Supporting Information

Manganese-Catalyzed Carboacylations of Alkenes with Alkyl Iodides

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General Methods

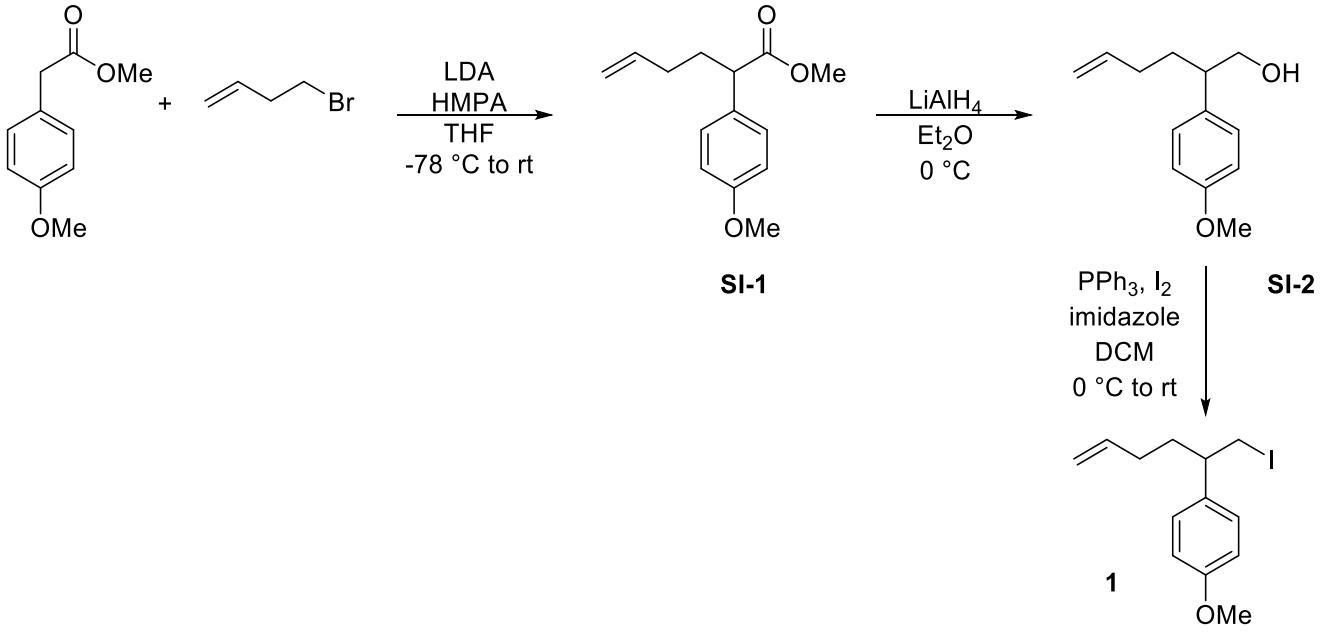
Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 or a Bruker AVANCE III 600 CryoProbe (^{1}H NMR at 400 MHz or 600 MHz and ^{13}C NMR at 151 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm or C_6D_6 at 7.16 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm or C_6D_6 at 128.06 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sxt = sextet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Thermo LTQ-FT-ICR-MS-7T mass spectrometer with positive ion electrospray ionization (ESI) or using an Agilent 6850 series gas chromatography system equipped with an Agilent 5973N mass selective detector. Thin layer chromatography (TLC) was performed on SiliaPlate 250μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), aqueous basic potassium permanganate solution, or ethanolic acidic *p*-anisaldehyde solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle. Tetrahydrofuran, diethyl ether and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. Acetone was dried over potassium carbonate. Ethanol, methanol, and benzene were sparged with argon and dried over molecular sieves. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. The sealed tubes used were purchased from Ace Glass. Pressure adapters were assembled from Swagelock parts (see photos below).

Compound Preparation

Substrate Preparation

Trans-2-(allyloxy)-3-iodotetrahydro-2H-pyran (**3**),[1] (E)-N-(2-iodoethyl)-4-methyl-N-(2-methylbut-2-en-1-yl)benzenesulfonamide (**9**),[2] (iodomethyl)diisopropyl((1-phenylbut-3-en-1-yl)oxy)silane (**13**),[3] and 3-(1-butoxy-2-iodoethoxy)cyclohex-1-ene (**19**),[4] were prepared according to literature procedures. All physical and spectral data were in accordance with literature data.

Synthesis of 1

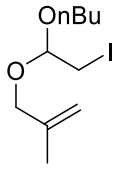


1) Enolate alkylation To a 0 °C solution of iPr_2NH (4.6 mL, 33 mmol) in THF (111 mL), n-BuLi (12.4 mL, 33 mmol, 2.66 M in hexanes) was added dropwise. The reaction was stirred at 0 °C for 10 minutes, then cooled to -78 ˚C. A solution of methyl 2-(4-methoxyphenyl)acetate (4.8 mL, 30 mmol) in THF (8 mL) was added dropwise and the reaction was stirred for 30 minutes. A solution of 4-bromobut-1-ene (3.7 mL, 36 mmol) in THF (8 mL) was added, followed by HMPA (3.13 mL, 18 mmol). The reaction was allowed to warm to room temperature and stirred overnight. It was then diluted with Et_2O and hexanes and washed with NH_4Cl and brine. The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (20:1 Hex:EtOAc) to provide 4.98 g (71%) of **SI-1** as a colorless oil. Analytical data for **SI-1**: IR (thin film, cm^{-1}) 2950, 2837, 1734, 1641, 1611, 1511, 1438, 1302, 1249, 1160, 1035, 914, 831, 531; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.22 (dd, *J*=8.80, 4.65 Hz, 2 H), 6.86 (dd, *J*=8.56, 4.65 Hz, 2 H), 5.77 (m, 1 H), 1.80 - 1.91 (m, 1 H), 4.96 - 5.03 (m, 2 H), 3.79 (s, 3 H), 3.65 (s, 3 H), 3.53 (t, *J*=7.58 Hz, 1 H), 2.07 - 2.20 (m, 1 H), 2.00 (dt, *J*=7.83, 6.85 Hz, 2 H); ^{13}C

NMR (151 MHz, $CDCl_3$) δ = 174.67, 158.72, 137.57, 130.90, 128.94, 115.34, 113.96, 55.20, 51.90, 49.78, 32.47, 31.42; HRMS (ESI) calculated for $[C_{14}H_{18}O_3+Na]^+$ = 257.1148, found = 257.1148.

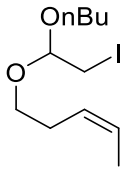
2) Reduction $LiAlH_4$ (1.46 g, 38.4 mmol) was stirred as a suspension in Et_2O (38 mL) at 0 ˚C. **SI-1** (4.5 g, 19.2 mmol) was added dropwise. The reaction was warmed to room temperature and stirred overnight. The reaction was then cooled to 0 ˚C and quenched with H_2O (1.5 mL), 10% NaOH (3.0 mL), and H_2O (4.5 mL) and stirred at room temperature for 20 minutes. The solids were filtered out and the filtrate was concentrated in vacuo. Purified by flash chromatography (2:1 Hex:EtOAc) to provide 3.48 g (88%) of **SI-2** as a white solid. Analytical data for **SI-2**: IR (thin film, cm^{-1}) 3371, 2930, 1640, 1611, 1511, 1460, 1300, 1247, 1179, 1035, 911, 830, 550; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.13 (dd, *J* = 4.6, 8.6 Hz, 2 H), 6.88 (dd, *J* = 4.9, 8.6 Hz, 2 H), 5.77 (m, *J* = 6.5, 10.4, 17.0 Hz, 1 H), 5.02 - 4.91 (m, 2 H), 3.80 (s, 3 H), 3.77 - 3.64 (m, 2 H), 2.91 - 2.71 (m, 1 H), 1.95 (m, *J* = 6.4, 7.6 Hz, 2 H), 1.84 - 1.71 (m, 1 H), 1.71 - 1.50 (m, 2 H), 1.31 (br. s., 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.38, 138.36, 133.75, 128.98, 114.71, 114.06, 67.54, 55.21, 47.07, 31.32, 31.21; HRMS (ESI) calculated for $[C_{13}H_{18}O_2+Na]^+$ = 229.1199, found = 229.1199.

3) Iodination A solution of PPh_3 (6.7 g, 25.4 mmol), imidazole (1.7 g, 25.4 mmol), and I_2 (6.4 g, 25.4 mmol) was stirred at 0 ˚C in DCM (64 mL). A solution of **SI-2** (3.48 g, 16.9 mmol) in DCM (42 mL) was added dropwise. The reaction was warmed to room temperature and stirred overnight. The reaction was quenched with H_2O and extracted with DCM (x3). The combined organic layers were washed with $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated in vacuo. Purified by column chromatography (10:1 Hex:EtOAc) to provide 4.87 g (92%) of **1** as a colorless oil. Analytical data for **1**: IR (thin film, cm^{-1}) 3073, 2997, 2929, 2834, 1640, 1610, 1583, 1511, 1457, 1301, 1248, 1177, 1106, 1036, 998, 913, 829, 734, 709, 602, 553; ^1H NMR (400MHz, $CDCl_3$) δ = 7.07 (dd, *J* = 4.6, 8.8 Hz, 2 H), 6.87 (dd, *J* = 4.6, 8.6 Hz, 2 H), 5.81 - 5.68 (m, 1 H), 5.08 - 4.92 (m, 2 H), 3.81 (s, 3 H), 3.35 (m, *J* = 2.4, 7.3 Hz, 2 H), 2.82 (m, *J* = 2.9, 3.9 Hz, 1 H), 2.03 - 1.85 (m, 3 H), 1.78 - 1.62 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.47, 137.91, 134.71, 128.33, 115.02, 113.90, 55.19, 46.69, 34.77, 31.58, 14.42; LR GC/MS calculated for $[C_{13}H_{17}OI]^+$ = 316.0324, found = 316.



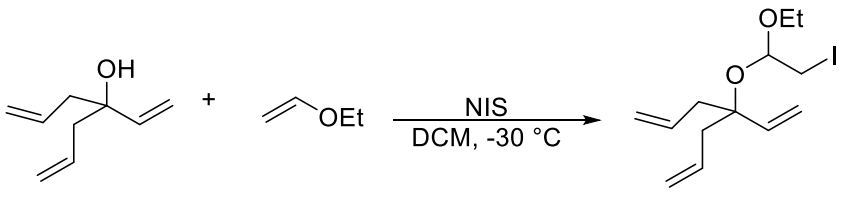
7

To a -30 °C solution of butyl vinyl ether (1.48 mL, 11.4 mmol) and 2-methyl-2-propen-1-ol (0.80 mL, 9.5 mmol) in DCM (9.5 mL), N-iodosuccinimide (2.14 g, 9.5 mmol) was added portionwise. The reaction was stirred at -30 °C for 4 hours. The reaction was allowed to warm to room temperature and stirred overnight. It was then diluted with DCM. It was washed with H_2O, $Na_2S_2O_3$, and brine. The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (30:1 Hex:EtOAc) to provide 2.07 g (73%) of **7** as a colorless oil. Analytical data for **7**: IR (thin film, cm^{-1}) 2958, 2932, 2870, 1657, 1455, 1342, 1177, 1112, 1036, 901, 605; ^1H NMR (400MHz, $CDCl_3$) δ = 5.00 (s, 1 H), 4.91 (s, 1 H), 4.64 (t, J=5.38 Hz, 1 H), 3.91 - 4.07 (m, 2 H), 3.55 - 3.70 (m, 1 H), 3.40 - 3.55 (m, 1 H), 3.24 (d, J=5.62 Hz, 2 H), 1.78 (s, 3 H), 1.52 - 1.64 (m, 2 H), 1.40 (sxt, J=7.43 Hz, 2 H), 0.93 (t, J=7.34 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.52, 112.75, 101.12, 70.23, 66.26, 31.69, 19.70, 19.29, 13.83, 5.21; LR GC/MS calculated for $[C_{10}H_{19}O_2\text{-}I]^+$ = 171.1385, found = 171.



11

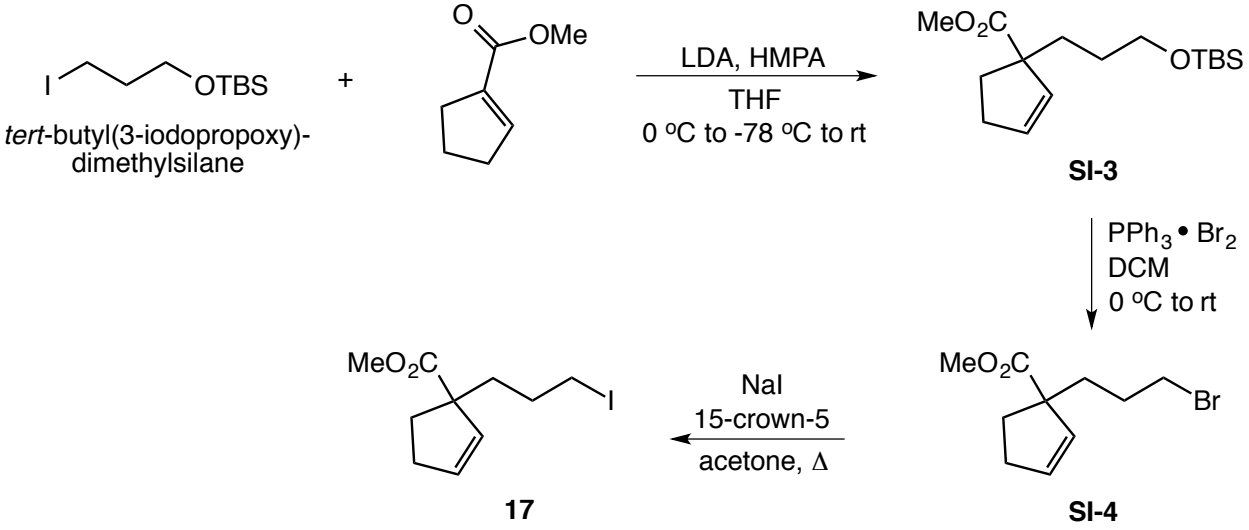
To a -30 °C solution of butyl vinyl ether (1.5 mL, 12 mmol) and cis-3-penten-1-ol (1.02 mL, 10 mmol) in DCM (10 mL), N-iodosuccinimide (2.25 g, 10 mmol) was added portionwise. The reaction was stirred at -30 °C for 4 hours. The reaction was allowed to warm to room temperature and then diluted with DCM. It was washed with H_2O, $Na_2S_2O_3$, and brine. The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (20:1 Hex:EtOAc) to provide 2.98 g (96%) of **11** as a colorless oil. Analytical data for **11**: IR (thin film, cm^{-1}) 3747, 3016, 2958, 2870, 2360, 1650, 1459, 1344, 1176, 1111, 1045, 706; ^1H NMR (600MHz, $CDCl_3$) δ = 5.62 - 5.48 (m, *J* = 4.4, 6.8, 6.8, 6.8, 6.8 Hz, 1 H), 5.47 - 5.37 (m, 1 H), 4.62 (t, *J* = 5.5 Hz, 1 H), 3.62 (q, *J* = 7.6 Hz, 2 H), 3.55 - 3.42 (m, 2 H), 3.22 (d, *J* = 5.4 Hz, 2 H), 2.36 (q, *J* = 6.8 Hz, 2 H), 1.69 - 1.54 (m, 5 H), 1.49 - 1.28 (m, 2 H), 0.93 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 126.15, 126.07, 101.85, 66.40, 65.91, 31.68, 27.47, 19.29, 13.84, 12.90, 5.33.



15

To a -30 °C solution of ethyl vinyl ether (0.82 mL, 8.68 mmol) and 4-vinylhepta-1,6-dien-4-ol[5] (1.0 g, 7.24 mmol) in DCM (7.1 mL), N-iodosuccinimide (1.63 g, 7.24 mmol) was added portionwise. The reaction was stirred at -30 °C for 4 hours. The reaction was allowed to warm to room temperature, stirred overnight, and then diluted with DCM. It was washed with H_2O, $Na_2S_2O_3$, and brine. The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (20:1 Hex:EtOAc) to provide 1.44 g (60%) of **15** as a colorless oil. Analytical data for **15**: IR (thin film, cm^{-1}) 3076, 2977, 2931, 1640, 1414, 1096, 1060, 1005, 916; ^1H NMR (400MHz, $CDCl_3$) δ = 5.78 - 5.94 (m, 3 H), 5.20 - 5.32 (m, 2 H), 5.03 - 5.11 (m, 4 H), 4.74 (t, J=5.38 Hz, 1 H), 3.53 (q, J=7.09 Hz, 2 H), 3.14 - 3.28 (m, 2 H), 2.36 - 2.51 (m, 4 H), 1.19 (t, J=6.97 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 140.63, 133.57, 133.33, 118.12, 117.96, 116.44, 96.61, 79.61, 60.20, 41.15, 40.54, 15.13, 7.10.

Synthesis of 17

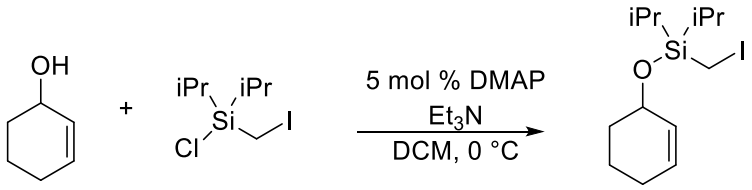


1) Alkylation To a 0 °C solution of iPr_2NH (0.99 mL, 7 mmol) in THF (7 mL), n-BuLi (2.4 mL, 6.3 mmol, 2.66 M in hexanes) was added dropwise. The reaction was cooled to -78 ˚C and stirred for 5 minutes. HMPA (1.1 mL, 6.3 mmol) was added and the reaction was stirred for 30 minutes. Methyl cyclopent-1-ene-1-carboxylate (0.61 mL, 5 mmol) was added dropwise and the reaction was stirred for 10 minutes. tert-butyl(3-iodopropoxy)dimethylsilane[6] (2.25 g, 7.5 mmol) was added and the reaction was stirred for 3 hours warming to room temperature. It was then diluted with Et_2O, quenched with NH_4Cl, and extracted with Et_2O (x3). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (25:1 Hex:EtOAc) to provide 832 mg (56%) of **SI-3** as a yellow oil. Analytical data for **SI-3**: IR (thin film, cm^{-1}) 2951, 2857, 2360, 1733, 1462, 1387, 1361, 1317, 1253, 1196, 1099, 1030, 836, 776, 725, 662, 511; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.80 (dt, *J*=5.62, 2.20 Hz, 1 H), 5.69 (dt, *J*=5.75, 2.02 Hz, 1 H), 3.67 (s, 3 H), 3.57 (t, *J*=6.48 Hz, 2 H), 2.30 - 2.46 (m, 3 H), 1.76 (m, *J*=8.56 Hz, 2 H), 1.62 (m, *J*=12.96 Hz, 1 H), 1.37 - 1.52 (m, 2 H), 0.88 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 176.92, 133.52, 132.27, 63.28, 59.83, 51.88, 34.84, 32.72, 31.75,

28.71, 25.96, 18.36, -5.26; HRMS (ESI) calculated for $[C_{16}H_{30}O_3Si+Na]^+$ = 321.1857, found = 321.1856.

2) Bromination To a 0 °C solution of **SI-3** (832 mg, 2.8 mmol) in DCM (28 mL), PPh_3•Br_2 (1.4 g, 3.4 mmol) was added. The reaction was stirred, warming to room temperature gradually. It was then concentrated in vacuo, redissolved in Et_2O, and filtered. The filtrate was concentrated in vacuo. Purified by flash chromatography (20:1 Hex:EtOAc) to provide 424 mg (61%) of **SI-4** as a pale orange oil. Analytical data for **SI-4**: IR (thin film, cm^{-1}) 2949, 2853, 1729, 1435, 1319, 1241, 1163, 1065, 993, 918, 727, 638, 559; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.84 (dt, *J*=5.50, 2.26 Hz, 1 H), 5.67 (dt, *J*=5.62, 1.96 Hz, 1 H), 3.68 (s, 3 H), 3.37 (t, *J*=6.11 Hz, 2 H), 2.34 - 2.48 (m, 3 H), 1.72 - 1.88 (m, 5 H), 1.58 (s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 176.54, 132.99, 132.90, 59.53, 52.04, 37.04, 33.74, 32.80, 31.81, 28.76; LR GC/MS calculated for $[C_{10}H_{15}O_2Br - CO_2CH_3]^+$ = 187.0122; found = 187.

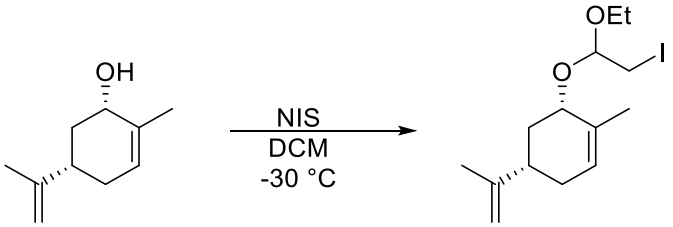
3) Iodination To a solution of **SI-4** (424 mg, 1.7 mmol) in acetone (7 mL), NaI (764 mg, 5.1 mmol) was added. 15-crown-5 (165 µL, 0.85 mmol) was added. The reaction was heated to reflux and stirred overnight. It was then diluted with DCM, washed with $Na_2S_2O_3$, and extracted with DCM (x3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (20:1 Hex:EtOAc) to provide 428 mg (86%) of **17** as a pale yellow oil. Analytical data for **17**: IR (thin film, cm^{-1}) 2947, 1728, 1433, 1217, 1162, 727; ^1H NMR (400MHz, $CDCl_3$) δ = 5.83 (dt, *J* = 2.3, 5.6 Hz, 1 H), 5.67 (dt, *J* = 2.1, 5.6 Hz, 1 H), 3.68 (s, 3 H), 3.14 (t, *J* = 6.2 Hz, 2 H), 2.47 - 2.34 (m, 3 H), 1.85 - 1.68 (m, 5 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 176.48, 132.99, 132.94, 59.40, 51.99, 39.26, 32.79, 31.75, 29.48; HRMS (APCI) calculated for $[C_{10}H_{15}O_2I+H]^+$ = 295.0195, found = 295.0188.



21

To a 0 ˚C solution of chloro(iodomethyl)diisopropylsilane[3] (937 mg, 3 mmol) and DMAP (18.3 mg, 0.15 mmol) in DCM (10 mL), triethylamine (418 µL, 3 mmol) was added. A solution of cyclohex-2-en-1-ol (323 µL, 3.3 mmol) in DCM (5 mL) was added. The reaction was stirred at 0 °C. The reaction was allowed to warm to room temperature, quenched with NH_4Cl and then extracted with DCM (x3). It was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (hexanes) to provide 675 mg (64%) of **21** as a colorless oil. Analytical data for **21**: IR (thin film, cm^{-1}) 3025, 2939, 2864, 1462, 1388, 1085, 1023, 881,

834, 797, 726; ^{1}H NMR (400MHz, $CDCl_3$) δ = 5.82 - 5.68 (m, 2 H), 4.38 (br. s., 1 H), 2.10 (s, 2 H), 2.06 - 1.97 (m, 1 H), 1.97 - 1.75 (m, 3 H), 1.69 - 1.43 (m, 2 H), 1.34 - 1.15 (m, 2 H), 1.09 (t, *J* = 6.8 Hz, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 130.63, 129.53, 66.98, 32.57, 24.91, 19.38, 17.72, 17.70, 17.43, 12.45, 12.43; LR GC/MS calculated for $[C_{13}H_{25}OSiI]^+$ = 352.0719, found = 352.



23

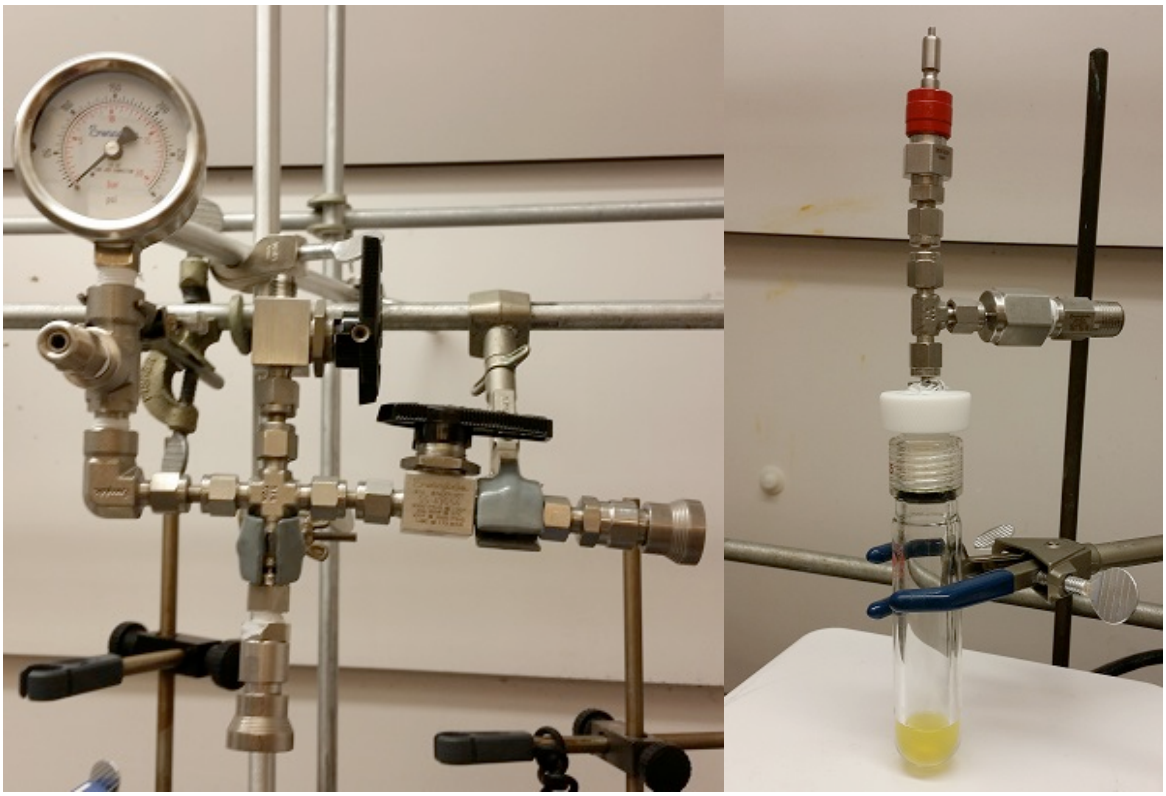
To a -30 °C solution of ethyl vinyl ether (0.75 mL, 7.9 mmol) and (1S,5S)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-ol)[7] (1.0 g, 6.6 mmol) in DCM (6.6 mL), N-iodosuccinimide (1.48 g, 6.6 mmol) was added portionwise. The reaction was stirred at -30 °C for 4 hours and allowed to warm to room temperature overnight. It was then diluted with DCM. It was washed with H_2O, $Na_2S_2O_3$, and brine. The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purified by flash chromatography (25:1 Hex:EtOAc) to provide 2.02 g (87%) of **23** as a colorless oil. Analytical data for **23**: IR (thin film, cm^{-1}) 3078, 2972, 2918, 1644, 1450, 1373, 1323, 1179, 1103, 1029, 924, 889, 810, 609, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.66 (d, *J*=19.44 Hz, 1 H) 5.53 (d, *J*=14.31 Hz, 1 H) 4.69 - 4.81 (m, 3 H) 4.06 - 4.27 (m, 1 H) 3.56 - 3.70 (m, 2 H) 3.19 - 3.29 (m, 2 H) 2.14 - 2.25 (m, 2 H) 2.00 - 2.07 (m, 1 H) 1.89 - 1.98 (m, 1 H) 1.68 - 1.83 (m, 6 H) 1.46 - 1.61 (m, 1 H) 1.24 (t, *J*=6.97 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.80, 148.79, 134.73, 134.56, 125.11, 125.05, 109.21, 109.12, 102.78, 99.83, 78.15, 75.31, 60.99, 60.98, 40.68, 40.50, 35.94, 34.59, 30.82, 30.77, 20.39, 20.37, 19.89, 19.50, 15.20, 15.08, 6.28, 5.56; HRMS (ESI) calculated for $[C_{14}H_{23}O_2I+Na]^+$ = 373.0640, found = 373.0629.

General Procedure for Manganese-Catalyzed Carboacylation Reactions

In a glovebox, the alkyl iodide (1.0 equiv), $KHCO_3$ (1.0 equiv), EtOH (0.2 M), and $Mn_2(CO)_{10}$ (2.5 mol %, unless otherwise noted) were combined in a sealed tube, the cap of which was fitted with a quick-connect adapter (see **Figure 1**). After removing the tube from the glovebox it was purged with 10 atm CO (x 3) and pressurized to 10 atm CO. The reaction was stirred at room temperature for 24 hours in a fume hood with the hood lights on. After 24 hours, the tube was depressurized and 3-5 drops of DBU were added. The reaction was allowed to stir for 1 hour, after which it was diluted with EtOAc and washed with brine. The aqueous layer was then extracted with EtOAc (x3). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The crude mixture was then filtered through a silica plug with 10:1

hexanes:ethyl acetate. The resulting product was purified by flash chromatography with the specified solvent system.

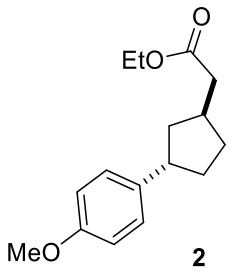
Figure 1. Photos of regulator used to pressurize CO reactions (left) and sealed tubes used to run CO reactions (right) – Each tube gets connected to the regulator via a quick-connect connection at the bottom connection on the regulator (left) and the red top connection on the tube adapter (right).



Product Modification - Oxidation Procedure:

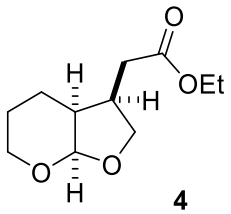
A solution of acetal product (30 mg, 0.12 mmol) in acetone (1.5 mL) was cooled to 0 ˚C. CrO_3 (60 mg, 0.60 mmol) was dissolved in 25% aqueous H_2SO_4 (375 µL) and that solution was added to acetone solution dropwise. The reaction was stirred at 0 ˚C for 2 hours. After completion, Et_2O was added, and the reaction was quenched with iPrOH and neutralized with saturated $NaHCO_3$. The mixture was extracted with Et_2O (x2) and the organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting product was purified by flash chromatography with the specified solvent system.

Table 2 – entries 1-9:



2

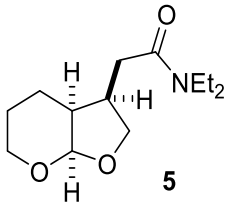
2 was synthesized according to the general procedure using **1** (94.9 mg, 0.30 mmol). The resulting ester was purified by flash chromatography (10:1 Hex:EtOAc) to afford **2** as a mixture of inseparable diastereomers (65.2 mg, 0.25 mmol, 83% yield, 2:1 d.r.) as a yellow oil. The major diastereomer was determined by 2D NMR analysis. Analytical data for **2**: IR (thin film, cm^{-1}) 2946, 2865, 2360, 1732, 1611, 1582, 1512, 1463, 1372, 1246, 1180, 1035, 828, 577, 539; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.17 - 7.09 (m, 2 H), 6.90 - 6.82 (m, 2 H), 4.13 (q, *J* = 7.0 Hz, 2 H), 3.79 (s, 3 H), 3.12 - 3.00 (m, 1 H), 3.05 - 2.99 (m, 1 H), 2.56 (td, *J* = 7.5, 15.0 Hz, 0.8 H), 2.46 - 2.36 (m, 2 H), 2.27 - 2.21 (m, 0.4 H), 2.12 - 1.98 (m, 2 H), 1.88 (m, 0.8 H), 1.77 (m, 0.8 H), 1.70 - 1.57 (m, 1 H), 1.49 - 1.41 (m, 0.4 H), 1.36 - 1.28 (m, 0.8 H), 1.26 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.14, 157.66, 157.61, 138.25, 137.71, 127.76, 113.60, 60.12, 55.18, 44.80, 43.44, 41.83, 41.02, 40.67, 40.06, 36.30, 35.49, 35.05, 33.28, 32.94, 31.47, 14.23; HRMS (ESI) calculated for $[C_{16}H_{22}O_3+H]^+$ = 263.1642, found = 263.1640.



4

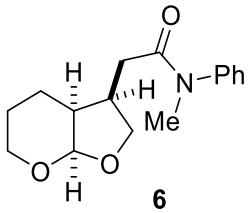
4 was synthesized according to the general procedure using **3** (80.4 mg, 0.30 mmol). The resulting ester was purified by flash chromatography (10:1 followed by 2:1 Hex:EtOAc) to afford **4** as a mixture of inseparable diastereomers (49.2 mg, 0.23 mmol, 77% yield, 10:1 d.r.) as a colorless oil. The major diastereomer was assigned based on 2D NMR analysis. Analytical data for **4**: IR (thin film, cm^{-1}) 2938, 1732, 1371, 1255, 1178, 1146, 1023, 950, 903; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.28 (d, *J* = 3.7 Hz, 0.9 H), 5.00 (d, *J* = 3.3 Hz, 0.1 H), 4.41 (t, J = 8.4 Hz, 0.1 H), 4.13 (q, *J* = 7.3 Hz, 2 H), 4.04 (t, *J* = 8.1 Hz, 0.9 H), 3.77 - 3.59 (m, 2.9 H), 3.42 (dt, *J* = 2.4, 11.6 Hz, 0.1 H), 2.80 - 2.72 (m, 1 H), 2.53 (dd, *J* = 4.8, 15.8 Hz, 0.1 H), 2.45 (dd, *J* = 7.3, 16.1 Hz, 0.9 H), 2.34 (dd, *J* = 8.1, 16.1 Hz, 0.9 H), 2.26 (dd, *J* = 9.7, 16.0 Hz, 0.1 H), 2.10 - 2.05 (m,

1 H), 1.71 - 1.53 (m, 3H), 1.43 - 1.36 (m, 1 H), 1.25 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major: 172.17, 101.67, 69.63, 61.06, 60.55, 36.90, 36.41, 32.59, 22.87, 19.49, 14.13; Minor: 101.59, 73.58, 64.38, 43.61, 37.25, 34.40, 22.14, 20.46; HRMS (ESI) calculated for $[C_{11}H_{18}O_4+Na]^+$ = 237.1098, found = 237.1096.



5

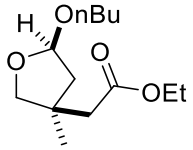
5 was synthesized according to the general procedure using **3** (80.4 mg, 0.30 mmol), 2 equiv $KHCO_3$ (60 mg, 0.60 mmol), and 2 equiv Et_2NH (62 μL, 0.60 mmol). The resulting amide was purified by flash chromatography (1:1 Hex:EtOAc) to afford **5** (48.7 mg, 0.20 mmol, 67% yield, 8:1 d.r.) as a pale orange oil. The major diastereomer was assigned by analogy to **4**. Analytical data for **5**: IR (thin film, cm^{-1}) 3492, 2934, 1638, 1434, 1379, 1251, 1221, 1142, 1100, 1021, 949, 902, 603; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.31 (d, J = 3.7 Hz, 0.85 H), 5.04 (d, J = 3.4 Hz, 0.15 H), 4.50 (t, J = 8.4 Hz, 0.15 H), 4.11 (t, J = 8.2 Hz, 0.85 H), 3.94 - 3.58 (m, 3 H), 3.48 - 3.27 (m, 4 H), 2.93 - 2.72 (m, 1 H), 2.60 (dd, J = 4.6, 15.9 Hz, 0.15 H), 2.51 - 2.43 (m, 0.85 H), 2.40 - 2.26 (m, 1 H), 2.19 (m, 1 H), 1.85 - 1.64 (m, 1 H), 1.63 - 1.56 (m, 2 H), 1.52 - 1.35 (m, 1 H), 1.20 (t, J = 7.2 Hz, 3 H), 1.12 (t, J = 7.1 Hz, 3 H) ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major: 170.17, 101.80, 70.15, 61.13, 41.84, 40.07, 37.02, 36.50, 31.09, 23.03, 19.75, 14.23, 13.00; Minor: 101.49, 74.21, 64.26, 43.58, 36.82, 34.87, 22.50, 20.63; HRMS (ESI) calculated for $[C_{13}H_{23}NO_3+H]^+$ = 242.1751, found = 242.1749.



6

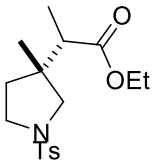
6 was synthesized according to the general procedure using **3** (80.4 mg, 0.30 mmol), 2 equiv $KHCO_3$ (60 mg, 0.60 mmol), and 2 equiv N-methylaniline (65 μL, 0.60 mmol). The resulting amide was purified by flash chromatography (1:1 Hex:EtOAc) to afford **6** (60.1 mg, 0.22 mmol, 73% yield, 10:1 d.r.) as a white solid. The major diastereomer was assigned by analogy to **4**. Analytical data for **6**: IR (thin film, cm^{-1}) 3503, 2938, 1655, 1594, 1495, 1421, 1390, 1293, 1251, 1205, 1144, 1020, 948, 903, 870, 776, 702, 649, 562, 523; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.46 (t, J = 7.8 Hz, 2 H), 7.41 - 7.36 (m, 1 H), 7.19 (d, J = 8.3 Hz, 2 H), 5.28 (d, J = 3.7 Hz, 0.9 H),

4.93 (d, *J* = 3.2 Hz, 0.1 H), 4.44 (t, *J* = 8.7 Hz, 0.1 H), 4.01 (t, *J* = 8.3 Hz, 0.9 H), 3.90 - 3.85 (m, 0.1 H), 3.75 - 3.53 (m, 2.9 H), 3.28 (s, 3 H), 2.92 - 2.65 (m, *J* = 8.8 Hz, 1 H), 2.27 - 2.00 (m, 3 H), 1.56 - 1.41 (m, 3 H), 1.30 - 1.16 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ =Major: 171.20, 143.67, 129.85, 127.94, 127.09, 101.63, 69.70, 60.87, 37.21, 37.17, 36.18, 32.11, 22.86, 19.41; Minor: 171.47, 143.74, 127.24, 101.38, 73.93, 64.21, 43.32, 37.53, 36.26, 34.93, 29.60, 22.22, 20.49; HRMS (ESI) calculated for $[C_{16}H_{21}NO_3+H]^+$ = 276.1594, found = 276.1593.



8

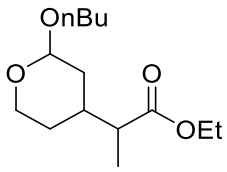
8 was synthesized according to the general procedure using **7** (89.5 mg, 0.30 mmol) and 5 mol % $Mn_2(CO)_{10}$ (5.8 mg, 0.015 mmol). The resulting ester was purified by flash chromatography (20:1 Hex:EtOAc) to afford **8** as a mixture of inseparable diastereomers (55.2 mg, 0.23 mmol, 77% yield, 8:1 d.r.) as a yellow oil. The major diastereomer was assigned based on 2D NMR analysis. Analytical data for **8**: IR (thin film, cm^{-1}) 2960, 2872, 1733, 1460, 1369, 1344, 1204, 1096, 1033, 931, 580; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.13 (dd, *J* = 2.8, 5.7 Hz, 0.89 H), 5.12 - 5.10 (m, 0.11 H), 4.12 (q, *J* = 7.3 Hz, 2 H), 3.80 (d, *J* = 8.8 Hz, 1 H), 3.70 - 3.62 (m, 2 H), 3.36 (td, *J* = 6.6, 9.5 Hz, 1 H), 2.50 (s, 1.8 H), 2.36 - 2.33 (m, 0.2 H), 1.96 (dd, *J* = 5.5, 13.6 Hz, 1 H), 1.83 (dd, *J* = 2.9, 13.6 Hz, 1 H), 1.57 - 1.50 (m, 2 H), 1.39 - 1.31 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.14 (s, 3 H), 0.90 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major: 171.79, 104.34, 77. 11, 67.49, 60.22, 46.27, 44.43, 40.50, 31.76, 24.97, 19.32, 14.20, 13.84; Minor: 104.50, 76.66, 64.20, 63.13, 45.69, 44.44, 41.24, 30.59, 23.61, 19.15, 15.23, 13.66; HRMS (ESI) calculated for $[C_{13}H_{24}O_4+Na]^+$ = 267.1567, found = 267.1564.



