Electronic Supplementary Material (ESI) for Chemical Communications.

An Expedient Synthesis of Functionalized 1,4-Diketone-Derived Compounds via Silyloxyallyl Cation Intermediates

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SUPPORTING INFORMATION

GENERAL INFORMATION

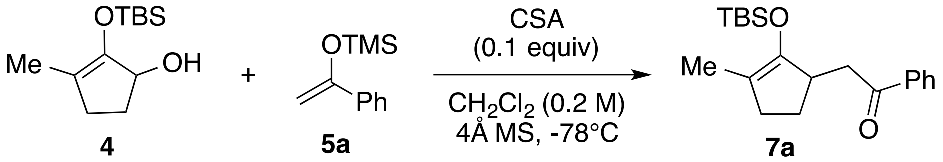
Unless otherwise noted, all materials were used as received from commercial suppliers without further purification. All anhydrous reactions were performed using oven-dried or flame-dried glassware, which was then cooled under vacuum and purged with nitrogen gas. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), acetonitrile, toluene, and diethyl ether (Et_2O) were filtered through activated 3Å molecular sieves under nitrogen contained in an M-Braun Solvent Purification System. All reactions were monitored by EMD analytical thin layer chromatography (TLC Silica Gel 60 F_{254}, Glass Plates) and analyzed with 254 nm UV light and / or anisaldehyde – sulfuric acid or potassium permanganate treatment. Silica gel for column chromatography was purchased from Dynamic Adsorbents, Inc. or Sigma Aldrich (Flash Silica Gel 32-63u).

Unless otherwise noted, all ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Ascend 400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C or Bruker Ascend 500 spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Chemical shifts (δ) are reported in ppm relative to residual $CHCl_3$ as an internal reference (^1H: 7.26 ppm, ^{13}C: 77.23 ppm). Coupling constants (J) are reported in Hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), x (septet), h (heptet), b (broad), and m (multiplet). FT-IR spectra were recorded on Bruker Tensor 27 spectrometer and OPUS 6.5 Data Collection Program, and absorption frequencies were reported in reciprocal centimeters (cm^{-1}). High Resolution Mass Spectrometry – Electron Spray Ionization (HRMS-ESI) analyses were performed by the Louisiana State University Mass Spectrometry Facility using an Agilent

6210 Instrument. X-ray structure analyses were performed by the Louisiana State University X-ray Structure Facility using a Bruker APEX-II CCD diffractometer.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION OF NEW COMPOUNDS

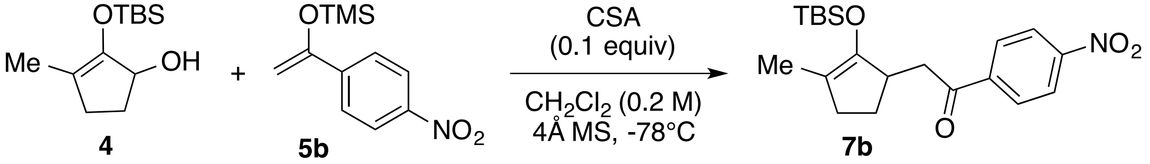
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-1-phenylethan-1-one (7a)



Starting material **4** (200 mg, 0.876 mmol) was dissolved in dry CH_2Cl_2 (4.4 mL), and 4Å molecular sieves (1.0 g) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (359 mL, 1.75 mmol) was added, followed by camphorsulfonic acid (20 mg, 0.088 mmol). The solution was stirred at -78°C for 7 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7a** (242 mg, 83%) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.97 (dd, J = 8.4, 1.4 Hz, 2H), 7.65 – 7.48 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 3.29 (dd, J = 16.9, 2.8 Hz, 1H), 3.10 (tdd, J = 8.3, 4.4, 2.4 Hz, 1H), 2.90 (dd, J = 16.9, 10.7 Hz, 1H), 2.28 – 2.11 (m, 3H), 1.58 (s, 3H), 1.51 – 1.40 (m, 1H), 0.96 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (125 MHz): δ = 199.81, 147.92, 137.23, 132.79, 128.43, 127.98, 113.74, 42.26, 41.33, 31.89, 26.94, 25.68, 18.03, 12.34, -4.10, -4.29. FT-IR: f (cm^{-1}) = 2929, 2857, 1685, 1251, 1210, 907, 854, 836, 778, 752, 729, 688, 648. HR-MS: $(M+H)^+$ = 331.2088 calculated for $C_{20}H_{31}O_2Si$; experimental = 331.2090.

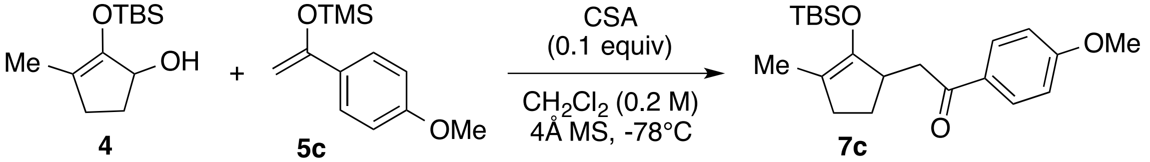
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-1-(4-nitrophenyl)ethan-1-one (7b)



Starting material **4** (100 mg, 0.438 mmol) was dissolved in dry CH_2Cl_2 (2.2 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5b** (208 mg, 0.876 mmol) was added, followed by camphorsulfonic acid (10 mg, 0.044 mmol). The solution was stirred at -78°C for 21 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7b** (97 mg, 59%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.30 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 3.30 (dd, *J* = 16.9, 3.0 Hz, 1H), 3.07 (m, 1H), 2.93 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.24 – 2.09 (m, 3H), 1.55 (s, 3H), 1.50 – 1.38 (m, 1H), 0.94 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (125 MH): δ = 198.57, 150.24, 147.43, 141.62, 129.06, 123.78, 114.34, 42.96, 41.52, 31.95, 26.86, 25.71, 18.08, 12.38, -4.05, -4.22. FT-IR: *f* (cm^{-1}) = 2954, 2929, 2856, 1687, 1603, 1526, 1471, 1443, 1344, 1329, 1252, 1209, 1086, 1009, 938, 894, 836, 778, 746, 732, 685. HR-MS: $(M+H)^+$ = 376.1939 calculated for $C_{20}H_{30}NO_4Si$; experimental = 376.1942.

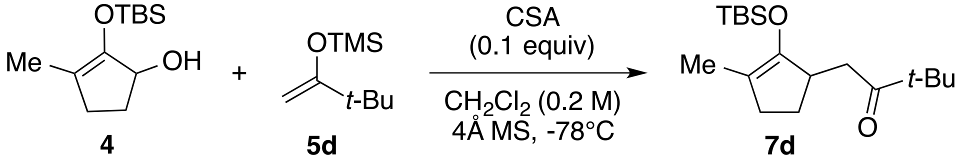
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-1-(4-methoxyphenyl)ethan-1-one (7c)



Starting material **4** (100 mg, 0.438 mmol) was dissolved in dry CH_2Cl_2 (2.2 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5c** (195 mg, 0.876 mmol) was added, followed by camphorsulfonic acid (10 mg, 0.044 mmol). The solution was stirred at -78°C for 21 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7c** (93 mg, 59%) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.95 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.22 (dd, *J* = 16.7, 2.8 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.85 (dd, *J* = 16.7, 10.8 Hz, 1H), 2.22 – 2.08 (m, 3H), 1.57 (s, 3H), 1.44 (ddd, *J* = 13.4, 7.4, 4.5 Hz, 1H), 0.95 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (125 MH): δ = 198.48, 163.29, 148.08, 130.45, 130.25, 113.74, 113.59, 55.38, 41.89, 41.46, 31.91, 26.95, 25.71, 18.07, 12.36, -4.08, -4.26. FT-IR: *f* (cm^{-1}) = 2954, 2929, 2855, 1677, 1599, 1575, 1509, 1442, 1328, 1280, 1252, 1211, 1167, 1073, 988, 938, 892, 855, 834, 777, 672. HR-MS: $(M+H)^+$ = 361.2193 calculated for $C_{21}H_{33}O_3Si$; experimental = 361.2206.

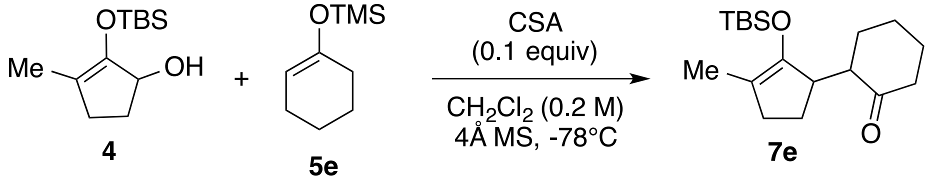
1-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-3,3-dimethylbutan-2-one (7d)



Starting material **4** (50 mg, 0.219 mmol) was dissolved in dry CH_2Cl_2 (1.1 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5d** (95 μL, 0.438 mmol) was added, followed by camphorsulfonic acid (5.1 mg, 0.022 mmol). The solution was stirred at -78°C for 36 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7d** (60 mg, 89%) as colorless oil.

^{1}H NMR (500 MHz): δ = 2.97 – 2.88 (m, 1H), 2.79 (dd, *J* = 18.0, 2.5 Hz, 1H), 2.45 (dd, *J* = 17.9, 11.0 Hz, 1H), 2.18 – 2.08 (m, 3H), 1.55 (s, 3H), 1.32 – 1.22 (m, 1H), 1.13 (s, 9H), 0.94 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (125 MH): δ = 215.65, 148.11, 113.58, 44.10, 40.68, 40.45, 31.90, 27.35, 26.40, 25.72, 18.09, 12.33, -4.13, -4.26. FT-IR: *f* (cm^{-1}) = 2959, 2930, 2858, 1707, 1689, 1473, 1380, 1362, 1328, 1258, 1211, 1081, 1012, 938, 858, 837, 796, 672. HR-MS: $(M+H)^+$ = 311.2401 calculated for $C_{18}H_{35}O_2Si$; experimental = 311.2403.

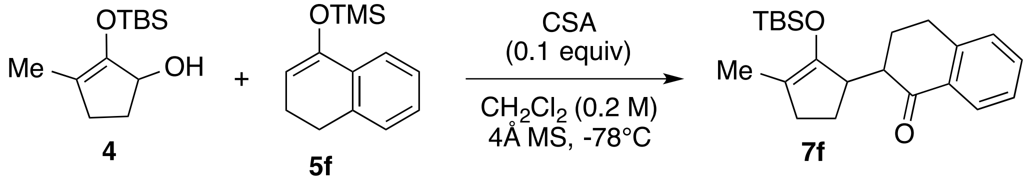
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)cyclohexan-1-one (7e)



Starting material **4** (100 mg, 0.438 mmol) was dissolved in dry CH_2Cl_2 (2.2 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5e** (170 μL, 0.876 mmol) was added, followed by camphorsulfonic acid (10 mg, 0.044 mmol). The solution was stirred at -78°C for 23 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7e** as an inseparable 1:1 mixture of diastereomer (59 mg, 44%) as colorless oil.

^1H NMR (500 MHz): δ = 3.15 – 3.06 (m, 1H), 2.70 (ddt, *J* = 7.6, 4.0, 1.9 Hz, 1H), 2.57 (dddd, *J* = 13.0, 5.6, 2.8, 1.3 Hz, 1H), 2.43 – 2.32 (m, 4H), 2.31 – 2.20 (m, 4H), 2.09 – 1.91 (m, 8H), 1.68 – 1.58 (m, 5H), 1.52 (s, 6H), 1.47 – 1.36 (m, 4H), 0.92 (s, 18H), 0.09 (s, 6H), 0.08 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (125 MHz, * denotes the other diastereomer): δ = 212.97*, 212.79, 148.50, 146.18*, 114.83*, 114.18, 55.02*, 51.71, 44.54*, 43.69, 42.54*, 42.30, 32.97, 32.24*, 31.86, 28.07*, 27.19, 26.95*, 26.37*, 25.78*, 25.72, 25.20, 25.10*, 22.64, 18.08*, 18.02, 12.61*, 12.23, -3.89, -4.14, -4.19*, -4.23*. FT-IR: *f* (cm^{-1}) = 2929, 2856, 1709, 1688, 1462, 1447, 1380, 1360, 1326, 1250, 1209, 1127, 1081, 1007, 939, 857, 835, 777, 675. HR-MS: $(M+Na)^+$ = 331.2064 calculated for $C_{18}H_{32}NaO_2Si$; experimental = 331.2066.

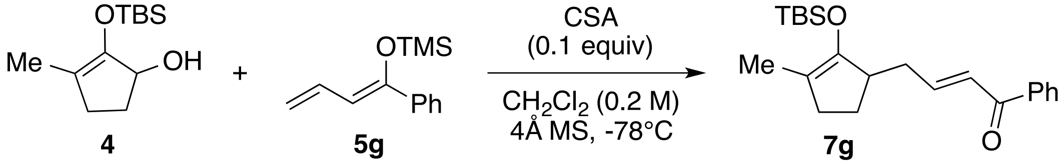
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (7f)



Starting material **4** (50 mg, 0.219 mmol) was dissolved in dry CH_2Cl_2 (1.1 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5f** (96 mg, 0.438 mmol) was added, followed by camphorsulfonic acid (5.1 mg, 0.022 mmol). The solution was stirred at -78°C for 5 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7f** as an inseparable 2.5:1 mixture of diastereomer (59 mg, 75%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.04 (d, *J* = 7.8 Hz, 0.4H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.38 (m, 1.4H), 7.33 – 7.23 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 3.57 – 3.53 (m, 0.4H), 3.28 – 3.22 (m, 1H), 3.07 – 2.89 (m, 3H), 2.79 (ddd, *J* = 13.6, 4.3, 3.1 Hz, 0.4H), 2.49 (dt, *J* = 11.7, 4.6 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.21 – 1.92 (m, 6H), 1.83 (tdd, *J* = 13.3, 11.7, 5.5 Hz, 04H), 1.66 – 1.61 (m, 1.2H), 1.58 (s, 3H), 1.54 (s, 3H), 0.94 (s, 3.6H), 0.82 (s, 9H), 0.15 (s, 1.2H), 0.12 (s, 4.2H), 0.07 (s, 3H). ^{13}C NMR (125 MHz, * denotes the minor diastereomer): δ = 200.03*, 199.01, 147.61, 146.36*, 144.51*, 144.15, 133.15*, 133.11, 133.06*, 132.73, 128.69*, 128.38 , 127.56*, 127.24 , 126.44*, 126.32, 114.89 , 114.59*, 51.73 , 49.72*, 45.34 , 44.37*, 32.81*, 32.67 , 29.67*, 29.09, 26.24*, 25.76 , 25.56 , 22.99*, 22.35*, 18.14*, 17.99, 12.73, 12.31*, -3.94*, -4.08. FT-IR: *ƒ* (cm^{-1}) = 2929, 2856, 1684, 1599, 1471, 1455, 1380, 1360, 1280, 1251, 1217, 1082, 1007, 922, 858, 838, 780, 744, 676. HR-MS: $(M+H)^+$ = 357.2244 calculated for $C_{22}H_{33}O_2Si$; experimental = 357.2245.

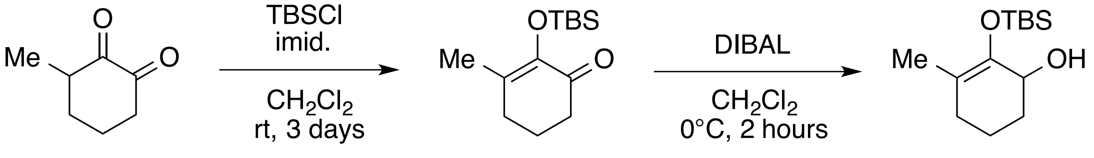
(E)-4-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclopent-2-en-1-yl)-1-phenylbut-2-en-1-one (7g)



Starting material **4** (50 mg, 0.219 mmol) was dissolved in dry CH_2Cl_2 (1.1 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5g** (96 mg, 0.438 mmol) was added, followed by camphorsulfonic acid (5.1 mg, 0.022 mmol). The solution was stirred at -78°C for 20 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **7g** (39 mg, 50%) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.92 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.03 (dt, *J* = 14.3, 7.1 Hz, 1H), 6.88 (d, *J* = 15.4 Hz, 1H), 2.70 – 2.61 (m, 2H), 2.28 – 2.10 (m, 3H), 2.05 – 1.95 (m, 1H), 1.56 (s, 3H), 1.56 – 1.49 (m, 1H), 0.96 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H). ^{13}C NMR (125 MHz): δ = 190.86, 148.59, 147.87, 138.02, 132.52, 128.53, 128.45, 127.06, 113.73, 44.64, 36.77, 31.96, 25.74, 25.71, 18.12, 12.33, -4.00, -4.17. FT-IR: *f* (cm^{-1}) = 2953, 2928, 2855, 1685, 1671, 1620, 1598, 1579, 1471, 1462, 1446, 1380, 1336, 1283, 1184, 1085, 1009, 983, 938, 891, 859, 836, 777, 733, 691. HR-MS: $(M+H)^+$ = 357.2244 calculated for $C_{22}H_{33}O_2Si$; experimental = 357.2252.

2-((tert-butyldimethylsilyl)oxy)-3-methylcyclohex-2-en-1-ol (8)

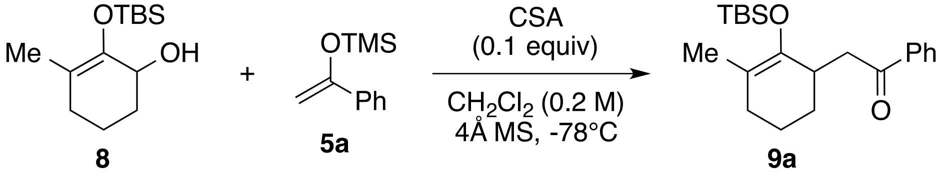


8

3-Methylcyclohexane-1,2-dione (3.00 g, 23.8 mmol) was dissolved in CH_2Cl_2 (60 mL). TBSCl (4.12 g, 27.3 mmol) was then added, followed by imidazole (2.43 g, 35.7 mmol). Upon stirring at room temperature for 3 days, the reaction was quenched with aqueous HCl (2 M solution, 20 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated under vacuum to yield crude product (6.25 g). This material was then dissolved in CH_2Cl_2 (65 mL) and cooled to 0°C. DIBAL (36.4 mL, 1.0 M solution in toluene) was added dropwise. Once the reaction was complete within 2 hours, as monitored by TLC, aqueous HCl (2 M solution, 100 mL) was added slowly. The resulting solid precipitate was filtered through pad of celite, and then the aqueous layer was then extracted with CH_2Cl_2 (3 x 30 mL). The combined CH_2Cl_2 layers were washed with brine, dried over Na_2SO_4 and concentrated in *vacuo* to obtain crude product. The crude material was purified with flash column chromatography with 90 : 10 hexanes : ethyl acetate → 80 : 20 hexanes : ethyl acetate → 70 : 30 hexanes : ethyl acetate to yield compound **8** in 68% yield (3.93 g, 16.2 mmol) over two steps as a clear, colorless oil.

^{1}H NMR (500 MHz): δ = 4.04 (s, 1H), 1.98 (dd, J = 15.0, 4.8 Hz, 3H), 1.89 – 1.77 (m, 1H), 1.80 – 1.63 (m, 2H), 1.60 (s, 3H), 1.58 – 1.46 (m, 1H), 0.97 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (125 MHz): δ = 144.01, 115.74, 67.81, 32.07, 30.72, 25.88, 18.43, 16.66, -3.96, -4.06. FT-IR: f (cm^{-1}) = 3424, 2929, 2857, 1678, 1472, 1462, 1441, 1389, 1360, 1252, 1192, 1119, 1075, 1007, 961, 922, 864, 828, 776, 707, 671. HR-MS: $(M+Na)^+$ = 265.1594 calculated for $C_{13}H_{26}NaO_2Si$; experimental = 265.1592.

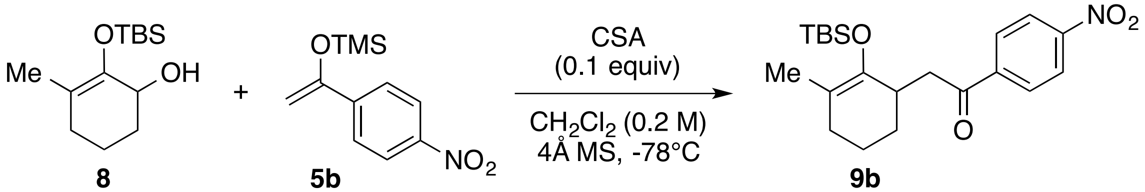
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclohex-2-en-1-yl)-1-phenylethan-1-one (9a)



Starting material **8** (100 mg, 0.412 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (169 μL, 0.824 mmol) was added, followed by camphorsulfonic acid (9.6 mg, 0.041 mmol). The solution was stirred at -78°C for 42 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **9a** (87 mg, 61%) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.98 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.32 (dd, *J* = 17.6, 2.3 Hz, 1H), 3.05 (dd, *J* = 17.5, 10.8 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.06 – 1.91 (m, 2H), 1.85 (dddd, *J* = 13.2, 9.7, 5.8, 3.3 Hz, 1H), 1.62 (s, 3H), 1.8 – 1.48 (m, 2H), 1.47 – 1.40 (m, 1H), 0.94 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (125 MHz): δ = 199.82, 144.60, 137.50, 132.87, 128.51, 127.96, 113.75, 41.14, 34.88, 30.67, 28.98, 25.92, 19.67, 18.27, 17.12, -3.73, -4.33. FT-IR: *f* (cm^{-1}) = 2928, 2857, 1683, 1597, 1471, 1461, 1448, 1359, 1254, 1217, 1199, 1165, 1124, 1002, 916, 858, 828, 814, 777, 750, 689, 673. HR-MS: $(M+H)^+$ = 345.2244 calculated for $C_{21}H_{33}O_2Si$; experimental = 345.2247.

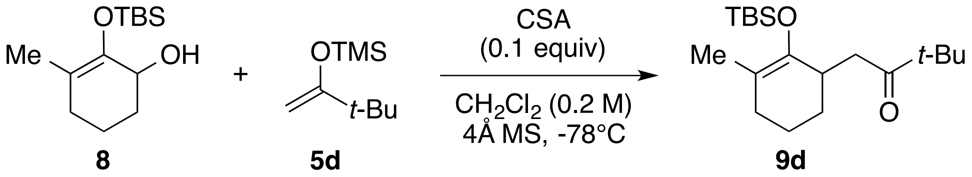
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclohex-2-en-1-yl)-1-(4-nitrophenyl)ethan-1-one (9b)



Starting material **8** (100 mg, 0.412 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5b** (196 mg, 0.824 mmol) was added, followed by camphorsulfonic acid (9.6 mg, 0.041 mmol). The solution was stirred at -78°C for 30 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **9b** (64 mg, 40%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.30 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 3.38 (dd, *J* = 17.7, 2.5 Hz, 1H), 3.05 (dd, *J* = 17.6, 10.4 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.05 – 1.82 (m, 3H), 1.61 (s, 3H), 1.58 – 1.40 (m, 3H), 0.92 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (125 MHz): δ = 198.39, 150.24, 143.99, 141.78, 128.97, 123.81, 114.26, 41.96, 35.00, 30.56, 29.04, 25.89, 19.67, 18.25, 17.13, -3.75, -4.32. FT-IR: *f* (cm^{-1}) = 2928, 2857, 1692, 1603, 1525, 1471, 1461, 1405, 1344, 1317, 1254, 1195, 1163, 1124, 1096, 1103, 91, 867, 854, 825, 813, 776, 745, 686, 675. HR-MS: $(M+H)^+$ = 390.2095 calculated for $C_{21}H_{32}NO_4Si$; experimental = 390.2105.

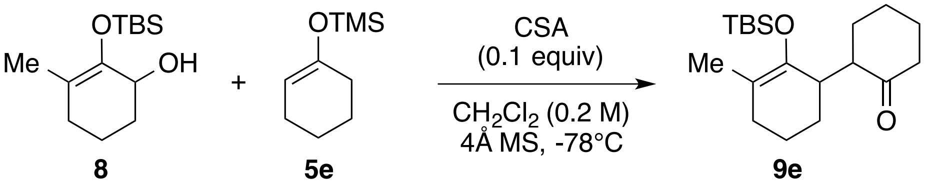
1-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclohex-2-en-1-yl)-3,3-dimethylbutan-2-one (9d)



Starting material **8** (50 mg, 0.206 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5d** (89 μL, 0.412 mmol) was added, followed by camphorsulfonic acid (4.9 mg, 0.021 mmol). The solution was stirred at -78°C for 48 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **9d** (45 mg, 67%) as colorless oil.

^{1}H NMR (500 MHz): δ = 2.79 (dd, *J* = 17.6, 1.8 Hz, 1H), 2.73 – 2.67 (m, 1H), 2.60 (dd, *J* = 17.6, 10.9 Hz, 1H), 1.94 (dtd, *J* = 22.4, 16.5, 6.3 Hz, 2H), 1.80 – 1.72 (m, 1H), 1.58 (s, 3H), 1.53 – 1.44 (m, 2H), 1.31 – 1.21 (m, 1H), 1.12 (s, 9H), 0.93 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (125 MHz): δ = 215.30, 144.79, 113.49, 44.10, 39.36, 34.34, 30.67, 28.92, 26.34, 25.91, 19.71, 18.27, 17.06, 1.02, -3.86, -4.35. FT-IR: *f* (cm^{-1}) = 2954, 2928, 2858, 1705, 1681, 1473, 1391, 1362, 1254, 1165, 1124, 1099, 1061, 1004, 916, 826, 813, 776, 672. HR-MS: $(M+H)^+$ =325.2557 calculated for $C_{19}H_{37}O_2Si$; experimental = 325.2558.

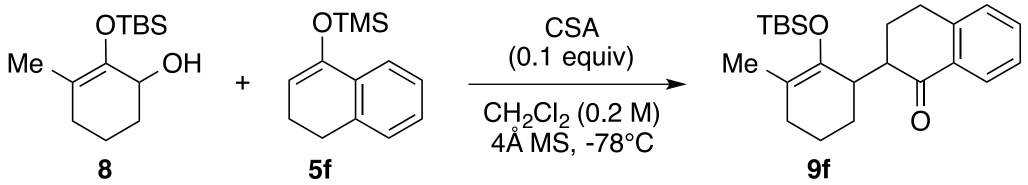
2'-((tert-butyldimethylsilyl)oxy)-3'-methyl-[1,1'-bi(cyclohexan)]-2'-en-2-one (9e)



Starting material **8** (100 mg, 0.412 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL), and 4Å molecular sieves (500 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5e** (160 μL, 0.824 mmol) was added, followed by camphorsulfonic acid (9.6 mg, 0.041 mmol). The solution was stirred at -78°C for 27 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **9e** as an inseparable 3:2 mixture of diastereomers (60 mg, 45%) as colorless oil.

^{1}H NMR (500 MHz): δ = 2.93 – 2.81 (m, 0.8H), 2.57 – 2.48 (m, 2.2H), 2.38 – 2.23 (m, 1.8H), 2.10 – 1.84 (m, 9.6H), 1.68 – 1.58 (m, 6H), 1.56 (s, 2H), 1.54 (s, 3H), 0.93 (s, 4H), 0.92 (s, 9H), 0.10 (s, 3H), 0.08 (s, 1.2H), 0.07 (s, 3H), 0.02 (s, 1.2H). ^{13}C NMR (125 MHz, * denotes the minor diastereomer): δ = 212.54*, 212.23, 144.36, 143.08*, 114.89*, 113.26, 54.02, 50.81*, 42.89, 42.22*, 37.60*, 37.49, 32.85, 30.75*, 30.33, 28.38, 27.82, 27.07*, 26.84*, 26.02, 25.94*, 25.91, 25.42*, 24.97*, 22.00*, 19.30, 18.28, 18.26, 17.31*, 17.10, 2.73*, -3.27, -4.04*, -4.15, -4.39*. FT-IR: *f* (cm^{-1}) = 2928, 2857, 1709, 1678, 1448, 1360, 1252, 1160, 1129, 1050, 1007, 916, 832, 775, 733, 670. HR-MS: $(M+H)^+$ = 323.2401 calculated for $C_{19}H_{35}O_2Si$; experimental = 323.2412.

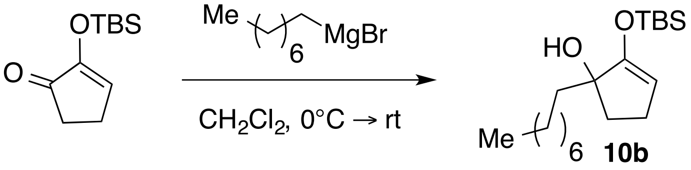
2-(2-((tert-butyldimethylsilyl)oxy)-3-methylcyclohex-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (9f)



Starting material **8** (50 mg, 0.206 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5f** (90 mg, 0.412 mmol) was added, followed by camphorsulfonic acid (4.9 mg, 0.021 mmol). The solution was stirred at -78°C for 23 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **9f** as an inseparable 2:1 mixture of diastereomers (48 mg, 63%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.05 (d, *J* = 7.8 Hz, 0.5H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.40 (m, 1.5H), 7.29 (dd, *J* = 14.3, 7.4 Hz, 1.5H), 7.22 (t, *J* = 8.7 Hz, 1.5H), 3.28 – 3.19 (m, 0.5H), 3.06 (ddd, *J* = 13.5, 4.5, 3.3 Hz, 0.5H), 3.02 – 2.94 (m, 3H), 2.89 – 2.85 (m, 1H), 2.64 – 2.54 (m, 1.5H), 2.17 – 1.95 (m, 6.5H), 1.91 – 1.80 (m, 3.5H), 1.61 (s, 1.5H), 1.59 (s, 3H), 1.57 – 1.45 (m, 5.5H), 1.33 – 1.18 (m, 3H), 0.94 (s, 4.5H), 0.84 (s, 9H), 0.12 (s, 1.5H), 0.09 (s, 4.5H), 0.06 (s, 3H). ^{13}C NMR (125 MHz, * denotes the minor diastereomer): δ = 199.76, 199.09, 144.53*, 144.19, 144.00, 143.16*, 133.23*, 132.99, 132.76, 128.65*, 128.47, 127.51, 127.27*, 126.43*, 126.33, 115.29*, 113.84, 51.2 , 49.30*, 38.92, 38.58*, 30.87*, 30.62, 29.09, 27.27*, 26.02, 25.93*, 24.81, 23.97*, 22.04*, 20.27, 18.24*, 17.31, -3.33, -3.82*, -4.01, -4.41*. FT-IR: *f* (cm^{-1}) = 2928, 2857, 1682, 1599, 1454, 1359, 1285, 1257, 1220, 1161, 1091, 1019, 920, 831, 797, 777, 744, 704, 669. HR-MS: $(M+H)^+$ = 393.2220 calculated for $C_{23}H_{34}NaO_2Si$; experimental = 393.2219.

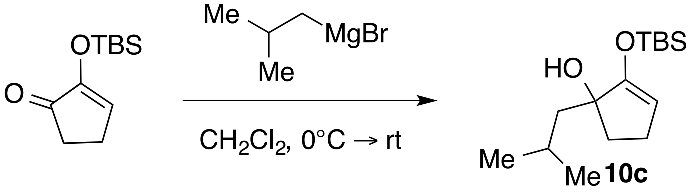
2-((tert-butyldimethylsilyl)oxy)-1-octylcyclopent-2-en-1-ol (10b)



2-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-one (150 mg, 0.708 mmol) was dissolved in CH_2Cl_2 (3.5 mL). After cooling to 0°C, octyl magnesium bromide (0.70 mL, 2M in Et_2O, 1.42 mmol) was added drop wise. The reaction mixture was then stirred at room temperature for 1 hour until the completion of reaction, as monitored by TLC. After cooling to 0°C, the reaction mixture was then quenched with water (15 mL). The resulting solid precipitate was filtered through a pad of celite, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was further purified by flash column chromatography (buffered with Et_3N) with 95:5 hexanes : EtOAc to afford product **10b** (118 mg, 51% yield) as colorless oil.

^{1}H NMR (500 MHz): δ = 4.64 (t, *J* = 2.4 Hz, 1H), 2.25 (ddt, *J* = 14.7, 8.7, 3.0 Hz, 1H), 2.12 – 2.04 (m, 1H), 2.04 – 1.96 (m, 1H), 1.84 (ddd, *J* = 13.8, 9.0, 4.9 Hz, 1H), 1.77 (s, 1H), 1.67 – 1.55 (m, 1H), 1.54 – 1.45 (m, 1H), 1.26 (s, 14H), 0.93 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.19 (s, 3H), 0.17 (s, 3H). ^{13}C NMR (125 MHz): δ = 155.87, 101.76, 82.51, 38.64, 34.27, 31.85, 30.12, 29.57, 29.24, 25.63, 24.55, 24.17, 22.64, 18.04, 14.07, -4.86, -5.03. FT-IR: *f* (cm^{-1}) = 3448, 2927, 2856, 1648, 1464, 1361, 1252, 1006, 908, 857, 837, 780, 732, 677. HR-MS: $(M-OH)^+$ = 309.2608 calculated for $C_{19}H_{37}OSi$; experimental = 309.2615.

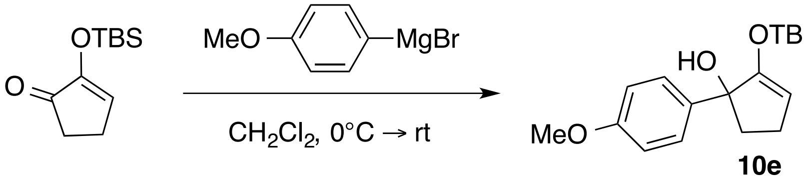
2-((tert-butyldimethylsilyl)oxy)-1-isobutylcyclopent-2-en-1-ol (10c)



2-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-one (150 mg, 0.708 mmol) was dissolved in CH_2Cl_2 (3.5 mL). After cooling to 0°C, isobutyl magnesium bromide (0.70 mL, 2M in Et_2O, 1.42 mmol) was added dropwise. The reaction mixture was then stirred at room temperature for 1 hour until the completion of reaction, as monitored by TLC. After cooling to 0°C, the reaction mixture was then quenched with water (15 mL). The resulting solid precipitate was filtered through a pad of celite, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was further purified by flash column chromatography (buffered with Et_3N) with 95:5 hexanes : EtOAc to afford product **10c** (56 mg, 29 % yield) as colorless oil.

^{1}H NMR (500 MHz): δ = 4.63 (s, 1H), 2.27 (m,1H), 2.17 – 2.02 (m, 2H), 1.88 (ddd, *J* = 13.5, 8.9, 3.8 Hz, 1H), 1.74 (dd, *J* = 12.9, 6.4 Hz, 1H), 1.69 (s, 1H), 1.59 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.42 (dd, *J* = 13.9, 6.5 Hz, 1H), 1.02 – 0.84 (m, 15H), 0.19 (s, 3H), 0.17 (s, 3H). ^{13}C NMR (125 MHz): δ = 156.46, 101.56, 82.53, 46.95, 34.76, 25.66, 24.84, 24.63, 24.61, 24.08, 18.07, -4.92, -4.98. FT-IR: *f* (cm^{-1}) = 3473, 2953, 2929, 2858, 1649, 1470, 1362, 1251, 1129, 1037, 1003, 837, 780, 732, 677. HR-MS: $(M-OH)^+$ = 253.1982 calculated for $C_{15}H_{29}OSi$; experimental = 253.1975.

