Supporting Information for

Late stage azidation of complex molecules

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A. General Experimental Details

All air-sensitive manipulations were conducted in a nitrogen-filled glovebox or by standard Schlenk techniques under nitrogen. All glassware were heated in an oven and cooled under an inert atmosphere prior to use. NMR spectra were acquired on 300, 400 MHz, 500 MHz, 600 MHz or 900 MHz Bruker instruments at the University of California, Berkeley. NMR spectra were processed with MestReNova 9.0 (Mestrelab Research SL). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.16 ppm for ^{13}C, Pyridine-d_4H in pyridine-d_5 8.74 for ^1H and 149.65 for ^{13}C, acetone-d_5H in acetone-d_6: 2.05 ppm for ^1H and 29.84 for ^{13}C). Coupling constants are reported in hertz. Flash column chromatography was performed with Silicycle SiliaFlash T60 TLC-grade silica gel. Products were visualized on TLC plates using a $KMnO_4$ stain or a CAM stain. GC analyses were obtained on an Agilent 6890 GC equipped with an HP- 5 column (25 m x 0.20 mm ID x 0.33 m film) and an FID detector. Preparative LC-MS purifications were carried out on Waters Acquity Ultra Performance LC with SQ mass detector with an xBridge C18 column (19 x 250 mm, 10 μm, 30 mL/min flow rate). High-resolution mass spectra were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. X-ray crystal structures were obtained via X-ray Crystallography Facility operated by the College of Chemistry, University of California, Berkeley.

Substrates (natural products and active pharmaceutical ingredients), *i*-PrPyBox (**L1**) and $Fe(OAc)_2$ were purchased from commercial sources and used without further purification unless mentioned otherwise. Acetonitrile, ethylacetate, dichloromethane (DCM) and tetrahydrofuran (THF) were degassed by purging with nitrogen for 45 minutes and dried with a solvent purification system containing a one-meter column of activated alumina. Iodine (III) azide reagent (**1**) was prepared according to reported procedures[1,2] and Togni's reagent (**5**) was purchased from commercial sources.

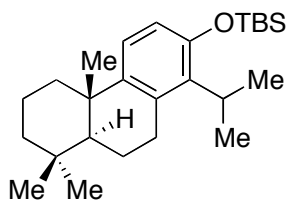
CAUTION: Azides are known to be potentially explosive compounds. As shown in equation below, azides with C/N ratio more than 3 are stable enough to be handled with proper safety measures.[3,4]

$$(N_c+N_o)/N_n \geq 3$$

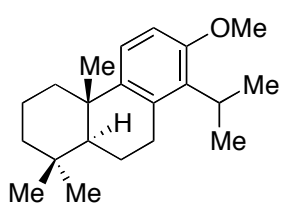
N_c = Number of carbon atom
N_o = Number of other atom about the same size
N_n = Number of nitrogen atoms

Azides with a C/N ratio greater than one and no more than 3 can be synthesized and isolated but should be stored below room temperature at no more than 1.0 M concentration and at a maximum of 5 grams of material. Organic azides with C/N less than 1 should never be isolated.[3,4] In general, aliphatic azides are more stable than olefinic, aromatic or carbonyl azides. All azidation reactions and subsequent workups were performed behind a blast shield with the sash positioned as low as possible. Once isolated, organic azides were stored in a freezer and away from sources of heat, light, pressure and shock. While we did not encounter any issues during their synthesis, proper precautions were taken.

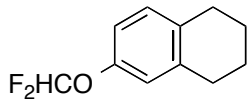
B. Synthesis of the starting materials.



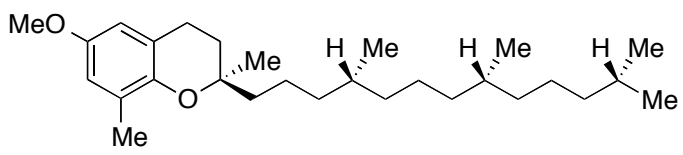
Totarol TBS ether S1: Totarol (100 mg, 0.349 mmol, 1 equiv) was dissolved in CH_2Cl_2 (2 mL) and cooled to 0 °C in an ice/water bath. Pyridine (282 ml, 3.49 mmol, 10 equiv) followed by TBSOTf (113 μl, 0.524 mmol, 1.5 equiv) was added. After stirring at this temperature for 30 min, the reaction mixture was diluted with diethyl ether (50 mL) and washed with a saturated solution of $NaHCO_3$ (30 mL). The ether layer was dried over $MgSO_4$, filtered and concentrated. The crude material was purified by flash column chromatography (hexanes) to give **S1** in 58% yield (81.5 mg). At ambient temperature **S1** exists as a mixture of two rotomers. ^{1}H and ^{13}C NMR spectra was recorded at 75 °C. **^{1}H NMR** (600 MHz, C_6D_6) δ 7.00 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 3.49 (bs, 1H), 2.94 (dd, *J* = 17.0, 7.3, 1H), 2.76 (ddd, *J* = 17.7, 11.0, 7.9 Hz, 1H), 2.19 (d, *J* = 12.8, 1H), 1.83 (m, 1H), 1.74 – 1.58 (m, 2H), 1.52 (dp, *J* = 14.1, 3.6 Hz, 1H), 1.46 (d, *J* = 0.85 Hz, 3H), 1.45 (d, *J* = 0.86 Hz, 3H), 1.42 (dt, *J* = 13.4, 3.3, 1H), 1.35 (td, *J* = 13.1, 3.9 Hz, 1H), 1.26 (dd, *J* = 12.6, 2.5 Hz, 1H), 1.19 (s, 3H), 1.15 (td, *J* = 13.4, 4.1 Hz, 1H), 1.06 (s, 9H), 0.92 (s, 3H), 0.91 (s, 3H), 0.26 (s, 6H); **^{13}C NMR** (151 MHz, C_6D_6) δ 152.34, 143.86, 135.11, 134.53, 122.95, 117.12, 50.22, 42.22, 40.21, 38.28, 33.54, 33.39, 29.29, 27.58, 26.60, 25.30, 21.85, 21.05, 21.00, 20.11, 19.99, 18.97, -3.30, -3.36; **EIHR** calc'd 400.3161, found 400.3167.



Totarol methyl ether S2: Totarol (100 mg, 0.349 mmol, 1 equiv) was dissolved in DMF (2 mL). K_2CO_3 (96.5 mg, 0.698 mmol, 2 equiv), followed by MeI (33.0 μl, 0.524 mmol, 1.5 equiv), was added. After stirring at ambient temperature for 16 hours, the reaction mixture was diluted with diethyl ether (50 mL) and washed with saturated solution of $NaHCO_3$ (30 mL). The ether layer was dried over $MgSO_4$, filtered and concentrated. The crude material was purified by flash column chromatography (hexanes:EtOAc 98:2) to give **S2** in 52% yield (54.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 3.28 (bs, 1H), 2.98 (dd, *J* = 17.1, 6.6 Hz, 1H), 2.79 (ddd, *J* = 17.8, 11.4, 8.0 Hz, 1H), 2.28 (d, *J* = 12.9, 1H), 1.94 (dd, *J* = 11.6, 8.0, 1H), 1.82 – 1.64 (m, 2H), 1.62 (dp, *J* = 14.1, 3.6 Hz, 1H), 1.49 (dt, *J* = 13.2, 3.4, 1H), 1.39 (td, *J* = 13.1, 3.7 Hz, 1H), 1.28-1.35 (m, 2H), 1.33 (d, *J* = 7.1 Hz, 3H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.26 – 1.22 (m, 1H), 1.22 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.49, 143.21, 133.51, 122.84, 120.26, 109.62, 55.15, 49.73, 41.78, 39.81, 37.85, 33.44, 33.40, 28.89, 27.71, 25.36, 21.76, 20.56 (2 overlapping resonances), 19.67, 19.59; **EIHR** calc'd 300.2453, found 300.2452.

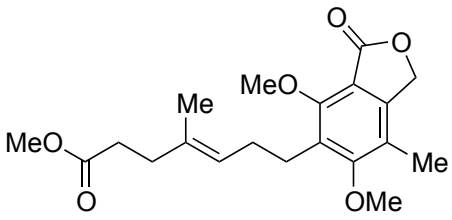


6-(difluoromethoxy)-1,2,3,4-tetrahydronaphthalene S3: Into a 20 mL vial was placed 5,6,7,8-tetrahydro-2-naphtol (74.0 mg, 0.5 mmol, 1 equiv) acetonitrile (1.0 mL) and 6 M aqueous KOH (1.0 mL). The mixture was stirred rapidly at room temperature, and HCF_2OTf (210 μl, 1.5 mmol, 3 equiv) was added at once. Note: the reaction is exothermic. The mixture was stirred vigorously for 2 minutes. The reaction was diluted with H_2O (8 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc 99:1) to give **S3** in 51% (51.0 mg) yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.2 Hz, 1H), 6.92 – 6.79 (m, 2H), 6.45 (t, *J* = 74.5 Hz, 1H), 3.08 – 2.53 (m, 4H), 2.08 – 1.65 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.01, 138.99, 134.50, 130.40, 119.97, 117.00, 116.34 (t, *J* = 258.6 Hz), 29.61, 28.89, 23.20, 22.97; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.36 (d, *J* = 74.6 Hz); **EIHR** calc'd 198.0856, found 198.0856.

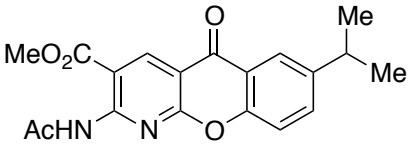


δ-tocopherol methyl ether S4: δ-tocopherol (403 mg, 1.00 mmol, 1 equiv)

was dissolved in DMF (5 mL). K_2CO_3 (276 mg, 2.00 mmol, 2 equiv) followed by MeI (93.0 μl, 1.50 mmol, 1.5 equiv) was added. After stirring at ambient temperature for 16 hours, the reaction mixture was diluted with diethylether (50 mL) and washed with a saturated solution of $NaHCO_3$ (30 mL). The ether layer was dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the ether layer was concentrated. The crude material was purified by flash column chromatography (hexanes:EtOAc 97:3) to give **S4** in 91% yield (382 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.59 (d, J = 3.0 Hz, 1H), 6.47 (d, J = 3.0 Hz, 1H), 3.75 (s, 3H), 2.75 (t, J = 8.2 Hz, 2H), 2.18 (s, 3H), 1.93 – 1.66 (m, 2H), 1.67 – 0.98 (m, 21H), 1.28 (s, 3H), 0.89 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.24, 146.26, 127.32, 121.06, 114.88, 111.13, 75.68, 55.73, 40.14, 39.53, 37.61 (2 overlapping resonances), 37.58, 37.44, 32.95, 32.84, 31.55, 28.14, 24.96, 24.61, 24.28, 22.88, 22.79, 21.14, 19.91, 19.82, 16.37; **EIHR** calc'd 416.3654, found 416.3659.



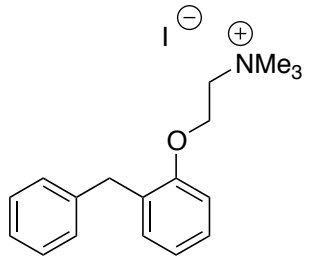
Mycophenolic acid derivative S5: Mycophenolic acid (160 mg, 0.500 mmol, 1 equiv) was dissolved in methanol (10 mL) at ambient temperature. A 2 M solution of $TMSCHN_2$ in ether (1.0 mL, 1.5 mmol, 4 equiv) was added, and the reaction mixture was stirred for 24 hours. The reaction mixture was concentrated and purified by flash column chromatography to yield methyl O-methyl mycophenolate in 87% yield. The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[5]



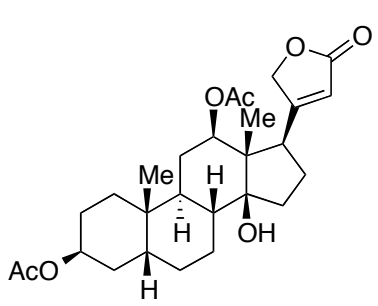
Pyridine derivative S6: To the solution of amlexanox (110 mg, 0.369 mmol, 1 equiv) in EtOAc (7 mL) and MeOH (2 mL) mixture was added 2 M solution of $TMSCHN_2$ in ether (553 μL, 1.11 mmol, 3 equiv) at ambient temperature. The reaction mixture was stirred at this temperature for 1 hour and concentrated. The crude product of this reaction was used in the next step without further purification.

To the solution of the crude product from the previous step (0.369 mmol, 1 equiv) in pyridine (2 mL) was added acetic anhydride (1 mL). The reaction was stirred for 24 hours at 80 °C. The reaction was diluted with EtOAc (75 mL) and washed once with $NaHCO_3$ (25 mL).

The organic layer was dried over $MgSO_4$, concentrated, and purified by flash column chromatography (hexanes:EtOAc 80:20) to give **S6** in 52% yield (67.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.27 (s, 1H), 9.29 (s, 1H), 8.11 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 4.00 (s, 3H), 3.05 (hept, *J* = 6.8 Hz, 1H), 2.55 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.40, 169.87, 166.43, 161.66, 155.01, 153.86, 146.32, 142.80, 134.72, 123.65, 121.45, 118.54, 111.13, 108.41, 53.17, 33.84, 26.67, 24.04: **ESIHR** (M+Na) calc'd 377.1108, found 377.1108.

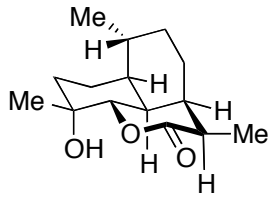


Tetraalkylammonium iodide S7: Phenyltoloxamine (2.55 g, 10.0 mmol, 1 equiv) was dissolved CH_2Cl_2 (15 mL) and MeI (1.25 ml, 20.0 mmol, 2 equiv) was added at ambient temperature. The reaction mixture was stirred at this temperature for 24 hours and concentrated to yield tetraalkyl ammonium iodide **S7** in quantitative yield (3.97 g) as a white solid. It was used in subsequent azidation reactions without further purification. **^{1}H NMR** (500 MHz, CDCl3) δ 7.37 – 6.75 (m, 9H), 4.44 – 4.24 (m, 2H), 4.06 – 3.85 (m, 4H), 3.22 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.20, 140.51, 131.66, 128.51, 128.26, 128.24 (2 overlapping resonances), 126.22, 122.13, 111.61, 65.33, 62.24, 54.63, 36.59; **ESIHR** (M) calc'd 270.1852, found 270.1851.

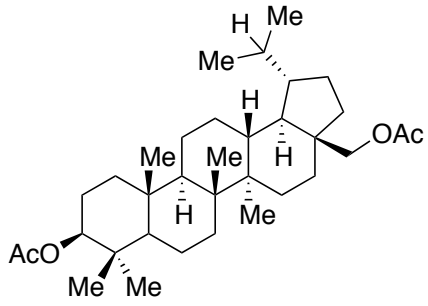


Digoxigenin diacetate 10b: To the solution of digoxigenin (110 mg, 0.256 mmol, 1 equiv) in pyridine (1.5 mL) was added acetic anhydride (1.0 mL). The reaction was stirred for 24 hours at ambient temperature. Excess Ac_2O and pyridine was removed under high vacuum, and the residue was purified by flash column chromatography (hexanes:EtOAc 1:1) to yield digoxigenin diacetate **10b** in 82% yield (110 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.79 (bs, 1H), 5.01 (bs, 1H), 4.87 (dd, *J* = 18.1, 1.8 Hz, 1H), 4.74 (dd, *J* = 18.0, 1.8 Hz, 1H), 4.57 (dd, *J* = 11.9, 4.0 Hz, 1H), 2.85 (dd, *J* = 9.2, 5.8 Hz, 1H), 2.21 (m, 1H), 2.10 (m, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.97 – 1.07 (m, 18H), 0.91 (s, 3H), 0.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.60, 174.02, 170.83, 170.66, 117.78, 85.53, 77.35, 73.48, 70.21, 54.08, 45.95, 41.14, 36.80, 35.12, 33.01,

32.24, 30.43, 30.35, 27.20, 26.41, 26.24, 24.96, 23.53, 21.48, 21.43, 21.27, 10.37; **ESIHR** (M+H) calc'd 516.2705, found 516.2716.



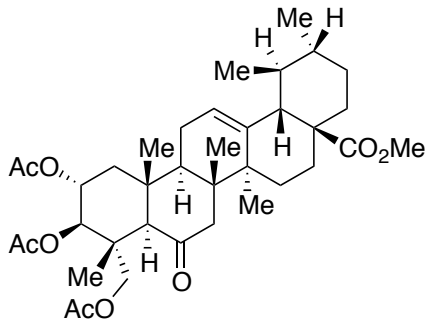
Artemisinic acid derivative 10d: Dihydroartemisinic acid methyl ester (100 mg, 0.399 mmol, 1 equiv) was dissolved in THF (3 mL) at ambient temperature. *N*-methylmorpholine *N*-oxide (70.2 mg, 0.599 mmol, 1.5 equiv) 2.5% solution of OsO_4 in *t*-BuOH (2.5 mL, 0.200 mmol, 0.5 equiv) was added, and the reaction mixture was stirred at ambient temperature for 3 days. The reaction was quenched by addition of Na_2SO_3 (500 mg) and water (3 mL) and stirred overnight. After this time, the reaction was diluted with EtOAc (100 mL), and washed with water (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography (hexane:EtOAc 4:1 to 1:1) to give **10d** in 78% yield (79 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) d 4.30 (d, *J* = 11.9 Hz, 1H), 2.68 (p, *J* = 7.0 Hz, 1H), 2.36 (dt, *J* = 12.0, 4.1 Hz, 1H), 1.97 (bs, 1H), 1.92 – 1.68 (m, 4H), 1.64 (m, 2H), 1.57 (m, 1H), 1.49 – 1.39 (m, 2H), 1.32 (s, 3H), 1.24 – 1.14 (m, 1H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.99 (qd, *J* = 13.1, 3.9 Hz, 1H), 0.85 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.25, 81.09, 70.76, 43.40, 40.51, 39.43, 37.39, 35.08, 32.82, 27.57, 27.30, 22.99, 22.34, 20.10, 13.43. **ESIHR** (M+Na) calc'd 275.1617, found 275.1621.



Betulin diacetate S8: Betulin (200 mg, 0.450 mmol, 1 equiv) was dissolved in a mixture of EtOAc and MeOH (15 mL/15 mL) in a 50 mL round-bottom flask. Pd/C (10%) (48.0 mg, 0.045 mmol, 0.1 equiv) was added, and the flask was evacuated and then backfilled with H_2 by attaching a balloon filled with hydrogen gas. The reaction mixture was vigorously stirred at ambient temperature for 24 hours. The reaction mixture was passed through a pad of Celite. The Celite layer was washed with EtOAc, and the combined EtOAc fractions were concentrated to obtain dihydrobetulin. The crude material was used in the next step without further purification

Dihydrobetulin was dissolved in pyridine (1.5 mL) at ambient temperature. Ac_2O (0.7 mL) was added, and the reaction mixture was stirred for 24 hours. Excess pyridine and Ac_2O was

removed under high vacuum, and the crude betulin diacetate was purified by flash column chromatography (hexanes:EtOAc 4:1) to give **S8** in 76% yield (180 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.46 (dd, *J* = 10.5, 5.8 Hz, 1H), 4.22 (d, *J* = 11.0 Hz, 1H), 3.80 (d, *J* = 11.0 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.93 – 1.52 (m, 12H), 1.51 – 1.13 (m, 12H), 1.02 (s, 3H), 0.99 – 0.96 (m, 1H), 0.93 (s, 3H), 0.85 – 0.80 (m, 12H), 0.80 – 0.76 (m, 1H), 0.75 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.76, 171.12, 80.98, 62.91, 55.38, 50.01, 48.16, 46.51, 44.56, 42.92, 40.98, 38.43, 37.87, 37.17, 37.09, 34.73, 34.26, 29.91, 29.52, 28.03, 26.98, 26.88, 23.77, 23.03, 21.68, 21.46, 21.20, 20.87, 18.26, 16.62, 16.21, 16.12, 15.00, 14.69. The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[6]

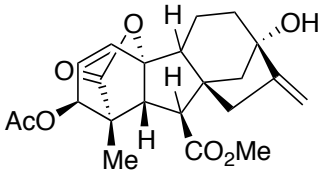


Synthesis of madecassic acid derivative S9: To the slurry of madecassic acid (104 mg, 0.200 mmol, 1 equiv) in a mixture of PhH (7 mL) and MeOH (2 mL) was added a 2 M solution of $TMSCHN_2$ in ether (0.2 mL, 0.400 mmol, 2 equiv) at ambient temperature. The reaction mixture was stirred at this temperature for 30 min and concentrated. The crude product was used in the next step without further purification.

To the solution of madecassic acid methyl ester (0.200 mmol, 1 equiv) in pyridine (2 mL) was added acetic anhydride (1 mL). The reaction was stirred for 24 hours at ambient temperature. Excess Ac_2O and pyridine was removed under high vacuum, and the residue was used in the subsequent step without further purification. The crude product was used in the next step without further purification. **ESIHR** (M+Na) calc'd 667.3816, found 667.3826.

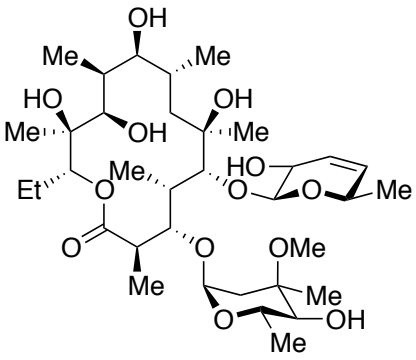
Crude methyl madecassate triacetate (0.200 mmol, 1 equiv) was dissolved in CH_2Cl_2 (10 mL). $NaHCO_3$, followed by Dess-Martin periodinane (127 mg, 0.300 mmol, 1.5 equiv), was added, and the reaction mixture was stirred at ambient temperate for 3 hours. A 1:1 mixture of a saturated solution of $NaHCO_3$ (5 mL) and a 20% aqueous solution of $Na_2S_2O_3$ (5 mL) were added to quench the reaction. The biphasic mixture was vigorously stirred for 30 min and then extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered and concentrated. Crude **S9** was purified by flash column chromatography to give **S9** in 86% yield (172 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.33 (t, *J* = 3.6 Hz, 1H), 5.16 (td,

J = 11.0, 4.8 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 3.94 (d, *J* = 11.6 Hz, 1H), 3.79 (d, *J* = 11.5 Hz, 1H), 3.61 (s, 3H), 2.68 (s, 1H), 2.52 (d, *J* = 13.1 Hz, 1H), 2.30 (d, *J* = 11.3 Hz, 1H), 2.24 – 2.13 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 – 2.10 (m, 3H), 2.00 (s, 3H), 1.95 (d, *J* = 13.1 Hz, 1H), 1.82 – 1.47 (m, 6H), 1.41 (dd, *J* = 13.0, 11.0 Hz, 2H), 1.34 (s, 3H), 1.22 (s, 3H), 1.14 (s, 3H), 1.10 – 0.93 (m, 2H), 0.98 (d, *J* = 6.2 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.29, 177.75, 170.58, 170.39, 170.32, 138.12, 124.73, 73.64, 69.18, 65.52, 57.38, 52.74, 51.68, 50.05, 48.04, 48.01, 46.14, 44.00, 43.29, 42.40, 40.60, 38.92, 38.87, 36.47, 30.61, 27.89, 24.01, 23.98, 23.79, 21.24, 21.10, 20.97, 20.81, 18.42, 17.59, 17.09, 14.11; **ESIHR** (M+Na) calc'd 665.3660, found 665.2692.

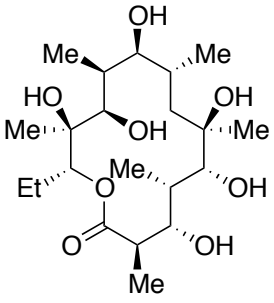


Synthesis of gibberellic acid derivative S10: To the solution of gibberrelic acid (172 mg, 0.497 mmol, 1 equiv) in a mixture of PhH (7 mL) and MeOH (2 mL) was added a 2 M solution of $TMSCHN_2$ in ether (0.5 mL, 1.00 mmol, 2 equiv) at ambient temperature. The reaction mixture was stirred at this temperature for 20 min and concentrated. The crude product was used in the next step without further purification.

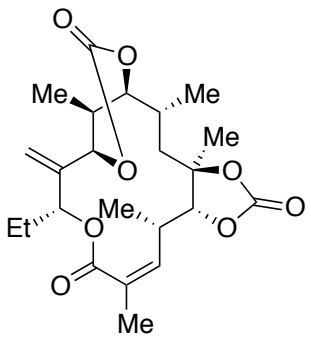
To the solution of gibberrelic acid methyl ester (0.497 mmol, 1 equiv) in pyridine (2 mL) was added acetic anhydride (1 mL). The reaction was stirred for 24 hours at ambient temperature. At this time, the reaction was diluted with EtOAc (75mL). The resulting solution was washed with 1M solution of HCl (2 x 25 mL) and then once with $NaHCO_3$ (25 mL). The organic solution was dried over $MgSO_4$, concentrated, and purified by flash column chromatography to give **S10** in 86% yield (172 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.42 (d, *J* = 9.4 Hz, 1H), 5.91 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.37 (d, *J* = 3.8 Hz, 1H), 5.32 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.01 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 3.36 (d, *J* = 10.8 Hz, 1H), 2.81 (d, *J* = 10.8 Hz, 1H), 2.26 (m, 1H), 2.20 (t, *J* = 3.0 Hz, 1H), 2.16 (s, 3H), 2.14 – 2.04 (m, 2H), 2.04 – 1.64 (m, 6H), 1.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.26, 172.50, 170.17, 156.98, 134.32, 129.28, 107.83, 90.28, 78.27, 70.37, 53.52, 52.32, 52.23, 51.14, 50.64, 50.49, 44.85, 43.20, 38.37, 20.97, 17.10, 14.43; **ESIHR** (M+Na) calc'd 425.1571, found 425.1570.



9-(S)-hydroxy erythromycin olefin derivative S11: 9-(S)-hydroxy erythromycin *N*-oxide[7] (1.30 g, 1.73 mmol, 1 equiv) was dissolved in $CHCl_3$ in a 1 L flask. The $CHCl_3$ was evaporated using a rotovap to obtain a thin layer of 9-(S)-hydroxyerythromycin covering the walls of the flask. This flask was then heated to 160 °C under vacuum (80 millitorr) for 6 hours. The flask was then cooled to room temperature, and the product was purified by flash column chromatography (hexanes:acetone 5:1 then 4:1) to yield **S11** in 69% yield (821 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.64 (s, 2H), 5.00 (dd, *J* = 10.3, 2.6 Hz, 1H), 4.87 (d, *J* = 4.2 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.45 (tt, *J* = 6.8, 4.7 Hz, 1H), 4.18 (dd, *J* = 6.8, 3.0 Hz, 1H), 4.12 (dq, *J* = 9.4, 6.3 Hz, 1H), 3.94 (dd, *J* = 8.7, 4.3 Hz, 1H), 3.78 (s, 1H), 3.65 (d, *J* = 3.8 Hz, 1H), 3.43 – 3.39 (m, 1H), 3.26 (s, 3H), 3.14 (s, 1H), 3.03 (d, *J* = 9.1 Hz, 1H), 2.71 – 2.59 (m, 1H), 2.38 – 2.30 (m, 1H), 2.32 – 2.20 (m, 1H), 1.99 (dtd, *J* = 14.5, 7.6, 2.6 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.75 (dd, *J* = 14.6, 7.6 Hz, 1H), 1.57 (dd, *J* = 15.2, 4.9 Hz, 1H), 1.49 (ddq, *J* = 14.4, 10.2, 7.2 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.29 – 1.09 (m, 6H), 1.27 (s, 3H), 1.25 (d, *J* = 5.9 Hz, 3H), 1.23 (d, *J* = 5.7 Hz, 3H), 1.22 (s, 3H), 1.16 (d, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.43, 131.44, 126.91, 104.57, 100.13, 98.27, 82.62, 80.48, 78.63, 77.58, 74.71, 73.65, 72.77, 72.04, 71.20, 68.06, 66.58, 49.49, 48.35, 41.64, 37.95, 35.09, 33.96, 32.23, 24.85, 21.99, 21.57, 21.28, 20.97, 17.87, 17.09, 16.55, 15.86, 11.20, 10.12; **ESIHR** calc'd (M+Na) 713.4082, found 713.4105.



9-(S)-hydroxyerythronolide S12: To the solution of the olefin **S11** (821 mg, 1.20 mmol, 1 equiv) in methanol (10 mL), acetyl chloride (0.5 mL) was added slowly. The reaction mixture was stirred at ambient temperature for 15 hours, and then solid $NaHCO_3$ (1.50 g) was added to quench the reaction. The solids were removed by filtration and washed with MeOH (2 x 5 mL). The combined MeOH fractions were concentrated to obtain a white solid. The crude 9-S-hydroxyerythronolide was purified by flash column chromatography (hexanes:acetone 4:1) to yield 9-(S)-hydroxyerythronolide **S12** in 79% yield (399 mg); The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[8]



Erythronolide bis-carbonate diene derivative S13: 9-(S)-hydroxyerythronolide **S12** (52.0 mg, 0.124 mmol, 1 equiv) and pyridine (200 μl, 2.47 mmol, 20 equiv) were dissolved in CH_2Cl_2, and the resulting solution was cooled to -78 C. Triphosgene (55.0 mg, 0.185 mmol, 1.5 equiv) was added as a solid. The cooling bath was removed to allow the reaction to warm to ambient temperature, and the reaction was stirred for 36 hours. MeOH (0.2 mL) and small piece of ice was added to quench the reaction. The reaction was filtered through a pad of Celite to remove the small amount of water, and concentrated. The product was purified by flash column chromatography to yield **S13** in 81% yield (44.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.14 (d, *J* = 9.8 Hz, 1H), 5.51 (s, 1H), 5.35 (dd, *J* = 9.7, 5.4 Hz, 1H), 5.30 (s, 1H), 5.15 (s, 1H), 4.48 (d, *J* = 10.4 Hz, 1H), 3.90 (d, *J* = 10.2 Hz, 1H), 2.83 (tq, *J* = 10.1, 6.6 Hz, 1H), 2.44 (qd, *J* = 7.1, 2.1 Hz, 1H), 2.36 (m, 1H), 1.94 (m, 1H), 1.89 (d, *J* = 1.4 Hz, 3H), 1.78 – 1.62 (m, 2H), 1.42 (m, 1H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.28 (s, 3H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.77, 152.69, 147.32, 138.33, 137.12, 131.03, 115.13, 88.38, 85.63, 82.78, 78.31, 74.93, 37.03, 33.63, 33.37, 28.15, 27.97, 22.89, 16.99, 15.65, 12.63, 11.75, 10.03. **ESIHR** (M+Na) calc'd 437.2170, found 437.2167.

C. C-H azidation of complex molecules

General procedures for the azidation reactions

Catalyst preparation: A 0.02 M solution of the catalyst was prepared according to the following procedure and used in all C-H azidation and trifluoromethyl azidation reactions: In an N_2-filled glovebox, to a dry 4 ml vial containing a magnetic stirbar, $Fe(OAc)_2$ (10.4 mg, 0.06 mmol, 1 equiv) and **L1** (19.9 mg, 0.066 mmol, 1.1 equiv) were added 3.0 mL of CH_3CN or EtOAc. The reaction mixture was stirred for 16 hours at room temperature, during which time the color of the solution changed from colorless to blue.

General procedure (A) for the iron-catalyzed azidation of C-H bonds.

In an N_2 filled glovebox, to a 4 ml vial containing the substrate (0.10 mmol), hypervalent iodine reagent **1** (2.0 – 3.0 equiv, 0.20 – 0.30 mmol) and a magnetic stir bar was added a 0.02 M

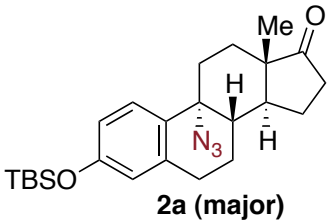
solution of (**L1**)$Fe(OAc)_2$ (0.5 ml, 0.1 equiv). The vial was sealed with a cap containing a PTFE septum and then kept at 23 or 50 °C for 48 h while monitoring by thin layer chromatography or GC for consumption of the starting material. The crude reaction mixture was then treated with 1 ml of EtOAc and filtered through a 30 x 6 mm plug of basic alumina (in a 9 mm pipette) into a 20 ml vial. The basic alumina was washed with 3 x 3.0 mL of EtOAc. The solvent was evaporated from the combined resulting solution, and the product was purified by flash column chromatography on silica gel. Ratios of products were determined by ^{1}H NMR analysis of crude reaction mixtures.

General guidelines for identifying C-H azidation products: During the azidation process a C-H bond was replaced with C-N_3 bond. We used DEPT135 and DEPT90 NMR experiments in combination with ^{13}C NMR to identify whether the C-H bond azidation occurred at primary, secondary or tertiary C-H bonds. The specific C-H bond that underwent azidation was identified by the change of the splitting pattern of the nearby hydrogens, or the appropriate 2D NMR correlations. The structures of nine compounds were determined unambiguously by X-ray diffraction of single crystals. For the products of azidation at secondary benzylic C-H bonds, the chemical shift of the tertiary C-H hydrogen (Ar$C\underline{H}(R)N_3$) was diagnostic of a benzylic azide (4.5-4.8 ppm). The presence of the azide functionality was further confirmed by IR spectroscopy and high-resolution mass spectroscopy.

Experimental procedures and NMR data for compounds 2a', 2h and 2i were previously reported by our research group.[9] The structure of **2a'** was originally assigned as the product from mono-azidation of a secondary benzylic C-H bond. We have now shown that the ratio of this product (**2a')** and a second azidation product arising from azidation of the tertiary C-H bond (**2a**) depends on conversion and that the product from azidation at the secondary benzylic position also contains one azide at the tertiary benzylic position. This product (**2a')** forms from azidation of the initial product (**2a**). Structural assignment of all azides **2a** and **2a'** with corresponding ^{1}H NMR, ^{13}C NMR, HRMS and IR data are provided below.

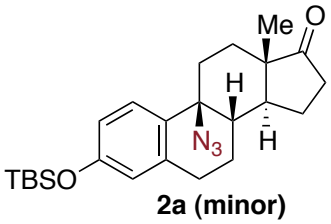
Azidation of estrone TBS ether: Azide **2a and 2a'** was prepared from estrone 3-TBS ether according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and

the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (benzene) to give 2 fractions. Each fraction was further purified by flash column chromatography (hexanes:CH_2Cl_2 50:50) to give 3 azidation products.



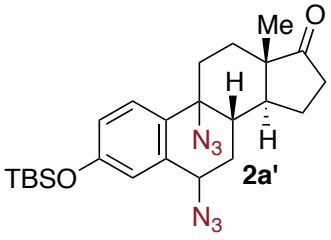
2a (major)

The major diastereomer of **2a** was obtained in 28% yield (11.9 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.61 (dt, *J* = 11.9, 2.3 Hz, 1H), 2.53 – 2.44 (m, 1H), 2.16 (dt, *J* = 19.2, 9.0 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.89 (td, *J* = 11.4, 11.0, 3.1 Hz, 1H), 1.85 – 1.69 (m, 5H), 1.62 – 1.53 (m, 1H), 0.98 (s, 9H), 0.90 (s, 3H), 0.20 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.07, 155.60, 138.25, 129.59, 126.25, 120.96, 117.65, 65.84, 47.69, 43.66, 41.16, 35.93, 29.77, 29.04, 28.02, 25.79, 21.43, 20.76, 18.31, 13.42, -4.22; **ESIHR** Calc'd (M-N_2+H) 398.2510, found 398.2514; **FT-IR** 2932, 2885, 2858, 2095 (N_3), 1742.



2a (minor)

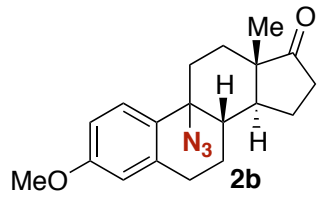
The minor diastereomer of **2a** was obtained in 14% yield (5.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 2.75 (dd, *J* = 10.9, 4.6 Hz, 2H), 2.68 (dt, *J* = 14.4, 3.4 Hz, 1H), 2.46 (dd, *J* = 19.4, 8.7 Hz, 1H), 2.31 – 2.21 (m, 1H), 2.12 – 1.87 (m, 4H), 1.82 – 1.73 (m, 1H), 1.71 – 1.63 (m, 2H), 1.61 – 1.53 (m, 1H), 1.14 (td, *J* = 13.9, 3.6 Hz, 1H), 1.01 (s, 3H), 0.98 (s, 9H), 0.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 219.18, 155.55, 138.72, 127.29, 125.51, 121.11, 118.29, 66.49, 47.59, 43.27, 39.76, 35.81, 30.80, 28.53, 25.79, 25.18, 21.97, 19.82, 18.29, 13.60, -4.18, -4.20; **ESIHR** Calc'd (M-N_2+H) 398.2510, found 398.2521; **FT-IR** 2931, 2858, 2091 (N_3), 1742.



2a'

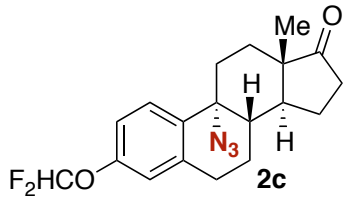
Bis-azidation product **2a'** was obtained in 24% yield (11.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 4.65 (dd, *J* = 4.6, 1.9 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.51 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.28 – 2.10 (m, 3H), 2.08 – 1.99 (m, 1H), 1.99 – 1.92 (m, 1H), 1.84 (tq, *J* = 11.1, 3.9 Hz, 3H), 1.73 (td, *J* = 13.6, 3.8 Hz, 1H), 1.63 (tt, *J* = 12.2, 8.9 Hz, 1H), 0.99 (s, 9H), 0.94 (s, 3H), 0.23 (s, 3H), 0.23 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.49, 156.10, 134.42,

129.68, 126.58, 121.92, 120.83, 65.43, 59.08, 47.78, 42.91, 36.48, 35.82, 29.07, 27.94, 27.50, 25.76, 21.23, 18.33, 13.45, -4.18, -4.26; **ESIHR** Calc'd (M-N_2+H) 439.2524, found 439.2533; **FT-IR** 2932, 2859, 2096 (N_3), 1742.



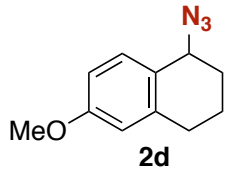
2b

Azidation of estrone methyl ether: Azide **2b** was prepared from estrone 3-methyl ether according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc, 95:5) to give a 2:1 diastereomeric mixture of **2b** as a white solid in 43% overall yield (14.1 mg). The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[10]



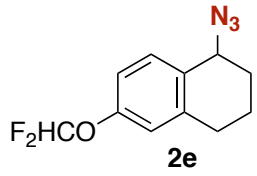
2c

Azidation of estrone difluoromethyl ether: Azide **2c** was prepared from estrone 3-difluoromethyl ether[11] according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc, 95:5) to give **2c** as a colorless oil in 50% yield (18.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.52 (t, *J* = 73.8 Hz, 1H), 3.03 – 2.86 (m, 2H), 2.65 – 2.57 (m, 1H), 2.50 (ddd, *J* = 19.1, 8.8, 1.0 Hz, 1H), 2.17 (dt, *J* = 19.2, 8.9 Hz, 1H), 2.07 – 1.95 (m, 2H), 1.89 (td, *J* = 10.9, 10.1, 2.7 Hz, 1H, H-8β) 1.86 – 1.70 (m, 5H), 1.65 – 1.52 (m, 1H), 0.90 (s, 3H); **^{13}C NMR** (126 MHz, CDCl3) δ 219.72, 150.98, 139.07, 133.80, 126.61, 120.48, 116.86, 115.87 (t, *J* = 259.9 Hz), 65.26, 47.59, 43.59, 40.84, 35.87, 29.54, 29.00, 27.93, 21.39, 20.44, 13.36. **ESIHR** Calc'd (M-N_2+H) 334.1613, found 334.1614; **FT-IR** 2096 (N_3), 1739. The configuration at C9 was determined by the $^{3}J_{H\text{-}H}$ coupling constant of H-8β. The td splitting pattern that was observed for this C8-H was consistent with the previously reported spectra of 3-methoxyestrone[10] and 3-acetoxyestrone[12] bearing a C9 azido group in the a configuration.



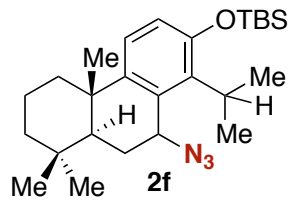
2d

Azidation 6-methoxy-1,2,3,4-tetrahydronaphthalene: Azide **2d** was prepared from 6-methoxy-1,2,3,4-tetrahydronaphthalene according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 99:1) to give **2d** as a colorless oil in 53% yield (10.8 mg). The regioselectivity of the azidation was determined to be 9:1. The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[13]



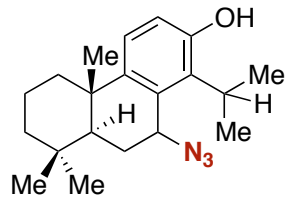
2e

Azidation of 6-(difluoromethoxy)-1,2,3,4-tetrahydronaphthalene: Azide **2e** was prepared from **S3** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 99:1) to give **2e** as a colorless oil in 57% yield (13.6 mg). The regioselectivity was determined to be 2:1. **^{1}H NMR** (500 MHz, $CDCl_3$) *for the major diastereomer*: δ 7.33 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.53 (t, *J* = 73.9 Hz, 1H), 4.59 (t, *J* = 4.6 Hz, 1H, C<u>H</u>N_3); *for the minor diastereomer* 7.16 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.52 (t, *J* = 74.0 Hz, 1H), 4.56 (t, *J* = 5.1 Hz, 1H, C<u>H</u>N_3); *for the major + minor diastereomers* δ 2.83 – 2.91 (m, 1H), 2.82 – 2.69 (m, 1H), 2.11 – 1.94 (m, 3H), 1.82 – 1.89 m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.78, 139.49, 135.49, 134.53, 131.01, 130.79, 130.69, 119.86, 119.77, 117.31, 115.86 (t, *J* = 259.5 Hz), 59.17, 58.82, 29.00, 28.96, 28.80, 28.22, 19.14, 18.70; **EIHR** calc'd 239.0870, found 239.0871; **FT-IR** 2940, 2869, 2098 (N_3).

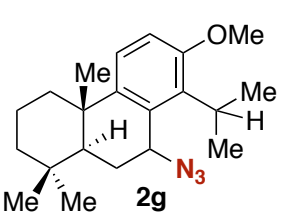


2f

Azidation of totarol TBS ether: Azide **2f** was prepared from **S1** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane) to give a 1.4:1 diastereomeric mixture of **2f** as a white solid in 43% yield (19.1 mg). **EIHR** Calc'd 441.3175, found 441.3175; **FT-IR** 2957, 2929, 2859, 2097 (N_3). At ambient temperature **2f** exists as a mixture of two rotomers caused by the large *i*-Pr and OTBS groups. TBS group was removed according to the following procedure for the characterization of this compound.

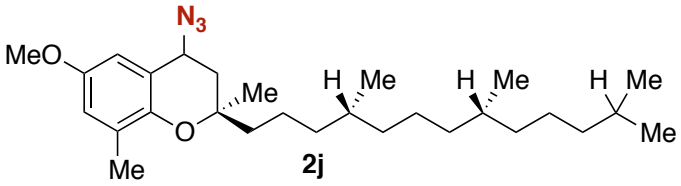


TBS deprotection of azide 2f: To the solution of **2f** (12.0 mg, 0.0272 mmol, 1 equiv) in THF (0.5 mL) was added 1 M solution of TBAF in THF (40.7 ml, 0.0407 mmol, 1.5 equiv). The reaction mixture was stirred at ambient temperature for 2 hours and then diluted with Et_2O (30 mL) and washed with H_2O (10 mL). The ether layer was dried over $MgSO_4$, filtered, and concentrated. The crude azide was purified by flash column chromatography (hexanes:EtOAc 95:5) to give azidototarol **S14** in 88% yield (7.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ *for the major diastereomer:* 7.07 (d, *J* = 8.7 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 4.75 (dd, *J* = 4.5, 2.0 Hz, 1H, C<u>H</u>N$_3$), 4.60 (s, 1H), 3.37 (m, 1H), 2.19 (dt, *J* = 14.3, 1.9 Hz, 1H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.39 (d, *J* = 7.1 Hz, 3H), 1.16 (s, 3H), 1.05 (s, 3H), 0.94 (s, 3H); *for the minor diastereomer:* 7.03 (d, *J* = 8.6 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 4.66 (t, *J* = 9.0 Hz, 1H, C<u>H</u>N$_3$), 4.60 (s, 1H), 3.37 (m, 1H), 2.46 (ddd, J = 13.6, 9.1, 2.5 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.35 (d, *J* = 7.1 Hz, 3H), 1.30 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H); *for the major + minor diastereomers:* 2.29 – 2.22 (m, 1H), 2.04 – 1.92 (m, 1H), 1.84 – 1.44 (m, 3H), 1.43 – 1.17 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ *for the major diastereomer:* 152.71, 143.56, 132.82, 129.64, 123.88, 117.78, 59.36, 45.29, 41.33, 39.11, 38.49, 33.29, 33.15, 28.25, 26.87, 24.92, 21.69, 20.94, 20.55, 19.34; *for the minor diastereomer:*152.95, 145.37, 133.22, 130.98, 123.06, 117.10, 58.37, 48.64, 41.49, 39.95, 37.82, 33.37, 32.99, 29.21, 27.19, 24.83, 21.51, 20.89, 20.47, 19.53; **ESIHR** (M-H) calc'd 326.2238, found 326.2234; **FT-IR** 3409, 2925, 2867, 2097 (N_3).



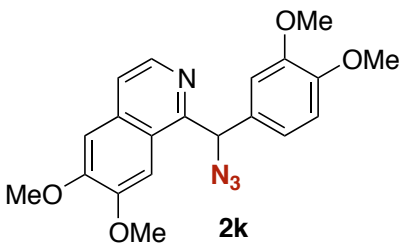
Azidation of totarol methyl ether: Azide **2g** was prepared from **S2** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 98:2) to give a 1.5:1 diastereomeric mixture of **2g** as a white solid in 50% yield (17.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) *for the major diastereomer*: δ 7.16 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 1H), 4.74 (dd, *J* = 4.4, 2.1 Hz, 1H, C<u>H</u>N$_3$), 3.80 (s, 3H), 3.39 – 3.24 (m, 1H), 2.17 (dt, *J* = 14.3, 1.9 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.15 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H); *for the minor diastereomer:* δ 7.12 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.66 (t, *J* = 9.0 Hz, 1H, C<u>H</u>N$_3$), 3.80 (s, 3H), 3.32 (m, 1H), 2.44 (ddd, *J* = 13.6, 9.1, 2.6 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.30 (s, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 0.97 (s, 3H), 0.95 (s, 3H); *for the major+minor*

diastereomers: δ 2.27 (dd, *J* = 10.1, 6.3 Hz, 1H), 2.05 – 1.90 (m, 1H), 1.75 (tt, *J* = 13.6, 3.5 Hz, 1H), 1.69 – 1.45 (m, 4H), 1.27 – 1.17 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) *for the major diastereomer*: δ 156.99, 143.14, 135.22, 129.29, 123.68, 112.76, 58.45, 55.21, 45.30, 41.35, 39.17, 38.46, 33.30, 33.16, 28.68, 26.96, 25.03, 21.71, 21.53, 20.60, 19.56; *for the minor diastereomer*: δ 157.23, 144.96, 135.69, 130.60, 122.80, 112.11, 59.32, 55.21, 48.63, 41.35, 40.00, 37.77, 33.38, 32.99, 29.65, 27.31, 24.85, 21.53, 21.04, 20.66, 19.36; **EIHR** Calc'd 341.2467, found ; **FT-IR** 2930, 2867, 2096 (N_3).



2j

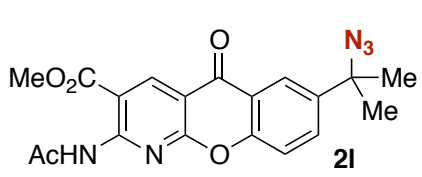
Azidation of tocopherol methyl ether: Azide **2j** was prepared from **S4** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:CH_2Cl_2 80:20) to give a 1:1 diastereomeric mixture of **2j** as a colorless oil in 25% yield (11.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) *for a 1:1 mixture of diastereomers*: δ 6.93 – 6.72 (m, 2H), 4.64 (m, 1H, C<u>H</u>N_3), 3.88 (s, 3H), 2.27 (s, *J* = 3.3 Hz, 3H), 2.08 (m, 1H), 1.81 – 1.75 (m, 1H), 1.73 – 1.57 (m, 3H), 1.57 – 1.43 (m, 3H), 1.50 (s, 3H), 1.43 – 1.30 (m, 6H), 1.36 (s, 3H), 1.30 – 1.11 (m, 6H), 1.04 – 0.91 (m, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) *for a 1:1 mixture of diastereomers*: δ 152.58 (2 overlapping resonances), 145.73, 145.65, 128.06, 128.02, 119.21, 119.03, 117.69, 117.59, 109.20, 108.91, 76.24, 76.21, 55.72, 55.69, 54.85, 54.60, 41.70, 39.38 (2 overlapping resonances), 38.54, 37.47, 37.44, 37.40, 37.39, 37.37, 37.34, 37.31, 37.29, 37.11, 32.84, 32.82, 32.69, 32.66, 28.01 (3 overlapping resonances), 25.50, 24.84 (2 overlapping resonances), 24.48, 24.46, 23.37, 22.76 (2 overlapping resonances), 22.67 (2 overlapping resonances), 21.09, 20.90, 19.78, 19.77, 19.70, 19.64, 16.37, 16.36; **EIHR** calc'd 457.3668, found 457.3672; **FT-IR** 2951. 2925, 2867, 2095 (N_3).



2k

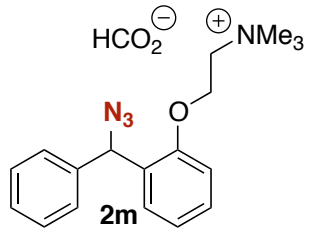
Azidation of pyridine derivative: Azide **2k** was prepared from papaverine according to the general procedure (A) on a 0.1 mmol scale. MeCN was used as the solvent, and the reaction was run at 25 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 60:40) to give

2k as a colorless oil in 45% yield (17.0 mg). The ^{1}H and ^{13}C NMR spectral data match those of the reported molecule.[12]



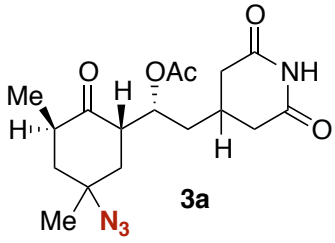
2l

Azidation of 2-amidopyridine derivative: Azide **2l** was prepared from **S6** according to the general procedure (A) on a 0.1 mmol scale. MeCN was used as the solvent, and the reaction was run at 50 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 70:30) to give **2l** as a colorless oil in 62% yield (24.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.30 (s, 1H), 9.31 (s, 1H), 8.31 (d, J = 1.4 Hz, 1H), 7.91 (dd, J = 8.8, 1.5 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 4.02 (s, 3H), 2.56 (s, 3H), 1.72 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.09, 169.87, 166.37, 161.69, 155.24, 154.72, 142.85, 142.47, 133.33, 123.09, 121.42, 119.13, 111.14, 108.74, 63.40, 53.23, 28.51, 26.67. **ESIHR** (M+Na) calc'd 418.1122, found 418.1129; **FT-IR** 3237, 2955, 2107 (N_3), 1687, 1665, 1601.



2m

Azidation of tetraalkyl ammonium salt S7: Azide **2m** was prepared from **S7** according to the general procedure (A) on a 0.1 mmol scale. MeCN was used as the solvent, and the reaction was run at 50 °C. The crude azide was first purified by UHPLC-MS (C-18 column, 30% MeCN in water to 95% MeCN in water with 0.1% formic acid). This UHPLC-MS purified material was contaminated with 2-iodobenzoic acid, which was removed by further purification by flash column chromatography (CH_2Cl_2:MeOH:H_2O:HCO_2H 90:10:0.6:0.6 then 70:30:5:5) to give **2m** as the formate salt in 27% yield (9.6 mg). **^{1}H NMR** (600 MHz, CD_3CN) δ 8.40 (s, 1H), 7.48 – 7.26 (m, 7H), 7.14 – 6.97 (m, 2H), 6.18 (s, 1H), 4.37 (s, 2H), 3.63 (s, 2H), 3.04 (s, 9H); **^{13}C NMR** (226 MHz, CD_3CN) δ 166.98, 155.61, 140.24, 130.62, 129.67, 129.42, 129.06, 128.57, 128.35, 122.76, 113.13, 66.35, 63.25, 63.07, 54.75; **ESIHR** (M) calc'd 311.1866, found 311.1864; **FT-IR** 2917, 2098 (N_3), 1619, 1598.



3a

Azidation of cycloheximide acetate: Azide **3a** was prepared from cycloheximide acetate[14] according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C. The crude azide was purified by flash column

chromatography (Hexane:EtOAc 60:40) to give **3a** as a colorless oil in 40% yield (14.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 5.39 (td, *J* = 8.1, 3.6 Hz, 1H), 2.95 (ddd, *J* = 17.3, 4.3, 1.8 Hz, 1H), 2.87 (ddd, *J* = 13.1, 7.7, 5.7 Hz, 1H), 2.77 (dt, *J* = 12.7, 6.2 Hz, 1H), 2.66 (ddd, *J* = 16.9, 4.2, 1.7 Hz, 1H), 2.36 (ddd, *J* = 36.3, 17.1, 10.6 Hz, 2H), 2.24 – 2.13 (m, 1H), 2.13 – 2.02 (m, 1H), 2.10 (s, 3H), 1.75 – 1.48 (m, 5H), 1.46 (s, 3H), 1.03 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.45, 171.86, 171.74, 170.64, 68.69, 60.73, 49.08, 46.24, 40.98, 40.13, 38.89, 38.42, 37.08, 27.38, 25.86, 21.09, 13.71. **ESIHR** (M+Na) calc'd 387.1639, found 387.1643; **FT-IR** 3462, 2102 (N_3), 1736.

*Structural assignment for the azide **3a**.*

To assign the structure of the C-H azidation product of the cycloheximide acetate we first identified ^{1}H resonances corresponding to the two methyl groups. These resonances were 1.46 (s, 3H) and 1.03 (d, *J* = 6.5 Hz, 3H). One these methyl groups is a singlet, indicating that the C-H bond α to this methyl group underwent C-H azidation. We then used HMBC correlations to identify which of the two C-H bonds α to the two methyl groups in the starting material (cycloheximide acetate) underwent C-H azidation. These key HMBC correlations are shown in Figure S1.

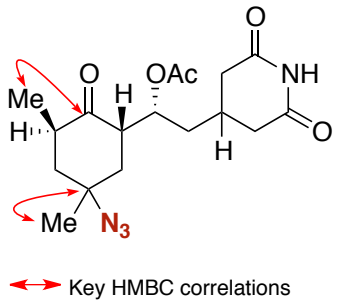
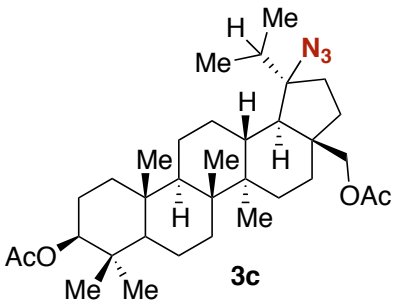


Figure S1 Key HMBC correlations of **3a**.



3c

Azidation of betulin diacetate: Azide **3b** was prepared from **S8** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C. The crude azide was purified by flash column chromatography (Hexane:CH_2Cl_2 70:30) to give **3b** as a colorless oil in 48% yield (17.7 mg). **^{1}H NMR** (900 MHz, $CDCl_3$) δ 4.48 (dd, *J* = 11.7, 4.6 Hz, 1H), 4.14 (d, *J* = 11.3 Hz, 1H), 4.01 (d, *J* = 11.3 Hz, 1H), 2.15 (h, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.92 (ddt, *J* = 15.4, 12.5, 5.8 Hz, 2H), 1.82 (d,

J = 13.2 Hz, 1H), 1.75 (dd, J = 12.8, 7.5 Hz, 1H), 1.71 – 1.57 (m, 6H), 1.51 (tt, J = 9.0, 4.8 Hz, 2H), 1.45 – 1.23 (m, 8H), 1.20 (td, J = 12.8, 12.3, 8.6 Hz, 1H), 1.03 (s, 3H), 1.02 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H), 0.88 (m, 1H), 0.86 (s, 3H), 0.84 (s, 3H), 0.84 (m, 3H), 0.81 (m, 2H); **^{13}C NMR** (226 MHz, $CDCl_3$) δ 171.30, 170.96, 80.79, 77.94, 62.41, 58.05, 55.26, 50.04, 45.73, 44.03, 41.10, 38.28, 37.77, 36.99, 35.07, 34.82, 34.00, 33.51, 31.58, 30.90, 27.90, 26.92, 25.12, 23.64, 21.31, 20.99, 20.71, 19.66, 19.31, 18.16, 16.45, 16.06, 16.03, 15.16. **ESIHR** (M-N_2+H) calc'd 542.4204, found 542.4195; **FT-IR** 2945, 2874, 2091 (N_3).

*Structural assignment for the azide **3b**.*

^{1}H-^{1}H COSY correlations (Figure S2) indicated that the protons on two CH_3 groups (C29 and C30) couple with C20-H, and this spin system does not couple with the rest of protons indicating that the C19 is a quaternary center. Based on these data, we deduced that the C19 carbon is connected to the N_3 group. This assignment was further confirmed by ^{1}H-^{13}C HMBC correlations shown in Figure S2.

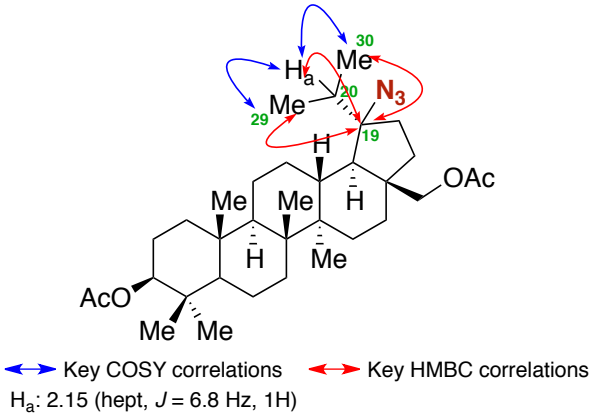
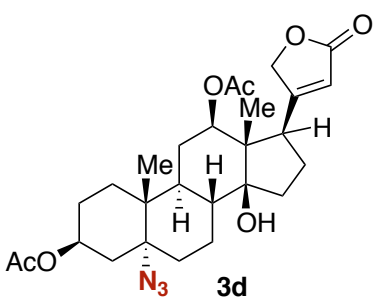


Figure S2 Key ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMBC correlations and coupling constants of **3b**.



3d

Azidation of digoxigenin diacetate: Azide **3d** was prepared from **10b** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C. The crude azide was purified by flash column chromatography (CH_2Cl_2:EtOAc 90:10) to give **3d** as a white solid in 68% yield (35.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.83 (q, J = 1.6 Hz, 1H), 5.03 (tt, J = 11.0, 5.4 Hz, 1H), 4.88 (dd, J = 18.1, 1.8 Hz, 1H), 4.76 (dd, J = 17.9, 1.8 Hz, 1H), 4.59 (dd, J = 11.9, 4.2 Hz, 1H), 2.87 (dd, J = 9.4, 6.2 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 2.05 – 1.97 (m, 1H), 1.97 – 1.86 (m, 4H), 1.85 – 1.77 (m, 2H)

1.75 – 1.57 (m, 6H) 1.57 – 1.30 (m, 4H), 1.21 (q, J = 12.1 Hz, 1H), 0.99 (s, 3H), 0.87 (s, 3H). **^{13}C NMR** (226 MHz, $CDCl_3$) δ 174.26, 173.25, 170.60, 170.37, 118.02, 85.54, 77.36, 73.28, 69.45, 68.78, 53.91, 45.83, 40.26, 38.31, 37.96, 35.67, 33.09, 30.52, 29.88, 27.11, 26.45, 26.30, 21.78, 21.28, 21.20, 15.36, 10.33; **ESIHR** (M+H) calc'd 516. 2704, found 516.2720; **FT-IR** 3463, 2949, 2102 (N_3), 1736.

*Structural assignment for the azide **3d**.*

As shown in Figure S3, the A/B ring system of digoxigenin diacetate (**S8**) (starting material for this azidation reaction) has a *cis*-decalin conformation. In this case C3-OAc occupies the axial position and C3-H occupies the equatorial position. The $^3J_{H\text{-}H}$ coupling constants involving C3-H at 5.01 ppm are smaller than those from a $^3J_{Hax\text{-}Hax}$ value. Thus, the observed coupling is due to $^3J_{Heq\text{-}Heq}$ and $^3J_{Heq\text{-}Hax}$ couplings. Because the two $^3J_{H\text{-}H}$ values are small and close in value to each other, the C3-H resonance in **S8** is a broad singlet. In azide **3d**, C3-H (labeled as H_a in Figure S3) resonates with a tt splitting pattern with coupling constants of 11.0 Hz and 5.4 Hz. The 11.0 Hz coupling constant corresponds to a $^3J_{Hax\text{-}Hax}$ coupling. This coupling indicates that H_a occupies an axial position and the A/B ring fusion has changed from a *cis*-decalin structure to a *trans*-decalin structure. COSY and HMBC correlations shown in Figure S3 were used to identify the position of the azido group.

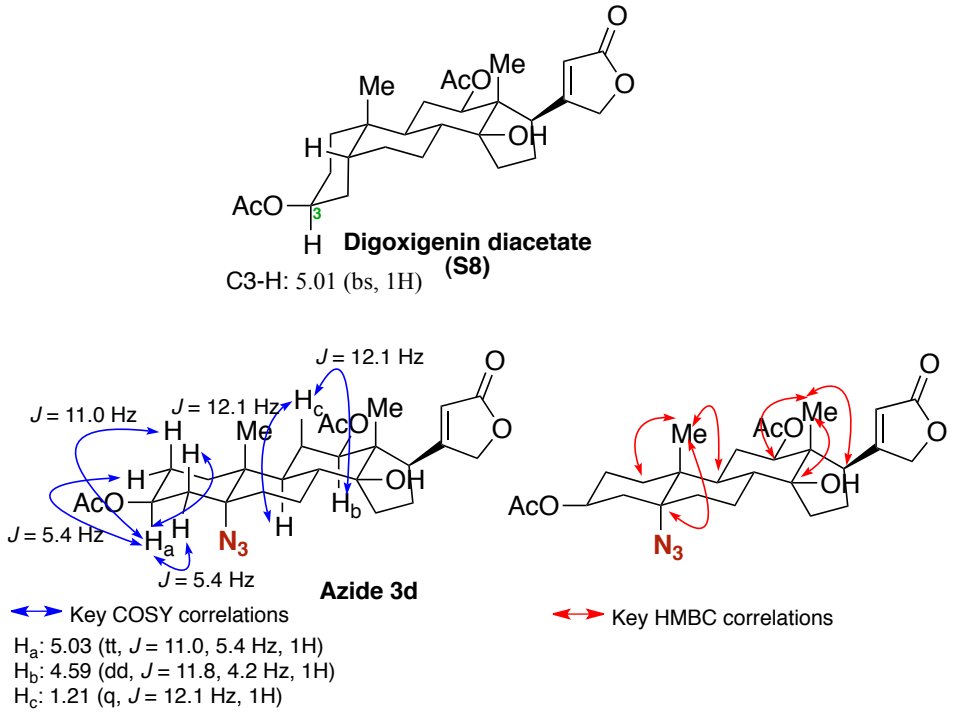
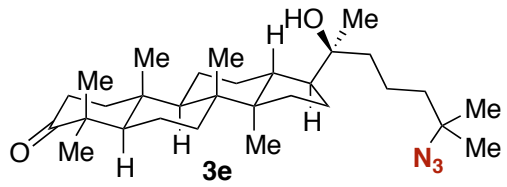


Figure S3 Key ^{1}H-^{1}H COSY and HMBC correlations and coupling constants of azide **3d**.



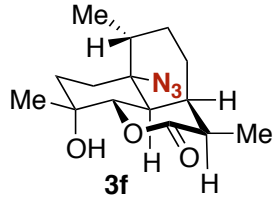
3e

Azidation of dihydrodipterocarpol: Azide **3e** was prepared from 24,25-dihydrodipterocarpol[15] according to the general procedure (A) on a 0.1 mmol scale. MeCN was used as the solvent, and the reaction was run at 50 °C. The crude azide was purified by flash column chromatography (Hexane:EtOAc 90:10) to give **3e** as a colorless oil in 63% yield (29.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.50 (ddd, *J* = 15.6, 9.6, 7.6 Hz, 1H), 2.42 (ddd, *J* = 15.6, 7.7, 4.4 Hz, 1H), 1.92 (ddd, *J* = 12.6, 7.7, 4.5 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.78 – 1.69 (m, 2H), 1.69 – 1.29 (m, 20H), 1.27 (s, 6H), 1.16 (m, 1H) 1.15 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 218.16, 75.41, 61.85, 55.51, 50.43, 50.14, 50.07, 47.57, 42.60, 42.23, 40.82, 40.44, 40.04, 36.99, 34.69, 34.26, 31.33, 27.65, 26.86, 26.30, 26.10, 25.74, 24.99, 22.18, 21.16, 19.80, 18.64, 16.52, 16.16, 15.34; **ESIHR** (M+Na) calc'd 508.3873, found 508.3866; **FT-IR** 2952, 2869, 2097 (N_3), 1704.

*Structural assignment for the azide **3e**.*

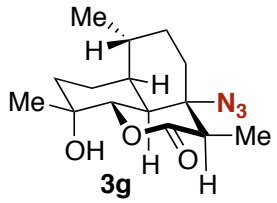
The structure was assigned based on the observation that all methyl groups resonated as singlets in the ^{1}H NMR spectrum.

Azidation of artemisinic acid derivative S9 was conducted according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C. The crude azide isomers were purified by flash column chromatography (Hexane:EtOAc 60:40) to give **3f-h** as white solids.

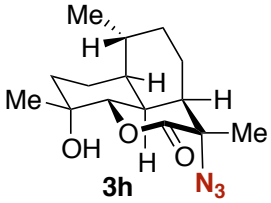


3f

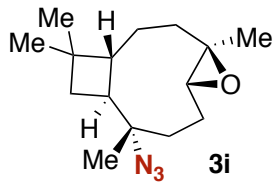
3f was obtained in 22% yield (6.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.29 (d, *J* = 11.6 Hz, 1H), 2.68 (p, *J* = 7.0 Hz, 1H), 2.42 (dd, *J* = 11.6, 3.8 Hz, 1H), 2.29 (m, 1H), 2.03 (td, *J* = 13.7, 4.4 Hz, 1H), 1.95 (m, 2H), 1.86 (m, 1H), 1.83 – 1.71 (m, 2H), 1.62 (m, 2H), 1.46 (m, 2H), 1.36 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.36, 80.55, 69.88, 66.37, 41.17, 40.14, 34.34, 32.93, 31.18, 30.00, 26.86, 26.69, 22.65, 15.10, 13.40; **FT-IR** 3442, 2927, 2095 (N_3), 1727. Single crystals suitable for **X-ray** diffraction were obtained by slow vapor diffusion of octane into a solution of **3f** in a mixture of ether and octane.



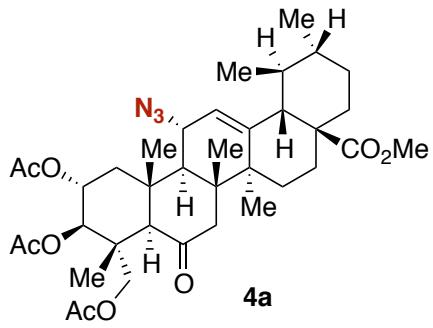
3g was obtained in 12% yield (3.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.19 (d, *J* = 11.7 Hz, 1H), 2.75 (q, *J* = 7.1 Hz, 1H), 2.32 (ddd, *J* = 11.8, 4.0, 1.9 Hz, 1H), 1.90 – 1.56 (m, 9H), 1.52 (td, *J* = 14.5, 4.3 Hz, 1H), 1.44 (td, *J* = 13.8, 3.9 Hz, 1H), 1.36 (s, 3H), 1.33 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.30, 80.88, 70.81, 64.81, 46.32, 40.87, 38.85, 32.89, 30.36, 27.44, 26.79, 26.33, 21.96, 19.77, 9.98; **FT-IR** 3505, 2924, 2853, 2101 (N_3), 1731. Single crystals suitable for **X-ray** diffraction were obtained by slow vapor diffusion of octane into the solution of **3g** in a mixture of ether and octane.



