Enantioselective Synthesis of 2-Arylbicyclo[1.1.0]butane Carboxylates

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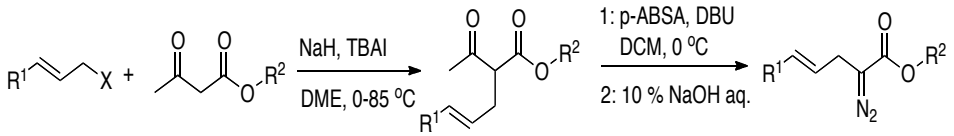
(1) General Method

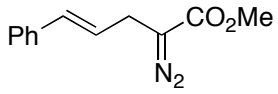
All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers unless otherwise stated. Dichloromethane, toluene, hexane, pentane, diethyl ether solvents were obtained from drying columns (Grubbs type solvent purifier), acetone and ethyl acetate were dried over calcium hydride under reflux and kept under argon atmosphere and 4 A molecular sieves. Flash chromatography was performed on silica gel 60 (230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium backed plates, pre-coated with silica gel (0.25 mm, 60 F_{254}) which were developed using standard visualizing agents: UV fluorescence (254 nm) and phosphomolybdic acid. ^{1}H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 600, 400 or 300 MHz. Tetramethylsilane (TMS) was used as an internal standard ($\delta = 0.00$). The NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, and br = broad), integration and coupling constants in Hz. ^{13}C NMR spectra were recorded at 150, 100 or 75 MHz using the given solvent as an internal standard ($CDCl_3$, $\delta = 77.0$) and ^{13}C NMR spectra were obtained with complete proton decoupling. Mass spectral determinations were carried out by APCI/ESI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Optical rotations were measured on Jasco P-2000 polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol/hexane as gradient.

(2) General procedure for the synthesis of α-allyldiazoacetates



Under an argon atmosphere, a solution of acetoacetate (1.5 equiv.) in anhydrous DME was added dropwise to a stirred suspension of NaH (dry powder, 95%, 1.5 equiv.) in anhydrous DME at 0 °C in 1 hour. Then, n-Bu_4NI (0.1 equiv.) was added in one portion, followed by slow addition of allyl halide derivative (1.0 equiv.) in anhydrous DME at 0 °C in 1 hour. Then, the resulting mixture was heated at 85 °C overnight. The mixture was cooled to 0 °C, diluted with 1 N HCl, and extracted with diethyl ether. The combined organic extracts were washed by brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. After a short flash chromatographic purification, the resulting α-allyl-β-ketoester was used directly without full characterization in the next step.

To a stirred solution of α-allyl-β-ketoester (1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.0 equiv.) in DCM, DBU (4.0 equiv.) was added dropwise at 0 °C. The reaction mixture was then stirring for another 2-3 h. Then, 10% NaOH aqueous was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed to afford the corresponding α-allyldiazoacetates.



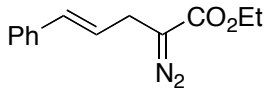
(*E*)-methyl 2-diazo-5-phenylpent-4-enoate (**1**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using cinnamyl chloride (23.0 g, 151 mmol, 1.0 equiv.) dissolving in 50 mL anhydrous DME, methyl acetoacetate (26.2 g, 226 mmol, 1.5 equiv.) dissolving in 50 mL anhydrous DME, sodium hydride (dry powder, 95%, 5.5 g, 226 mmol, 1.5 equiv.) dissolving in 50 mL anhydrous DME and n-Bu_4NI (5.6 g, 15.1 mmol, 0.1 equiv.). After removal of all volatile compounds, the resulting α-allyl-β-ketoester derivative was obtained after a short flash chromatographic purification and used without full characterization in the next step.

The resulting α-allyl-β-ketoester derivative (2.32 g, ca. 10 mmol) was dissolved in DCM (60 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (4.8 g, 20 mmol) was added at 0 °C under argon atmosphere. DBU (6.0 ml, 40 mmol) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 3 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 100/1) afforded **1**(1.46 g, 67%, two steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.29 (m, 4H), 7.24-7.21 (m, 1H), 6.81-6.79 (m, 2H), 6.49 (d, J = 16.0 Hz, 1H), 6.19 (dt, J = 6.8, 16.0 Hz, 1H), 3.76 (s, 3H), 3.20 (d, J = 6.8 Hz, 1H). The NMR spectral data are consistent with published results.[1]

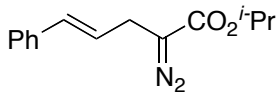
[1] Taber, D. F.; Herr, R. J.; Pack, S. K.; Geremia, J. M. *J. Org. Chem.* **1996**, *61*, 2908.



(*E*)-ethyl 2-diazo-5-phenylpent-4-enoate (**6a**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using cinnamyl bromide (3.92 g, 20 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, ethyl acetoacetate (3.90 g, 30 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 758 mg, 30 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME and n-Bu_4NI (738 mg, 2.0 mmol, 0.1 equiv.). After a short flash chromatographic purification, the resulting α-allyl-β-ketoester derivative was obtained and used without full characterization. The resulting α-allyl-β-ketoester derivative (1.23 g, ca. 5 mmol, 1.0 equiv.) was dissolved in DCM (40 mL), *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10 mmol, 2.0 equiv.) was added at 0 °C under argon atmosphere. DBU (3.0 ml, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (15 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6a** (665.9 mg, 58%, two steps) as a yellow oil.

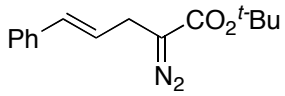
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.22 (m, 5H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.19 (dt, *J* = 6.4, 16.0 Hz, 1H), 4.23 (q, *J* = 7.6 Hz, 2H), 3.20 (d, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 132.5, 128.4, 127.4, 126.1, 123.9, 60.7, 26.6, 14.4; IR (neat): 2982, 2080, 1686, 1370, 1108; HRMS (APCI) calcd for $C_{13}H_{15}O_2N_2$ $(M+H)^+$ 231.11280 found 231.11253.



(*E*)-isopropyl 2-diazo-5-phenylpent-4-enoate (**6b**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using cinnamyl bromide (3.92 g, 20 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, isopropyl acetoacetate (4.32 g, 30 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 758 mg, 30 mmol, 1.5 equiv.) dissolving in 15 mL anhydrous DME and n-Bu_4NI (738 mg, 2.0 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester derivative was obtained and used without full characterization. The resulting α-allyl-β-ketoester derivative (1.3 g, ca. 5.0 mmol, 1.0 equiv.) was dissolved in DCM (30 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10 mmol, 2.0 equiv.) was added at 0 °C under argon atmosphere. DBU (3.0 mL, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (15 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6b** (507.9 mg, 42%, two steps) as a yellow oil.

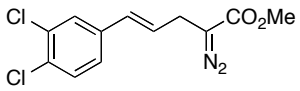
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 5H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 6.9, 15.6 Hz, 1H), 5.15-5.09 (m, 1H), 3.20 (d, *J* = 6.9 Hz, 2H), 1.27 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.4, 128.3, 127.3, 126.0, 123.9, 68.1, 26.5, 21.8; IR (neat): 2980, 2078, 1684, 1364, 1102; HRMS (ESI) calcd for $C_{14}H_{17}O_2N_2$ $(M+H)^+$ 245.12845 found 245.12819.



(*E*)-*tert*-butyl 2-diazo-5-phenylpent-4-enoate (**6c**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using cinnamyl bromide (3.92 g, 20 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, isopropyl acetoacetate (4.74 g, 30 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 758 mg, 30 mmol, 1.5 equiv.) dissolving in 15 mL anhydrous DME and n-Bu_4NI (738 mg, 2.0 mmol, 0.1 equiv.). After general work up, the crude ester was obtained and used without full characterization. The resulting α-allyl-β-ketoester derivative (1.37 g, ca. 5.0 mmol, 1.0 equiv.) was dissolved in DCM (30 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10 mmol, 2.0 equiv.) was added at 0 °C under argon atmosphere. DBU (3.0 mL, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (15 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6c** (669.9 mg, 52%, two steps) as a yellow oil.

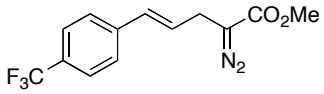
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 5H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.17 (dt, *J* = 7.2, 16.0 Hz, 1H), 3.14 (d, *J* = 7.2 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 132.5, 128.5, 127.5, 126.2, 124.2, 81.2, 28.3, 26.7; IR (neat): 2977, 2076, 1682, 1392, 1108; HRMS (APCI) calcd for $C_{15}H_{19}O_2$ $(M-N_2+H)^+$ 231.13796 found 231.13762.



(*E*)-methyl 2-diazo-5-(3,4-dichlorophenyl)pent-4-enoate (**6d**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using (*E*)-4-(3-bromoprop-1-en-1-yl)-1,2-dichlorobenzene (12.0 g, 45.5 mmol, 1.0 equiv.) dissolving in 50 mL anhydrous DME, methyl acetoacetate (7.92 g, 68.3 mmol, 1.5 equiv.) dissolving in 50 mL anhydrous DME, sodium hydride (dry powder, 95%, 1.73 g, 68.3 mmol, 1.5 equiv.) dissolving in 25 mL anhydrous DME and n-Bu_4NI (1.68 g, 4.55 mmol, 0.1 equiv.). After a short flash chromatographic purification, the resulting α-allyl-β-ketoester was obtained and used directly without full characterization in the next step. The ester derivative (1.50 g, ca. 5.0 mmol, 1.0 equiv.) was dissolved in DCM (40 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10 mmol, 2.0 equiv.) was added at 0 °C under argon atmophere. DBU (3.0 ml, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (15 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6d** (901.1 mg, 63%, two steps) as a yellow oil.

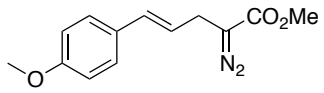
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.17 (dd, *J* = 2.0, 8.3 Hz, 1H), 3.79 (s, 3H), 3.20 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 136.5, 132.2, 130.8, 130.0, 129.8, 127.6, 126.0, 125.2, 51.7, 26.5; IR (neat): 2977, 2076, 1682, 1392, 1108; HRMS (APCI) calcd for $C_{12}H_{11}O_2N_2Cl_2$ $(M+H)^+$ 285.01921 found 285.01965.



(*E*)-methyl 2-diazo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (**6e**)

Prepared according to general procedure for the synthesis of α -allyldiazoacetates using (*E*)-1-(3-bromoprop-1-en-1-yl)-4-(trifluoromethyl)benzene (6.0 g, 23.0 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, methyl acetoacetate (4.0 g, 34.5 mmol, 1.5 equiv.) dissolving in 25 mL anhydrous DME, sodium hydride (dry powder, 95%, 872 mg, 34.5 mmol, 1.5 equiv.) dissolving in 25 mL anhydrous DME and n-Bu_4NI (849 mg, 2.3 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester was obtained and used directly without full characterization. The resulting α-allyl-β-ketoester derivative (1.5 g, ca. 5.0 mmol, 1.0 equiv.) was dissolved in DCM (30 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10 mmol, 2.0 equiv.) was added at 0 °C under argon atmophere. DBU (3.0 ml, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 100/1) afforded **6e** (440.2 mg, 29%, two steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 6.8, 16.0 Hz, 1H), 3.78 (s, 3H), 3.22 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 140.0, 131.1, 129.4, 129.1, 128.7, 128.1, 126.9, 126.3, 126.1, 125.42, 125.38, 125.34, 125.30, 122.7, 120.0, 51.9, 26.7; IR (neat): 2955, 1716, 1620, 1326, 1121, 1068; HRMS (APCI) calcd for $C_{13}H_{12}O_2F_3N_2$ $(M+H)^+$ 285.08454 found 285.08401.

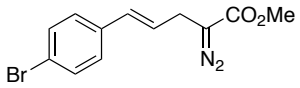


(E)-methyl 2-diazo-5-(4-methoxyphenyl)pent-4-enoate (**6f**)

Prepared according to general procedure for the synthesis of α -allyldiazoacetates using (*E*)-1-(3-bromoprop-1-en-1-yl)-4-methoxybenzene (2.2 g, 9.7 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, methyl acetoacetate (1.7 g, 14.6 mmol, 1.5 equiv.) dissolving in 16 mL anhydrous DME, sodium hydride (dry powder, 95%, 369 mg, 14.6 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME and n-Bu_4NI (358 mg, 0.97 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester was obtained and used directly without full full characterization. The resulting α-allyl-β-ketoester derivative (2.6 g, ca. 10.0 mmol, 1.0 equiv.) was dissolved in DCM (50 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (4.8 g, 20 mmol, 2.0 equiv.) was added at 0 °C under argon atmophere. DBU (6.0 ml, 40 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-

allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 100/1) afforded **6f** (1.29 mg, 54%, two steps) as a sticky yellow oil.

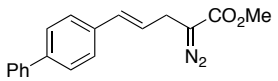
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.04 (dt, *J* = 6.8, 15.6 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.18 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 132.1, 129.4, 127.4, 121.6, 113.9, 55.2, 51.9, 26.8; IR (neat): 2953, 2837, 2080, 1689, 1511, 1247; HRMS (APCI) calcd for $C_{13}H_{15}O_3N_2$ $(M+H)^+$ 247.10772 found 247.10796.



(*E*)-methyl 5-(4-bromophenyl)-2-diazopent-4-enoate (**6g**)

Prepared according to general procedure for the synthesis of α -allyldiazoacetates using (*E*)-1-bromo-4-(3-bromoprop-1-en-1-yl)benzene (5.1 g, 18.6 mmol, 1.0 equiv.) dissolving in 20 mL anhydrous DME, methyl acetoacetate (3.2 g, 27.9 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 705 mg, 27.9 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME and n-Bu_4NI (686 mg, 1.86 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester was obtained and used without full characterizaition. The resulting α-allyl-β-ketoester derivative (1.55 g, ca. 5.0 mmol, 1.0 equiv.) was dissolved in DCM 50 mL and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.4 g, 10.0 mmol, 2.0 equiv.) was added at 0 °C under argon atmophere. DBU (3.0 ml, 20 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6g** (977.8 mg, 66%, two steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 7.2, 16.0 Hz, 1H), 3.79 (s, 3H), 3.20 (d, *J* = 7.2 Hz, 2H), 3.01 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 131.6, 131.5, 127.8, 124.9, 121.4, 52.0, 26.8; IR (neat): 2950, 2078, 1686, 1339; HRMS (APCI) calcd for $C_{12}H_{12}O_2N_2Br$ $(M+H)^+$ 295.00767found 295.00801.

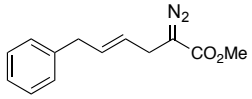


(*E*)-methyl 5-([1,1'-biphenyl]-4-yl)-2-diazopent-4-enoate (**6h**)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using (*E*)-4-(3-bromoprop-1-en-1-yl)-1,1'-biphenyl (5.16 g, 19.0 mmol, 1.0 equiv.) dissolving in 60 mL anhydrous DME (note: 15 mL DCM was also added to increase the solubility and the resulting solution was dropped within 1 hour by use of pressure constant funnel under argon), methyl acetoacetate (3.48 g, 30 mmol, 1.58 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 758 mg, 30 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME and n-Bu_4NI (738 mg, 1.9 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester was obtained and used without full characterization. The resulting α-allyl-β-ketoester derivative (0.8 g, ca. 2.6 mmol, 1.0 equiv.) was dissolved in DCM 50 mL and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.25 g, 5.2 mmol, 2.0 equiv.) was added at 0 °C under argon atmophere. DBU (1.54 ml, 10.4 mmol, 4.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring

for another 2 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6h** (467.3 mg, 62%, two steps) as a yellow solid.

Mp: 71-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.59 (m, 4H), 7.51-7.47 (m, 4H), 7.42-7.38 (m, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.29 (dt, *J* = 6.8, 15.6 Hz, 1H), 3.85 (s, 3H), 3.27 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 140.2, 135.5, 132.1, 128.6, 127.2, 127.1, 126.7, 126.6, 123.9, 51.9, 26.7; IR (neat): 3031, 2080, 1692, 1437, 1341; HRMS (APCI) calcd for $C_{18}H_{17}O_2$ (M-N_2+H)$^+$ 265.12231 found 265.12283.

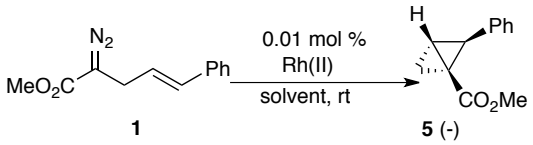


(*E*)-methyl 2-diazo-6-phenylhex-4-enoate (6i)

Prepared according to general procedure for the synthesis of α-allyldiazoacetates using (*E*)-(4-bromobut-2-en-1-yl)benzene (3.78 g, 18.0 mmol, 1.0 equiv.) dissolving in 50 mL anhydrous DME, methyl acetoacetate (3.13 g, 27 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME, sodium hydride (dry powder, 95%, 682 mg, 27 mmol, 1.5 equiv.) dissolving in 20 mL anhydrous DME and n-Bu_4NI (664 mg, 1.8 mmol, 0.1 equiv.). After general work up, the resulting α-allyl-β-ketoester was obtained and used without full characterization. The resulting α-allyl-β-ketoester derivative (1.1 g, ca. 4.5 mmol, 1.0 equiv.) was dissolved in DCM 20 mL and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (3.24 g, 13.5 mmol, 3.0 equiv.) was added at 0 °C under argon atmosphere. DBU (4.0 ml, 27 mmol, 6.0 equiv.) was added dropwise at 0 °C in 1 hour. The reaction mixture was then stirring for another 2 h. Then, 10% NaOH (20 mL) was added at 0 °C. The resulting mixture was warmed to room temperature. The crude α-allyldiazoester was extracted with DCM (20 x 3 mL), washed by brine (10 x 3 mL), dried over anhydrous $MgSO_4$. Flash chromatographic purification (hexanes/ethyl acetate = 50/1) afforded **6i** (462.2 mg, 45%, two steps) as a yellow sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.13 (m, 5H), 5.76-5.68 (m, 1H), 5.68-5.45 (m, 1H), 3.74 (s, 3H), 3.34 (d, *J* = 7.0 Hz, 2H), 3.01 (d, *J* = 7.0 Hz, 2H);; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 132.6, 128.3, 128.1, 125.9, 125.2, 51.7, 38.5, 25.9; IR (neat): 3027, 2952, 2079, 1689, 1339; HRMS (APCI) calcd for $C_{13}H_{14}O_2N_2Na$ (M+Na)$^+$ 253.09475 found 253.09463.

(3) General procedure for examination of catalysts and solvent effects



1 **5** (-)

To a 25 mL flame-dried round-bottom flask, kept under a dry atmosphere of argon at given temperature, was added the given dry solvent (1.0 mL) and the given catalyst. The diazo compound (0.4 mmol, 1.0 equiv.), dissolved in the given dry solvent (2 mL), was then added to the former solution drop-wise over 0.5 hour at given temperature. The mixture was allowed to stir for another 15 min

after the addition at room temperature or was allowed to warm to around 10 °C; when the diazo compound was fully consumed by TLC analysis, the reaction mixture was concentrated *in vacuo*. The crude residue was analyzed by ^{1}H NMR with C_6D_6 or freshly opened $CDCl_3$, which was kept under potassium carbonate, as solvent, and purified by flash column chromatography (hexanes/ethyl acetate) to afford the pure bicyclo[1.1.0]butane derivatives.

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*R*-DOSP)$_4$ (0.1 mL, 0.76 mg/mL in dry dichloromethane, 0.01 mol%), dichloromethane as solvent, room temperature, 45 min. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (49.1 mg, 65% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 13.8 min and 15.3 min (minor), 0% ee.

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*S*-PTAD)$_4$ (0.12 mL, 0.62 mg/mL in dry dichloromethane, 0.012 mol%), dichloromethane as solvent, room temperature, 45 min. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (48.4 mg, 64% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 13.3 min (minor) and 14.9 min (major), 47% ee.

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*S*-PTTL)$_4$ (0.12 mL, 0.50 mg/mL in dry dichloromethane, 0.012 mol%), dichloromethane as solvent, room temperature, 45 min. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (52.1 mg, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 14.0 min (minor) and 15.6 min (major), 52% ee.

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(4*S*-MEOX)$_4$ (0.1 mL, 0.35 mg/mL in dry dichloromethane, 0.01 mol%), dichloromethane as solvent, room temperature, 45 min. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (31.5 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, J = 1.2 Hz, 1H), 2.28 (d, J = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 14.3 min (major) and 15.8 min (minor), -23% ee.

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*R*-BTPCP)$_4$ (0.1 mL, 0.70 mg/mL in dry dichloromethane, 0.01 mol%), dichloromethane as solvent, room temperature, 45 min. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (54.2 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, J = 1.2 Hz, 1H), 2.28 (d, J = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 13.3 min (minor) and 14.8 min (major), 90% ee

Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*R*-BTPCP)$_4$ (0.1 mL, 0.70 mg/mL in dry dichloromethane, 0.01 mol%), and the dichloromethane solvent was removed away with flushed argon gas, dry hexane as solvent, room temperature. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (47.9 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, J = 1.2 Hz, 1H), 2.28 (d, J = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 15.3 min (minor) and 17.2 min (minor), 88% ee

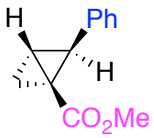
Prepared according to the general procedure for examination of catalysts, temperature and solvent effects using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.), Rh_2(*R*-BTPCP)$_4$ (0.1 mL, 0.70 mg/mL in dry dichloromethane, 0.01 mol%), and the dichloromethane solvent was removed away with flushed argon gas, dry acetone as solvent, room temperature. The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (45.4 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, J = 1.2 Hz, 1H), 2.28 (d, J = 3.2 Hz, 1H), 1.14 (s, 1H); HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 15.2 min (major) and 16.9 min (minor), 94% ee.

(4) General procedure for Rh_2(*R*-BTPCP)$_4$-catalyzed enantioselective synthesis of 2-arylbicyclo[1.1.0]butane carboxylate

To a 25 mL flame-dried round-bottom flask, kept under a dry atmosphere of argon, was added dry ethyl acetate (1.0 mL) and Rh_2(*R*-BTPCP)$_4$ (0.1 mL, c = 0.70 mg/ mL in ethyl acetate, 0.0001 equiv.). The diazo compound (0.4 mmol, 1.0 equiv.), dissolved in dry ethyl acetate (2 mL), was then added to the former solution drop-wise over 0.5 hour at room temperature. The mixture was allowed to stir for another 15 min after the addition; when the diazo compound was fully consumed by TLC analysis, the reaction mixture was

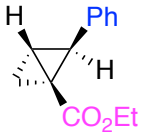
concentrated *in vacuo*. The crude residue was analyzed by ^{1}H NMR with C_6D_6 or freshly opened $CDCl_3$ kept under potassium carbonate as solvent and purified by flash column chromatography (hexanes/ethyl acetate) to afford the pure bicyclo[1.1.0]butane derivatives.



(1*S*,2*S*,3*R*)-methyl 2-phenylbicyclo[1.1.0]butane-1-carboxylate (**5**)

Prepared according to the general procedure for enantioselective synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **5** as a colorless oil (52.4 mg, 70% yield).

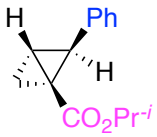
$[\alpha]^{20}_D$ -38.1° (c = 1.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.17-7.15 (m, 2H), 3.55 (s, 3H), 2.75-2.74 (m, 1H), 2.39 (d, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 3.2 Hz, 1H), 1.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 134.6, 127.9, 127.2, 51.5, 50.5, 31.1, 19.8, 15.1; IR (neat): 2951, 1708, 1439, 1389, 1196, 1135; HRMS (APCI) calcd for $C_{12}H_{13}O_2$ $(M+H)^+$ 189.09101 found 189.09086; HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 15.7 min (minor) and 17.7 min (major), 94% ee.



(1*S*,2*S*,3*R*)-ethyl 2-phenylbicyclo[1.1.0]butane-1-carboxylate (**7a**)

Prepared according to the general procedure for enantioselective synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-ethyl 2-diazo-5-phenylpent-4-enoate 9 (0.4 mmol, 92.0 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7a** as colorless oil (59.7 mg, 74% yield).

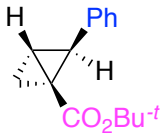
$[\alpha]^{20}_D$ -35.9° (c = 5.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 3H), 7.17-7.15 (m, 2H), 4.07-3.94 (m, 2H), 2.73-2.72 (m, 1H), 2.39 (d, *J* = 1.6 Hz, 1H), 2.29 (d, *J* = 3.2 Hz, 1H), 1.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 134.8, 127.7, 127.2, 127.1, 60.2, 50.4, 31.0, 19.4, 15.4, 13.8; IR (neat): 2982, 1723, 1454, 1202; HRMS (APCI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$ 203.10666 found 203.10640. HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 11.5 min (minor) and 12.5 min (major), 94% ee.



(1*S*,2*S*,3*R*)-isopropyl 2-phenylbicyclo[1.1.0]butane-1-carboxylate (**7b**)

Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-isopropyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 97.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7b** as colorless oil (55.3 mg, 64% yield).

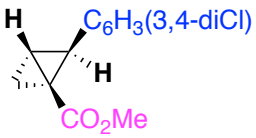
$[\alpha]^{20}_D$ -23.8° (c = 5.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.21 (m, 3H), 7.17-7.15 (m, 2H), 4.93-4.87 (m, 1H), 2.71-2.69 (m, 1H), 2.38 (d, *J* = 1.2 Hz, 1H), 2.28 (d, *J* = 1.2 Hz, 1H), 1.12 (s, 1H), 1.05 (d, *J* = 1.2 Hz, 1H), 1.08 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 134.9, 127.7, 127.3, 126.9, 67.6, 50.3, 31.0, 21.6, 21.2, 18.9, 15.8; IR (neat): 2979, 1703, 1404, 1208; HRMS (APCI) calcd for $C_{14}H_{17}O_2$ $(M+H)^+$ 217.12231 found 217.12202. HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 9.6 min (minor) and 10.3 min (major), 93% ee.



(1*S*,2*S*,3*R*)-*tert*-butyl 2-phenylbicyclo[1.1.0]butane-1-carboxylate (**7c**)

Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-tert-butyl 2-diazo-5-phenylpent-4-enoate (0.4 mmol, 103.3 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7c** as colorless oil (41.7 mg, 45% yield).

$[\alpha]^{20}_D$ -16.3° (c = 4.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 3H), 7.16-7.14 (m, 2H), 2.68-2.66 (m, 1H), 2.34 (d, *J* = 1.2 Hz, 1H), 2.30 (d, *J* = 3.6 Hz, 1H), 1.18 (s, 9H), 1.07 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 135.3, 127.7, 127.2, 126.9, 80.4, 50.1, 30.2, 27.6, 18.6, 16.8; IR (neat): 2976, 1699, 1394, 1221; HRMS (APCI) calcd for $C_{15}H_{19}O_2$ $(M+H)^+$ 231.13796 found 231.13770. HPLC (S, S-Whelk, 0.5% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 230 nm) retention times of 6.2 min (minor) and 7.2 min (major), 70% ee.

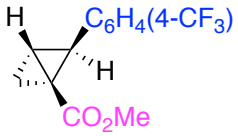


(1*S*,2*S*,3*R*)-methyl 2-(3,4-dichlorophenyl)bicyclo[1.1.0]butane-1-carboxylate (**7d**)

Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 2-diazo-5-(3,4-dichlorophenyl)pent-4-enoate (0.4 mmol, 113.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7d** as colorless oil (66.3 mg, 65% yield).

$[\alpha]^{20}_D$ -38.2 ° (c = 3.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 2.1, 8.3 Hz, 1H), 3.56 (s, 3H), 2.74-2.72 (m, 1H), 2.29-2.25 (m, 2H), 1.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 134.9, 131.1, 129.8, 129.3, 126.6, 51.6, 48.9, 30.8, 19.7, 13.3; IR (neat): 2951, 1712, 1474, 1439, 1199, 1134; HRMS (APCI) calcd for $C_{12}H_{11}O_2Cl_2$

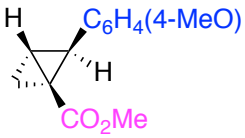
$(M+H)^+$ 257.01306 found 257.01279. HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 210 nm) retention times of 14.0 min (minor) and 18.0 min (major), 90% ee.



(1*S*,2*S*,3*R*)-methyl 2-(4-(trifluoromethyl)phenyl)bicyclo[1.1.0]butane-1-carboxylate (**7e**)

Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 2-diazo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (0.4 mmol, 113.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7e** as colorless oil (64.6 mg, 63% yield).

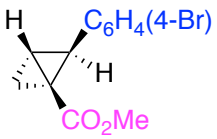
$[\alpha]^{20}_D$ -11.4 ° (c = 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 3.19 (s, 3H), 2.20-2.18 (m, 1H), 2.11 (app. dd, *J* = 0.8, 3.2 Hz, 1H), 1.90 (d, *J* = 1.6 Hz, 1H), 0.77-0.76 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.1, 139.2, 131.1, 128.2, 127.9, 127.7, 124.8 (q), 51.0, 49.5, 30.8, 19.4, 15.7; IR (neat): 2955, 1716, 1620, 1326, 1121, 1068; HRMS (APCI) calcd for $C_{13}H_{12}O_2F_3$ $(M+H)^+$ 257.07839 found 257.07791. HPLC (S-250, 0% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 60 min, UV 210 nm) retention times of 45.6 min (minor) and 48.3 min (major), 94% ee.



(1S,2S,3R)-methyl 2-(4-methoxyphenyl)bicyclo[1.1.0]butane-1-carboxylate (**7f**)

Prepared according to the general procedure for Rh_2(*R*-BTPCP)$_4$-catalyzed synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 2-diazo-5-(4-methoxyphenyl)pent-4-enoate xx (0.4 mmol, 98.4 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7f** as colorless oil (57.4 mg, 66% yield).

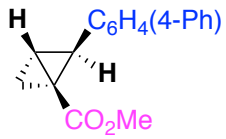
$[\alpha]^{20}_D$ -30.1° (c = 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.59 (s, 3H), 2.69-2.68 (m, 1H), 2.38 (d, *J* = 1.6 Hz, 1H), 2.28 (app. dd, *J* = 1.2, 3.6 Hz, 1H), 1.29 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.9, 158.7, 128.2, 126.8, 113.3, 55.2, 51.5, 50.2, 30.9, 19.8, 14.8; IR (neat): 2952, 2836, 1706, 1516, 1439, 1038; HRMS (APCI) calcd for $C_{13}H_{15}O_3$ $(M+H)^+$ 219.10157 found 219.10144; HPLC (ADH, 1.0 % isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 230 nm) retention times of 19.8 min (minor) and 20.8 min (major), 85% ee. (-78-0 °C, 59% yield, 88% ee).



(1S,2S,3R)-methyl 2-(4-bromophenyl)bicyclo[1.1.0]butane-1-carboxylate (**7g**)

Prepared according to the general procedure for Rh_2(*R*-BTPCP)$_4$-catalyzed synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 5-(4-bromophenyl)-2-diazopent-4-enoate (0.4 mmol, 117.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7g** as colorless oil (70.4 mg, 66% yield).

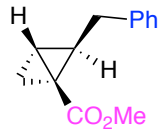
$[\alpha]^{20}_D$ -30.4° (c = 3.13, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.58 (s, 3H), 2.35 (d, *J* = 1.6 Hz, 1H), 2.29 (app. dd, *J* = 1.2, 3.6 Hz, 1H), 1.15 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.4, 133.7, 130.9, 128.9, 121.1, 51.6, 49.7, 30.9, 19.7, 15.2; IR (neat): 2949, 1709, 1207, 1135; HRMS (APCI) calcd for $C_{12}H_{12}O_2Br$ $(M+H)^+$ 267.00152 found 267.00189; HPLC (S250, 0 % isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 230 nm) retention times of 16.3 min (minor) and 18.9 min (major), 93% ee.



(1S,2S,3R)-methyl 2-([1,1'-biphenyl]-4-yl)bicyclo[1.1.0]butane-1-carboxylate (**7h**)

Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 5-(4-bromophenyl)-2-diazopent-4-enoate (0.4 mmol, 116.8 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7h** as colorless oil (64.3 mg, 61% yield).

Mp; 99-101 °C; $[\alpha]^{20}_D$ -37.4° (c = 1.17, CH_3CN); ^{1}H NMR (400 MHz, C_6D_6): δ 7.60-7.58 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 745-7.41 (m, 2H), 7.35-7.33 (m, 1H), 7.26-7.25 (m, 2H), 3.60 (s, 3H), 2.80-2.79 (m, 1H), 2.45 (app. d, *J* = 1.2 Hz, 1H), 2.32 (app. dd, *J* = 1.2, 4.2 Hz, 1H), 1.18 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 171.7, 140.8, 140.0, 133.7, 128.7, 127.7, 127.2, 126.9, 126.6, 51.6, 50.3, 31.1, 20.1, 15.2; IR (neat): 3030, 2949, 1712, 1207, 1135; HRMS (APCI) calcd for $C_{18}H_{17}O_2$ $(M+H)^+$ 265.12231 found 265.12283; HPLC (ODH, 0.5% isopropanol in hexane, 0.5 mL/min, 1 mg/mL, 60 min, UV 230 nm) retention times of 16.5 min (minor) and 41.8 min (major), 91% ee.



(1S,2S,3R)-methyl 2-([1,1'-biphenyl]-4-yl)bicyclo[1.1.0]butane-1-carboxylate (**7i**)

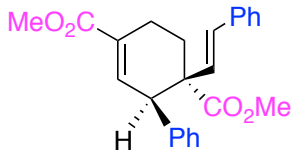
Prepared according to the general procedure for synthesis of bicyclo[1.1.0]butane derivatives using (*E*)-methyl 2-diazo-6-phenylhex-4-enoate (0.4 mmol, 92.0 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **7i** as colorless oil (59.4 mg, 74% yield).

$[\alpha]^{20}_D$ -6.8° (c = 2.43, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ 7.33-7.21 (m, 5H), 3.73 (s, 3H), 3.26 (dd, *J* = 4.4, 15.0 Hz, 1H), 2.83 (dd, *J* = 8.0, 15.0 Hz, 1H), 2.29 (s, 2H), 1.64-1.60 (m, 1H), 1.05 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 173.1, 140.4, 128.3, 126.1, 51.6, 49.7, 34.0, 32.9, 21.3, 12.4; IR (neat): 2952, 1713, 1209, 1128; HRMS (APCI) calcd for $C_{13}H_{14}O_2Na$ $(M+Na)^+$ 225.08860 found

225.08834; HPLC (ODR, 0.25% isopropanol in hexane, 1.0 mL/min, 1 mg/mL, 30 min, UV 230 nm) retention times of 5.9 min (minor) and 6.5 min (major), 51% ee.

(5) General procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives

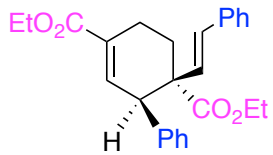
To a 25 mL flame-dried round-bottom flask, kept under a dry atmosphere of argon, was added dry and degassed hexane (1.0 mL) and $Rh_2(TPA)_4$ (5.4 mg, 0.01 equiv.). The diazo compound (0.4 mmol, 1.0 equiv.), dissolved in dry and degassed hexane (2 mL), was then added to the former solution drop-wise over 0.5 hour at room temperature. The mixture was allowed to stir for another 12-48 hours after the addition. Then, the reaction mixture was concentrated *in vacuo*. The crude residue was analyzed by ^{1}H NMR with C_6D_6 or freshly opened $CDCl_3$, which was kept under potassium carbonate, as solvent and purified by flash column chromatography (hexanes/ethyl acetate) to afford the pure cyclohexene derivatives.



(1*R*,2*R*)-dimethyl 2-((*E*)-styryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**4**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-methyl 2-diazo-4-methyl-5-phenylpent-4-enoate xx (0.4 mmol, 86.4 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **4** as a white but amorphous solid (60.1 mg, 80% yield).

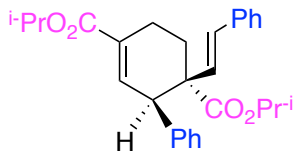
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.09 (m, 10H), 7.05 (d, *J* = 5.2 Hz, 1H), 6.18 (d, *J* = 16.6 Hz, 1H), 5.74 (d, *J* = 16.6 Hz, 1H), 4.40 (d, *J* = 5.2 Hz, 1H), 3.74 (s, 3H), 2.63 (dd, *J* = 5.8, 18.6 Hz, 1H), 2.50-2.46 (m, 1H), 1.89 (ddd, *J* = 6.4, 10.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 167.4, 139.5, 138.0, 136.8, 131.4, 130.6, 129.9, 129.5, 128.4, 127.9, 127.5, 127.3, 126.2, 52.5, 51.7, 51.3, 47.7, 24.5, 22.2; IR (neat): 3026, 2949, 1712, 1435, 1256, 1229; HRMS (APCI) calcd for $C_{24}H_{25}O_4$ $(M+H)^+$ 377.17474 found 377.17493.



(1*R*,2*R*)-diethyl 2-((*E*)-styryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8a**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-ethyl 2-diazo-5-phenylpent-4-enoate xx (0.4 mmol, 92 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8a** as a white solid (65.7 mg, 81% yield).

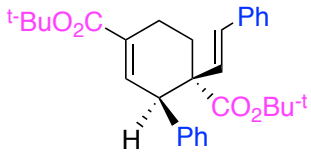
Mp: 101-103 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.06 (m, 10H), 6.21 (d, *J* = 16.4 Hz, 1H), 5.73 (d, *J* = 16.4 Hz, 1H), 4.41 (d, *J* = 5.1 Hz, 1H), 4.24-4.16 (m, 4H), 2.64 (dd, *J* = 5.7, 18.8 Hz, 1H), 2.52-2.43 (m, 1H), 2.31 (dd, *J* = 6.4, 13.7 Hz, 1H), 1.89 (ddd, *J* = 6.4, 10.8, 13.6 Hz, 1H), 1.27 (q, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 166.9, 139.3, 138.2, 136.8, 131.7, 130.7, 130.1, 129.4, 128.4, 127.9, 127.4, 127.2, 126.2, 61.2, 60.5, 51.1, 47.6, 24.5, 22.1, 14.2; IR (neat): 3027, 2979, 1716, 1255, 1229, 1088; HRMS (APCI) calcd for $C_{26}H_{29}O_4$ $(M+H)^+$ 405.20604 found 405.20536.



(1*R*,2*R*)-diisopropyl 2-((*E*)-styryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8b**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-isopropyl 2-diazo-5-phenylpent-4-enoate xx (0.4 mmol, 97.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8b** as a white solid (39.5 mg, 46% yield).

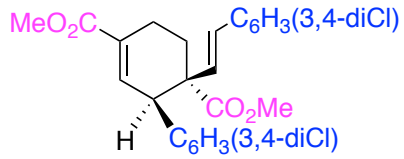
Mp: 133-135 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.10 (m, 10H), 7.04 (d, *J* = 5.4 Hz, 1H), 6.23 (d, *J* = 16.6 Hz, 1H), 5.70 (d, *J* = 16.6 Hz, 1H), 5.14-5.06 (m, 2H), 4.40 (d, *J* = 5.4 Hz, 1H), 2.63 (dd, *J* = 6.6, 19.2 Hz, 1H), 2.61-2.44 (m, 1H), 2.29 (dd, *J* = 6.6, 13.8 Hz, 1H), 1.90-1.85 (m, 1H), 1.28-1.24 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 166.5, 139.1, 138.3, 136.9, 132.0, 130.7, 130.4, 129.4, 128.4, 127.9, 127.4, 127.2, 126.2, 68.6, 67.8, 51.1, 47.6, 24.6, 22.1, 21.9, 21.7, 21.6; IR (neat): 2979, 2936, 1710, 1452, 1106; HRMS (APCI) calcd for $C_{28}H_{33}O_4$ $(M+H)^+$ 433.23734 found 433.23679.



(1*R*,2*R*)-di-*tert*-butyl 2-((*E*)-styryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8c**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-tert-butyl 2-diazo-5-phenylpent-4-enoate xx (0.4 mmol, 103.3 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8c** as a white but amorphous solid (17.6 mg, 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.07 (m, 10H), 6.94 (d, *J* = 5.4 Hz, 1H), 6.23 (d, *J* = 16.4 Hz, 1H), 5.67 (d, *J* = 16.4 Hz, 1H), 4.30 (d, *J* = 5.2 Hz, 1H), 2.55 (dd, *J* = 6.2, 18.1 Hz, 1H), 2.48-2.39 (m, 1H), 2.22-2.17 (m, 1H), 1.79 (ddd, *J* = 6.6, 10.7, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 166.4, 138.6, 137.1, 132.4, 131.5, 130.8, 129.1, 128.4, 127.8, 127.3, 127.1, 126.2, 81.3, 80.3, 51.6, 47.4, 28.1, 27.9, 24.8, 22.2; IR (neat): 2976, 2931, 1705, 1367, 1155; HRMS (APCI) calcd for $C_{30}H_{35}O_4$ $(M-H)^+$ 459.25408 found 459.25464.

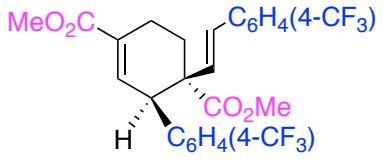


(1*R*,2*R*)-dimethyl 3',4'-dichloro-2-((*E*)-3,4-dichlorostyryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8d**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-methyl 2-diazo-5-(3,4-dichlorophenyl)pent-4-enoate xx (0.4 mmol, 113.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8d** as a white and amorphous solid (87.4 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 3.6, 8.4 Hz, 2H), 7.18 (dd, *J* = 2.0, 10.4 Hz, 2H), 6.94 (app. dd, *J* = 2.0, 6.8 Hz, 2H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.11 (d, *J* = 16.4 Hz, 1H), 5.73 (d, *J* = 16.4 Hz, 1H), 4.34 (d, *J* = 4.8 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.63 (app.

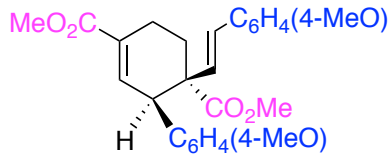
dd, J = 6.0, 19.2 Hz, 1H), 2.48-2.39 (m, 1H), 2.29 (app. dd, J = 6.4, 14.0 Hz, 1H), 1.78 (ddd, J = 6.4, 10.4, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 166.9, 138.3, 137.8, 136.4, 132.5, 132.2, 132.1, 130.9, 130.5, 129.8, 128.2, 128.1, 125.3, 52.8, 51.9, 51.2, 46.7, 24.3, 22.0; IR (neat): 2950, 1720, 1470, 1255; HRMS (APCI) calcd for $C_{24}H_{21}O_4Cl_4$ $(M+H)^+$ 513.01885 found 513.01874.



(1*R*,2*R*)-dimethyl 4'-(trifluoromethyl)-2-((*E*)-4-(trifluoromethyl)styryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8e**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-methyl 2-diazo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate xx (0.4 mmol, 113.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8e** as a white and amorphous solid (91.3 mg, 89% yield).

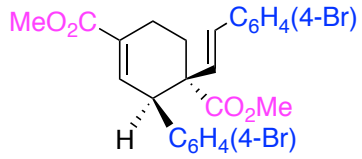
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, J = 8.4, 12.4 Hz, 4H), 7.23 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.0 (d, J = 5.2 Hz, 1H), 6.22 (d, J = 16.6 Hz, 1H), 5.80 (d, J = 16.6 Hz, 1H), 4.47 (d, J = 4.8 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.70 (dd, J = 5.6, 18.9 Hz, 1H), 2.53-2.50 (m, 1H), 2.36 (dd, J = 5.8, 13.8 Hz, 1H), 1.89 (ddd, J = 6.3, 12.1, 13.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 167.1, 142.2, 139.8, 138.2, 133.2, 130.9, 130.8, 129.1, 126.4, 125.6, 125.5, 124.9, 52.8, 51.9, 51.3, 47.4, 24.6, 22.1; IR (neat): 2953, 1723, 1325, 1124; HRMS (ESI) calcd for $C_{26}H_{23}O_4F_6$ $(M+H)^+$ 513.14951 found 513.15025.



(1*R*,2*R*)-dimethyl 4'-methoxy-2-((*E*)-4-methoxystyryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8f**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-methyl 2-diazo-5-(4-methoxyphenyl)pent-4-enoate (0.4 mmol, 98.4 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8f** as a white and amorphous solid (72.6 mg, 83% yield).

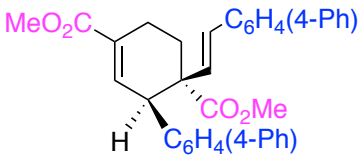
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.01 (m, 5H), 6.81-6.74 (m, 4H), 6.12 (d, J = 16.4 Hz, 1H), 5.60 (d, J = 16.4 Hz, 1H), 4.32 (d, J = 4.4 Hz, 1H), 3.75 -3.73 (m, 12H), 2.60 (app. dd, J = 5.6, 18.8 Hz, 1H), 2.47-2.40 (m, 1H), 2.27 (app. dd, J = 4.8, 13.6 Hz, 1H), 1.84 (ddd, J = 6.4, 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 167.7, 159.4, 158.9, 140.2, 131.9, 130.3, 129.8, 129.7, 129.1, 127.6, 114.1, 113.5, 55.5, 55.4, 52.6, 51.9, 51.5, 47.2, 24.8, 22.4; IR (neat): 2950, 2837, 1713, 1510, 1245; HRMS (APCI) calcd for $C_{26}H_{29}O_6$ $(M+H)^+$ 437.19587 found 437.19653.



(1*R*,2*R*)-dimethyl 4'-bromo-2-((*E*)-4-bromostyryl)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,5-dicarboxylate (**8g**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-methyl 5-(4-bromophenyl)-2-diazopent-4-enoate (0.4 mmol, 117.6 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8g** as a white and amorphous solid (86.9 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 4H), 7.01-6.98 (m, 5H), 6.13 (d, *J* = 16.0 Hz, 1H), 5.73 (d, *J* = 16.0 Hz, 1H), 4.36 (d, *J* = 4.8 Hz, 1H), 3.76 (s, 6H), 2.63 (app. dd, *J* = 5.6, 18.8 Hz, 1H), 2.51-2.42 (m, 1H), 2.31 (app. dd, *J* = 6.4, 14.0 Hz, 1H), 1.84 (ddd, *J* = 6.0, 10.4, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 167.1, 138.7, 137.0, 135.4, 132.2, 131.6, 131.1, 130.3, 128.9, 127.7, 121.5, 52.6, 51.8, 51.2, 47.1, 24.4, 22.1; IR (neat): 2949, 1716, 1487, 1258, 1229; HRMS (APCI) calcd for $C_{24}H_{22}O_4Br_2Cl$ $(M+Cl)^+$ 566.95788 found 566.95802.