10

10 was synthesized according to the general procedure using **9** (118 mg, 0.30 mmol) and 5 mol % $Mn_2(CO)_{10}$ (5.8 mg, 0.015 mmol). The resulting ester was purified by flash chromatography (2:1 Hex:EtOAc) to afford **10** as a mixture of inseparable diastereomers (80.4 mg, 0.24 mmol, 79% yield, 1:1 d.r.) as a pale orange oil. Analytical data for **10**: IR (thin film, $cm^{-1)}$ 2977, 2880, 1727, 1597, 1453, 1344, 1192, 1159, 1094, 1058, 860, 816, 731, 709, 663, 593, 548; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 3.1, 8.3 Hz, 2 H), 7.32 (dd, *J* = 1.5, 8.4 Hz, 2 H), 4.14 - 4.05 (m, 2 H), 3.39 - 3.34 (m, 1 H), 3.27 - 3.21 (m, 1 H), 3.21 - 3.14 (m, 1 H), 3.04 (s, 1 H), 2.43 (s, 3

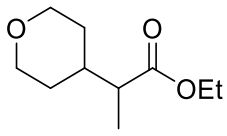
H), 2.35 - 2.31 (m, 1 H), 1.83 (td, *J* = 9.2, 12.8 Hz, 0.5 H), 1.64 - 1.55 (m, 1.5 H), 1.22 (dt, *J* = 7.1, 18.2 Hz, 3 H), 1.07 – 1.06 (d, *J* = 4.4 Hz, 3 H), 0.84 (s, 1.5 H), 0.78 (s, 1.5 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.18, 174.03, 143.37, 143.29, 133.72, 133.56, 129.56, 129.54, 127.36, 60.35, 60.26, 58.66, 58.02, 46.92, 46.55, 46.14, 43.78, 43.74, 36.68, 36.53, 21.46, 19.97, 19.46, 14.16, 14.14, 12.94, 12.56; HRMS (ESI) calculated for $[C_{17}H_{25}NO_4S+H]^+$ = 340.1577, found = 340.1575.



12

12 was synthesized according to the general procedure using **11** (93.7 mg, 0.30 mmol) and 5 mol % $Mn_2(CO)_{10}$ (5.8 mg, 0.015 mmol). The resulting ester was purified by flash chromatography (20:1 Hex:EtOAc) to afford **12** as a complex mixture of diastereomers (49.3 mg, 0.19 mmol, 64% yield) as a colorless oil. Analytical data for **12**: IR (thin film, cm^{-1}) 2958, 2935, 2874, 2360, 1733, 1461, 1374, 1342, 1246, 1176, 1129, 1073, 985, 892, 851, 812; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.83 (dd, *J* = 2.9, 9.3 Hz, 0.75 H), 4.38 - 4.34 (m, 0.25 H), 4.20 - 4.11 (m, 2 H), 4.10 - 4.00 (m, 0.25 H), 3.90 - 3.75 (m, 1 H), 3.70 - 3.58 (m, 1.5 H), 3.50 - 3.41 (m, 0.5 H), 3.41 - 3.33 (m, 0.75 H), 2.34 - 2.26 (m, 0.25 H), 2.26 - 2.13 (m, 1.5 H), 1.92 - 1.86 (m, 0.25 H), 1.83 - 1.76 (m, 0.25 H), 1.69 - 1.49 (m, 4 H), 1.47 - 1.32 (m, 4 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.20 - 1.11 (m, 3 H), 0.98 - 0.90 (m, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 175.83, 175.80, 175.77, 175.68, 101.72, 101.63, 96.65, 68.74, 66.76, 66.73, 64.99, 64.78, 60.34, 60.31, 60.17, 59.31, 59.23, 45.22, 44.79, 44.74, 44.72, 37.25, 37.18, 36.23, 34.88, 34.85, 34.48, 33.97, 32.39, 32.16, 31.86, 31.85, 31.77, 31.61, 29.91, 29.88, 28.91, 28.42, 22.68, 19.49, 19.32, 19.29, 18. 91, 14.33, 14.31, 14.30, 14.27, 14.07, 14.04, 14.03, 13.96, 13.92, 13.44; HRMS (ESI) calculated for $[C_{14}H_{26}O_4+Na]^+$ = 281.1724, found = 281.1722.

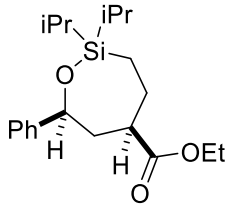
Reduced product:



SI-5

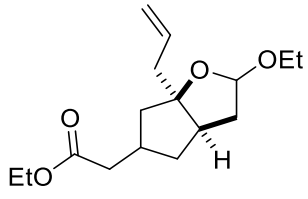
SI-5 was synthesized by dissolving **12** (25 mg, 0.10 mmol) in DCM (2.5 mL) at -30 ˚C and adding Et_3SiH (16 µL, 0.10 mmol) and BF_3•OEt_2 (7.7 µL, 0.03 mmol). The reaction was warmed to -10 ˚C and stirred for 4 hours. An additional 16 µL of Et_3SiH was then added and the mixture

stirred overnight at room temperature and then concentrated. The resulting tetrahydropyran was purified by flash chromatography (5:1 Hex:EtOAc) to afford **SI-5** (11.7 mg, 0.062 mmol, 64% yield) as a colorless oil. Analytical data for **SI-5**: IR (thin film, cm^{-1}) 2931, 1732, 1453, 1176, 1093; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.15 (q, *J* = 7.1 Hz, 2 H), 4.05 - 3.93 (m, 2 H), 3.48 - 3.33 (m, 2 H), 2.27 (quin, *J* = 7.3 Hz, 1 H), 1.85 - 1.73 (m, 1 H), 1.71 - 1.57 (m, 1 H), 1.57 - 1.48 (m, 1 H), 1.47 - 1.31 (m, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.15 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 175.88, 67.95, 67.85, 60.17, 45.09, 38.00, 30.95, 29.73, 14.26, 13.90; HRMS (ESI) calculated for $[C_{10}H_{18}O_3+H]^+$ = 187.1329, found = 187.1327.



14

14 was synthesized according to the general procedure using **13**[3] (120.7 mg, 0.30 mmol) and 5 mol % $Mn_2(CO)_{10}$ (5.8 mg, 0.015 mmol). The resulting ester was purified by flash chromatography (hexanes, then 2:1 Hex:EtOAc) to afford **14** (81.4 mg, 0.23 mmol, 78% yield, 3:1 d.r.) as colorless oil. The major diastereomer was assigned based on 2D NMR analysis. Analytical data for **14**: IR (thin film, cm^{-1}) 2939, 2864, 2360, 1730, 1462, 1369, 1306, 1236, 1159, 1095, 1067, 1037, 884, 797, 737, 698; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.0 Hz, 0.5 H), 7.39 (d, *J* = 7.3 Hz, 1.5 H), 7.32 (t, *J* = 7.5 Hz, 2.25 H), 7.25 - 7.22 (m, 0.75 H), 5.25 (d, *J* = 7.3 Hz, 0.25 H), 4.85 (d, *J* = 9.9 Hz, 0.75 H), 4.20 - 4.16 (m, 0.5 H), 4.11 - 4.05 (m, 1.5 H), 2.76 - 2.71 (m, 0.25 H), 2.50 - 2.45 (m, 0.75 H), 2.35 - 2.16 (m, 2 H), 2.03 - 1.76 (m, 2 H), 1.29 (t, *J* = 7.2 Hz, 0.75 H), 1.22 (t, *J* = 7.2 Hz, 2.25 H), 1.12 - 1.00 (m, 8 H), 0.99 - 0.94 (m, 6.5 H), 0.91 - 0.79 (m, 1.5 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major: 176.02, 145.86, 128.07, 127.99, 126.84, 125.22, 125.14, 75.62, 60.40, 49.26, 45.05, 26.86, 17.88, 17.76, 17.64, 17.42, 13.49, 9.61; Minor: 175.54, 145.79, 128.20, 126.95, 126.49, 126.40, 125.19, 60.34, 60.24, 45.56, 42.49, 41.80, 24.71, 17.85, 17.67, 17.51, 14.32, 12.87, 7.17; HRMS (ESI) calculated for $[C_{20}H_{32}O_3Si+Na]^+$ = 371.2013, found = 371.2009.

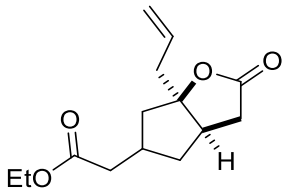


16

16 was synthesized according to the general procedure using **15** (100.9 mg, 0.30 mmol) and 5 mol % $Mn_2(CO)_{10}$ (5.8 mg, 0.015 mmol). The resulting ester was purified by flash

chromatography (10:1 Hex:EtOAc) to afford **16** (65.4 mg, 0.23 mmol, 77% yield) as a pale yellow oil. **16** was formed in 1.5:1 d.r. with respect to cyclization/carbonylation. This ratio was determined by analysis of oxidized product **SI-6** (see below). Analytical data for **16**: IR (thin film, cm^{-1}) 3074, 2976, 2938, 1735, 1640, 1443, 1374, 1339, 1242, 1159, 1101, 1002, 916; ^1H NMR (400 MHz ,$CDCl_3$) δ = 5.95 - 5.73 (m, 1 H), 5.22 - 5.03 (m, 3 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.83 - 3.65 (m, 1 H), 3.44 - 3.32 (m, 1 H), 2.63 - 2.48 (m, 1 H), 2.45 - 2.19 (m, 5 H), 2.17 - 2.02 (m, 2 H), 1.96 - 1.70 (m, 2 H), 1.68 - 1.57 (m, 1 H), 1.47 - 1.32 (m, 1 H), 1.27 - 1.14 (m, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.99, 172.97, 172.82, 172.79, 135.02, 134.71, 134.10, 117.82, 117.45, 117.39, 117.26, 106.20, 105.93, 104.63, 104.40, 96.19, 95.10, 94.95, 94.93, 62.77, 62.44, 62.05, 60.21, 60.19, 60.16, 60.06, 46.68, 46.24, 46.23, 45.35, 45.28, 45.26, 45.16, 45.07, 44.65, 44.27, 44.08, 43.69, 41.42, 41.07, 40.48, 40.23, 39.99, 39.91, 39.83, 39.80, 39.63, 39.49, 38.94, 38.40, 37.14, 36.78, 33.74, 33.63, 15.17, 15.08, 15.02, 14.21; HRMS (ESI) calculated for $[C_{16}H_{26}O_4+Na]^+$ = 305.1724, found = 305.1720.

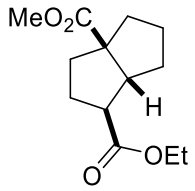
Oxidized product:



SI-6

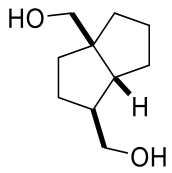
SI-6 was synthesized according to the general oxidation procedure using **16** (30 mg, 0.11 mmol). The resulting lactone was purified by flash chromatography (2:1 Hex:EtOAc) to afford **SI-6** as a mixture of inseparable diastereomers (25 mg, 0.10 mmol, 90% yield, 1.5:1 d.r.) as a colorless oil. The d.r. is determined to reflect a cis ring junction and a mixture of diastereomers at the final cyclization/carbonylation center. Analytical data for **SI-6**: IR (thin film, cm^{-1}) 3525, 2935, 1771, 1731, 1641, 1418, 1378, 1206, 1156, 1028, 979, 926; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.81 - 5.73 (m, 1 H), 5.20 - 5.15 (m, 2 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 2.87 - 2.81 (m, 0.65 H), 2.74 - 2.64 (m, 1 H), 2.56 - 2.45 (m, 2 H), 2.43 - 2.19 (m, 6 H), 1.77 (dd, *J* = 6.2, 13.2 Hz, 0.65 H), 1.71 - 1.55 (m, 1.35 H), 1.34 (dd, *J* = 12.1, 13.6 Hz, 0.65 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.20 - 1.12 (m, 0.35 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 177.02, 176.58, 172.34, 172.12, 131.87, 131.53, 120.20, 119.84, 96.56, 95.58, 60.46, 44.07, 44.00, 43.78, 43.21, 42.22, 40.76, 40.47, 39.98, 38.86, 38.65, 37.29, 35.56, 35.25, 33.85, 14.20; HRMS (ESI) calculated for $[C_{14}H_{20}O_4+H]^+$ = 253.1434, found = 253.1433.

Table 3 (entries 1-4):



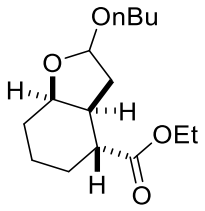
18

18 was synthesized according to the general procedure using **17** (88.2 mg, 0.30 mmol). The resulting ester was purified by flash chromatography (10:1 Hex:EtOAc) to afford **18** (64.2 mg, 0.27 mmol, 89% yield, 7:1 d.r.) as a colorless oil. The major diastereomer was determined by 2D NMR analysis of reduced product **SI-7** (see below). Analytical data for **18**: IR (thin film, cm^{-1}) 2953, 2870, 1730, 1451, 1375, 1271, 1230, 1164, 1038; ^{1}H NMR (600 MHz, C_6D_6) δ = 3.98 - 3.92 (m, 2 H), 3.32 - 3.29 (m, 3 H), 3.29 - 3.24 (m, 0.88 H), 3.14 - 3.08 (m, 0.12 H), 2.88 - 2.83 (m, 0.12 H), 2.50 (ddd, *J* = 3.5, 6.5, 12.7 Hz, 0.88 H), 2.37 - 2.31 (m, 0.12 H), 2.26 - 2.21 (m, 0.88 H), 2.10 - 1.94 (m, 2 H), 1.79 - 1.73 (m, 2 H), 1.55 - 1.44 (m, 2 H), 1.41 - 1.29 (m, 2 H), 1.19 - 1.14 (m, 1 H), 0.98 - 0.92 (m, 3 H); ^{13}C NMR (151 MHz, C_6D_6) δ = Major: 177.41, 173.99, 59.87, 59.82, 52.80, 51.67, 51.26, 38.24, 36.90, 33.01, 30.54, 25.50, 13.93; Minor: 177.33, 172.54, 59.58, 59.37, 51.22, 50.69, 48.26, 38.67, 36.03, 30.01, 26.97, 26.91, 14.02; HRMS (ESI) calculated for $[C_{13}H_{20}O_4+Na]^+$ = 263.1254; found = 263.1254.



SI-7

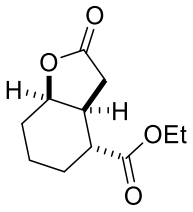
SI-7 was made from **18** (12 mg, 0.05 mmol), added dropwise to a slurry of $LiAlH_4$ (5 mg, 0.13 mmol) in Et_2O (600 μL) at 0 ˚C. The reaction was warmed to room temperature and stirred overnight. It was quenched with water and 10% NaOH, extracted with Et_2O, dried over $MgSO_4$, and concentrated in vacuo. The resulting diol was purified by flash chromatography (1:2 Hex:EtOAc) to afford **SI-7** (0.05 mmol, quantitative yield) as a colorless oil. The major diastereomer was determined by 2D NMR analysis. Analytical data for **SI-7**: IR (thin film, cm^{-1}) 3326, 2934, 2856, 1466, 1034, 527; ^{1}H NMR (600 MHz, C_6D_6) δ = 3.44 - 3.36 (m, 2 H), 3.26 - 3.20 (m, 2 H), 1.84 - 1.78 (m, 1 H), 1.73 (dt, *J* = 3.1, 7.4 Hz, 1 H), 1.68 - 1.61 (m, 1 H), 1.61 - 1.56 (m, 1 H), 1.54 - 1.46 (m, 3 H), 1.41 - 1.26 (m, 5 H), 1.20 (ddd, *J* = 6.6, 9.8, 12.6 Hz, 2 H); ^{13}C NMR (151 MHz, C_6D_6) δ = 69.58, 65.87, 55.95, 50.33, 48.53, 37.05, 35.87, 33.44, 29.30, 25.51; HRMS (ESI) calculated for $[C_{10}H_{18}O_2+H]^+$ = 171.1380, found = 171.1378.



20

20 was synthesized according to the general procedure using **19** (97.3 mg, 0.30 mmol). The resulting ester was purified by flash chromatography (10:1 Hex:EtOAc) to afford **20** (73.2 mg, 0.27 mmol, 90% yield) as a pale orange oil. **20** was formed in 7:1 d.r. with respect to cyclization/carbonylation. This ratio was determined by analysis of oxidized product **SI-8** (see below). The assignment of the major diastereomer was based on analogy to similar radical cyclizations.[1,8,9] Analytical data for **20**: IR (thin film, cm^{-1}) 2937, 2868, 1730, 1450, 1375, 1292, 1256, 1175, 1094, 1069, 1027, 909; ^1H NMR (400MHz, C_6D_6) δ = 5.19 - 5.03 (m, 1 H), 4.21 - 4.08 (m, 2.5 H), 4.08 - 4.03 (m, 0.5 H), 3.77 - 3.63 (m, 1 H), 3.43 - 3.31 (m, 1 H), 2.84 (m, 1 H), 2.30 - 2.21 (m, 1 H), 2.18 - 2.10 (m, 1 H), 2.08 - 1.82 (m, 3 H), 1.63 - 1.47 (m, 5 H), 1.42 - 1.29 (m, 3 H), 1.28 - 1.21 (m, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (151 MHz, C_6D_6) δ = Major: 176.01, 175.57, 103.71, 103.17, 77.56, 74.39, 67.94, 67.55, 60.31, 60.16, 45.06, 43.02, 39.67, 39.33, 38.85, 37.53, 31.73, 28.10, 27.99, 27.89, 26.80, 19.41, 19.39, 19.34, 19.28, 14.19, 14.17, 13.81, 13.79; Minor: 174.21, 173.89, 102.91, 77.94, 68.11, 66.98, 60.30, 60.24, 41.65, 39.28, 36.35, 32.16, 31.83, 31.68, 29.21, 29.08, 22.09, 21.92, 20.92, 19.29, 13.77; HRMS (ESI) calculated for $[C_{15}H_{26}O_4+Na]^+$ = 293.1724, found = 293.1721.

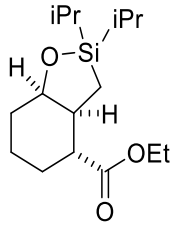
Oxidized product:



SI-8

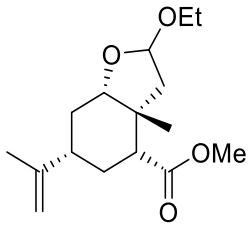
SI-8 was synthesized according to the general oxidation procedure using **20** (30 mg, 0.11 mmol). The resulting lactone was purified by flash chromatography (2:1 Hex:EtOAc) to afford **SI-8** as a mixture of inseparable diastereomers (18 mg, 0.08 mmol, 77% yield, 7:1 d.r.) as a colorless oil. Analytical data for **SI-8**: IR (thin film, cm^{-1}) 2938, 1778, 1727, 1297, 1155, 559; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.59 (q, *J* = 3.5 Hz, 0.88 H), 4.57 - 4.53 (m, 0.12 H), 4.17 - 4.12 (m, 2 H), 3.11 - 3.03 (m, 0.12 H), 2.70 (dd, *J* = 6.8, 17.1 Hz, 0.88 H), 2.66 - 2.61 (m, 0.88 H), 2.52 - 2.45 (m, 0.12 H), 2.41 - 2.35 (m, 1 H), 2.26 - 2.19 (m, 1.76 H), 2.17 - 2.11 (m, 0.12 H), 2.00 - 1.95 (m, 0.88 H), 1.93 - 1.87 (m, 0.12 H), 1.87 - 1.80 (m, 0.12 H), 1.68 - 1.57 (m, 2 H), 1.54 - 1.47 (m, 1 H), 1.41 - 1.34 (m, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major:

176.62, 174.18, 78.51, 60.89, 43.59, 37.37, 37.15, 26.90, 26.86, 18.81, 14.15; Minor: 176.09, 172.78, 42.08, 36.22, 28.69, 28.32, 21.93, 21.07; HRMS (ESI) calculated for $[C_{11}H_{16}O_4+H]^+$ = 213.1121, found = 213.1120.



22

22 was synthesized according to the general procedure using **21** (105.7 mg, 0.30 mmol). The resulting ester was purified by flash chromatography (10:1 Hex:EtOAc) to afford **22** (64.7 mg, 0.22 mmol, 72% yield, 9:1 d.r.) as a colorless oil. The assignment of the major diastereomer was based on analogy to similar radical cyclizations.[1,8,9] Analytical data for **22**: IR (thin film, cm^{-1}) 2938, 2864, 1732, 1463, 1372, 1288, 1243, 1164, 1141, 1068, 1035, 977, 906, 882, 832, 792, 714, 613; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.22 - 4.06 (m, 2 H), 4.06 - 3.97 (m, 0.9 H), 3.78 - 3.75 (m, 0.1 H), 2.72 - 2.65 (m, 0.1 H), 2.65 - 2.59 (m, 0.1 H), 2.36 - 2.25 (m, 1.8 H), 2.04 - 1.87 (m, 1 H), 1.85 - 1.70 (m, 1 H), 1.61 - 1.42 (m, 4 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.12 - 0.97 (m, 15 H), 0.95 - 0.88 (m, 1 H), 0.64 (dd, *J* = 1.8, 15.0 Hz, 0.9 H), 0.48 - 0.44 (m, 0.1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = Major: 175.90, 75.88, 60.14, 45.49, 39.35, 30.63, 28.00, 19.13, 17.95, 17.84, 17.46, 17.32, 14.24, 13.02, 12.99, 11.68; Minor: 174.21, 77.49, 60.04, 44.80, 39.78, 30.90, 22.58, 21.20, 17.69, 17.45, 17.35, 14.29, 13.06, 12.77, 4.21; HRMS (ESI) calculated for $[C_{16}H_{30}O_3Si+H]^+$ = 299.2037, found = 299.2035.

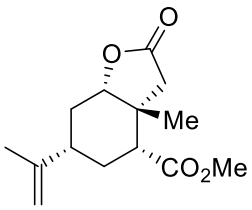


24

24 was synthesized according to the general procedure using **23** (105 mg, 0.30 mmol) and 10 mol% $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol) in MeOH (2.3 mL) instead of EtOH. The resulting ester was purified by flash chromatography (10:1 Hex:EtOAc) to afford **24** (56.6 mg, 0.20 mmol, 67% yield) as colorless oil. **24** was formed in 3:1 d.r. with respect to cyclization/carbonylation. This ratio was determined by analysis of oxidized product **SI-9** (see below). The major diastereomer was determined via 2D NMR analysis of the oxidized product **SI-9**. Analytical data for **24**: IR (thin film, cm^{-1}) 2948, 1734, 1647, 1437, 1375, 1192, 1115, 1003, 891; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.26 - 5.17 (m, 0.8 H), 5.10 (dd, *J* = 2.1, 5.7 Hz, 0.2 H), 4.77 - 4.71 (m, 2 H), 3.98

(dd, *J* = 6.2, 10.4 Hz, 0.2 H), 3.91 - 3.72 (m, 1.6 H), 3.72 - 3.65 (m, 3.2 H), 3.53 - 3.43 (m, 1 H), 2.97 (t, *J* = 5.1 Hz, 0.2 H), 2.65 - 2.45 (m, 1.2 H), 2.39 - 2.33 (m, 0.2 H), 2.21 (dd, *J* = 5.4, 13.7 Hz, 0.4 H), 2.00 - 1.84 (m, 2.4 H), 1.81 - 1.57 (m, 6.6 H), 1.29 - 1.16 (m, 5.4 H), 1.10 (s, 0.6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ =175.03, 174.94, 174.35, 174.17, 148.56, 148.17, 148.06, 109.31, 109.29, 108.88, 108.83, 104.86, 103.81, 103.52, 102.37, 85.39, 84.48, 82.85, 63.74, 63.61, 63.51, 62.87, 51.48, 51.47, 51.41, 51.38, 50.32, 46.29, 46.01, 44.91, 43.50, 43.21, 41.97, 41.92, 41.73, 41.01, 40.89, 38.92, 38.38, 36.90, 35.87, 35.78, 35.69, 34.21, 30.36, 30.30, 30.22, 30.14, 28.37, 27.50, 27.24, 26.79, 24.40, 21.73, 21.20, 21.05, 20.79, 20.77, 15.32, 15.25; HRMS (ESI) calculated for $[C_{16}H_{26}O_4+Na]^+$ = 305.1724, found = 305.1725.

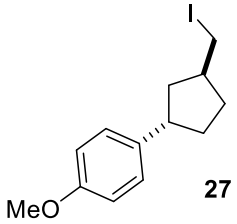
Oxidized product:



SI-9

SI-9 was synthesized according to the general oxidation procedure using **24** (30 mg, 0.106 mmol). The resulting lactone was purified by flash chromatography (2:1 Hex:EtOAc) to afford **SI-9** as a mixture of inseparable diastereomers (11.4 mg, 0.045 mmol, 43% yield, 3:1 d.r.) as a colorless oil. The major diastereomer was assigned by 2D NMR analysis. Analytical data for **SI-9**: IR (thin film, cm^{-1}) 2950, 1779, 1732, 1646, 1437, 1364, 1267, 1231, 1194, 1158, 1067, 998, 894, 836; ^{1}H NMR (400 MHz, C_6D_6) δ = 4.65 (t, *J* = 25.7 Hz, 1 H), 4.51 (s, 1 H), 4.10 (dd, *J* = 5.9, 9.5 Hz, 0.3 H), 3.44 (dd, *J* = 6.2, 11.0 Hz, 0.7 H), 3.20 (s, 2.1 H), 3.16 (s, 0.9 H), 2.58 (d, 0.7 H), 2.35 (t, *J* = 5.3 Hz, 0.3 H), 2.26 (d, *J* = 16.9 Hz, 0.3 H), 2.10 (d, *J* = 17.6 Hz, 0.7 H), 1.99 (dd, *J* = 3.9, 12.7 Hz, 0.7 H), 1.87 - 1.74 (m, 1 H), 1.63 (d, *J* = 17.2 Hz, 0.3 H), 1.56 - 1.48 (m, 1 H), 1.45 (s, 0.9 H), 1.39 (s, 2.1 H), 1.33 (ddd, *J* = 4.4, 9.5, 14.3 Hz, 0.7 H), 1.28 - 1.15 (m, 1 H), 1.13 - 1.06 (m, 0.3 H), 0.88 - 0.87 (m, 2.1 H), 0.87 - 0.83 (m, 0.9 H), 0.82 - 0.81 (m, 1 H); ^{13}C NMR (151 MHz, C_6D_6) δ = Major: 174.80, 172.72, 147.05, 110.06, 83.78, 51.14, 49.41, 40.14, 39.87, 36.13, 35.11, 30.31, 26.24, 20.55; Minor: 174.20, 173.58, 109.91, 82.93, 51.04, 45.23, 39.92, 39.30, 35.94, 33.03, 27.92, 22.67, 21.04; HRMS (ESI) calculated for $[C_{14}H_{20}O_4+H]^+$ = 253.1434, found = 253.1437.

Scheme 1:



27

27 was synthesized according to the general procedure using **1** (189.7 mg, 0.60 mmol) and $KHCO_3$ (60 mg, 0.60 mmol), with no CO pressure and benzene (4.6 mL) instead of EtOH. The resulting ester was purified by flash chromatography (hexanes) to afford **27** as a mixture of inseparable diastereomers (173 mg, 0.55 mmol, 90% yield, 3:1 d.r.) as a pale yellow oil. The major diastereomer was assigned by analogy to **2**. Analytical data for **27**: IR (thin film, cm^{-1}) 2947, 2859, 2360, 1611, 1511, 1460, 1245, 1178, 1036, 828, 585, 537; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.19 - 7.08 (m, 2 H), 6.90 - 6.84 (m, 2 H), 3.81 (s, 3 H), 3.35 - 3.25 (m, 2 H), 3.14 (d, *J* = 7.1 Hz, 1 H), 2.54 - 2.45 (m, 0.75 H), 2.39 - 2.28 (m, 0.5 H), 2.21 - 2.08 (m, 1.75 H), 1.93 - 1.84 (m, 1.5 H), 1.79 - 1.64 (m, 1 H), 1.60 - 1.51 (m, 0.5 H), 1.45 - 1.30 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.76, 157.70, 137.66, 137.18, 127.78, 127.74, 113.64, 55.22, 45.29, 43.72, 42.80, 42.21, 41.64, 40.99, 35.26, 34.05, 33.59, 32.36, 14.93, 14.22; LR GC/MS calculated for $[C_{13}H_{17}OI]^+$ = 316.0324, found = 316.

References

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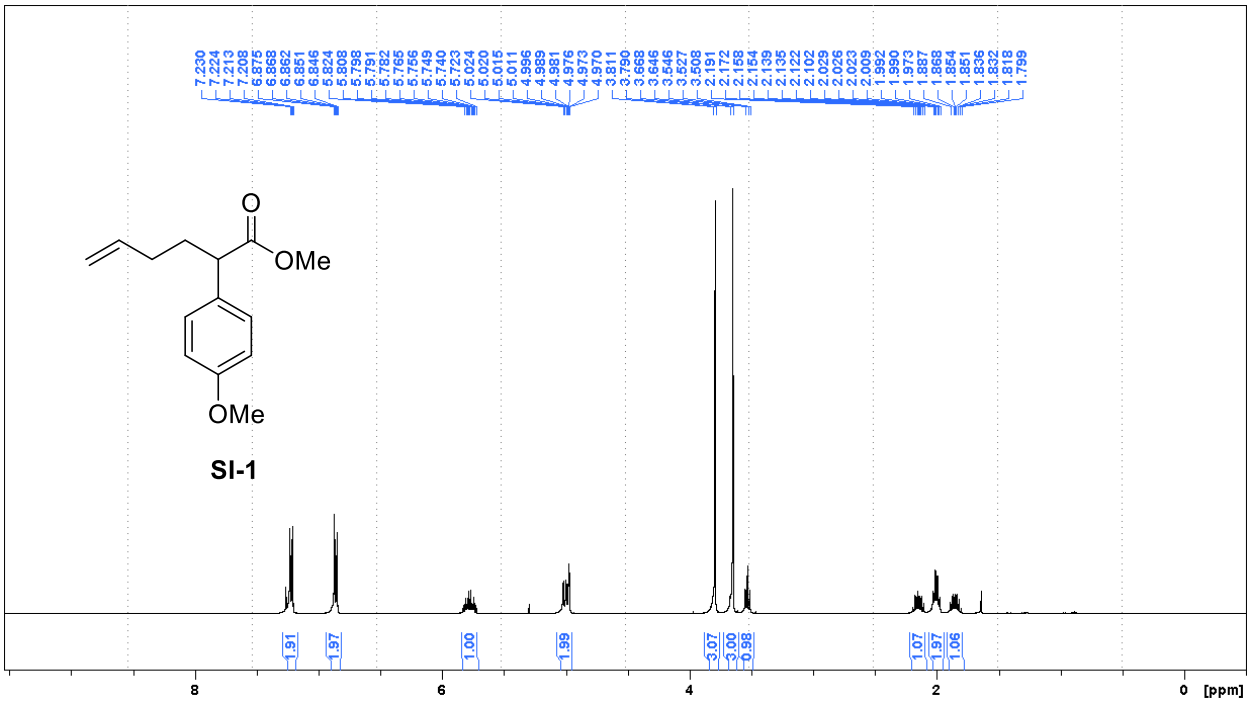
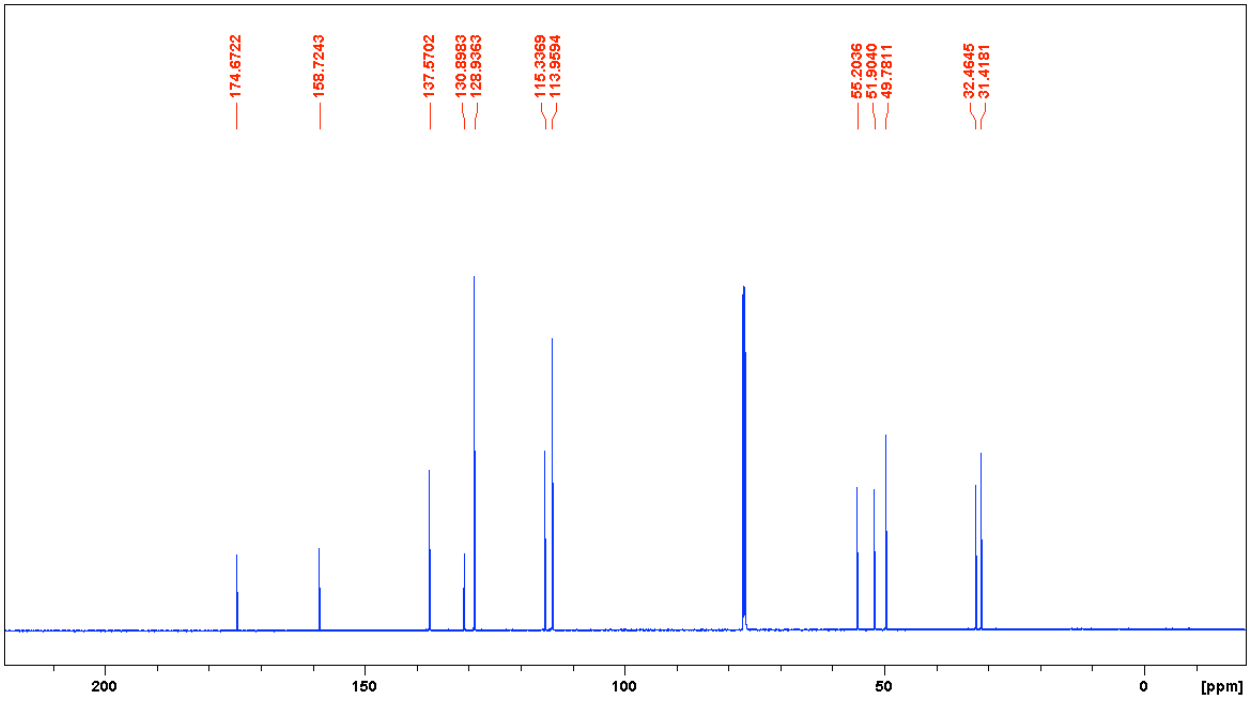
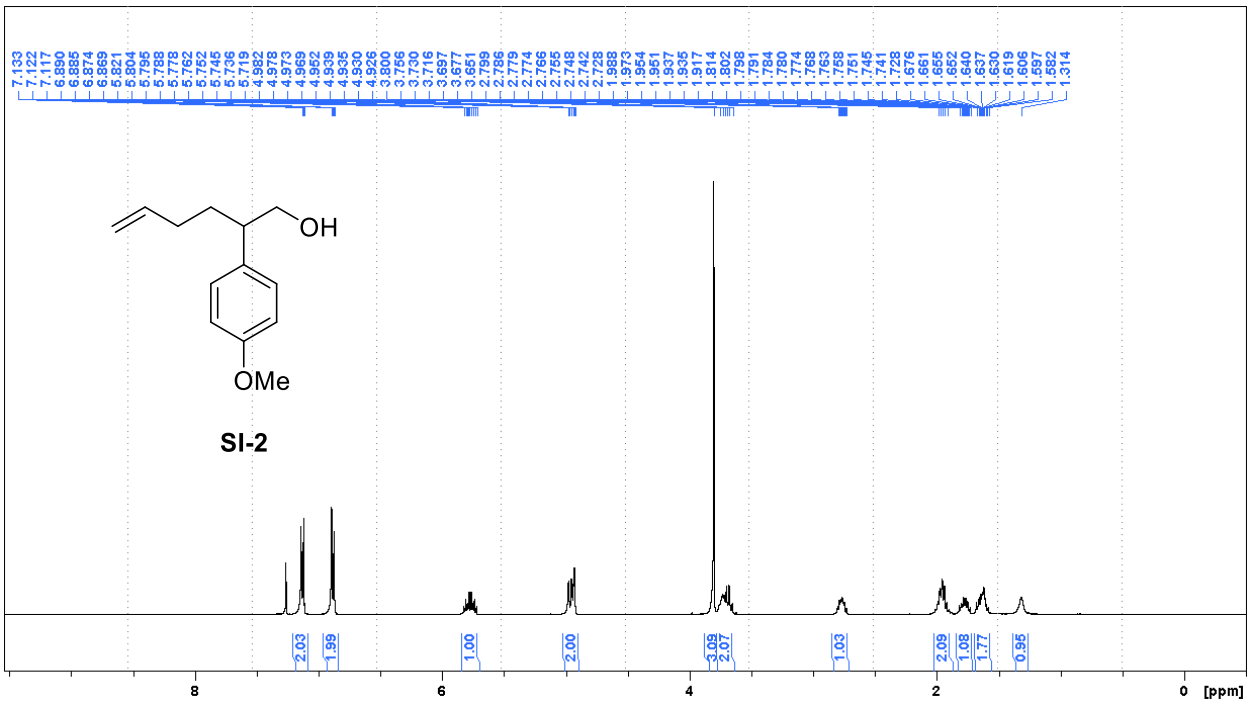
Substrate Spectra:



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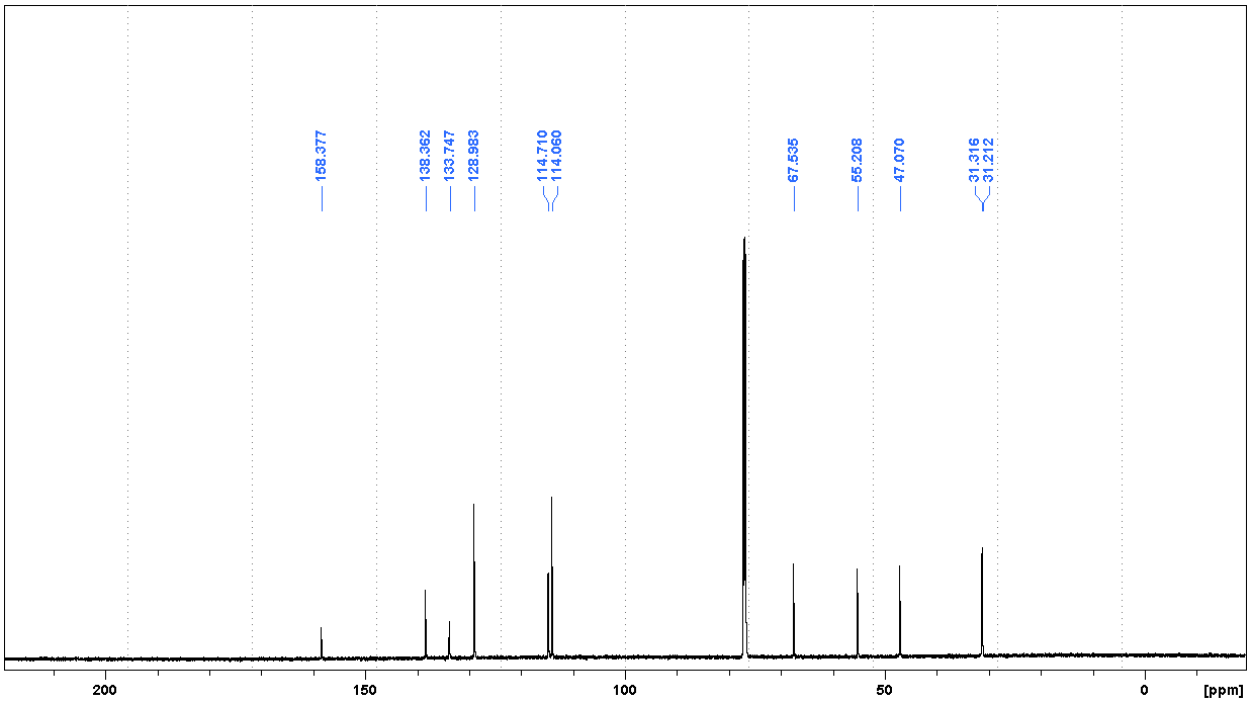
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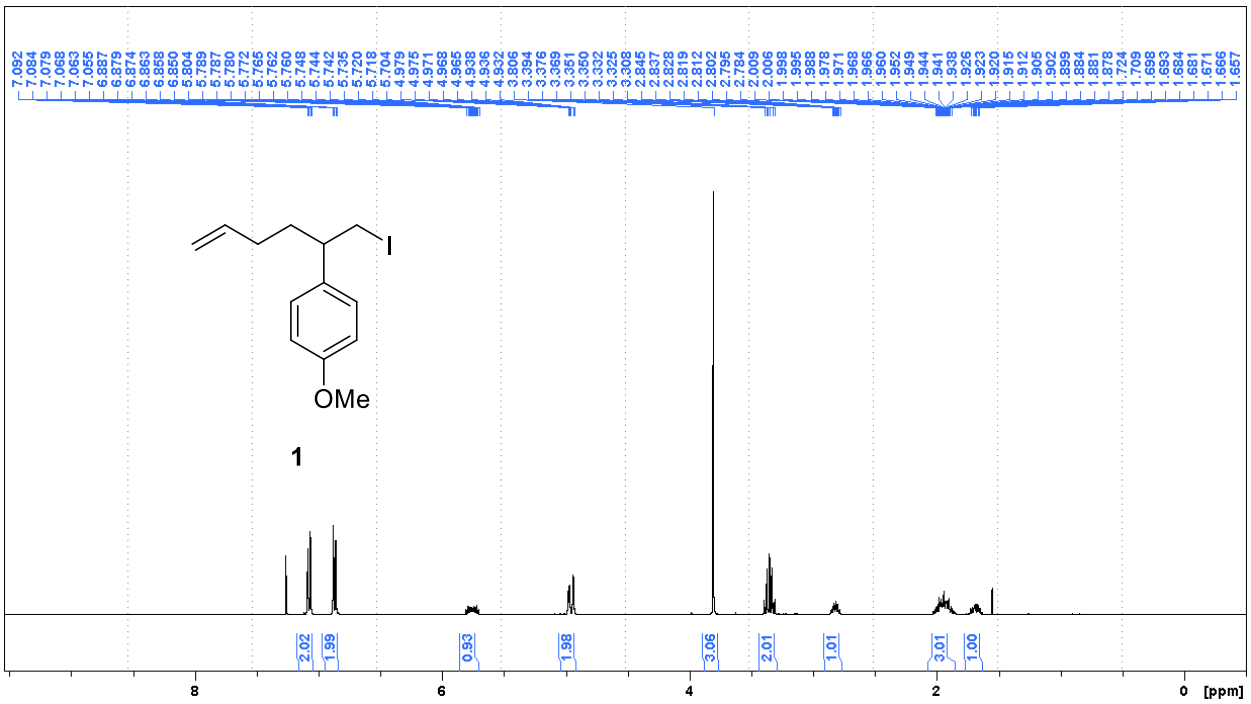
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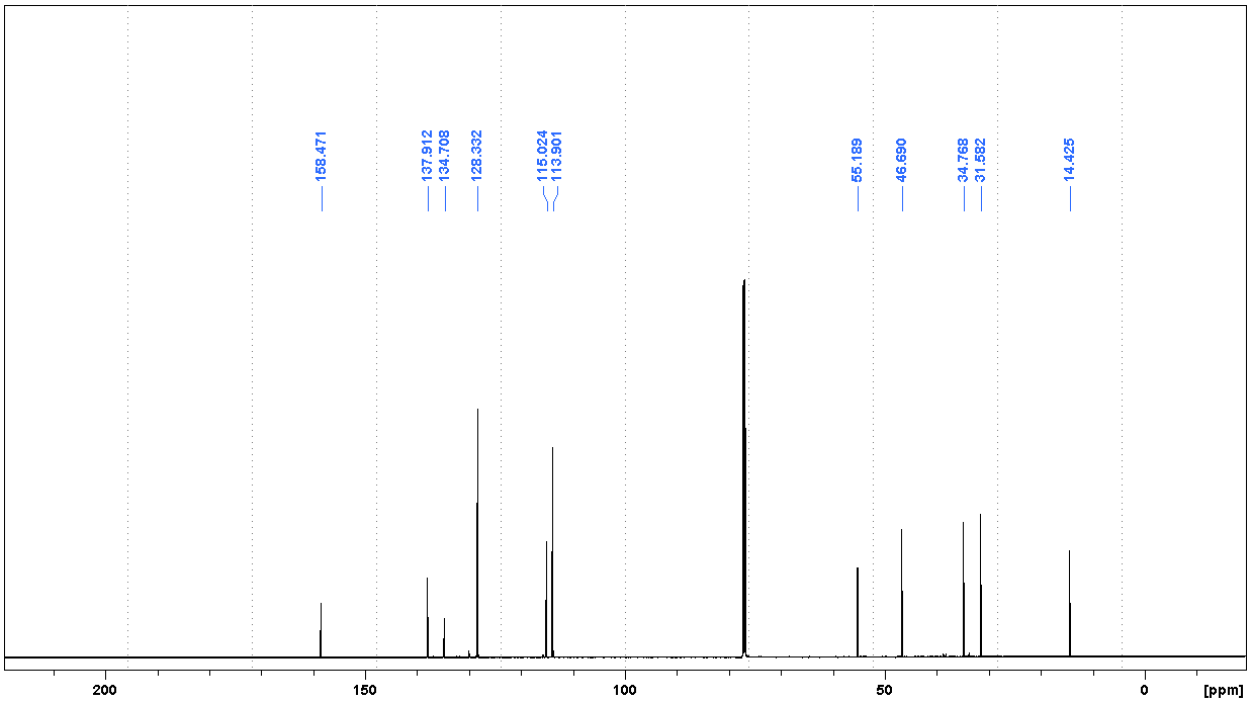
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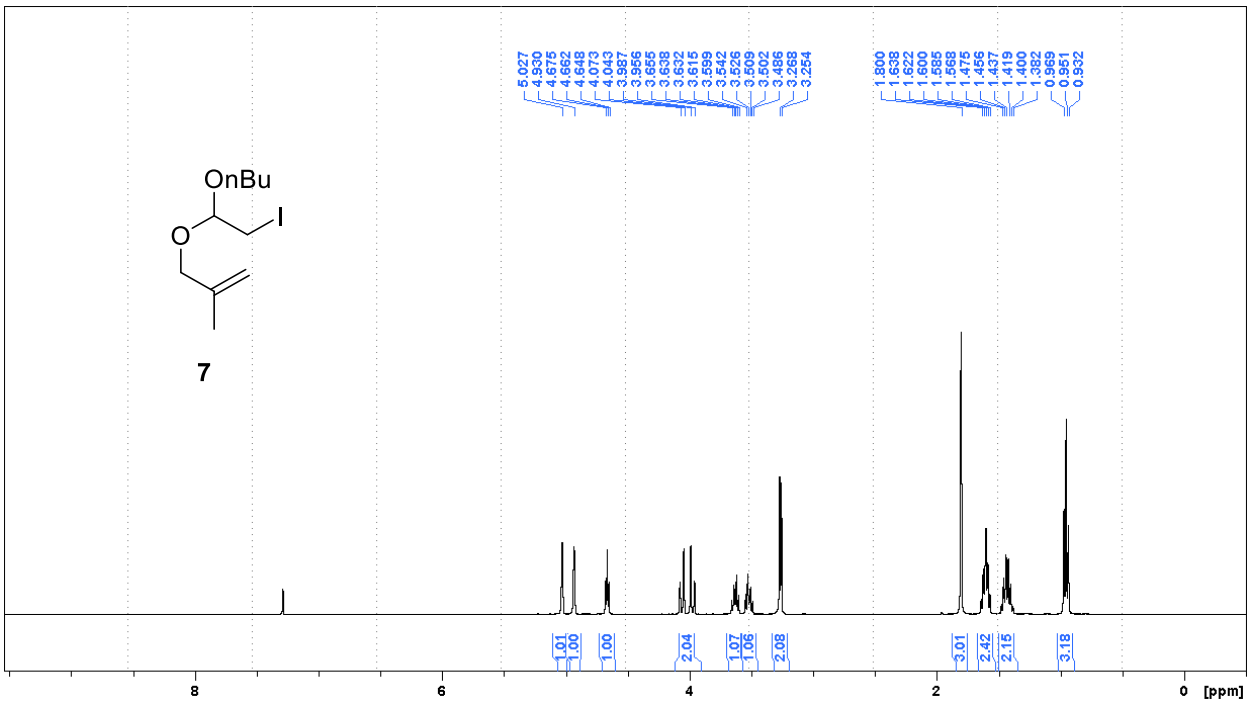
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0.932
1.01
1.00
1.00
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1.07
1.06
2.08
3.01
2.42
2.15
3.18
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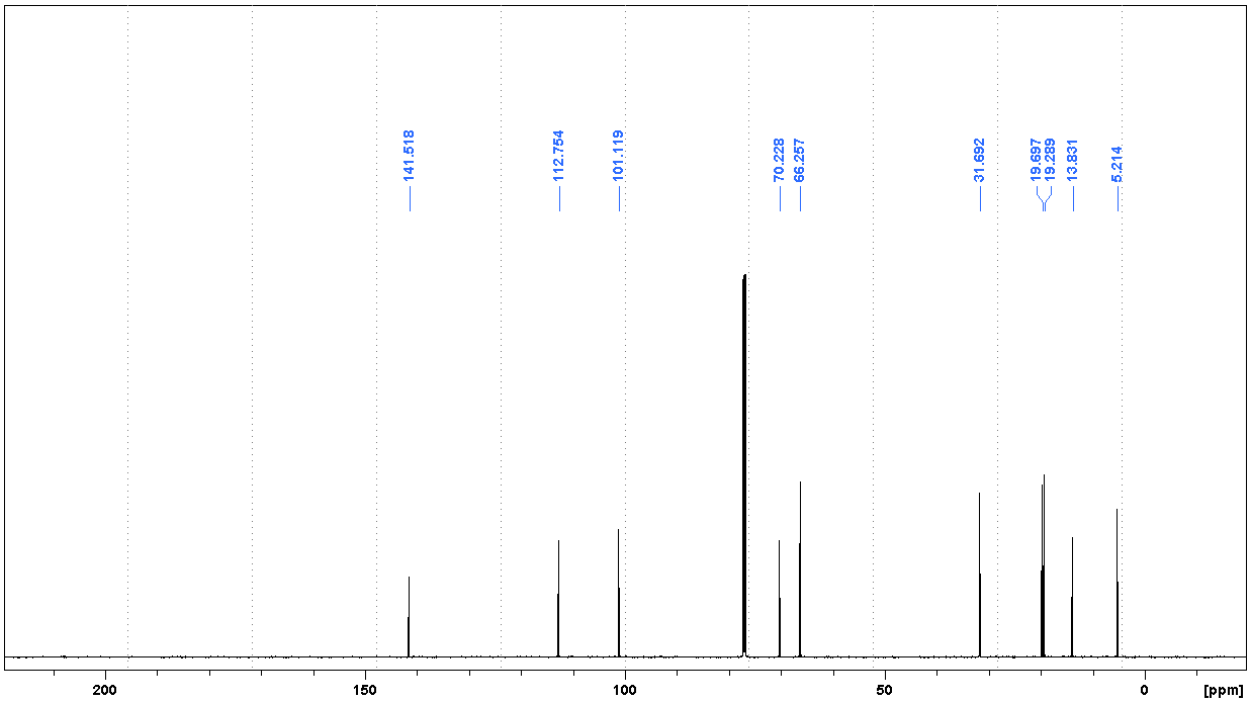
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19.697
19.289
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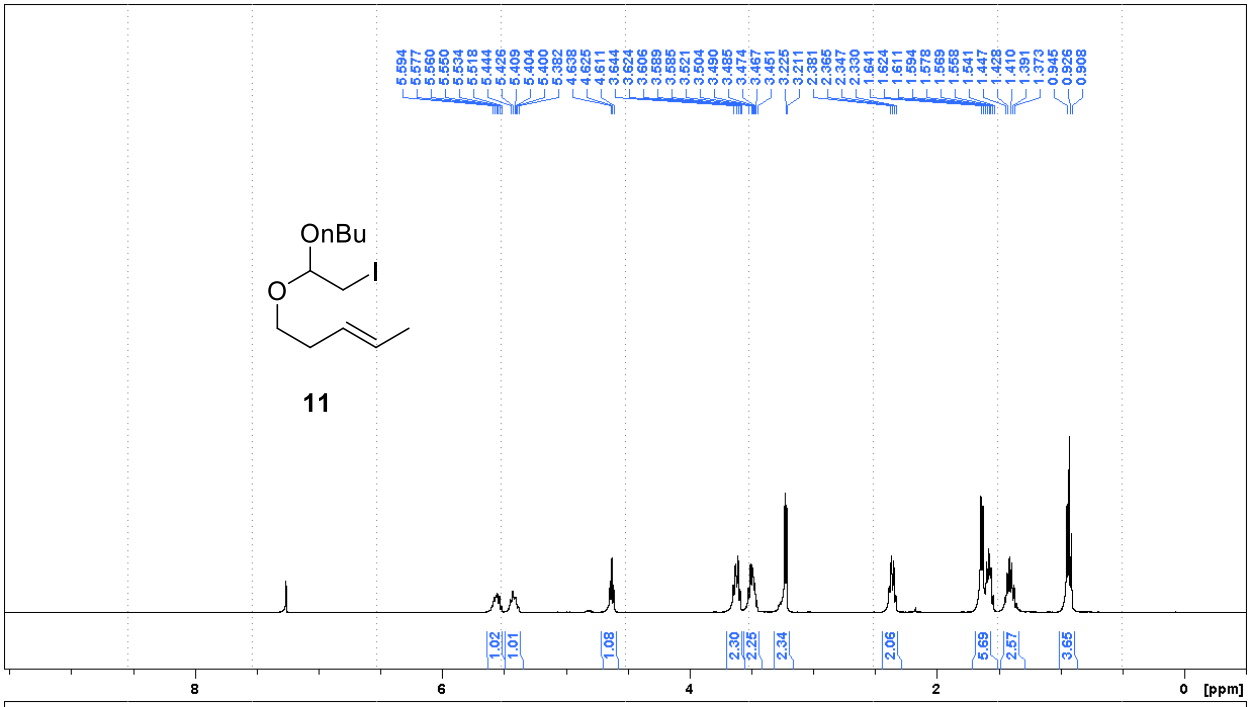
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5.382
4.638
4.625
4.611
3.644
3.624
3.606
3.589
3.585
3.521
3.504
3.490
3.485
3.474
3.467
3.451
3.225
3.211
2.381
2.365
2.347
2.330
1.641
1.624
1.611
1.594
1.578
1.569
1.558
1.541
1.447
1.428
1.410
1.391
1.373
0.945
0.926
0.908
OnBu
O
I
11
1.02
1.01
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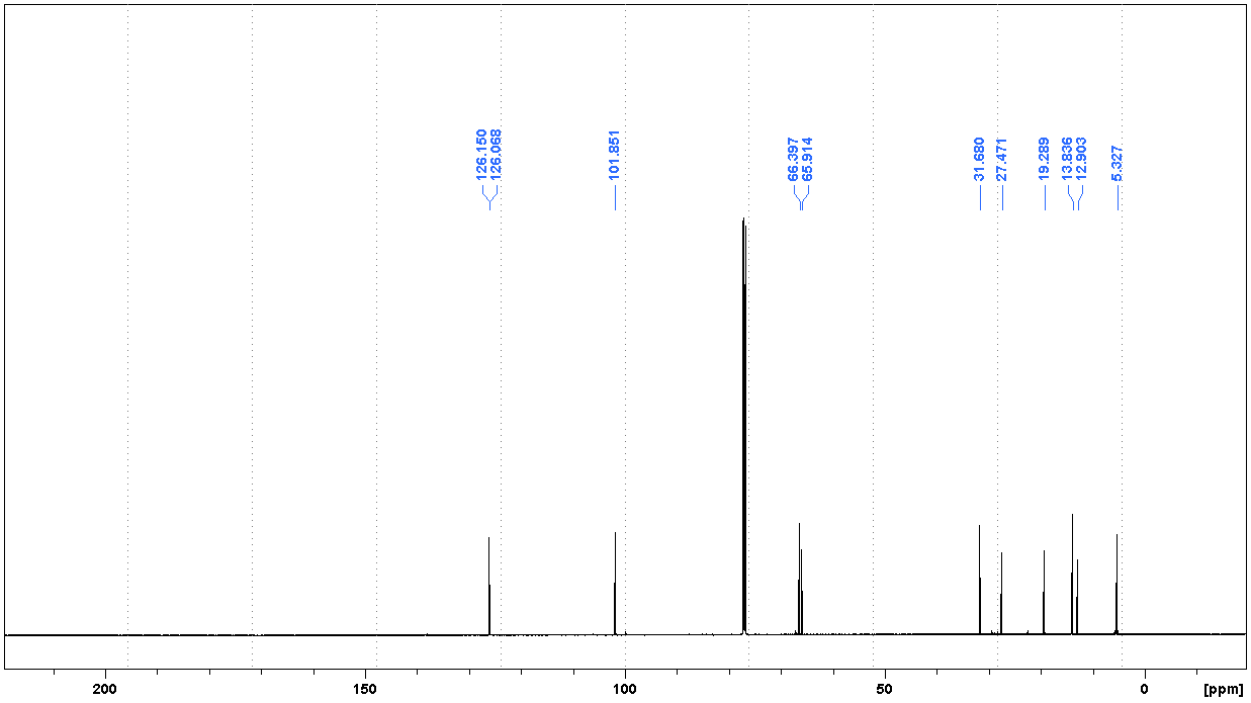
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101.851
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19.289
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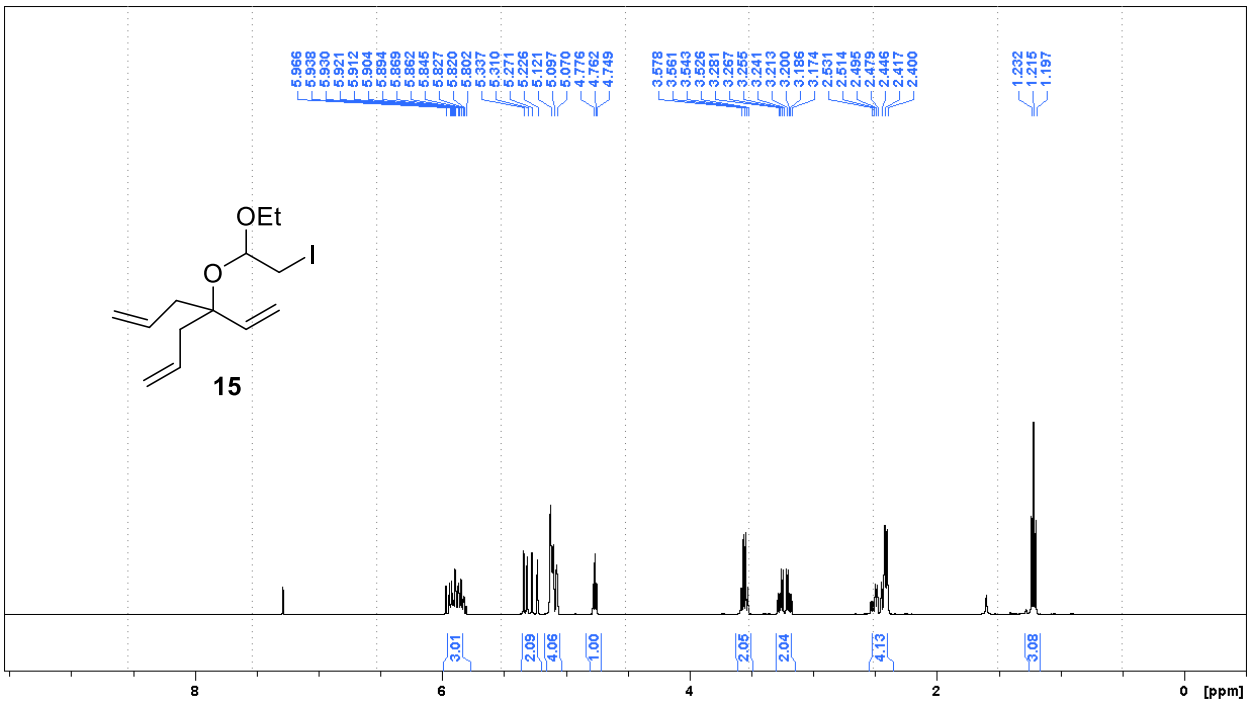
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5.827
5.820
5.802
5.337
5.310
5.271
5.226
5.121
5.057
5.070
4.776
4.762
4.749
3.578
3.561
3.543
3.526
3.281
3.267
3.255
3.241
3.213
3.200
3.186
3.174
2.531
2.514
2.495
2.479
2.446
2.417
2.400
1.232
1.215
1.197
OEt
O
I
15
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1.00
2.05
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3.08
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2
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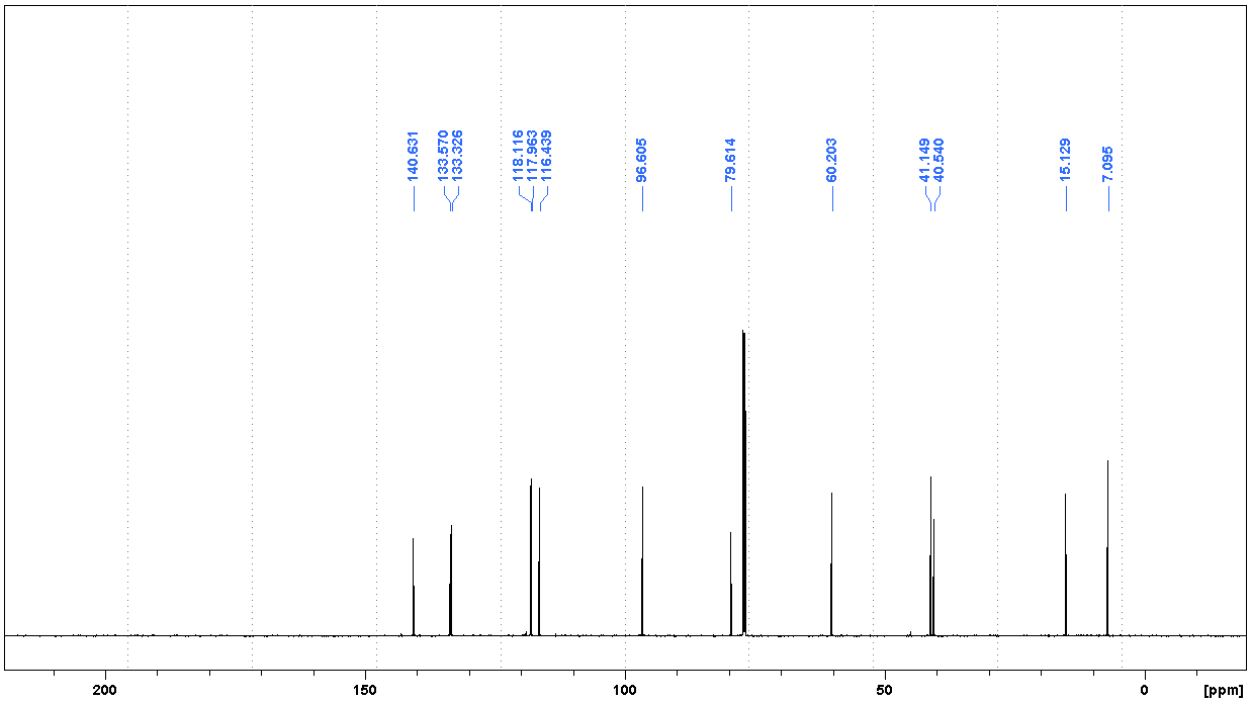
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133.326
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79.614
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41.149
40.540
15.129
7.095
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50
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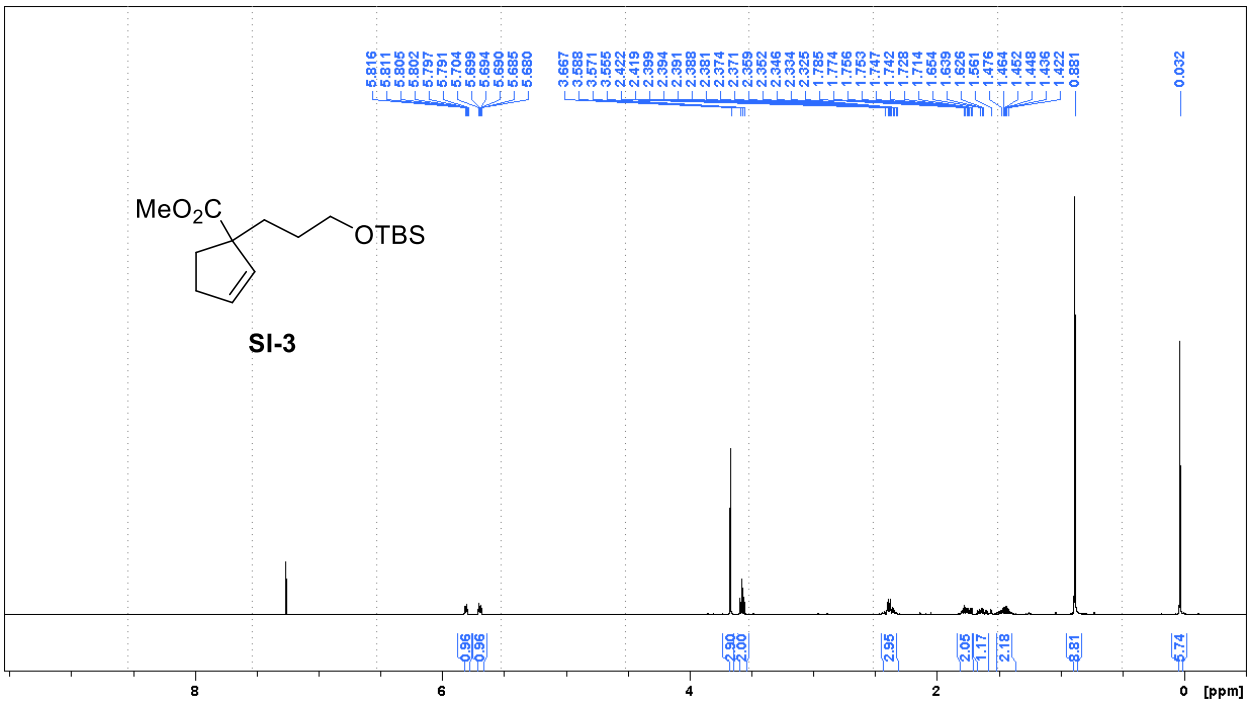
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5.699
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5.690
5.685
5.680
3.667
3.588
3.571
3.555
2.422
2.419
2.399
2.394
2.391
2.388
2.381
2.374
2.371
2.359
2.352
2.346
2.334
2.325
1.785
1.774
1.756
1.753
1.747
1.742
1.728
1.714
1.654
1.639
1.626
1.561
1.476
1.464
1.452
1.448
1.436
1.422
0.881
0.032
MeO2C
OTBS
SI-3
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0.96
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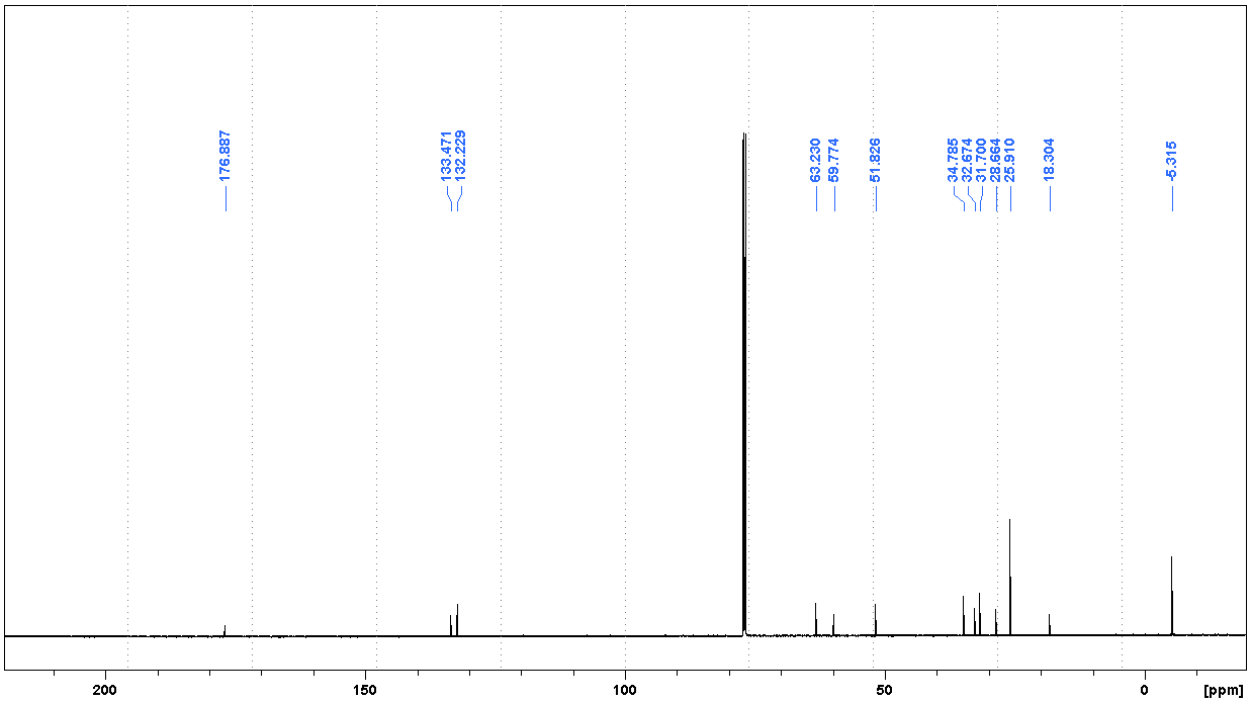
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63.230
59.774
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34.785
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25.910
18.304
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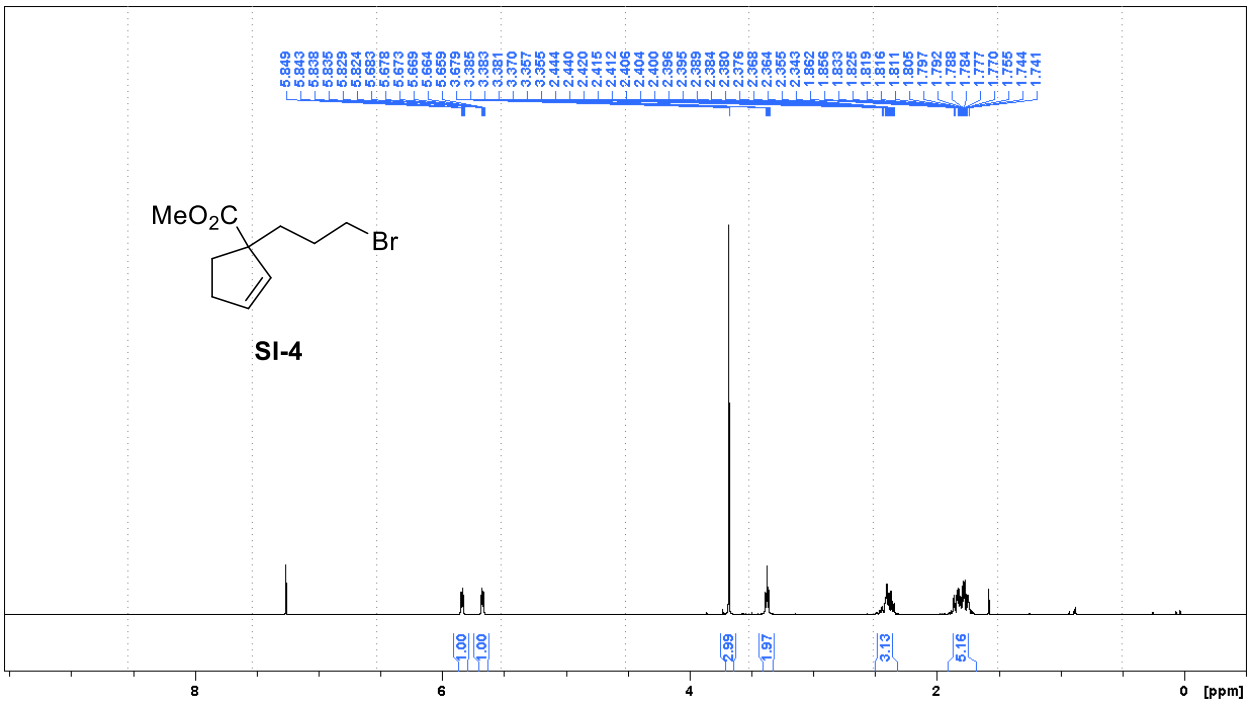
100
50
0
[ppm]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5.824
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5.673
5.669
5.664
5.659
3.679
3.385
3.383
3.381
3.370
3.357
3.355
2.444
2.440
2.420
2.415
2.412
2.406
2.404
2.400
2.396
2.395
2.389
2.384
2.380
2.376
2.368
2.364
2.355
2.343
1.862
1.856
1.833
1.825
1.819
1.816
1.811
1.805
1.797
1.792
1.788
1.784
1.777
1.770
1.755
1.744
1.741
MeO2C
Br
SI-4
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4
2
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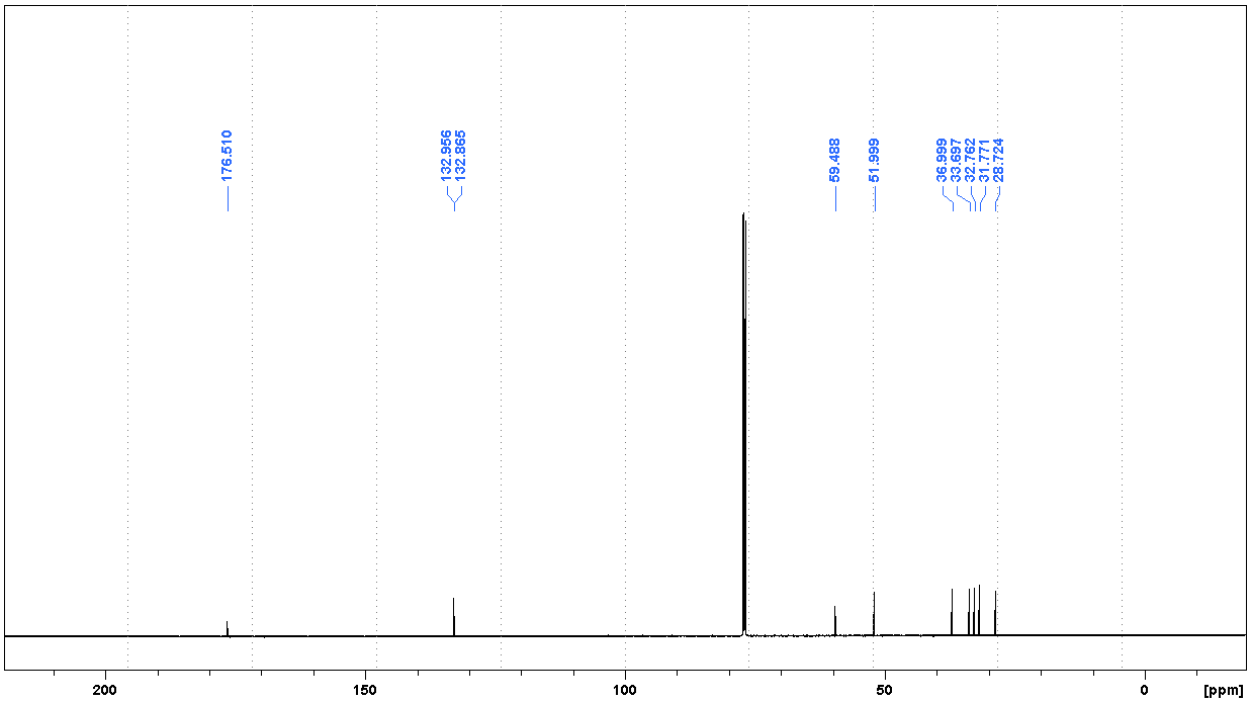
[ppm]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32.762
31.771
28.724
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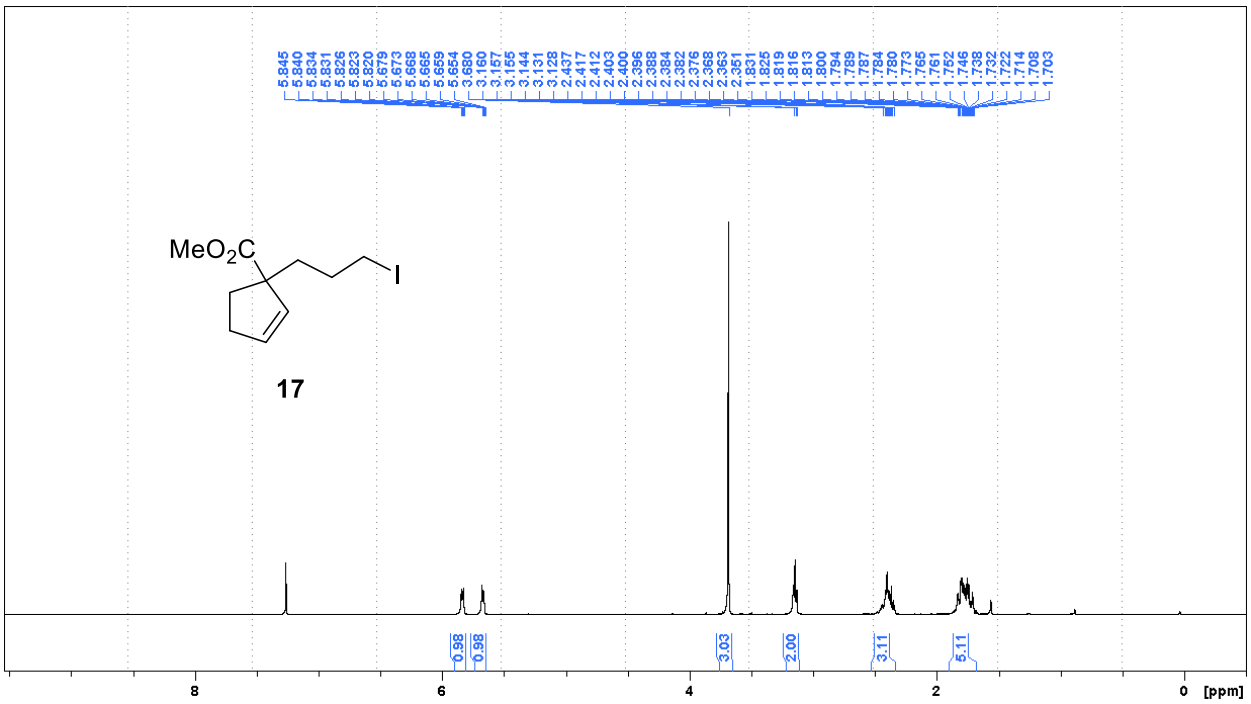
150
100
50
0
[ppm]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5.831
5.826
5.823
5.820
5.679
5.673
5.668
5.665
5.659
5.654
3.160
3.157
3.155
3.144
3.131
3.128
2.437
2.417
2.412
2.403
2.400
2.396
2.388
2.384
2.382
2.376
2.368
2.363
2.351
1.831
1.825
1.819
1.816
1.813
1.800
1.794
1.789
1.787
1.784
1.780
1.773
1.765
1.761
1.752
1.746
1.738
1.732
1.722
1.714
1.708
1.703
MeO2C
I
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0.98
0.98
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2.00
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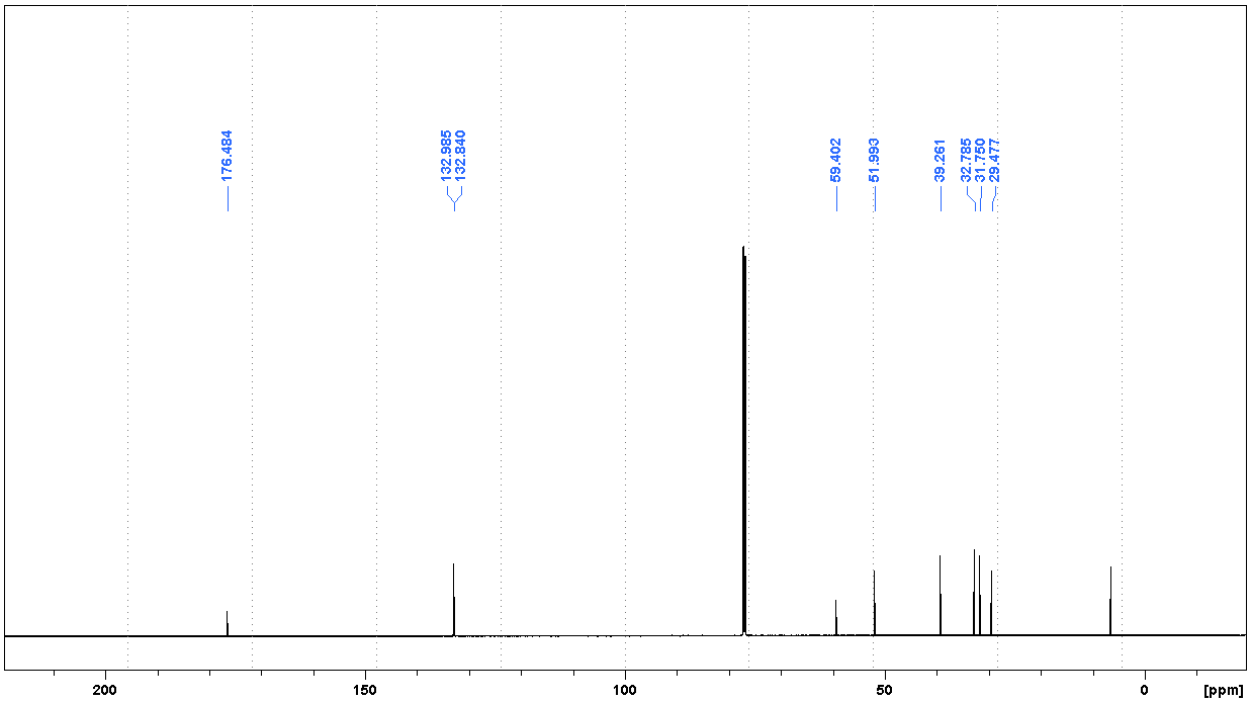
5.11
8
6
4
2
0
[ppm]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31.750
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100
50
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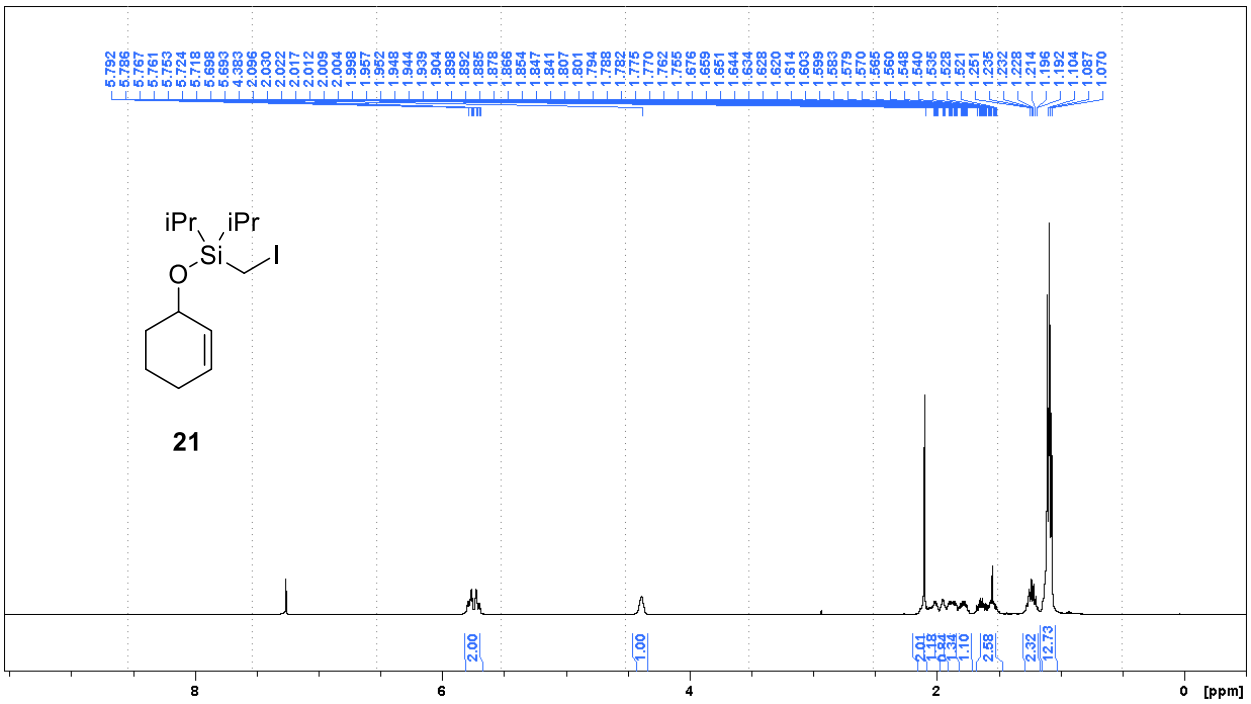
iPr
iPr
Si
O
I
21
8
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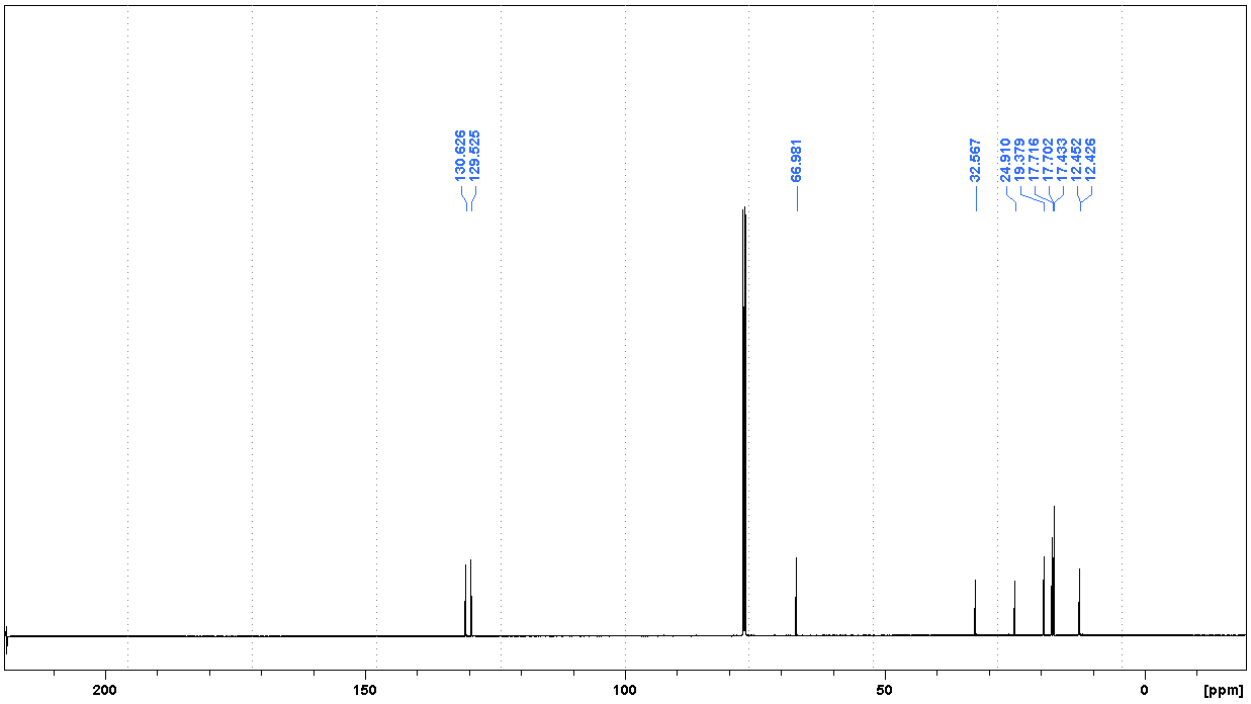
4
2
0
[ppm]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129.525
66.981
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24.910
19.379
17.716
17.702
17.433
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12.426
200
150
100
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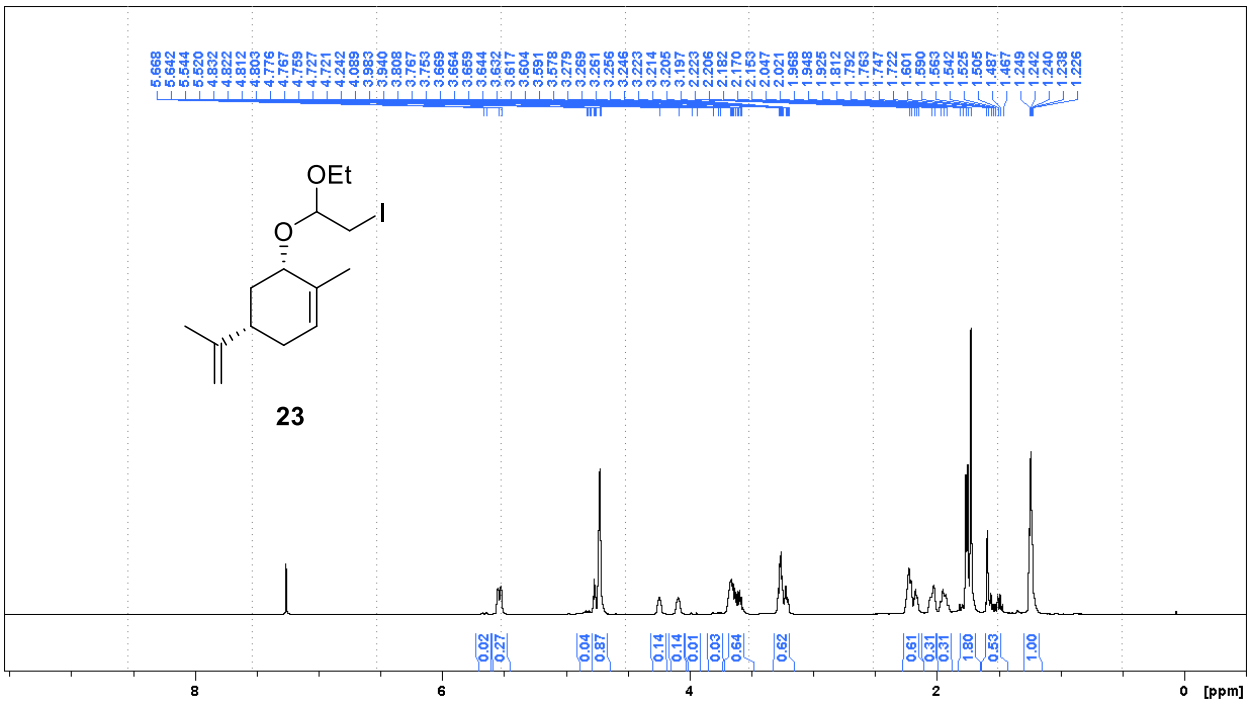
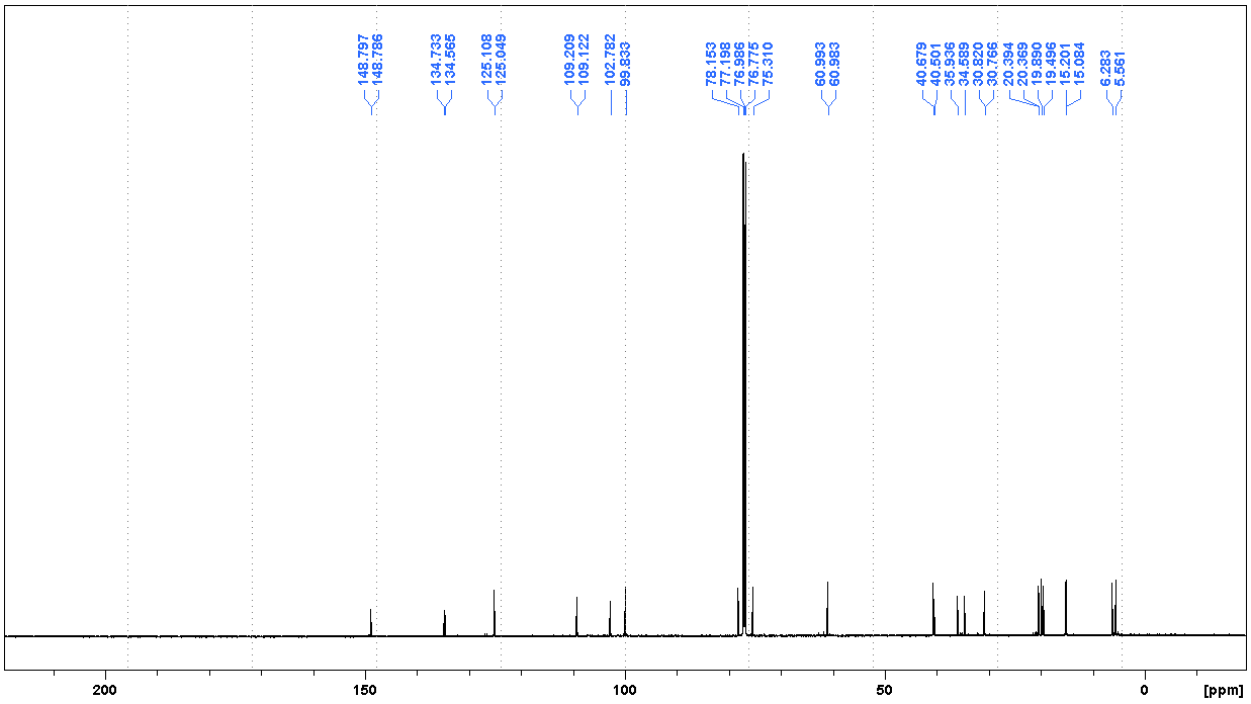
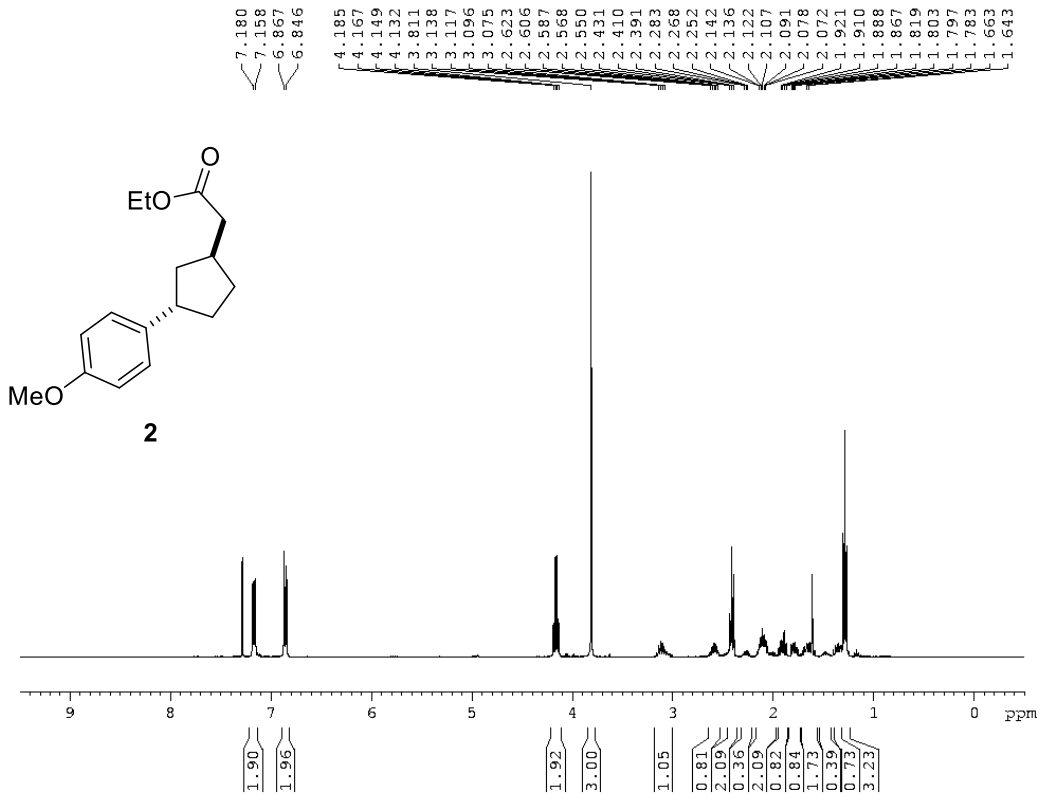
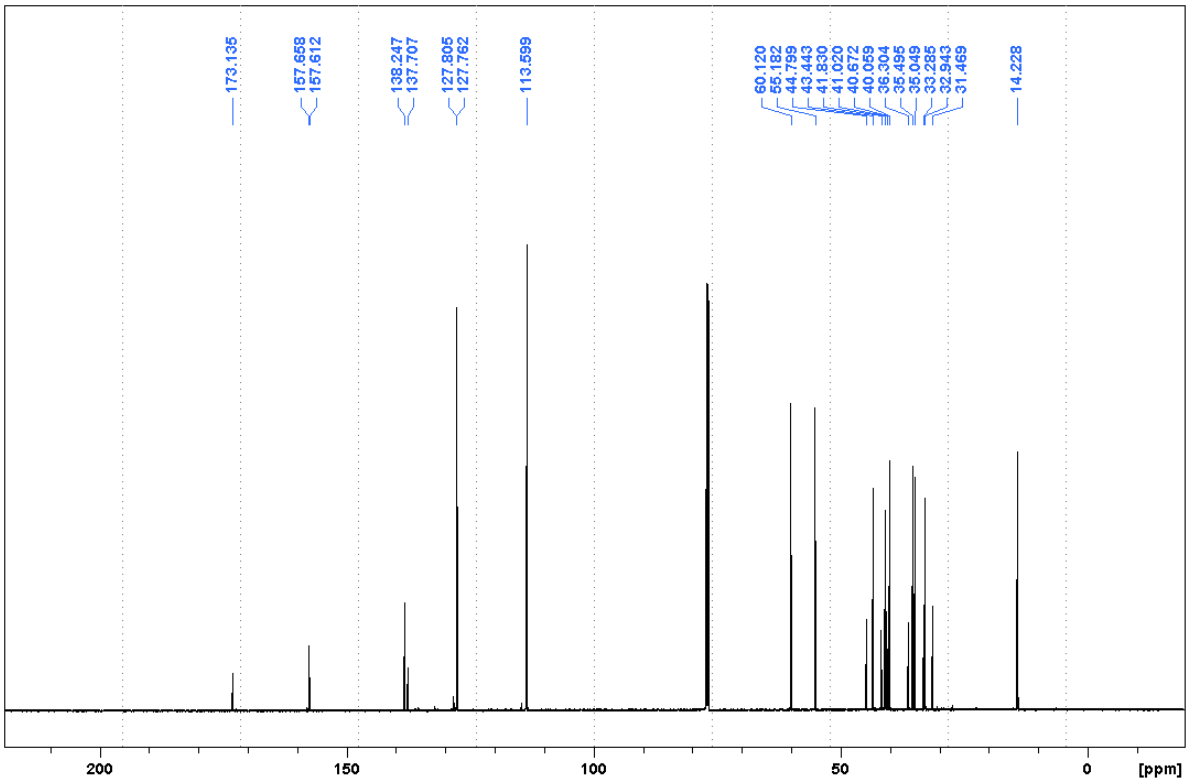
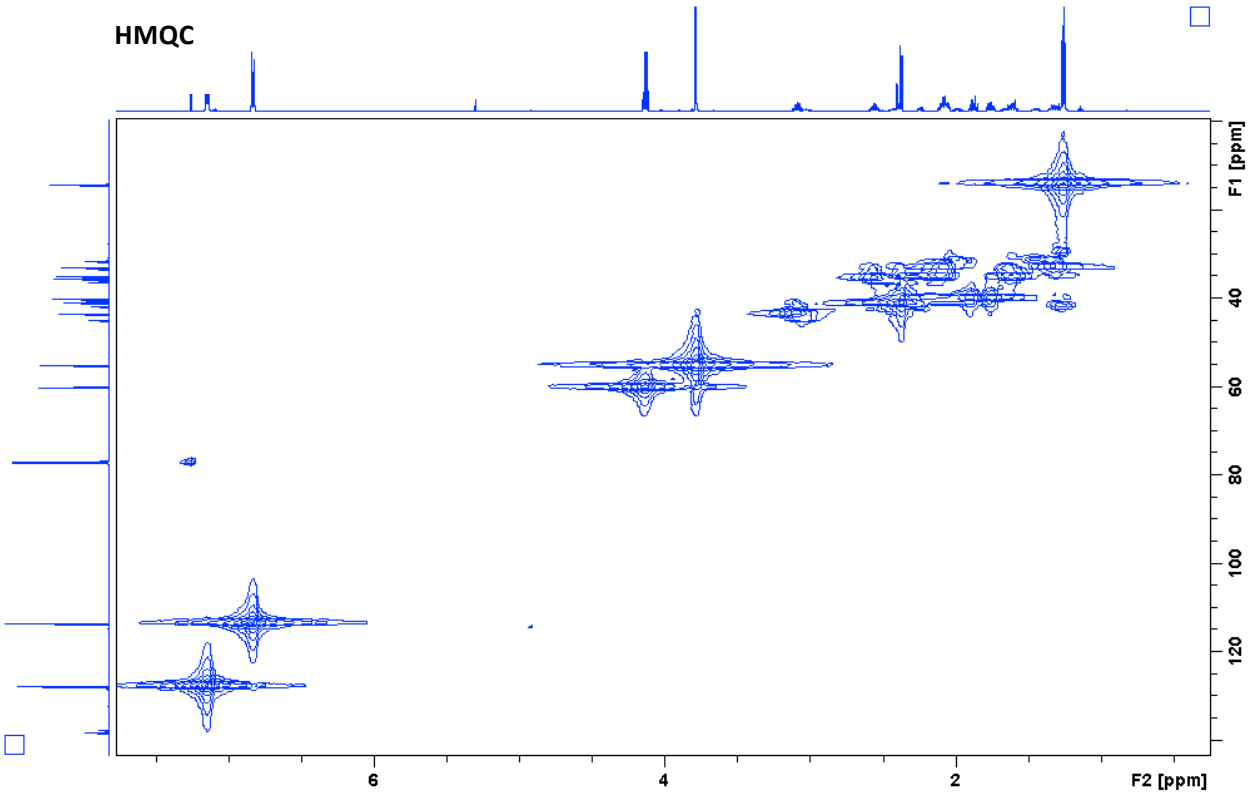

