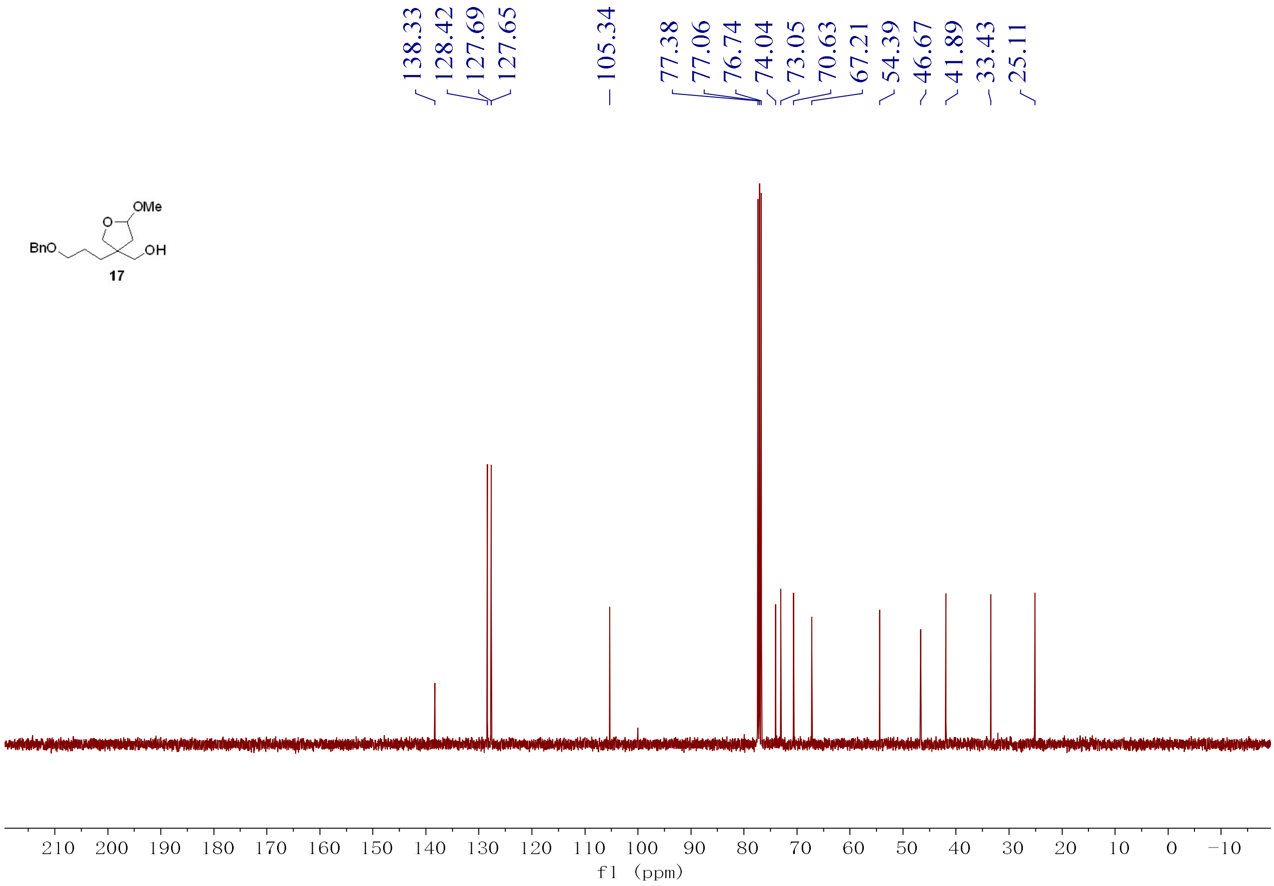
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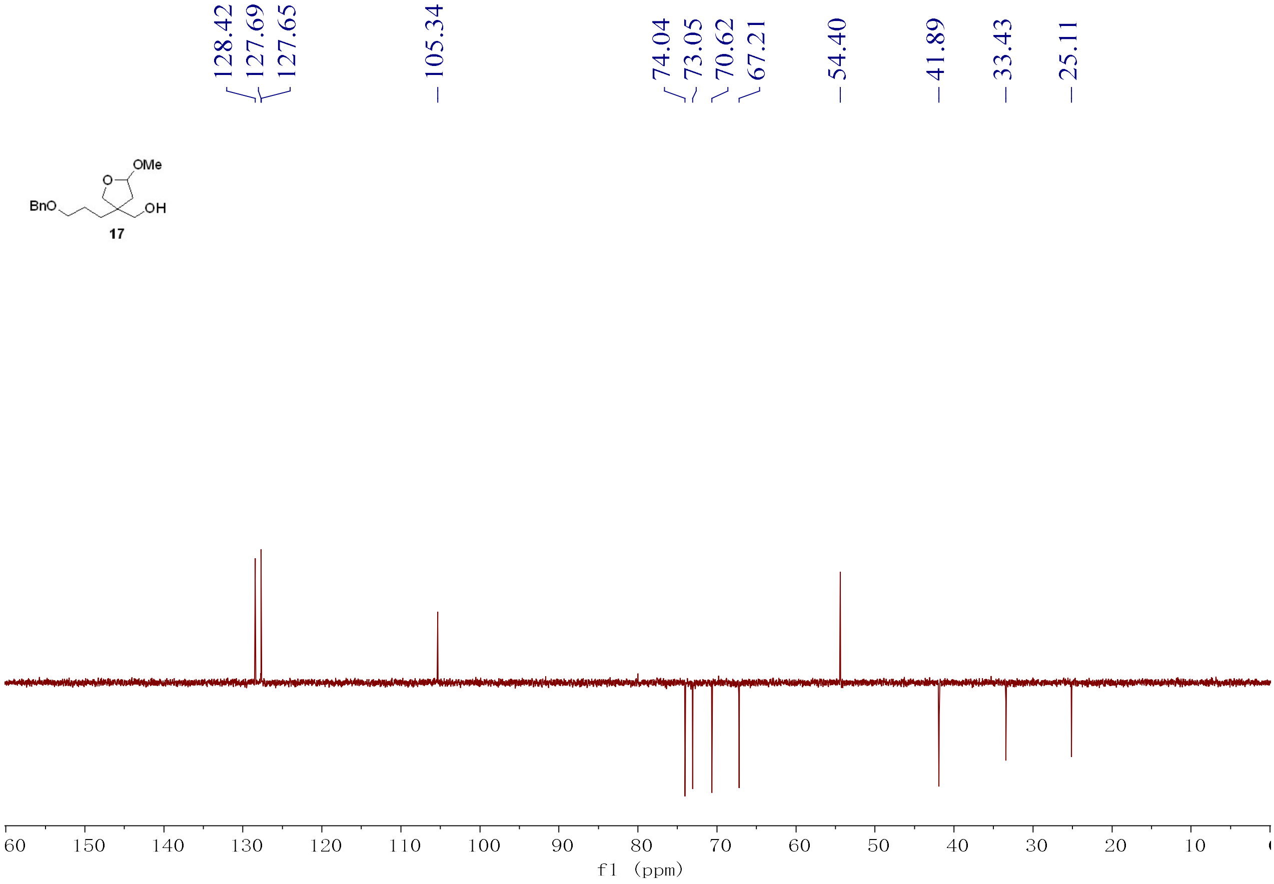
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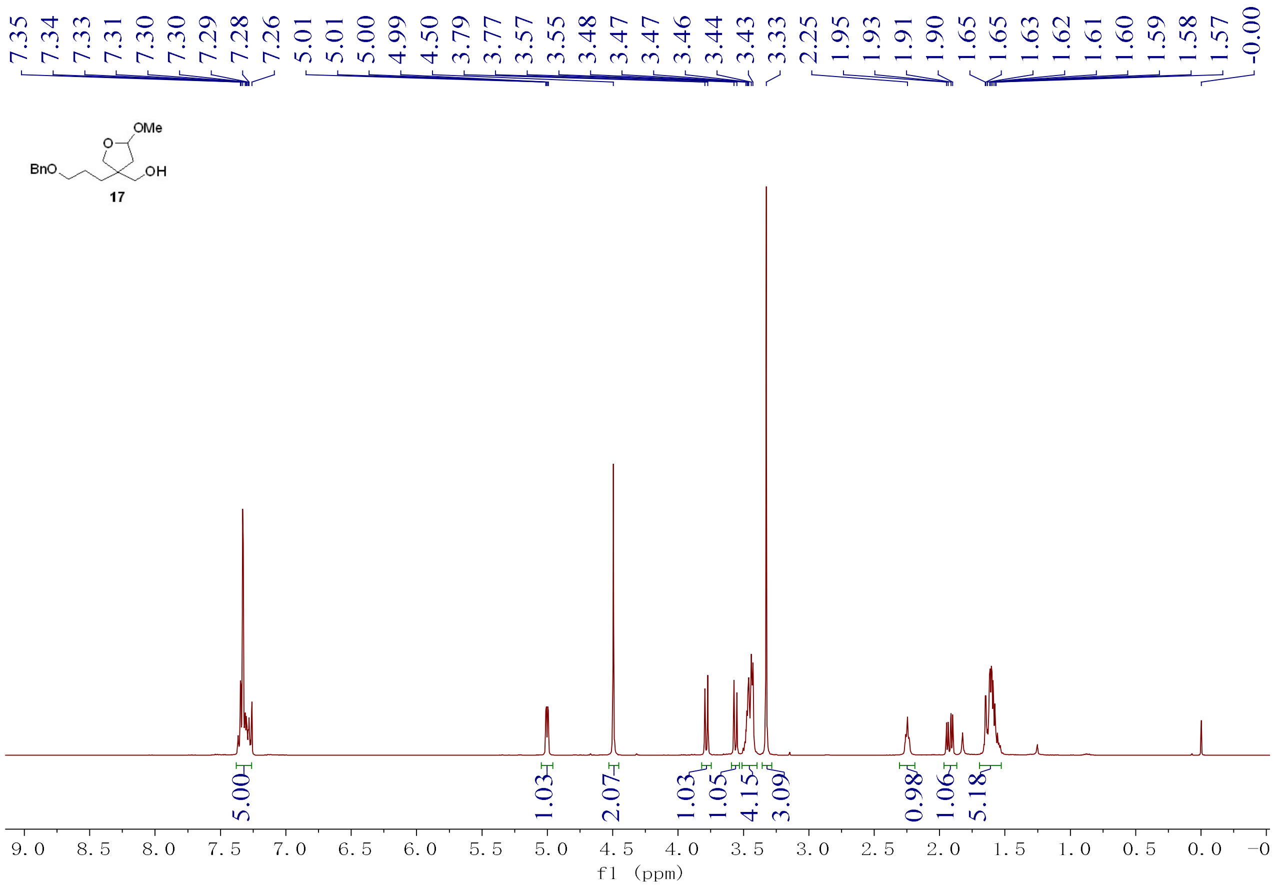
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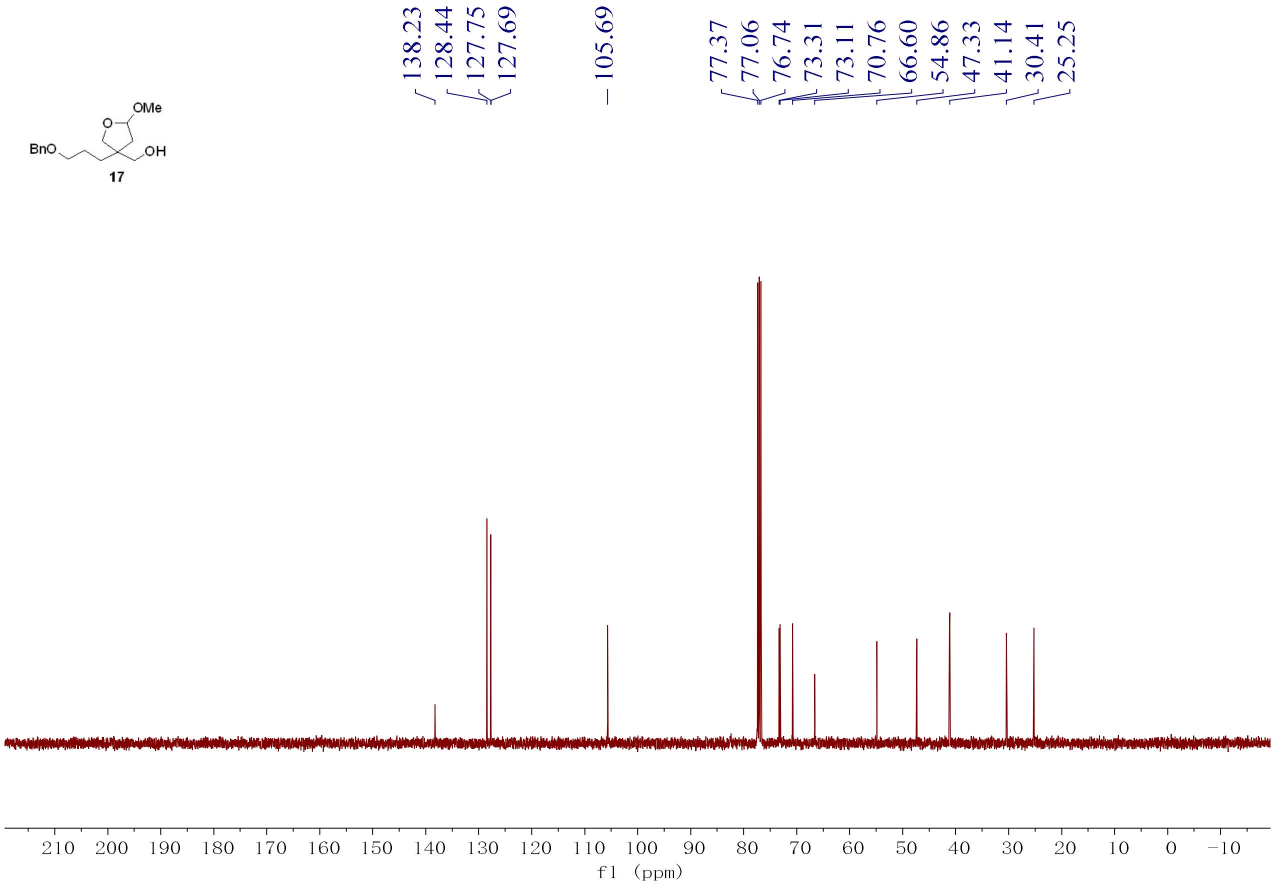
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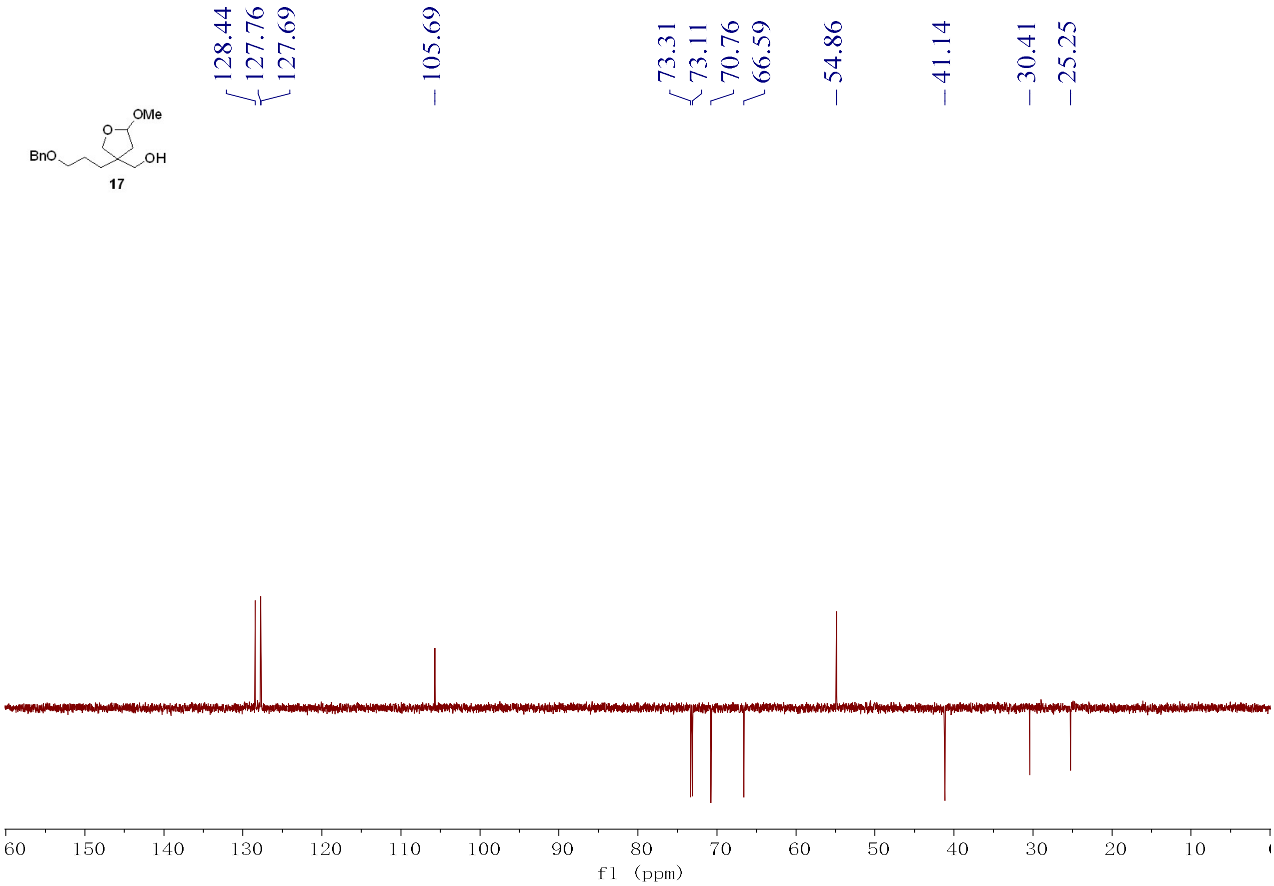
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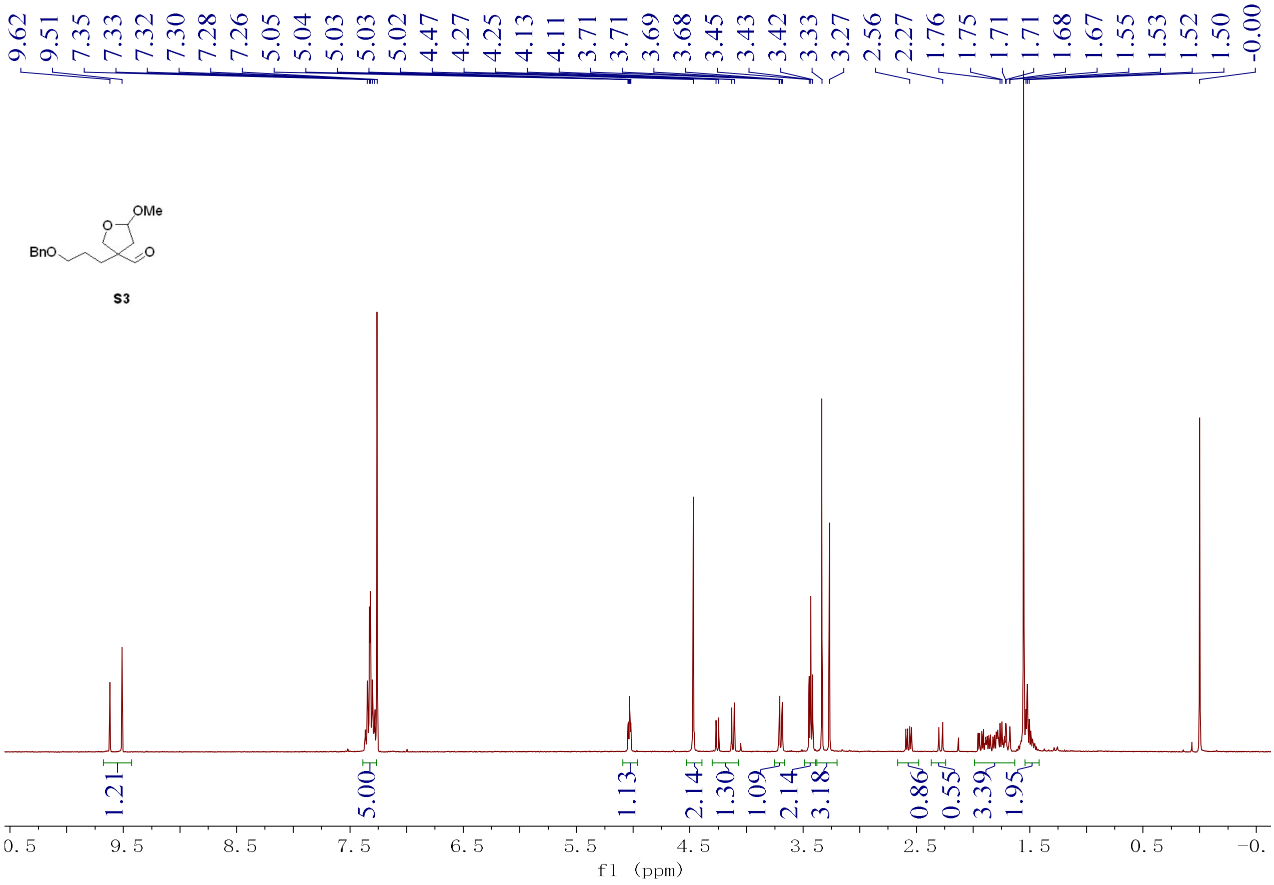
20
10
f1 (ppm)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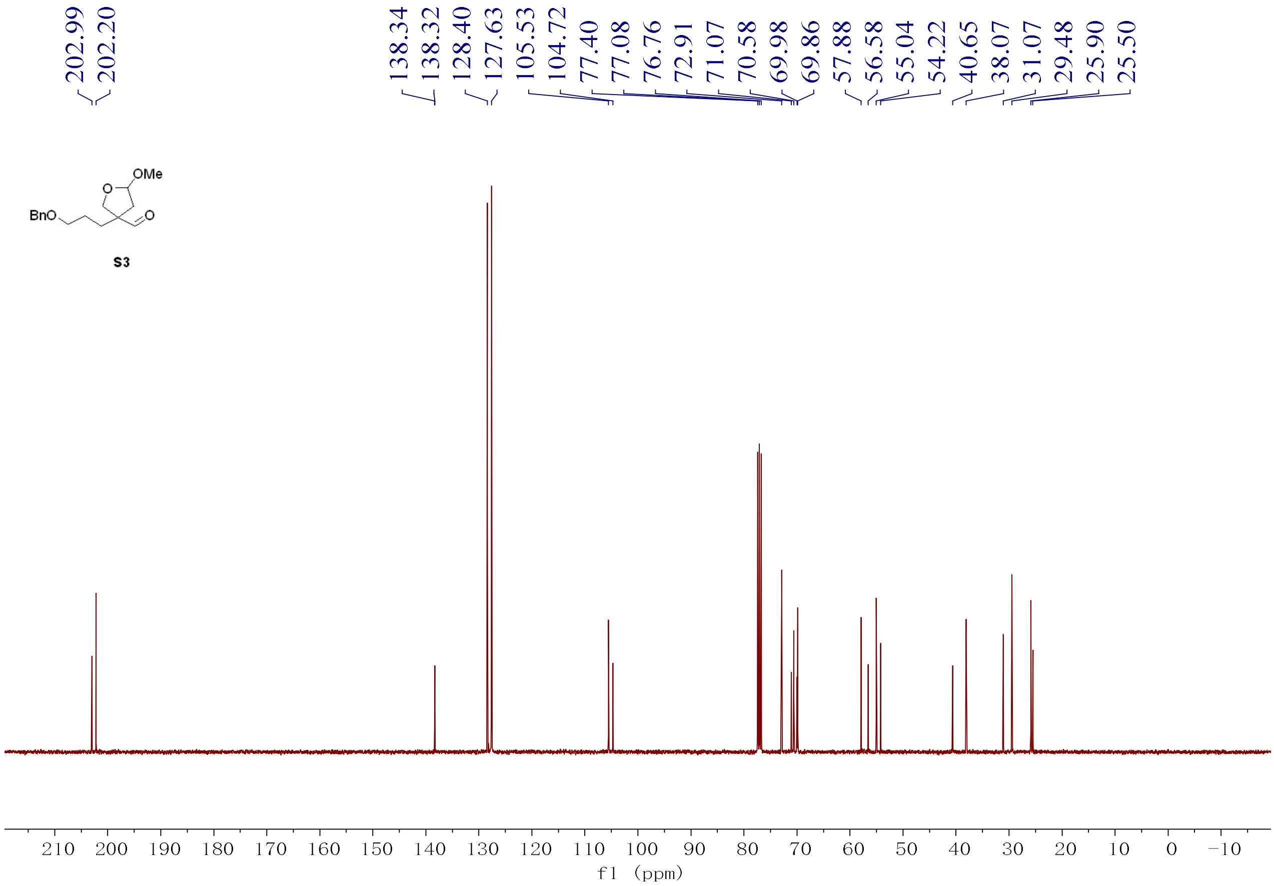
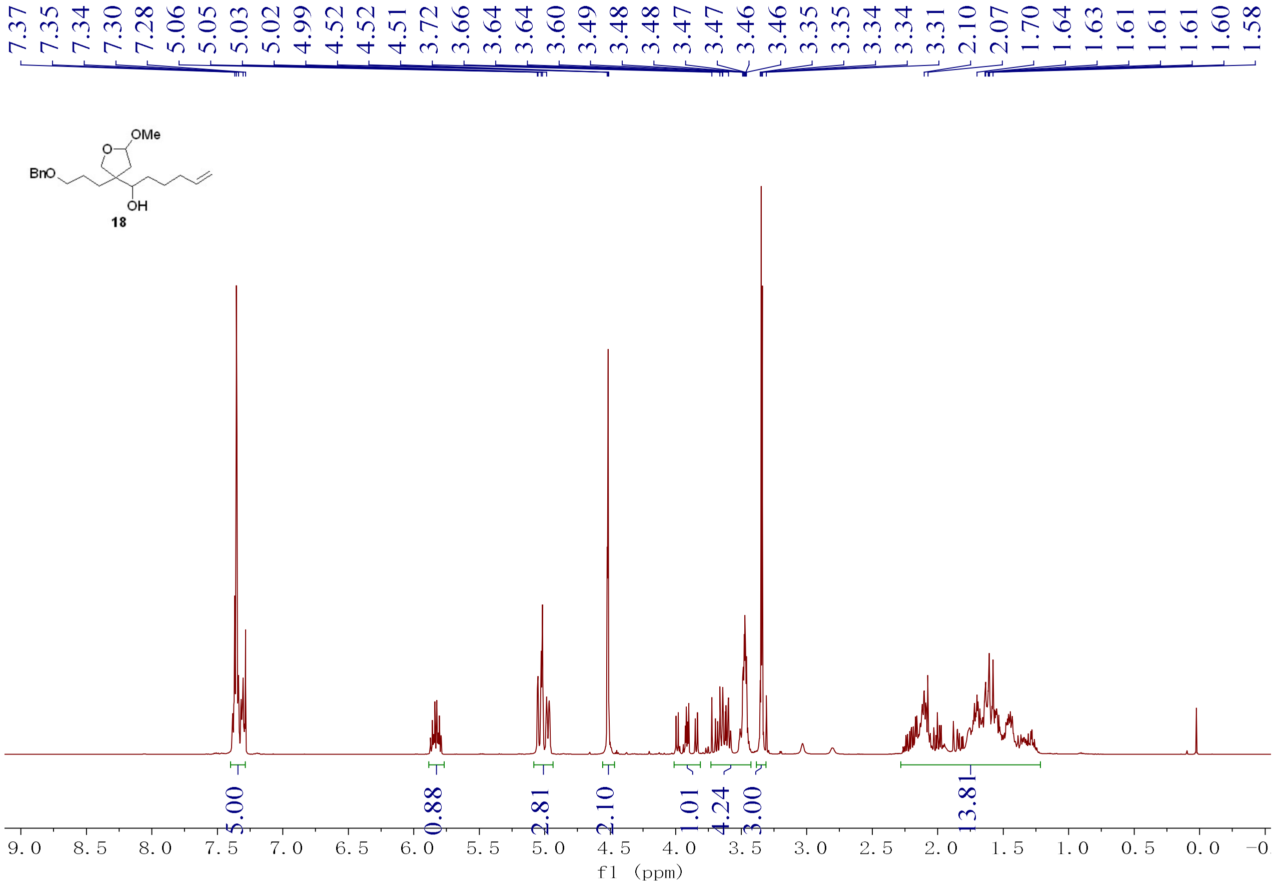
9.51
7.35
7.33
7.32
7.30
7.28
7.26
5.05
5.04
5.03
5.03
5.02
4.47
4.27
4.25
4.13
4.11
3.71
3.71
3.69
3.68
3.45
3.43
3.42
3.33
3.27
2.56
2.27
1.76
1.75
1.71
1.71
1.68
1.67
1.55
1.53
1.52
1.50
-0.00
OMe
O
BnO
O
S3
1.21
5.00
1.13
2.14
1.30
1.09
2.14
3.18
0.86
0.55
3.39
1.95
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)


202.99
202.20
138.34
138.32
128.40
127.63
105.53
104.72
77.40
77.08
76.76
72.91
71.07
70.58
69.98
69.86
57.88
56.58
55.04
54.22
40.65
38.07
31.07
29.48
25.90
25.50
OMe
O
BnO
O
S3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.35
7.34
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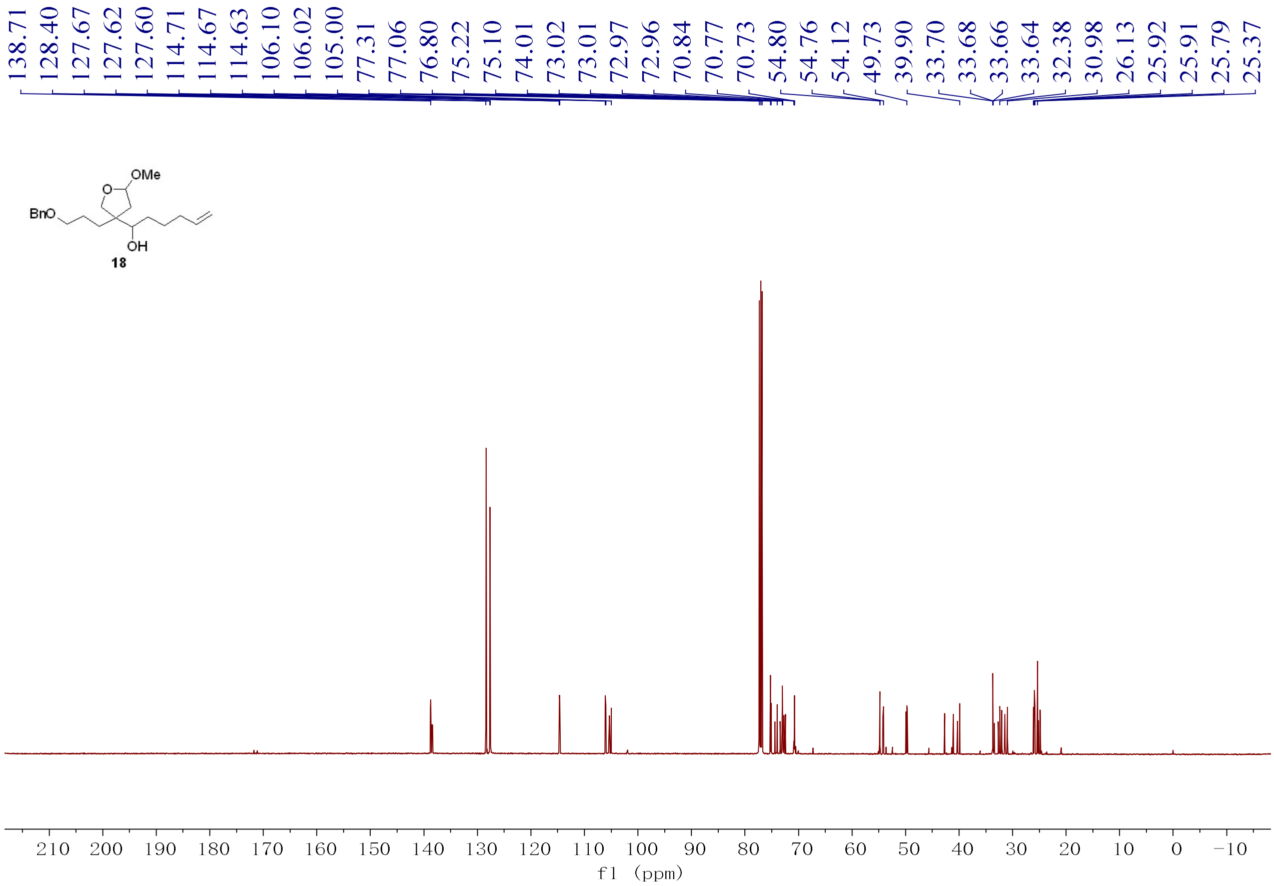
5.05
5.03
5.02
4.99
4.52
4.52
4.51
3.72
3.66
3.64
3.64
3.60
3.49
3.48
3.48
3.47
3.47
3.46
3.46
3.35
3.35
3.34
3.34
3.31
2.10
2.07
1.70
1.64
1.63
1.61
1.61
1.61
1.60
1.58
OMe
O
BnO
OH
18
5.00
0.88
2.81
2.10
1.01
4.24
3.00
13.81
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)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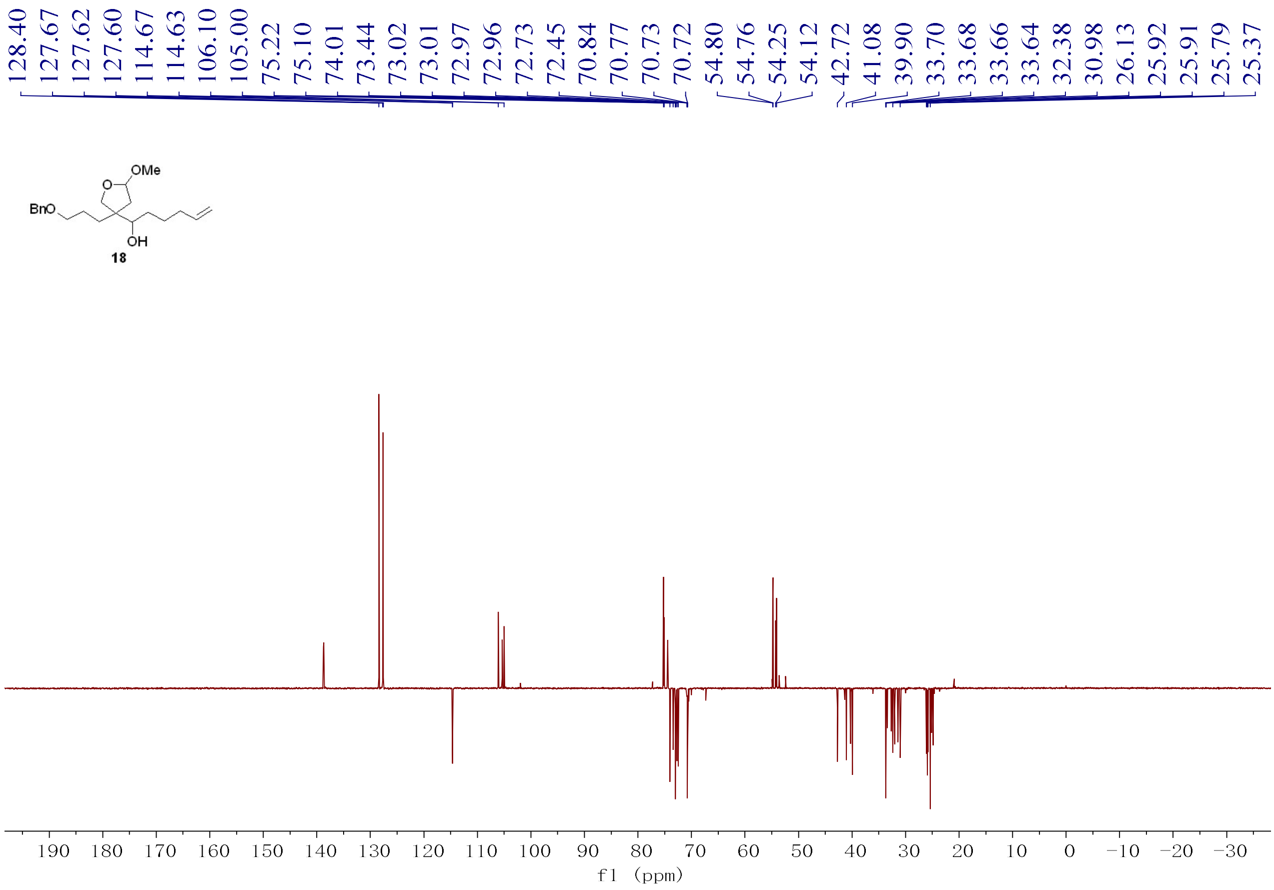
127.67
127.62
127.60
114.71
114.67
114.63
106.10
106.02
105.00
77.31
77.06
76.80
75.22
75.10
74.01
73.02
73.01
72.97
72.96
70.84
70.77
70.73
54.80
54.76
54.12
49.73
39.90
33.70
33.68
33.66
33.64
32.38
30.98
26.13
25.92
25.91
25.79
25.37
OMe
O
BnO
OH
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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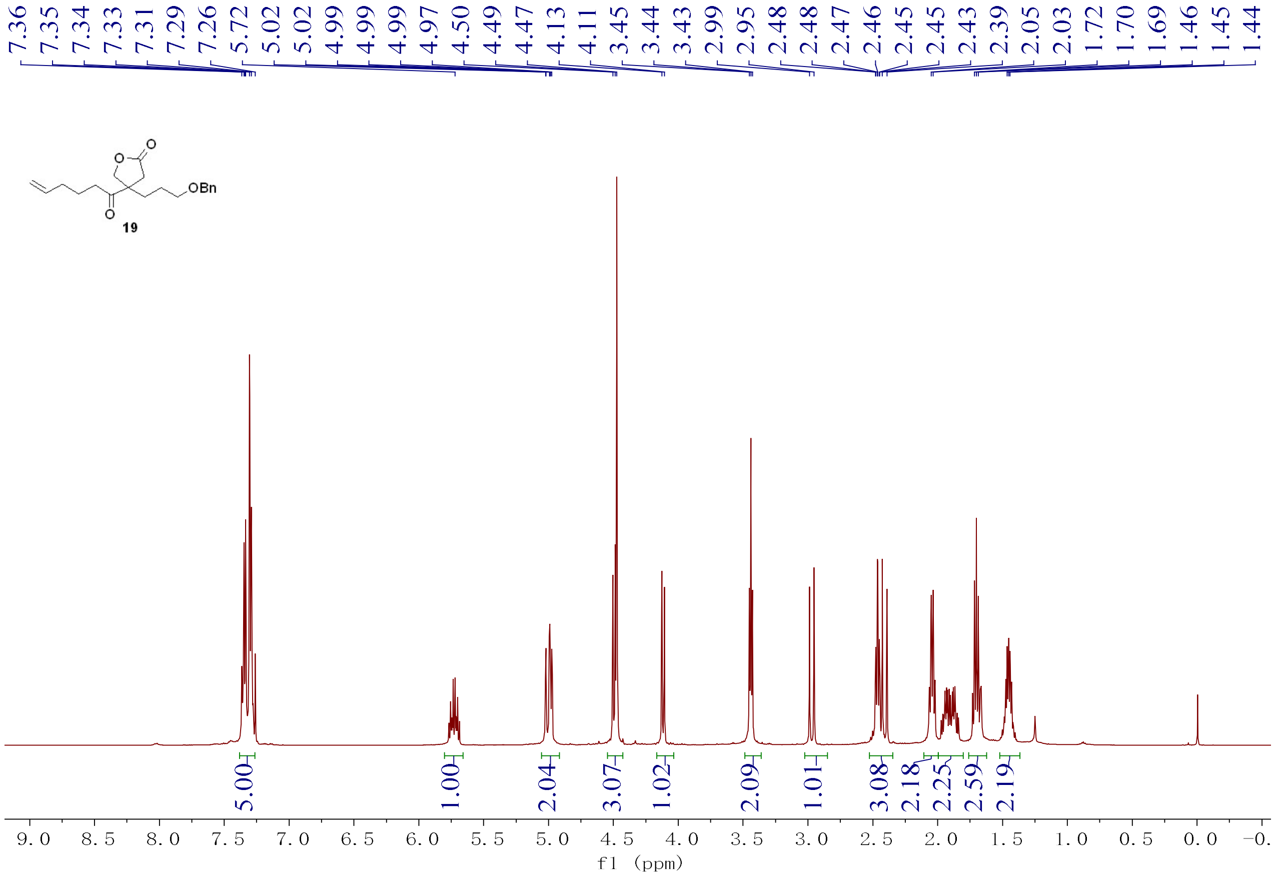
127.67
127.62
127.60
114.67
114.63
106.10
105.00
75.22
75.10
74.01
73.44
73.02
73.01
72.97
72.96
72.73
72.45
70.84
70.77
70.73
70.72
54.80
54.76
54.25
54.12
42.72
41.08
39.90
33.70
33.68
33.66
33.64
32.38
30.98
26.13
25.92
25.91
25.79
25.37
OMe
O
BnO
OH
18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)


