Gold(I)-Catalyzed Enantioselective Polycyclization Reactions

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Supporting Information

General Information

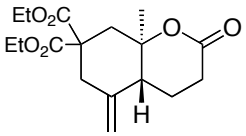
Unless otherwise stated, all commercial materials were used without further purification. Solvents were purchased from EM-Science and were dried by passage through activated alumina, except *meta*-xylene. Solvents used in polycyclization reactions were stored over 4Å molecular sieves. Silver tetrafluoroborate ($AgBF_4$), silver perchlorate ($AgClO_4$) and silver hexafluoroantimonate ($AgSbF_6$) were obtained from Aldrich Chemical Company and stored in the dark under an inert atmosphere. Silver salts kept under argon in a sealed vial and protected from light could be used several times before succumbing to deliquescence. Bisphosphine ligands were obtained from Solvias and Takasago. $AuCl_3$ was provided by Johnson Matthey. Chiral digold chloride complexes were prepared as previously described by previous work from this lab.[1] Complexes used for ligand optimization provided spectra in agreement with those previously described.[2] Except for the inhomogenous mixture arising in the synthesis of **2c**, small scale reactions were not stirred beyond a brief mixing upon addition of the catalyst. Thin layer chromatography (TLC) analysis of reaction mixtures was performed on Merck silica gel 60 F_{254} TLC plates and flash chromatography was carried out on Sorbent Technologies 40-63 D 60 Å silica gel. ^1H and ^{13}C NMR spectra were recorded with Bruker AVQ-400, AVB-400, AV-500 or AV-600 spectrometers using either $CDCl_3$ or C_6D_6, and are internally referenced to residual protio solvent signals. ^1H NMR multiplicities are reported as follows: m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet. All ^{13}C NMR spectra were obtained with proton decoupling. Enantiomeric ratios were measured by chiral HPLC employing a Shimidzu VP Series instrument equipped with SPD-M10A microdiode array detector using a Chiral PAK AD-H column.

General Procedure for Enantioselective Polycyclizations

A mixture of $AgSbF_6$ (0.8 mg, 2.2 μmol) and the bisphosphine digold(I) chloride complex (3.32 mg, 2.22 μmol) is suspended in 300 μL of *m*–xylene in a sealed vial, and sonicated or stirred

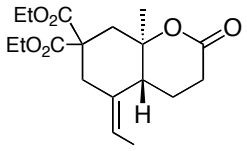
magnetically for 15 min at room temperature). The resulting suspension is filtered through a glass microfiber plug directly into a solution of substrate (15 mg, 0.044 mmol) in 600 μl of *m*-xylene, thourough mixing is ensured and the resulting homogenous solution is allowed stand until such time as the substrate was fully consumed as judged by TLC or ^{1}H NMR analysis. Determination of yield was made by calibration with an internal standard (9-bromophenanthrene) prior to addition of catalyst. Upon consumption of the starting material, an aliquot containing ca. 4 mg. of crude product was concentrated under a stream of N_2 until a thick oil was obtained. This was dissolved in 100 μL C_6D_6 and concentrated under flowing N_2 twice, providing a residual oil free from excessive *m*-xylene which was subsequently analyzed by ^{1}H NMR. The product was isolated in analytically pure form by evaporation of the reaction mixture to a volume of ca. 100 μL which was then eluted through a short silica column. Products **2a** and **15** provided crystals suitable for x-ray analysis, permitting assignment of the absolute stereochemistry. Notably, cyclization by the catalyst derived from (R)-DTB,MeO-Biphep(AuCl)$_2$ proceeded with the same sense of enantioselectivity in both cases. Crystallographic data provided

Experimental Details

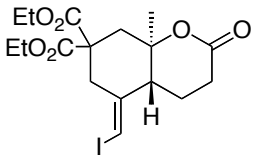


(4R,8R)-Diethyl-8-methyl-5-methylene-2-oxohexahydro-2*H*-chromene-7,7(3*H*)-dicarboxylate (2a). Prepared from **1a** in accord with the general procedure for cyclization. Chromatography (1:1 hexanes : diethyl ether) provided a clear oil which was recrystallized by slow evaporation (3:2 dichloromethane : hexanes) to provide transparent crystals suitable for x-ray analysis, crystallographic data provided. **^{1}H NMR** (600 MHz, C_6D_6): δ 7.07 (dd, *J* = 7.0, 1.4 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.87-6.85 (m, 1H), 5.16 (d, *J* = 1.0 Hz, 1H), 4.73 (d, *J* = 1.1 Hz, 1H), 3.97-3.83 (m, 4H), 3.38 (dd, *J* = 13.5, 2.2 Hz, 1H), 3.16 (dd, *J* = 13.6, 2.1 Hz, 1H), 2.74 (d, *J* = 13.7 Hz, 1H), 2.58 (dd, *J* = 16.0, 12.8 Hz, 1H), 2.36 (dd, *J* = 16.1, 4.6 Hz, 1H), 2.24 (s, 1H), 1.04 (s, 3H), 0.86 (t, *J* = 8.0 Hz, 6H). **^{13}C NMR** (151 MHz, C-

$_6D_6$): δ 170.67, 169.91, 152.81, 142.91, 129.65, 121.06, 120.0`4, 117.39, 111.03, 99.96, 76.53, 61.29, 60.84, 54.51, 43.92, 43.16, 40.00, 24.38, 17.24, 13.49. **MS** HRMS (ESI) calc. for $[C_{21}H_{27}O_5]^+$: 359.1850, found: 358.1853. **HPLC** (95:5 hexanes : isopropanol, 0.7 mL/min, λ_{max}= 205 nm). t_R 27.58 min (major), 25.31 (minor): 91% *ee.*

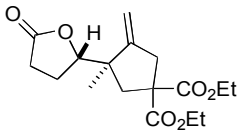


(4R,8R,Z)-diethyl-5-ethylidene-8a-methyl-2-oxohexahydro-2H-chromene-7,7(3H)-dicarboxylate (2b). Prepared from **1b** in accord with the general procedure for cyclization. Flash chromatography (1:1 hexanes : diethyl ether) provided the lactone as a clear oil. **^{1}H-NMR** (600 MHz, C_6D_6): δ 5.55 (t, *J* = 7.0 Hz, 1H), 5.30 (td, *J* = 7.0, 1.2 Hz, 1H), 5.27 (d, *J* = 6.9 Hz, 1H), 4.04-3.93 (m, 4H), 3.38 (s, 5H), 3.23 (s, 2H), 3.14 (d, *J* = 2.7 Hz, 2H), 2.63 (dt, *J* = 16.8, 8.2 Hz, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.77 (dt, *J* = 5.4, 2.7 Hz, 1H), 1.61 (s, 3H), 1.52 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (150 MHz, C_6D_6): δ 170.59, 169.81, 167.36, 131.57, 124.38, 82.75, 61.50, 60.91, 55.01, 48.10, 43.88, 43.61, 30.73, 21.35, 21.22, 13.61, 13.24. **MS** HRMS (ESI) calc. for $[C_{18}H_{27}O_6]^+$**:** 339.1802, found: 339.1809. **HPLC** (95:5 hexanes : isopropanol, 0.4 mL/min, λ_{ax}= 205 nm). t_R 26.86 min (major), 25.46 min (minor): 92% *ee.*

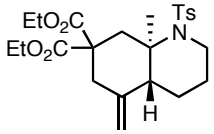


(4R,8R,E)-diethyl-5-(iodomethylene)-8a-methyl-2-oxohexahydro-2H-chromene-7,7(3H)-dicarboxylate (2c). Prepared from **1a** in accord with the general procedure for cyclization with the following modification: Immedietly before the addtion of catalyst, 2.1 equivalents of N-iodosuccinimide were added at -40°C, and this temperature was maintained for 18 hours. Purified by flash chromatography (1:1 hexanes : diethyl ether) to provide the lactone as a slightly tan oil. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.29-5.26 (m, 1H), 4.16 (qq, *J* = 10.1, 7.0 Hz, 4H), 2.75 (s, 2H), 2.68 (d, *J* = 2.5 Hz, 2H), 2.36-2.29 (m, 4H), 1.74 (t, *J* = 2.5 Hz, 3H), 1.23 (d, *J* = 14.2 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 170.36, 170.34, 169.50, 143.95, 82.27, 78.29, 62.47, 62.04, 54.51, 47.77, 43.02, 40.54, 29.14, 21.00, 19.09, 14.21, 14.11. **MS** HRMS (EI) calc. for $[C_{17}H_{23}O_6I]^+$: 473.0432, found:

473.0438. **HPLC** (95:5 hexanes : isopropanol, 0.4 mL/min, λ_{ax}= 225 nm). t_R 65.14 min (major), 59.83 min (minor): 96 % *ee.*

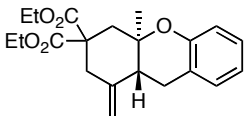


(R)-diethyl 3-methyl-4-methylene-3-((S)-5-oxotetrahydrofuran-2-yl)cyclopentane-1,1-dicarboxylate (3). Prepared from **1** in accord with the general procedure for cyclization, isolated by flash chromatography (2:3 diethyl ether : hexanes) as a minor product along with **2a.** Analytically pure material was obtained from the cyclization of triester **10**, providing **3** as the major isolable product along with **1** as further purified by trituration with cold pentane isolation of the supernate. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 4.93 (t, *J* = 2.0 Hz, 1H), 4.73 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.03-3.92 (m, 4H), 3.73 (t, *J* = 7.9 Hz, 1H), 3.21 (t, *J* = 2.6 Hz, 1H), 3.20 (d, *J* = 1.3 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H), 2.44 (dd, *J* = 14.0, 1.1 Hz, 1H), 1.90-1.84 (m, 1H), 1.72 (dt, *J* = 17.4, 10.3 Hz, 1H), 1.20-1.14 (m, 3H), 0.94-0.89 (m, 11H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 175.73, 172.20, 171.84, 154.60, 108.52, 85.63, 62.19, 61.99, 58.57, 48.37, 43.38, 42.76, 29.33, 24.33, 23.52, 14.45, 14.45. **MS** HRMS (ESI) calc. for $[C_{17}H_{24}O_6Na]^+$: 347.1465, found: 347.1463.

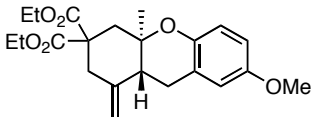


(4R,8R)-diethyl-8a-methyl-5-methylene-1-tosyloctahydroquinoline-7,7(1H)-dicarboxylate (5). Prepared from **4** in accord with the general procedure for cyclization. Purified by flash chromatography (1:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.87 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 7.9 Hz, 2H), 5.13 (d, J = 1.3 Hz, 1H), 4.59 (d, J = 1.5 Hz, 1H), 4.06 (dt, J = 13.1, 3.5 Hz, 1H), 4.03-3.80 (m, 5H), 3.33 (dd, J = 13.3, 1.9 Hz, 1H), 2.90 (td, J = 12.5, 3.6 Hz, 1H), 2.71 (d, J = 14.0 Hz, 1H), 2.13 (d, J = 13.4 Hz, 1H), 1.87-1.84 (m, 4H), 1.37-1.25 (m, 2H), 1.20-1.16 (m, 1H), 1.07 (q, J = 6.0 Hz, 4H), 0.95 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 7.1 Hz, 3 H). **^{13}C-NMR** (100 MHz, C_6D_6): δ 178.83, 171.49, 171.21, 143.69, 143.12, 140.47, 129.80, 127.40, 112.64, 63.64, 62.11, 61.63, 55.14, 50.42, 43.66, 41.98, 40.27, 25.76, 22.52, 21.86, 14.67, 14.31, 14.22. **MS** HRMS (ESI) calc. for $[C_{24}H_{34}NO_6S]^+$: 464.2101, found:

464.2105. **HPLC** (95:5 hexanes : isopropanol, 1 mL/min, λ_{max}= 206 nm). t_R min 20.26 (major), 15.71 min (minor): 90% ee.

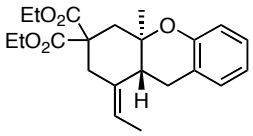


(4R,9R)-diethyl 4-methyl-1-methylene-4,4,9,9-tetrahydro-1H-xanthene-3,3(2*H*)-dicarboxylate (7a). Prepared from **6a** in accord with the general procedure for cyclization. Purified by flash chromatography (4:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H NMR** δ (600 MHz, C_6H_6): δ 7.09-7.02 (m, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.86 (td, J = 6.9, 2.6 Hz, 1H), 5.16 (d, J = 1.0 Hz, 1H), 4.73 (d, J = 1.1 Hz, 1H), 3.98-3.82 (m, 4H), 3.38 (dd, J = 13.5, 2.2 Hz, 1H), 3.16 (dd, J = 13.6, 2.1 Hz, 1H), 2.74 (d, J = 13.7 Hz, 1H), 2.58 (dd, J = 16.0, 12.8 Hz, 1H), 2.36 (dd, J = 16.1, 4.6 Hz, 1H), 2.23 (d, J = 13.5 Hz, 1H), 2.09-2.06 (m, 1H), 1.04 (s, 3H), 0.86 (t, J = 8.0 Hz, 6H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 170.67, 169.91, 152.81, 142.91, 129.65, 121.06, 120.04, 117.39, 111.03, 99.96, 76.53, 61.29, 60.84, 54.51, 43.92, 43.16, 40.00, 24.38, 17.24, 13.53, 13.49. **MS** HRMS (ESI) calc. for [C0H0O0]+ : 0, found: 0. **HPLC** Chiralpak AD-H column (98:2 hexanes : ethanol, 0.5 mL/min) t_R 19.84 min (major), 14.95 min (minor): 92% *ee*.

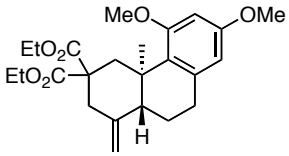


(4R,9R)-diethyl 7- methoxy-4-methyl-1-methylene-4,4,9,9-tetrahydro-1H-xanthene-3,3(2H)-dicarboxylate (7b). Prepared from **6b** in accord with the general procedure for cyclization. (4:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H-NMR** (400 MHz, CDCl): δ 6.75-6.69 (m, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 5.16 (s, 1H), 4.91 (s, 1H), 4.26-4.10 (m, 4H), 3.75 (s, 3H), 3.20 (dd, *J* = 13.7, 2.1 Hz, 1H), 2.81-2.73 (m, 2H), 2.65 (dd, *J* = 16.3, 4.8 Hz, 1H), 2.45 (d, *J* = 13.7 Hz, 1H), 2.38 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.32 (d, *J* = 13.7 Hz, 1H), 1.26 (td, *J* = 7.1, 3.4 Hz, 7H), 0.92 (s, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 171.05, 170.56, As153.15, 146.31, 142.73, 121.66, 117.73, 114.09, 113.68, 111.48, 76.38, 61.90, 61.40, 55.67, 54.53, 44.13, 42.75, 40.00, 24.80, 17.06, 14.01, 13.92. **MS** HRMS (ESI) calc. for $[C_{22}H_{28}O_6Na]^+$: 411.1778, found: 411.1782.

HPLC (98:2 hexanes : ethanol, 0.5 mL/min, λ_{max}= 226) t_r 18.62 min (major), 16.40 min (minor): 93% *ee*

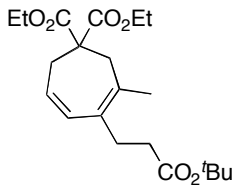


(4*R*,9*R*,*Z*)-diethyl 1-ethylidene-4-methyl-4,4,9,9-tetrahydro-1*H*-xanthene-3,3(2*H*)-dicarboxylate (7c). Prepared from **6c** in accord with the general procedure for cyclization. Purified by flash chromatography (4:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.06 (dt, J = 18.8, 8.8 Hz, 2H), 6.95 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.3 Hz, 1H), 5.69 (q, *J* = 7.4 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.94-3.84 (m, 3H), 3.19 (ddd, *J* = 13.3, 8.1, 1.7 Hz, 2H), 3.14 (d, *J* = 14.5 Hz, 1H), 2.76-2.71 (m, 2H), 2.36 (t, *J* = 13.4 Hz, 2H), 1.57 (d, *J* = 7.4 Hz, 3H), 1.21 (s, 3H), 0.87 (dt, *J* = 17.9, 7.1 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 170.91, 170.06, 152.69, 132.02, 129.58, 124.32, 121.24, 119.84, 117.30, 77.29, 65.61, 61.31, 60.77, 55.05, 45.95, 43.80, 27.19, 18.80, 15.29, 13.62, 13.61. **MS** HRMS (EI) calc. for $[C_{22}H_{28}O_5Na]^+$: 395.1829, found: 395.1826. **HPLC** (99:1 hexanes : ethanol, 0.3 mL/min, λ_{ax}= 274 nm). t_R 25.82 min (major), 30.62 min (minor): 93% *ee*

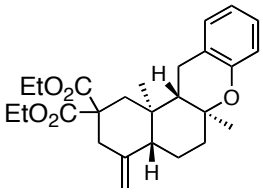


(4*R*,10*R*)-diethyl-5,7-dimethoxy-4-methyl-1-methylene-1,2,4,4,10,10-hexahydrophenanthrene-3,3(9*H*)-dicarboxylate (9). Prepared from **8** in accord with the general procedure for cyclization. Purified by flash chromatography (4:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H-NMR** (600 MHz,C_6D_6): δ 6.32 (d, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 5.33 (d, *J* = 1.1 Hz, 1H), 4.41 (dd, *J* = 14.1, 1.9 Hz, 1H), 4.16-4.08 (m, 2H), 3.94-3.83 (m, 2H), 3.61 (dd, *J* = 13.3, 1.9 Hz, 1H), 3.42 (s, 3H), 3.28 (s, 3H), 2.78-2.72 (m, 1H), 2.62 (dt, *J* = 16.9, 3.3 Hz, 1H), 2.45 (dd, *J* = 37.6, 13.8 Hz, 2H), 2.23 (t, *J* = 7.1 Hz, 1H), 1.65-1.61 (m, 2H), 1.34 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.28, 172.14, 159.58, 158.08, 145.47, 137.99, 126.70, 109.94, 104.80, 97.27, 61.31, 60.86, 55.11, 54.99, 54.93, 50.44,

40.36, 39.70, 39.07, 31.89, 20.63, 17.72, 13.86, 13.84. **MS** HRMS (ESI) calc. for $[C_{24}H_{32}O_6Na]^+$: 439.2091, found: 439.2091. **HPLC** (99:1 hexanes : ethanol, 0.85 mL/min, λ_{max}= 208 nm). t_R 19.216 min (major), 22.57 min (minor): 94% *ee*

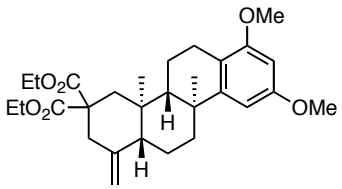


diethyl 4-(3-tert-butoxy-3-oxopropyl)-3-methylcyclohepta-3,5-diene-1,1-dicarboxylate (11). Prepared from **10** in accord with the general procedure for cyclization. Purified by flash chromatography (5:1 hexanes : diethyl ether). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.27 (d, J = 15.6 Hz, 1H), 5.46 (dt, J = 15.0, 7.3 Hz, 1H), 3.97 (sextet, J = 6.4 Hz, 4H), 3.43 (s, 2H), 3.22 (s, 2H), 2.33 (q, J = 7.1 Hz, 2H), 2.17 (d, J = 7.4 Hz, 2H), 1.50 (s, 3H), 1.37 (d, J = 0.8 Hz, 9H), 0.91 (t, J = 7.1 Hz, 6H). **13C-NMR** (150 MHz, C_6D_6): δ 185.92, 172.11, 171.85, 132.70, 131.19, 129.19, 125.06, 79.65, 79.65, 61.37, 57.65, 46.78, 41.76, 35.53, 29.04, 28.17, 14.04, 13.33. **MS** HRMS (ESI) calc. for $[C_{21}H_{32}O_6Na]^+$: 403.2091, found: 403.2095.

