Supporting Information

Ruthenium-Catalyzed Benzylic Substitution of Benzyl Esters with Stabilized Carbon Nucleophiles

Koki Suzuki, Hiroaki Tsuji* and Motoi Kawatsura*

Department of Chemistry, College of Humanities & Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

tsuji@chs.nihon-u.ac.jp
kawatsur@chs.nihon-u.ac.jp

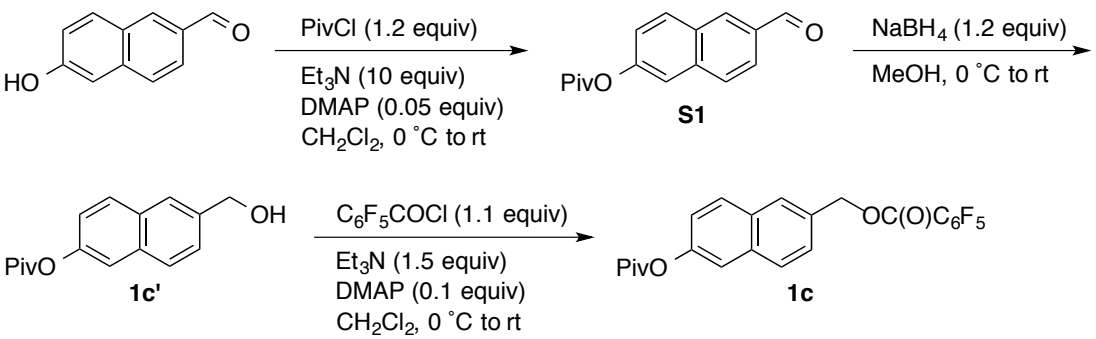
Table of Contents

1. General experimental remarks

Commercially available chemicals were purchased from Aldrich, TCI, Kanto, and Wako and used without further purification unless otherwise noted. Benzyl 2,3,4,5,6-pentafluorobenzoates **1a**, **1b**, **1f**, **1h**, **1i**, **1j**, and **1k** were prepared according to the our previously reported method.[1] Ruthenium(III) chloride hydrate was purchased from Oakwood chemical. $[Cp^*RuCl_2]_2$ was prepared according to the literature.[2] NMR spectra were recorded at 25 ˚C on a JEOL EX-270 spectrometer (270 MHz for ^1H, 67.9 MHz for ^{13}C) or a JEOL JNM ECP-500 spectrometer (500 MHz for ^1H, 126 MHz for ^{13}C, 471 MHz for ^{19}F). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane (0 ppm) for ^1H NMR. Chemical shifts of ^{13}C NMR are given relative to the solvent peak as an internal standard. ^{19}F NMR data are reported relative to external α,α,α-trifluorotoluene (–63.7 ppm). Multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). Melting points were measured on a Yanako MP-500P. Infrared (IR) spectra were recorded on JASCO FT/IR–400 plus. GC-MS measurements were carried out with JEOL JMS-Q1000GC/K9. HRMS analyses were carried out using a JEOL AccuTOF LCplus for ESI-MS and APCI-MS, Waters G2-S Q-Tof for ESI-MS, and JEOL GCmate for EI-MS. Column chromatography and preparative thin-layer chromatography were conducted with silica gel 60N (KANTO CHEMICAL, spherical, neutral, 40-50 or 63-210 μm) and Wakogel® B-5F (45 μm), respectively. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), phosphomolybdic acid, and I_2/SiO_2.

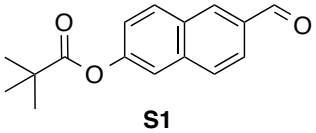
2. General procedure for the preparation of benzyl 2,3,4,5,6-pentafluorobenzoates 1c–e and 1g

Scheme S1. Preparation of benzyl 2,3,4,5,6-pentafluorobenzoate **1c**



Preparation of 6-formylnaphthalen-2-yl pivalate (**S1**):

6-Hydroxy-2-naphthaldehyde (861 mg, 5.00 mmol) and DMAP (30.5 mg, 0.25 mmol, 0.05 equiv) were charged into a round flask and the flask was refilled with N_2. CH_2Cl_2 (10 mL) and triethylamine (7.0 mL, 50 mmol, 10 equiv) were added to the flask. Pivaroyl chloride (0.74 mL, 6.0 mmol, 1.2 equiv) was added dropwise to the mixture at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched with water and the resulting aqueous phase was extracted with CH_2Cl_2 (70 mL×3). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography to give 6-formylnaphthalen-2-yl pivalate (**S1**) as a white solid (1.10 g, 4.29 mmol, 86% yield).

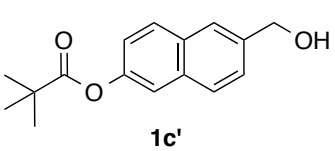


S1

M.p. 98.3–99.6 ˚C; IR (KBr) 2983, 2876, 1745, 1692, 1472, 1105, 913, 817 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.42 (s, 9H), 7.32 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.97 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 8.34 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 27.1, 39.2, 118.8, 122.5, 123.5, 128.7, 130.4, 131.0, 133.9, 134.1, 137.1, 151.3, 176.9, 192.0; HRMS (APCI/TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}O_3$ 257.1178; Found 257.1187.

Preparation of 6-(hydroxymethyl)naphthalen-2-yl pivalate (**1c'**):

$NaBH_4$ (174 mg, 4.60 mmol, 1.2 equiv) was added to a solution of 6-formylnaphthalen-2-yl pivalate (**S3**) (981 mg, 3.8 mmol) in MeOH (13 mL) at 0 ˚C. The resulting mixture was stirred for 2 h at room temperature. MeOH was removed by evaporation and the resulting mixture was transferred to a separating funnel with EtOAc and water. The aqueous phase was extracted with EtOAc (80 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 5/1, 4/1, 10/3, 20/7) to give 6-(hydroxymethyl)naphthalen-2-yl pivalate (**1c'**) as a white solid (458 mg, 1.77 mmol, 47% yield).

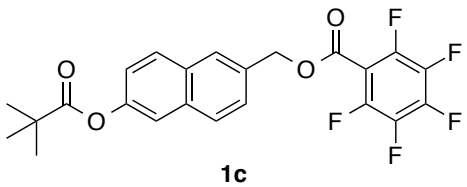


1c'

M.p. 126.3–127.4 ˚C; IR (KBr) 3326, 2962, 2932, 2871, 1749, 1476, 1279, 1150, 1030, 906, 816 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.72 (bs, 1H), 4.85 (s, 2H), 7.20 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.77–7.84 (m, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 27.1, 39.1, 65.1, 118.2, 121.4, 125.2, 125.8, 127.9, 129.2, 131.2, 133.2, 138.1, 148.7, 177.3; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{18}O_3Na$ 281.1154; Found 281.1152.

Preparation of (6-(pivaloyloxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1c**):

6-(Hydroxymethyl)naphthalen-2-yl pivalate (**1c'**) (450 mg, 1.74 mmol) and DMAP (21.3 mg, 0.174 mmol, 0.1 equiv) were charged into a round flask and the flask was refilled with N_2. THF (6 mL) and triethylamine (0.36 mL, 2.60 mmol, 1.5 equiv) were added to the flask. Pentafluorobenzoyl chloride (0.30 mL, 1.91 mmol, 1.1 equiv) was added dropwise to the mixture at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stirred for 20 min. The reaction was quenched with water and the resulting aqueous phase was extracted with EtOAc (50 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 95/5, 92/8, 9/1) to give (6-(pivaloyloxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1c**) as a white solid (643 mg, 1.42 mmol, 84% yield).

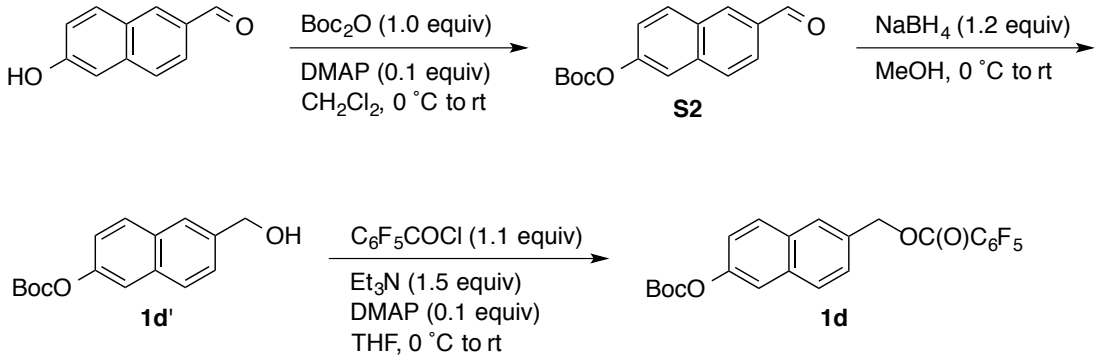


1c

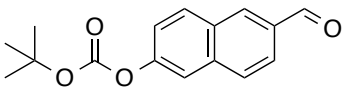
M.p. 114.9–115.4 ˚C; IR (KBr) 2983, 2876, 1756, 1731, 1655, 1498, 1322, 1230, 1140, 1013, 907, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.41 (s, 9H), 5.56 (s, 2H), 7.23 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 (d, *J* = 2.3 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.1, 39.1, 68.4, 108.0 (m), 118.3, 121.8, 126.4, 127.6, 128.3, 129.4, 131.0, 131.7, 133.7, 137.7 (dm, J_{CF} = 256 Hz), 143.3 (dm, J_{CF} = 261 Hz), 145.5 (dm, J_{CF} = 258 Hz), 149.4, 158.9, 177.1; ^{19}F NMR (471 MHz, $CDCl_3$): δ -138.7 – -138.8 (m,

2F), -149.1 (tt, J = 21.2, 4.9 Hz, 1F), -161.1 – -161.2 (m, 2F); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{23}H_{17}O_4F_5$ 452.1047; Found 452.1047.

Scheme S2. Preparation of benzyl 2,3,4,5,6-perfluorobenzoate **1d**



Preparation of *tert*-butyl (6-formylnaphthalen-2-yl) carbonate (**S2**):
6-Hydroxy-2-naphthaldehyde (861 mg, 5.00 mmol) and DMAP (61.1 mg, 0.50 mmol, 0.1 equiv) were charged into a round flask and the flask was refilled with N_2. CH_2Cl_2 (10 mL) was added to the flask. A solution of Boc_2O (1.09 g, 5.00 mmol, 1.0 equiv) in CH_2Cl_2 was added dropwise to the resulting mixture at 0 ˚C. After stirring the reaction mixture at room temperature for 1 h, the reaction was quenched with water and the resulting aqueous phase was extracted with CH_2Cl_2 (80 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 9/1, 85/15) to give *tert*-butyl (6-formylnaphthalen-2-yl) carbonate (**S2**) as a white solid (1.23 g, 4.52 mmol, 90% yield).

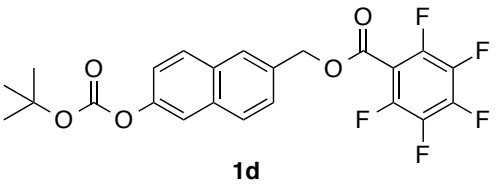


S2

M.p. 105.7–106.8 ˚C; IR (KBr) 2979, 2942, 2863, 1751, 1693, 1476, 1374, 1288, 1257, 1147, 899, 823, 778 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.60 (s, 9H), 7.43 (dd, J = 8.9, 2.3 Hz, 1H), 7.73 (d, J = 2.3 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.97 (dd, J = 8.6, 1.4 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 8.34 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 27.7, 84.1, 118.4, 122.2, 123.5, 128.8, 130.4, 131.0, 133.9, 134.0, 137.0, 151.1, 151.5, 191.9; HRMS (APCI/TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}O_4$ 273.1127; Found 273.1120.

Preparation of (6-((*tert*-butoxycarbonyl)oxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1d**):

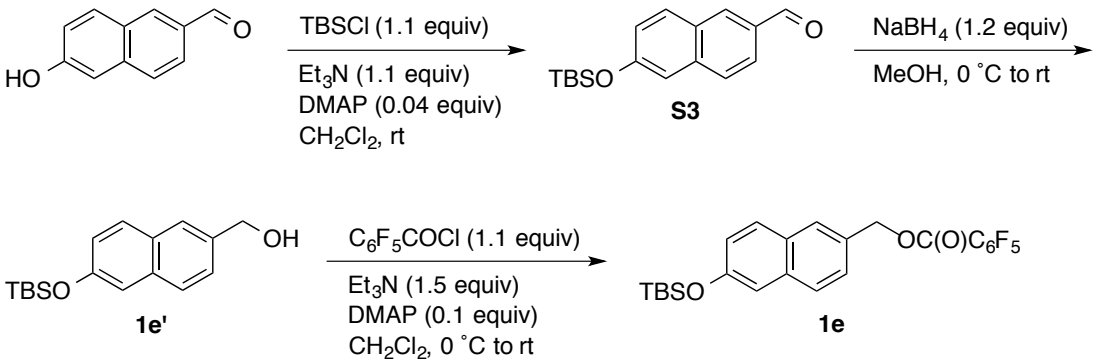
$NaBH_4$ (182 mg, 4.80 mmol, 1.2 equiv) was added to a solution of *tert*-butyl (6-formylnaphthalen-2-yl) carbonate (**S2**) (1.10 g, 4.0 mmol) in MeOH (13 mL) at 0 ˚C. The resulting mixture was stirred overnight at room temperature. MeOH was removed by evaporation and the resulting mixture was transferred to a separating funnel with EtOAc and water. The aqueous phase was extracted with EtOAc (80 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, alcohol **1d'** was obtained as a crude mixture and this mixture was used next step without further purification. The crude mixture and DMAP (49.0 mg, 0.40 mmol, 0.1 equiv) were placed in a round flask and refilled with N_2. THF (12 mL) and triethylamine (0.82 mL, 5.90 mmol, 1.5 equiv) were added to the flask. Pentafluorobenzoyl chloride (0.60 mL, 4.30 mmol, 1.1 equiv) was added dropwise to the mixture at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with water and the resulting aqueous phase was extracted with EtOAc (80 mL×3). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 92/8, 9/1, 88/12) to give (6-((*tert*-butoxycarbonyl)oxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1d**) as a white solid (1.50 g, 3.20 mmol, 82% yield).



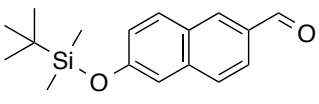
1d

M.p. 107.6–109.8 ˚C; IR (KBr) 2985, 2936, 1752, 1739, 1651, 1496, 1325, 1226, 1142, 1005, 895 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.59 (s, 9H), 5.55 (s, 2H), 7.35 (dd, J = 8.5, 2.5 Hz, 1H), 7.53 (dd, J = 8.3, 1.8 Hz, 1H), 7.66 (d, J = 2.5 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.89 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.7, 68.4, 83.8, 108.0 (m), 118.1, 121.5, 126.4, 127.6. 128.4, 129.5, 131.0, 131.8, 13 3.6, 137.7 (dm, J_{CF} = 256 Hz), 143.3 (dm, J_{CF} = 261 Hz), 145.5 (dm, J_{CF} = 262 Hz), 149.3, 151.8, 158.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ -138.7– -138.8 (m, 2F), 149.1 (tt, J = 20.7, 4.8 Hz, 1F), -161.1– -161.2 (m, 2F); HRMS (ESI/QTOF) $[M+Na]^+$ Calcd for $C_{23}H_{17}F_5O_5Na$, 491.0894; Found 491.0897.

Scheme S3. Preparation of benzyl 2,3,4,5,6-perfluorobenzoate **1e**



Preparation of 6-((*tert*-butyldimethylsilyl)oxy)-2-naphthaldehyde (**S3**):
6-Hydroxy-2-naphthaldehyde (861 mg, 5.00 mmol), TBSCl (829 mg, 5.50 mmol, 1.1 equiv), and DMAP (24.4 mg, 0.20 mmol, 0.04 equiv) were charged into a round flask and the flask was refilled with N_2. CH_2Cl_2 (17 mL) and triethylamine (0.8 mL, 5.5 mmol, 1.1 equiv) were added to the flask. The resulting mixture was stirred at room temperature for 3 hours. The reaction was quenched with water and the resulting aqueous phase was extracted with CH_2Cl_2 (80 mL × 2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 95/5, 9/1) to give 6-((*tert*-butyldimethylsilyl)oxy)-2-naphthaldehyde (**S3**) as a white solid (1.29 g, 4.50 mmol, 90% yield).

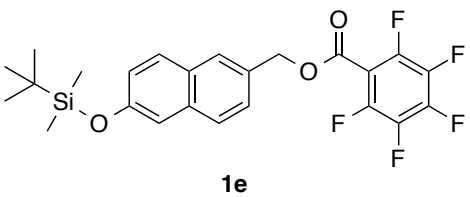


S3

M.p. 46.9–48.1 ˚C; IR (KBr) 2958, 2928, 2855, 1686, 1622, 1475, 1264, 1168, 873, 816, 778 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.28 (s, 6H), 1.03 (s, 9H), 7.17 (dd, J = 8.8, 2.2 Hz, 1H), 7.23 (d, J = 2.2 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.88–7.92 (m, 2H), 8.26 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ -4.36, 18.2, 25.6, 115.1, 123.2, 127.6, 128.1, 131.2, 132.4, 134.4, 138.1, 156.5, 192.0, one peak for aromatic carbon was not found probably due to overlapping; HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{23}O_2Si$ 287.1467; Found 287.1463.

Preparation of (6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1e**):

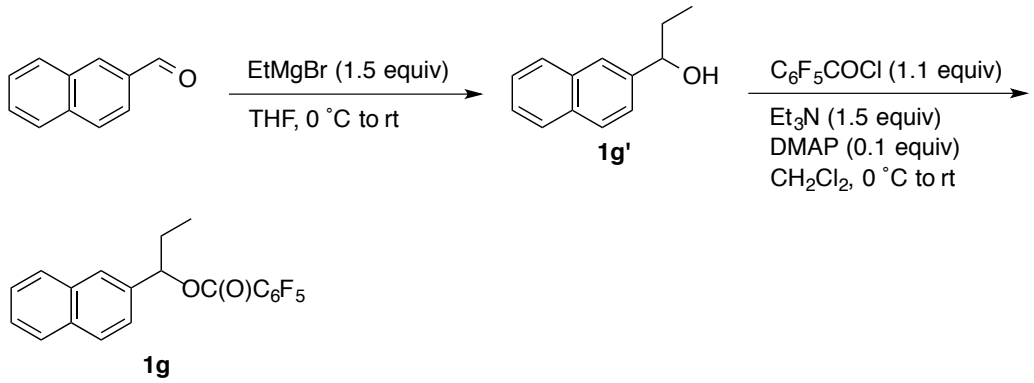
$NaBH_4$ (182 mg, 4.80 mmol, 1.2 equiv) was added to a solution of 6-((*tert*-butyldimethylsilyl)oxy)-2-naphthaldehyde (**S3**) in MeOH (13 mL) at 0 ˚C. The resulting mixture was stirred for 2 h at room temperature. MeOH was removed by evaporation and the resulting mixture was transferred to a separating funnel with EtOAc and water. The aqueous phase was extracted with EtOAc (60 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, alcohol **1e'** was obtained as a crude mixture and this mixture was used next step without further purification. The crude mixture and DMAP (49.0 mg, 0.40 mmol, 0.1 equiv) were placed in a round flask and refilled with N_2. THF (13 mL) and triethylamine (0.8 mL, 6.00 mmol, 1.5 equiv) were added to the flask. Pentafluorobenzoyl chloride (0.6 mL, 4.40 mmol, 1.1 equiv) was added dropwise to the mixture at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stirred for 30 min. The reaction was quenched with water and the resulting aqueous phase was extracted with EtOAc (100 mL×2). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 97/3, 95/5) to give (6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1e**) as a white solid (693 mg, 1.44 mmol, 36% yield).



1e

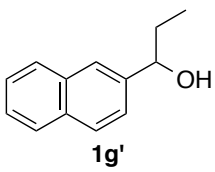
M.p. 124.4–125.4 ˚C; IR (KBr) 2930, 2861, 1738, 1525, 1496, 1325, 1219, 1006, 940, 834 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.25 (s, 6H), 1.02 (s, 9H), 5.52 (s, 2H), 7.11 (dd, J = 8.8, 2.4 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.46 (dd, J = 8.3, 1.3 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.82 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ -4.4, 18.2, 25.7, 68.8, 108.1 (m), 114.8, 122.7, 126.2, 127.4, 127.9, 128.8, 129.5, 129.7, 134.6, 137.6 (dm, J_{CF} = 256 Hz), 143.2 (dm, J_{CF} = 261 Hz), 145.4 (dm, J_{CF} = 258 Hz), 154.2, 158.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ -138.7 – -138.8 (m, 2F), -149.3 (tt, J = 21.2, 4.7 Hz, 1F), -161.2 – -161.3 (m, 2F); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{23}O_3F_5Si$ 482.1336; Found 482.1340.

Scheme S4. Preparation of benzyl 2,3,4,5,6-perfluorobenzoate **1g**



Preparation of 1-(naphthalen-2-yl)propan-1-ol (**1g'**)[3]:

Magnesium turnings (219 mg, 9.00 mmol) was charged into a two-necked round flask equipped with a condenser and a dropping funnel and the equipment was refilled with N_2. After addition of a small amount of THF, a solution of bromoethane (818 mg, 0.58 mL, 7.50 mmol, 1.5 equiv) in THF (20 mL) was added dropwise to the mixture. The reaction mixture was cooled to room temperature and a solution of 2-naphthaldehyde (781 mg, 5.00 mmol) in THF (20 mL) was added to the mixture at 0 ˚C. The resulting mixture was stirred at room temperature for 2.5 h. The reaction was quenched with 1N HCl (20 mL) and the resulting aqueous phase was extracted with EtOAc (100 mL×2). The combined organic phase was washed with brine, dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 85/15, 4/1) to give 1-(naphthalen-2-yl)propan-1-ol (**1g'**) as a pale yellow oil (877 mg, 4.71 mmol, 94% yield).

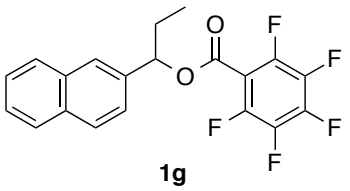


^{1}H NMR (270 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3H), 1.75–1.95 (m, 2H), 1.98 (s, 1H), 4.74 (t, J = 6.6 Hz, 1H), 7.42–7.51 (m, 3H), 7.76 (d, J = 1.4 Hz, 1H), 7.80–7.85 (m, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 10.1, 31.7, 76.1, 124.1, 124.7, 125.7, 126.1, 127.6, 127.9, 128.2, 132.9, 133.2, 141.9; GC-MS (EI) *m/z*: 186 $[M]^+$.

Preparation of 1-(naphthalen-2-yl)propyl 2,3,4,5,6-pentafluorobenzoate (**1g**):

1-(Naphthalen-2-yl)propan-1-ol (**1g'**) (689 mg, 3.70 mmol) and DMAP (49.0 mg, 0.40 mmol, 0.1 equiv) were placed in a round flask and refilled with N_2. THF (12 mL) and

triethylamine (0.78 mL, 5.60 mmol, 1.5 equiv) were added to the flask. Pentafluorobenzoyl chloride (0.57 mL, 4.10 mmol, 1.1 equiv) was added dropwise to the mixture at 0 ˚C. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with water and the resulting aqueous phase was extracted with EtOAc (60 mL×3). The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 95/5, 9/1) to give 1-(naphthalen-2-yl)propyl 2,3,4,5,6-pentafluorobenzoate (**1g**) as a white solid (1.10 g, 2.89 mmol, 78% yield).



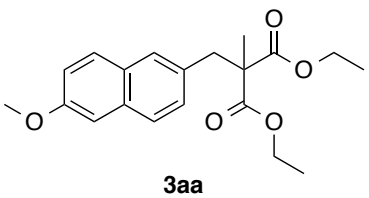
1g

M.p. 119.0–119.8 ˚C; IR (KBr) 2978, 2944, 1747, 1655, 1503, 1321, 1227, 995, 957, 818, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, J = 7.5 Hz, 3H), 2.01–2.08 (m, 1H), 2.11–2.18 (m, 1H), 6.10 (t, J = 6.8 Hz, 1H), 7.47–7.51 (m, 3H), 7.83–7.87 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.82, 29.2, 80.7, 108.4 (m), 124.1, 126.1, 126.3 (2C), 127.7, 128.1, 128.5, 133.0, 133.2, 136.4, 137.6 (dm, J_{CF} = 255 Hz), 143.1 (dm, J_{CF} = 261 Hz), 145.4 (dm, J_{CF} = 258 Hz), 158.4; ^{19}F NMR (471 MHz, $CDCl_3$): δ -139.0 – -139.1 (m, 2F), -149.7 (tt, J = 21.2, 4.2 Hz, 1F), -161.3 – -161.4 (m, 2F); HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{13}O_2F_5$ 380.0835; Found 380.0835.

3. General procedure for the ruthenium-catalyzed benzylic substitution of benzyl esters with stabilized carbon nucleophiles

(6-Methoxynaphthalen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate (**1a**) (0.25 mmol, 95.6 mg), $[Cp^*RuCl_2]_2$ (3.8 mg, 0.00625 mmol, 0.025 equiv), picolinic acid (**L1**) (1.5 mg, 0.0125 mmol, 0.05 equiv), Cs_2CO_3 (89.6 mg, 0.275 mmol, 1.1 equiv) were charged into a screw cap vial. The resulting mixture was carefully evacuated and refilled with N_2 five times. After the addition of CH_3CN (1 mL) and diethyl methylmalonate (**2a**) (47 μL, 0.275 mmol, 1.1 equiv), the resulting yellow suspension was stirred at 60 ˚C for 18 h. The reaction was allowed to cool to room temperature and quenched with water (1 mL). The resulting aqueous phase was extracted with EtOAc (3 mL × 1). The organic phase was washed with brine and dried over $MgSO_4$. After removal of the

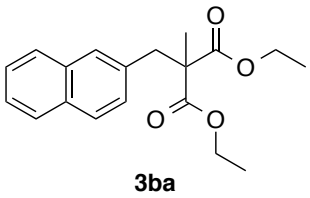
solvent, the resulting crude mixture was purified by preparative thin-layer chromatography (Hexane/EtOAc = 4/1) to give diethyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-methylmalonate (**3aa**)[1] as a pale yellow oil (76.8 mg, 0.223 mmol, 89% yield).



3aa

^{1}H NMR (270 MHz, $CDCl_3$): δ 1.26 (t, *J* = 7.1 Hz, 6H), 1.37 (s, 3H), 3.36 (s, 2H), 3.91 (s, 3H), 4.21 (q, *J* = 7.1 Hz, 4H), 7.10-7.14 (m, 2H), 7.21 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.52 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 19.8, 41.0, 54.9, 55.2, 61.3, 105.4, 118.7, 126.4, 128.7, 128.8 (2C), 129.0, 131.3, 133.4, 157.4, 172.0; GC-MS (EI): *m*/*z* 344 $[M]^+$.

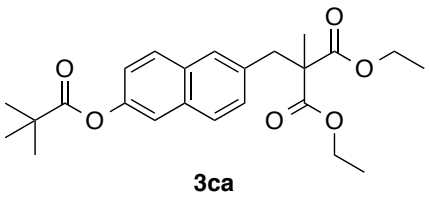
Diethyl 2-methyl-2-(naphthalen-2-ylmethyl)malonate (**3ba**)[4]



3ba

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 95/5 ×2). Pale yellow oil (70.0 mg, 0.223 mmol, 89% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.26 (t, *J* = 7.0 Hz, 6H), 1.38 (s, 3H), 3.40 (s, 2H), 4.21 (q, *J* = 7.0 Hz, 4H), 7.25 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.40–7.49 (m, 2H), 7.60 (s, 1H), 7.72–7.81 (m, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 19.8, 41.2, 54.9, 61.3, 125.6, 126.0, 127.5, 127.6 (2C), 128.4, 129.0, 132.4, 133.2, 133.8, 172.0; GC-MS (EI): *m*/*z* 314 $[M]^+$.

Diethyl 2-methyl-2-((6-(pivaloyloxy)naphthalen-2-yl)methyl)malonate (**3ca**)

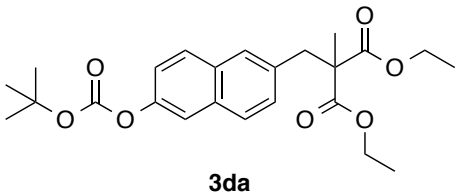


3ca

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1 × 3). White solid (84.1 mg, 0.203 mmol, 81% yield); M.p. 80.5–82.3 ˚C; IR (KBr) 2983, 2940, 1749, 1731, 1607, 1466, 1286, 1187, 1107, 908 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 6H), 1.37 (s, 3H), 1.40 (s, 9H), 3.38 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 7.16 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.26 (dd, *J* = 8.4,

1.6 Hz, 2H), 7.47 (d, 1H), 7.59 (s, 1H), 7.68 (d, J = 8.6 Hz) 7.76 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 20.3 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 19.8, 27.1, 39.1, 41.1, 54.9, 61.3, 118.1, 121.3, 127.3, 128.8, 128.9, 129.0, 131.1, 132.7, 133.6, 148.6, 171.9, 177.2; HRMS (ESI/TOF) $[M+Na]^+$ Calcd for $C_{24}H_{30}O_6Na$ 437.1940; Found 437.1934.

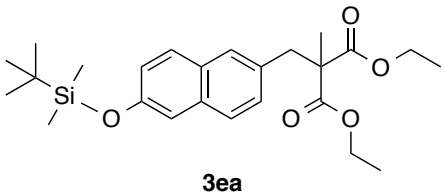
Diethyl 2-((6-((*tert*-butoxycarbonyl)oxy)naphthalen-2-yl)methyl)-2-methylmalonate (**3da**)



3da

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = Hexane/EtOAc = 9/1×2). Pale yellow oil (102 mg, 0.237 mmol, 95% yield); IR (neat) 2983, 2938, 1732, 1607, 1508, 1463, 1371, 1246, 1021, 899, 862, 813, 781 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 6H), 1.37 (s, 3H), 1.58 (s, 9H), 3.38 (s, 2H), 4.20 (q, J = 7.2 Hz, 4H), 7.26 (dd, J = 8.6, 1.6 Hz, 1H), 7.28 (dd, J = 8.8, 2.3 Hz, 1H), 7.59–7.59 (m, 2H), 7.76 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 19.8, 27.7, 41.1, 54.9, 61.3, 83.6, 117.9, 121.0, 127.4, 128.8, 129.0, 129.1, 131.2, 132.6, 133.7, 148.5, 151.9, 171.9; HRMS (ESI/TOF) $[M+Na]^+$ Calcd for $C_{24}H_{30}O_7Na$ 453.1889; Found 453.1886.

Diethyl 2-((6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)methyl)-2-methylmalonate (**3ea**)

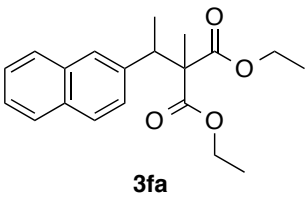


3ea

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1×3). Pale yellow oil (44.7 mg, 0.101 mmol, 40% yield); IR (neat) 2933, 2858, 1733, 1604, 1473, 1376, 1245, 1022, 976, 937, 781 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.22–0.25 (m, 6H), 0.99–1.03 (m, 9H), 1.25 (t, J = 7.1 Hz, 6H), 1.38 (s, 3H), 3.35 (s, 2H), 4.21 (q, J = 7.1 Hz, 4H), 7.04 (dd, J = 8.8, 2.6 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 7.18 (dd, J = 8.6, 1.8 Hz, 1H), 7.51 (s, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ -4.37, 14.0, 18.2, 19.8, 25.7, 41.1, 55.0, 61.3, 114.6, 122.2, 126.4, 128.6, 128.7, 129.0, 129.1, 131.5, 133.5, 153.3,

172.0; HRMS (ESI/TOF) $[M+Na]^+$ Calcd for $C_{25}H_{36}O_5SiNa$ 467.2230; Found 467.2224.

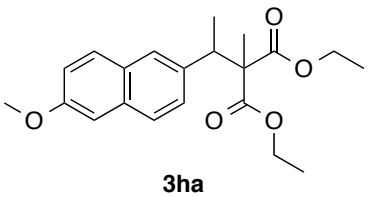
Diethyl 2-methyl-2-(1-(naphthalen-2-yl)ethyl)malonate (**3fa**)[1]



3fa

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 99/1, 96/4, 94/6, 92/8) and preparative thin-layer chromatography (Toluene/ EtOAc = 9/1). Pale yellow oil (65.7 mg, 0.200 mmol, 80% yield); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.42 (s, 3H), 1.49 (d, *J* = 7.1 Hz, 3H), 3.86 (q, *J* = 7.1 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 4.19–4.28 (m, 2H), 7.37 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.40–7.47 (m, 2H), 7.68 (d, *J* = 1.4 Hz, 1H), 7.73–7.81 (m, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.8, 14.0, 17.2, 17.3, 43.9, 58.4, 61.1, 61.2, 125.5, 125.8, 127.1, 127.4 (2C), 127.7, 127.9, 132.5, 133.1, 139.2, 171.4, 171.5; GC-MS (EI): *m/z* 328 $[M]^+$.

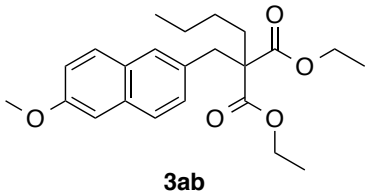
Diethyl 2-(1-(6-methoxynaphthalen-2-yl)ethyl)-2-methylmalonate (**3ha**)



3ha

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/Et_2O = 9/1 × 2). Pale yellow oil (74.5 mg, 0.208 mmol, 83% yield); IR (neat) 2976, 2841, 1747, 1633, 1607, 1455, 1393, 1216, 852, 811 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.41 (s, 3H), 1.47 (d, *J* = 7.2 Hz, 3H), 3.82 (q, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 4.03 (q, *J* = 7.0 Hz, 2H), 4.17–4.28 (m, 2H), 7.09–7.14 (m, 2H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.62–7.68 (m, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 14.0, 17.2, 17.3, 43.7, 55.2, 58.4, 61.1, 61.2, 105.4, 118.7, 126.2, 127.6, 127.7, 128.6, 129.2, 133.5, 136.8, 157.4, 171.4, 171.5; HRMS (ESI/TOF) $[M+Na]^+$ Calcd for $C_{21}H_{26}O_5Na$ 381.1678; Found 381.1672.

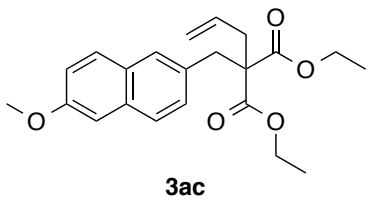
Diethyl 2-butyl-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ab**)



3ab

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1×2). Pale yellow oil (77.9 mg, 0.202 mmol, 81% yield); IR (neat) 2959, 2871, 1732, 1606, 1485, 1203, 1033, 856, 757 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.92 (t, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 6H), 1.28–1.37 (m, 4H), 1.77–1.83 (m, 2H), 3.37 (s, 2H), 3.90 (s, 3H), 4.11–4.27 (m, 4H), 7.08–7.13 (m, 2H), 7.16 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.47 (d, *J* = 1.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 14.0, 22.8, 26.3, 31.5, 37.9, 55.2, 58.9, 61.1, 105.4, 118.7, 126.5, 128.5 (2C), 128.8, 129.0, 131.5, 133.4, 157.4, 171.4; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{30}O_5Na$ 409.1991; Found 409.1977.

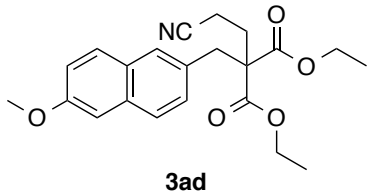
Diethyl 2-allyl-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ac**)



3ac

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 88/15). Colorless oil (74.3 mg, 0.201 mmol, 80% yield); IR (neat) 3060, 2980, 2938, 1732, 1606, 1207, 1034, 856, 757 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.2 Hz, 6H), 2.60 (d, *J* = 7.3 Hz, 2H), 3.37 (s, 2H), 3.91 (s, 3H), 4.11–4.27 (m, 4H), 5.14–5.17 (m, 1H), 5.20–5.21 (m, 1H), 5.75–5.90 (m, 1H), 7.08–7.14 (m, 2H), 7.19 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.51 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 36.6, 38.0, 52.2, 58.9, 61.2, 105.5, 118.8, 119.2, 126.6, 128.6, 128.7, 128.8, 129.0, 131.2, 132.7, 133.5, 157.5, 170.8; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{26}O_5Na$ 393.1678; Found 393.1679.

Diethyl 2-(2-cyanoethyl)-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ad**)

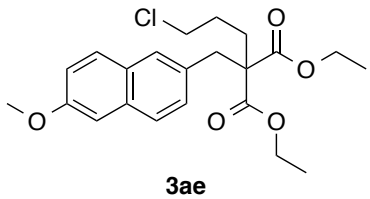


3ad

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by silica gel column chromatography

(Hexane/EtOAc = 9/1, 4/1, 7/3) and preparative thin-layer chromatography (Toluene/EtOAc= 9/1×2). Pale yellow oil (95.5 mg, 0.249 mmol, >99% yield); IR (neat) 2981, 2906, 2249, 1730, 1606, 1485, 1120, 1028, 858, 759 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7.2 Hz, 6H), 2.13–2.19 (m, 2H), 2.44–2.50 (m, 2H), 3.40 (s, 2H), 3.92 (s, 3H), 4.25 (q, *J* = 7.2 Hz, 4H), 7.09–7.16 (m, 3H), 7.48 (d, *J* = 0.81 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.1, 13.9, 28.8, 39.5, 55.2, 57.8, 61.8, 105.4, 119.0, 119.1, 126.9, 128.1, 128.6, 128.7, 129.0, 129.9, 133.6, 157.6, 170.0; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{25}NO_5Na$ 406.1630; Found 406.1630.

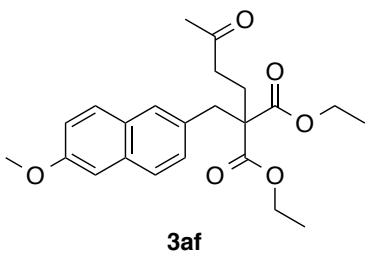
Diethyl 2-(3-chloropropyl)-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ae**)



3ae

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1×3). Pale yellow oil (95.3 mg, 0.234 mmol, 93% yield); IR (neat) 2979, 2905, 1731, 1606, 1485, 1267, 1030, 857, 758 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.0 Hz, 6H), 1.78–1.89 (m, 2H), 1.91–1.99 (m, 2H), 3.38 (s, 2H), 3.52 (t, *J* = 6.1 Hz, 2H), 3.91 (s, 3H), 4.15–4.26 (m 4H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.12 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.17 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 14.0, 27.7, 29.6, 38.3, 44.7, 55.2, 58.5, 61.3, 105.4, 118.9, 126.7, 128.4, 128.5, 128.7, 129.0, 130.9, 133.5, 157.5, 171.0; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{27}O_5ClNa$ 429.1445; Found 429.1442.

Diethyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-(3-oxobutyl)malonate (**3af**)

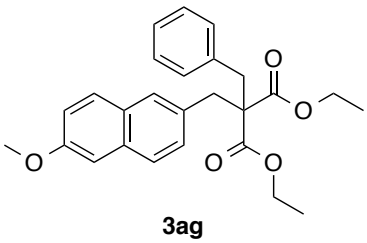


3af

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 85/15, 7/3) and preparative thin-layer chromatography (Toluene/EtOAc = 4/1×3). Colorless oil (84.8 mg, 0.212 mmol, 85% yield); IR (neat) 2980, 2905, 1731, 1606, 1485, 1175, 1030, 858, 757 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.1 Hz, 6H), 2.08–2.14 (m, 5H), 2.50–2.56 (m, 2H), 3.37 (s, 2H), 3.90 (s,

3H), 4.18 (q, J = 7.1 Hz, 4H), 7.08 (d, J = 2.6 Hz, 1H), 7.12 (dd, J = 8.9, 2.6 Hz, 1H), 7.17 (dd, J = 8.5, 1.6 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 26.4, 29.8, 38.8, 39.3, 55.2, 58.1, 61.3, 105.4, 118.8, 126.7, 128.4, 128.6, 128.7, 129.0, 130.8, 133.5, 157.5, 170.9, 207.2; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{28}O_6Na$ 423.1784; Found 423.1783.

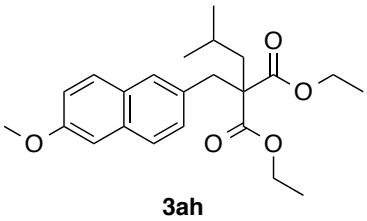
Diethyl 2-benzyl-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ag**)



3ag

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1 × 2). Pale yellow oil (95.7 mg, 0.228 mmol, 91% yield); IR (neat) 3030, 2980, 2938, 2904, 1730, 1606, 1485, 1265, 1034, 857, 756, 702 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.14 (t, J = 7.2 Hz, 6H), 3.27 (s, 2H), 3.35 (s, 2H), 3.91 (s, 3H), 4.11 (q, J = 7.2 Hz, 4H), 7.09–7.14 (m, 2H), 7.18–7.21 (m, 2H), 7.24–7.32 (m, 4H), 7.55 (d, J = 1.4 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.8, 39.1, 39.2, 55.2, 60.2, 61.2, 105.4, 118.8, 126.5, 126.8, 128.1, 128.7, 128.8, 129.1, 130.1, 131.4, 133.4, 136.3, 157.4, 171.0, one peak for aromatic carbon was not found probably due to overlapping; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{28}O_5Na$ 443.1834; Found 443.1830.

Diethyl 2-isobutyl-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ah**)

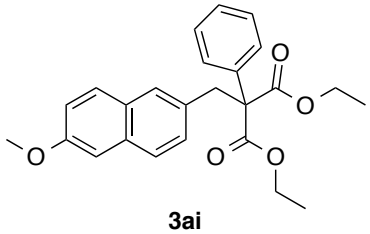


3ah

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1 × 2). Colorless oil (71.9 mg, 0.186 mmol, 75% yield); IR (neat) 2958, 2871, 1731, 1606, 1229, 1126, 1035, 856 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.91 (d, J = 6.8 Hz, 6H), 1.22 (t, J = 7.1 Hz, 6H), 1.79 (d, J = 5.9 Hz, 2H), 1.86–2.00 (m, 1H), 3.41 (s, 2H), 3.90 (s, 3H), 4.16 (q, J = 7.1 Hz, 4H), 7.08–7.13 (m, 2H), 7.18 (dd, J = 8.5, 1.6 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 23.6, 24.0, 38.7, 40.8, 55.2, 58.3, 61.0, 105.4, 118.7, 126.5,

128.6 (2C), 128.8, 129.0, 131.5, 133.4, 157.4, 171.8; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{30}O_5Na$ 409.1991; Found 409.1986.

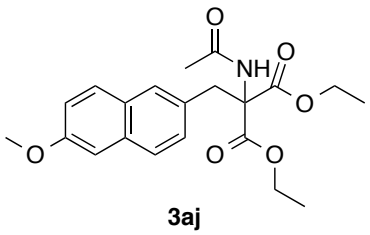
Diethyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-phenylmalonate (**3ai**)



3ai

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Pentane/EtOAc = 9/1 and Toluene/EtOAc = 19/1 × 2). Pale yellow oil (98.9 mg, 0.243 mmol, 97% yield); IR (neat) 3059, 2980, 2904, 1738, 1606, 1484, 1228, 1033, 857, 755 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.20 (t, *J* = 7.1 Hz, 6H), 3.73 (s, 2H), 3.89 (s, 3H), 4.21 (q, *J* = 7.1 Hz, 4H), 6.95 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.05–7.09 (m, 2H), 7.23–7.29 (m, 6H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.8, 42.9, 55.1, 61.5, 64.4, 105.3, 118.5, 125.9, 127.4, 127.8, 128.3, 128.5, 129.1 (2C), 129.2, 131.2, 133.3, 137.0, 157.4, 170.1; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{26}O_5Na$ 429.1678; Found 429.1677.

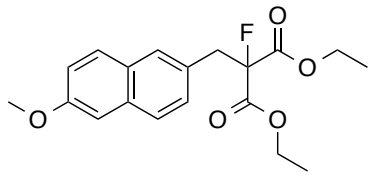
Diethyl 2-acetamido-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3aj**)



3aj

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 1/1 × 2). White solid (88.8 mg, 0.229 mmol, 91% yield); M.p. 136.7–137.9 ˚C; IR (KBr) 3266, 3048, 2986, 2941, 1747, 1644, 1515, 1187, 1030, 848, 667, 612 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.2 Hz, 6H), 2.04 (s, 3H), 3.78 (s, 2H), 3.91 (s, 3H), 4.29 (q, *J* = 7.2 Hz, 4H), 6.52 (brs, 1H), 7.06–7.14 (m, 3H), 7.40 (d, *J* = 0.81 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 22.9, 37.7, 55.2, 62.5, 67.3, 105.4, 118.9, 126.6, 128.2, 128.5, 128.7, 128.9, 130.2, 133.5, 157.5, 167.5, 169.1; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{25}NO_6Na$ 410.1580; Found 410.1580.

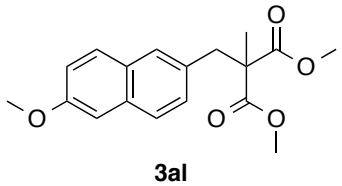
Diethyl 2-fluoro-2-((6-methoxynaphthalen-2-yl)methyl)malonate (**3ak**)



3ak

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1 × 3). Yellow oil (35.3 mg, 0.101 mmol, 40% yield); IR (neat) 2983, 2939, 1751, 1608, 1485, 1250, 1045, 857 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.23 (t, J = 7.1 Hz, 6H), 3.60 (d, J_{HF} = 25.7 Hz, 2H), 3.91 (s, 3H), 4.24 (q, J = 7.1 Hz, 4H), 7.09–7.15 (m, 2H), 7.32–7.36 (m, 1H), 7.65–7.69 (m, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 40.2 (d, J_{CF} = 20.6 Hz), 55.2, 62.6, 94.8 (d, J_{CF} = 202 Hz), 105.5, 118.9, 126.8, 128.1, 128.7 (2C), 129.1 (d, J_{CF} = 1.1 Hz), 129.2, 133.8, 157.7, 165.8 (d, J_{CF} = 25.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -165.4 (t, J_{HF} = 25.7 Hz); HRMS (ESI/TOF) *m/z*: [M+Na^+] Calcd for $C_{19}H_{21}FO_5Na$ 371.1271; Found 371.1278.

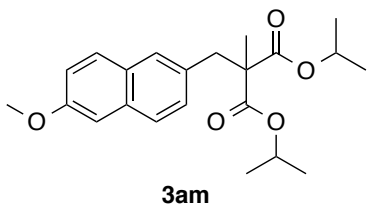
Dimethyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-methylmalonate (**3al**)



3al

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Toluene/EtOAc = 9/1 × 2). White solid (69.5 mg, 0.220 mmol, 88% yield); M.p. 118.0–118.8 ˚C; IR (KBr) 2990, 2940, 2845, 1733, 1604, 1441, 1232, 1113, 1027, 858, 678 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.39 (s, 3H), 3.36 (s, 2H), 3.74 (s, 6H), 3.91 (s, 3H), 7.09–7.14 (m, 2H), 7.18 (dd, J = 8.2, 1.6 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 19.8, 41.2, 52.5, 55.0, 55.2, 105.4, 118.8, 126.5, 128.7 (2C), 129.1, 131.1, 133.5, 157.5, 172.4. one peak for the aromatic carbon was not found probably due to overlapping; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{20}O_5Na$ 339.1208; Found 339.1210.

Diisopropyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-methylmalonate (**3am**)

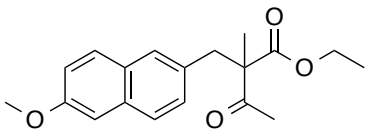


3am

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer

chromatography (Hexane/EtOAc = 9/1×2). Pale yellow oil (68.0 mg, 0.183 mmol, 73% yield); IR (neat) 2981, 2938, 1727, 1607, 1485, 1247, 1097, 1033, 854, 757 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.22 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H), 1.35 (s, 3H), 3.34 (s, 2H), 3.90 (s, 3H), 5.06 (sep, *J* = 6.2 Hz, 2H), 7.09–7.13 (m, 2H), 7.23 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.53 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 19.8, 21.5, 21.6, 40.8, 54.9, 55.2, 68.8, 105.5, 118.7, 126.4, 128.7, 128.8, 129.0 (2C), 131.5, 133.4, 157.4, 171.5; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{28}O_5Na$ 395.1834; Found 395.1844.

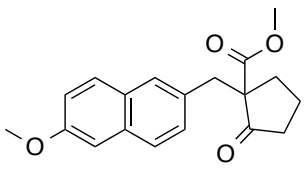
Ethyl 2-((6-methoxynaphthalen-2-yl)methyl)-2-methyl-3-oxobutanoate (**5aa**)



5aa

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 95/5, 9/1, 85/15). Pale yellow oil (70.4 mg, 0.224 mmol, 90% yield); IR (neat) 2982, 2938, 1712, 1606, 1484, 1231, 1095, 1030, 856, 757 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 2.18 (s, 3H), 3.18 (d, *J* = 13.8 Hz, 1H), 3.40 (d, *J* = 13.8 Hz, 1H), 3.91 (s, 3H), 4.14–4.27 (m, 2H), 7.09–7.14 (m, 2H), 7.18 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 19.1, 26.5, 40.4, 55.2, 60.9, 61.4, 105.4, 118.8, 126.5, 128.7 (2C), 128.8, 129.0, 131.5, 133.4, 157.4, 172.4, 205.5; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{22}O_4Na$ 337.1416; Found 337.1404.

Methyl 1-((6-methoxynaphthalen-2-yl)methyl)-2-oxocyclopentanecarboxylate (**5ab**)

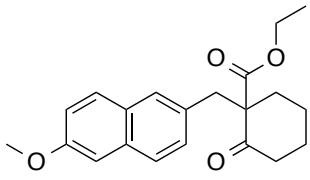


5ab

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Toluene/EtOAc = 9/1). Light brown solid (76.8 mg, 0.246 mmol, 98% yield); M.p. 92.7–94.4 ˚C; IR (KBr) 2963, 2946, 2896, 1748, 1720, 1605, 1487, 1230, 1198, 1024, 850, 822 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.51–1.65 (m, 1H), 1.79–1.93 (m, 1H), 1.95–2.09 (m, 2H), 2.32–2.48 (m, 2H), 3.27 (d, *J* = 13.8 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.74 (s, 3H), 3.91 (s, 3H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.21 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.52 (s, 1H), 7.64 (d,

J = 9.2 Hz, 1H), 7.67 (d, J = 9.5 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 19.4, 31.6, 38.3, 39.0, 52.6, 55.2, 61.6, 105.4, 118.9, 126.8, 128.7 (3C), 129.1, 131.6, 133.3, 157.5, 171.4, 215.0; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}O_4Na$ 335.1259; Found 335.1250.

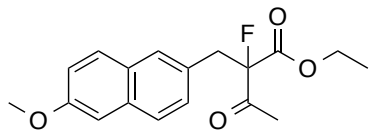
Ethyl 1-((6-methoxynaphthalen-2-yl)methyl)-2-oxocyclohexanecarboxylate (**5ac**)



5ac

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Toluene/EtOAc = 9/1 × 2). White solid (62.9 mg, 0.185 mmol, 74% yield); M.p. 81.0–83.0 ˚C; IR (KBr) 2939, 2862, 1735, 1710, 1606, 1487, 1185, 1125, 1030, 855, 830 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.14 (t, J = 7.2 Hz, 3H), 1.44–1.77 (m, 4H), 1.96–2.06 (m, 1H), 2.37–2.55 (m, 3H), 3.03 (d, J = 13.9 Hz, 1H), 3.42 (d, J = 13.9 Hz, 1H), 3.91 (s, 3H), 4.00–4.17 (m, 2H), 7.09–7.13 (m, 2H), 7.23 (dd, J = 8.4, 1.4 Hz, 1H), 7.50 (d, J = 1.4 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.65 (d, J = 9.5 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 22.5, 27.5, 35.9, 40.3, 41.2, 55.2, 61.2, 62.3, 105.4, 118.6, 126.2, 128.7, 128.8, 129.0, 129.1, 131.8, 133.3, 157.3, 171.1, 207.4; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{24}O_4Na$ 363.1572; Found 363.1572.

