Single-Flask Multicomponent Synthesis of Highly Substituted α-Pyrones via a Sequential Enolate Arylation and Alkenylation Strategy

Supporting Information

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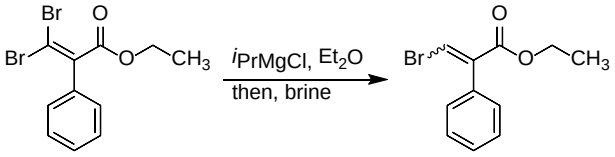
Table of Contents

I. General Experimental Details

All reactions were conducted in oven-dried glassware under an atmosphere of argon. Tetrahydrofuran (inhibitor-free) was purified by passage through a solvent purification system (Innovative Technology) and stored in a glovebox over 4Å molecular sieves. Dichloromethane was freshly distilled over CaH_2 prior to use. Methyl (*E*)-3-bromo-2-methylacrylate,[1] 1-(4-(dimethylamino)phenyl)propan-1-one,[2] methyl (*E*)-3-bromoacrylate,[3] methyl (*Z*)-3-bromoacrylate,[4] methyl (*Z*)-2,3-dibromoacrylate,[5] methyl (*Z*)-3-bromo-2-methoxyacrylate,[6] and 1,2-bis(perfluorophenyl)ethyne[7] were synthesized according to literature procedures. All other reagents were used as received from commercial sources. MPLC was performed to obtain analytically pure material using a Biotage Isolera Prime (Version 1.5.2) system with Silicycle, Inc. SiliaSep 12-g or 25-g cartridges (FLH-R10030B-ISO12 or FLH-R10030B-ISO25, respectively). ^{1}H and ^{13}C spectra were obtained using either a Bruker AVANCE III HD 400 instrument operating at 400 MHz and 100 MHz, respectively, or a Bruker AVANCE III HD 500 instrument operating at 500 MHz and 125 MHz, respectively. All ^{1}H and ^{13}C spectral data are reported in ppm (δ) relative to the residual $CDCl_3$ peak at 7.26 ppm and 77.23 ppm, respectively. ^{19}F spectral data were obtained on a Bruker AVANCE III HD 500 instrument operating at 471 MHz. Coupling constants (*J*) are reported in Hz. High-resolution mass spectrometry (HRMS) was performed on a Bruker micrOTOF-Q II instrument. X-ray diffraction collections were obtained on a Bruker APEX-II diffractometer.

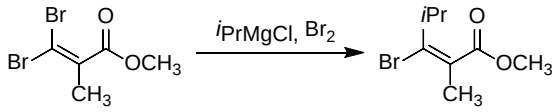
Synthesis of Substrates



Ethyl (*E*/*Z*)-3-bromo-2-phenylacrylate

The title compound was synthesized by a modified procedure reported by Vu, et. al.[8]

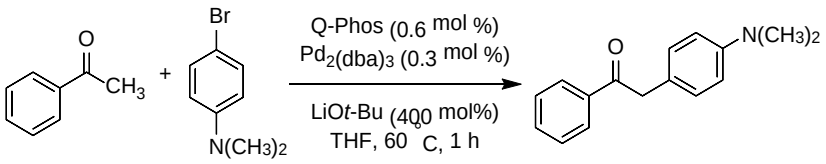
To an oven-dried two-neck flask under an atmosphere of Ar and equipped with a magnetic stirring bar was added ethyl 3,3-dibromo-2-phenylacrylate[8] (785 mg, 2.35 mmol) in anhydrous diethyl ether (8 ml). The mixture was stirred and cooled to -78 ˚C, then 2*M* *i*PrMgCl (1.17 ml, 2.35 mmol) was added over 10 min. After stirring for 15 min at -78 ˚C, then -50 ˚C for 1 h, brine (1 ml) was added dropwise, and the reaction was stirred at 22 ˚C. After 14 h, brine (5 ml) was added and extracted with diethyl ether (3x10 ml). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The crude oil was purified by column chromatography (10% diethyl ether in hexanes) to afford 270 mg (45%) as a yellow oil. The purified compound was determined to be ~1:1 mixture of *cis*/*trans* isomers by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.44 – 7.27 (m, 10H), 6.78 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.85, 164.76, 141.27, 139.14, 135.27, 134.51, 129.58, 129.11, 129.01, 128.58, 128.28, 126.69, 124.08, 109.00, 61.97, 61.86, 14.38; HRMS (ESI) calcd for $C_{11}H_{11}BrO_2$ [M + H] 255.0015 & 257.0079, found 255.0027 & 257.0006



Methyl (*E*)-3-bromo-2,4-dimethylpent-2-enoate

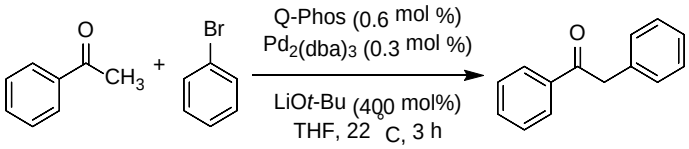
The title compound was synthesized by a modified procedure reported by Vu, et. al.[8]

To an oven-dried two-neck flask under an atmosphere of Ar and equipped with a magnetic stirring bar was added methyl 3,3-dibromo-2-methylacrylate[8] (2.58 g, 10 mmol) in anhydrous diethyl ether (30 ml). The reaction mixture was stirred and cooled to -78 ˚C, then 2*M* *i*PrMgCl (11.0 ml, 22 mmol) was added over 30 min. After stirring for 15 min at -78 ˚C, then -0 ˚C for 3 h, a solution of bromine (1.08 ml, 21 mmol) in diethyl ether (30 ml) was added over 1 h. The reaction was warmed to 22 ˚C over a period of 14 h. The reaction mixture was quenched with brine and extracted with diethyl ether (3x). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (5% diethyl ether in hexanes) to afford 470 mg (21%) of a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 2.90 (hept, *J* = 6.6 Hz, 1H), 1.95 (s, 3H), 1.08 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.00, 135.12, 128.00, 52.29, 32.49, 21.39, 17.01; HRMS (ESI) calcd for $C_8H_{13}BrO_2$ [M + H] 221.0172 & 223.0085., found 221.0165 & 223.0094.



2-(4-(Dimethylamino)phenyl)-1-phenylethan-1-one (**3a**)

In a glove box, $LiOtBu_{(s)}$ (961 mg, 12.0 mmol), 4-bromo-N,N-dimethylaniline (600 mg, 3.0 mmol), $Pd_2(dba)_3$ (8.24 mg, 0.009 mmol), and Q-Phos (12.8 mg, 0.018 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (6 mL) was added, and the vial was taken out of the glove box and stirred at 22 °C. Acetophenone (360 mg, 3 mmol) was added dropwise to the stirred solution. After 5 min, bromobenzene (3 mmol) was added and stirred at 60 °C for 1 h. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (40 ml), and concentrated. Purification by MPLC (silica gel, hexane/EtOAc 90/10 to 85/15) afforded 669 mg (93%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.57, 149.86, 137.06, 133.18, 130.31, 128.95, 128.83, 122.49, 113.25, 44.94, 40.89. (lit.[9] ^{1}H NMR)



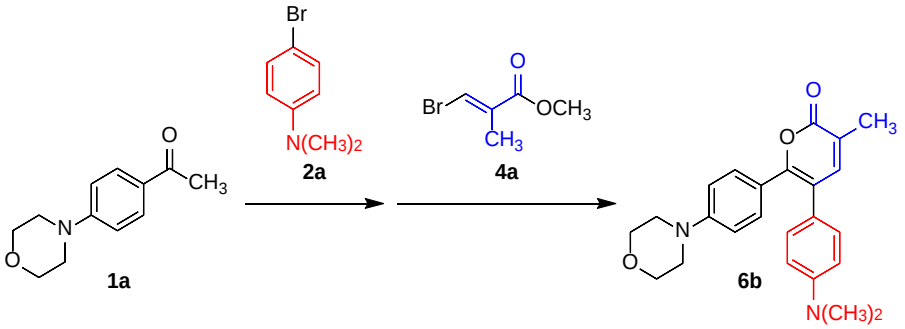
1,2-Diphenylethan-1-one (**3b**)

In a glove box, $LiOtBu_{(s)}$ (961 mg, 12.0 mmol), $Pd_2(dba)_3$ (8.24 mg, 0.009 mmol), and Q-Phos (12.8 mg, 0.018 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (6 mL) was added, and the vial was taken out of the glove box and stirred at 22 °C. Acetophenone (360 mg, 3 mmol) was added dropwise to the stirred solution. After 5 min, bromobenzene (471 mg, 3 mmol) was added and stirred at 22 °C for 3h. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (40 ml), and concentrated. Purification by MPLC (silica gel, hexane/EtOAc 98/2) afforded 540 mg (92%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.27 (m, 5H), 4.32 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.88, 136.92, 134.92, 133.48, 129.83, 128.99, 128.97, 128.93, 127.20, 45.78. (lit.[10] ^{1}H NMR)

Three-Component Synthesis of α-Pyrones: Experimental Details

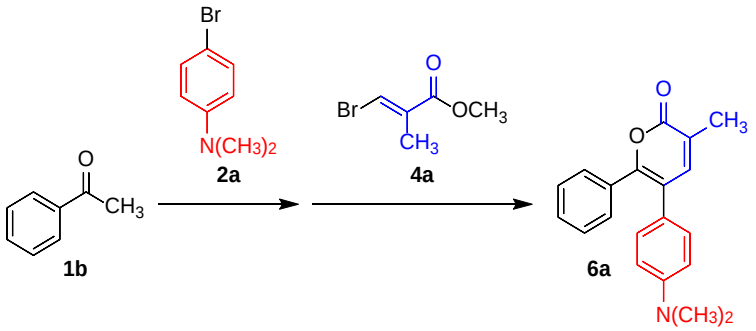
General Procedure for Three-Component Synthesis of α-Pyrones Employing a Palladium Catalyst

In a glove box, $LiOtBu_{(s)}$ (160 mg, 2.0 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), and Q-Phos (3.6 mg, 0.005 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (2 mL) was added, and the vial was taken out of the glove box and stirred at 22 °C. A ketone (0.5 mmol) was added dropwise to the stirred solution. After 5 min, an aryl bromide (0.500 mmol) was added and stirred for 1–4 h at either 22 °C or 40 °C. After the starting ketone had been consumed, a β-bromoacrylate (0.525 mmol) was added and stirred at either 22 °C or 40 °C for 16 h as a standard reaction time. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Purification by MPLC (silica gel, hexane/EtOAc) afforded the coupled product**.**



5-(4-(Dimethylamino)phenyl)-3-methyl-6-(4-morpholinophenyl)-2H-pyran-2-one (**6b**)

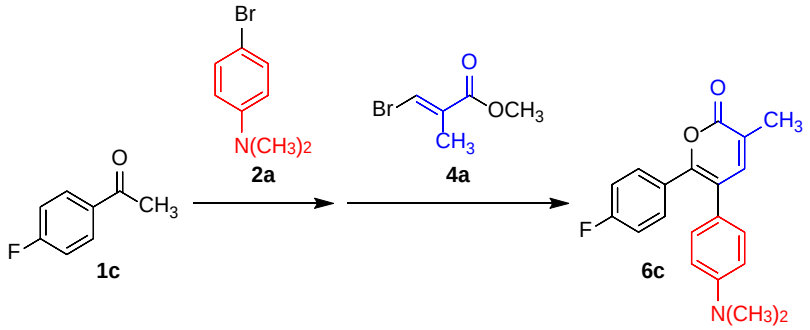
Following the representative three-component procedure, **1a** (103 mg, 0.50 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 60/40 to 50/50) to afford 181 mg (93%) of **6b** as a yellow solid. mp = 189-191 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 9.1 Hz, 2H), 7.22 (d, *J* = 1.2 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.84 – 3.78 (m, 4H), 3.20 – 3.14 (m, 4H), 2.96 (s, 6H), 2.15 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.82, 155.06, 151.47, 149.96, 145.45, 130.20, 130.05, 124.73, 123.54, 122.03, 116.98, 114.08, 112.80, 66.88, 48.24, 40.59, 16.61; HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3$ [M + H] 391.2016, found 391.2009.



5-(4-(Dimethylamino)phenyl)-3-methyl-6-phenyl-2H-pyran-2-one (**6a**)

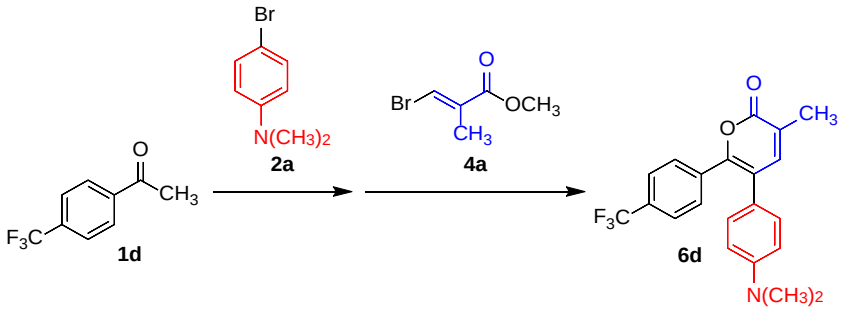
Following the representative three-component procedure, **1b** (60 mg, 0.500 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 139 mg (91%) of **6a** as a yellow solid. mp = 144-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J*

= 8.2, 1.6 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 2.96 (s, 6H), 2.18 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.66, 154.66, 150.06, 145.01, 132.98, 130.07, 129.37, 129.20, 128.26, 124.00, 123.61, 118.33, 112.71, 40.58, 16.73; HRMS (ESI) calcd for $C_{20}H_{19}NO_2$ [M + H] 306.1489, found 306.1477.



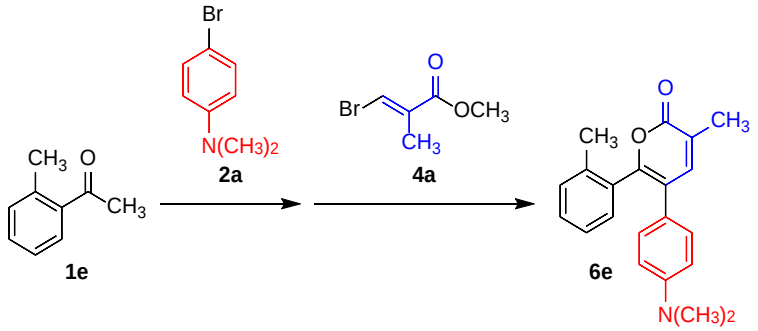
5-(4-(Dimethylamino)phenyl)-6-(4-fluorophenyl)-3-methyl-2H-pyran-2-one (**6c**)

Following the representative three-component procedure, **1c** (103 mg, 0.50 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 90/10 to 85/15) to afford 142 mg (88%) of **6c** as a yellow solid. mp = 147-149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.26 (d, *J* = 1.1 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 2.96 (s, 6H), 2.17 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.50, 163.15 (d, *J* = 253.3 Hz), 153.62, 150.12, 144.96, 131.23 (d, *J* = 8.8 Hz), 130.02, 129.12 (d, *J* = 3.8 Hz), 123.68, 123.65, 118.23, 115.41 (d, *J* = 21.4 Hz), 112.71, 40.53, 16.72; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.99; HRMS (ESI) calcd for $C_{20}H_{18}FNO_2$ [M + H] 324.1394, found 324.1381.



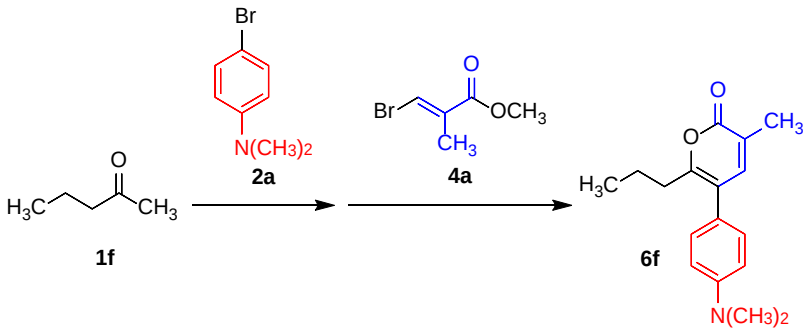
5-(4-(Dimethylamino)phenyl)-3-methyl-6-(4-(trifluoromethyl)phenyl)-2H-pyran-2-one (**6d**)

Following the representative three-component procedure, **1d** (94 mg, 0.50 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 2 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 77 mg (41%) of **6d** as a yellow solid. A separate reaction was conducted in which the second coupling was conducted at 40 °C for 16 h, producing 87 mg (47%) of **6d**. mp = 48-50 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (q, *J* = 8.6 Hz, 4H), 7.28 (d, *J* = 1.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 2.98 (s, 6H), 2.19 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.18, 152.62, 150.32, 144.72, 136.40, 130.88 (q, *J* = 32.5 Hz), 130.02, 129.40, 125.22 (q, *J* = 3.7 Hz), 124.82, 124.05 (q, *J* = 272.2 Hz), 123.10, 119.59, 112.76, 40.49, 16.79; ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.01; HRMS (ESI) calcd for $C_{21}H_{18}F_3NO_2$ [M + H] 374.1362, found 374.1346.



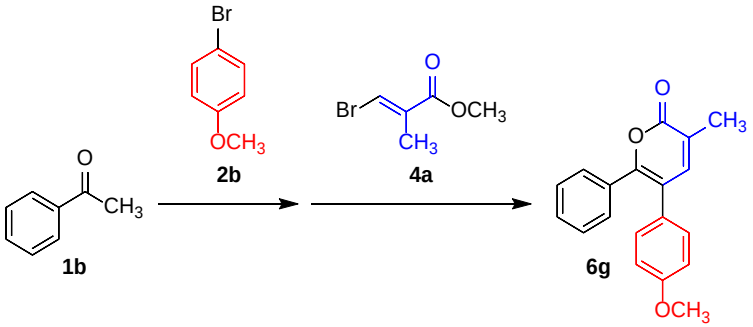
5-(4-(Dimethylamino)phenyl)-3-methyl-6-(o-tolyl)-2H-pyran-2-one (**6e**)

Following the representative three-component procedure, **1e** (67 mg, 0.500 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 2 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 90/10 to 80/20) to afford 139 mg (87%) of **6e** as a yellow solid. mp = 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.2 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.15 – 7.06 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 2.88 (s, 6H), 2.20 (d, *J* = 1.2 Hz, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77, 155.55, 149.79, 143.91, 137.30, 133.13, 130.71, 130.61, 129.57, 129.50, 125.87, 124.10, 123.29, 119.32, 112.35, 40.45, 20.08, 16.86; HRMS (ESI) calcd for $C_{21}H_{21}NO_2$ [M + H] 320.1645, found 320.1627.



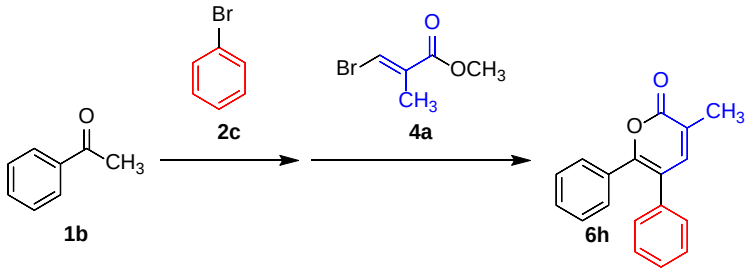
5-(4-(Dimethylamino)phenyl)-3-methyl-6-propyl-2H-pyran-2-one (**6f**)

Following the representative three-component procedure, **1f** (43 mg, (0.500 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 2 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 100 mg (74%) of **6f** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 1.2 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 2.99 (s, 6H), 2.51 – 2.42 (m, 2H), 2.10 (d, *J* = 1.2 Hz, 3H), 1.68 (sex, 0.88 *J* = 7.5 Hz, 2H), (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.38, 159.74, 150.09, 144.14, 129.81, 124.09, 122.21, 118.32, 112.54, 40.67, 33.24, 21.45, 16.64, 13.94; HRMS (ESI) calcd for $C_{17}H_{21}NO_2$ [M + H] 272.1645, found 272.1646.



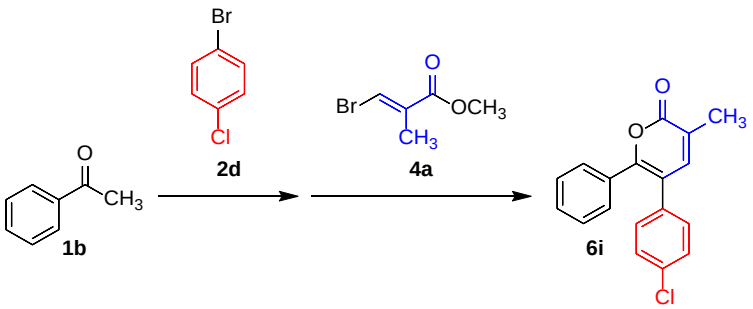
5-(4-Methoxyphenyl)-3-methyl-6-phenyl-2H-pyran-2-one (**6g**)

Following the representative three-component procedure, **1b** (60 mg, 0.500 mmol) and **2b** (94 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 80/20) to afford 132 mg (90%) of **6g** as a white solid. mp = 86-88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.0 Hz, 2H), 7.29 – 7.19 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.17 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.46, 159.41, 155.21, 144.56, 132.60, 130.55, 129.62, 129.23, 128.86, 128.32, 123.81, 117.85, 114.55, 55.49, 16.74; HRMS (ESI) calcd for $C_{19}H_{16}O_3$ [M + H] 293.1172, found 293.1186.



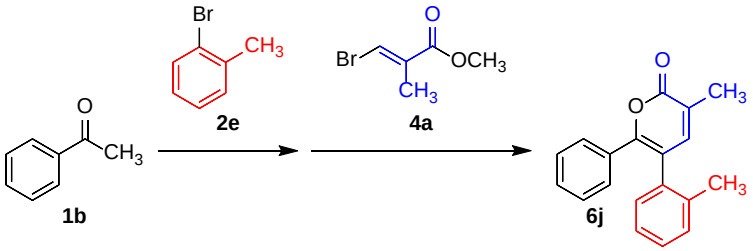
3-Methyl-5,6-diphenyl-2H-pyran-2-one (**6h**)

Following the representative three-component procedure, **1b** (60 mg, 0.500 mmol) and **2c** (79 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 77 mg (59%) of **6h** as a colorless oil. A separate reaction was conducted in which the second coupling was conducted at 40 °C for 16 h, producing 80 mg (61%) of **6h**. mp = 93-95 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.25 (d, *J* = 6.3 Hz, 2H), 6.98 – 6.91 (m, 3H), 6.89 – 6.77 (m, 5H), 6.46 (d, *J* = 1.3 Hz, 1H), 1.88 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.37, 155.64, 144.23, 136.83, 132.46, 129.76, 129.45, 129.31, 129.11, 128.32, 128.00, 123.96, 118.23, 16.70; HRMS (ESI) calcd for $C_{13}H_{12}O_2$ [M + H] 201.0910, found 201.0917. (lit.[12] ^{13}C NMR)



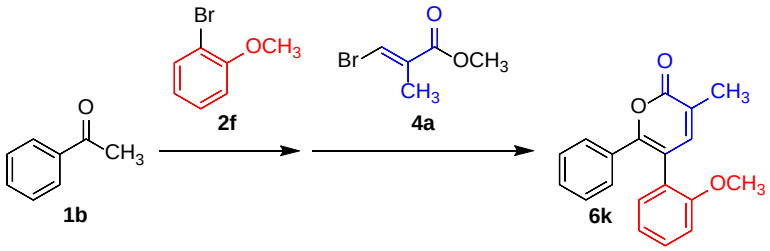
5-(4-Chlorophenyl)-3-methyl-6-phenyl-2H-pyran-2-one (**6i**)

Following the representative three-component procedure, **1b** (60 mg, 0.500 mmol) and **2d** (96 mg, 0.500 mmol) were stirred for 3 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 40 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 90/10) to afford 33 mg (22%) of **6i** as a white solid. mp = 63-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 8H), 7.11 (d, *J* = 8.6 Hz, 2H), 2.19 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.04, 157.84, 145.55, 137.22, 136.02, 134.11, 132.70, 131.92, 131.29, 131.22, 130.40, 126.18, 118.94, 18.64; HRMS (ESI) calcd for $C_{18}H_{13}ClO_2$ [M + H] 297.0677, found 297.0683.



3-Methyl-6-phenyl-5-(o-tolyl)-2H-pyran-2-one (**6j**)

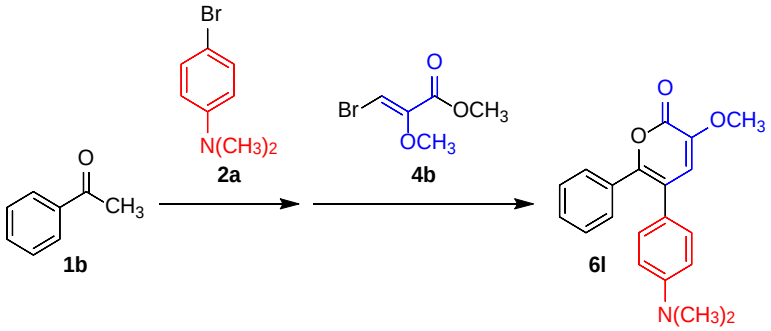
Following the representative three-component procedure, **1b** (60 mg, 0.50 mmol) and **2e** (86 mg, 0.500 mmol) were stirred for 3 h at 40 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 40 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5) to afford 75 mg (55%) of **6j** as a white solid. mp = 132-134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.09 (m, 10H), 2.18 (d, *J* = 0.7 Hz, 3H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.50, 155.17, 144.52, 136.41, 136.19, 132.55, 130.93, 130.20, 129.73, 128.61, 128.37, 128.26, 126.83, 123.75, 117.29, 20.02, 16.72; HRMS (ESI) calcd for $C_{19}H_{16}O_2$ [M + H] 277.1223, found 277.1217.



5-(2-Methoxyphenyl)-3-methyl-6-phenyl-2H-pyran-2-one (**6k**)

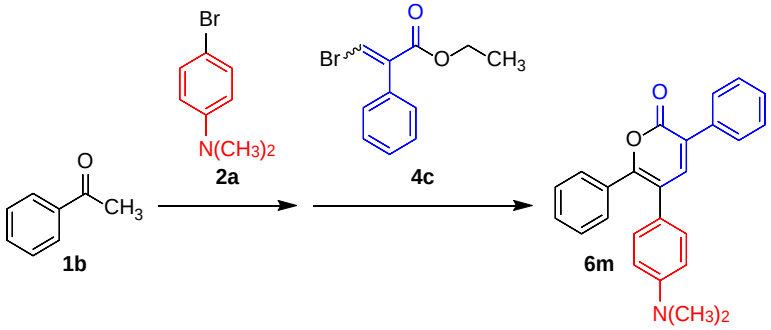
Following the representative three-component procedure, **1b** (60 mg, 0.500 mmol) and **2f** (94 mg, 0.500 mmol) were stirred for 3 h at 40 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 40 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 80/20 to 75/25)

to afford 121 mg (83%) of **6k** as a light orange solid. mp = 135-137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.27 – 7.22 (m, 1H), 7.21 – 7.17 (m, 3H), 7.02 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.91 – 6.86 (m, 2H), 3.63 (s, 3H), 2.17 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.60, 156.96, 155.99, 144.99, 133.04, 131.44, 129.90, 129.50, 128.47, 128.12, 125.50, 123.15, 121.27, 114.65, 111.52, 55.53, 16.71; HRMS (ESI) calcd for $C_{19}H_{16}O_3$ [M + H] 293.1172, found 293.1154.



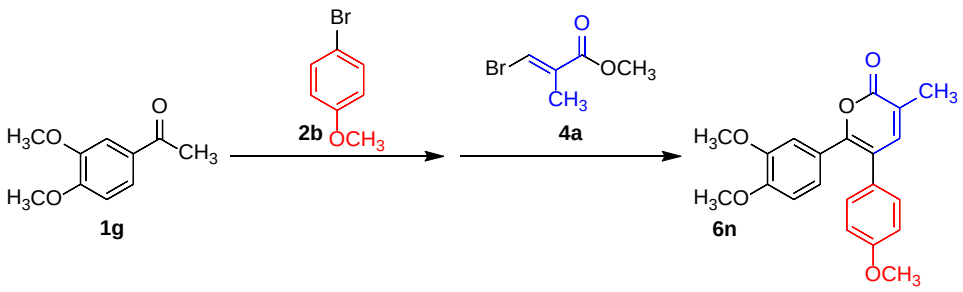
5-(4-(Dimethylamino)phenyl)-3-methoxy-6-phenyl-2H-pyran-2-one (**6l**)

Following the representative three-component procedure, **1b** (60 mg, 0.50 mmol) and **2a** (100 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4b** (102 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 85/15 to 60/40) to afford 118 mg (73%) of **6l** as a orange solid. mp = 141-143 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.33 (m, 2H), 7.25 – 7.18 (m, 3H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.62 (s, 1H), 3.86 (s, 3H), 2.97 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 150.21, 148.68, 144.35, 132.75, 130.14, 129.01, 128.93, 128.25, 124.26, 119.00, 117.83, 112.71, 56.47, 40.59; HRMS (ESI) calcd for $C_{20}H_{19}NO_3$ [M + H] 322.1438, found 322.1442.



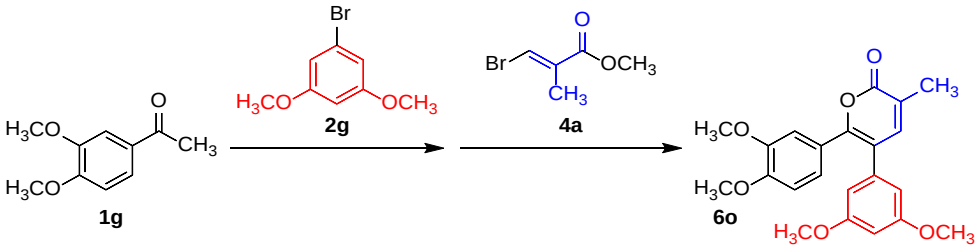
5-(4-(Dimethylamino)phenyl)-3,6-diphenyl-2H-pyran-2-one (**6m**)

Following the representative three-component procedure, **1b** (30 mg, (0.25 mmol) and **2a** (50 mg, 0.25 mmol) were stirred for 1 h at 22 °C. Then, **4c** (67 mg, 0.266 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 80/20) to afford 41 mg (45%) of **6m** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.1 Hz, 2H), 7.64 (s, 1H), 7.52 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 2.98 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.74, 156.08, 150.19, 145.38, 134.93, 132.70, 130.13, 129.75, 129.32, 128.68, 128.47, 128.34, 125.58, 123.80, 118.98, 112.75, 40.57; HRMS (ESI) calcd for $C_{25}H_{21}NO_2$ [M + H] 368.1645, found 368.1627.



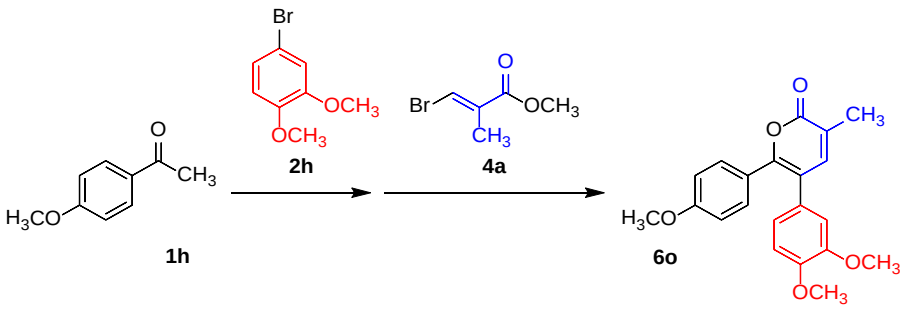
6-(3,4-Dimethoxyphenyl)-5-(4-methoxyphenyl)-3-methyl-2H-pyran-2-one (**6n**)

Following the representative three-component procedure, **1g** (360 mg, 2.0 mmol) and **2b** (374 mg, 2.0 mmol) were stirred for 1 h at 22 °C. Then, **4a** (376 mg, 2.1 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 75/25 to 55/45) to afford 585 mg (83%) of **6n** as a yellow solid. mp = 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 1.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.01 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 2.16 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.58, 159.37, 155.21, 150.18, 148.37, 144.77, 130.65, 129.46, 124.99, 122.95, 122.53, 117.05, 114.63, 112.03, 110.68, 56.05, 55.78, 55.56, 16.69; HRMS (ESI) calcd for $C_{21}H_{20}O_5$ [M + H] 353.1384, found 353.1393.



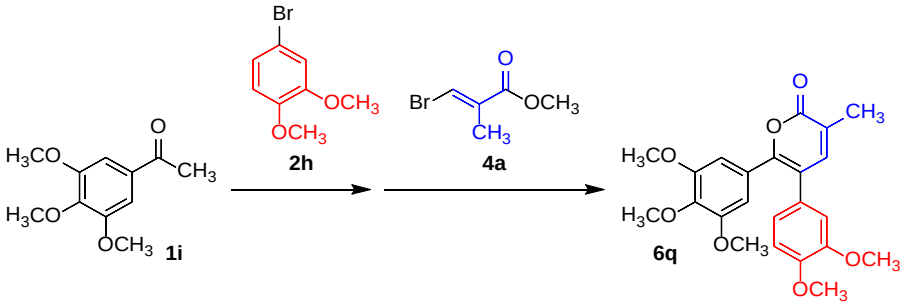
6-(3,4-Dimethoxyphenyl)-5-(3,5-dimethoxyphenyl)-3-methyl-2H-pyran-2-one (**6o**)

Following the representative three-component procedure, **1g** (90 mg, 0.50 mmol) and **2g** (109 mg, 0.500 mmol) were stirred for 1 h at 22 °C. Then, **4a** (94 mg, 0.525 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 70/30 to 55/45) to afford 160 mg (84%) of **6o** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.2 Hz, 1H), 7.07 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.39 (t, *J* = 2.3 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 2H), 3.85 (s, 3H), 3.70 (s, 6H), 3.61 (s, 3H), 2.16 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.38, 161.47, 155.37, 150.41, 148.43, 144.20, 139.31, 124.72, 122.87, 122.48, 117.32, 112.00, 110.72, 107.57, 99.95, 56.05, 55.83, 55.62, 16.60; HRMS (ESI) calcd for $C_{22}H_{22}O_6$ [M + Na] 405.1309, found 405.1321.