7.36
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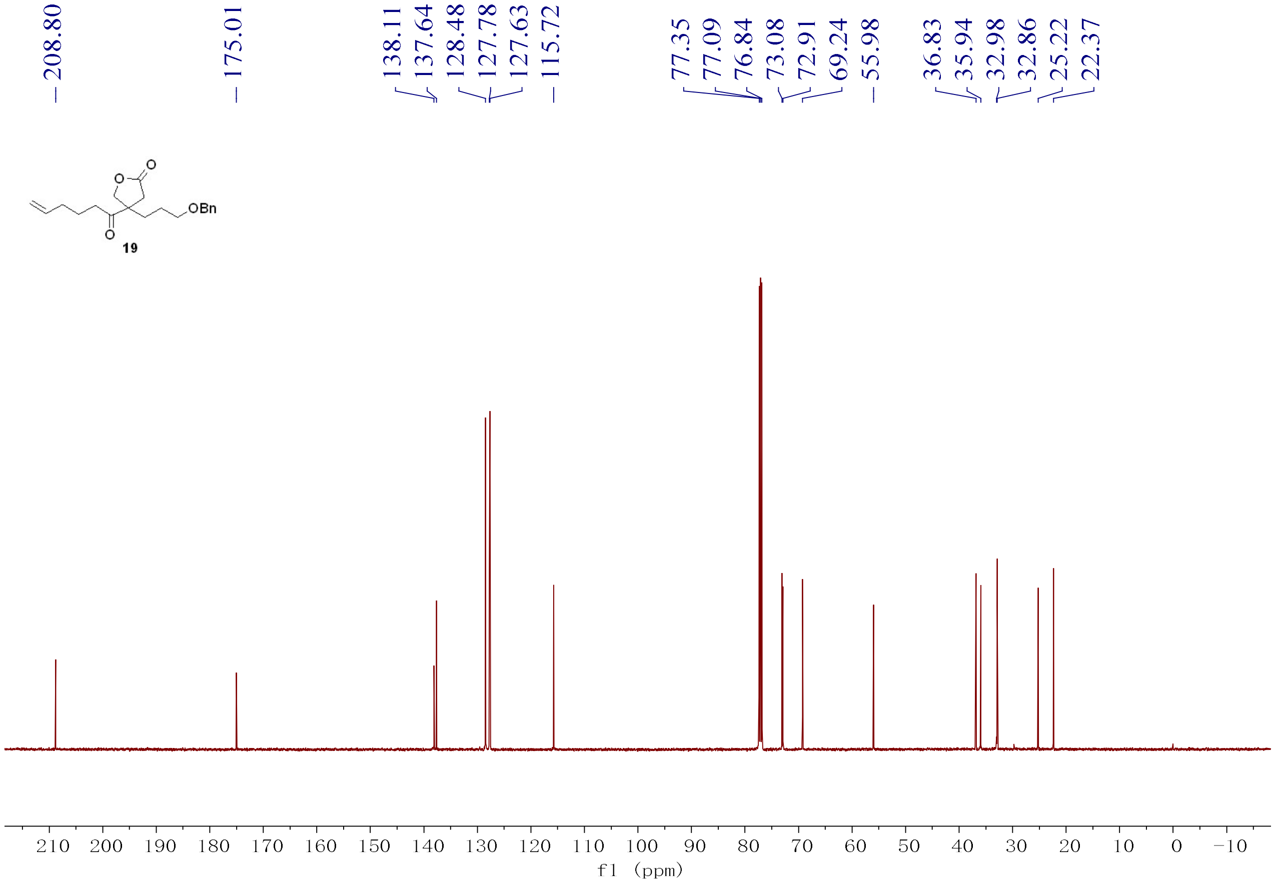
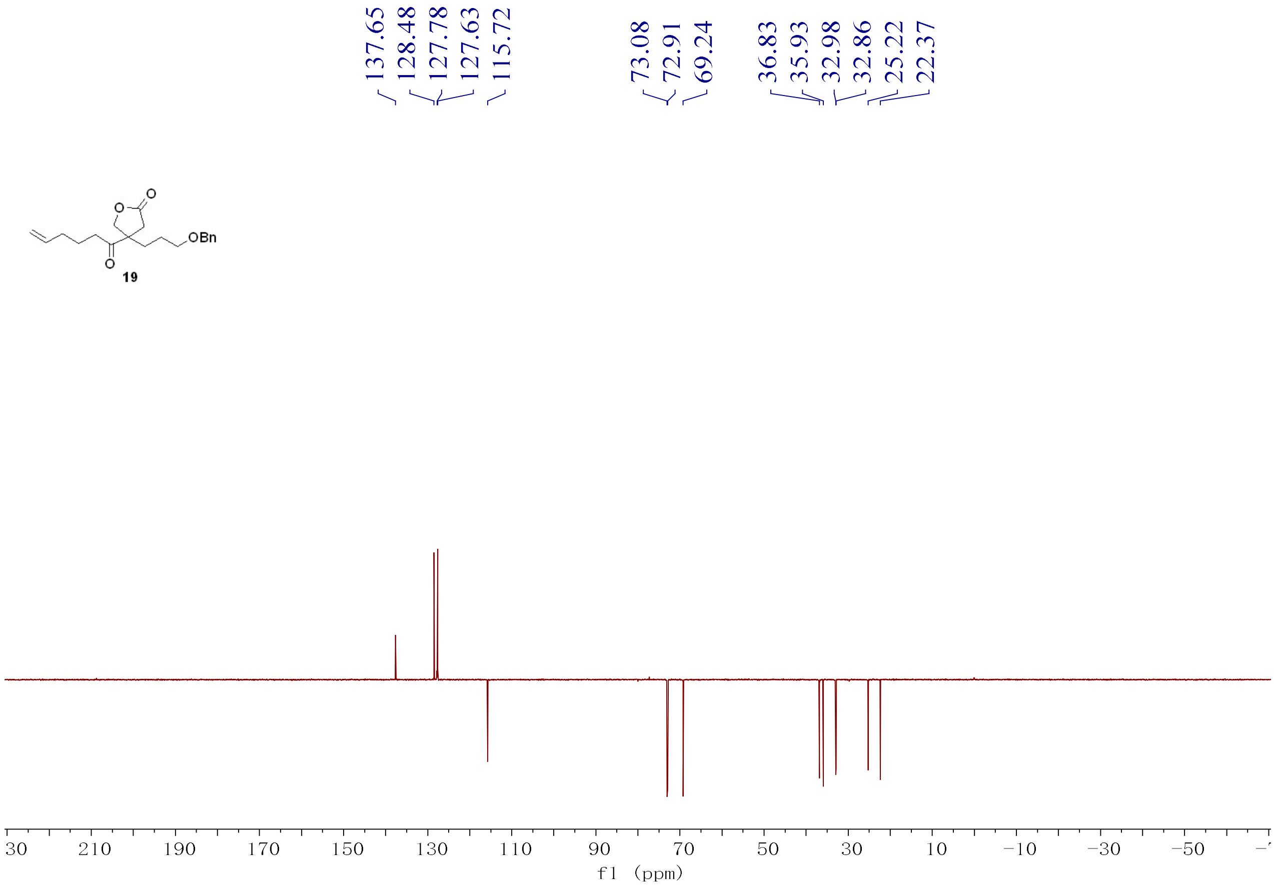
7.34
7.33
7.31
7.29
7.26
5.72
5.02
5.02
4.99
4.99
4.99
4.97
4.50
4.49
4.47
4.13
4.11
3.45
3.44
3.43
2.99
2.95
2.48
2.48
2.47
2.46
2.45
2.45
2.43
2.39
2.05
2.03
1.72
1.70
1.69
1.46
1.45
1.44
O
O
O
OBn
19
5.00
1.00
2.04
3.07
1.02
2.09
1.01
3.08
2.18
2.25
2.59
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


208.80
175.01
138.11
137.64
128.48
127.78
127.63
115.72
77.35
77.09
76.84
73.08
72.91
69.24
55.98
36.83
35.94
32.98
32.86
25.22
22.37
O
O
O
OBn
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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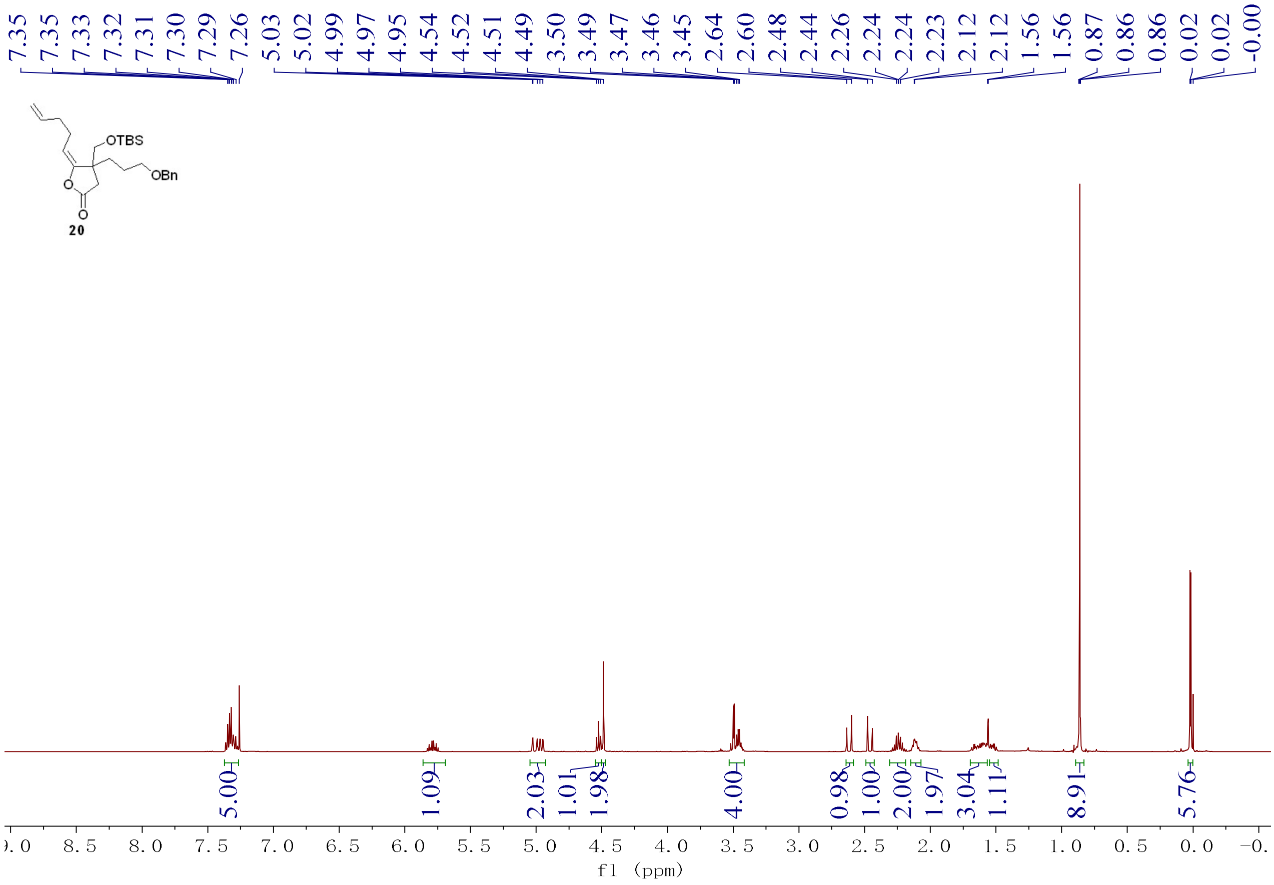
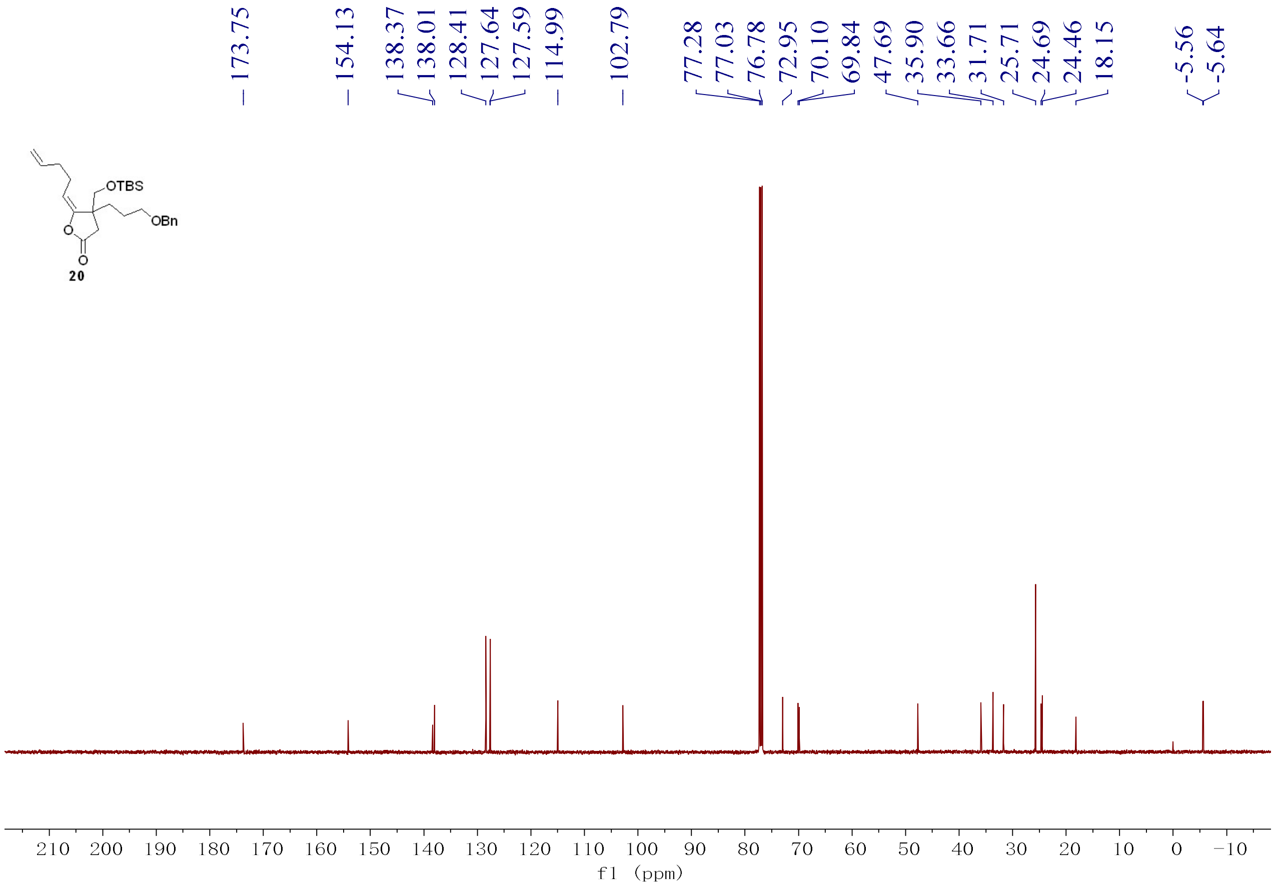
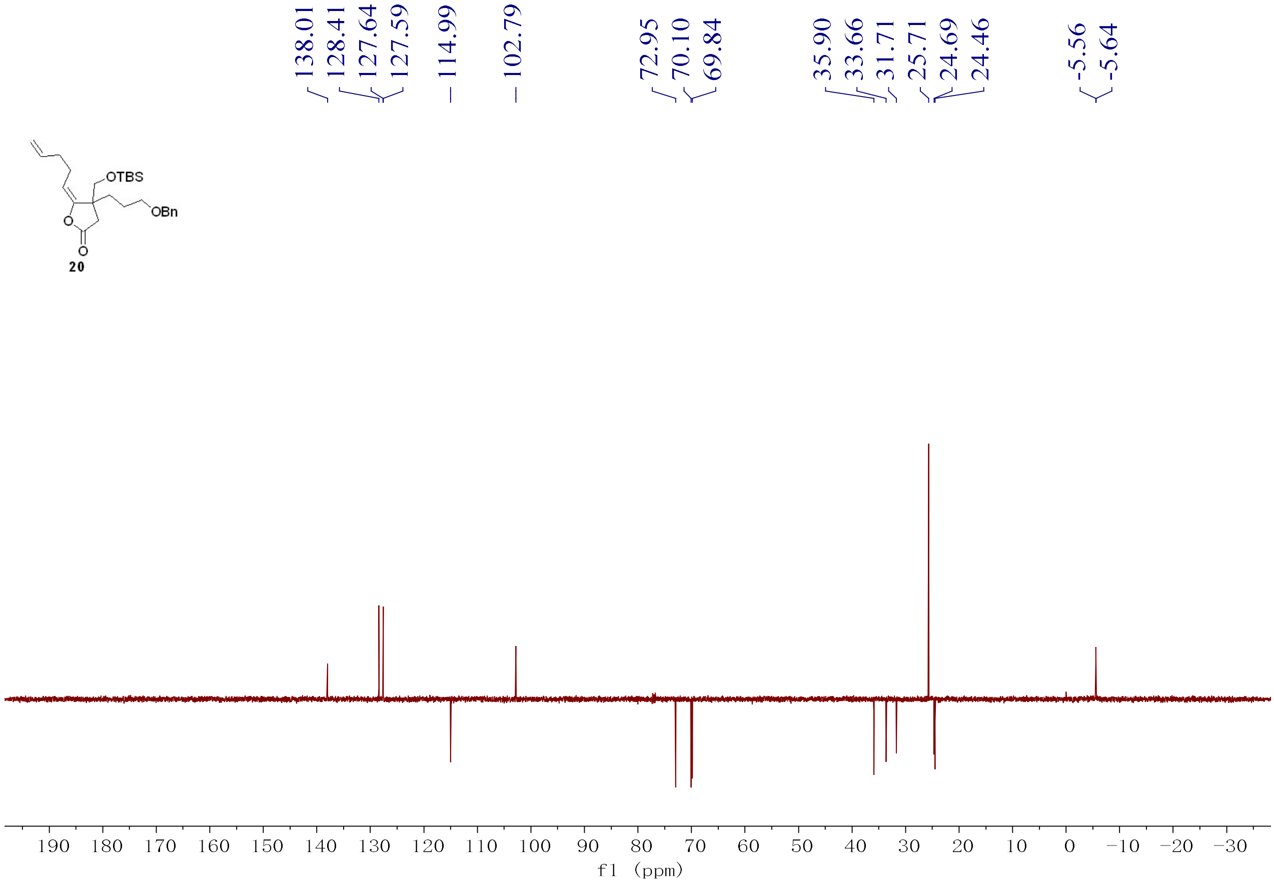
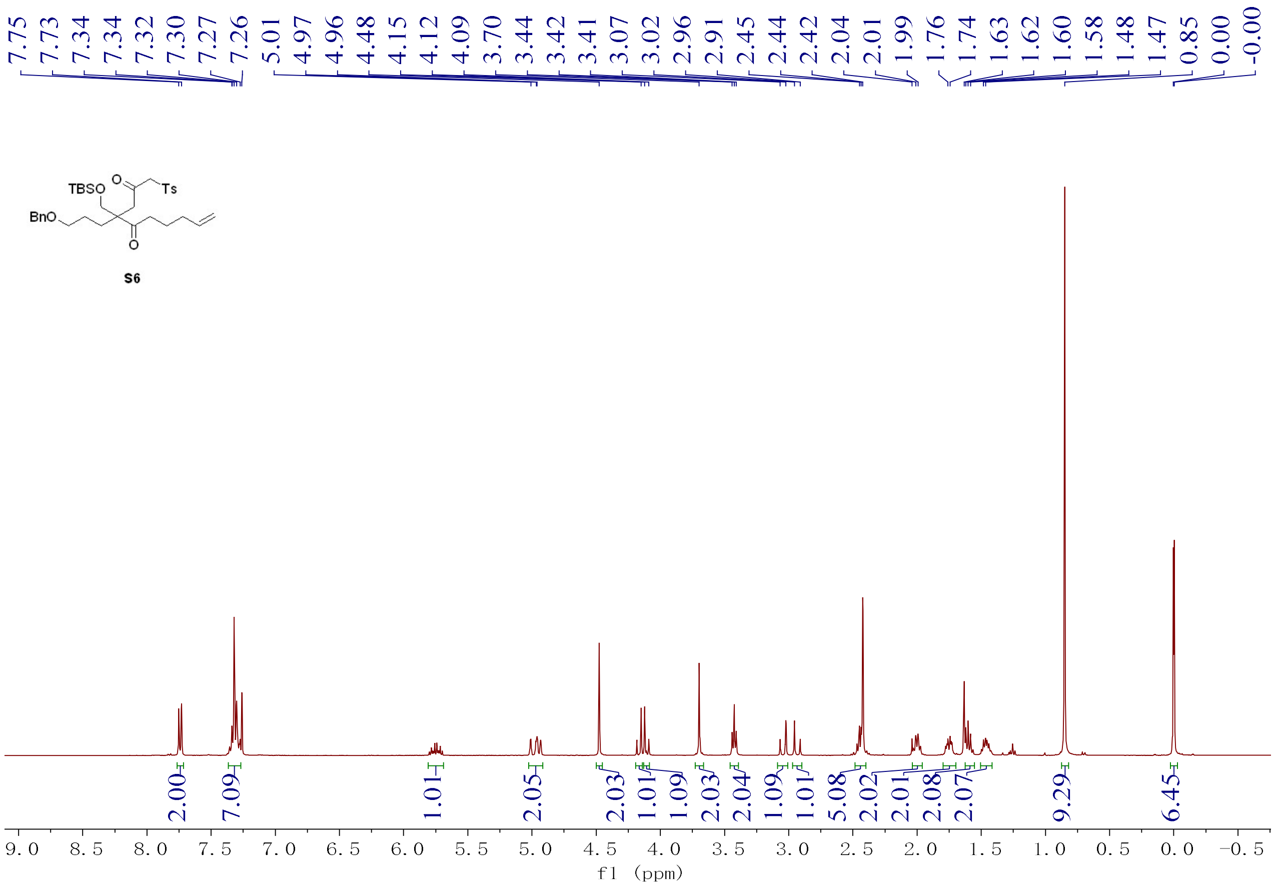
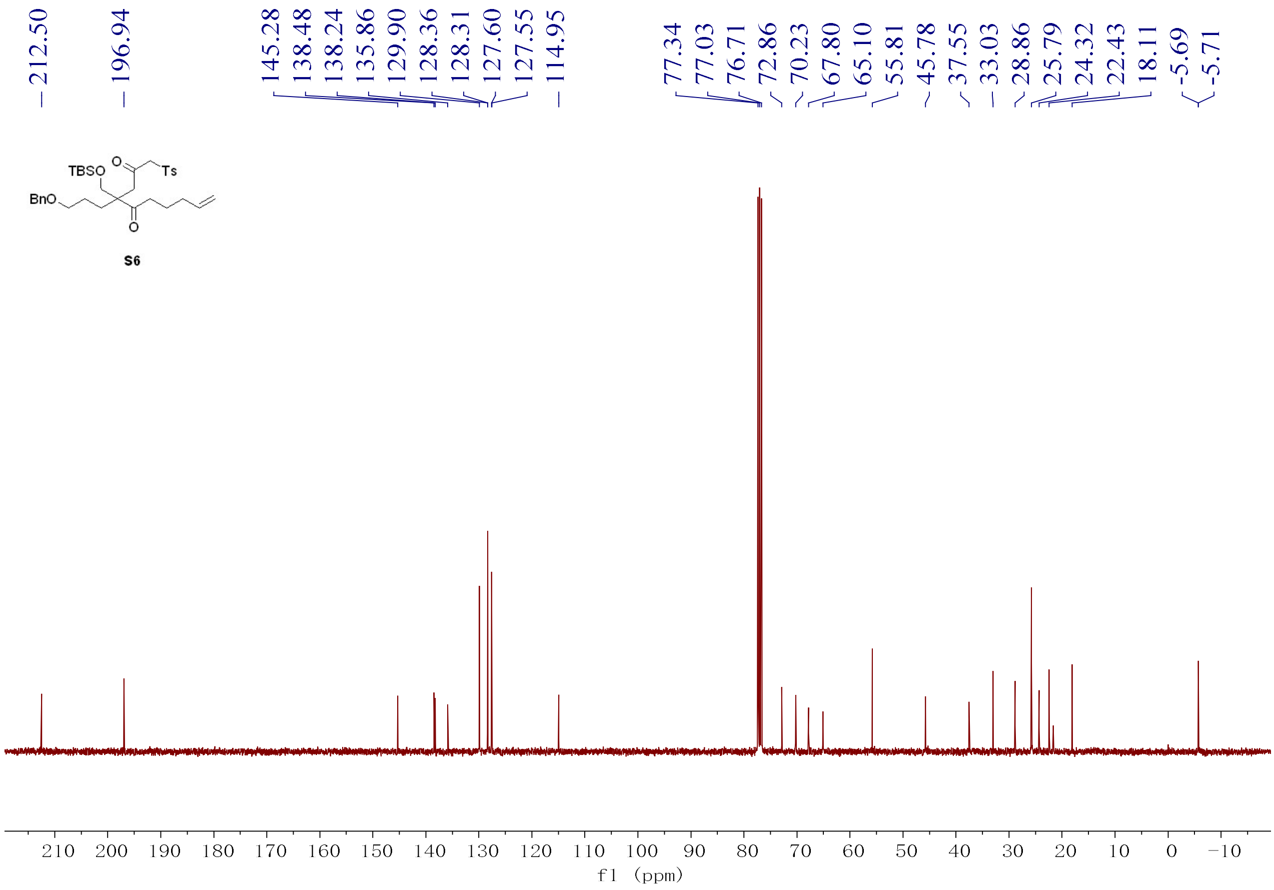
128.48
127.78
127.63
115.72
73.08
72.91
69.24
36.83
35.93
32.98
32.86
25.22
22.37
O
O
O
OBn
19
30
210
190
170
150
130
110
90
70
50
30
10
−10
−30
−50
f1 (ppm)

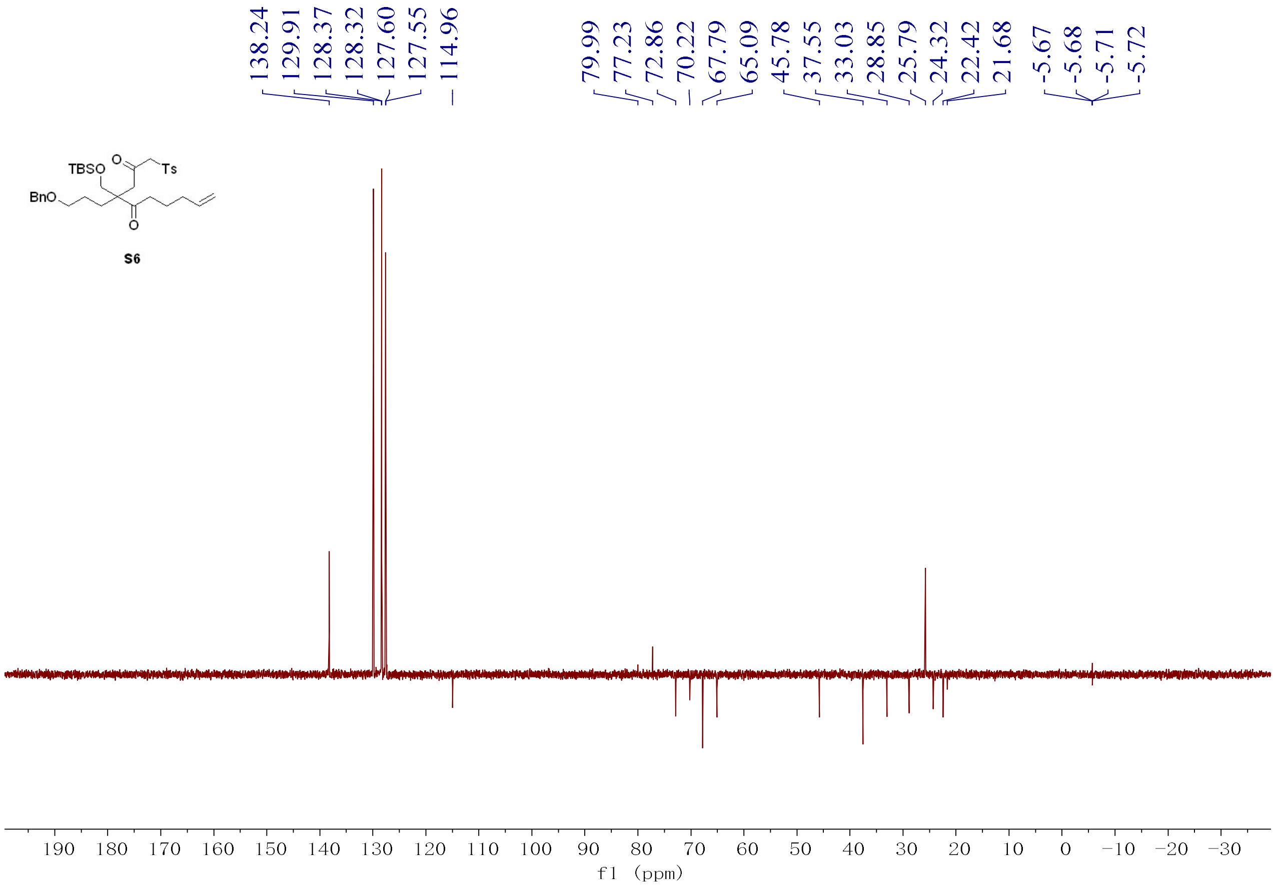

7.35
7.35
7.33
7.32
7.31
7.30
7.29
7.26
5.03
5.02
4.99
4.97
4.95
4.54
4.52
4.51
4.49
3.50
3.49
3.47
3.46
3.45
2.64
2.60
2.48
2.44
2.26
2.24
2.24
2.23
2.12
2.12
1.56
1.56
0.87
0.86
0.86
0.02
0.02
-0.00
OTBS
OBn
O
O
20
5.00
1.09
2.03
1.01
1.98
4.00
0.98
1.00
2.00
1.97
3.04
1.11
8.91
5.76
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

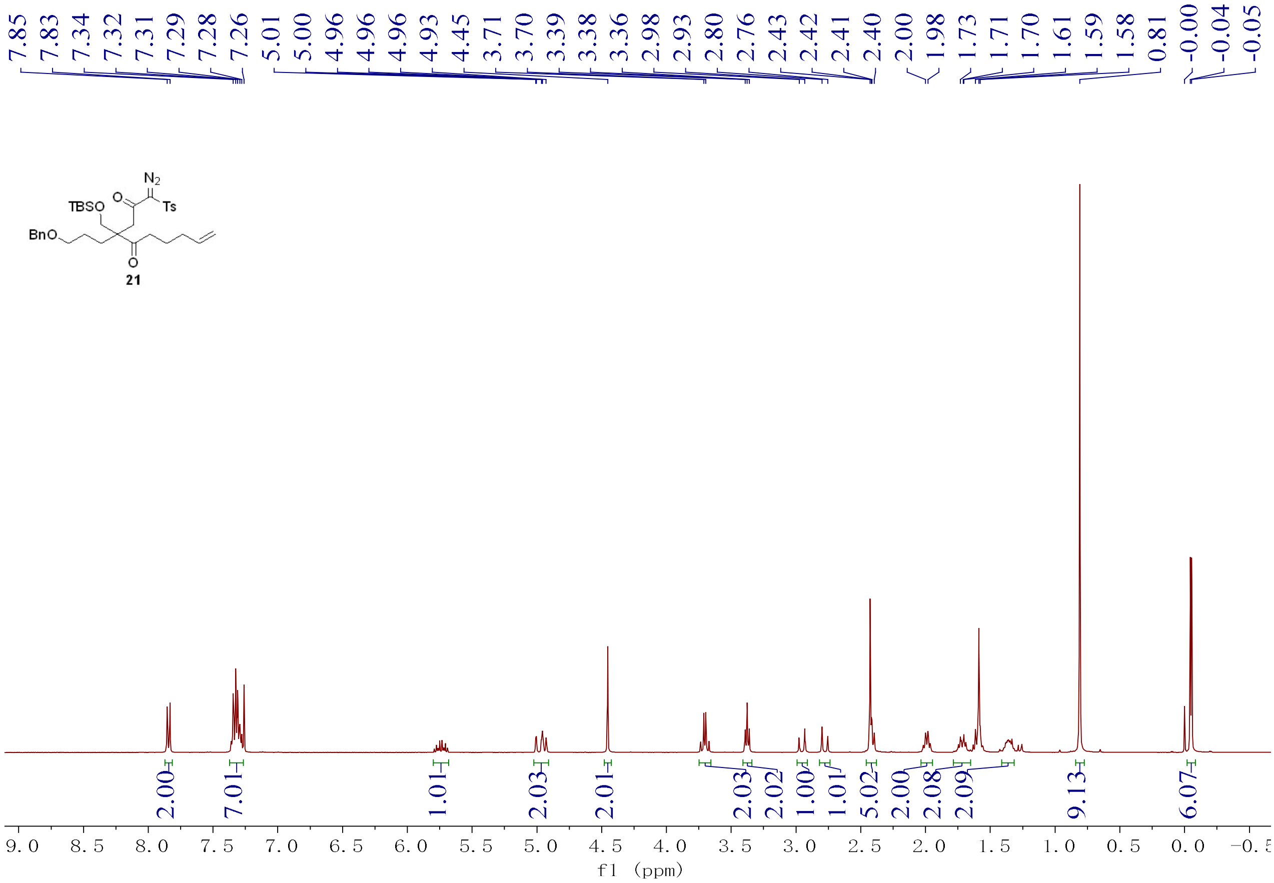

173.75
154.13
138.37
138.01
128.41
127.64
127.59
114.99
102.79
77.28
77.03
76.78
72.95
70.10
69.84
47.69
35.90
33.66
31.71
25.71
24.69
24.46
18.15
-5.56
-5.64
OTBS
OBn
O
O
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

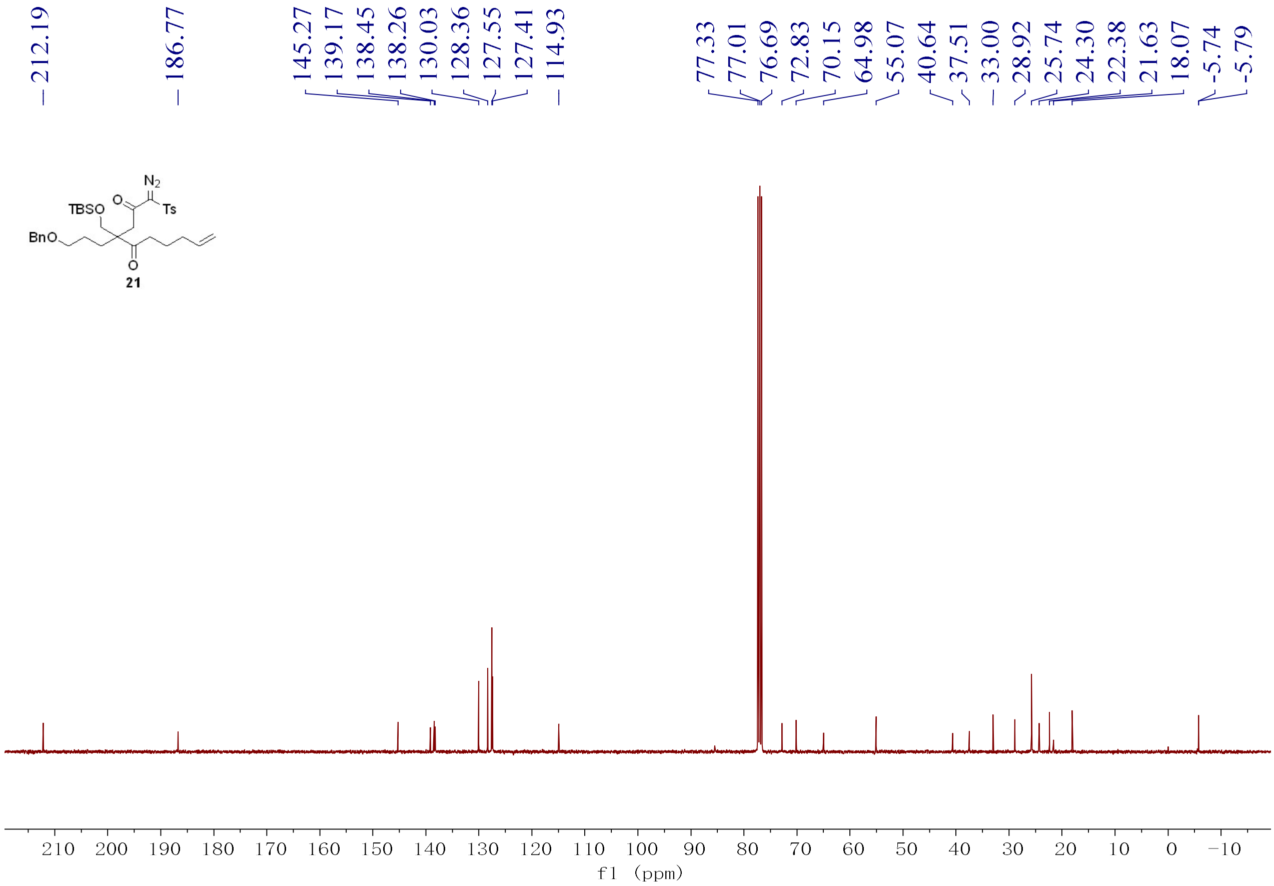

138.01
128.41
127.64
127.59
114.99
102.79
72.95
70.10
69.84
35.90
33.66
31.71
25.71
24.69
24.46
-5.56
-5.64
OTBS
OBn
O
O
20
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.75
7.73
7.34
7.34
7.32
7.30
7.27
7.26
5.01
4.97
4.96
4.48
4.15
4.12
4.09
3.70
3.44
3.42
3.41
3.07
3.02
2.96
2.91
2.45
2.44
2.42
2.04
2.01
1.99
1.76
1.74
1.63
1.62
1.60
1.58
1.48
1.47
0.85
0.00
-0.00
TBSO
Ts
BnO
O
O
S6
2.00
7.09
1.01
2.05
2.03
1.01
1.09
2.03
2.04
1.09
1.01
5.08
2.02
2.01
2.08
2.07
9.29
6.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


212.50
196.94
145.28
138.48
138.24
135.86
129.90
128.36
128.31
127.60
127.55
114.95
77.34
77.03
76.71
72.86
70.23
67.80
65.10
55.81
45.78
37.55
33.03
28.86
25.79
24.32
22.43
18.11
-5.69
-5.71
TBSO
Ts
BnO
O
O
S6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


138.24
129.91
128.37
128.32
127.60
127.55
114.96
79.99
77.23
72.86
70.22
67.79
65.09
45.78
37.55
33.03
28.85
25.79
24.32
22.42
21.68
-5.67
-5.68
-5.71
-5.72
TBSO
O
Ts
BnO
O
S6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)