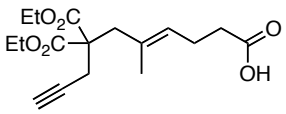


(4*R*,6*S*,12*S*,12*R*)-diethyl-6,12b-dimethyl-4-methylene-3,4,4,5,6,6,12,12a-octahydro-1*H*-benzo[*a*]xanthene-2,2(12b*H*)-dicarboxylate (13). Prepared from **12** in accord with the general procedure for cyclization. Purified by flash chromatography (4:1 hexanes : diethyl ether), providing the title compound as a clear oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (t, *J* = 6.2 Hz, 2H), 6.86 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.31 (t, *J* = 7.3 Hz, 2H), 5.24 (s, 1H), 4.19 (qq, *J* = 10.9, 7.2 Hz, 4H), 3.37 (d, *J* = 7.1 Hz, 1H), 2.79-2.77 (m, 4H), 2.16-2.06 (m, 4H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.76 (s, 3H), 1.53 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (151 MHz, C_6D_6): δ 171.52, 171.00, 153.62, 144.90, 129.78, 127.94, 121.98, 119.72, 117.16, 109.54, 76.02, 61.16, 60.81, 54.65, 51.05, 49.87, 43.10, 40.41, 39.31, 38.26, 29.82, 22.98, 21.44, 20.71, 13.60, 13.03. **MS** HRMS (ESI) calc. for $[C_{26}H_{34}O_5Na]^+$: 449.2298, found: 449.2300. **HPLC** (98:2:

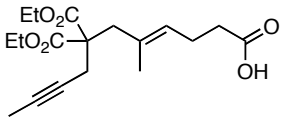
hexanes:isopropanol, 0.6 mL/min, λ_{ax}= 205 nm). t_{Rs} 11.37 min (major), 16.88 min (minor). 88 % *ee.*



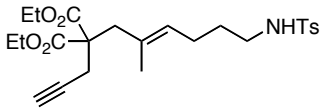
(4*R*,4*S*,10*S*,12*R*)-diethyl-7,9-dimethoxy-4,10b-dimethyl-1-methylene-1,2,4,4,5,6,10b,11,12,12a-decahydrochrysene-3,3(4*H*)-dicarboxylate (15). Prepared from **14** in accord with the general procedure for cyclization. Purified by flash chromatography (5:1 hexanes : diethyl ether) to give a clear oil which solidified on standing. A solution of this material crystallized on slow evaporation of a solution in 3:2 MTBE : pentanes. **^{1}H-NMR** (600 MHz, C_6D_6): δ 6.37 (d, J = 2.0 Hz, 1H), 6.20 (d, J = 1.9 Hz, 1H), 5.25 (s, 1H), 4.84 (s, 1H), 4.12-4.01 (m, 2H), 3.98-3.87 (m, 2H), 3.55 (d, J = 13.4 Hz, 1H), 3.42 (s, 3H), 3.28 (s, 3H), 3.06 (d, J = 13.6 Hz, 1H), 2.74-2.63 (m, 2H), 2.37 (d, J = 13.4 Hz, 1H), 2.04 (d, J = 13.7 Hz, 1H), 1.84-1.78 (m, 2H), 1.73 (qd, J = 12.9, 2.6 Hz, 1H), 1.60-1.58 (m, 1H), 1.45 (s, 2H), 1.43-1.40 (m, 1H), 1.36 (t, J = 5.6 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H), 0.86 (s, 3H).**^{13}C-NMR** (100 MHz, C_6D_6): δ 171.99, 171.42, 159.50, 158.33, 145.87, 138.43, 130.15, 108.88, 105.02, 97.91, 61.09, 60.79, 55.11, 54.91, 54.43, 54.25, 51.68, 43.94, 40.46, 39.59, 39.51, 36.83, 33.37, 29.87, 21.37, 21.15, 18.65, 14.53, 13.65. **MS** HRMS (ESI) calc. for $C_{29}H_{40}O_6Na$: 507.2717, found: 507.2708. **HPLC** (99:1 hexanes : isopropanol, 0.65 mL/min, λ_{ax}= 207 nm). t_R 20.60 min (major), 42.16 min (minor). 96% *ee.*



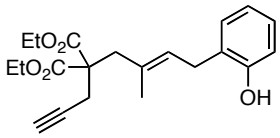
(*E*)-7,7-bis(ethoxycarbonyl)-5-methyldec-4-en-9-ynoic acid (1a). **^{1}H NMR (400 MHz,** $CDCl_3$**):** δ 1.24 (t, *J* = 7.2 Hz, 6H), 1.55–1.57 (m, 3H), 2.00–2.02 (m, 1H), 2.26–2.34 (m, 2H), 2.35–2.41 (m, 2H), 2.75 (d, *J* = 2.7 Hz, 2H), 2.79 (s, 2H), 4.11–4.25 (m, 4H), 5.29–5.34 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$**):** δ 179.0, 170.2, 131.2, 128.5, 79.3, 71.6, 61.6, 56.5, 41.2, 33.7, 23.3, 22.4, 16.8, 14.0. **MS** HRMS (ESI) calc. for $[C_{17}H_{24}O_6Na]^+$: 347.1465, found: 347.1467.



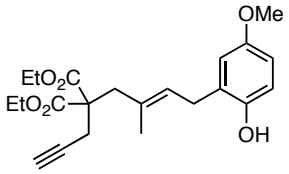
(*E*)-7,7-bis(ethoxycarbonyl)-5-methylundec-4-en-9-ynoic acid (1b). ^{1}H NMR (400 MHz, $CDCl_3$)**:** δ 1.23 (t, *J* = 7.1 Hz, 6H), 1.56 (s, 3H), 1.74 (t, *J* = 2.6 Hz, 3H), 2.25–2.34 (m, 2H), 2.34–2.40 (m, 2H), 2.69 (q, *J* = 2.4 Hz, 2H), 2.76 (s, 2H), 4.10–4.23 (m, 4H), 5.28 (t, *J* = 6.5 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$)**:** δ 3.4, 14.0, 16.9, 22.8, 23.3, 33.8, 41.1, 57.0, 61.4, 73.8, 79.0, 128.1, 131.5, 170.5, 179.2. **MS** HRMS (ESI) calc. for $[C_{18}H_{26}O_6Na]^+$: 361.1622, found: 361.1624.



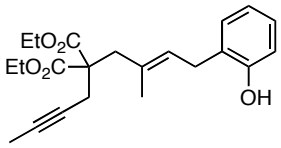
(*E*)-diethyl 2-(2-methyl-6-(4-methylphenylsulfonamido)hex-2-enyl)-2-(prop-2-ynyl)malonate (4). 1H-NMR (400 MHz, CDCl3): δ 7.77-7.75 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.23 (t, *J* = 7.1 Hz, 1H), 4.40 (td, *J* = 6.2, 0.3 Hz, 1H), 4.26-4.12 (m, 4H), 2.93 (d, *J* = 6.7 Hz, 2H), 2.77 (s, 2H), 2.72 (d, *J* = 2.7 Hz, 2H), 2.44 (s, 3H), 2.02-1.97 (m, 3H), 1.53-1.50 (m, 5H), 1.26 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 170.18, 143.36, 142.23, 136.90, 130.63, 129.69, 129.33, 127.08, 79.33, 71.65, 61.59, 56.54, 42.77, 41.18, 29.39, 25.07, 22.47, 21.51, 16.86, 14.00. **MS** HRMS (ESI) calc. for $[C_{24}H_{34}NO_6S]^+$: 464.2101, found: 464.2103.



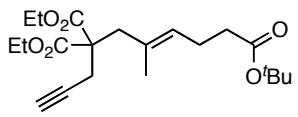
(*E*)-diethyl 2-(4-(2-hydroxyphenyl)-2-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (6a). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 8.5 Hz, 1H), 6.65 (td, *J* = 8.5, 3.0 Hz, 2H), 5.48 (t, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 3.31 (d, *J* = 7.2 Hz, 2H), 2.87 (s, 2H), 2.81 (d, *J* = 2.6 Hz, 2H), 2.02 (t, *J* = 2.6 Hz, 1H), 1.70 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 170.20, 153.84, 131.73, 129.86, 128.21, 127.41, 126.73, 120.86, 115.65, 79.29, 71.75, 61.64, 56.84, 41.32, 29.29, 22.78, 17.16, 13.95. **MS** HRMS (ESI) calc. for $[C_{21}H_{26}O_5Na]^+$: 381.1672, found: 381.1676.



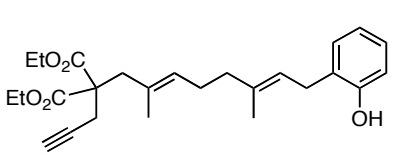
(*E*)-diethyl 2-(4-(2-hydroxy-5-methoxyphenyl)-2-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (6b). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.7 Hz, 1H), 6.68 (dt, *J* = 12.5, 4.1 Hz, 2H), 5.51 (td, *J* = 7.3, 1.2 Hz, 1H), 5.16 (s, 2H), 4.17 (qq, *J* = 11.3, 7.1 Hz, 4H), 3.76 (s, 3H), 3.70 (s, 2H), 3.32 (d, *J* = 7.3 Hz, 2H), 2.85 (s, 2H), 2.82 (d, *J* = 2.7 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.65 (t, *J* = 0.5 Hz, 3H), 1.23 (td, *J* = 7.1, 1.1 Hz, 10H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 170.28, 154.48, 149.34, 131.38, 130.60, 128.83, 115.59, 115.18, 111.56, 94.11, 79.49, 71.70, 64.13, 61.61, 56.73, 55.67, 41.42, 28.83, 22.66, 17.01, 15.19, 14.04. **MS** HRMS (ESI) calc. for $[C_{22}H_{28}O_6Na]^+$: 411.1778, found: 411.1774



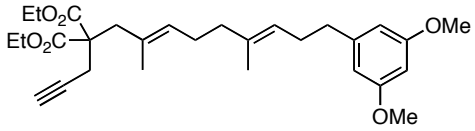
(*E*)-diethyl 2-(but-2-ynyl)-2-(4-(2-hydroxyphenyl)-2-methylbut-2-enyl)malonate (6c). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 8.5 Hz, 1H), 6.65 (td, *J* = 8.5, 3.0 Hz, 2H), 5.48 (t, *J* = 6.8 Hz, 1H), 4.56 (s, 1H), 4.16 (qq, *J* = 12.3, 7.0 Hz, 4H), 3.76 (s, 3H), 3.31 (d, *J* = 7.2 Hz, 2H), 2.87 (s, 2H), 2.81 (d, *J* = 2.6 Hz, 2H), 2.02 (t, *J* = 2.6 Hz, 1H), 1.70 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (10\1 MHz, $CDCl_3$): δ 170.20, 153.84, 131.73, 129.86, 128.21, 127.41, 126.73, 120.86, 115.65, 79.29, 71.75, 61.64, 56.84, 41.32, 29.29, 22.78, 17.16, 13.95. **MS** HRMS (EI) calc. for $[C_{22}H_{28}O_5Na]^+$: 395.1829, found: 395.1831.



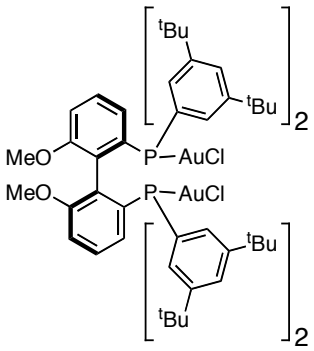
(E)-1-tert-butyl 6,6-diethyl 4-methylnon-3-en-8-yne-1,6,6-tricarboxylate (10). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.30 (t, J = 6.4 Hz, 1H), 4.18 (qq, J = 10.5, 7.1 Hz, 5H), 2.77 (d, J = 4.4 Hz, 2H), 2.29-2.20 (m, 4H), 2.00 (d, J = 2.6 Hz, 1H), 1.43 (s, 9H), 1.24 (t, J = 7.1 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.47, 170.18, 130.47, 129.18, 80.13, 79.40, 71.57, 61.54, 56.50, 41.21, 35.27, 28.06, 23.76, 22.41, 16.80, 13.99.**MS** HRMS (ESI) calc. for $[C_{21}H_{32}O_6Na]^+$: 403.2091, found: 403.2089.



diethyl 2-((2*E*,6*E*)-8-(2-hydroxyphenyl)-2,6-dimethylocta-2,6-dienyl)-2-(prop-2-ynyl)malonate (12). **^{1}H-NMR** (600 MHz, C_6D_6):6.37 (d, J = 2.0 Hz, 1H), 6.20 (d, J = 1.9 Hz, 1H), 5.25 (s, 1H), 4.84 (s, 1H), 4.12-4.01 (m, 2H), 3.98-3.87 (m, 2H), 3.55 (d, J = 13.4 Hz, 1H), 3.42 (s, 3H), 3.28 (s, 3H), 3.06 (d, J = 13.6 Hz, 1H), 2.74-2.63 (m, 2H), 2.37 (d, J = 13.4 Hz, 1H), 2.04 (d, J = 13.7 Hz, 1H), 1.84-1.78 (m, 2H), 1.73 (qd, J = 12.9, 2.6 Hz, 1H), 1.60-1.58 (m, 1H), 1.45 (s, 2H), 1.43-1.40 (m, 1H), 1.36 (t, J = 5.6 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H), 0.86 (s, 3H).**^{13}C-NMR** (100 MHz, C_6D_6): δ 171.99, 171.42, 159.50, 158.33, 145.87, 138.43, 130.15, 108.88, 105.02, 97.91, 61.09, 60.79, 55.11, 54.91, 54.43, 54.25, 51.68, 43.94, 40.46, 39.59, 39.51, 36.83, 33.37, 29.87, 21.37, 21.15, 18.65, 14.53, 13.65. **MS** HRMS (ESI) calc. for $[C_{29}H_{40}O_6Na]^+$: 507.2717, found: 507.2708.



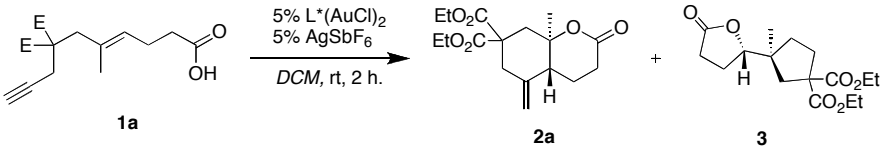
diethyl 2-((2*E*,6*E*)-9-(3,5-dimethoxyphenyl)-2,6-dimethylnona-2,6-dienyl)-2-(prop-2-ynyl)malonate (14). **^{1}H-NMR** (600 MHz, C_6D_6): δ 6.53 (d, *J* = 2.3 Hz, 2H), 6.49 (t, *J* = 2.2 Hz, 1H), 5.56-5.54 (m, 1H), 5.30 (t, *J* = 7.1 Hz, 1H), 4.04-3.93 (m, 4H), 3.39 (d, *J* = 1.8 Hz, 1H), 3.23 (d, *J* = 2.7 Hz, 2H), 3.14 (d, *J* = 2.7 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.39 (q, *J* = 7.5 Hz, 2H), 2.10 (t, *J* = 7.3 Hz, 2H), 2.05-2.02 (m, 2H), 1.77 (t, *J* = 2.7 Hz, 1H), 1.67 (d, *J* = 1.3 Hz,), 1.61 (s, 3H), 1.53-1.50 (m, 3H), 0.93 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 171.21, 143.42, 142.82, 140.22, 129.51, 127.12, 112.34, 63.37, 61.82, 61.34, 54.87, 50.14, 43.37, 41.71, 39.99, 25, 22.24, 21.56, 14.41, 14.02, 13.93. **MS** HRMS (ESI) calc. for $[C_{29}H_{40}O_6Na]^+$: 507.2717, found: 507.2716.



(R)-DTB,MeO-biphep(AuCl)$_2$, Prepared from treatment of the commercially available ligand with AuCl, generated *in-situ* from $AuCl_3$ and thiodiglycol, as described recently by this group.[1] The crude product, as an oil concentrated from benzene, was recrystallized from a concentrated solution of 5% benzene in pentane, layered underneath a fivefold excess of pentane and kept at 0°C for ten days. The crystalline material thus obtained proved suitable for x-ray analysis, crystallographic data provided. **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ 7.59 (q, *J* = 1.8 Hz, 3H), 7.55 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.52 (q, *J* = 1.7 Hz, 2H), 7.41 (dd, *J* = 14.1, 1.8 Hz, 4H), 7.12 (dd, *J* = 14.2, 1.6 Hz, 4H), 6.97 (ddd, *J* = 10.7, 7.8, 0.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 6H), 1.26 (d, *J* = 8.5 Hz, 73H). **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 158.96, 158.83, 151.68, 151.19, 151.08, 130.34-130.16, 129.67, 129.50, 129.45-129.40, 129.08, 128.87, 128.80, 128.72, 128.66-128.57, 128.44, 128.29, 128.25, 128.19, 128.15, 125.74, 125.27, 113.21, 34.96, 31.05. **^{31}P-NMR** (162 MHz; C_6D_6): δ 24.96. **MS** HRMS (ESI) calc. for $[C_{70}H_{96}O_2Au_2Cl]^+$: 1459.5900, found: 1459.5902.