3h was obtained in 7% yield (2.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.34 (d, *J* = 12.0 Hz, 1H), 2.70 (dt, *J* = 12.2, 4.1 Hz, 1H), 1.94 – 1.75 (m, 3H), 1.68 (m, 4H), 1.56 (m, 1H), 1.51 (s, 3H), 1.49 – 1.37 (m, 2H), 1.34 (s, 3H), 1.33 – 1.22 (m, 1H), 1.15 – 0.96 (m, 1H), 0.86 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.03, 82.06, 70.64, 65.62, 44.08, 42.87, 34.89, 32.82, 32.57, 27.16 (2 overlapping resonances), 23.15, 22.25, 19.96, 19.26; **FT-IR** 3435, 2937, 2109 (N_3), 1722. Single crystals suitable for **X-Ray** analysis were obtained by slow vapor diffusion of octane into the solution of **3h** in a mixture of ether and octane.



Azidation of dihydrocaryophyllene oxide: Azide **3i** was prepared from dihydrocaryophyllene oxide[16] according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C for 15 hours. The crude azide was purified by flash column chromatography (Hexane:EtOAc 95:5) to give **3i** as a colorless oil in 44% yield (11.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.75 (dd, *J* = 9.7, 5.7 Hz, 1H), 2.21 (m, 2H), 2.09 (dt, *J* = 13.0, 3.6 Hz, 1H), 2.05 (ddd, *J* = 14.2, 5.6, 2.9 Hz, 1H), 1.84 (td, *J* = 13.5, 5.4 Hz, 1H), 1.78 (dd, *J* = 11.7, 9.0 Hz, 1H), 1.74 – 1.59 (m, 3H), 1.50 (m, 1H), 1.43 (m, 1H), 1.31 (s, 3H), 1.30 (s, 3H), 0.98 (s, 3H), 0.96 (s, 3H), 0.93 (dd, *J* = 13.5, 4.0 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 67.30, 60.47, 59.29, 50.57, 47.11, 40.10, 37.36, 36.36, 32.42, 30.23, 28.80, 24.78, 23.27, 17.48, 16.38; **ESIHR** (M-N_2+H) calc'd 236.2009, found 236.2008; **FT-IR** 2932, 2857, 2089 (N_3); Single crystals suitable for **X-Ray** analysis were obtained by slow evaporation of octane from a solution of **3i** in octane.



4a

Azidation of the madecassic acid derivative: Azide **4a** was prepared from **S9** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C for 15 hours. The crude azide was purified by flash column chromatography (Hexane:EtOAc 95:5) to give **4a** as a white solid in 42% yield (28.8 mg). A side product, diene **S15**, was obtained in 16% yield. (10.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.48 (d, *J* = 3.5 Hz, 1H), 5.22 (td, *J* = 11.0, 4.7 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 3.93 (d, *J* = 11.6 Hz, 1H), 3.87 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.82 (d, *J* = 11.6 Hz, 1H), 3.63 (s, 3H), 2.74 (s, 1H), 2.59 (dd, *J* = 13.0, 4.7 Hz, 1H), 2.52 (d, *J* = 12.3 Hz, 1H), 2.40 (d, *J* = 11.2 Hz, 1H), 2.28 (d, *J* = 9.2 Hz, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.92 (d, *J* = 12.3 Hz, 1H), 1.81 – 1.54 (m, 8H), 1.37 (s, 3H), 1.32 (s, 3H), 1.20 – 1.42 (m, 3H) 1.24 (s, 3H), 1.05 (d, *J* = 6.5 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.83 (s, 3H); **^{13}C NMR** (226 MHz, $CDCl_3$) δ 209.36, 177.45, 170.66, 170.41, 170.30, 143.73, 123.74, 73.38, 68.67, 65.49, 58.04, 57.15, 52.16, 51.90, 51.67, 50.07, 48.29, 47.64, 44.98, 44.78, 42.33, 40.60, 38.73, 37.92, 36.29, 30.40, 28.22, 24.26, 23.80, 21.29, 21.22, 21.08, 20.83, 19.42, 18.31, 17.17, 14.28.; **ESIHR** (M+Na) calc'd 706.3674, found 706.3702; **FT-IR** 2929, 2090 (N_3), 1744.

*Structural assignment for the azide **4a**.*

The structure of azide **4a** was assigned based on the ^{1}H-^{1}H COSY correlations that are shown in Figure S4. The configuration of the carbon to which the N_3 group is bound was assigned on the basis of the coupling constant $^3J_{Hd\text{-}Hc}$ = 9.3 Hz. This coupling constant indicates that H_d occupies an axial position on ring C.

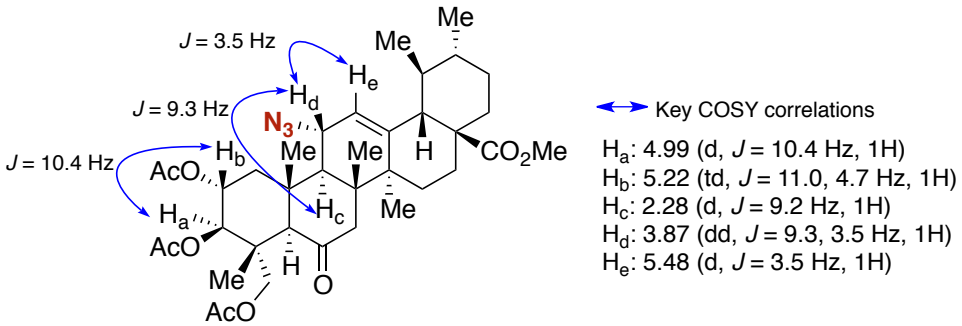
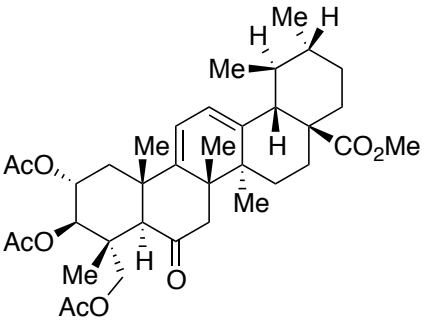
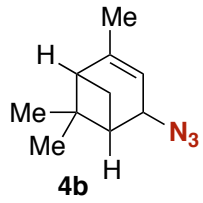


Figure S4 Key ^{1}H-^{1}H COSY correlations and coupling constants of **4a**.

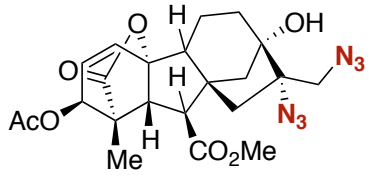


Diene **S15** was obtained in 16% yield as the main side product of the azidation of the madecassic acid derivative. **^{1}H NMR** (900 MHz, $CDCl_3$) δ 5.69 (d, *J* = 5.8 Hz, 1H), 5.66 (d, *J* = 5.8 Hz, 1H), 5.22 (ddd, *J* = 11.8, 10.3, 4.4 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.29 (d, *J* = 11.3 Hz, 1H), 3.72 (d, *J* = 11.4 Hz, 1H), 3.62 (s, 3H), 2.73 (s, 1H), 2.66 (d, *J* = 17.6 Hz, 1H), 2.41 (dd, *J* = 11.2, 2.0 Hz, 1H), 2.33 (dd, *J* = 12.6, 4.5 Hz, 1H), 2.11 (d, *J* = 17.6 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.90 – 1.81 (m, 2H), 1.78 (m, 1H), 1.74 (dt, *J* = 13.3, 3.4 Hz, 1H), 1.63 (dd, *J* = 13.6, 4.4 Hz, 1H), 1.61 (s, 3H), 1.52 (m, 1H), 1.35 (s, 3H), 1.34 – 1.25 (m, 3H), 1.25 (s, 3H), 1.21 – 1.16 (m, 2H), 1.06 (s, 3H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.93 (s, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (226 MHz, $CDCl_3$) δ 210.39, 177.73, 170.54, 170.49, 170.40, 148.39, 140.80, 123.63, 115.95, 77.36, 73.73, 69.36, 65.74, 52.70, 51.89, 51.64, 47.56, 47.09, 45.23, 41.88, 41.82, 41.48, 41.07, 38.77, 38.43, 36.18, 30.53, 27.04, 26.20, 24.40, 23.86, 21.37, 21.21, 20.89, 18.75, 17.07, 13.98; **ESIHR** (M+Na) calc'd 663.3504, found 663.3507.



4b

Azidation of a-pinene: Azide **4b** was prepared from a-pinene according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C for 15 hours. The crude azide was purified by flash column chromatography (Hexanes) to give **4b** as a colorless oil in 26% yield (5.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.33 (dq, *J* = 3.5, 1.7 Hz, 1H), 4.03 (s, 1H), 2.30 (dt, *J* = 9.3, 5.5 Hz, 1H), 2.27 – 2.21 (m, 1H), 2.05 (td, *J* = 5.6, 1.4 Hz, 1H), 1.76 (t, *J* = 1.7 Hz, 3H), 1.46 – 1.35 (m, 1H), 1.34 (s, 3H), 0.88 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.64, 114.04, 61.63, 47.34, 45.44, 44.84, 28.61, 26.33, 22.75, 20.38. The ^{1}H NMR spectral data match those of the reported molecule.[17]



4c

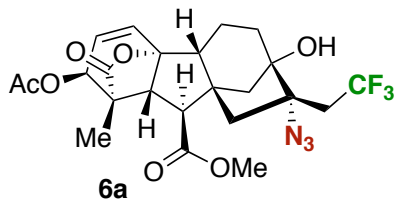
Azidation of the gibberellic acid derivative: Azide **4c** was prepared from **S10** according to the general procedure (A) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 50 °C for 15 hours. The crude azide was purified by flash column chromatography (Hexane:EtOAc 65:35) to give **4c**

as a white solid in 56% yield (27.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.36 (d, *J* = 9.3 Hz, 1H), 5.89 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.32 (d, *J* = 3.8 Hz, 1H), 3.80 (s, 3H), 3.66 – 3.56 (m, 2H), 3.30 (d, *J* = 10.7 Hz, 1H), 2.75 (d, *J* = 10.7 Hz, 1H), 2.11 (s, 3H), 2.02 – 1.66 (m, 10H), 1.13 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.95, 172.42, 170.11, 133.64, 129.70, 89.94, 79.55, 73.12, 70.26, 56.08, 53.70, 53.46, 52.73, 52.31, 51.98, 49.07, 45.08, 43.26, 29.34, 20.93, 16.18, 14.38. **FT-IR** 3506, 2951, 2108 (N_3), 1776, 1735; Single crystals suitable for **X-ray** diffraction were obtained by slow vapor diffusion of octane into a solution of **4c** in a mixture of acetone and octane.

D. Trifluoromethylazidation of olefins in natural products

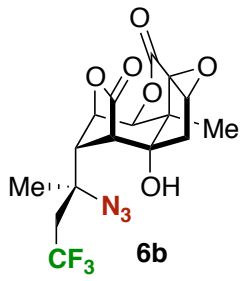
General procedure (B) for iron-catalyzed trifluoromethyl azidation of olefins. In an N_2 filled glovebox, to a 4 mL vial containing alkene (0.1 mmol) and Togni's reagent (**5**) (1.5-2.0 equiv, 0.15-0.2 mmol) was added EtOAc (0.3 mL). In a separate vial, to the solution of the $Fe(OAc)_2$(PyBox) catalyst (0.5 mL), was added $TMSN_3$ (1.2 equiv). Both vials were allowed to stir for 5 min at ambient temperature, at which time the contents of the second vial (containing the Fe catalyst and $TMSN_3$) was transferred into the first vial. The vial containing the reaction mixture was then sealed with a cap containing a PTFE septum and kept at 23 °C for 24 hours. The crude reaction mixture was then treated with 1 ml of EtOAc. The resulting mixture was filtered through a 30 x 6 mm plug of basic alumina (in a 9 mm pipette) and collected in a 20 ml vial. The basic alumina was washed with 3 x 3.0 mL of EtOAc. The solvent was evaporated from the combined resulting solution, and the product was purified by flash column chromatography on silica gel.

General guidelines for identifying trifluoromethyl azidation products: The absence of resonances in the ^{1}H and ^{13}C NMR spectra due to an alkene and the presence of a signal in the ^{19}F NMR spectrum, as well as the presence of a stretch for an N_3 group in the IR spectrum indicated that the product resulted from addition of a trifluoromethyl group and an azide to the alkene. The regioselectivity of the addition to the alkene was determined by the splitting pattern of the CF_3 group in the ^{19}F NMR spectrum. In addition, the structures of four compounds were determined unambiguously by X-ray diffraction of single crystals.



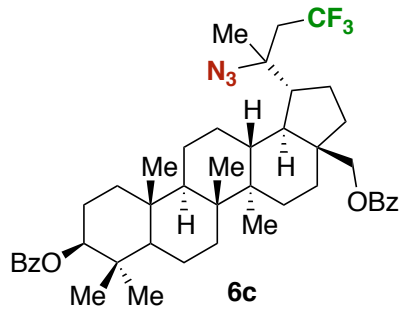
6a

Trifluromethylazidation of the gibberellic acid derivative: Trifluoromethylazide **6a** was prepared from **S10** according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:EtOAc 65:35) to give **6a** as a white solid in 75% yield (39.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.36 (d, *J* = 9.4 Hz, 1H), 5.89 (dd, *J* = 9.3, 3.6 Hz, 1H), 5.33 (d, *J* = 3.8 Hz, 1H), 3.79 (s, 3H), 3.32 (d, *J* = 10.6 Hz, 1H), 2.74 (d, *J* = 10.6 Hz, 1H), 2.63 – 2.53 (m, 2H), 2.43 (dq, *J* = 15.2, 10.6 Hz, 1H), 2.11 (s, 3H), 2.08 (d, *J* = 16.0 Hz, 1H), 2.00 (s, 2H), 1.98 – 1.90 (m, 3H), 1.84 (d, *J* = 15.9 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.14 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.98, 172.53, 170.10, 133.52, 129.78, 126.36 (q, *J* = 278.3 Hz), 89.77, 80.82, 70.31, 70.04, 54.74, 53.84, 52.95, 52.35, 52.24, 48.92, 45.24, 41.80, 37.65 (q, *J* = 28.2 Hz), 29.40, 20.93, 16.25, 14.35; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.60 (t, *J* = 10.5 Hz); **FT-IR** 3510, 2954, 2118 (N_3), 1778, 1735.



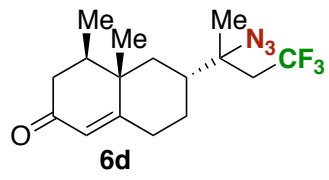
6b

Trifluromethylazidation of picrotoxinin: Trifluoromethylazide **6b** was prepared from picrotoxinin according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:acetone 70:30) to give **6b** as a white solid in 78% yield (31.5 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 5.39 (s, 1H), 5.16 (t, *J* = 4.1 Hz, 1H), 5.10 (d, *J* = 3.4 Hz, 1H), 3.59 (d, *J* = 3.4 Hz, 1H), 3.14 (t, *J* = 4.4 Hz, 1H), 3.11 – 2.72 (m, 5H), 2.17 (d, *J* = 15.0 Hz, 1H), 2.09 (s, 1H), 1.81 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 174.33, 170.09, 127.17 (q, *J* = 277.4 Hz), 86.28, 80.99, 77.66, 73.67, 62.02, 58.34, 58.32, 53.51, 50.79, 48.47, 45.27, 43.82 (q, *J* = 26.4 Hz), 20.29, 15.82; **^{19}F NMR** (376 MHz, Acetone-d_6) δ -59.99 (t, *J* = 11.4 Hz); **FT-IR** 2924, 2853, 2127 (N_3), 1793. Single crystals suitable for **X-Ray** analysis were obtained by slow evaporation of dichloromethane from a solution of **6b** in a mixture of dichloromethane and octane.



6c

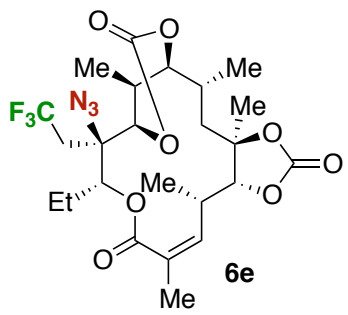
Trifluromethylazidation of betulin dibenzoate: Trifluoromethylazide **6c** was prepared betulin dibenzoate[18] according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:ether 90:10) to give **6c** as a white solid in 80% overall yield (61.0 mg). *For the major diastereomer:* **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 – 7.92 (m, 4H), 7.70 – 7.49 (m, 2H), 7.44 (dt, *J* = 9.3, 7.8 Hz, 4H), 4.74 (dd, *J* = 11.3, 4.6 Hz, 1H), 4.63 (d, *J* = 11.3 Hz, 1H), 4.03 (d, *J* = 11.2 Hz, 1H), 2.48 – 2.27 (m, 2H), 2.13 – 2.06 (m, 1H), 2.06 – 1.50 (m, 12H), 1.50 – 1.44 (m, 4H), 1.43 (s, 3H), 1.41 – 1.19 (m, 5H), 1.15 (s, 3H), 1.11 (m, 2H), 1.06 (s, 3H), 1.01 (s, 3H), 0.93 (s, 6H), 0.91 – 0.80 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.86, 166.40, 133.15, 132.82, 131.18, 130.42, 129.70, 129.67, 128.57, 128.45, 125.83 (q, *J* = 278.6 Hz), 81.69, 63.18, 63.00, 55.51, 50.39, 48.81, 48.59, 47.36, 43.79, 43.73, 43.64 (q, *J* = 26.6 Hz), 41.82, 38.60, 38.37, 37.22, 34.58, 34.37, 30.80, 29.85, 28.45, 28.29, 27.95, 27.51, 23.90, 21.72, 18.38, 16.96, 16.45, 16.41, 15.37; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.23 (d, *J* = 10.8 Hz); **FT-IR** 2950, 2107 (N_3), 1716. Single crystals suitable for **X-Ray** analysis were obtained by slow evaporation of dichloromethane from a solution of **6c** (major diastereomer) in dichloromethane/octane mixture. *For the minor diastereomer*: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 – 7.98 (m, 4H), 7.56 (m, 2H), 7.45 (m, 4H), 4.74 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.04 (d, *J* = 11.1 Hz, 1H), 2.32 (m, 2H), 2.15 – 1.67 (m, 9H), 1.58 (m, 5H), 1.54 (s, 3H), 1.50 – 1.18 (m, 8H), 1.14 (s, 3H), 1.13 – 1.06 (m, 3H), 1.04 (s, 3H), 1.01 (s, 3H), 0.93 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.91, 166.43, 133.15, 132.84, 131.15, 130.42, 129.70, 129.67, 128.57, 128.45, 126.1 (q, J = 279.1 Hz), 81.67, 63.41, 63.30, 55.50, 50.40, 49.21, 48.62, 48.54, 43.78, 41.79, 40.94 (q, J = 27.3 Hz), 38.62, 38.36, 37.22, 37.04, 34.57, 34.23, 30.84, 29.18, 28.27, 27.96, 27.47, 23.90, 23.64, 21.76, 18.34, 16.97, 16.44, 16.42, 15.32; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.82 (t, *J* = 11.0 Hz); **FT-IR** 2953, 2107 (N_3), 1716.



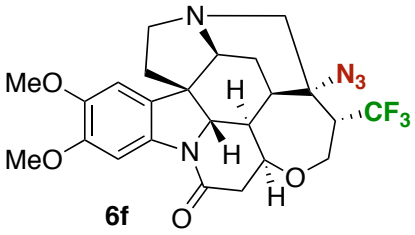
6d

Trifluromethylazidation of nootkatone: Azide **6d** was prepared from nootkatone according to the general procedure (B) on a 0.1 mmol scale. EtOAc was used as the solvent, and the reaction was run at 25 °C for 15 hours. The crude azide was purified by flash

column chromatography (Hexane:EtOAc 65:35) to give **6d** as a white solid in 56% yield (23.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) *for the mixture of diastereomers:* δ 5.74 (d, *J* = 1.7 Hz, 1H), 2.55 – 2.12 (m, 6H), 2.09 – 1.76 (m, 4H), 1.42 (two overlapping singlets, 3H), 1.24 (m, 1H), 1.07 (s, 3H), 1.04 (d, *J* = 12.8 Hz, 1H), 0.97 (two overlapping doublets, *J* = 6.9, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *for the mixture of diastereomers:* δ 199.25, 199.21, 168.85, 168.82, 125.86 (q, *J* = 278.4 Hz), 125.80 (q, *J* = 278.4 Hz), 124.93, 124.91, 62.70 (2 overlapping resonances), 42.21, 42.05 (2 overlapping resonances), 41.88, 40.57 (2 overlapping resonances), 40.75 (q, *J* = 27.4 Hz), 40.22 (q, *J* = 27.4 Hz), 39.28, 39.25, 39.16, 38.99, 32.51 (2 overlapping resonances), 27.35, 27.27, 20.28, 20.17, 16.82 (2 overlapping resonances), 15.06 (2 overlapping resonances); **^{19}F NMR** (376 MHz, $CDCl_3$) *for the mixture of diastereomers:* δ -59.15 (t, *J* = 10.9 Hz), -59.24 (t, *J* = 10.9 Hz); **ESIHR** (M+H) calc'd 330.1788, found 330.1788; **FT-IR** 3376, 2959, 2108 (N_3), 1664.

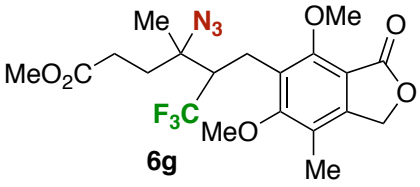


Trifluromethylazidation of the erythronolide derivative S13: Trifluoromethylazide **6e** was prepared from **S13** according to the general procedure (B) on a 0.055 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:acetone 70:30) to give **6e** as a white solid in 60% yield (18.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.96 (dd, *J* = 9.7, 1.6 Hz, 1H), 5.29 (bs, 1H), 5.02 (bs, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 3.86 (d, *J* = 9.9 Hz, 1H), 3.15 (bs, 1H), 2.86 (m, 1H), 2.54 (m, 2H), 2.29 (bs, 1H), 1.97 –1.94 (m, 1H), 1.94 (d, *J* = 1.5 Hz, 3H), 1.97 (m, 1H), 1.75 (t, *J* = 13.8 Hz, 1H), 1.67 (dd, *J* = 15.2, 3.5 Hz, 1H), 1.31 (m, 9H), 1.28 (d, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (226 MHz, Acetone-d_6) δ 167.98, 153.39, 146.51, 138.43, 131.53, 126.88 (q, *J* = 277.6 Hz), 91.83, 86.80, 83.47, 81.74, 79.00, 69.25, 37.40, 34.47, 33.69 (q, *J* = 28.8 Hz), 33.44, 28.64, 25.46, 23.10, 17.00, 16.08, 14.16, 13.14, 11.84; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.35; **FT-IR** 2977, 2919, 2849, 2128 (N_3), 1801, 1788, 1743. Single crystals suitable for **X-Ray** analysis were obtained by slow vapor diffusion of octane into the solution of **6e** in acetone/octane mixture.



6f

Trifluromethylazidation of brucine: Trifluoromethylazide **6f** was prepared from brucine according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:Et_2O 50:50) to give **6f** as a white solid in 70% yield (35.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.66 (s, 1H), 4.12 (dd, *J* = 13.4, 2.4 Hz, 1H), 4.07 (dt, *J* = 8.2, 5.4 Hz, 1H), 3.89 (d, *J* = 3.8 Hz, 3H), 3.87 (s, 3H), 3.80 (dd, *J* = 13.4, 9.2 Hz, 1H), 3.48 (t, *J* = 3.2 Hz, 1H), 3.30 (d, *J* = 13.7 Hz, 1H), 3.20 (dt, *J* = 12.6, 9.3 Hz, 1H), 2.99 (dd, *J* = 16.0, 8.2 Hz, 1H), 2.90 (ddd, *J* = 12.8, 8.7, 2.2 Hz, 1H), 2.74 (dt, *J* = 14.3, 3.6 Hz, 1H), 2.64 – 2.52 (m, 2H), 2.49 – 2.35 (m, 3H), 2.04 (ddd, *J* = 14.4, 9.4, 2.3 Hz, 1H), 1.75 (dq, *J* = 5.4, 3.7 Hz, 1H), 1.60 (dt, *J* = 14.3, 2.9 Hz, 1H) 1.33 – 1.27 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.06, 149.33, 146.75, 134.28, 125.40 (q, *J* = 280.8 Hz), 124.95, 105.17, 100.58, 74.93, 67.72, 64.05, 63.14, 62.53, 58.78, 56.53, 56.20, 55.25 (q, *J* = 22.1 Hz), 53.82, 52.02, 51.43, 45.81, 40.45, 34.73, 28.16; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.84 (d, *J* = 10.5 Hz); Single crystals suitable for **X-Ray** analysis were obtained by slow evaporation of solution of **6f** in dichloromethane/$CHCl_3$/octane mixture.

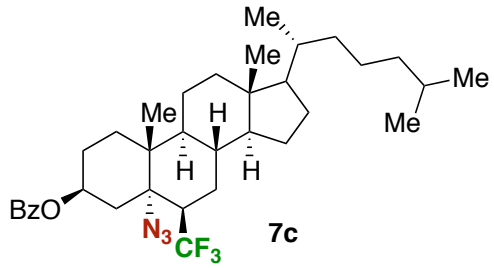


6g

Trifluromethylazidation of the mycophenollic acid derivative S5: Trifluoromethylazide **6g** was prepared from **S5** according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:CH_2Cl_2 70:30 to 50:50) to give **6g** as a light yellow colored oil in 67% overall yield (30.8 mg). *For the major diastereomer:* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.15 (s, 2H), 4.12 (s, 3H), 3.81 (s, 3H), 3.70 (s, 3H), 3.21 (dd, *J* = 15.1, 10.1 Hz, 1H), 3.00 – 2.88 (m, 2H), 2.48 (ddd, *J* = 9.5, 6.2, 4.8 Hz, 2H), 2.23 – 2.16 (m, 1H), 2.18 (s, 3H), 2.11 (ddd, *J* = 15.2, 9.6, 6.6 Hz, 1H), 1.52 – 1.44 (s, 3H); **^{13}C NMR** (226 MHz, $CDCl_3$) δ 173.26, 168.86, 163.05, 156.84, 147.82, 127.21 (q, *J* = 282.7 Hz), 126.14, 119.70, 112.24, 68.46, 64.11, 62.93, 61.06, 51.98, 48.81 (q, *J* = 22.8 Hz), 34.35, 28.94, 20.98, 20.40, 11.81; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.09 (d, *J* = 9.1 Hz); **ESIHR** (M) calc'd 482.1509, found 482.1506; **FT-IR** 2953, 2108 (N_3), 1759.

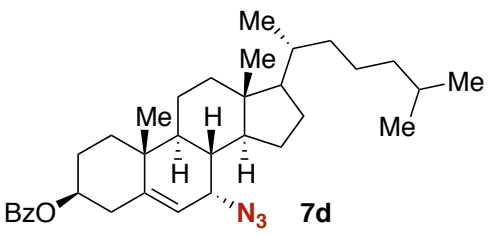
For the minor diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.15 (s, 2H), 4.14 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 3.18 (dd, *J* = 14.9, 10.3 Hz, 1H), 3.05 – 2.89 (m, 2H), 2.46 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 2H), 2.19 (s, 3H), 2.10 – 2.02 (m, 1H), 2.02 – 1.94 (m, 1H), 1.53 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (226 MHz, $CDCl_3$) δ 173.47, 168.83, 163.01, 156.86, 147.96, 127.22 (q, *J* = 283.2 Hz), 125.84, 119.58, 112.15, 68.46, 64.00, 62.97, 61.03, 51.97, 50.76 (q, *J* = 22.6 Hz), 31.85, 28.96, 21.75, 20.87, 11.87; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.54 (d, *J* = 9.3 Hz); **ESIHR** (M) calc'd 482.1509, found 482.1503; **FT-IR** 2954, 2108 (N_3), 1759.

E. Azidation of the cholesterol scaffold.



7c

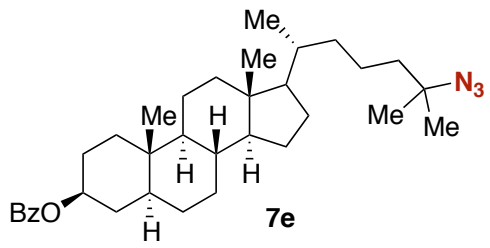
Trifluoromethylazidation of the cholesterol benzoate derivative: Trifluoromethylazide **7c** was prepared from cholesterol benzoate according to the general procedure (B) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:acetone 70:30) to give **7c** as a white solid in 60% yield (36.1 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.62 – 7.50 (m, 1H), 7.50 – 7.37 (m, 2H), 5.27 (dq, *J* = 10.9, 5.4 Hz, 1H), 2.48 – 2.19 (m, 3H), 2.12 – 1.94 (m, 2H), 1.93 – 1.15 (m, 18H), 1.19 – 1.04 (m, 6H), 1.12 (s, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.4 Hz, 3H), 0.86 (d, *J* = 1.4 Hz, 3H), 0.67 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.05, 133.05, 130.65, 129.78, 128.47,127.07 (q, *J* = 281.7Hz), 71.25, 70.64, 56.39, 55.99, 46.17, 46.17 (q, *J* = 26.1 Hz) 42.92, 39.95, 39.70, 38.52, 36.34, 35.93, 35.26 (q, *J* = 3.2 Hz), 33.47, 31.86, 28.32, 28.17, 27.10, 26.85, 24.17, 24.03, 22.94, 22.70, 21.23, 18.82, 16.57 (q, *J* = 3.8 Hz), 12.38; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.12 (d, *J* = 11.8 Hz); **EIHR** (M-H) calc'd 601.3810, found 601.3803; **FT-IR** 2950, 2865, 2101 (N_3), 1720.



7d

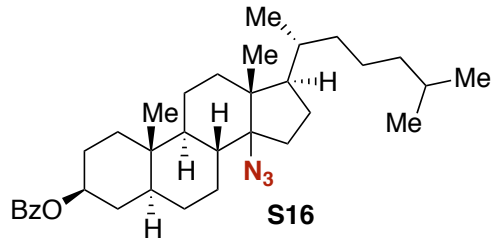
Azidation of the cholesterol benzoate derivative: Azide **7d** was prepared from cholesterol benzoate according to the general procedure (A) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (Hexane:acetone 97:3) to give **7d** as a white solid in 43% yield (22.9 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0

Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.61 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.93 (tt, *J* = 10.9, 5.0 Hz, 1H), 3.68 – 3.49 (m, 1H), 2.67 – 2.52 (m, 2H), 2.11 – 2.04 (m, 1H), 2.02 (dt, *J* = 12.7, 3.5 Hz, 1H), 1.95 (dt, *J* = 14.0, 3.9 Hz, 1H), 1.90 (ddd, *J* = 13.4, 9.5, 6.1 Hz, 1H), 1.76 (dtd, *J* = 15.3, 12.0, 3.8 Hz, 1H), 1.68 (ddd, *J* = 12.2, 6.8, 2.7 Hz, 1H), 1.62 (td, *J* = 11.5, 4.2 Hz, 1H), 1.59 – 0.99 (m, 17H), 1.08 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 3.0 Hz, 3H), 0.87 (d, *J* = 3.0 Hz, 3H), 0.68 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.77, 147.30, 132.77, 130.60, 129.51, 128.25, 119.22, 74.25, 58.22, 55.78, 50.42, 43.27, 42.18, 39.48, 38.97, 38.00, 37.48, 36.99, 36.75, 36.10, 35.70, 28.10, 27.99, 27.51, 24.02, 23.70, 22.78, 22.53, 20.73, 18.69, 18.52, 11.62; **ESIHR** (M+Na) calc'd 554.3717, found 554.3714; **FT-IR** 2949, 2096 (N_3), 1718.



7e

Azidation of the dihydrocholesterol benzoate derivative: Azide **7e** was prepared according to the general procedure (A) on a 0.1 mmol scale using EtOAc as a solvent. The crude azide was purified by flash column chromatography (first hexane:ether 95:5. The 4 fractions obtained were concentrated and repurified by flash column chromatography using hexanes:CH_2Cl_2) to give **7e** as a white solid in 23% yield (12.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.59 – 7.48 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.94 (tt, *J* = 11.1, 4.9 Hz, 1H), 1.97 (dt, *J* = 12.8, 3.4 Hz, 1H), 1.86 – 1.27 (m, 19H), 1.25 (s, 6H), 1.24 – 0.95 (m, 8H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 4.4 Hz, 3H), 0.85 – 0.79 (m, 1H), 0.72 – 0.67 (m, 1H), 0.66 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.29, 132.80, 131.06, 129.65, 128.38, 74.51, 61.97, 56.53, 56.30, 54.34, 44.84, 42.76, 42.04, 40.10, 36.93, 36.29, 35.86, 35.66, 34.26, 32.14, 29.86, 28.77, 28.41, 27.72, 26.22, 26.16, 24.35, 21.36, 20.90, 18.75, 12.45, 12.23; **ESIHR** (M-N_2+H) calc'd 506.3993, found 506.3984; **FT-IR** 2930, 2850, 2095 (N_3), 1712.



S16

S16 was obtained as a minor product in 7% yield (3.7 mg) from the azidation of the dihydrocholesterol benzoate. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.94 (tt, *J* = 11.0, 4.9 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.92 – 1.13 (m, 26H), 1.13 – 1.05 (m, 1H), 1.04 (s, 3H), 0.97 (m, 2H), 0.89 (d, *J* = 6.3 Hz, 3H),

0.88 (d, J = 2.2 Hz, 3H), 0.88 (s, 3H), 0.87 (d, J = 1.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.28, 132.86, 131.01, 129.67, 128.41, 79.58, 74.23, 56.72, 49.59, 48.28, 44.39, 43.25, 40.25, 39.67, 37.07, 36.15, 34.29, 34.02, 33.06, 28.76, 28.76, 28.58, 28.11, 27.57, 25.39, 24.58, 22.87, 22.81, 21.15, 20.99, 16.97, 12.32; **ESIHR** (M-N_2+H) calc'd 506.3993, found 506.3996; **FT-IR** 2950, 2866, 2099 (N_3), 1715.

Key ^{1}H-^{13}C HMBC correlations that were used to assign the structure are shown in Figure S5.

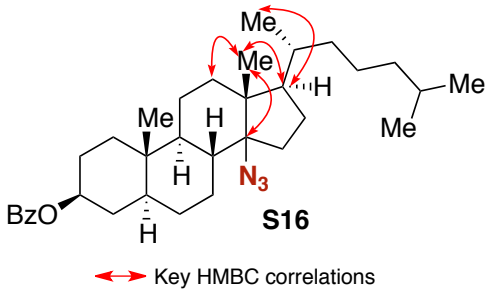
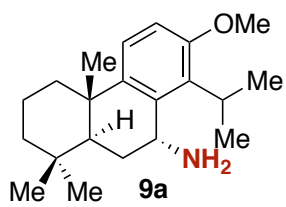
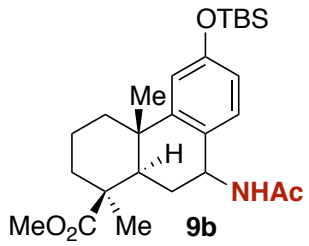


Figure S5 Key HMBC correlations for **S16**.

F. Derivatization of azides.

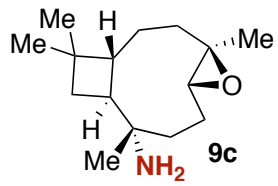


Preparation of amine 9a: In a 4 mL vial, totarol azide **2g** (dr = 5:1, 8.0 mg, 0.023 mmol, 1 equiv) was dissolved in THF (0.3 mL). A 1 M solution of Me_3P (500 µl, 0.500 mmol, 21 equiv) was added, followed by H_2O (4.2 µl, 0.23 mmol, 10 equiv). The reaction mixture was stirred at ambient temperature for 24 hours. The volatile materials were evaporated using a stream of N_2, and the crude amine was purified by flash column chromatography (hexanes:Et_3N 98:2) to give **9a** in 78% yield (7.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 4.29 (dd, J = 4.9, 1.9 Hz, 1H), 3.78 (s, 3H), 3.53 – 3.40 (m, 1H), 2.26 (dd, J = 12.8, 3.7 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.76 (dd, J = 13.8, 2.7 Hz, 2H), 1.67 (dd, J = 12.9, 1.6 Hz, 1H), 1.62 (m, 1H), 1.51 (m, 1H), 1.49 – 1.43 (m, 1H), 1.41 (d, J = 7.0 Hz, 3H), 1.37 (dd, J = 13.0, 3.9 Hz, 1H), 1.32 (d, J = 7.0 Hz, 3H), 1.31 – 1.24 (m, 3H), 1.13 (s, 3H), 0.99 (s, 3H), 0.92 (s, 3H), 0.90 – 0.83 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.21, 142.06, 137.40, 134.36, 123.53, 111.17, 55.15, 47.11, 44.24, 41.61, 39.36, 38.77, 33.35, 33.00, 29.24, 28.24, 25.38, 21.92, 21.18, 21.15, 19.73; **ESIHR** (M+H) calc'd 316.2635, found 316.2594.



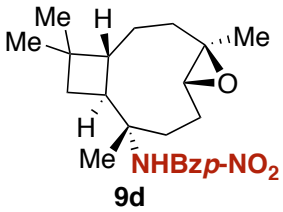
9b

Preparation of acetamide 9b: In a 4 mL vial, the azide **2i** (dr = 5:1, 11.0 mg, 0.0248 mmol, 1 equiv) was dissolved in THF (0.3 mL). A 1M solution of Me_3P (500 µl, 0.500 mmol, 20 equiv) was added followed by H_2O (4.5 µl, 0.25 mmol, 10 equiv). The reaction mixture was stirred at ambient temperature for 24 hours. The volatile materials were evaporated using a stream of N_2, and the crude amine was kept under high vacuum for 2 hours. This crude amine was then dissolved in a mixture of pyridine (0.6 mL) and Ac_2O (0.3 mL) and allowed to stir for 15 hours. Excess pyridine and A_2O were removed under high vacuum, and the residue was purified by flash column chromatography (hexanes:EtOAc 80:20) to give **9b** in 63% yield (7.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.69 (d, *J* = 7.0 Hz, 1H), 5.05 (t, *J* = 5.5 Hz, 1H), 3.64 (s, 3H), 2.39 (d, *J* = 14.6 Hz, 1H), 2.32 (d, *J* = 13.6 Hz, 1H), 2.23 – 2.11 (m, 2H), 1.99 (s, 3H), 1.35 (td, *J* = 13.3, 4.0 Hz, 1H), 1.29 – 1.22 (m, 2H), 1.20 (s, 3H), 1.16 – 1.02 (m, 2H), 0.97 (s, 12H), 0.17 (dd, *J* = 4.3, 1.6 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.72, 168.84, 155.54, 150.48, 131.44, 126.94, 118.65, 116.88, 51.45, 48.40, 47.41, 43.66, 39.37, 38.52, 37.83, 28.45, 27.36, 25.86, 23.71, 22.05, 19.95, 18.39, -4.21, -4.22; **ESIHR** (M+H) calc'd 460.2878, found.



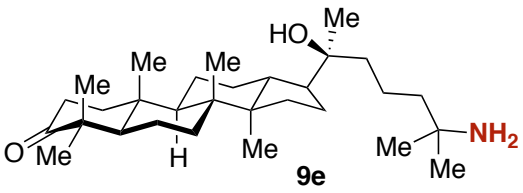
9c

Preparation of amine 9c: Caryophyllene azide **3i** (20.0 mg, 0.0759 mmol, 1 equiv) was dissolved in EtOAc (1 mL) in a 20 mL vial. Pd/C (10%, 16.2 mg, 0.0152 mmol, 0.2 equiv) was added, vial was closed with septa and a balloon containing hydrogen was attached. The reaction mixture was allowed to stir at ambient temperature for 20 hours. Pd/C was removed by filtration and washed with EtOAc (2 x 5 mL). The combined EtOAc solution was concentrated to yield amine **9c** in 98% yield (17.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.82 (dd, *J* = 9.7, 5.7 Hz, 1H), 2.18 (ddt, *J* = 14.2, 12.3, 6.2 Hz, 1H), 2.08 (dt, *J* = 12.8, 3.6 Hz, 1H), 1.98 (q, *J* = 9.2 Hz, 1H), 1.75 – 1.61 (m, 4H), 1.56 (m, 2H), 1.53 – 1.30 (m, 5H), 1.29 (s, 3H), 1.21 (s, 3H), 0.96 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 61.01, 59.42, 53.96, 53.40, 47.36, 40.45, 40.44, 35.62, 31.89, 30.26, 29.09, 25.32, 23.32, 21.68, 16.37; **ESIHR** (M+H) calc'd 238.2165, found 238.2177.



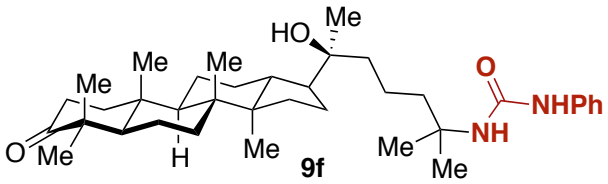
9d

Preparation of amide 9d: Caryophyllene oxide amine **9c** (11.0 mg, 0.0463 mmol, 1 equiv) was dissolved in CH_2Cl_2 (1.0 mL) and cooled to 0 °C. Pyridine (19 µl, 0.23 mmol, 5 equiv) and a small crystal of DMAP, followed by *p*-NO_2BzCl (12.9 mg, 0.0695 mmol, 1.5 equiv), were added, and the cooling bath was removed. The reaction mixture was stirred at ambient temperature for 24 hours then diluted with ether (30 mL). The organic layer was washed with a saturated solution of $NaHCO_3$ (15 mL) and dried over $MgSO_4$. $MgSO_4$ was removed by filtration and the resulting solution was concentrated. The crude amide was purified by flash column chromatography to give **9d** in 92% yield as off white solid (16.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 5.87 (s, 1H), 2.88 (q, *J* = 9.3 Hz, 1H), 2.82 (dd, *J* = 9.6, 5.5 Hz, 1H), 2.46 – 2.21 (m, 3H), 2.12 (dt, *J* = 13.0, 3.6 Hz, 1H), 1.78 – 1.54 (m, 6H), 1.53 (s, 3H), 1.46 – 1.38 (m, 1H), 1.36 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.45, 149.55, 141.56, 127.90, 123.98, 60.96, 60.19, 59.38, 48.74, 46.15, 40.31, 36.90, 35.92, 32.06, 30.34, 29.00, 24.98, 23.42, 18.69, 16.53; **ESIHR** (M+H) calc'd 387.2278, found 387.2274.



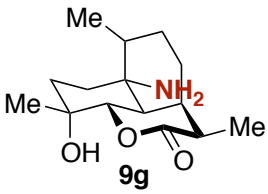
9e

Preparation of amine 9e: Azide **3e** (10.0 mg, 0.0206 mmol, 1 equiv) was dissolved in EtOAc (1 mL). Pd/C (10%, 4.4 mg, 0.041 mmol, 0.2 equiv) was added, and a balloon containing hydrogen was attached. The reaction mixture was allowed to stir at ambient temperature for 20 hours. The Pd/C was removed by filtration, and the resulting solution was concentrated to yield amine **9e** in 99% yield (9.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.50 (ddd, *J* = 16.5, 9.5, 7.7 Hz, 1H), 2.42 (ddd, *J* = 15.5, 7.7, 4.4 Hz, 1H), 1.90 (ddd, *J* = 12.5, 7.6, 4.4 Hz, 1H), 1.85 – 1.18 (m, 26H), 1.43 (s, 3H), 1.42 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H), 1.01 (s, 3H), 0.93 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 218.29, 75.86, 55.42, 50.51, 50.41, 50.10, 47.56, 42.62, 41.21, 40.42, 40.36, 40.02, 36.94, 34.63, 34.24, 31.35, 27.63, 26.82, 26.47, 25.68, 25.17, 24.67, 22.16, 21.14, 19.76, 18.08, 16.56, 16.18, 15.31, 14.28; **ESIHR** (M+H) calc'd 460.4149, found 460.4154.



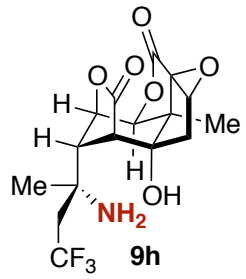
9f

Preparation of urea 9f: Dipterocarpol amine **9e** (7.0 mg, 0.0152 mmol, 1 equiv) was dissolved in CH_2Cl_2 (1.0 mL) and cooled to 0 °C. Pyridine (13 µl, 0.16 mmol, 11 equiv), followed by phenylisocyanate (5 µl, 0.05 mmol, 3 equiv) was added, and the cooling bath was removed. The reaction mixture was stirred at ambient temperature for 24 hours, then diluted with ether (30 mL) and washed with a saturated solution of $NaHCO_3$ (15 mL). The ether layer was dried over $MgSO_4$, filtered, and concentrated. The crude urea was purified by flash column chromatography to give **9f** in 83% yield as white solid (7.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.09 – 6.99 (m, 1H), 6.28 (s, 1H), 4.63 (s, 1H), 2.56 – 2.36 (m, 2H), 1.88 (ddd, *J* = 12.7, 7.5, 4.5 Hz, 1H), 1.84 – 1.15 (m, 24H), 1.33 (s, 3H), 1.33 (s, 3H) 1.12 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (151 MHz, DMSO) δ 218.32, 154.99, 138.87, 129.43, 123.85, 121.11, 75.79, 55.52, 53.66, 50.40, 50.22, 50.13, 47.60, 42.61, 41.48, 40.58, 40.40, 40.03, 36.96, 34.68, 34.28, 31.31, 29.85, 27.75, 27.63, 26.83, 25.51, 25.06, 22.16, 21.17, 19.78, 18.35, 16.49, 16.15, 15.33; **ESIHR** (M+Na) calc'd 601.4340, found 601.4343.

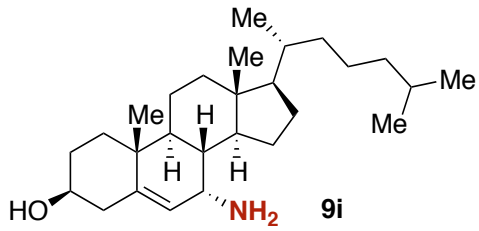


9g

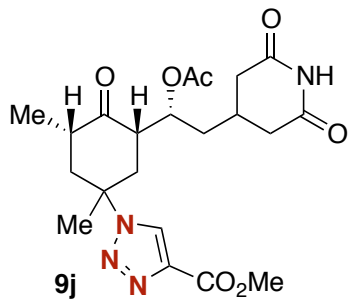
Preparation of amine 9g: Azide **3f** (10.0 mg, 0.0341 mmol, 1 equiv) was dissolved in MeOH (0.5 mL). PtO_2 (1.6 mg, 0.0068 mmol, 0.2 equiv) was added, and a balloon containing hydrogen was attached. The reaction mixture was allowed to stir at ambient temperature for 20 hours. PtO_2 was removed by filtration and the resulting solution was concentrated. The crude amine was purified by flash column chromatography ($CHCl_3$:MeOH:Et_3N 97:2:1) to yield amine **9g** in 86% yield (7.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.34 (d, *J* = 11.8 Hz, 1H), 2.70 – 2.57 (m, 1H), 2.33 (ddt, *J* = 13.6, 5.8, 3.9 Hz, 1H), 2.11 (dd, *J* = 11.7, 3.6 Hz, 1H), 1.83 –1.36 (m, 12H), 1.34 (s, 3H), 1.21 (d, *J* = 7.3 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.00, 81.00, 70.27, 53.99, 44.61, 40.39, 33.86, 33.12, 32.58, 30.28, 29.82, 27.16, 22.81, 14.55, 13.53; **ESIHR** (M+H) calc'd 268.1907, found 268.1890, (2M+H) calc'd 535.3742, found 535.3722.



Preparation of picrotoxinin amine 9h: Picrotoxinin azide **6b** (18.0 mg, 0.0449 mmol, 1 equiv) was dissolved in MeOH (1 mL). PtO_2 (2.04 mg, 0.00897 mmol, 0.2 equiv) was added, and a balloon containing hydrogen was attached. The reaction mixture was allowed to stir at ambient temperature for 20 hours. PtO_2 was removed by filtration, and the resulting solution was concentrated to yield amine **9h** in 98% yield (16.5 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 5.28 – 5.10 (m, 2H), 3.64 – 3.56 (m, 1H), 3.09 (t, J = 4.3 Hz, 1H), 2.97 – 2.77 (m, 3H), 2.73 (dd, J = 14.8, 3.5 Hz, 1H), 2.11 – 2.06 (m, 3H), 1.99 (d, J = 14.9 Hz, 1H), 1.57 – 1.50 (s, 3H), 1.25 (s, 3H); **^{13}C NMR** (151 MHz, Acetone-d_6) δ 174.80, 170.12, 127.47 (q, J = 278.0 Hz), 85.60, 80.41, 78.10, 74.23, 62.80, 54.41, 51.38, 50.39, 48.45, 45.09 (q, J = 25.7 Hz), 43.93, 26.28 (q, J = 1.27 Hz), 16.52; **^{19}F NMR** (376 MHz, Acetone-d_6) δ -59.25 (t, J = 11.5 Hz); **ESIHR** (M+Na) calc'd 400.0978, found 400.0932.

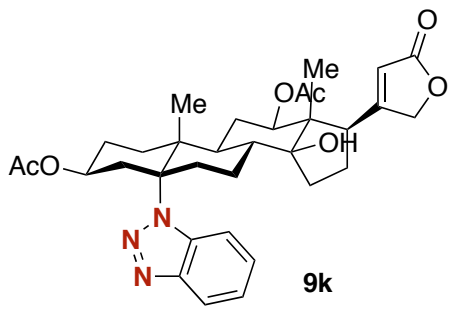


Preparation of amine 9i: In an N_2 filled glovebox, in a 4 mL vial, azide **7e** (14.0 mg, 0.0263 mmol, 1 equiv) was dissolved in THF (1.0 mL), and $LiAlH_4$ (3.0 mg, 0.079 mmol, 3 equiv) was added at ambient temperature. The vial was sealed with a PTFE lined cap and heated at 65 °C for 6 hours. The reaction mixture was cooled to ambient temperature and sequentially treated with H_2O (3 µl), a 20% NaOH solution (3 µl), and H_2O (9 µl). The solids were removed by filtration and the resulting solution was concentrated. The crude mixture was purified by flash column chromatography ($CHCl_3$:MeOH:Et_3N 95:4:1) to yield **9i** in 77% yield (8.1 mg). The ^{1}H and ^{13}C NMR data match those of the reported molecule.[19]



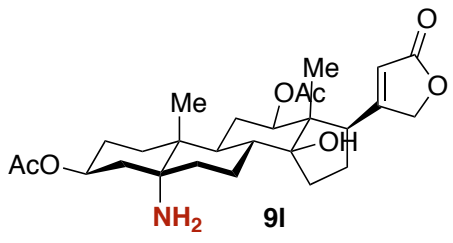
Preparation of triazole 9j: Cycloheximide azide **3a** (8.0 mg, 0.022 mmol, 1 equiv) was dissolved in methyl propiolate (400 µl, 4.39 mmol, 200 equiv) and heated to 65 °C. The reaction mixture was stirred at this temperature for 4 hours and concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc 30:70) to give **9j** in 71% yield (7.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.10 – 7.92 (m, 1H), 5.41 (ddd, J = 9.4, 6.8, 3.2 Hz, 1H), 3.98

(s, 3H), 3.07 (dt, J = 14.4, 4.6 Hz, 1H), 2.91 (ddd, J = 17.3, 4.3, 1.8 Hz, 1H), 2.84 (dt, J = 14.7, 4.8 Hz, 1H), 2.68 – 2.56 (m, 2H), 2.45 – 2.20 (m, 3H), 2.15 (dq, J = 9.5, 4.7 Hz, 1H), 2.10 (s, 3H), 2.08 – 1.90 (m, 2H), 1.76 – 1.62 (m, 2H), 1.60 (s, 3H), 1.03 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.91, 171.71, 171.61, 170.69, 161.26, 140.78, 125.52, 68.28, 62.31, 52.59, 48.75, 46.25, 40.61, 39.12, 38.73, 38.28, 37.05, 31.29, 27.26, 21.17, 13.81; **ESIHR** (M+Na) calc'd 471.1850, found 471.1840.



9k

Preparation of benzotriazole 9k: In an N_2 filled glovebox to the solution of azide **3d** (8.7 mg, 0.017 mmol, 1 equiv) and 2-(trimethylsilyl)phenyl triflate (7.6 mg, 0.025 mmol, 1.5 equiv) in acetonitrile was added CsF (7.7 mg, 0.051 mmol, 3 equiv). The reaction mixture was stirred at ambient temperature for 48 hours. The solids were removed by filtration, and the resulting solution was concentrated. The crude product was purified by preparative thin layer chromatography (hexane:EtOAc 70:30) to give **9k** in 37% yield (3.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 5.80 (d, J = 1.8 Hz, 1H), 4.81 (dd, J = 18.0, 1.8 Hz, 1H), 4.75 – 4.65 (m, 2H), 3.90 (p, J = 6.0 Hz, 1H), 3.38 (td, J = 12.4, 3.1 Hz, 1H), 3.17 – 3.04 (m, 1H), 2.97 – 2.80 (m, 2H), 2.57 (dt, J = 14.5, 3.4 Hz, 1H), 2.21 – 1.64 (m, 16H), 1.39 (s, 3H), 1.34 – 1.22 (m, 4H), 0.91 (s, 3H), 0.23 (qd, J = 13.4, 3.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.48, 173.58, 170.61, 170.08, 146.42, 131.96, 126.91, 124.07, 120.76, 118.02, 113.28, 85.58, 73.46, 71.70, 69.34, 54.35, 46.01, 41.56, 40.96, 36.19, 36.15, 32.81, 31.12, 29.47, 27.51, 27.33, 26.49, 21.37, 21.37, 21.27, 19.28, 10.62 (one carbon was not observed because the signal overlapped with that of the $CDCl_3$). **ESIHR** (M+Na) calc'd 614.2837, found 614.2825.



9l

Under an N_2 atmosphere, finely grinded $CuSO_4$ (1.4 mg, 0.0054 mmol, 0.2 equiv.) and $NaBH_4$ (20.5 mg, 0.543 mmol, 20 equiv.) were added to dry MeOH (0.5 mL) that was cooled to 0 ºC. A dark suspension formed. Then, a solution of the azide **3d** (14.0 mg, 0.0272 mmol, 1 equiv)

in THF (0.5 mL) was added dropwise to the above mixture at the same temperature. The resulting mixture was allowed to warm to ambient temperature slowly, and the reaction mixture was stirred until the substrate **3d** was completely consumed. Water (2 mL) was added to quench the reaction. The mixture was diluted with ethyl acetate (30 mL), and the organic layer was washed with saturated solution of $NaHCO_3$ (15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (hexanes:acetone 70:40 with 1% Et_3N) to yield **9l** (11.2 mg, 84% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.84 (s, 1H), 5.15 (tt, *J* = 11.0, 5.5 Hz, 1H), 4.87 (dd, *J* = 18.0, 1.8 Hz, 1H), 4.77 (dd, *J* = 17.9, 1.8 Hz, 1H), 4.62 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.89 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.08 (s, 3H), 2.05-1.99 (m, 1H), 2.01 (s, 3H), 1.98 – 1.86 (m, 2H), 1.85 – 1.79 (m, 1H), 1.76 – 1.49 (m, 10H), 1.41 – 1.34 (m, 2H), 1.30 – 1.21 (m, 1H), 1.20 – 1.15 (m, 1H), 1.00 (s, 3H), 0.89 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.36, 173.42, 170.80, 170.77, 118.19, 85.95, 77.55, 73.43, 70.33, 54.39, 54.15, 46.12, 40.99, 40.70, 38.76, 37.51, 34.97, 33.29, 30.61, 27.35, 26.98, 26.74, 21.54, 21.36, 21.17, 15.60, 10.54; **ESIHR** (M+H) calc'd 490.2799, found 490.2790.

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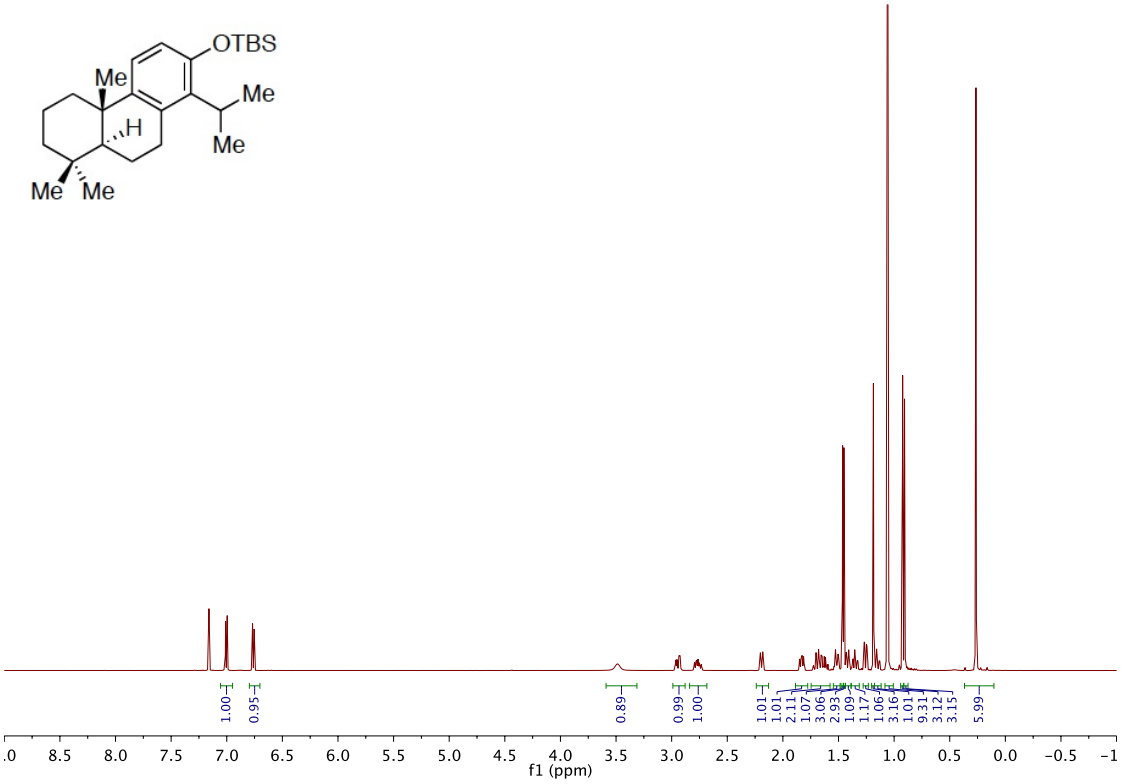
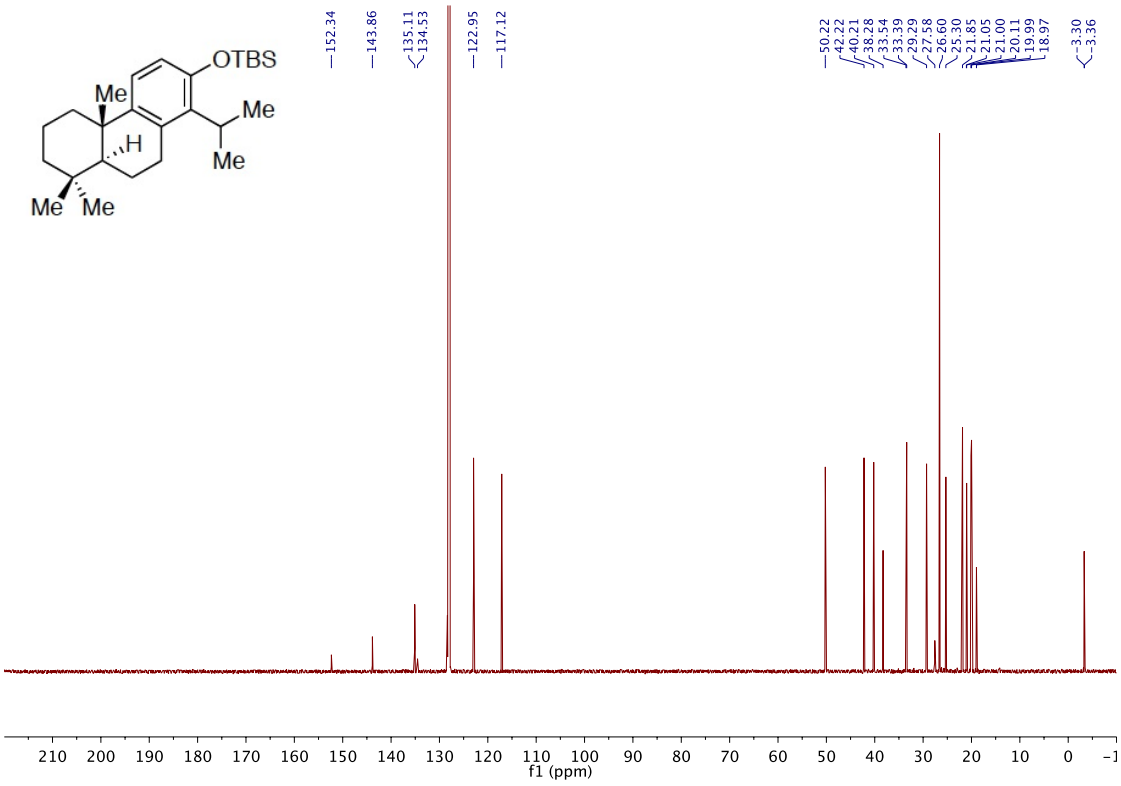
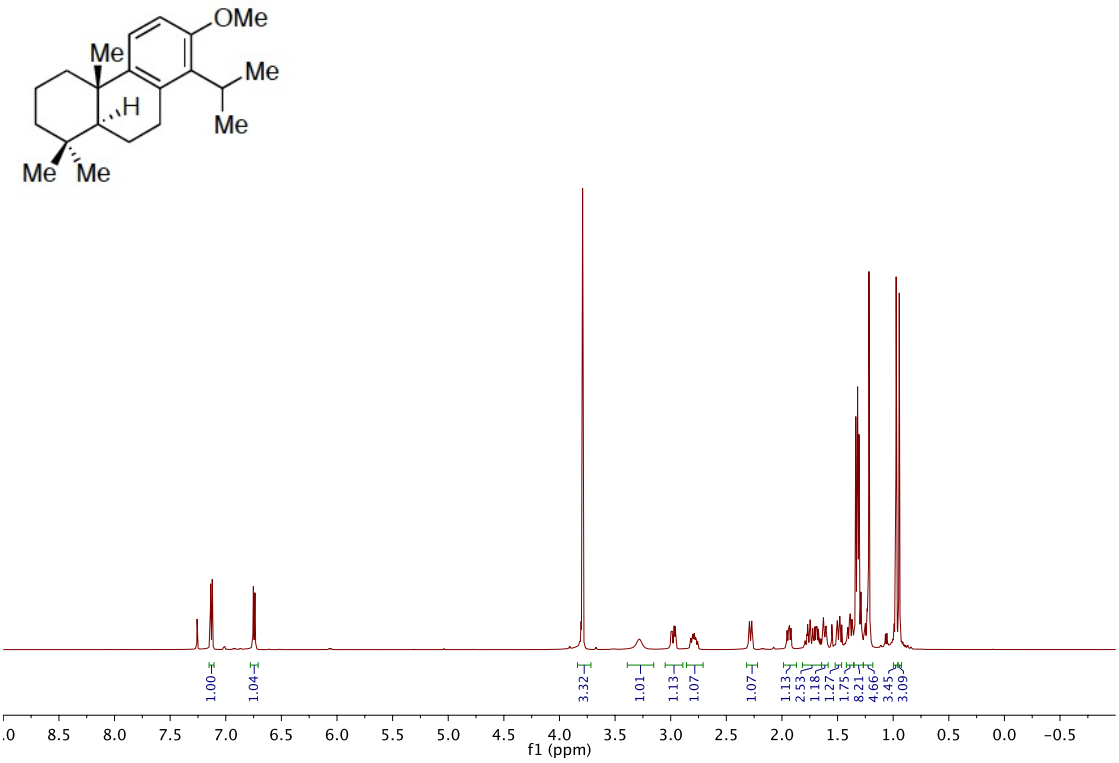
H. NMR Spectra