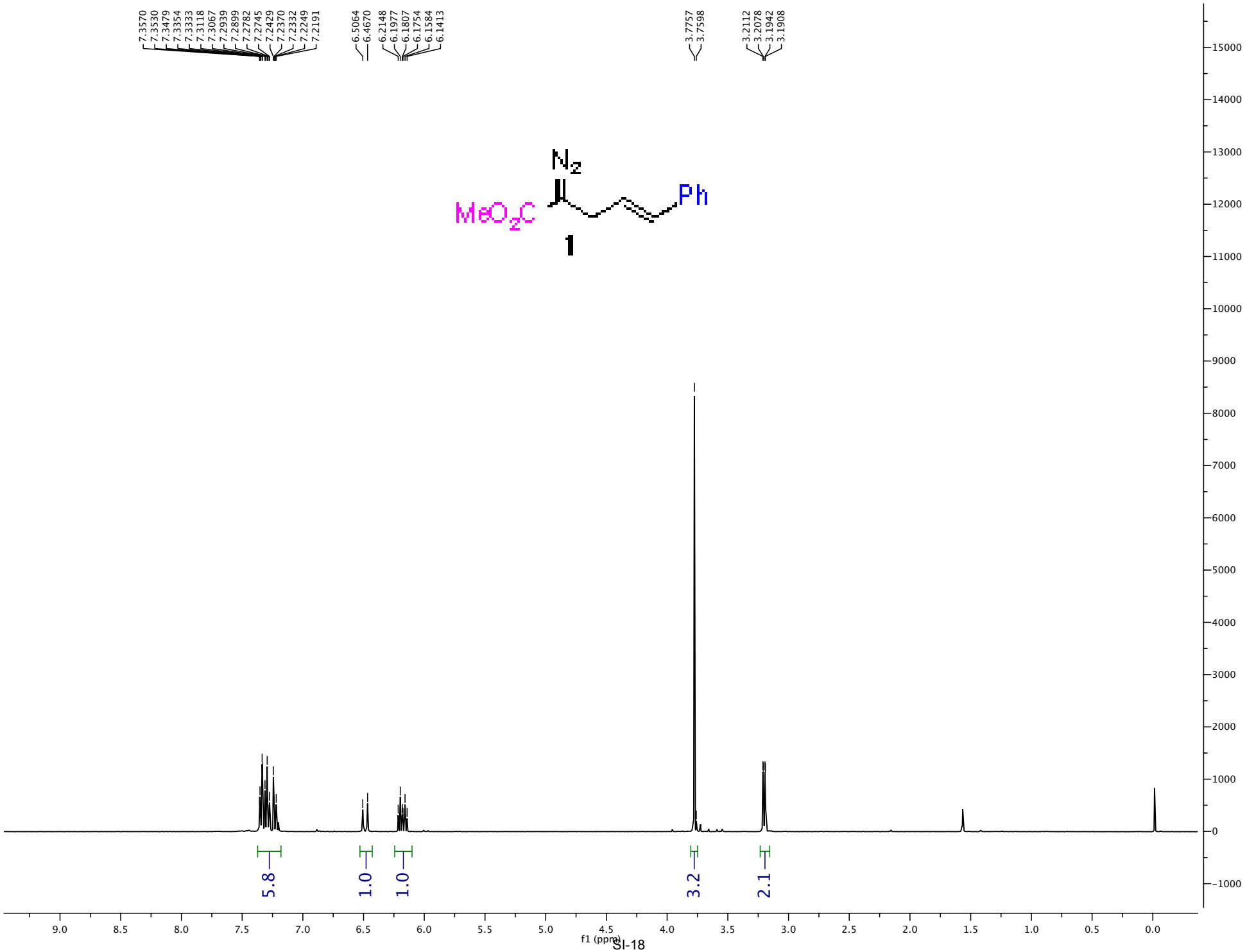
(1*R*,2*R*)-dimethyl 2-((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-1,2,3,4-tetrahydro-[1,1':4',1"-terphenyl]-2,5-dicarboxylate (**8h**)

Prepared according to the general procedure for $Rh_2(TPA)_4$-catalyzed synthesis of cyclohexene derivatives using (*E*)-4-(3-bromoprop-1-en-1-yl)-1,1'-biphenyl (0.4 mmol, 116.8 mg, 1.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography (hexanes/ethyl acetate = 50/1) to afford **8h** as a white foam solid (87.4 mg, 83% yield).

Mp: 73-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.39 (m, 8H), 7.36-7.32 (m, 4H), 7.27-7.23 (m, 2H), 7.17-7.13 (m, 4H), 7.02 (d, *J* = 5.2 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 5.78 (d, *J* = 16.4 Hz, 1H), 4.40 (d, *J* = 5.2 Hz, 1H), 3.70 (s, 6H), 2.60 (app. dd, *J* = 4.8, 18.0 Hz, 1H), 2.47-2.38 (m, 1H), 2.28 (app. dd, *J* = 6.0, 13.2 Hz, 1H), 1.89 (ddd, *J* = 6.4, 10.8, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 167.4, 140.6, 140.5, 140.3, 140.1, 139.5, 137.1, 135.7, 131.4, 131.1, 130.0, 129.3, 128.7, 127.3, 127.2, 127.0, 126.9, 126.7, 126.6, 52.5, 51.8, 51.4, 47.4, 24.7, 22.2; IR (neat): 3027, 2949, 1723, 1258, 1231; HRMS (APCI) calcd for $C_{36}H_{33}O_4$ $(M+H)^+$ 529.23734 found 529.23773.

(6) Method on calculation the yield ratio of product 2,4,5 in Table 1.

The ratio of product **2**:**4**:**5** represents the molar conversion of starting materials to the products determined in NMR. 2.0 mole of starting material **1** generates 1.0 mole of product **4**. Therefore, a value of 10:5:85 for product **2**:**4**:**5** represents around 10:10:80 molar conversion to the products.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7.3118
7.3067
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7.2899
7.2782
7.2745
7.2429
7.2370
7.2332
7.2249
7.2191
6.5064
6.4670
6.2148
6.1977
6.1807
6.1754
6.1584
6.1413
3.7757
3.7598
3.2112
3.2078
3.1942
3.1908
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MeO2C
Ph
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5.8
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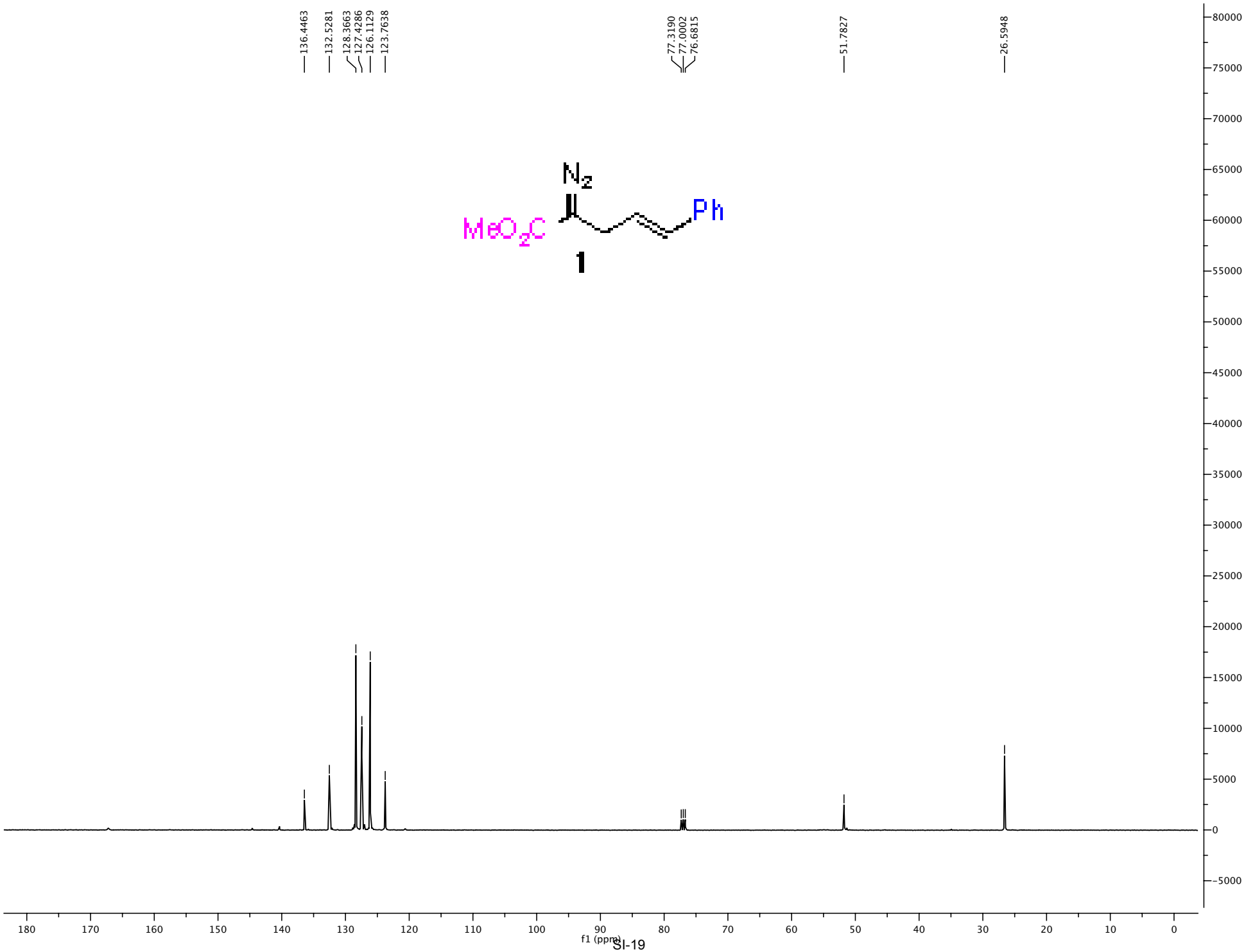
1.0
3.2
2.1
f1 (ppm)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77.3190
77.0002
76.6815
51.7827
26.5948
N2
MeO2C
Ph
1
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
180
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160
150
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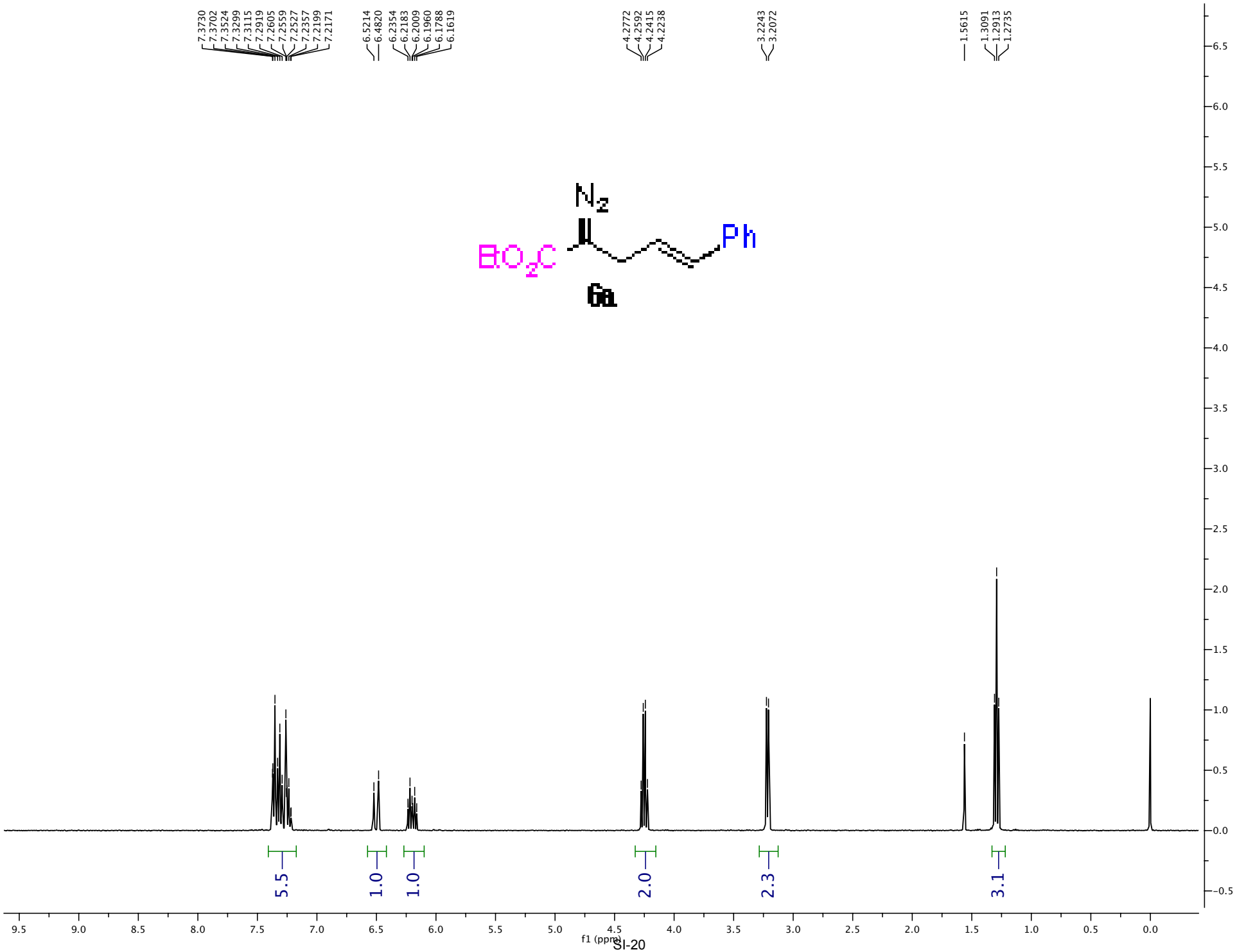
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3115
7.2919
7.2605
7.2559
7.2527
7.2357
7.2199
7.2171
6.5214
6.4820
6.2354
6.2183
6.2009
6.1960
6.1788
6.1619
4.2772
4.2592
4.2415
4.2238
3.2243
3.2072
1.5615
1.3091
1.2913
1.2735
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BO2C
Ph
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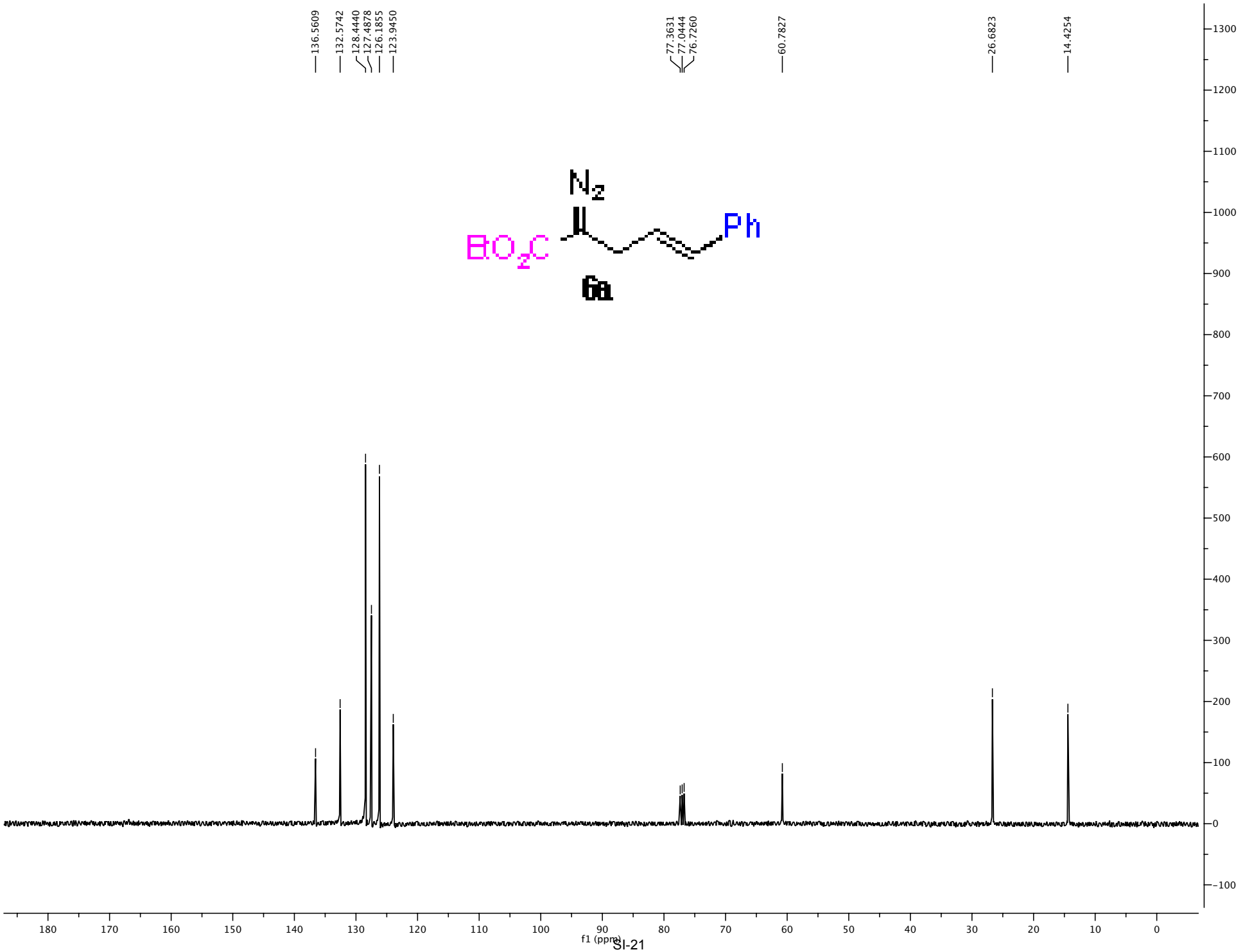
1.0
1.0
2.0
2.3
3.1
f1 (ppm)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123.9450
77.3631
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76.7260
60.7827
26.6823
14.4254
N2
BnO2C
Ph
6a
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180
170
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150
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130
120
110
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90
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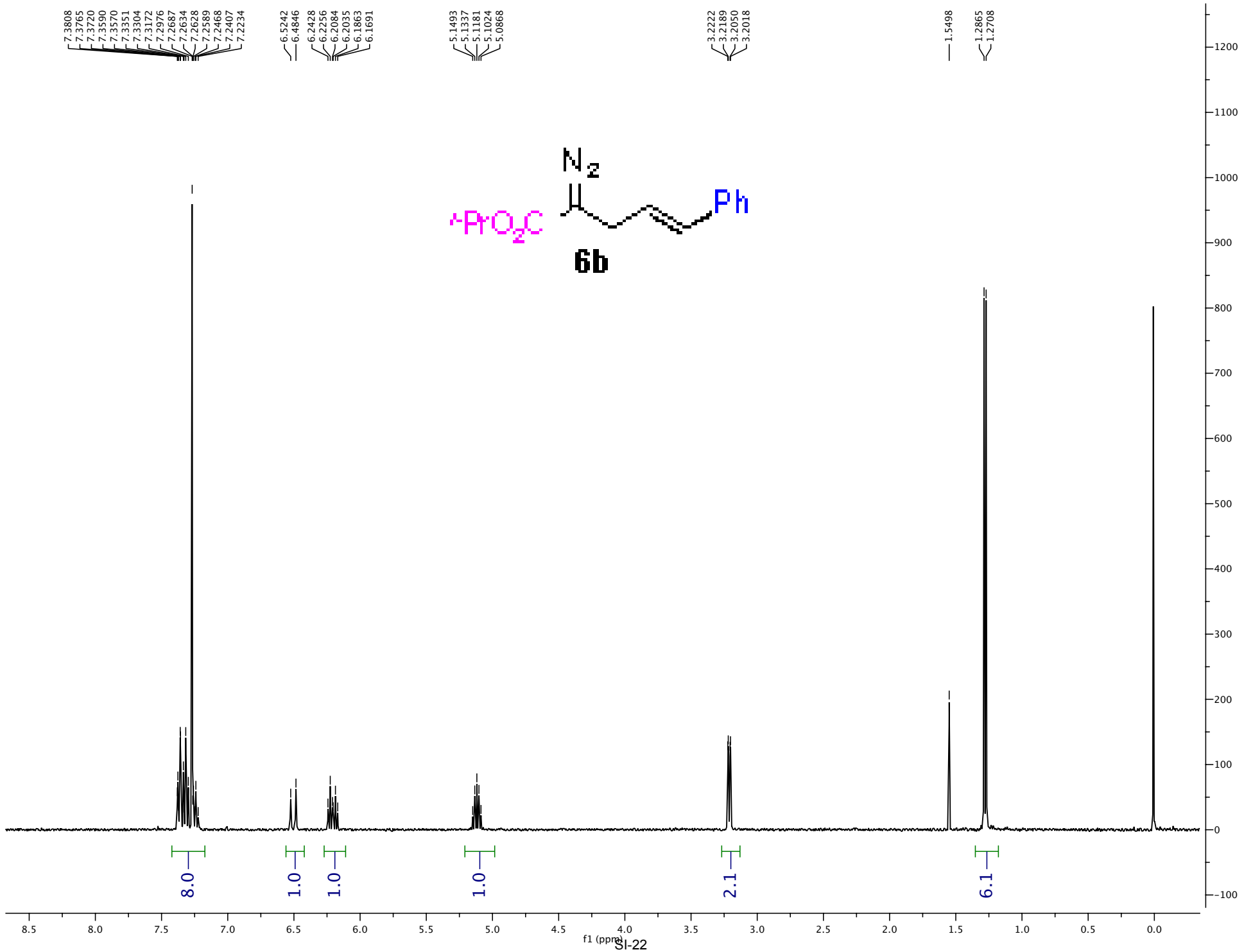
50
40
30
20
10
0
f1 (ppm)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7.3351
7.3304
7.3172
7.2976
7.2687
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7.2628
7.2589
7.2468
7.2407
7.2234
6.5242
6.4846
6.2428
6.2256
6.2084
6.2035
6.1863
6.1691
5.1493
5.1337
5.1181
5.1024
5.0868
3.2222
3.2189
3.2050
3.2018
1.5498
1.2865
1.2708
N2
Ph
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6b
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1.0
1.0
1.0
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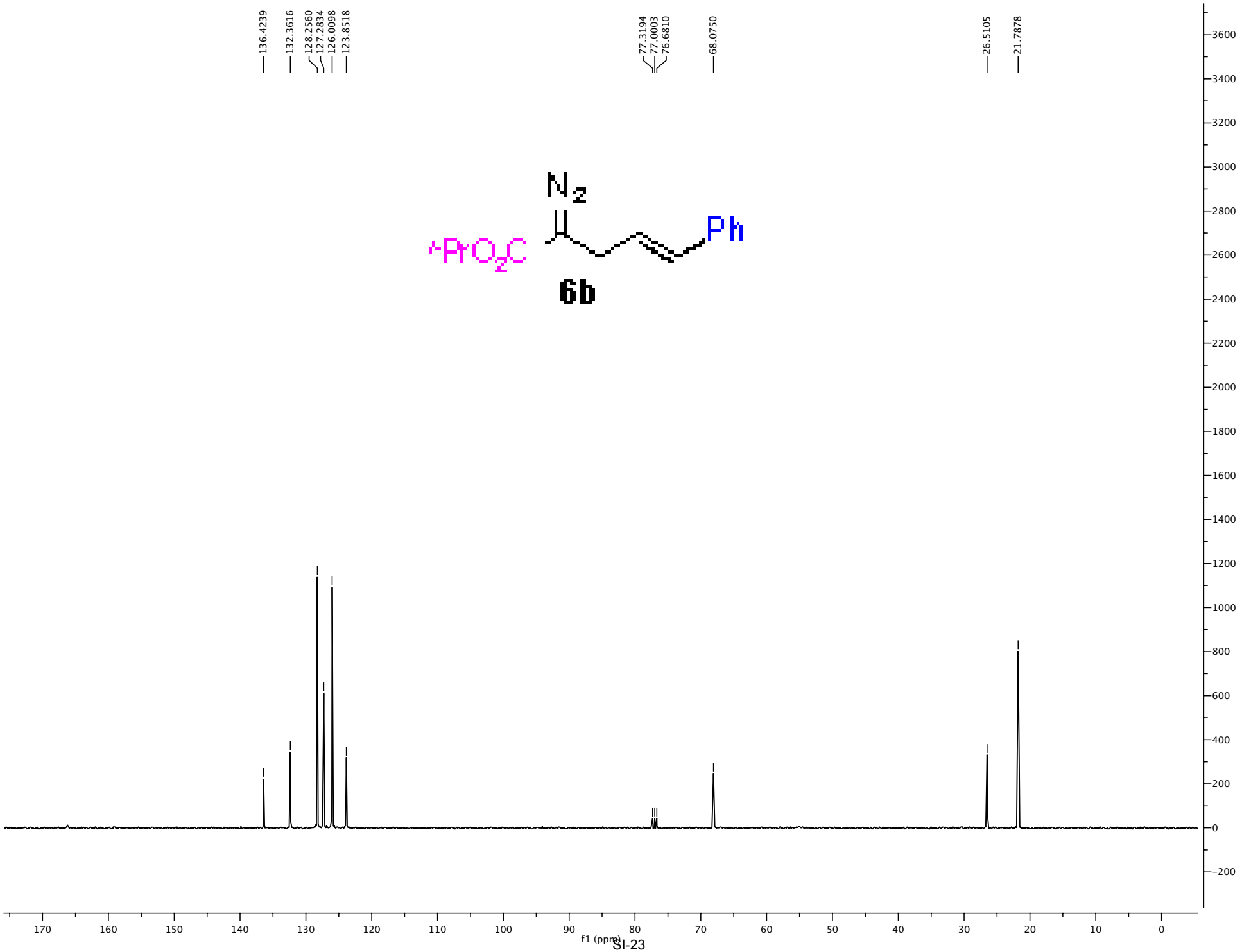
6.1
f1 (ppm)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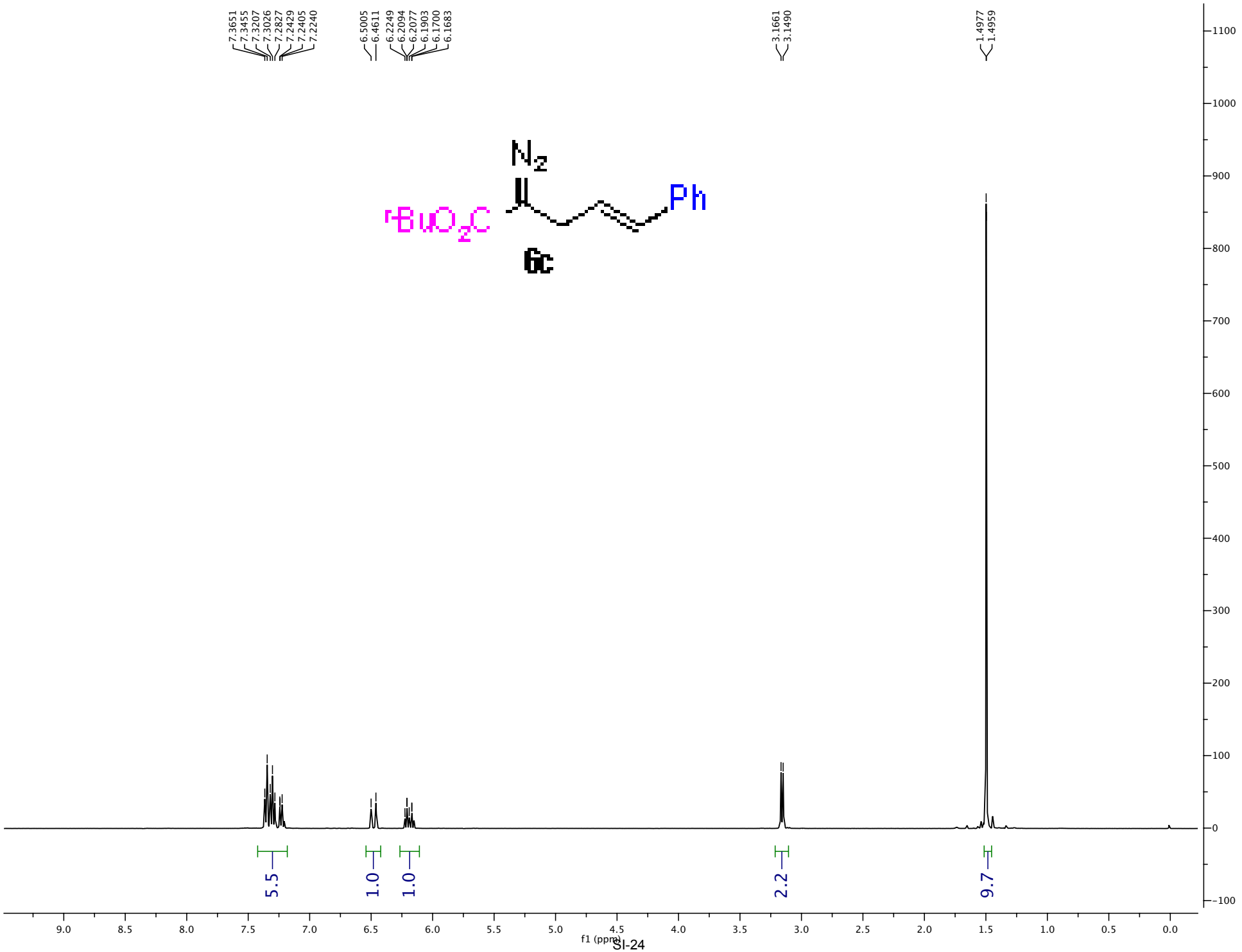
N2
Ph
6b
f1 (ppm)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7.3026
7.2827
7.2429
7.2405
7.2240
6.5005
6.4611
6.2249
6.2094
6.2077
6.1903
6.1700
6.1683
3.1661
3.1490
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1.4959
N2
tBuO2C
Ph
6c
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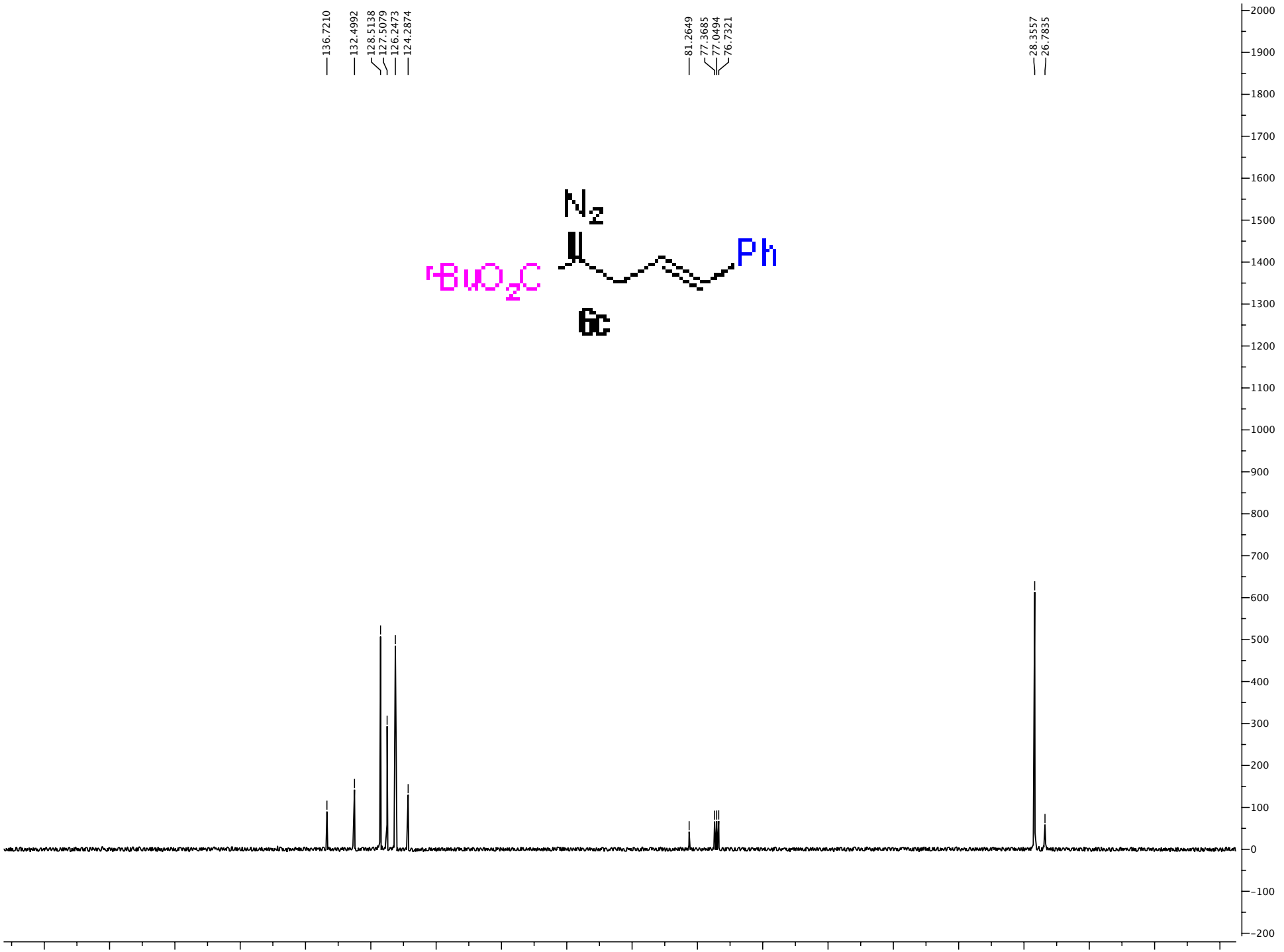
1.0
2.2
9.7
f1 (ppm)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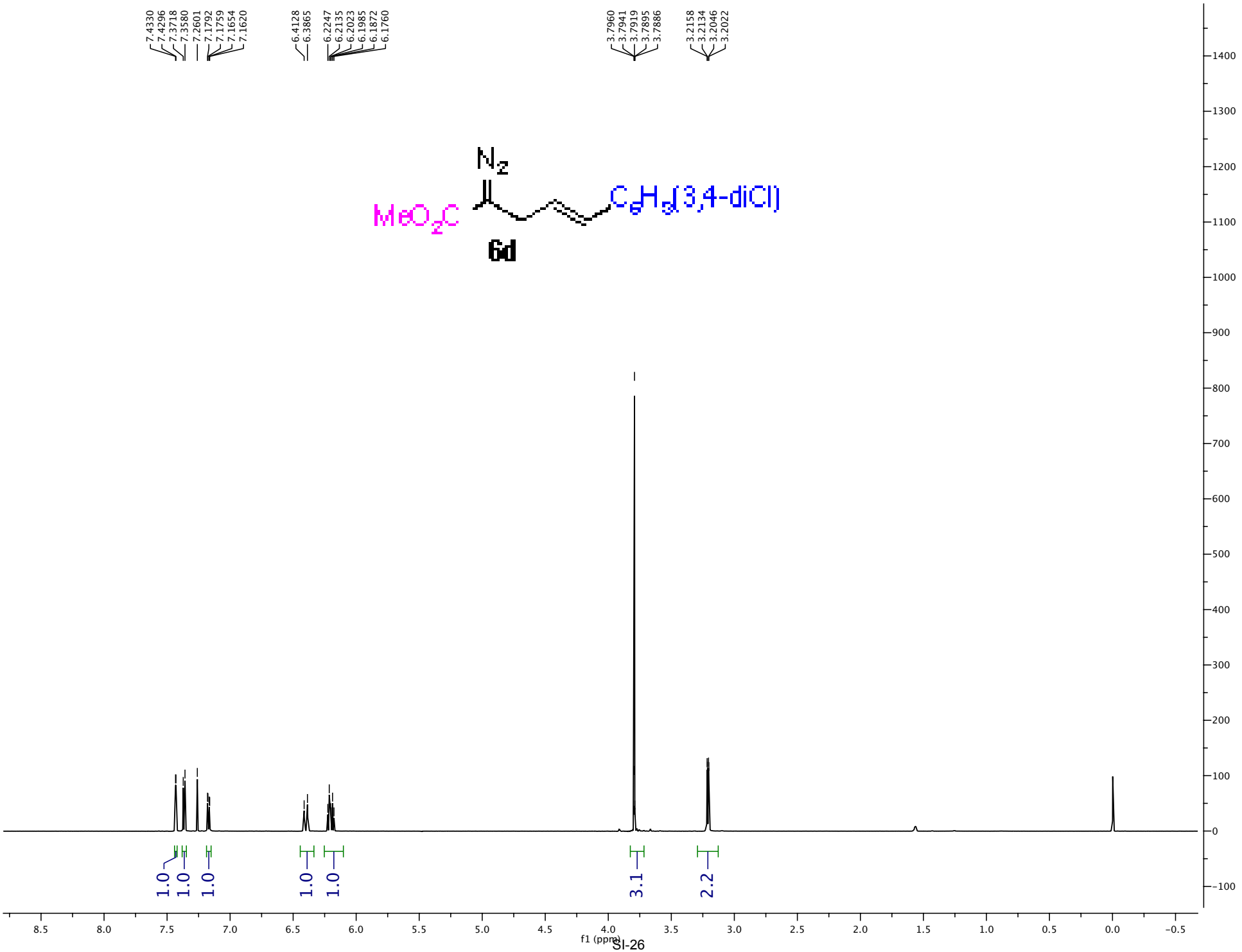
28.3557
26.7835
N2
tBuO2C
Ph
6c
f1 (ppm)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7.2601
7.1792
7.1759
7.1654
7.1620
6.4128
6.3865
6.2247
6.2135
6.2023
6.1985
6.1872
6.1760
3.7960
3.7941
3.7919
3.7895
3.7886
3.2158
3.2134
3.2046
3.2022
N2
MeO2C
C6H3(3,4-diCl)
6d
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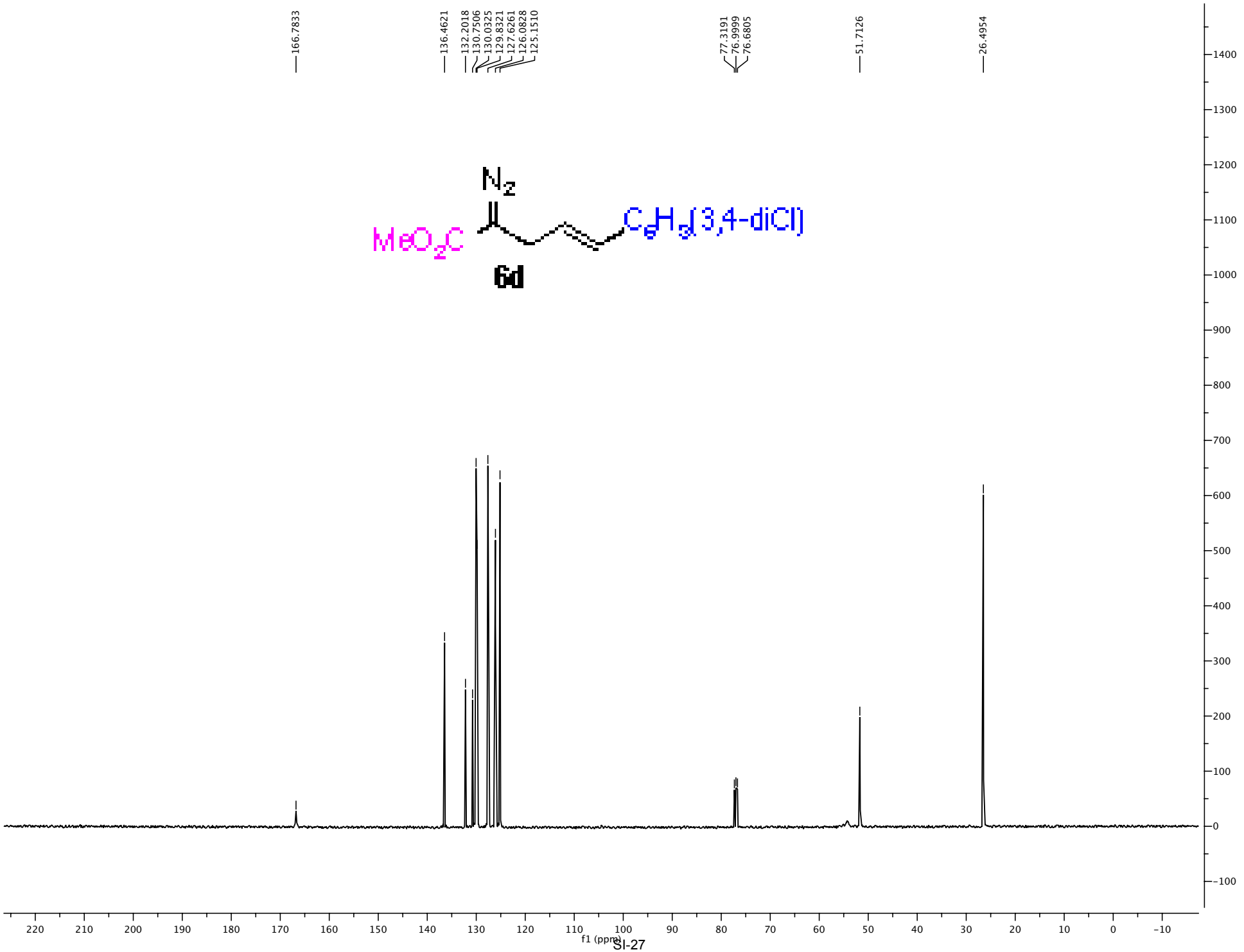
1.0
1.0
1.0
1.0
3.1
2.2
f1 (ppm)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125.1510
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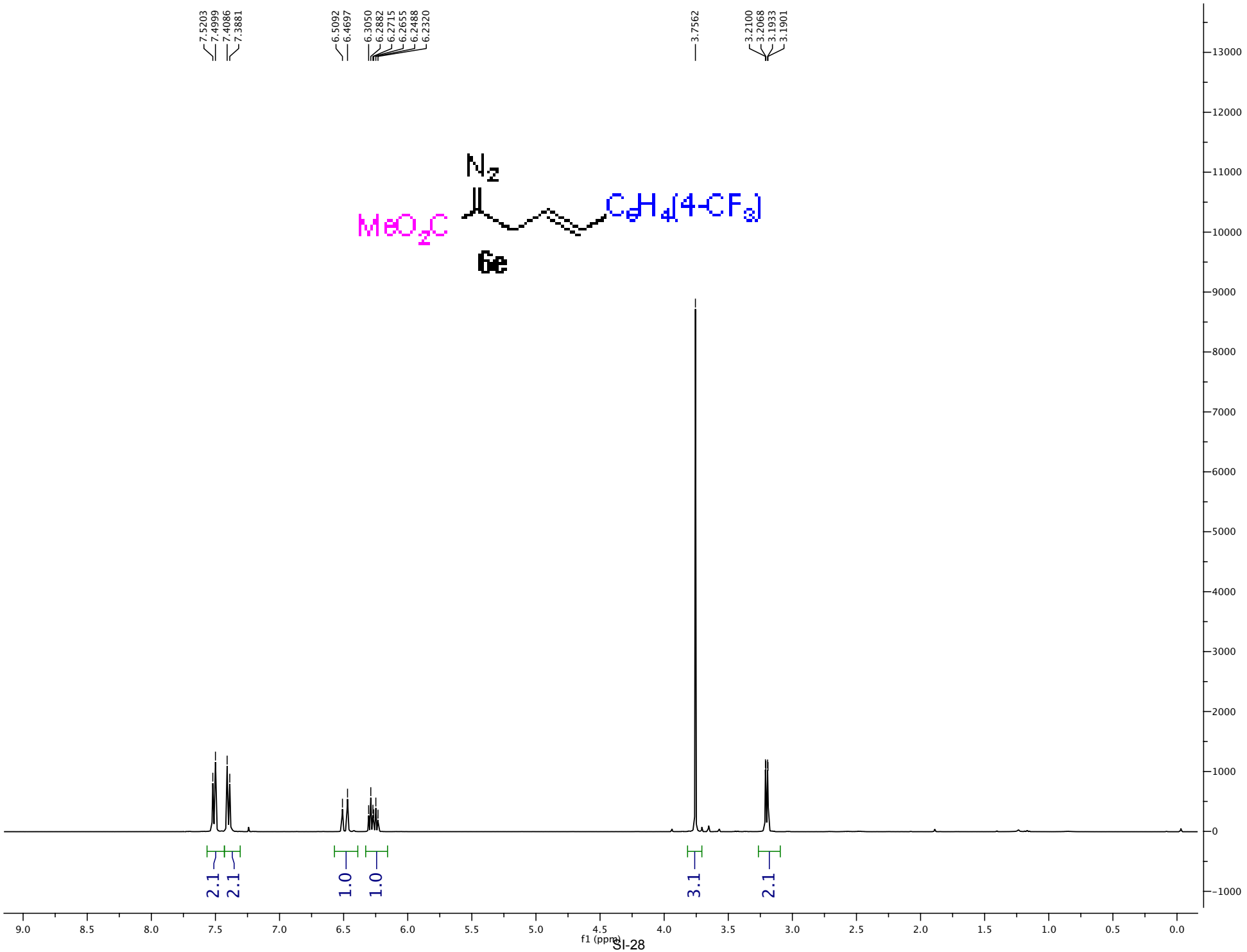
26.4954
N2
MeO2C
C6H3(3,4-diCl)
6d
f1 (ppm)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6.2715
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6.2488
6.2320
3.7562
3.2100
3.2068
3.1933
3.1901
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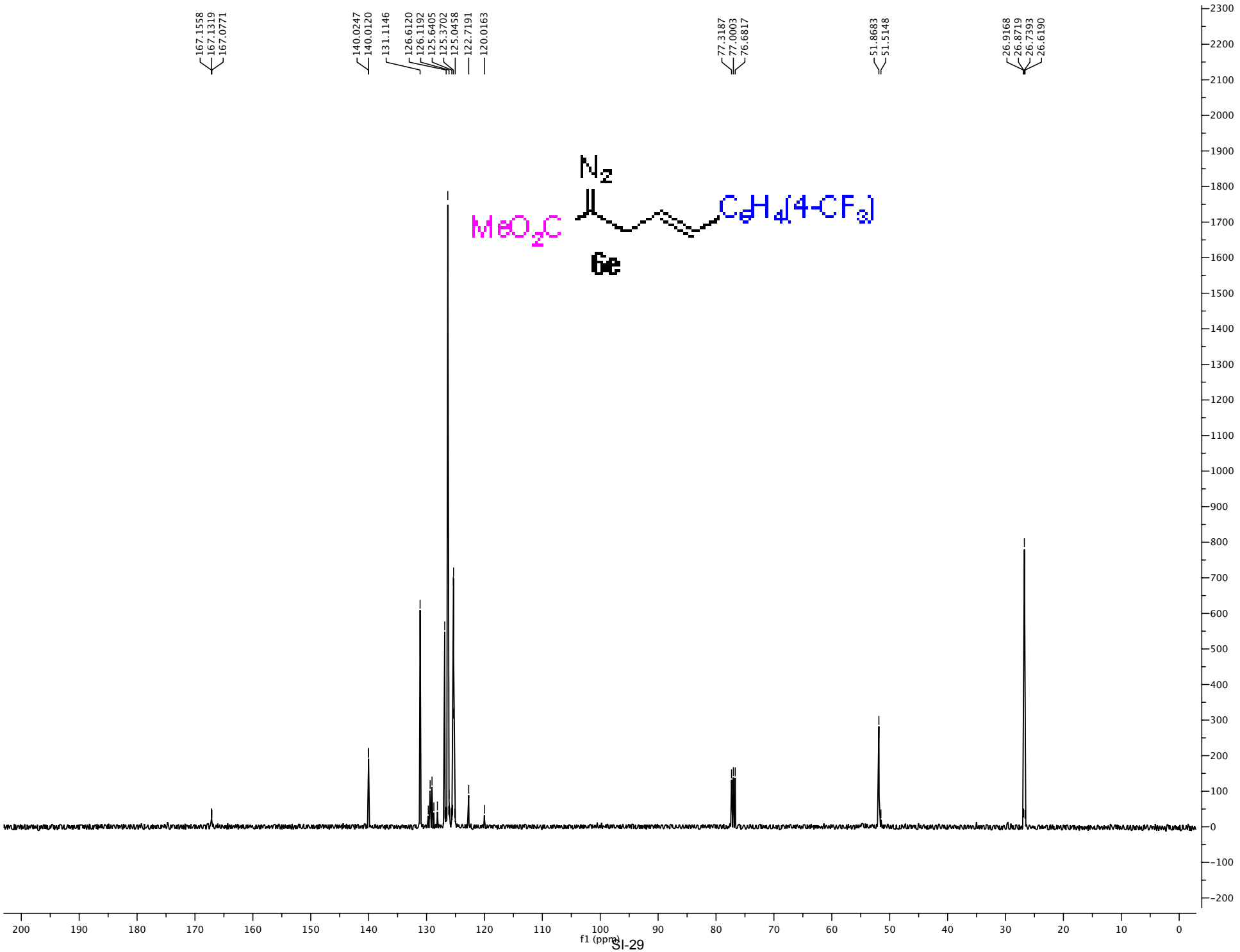
MeO2C
C6H4(4-CF3)
6e
2.1
2.1
1.0
1.0
3.1
2.1
f1 (ppm)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76.6817
51.8683
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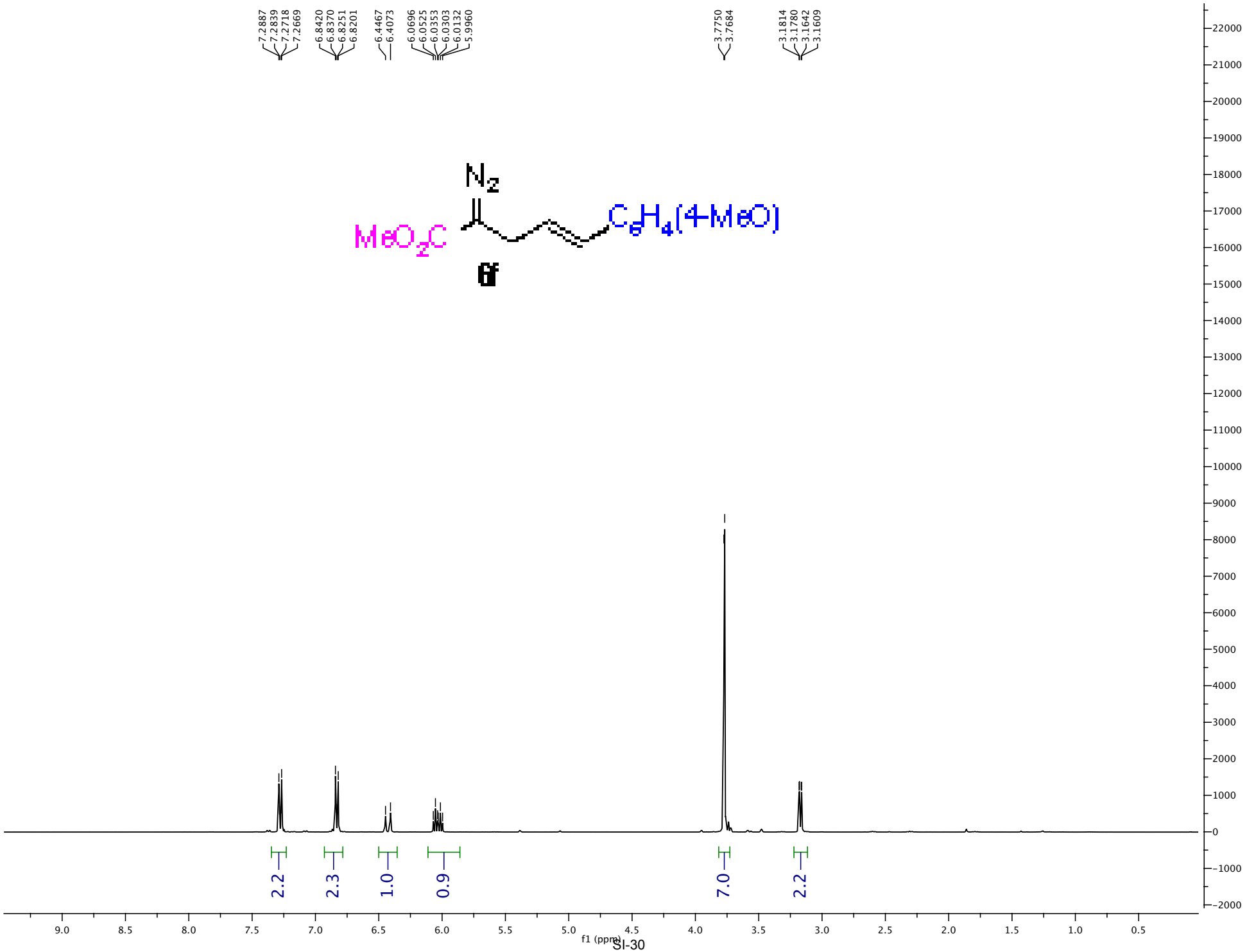
MeO2C
C6H4(4-CF3)
6e
f1 (ppm)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6.0696
6.0525
6.0353
6.0303
6.0132
5.9960
3.7750
3.7684
3.1814
3.1780
3.1642
3.1609
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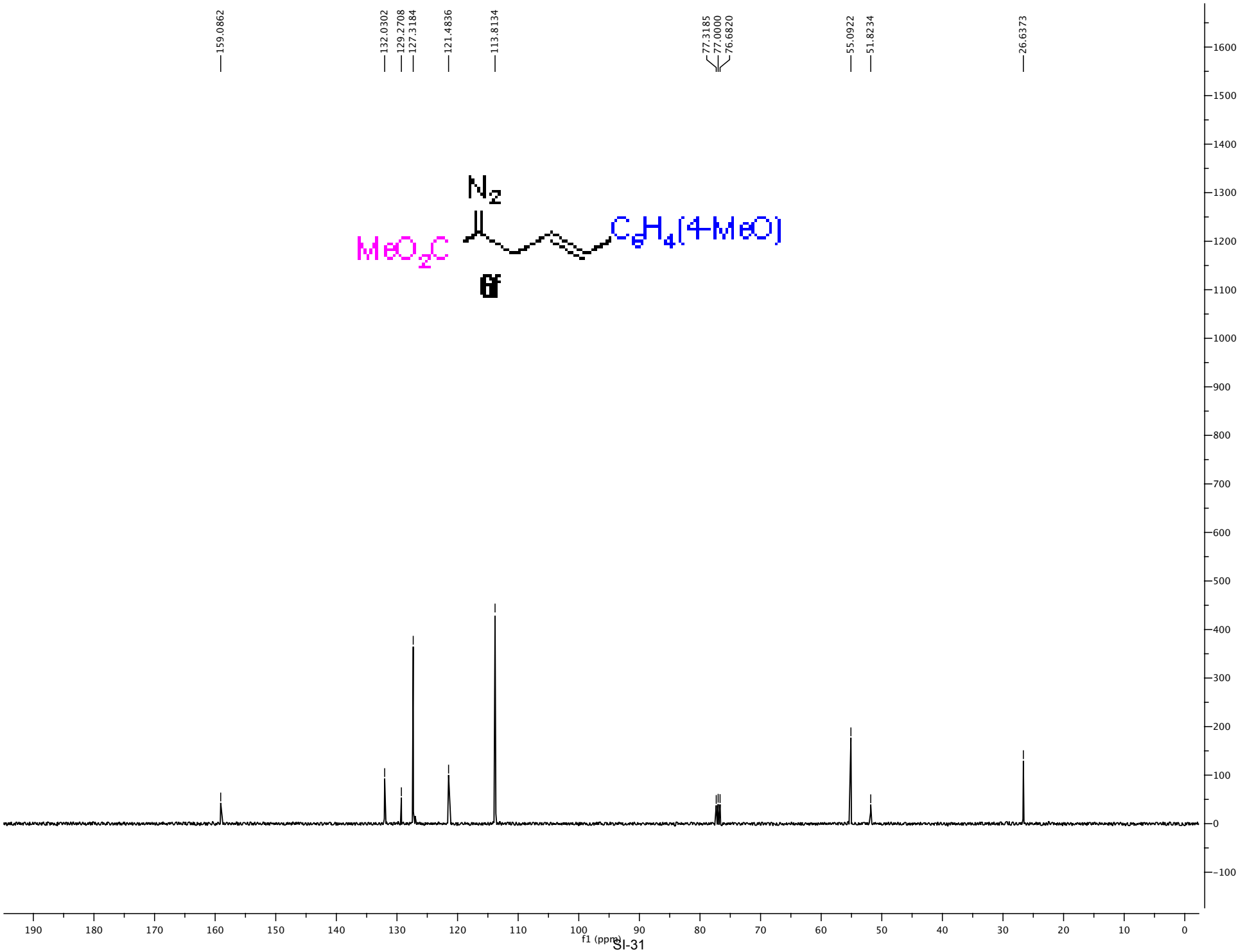
2.2
f1 (ppm)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77.0000
76.6820
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51.8234
26.6373
N2
MeO2C
C6H4(4-MeO)
6f
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
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140
130
120
110
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90
80
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50
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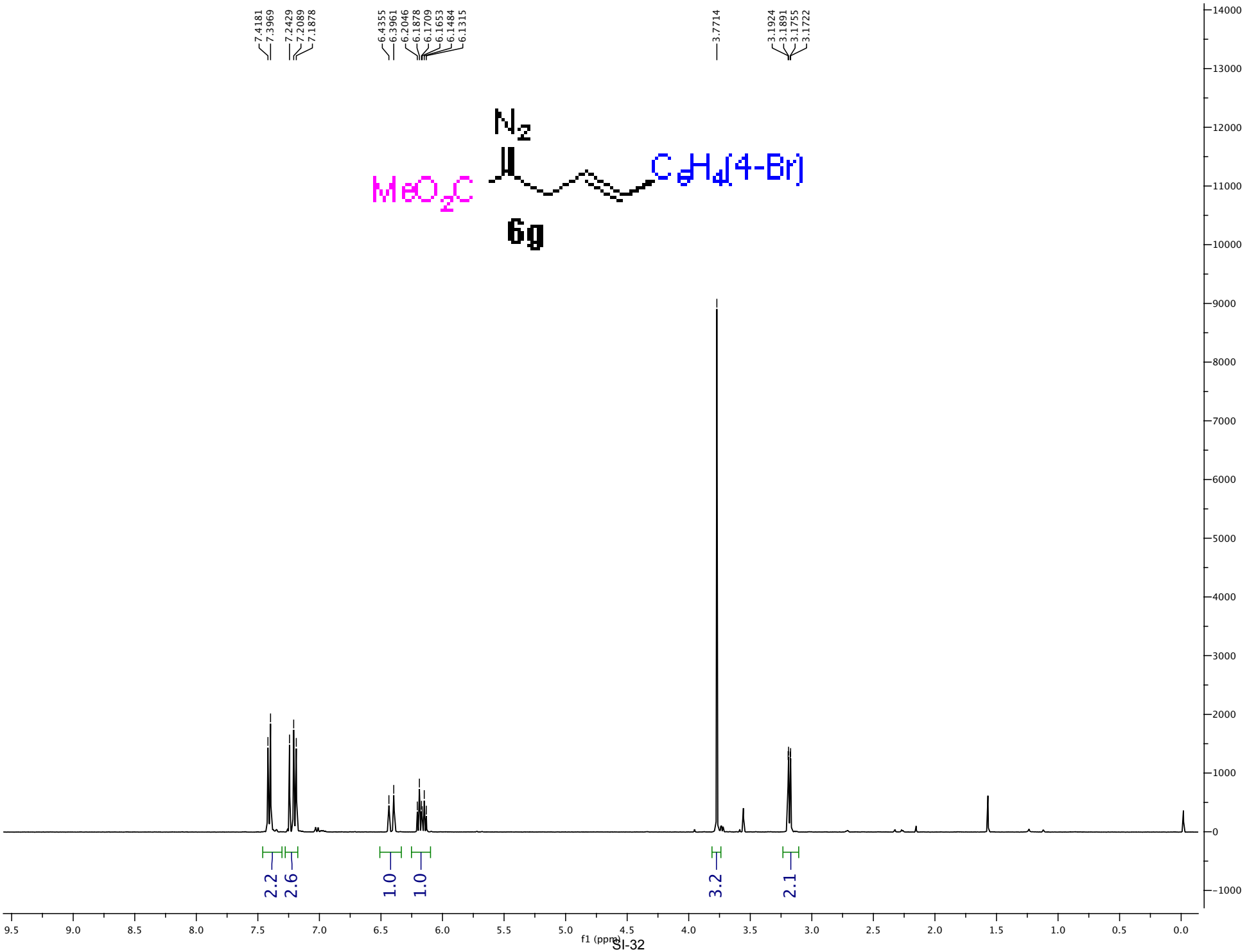
f1 (ppm)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6.3961
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6.1878
6.1709
6.1653
6.1484
6.1315
3.7714
3.1924
3.1891
3.1755
3.1722
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MeO2C
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6g
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2.6
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1.0
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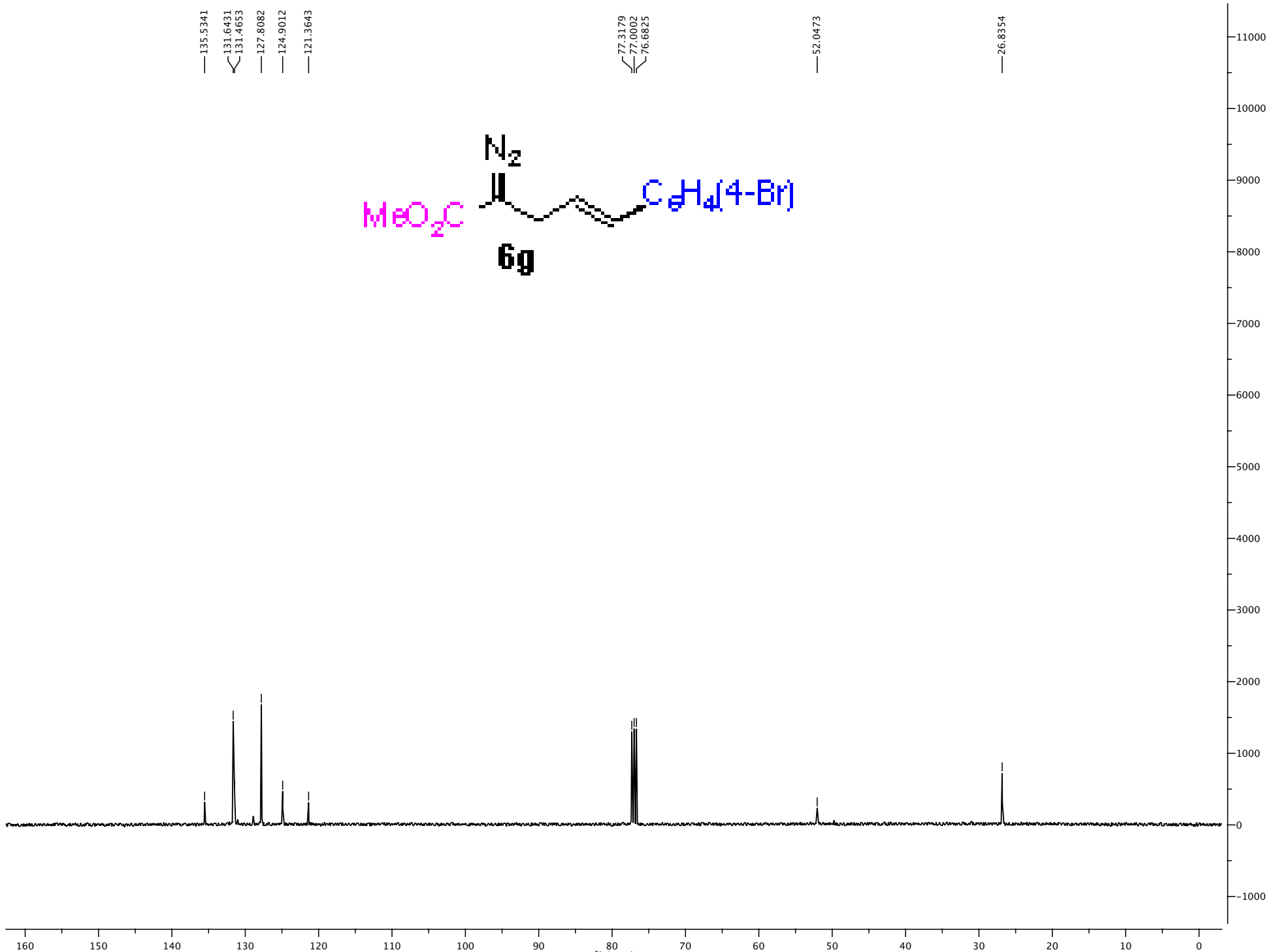
2.1
f1 (ppm)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26.8354
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C6H4(4-Br)
6g
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10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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130
120
110
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90
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50
40
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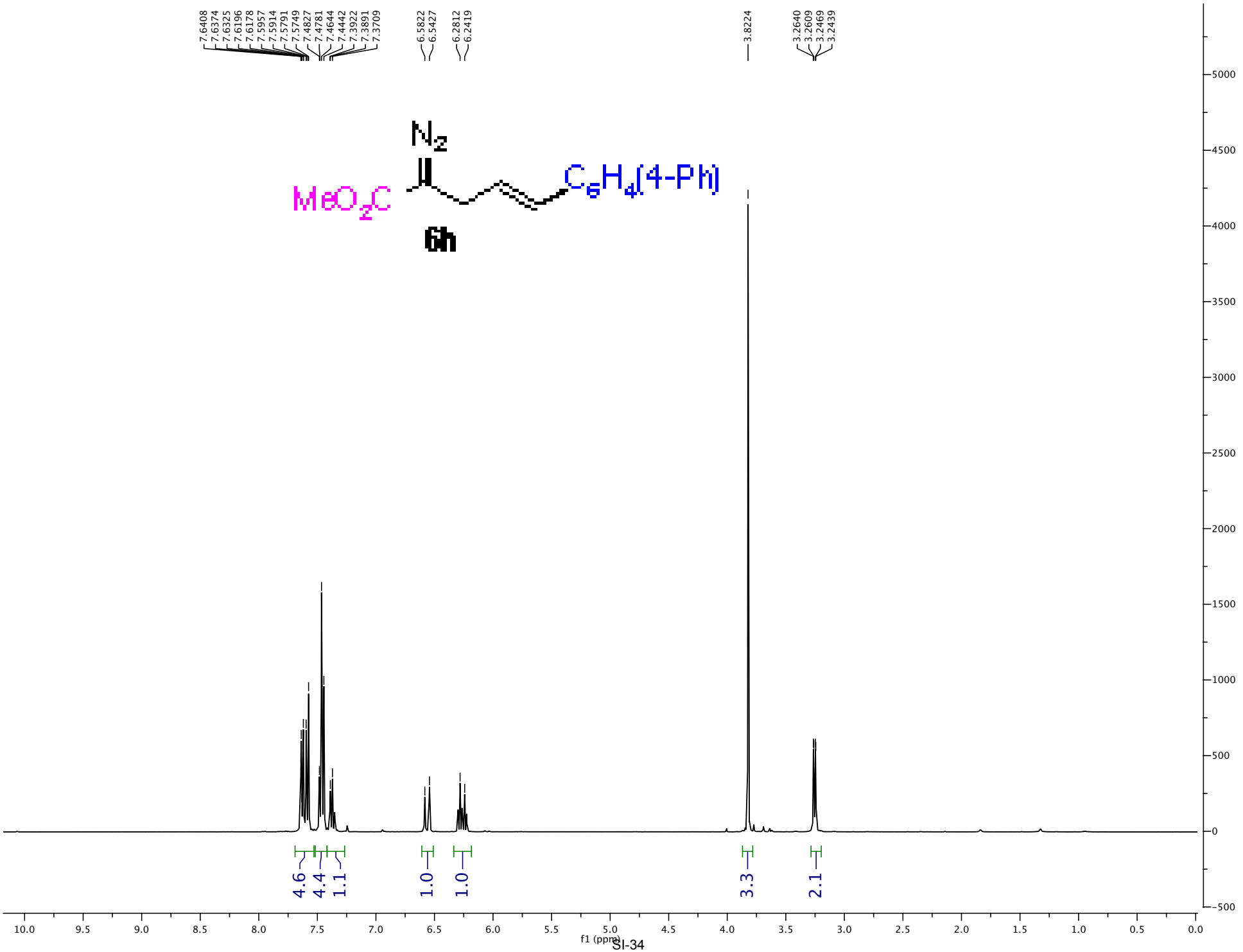
f1 (ppm)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7.4781
7.4644
7.4442
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7.3891
7.3709
6.5822
6.5427
6.2812
6.2419
3.8224
3.2640
3.2609
3.2469
3.2439
N2
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6h
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4.4
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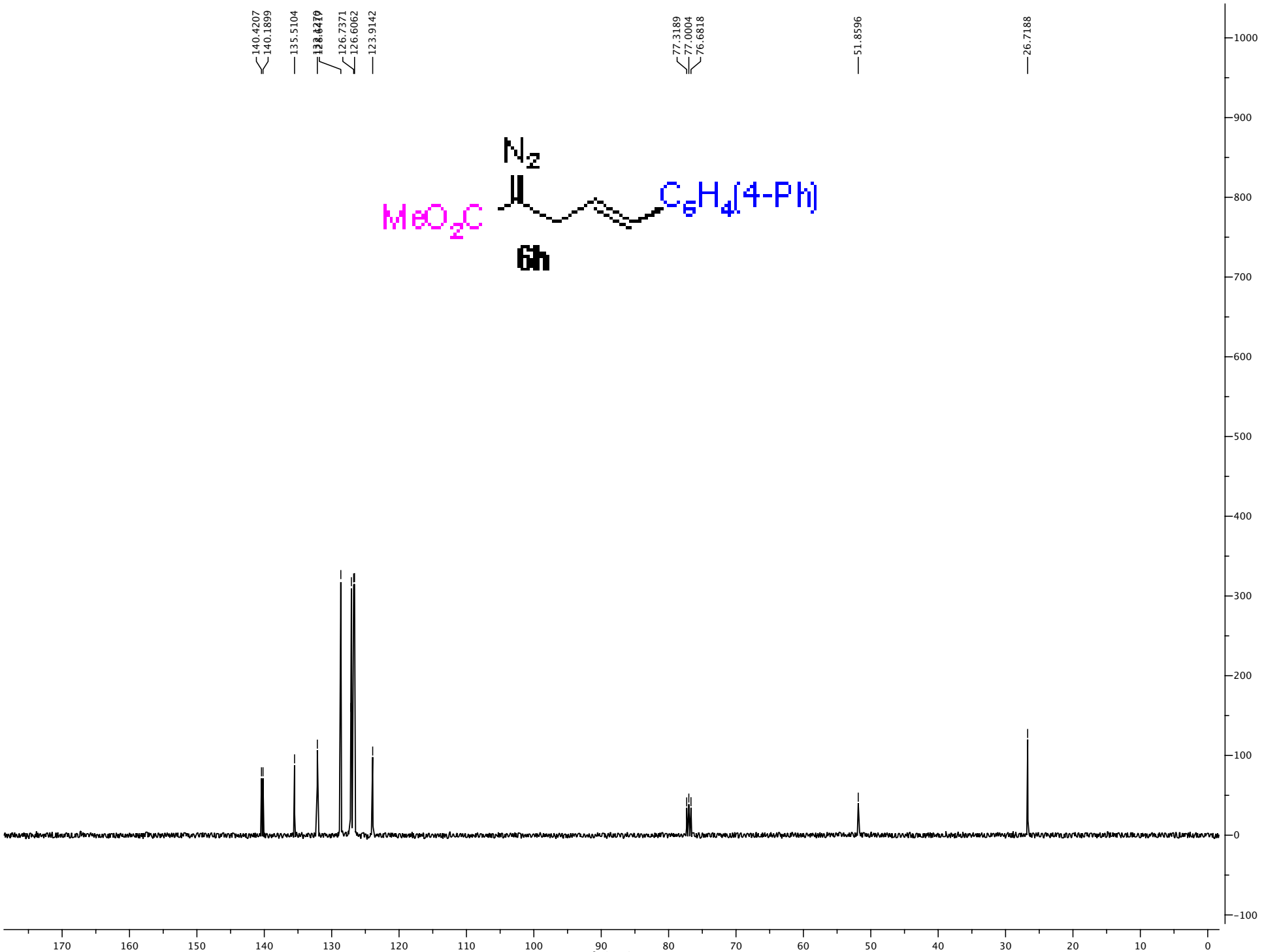
1.0
3.3
2.1
f1 (ppm)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26.7188
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MeO2C
C6H4(4-Ph)
6h
1000
900
800
700
600
500
400
300
200
100
0
-100
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160
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130
120
110
100
90
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70
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50
40
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20
10
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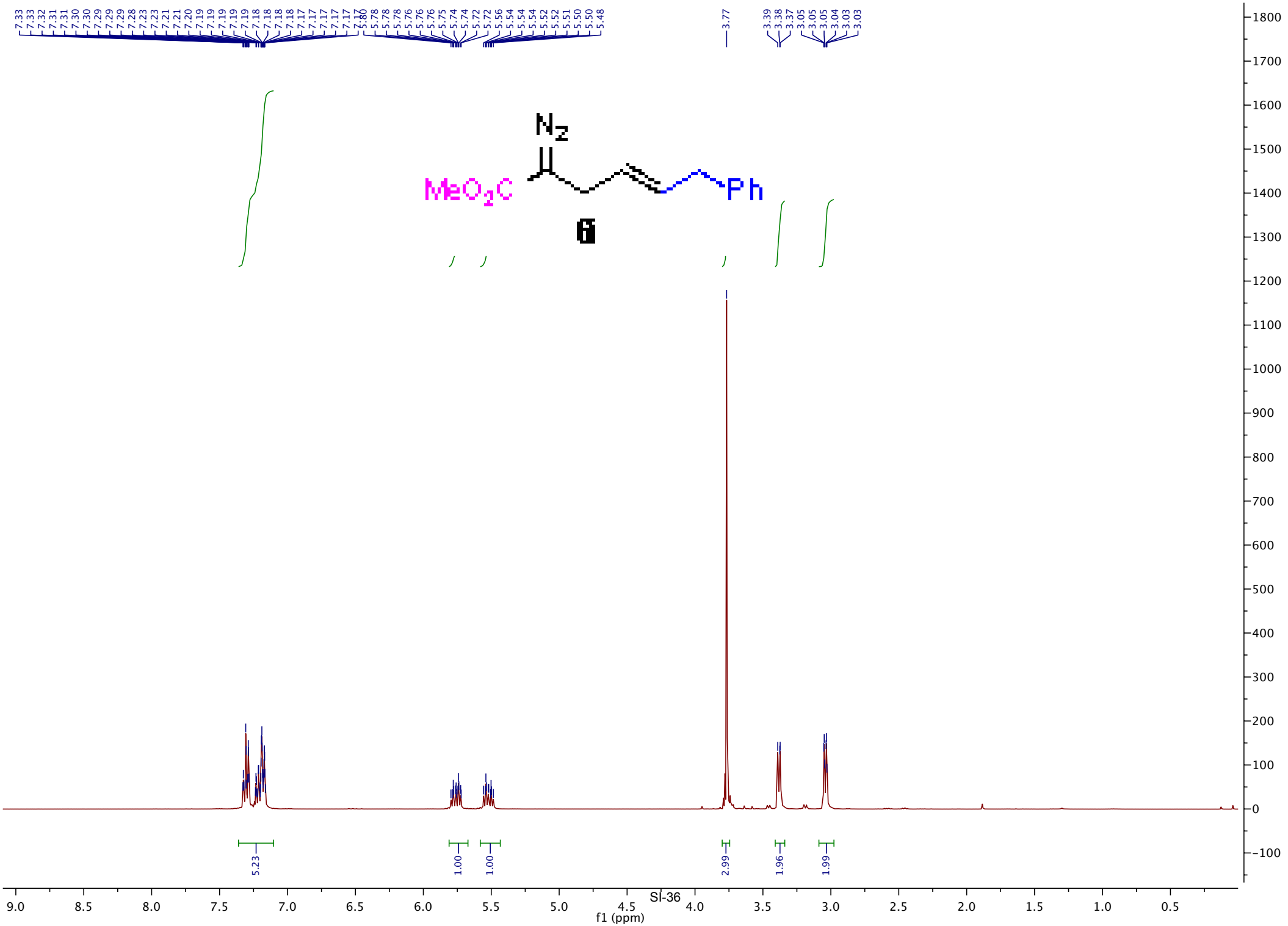
f1 (ppm)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3.77
3.39 3.38 3.37 3.05 3.05 3.05 3.04 3.03 3.03
N2
MeO2C
Ph
6
1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100
5.23
1.00
1.00
2.99
1.96
1.99
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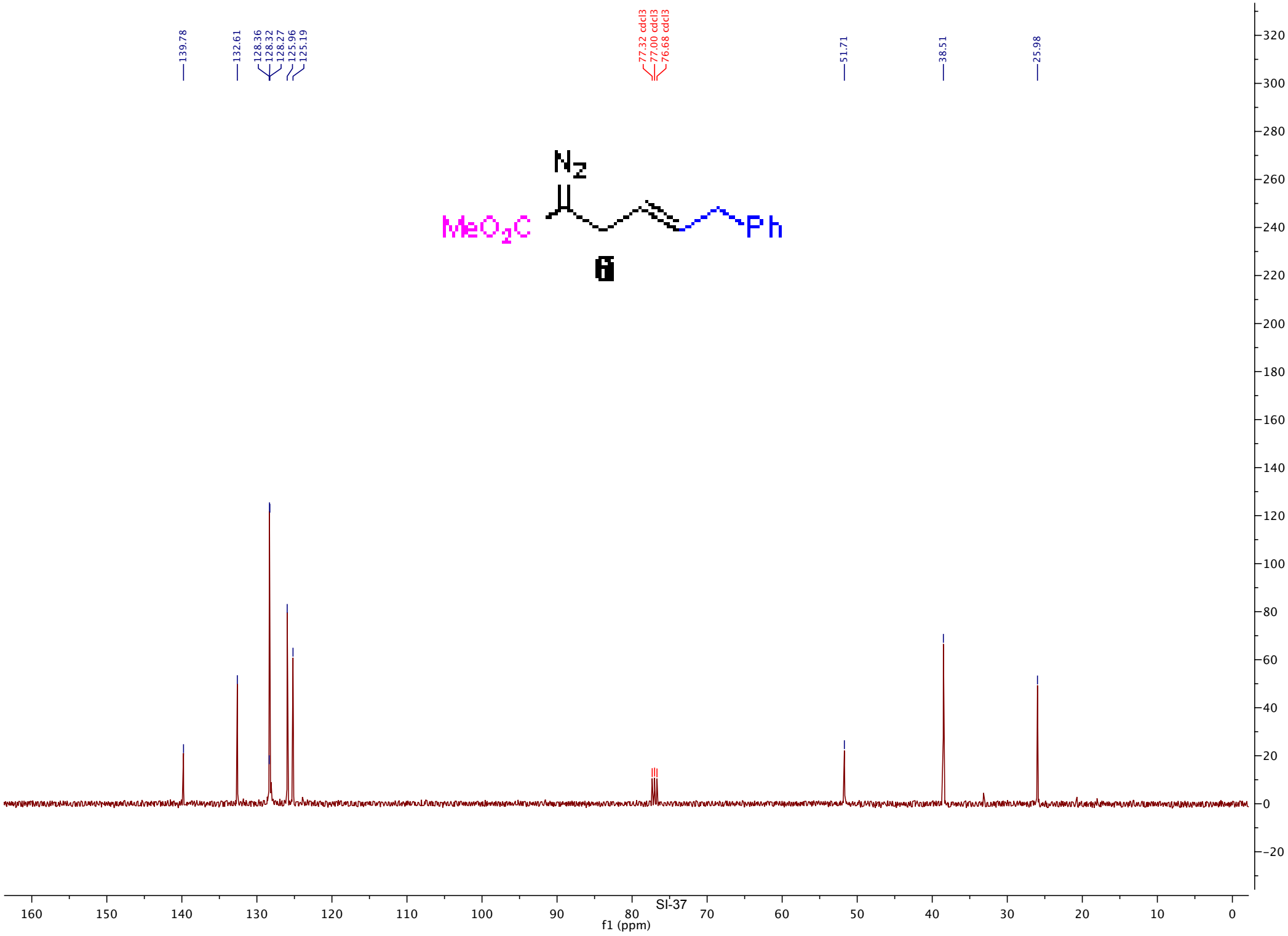
f1 (ppm)