Ethyl 2-fluoro-2-((6-methoxynaphthalen-2-yl)methyl)-3-oxobutanoate (**5ad**)

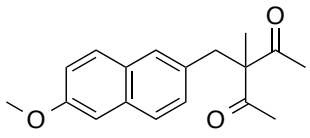


5ad

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1 × 3). White solid (41.9 mg, 0.132 mmol, 53% yield); M.p. 62.2–64.6 ˚C; IR (KBr) 2992, 2939, 1752, 1731, 1607, 1192, 1028, 856, 813 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.24 (t, J = 7.2 Hz, 3H), 2.12 (d, J_{CF} = 5.4 Hz, 3H), 3.43–3.65 (m, 2H), 3.92 (s, 3H), 4.17–4.28 (m, 2H), 7.10 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 8.8, 2.5 Hz, 1H), 7.29–7.33 (m, 1H), 7.61 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.9, 26.3, 39.7 (d, J_{CF} = 20.7 Hz), 55.2, 62.6, 100.2 (d, J_{CF} = 200 Hz), 105.4, 119.0, 126.8, 128.1, 128.7 (d, J_{CF} =3.4 Hz), 128.7, 129.1, 129.2 (d, J_{CF} = 4.5 Hz), 133.7, 157.7, 165.7 (d, J_{CF} = 25.7 Hz), 202.6 (d, J_{CF} = 29.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -165.3 –

-165.4 (m); HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{19}FO_4Na$ 341.1165; Found 341.1155.

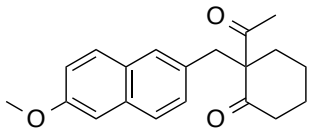
3-((6-Methoxynaphthalen-2-yl)methyl)-3-methylpentane-2,4-dione (**5ae**)



5ae

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 9/1×2 and Pentane/EtOAc = 4/1×2). Colorless oil (53.5 mg, 0.188 mmol, 75% yield); IR (neat) 3058, 2999, 2937, 2841, 1697, 1606, 1484, 1358, 1229, 1031, 855, 756 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.33 (s, 3H), 2.13 (s, 6H), 3.31 (s, 2H), 3.91 (s, 3H), 7.09 (d, *J* = 2.6 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.15 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 18.3, 27.3, 40.2, 55.2, 67.4, 105.4, 118.9, 126.7, 128.6, 128.7 (2C), 129.1, 131.5, 133.3, 157.5, 207.2; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{20}O_3Na$ 307.1310; Found 307.1306.

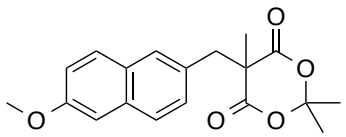
2-Acetyl-2-((6-methoxynaphthalen-2-yl)methyl)cyclohexanone (**5af**)



5af

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by silica gel column chromatography (Hexane/EtOAc = 95/5, 9/1, 4/1) and preparative thin-layer chromatography (Toluene/EtOAc = 9/1×2). Light brown solid (32.1 mg, 0.103 mmol, 41% yield); M.p. 85.3–86.3 ˚C; IR (KBr) 2960, 2937, 2868, 1690, 1607, 1485, 1265, 1233, 1165, 1121, 1033, 849, 817 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.42–1.74 (m, 4H), 1.91–2.03 (m, 1H), 2.12 (s, 3H), 2.20–2.32 (m, 1H), 2.36–2.44 (m, 1H), 2.49–2.57 (m, 1H), 3.25 (s, 2H), 3.91 (s, 3H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.12 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 22.2, 26.9 (2C), 33.9, 39.8, 42.0, 55.2, 68.8, 105.4, 118.8, 126.5, 128.7, 128.8, 129.0, 129.1, 131.3, 133.3, 157.5, 206.0, 209.5; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{22}O_3Na$ 333.1467; Found 333.1456.

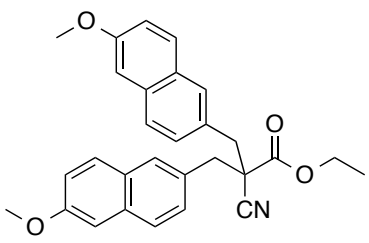
5-((6-Methoxynaphthalen-2-yl)methyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (**5ag**)



5ag

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 4/1). Pale yellow solid (69.9 mg, 0.213 mmol, 85% yield); M.p. 139.1–140.9 ˚C; IR (KBr) 2994, 2943, 1768, 1736, 1606, 1336, 1284, 1066, 816 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.79 (s, 3H), 1.57–1.58 (m, 3H), 1.79 (s, 3H), 3.46 (s, 2H), 3.90 (s, 3H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.12 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.25 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 9.7 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 25.8, 28.3, 29.3, 44.9, 52.2, 55.2, 105.2, 105.3, 119.0, 127.1, 128.3, 128.7, 128.9, 129.4, 130.3, 133.8, 157.7, 169.9; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{20}O_5Na$ 351.1208; Found 351.1209.

Ethyl 2-cyano-3-(6-methoxynaphthalen-2-yl)-2-((6-methoxynaphthalen-2-yl)methyl)propanoate (**5ah**)

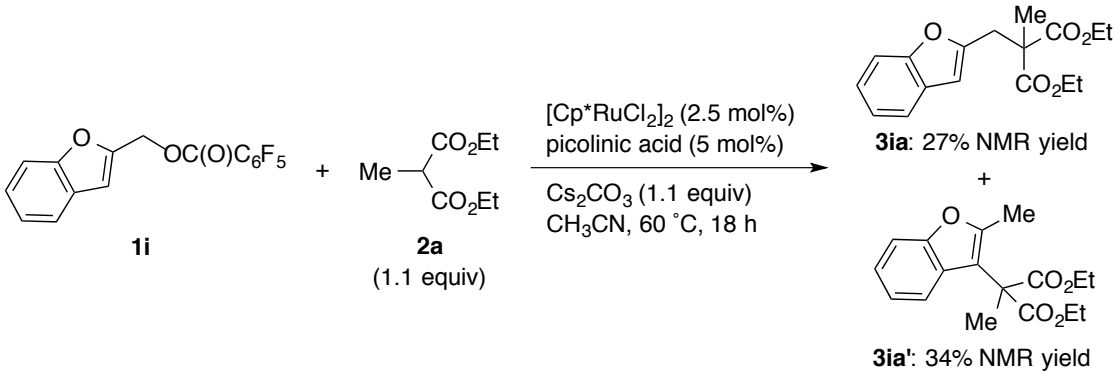


5ah

This compound was prepared according to the same method to **3aa** and the desired product was obtained after purification by preparative thin-layer chromatography (Hexane/EtOAc = 85/15 × 2 and Toluene/EtOAc = 9/1 × 2). Brown solid (35.0 mg, 0.0772 mmol, 62% yield); M.p. 106.5–107.7 ˚C; IR (KBr) 2965, 2939, 2246, 1733, 1606, 1484, 1392, 1237, 1198, 1027, 857 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.1 Hz, 3H), 3.27 (d, *J* = 13.5 Hz, 2H), 3.50 (d, *J* = 13.5 Hz, 2H), 3.92 (s, 6H), 3.97 (q, *J* = 7.1 Hz, 2H), 7.11–7.16 (m, 4H), 7.41 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.69–7.72 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.6, 43.3, 53.4, 55.3, 62.6, 105.5, 118.8, 119.1, 127.0, 128.3, 128.7, 128.9, 129.2, 129.3, 134.0, 157.8, 168.4; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{27}NO_4Na$ 476.1838; Found 476.1833.

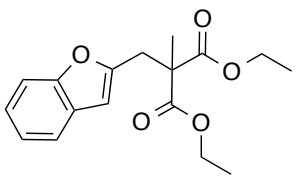
4. Experimental details for the mechanistic experiments

Scheme S5. Reaction of benzofuran-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (**1i**)



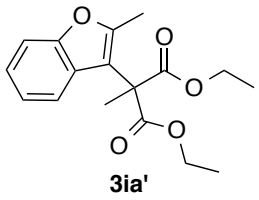
Benzofuran-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (**1i**) (85.6 mg, 0.25 mmol), $[Cp^*RuCl_2]_2$ (3.8 mg, 0.00625 mmol, 0.025 equiv), picolinic acid (**L1**) (1.5 mg, 0.0125 mmol, 0.05 equiv), Cs_2CO_3 (89.6 mg, 0.275 mmol, 1.1 equiv) were charged into a screw cap vial. The resulting mixture was carefully evacuated and refilled with N_2 five times. After the addition of CH_3CN (1 mL) and diethyl methylmalonate (**2a**) (47 μL, 0.275 mmol, 1.1 equiv), the resulting yellow suspension was stirred at 60 ˚C for 18 h. The reaction was allowed to cool to room temperature and quenched with water (1 mL). The resulting aqueous phase was extracted with EtOAc (3 mL × 1). The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the yields of benzylic alkylation product **3ia** and aromatic substitution **3ia'** were determined to be 27% and 34%, respectively, by ^{1}H NMR analyses of the crude reaction mixture. The resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 95/5) and preparative thin-layer chromatography (Pentane/EtOAc = 95/5) to give **3ia** in 18% yield (13.4 mg, 0.0440 mmol, 18% yield) and **3ia'** in 19% yield (14.8 mg, 0.0486 mmol, 19% yield), respectively.

Diethyl 2-(benzofuran-2-ylmethyl)-2-methylmalonate (**3ia**)[1]


3ia

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, J = 7.0 Hz, 6H), 1.46 (s, 3H), 3.41 (s, 2H), 4.19–4.28 (m, 4H), 6.47 (s, 1H), 7.17 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H), 7.21 (ddd, J = 7.6, 7.6, 1.7 Hz, 1H), 7.36–7.38 (m, 1H), 7.48 (dd, J = 7.0, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.0, 19.9, 34.5, 53.7, 61.6, 105.3, 110.9, 120.5, 122.5, 123.6, 128.5, 154.1, 154.8, 171.4; GC-MS (EI) m/z: 304 $[M]^+$.

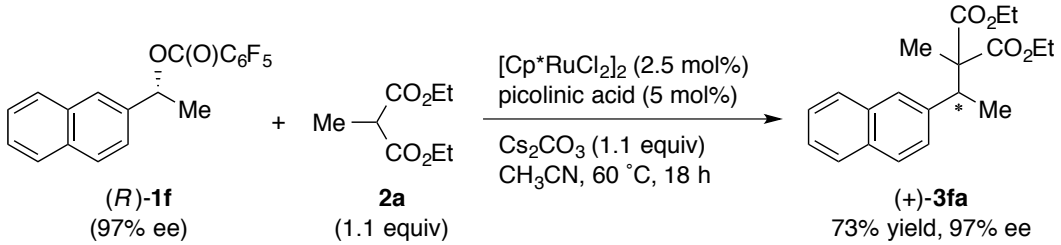
Diethyl 2-methyl-2-(2-methylbenzofuran-3-yl)malonate (**3ia'**)



3ia'

IR (neat) 2983, 2939, 1733, 1603, 1586, 1455, 1242, 1110, 1021, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.0 H, 6H), 1.95 (s, 3H), 2.38 (s, 3H), 4.19–4.32 (m, 4H), 7.14 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.19 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 22.3, 53.7, 61.9, 110.7, 112.9, 120.5, 122.1, 123.2, 128.1, 151.4, 153.3, 170.9, one peak was not found probably due to overlapping; HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{20}O_5Na$ 327.1208; Found 327.1211.

Scheme S6. Reaction of (*R*)-1-(naphthalen-2-yl)ethyl 2,3,4,5,6-pentafluorobenzoate ((*R*)-**1f**)



Preparation of (*R*)-1-(naphthalen-2-yl)ethyl 2,3,4,5,6-pentafluorobenzoate ((*R*)-**1f**):

(*R*)-**1f** was prepared according to the our previously reported method using (*R*)-1-(2-naphthyl)methanol as a chiral alcohol.[1] Pale yellow solid (941 mg, 2.57 mmol, 88% yield, 97% ee). $[\alpha]_D^{28}$ = –13.3 (*c* 1.02, $CHCl_3$); HPLC conditions: DAICEL CHIRALPAK AD-H, Hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 224 nm, retention time; t_R (major) = 6.34 min, t_R (minor) = 7.82 min.

Reaction of (*R*)-**1f** with diethyl methylmalonate (**2a**):

(*R*)-1-(Naphthalen-2-yl)ethyl 2,3,4,5,6-pentafluorobenzoate ((*R*)-**1f**)) (91.6 mg, 0.25 mmol), $[Cp^*RuCl_2]_2$ (3.8 mg, 0.00625 mmol, 0.025 equiv), picolinic acid (**L1**) (1.5 mg, 0.0125 mmol, 0.05 equiv), Cs_2CO_3 (89.6 mg, 0.275 mmol, 1.1 equiv) were charged into a screw cap vial. The resulting mixture was carefully evacuated and refilled with N_2 five times. After the addition of CH_3CN (1 mL) and diethyl methylmalonate (**2a**) (47 μL, 0.275 mmol, 1.1 equiv), the resulting yellow suspension was stirred at 60 ˚C for 18 h. The reaction was allowed to cool to room temperature and quenched with water (1

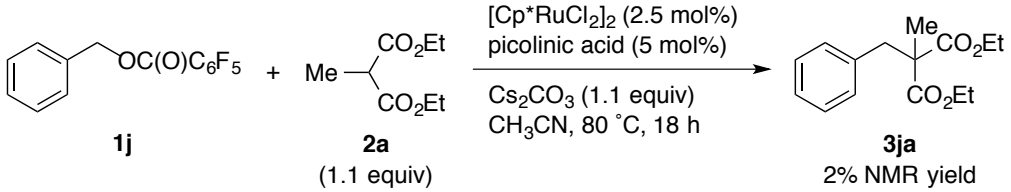
mL). The resulting aqueous phase was extracted with EtOAc (3 mL × 1). The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 97/3, 95/5, 92/8) and preparative thin-layer chromatography (Toluene/EtOAc = 9/1) to give (+)-**3fa** as a colorless oil (60.1 mg, 0.183 mmol, 73% yield, 97% ee).

(+)-Diethyl 2-methyl-2-(1-(naphthalen-2-yl)ethyl)malonate ((+)-**3fa**)

$[\alpha]_D^{28}$ = +60.1 (*c* 0.91, $CHCl_3$); HPLC conditions: DAICEL CHIRALPAK AD-H, Hexane/*i*-PrOH = 49/1, flow rate = 1.0 mL/min, λ = 224 nm, retention time; t_R (minor) = 7.94 min, t_R (major) = 9.19 min.

5. Experimental details for the reaction of non-fused aromatic substrates

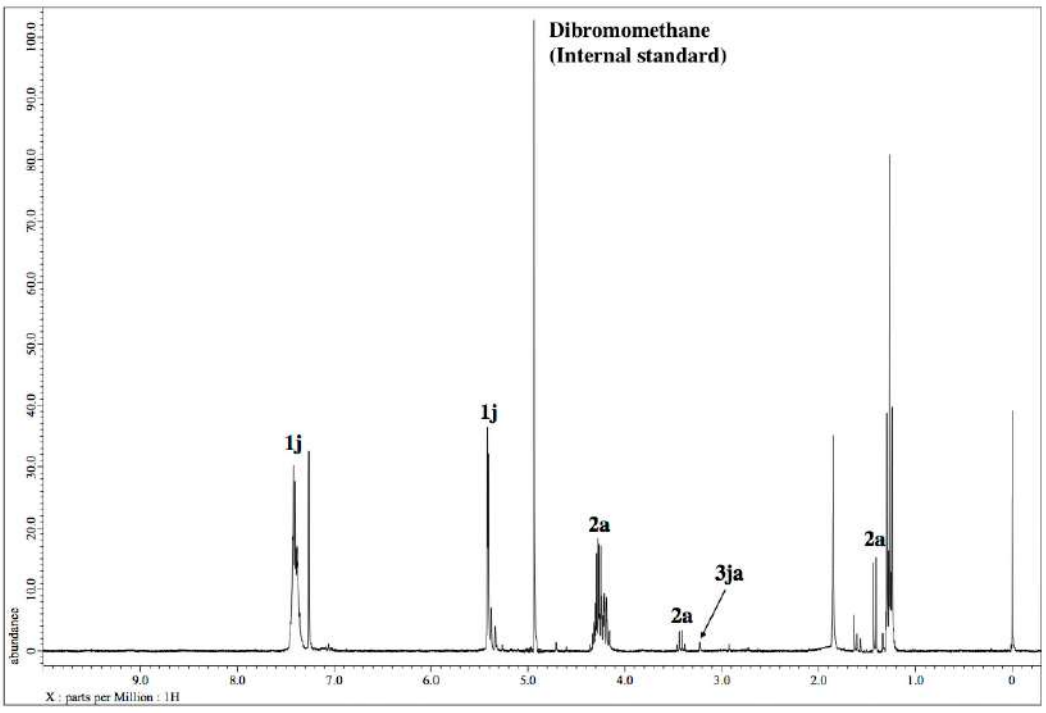
Scheme S7. Reaction of benzyl 2,3,4,5,6-pentafluorobenzoates (**1j**):



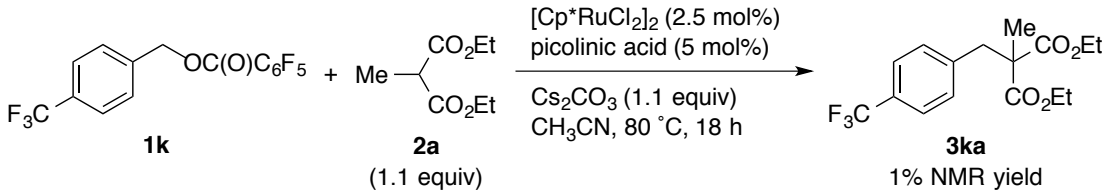
1j **2a** (1.1 equiv) **3ja** 2% NMR yield

Benzyl 2,3,4,5,6-pentafluorobenzoate (**1j**) (75.6 mg, 0.25 mmol), $[Cp^*RuCl_2]_2$ (3.8 mg, 0.00625 mmol, 0.025 equiv), picolinic acid (**L1**) (1.5 mg, 0.0125 mmol, 0.05 equiv), Cs_2CO_3 (89.6 mg, 0.275 mmol, 1.1 equiv) were charged into a screw cap vial. The resulting mixture was carefully evacuated and refilled with N_2 five times. After the addition of CH_3CN (1 mL) and diethyl methylmalonate (**2a**) (47 μL, 0.275 mmol, 1.1 equiv), the resulting yellow suspension was stirred at 80 ˚C for 18 h. The reaction was allowed to cool to room temperature and quenched with water (1 mL). The resulting aqueous phase was extracted with EtOAc (3 mL × 1). The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the yield of benzylic alkylation product **3ja** was determined to be 2% by ^{1}H NMR analyses of the crude reaction mixture.

Chart S1. ^{1}H NMR spectrum of the reaction of **1j**

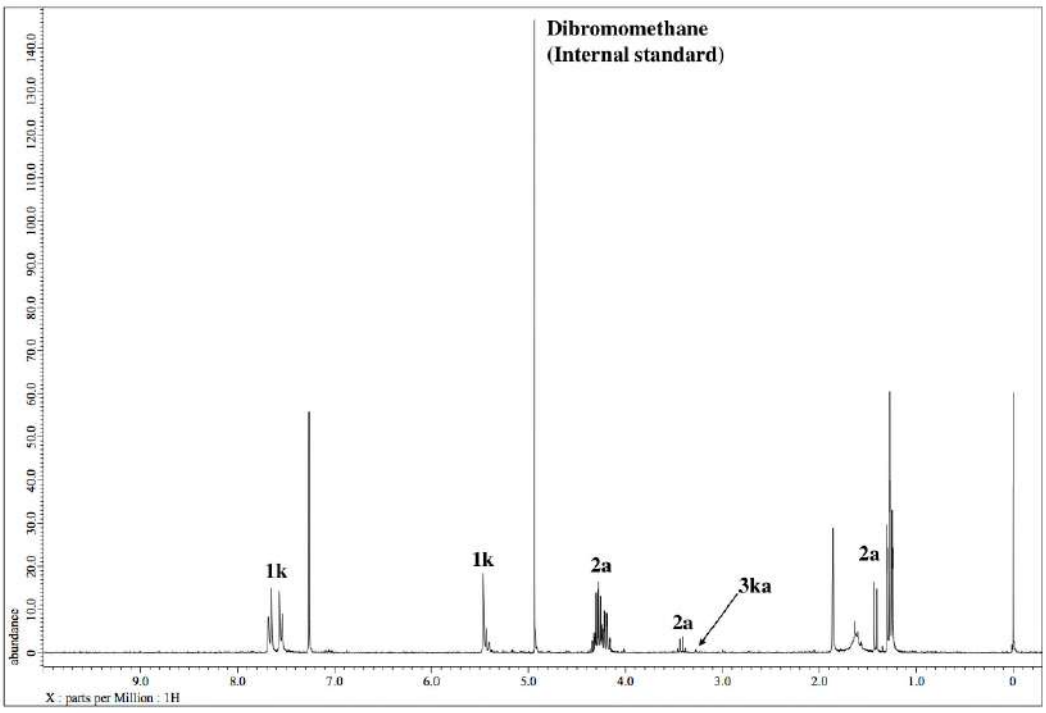


Scheme S8. Reaction of 4-(trifluoromethyl)benzyl 2,3,4,5,6-pentafluorobenzoates (**1k**)



4-(Trifluoromethyl)benzyl 2,3,4,5,6-pentafluorobenzoate (**1k**) (92.6 mg, 0.25 mmol), $[Cp^*RuCl_2]_2$ (3.8 mg, 0.00625 mmol, 0.025 equiv), picolinic acid (**L1**) (1.5 mg, 0.0125 mmol, 0.05 equiv), Cs_2CO_3 (89.6 mg, 0.275 mmol, 1.1 equiv) were charged into a screw cap vial. The resulting mixture was carefully evacuated and refilled with N_2 five times. After the addition of CH_3CN (1 mL) and diethyl methylmalonate (**2a**) (47 μL, 0.275 mmol, 1.1 equiv), the resulting yellow suspension was stirred at 80 ˚C for 18 h. The reaction was allowed to cool to room temperature and quenched with water (1 mL). The resulting aqueous phase was extracted with EtOAc (3 mL × 1). The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the yield of benzylic alkylation product **3ka** was determined to be 1% by ^{1}H NMR analyses of the crude reaction mixture.

Chart S2. ^{1}H NMR spectrum of the reaction of **1k**



6. References

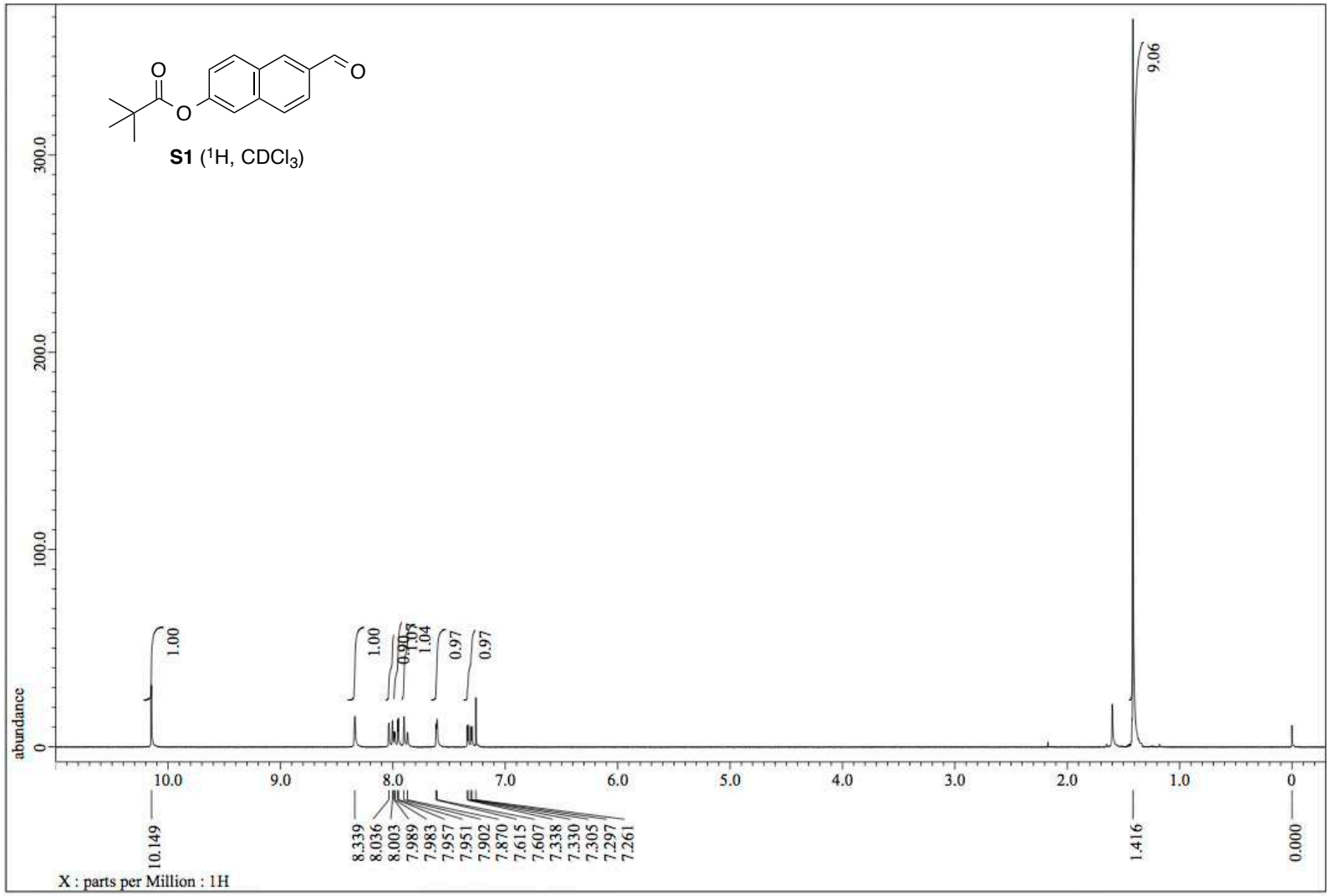
1. Tsuji, H.; Hashimoto, K.; Kawatsura, M. *Org. Lett.* **2019**, *21*, 8837–8841.

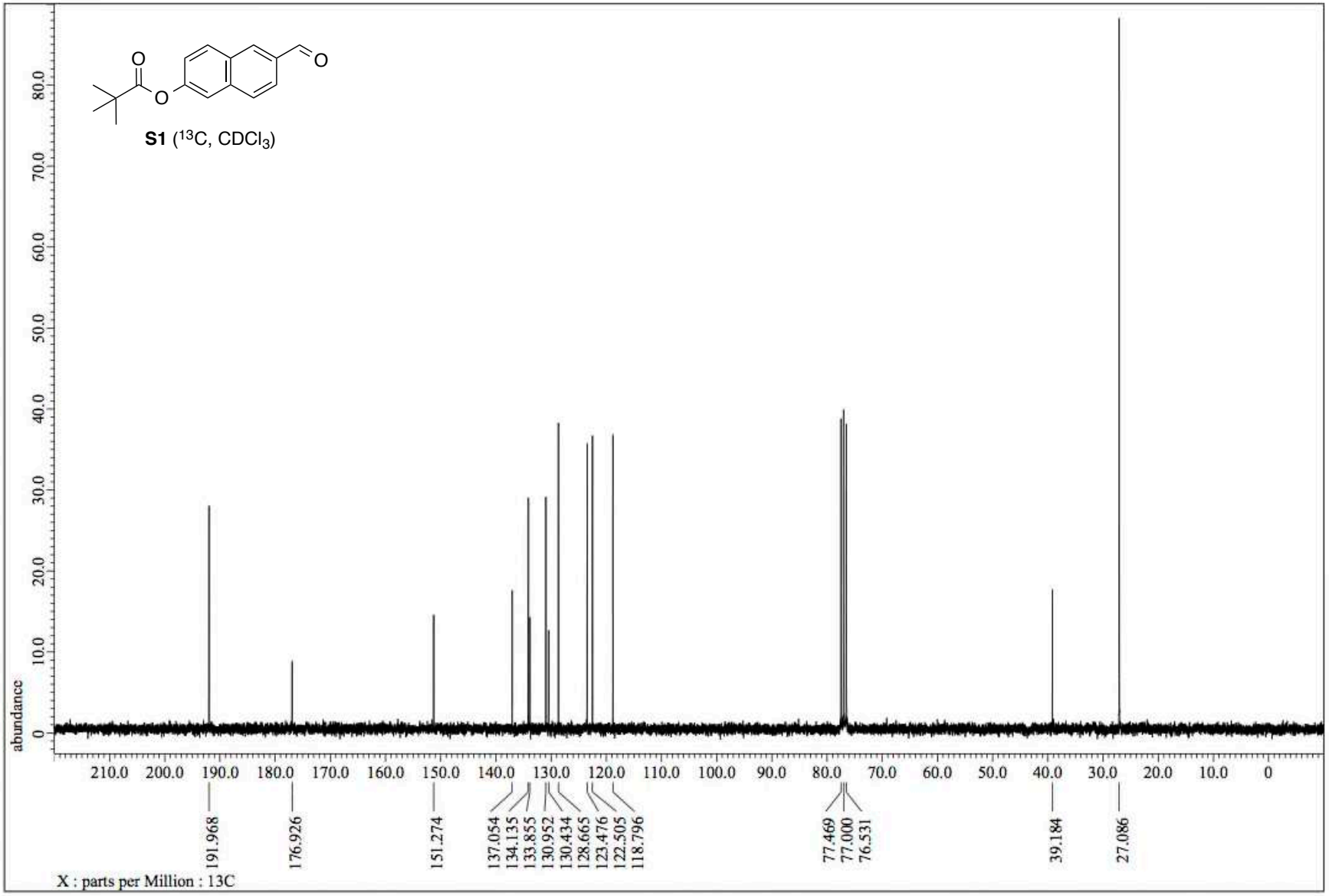
2. Mercier, A.; Yeo, W. C.; Chou, J.; Chaudhuri, P. D.; Bernardinelli, G.; Kündig, E. P. *Chem. Commun.* **2009**, 5227–5229.

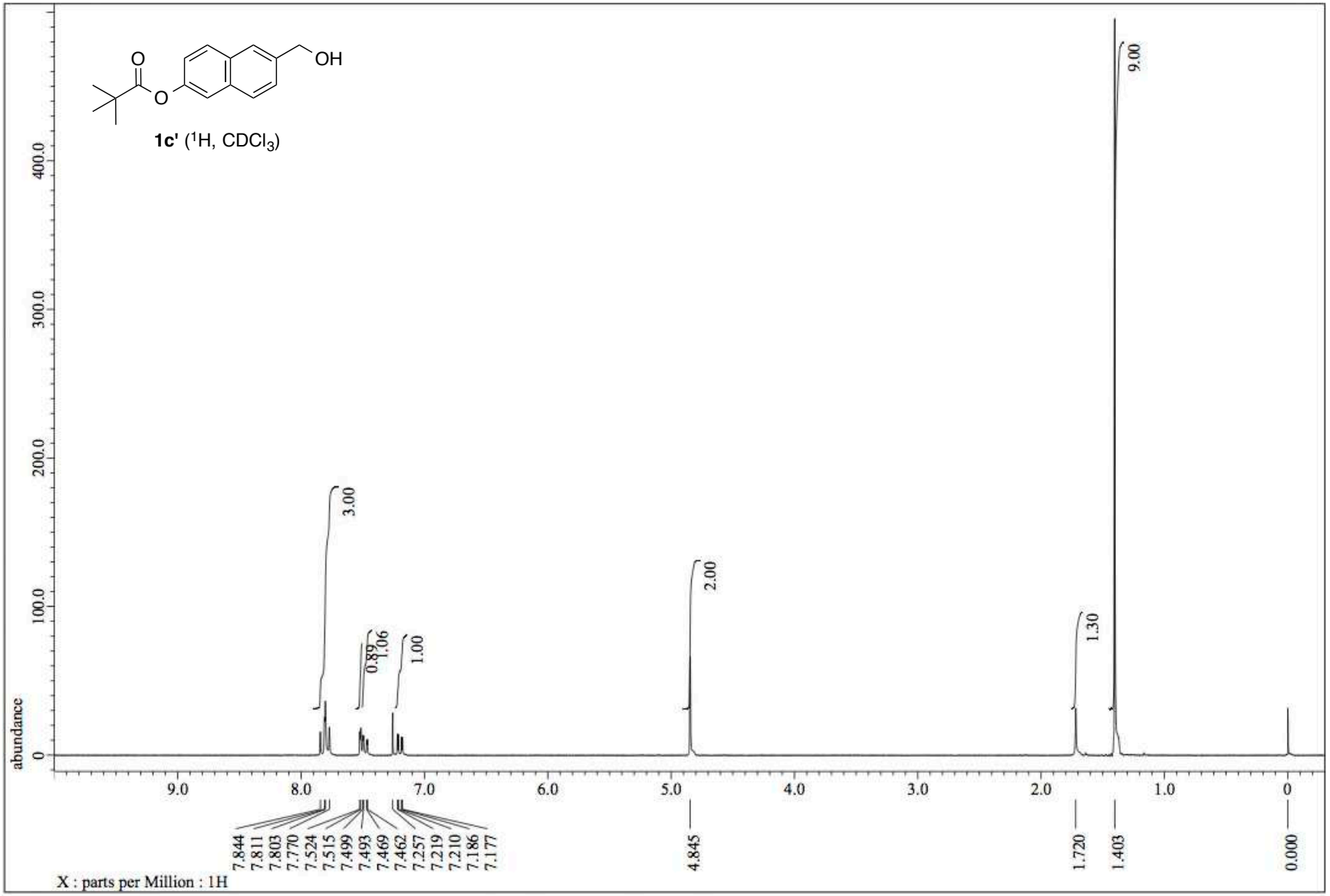
3. Beckendorf, S.; Mancheño, O. G. *Synthesis* **2012**, *44*, 2162–2172.

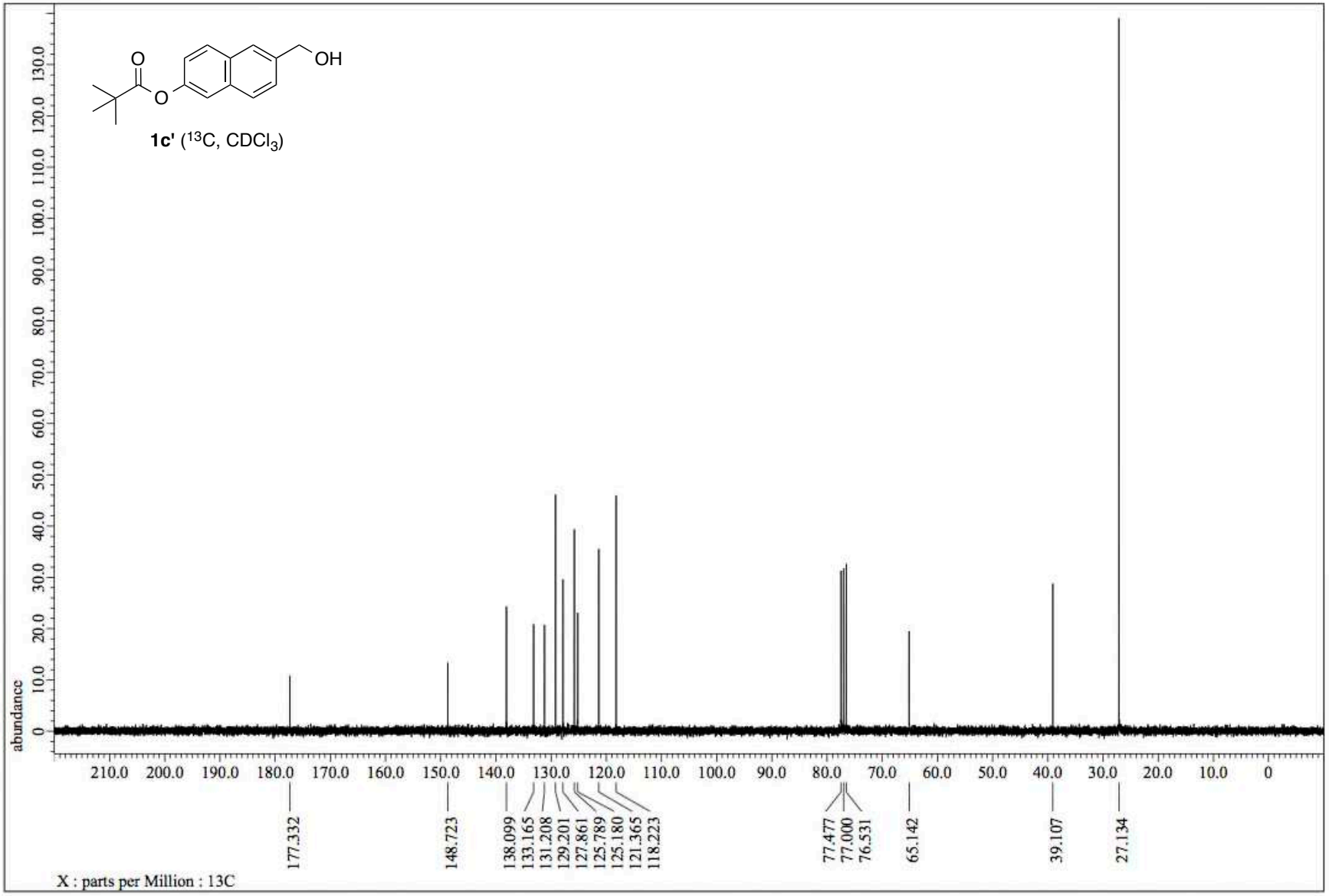
4. Kuwano, R.; Kondo, Y.; Matsuyama, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12104–12105.

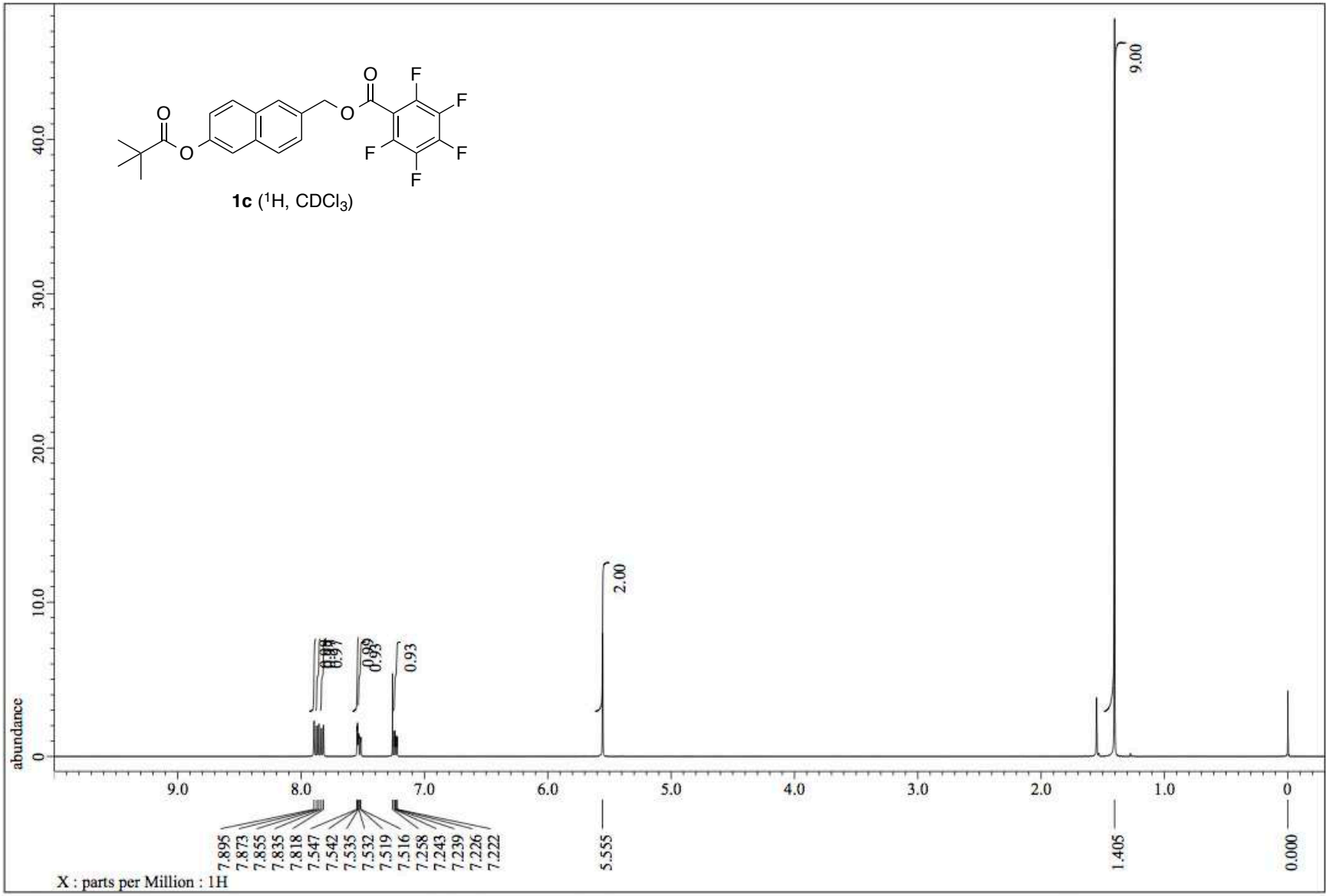
7. Copies of NMR spectra (^{1}H, ^{13}C, and ^{19}F) and HPLC chromatograms

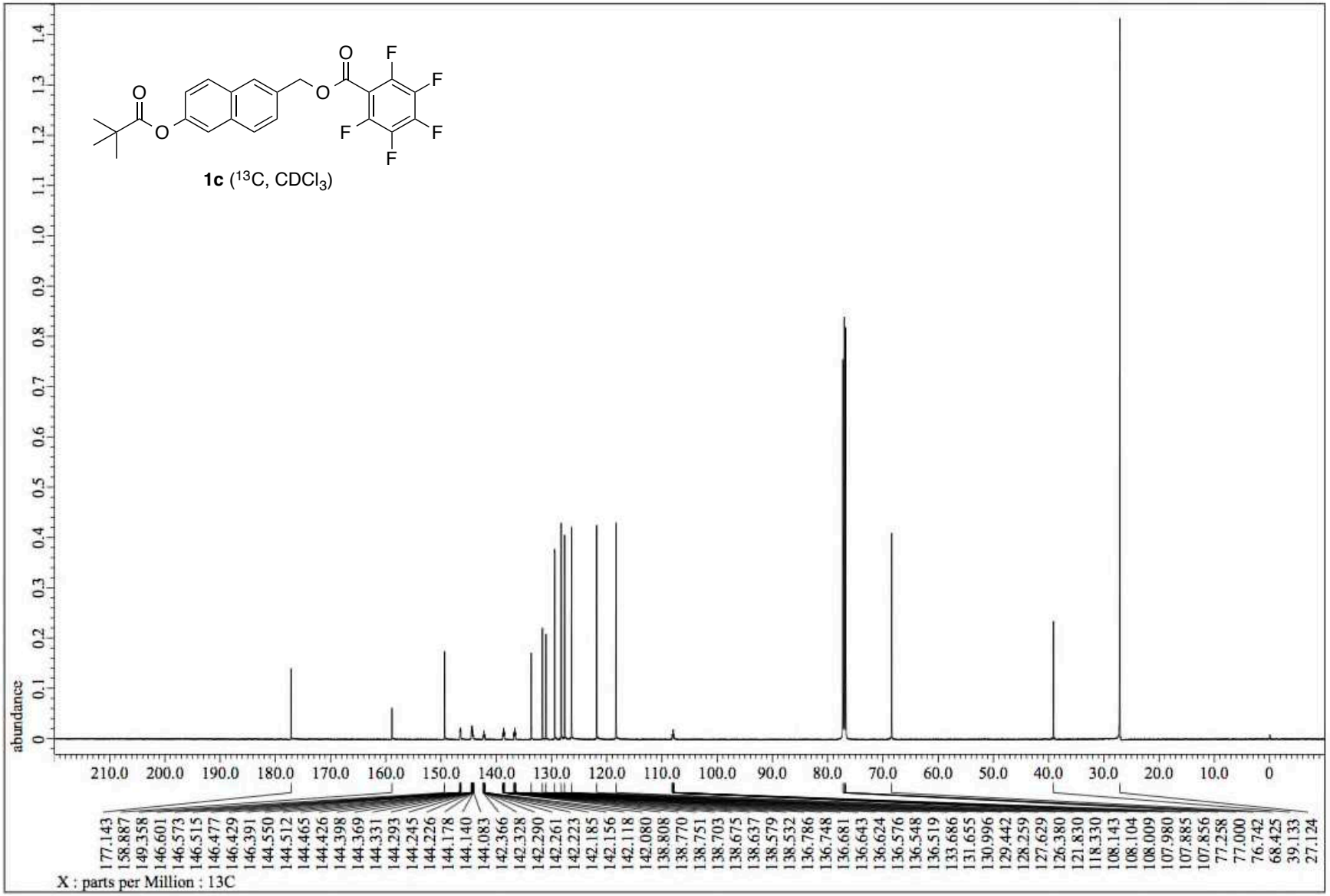


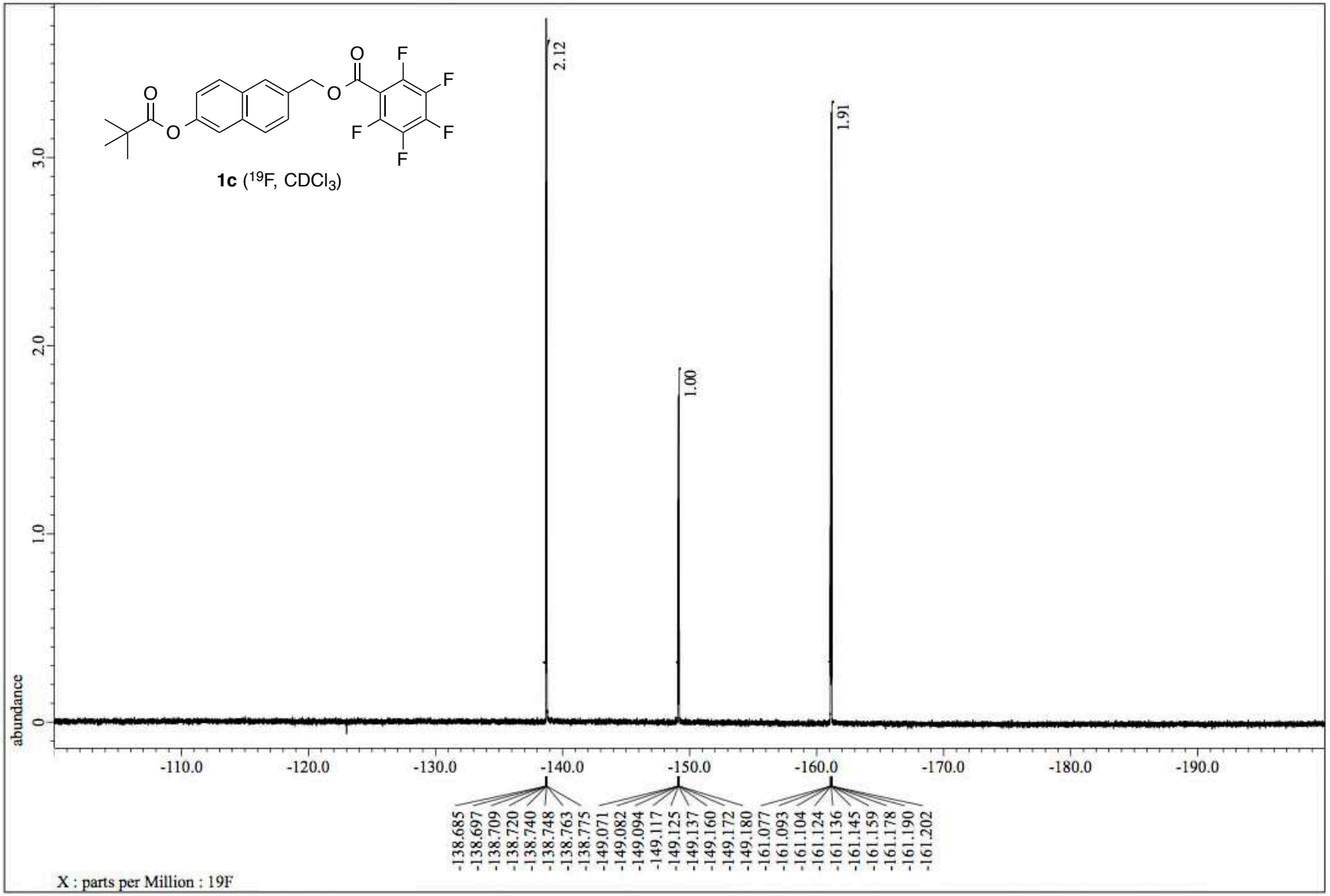

S1 (13C, CDCl3)
abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.968
176.926
151.274
137.054
134.135
133.855
130.952
130.434
128.665
123.476
122.505
118.796
77.469
77.000
76.531
39.184
27.086
X : parts per Million : 13C

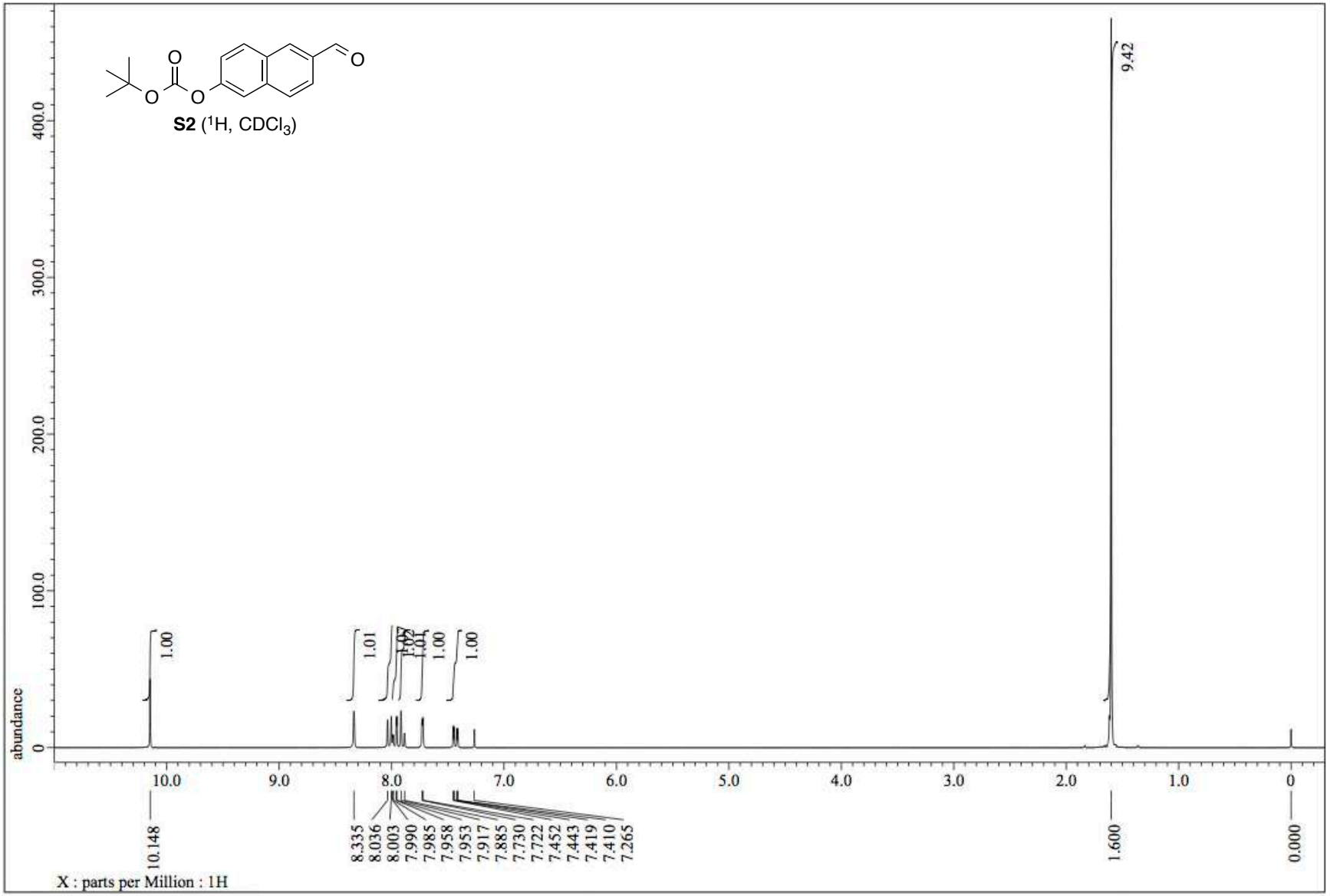

O
O
OH
1c' (1H, CDCl3)
abundance
400.0
300.0
200.0
100.0
0
3.00
0.89
1.06
1.00
2.00
1.30
9.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.844
7.811
7.803
7.770
7.524
7.515
7.499
7.493
7.469
7.462
7.257
7.219
7.210
7.186
7.177
4.845
1.720
1.403
0.000
X : parts per Million : 1H