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Me
H
Me
Me
Me
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1.01
1.13
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2.53
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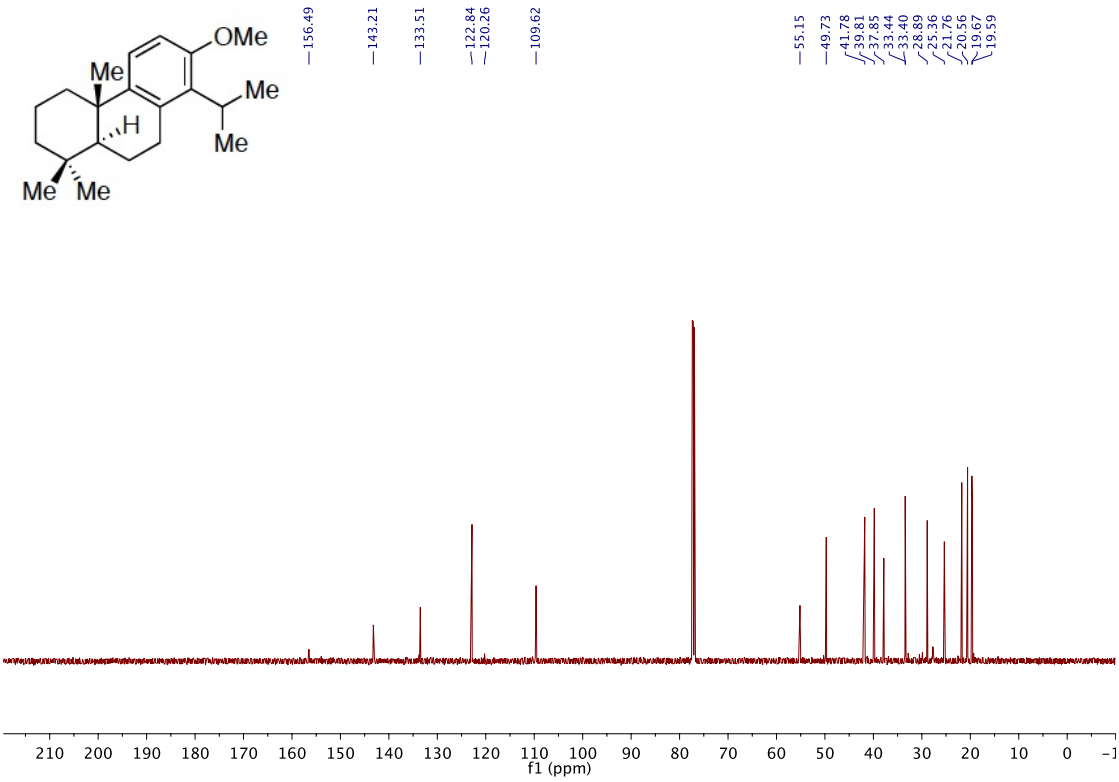
1.27
1.75
8.21
4.66
3.45
3.09
f1 (ppm)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Me
Me
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Me
Me
Me
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28.89
25.36
21.76
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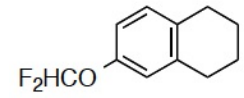
19.59
f1 (ppm)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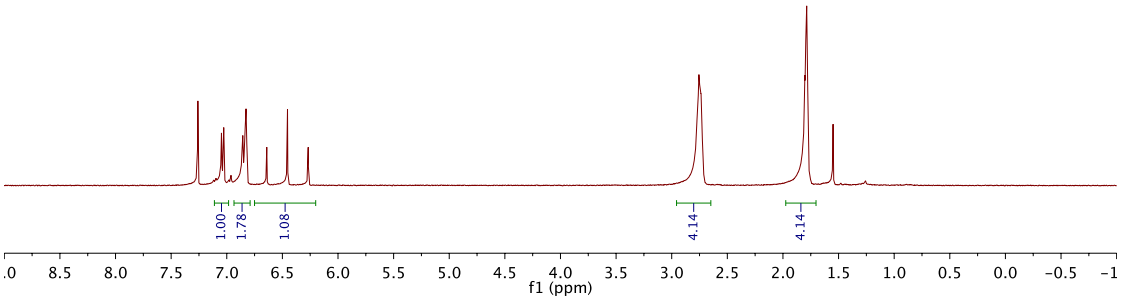
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1.08
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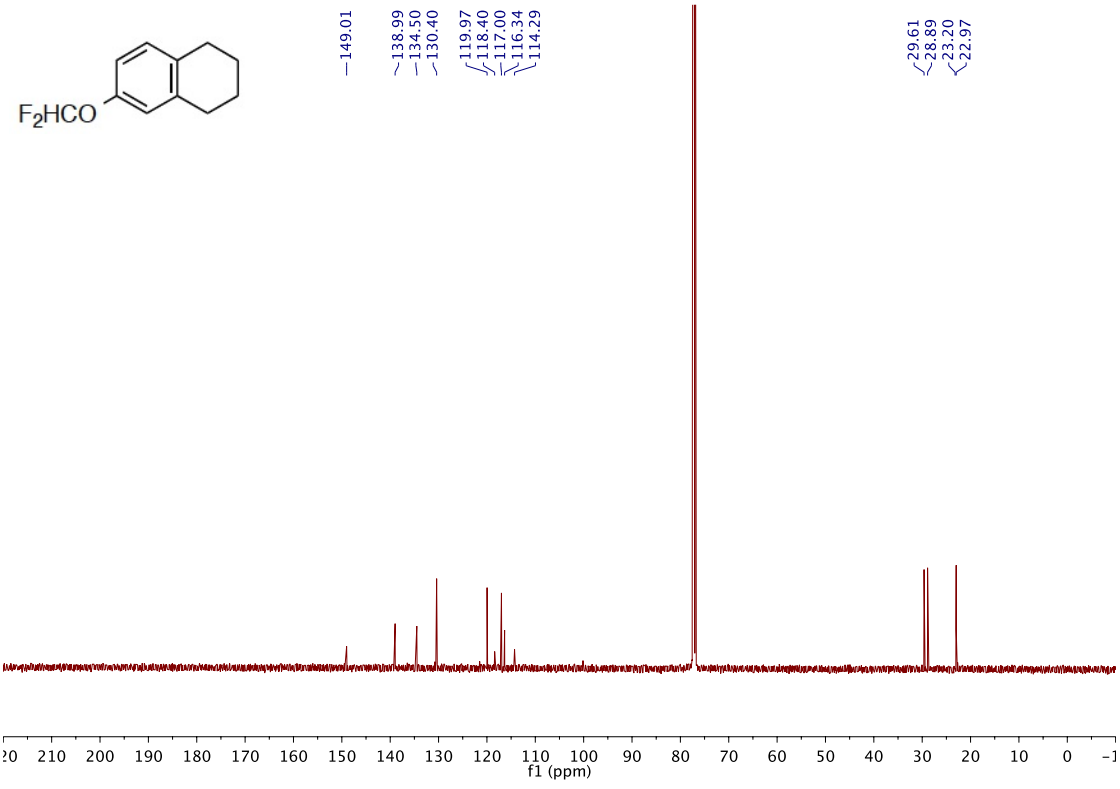
4.14
f1 (ppm)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114.29
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28.89
23.20
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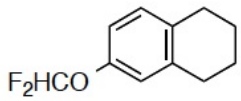
f1 (ppm)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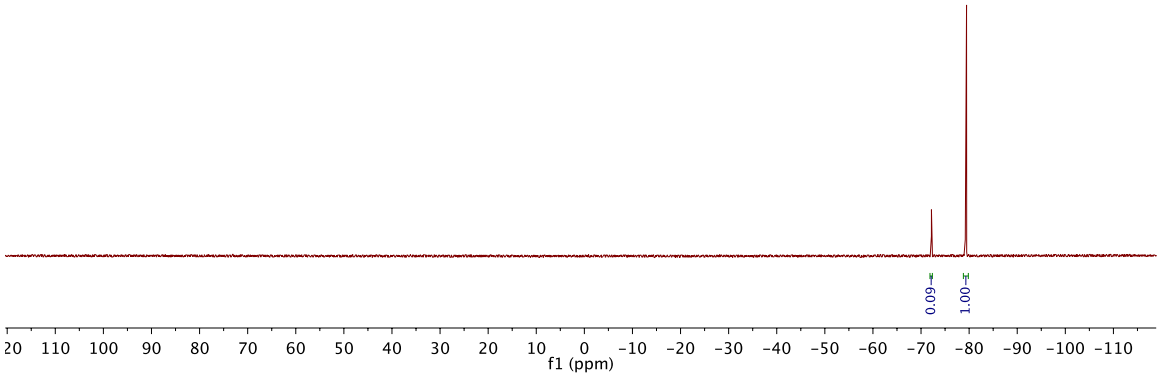
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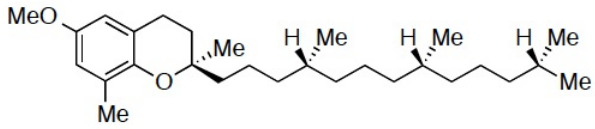
f1 (ppm)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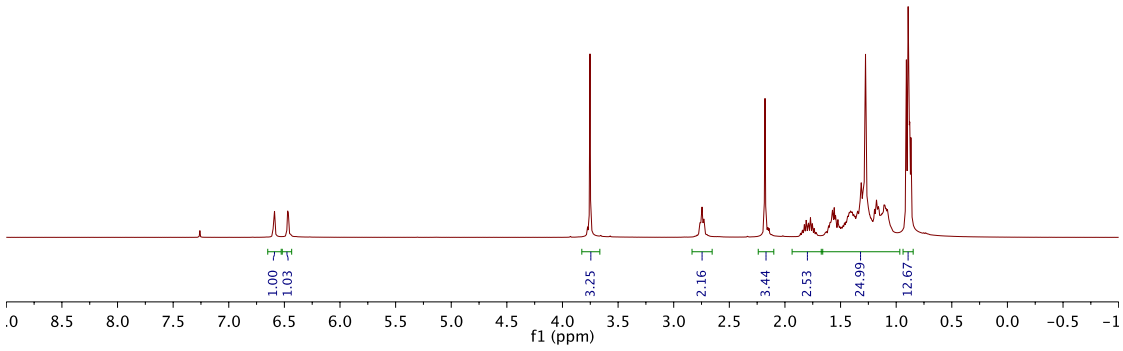
O
Me
H
Me
H
Me
H
Me
Me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2.16
3.44
2.53
24.99
12.67
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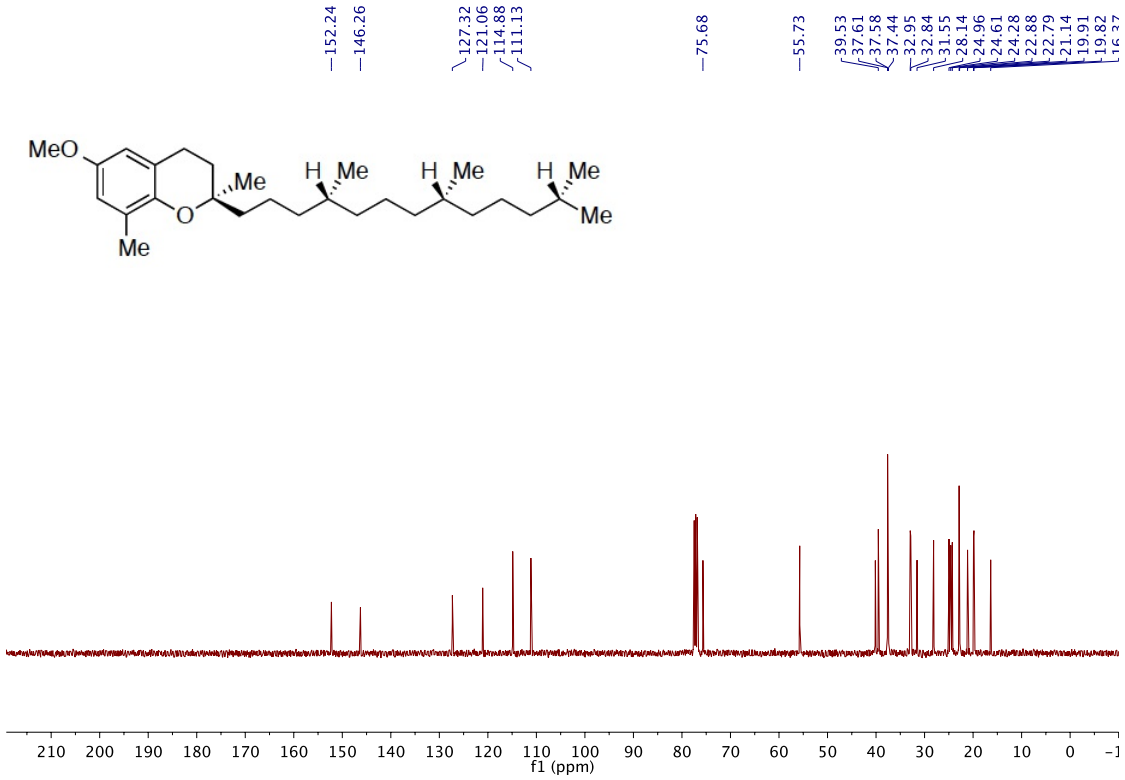
f1 (ppm)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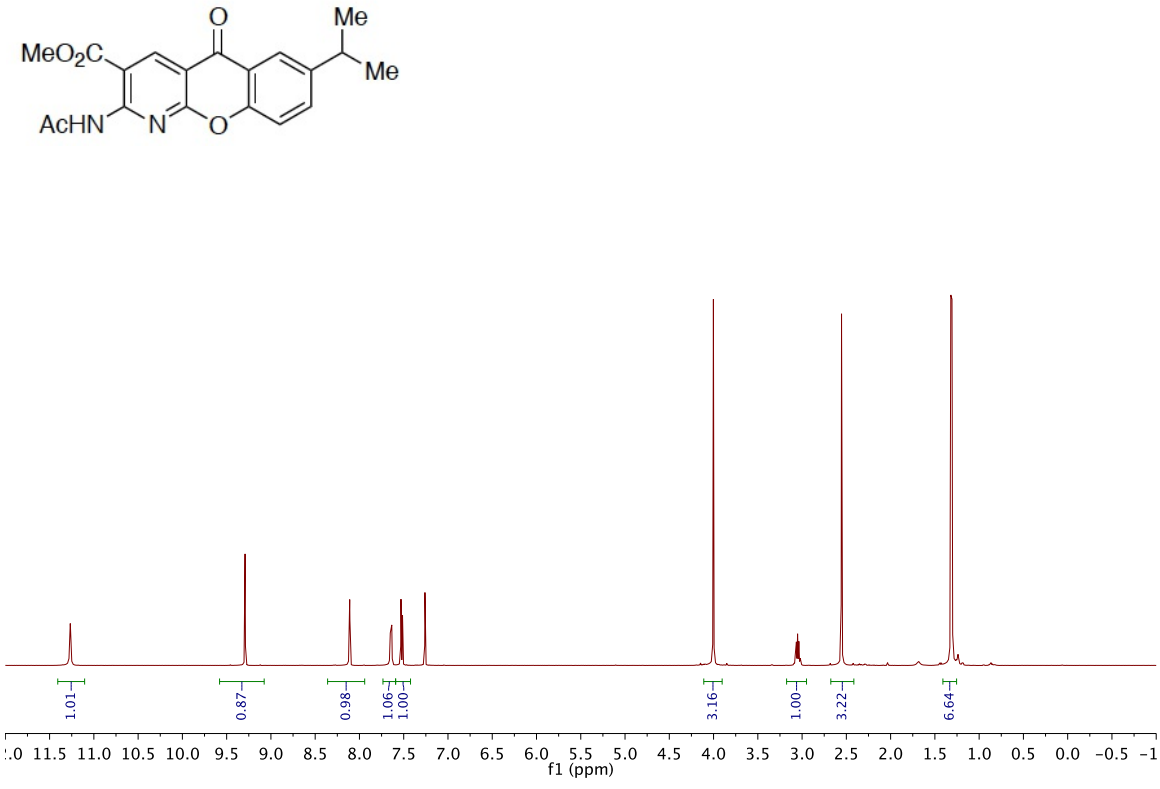
127.32
121.06
114.88
111.13
75.68
55.73
39.53
37.61
37.58
37.44
32.95
32.84
31.55
28.14
24.96
24.61
24.28
22.88
22.79
21.14
19.91
19.82
MeO
Me
H Me
H Me
H Me
Me
Me
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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Me
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O
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1.00
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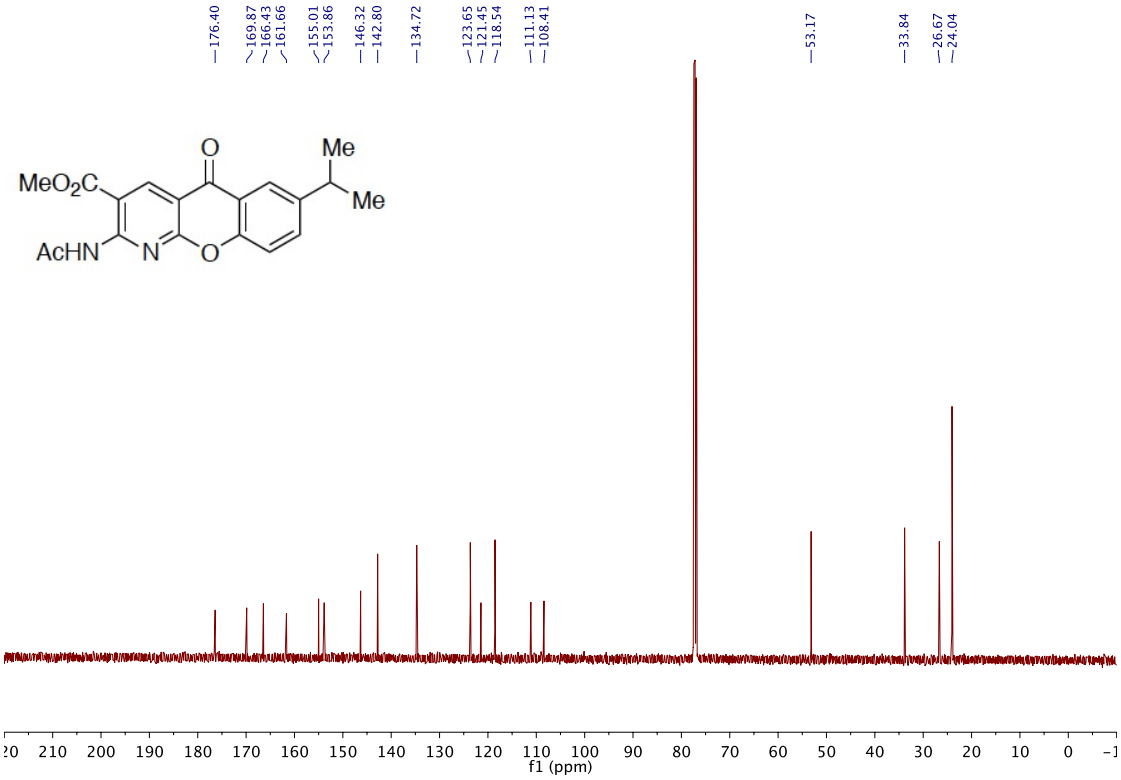
1.00
3.22
6.64
f1 (ppm)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161.66
155.01
153.86
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142.80
134.72
123.65
121.45
118.54
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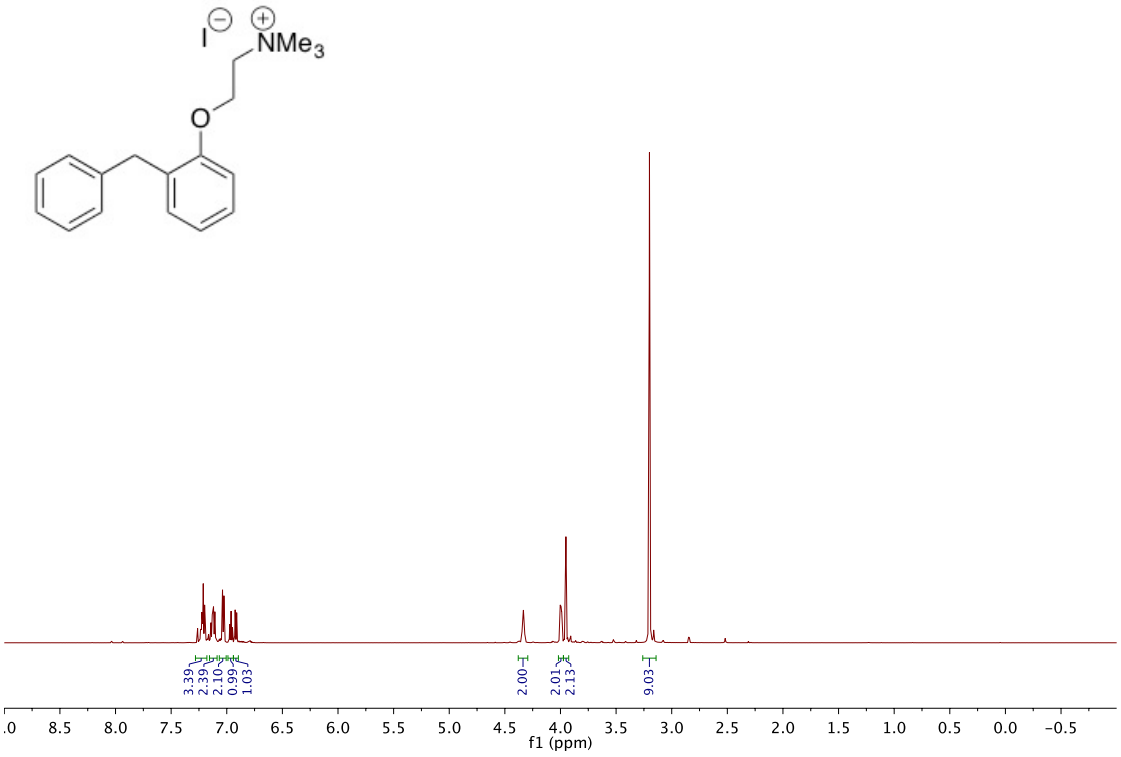
53.17
33.84
26.67
24.04
MeO2C
AcHN
N
O
Me
Me
f1 (ppm)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O
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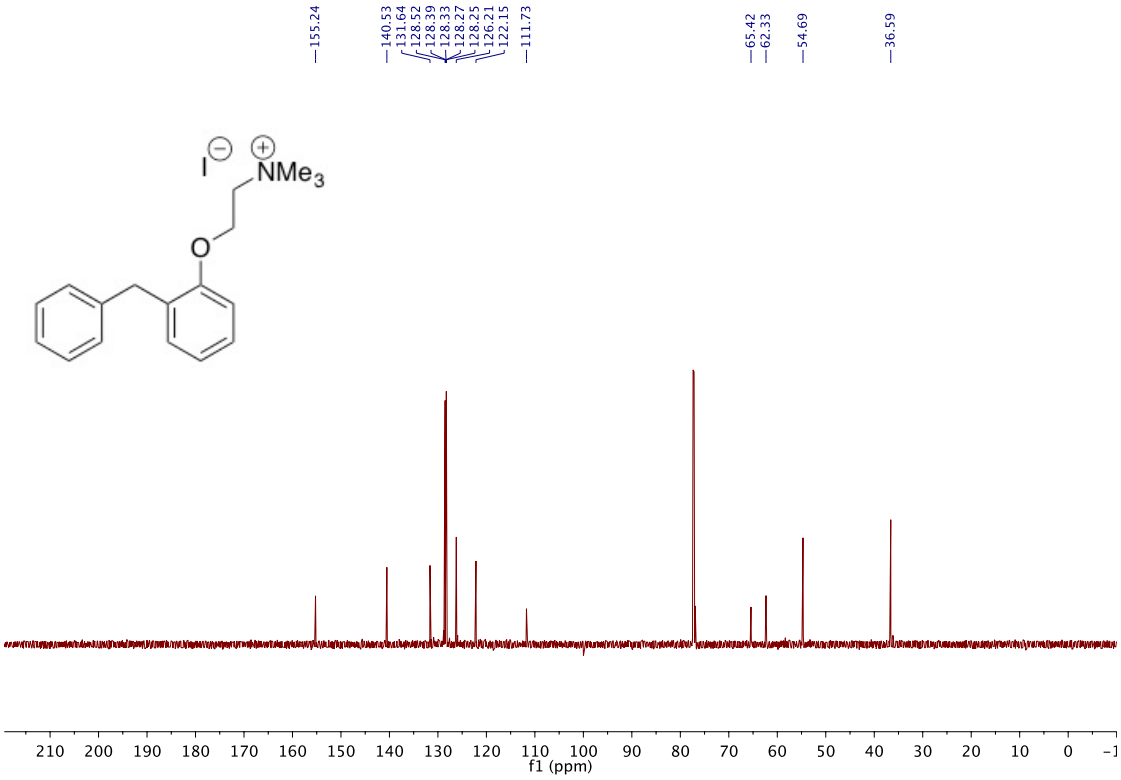
0.99
1.03
2.00
2.01
2.13
9.03
f1 (ppm)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140.53
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128.52
128.39
128.33
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128.25
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122.15
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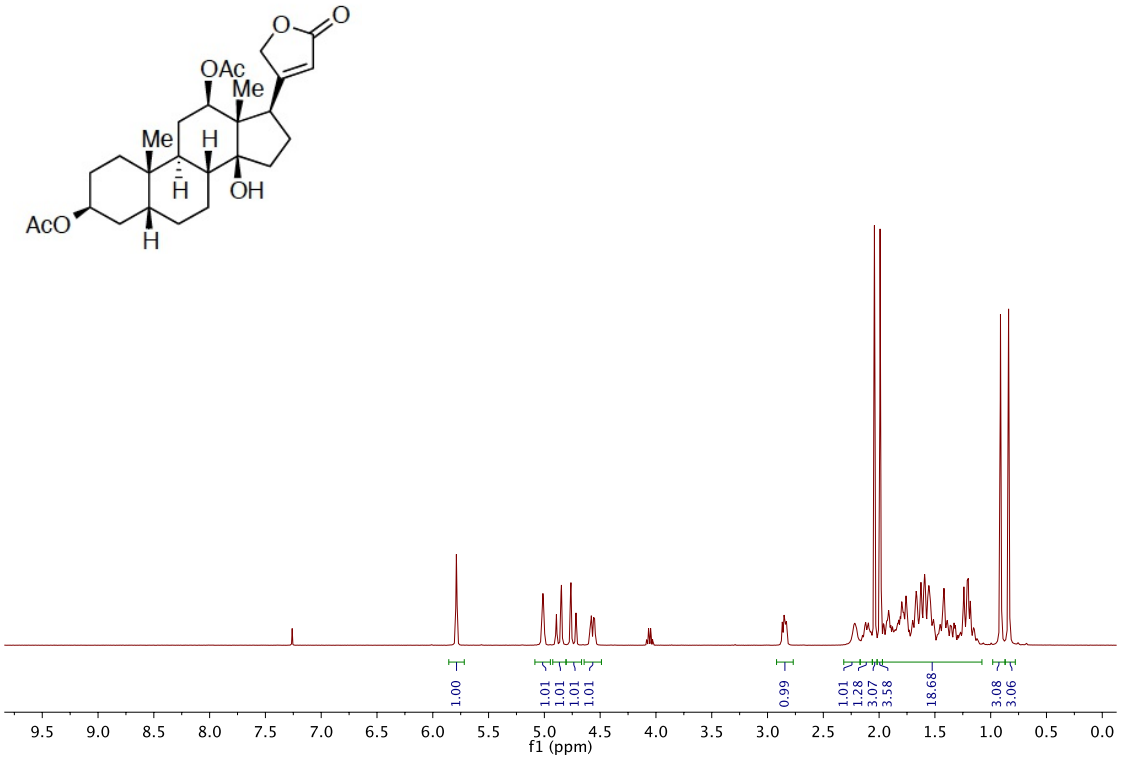
54.69
36.59
I
NMe3
O
f1 (ppm)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O
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Me
Me
H
H
OH
AcO
H
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1.28
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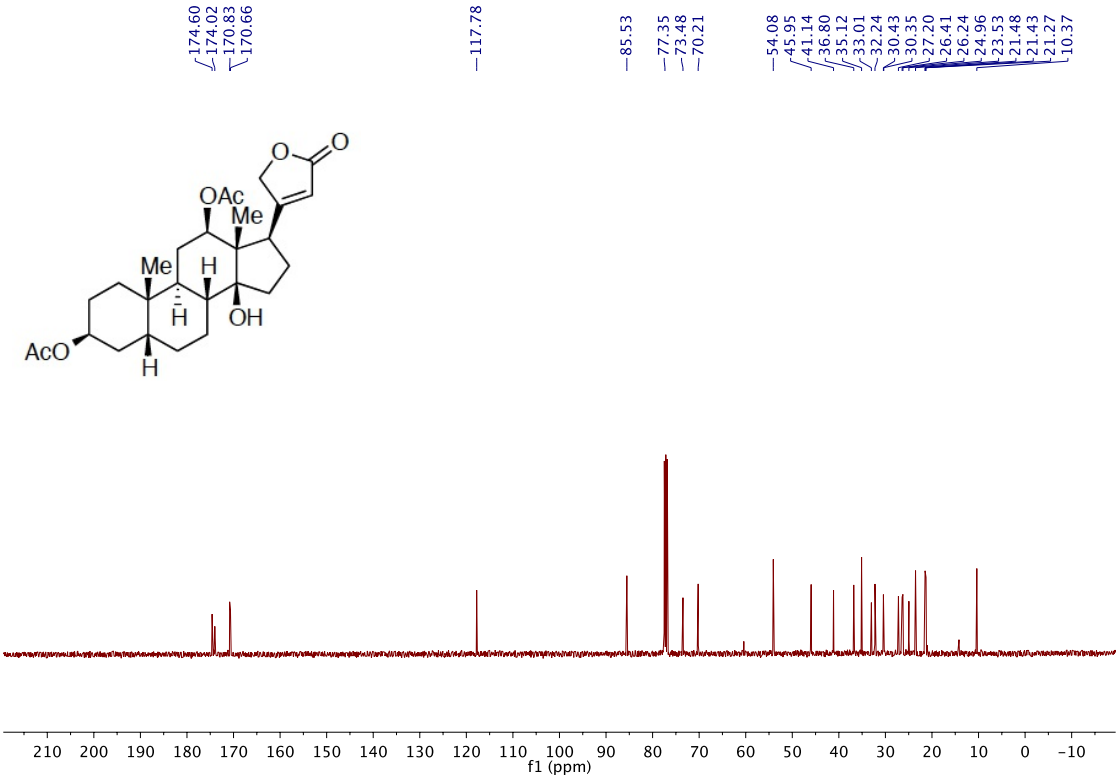
18.68
3.08
3.06
f1 (ppm)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73.48
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54.08
45.95
41.14
36.80
35.12
33.01
32.24
30.43
30.35
27.20
26.41
26.24
24.96
23.53
21.48
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21.27
10.37
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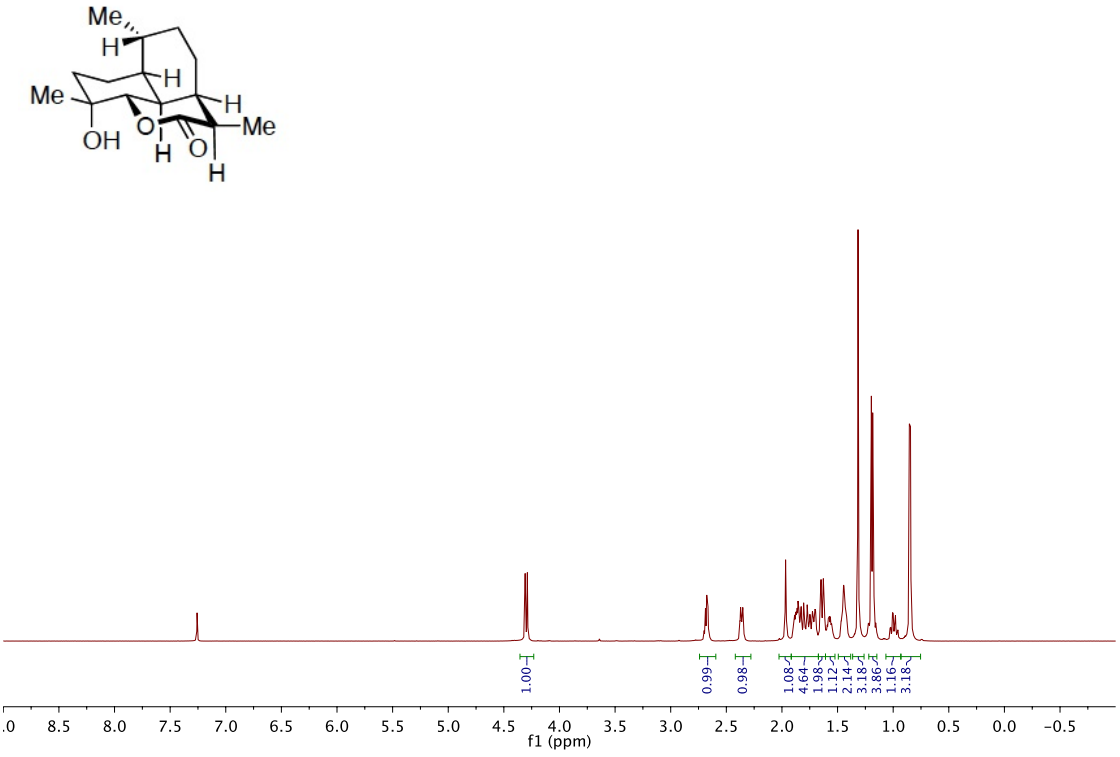
Me
Me
H
H
OH
AcO
H
O
O
f1 (ppm)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H
H
Me
OH
O
H
O
H
Me
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0.99
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1.12
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3.86
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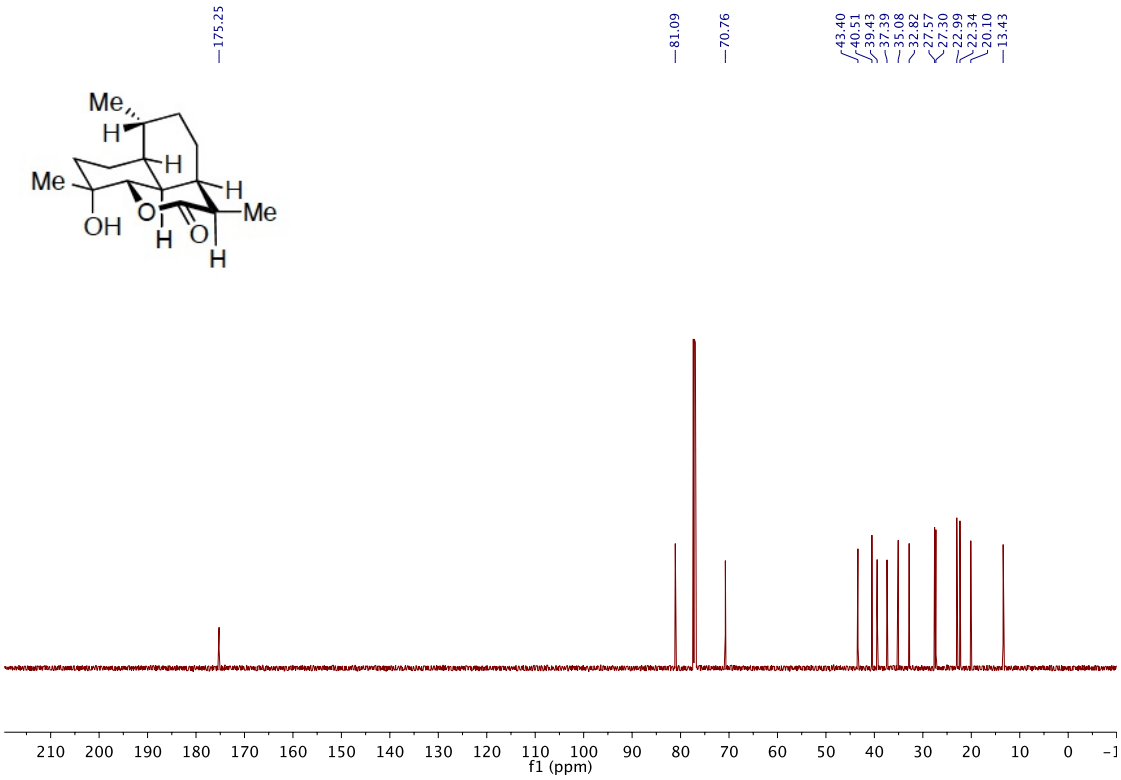
3.18
f1 (ppm)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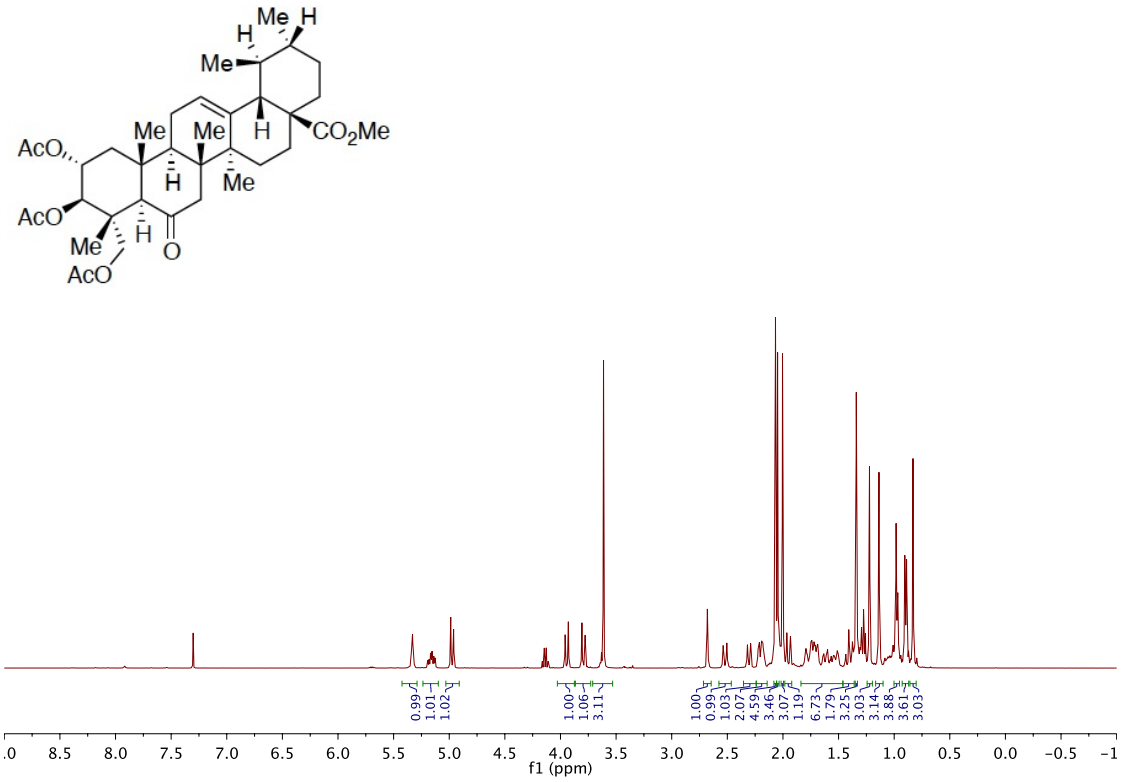
22.99
22.34
20.10
13.43
Me
H
H
Me
H
OH
O
Me
H
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)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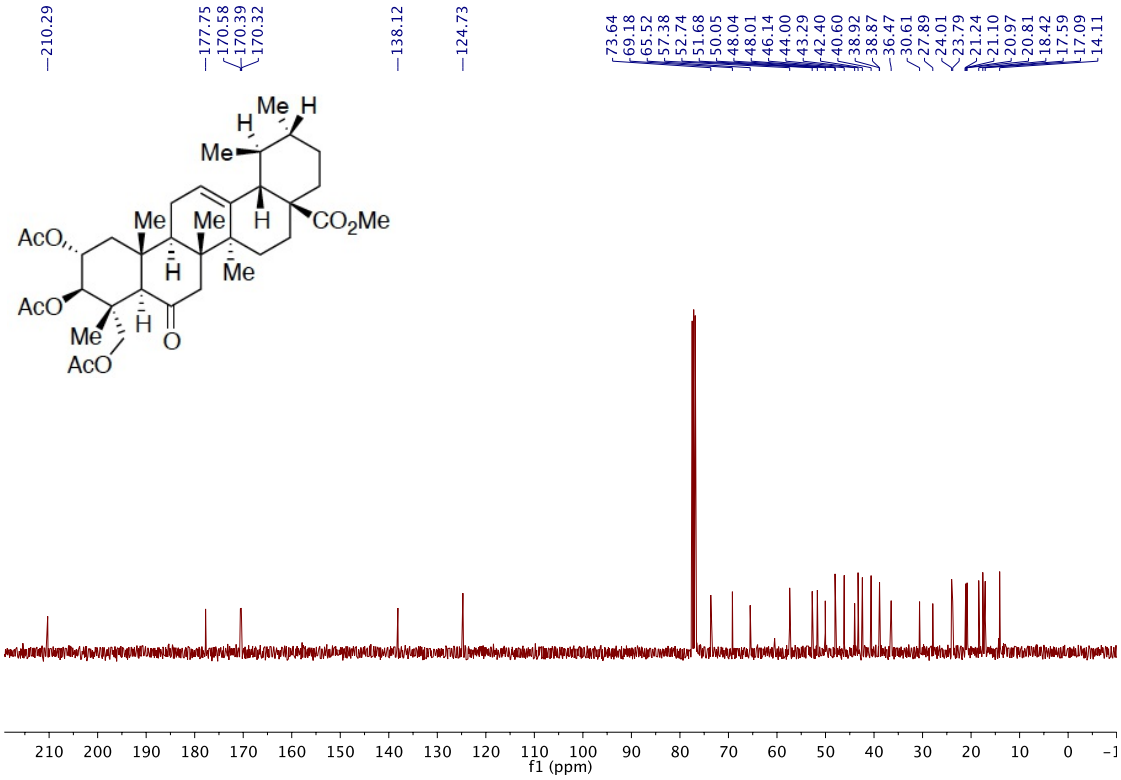
H
H
Me
Me
Me
H
CO2Me
AcO
Me
H
AcO
H
Me
O
AcO
0.99
1.01
1.02
1.00
1.06
3.11
1.00
0.99
1.03
2.07
4.59
3.46
3.07
1.19
6.73
1.79
3.25
3.03
3.14
3.88
3.61
3.03
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)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73.64
69.18
65.52
57.38
52.74
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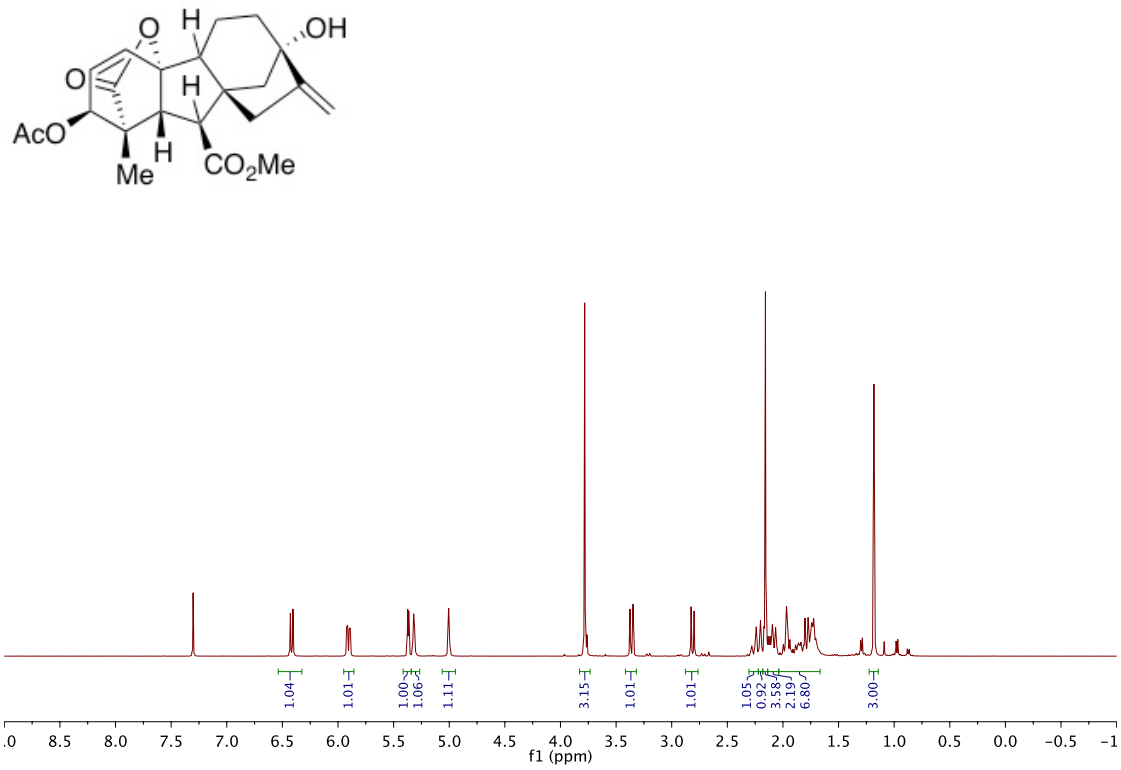
50.05
48.04
48.01
46.14
44.00
43.29
42.40
40.60
38.92
38.87
36.47
30.61
27.89
24.01
23.79
21.24
21.10
20.97
20.81
18.42
17.59
17.09
14.11
Me
H
Me
H
Me
Me
H
CO2Me
AcO
AcO
H
Me
Me
H
O
AcO
f1 (ppm)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H
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O
H
AcO
H
Me
CO2Me
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1.01
1.00
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1.01
1.01
1.05
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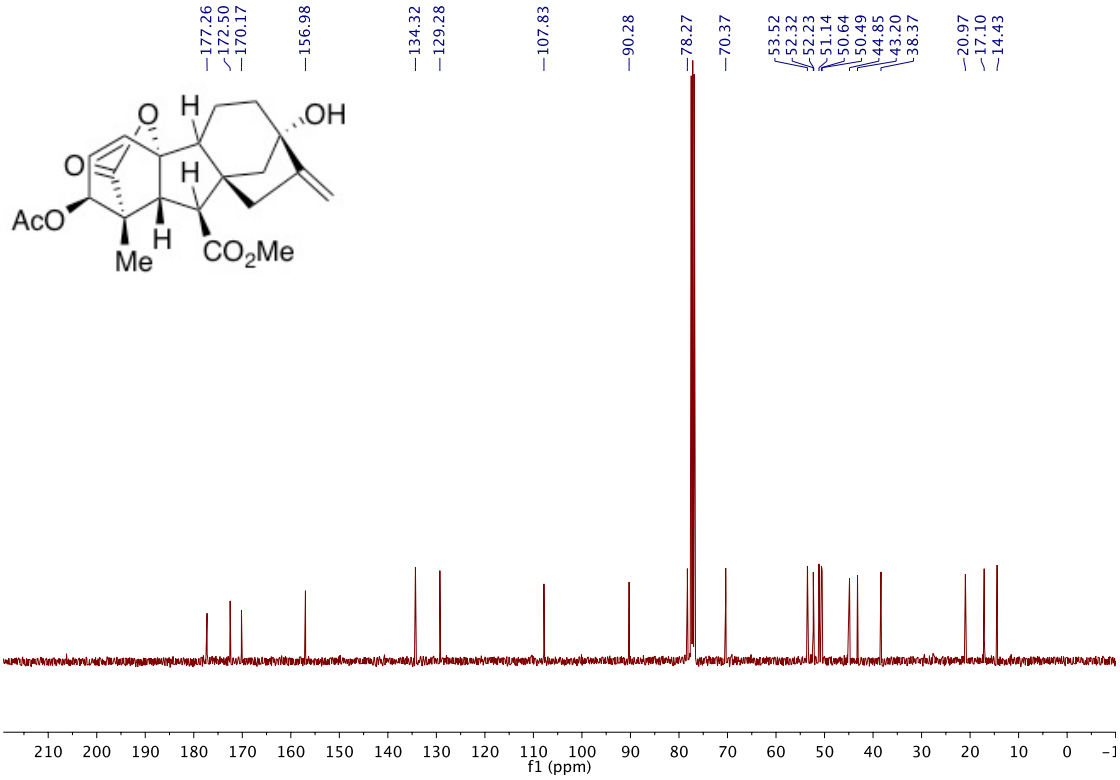
3.00
f1 (ppm)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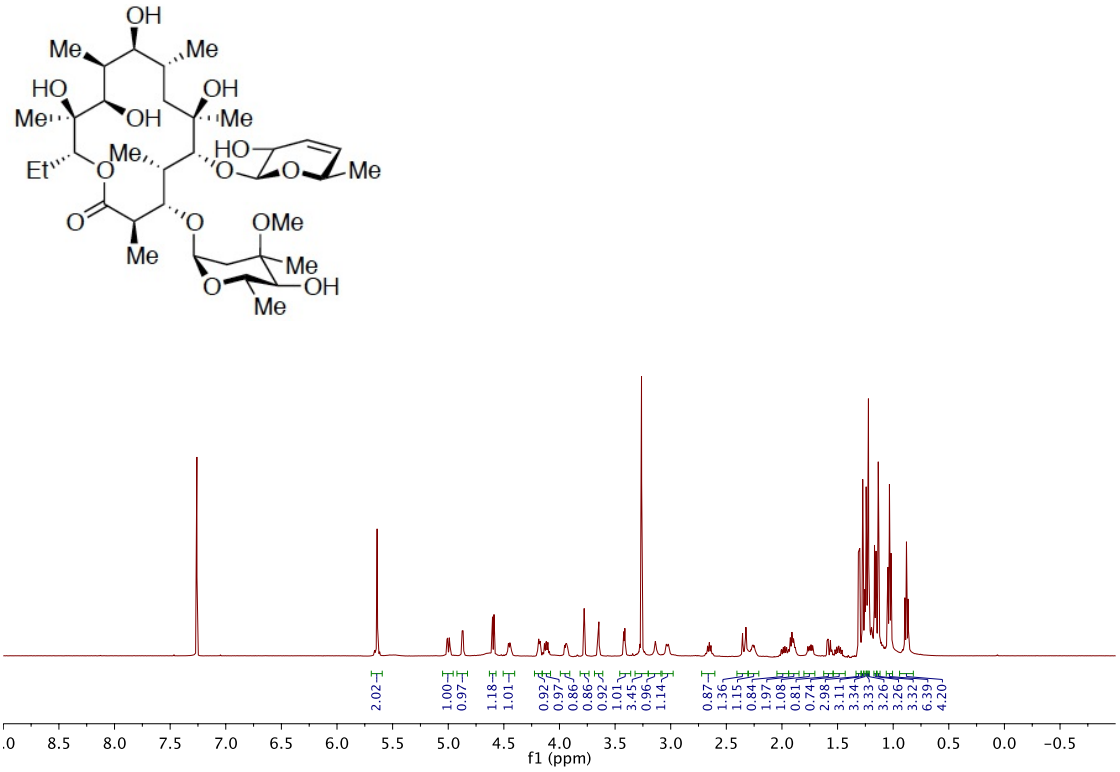
129.28
107.83
90.28
78.27
70.37
53.52
52.32
52.23
51.14
50.64
50.49
44.85
43.20
38.37
20.97
17.10
14.43
O
H
OH
O
H
AcO
H
Me
CO2Me
f1 (ppm)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Me
Me
HO
OH
Me
Me
OH
Me
HO
Et
O
O
Me
Me
O
O
OMe
Me
Me
OH
O
Me
2.02
1.00
0.97
1.18
1.01
0.92
0.97
0.86
0.86
0.92
1.01
3.45
0.96
1.14
0.87
1.36
1.15
0.84
1.97
1.08
0.81
0.74
2.98
3.11
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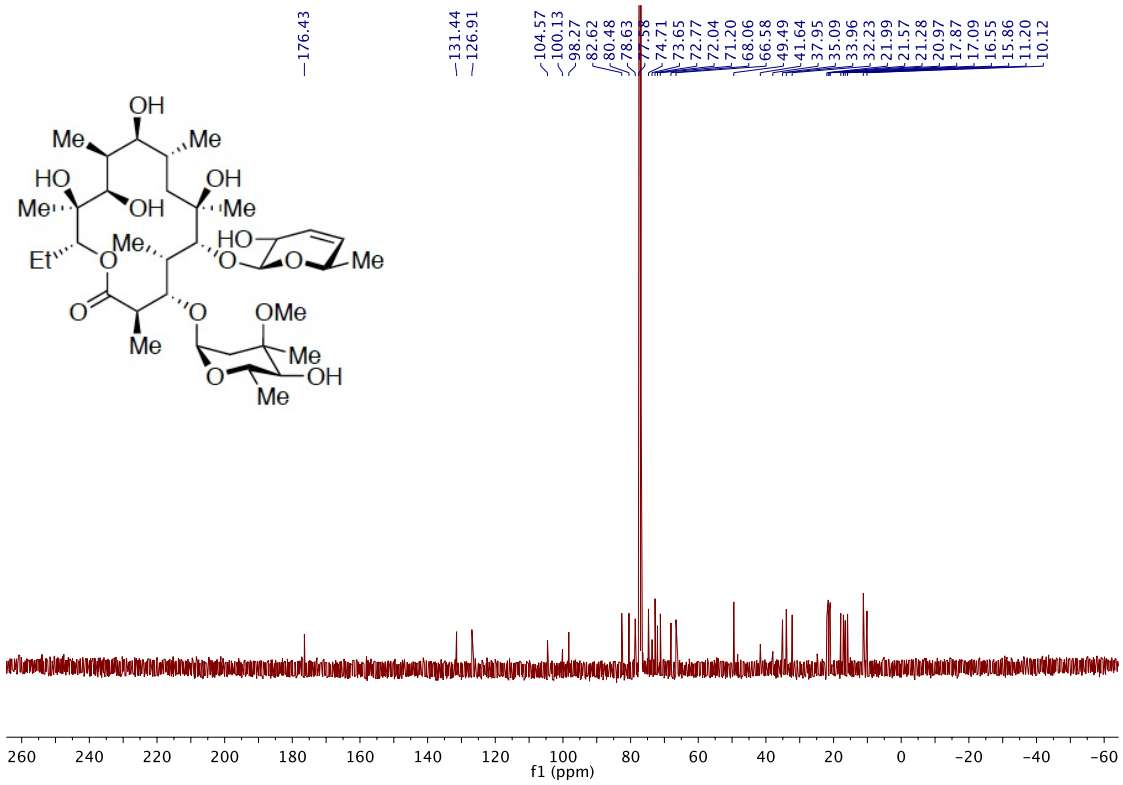
3.33
3.26
3.26
3.32
6.39
4.20
f1 (ppm)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78.63
77.58
74.71
73.65
72.77
72.04
71.20
68.06
66.58
49.49
41.64
37.95
35.09
33.96
32.23
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17.87
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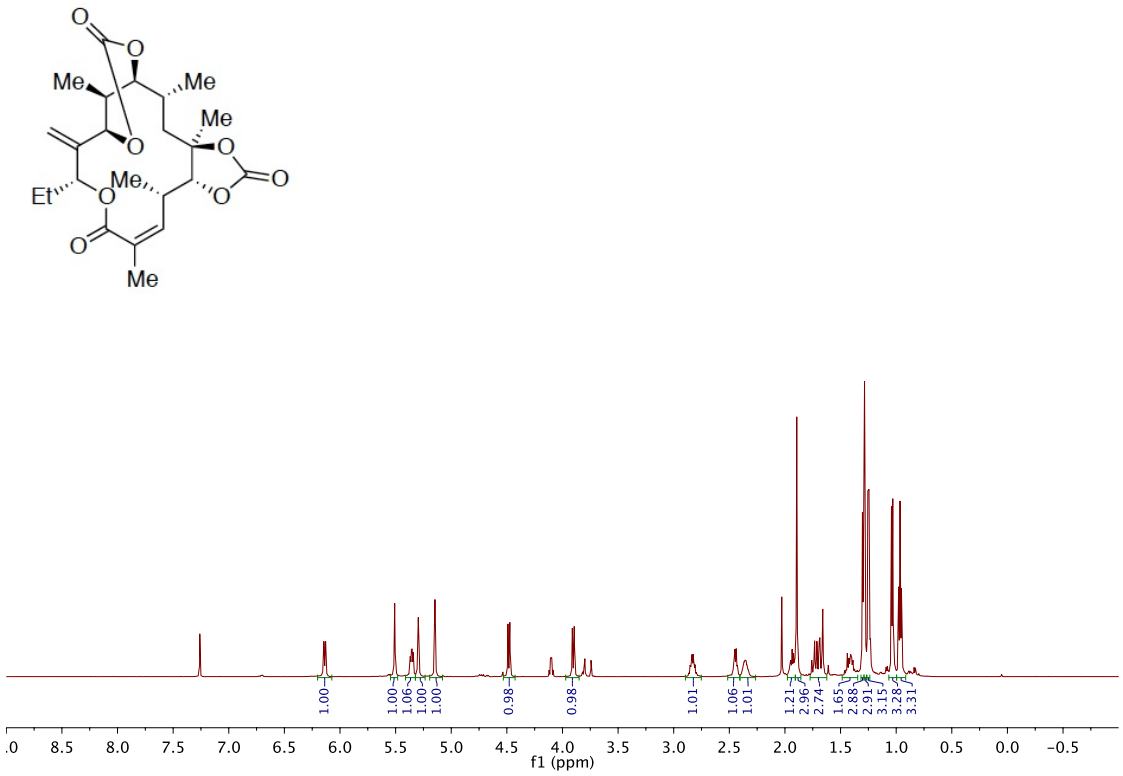
15.86
11.20
10.12
f1 (ppm)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1.00
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1.00
0.98
0.98
1.01
1.06
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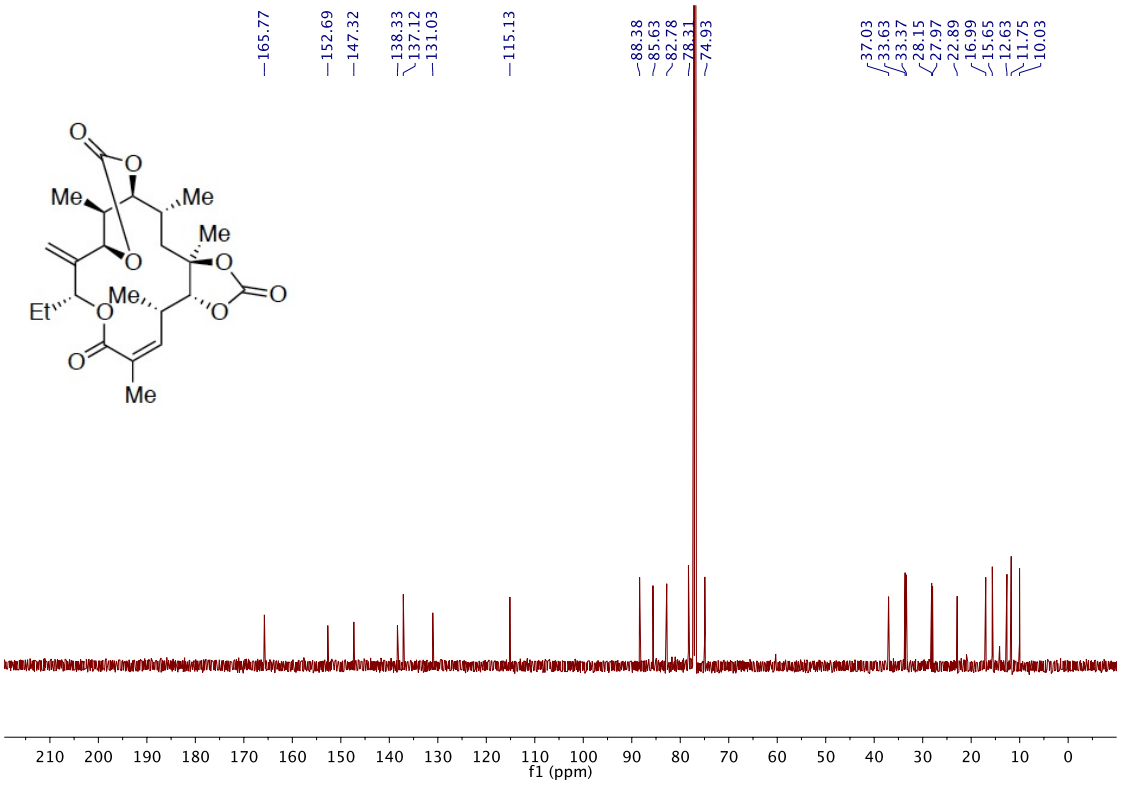
2.74
1.65
2.88
2.91
3.15
3.28
3.31
f1 (ppm)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137.12
131.03
115.13
88.38
85.63
82.78
78.31
74.93
37.03
33.63
33.37
28.15
27.97
22.89
16.99
15.65
12.63
11.75
10.03
O
O
Me
Me
Me
O
O
O
Me
Et
O
O
O
Me
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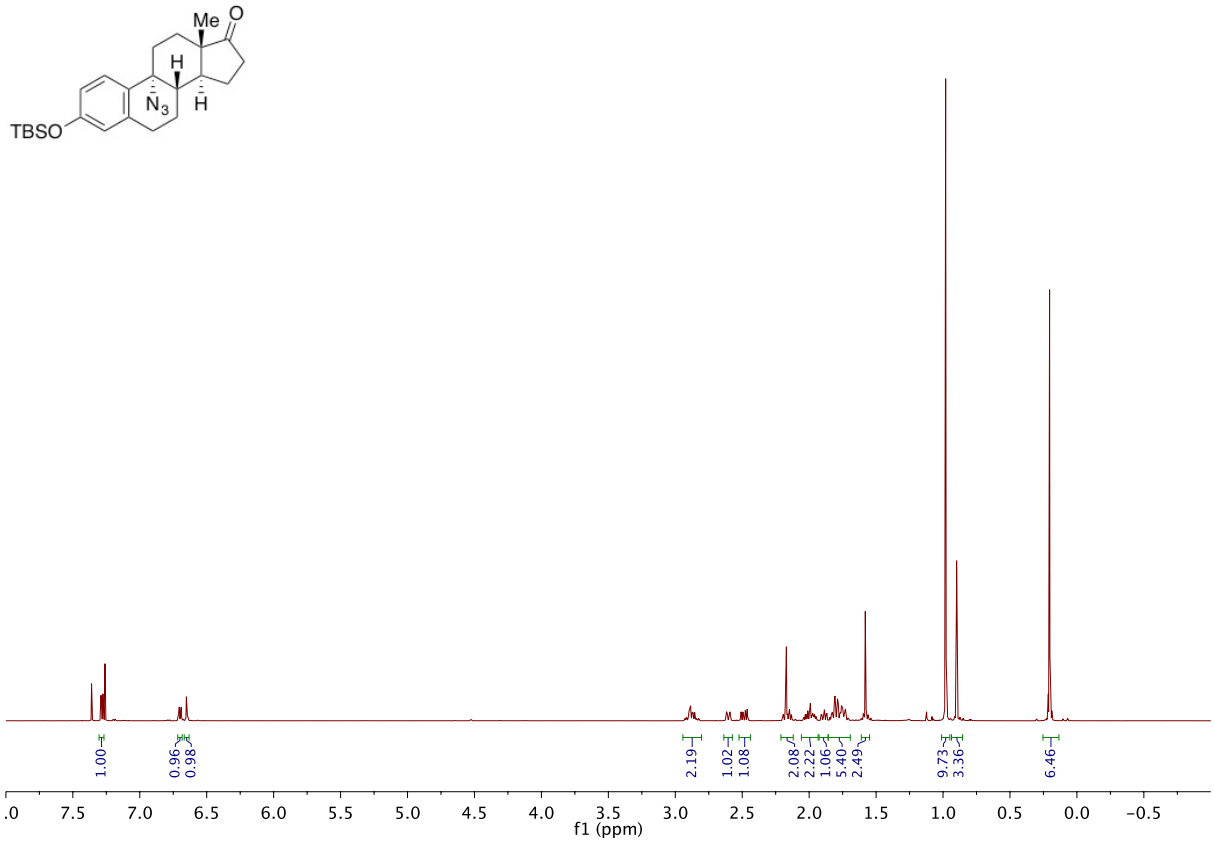
f1 (ppm)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H
N3
H
TBSO
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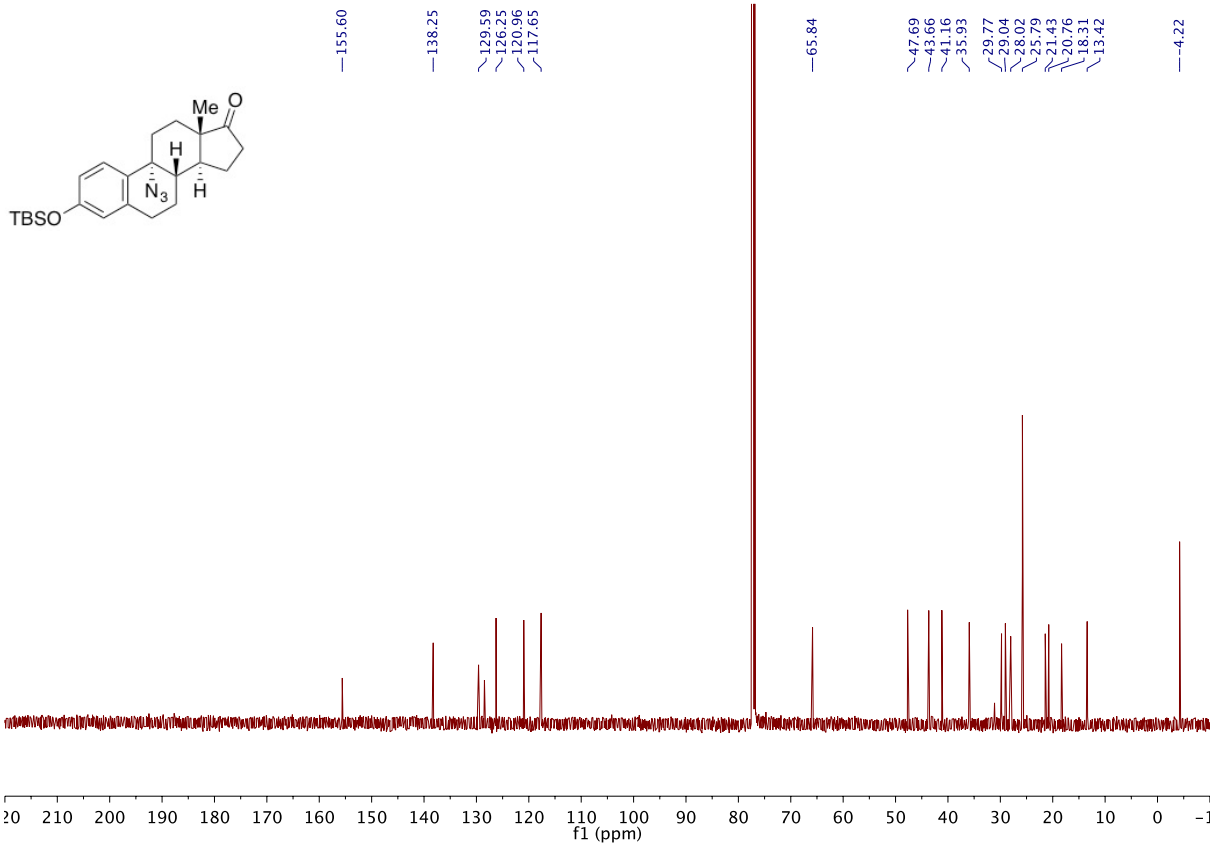
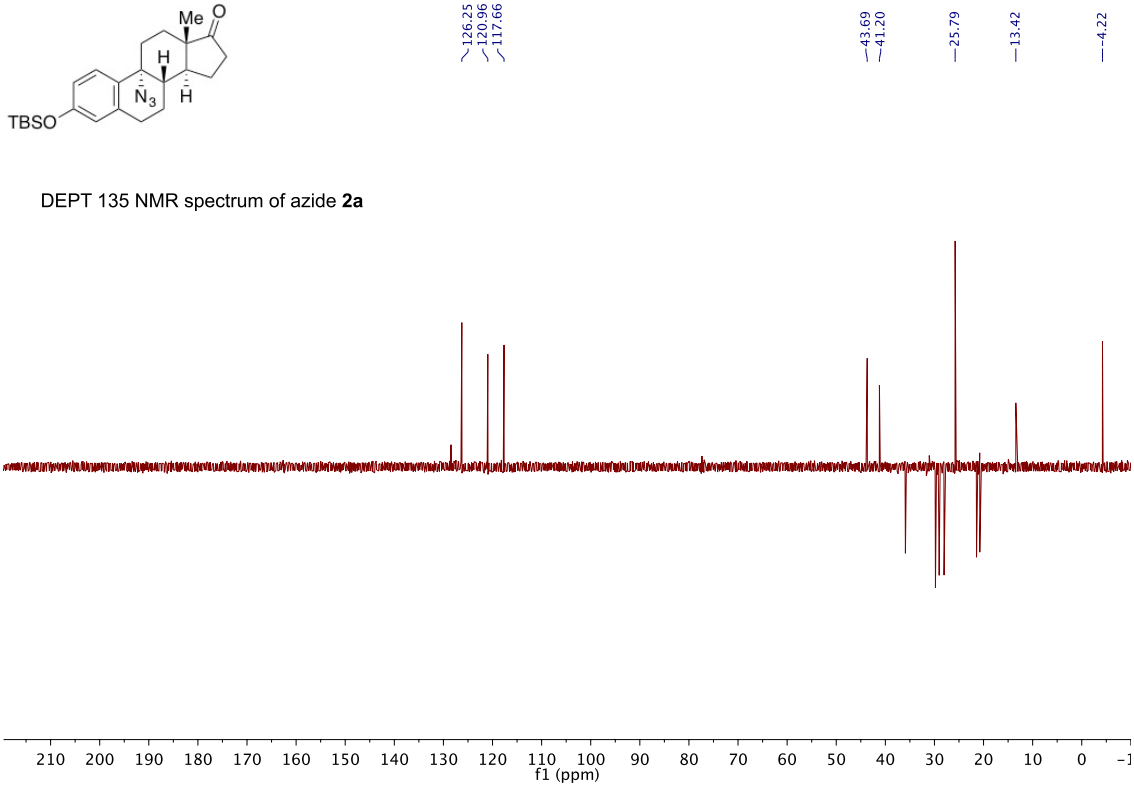
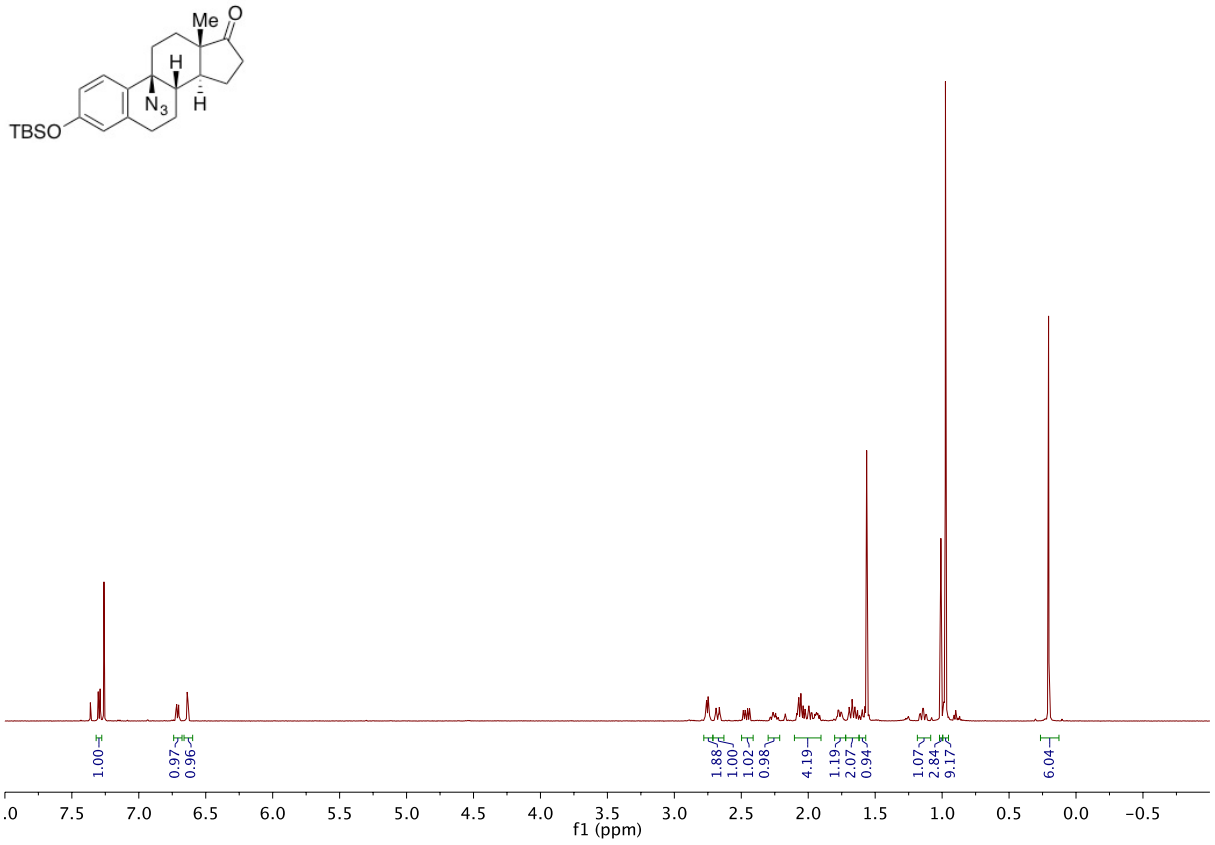
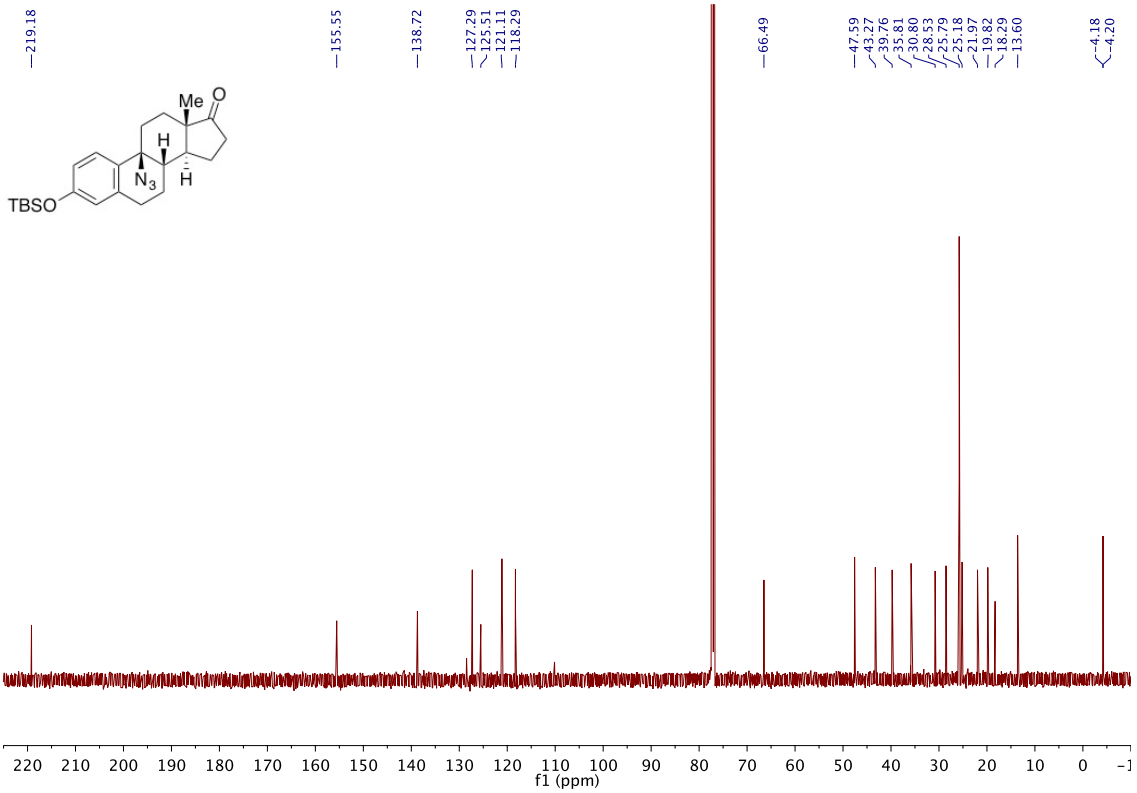
0.96
0.98
2.19
1.02
1.08
2.08
2.22
1.06
5.40
2.49
9.73
3.36
6.46
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