7.85
7.83
7.34
7.32
7.31
7.29
7.28
7.26
5.01
5.00
4.96
4.96
4.96
4.93
4.45
3.71
3.70
3.39
3.38
3.36
2.98
2.93
2.80
2.76
2.43
2.42
2.41
2.40
2.00
1.98
1.73
1.71
1.70
1.61
1.59
1.58
0.81
-0.00
-0.04
-0.05
N_2
TBSO
O
Ts
BnO
O
21
2.00
7.01
1.01
2.03
2.01
2.03
2.02
1.00
1.01
5.02
2.00
2.08
2.09
9.13
6.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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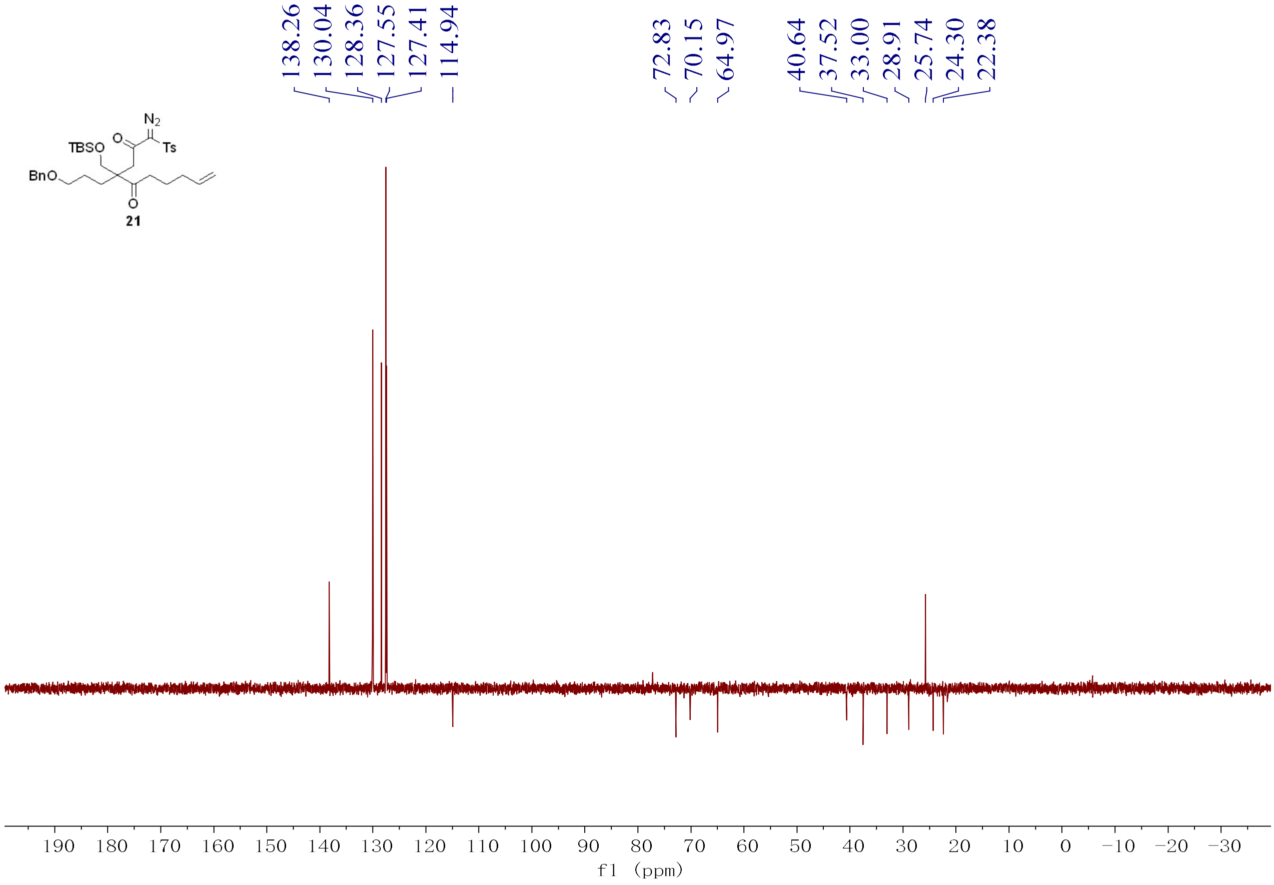
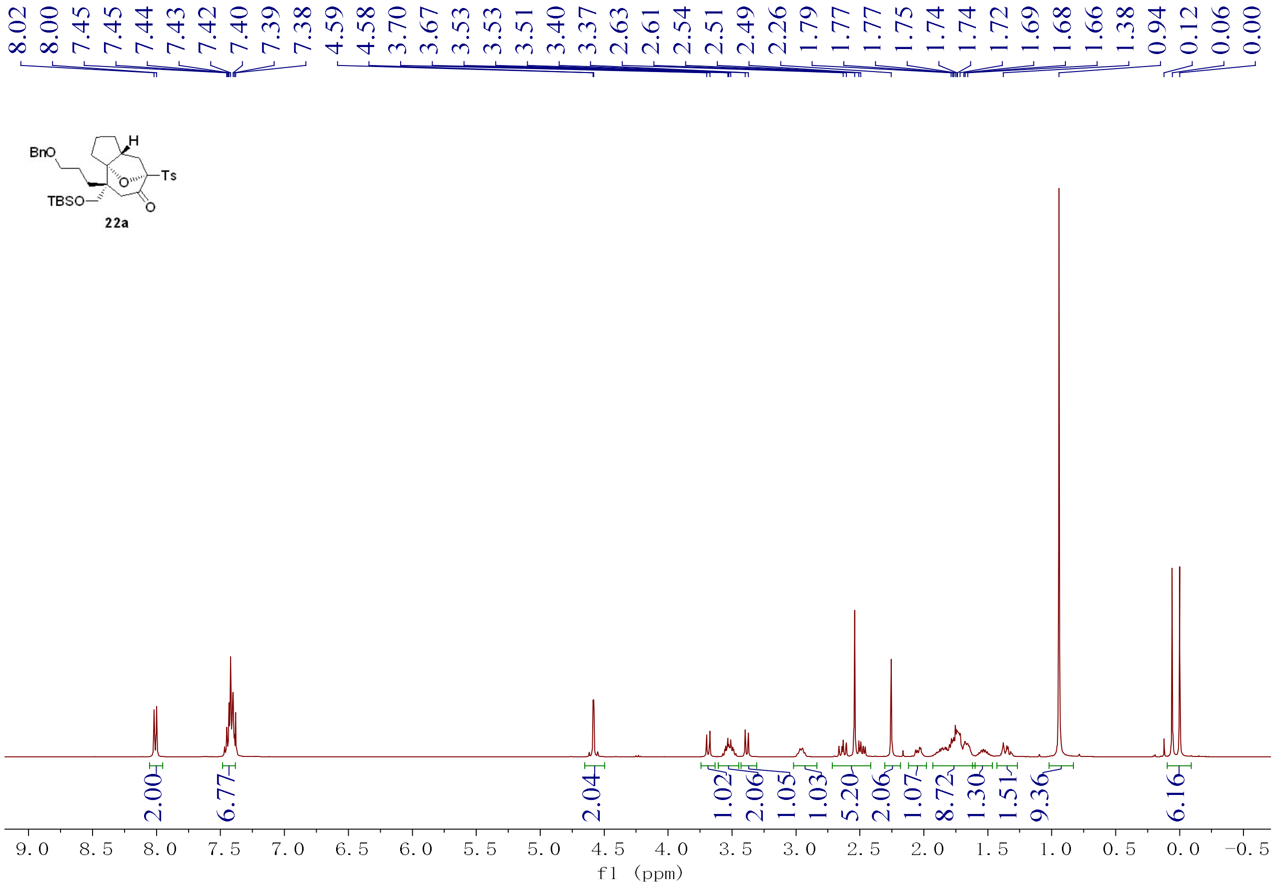
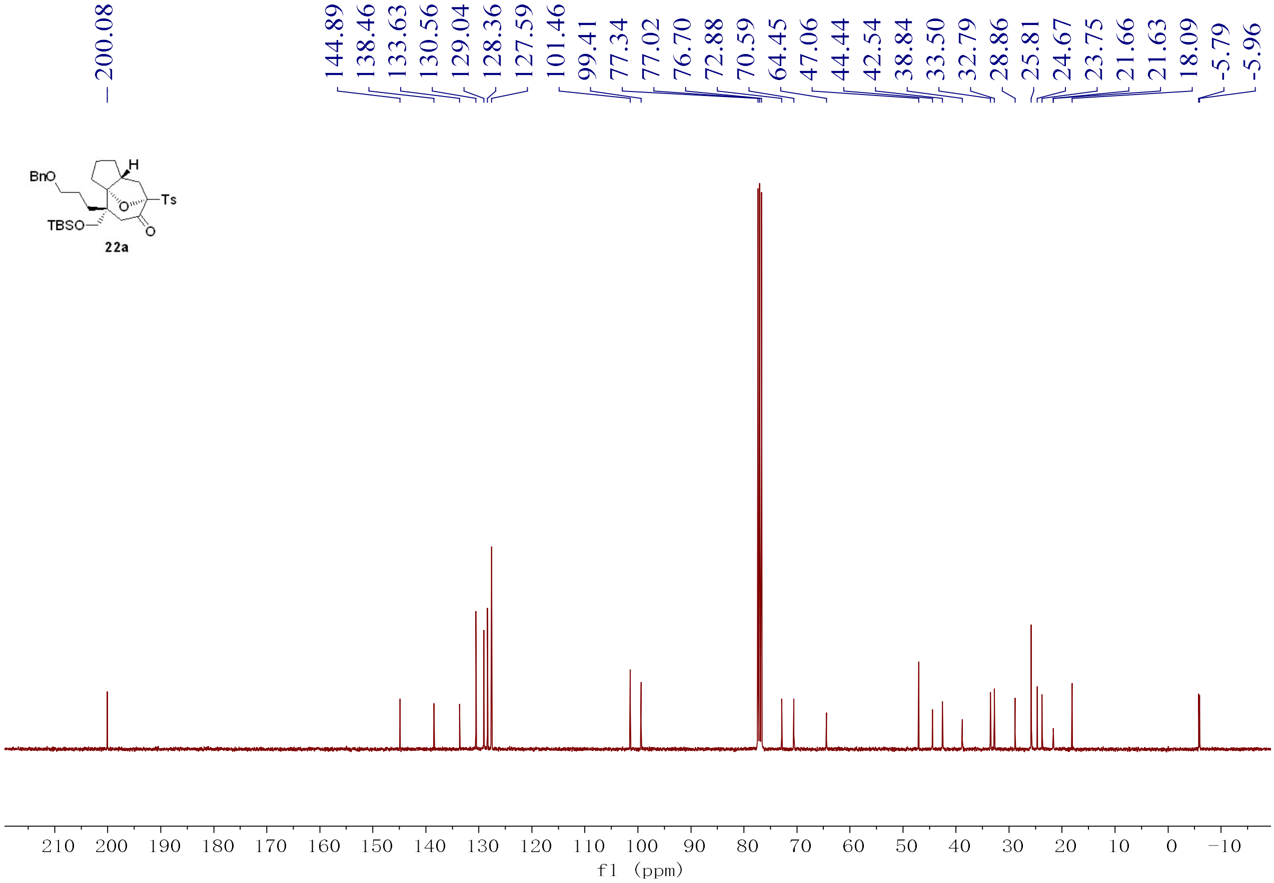
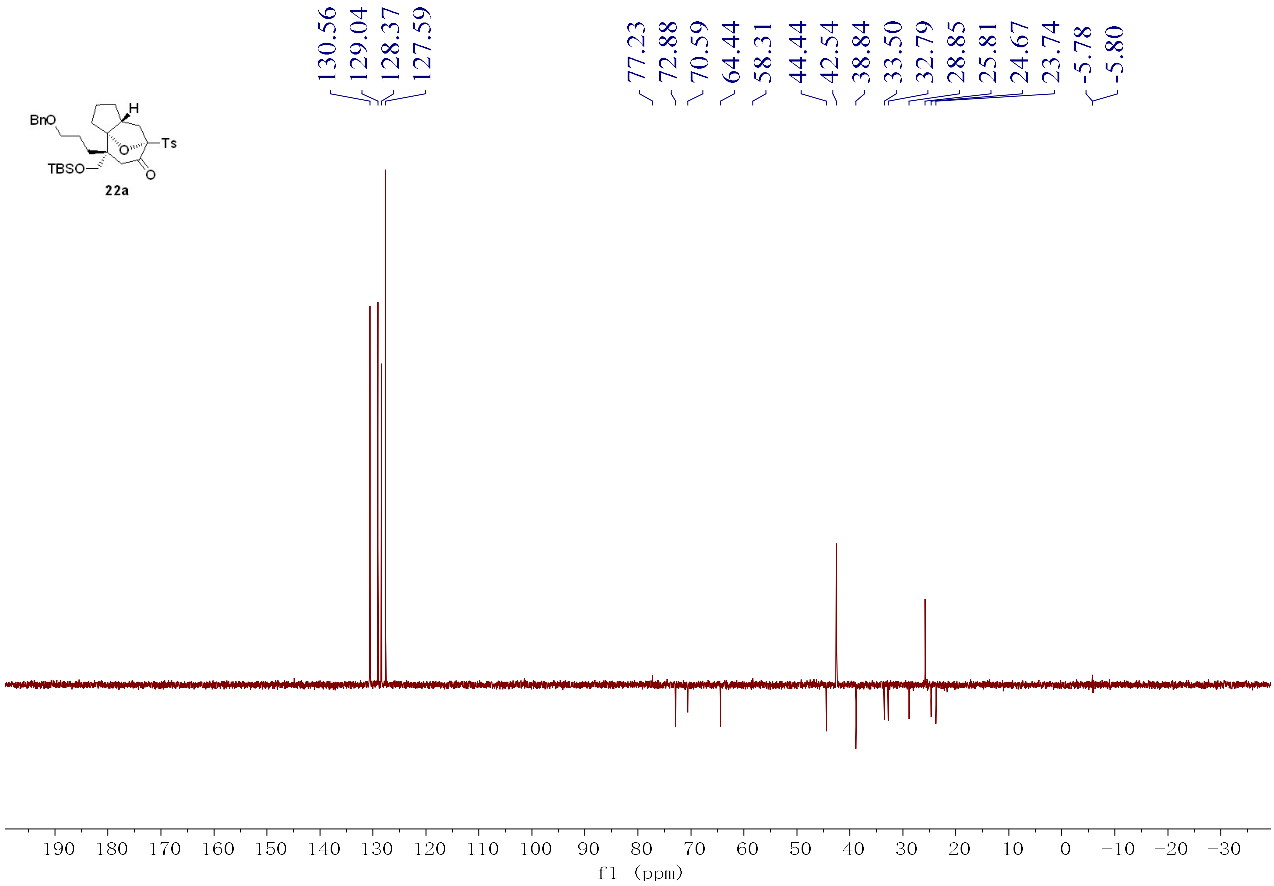
139.17
138.45
138.26
130.03
128.36
127.55
127.41
114.93
77.33
77.01
76.69
72.83
70.15
64.98
55.07
40.64
37.51
33.00
28.92
25.74
24.30
22.38
21.63
18.07
-5.74
-5.79
N2
TBSO
O
Ts
BnO
O
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


138.26
130.04
128.36
127.55
127.41
114.94
72.83
70.15
64.97
40.64
37.52
33.00
28.91
25.74
24.30
22.38
N2
TBSO
O
Ts
BnO
O
21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

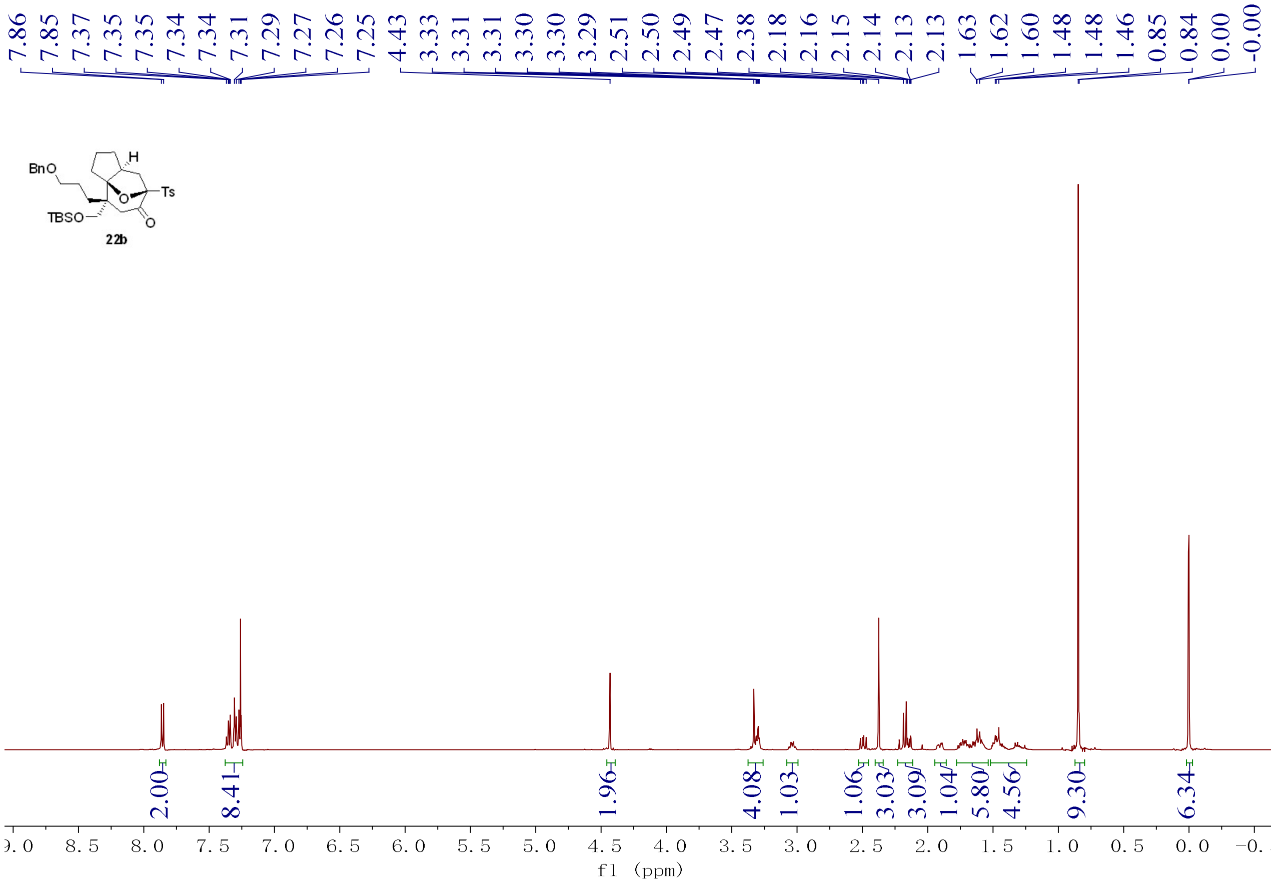

8.02
8.00
7.45
7.45
7.44
7.43
7.42
7.40
7.39
7.38
4.59
4.58
3.70
3.67
3.53
3.53
3.51
3.40
3.37
2.63
2.61
2.54
2.51
2.49
2.26
1.79
1.77
1.77
1.75
1.74
1.74
1.72
1.69
1.68
1.66
1.38
0.94
0.12
0.06
0.00
BnO
H
Ts
O
TBSO
O
22a
2.00
6.77
2.04
1.02
2.06
1.05
1.03
5.20
2.06
1.07
8.72
1.30
1.51
9.36
6.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


200.08
144.89
138.46
133.63
130.56
129.04
128.36
127.59
101.46
99.41
77.34
77.02
76.70
72.88
70.59
64.45
47.06
44.44
42.54
38.84
33.50
32.79
28.86
25.81
24.67
23.75
21.66
21.63
18.09
-5.79
-5.96
BnO
H
Ts
O
TBSO
O
22a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



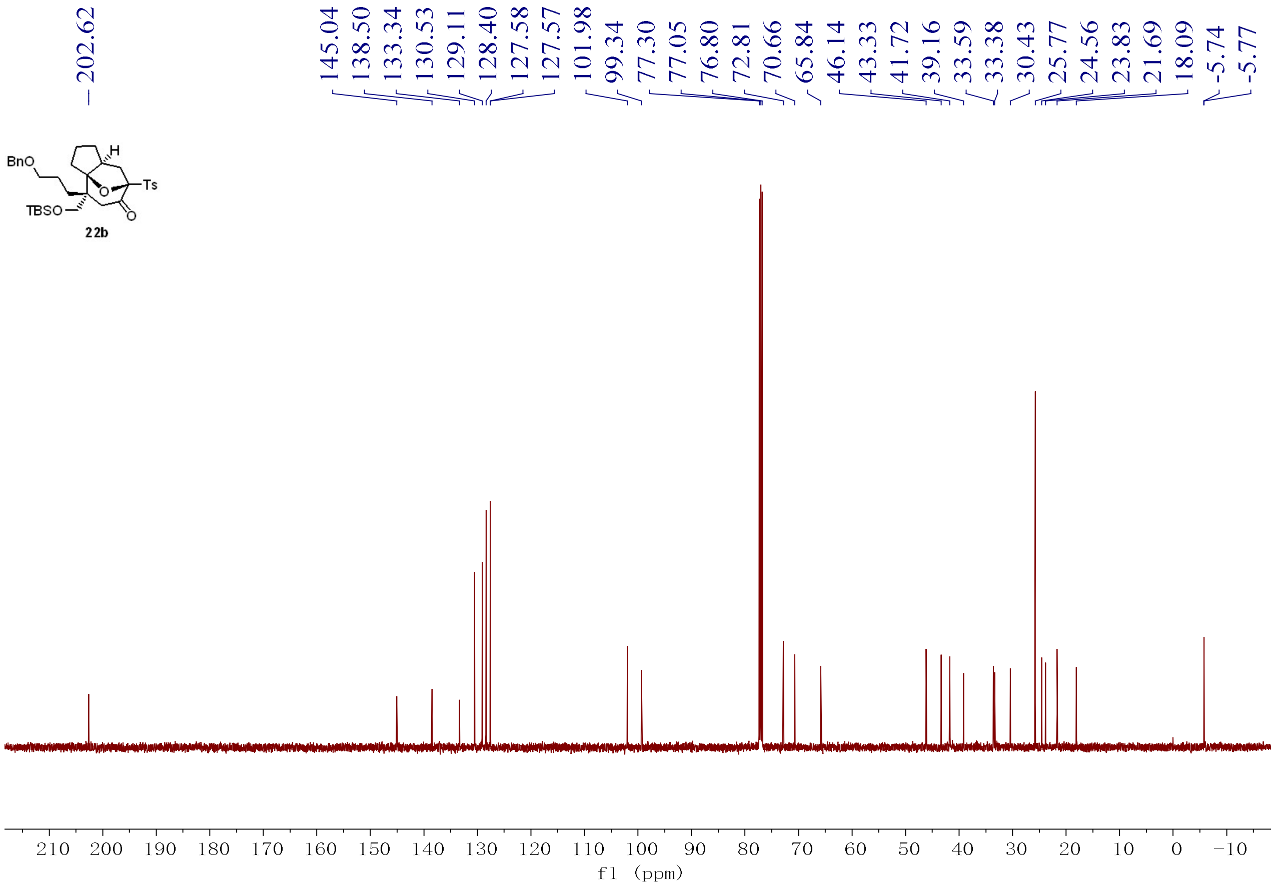
130.56
129.04
128.37
127.59
77.23
72.88
70.59
64.44
58.31
44.44
42.54
38.84
33.50
32.79
28.85
25.81
24.67
23.74
-5.78
-5.80
BnO
H
Ts
O
TBSO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

22a



7.86
7.85
7.37
7.35
7.35
7.34
7.34
7.31
7.29
7.27
7.26
7.25
4.43
3.33
3.31
3.31
3.30
3.30
3.29
2.51
2.50
2.49
2.47
2.38
2.18
2.16
2.15
2.14
2.13
2.13
1.63
1.62
1.60
1.48
1.48
1.46
0.85
0.84
0.00
-0.00
BnO
H
Ts
O
TBSO
O
2.00
8.41
1.96
4.08
1.03
1.06
3.03
3.09
1.04
5.80
4.56
9.30
6.34
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