Additional Optimization Data

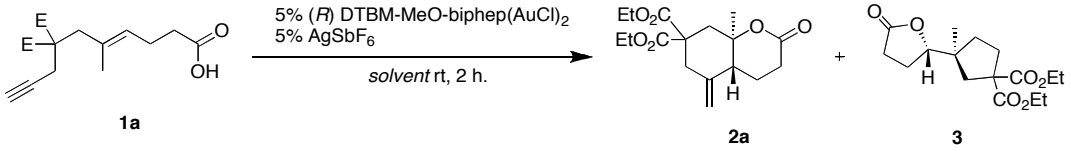
Table S1: Catalyst Optimization



1a 2a 3

entry	ligand	ee (%)	yield 2a (%)	yield 3 (%)
1	(*R*)-DTBM-MeO-biphep	-46	81	10
2	*(R)-xyl*-MeO-BIPHEP	-36	66	11
3	*(R)-xyl*-BINAP	-40	71	12
4	*(R)-tol*-BINAP	-23	75	10
5	*(S)*-BINAP	13	81	8
6	*(R)*-C_3-Tunephos	7	72	8
7	*(R)*-SEGPHOS	-3	88	6
8	*(S)*-Difluorphos	-3	80	-
9	*(R)*-DTBM-SEGPHOS	-2	78	10

Table S2: Solvent Optimization



1a 2a 3

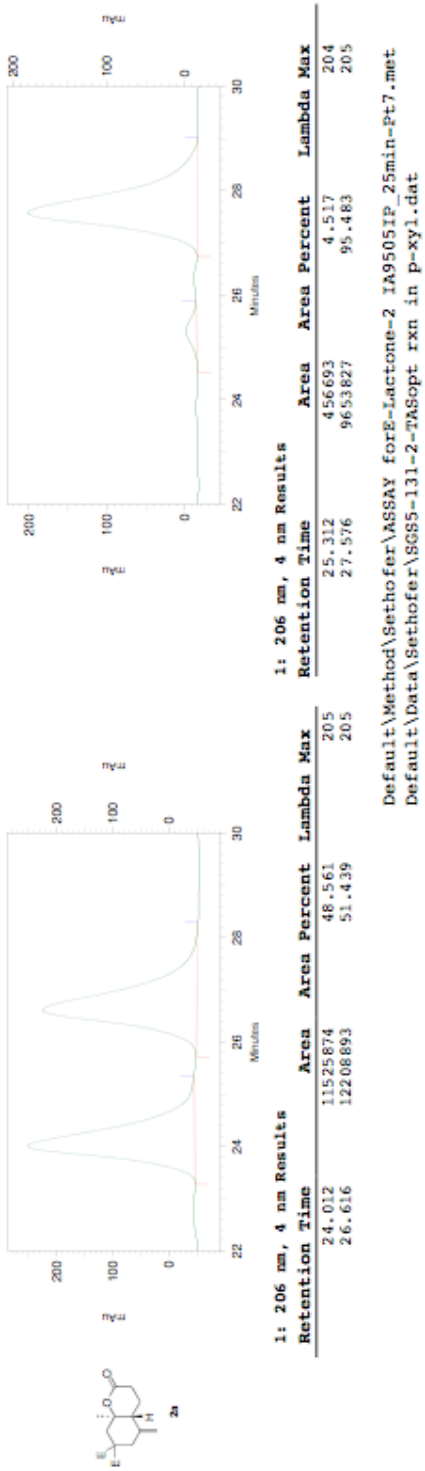
entry	solvent	ee (%)	yield 2a (%)	yield 3 (%)
1	DCM	-46	81	10
2	benzene	-83	83	11
3	toluene	-85	81	11
4	*m*-xylene	-87	83	14
5	fluorobenzene	-73	88	7
6	nitromethane	-47	79	3
7	THF	-58	83	13

References

[1] Kleinbeck, F.; Toste, F. D. *J. Am. Chem. Soc.*, **2009**, *131*, 9178

[2] Melhado, A. D.; Luparia M.; Toste, F.D. . *J. Am. Chem. Soc.*, **2007**, *129*, 12638

HPLC Data



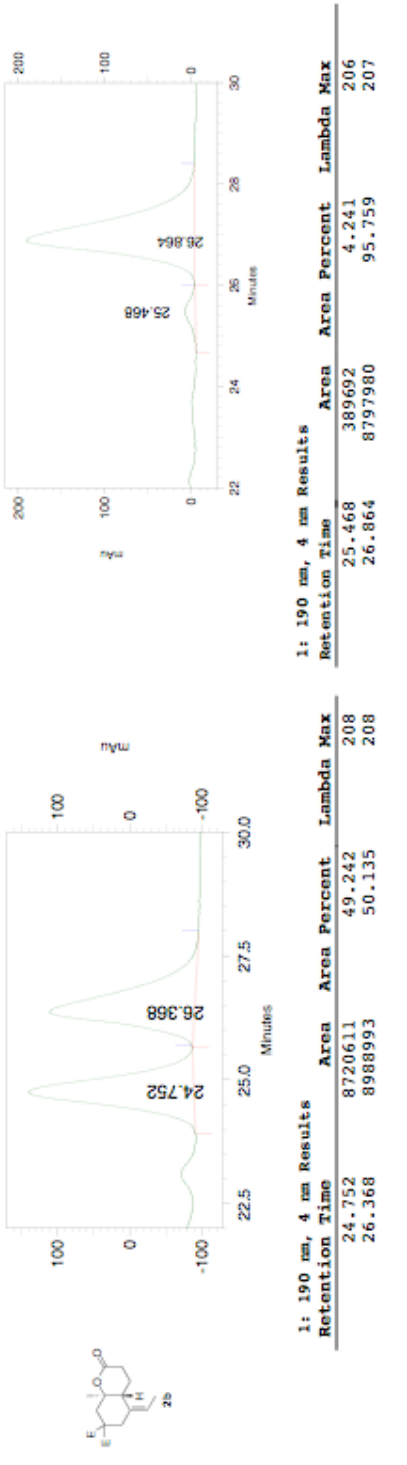
1: 206 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
24.012	11525874	48.561	205
26.616	12208893	51.439	205

1: 206 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
25.312	456693	4.517	204
27.576	9653827	95.483	205

Default\Method\Sethofer\ASSAY forE-Lactone-2 IA9505IP_25min-Pt7.met
Default\Data\Sethofer\SGS5-131-2-7ASopt rxn in p-xyl.dat



1: 190 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
24.752	8720611	49.242	208
26.368	8988993	50.135	208

1: 190 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
25.468	389692	4.241	206
26.864	8797980	95.759	207

Default\Method\Sethofer\IA9505IP_25min-tASSAY_Me Alkyne Pt4.m
Default\Data\Sethofer\SGS5-131-1-MTAS opt rxn.dat

1: 236 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
59.83	837322	2.036	232
65.14	40284356	97.964	225

Default\Method\SethoferASSAY for E-Lactone Internal IA9505IP_75min-Pt4.met
Default\Data\Sethofer\SG55-131-3-TAS rxn with xs NIS, rac look forassay-4.dat

60.116
65.704

1: 225 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
59.236	23701724	48.979	225
65.328	24689862	51.020	225

1: 207 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
15.712	199233	4.488	206
20.264	4240282	95.512	206

1: 207 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
15.828	8092698	50.168	206
20.232	8038556	49.832	206

Default\Method\Sethofer\ASSAY for TsN IA9505IP with207nm clean_25min.met
Default\Sequence\Sethofer\09082502_TsN_ASSAY.seq

2: 280 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
23.643	18537834	49.290	274
27.115	19071776	50.710	274

2: 280 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
25.819	11156281	96.404	274
30.619	416116	3.596	272

Default\Data\Sethofer\SGS5-24A-Rac-3
Default\Data\Sethofer\SGS5-24Al-3
Default\Method\Sethofer\MeAlk-Assay-AD9901ET-30min-pt3.met

1: 217 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
19.216	11863681	50.198	208
22.203	11770065	49.802	208

1: 217 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
19.189	35727132	96.895	208
22.565	1462552	3.185	208

Projects\Default\Data\Sethofer\2FCASSAY-WB9901ET_pt85-SGS4-207
Projects\Default\Method\Sethofer\ASSAY_FC_WB9901ET_30min_pt85.met

2: 269 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
11.620	1618601	49.865	205
17.128	1627335	50.135	205

2: 269 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
11.368	7178906	93.908	207
16.880	465708	6.092	204

Projects\Default\Method\Sethofer\IA98021P_45min_pt6.met
Projects\Default\Data\Sethofer\PYDE-IA98021P-SG55-103Pt6.dat

1: 214 nm, 4 nm Results

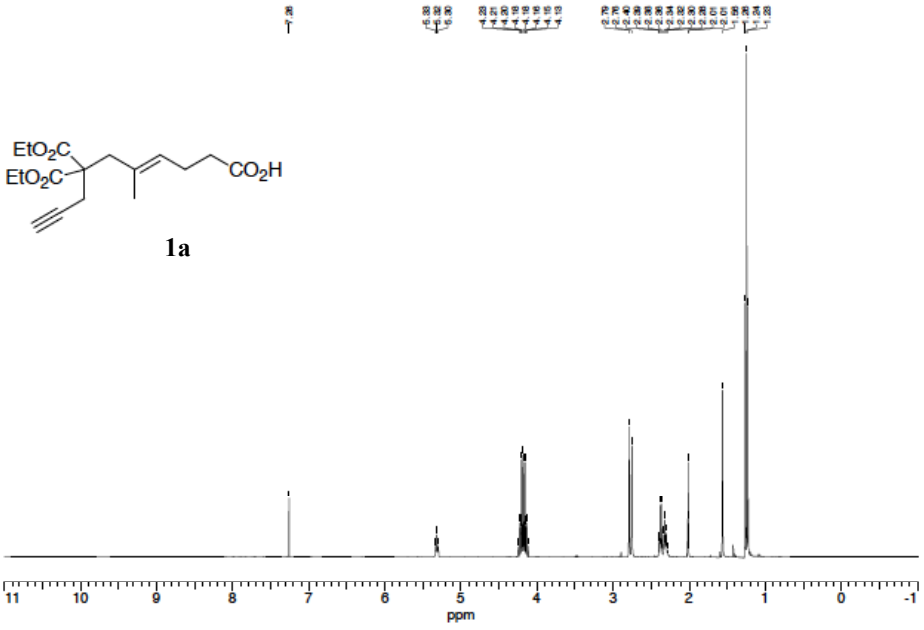
Retention Time	Area	Area Percent	Lambda Max
19.744	5682768	49.536	207
40.976	5789122	50.464	207

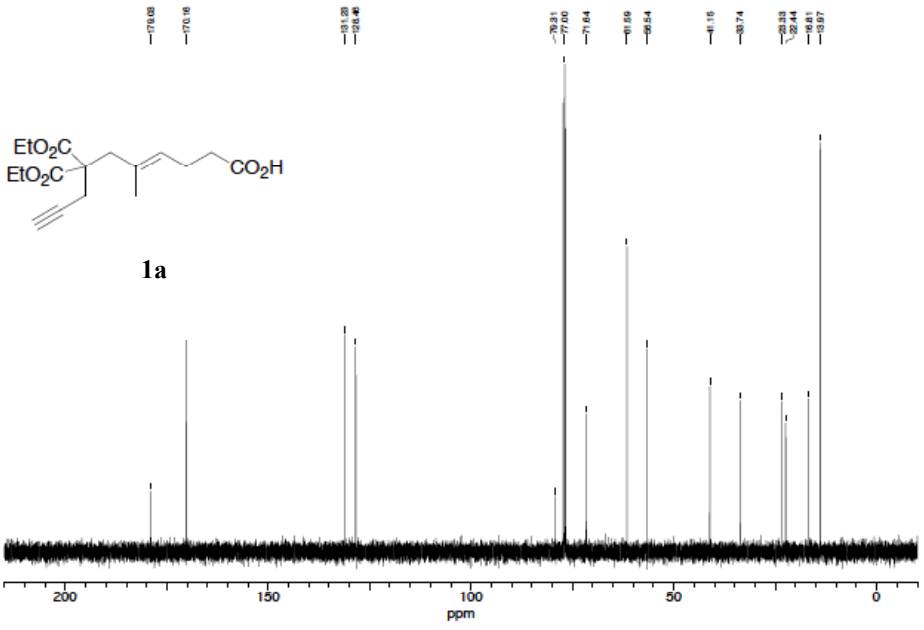
1: 214 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
20.596	110283653	97.966	208
42.156	2289649	2.034	208

Projects\Default\Method\Sethofer\IA99011P_pt65_ASSAY for FCDE.met
Projects\Default\Data\Sethofer\PYDE-IA98021P-SG55-103Pt6.dat SG55-153-FCDE

NMR spectra


EtO2C
EtO2C
CO2H
1a
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm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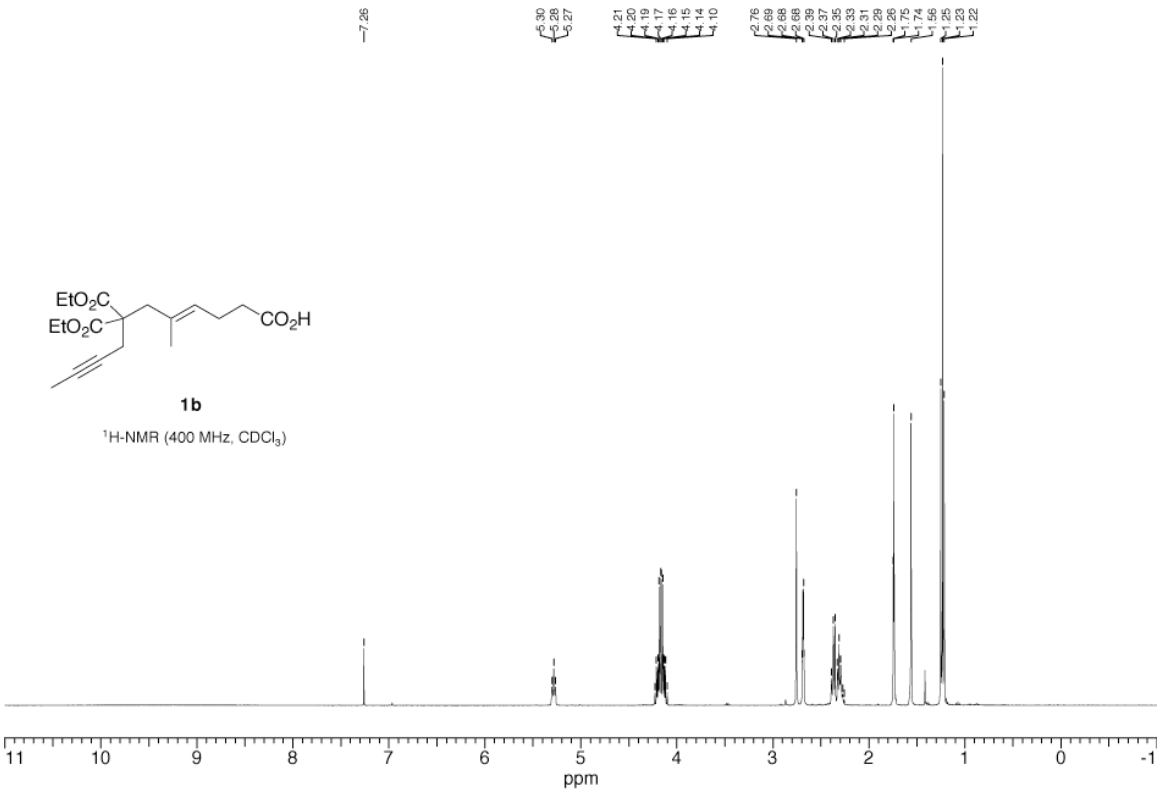
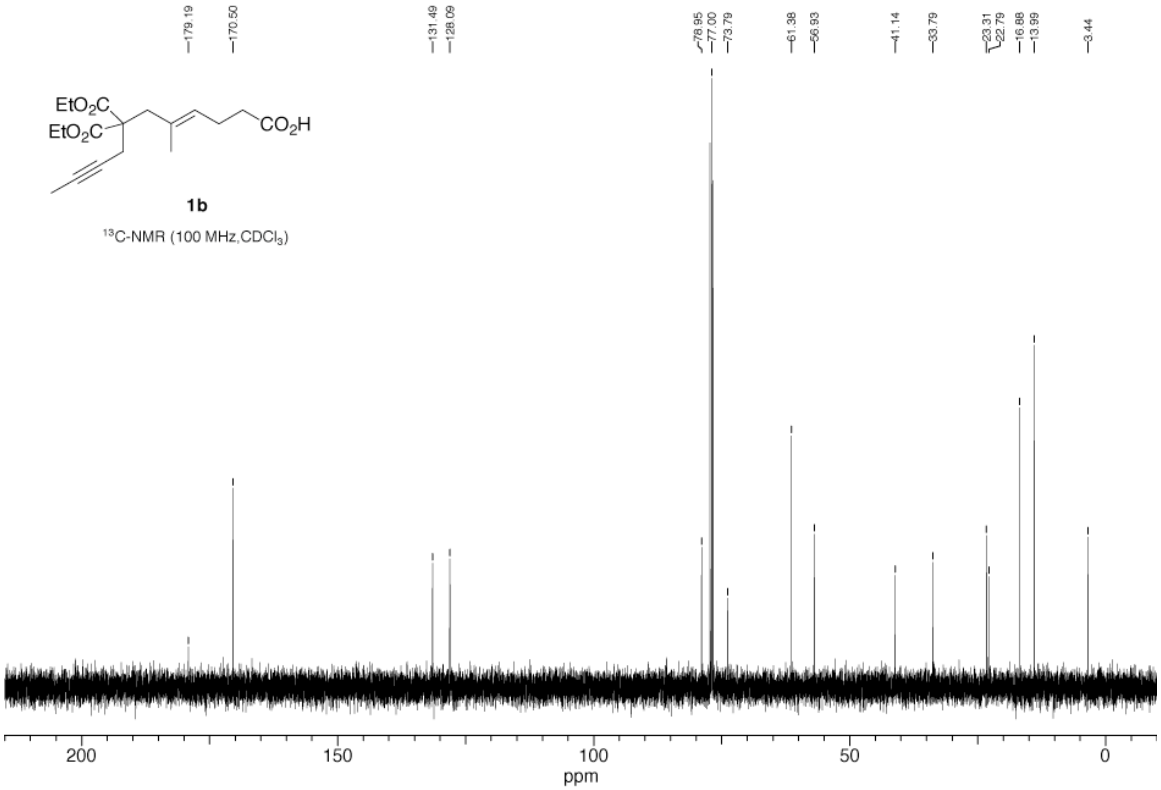
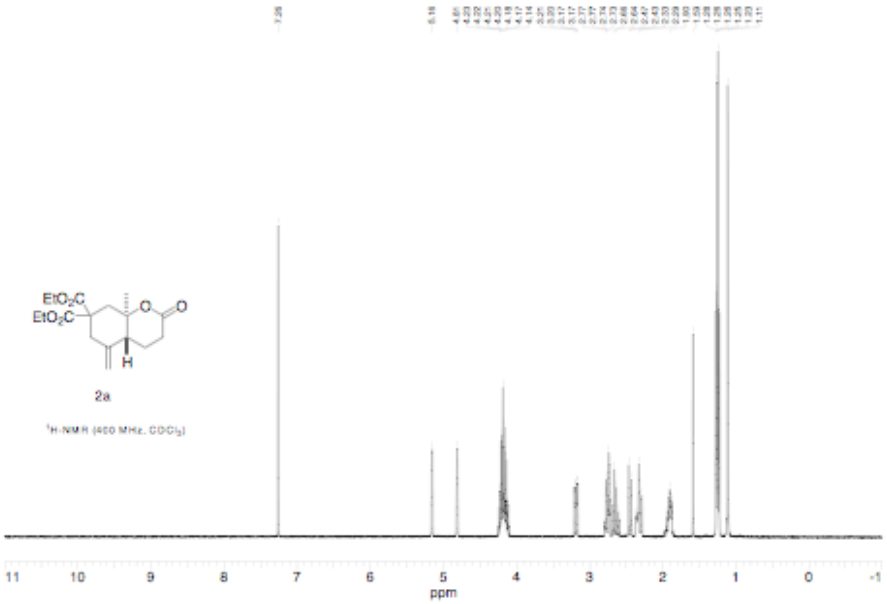
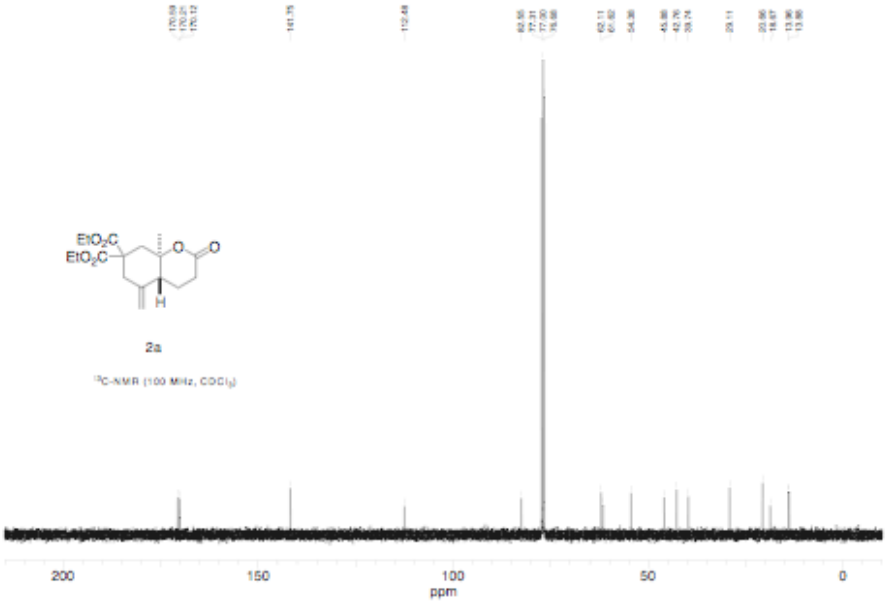
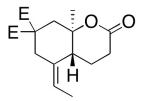
EtO2C
CO2H
1a
200
150
100
50
0
ppm