DEPT 135 NMR spectrum of azide **2a**




Me
O
H
N3
H
TBSO
1.00
0.97
0.96
1.88
1.00
1.02
0.98
4.19
1.19
2.07
0.94
1.07
2.84
9.17
6.04
f1 (ppm)


219.18
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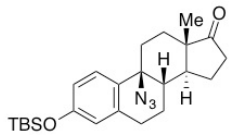
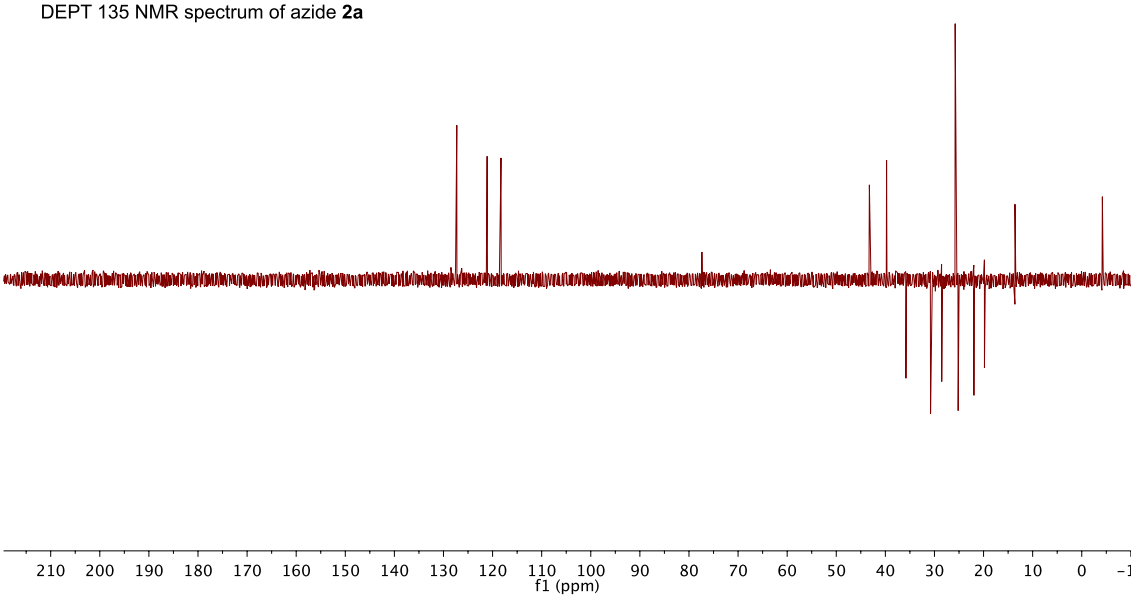
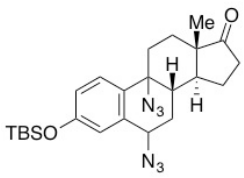
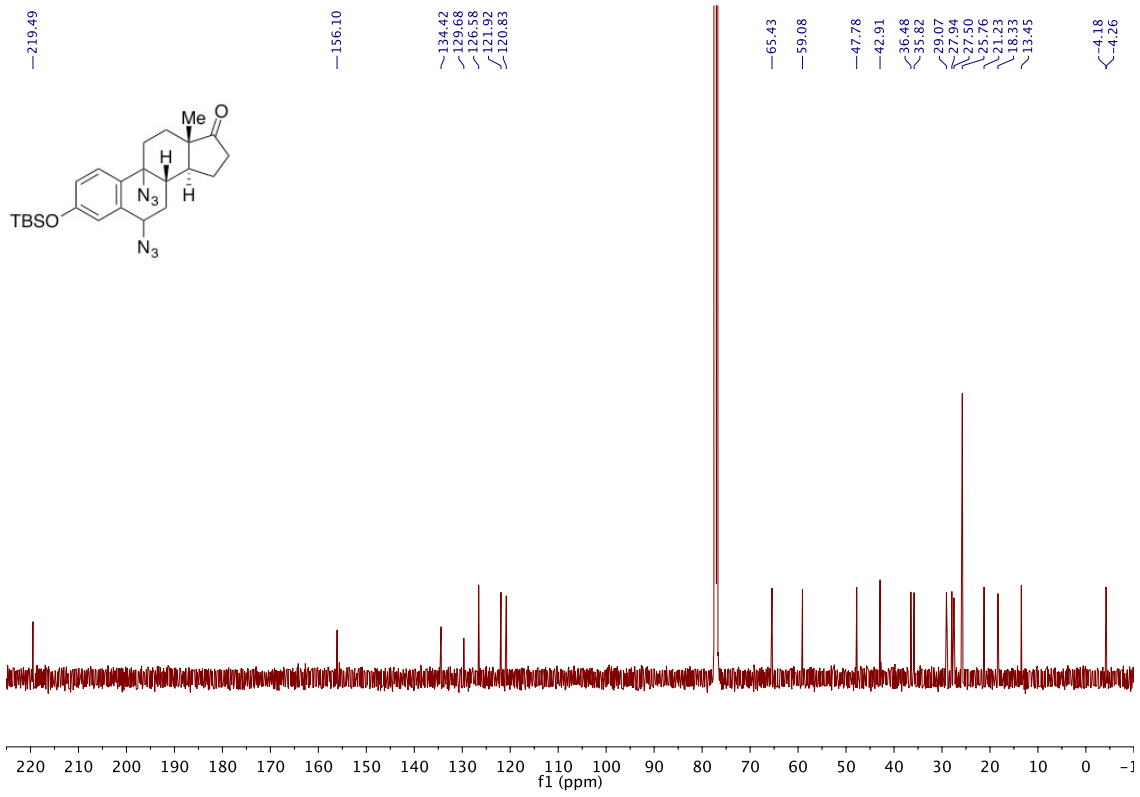
127.29
125.51
121.11
118.29
66.49
47.59
43.27
39.76
35.81
30.80
28.53
25.79
25.18
21.97
19.82
18.29
13.60
-4.18
-4.20
Me
O
H
N3
H
TBSO
f1 (ppm)

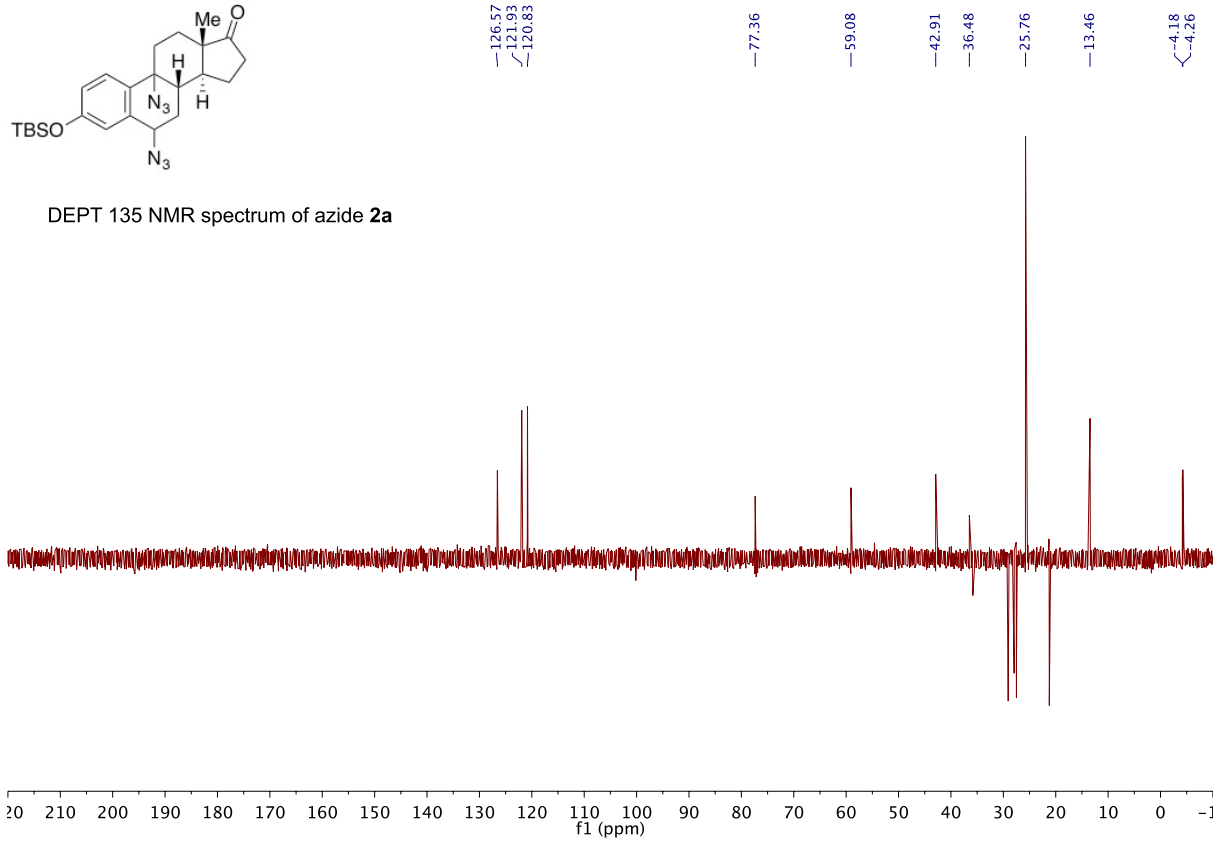


DEPT 135 NMR spectrum of azide **2a**

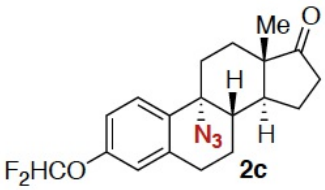


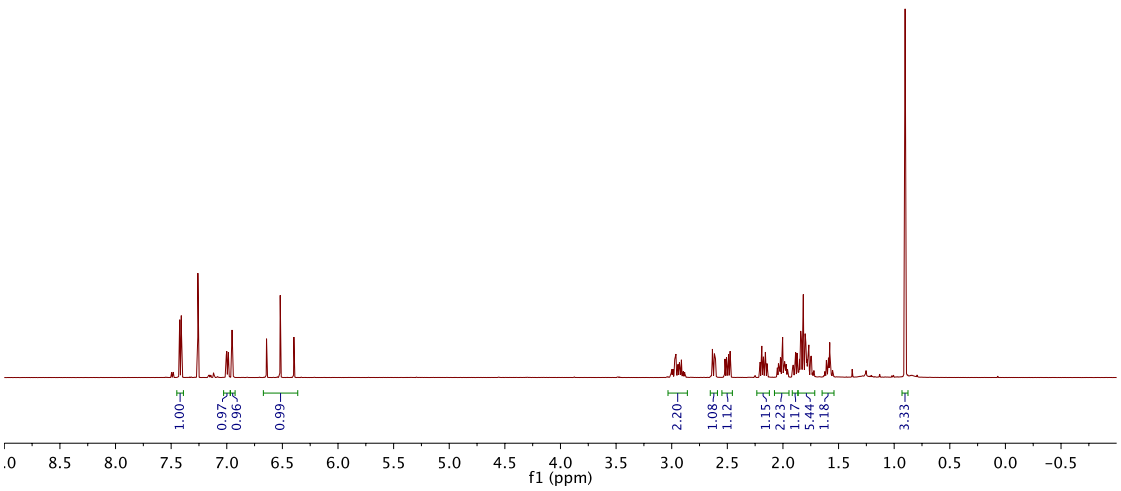


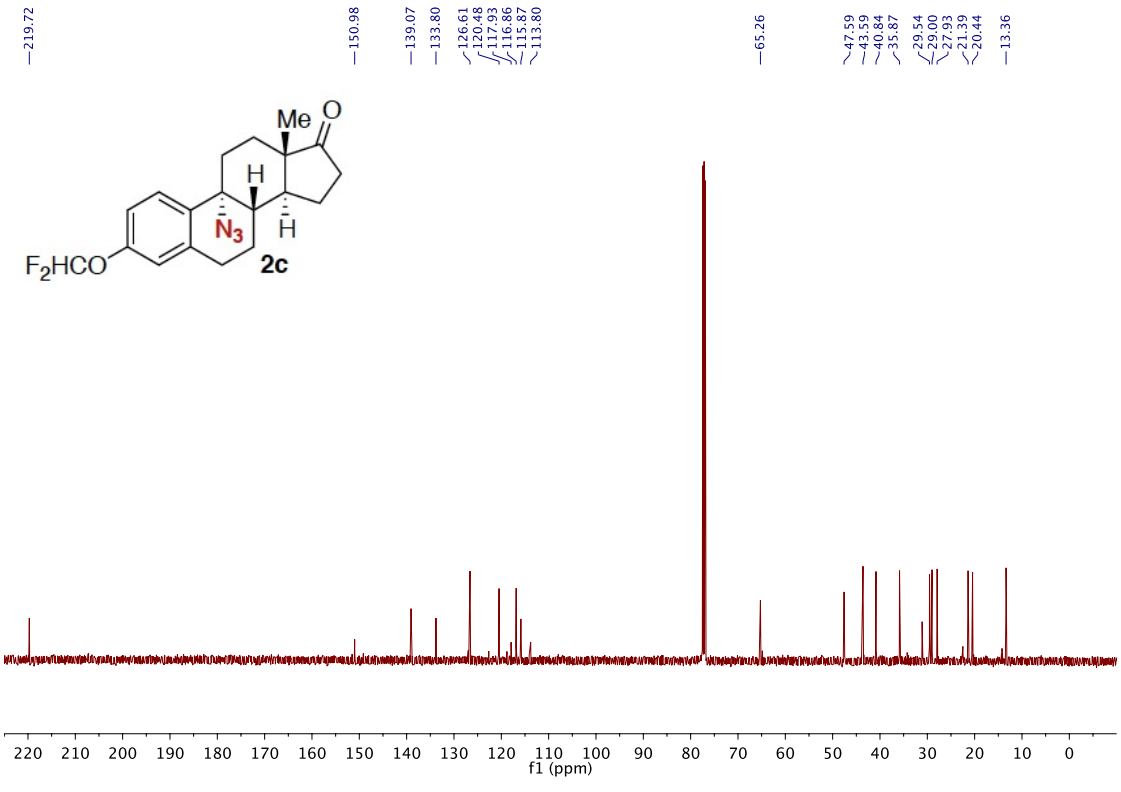




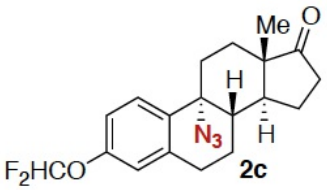
DEPT 135 NMR spectrum of azide **2a**


Me
O
H
N3
H
F2HCO
2c

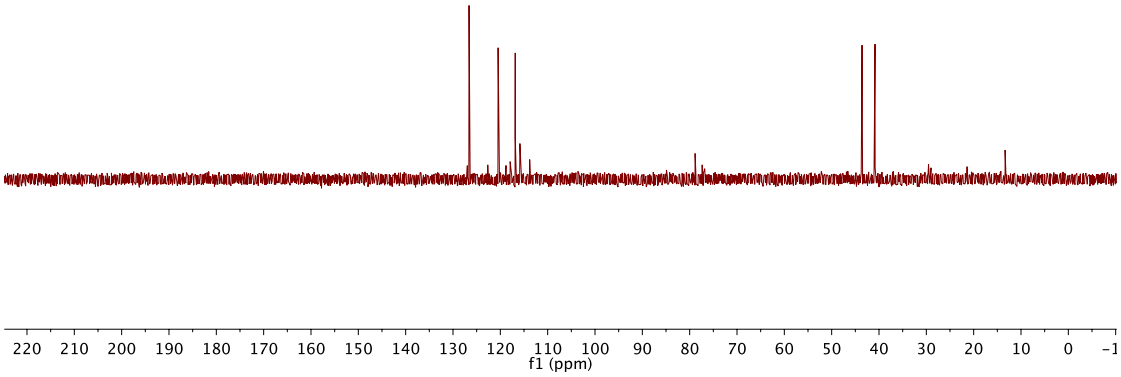

1.00
0.97
0.96
0.99
2.20
1.08
1.12
1.15
2.23
1.17
5.44
1.18
3.33
f1 (ppm)

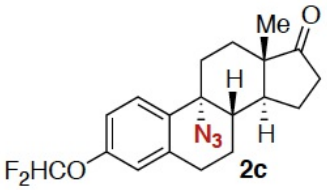

219.72
150.98
139.07
133.80
126.61
120.48
117.93
116.86
115.87
113.80
65.26
47.59
43.59
40.84
35.87
29.54
29.00
27.93
21.39
20.44
13.36
f1 (ppm)

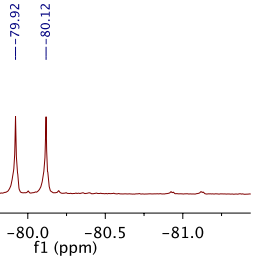
Me
O
H
N3
H
F2HCO
2c

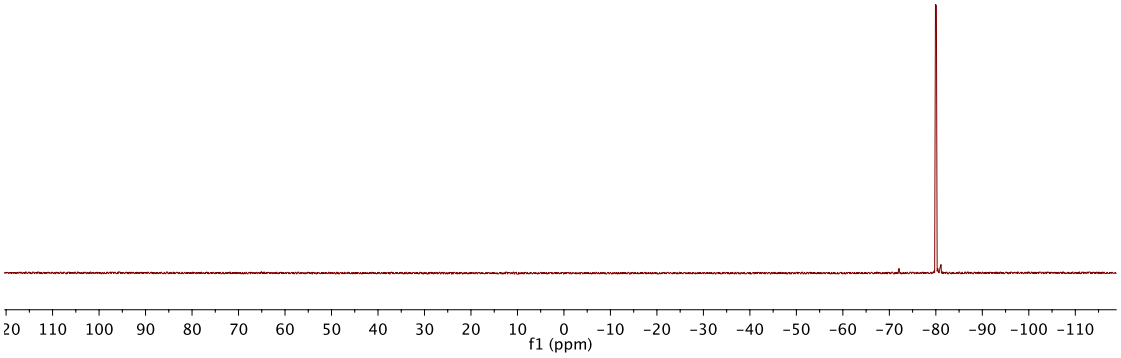


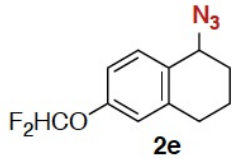
DEPT 90 NMR spectrum of azide **2c**



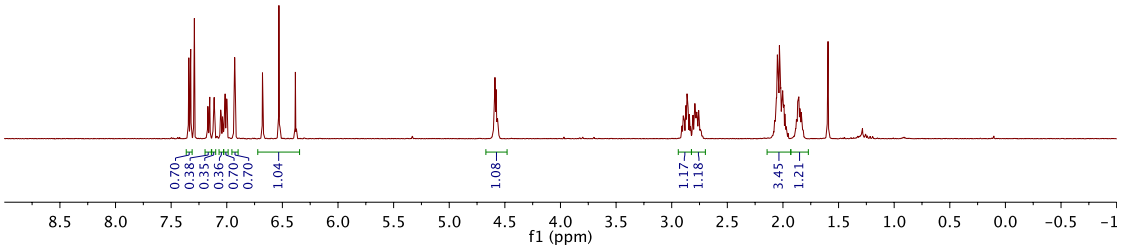


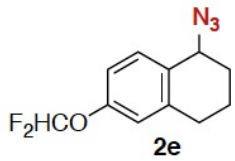





N3
F2HCO

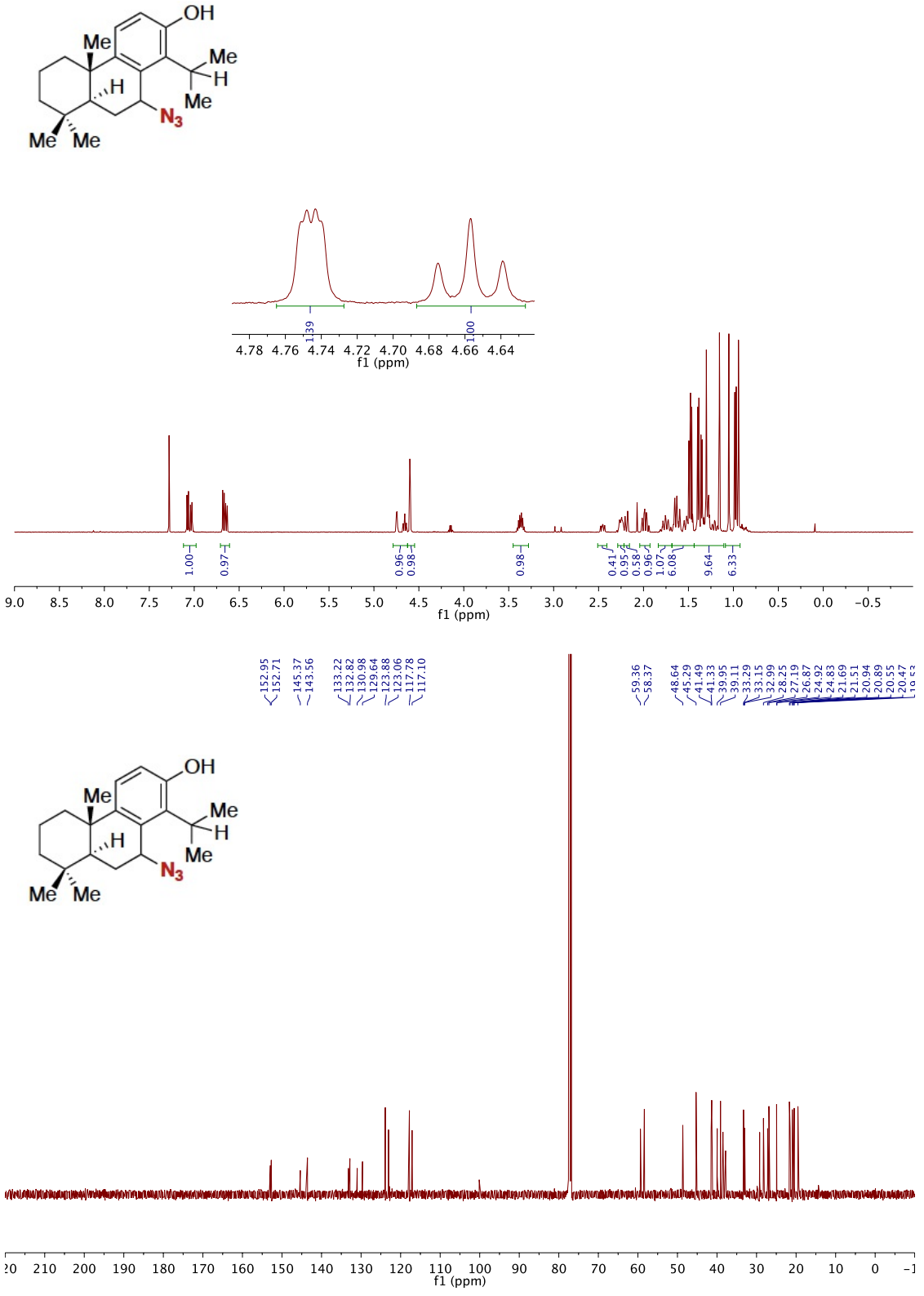
2e

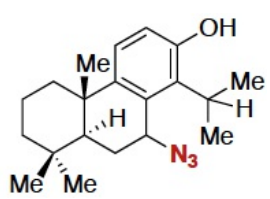

0.70
0.38
0.35
0.36
0.70
0.70
1.04
1.08
1.17
1.18
3.45
1.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


N3
F2HCO

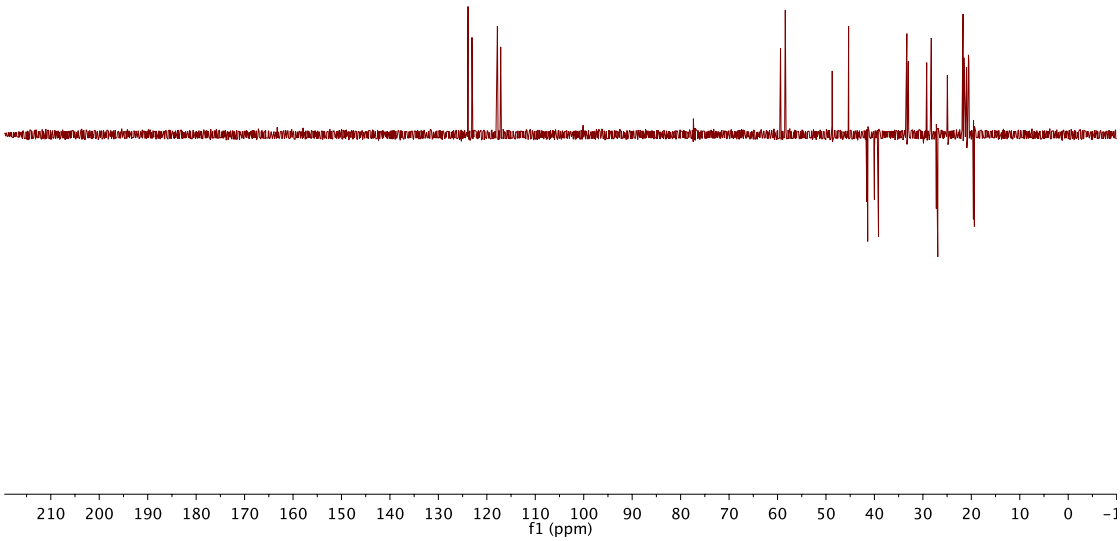
2e

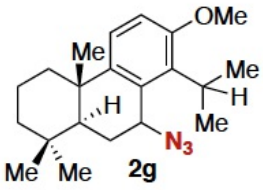
150.78
139.49
135.49
134.53
131.01
130.79
130.69
119.86
119.77
117.93
117.31
115.86
113.80
59.17
58.82
29.00
28.96
28.80
28.22
19.14
18.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


OH
Me
Me
H
H
Me
N3
Me
Me
1.39
1.00
4.78 4.76 4.74 4.72 4.70 4.68 4.66 4.64
f1 (ppm)
1.00
0.97
0.96
0.98
0.98
0.41
0.95
0.58
0.96
1.07
6.08
9.64
6.33
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)
152.95
152.71
145.37
143.56
133.22
132.82
130.98
129.64
123.88
123.06
117.78
117.10
59.36
58.37
48.64
45.29
41.49
41.33
39.95
39.11
33.29
33.15
32.99
32.91
28.25
27.19
26.87
24.92
24.83
21.69
21.51
20.94
20.89
20.55
20.47
OH
Me
Me
H
H
Me
N3
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

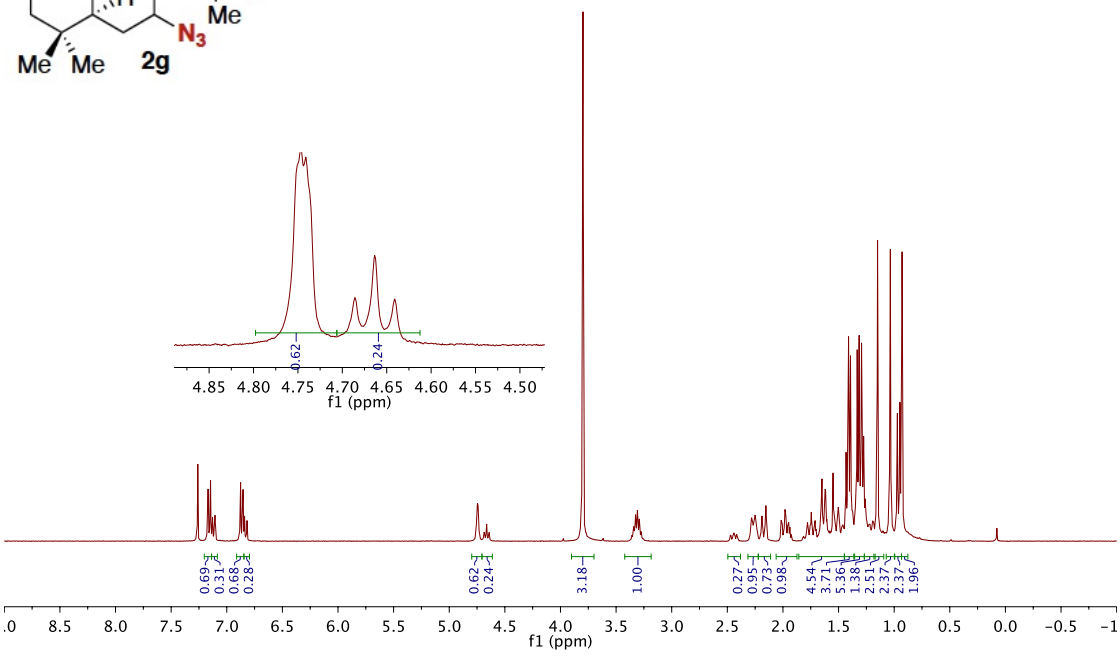


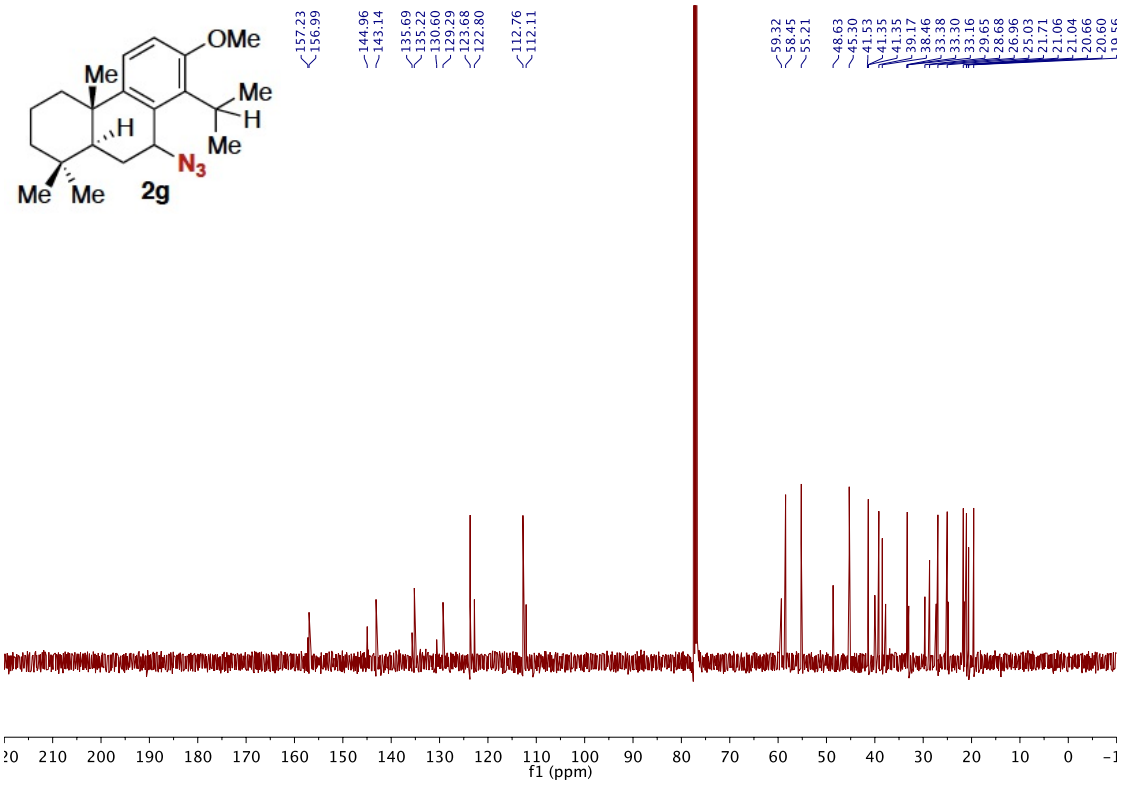
DEPT135 NMR spectrum of azide **S14**

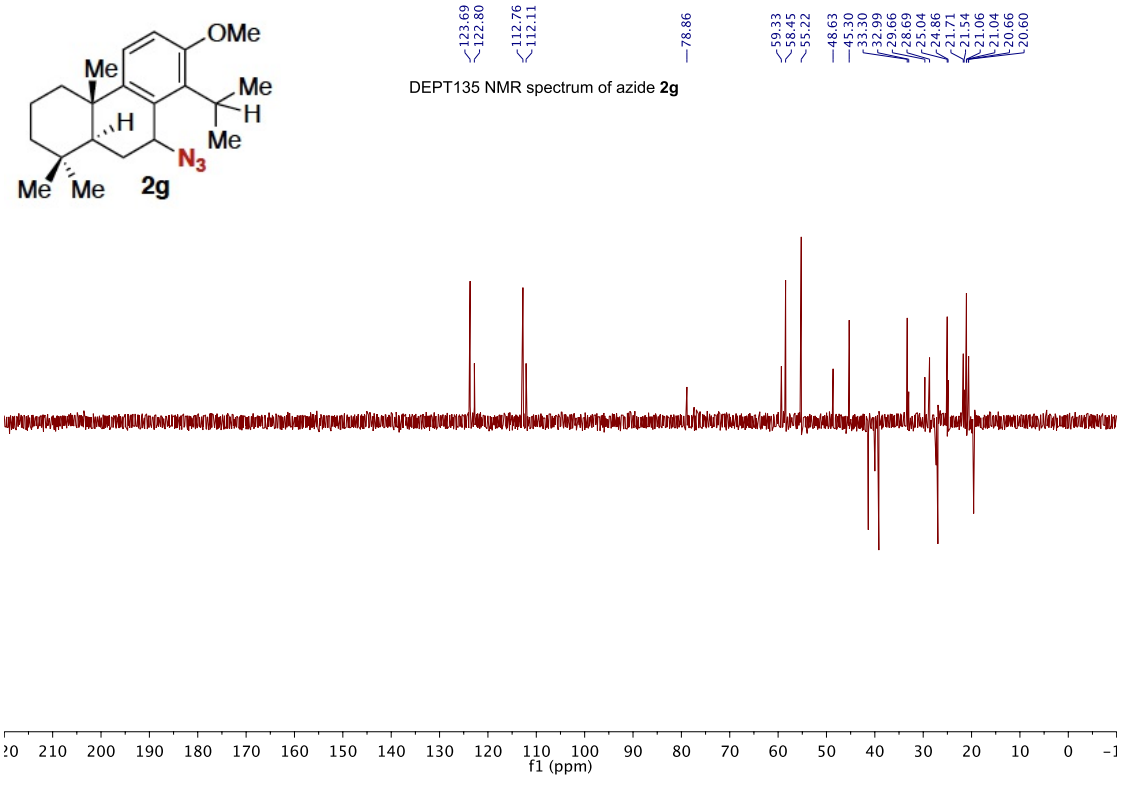




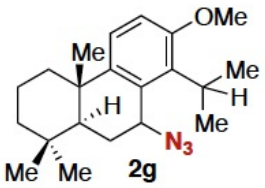
2g



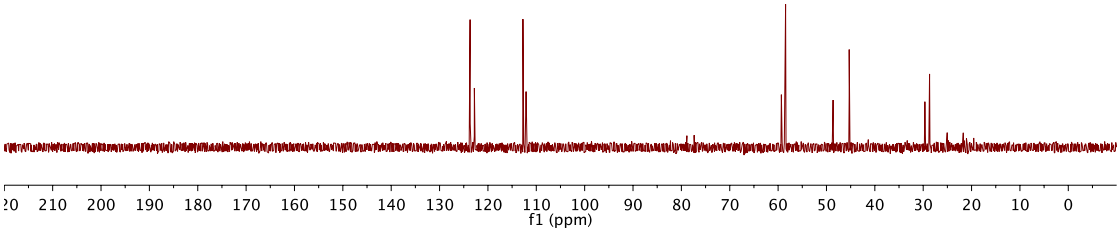


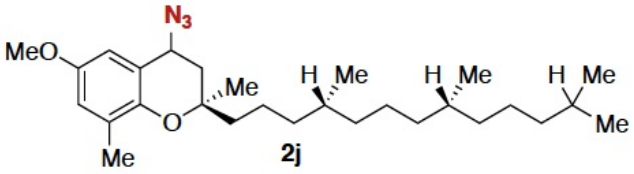


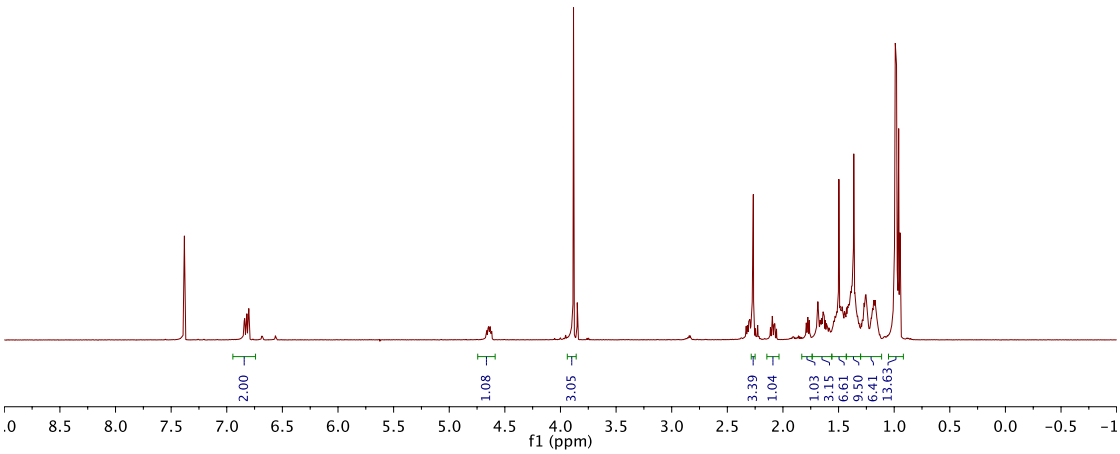
DEPT135 NMR spectrum of azide **2g**

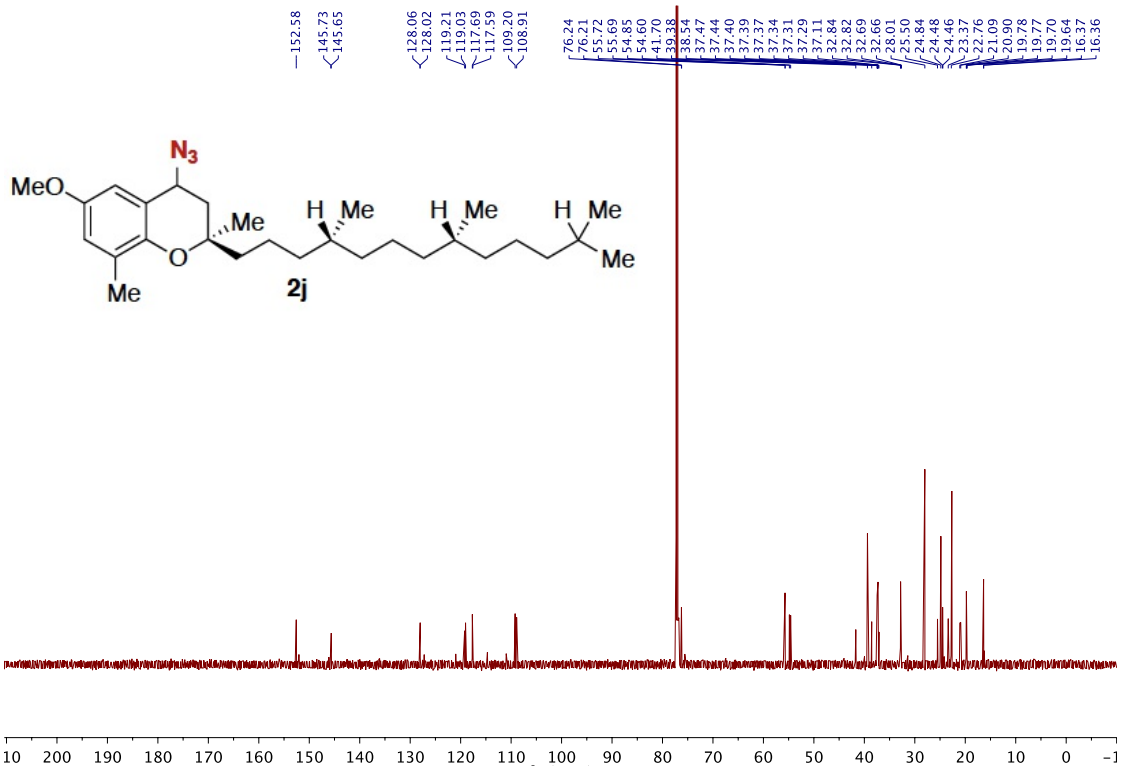


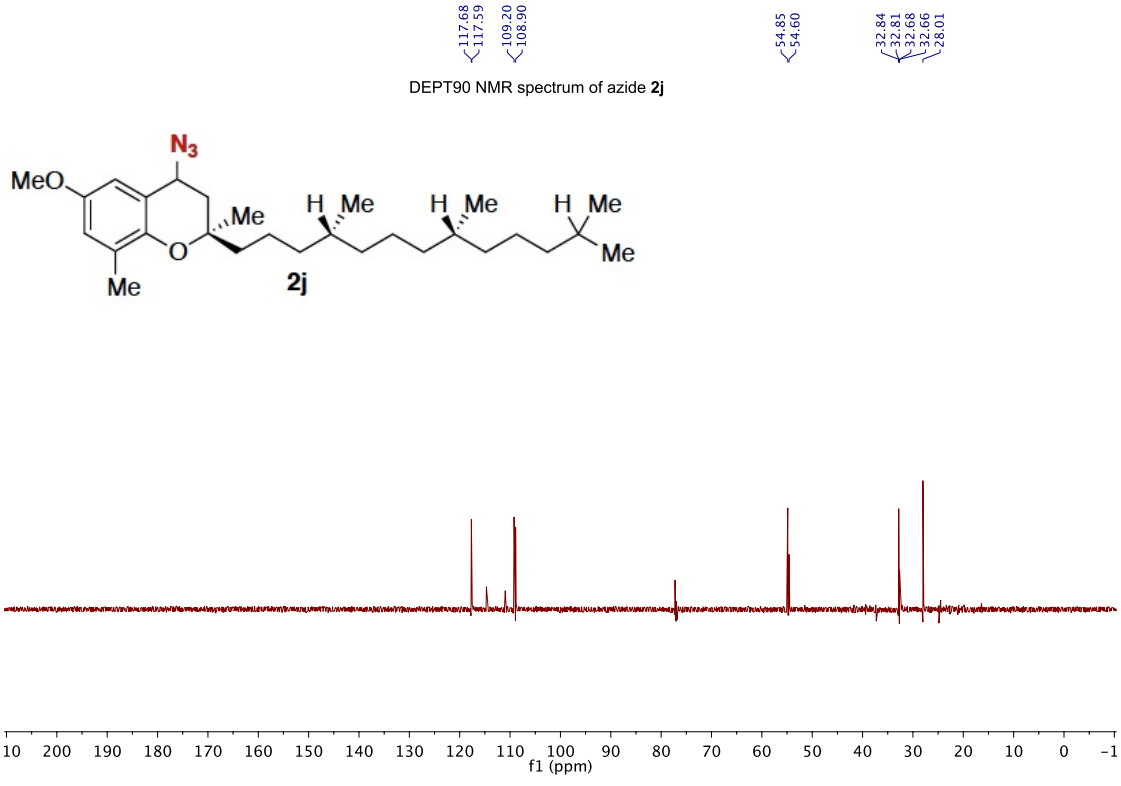
DEPT90 NMR spectrum of azide **2g**



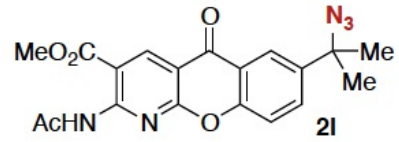




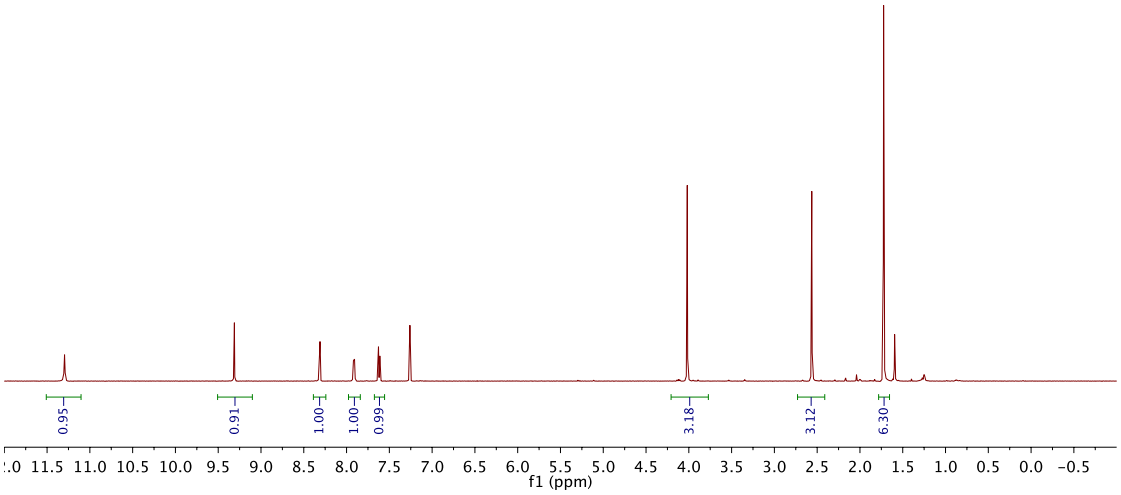


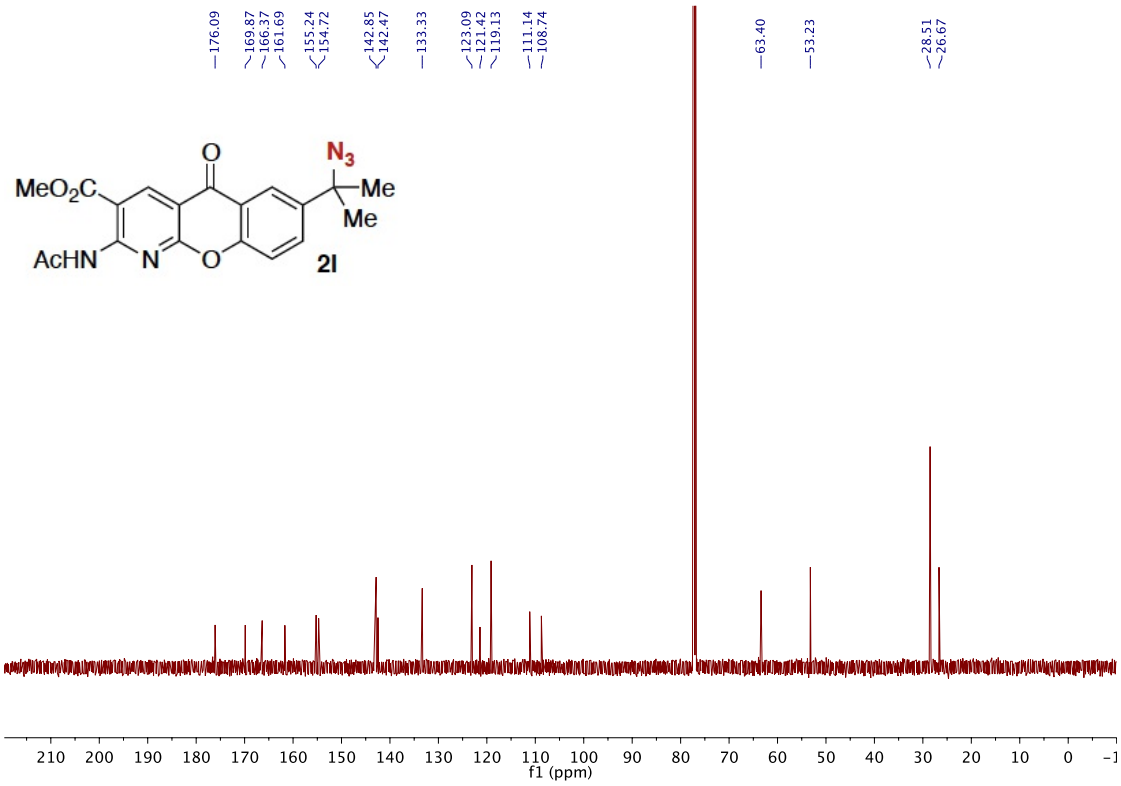


DEPT90 NMR spectrum of azide **2j**


O
N3
MeO2C
Me
Me
AcHN
N
O

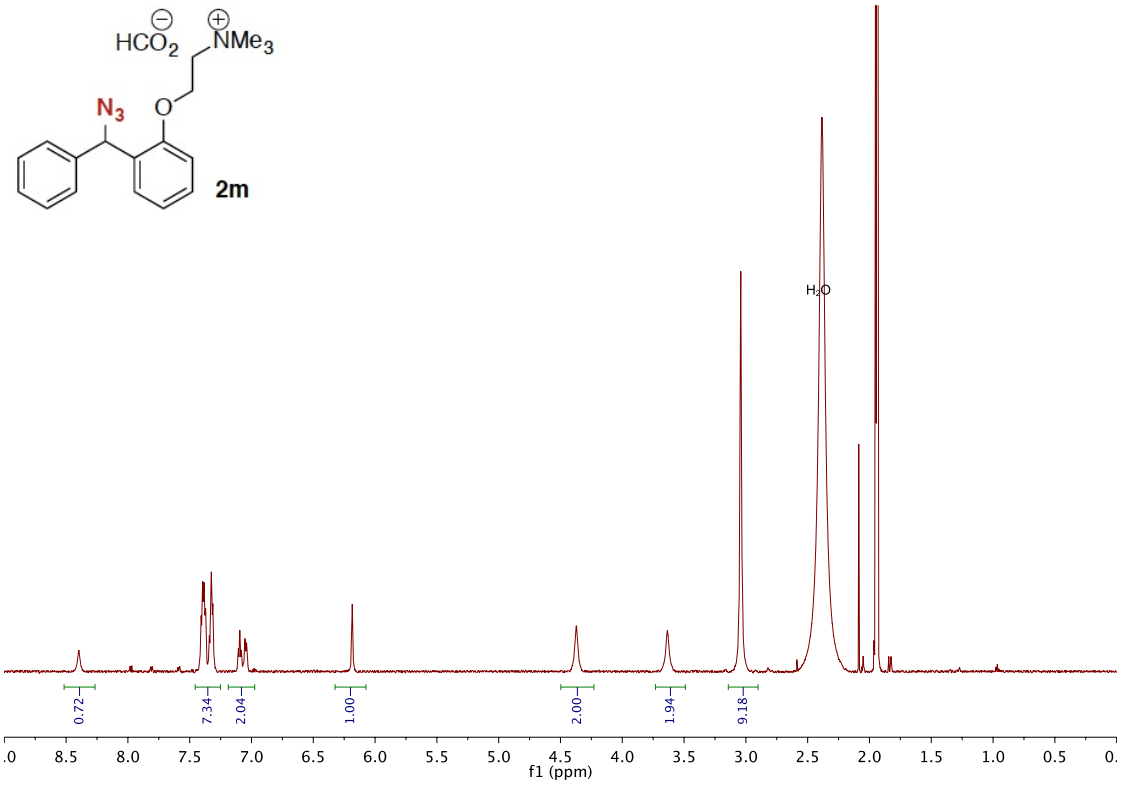
2l

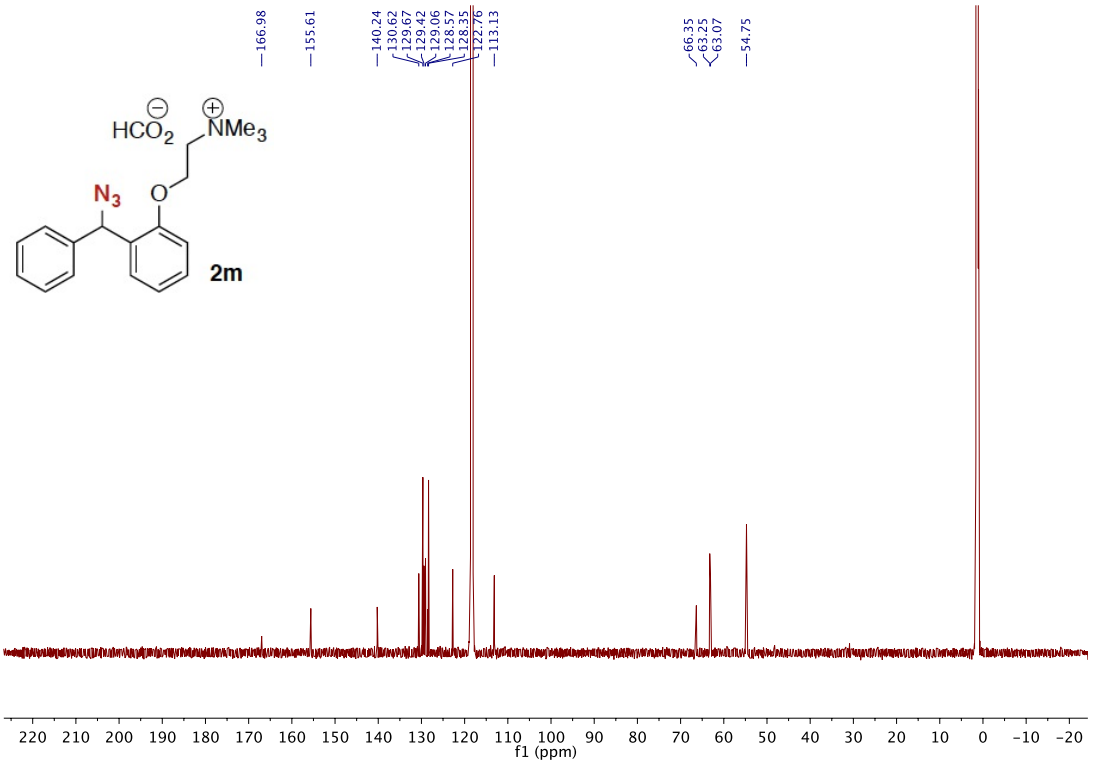

0.95
0.91
1.00
1.00
0.99
3.18
3.12
6.30
f1 (ppm)

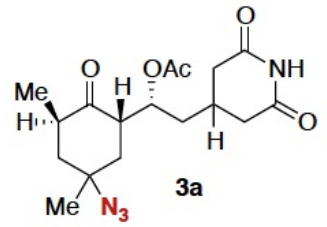

176.09
169.87
166.37
161.69
155.24
154.72
142.85
142.47
133.33
123.09
121.42
119.13
111.14
108.74
63.40
53.23
28.51
26.67
f1 (ppm)

O
N3
MeO2C
Me
Me
AcHN
N
O

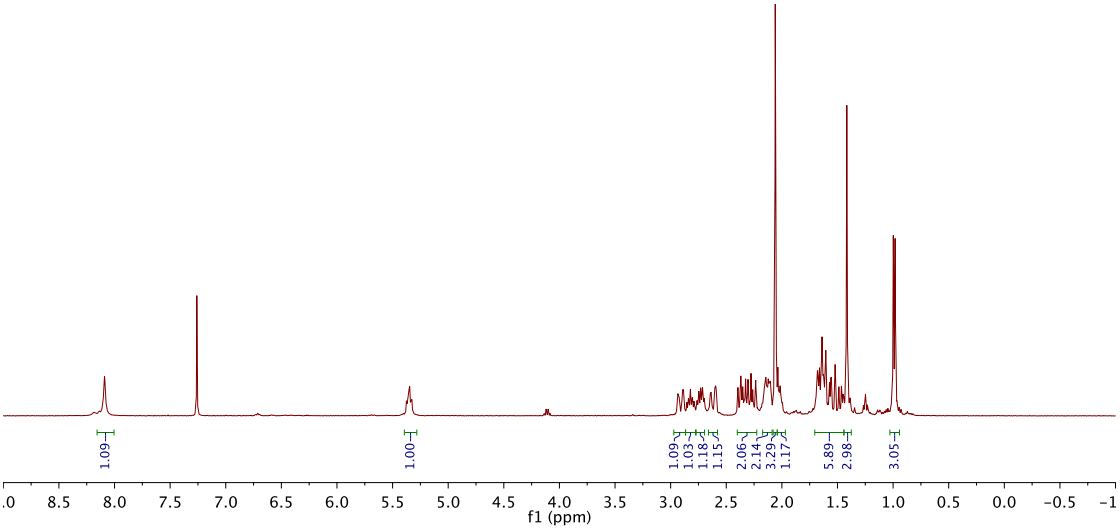
2l

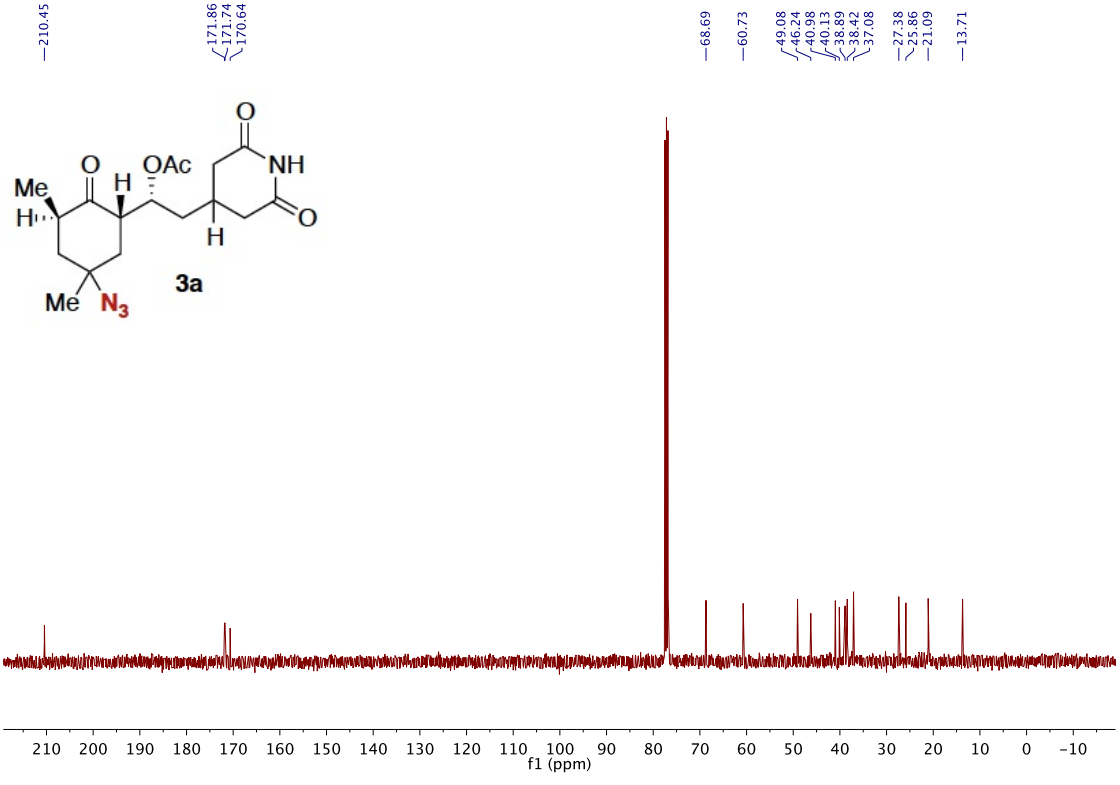

HCO2
NMe3
N3
O
2m
H2O
0.72
7.34
2.04
1.00
2.00
1.94
9.18
f1 (ppm)


166.98
155.61
140.24
130.62
129.67
129.42
129.06
128.57
128.35
122.76
113.13
66.35
63.25
63.07
54.75
HCO2
NMe3
N3
O
2m
f1 (ppm)


O
NH
OAc
O
H
Me
H
O
H
Me
N3

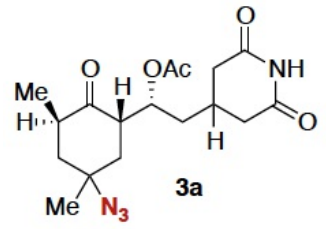
3a


1.09
1.00
1.09
1.03
1.18
1.15
2.06
2.14
3.29
1.17
5.89
2.98
3.05
f1 (ppm)


210.45
171.86
171.74
170.64
68.69
60.73
49.08
46.24
40.98
40.13
38.89
38.42
37.08
27.38
25.86
21.09
13.71
f1 (ppm)