139.78
132.61
128.36
128.32
128.27
125.96
125.19
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76.68 cdcl3
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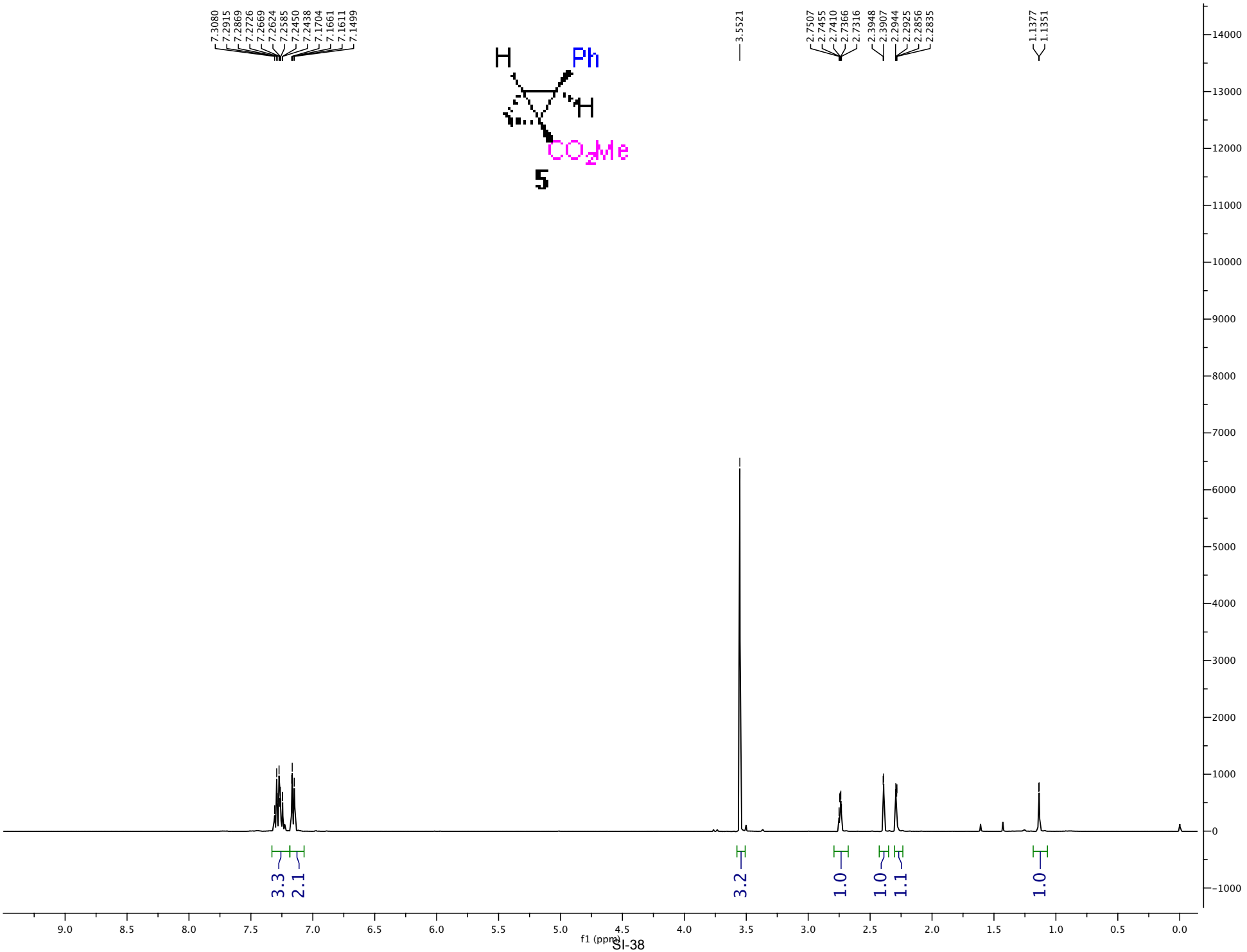
38.51
25.98
N2
MeO2C
Ph
6i
f1 (ppm)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7.2450
7.2438
7.1704
7.1661
7.1611
7.1499
3.5521
2.7507
2.7455
2.7410
2.7366
2.7316
2.3948
2.3907
2.2944
2.2925
2.2856
2.2835
1.1377
1.1351
H
Ph
H
CO2Me
5
3.3
2.1
3.2
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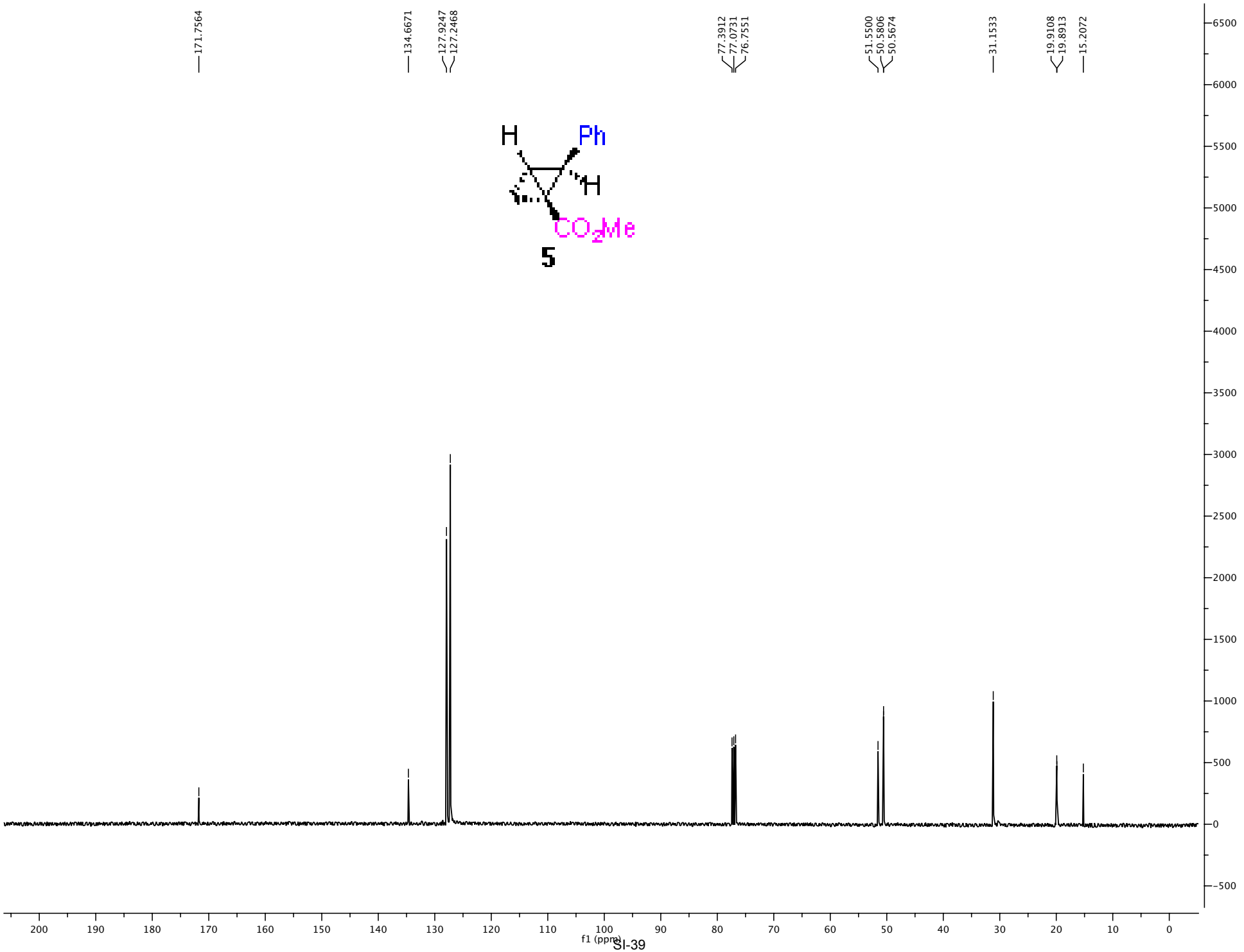
1.0
1.1
1.0
f1 (ppm)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76.7551
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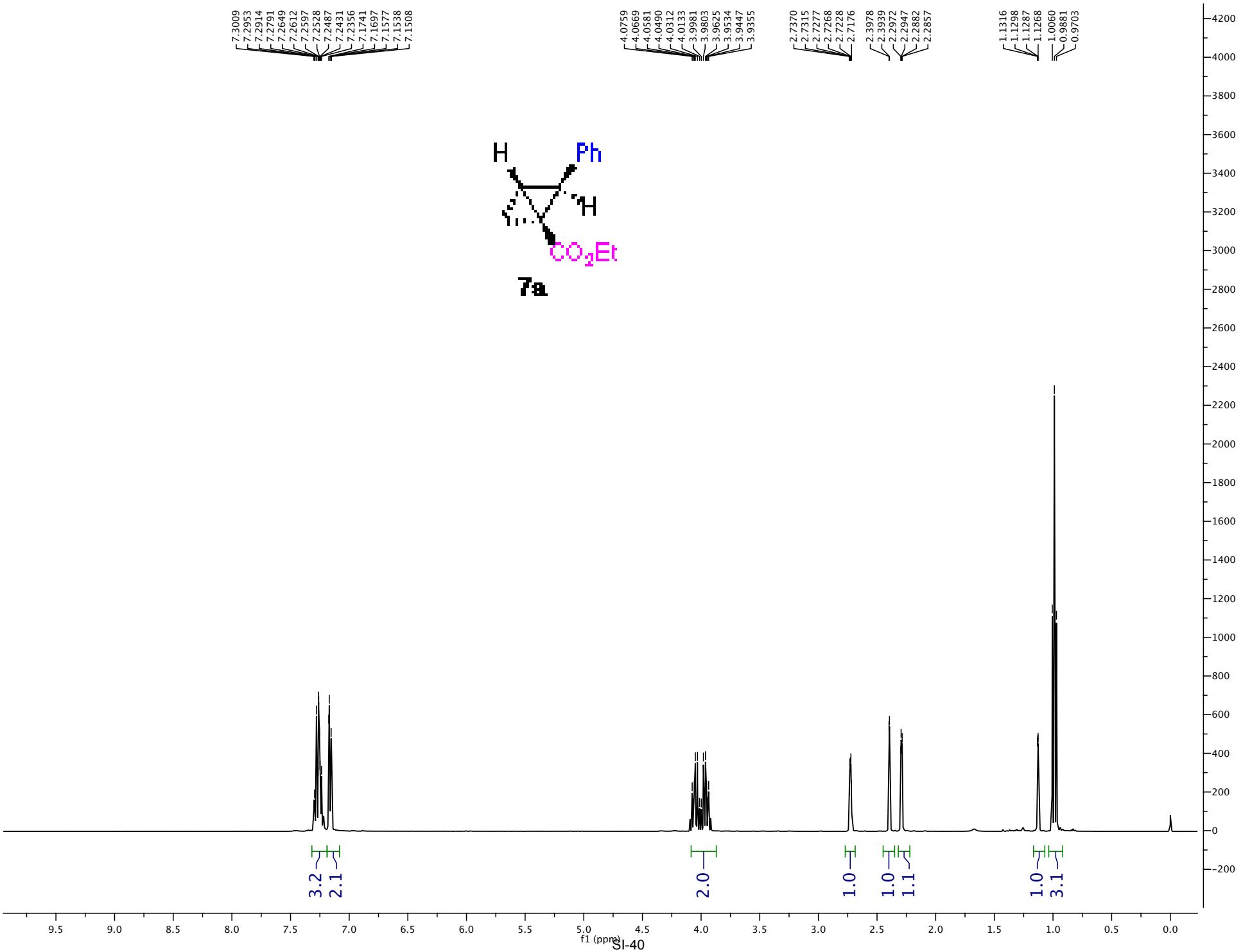
31.1533
19.9108
19.8913
15.2072
H
Ph
H
CO2Me
5
f1 (ppm)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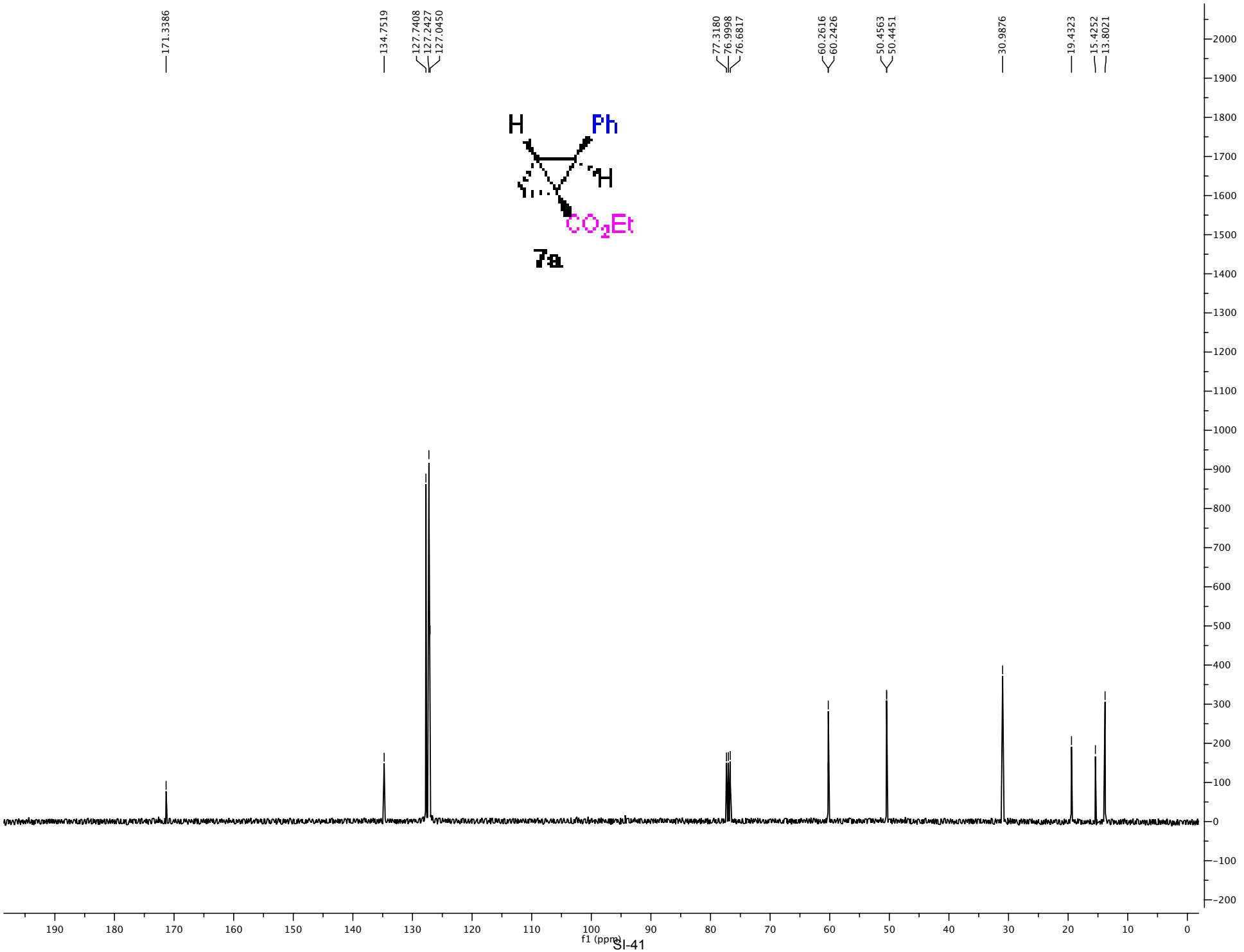
7.2597
7.2528
7.2487
7.2431
7.2356
7.1741
7.1697
7.1577
7.1538
7.1508
4.0759
4.0669
4.0581
4.0490
4.0312
4.0133
3.9981
3.9803
3.9625
3.9534
3.9447
3.9355
2.7370
2.7315
2.7277
2.7268
2.7228
2.7176
2.3978
2.3939
2.2972
2.2947
2.2882
2.2857
1.1316
1.1298
1.1287
1.1268
1.0060
0.9881
0.9703
H
Ph
H
CO2Et
7a
3.2
2.1
2.0
1.0
1.0
1.1
1.0
3.1
f1 (ppm)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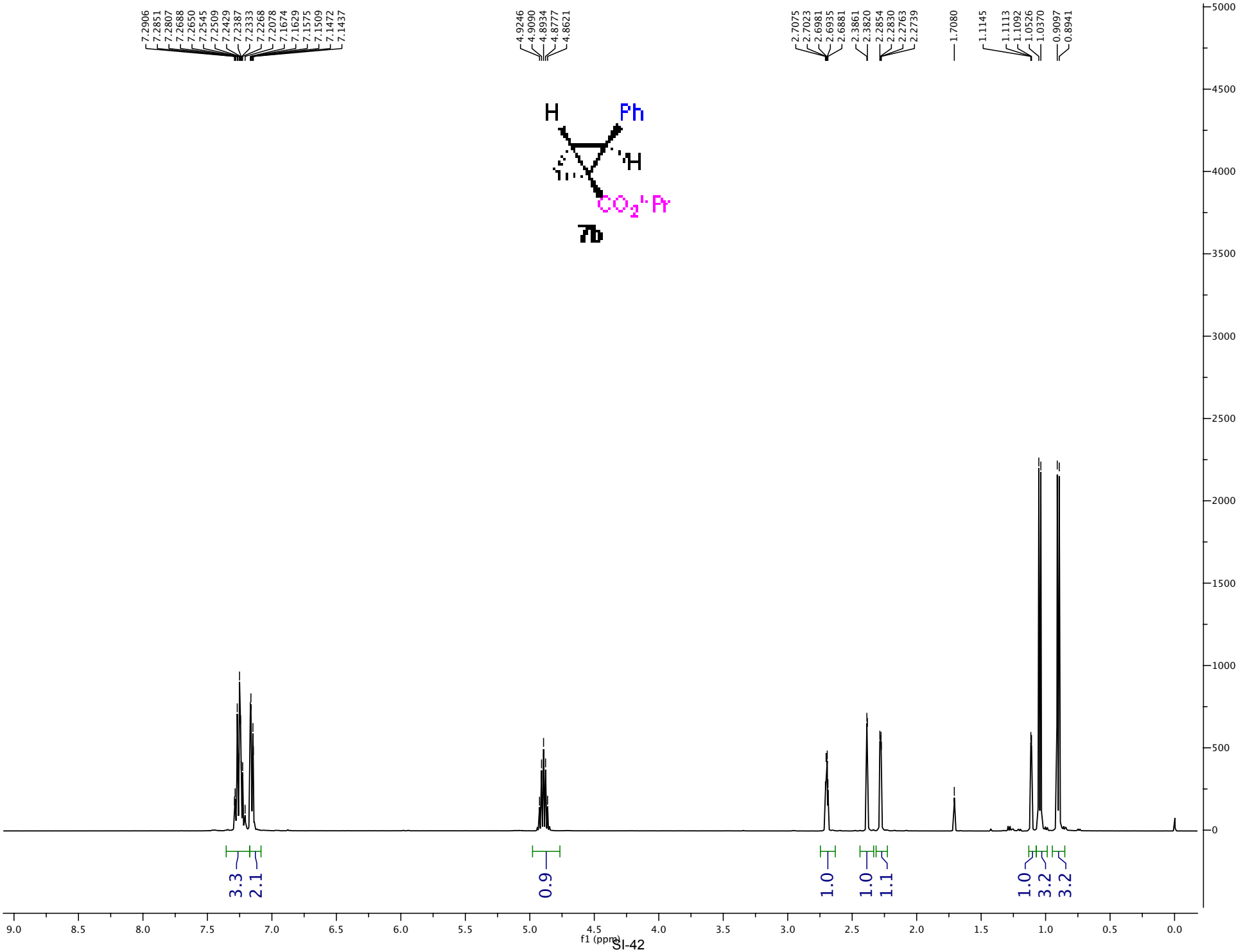
30.9876
19.4323
15.4252
13.8021
H
Ph
H
CO2Et
7a
f1 (ppm)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7.2851
7.2807
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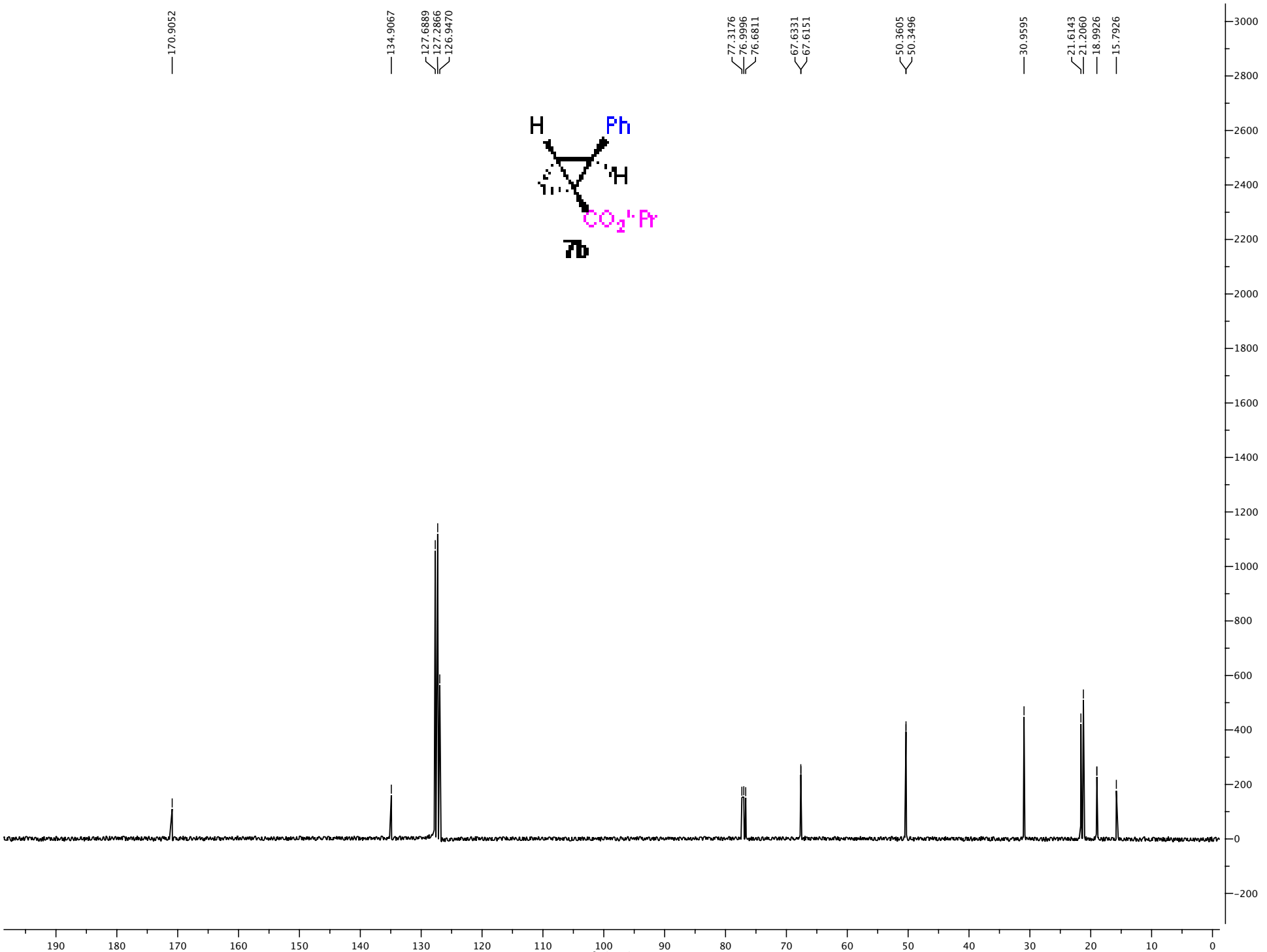
7.2650
7.2545
7.2509
7.2429
7.2387
7.2333
7.2268
7.2078
7.1674
7.1629
7.1575
7.1509
7.1472
7.1437
4.9246
4.9090
4.8934
4.8777
4.8621
2.7075
2.7023
2.6981
2.6935
2.6881
2.3861
2.3820
2.2854
2.2830
2.2763
2.2739
1.7080
1.1145
1.1113
1.1092
1.0526
1.0370
0.9097
0.8941
H
Ph
H
CO2iPr
7b
3.3
2.1
0.9
1.0
1.0
1.1
1.0
3.2
3.2
f1 (ppm)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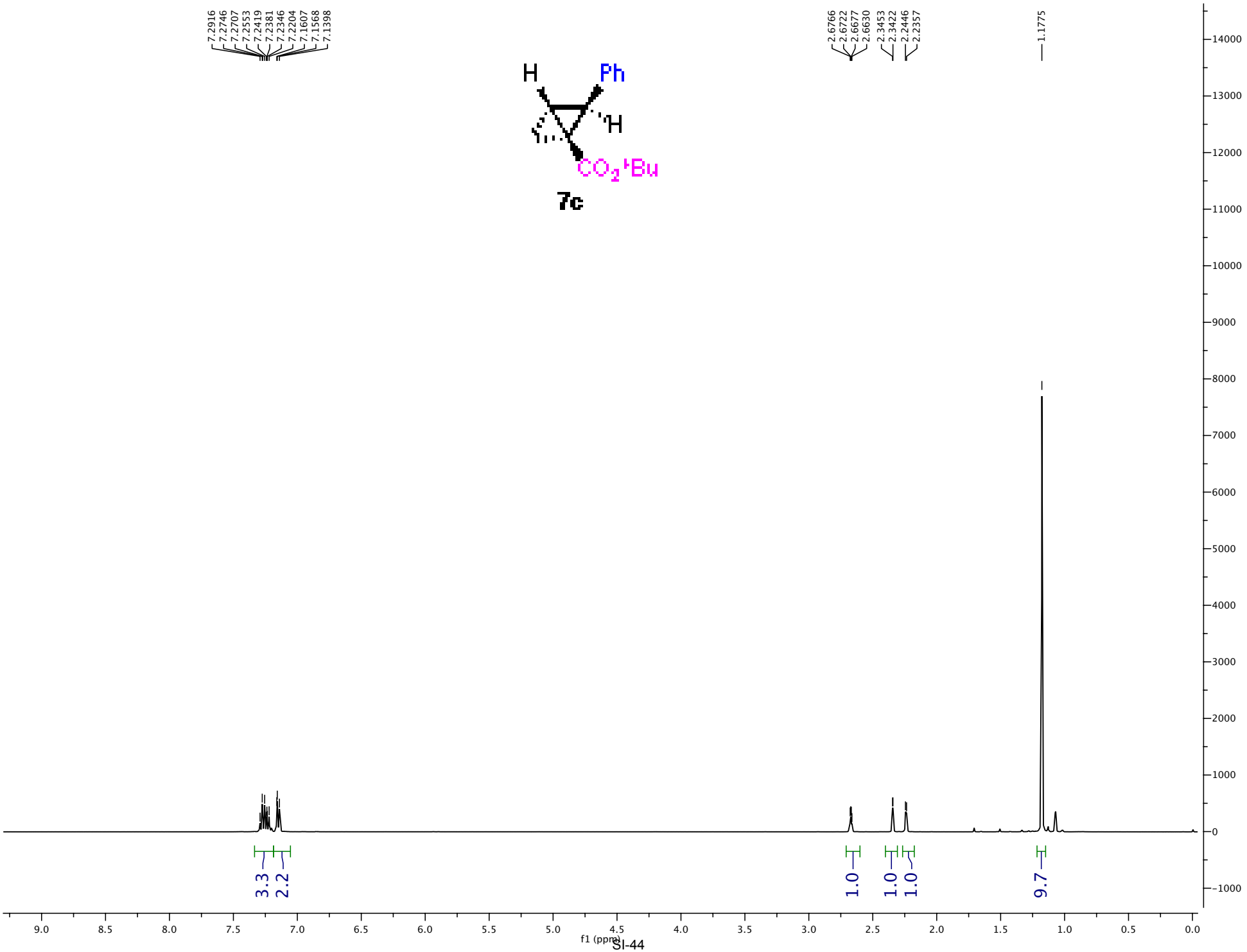
127.6889
127.2866
126.9470
77.3176
76.9996
76.6811
67.6331
67.6151
50.3605
50.3496
30.9595
21.6143
21.2060
18.9926
15.7926
H
Ph
H
CO2iPr
7b
f1 (ppm)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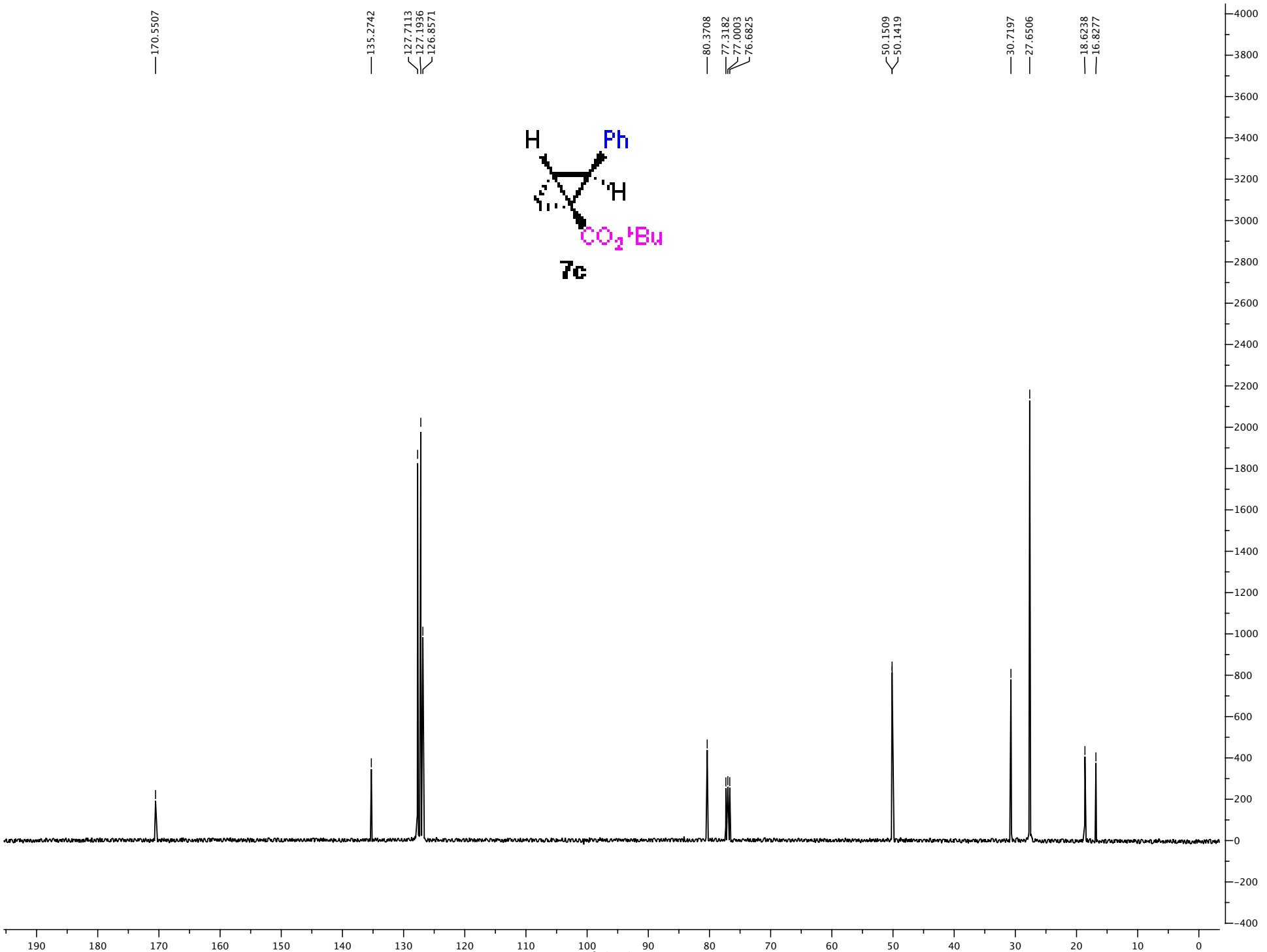
7.2707
7.2553
7.2419
7.2381
7.2346
7.2204
7.1607
7.1568
7.1398
2.6766
2.6722
2.6677
2.6630
2.3453
2.3422
2.2446
2.2357
1.1775
H
Ph
H
CO2tBu
7c
3.3
2.2
1.0
1.0
1.0
9.7
f1 (ppm)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127.7113
127.1936
126.8571
80.3708
77.3182
77.0003
76.6825
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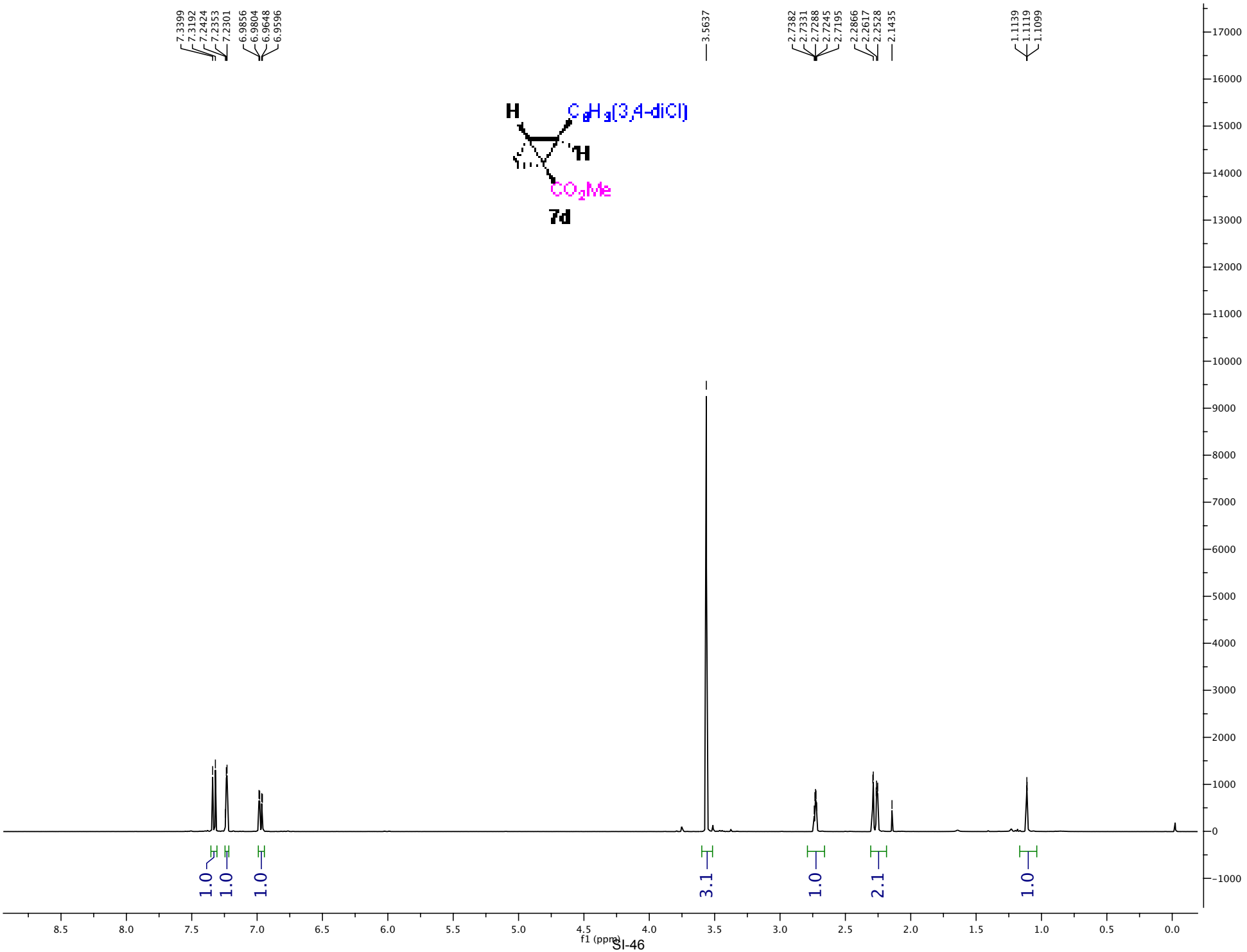
50.1419
30.7197
27.6506
18.6238
16.8277
H
Ph
H
CO2tBu
7c
f1 (ppm)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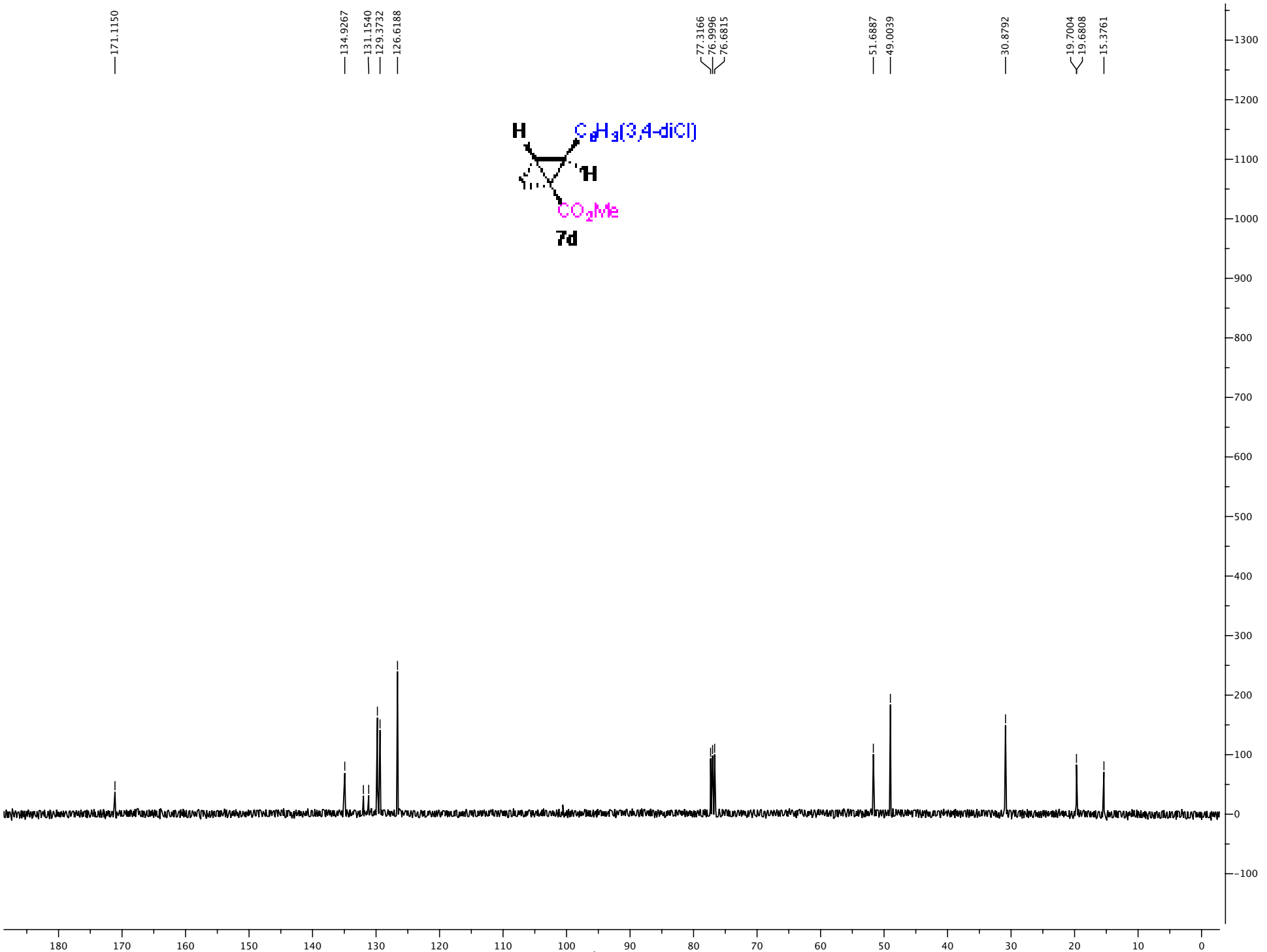
7.3192
7.2424
7.2353
7.2301
6.9856
6.9804
6.9648
6.9596
3.5637
2.7382
2.7331
2.7288
2.7245
2.7195
2.2866
2.2617
2.2528
2.1435
1.1139
1.1119
1.1099
H
C6H3(3,4-diCl)
H
CO2Me
7d
1.0
1.0
1.0
3.1
1.0
2.1
1.0
f1 (ppm)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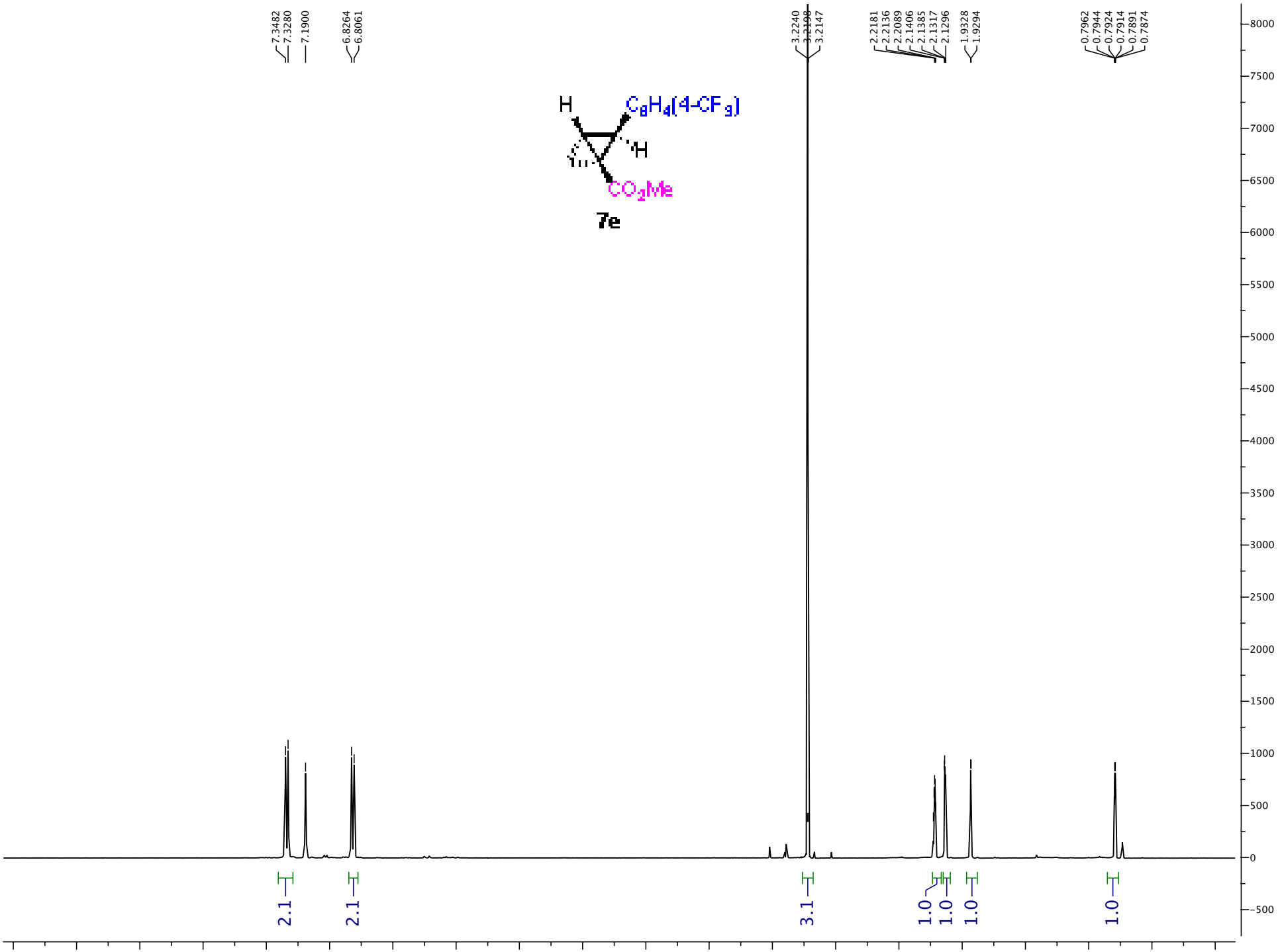
129.3732
126.6188
77.3166
76.9996
76.6815
51.6887
49.0039
30.8792
19.7004
19.6808
15.3761
H
C6H3(3,4-diCl)
H
CO2Me
7d
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.1900
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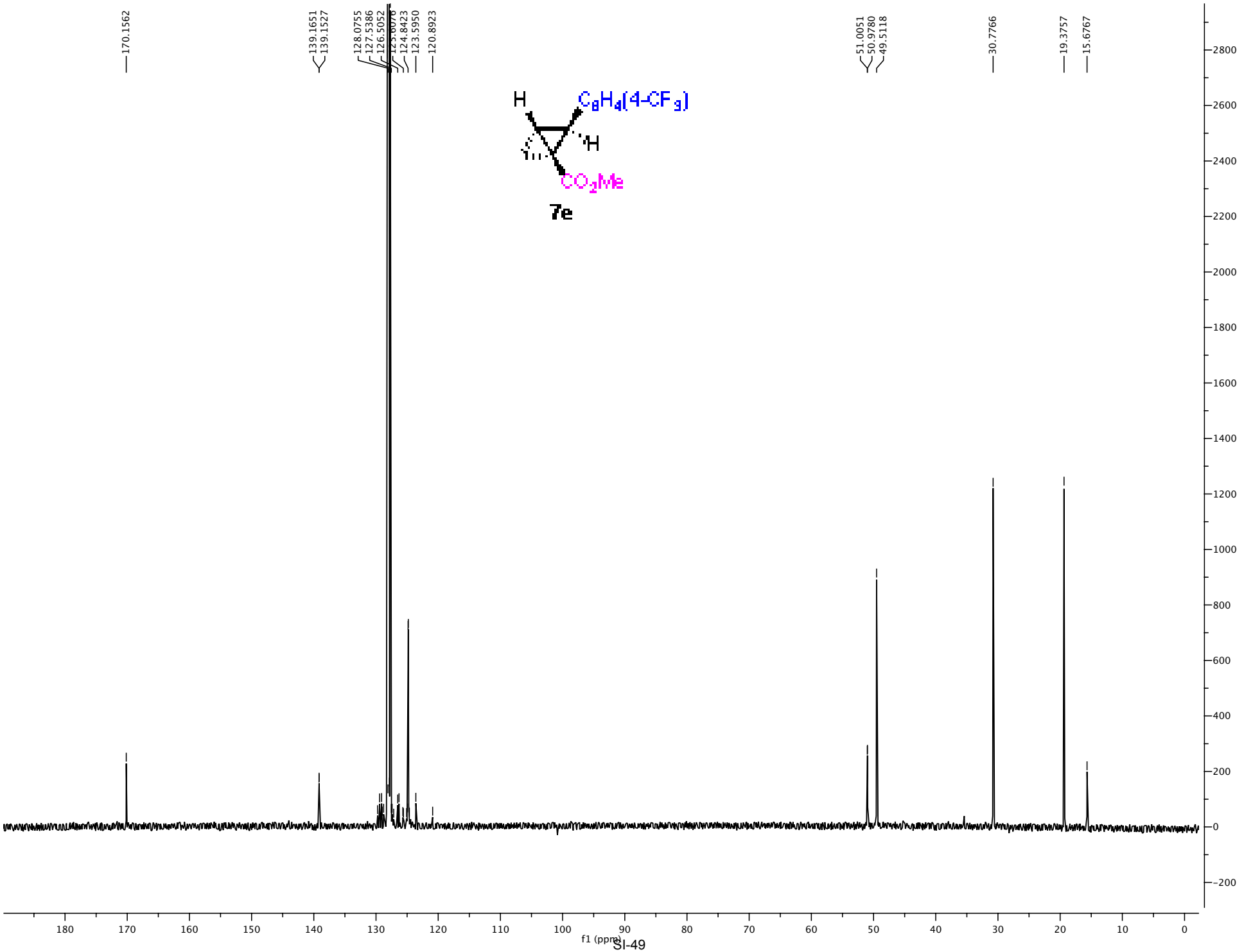
6.8061
3.2240
3.2198
3.2147
2.2181
2.2136
2.2089
2.1406
2.1385
2.1317
2.1296
1.9328
1.9294
0.7962
0.7944
0.7924
0.7914
0.7891
0.7874
H
C6H4(4-CF3)
H
CO2Me
7e
2.1
2.1
3.1
1.0
1.0
1.0
1.0
f1 (ppm)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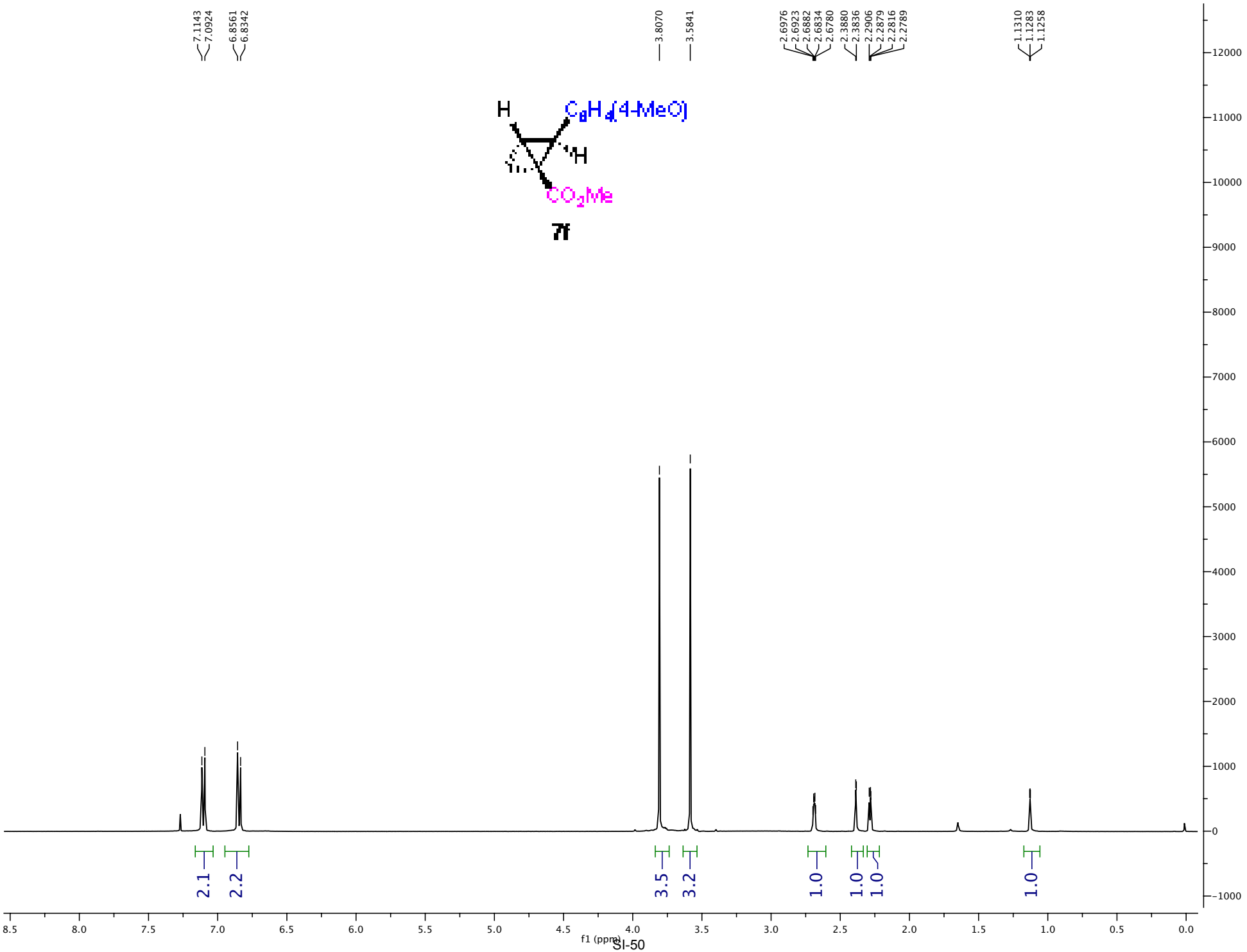
139.1527
128.0755
127.5386
126.5052
125.8078
124.8423
123.5950
120.8923
51.0051
50.9780