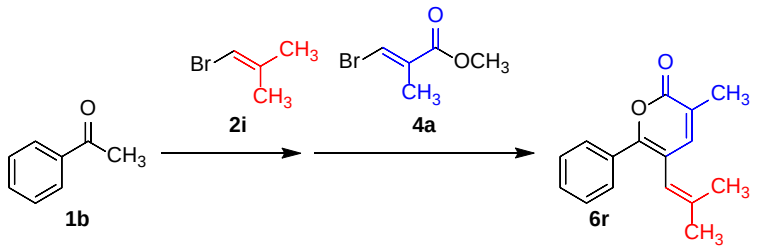
5-(3,4-Dimethoxyphenyl)-6-(4-methoxyphenyl)-3-methyl-2H-pyran-2-one (**6p**)

Following the representative three-component procedure, **1h** (300 mg, 2.0 mmol) and **2h** (434 mg, 2.0 mmol) were stirred for 1 h at 22 °C. Then, **4a** (376 mg, 2.1 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 70/30 to 55/45) to afford 587 mg (83%) of **6p** as a yellow solid. mp = 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 1.3 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.76 – 6.69 (m, 3H), 6.63 (d, *J* = 2.0 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.69 (s, 3H), 2.14 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.44, 160.56, 155.31, 149.27, 148.76, 144.53, 130.60, 129.47, 124.84, 122.75, 121.61, 116.93, 113.64, 112.62, 111.67, 56.00, 55.98, 55.38, 16.53; HRMS (ESI) calcd for $C_{21}H_{20}O_5$ [M + H] 353.1384, found 353.1372.



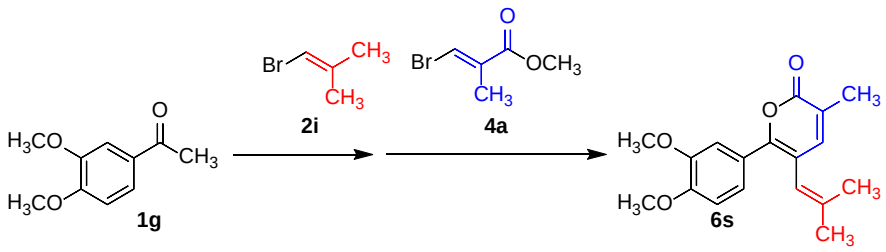
5-(3,4-Dimethoxyphenyl)-3-methyl-6-(3,4,5-trimethoxyphenyl)-2H-pyran-2-one (**6q**)

Following the representative three-component procedure, **1i** (420 mg, 2.0 mmol) and **2h** (434 mg, 2.0 mmol) were stirred for 1 h at 22 °C. Then, **4a** (376 mg, 2.1 mmol) was added to the reaction mixture and stirred for 16 h at 22 °C. Purification was achieved by MPLC (silica gel, hexane/EtOAc 70/30 to 55/45) to afford 665 mg (81%) of **6q** as a yellow solid. mp = 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 1.2 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.65 (d, *J* = 2.0 Hz, 1H), 6.57 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.57 (s, 6H), 2.13 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.24, 154.90, 152.83, 149.52, 148.96, 144.41, 139.29, 129.60, 127.43, 123.46, 121.83, 117.74, 112.71, 111.84, 106.54, 61.06, 56.22, 56.19, 56.10, 16.65; HRMS (ESI) calcd for $C_{23}H_{24}O_7$ [M + H] 413.1595, found 413.1578.



3-Methyl-5-(2-methylprop-1-en-1-yl)-6-phenyl-2H-pyran-2-one (**6r**)

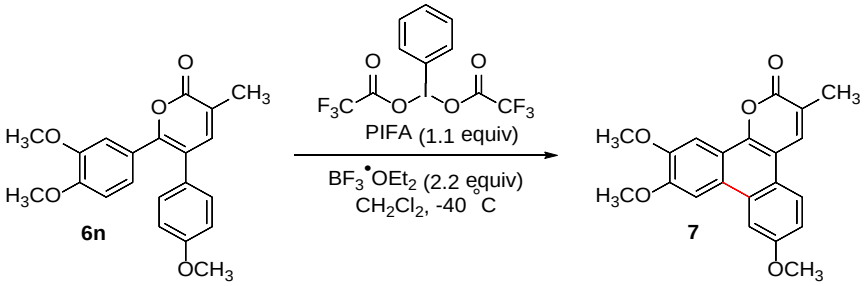
In a glove box, $LiOtBu_{(s)}$ (160 mg, 2.00 mmol), $Pd_2(dba)_3$ (0.69 mg, 0.000750 mmol), and Q-Phos (1.07 mg, 0.00150 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (1 mL) was added, and the vial was taken out of the glove box and stirred at 22 °C. Then, **1b** (60 mg, 0.500 mmol) was added dropwise to the stirred solution. After 5 min, **2i** (68 mg, 0.500 mmol) was added and stirred for 3 h at 40 °C. Then, **4a** (94 mg, 0.525 mmol) was added and stirred at 40 °C for 8 h. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Purification by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 83 mg (69%) of **6r** as a yellow solid. mp = 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.13 (d, *J* = 1.2 Hz, 1H), 5.93 – 5.87 (m, 1H), 2.15 (d, *J* = 1.2 Hz, 3H), 1.84 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41, 155.24, 144.49, 137.96, 133.04, 129.68, 128.65, 128.37, 123.21, 119.88, 114.31, 25.91, 19.84, 16.70; HRMS (ESI) calcd for $C_{16}H_{16}O_2$ [M + H] 241.1223, found 241.1220.



6-(3,4-Dimethoxyphenyl)-3-methyl-5-(2-methylprop-1-en-1-yl)-2H-pyran-2-one (**6s**)

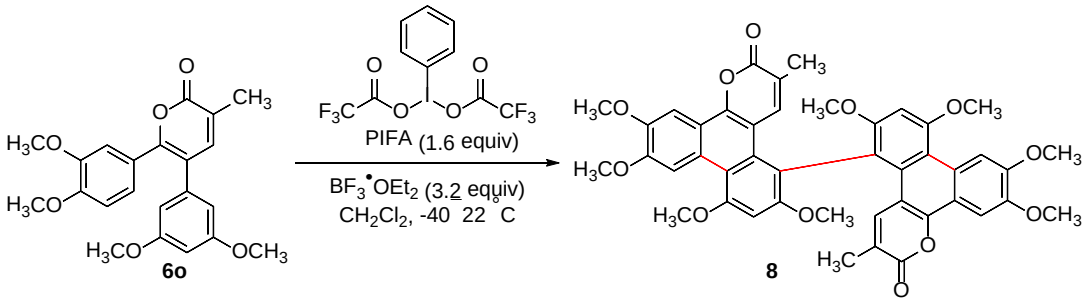
In a glove box, $LiOtBu_{(s)}$ (640 mg, 8.00 mmol), $Pd_2(dba)_3$ (1.83 mg, 0.002 mmol), Q-Phos (2.84 mg, 0.004 mmol), and **1g** (360 mg, 2.00 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (6 mL) was added, and the vial was taken out of the glove box and stirred at 22 °C for 5 min. Then, **2i** (270 mg, 2.00 mmol) was added and stirred for 4 h at 40 °C. Then, **4a** (376 mg, 2.10 mmol) was added and stirred at 40 °C for 8 h. The reaction mixture was cooled to ambient temperature, diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (40 ml), and concentrated. Purification by MPLC (silica gel, hexane/EtOAc 85/15 to 75/25) to afford 465 mg (76%) of **6s** as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 1.2 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.88 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.09 (d, *J* = 1.2 Hz, 3H), 1.81 (d, *J* = 1.4 Hz, 3H), 1.64 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.35, 154.98, 150.18, 148.53, 144.64, 137.35, 125.47, 122.14, 122.01, 120.28, 113.28, 111.22, 110.59, 55.98, 55.96, 25.75, 19.70, 16.53; HRMS (ESI) calcd for $C_{18}H_{20}O_4$ [M + H] 301.1434, found 301.1450.

Further Transformations of α-Pyrones



7,10,11-Trimethoxy-3-methyl-2H-dibenzo[f,h]chromen-2-one (**7**)

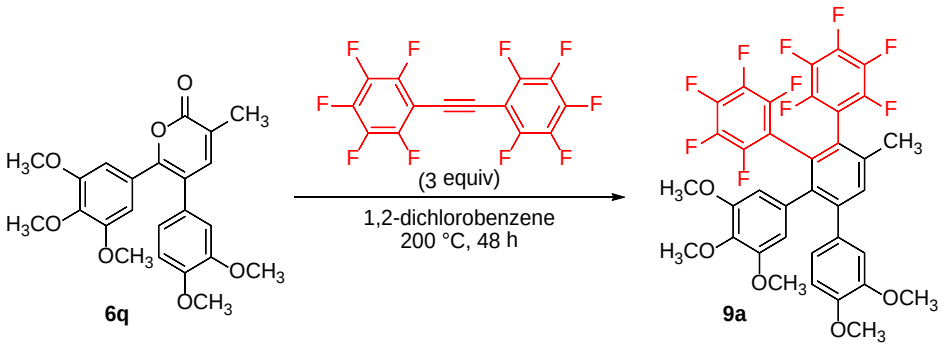
Following the experimental procedure reported by Tohma, et. al,[13] to a stirred solution of **6n** (36 mg, 0.102 mmol) in dichloromethane (3 ml) under argon was added dropwise a solution of PIFA (48 mg, 0.112 mmol) and BF_3•Et_2O (32 mg, 0.225 mmol) in dichloromethane (3 ml) at -40 °C. The reaction was stirred at -40 °C for 5 h, then quenched with $NaHCO_3$ (aq) and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 65/35 to 15/85) to afford 33 mg (92%) of **7** as a yellow solid. mp = 218-220; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 0.8 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.65 (s, 2H), 7.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.10 (s, 3H), 4.06 (s, 3H), 4.01 (s, 3H), 2.29 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56, 158.08, 150.99, 150.25, 148.04, 136.12, 128.57, 125.97, 123.77, 123.67, 120.74, 118.26, 115.85, 109.95, 105.32, 103.50, 102.78, 56.56, 56.27, 55.76, 17.67; HRMS (ESI) calcd for $C_{21}H_{18}O_5$ [M + H] 351.1227, found 351.1214.



6,6',8,8',10,10',11,11'-Octamethoxy-3,3'-dimethyl-2H,2'H-[5,5'-bidibenzo[f,h]chromene]-2,2'-dione (**8**)

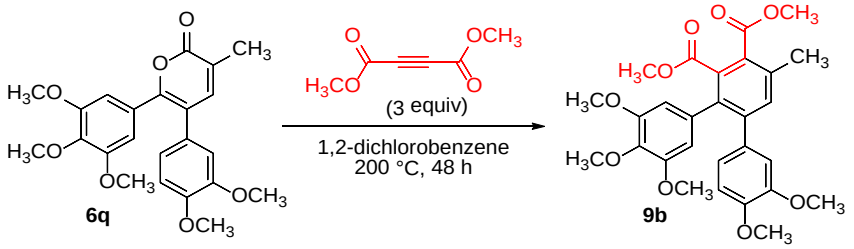
Following the experimental procedure reported by Tohma, et. al.,[13] to a stirred solution of **6o** (46 mg, 0.120 mmol) in dichloromethane (3 ml) under argon was added dropwise a solution of PIFA (57 mg, 0.132 mmol) and BF_3•Et_2O (38 mg, 0.265 mmol) in dichloromethane (3 ml) at -40 °C. The reaction was stirred at -40 °C for 2 h, then was gradually warmed to 22 °C over 12 h. The reaction mixture was quenched with $NaHCO_3$ (aq) and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 45/55 to 5/95) to afford 20 mg (60% based on PIFA as the limiting reagent) of **8** as a yellow solid. mp > 260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.91 (s, 1H), 7.33 (d, *J* = 1.2 Hz, 1H), 6.97 (s, 1H), 4.23 (s, 3H), 4.13 (s, 3H), 4.10 (s, 3H), 3.68 (s, 3H), 1.57 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96, 159.70, 156.02, 151.96, 150.67, 148.84, 139.47, 130.25, 127.21, 120.08, 117.91, 115.72, 114.65, 110.97,

109.60, 102.74, 95.97, 56.68, 56.59, 56.45, 56.05, 17.25; HRMS (ESI) calcd for $C_{44}H_{38}O_{12}$ [M + Na] 781.2255, found 781.2268.



4'-(3,4-Dimethoxyphenyl)-2,2",3,3",4,4",5,5",6,6"-decafluoro-6'-methyl-3'-(3,4,5-trimethoxyphenyl)-1,1':2',1"-terphenyl (**9a**)

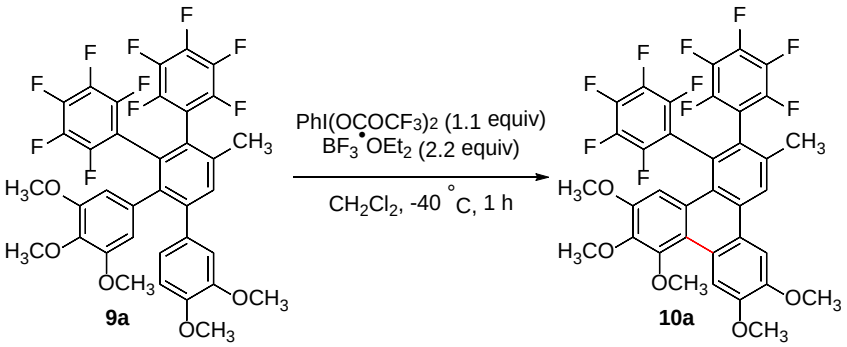
To a 10-ml crimp cap vial equipped with a magnetic stirring bar was added **6q** (82 mg, 0.20 mmol), 1,2-bis(perfluorophenyl)ethyne (215 mg, 0.60 mmol), and 1,2-dichlorobenzene (0.5 ml). The vial was then crimped and an evacuation/backfill cycle with Ar was done three times. The vial was stirred and heated to 200 °C for 48 h. The reaction was cooled, dissolved in dichloromethane and purified by MPLC (silica gel, hexane/EtOAc 80/20 to 60/40) to afford 135 mg (93%) of **9a** as a tan solid. mp = 146-148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 0.6 Hz, 1H), 6.85 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 6.16 (s, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.59 (s, 3H), 3.54 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.68, 148.31, 148.23, 144.98 – 144.66 (m), 143.30 – 143.03 (m), 141.79 (dt, *J* = 58.5, 13.6 Hz) , 140.45 – 139.77 (m), 138.55 – 137.76 (m), 137.85, 137.21, 136.45 (dt, *J* = 81.3, 14.5 Hz), 134.03, 133.49, 132.82, 127.75, 126.08, 121.94, 114.39 (td, *J* = 19.8, 3.3 Hz), 113.20 – 112.95 (m), 113.01, 110.77, 107.32, 61.05, 56.13, 55.97, 55.78, 20.21; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.98 – -141.49 (m), -142.03 – -142.52 (m), -155.72 (t, *J* = 21.0 Hz), -155.89 (t, *J* = 21.1 Hz), -163.89 (td, *J* = 23.0, 8.4 Hz), -165.11 (td, *J* = 23.1, 8.1 Hz); HRMS (ESI) calcd for $C_{36}H_{24}F_{10}O_5$ [M + H] 727.1537, found 727.1569.



Dimethyl 3,3",4,4",5"-pentamethoxy-5'-methyl-[1,1':2',1"-terphenyl]-3',4'-dicarboxylate (**9b**)

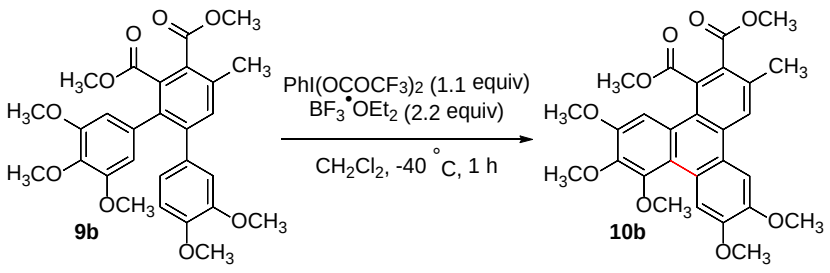
To a 10-ml crimp cap vial equipped with a magnetic stirring bar was added **6q** (129 mg, 0.312 mmol), dimethyl but-2-ynedioate (133 mg, 0.936 mmol), and 1,2-dichlorobenzene (0.7 ml). The vial was then crimped and an evacuation/backfill cycle with Ar was done three times. The vial was stirred and heated to 200 °C for 48 h. The reaction was cooled, dissolved in dichloromethane, and concentrated. The crude oil was purified by MPLC (silica gel, hexane/EtOAc 60/40 to 45/55) to afford 150 mg (94%) of **9b** as a yellow solid. mp = 84-86; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 0.6 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.71 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.45 (d, *J* = 1.9 Hz, 1H), 6.27 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.79

(s, 3H), 3.61 (s, 6H), 3.55 (d, *J* = 1.3 Hz, 6H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.48, 168.30, 152.88, 148.49, 148.42, 143.58, 137.38, 136.83, 136.29, 134.73, 133.96, 133.85, 132.86, 129.73, 121.89, 113.22, 110.98, 107.92, 61.11, 56.28, 56.09, 55.91, 52.60, 52.48, 20.40; HRMS (ESI) calcd for $C_{28}H_{30}O_9$ [M + H] 511.1963, found 511.1968.



1,2,3,10,11-Pentamethoxy-7-methyl-5,6-bis(perfluorophenyl)triphenylene (**10a**)

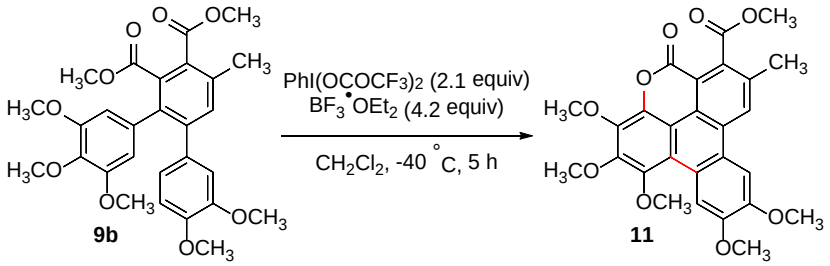
Following the experimental procedure reported by Tohma, et. al,[13] to a stirred solution of **9a** (45 mg, 0.062 mmol) in dichloromethane (4 ml) under argon was added dropwise a solution of PIFA (29.2 mg, 0.068 mmol) and BF_3•Et_2O (19.3 mg, 0.136 mmol) in dichloromethane (4 ml) at -40 °C. The reaction was stirred at -40 °C for 5 h, then quenched with $NaHCO_3$ (aq) and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 75/25) to afford 41 mg (91%) of **10a** as a tan solid. Crystals suitable for x-ray diffraction were obtained by slow vapor diffusion of hexane into ethyl acetate at 22 °C. mp = 199-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.52 (s, 1H), 7.98 (s, 1H), 6.88 (s, 1H), 4.15 (s, 3H), 4.10 (s, 3H), 4.02 (s, 3H), 3.93 (s, 3H), 3.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.91, 150.87, 149.87, 148.89, 145.85 – 144.89 (m), 143.32, 143.24 – 142.77 (m), 142.77 – 141.97 (m), 140.32 – 139.49 (m), 139.49 – 138.53 (m), 137.01 – 136.05 (m), 135.90, 132.77, 129.12, 127.02, 125.71, 124.63, 123.96, 123.35, 120.17, 117.68 (td, *J* = 19.1, 4.1 Hz), 113.70 (td, *J* = 19.9, 3.7 Hz), 109.35, 108.80, 105.44, 104.91, 61.42, 60.79, 56.24, 56.11, 55.21, 21.05; ^{19}F NMR (471 MHz, $CDCl_3$) δ -140.80 – -141.44 (m), -141.53 – -142.04 (m), -155.69 (t, *J* = 20.9 Hz), -156.17 (t, *J* = 20.9 Hz), -163.93 (td, *J* = 22.9, 8.2 Hz), -164.13 (td, *J* = 23.2, 8.3 Hz); HRMS (ESI) calcd for $C_{36}H_{22}F_{10}O_5$ [M + H] 725.1380, found 725.140.



Dimethyl 6,7,9,10,11-pentamethoxy-3-methyltriphenylene-1,2-dicarboxylate (**10b**)

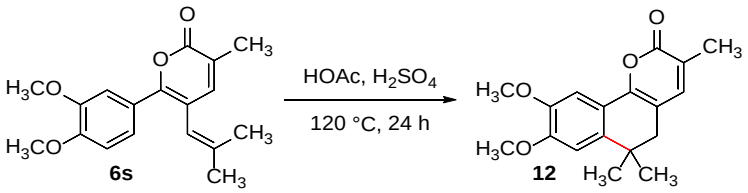
Following the experimental procedure reported by Tohma, et. al,[13] to a stirred solution of **9b** (40 mg, 0.078 mmol) in dichloromethane (4 ml) under argon was added dropwise a solution of PIFA (37.1 mg, 0.086 mmol) and BF_3•Et_2O (24.5 mg, 0.172 mmol) in dichloromethane (4 ml) at -40 °C. The reaction was

stirred at -40 °C for 1 h, then quenched with $NaHCO_3$ (aq) and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 50/50) to afford 36 mg (90%) of **10b** as a white solid. mp = 129-131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.29 (s, 1H), 7.87 (s, 1H), 7.44 (s, 1H), 4.12 (s, 3H), 4.09 (s, 3H), 4.06 (s, 3H), 3.96 (s, 3H), 3.94 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.85, 169.46, 151.79, 151.46, 149.68, 148.57, 143.42, 133.46, 132.28, 131.37, 130.33, 126.02, 125.80, 125.40, 124.76, 122.91, 119.35, 109.13, 105.81, 104.59, 61.49, 60.76, 56.15, 56.06, 56.04, 53.13, 52.86, 20.58; HRMS (ESI) calcd for $C_{26}H_{24}O_7$ [M + Na] 471.1414, found 471.1400.



Methyl 1,2,3,10,11-pentamethoxy-7-methyl-5-oxo-5H-phenanthro[1,10,9-cde]chromene-6-carboxylate (**11**)

To a stirred solution of **9b** (37 mg, 0.072 mmol) in dichloromethane (3 ml) under argon was added dropwise a solution of PIFA (65.4 mg, 0.152 mmol) and BF_3•Et_2O (43.2 mg, 0.304 mmol) in dichloromethane (3 ml) at -40 °C. The reaction was stirred at -40 °C for 5 h, then quenched with $NaHCO_3$ (aq) and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 50/50) and could be recrystallized from hexanes/EtOAc to afford 32 mg (90%) of **11** as a red solid. Crystals suitable for x-ray diffraction were obtained by slow vapor diffusion of pentane into dichloromethane at -30 °C. mp = 176-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.48 (s, 1H), 7.87 (s, 1H), 4.17 (s, 6H), 4.16 (s, 3H), 4.12 (s, 3H), 4.09 (s, 3H), 3.98 (s, 7H), 2.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.84, 159.48, 150.13, 149.33, 148.54, 147.81, 140.03, 139.67, 134.56, 134.37, 128.86, 128.73, 125.27, 123.87, 122.70, 117.90, 116.22, 109.69, 109.49, 104.39, 62.33, 62.07, 61.05, 56.13, 56.03, 53.21, 19.88; HRMS (ESI) calcd for $C_{27}H_{24}O_9$ [M + H] 493.1499, found 493.1498.



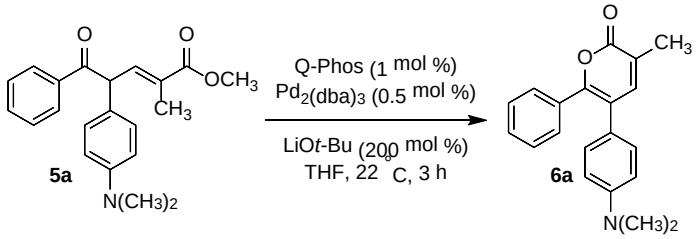
8,9-Dimethoxy-3,6,6-trimethyl-5,6-dihydro-2H-benzo[h]chromen-2-one (**12**)

To a 100-ml round-bottomed flask equipped with a magnetic stirring bar was added **6s** (140 mg, 0.466 mmol), AcOH (14 ml), and H_2SO_4 (0.1 ml). The flask was equipped with a reflux condenser, and the reaction was stirred and heated at 120 °C for 24 hours. The mixture was cooled and concentrated. The residue was dissolved in dichloromethane, and the mixture was washed three times with $NaHCO_3$ (aq). The organic layer was dried over Na_2SO_4 and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc 75/25 to 55/45) to afford 114 mg (81%) of **12** as a yellow solid. mp = 140-142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.04 (d, *J* = 1.1 Hz, 1H), 6.81 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H),

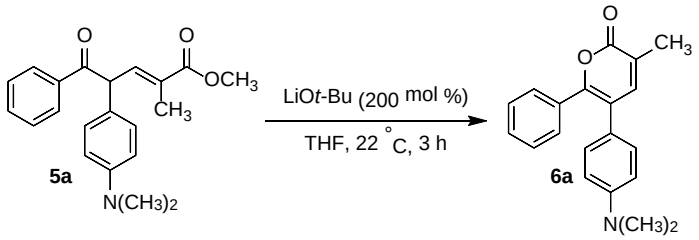
2.48 (s, 2H), 2.10 (d, J = 1.0 Hz, 3H), 1.24 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.81, 152.40, 150.66, 147.83, 142.82, 138.93, 122.24, 119.72, 109.70, 107.80, 106.12, 56.37, 56.11, 39.82, 34.06, 28.48, 16.93; HRMS (ESI) calcd for $C_{18}H_{20}O_4$ [M + H] 301.1434, found 301.1408.

Mechanistic Experimental Details

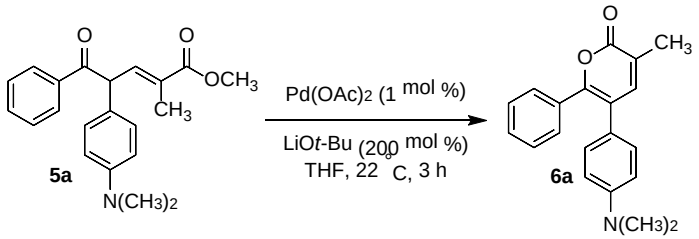
Experimental details for Table 1:



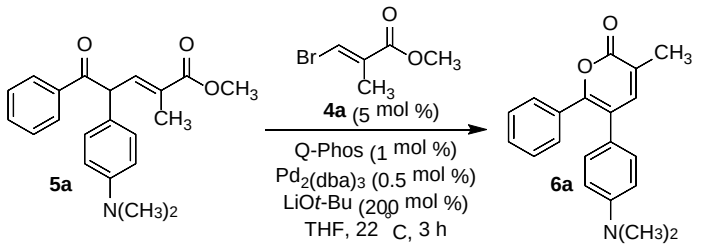
In an Ar filled glovebox, **5a** (5 mg, 0.015 mmol) prepared by the standard published procedure[11], LiO*t*-Bu (5 mg, 0.060 mmol), a solution of $Pd_2(dba)_3$ and Q-Phos (15 µL, 0.005*M* and 0.01*M*, respectively) in THF and THF (85 µl) were added to a crimp vial. The vial was crimped, taken out of the glovebox, and stirred at 22 ˚C. After 3 h, trimethoxybenzene (44 µl, 0.1*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 50% of **6a** was formed (Table 1, entry 1).



In an Ar filled glovebox, **5a** (5 mg, 0.015 mmol) prepared by the standard published procedure[11], LiO*t*-Bu (5 mg, 0.060 mmol), and THF (0.1 ml) were added to crimp vial. The vial was crimped, taken out of the glovebox, and stirred at 22 ˚C. After 3 h, trimethoxybenzene (44 µl, 0.1*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 52% of **6a** was formed (Table 1, entry 2).

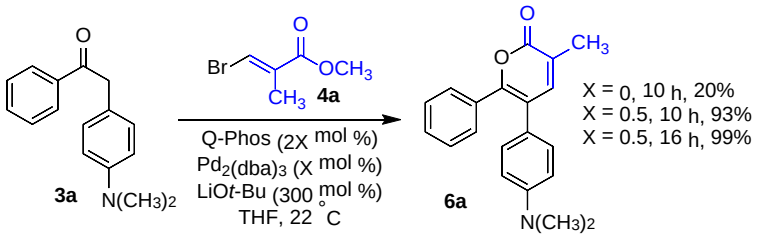


In an Ar filled glovebox, **5a** (5 mg, 0.015 mmol) prepared by the standard published procedure[11], LiO*t*-Bu (5 mg, 0.060 mmol), a solution of $Pd(OAc)_2$ (15 µL, 0.01*M* in THF, 0.00015 mmol) and THF (85 µl) were added to a crimp vial. The vial was crimped, taken out of the glovebox, and stirred at 22 ˚C. After 3 h, trimethoxybenzene (44 µl, 0.1*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 99% of **6a** was formed (Table 1, entry 3).



In an Ar filled glovebox, **5a** (5 mg, 0.015 mmol) prepared by the standard published procedure[11], LiO*t*-Bu (5 mg, 0.060 mmol), a solution of $Pd_2(dba)_3$ and Q-Phos (15 µL, 0.005*M* and 0.01*M*, respectively) in THF and THF (70 µl) were added to a crimp vial. The vial was crimped, taken out of the glovebox, **4a** (15 µL, 0.05*M* in THF, 0.00075 mmol) was added and stirred at 22 ˚C. After 3 h, trimethoxybenzene (44 µl, 0.1*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 99% of **6a** was formed (Table 1, entry 4).

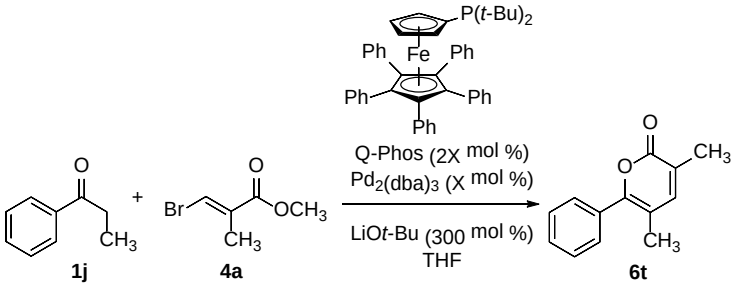
Experimental details for Figure 2:



In an Ar filled glovebox, **3a** (120 mg, 0.5 mmol), LiO*t*-Bu (120 mg, 1.5 mmol), and THF (2 ml) were added to a crimp vial. The vial was crimped, taken out of the glovebox, **4a** (94 mg, 0.525 mmol) was added and stirred at 22 ˚C. After 10 h, trimethoxybenzene (0.5 ml, 0.33*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 20% of **6a** was formed.

In an Ar filled glovebox, **3a** (120 mg, 0.5 mmol), LiO*t*-Bu (120 mg, 1.5 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) and Q-Phos (3.6 mg, 0.005 mmol) and THF (2 ml) were added to a crimp vial. The vial was crimped, taken out of the glovebox, **4a** (94 mg, 0.525 mmol) was added and stirred at 22 ˚C. After 10 h, trimethoxybenzene (0.5 ml, 0.33*M* in toluene) was added as an internal standard. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Crude NMR indicated that 93% of **6a** was formed. The same reaction was conducted for 16 h and resulted in the formation of 99% of **6a**, as determined by crude NMR.

Two-Component Synthesis of α-Pyrones Optimization and Scope



1j **4a** **6t**

entry	X	base	time (h)	temperature (˚C)	yield (%)
1	0.5	LiOtBu	0.5	22	99
2	0.25	LiOtBu	1.5	22	93
3	0.001	LiOtBu	16	22	99
4	0	LiOtBu	16	22	99
5	0	LiOtBu	4	0	78
6	0	LiOtBu	16	0→22	99
7	0.5	LiOtBu	16	0→22	99
8	0	NaOtBu	16	22	23
9	0	KOtBu	16	22	18
10	0	LiHMDS	1	22	5
11	0	LiTMP	16	22	48

Reactions were conducted on a 0.5-mmol scale. Yields are based on NMR internal standard.

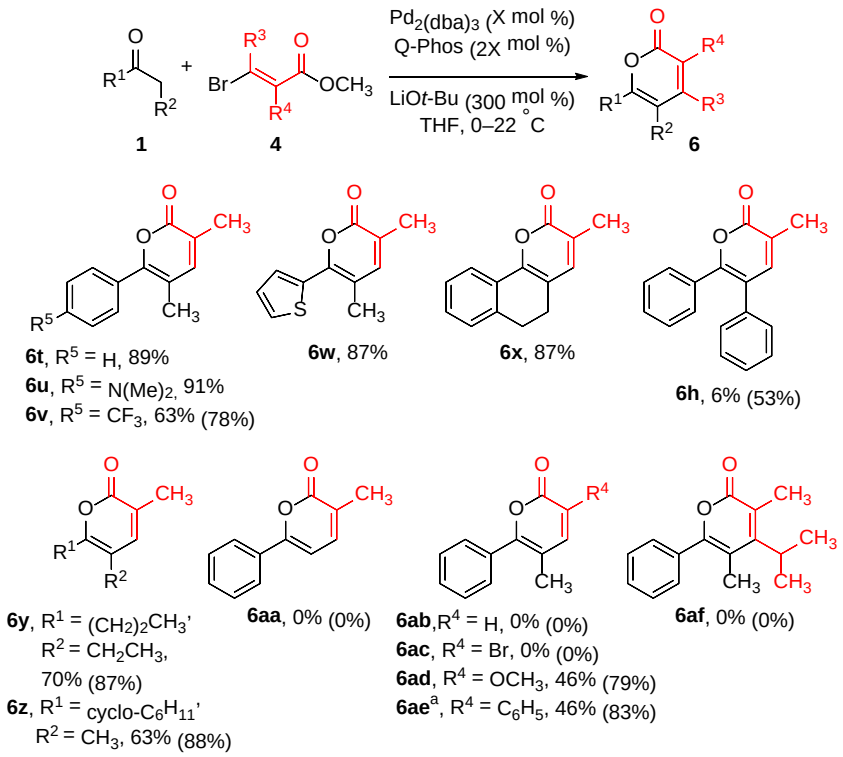


Figure SI1. Assessment of ketone and α-bromoacrylate substrates suitable for two-component α-pyrone synthesis. Isolated yields are shown for reactions without (no parentheses) and with Pd catalyst (in parentheses) in which X = 0 and X = 0.5, respectively. Reactions were conducted on a 0.5-mmol scale. [a]The corresponding ethyl acrylate was employed.