2-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)cyclopent-2-en-1-ol (10e)

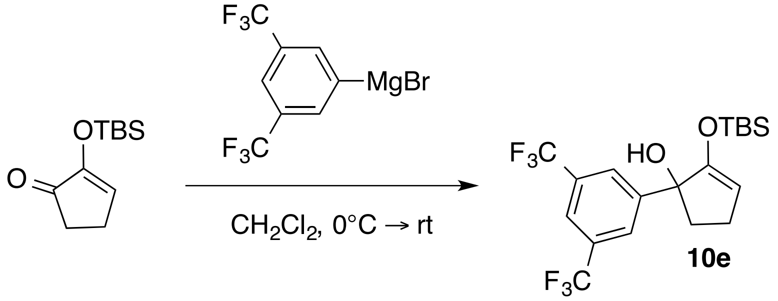


10e

2-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-one (200 mg, 0.943 mmol) was dissolved in CH_2Cl_2 (4.7 mL). After cooling to 0°C, 4-methoxyphenyl magnesium bromide (3.8 mL, 0.5M in THF, 1.87 mmol) was added drop wise. The reaction mixture was then stirred at room temperature for 1 hour until the completion of reaction, as monitored by TLC. After cooling to 0°C, the reaction mixture was then quenched with water (15 mL). The resulting solid precipitate was filtered through a pad of celite, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was further purified by flash column chromatography (buffered with Et_3N) with 95:5 hexanes : EtOAc to afford product **10e** (113 mg, 37% yield) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.34 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.87 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 3H), 2.43 – 2.30 (m, 2H), 2.32 – 2.05 (m, 3H), 0.80 (s, 9H), 0.17 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz): δ = 158.41, 155.82, 137.96, 126.28, 113.31, 103.09, 83.76, 55.22, 39.65, 25.50, 24.72, 17.96, -4.81, -5.20. FT-IR: *f* (cm^{-1}) = 3470, 2930, 2856, 1648, 1610, 1463, 1243, 1175, 1055, 1037, 1004, 912, 831, 779, 732, 677, 568. HR-MS: $(M-H_2O)^+$ = 303.1775 calculated for $C_{18}H_{27}O_2Si$; experimental = 303.1776.

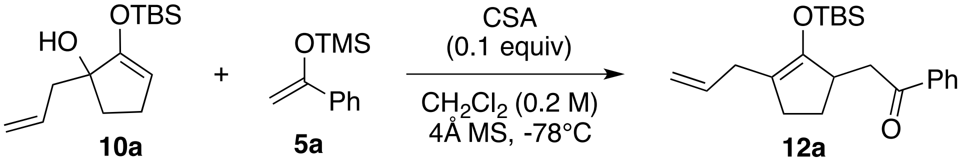
1-(3,5-bis(trifluoromethyl)phenyl)-2-((tert-butyldimethylsilyl)oxycyclopent-2-en-1-ol (10f)



2-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-one (200 mg, 0.943 mmol) was dissolved in CH_2Cl_2 (4.7 mL). After cooling to 0°C, 3,5-bis-(trifluoromethyl)phenyl magnesium bromide (3.8 mL, 0.5M in THF, 1.87 mmol) was added drop wise. The reaction mixture was then stirred at room temperature for 1 hour until the completion of reaction, as monitored by TLC. After cooling to 0°C, the reaction mixture was then quenched with water (15 mL). The resulting solid precipitate was filtered through a pad of celite, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was further purified by flash column chromatography (buffered with Et_3N) with 95:5 hexanes : EtOAc to afford product **10f** (194 mg, 48 % yield) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.13 – 7.83 (m, 2H), 7.75 (s, 1H), 4.99 (t, J = 2.2 Hz, 1H), 2.60 – 2.40 (m, 2H), 2.34 (ddd, J = 11.4, 10.2, 5.1 Hz, 2H), 2.30 – 2.03 (m, 1H), 0.75 (s, 9H), 0.18 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz): δ = 154.48, 148.69, 131.35 (q, J = 33.1 Hz), 125.78 (d, J = 4.0 Hz), 123.50 (q, J = 272.7 Hz), 120.76 (p, J = 3.8 Hz), 104.59, 84.02, 39.55, 25.24, 24.90, 17.83, -4.87, -5.61. FT-IR: f (cm^{-1}) = 3447, 2933, 2861, 1650, 1468, 1374, 1275, 1171, 1128, 1058, 897, 839, 781, 735, 707, 680. HR-MS: $(M-H_2O)^+$ = 409.1417 calculated for $C_{19}H_{23}F_6OSi$; experimental = 409.1407.

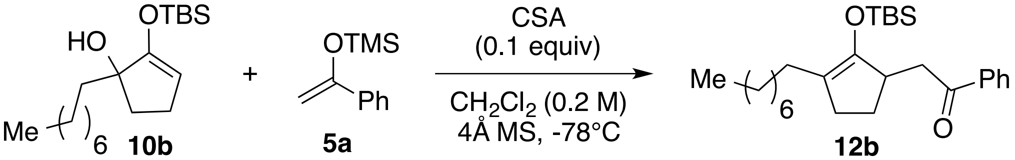
2-(3-allyl-2-((tert-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)-1-phenylethan-1-one (12a)



Starting material **10a** (50 mg, 0.197 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (80 μL, 0.393 mmol) was added, followed by camphorsulfonic acid (4.6 mg, 0.020 mmol). The solution was stirred at -78°C for 47 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **12a** (33 mg, 47%) as colorless oil.

^{1}H NMR (500 MHz): δ = 7.97 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.74 (ddt, *J* = 16.8, 10.0, 6.6 Hz, 1H), 5.06 – 4.96 (m, 2H), 3.27 (dd, *J* = 17.0, 2.8 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.94 (dd, *J* = 16.9, 10.6 Hz, 1H), 2.80 (qd, *J* = 15.0, 6.6 Hz, 2H), 2.24 – 2.06 (m, 3H), 1.53 – 1.40 (m, 1H), 0.95 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (125 MHz): δ = 199.87, 148.53, 137.26, 136.03, 128.51, 128.05, 115.82, 115.17, 42.16, 41.43, 31.30, 29.21, 26.91, 25.72, 18.09, -3.99, -4.32. FT-IR: *f* (cm^{-1}) = 3076, 2954, 2929, 2893, 2856, 1682, 1638, 1597, 1462, 1360, 1335, 1287, 1250, 1210, 1046, 995, 895, 853, 836, 778, 751, 689, 575. HR-MS: $(M+H)^+$ = 357.2244 calculated for $C_{22}H_{32}O_2Si$; experimental = 357.2230.

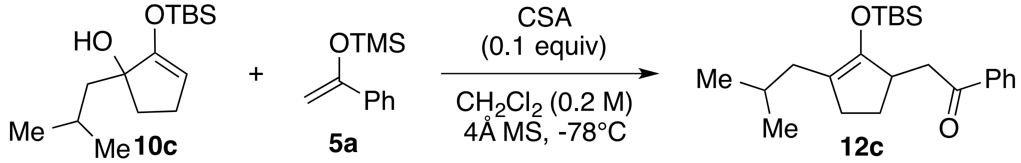
2-(3-octyl-2-((tert-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)-1-phenylethan-1-one (12b)



Starting material **10b** (50 mg, 0.153 mmol) was dissolved in dry CH_2Cl_2 (0.80 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (63 μL, 0.306 mmol) was added, followed by camphorsulfonic acid (3.5 mg, 0.015 mmol). The solution was stirred at -78°C for 49 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **12b** (45 mg, 68%) as colorless oil.

^{1}H NMR (400 MHz): δ = 7.97 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.27 (dd, *J* = 16.8, 2.8 Hz, 1H), 3.14 – 3.03 (m, 1H), 2.90 (dd, *J* = 16.8, 10.6 Hz, 1H), 2.27 – 2.08 (m, 3H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.46 (tt, *J* = 8.2, 4.2 Hz, 1H), 1.28 (bs, 14H), 0.95 (s, 9H), 0.89 (t, *J* = 5.2 Hz, 3H), 0.13 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz): δ = 200.04, 147.65, 137.37, 132.84, 128.48, 128.06, 118.42, 42.28, 41.55, 31.89, 29.76, 29.48, 29.30, 29.23, 27.68, 26.95, 26.63, 25.75, 22.67, 18.11, 14.09, -3.98, -4.34. FT-IR: *f* (cm^{-1}) = 2954, 2927, 2855, 1680, 1589, 1580, 1462, 1448, 1252, 1209, 1180, 906, 856, 837, 779, 729, 688, 648, 582. HR-MS: $(M+H)^+$ = 429.3183 calculated for $C_{27}H_{45}O_2Si$; experimental = 429.3190.

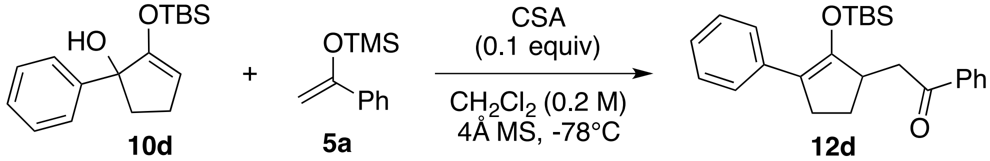
2-(2-((tert-butyldimethylsilyl)oxy)-3-isobutylcyclopent-2-en-1-yl)-1-phenylethan-1-one (12c)



Starting material **10c** (56 mg, 0.207 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL), and 4Å molecular sieves (280 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (85 μL, 0.414 mmol) was added, followed by camphorsulfonic acid (4.8 mg, 0.021 mmol). The solution was stirred at -78°C for 18 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **12c** (45 mg, 59%) as colorless oil.

^{1}H NMR (400 MHz): δ = 7.98 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.27 (dd, *J* = 16.9, 2.6 Hz, 1H), 3.15 – 3.01 (m, 1H), 2.90 (dd, *J* = 16.9, 10.6 Hz, 1H), 2.31 – 2.05 (m, 3H), 1.95 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.71 (dp, *J* = 13.9, 6.7 Hz, 1H), 0.94 (s, 9H), 0.88 (d, *J* = 10.4 Hz, 3H), 0.86 (d, *J* = 10.2 Hz, 3H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz): δ = 200.07, 148.80, 137.29, 132.89, 128.50, 128.07, 117.45, 42.20, 41.48, 35.89, 29.60, 26.96, 26.70, 25.78, 23.05, 22.41, 18.10, -3.82, -4.28. FT-IR: *f* (cm^{-1}) = 2953, 2929, 2893, 2858, 1680, 1462, 1347, 1251, 1195, 1103, 1044, 1021, 1002, 907, 854, 836, 778, 752, 731, 688. HR-MS: $(M+H)^+$ = 373.2557 calculated for $C_{23}H_{37}O_2Si$; experimental = 373.2548.

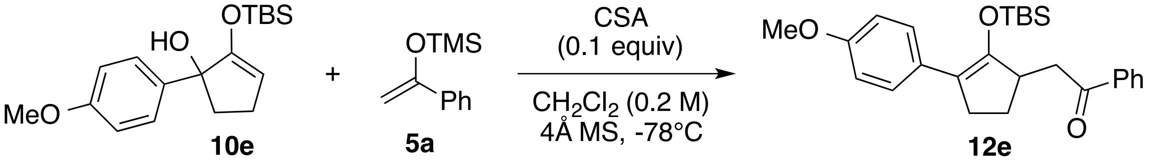
2-(2-((tert-butyldimethylsilyl)oxy)-3-phenylcyclopent-2-en-1-yl)-1-phenylethan-1-one (12d)



Starting material **10d** (50 mg, 0.172 mmol) was dissolved in dry CH_2Cl_2 (0.90 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (71 μL, 0.344 mmol) was added, followed by camphorsulfonic acid (4.0 mg, 0.017 mmol). The solution was stirred at -78°C for 10 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **12d** (56 mg, 83%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.01 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.61 – 7.54 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.38 (dd, *J* = 17.4, 2.5 Hz, 2H), 3.17 – 3.04 (m, 1H), 2.79 (dddd, *J* = 14.2, 9.3, 4.9, 1.2 Hz, 1H), 2.56 (dddd, *J* = 14.5, 8.8, 5.7, 2.0 Hz, 1H), 2.39 – 2.24 (m, 1H), 1.58 (ddt, *J* = 13.3, 9.0, 4.6 Hz, 1H), 0.96 (s, 9H), 0.13 (s, 3H), -0.01 (s, 3H). ^{13}C NMR (125 MHz): δ = 199.45, 151.54, 137.33, 136.43, 132.98, 128.57, 128.06, 127.79, 127.04, 125.72, 116.05, 42.88, 42.28, 29.80, 26.85, 25.84, 18.19, -3.74, -4.14. FT-IR: *f* (cm^{-1}) = 3056, 2929, 2856, 1684, 1637, 1598, 1469, 1350, 1280, 1255, 1099, 1064, 1002, 968, 937, 909, 835, 779, 752, 689. HR-MS: $(M+H)^+$ = 393.2244 calculated for $C_{25}H_{33}O_2Si$; experimental = 393.2259.

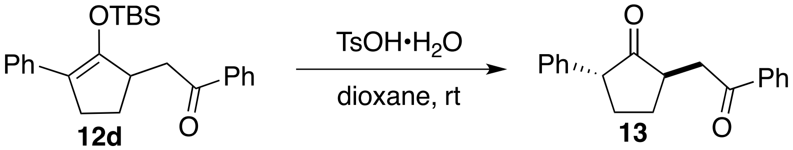
2-(2-((tert-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)cyclopent-2-en-1-yl)-1-phenylethan-1-one (12e)



Starting material **10e** (50 mg, 0.156 mmol) was dissolved in dry CH_2Cl_2 (0.80 mL), and 4Å molecular sieves (250 mg) were added. After cooling the reaction mixture to -78°C, silylenol ether **5a** (64 μL, 0.312 mmol) was added, followed by camphorsulfonic acid (3.6 mg, 0.016 mmol). The solution was stirred at -78°C for 10 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **12e** (52 mg, 79%) as colorless oil.

^{1}H NMR (500 MHz): δ = 8.00 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 3.36 – 3.28 (m, 2H), 3.07 (ddd, *J* = 16.9, 10.7, 1.9 Hz, 1H), 2.73 (ddd, *J* = 14.1, 9.2, 4.5 Hz, 1H), 2.61 (s, 1H), 2.58 – 2.46 (m, 1H), 2.36 – 2.20 (m, 1H), 1.58 – 1.49 (m, 1H), 0.94 (s, 9H), 0.11 (s, 3H), -0.01 (s, 3H). ^{13}C NMR (125 MHz): δ = 199.63, 157.54, 149.92, 137.25, 129.17, 128.56, 128.29, 128.11, 128.06, 115.47, 113.20, 55.20, 42.72, 42.32, 29.84, 26.72, 25.86, 18.20, -3.72, -4.10. FT-IR: *f* (cm^{-1}) = 2953, 2929, 2855, 1685, 1640, 1607, 1511, 1462, 1447, 1358, 1342, 1288, 1246, 1211, 1177, 1089, 1035, 834, 779, 752, 689. HR-MS: $(M+H)^+$ = 423.2350 calculated for $C_{26}H_{35}O_3Si$; experimental = 423.2360.

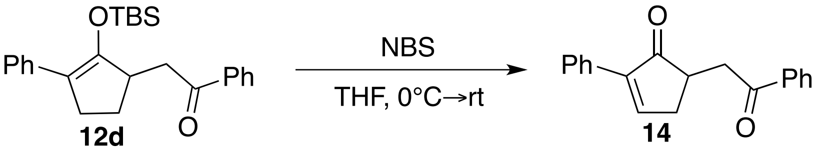
(2R,5R)-2-(2-oxo-2-phenylethyl)-5-phenylcyclopentan-1-one (13*)*



Compound **12d** (50 mg, 0.127 mmol) was dissolved in dioxane (2.0 mL), TsOH•H_2O (48 mg, 0.254 mmol) was added, and the reaction mixture was stirred for 1 hour until the completion of reaction, as monitored by TLC. The reaction mixture was neutralized with aqueous sodium bicarbonate (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was further purified by flash column chromatography with 80:20 hexanes : EtOAc to afford product **13** as an 4:1 mixture of inseparable diastereomers (29 mg, 82% yield) as a white solid. The *trans* relative stereochemistry in the major product was determined by NOE experiments.

^{1}H NMR (500 MHz): δ= 7.91 – 7.84 (m, 2H), 7.51 – 7.44 (m, 1H), 7.40 – 7.35 (m, 2H), 7.26 – 7.22 (m, 2H), 7.17 – 7.11 (m, 3H), 3.51 (dd, *J* = 18.1, 3.2 Hz, 1H), 3.45 (dd, *J* = 12.3, 8.5 Hz, 1H), 3.10 (dd, *J* = 18.1, 7.7 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.49 – 2.41 (m, 1H), 2.37 – 2.31 (m, 1H), 2.00 (qd, *J* = 12.5, 6.3 Hz, 1H), 1.62 (qd, *J* = 12.3, 6.2 Hz, 1H). ^{13}C NMR (125 MHz, *denotes minor diastereomer): δ= 218.50*, 218.06, 208.50*, 197.79, 157.54*, 138.87, 136.54, 133.33*, 133.28 , 133.26*, 131.63*, 128.13 , 128.08*, 128.04 , 127.01*, 126.84 , 126.82*, 54.89, 53.73*, 45.82, 43.63, 42.47*, 40.13*, 39.64, 38.90, 34.00*, 30.11, 28.92*, 27.54, 27.48*. FT-IR: *f* (cm^{-1}) = 3059, 3027, 2961, 2873, 173, 1680, 1596, 1580, 1495, 1448, 1401, 1361, 1322, 1259, 1222, 1181, 1152, 1099, 1075, 998, 801, 752, 689. HR-MS $(M + H)^+$ = 279.1380 calculated for $C_{19}H_{19}O_2$; experimental = 279.1377.

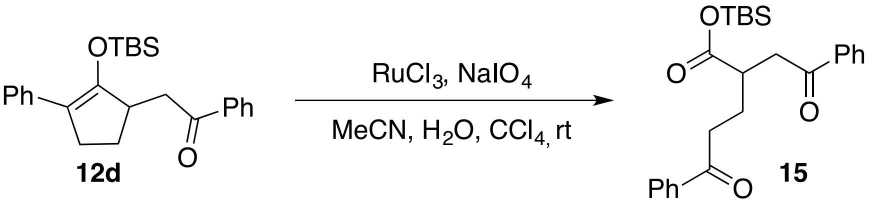
5-(2-oxo-2-phenylethyl)-2-phenylcyclopent-2-en-1-one (14)



In a round bottom flask, a solution of N-bromosuccinimide (51 mg, 0.287 mmol) in dry THF (1.9 mL) was added dropwise into a solution of **12d** (75 mg, 0.191 mmol) in dry THF (1.9 mL) at 0°C. The reaction mixture was stirred at 0°C for 7 hours and then room temperature for 12 hours. The reaction was then quenched with a saturated solution of sodium thiosulfate (5 mL) and a saturated aqueous solution of sodium bicarbonate (5 mL). The reaction mixture was then partitioned between EtOAc and H_2O (50 mL, 1:1). The aqueous layer extracted with EtOAc (3 x 20mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was further purified by flash column chromatography with 90 : 10 hexanes : ethyl acetate to afford **14** as yellow oil (42 mg, 80 %).

^{1}H NMR (500 MHz): δ= 7.99 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.84 (t, *J* = 2.8 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.60 – 7.56 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 3.72 (dd, *J* = 17.1, 2.3 Hz, 1H), 3.22 – 3.05 (m, 3H), 2.43 (dt, *J* = 19.1, 2.3 Hz, 1H). ^{13}C NMR (125 MHz): δ= 208.48, 198.03, 157.53, 142.58, 136.44, 133.33, 131.63, 128.66, 128.42, 128.40, 128.06, 127.01, 77.20, 42.47, 40.12, 34.00. FT-IR: *f* (cm^{-1}) = 3057, 2962, 2920, 1680, 1618, 1596, 1579, 1492, 1447, 1404, 1360, 1303, 1222, 1180, 1074, 1022, 979, 916, 873, 803, 753, 689, 616, 578. HR-MS $(M + H)^+$ = 277.1223 calculated for $C_{19}H_{17}O_2$; experimental = 277.1223.

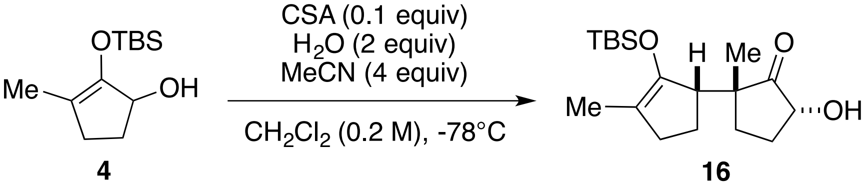
tert-butyldimethylsilyl 5-oxo-2-(2-oxo-2-phenylethyl)-5-phenylpentanoate (15)



Compound **12d** (75 mg, 0.191 mmol) was dissolved in a mixture of H_2O:CCl_4:MeCN (3:2:2, 4.2 mL). $NaIO_4$ (163 mg, 0.764 mmol) was then added, followed by $RuCl_3$ (2.0 mg, 0.0096 mmol). The reaction mixture was stirred at room temperature for 4 hours until the completion of reaction, as monitored by TLC. The reaction mixture was quenched with saturated aqueous sodium thiosulfate (5mL), stirred for 15 min, and then extracted with dichloromethane (3 x 5 mL). The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was further purified by flash column chromatography with 90:10 hexanes : EtOAc to afford product **15** (66 mg, 81% yield) as a clear oil.

^{1}H NMR (500 MHz): δ= 8.08 – 7.85 (m, 4H), 7.65 – 7.52 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 3.55 – 3.45 (m, 1H), 3.19 – 3.07 (m, 4H), 2.17 – 2.07 (m, 2H), 0.88 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (125 MHz): δ= 199.12, 197.75, 175.09, 136.71, 136.63, 133.15, 133.10, 128.59, 128.57, 127.98, 41.26, 40.86, 36.20, 26.21, 25.49, 17.56, -4.90, -4.92. FT-IR: *f* (cm^{-1}) = 3062, 2954, 2930, 2858, 1712, 1683, 1597, 1580, 1467, 1448, 1364, 1255, 1214, 1176, 1096, 1002, 971, 938, 912, 82, 841, 823, 790, 752, 731, 688, 602. HR-MS $(M + H)^+$ = 425.2143 calculated for $C_{25}H_{33}O_4Si$; experimental = 425.2147.

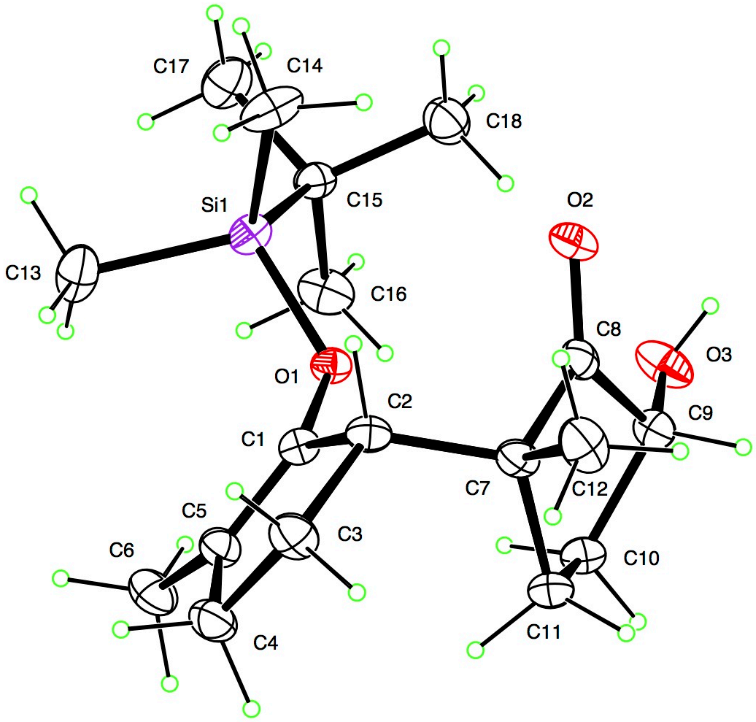
(1*R*,1'*S*,3*R*)-2'-((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-1,3'-dimethyl-[1,1'-bi(cyclopentan)]-2'-en-2-one (16)

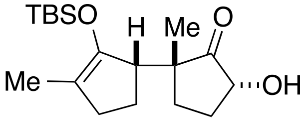


Starting material **4** (100 mg, 0.438 mmol), and MeCN (91 μL, 1.75 mmol) were dissolved in dry CH_2Cl_2 (2.2 mL). After cooling the reaction mixture to -78°C deionized water (16 μL, 0.876 mmol) and camphorsulfonic acid (20 mg, 0.088 mmol) were added. The solution was stirred at -78°C for 22 hours until the completion of reaction, as monitored by TLC. The reaction was quenched with triethylamine (0.1 mL) and was directly purified by flash column chromatography with 50:50 hexanes : CH_2Cl_2 to afford product **16** (40 mg, 57%) as white solid.

^{1}H NMR (500 MHz): δ = 4.04 (ddd, *J* = 10.6, 8.0, 4.1 Hz, 1H), 2.70 (d, *J* = 9.7 Hz, 1H), 2.61 (d, *J* = 4.7 Hz, 1H), 2.27 – 2.09 (m, 3H), 2.06 (ddd, *J* = 13.5, 7.5, 2.4 Hz, 1H), 2.03 – 1.91 (m, 1H), 1.75 (ddt, *J* = 13.7, 8.8, 2.3 Hz, 1H), 1.67 (dtd, *J* = 12.2, 11.1, 7.5 Hz, 1H), 1.57 (bs, 2H), 1.54 (s, 3H), 1.37 (ddd, *J* = 13.5, 11.4, 6.8 Hz, 1H), 1.05 (s, 3H), 0.94 (s, 9H), 0.14 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz): δ = 220.61, 146.77, 117.23, 74.90, 51.96, 48.84, 33.02, 28.90, 27.71, 26.00, 24.58, 22.13, 18.19, 12.94, -3.62, -4.37. FT-IR: *f* (cm^{-1}) = 3468, 2955, 2927, 2855, 1742, 1681, 1462, 1379, 1362, 1336, 1298, 1275, 1251, 1205, 1135, 1115, 1086, 1045, 1023, 1005, 974, 926, 881, 855, 836, 803, 778, 734, 677. HR-MS: $(M+Na)^+$ = 347.2013 calculated for $C_{18}H_{32}NaO_3Si$; experimental = 347.2019

X-RAY CRYSTAL DATA





16

Crystal data

$C_{18}H_{32}O_3Si$	$F(000) = 1424$
$M_r = 324.53$	$D_x = 1.094$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 3436 reflections
$a = 29.017$ (4) Å	$\theta = 2.6–26.4°$
$b = 11.4978$ (17) Å	$\mu = 0.13$ mm^{-1}
$c = 12.6967$ (16) Å	$T = 90$ K
$\beta = 111.472$ (8)°	Plate, colorless
$V = 3942.0$ (9) Å^3	0.30 × 0.28 × 0.08 mm
$Z = 8$	

Data collection

Nonius KappaCCD diffractometer	3950 independent reflections
Radiation source: fine-focus sealed tube	2423 reflections with $I > 2\sigma(I)$
graphite	$R_{\mathrm{int}} = 0.060$
ϕ and ω scans	$\theta_{\max} = 26.3°$, $\theta_{\min} = 2.8°$
Absorption correction: multi-scan *DENZO* & *SCALEPACK* (Otwinowski & Minor, 1997)	$h = -35 – 36$
$T_{\min} = 0.944$, $T_{\max} = 0.990$	$k = -14 – 12$
10745 measured reflections	$l = -15 – 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.069$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.145$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 9.0605P]$ where $P = (F_o^2 + 2F_c^2)/3$
3950 reflections	$(\Delta/\sigma)_{\max} < 0.001$
209 parameters	$\Delta\rangle_{\max} = 0.27$ e Å^{-3}
0 restraints	$\Delta\rangle_{\min} = -0.23$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$	

Si1	0.58731 (3)	0.16366 (8)	0.46049 (7)	0.0302 (2)	
O1	0.61758 (7)	0.26041 (17)	0.55928 (16)	0.0262 (5)	
O2	0.69316 (8)	0.35988 (19)	0.45389 (18)	0.0353 (6)	
C1	0.59887 (11)	0.3687 (3)	0.5703 (2)	0.0280 (7)	
O3	0.75160 (10)	0.2410 (2)	0.6616 (2)	0.0466 (7)	
H3O	0.7663 (15)	0.236 (4)	0.620 (3)	0.070*	
C15	0.62385 (12)	0.0248 (3)	0.4983 (3)	0.0310 (8)	
C13	0.52378 (12)	0.1432 (3)	0.4616 (3)	0.0479 (10)	
H13A	0.5259	0.1068	0.5330	0.072*	
H13B	0.5046	0.0931	0.3983	0.072*	
H13C	0.5074	0.2189	0.4541	0.072*	
C7	0.66996 (12)	0.4998 (3)	0.5702 (3)	0.0296 (7)	
C11	0.69089 (12)	0.5071 (3)	0.7021 (3)	0.0383 (9)	
H11A	0.7156	0.5704	0.7284	0.046*	
H11B	0.6639	0.5221	0.7305	0.046*	
C8	0.69902 (11)	0.3991 (3)	0.5472 (3)	0.0294 (7)	
C5	0.57198 (11)	0.3918 (3)	0.6332 (3)	0.0316 (8)	
C9	0.73799 (12)	0.3581 (3)	0.6577 (3)	0.0338 (8)	
H9	0.7684	0.4067	0.6733	0.041*	
C6	0.55711 (13)	0.3073 (3)	0.7049 (3)	0.0436 (9)	
H6A	0.5212	0.2949	0.6721	0.065*	
H6B	0.5662	0.3386	0.7816	0.065*	

H6C	0.5742	0.2331	0.7078	0.065*	
C12	0.68169 (14)	0.6096 (3)	0.5148 (3)	0.0457 (9)	
H12A	0.7176	0.6202	0.5410	0.069*	
H12B	0.6666	0.6776	0.5360	0.069*	
H12C	0.6682	0.6006	0.4323	0.069*	
C2	0.61372 (11)	0.4744 (3)	0.5200 (3)	0.0295 (7)	
H2	0.6032	0.4636	0.4363	0.035*	
C10	0.71509 (12)	0.3890 (3)	0.7440 (3)	0.0373 (8)	
H10A	0.7407	0.3953	0.8210	0.045*	
H10B	0.6902	0.3306	0.7446	0.045*	
C14	0.58236 (15)	0.2184 (3)	0.3189 (3)	0.0495 (10)	
H14A	0.5581	0.2818	0.2959	0.074*	
H14B	0.5716	0.1551	0.2636	0.074*	
H14C	0.6147	0.2472	0.3227	0.074*	
C4	0.56079 (13)	0.5194 (3)	0.6308 (3)	0.0408 (9)	
H4A	0.5775	0.5547	0.7064	0.049*	
H4B	0.5247	0.5329	0.6065	0.049*	
C3	0.58121 (13)	0.5704 (3)	0.5442 (3)	0.0380 (8)	
H3A	0.6013	0.6407	0.5754	0.046*	
H3B	0.5537	0.5921	0.4736	0.046*	
C16	0.63830 (14)	-0.0020 (3)	0.6244 (3)	0.0457 (9)	
H16A	0.6084	-0.0076	0.6426	0.069*	
H16B	0.6595	0.0603	0.6692	0.069*	
H16C	0.6563	-0.0760	0.6420	0.069*	
C17	0.59231 (13)	-0.0750 (3)	0.4285 (3)	0.0466 (10)	

H17A	0.6121	-0.1465	0.4432	0.070*	
H17B	0.5812	-0.0558	0.3479	0.070*	
H17C	0.5634	-0.0867	0.4499	0.070*	
C18	0.67148 (13)	0.0341 (3)	0.4717 (3)	0.0439 (9)	
H18A	0.6923	0.0968	0.5168	0.066*	
H18B	0.6628	0.0509	0.3910	0.066*	
H18C	0.6897	-0.0396	0.4904	0.066*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0340 (5)	0.0254 (5)	0.0278 (5)	-0.0022 (4)	0.0074 (4)	0.0016 (4)
O1	0.0321 (12)	0.0224 (12)	0.0253 (11)	-0.0006 (9)	0.0120 (9)	-0.0003 (9)
O2	0.0458 (14)	0.0354 (14)	0.0326 (13)	0.0016 (11)	0.0235 (11)	-0.0019 (11)
C1	0.0306 (17)	0.0270 (18)	0.0251 (17)	-0.0006 (14)	0.0088 (14)	-0.0019 (14)
O3	0.0598 (17)	0.0493 (16)	0.0418 (15)	0.0212 (13)	0.0318 (13)	0.0142 (13)
C15	0.0363 (18)	0.0311 (19)	0.0259 (17)	-0.0028 (15)	0.0117 (15)	-0.0018 (14)
C13	0.0330 (19)	0.040 (2)	0.063 (2)	-0.0006 (17)	0.0088 (18)	-0.001 (2)
C7	0.0379 (18)	0.0206 (16)	0.0353 (18)	-0.0022 (14)	0.0194 (15)	-0.0031 (14)
C11	0.041 (2)	0.039 (2)	0.038 (2)	-0.0047 (17)	0.0175 (17)	-0.0162 (17)
C8	0.0314 (18)	0.0267 (18)	0.0362 (19)	-0.0052 (14)	0.0194 (15)	-0.0017 (15)
C5	0.0325 (18)	0.036 (2)	0.0296 (18)	0.0000 (15)	0.0147 (15)	0.0002 (15)

C9	0.0348 (18)	0.037 (2)	0.0326 (18)	-0.0008 (16)	0.0159 (15)	-0.0028 (16)
C6	0.048 (2)	0.052 (2)	0.040 (2)	0.0018 (19)	0.0270 (17)	0.0051 (18)
C12	0.050 (2)	0.030 (2)	0.066 (3)	-0.0016 (18)	0.032 (2)	0.0025 (19)
C2	0.0388 (19)	0.0244 (17)	0.0267 (17)	0.0018 (15)	0.0137 (15)	-0.0009 (14)
C10	0.0383 (19)	0.047 (2)	0.0261 (18)	-0.0017 (17)	0.0114 (15)	-0.0070 (16)
C14	0.071 (3)	0.036 (2)	0.0289 (19)	-0.010 (2)	0.0044 (18)	-0.0025 (17)
C4	0.044 (2)	0.040 (2)	0.046 (2)	0.0015 (17)	0.0250 (18)	-0.0082 (18)
C3	0.045 (2)	0.0247 (18)	0.049 (2)	0.0039 (16)	0.0228 (17)	-0.0014 (16)
C16	0.059 (2)	0.042 (2)	0.038 (2)	0.0151 (19)	0.0202 (19)	0.0110 (18)
C17	0.049 (2)	0.030 (2)	0.055 (2)	-0.0017 (18)	0.0114 (19)	-0.0041 (18)
C18	0.042 (2)	0.044 (2)	0.049 (2)	0.0020 (18)	0.0210 (18)	-0.0027 (19)

Geometric parameters (Å, º)

Si1—O1	1.666 (2)	C6—H6A	0.9800
Si1—C14	1.860 (3)	C6—H6B	0.9800
Si1—C13	1.864 (3)	C6—H6C	0.9800
Si1—C15	1.879 (3)	C12—H12A	0.9800
O1—C1	1.386 (4)	C12—H12B	0.9800
O2—C8	1.220 (3)	C12—H12C	0.9800
C1—C5	1.331 (4)	C2—C3	1.554 (4)
C1—C2	1.508 (4)	C2—H2	1.0000
O3—C9	1.399 (4)	C10—H10A	0.9900