7.26
5.30
5.28
5.27
4.21
4.20
4.19
4.17
4.16
4.15
4.14
4.10
2.76
2.69
2.68
2.68
2.68
2.39
2.37
2.35
2.33
2.31
2.29
2.26
1.75
1.74
1.56
1.25
1.23
1.22
EtO2C
EtO2C
CO2H
1b
1H-NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

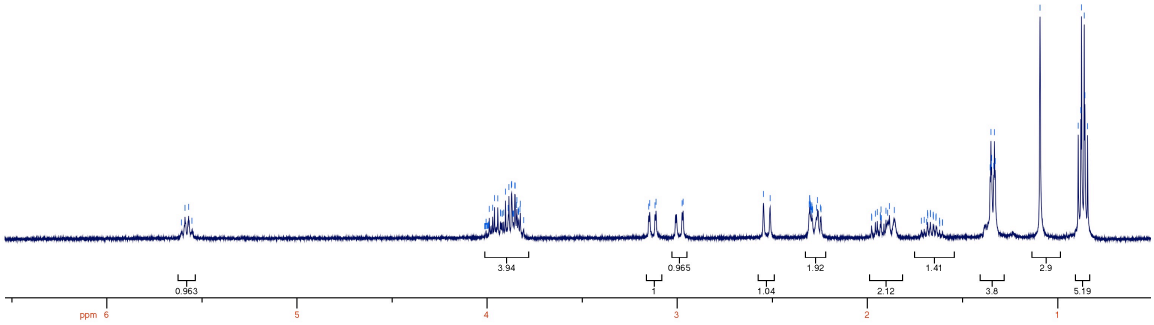

179.19
170.50
131.49
128.09
78.95
77.00
73.79
61.38
56.93
41.14
33.79
23.31
22.79
16.88
13.99
3.44
EtO2C
EtO2C
CO2H
1b
13C-NMR (100 MHz,CDCl3)
200
150
100
50
0
ppm


EtO2C
EtO2C
O
O
H
2a
1H-NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


EtO2C
EtO2C
O
O
H
2a
13C-NMR (100 MHz, CDCl3)
200
150
100
50
0
ppm


E
E
O
O
H

2b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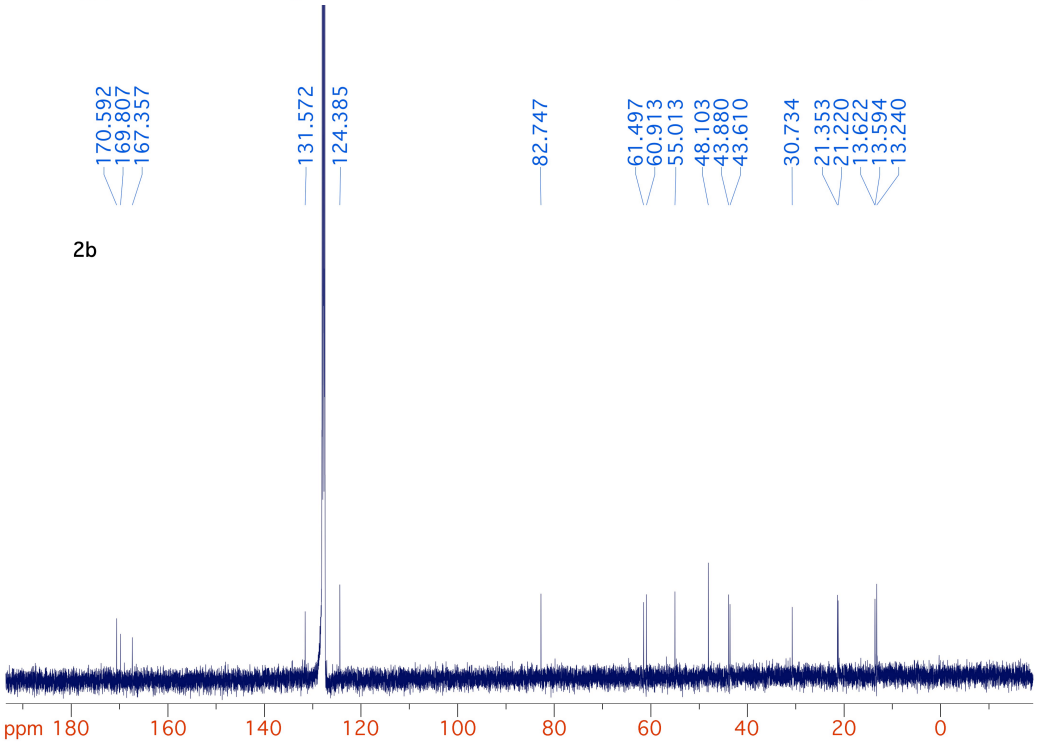
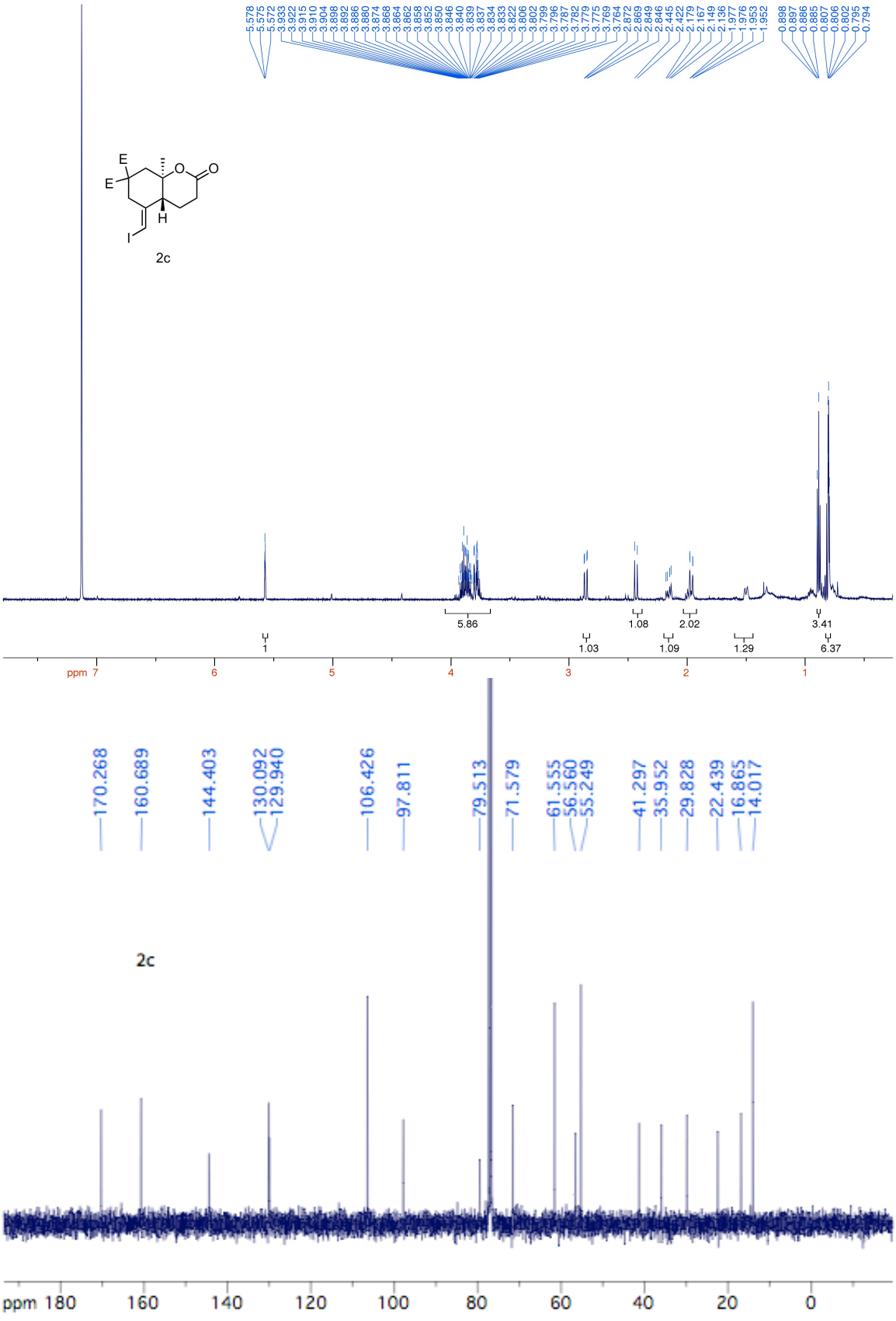
3.94
0.965
1
1.04
1.92
2.12
1.41
3.8
2.9
5.19
ppm 6
5
4
3
2
1


170.592
169.807
167.357
131.572
124.385
82.747
61.497
60.913
55.013
48.103
43.880
43.610
30.734
21.353
21.220
13.622
13.594
13.240
ppm 180
160
140
120
100
80
60
40
20
0