OEt
O
I
23
8
6
4
2
0
[ppm]

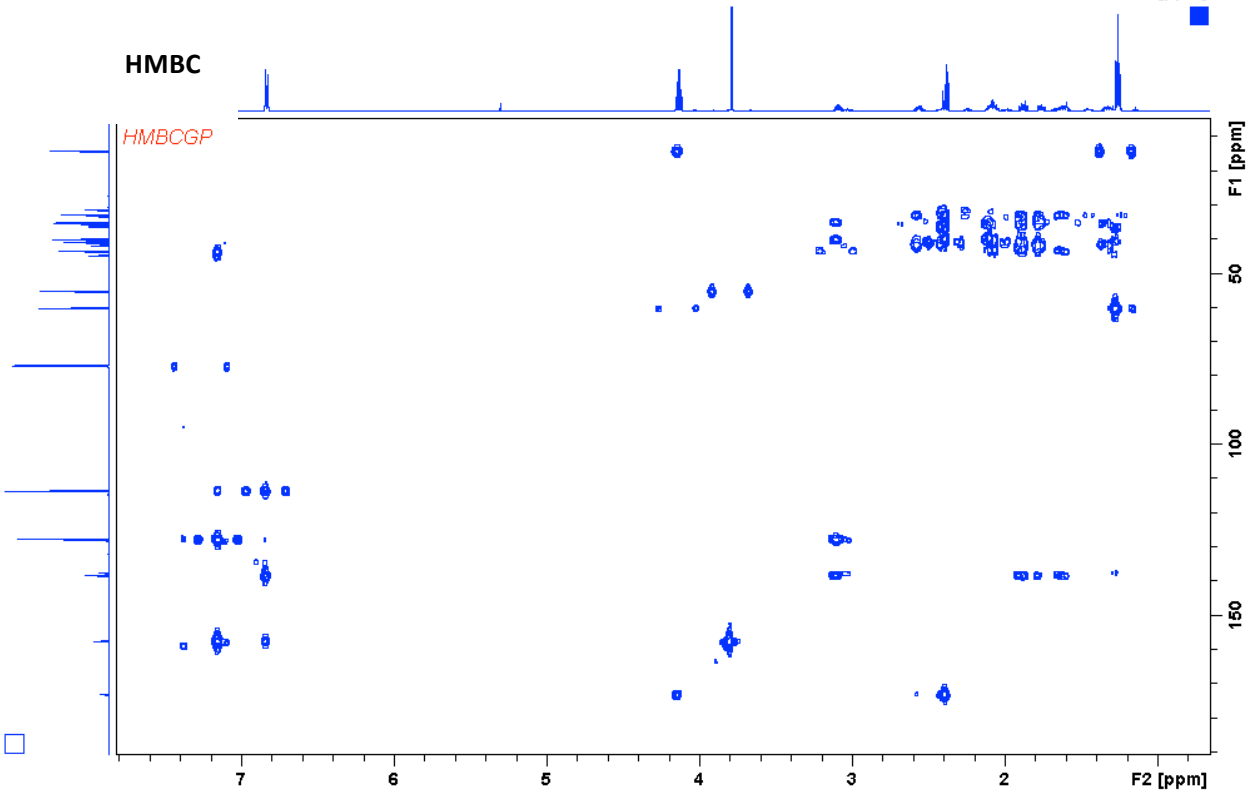

200
150
100
50
0
[ppm]

Product Spectra:

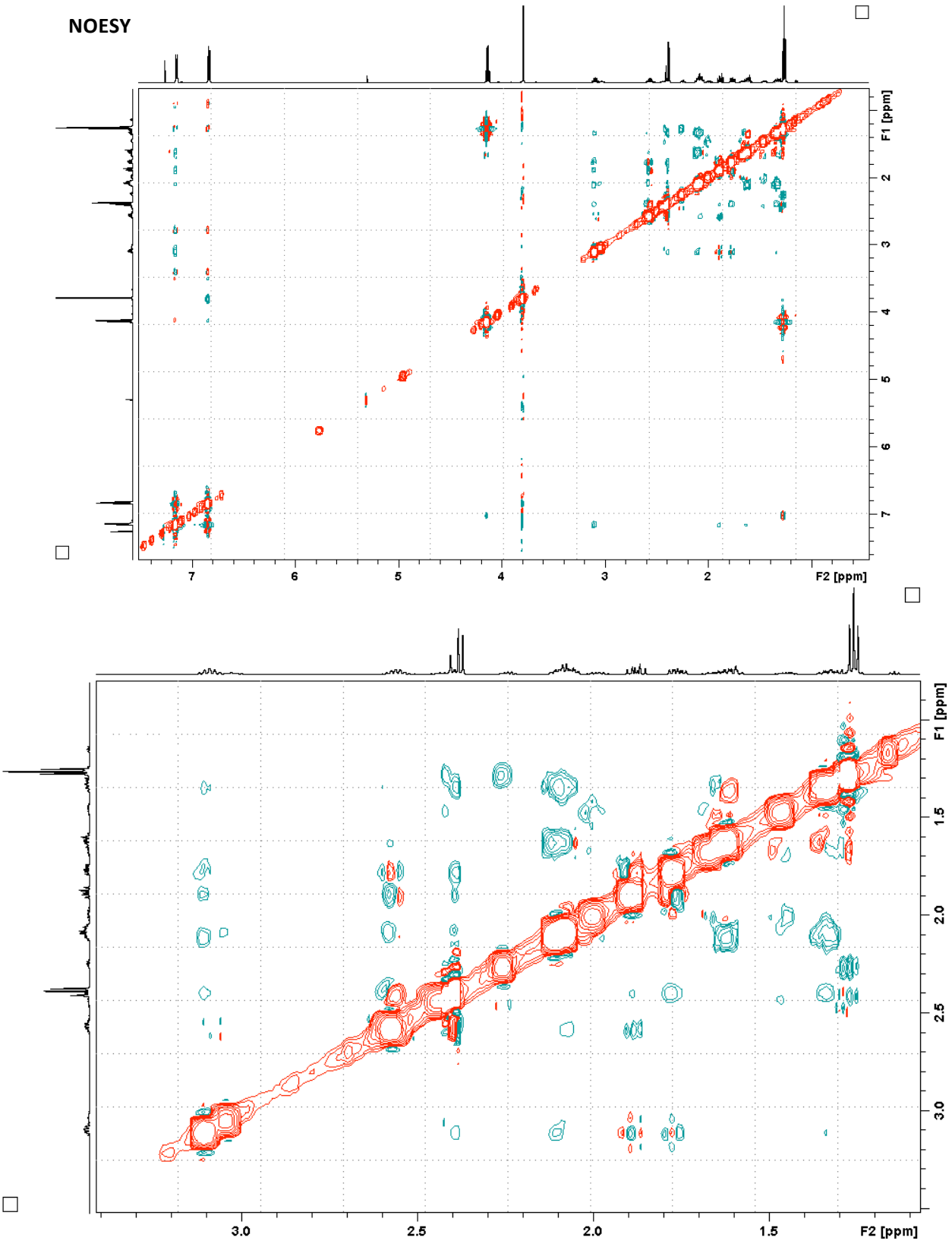





HMQC
F1 [ppm]
40
60
80
100
120
6
4
2
F2 [ppm]


HMBC
HMBCGP
F1 [ppm]
50
100
150
7
6
5
4
3
2
F2 [ppm]

NOESY




5.308
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4.164
4.146
4.128
4.093
4.072
4.052
3.784
3.778
3.774
3.750
3.736
3.715
3.712
3.691
3.674
3.668
3.664
3.659
3.655
3.640
3.636
2.798
2.778
2.506
2.487
2.466
2.447
2.394
2.374
2.354
2.334
2.119
2.109
2.092
2.082
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1.684
1.647
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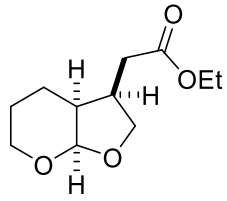
O
H
OEt
H
O
O
H

4

9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.11
0.13
2.27
1.03
3.26
0.14
1.12
0.15
1.06
1.05
0.16
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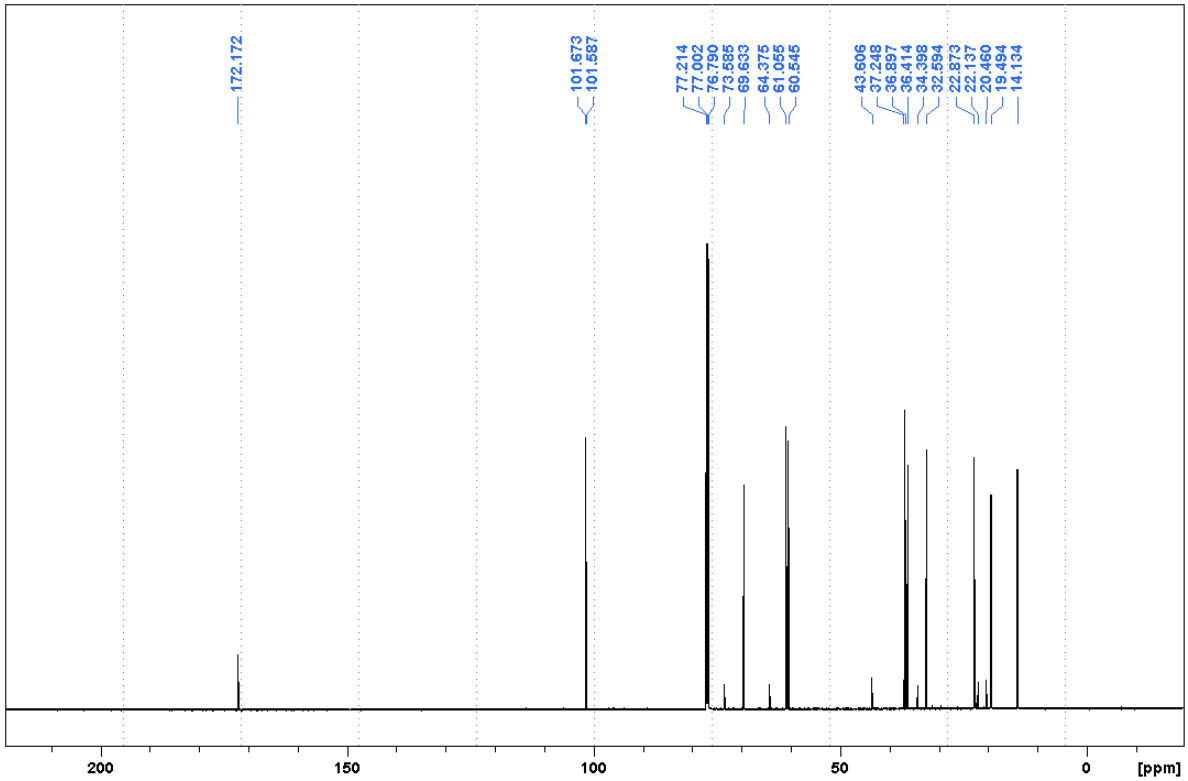
4.20
1.27
3.58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101.587
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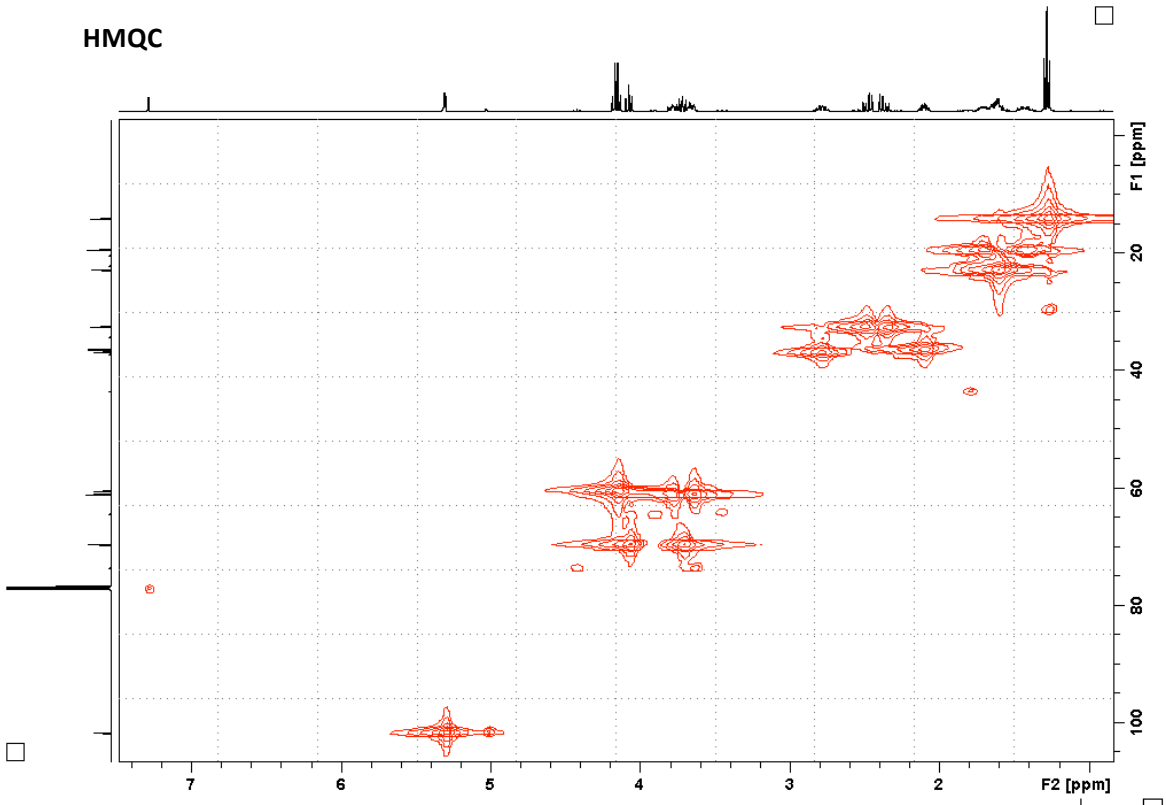
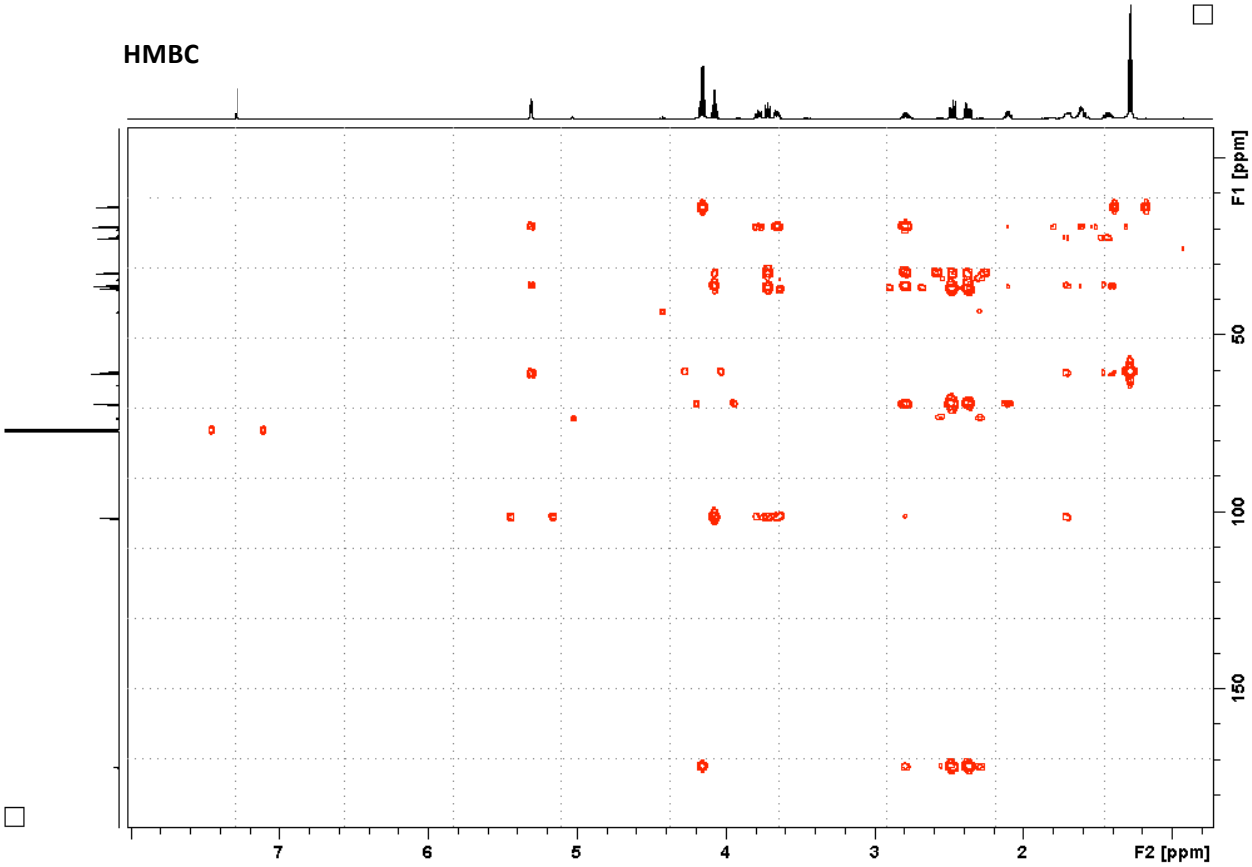
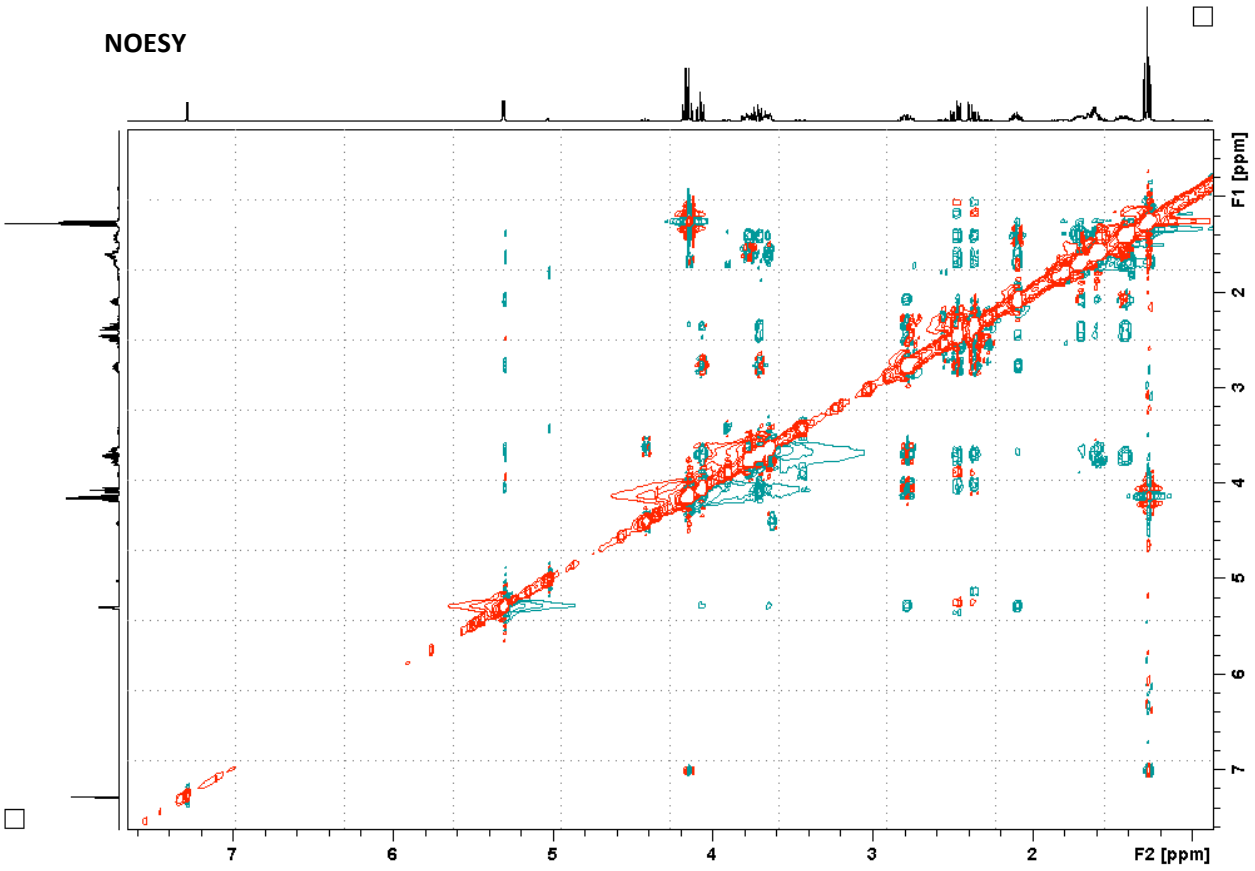
77.002
76.790
73.585
69.633
64.375
61.055
60.545
43.606
37.248
36.897
36.414
34.398
32.594
22.873
22.137
20.460
19.494
14.134
200
150
100
50
0
[ppm]