O3—H3O	0.80 (4)	C10—H10B	0.9900
C15—C16	1.531 (4)	C14—H14A	0.9800
C15—C17	1.531 (4)	C14—H14B	0.9800
C15—C18	1.542 (4)	C14—H14C	0.9800
C13—H13A	0.9800	C4—C3	1.544 (4)
C13—H13B	0.9800	C4—H4A	0.9900
C13—H13C	0.9800	C4—H4B	0.9900
C7—C8	1.522 (4)	C3—H3A	0.9900
C7—C12	1.542 (4)	C3—H3B	0.9900
C7—C2	1.547 (4)	C16—H16A	0.9800
C7—C11	1.560 (4)	C16—H16B	0.9800
C11—C10	1.532 (5)	C16—H16C	0.9800
C11—H11A	0.9900	C17—H17A	0.9800
C11—H11B	0.9900	C17—H17B	0.9800
C8—C9	1.519 (4)	C17—H17C	0.9800
C5—C6	1.499 (4)	C18—H18A	0.9800
C5—C4	1.500 (5)	C18—H18B	0.9800
C9—C10	1.517 (4)	C18—H18C	0.9800
C9—H9	1.0000		
O1—Si1—C14	109.53 (14)	C7—C12—H12B	109.5
O1—Si1—C13	109.21 (14)	H12A—C12—H12B	109.5
C14—Si1—C13	108.88 (18)	C7—C12—H12C	109.5
O1—Si1—C15	106.41 (12)	H12A—C12—H12C	109.5
C14—Si1—C15	111.78 (16)	H12B—C12—H12C	109.5
C13—Si1—C15	110.98 (15)	C1—C2—C7	113.5 (3)
C1—O1—Si1	123.92 (18)	C1—C2—C3	101.6 (2)
C5—C1—O1	125.2 (3)	C7—C2—C3	114.2 (3)
C5—C1—C2	114.5 (3)	C1—C2—H2	109.1
O1—C1—C2	119.9 (2)	C7—C2—H2	109.1
C9—O3—H3O	105 (3)	C3—C2—H2	109.1

C16—C15—C17	109.3 (3)	C9—C10—C11	102.9 (3)
C16—C15—C18	108.6 (3)	C9—C10—H10A	111.2
C17—C15—C18	108.6 (3)	C11—C10—H10A	111.2
C16—C15—Si1	110.5 (2)	C9—C10—H10B	111.2
C17—C15—Si1	109.1 (2)	C11—C10—H10B	111.2
C18—C15—Si1	110.7 (2)	H10A—C10—H10B	109.1
Si1—C13—H13A	109.5	Si1—C14—H14A	109.5
Si1—C13—H13B	109.5	Si1—C14—H14B	109.5
H13A—C13—H13B	109.5	H14A—C14—H14B	109.5
Si1—C13—H13C	109.5	Si1—C14—H14C	109.5
H13A—C13—H13C	109.5	H14A—C14—H14C	109.5
H13B—C13—H13C	109.5	H14B—C14—H14C	109.5
C8—C7—C12	107.8 (2)	C5—C4—C3	104.4 (3)
C8—C7—C2	110.6 (2)	C5—C4—H4A	110.9
C12—C7—C2	110.0 (3)	C3—C4—H4A	110.9
C8—C7—C11	102.8 (3)	C5—C4—H4B	110.9
C12—C7—C11	112.4 (3)	C3—C4—H4B	110.9
C2—C7—C11	113.0 (2)	H4A—C4—H4B	108.9
C10—C11—C7	105.9 (2)	C4—C3—C2	106.9 (3)
C10—C11—H11A	110.6	C4—C3—H3A	110.3
C7—C11—H11A	110.6	C2—C3—H3A	110.3
C10—C11—H11B	110.6	C4—C3—H3B	110.3
C7—C11—H11B	110.6	C2—C3—H3B	110.3
H11A—C11—H11B	108.7	H3A—C3—H3B	108.6
O2—C8—C9	125.0 (3)	C15—C16—H16A	109.5
O2—C8—C7	125.3 (3)	C15—C16—H16B	109.5
C9—C8—C7	109.7 (3)	H16A—C16—H16B	109.5
C1—C5—C6	126.7 (3)	C15—C16—H16C	109.5
C1—C5—C4	110.7 (3)	H16A—C16—H16C	109.5
C6—C5—C4	122.5 (3)	H16B—C16—H16C	109.5
O3—C9—C10	113.1 (3)	C15—C17—H17A	109.5

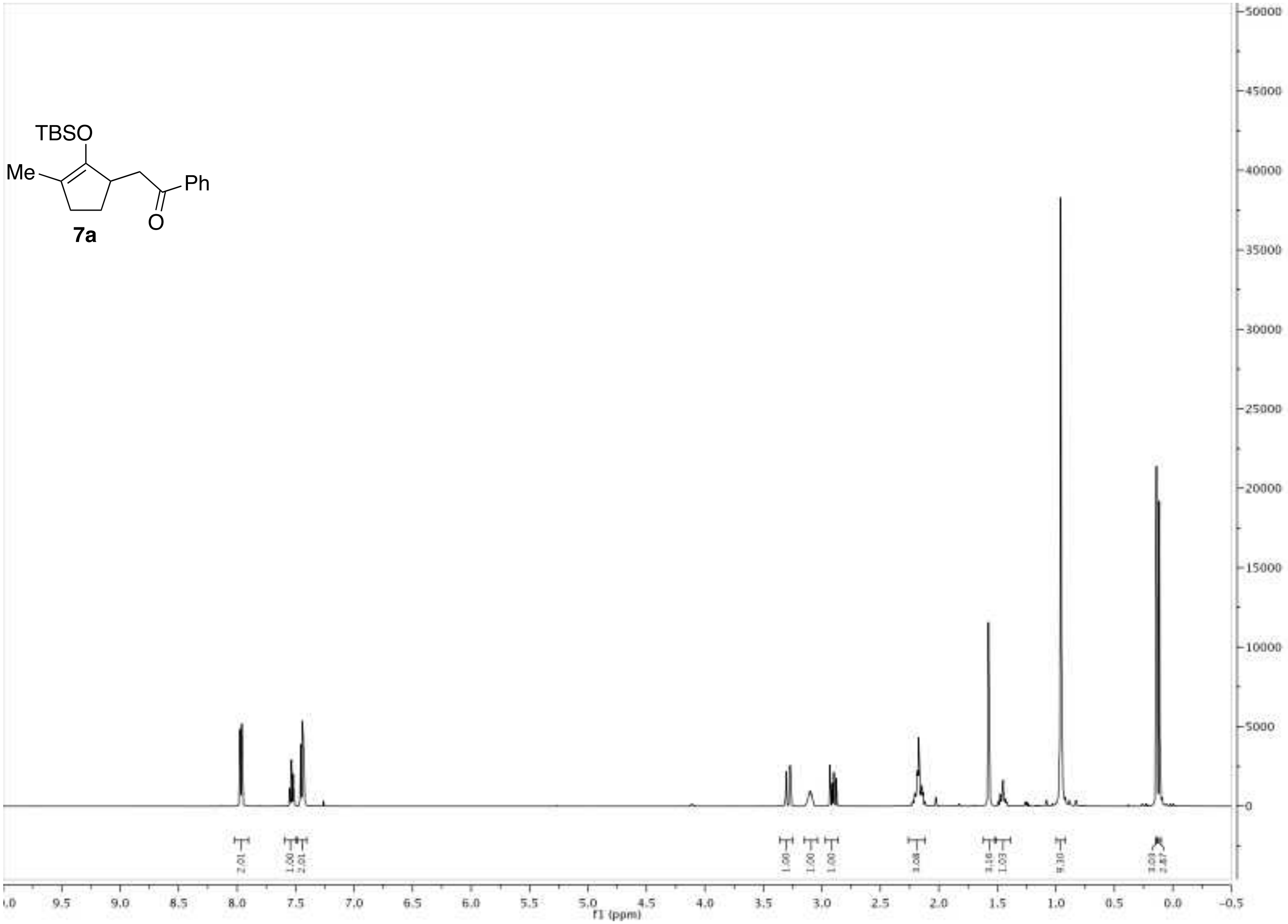
O3—C9—C8	115.9 (3)	C15—C17—H17B	109.5
C10—C9—C8	102.7 (3)	H17A—C17—H17B	109.5
O3—C9—H9	108.3	C15—C17—H17C	109.5
C10—C9—H9	108.3	H17A—C17—H17C	109.5
C8—C9—H9	108.3	H17B—C17—H17C	109.5
C5—C6—H6A	109.5	C15—C18—H18A	109.5
C5—C6—H6B	109.5	C15—C18—H18B	109.5
H6A—C6—H6B	109.5	H18A—C18—H18B	109.5
C5—C6—H6C	109.5	C15—C18—H18C	109.5
H6A—C6—H6C	109.5	H18A—C18—H18C	109.5
H6B—C6—H6C	109.5	H18B—C18—H18C	109.5
C7—C12—H12A	109.5		
C14—Si1—O1—C1	68.4 (3)	O1—C1—C5—C4	176.5 (3)
C13—Si1—O1—C1	-50.7 (3)	C2—C1—C5—C4	3.6 (4)
C15—Si1—O1—C1	-170.6 (2)	O2—C8—C9—O3	-30.5 (4)
Si1—O1—C1—C5	89.9 (3)	C7—C8—C9—O3	151.9 (3)
Si1—O1—C1—C2	-97.6 (3)	O2—C8—C9—C10	-154.3 (3)
O1—Si1—C15—C16	46.4 (3)	C7—C8—C9—C10	28.1 (3)
C14—Si1—C15—C16	166.0 (2)	C5—C1—C2—C7	111.9 (3)
C13—Si1—C15—C16	-72.3 (3)	O1—C1—C2—C7	-61.4 (4)
O1—Si1—C15—C17	166.6 (2)	C5—C1—C2—C3	-11.2 (4)
C14—Si1—C15—C17	-73.8 (3)	O1—C1—C2—C3	175.6 (3)
C13—Si1—C15—C17	47.9 (3)	C8—C7—C2—C1	61.6 (3)
O1—Si1—C15—C18	-73.9 (2)	C12—C7—C2—C1	-179.5 (3)
C14—Si1—C15—	45.6 (3)	C11—C7—C2—C1	-53.0 (3)

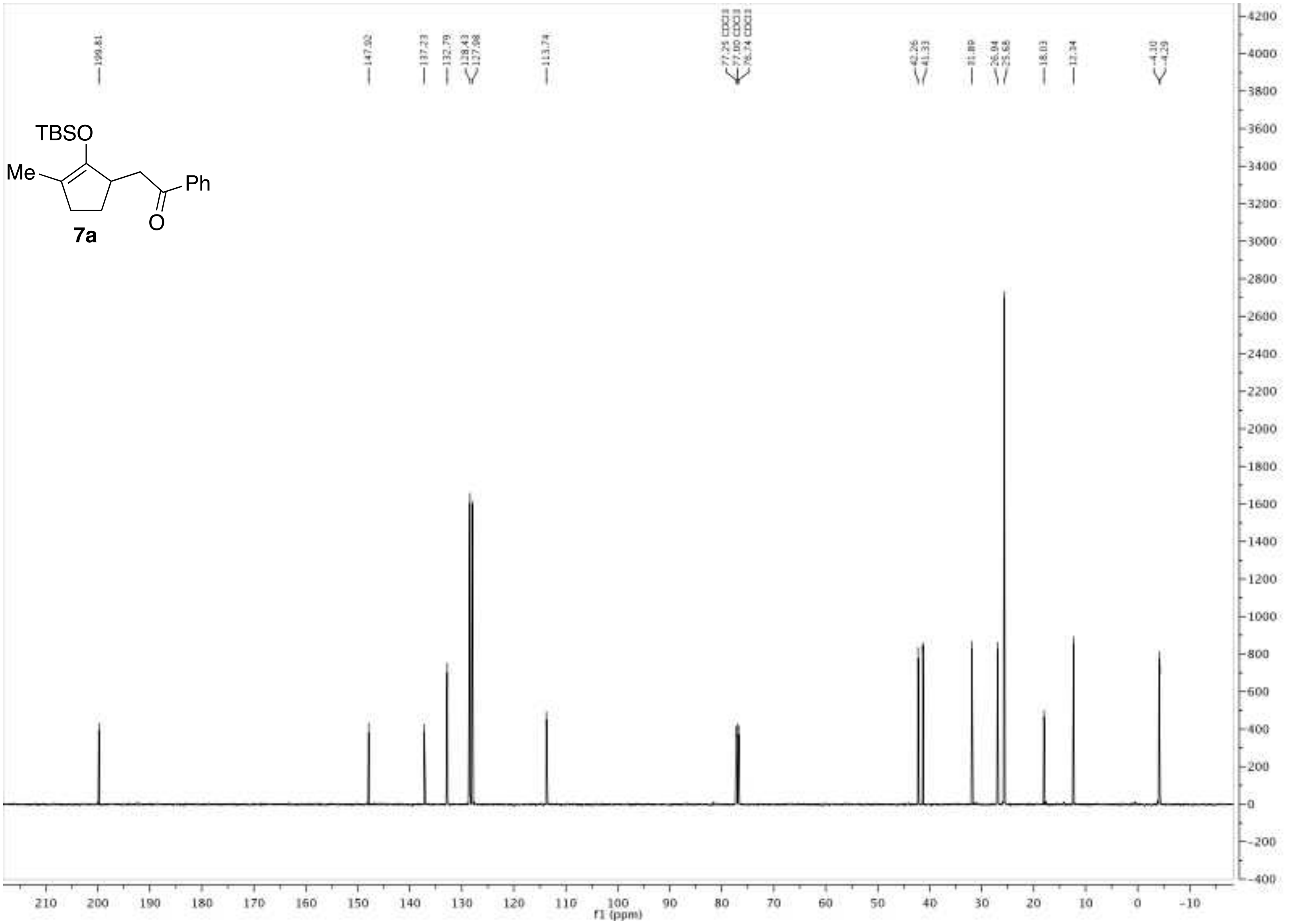
C18			
C13—Si1—C15—C18	167.4 (2)	C8—C7—C2—C3	177.4 (3)
C8—C7—C11—C10	-19.5 (3)	C12—C7—C2—C3	-63.7 (3)
C12—C7—C11—C10	-135.1 (3)	C11—C7—C2—C3	62.8 (3)
C2—C7—C11—C10	99.7 (3)	O3—C9—C10—C11	-164.9 (3)
C12—C7—C8—O2	-64.0 (4)	C8—C9—C10—C11	-39.2 (3)
C2—C7—C8—O2	56.3 (4)	C7—C11—C10—C9	37.1 (3)
C11—C7—C8—O2	177.1 (3)	C1—C5—C4—C3	5.7 (4)
C12—C7—C8—C9	113.5 (3)	C6—C5—C4—C3	-178.3 (3)
C2—C7—C8—C9	-126.2 (3)	C5—C4—C3—C2	-12.3 (4)
C11—C7—C8—C9	-5.3 (3)	C1—C2—C3—C4	13.8 (3)
O1—C1—C5—C6	0.8 (5)	C7—C2—C3—C4	-108.8 (3)
C2—C1—C5—C6	-172.1 (3)		

Hydrogen-bond geometry (Å, º)

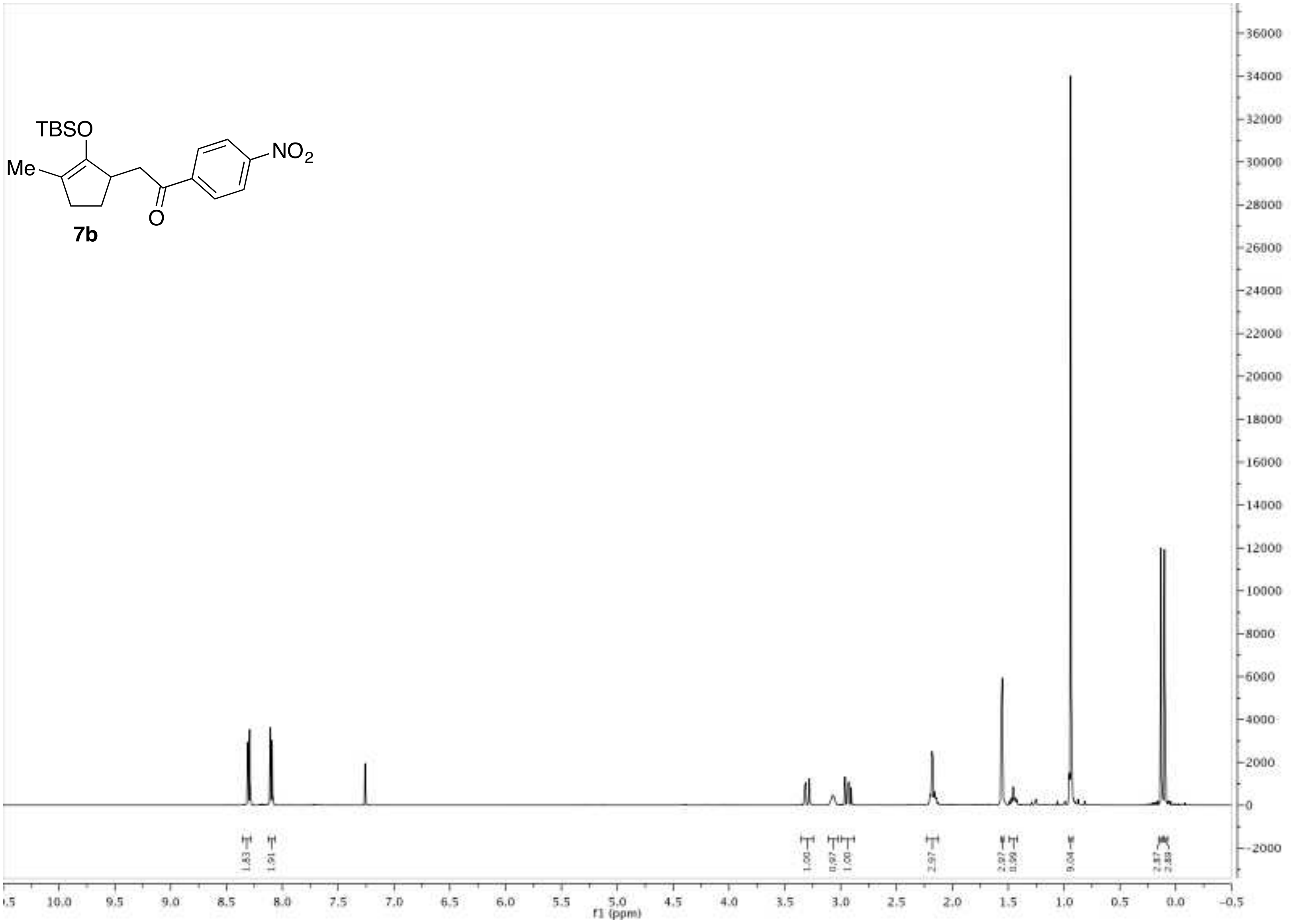
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O2^{i}	0.80 (4)	2.07 (4)	2.790 (3)	151 (4)

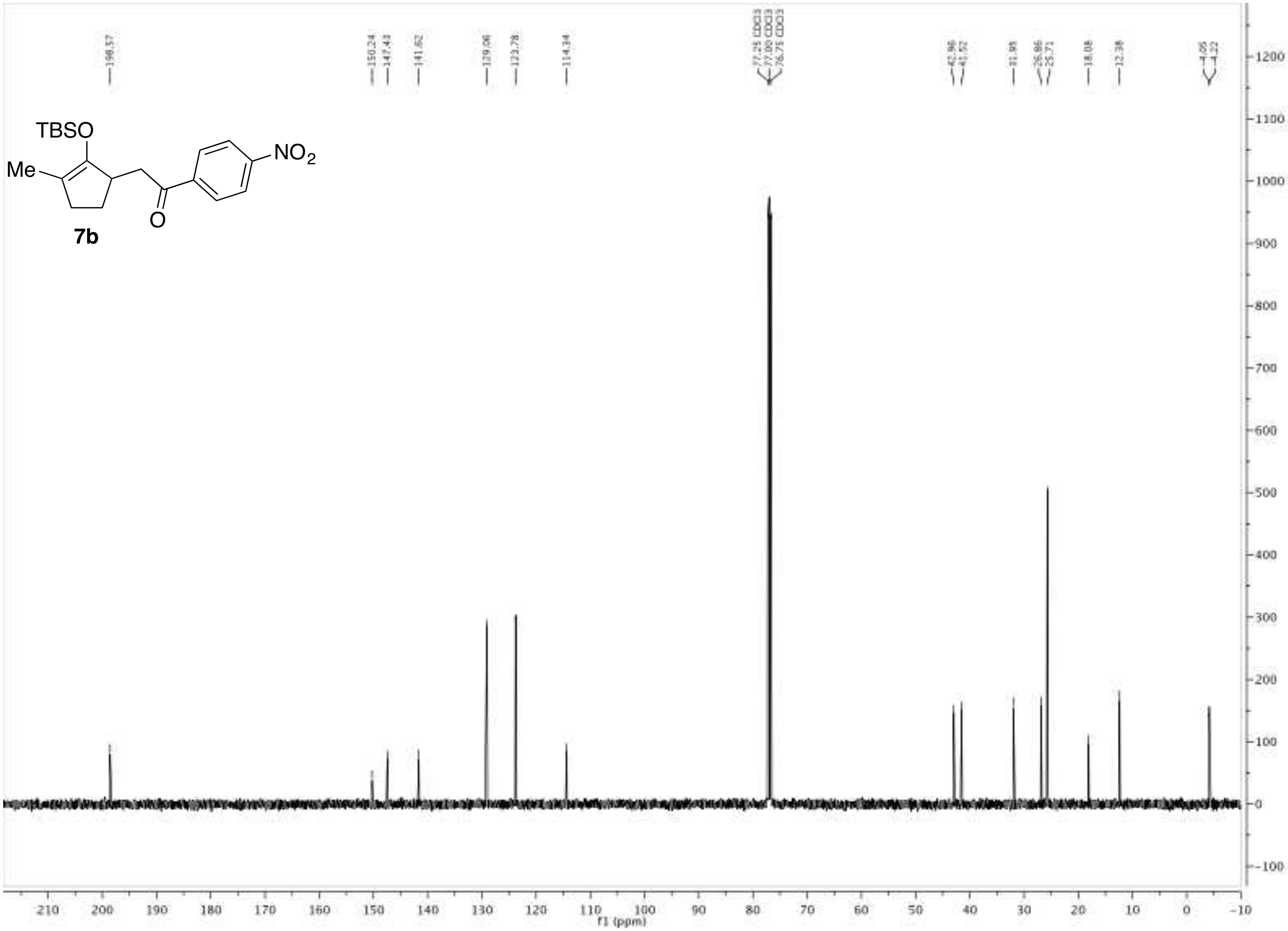
Symmetry code: (i) -*x*+3/2, -*y*+1/2, -*z*+1.


TBSO
Me
Ph
O
7a
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.01
1.00
2.01
1.00
1.00
1.00
3.08
3.16
1.03
9.30
3.03
2.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

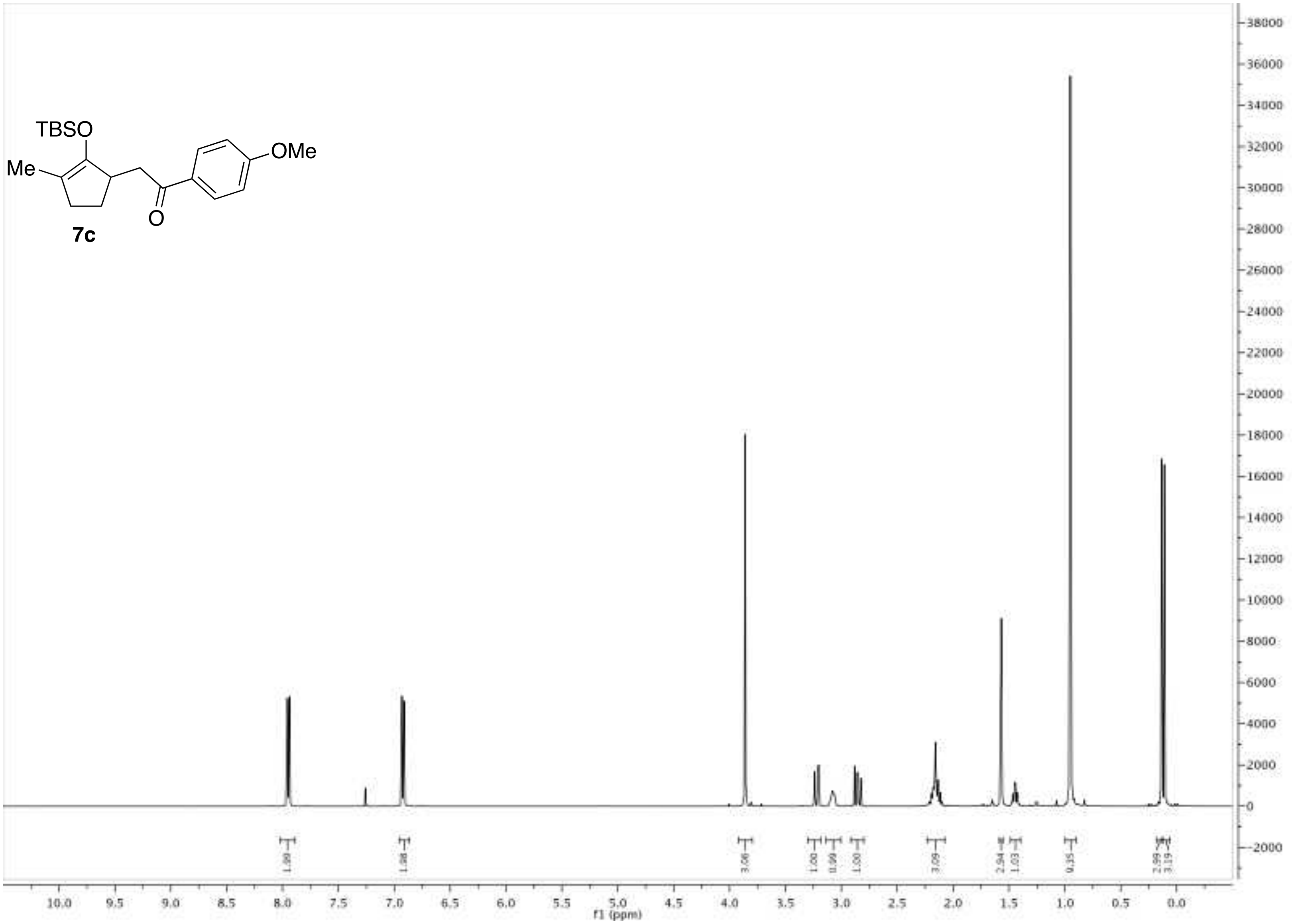

199.81
147.92
137.23
132.79
128.43
127.98
113.74
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
42.26
41.33
31.89
26.94
25.68
18.03
12.34
-4.10
-4.29
TBSO
Me
Ph
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400

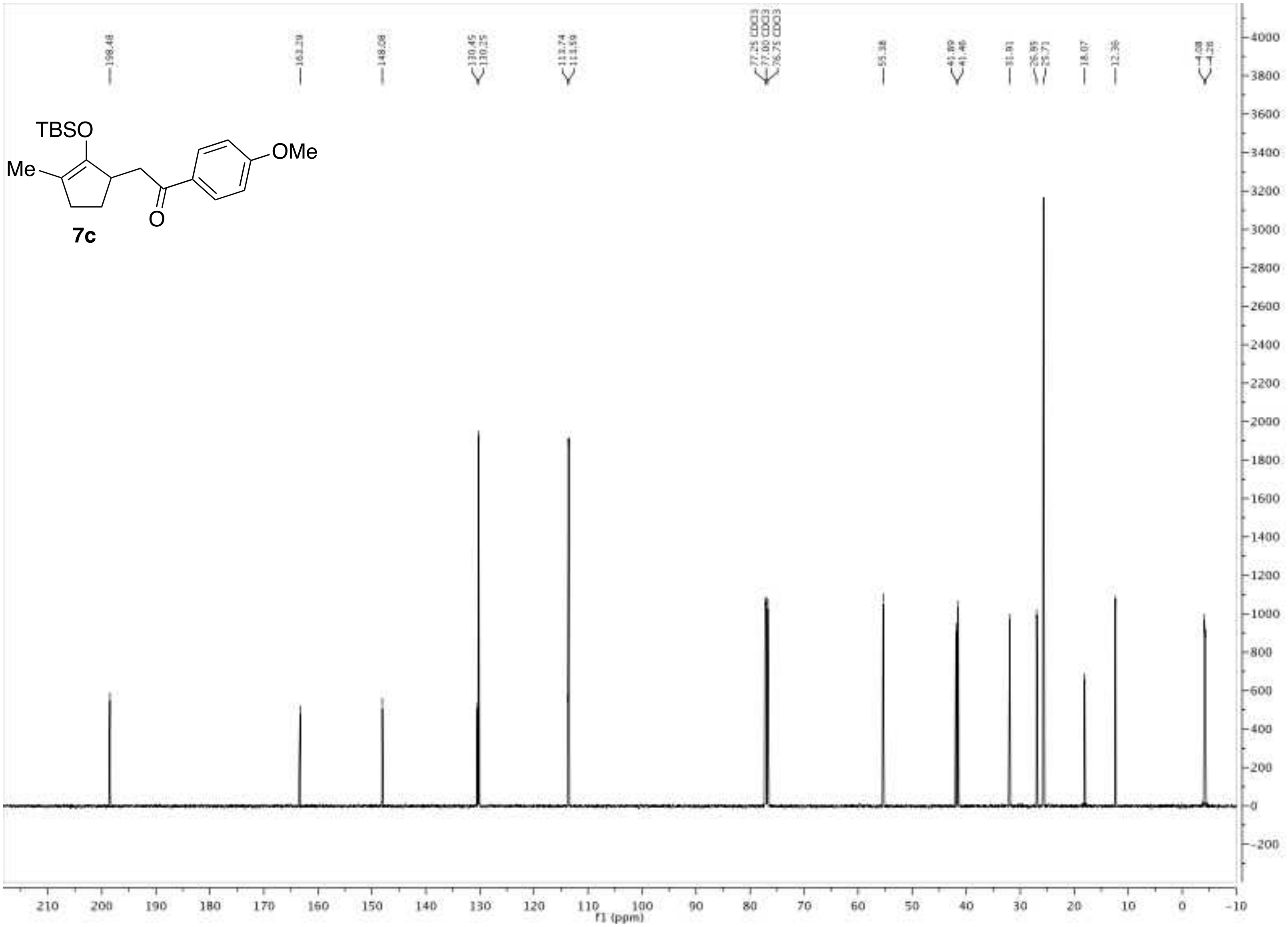
7a

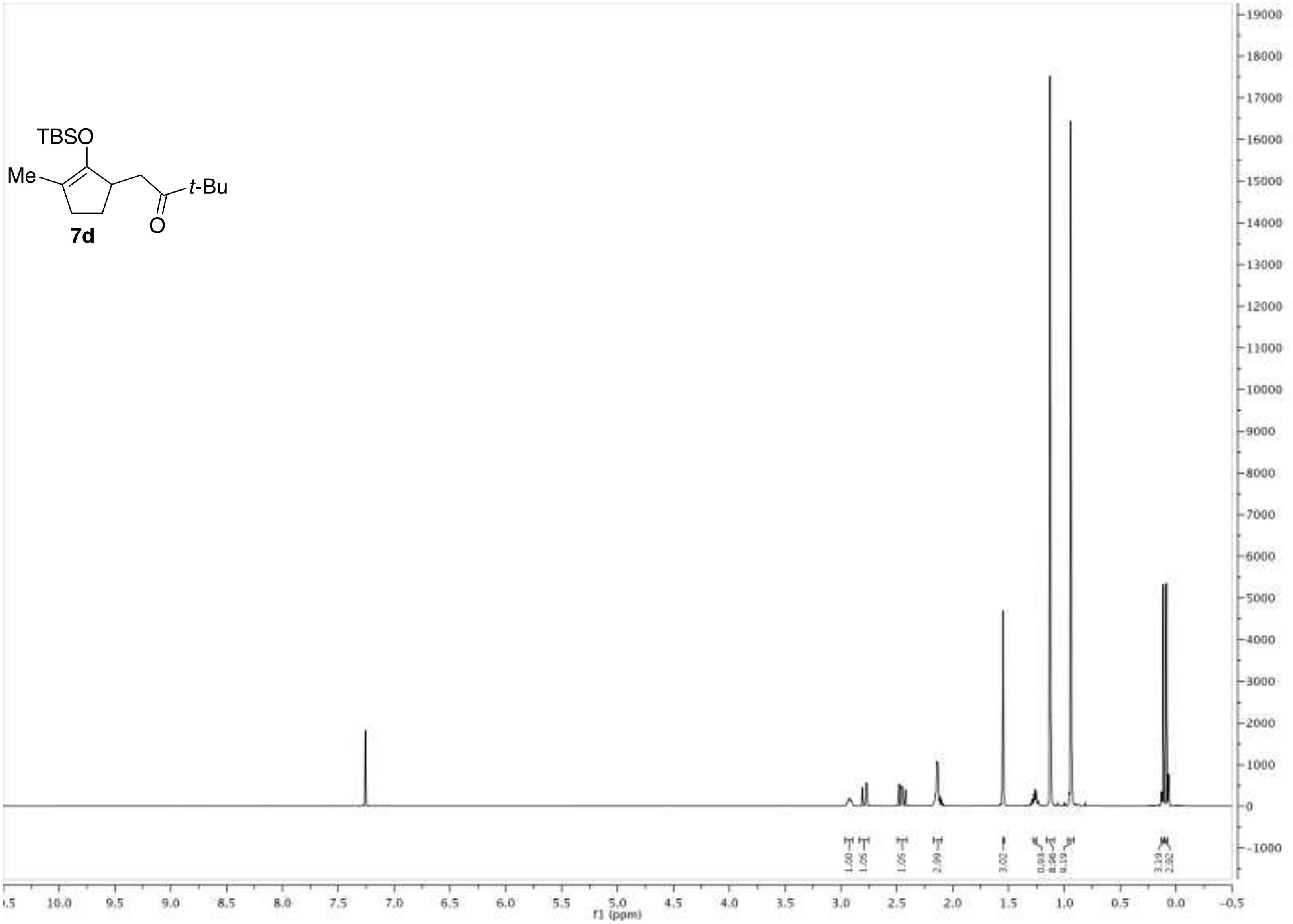

TBSO
Me
NO2
O
7b
1.83
1.91
1.00
0.97
1.00
2.97
2.97
0.99
9.04
2.87
2.89
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


198.57
150.24
147.43
141.62
129.06
123.78
114.34
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
42.96
41.52
31.95
26.86
25.71
18.08
12.38
-4.05
-4.22
TBSO
Me
NO2
O
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7b