49.5118
30.7766
19.3757
15.6767
H
C6H4(4-CF3)
H
CO2Me
7e
f1 (ppm)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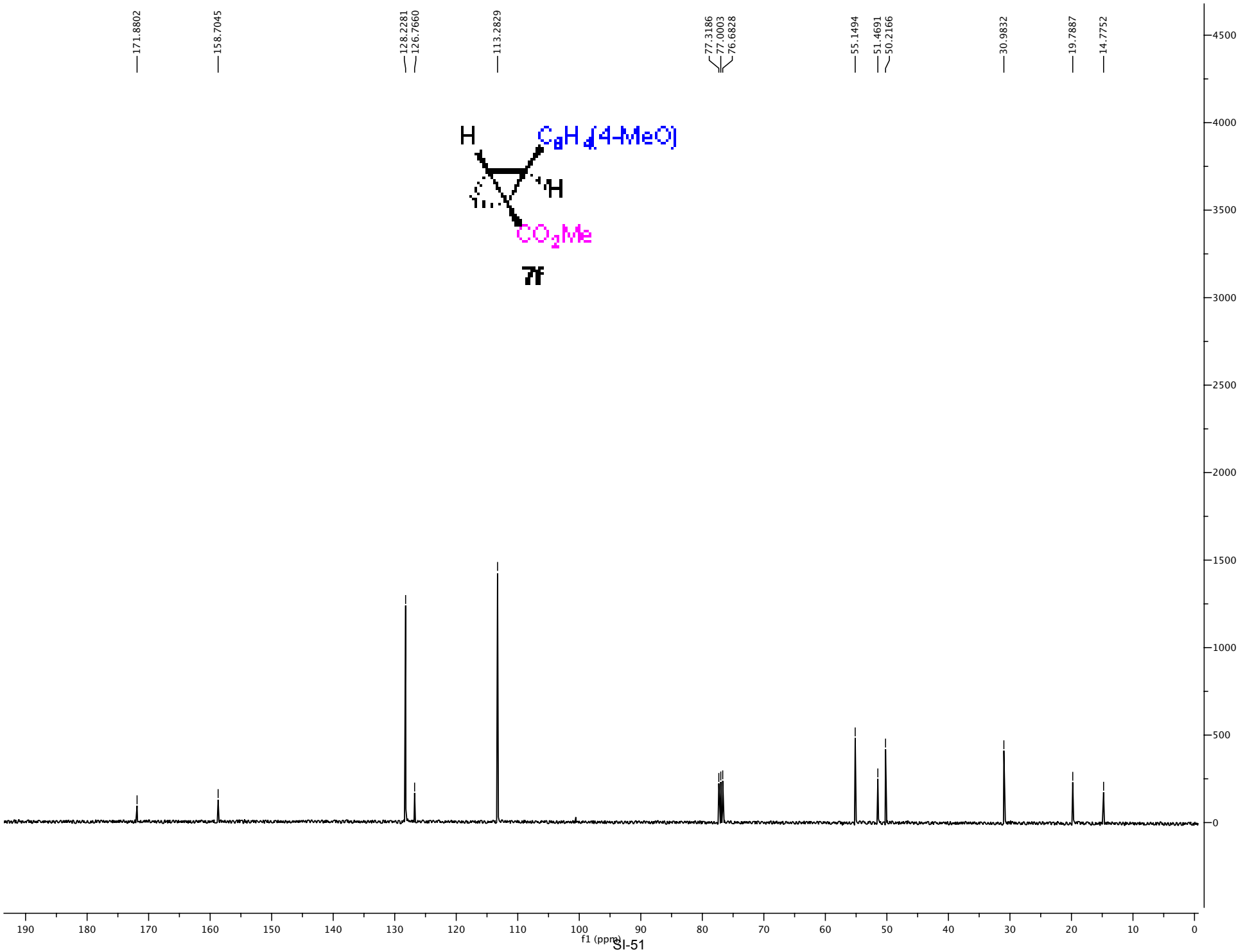
7.0924
6.8561
6.8342
3.8070
3.5841
2.6976
2.6923
2.6882
2.6834
2.6780
2.3880
2.3836
2.2906
2.2879
2.2816
2.2789
1.1310
1.1283
1.1258
H
C6H4(4-MeO)
H
CO2Me
7f
2.1
2.2
3.5
3.2
1.0
1.0
1.0
1.0
f1 (ppm)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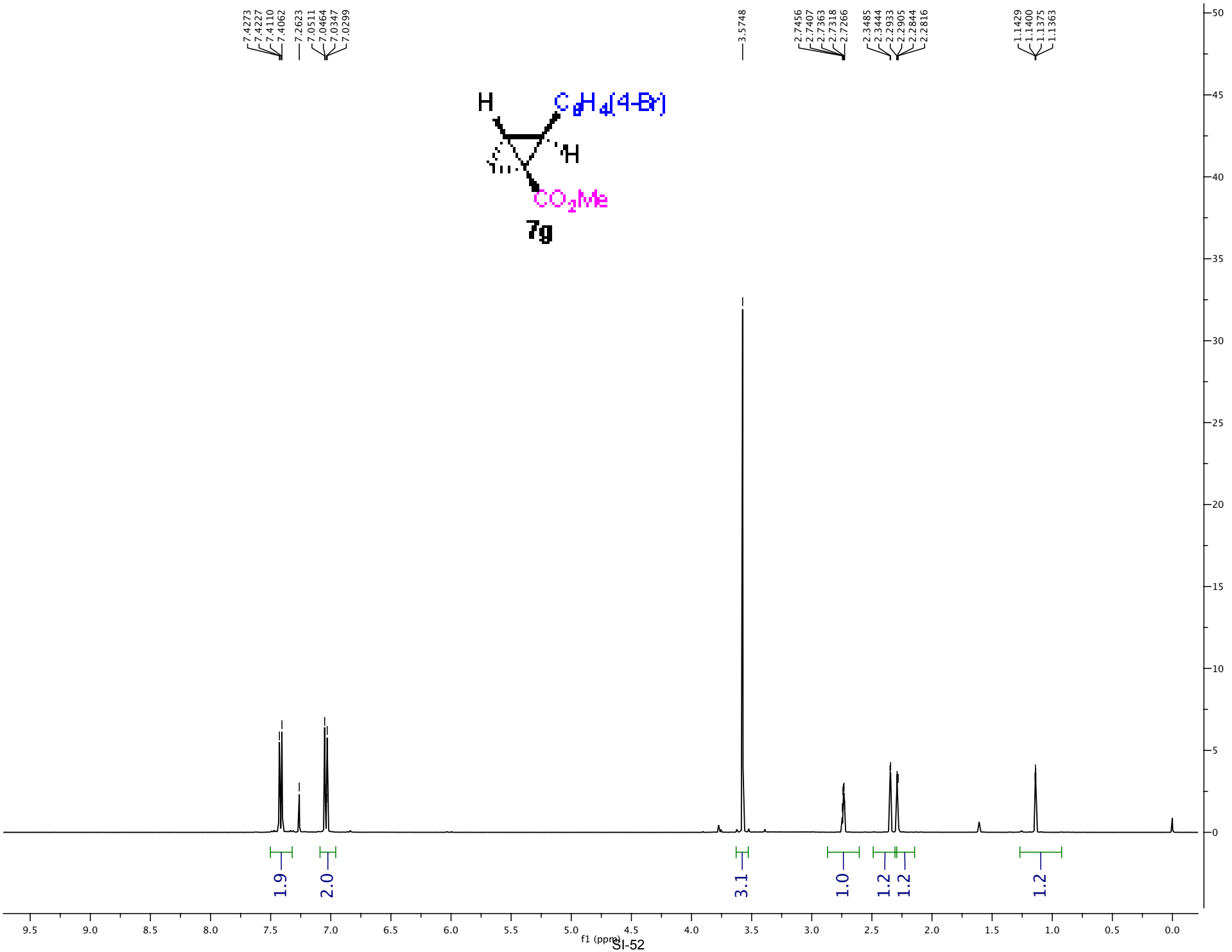
113.2829
77.3186
77.0003
76.6828
55.1494
51.4691
50.2166
30.9832
19.7887
14.7752
H
C6H4(4-MeO)
H
CO2Me
7f
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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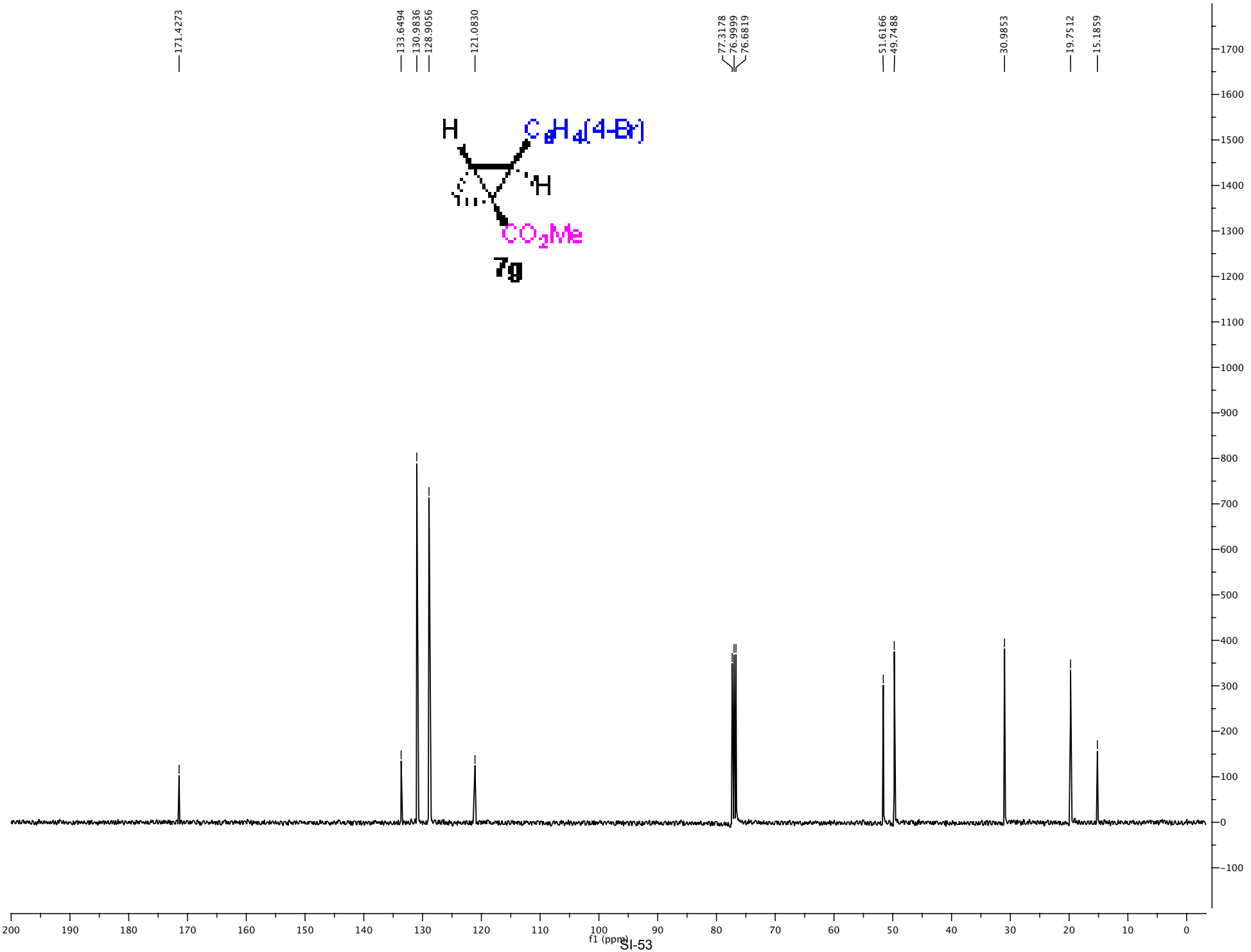
7.0464
7.0347
7.0299
3.5748
2.7456
2.7407
2.7363
2.7318
2.7266
2.3485
2.3444
2.2933
2.2905
2.2844
2.2816
1.1429
1.1400
1.1375
1.1363
H
C6H4(4-Br)
H
CO2Me
7g
1.9
2.0
3.1
1.0
1.2
1.2
1.2
f1 (ppm)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76.9999
76.6819
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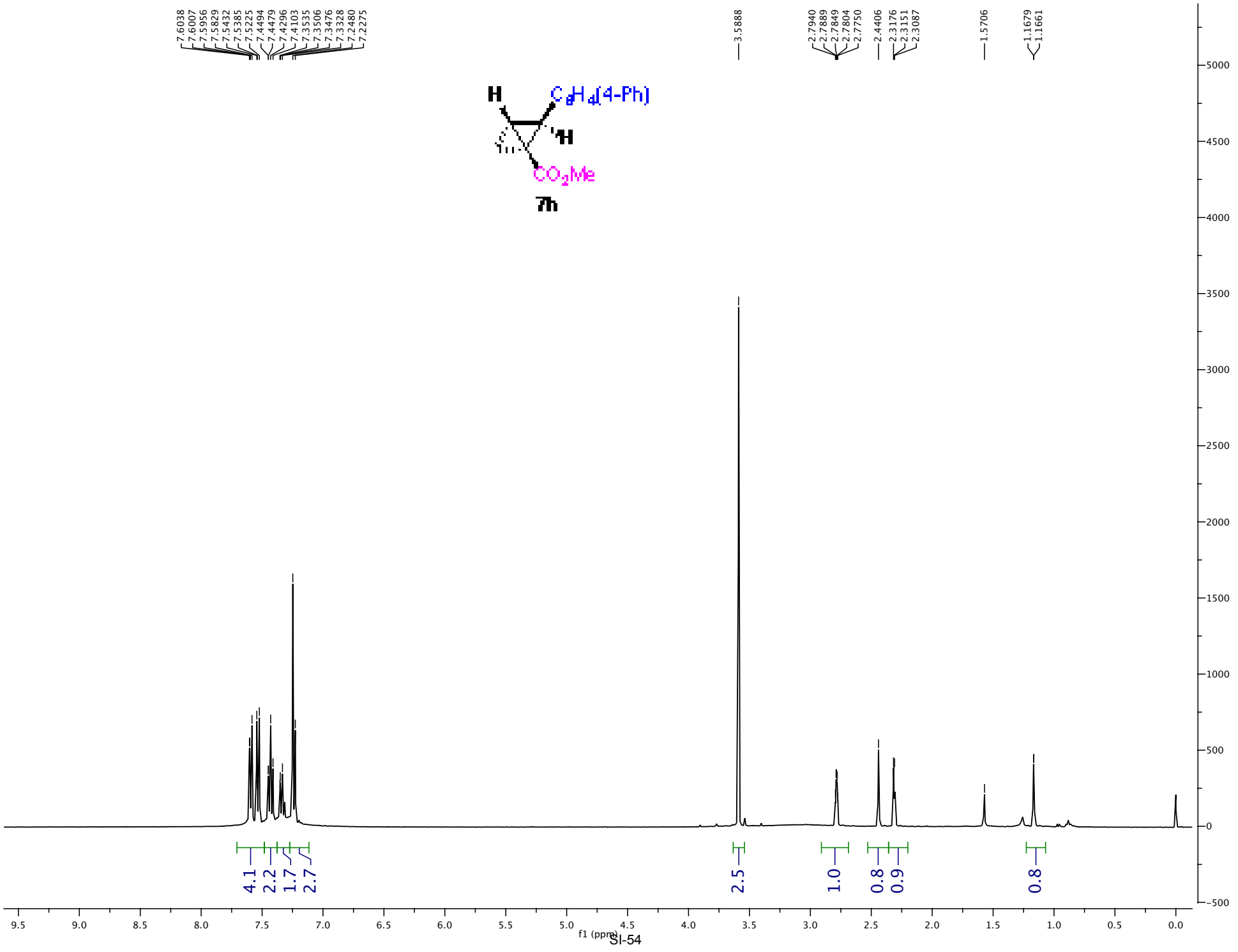
49.7488
30.9853
19.7512
15.1859
H
C6H4(4-Br)
H
CO2Me
7g
f1 (ppm)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7.4479
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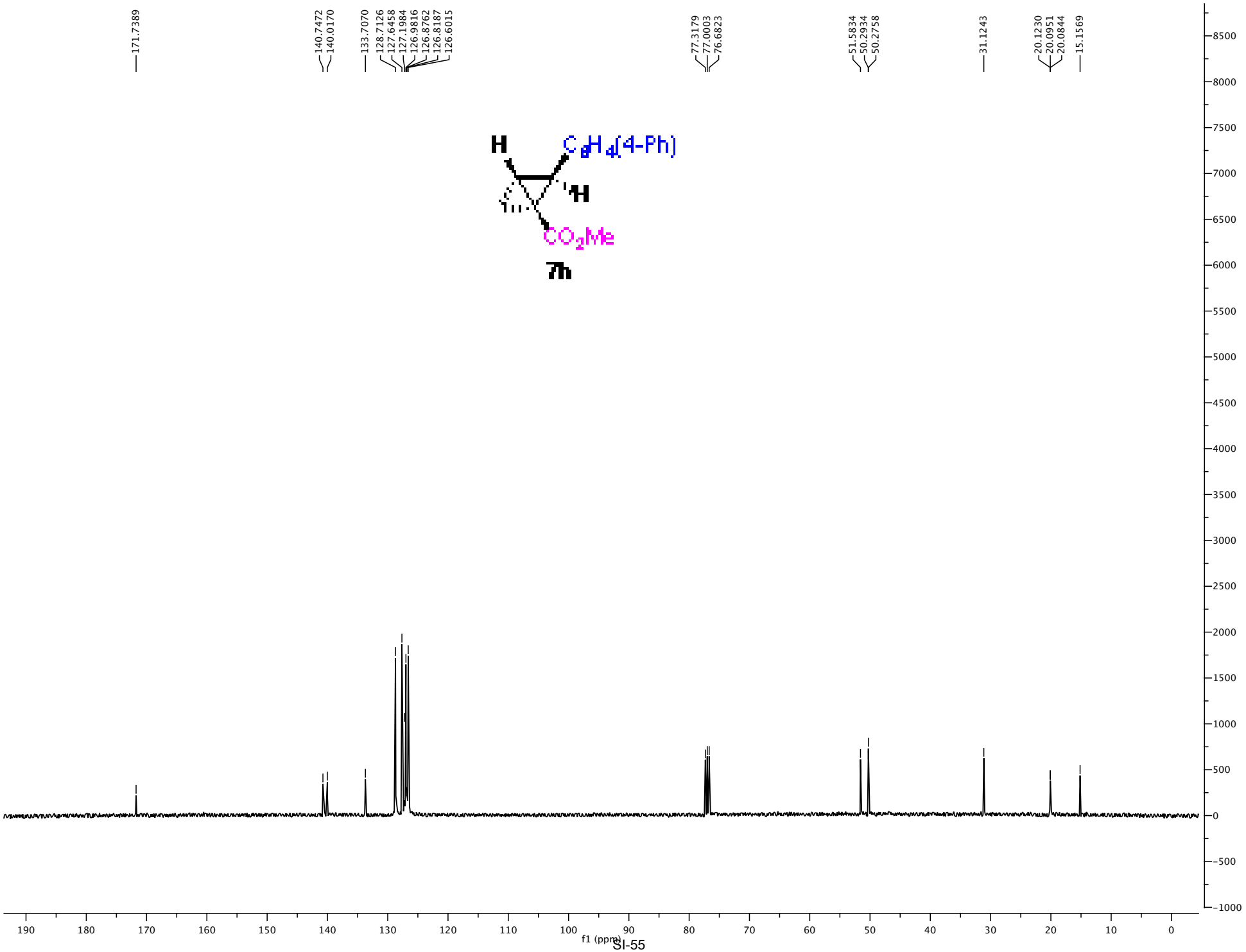
7.4103
7.3535
7.3506
7.3476
7.3328
7.2480
7.2275
3.5888
2.7940
2.7889
2.7849
2.7804
2.7750
2.4406
2.3176
2.3151
2.3087
1.5706
1.1679
1.1661
H
C6H4(4-Ph)
H
CO2Me
Ph
4.1
2.2
1.7
2.7
2.5
1.0
0.8
0.9
0.8
f1 (ppm)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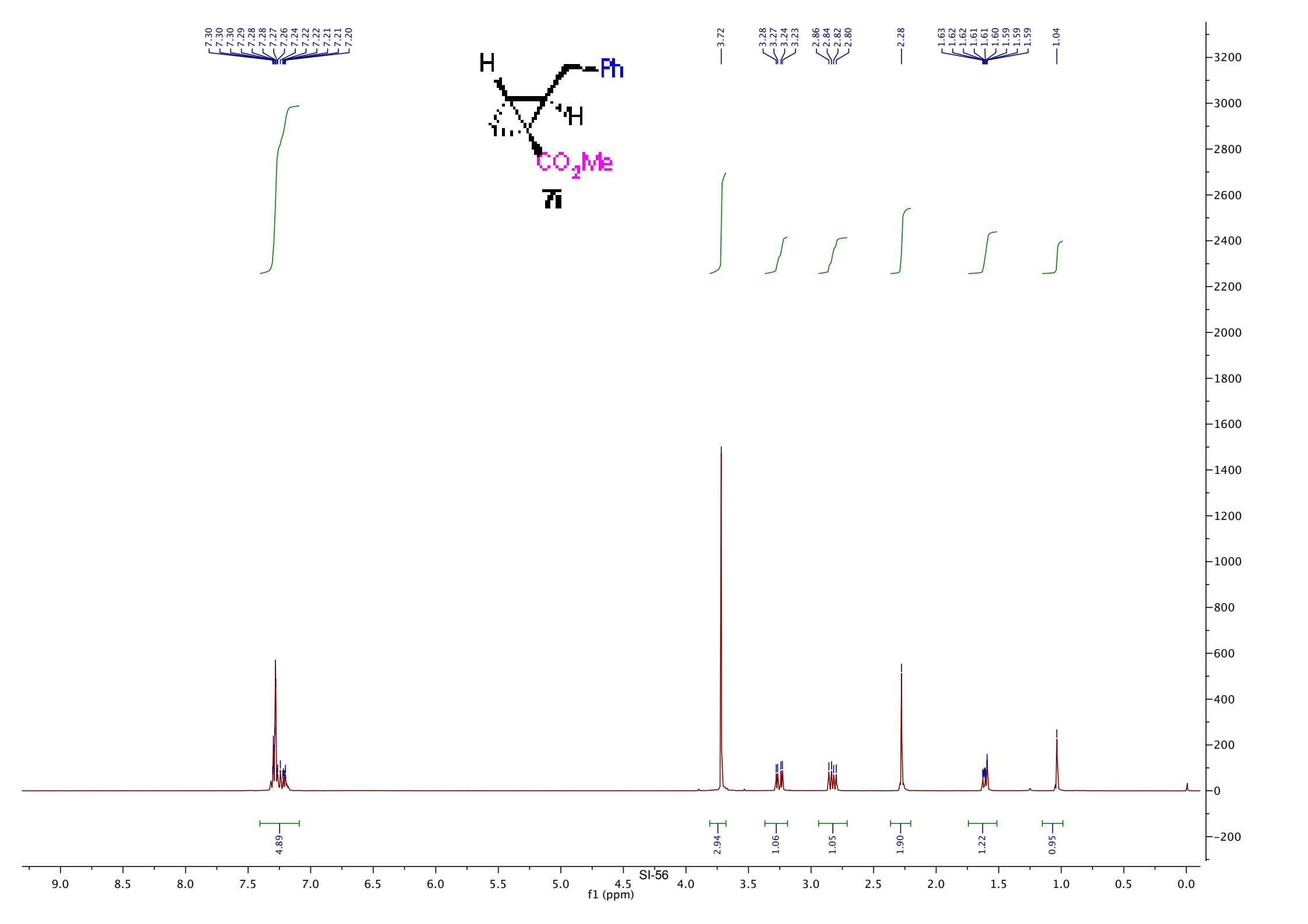
126.8187
126.6015
77.3179
77.0003
76.6823
51.5834
50.2934
50.2758
31.1243
20.1230
20.0951
20.0844
15.1569
H
C6H4(4-Ph)
H
CO2Me
7h
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
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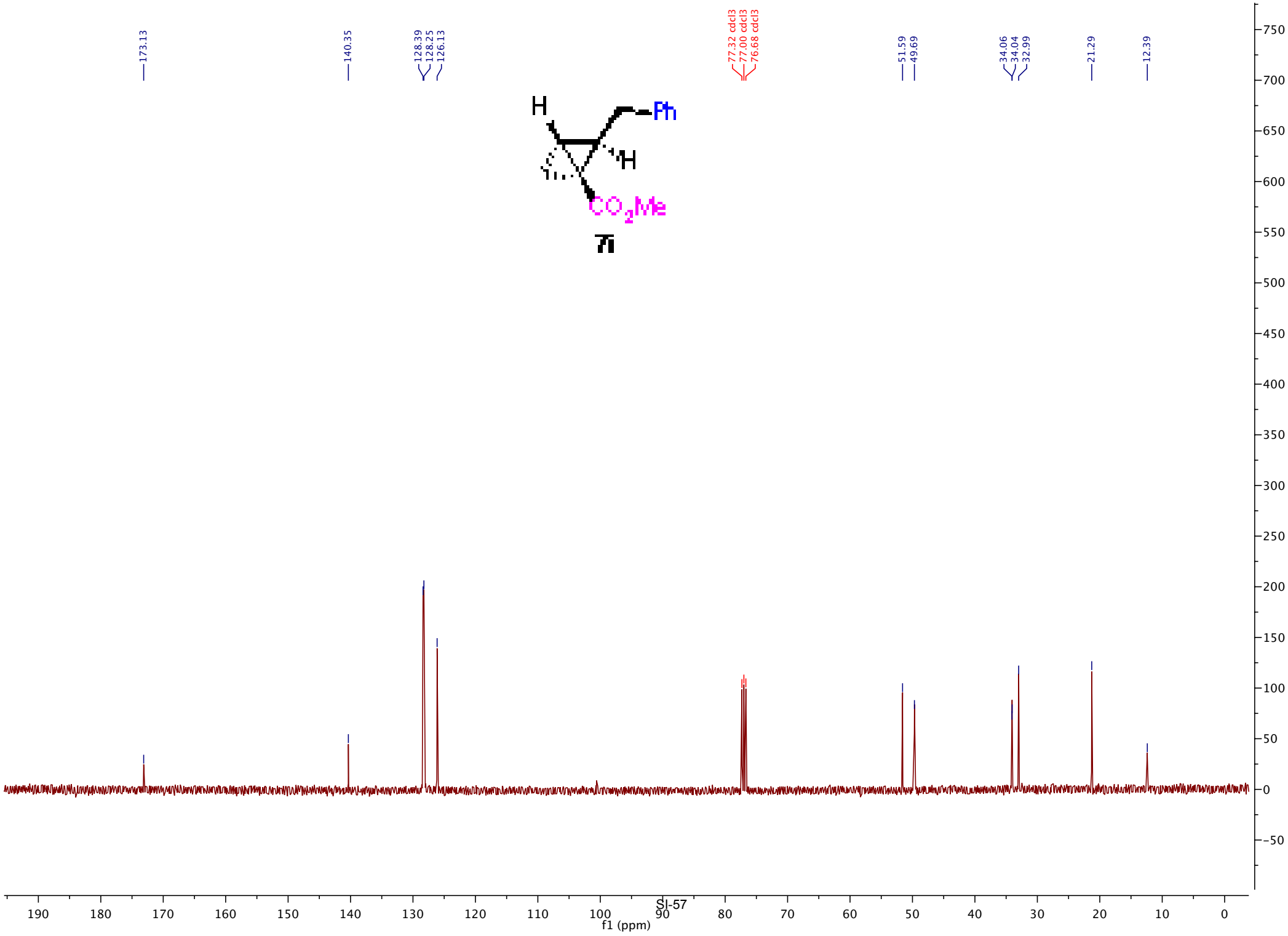
7.22
7.22
7.21
7.21
7.20
3.72
3.28
3.27
3.24
3.23
2.86
2.84
2.82
2.80
2.28
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.59
1.59
1.04
H
Ph
H
CO2Me
4.89
2.94
1.06
1.05
1.90
1.22
0.95
f1 (ppm)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128.39
128.25
126.13
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77.00 cdcl3
76.68 cdcl3
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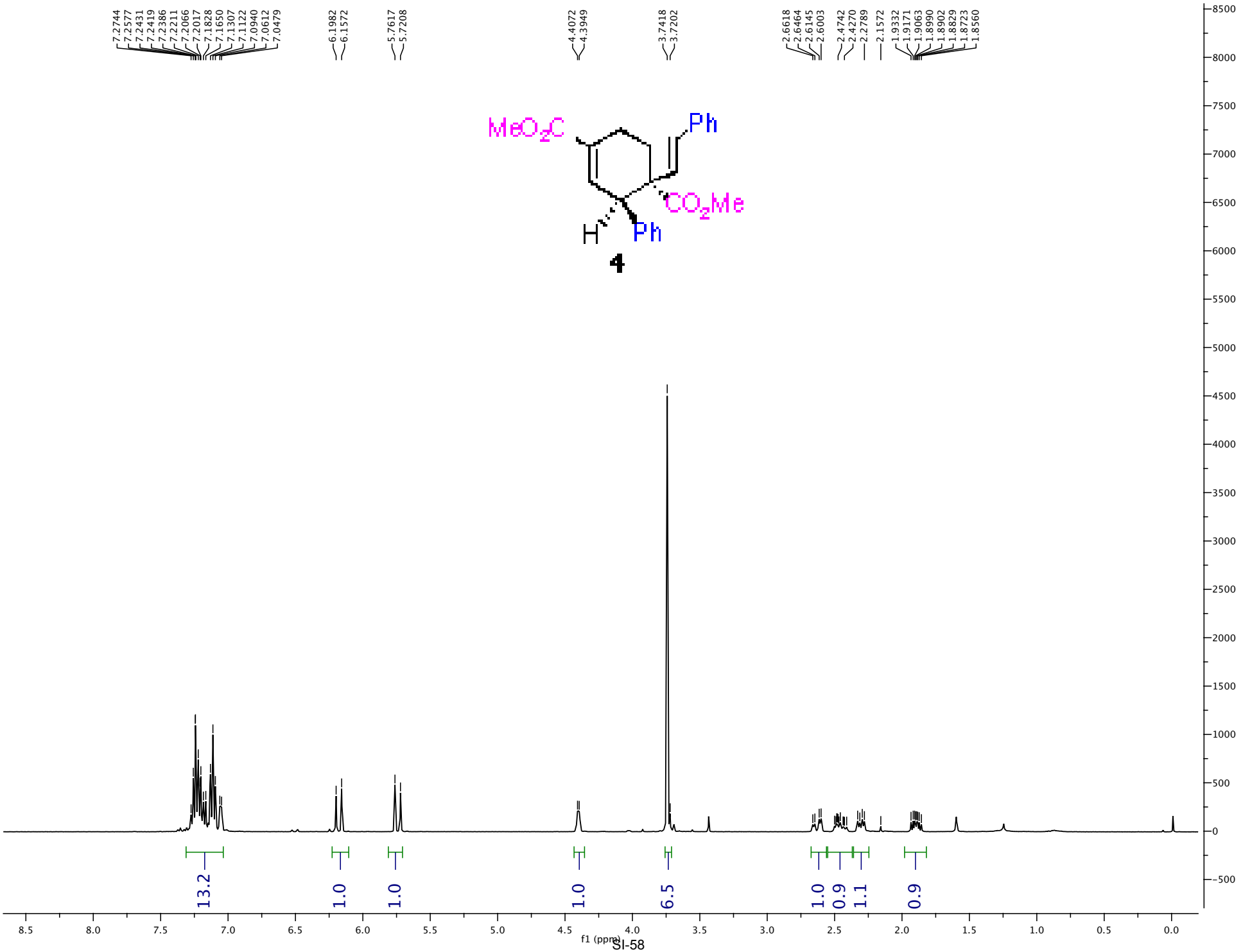
34.06
34.04
32.99
21.29
12.39
H
Ph
H
CO2Me
f1 (ppm)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7.2017
7.1828
7.1650
7.1307
7.1122
7.0940
7.0612
7.0479
6.1982
6.1572
5.7617
5.7208
4.4072
4.3949
3.7418
3.7202
2.6618
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2.6145
2.6003
2.4742
2.4270
2.2789
2.1572
1.9332
1.9171
1.9063
1.8990
1.8902
1.8829
1.8723
1.8560
MeO2C
Ph
CO2Me
H
Ph
4
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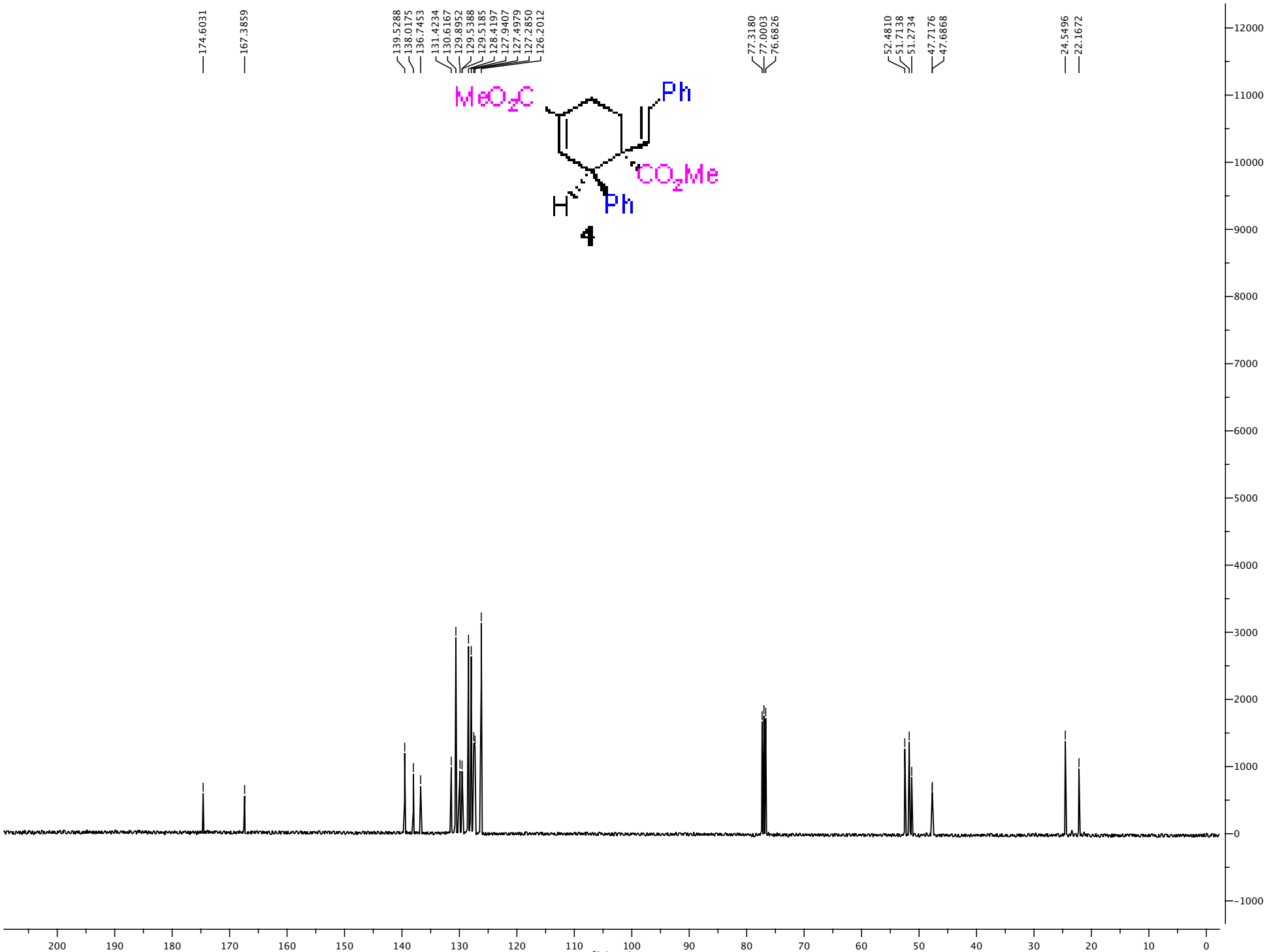
1.0
1.0
1.0
6.5
1.0
0.9
1.1
0.9
f1 (ppm)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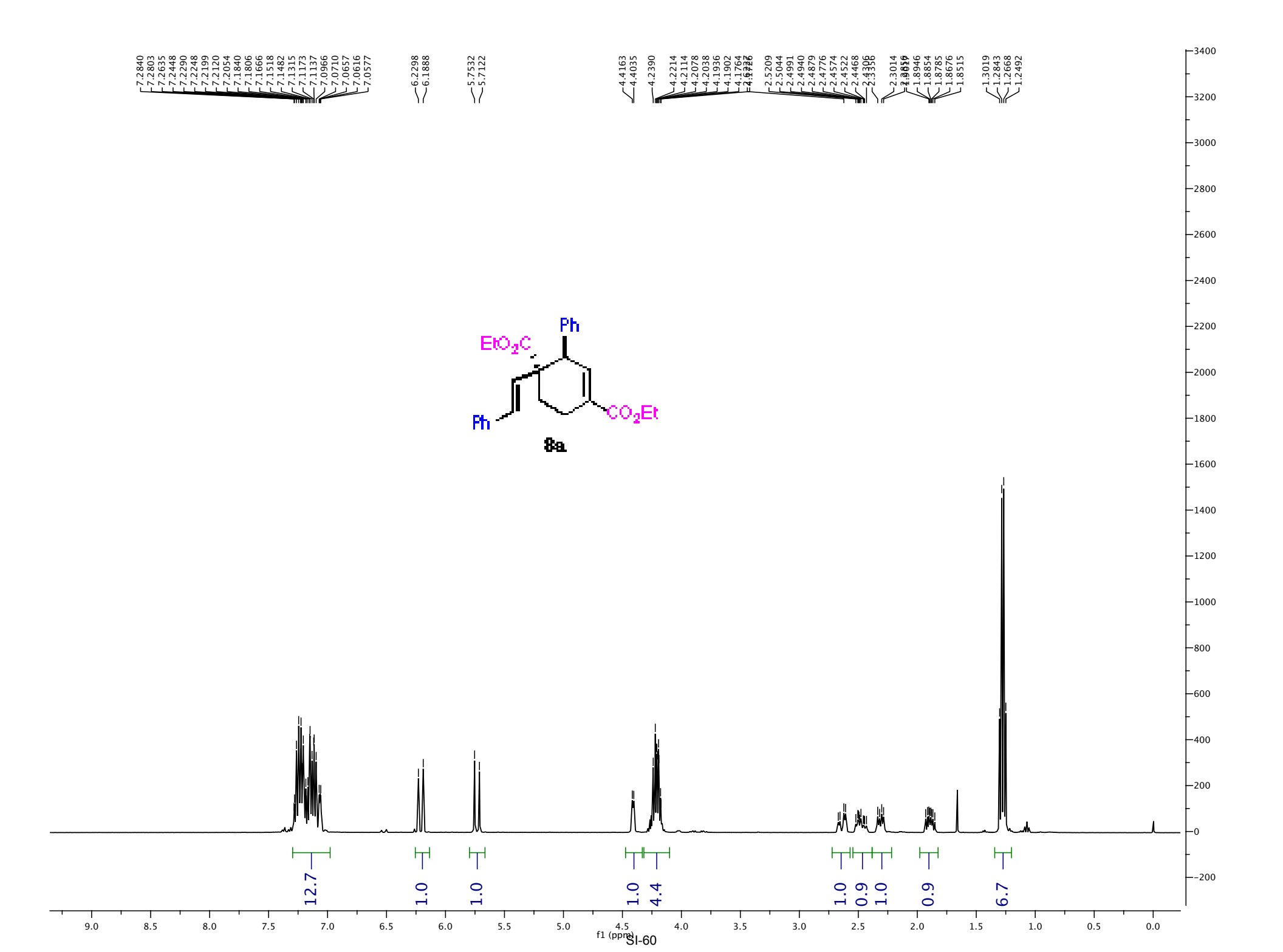
127.9407
127.4979
127.2850
126.2012
77.3180
77.0003
76.6826
52.4810
51.7138
51.2734
47.7176
47.6868
24.5496
22.1672
MeO2C
Ph
CO2Me
H
Ph
4
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.1806
7.1666
7.1518
7.1482
7.1315
7.1173
7.1137
7.0966
7.0710
7.0657
7.0616
7.0577
6.2298
6.1888
5.7532
5.7122
4.4163
4.4035
4.2390
4.2214
4.2114
4.2078
4.2038
4.1936
4.1902
4.1764
2.5209
2.5044
2.4991
2.4940
2.4879
2.4776
2.4574
2.4522
2.4468
2.4306
2.3014
1.8946
1.8854
1.8785
1.8676
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1.3019
1.2843
1.2668
1.2492
Ph
EtO2C
CO2Et
Ph
8a
12.7
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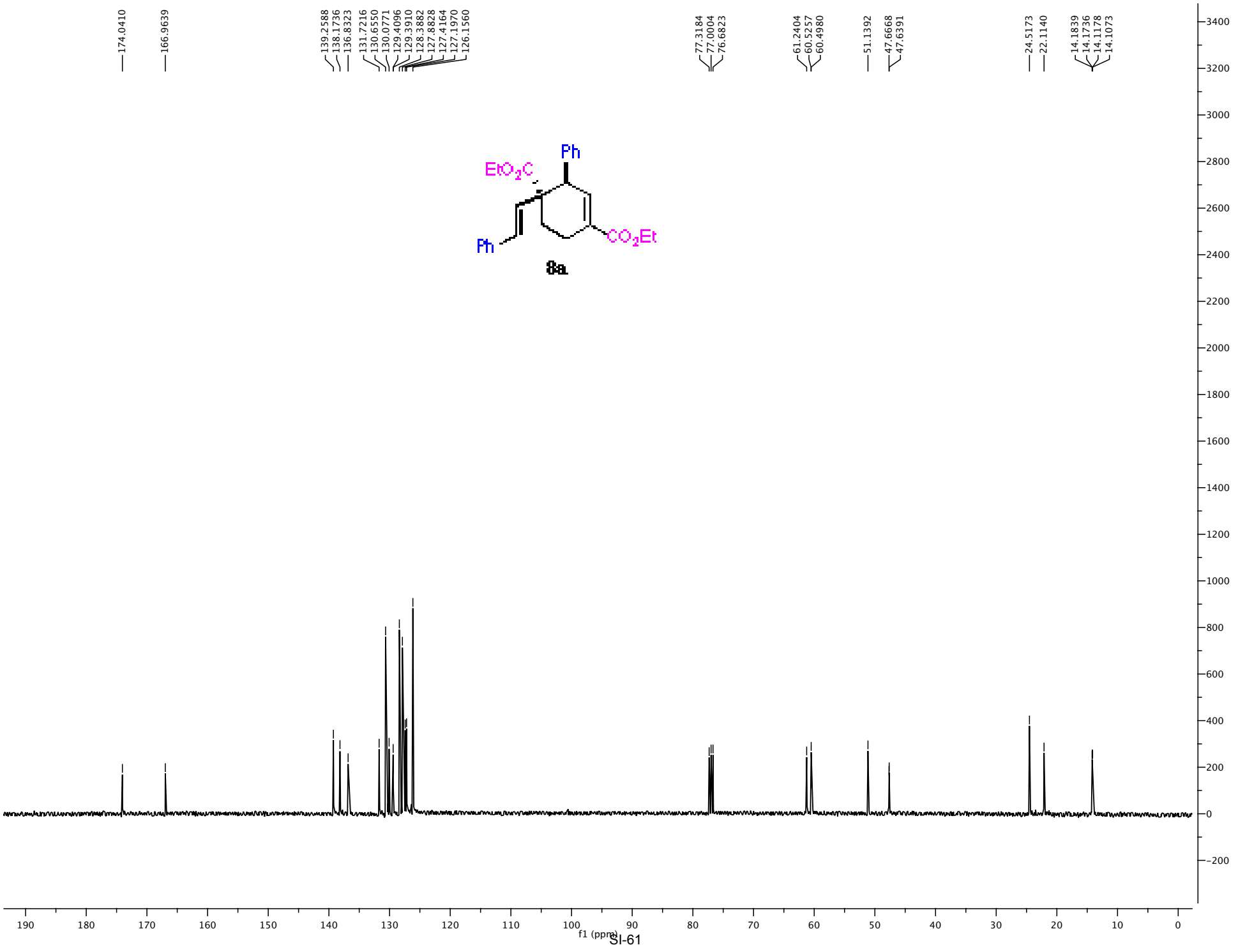
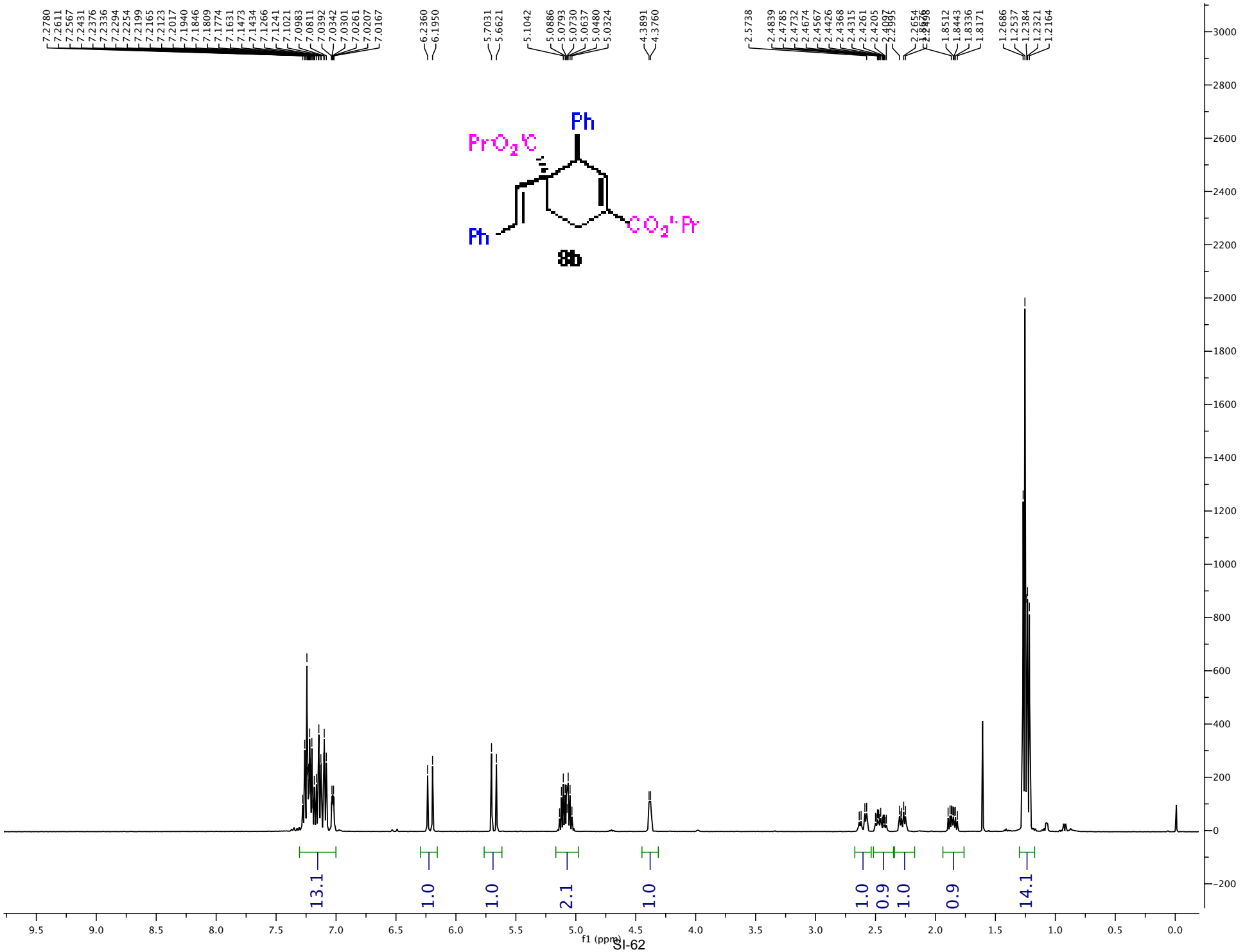
1.0
1.0
4.4
1.0
0.9
1.0
0.9
6.7
f1 (ppm)