HMQC


F1 [ppm]
20
40
60
80
100
7
6
5
4
3
2
F2 [ppm]

HMBC


F1 [ppm]
50
100
150
7
6
5
4
3
2
F2 [ppm]


NOESY
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
1


5.309
5.299
4.127
4.106
4.086
3.789
3.774
3.770
3.756
3.736
3.713
3.692
3.660
3.656
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3.285
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2.318
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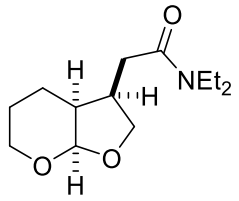
1.104


O
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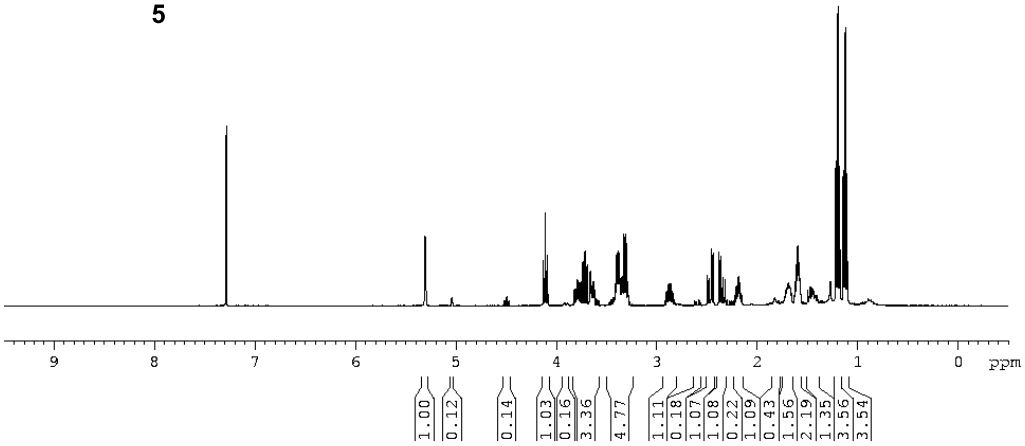
NEt2
H
O
O
H

5


9
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6
5
4
3
2
1
0
ppm
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0.12
0.14
1.03
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3.36
4.77
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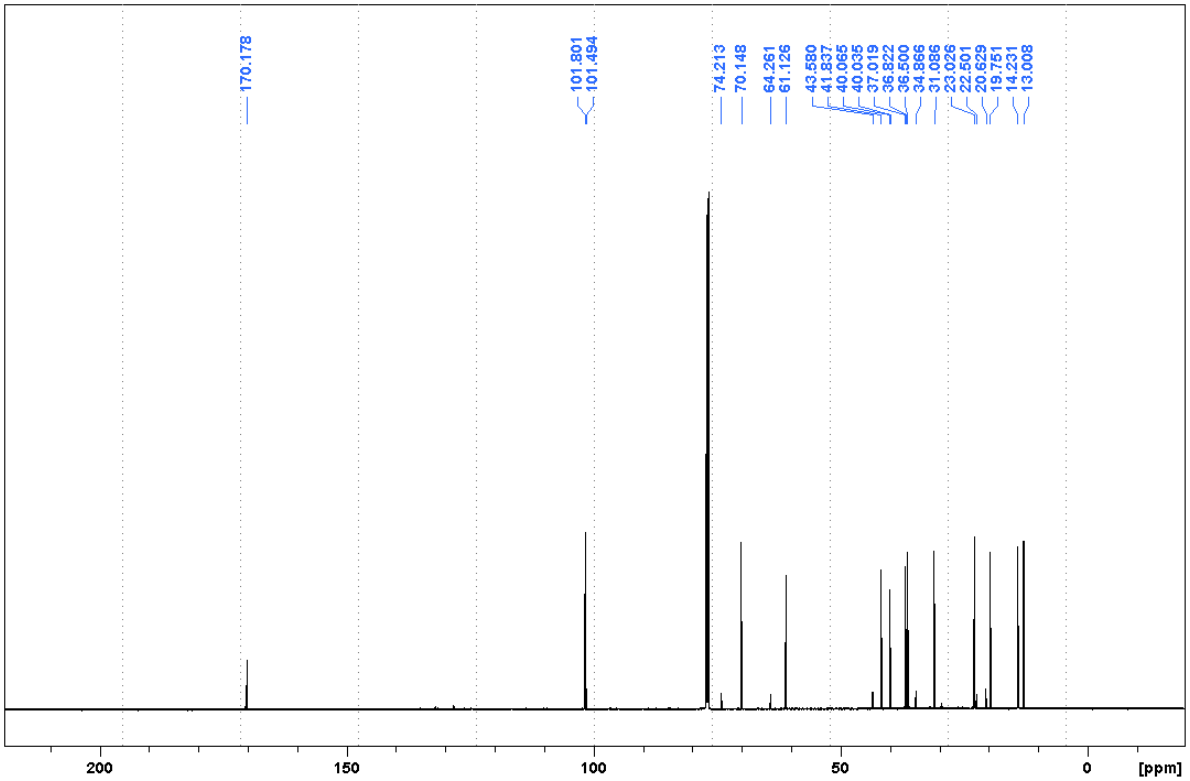
1.08
0.22
1.09
0.43
1.56
2.19
1.35
3.56
3.54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40.065
40.035
37.019
36.822
36.500
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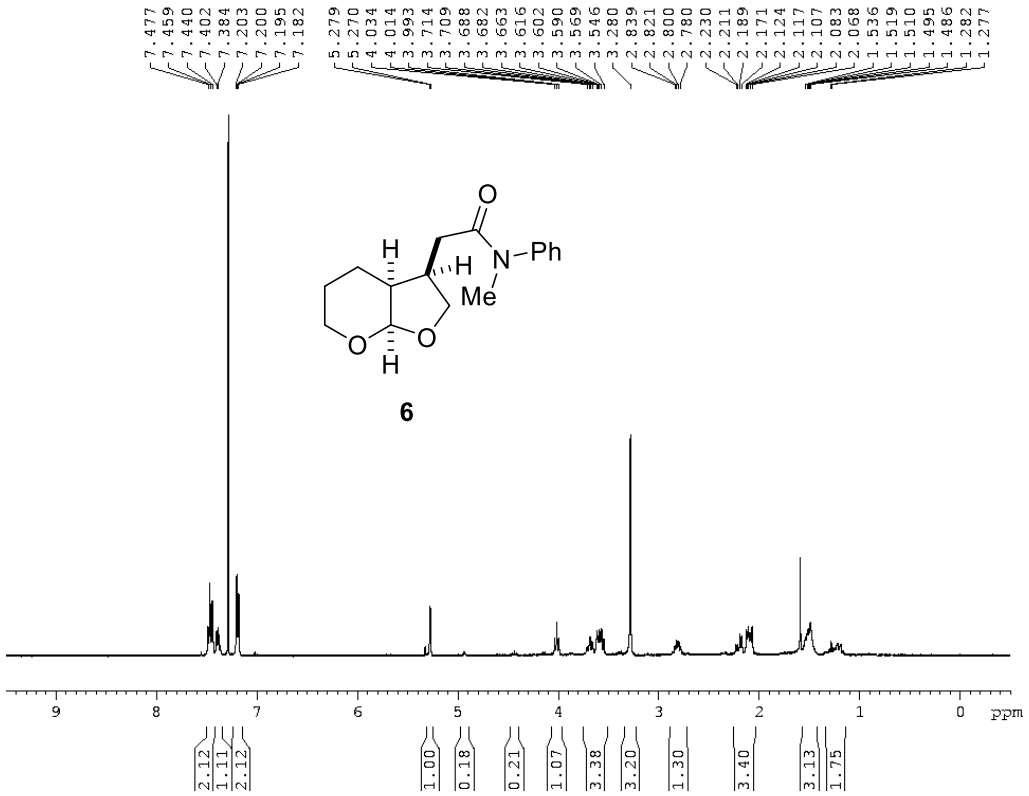
[ppm]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5.279
5.270
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4.014
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3.709
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3.602
3.590
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3.280
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2.821
2.800
2.780
2.230
2.211
2.189
2.171
2.124
2.117
2.107
2.083
2.068
1.536
1.519
1.510
1.495
1.486
1.282
1.277
O
H
H
N–Ph
Me
O
O
H
9
8
7
6
5
4
3
2
1
0
ppm
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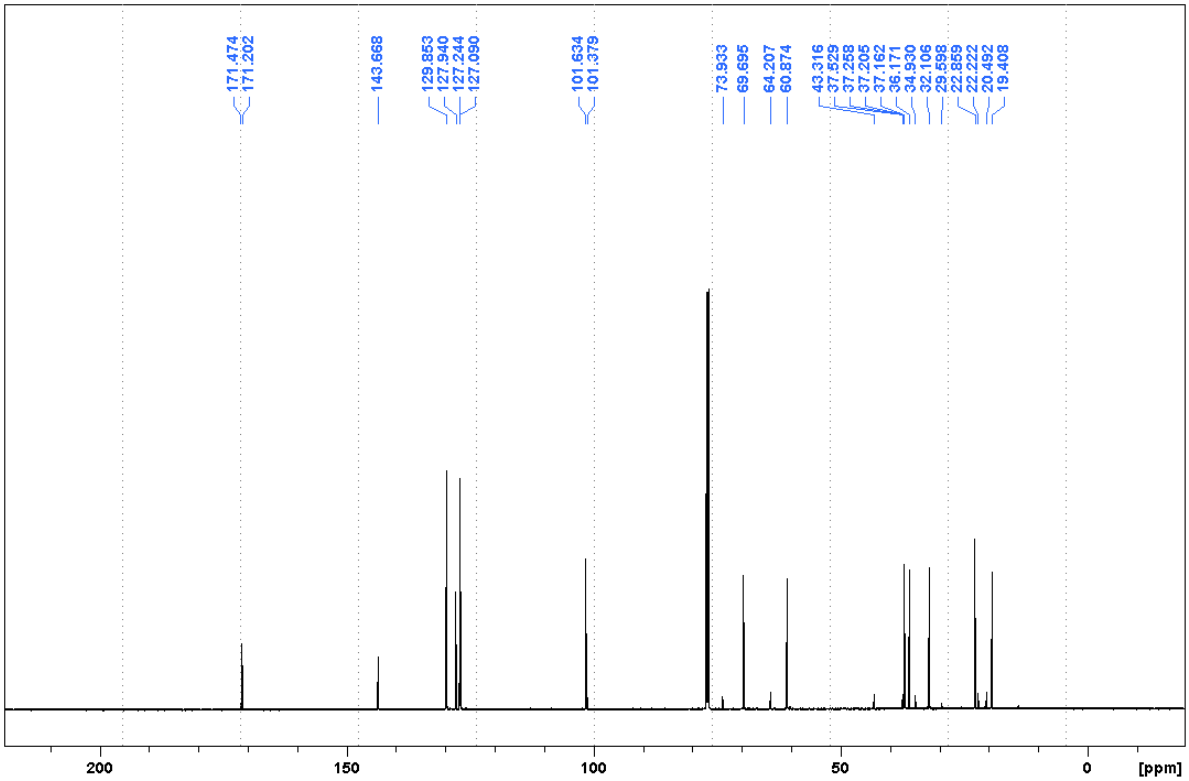
3.13
1.75

6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73.933
69.695
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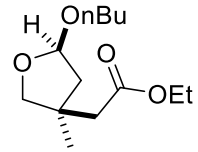
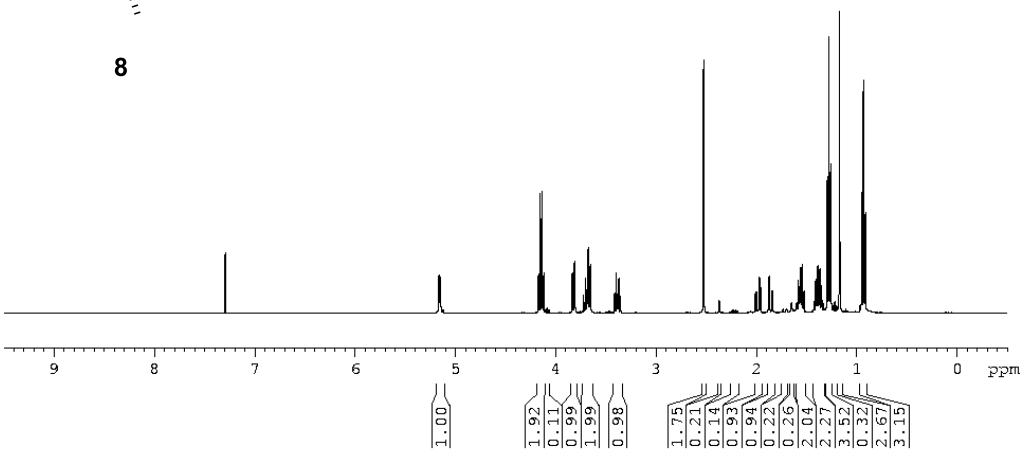
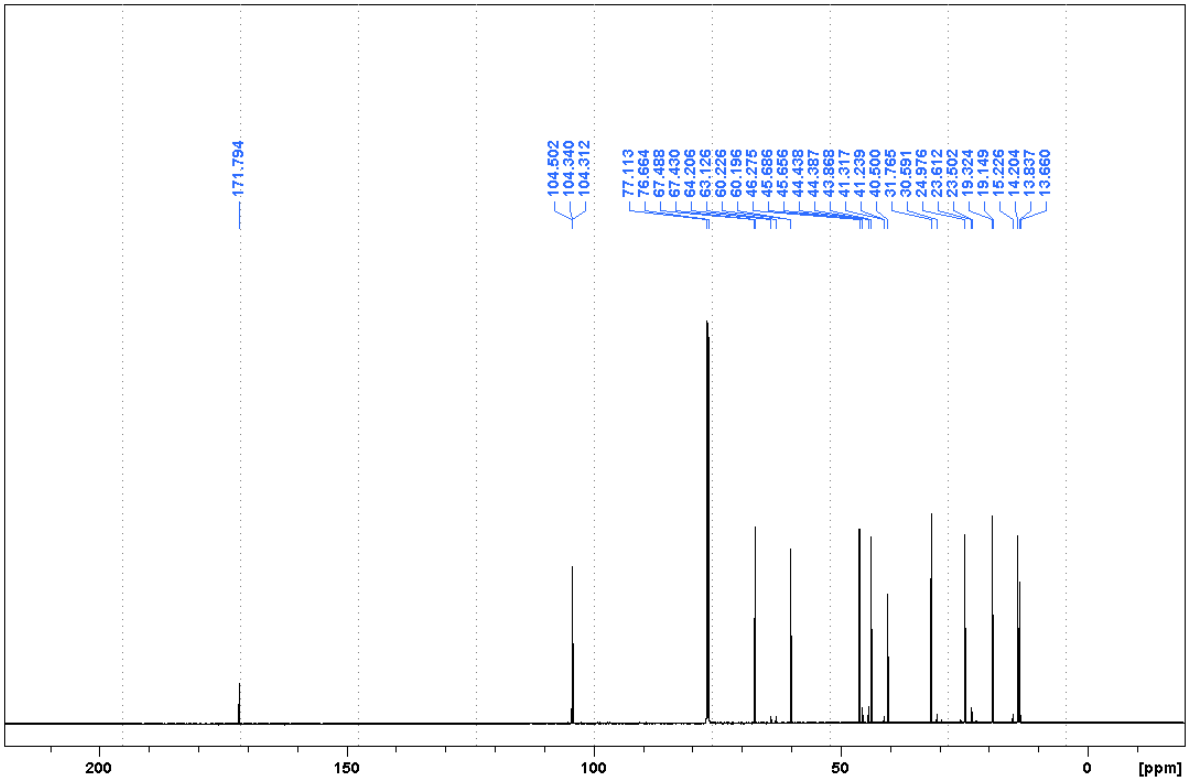
60.874
43.316
37.529
37.258
37.205
37.162
36.171
34.930
32.106
29.598
22.859
22.222
20.492
19.408
200
150
100
50
0
[ppm]


5.168
5.161
5.154
5.147
4.170
4.152
4.134
4.117
3.833
3.812
3.720
3.703
3.696
3.686
3.679
3.674
3.663
3.653
3.410
3.394
3.387
3.377
3.370
3.354
2.525
2.370
2.007
1.993
1.973
1.959
1.877
1.870
1.843
1.836
1.579
1.576
1.571
1.562
1.558
1.546
1.541
1.524
1.404
1.386
1.366
1.348
1.292
1.274
1.256
1.170
0.949
0.930
0.912


H
OnBu
O
O
OEt

8


9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.92
0.11
0.99
1.99
0.98
1.75
0.21
0.14
0.93
0.94
0.22
0.26
2.04
2.27
3.52
0.32
2.67
3.15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104.502
104.340
104.312
77.113
76.664
67.488
67.430
64.206
63.126
60.226
60.196
46.275
45.686
45.656
44.438
44.387
43.868
41.317
41.239
40.500
31.765
30.591
24.976
23.612
23.502
19.324
19.149
15.226
14.204
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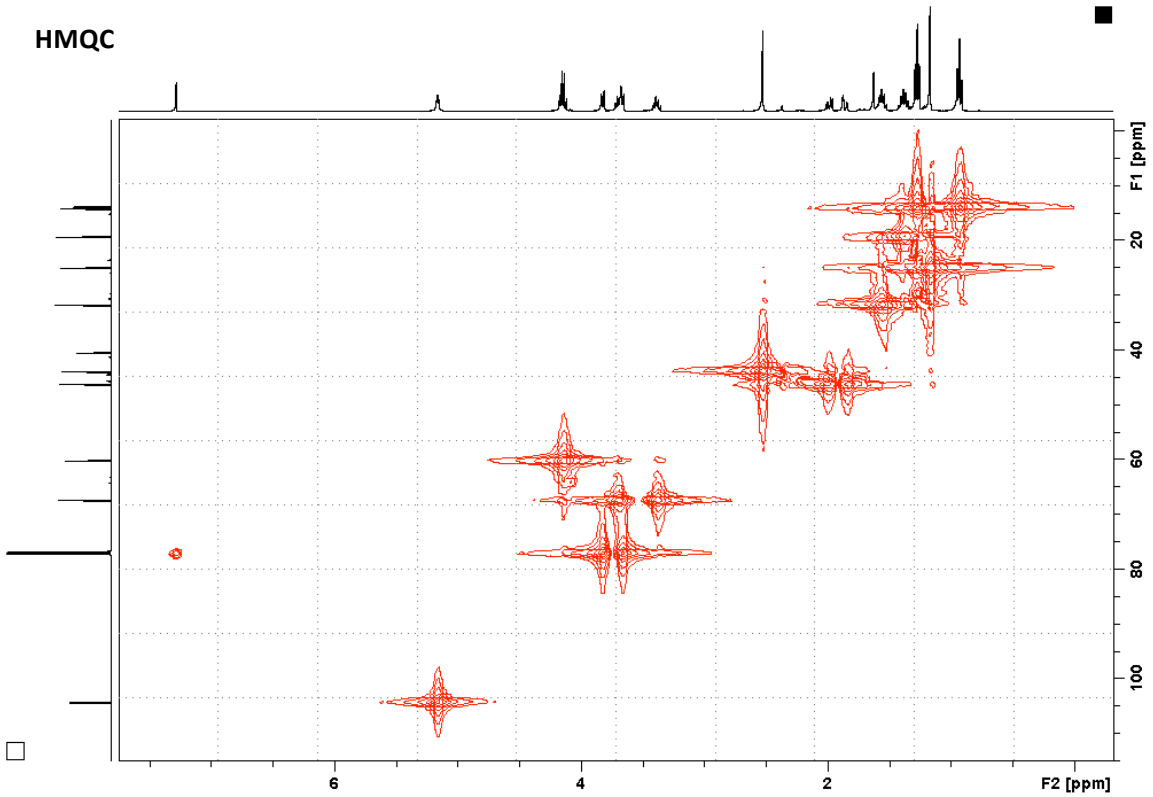
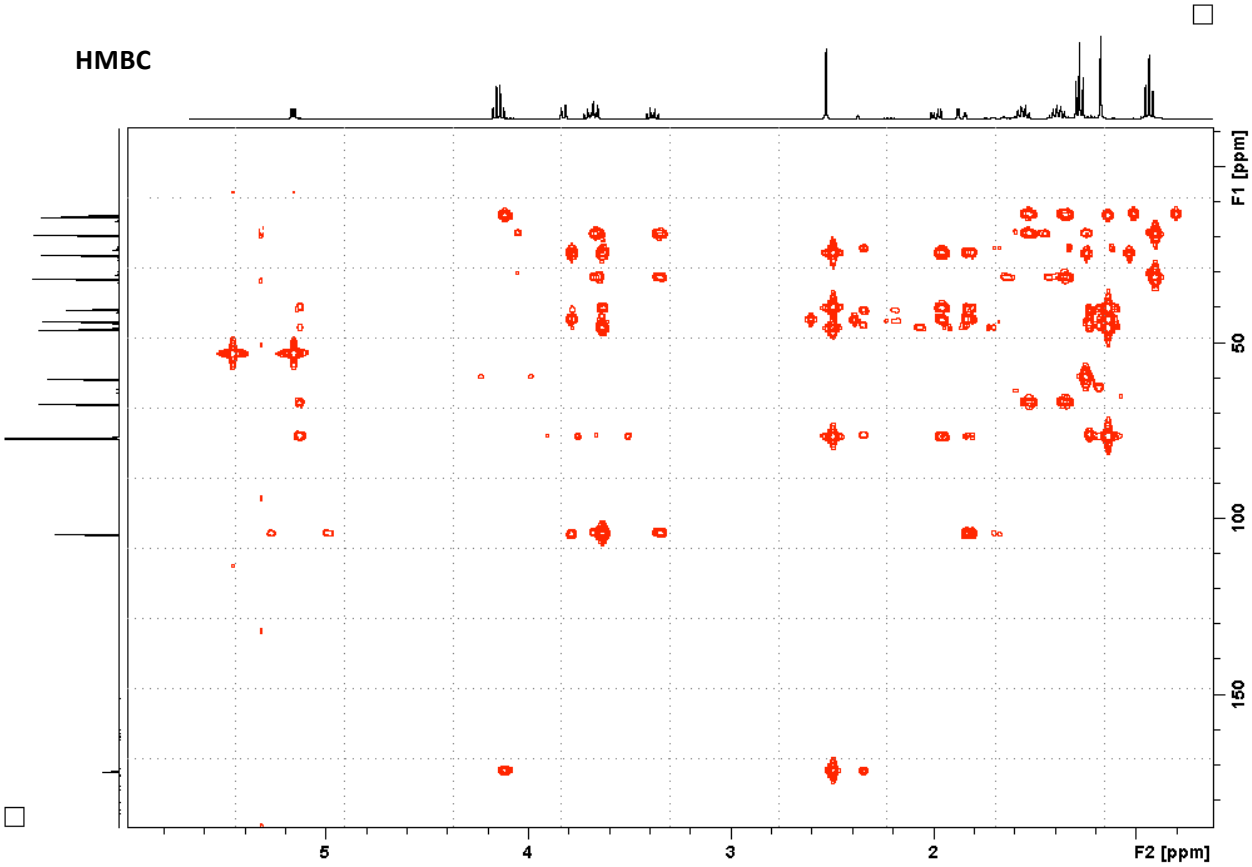
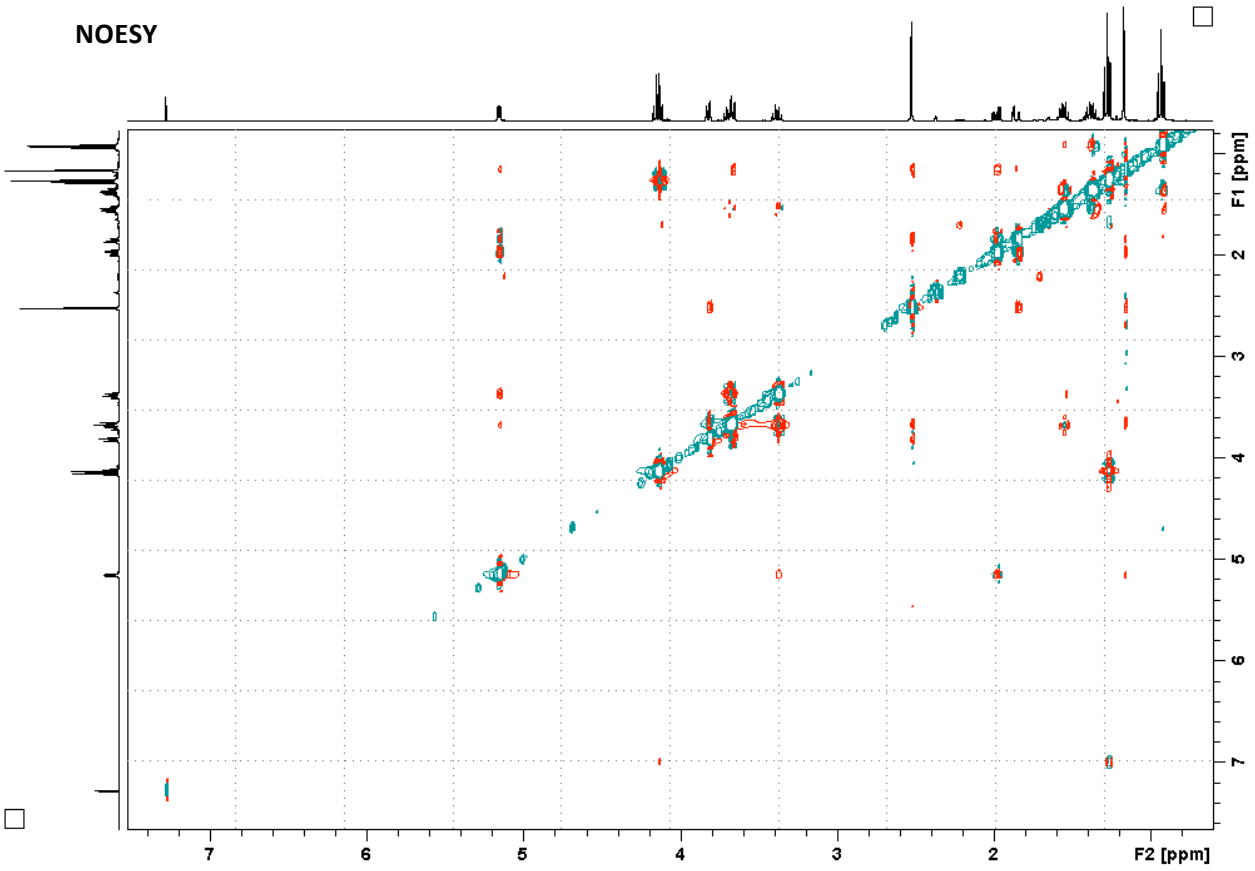
13.660
200
150
100
50
0
[ppm]

HMQC



HMBC




NOESY
F1 [ppm]
F2 [ppm]
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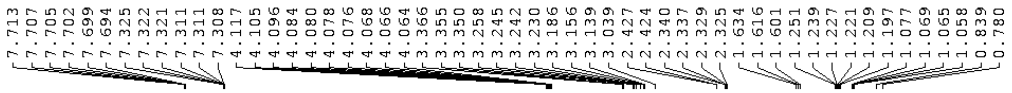
2
3
4
5
6
7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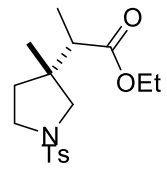
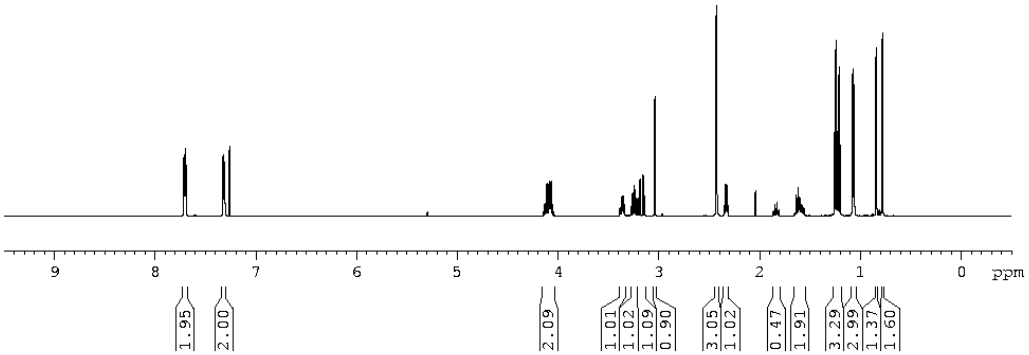
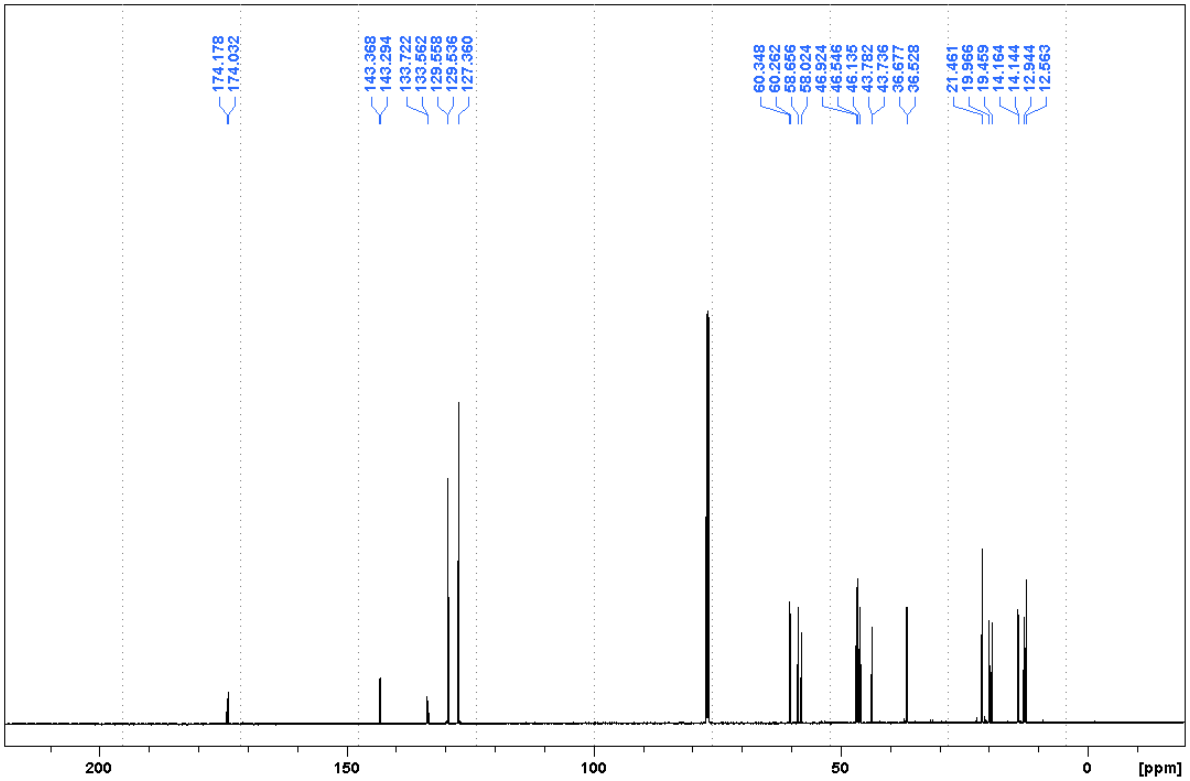
7.707
7.705
7.702
7.699
7.694
7.325
7.322
7.321
7.311
7.311
7.308
4.117
4.105
4.096
4.084
4.080
4.078
4.076
4.068
4.066
4.064
3.366
3.355
3.350
3.258
3.245
3.242
3.230
3.186
3.156
3.139
3.039
2.427
2.424
2.340
2.337
2.329
2.325
1.634
1.616
1.601
1.251
1.239
1.227
1.221
1.209
1.197
1.077
1.069
1.065
1.058
0.839
0.780

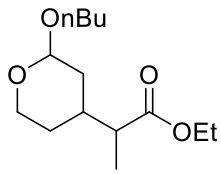

O
OEt
N
Ts

10

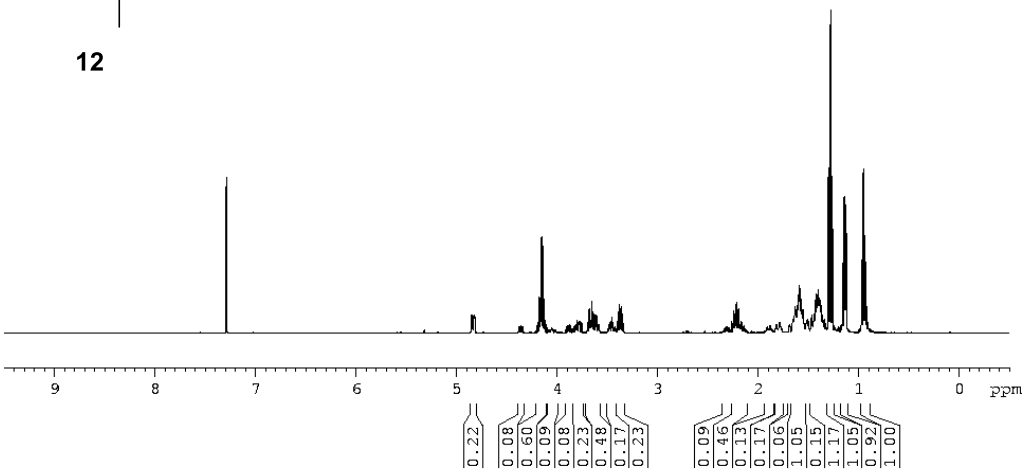

9
8
7
6
5
4
3
2
1
0
ppm
1.95
2.00
2.09
1.01
1.02
1.09
0.90
3.05
1.02
0.47
1.91
3.29
2.99
1.37
1.60