2b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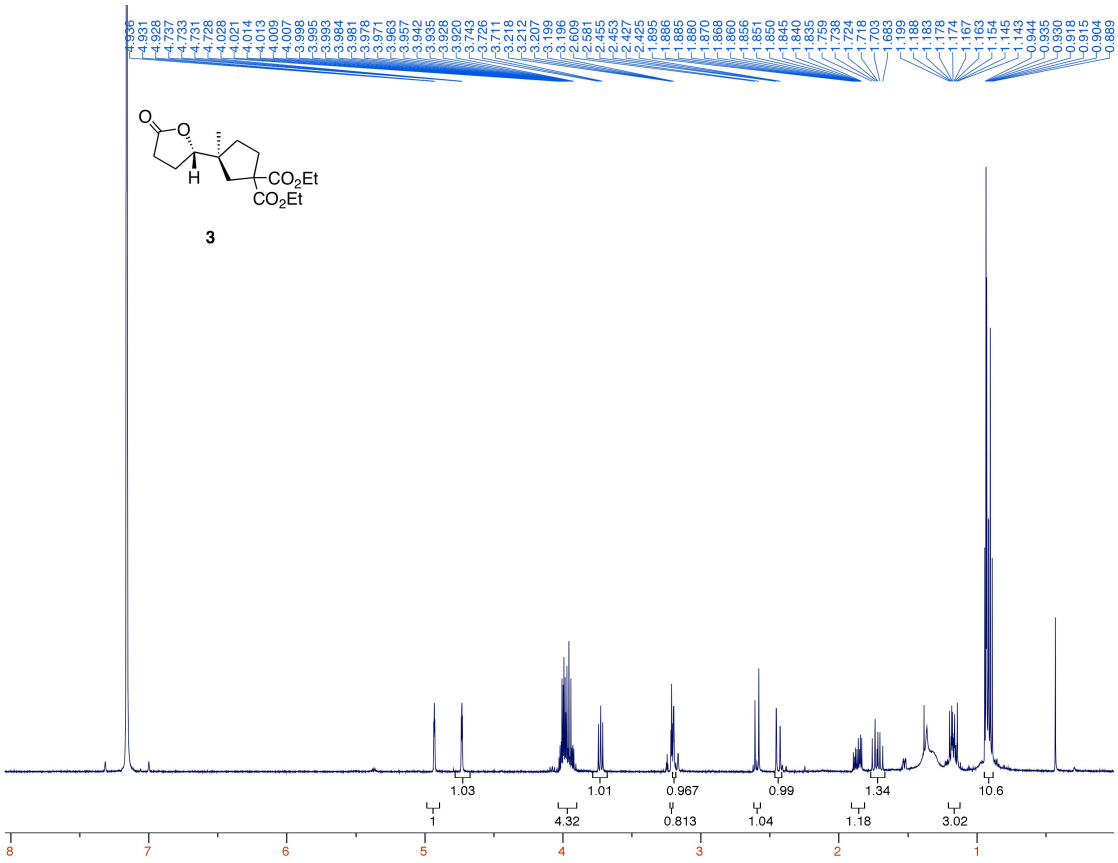
5.575
5.572
3.923
3.915
3.910
3.904
3.898
3.892
3.886
3.880
3.874
3.868
3.864
3.862
3.858
3.852
3.850
3.846
3.840
3.839
3.837
3.834
3.833
3.822
3.806
3.802
3.799
3.796
3.787
3.782
3.779
3.775
3.769
3.764
2.872
2.869
2.849
2.846
2.445
2.422
2.179
2.167
2.149
2.136
1.977
1.976
1.953
1.952
0.898
0.897
0.886
0.885
0.807
0.806
0.802
0.795
0.794
E
E
O
O
H
I
2c
5.86
1.08
2.02
3.41
1
1.03
1.09
1.29
6.37
ppm 7
6
5
4
3
2
1
170.268
160.689
144.403
130.092
129.940
106.426
97.811
79.513
71.579
61.555
56.560
55.249
41.297
35.952
29.828
22.439
16.865
14.017
2c
ppm 180
160
140
120
100
80
60
40
20
0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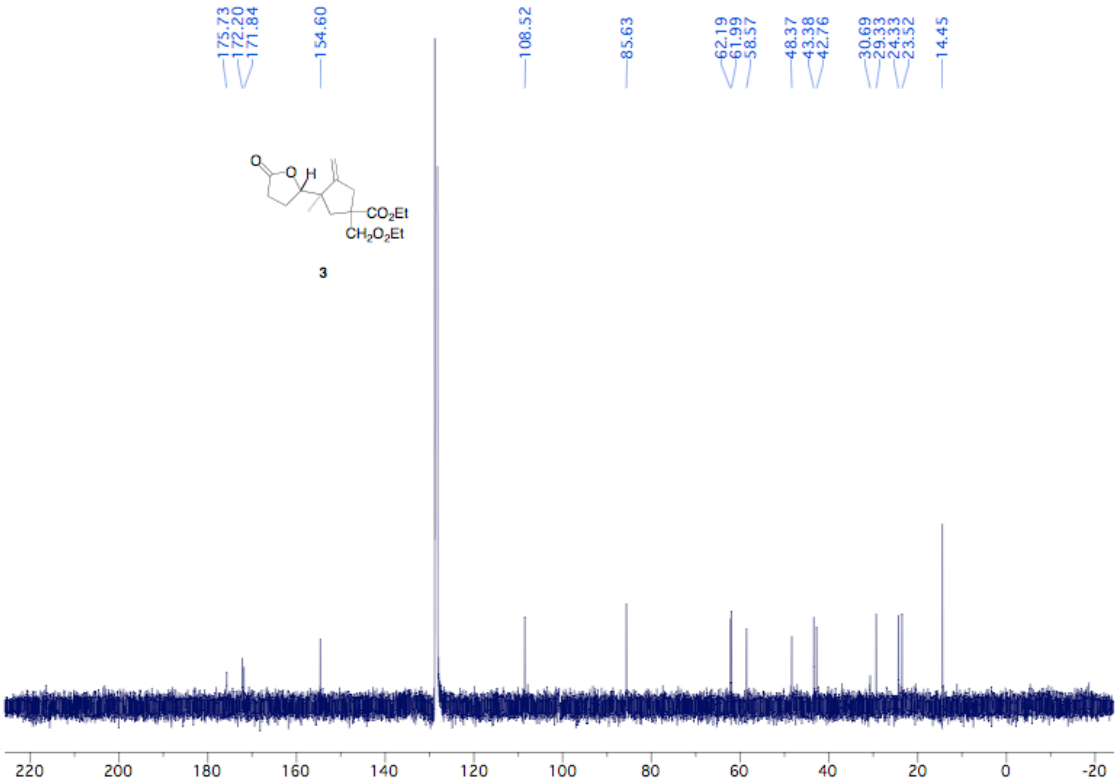
4.928
4.737
4.733
4.731
4.728
4.028
4.021
4.014
4.013
4.009
4.007
3.998
3.995
3.993
3.984
3.981
3.978
3.971
3.963
3.957
3.942
3.935
3.928
3.920
3.743
3.726
3.711
3.218
3.212
3.207
3.199
3.196
3.009
2.581
2.451
2.445
2.427
2.425
1.895
1.886
1.885
1.880
1.870
1.868
1.860
1.856
1.851
1.850
1.845
1.840
1.835
1.759
1.738
1.724
1.718
1.703
1.683
1.199
1.188
1.183
1.178
1.174
1.167
1.163
1.154
1.145
1.143
0.944
0.935
0.930
0.918
0.915
0.904
0.889
O
O
H
CO2Et
CO2Et
3
1.03
1.01
0.967
0.99
1.34
10.6
1
4.32
0.813
1.04
1.18
3.02
8
7
6
5
4
3
2
1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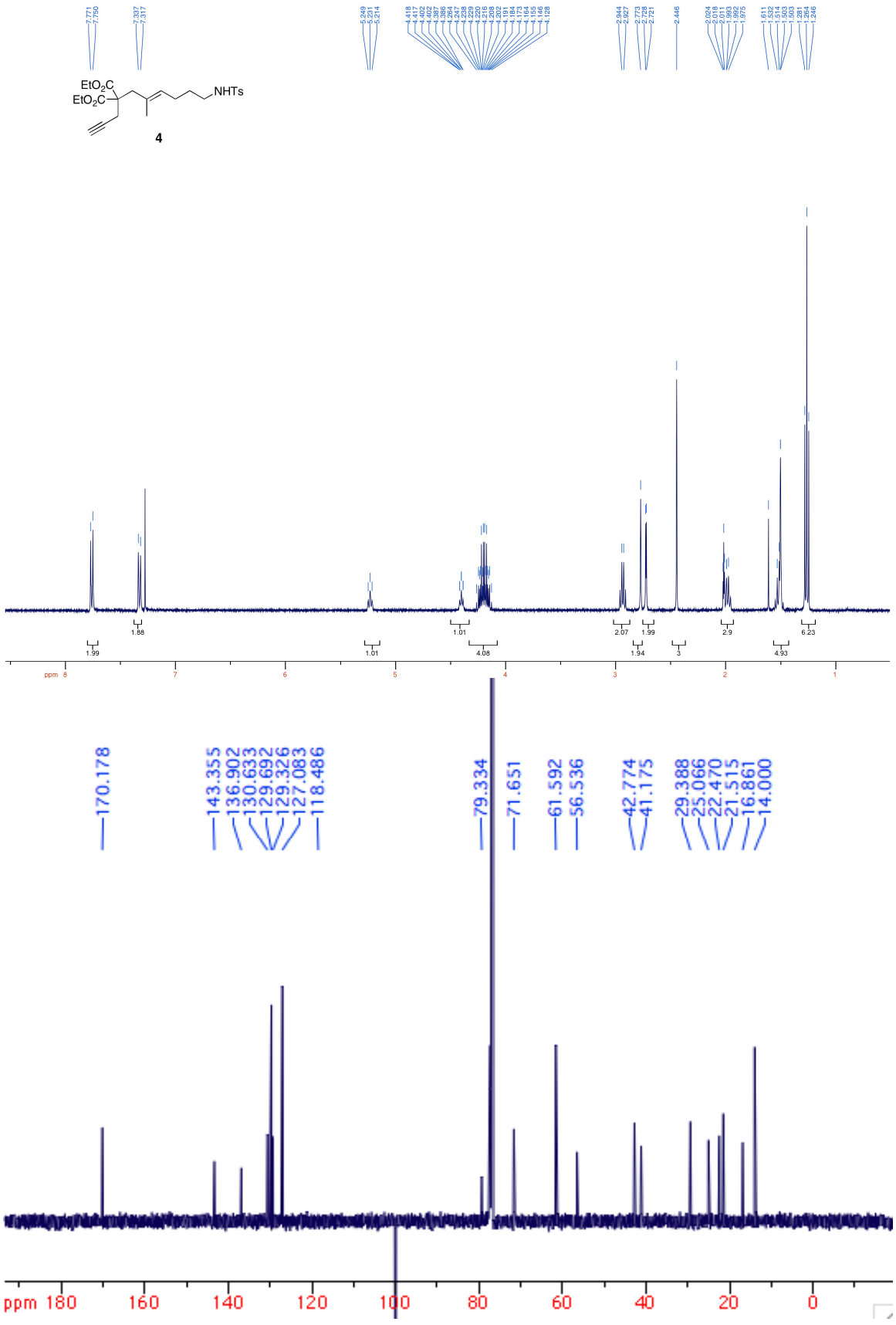
172.20
171.84
154.60
108.52
85.63
62.19
61.99
58.57
48.37
43.38
42.76
30.69
29.33
24.33
23.52
14.45
O
O
H
CO2Et
CH2O2Et
3
220
200
180
160
140
120
100
80
60
40
20
0
-20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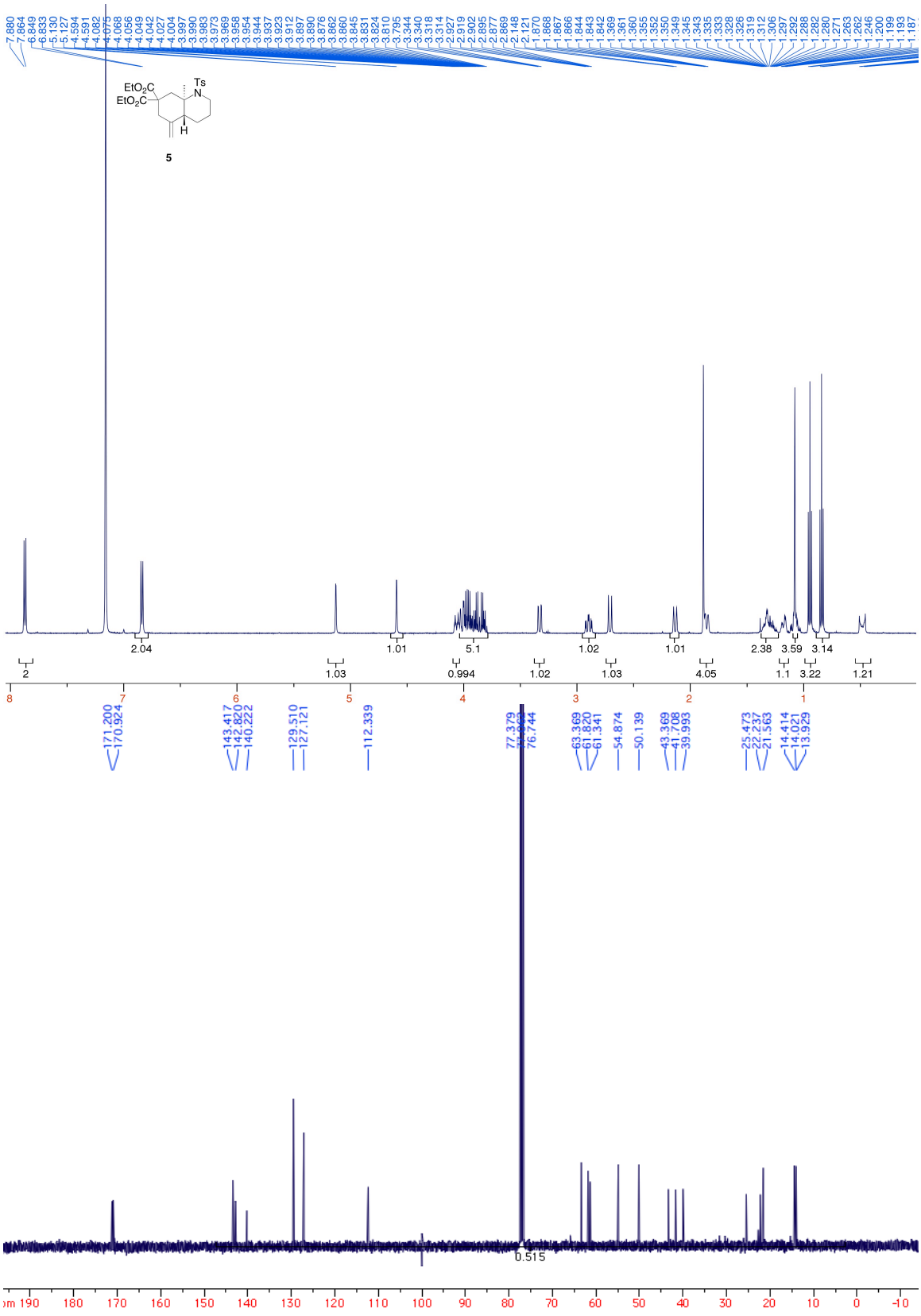
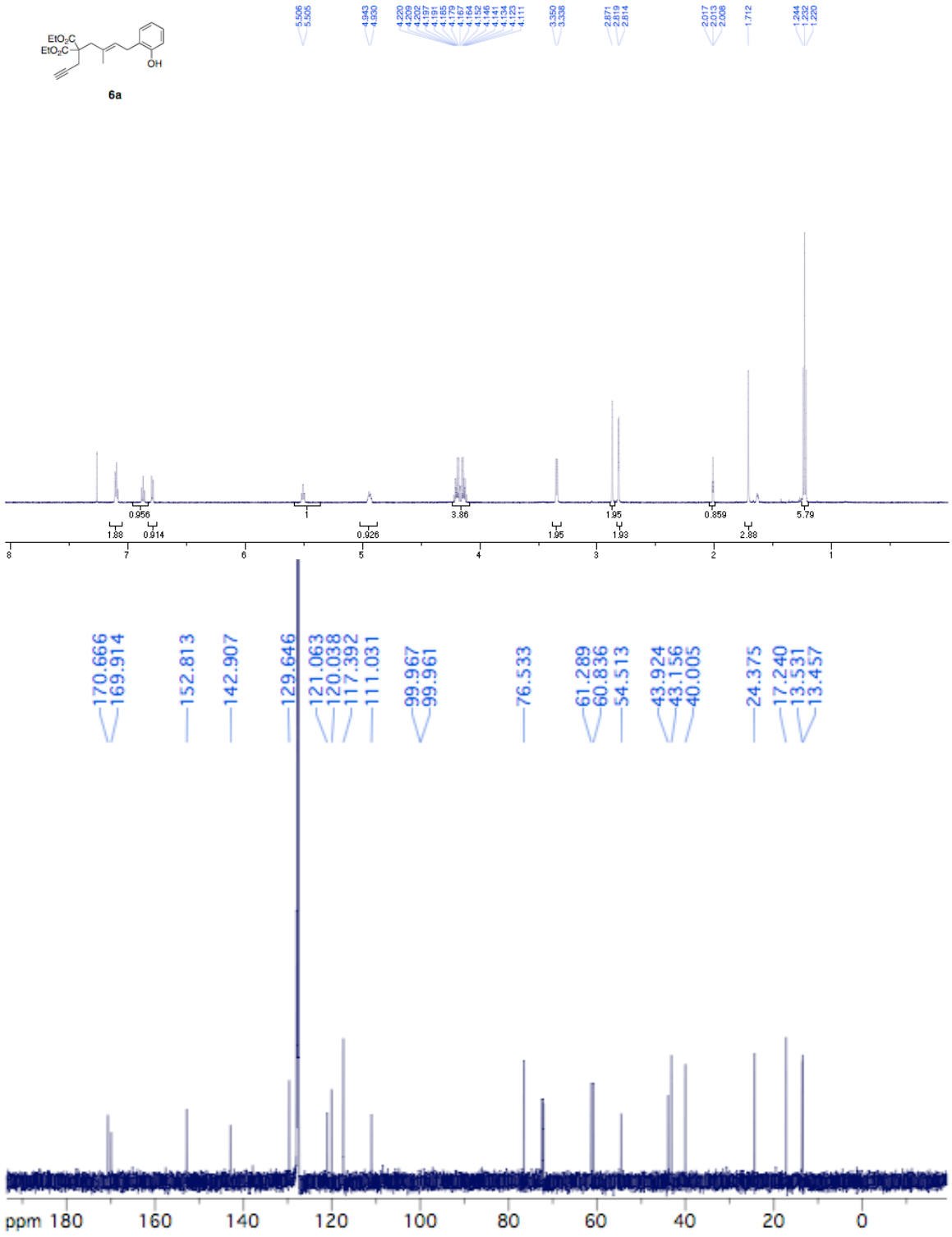
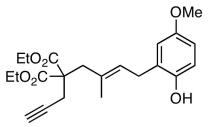
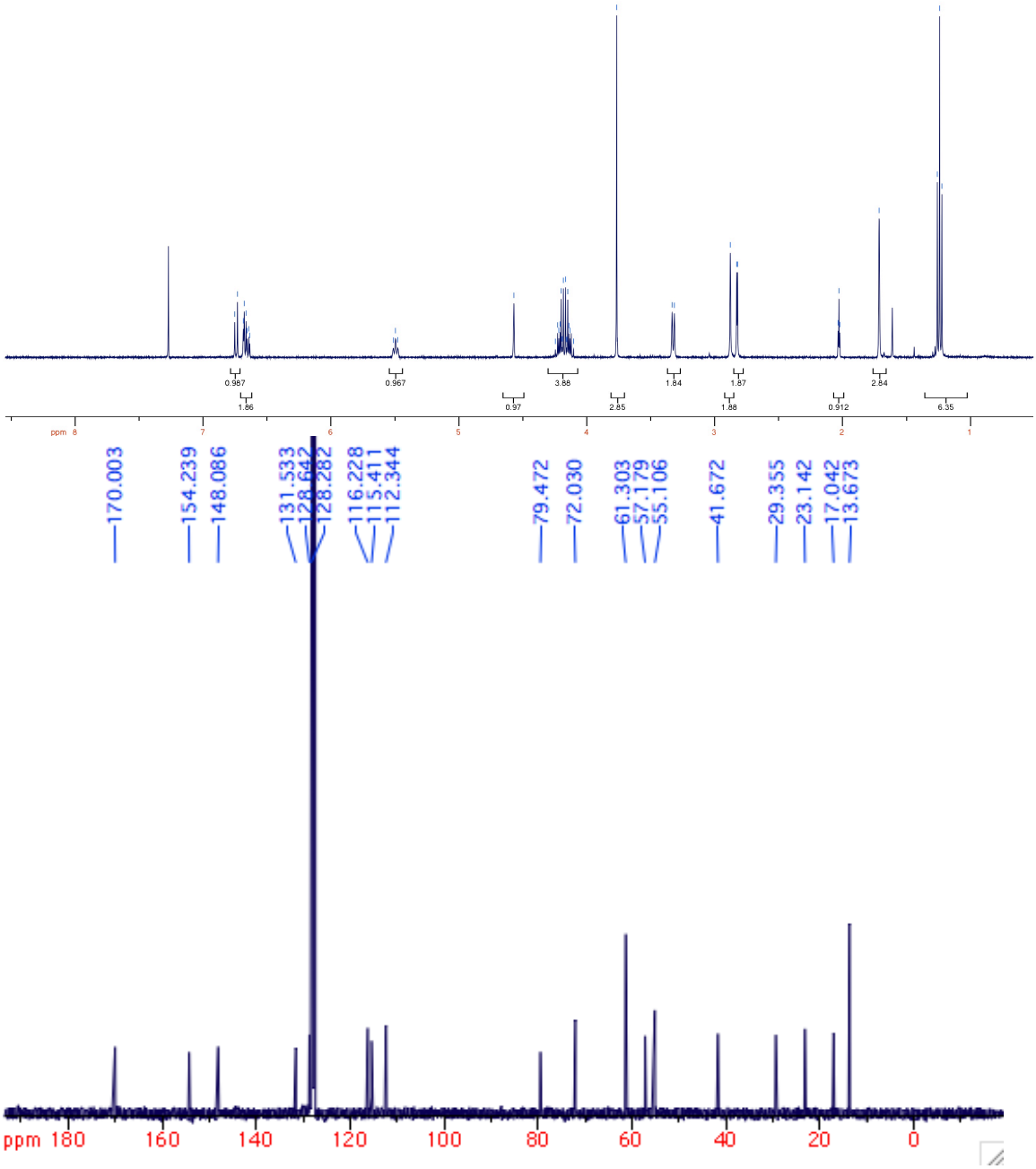
7.750
7.337
7.317
5.249
5.231
5.214
4.418
4.417
4.402
4.387
4.386
4.264
4.247
4.229
4.226
4.208
4.202
4.191
4.184
4.173
4.164
4.155
4.146
4.128
2.844
2.827
2.773
2.728
2.721
2.446
2.024
2.016
2.011
1.993
1.980
1.975
1.611
1.532
1.514
1.503
1.393
1.381
1.264
1.246
EtO2C
EtO2C
NHTs
4
1.99
1.88
1.01
4.08
1.01
2.07
1.99
1.94
3
2.9
4.93
6.23
ppm 8
7
6
5
4
3
2
1
170.178
143.355
136.902
130.633
129.692
129.326
127.083
118.486
79.334
71.651
61.592
56.536
42.774
41.175
29.388
25.066
22.470
21.515
16.861
14.000
ppm 180
160
140
120
100
80
60
40
20
0


EtO2C
EtO2C
Ts
N
H
5


EtO2C
EtO2C
OH
6a
5.506
5.505
4.943
4.930
4.220
4.209
4.202
4.197
4.191
4.185
4.179
4.157
4.164
4.152
4.146
4.141
4.134
4.123
4.111
3.350
3.338
2.871
2.819
2.814
2.017
2.013
2.008
1.712
1.244
1.232
1.220
0.956
1.88
0.914
1
0.926
3.86
1.95
1.95
1.93
0.859
2.88
5.79
170.666
169.914
152.813
142.907
129.646
121.063
120.038
117.392
111.031
99.967
99.961
76.533
61.289
60.836
54.513
43.924
43.156
40.005
24.375
17.240
13.531
13.457
ppm 180
160
140
120
100
80
60
40
20
0