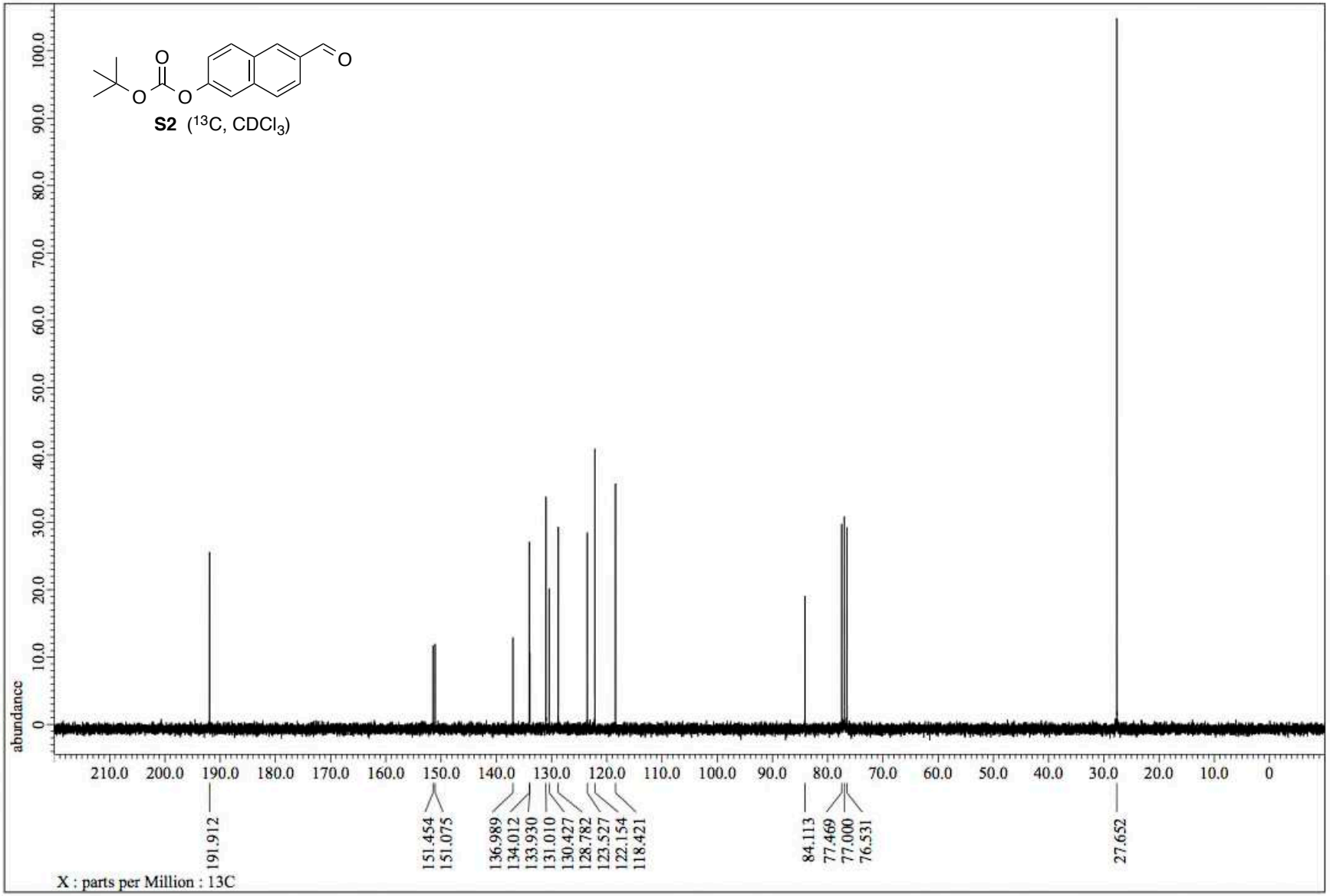

O
O
OH
1c' (13C, CDCl3)
abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
177.332
148.723
138.099
133.165
131.208
129.201
127.861
125.789
125.180
121.365
118.223
77.477
77.000
76.531
65.142
39.107
27.134
X : parts per Million : 13C

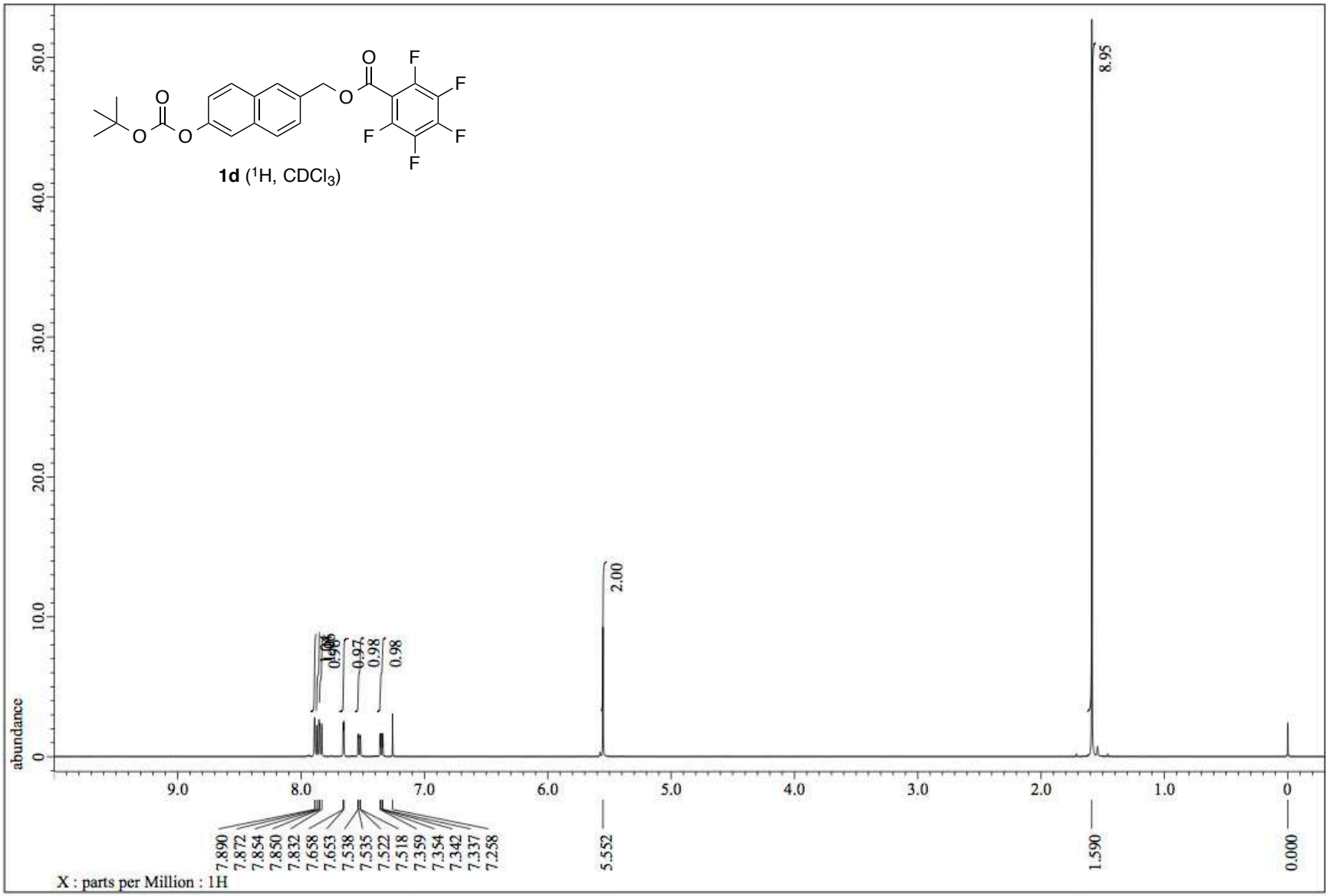

O
O
O
F
F
F
F
F
1c (1H, CDCl3)
abundance
40.0
30.0
20.0
10.0
0
9.00
2.00
0.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.895
7.873
7.855
7.835
7.818
7.547
7.542
7.535
7.532
7.519
7.516
7.258
7.243
7.239
7.226
7.222
5.555
1.405
0.000
X : parts per Million : 1H

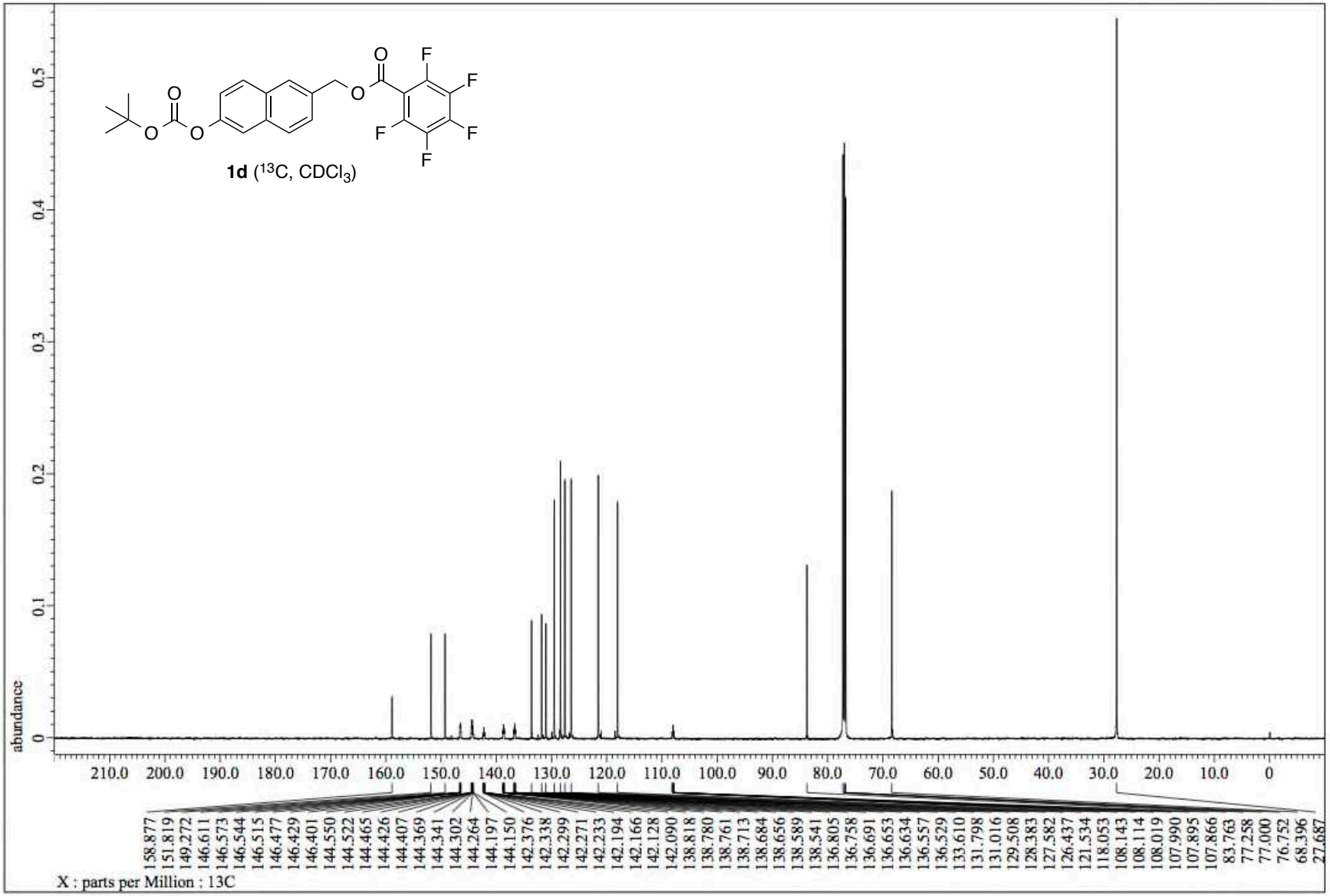

1c (13C, CDCl3)
abundance
X : parts per Million : 13C

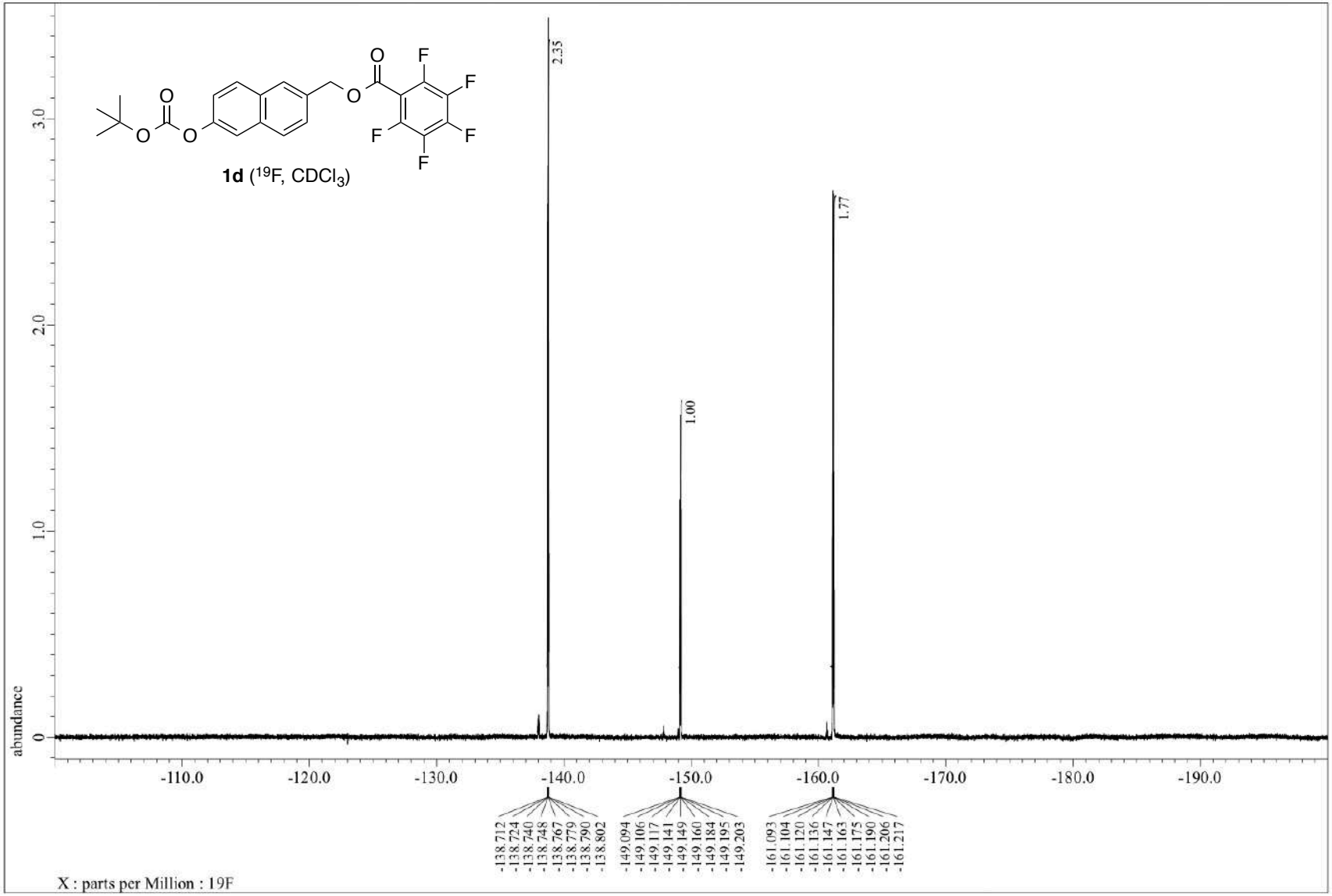

1c (19F, CDCl3)
2.12
1.91
1.00
abundance
X : parts per Million : 19F
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
-138.685
-138.697
-138.709
-138.720
-138.740
-138.748
-138.763
-138.775
-149.071
-149.082
-149.094
-149.117
-149.125
-149.137
-149.160
-149.172
-149.180
-161.077
-161.093
-161.104
-161.124
-161.136
-161.145
-161.159
-161.178
-161.190
-161.202

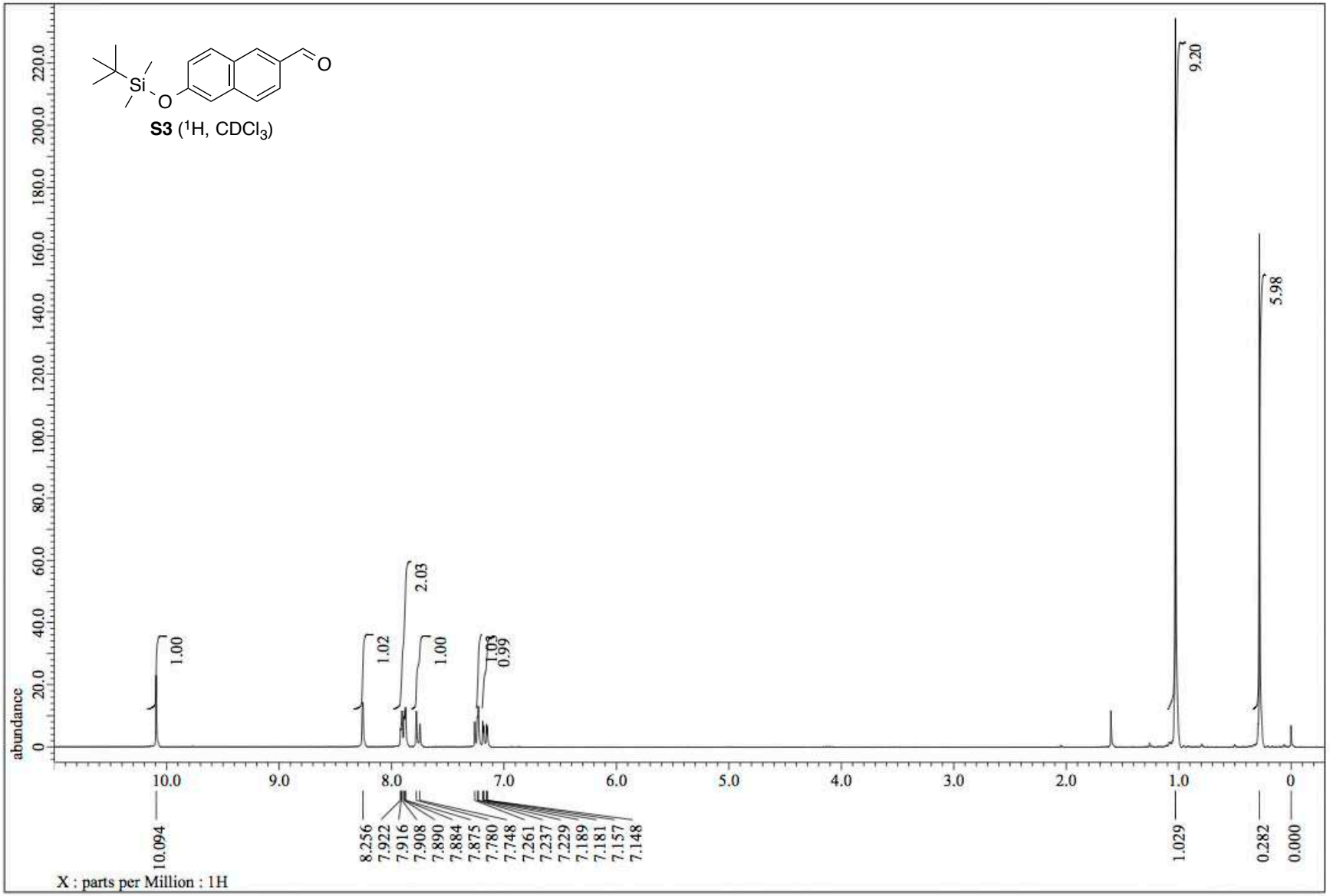

S2 (1H, CDCl3)
abundance
X : parts per Million : 1H
9.42
1.00
1.01
1.00
1.00
10.148
8.335
8.036
8.003
7.990
7.985
7.958
7.953
7.917
7.885
7.730
7.722
7.452
7.443
7.419
7.410
7.265
1.600
0.000

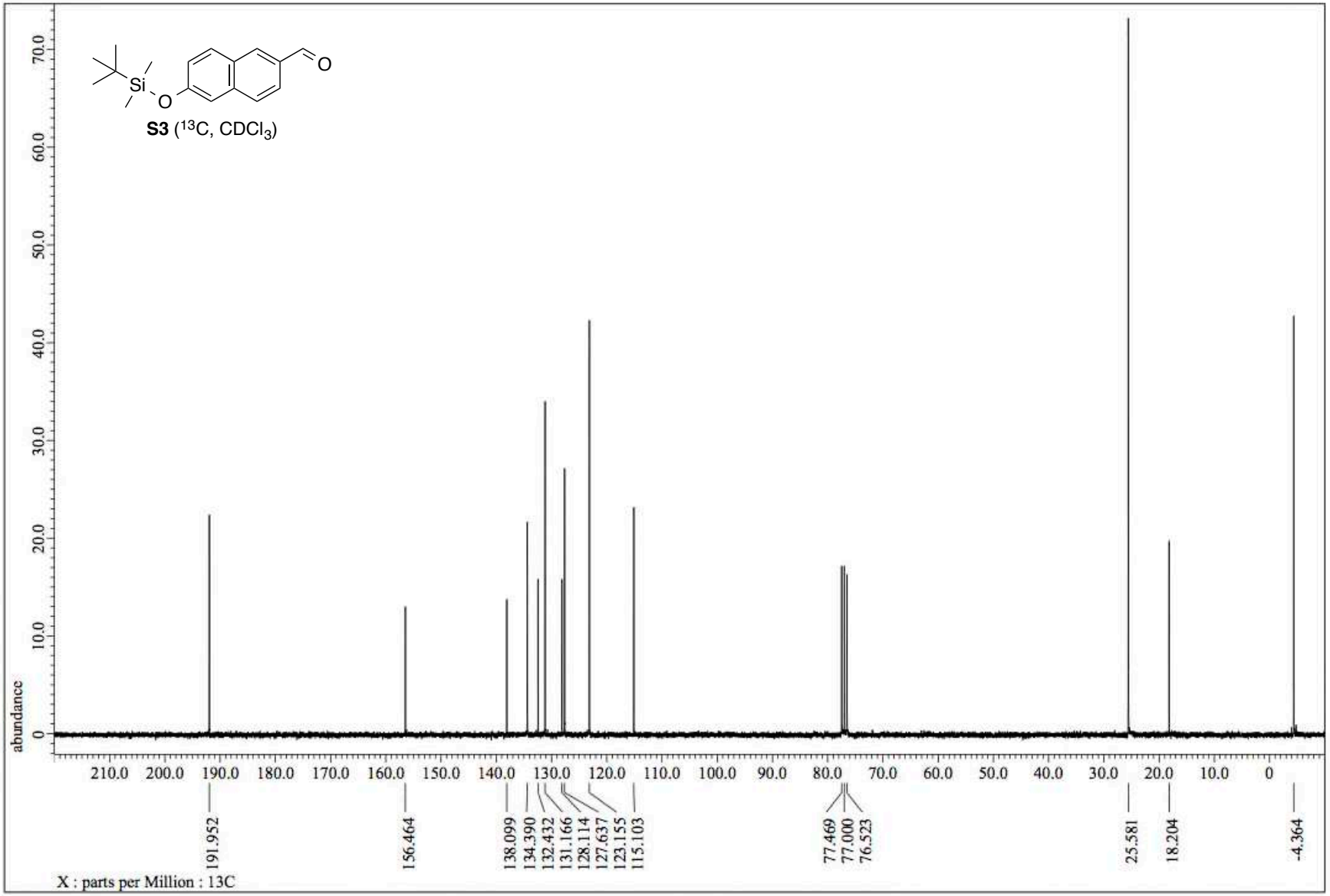

S2 (13C, CDCl3)
abundance
X : parts per Million : 13C
191.912
151.454
151.075
136.989
134.012
133.930
131.010
130.427
128.782
123.527
122.154
118.421
84.113
77.469
77.000
76.531
27.652

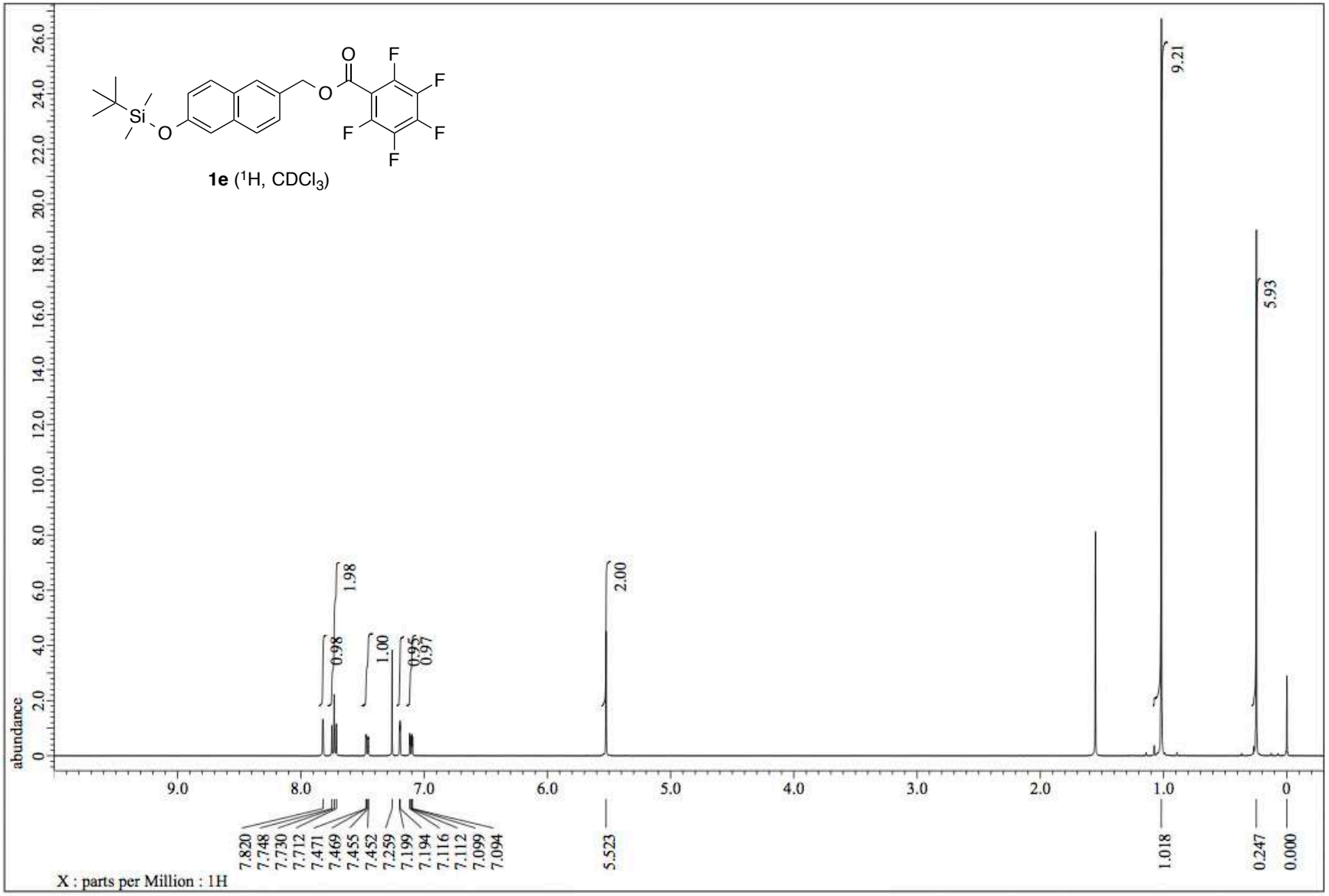

1d (1H, CDCl3)
abundance
X : parts per Million : 1H
8.95
2.00
0.97
0.98
0.98
7.890
7.872
7.854
7.850
7.832
7.658
7.653
7.538
7.535
7.522
7.518
7.359
7.354
7.342
7.337
7.258
5.552
1.590
0.000

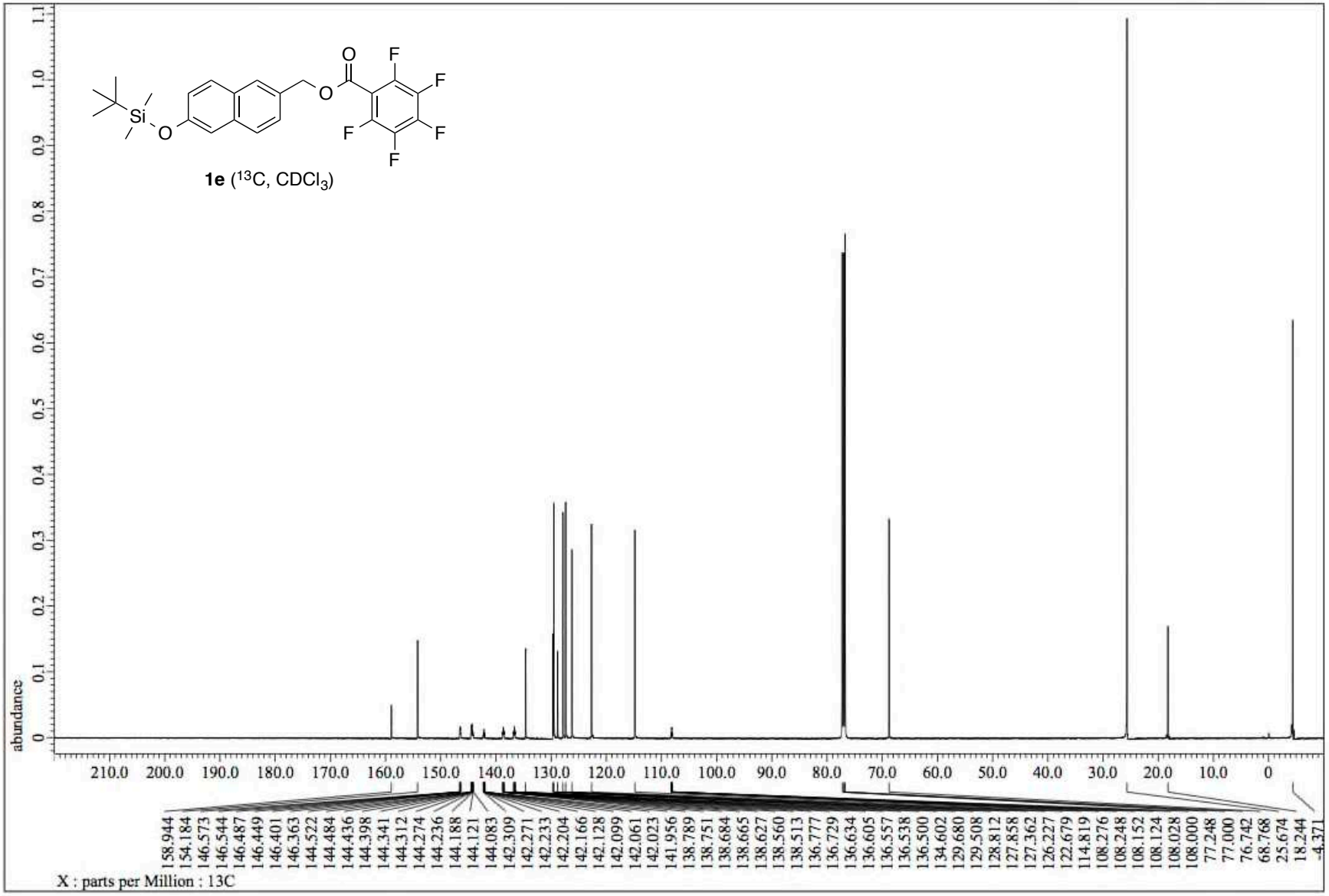

1d (13C, CDCl3)
abundance
X : parts per Million : 13C

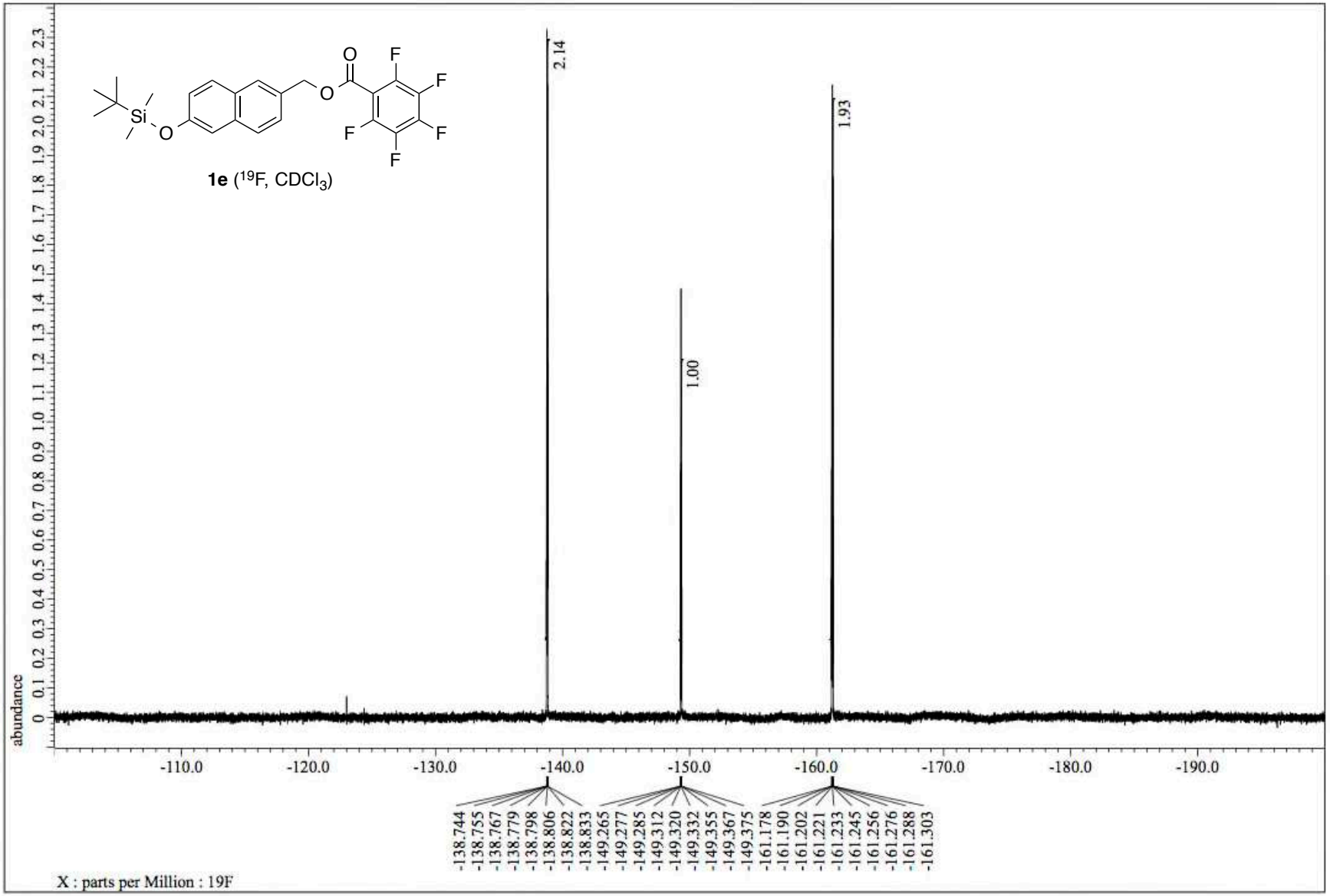

1d (19F, CDCl3)
2.35
1.77
1.00
abundance
3.0
2.0
1.0
0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
-138.712
-138.724
-138.740
-138.748
-138.767
-138.779
-138.790
-138.802
-149.094
-149.106
-149.117
-149.141
-149.149
-149.160
-149.184
-149.195
-149.203
-161.093
-161.104
-161.120
-161.136
-161.147
-161.163
-161.175
-161.190
-161.206
-161.217
X : parts per Million : 19F

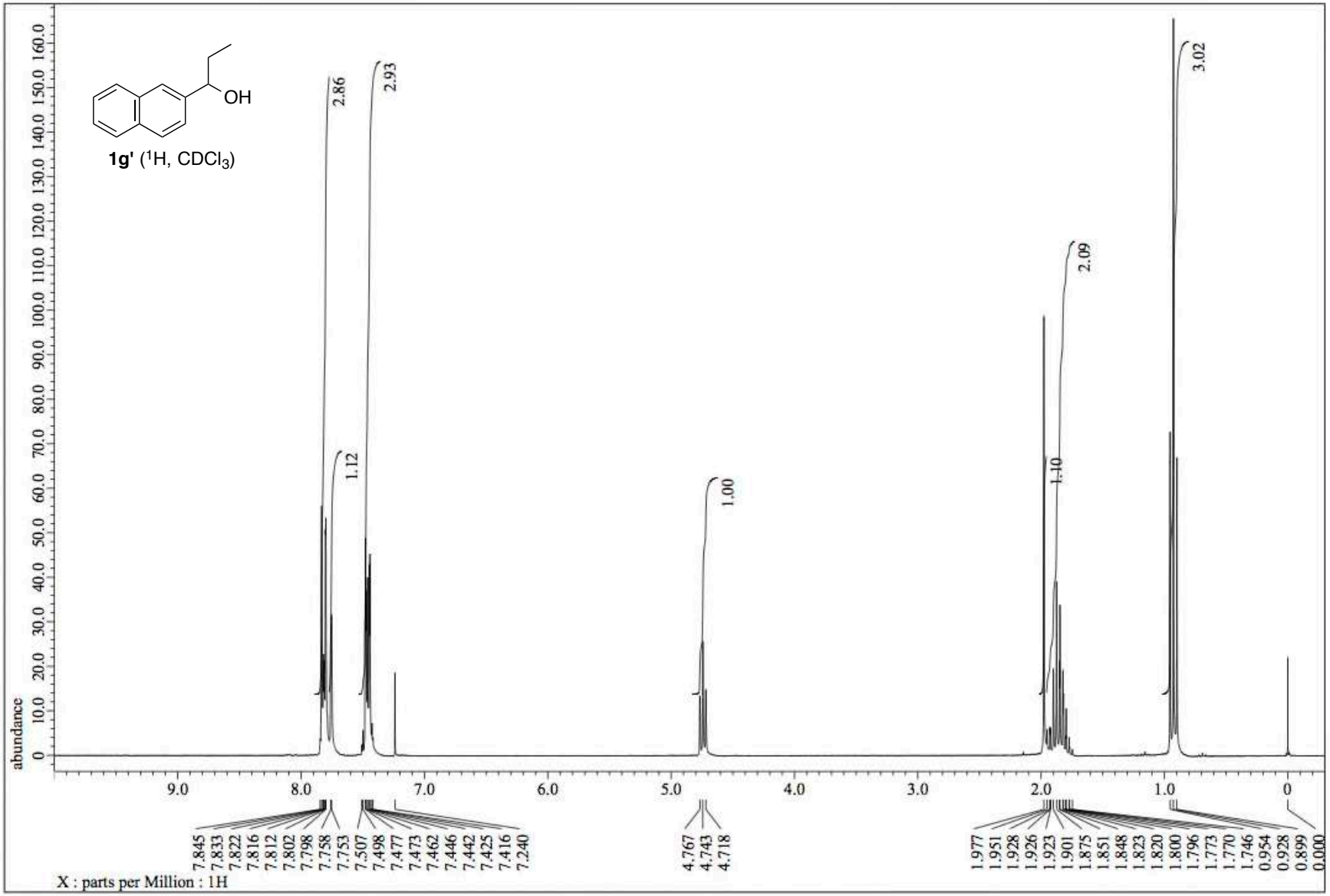

S3 (1H, CDCl3)
abundance
X : parts per Million : 1H
10.094
8.256
7.922
7.916
7.908
7.890
7.884
7.875
7.780
7.748
7.261
7.237
7.229
7.189
7.181
7.157
7.148
1.029
0.282
0.000
1.00
1.02
2.03
1.00
1.03
0.99
9.20
5.98

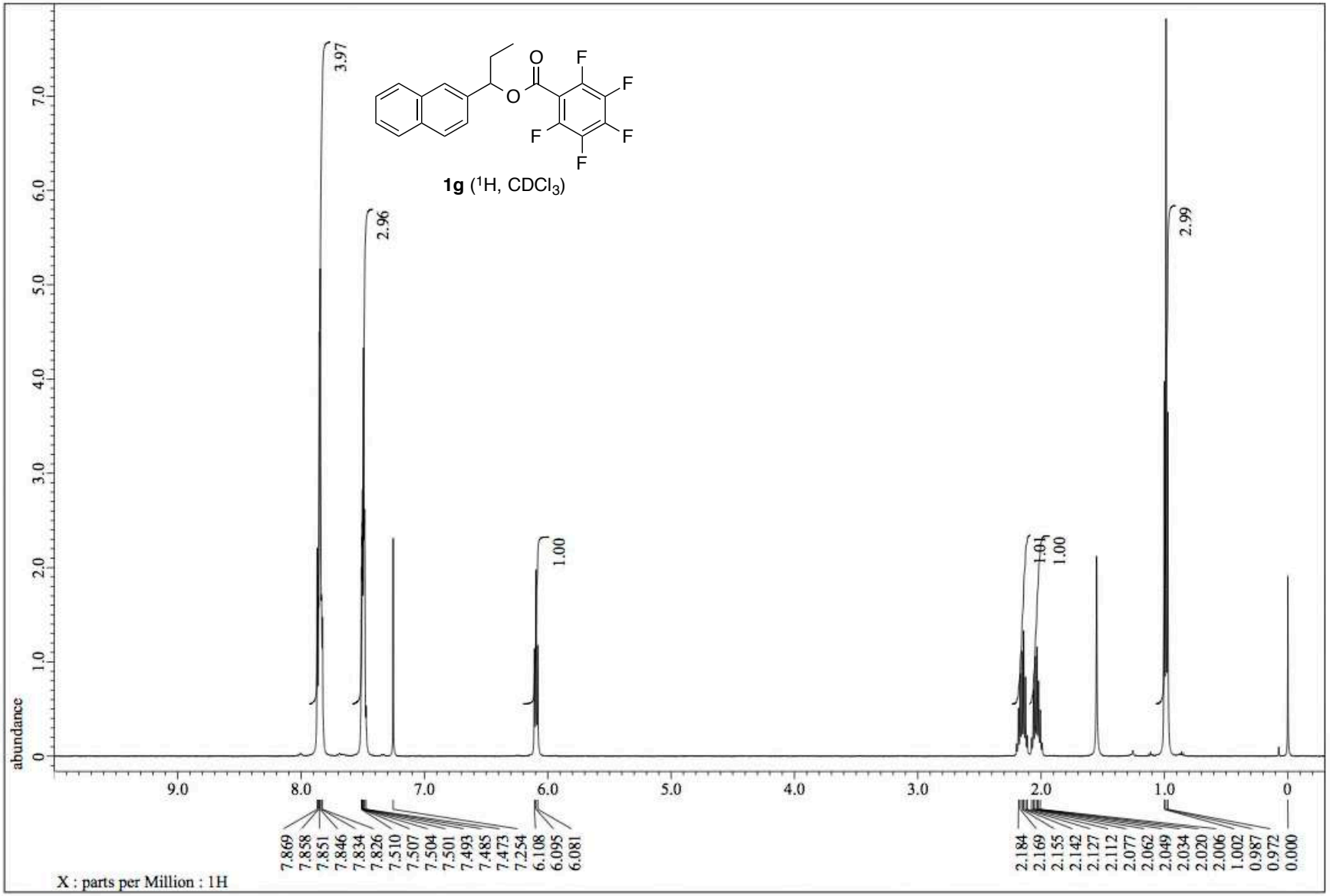

S3 (13C, CDCl3)
abundance
X : parts per Million : 13C
191.952
156.464
138.099
134.390
132.432
131.166
128.114
127.637
123.155
115.103
77.469
77.000
76.523
25.581
18.204
-4.364


1e (1H, CDCl3)
abundance
X : parts per Million : 1H
9.21
5.93
1.98
2.00
0.98
1.00
0.95
0.97
7.820
7.748
7.730
7.712
7.471
7.469
7.455
7.452
7.259
7.199
7.194
7.116
7.112
7.099
7.094
5.523
1.018
0.247
0.000

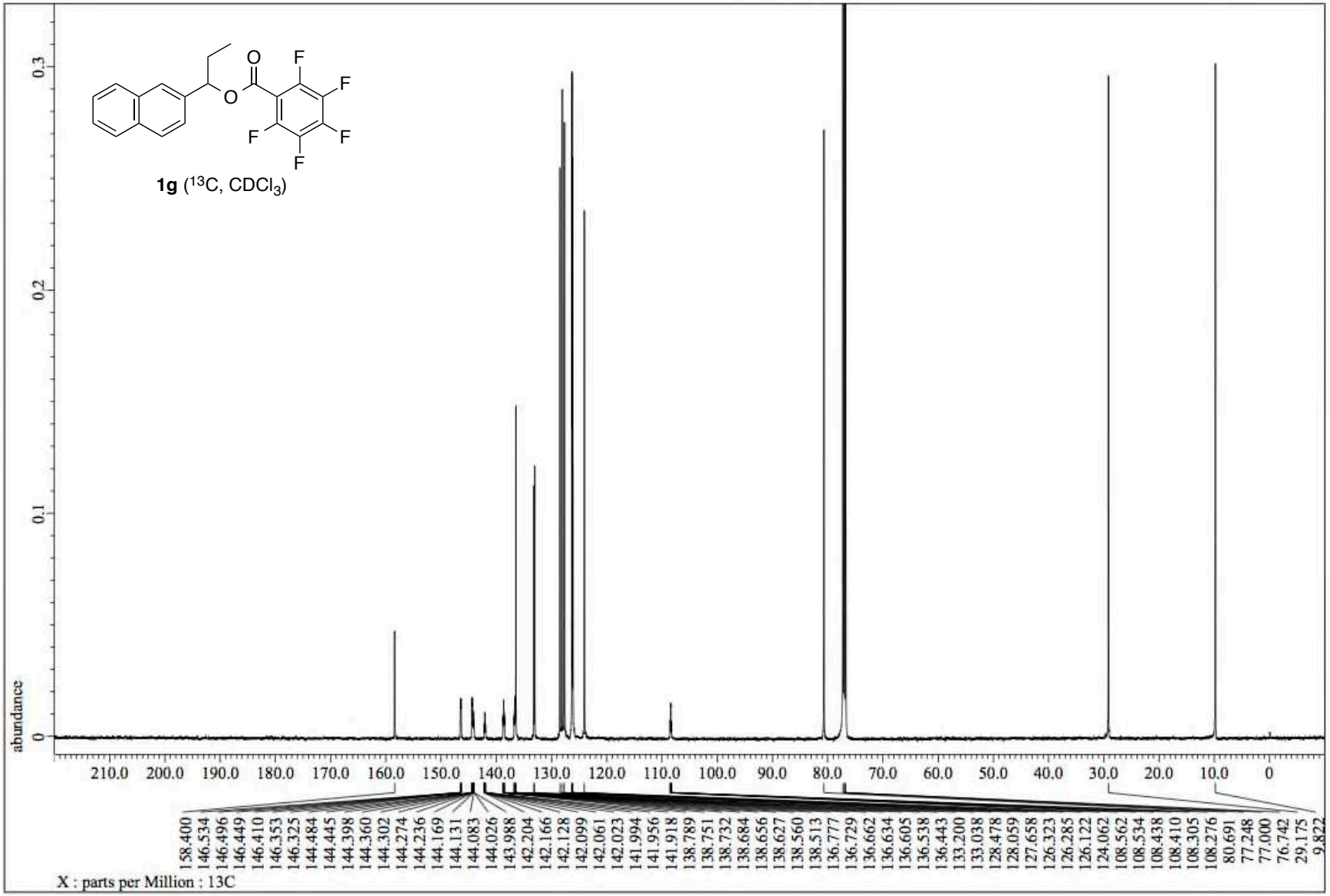

1e (13C, CDCl3)
abundance
X : parts per Million : 13C

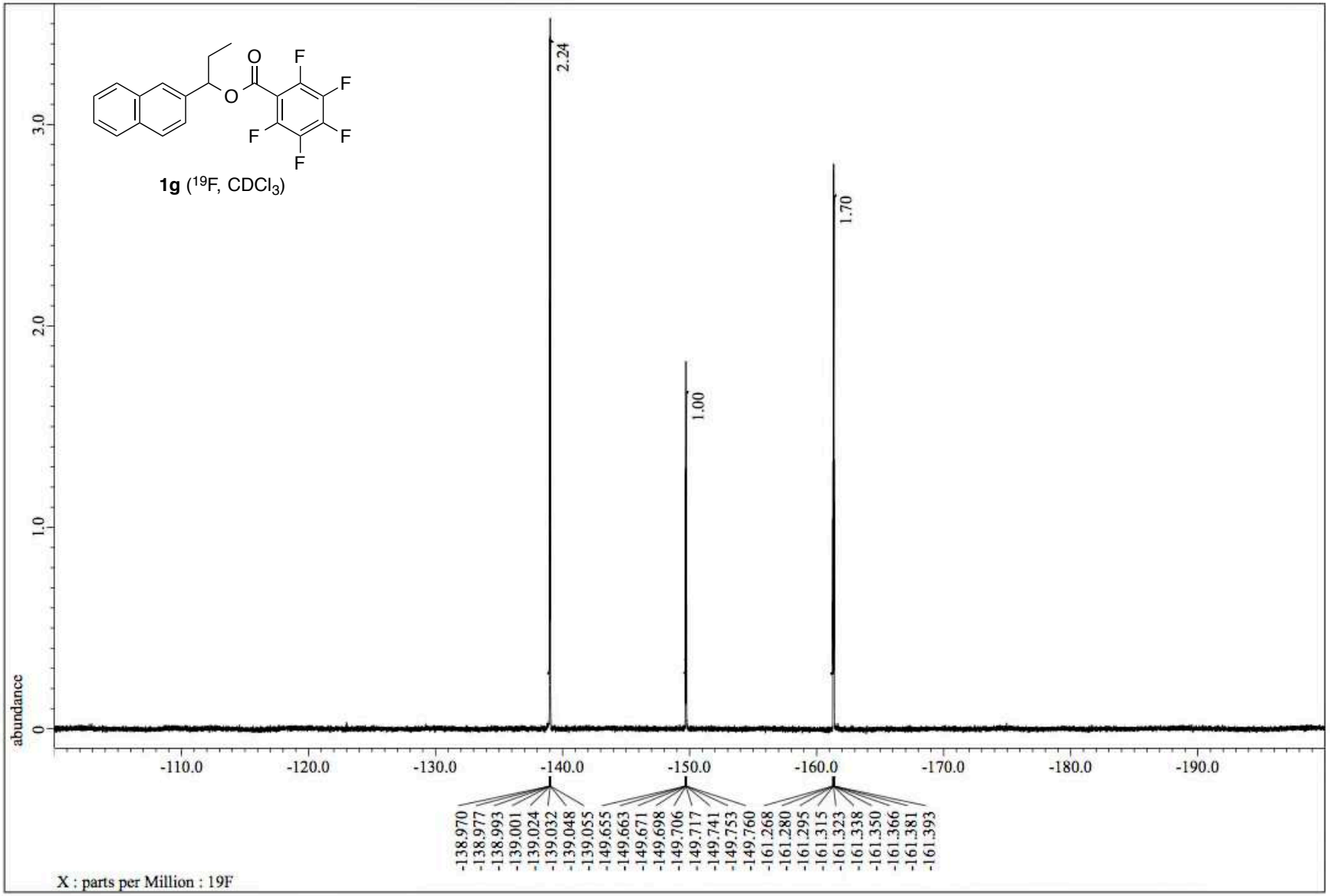

1e (19F, CDCl3)
2.14
1.00
1.93
abundance
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
-138.744
-138.755
-138.767
-138.779
-138.798
-138.806
-138.822
-138.833
-149.265
-149.277
-149.285
-149.312
-149.320
-149.332
-149.355
-149.367
-149.375
-161.178
-161.190
-161.202
-161.221
-161.233
-161.245
-161.256
-161.276
-161.288
-161.303
X : parts per Million : 19F