Two-Component Synthesis of α-Pyrones: Experimental Details

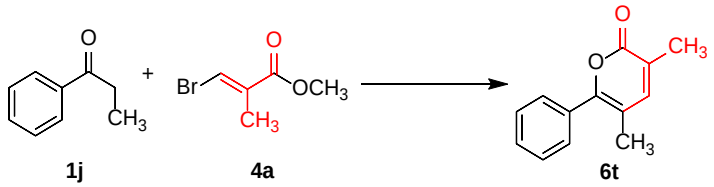
General Procedure for Two-Component Catalyst- and Ligand-Free α-Pyrone Synthesis

In a glove box, $LiOtBu_{(s)}$ (120 mg, 1.5 mmol) was added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (1 mL) was added, and the vial was taken out of the glove box and stirred at 0 °C. The ketone (0.500 mmol) was added dropwise to the stirred solution. After 5 min, the β-bromoacrylate (0.525 mmol) was added and stirred at 0 °C and was warmed to 22 °C over 16 h as a standard reaction time. The reaction mixture was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc) to afford the α-pyrone.

General Procedure for Two-Component Synthesis of α-Pyrones Employing a Palladium Catalyst

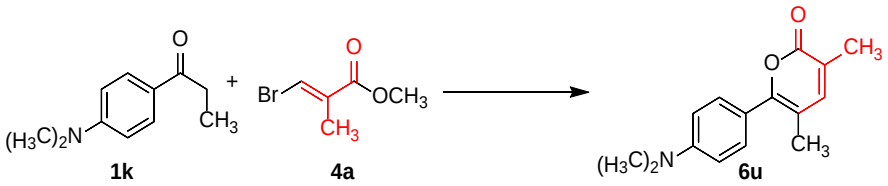
In a glove box, $LiOtBu_{(s)}$ (120 mg, 1.5 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), and Q-Phos (3.6 mg, 0.005 mmol) were added to a 10-mL crimp cap vial containing a stir bar. The vial was crimped, THF (1 mL) was added, and the vial was taken out of the glove box and stirred at 0 °C. The ketone (0.500 mmol) was added dropwise to the stirred solution. After 5 min, the β-bromoacrylate (0.525 mmol) was added and stirred at 0 °C and was warmed to 22 °C over 16 h as a standard reaction time. The reaction mixture

was diluted with ethyl acetate (5 ml), passed through a silica plug with ethyl acetate as eluent (20 ml), and concentrated. Purification was achieved by MPLC (silica gel, hexane/EtOAc) to afford the α-pyrone.



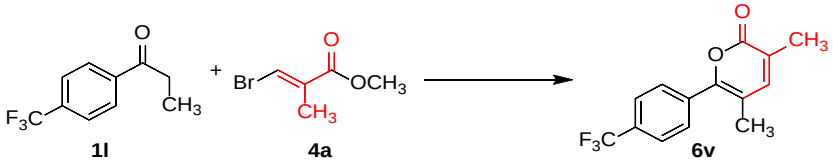
3,5-Dimethyl-6-phenyl-2H-pyran-2-one (**6t**)

Following the representative catalyst- and ligand-free procedure, **1j** (67 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 89 mg (89%) of **6t** as a white solid. mp = 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.45 – 7.36 (m, 3H), 7.09 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.76, 155.18, 144.95, 132.88, 129.64, 128.81, 128.51, 124.07, 111.56, 16.91, 16.59; HRMS (ESI) calcd for $C_{13}H_{12}O_2$ [M + H] 201.0910, found 201.0917. (lit[11] ^{1}H NMR, ^{13}C NMR)



6-(4-(Dimethylamino)phenyl)-3,5-dimethyl-2H-pyran-2-one (**6u**)

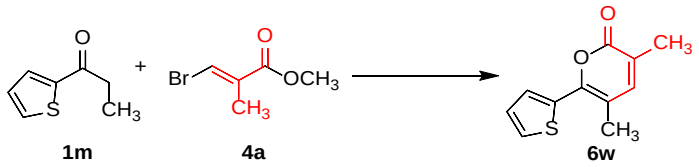
Following the representative catalyst- and ligand-free procedure, **1k** (89 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 90/10 to 80/20) to afford 111 mg (91%) of **6u** as a yellow solid. mp = 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.1 Hz, 2H), 7.05 (d, *J* = 1.1 Hz, 1H), 6.69 (d, *J* = 9.1 Hz, 2H), 2.99 (s, 6H), 2.14 (s, 3H), 2.09 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.29, 156.22, 151.04, 145.75, 129.81, 121.82, 120.40, 111.52, 109.75, 40.32, 17.37, 16.47; HRMS (ESI) calcd for $C_{15}H_{17}NO_2$ [M + H] 244.1332, found 244.1362.



3,5-Dimethyl-6-(4-(trifluoromethyl)phenyl)-2H-pyran-2-one (**6v**)

Following the representative catalyst- and ligand-free procedure, **1l** (101 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5) to afford 84 mg (63%) of **6v** as a white solid.

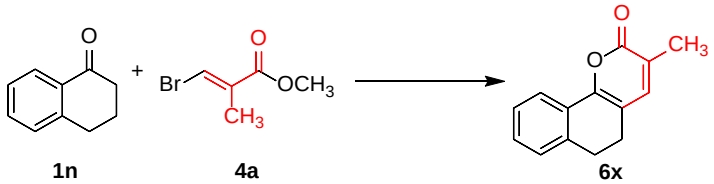
Following the representative procedure employing a Pd catalyst, 104 mg (78%) of **6v** was obtained after MPLC purification. mp = 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.11 (d, *J* = 1.2 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23, 153.25, 144.66, 136.18, 131.33 (q, *J* = 32.8 Hz), 129.12, 125.486 (q, *J* = 3.7 Hz), 125.20, 124.00 (q, *J* = 270.8 Hz), 112.75, 16.83, 16.61; ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.03; HRMS (ESI) calcd for $C_{14}H_{11}F_3O_2$ [M + H] 269.0784, found 269.0760.



1m **4a** **6w**

3,5-Dimethyl-6-(thiophen-2-yl)-2H-pyran-2-one (**6w**)

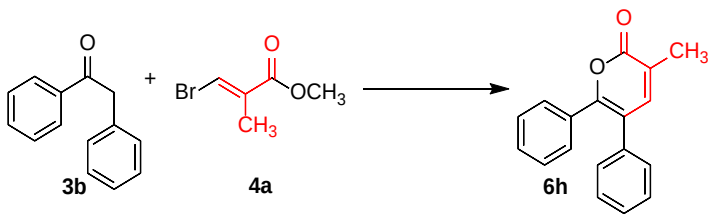
Following the representative catalyst- and ligand-free procedure, **1m** (70 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 80/20) to afford 90 mg (87%) of **6w** as a yellow solid. mp = 95-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.05 – 7.02 (m, 1H), 2.22 (s, 3H), 2.08 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.83, 150.25, 145.62, 135.27, 128.39, 128.30, 127.76, 123.41, 110.63, 17.79, 16.64; HRMS (ESI) calcd for $C_{11}H_{10}O_2S$ [M + H] 207.0474, found 207.0450.



1n **4a** **6x**

3-Methyl-5,6-dihydro-2H-benzo[h]chromen-2-one (**6x**)

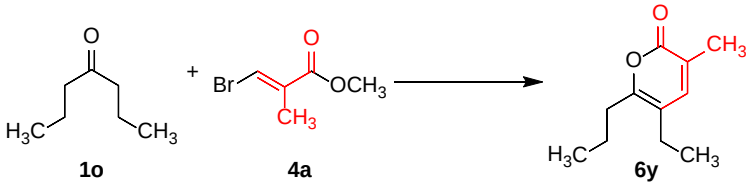
Following the representative catalyst- and ligand-free procedure, **1n** (73 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 90/10 to 75/25) to afford 92 mg (87%) of **6x** as a white solid. mp = 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 1H), 7.27 – 7.24 (m, 2H), 7.19 – 7.13 (m, 1H), 7.08 – 7.04 (m, 1H), 2.89 (d, *J* = 7.6 Hz, 2H), 2.63 (d, *J* = 7.6 Hz, 2H), 2.12 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54, 152.82, 142.20, 136.78, 129.80, 128.41, 128.03, 127.29, 123.95, 122.92, 112.46, 27.73, 24.69, 17.04; HRMS (ESI) calcd for $C_{14}H_{12}O_2$ [M + H] 213.0910, found 213.0887.



3-Methyl-5,6-diphenyl-2H-pyran-2-one (**6h**)

Following the representative catalyst- and ligand-free procedure, **3b** (98 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5 to 85/15) to afford 8 mg (6%) of **6h** as a white solid.

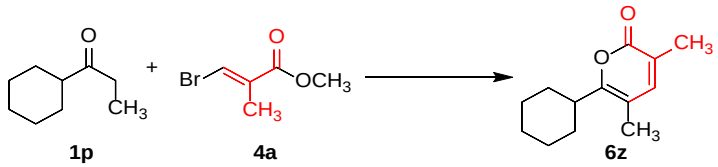
Following the representative procedure employing a Pd catalyst, 69 mg (53%) of **6h** was obtained after MPLC purification. mp = 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 11H), 2.20 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ163.42, 155.61, 144.30, 136.77, 132.41, 129.77, 129.43, 129.30, 129.11, 128.32, 128.00, 123.94, 118.23, 16.74; HRMS (ESI) calcd for $C_{18}H_{14}O_2$ [M + H] 263.1067, found 263.1083. (lit.[14] ^{1}H NMR, ^{13}C NMR)



5-Ethyl-3-methyl-6-propyl-2H-pyran-2-one (**6y**)

Following the representative catalyst- and ligand-free procedure, **1o** (51 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5) to afford 63 mg (70%) of **6y** as a colorless oil.

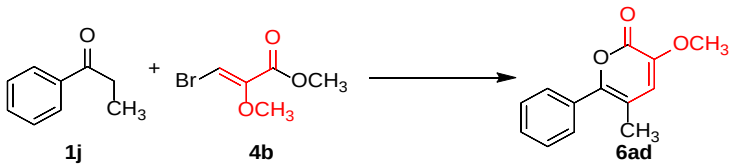
Following the representative procedure employing a Pd catalyst, 78 mg (87%) of **6y** was obtained after MPLC purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 1.2 Hz, 1H), 2.41 (t, *J* = 7.6, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 2.03 (d, *J* = 1.1 Hz, 3H), 1.64 (sex, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.42, 158.64, 143.03, 122.92, 116.83, 32.38, 22.69, 21.34, 16.55, 14.92, 13.84; HRMS (ESI) calcd for $C_{11}H_{16}O_2$ [M + H] 181.1223, found 181.1198.



6-Cyclohexyl-3,5-dimethyl-2H-pyran-2-one (**6z**)

Following the representative catalyst- and ligand-free procedure, **1p** (70 mg, 0.500 mmol) and **4a** (94 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 95/5) to afford 65 mg (63%) of **6z** as a colorless oil.

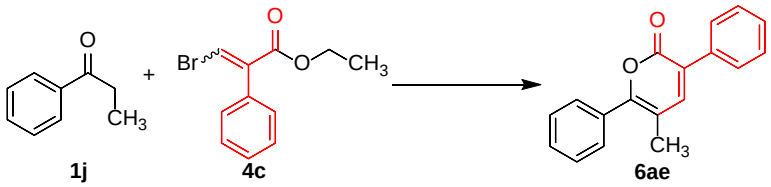
Following the representative procedure employing a Pd catalyst, 91 mg (88%) of **6z** was obtained after MPLC purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (d, *J* = 1.0 Hz, 1H), 2.55 – 2.44 (m, 1H), 1.98 (d, *J* = 1.0 Hz, 3H), 1.91 (s, 3H), 1.82 – 1.72 (m, 2H), 1.67 – 1.56 (m, 5H), 1.30 – 1.13 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.48, 162.29, 144.87, 122.10, 108.99, 39.66, 29.90, 26.31, 25.75, 16.47, 15.00; HRMS (ESI) calcd for $C_{13}H_{18}O_2$ [M + H] 207.1380, found 207.1400.



3-Methoxy-5-methyl-6-phenyl-2H-pyran-2-one (**6ad**)

Following the representative catalyst- and ligand-free procedure, **1j** (67 mg, 0.500 mmol) and **4b** (102 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 80/20 to 40/60) to afford 50 mg (46%) of **6ad** as a white solid.

Following the representative procedure employing a Pd catalyst, 85 mg (79%) of **6ad** was obtained after MPLC purification. mp = 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.42 – 7.32 (m, 3H), 6.43 (s, 1H), 3.82 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 149.08, 144.56, 132.58, 129.29, 128.75, 128.51, 118.66, 111.30, 56.38, 17.59; HRMS (ESI) calcd for $C_{13}H_{12}O_3$ [M + H] 217.0859, found 217.0862.



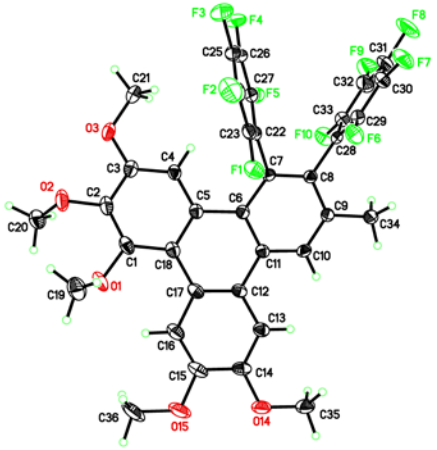
5-Methyl-3,6-diphenyl-2H-pyran-2-one (**6ae**)

Following the representative catalyst- and ligand-free procedure, **1j** (67 mg, 0.500 mmol) and **4c** (127 mg, 0.525 mmol) were stirred at 0 °C and warmed to 22 °C over 16 h. Purification was achieved by MPLC (silica gel, hexane/EtOAc 90/10 to 65/35) to afford 60 mg (46%) of **6ae** as a white solid.

Following the representative procedure employing a Pd catalyst, 109 mg (83%) of **6ae** was obtained after MPLC purification. mp = 162-164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.50 – 7.41 (m, 6H), 7.40 – 7.35 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 161.90, 156.76, 145.43, 134.83, 132.61, 130.02, 128.91, 128.72, 128.67, 128.62, 128.45, 126.04, 112.21, 17.20; HRMS (ESI) calcd for $C_{18}H_{14}O_2$ [M + H] 263.1067, found 263.1055.

X-Ray Crystallographic Data



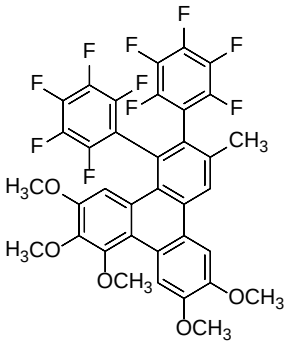
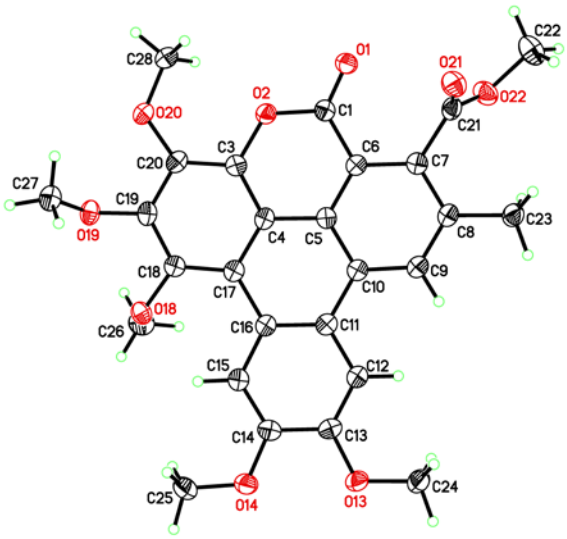


Table S1. Crystal data and structure refinement for **10a**

Identification code	nd1609
Empirical formula	$C_{76}H_{52}F_{20}O_{12}$
Formula weight	1537.17
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.1826(9) Å α = 90°
	b = 25.666(3) Å β = 95.407(2)°
	c = 31.715(4) Å γ = 90°
Volume	6631.0(13) $Å^3$
Z	4
Density (calculated)	1.540 $g.cm^{-3}$
Absorption coefficient (μ)	0.140 mm^{-1}
F(000)	3136
Crystal color, habit	colorless, rod
Crystal size	0.237 × 0.112 × 0.078 mm^3
θ range for data collection	1.022 to 26.378°
Index ranges	$-10 \le h \le 10$, $-32 \le k \le 32$, $-39 \le l \le 39$
Reflections collected	113081
Independent reflections	13556 [R_{int} = 0.0461]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 0.9362
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13556 / 6 / 998
Goodness-of-fit on F^2	1.027
Final R indices [I>2σ(I)]	R_1 = 0.0545, wR_2 = 0.1366
R indices (all data)	R_1 = 0.0770, wR_2 = 0.1502
Extinction coefficient	n/a
Largest diff. peak and hole	1.606 and -0.830 $e^-.Å^{-3}$



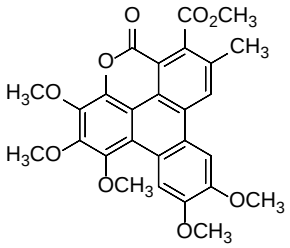


Table S2. Crystal data and structure refinement for **11**

Empirical formula	$C_{112}H_{106}Cl_8O_{37}$
Formula weight	2327.56
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 27.9493(7) Å α = 90°
	b = 14.6228(4) Å β = 105.0980(10)°
	c = 26.5088(7) Å γ = 90°
Volume	10460.1(5) $Å^3$
Z	4
Density (calculated)	1.478 $g.cm^{-3}$
Absorption coefficient (μ)	2.727 mm^{-1}
F(000)	4840
Crystal color, habit	yellow, tablet
Crystal size	0.336 × 0.156 × 0.044 mm^3
θ range for data collection	1.637 to 72.039°
Index ranges	$-34 \le h \le 34$, $-17 \le k \le 17$, $-32 \le l \le 32$
Reflections collected	250239
Independent reflections	20394 [R_{int} = 0.0470]
Completeness to θ = 67.679°	99.8 %
Absorption correction	Numerical
Max. and min. transmission	0.8644 and 0.6454
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20394 / 0 / 1451
Goodness-of-fit on F^2	1.076
Final R indices [I>2σ(I)]	R_1 = 0.0722, wR_2 = 0.1908
R indices (all data)	R_1 = 0.0756, wR_2 = 0.1934
Extinction coefficient	n/a
Largest diff. peak and hole	1.842 and -1.934 $e^-.Å^{-3}$

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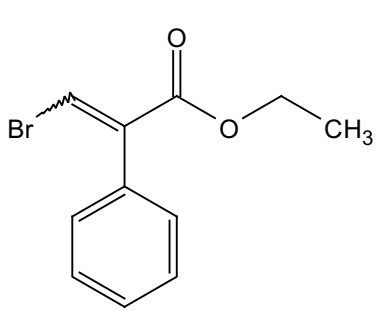

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4.26
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4.23
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1.37
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1.28

1.00
12.18
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2.80
3.86
4.30

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
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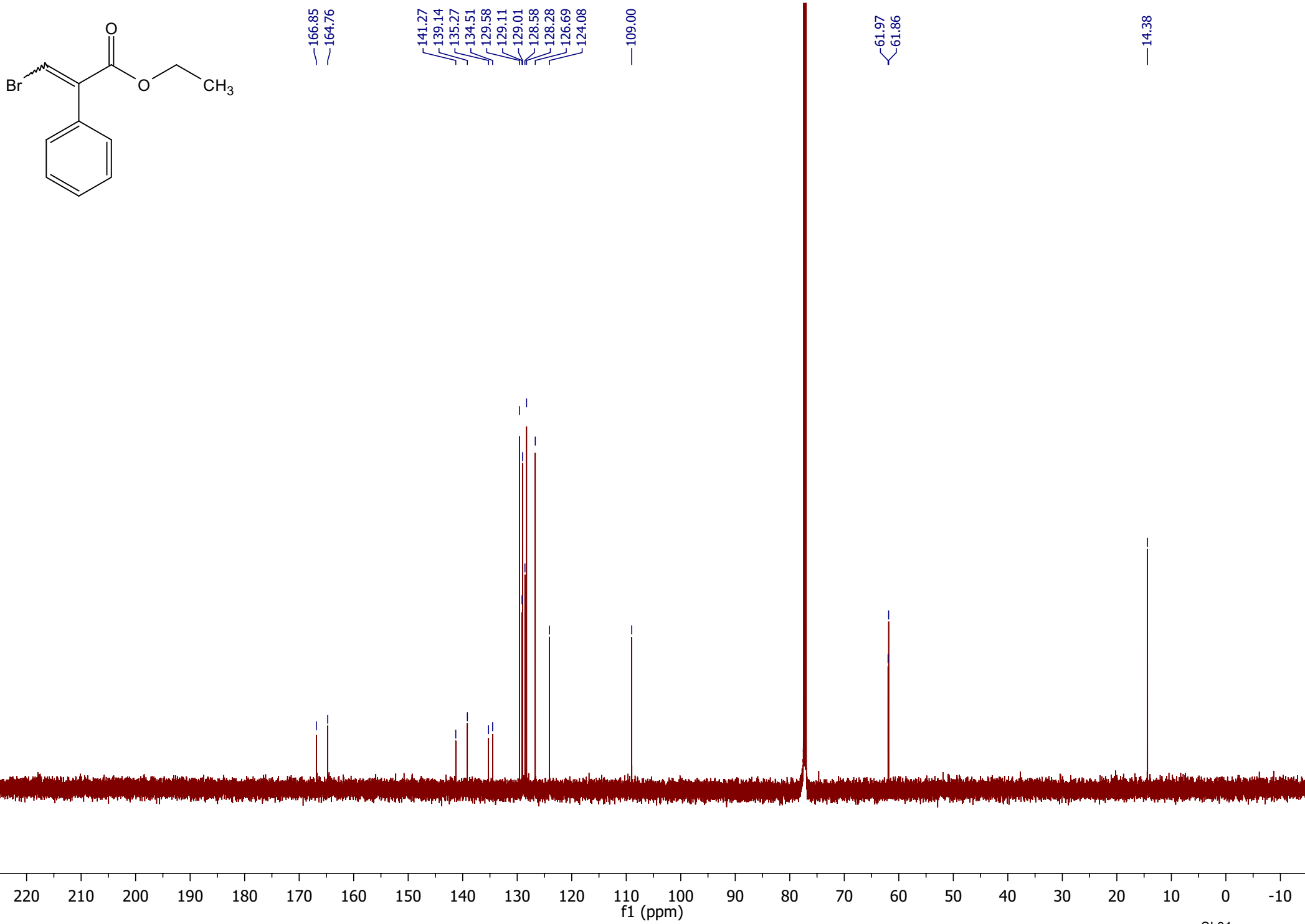
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200
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180
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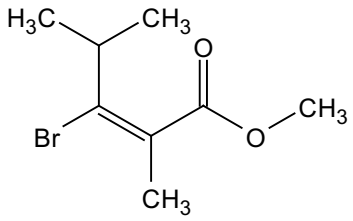
f1 (ppm)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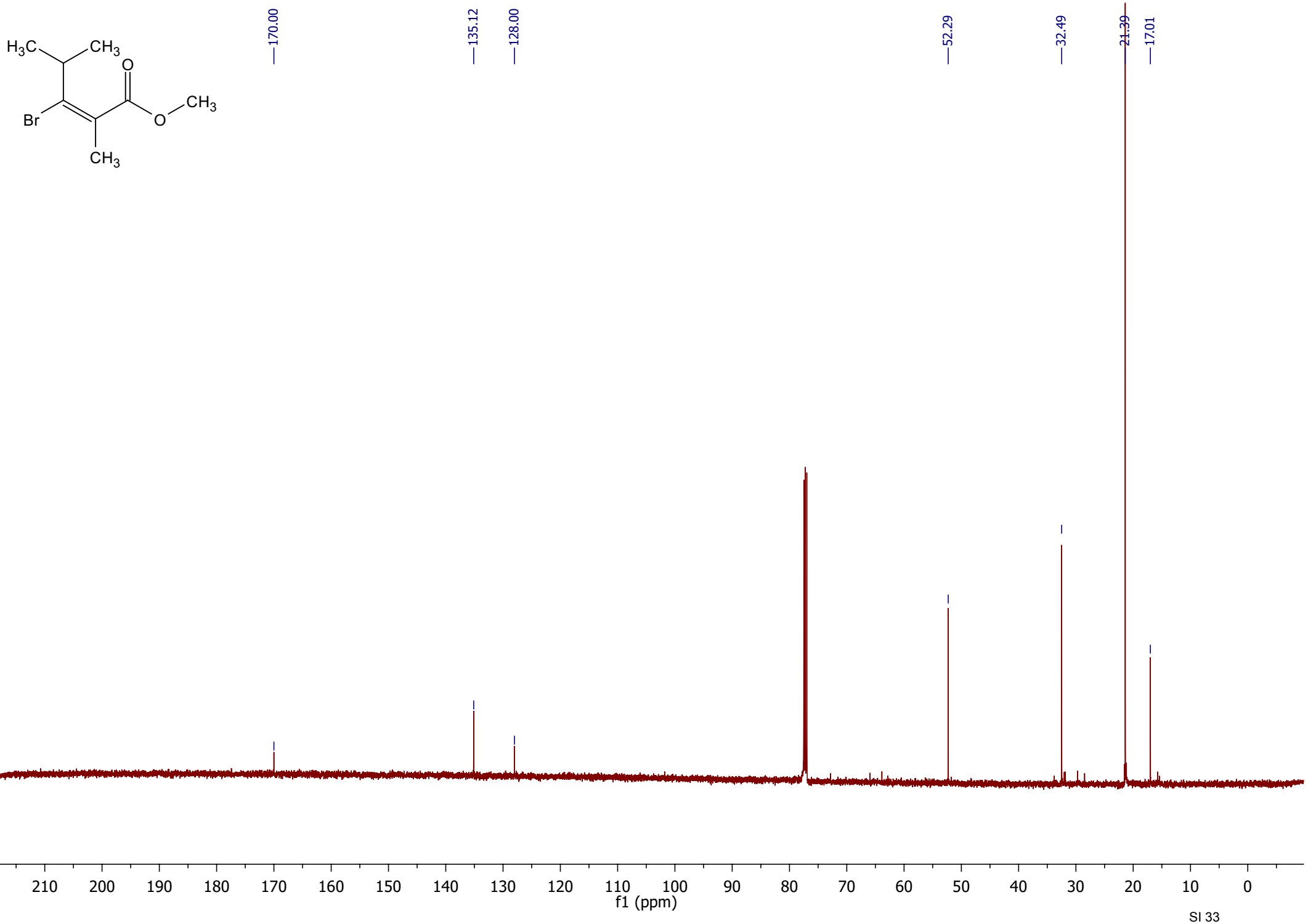
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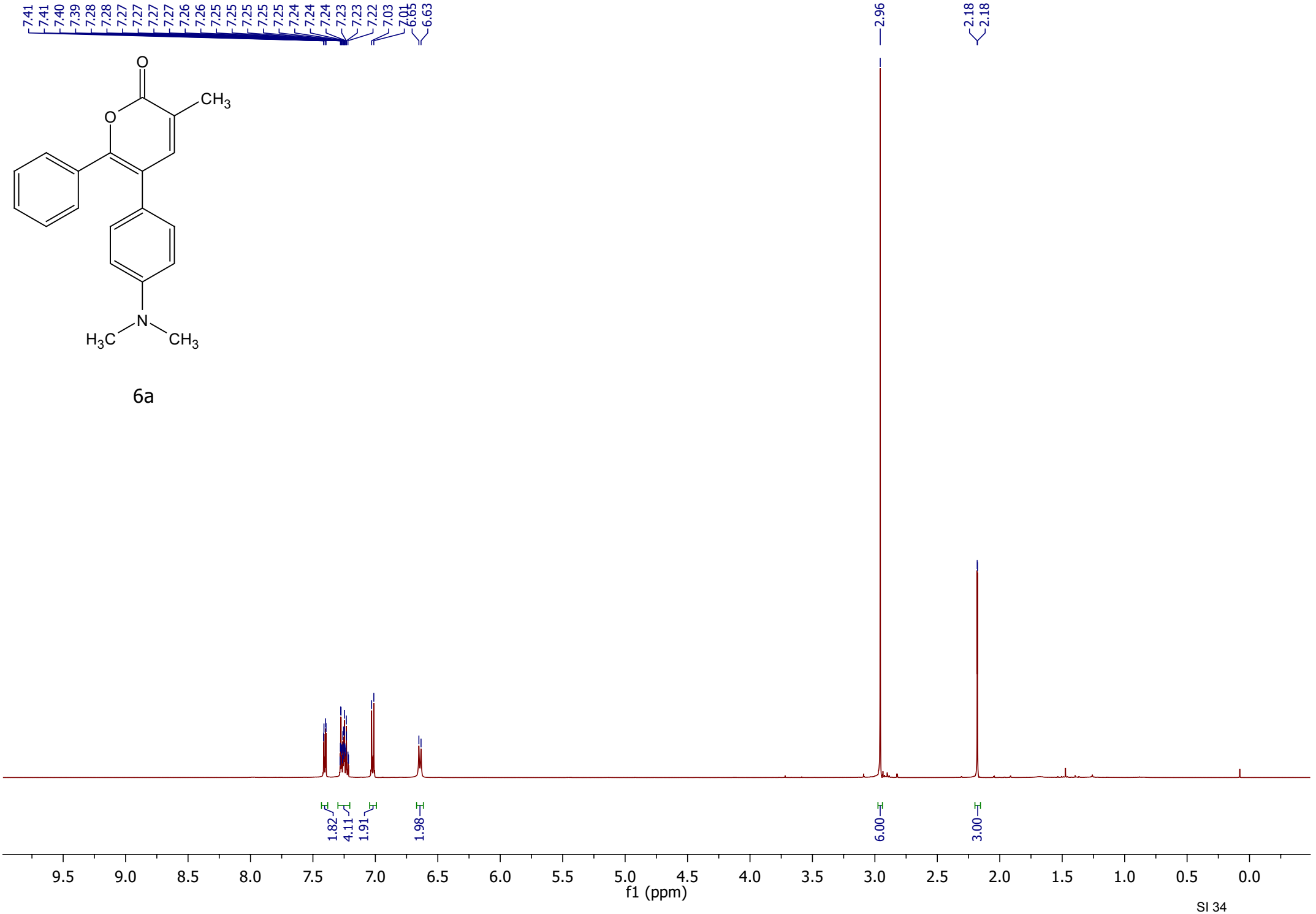
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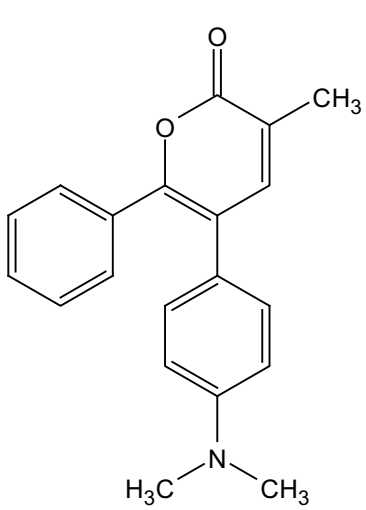
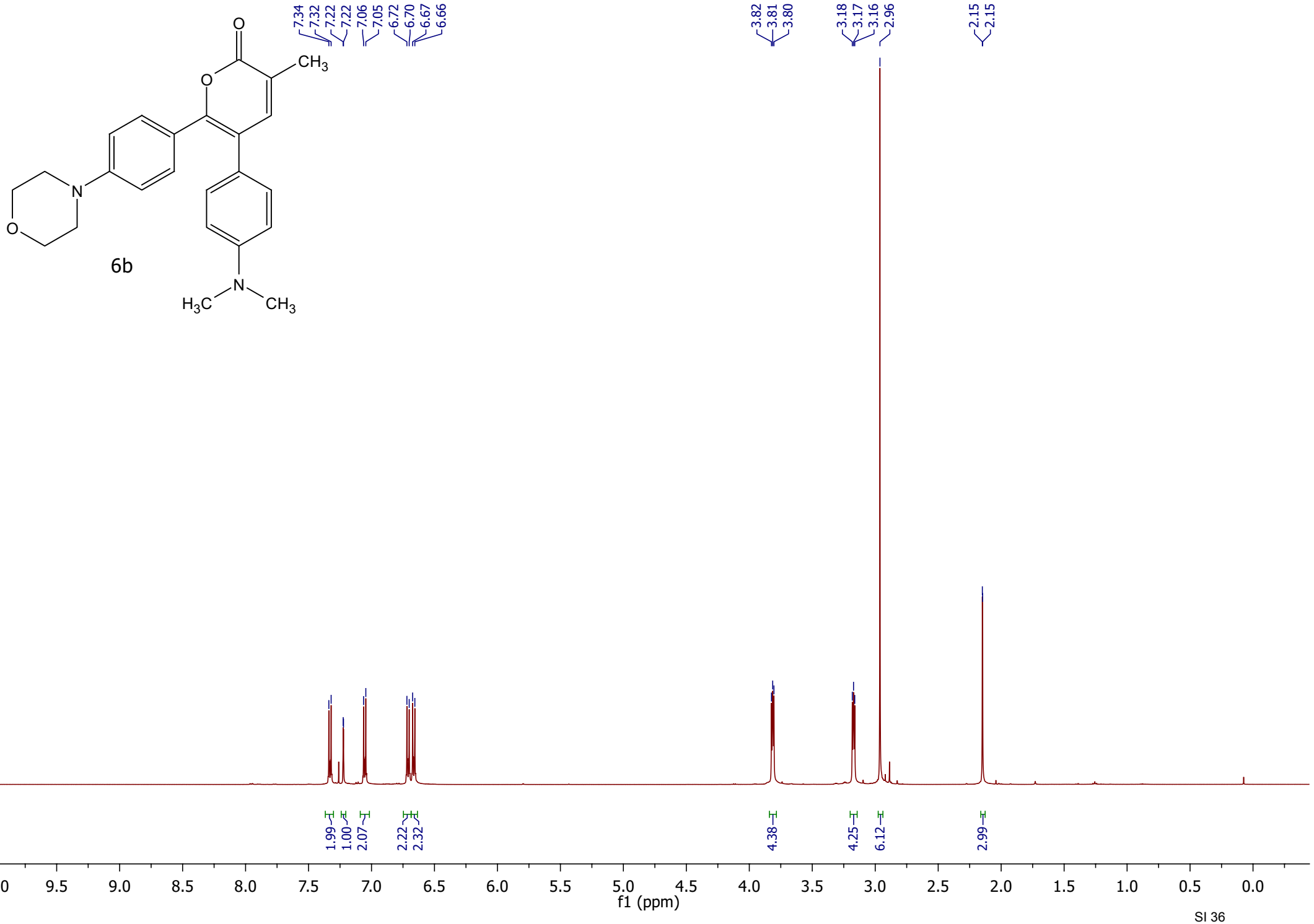
7.24
7.24
7.23
7.23
7.22
7.03
7.01
6.85
6.63
2.96
2.18
2.18
O
O
CH3
N
H3C
CH3
1.82
4.11
1.91
1.98
6.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