OMe
EtO2C
EtO2C
OH

6b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128.642
128.282
116.228
115.411
112.344
79.472
72.030
61.303
57.179
55.106
41.672
29.355
23.142
17.042
13.673
ppm 180
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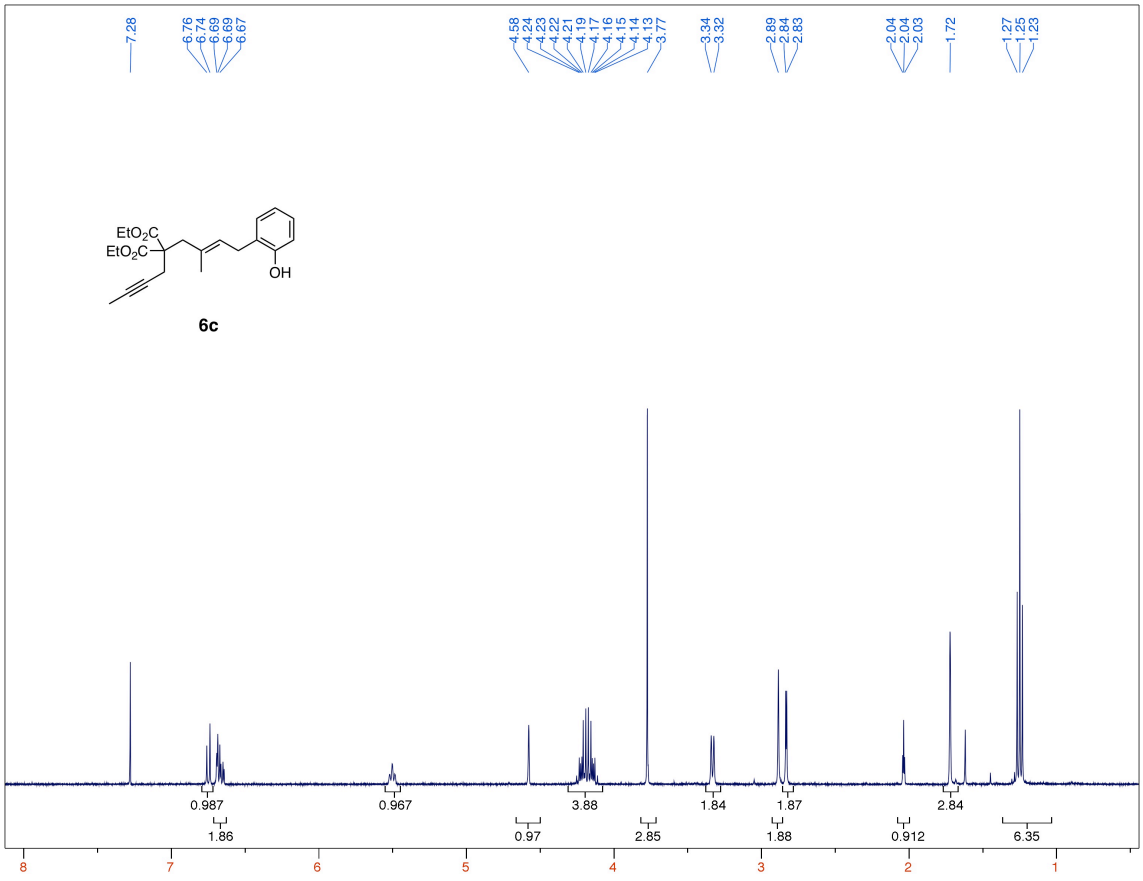
140
120
100
80
60
40
20
0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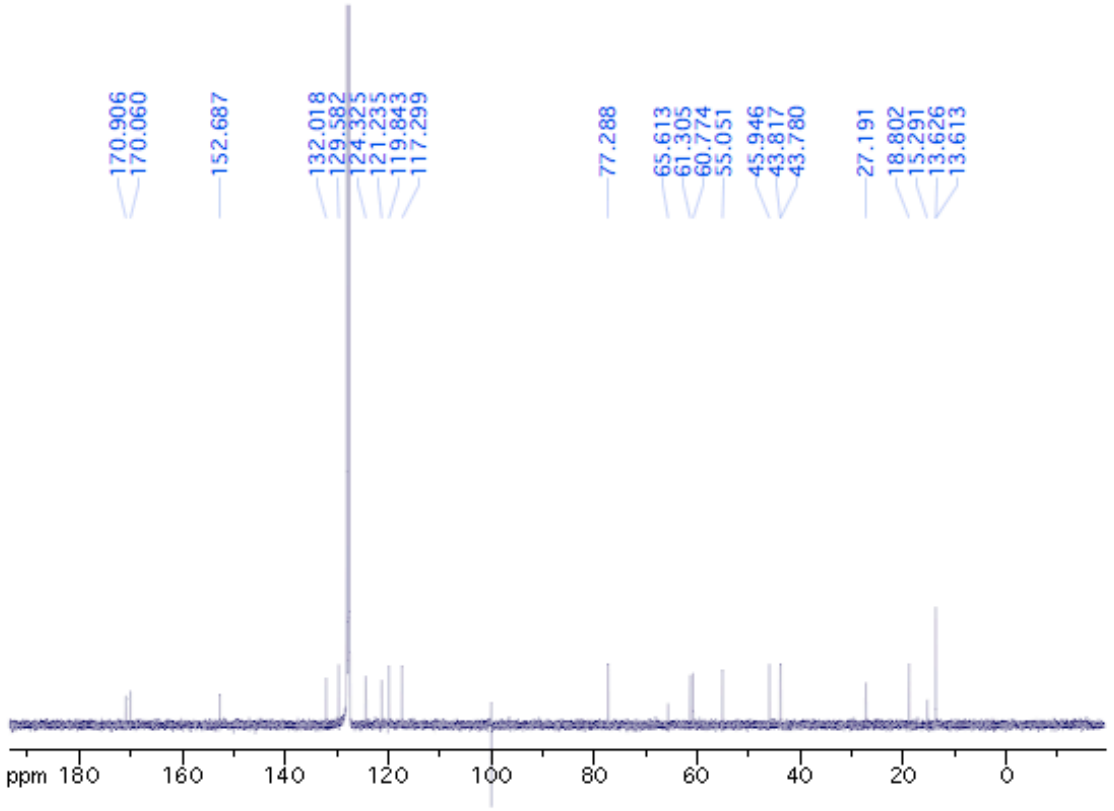
6.76
6.74
6.69
6.69
6.67
4.58
4.24
4.23
4.22
4.21
4.19
4.17
4.16
4.15
4.14
4.13
3.77
3.34
3.32
2.89
2.84
2.83
2.04
2.04
2.03
1.72
1.27
1.25
1.23
EtO2C
EtO2C
OH
6c
0.987
1.86
0.967
0.97
3.88
2.85
1.84
1.87
1.88
2.84
0.912
6.35
8
7
6
5
4
3
2
1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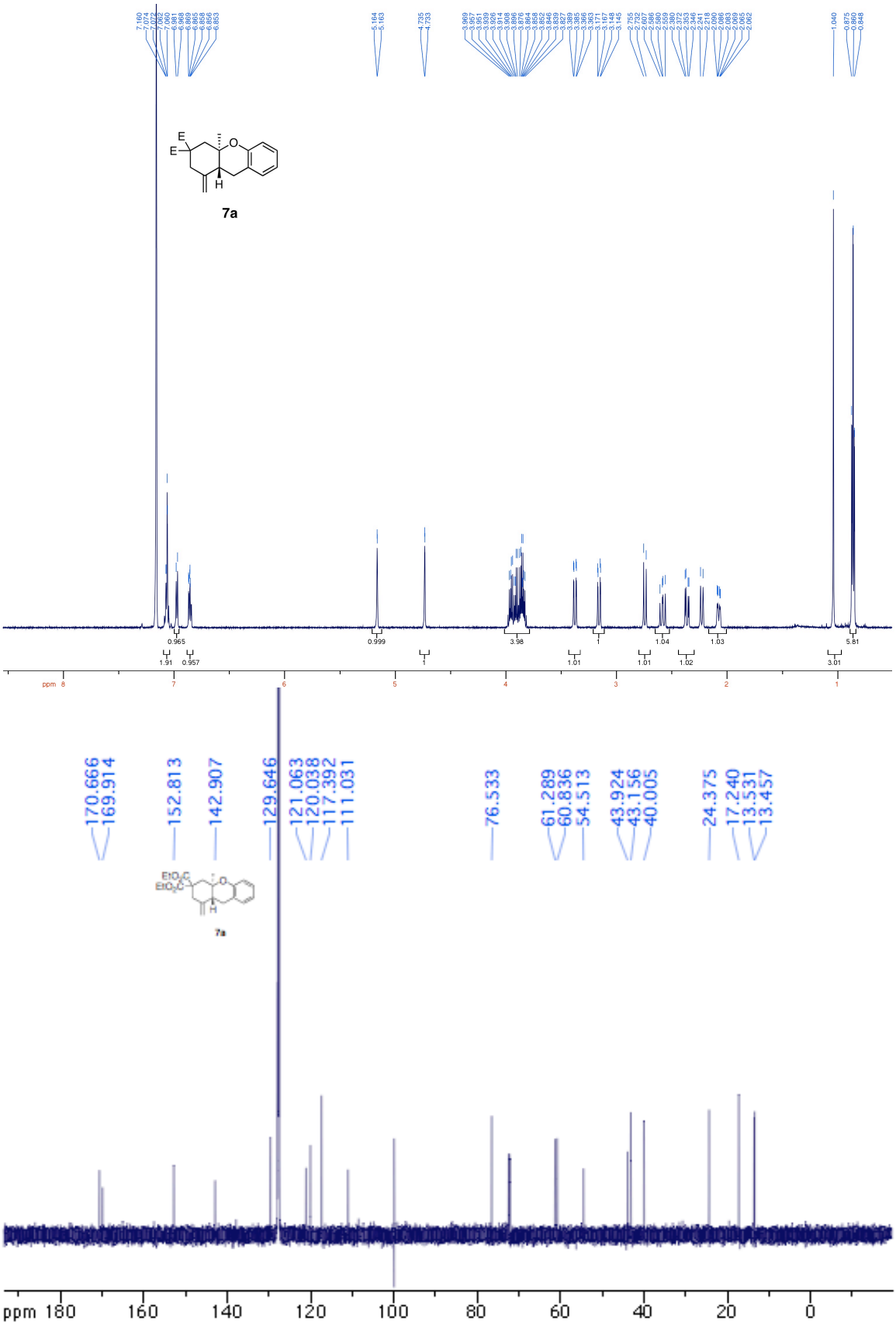
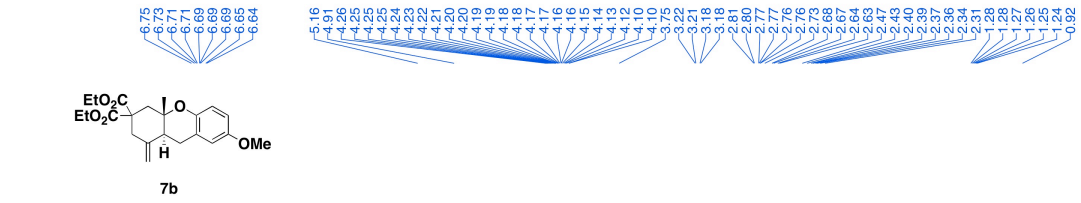
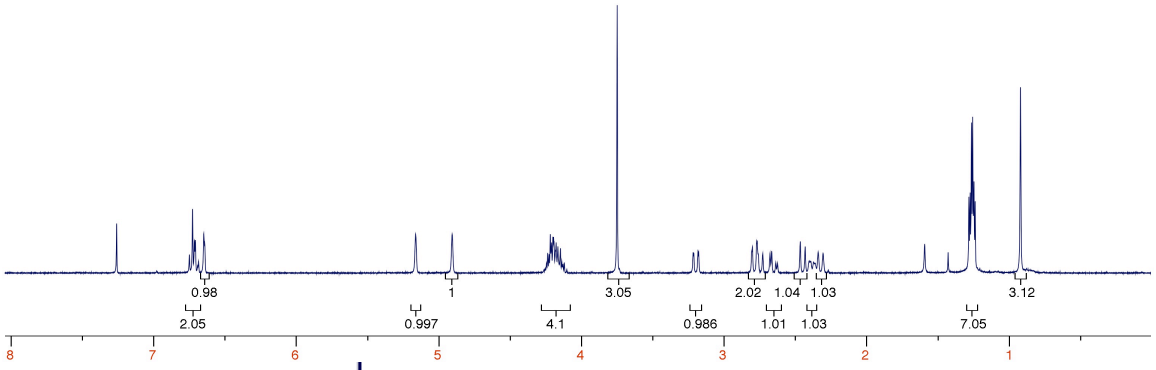
170.060
152.687
132.018
129.582
124.325
121.235
119.843
117.299
77.288
65.613
61.305
60.774
55.051
45.946
43.817
43.780
27.191
18.802
15.291
13.626
13.613
ppm 180
160
140
120
100
80
60
40
20
0


7a
ppm 180
160
140
120
100
80
60
40
20
0


6.75
6.73
6.71
6.69
6.69
6.69
6.65
6.64
5.16
4.91
4.26
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.18
4.17
4.17
4.16
4.16
4.15
4.14
4.13
4.12
4.10
4.10
3.75
3.22
3.21
3.18
3.18
2.81
2.80
2.77
2.77
2.76
2.76
2.73
2.68
2.67
2.64
2.63
2.47
2.43
2.40
2.39
2.37
2.36
2.34
2.31
1.28
1.28
1.27
1.26
1.25
1.24
0.92

EtO2C
EtO2C
O
H
OMe

7b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1
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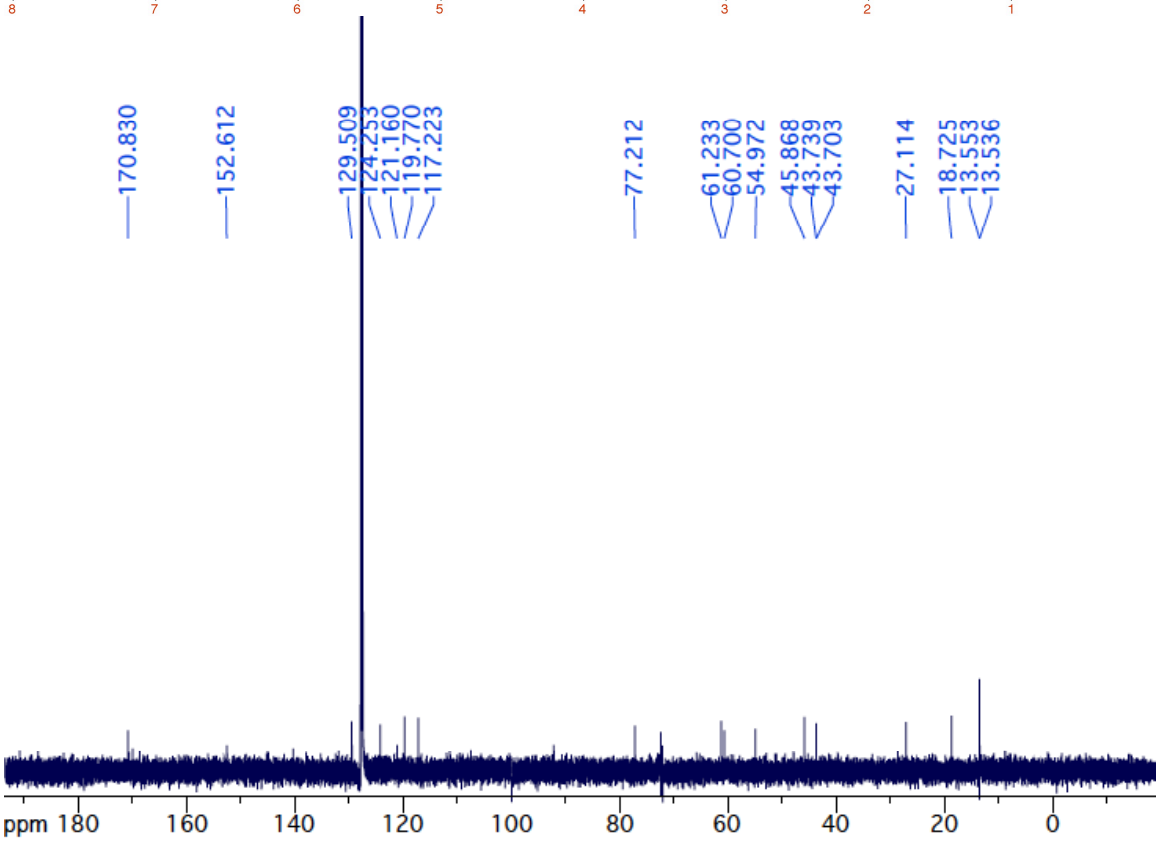
2.02
1.04
1.03
3.12
2.05
0.997
4.1
0.986
1.01
1.03
7.05
8
7
6
5
4
3
2
1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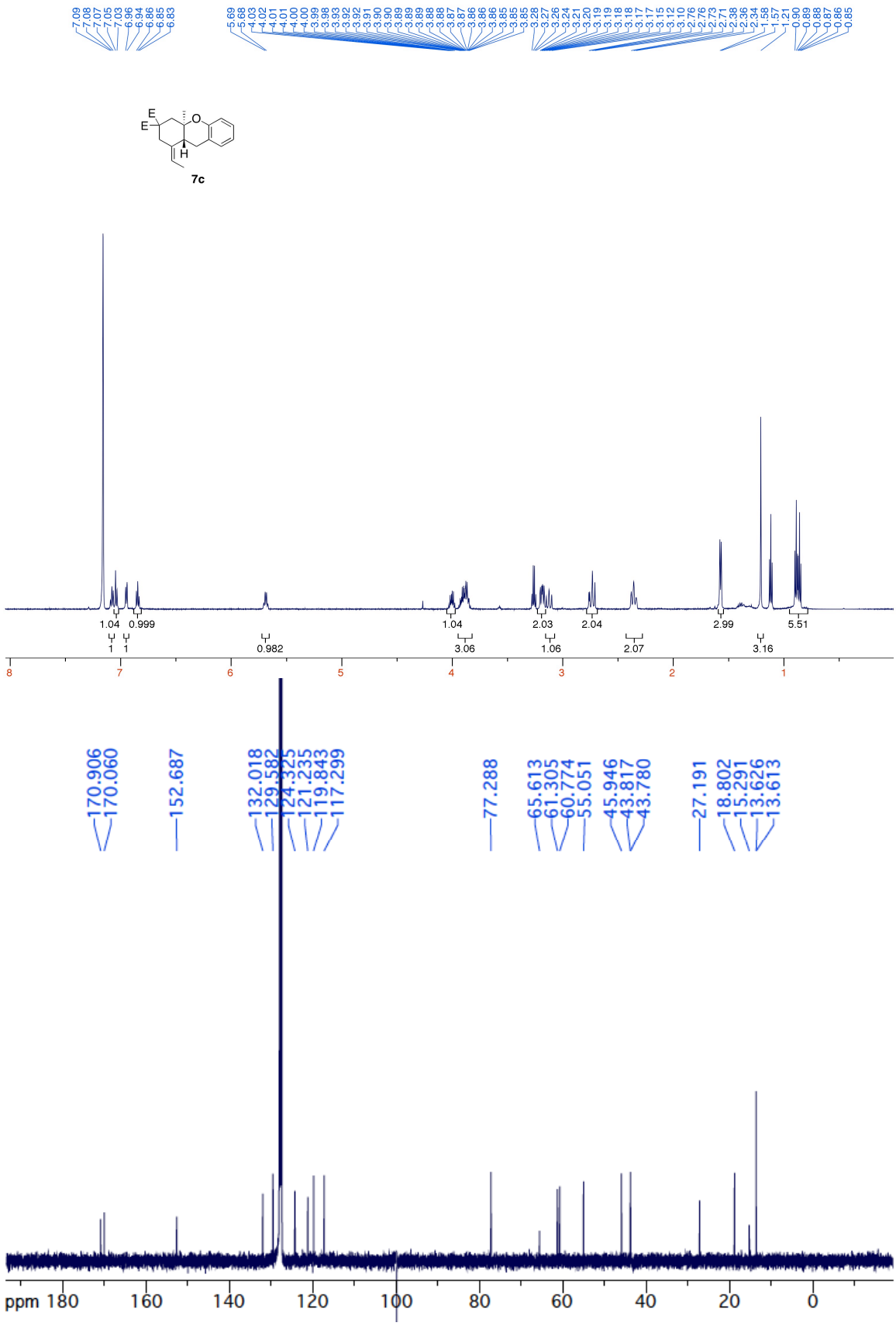
129.509
124.253
121.160
119.770
117.223
77.212
61.233
60.700
54.972
45.868
43.739
43.703
27.114
18.725
13.553
13.536
ppm 180
160
140
120
100
80
60
40
20
0