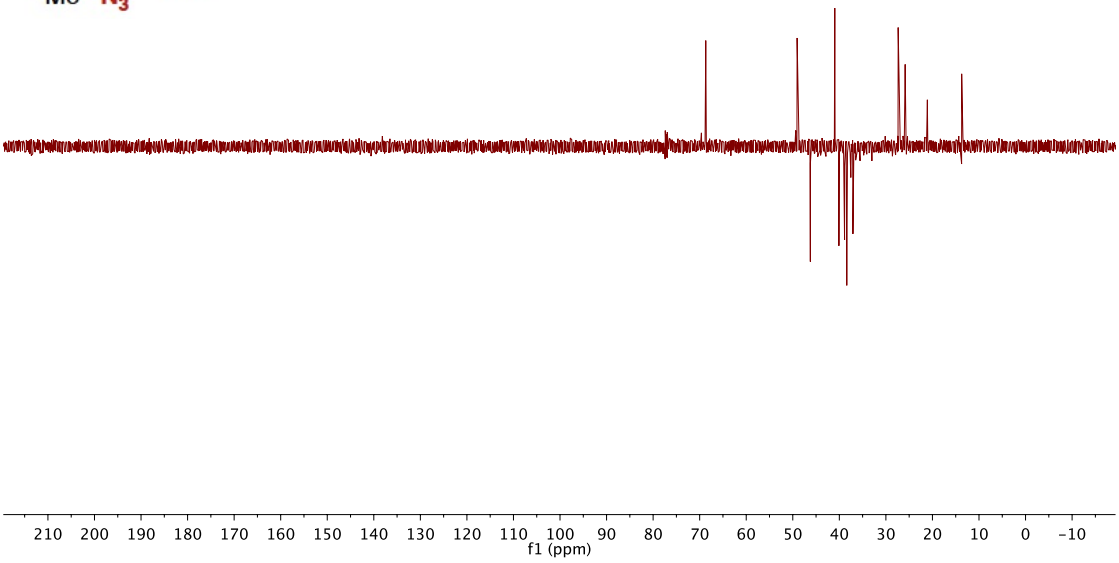
O
NH
OAc
O
H
Me
H
O
H
Me
N3

3a

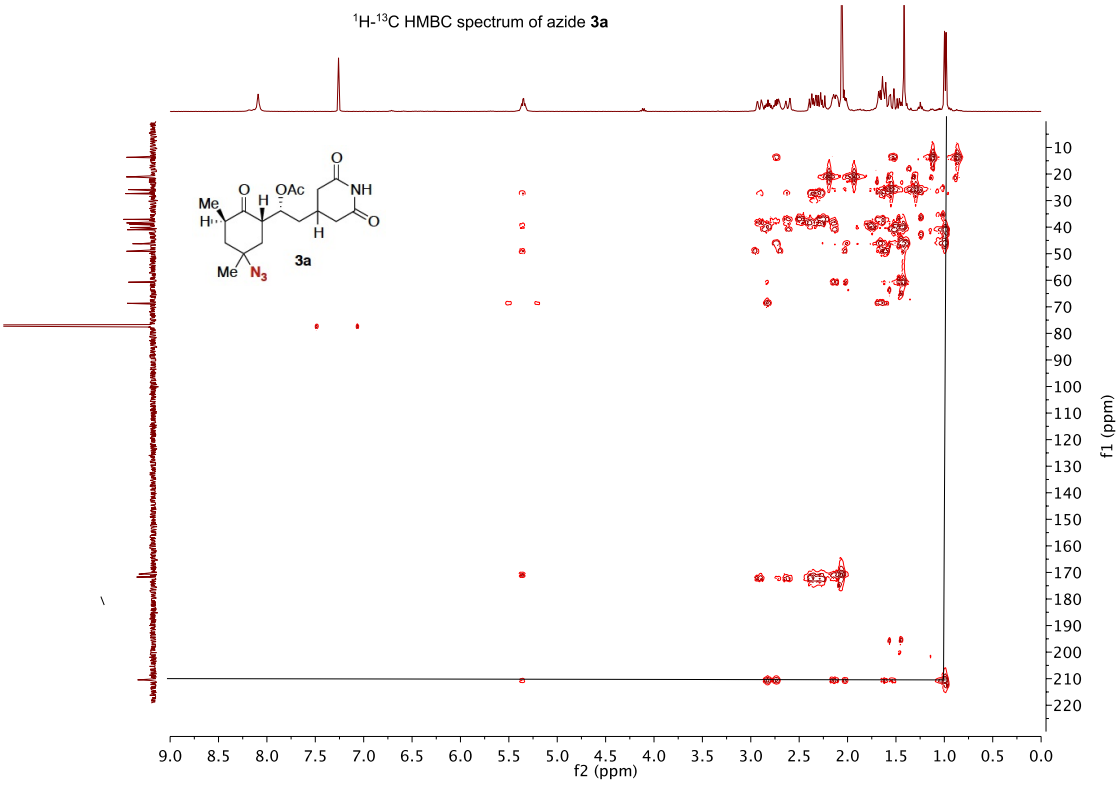


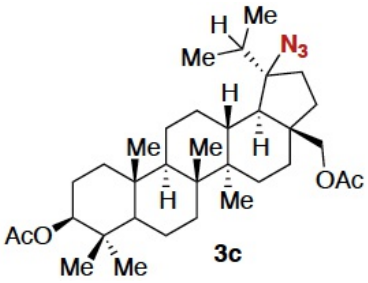
3a

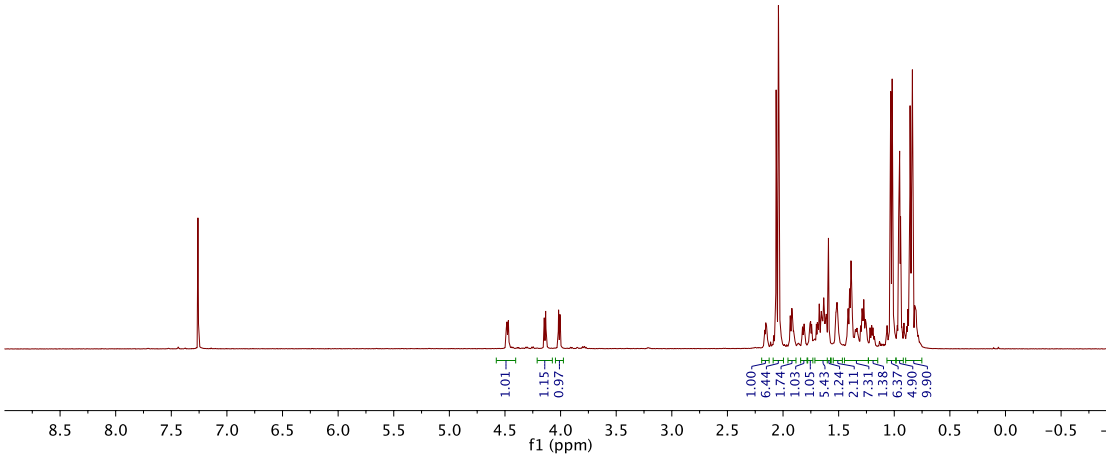
DEPT135 NMR spectrum of azide **3a**

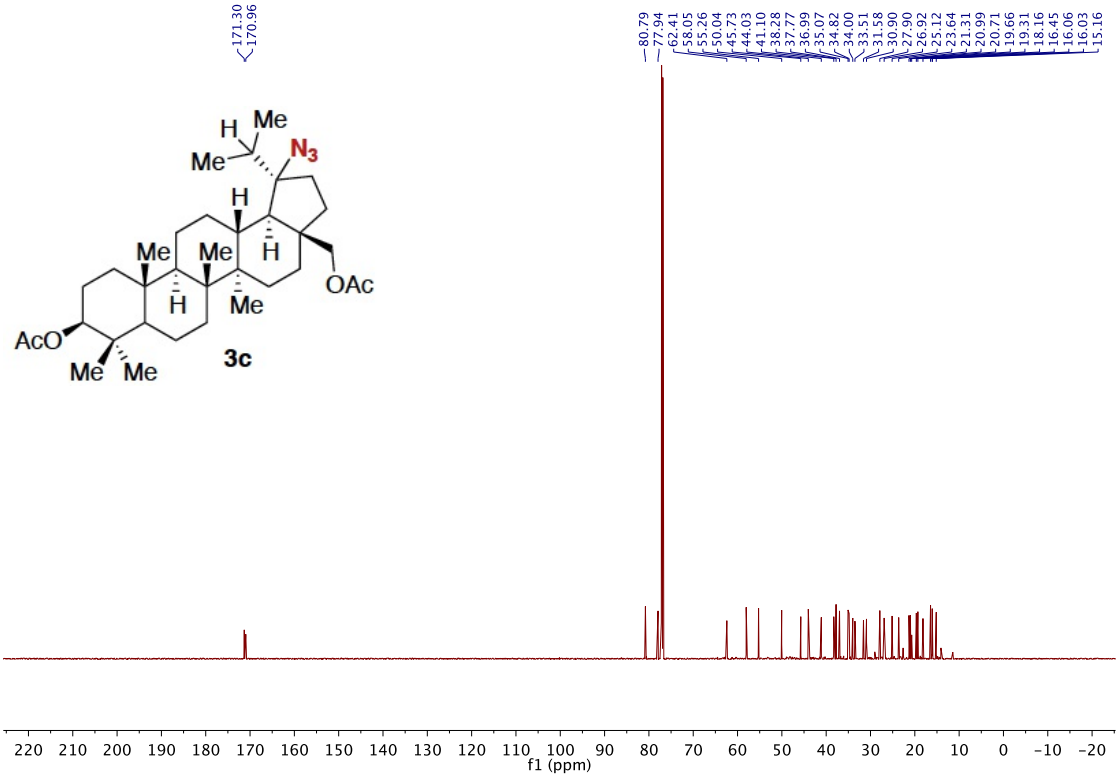


^{1}H-^{13}C HMBC spectrum of azide **3a**

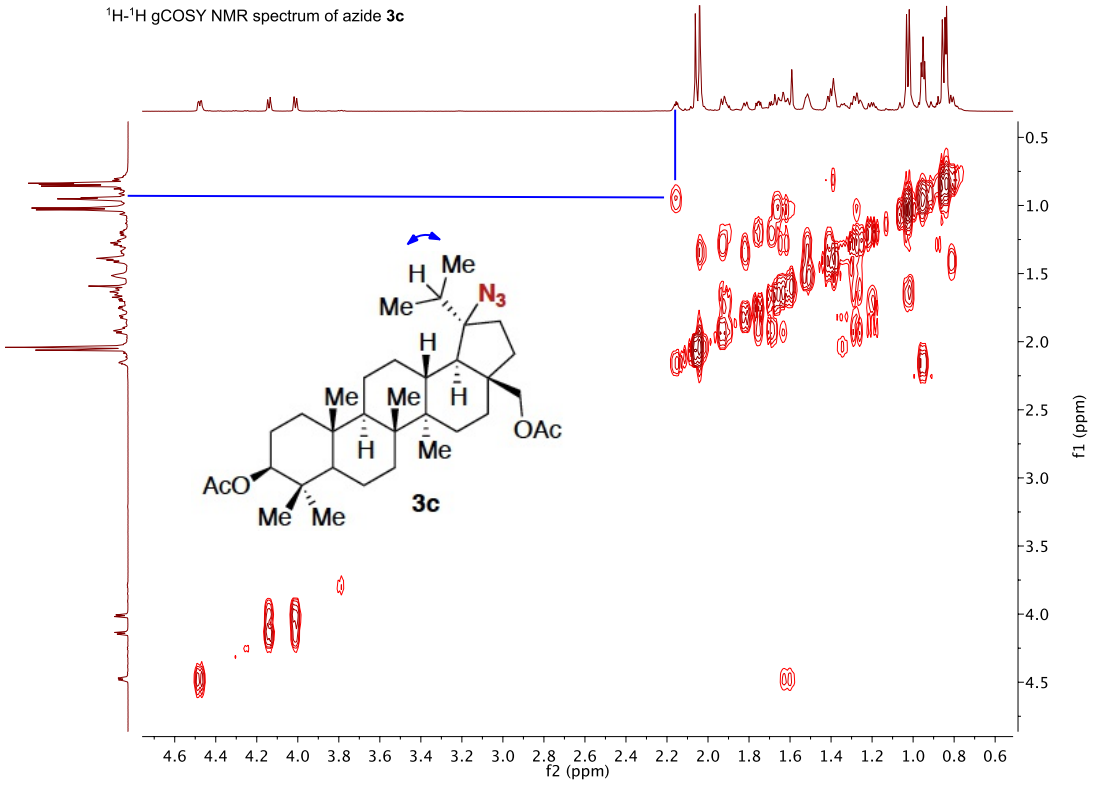



H
Me
Me
N3
H
Me
Me
H
OAc
H
Me
AcO
Me
Me
3c

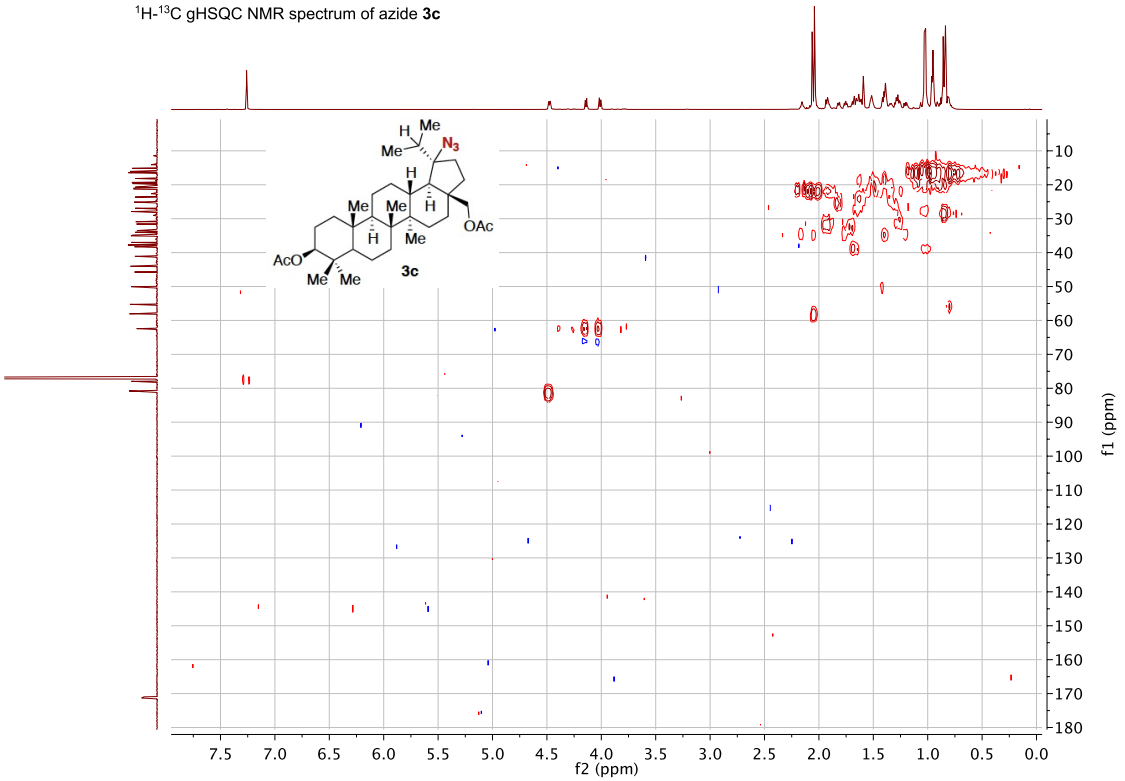

1.01
1.15
0.97
1.00
6.44
1.74
1.03
1.05
5.43
1.24
2.11
7.31
1.38
6.37
4.90
9.90
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.30
170.96
80.79
77.94
62.41
58.05
55.26
50.04
45.73
44.03
41.10
38.28
37.77
36.99
35.07
34.82
34.00
33.51
31.58
30.90
27.90
26.92
25.12
23.64
21.31
20.99
20.71
19.66
19.31
18.16
16.45
16.06
16.03
15.16
H
Me
Me
N3
H
Me
Me
H
OAc
H
Me
AcO
Me
Me
3c
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)

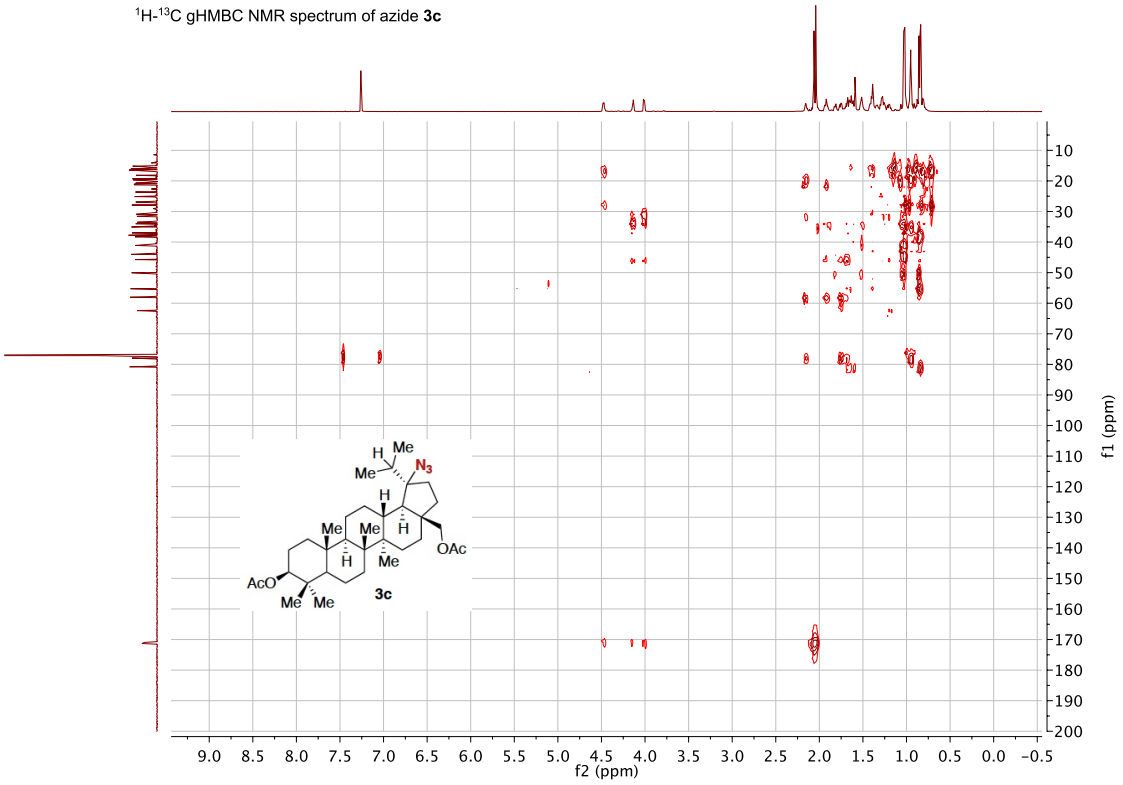
^{1}H-^{1}H gCOSY NMR spectrum of azide **3c**

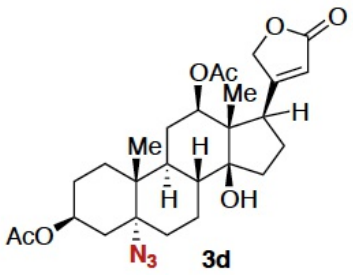


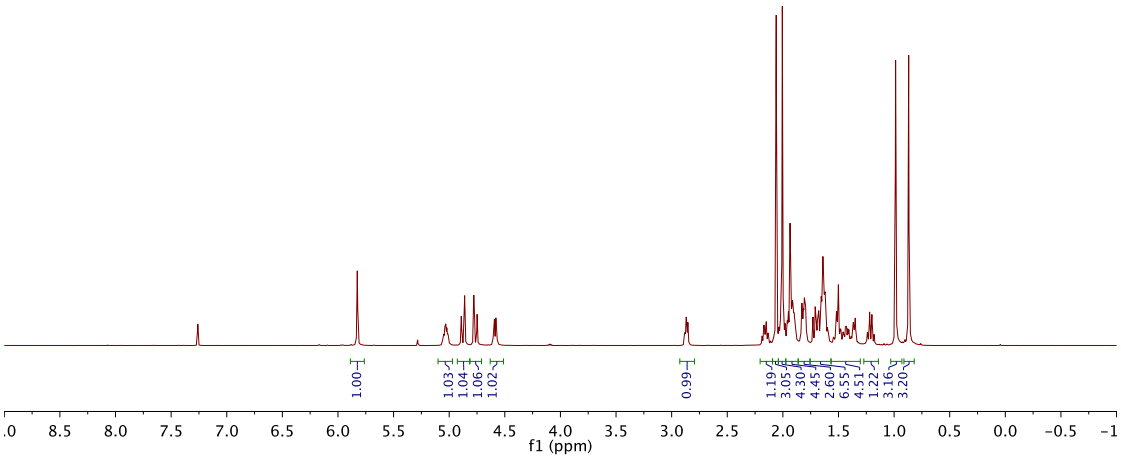
^{1}H-^{13}C gHSQC NMR spectrum of azide **3c**

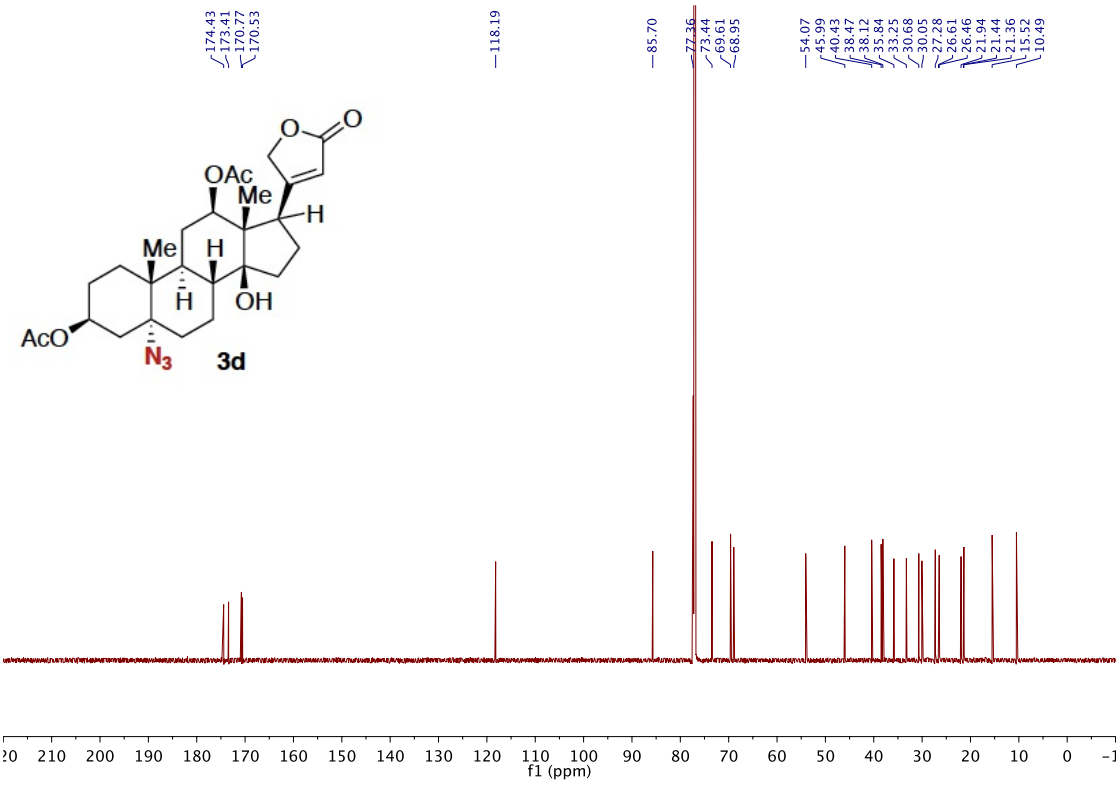


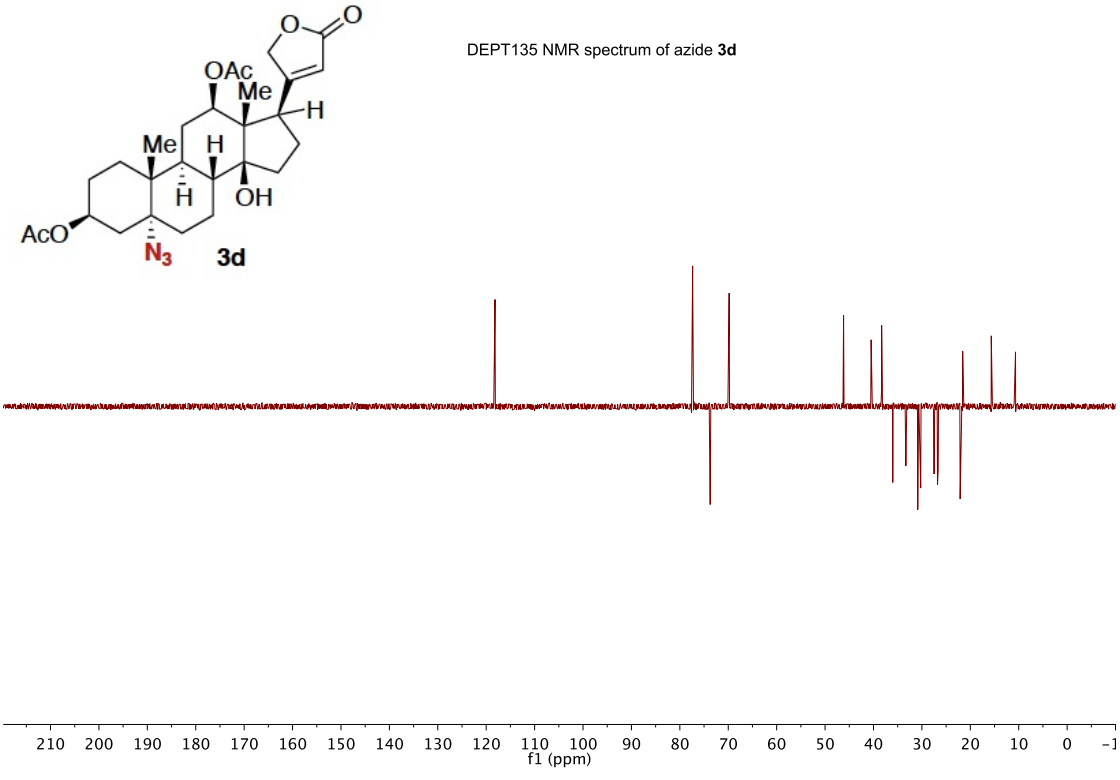
^{1}H-^{13}C gHMBC NMR spectrum of azide **3c**





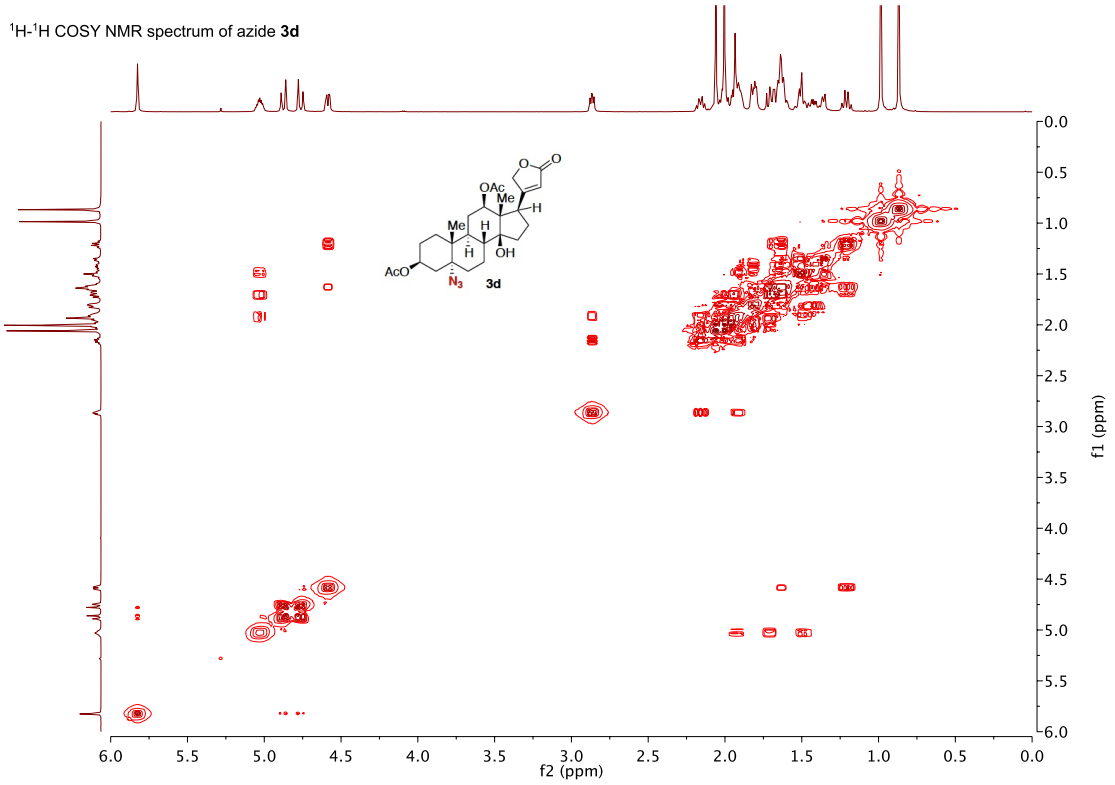




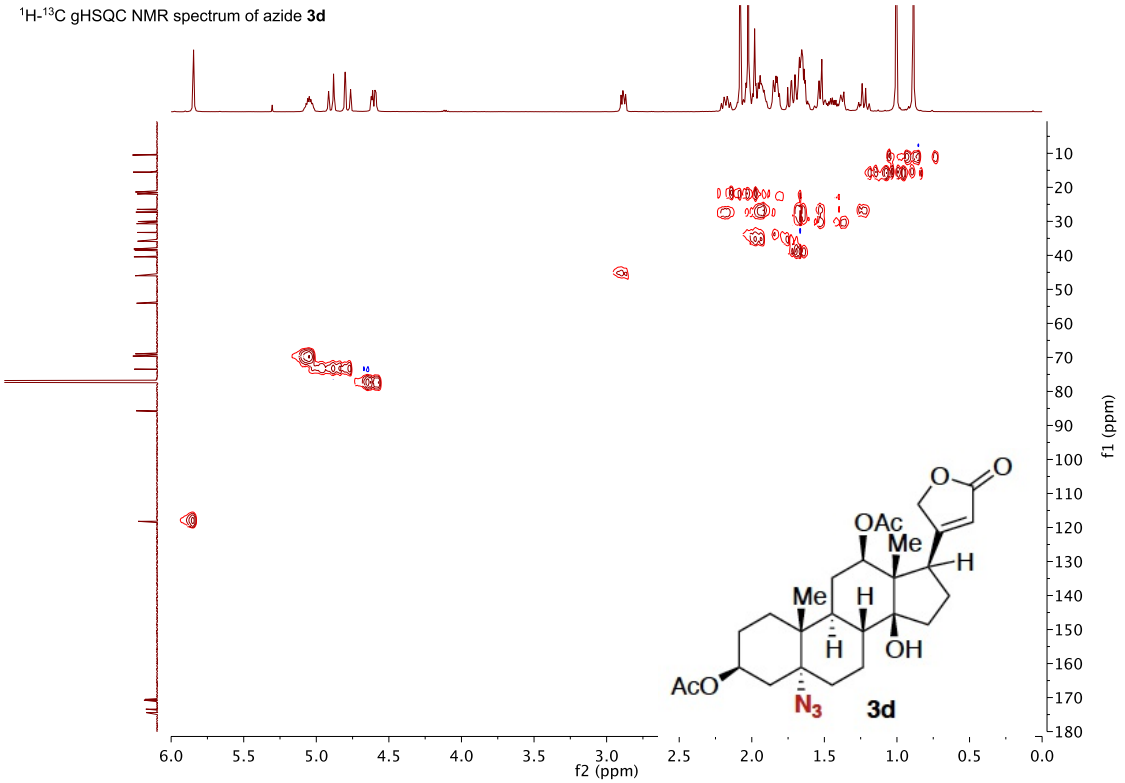


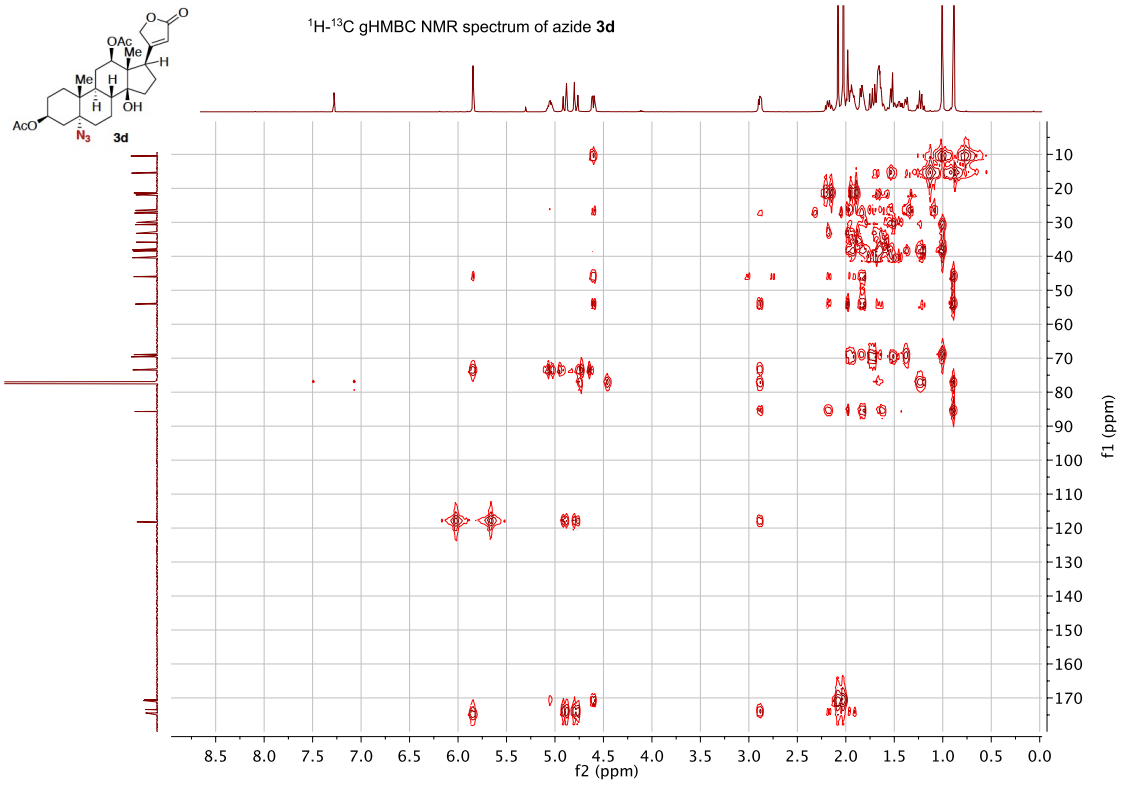
DEPT135 NMR spectrum of azide **3d**

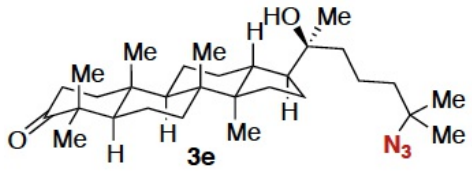
^{1}H-^{1}H COSY NMR spectrum of azide **3d**

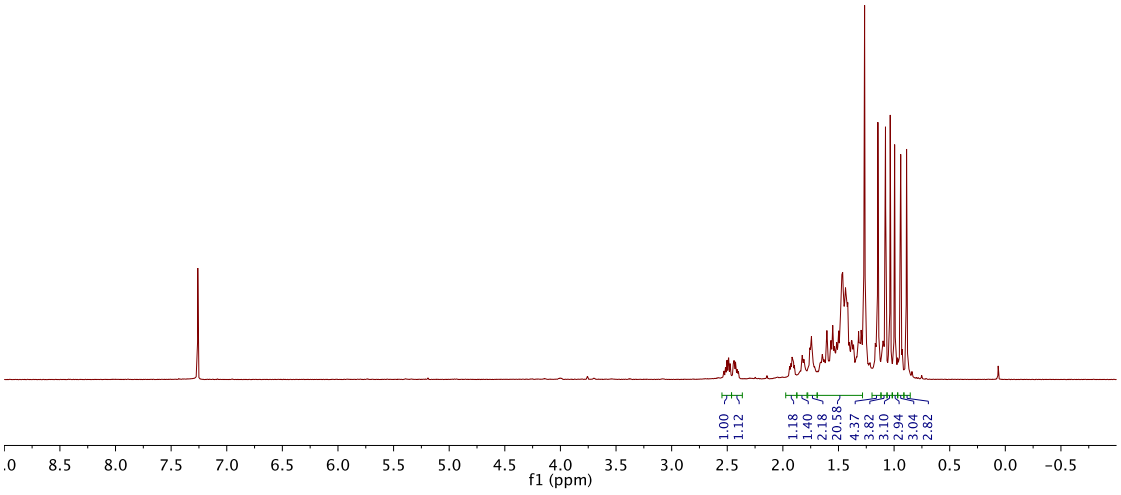


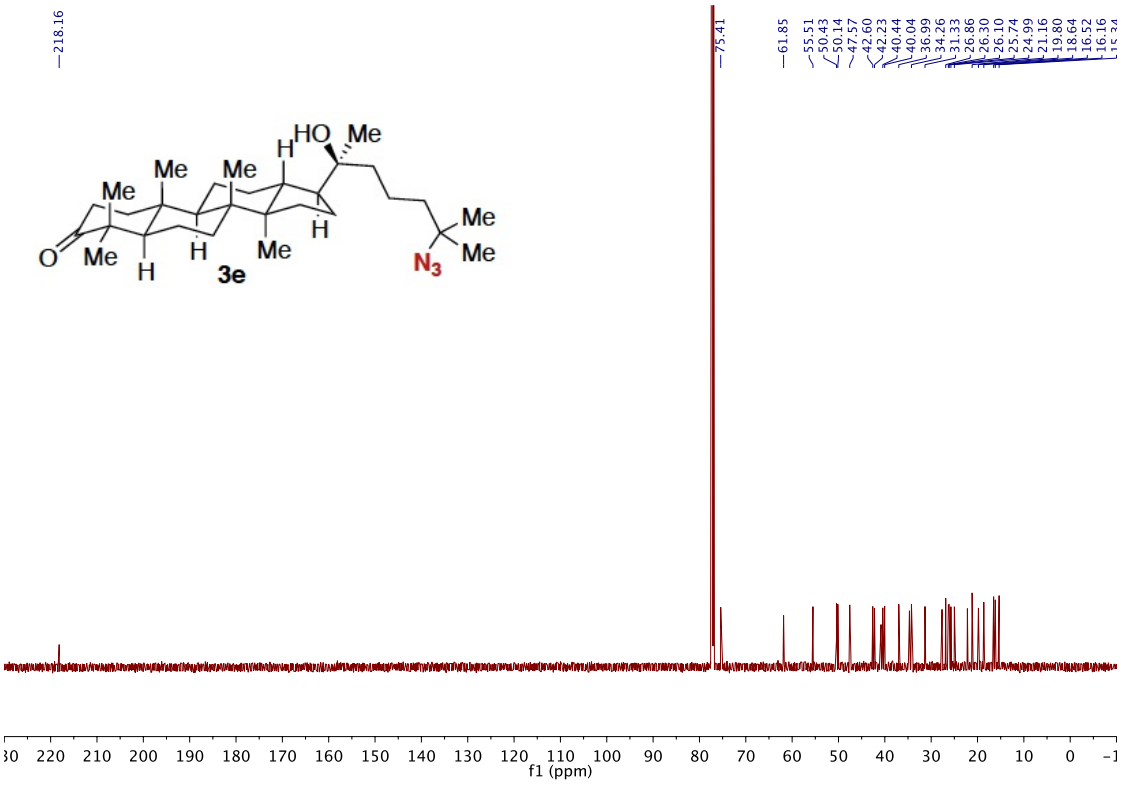
^{1}H-^{13}C gHSQC NMR spectrum of azide **3d**

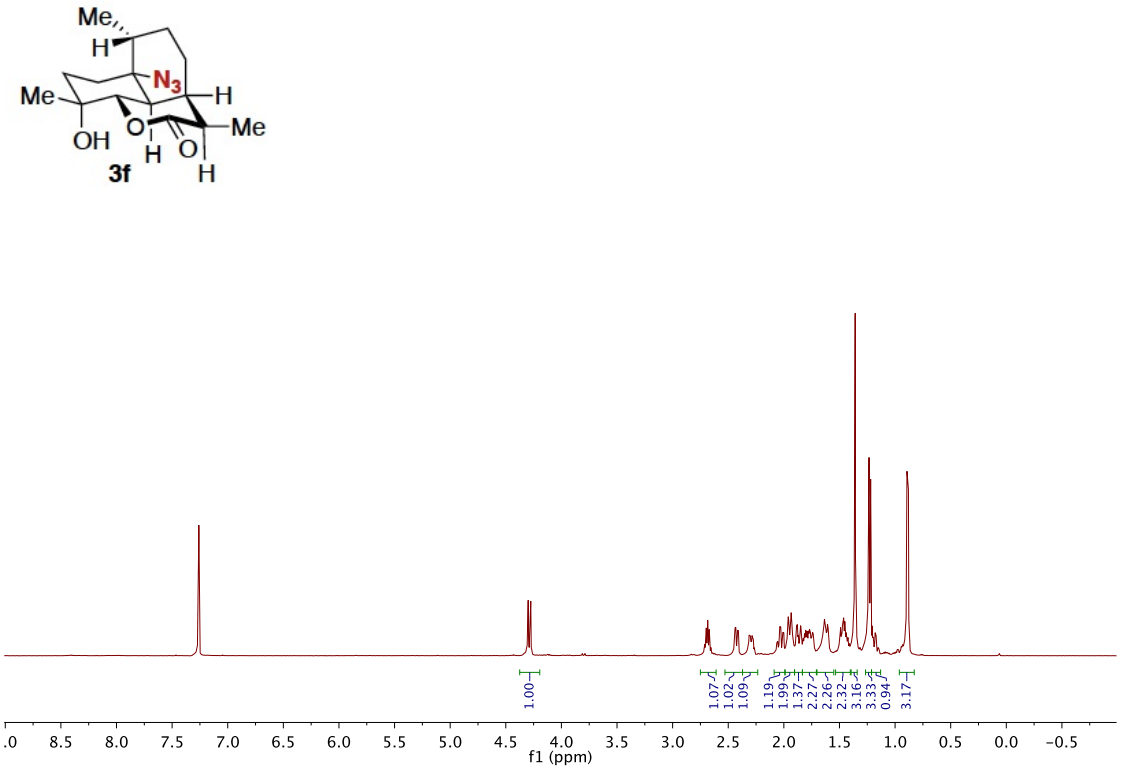


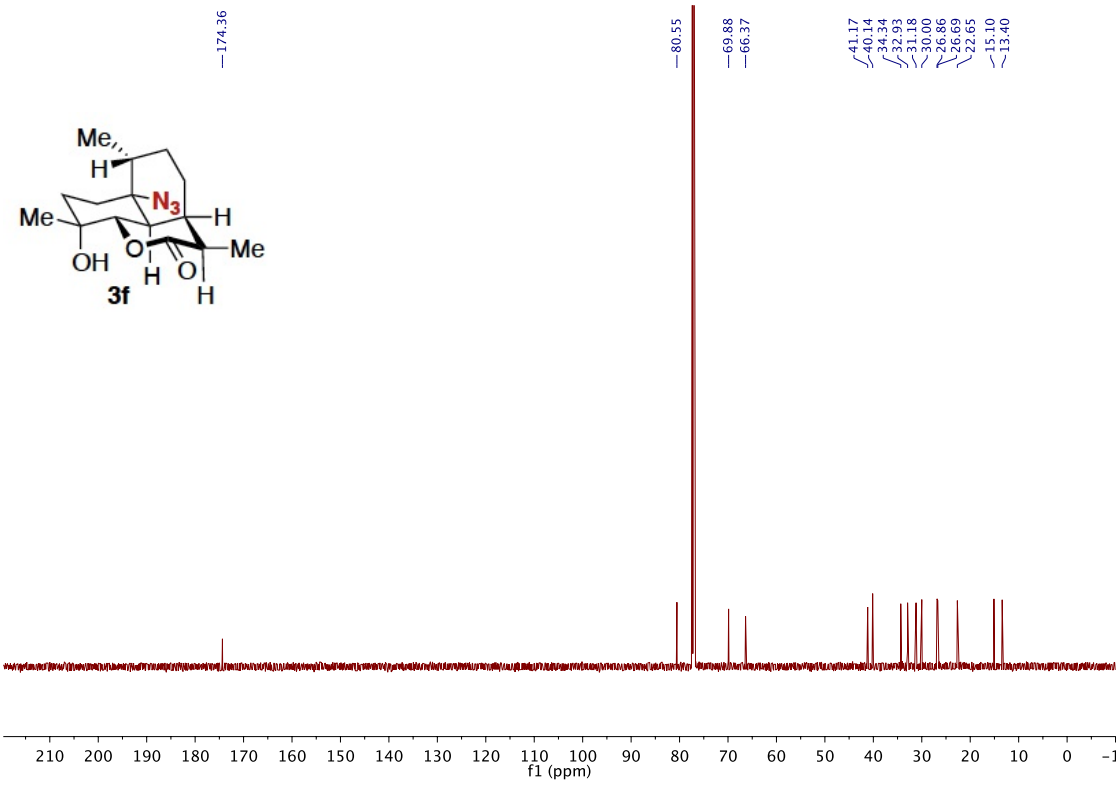

^{1}H-^{13}C gHMBC NMR spectrum of azide **3d**
OAc
Me
H
Me
H
H
OH
AcO
N_3
3d
f2 (ppm)
f1 (ppm)

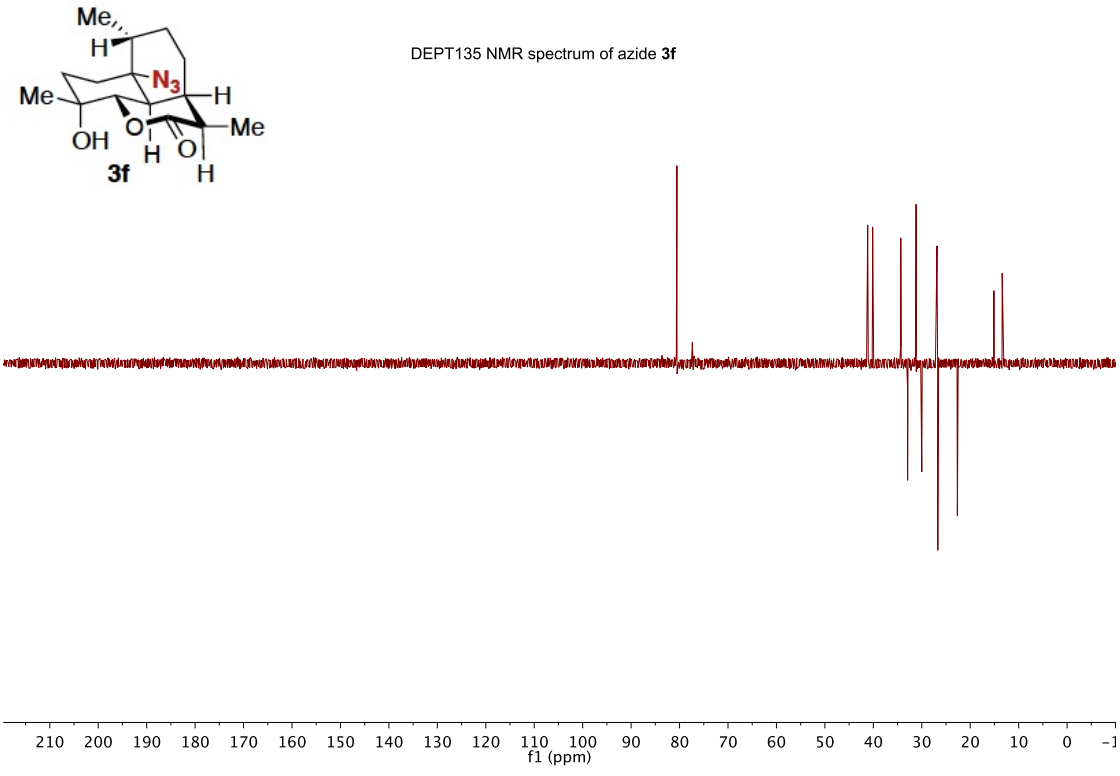

HO
Me
H
Me
Me
Me
H
Me
O
Me
H
H
Me
Me
N_3
3e


1.00
1.12
1.18
1.40
2.18
20.58
4.37
3.82
3.10
2.94
3.04
2.82
f1 (ppm)

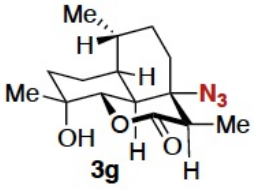

218.16
75.41
61.85
55.51
50.43
50.14
47.57
42.60
42.23
40.44
40.04
36.99
34.26
31.33
26.86
26.30
26.10
25.74
24.99
21.16
19.80
18.64
16.52
16.16
HO
Me
H
Me
Me
Me
Me
H
H
Me
Me
O
Me
H
3e
N3
Me
f1 (ppm)

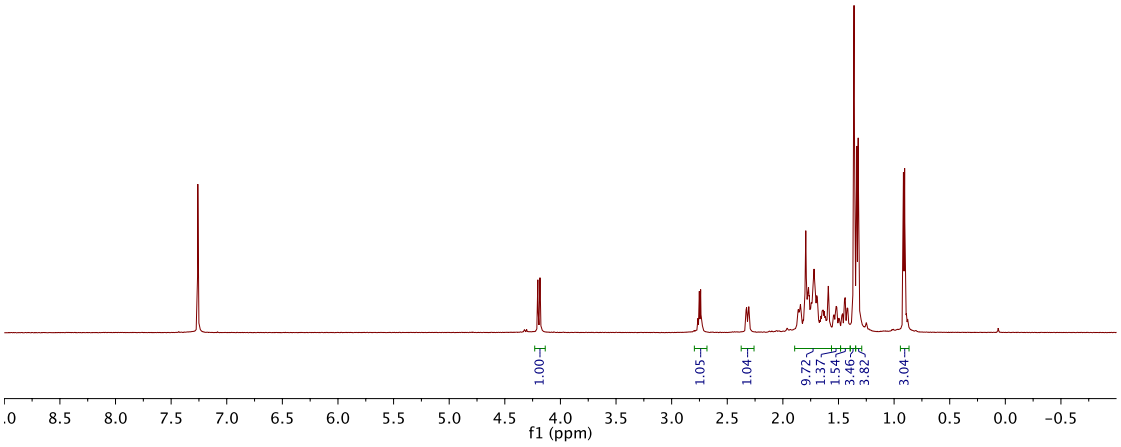

Me
H
N3
H
Me
O
Me
OH
H
O
H
3f
1.00
1.07
1.02
1.09
1.19
1.99
1.37
2.27
2.26
2.32
3.16
3.33
0.94
3.17
f1 (ppm)

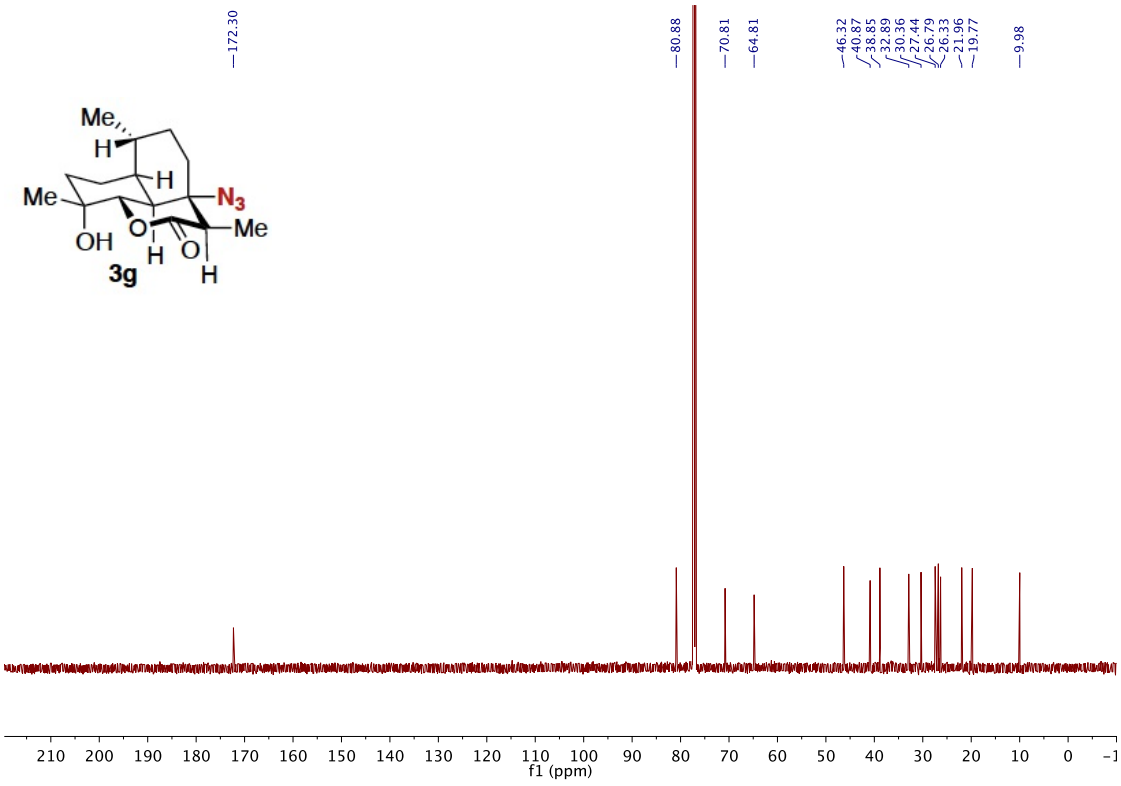




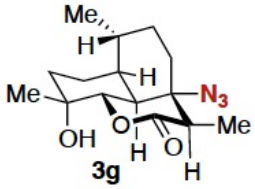
DEPT135 NMR spectrum of azide **3f**


Me
H
H
Me
N3
OH
O
Me
H
O
H
3g

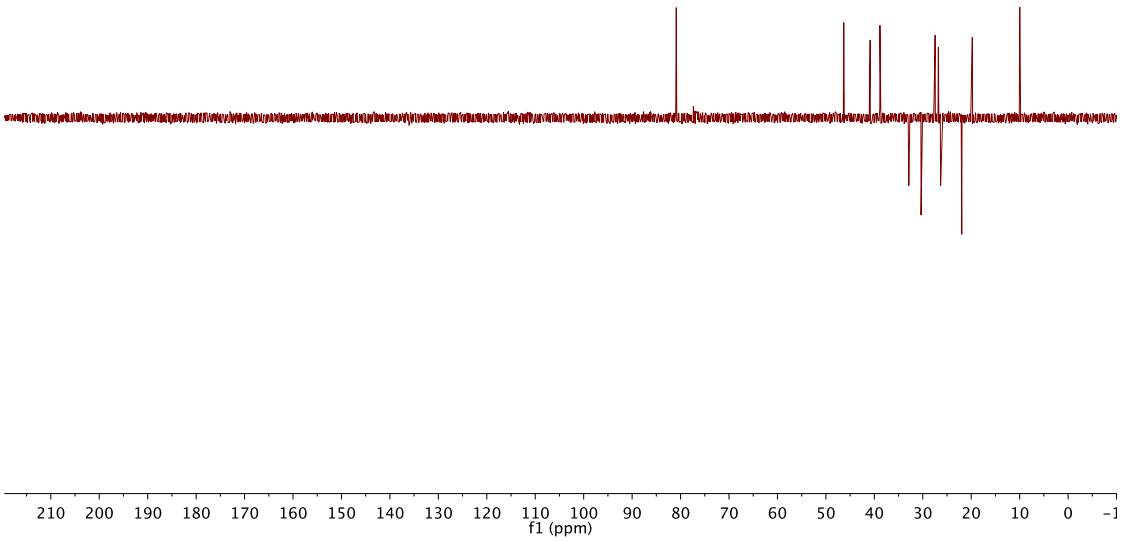

1.00
1.05
1.04
9.72
1.37
1.54
3.46
3.82
3.04
f1 (ppm)

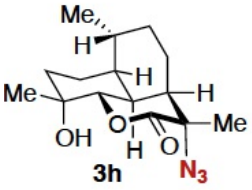

172.30
80.88
70.81
64.81
46.32
40.87
38.85
32.89
30.36
27.44
26.79
26.33
21.96
19.77
9.98
f1 (ppm)

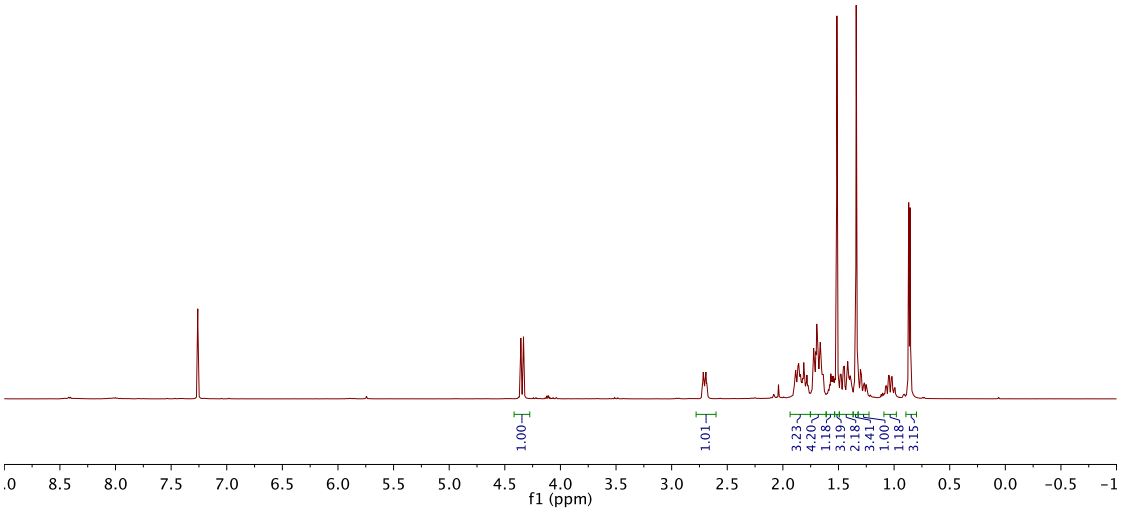
Me
H
H
Me
N3
OH
O
Me
H
O
H
3g

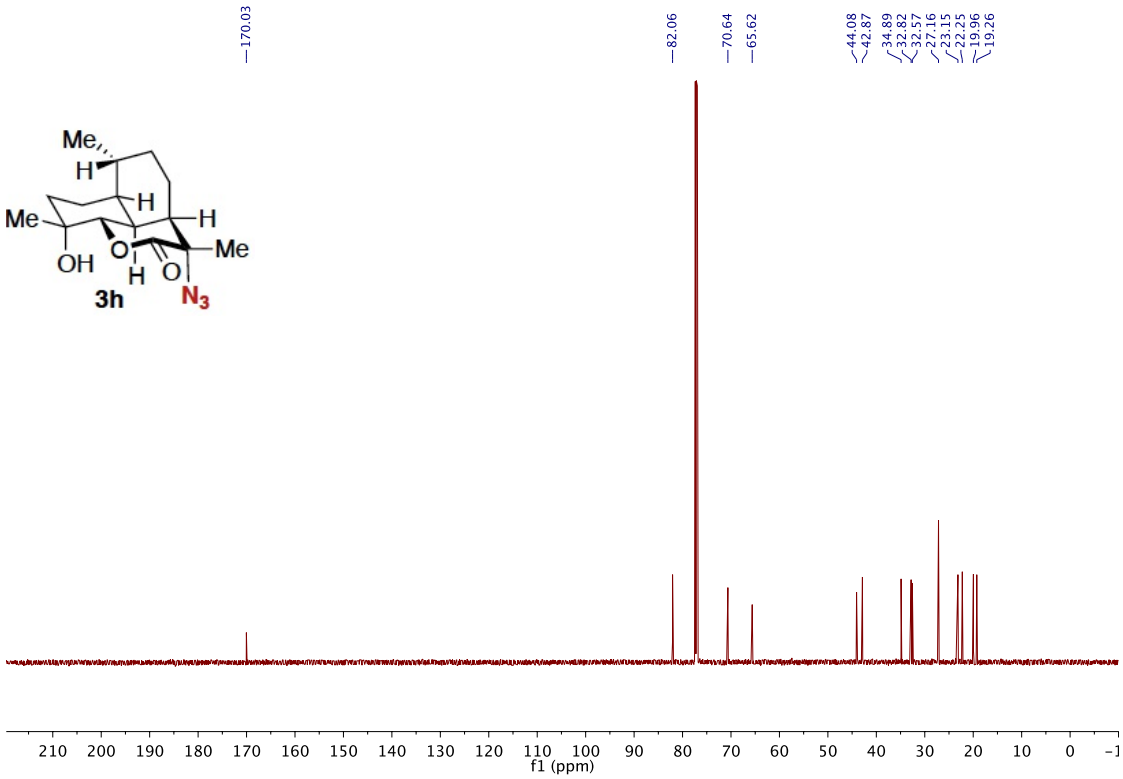


DEPT135 NMR spectrum of azide **3g**

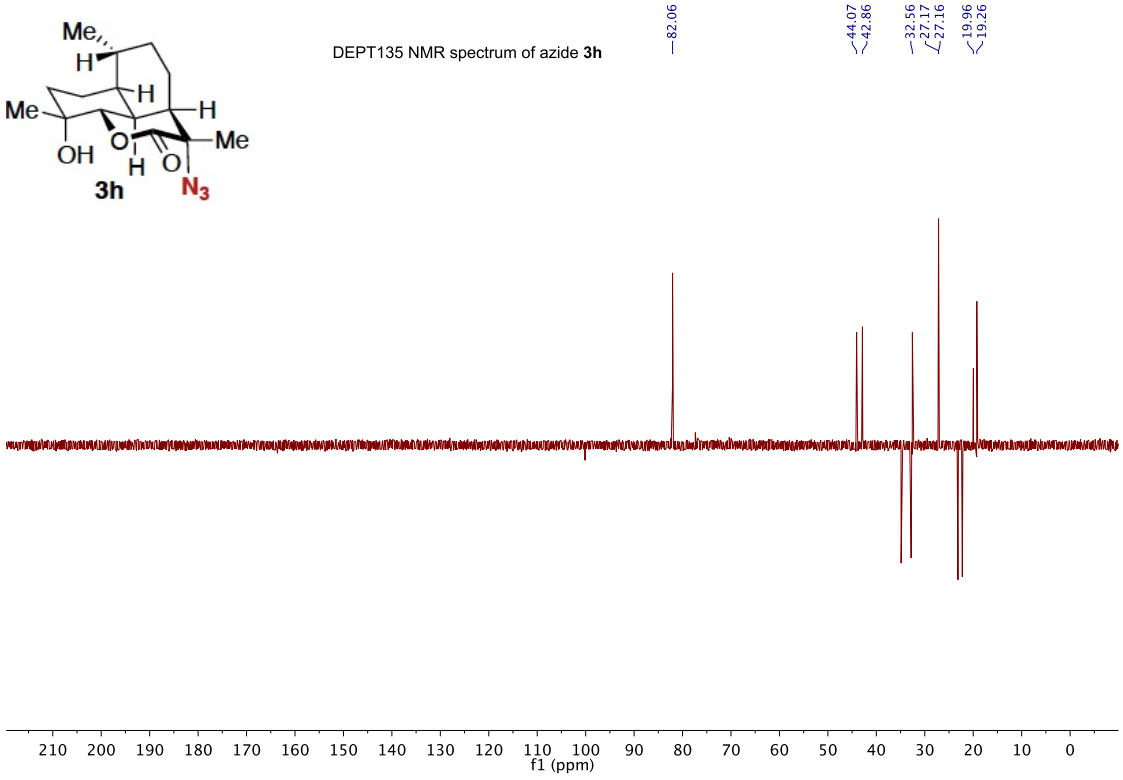


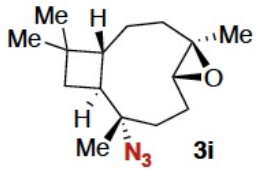






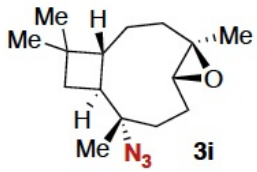
DEPT135 NMR spectrum of azide **3h**




Me
H
Me
Me
O
H
Me
N3

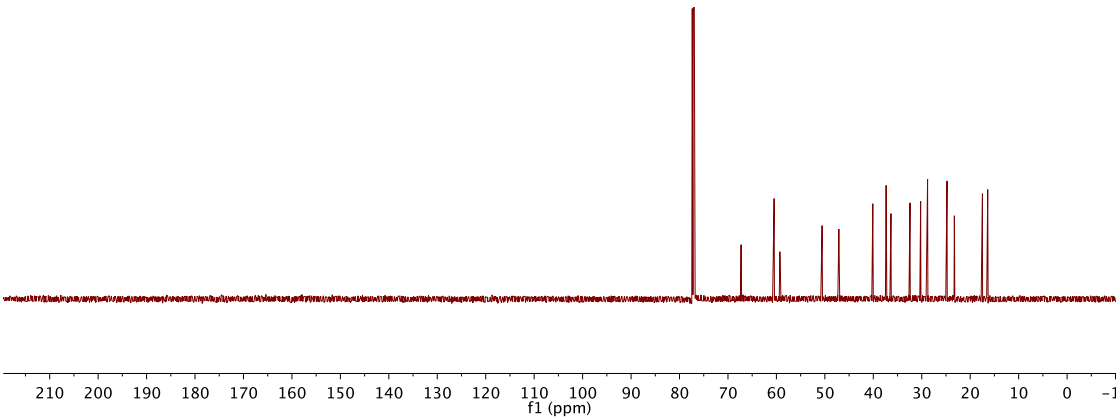
3i

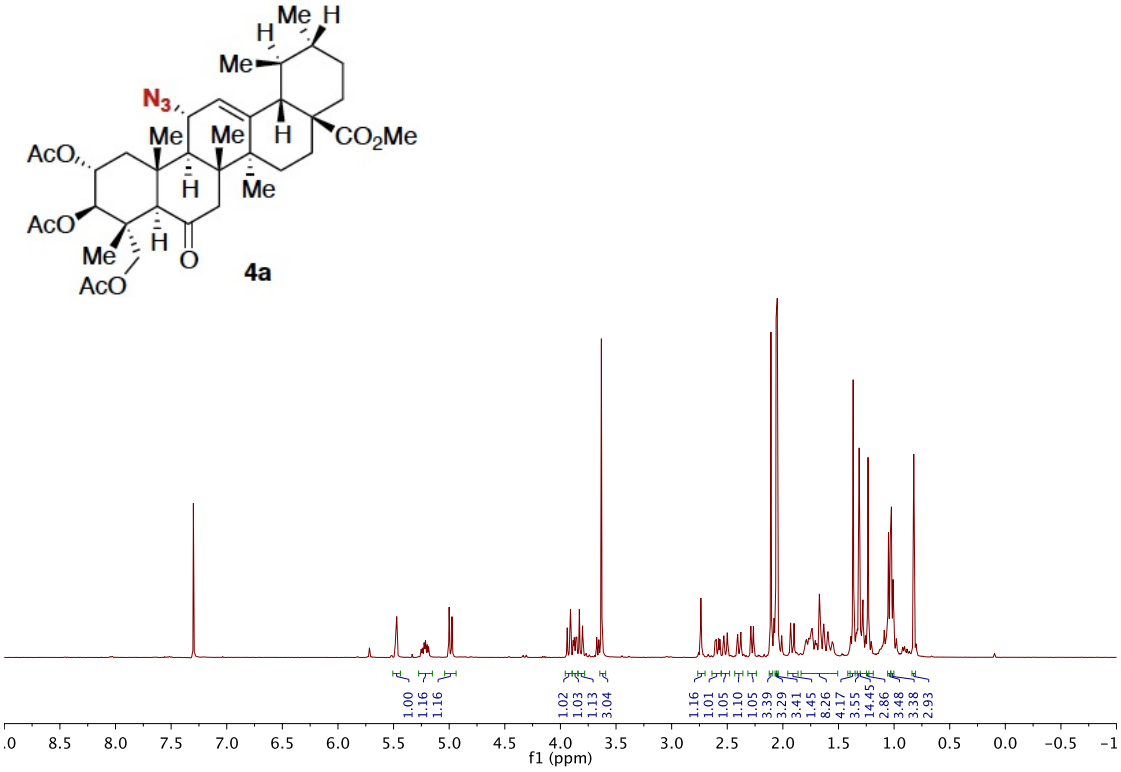
1.00
2.06
1.03
1.01
1.09
1.09
3.22
0.97
1.28
2.79
2.84
2.86
3.03
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

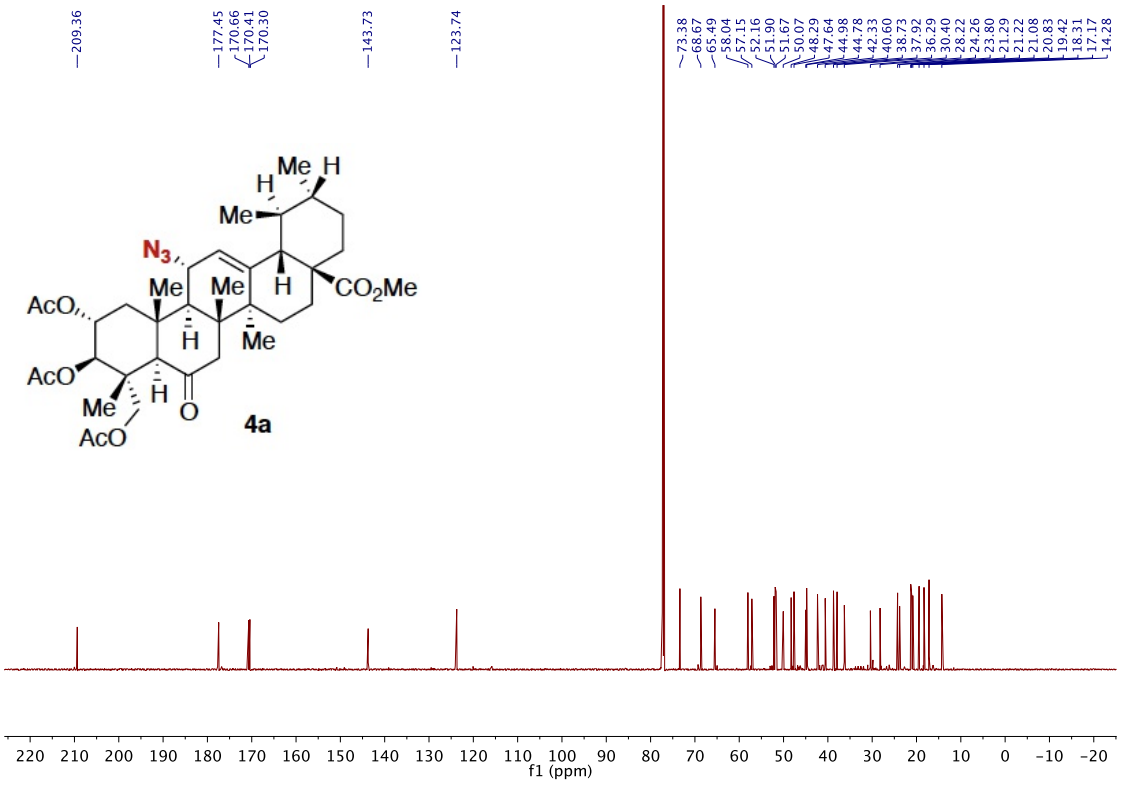

Me
H
Me
Me
O
H
Me
N3

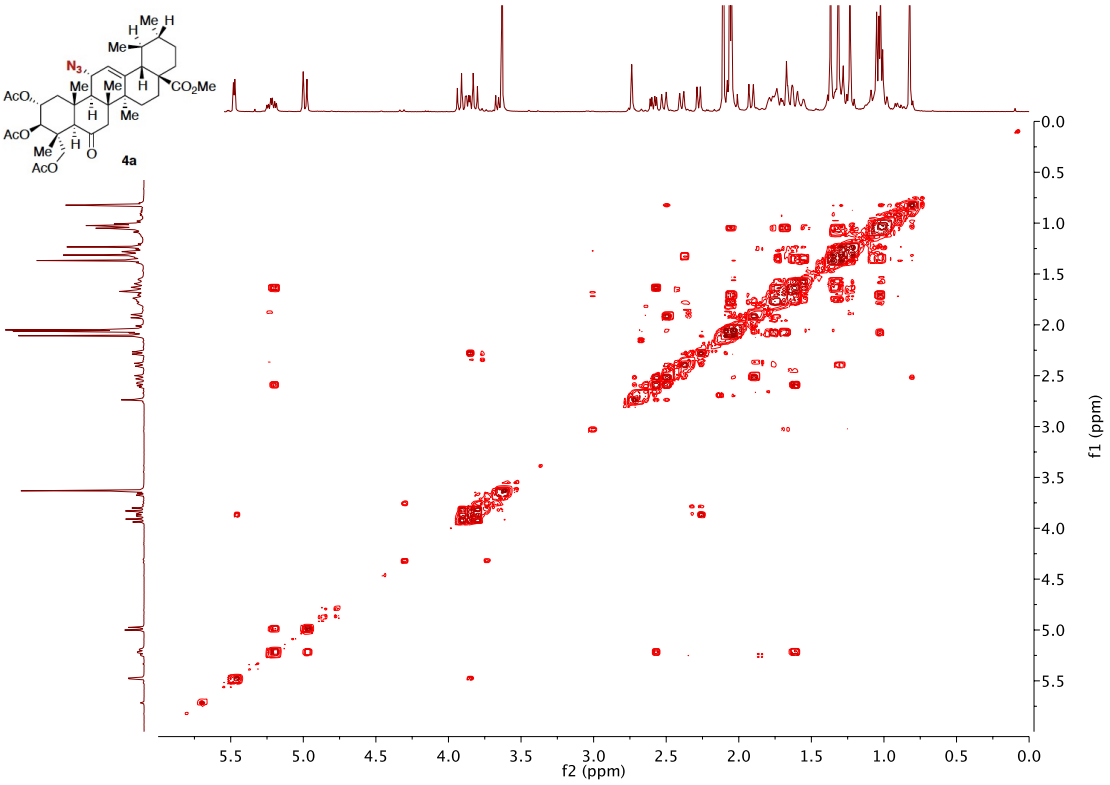
3i

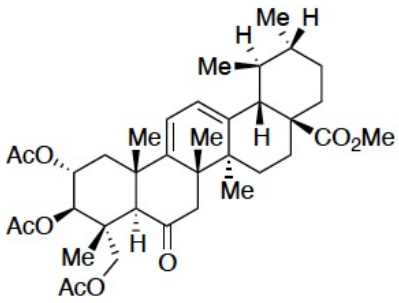

77.37
77.16
76.95
67.30
60.47
59.29
50.57
47.11
40.10
37.36
36.36
32.42
30.23
28.80
24.78
23.27
17.48
16.38