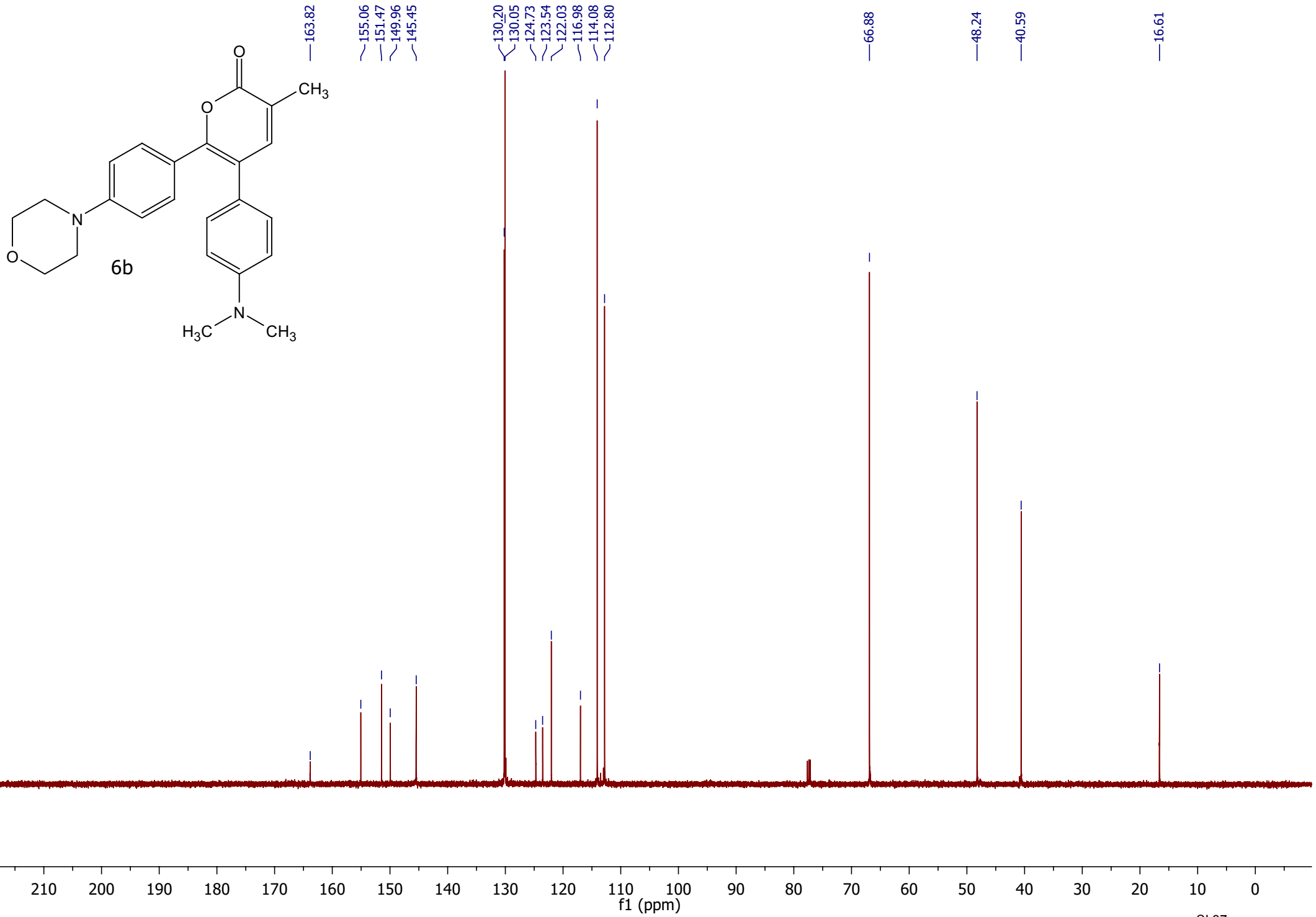
6a

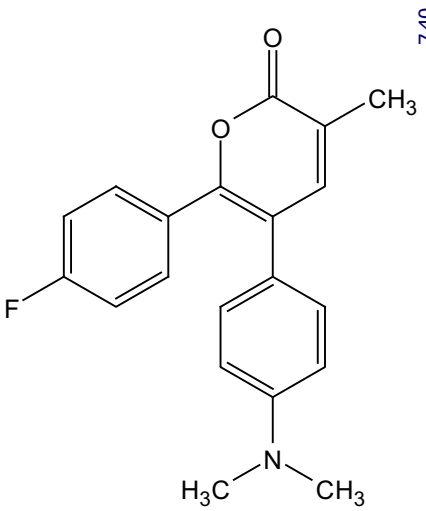

O
O
CH3
N
H3C
CH3

6a

163.66
154.66
150.06
145.01
132.98
130.07
129.37
129.20
128.26
124.00
123.61
118.33
112.71
40.58
16.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

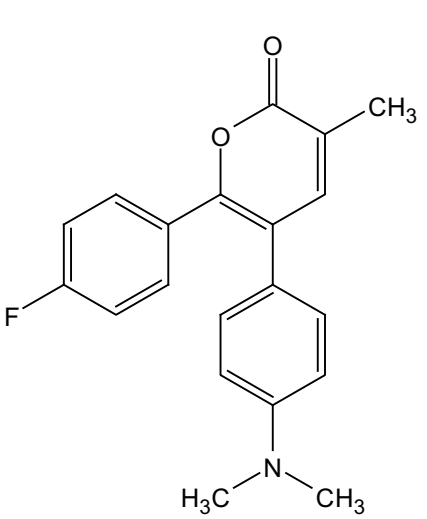

7.34
7.32
7.22
7.22
7.06
7.05
6.72
6.70
6.67
6.66
3.82
3.81
3.80
3.18
3.17
3.16
2.96
2.15
2.15
O
O
CH3
N
O
6b
N
H3C
CH3
1.99
1.00
2.07
2.22
2.32
4.38
4.25
6.12
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.82
155.06
151.47
149.96
145.45
130.20
130.05
124.73
123.54
122.03
116.98
114.08
112.80
66.88
48.24
40.59
16.61
O
O
CH3
N
O
6b
N
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
F
N
H3C
CH3

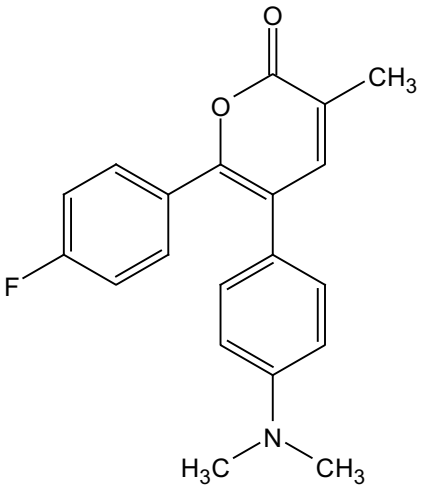
6c

7.40
7.39
7.38
7.37
7.26
7.26
7.01
6.99
6.93
6.92
6.90
6.65
6.63
2.96
2.17
2.17
1.63
0.94
1.87
1.77
2.00
5.58
2.82
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)


O
O
CH3
F
N
H3C
CH3

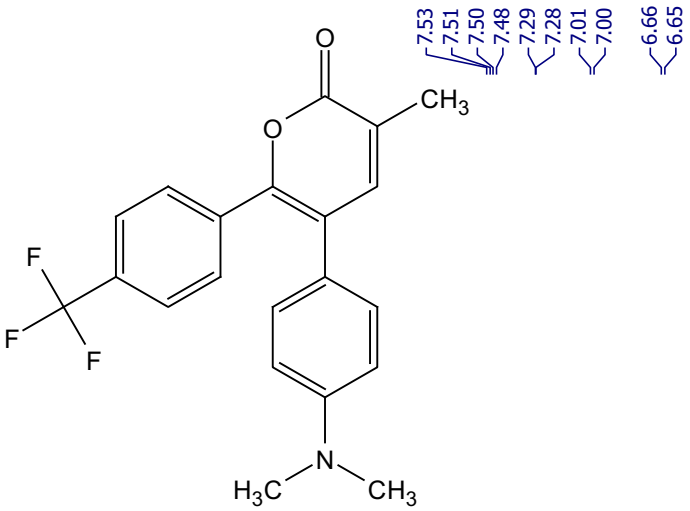
6c

164.15
163.50
162.16
153.62
150.12
144.96
131.26
131.19
130.02
129.14
129.11
123.68
123.65
118.23
115.50
115.33
112.71
40.53
16.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
F
N
H3C
CH3

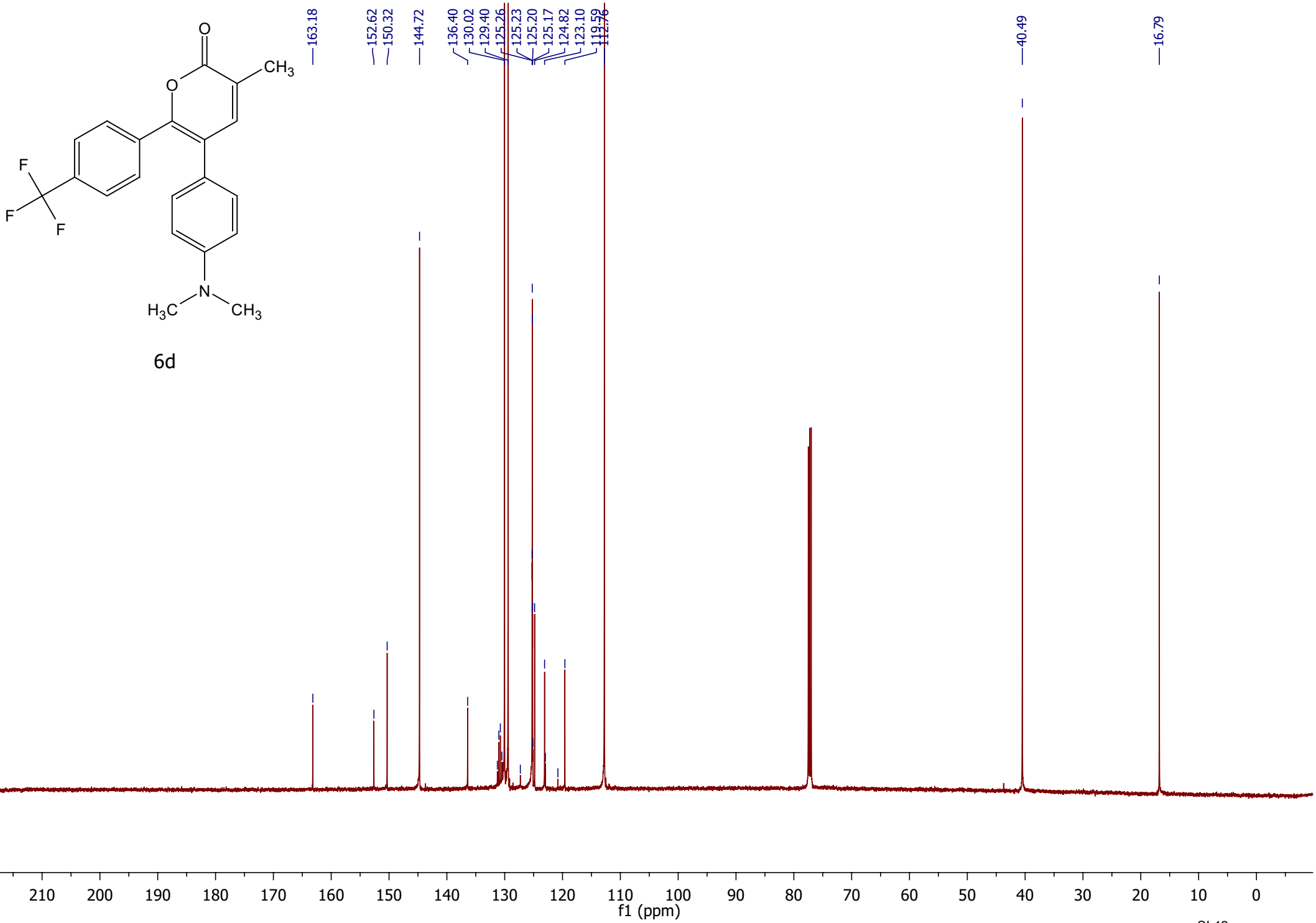
6c

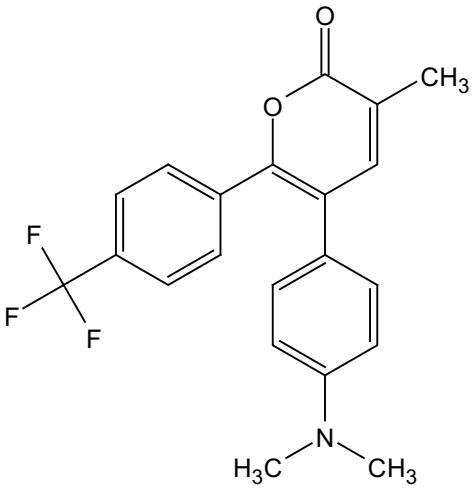
113.99
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


O
O
CH3
F
F
F
N
H3C
CH3

6d

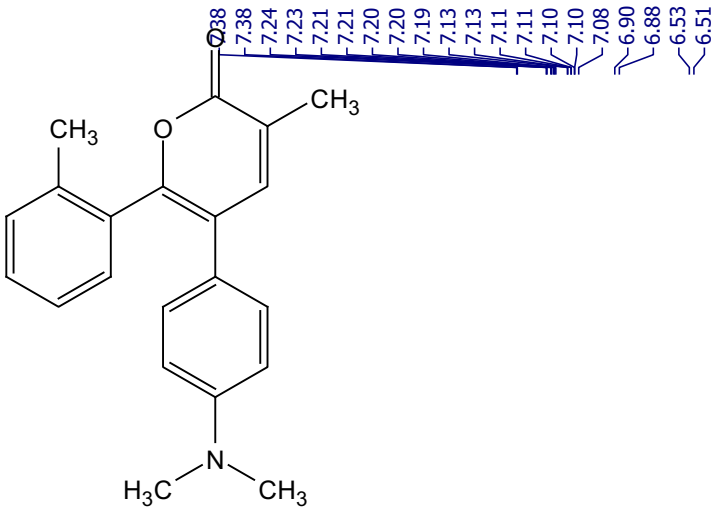
7.53
7.51
7.50
7.48
7.29
7.28
7.01
7.00
6.66
6.65
2.98
2.20
2.19
4.05
0.81
2.00
2.31
6.64
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
CH3
F
F
F
N
H3C
CH3
6d
163.18
152.62
150.32
144.72
136.40
130.02
129.40
125.26
125.23
125.20
125.17
124.82
123.10
119.59
112.78
40.49
16.79
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
F
F
F
N
H3C
CH3

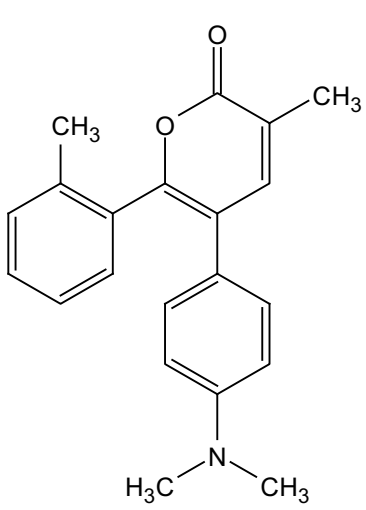
6d

66.01
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


O
CH3
CH3
O
N
H3C
CH3

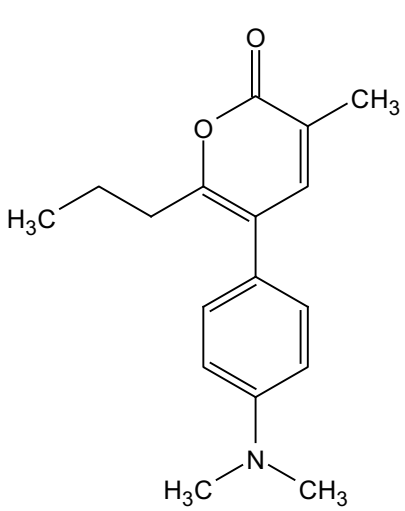
6e

7.38
7.38
7.24
7.23
7.21
7.21
7.20
7.20
7.19
7.13
7.13
7.11
7.11
7.10
7.10
7.08
6.90
6.88
6.53
6.51
2.88
2.20
2.20
2.13
1.00
1.92
2.04
2.07
2.21
6.53
3.23
3.13
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)


O
CH3
CH3
O
N
H3C
CH3

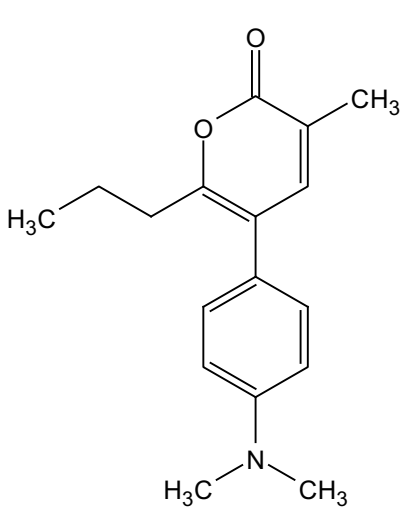
6e

163.77
155.55
149.79
143.91
137.30
133.13
130.71
130.61
129.57
129.50
125.87
124.10
123.29
119.32
112.35
40.45
20.08
16.86
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
H3C
N
H3C
CH3

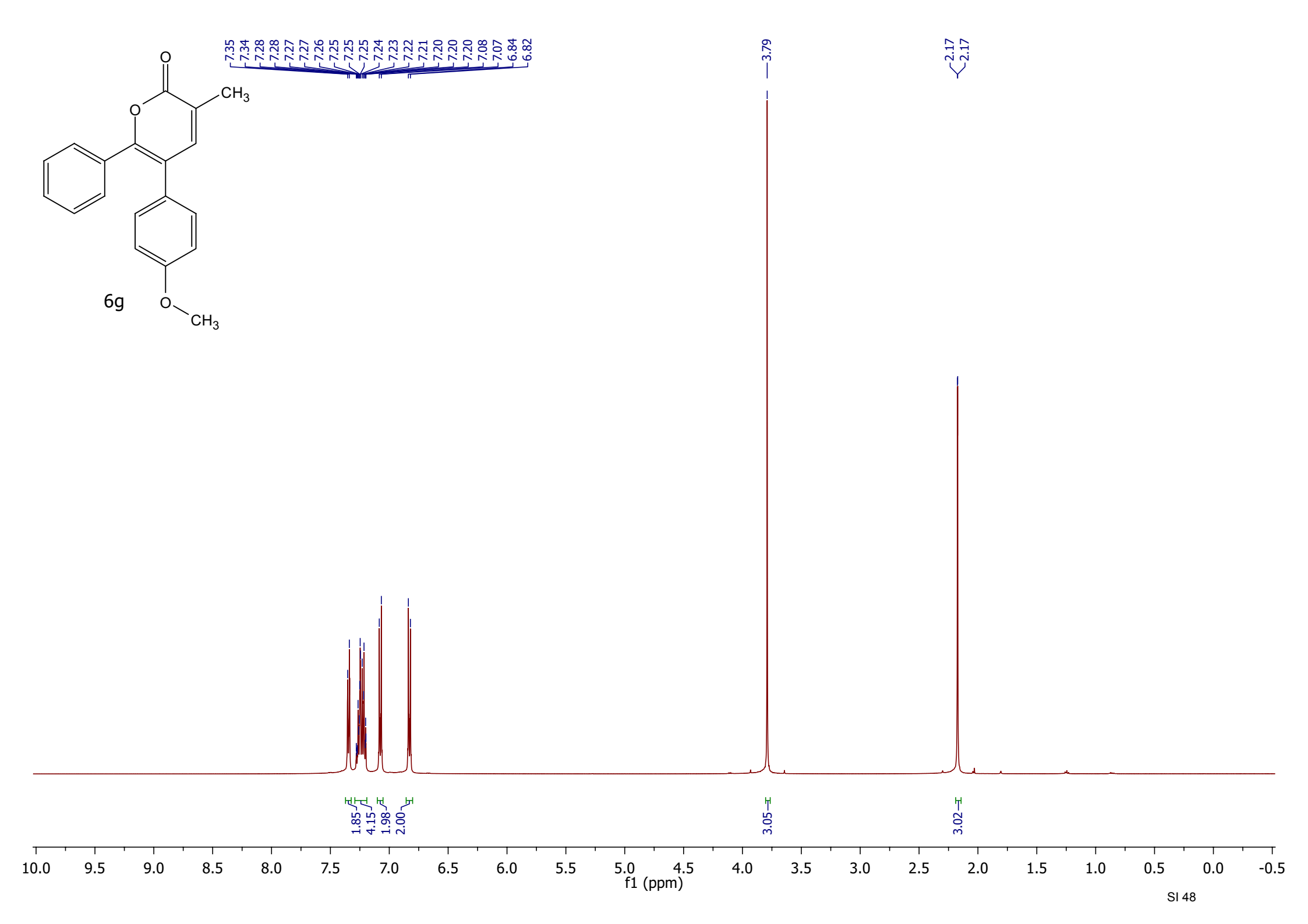
6f

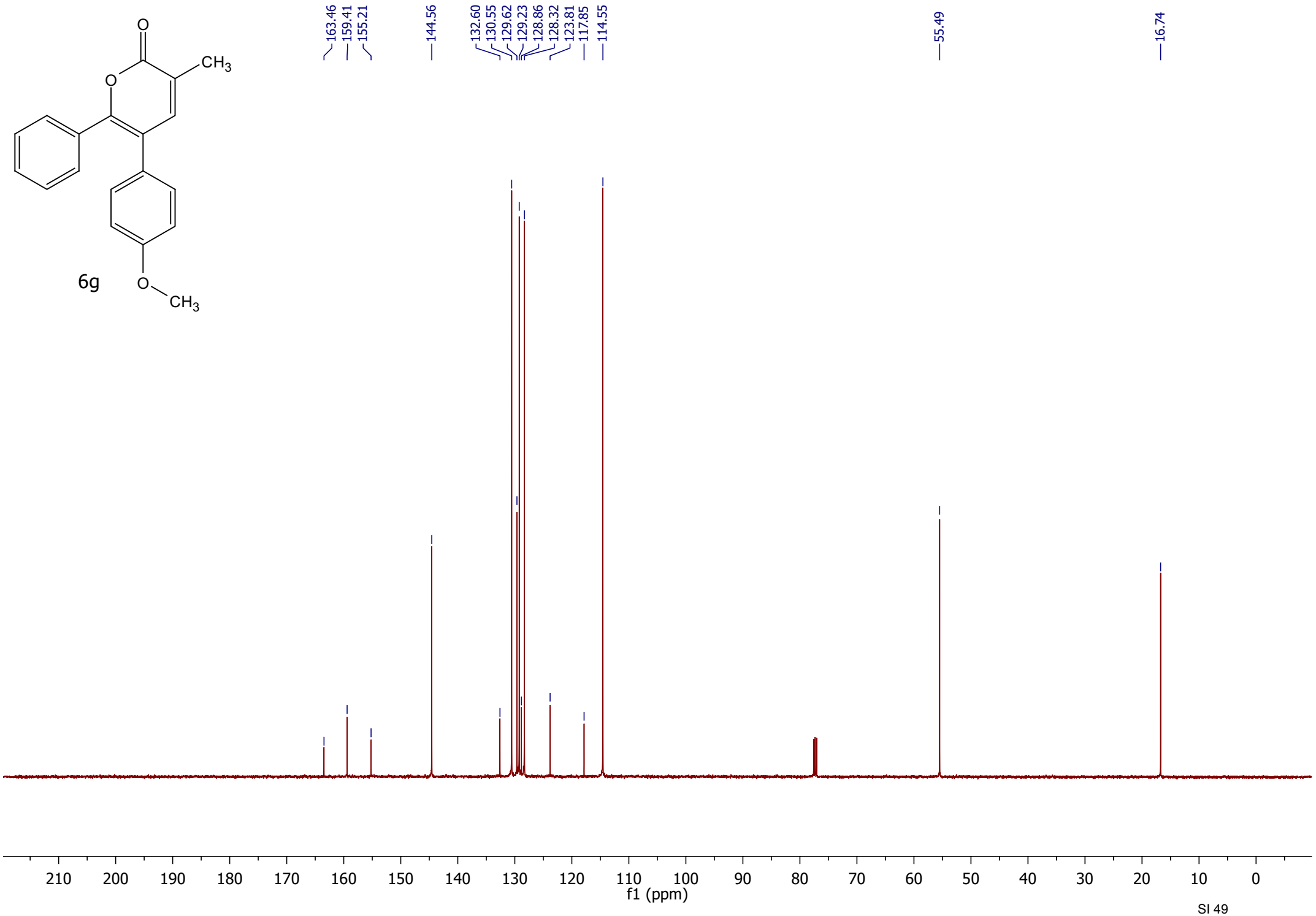
7.12
7.12
7.10
7.07
6.75
6.73
2.99
2.49
2.47
2.45
2.10
2.10
1.74
1.72
1.70
1.68
1.66
1.64
0.90
0.88
0.86
0.82
1.80
2.02
5.83
2.15
3.00
2.18
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

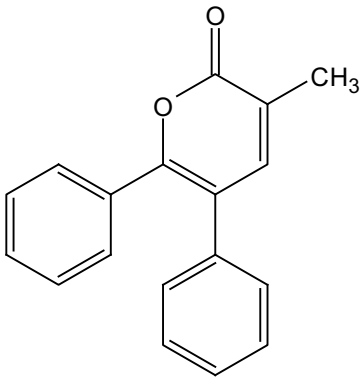

O
O
CH3
H3C
N
H3C
CH3

6f

164.38
159.74
150.09
144.14
129.81
124.09
122.21
118.32
112.54
40.67
33.24
21.45
16.64
13.94
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

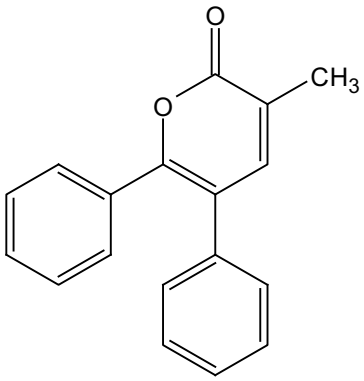

7.35
7.34
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.20
7.08
7.07
6.84
6.82
3.79
2.17
2.17
O
O
CH3
6g
O
CH3
1.85
4.15
1.98
2.00
3.05
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.46
159.41
155.21
144.56
132.60
130.55
129.62
129.23
128.86
128.32
123.81
117.85
114.55
55.49
16.74
O
O
CH3
6g
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3

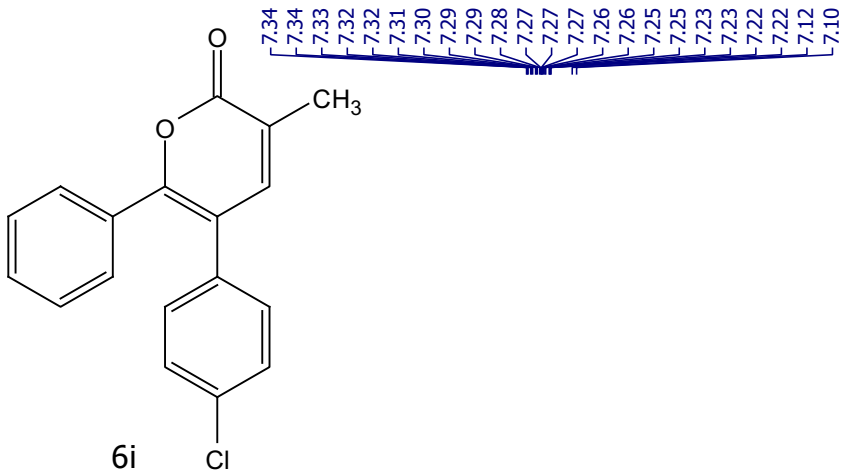
6h

7.25
7.24
6.96
6.95
6.84
6.84
6.46
6.46
1.88
1.87
2.09
2.92
4.84
1.01
3.00
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
f1 (ppm)


O
O
CH3

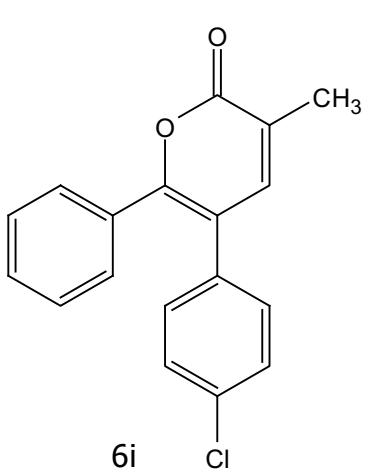
6h

163.37
155.64
144.23
136.83
129.76
129.45
129.31
129.11
128.32
128.00
123.96
118.23
16.70
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
Cl

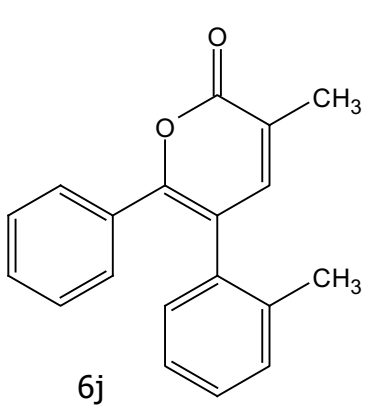
6i

7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.22
7.22
7.12
7.10
2.20
2.19
8.09
2.00
3.35
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)

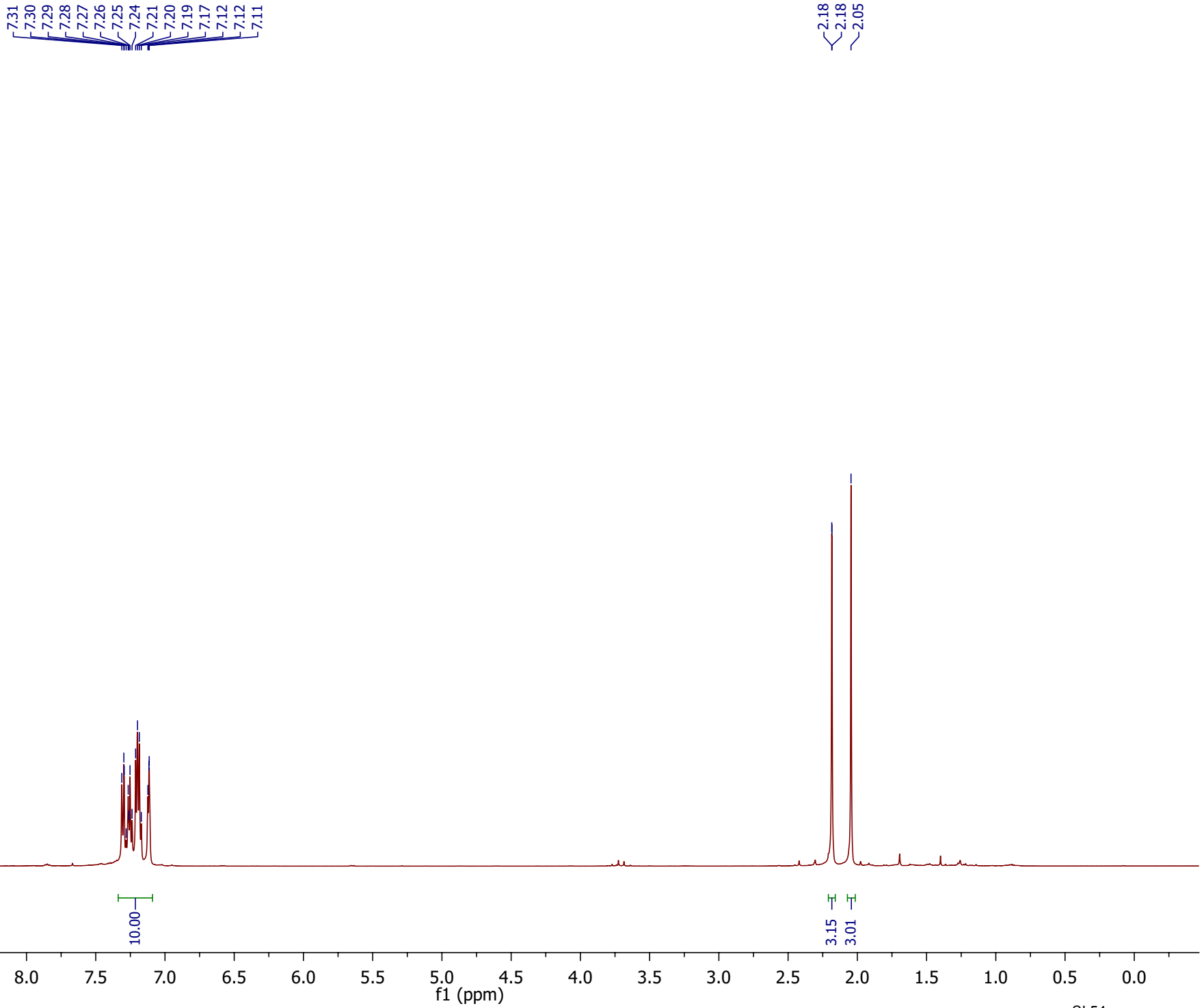

O
O
CH3
Cl

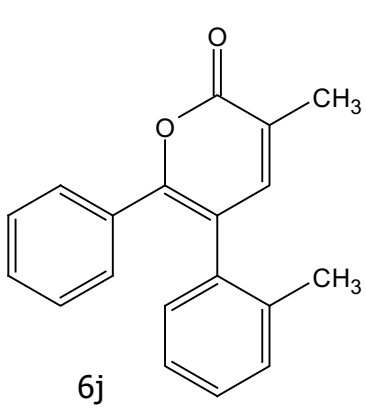
6i

165.04
157.84
145.55
137.22
136.02
132.70
131.92
131.29
131.22
130.40
18.64
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
CH3