22b


202.62
145.04
138.50
133.34
130.53
129.11
128.40
127.58
127.57
101.98
99.34
77.30
77.05
76.80
72.81
70.66
65.84
46.14
43.33
41.72
39.16
33.59
33.38
30.43
25.77
24.56
23.83
21.69
18.09
-5.74
-5.77
BnO
H
Ts
O
TBSO
O
22b
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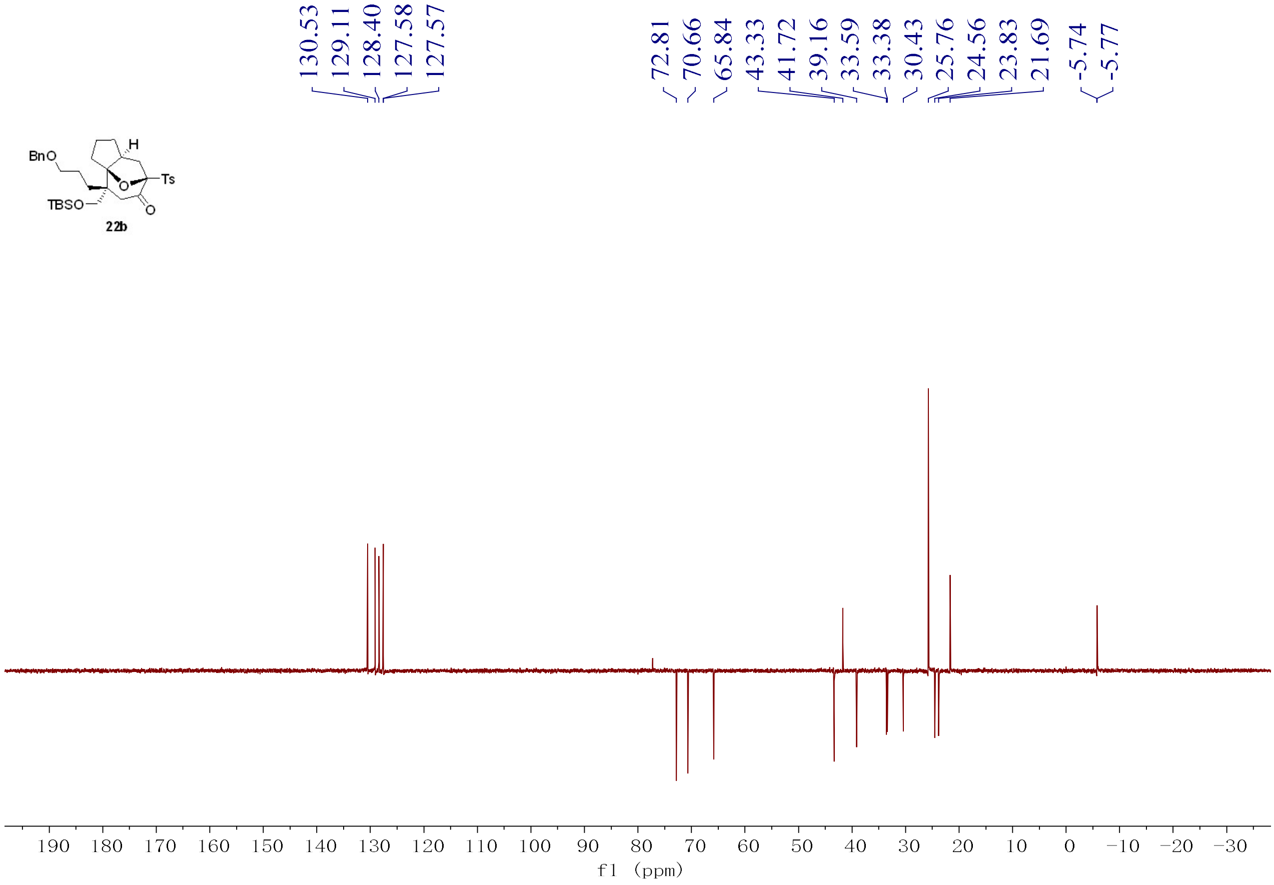
f1 (ppm)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30.43
25.76
24.56
23.83
21.69
-5.74
-5.77
BnO
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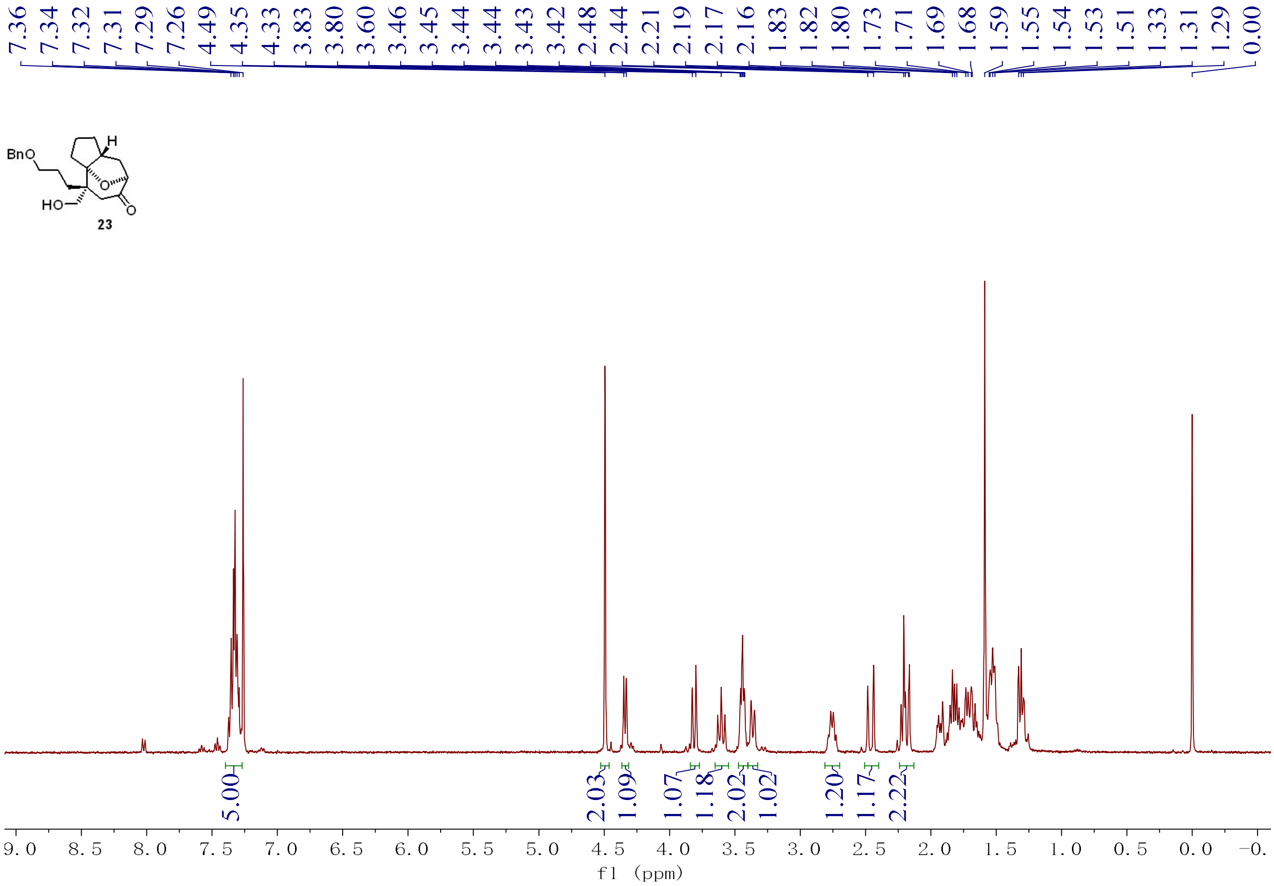
Ts
O
TBSO
O
22b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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3.43
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2.19
2.17
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1.71
1.69
1.68
1.59
1.55
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1.53
1.51
1.33
1.31
1.29
0.00
BnO
H
O
HO
O
23
5.00
2.03
1.09
1.07
1.18
2.02
1.02
1.20
1.17
2.22
9.0
8.5
8.0
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7.0
6.5
6.0
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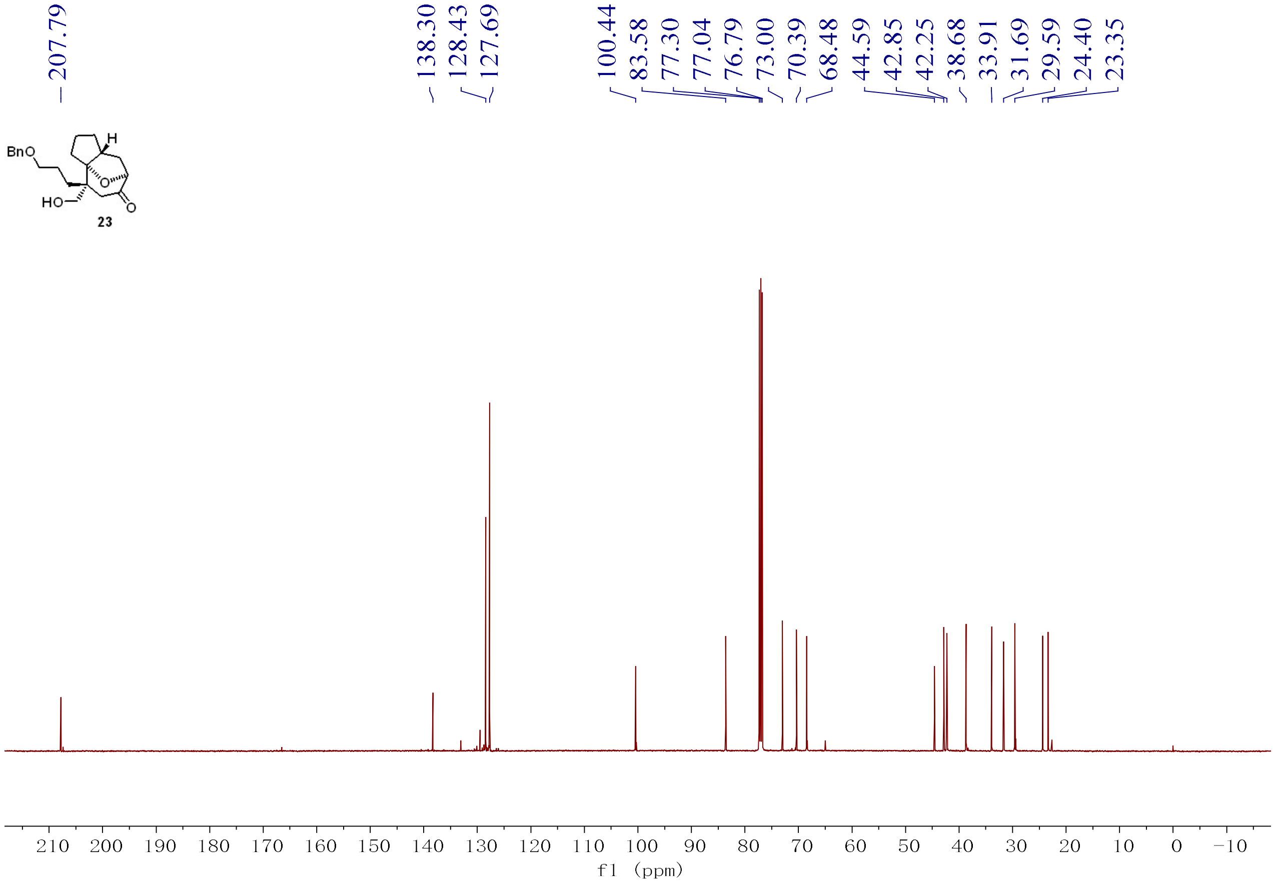
f1 (ppm)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42.25
38.68
33.91
31.69
29.59
24.40
23.35
BnO
H
O
HO
O
23
210
200
190
180
170
160
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100
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80
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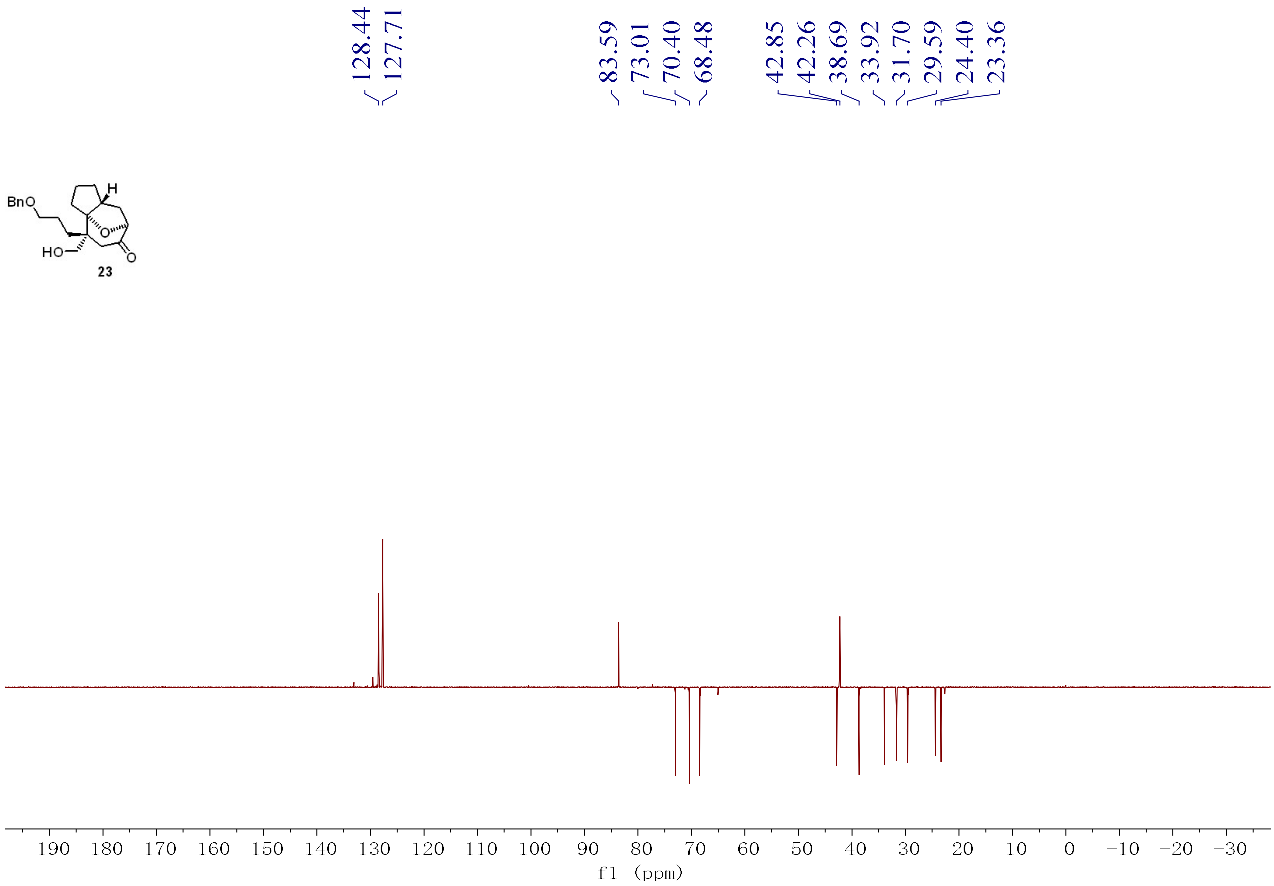
-10
f1 (ppm)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24.40
23.36
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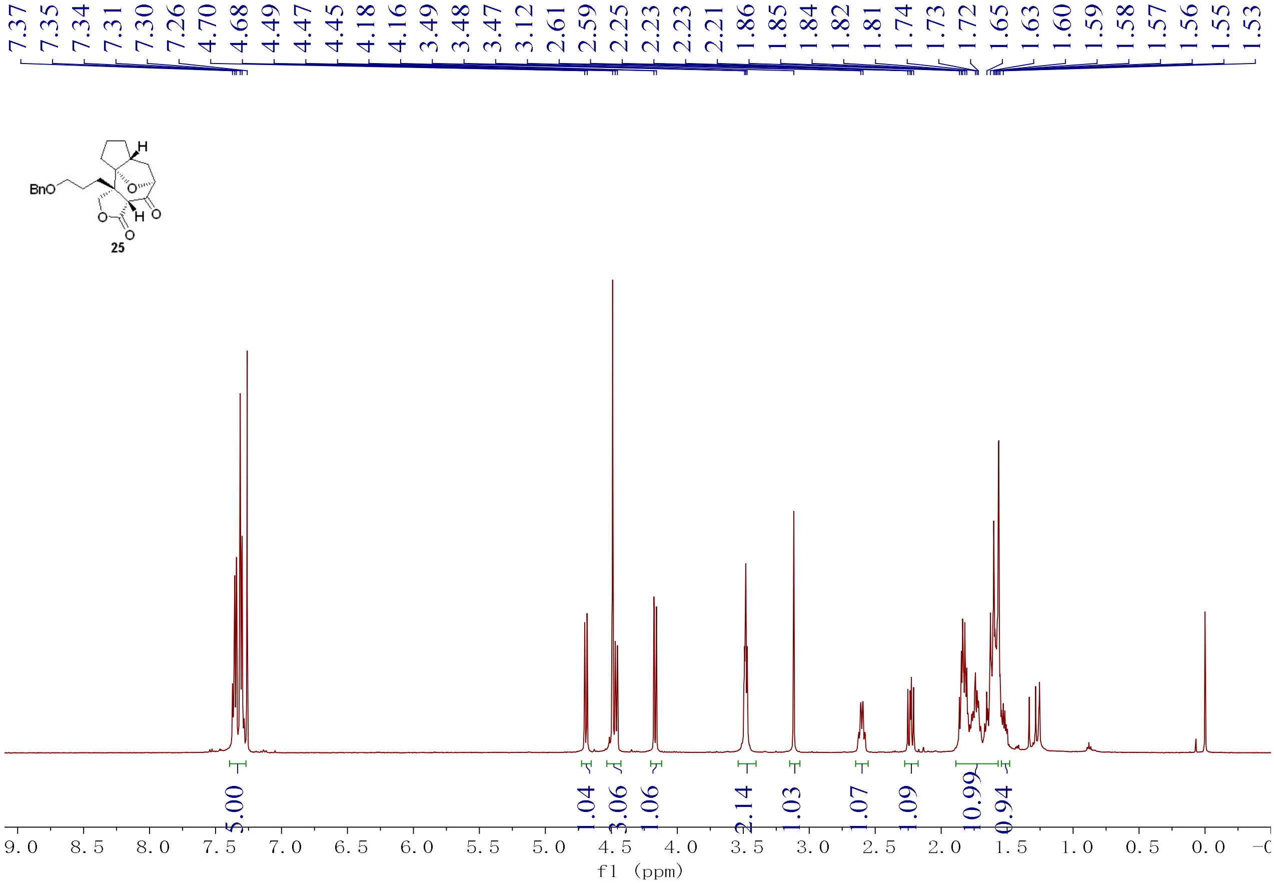
HO
O
23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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4.47
4.45
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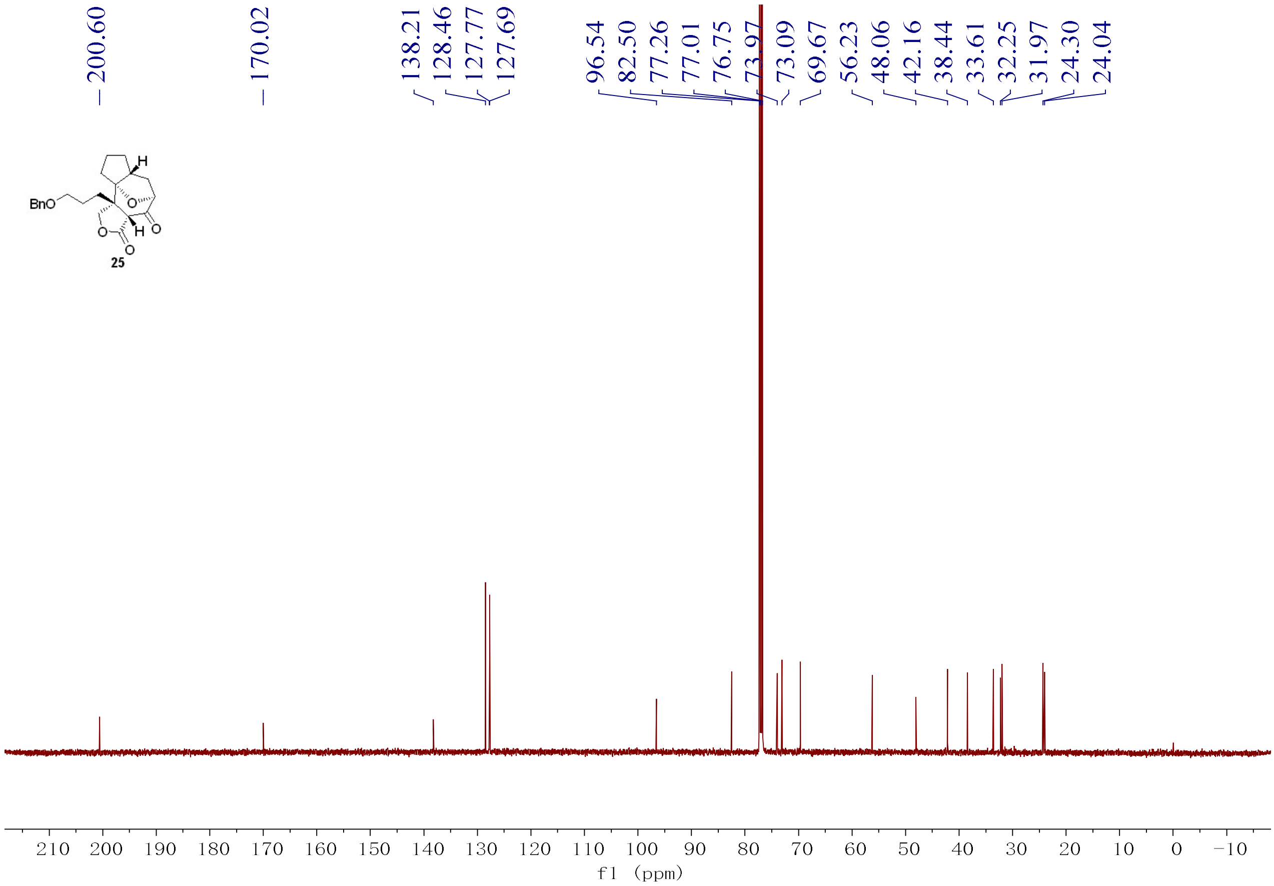
4.16
3.49
3.48
3.47
3.12
2.61
2.59
2.25
2.23
2.23
2.21
1.86
1.85
1.84
1.82
1.81
1.74
1.73
1.72
1.65
1.63
1.60
1.59
1.58
1.57
1.56
1.55
1.53
BnO
H
O
H
O
O
O
25
5.00
1.04
3.06
1.06
2.14
1.03
1.07
1.09
10.99
0.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)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76.75
73.97
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69.67
56.23
48.06
42.16
38.44
33.61
32.25
31.97
24.30
24.04
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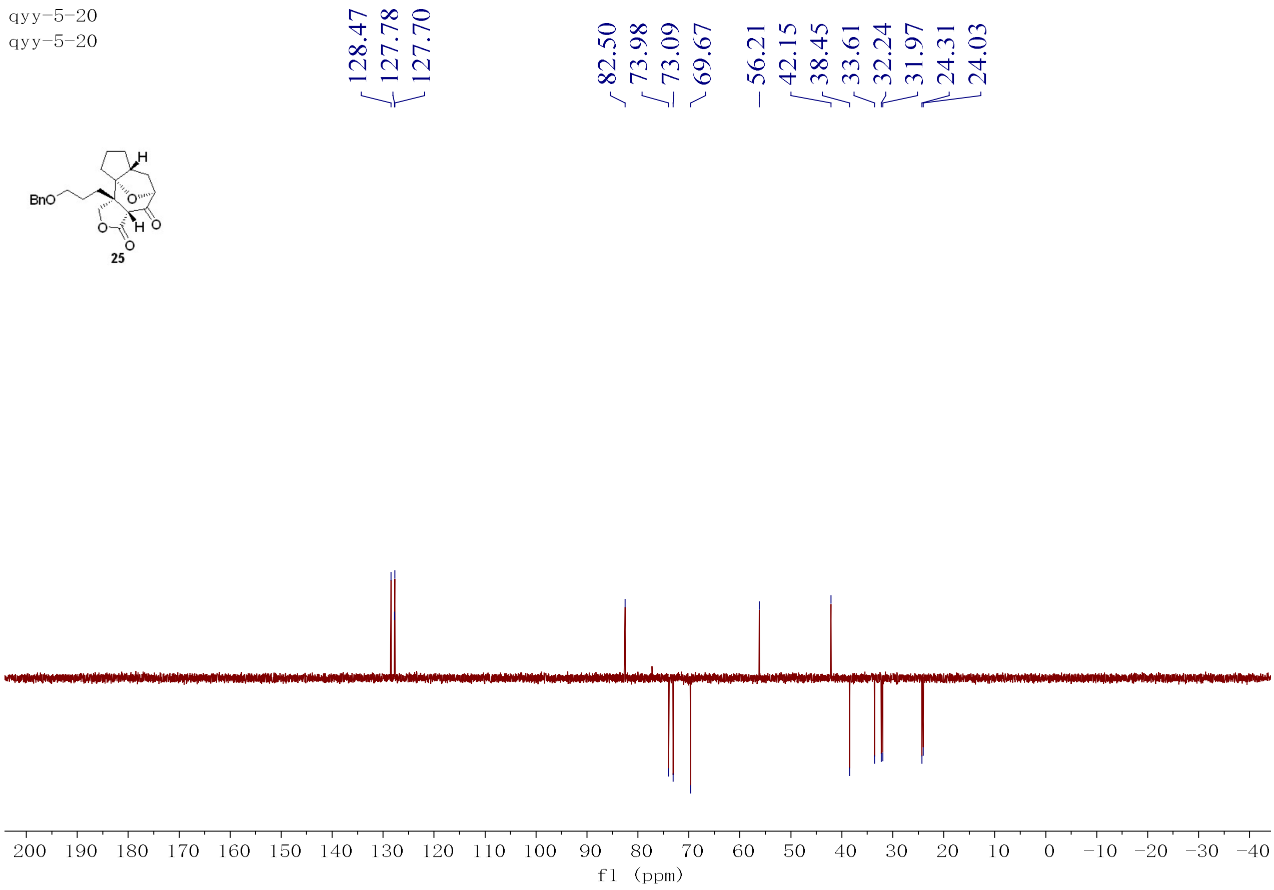
f1 (ppm)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qyy-5-20
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127.70
82.50
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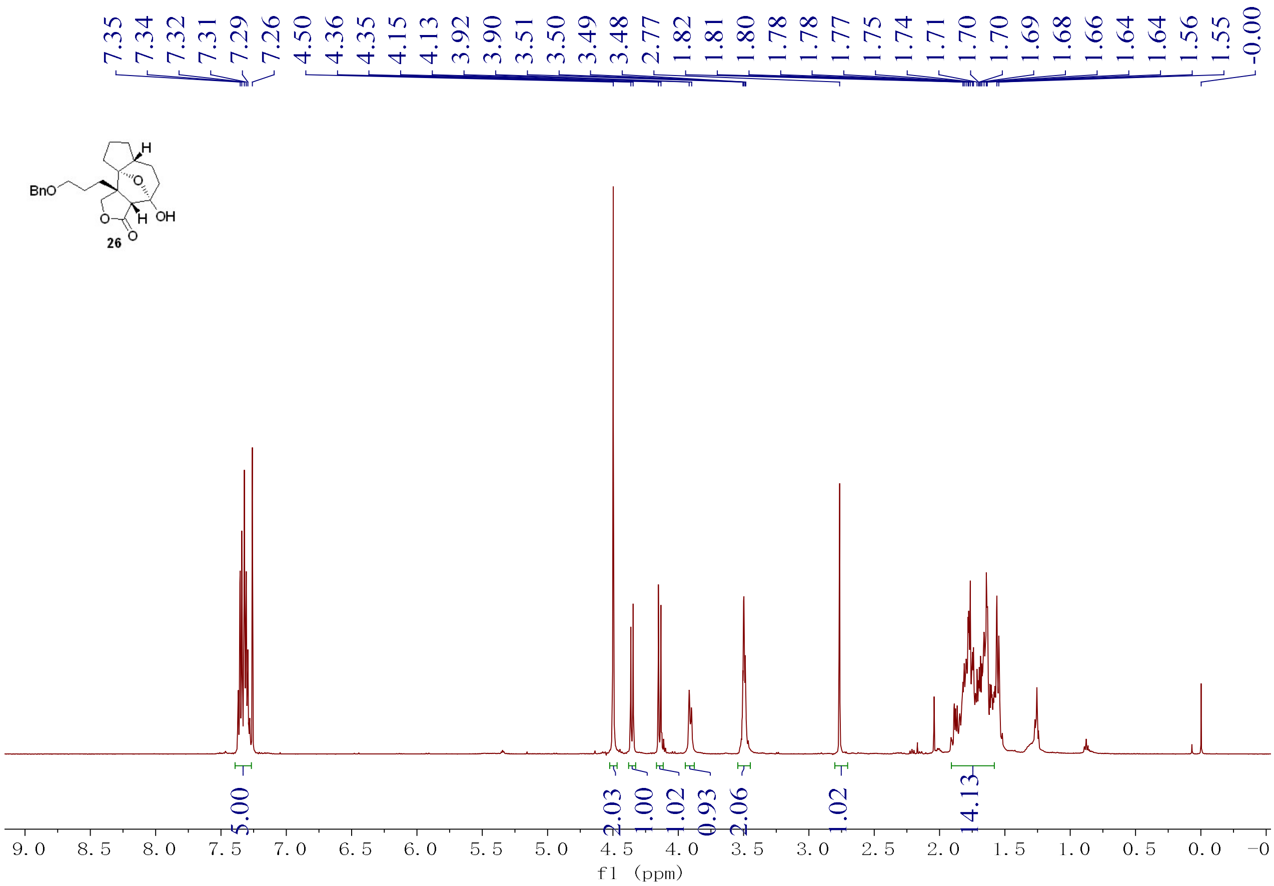
69.67
56.21
42.15
38.45
33.61
32.24
31.97
24.31
24.03
BnO
H
O
H
O
O
O
25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)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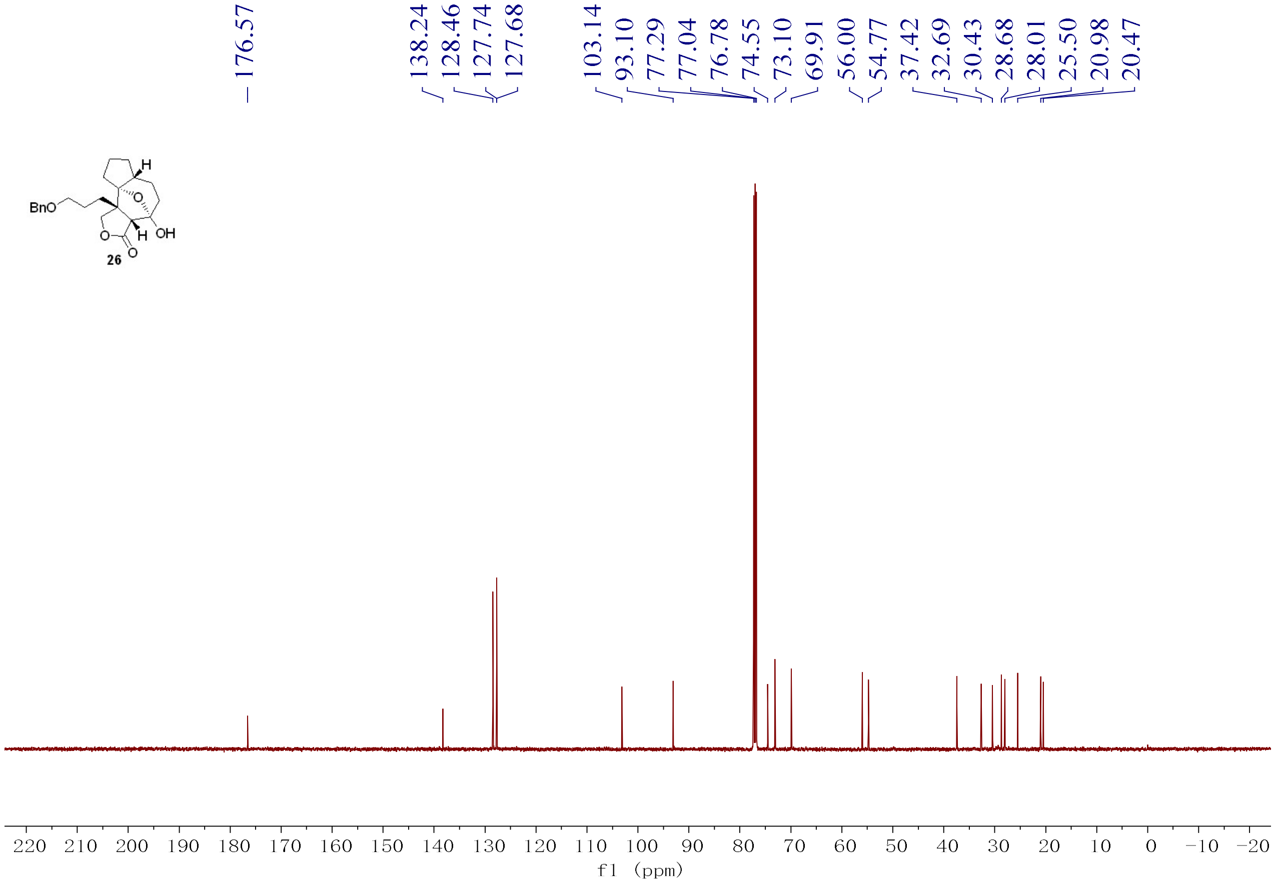
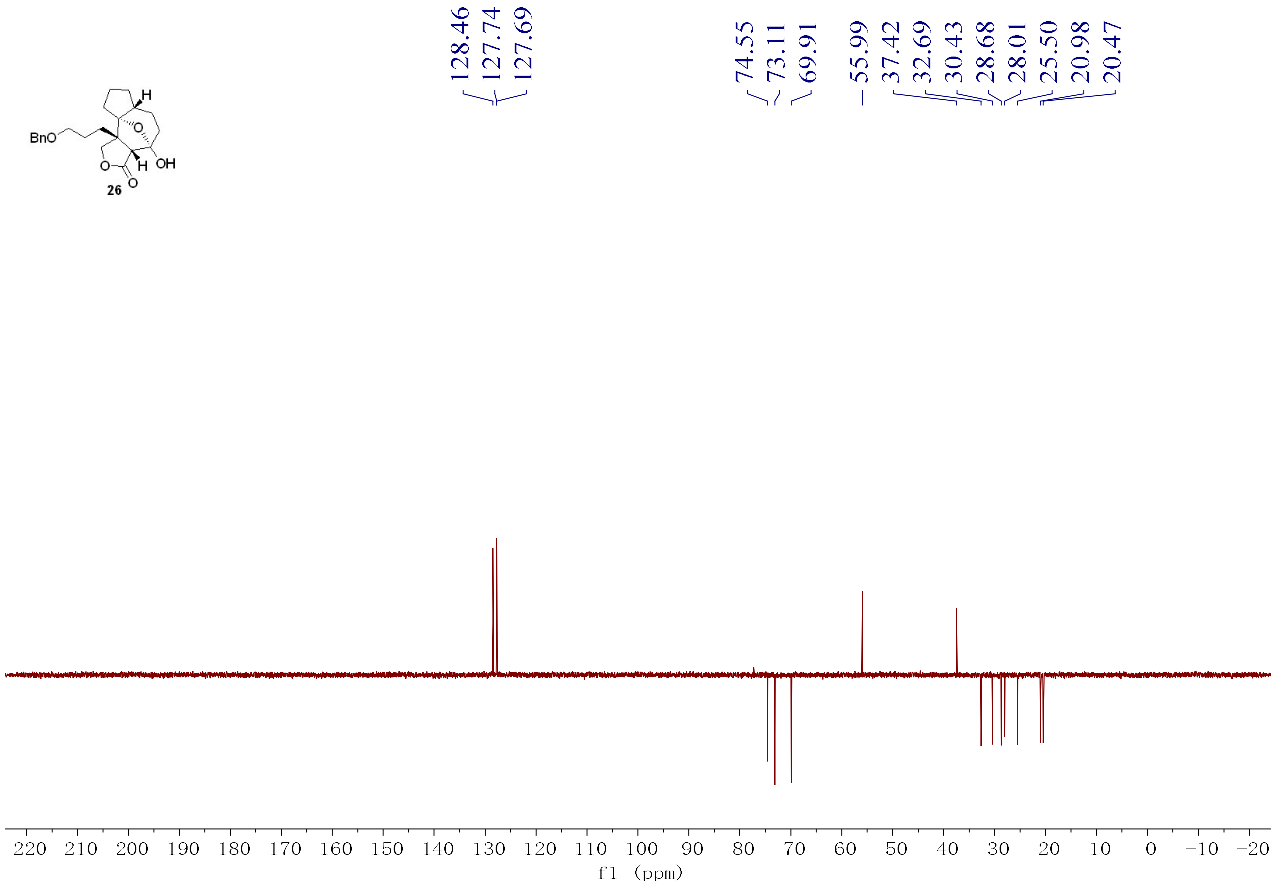
BnO
H
O
H
OH
O
26
5.00
2.03
1.00
1.02
0.93
2.06
1.02
14.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


176.57
138.24 128.46 127.74 127.68
103.14 93.10 77.29 77.04 76.78 74.55 73.10 69.91 56.00 54.77 37.42 32.69 30.43 28.68 28.01 25.50 20.98 20.47
BnO
H
O
H
OH
O
26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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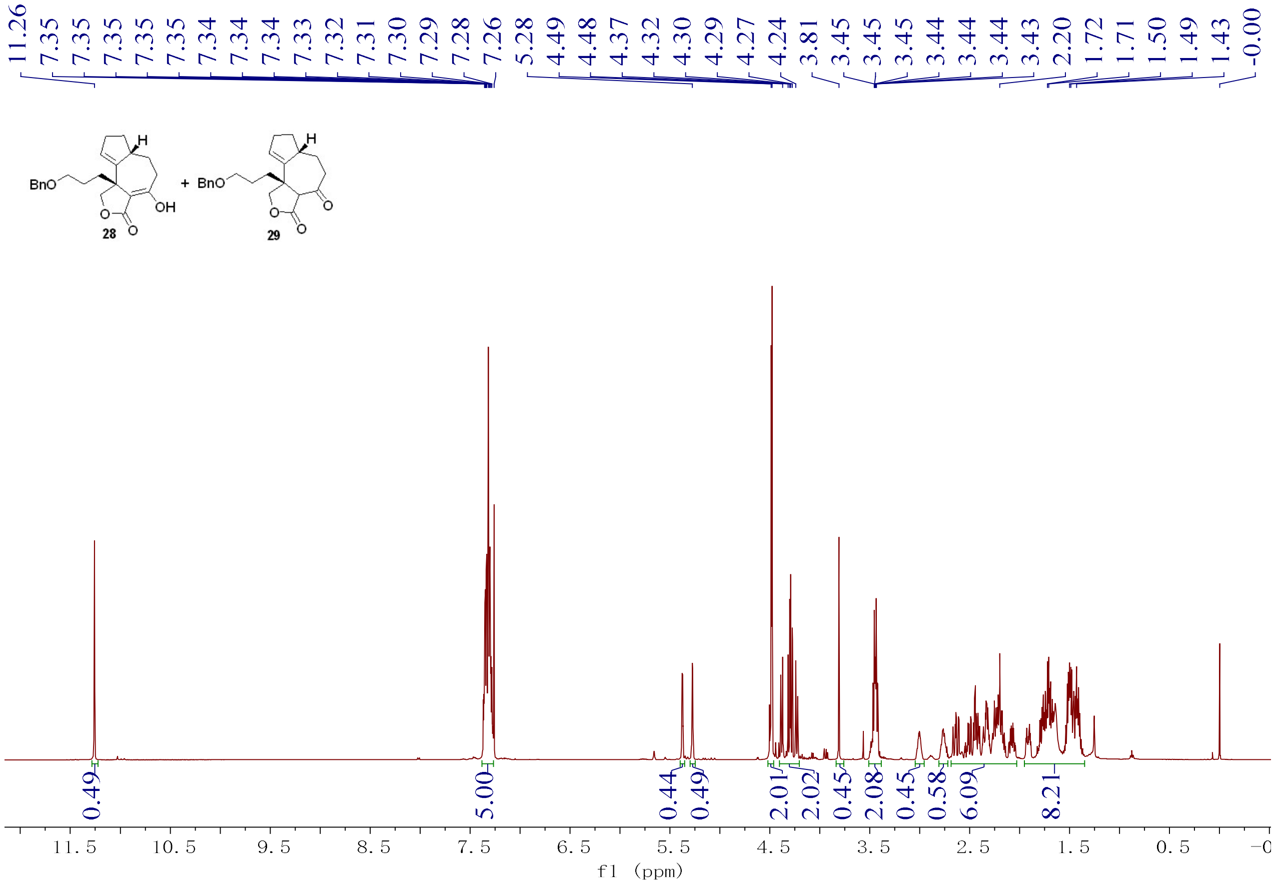
74.55
73.11
69.91
55.99
37.42
32.69
30.43
28.68
28.01
25.50
20.98
20.47
BnO
H
O
OH
H
O
O
26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)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7.30
7.29
7.28
7.26
5.28
4.49
4.48
4.37
4.32
4.30
4.29
4.27
4.24
3.81
3.45
3.45
3.45
3.44
3.44
3.44
3.43
2.20
1.72
1.71
1.50
1.49
1.43
-0.00
BnO
H
OH
O
O
28
+
BnO
H
O
O
O
29
0.49
5.00
0.44
0.49
2.01
2.02
0.45
2.08
0.45
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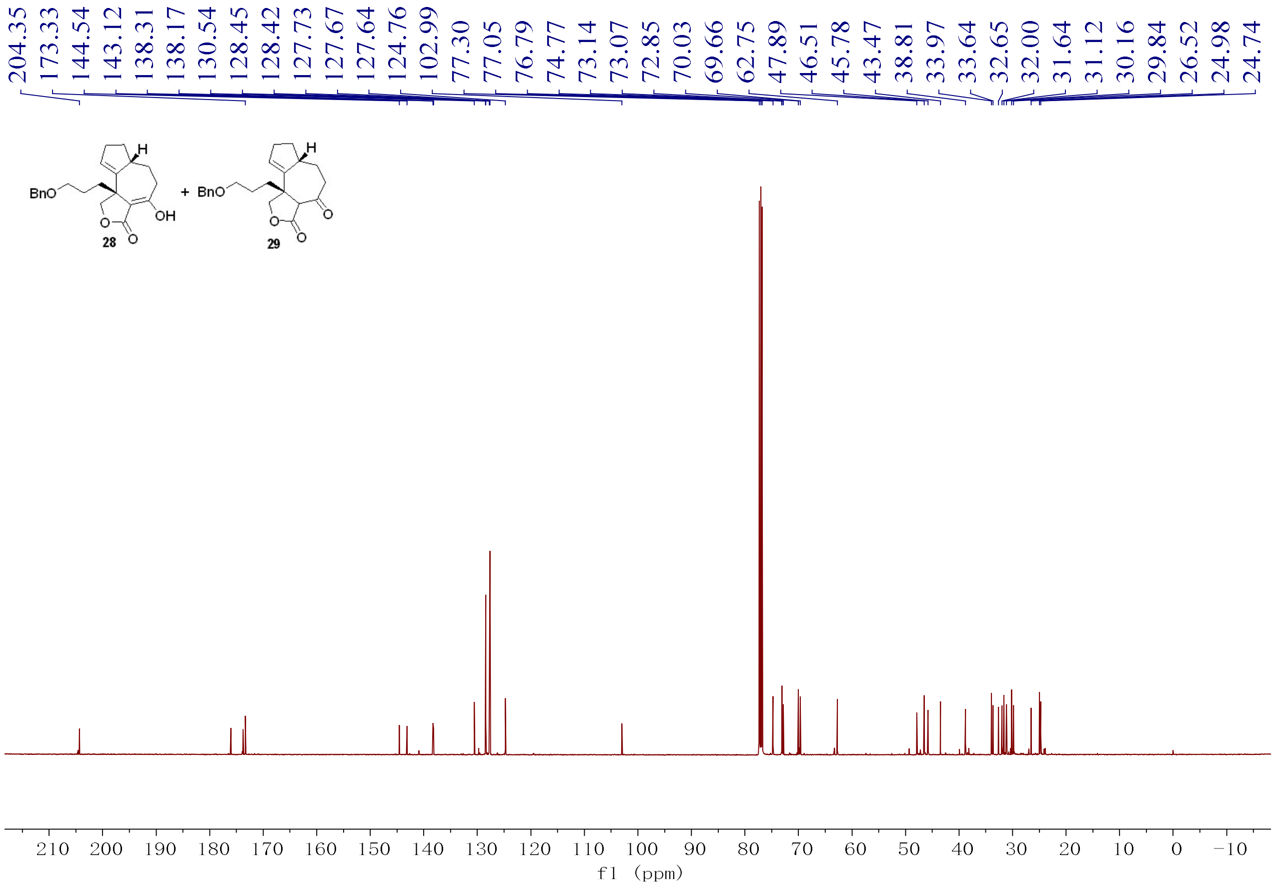
8.21
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)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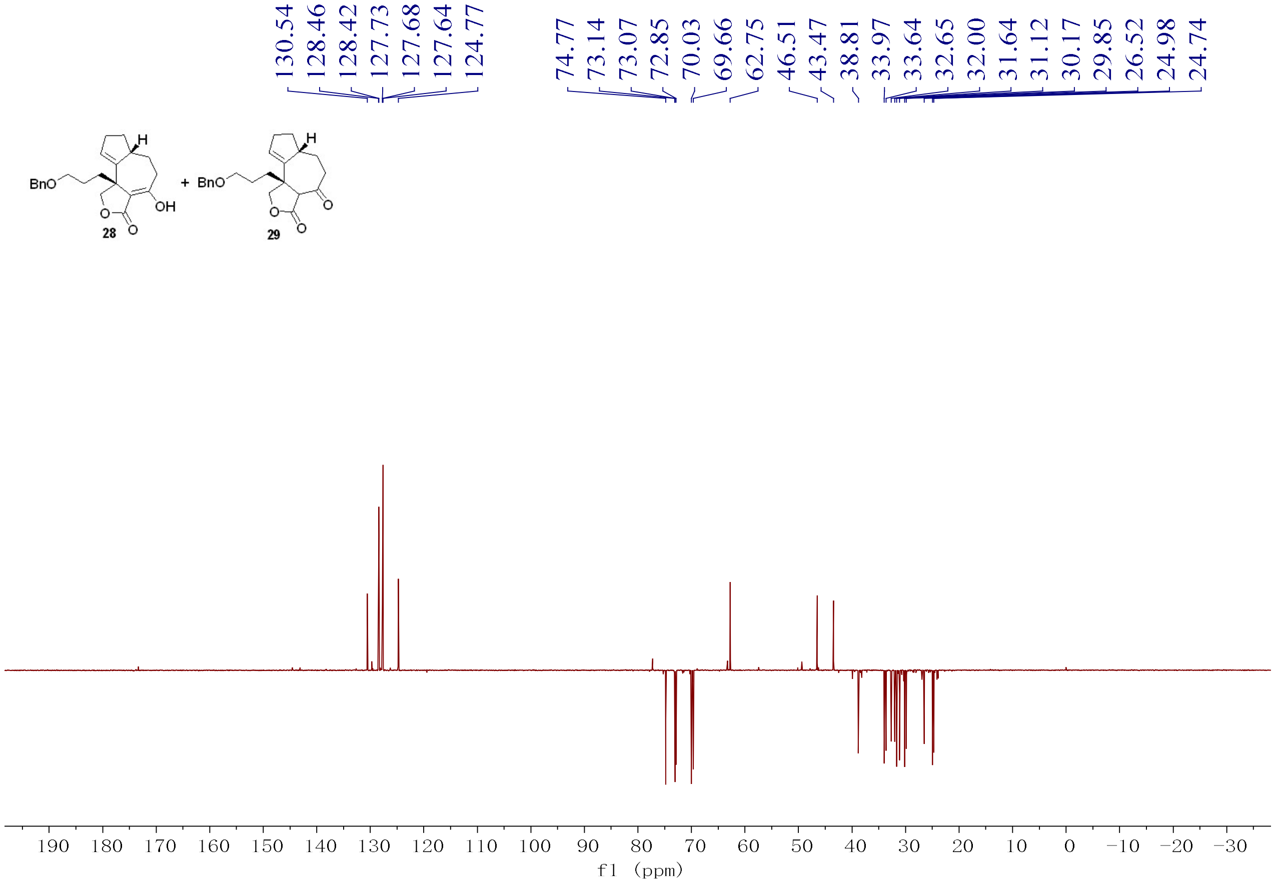
127.67
127.64
124.76
102.99
77.30
77.05
76.79
74.77
73.14
73.07
72.85
70.03
69.66
62.75
47.89
46.51
45.78
43.47
38.81
33.97
33.64
32.65
32.00
31.64
31.12
30.16
29.84
26.52
24.98
24.74
BnO
H
OH
O
O
28
+ BnO
H
O
O
O
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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62.75
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43.47
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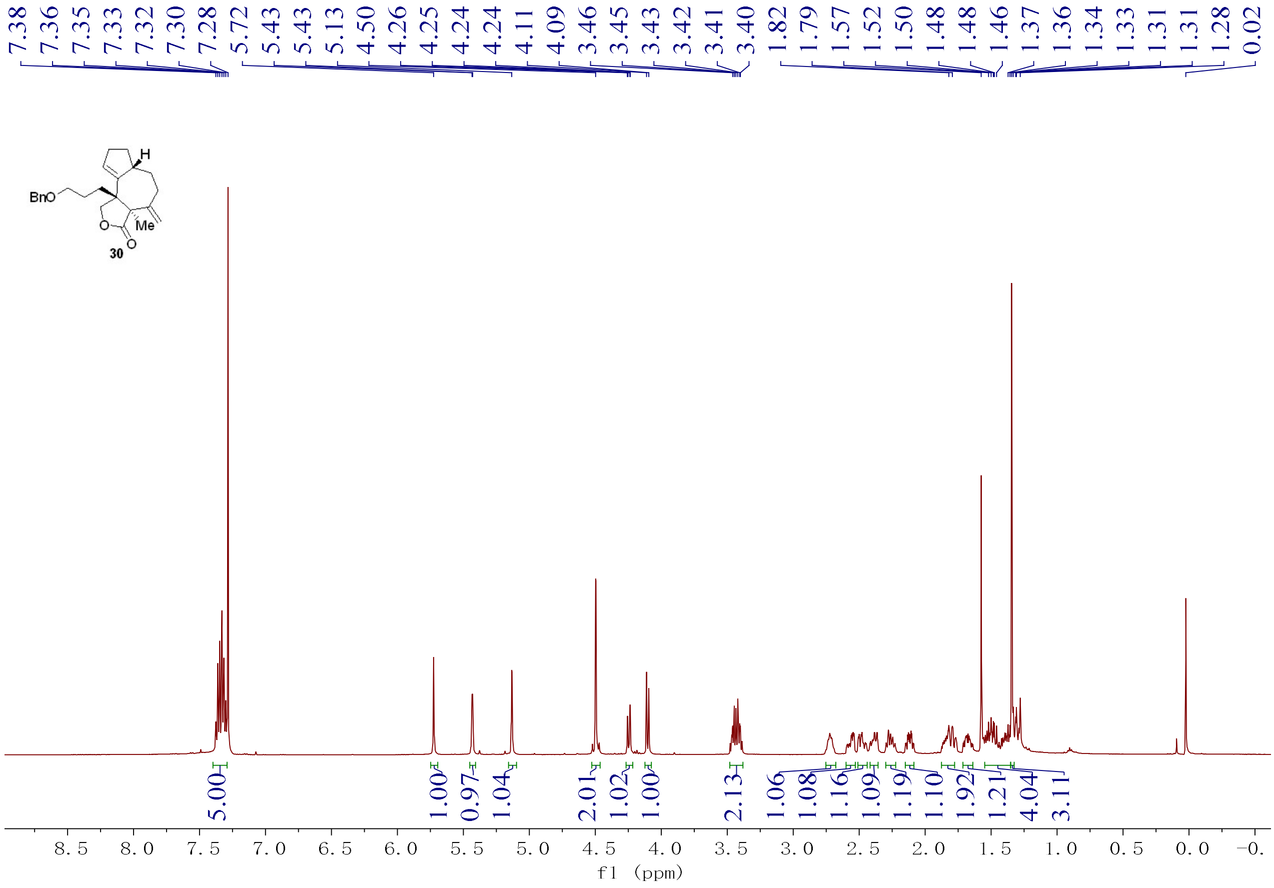
33.97
33.64
32.65
32.00
31.64
31.12
30.17
29.85
26.52
24.98
24.74
BnO
H
OH
O
O
28
+ BnO
H
O
O
O
29
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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5.13
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4.26
4.25
4.24
4.24
4.11
4.09
3.46
3.45
3.43
3.42
3.41
3.40
1.82
1.79
1.57
1.52
1.50
1.48
1.48
1.46
1.37
1.36
1.34
1.33
1.31
1.31
1.28
0.02
H
BnO
O
Me
O
30
5.00
1.00
0.97
1.04
2.01
1.02
1.00
2.13
1.06
1.08
1.16
1.09
1.19
1.10
1.92
1.21
4.04
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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0.5
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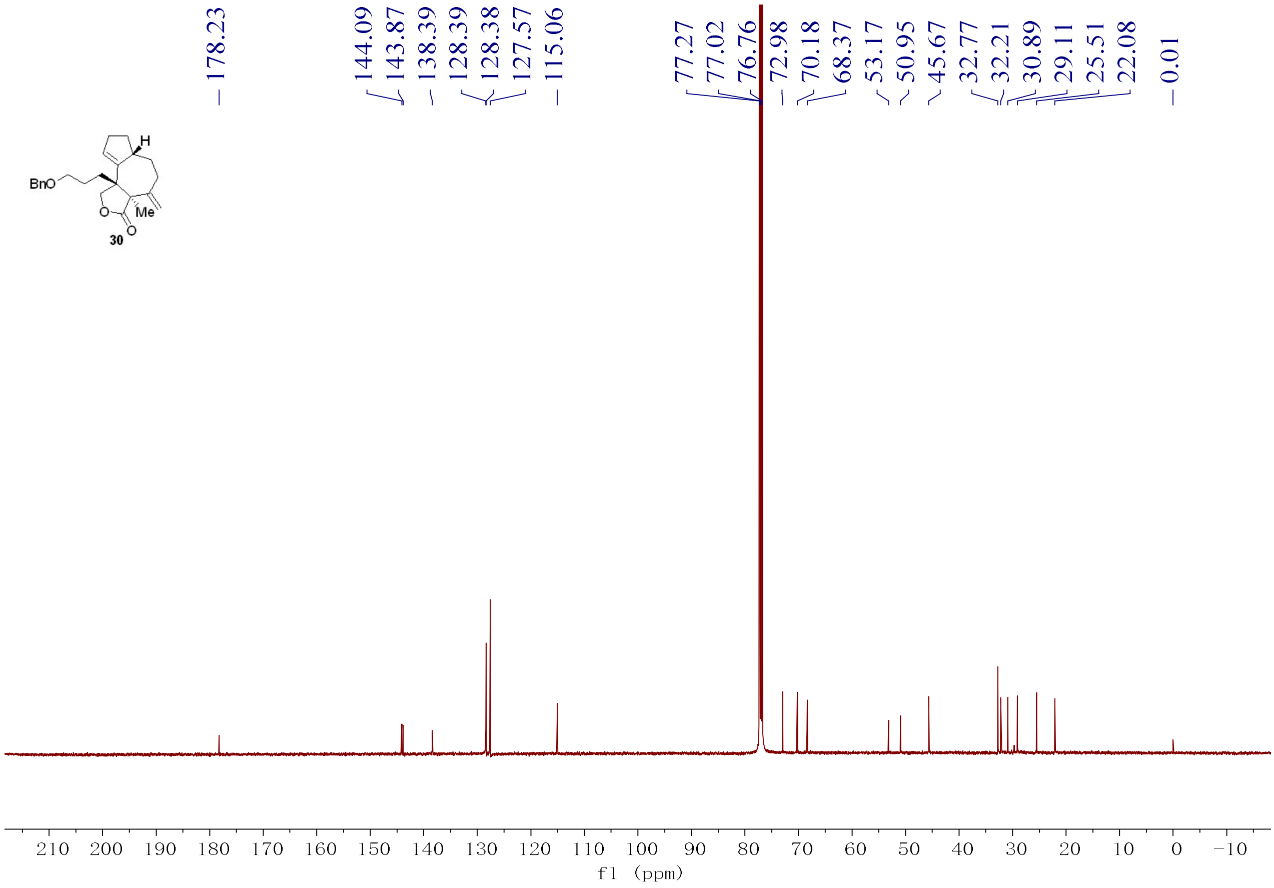
-0.
f1 (ppm)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72.98
70.18
68.37
53.17
50.95
45.67
32.77
32.21
30.89
29.11
25.51
22.08
0.01
H
BnO
O
Me
O
30
210
200
190
180
170
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100
90
80
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40
30
20
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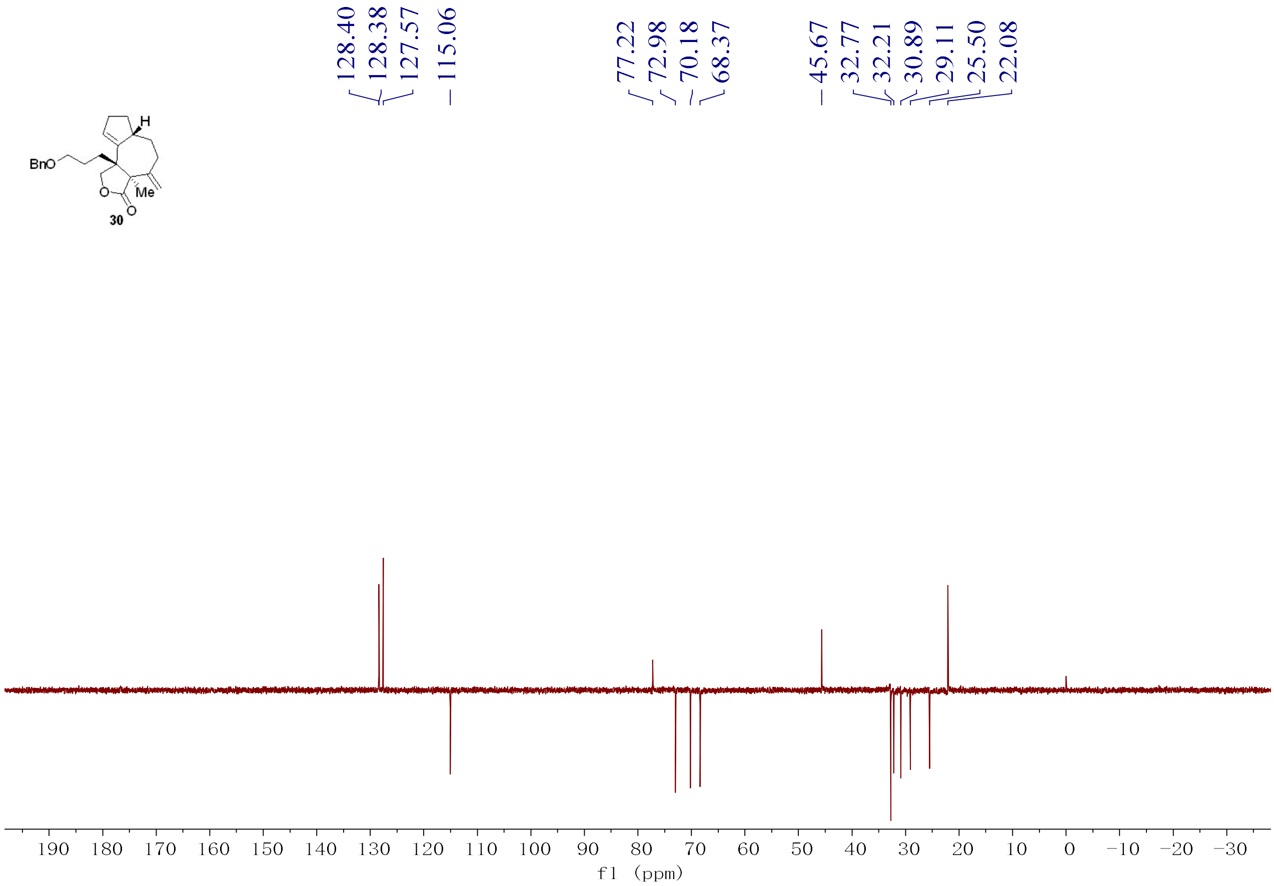
-10
f1 (ppm)