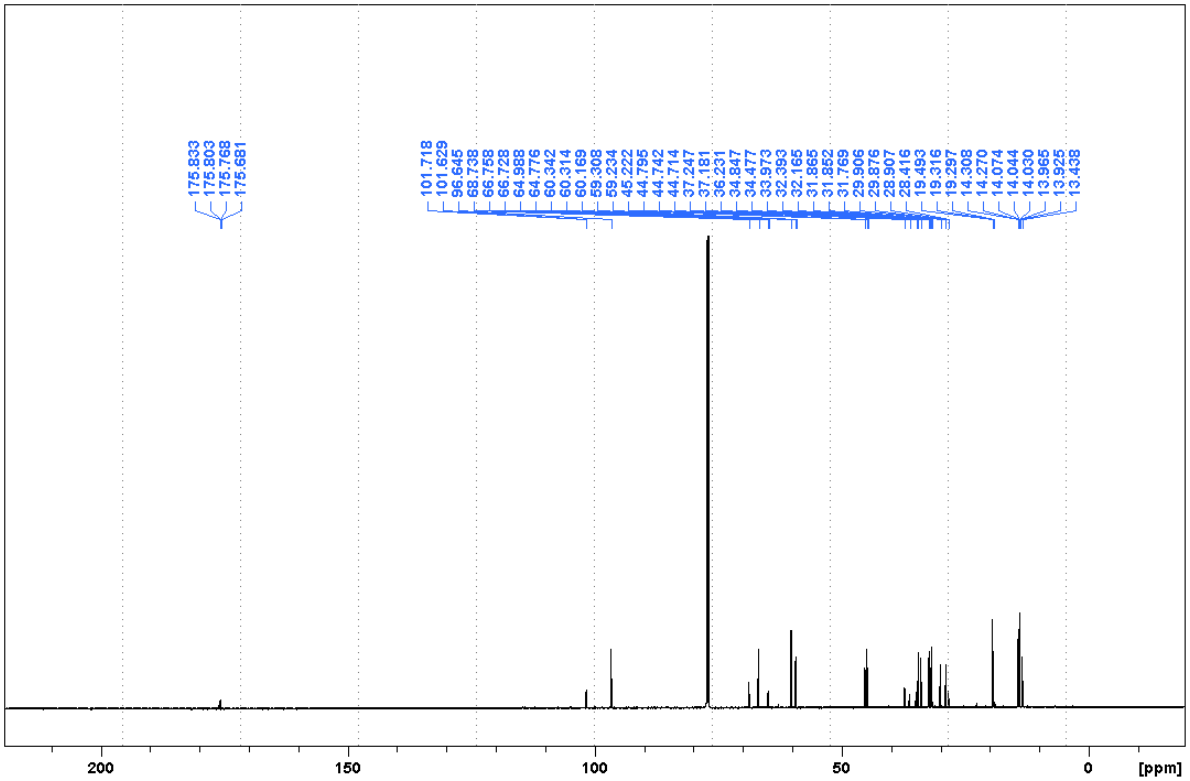

174.178
174.032
143.368
143.294
133.722
133.562
129.558
129.536
127.360
60.348
60.262
58.656
58.024
46.924
46.546
46.135
43.782
43.736
36.677
36.528
21.461
19.966
19.459
14.164
14.144
12.944
12.563
200
150
100
50
0
[ppm]


4.178
4.169
4.160
4.154
4.151
4.142
4.136
4.125
3.673
3.654
3.649
3.377
3.361
2.211
2.194
1.629
1.612
1.606
1.595
1.589
1.583
1.573
1.567
1.550
1.430
1.426
1.420
1.416
1.412
1.408
1.403
1.397
1.389
1.384
1.379
1.372
1.295
1.277
1.263
1.259
1.158
1.143
1.138
1.126
1.121
0.970
0.966
0.957
0.951
0.947
0.939
0.932
0.929
0.920


OnBu
O
O
OEt

12


9
8
7
6
5
4
3
2
1
0
ppm
0.22
0.08
0.60
0.09
0.08
0.23
0.48
0.17
0.23
0.09
0.46
0.13
0.17
0.06
1.05
0.15
1.17
1.05
0.92
1.00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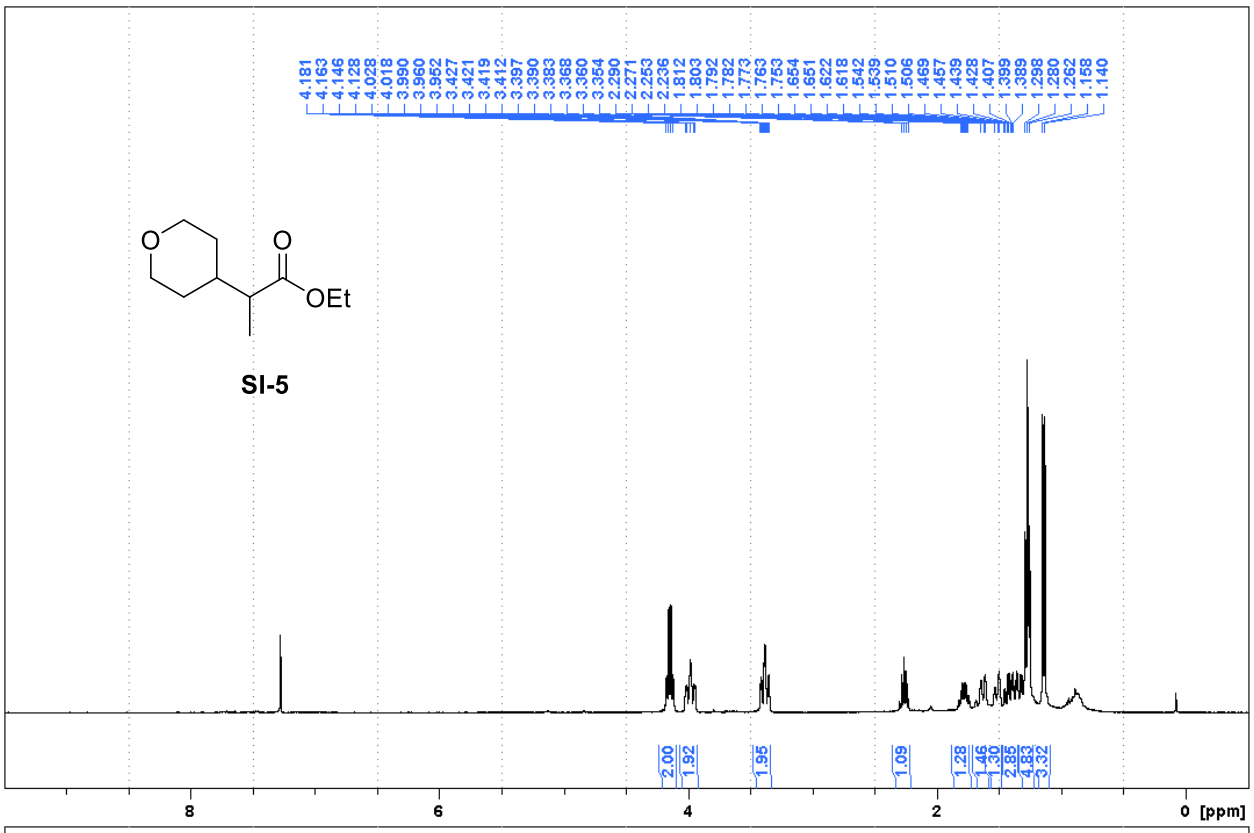
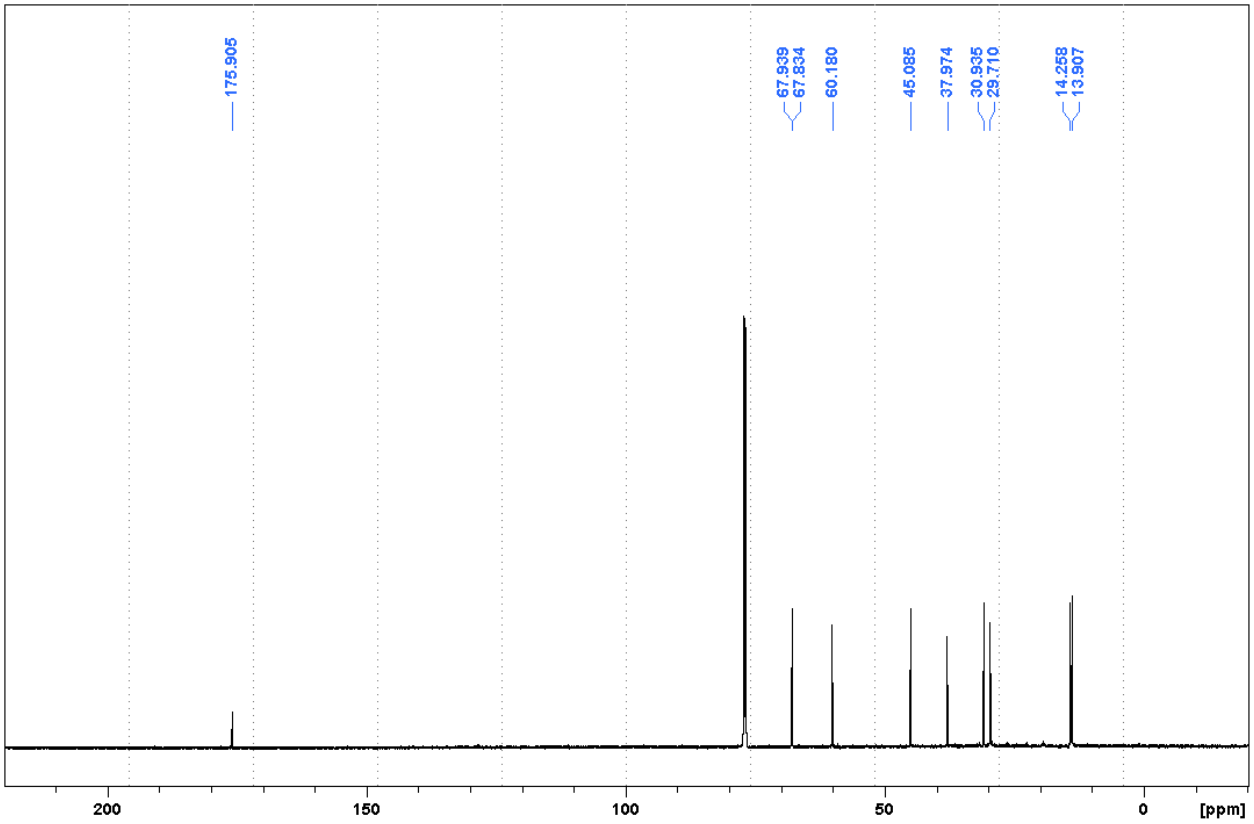
175.803
175.768
175.681
101.718
101.629
96.645
68.738
66.768
66.728
64.988
64.776
60.342
60.314
60.169
59.308
59.234
45.222
44.795
44.742
44.714
37.247
37.181
36.231
34.847
34.477
33.973
32.393
32.165
31.865
31.852
31.769
29.906
29.876
28.907
28.416
19.493
19.316
19.297
14.308
14.270
14.074
14.044
14.030
13.965
13.925
13.438
200
150
100
50
0
[ppm]


4.181
4.163
4.146
4.128
4.028
4.018
3.990
3.960
3.952
3.427
3.421
3.419
3.412
3.397
3.390
3.383
3.368
3.360
3.354
2.290
2.271
2.253
2.236
1.812
1.803
1.792
1.782
1.773
1.763
1.753
1.654
1.651
1.622
1.618
1.542
1.539
1.510
1.506
1.469
1.457
1.439
1.428
1.407
1.399
1.389
1.298
1.280
1.262
1.158
1.140
O
O
OEt
2.00
1.92
1.95
1.09
1.28
1.46
1.30
2.85
4.82
3.32
8
6
4
2
0 [ppm]

SI-5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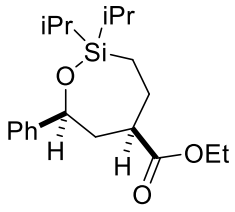
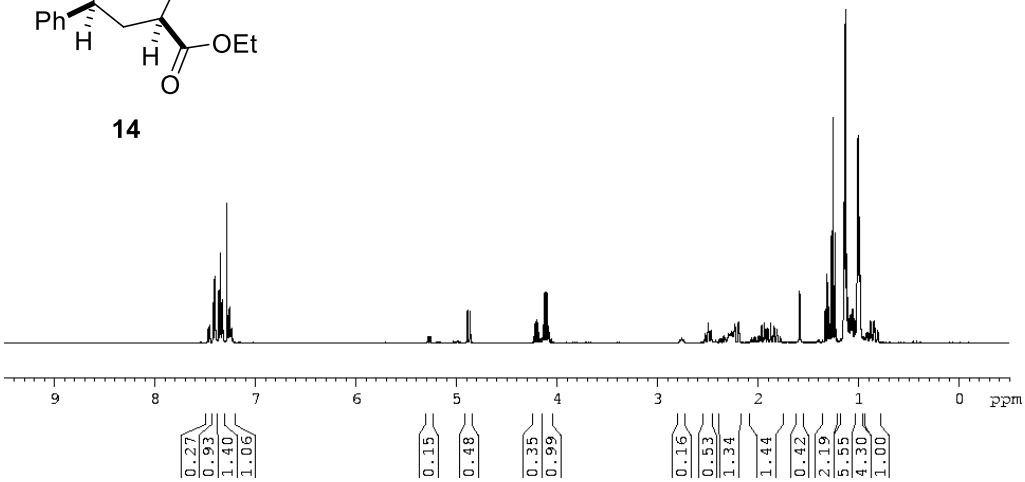
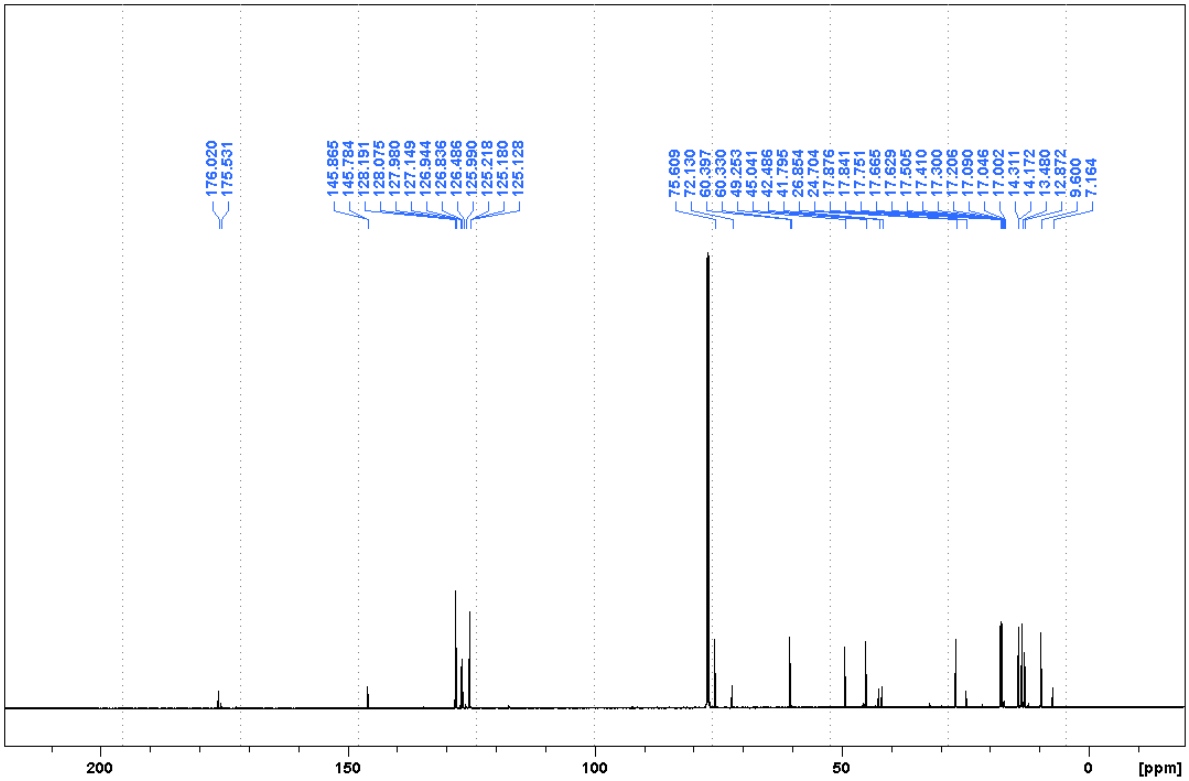
67.939
67.834
60.180
45.085
37.974
30.935
29.710
14.258
13.907
200
150
100
50
0
[ppm]


7.452
7.422
7.418
7.401
7.363
7.345
7.325
7.285
7.273
7.255
4.887
4.862
4.213
4.195
4.120
4.115
4.102
4.097
2.494
2.231
2.194
2.191
2.188
1.933
1.871
1.584
1.328
1.311
1.293
1.287
1.267
1.249
1.231
1.150
1.139
1.129
1.118
1.108
1.095
1.093
1.078
1.073
1.058
1.054
1.038
1.035
1.011
1.004
0.991
0.982
0.882
0.875
0.848
0.842


iPr
iPr
Si
O
Ph
H
H
OEt
O

14


9
8
7
6
5
4
3
2
1
0
ppm
0.27
0.93
1.40
1.06
0.15
0.48
0.35
0.99
0.16
0.53
1.34
1.44
0.42
2.19
5.55
4.30
1.00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175.531
145.865
145.784
128.191
128.075
127.980
127.149
126.944
126.836
126.486
125.990
125.218
125.180
125.128
75.609
72.130
60.397
60.330
49.253
45.041
42.486
41.795
26.854
24.704
17.876
17.841
17.751
17.665
17.629
17.505
17.410
17.300
17.206
17.090
17.046
17.002
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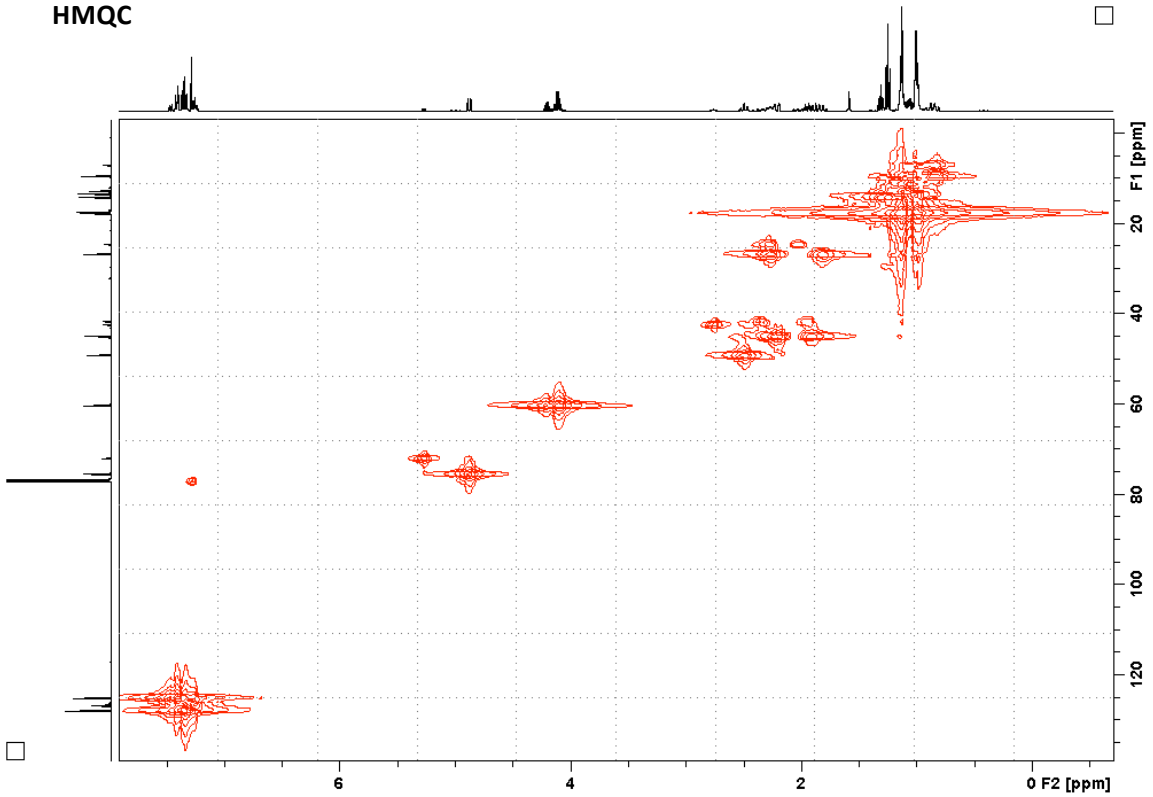
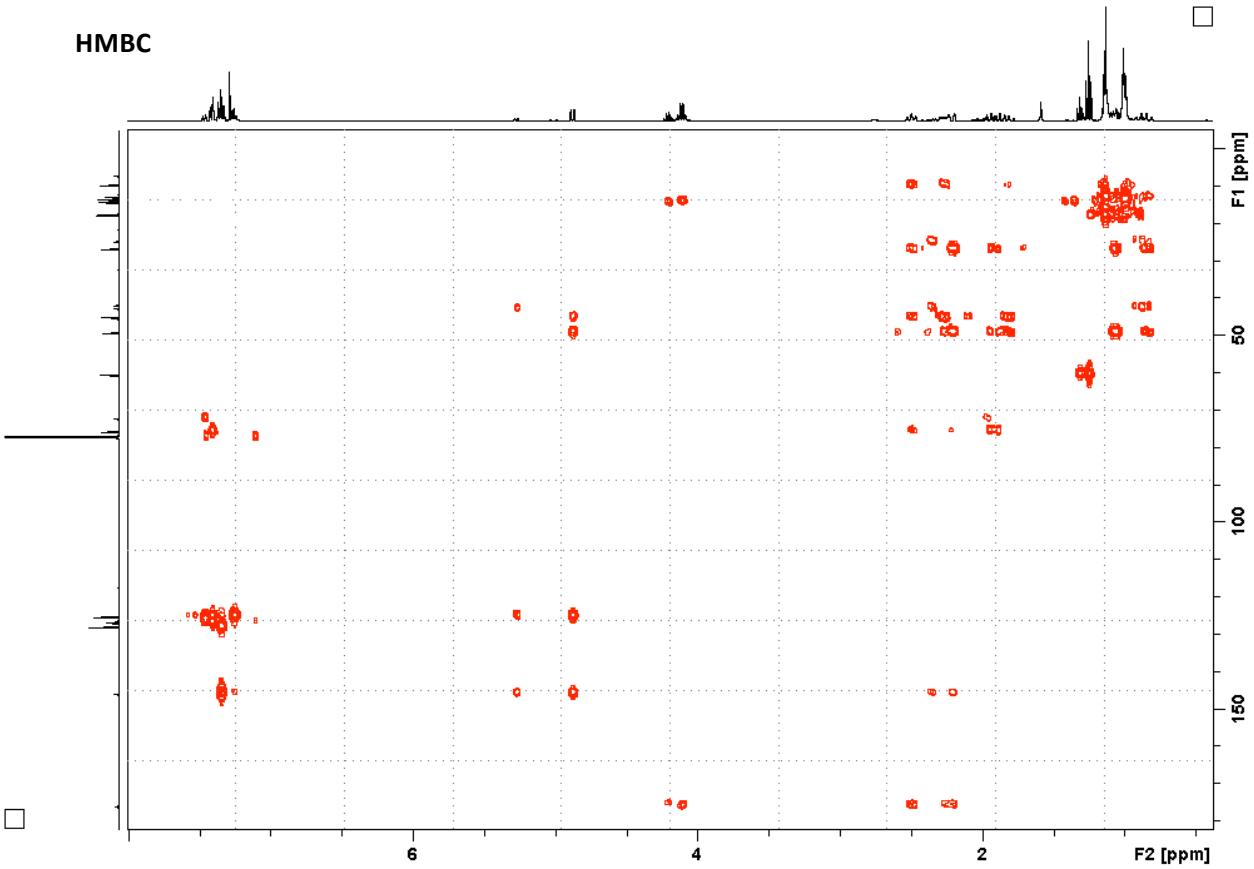
14.172
13.480
12.872
9.600
7.164
200
150
100
50
0
[ppm]

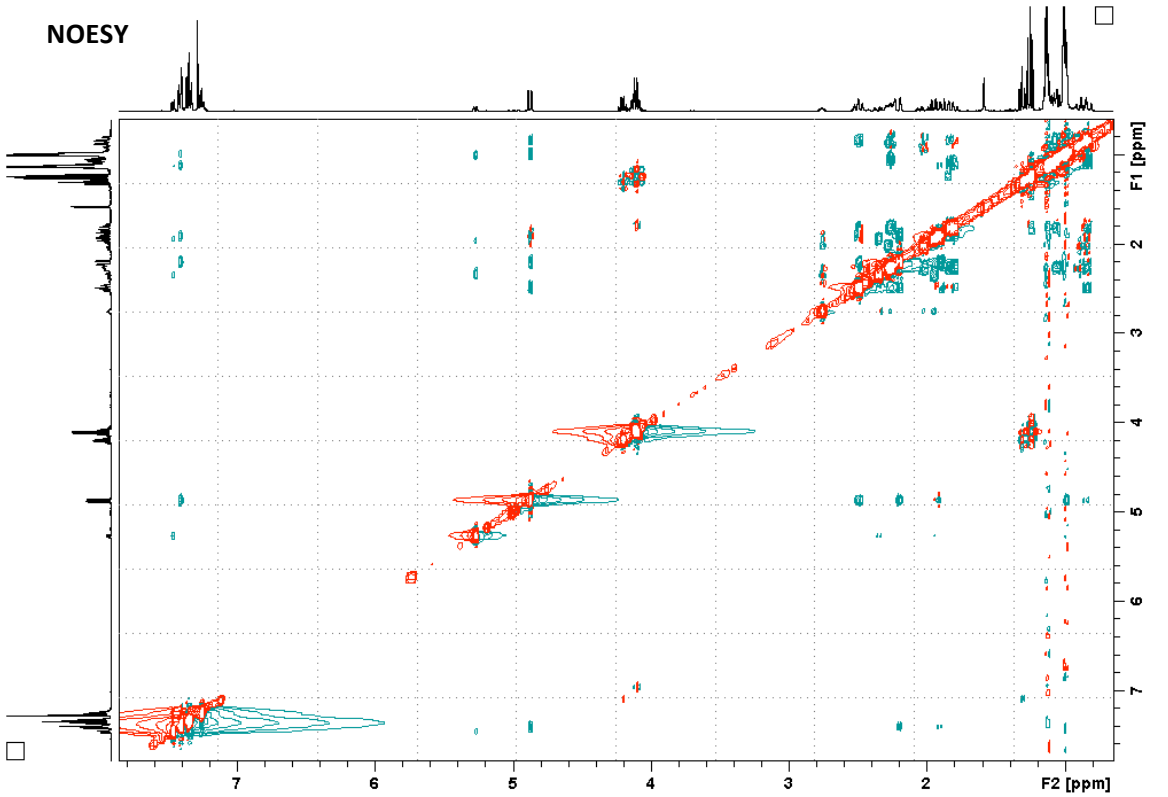
HMQC

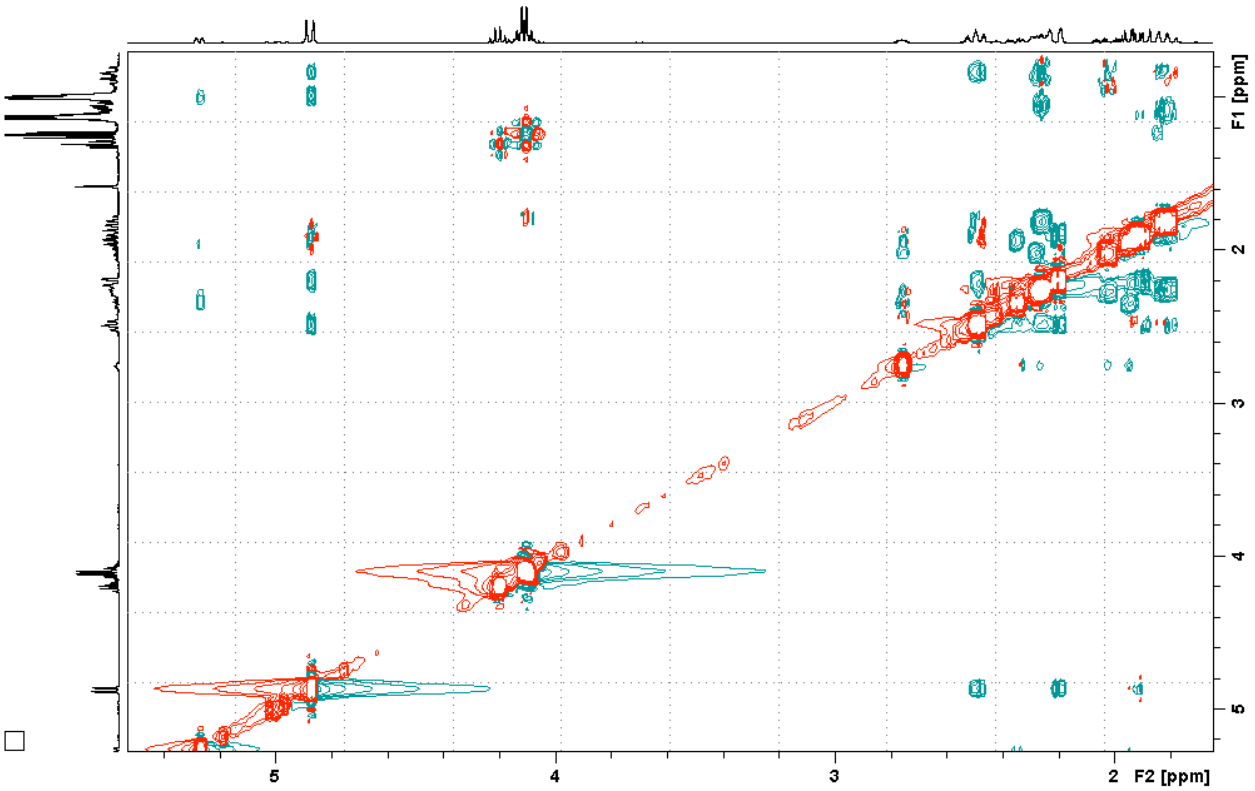


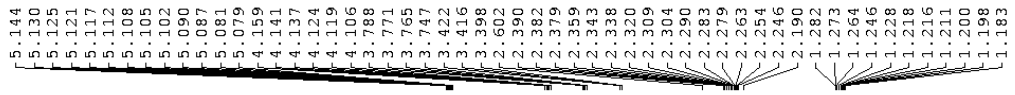
HMBC



NOESY






5.144
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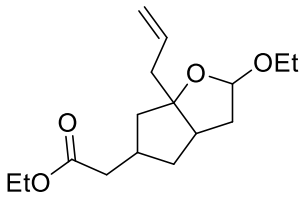
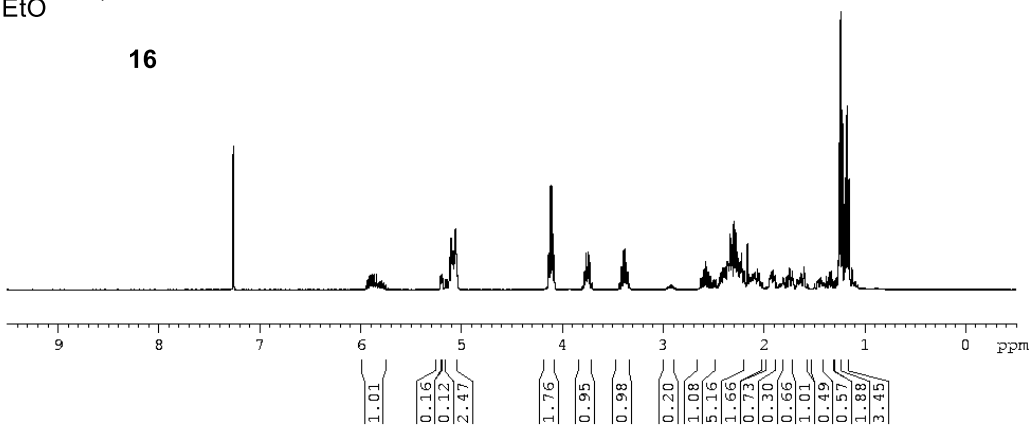
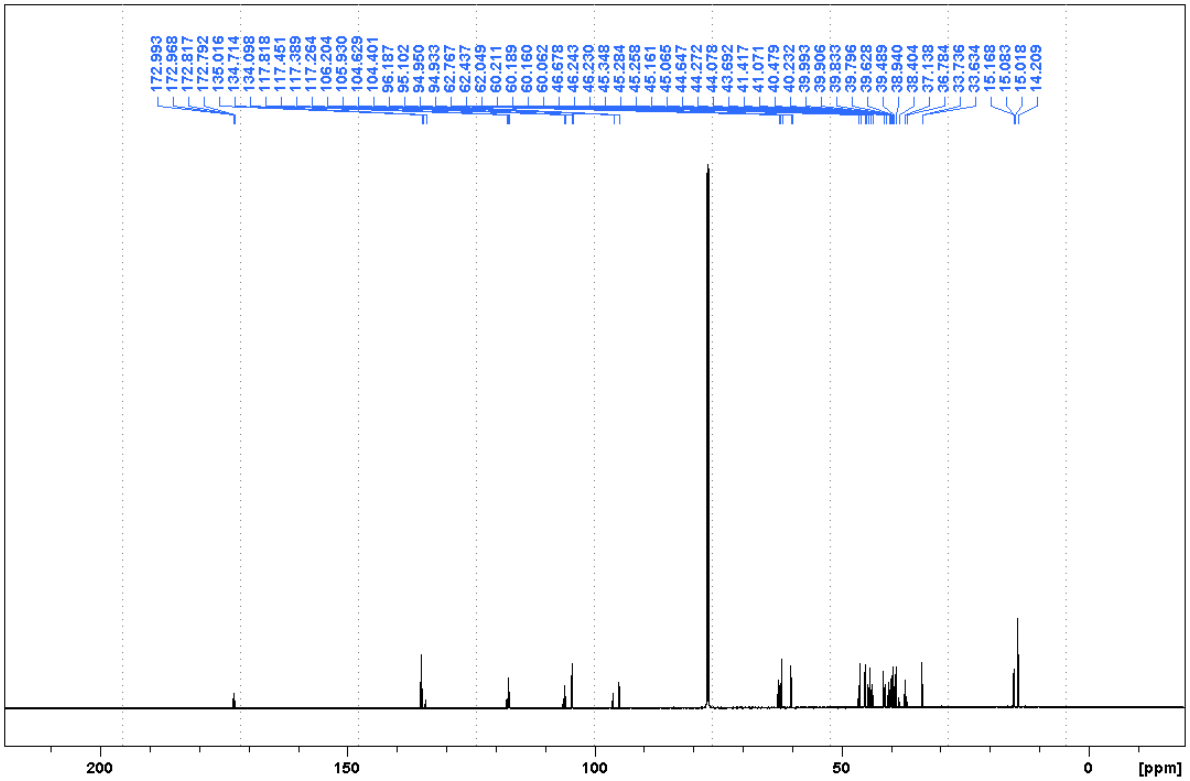
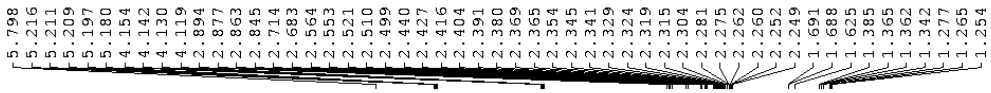
5.125
5.121
5.117
5.112
5.108
5.105
5.102
5.090
5.087
5.081
5.079
4.159
4.141
4.137
4.124
4.119
4.106
3.788
3.771
3.765
3.747
3.422
3.416
3.398
2.602
2.390
2.382
2.379
2.359
2.343
2.338
2.320
2.309
2.304
2.290
2.283
2.279
2.263
2.254
2.246
2.190
1.282
1.273
1.264
1.246
1.228
1.218
1.216
1.211
1.200
1.198
1.183

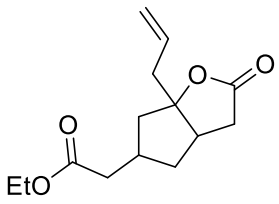

O
OEt
O
EtO

16

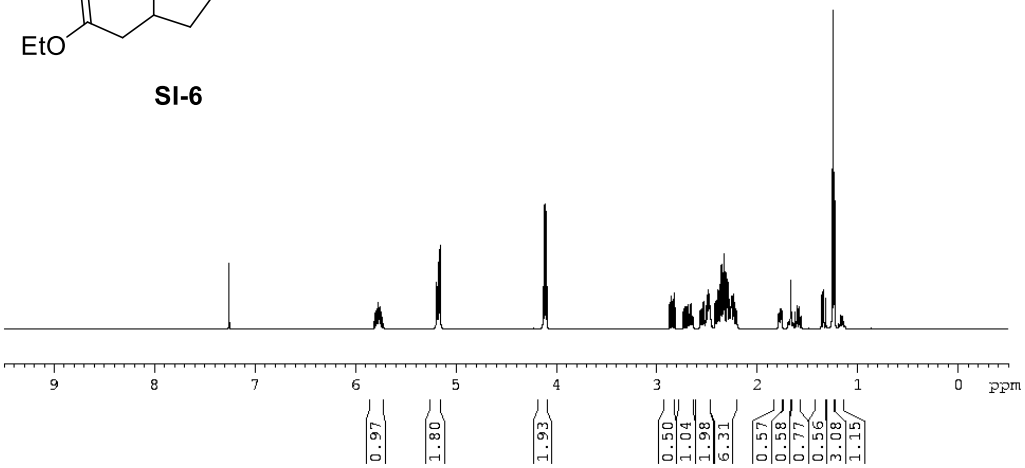

9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.16
0.12
2.47
1.76
0.95
0.98
0.20
1.08
5.16
1.66
0.73
0.30
0.66
1.01
0.49
0.57
1.88
3.45

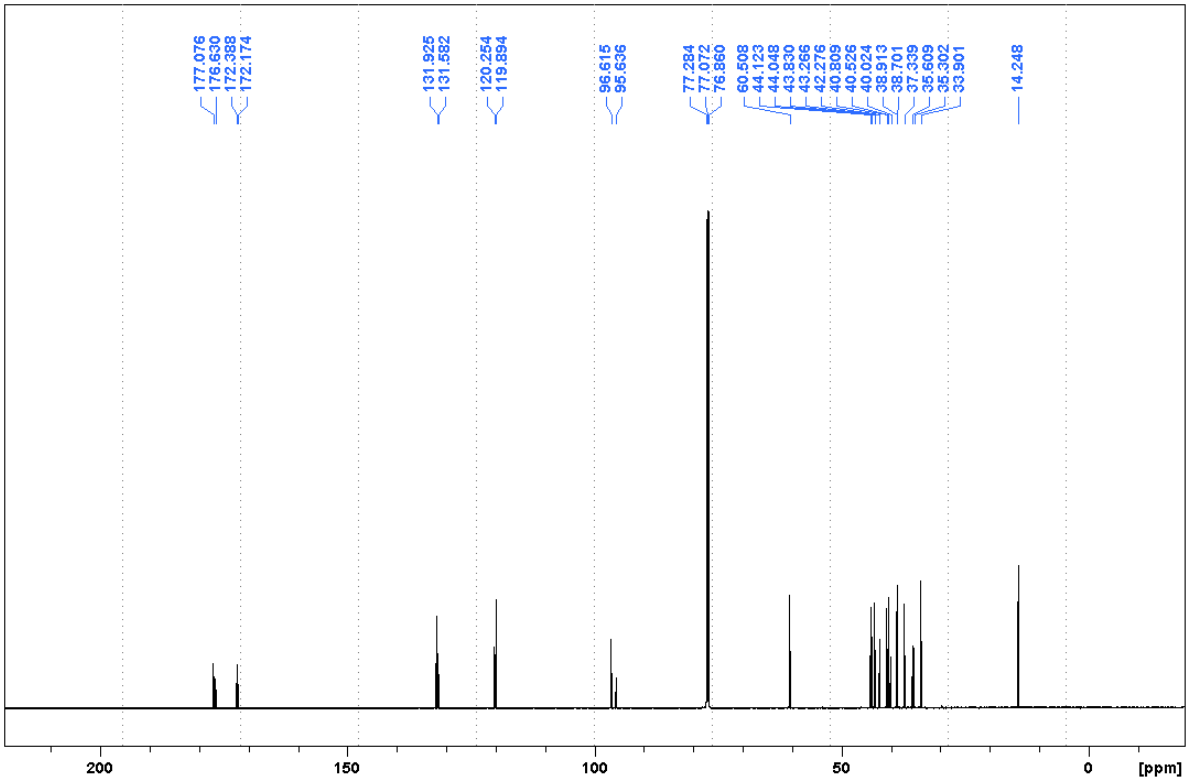

172.993
172.968
172.817
172.792
135.016
134.714
134.098
117.818
117.451
117.389
117.264
106.204
105.930
104.629
104.401
96.187
95.102
94.950
94.933
62.767
62.437
62.049
60.211
60.189
60.160
60.062
46.678
46.243
46.230
45.348
45.284
45.258
45.161
45.065
44.647
44.272
44.078
43.692
41.417
41.071
40.479
40.232
39.993
39.906
39.833
39.796
39.628
39.489
38.940
38.404
37.138
36.784
33.736
33.634
15.168
15.083
15.018
14.209
200
150
100
50
0
[ppm]