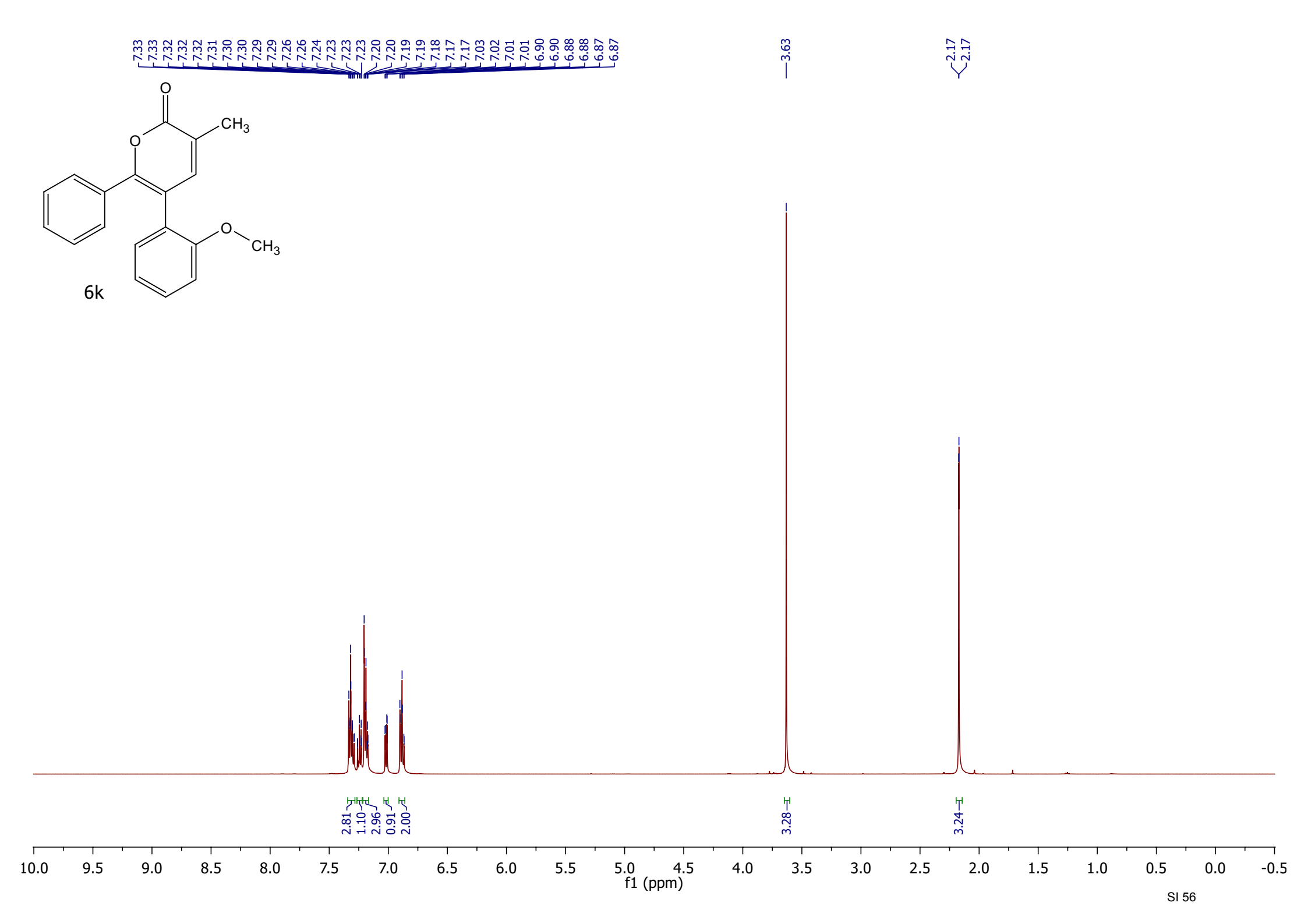
6j

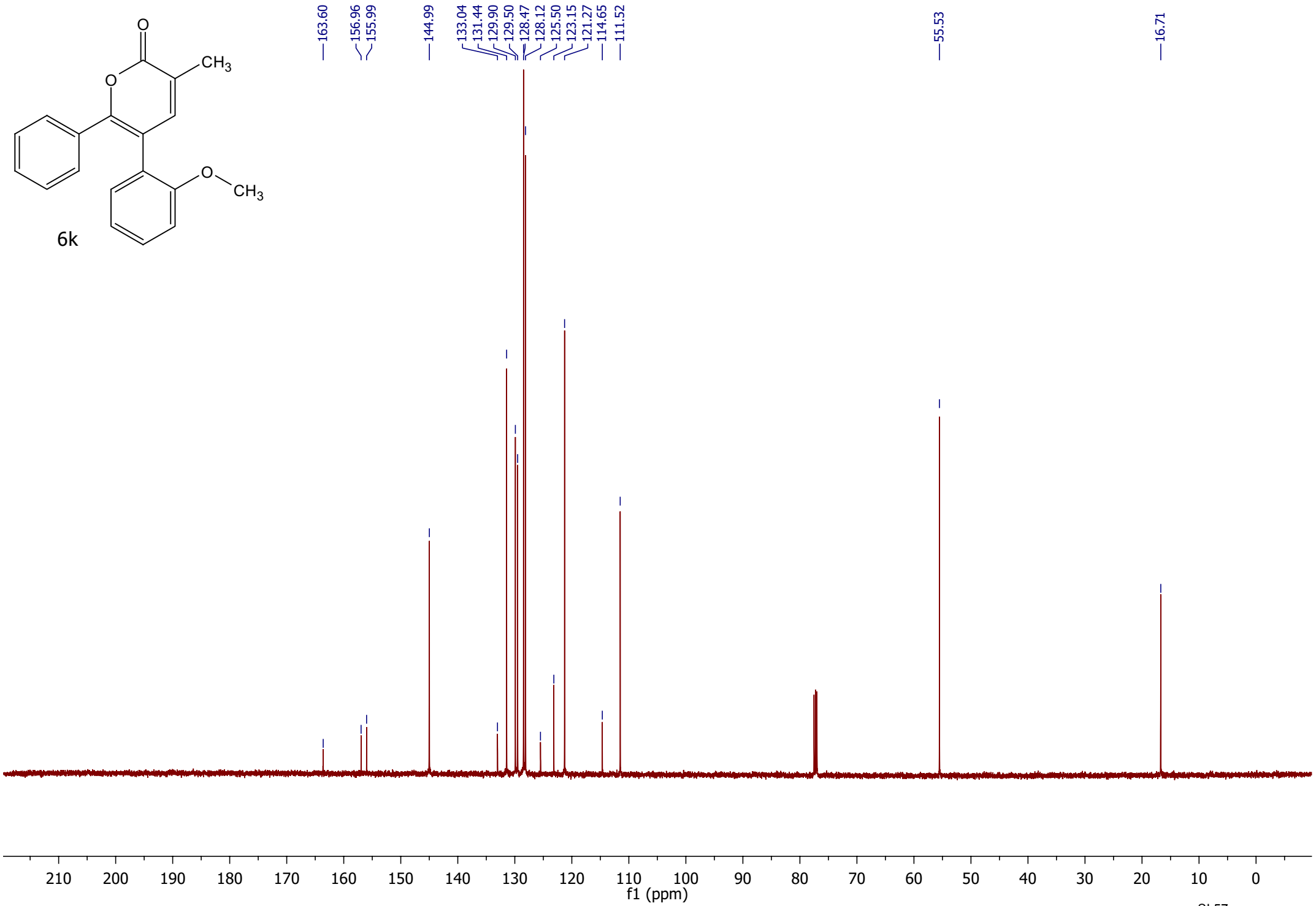

7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.21
7.20
7.19
7.17
7.12
7.12
7.11
2.18
2.18
2.05
10.00
3.15
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
CH3
CH3

6j

163.50
155.17
144.52
130.93
130.20
129.73
128.61
128.37
128.26
126.83
123.75
117.29
20.02
16.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.26
7.26
7.24
7.23
7.23
7.23
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.03
7.02
7.01
7.01
6.90
6.90
6.88
6.88
6.87
6.87
3.63
2.17
2.17
O
O
CH3
O
CH3
6k
2.81
1.10
2.96
0.91
2.00
3.28
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)


O
O
CH3
O
CH3
6k
163.60
156.96
155.99
144.99
133.04
131.44
129.90
129.50
128.47
128.12
125.50
123.15
121.27
114.65
111.52
55.53
16.71
210
200
190
180
170
160
150
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130
120
110
100
90
80
70
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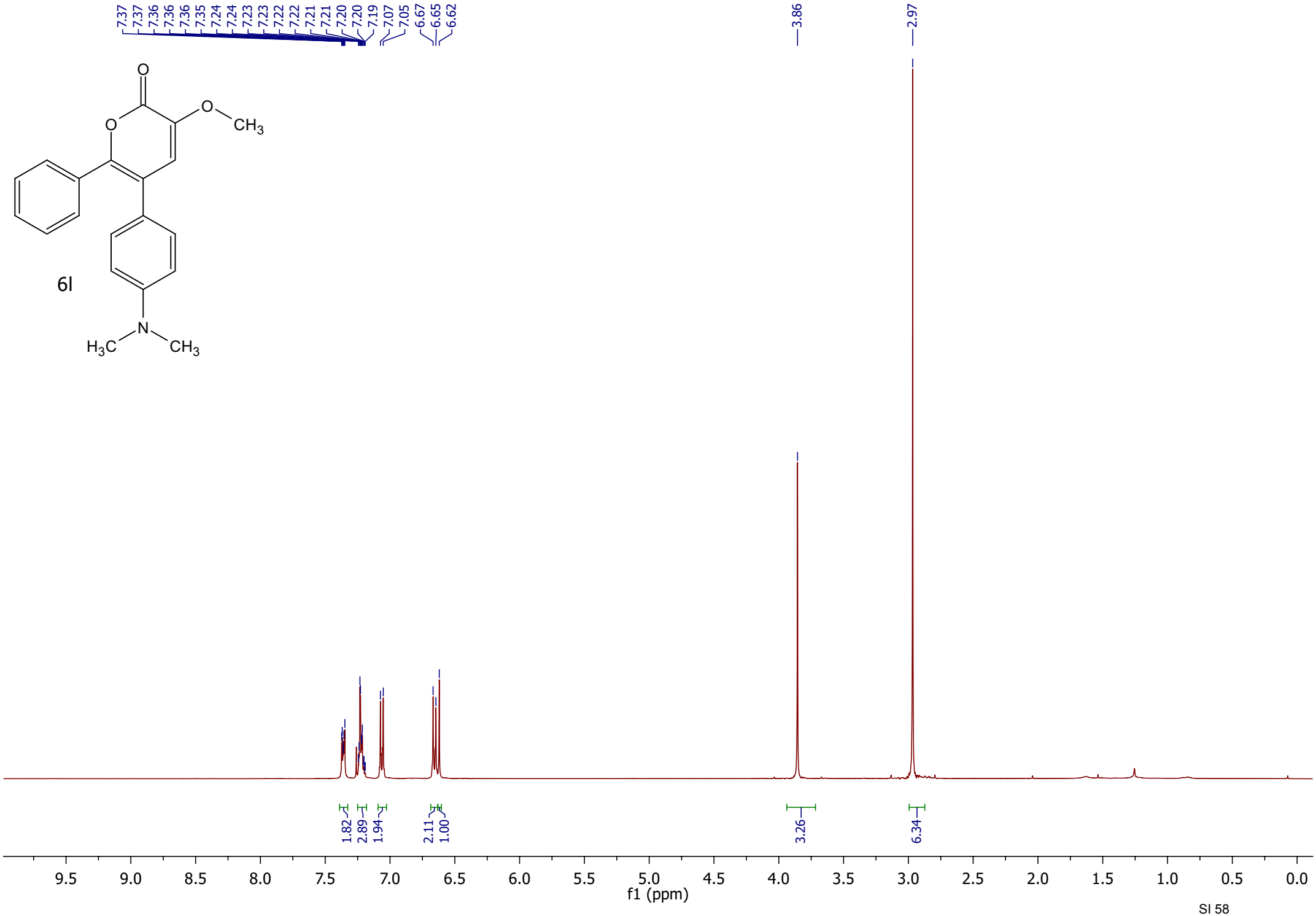
50
40
30
20
10
0
f1 (ppm)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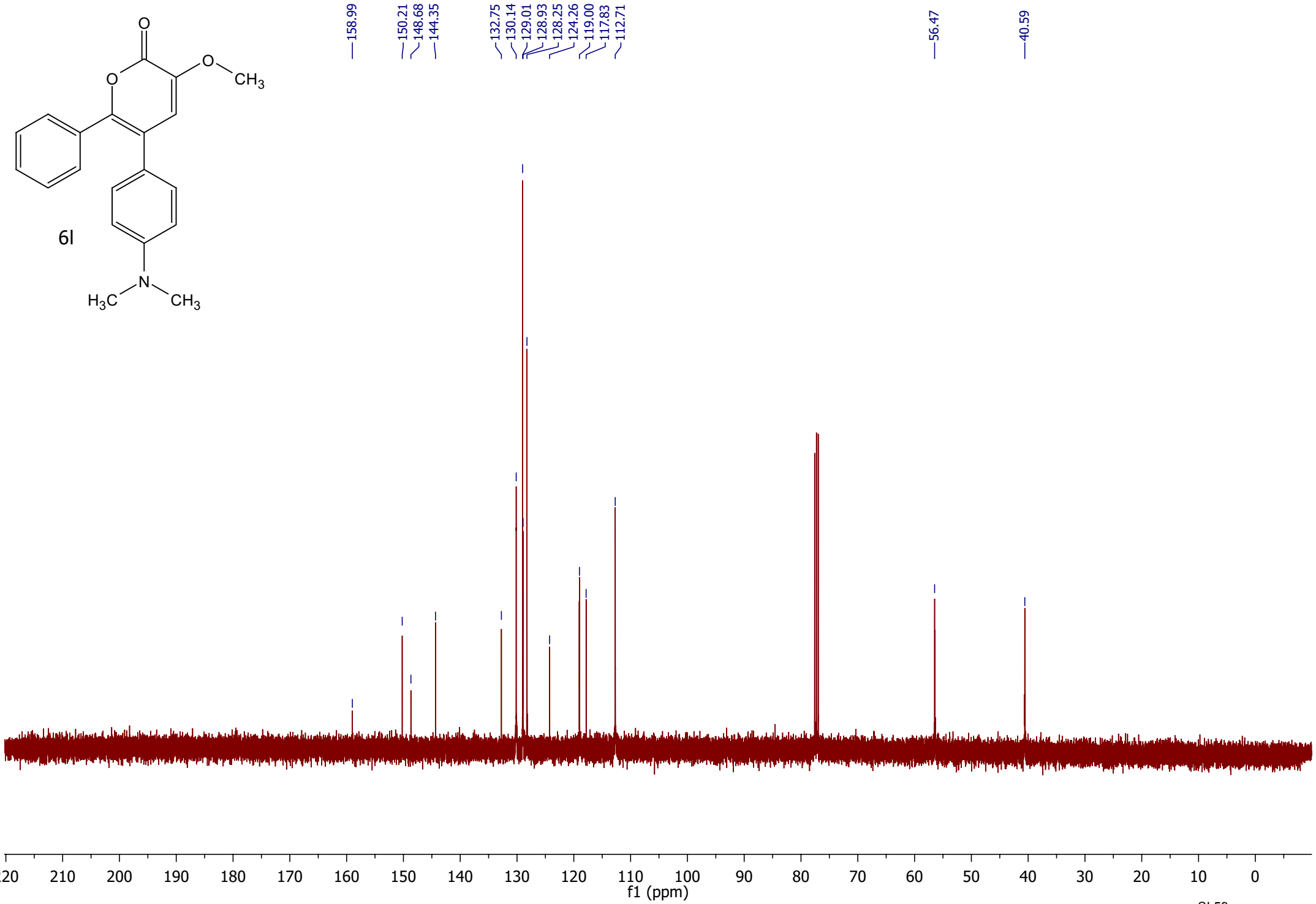
7.36
7.35
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.07
7.05
6.67
6.65
6.62
3.86
2.97
O
O
O
CH3
6l
N
H3C
CH3
1.82
2.89
1.94
2.11
1.00
3.26
6.34
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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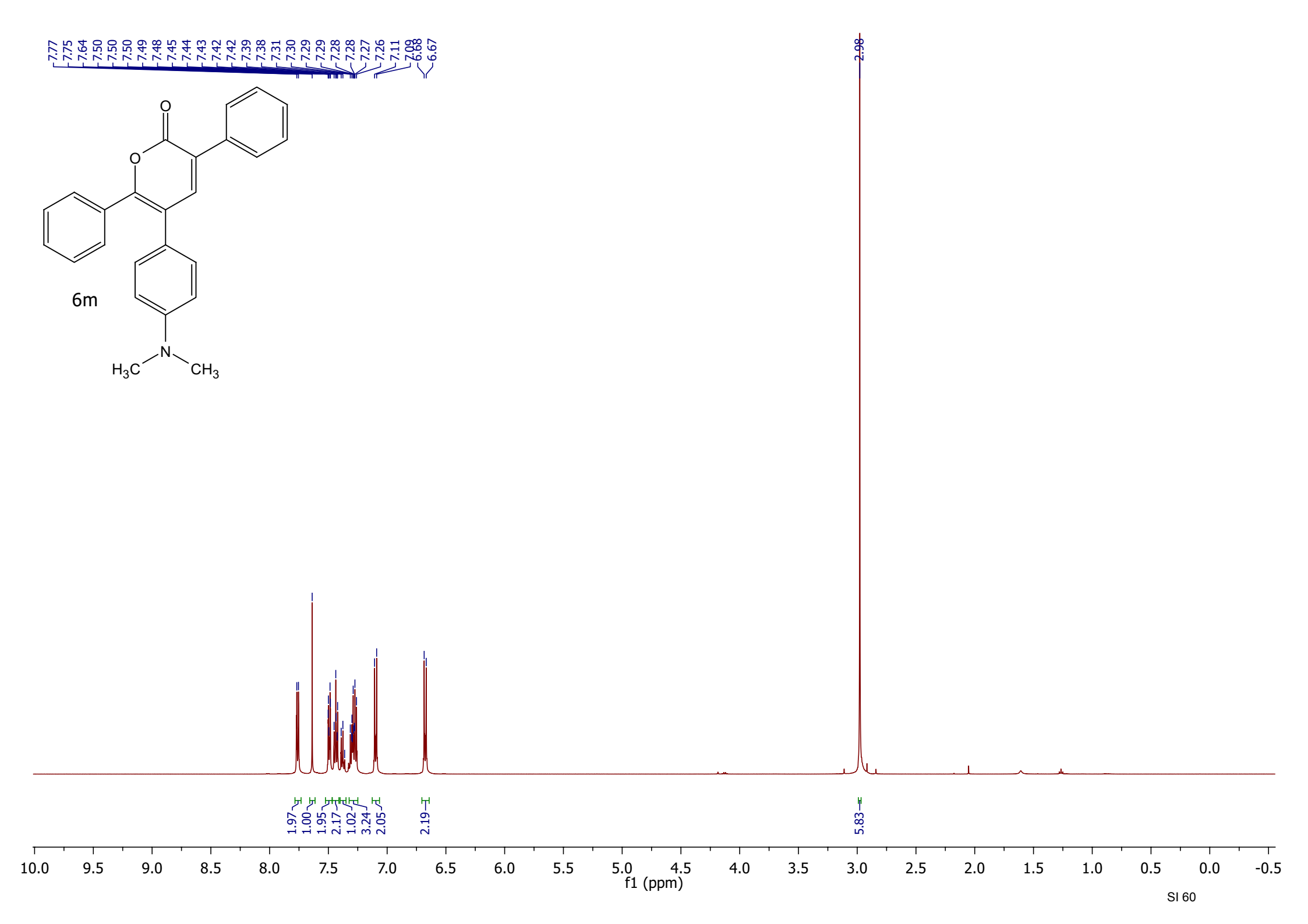
130.14
129.01
128.93
128.25
124.26
119.00
117.83
112.71
56.47
40.59
O
O
O
CH3
6l
N
H3C
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.50
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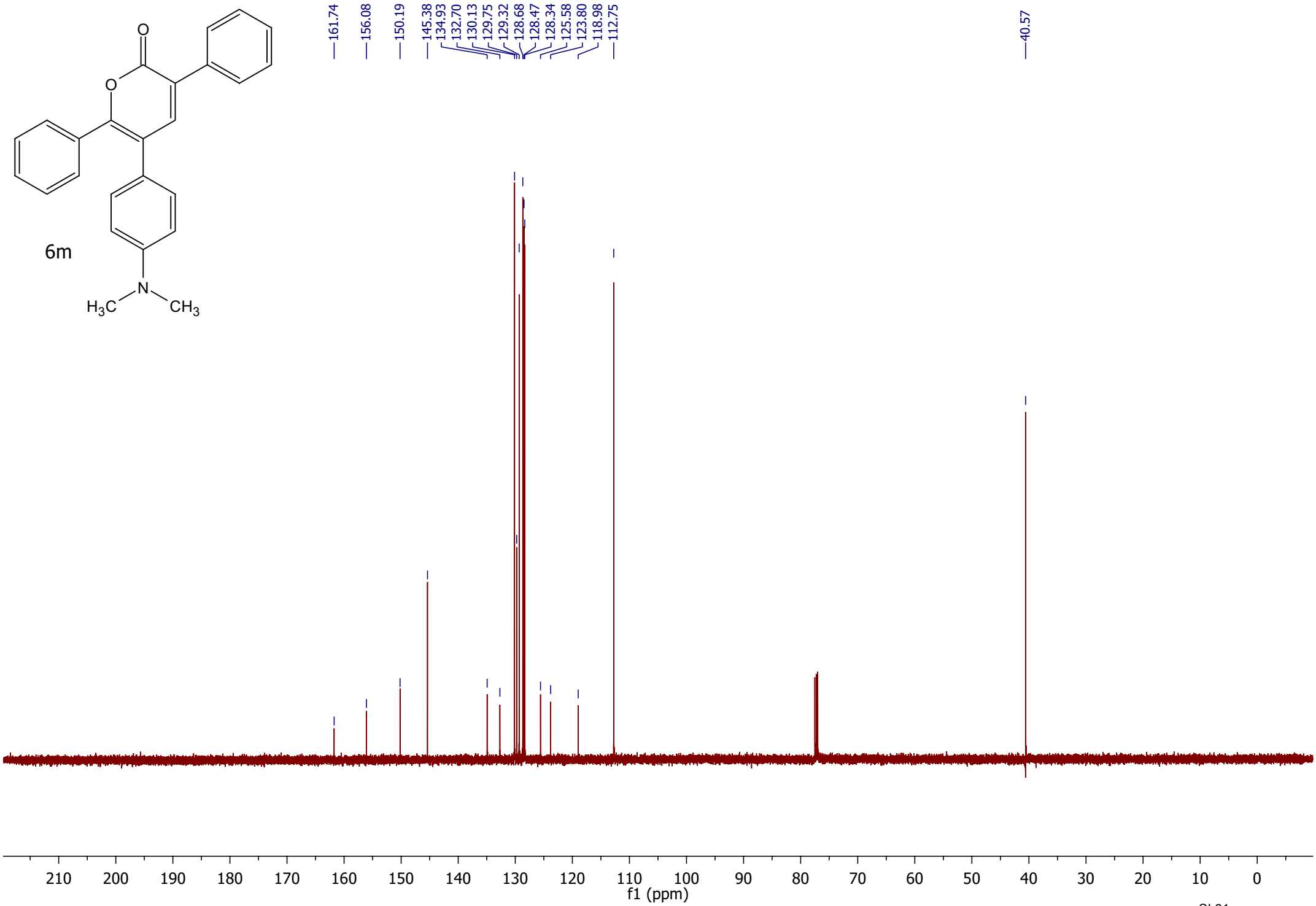
7.48
7.45
7.44
7.43
7.42
7.42
7.39
7.38
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.11
7.09
6.68
6.67
2.98
O
O
6m
N
H3C
CH3
1.97
1.00
1.95
2.17
1.02
3.24
2.05
2.19
5.83
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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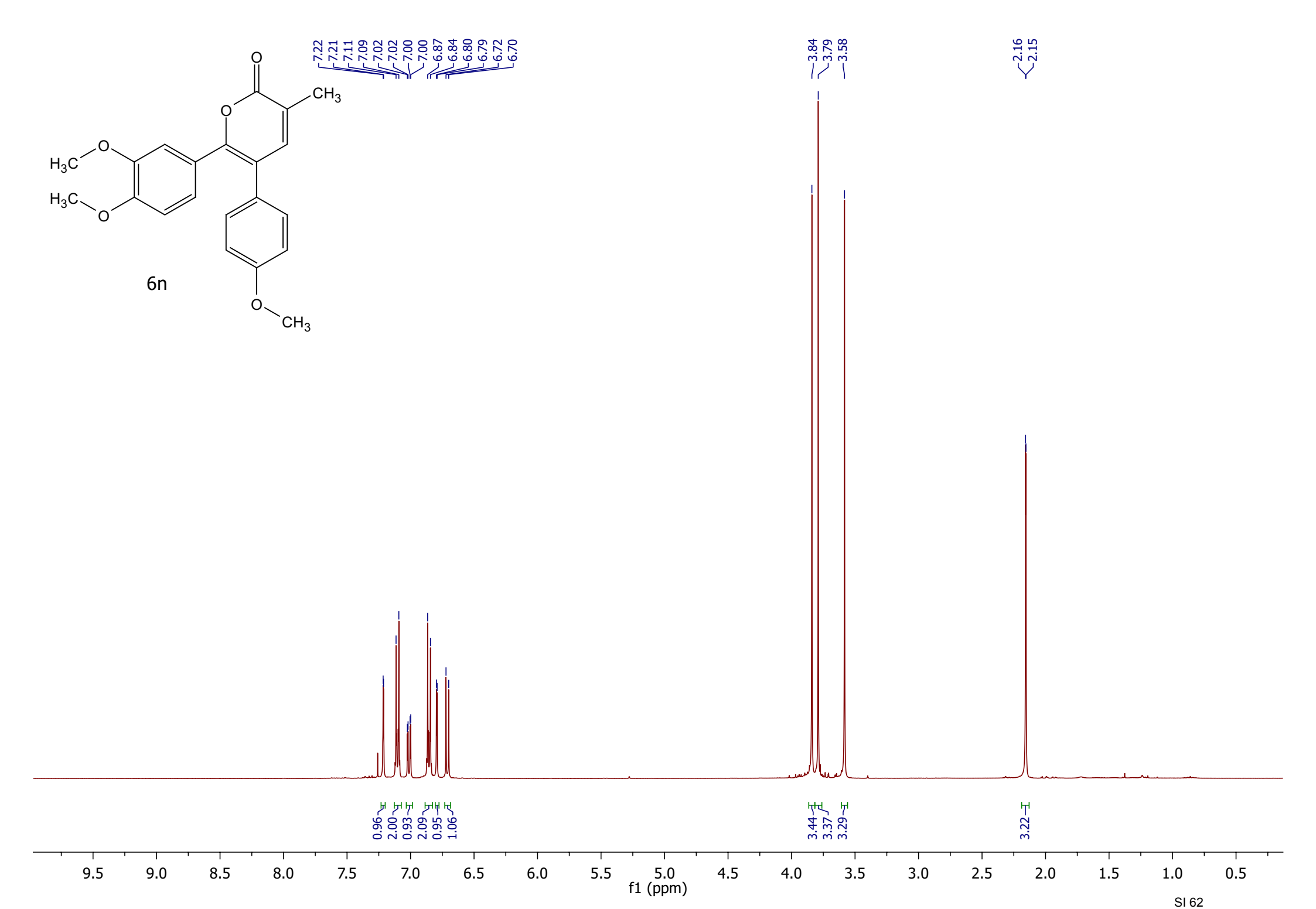
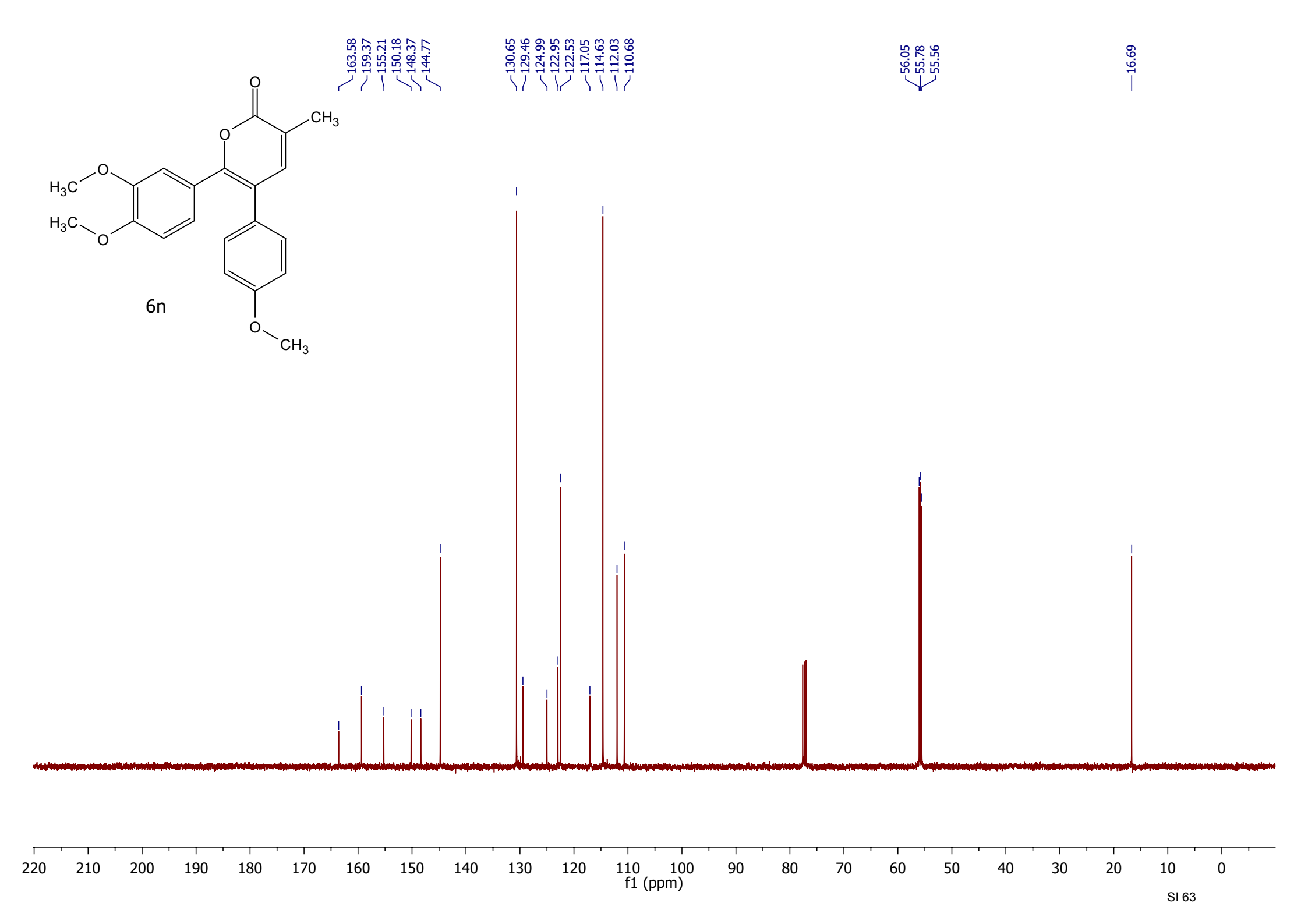
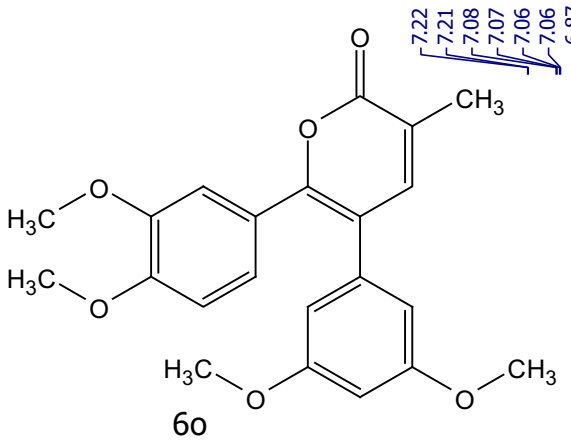
156.08
150.19
145.38
134.93
132.70
130.13
129.75
129.32
128.68
128.47
128.34
125.58
123.80
118.98
112.75
40.57
O
O
6m
N
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