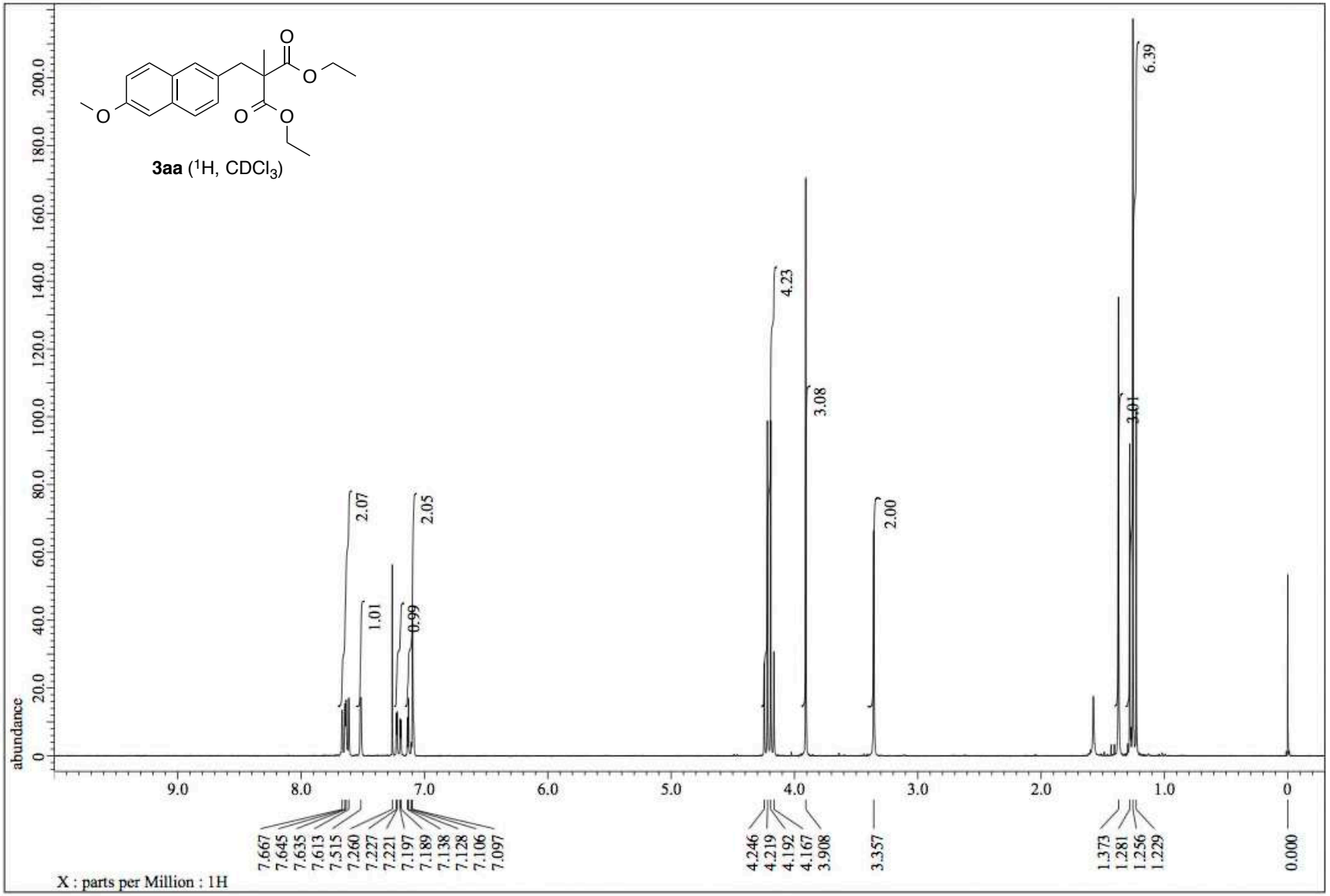

OH
1g' (1H, CDCl3)
abundance
X : parts per Million : 1H
2.86
2.93
1.12
1.00
1.10
2.09
3.02
7.845
7.833
7.822
7.816
7.812
7.802
7.798
7.758
7.753
7.507
7.498
7.477
7.473
7.462
7.446
7.442
7.425
7.416
7.240
4.767
4.743
4.718
1.977
1.951
1.928
1.926
1.923
1.901
1.875
1.851
1.848
1.823
1.820
1.800
1.796
1.773
1.770
1.746
0.954
0.928
0.899
0.000

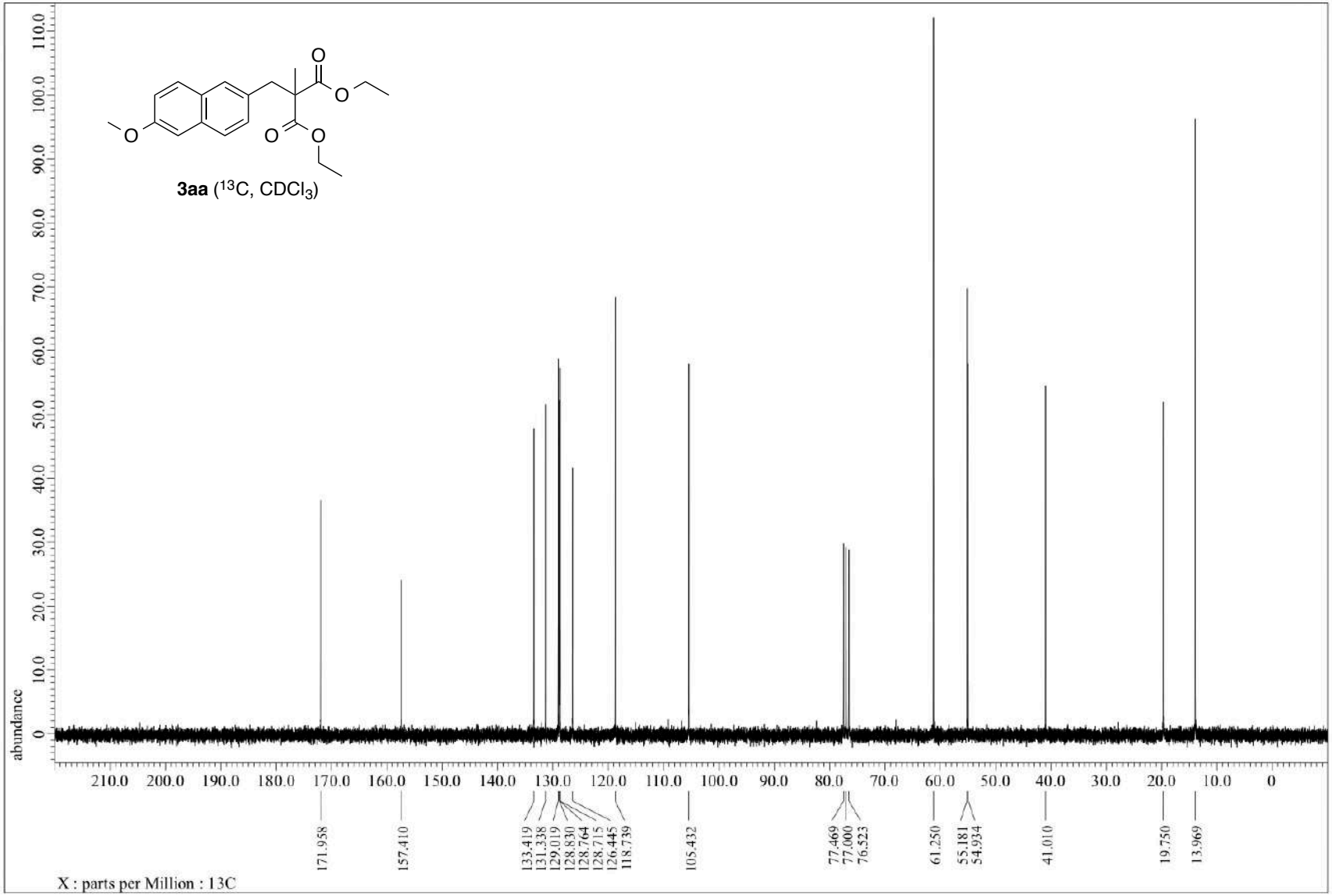

3.97
2.96
1.00
1.01
1.00
2.99
O
O
F
F
F
F
F
abundance
X : parts per Million : 1H
7.869
7.858
7.851
7.846
7.834
7.826
7.510
7.507
7.504
7.501
7.493
7.485
7.473
7.254
6.108
6.095
6.081
2.184
2.169
2.155
2.142
2.127
2.112
2.077
2.062
2.049
2.034
2.020
2.006
1.002
0.987
0.972
0.000

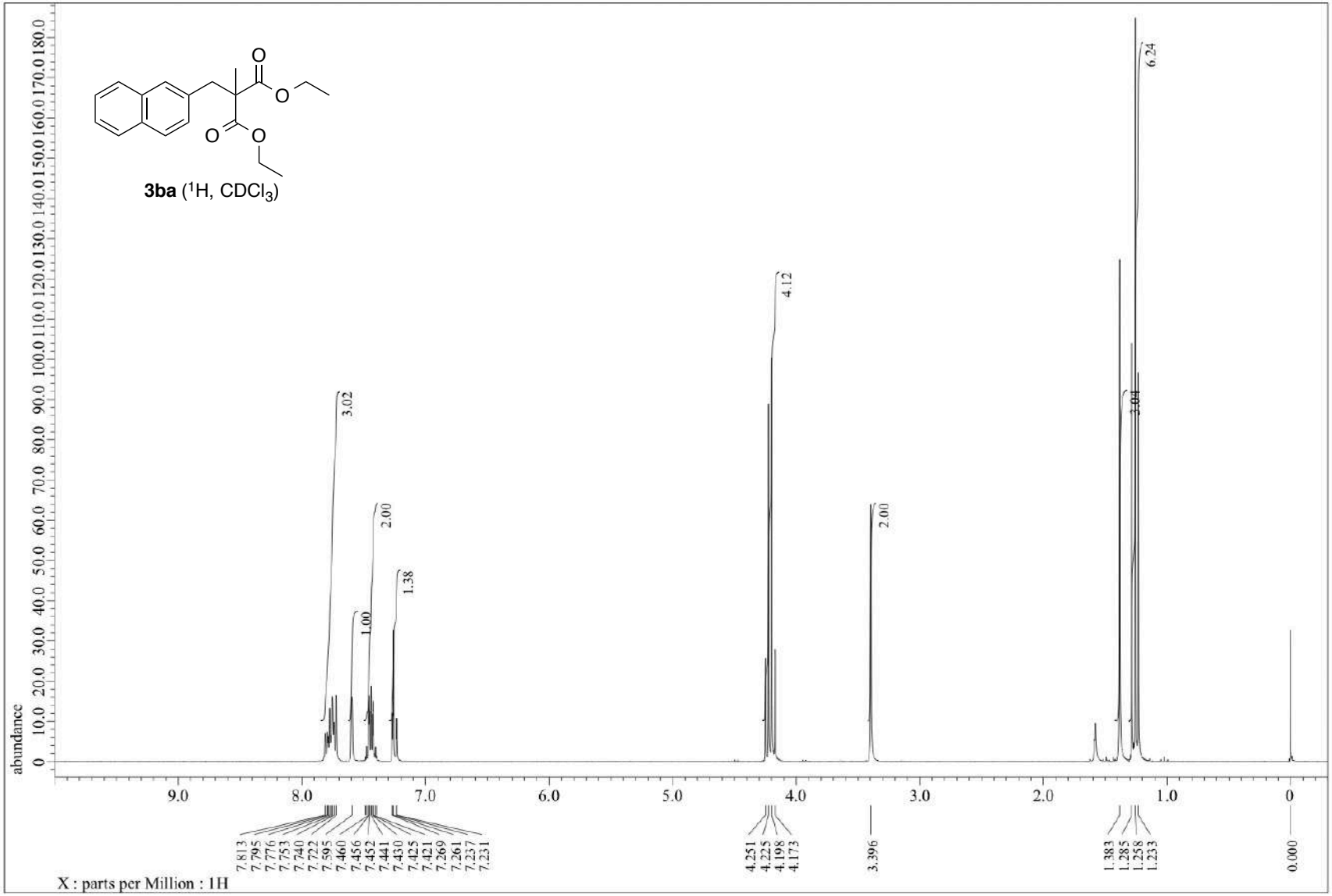
1g (^{1}H, $CDCl_3$)

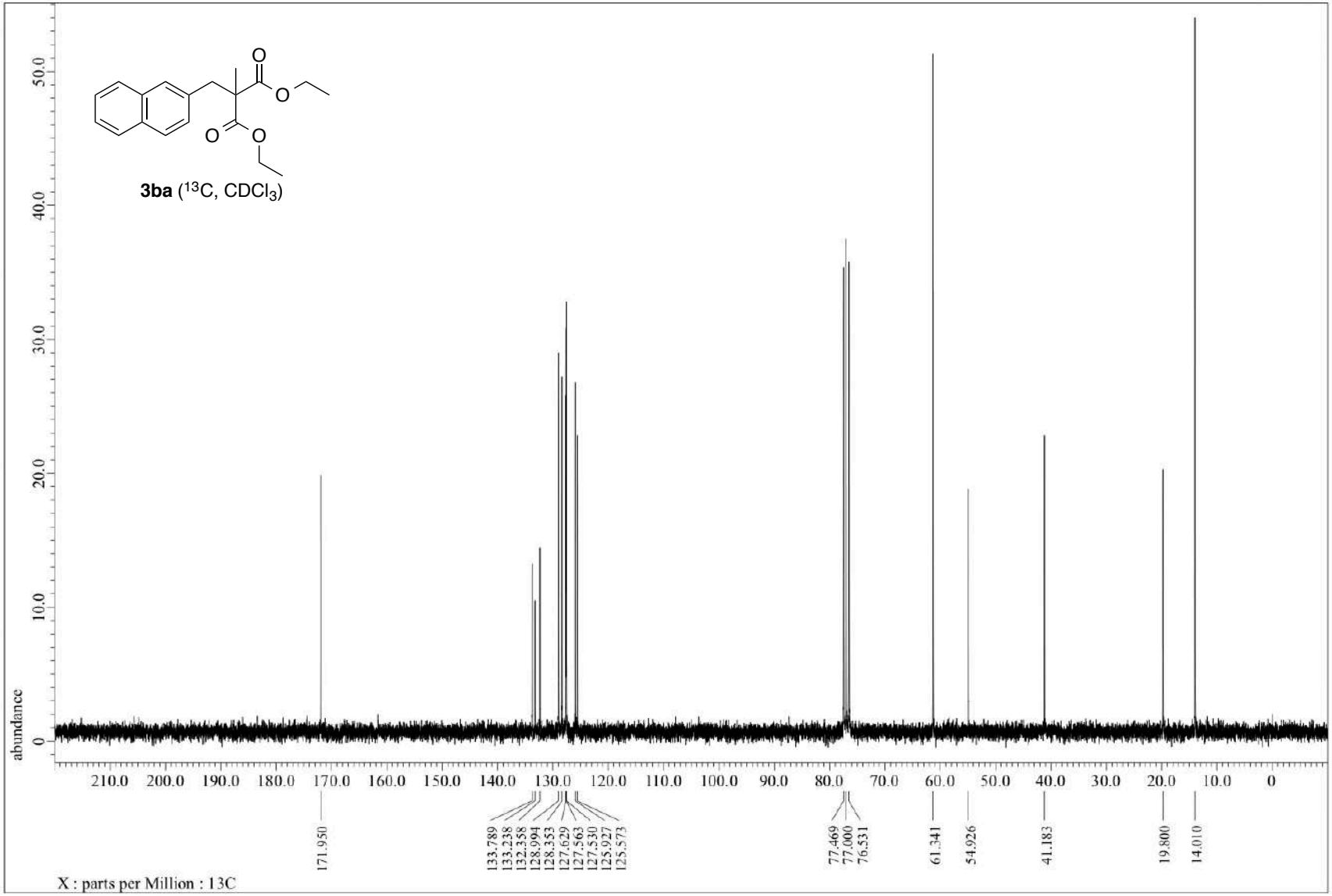

O
O
F
F
F
F
F
1g (13C, CDCl3)
abundance
0.3
0.2
0.1
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
158.400
146.534
146.496
146.449
146.410
146.353
146.325
144.484
144.445
144.398
144.360
144.302
144.274
144.236
144.169
144.131
144.083
144.026
143.988
142.204
142.166
142.128
142.099
142.061
142.023
141.994
141.956
141.918
138.789
138.751
138.732
138.684
138.656
138.627
138.560
138.513
136.777
136.729
136.662
136.634
136.605
136.538
136.443
133.200
133.038
128.478
128.059
127.658
126.323
126.285
126.122
124.062
108.562
108.534
108.438
108.410
108.305
108.276
80.691
77.248
77.000
76.742
29.175
9.822
X : parts per Million : 13C

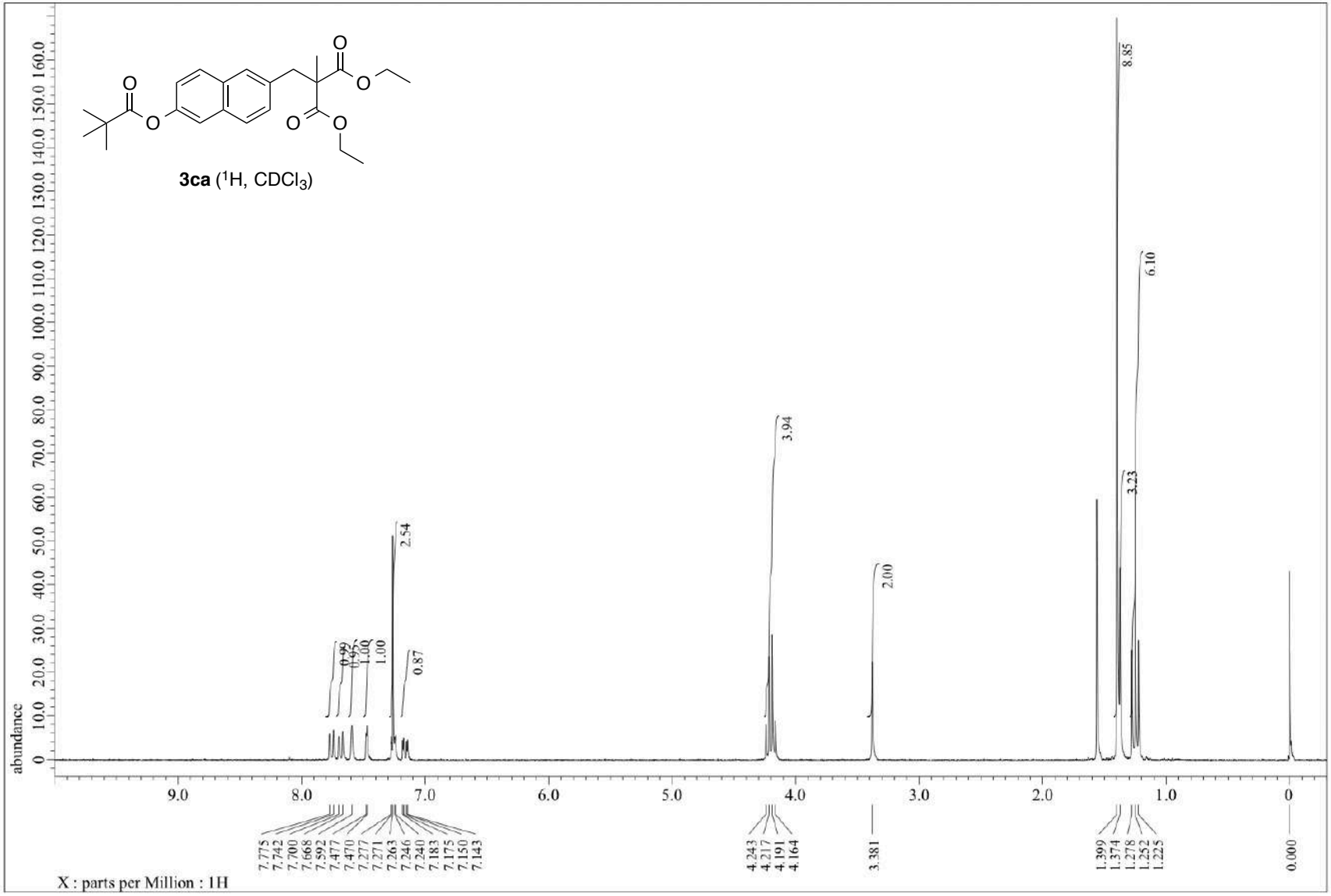

1g (^{19}F, $CDCl_3$)
2.24
1.70
1.00
abundance
3.0
2.0
1.0
0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
-138.970
-138.977
-138.993
-139.001
-139.024
-139.032
-139.048
-139.055
-149.655
-149.663
-149.671
-149.698
-149.706
-149.717
-149.741
-149.753
-149.760
-161.268
-161.280
-161.295
-161.315
-161.323
-161.338
-161.350
-161.366
-161.381
-161.393
X : parts per Million : 19F

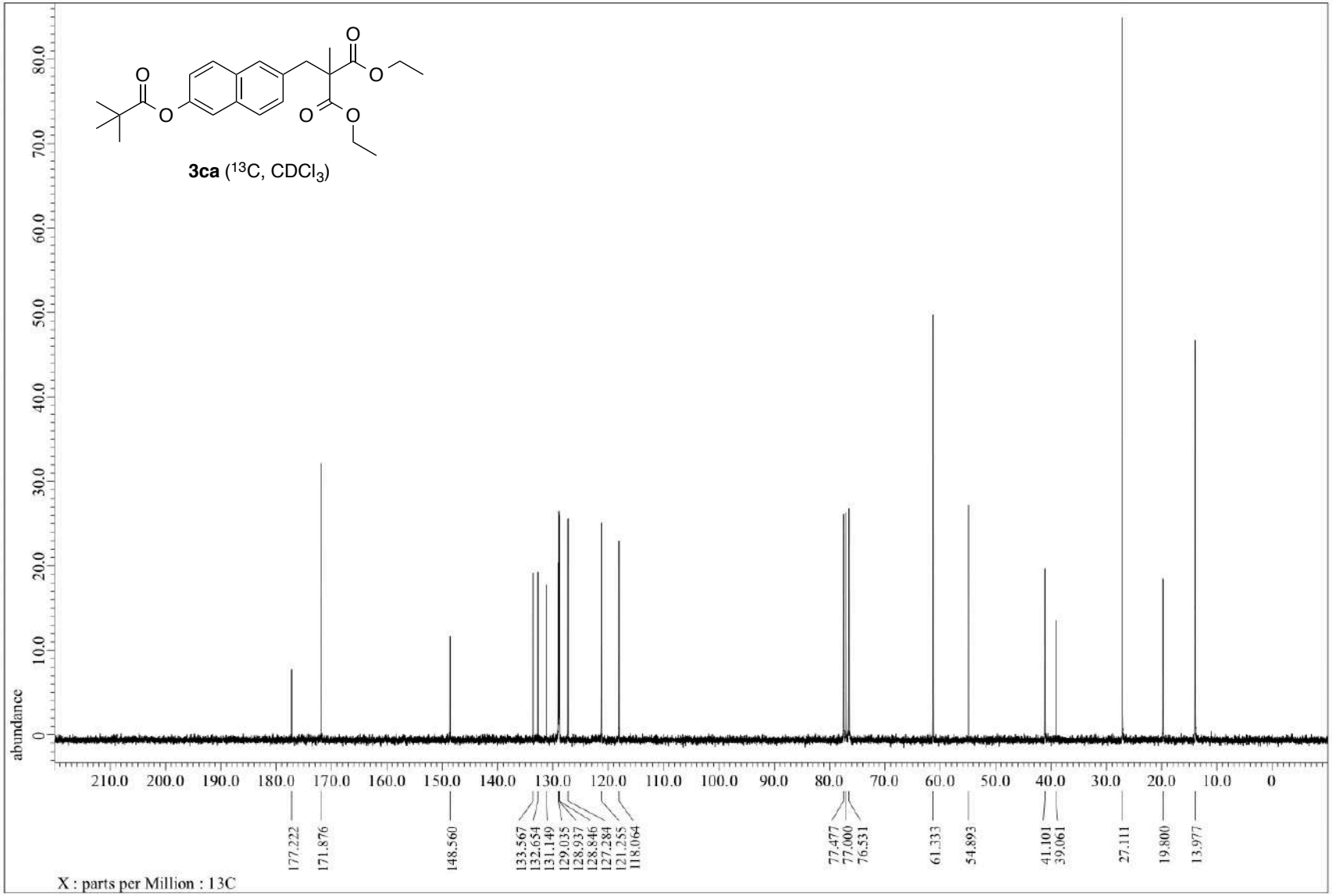

3aa (1H, CDCl3)
abundance
X : parts per Million : 1H
2.07
1.01
0.99
2.05
4.23
3.08
2.00
3.01
6.39
7.667
7.645
7.635
7.613
7.515
7.260
7.227
7.221
7.197
7.189
7.138
7.128
7.106
7.097
4.246
4.219
4.192
4.167
3.908
3.357
1.373
1.281
1.256
1.229
0.000

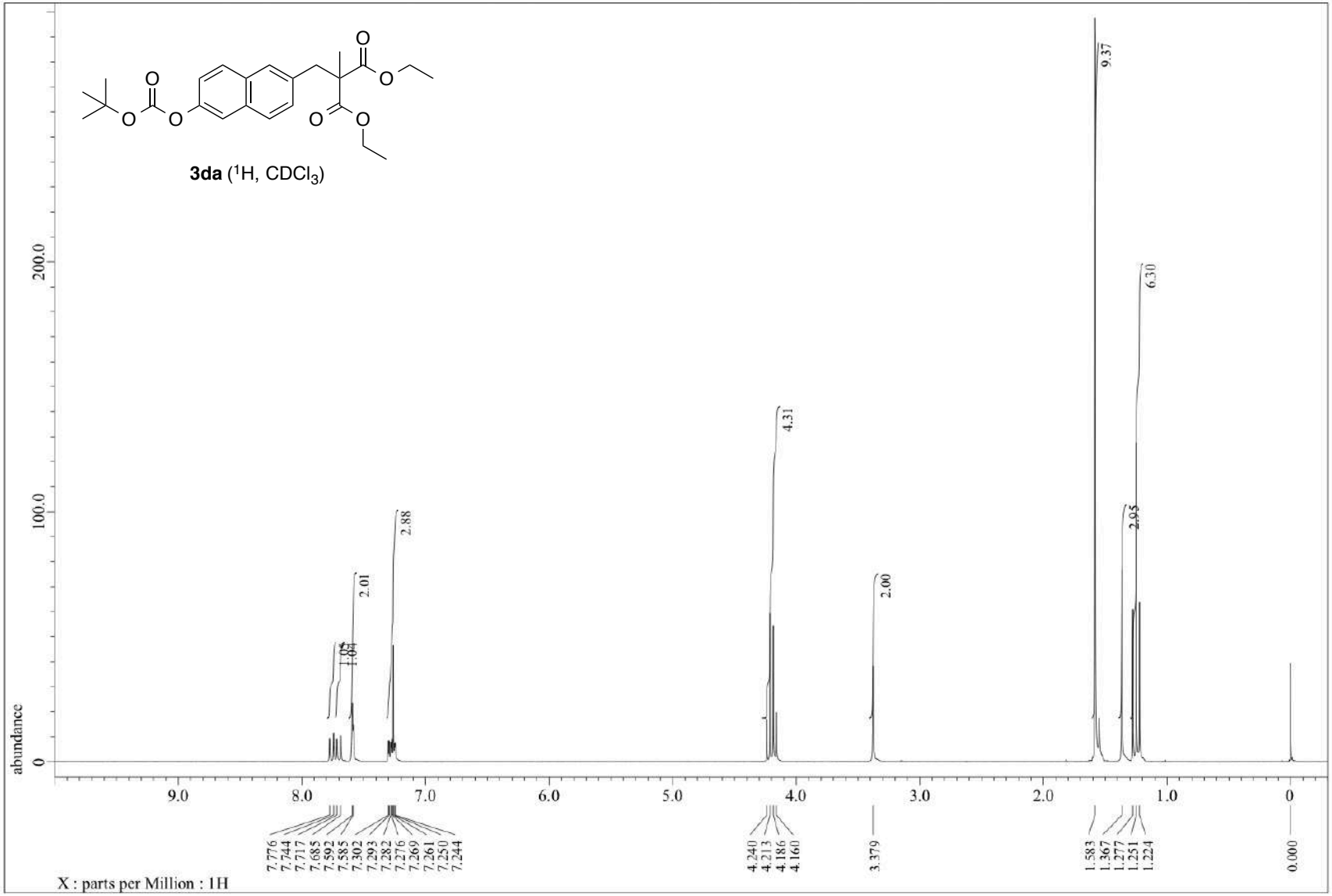

3aa (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
171.958
157.410
133.419
131.338
129.019
128.830
128.764
128.715
126.445
118.739
105.432
77.469
77.000
76.523
61.250
55.181
54.934
41.010
19.750
13.969

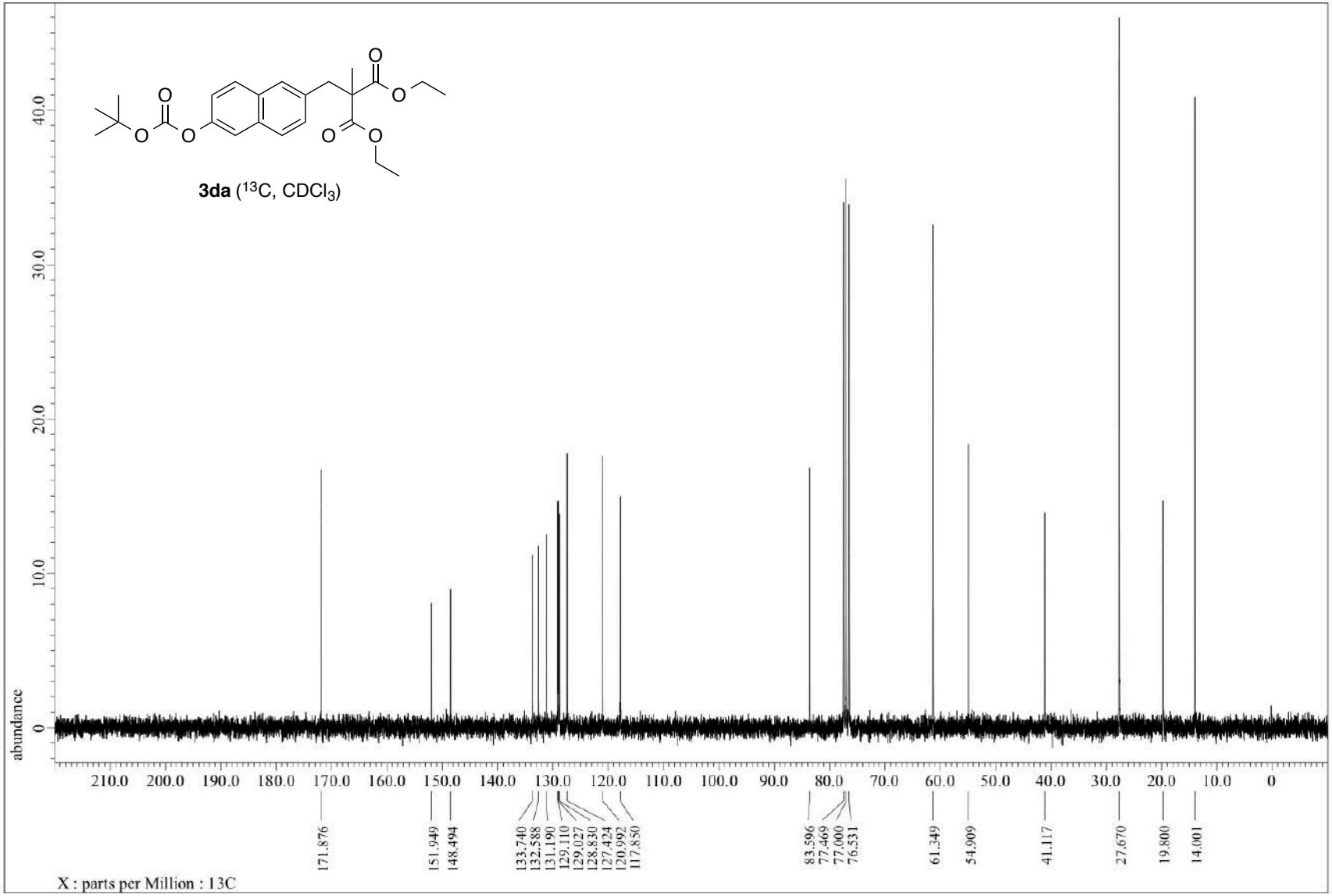

3ba (1H, CDCl3)
abundance
X : parts per Million : 1H
3.02
1.00
2.00
1.38
4.12
2.00
3.04
6.24
7.813
7.795
7.776
7.753
7.740
7.722
7.595
7.460
7.456
7.452
7.441
7.430
7.425
7.421
7.269
7.261
7.237
7.231
4.251
4.225
4.198
4.173
3.396
1.383
1.285
1.258
1.233
0.000

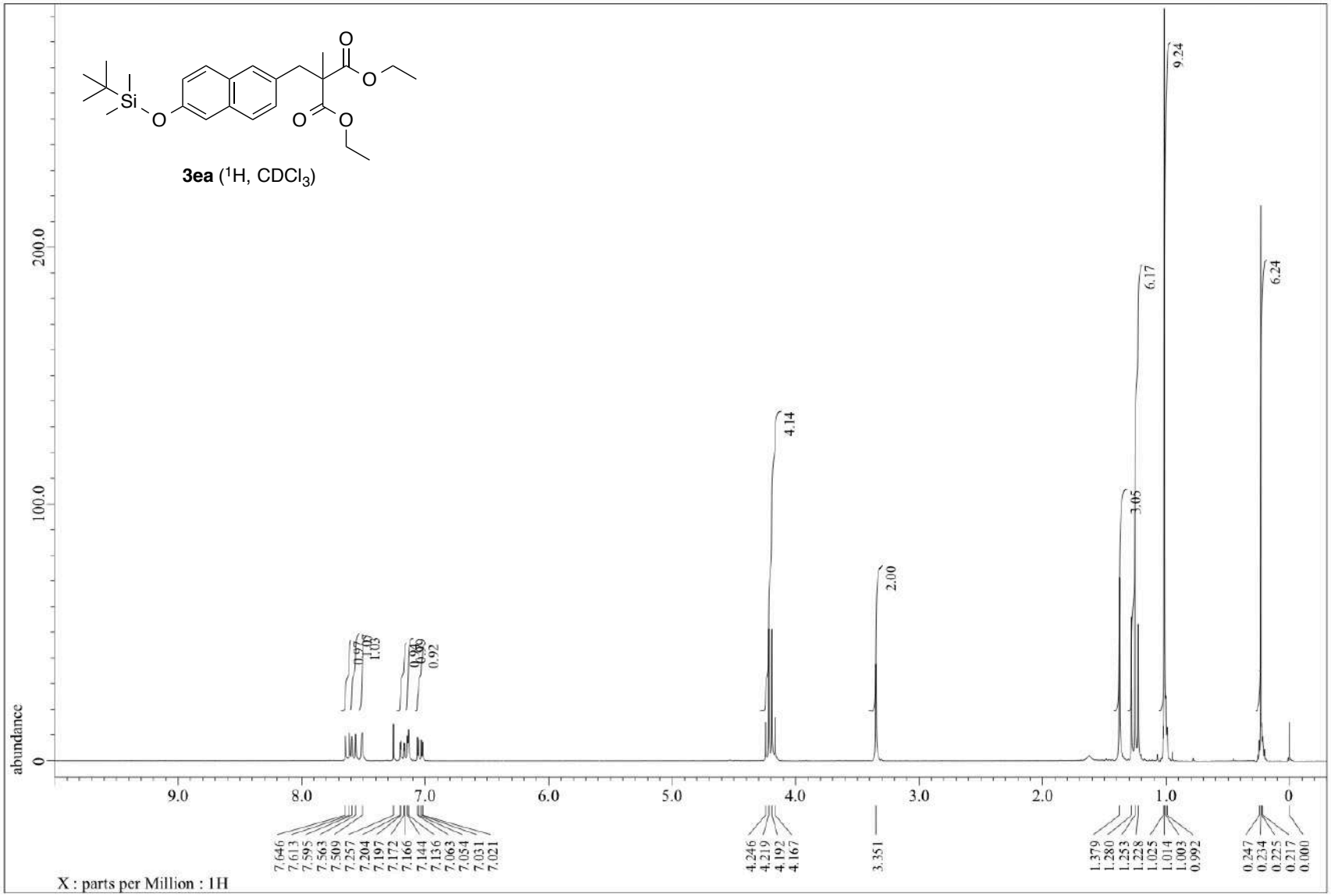

3ba (13C, CDCl3)
abundance
50.0
40.0
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
171.950
133.789
133.238
132.358
128.994
128.353
127.629
127.563
127.530
125.927
125.573
77.469
77.000
76.531
61.341
54.926
41.183
19.800
14.010
X : parts per Million : 13C

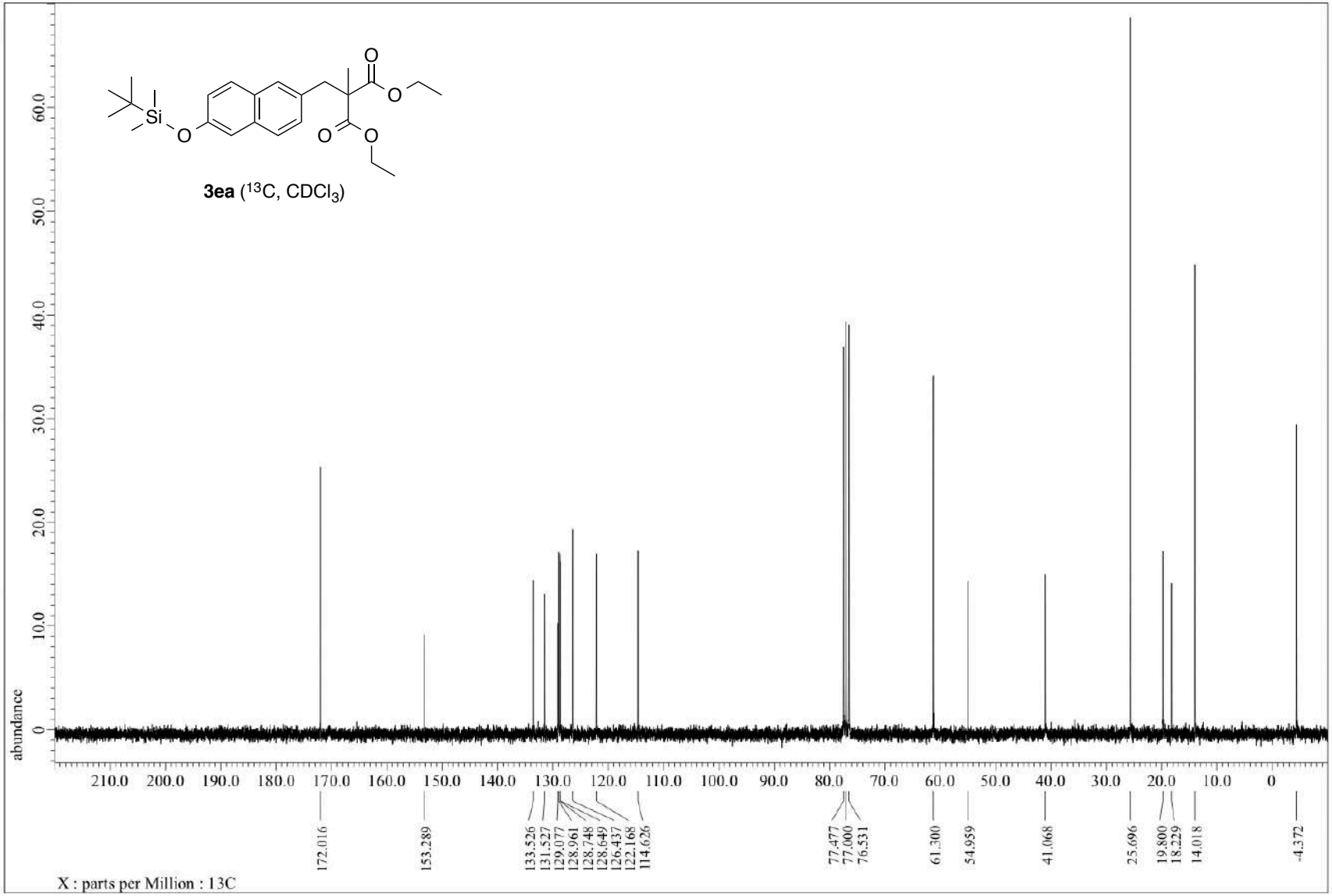

3ca (1H, CDCl3)
abundance
X : parts per Million : 1H
8.85
6.10
3.94
3.23
2.54
2.00
1.00
0.87
7.775
7.742
7.700
7.668
7.592
7.477
7.470
7.277
7.271
7.263
7.246
7.240
7.183
7.175
7.150
7.143
4.243
4.217
4.191
4.164
3.381
1.399
1.374
1.278
1.252
1.225
0.000

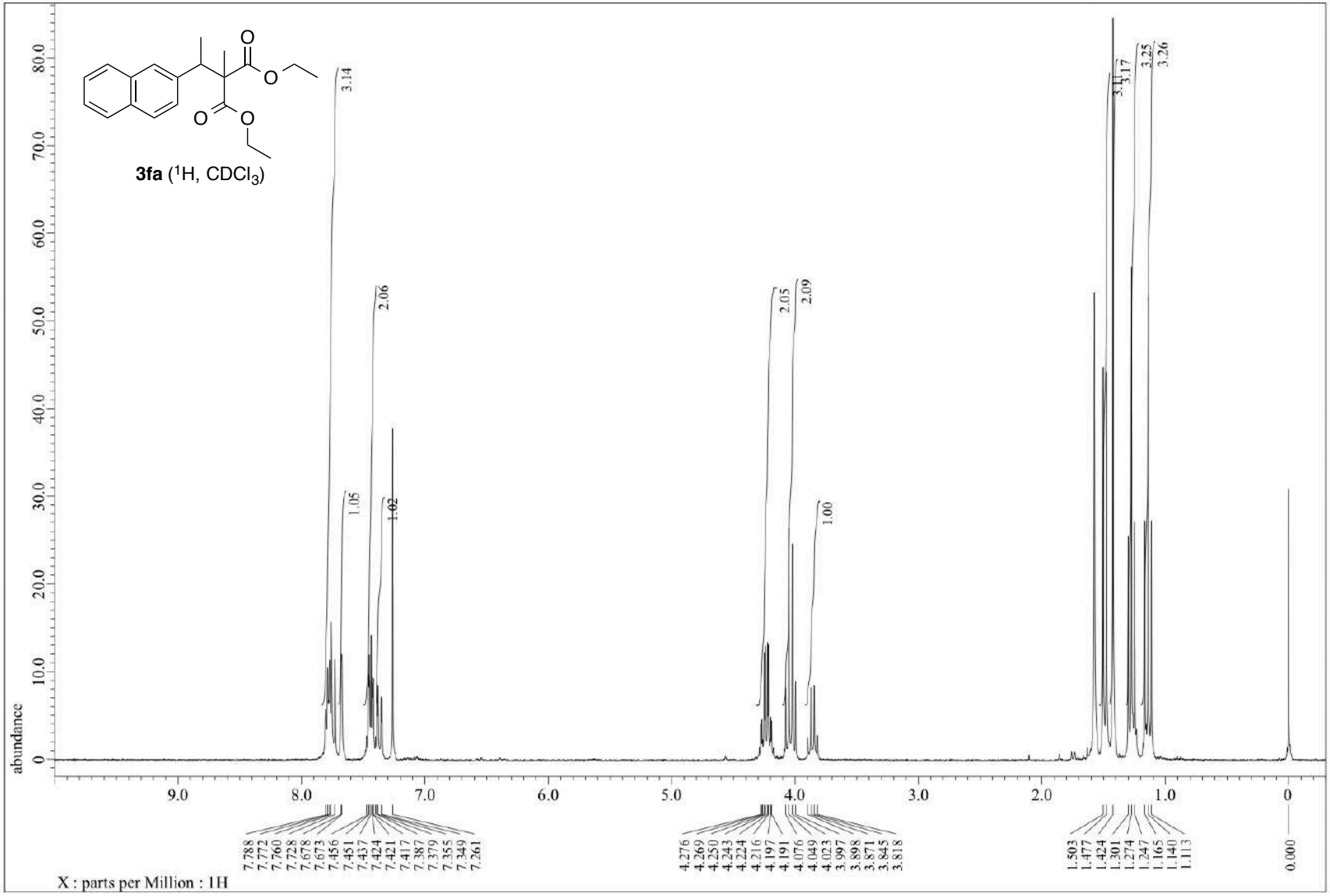

3ca (13C, CDCl3)
abundance
X : parts per Million : 13C
177.222
171.876
148.560
133.567
132.654
131.149
129.035
128.937
128.846
127.284
121.255
118.064
77.477
77.000
76.531
61.333
54.893
41.101
39.061
27.111
19.800
13.977

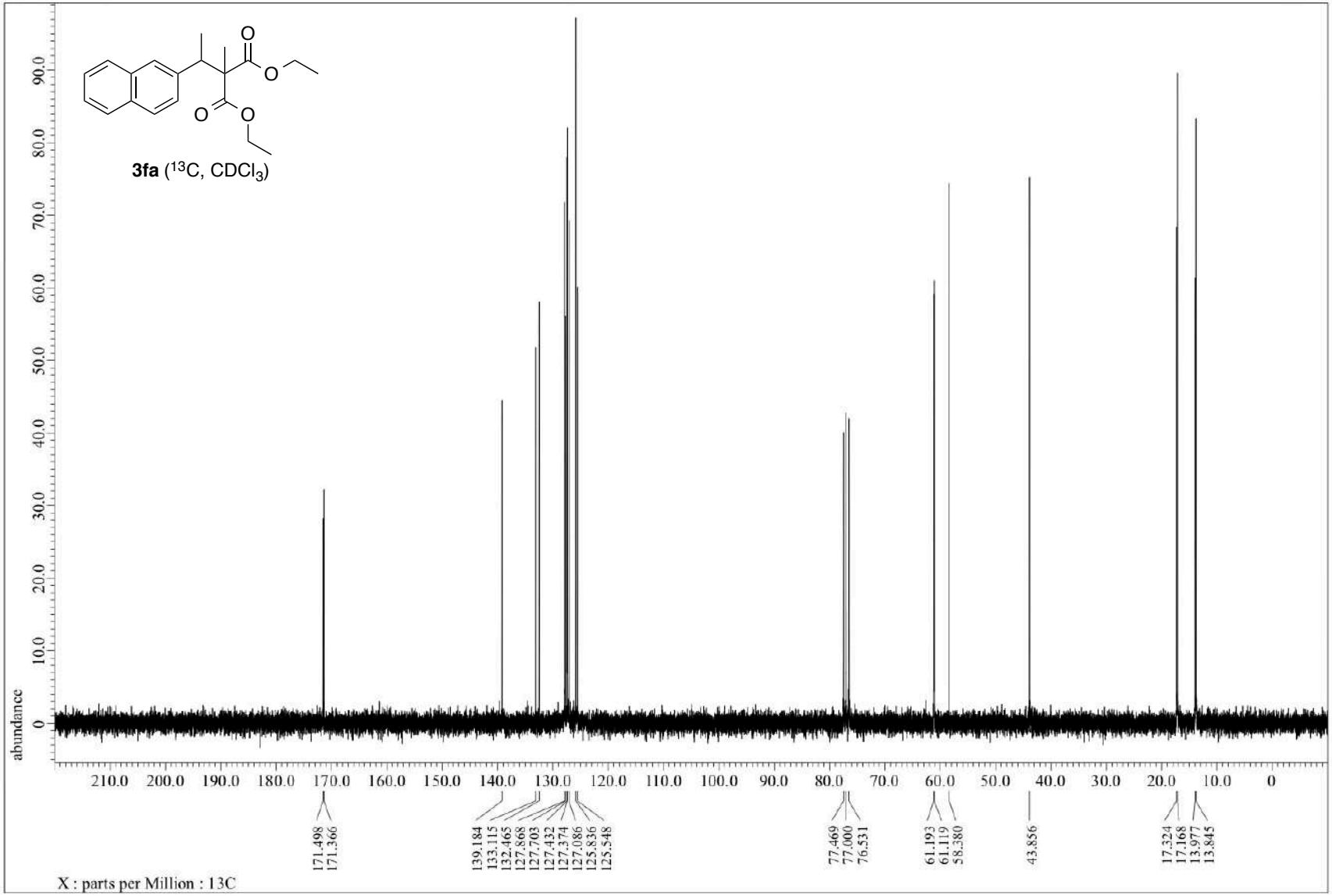

3da (1H, CDCl3)
abundance
X : parts per Million : 1H
9.37
6.30
4.31
2.88
2.01
2.00
2.93
7.776
7.744
7.717
7.685
7.592
7.585
7.302
7.293
7.282
7.276
7.269
7.261
7.250
7.244
4.240
4.213
4.186
4.160
3.379
1.583
1.367
1.277
1.251
1.224
0.000