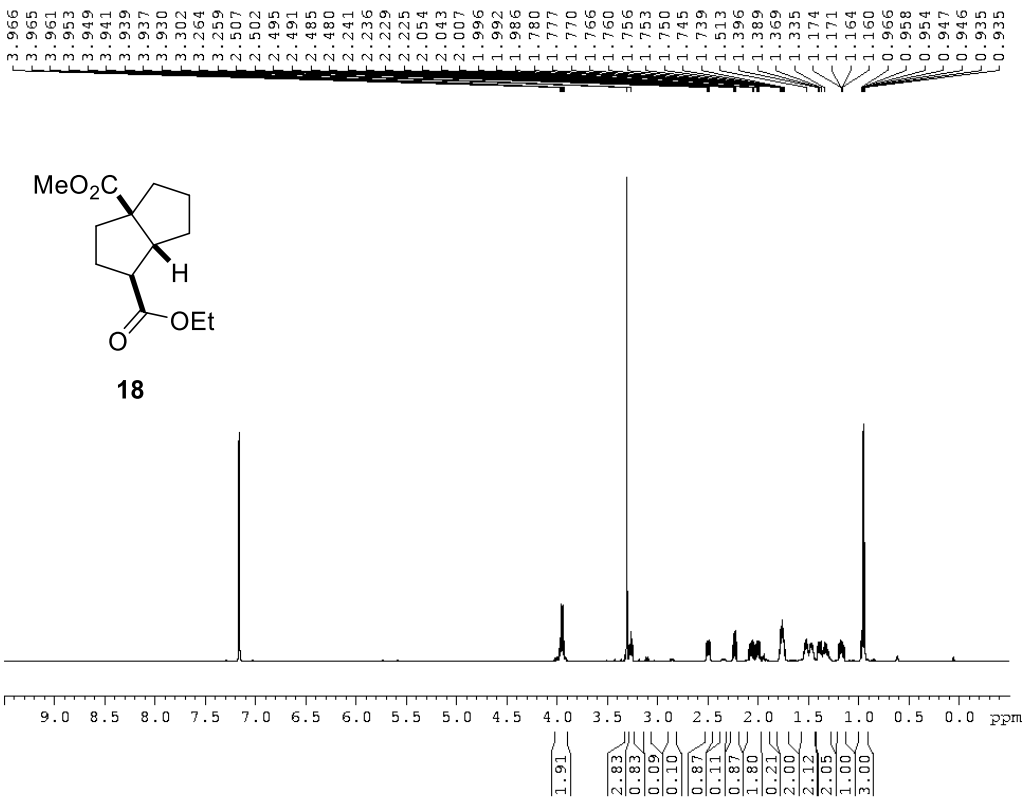

5.798
5.216
5.211
5.209
5.197
5.180
4.154
4.142
4.130
4.119
2.894
2.877
2.863
2.845
2.714
2.683
2.564
2.553
2.521
2.510
2.499
2.440
2.427
2.416
2.404
2.391
2.380
2.369
2.365
2.354
2.345
2.341
2.329
2.324
2.319
2.315
2.304
2.281
2.275
2.262
2.260
2.252
2.249
1.691
1.688
1.625
1.385
1.365
1.362
1.342
1.277
1.265
1.254

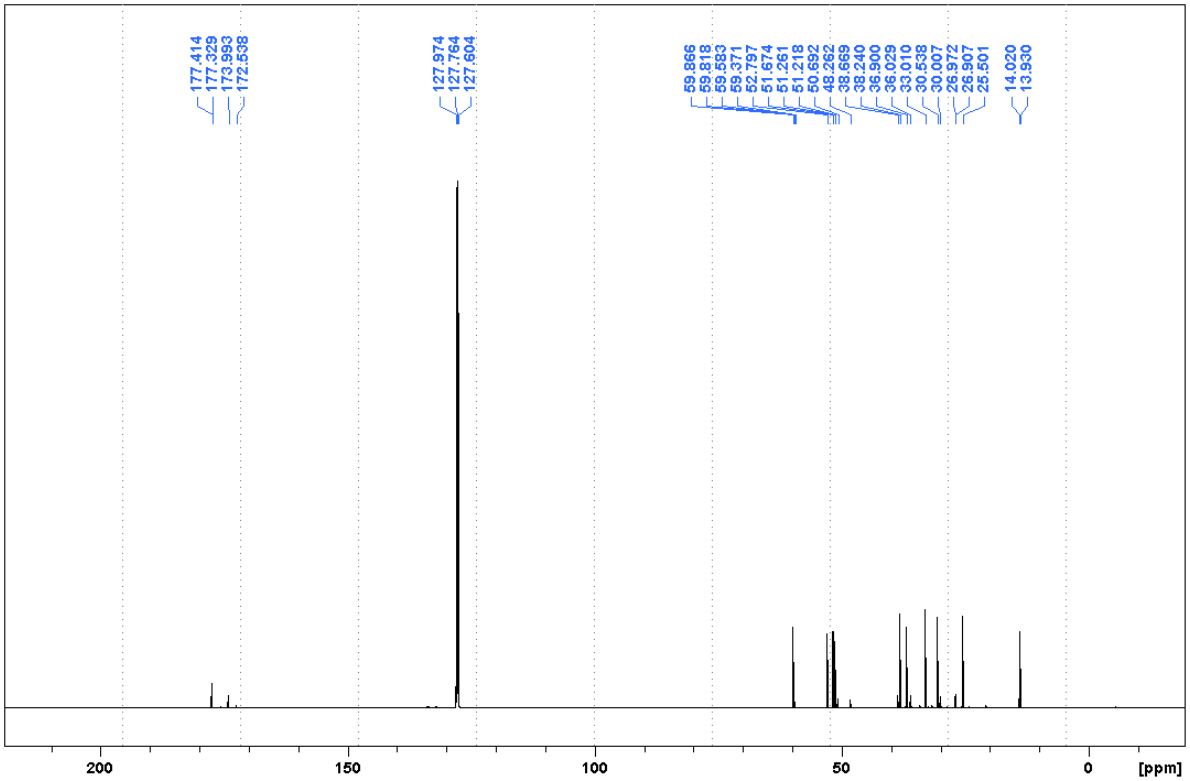

O
O
O
EtO

SI-6

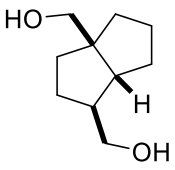

9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.80
1.93
0.50
1.04
1.98
6.31
0.57
0.58
0.77
0.56
3.08
1.15


177.076
176.630
172.388
172.174
131.925
131.582
120.254
119.894
96.615
95.636
77.284
77.072
76.860
60.508
44.123
44.048
43.830
43.266
42.276
40.809
40.526
40.024
38.913
38.701
37.339
35.609
35.302
33.901
14.248
200
150
100
50
0
[ppm]

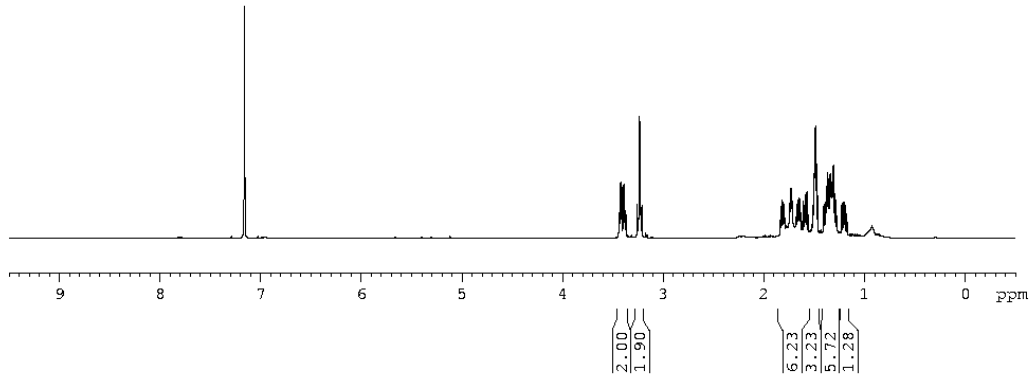

3.966
3.965
3.961
3.953
3.949
3.941
3.939
3.937
3.930
3.302
3.264
3.259
2.507
2.502
2.495
2.491
2.485
2.480
2.241
2.236
2.229
2.225
2.054
2.043
2.007
1.996
1.992
1.986
1.780
1.777
1.770
1.766
1.760
1.756
1.753
1.750
1.745
1.739
1.513
1.396
1.389
1.369
1.335
1.174
1.171
1.164
1.160
0.966
0.958
0.954
0.947
0.946
0.935
0.935
MeO2C
H
OEt
O
18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.91
2.83
0.83
0.09
0.10
0.87
0.11
0.87
1.80
0.21
2.00
2.12
2.05
1.00
3.00

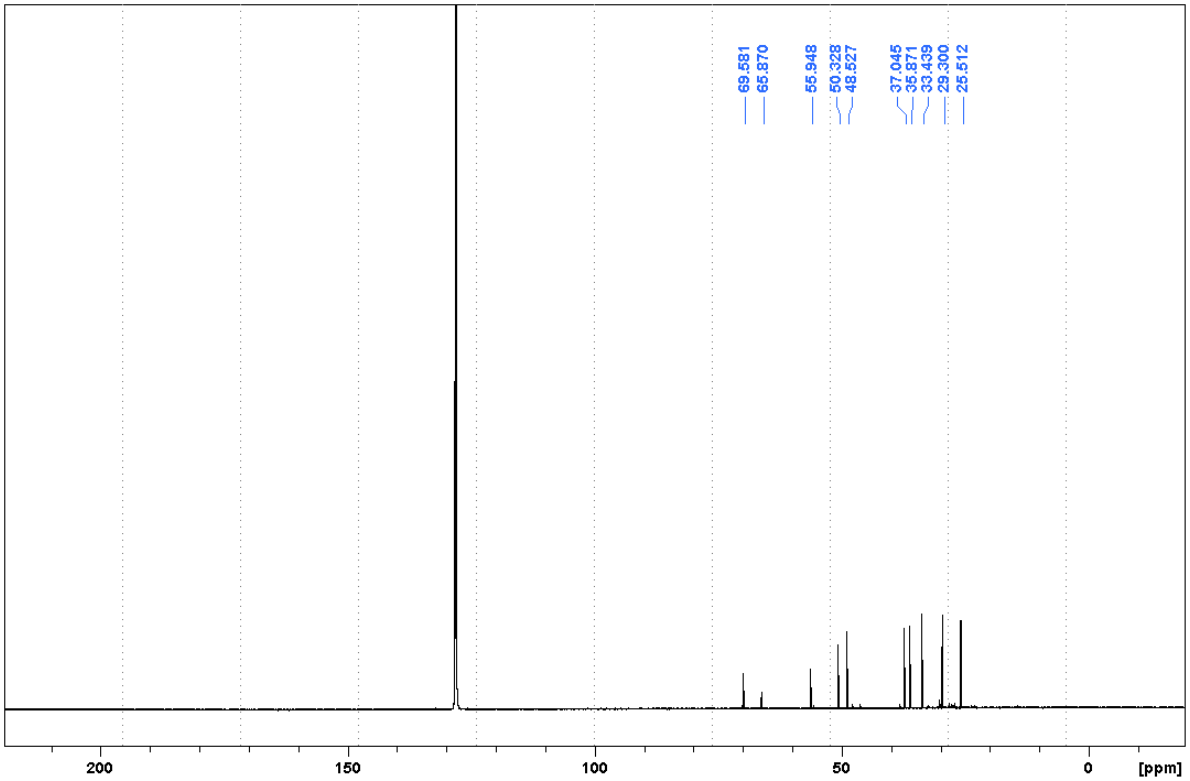

177.414
177.329
173.993
172.538
127.974
127.764
127.604
59.866
59.618
59.583
59.371
52.797
51.674
51.261
51.218
50.692
48.262
38.669
38.240
36.900
36.029
33.010
30.538
30.007
26.972
26.907
25.501
14.020
13.930
200
150
100
50
0
[ppm]


3.421
3.411
3.395
3.385
3.255
3.238
3.226
1.814
1.812
1.805
1.794
1.740
1.733
1.728
1.721
1.716
1.665
1.658
1.646
1.638
1.603
1.590
1.583
1.570
1.500
1.497
1.494
1.486
1.478
1.473
1.464
1.400
1.388
1.386
1.379
1.373
1.367
1.365
1.358
1.353
1.346
1.342
1.337
1.331
1.326
1.322
1.315
1.311
1.306
1.295
1.285
1.221
1.210
1.200

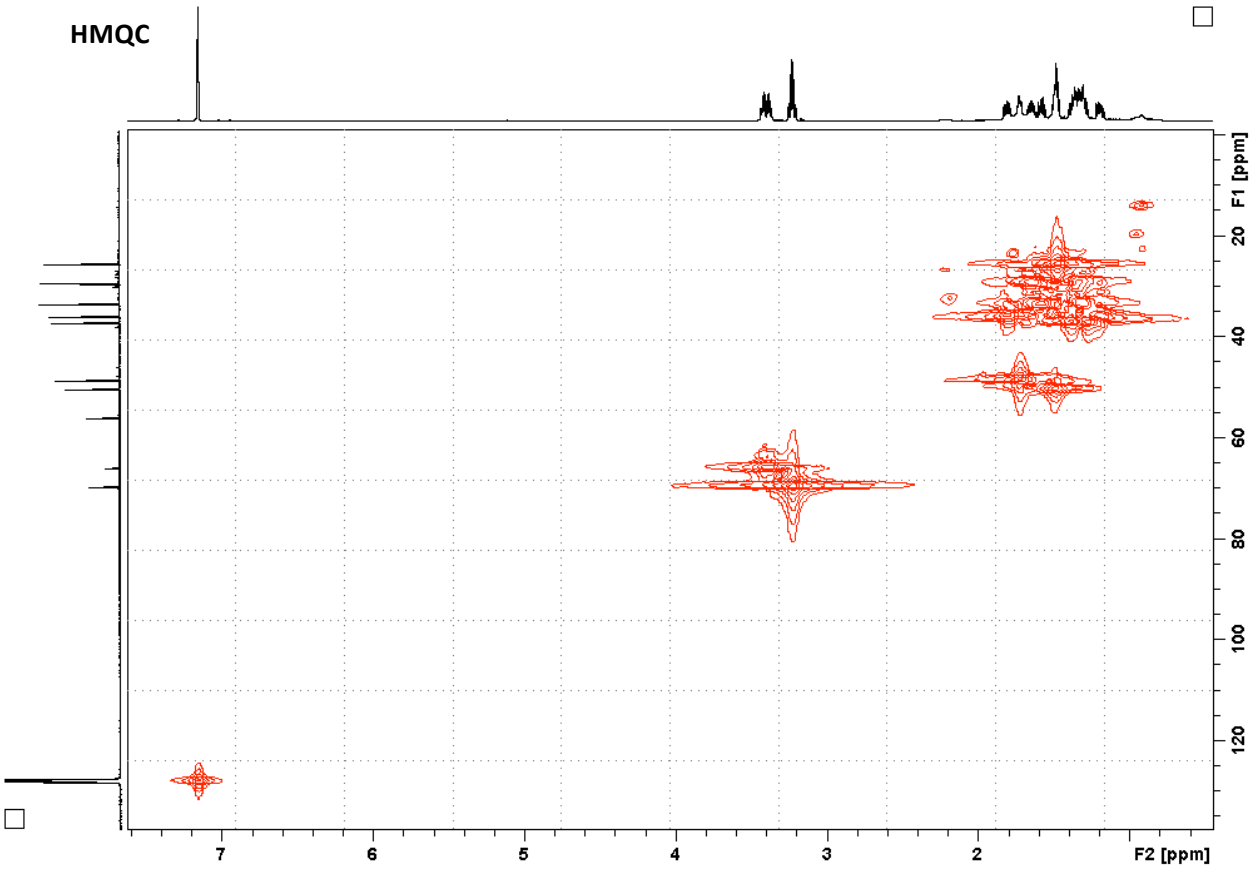

HO
H
OH

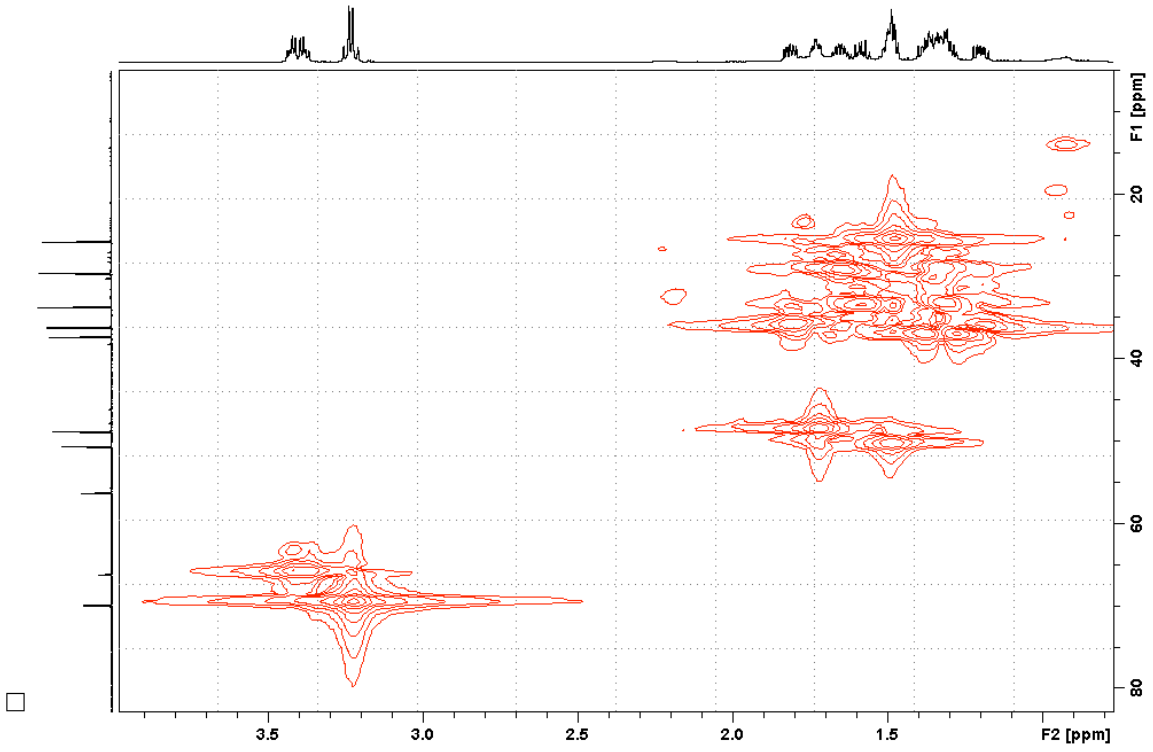
SI-7

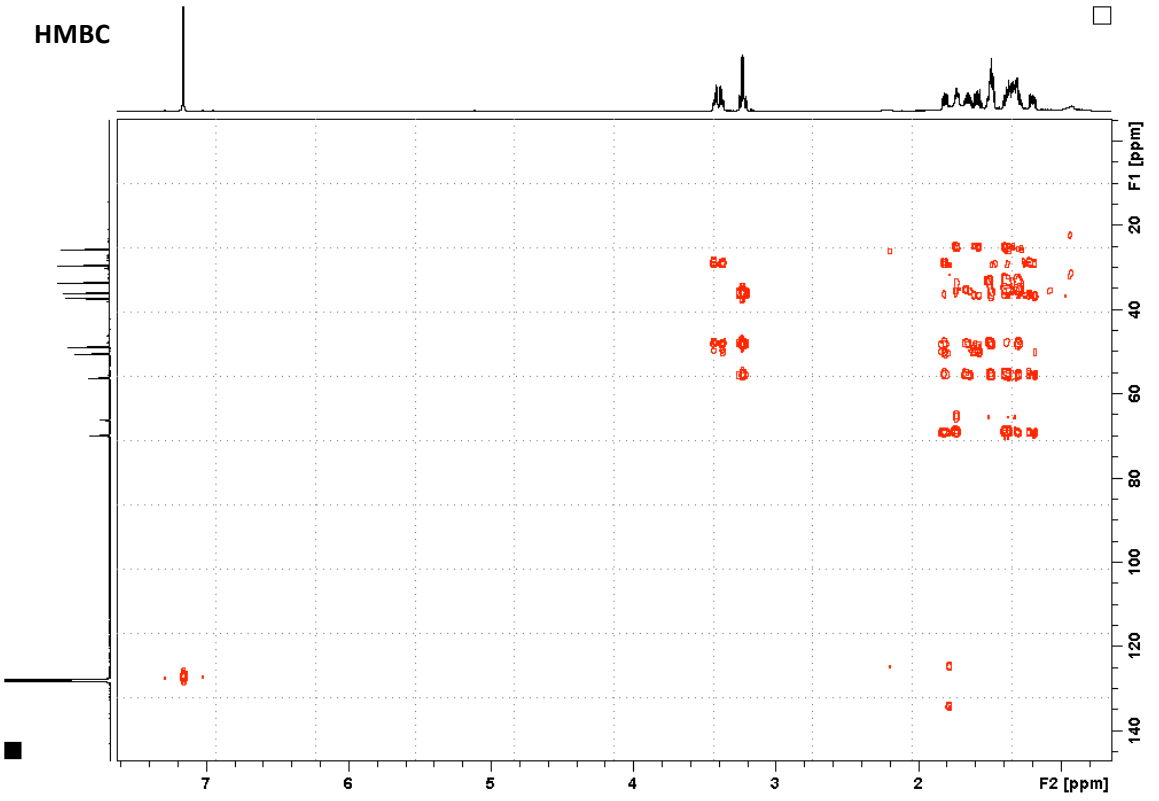

9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.90
6.23
3.23
5.72
1.28

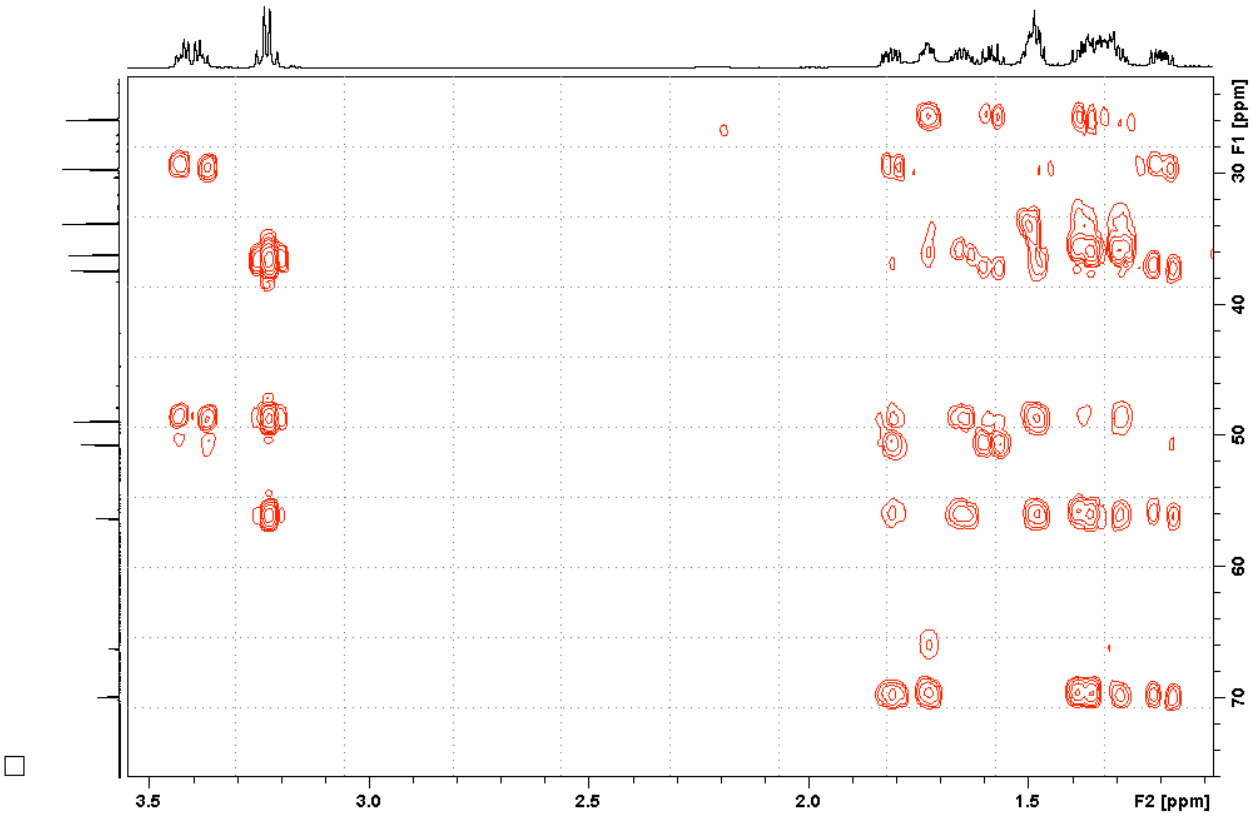

69.581
65.870
55.948
50.328
48.527
37.045
35.871
33.439
29.300
25.512
200
150
100
50
0
[ppm]

HMQC

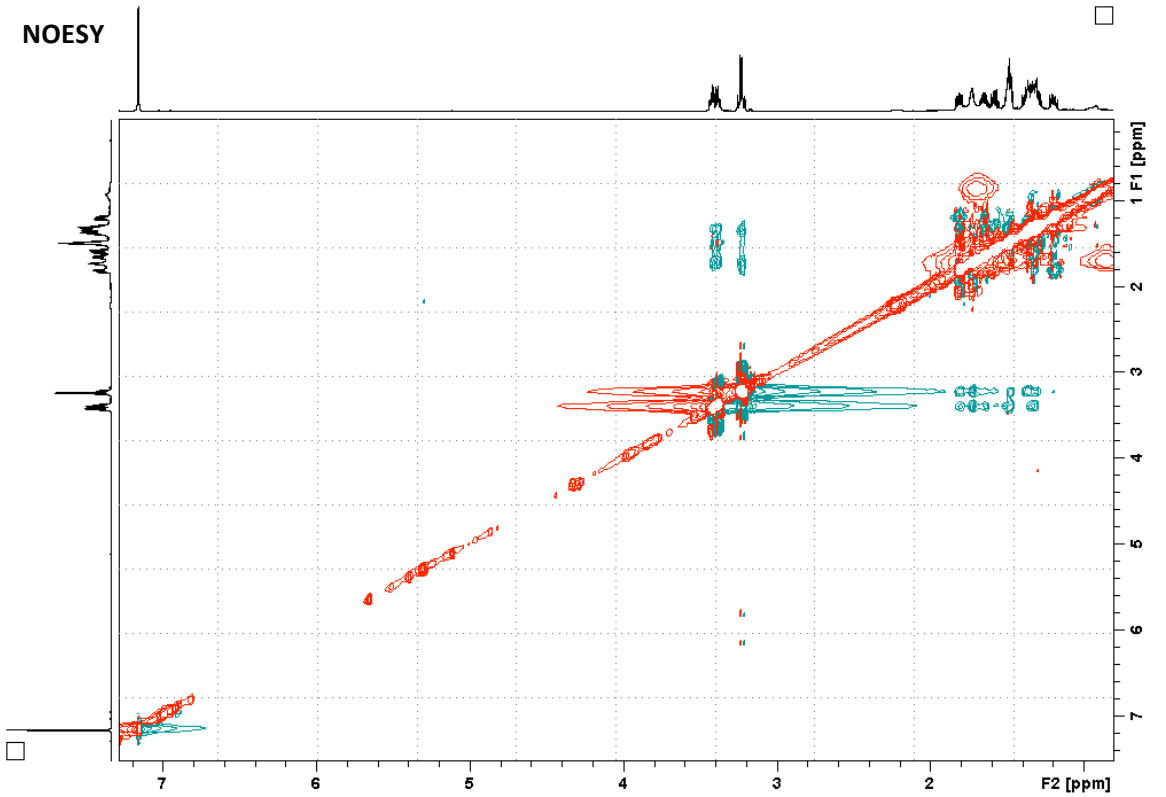

F1 [ppm]
20
40
60
80
100
120
7
6
5
4
3
2
F2 [ppm]

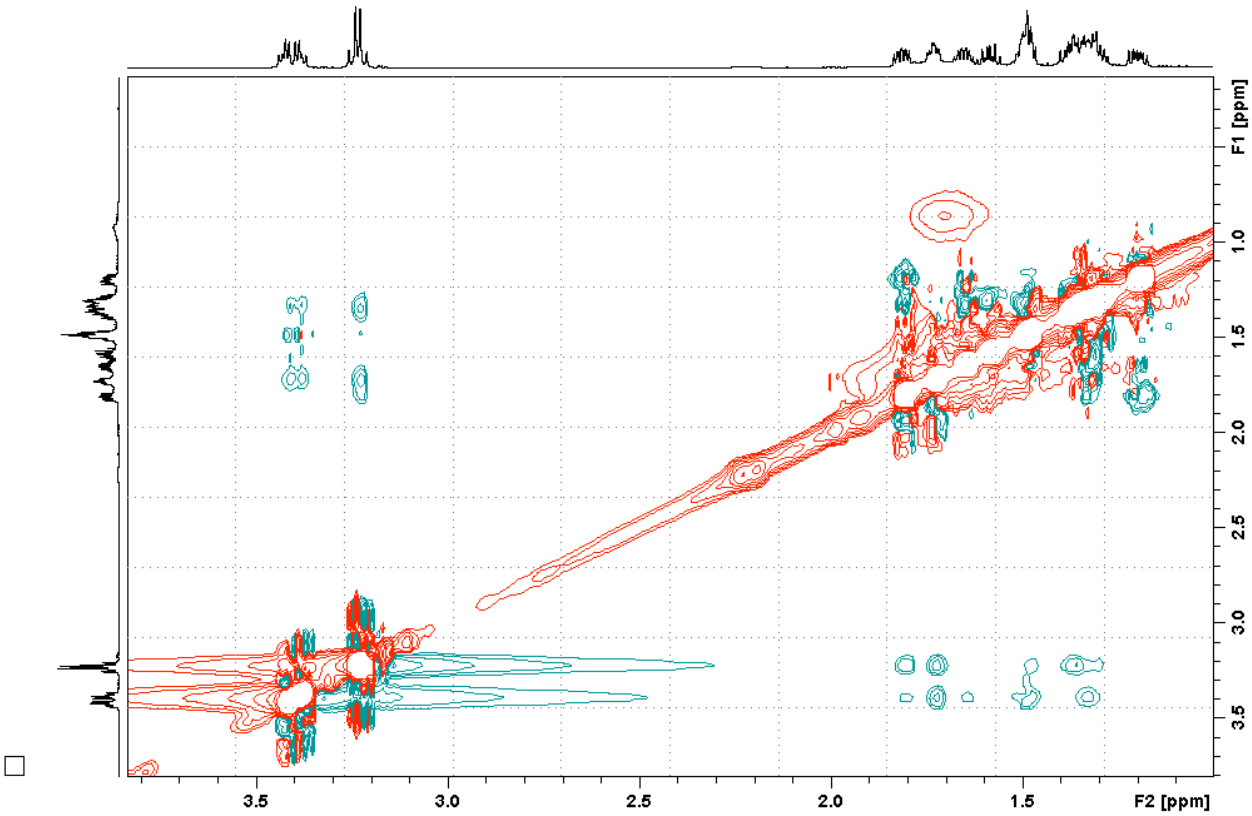

F1 [ppm]
20
40
60
80
3.5
3.0
2.5
2.0
1.5
F2 [ppm]


HMBC
F1 [ppm]
20
40
60
80
100
120
140
7
6
5
4
3
2
F2 [ppm]

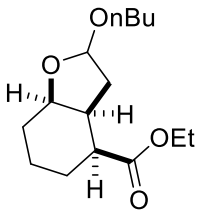

F1 [ppm]
30
40
50
60
70
3.5
3.0
2.5
2.0
1.5
F2 [ppm]

NOESY


F1 [ppm]
1
2
3
4
5
6
7
7
6
5
4
3
2
F2 [ppm]

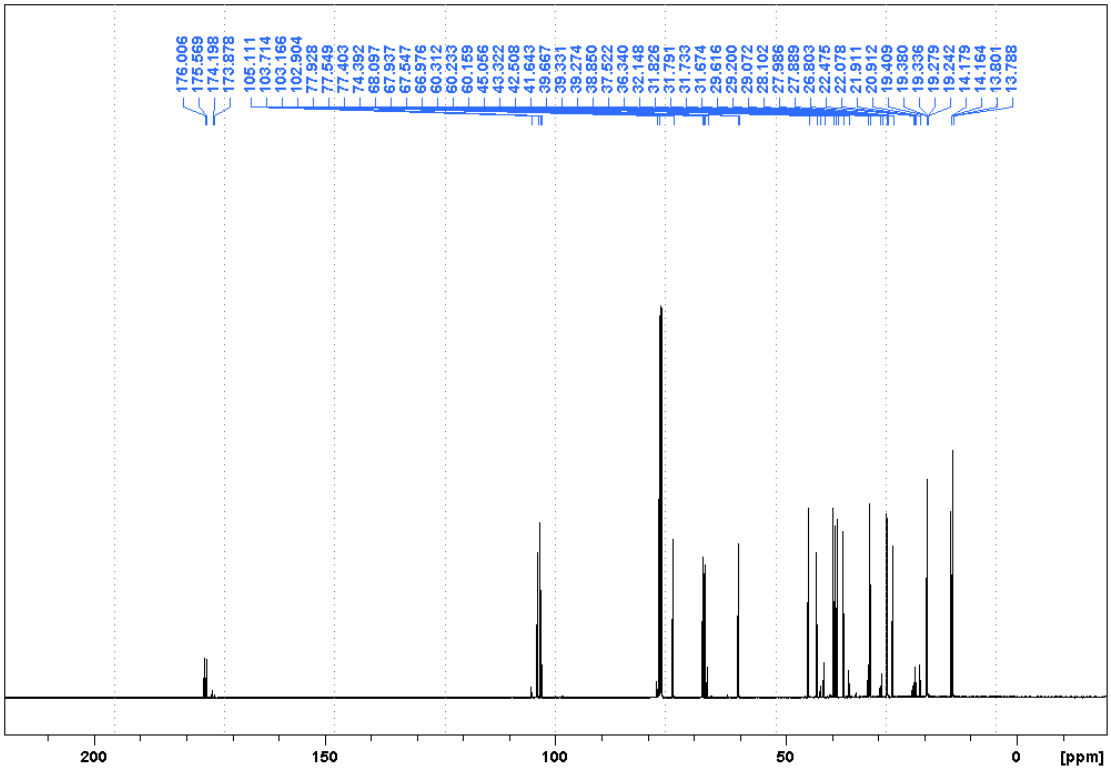

F1 [ppm]
1.0
1.5
2.0
2.5
3.0
3.5
3.5
3.0
2.5
2.0
1.5
F2 [ppm]


5.065
5.052
4.149
4.143
4.141
4.139
4.132
4.125
4.123
4.122
4.114
4.106
3.705
3.699
3.681
3.395
3.364
2.165
2.130
1.859
1.621
1.581
1.576
1.573
1.570
1.564
1.562
1.553
1.548
1.545
1.543
1.540
1.537
1.531
1.526
1.382
1.379
1.365
1.360
1.346
1.342
1.268
1.266
1.250
1.248
1.232
1.230
0.936
0.923
0.918
0.905
0.900
0.886


OnBu
O
H
H
OEt
H
O

20

9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.19
0.97
0.20
5.19
1.00
2.21
2.19
0.18
0.99
0.47
1.95
2.20
3.02
4.23
0.82
9.77
6.39
7.48
6.83


176.006
175.569
174.198
173.878
105.111
103.714
103.166
102.904
77.928
77.549
77.403
74.392
68.097
67.937
67.547
66.976
60.312
60.233
60.159
45.056
43.322
42.508
41.643
39.667
39.331
39.274
38.850
37.622
36.340
32.148
31.826
31.791
31.733
31.674
29.616
29.200
29.072
28.102
27.986
27.889
26.803
22.475
22.078
21.911
20.912
19.409
19.380
19.336
19.279
19.242
14.179
14.164
13.801
13.788
200
150
100
50
0
[ppm]