7.09
7.08
7.07
7.05
7.03
6.96
6.94
6.86
6.85
6.83
5.69
5.68
4.03
4.02
4.01
4.01
4.00
4.00
3.99
3.98
3.93
3.92
3.92
3.91
3.90
3.90
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3.89
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3.88
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3.87
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3.86
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3.85
3.85
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3.18
3.18
3.17
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3.10
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2.76
2.73
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0.86
0.85
E
E
O
H
7c
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2.03
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121.235
119.843
117.299
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65.613
61.305
60.774
55.051
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43.817
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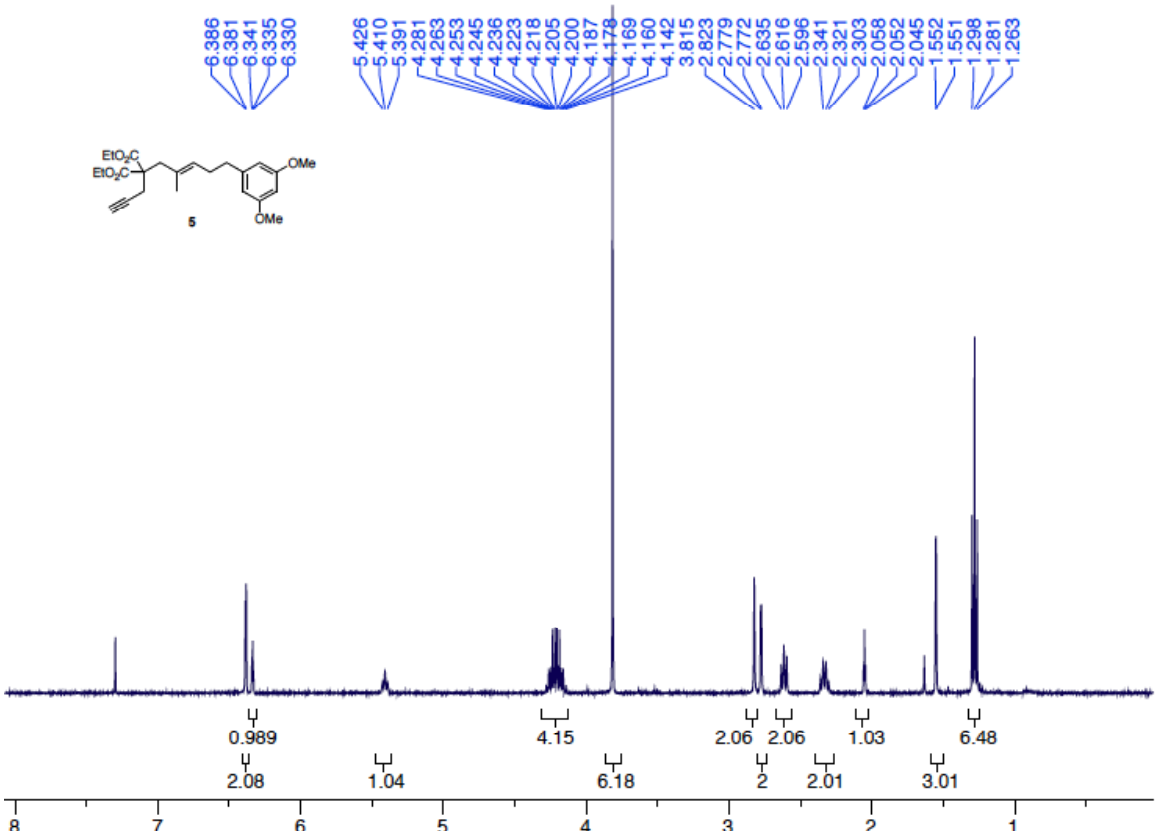
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4.223
4.218
4.205
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3.815
2.823
2.779
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EtO2C
EtO2C
OMe
OMe
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2.06
2.06
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3.01
8
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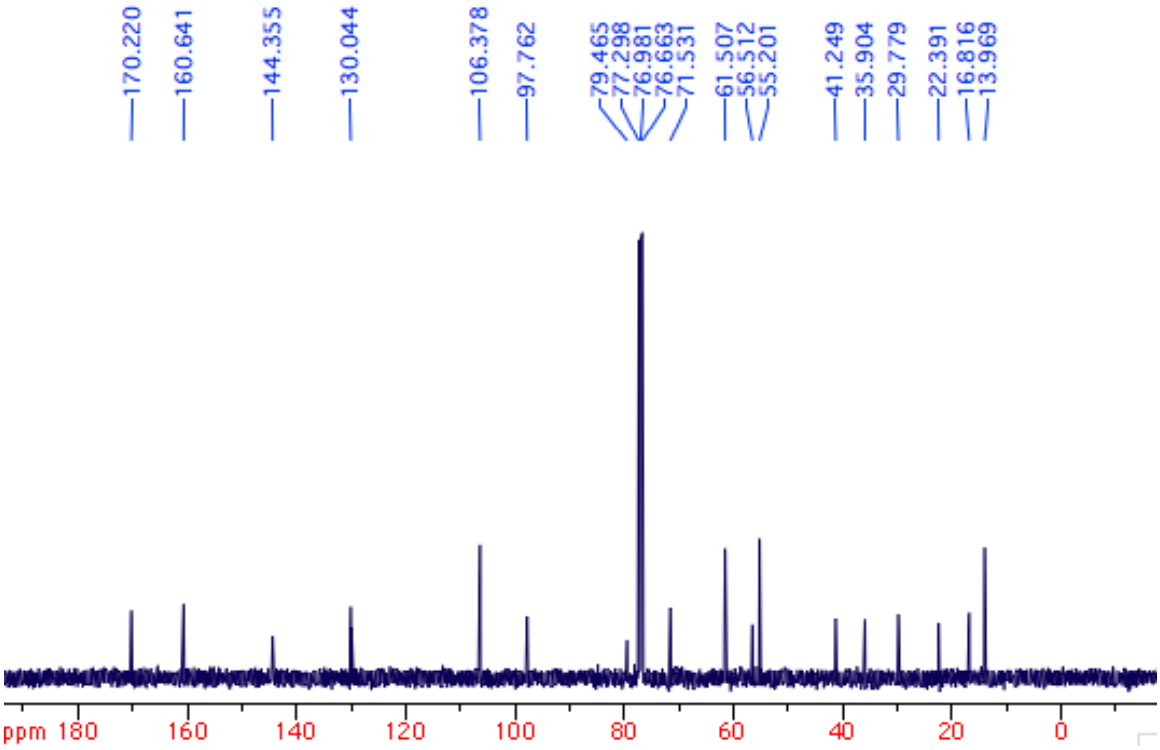
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77.298
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56.512
55.201
41.249
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22.391
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13.969
ppm 180
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140
120
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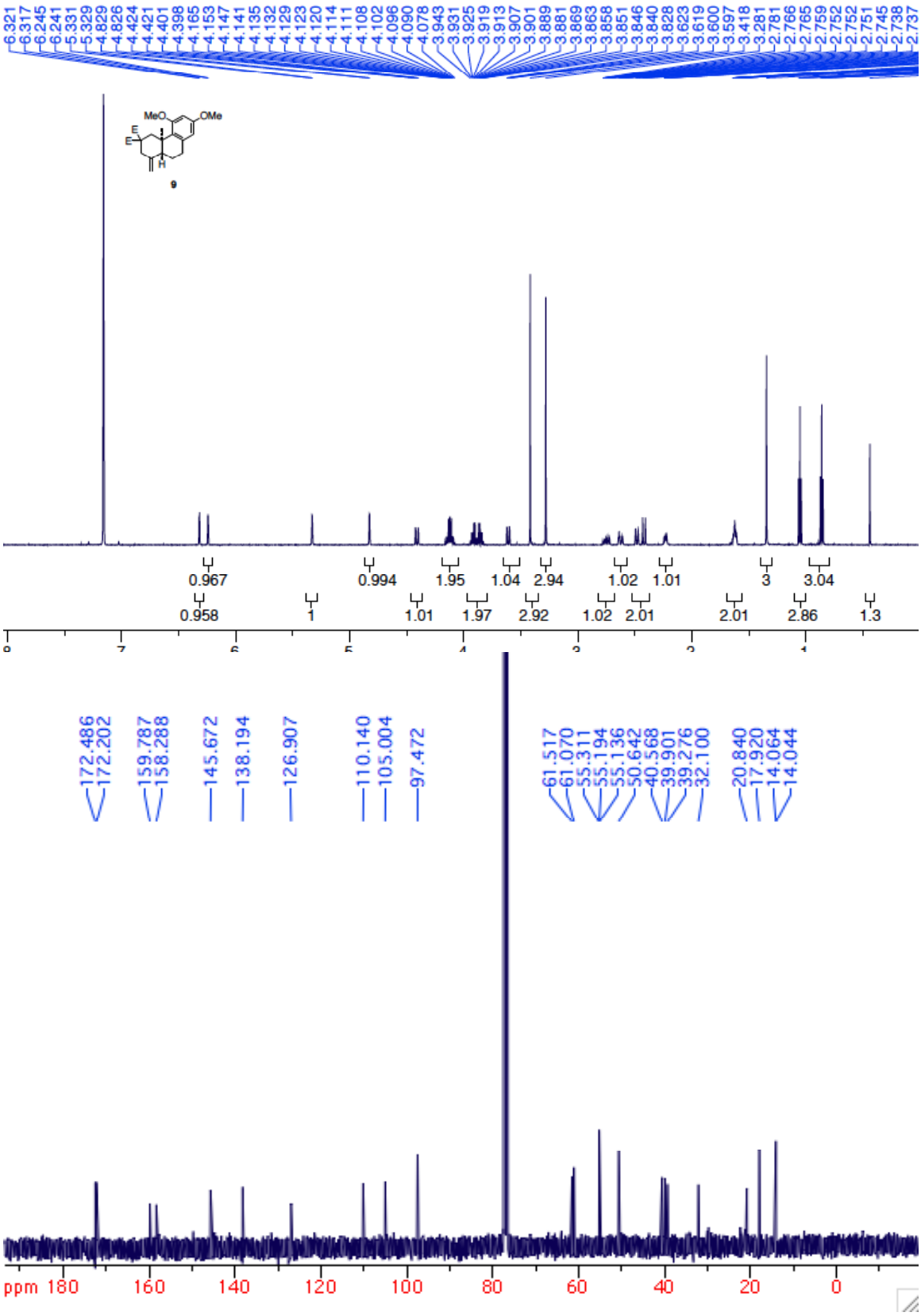
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4.153
4.147
4.141
4.135
4.132
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4.120
4.114
4.111
4.108
4.102
4.096
4.090
4.078
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3.931
3.925
3.919
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3.907
3.901
3.889
3.881
3.869
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3.858
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3.846
3.840
3.828
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3.281
2.781
2.766
2.765
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2.752
2.752
2.751
2.745
2.738
2.737
MeO
OMe
Et
Et
H
9
0.967
0.994
1.95
1.04
2.94
1.02
1.01
3
3.04
0.958
1
1.01
1.97
2.92
1.02
2.01
2.01
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1.3
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158.288
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126.907
110.140
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61.070
55.311
55.194
55.136
50.642
40.568
39.901
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120
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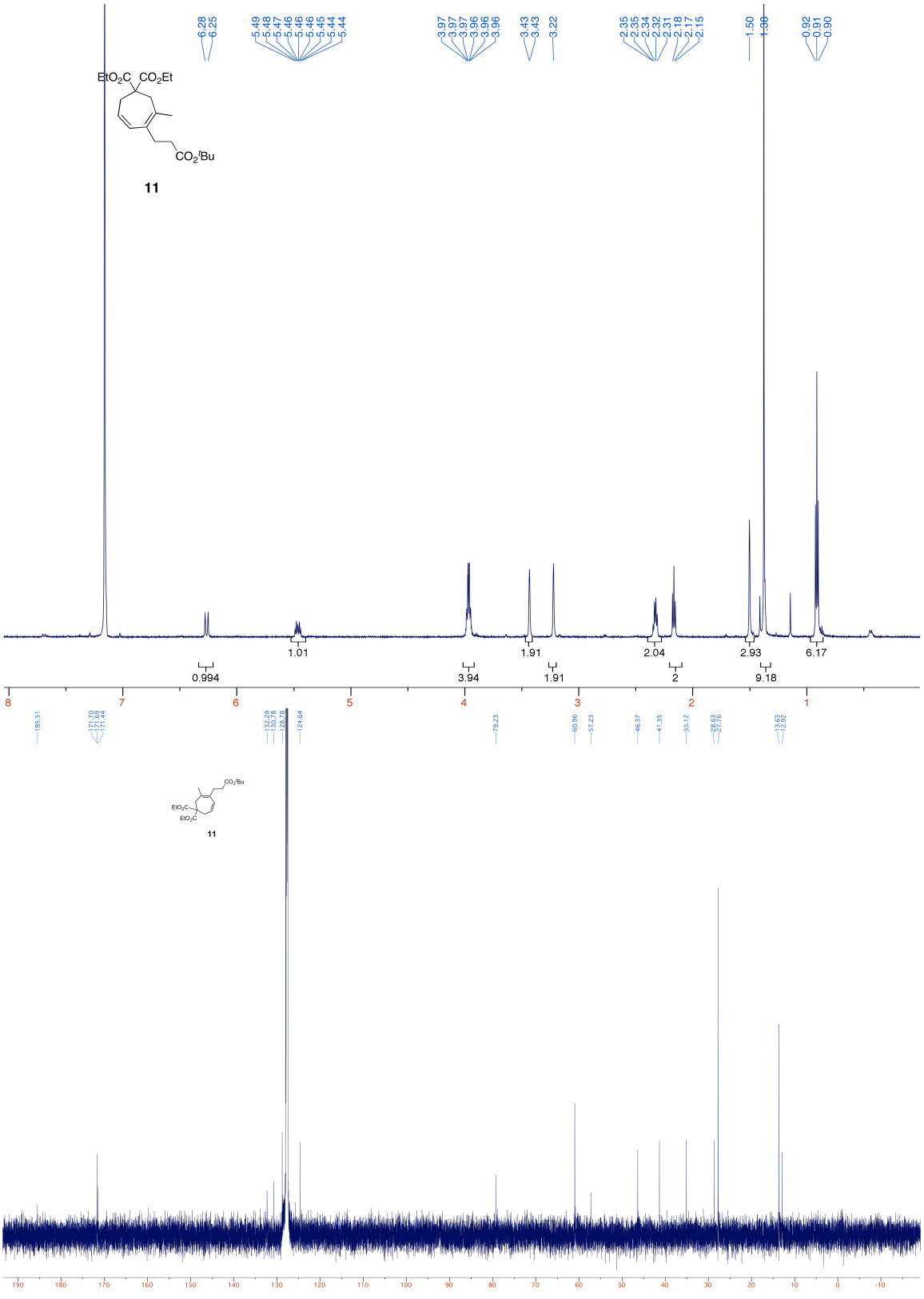
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3.97
3.96
3.96
3.96
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3.43
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2.35
2.35
2.34
2.32
2.31
2.18
2.17
2.15
1.50
1.30
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0.91
0.90
EtO2C CO2Et
CO2tBu
11
1.01
0.994
3.94
1.91
1.91
2.04
2
2.93
9.18
6.17
8
7
6
5
4
3
2
1
185.51
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171.69
171.44
132.29
130.78
129.76
124.64
79.23
60.96
57.23
46.37
41.35
35.12
28.63
27.76
13.63
12.82
CO2tBu
EtO2C
EtO2C
11
190
180
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120
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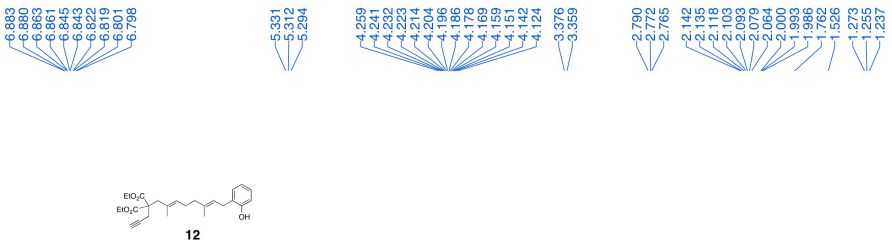
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4.241
4.232
4.223
4.214
4.204
4.196
4.186
4.178
4.169
4.159
4.151
4.142
4.124
3.376
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2.772
2.765
2.142
2.135
2.118
2.103
2.093
2.079
2.064
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1.986
1.762
1.526
1.273
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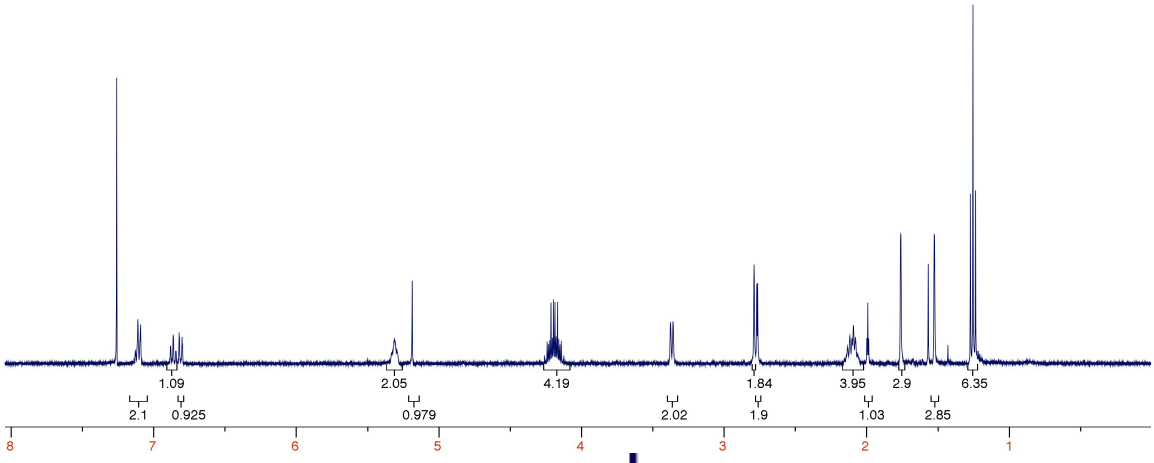
1.237

EtO2C
EtO2C
OH

12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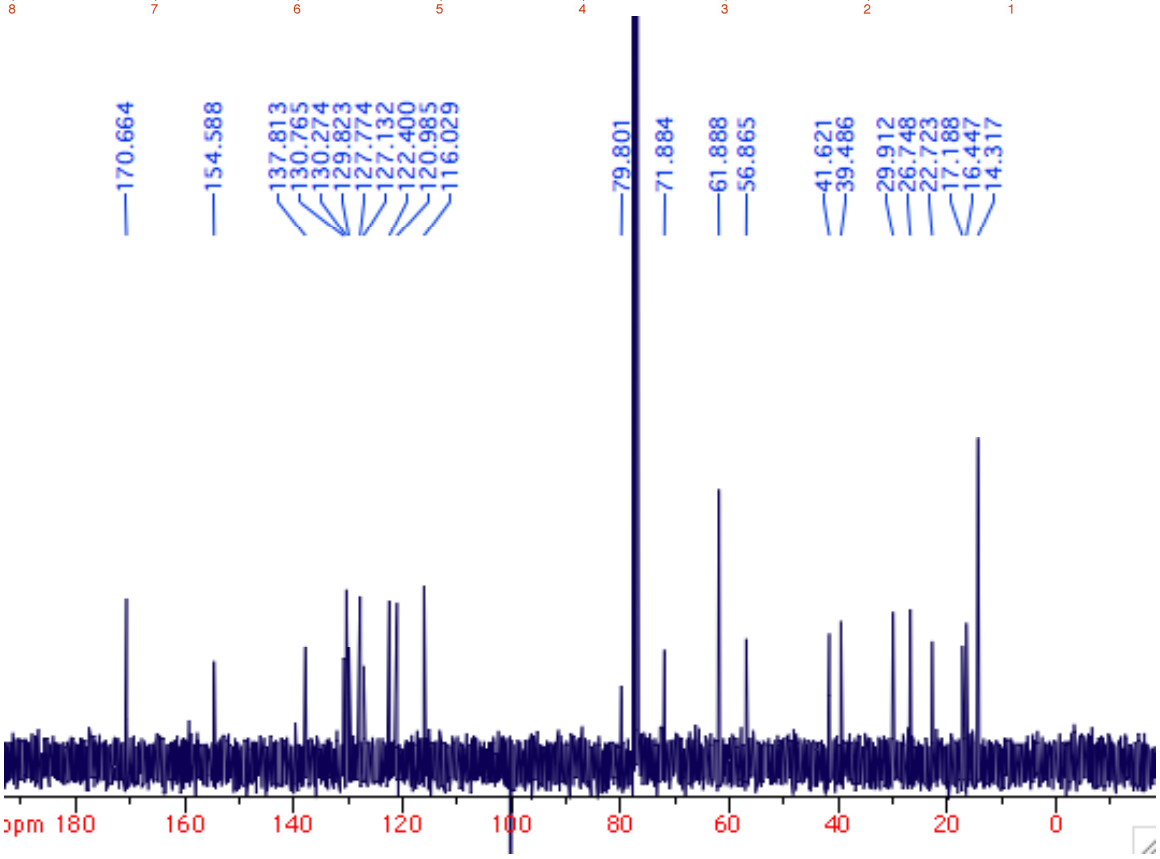
8
7
6
5
4
3
2
1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127.132
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61.888
56.865
41.621
39.486
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17.188
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ppm 180
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140
120
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80
60
40
20
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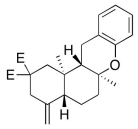
E
E
H
O
H