BnO
H
O
O
Me
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127.57
115.06
77.22
72.98
70.18
68.37
45.67
32.77
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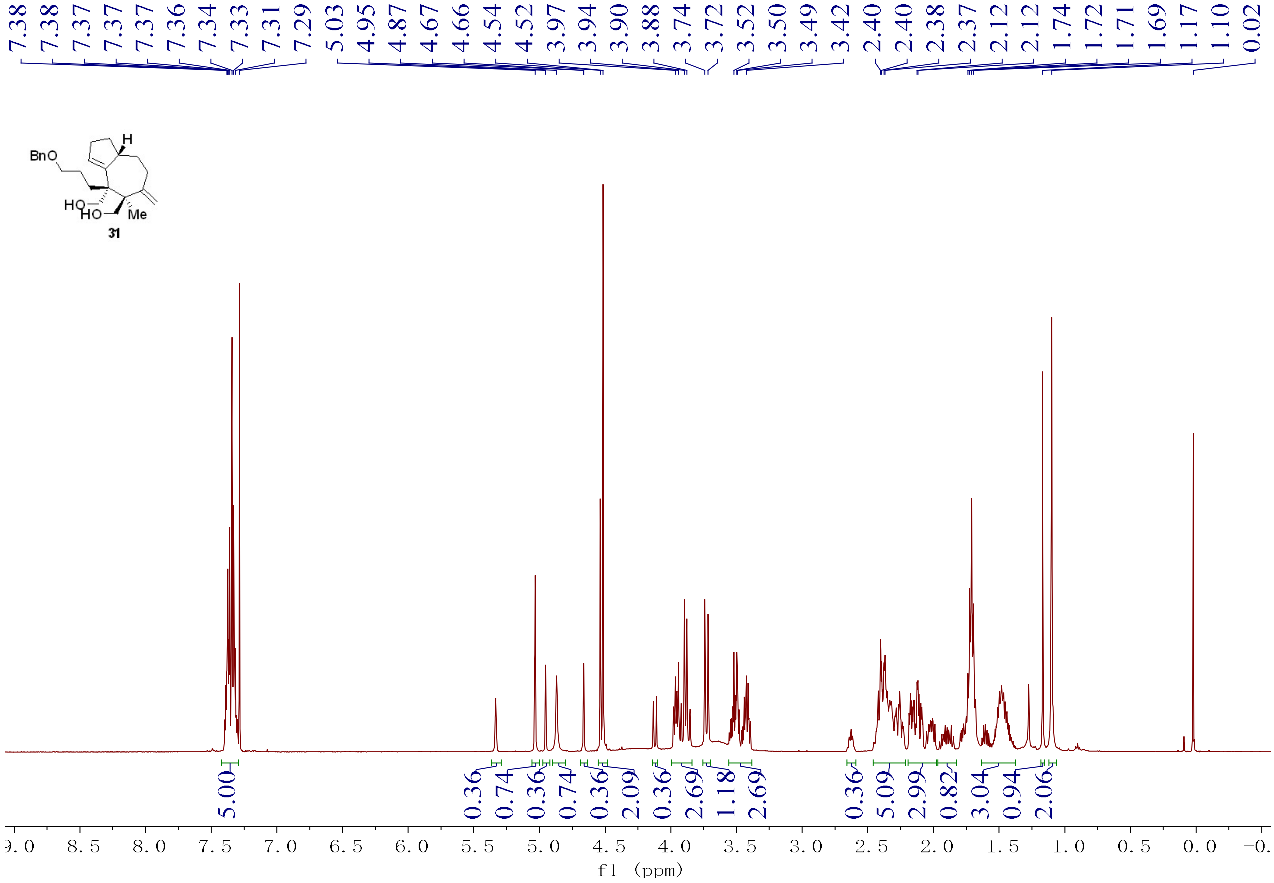
30.89
29.11
25.50
22.08
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)


BnO
H
HO
HO
Me
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7.38
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7.37
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7.31
7.29
5.03
4.95
4.87
4.67
4.66
4.54
4.52
3.97
3.94
3.90
3.88
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3.52
3.50
3.49
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2.40
2.40
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2.12
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1.71
1.69
1.17
1.10
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5.00
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0.74
0.36
0.74
0.36
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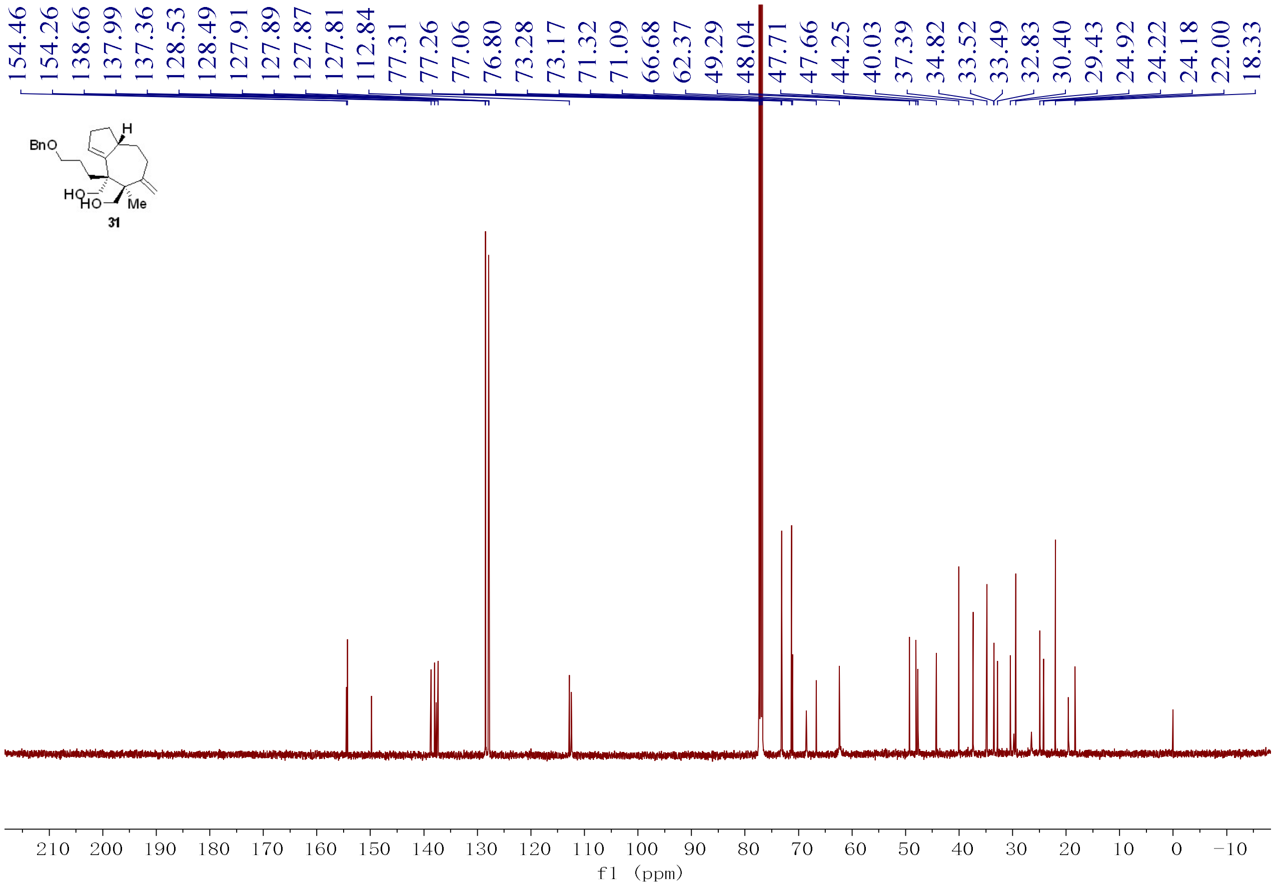
0.36
0.36
2.69
1.18
2.69
0.36
5.09
2.99
0.82
3.04
0.94
2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)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77.26
77.06
76.80
73.28
73.17
71.32
71.09
66.68
62.37
49.29
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47.66
44.25
40.03
37.39
34.82
33.52
33.49
32.83
30.40
29.43
24.92
24.22
24.18
22.00
18.33
BnO
H
HO
HO
Me
31
210
200
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180
170
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100
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40
30
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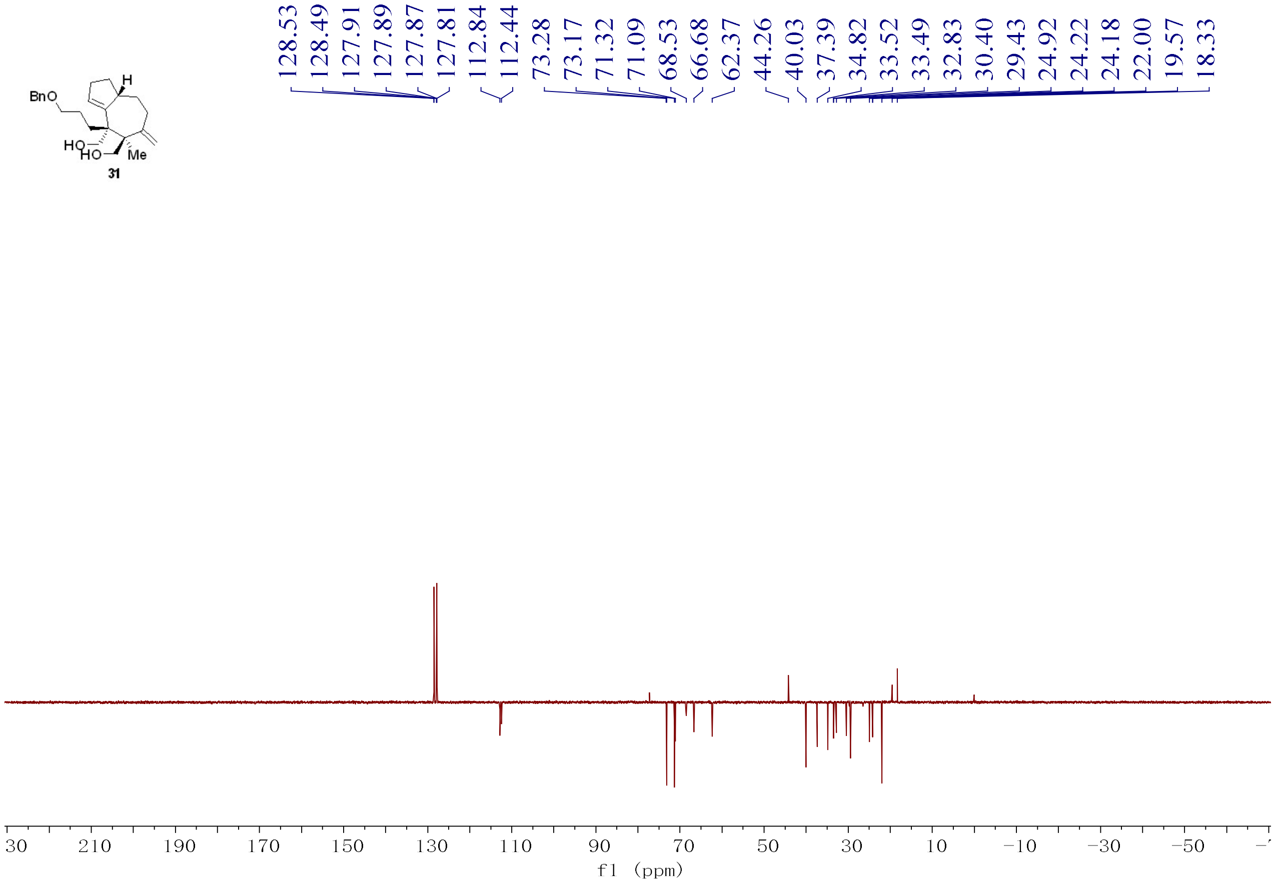
−10
f1 (ppm)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68.53
66.68
62.37
44.26
40.03
37.39
34.82
33.52
33.49
32.83
30.40
29.43
24.92
24.22
24.18
22.00
19.57
18.33
BnO
H
HO
HO
Me
31
30
210
190
170
150
130
110
90
70
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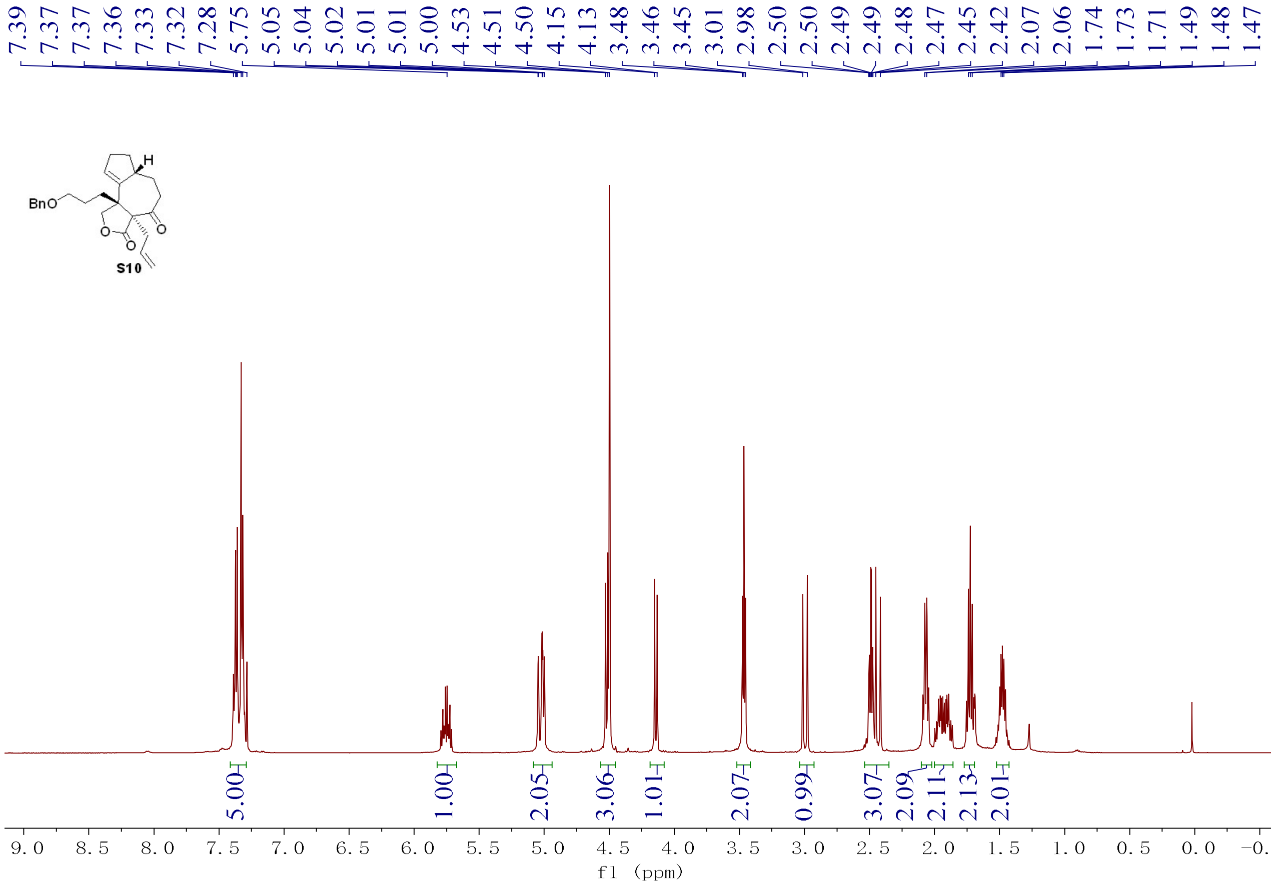
30
10
−10
−30
−50
f1 (ppm)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5.01
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2.49
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2.47
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2.06
1.74
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1.71
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1.48
1.47
BnO
H
O
O
O
S10
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1.00
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3.06
1.01
2.07
0.99
3.07
2.09
2.11
2.13
2.01
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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0.0
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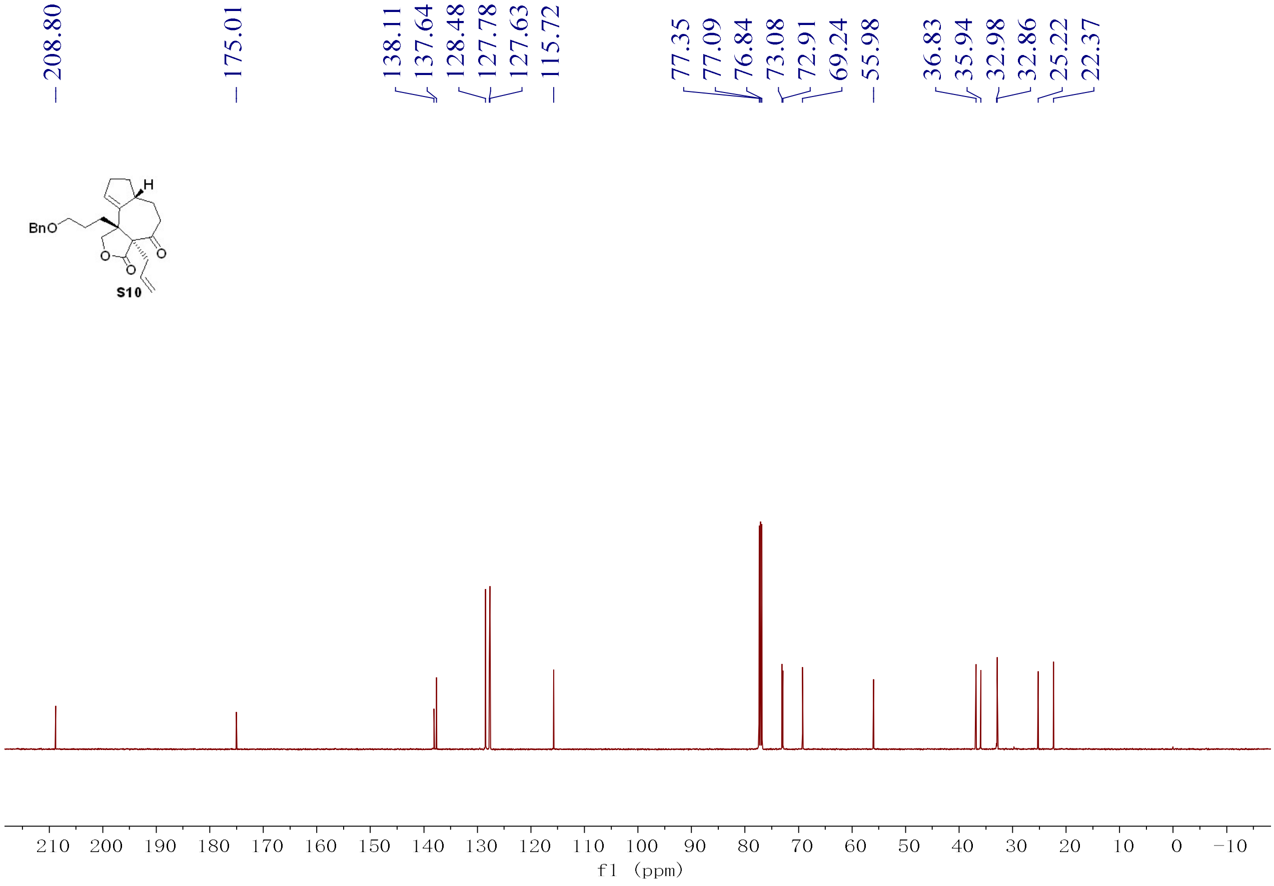
f1 (ppm)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73.08
72.91
69.24
55.98
36.83
35.94
32.98
32.86
25.22
22.37
BnO
H
O
O
O
S10
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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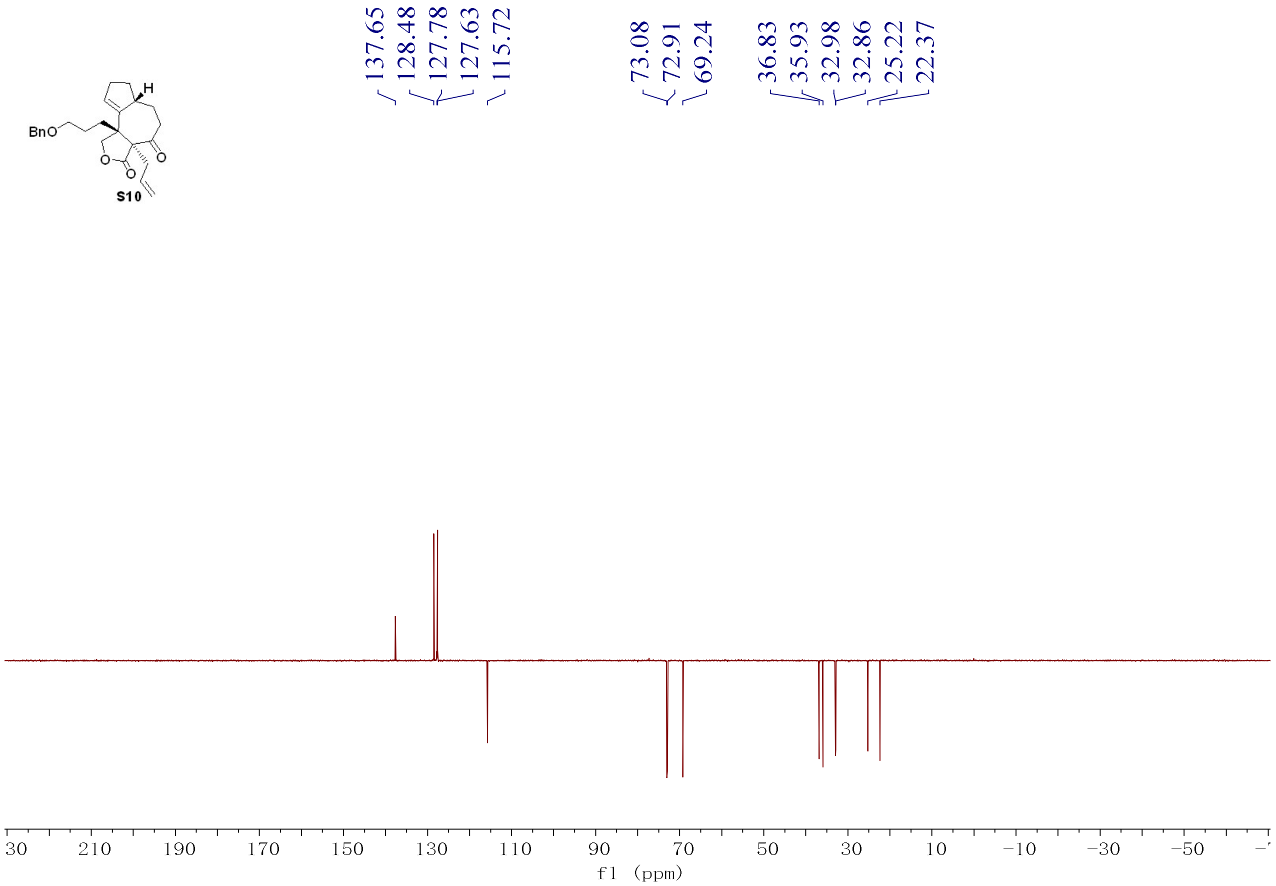
40
30
20
10
0
-10
f1 (ppm)


BnO
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S10
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35.93
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32.86
25.22
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150
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110
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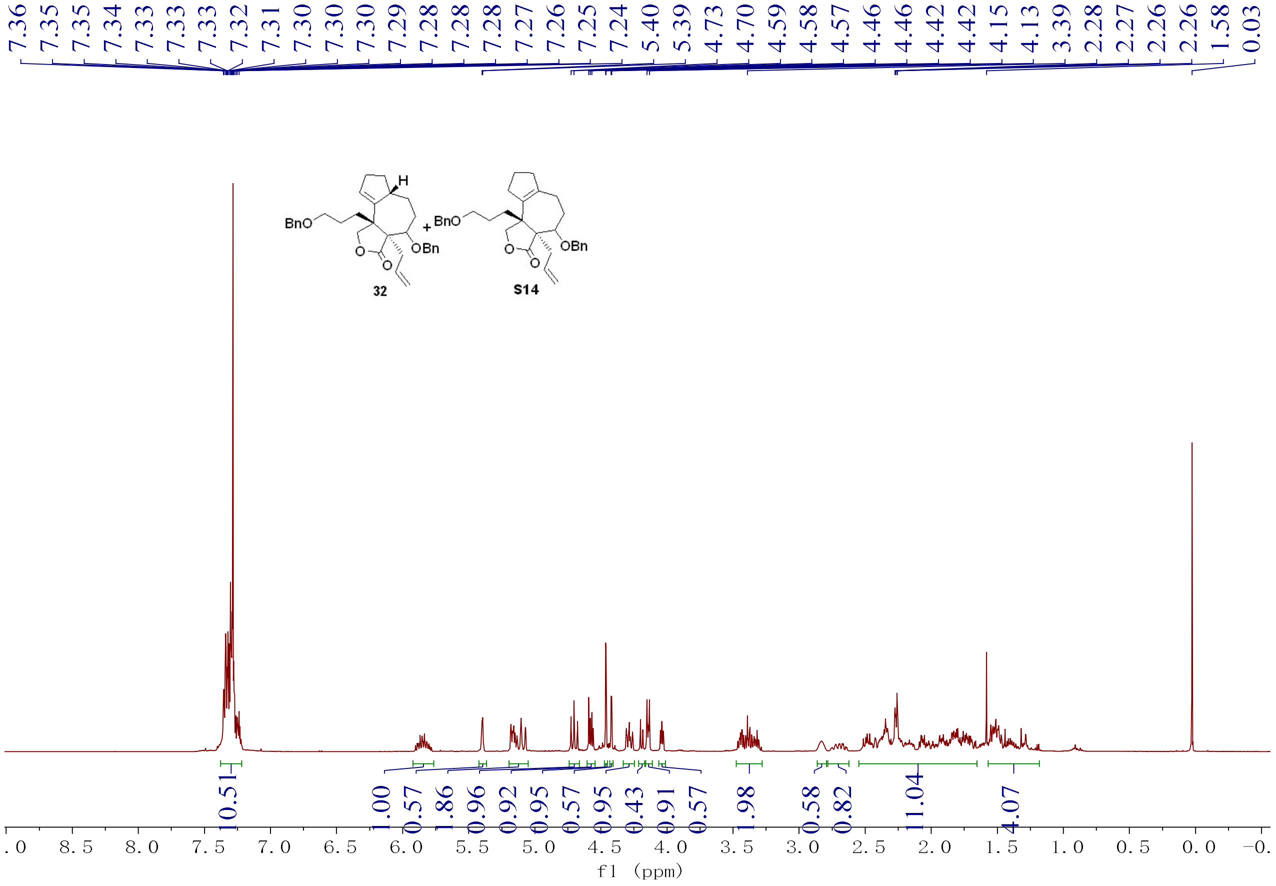
30
10
−10
−30
−50
f1 (ppm)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2.26
1.58
0.03
BnO
H
OBn
O
O
32
+
BnO
OBn
O
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S14
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0.57
0.95
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0.57
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0.58
0.82
11.04
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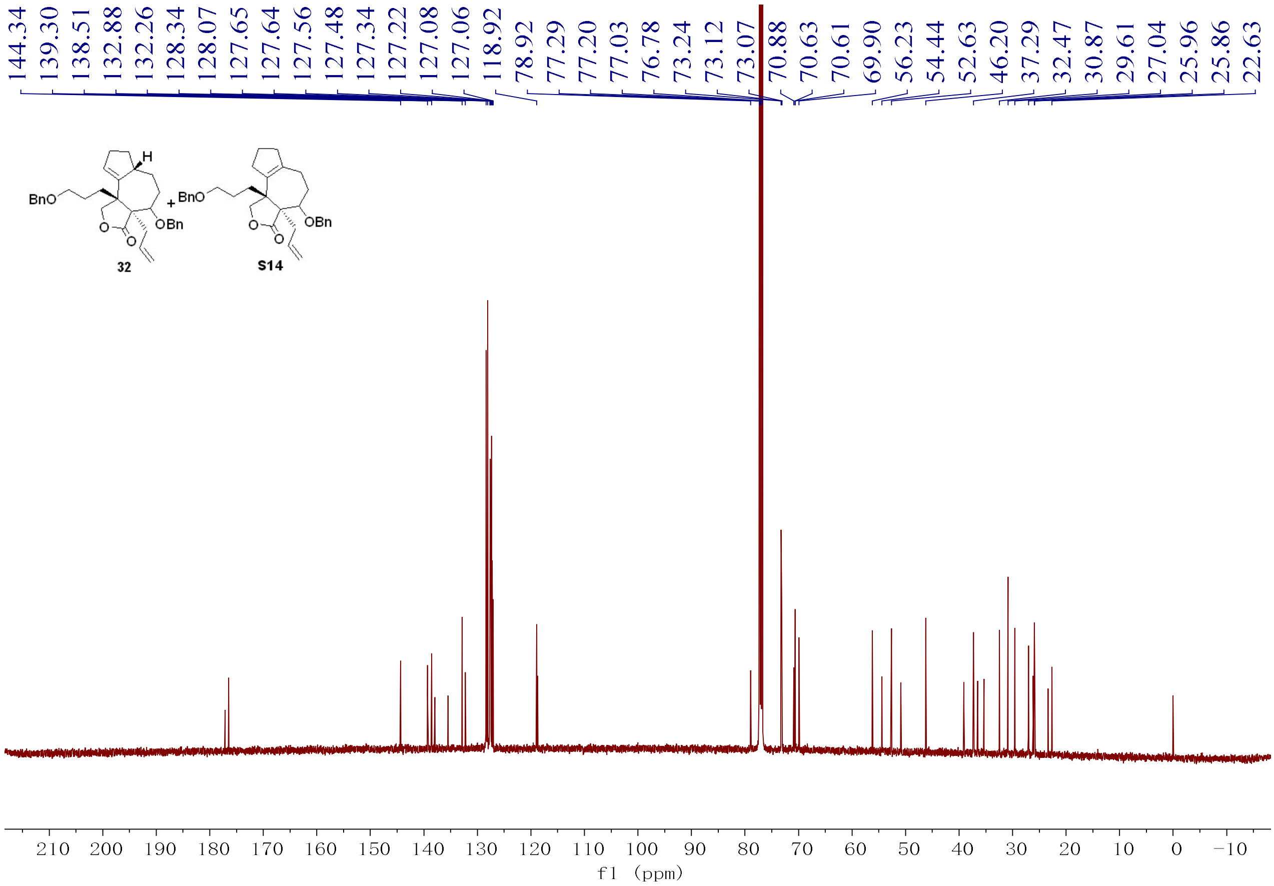
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)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139.30
138.51
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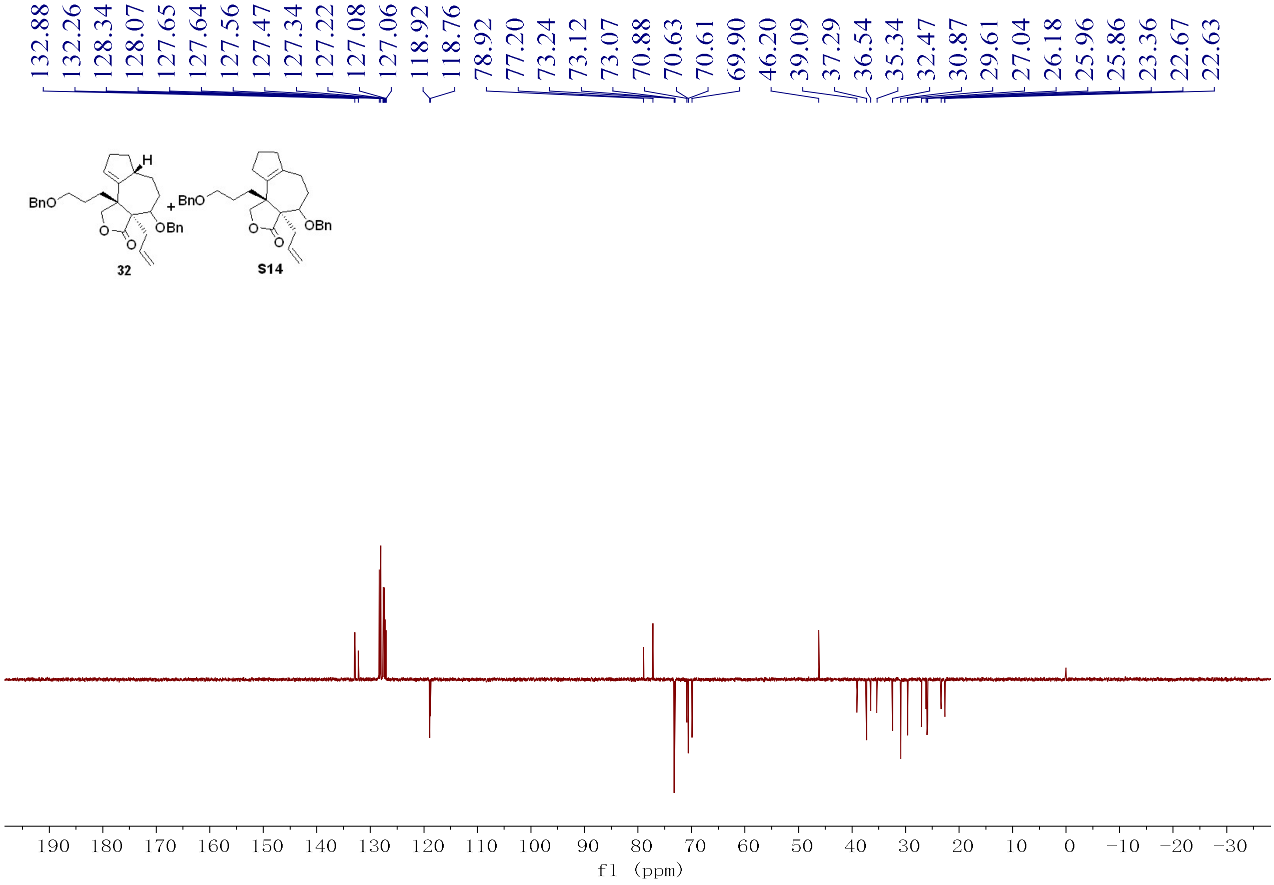
132.26
128.34
128.07
127.65
127.64
127.56
127.48
127.34
127.22
127.08
127.06
118.92
78.92
77.29
77.20
77.03
76.78
73.24
73.12
73.07
70.88
70.63
70.61
69.90
56.23
54.44
52.63
46.20
37.29
32.47
30.87
29.61
27.04
25.96
25.86
22.63
H
BnO
+
BnO
OBn
OBn
O
O
O
O
32
S14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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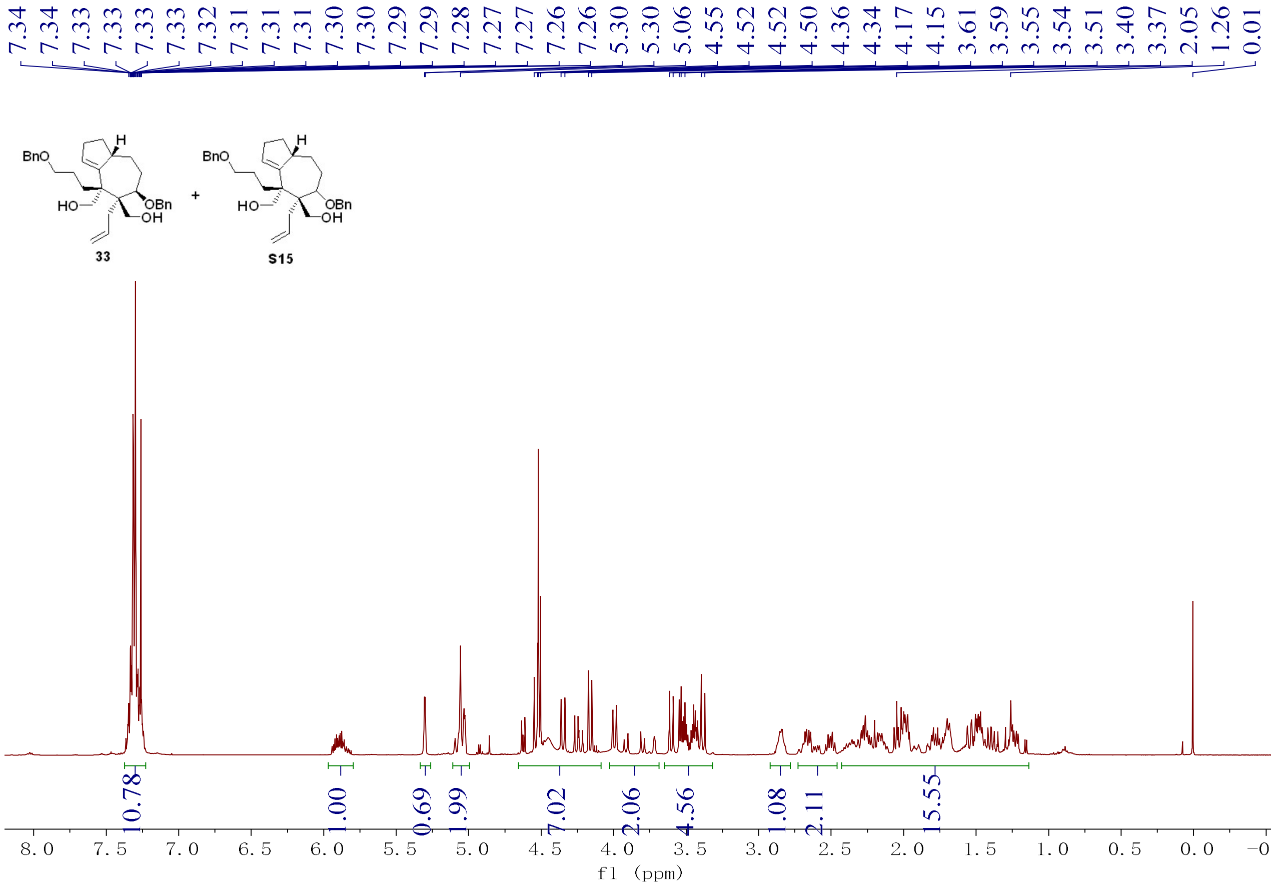
132.26
128.34
128.07
127.65
127.64
127.56
127.47
127.34
127.22
127.08
127.06
118.92
118.76
78.92
77.20
73.24
73.12
73.07
70.88
70.63
70.61
69.90
46.20
39.09
37.29
36.54
35.34
32.47
30.87
29.61
27.04
26.18
25.96
25.86
23.36
22.67
22.63
H
BnO
+
BnO
OBn
OBn
O
O
O
O
32
S14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)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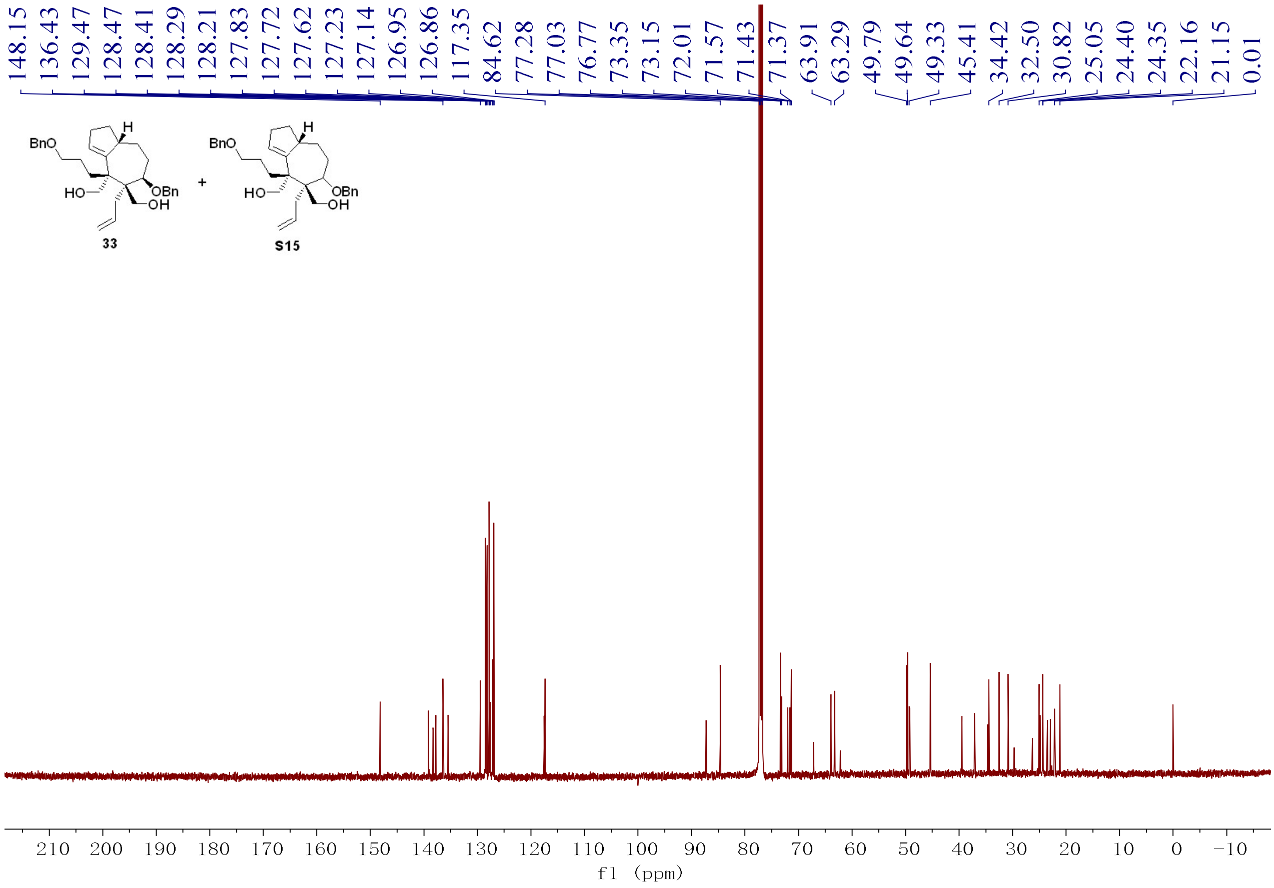
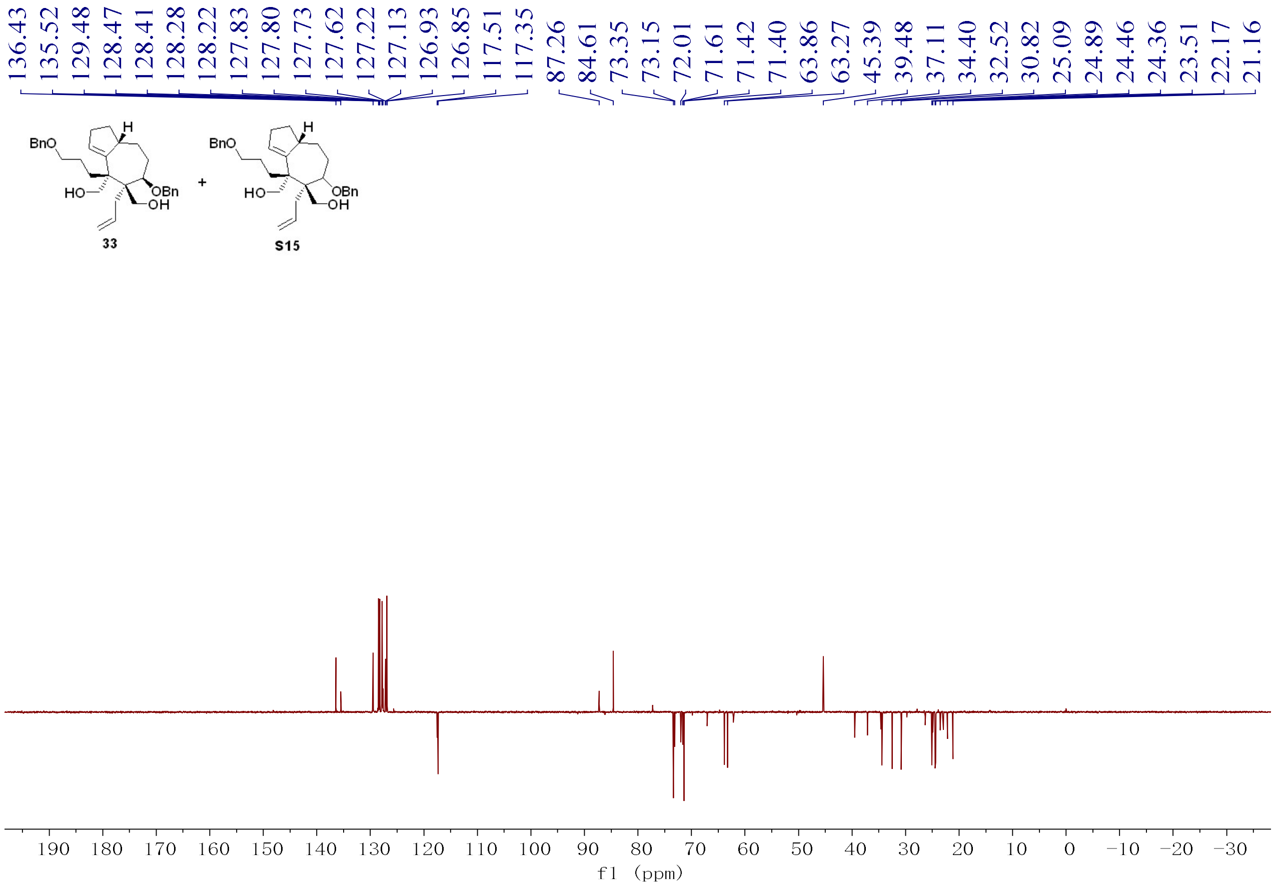
BnO
H
HO
OBn
OH
+
33
S15
10.78
1.00
0.69
1.99
7.02
2.06
4.56
1.08
2.11
15.55
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)