174.0410
166.9639
139.2588
138.1736
136.8323
131.7216
130.6550
130.0771
129.4096
129.3910
128.3882
127.8828
127.4164
127.1970
126.1560
77.3184
77.0004
76.6823
61.2404
60.5257
60.4980
51.1392
47.6668
47.6391
24.5173
22.1140
14.1839
14.1736
14.1178
14.1073
Ph
EtO2C
Ph
CO2Et
8a
f1 (ppm)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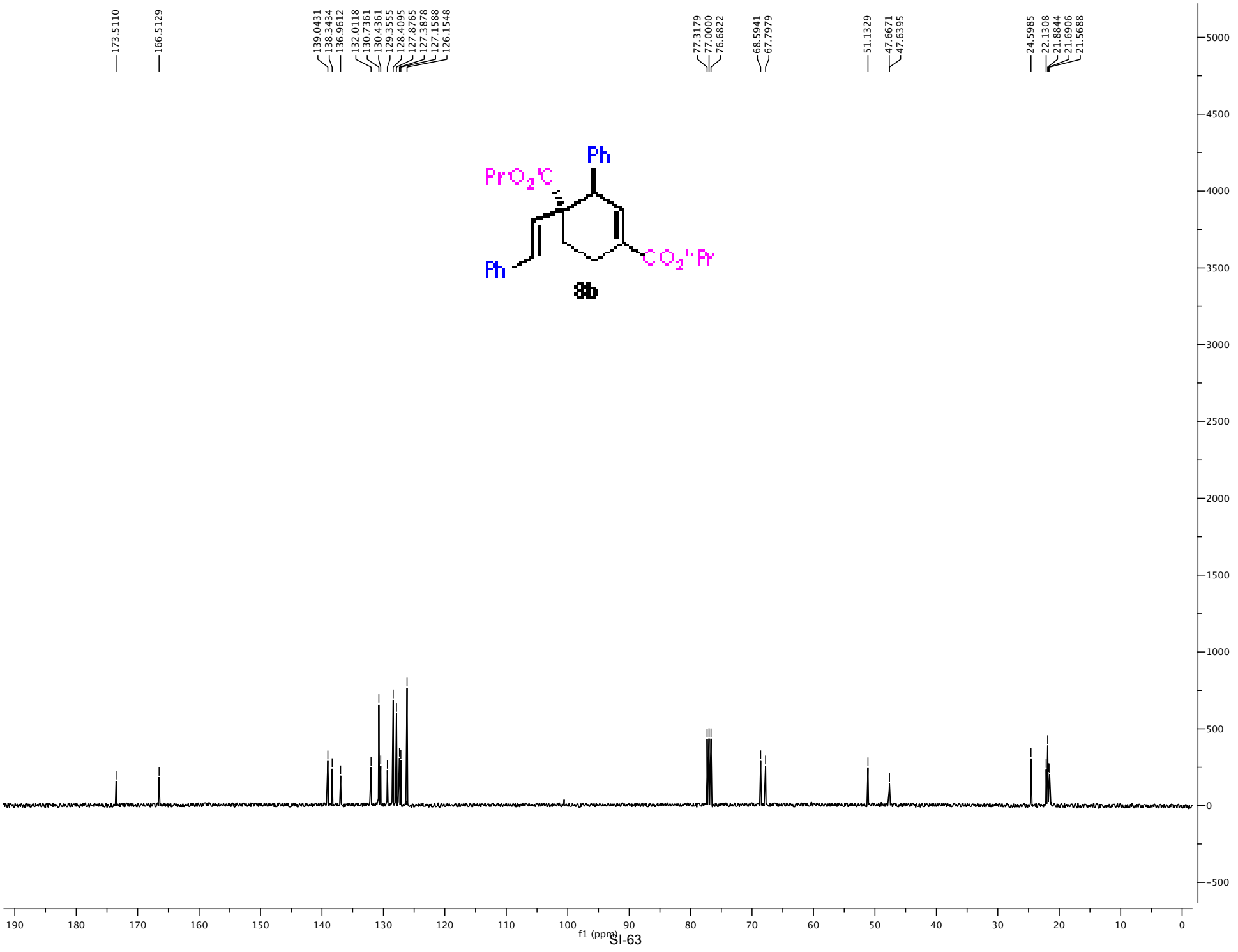
7.2611
7.2567
7.2431
7.2376
7.2336
7.2294
7.2254
7.2199
7.2165
7.2123
7.2017
7.1940
7.1846
7.1809
7.1774
7.1631
7.1473
7.1434
7.1266
7.1241
7.1021
7.0983
7.0811
7.0392
7.0342
7.0301
7.0261
7.0207
7.0167
6.2360
6.1950
5.7031
5.6621
5.1042
5.0886
5.0793
5.0730
5.0637
5.0480
5.0324
4.3891
4.3760
2.5738
2.4839
2.4785
2.4732
2.4674
2.4567
2.4426
2.4368
2.4315
2.4261
2.4205
2.4097
2.3995
2.2654
1.8512
1.8443
1.8336
1.8171
1.2686
1.2537
1.2384
1.2321
1.2164
Ph
PrO2C
Ph
CO2Pr
3b
13.1
1.0
1.0
2.1
1.0
1.0
0.9
1.0
0.9
14.1
f1 (ppm)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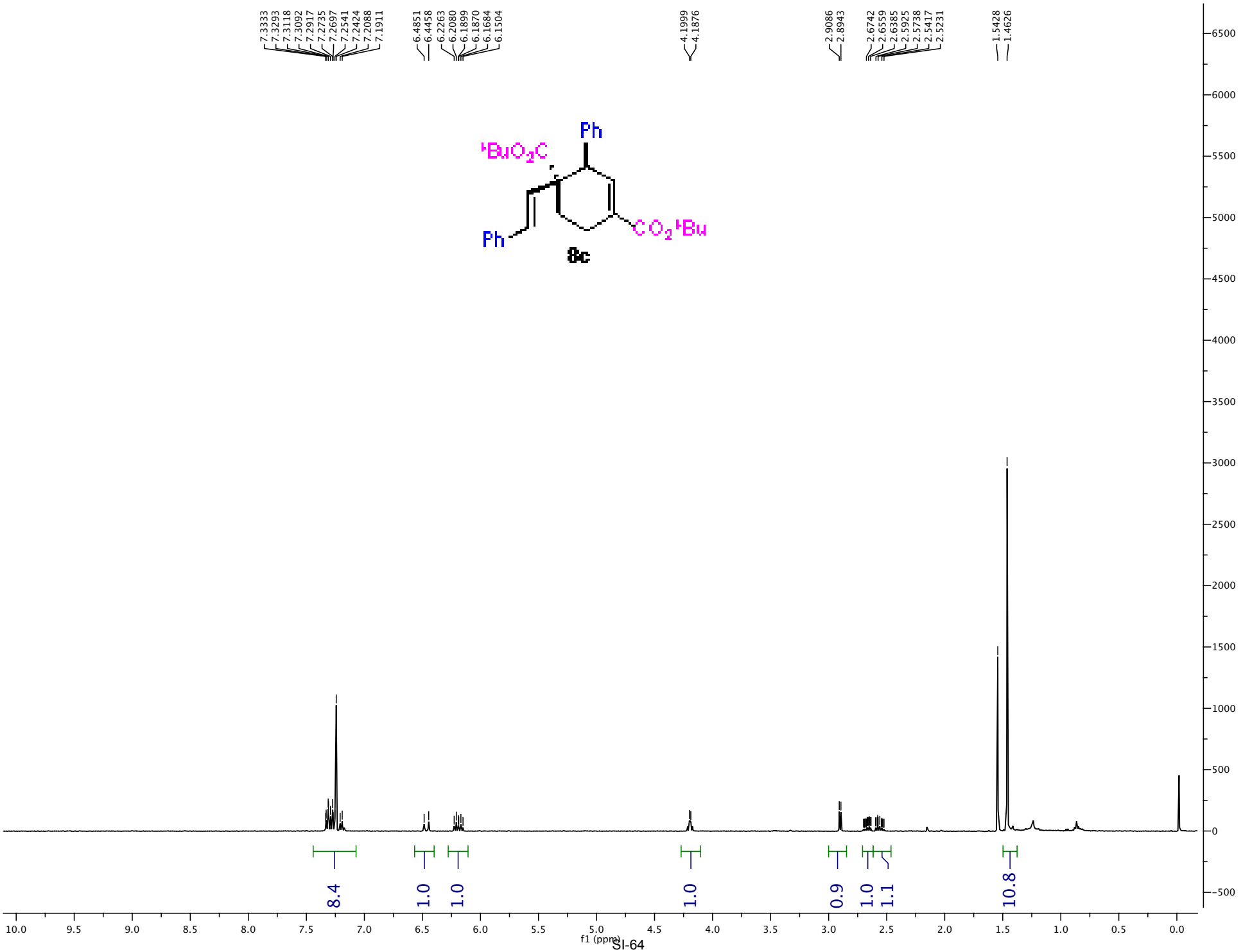
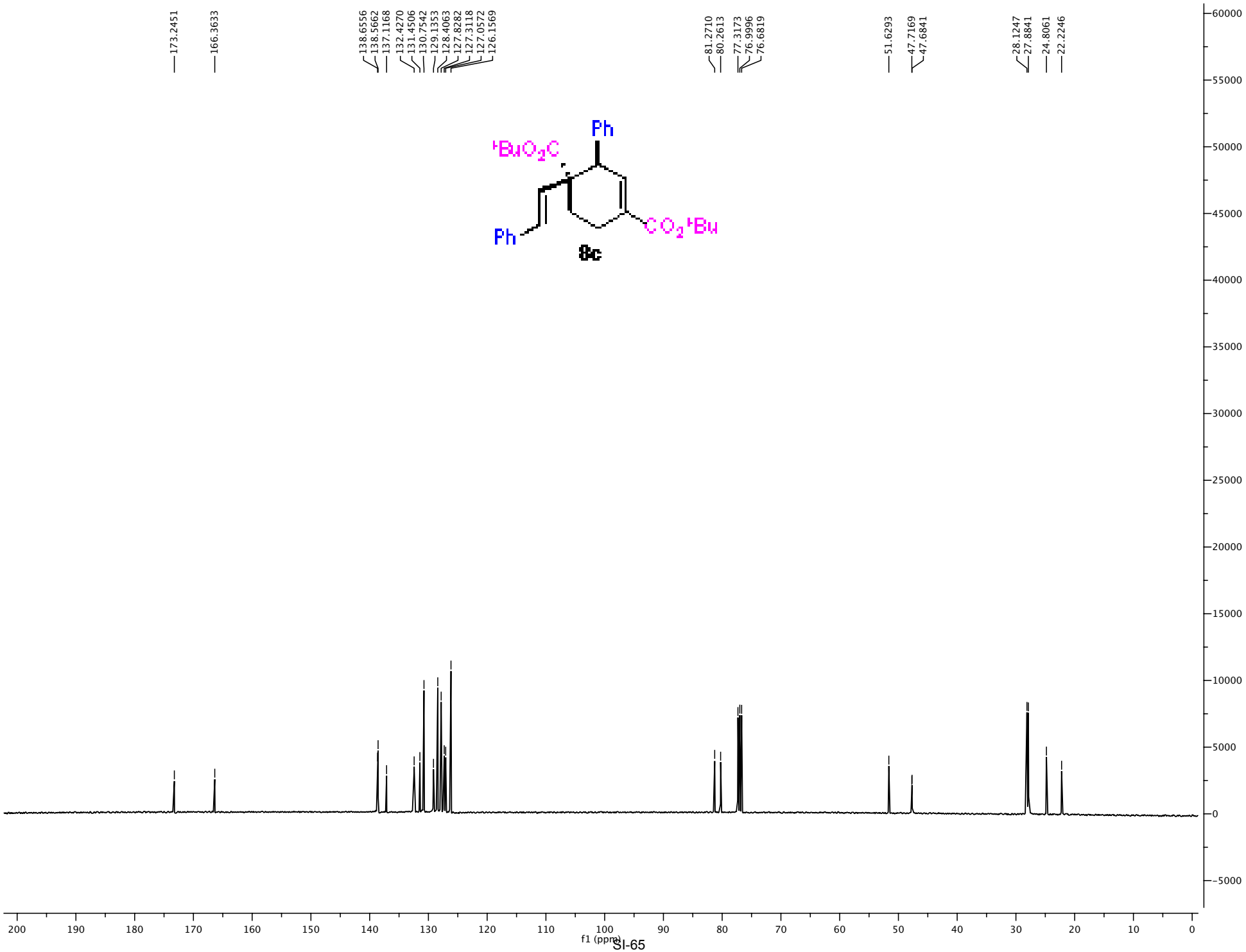
139.0431
138.3434
136.9612
132.0118
130.7361
130.4361
129.3555
128.4095
127.8765
127.3878
127.1588
126.1548
77.3179
77.0000
76.6822
68.5941
67.7979
51.1329
47.6671
47.6395
24.5985
22.1308
21.8844
21.6906
21.5688
Ph
PrO2C
CO2iPr
Ph
8b
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.3333
7.3293
7.3118
7.3092
7.2917
7.2735
7.2697
7.2541
7.2424
7.2088
7.1911
6.4851
6.4458
6.2263
6.2080
6.1899
6.1870
6.1684
6.1504
4.1999
4.1876
2.9086
2.8943
2.6742
2.6559
2.6385
2.5925
2.5738
2.5417
2.5231
1.5428
1.4626
Ph
tBuO2C
CO2tBu
Ph
8c
8.4
1.0
1.0
1.0
0.9
1.0
1.1
10.8
f1 (ppm)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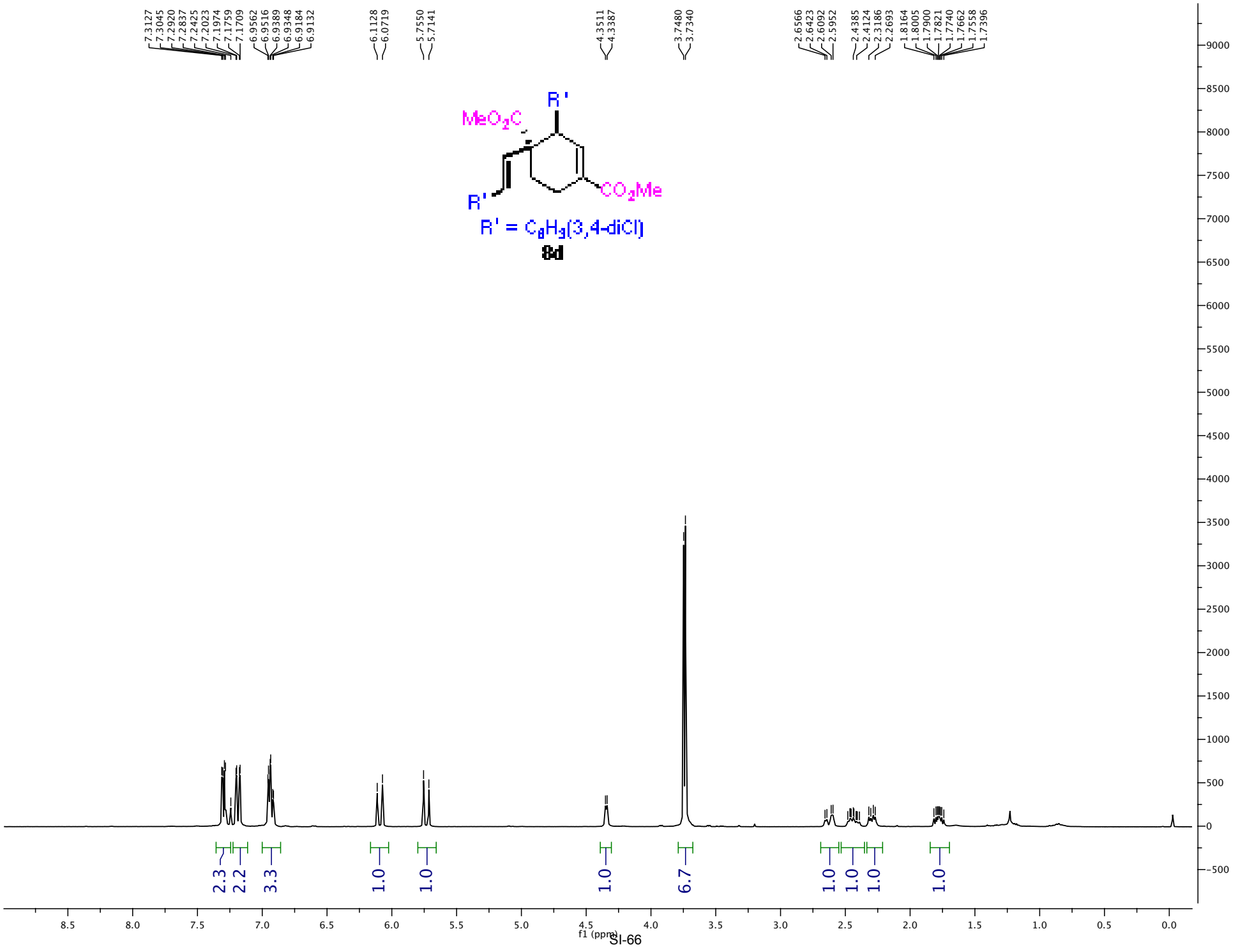
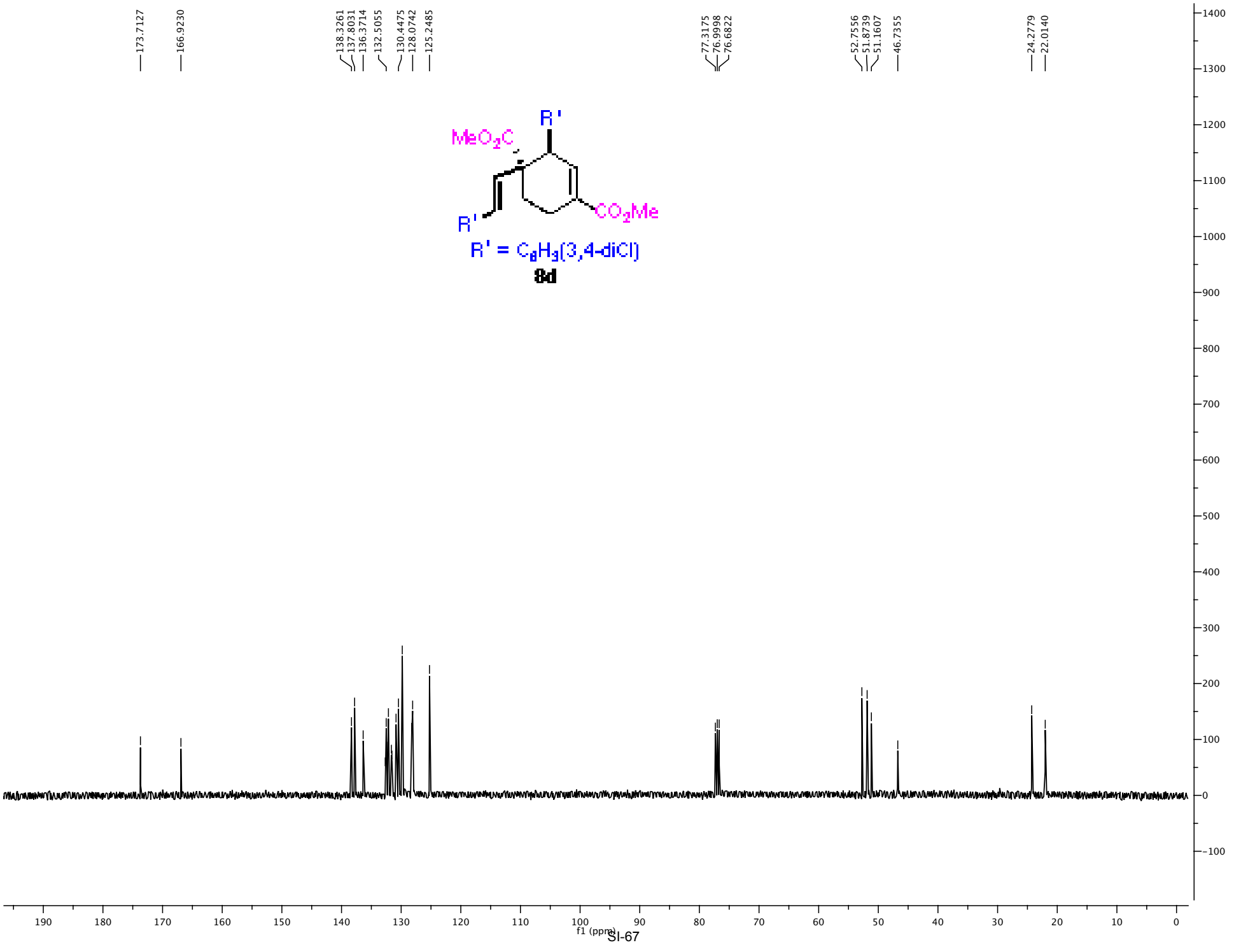
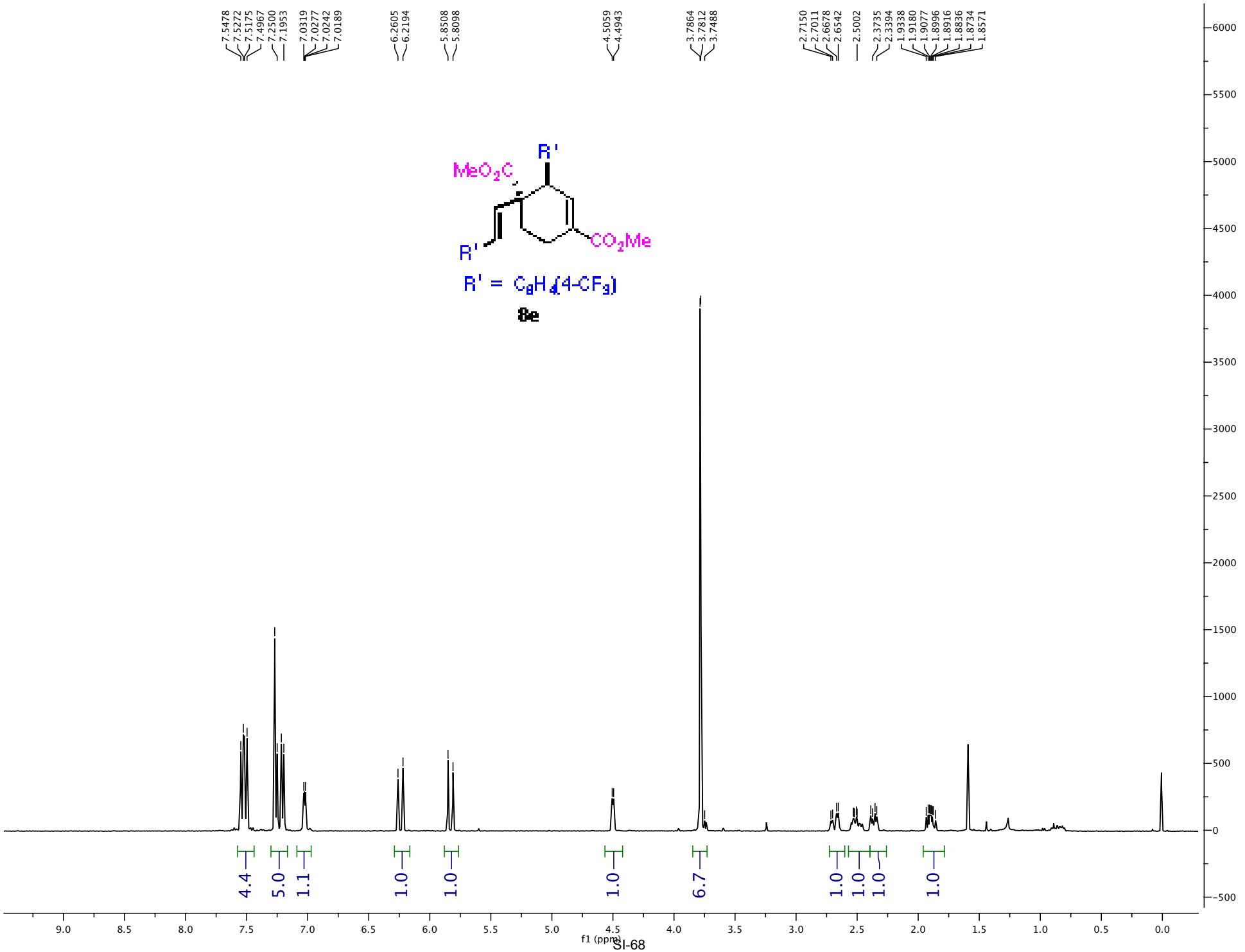
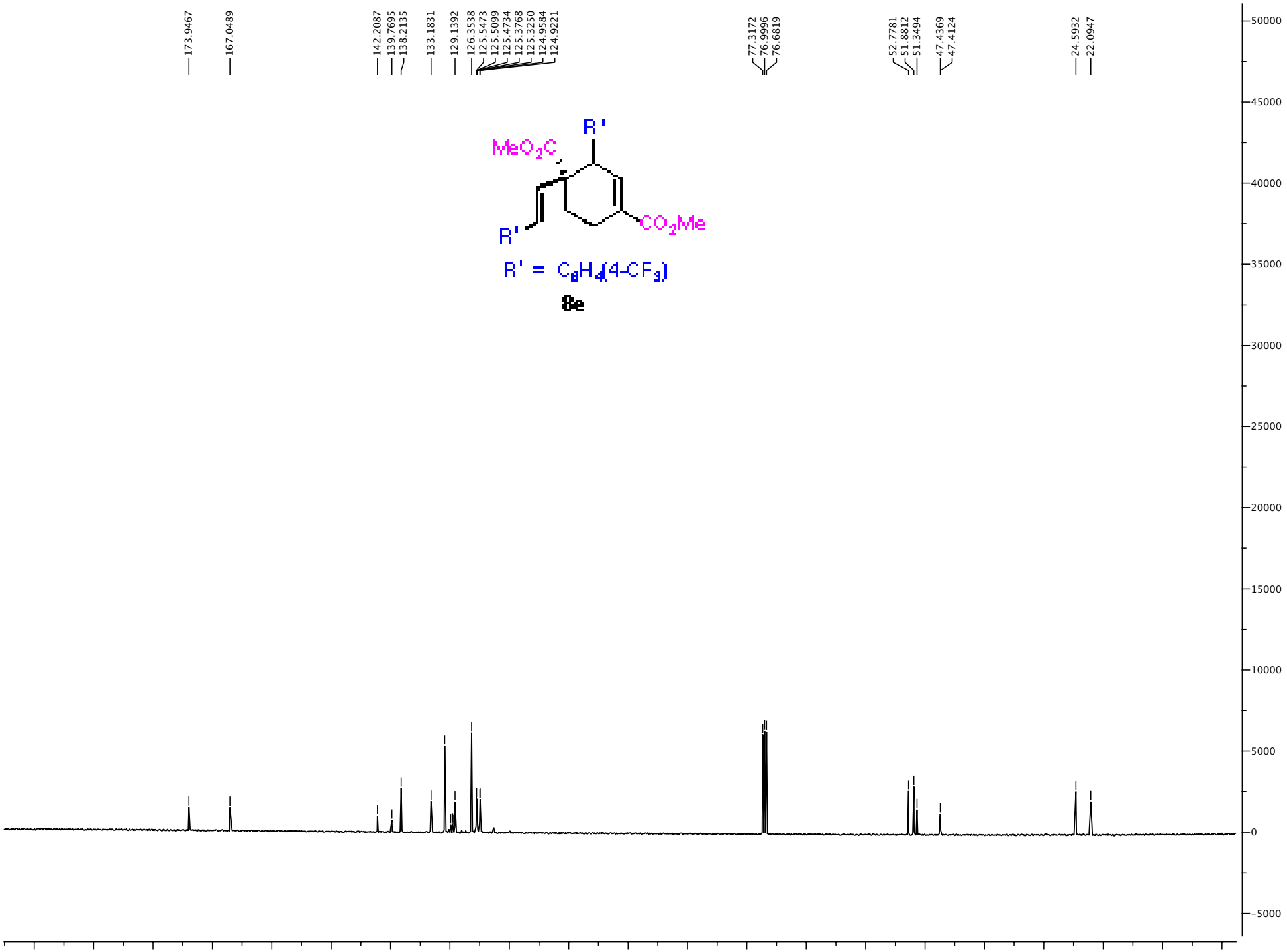
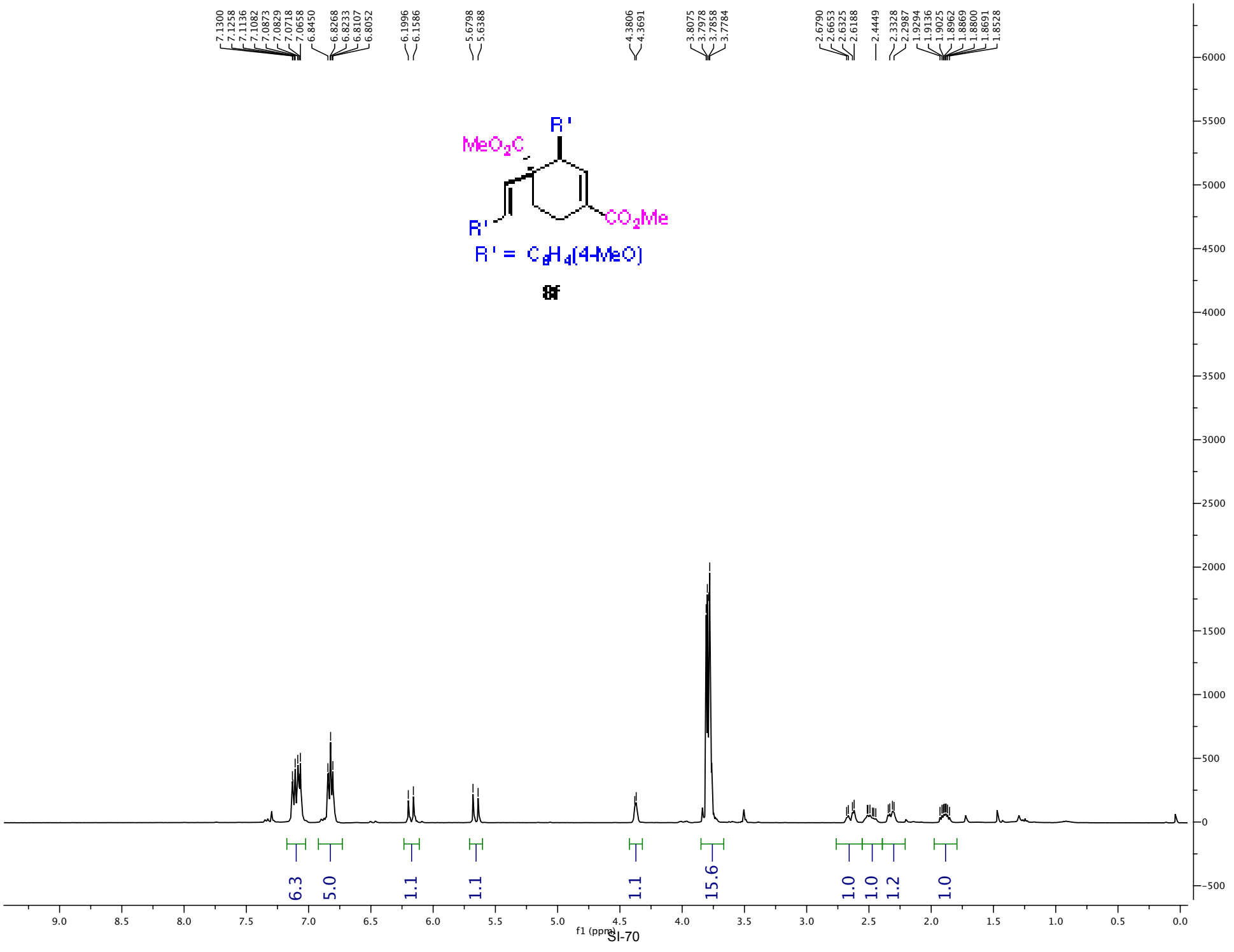
138.6556
138.5662
137.1168
132.4270
131.4506
130.7542
129.1353
128.4063
127.8282
127.3118
127.0572
126.1569
81.2710
80.2613
77.3173
76.9996
76.6819
51.6293
47.7169
47.6841
28.1247
27.8841
24.8061
22.2246
Ph
tBuO2C
Ph
CO2tBu
8c
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.3127
7.3045
7.2920
7.2837
7.2425
7.2023
7.1974
7.1759
7.1709
6.9562
6.9516
6.9389
6.9348
6.9184
6.9132
6.1128
6.0719
5.7550
5.7141
4.3511
4.3387
3.7480
3.7340
2.6566
2.6423
2.6092
2.5952
2.4385
2.4124
2.3186
2.2693
1.8164
1.8005
1.7900
1.7821
1.7740
1.7662
1.7558
1.7396
R'
MeO2C
CO2Me
R'
R' = C6H3(3,4-diCl)
8d
2.3
2.2
3.3
1.0
1.0
1.0
6.7
1.0
1.0
1.0
1.0
f1 (ppm)