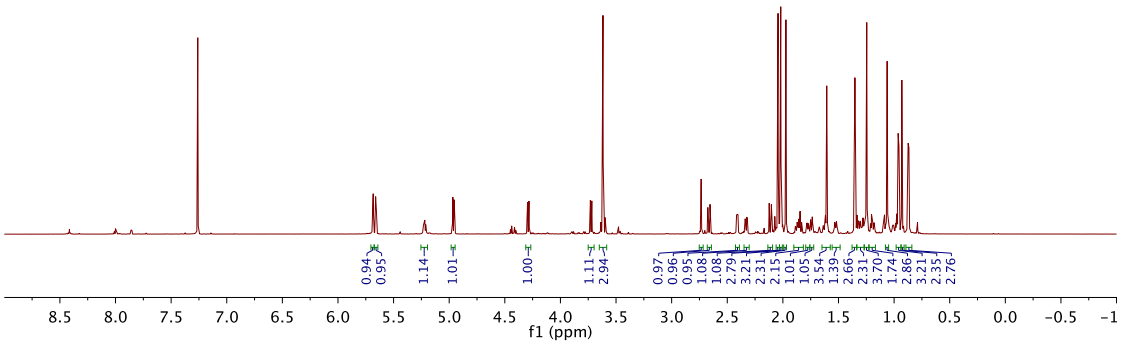

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

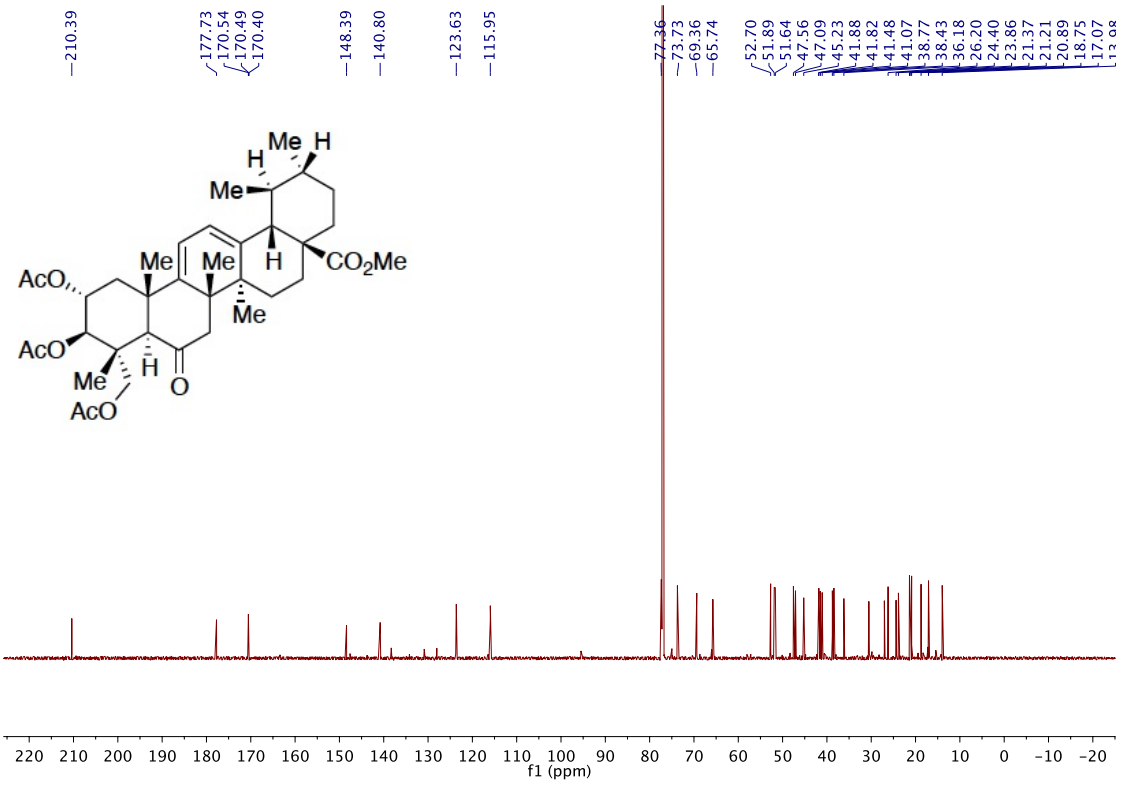

Me H
H
Me
N3
Me
Me
H
CO2Me
AcO
H
Me
AcO
Me
H
O
AcO
4a
1.00
1.16
1.16
1.02
1.03
1.13
3.04
1.16
1.01
1.05
1.10
1.05
3.39
3.29
3.41
1.45
8.26
4.17
3.55
14.45
2.86
3.48
3.38
2.93
f1 (ppm)

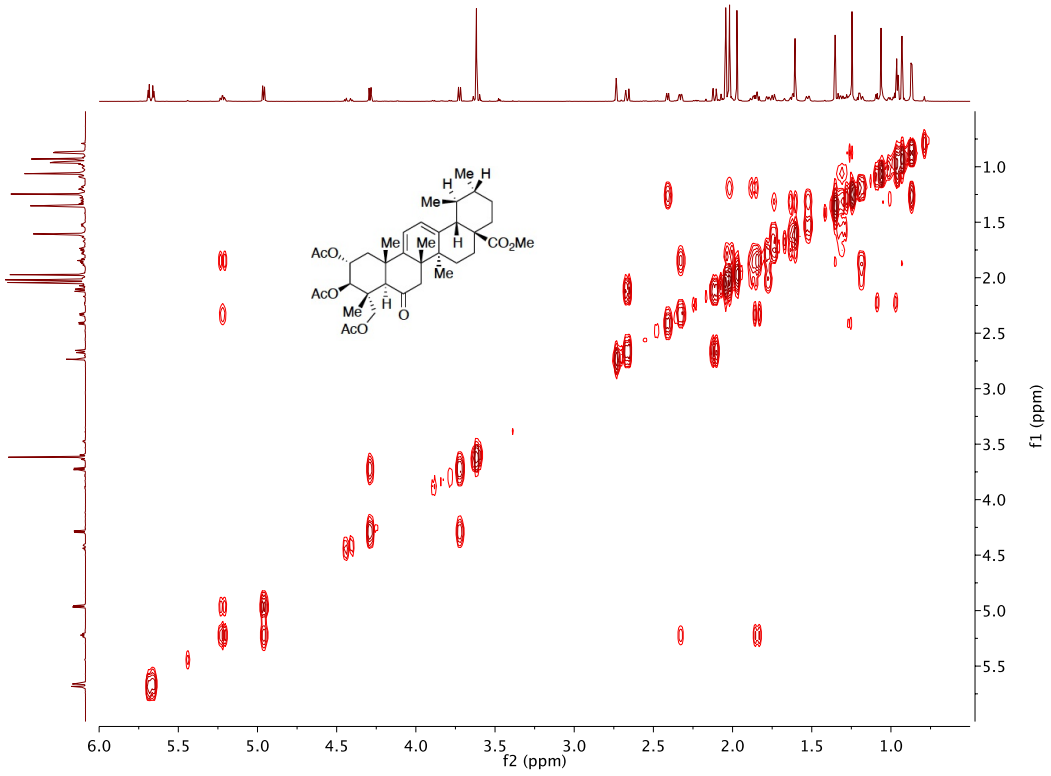

209.36
177.45
170.66
170.41
170.30
143.73
123.74
73.38
68.67
65.49
58.04
57.15
52.16
51.90
51.67
50.07
48.29
47.64
44.98
44.78
42.33
40.60
38.73
37.92
36.29
30.40
28.22
24.26
23.80
21.29
21.22
21.08
20.83
19.42
18.31
17.17
14.28
Me H
H
Me
N3
Me
Me
H
CO2Me
AcO
H
Me
AcO
Me
H
O
AcO
4a
f1 (ppm)

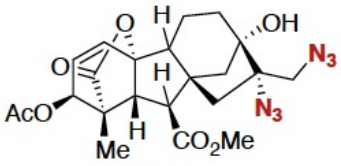

4a
f2 (ppm)
f1 (ppm)



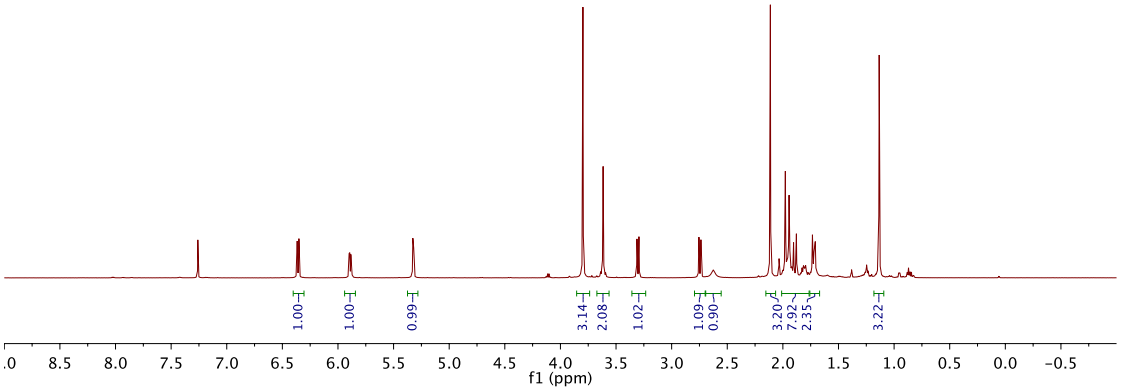

f1 (ppm)

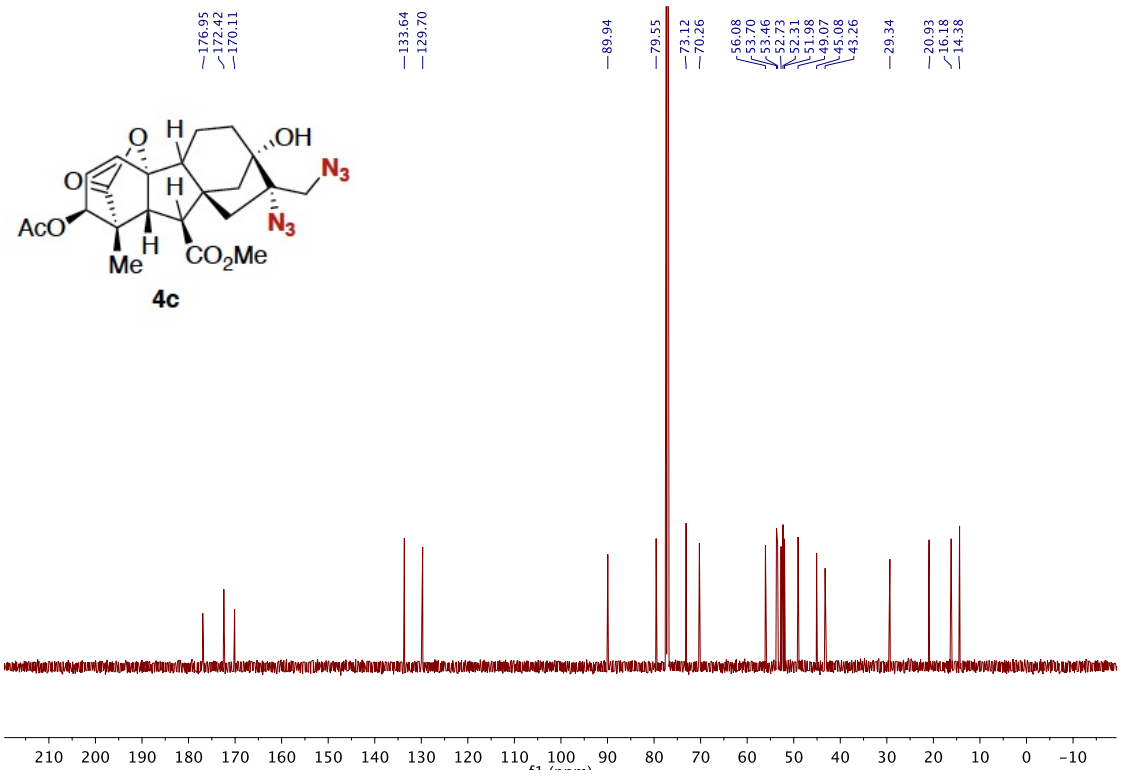

210.39
177.73
170.54
170.49
170.40
148.39
140.80
123.63
115.95
77.36
73.73
69.36
65.74
52.70
51.89
51.64
47.56
47.09
45.23
41.88
41.82
41.48
41.07
38.77
38.43
36.18
26.20
24.40
23.86
21.37
21.21
20.89
18.75
17.07
Me H
H
Me
Me
Me
H
CO2Me
AcO
AcO
Me
H
O
AcO
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


Me H
H
Me
Me
Me
H
CO2Me
AcO
AcO
Me
H
O
AcO
Me
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)


O
H
OH
N3
O
H
AcO
N3
H
Me
CO2Me

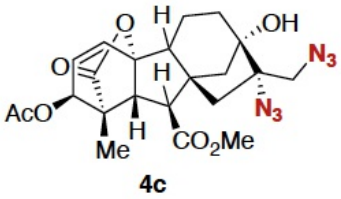
4c


1.00
1.00
0.99
3.14
2.08
1.02
1.09
0.90
3.20
7.92
2.35
3.22
f1 (ppm)


176.95
172.42
170.11
133.64
129.70
89.94
79.55
73.12
70.26
56.08
53.70
53.46
52.73
52.31
51.98
49.07
45.08
43.26
29.34
20.93
16.18
14.38

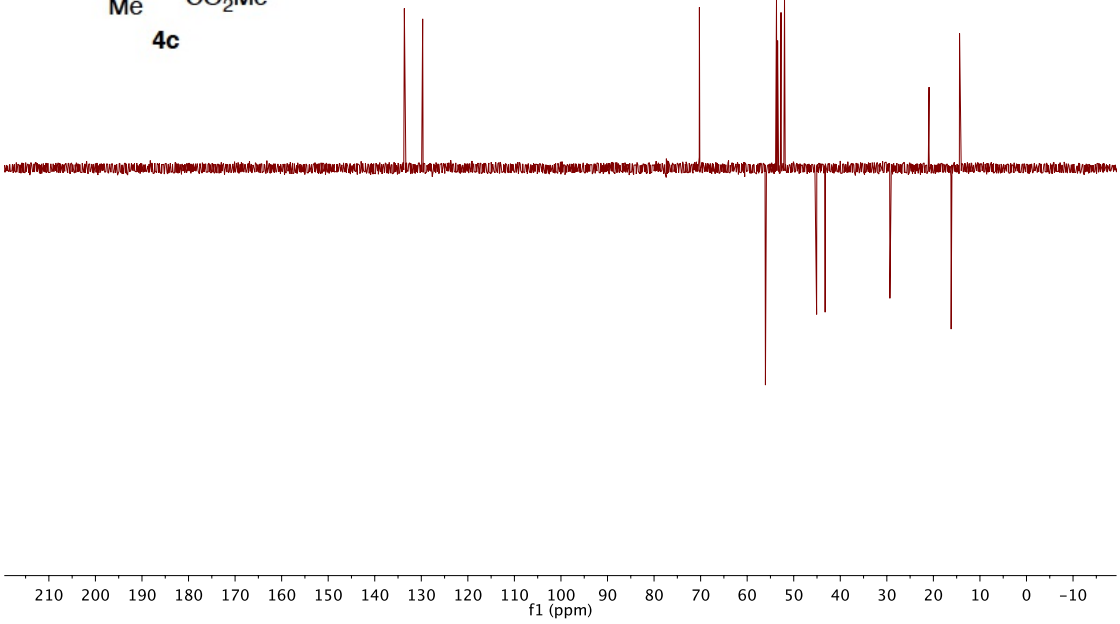
O
H
OH
N3
O
H
AcO
N3
H
Me
CO2Me

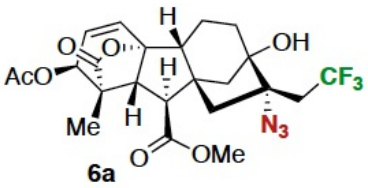
4c



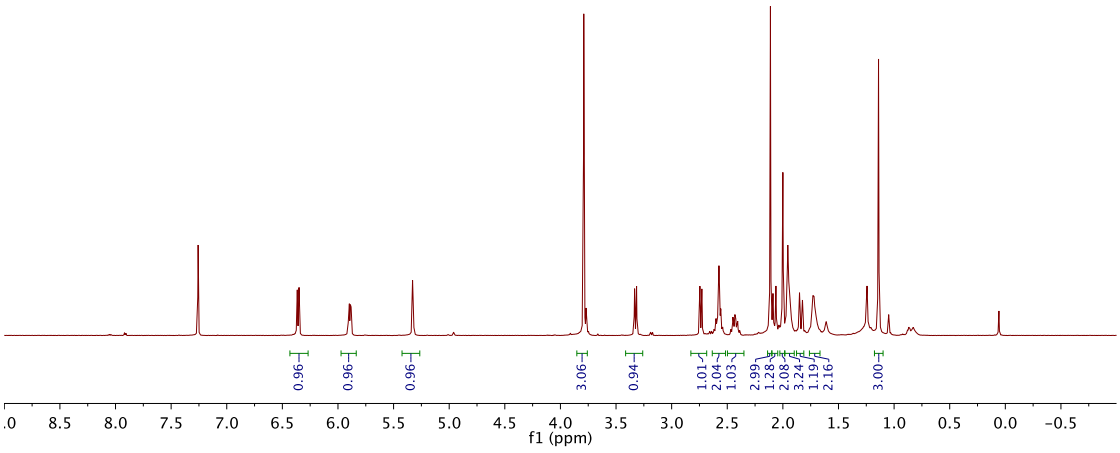
4c

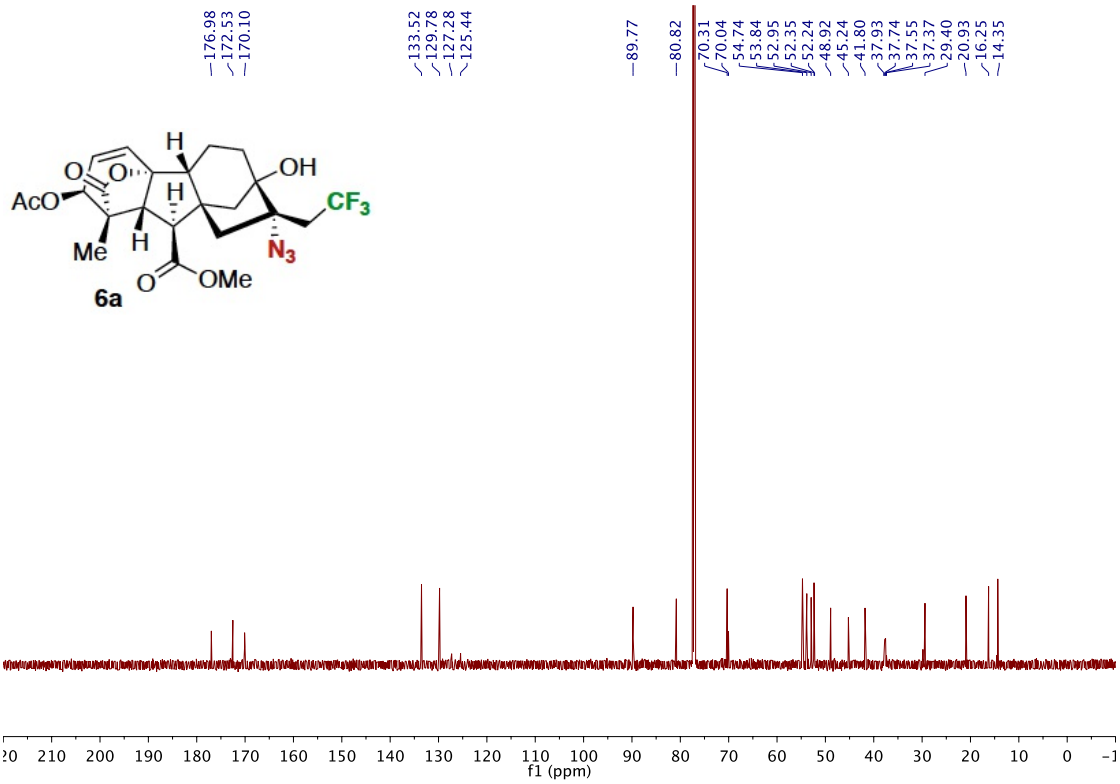
DEPT135 NMR spectrum of azide **4c**

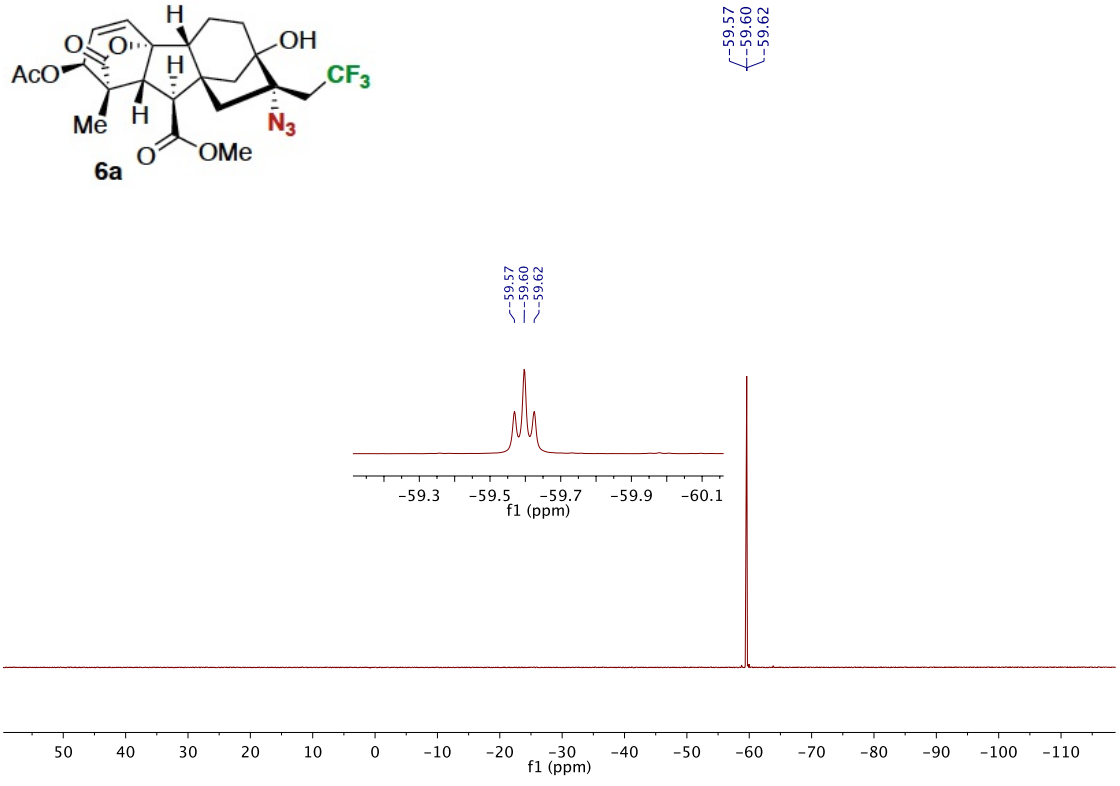


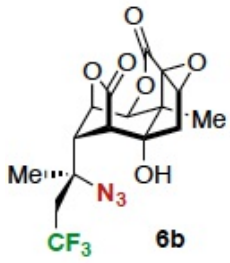


6a

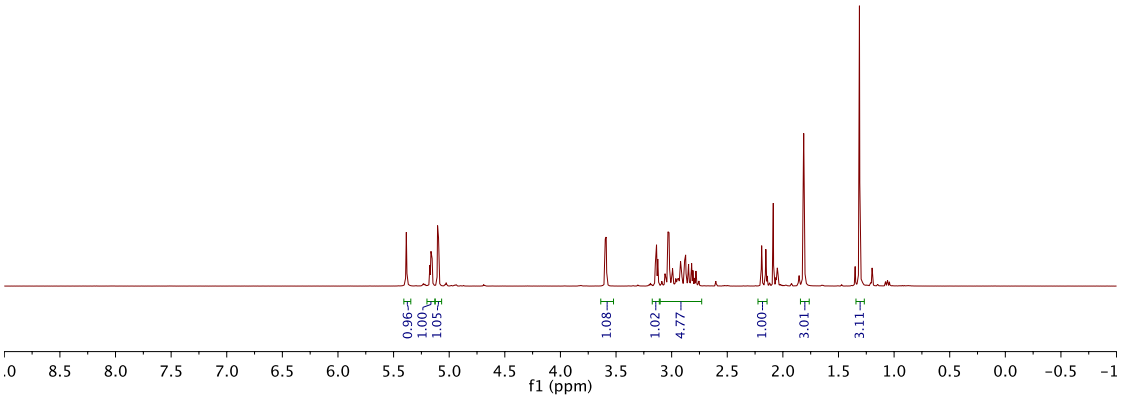


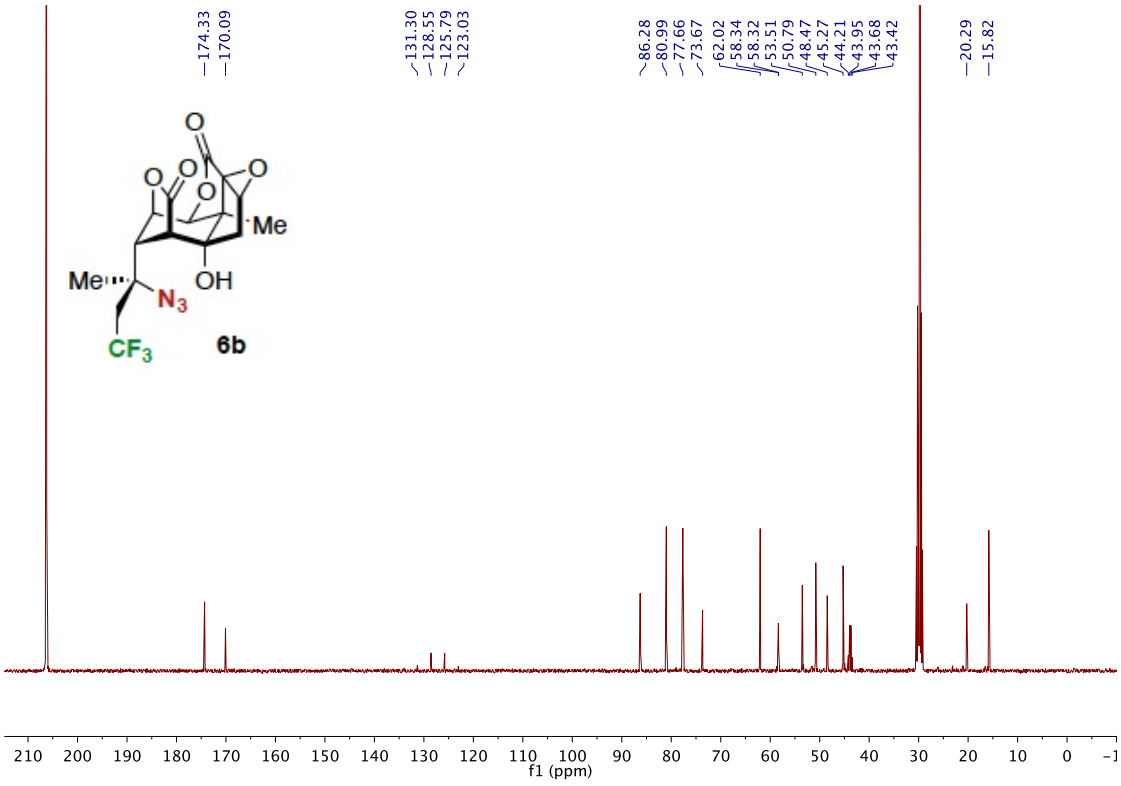

176.98
172.53
170.10
133.52
129.78
127.28
125.44
89.77
80.82
70.31
70.04
54.74
53.84
52.95
52.35
52.24
48.92
45.24
41.80
37.93
37.74
37.55
37.37
29.40
20.93
16.25
14.35
H
O
O
AcO
H
OH
CF3
Me
H
N3
O
OMe
6a
f1 (ppm)


59.57
59.60
59.62
H
O
O
AcO
H
OH
CF3
Me
H
N3
O
OMe
6a
59.57
59.60
59.62
f1 (ppm)
f1 (ppm)


O
O
O
O
O
O
Me
Me
N3
OH
CF3

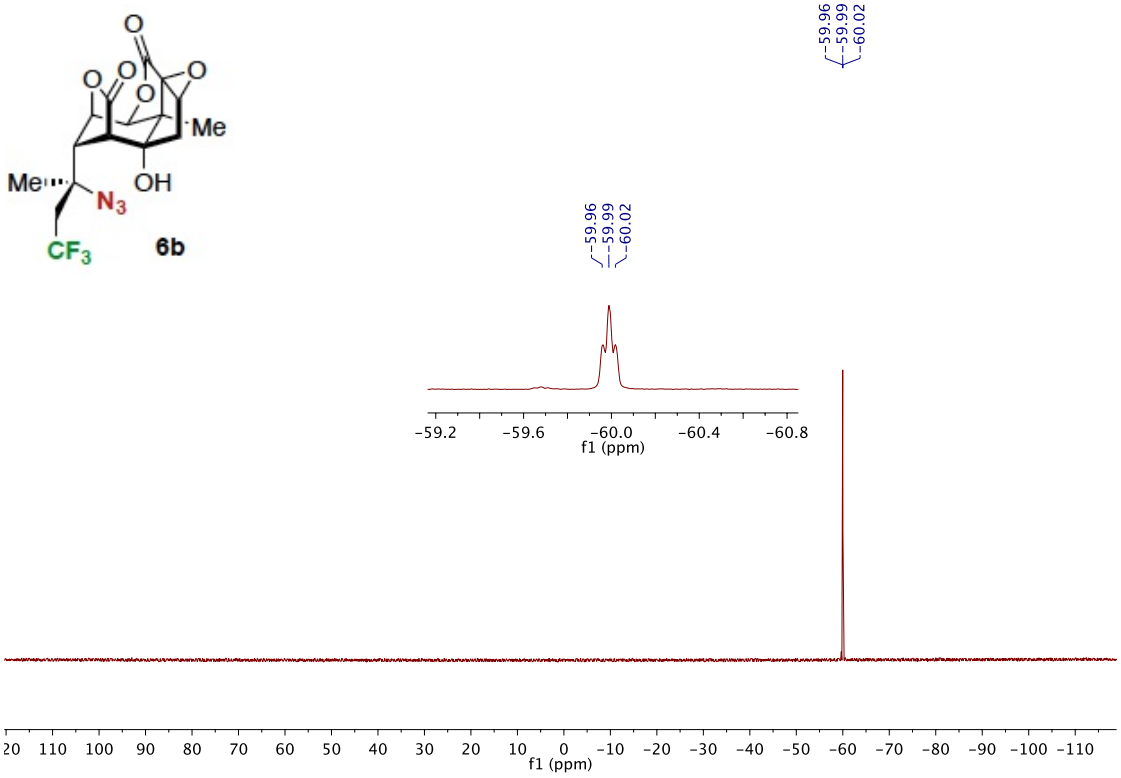
6b

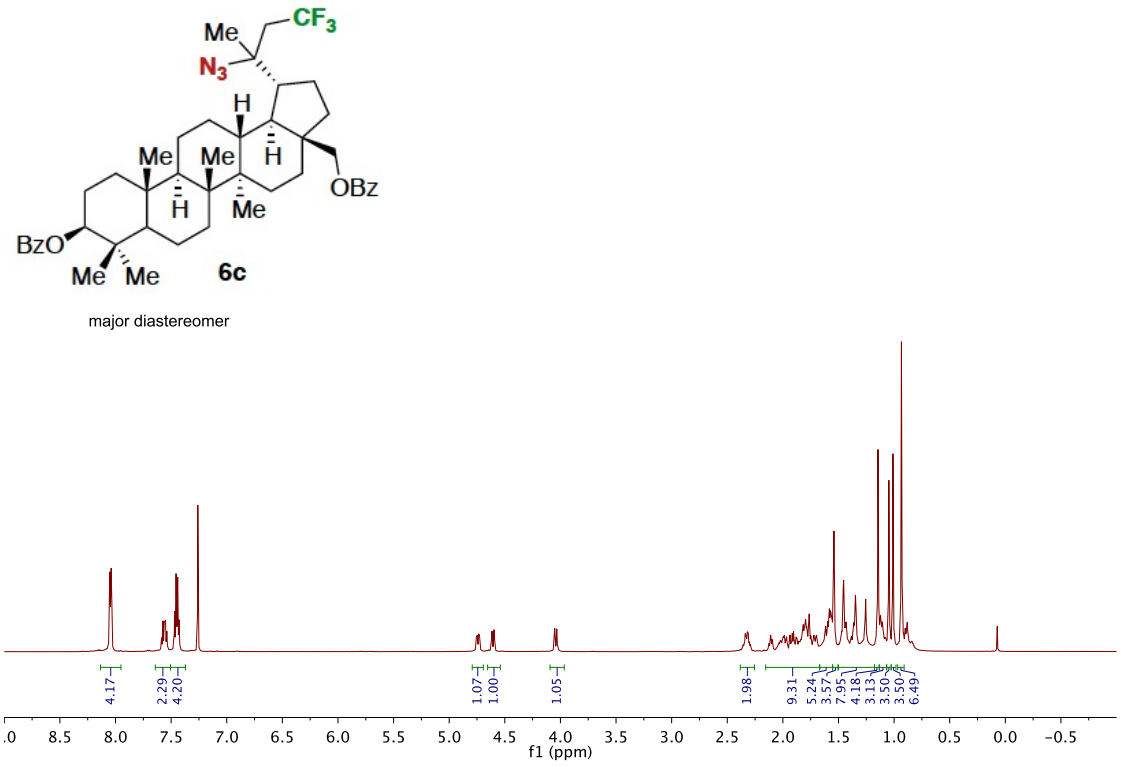

0.96
1.00
1.05
1.08
1.02
4.77
1.00
3.01
3.11
f1 (ppm)

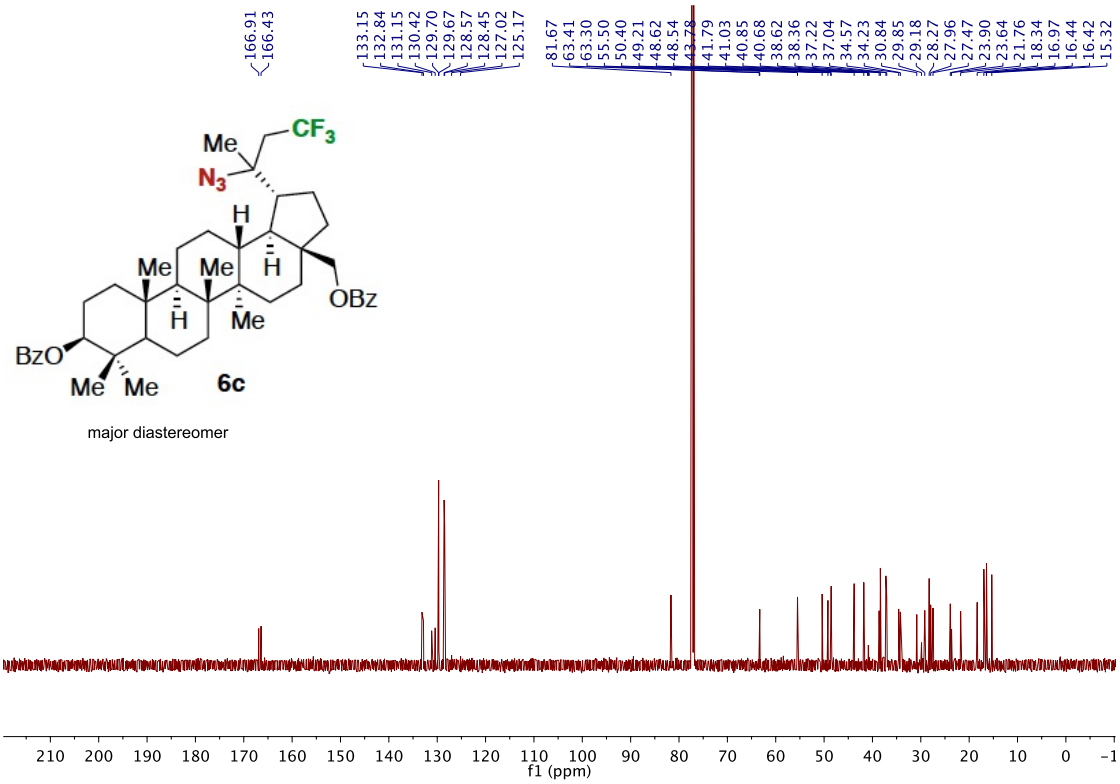

174.33
170.09
131.30
128.55
125.79
123.03
86.28
80.99
77.66
73.67
62.02
58.34
58.32
53.51
50.79
48.47
45.27
44.21
43.95
43.68
43.42
20.29
15.82
f1 (ppm)

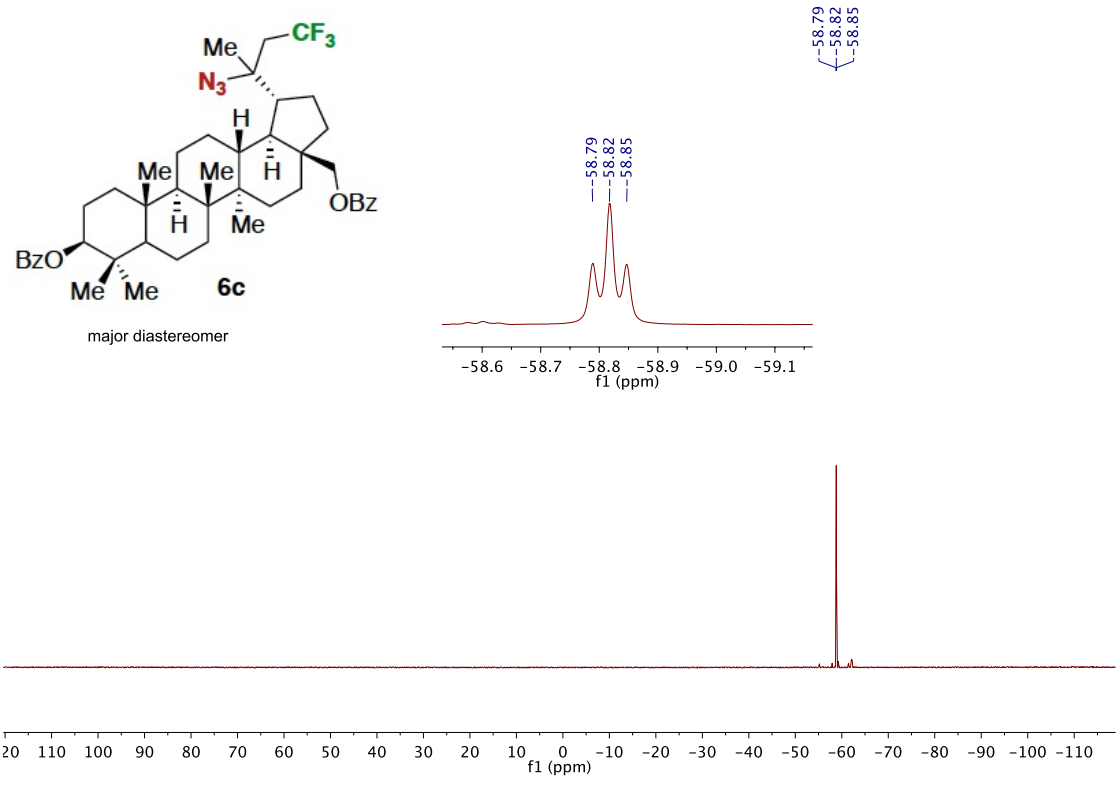
O
O
O
O
O
O
Me
Me
N3
OH
CF3

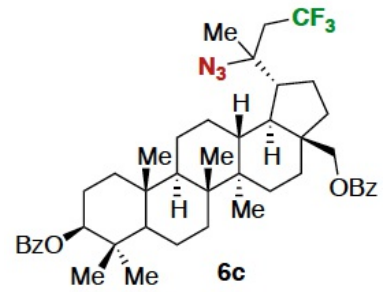
6b


Me
OH
N3
CF3
6b
-59.96
-59.99
-60.02
-59.2
-59.6
-60.0
-60.4
-60.8
f1 (ppm)
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

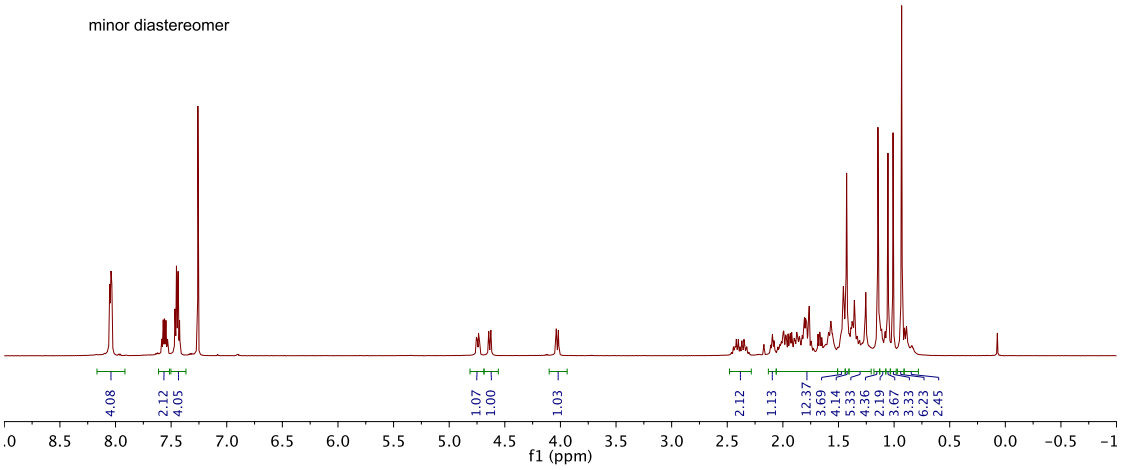

Me
CF3
N3
H
Me
Me
H
OBz
H
Me
BzO
Me
Me
6c
major diastereomer
4.17
2.29
4.20
1.07
1.00
1.05
1.98
9.31
5.24
3.57
7.95
4.18
3.13
3.50
3.50
6.49
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

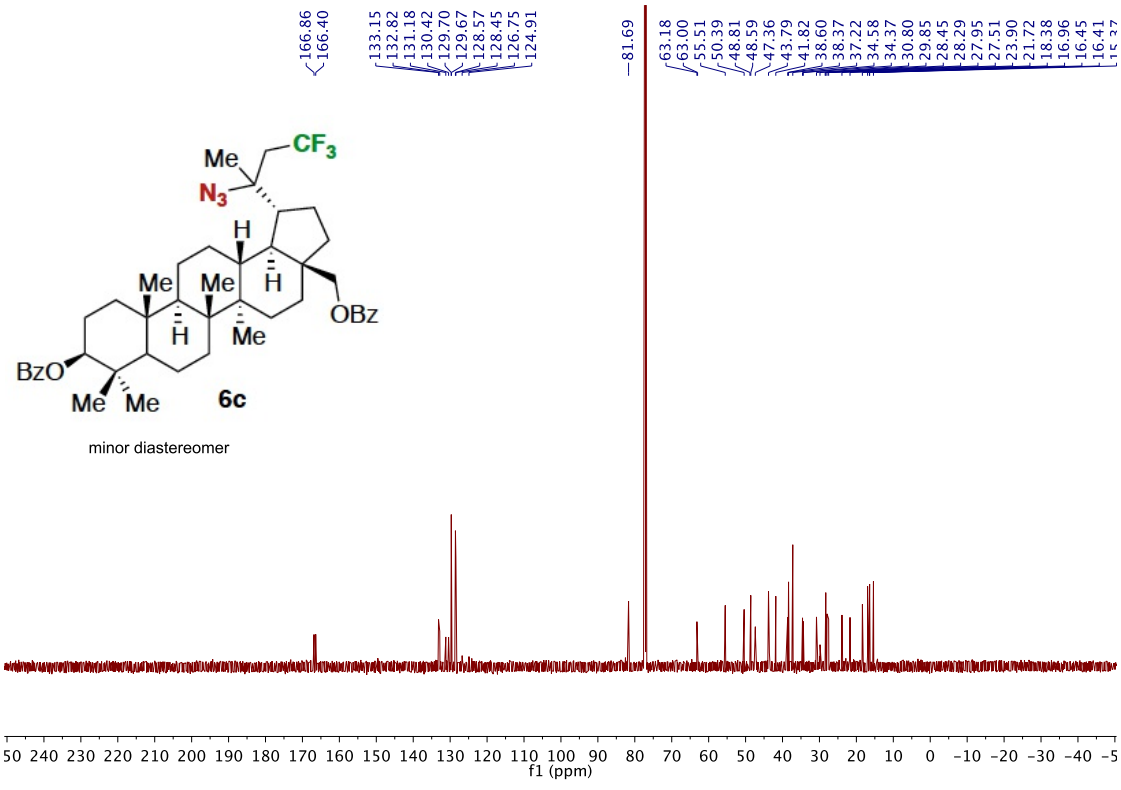

166.91
166.43
133.15
132.84
131.15
130.42
129.70
129.67
128.57
128.45
127.02
125.17
81.67
63.41
63.30
55.50
50.40
49.21
48.62
48.54
43.78
41.79
41.03
40.85
40.68
38.62
38.36
37.22
37.04
34.57
34.23
30.84
29.85
29.18
28.27
27.96
27.47
23.90
23.64
21.76
18.34
16.97
16.44
16.42
15.32
Me
CF3
N3
H
Me
Me
H
OBz
H
Me
BzO
Me
Me
6c
major diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)


Me
CF3
N3
H
Me
Me
H
OBz
H
Me
BzO
Me
Me
6c
major diastereomer
−58.79
−58.82
−58.85
−58.6 −58.7 −58.8 −58.9 −59.0 −59.1
f1 (ppm)
20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110
f1 (ppm)

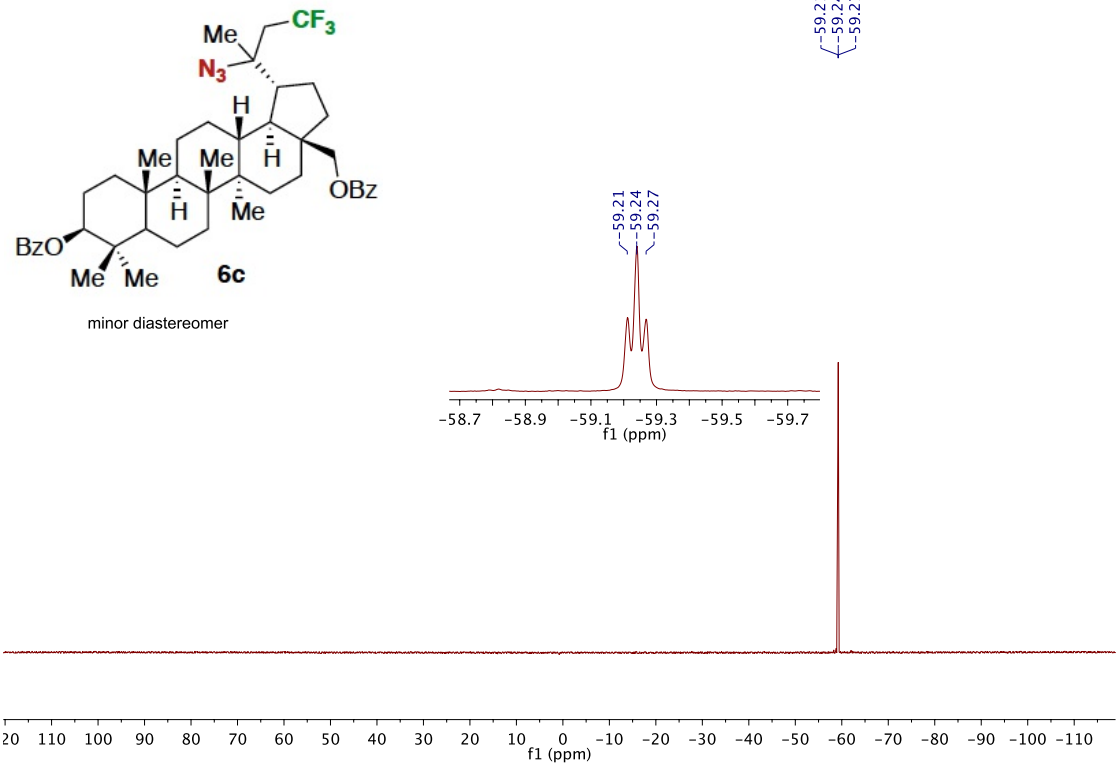


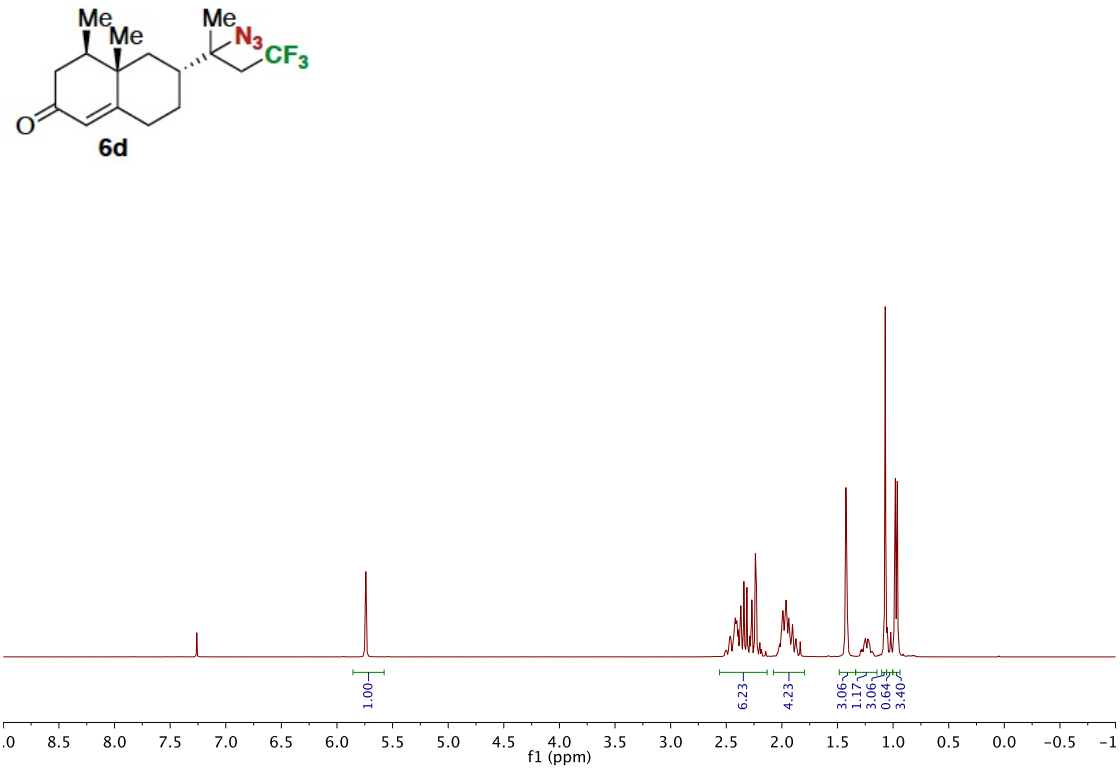
minor diastereomer

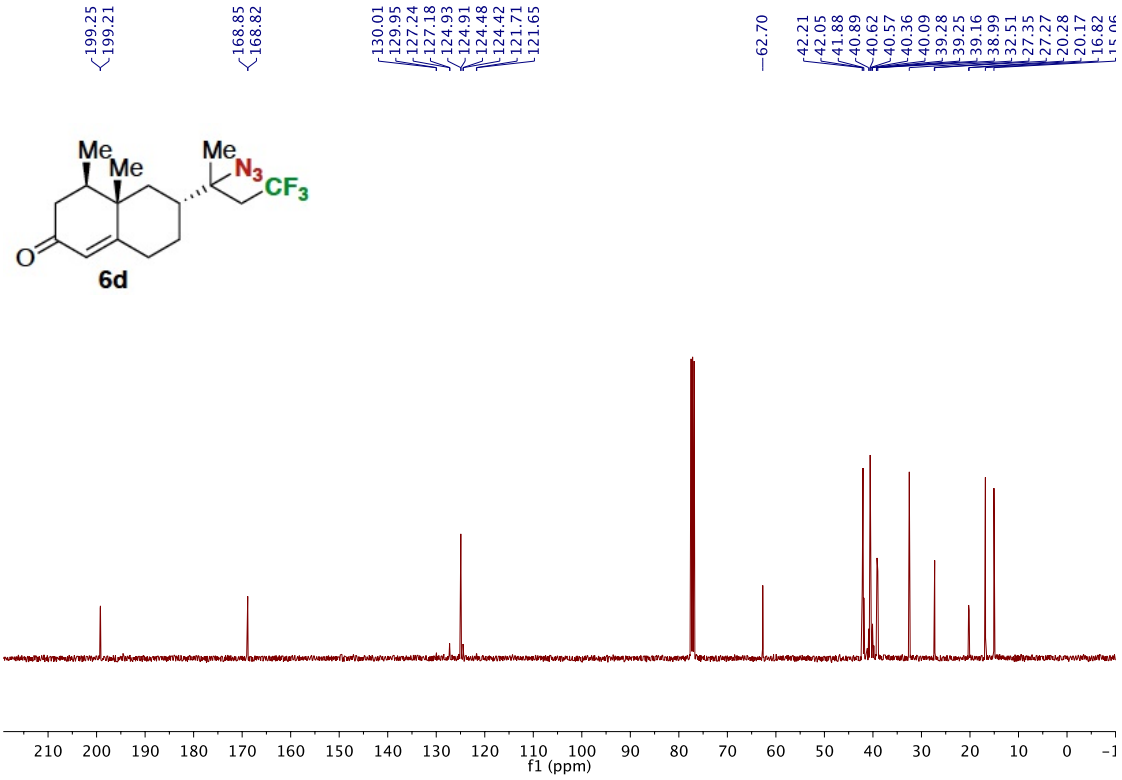


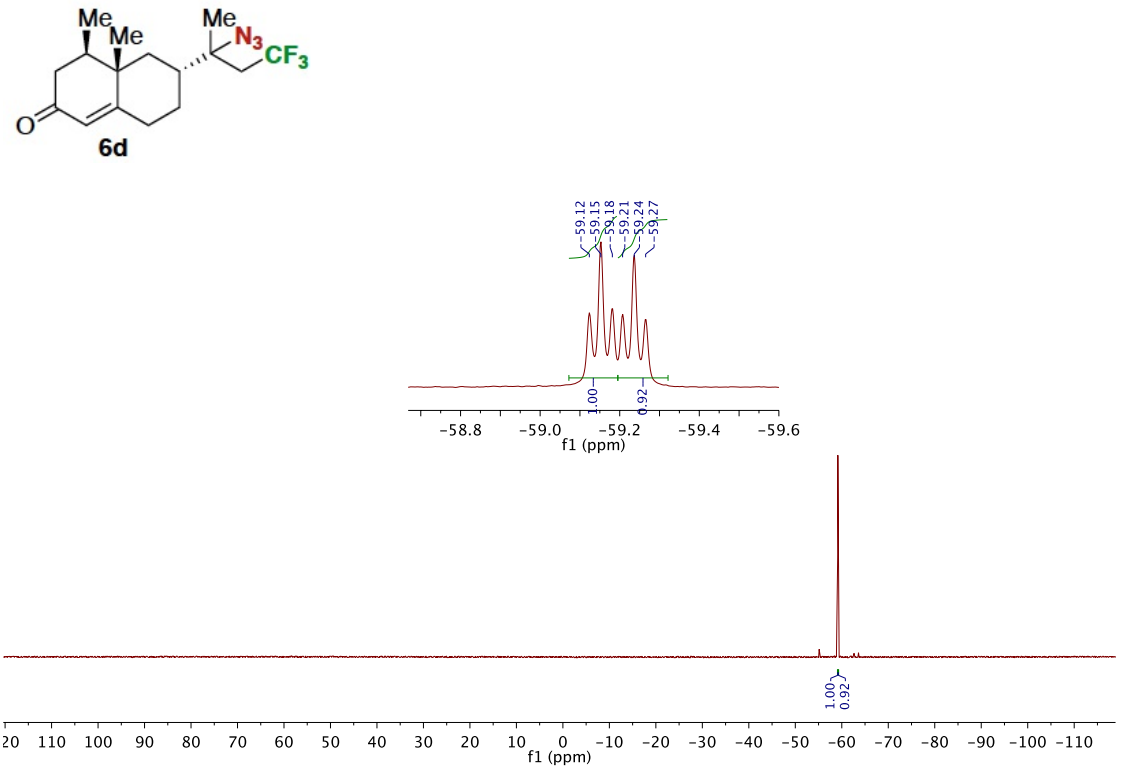


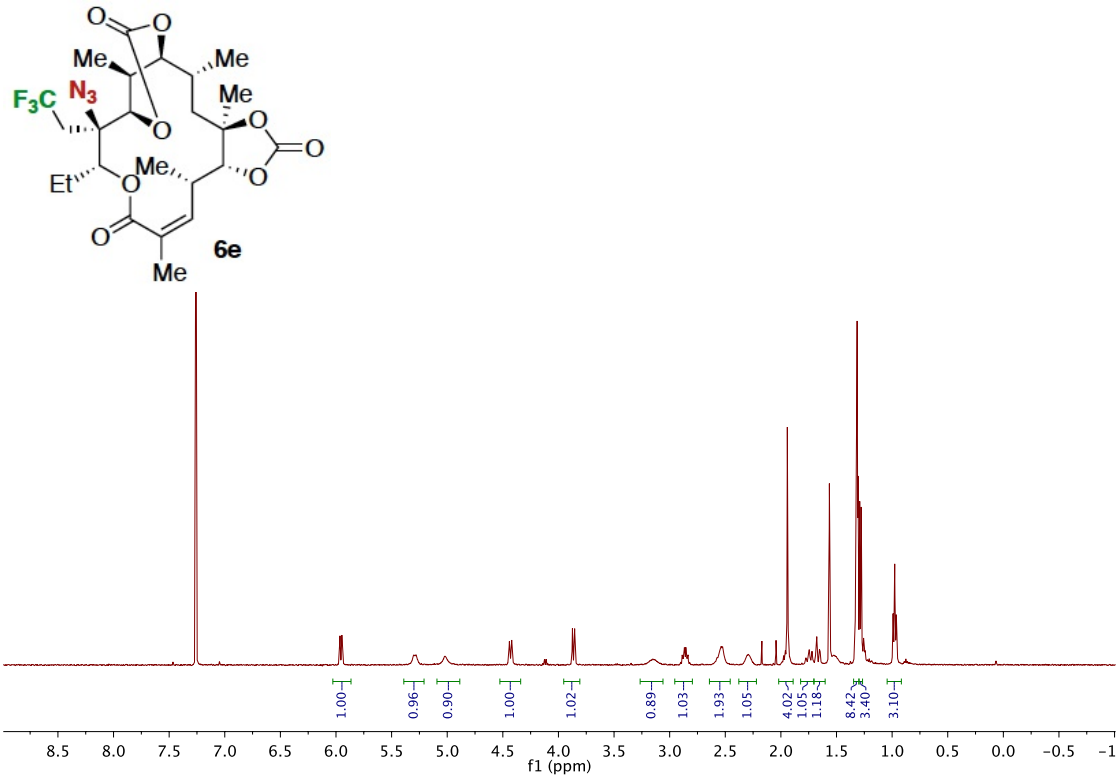
minor diastereomer

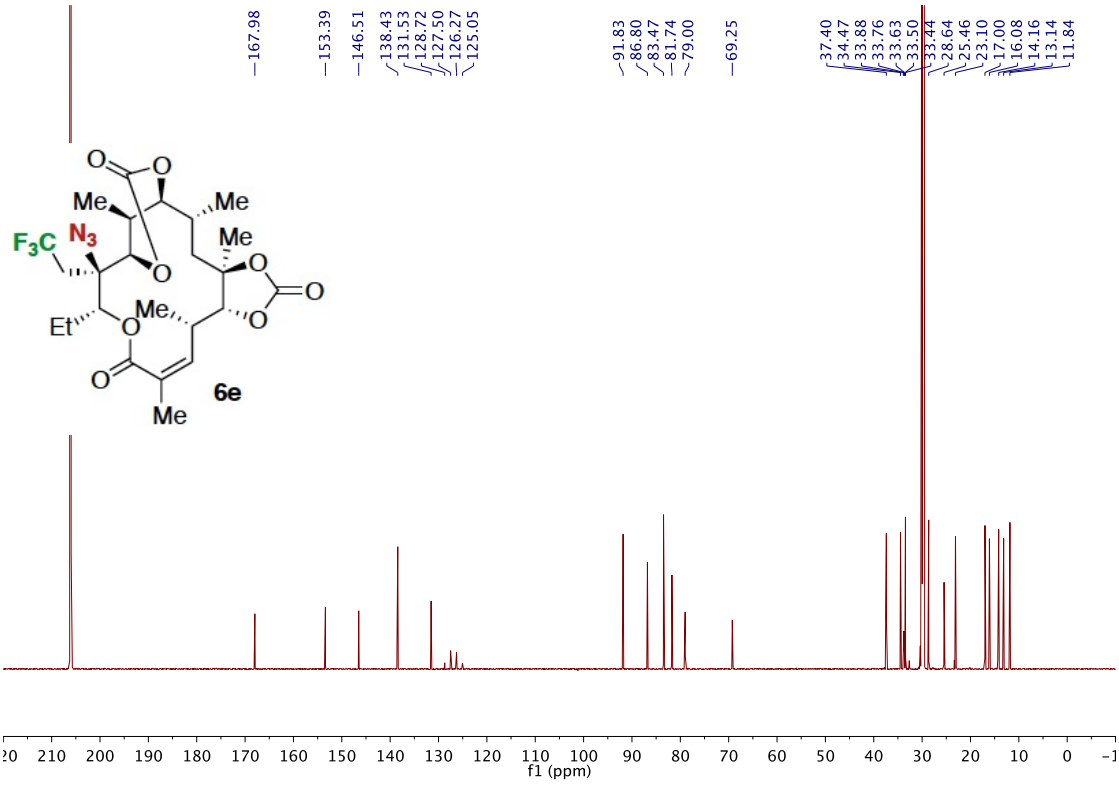

Me
CF3
N3
H
Me
Me
H
OBz
H
Me
BzO
Me
Me
6c
minor diastereomer
59.21
59.24
59.27
−58.7
−58.9
−59.1
−59.3
−59.5
−59.7
f1 (ppm)
20
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
f1 (ppm)

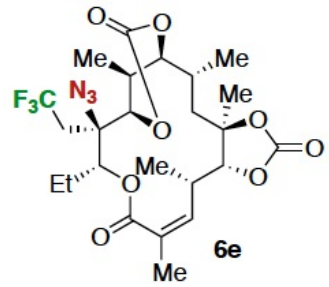

Me
Me
Me
N3
CF3
O
6d
1.00
6.23
4.23
3.06
1.17
3.06
0.64
3.40
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)


199.25
199.21
168.85
168.82
130.01
129.95
127.24
127.18
124.93
124.91
124.48
124.42
121.71
121.65
62.70
42.21
42.05
41.88
40.89
40.62
40.57
40.36
40.09
39.28
39.25
39.16
38.99
32.51
27.35
27.27
20.28
20.17
16.82
Me
Me
Me
N3
CF3
O
6d
f1 (ppm)

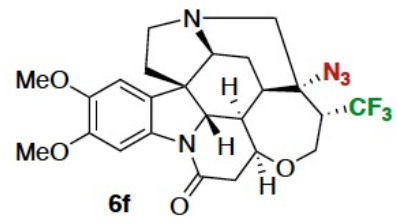

Me
Me
Me
N3
CF3
O
6d
59.12
59.15
59.18
59.21
59.24
59.27
1.00
0.92
f1 (ppm)
1.00
0.92
f1 (ppm)

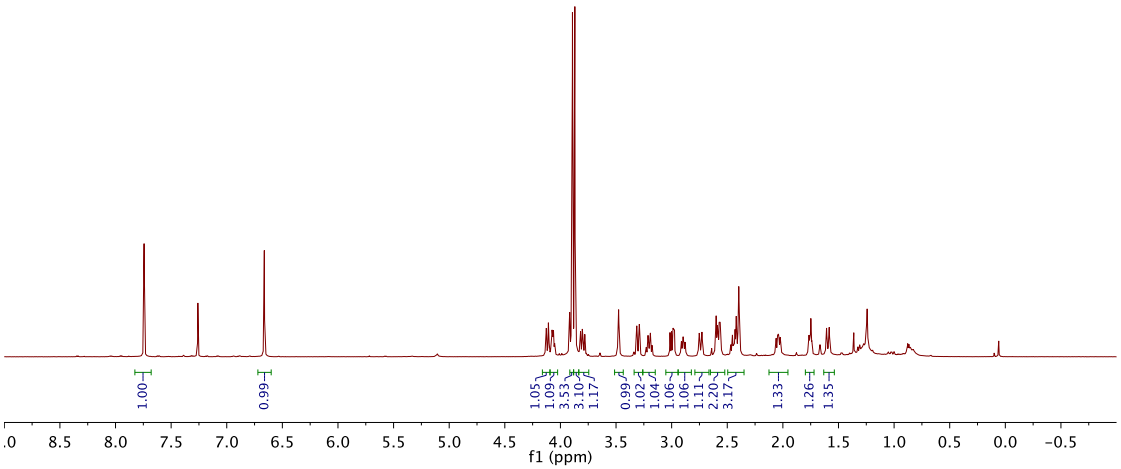

6e
1.00
0.96
0.90
1.00
1.02
0.89
1.03
1.93
1.05
4.02
1.05
1.18
8.42
3.40
3.10
f1 (ppm)