148.15 136.43 129.47 128.47 128.41 128.29 128.21 127.83 127.72 127.62 127.23 127.14 126.95 126.86 117.35 84.62 77.28 77.03 76.77 73.35 73.15 72.01 71.57 71.43 71.37 63.91 63.29 49.79 49.64 49.33 45.41 34.42 32.50 30.82 25.05 24.40 24.35 22.16 21.15 0.01
BnO
H
HO
OBn
OH
+
33
S15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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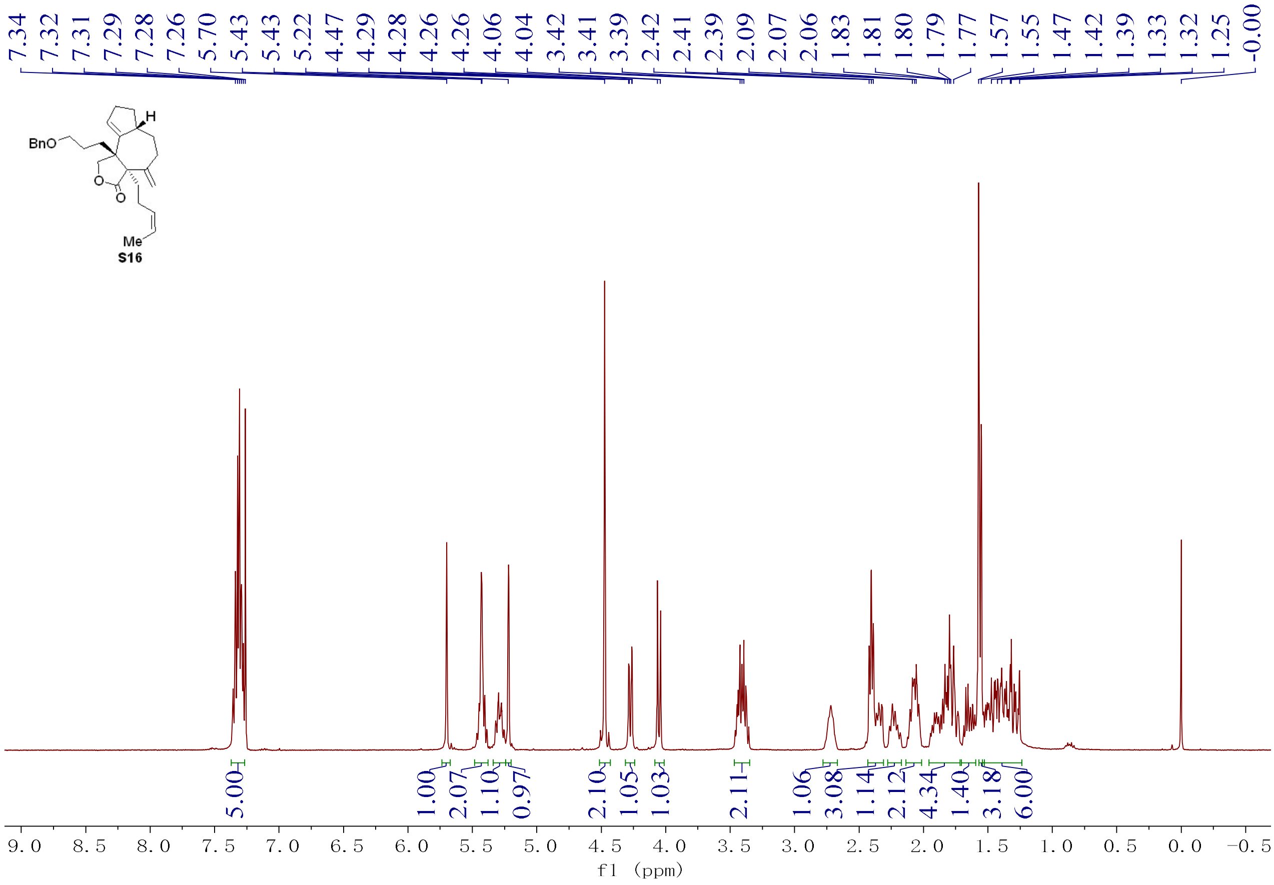
127.73
127.62
127.22
127.13
126.93
126.85
117.51
117.35
87.26
84.61
73.35
73.15
72.01
71.61
71.42
71.40
63.86
63.27
45.39
39.48
37.11
34.40
32.52
30.82
25.09
24.89
24.46
24.36
23.51
22.17
21.16
BnO
H
HO
OBn
OH
+
33
S15
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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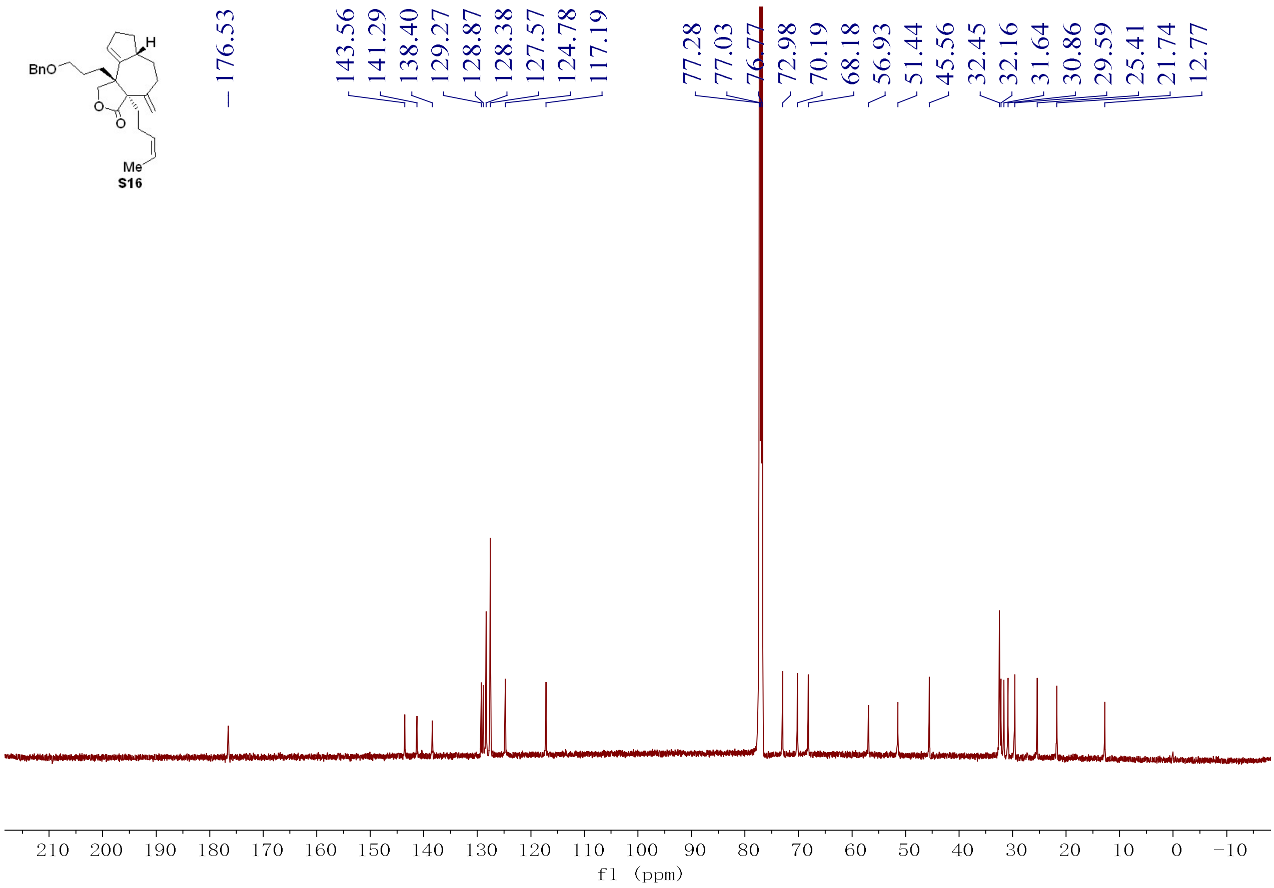
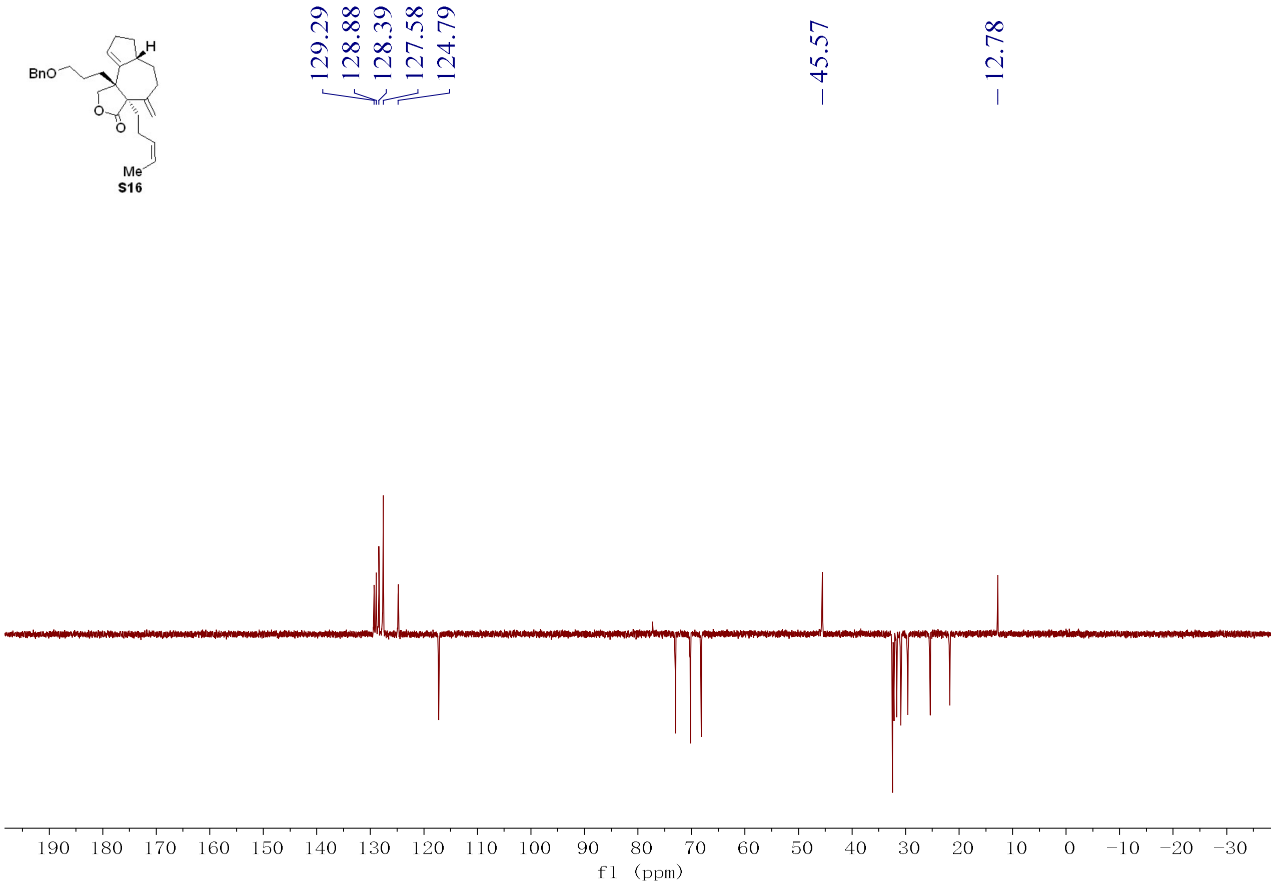
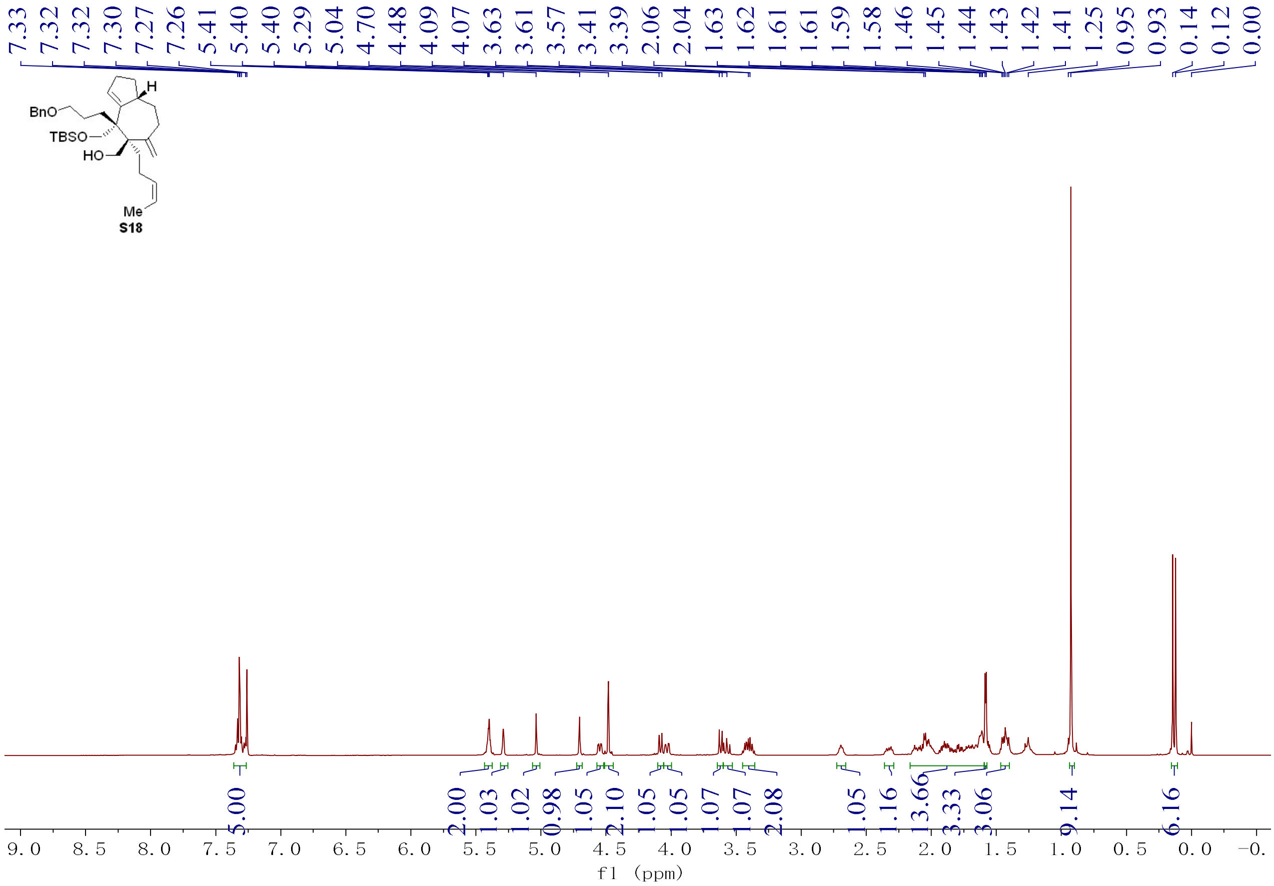
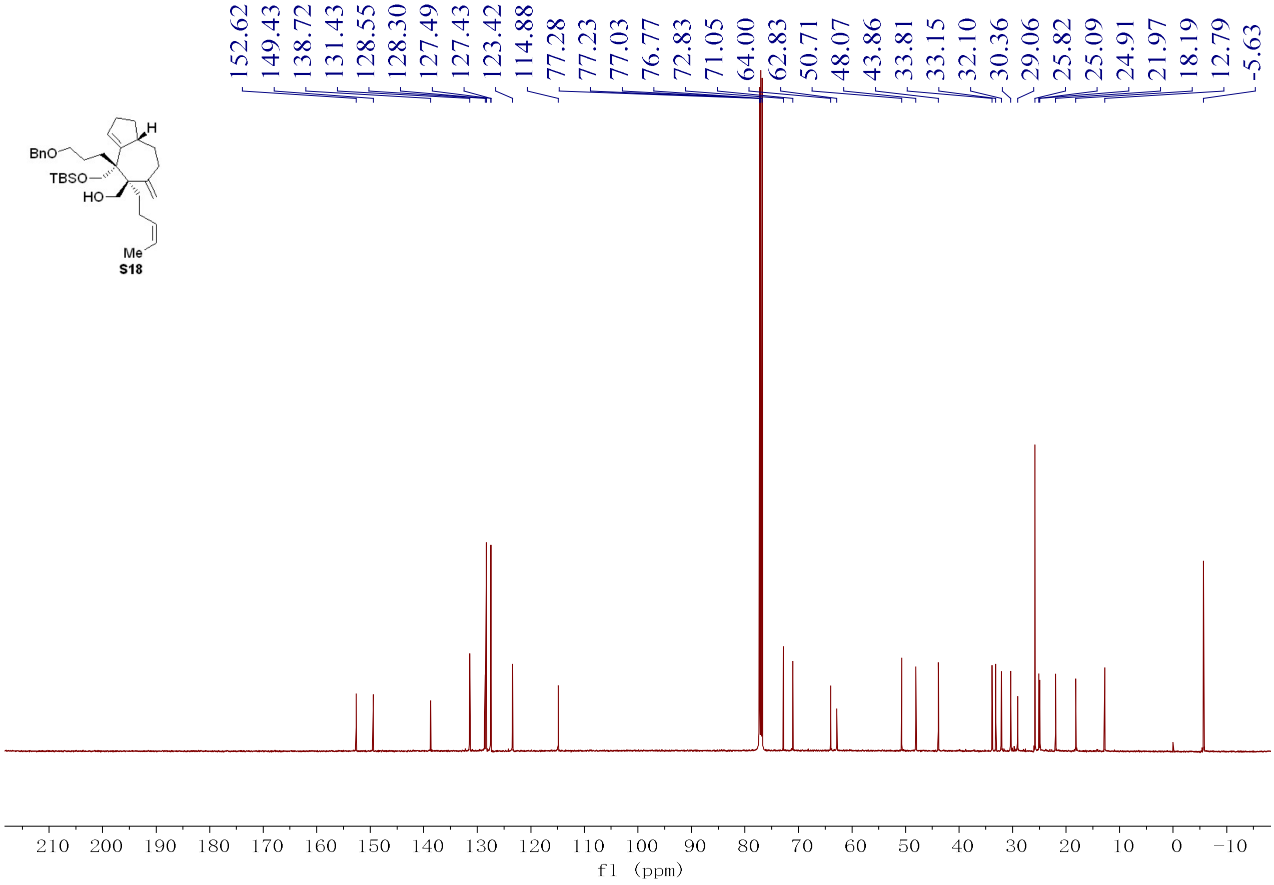
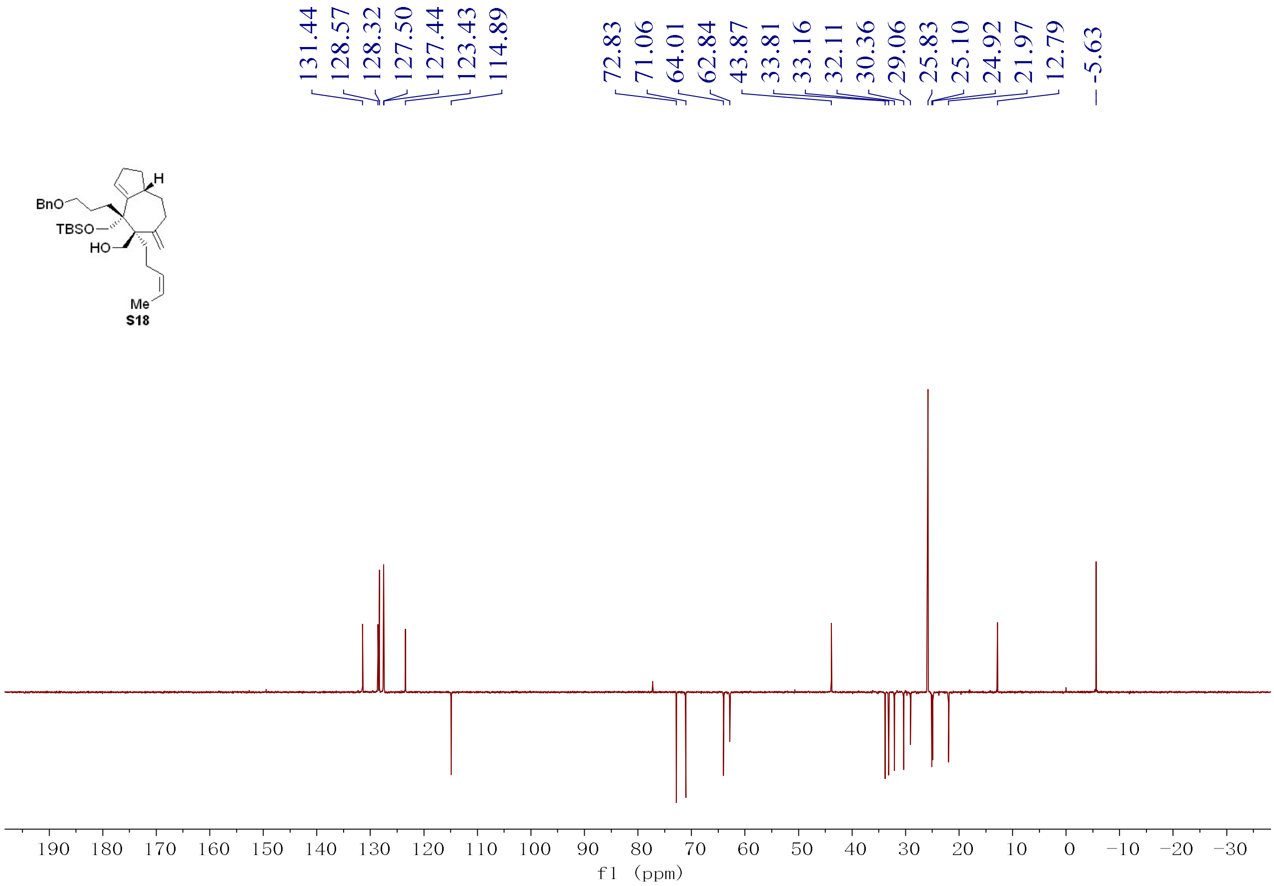
7.32
7.31
7.29
7.28
7.26
5.70
5.43
5.43
5.22
4.47
4.29
4.28
4.26
4.26
4.06
4.04
3.42
3.41
3.39
2.42
2.41
2.39
2.09
2.07
2.06
1.83
1.81
1.80
1.79
1.77
1.57
1.55
1.47
1.42
1.39
1.33
1.32
1.25
-0.00
BnO
H
O
O
Me
S16
5.00
1.00
2.07
1.10
0.97
2.10
1.05
1.03
2.11
1.06
3.08
1.14
2.12
4.34
1.40
3.18
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

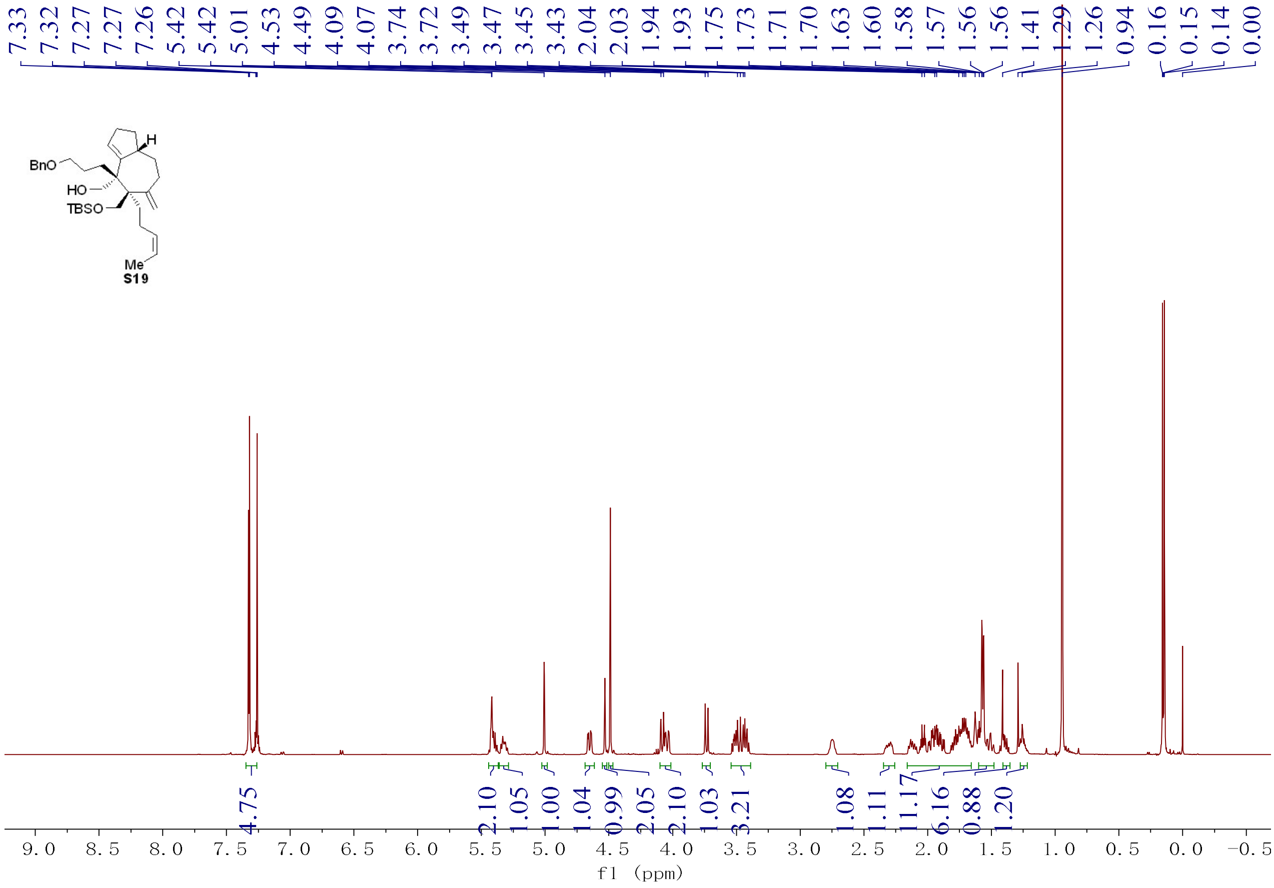

BnO
H
O
O
Me
S16
176.53
143.56
141.29
138.40
129.27
128.87
128.38
127.57
124.78
117.19
77.28
77.03
76.77
72.98
70.19
68.18
56.93
51.44
45.56
32.45
32.16
31.64
30.86
29.59
25.41
21.74
12.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

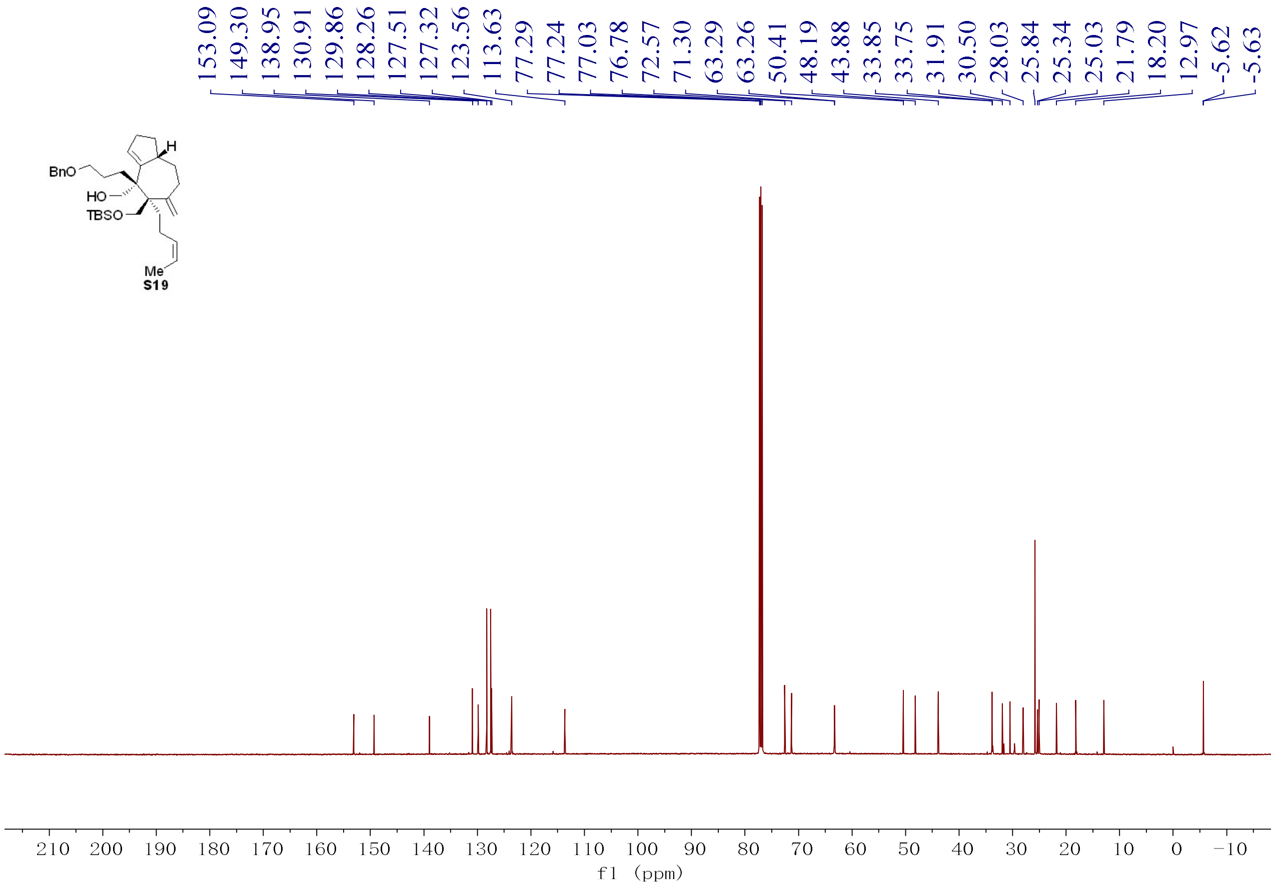

BnO
H
O
O
Me
S16
129.29
128.88
128.39
127.58
124.79
45.57
12.78
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