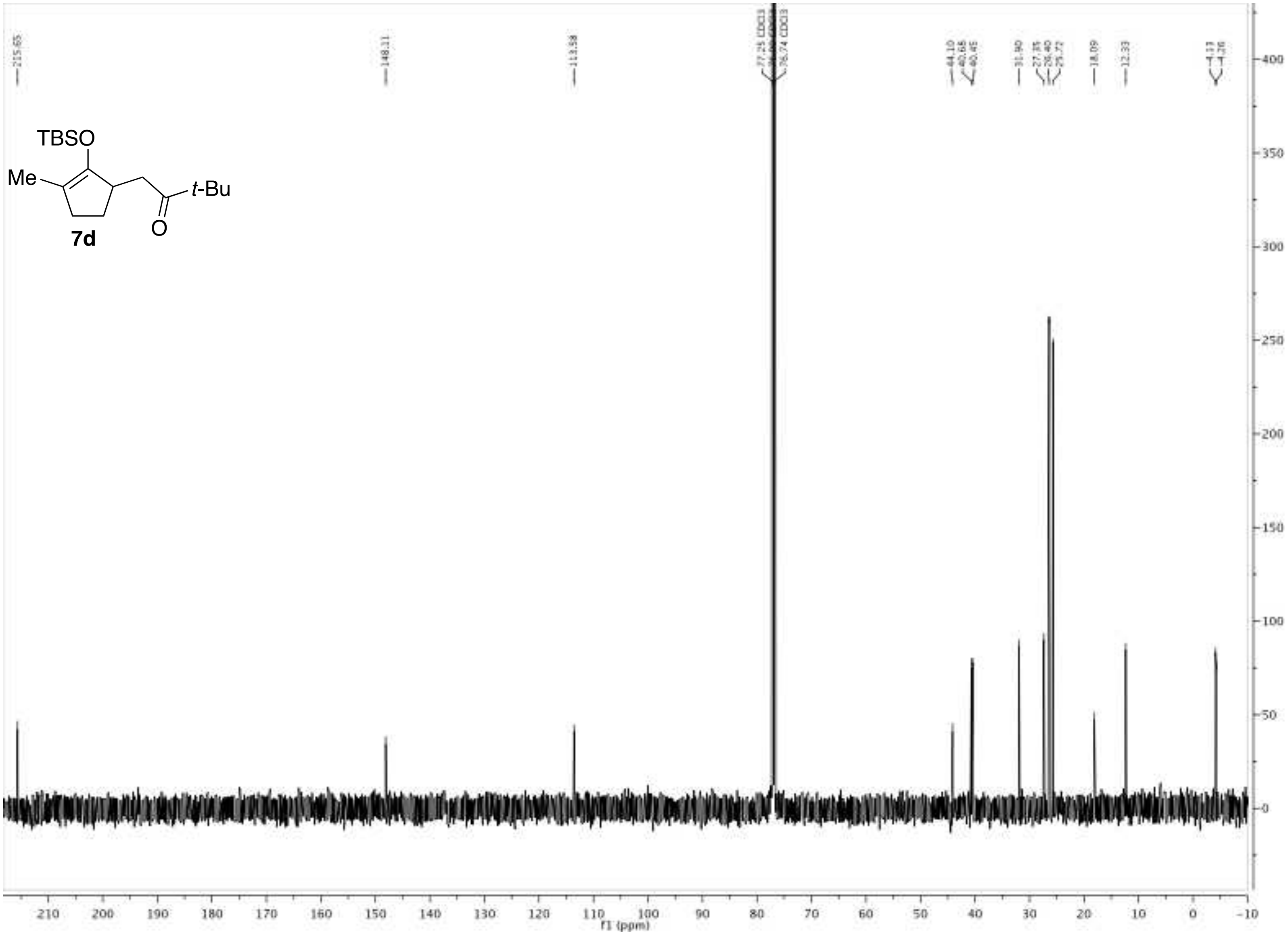

TBSO
Me
OMe
O
7c
1.80
1.88
3.06
1.00
0.99
1.00
3.09
2.94
1.03
9.35
2.99
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

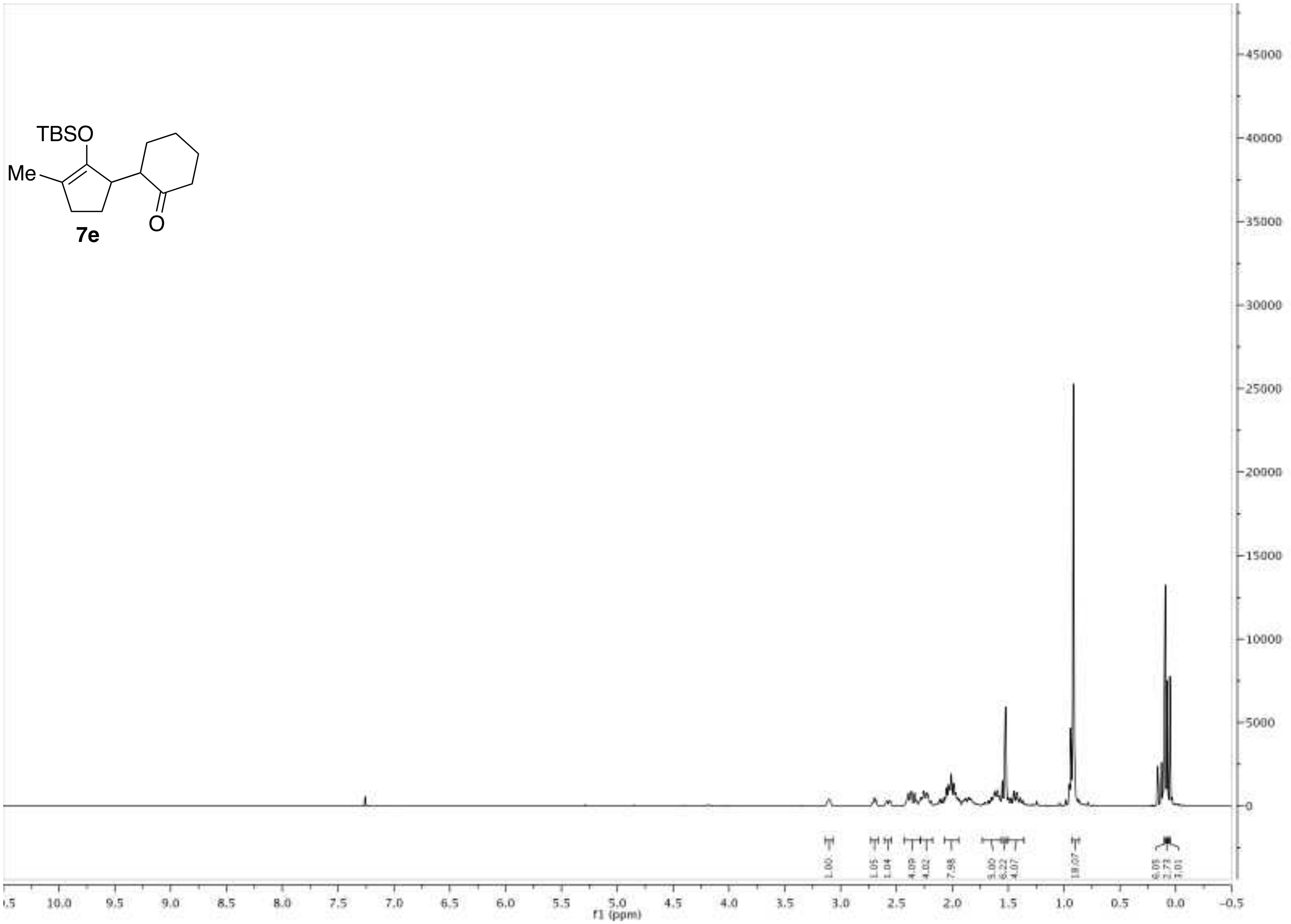

198.48
163.29
148.08
130.45
130.25
113.74
113.59
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.38
41.89
41.46
31.91
26.95
25.71
18.07
12.36
-4.08
-4.28
TBSO
Me
OMe
O
7c
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



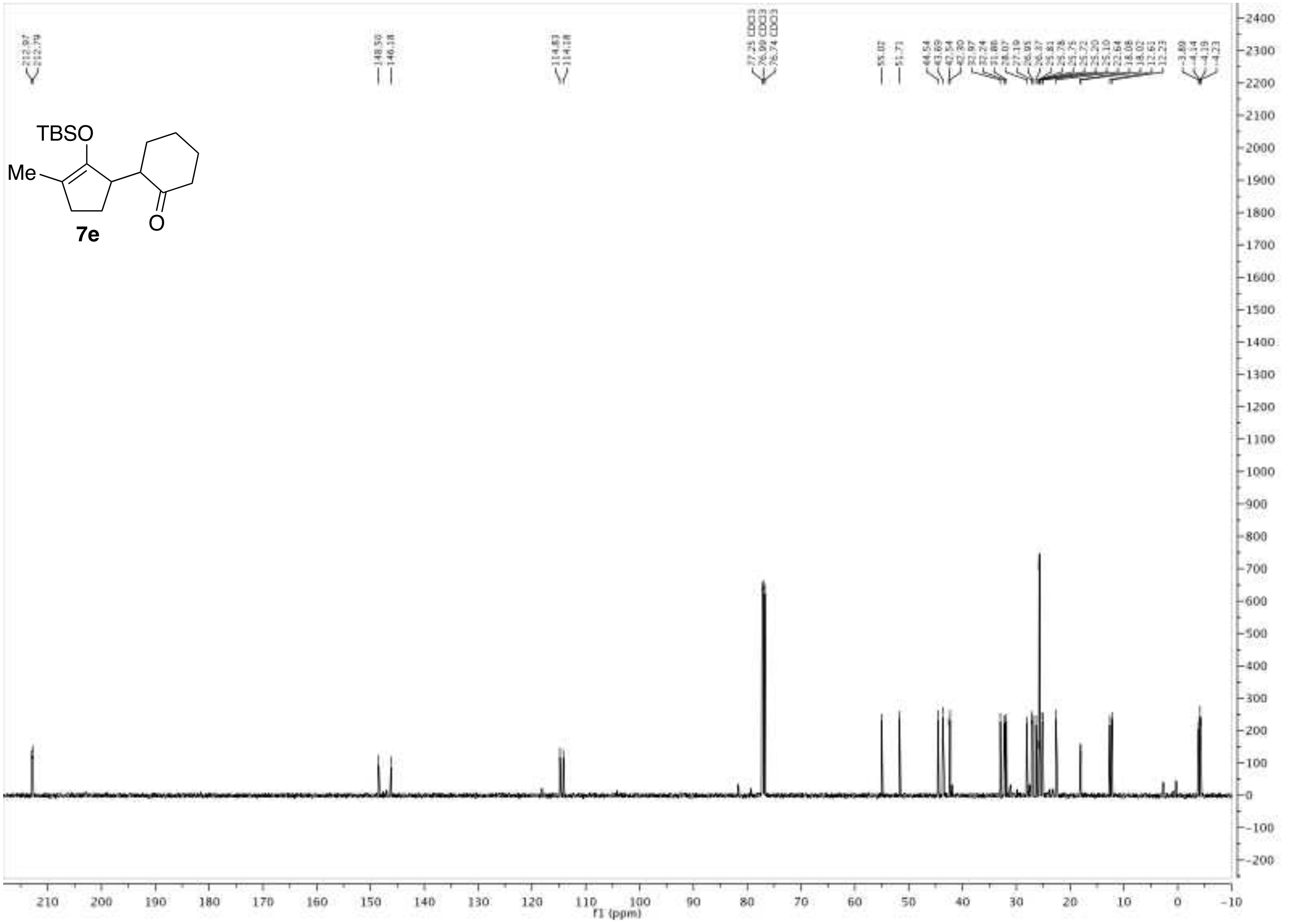
7d

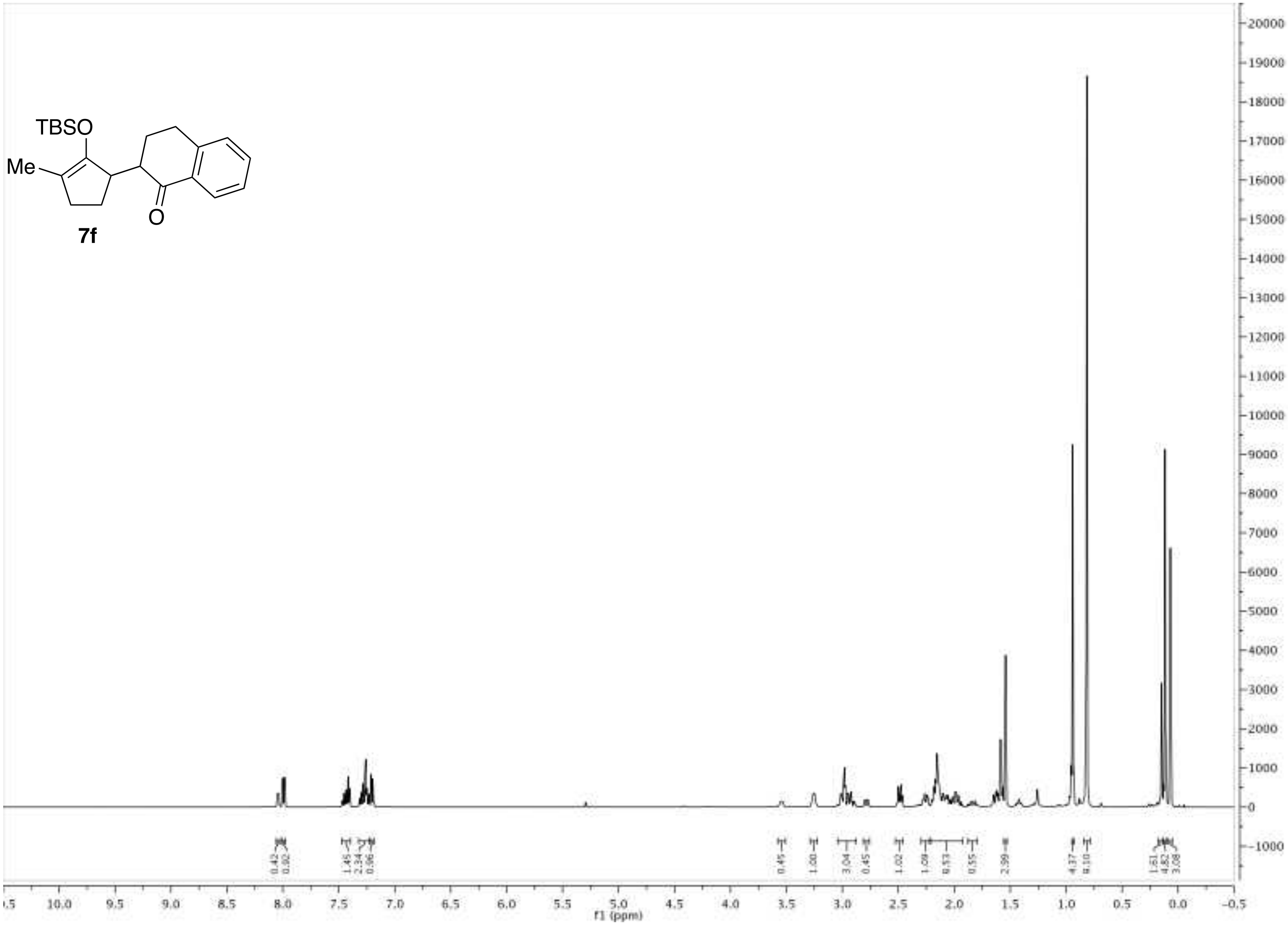
TBSO
Me
t-Bu
O
1.00
1.06
1.05
2.99
3.02
0.93
8.96
9.19
3.19
2.92
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


215.65
148.11
113.58
77.25 CDCl3
76.74 CDCl3
44.10
40.68
40.45
31.90
27.35
26.40
25.72
18.09
12.33
-4.13
-4.26
TBSO
Me
t-Bu
O
7d
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



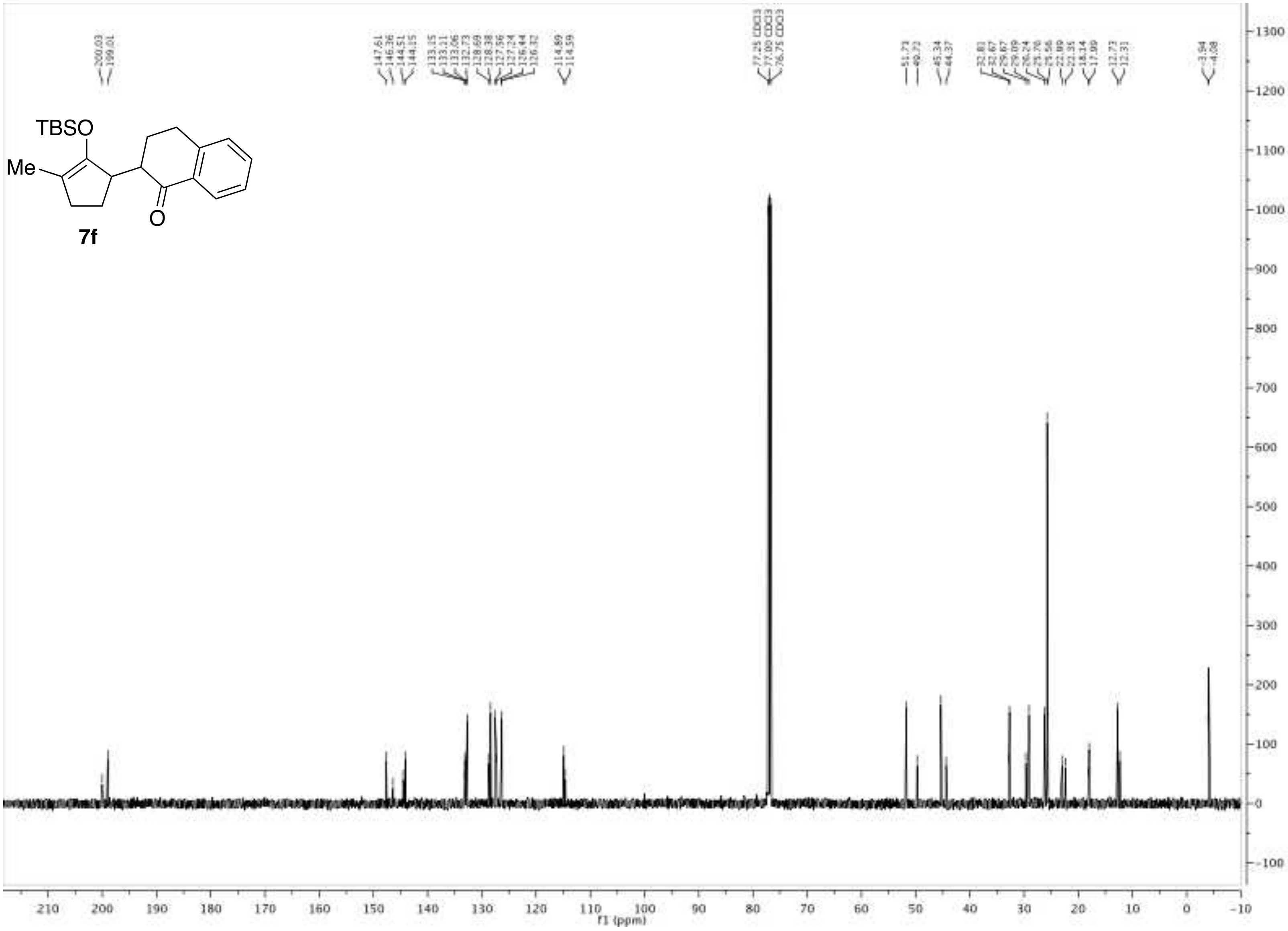
TBSO
Me
O
7e
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.05
1.04
4.09
4.02
7.98
5.00
6.22
4.07
18.07
6.05
2.73
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


212.97
212.79
148.50
146.18
114.83
114.18
77.25 CDCl3
76.99 CDCl3
76.74 CDCl3
55.02
51.71
44.54
43.69
42.54
42.30
32.97
32.24
31.88
28.07
27.19
26.95
26.37
25.81
25.78
25.75
25.72
25.20
25.10
22.64
18.08
18.02
12.61
12.23
-3.89
-4.14
-4.19
-4.23
TBSO
Me
O
7e
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

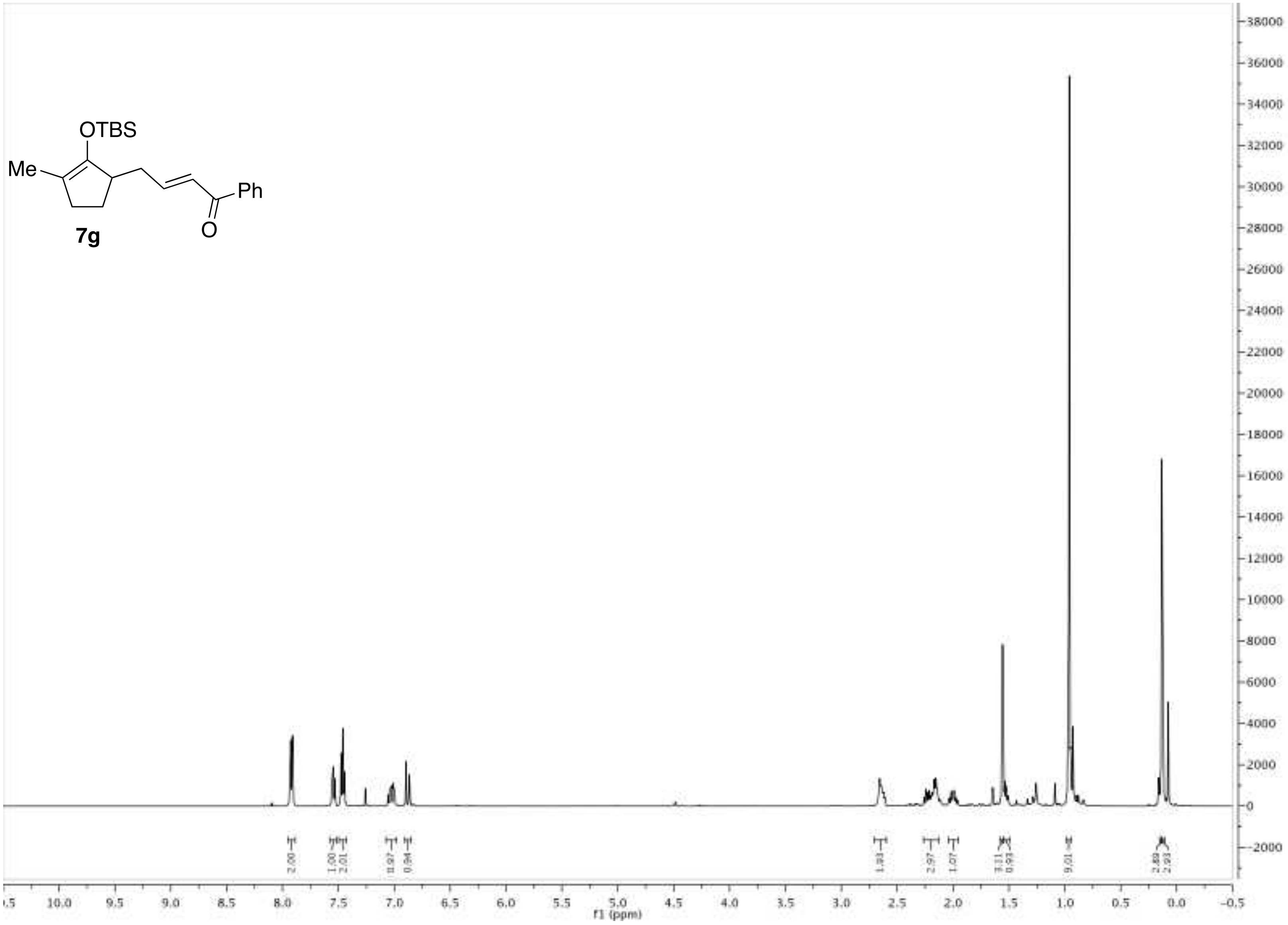


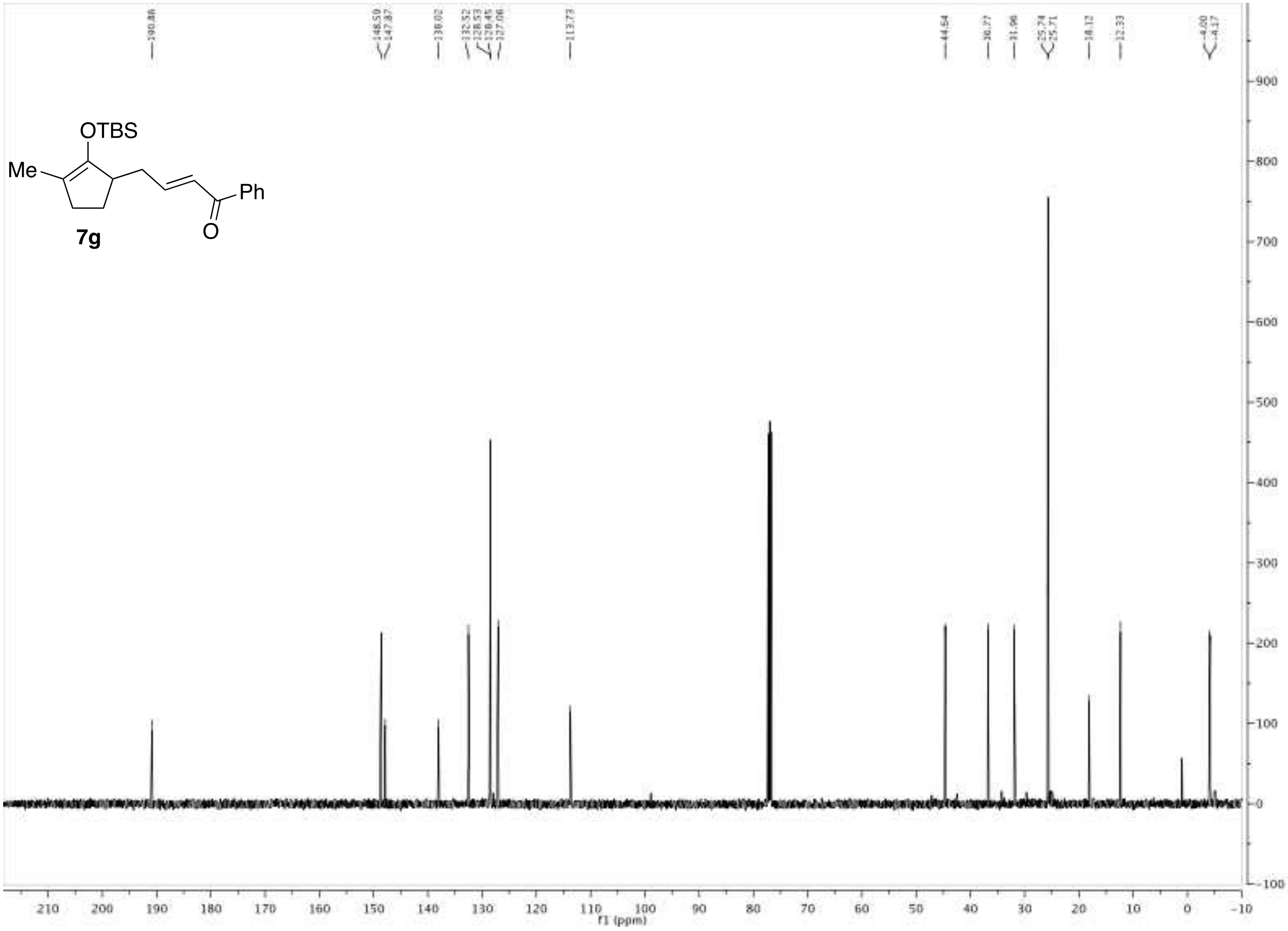
7f

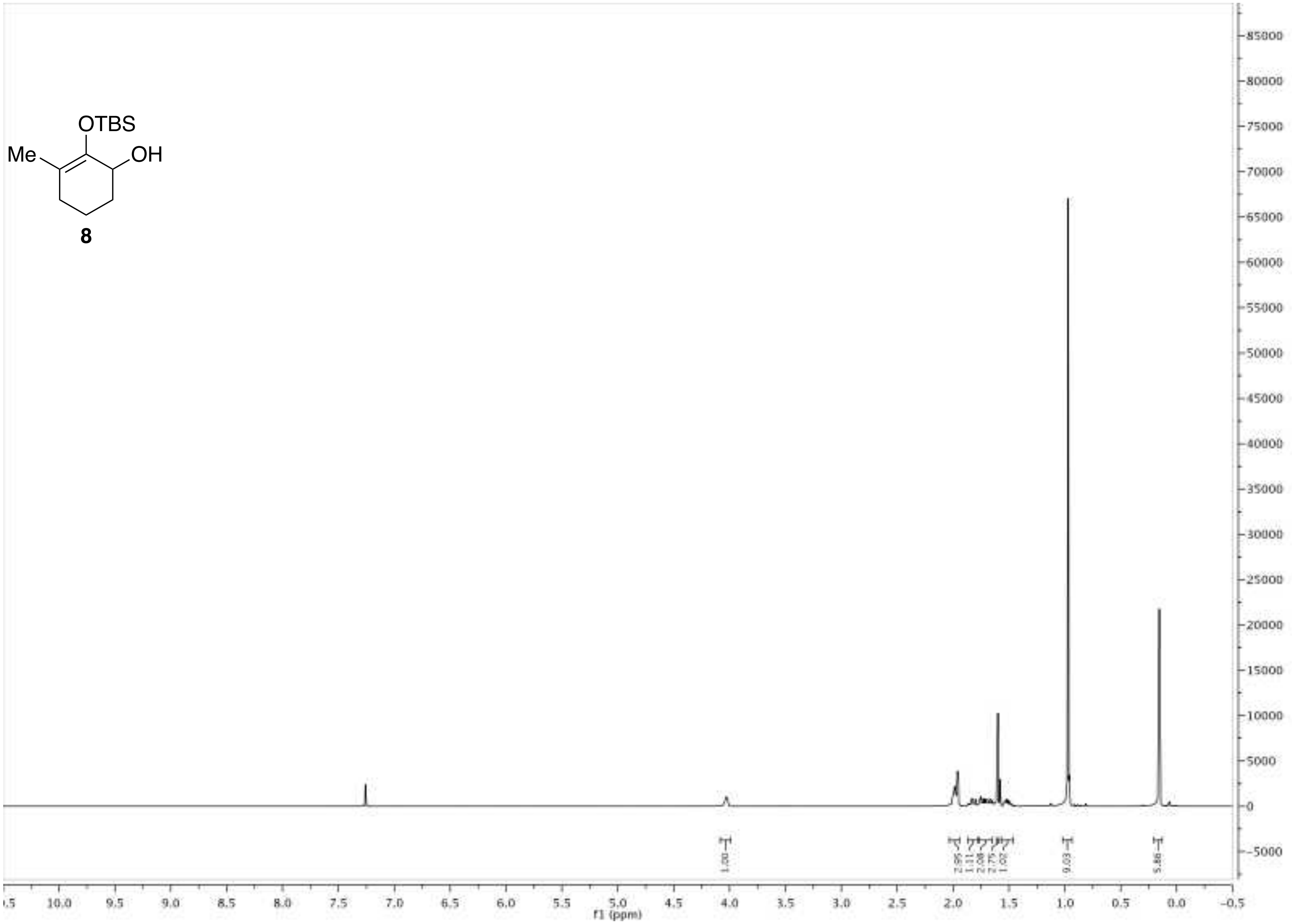
TBSO
Me
O
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.42
0.82
1.45
2.34
0.96
0.45
1.00
3.04
0.45
1.02
1.09
6.53
0.55
2.99
4.37
9.10
1.61
4.82
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

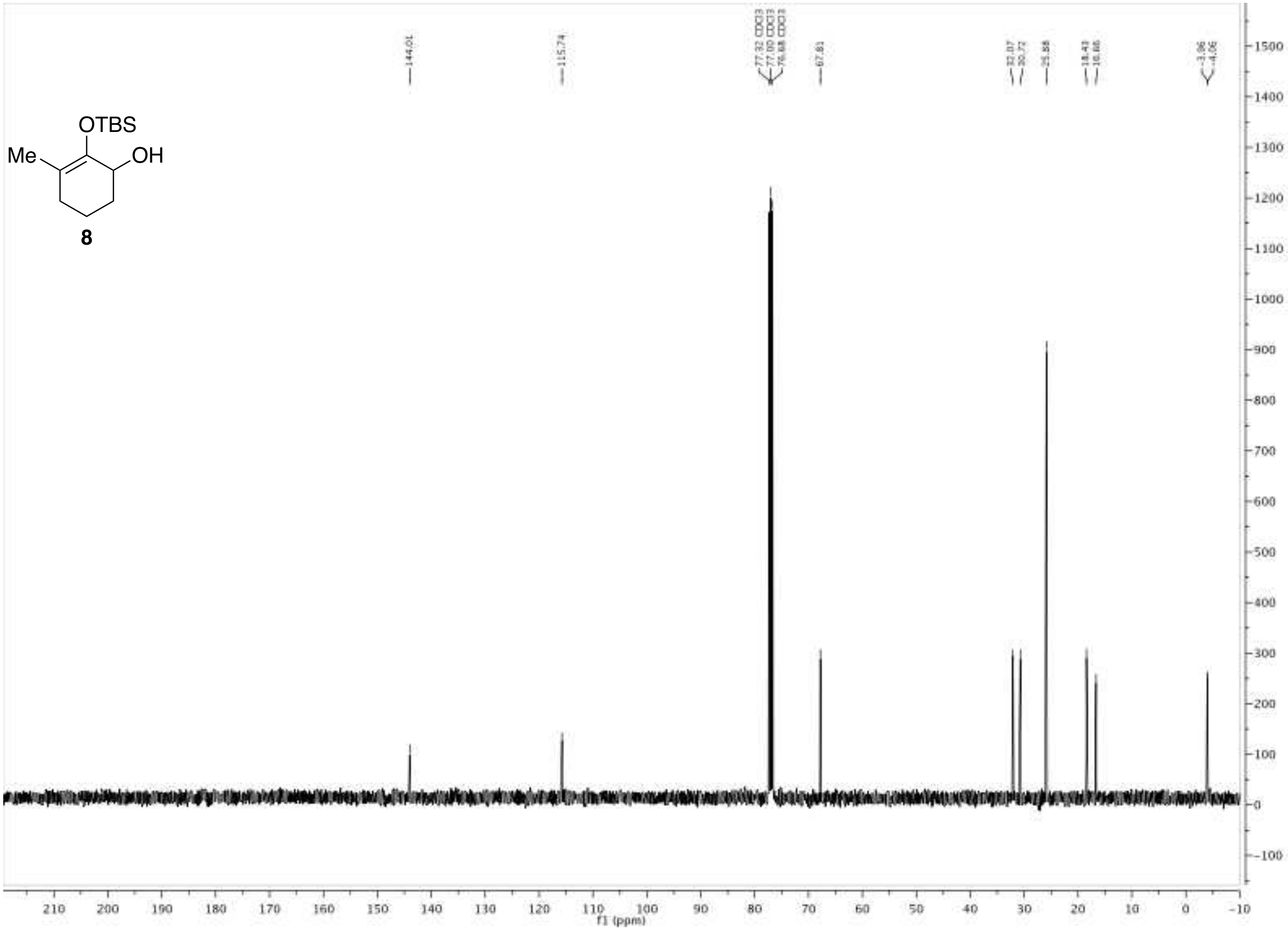

7f

200.03
199.01
147.61
146.36
144.51
144.15
133.15
133.11
133.06
132.73
128.69
128.38
127.56
127.24
126.44
126.32
114.89
114.59
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
51.73
49.72
45.34
44.37
32.81
32.67
29.67
29.09
26.24
25.76
25.56
22.89
22.35
18.14
17.99
12.73
12.31
-3.94
-4.08
TBSO
Me
O
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