173.7127
166.9230
138.3261
137.8031
136.3714
132.5055
130.4475
128.0742
125.2485
77.3175
76.9998
76.6822
52.7556
51.8739
51.1607
46.7355
24.2779
22.0140
MeO2C
R'
CO2Me
R'
R' = C6H3(3,4-diCl)
8d
f1 (ppm)


7.5478
7.5272
7.5175
7.4967
7.2500
7.1953
7.0319
7.0277
7.0242
7.0189
6.2605
6.2194
5.8508
5.8098
4.5059
4.4943
3.7864
3.7812
3.7488
2.7150
2.7011
2.6678
2.6542
2.5002
2.3735
2.3394
1.9338
1.9180
1.9077
1.8996
1.8916
1.8836
1.8734
1.8571
R'
MeO2C
CO2Me
R'
R' = C6H4(4-CF3)
8e
4.4
5.0
1.1
1.0
1.0
1.0
6.7
1.0
1.0
1.0
1.0
f1 (ppm)


173.9467
167.0489
142.2087
139.7695
138.2135
133.1831
129.1392
126.3538
125.5473
125.5099
125.4734
125.3768
125.3250
124.9584
124.9221
77.3172
76.9996
76.6819
52.7781
51.8812
51.3494
47.4369
47.4124
24.5932
22.0947
R'
MeO2C
CO2Me
R'
R' = C6H4(4-CF3)
8e
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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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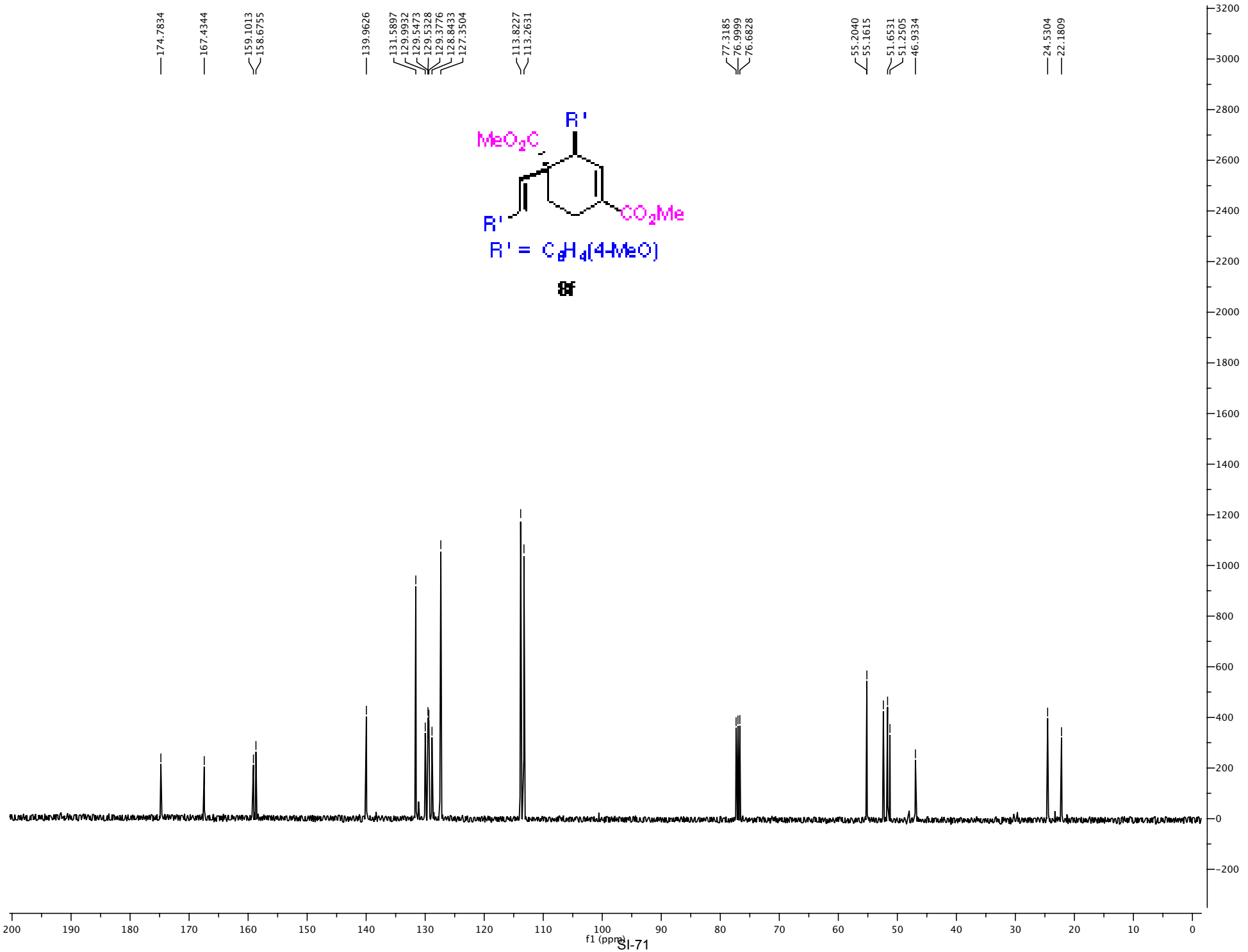
7.1258
7.1136
7.1082
7.0873
7.0829
7.0718
7.0658
6.8450
6.8268
6.8233
6.8107
6.8052
6.1996
6.1586
5.6798
5.6388
4.3806
4.3691
3.8075
3.7978
3.7858
3.7784
2.6790
2.6653
2.6325
2.6188
2.4449
2.3328
2.2987
1.9294
1.9136
1.9025
1.8962
1.8869
1.8800
1.8691
1.8528
R'
MeO2C
CO2Me
R'
R' = C6H4(4-MeO)
8f
6.3
5.0
1.1
1.1
1.1
15.6
1.0
1.0
1.2
1.0
f1 (ppm)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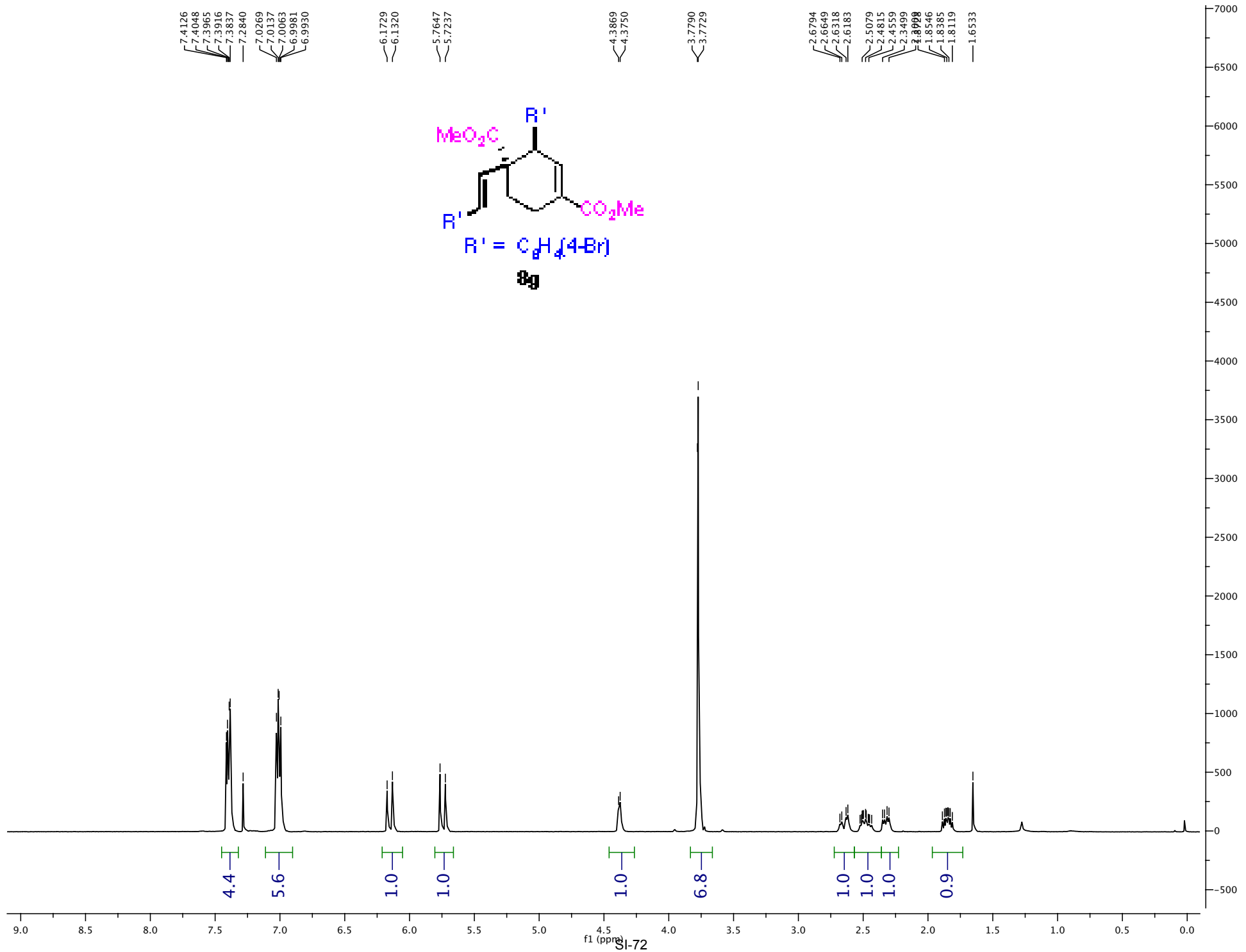
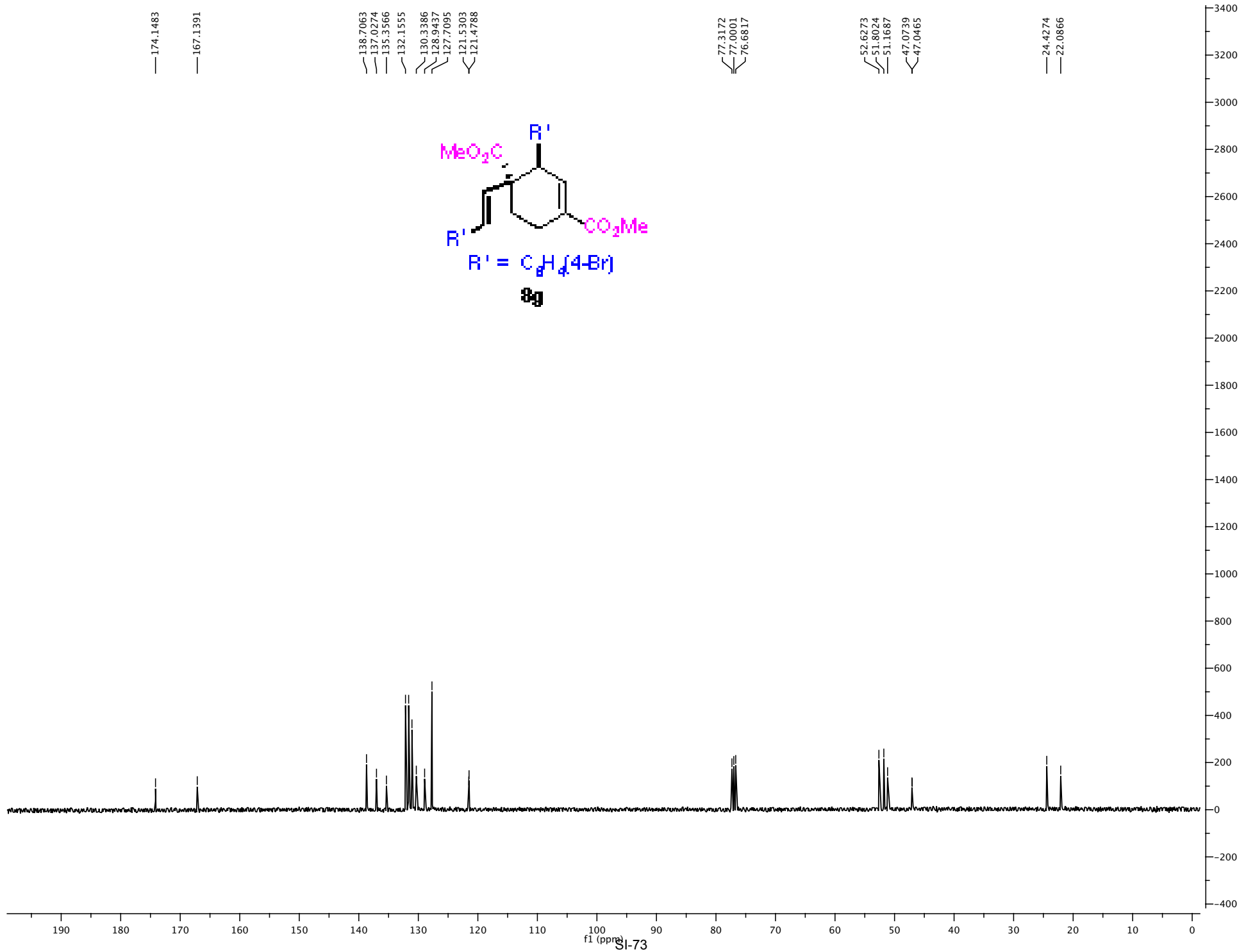
167.4344
159.1013
158.6755
139.9626
131.5897
129.9932
129.5473
129.5328
129.3776
128.8433
127.3504
113.8227
113.2631
77.3185
76.9999
76.6828
55.2040
55.1615
51.6531
51.2505
46.9334
24.5304
22.1809
MeO2C
R'
R'
CO2Me
R' = C6H4(4-MeO)
8f
f1 (ppm)