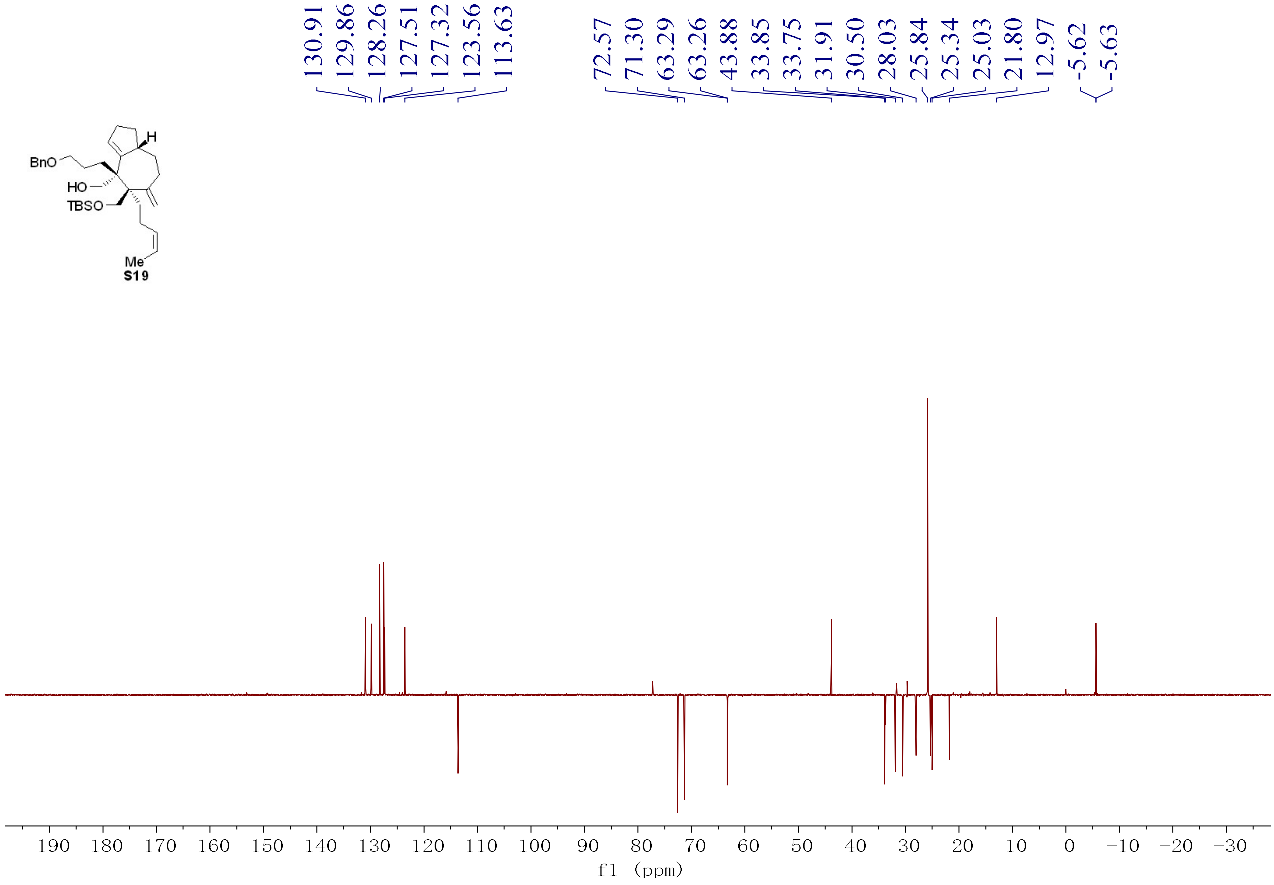

7.33
7.32
7.32
7.30
7.27
7.26
5.41
5.40
5.40
5.29
5.04
4.70
4.48
4.09
4.07
3.63
3.61
3.57
3.41
3.39
2.06
2.04
1.63
1.62
1.61
1.61
1.59
1.58
1.46
1.45
1.44
1.43
1.42
1.41
1.25
0.95
0.93
0.14
0.12
0.00
BnO
TBSO
HO
H
Me
S18
5.00
2.00
1.03
1.02
0.98
1.05
2.10
1.05
1.05
1.07
1.07
2.08
1.05
1.16
13.66
3.33
3.06
9.14
6.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


152.62
149.43
138.72
131.43
128.55
128.30
127.49
127.43
123.42
114.88
77.28
77.23
77.03
76.77
72.83
71.05
64.00
62.83
50.71
48.07
43.86
33.81
33.15
32.10
30.36
29.06
25.82
25.09
24.91
21.97
18.19
12.79
-5.63
BnO
TBSO
HO
H
Me
S18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S18
131.44
128.57
128.32
127.50
127.44
123.43
114.89
72.83
71.06
64.01
62.84
43.87
33.81
33.16
32.11
30.36
29.06
25.83
25.10
24.92
21.97
12.79
-5.63
BnO
TBSO
HO
H
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


S19
7.33
7.32
7.27
7.27
7.26
5.42
5.42
5.01
4.53
4.49
4.09
4.07
3.74
3.72
3.49
3.47
3.45
3.43
2.04
2.03
1.94
1.93
1.75
1.73
1.71
1.70
1.63
1.60
1.58
1.57
1.56
1.56
1.41
1.29
1.26
0.94
0.16
0.15
0.14
0.00
BnO
HO
TBSO
H
Me
4.75
2.10
1.05
1.00
1.04
0.99
2.05
2.10
1.03
3.21
1.08
1.11
11.17
6.16
0.88
1.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


153.09
149.30
138.95
130.91
129.86
128.26
127.51
127.32
123.56
113.63
77.29
77.24
77.03
76.78
72.57
71.30
63.29
63.26
50.41
48.19
43.88
33.85
33.75
31.91
30.50
28.03
25.84
25.34
25.03
21.79
18.20
12.97
-5.62
-5.63
BnO
HO
TBSO
H
Me
S19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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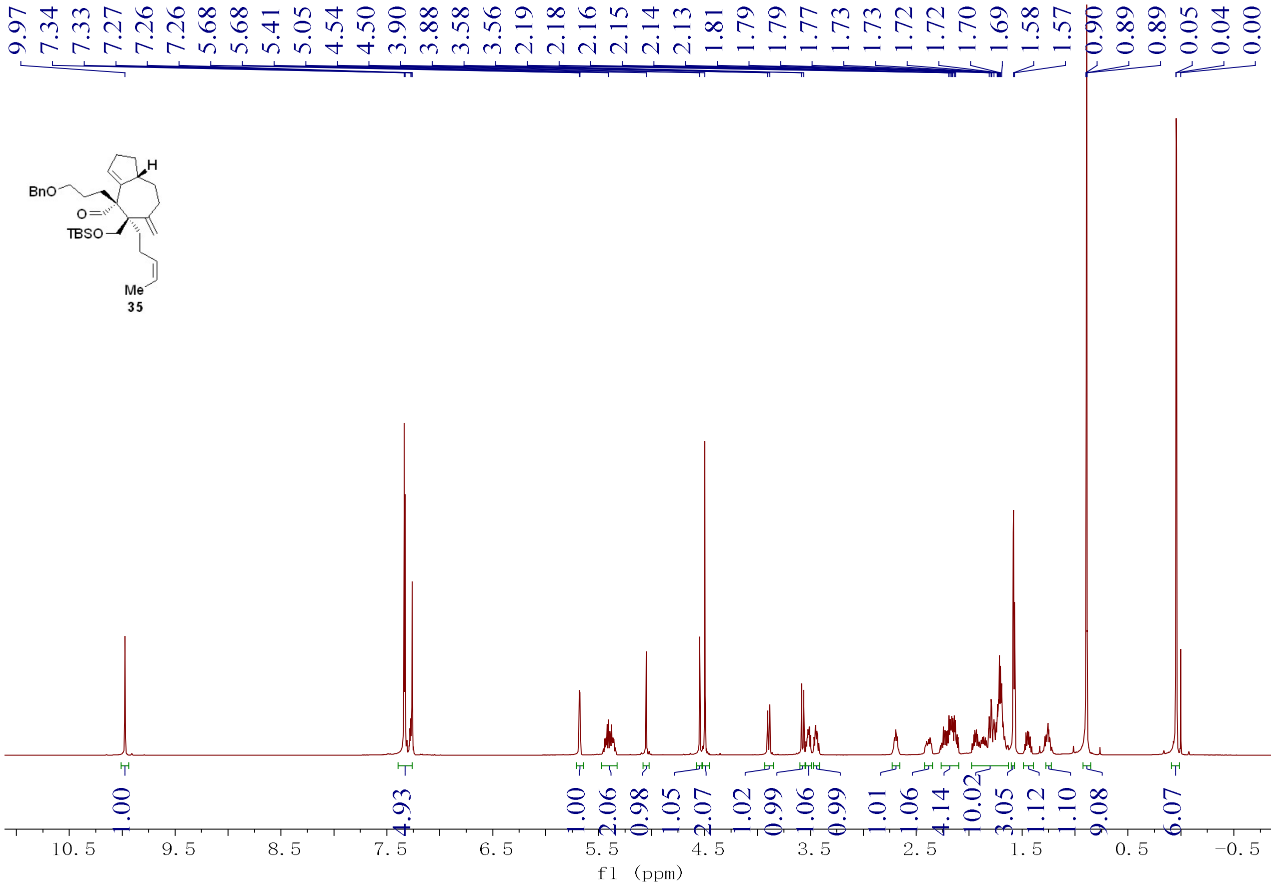
129.86
128.26
127.51
127.32
123.56
113.63
72.57
71.30
63.29
63.26
43.88
33.85
33.75
31.91
30.50
28.03
25.84
25.34
25.03
21.80
12.97
-5.62
-5.63
BnO
HO
TBSO
H
Me
S19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


9.97
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7.33
7.27
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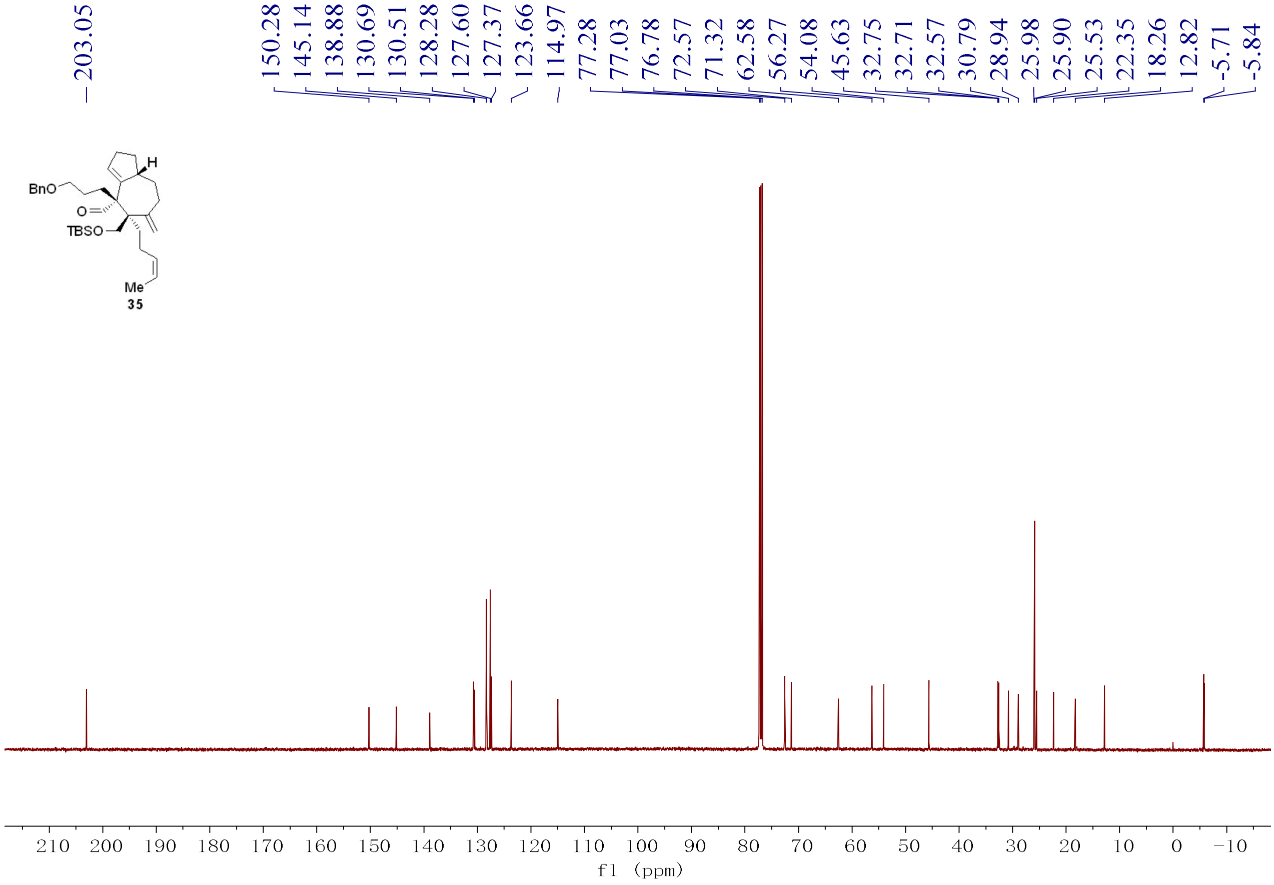
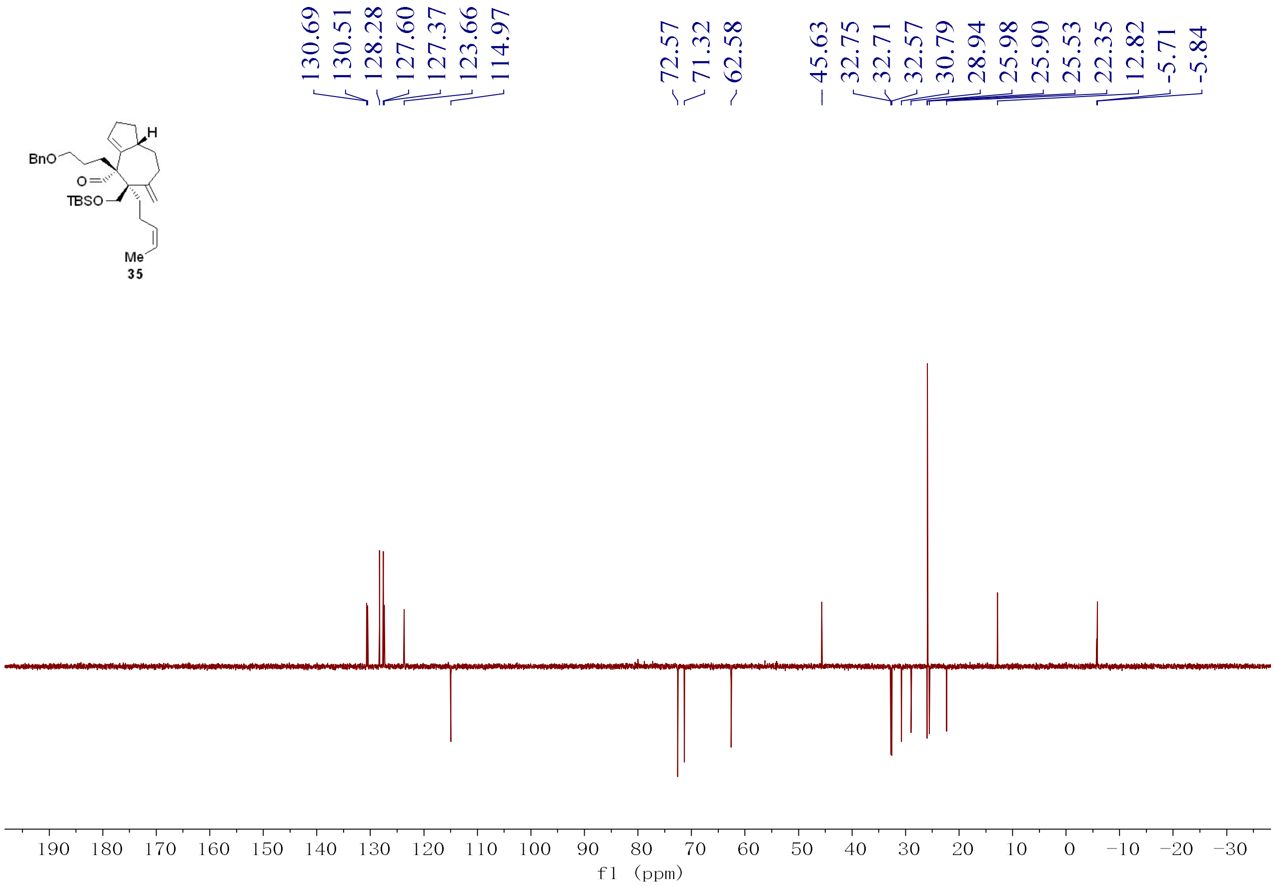
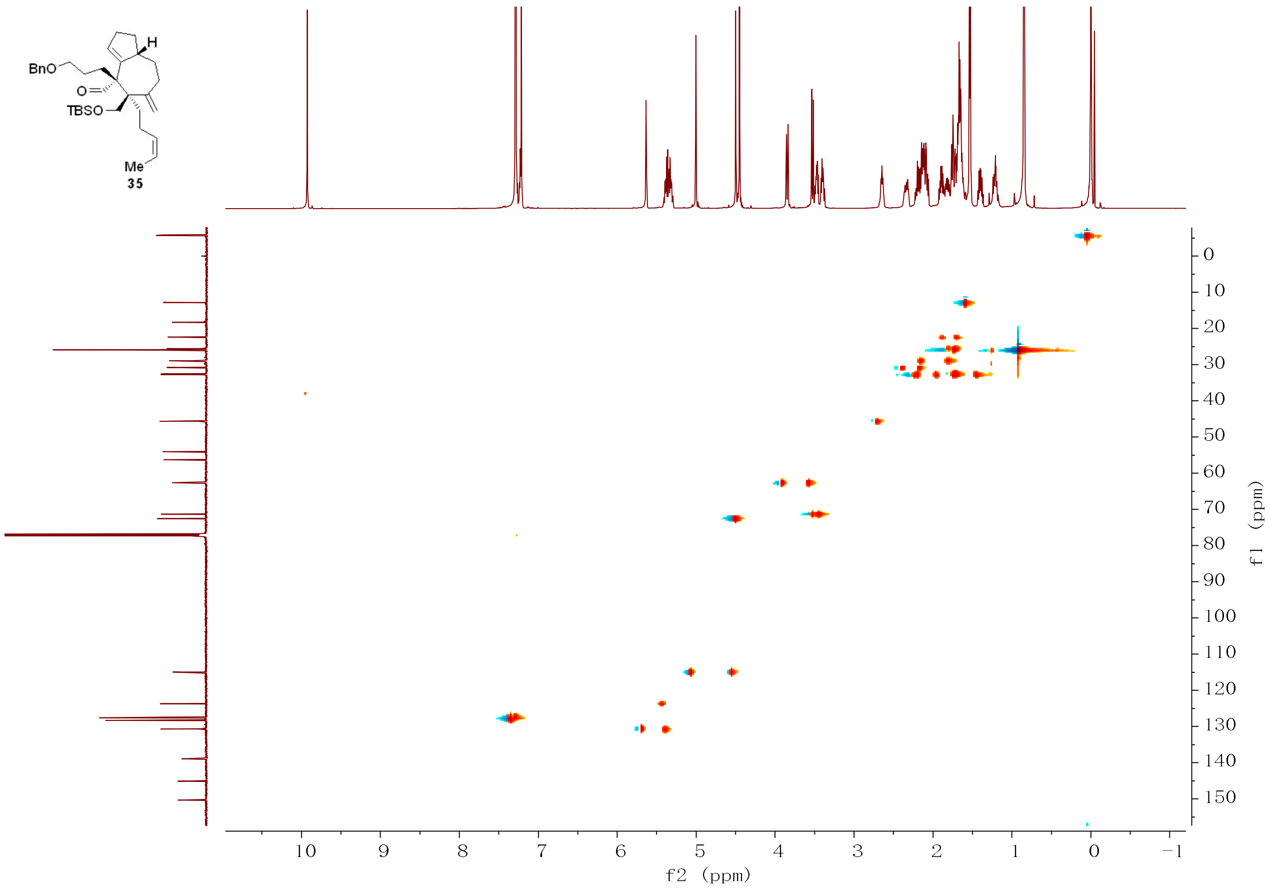
7.26
5.68
5.68
5.41
5.05
4.54
4.50
3.90
3.88
3.58
3.56
2.19
2.18
2.16
2.15
2.14
2.13
1.81
1.79
1.79
1.77
1.73
1.73
1.72
1.72
1.70
1.69
1.58
1.57
0.90
0.89
0.89
0.05
0.04
0.00
BnO
H
O
TBSO
Me
35
1.00
4.93
1.00
2.06
0.98
1.05
2.07
1.02
0.99
1.06
0.99
1.01
1.06
4.14
10.02
3.05
1.12
1.10
9.08
6.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

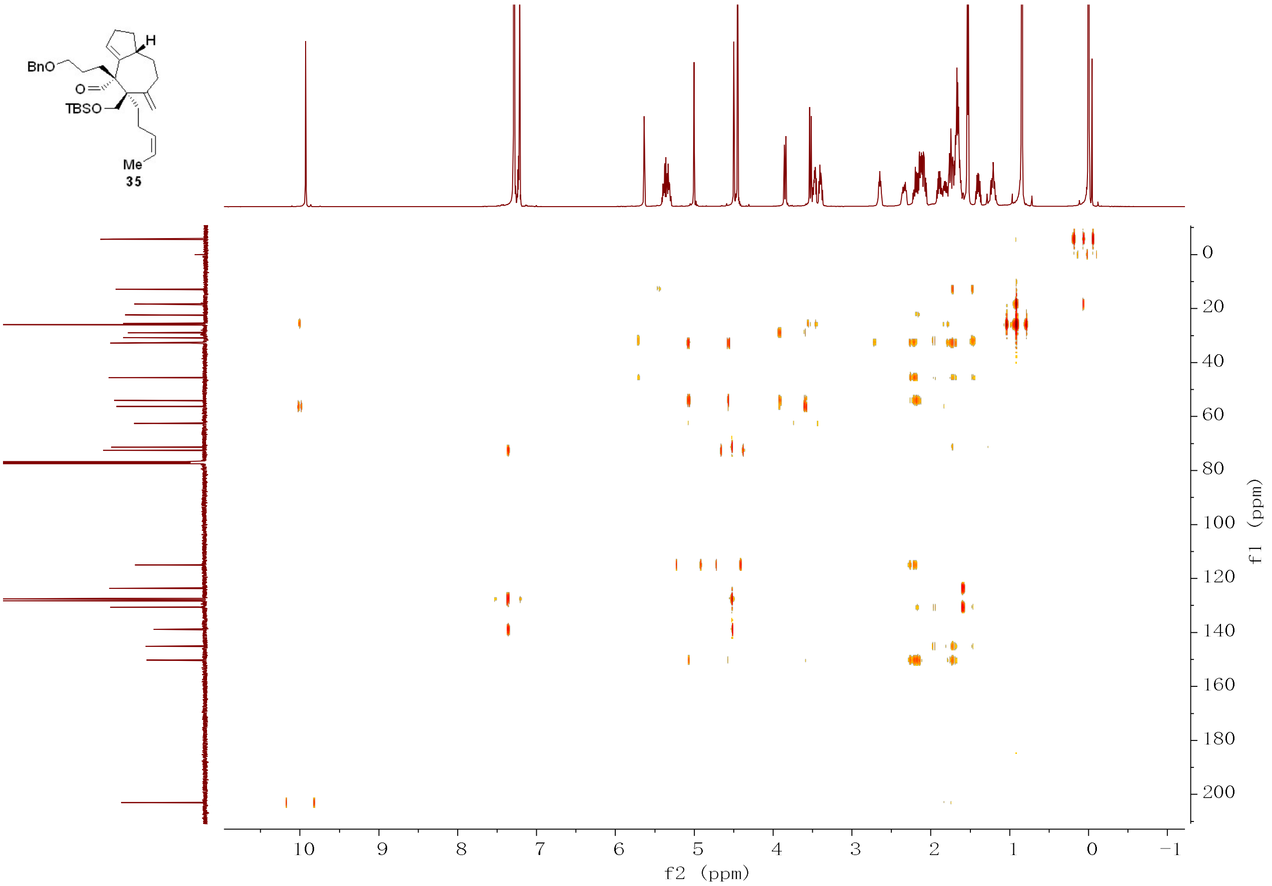

203.05
150.28
145.14
138.88
130.69
130.51
128.28
127.60
127.37
123.66
114.97
77.28
77.03
76.78
72.57
71.32
62.58
56.27
54.08
45.63
32.75
32.71
32.57
30.79
28.94
25.98
25.90
25.53
22.35
18.26
12.82
-5.71
-5.84
BnO
H
O
TBSO
Me
35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

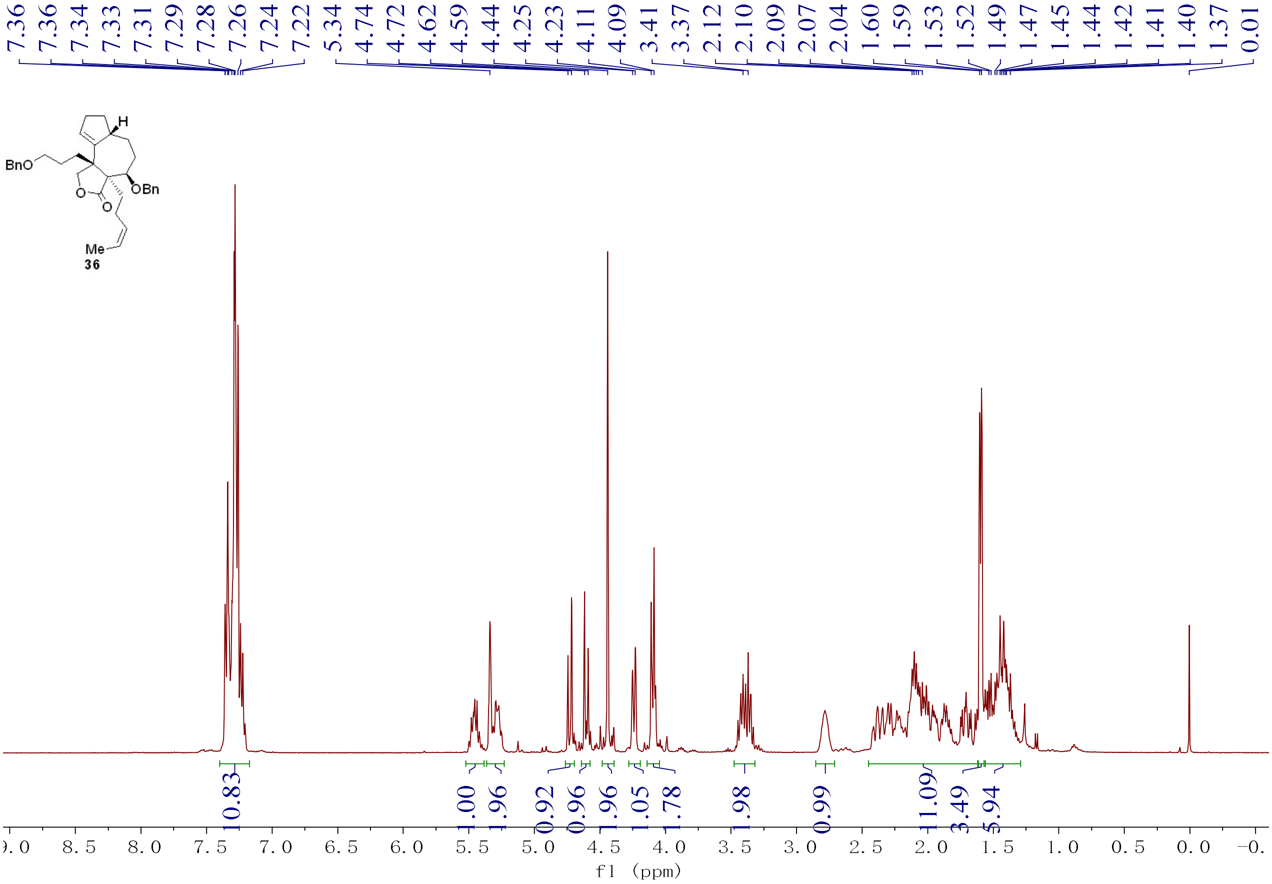

130.69
130.51
128.28
127.60
127.37
123.66
114.97
72.57
71.32
62.58
45.63
32.75
32.71
32.57
30.79
28.94
25.98
25.90
25.53
22.35
12.82
-5.71
-5.84
BnO
O
TBSO
H
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

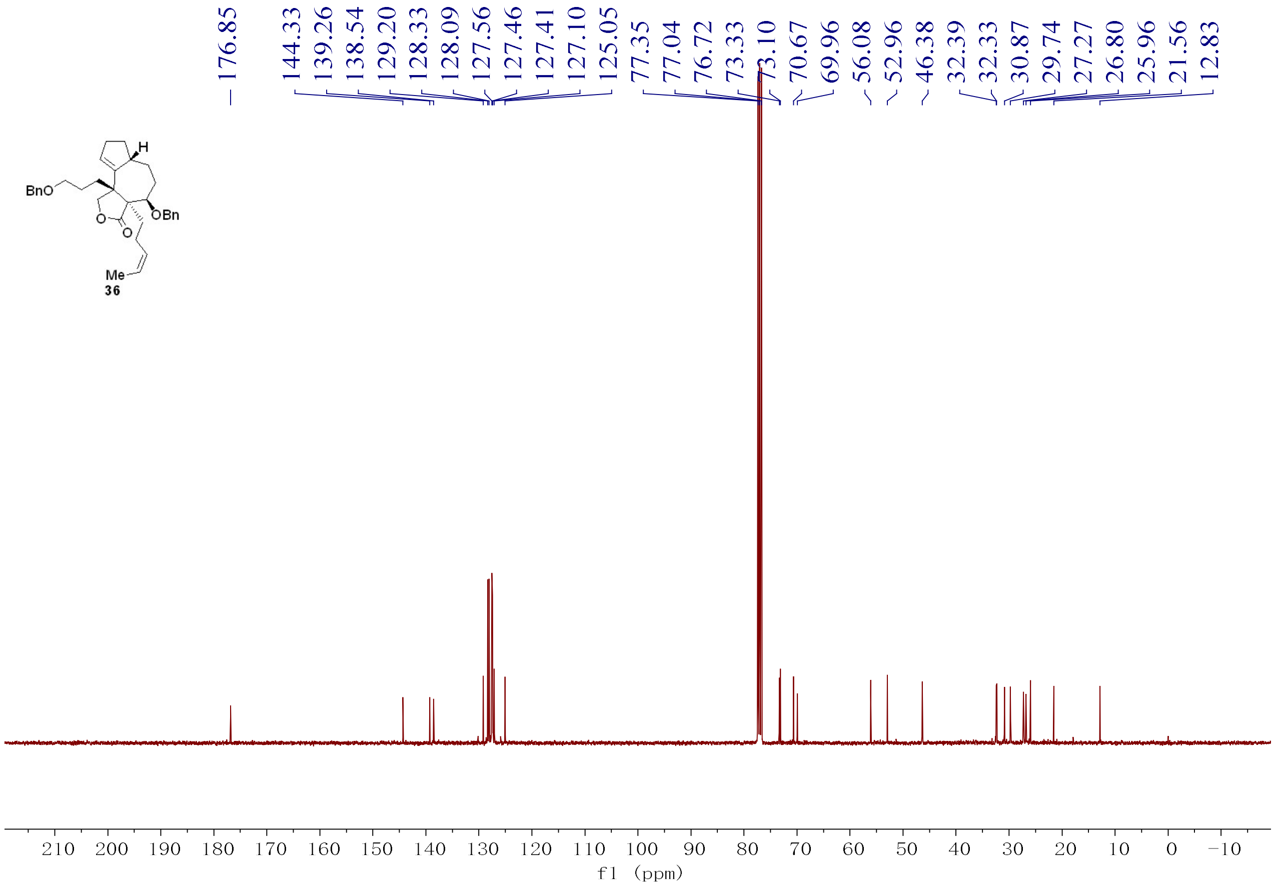
35

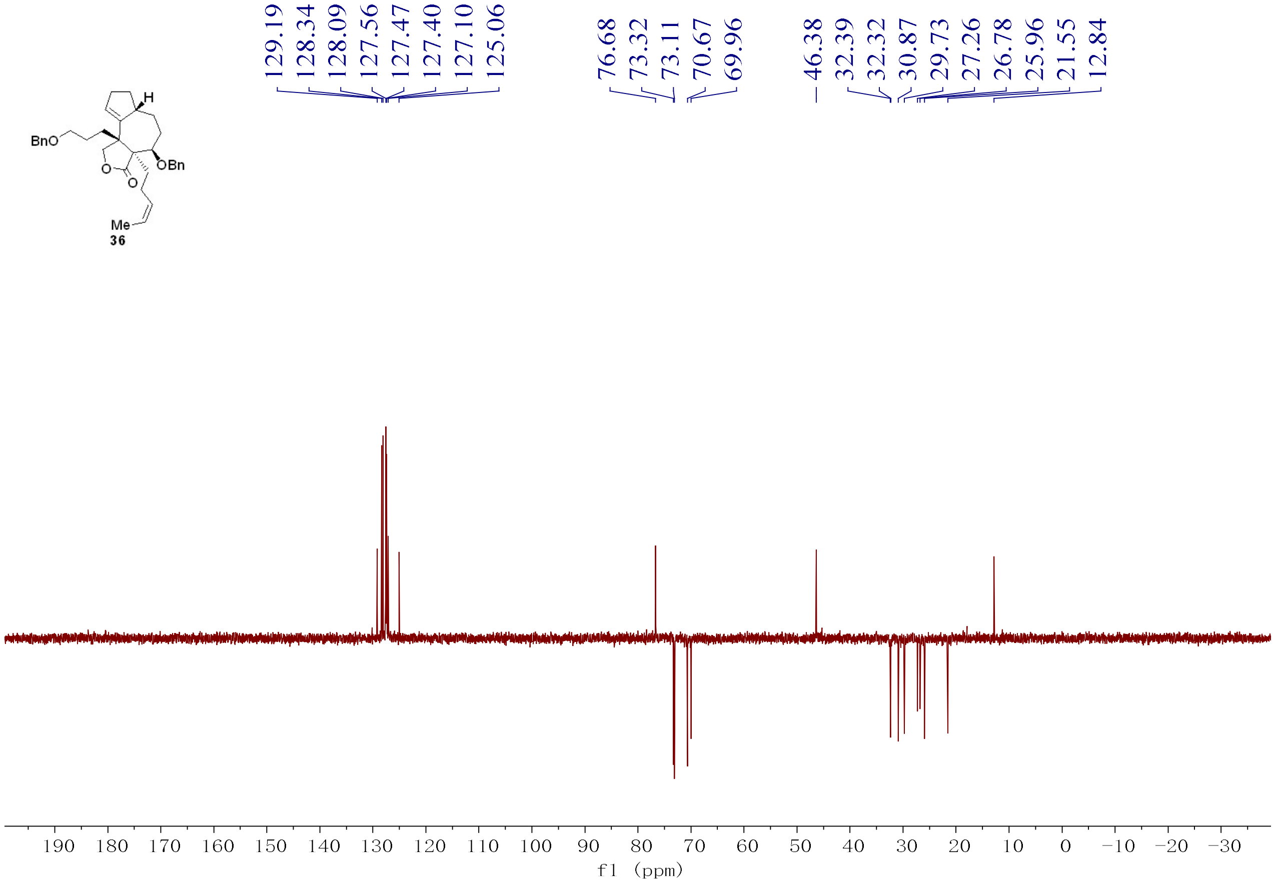

BnO
O
TBSO
H
Me
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
10 9 8 7 6 5 4 3 2 1 0 −1
f2 (ppm)

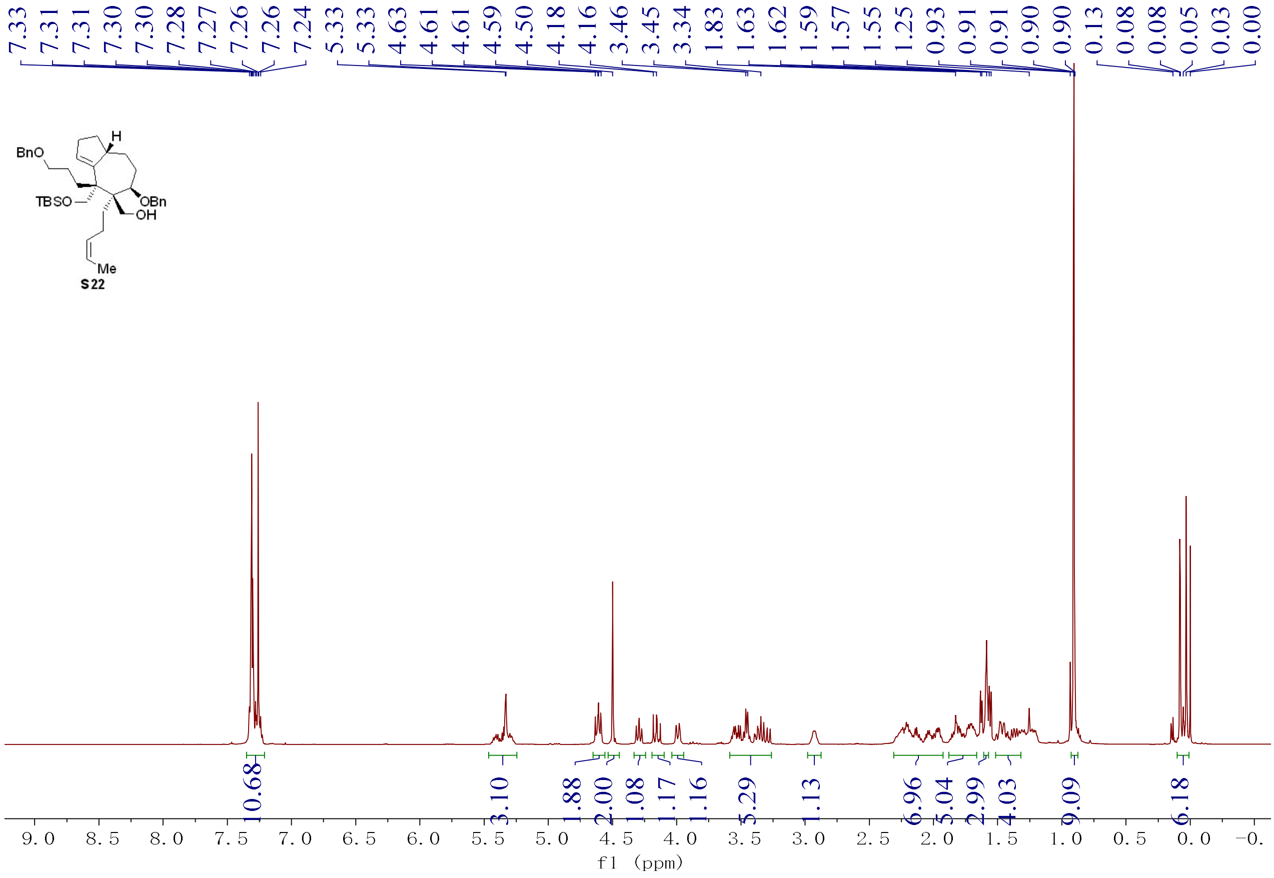
35

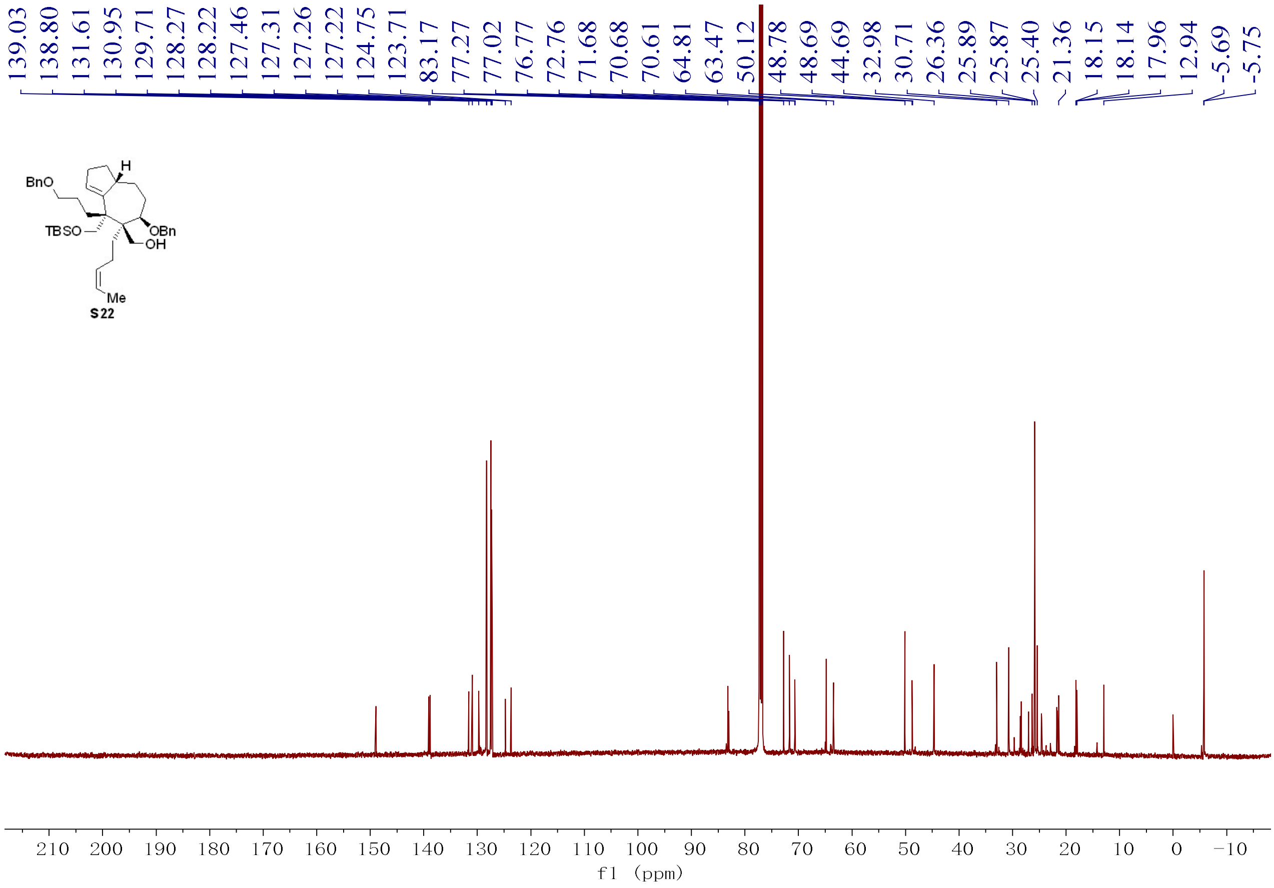

BnO
O
TBSO
H
Me
35
10
9
8
7
6
5
4
3
2
1
0
−1
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)