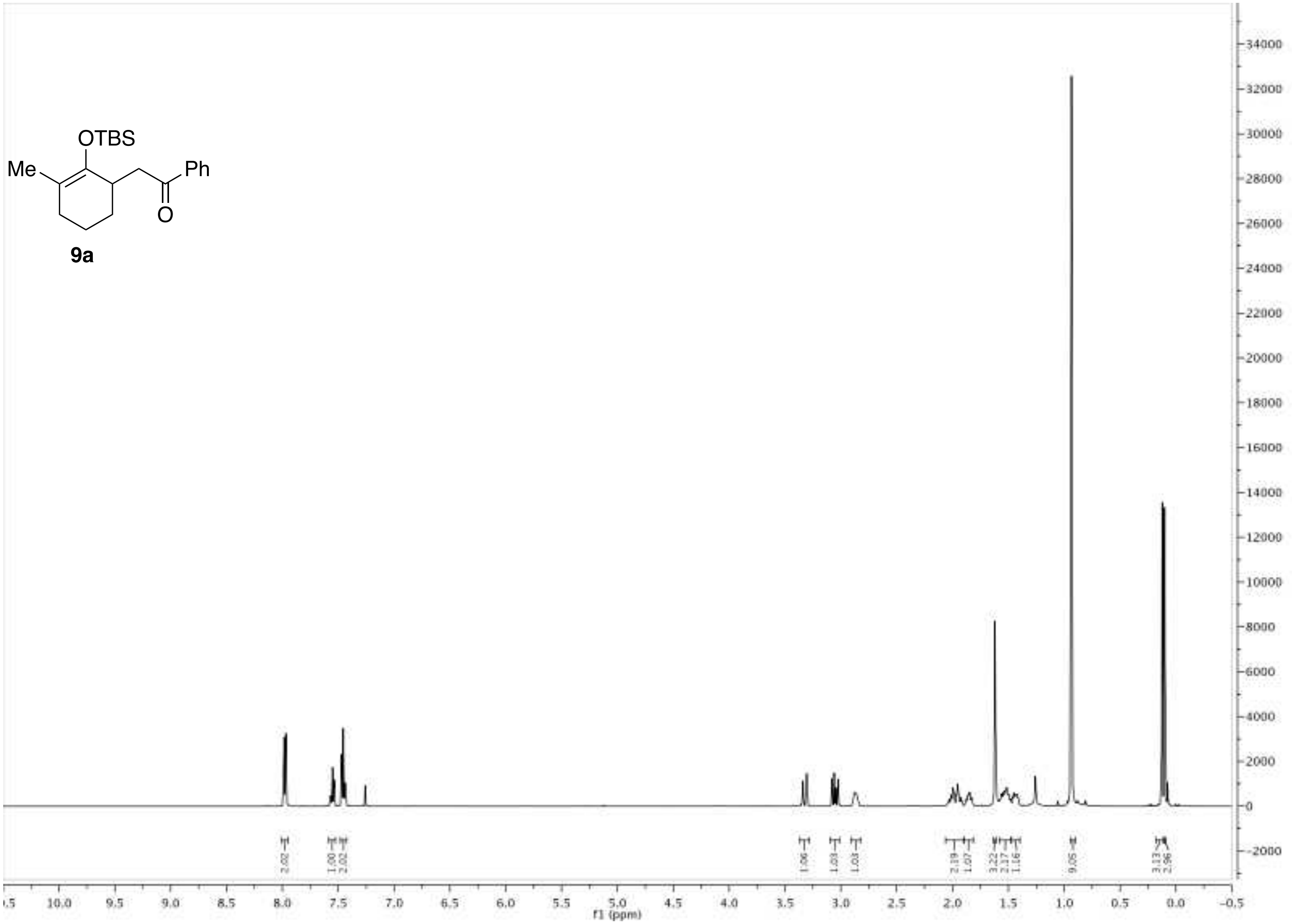

OTBS
Me
Ph
O
7g
2.00
1.00
2.01
0.97
0.94
1.93
2.97
1.07
3.11
0.93
9.01
2.89
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

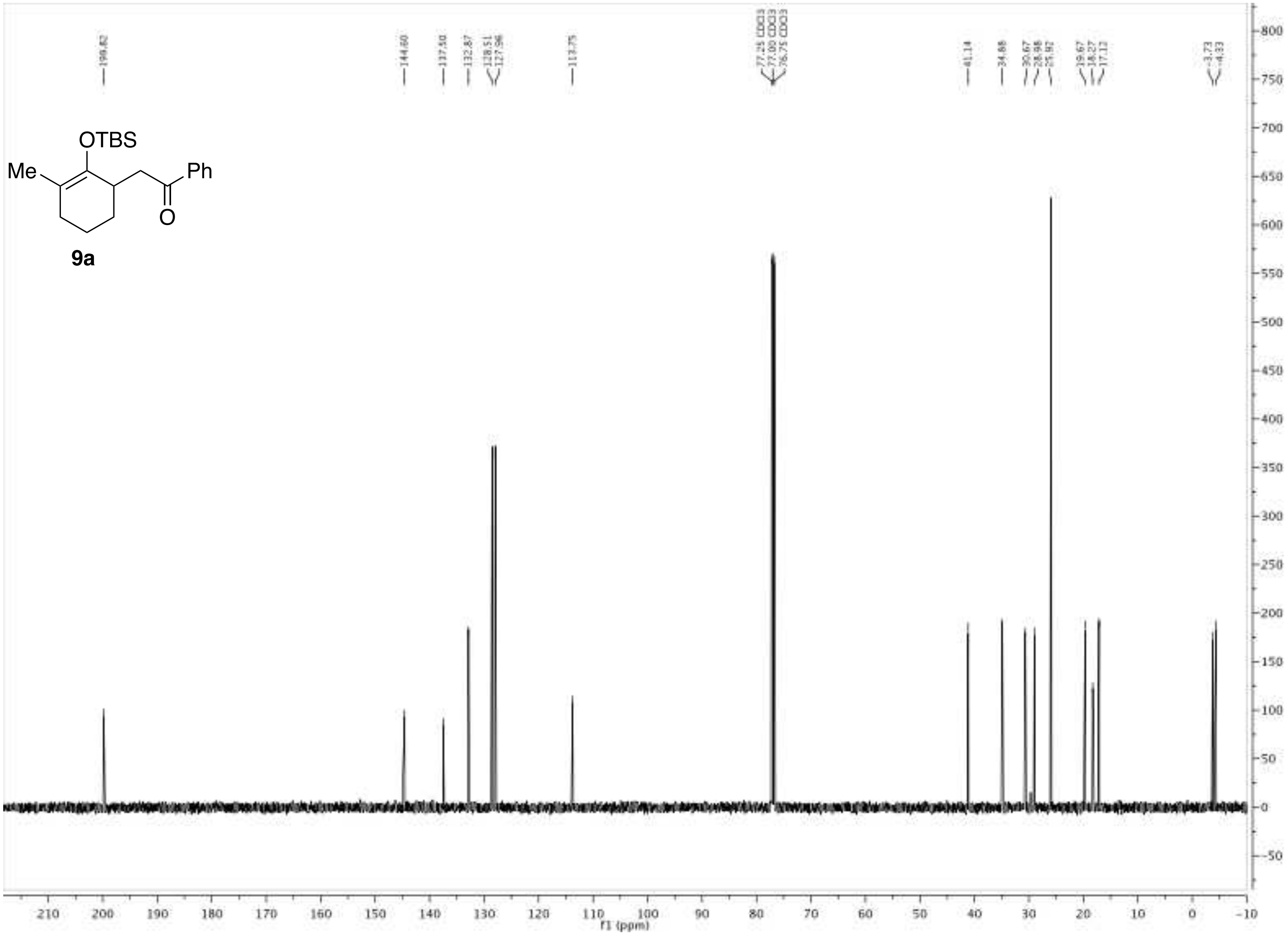

190.86
148.50
147.87
138.02
132.52
128.53
128.45
127.06
113.73
44.64
36.77
31.96
25.74
25.71
18.12
12.33
-4.00
-4.17
OTBS
Me
Ph
O
7g
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

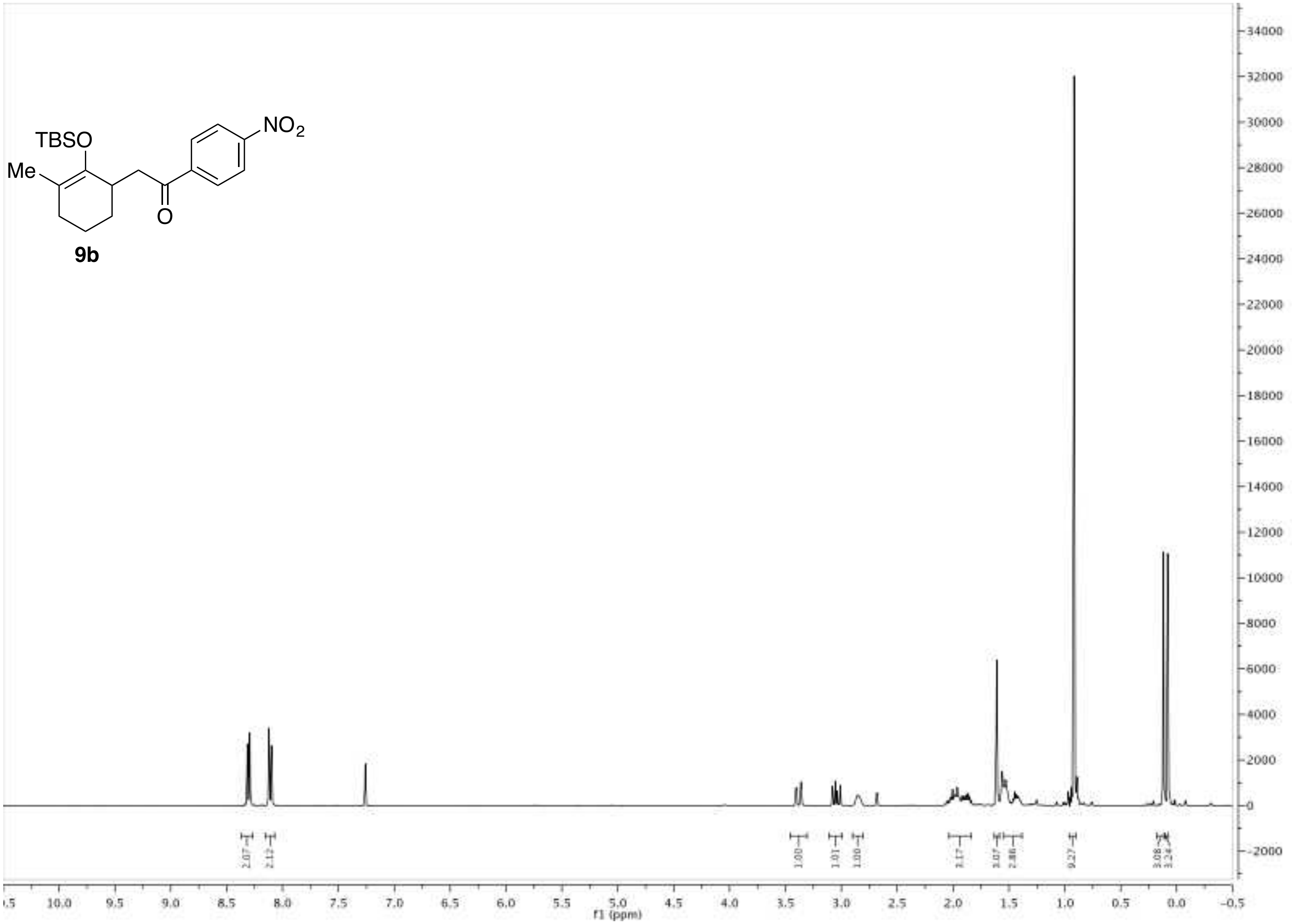

OTBS
Me
OH
8
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
1.00
2.95
1.11
2.08
2.75
1.02
9.03
5.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OTBS
Me
OH
144.01
115.74
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.81
32.07
30.72
25.88
18.43
16.66
-3.96
-4.06
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

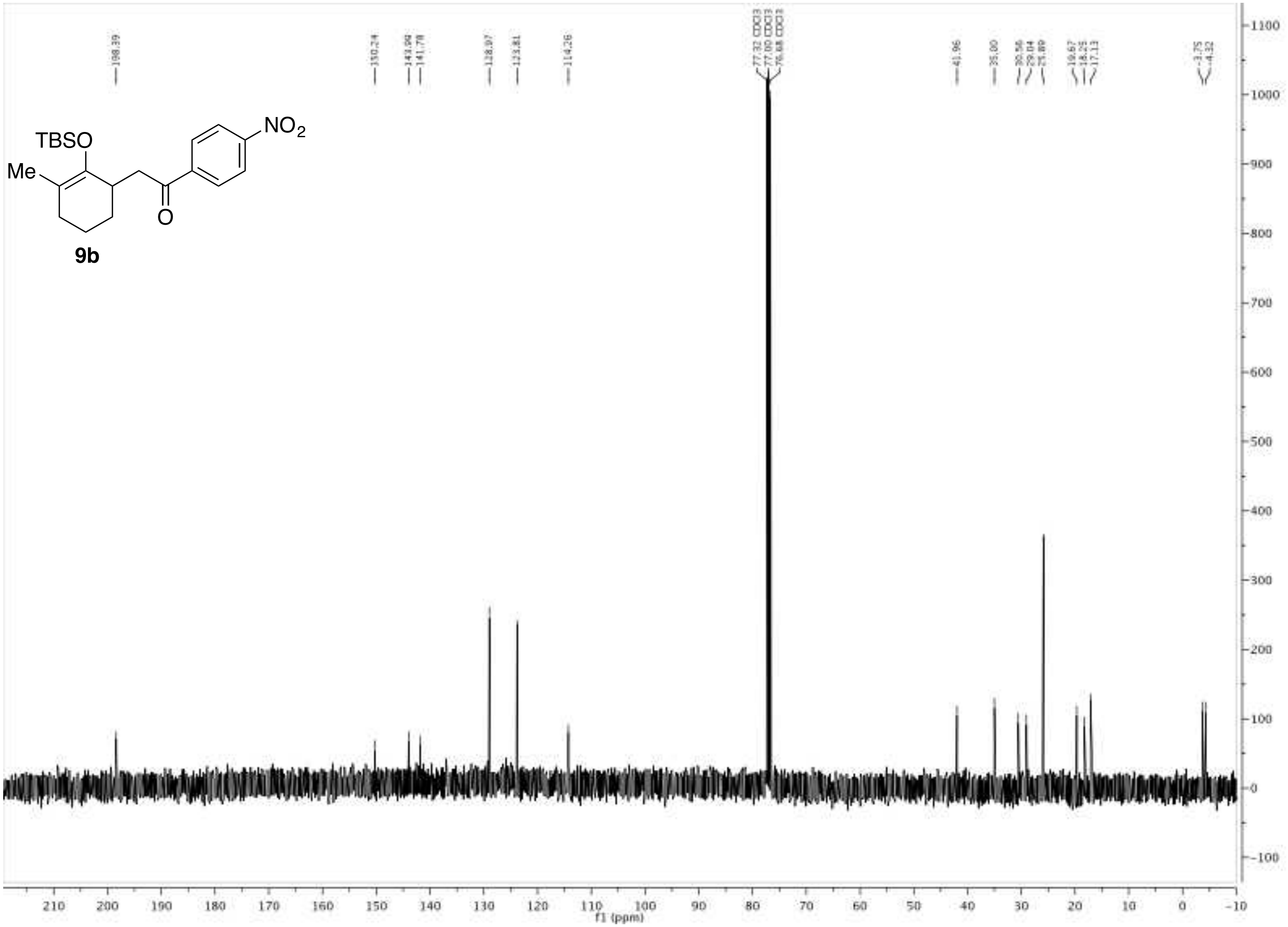
8


9a
OTBS
Me
Ph
O
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
2.02
1.00
2.02
1.06
1.03
1.03
2.19
1.07
3.22
2.17
1.16
9.05
3.13
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

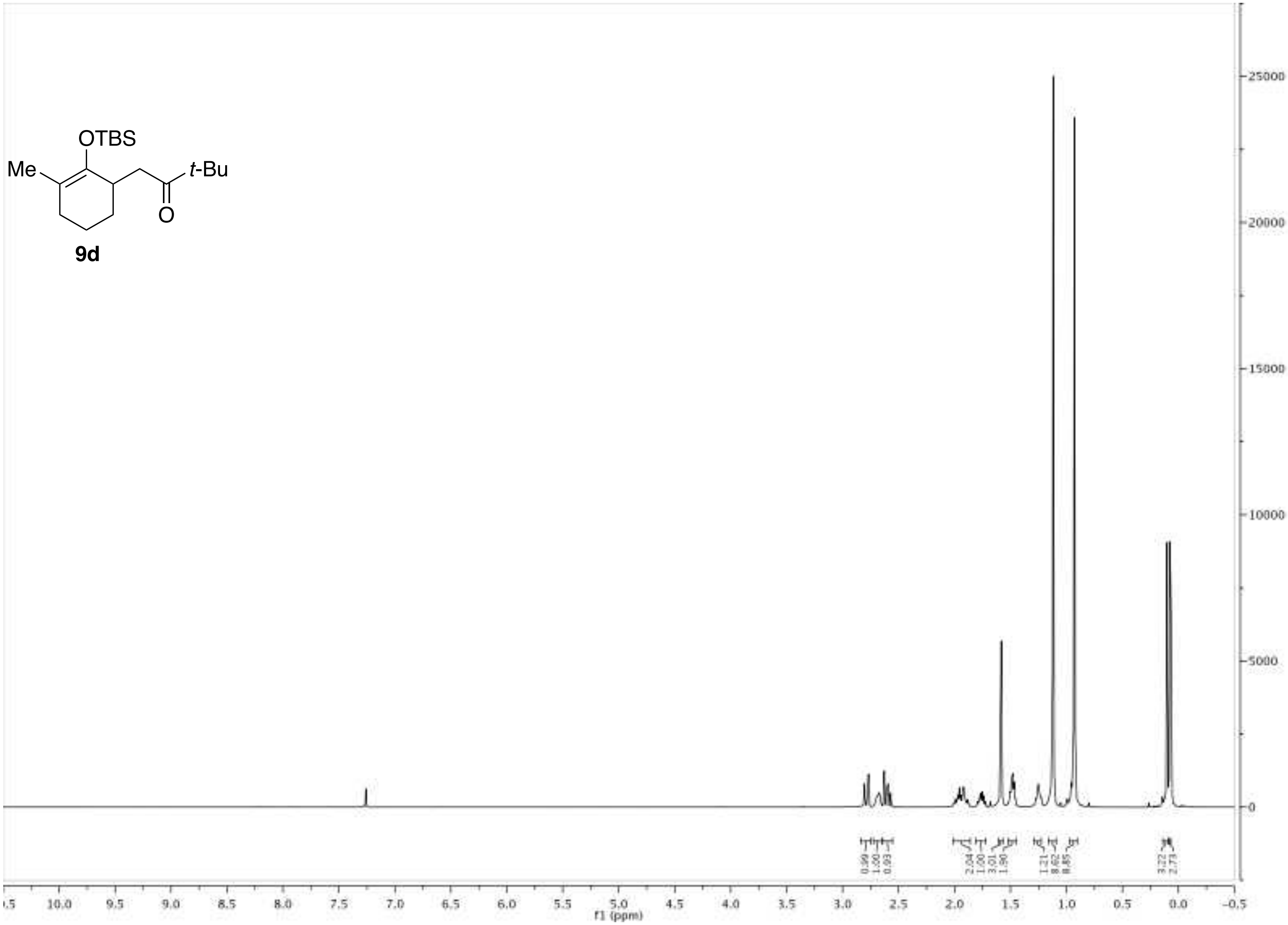

OTBS
Me
Ph
O
9a
199.82
144.60
137.50
132.87
128.51
127.96
113.75
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.14
34.88
30.67
28.98
25.92
19.67
18.27
17.12
-3.73
-4.33
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

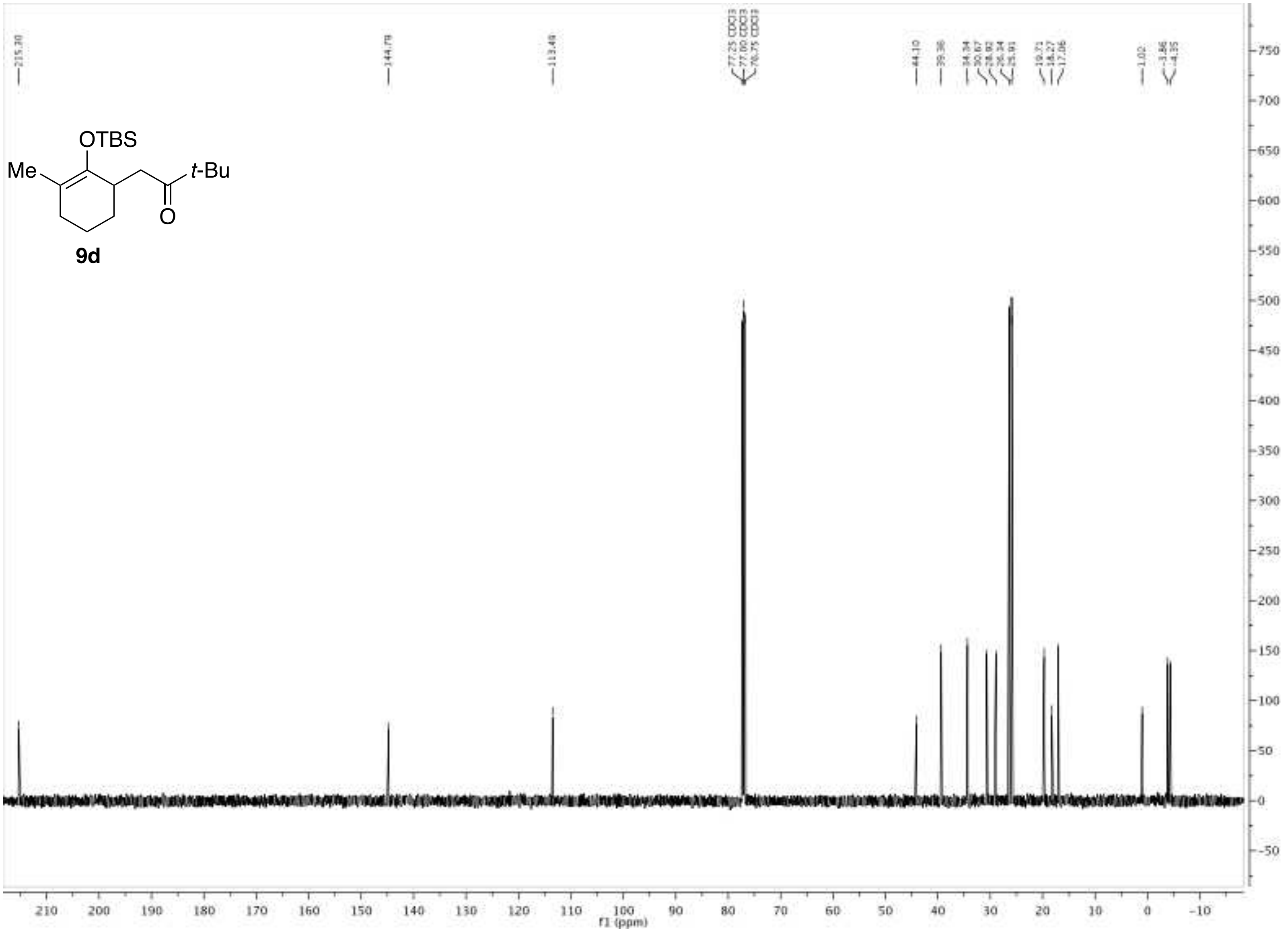

9b

TBSO
Me
O
NO2
2.07
2.12
1.00
1.01
1.00
3.17
3.07
2.86
9.27
3.08
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000



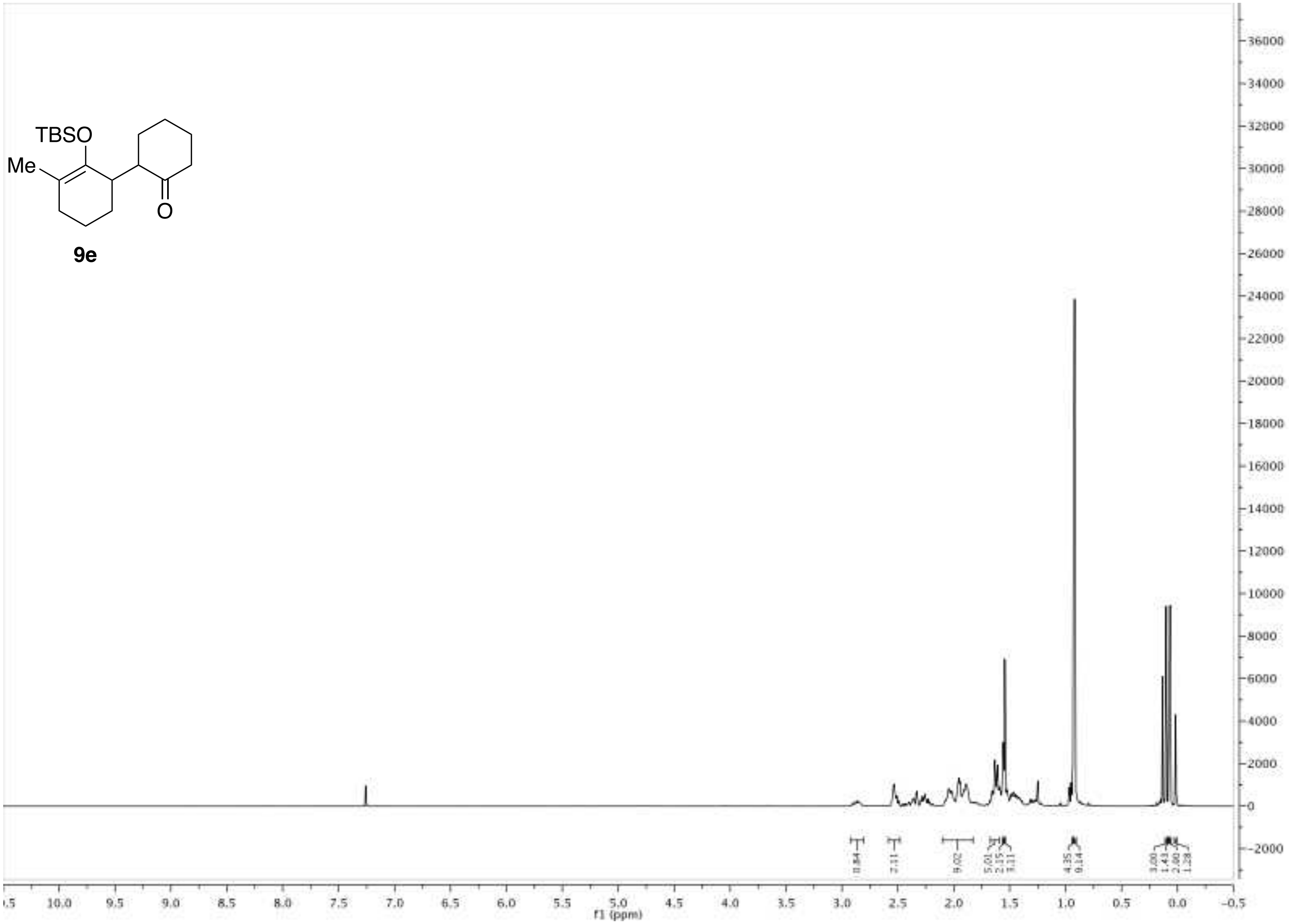
198.39
150.24
143.99
141.78
128.97
123.81
114.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
41.96
35.00
30.56
29.04
25.89
19.67
18.25
17.13
-3.75
-4.32
TBSO
Me
NO2
O
9b
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
Me
t-Bu
O
9d
0.99
1.00
0.93
2.04
1.00
3.01
1.90
1.21
8.62
8.85
3.22
2.73
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

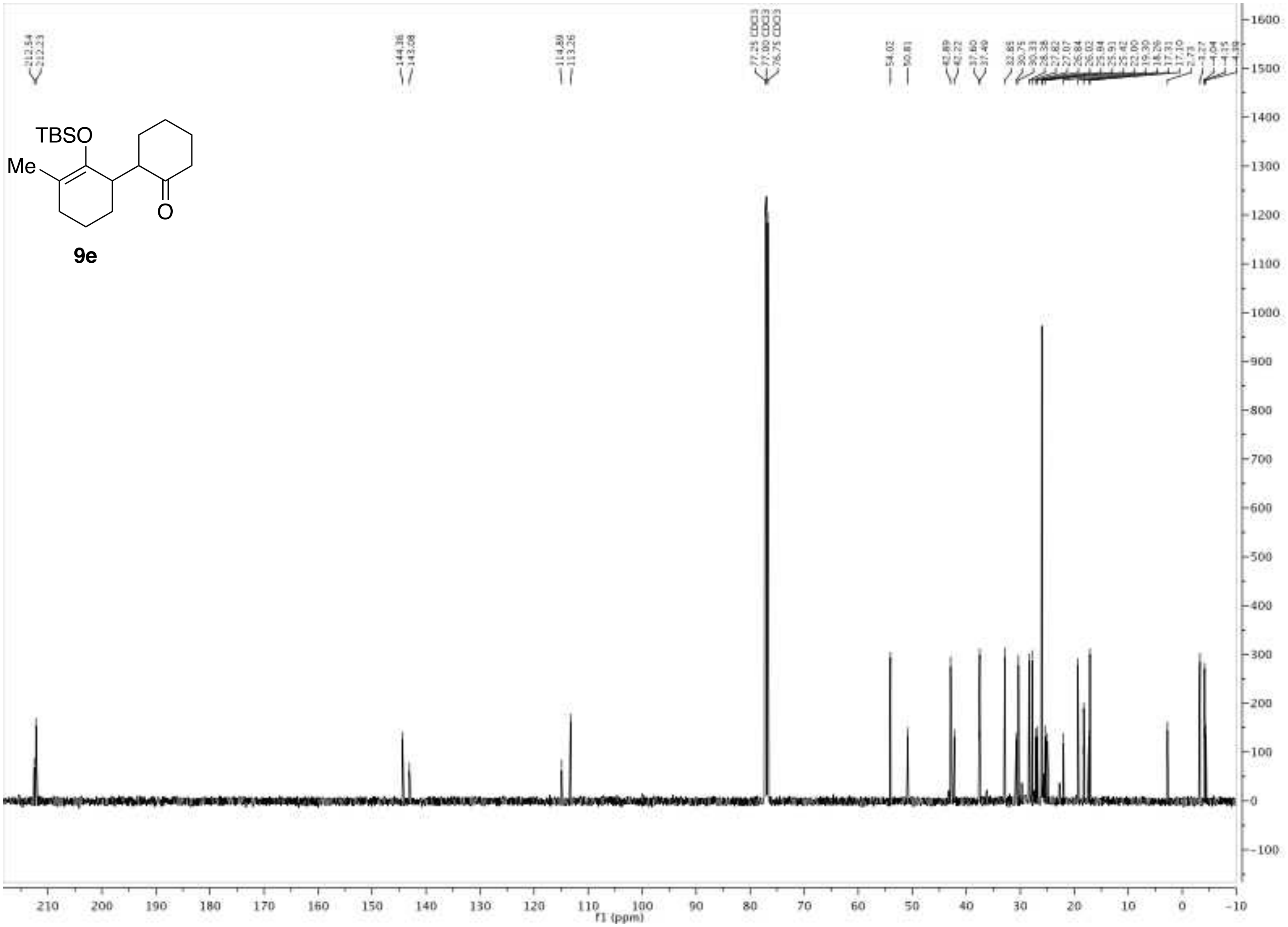


9d

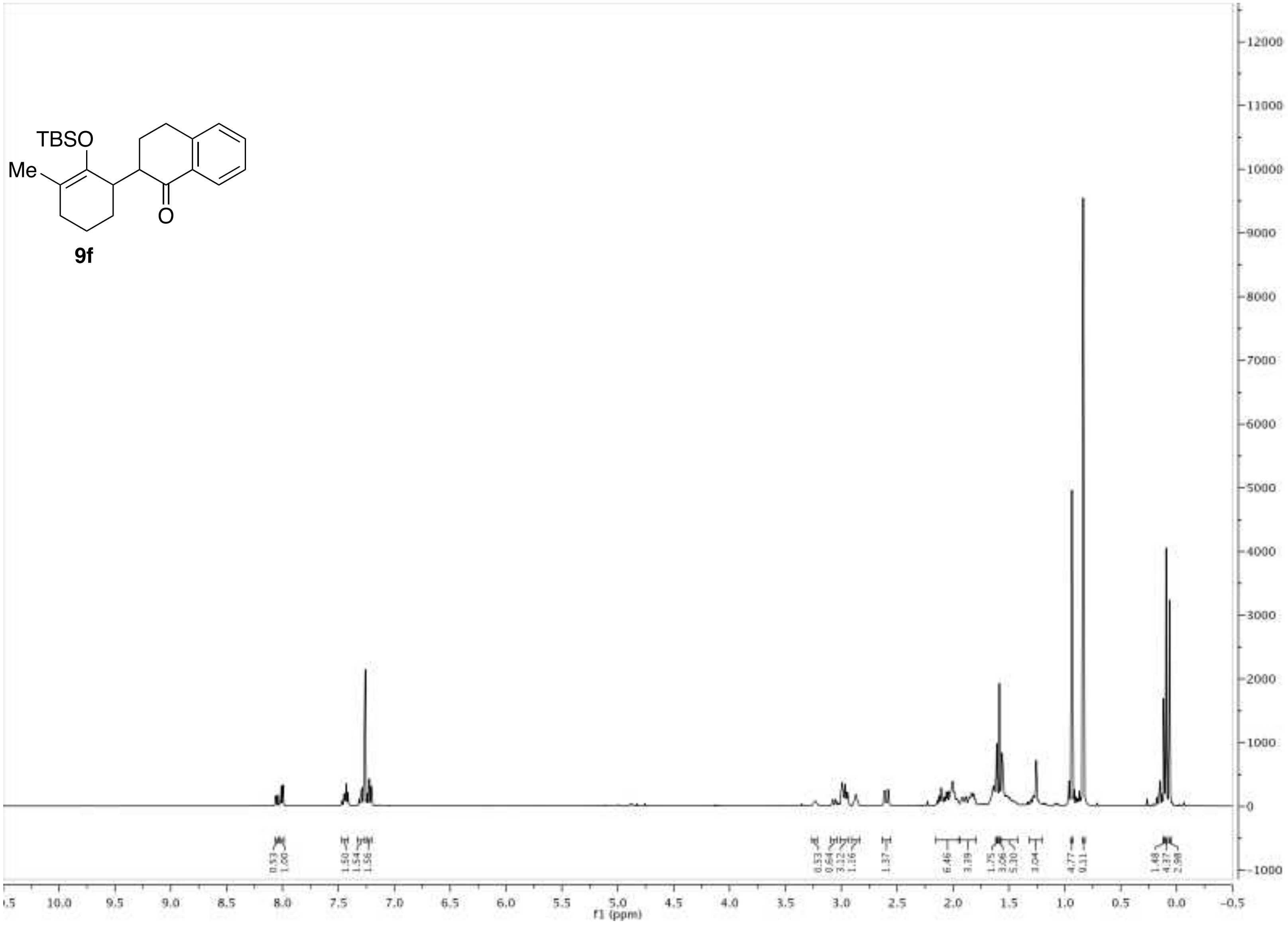
215.30
144.79
113.49
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
44.10
39.36
34.34
30.67
28.92
26.34
25.91
19.71
18.27
17.06
1.02
-3.86
-4.35
OTBS
Me
t-Bu
O
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