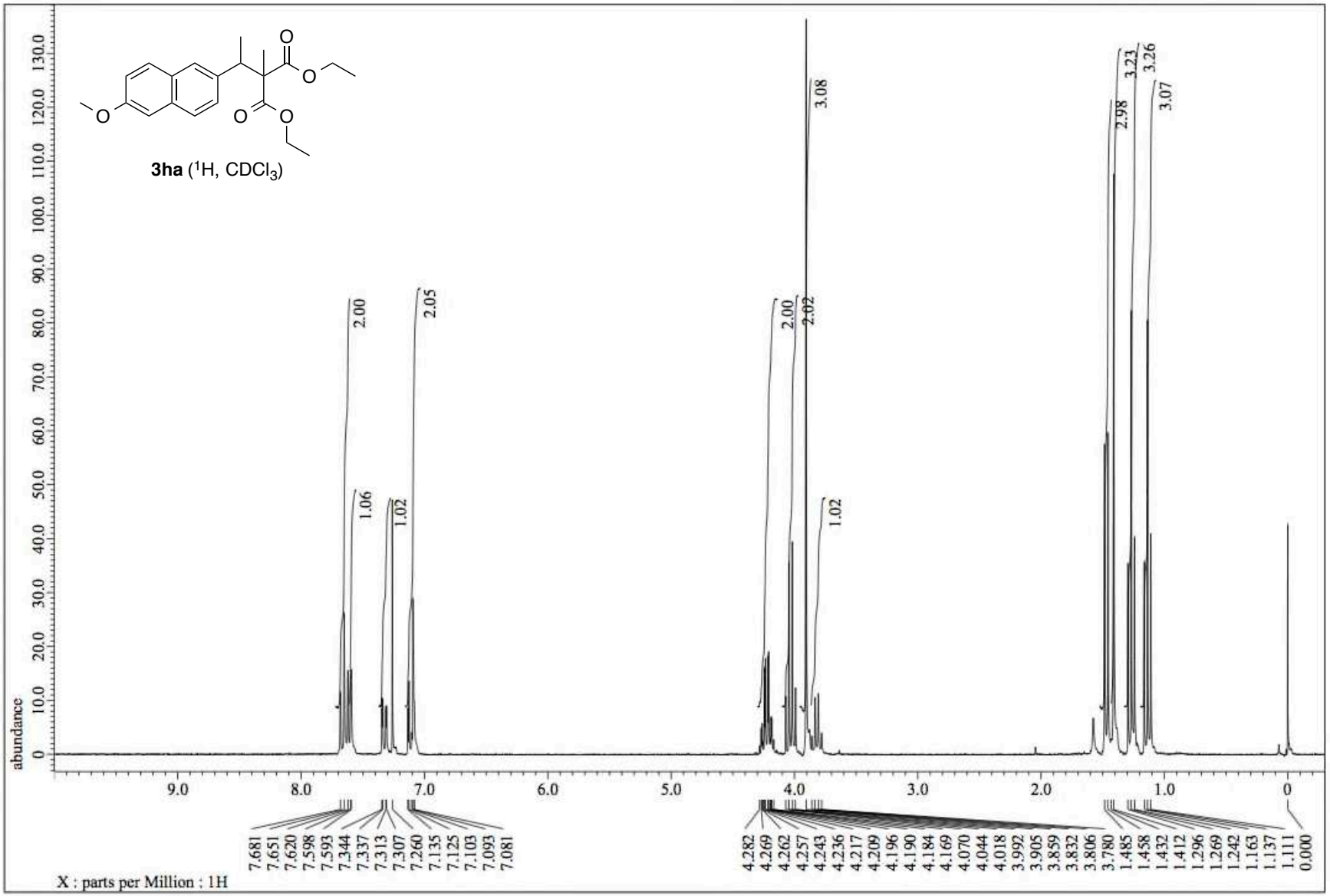

3da (13C, CDCl3)
abundance
X : parts per Million : 13C
171.876
151.949
148.494
133.740
132.588
131.190
129.110
129.027
128.830
127.424
120.992
117.850
83.596
77.469
77.000
76.531
61.349
54.909
41.117
27.670
19.800
14.001

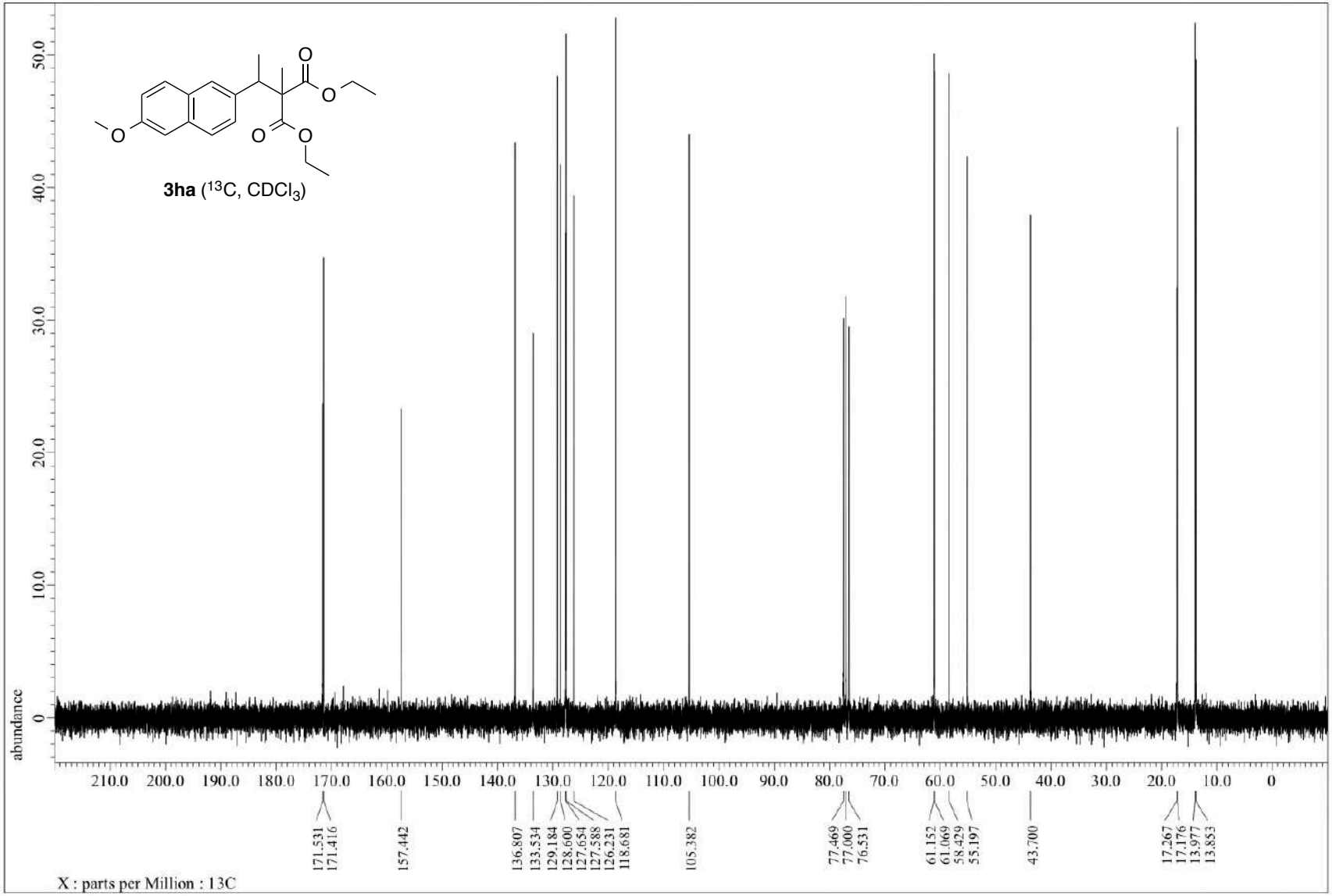

3ea (1H, CDCl3)
abundance
X : parts per Million : 1H
9.24
6.24
6.17
4.14
3.05
2.00
1.05
0.97
0.92
7.646
7.613
7.595
7.563
7.509
7.257
7.204
7.197
7.172
7.166
7.144
7.136
7.063
7.054
7.031
7.021
4.246
4.219
4.192
4.167
3.351
1.379
1.280
1.253
1.228
1.025
1.014
1.003
0.992
0.247
0.234
0.225
0.217
0.000

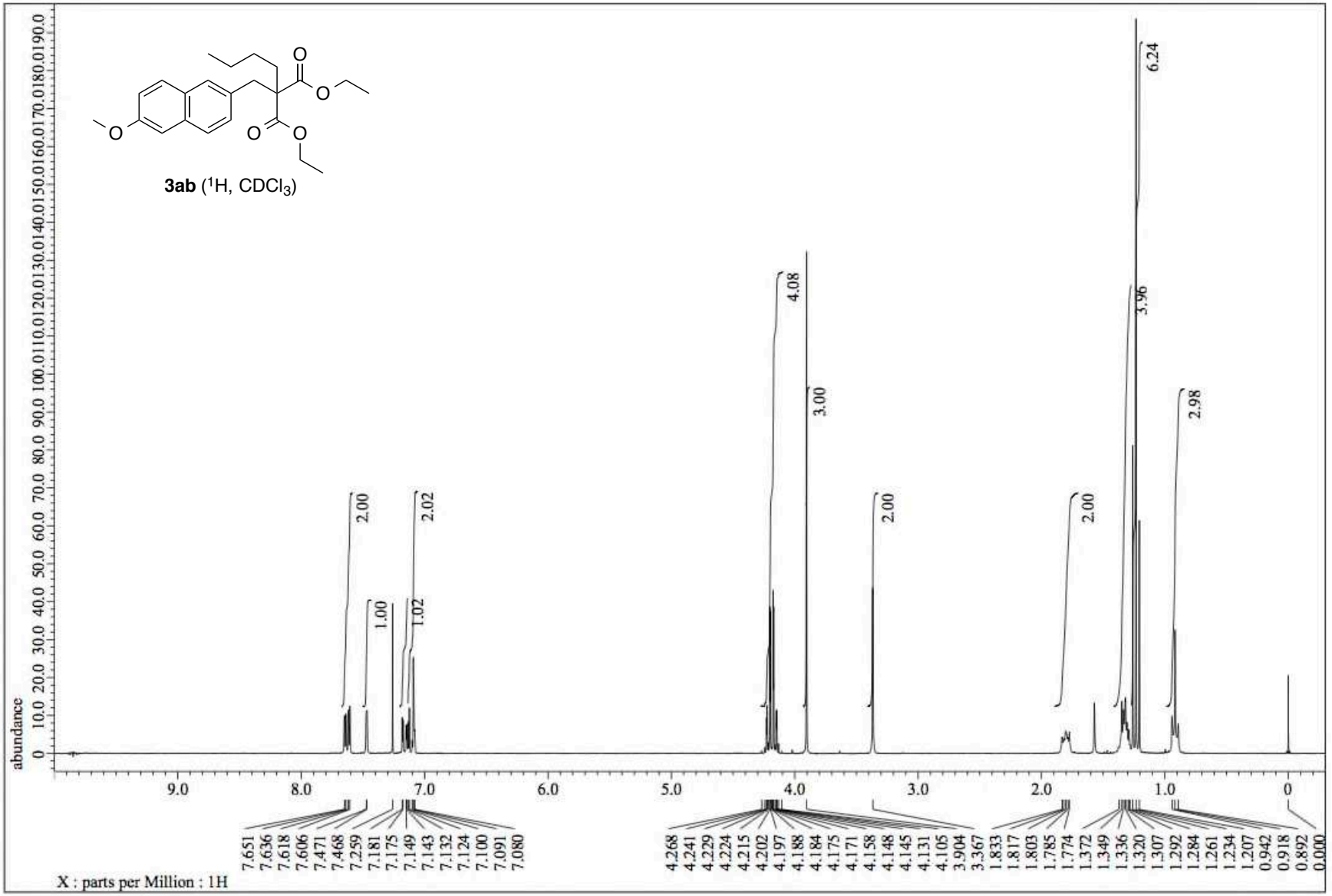

3ea (13C, CDCl3)
abundance
X : parts per Million : 13C
172.016
153.289
133.526
131.527
129.077
128.961
128.748
128.649
126.437
122.168
114.626
77.477
77.000
76.531
61.300
54.959
41.068
25.696
19.800
18.229
14.018
-4.372

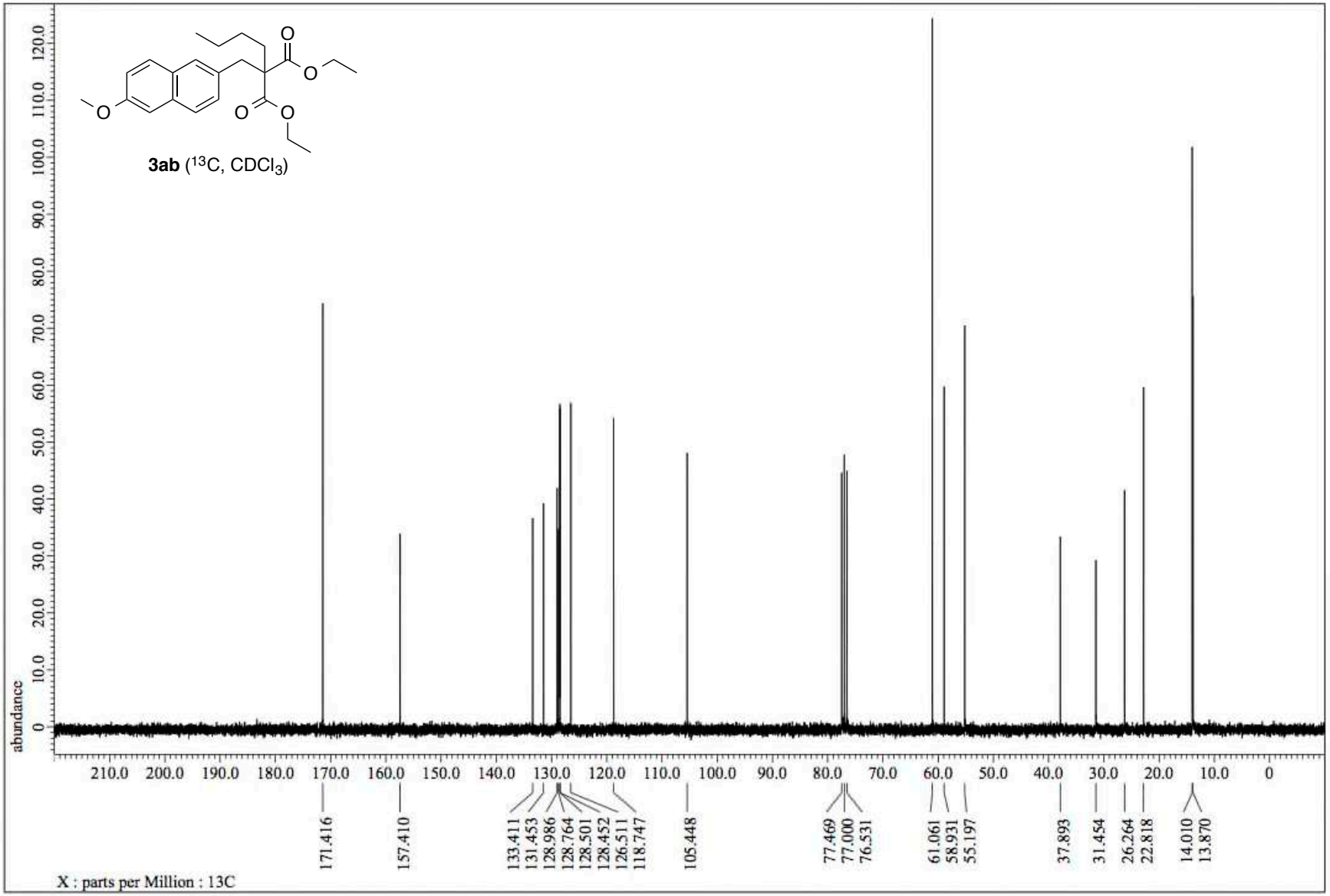

3fa (1H, CDCl3)
abundance
X : parts per Million : 1H
3.14
1.05
2.06
1.02
2.05
2.09
1.00
3.11
3.17
3.25
3.26
7.788
7.772
7.760
7.728
7.678
7.673
7.456
7.451
7.437
7.424
7.421
7.417
7.387
7.379
7.355
7.349
7.261
4.276
4.269
4.250
4.243
4.224
4.216
4.197
4.191
4.076
4.049
4.023
3.997
3.898
3.871
3.845
3.818
1.503
1.477
1.424
1.301
1.274
1.247
1.165
1.140
1.113
0.000

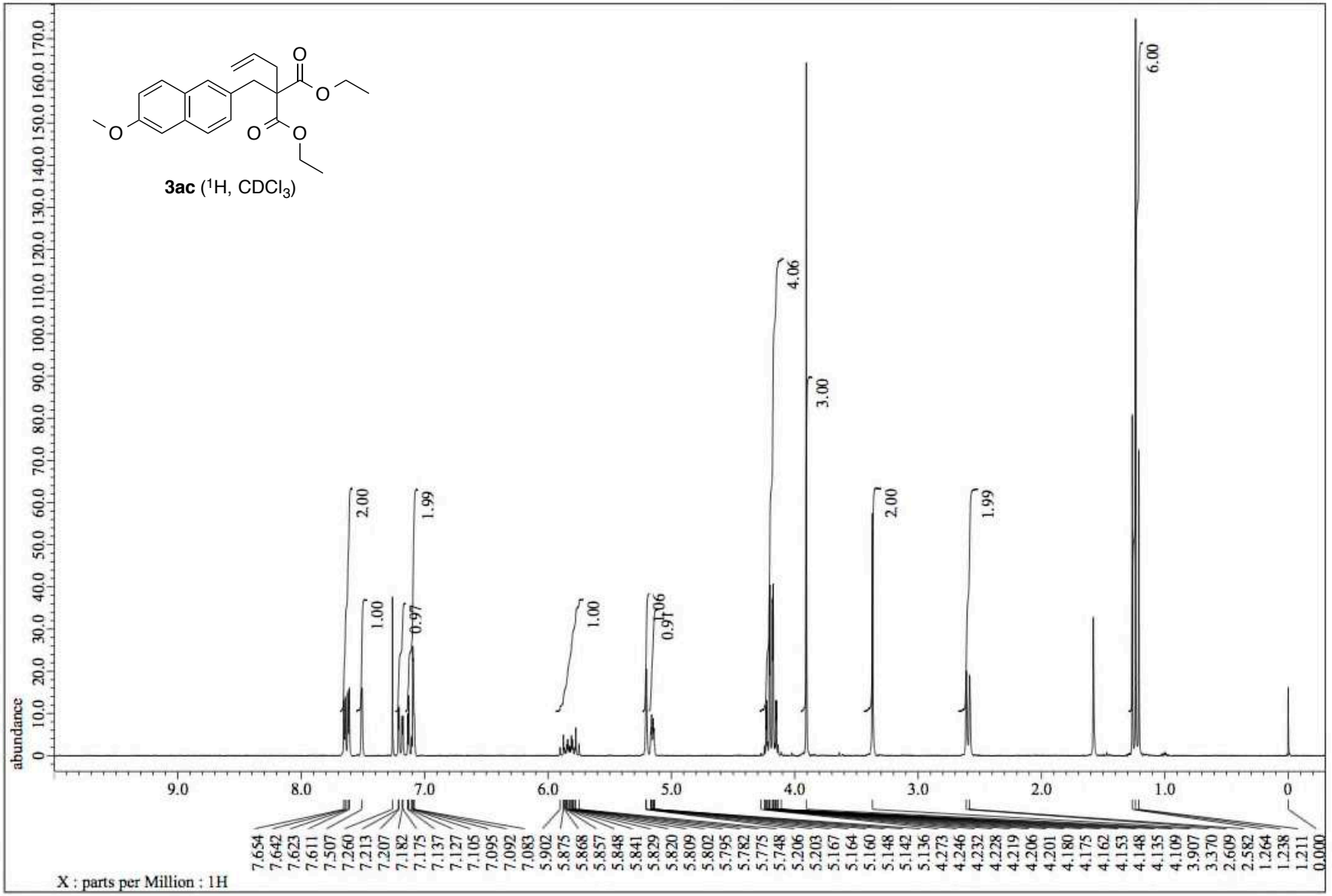

3fa (13C, CDCl3)
abundance
X : parts per Million : 13C
171.498
171.366
139.184
133.115
132.465
127.868
127.703
127.432
127.374
127.086
125.836
125.548
77.469
77.000
76.531
61.193
61.119
58.380
43.856
17.324
17.168
13.977
13.845

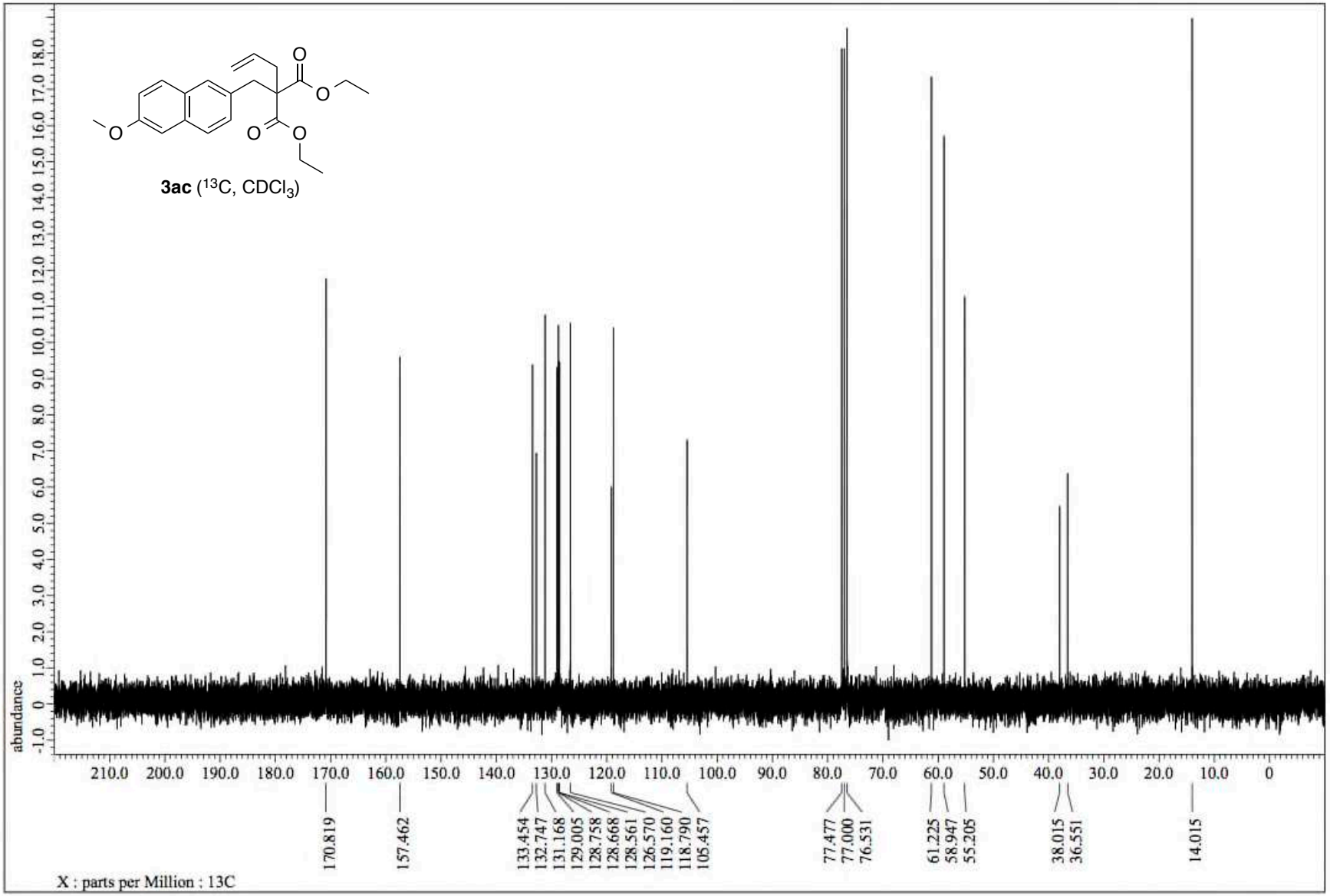

3ha (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
1.06
1.02
2.05
2.00
2.02
3.08
1.02
2.98
3.23
3.26
3.07
7.681
7.651
7.620
7.598
7.593
7.344
7.337
7.313
7.307
7.260
7.135
7.125
7.103
7.093
7.081
4.282
4.269
4.262
4.257
4.243
4.236
4.217
4.209
4.196
4.190
4.184
4.169
4.070
4.044
4.018
3.992
3.905
3.859
3.832
3.806
3.780
1.485
1.458
1.432
1.412
1.296
1.269
1.242
1.163
1.137
1.111
0.000

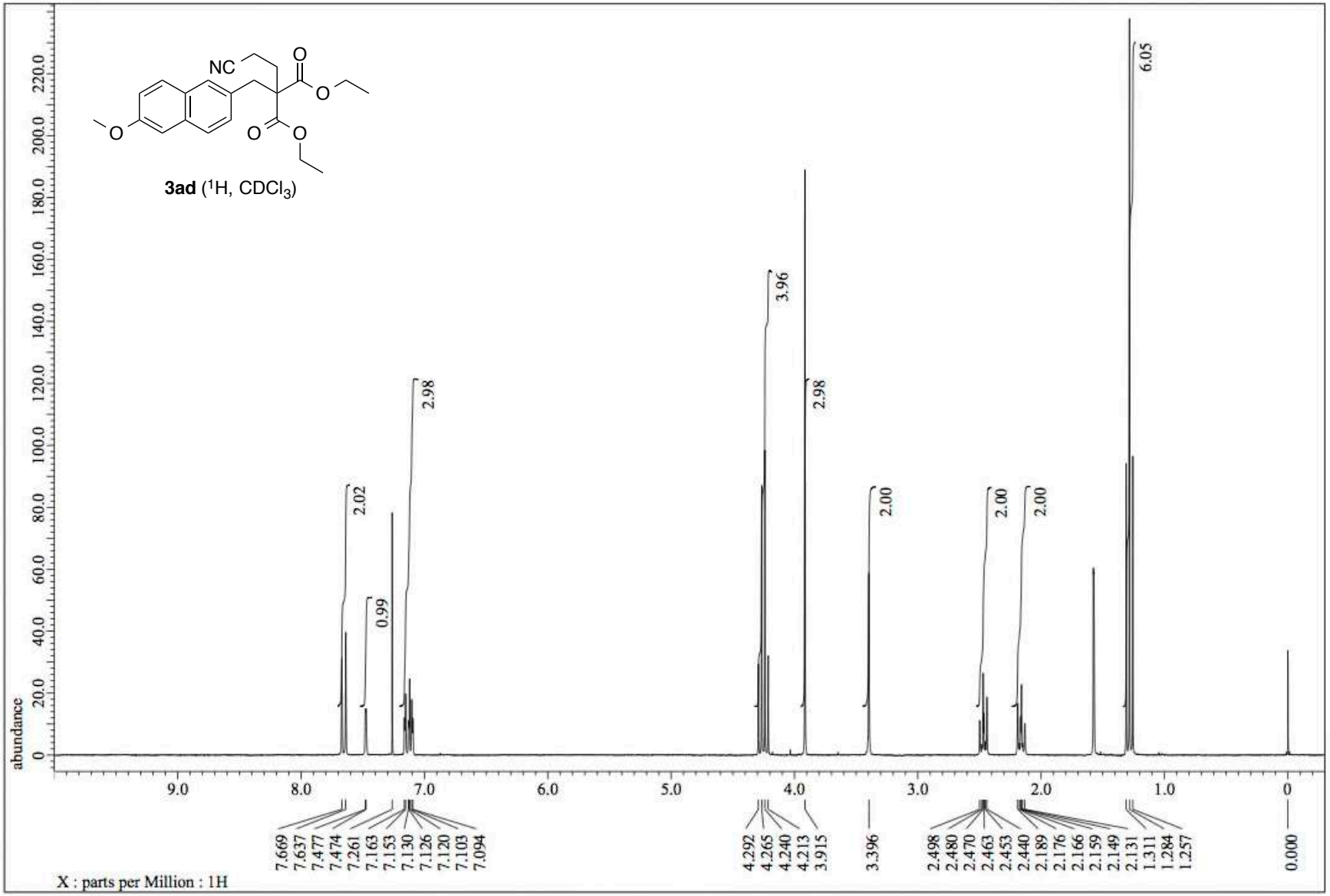

3ha (13C, CDCl3)
abundance
X : parts per Million : 13C
171.531
171.416
157.442
136.807
133.534
129.184
128.600
127.654
127.588
126.231
118.681
105.382
77.469
77.000
76.531
61.152
61.069
58.429
55.197
43.700
17.267
17.176
13.977
13.853

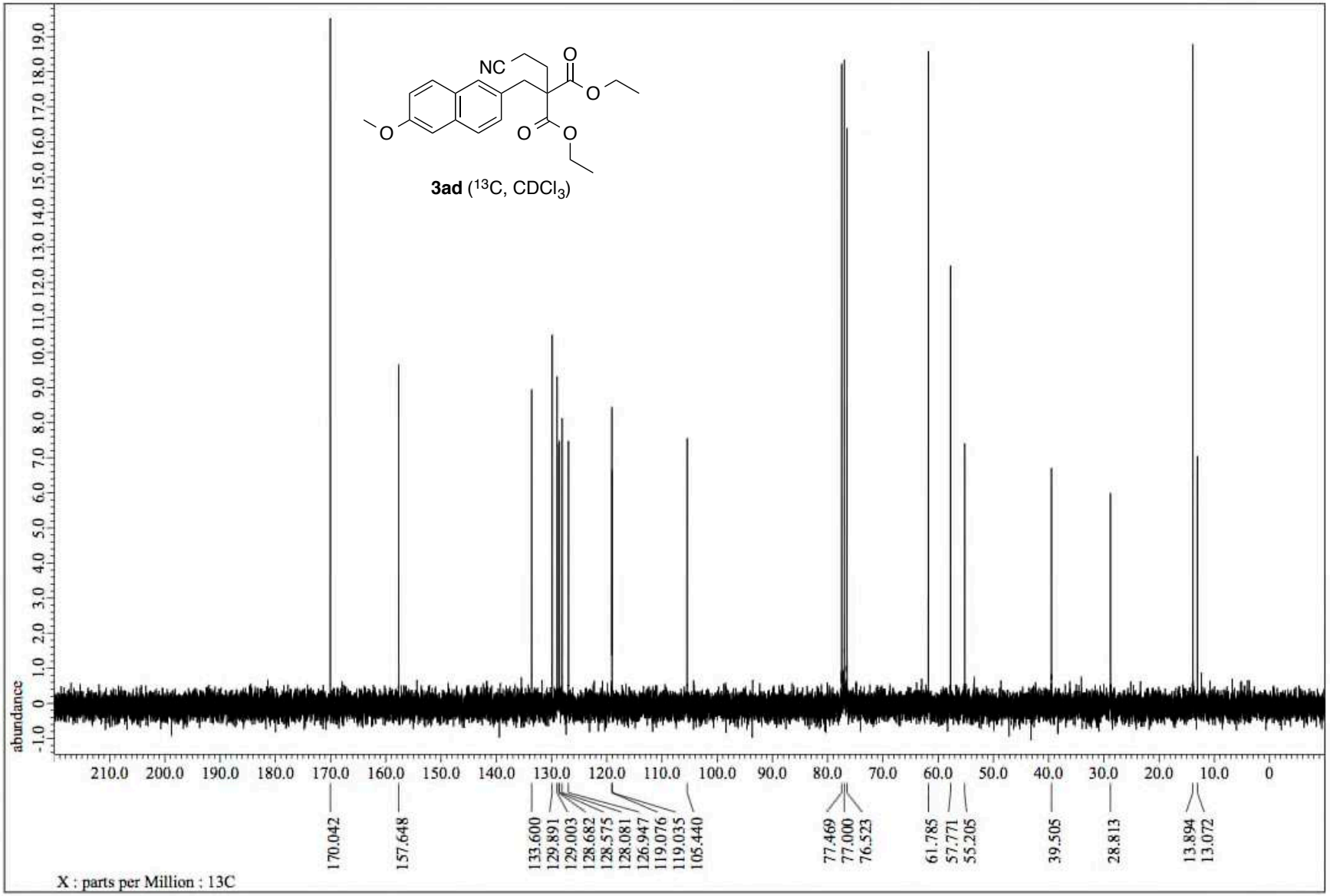

3ab (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
1.00
2.02
1.02
4.08
3.00
2.00
2.00
3.96
6.24
2.98

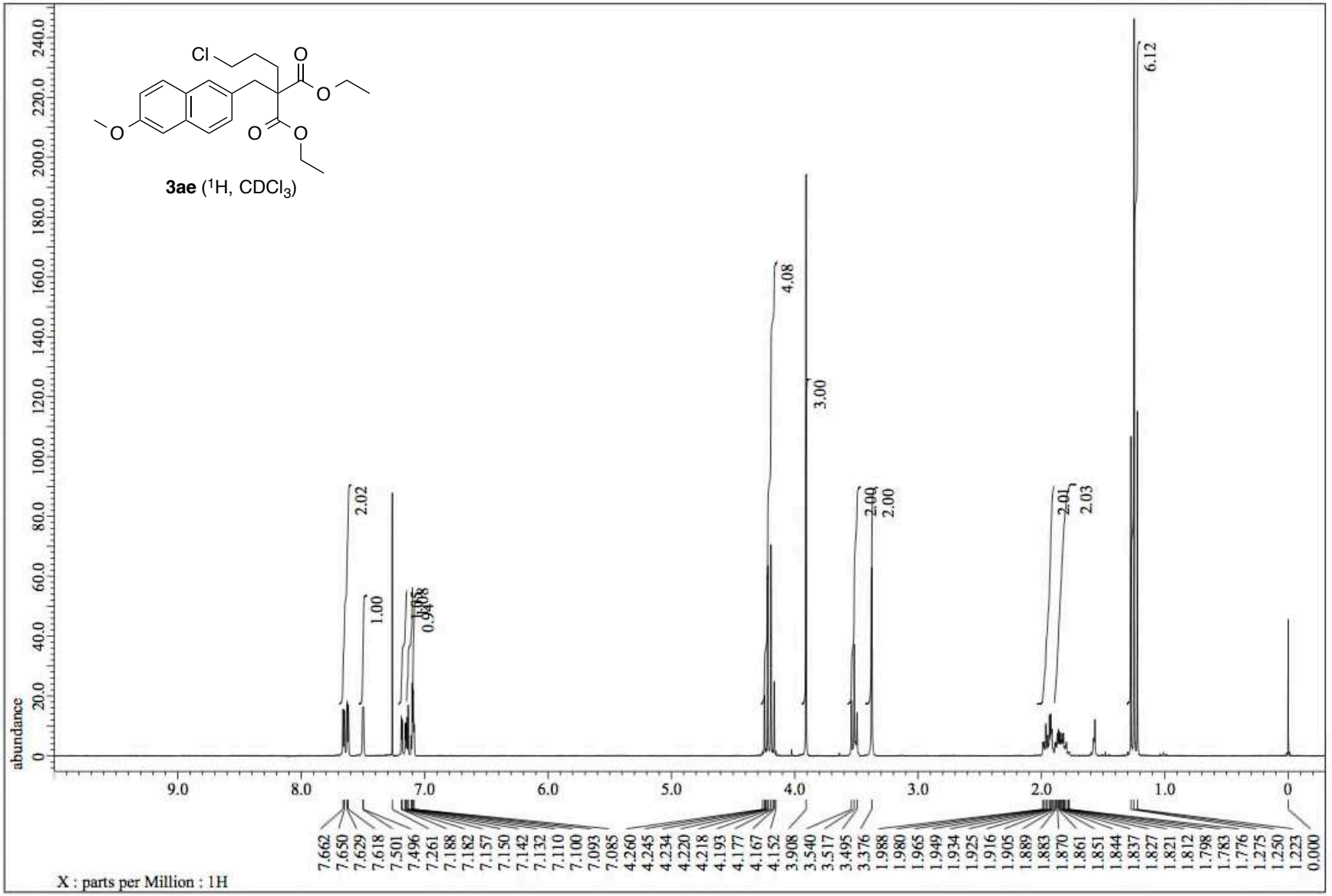

3ab (13C, CDCl3)
abundance
X : parts per Million : 13C
171.416
157.410
133.411
131.453
128.986
128.764
128.501
128.452
126.511
118.747
105.448
77.469
77.000
76.531
61.061
58.931
55.197
37.893
31.454
26.264
22.818
14.010
13.870

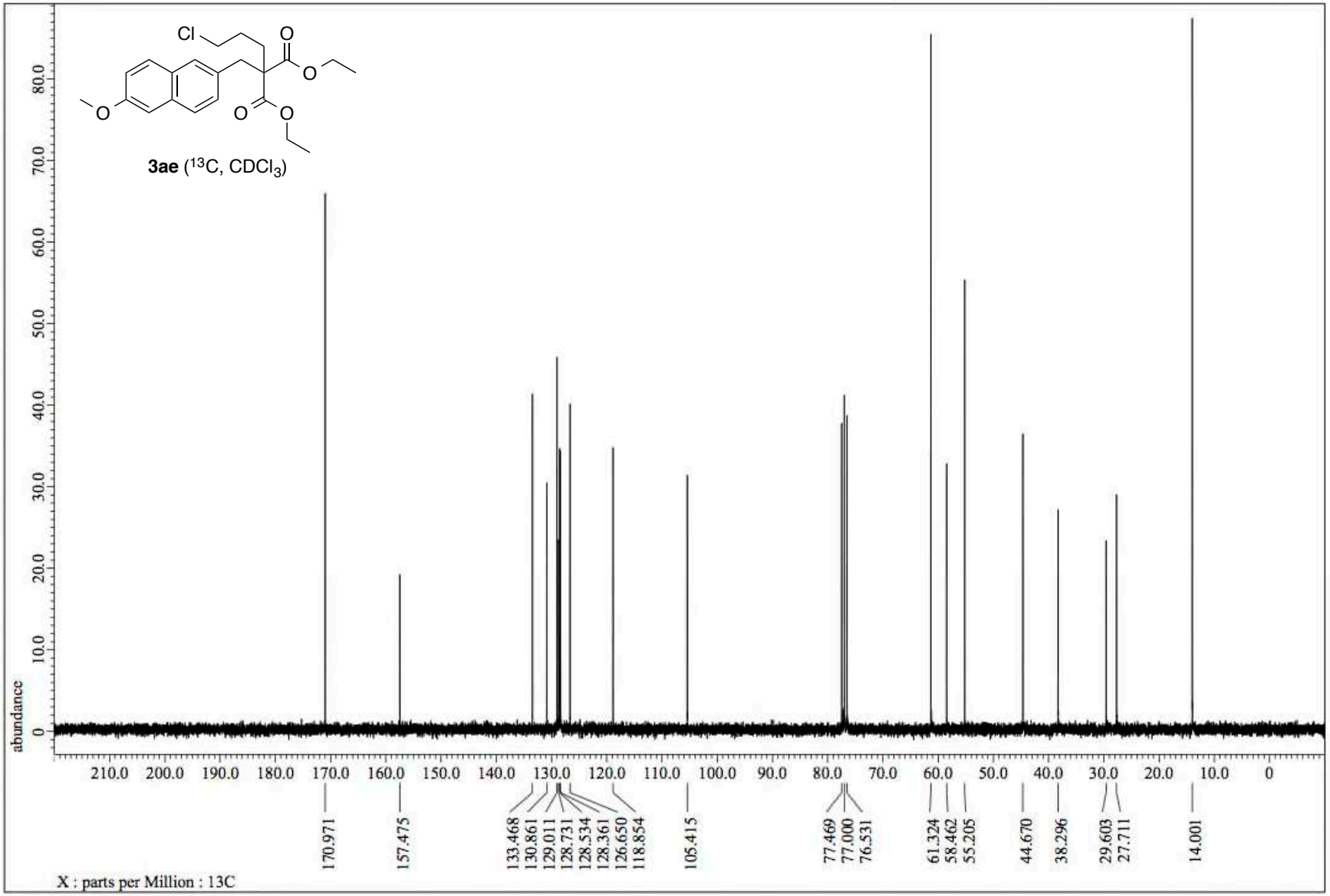

3ac (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
1.00
0.97
1.99
1.00
0.91
4.06
3.00
2.00
1.99
6.00

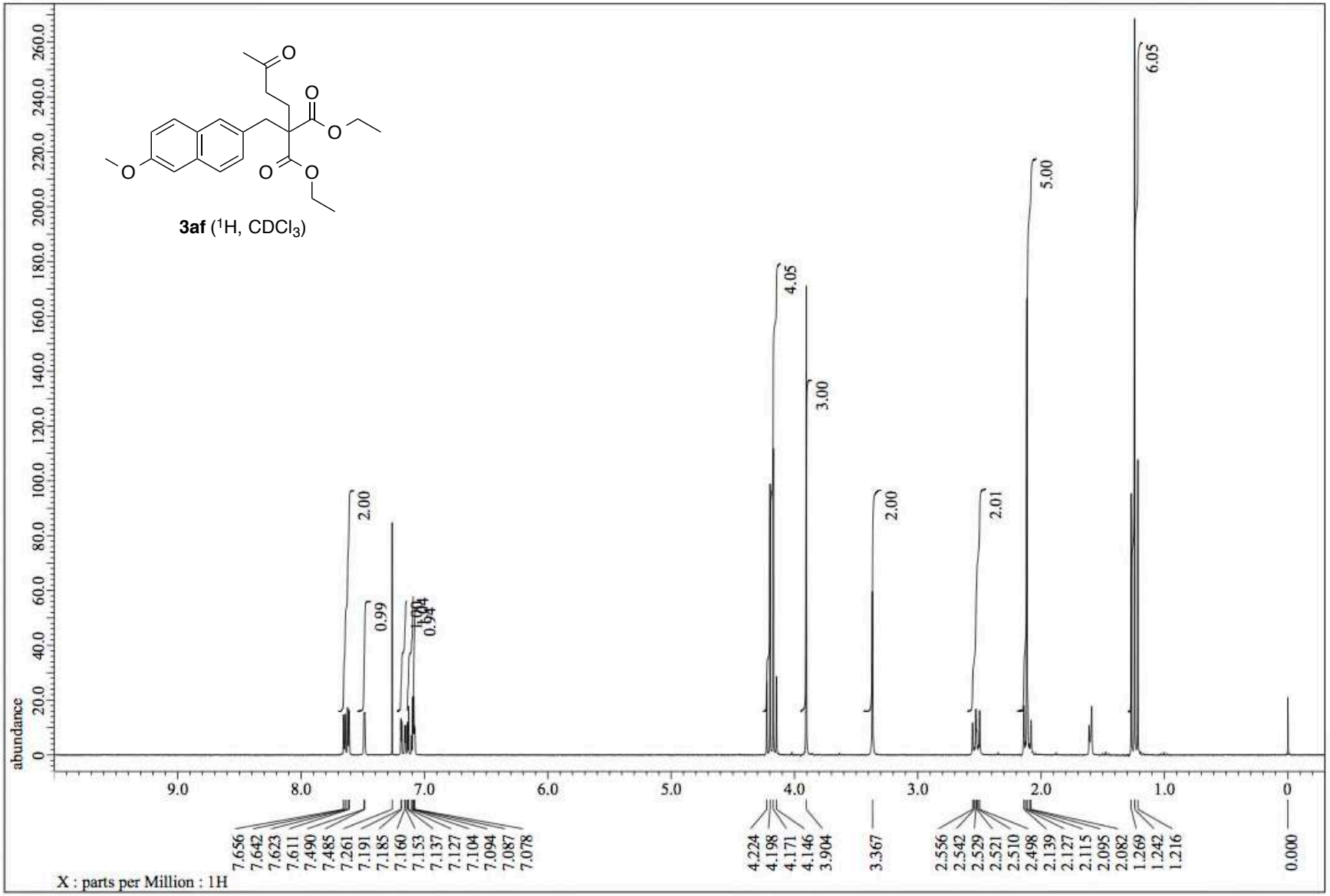

3ac (13C, CDCl3)
abundance
X : parts per Million : 13C
170.819
157.462
133.454
132.747
131.168
129.005
128.758
128.668
128.561
126.570
119.160
118.790
105.457
77.477
77.000
76.531
61.225
58.947
55.205
38.015
36.551
14.015

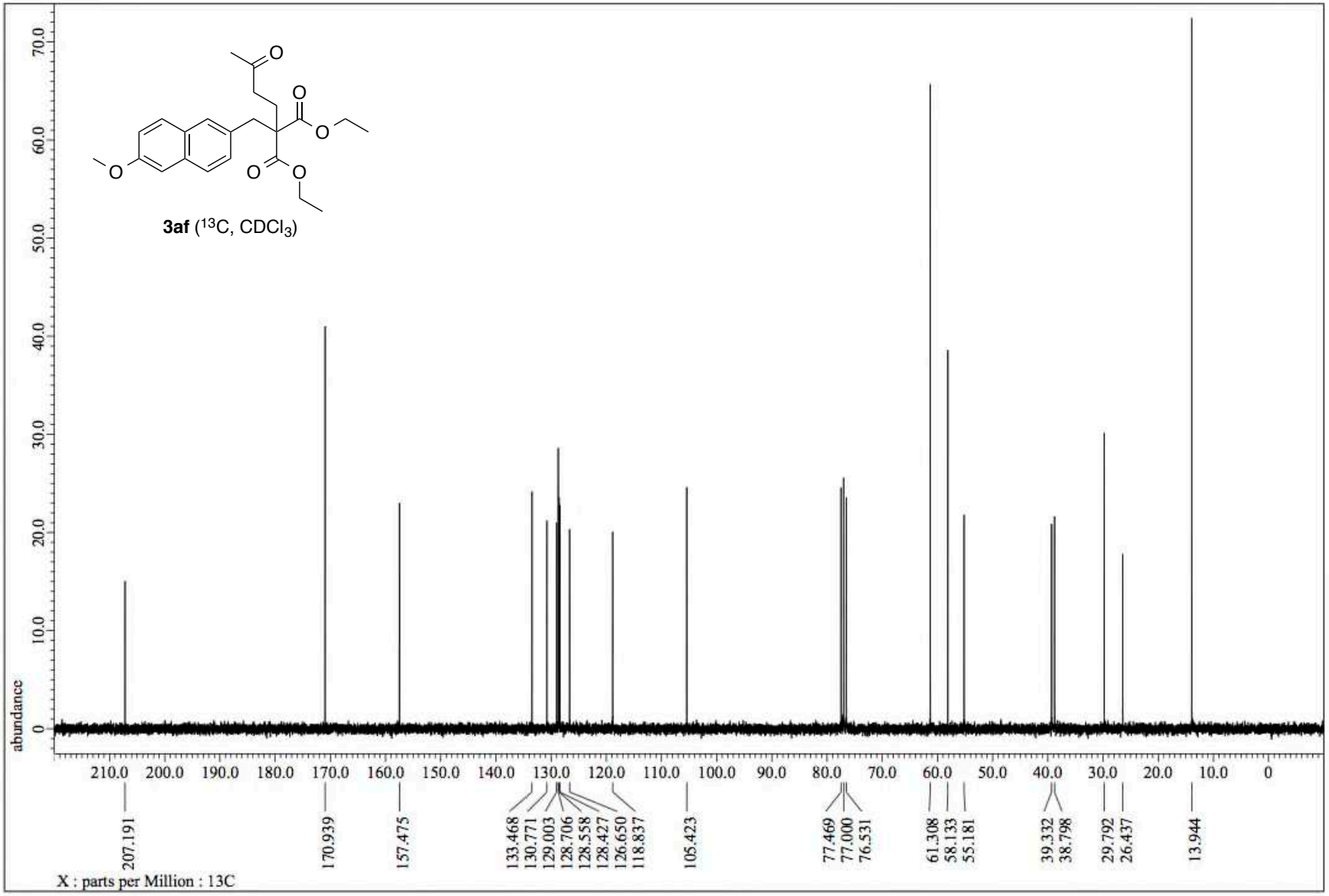

NC
O
O
O
O
O
3ad (1H, CDCl3)
abundance
X : parts per Million : 1H
7.669
7.637
7.477
7.474
7.261
7.163
7.153
7.130
7.126
7.120
7.103
7.094
4.292
4.265
4.240
4.213
3.915
3.396
2.498
2.480
2.470
2.463
2.453
2.440
2.189
2.176
2.166
2.159
2.149
2.131
1.311
1.284
1.257
0.000
2.02
0.99
2.98
3.96
2.98
2.00
2.00
2.00
6.05

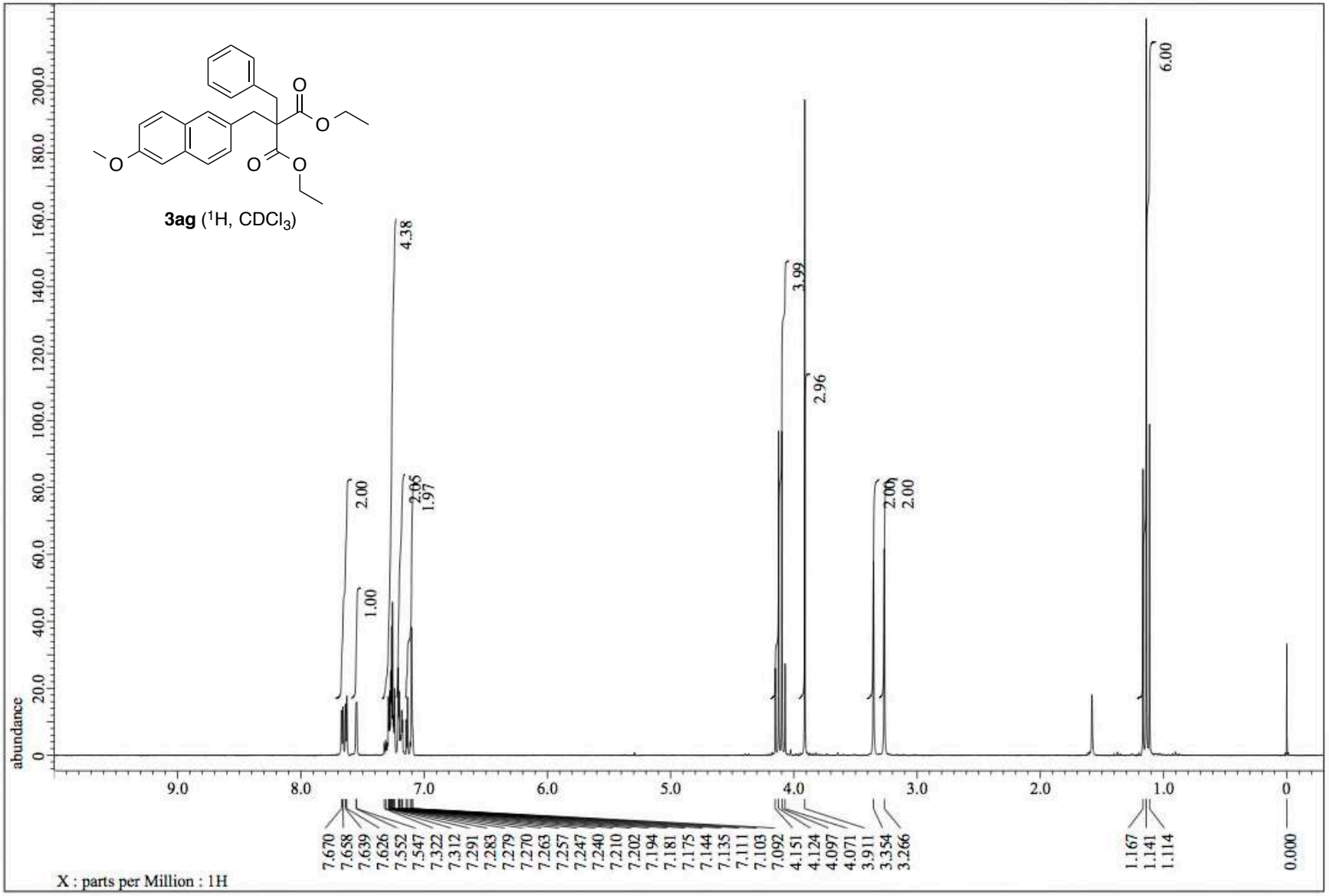

NC
O
O
O
O
O
3ad (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
170.042
157.648
133.600
129.891
129.003
128.682
128.575
128.081
126.947
119.076
119.035
105.440
77.469
77.000
76.523
61.785
57.771
55.205
39.505
28.813
13.894
13.072