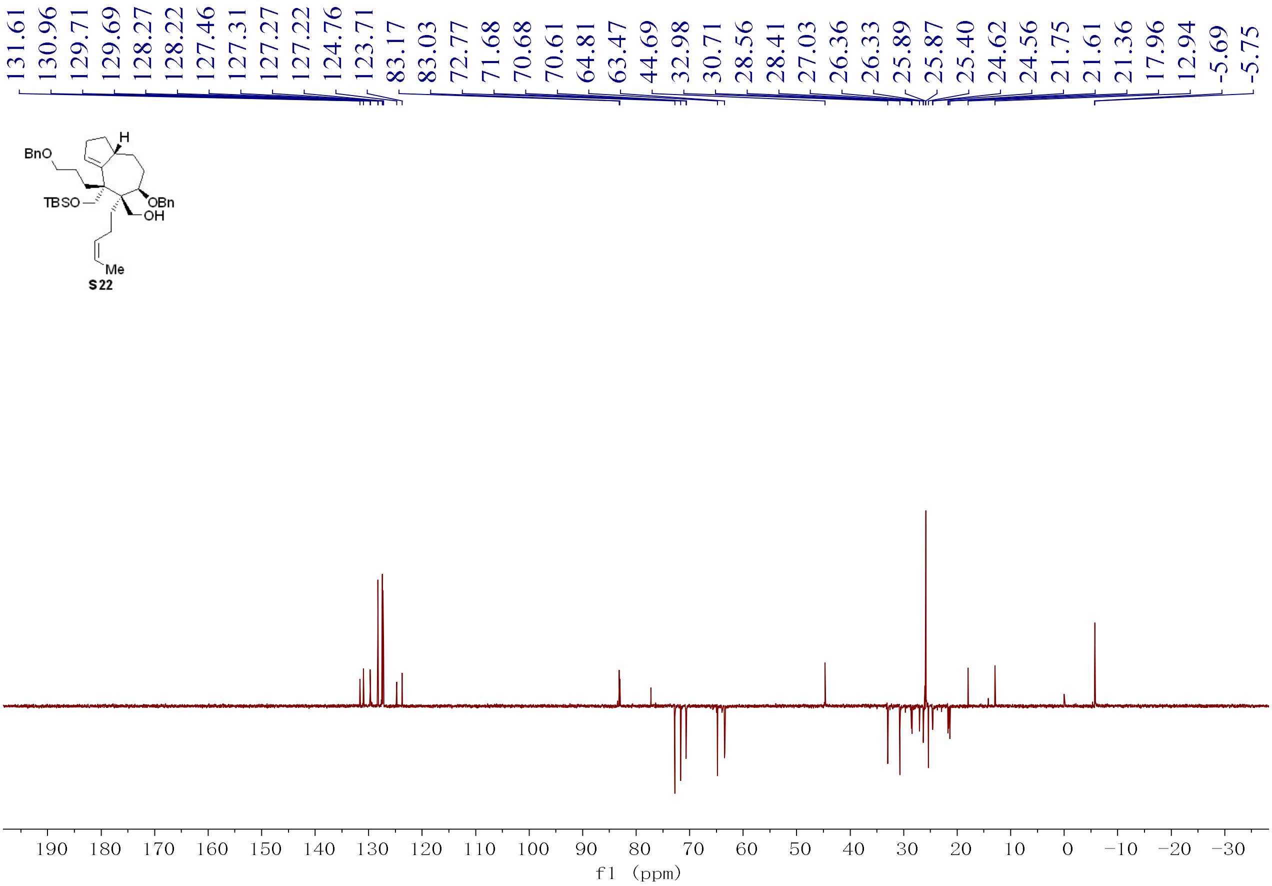

7.36
7.36
7.34
7.33
7.31
7.29
7.28
7.26
7.24
7.22
5.34
4.74
4.72
4.62
4.59
4.44
4.25
4.23
4.11
4.09
3.41
3.37
2.12
2.10
2.09
2.07
2.04
1.60
1.59
1.53
1.52
1.49
1.47
1.45
1.44
1.42
1.41
1.40
1.37
0.01
BnO
H
O
O
OBn
Me
36
10.83
1.00
1.96
0.92
0.96
1.96
1.05
1.78
1.98
0.99
11.09
3.49
5.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


176.85
144.33
139.26
138.54
129.20
128.33
128.09
127.56
127.46
127.41
127.10
125.05
77.35
77.04
76.72
73.33
73.10
70.67
69.96
56.08
52.96
46.38
32.39
32.33
30.87
29.74
27.27
26.80
25.96
21.56
12.83
BnO
H
O
O
OBn
Me
36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

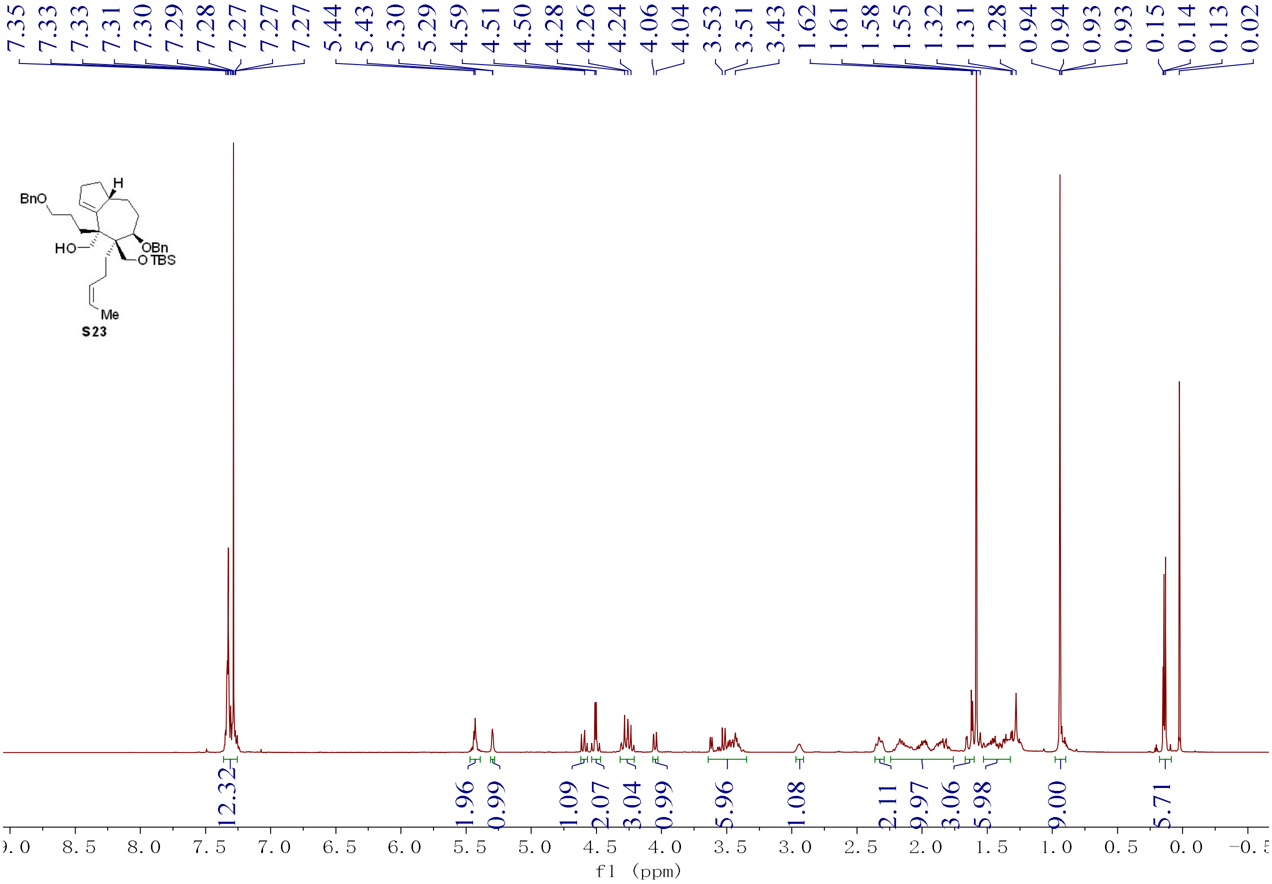

129.19
128.34
128.09
127.56
127.47
127.40
127.10
125.06
76.68
73.32
73.11
70.67
69.96
46.38
32.39
32.32
30.87
29.73
27.26
26.78
25.96
21.55
12.84
BnO
H
O
O
OBn
Me
36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.33 7.31 7.31 7.30 7.30 7.28 7.27 7.26 7.26 7.24 5.33 5.33 4.63 4.61 4.61 4.59 4.50 4.18 4.16 3.46 3.45 3.34 1.83 1.63 1.62 1.59 1.57 1.55 1.25 0.93 0.91 0.91 0.90 0.90 0.13 0.08 0.08 0.05 0.03 0.00
BnO
H
TBSO
OBn
OH
Me
S22
10.68 3.10 1.88 2.00 1.08 1.17 1.16 5.29 1.13 6.96 5.04 2.99 4.03 9.09 6.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

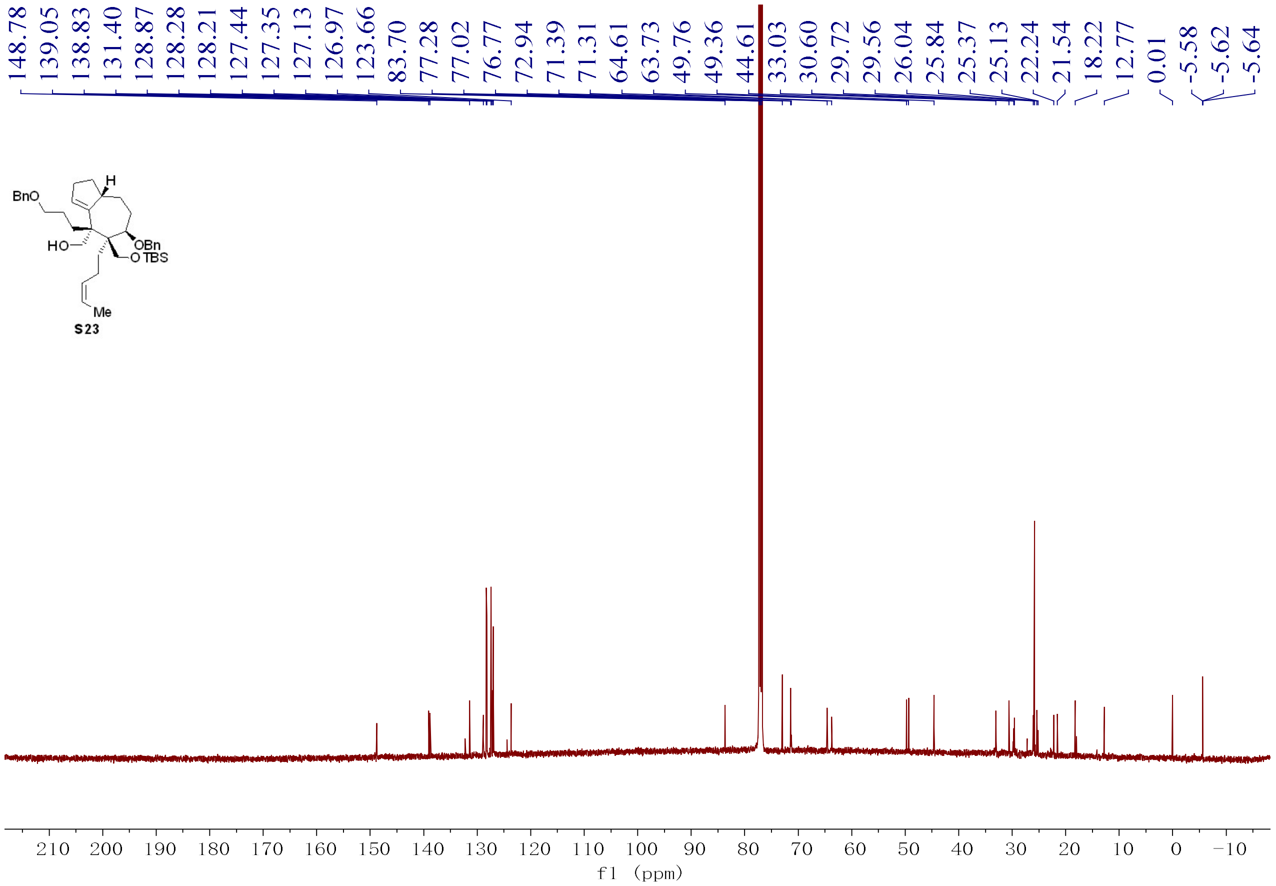

139.03 138.80 131.61 130.95 129.71 128.27 128.22 127.46 127.31 127.26 127.22 124.75 123.71 83.17 77.27 77.02 76.77 72.76 71.68 70.68 70.61 64.81 63.47 50.12 48.78 48.69 44.69 32.98 30.71 26.36 25.89 25.87 25.40 21.36 18.15 18.14 17.96 12.94 -5.69 -5.75
BnO
H
TBSO
OBn
OH
Me
S22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

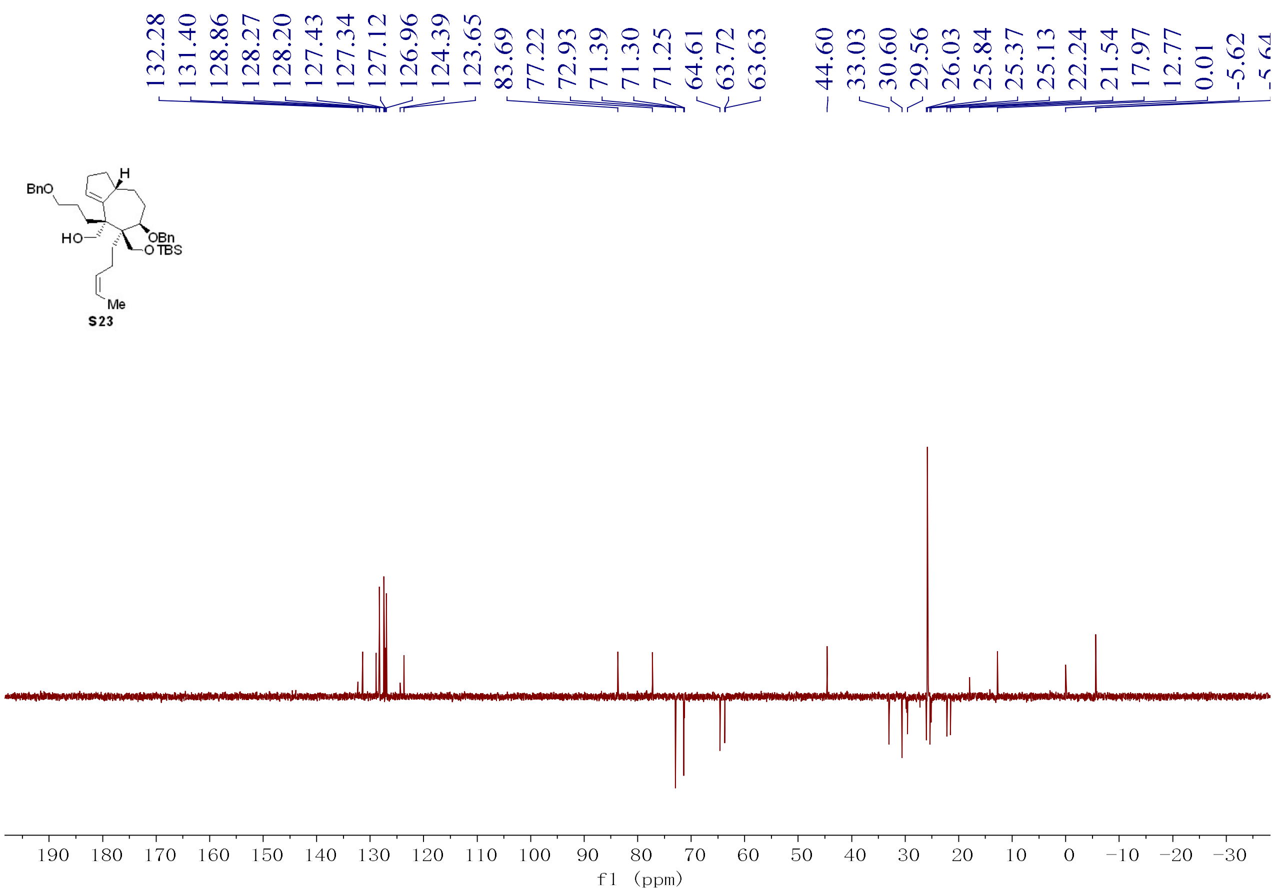

131.61
130.96
129.71
129.69
128.27
128.22
127.46
127.31
127.27
127.22
124.76
123.71
83.17
83.03
72.77
71.68
70.68
70.61
64.81
63.47
44.69
32.98
30.71
28.56
28.41
27.03
26.36
26.33
25.89
25.87
25.40
24.62
24.56
21.75
21.61
21.36
17.96
12.94
-5.69
-5.75
BnO
H
TBSO
OBn
OH
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

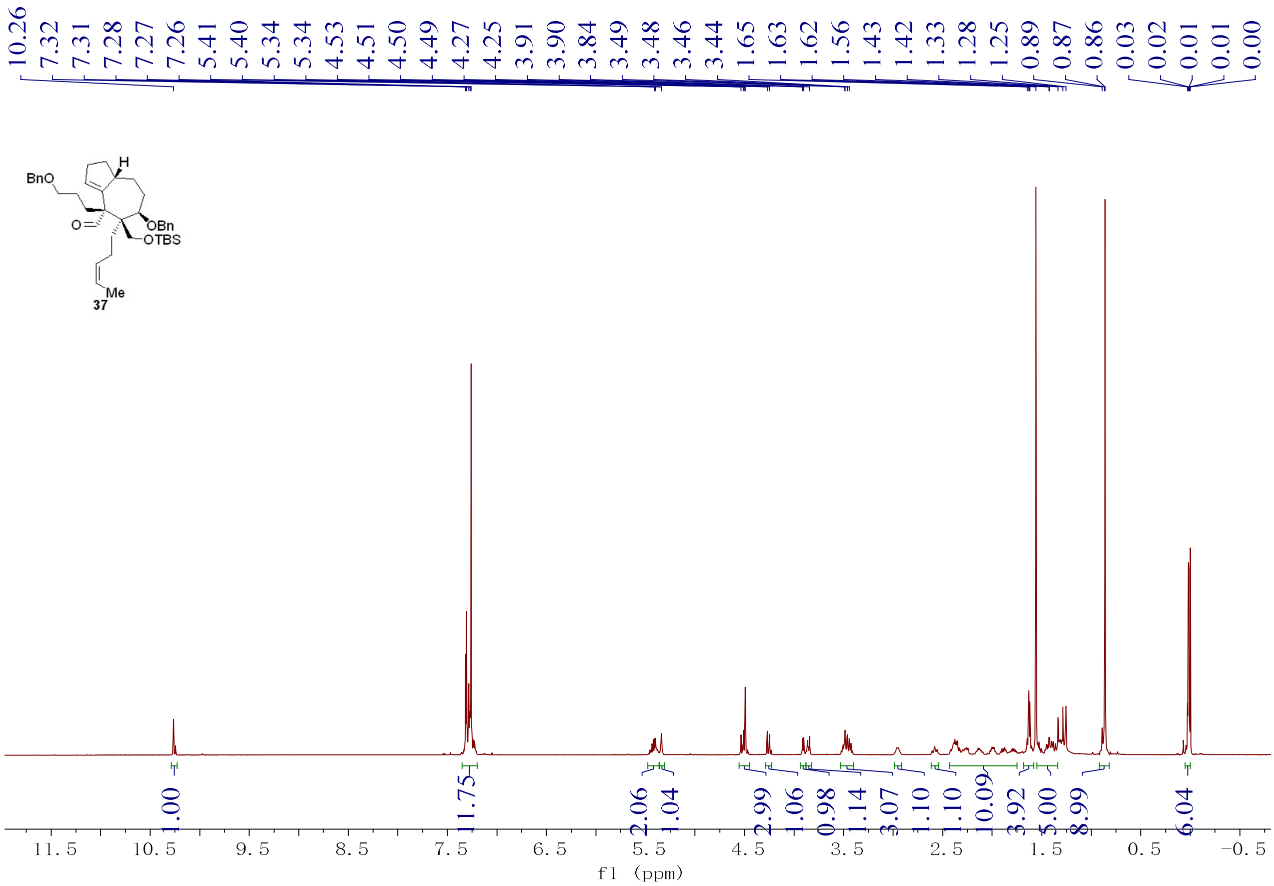
S22

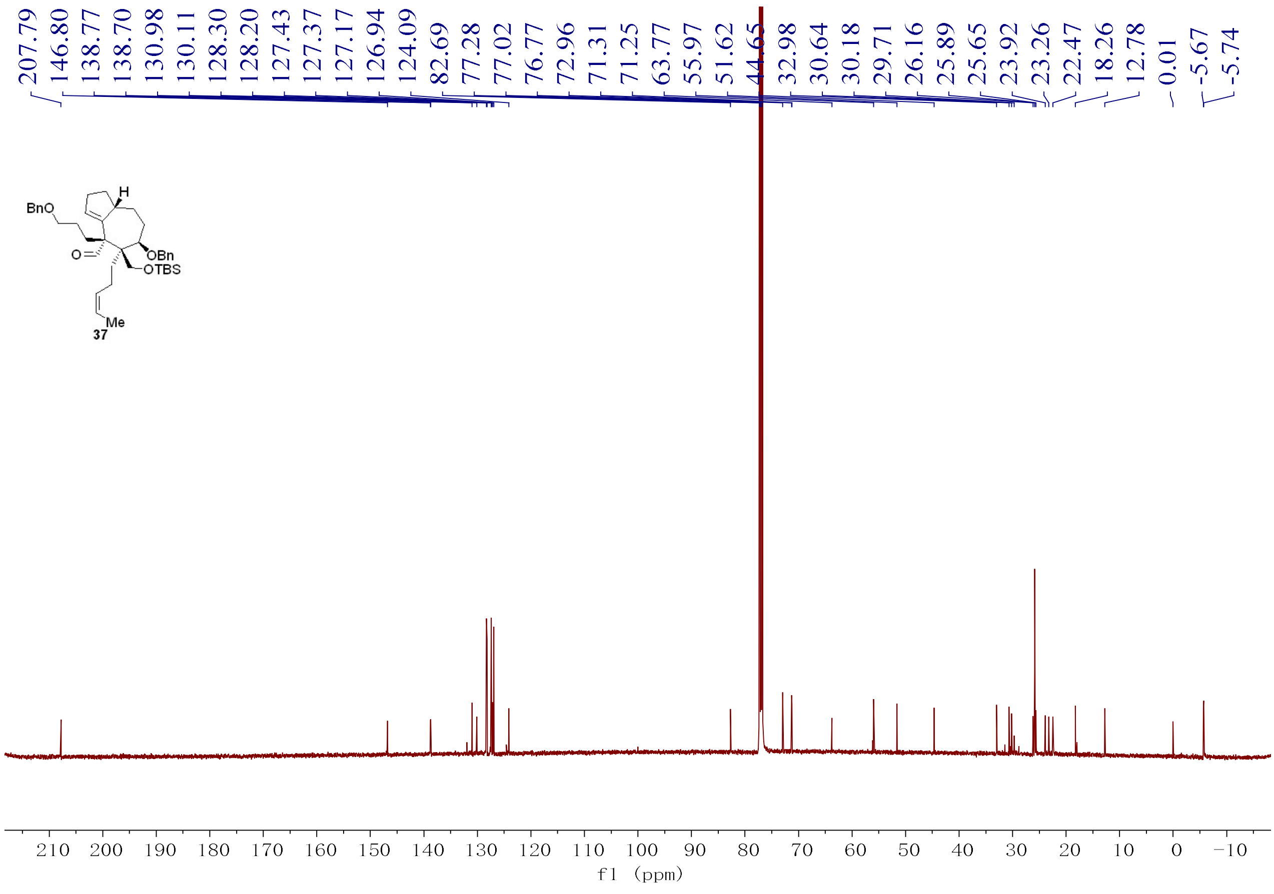

7.35
7.33
7.33
7.31
7.30
7.29
7.28
7.27
7.27
7.27
5.44
5.43
5.30
5.29
4.59
4.51
4.50
4.28
4.26
4.24
4.06
4.04
3.53
3.51
3.43
1.62
1.61
1.58
1.55
1.32
1.31
1.28
0.94
0.94
0.93
0.93
0.15
0.14
0.13
0.02
BnO
H
HO
OBn
O TBS
Me
12.32
1.96
0.99
1.09
2.07
3.04
0.99
5.96
1.08
2.11
9.97
3.06
5.98
9.00
5.71
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

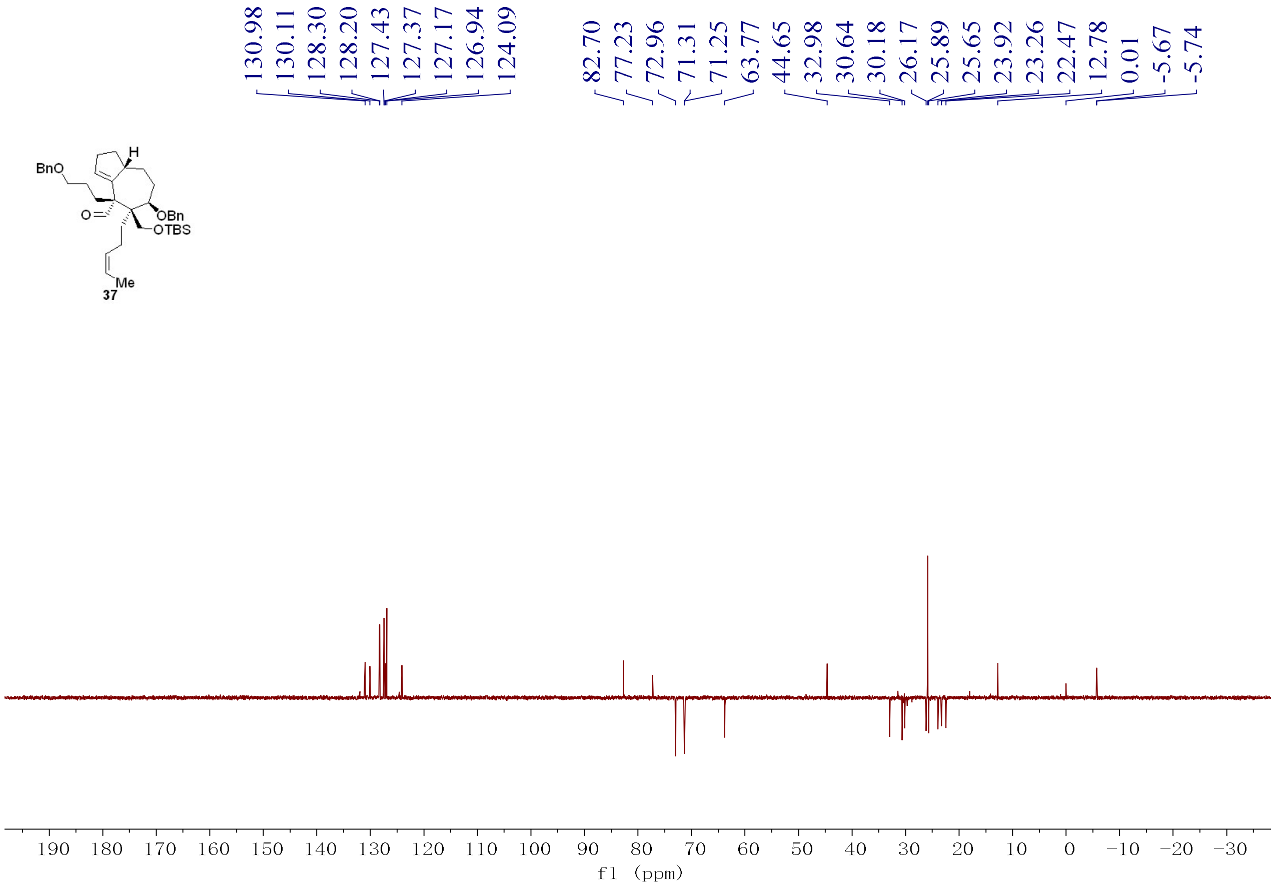
S23

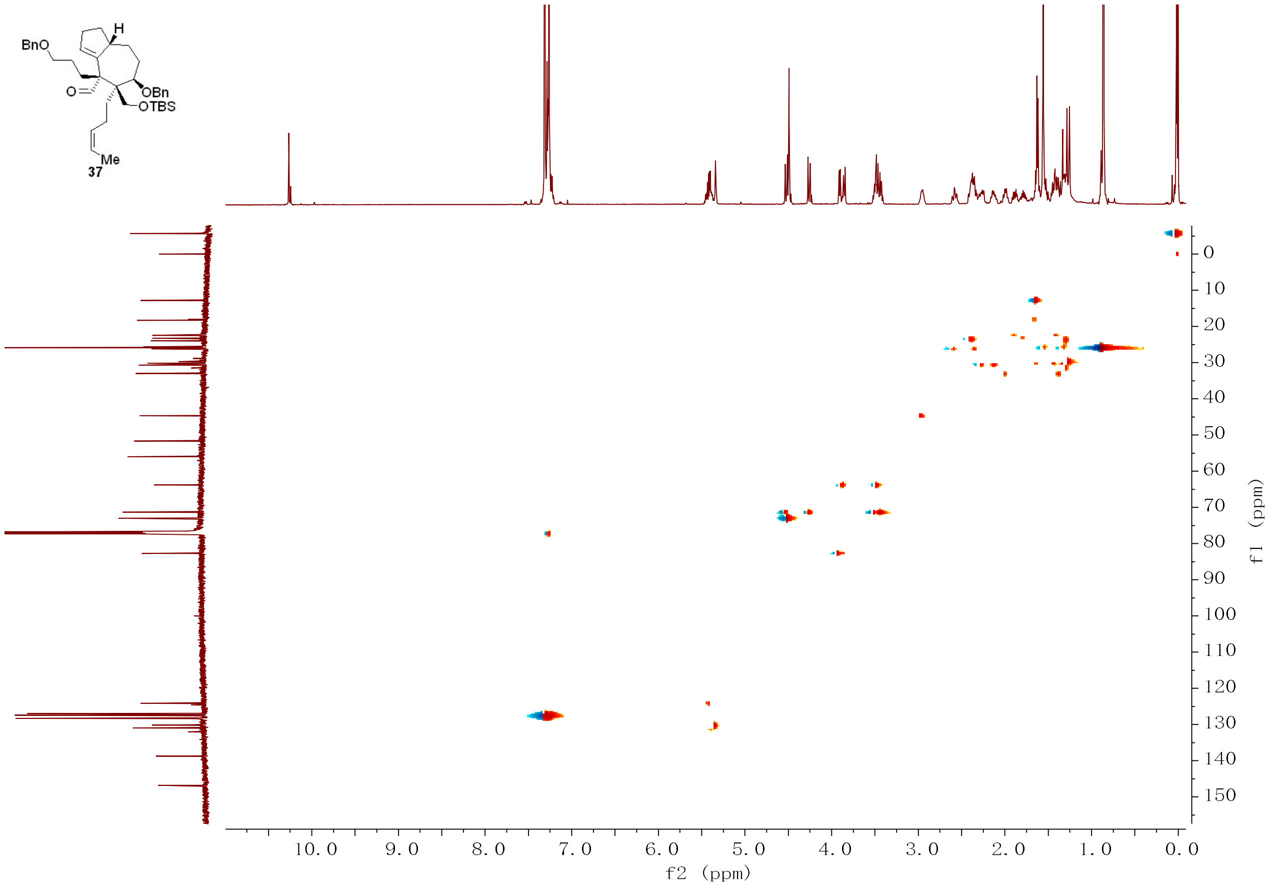

148.78
139.05
138.83
131.40
128.87
128.28
128.21
127.44
127.35
127.13
126.97
123.66
83.70
77.28
77.02
76.77
72.94
71.39
71.31
64.61
63.73
49.76
49.36
44.61
33.03
30.60
29.72
29.56
26.04
25.84
25.37
25.13
22.24
21.54
18.22
12.77
0.01
-5.58
-5.62
-5.64
BnO
H
HO
OBn
OTBS
Me
S23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

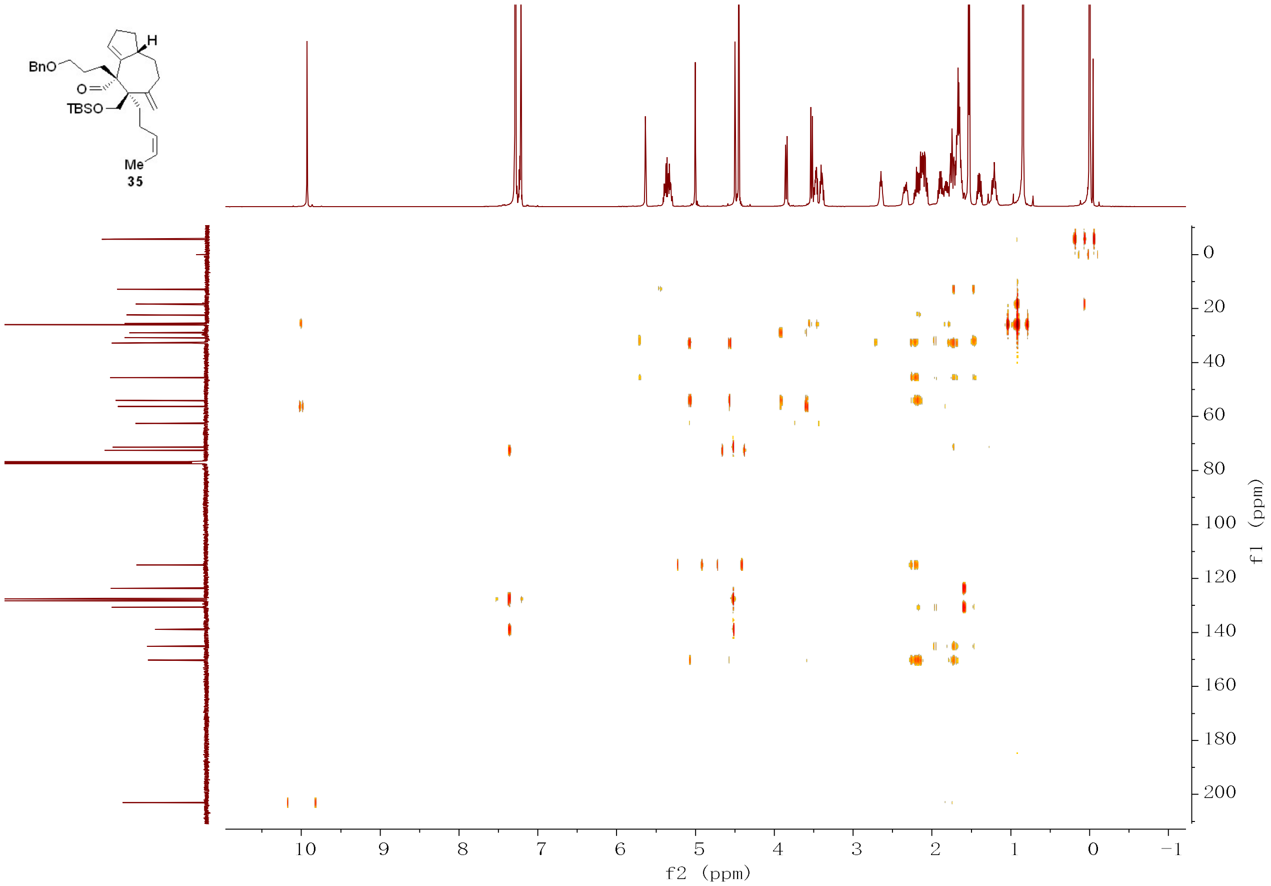

132.28
131.40
128.86
128.27
128.20
127.43
127.34
127.12
126.96
124.39
123.65
83.69
77.22
72.93
71.39
71.30
71.25
64.61
63.72
63.63
44.60
33.03
30.60
29.56
26.03
25.84
25.37
25.13
22.24
21.54
17.97
12.77
0.01
-5.62
-5.6
BnO
H
HO
OBn
OTBS
Me
S23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


10.26
7.32
7.31
7.28
7.27
7.26
5.41
5.40
5.34
5.34
4.53
4.51
4.50
4.49
4.27
4.25
3.91
3.90
3.84
3.49
3.48
3.46
3.44
1.65
1.63
1.62
1.56
1.43
1.42
1.33
1.28
1.25
0.89
0.87
0.86
0.03
0.02
0.01
0.01
0.00
BnO
H
O
OBn
OTBS
Me
37
1.00
11.75
2.06
1.04
2.99
1.06
0.98
1.14
3.07
1.10
1.10
10.09
3.92
5.00
8.99
6.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


207.79
146.80
138.77
138.70
130.98
130.11
128.30
128.20
127.43
127.37
127.17
126.94
124.09
82.69
77.28
77.02
76.77
72.96
71.31
71.25
63.77
55.97
51.62
44.65
32.98
30.64
30.18
29.71
26.16
25.89
25.65
23.92
23.26
22.47
18.26
12.78
-0.01
-5.67
-5.74
BnO
H
O
OBn
OTBS
Me
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


130.98
130.11
128.30
128.20
127.43
127.37
127.17
126.94
124.09
82.70
77.23
72.96
71.31
71.25
63.77
44.65
32.98
30.64
30.18
26.17
25.89
25.65
23.92
23.26
22.47
12.78
0.01
-5.67
-5.74
BnO
H
O
OBn
OTBS
Me
37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)


BnO
H
O
OBn
OTBS
Me
37
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f2 (ppm)


BnO
O
TBSO
H
Me
35
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
10
9
8
7
6
5
4
3
2
1
0
−1
f2 (ppm)