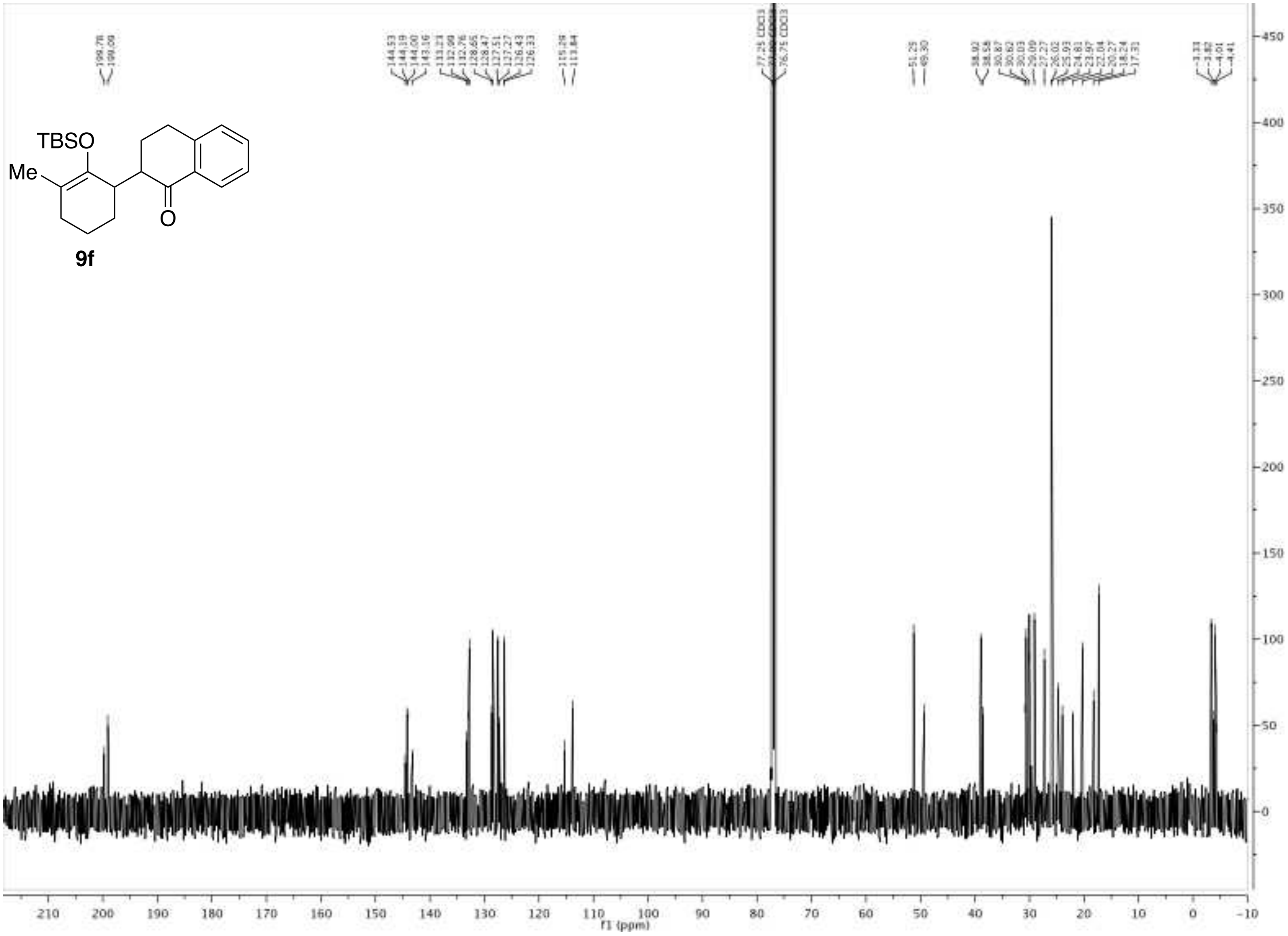

TBSO
Me
O
0.84
2.11
9.02
5.01
2.15
3.11
4.35
9.14
3.00
1.43
2.00
1.28
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

9e

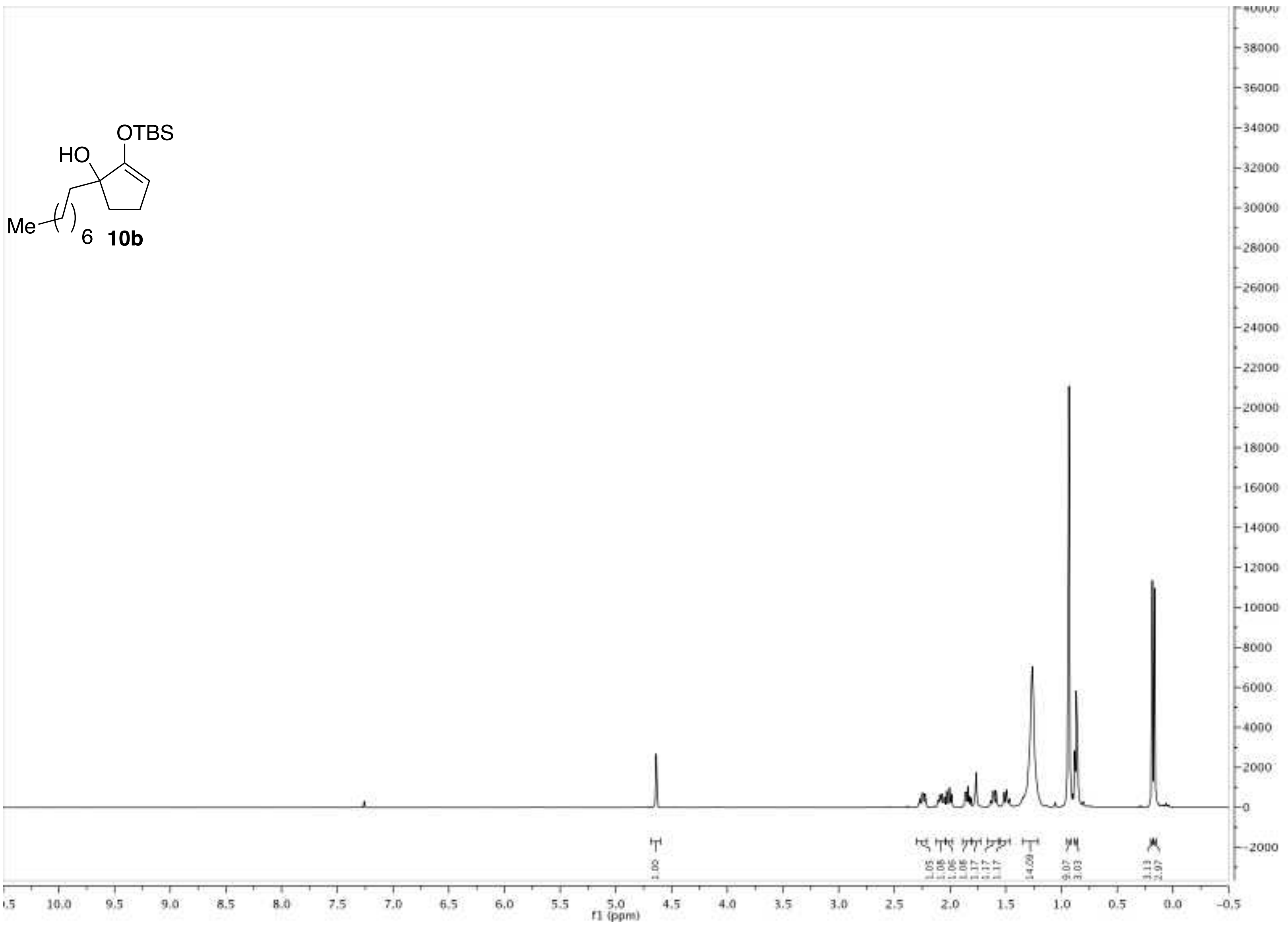

212.54
212.23
144.36
143.08
114.89
113.26
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
54.02
50.81
42.89
42.22
37.60
37.49
32.85
30.75
30.33
28.38
27.82
27.07
26.84
26.02
25.94
25.91
25.42
22.00
19.30
18.26
17.31
17.10
2.73
-3.27
-4.04
-4.15
39
TBSO
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

9e

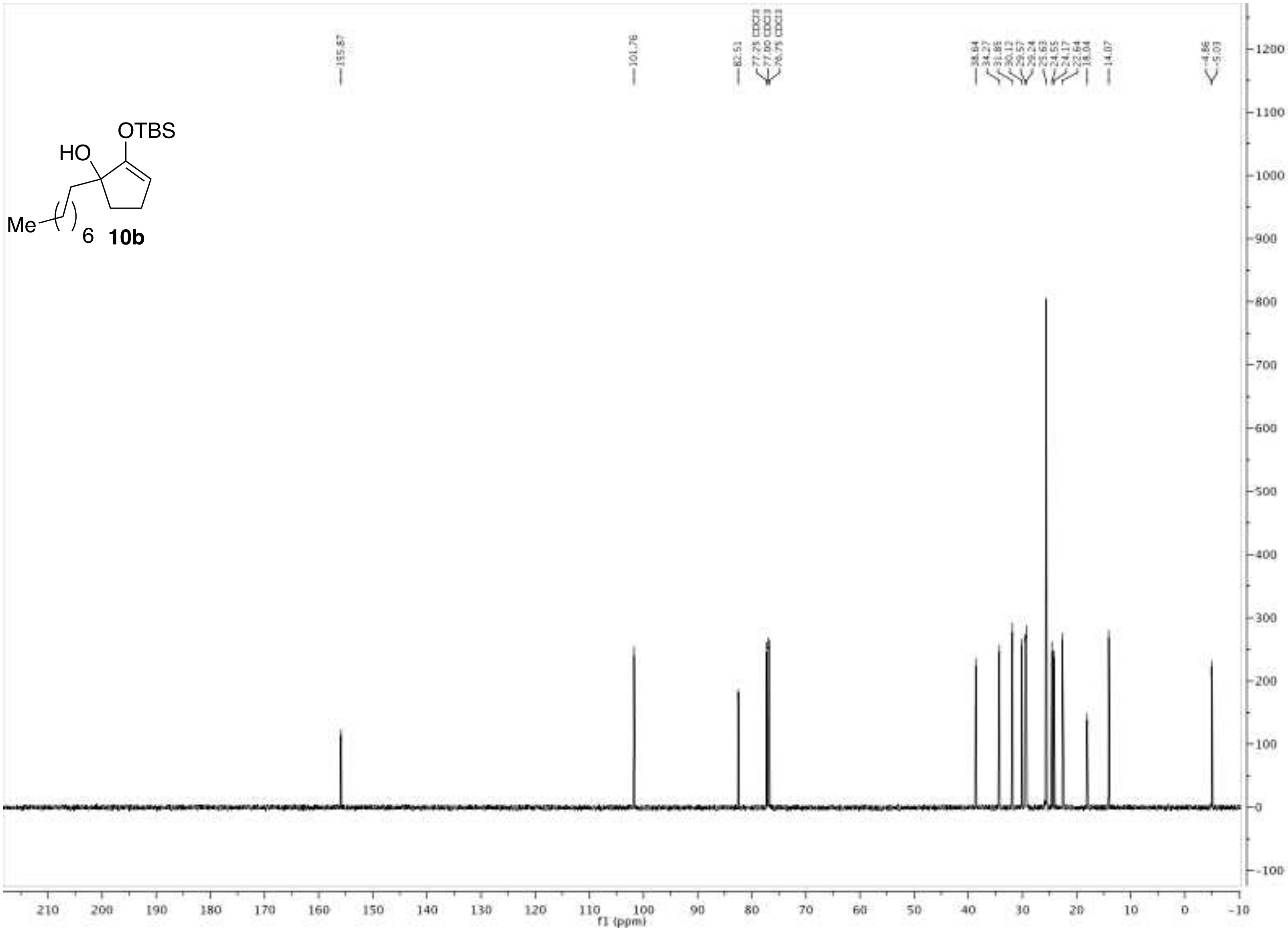

TBSO
Me
O
9f
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.53
1.00
1.50
1.54
1.56
0.53
0.64
3.12
1.16
1.37
6.46
3.39
1.75
3.06
5.30
3.04
4.77
9.11
1.48
4.37
2.98
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

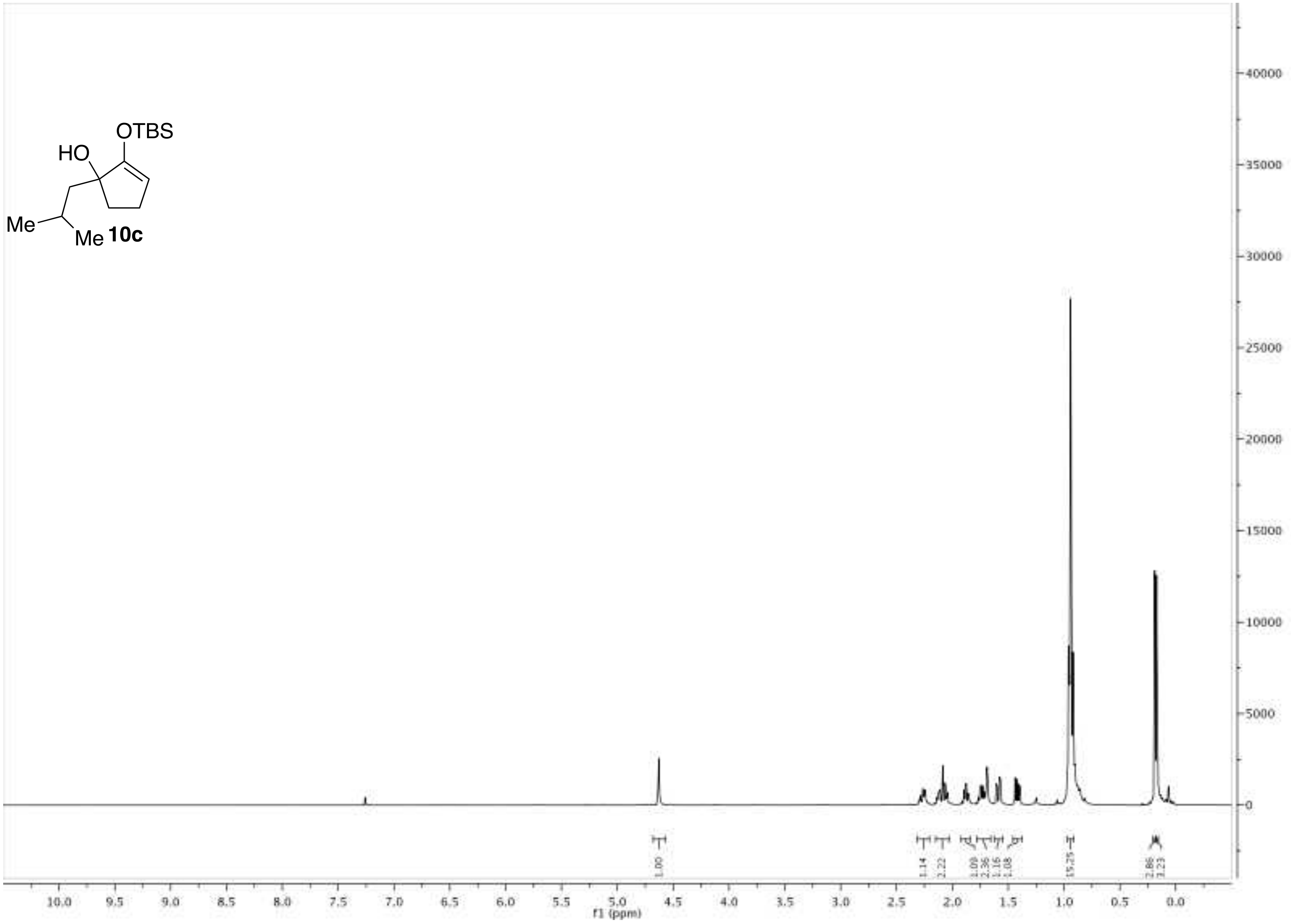

TBSO
Me
O
199.78
199.09
144.53
144.19
144.00
143.16
133.23
132.99
132.76
128.65
128.47
127.51
127.27
126.43
126.33
115.29
113.84
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
51.25
49.30
38.92
38.58
30.87
30.62
30.03
29.09
27.27
26.02
25.93
24.81
23.97
22.04
20.27
18.24
17.31
-3.33
-3.82
-4.01
-4.41
450
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

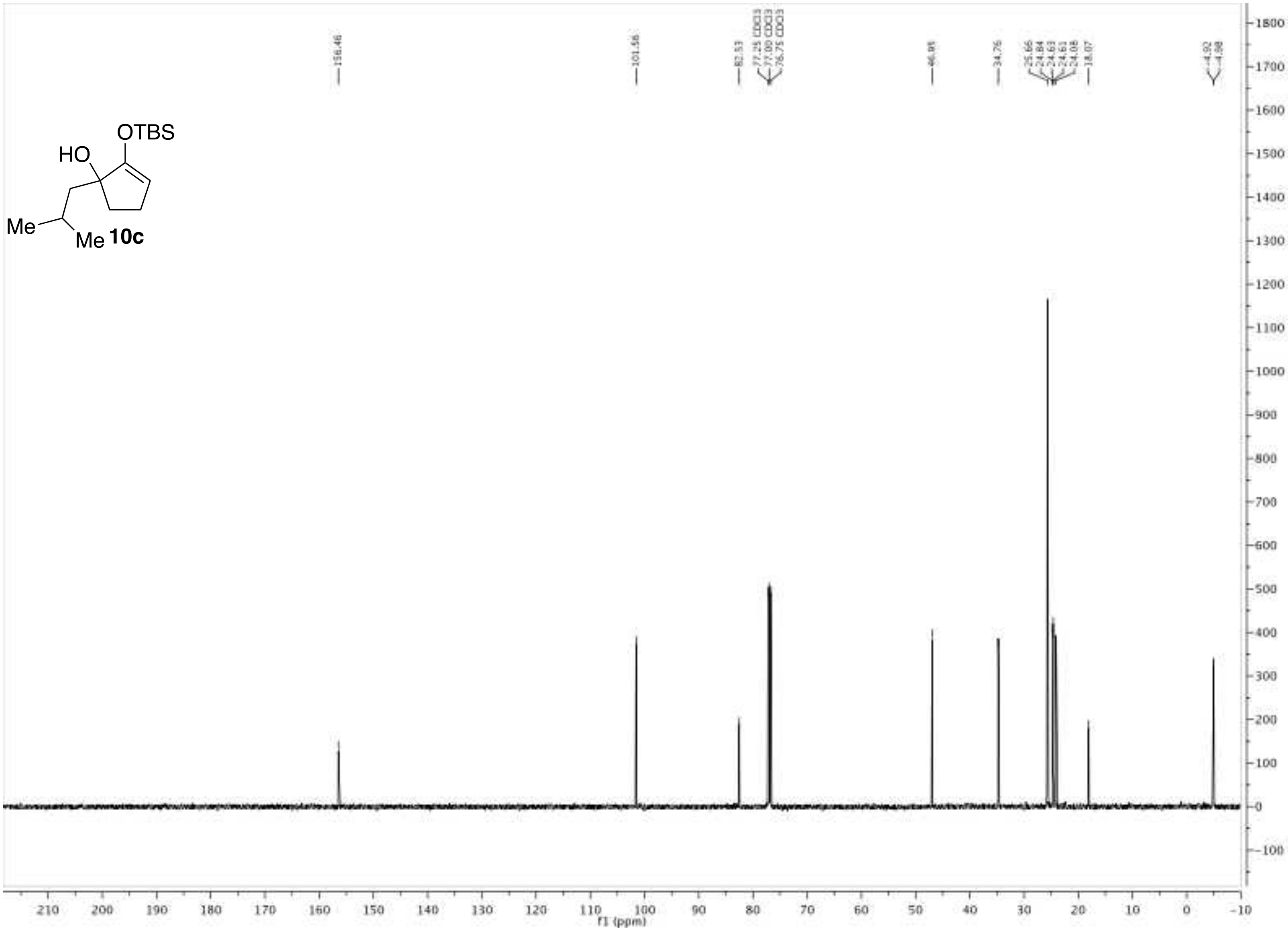
9f



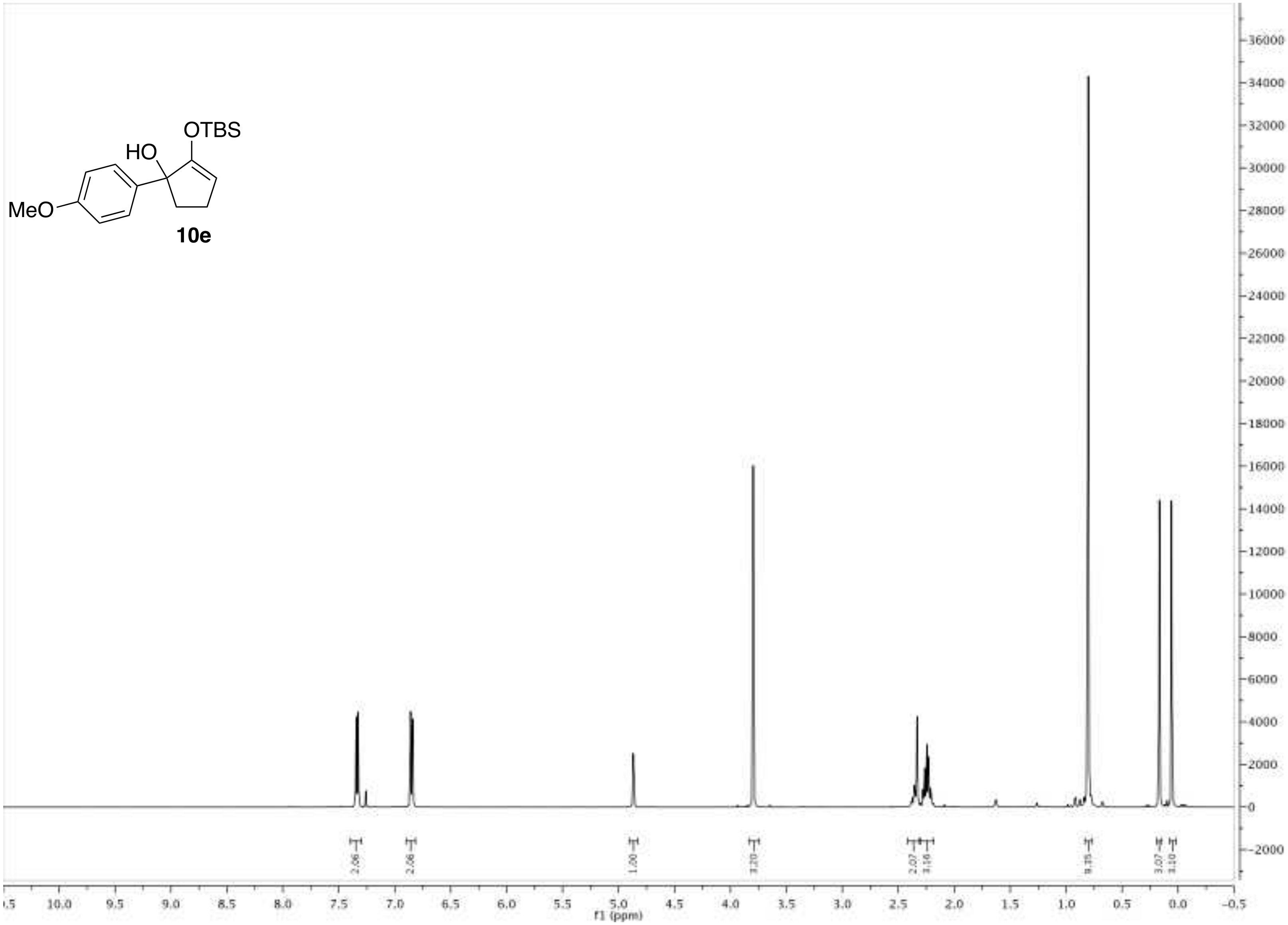
OTBS
HO
Me
6
10b
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
1.05
1.08
1.06
1.08
1.17
1.17
1.17
14.09
9.07
3.03
3.13
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

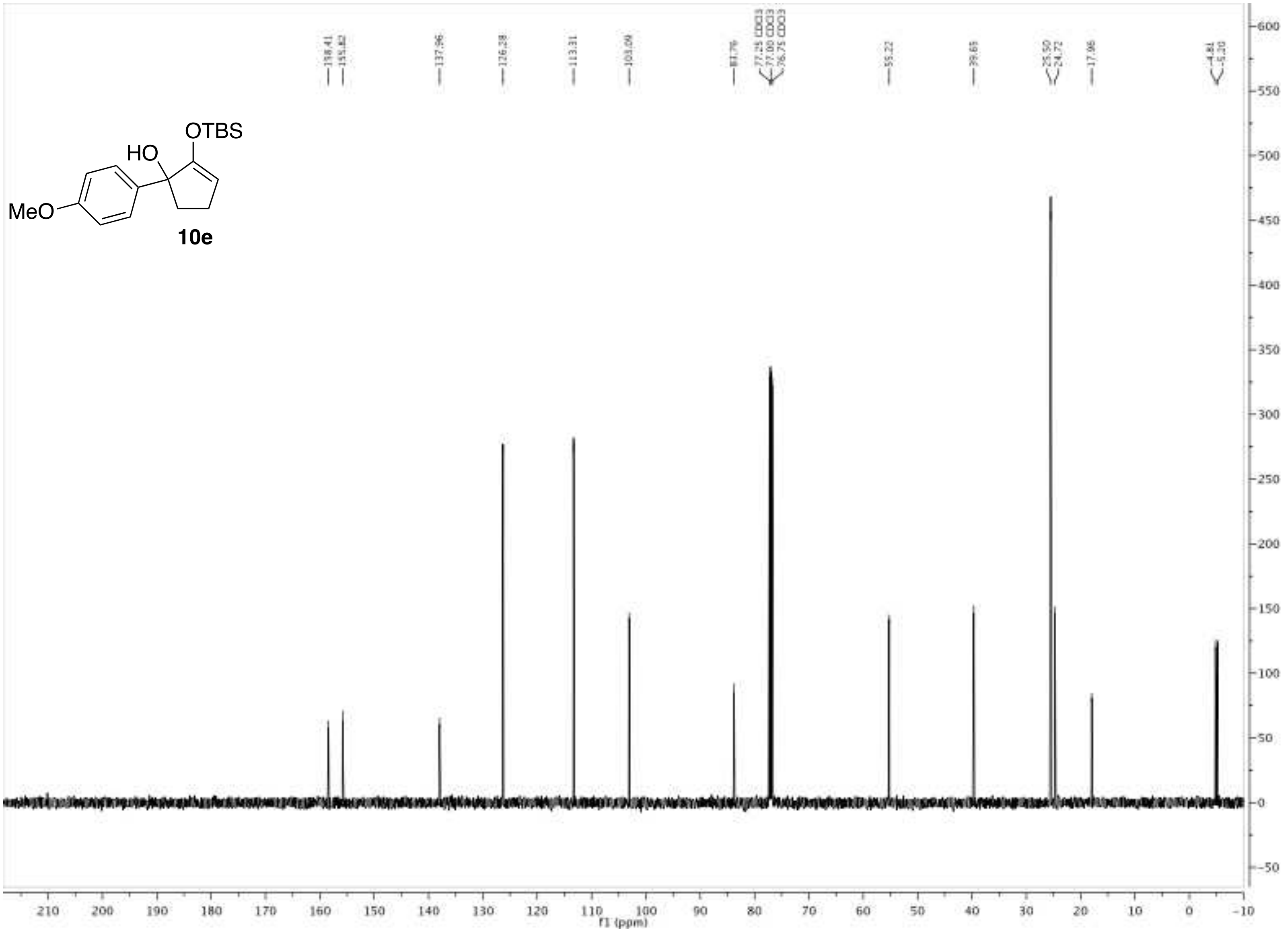

OTBS
HO
Me
6
10b
155.87
101.76
82.51
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
38.64
34.27
31.85
30.12
29.57
29.24
25.63
24.55
24.17
22.64
18.04
14.07
-4.86
-5.03
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

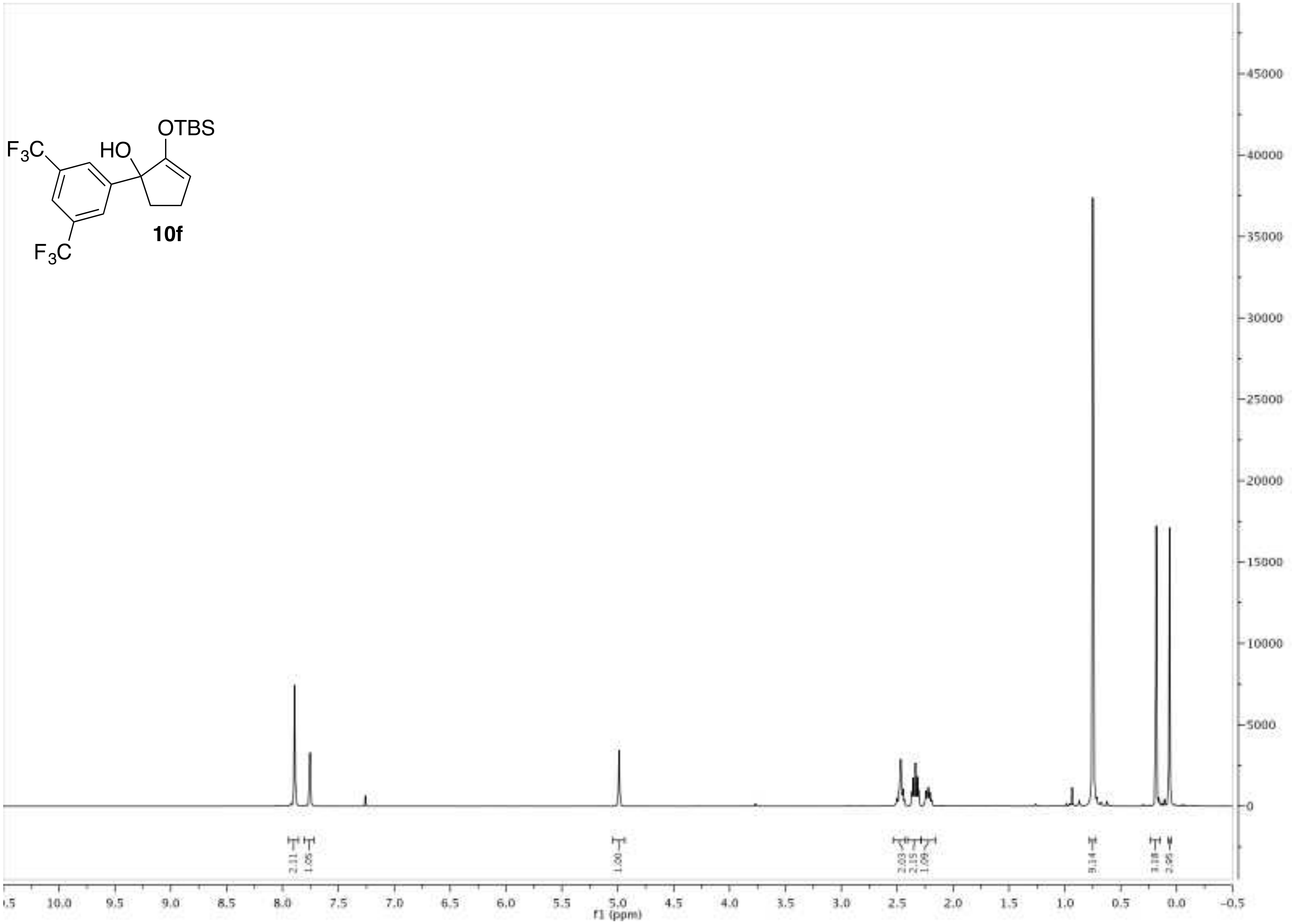

OTBS
HO
Me
Me
10c
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.14
2.22
1.09
2.36
1.16
1.08
15.25
2.86
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

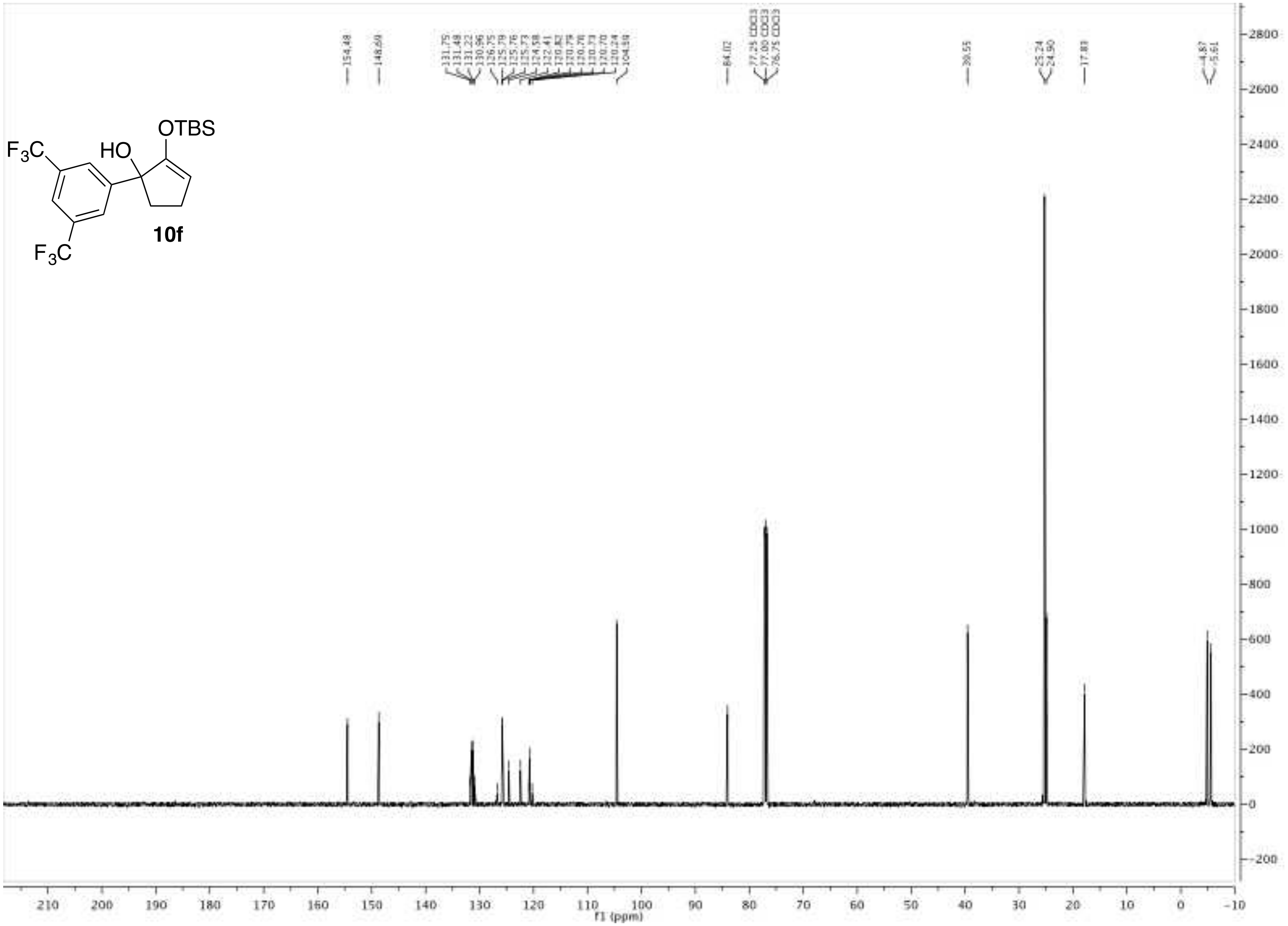


OTBS
HO
Me
Me
10c
156.46
101.56
82.53
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
46.96
34.76
25.66
24.84
24.63
24.61
24.08
18.07
-4.92
-4.98
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
HO
MeO
10e
2.06
2.08
1.00
3.20
2.07
3.16
9.35
3.07
3.10
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