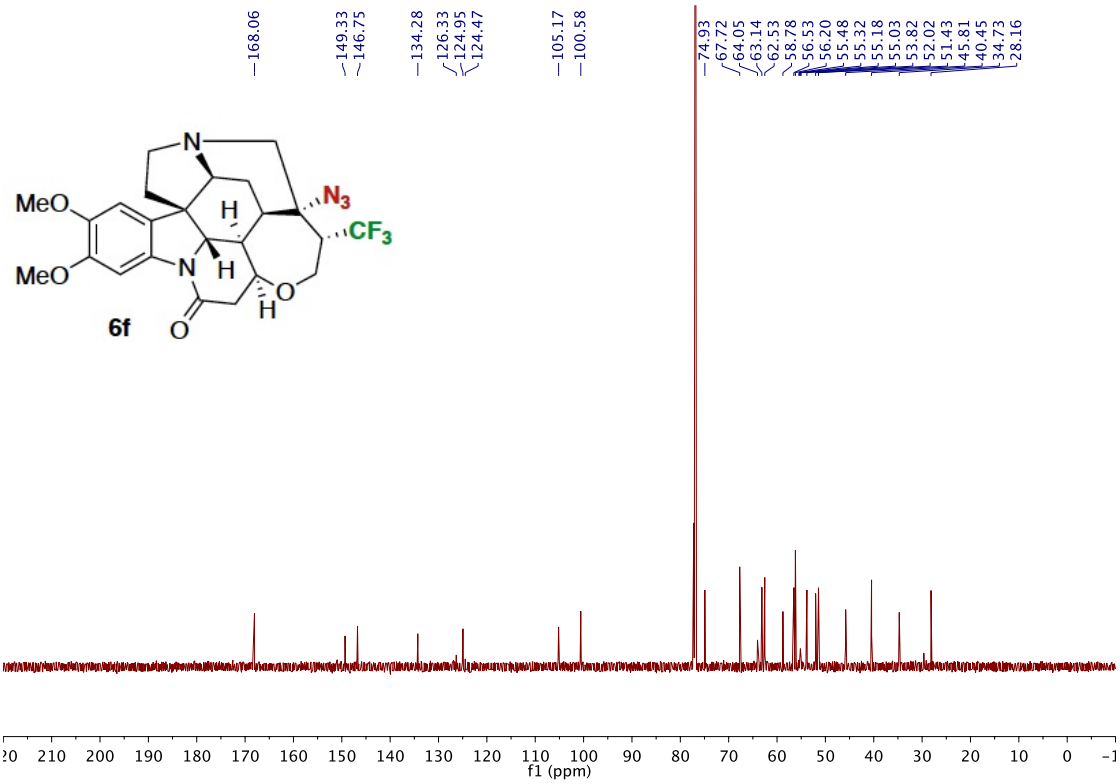

167.98
153.39
146.51
138.43
131.53
128.72
127.50
126.27
125.05
91.83
86.80
83.47
81.74
79.00
69.25
37.40
34.47
33.88
33.76
33.63
33.50
33.44
28.64
25.46
23.10
17.00
16.08
14.16
13.14
11.84
6e
f1 (ppm)

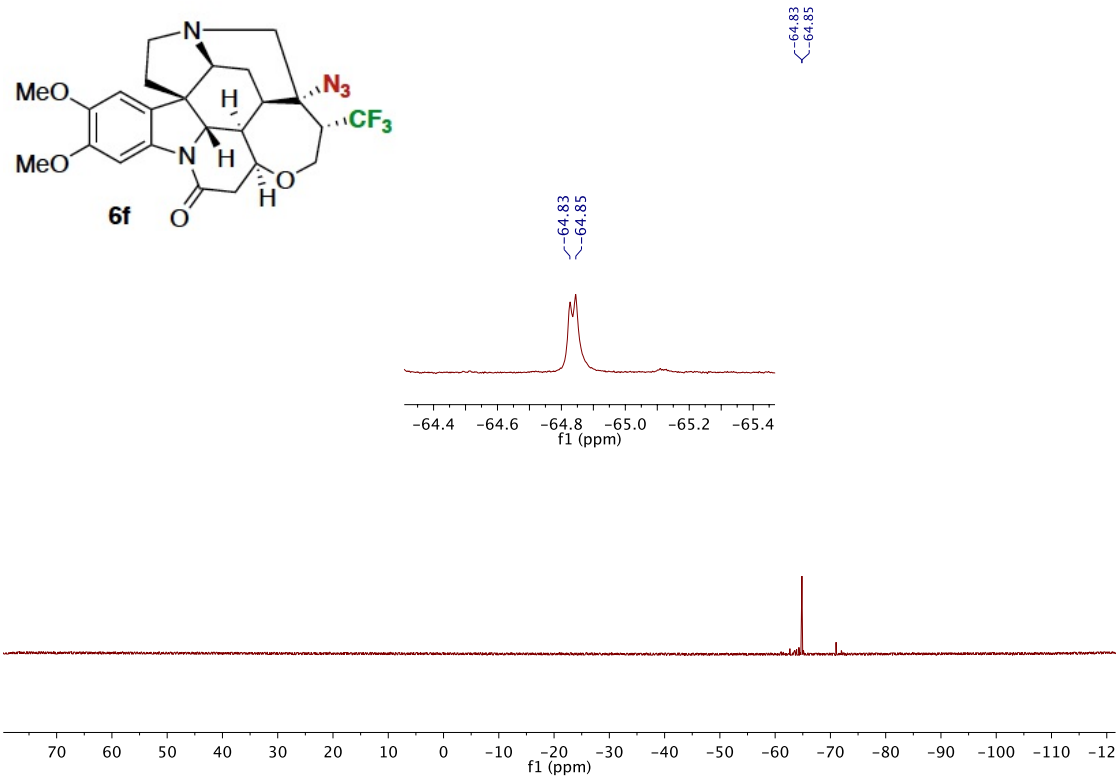

Me
Me
F3C
N3
Me
Et
Me
6e
Me

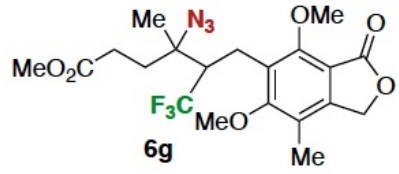
-58.35
-58.35
-53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63
f1 (ppm)
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


MeO
MeO
N
H
N
H
O
H
N3
CF3
O
6f

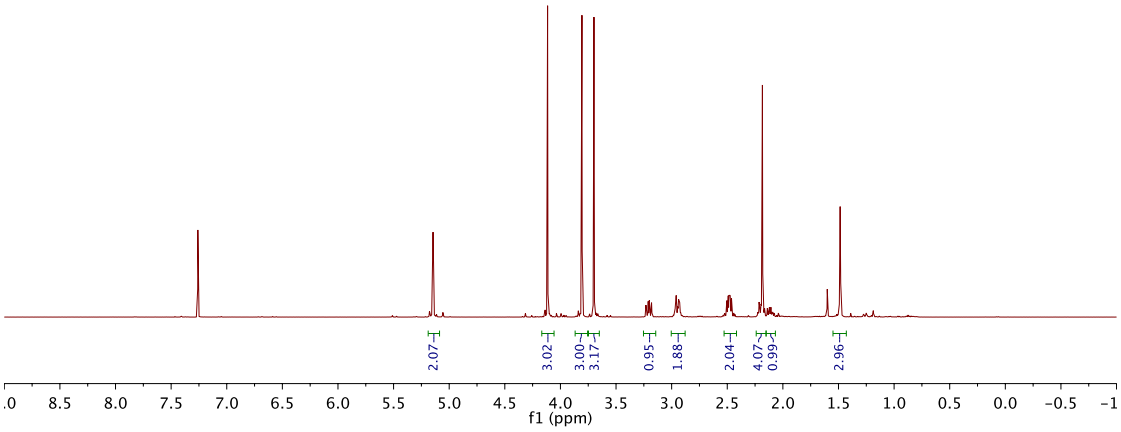

1.00
0.99
1.05
1.09
3.53
3.10
1.17
0.99
1.02
1.04
1.06
1.06
1.11
2.20
3.17
1.33
1.26
1.35
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

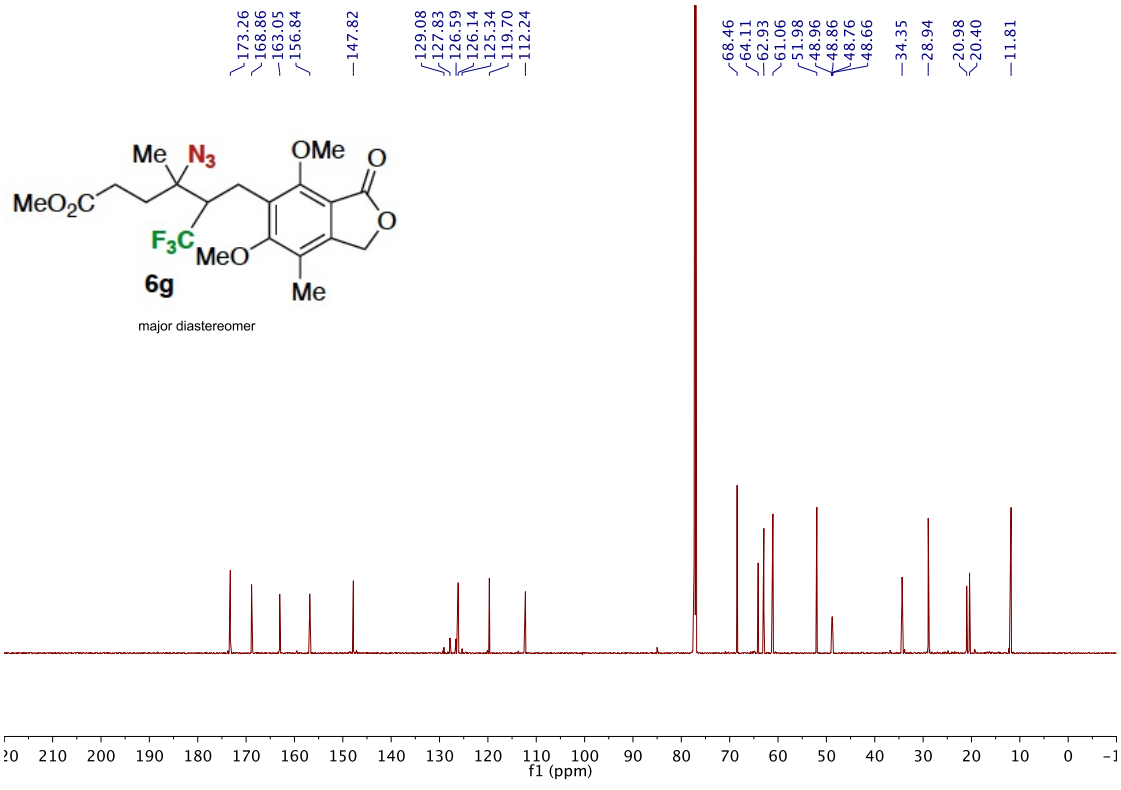

168.06
149.33
146.75
134.28
126.33
124.95
124.47
105.17
100.58
74.93
67.72
64.05
63.14
62.53
58.78
56.53
56.20
55.48
55.32
55.18
55.03
53.82
52.02
51.43
45.81
40.45
34.73
28.16
MeO
MeO
N3
CF3
6f
f1 (ppm)


64.83
64.85
MeO
MeO
N3
CF3
6f
f1 (ppm)

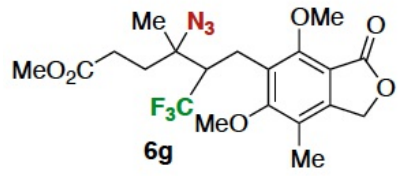


major diastereomer

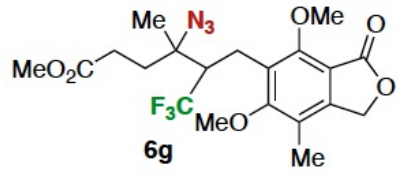




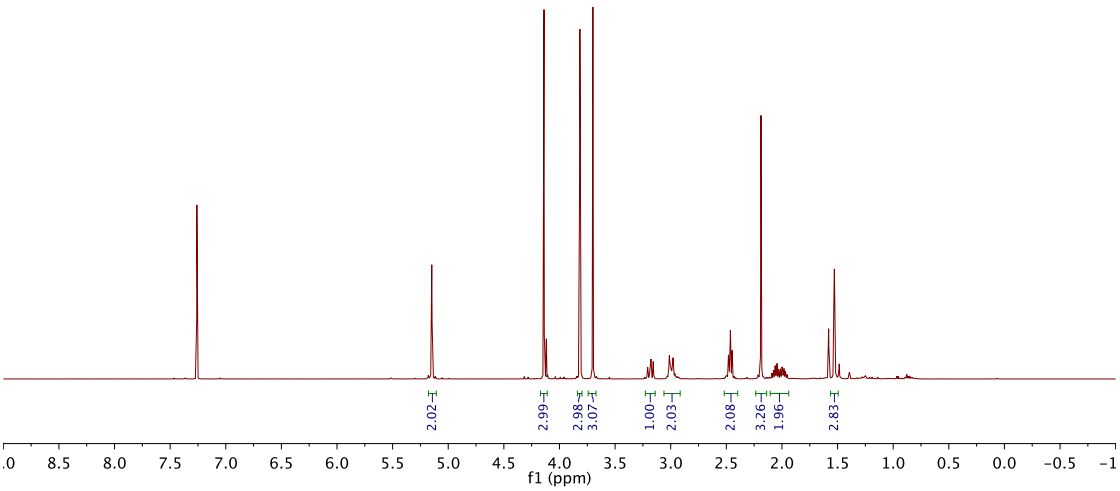
major diastereomer

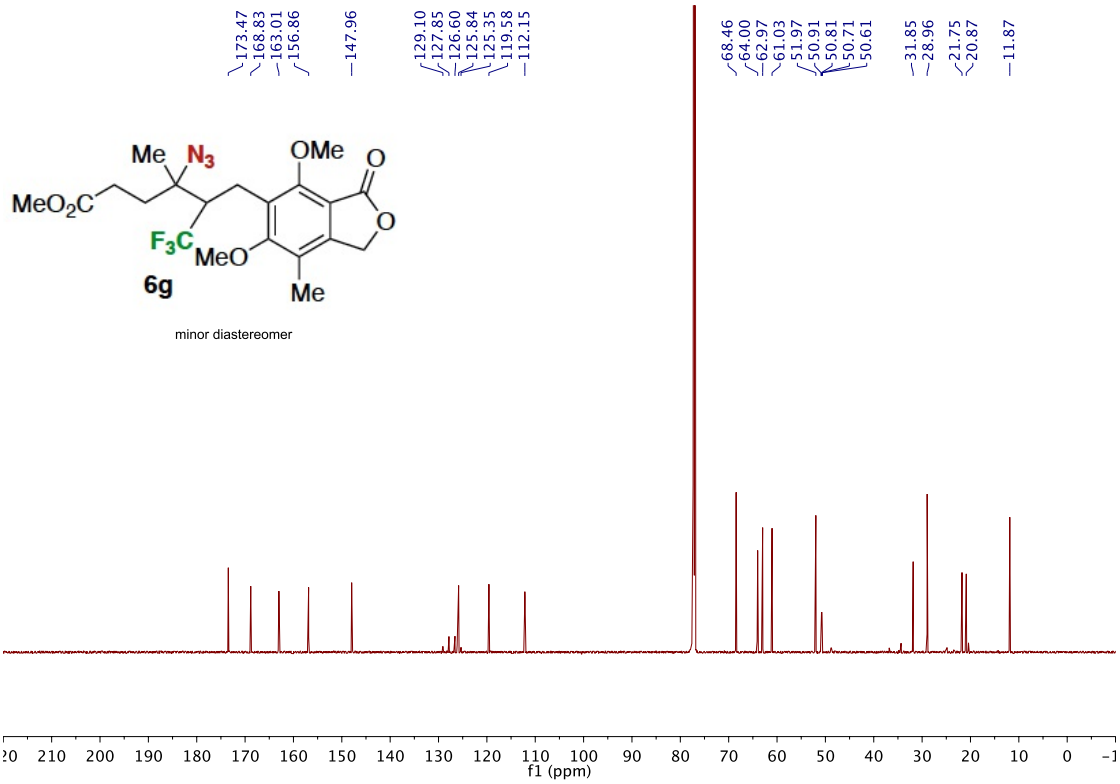


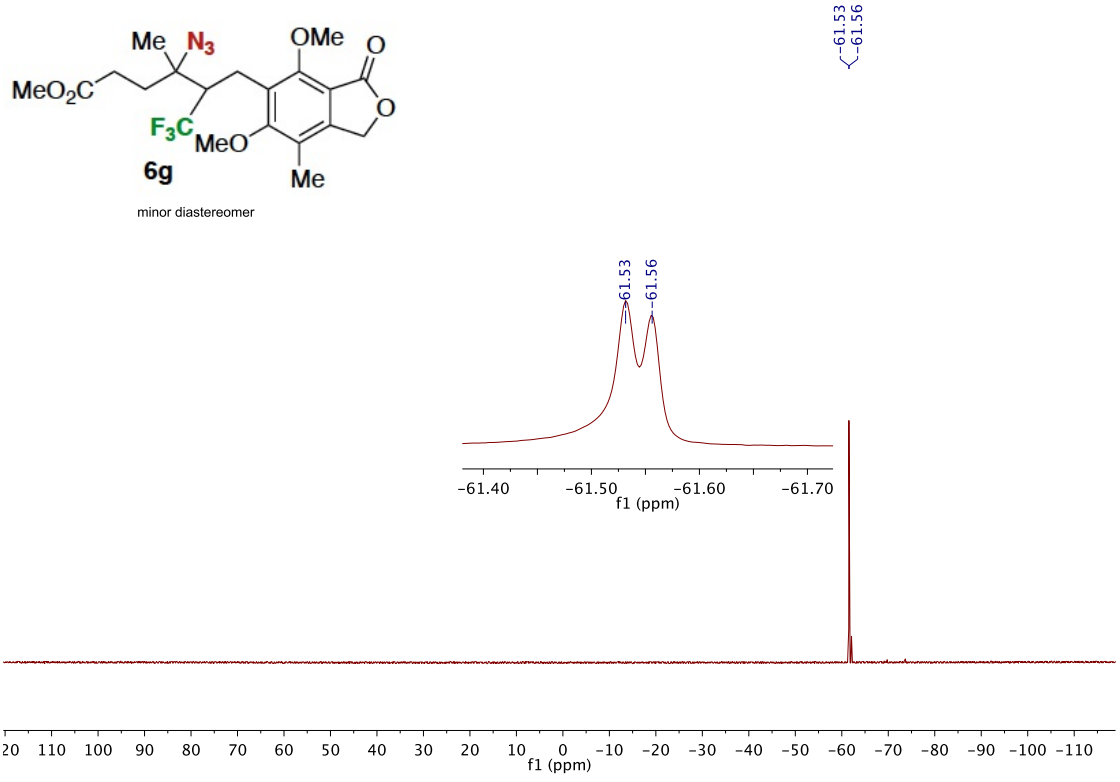
major diastereomer

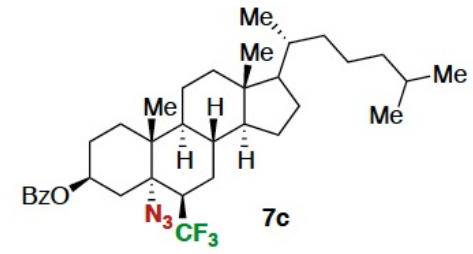


minor diastereomer

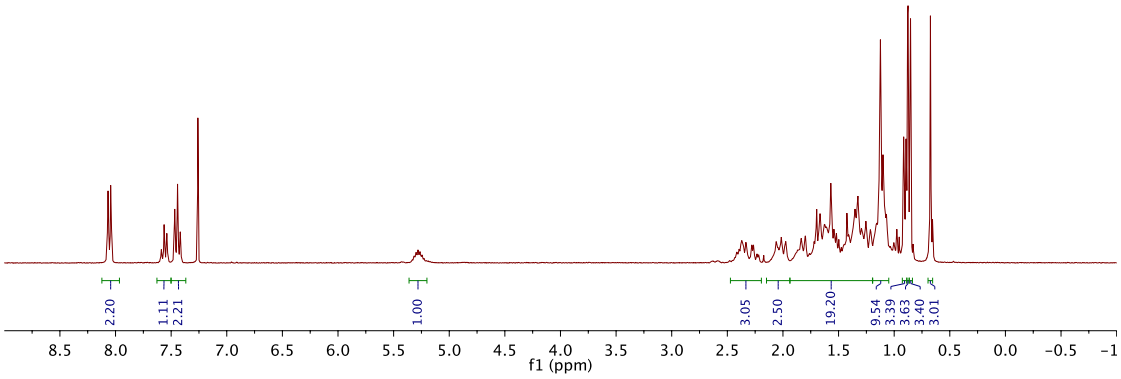



173.47
168.83
163.01
156.86
147.96
129.10
127.85
126.60
125.84
125.35
119.58
112.15
68.46
64.00
62.97
61.03
51.97
50.91
50.81
50.71
50.61
31.85
28.96
21.75
20.87
11.87
Me
N3
OMe
O
MeO2C
F3C
MeO
O
6g
Me
minor diastereomer
f1 (ppm)

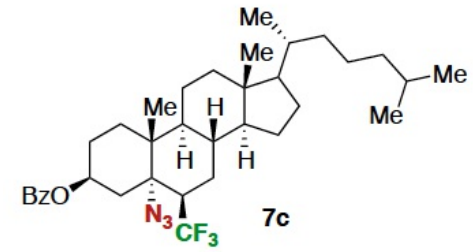

61.53
61.56
Me
N3
OMe
O
MeO2C
F3C
MeO
O
6g
Me
minor diastereomer
61.53
61.56
f1 (ppm)
f1 (ppm)


Me
Me
Me
Me
Me
H
H
H
BzO
N3
CF3

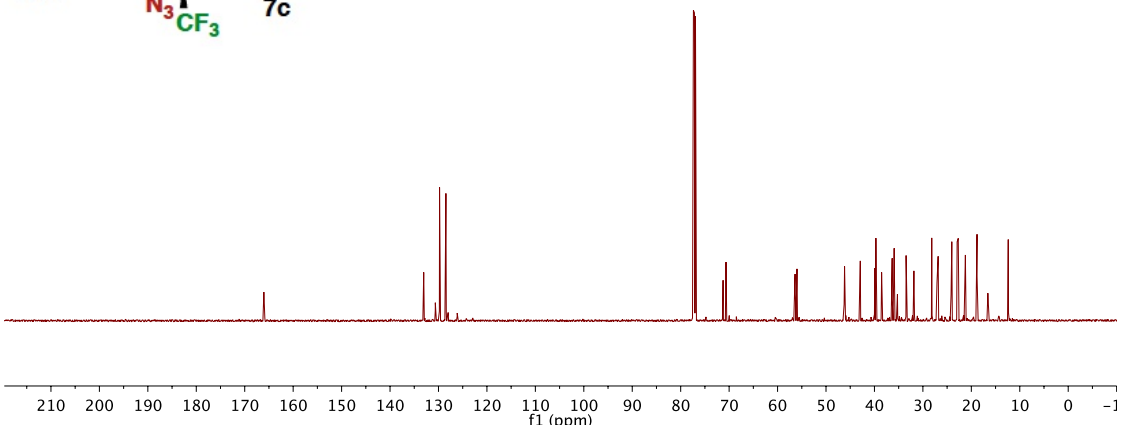
7c

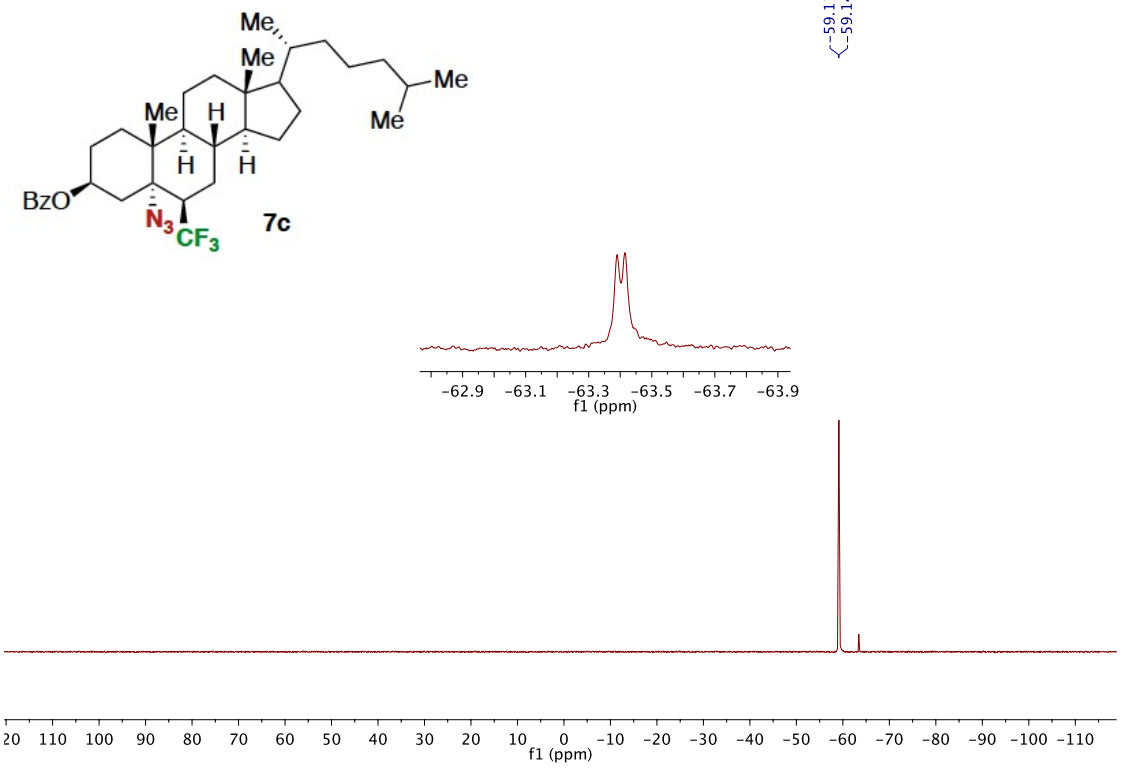

2.20
1.11
2.21
1.00
3.05
2.50
19.20
9.54
3.39
3.63
3.40
3.01
f1 (ppm)

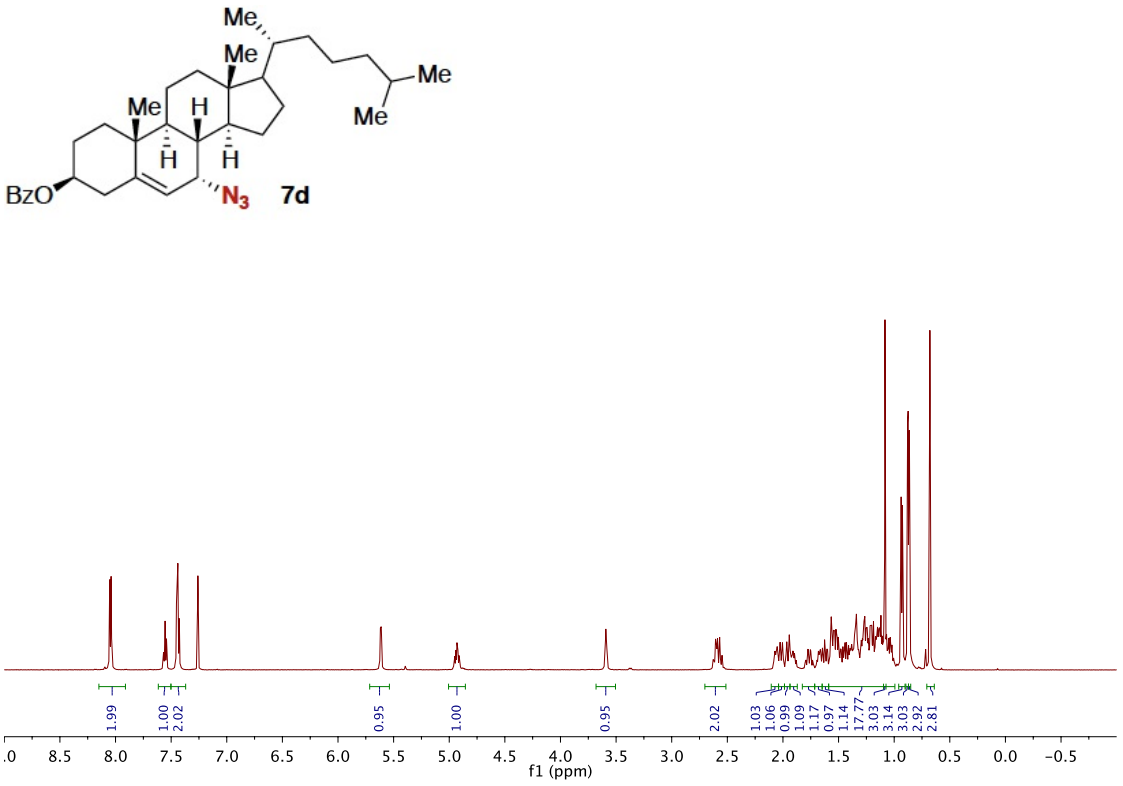

166.05
133.05
129.87
129.78
128.47
128.00
126.14
124.27
71.25
70.64
56.39
55.99
46.43
46.26
46.17
46.09
45.92
42.92
39.95
39.70
38.52
36.34
35.93
35.27
35.25
33.47
31.86
28.32
28.17
27.10
26.85
24.17
24.03
22.94
22.70
21.23
18.82
16.59
16.56
12.38

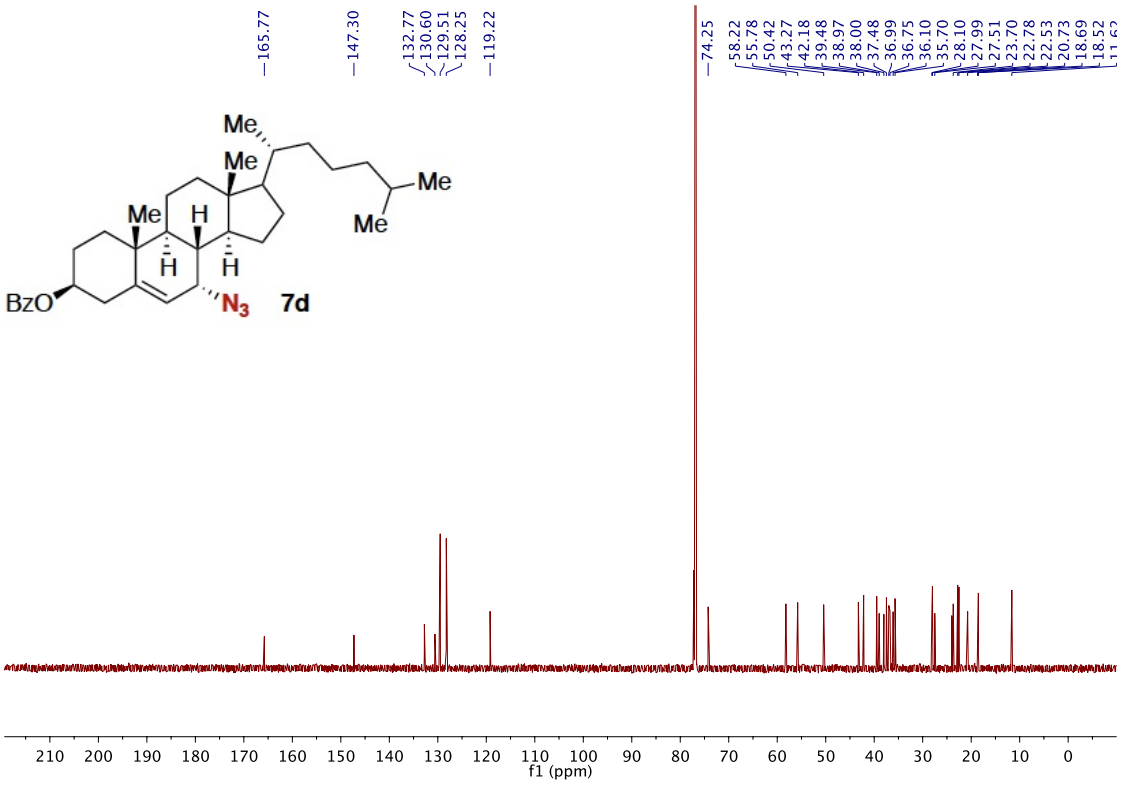

Me
Me
Me
Me
Me
H
H
H
BzO
N3
CF3

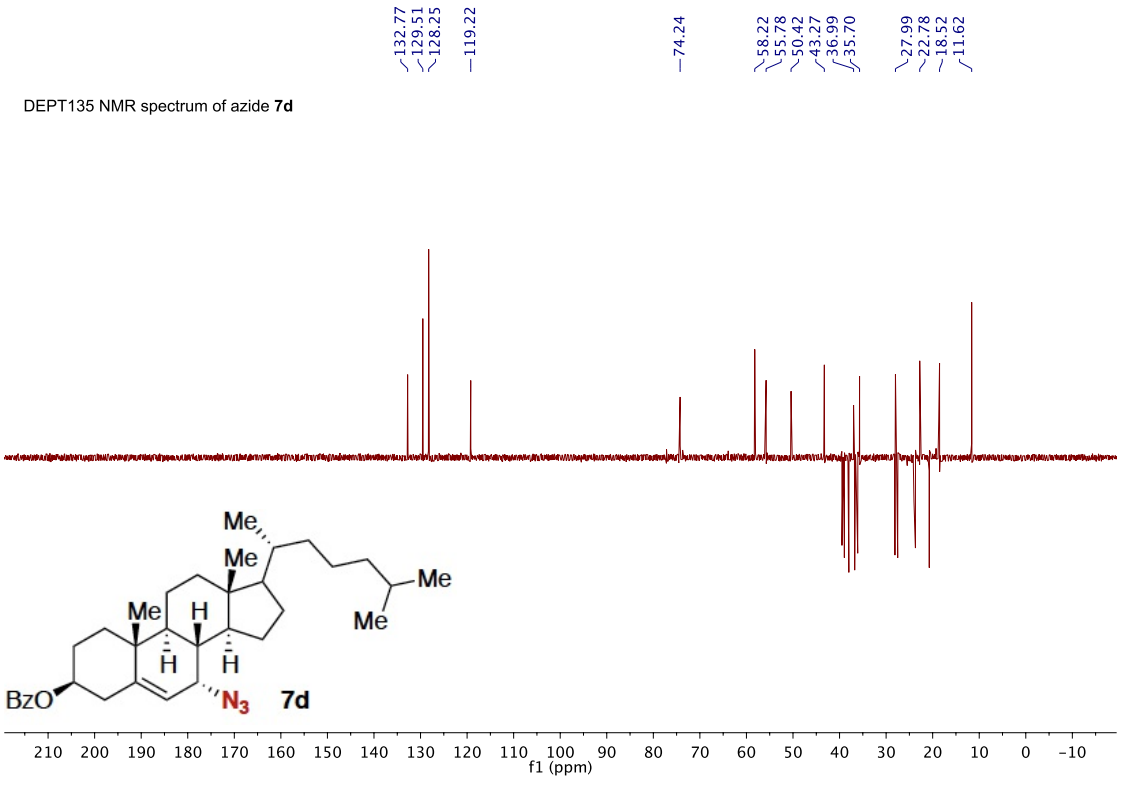
7c


f1 (ppm)

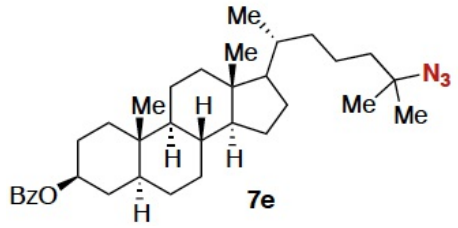

Me
Me
Me
Me
Me
H
H
H
BzO
N3
CF3
7c
-59.11
-59.14
-62.9
-63.1
-63.3
-63.5
-63.7
-63.9
f1 (ppm)
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

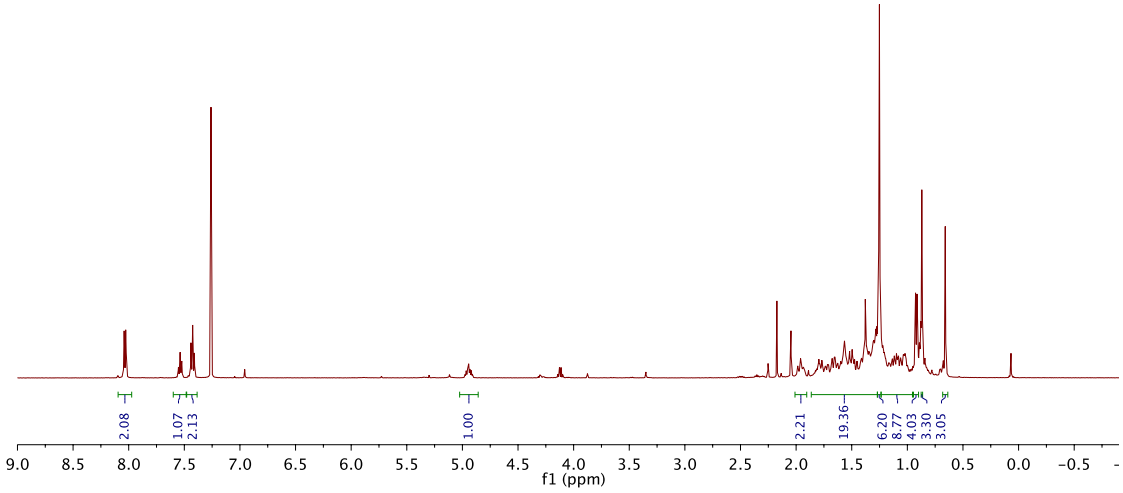

Me
Me
Me
Me
Me
H
H
H
BzO
N3
7d
1.99
1.00
2.02
0.95
1.00
0.95
2.02
1.03
1.06
0.99
1.09
1.17
0.97
1.14
17.77
3.03
3.14
3.03
2.92
2.81
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

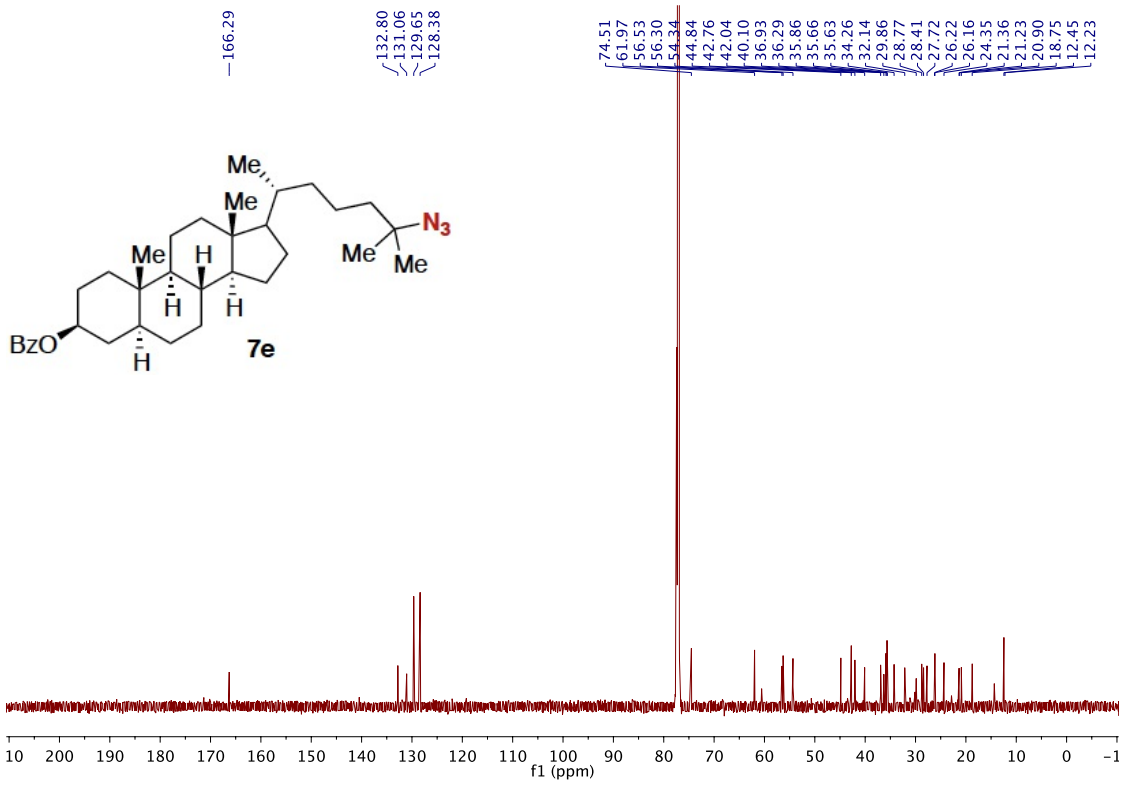




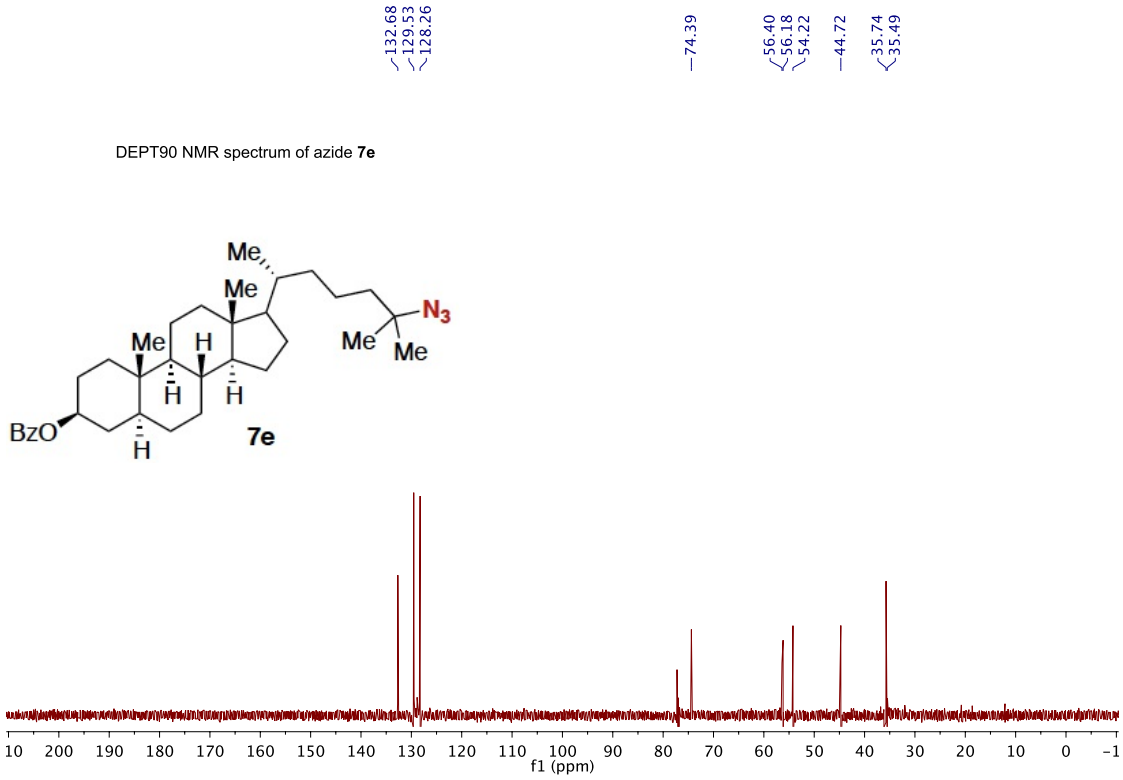
DEPT135 NMR spectrum of azide **7d**


Me
Me
N3
Me
Me
Me
H
H
H
H
BzO
7e

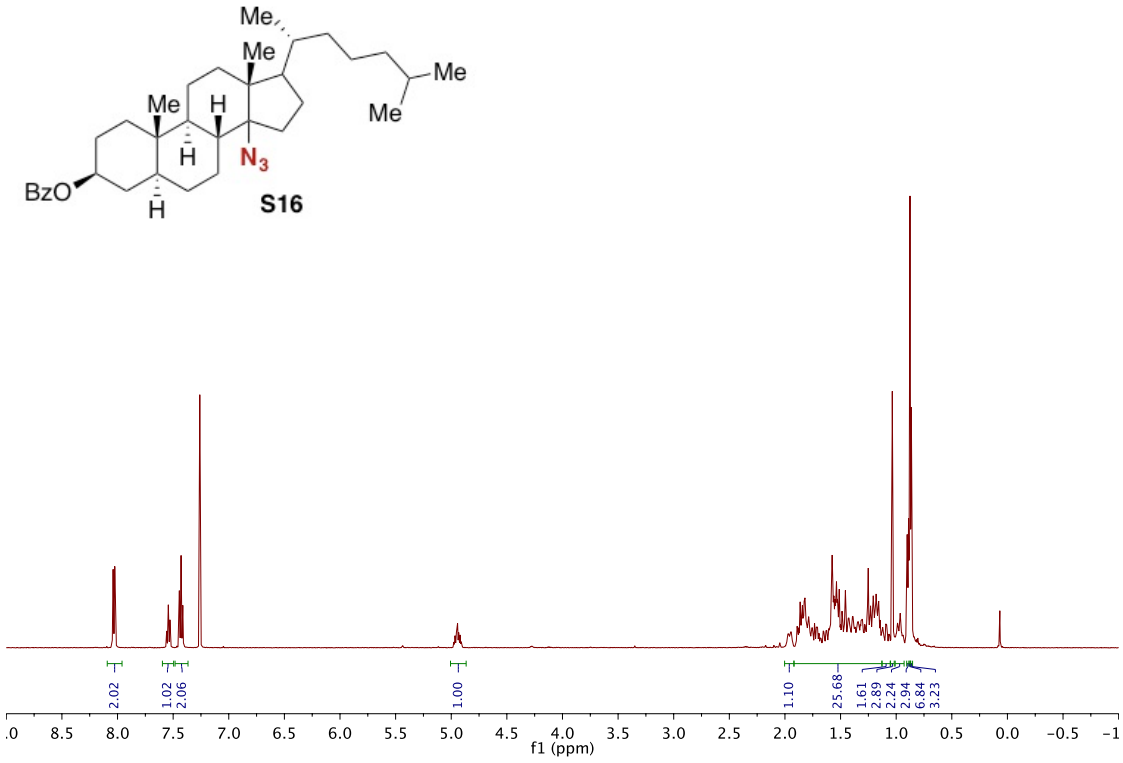

2.08
1.07
2.13
1.00
2.21
19.36
6.20
8.77
4.03
3.30
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

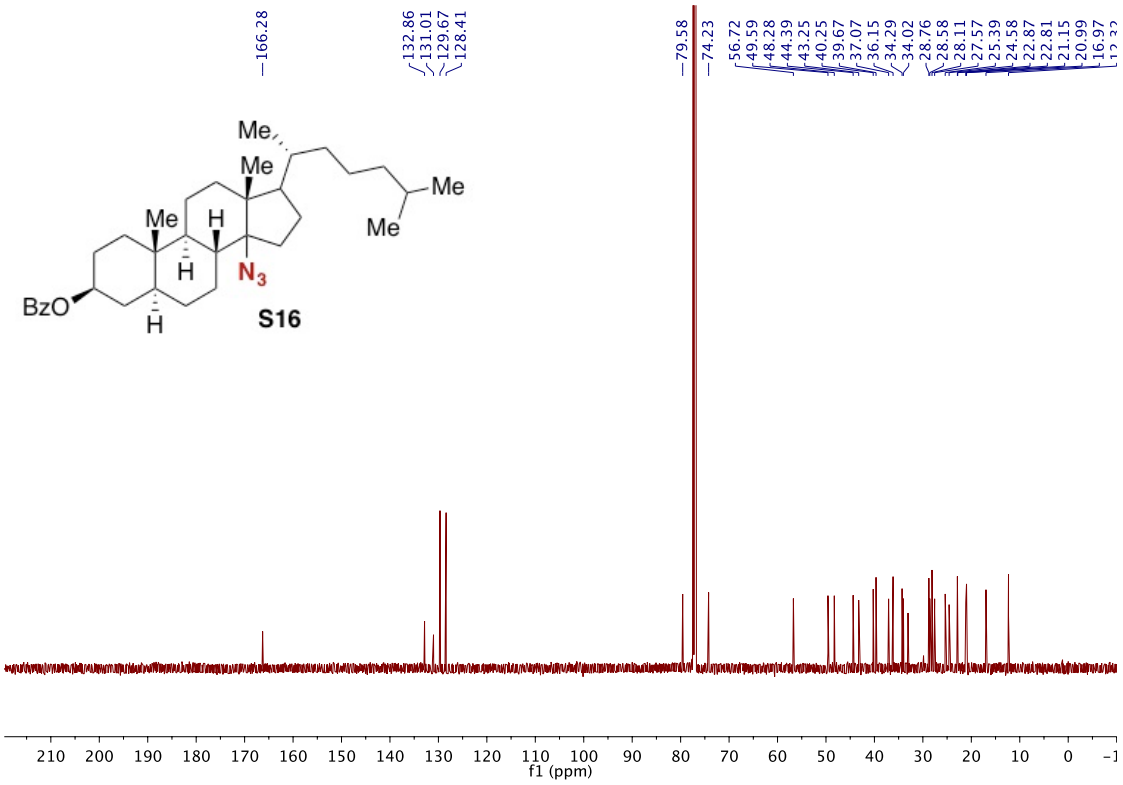

166.29
132.80
131.06
129.65
128.38
74.51
61.97
56.53
56.30
54.34
44.84
42.76
42.04
40.10
36.93
36.29
35.86
35.66
35.63
34.26
32.14
29.86
28.77
28.41
27.72
26.22
26.16
24.35
21.36
21.23
20.90
18.75
12.45
12.23
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Me
Me
N3
Me
Me
Me
H
H
H
H
BzO
7e

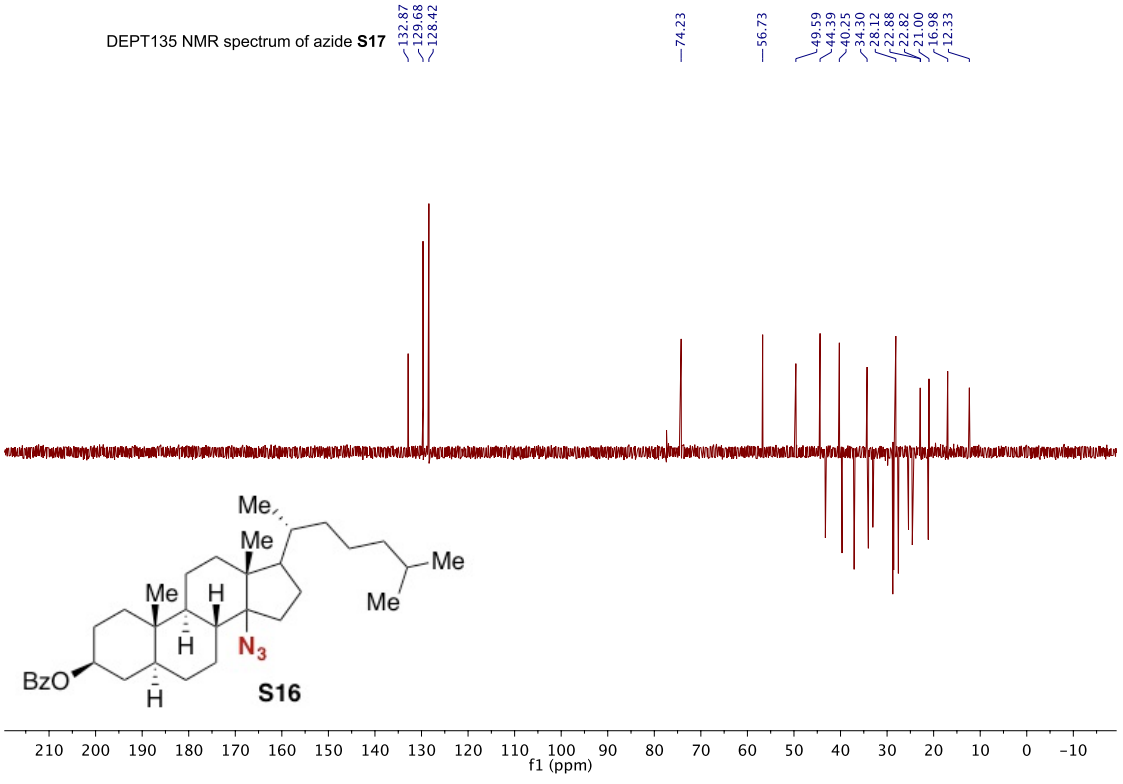


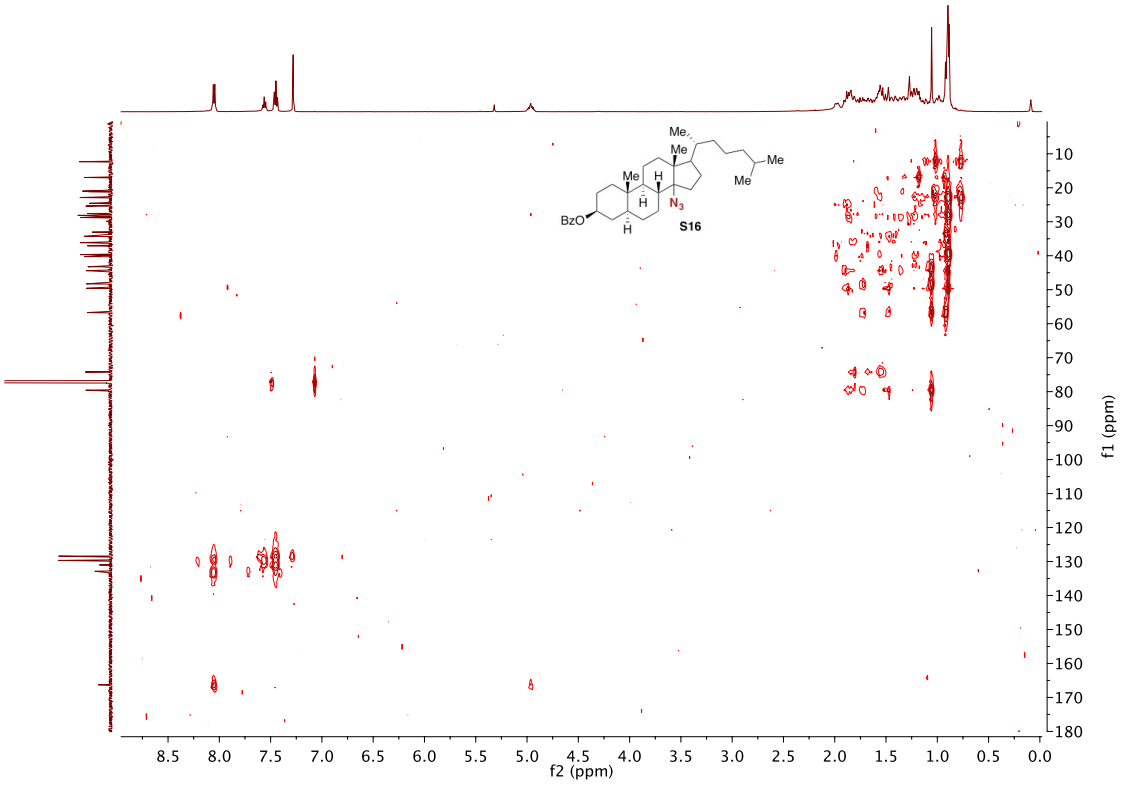
DEPT90 NMR spectrum of azide **7e**

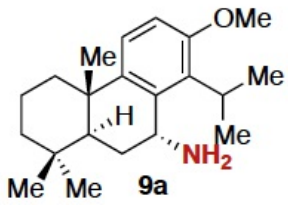




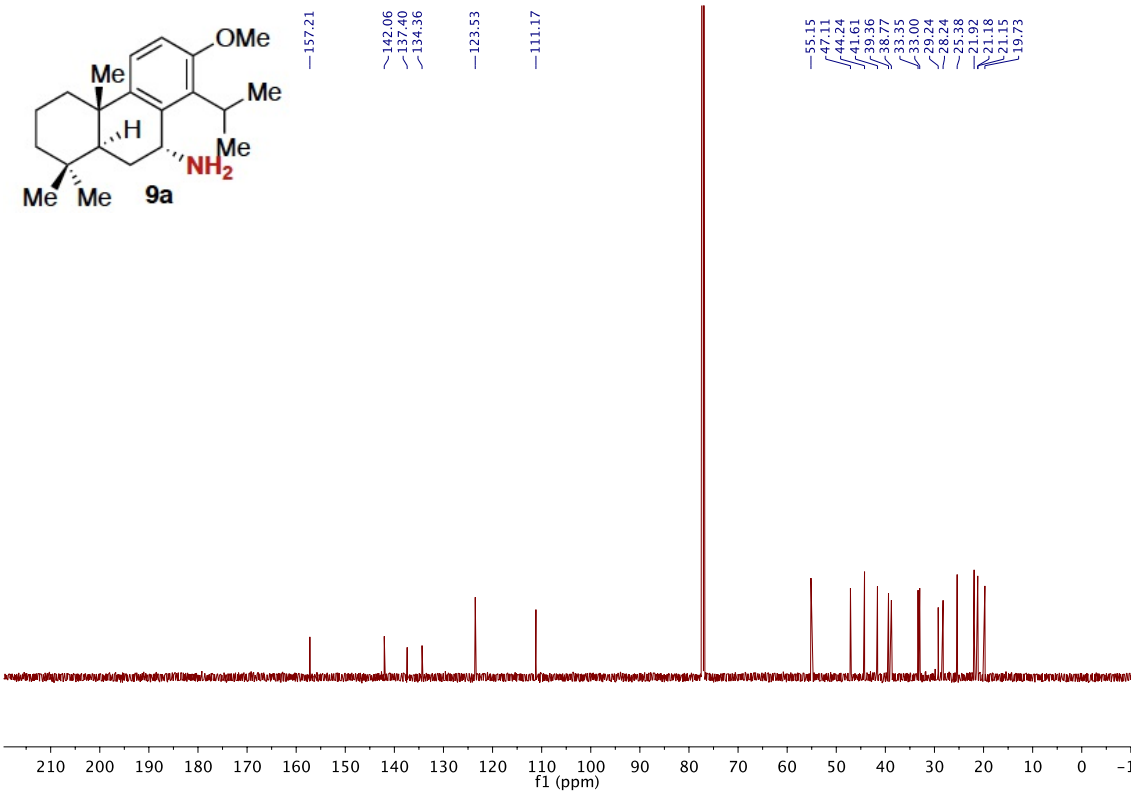
DEPT135 NMR spectrum of azide **S17**

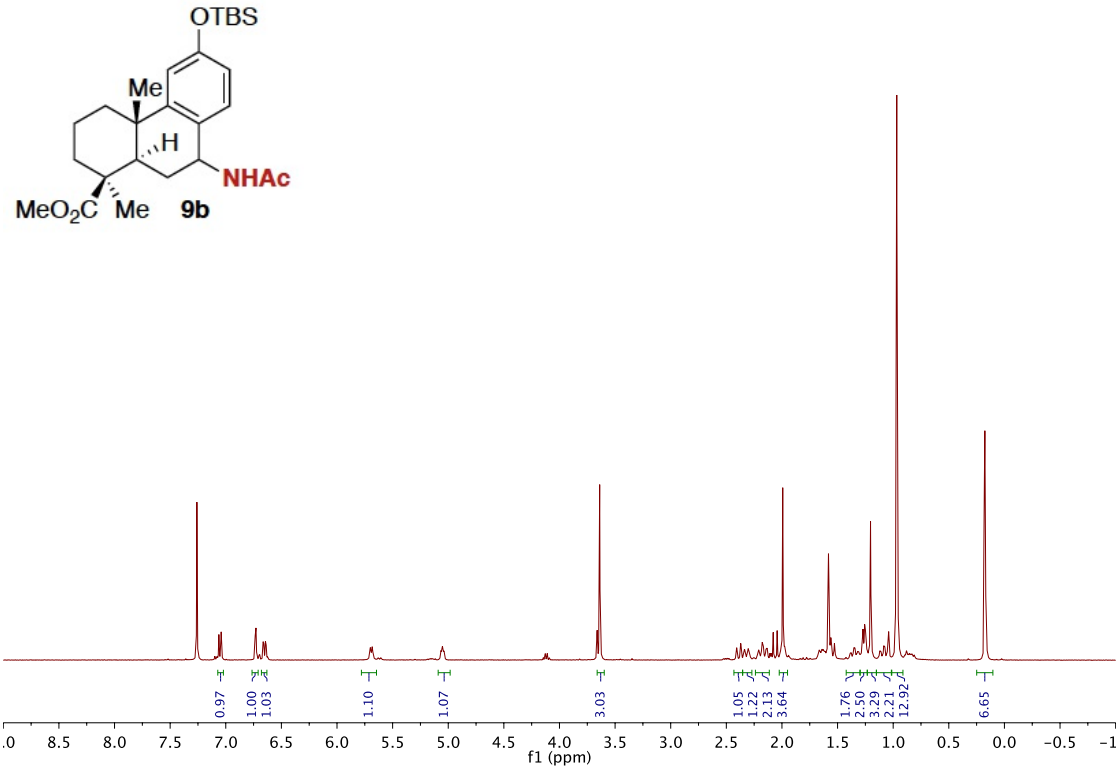


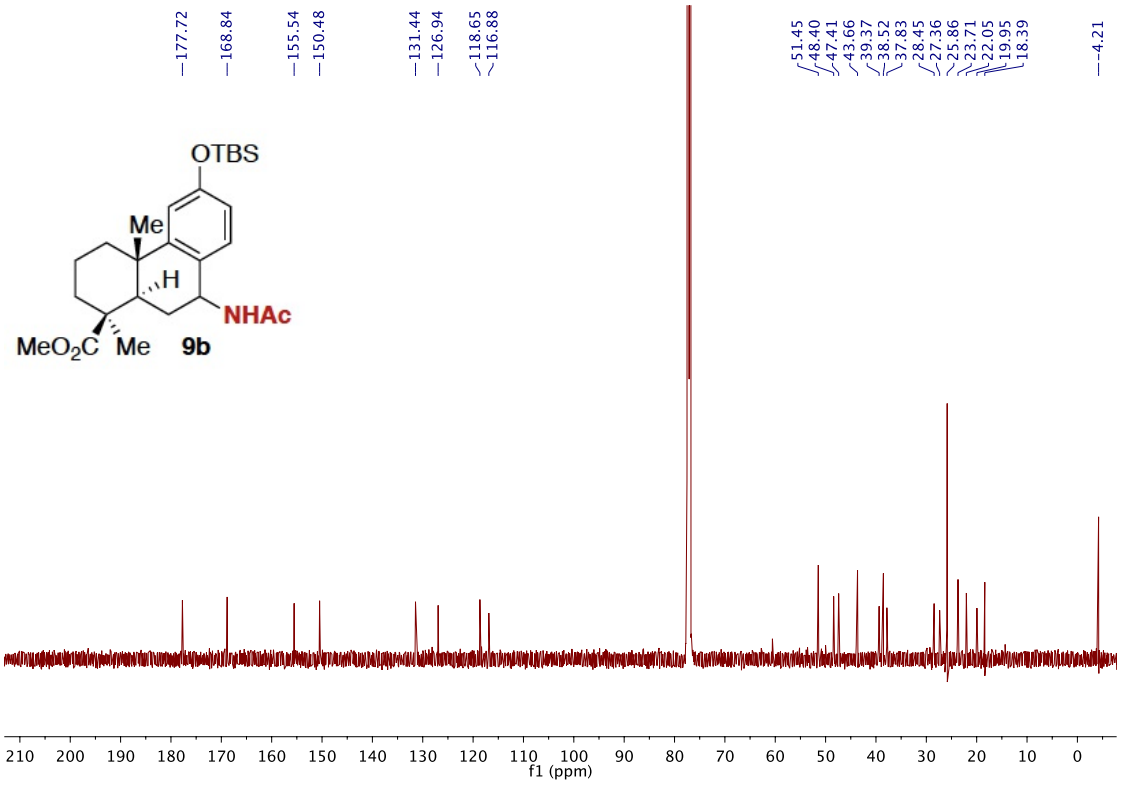

Me
Me
Me
H
Me
Me
H
N3
BzO
H
S16
f2 (ppm)
f1 (ppm)

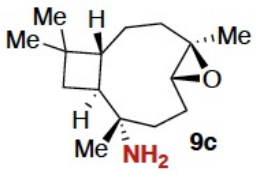

OMe
Me
Me
H
Me
NH2
Me
Me
9a

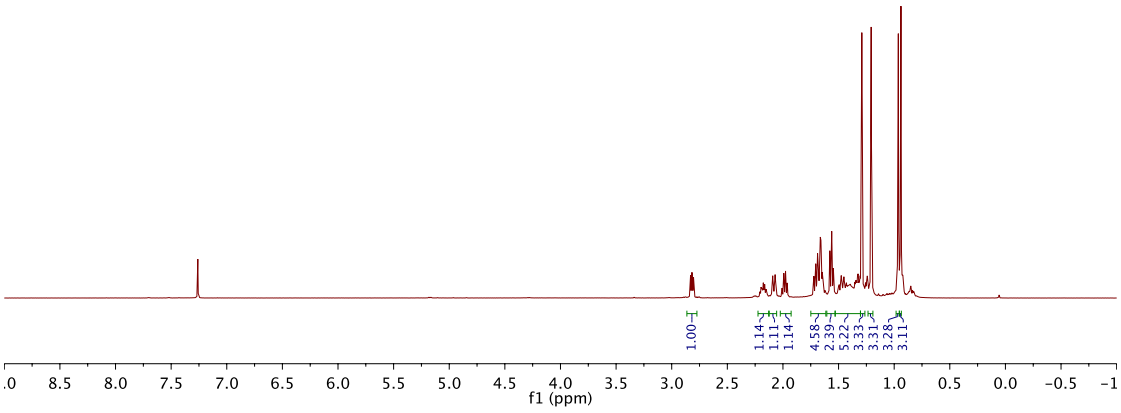
1.02
0.95
1.00
3.03
0.96
1.03
1.12
2.20
1.11
1.31
1.72
1.29
3.61
1.31
3.46
3.17
3.02
3.04
3.14
1.50
f1 (ppm)

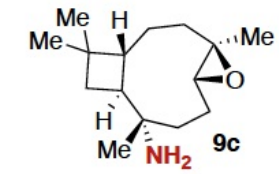

OMe
Me
Me
H
NH2
Me Me
9a
157.21
142.06
137.40
134.36
123.53
111.17
55.15
47.11
44.24
41.61
39.36
38.77
33.35
33.00
29.24
28.24
25.38
21.92
21.18
21.15
19.73
f1 (ppm)


OTBS
Me
H
NHAc
MeO2C Me
9b
0.97
1.00
1.03
1.10
1.07
3.03
1.05
1.22
2.13
3.64
1.76
2.50
3.29
2.21
12.92
6.65
f1 (ppm)


177.72
168.84
155.54
150.48
131.44
126.94
118.65
116.88
51.45
48.40
47.41
43.66
39.37
38.52
37.83
28.45
27.36
25.86
23.71
22.05
19.95
18.39
4.21
OTBS
Me
H
NHAc
MeO2C Me
9b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

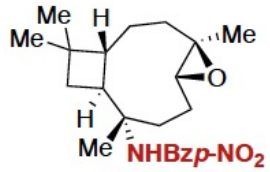

Me
H
Me
Me
O
H
Me
NH2
9c


1.00
1.14
1.11
1.14
4.58
2.39
5.22
3.33
3.31
3.28
3.11
.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 -1
f1 (ppm)