4.628
4.622
4.616
4.610
4.187
4.184
4.181
4.175
4.172
4.163
4.160
4.154
4.151
4.148
2.748
2.737
2.720
2.709
2.672
2.665
2.654
2.647
2.428
2.400
2.281
2.274
2.261
2.255
2.243
2.236
2.219
2.014
2.009
1.992
1.986
1.697
1.692
1.676
1.670
1.664
1.645
1.630
1.624
1.621
1.599
1.540
1.518
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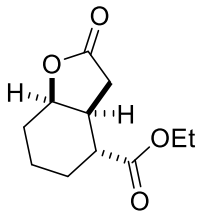
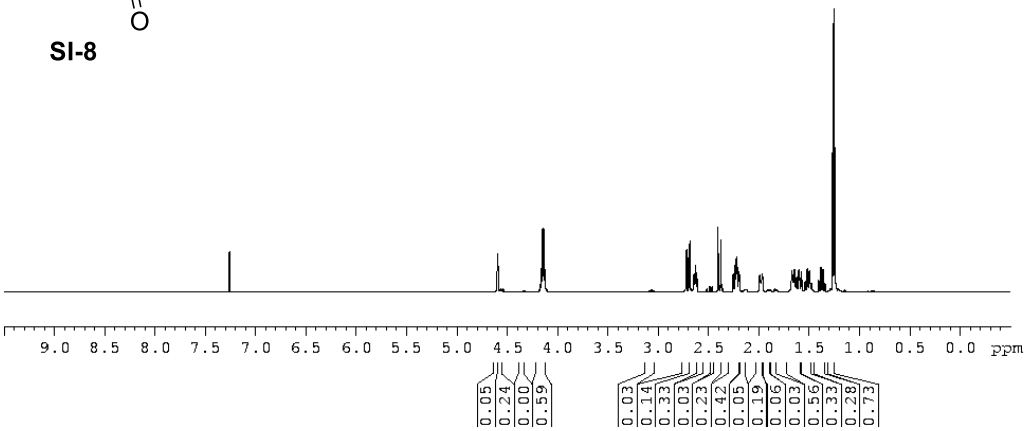
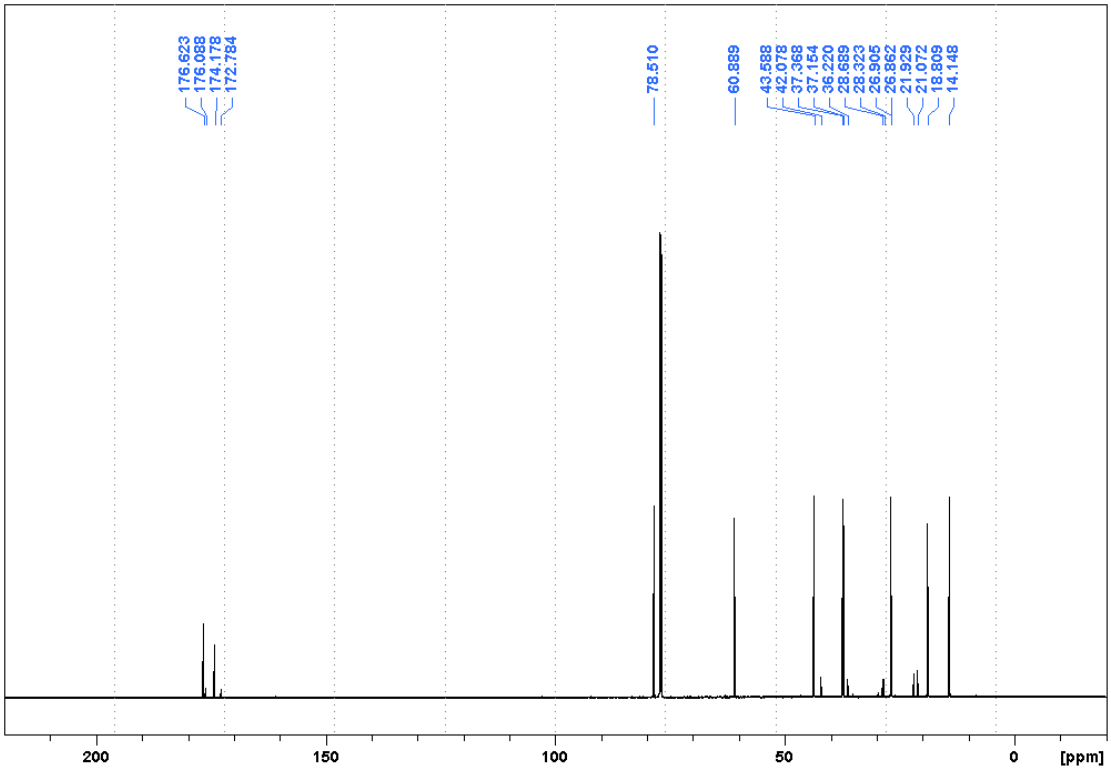
1.404
1.388
1.382
1.289
1.277
1.265

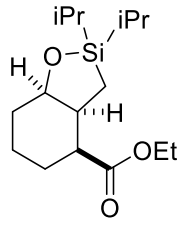

O
O
H
H
OEt
O

SI-8

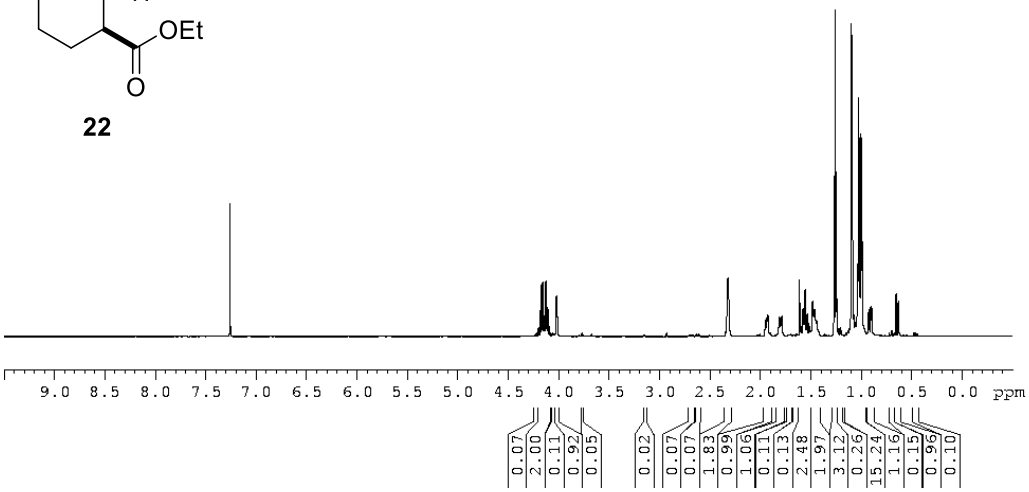

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.05
0.24
0.00
0.59
0.03
0.14
0.33
0.03
0.23
0.42
0.05
0.19
0.06
0.03
0.56
0.33
0.28
0.73

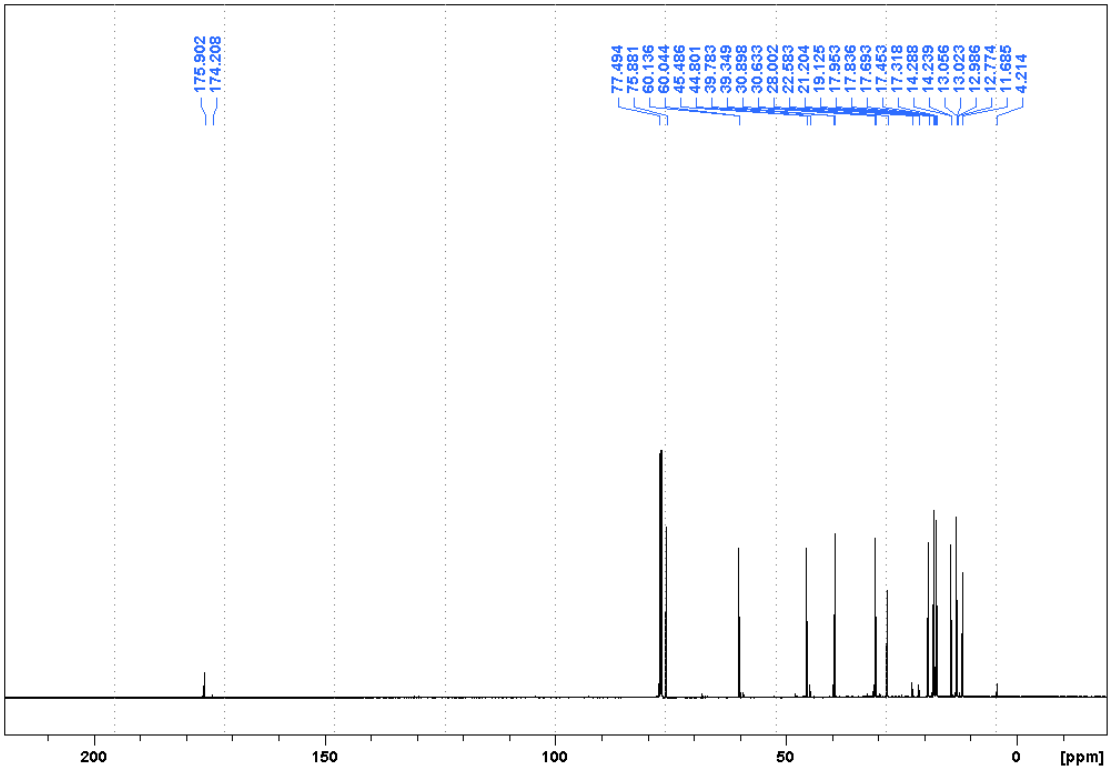

176.623
176.088
174.178
172.784
78.510
60.889
43.588
42.078
37.368
37.154
36.220
28.689
28.323
26.905
26.862
21.929
21.072
18.809
14.148
200
150
100
50
0
[ppm]

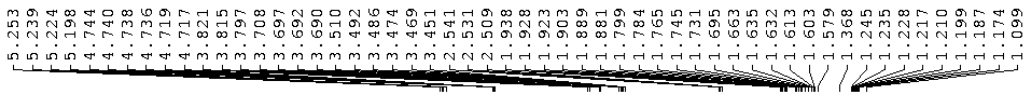

4.183
4.171
4.165
4.153
4.134
4.122
4.116
4.110
4.104
4.021
4.016
2.329
2.324
2.319
2.315
1.926
1.610
1.574
1.569
1.556
1.554
1.535
1.484
1.477
1.471
1.463
1.460
1.455
1.268
1.256
1.244
1.097
1.095
1.092
1.085
1.078
1.041
1.039
1.034
1.029
1.024
1.016
1.009
1.001
0.992
0.986
0.930
0.918
0.905
0.893
0.657
0.654
0.631
0.628

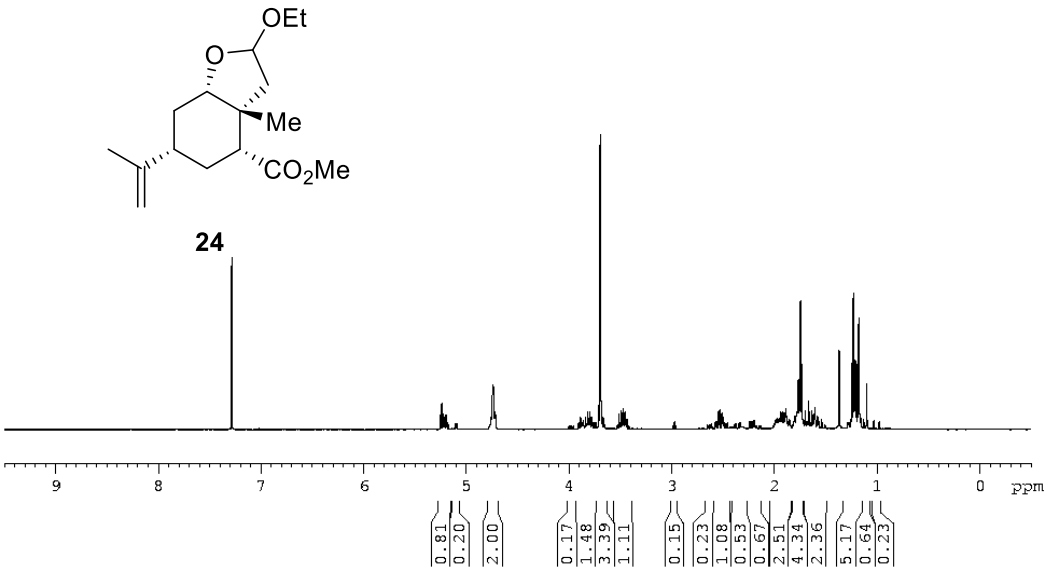

iPr
iPr
Si
O
H
H
OEt
O

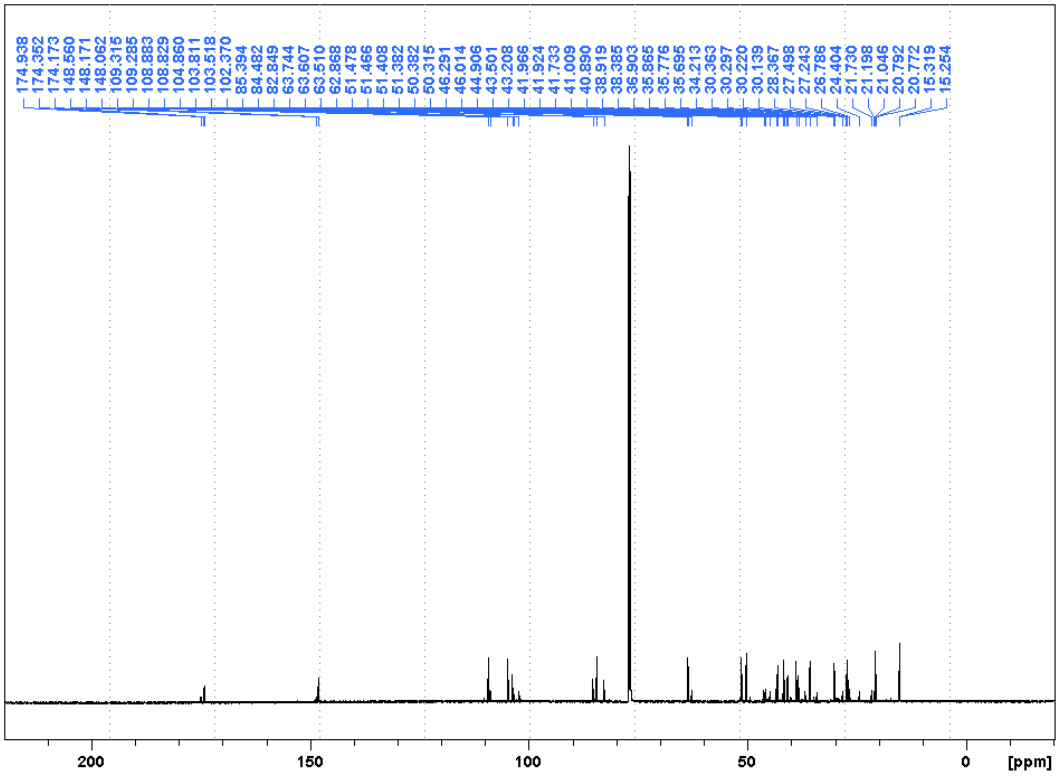
22

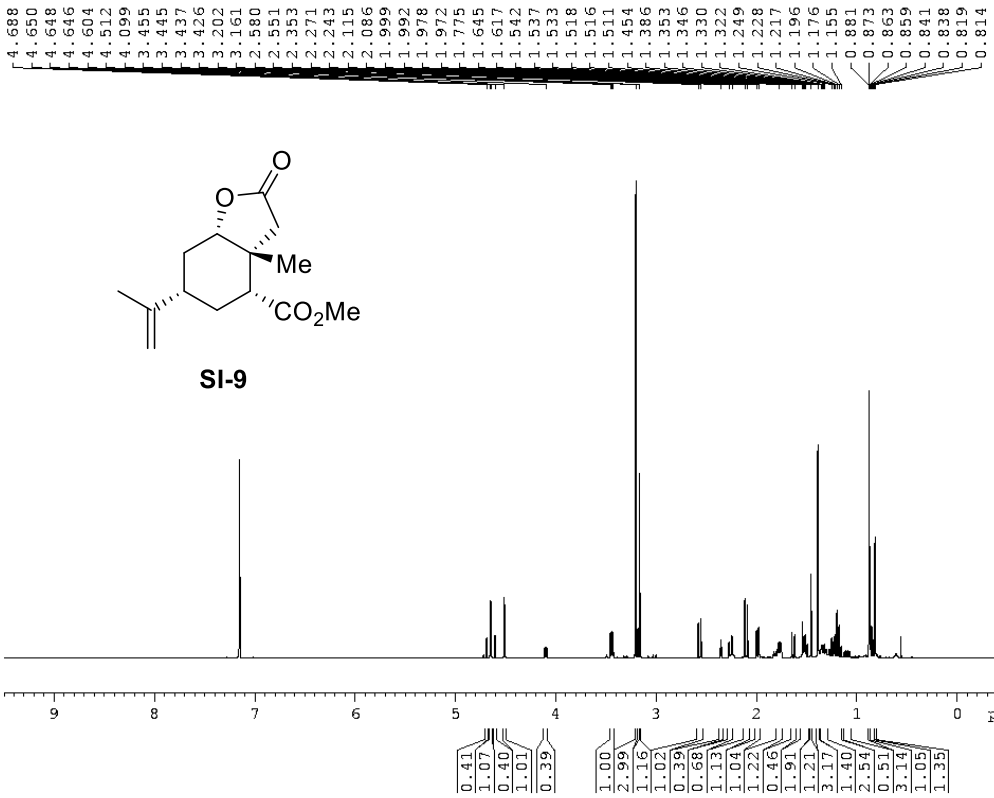

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.07
2.00
0.11
0.92
0.05
0.02
0.07
0.07
1.83
0.99
1.06
0.11
0.13
2.48
1.97
3.12
0.26
15.24
1.16
0.15
0.96
0.10

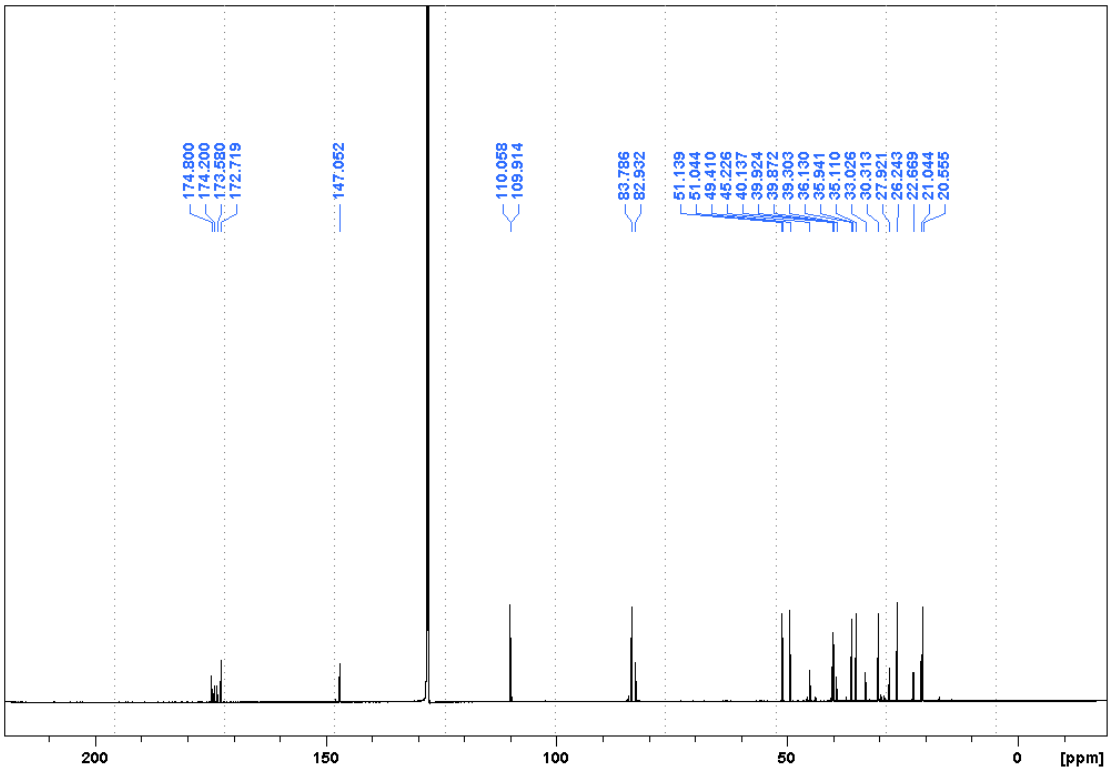

175.902
174.208
77.494
75.881
60.136
60.044
45.486
44.801
39.783
39.349
30.898
30.633
28.002
22.583
21.204
19.125
17.953
17.836
17.693
17.453
17.318
14.288
14.239
13.056
13.023
12.986
12.774
11.685
4.214
200
150
100
50
0
[ppm]


5.253
5.239
5.224
5.198
4.744
4.740
4.738
4.736
4.719
4.717
3.821
3.815
3.797
3.708
3.697
3.692
3.690
3.510
3.492
3.486
3.474
3.469
3.451
2.541
2.531
2.509
1.938
1.928
1.923
1.903
1.889
1.881
1.799
1.784
1.765
1.745
1.731
1.695
1.663
1.635
1.632
1.613
1.603
1.579
1.368
1.245
1.235
1.228
1.217
1.210
1.199
1.187
1.174
1.099

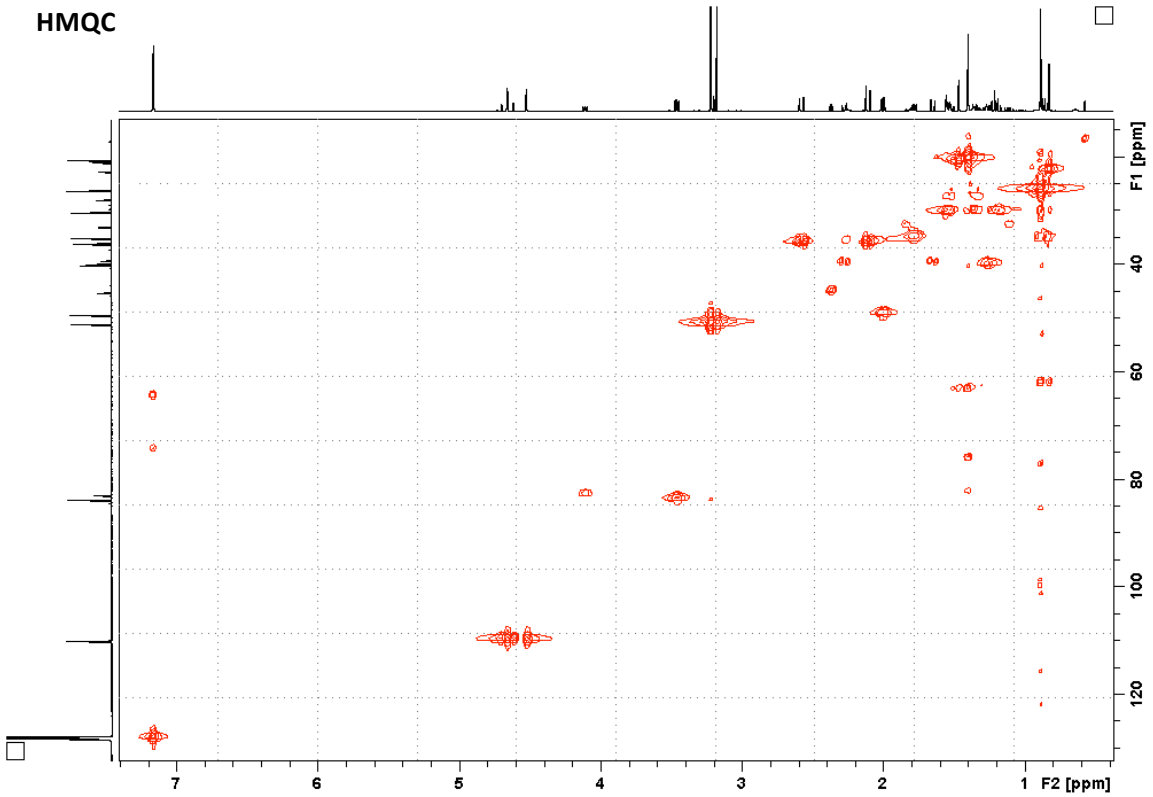

OEt
O
Me
CO2Me
24
9
8
7
6
5
4
3
2
1
0
ppm
0.81
0.20
2.00
0.17
1.48
3.39
1.11
0.15
0.23
1.08
0.53
0.67
2.51
4.34
2.36
5.17
0.64
0.23


174.938
174.352
174.173
148.560
148.171
148.062
109.315
109.285
108.883
108.829
104.860
103.811
103.518
102.370
85.394
84.482
82.849
63.744
63.607
63.510
62.868
51.478
51.466
51.408
51.382
50.382
50.315
46.291
46.014
44.906
43.501
43.208
41.966
41.924
41.733
41.009
40.890
38.919
38.385
36.903
35.865
35.776
35.695
34.213
30.363
30.297
30.220
30.139
28.367
27.498
27.243
26.786
24.404
21.730
21.198
21.046
20.792
20.772
15.319
15.254
200
150
100
50
0
[ppm]

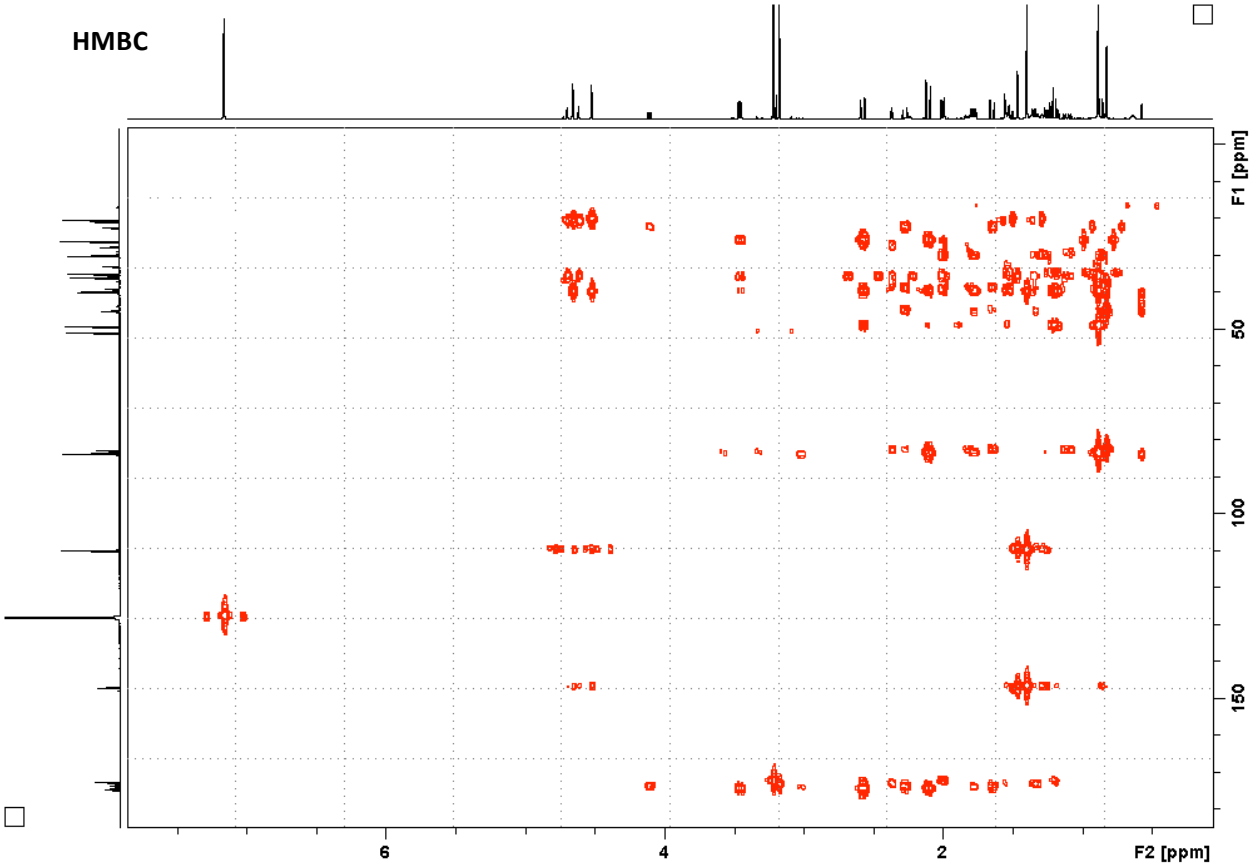

4.688
4.650
4.648
4.646
4.604
4.512
4.099
3.455
3.445
3.437
3.426
3.202
3.161
2.580
2.551
2.353
2.271
2.243
2.115
2.086
1.999
1.992
1.978
1.972
1.775
1.645
1.617
1.542
1.537
1.533
1.518
1.516
1.511
1.454
1.386
1.353
1.346
1.330
1.322
1.249
1.228
1.217
1.196
1.176
1.155
0.881
0.873
0.863
0.859
0.841
0.838
0.819
0.814
O
O
Me
CO2Me
SI-9
9
8
7
6
5
4
3
2
1
0
ppm
0.41
1.07
0.40
1.01
0.39
1.00
2.99
1.16
1.02
0.39
0.68
1.13
1.04
1.22
0.46
1.91
1.21
3.17
1.40
2.54
0.51
3.14
1.05
1.35


174.800
174.200
173.580
172.719
147.052
110.058
109.914
83.786
82.932
51.139
51.044
49.410
45.226
40.137
39.924
39.872
39.303
39.130
38.941
35.110
33.026
30.313
27.921
26.243
22.669
21.044
20.555
200
150
100
50
0
[ppm]

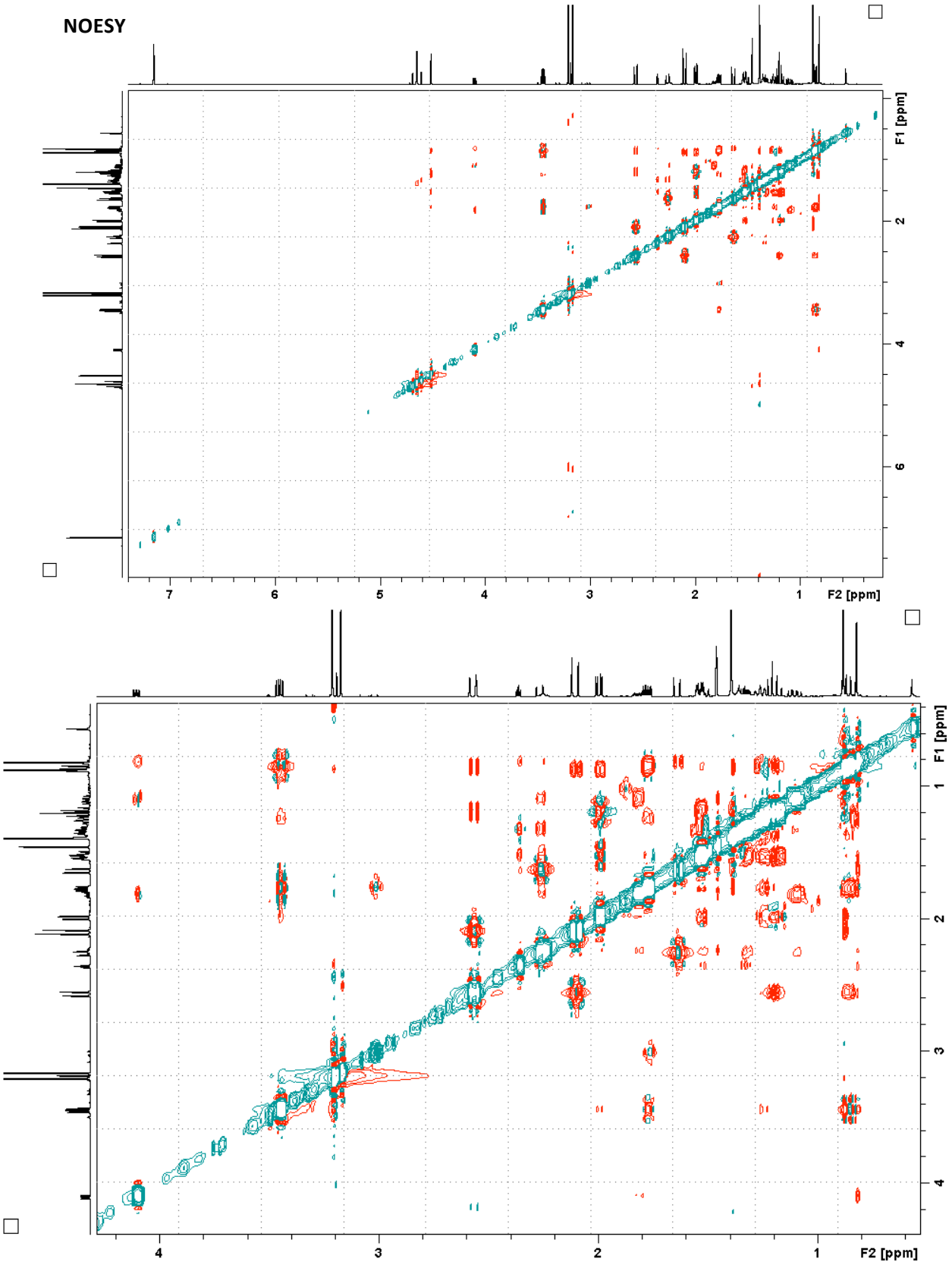
HMQC

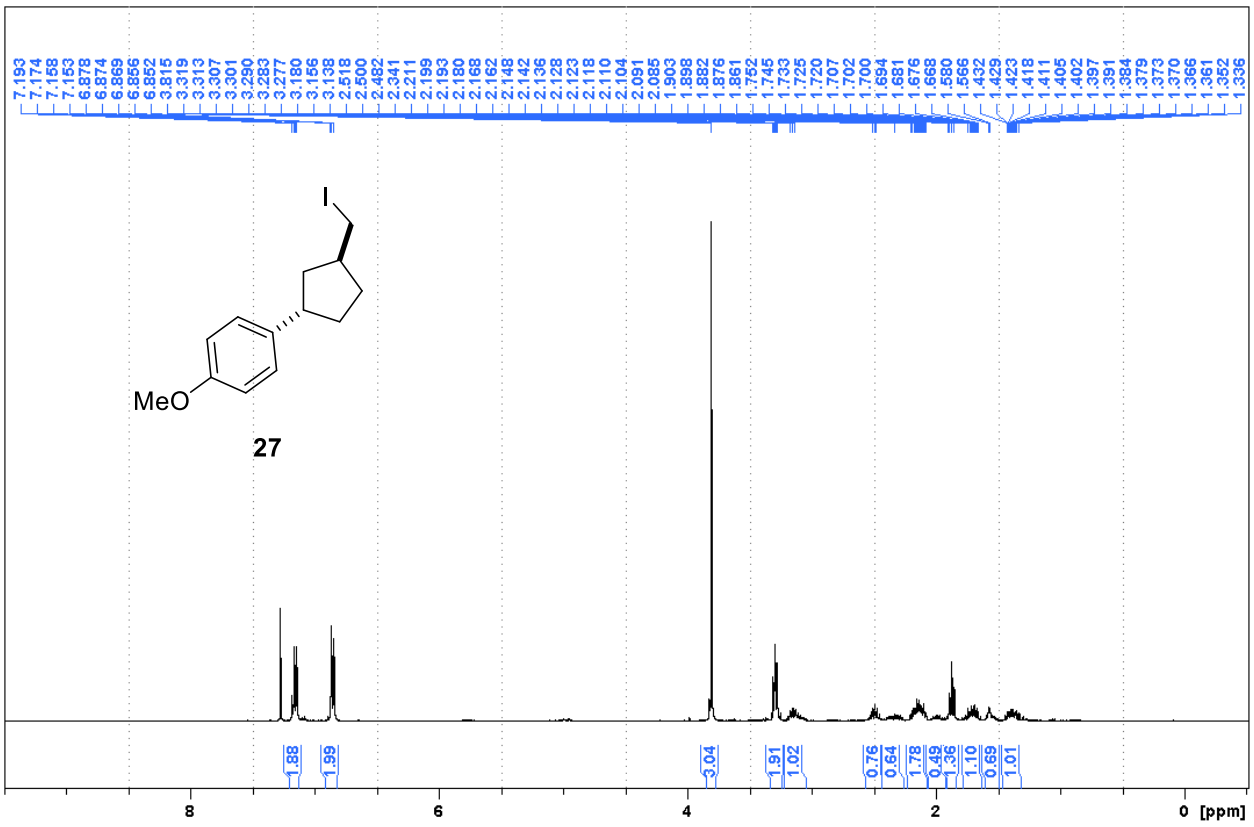

F1 [ppm]
40
60
80
100
120
7
6
5
4
3
2
1
F2 [ppm]

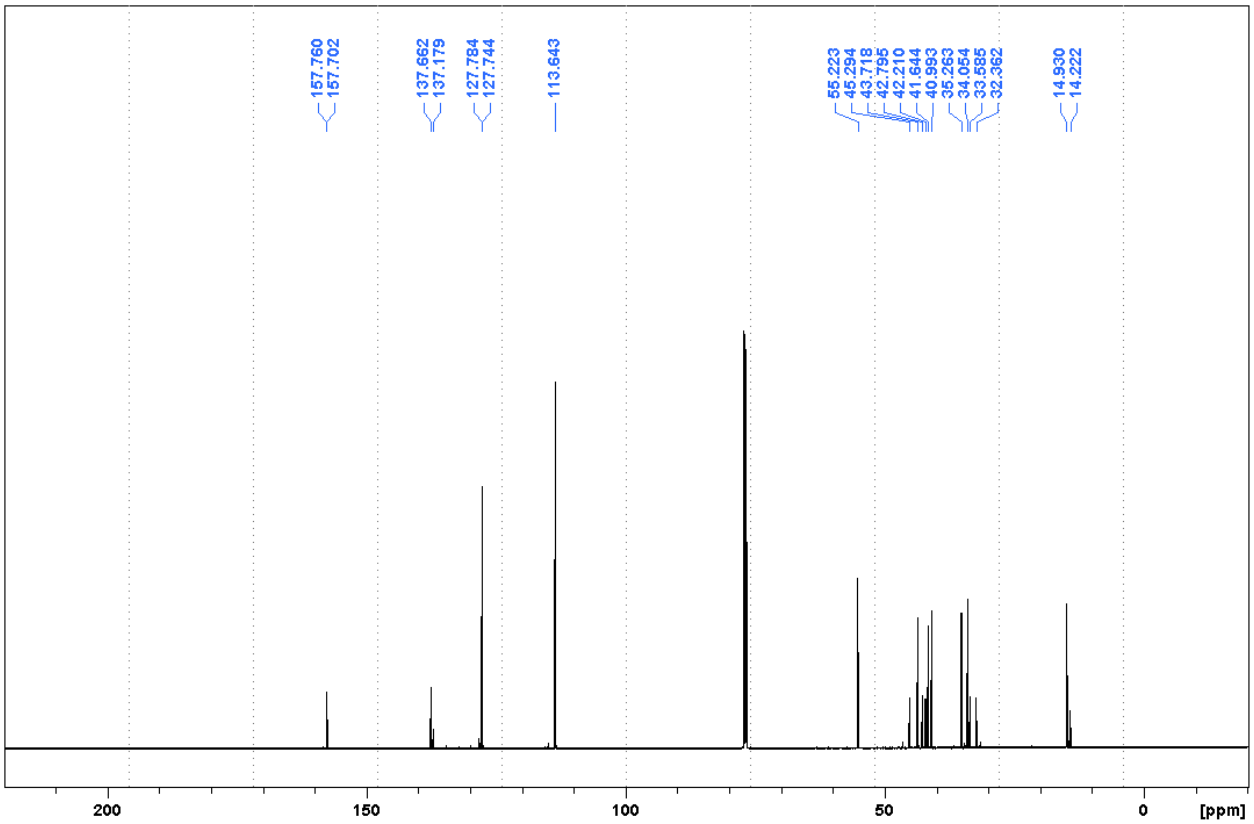
HMBC


F1 [ppm]
50
100
150
6
4
2
F2 [ppm]

NOESY




7.193
7.174
7.158
7.153
6.878
6.874
6.869
6.856
6.852
3.815
3.319
3.313
3.307
3.301
3.290
3.283
3.277
3.180
3.156
3.138
2.518
2.500
2.482
2.341
2.211
2.199
2.193
2.180
2.168
2.162
2.148
2.142
2.136
2.128
2.123
2.118
2.110
2.104
2.091
2.085
1.903
1.898
1.882
1.876
1.861
1.752
1.745
1.733
1.725
1.720
1.707
1.702
1.700
1.694
1.681
1.676
1.668
1.580
1.566
1.432
1.429
1.423
1.418
1.411
1.405
1.402
1.397
1.391
1.384
1.379
1.373
1.370
1.366
1.361
1.352
1.336
I
MeO
27
1.88
1.99
3.04
1.91
1.02
0.76
0.64
1.78
0.49
1.36
1.10
0.69
1.01
8
6
4
2
0
[ppm]


157.760
157.702
137.662
137.179
127.784
127.744
113.643
55.223
45.294
43.718
42.795
42.210
41.644
40.993
35.263
34.054
33.585
32.362
14.930
14.222
200
150
100
50
0
[ppm]