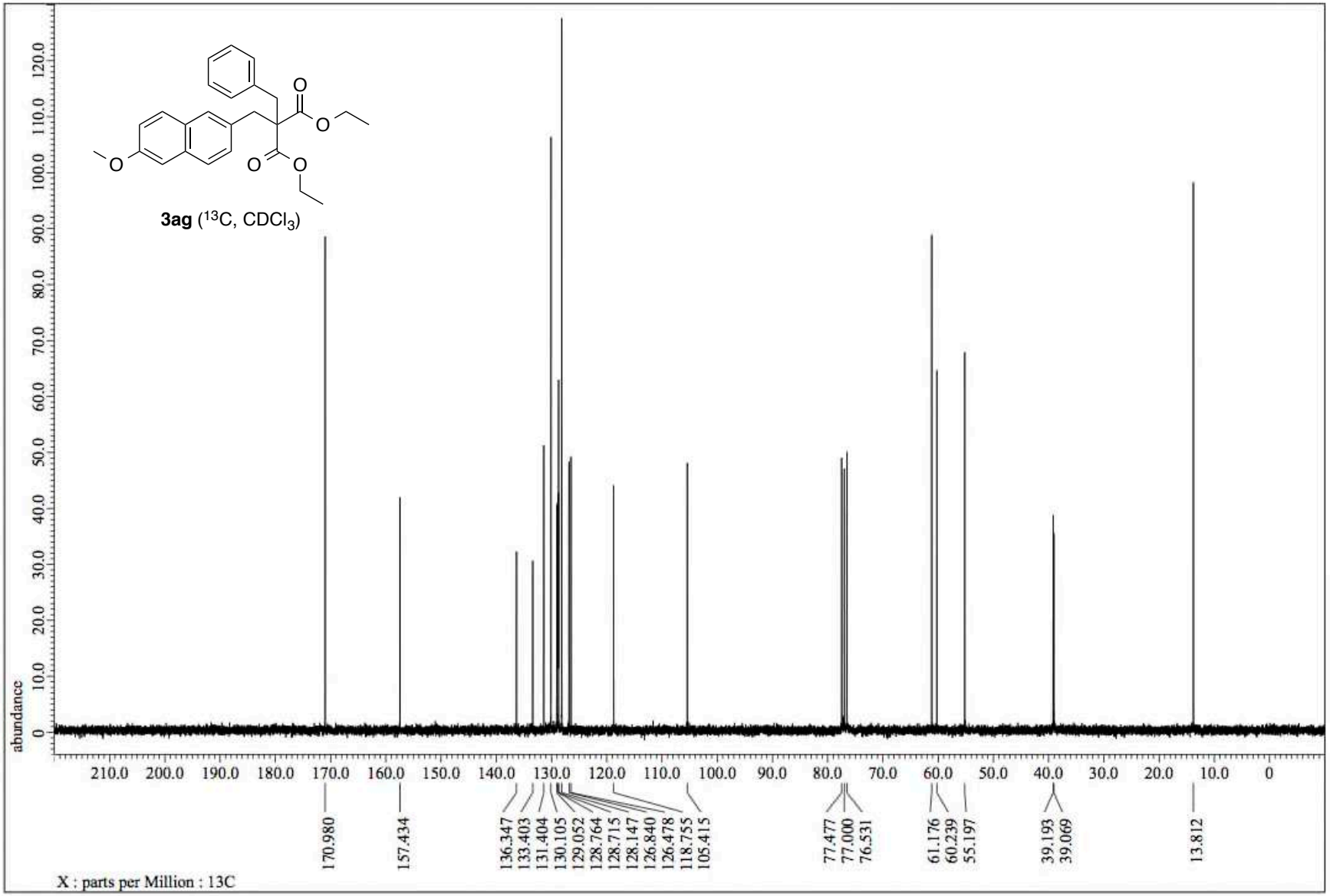

Cl
O
O
O
O
O
3ae (1H, CDCl3)
abundance
X : parts per Million : 1H
6.12
4.08
3.00
2.02
2.00
2.01
2.03
1.00

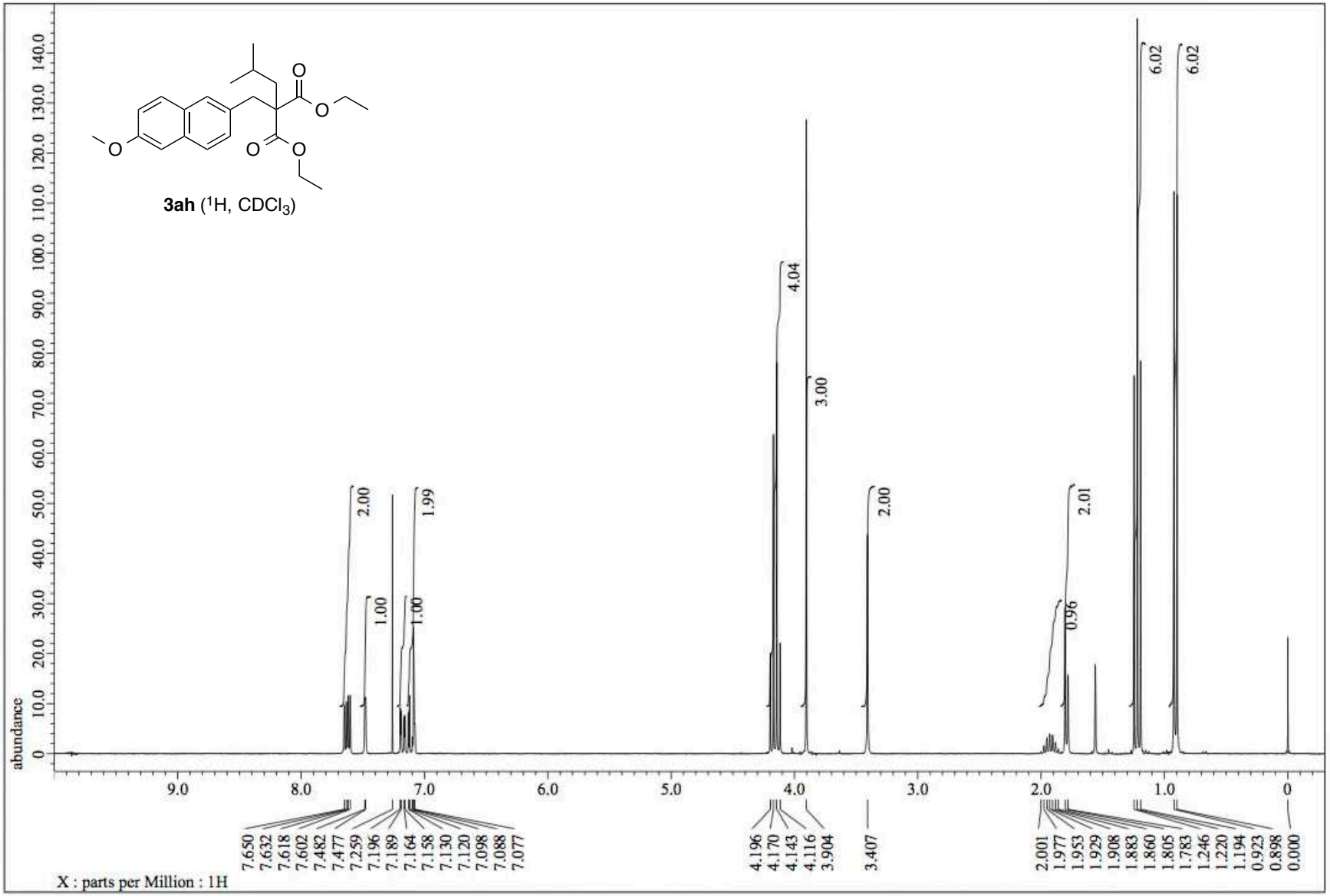

Cl
O
O
O
O
O
3ae (13C, CDCl3)
abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.971
157.475
133.468
130.861
129.011
128.731
128.534
128.361
126.650
118.854
105.415
77.469
77.000
76.531
61.324
58.462
55.205
44.670
38.296
29.603
27.711
14.001
X : parts per Million : 13C

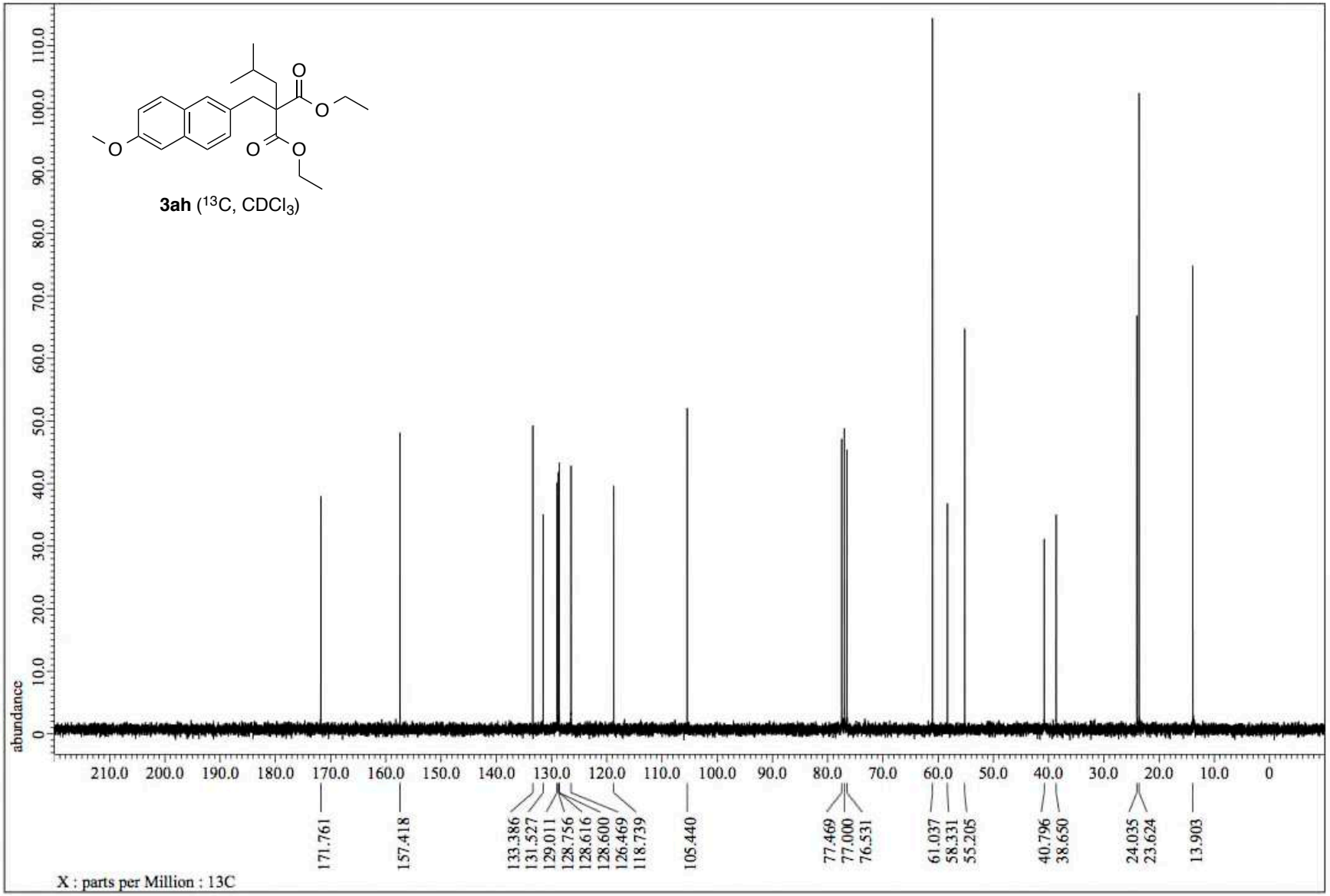

3af (1H, CDCl3)
abundance
X : parts per Million : 1H
7.656
7.642
7.623
7.611
7.490
7.485
7.261
7.191
7.185
7.160
7.153
7.137
7.127
7.104
7.094
7.087
7.078
4.224
4.198
4.171
4.146
3.904
3.367
2.556
2.542
2.529
2.521
2.510
2.498
2.139
2.127
2.115
2.095
2.082
1.269
1.242
1.216
0.000
2.00
0.99
0.94
4.05
3.00
2.00
2.01
5.00
6.05

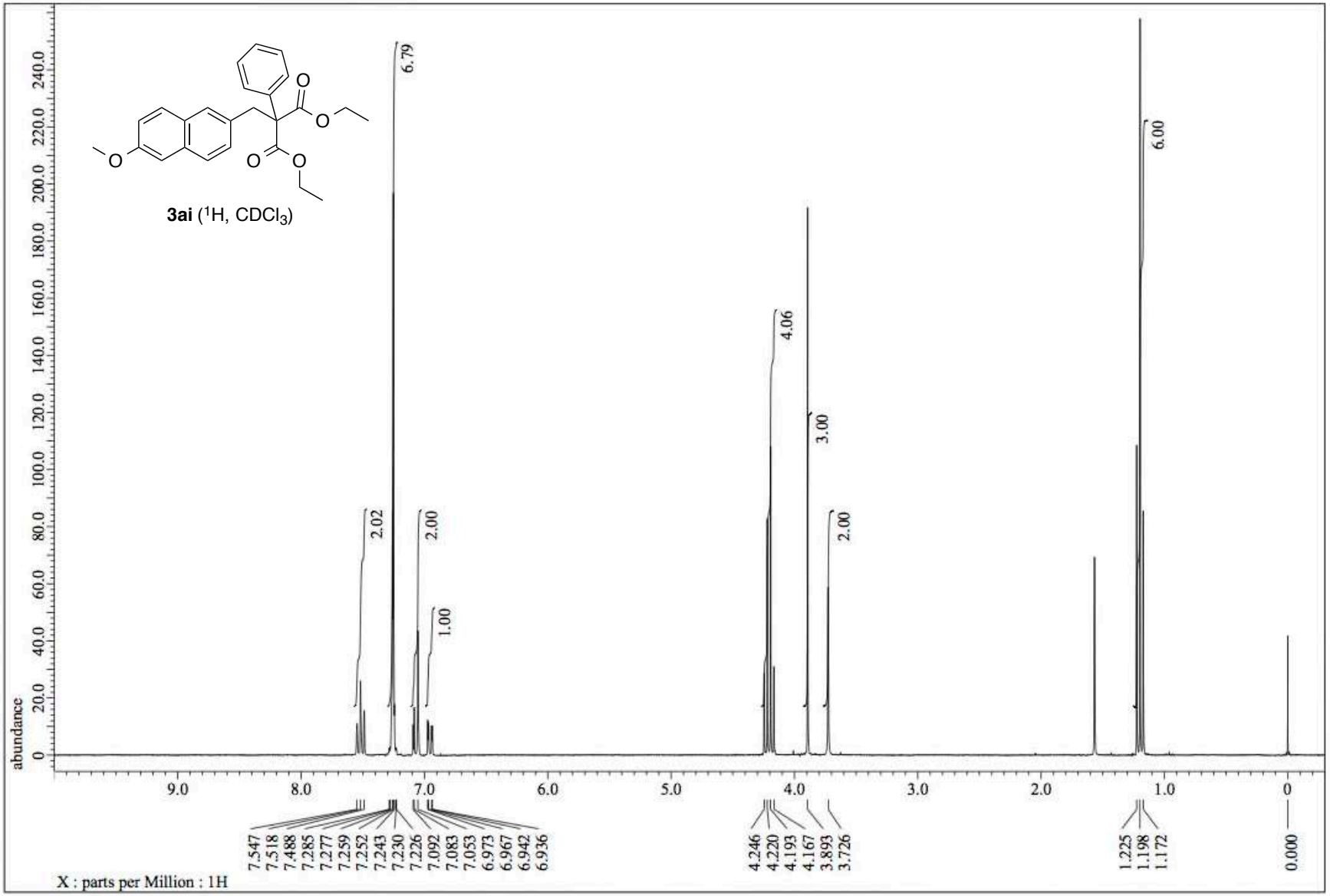

3af (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
207.191
170.939
157.475
133.468
130.771
129.003
128.706
128.558
128.427
126.650
118.837
105.423
77.469
77.000
76.531
61.308
58.133
55.181
39.332
38.798
29.792
26.437
13.944

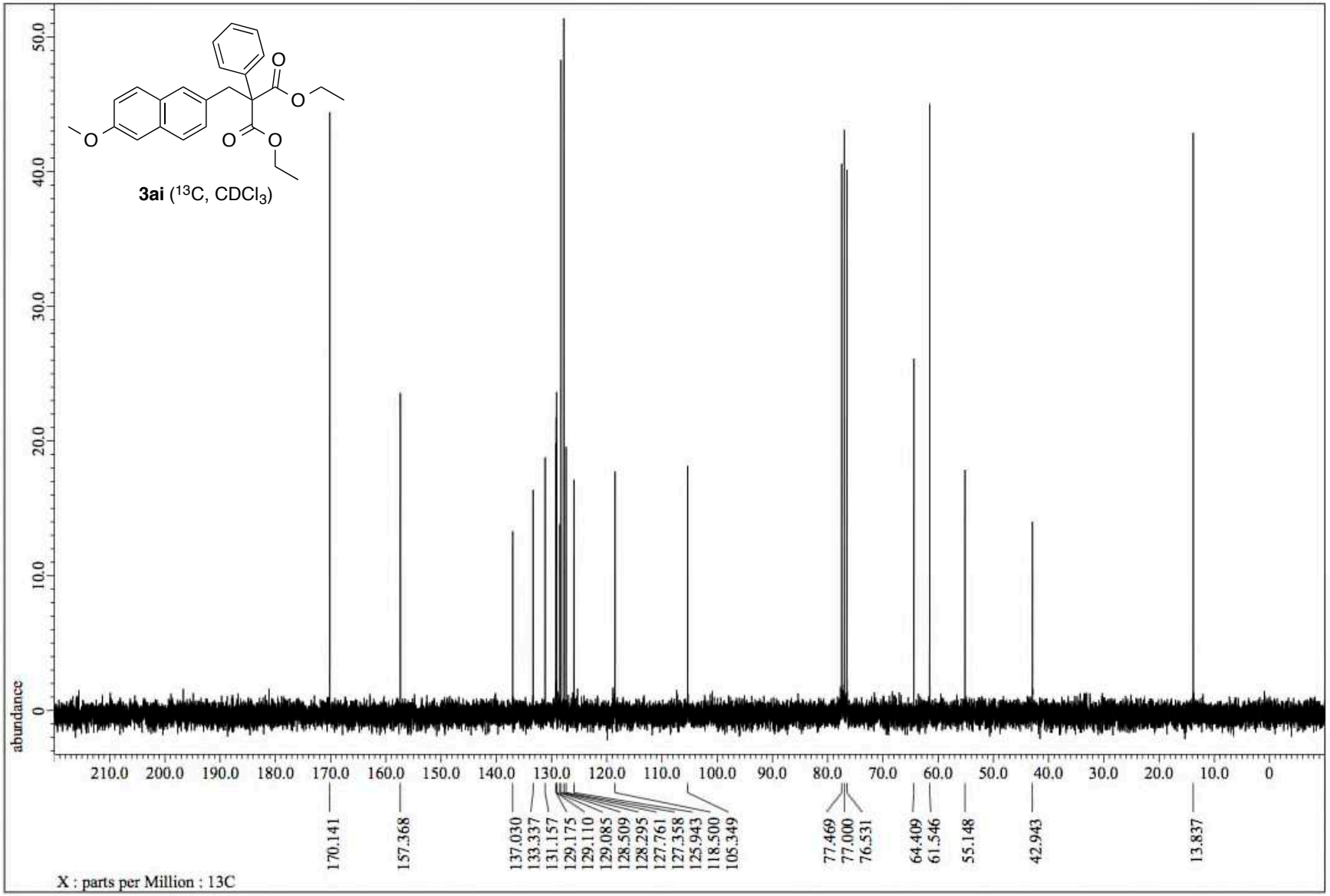

3ag (1H, CDCl3)
abundance
X : parts per Million : 1H
4.38
3.99
2.96
6.00
2.00
1.00
2.05
1.97
2.00
2.00
7.670
7.658
7.639
7.626
7.552
7.547
7.322
7.312
7.291
7.283
7.279
7.270
7.263
7.257
7.247
7.240
7.210
7.202
7.194
7.181
7.175
7.144
7.135
7.111
7.103
7.092
4.151
4.124
4.097
4.071
3.911
3.354
3.266
1.167
1.141
1.114
0.000

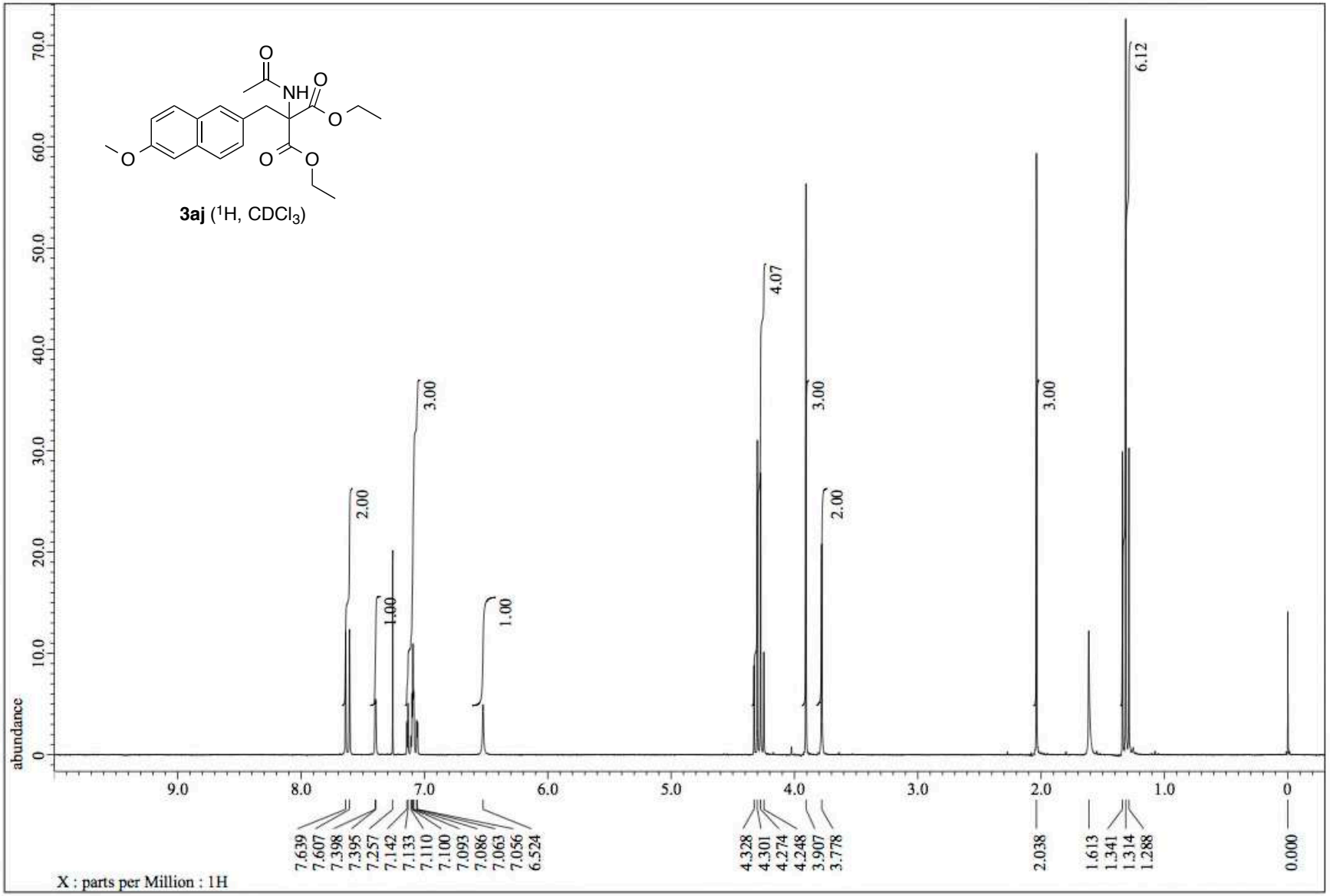

3ag (13C, CDCl3)
abundance
X : parts per Million : 13C
170.980
157.434
136.347
133.403
131.404
130.105
129.052
128.764
128.715
128.147
126.840
126.478
118.755
105.415
77.477
77.000
76.531
61.176
60.239
55.197
39.193
39.069
13.812

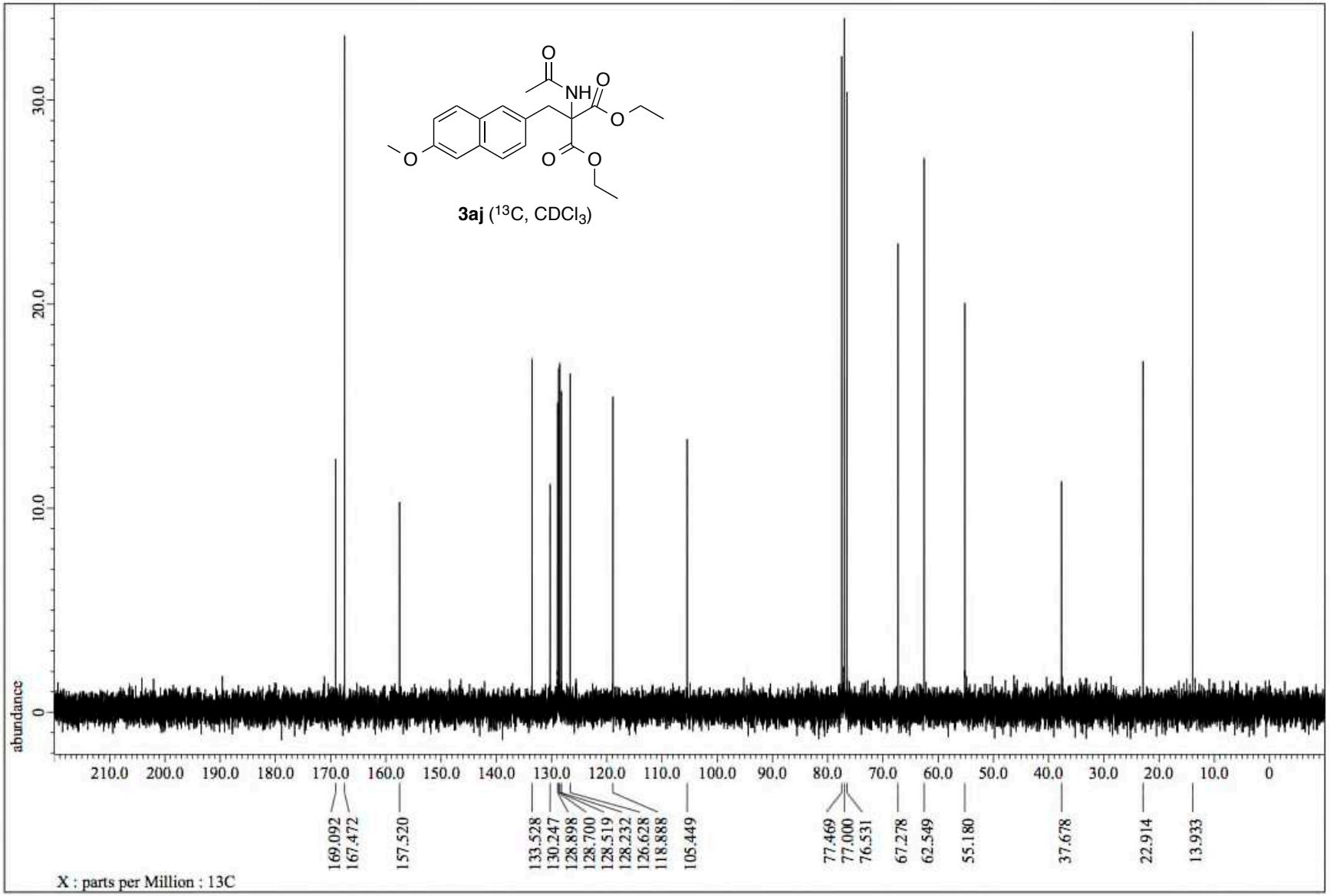

3ah (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
1.00
1.00
1.99
4.04
3.00
2.00
0.96
2.01
6.02
6.02
7.650
7.632
7.618
7.602
7.482
7.477
7.259
7.196
7.189
7.164
7.158
7.130
7.120
7.098
7.088
7.077
4.196
4.170
4.143
4.116
3.904
3.407
2.001
1.977
1.953
1.929
1.908
1.883
1.860
1.805
1.783
1.246
1.220
1.194
0.923
0.898
0.000

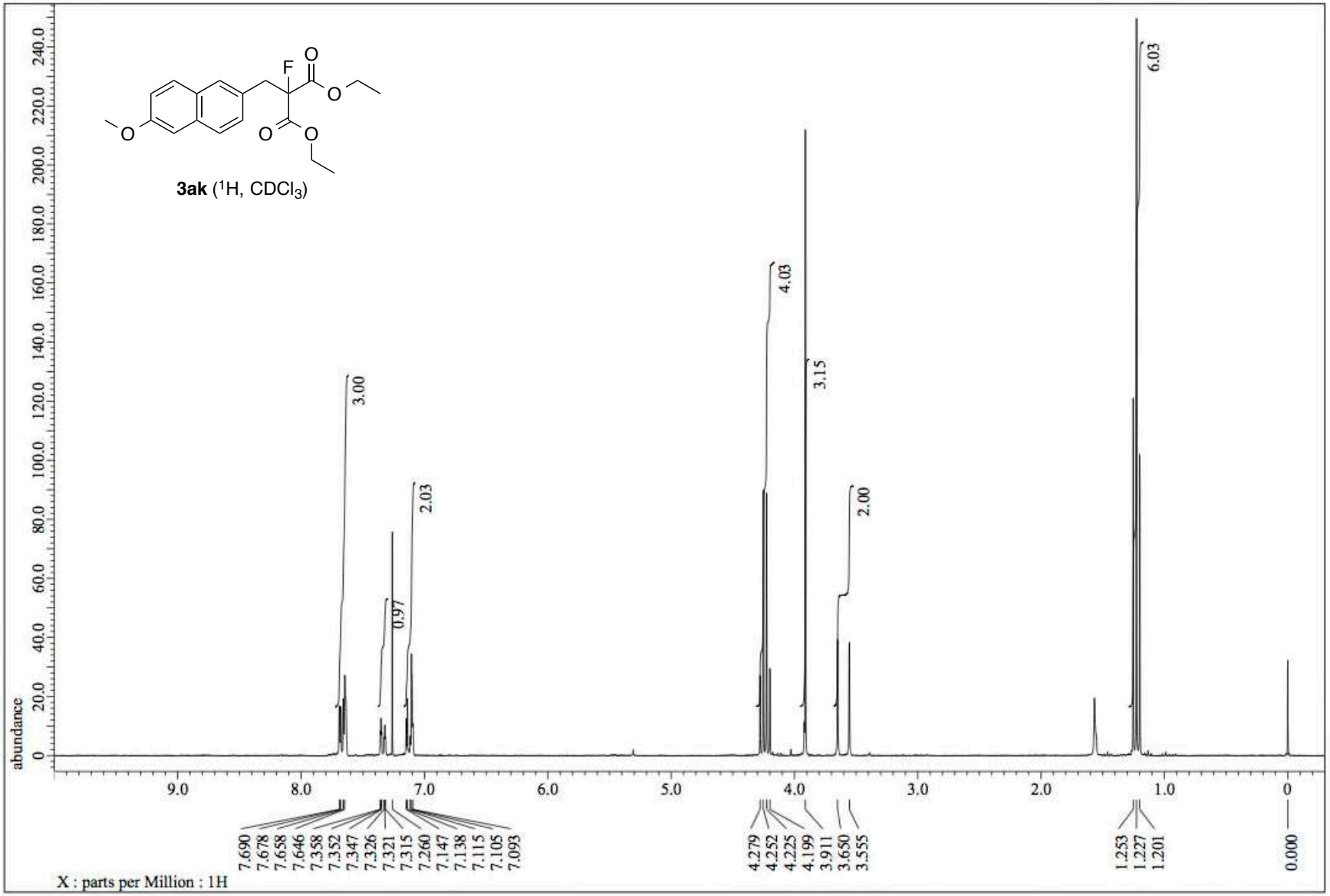

3ah (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
171.761
157.418
133.386
131.527
129.011
128.756
128.616
128.600
126.469
118.739
105.440
77.469
77.000
76.531
61.037
58.331
55.205
40.796
38.650
24.035
23.624
13.903

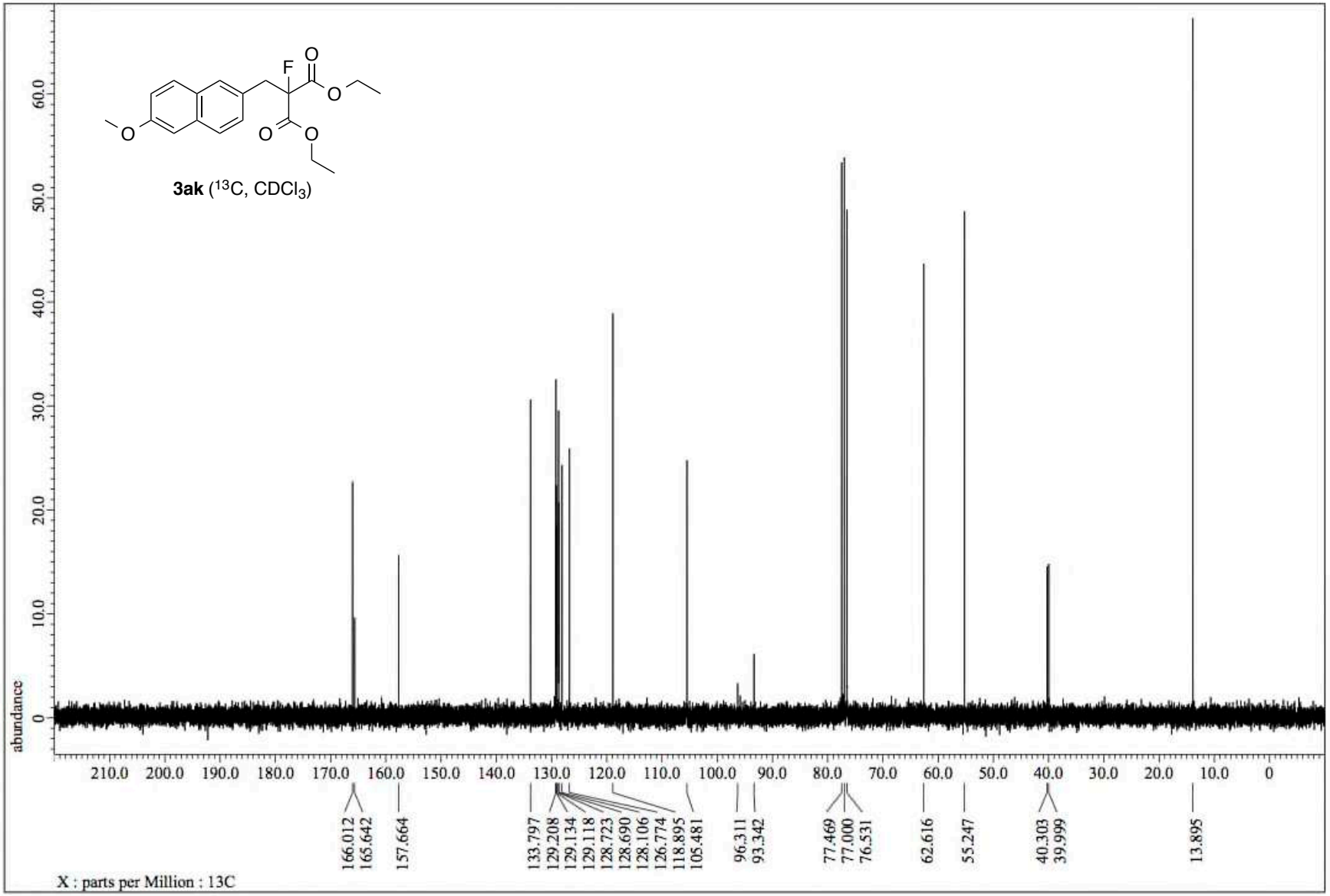

3ai (1H, CDCl3)
abundance
X : parts per Million : 1H
6.79
2.02
2.00
1.00
4.06
3.00
2.00
6.00
7.547
7.518
7.488
7.285
7.277
7.259
7.252
7.243
7.230
7.226
7.092
7.083
7.053
6.973
6.967
6.942
6.936
4.246
4.220
4.193
4.167
3.893
3.726
1.225
1.198
1.172
0.000

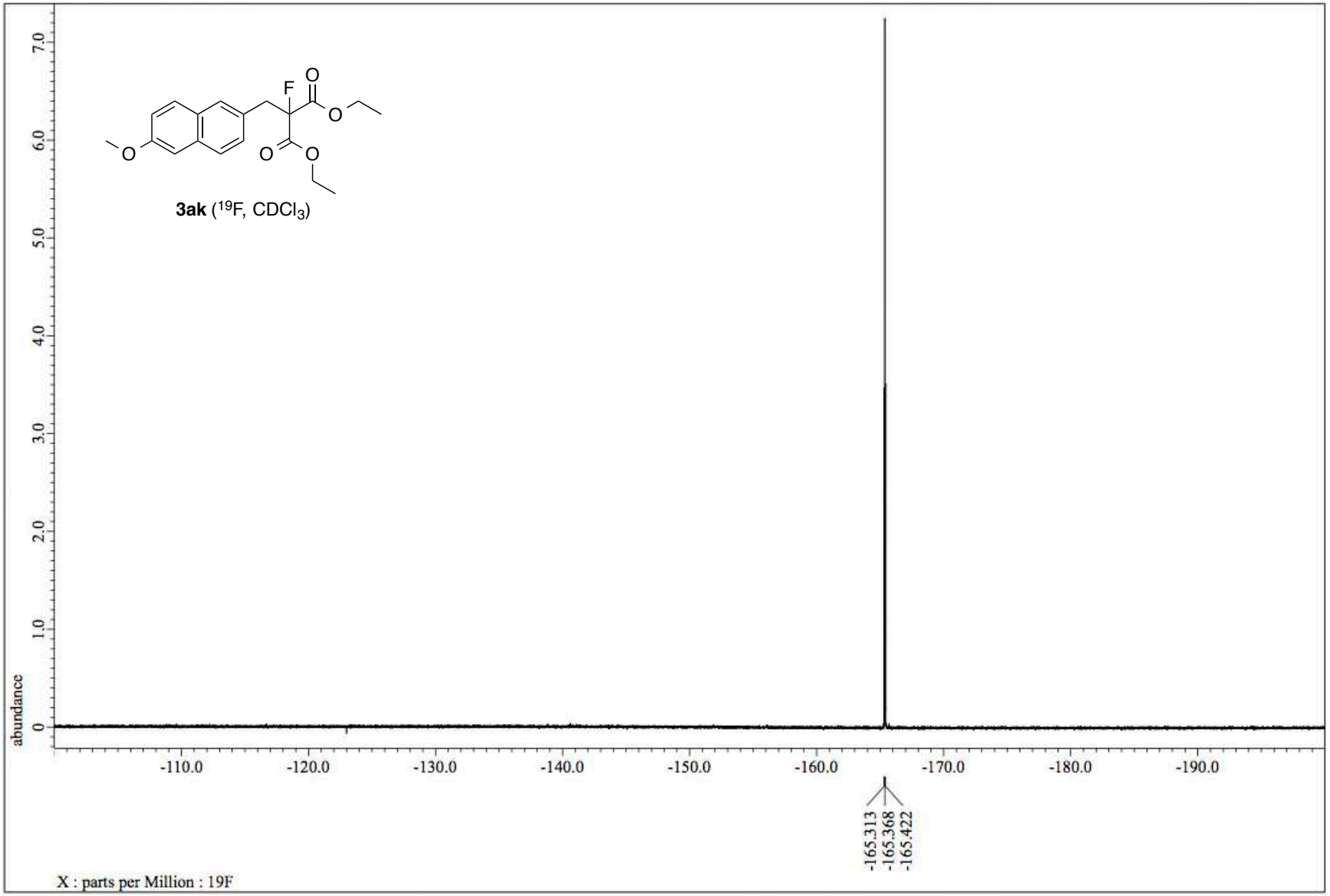

3ai (13C, CDCl3)
abundance
X : parts per Million : 13C
170.141
157.368
137.030
133.337
131.157
129.175
129.110
129.085
128.509
128.295
127.761
127.358
125.943
118.500
105.349
77.469
77.000
76.531
64.409
61.546
55.148
42.943
13.837


3aj (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
1.00
3.00
1.00
4.07
3.00
2.00
3.00
6.12
7.639
7.607
7.398
7.395
7.257
7.142
7.133
7.110
7.100
7.093
7.086
7.063
7.056
6.524
4.328
4.301
4.274
4.248
3.907
3.778
2.038
1.613
1.341
1.314
1.288
0.000

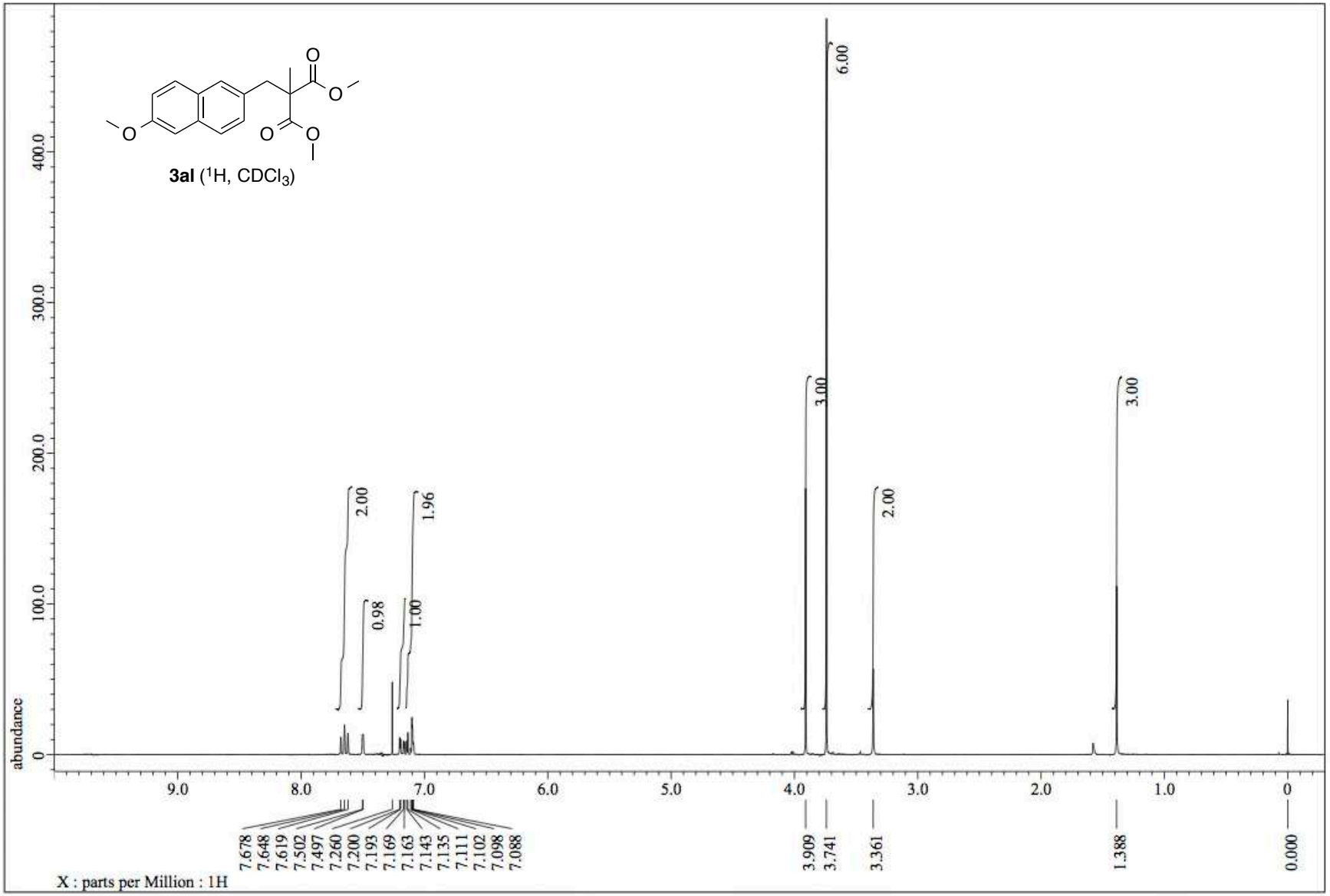

3aj (13C, CDCl3)
abundance
X : parts per Million : 13C
169.092
167.472
157.520
133.528
130.247
128.898
128.700
128.519
128.232
126.628
118.888
105.449
77.469
77.000
76.531
67.278
62.549
55.180
37.678
22.914
13.933

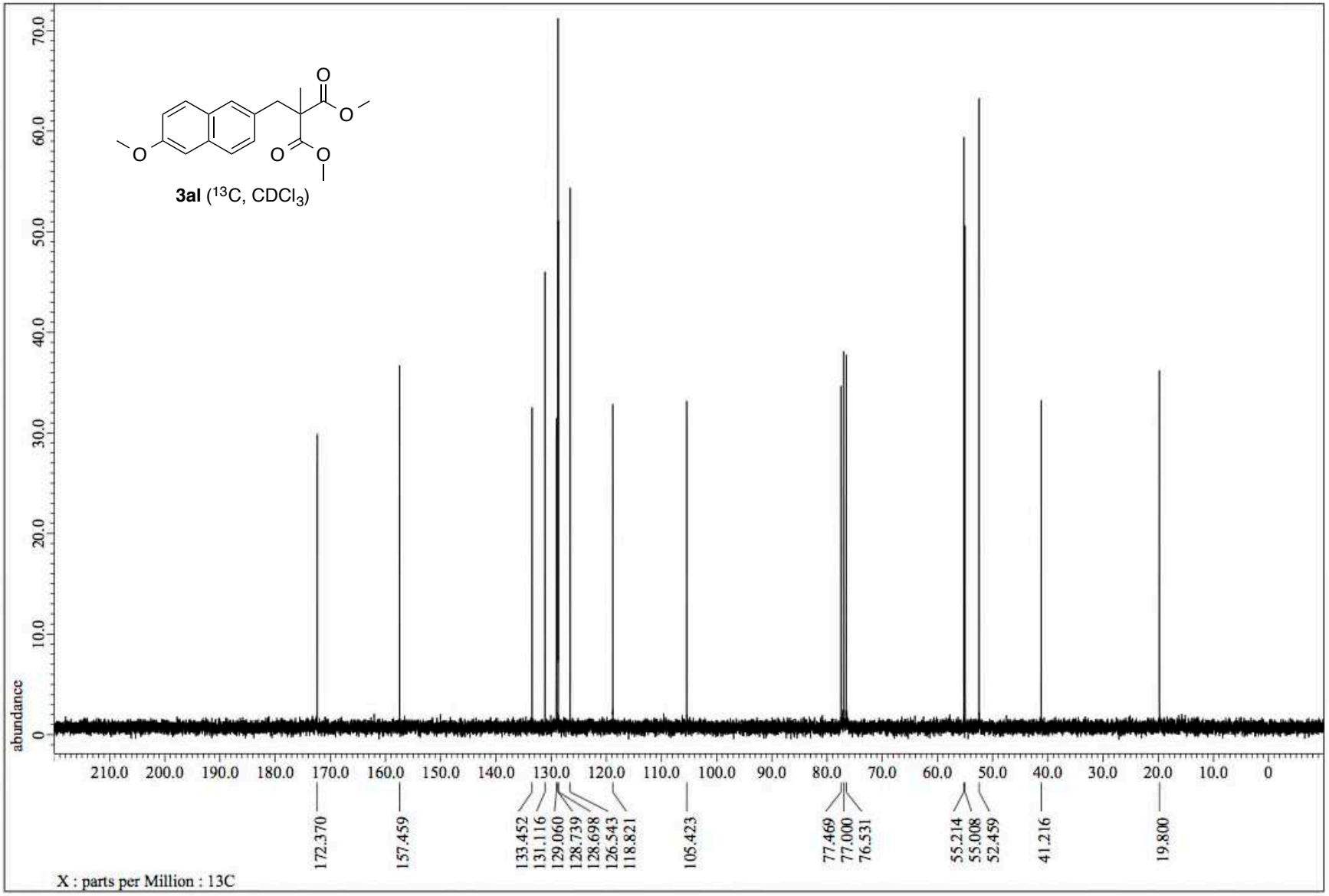

3ak (1H, CDCl3)
abundance
X : parts per Million : 1H
3.00
0.97
2.03
4.03
3.15
2.00
6.03
7.690
7.678
7.658
7.646
7.358
7.352
7.347
7.326
7.321
7.315
7.260
7.147
7.138
7.115
7.105
7.093
4.279
4.252
4.225
4.199
3.911
3.650
3.555
1.253
1.227
1.201
0.000

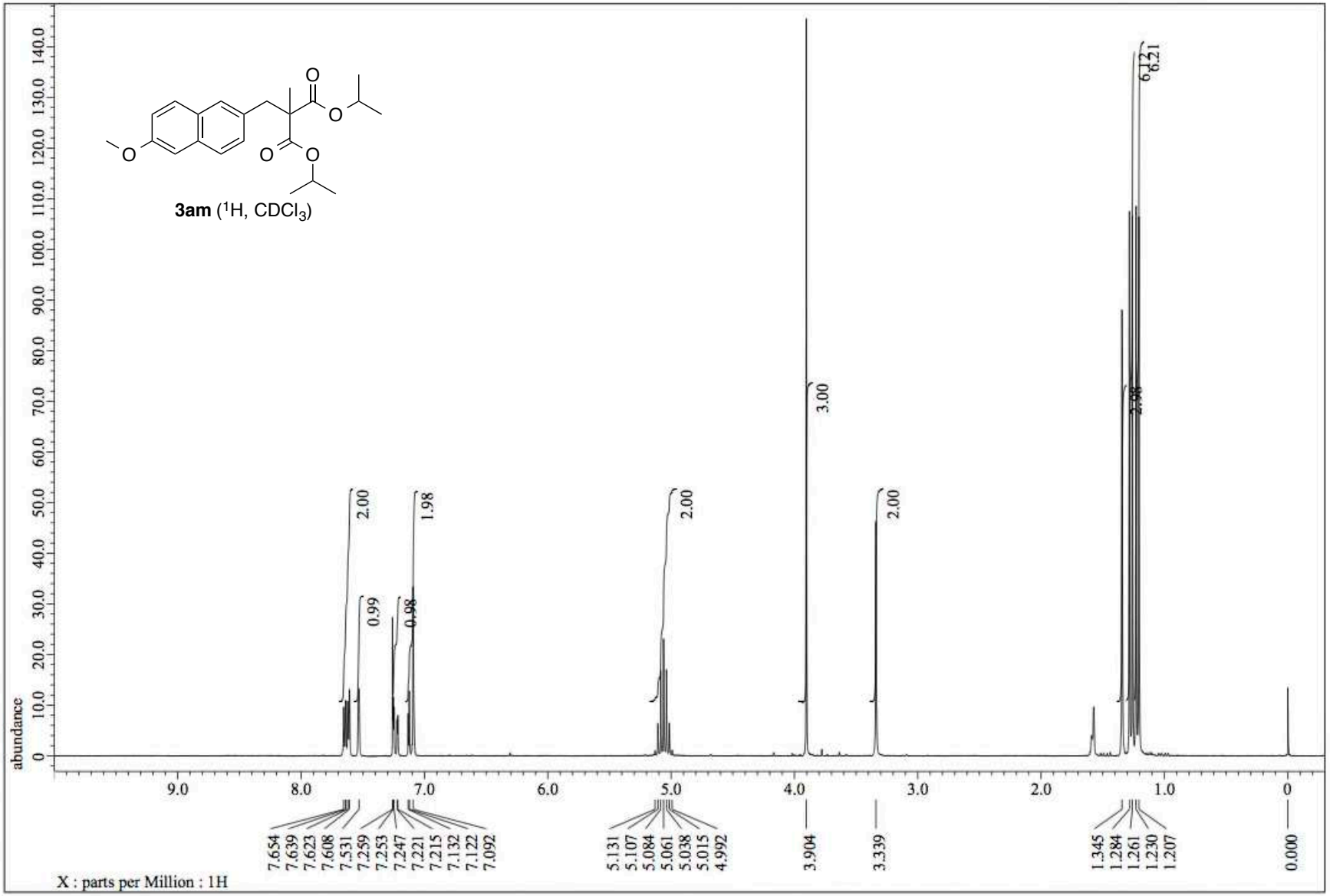

F
O
O
O
O
O
3ak (13C, CDCl3)
abundance
60.0
50.0
40.0
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.012
165.642
157.664
133.797
129.208
129.134
129.118
128.723
128.690
128.106
126.774
118.895
105.481
96.311
93.342
77.469
77.000
76.531
62.616
55.247
40.303
39.999
13.895
X : parts per Million : 13C