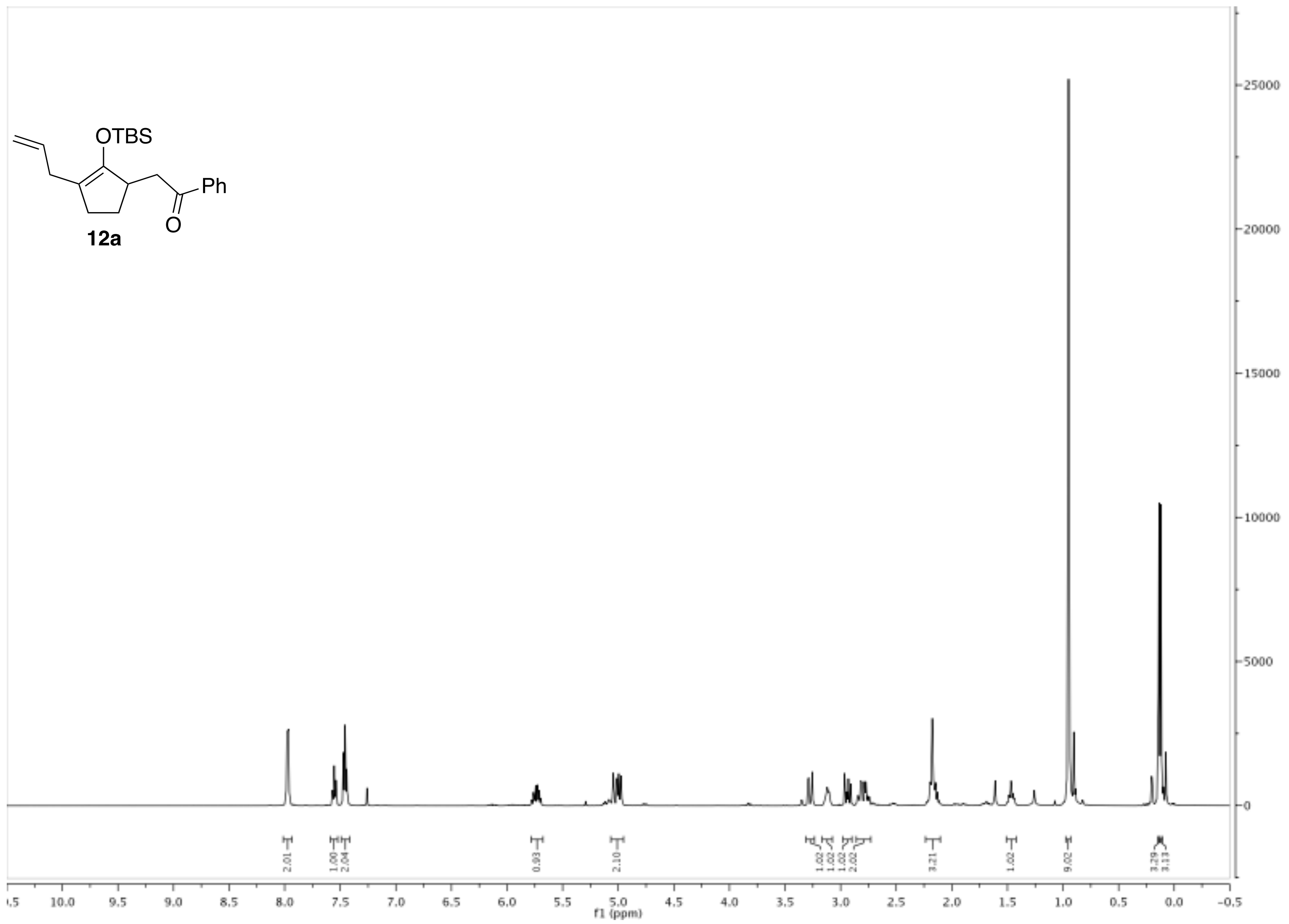

158.41
155.82
137.96
126.28
113.31
103.09
83.76
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.22
39.65
25.50
24.72
17.96
-4.81
-5.20
OTBS
HO
MeO
10e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

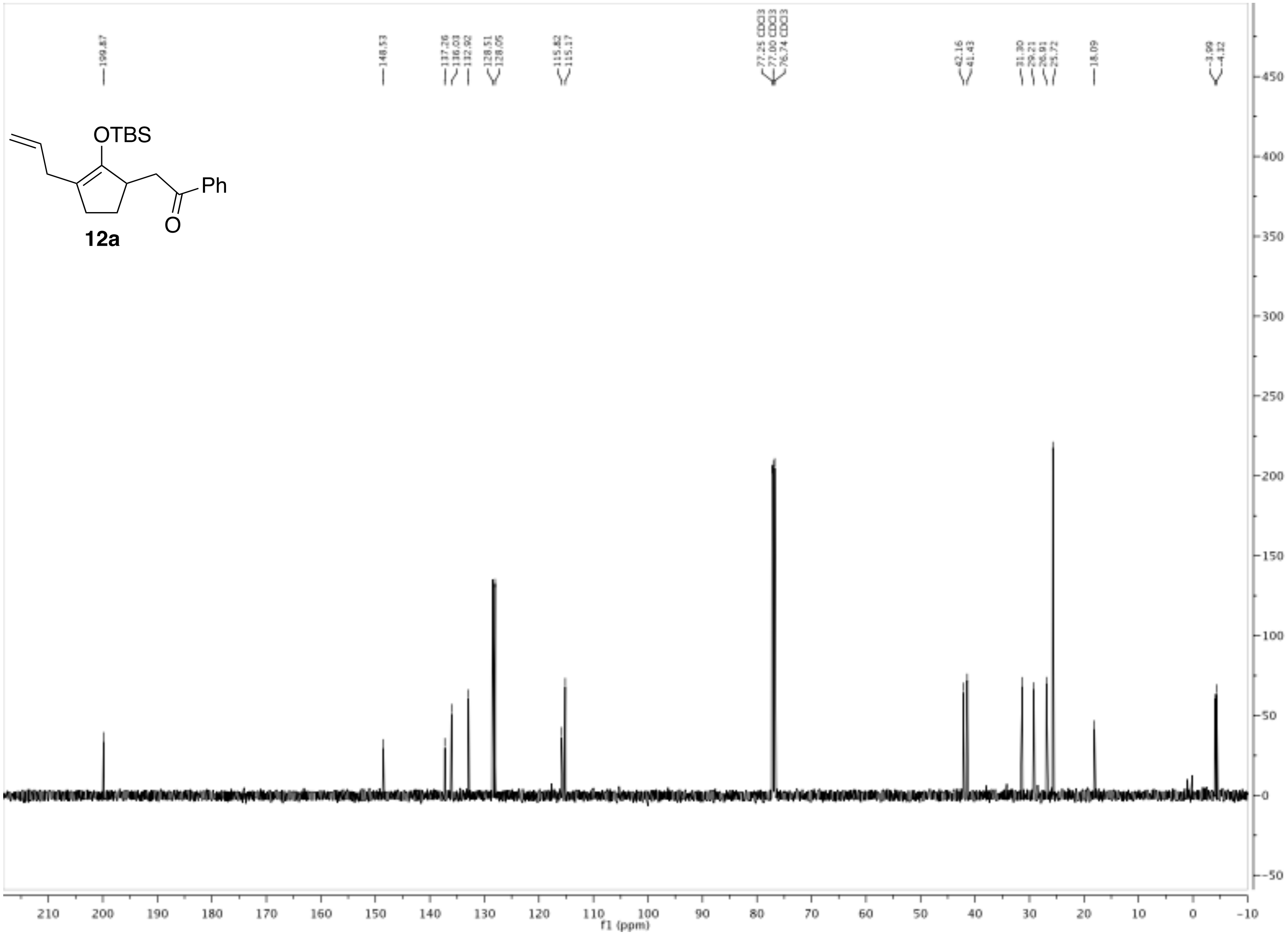

OTBS
HO
F_3C
F_3C
10f
2.11
1.05
1.00
2.03
2.15
1.09
9.14
3.18
2.95
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



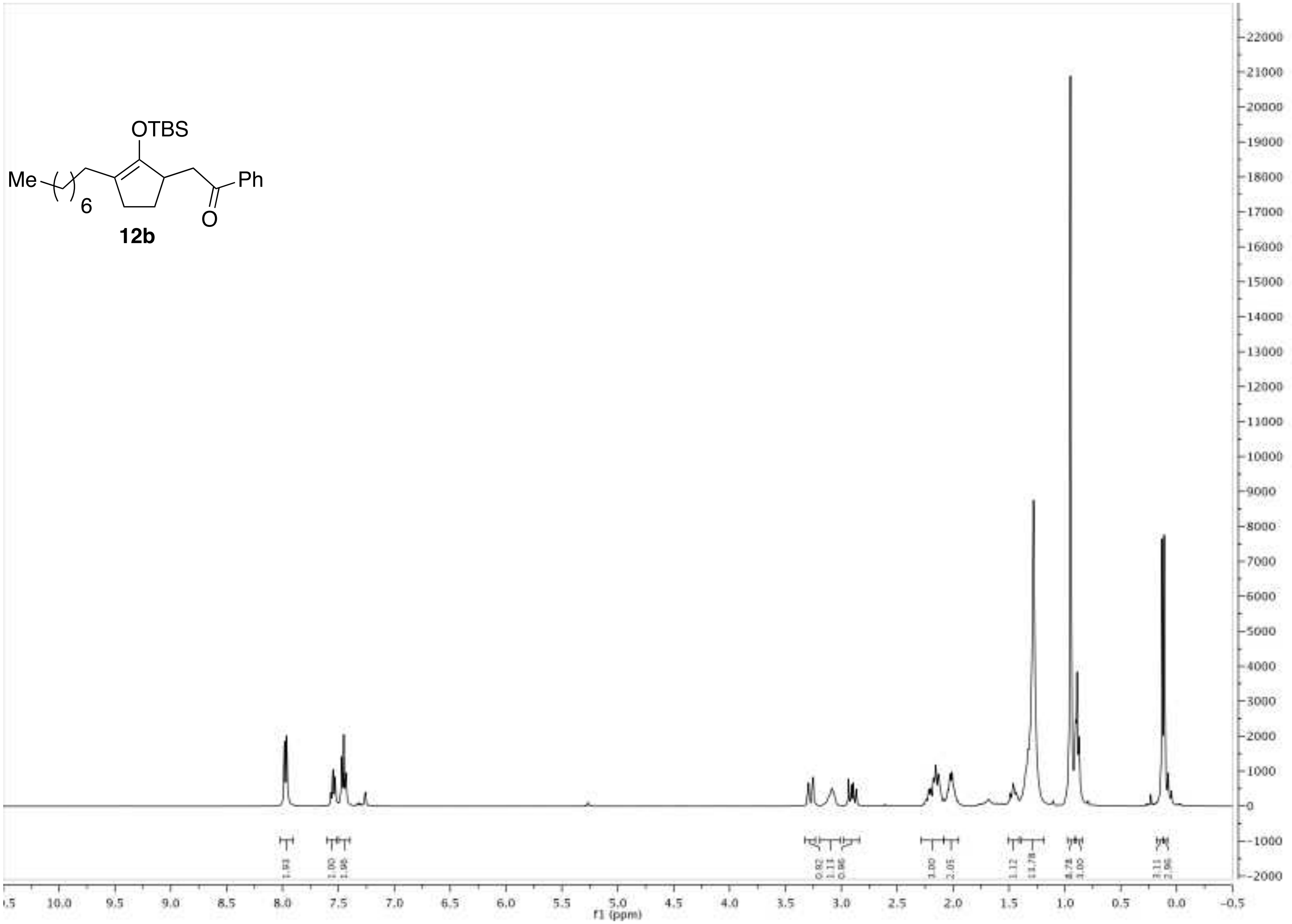
OTBS
HO
F3C
F3C
154.48
148.60
131.75
131.48
131.22
130.96
126.75
125.79
125.76
125.73
124.58
122.41
120.82
120.79
120.76
120.73
120.70
120.24
104.59
84.02
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
39.55
25.24
24.90
17.83
-4.87
-5.61
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10f


OTBS
Ph
O
12a
2.01
1.00
2.04
0.93
2.10
1.02
1.02
1.02
2.02
3.21
1.02
9.02
3.29
3.13
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

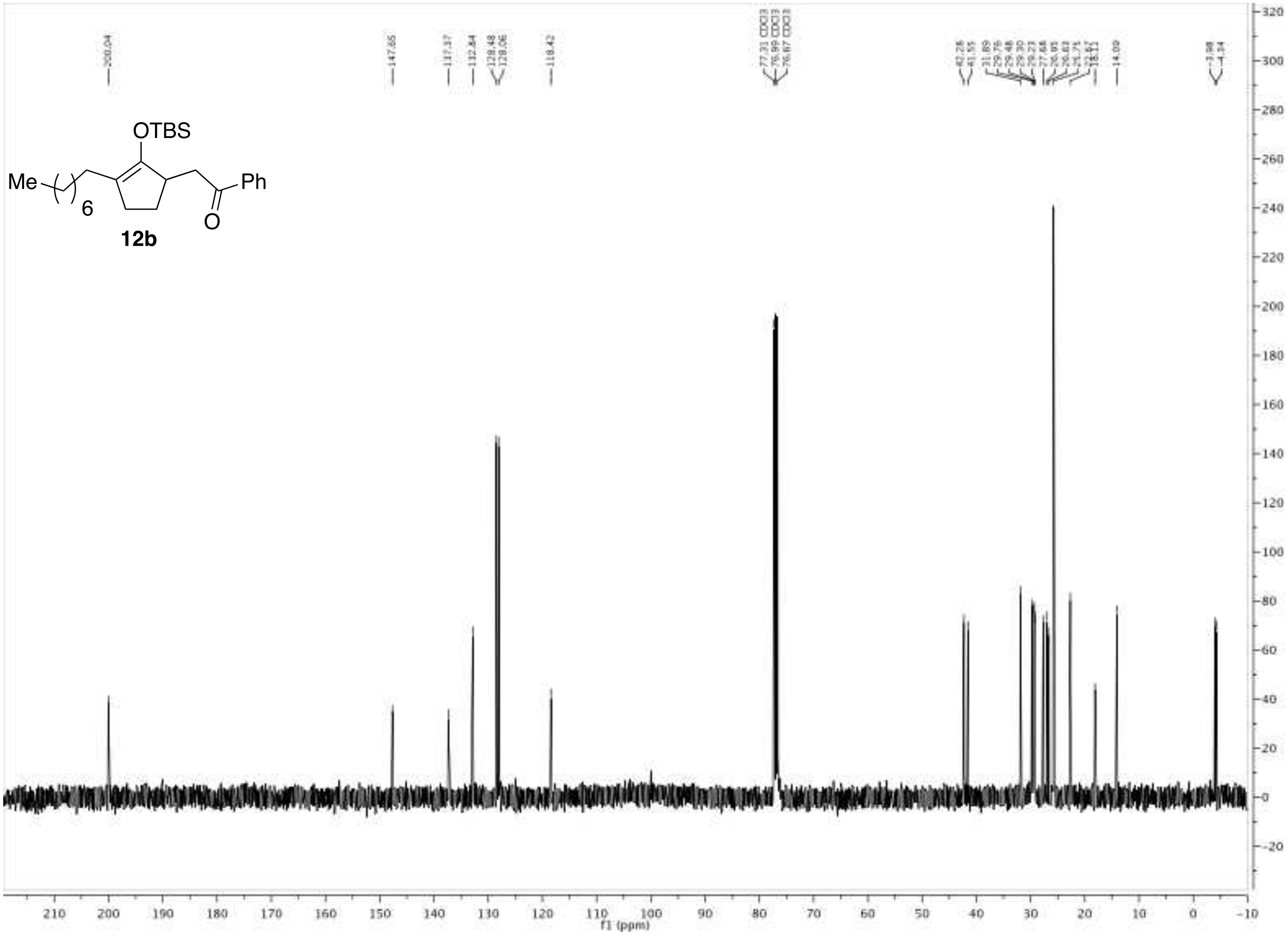


OTBS
Ph
O
12a
199.87
148.53
137.26
136.03
132.92
128.51
128.05
115.82
115.17
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
42.16
41.43
31.30
29.21
26.91
25.72
18.09
-3.99
-4.32
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



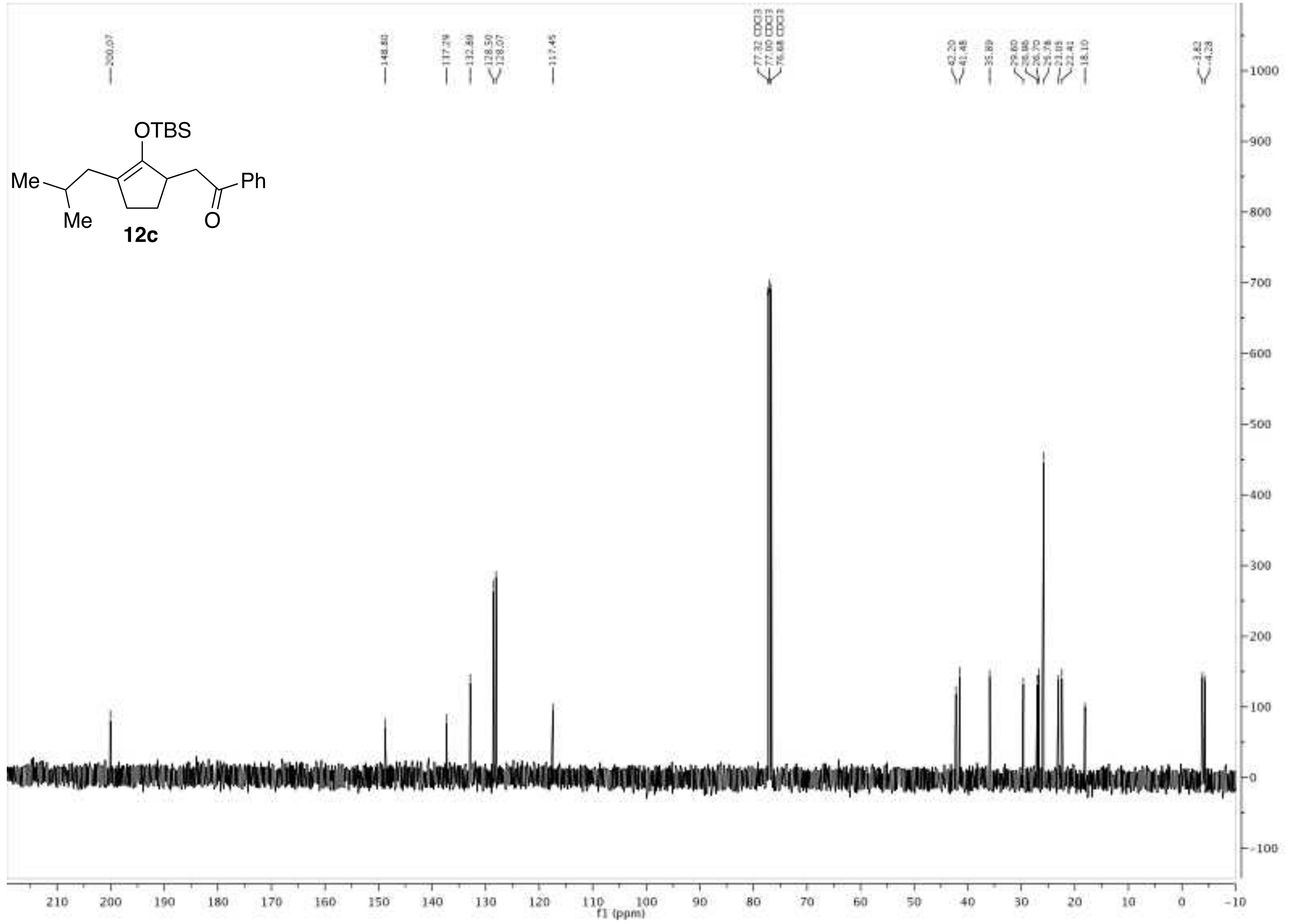
OTBS
Me
6
O
Ph
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
1.93
1.00
1.96
0.92
1.13
0.96
3.00
2.05
1.12
13.78
8.78
3.00
3.11
2.96
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

12b

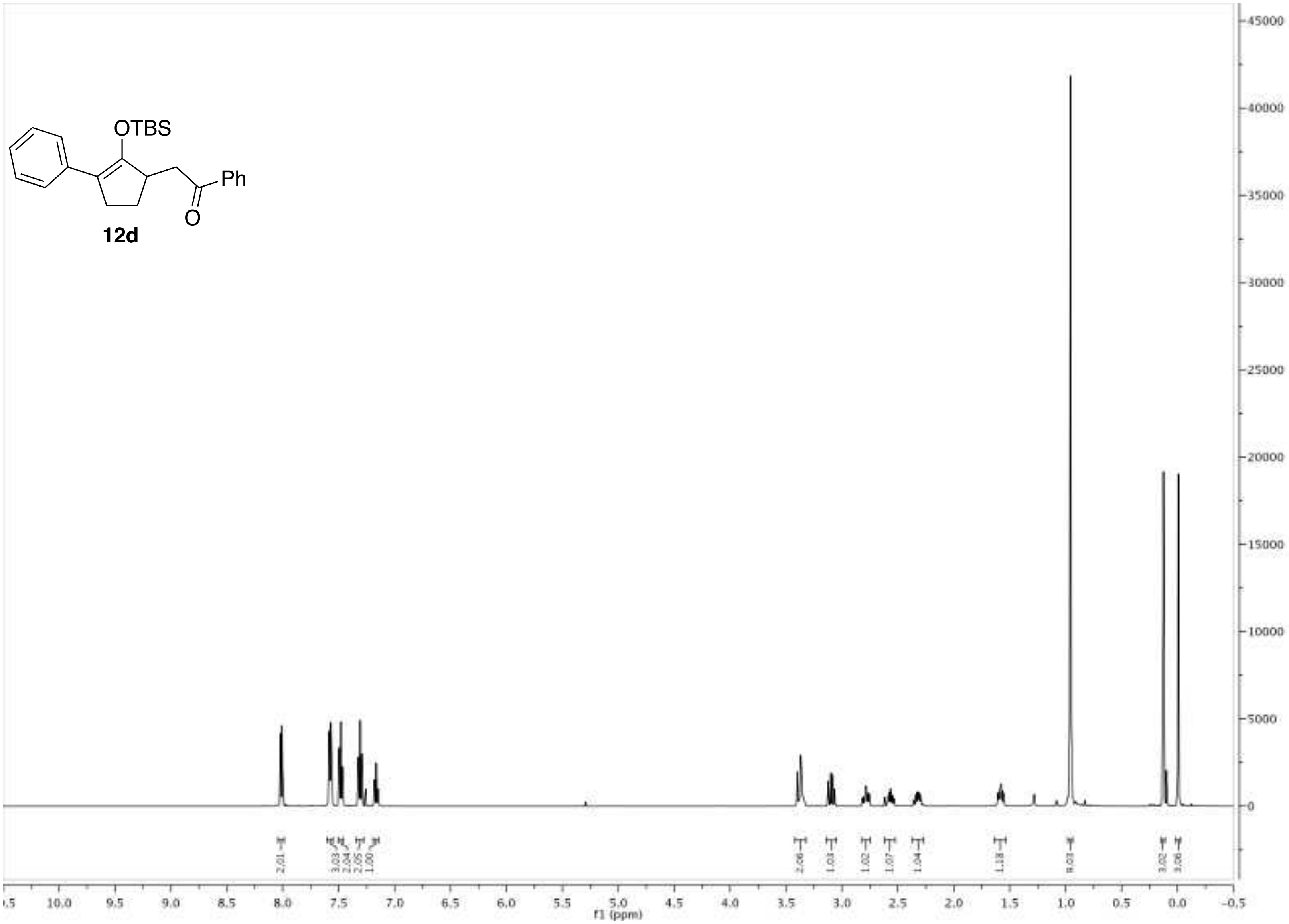

OTBS
Me
6
O
Ph
200.04
147.65
137.37
132.84
128.48
128.06
118.42
77.31 CDCl3
76.99 CDCl3
76.67 CDCl3
42.28
41.55
31.89
29.76
29.48
29.30
29.23
27.68
26.95
26.83
25.75
22.67
18.13
14.09
-3.98
-4.34
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

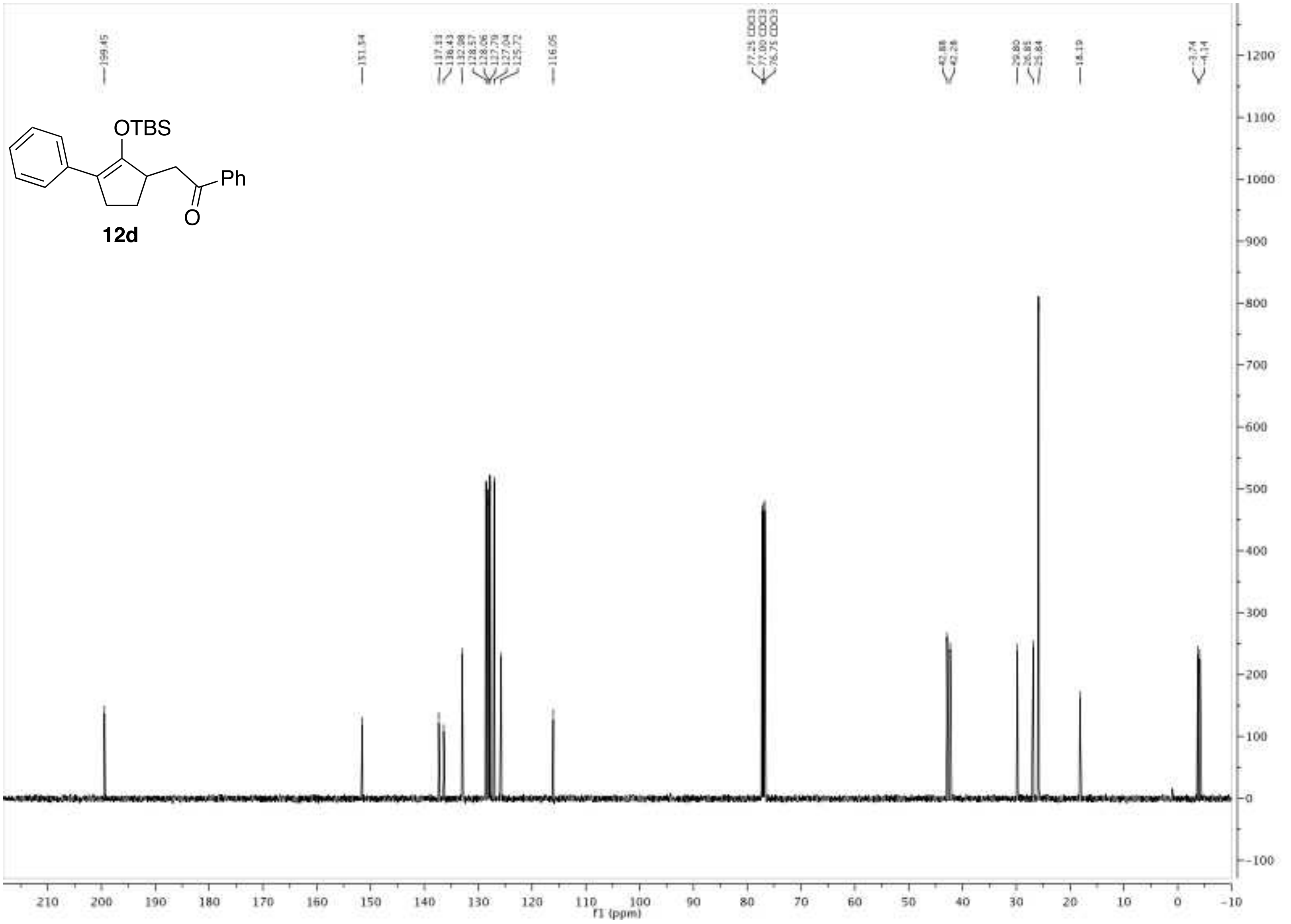
12b

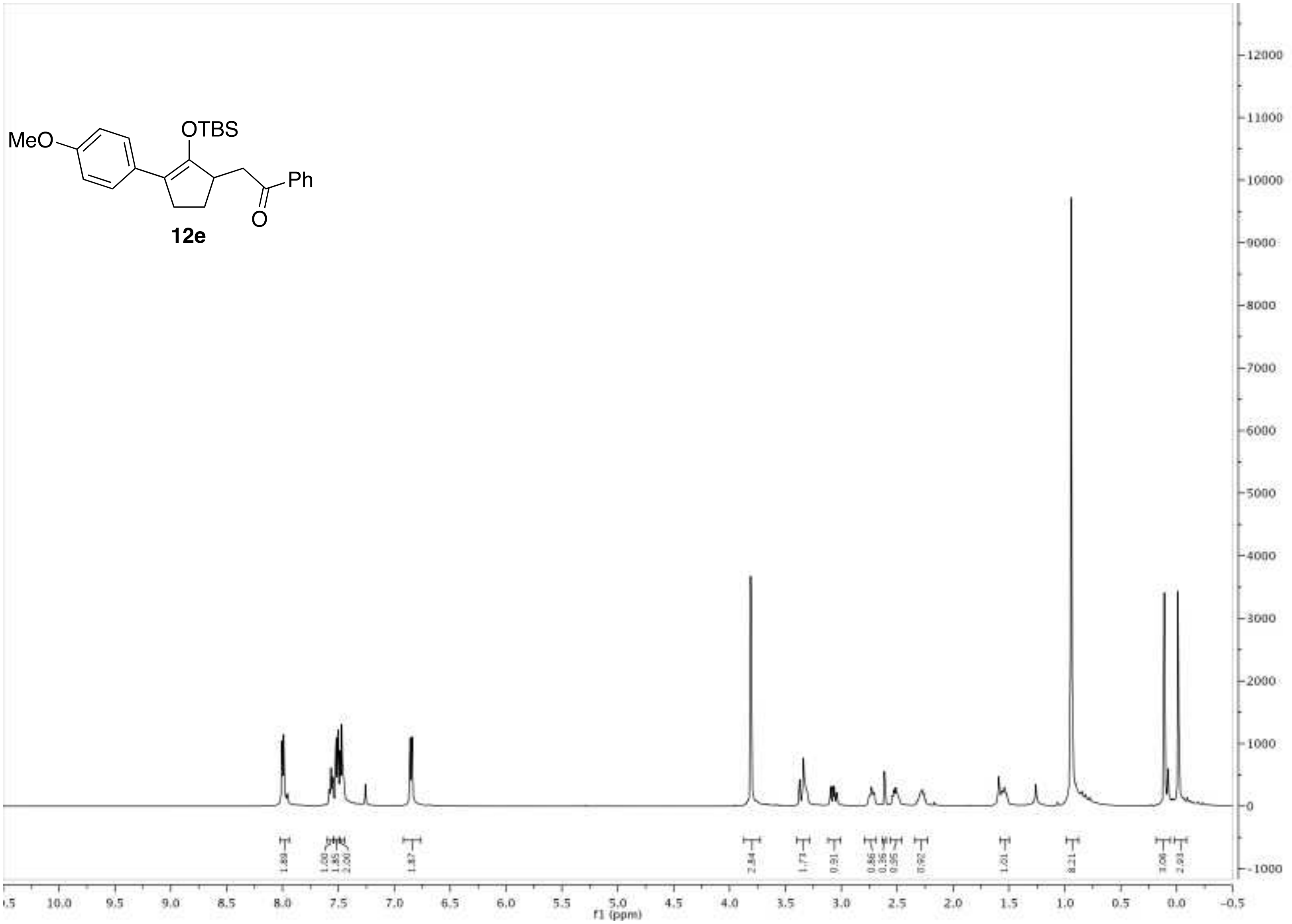

OTBS
Me
Me
Ph
O
12c
2.00
1.00
2.03
1.01
1.06
1.01
3.16
1.07
1.04
1.13
8.48
6.26
3.04
3.18
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

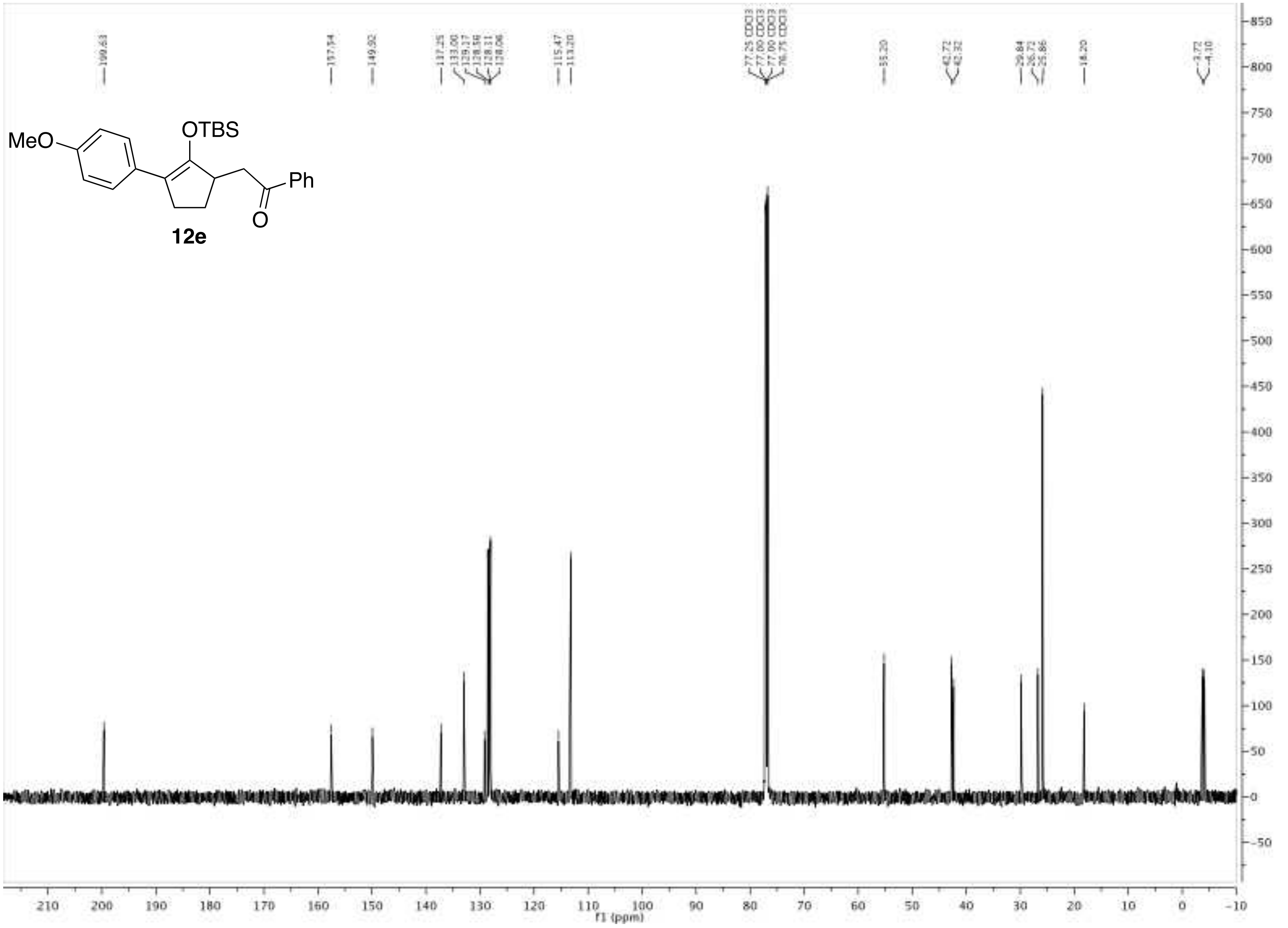

200.07
148.80
137.29
132.89
128.50
128.07
117.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
42.20
41.48
35.89
29.60
26.86
26.70
25.78
23.05
22.41
18.10
-3.82
-4.28
OTBS
Me
Me
Ph
O
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