13

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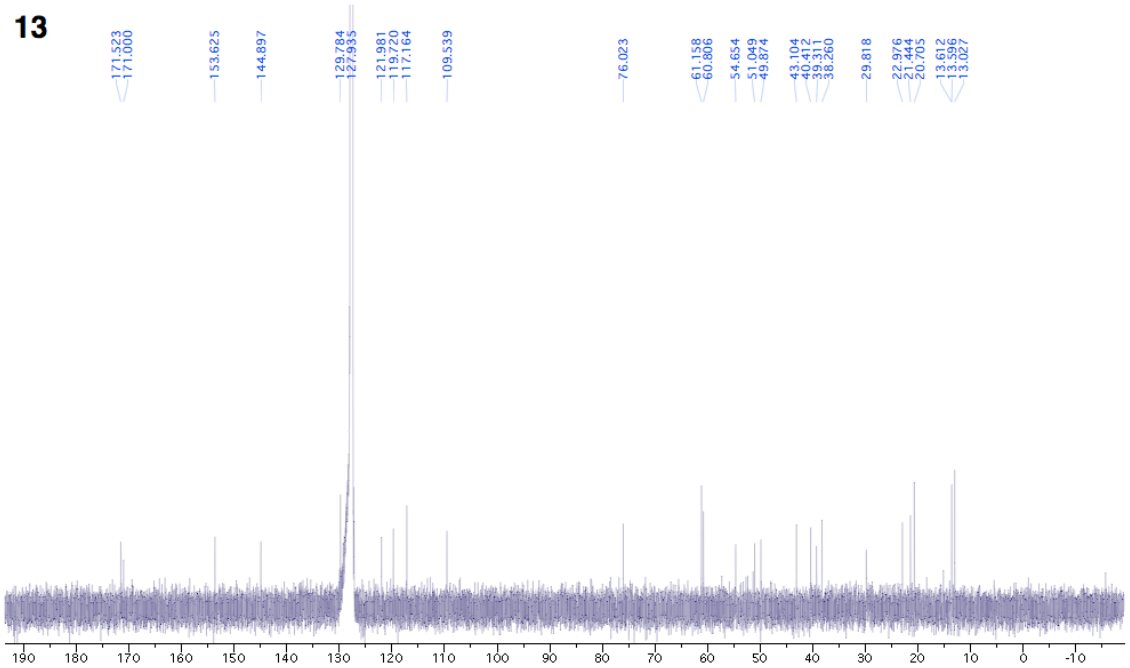
10.5

13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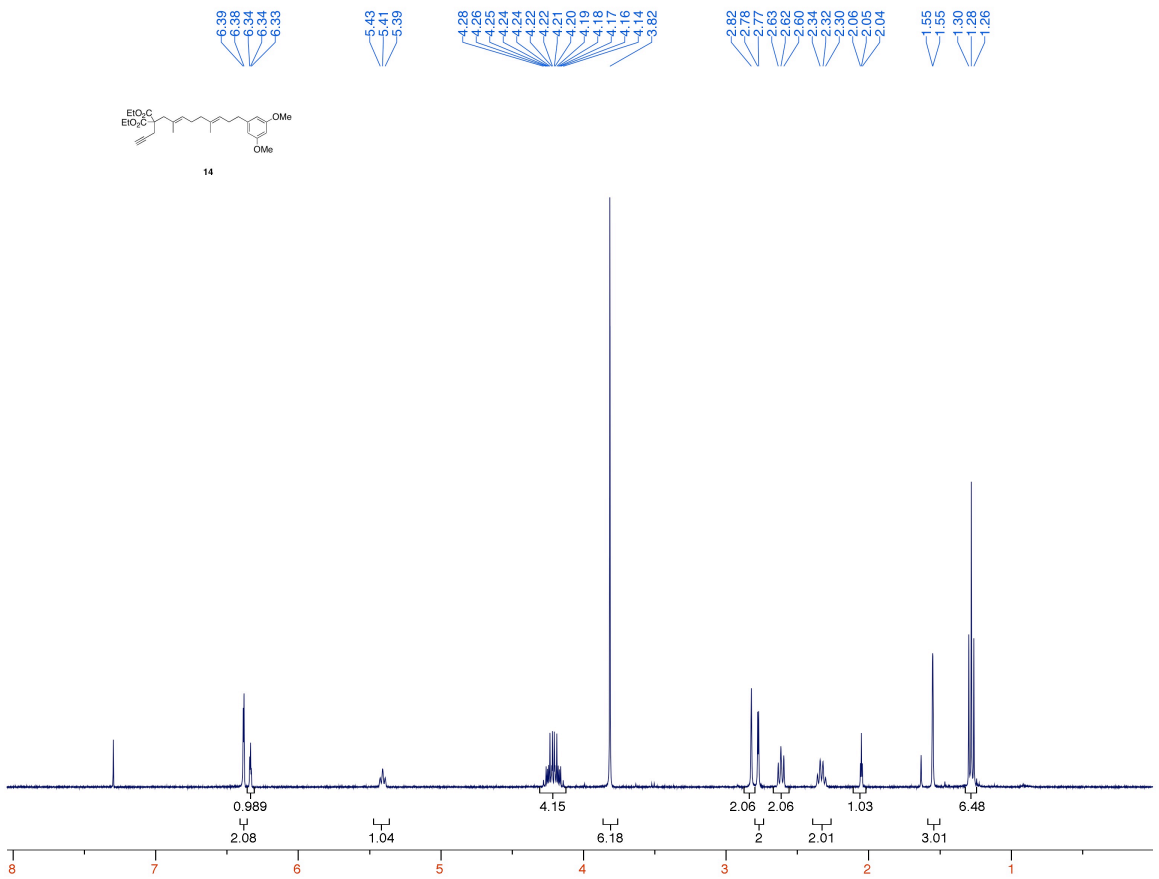
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5.39
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4.26
4.25
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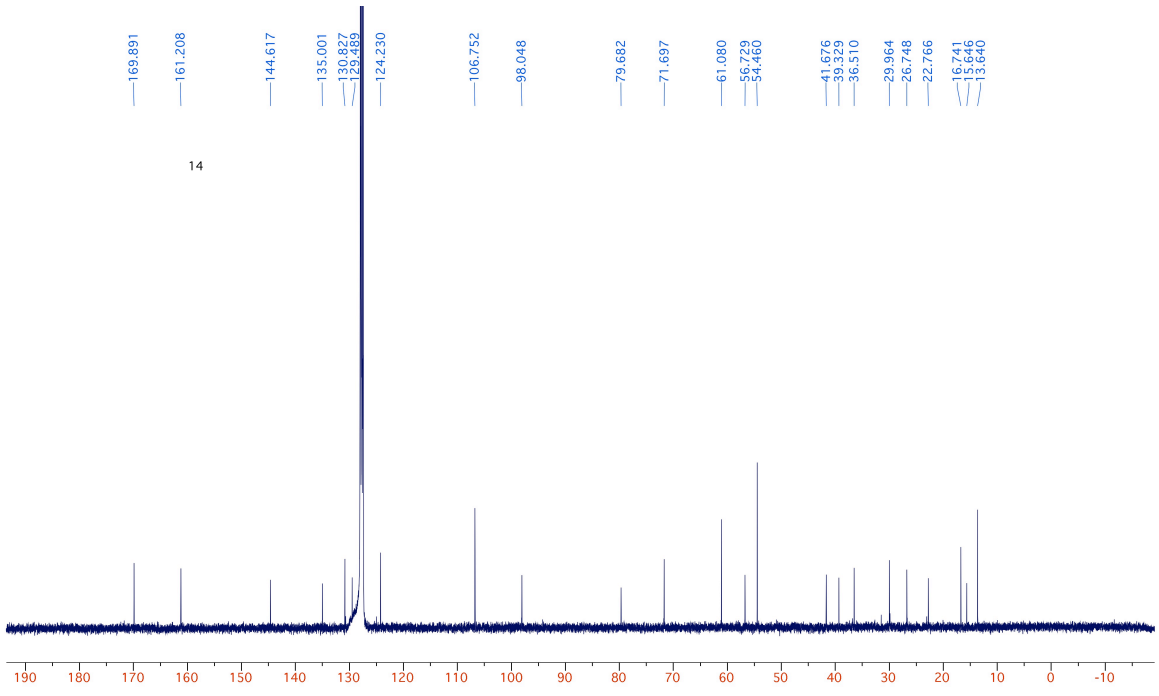
4.24
4.22
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.14
3.82
2.82
2.78
2.77
2.63
2.62
2.60
2.34
2.32
2.30
2.06
2.05
2.04
1.55
1.55
1.30
1.28
1.26
EtO2C
EtO2C
OMe
OMe
14
0.989
4.15
2.06
2.06
1.03
6.48
2.08
1.04
6.18
2
2.01
3.01
8
7
6
5
4
3
2
1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61.080
56.729
54.460
41.676
39.329
36.510
29.964
26.748
22.766
16.741
15.646
13.640
14
190
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140
130
120
110
100
90
80
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60
50
40
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20
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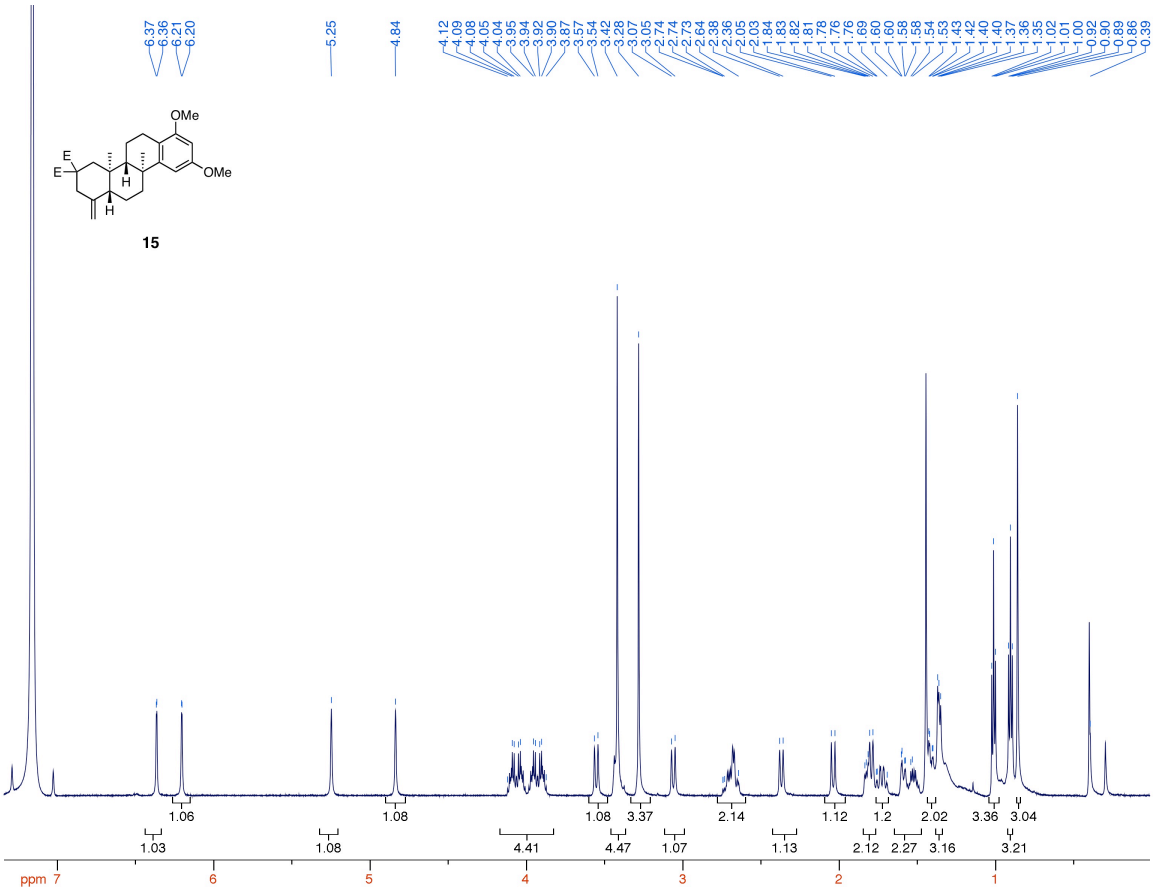
0
-10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4.09
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4.05
4.04
3.95
3.94
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3.90
3.87
3.57
3.54
3.42
3.28
3.07
3.05
2.74
2.74
2.73
2.64
2.38
2.36
2.05
2.03
1.84
1.83
1.82
1.81
1.78
1.76
1.76
1.69
1.60
1.60
1.58
1.58
1.54
1.53
1.43
1.42
1.40
1.40
1.37
1.36
1.35
1.02
1.01
1.00
0.92
0.90
0.89
0.88
0.39
OMe
OMe
E
E
H
H
15
1.06
1.08
1.08
3.37
2.14
1.12
1.2
2.02
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1.08
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1.13
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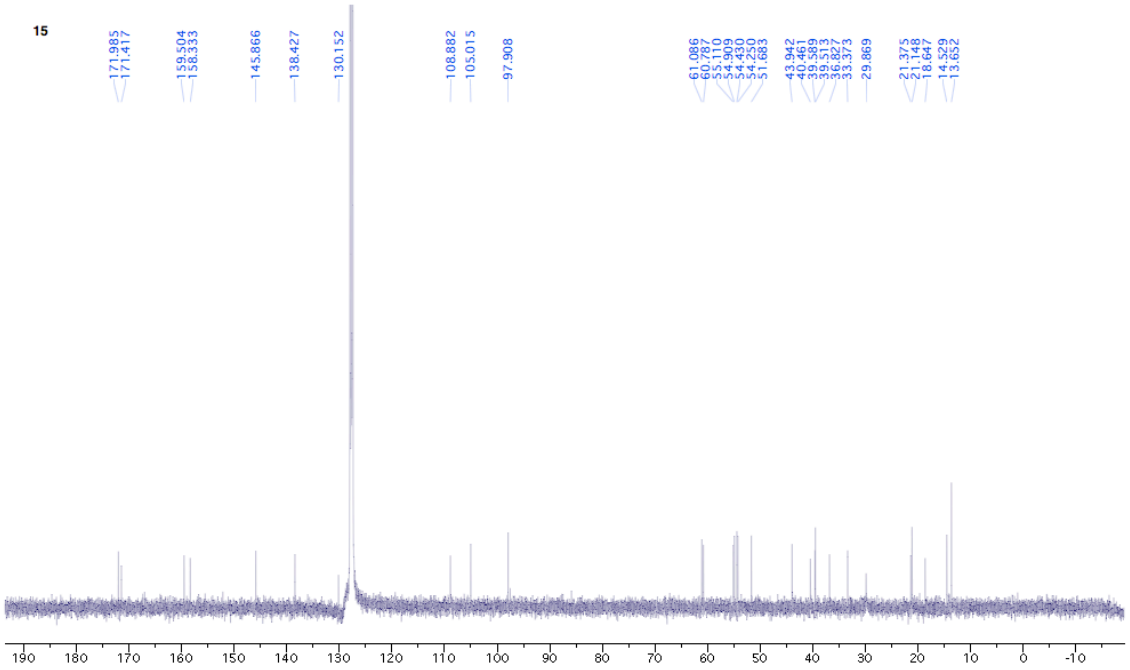
2
1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53.110
54.990
54.430
54.250
51.683
43.942
40.461
39.593
39.313
36.827
33.373
29.869
21.375
21.148
18.647
14.529
13.652
190
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100
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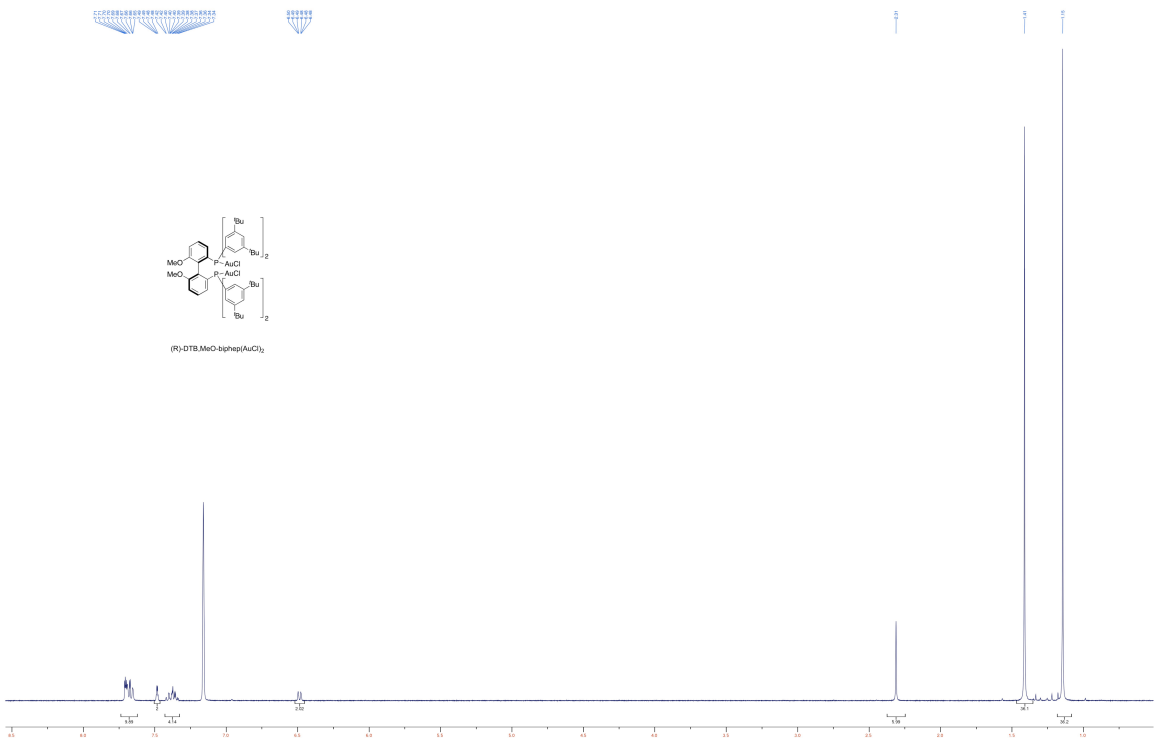
tBu
tBu
MeO
MeO
P→AuCl
P→AuCl
tBu
tBu
(R)-DTB,MeO-biphep(AuCl)2