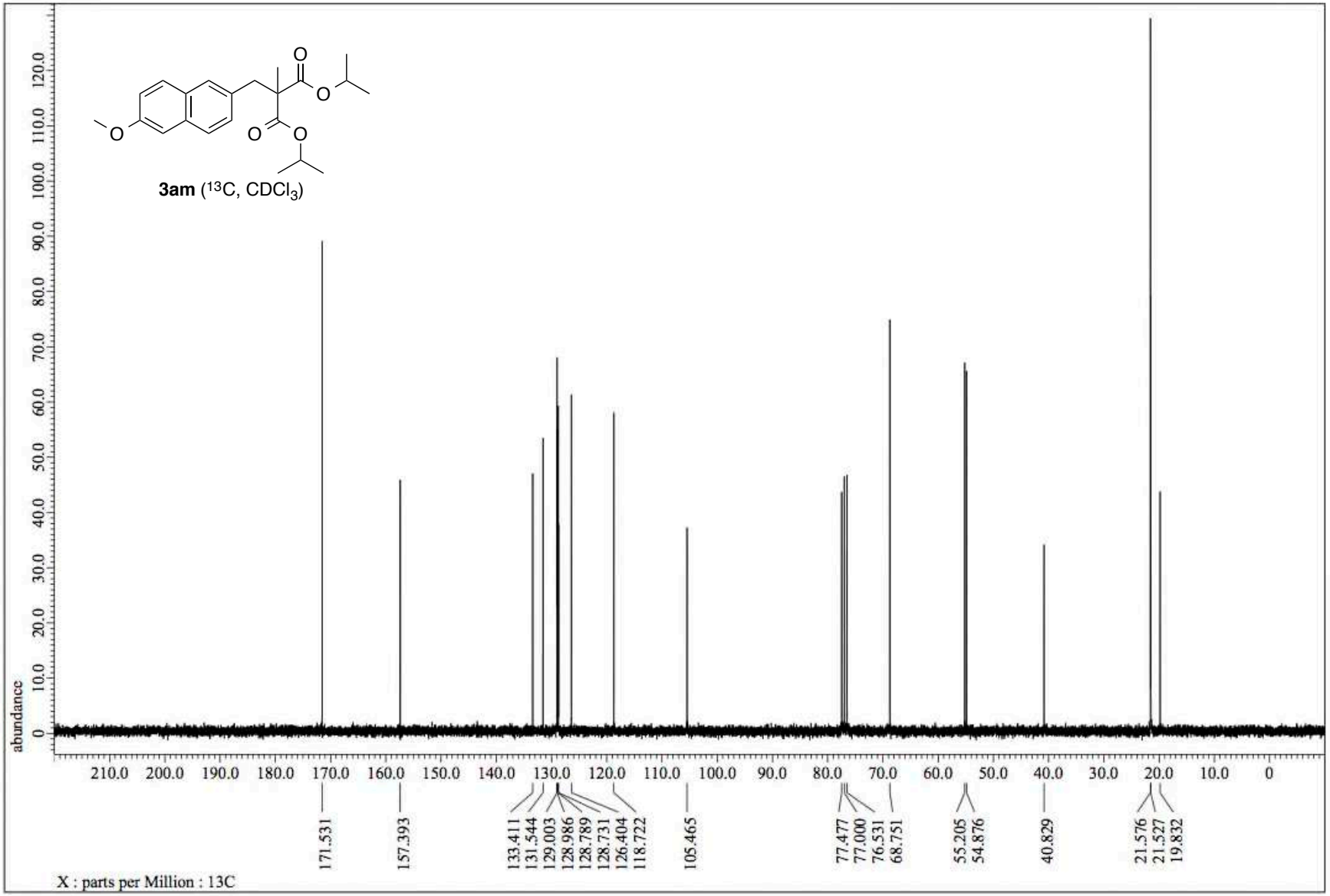


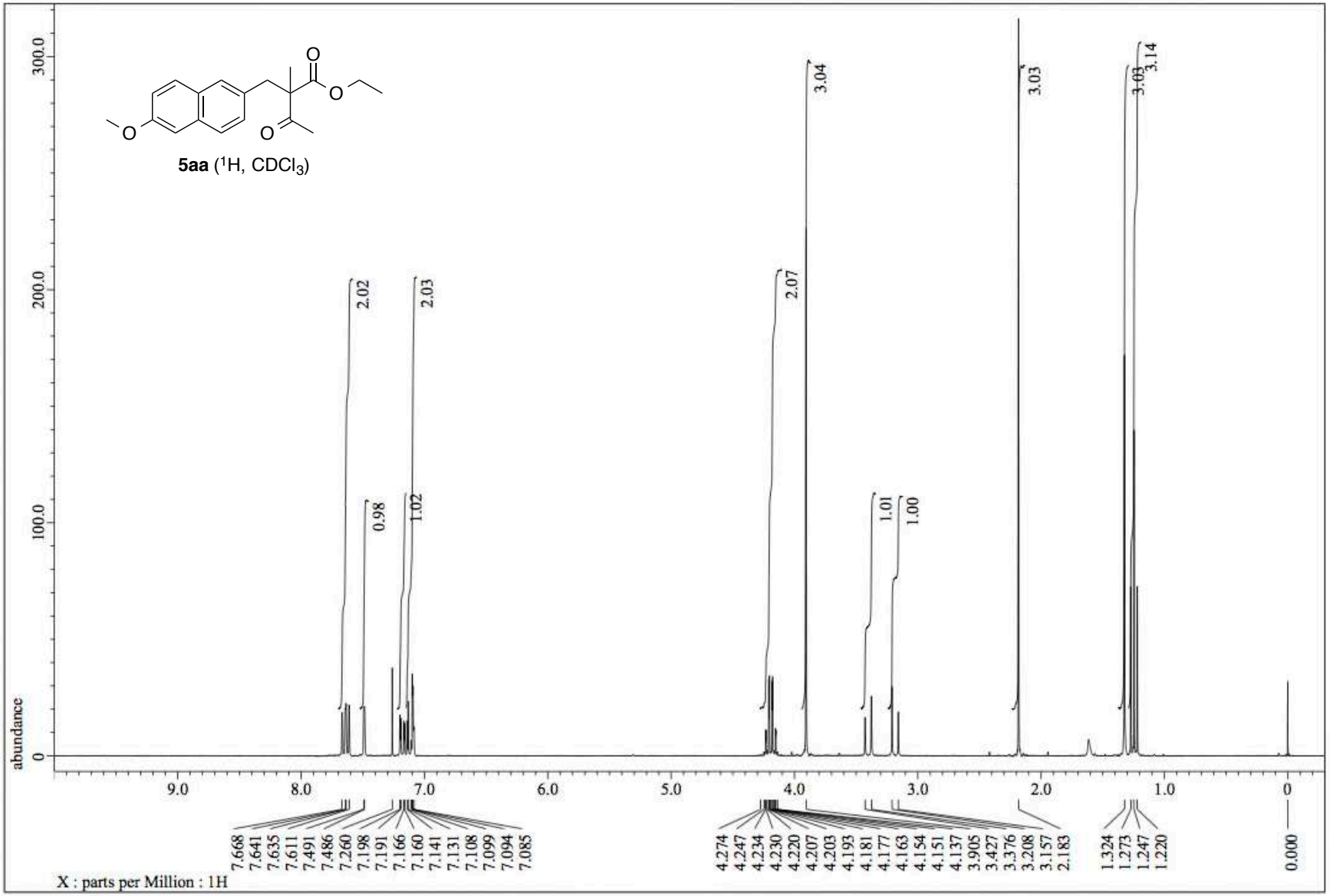
3ak (^{19}F, $CDCl_3$)

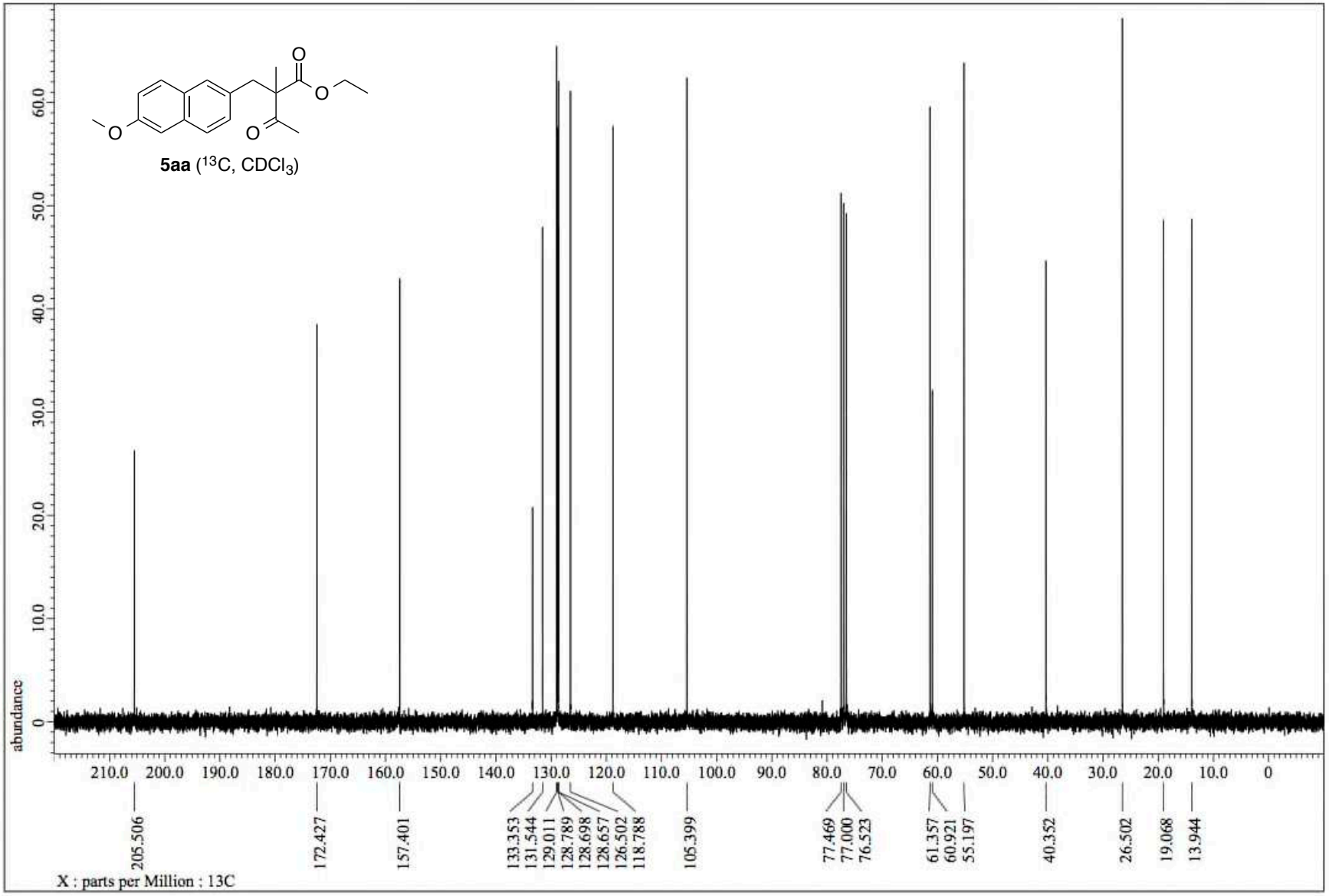

3al (1H, CDCl3)
abundance
X : parts per Million : 1H
6.00
3.00
3.00
2.00
2.00
1.96
1.00
0.98
7.678
7.648
7.619
7.502
7.497
7.260
7.200
7.193
7.169
7.163
7.143
7.135
7.111
7.102
7.098
7.088
3.909
3.741
3.361
1.388
0.000

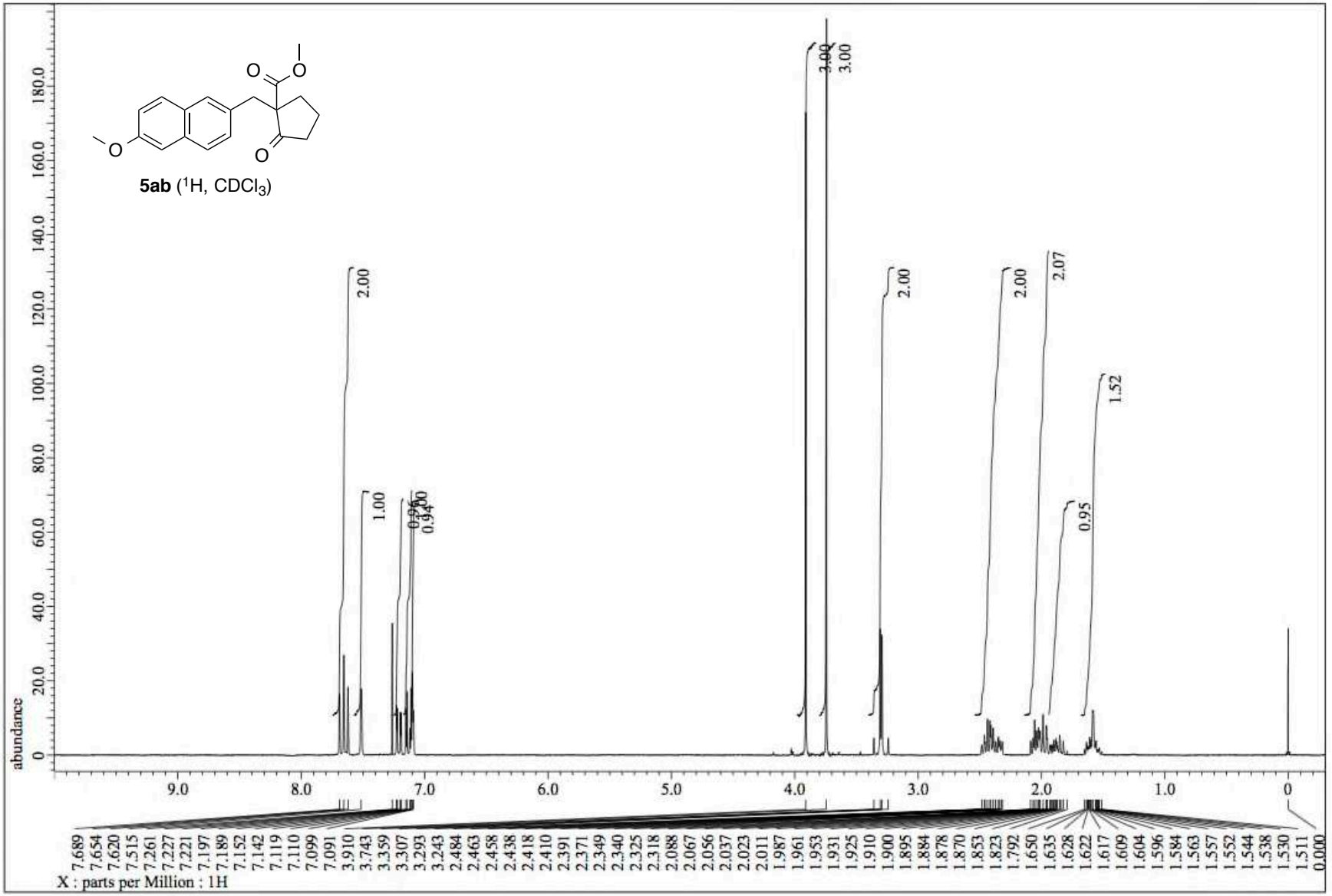

3al (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
172.370
157.459
133.452
131.116
129.060
128.739
128.698
126.543
118.821
105.423
77.469
77.000
76.531
55.214
55.008
52.459
41.216
19.800

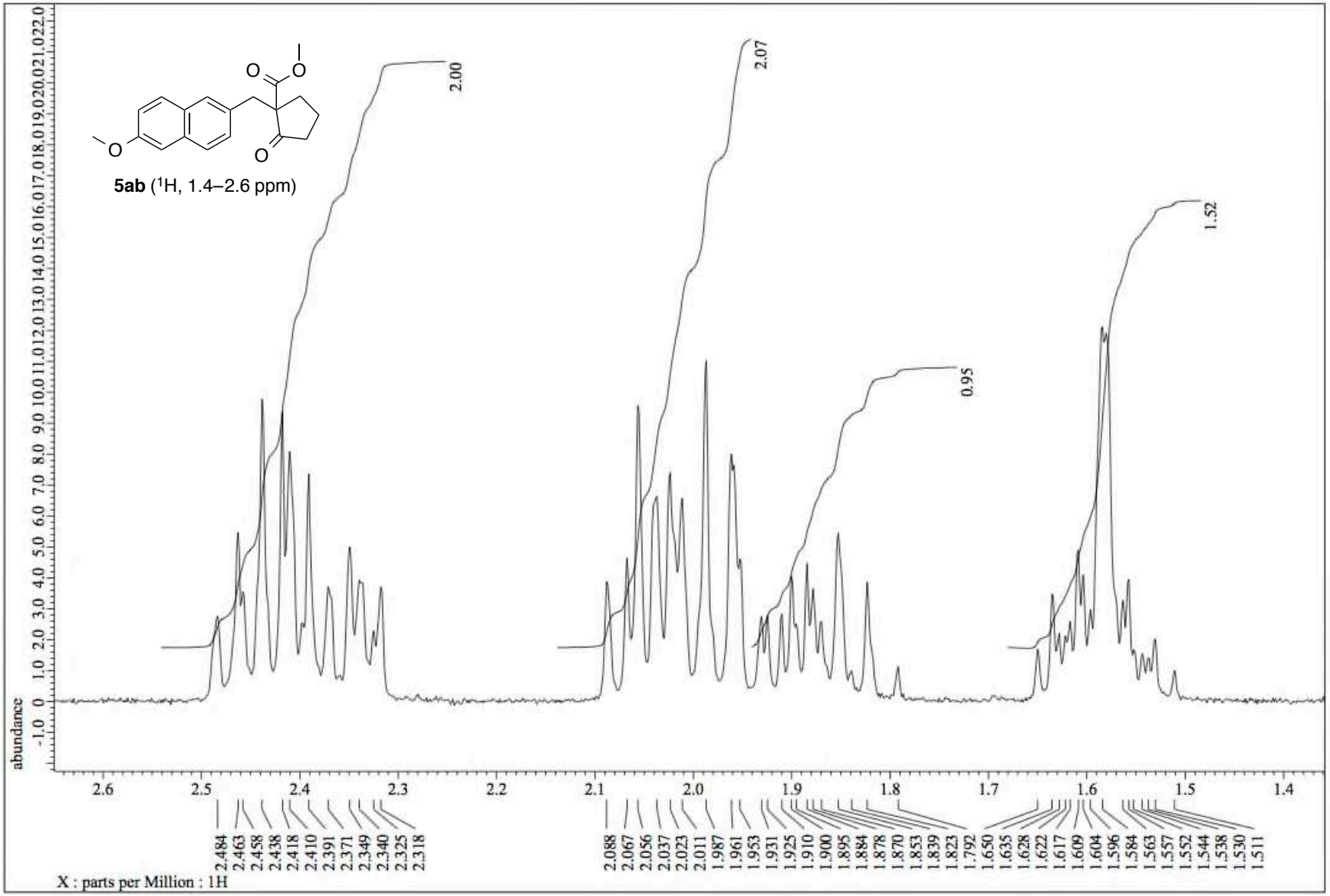

3am (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
0.99
0.98
1.98
2.00
3.00
2.00
6.12
6.21
7.654
7.639
7.623
7.608
7.531
7.259
7.253
7.247
7.221
7.215
7.132
7.122
7.092
5.131
5.107
5.084
5.061
5.038
5.015
4.992
3.904
3.339
1.345
1.284
1.261
1.230
1.207
0.000

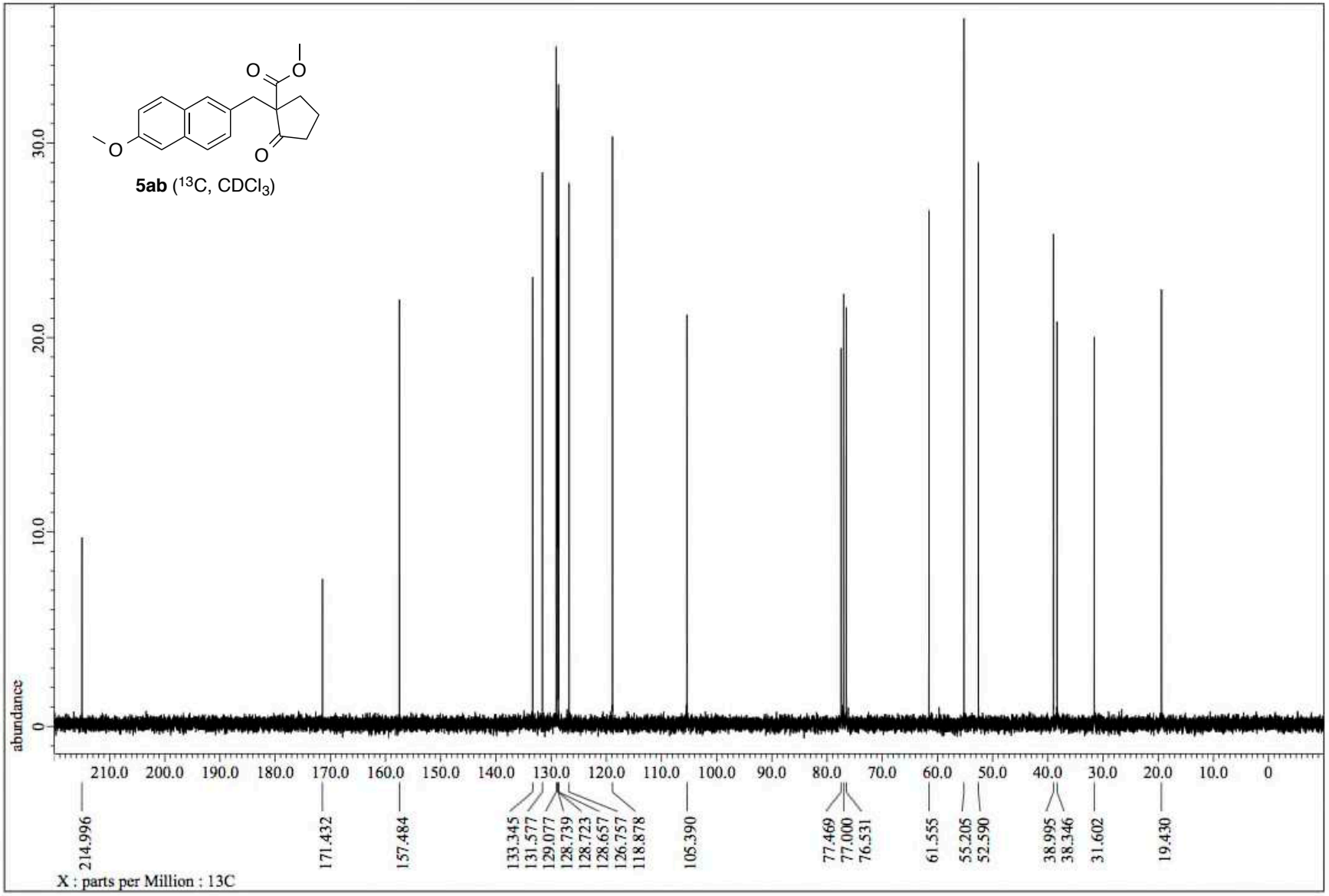

3am (13C, CDCl3)
abundance
X : parts per Million : 13C
171.531
157.393
133.411
131.544
129.003
128.986
128.789
128.731
126.404
118.722
105.465
77.477
77.000
76.531
68.751
55.205
54.876
40.829
21.576
21.527
19.832

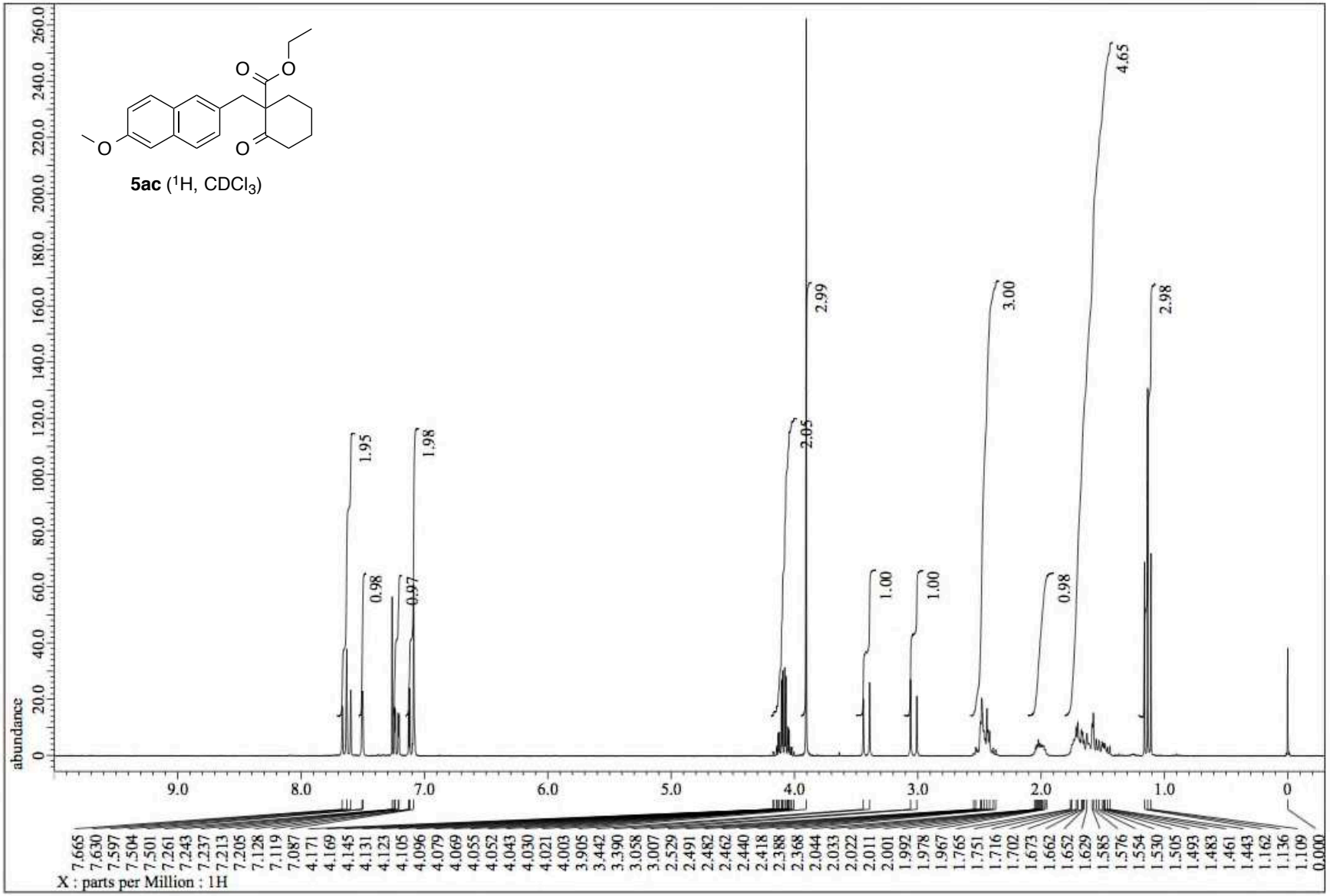

5aa (1H, CDCl3)
abundance
X : parts per Million : 1H
2.02
0.98
1.02
2.03
2.07
3.04
3.03
1.01
1.00
3.03
3.14
7.668
7.641
7.635
7.611
7.491
7.486
7.260
7.198
7.191
7.166
7.160
7.141
7.131
7.108
7.099
7.094
7.085
4.274
4.247
4.234
4.230
4.220
4.207
4.203
4.193
4.181
4.177
4.163
4.154
4.151
4.137
3.905
3.427
3.376
3.208
3.157
2.183
1.324
1.273
1.247
1.220
0.000

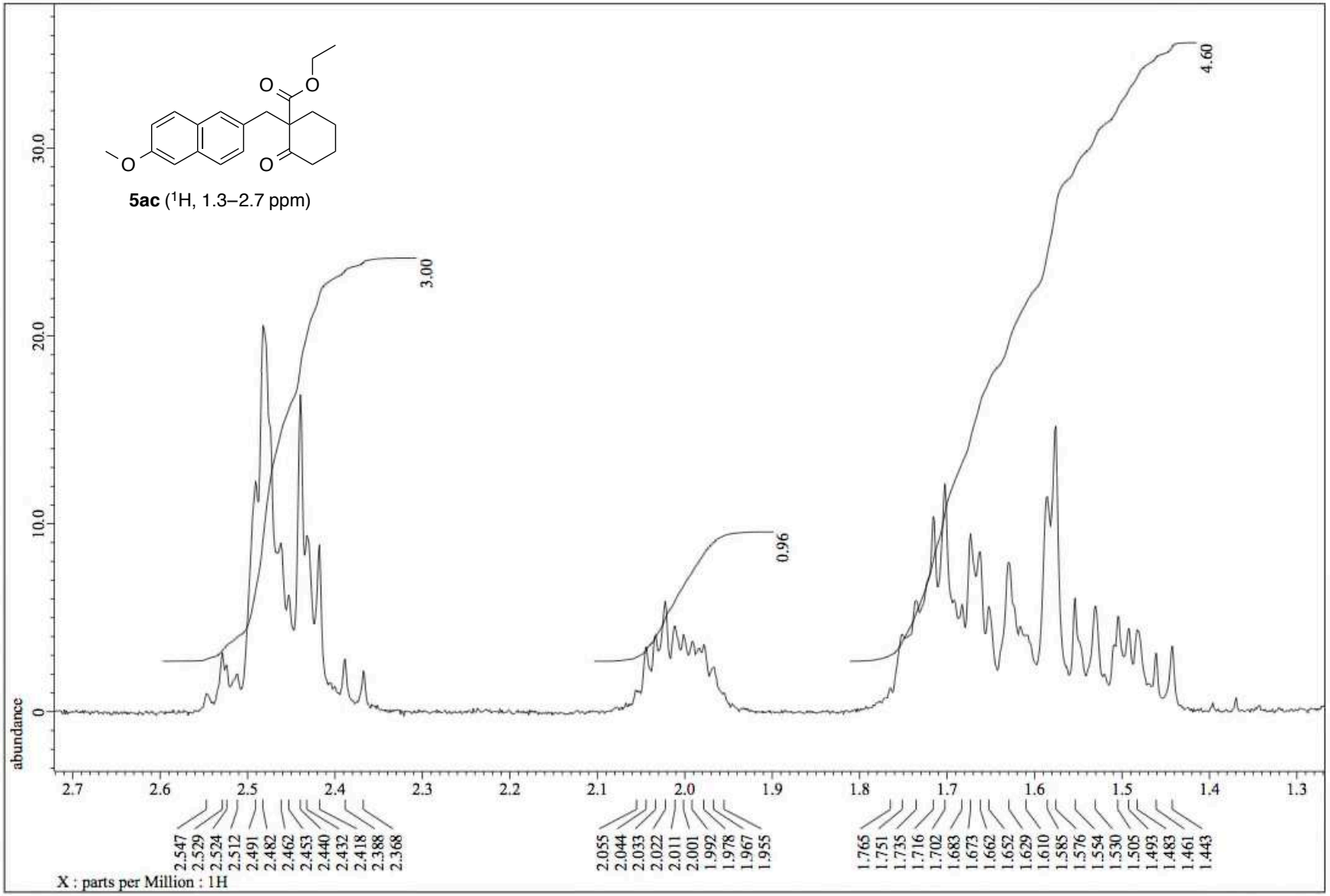

5aa (^{13}C, $CDCl_3$)
abundance
X : parts per Million : 13C
205.506
172.427
157.401
133.353
131.544
129.011
128.789
128.698
128.657
126.502
118.788
105.399
77.469
77.000
76.523
61.357
60.921
55.197
40.352
26.502
19.068
13.944

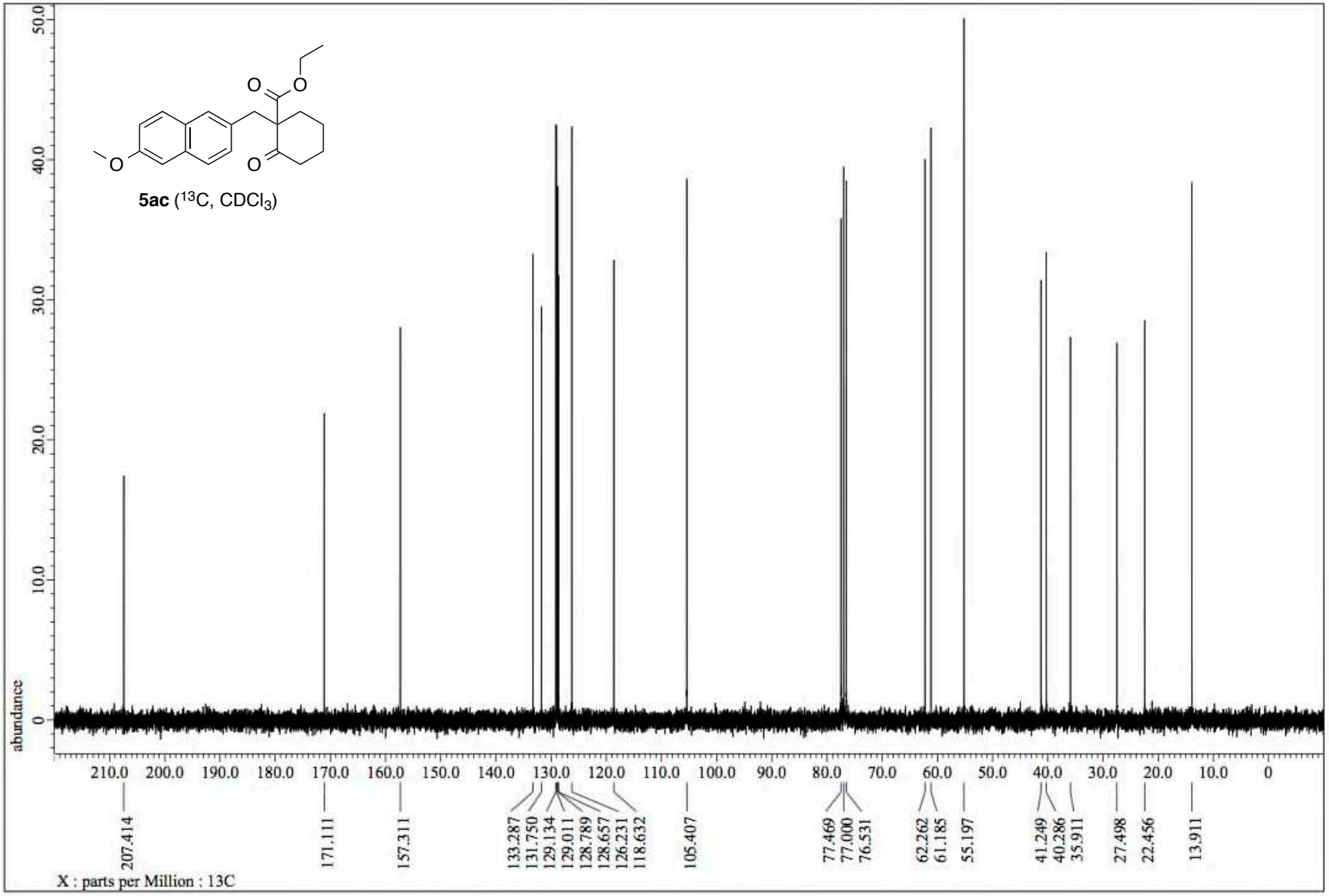

5ab (1H, CDCl3)
abundance
X : parts per Million : 1H

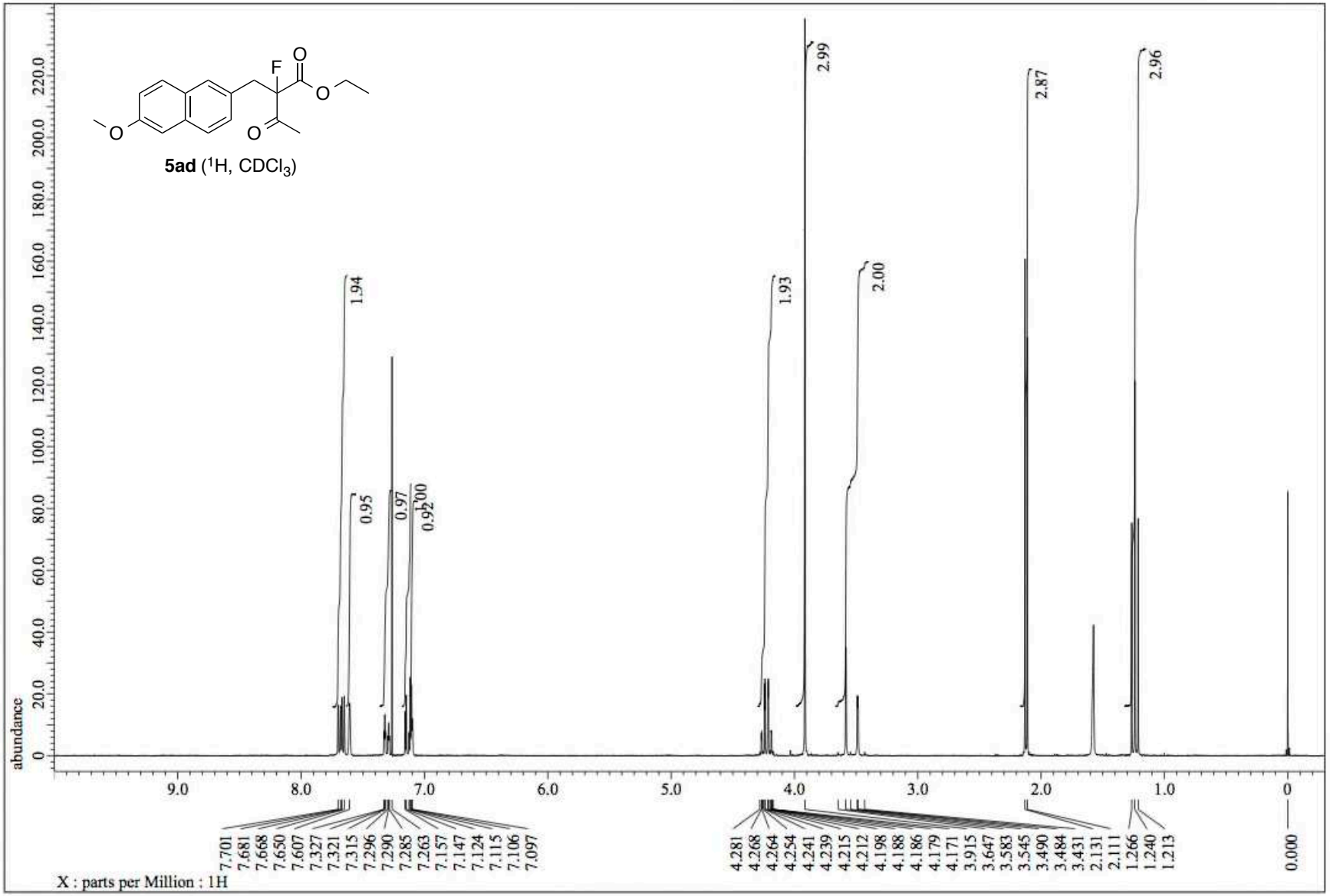

5ab (1H, 1.4–2.6 ppm)
2.00
2.07
0.95
1.52
abundance
X : parts per Million : 1H

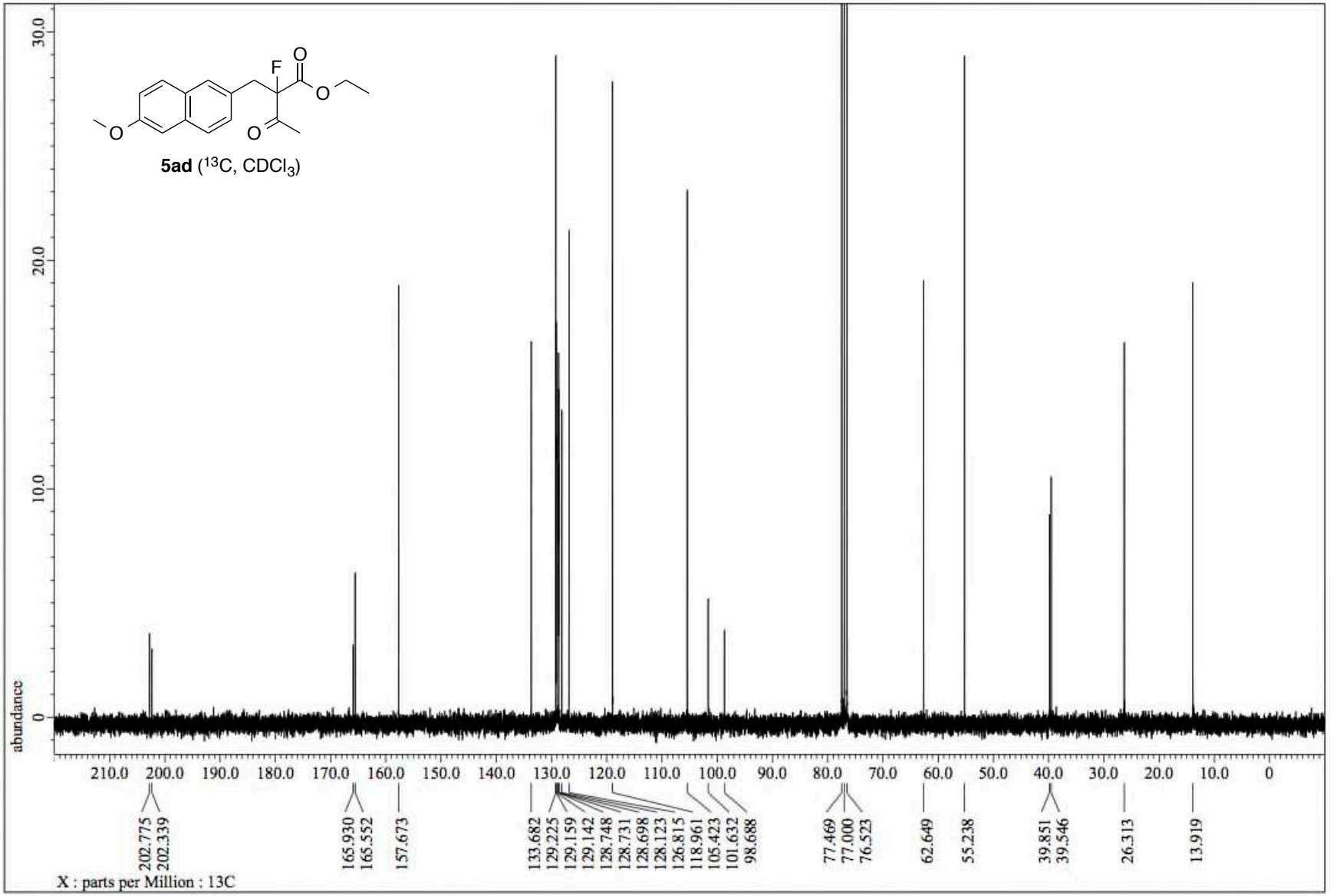

5ab (13C, CDCl3)
abundance
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
214.996
171.432
157.484
133.345
131.577
129.077
128.739
128.723
128.657
126.757
118.878
105.390
77.469
77.000
76.531
61.555
55.205
52.590
38.995
38.346
31.602
19.430
X : parts per Million : 13C

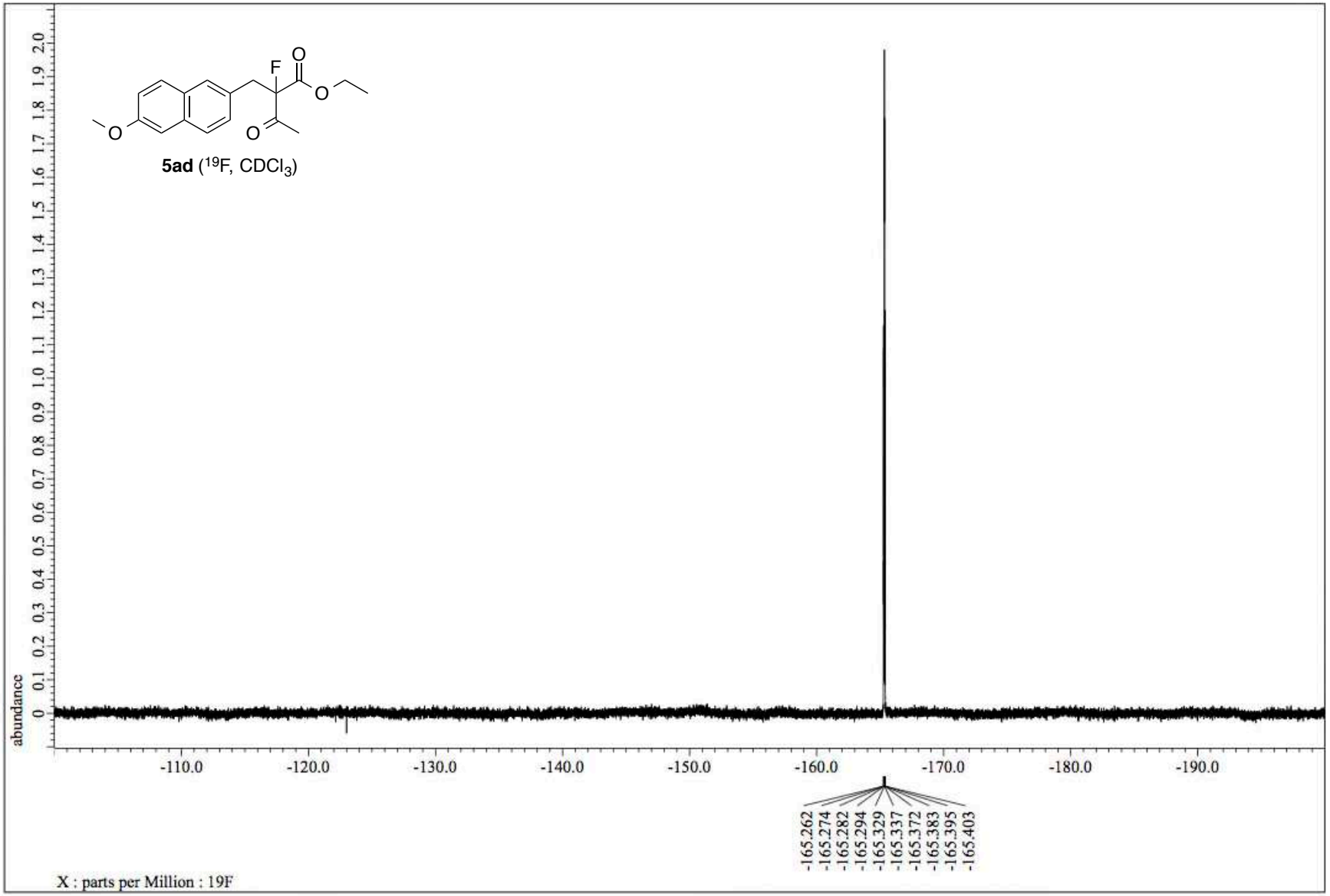

5ac (1H, CDCl3)
abundance
X : parts per Million : 1H
1.95
0.98
0.97
1.98
2.05
2.99
1.00
1.00
3.00
0.98
4.65
2.98

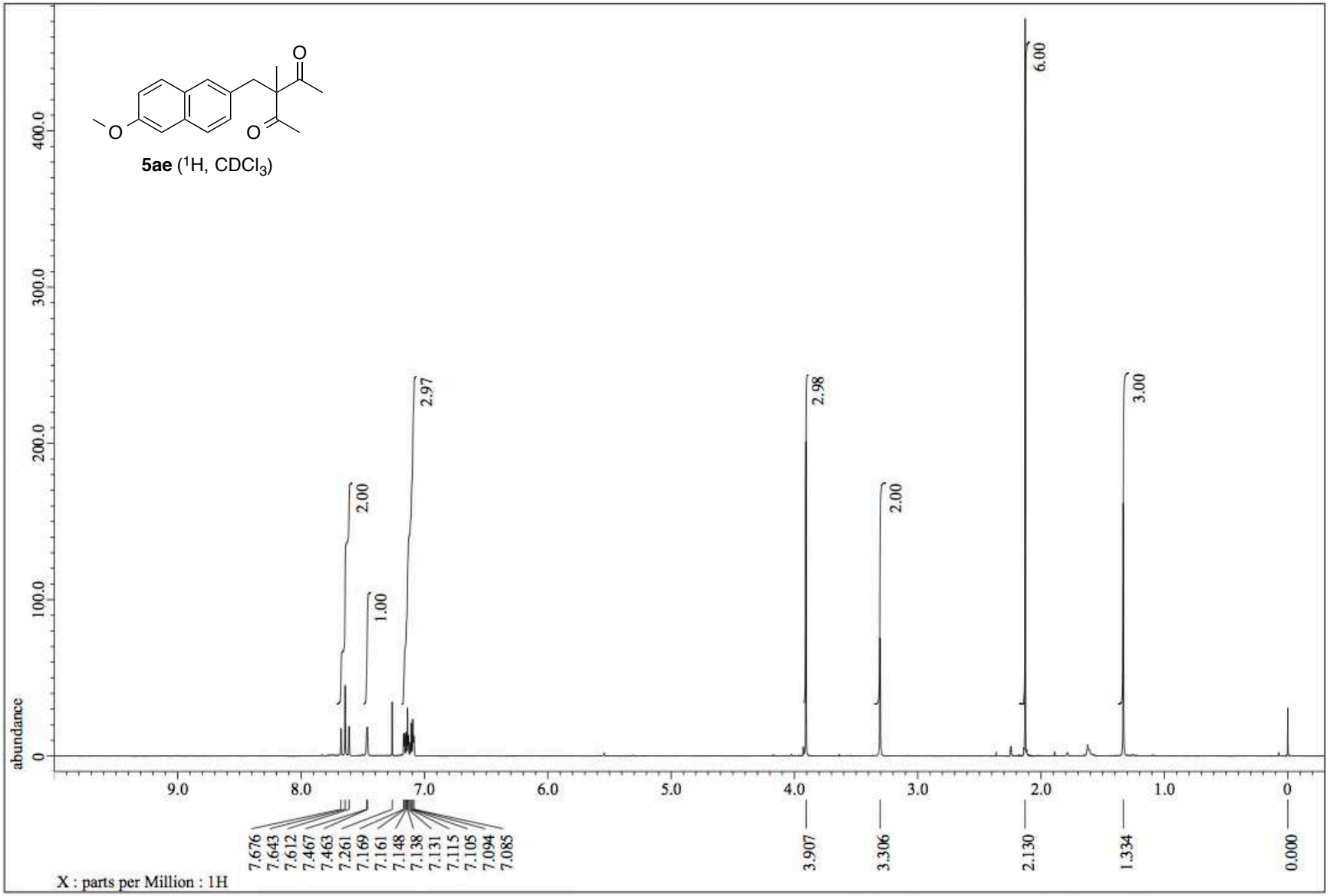

5ac (1H, 1.3–2.7 ppm)
abundance
30.0
20.0
10.0
0
3.00
0.96
4.60
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
2.547
2.529
2.524
2.512
2.491
2.482
2.462
2.453
2.440
2.432
2.418
2.388
2.368
2.055
2.044
2.033
2.022
2.011
2.001
1.992
1.978
1.967
1.955
1.765
1.751
1.735
1.716
1.702
1.683
1.673
1.662
1.652
1.629
1.610
1.585
1.576
1.554
1.530
1.505
1.493
1.483
1.461
1.443
X : parts per Million : 1H