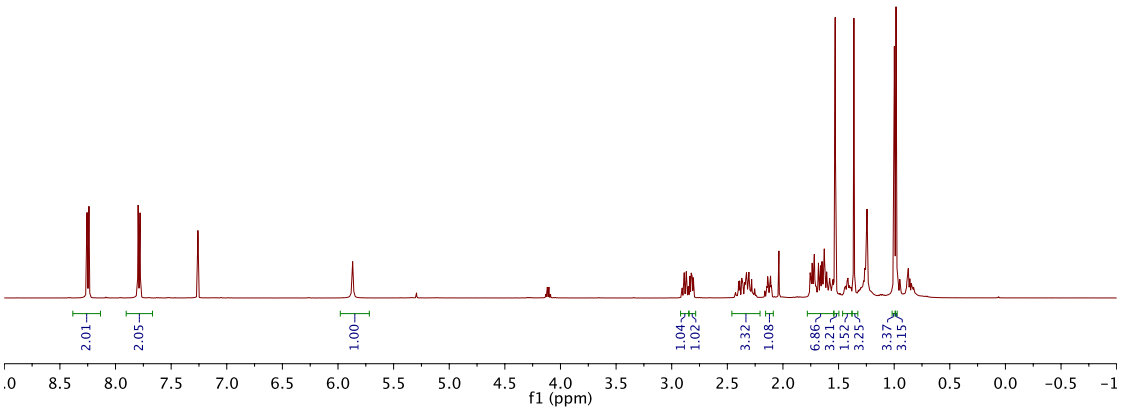

Me
H
Me
Me
O
H
Me
NH2

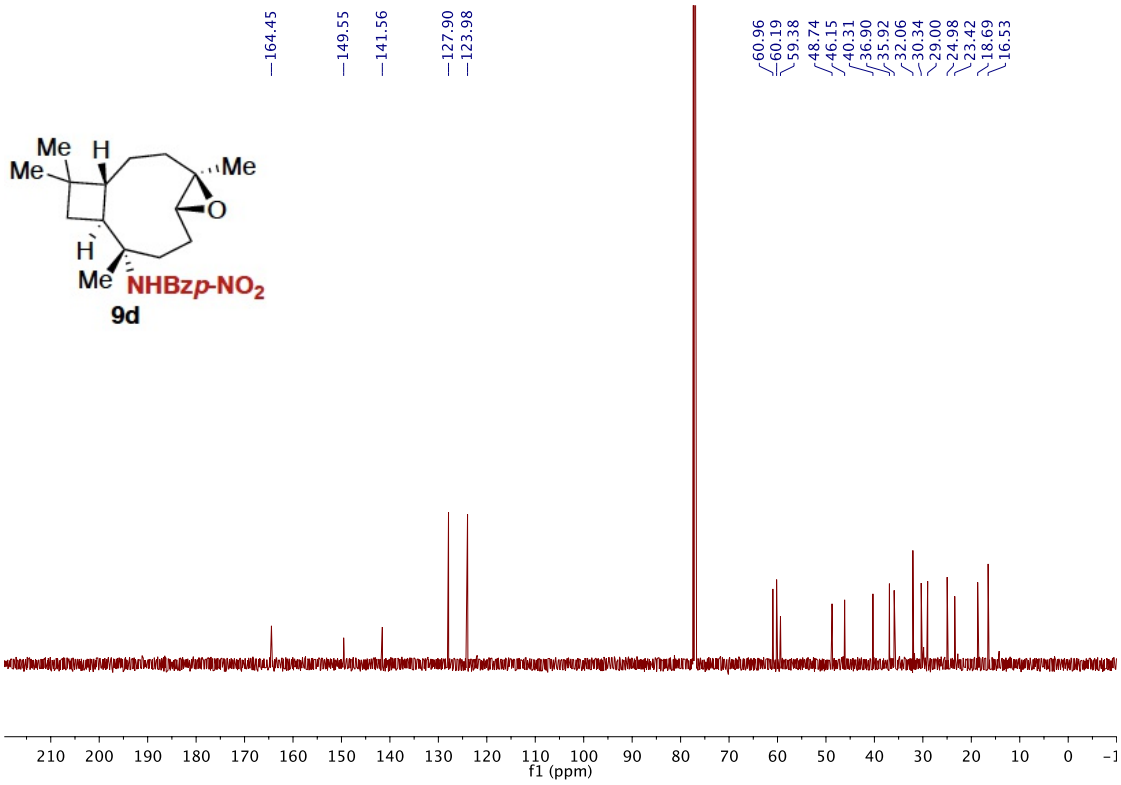
9c

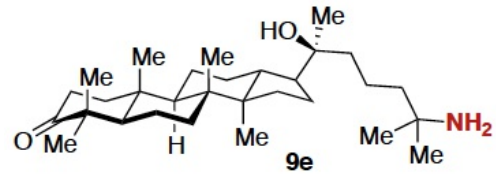
61.01
59.42
53.96
53.40
47.36
40.45
40.44
35.62
31.89
30.26
29.09
25.32
23.32
21.68
16.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

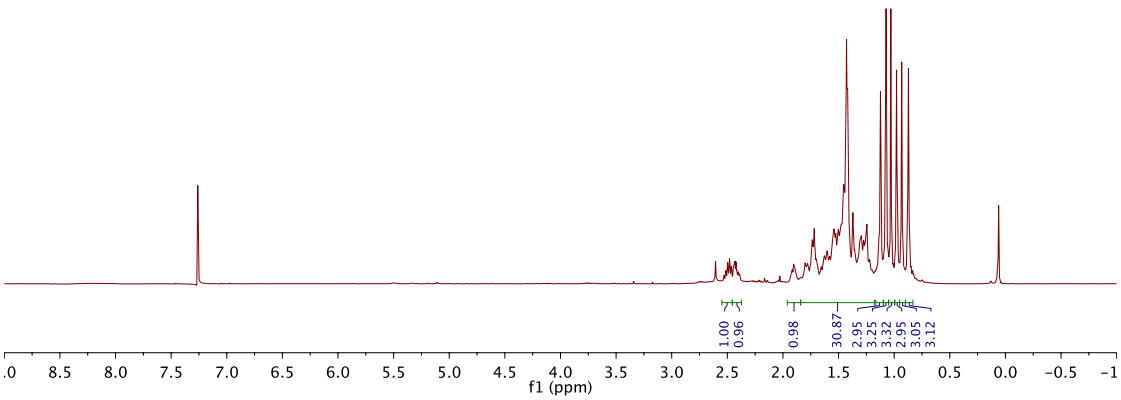

Me
H
Me
Me
O
H
Me
NHBzp-NO2

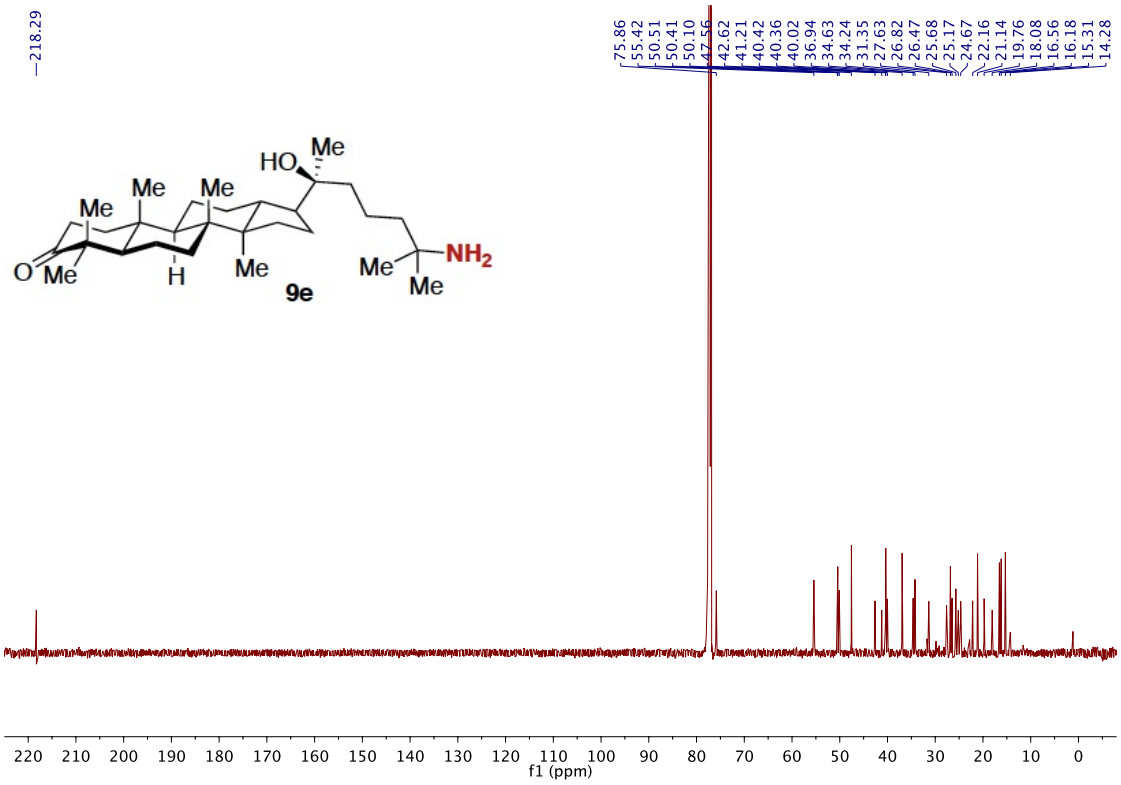
9d

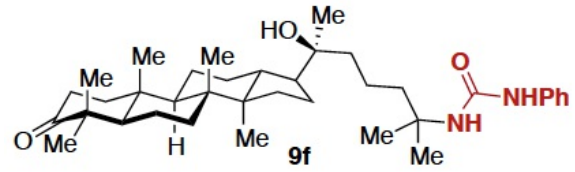

2.01
2.05
1.00
1.04
1.02
3.32
1.08
6.86
3.21
1.52
3.25
3.37
3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

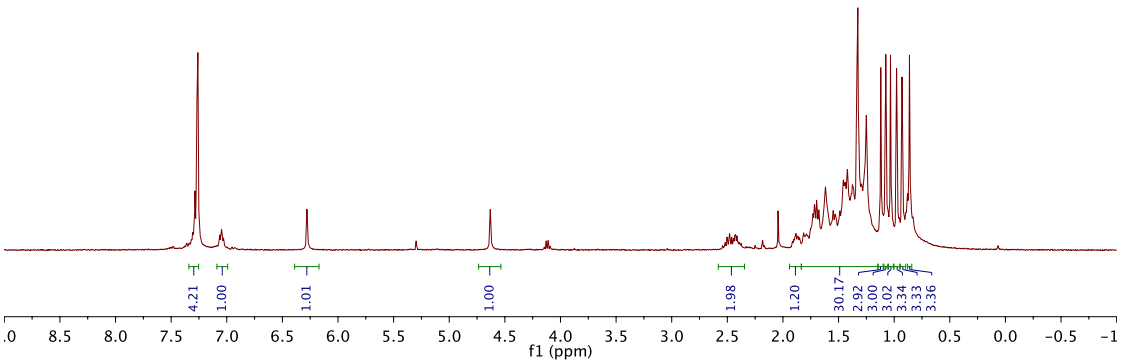

164.45
149.55
141.56
127.90
123.98
60.96
60.19
59.38
48.74
46.15
40.31
36.90
35.92
32.06
30.34
29.00
24.98
23.42
18.69
16.53
Me
H
Me
Me
O
H
Me
NHBzp-NO2
9d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

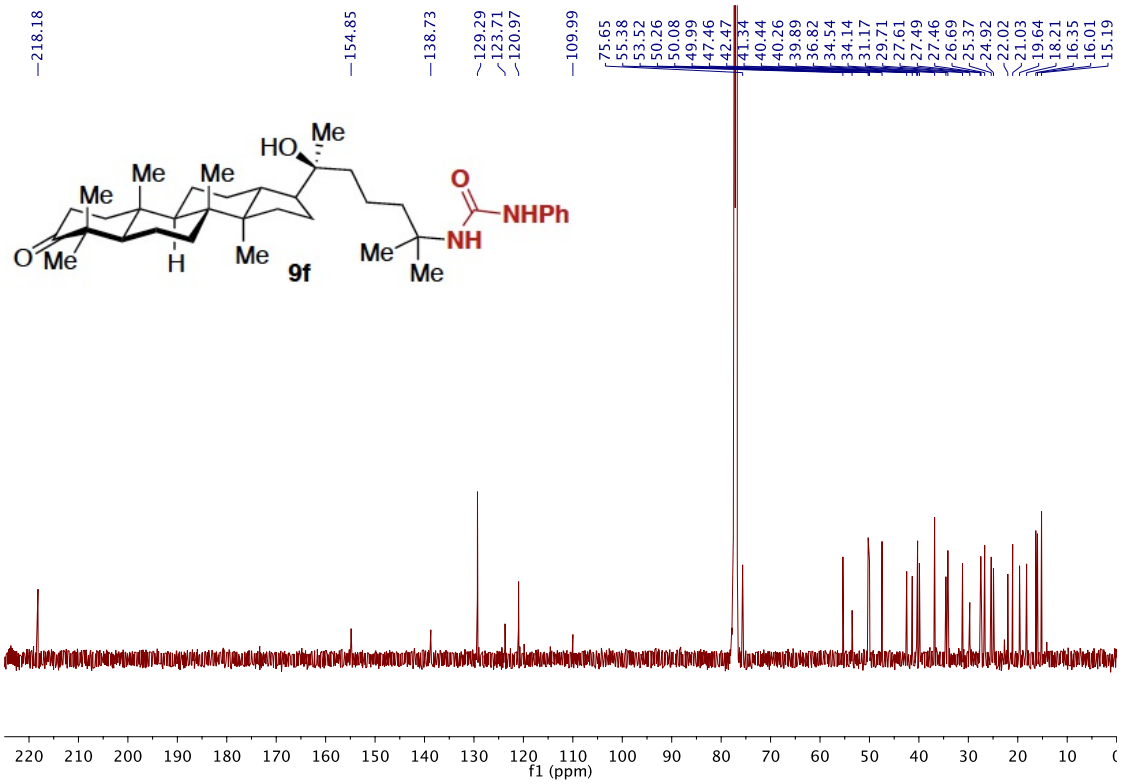

HO
Me
Me
Me
Me
O
Me
H
Me
Me
NH2
Me
9e

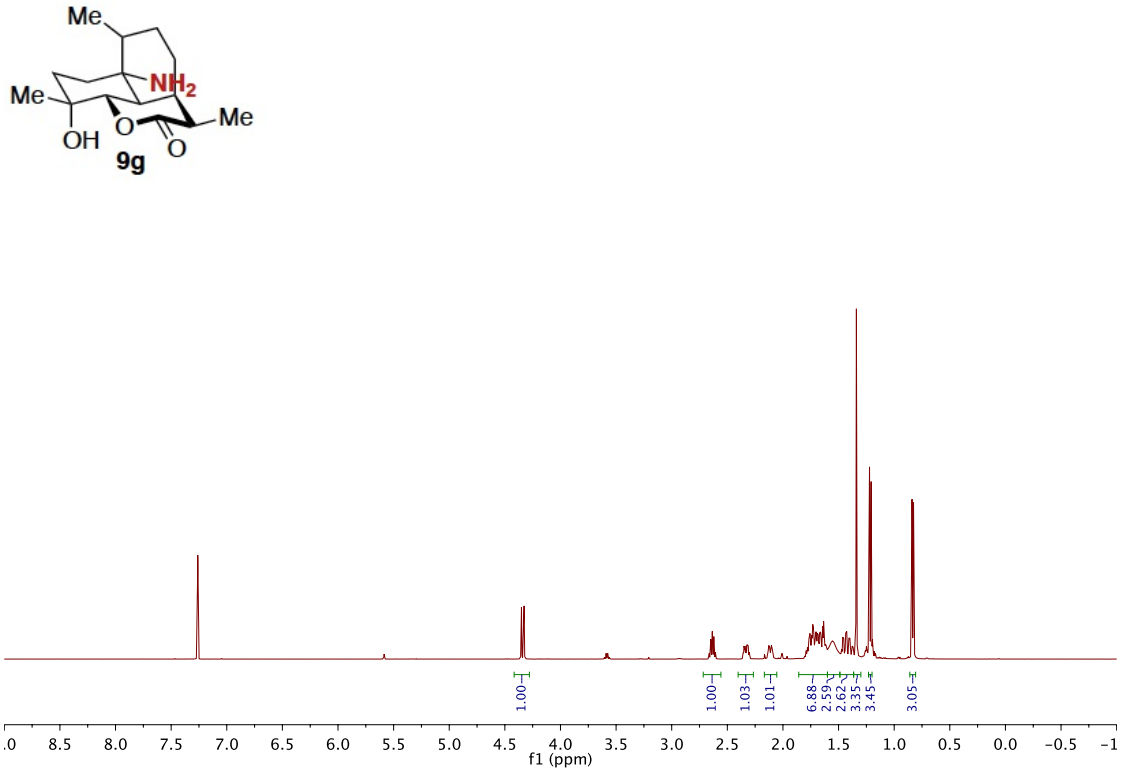

1.00
0.96
0.98
30.87
2.95
3.25
3.32
2.95
3.05
3.12
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

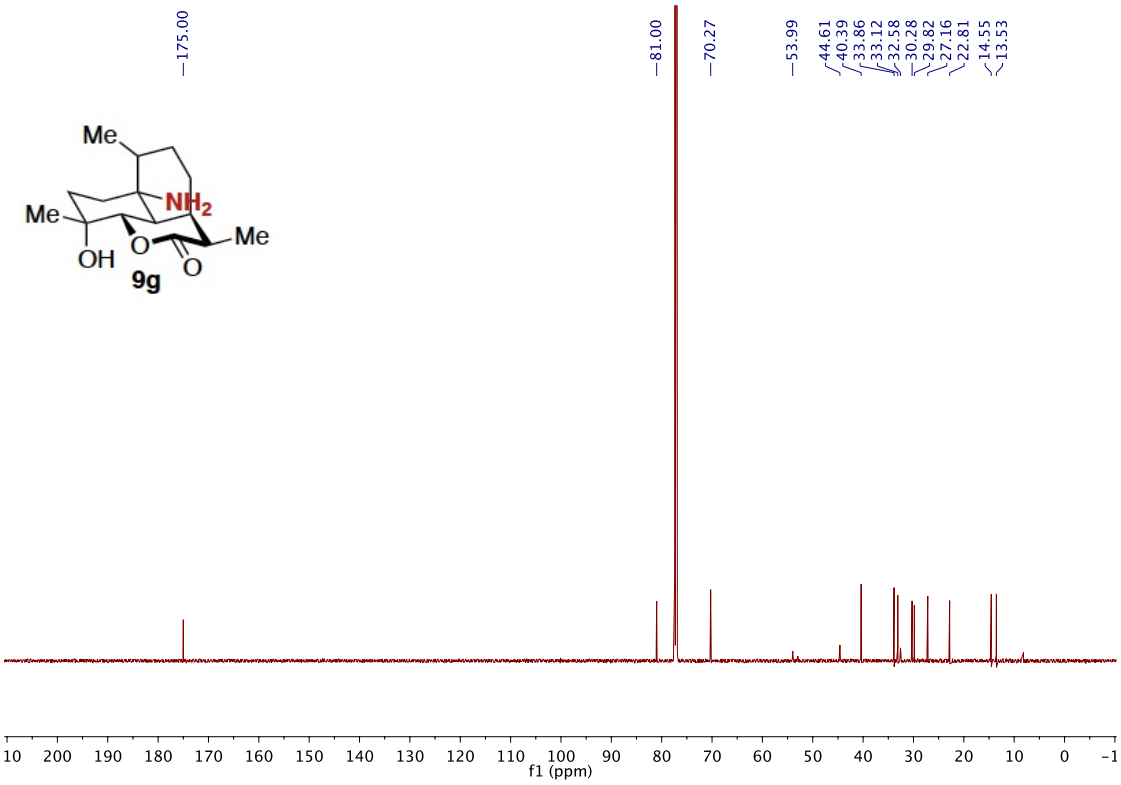

218.29
75.86
55.42
50.51
50.41
50.10
47.56
42.62
41.21
40.42
40.36
40.02
36.94
34.63
34.24
31.35
27.63
26.82
26.47
25.68
25.17
24.67
22.16
21.14
19.76
18.08
16.56
16.18
15.31
14.28
HO
Me
Me
Me
Me
O
Me
H
Me
Me
Me
NH2
Me
9e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

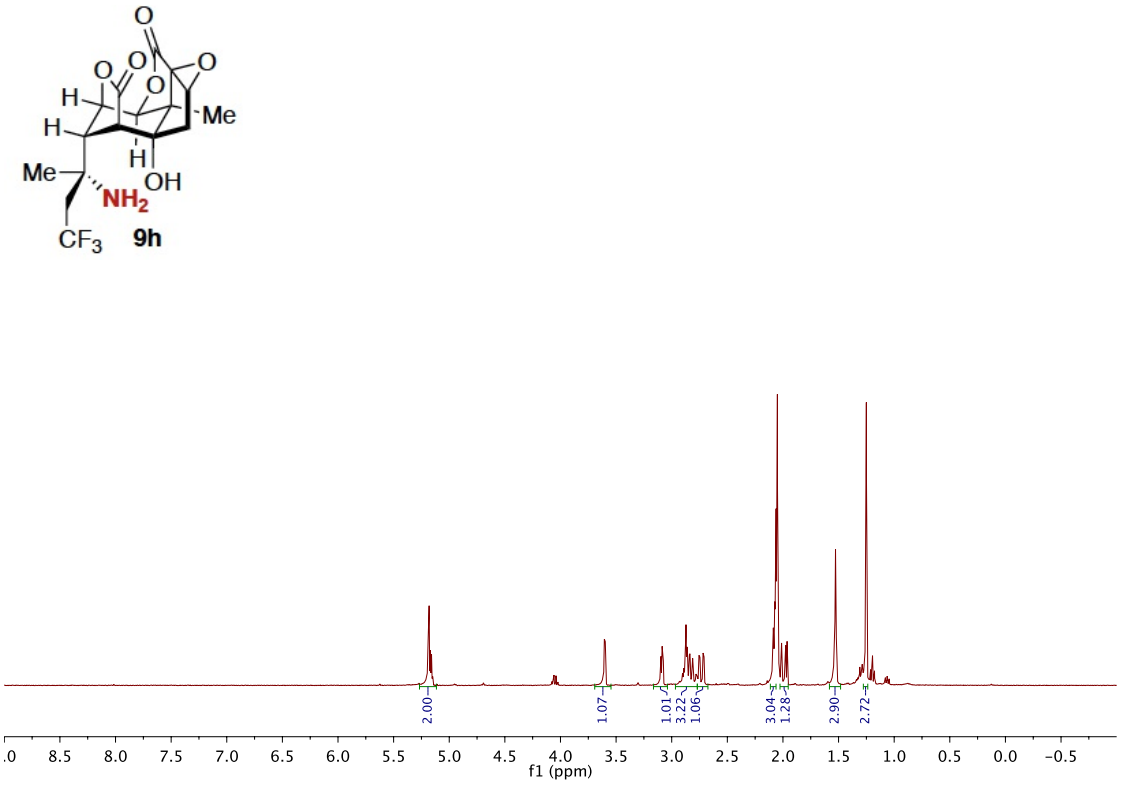

HO
Me
Me
Me
Me
O
Me
H
Me
Me
Me
O
NHPh
NH
Me
9f

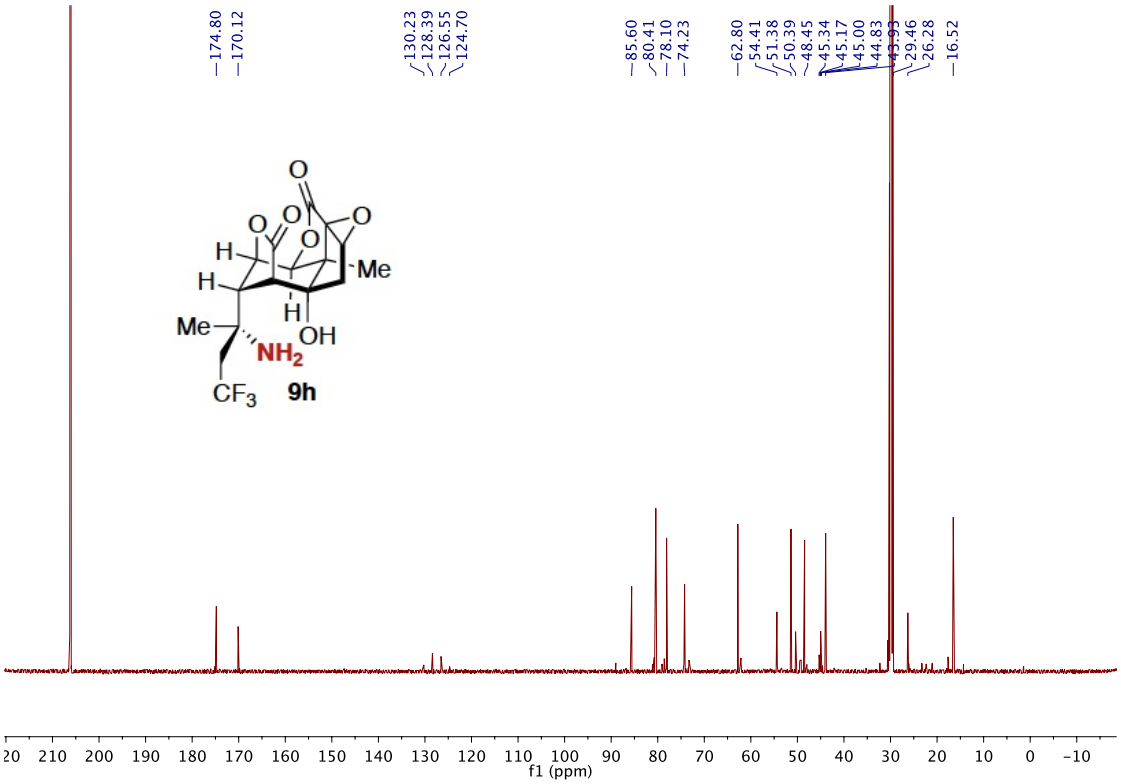

4.21
1.00
1.01
1.00
1.98
1.20
30.17
2.92
3.00
3.02
3.34
3.33
3.36
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

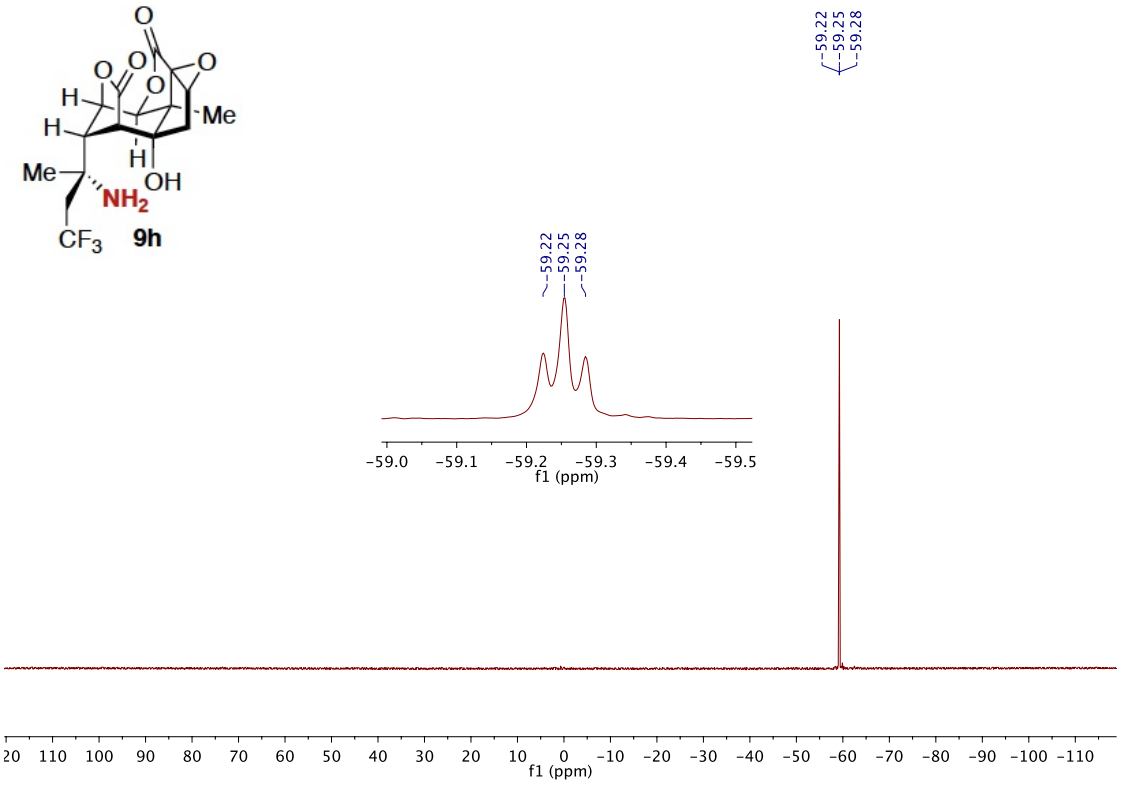

218.18
154.85
138.73
129.29
123.71
120.97
109.99
75.65
55.38
53.52
50.26
50.08
49.99
47.46
42.47
41.34
40.44
40.26
39.89
36.82
34.54
34.14
31.17
29.71
27.61
27.49
27.46
26.69
25.37
24.92
22.02
21.03
19.64
18.21
16.35
16.01
15.19
HO
Me
Me
Me
Me
O
Me
H
Me
9f
O
NHPh
NH
Me
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

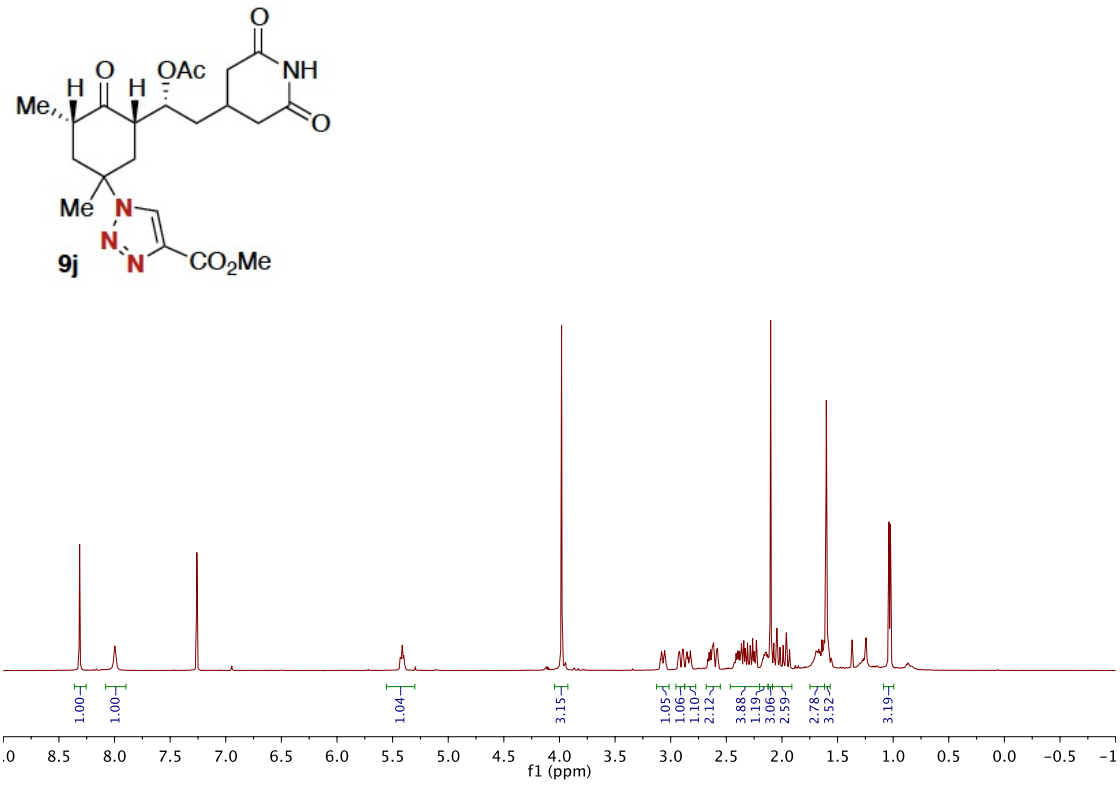

Me
NH2
Me
OH
O
Me
O
9g
1.00
1.00
1.03
1.01
6.88
2.59
2.62
3.35
3.45
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

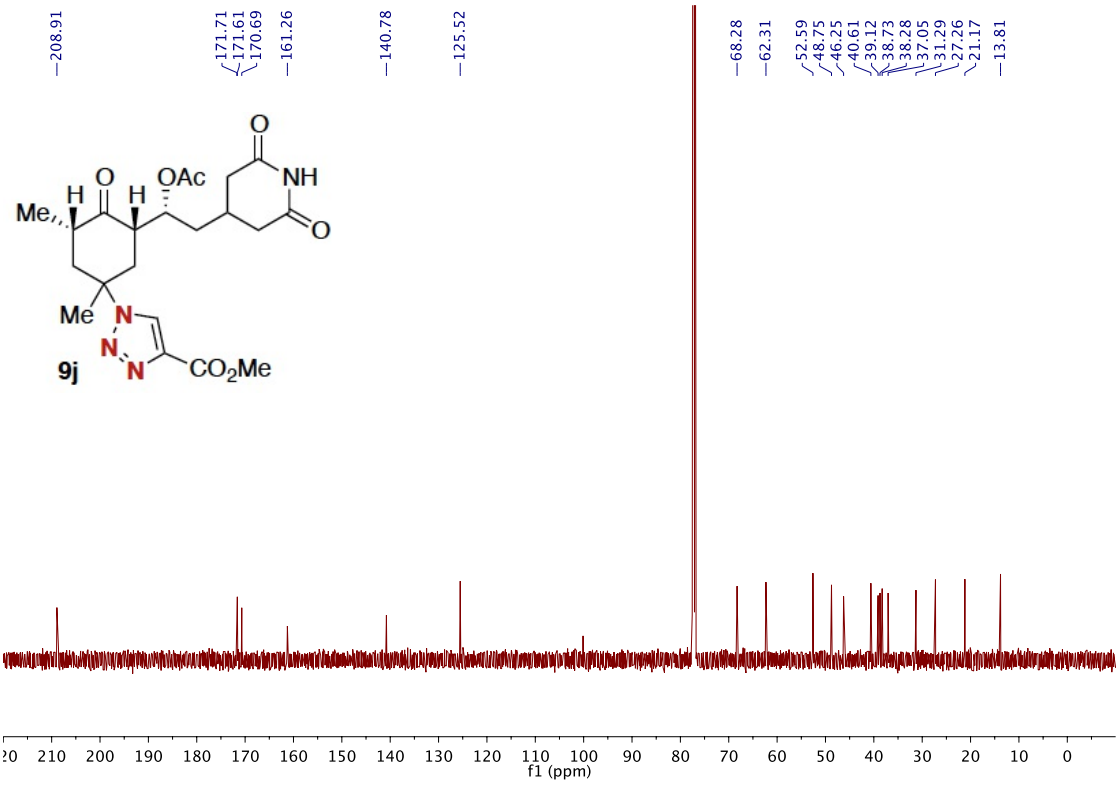

175.00
81.00
70.27
53.99
44.61
40.39
33.86
33.12
32.58
30.28
29.82
27.16
22.81
14.55
13.53
Me
NH2
Me
OH
O
O
Me
9g
f1 (ppm)

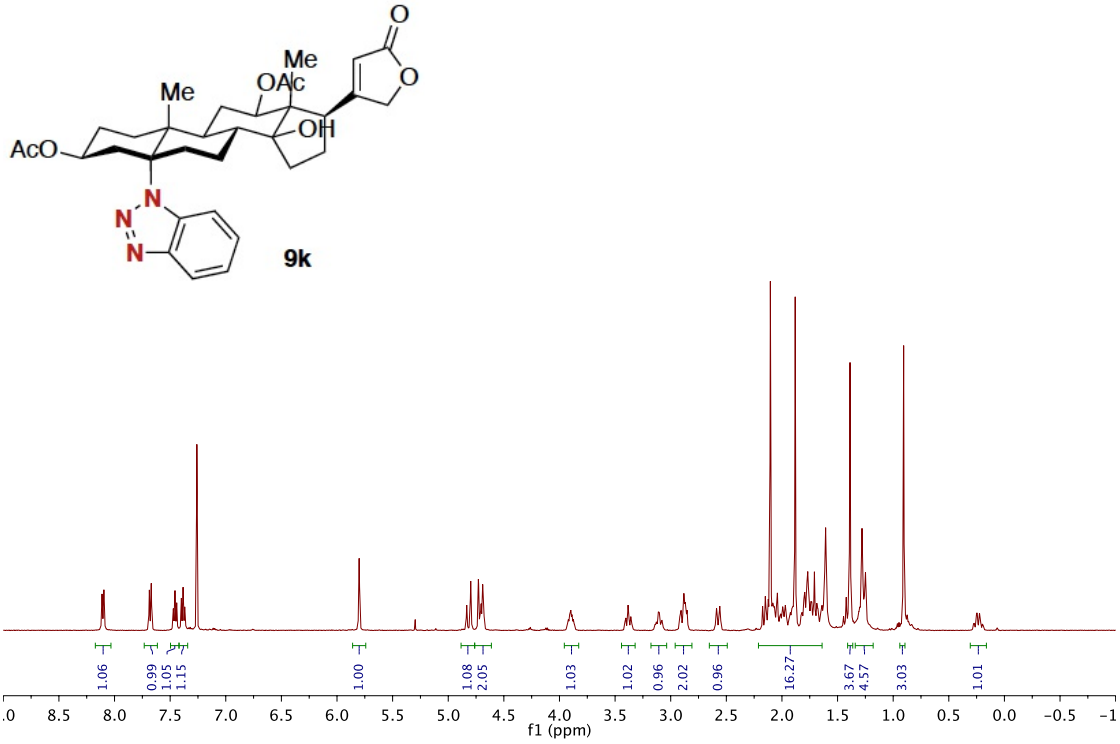

O
O
O
O
O
H
H
Me
H
Me
OH
NH2
CF3
9h
2.00
1.07
1.01
3.22
1.06
3.04
1.28
2.90
2.72
f1 (ppm)

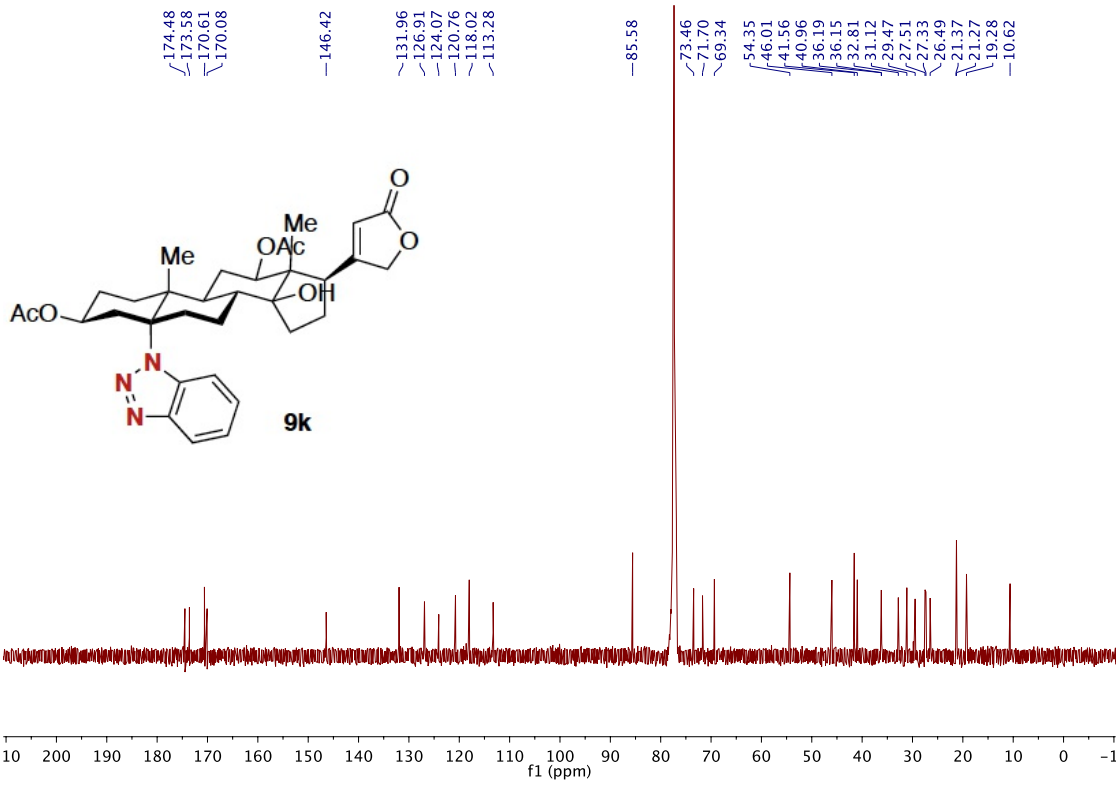

174.80
170.12
130.23
128.39
126.55
124.70
85.60
80.41
78.10
74.23
62.80
54.41
51.38
50.39
48.45
45.34
45.17
45.00
44.83
43.93
29.46
26.28
16.52
Me
H
H
Me
NH2
OH
CF3
9h
f1 (ppm)


59.22
59.25
59.28
Me
H
H
Me
NH2
OH
CF3
9h
f1 (ppm)


O
OAc
NH
H
H
Me
O
O
Me
N
N
N
CO2Me
9j
1.00
1.00
1.04
3.15
1.05
1.06
1.10
2.12
3.88
1.19
3.06
2.59
2.78
3.52
3.19
f1 (ppm)


208.91
171.71
171.61
170.69
161.26
140.78
125.52
68.28
62.31
52.59
48.75
46.25
40.61
39.12
38.73
38.28
37.05
31.29
27.26
21.17
13.81
O
OAc
NH
H
H
Me
O
O
Me
N
N
N
CO2Me
9j
f1 (ppm)


O
Me
OAc
O
Me
OH
AcO
N
N
N
9k
1.06
0.99
1.05
1.15
1.00
1.08
2.05
1.03
1.02
0.96
2.02
0.96
16.27
3.67
4.57
3.03
1.01
f1 (ppm)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69.34
54.35
46.01
41.56
40.96
36.19
36.15
32.81
31.12
29.47
27.51
27.33
26.49
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OAc
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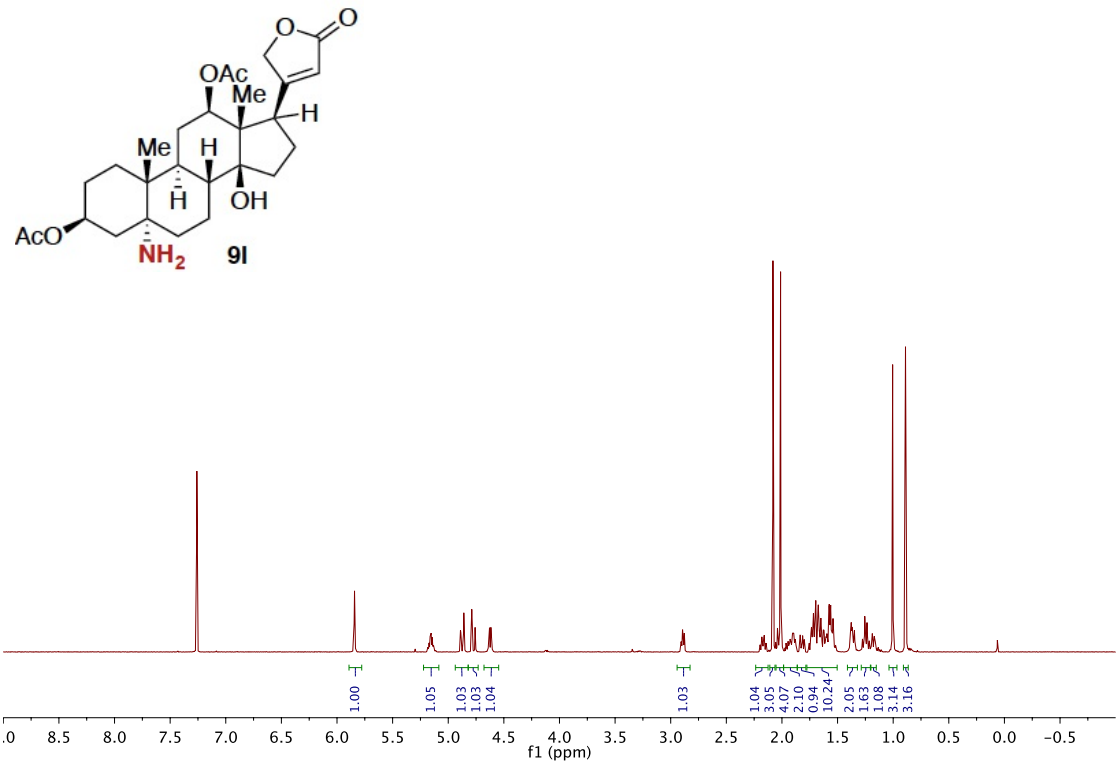
Me
OH
AcO
N
N
N
9k
f1 (ppm)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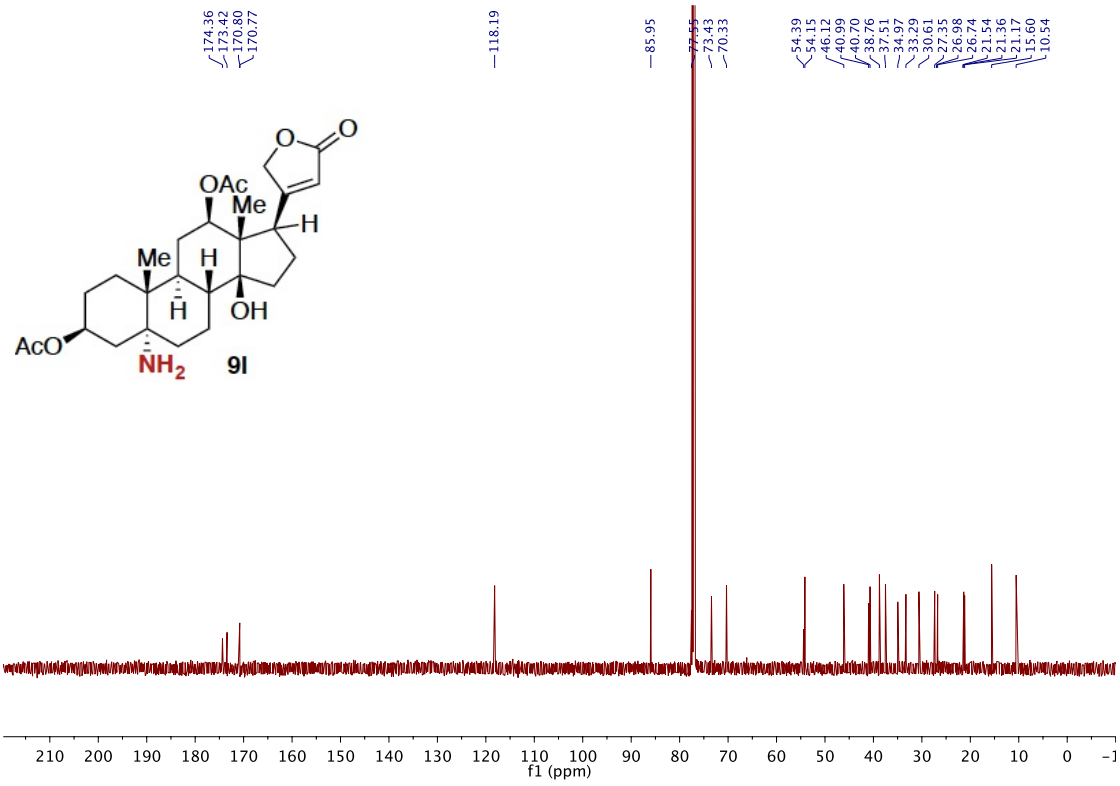
Me
H
Me
H
H
OH
AcO
NH2
9l
1.00
1.05
1.03
1.03
1.04
1.03
1.04
3.05
4.07
2.10
0.94
10.24
2.05
1.63
1.08
3.14
3.16
f1 (ppm)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33.29
30.61
27.35
26.98
26.74
21.54
21.36
21.17
15.60
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Me
H
Me
H
H
OH
AcO
NH2
9l
f1 (ppm)

I. X-ray structures

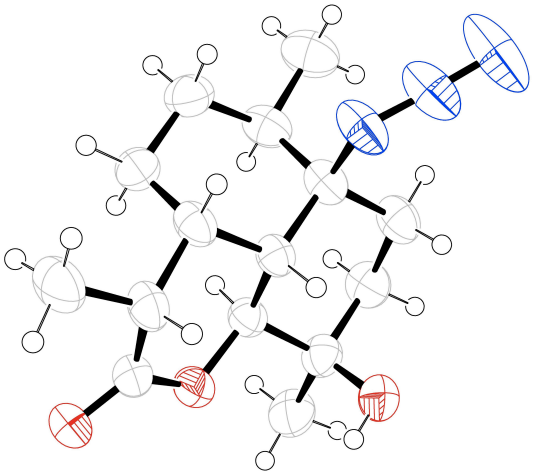

Figure S6 ORTEP drawing of azide **3f**.

A colorless plate 0.080 x 0.050 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 200(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 2 seconds per frame using a scan width of 2.0°. Data collection was 99.7% complete to 67.000° in θ. A total of 12040 reflections were collected covering the indices, -12<=*h*<=12, -7<=*k*<=6, -14<=*l*<=14. 2578 reflections were found to be symmetry independent, with an R_{int} of 0.0496. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C1, C4, C7, C8, C11, and C12, and *S* at C5, respectively.

Table S1. Crystal data and structure refinement for azide **3f**.

Empirical formula	C15 H23 N3 O3	
Formula weight	293.36	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.1594(5) Å	α= 90°.
	b = 6.5226(3) Å	β= 100.773(3)°.
	c = 11.7589(5) Å	γ = 90°.
Volume	765.48(6) $Å^3$	
Z	2	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	316	
Crystal size	0.080 x 0.050 x 0.030 mm^3	
Theta range for data collection	3.826 to 68.341°.	
Index ranges	-12<=h<=12, -7<=k<=6, -14<=l<=14	
Reflections collected	12040	
Independent reflections	2578 [R(int) = 0.0496]	
Completeness to theta = 67.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.725	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2578 / 1 / 194	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1239	
R indices (all data)	R1 = 0.0559, wR2 = 0.1310	
Absolute structure parameter	0.02(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.187 and -0.150 $e.Å^{-3}$	

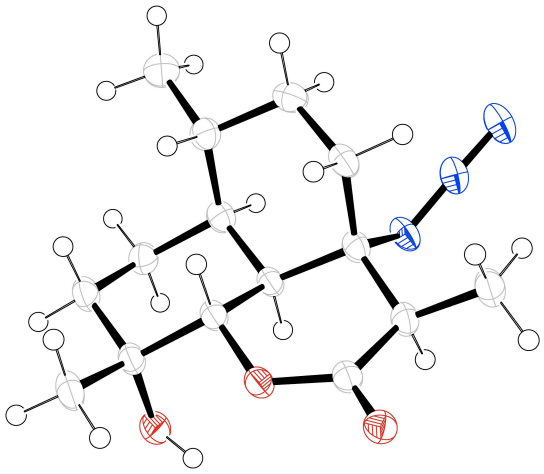

Figure S7 ORTEP drawing of azide **3g**.

A colorless blade 0.080 x 0.040 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.9% complete to 67.000° in θ. A total of 19107 reflections were collected covering the indices, -21<=*h*<=21, -6<=*k*<=6, -17<=*l*<=17. 2560 reflections were found to be symmetry independent, with an R_{int} of 0.0681. Indexing and unit cell refinement indicated a C-centered, monoclinic lattice. The space group was found to be C 2 (No. 5). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C4, C8, and C11, and *S* at C1, C5, C9, and C12, respectively.

Table S2. Crystal data and structure refinement for azide **3g**.

Empirical formula	C15 H23 N3 O3	
Formula weight	293.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 17.681(2) Å	α= 90°.
	b = 5.8685(7) Å	β= 98.134(8)°.
	c = 14.2464(19) Å	γ = 90°.
Volume	1463.4(3) $Å^3$	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.764 mm^{-1}	
F(000)	632	
Crystal size	0.080 x 0.040 x 0.020 mm^3	
Theta range for data collection	3.133 to 68.446°.	
Index ranges	-21<=h<=21, -6<=k<=6, -17<=l<=17	
Reflections collected	19107	
Independent reflections	2560 [R(int) = 0.0681]	
Completeness to theta = 67.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.748	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2560 / 1 / 194	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1121	
R indices (all data)	R1 = 0.0456, wR2 = 0.1151	
Absolute structure parameter	0.09(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.373 and -0.159 $e.Å^{-3}$	

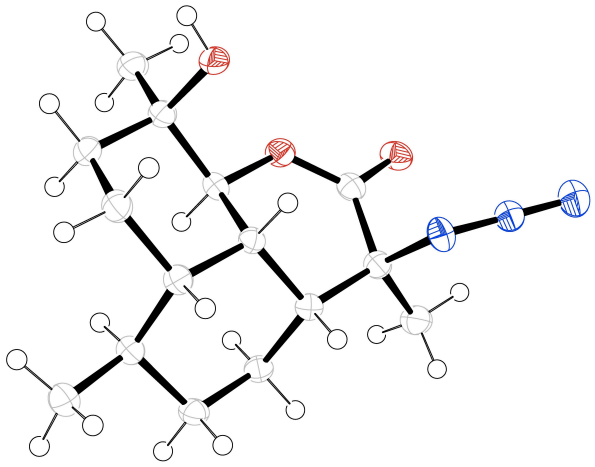

Figure S8 ORTEP drawing of azide **3h**.

A colorless plate 0.070 x 0.050 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 98.5% complete to 67.000° in θ. A total of 34567 reflections were collected covering the indices, -7<=*h*<=5, -12<=*k*<=12, -27<=*l*<=27. 2678 reflections were found to be symmetry independent, with an R_{int} of 0.0414. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C2, C5 and C9, and *S* at C1, C6, C10, and C12, respectively.

Table S3. Crystal data and structure refinement for azide **3h**.

Empirical formula	C15 H23 N3 O3	
Formula weight	293.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.1715(3) Å	α= 90°.
	b = 10.4190(6) Å	β= 90°.
	c = 22.9681(13) Å	γ = 90°.
Volume	1476.87(14) $Å^3$	
Z	4	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.757 mm^{-1}	
F(000)	632	
Crystal size	0.070 x 0.050 x 0.030 mm^3	
Theta range for data collection	3.849 to 68.240°.	
Index ranges	-7<=h<=5, -12<=k<=12, -27<=l<=27	
Reflections collected	34567	
Independent reflections	2678 [R(int) = 0.0414]	
Completeness to theta = 67.000°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2678 / 0 / 194	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0825	
R indices (all data)	R1 = 0.0301, wR2 = 0.0826	
Absolute structure parameter	0.05(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.231 and -0.154 $e.Å^{-3}$	

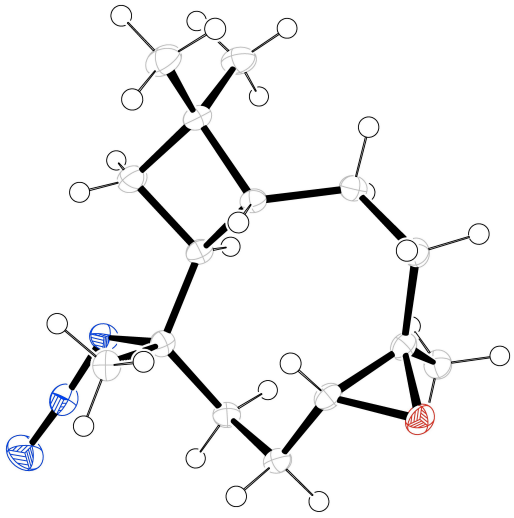

Figure S9 ORTEP drawing of azide **3i**.

A colorless plate 0.060 x 0.030 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 2 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 14137 reflections were collected covering the indices, -7<=*h*<=5, -16<=*k*<=16, -22<=*l*<=22. 2693 reflections were found to be symmetry independent, with an R_{int} of 0.0473. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at CC5, C8, and C9, and *S* at C1 and C2, respectively.

Table S4. Crystal data and structure refinement for azide **3i**.

Empirical formula	C15 H25 N3 O	
Formula weight	263.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.8607(3) Å	α= 90°.
	b = 13.4039(7) Å	β= 90°.
	c = 18.8487(10) Å	γ = 90°.
Volume	1480.68(13) $Å^3$	
Z	4	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	576	
Crystal size	0.060 x 0.030 x 0.030 mm^3	
Theta range for data collection	4.047 to 68.241°.	
Index ranges	-7<=h<=5, -16<=k<=16, -22<=l<=22	
Reflections collected	14137	
Independent reflections	2693 [R(int) = 0.0473]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.828	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2693 / 0 / 176	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0779	
R indices (all data)	R1 = 0.0309, wR2 = 0.0785	
Absolute structure parameter	0.05(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.184 and -0.148 $e.Å^{-3}$	

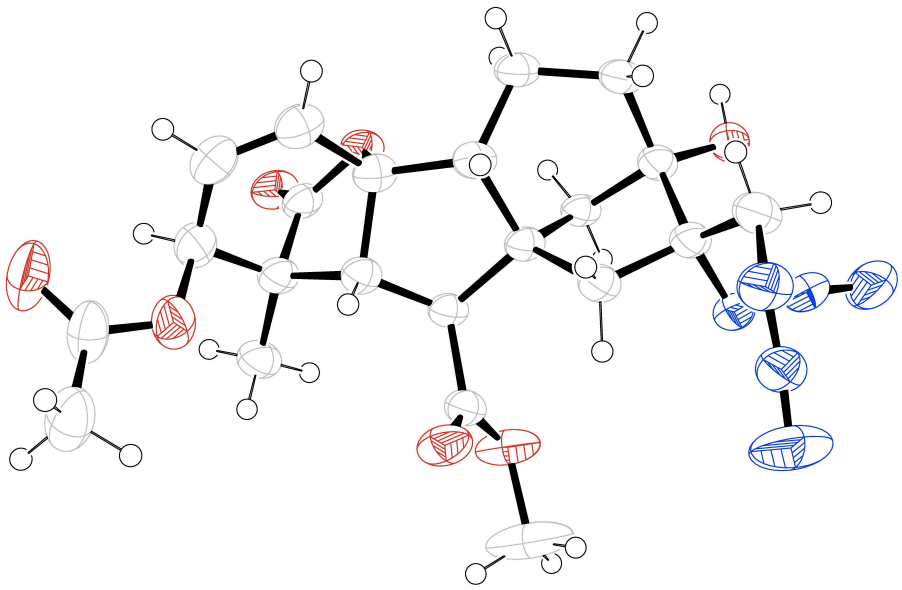

Figure S10 ORTEP drawing of azide **4c**.

A colorless plate 0.070 x 0.060 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 200(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 1 seconds per frame using a scan width of 2.0°. Data collection was 99.9% complete to 67.000° in q. A total of 15676 reflections were collected covering the indices, -8<=*h*<=9, -12<=*k*<=12, -16<=*l*<=16. 4236 reflections were found to be symmetry independent, with an R_{int} of 0.0530. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C5, C9, and C10, and *S* at C1, C3, C4, C6, C13, and C16, respectively.

Table S5. Crystal data and structure refinement for azide **4c**.

Empirical formula	C22 H26 N6 O7	
Formula weight	486.49	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.1836(2) Å	α= 90°.
	b = 10.5248(2) Å	β= 103.0580(10)°.
	c = 13.9957(3) Å	γ = 90°.
Volume	1174.29(4) Å^3	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.879 mm^{-1}	
F(000)	512	
Crystal size	0.070 x 0.060 x 0.030 mm^3	
Theta range for data collection	3.241 to 68.381°.	
Index ranges	-8<=h<=9, -12<=k<=12, -16<=l<=16	
Reflections collected	15676	
Independent reflections	4236 [R(int) = 0.0530]	
Completeness to theta = 67.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.807	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4236 / 3 / 335	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0963	
R indices (all data)	R1 = 0.0439, wR2 = 0.1005	
Absolute structure parameter	0.11(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.149 and -0.187 e.Å^{-3}	

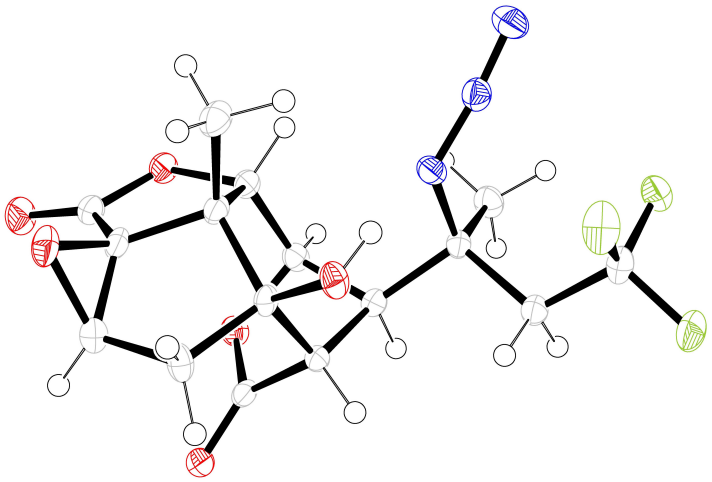

Figure S11 ORTEP drawing of azide **6b**.

A colorless rod 0.060 x 0.030 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 65071 reflections were collected covering the indices, -21<=*h*<=21, -20<=*k*<=21, -12<=*l*<=12. 3324 reflections were found to be symmetry independent, with an R_{int} of 0.0907. Indexing and unit cell refinement indicated a primitive, hexagonal lattice. The space group was found to be P 61 (No. 169). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C1, C3, C5, C9, and C11, and *S* at C2, C6, C8, and C13, respectively.

Table S6. Crystal data and structure refinement for azide **6b**.

Empirical formula	C16 H16 F3 N3 O6	
Formula weight	403.32	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	P 61	
Unit cell dimensions	a = 17.5978(5) Å	α= 90°.
	b = 17.5978(5) Å	β= 90°.
	c = 10.1363(4) Å	γ = 120°.
Volume	2718.48(19) $Å^3$	
Z	6	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	1.167 mm^{-1}	
F(000)	1248	
Crystal size	0.060 x 0.030 x 0.020 mm^3	
Theta range for data collection	2.899 to 68.250°.	
Index ranges	-21<=h<=21, -20<=k<=21, -12<=l<=12	
Reflections collected	65071	
Independent reflections	3324 [R(int) = 0.0907]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3324 / 1 / 256	
Goodness-of-fit on F^2	1.170	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1389	
R indices (all data)	R1 = 0.0467, wR2 = 0.1404	
Absolute structure parameter	0.08(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.188 and -0.237 $e.Å^{-3}$	

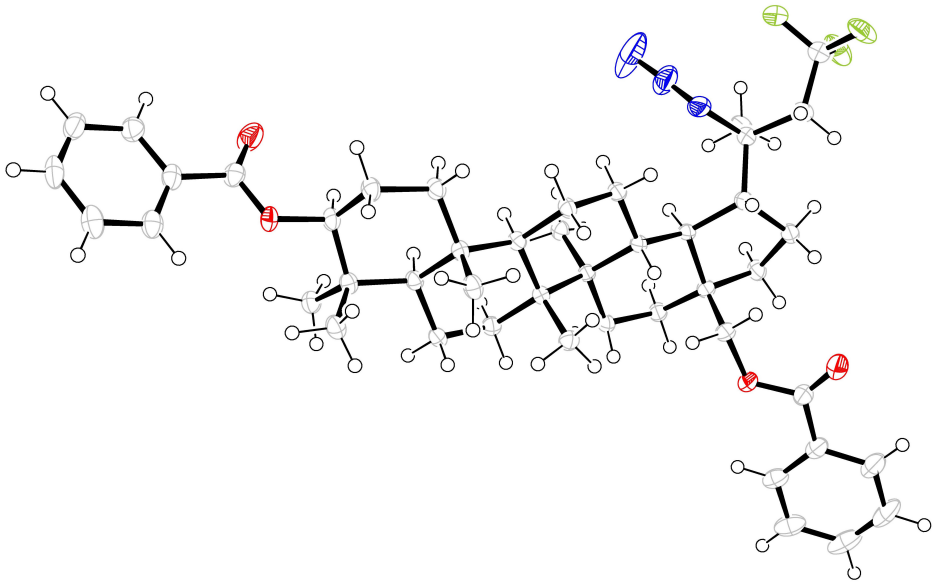

Figure S12 ORTEP drawing of azide **6c**.

A colorless prism 0.060 x 0.040 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 7275 reflections were collected covering the indices, -15<=*h*<=15, -13<=*k*<=13, -16<=*l*<=16. 7275 reflections were found to be symmetry independent, with an R_{int} of 0.0478. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C1, C7, C8, C11, C16, C17, and C20, and *S* at C4, C13, C20, and C21, respectively.

Table S7. Crystal data and structure refinement for azide **6c**.

Empirical formula	C45 H58 F3 N3 O4	
Formula weight	761.94	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.8744(7) Å	α= 90°.
	b = 11.4434(7) Å	β= 107.307(2)°.
	c = 13.9437(8) Å	γ = 90°.
Volume	1961.3(2) Å^3	
Z	2	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.746 mm^{-1}	
F(000)	816	
Crystal size	0.060 x 0.040 x 0.020 mm^3	
Theta range for data collection	3.320 to 68.406°.	
Index ranges	-15<=h<=15, -13<=k<=13, -16<=l<=16	
Reflections collected	7275	
Independent reflections	7275 [R(int) = 0.0478]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.421	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7275 / 1 / 503	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.1030	
R indices (all data)	R1 = 0.0395, wR2 = 0.1041	
Absolute structure parameter	0.02(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.396 and -0.288 e.Å^{-3}	

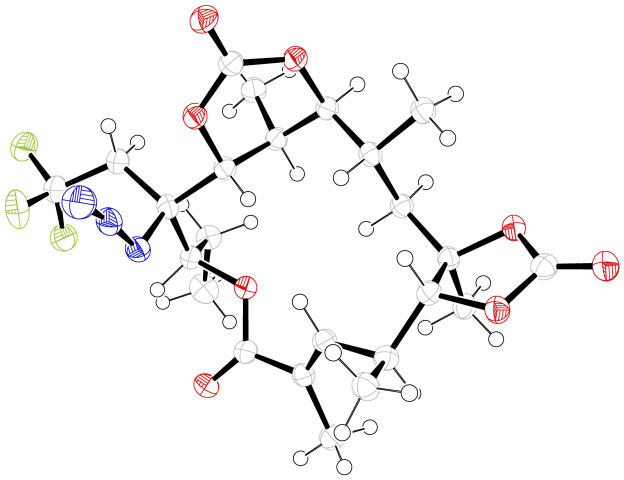

Figure S13 ORTEP drawing of azide **6e**.

A colorless plate 0.060 x 0.040 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.9% complete to 67.000° in θ. A total of 43193 reflections were collected covering the indices, -9<=*h*<=9, -11<=*k*<=12, -20<=*l*<=20. 5190 reflections were found to be symmetry independent, with an R_{int} of 0.0479. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C1, C2, C5, C7, C9, C11, and C16, and *S* at C4 and C12, respectively.

Table S8. Crystal data and structure refinement for azide **6e**.

Empirical formula	C27 H38 F3 N3 O9	
Formula weight	605.60	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.9614(5) Å	α= 90°.
	b = 10.5937(7) Å	β= 93.179(3)°.
	c = 17.3592(11) Å	γ = 90°.
Volume	1461.83(16) Å^3	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.985 mm^{-1}	
F(000)	640	
Crystal size	0.060 x 0.040 x 0.030 mm^3	
Theta range for data collection	2.549 to 68.626°.	
Index ranges	-9<=h<=9, -11<=k<=12, -20<=l<=20	
Reflections collected	43193	
Independent reflections	5190 [R(int) = 0.0479]	
Completeness to theta = 67.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.754	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5190 / 1 / 387	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1050	
R indices (all data)	R1 = 0.0394, wR2 = 0.1056	
Absolute structure parameter	0.04(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.281 and -0.246 e.Å^{-3}	

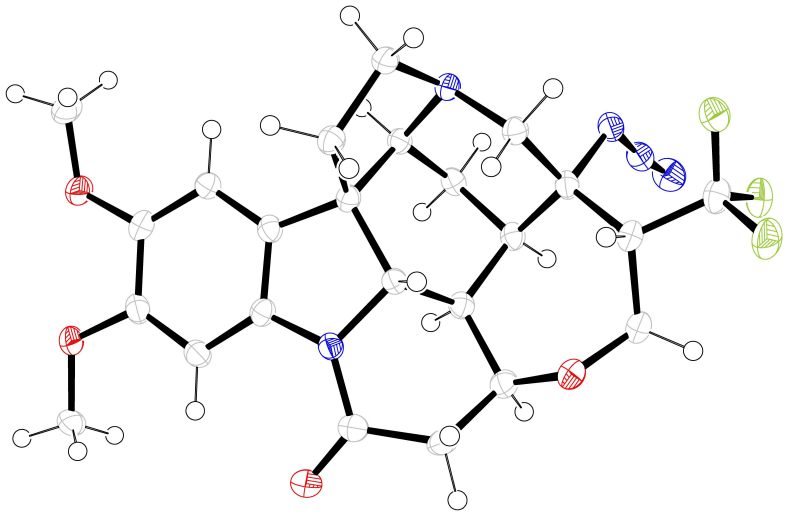

Figure S14 ORTEP drawing of azide **6f**.

A colorless prism 0.070 x 0.050 x 0.050 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 98.3% complete to 67.000° in θ. A total of 27080 reflections were collected covering the indices, -11<=*h*<=11, -12<=*k*<=12, -13<=*l*<=13. 3858 reflections were found to be symmetry independent, with an R_{int} of 0.0406. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C17 and C21, and *S* at C1, C14, C16, C19, and C20, respectively.

Table S9. Crystal data and structure refinement for azide **6f**.

Empirical formula	C24 H26 F3 N5 O4	
Formula weight	505.50	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.5910(6) Å	α= 90°.
	b = 10.1778(6) Å	β= 102.570(2)°.
	c = 11.4314(7) Å	γ = 90°.
Volume	1089.13(12) $Å^3$	
Z	2	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	1.056 mm^{-1}	
F(000)	528	
Crystal size	0.070 x 0.050 x 0.050 mm^3	
Theta range for data collection	3.962 to 68.228°.	
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=13	
Reflections collected	27080	
Independent reflections	3858 [R(int) = 0.0406]	
Completeness to theta = 67.000°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3858 / 1 / 327	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0766	
R indices (all data)	R1 = 0.0291, wR2 = 0.0767	
Absolute structure parameter	0.09(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.250 and -0.193 $e.Å^{-3}$	