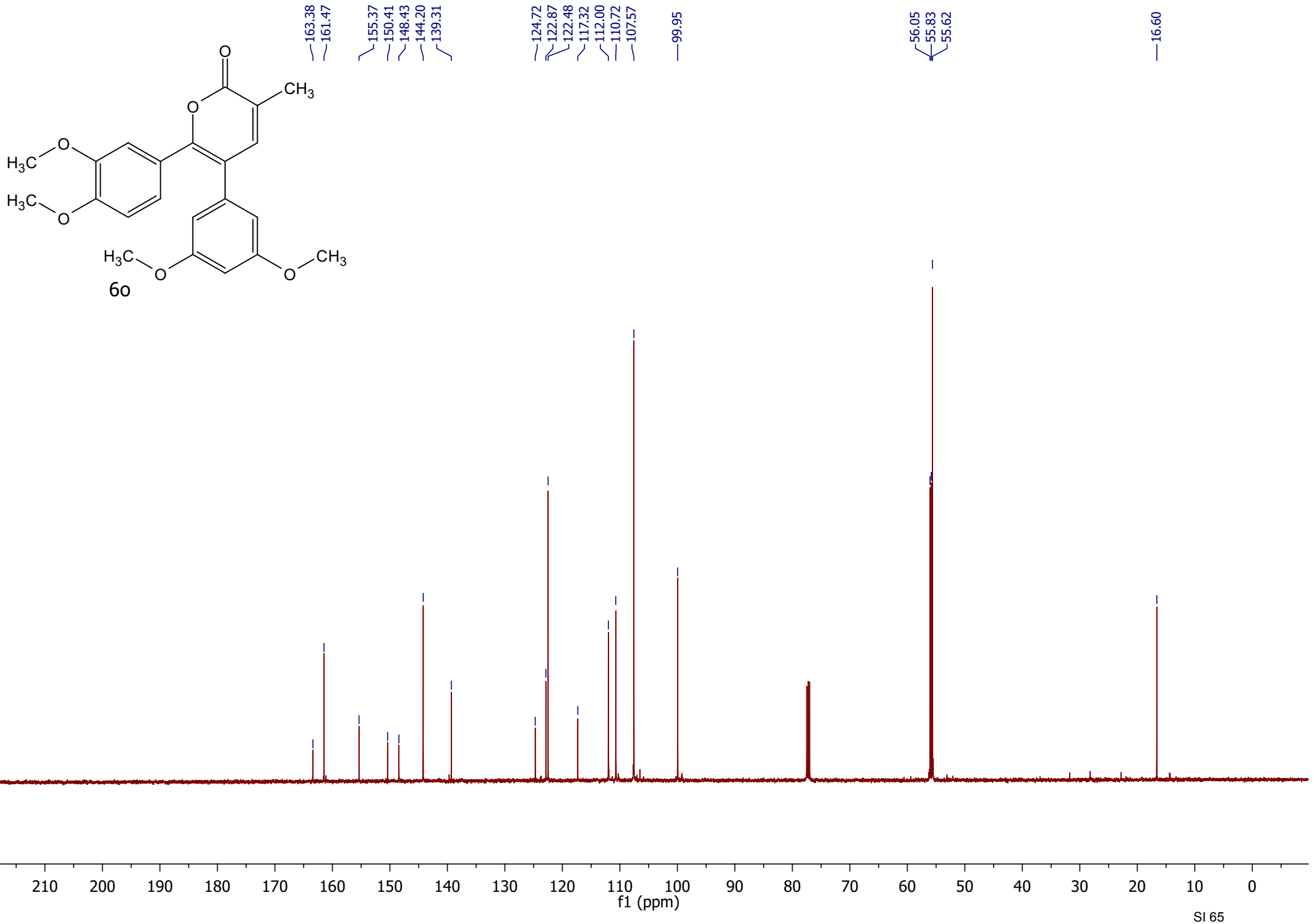

7.22
7.21
7.11
7.09
7.02
7.02
7.00
7.00
6.87
6.84
6.80
6.79
6.72
6.70
3.84
3.79
3.58
2.16
2.15
O
CH3
O
H3C
O
H3C
O
O
CH3
6n
0.96
2.00
0.93
2.09
0.95
1.06
3.44
3.37
3.29
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

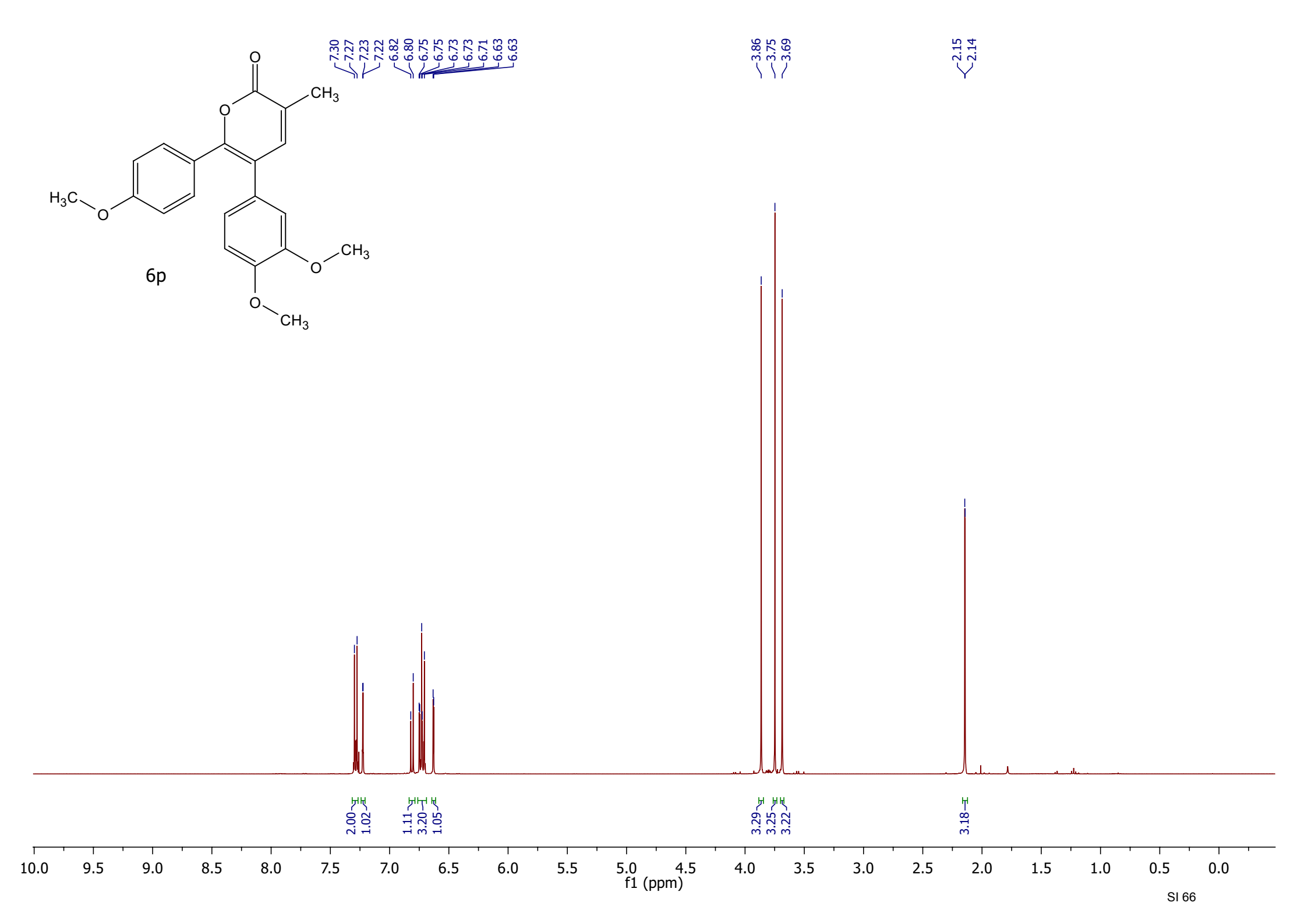

163.58
159.37
155.21
150.18
148.37
144.77
130.65
129.46
124.99
122.95
122.53
117.05
114.63
112.03
110.68
56.05
55.78
55.56
16.69
O
O
CH3
O
H3C
O
H3C
O
CH3
6n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

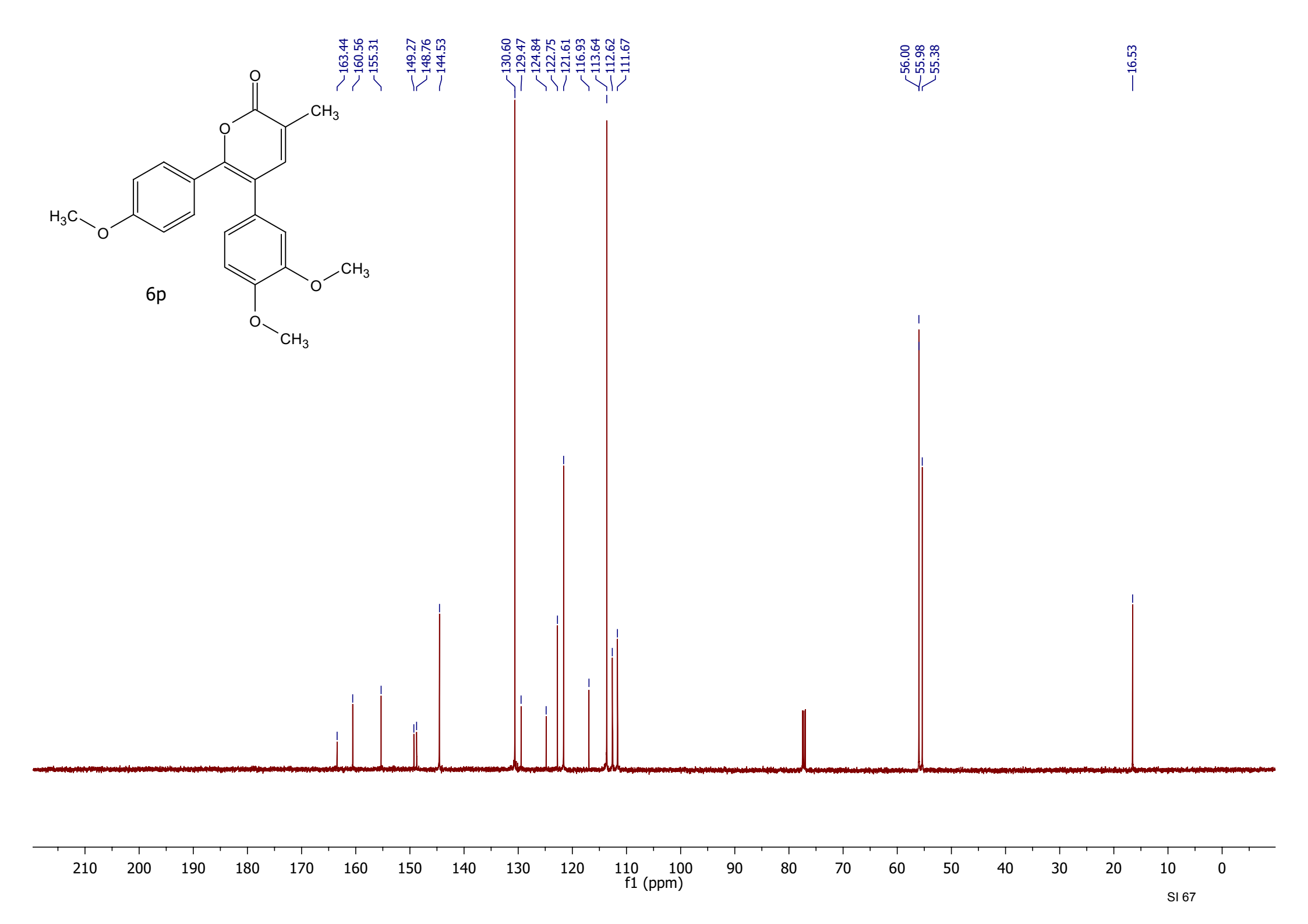

O
CH3
O
H3C
O
H3C
O
H3C
O
O
CH3

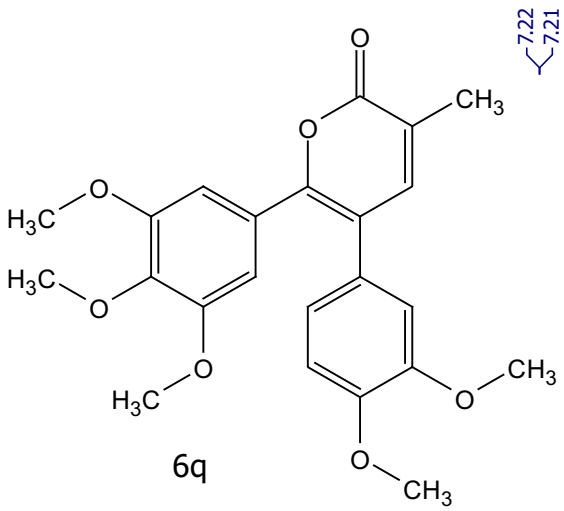
6o

7.22
7.21
7.08
7.07
7.06
7.06
6.87
6.87
6.73
6.72
6.40
6.39
6.39
6.35
6.34
3.85
3.70
3.61
2.16
2.16
1.00
0.99
1.01
1.10
0.99
1.98
3.25
6.67
3.28
3.21
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)


163.38
161.47
155.37
150.41
148.43
144.20
139.31
124.72
122.87
122.48
117.32
112.00
110.72
107.57
99.95
56.05
55.83
55.62
16.60
O
O
CH3
O
H3C
O
H3C
O
H3C
O
O
CH3
6o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

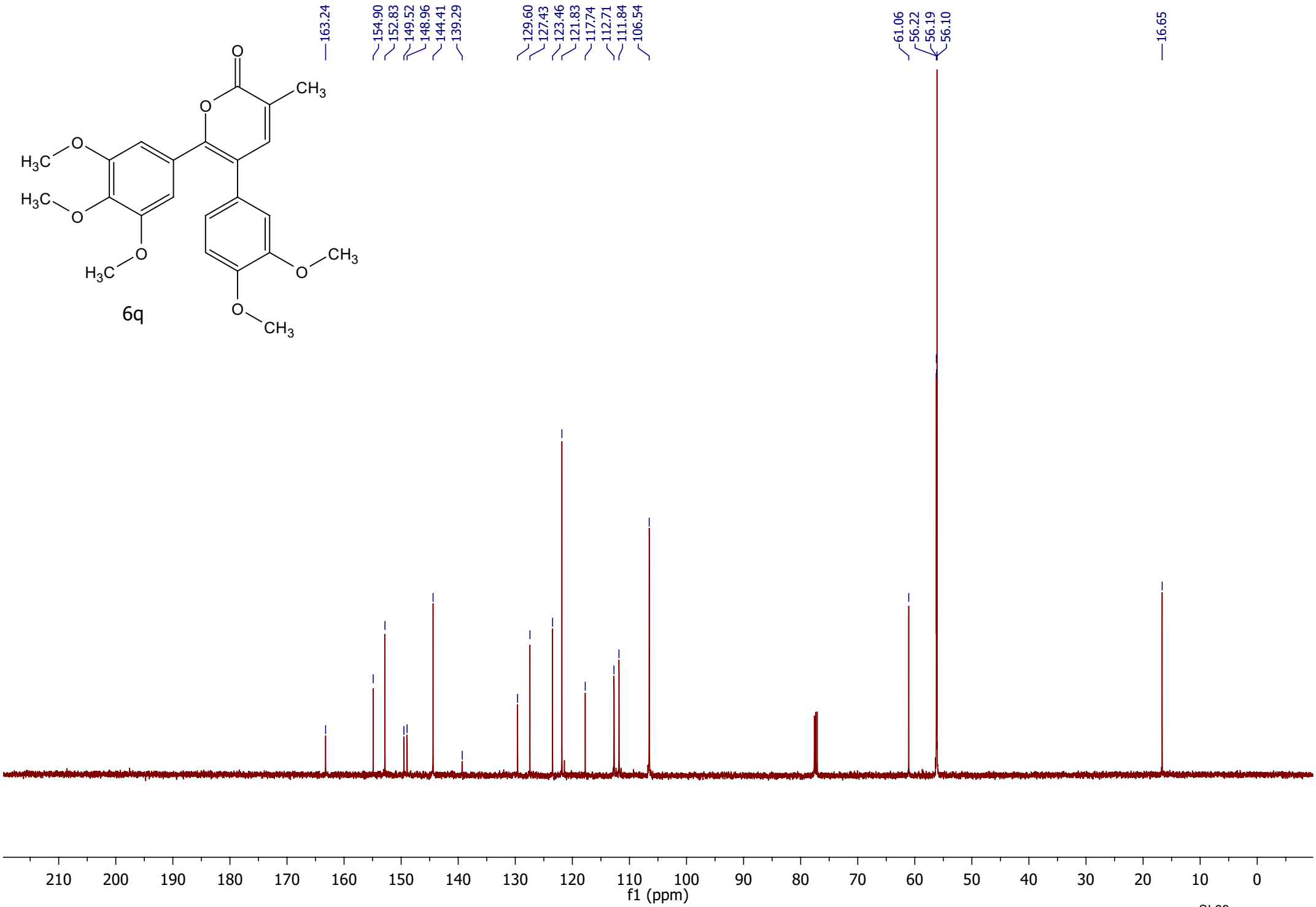

7.30
7.27
7.23
7.22
6.82
6.80
6.75
6.75
6.73
6.73
6.71
6.63
6.63
3.86
3.75
3.69
2.15
2.14
O
CH3
O
H3C
O
6p
CH3
O
O
CH3
2.00
1.02
1.11
3.20
1.05
3.29
3.25
3.22
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

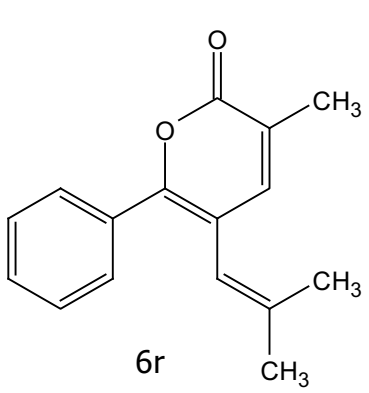

163.44
160.56
155.31
149.27
148.76
144.53
130.60
129.47
124.84
122.75
121.61
116.93
113.64
112.62
111.67
56.00
55.98
55.38
16.53
O
O
CH3
H3C
O
CH3
O
O
CH3
6p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CH3
O
H3C
O
H3C
O
O
H3C
O
CH3
O
CH3

6q

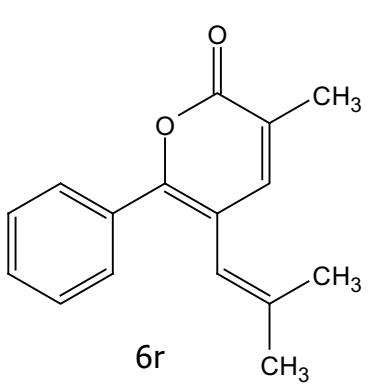
7.22
7.21
6.83
6.81
6.76
6.75
6.74
6.73
6.65
6.64
6.57
3.83
3.77
3.70
3.57
2.13
2.13
1.00
1.10
1.18
1.06
2.08
3.40
3.27
3.12
6.28
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.24
154.90
152.83
149.52
148.96
144.41
139.29
129.60
127.43
123.46
121.83
117.74
112.71
111.84
106.54
61.06
56.22
56.19
56.10
16.65
O
CH3
O
H3C
O
H3C
O
O
H3C
O
CH3
O
CH3
6q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
CH3
CH3

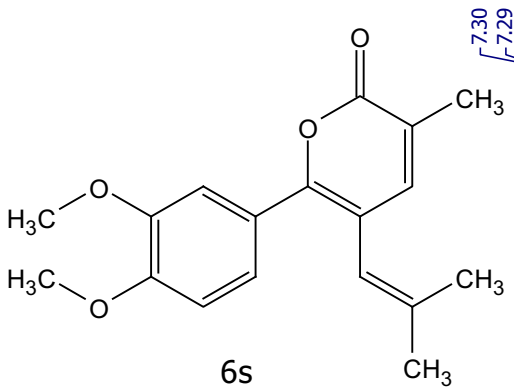
6r

7.71
7.70
7.69
7.69
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.13
7.13
5.91
5.90
5.90
2.15
2.15
1.84
1.84
1.65
1.65
1.91
3.00
0.98
0.98
3.49
3.59
3.55
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)


O
O
CH3
CH3
CH3

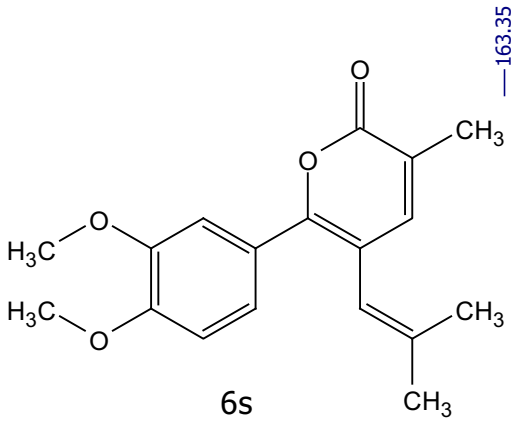
6r

163.41
155.24
144.49
137.96
133.04
129.68
128.65
128.37
123.21
119.88
114.31
25.91
19.84
16.70
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
H3C
O
H3C
O
CH3
CH3

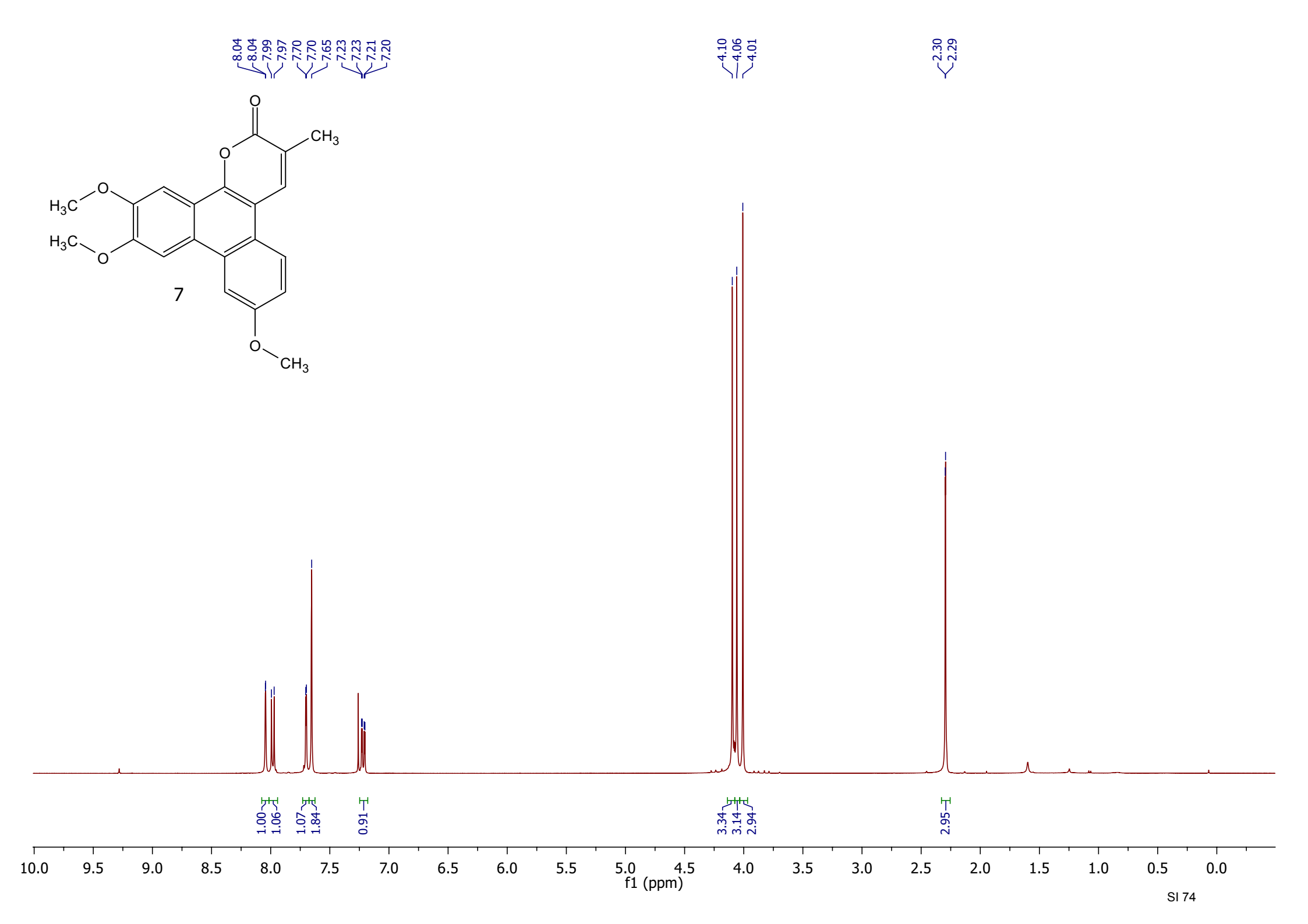
6s

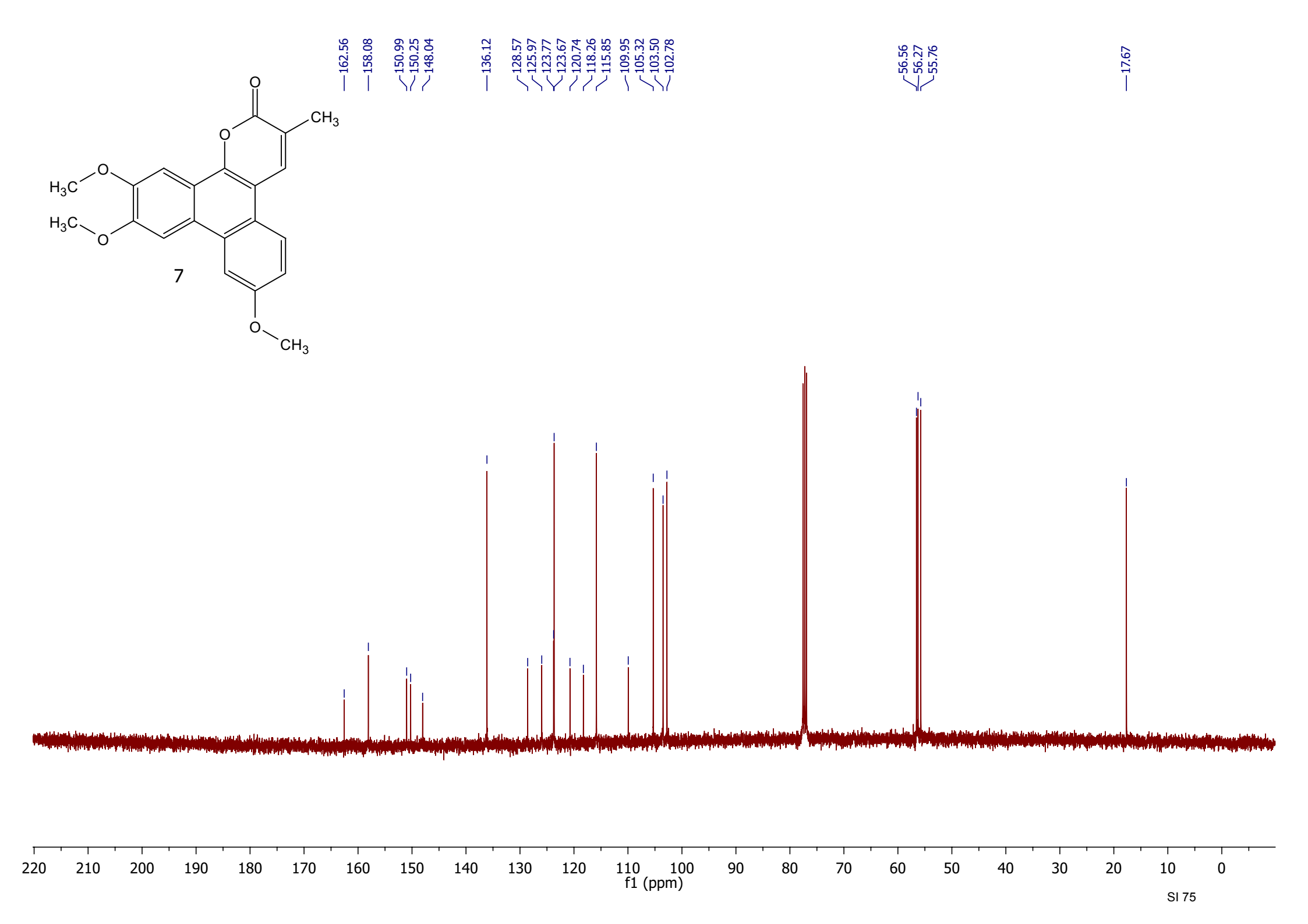
7.30
7.29
7.27
7.27
7.25
7.24
7.07
7.07
6.84
6.82
5.88
3.87
3.84
2.09
2.09
1.81
1.81
1.64
1.63
1.00
0.97
1.00
1.13
1.00
3.35
3.36
3.26
3.38
3.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

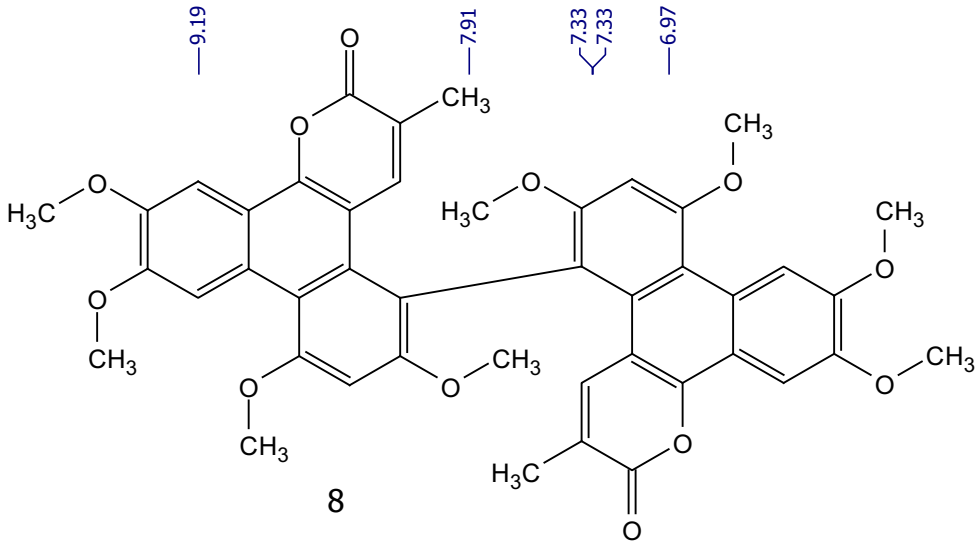

O
O
CH3
H3C
O
H3C
O
CH3
CH3

6s

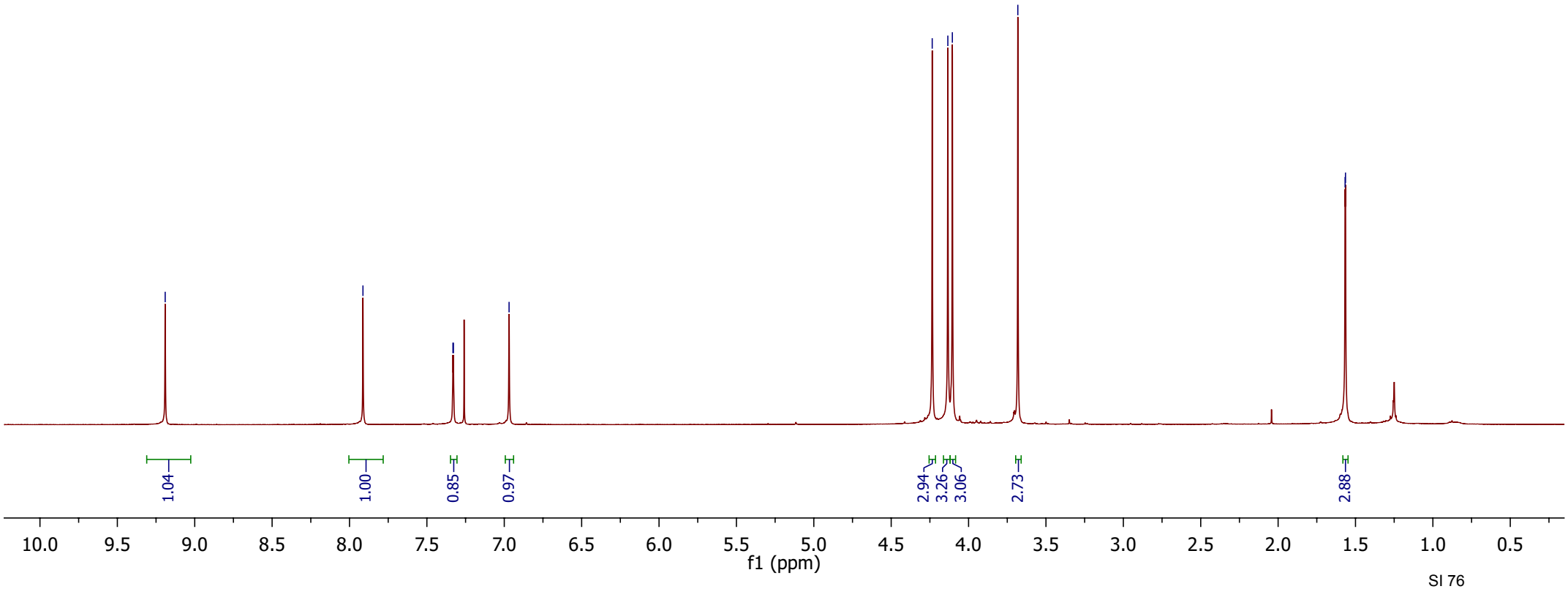
163.35
154.98
150.18
148.53
144.64
137.35
125.47
122.14
122.01
120.28
113.28
111.22
110.59
55.98
55.96
25.75
19.70
16.53
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