7.4126
7.4048
7.3965
7.3916
7.3837
7.2840
7.0269
7.0137
7.0063
6.9981
6.9930
6.1729
6.1320
5.7647
5.7237
4.3869
4.3750
3.7790
3.7729
2.6794
2.6649
2.6318
2.6183
2.5079
2.4815
2.4559
2.3499
1.8546
1.8385
1.8119
1.6533
R'
MeO2C
CO2Me
R'
R' = C6H4(4-Br)
3g
4.4
5.6
1.0
1.0
1.0
6.8
1.0
1.0
1.0
0.9
f1 (ppm)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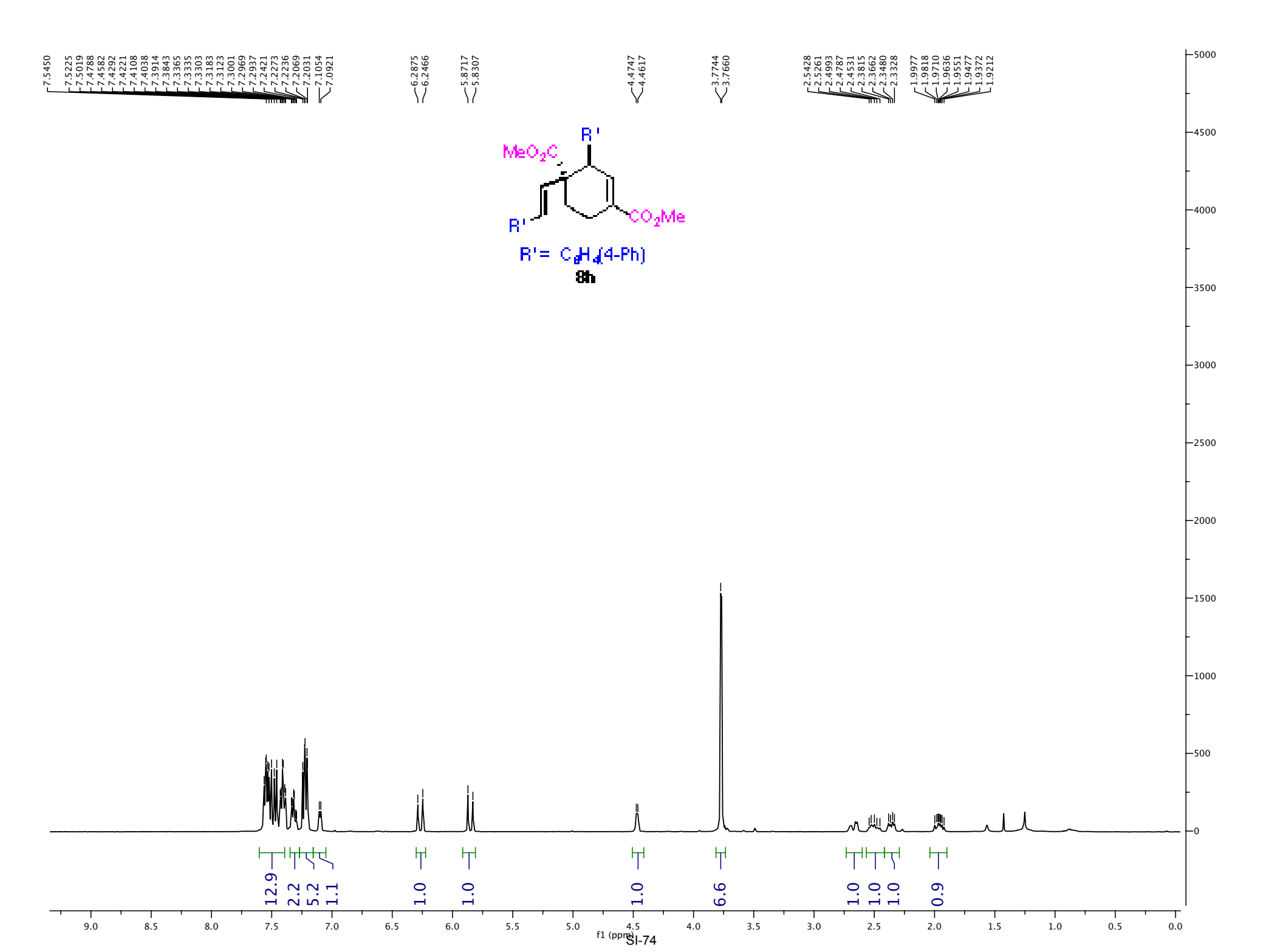
167.1391
138.7063
137.0274
135.3566
132.1555
130.3386
128.9437
127.7095
121.5303
121.4788
77.3172
77.0001
76.6817
52.6273
51.8024
51.1687
47.0739
47.0465
24.4274
22.0866
R'
MeO2C
CO2Me
R'
R' = C6H4(4-Br)
8g
f1 (ppm)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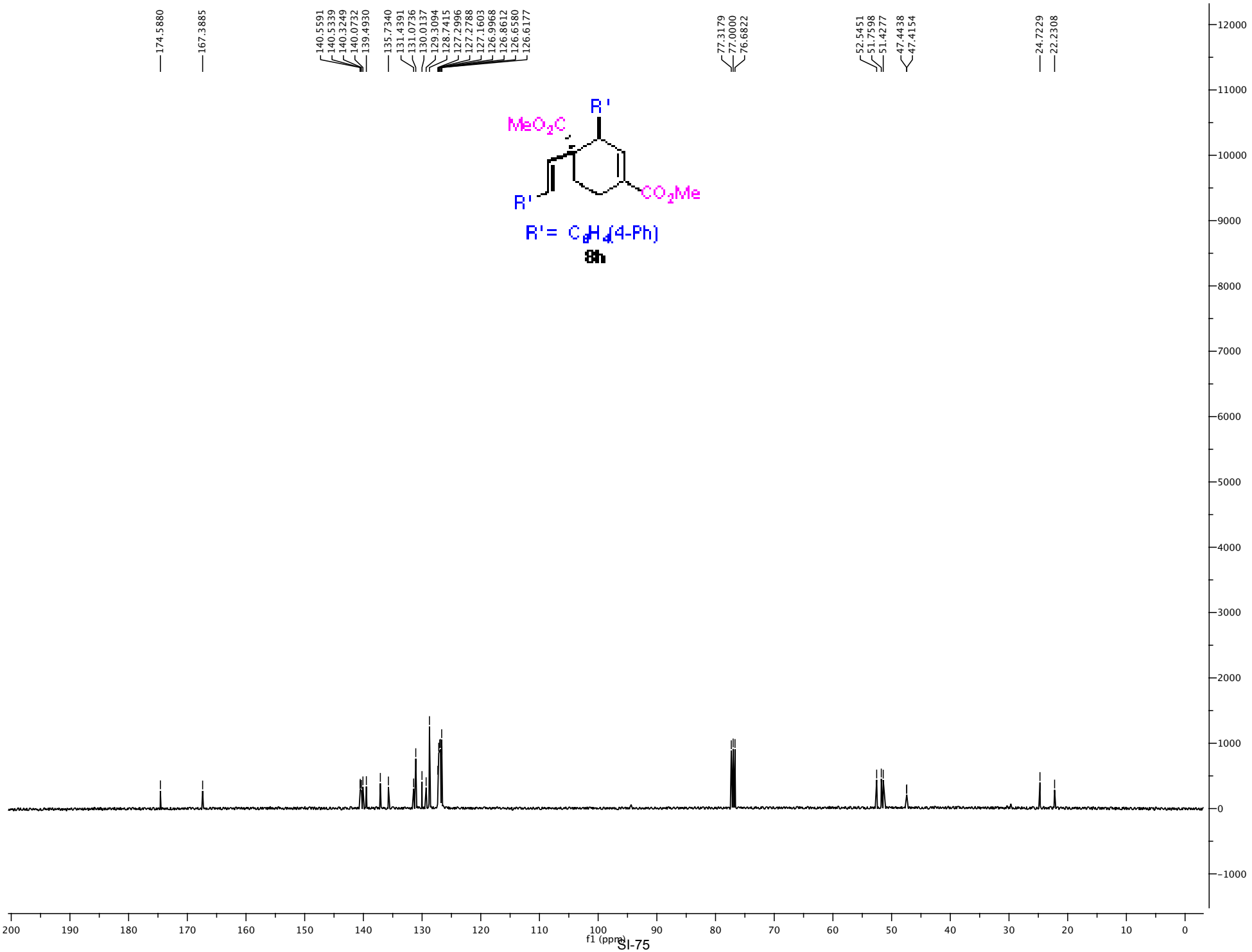
7.5019
7.4788
7.4582
7.4292
7.4221
7.4108
7.4038
7.3914
7.3843
7.3365
7.3335
7.3303
7.3183
7.3123
7.3001
7.2969
7.2937
7.2421
7.2273
7.2236
7.2069
7.2031
7.1054
7.0921
6.2875
6.2466
5.8717
5.8307
4.4747
4.4617
3.7744
3.7660
2.5428
2.5261
2.4993
2.4787
2.4531
2.3815
2.3662
2.3480
2.3328
1.9977
1.9818
1.9710
1.9636
1.9551
1.9477
1.9372
1.9212
R'
MeO2C
CO2Me
R'
R' = C6H4(4-Ph)
8h
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
12.9
2.2
5.2
1.1
1.0
1.0
1.0
6.6
1.0
1.0
1.0
0.9
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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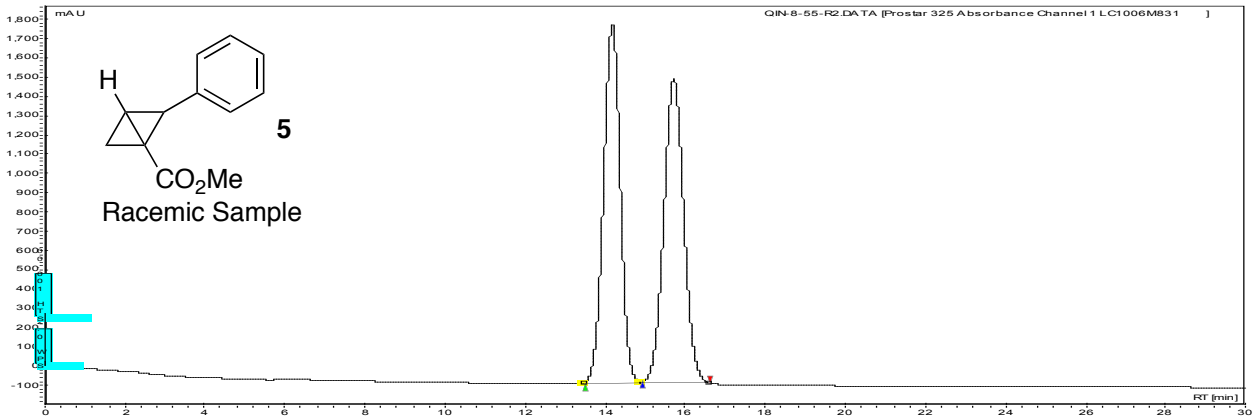
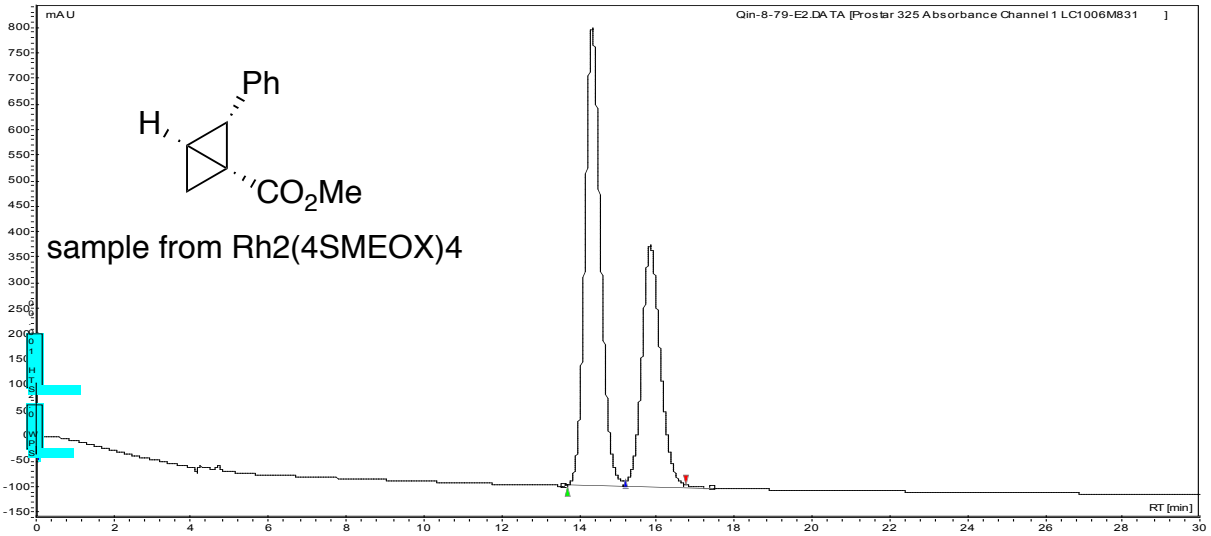
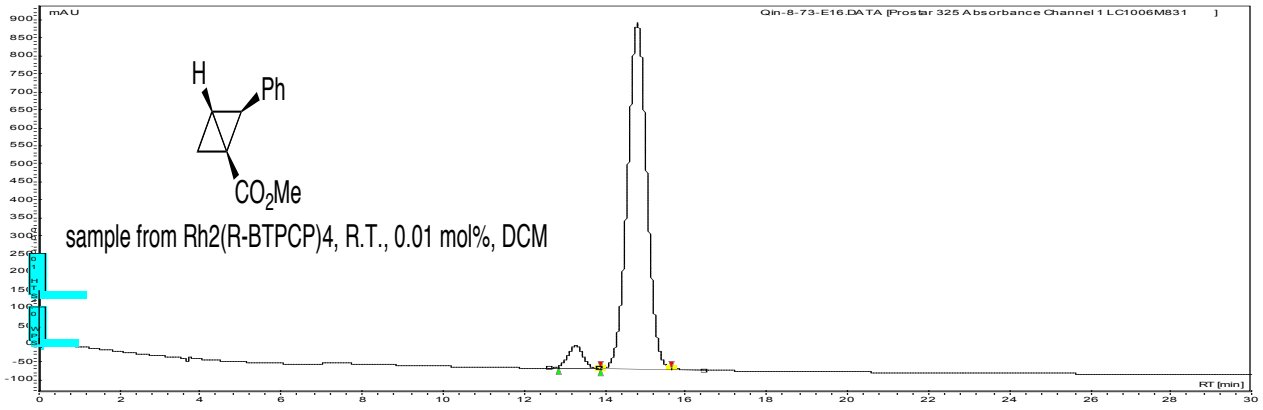
140.5591
140.5339
140.3249
140.0732
139.4930
135.7340
131.4391
131.0736
130.0137
129.3094
128.7415
127.2996
127.2788
127.1603
126.9968
126.8612
126.6580
126.6177
77.3179
77.0000
76.6822
52.5451
51.7598
51.4277
47.4438
47.4154
24.7229
22.2308
R'
MeO2C
CO2Me
R'
R'= C6H4(4-Ph)
8h
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

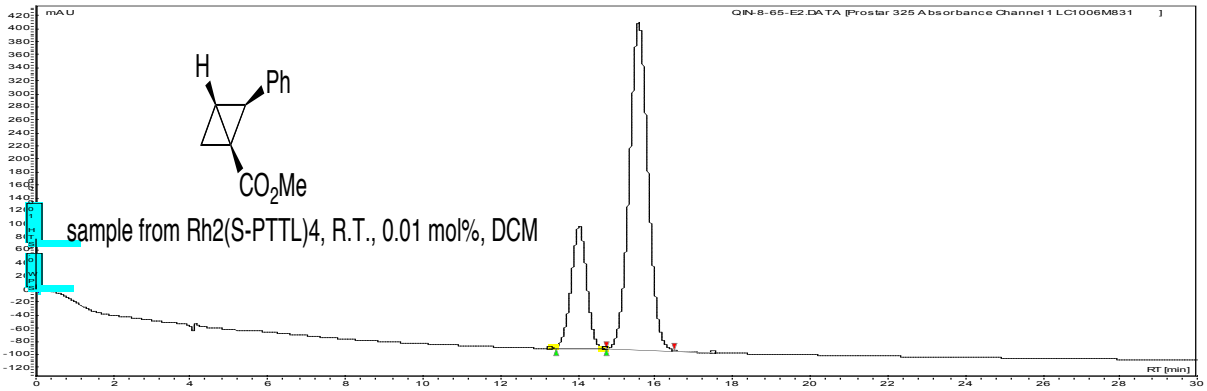




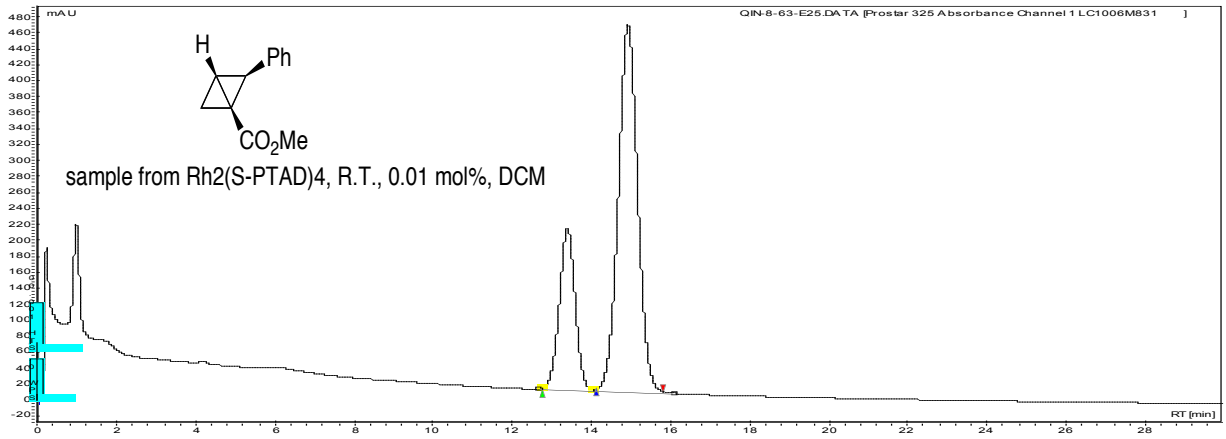
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.33	61.58	896.6	423.4	61.585
2	UNKNOWN	15.83	38.42	473.9	264.1	38.415
Total			100.00	1370.6	687.5	100.000



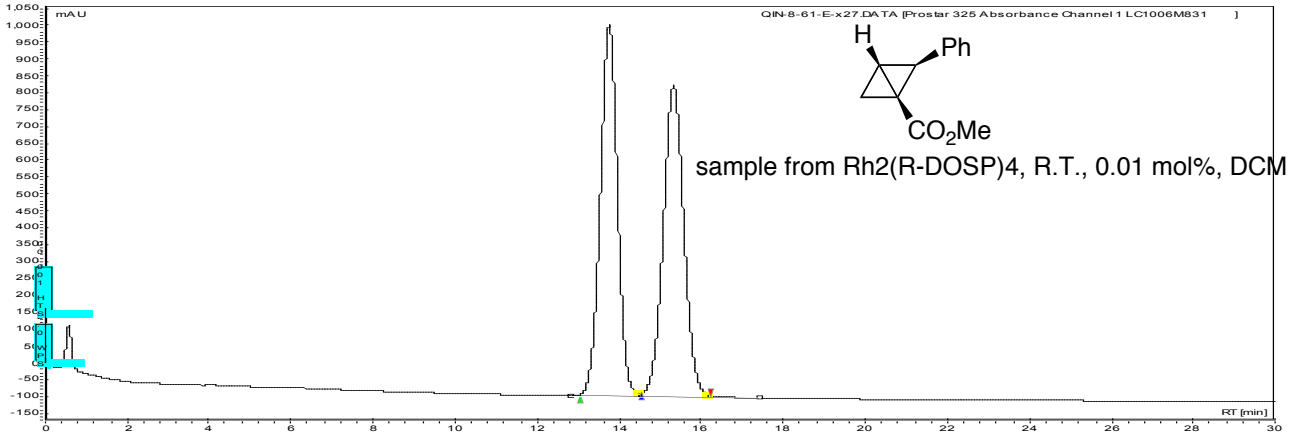
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.28	4.91	63.4	27.7	4.905
2	UNKNOWN	14.80	95.09	961.2	537.2	95.095
Total			100.00	1024.6	564.9	100.000



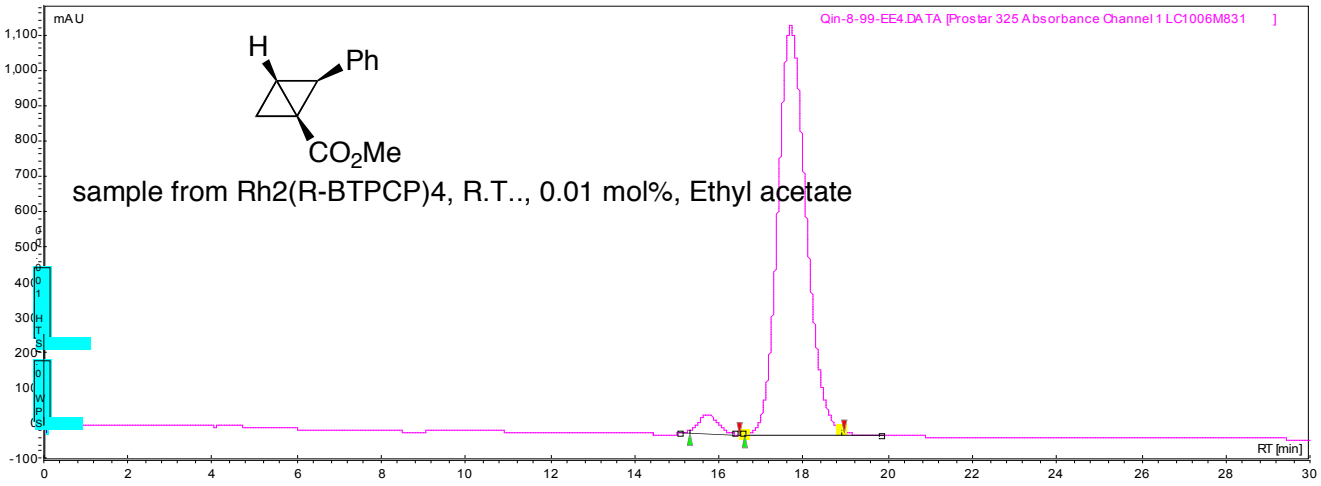
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.03	23.82	188.5	87.9	23.821
2	UNKNOWN	15.57	76.18	502.4	281.0	76.179
Total			100.00	690.9	368.9	100.00



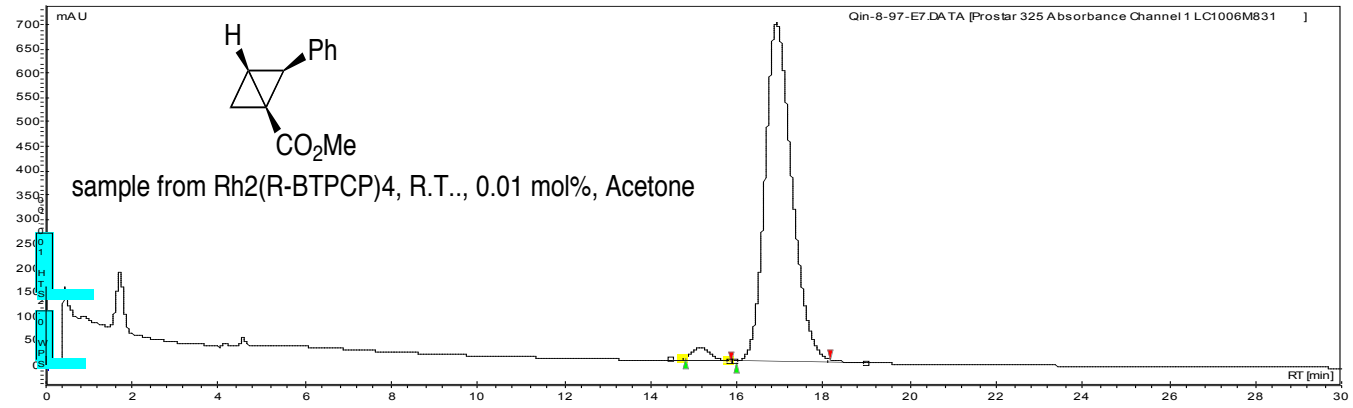
#	Name	Time [Min]	Quantity [% Area] [%]	Height [mAU]	Area [mAU.Min]	Area %
1	UNKNOWN	13.39	26.48	202.8	94.3	26.482
2	UNKNOWN	14.92	73.52	459.7	261.8	73.518
Total			100.00	662.5	356.1	100.000



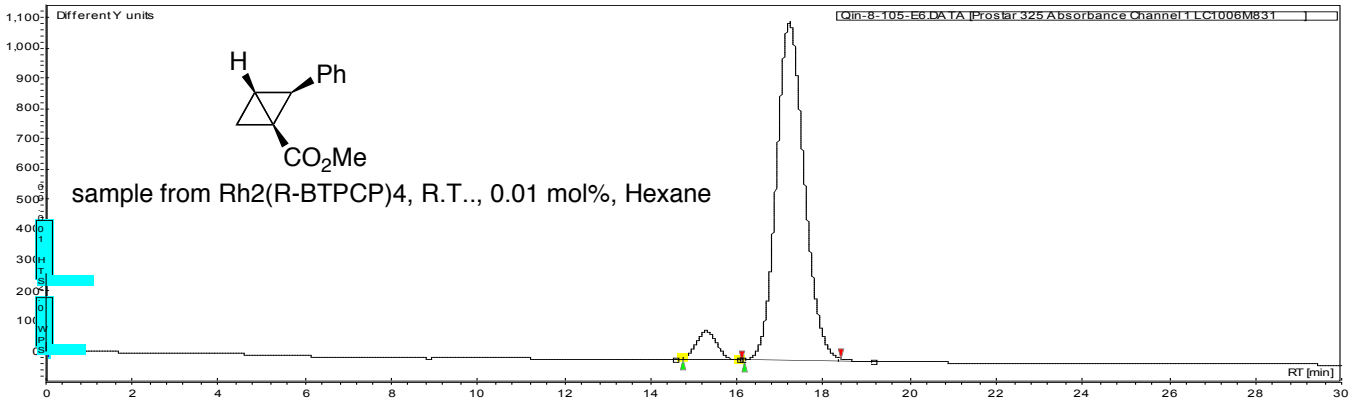
#	Name	Time [Min]	Quantity [% Area] [%]	Height [mAU]	Area [mAU.Min]	Area %
1	UNKNOWN	13.76	49.87	1099.2	536.1	49.867
2	UNKNOWN	15.32	50.13	922.5	538.9	50.133
Total			100.00	2021.7	1075.0	100.000



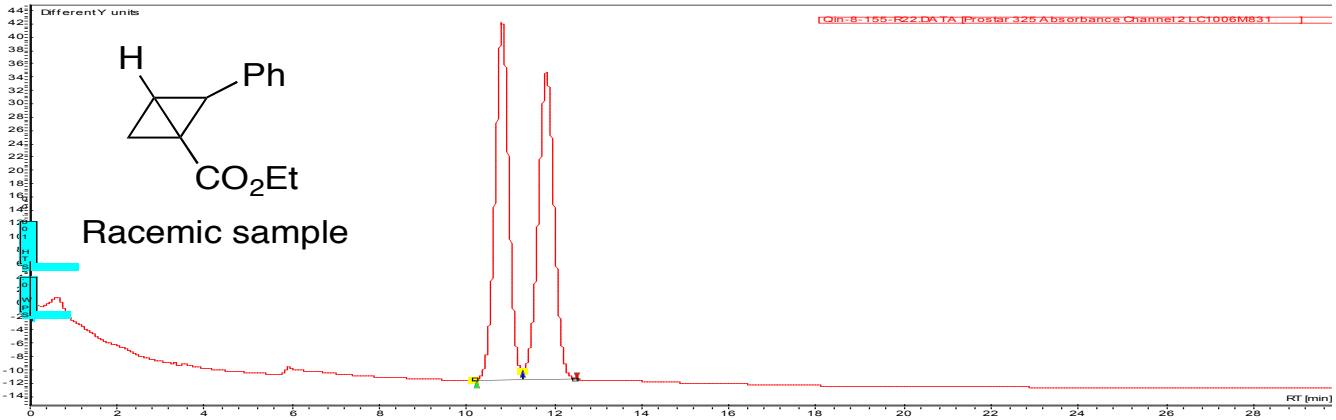
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.74	3.22	54.4	30.1	3.217
2	UNKNOWN	17.69	96.78	1154.2	904.7	96.783
Total			100.00	1208.5	934.8	100.000

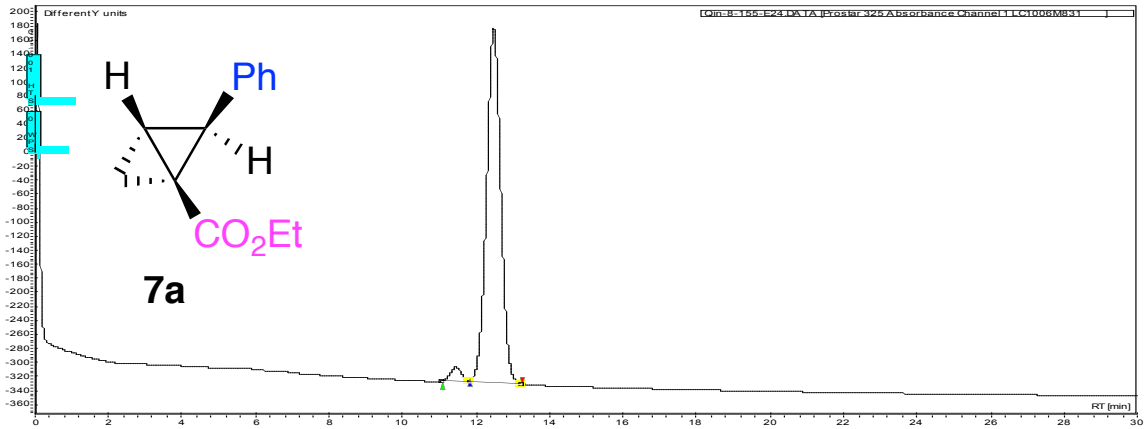


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.15	2.76	27.0	14.4	2.762
2	UNKNOWN	16.91	97.24	694.4	505.2	97.238
Total			100.00	721.5	519.6	100.00

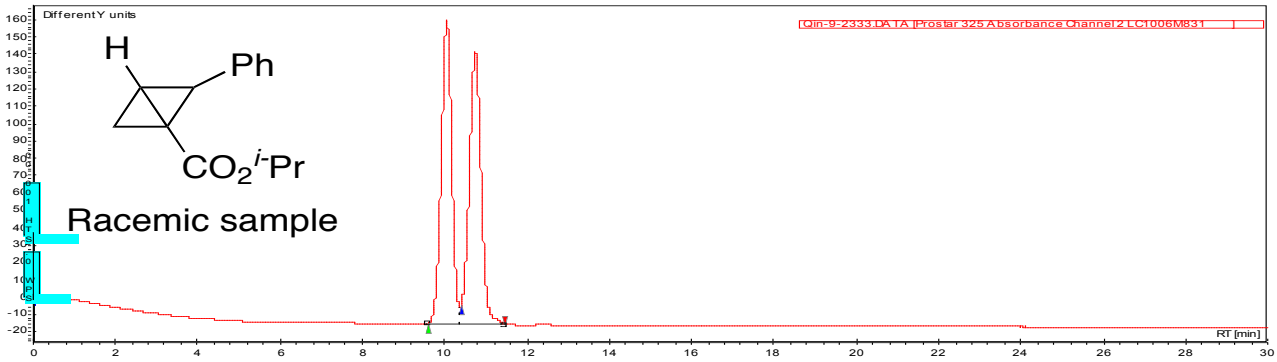


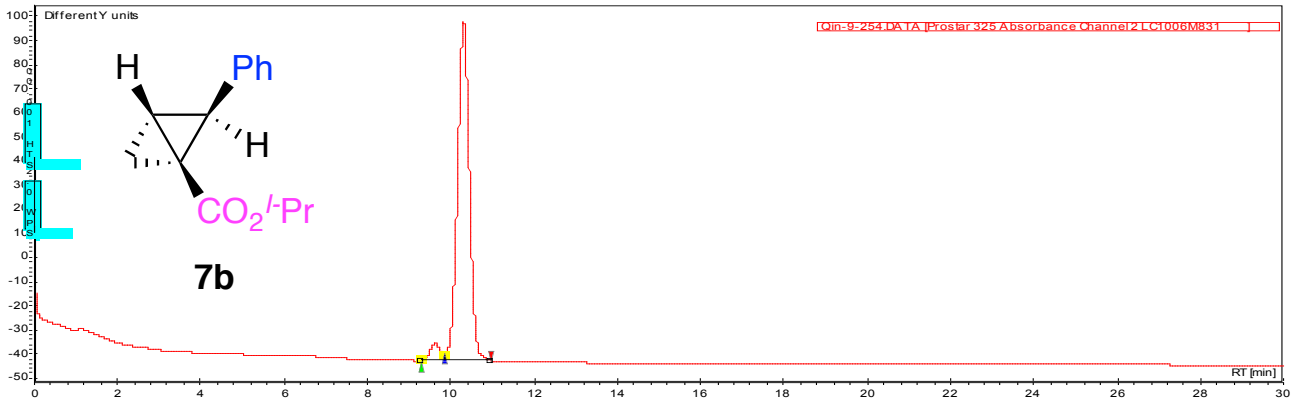
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.29	6.03	96.2	53.7	6.026
2	UNKNOWN	17.21	93.97	1113.5	838.1	93.974
Total			100.00	1209.7	891.8	100.000



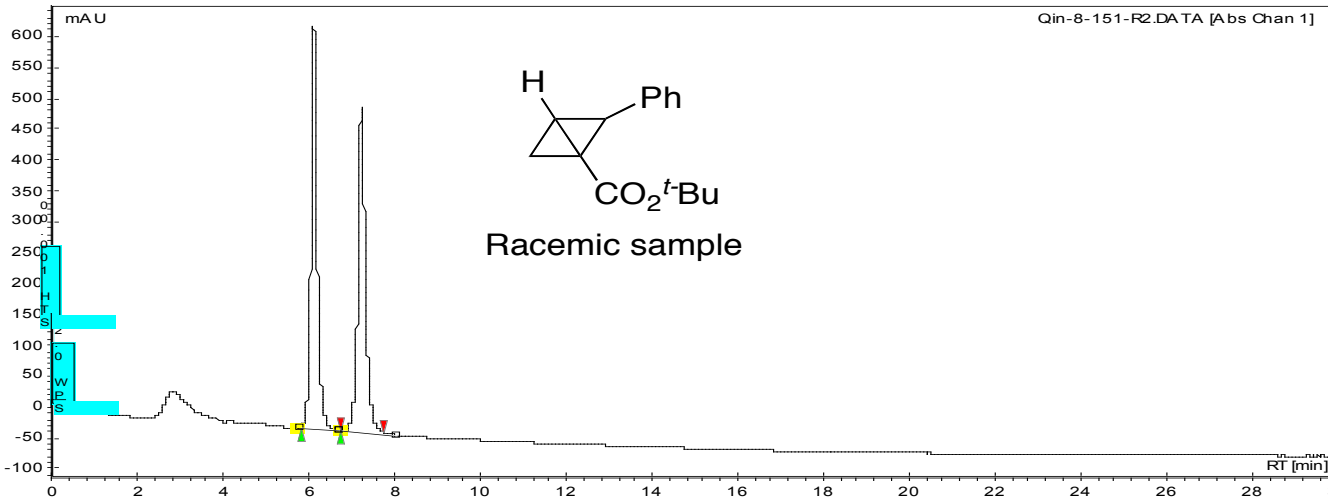


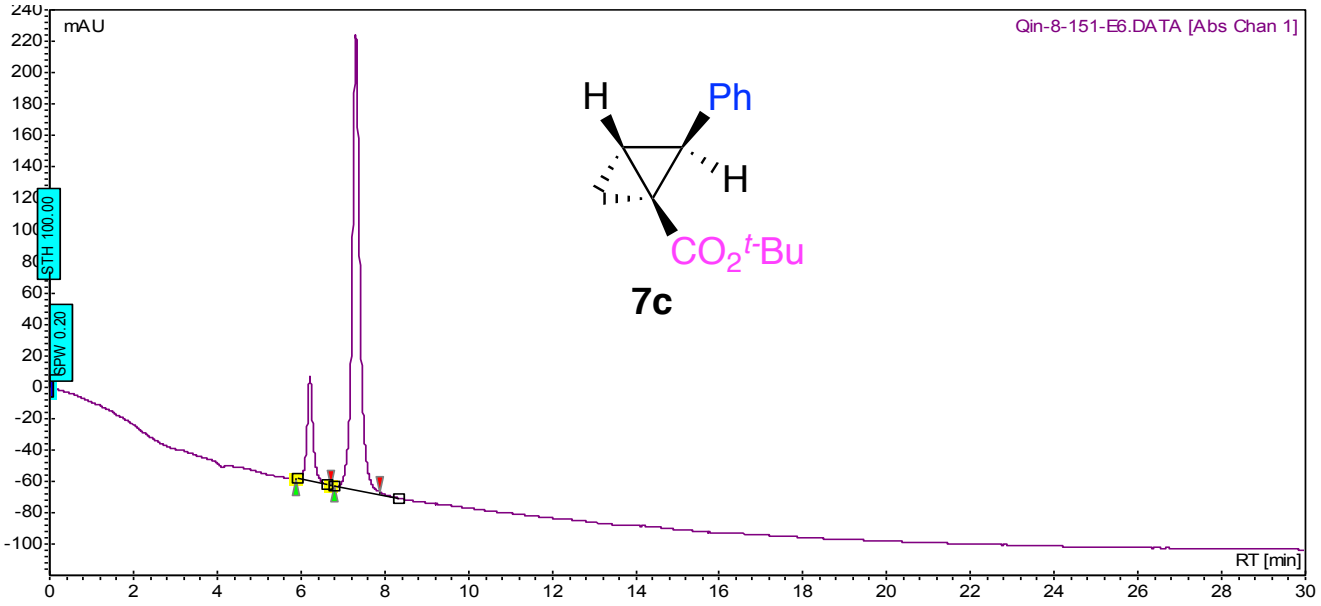
#	Name	Time [Min]	Quantity [% Area] [%]	Height [mAU]		Area [mAU.Min]	Area %
1	UNKNOWN	11.46	3.07	20.4	7.2	3.069	
2	UNKNOWN	12.48	96.93	505.0	227.0	96.931	
Total			100.00	525.4	234.2	100.000	



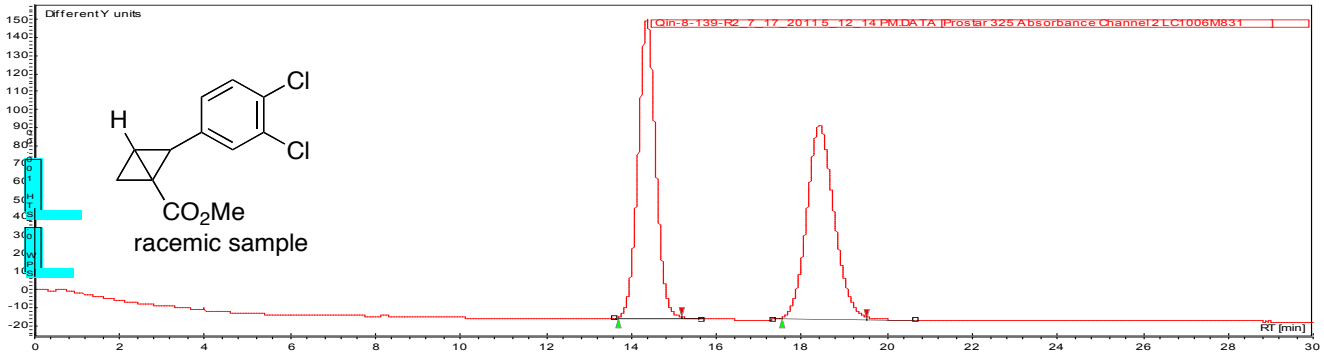


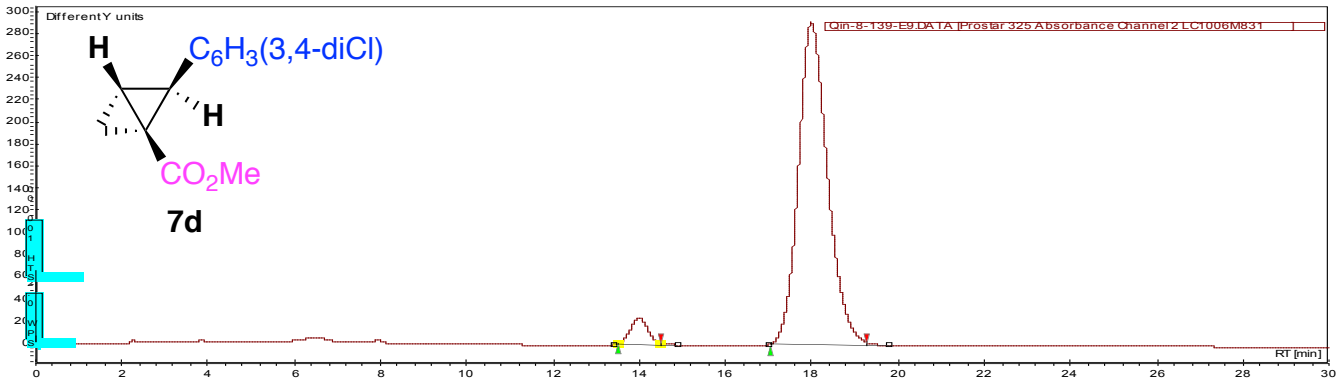
#	Name	Time [Min]	Quantity [% Area] [%]	Height [mAU]		Area [mAU.Min]	Area %
1	UNKNOWN	9.63	4.12	7.2	2.0	4.125	
2	UNKNOWN	10.31	95.88	140.1	46.4	95.875	



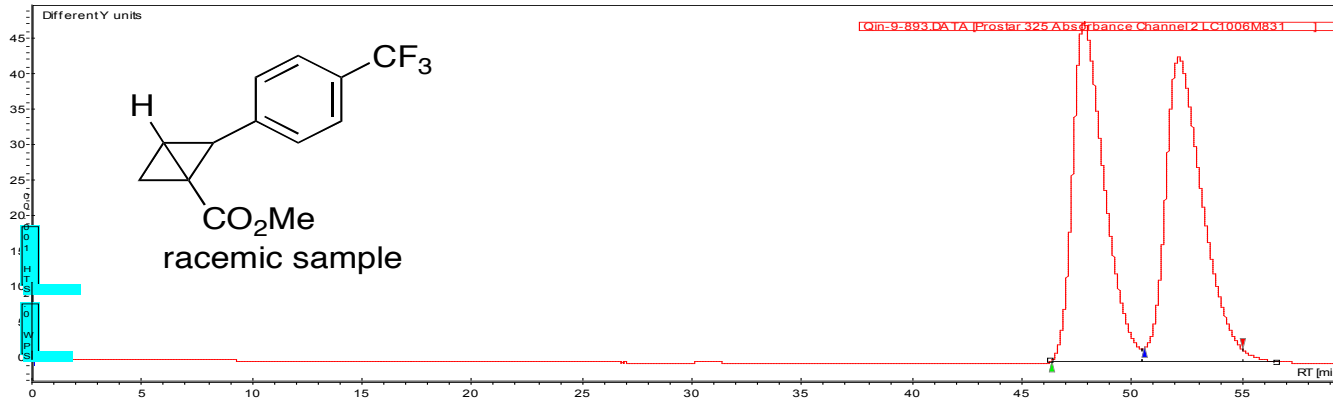


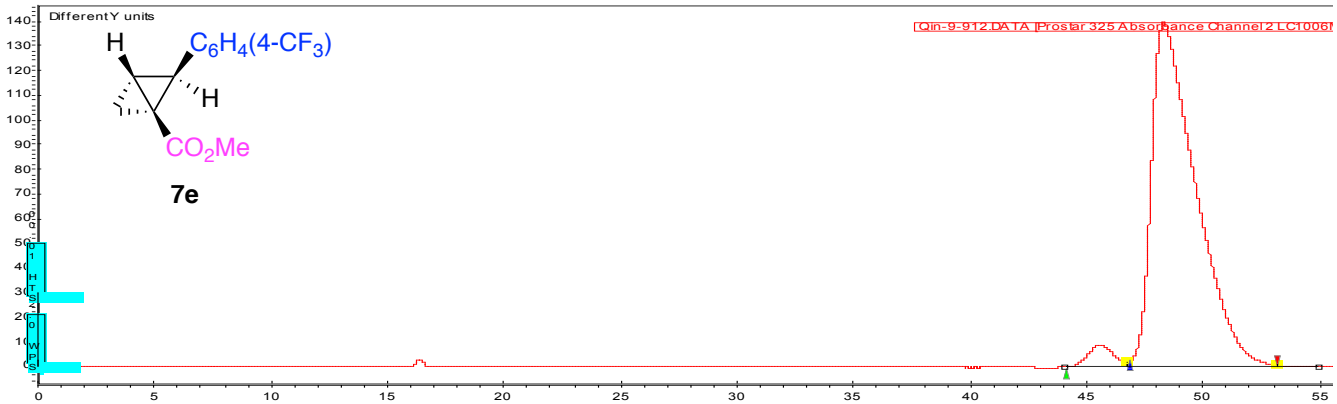
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.21	14.97	66.2	11.0	14.971
2	UNKNOWN	7.31	85.03	289.3	62.2	85.029
Total			100.00	355.5	73.2	100.000



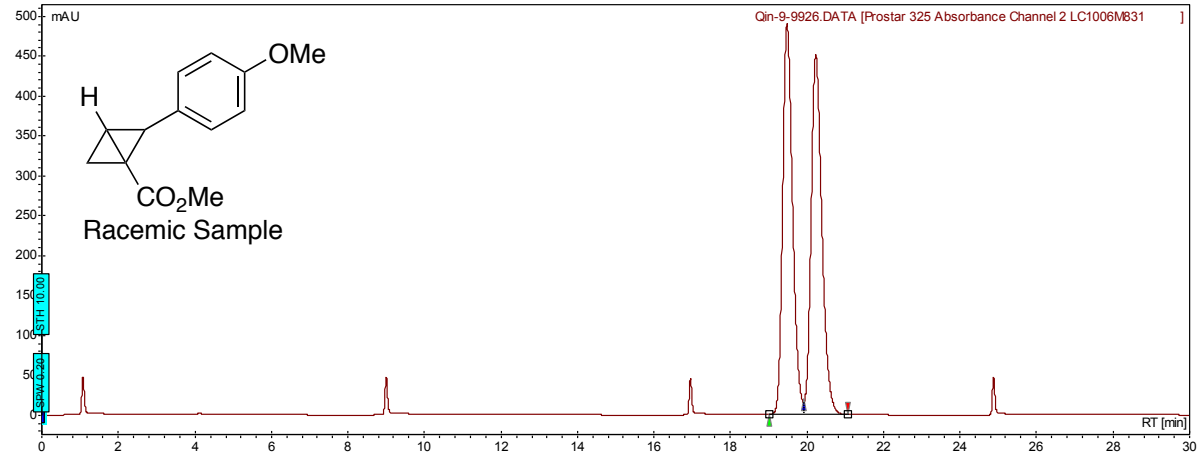


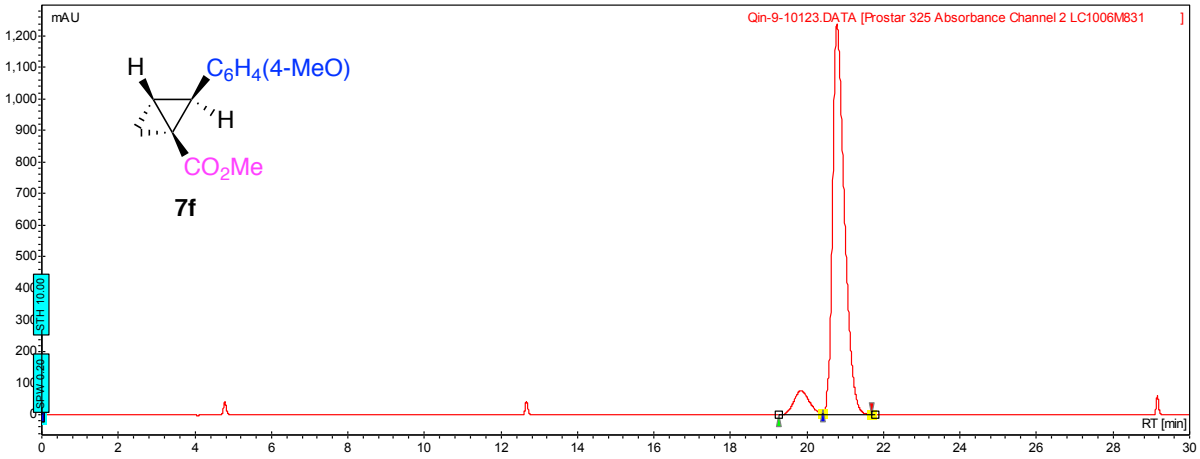
#	Name	Time [Min]	Quantity [% Area] [%]	Height [mAU]	Area [mAU.Min]	Area %
1	UNKNOWN	14.00	4.83	24.6	11.6	4.829
2	UNKNOWN	17.99	95.17	291.2	229.4	95.171
Total		100.00	315.7	241.1	100.000	





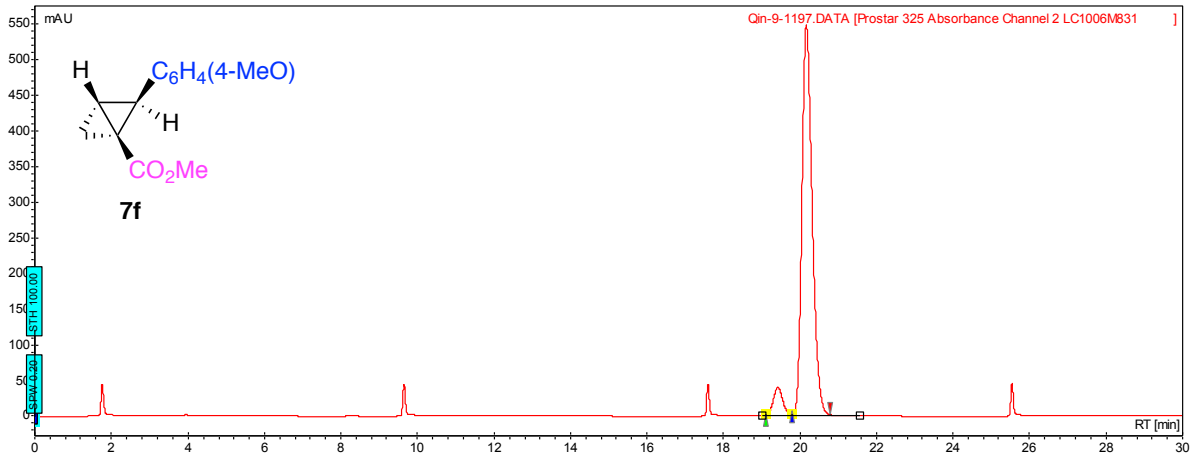
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	45.55	3.62	9.2	11.6	3.618
2	UNKNOWN	48.28	96.38	139.8	308.5	96.382
	Total		100.00	149.0	320.1	100.000