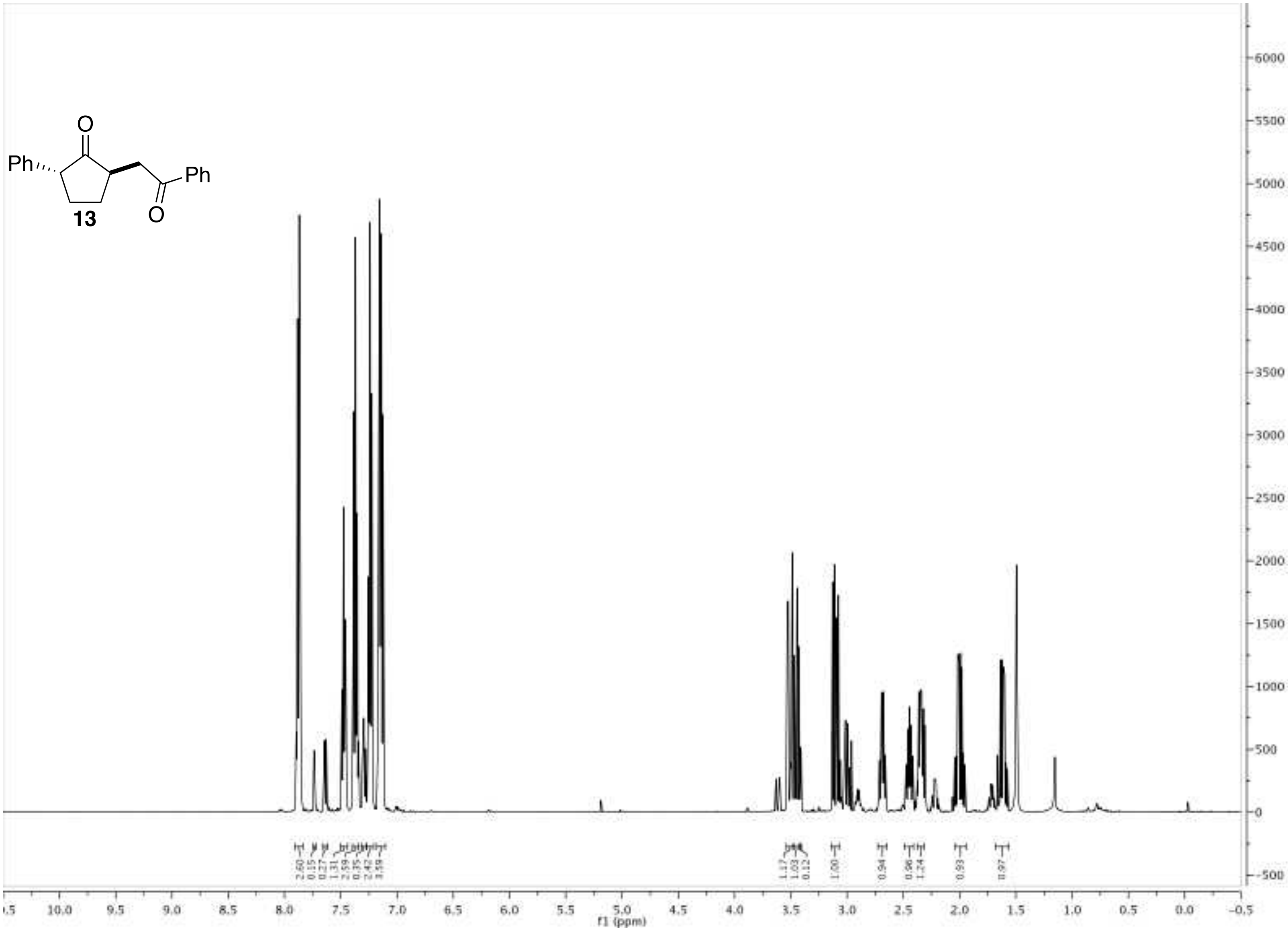
12c

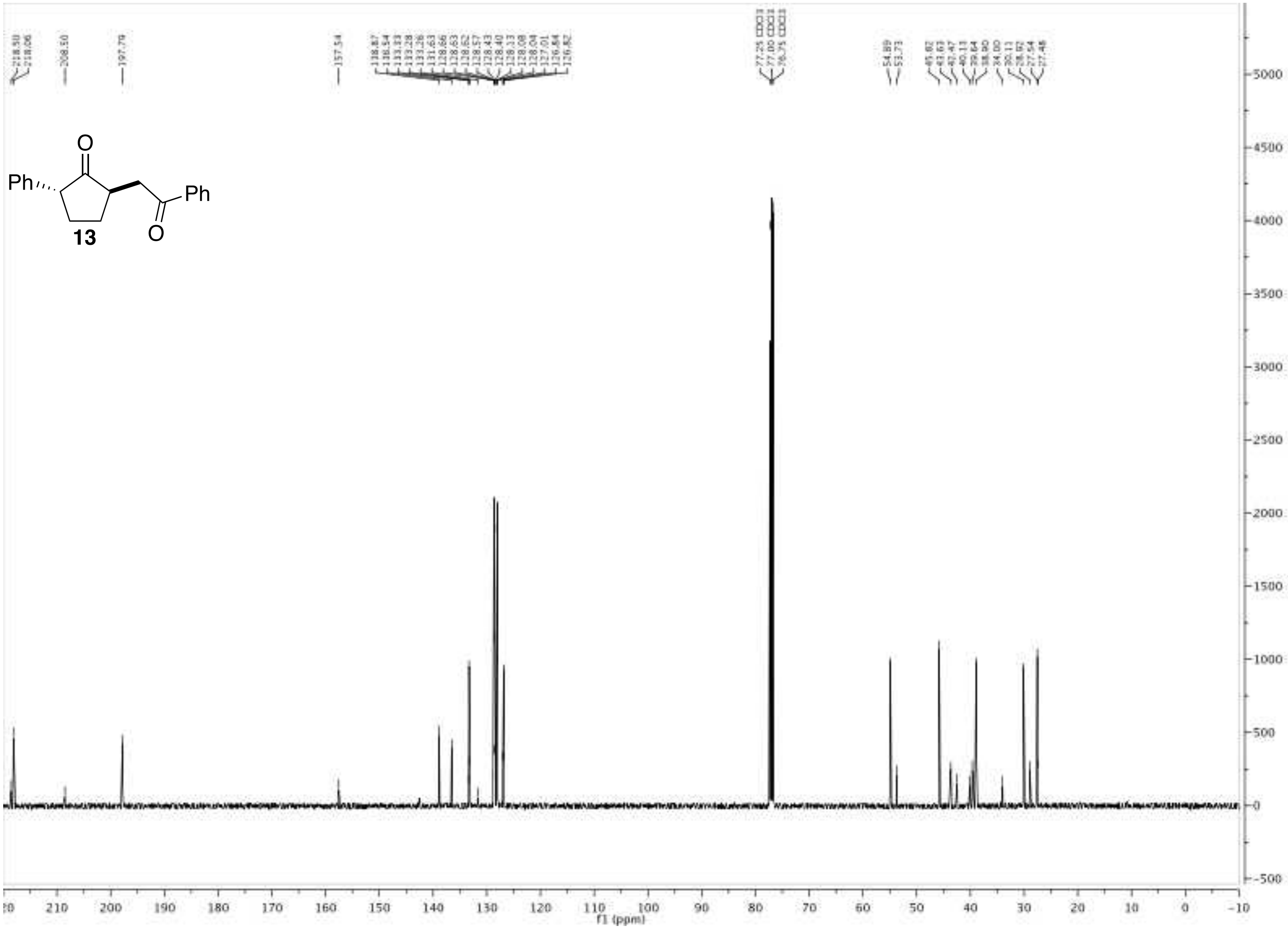

OTBS
Ph
O
12d
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.01
3.03
2.04
2.05
1.00
2.06
1.03
1.02
1.07
1.04
1.18
9.03
3.02
3.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


199.45
151.54
137.33
136.43
132.88
128.57
128.06
127.79
127.04
125.72
116.05
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
42.88
42.28
29.80
26.85
25.84
18.19
-3.74
-4.14
OTBS
Ph
O
12d
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

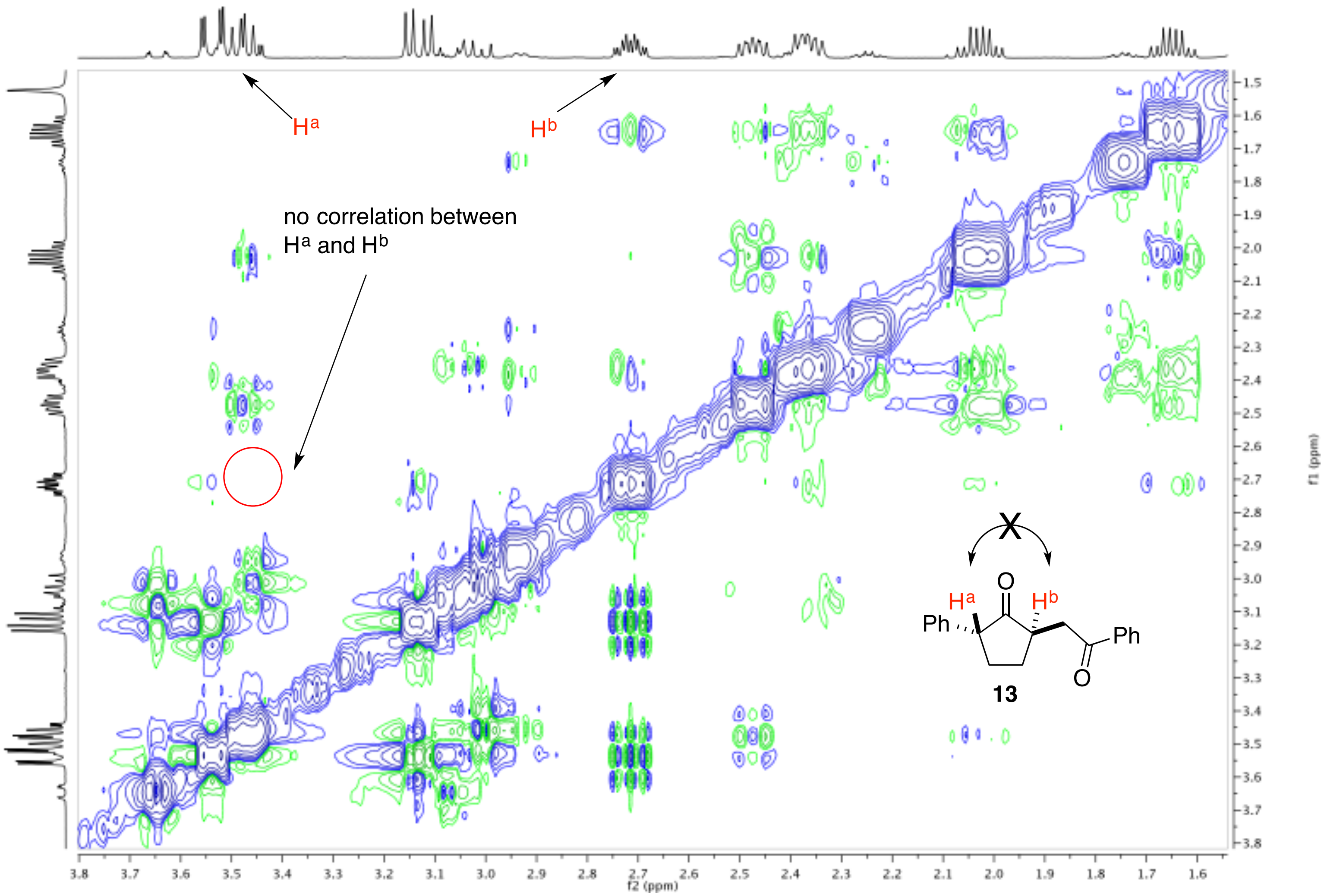

MeO
OTBS
Ph
O
12e
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.89
1.00
1.85
2.00
1.87
2.84
1.73
0.91
0.86
0.36
0.95
0.92
1.01
8.21
3.06
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

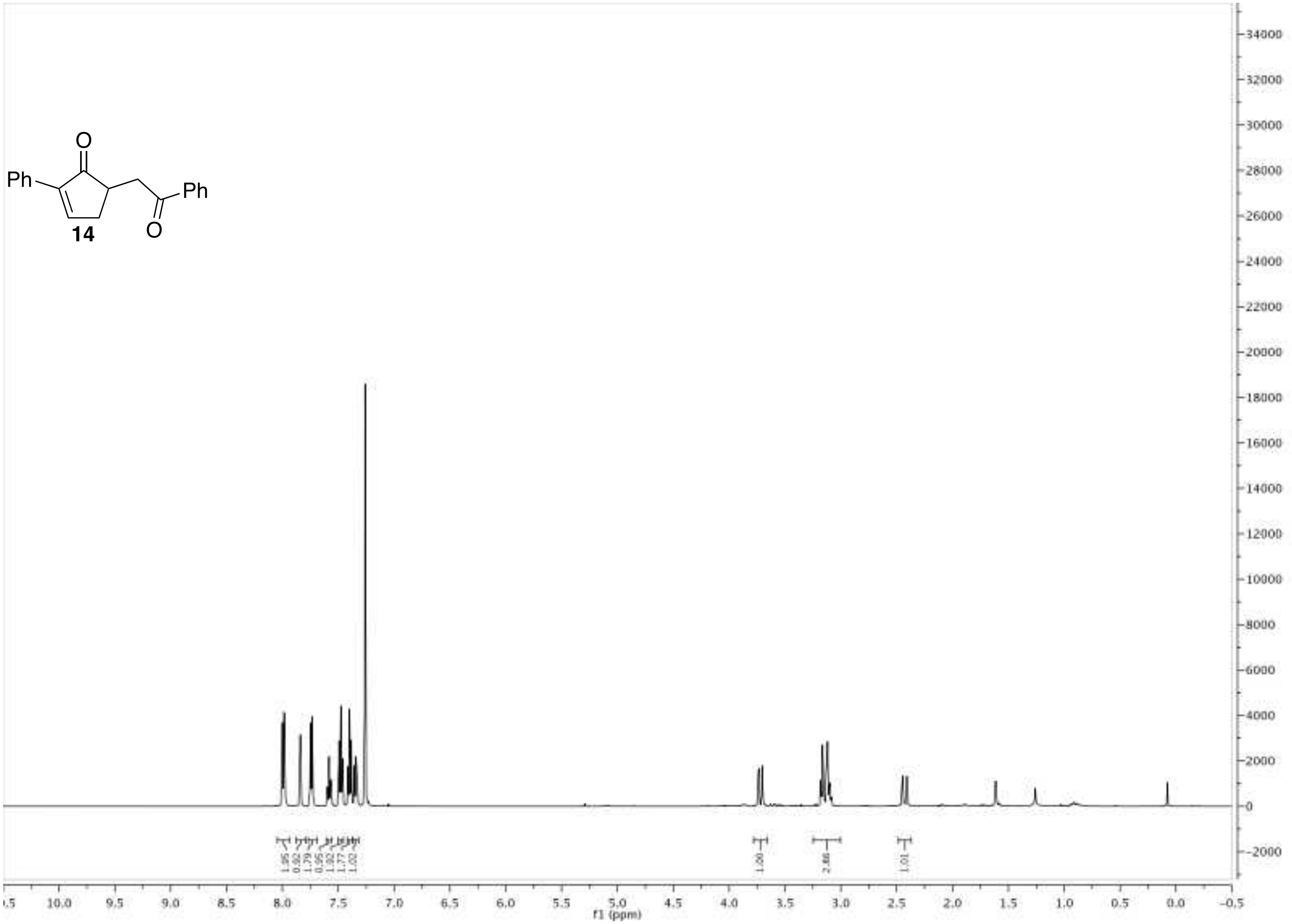

199.63
157.54
149.92
137.25
133.00
129.17
128.56
128.11
128.06
115.47
113.20
77.25 CDCl3
77.00 CDCl3
77.00 CDCl3
76.75 CDCl3
55.20
42.72
42.32
29.84
26.72
25.86
18.20
-3.72
-4.10
MeO
OTBS
Ph
O
12e
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

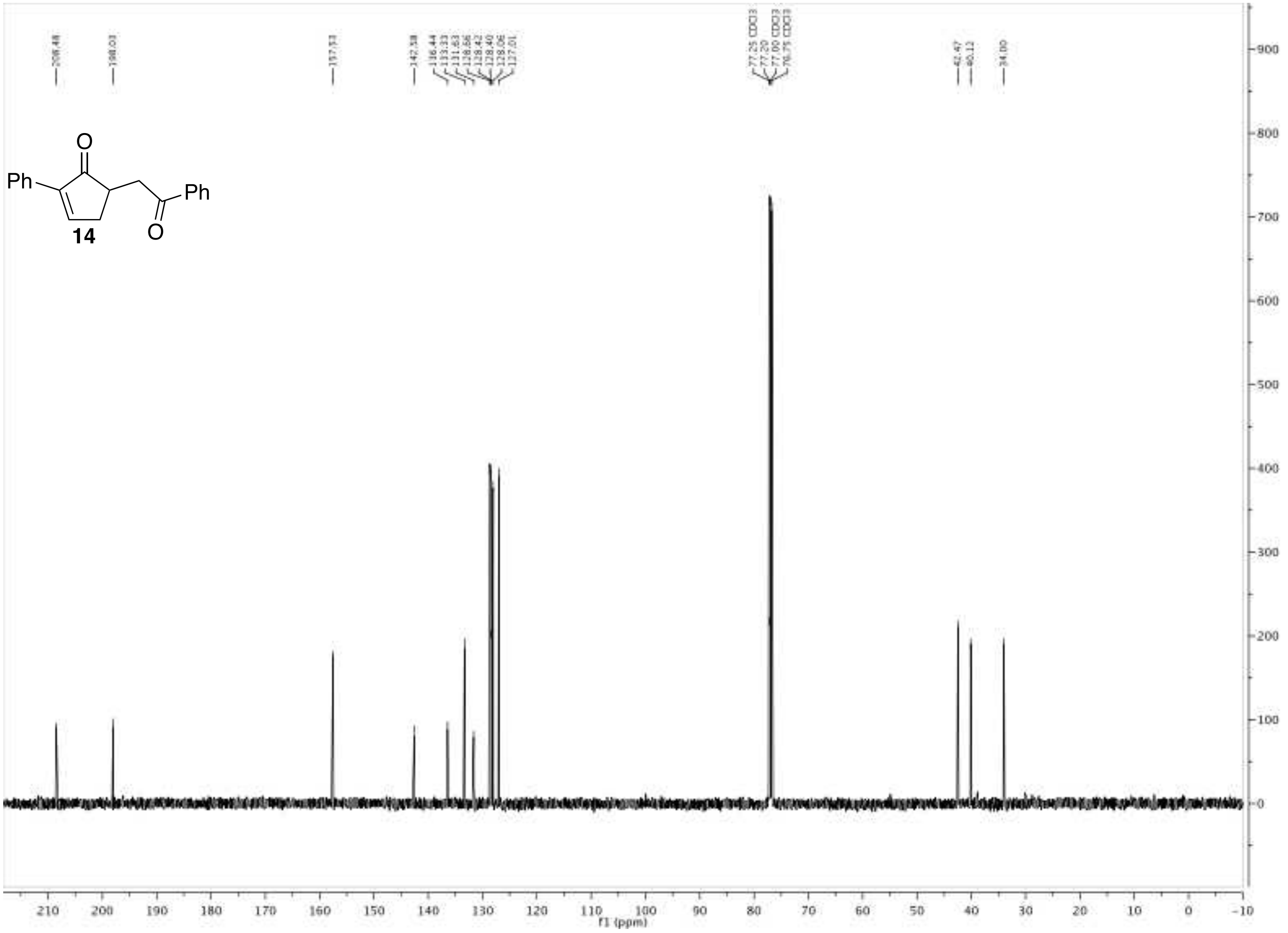

O
Ph
Ph
O
13
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
2.60
0.15
0.27
1.31
2.59
0.35
2.42
3.59
1.17
1.03
0.12
1.00
0.94
0.96
1.24
0.93
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

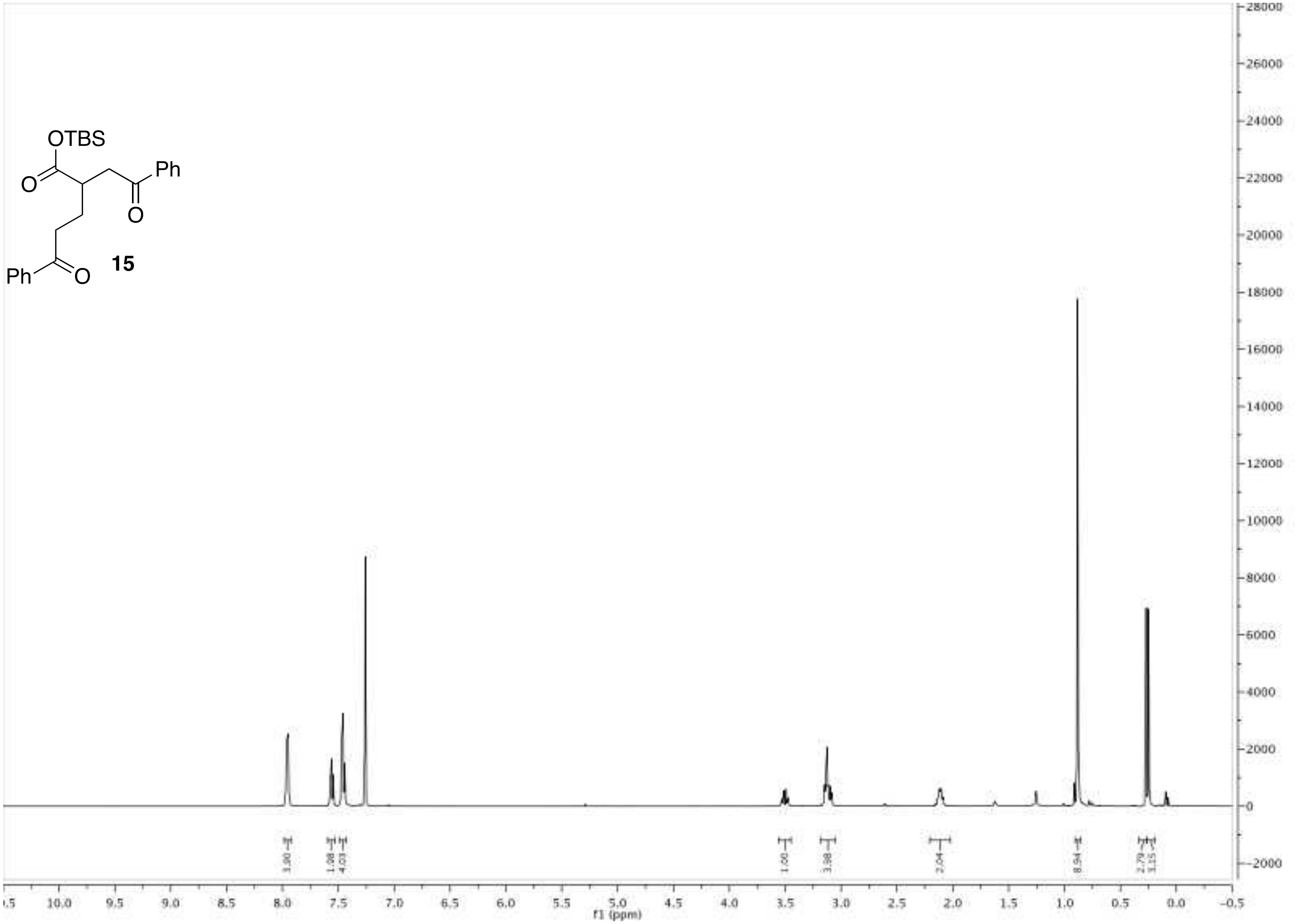

13

218.50
218.06
208.50
197.79
157.54
138.87
136.54
133.33
133.28
133.26
131.63
128.66
128.63
128.62
128.57
128.43
128.40
128.13
128.08
128.04
127.01
126.84
126.82
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
54.89
53.73
45.82
43.63
42.47
40.13
39.64
38.90
34.00
30.11
28.92
27.54
27.48
O
Ph
Ph
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Hᵃ
Hᵇ
no correlation between
Hᵃ and Hᵇ
X
O
Hᵃ
Hᵇ
Ph
Ph
O
13
f2 (ppm)
f1 (ppm)
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5

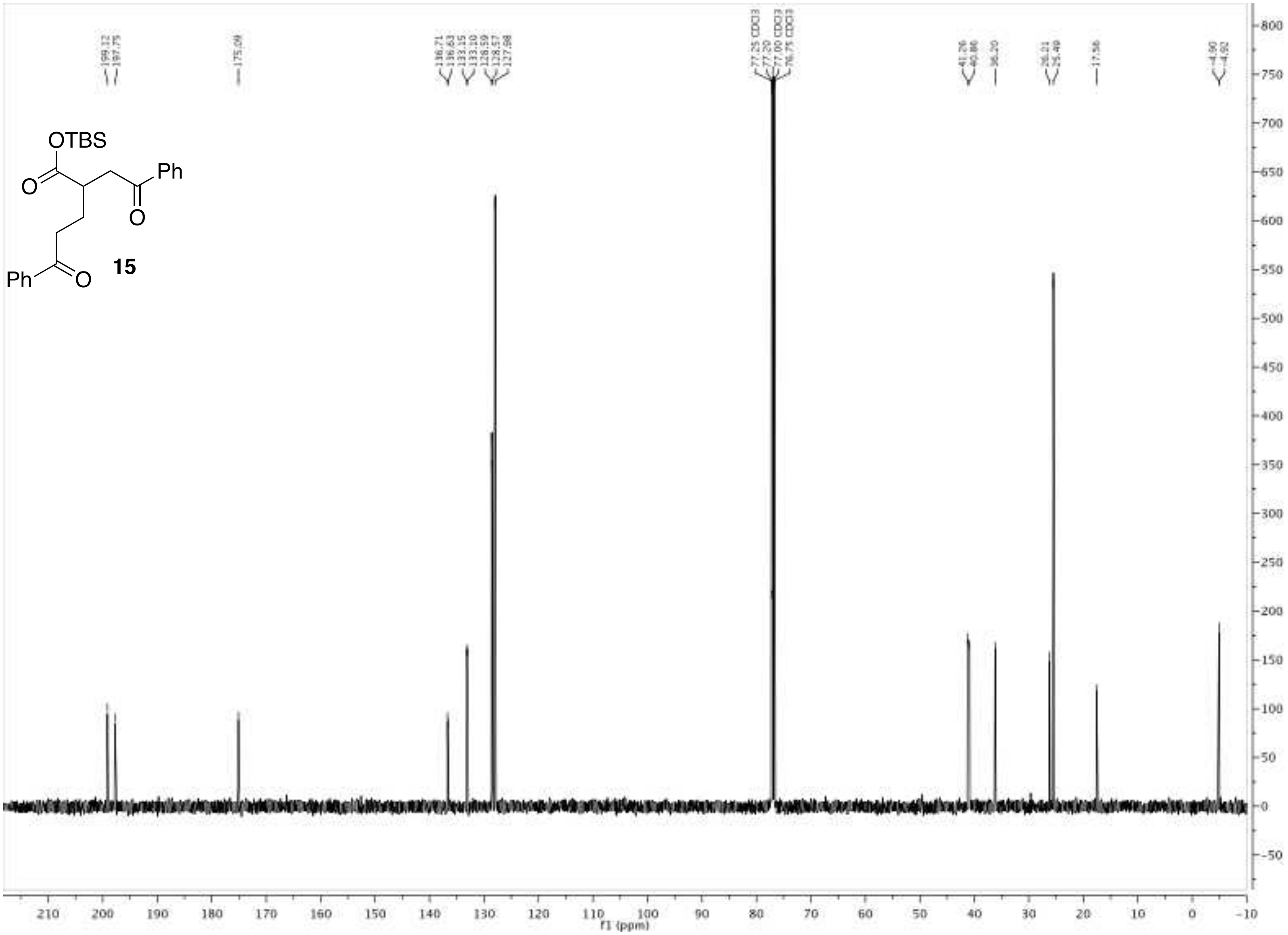

O
Ph
Ph
O
14
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.95
0.92
1.79
0.95
1.92
1.77
1.02
1.00
2.86
1.01
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

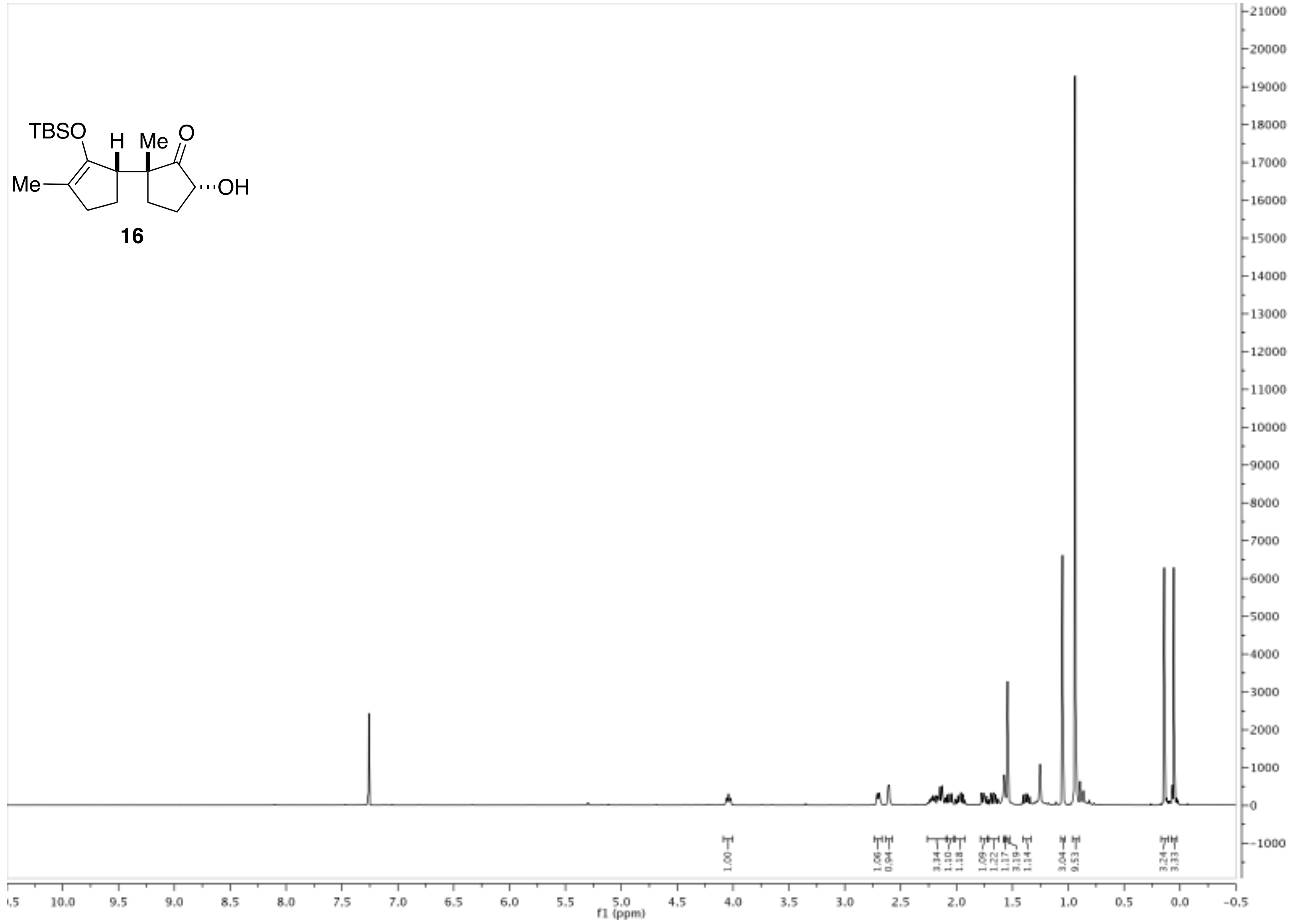

14
Ph
O
Ph
O
208.48
198.03
157.53
142.58
136.44
133.33
131.63
128.66
128.42
128.40
128.06
127.01
77.25 CDCl3
77.20
77.00 CDCl3
76.75 CDCl3
42.47
40.12
34.00
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

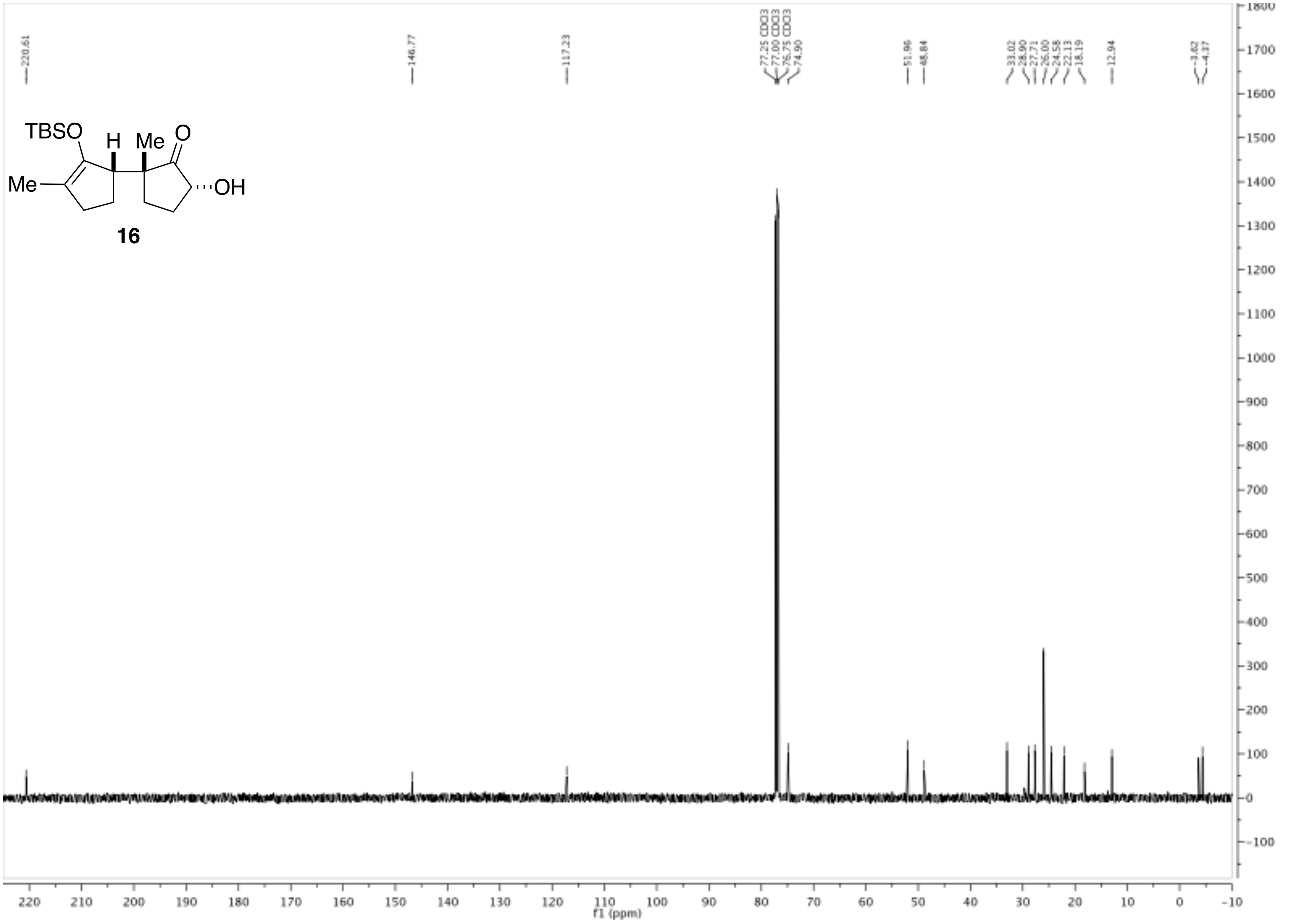


15

OTBS
O
Ph
O
Ph
O
3.90
1.08
4.03
1.00
3.98
2.04
8.94
2.79
3.15
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OTBS
O
Ph
O
Ph
O
15
199.12
197.75
175.09
136.71
136.63
133.15
133.10
128.59
128.57
127.98
77.25 CDCl3
77.20
77.00 CDCl3
76.75 CDCl3
41.26
40.86
36.20
26.21
25.49
17.56
-4.90
-4.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50


TBSO
H
Me
O
Me
OH
16
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.06
0.94
3.34
1.10
1.18
1.09
1.22
1.17
3.19
1.14
3.04
9.53
3.24
3.33
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.61
146.77
117.23
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
74.90
51.96
48.84
33.02
28.90
27.71
26.00
24.58
22.13
18.19
12.94
-3.82
-4.37
TBSO
H
Me
O
Me
OH
16
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)