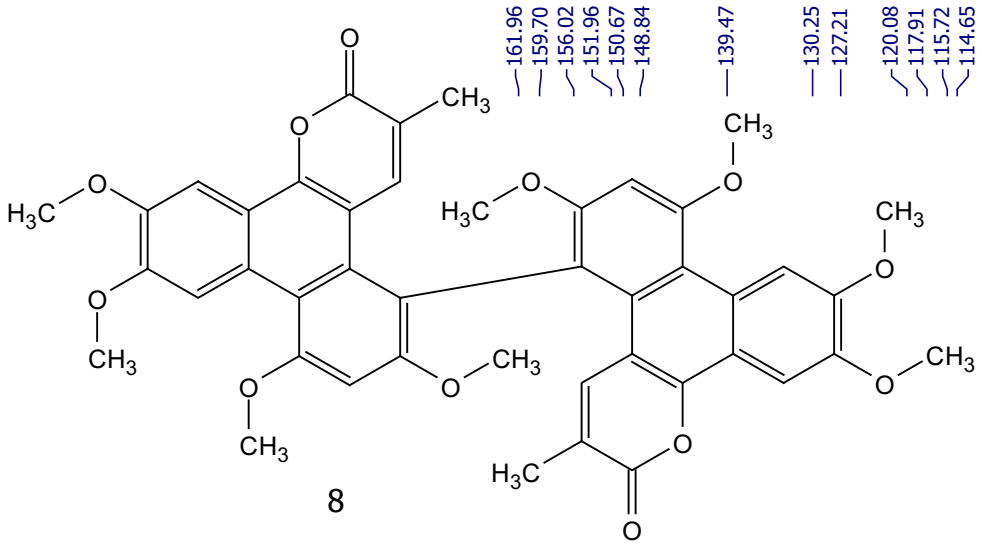

8.04
8.04
7.99
7.97
7.70
7.70
7.65
7.23
7.23
7.21
7.20
4.10
4.06
4.01
2.30
2.29
O
CH3
O
H3C
O
H3C
O
7
O
CH3
1.00
1.06
1.07
1.84
0.91
3.34
3.14
2.94
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.56
158.08
150.99
150.25
148.04
136.12
128.57
125.97
123.77
123.67
120.74
118.26
115.85
109.95
105.32
103.50
102.78
56.56
56.27
55.76
17.67
O
O
CH3
O
H3C
O
H3C
O
CH3
7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.19
7.91
7.33
7.33
6.97
4.23
4.13
4.10
3.68
1.57
1.56
O
CH3
O
H3C
O
O
CH3
O
CH3
O
CH3
O
CH3
O
CH3
O
H3C
O
O
CH3
O
CH3
O
H3C
O
O

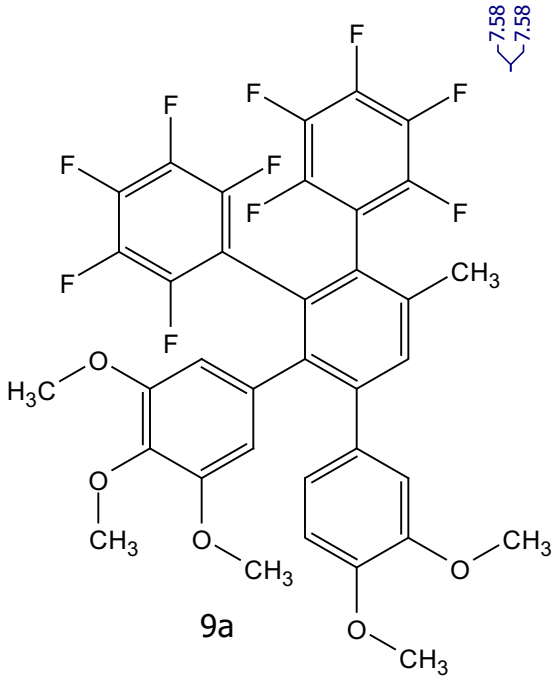
8


1.04
1.00
0.85
0.97
2.94
3.26
3.06
2.73
2.88
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
f1 (ppm)



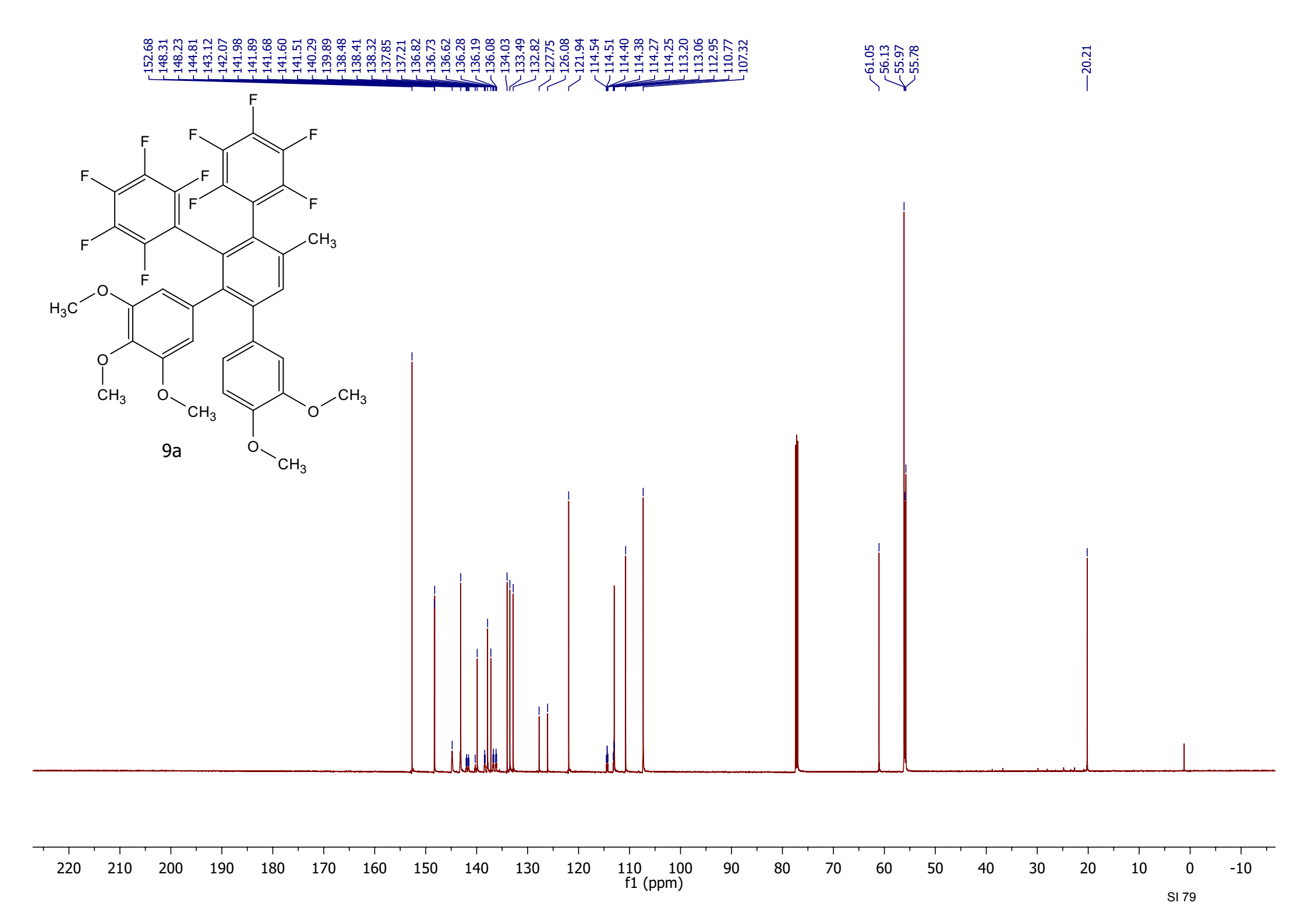
8

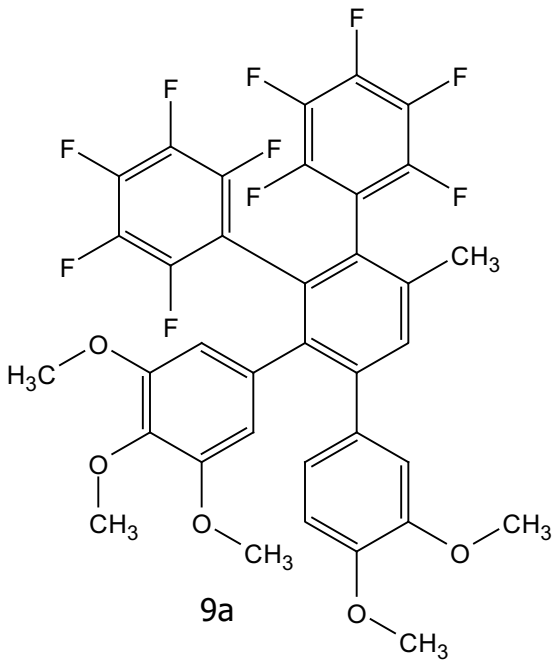
161.96
159.70
156.02
151.96
150.67
148.84
139.47
130.25
127.21
120.08
117.91
115.72
114.65
110.97
109.60
102.74
95.97
56.68
56.59
56.45
56.05
17.25
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3

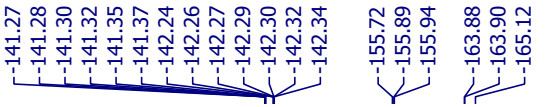
9a

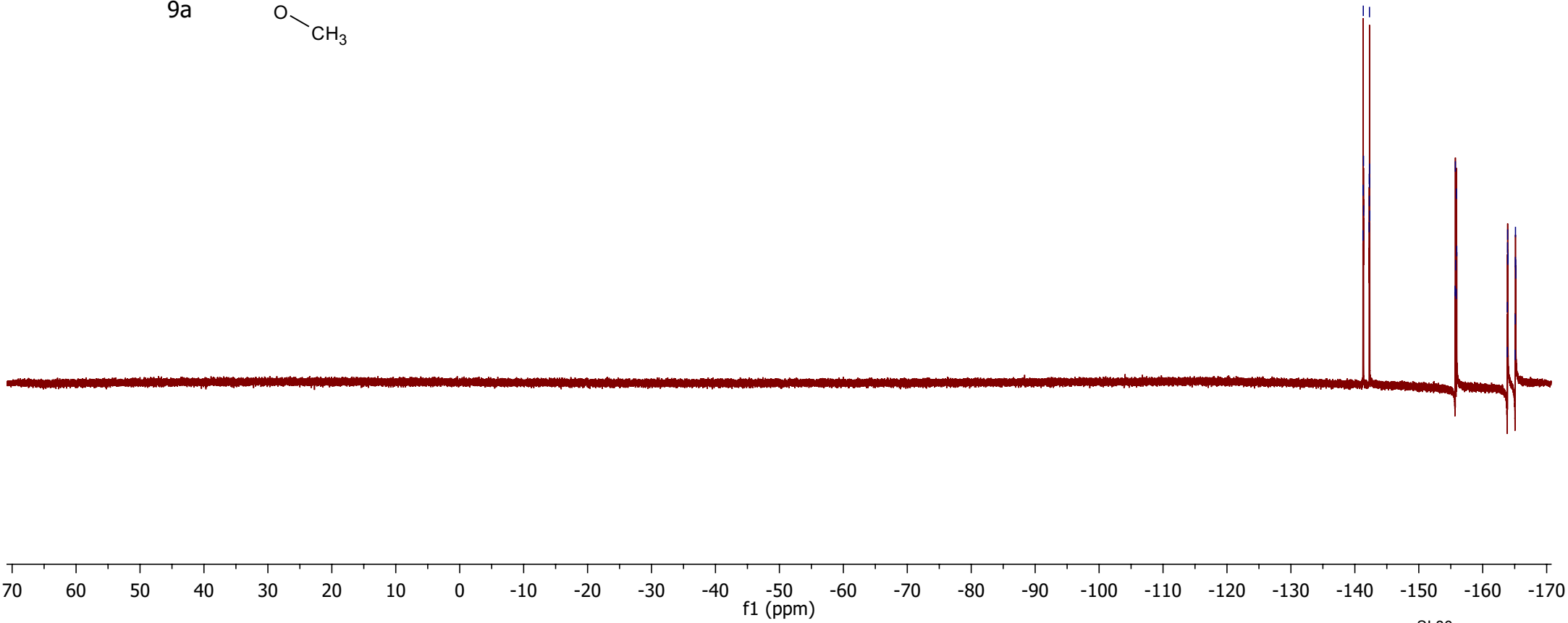
7.58
7.58
6.86
6.86
6.85
6.84
6.80
6.78
6.59
6.59
6.16
3.85
3.73
3.59
3.54
2.24
0.32
0.34
0.35
0.33
0.66
1.04
0.99
1.07
2.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

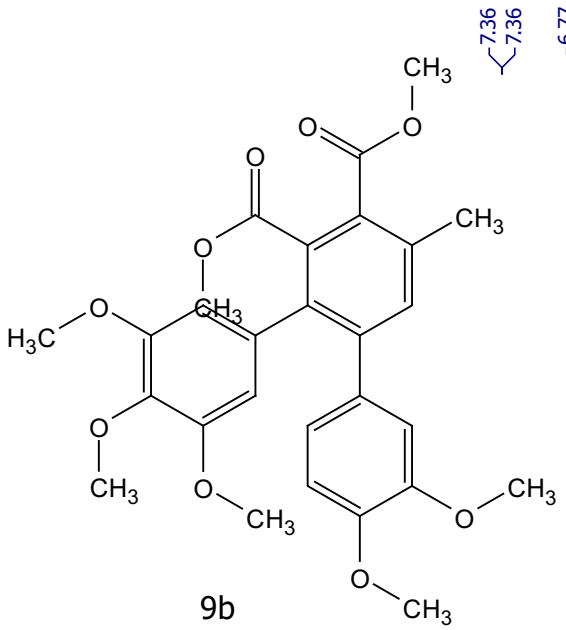

152.68
148.31
148.23
144.81
143.12
142.07
141.98
141.89
141.68
141.60
141.51
140.29
139.89
138.48
138.41
138.32
137.85
137.21
136.82
136.73
136.62
136.28
136.19
136.08
134.03
133.49
132.82
127.75
126.08
121.94
114.54
114.51
114.40
114.38
114.27
114.25
113.20
113.06
112.95
110.77
107.32
61.05
56.13
55.97
55.78
20.21
F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3
9a
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)


F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3

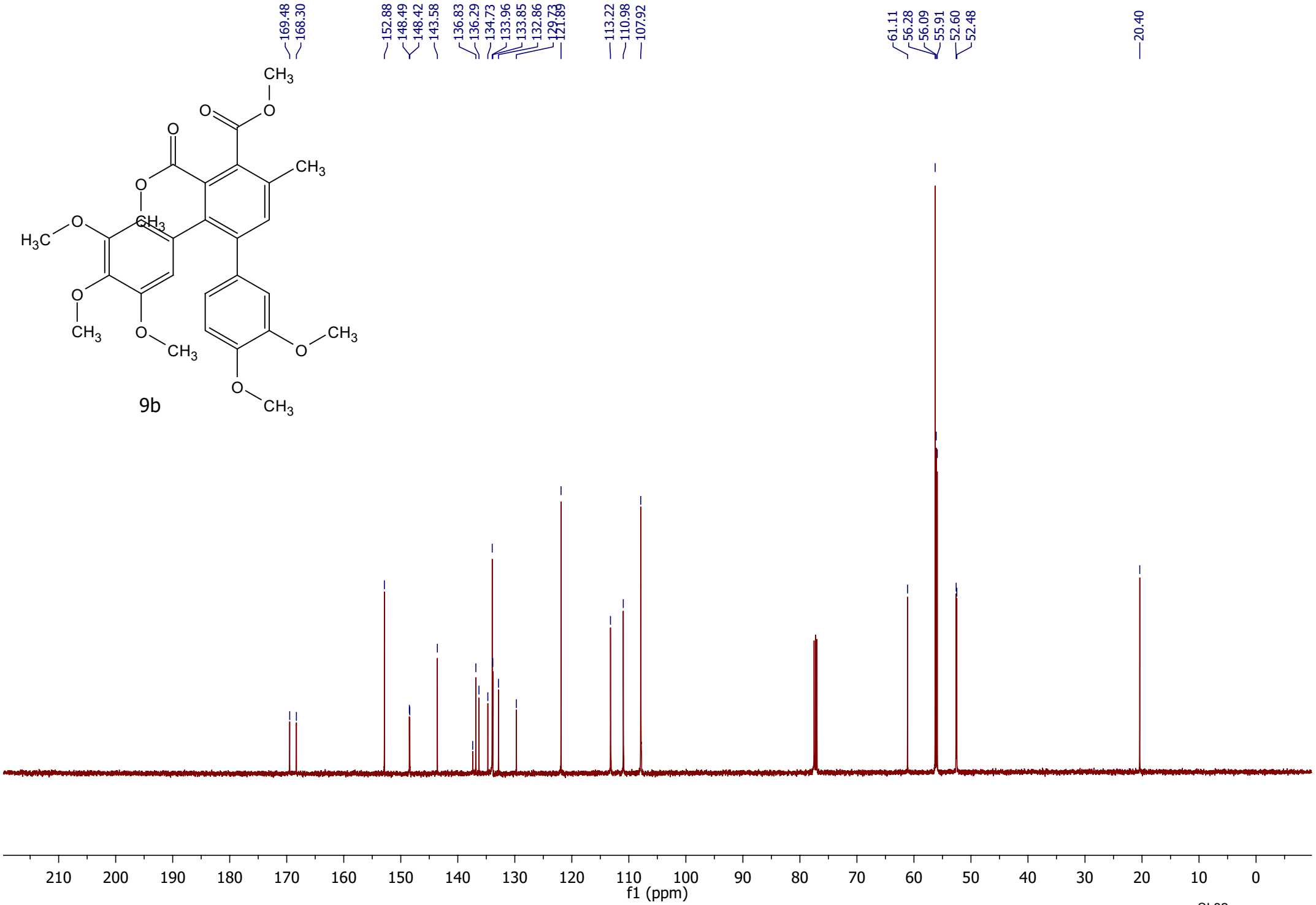
9a

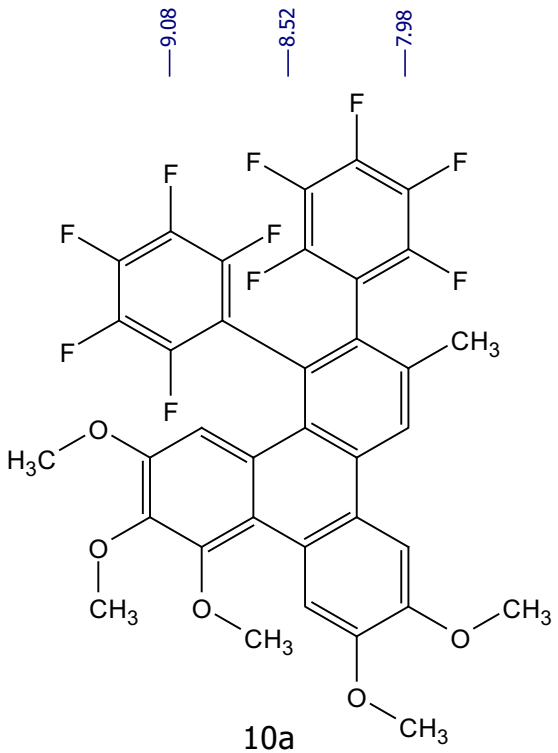

141.27
141.28
141.30
141.32
141.35
141.37
142.24
142.26
142.27
142.29
142.30
142.32
142.34
155.72
155.89
155.94
163.88
163.90
165.12


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



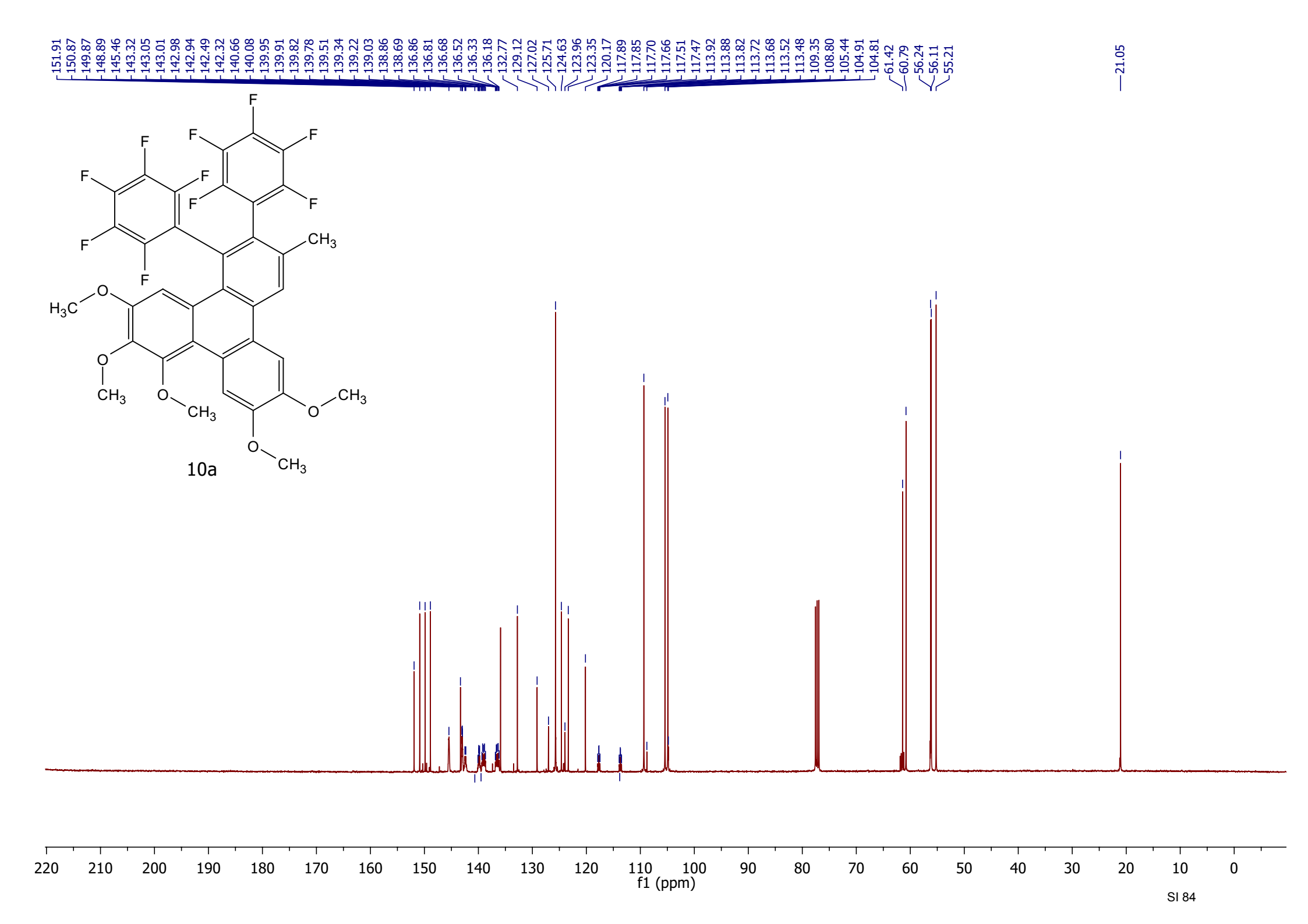
9b

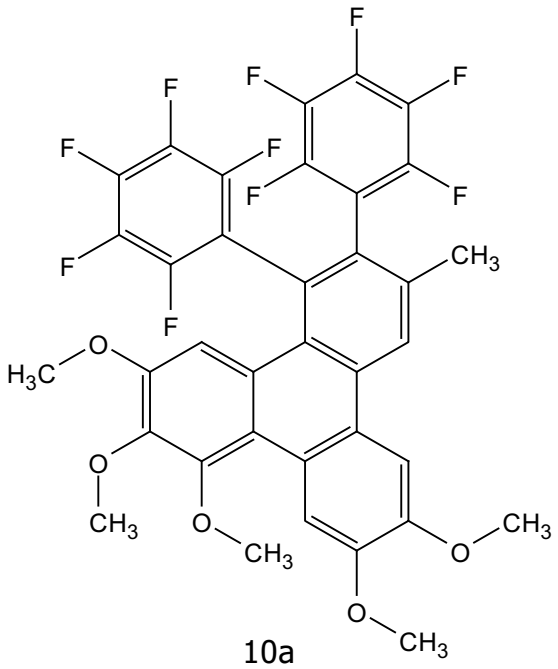

169.48
168.30
152.88
148.49
148.42
143.58
136.83
136.29
134.73
133.96
133.85
132.86
129.73
121.89
113.22
110.98
107.92
61.11
56.28
56.09
55.91
52.60
52.48
20.40
9b
f1 (ppm)


F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3

10a

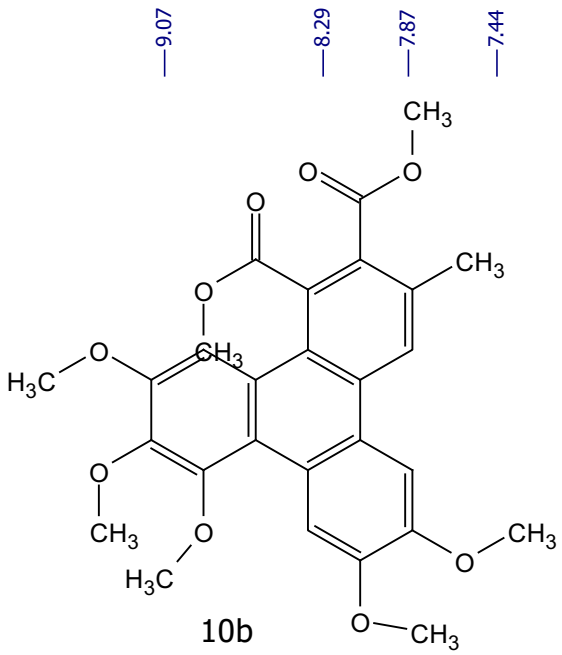
9.08
8.52
7.98
4.15
4.10
4.02
3.93
3.45
2.38
1.00
1.03
1.03
0.99
3.02
3.01
2.84
2.89
3.17
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

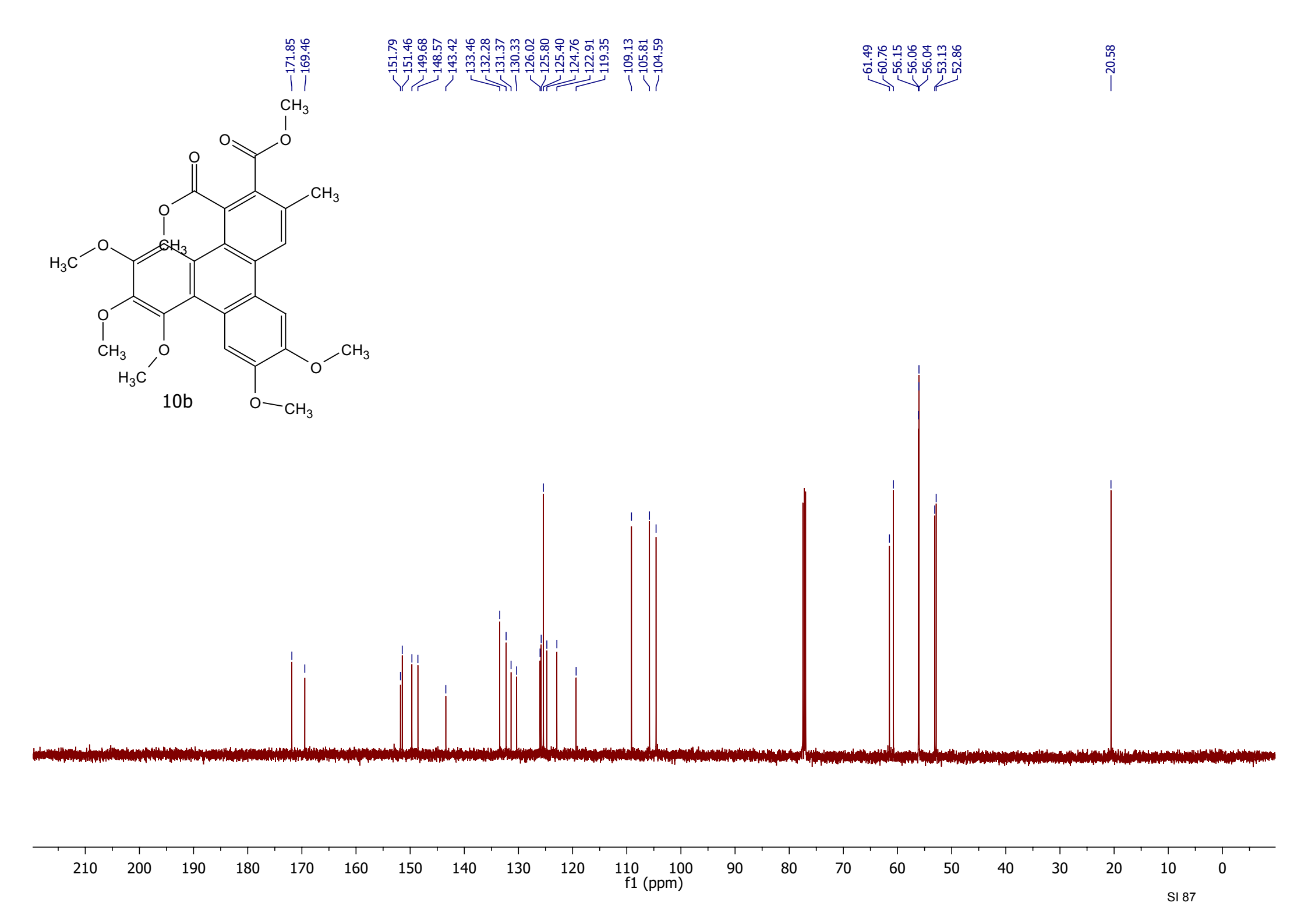

151.91
150.87
149.87
148.89
145.46
143.32
143.05
143.01
142.98
142.94
142.49
142.32
140.66
140.08
139.95
139.91
139.82
139.78
139.51
139.34
139.22
139.03
138.86
138.69
136.86
136.81
136.68
136.52
136.33
136.18
132.77
129.12
127.02
125.71
124.63
123.96
123.35
120.17
117.89
117.85
117.70
117.66
117.51
117.47
113.92
113.88
113.82
113.72
113.68
113.52
113.48
109.35
108.80
105.44
104.91
104.81
61.42
60.79
56.24
56.11
55.21
21.05
F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3
10a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

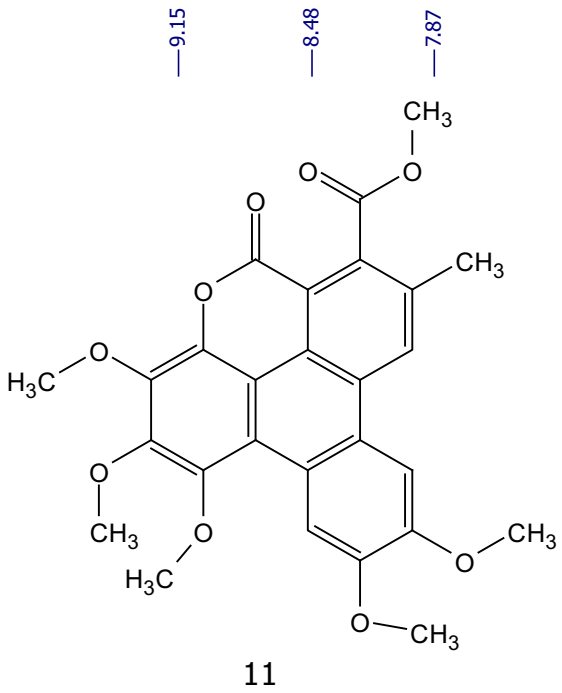

F
F
F
F
F
F
F
F
F
CH3
O
H3C
O
CH3
O
CH3
O
CH3
O
CH3

10a

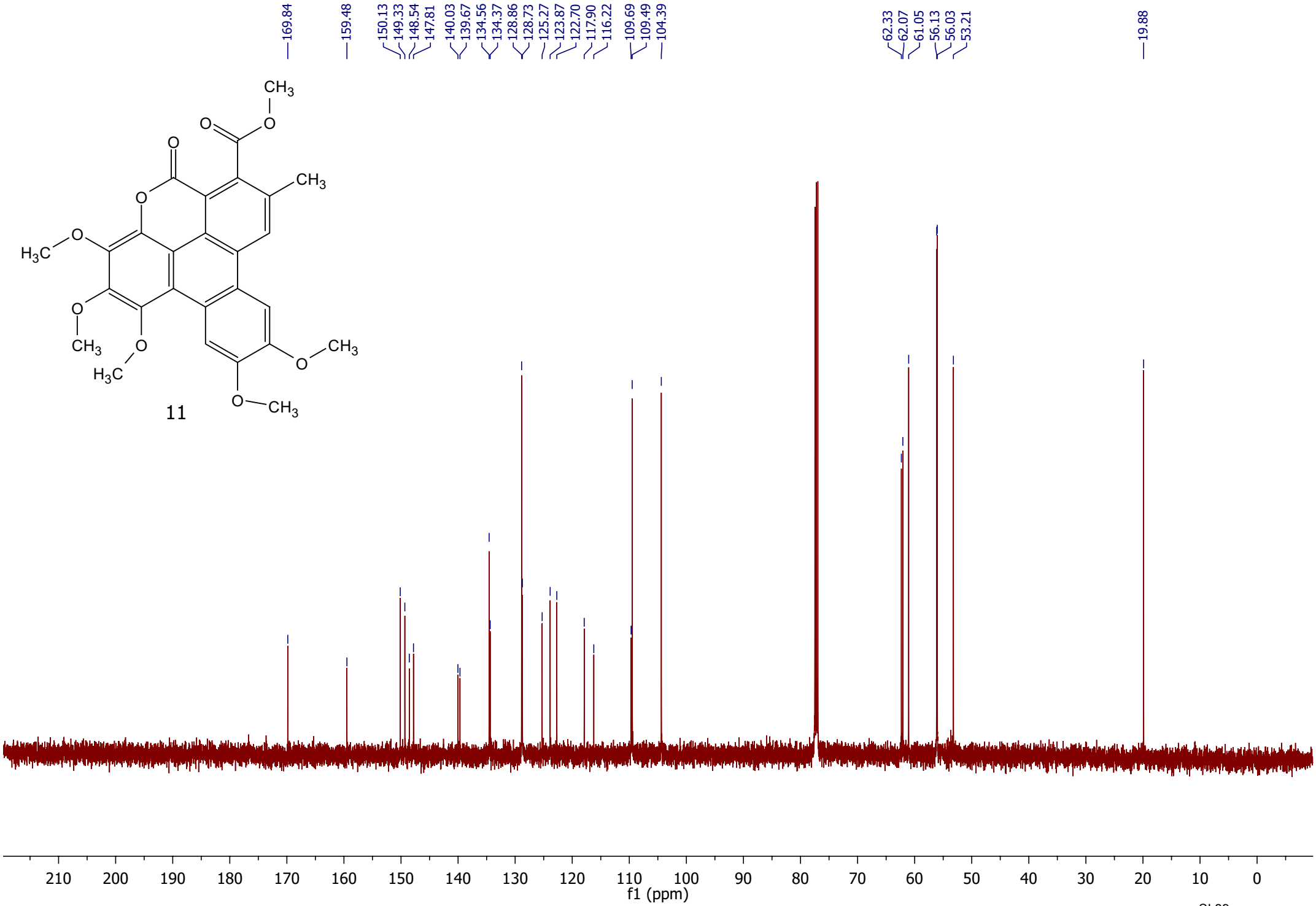
141.17
141.19
141.22
141.24
141.26
141.82
141.84
141.87
141.89
141.91
155.69
156.17
156.21
163.94
164.12
164.14
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