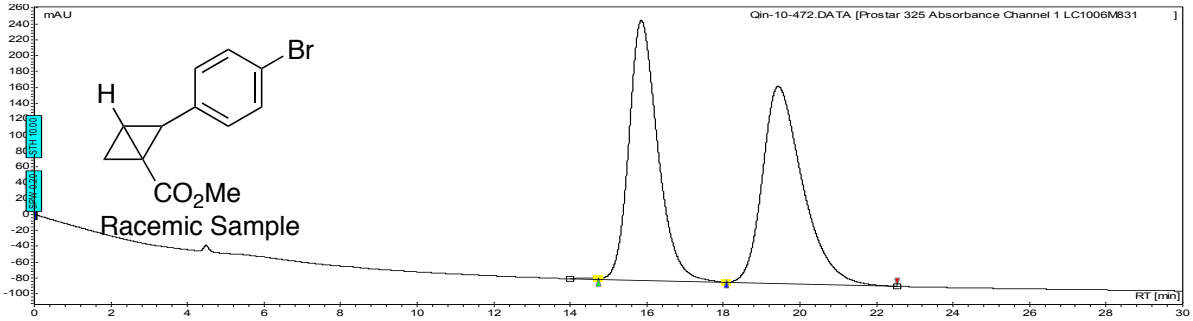


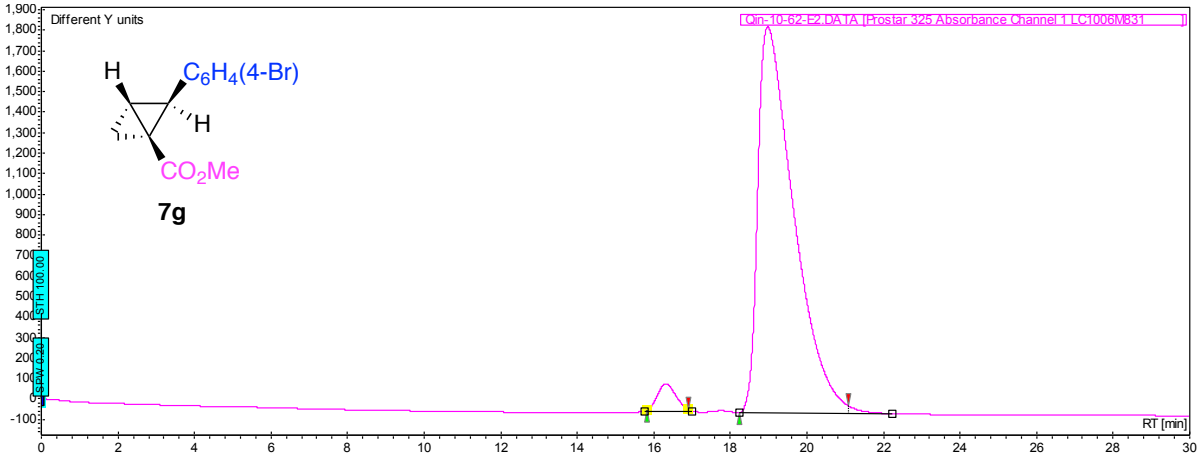
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.84	7.74	76.9	37.1	7.737
2	UNKNOWN	20.78	92.26	1234.6	442.1	92.263
Total			100.00	1311.5	479.1	100.000

When reaction was run at -78 °C, the ee was increased to 88%, as follows:



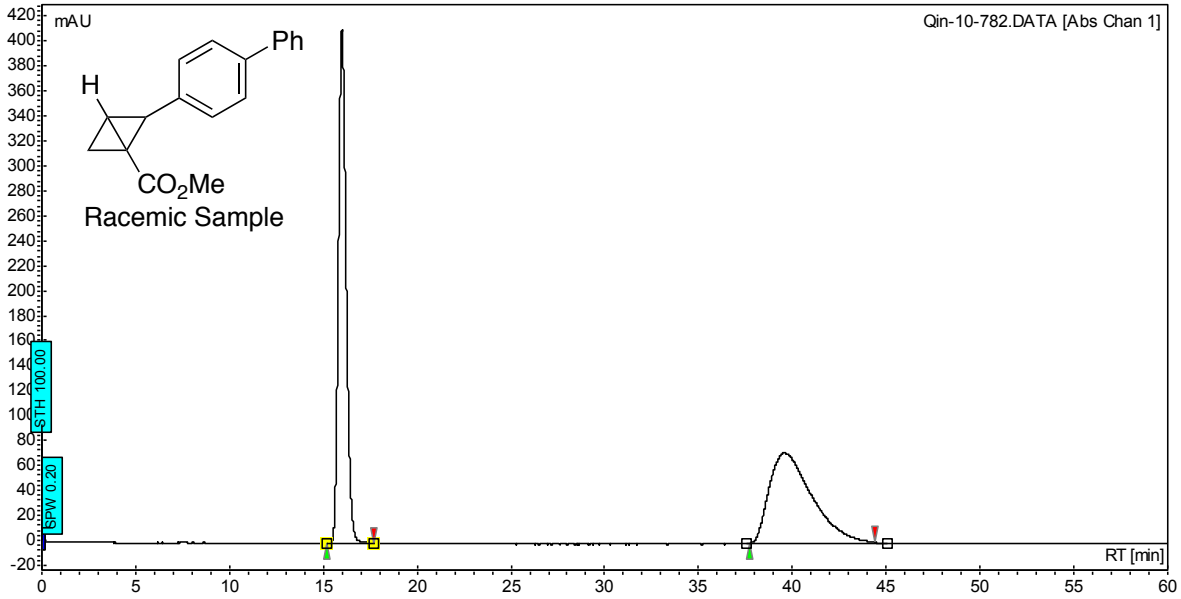
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.42	6.17	39.2	11.1	6.168
2	UNKNOWN	20.17	93.83	546.1	169.1	93.832
Total			100.00	585.3	180.2	100.000

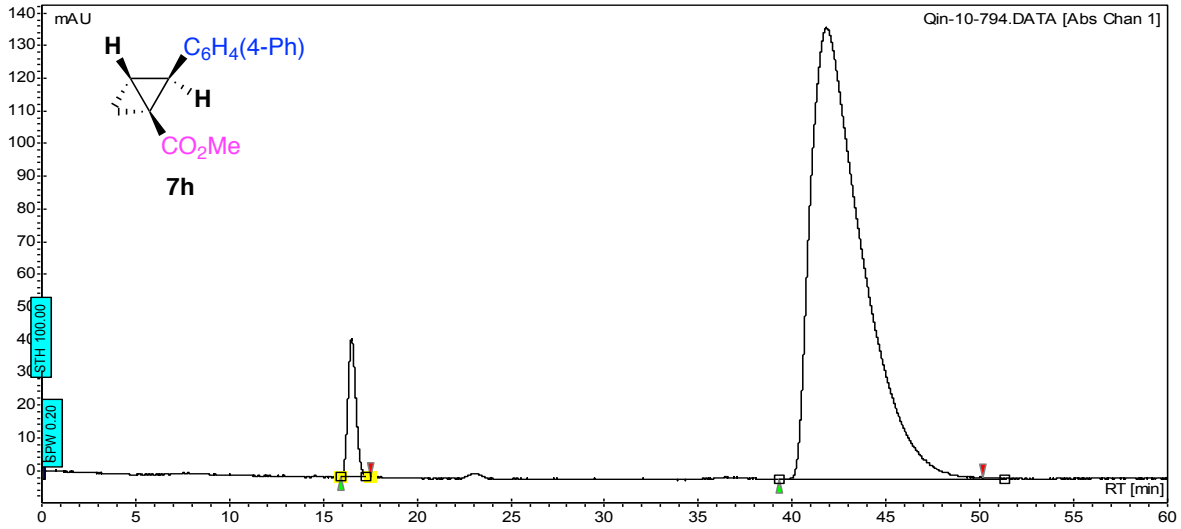




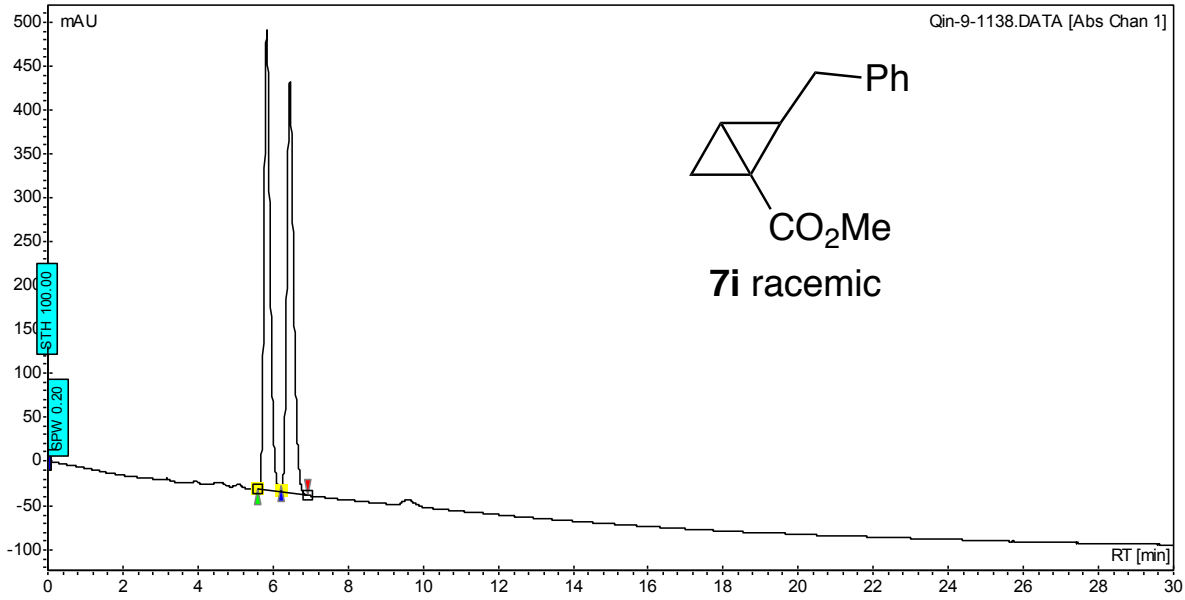
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]

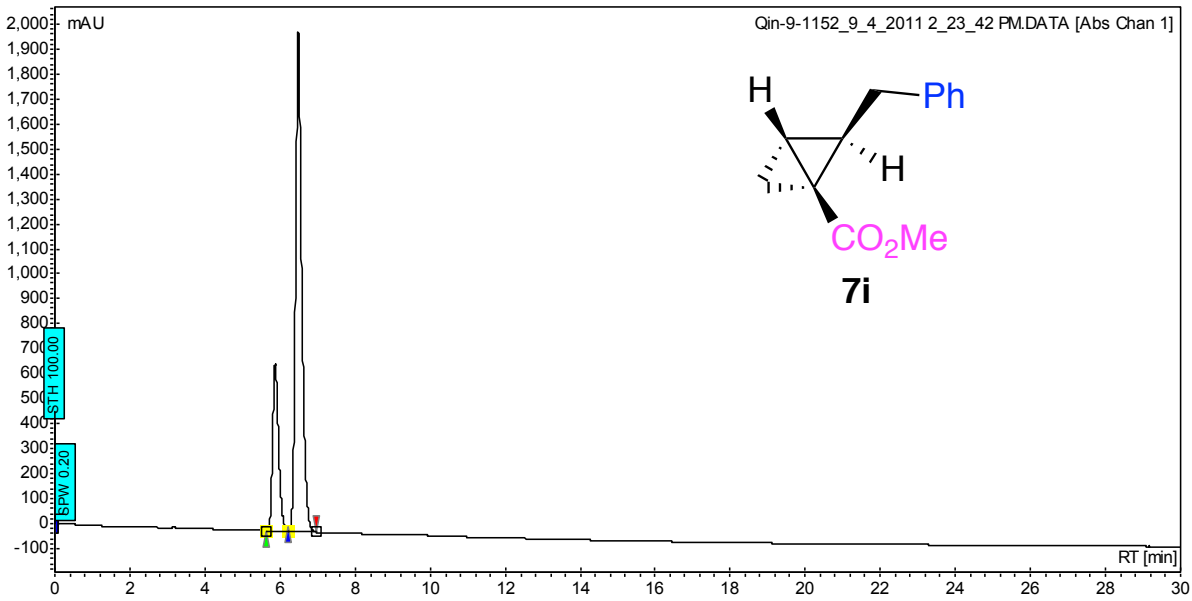
1	UNKNOWN	16.31	3.52	132.6	74.7	3.518
2	UNKNOWN	18.97	96.48	1885.8	2048.6	96.482
Total		100.00	2018.4	2123.3	100.000	





#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.51	4.50	42.0	20.6	4.495
2	UNKNOWN	41.83	95.50	138.2	437.7	95.505
Total			100.00	180.3	458.3	100.000





#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.87	24.60	670.8	123.5	24.603
2	UNKNOWN	6.49	75.40	2001.2	378.6	75.397
Total			100.00	2672.0	502.2	100.000

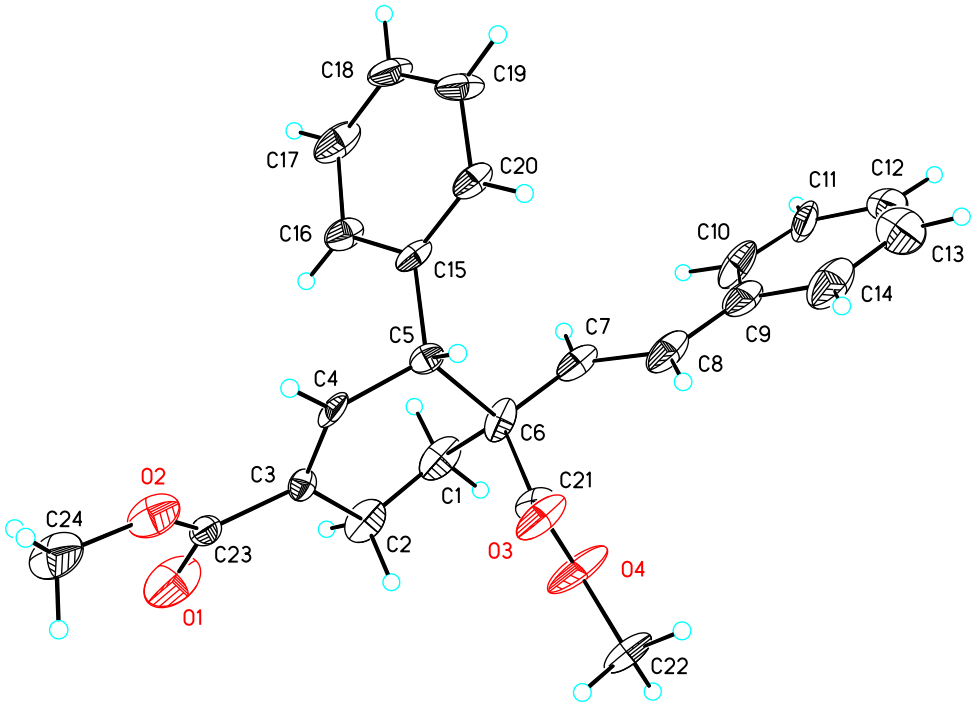


Table 1. Crystal data and structure refinement for QIN_4_133.

Identification code	qin_4_133	
Empirical formula	C24 H24 O4	
Formula weight	376.43	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2295(3) Å	⟨= 86.591(2)°.
	b = 10.3951(4) Å	®= 69.851(2)°.
	c = 11.3783(5) Å	© = 79.622(2)°.
Volume	1008.07(7) Å^3	
Z	2	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.672 mm^{-1}	
F(000)	400	

Crystal size	0.45 x 0.26 x 0.13 mm^3
Theta range for data collection	4.14 to 69.41°.
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=13
Reflections collected	6798
Independent reflections	3018 [R(int) = 0.0115]
Completeness to theta = 69.41°	79.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9177 and 0.7518
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3018 / 0 / 253
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.1114, wR2 = 0.2482
R indices (all data)	R1 = 0.1686, wR2 = 0.3947
Largest diff. peak and hole	1.170 and -0.883 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for QIN_4_133. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	11428(8)	252(7)	861(6)	25(2)
C(2)	12495(8)	1272(7)	566(6)	27(2)
C(3)	11756(7)	2460(6)	1385(6)	19(1)
C(4)	10483(7)	2491(6)	2420(6)	20(1)
C(5)	9653(7)	1358(6)	2889(6)	17(1)
C(6)	10670(8)	21(6)	2289(6)	23(2)
C(7)	9745(8)	-1050(7)	2489(7)	28(2)
C(8)	9519(8)	-1906(7)	3426(6)	29(2)
C(9)	8652(8)	-2994(7)	3598(7)	29(2)
C(10)	8123(9)	-3388(7)	2709(8)	36(2)
C(11)	7301(9)	-4426(8)	2899(9)	40(2)
C(12)	6996(9)	-5077(7)	4056(9)	43(2)
C(13)	7490(12)	-4710(9)	4909(8)	50(2)
C(14)	8358(10)	-3679(9)	4744(8)	42(2)
C(15)	8027(7)	1591(6)	2818(6)	20(1)
C(16)	7677(8)	2218(7)	1774(6)	25(1)
C(17)	6203(9)	2456(8)	1744(7)	33(2)
C(18)	4974(8)	2027(8)	2695(7)	33(2)
C(19)	5297(8)	1407(7)	3741(7)	28(2)
C(20)	6786(8)	1180(6)	3758(6)	24(1)
C(21)	11948(7)	-351(6)	2874(6)	19(1)
C(22)	14317(8)	-1792(8)	2684(7)	33(2)
C(23)	12501(7)	3647(7)	979(6)	23(1)
C(24)	12695(11)	5733(8)	1527(9)	46(2)
O(1)	11963(6)	57(5)	3830(4)	32(1)
O(2)	13094(6)	-1287(5)	2175(5)	34(1)
O(3)	13446(7)	3754(6)	-46(5)	46(2)
O(4)	12059(6)	4556(5)	1855(5)	34(1)

Table 3. Bond lengths [Å] and angles [°] for QIN_4_133.

C(1)-C(2)	1.520(10)
C(1)-C(6)	1.555(9)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.502(9)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.344(9)
C(3)-C(23)	1.492(9)
C(4)-C(5)	1.492(8)
C(4)-H(4A)	0.9500
C(5)-C(15)	1.506(8)
C(5)-C(6)	1.575(8)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.483(10)
C(6)-C(21)	1.526(8)
C(7)-C(8)	1.331(11)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.467(11)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.374(11)
C(9)-C(14)	1.414(12)
C(10)-C(11)	1.393(12)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.406(13)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.307(14)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.417(13)
C(13)-H(13A)	0.9500
C(14)-H(14A)	0.9500
C(15)-C(20)	1.385(10)
C(15)-C(16)	1.427(9)
C(16)-C(17)	1.350(10)

C(16)-H(16A)	0.9500
C(17)-C(18)	1.391(11)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.416(10)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.358(9)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500
C(21)-O(1)	1.196(8)
C(21)-O(2)	1.356(7)
C(22)-O(2)	1.444(8)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(3)	1.205(9)
C(23)-O(4)	1.321(8)
C(24)-O(4)	1.426(10)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800

C(2)-C(1)-C(6)	113.1(5)
C(2)-C(1)-H(1A)	109.0
C(6)-C(1)-H(1A)	109.0
C(2)-C(1)-H(1B)	109.0
C(6)-C(1)-H(1B)	109.0
H(1A)-C(1)-H(1B)	107.8
C(3)-C(2)-C(1)	111.7(5)
C(3)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	107.9
C(4)-C(3)-C(23)	120.5(6)
C(4)-C(3)-C(2)	123.2(6)
C(23)-C(3)-C(2)	116.3(6)

C(3)-C(4)-C(5)	124.2(6)
C(3)-C(4)-H(4A)	117.9
C(5)-C(4)-H(4A)	117.9
C(4)-C(5)-C(15)	112.6(5)
C(4)-C(5)-C(6)	112.6(5)
C(15)-C(5)-C(6)	113.6(5)
C(4)-C(5)-H(5A)	105.7
C(15)-C(5)-H(5A)	105.7
C(6)-C(5)-H(5A)	105.7
C(7)-C(6)-C(21)	109.5(5)
C(7)-C(6)-C(1)	109.5(5)
C(21)-C(6)-C(1)	109.7(5)
C(7)-C(6)-C(5)	113.1(5)
C(21)-C(6)-C(5)	107.6(5)
C(1)-C(6)-C(5)	107.4(5)
C(8)-C(7)-C(6)	126.6(6)
C(8)-C(7)-H(7A)	116.7
C(6)-C(7)-H(7A)	116.7
C(7)-C(8)-C(9)	126.5(7)
C(7)-C(8)-H(8A)	116.7
C(9)-C(8)-H(8A)	116.7
C(10)-C(9)-C(14)	118.5(8)
C(10)-C(9)-C(8)	123.9(7)
C(14)-C(9)-C(8)	117.6(7)
C(9)-C(10)-C(11)	122.7(8)
C(9)-C(10)-H(10A)	118.7
C(11)-C(10)-H(10A)	118.7
C(10)-C(11)-C(12)	117.9(8)
C(10)-C(11)-H(11A)	121.1
C(12)-C(11)-H(11A)	121.1
C(13)-C(12)-C(11)	120.0(8)
C(13)-C(12)-H(12A)	120.0
C(11)-C(12)-H(12A)	120.0
C(12)-C(13)-C(14)	123.9(9)
C(12)-C(13)-H(13A)	118.1
C(14)-C(13)-H(13A)	118.1

C(9)-C(14)-C(13)	117.0(8)
C(9)-C(14)-H(14A)	121.5
C(13)-C(14)-H(14A)	121.5
C(20)-C(15)-C(16)	116.1(6)
C(20)-C(15)-C(5)	121.5(6)
C(16)-C(15)-C(5)	122.4(6)
C(17)-C(16)-C(15)	121.5(6)
C(17)-C(16)-H(16A)	119.2
C(15)-C(16)-H(16A)	119.2
C(16)-C(17)-C(18)	121.4(7)
C(16)-C(17)-H(17A)	119.3
C(18)-C(17)-H(17A)	119.3
C(17)-C(18)-C(19)	117.8(6)
C(17)-C(18)-H(18A)	121.1
C(19)-C(18)-H(18A)	121.1
C(20)-C(19)-C(18)	119.9(7)
C(20)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19A)	120.0
C(19)-C(20)-C(15)	123.1(6)
C(19)-C(20)-H(20A)	118.5
C(15)-C(20)-H(20A)	118.5
O(1)-C(21)-O(2)	122.6(6)
O(1)-C(21)-C(6)	127.1(5)
O(2)-C(21)-C(6)	110.2(5)
O(2)-C(22)-H(22A)	109.5
O(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(3)-C(23)-O(4)	123.0(7)
O(3)-C(23)-C(3)	123.0(6)
O(4)-C(23)-C(3)	114.0(6)
O(4)-C(24)-H(24A)	109.5
O(4)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5

O(4)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(21)-O(2)-C(22)	115.4(5)
C(23)-O(4)-C(24)	117.2(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for QIN_4_133. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(3)	26(3)	16(3)	-6(3)	-8(2)	2(3)
C(2)	29(3)	32(4)	17(3)	-7(3)	-6(3)	3(3)
C(3)	17(3)	18(3)	22(3)	1(3)	-9(2)	-2(2)
C(4)	16(3)	17(3)	24(3)	3(3)	-6(2)	0(2)
C(5)	20(3)	14(3)	18(3)	-3(2)	-6(2)	-1(2)
C(6)	29(3)	20(3)	18(3)	-10(3)	-12(3)	9(3)
C(7)	25(3)	26(3)	31(4)	-4(3)	-13(3)	6(3)
C(8)	29(4)	31(4)	23(3)	-3(3)	-7(3)	2(3)
C(9)	22(3)	26(3)	36(4)	-4(3)	-8(3)	5(3)
C(10)	42(4)	24(4)	48(5)	2(4)	-26(4)	0(3)
C(11)	33(4)	28(4)	63(5)	-3(4)	-23(4)	0(3)
C(12)	27(4)	22(4)	64(6)	1(4)	4(4)	-5(3)
C(13)	60(6)	40(5)	36(4)	6(4)	4(4)	-15(4)
C(14)	46(5)	39(4)	35(4)	-1(4)	-5(3)	-7(4)
C(15)	20(3)	21(3)	19(3)	-3(3)	-9(2)	5(2)
C(16)	25(3)	32(4)	16(3)	10(3)	-6(2)	-3(3)
C(17)	35(4)	40(4)	26(3)	6(3)	-18(3)	1(3)
C(18)	20(3)	40(4)	39(4)	7(4)	-14(3)	-1(3)
C(19)	20(3)	34(4)	30(4)	6(3)	-9(3)	-8(3)
C(20)	25(3)	22(3)	24(3)	3(3)	-9(3)	0(2)
C(21)	15(3)	18(3)	23(3)	-6(3)	-7(2)	0(2)
C(22)	25(3)	35(4)	42(4)	-13(3)	-20(3)	12(3)
C(23)	16(3)	26(3)	26(3)	2(3)	-6(2)	-1(2)
C(24)	45(5)	31(4)	50(5)	-3(4)	-2(4)	-4(3)
O(1)	31(3)	37(3)	23(2)	-6(2)	-14(2)	13(2)
O(2)	31(3)	32(3)	32(3)	-12(2)	-13(2)	19(2)
O(3)	49(3)	42(3)	32(3)	6(3)	7(2)	-12(3)
O(4)	32(3)	23(3)	40(3)	-7(2)	-4(2)	-4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for QIN_4_133.

	x	y	z	U(eq)
H(1A)	12041	-585	456	30
H(1B)	10587	537	500	30
H(2A)	13494	884	687	33
H(2B)	12732	1534	-323	33
H(4A)	10085	3285	2883	24
H(5A)	9511	1288	3801	21
H(7A)	9264	-1134	1888	33
H(8A)	9965	-1801	4045	35
H(10A)	8327	-2935	1935	43
H(11A)	6957	-4686	2266	48
H(12A)	6430	-5784	4217	52
H(13A)	7254	-5161	5685	60
H(14A)	8727	-3458	5377	51
H(16A)	8501	2475	1084	30
H(17A)	6001	2925	1059	40
H(18A)	3952	2147	2644	39
H(19A)	4473	1149	4430	33
H(20A)	6985	717	4447	29
H(22A)	15089	-2456	2116	50
H(22B)	13861	-2186	3503	50
H(22C)	14830	-1077	2778	50
H(24A)	12285	6324	2251	69
H(24B)	12397	6156	832	69
H(24C)	13839	5528	1274	69

Table 6. Torsion angles [°] for QIN_4_133.

C(6)-C(1)-C(2)-C(3)	-45.3(7)
C(1)-C(2)-C(3)-C(4)	13.7(9)
C(1)-C(2)-C(3)-C(23)	-165.3(5)
C(23)-C(3)-C(4)-C(5)	179.4(5)
C(2)-C(3)-C(4)-C(5)	0.4(10)
C(3)-C(4)-C(5)-C(15)	-113.6(7)
C(3)-C(4)-C(5)-C(6)	16.4(8)
C(2)-C(1)-C(6)-C(7)	-176.0(5)
C(2)-C(1)-C(6)-C(21)	-55.8(7)
C(2)-C(1)-C(6)-C(5)	60.9(7)
C(4)-C(5)-C(6)-C(7)	-165.5(5)
C(15)-C(5)-C(6)-C(7)	-36.0(8)
C(4)-C(5)-C(6)-C(21)	73.4(7)
C(15)-C(5)-C(6)-C(21)	-157.1(5)
C(4)-C(5)-C(6)-C(1)	-44.6(7)
C(15)-C(5)-C(6)-C(1)	84.9(7)
C(21)-C(6)-C(7)-C(8)	27.6(9)
C(1)-C(6)-C(7)-C(8)	147.9(7)
C(5)-C(6)-C(7)-C(8)	-92.5(8)
C(6)-C(7)-C(8)-C(9)	-177.6(6)
C(7)-C(8)-C(9)-C(10)	9.3(11)
C(7)-C(8)-C(9)-C(14)	-171.3(7)
C(14)-C(9)-C(10)-C(11)	0.6(11)
C(8)-C(9)-C(10)-C(11)	-180.0(7)
C(9)-C(10)-C(11)-C(12)	0.7(11)
C(10)-C(11)-C(12)-C(13)	-0.6(12)
C(11)-C(12)-C(13)-C(14)	-0.8(14)
C(10)-C(9)-C(14)-C(13)	-1.8(11)
C(8)-C(9)-C(14)-C(13)	178.7(7)
C(12)-C(13)-C(14)-C(9)	2.0(14)
C(4)-C(5)-C(15)-C(20)	-140.7(6)
C(6)-C(5)-C(15)-C(20)	89.8(7)
C(4)-C(5)-C(15)-C(16)	40.8(8)
C(6)-C(5)-C(15)-C(16)	-88.7(7)

C(20)-C(15)-C(16)-C(17)	3.5(10)
C(5)-C(15)-C(16)-C(17)	-177.9(6)
C(15)-C(16)-C(17)-C(18)	-4.1(11)
C(16)-C(17)-C(18)-C(19)	4.1(12)
C(17)-C(18)-C(19)-C(20)	-3.8(11)
C(18)-C(19)-C(20)-C(15)	3.6(11)
C(16)-C(15)-C(20)-C(19)	-3.3(10)
C(5)-C(15)-C(20)-C(19)	178.1(6)
C(7)-C(6)-C(21)-O(1)	-104.4(8)
C(1)-C(6)-C(21)-O(1)	135.5(7)
C(5)-C(6)-C(21)-O(1)	18.9(10)
C(7)-C(6)-C(21)-O(2)	72.9(7)
C(1)-C(6)-C(21)-O(2)	-47.3(7)
C(5)-C(6)-C(21)-O(2)	-163.8(6)
C(4)-C(3)-C(23)-O(3)	-165.8(7)
C(2)-C(3)-C(23)-O(3)	13.3(9)
C(4)-C(3)-C(23)-O(4)	15.8(8)
C(2)-C(3)-C(23)-O(4)	-165.1(5)
O(1)-C(21)-O(2)-C(22)	1.8(10)
C(6)-C(21)-O(2)-C(22)	-175.6(6)
O(3)-C(23)-O(4)-C(24)	3.0(10)
C(3)-C(23)-O(4)-C(24)	-178.6(6)

Symmetry transformations used to generate equivalent atoms:

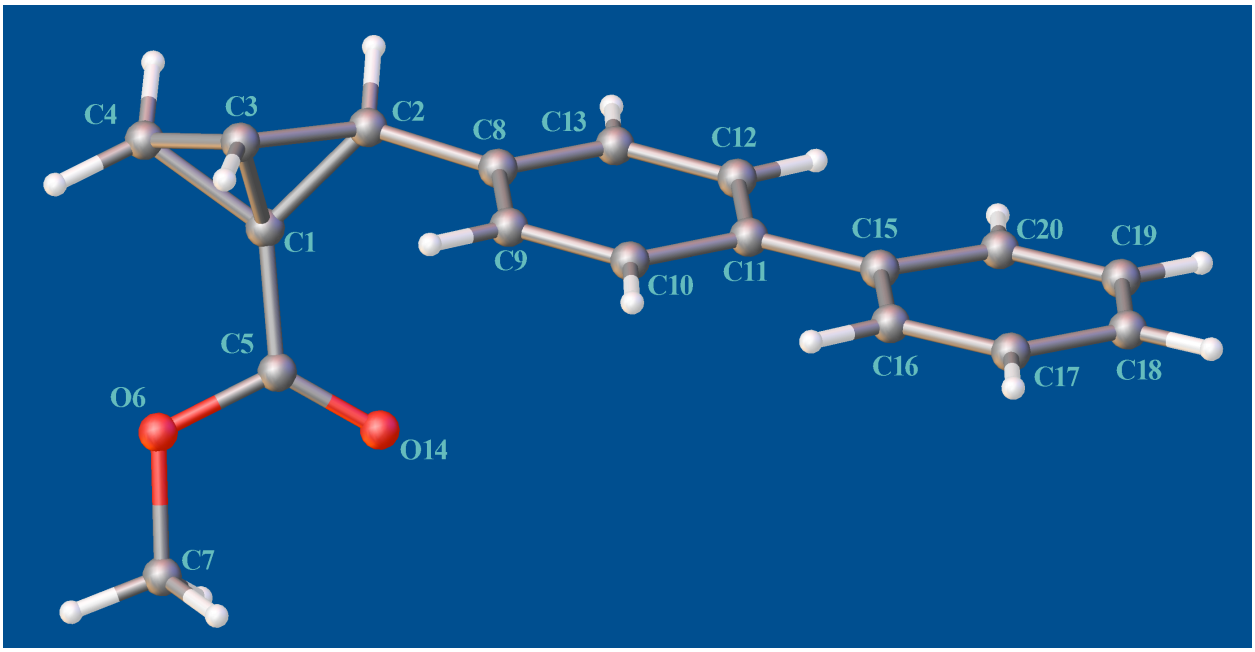


Table 2. Crystal data and structure refinement for QIN1079_fin.

Identification code	28shells	
Empirical formula	C18 H16 O2	
Formula weight	264.31	
Temperature	173 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.1737(19) Å	α= 90°.
	b = 5.6370(11) Å	β= 110.394(14)°.
	c = 12.798(3) Å	γ = 90°.
Volume	687.9(2) $Å^3$	
Z	2	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	280	
Crystal size	0.46 x 0.13 x 0.05 mm^3	
Theta range for data collection	3.68 to 60.00°.	
Index ranges	-10<=h<=8, -6<=k<=6, -14<=l<=13	
Reflections collected	8441	
Independent reflections	1751 [R(int) = 0.0679]	
Completeness to theta = 60.00°	95 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8643 and 0.7638
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1751 / 7 / 198
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1096
R indices (all data)	R1 = 0.0852, wR2 = 0.1355
Absolute structure parameter	0.1(6)
Largest diff. peak and hole	0.165 and -0.201 e.$Å^{-3}$

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for QIN1079_fin. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(6)	7910(3)	8485(6)	5536(3)	56(1)
O(14)	6572(3)	6628(7)	6352(3)	59(1)
C(1)	8777(4)	5037(9)	6520(3)	45(2)
C(2)	9194(4)	3435(9)	7530(4)	45(2)
C(3)	10213(4)	5255(10)	7420(4)	48(2)
C(4)	10088(5)	4814(10)	6248(4)	54(2)
C(5)	7631(4)	6751(9)	6149(4)	46(2)
C(7)	6787(5)	10205(11)	5097(4)	65(2)
C(8)	8555(4)	3648(9)	8411(3)	41(2)
C(9)	8806(4)	5551(8)	9138(4)	51(2)
C(10)	8231(4)	5668(8)	9958(4)	48(2)
C(11)	7389(4)	3905(8)	10128(3)	38(2)
C(12)	7132(4)	1986(8)	9386(4)	50(2)
C(13)	7699(4)	1879(9)	8553(4)	52(2)
C(15)	6811(4)	3994(8)	11039(3)	39(2)
C(16)	7108(5)	5863(9)	11789(4)	59(2)
C(17)	6603(5)	5970(10)	12654(4)	64(2)
C(18)	5748(4)	4213(9)	12797(4)	50(2)
C(19)	5410(4)	2359(9)	12056(4)	51(2)
C(20)	5923(4)	2255(9)	11190(4)	52(2)

Table 4. Bond lengths [Å] and angles [°] for QIN1079_fin.

O(6)-C(5)	1.344(6)
O(6)-C(7)	1.454(7)
O(14)-C(5)	1.195(6)
C(1)-C(2)	1.511(6)
C(1)-C(3)	1.518(6)
C(1)-C(4)	1.497(7)
C(1)-C(5)	1.460(7)
C(2)-C(3)	1.500(7)
C(2)-C(8)	1.490(6)
C(3)-C(4)	1.482(7)
C(8)-C(9)	1.384(6)
C(8)-C(13)	1.377(7)
C(9)-C(10)	1.370(7)
C(10)-C(11)	1.378(6)
C(11)-C(12)	1.403(6)
C(11)-C(15)	1.478(6)
C(12)-C(13)	1.379(7)
C(15)-C(16)	1.386(6)
C(15)-C(20)	1.392(6)
C(16)-C(17)	1.375(7)
C(17)-C(18)	1.372(7)
C(18)-C(19)	1.372(7)
C(19)-C(20)	1.381(7)
C(2)-H(2)	1.03(3)
C(3)-H(3)	1.03(4)
C(4)-H(4A)	1.03(3)
C(4)-H(4B)	1.03(5)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500

C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500

C(5)-O(6)-C(7)	114.4(4)
C(2)-C(1)-C(3)	59.4(3)
C(2)-C(1)-C(4)	98.1(4)
C(2)-C(1)-C(5)	128.9(4)
C(3)-C(1)-C(4)	58.9(3)
C(3)-C(1)-C(5)	129.9(4)
C(4)-C(1)-C(5)	130.9(4)
C(1)-C(2)-C(3)	60.5(3)
C(1)-C(2)-C(8)	122.2(4)
C(3)-C(2)-C(8)	120.9(4)
C(1)-C(3)-C(2)	60.1(3)
C(1)-C(3)-C(4)	59.9(3)
C(2)-C(3)-C(4)	99.3(4)
C(1)-C(4)-C(3)	61.3(3)
O(6)-C(5)-O(14)	124.0(5)
O(6)-C(5)-C(1)	111.3(4)
O(14)-C(5)-C(1)	124.7(5)
C(2)-C(8)-C(9)	123.0(4)
C(2)-C(8)-C(13)	120.3(4)
C(9)-C(8)-C(13)	116.7(4)
C(8)-C(9)-C(10)	121.6(4)
C(9)-C(10)-C(11)	122.8(4)
C(10)-C(11)-C(12)	115.4(4)
C(10)-C(11)-C(15)	122.7(4)
C(12)-C(11)-C(15)	121.9(4)
C(11)-C(12)-C(13)	121.9(4)
C(8)-C(13)-C(12)	121.6(4)
C(11)-C(15)-C(16)	121.4(4)
C(11)-C(15)-C(20)	122.8(4)
C(16)-C(15)-C(20)	115.8(4)

C(15)-C(16)-C(17)	122.6(5)
C(16)-C(17)-C(18)	120.5(5)
C(17)-C(18)-C(19)	118.4(4)
C(18)-C(19)-C(20)	120.9(4)
C(15)-C(20)-C(19)	121.8(4)
C(1)-C(2)-H(2)	113(3)
C(3)-C(2)-H(2)	117(2)
C(8)-C(2)-H(2)	114(3)
C(1)-C(3)-H(3)	124(3)
C(2)-C(3)-H(3)	130(3)
C(4)-C(3)-H(3)	127(3)
C(1)-C(4)-H(4A)	110(2)
C(1)-C(4)-H(4B)	118(3)
C(3)-C(4)-H(4A)	116(3)
C(3)-C(4)-H(4B)	113(3)
H(4A)-C(4)-H(4B)	123(4)
O(6)-C(7)-H(7A)	109.00
O(6)-C(7)-H(7B)	110.00
O(6)-C(7)-H(7C)	110.00
H(7A)-C(7)-H(7B)	109.00
H(7A)-C(7)-H(7C)	109.00
H(7B)-C(7)-H(7C)	109.00
C(8)-C(9)-H(9)	119.00
C(10)-C(9)-H(9)	119.00
C(9)-C(10)-H(10)	119.00
C(11)-C(10)-H(10)	119.00
C(11)-C(12)-H(12)	119.00
C(13)-C(12)-H(12)	119.00
C(8)-C(13)-H(13)	119.00
C(12)-C(13)-H(13)	119.00
C(15)-C(16)-H(16)	119.00
C(17)-C(16)-H(16)	119.00
C(16)-C(17)-H(17)	120.00
C(18)-C(17)-H(17)	120.00
C(17)-C(18)-H(18)	121.00
C(19)-C(18)-H(18)	121.00

C(18)-C(19)-H(19)	120.00
C(20)-C(19)-H(19)	120.00
C(15)-C(20)-H(20)	119.00
C(19)-C(20)-H(20)	119.00

Table 5. Anisotropic displacement parameters ($Å^2$x 10^3)for QIN1079_fin. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(6)	45(2)	62(2)	64(2)	12(2)	21(1)	8(1)
O(14)	43(2)	68(2)	71(2)	17(2)	25(2)	10(1)
C(1)	30(2)	54(3)	51(3)	6(3)	14(2)	8(2)
C(2)	39(2)	45(3)	50(3)	3(3)	13(2)	6(2)
C(3)	39(2)	57(4)	49(3)	1(3)	17(2)	7(2)
C(4)	50(3)	62(4)	56(3)	-1(3)	27(2)	10(3)
C(5)	41(3)	56(3)	41(3)	-7(3)	15(2)	-9(2)
C(7)	59(3)	64(4)	66(3)	16(3)	14(2)	16(3)
C(8)	33(2)	39(3)	46(3)	1(3)	7(2)	5(2)
C(9)	47(3)	44(3)	65(3)	-1(3)	25(2)	-10(2)
C(10)	46(3)	40(3)	63(3)	-10(3)	26(2)	-10(2)
C(11)	30(2)	31(3)	46(3)	-1(2)	5(2)	2(2)
C(12)	48(3)	39(3)	67(3)	-3(3)	25(2)	-13(2)
C(13)	48(3)	41(3)	65(3)	-16(3)	19(2)	-6(2)
C(15)	30(2)	37(3)	46(3)	1(2)	8(2)	3(2)
C(16)	60(3)	52(4)	79(4)	-25(3)	41(3)	-25(2)
C(17)	66(3)	63(4)	78(4)	-22(3)	43(3)	-20(2)
C(18)	40(3)	58(4)	51(3)	7(3)	14(2)	3(2)
C(19)	47(3)	52(4)	57(3)	8(3)	21(2)	-8(2)
C(20)	48(3)	43(3)	66(4)	-9(3)	20(2)	-12(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for QIN1079_fin.

	x	y	z	U(eq)
H(2)	9370(40)	1710(50)	7350(40)	58(13)
H(3)	10580(50)	6770(70)	7880(40)	91(18)
H(4A)	10210(40)	3080(50)	6040(40)	46(12)
H(4B)	10400(50)	6250(70)	5890(40)	84(17)
H(7A)	6626	11028	5716	97
H(7B)	5926	9386	4646	97
H(7C)	7050	11362	4633	97
H(9)	9391	6807	9066	60
H(10)	8421	7022	10430	57
H(12)	6550	725	9458	60
H(13)	7495	551	8066	62
H(16)	7683	7120	11702	71
H(17)	6848	7271	13157	77
H(18)	5399	4278	13395	60
H(19)	4815	1131	12140	62
H(20)	5662	961	10683	63

Table 7. Torsion angles [°] for QIN1079_fin.

C(7)-O(6)-C(5)-O(14)	-1.9(7)
C(7)-O(6)-C(5)-C(1)	177.5(4)
C(4)-C(1)-C(2)-C(8)	156.3(4)
C(3)-C(1)-C(2)-C(8)	110.0(5)
C(4)-C(1)-C(2)-C(3)	46.2(4)
C(2)-C(1)-C(3)-C(4)	123.4(4)
C(4)-C(1)-C(3)-C(2)	-123.4(4)
C(5)-C(1)-C(3)-C(2)	117.1(5)
C(5)-C(1)-C(3)-C(4)	-119.5(6)
C(2)-C(1)-C(4)-C(3)	-46.5(4)
C(5)-C(1)-C(2)-C(3)	-118.7(6)
C(5)-C(1)-C(2)-C(8)	-8.7(7)
C(2)-C(1)-C(5)-O(14)	-26.6(8)
C(3)-C(1)-C(5)-O(6)	74.4(6)
C(3)-C(1)-C(5)-O(14)	-106.3(6)
C(4)-C(1)-C(5)-O(6)	-6.0(7)
C(4)-C(1)-C(5)-O(14)	173.3(5)
C(5)-C(1)-C(4)-C(3)	117.9(6)
C(2)-C(1)-C(5)-O(6)	154.0(5)
C(1)-C(2)-C(3)-C(4)	-47.1(4)
C(1)-C(2)-C(8)-C(9)	-69.6(6)
C(1)-C(2)-C(8)-C(13)	112.1(5)
C(3)-C(2)-C(8)-C(9)	2.9(7)
C(3)-C(2)-C(8)-C(13)	-175.4(4)
C(8)-C(2)-C(3)-C(1)	-112.0(5)
C(8)-C(2)-C(3)-C(4)	-159.1(4)
C(2)-C(3)-C(4)-C(1)	47.2(4)
C(2)-C(8)-C(9)-C(10)	-178.3(4)
C(13)-C(8)-C(9)-C(10)	0.0(7)
C(2)-C(8)-C(13)-C(12)	177.7(4)
C(9)-C(8)-C(13)-C(12)	-0.7(7)
C(8)-C(9)-C(10)-C(11)	1.0(7)
C(9)-C(10)-C(11)-C(12)	-1.3(7)
C(9)-C(10)-C(11)-C(15)	177.7(4)

C(10)-C(11)-C(12)-C(13)	0.6(6)
C(15)-C(11)-C(12)-C(13)	-178.4(4)
C(10)-C(11)-C(15)-C(16)	-1.0(7)
C(10)-C(11)-C(15)-C(20)	177.8(4)
C(12)-C(11)-C(15)-C(16)	177.9(4)
C(12)-C(11)-C(15)-C(20)	-3.3(7)
C(11)-C(12)-C(13)-C(8)	0.4(7)
C(11)-C(15)-C(16)-C(17)	-178.9(5)
C(20)-C(15)-C(16)-C(17)	2.2(7)
C(11)-C(15)-C(20)-C(19)	179.1(4)
C(16)-C(15)-C(20)-C(19)	-2.0(7)
C(15)-C(16)-C(17)-C(18)	-1.2(8)
C(16)-C(17)-C(18)-C(19)	-0.1(8)
C(17)-C(18)-C(19)-C(20)	0.3(7)
C(18)-C(19)-C(20)-C(15)	0.8(7)