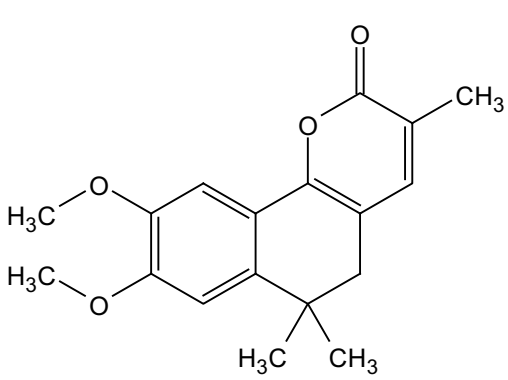

10b


171.85
169.46
151.79
151.46
149.68
148.57
143.42
133.46
132.28
131.37
130.33
126.02
125.80
125.40
124.76
122.91
119.35
109.13
105.81
104.59
61.49
60.76
56.15
56.06
56.04
53.13
52.86
20.58
10b
f1 (ppm)


9.15
8.48
7.87
4.17
4.16
4.12
4.09
3.98
2.64
CH3
O
O
O
CH3
O
H3C
O
O
CH3
O
CH3
H3C
O
CH3
O
CH3
1.15
1.20
1.21
6.00
2.69
3.00
2.68
2.61
3.46
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)

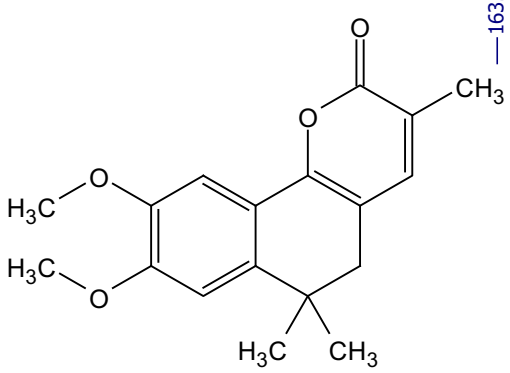
11


169.84
159.48
150.13
149.33
148.54
147.81
140.03
139.67
134.56
134.37
128.86
128.73
125.27
123.87
122.70
117.90
116.22
109.69
109.49
104.39
62.33
62.07
61.05
56.13
56.03
53.21
19.88
11
f1 (ppm)


O
O
CH3
O
H3C
O
H3C
O
H3C
CH3

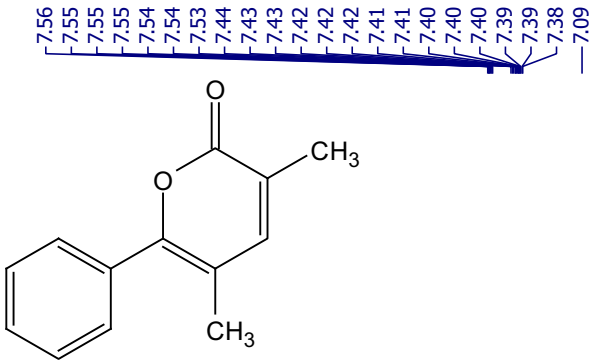
12

7.30
7.04
7.03
6.81
3.91
3.90
2.48
2.10
2.10
1.24
1.00
1.06
1.14
3.41
3.15
2.65
3.92
6.46
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)

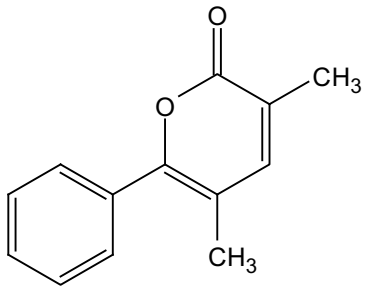

O
O
CH3
O
H3C
O
H3C
O
H3C
CH3

12

163.81
152.40
150.66
147.83
142.82
138.93
122.24
119.72
109.70
107.80
106.12
56.37
56.11
39.82
34.06
28.48
16.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

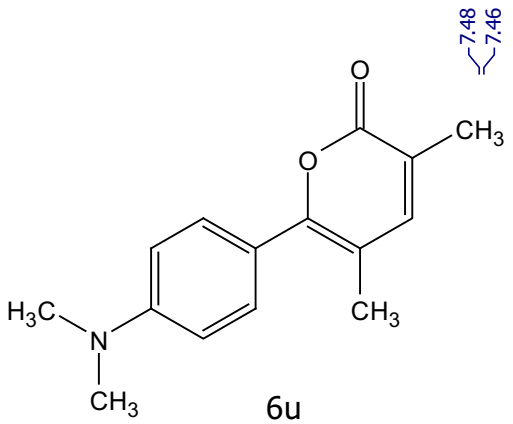

7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.09
2.13
O
O
CH3
CH3
1.94
3.02
1.00
7.65
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

6t


O
O
CH3
CH3

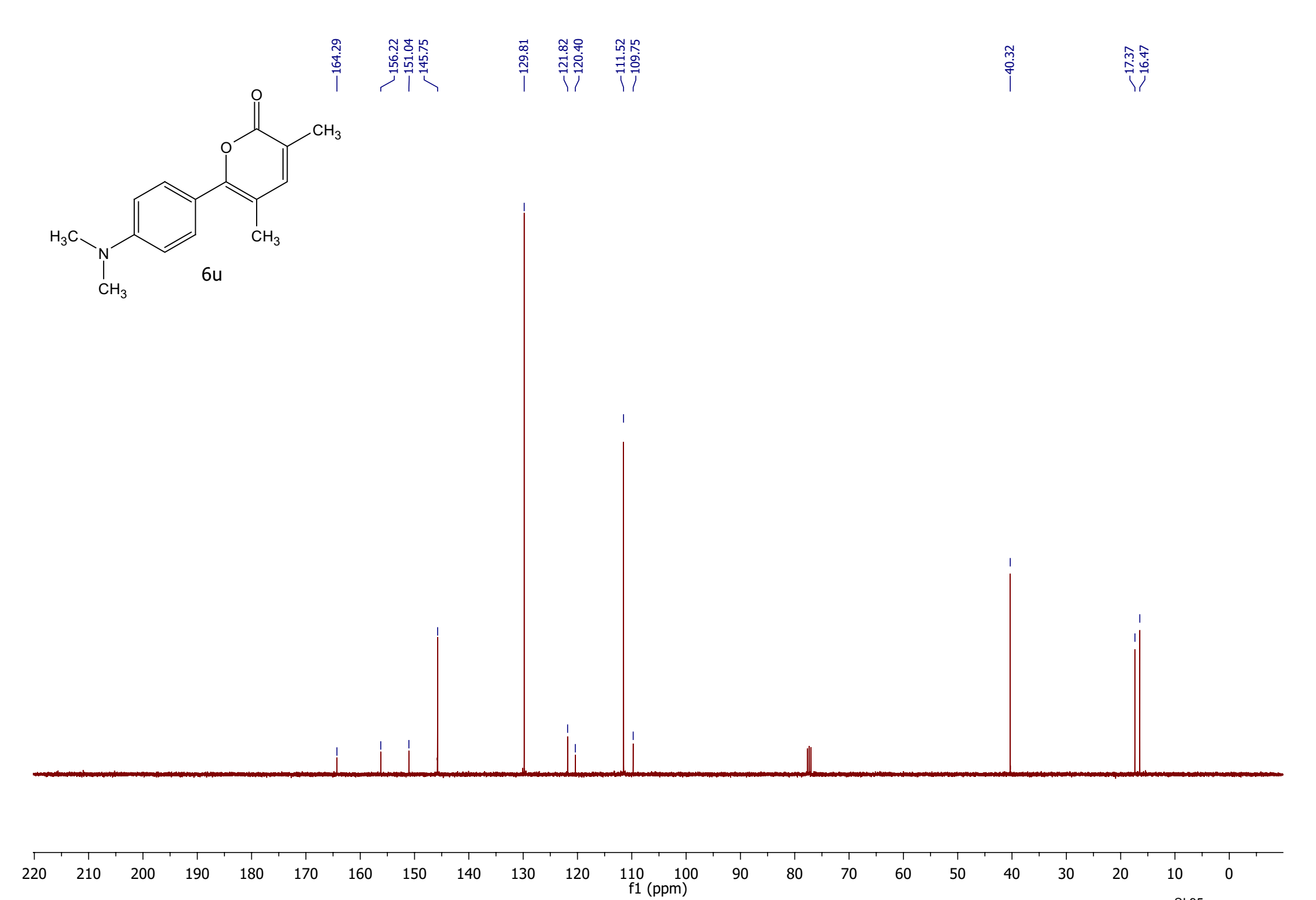
6t

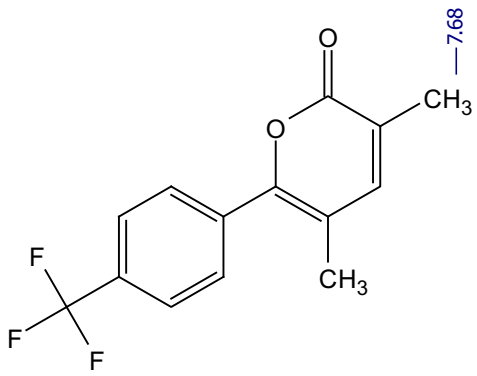
163.76
155.18
144.95
132.88
129.64
128.81
128.51
124.07
111.56
16.91
16.59
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
CH3
H3C
N
CH3

6u

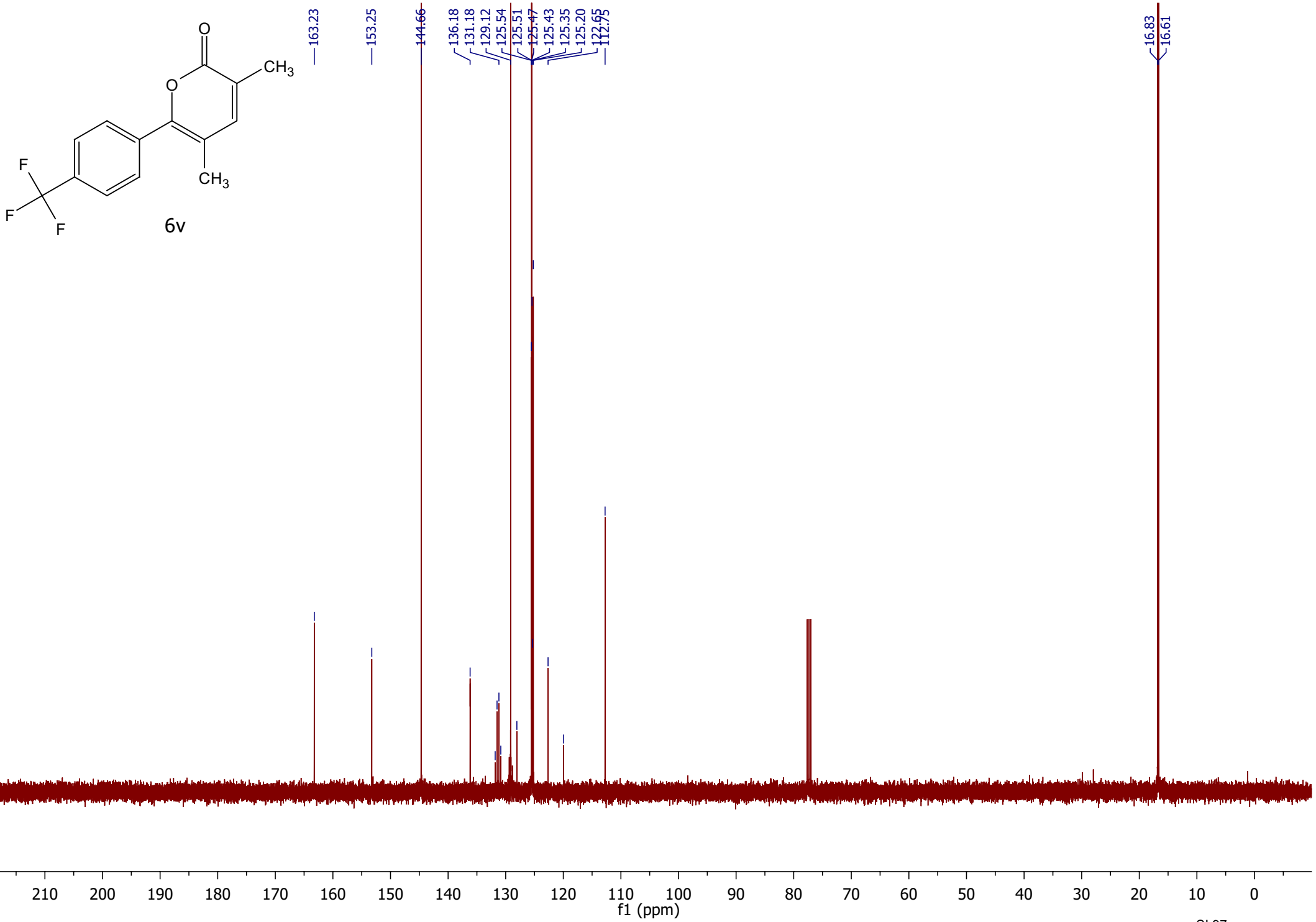
7.48
7.46
7.05
7.04
6.70
6.67
2.99
2.14
2.09
2.09
1.79
0.86
2.12
6.28
3.05
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

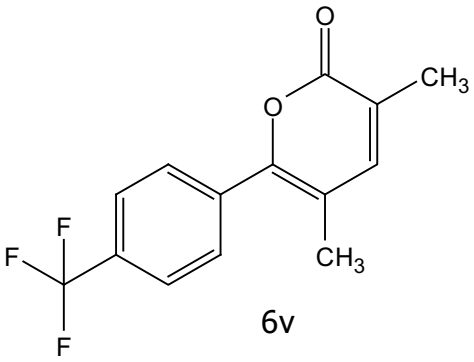

164.29
156.22
151.04
145.75
129.81
121.82
120.40
111.52
109.75
40.32
17.37
16.47
O
O
CH3
CH3
H3C
N
CH3
6u
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
CH3
F
F
F

6v

7.68
7.11
7.10
2.15
4.00
0.96
7.20
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)


O
O
CH3
CH3
F
F
F
6v
163.23
153.25
144.66
136.18
131.18
129.12
125.54
125.51
125.47
125.43
125.35
125.20
122.65
112.75
16.83
16.61
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

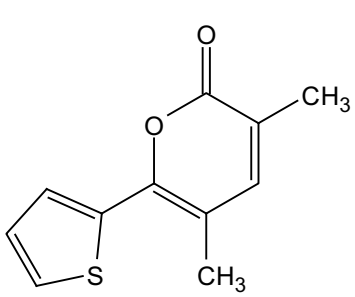


6v

-66.03

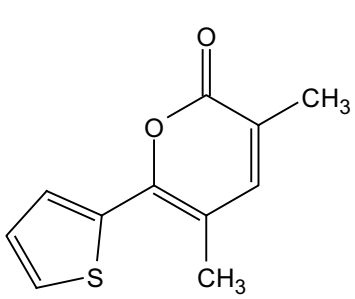
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170

f1 (ppm)


O
O
CH3
S
CH3

6w

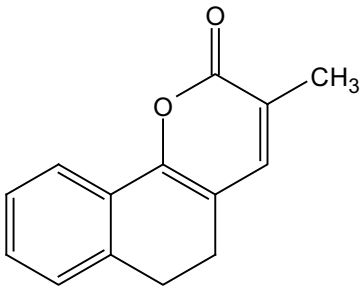
7.49
7.49
7.48
7.48
7.44
7.44
7.43
7.43
7.10
7.10
7.09
7.09
7.04
7.04
7.04
2.22
2.08
2.08
0.94
0.82
0.98
1.00
3.64
3.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
CH3
S
CH3

6w

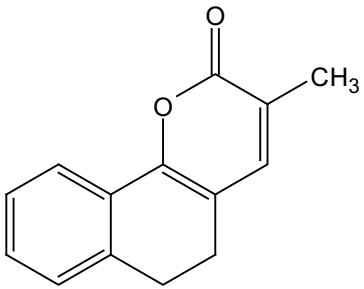
162.83
150.25
145.62
135.27
128.39
128.30
127.76
123.41
110.63
17.79
16.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

SI 100


O
O
CH3

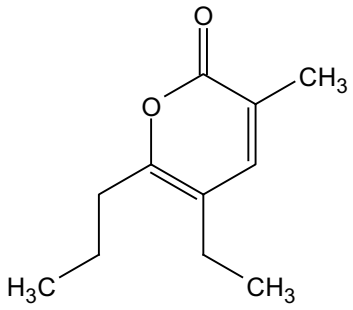
6x

7.78
7.77
7.77
7.76
7.76
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.17
7.17
7.16
7.16
7.16
7.15
7.06
7.06
7.06
2.91
2.89
2.87
2.65
2.63
2.61
2.12
2.11
1.00
2.18
1.15
1.13
3.09
3.07
4.29
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)


O
O
CH3

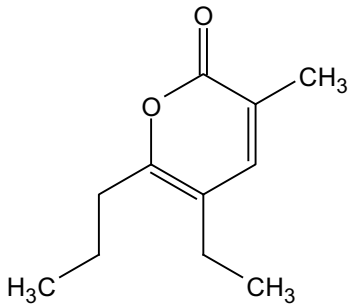
6x

163.54
152.82
142.20
136.78
129.80
128.41
128.03
127.29
123.95
122.92
112.46
27.73
24.69
17.04
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
H3C
CH3

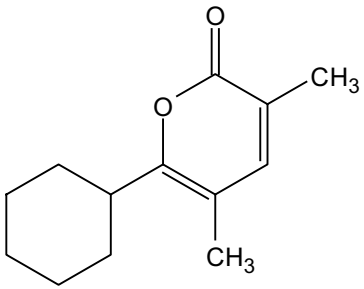
6y

6.96
6.96
2.43
2.41
2.39
2.29
2.27
2.25
2.23
2.03
2.03
1.67
1.65
1.63
1.61
1.09
1.07
1.05
0.93
0.91
0.89
0.80
2.06
2.19
3.00
2.09
3.25
3.00
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)


O
O
CH3
H3C
CH3

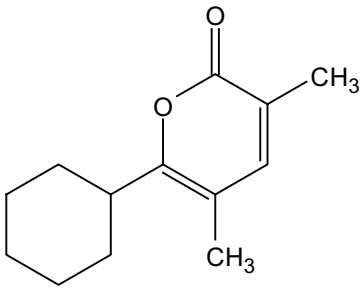
6y

164.42
158.64
143.03
122.92
116.83
32.38
22.69
21.34
16.55
14.92
13.84
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3
CH3

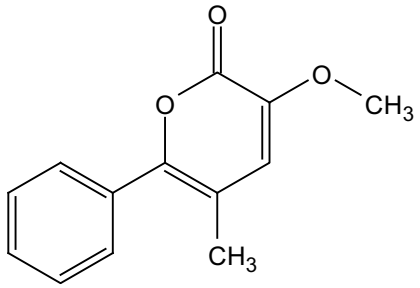
6z

6.90
6.90
2.51
2.51
2.49
2.48
2.48
2.46
1.98
1.98
1.91
1.62
1.61
1.61
1.26
1.26
1.24
1.24
1.23
1.23
1.21
1.21
1.20
1.19
1.18
1.17
0.87
1.00
3.27
3.07
2.27
5.44
3.42
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)


O
O
CH3
CH3

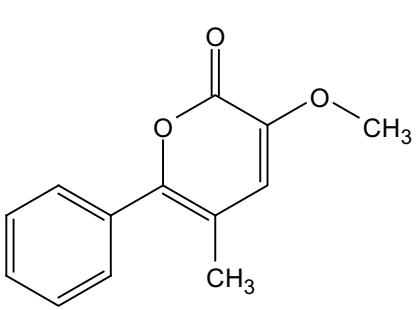
6z

164.48
162.29
144.87
122.10
108.99
39.66
29.90
26.31
25.75
16.47
15.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
CH3
CH3

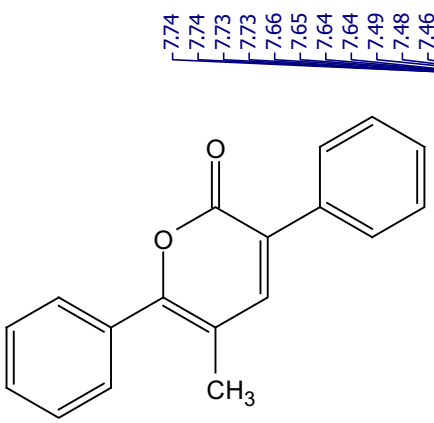
6ad

7.50
7.50
7.49
7.49
7.48
7.48
7.41
7.41
7.41
7.39
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
6.43
3.82
2.15
1.70
2.60
1.00
3.45
3.29
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)


O
O
O
CH3
CH3

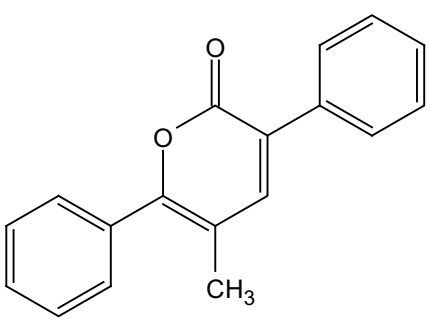
6ad

159.12
149.08
144.56
132.58
129.29
128.75
128.51
118.66
111.30
56.38
17.59
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CH3

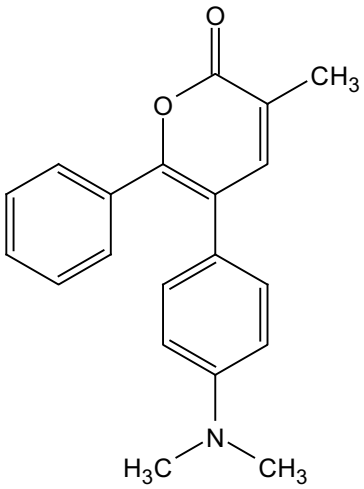
6ae

7.74
7.74
7.73
7.73
7.66
7.65
7.64
7.64
7.49
7.48
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.39
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
2.26
1.95
1.93
6.00
0.99
3.41
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)


O
O
CH3

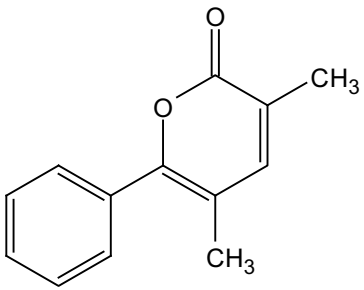
6ae

161.90
156.76
145.43
134.83
132.61
130.02
128.91
128.72
128.67
128.62
128.45
126.04
112.21
17.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

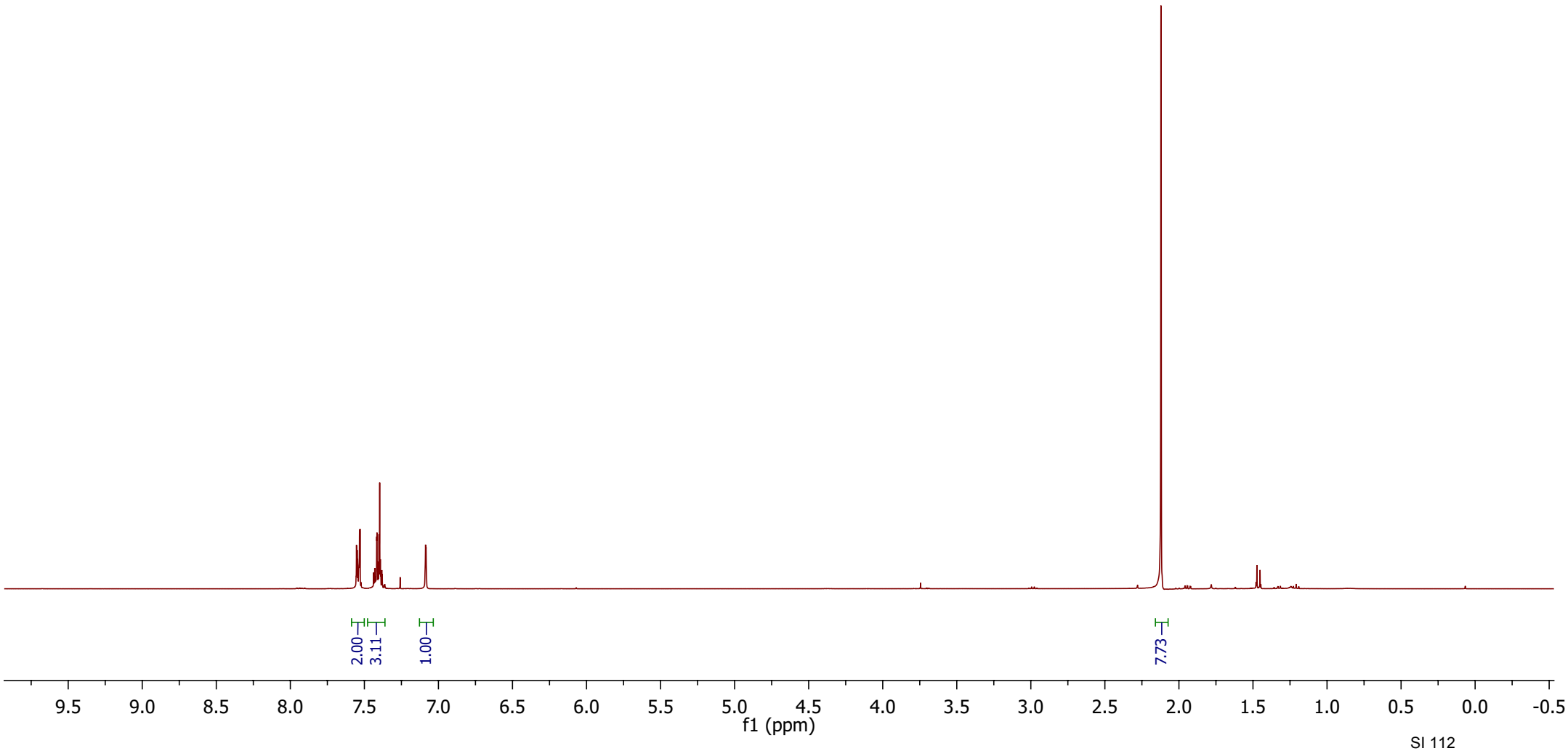

O
O
CH3
N
H3C
CH3

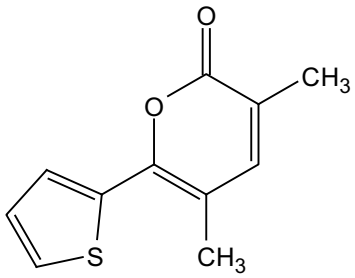
6a - CRUDE

1.75
4.17
2.00
2.43
6.86
3.29
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)

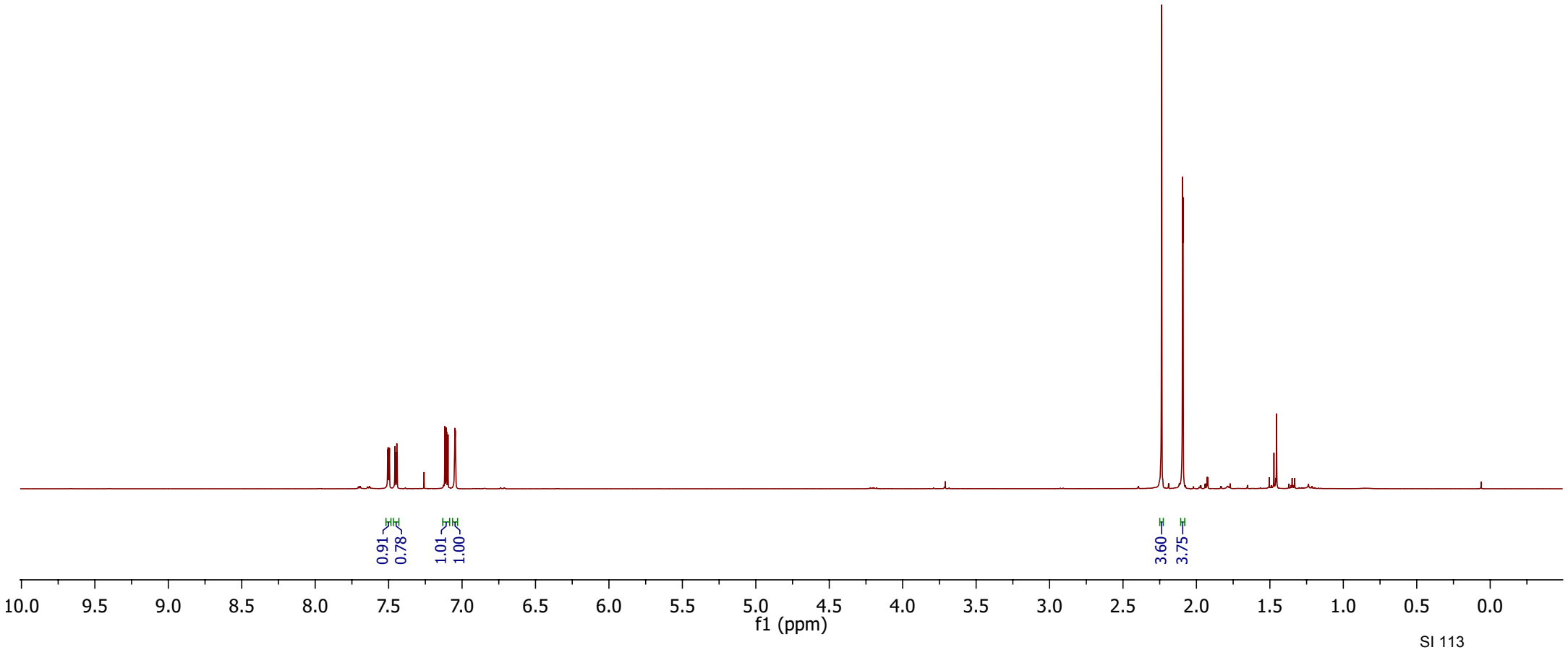

O
O
CH3
CH3

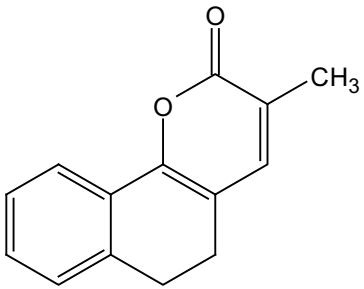
6t - CRUDE


2.00
3.11
1.00
7.73
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)

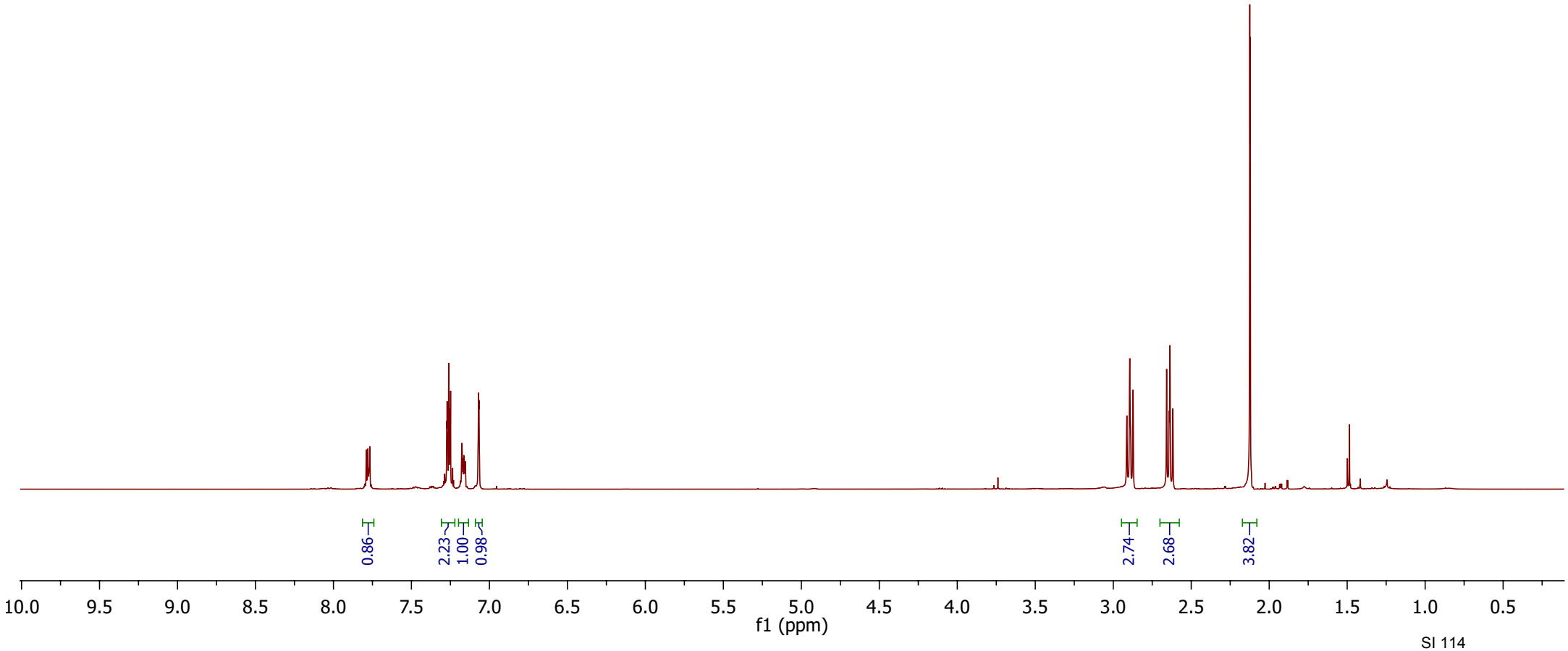

O
O
CH3
S
CH3

6w - CRUDE


0.91
0.78
1.01
1.00
3.60
3.75
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)


O
O
CH3

6x - CRUDE


0.86
2.23
1.00
0.98
2.74
2.68
3.82
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
f1 (ppm)