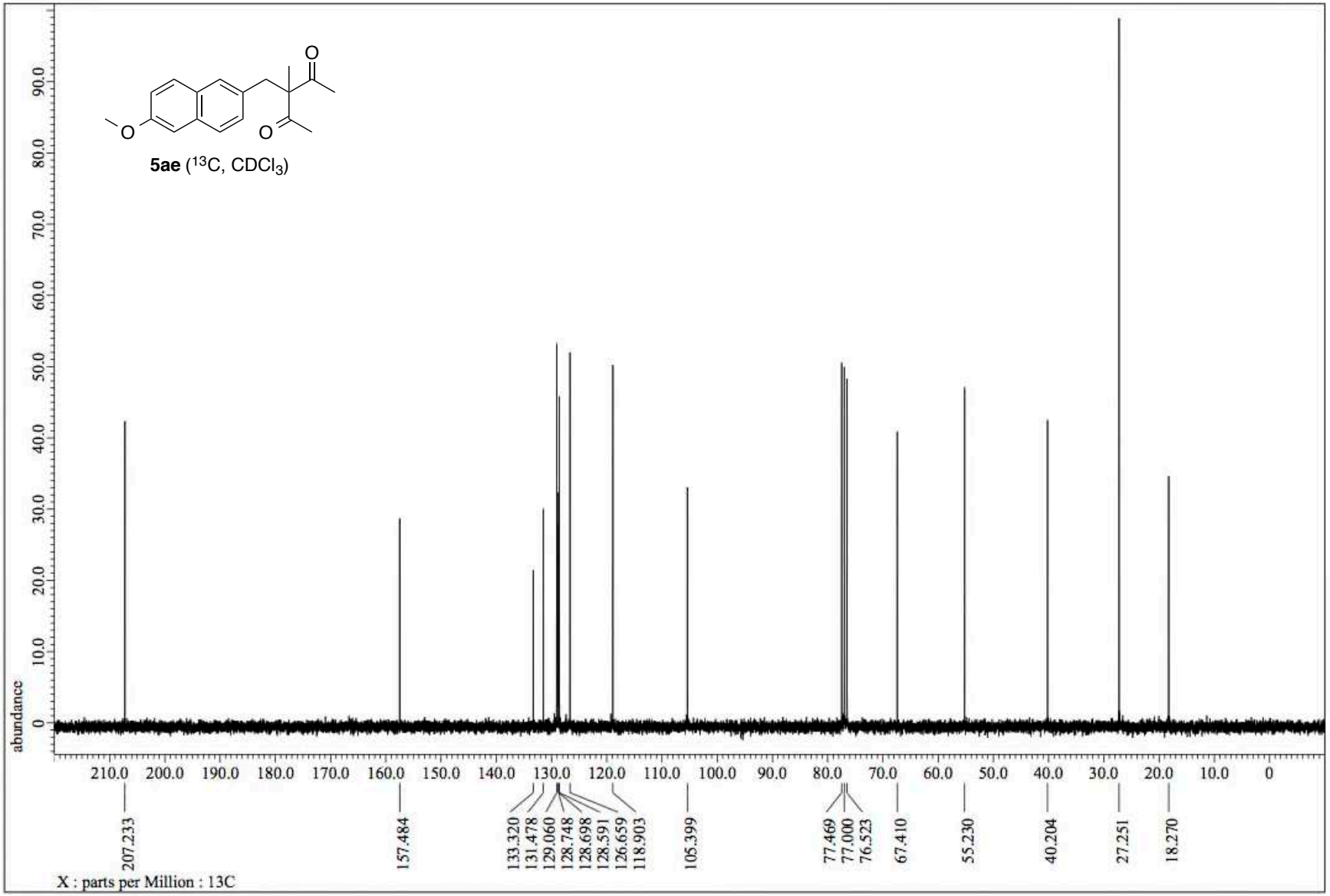

5ac (13C, CDCl3)
abundance
X : parts per Million : 13C
207.414
171.111
157.311
133.287
131.750
129.134
129.011
128.789
128.657
126.231
118.632
105.407
77.469
77.000
76.531
62.262
61.185
55.197
41.249
40.286
35.911
27.498
22.456
13.911

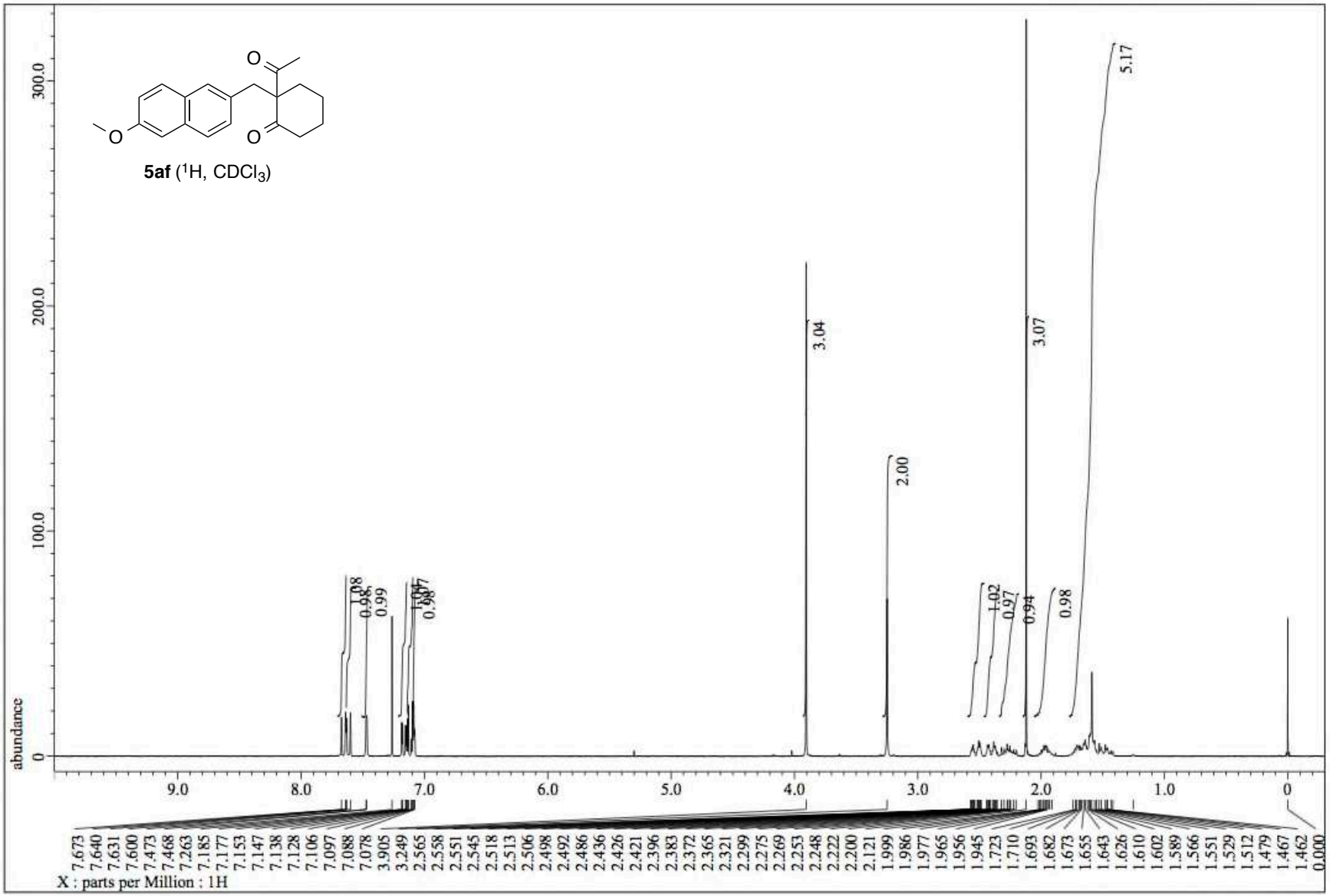

5ad (1H, CDCl3)
abundance
X : parts per Million : 1H
1.94
0.95
0.97
0.92
1.00
1.93
2.99
2.00
2.87
2.96
7.701
7.681
7.668
7.650
7.607
7.327
7.321
7.315
7.296
7.290
7.285
7.263
7.157
7.147
7.124
7.115
7.106
7.097
4.281
4.268
4.264
4.254
4.241
4.239
4.215
4.212
4.198
4.188
4.186
4.179
4.171
3.915
3.647
3.583
3.545
3.490
3.484
3.431
2.131
2.111
1.266
1.240
1.213
0.000

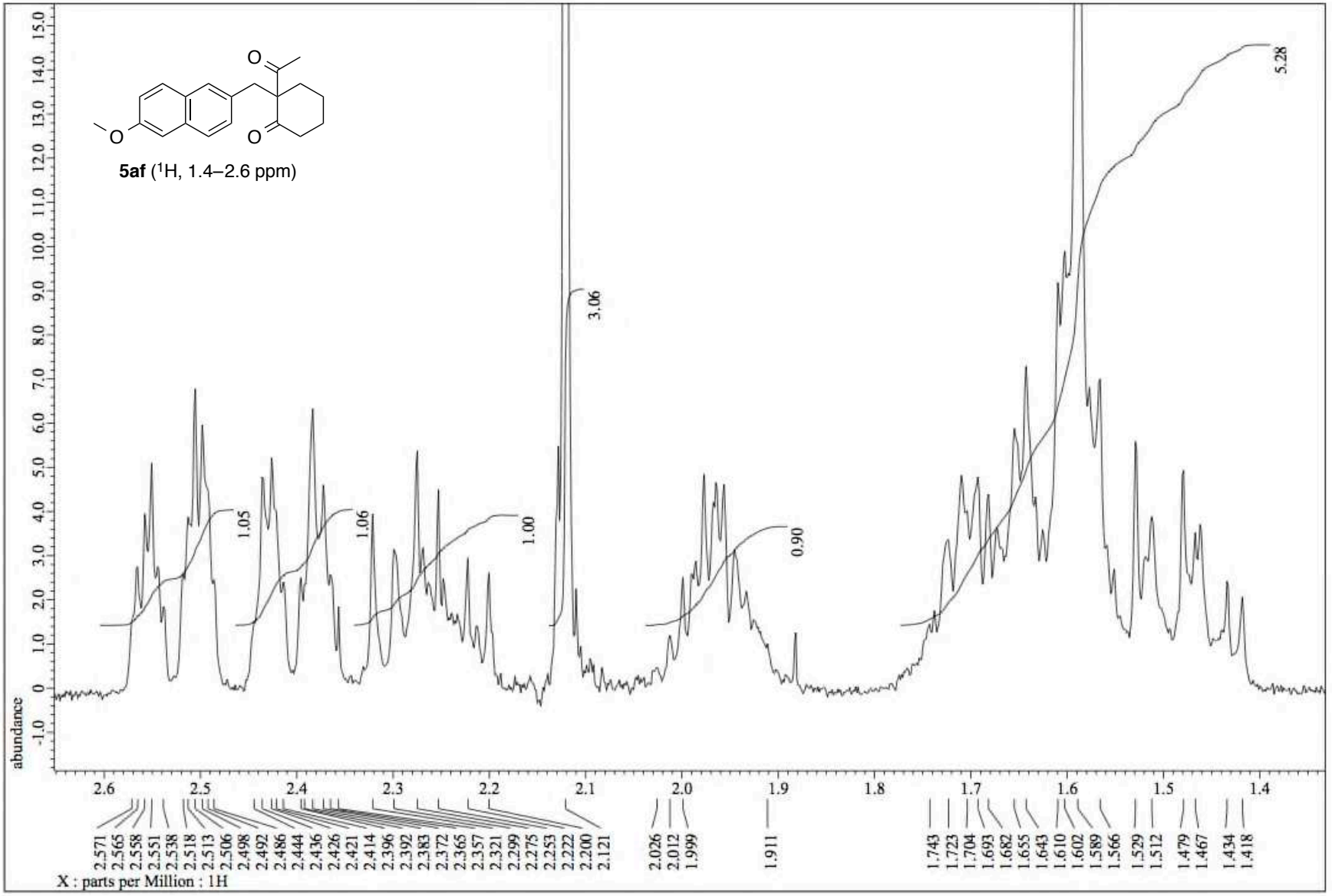

5ad (13C, CDCl3)
abundance
X : parts per Million : 13C
202.775
202.339
165.930
165.552
157.673
133.682
129.225
129.159
129.142
128.748
128.731
128.698
128.123
126.815
118.961
105.423
101.632
98.688
77.469
77.000
76.523
62.649
55.238
39.851
39.546
26.313
13.919

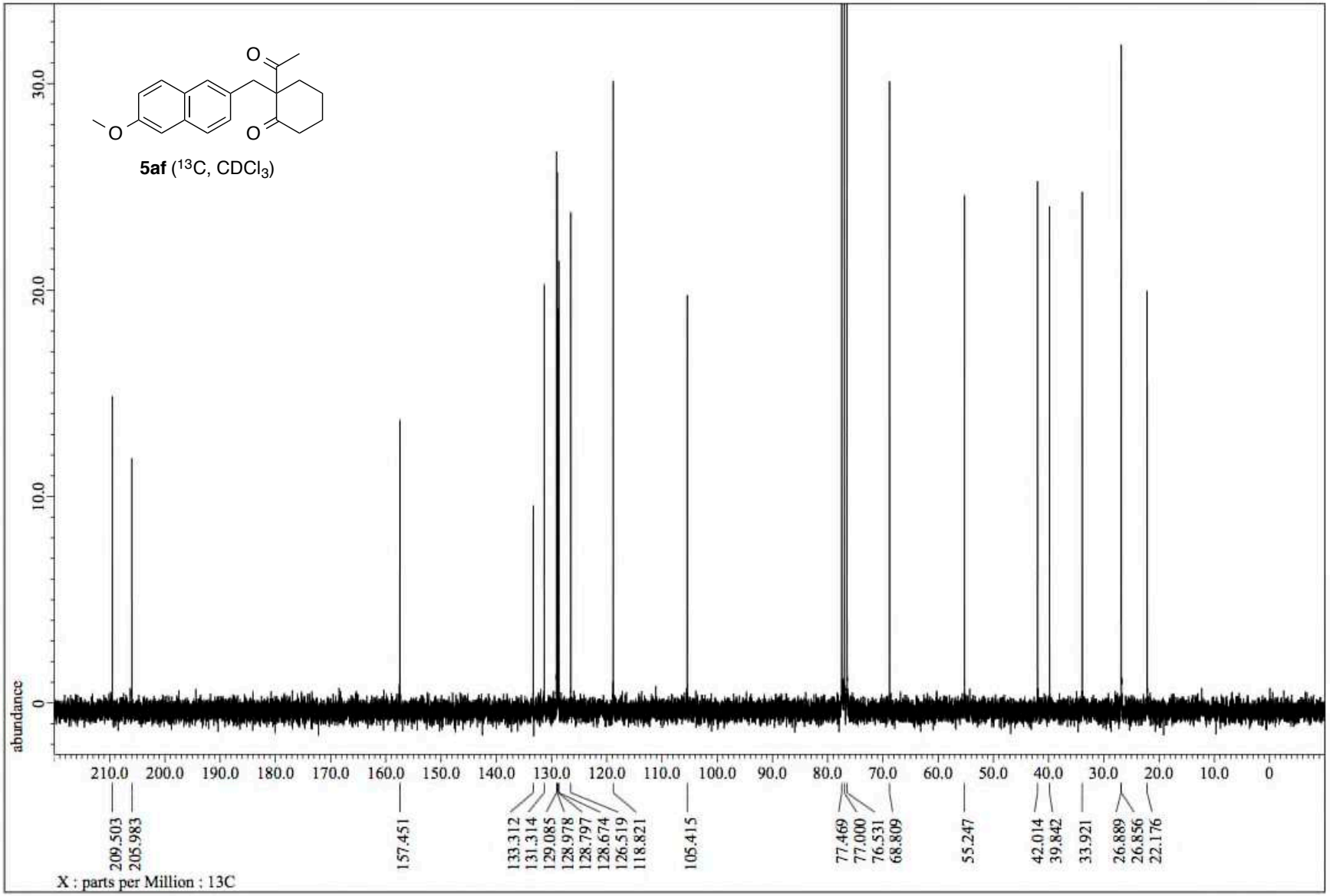

F
O
O
O
O
5ad (^{19}F, $CDCl_3$)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
-190.0
-165.262
-165.274
-165.282
-165.294
-165.329
-165.337
-165.372
-165.383
-165.395
-165.403
X : parts per Million : 19F

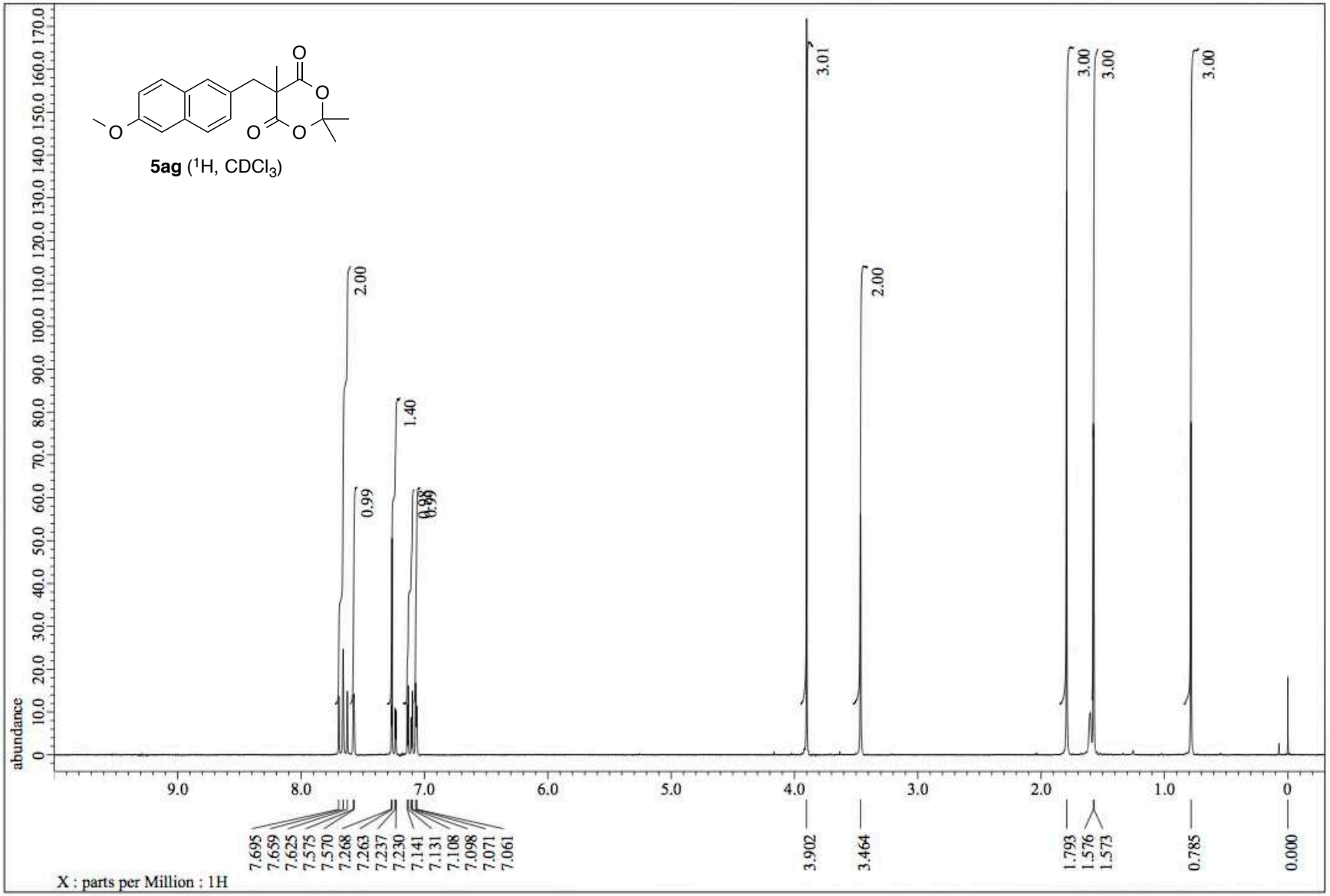

5ae (1H, CDCl3)
abundance
X : parts per Million : 1H
6.00
2.98
3.00
2.97
2.00
2.00
1.00
7.676
7.643
7.612
7.467
7.463
7.261
7.169
7.161
7.148
7.138
7.131
7.115
7.105
7.094
7.085
3.907
3.306
2.130
1.334
0.000

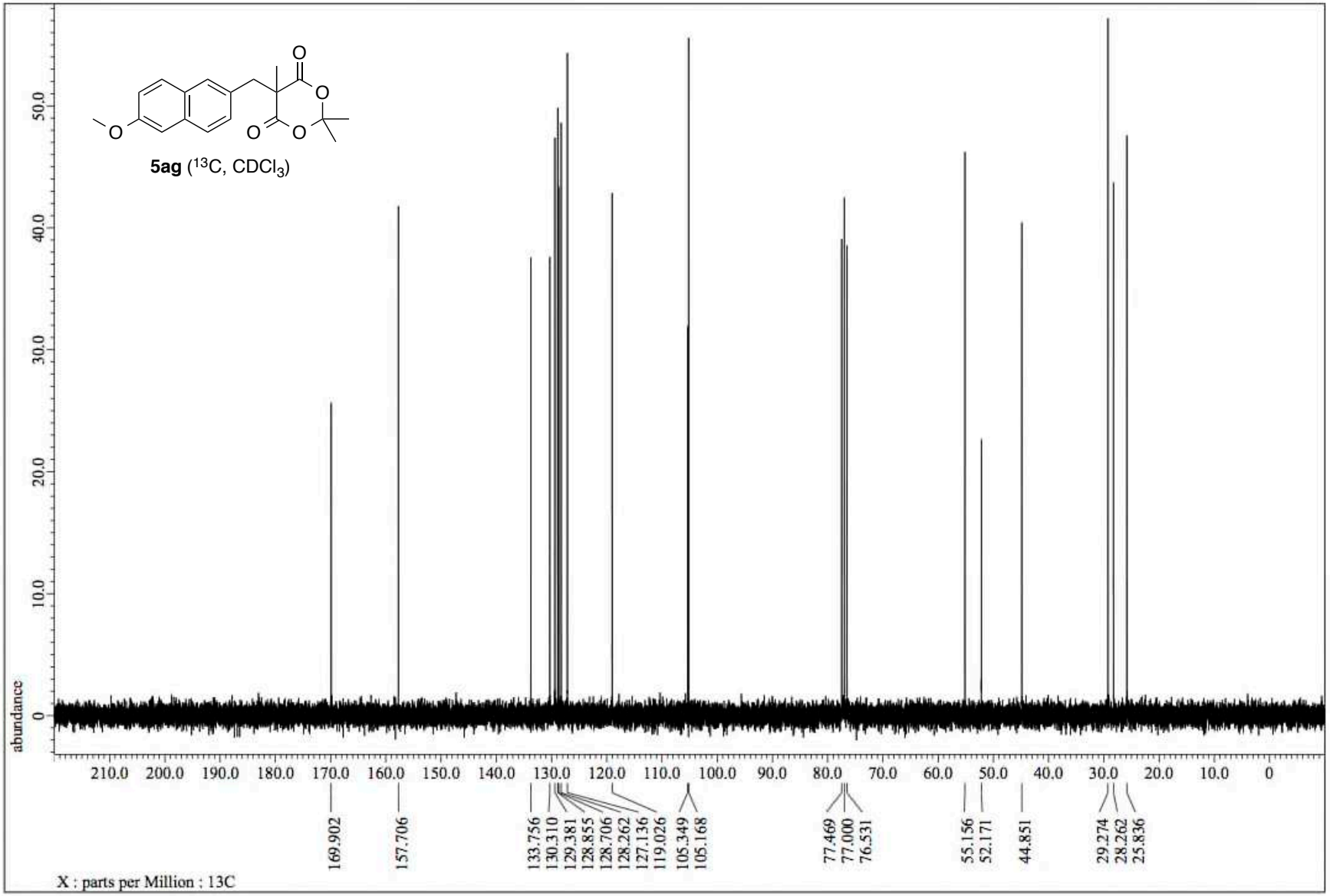

5ae (13C, CDCl3)
abundance
X : parts per Million : 13C
207.233
157.484
133.320
131.478
129.060
128.748
128.698
128.591
126.659
118.903
105.399
77.469
77.000
76.523
67.410
55.230
40.204
27.251
18.270

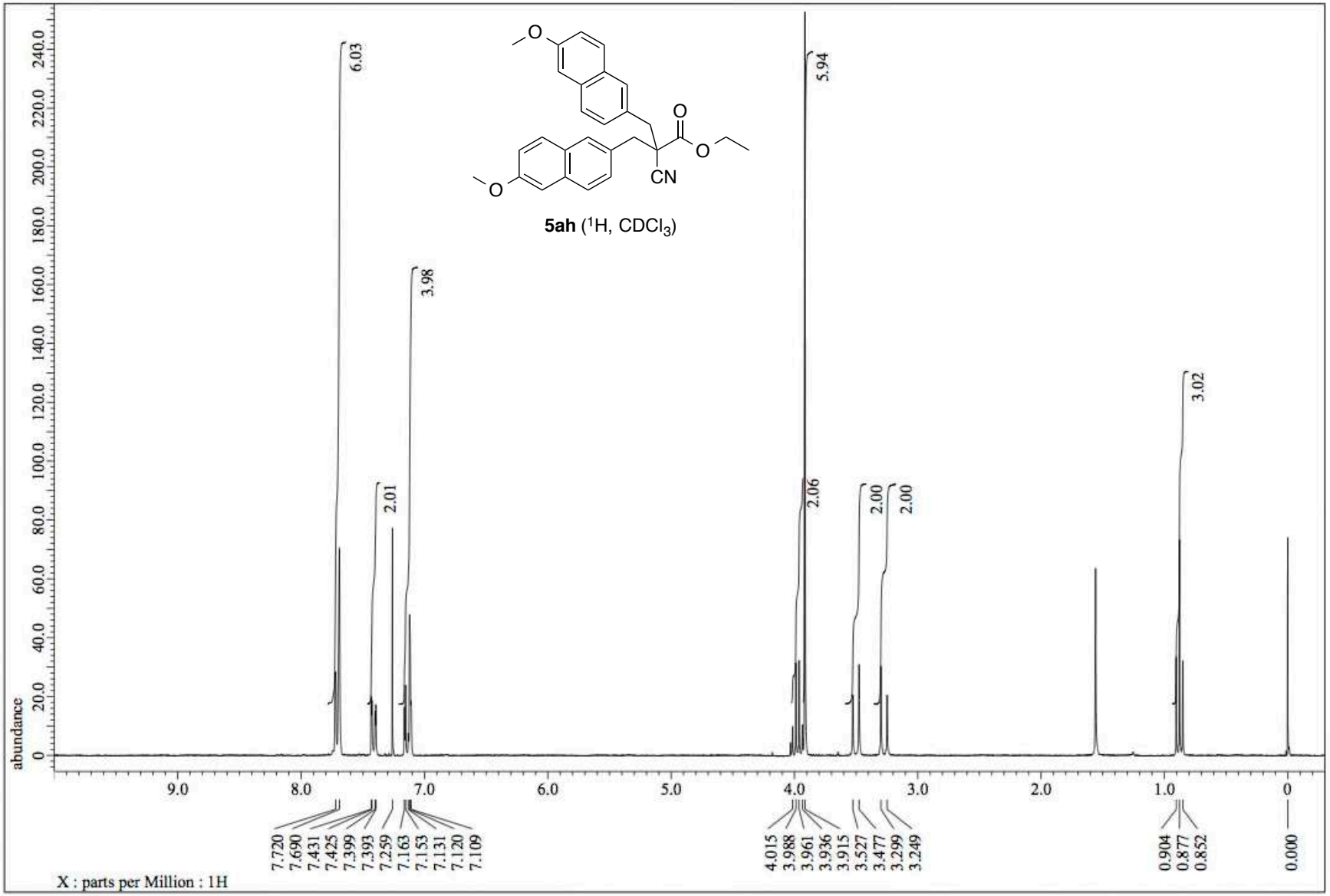

O
O
O
5af (1H, CDCl3)
abundance
300.0
200.0
100.0
0
3.04
2.00
3.07
5.17
1.02
0.97
0.94
0.98
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


5af (1H, 1.4–2.6 ppm)
abundance
X : parts per Million : 1H
1.05
1.06
1.00
3.06
0.90
5.28
2.571
2.565
2.558
2.551
2.538
2.518
2.513
2.506
2.498
2.492
2.486
2.444
2.436
2.426
2.421
2.414
2.396
2.392
2.383
2.372
2.365
2.357
2.321
2.299
2.275
2.253
2.222
2.200
2.121
2.026
2.012
1.999
1.911
1.743
1.723
1.704
1.693
1.682
1.655
1.643
1.610
1.602
1.589
1.566
1.529
1.512
1.479
1.467
1.434
1.418

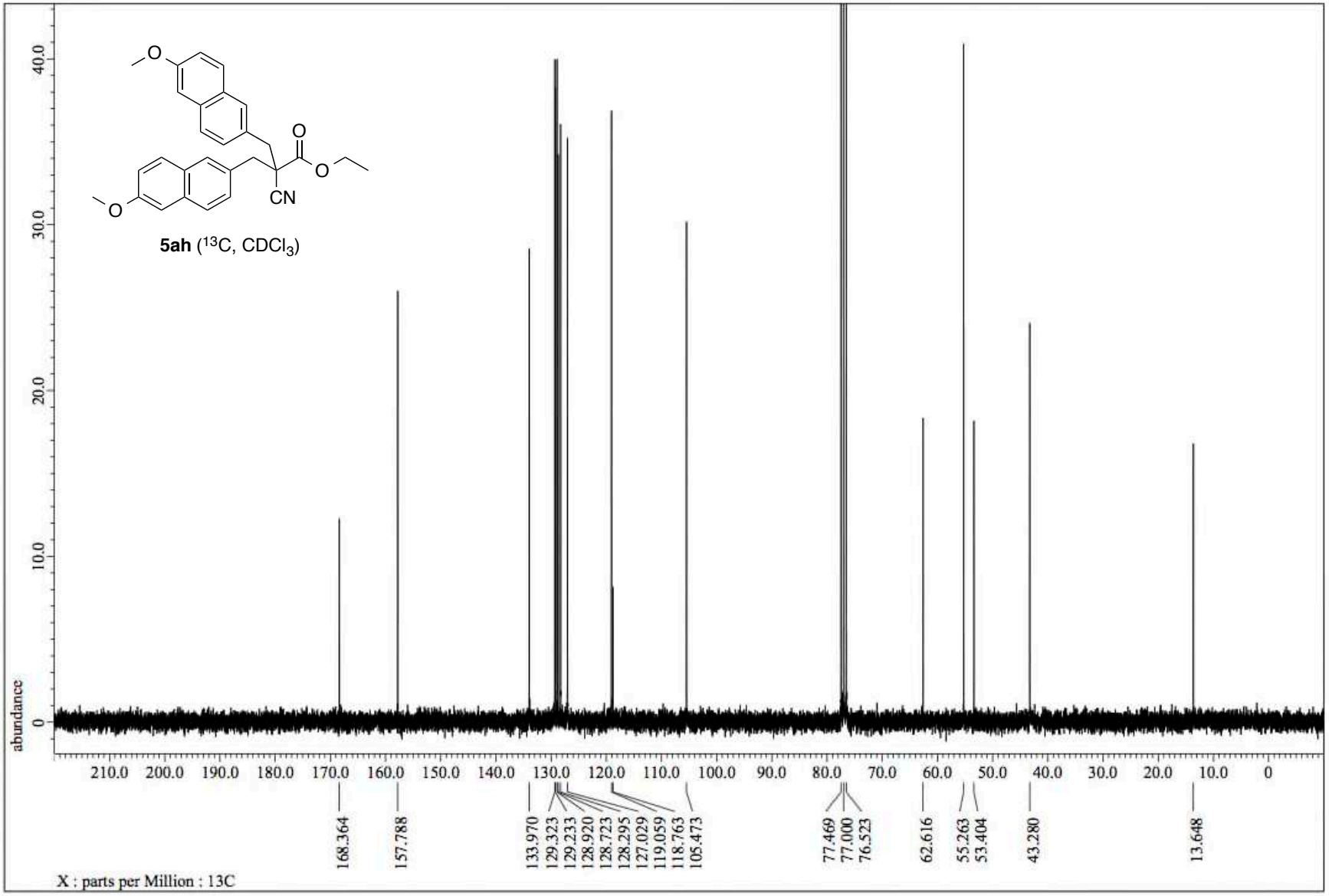

5af (13C, CDCl3)
abundance
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
209.503
205.983
157.451
133.312
131.314
129.085
128.978
128.797
128.674
126.519
118.821
105.415
77.469
77.000
76.531
68.809
55.247
42.014
39.842
33.921
26.889
26.856
22.176
X : parts per Million : 13C

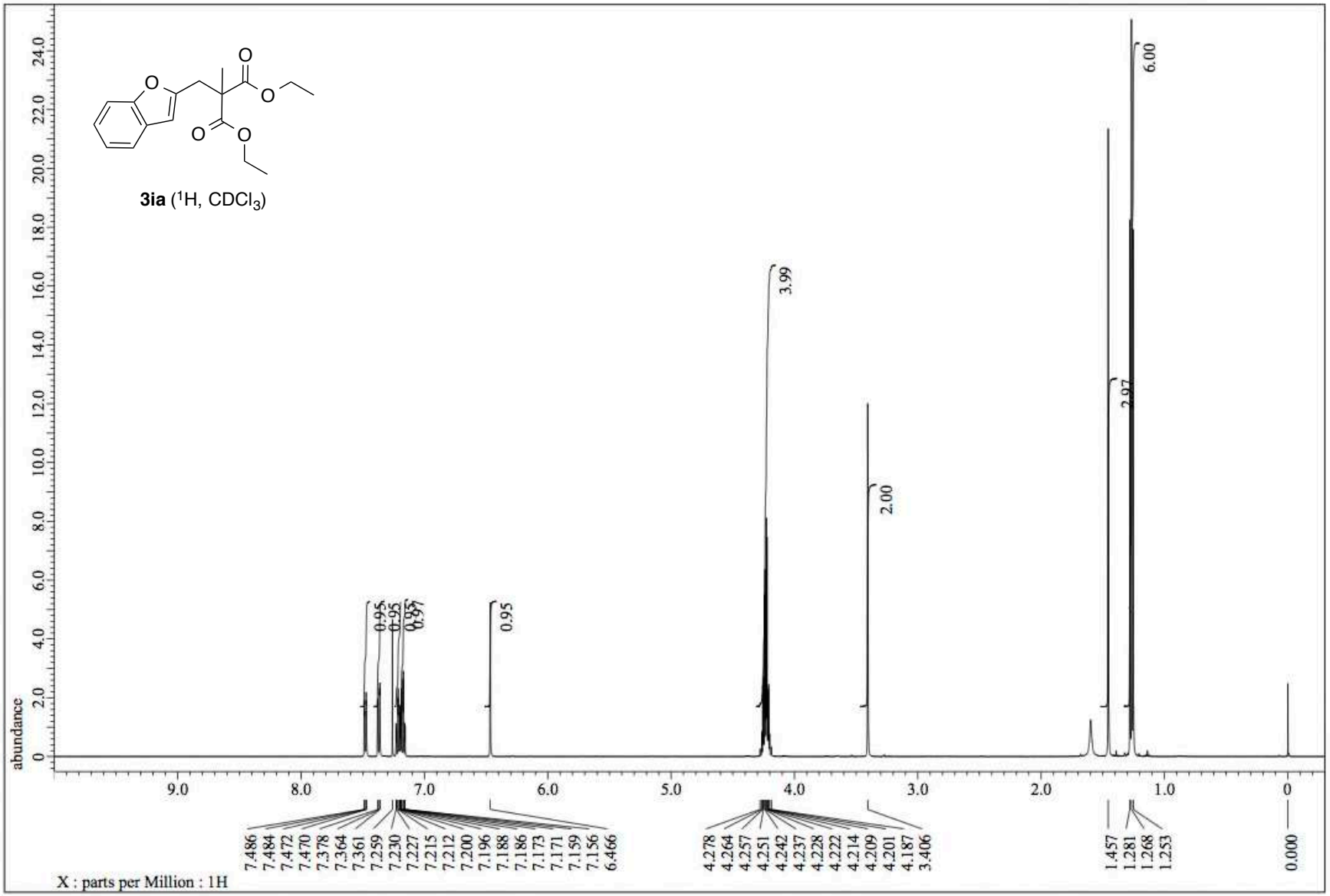

5ag (1H, CDCl3)
abundance
X : parts per Million : 1H
2.00
0.99
1.40
3.01
2.00
3.00
3.00
3.00
7.695
7.659
7.625
7.575
7.570
7.268
7.263
7.237
7.230
7.141
7.131
7.108
7.098
7.071
7.061
3.902
3.464
1.793
1.576
1.573
0.785
0.000

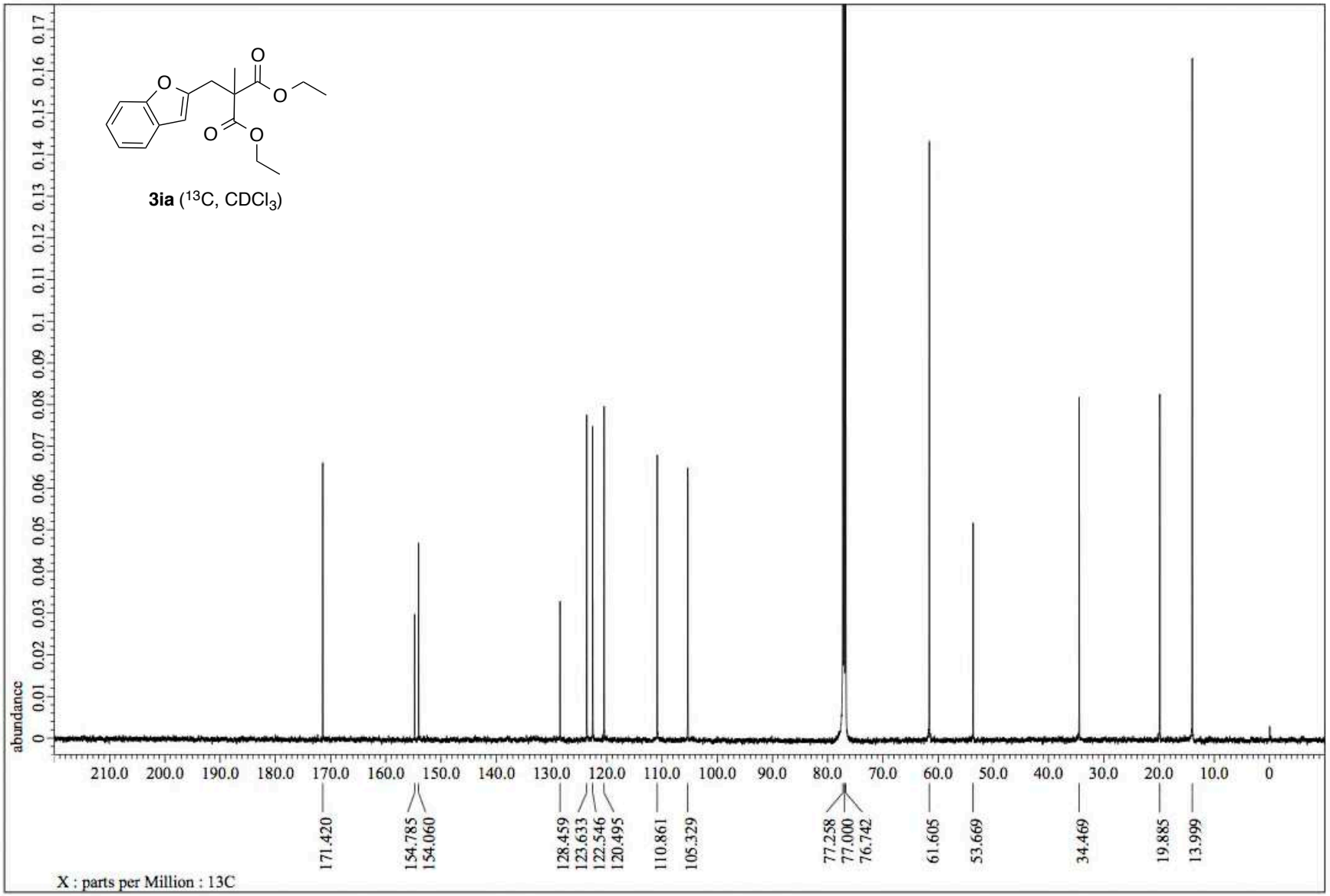

5ag (13C, CDCl3)
abundance
50.0
40.0
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
169.902
157.706
133.756
130.310
129.381
128.855
128.706
128.262
127.136
119.026
105.349
105.168
77.469
77.000
76.531
55.156
52.171
44.851
29.274
28.262
25.836
X : parts per Million : 13C

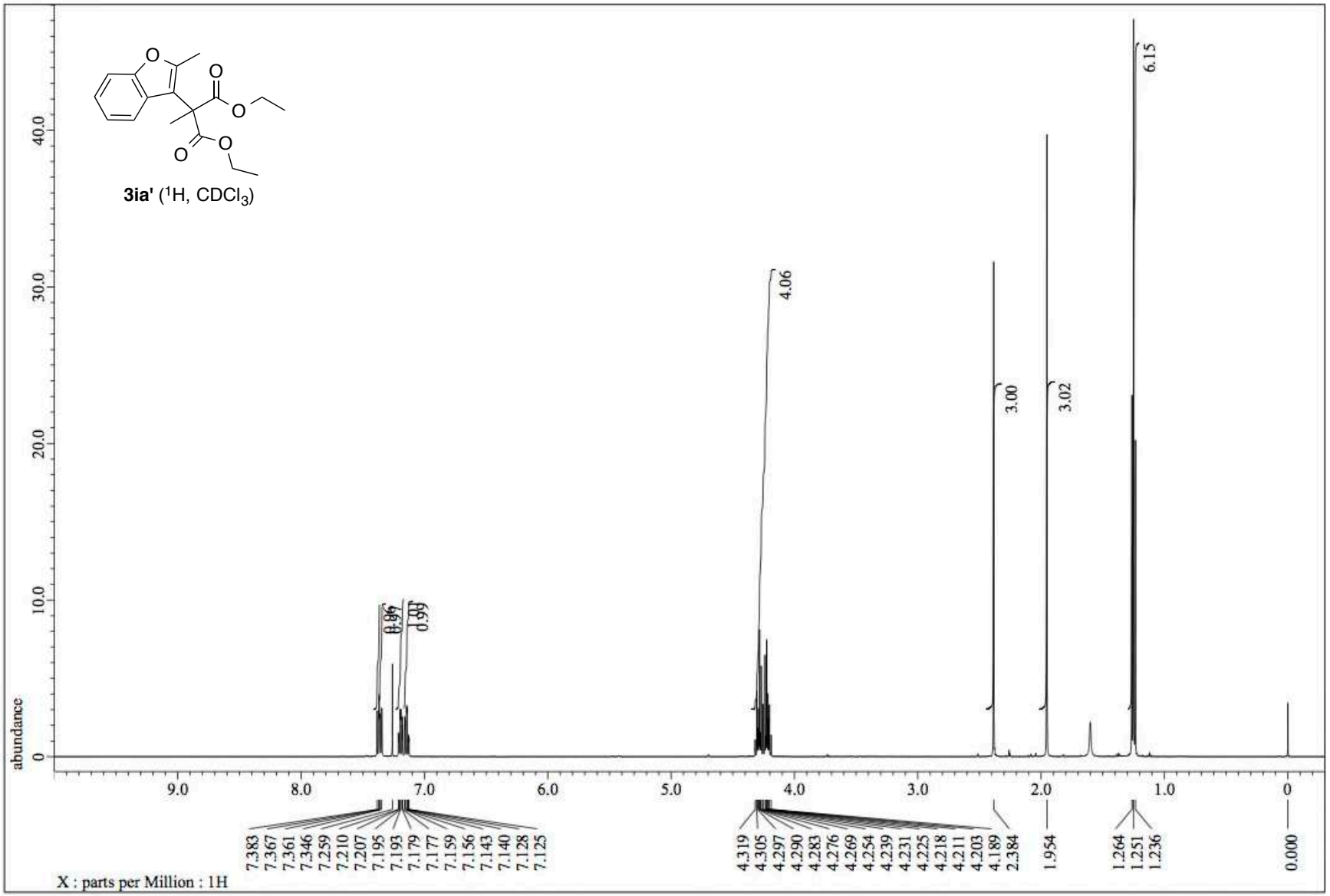

O
O
O
O
CN
6.03
5.94
3.98
2.01
2.06
2.00
2.00
3.02
abundance
X : parts per Million : 1H
7.720
7.690
7.431
7.425
7.399
7.393
7.259
7.163
7.153
7.131
7.120
7.109
4.015
3.988
3.961
3.936
3.915
3.527
3.477
3.299
3.249
0.904
0.877
0.852
0.000

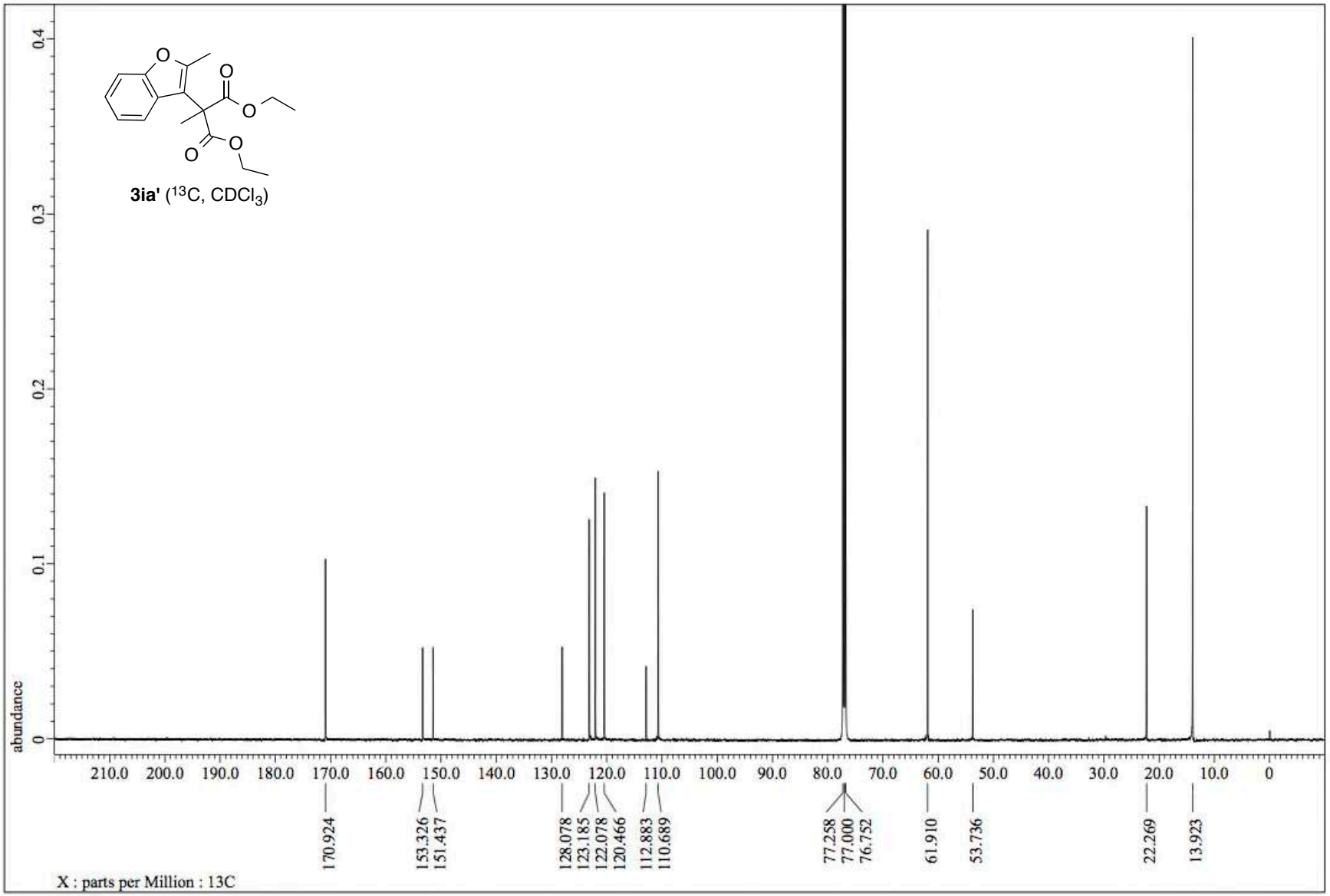
5ah (^{1}H, $CDCl_3$)


5ah (13C, CDCl3)
abundance
X : parts per Million : 13C
168.364
157.788
133.970
129.323
129.233
128.920
128.723
128.295
127.029
119.059
118.763
105.473
77.469
77.000
76.523
62.616
55.263
53.404
43.280
13.648

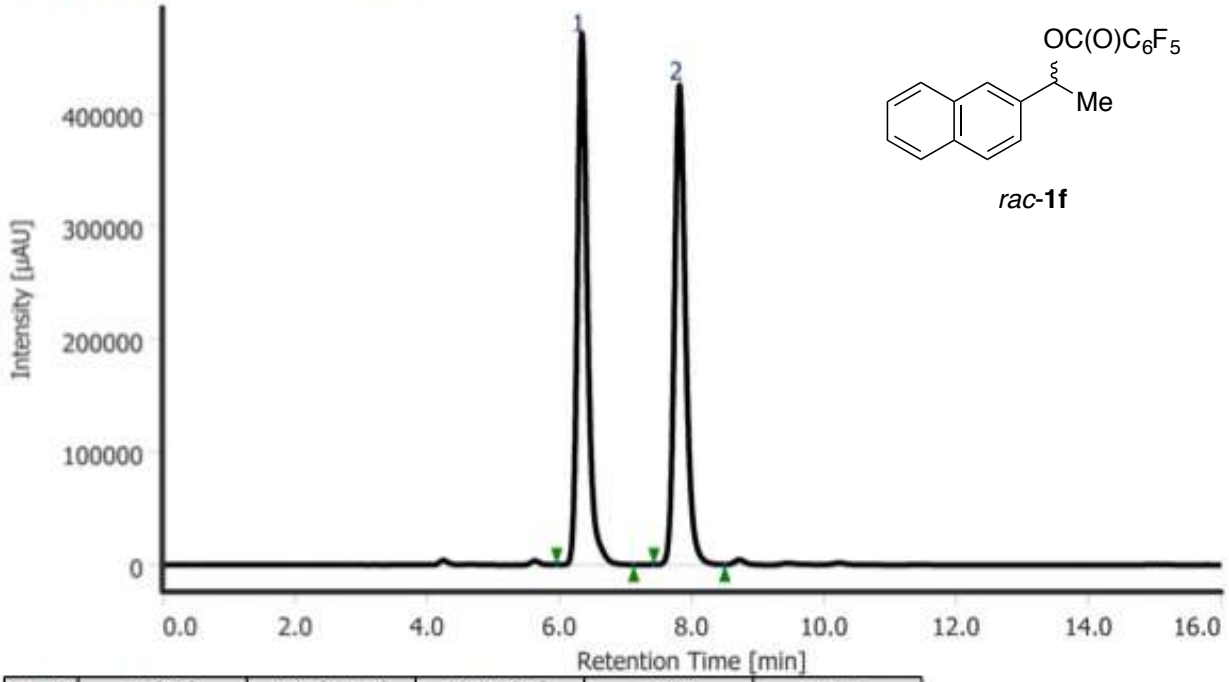

3ia (1H, CDCl3)
abundance
X : parts per Million : 1H
3.99
2.00
2.97
6.00
0.95


3ia (13C, CDCl3)
abundance
X : parts per Million : 13C
171.420
154.785
154.060
128.459
123.633
122.546
120.495
110.861
105.329
77.258
77.000
76.742
61.605
53.669
34.469
19.885
13.999


3ia' (1H, CDCl3)
abundance
X : parts per Million : 1H
4.06
3.00
3.02
6.15
7.383
7.367
7.361
7.346
7.259
7.210
7.207
7.195
7.193
7.179
7.177
7.159
7.156
7.143
7.140
7.128
7.125
4.319
4.305
4.297
4.290
4.283
4.276
4.269
4.254
4.239
4.231
4.225
4.218
4.211
4.203
4.189
2.384
1.954
1.264
1.251
1.236
0.000


3ia' (13C, CDCl3)
abundance
0.4
0.3
0.2
0.1
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.924
153.326
151.437
128.078
123.185
122.078
120.466
112.883
110.689
77.258
77.000
76.752
61.910
53.736
22.269
13.923
X : parts per Million : 13C

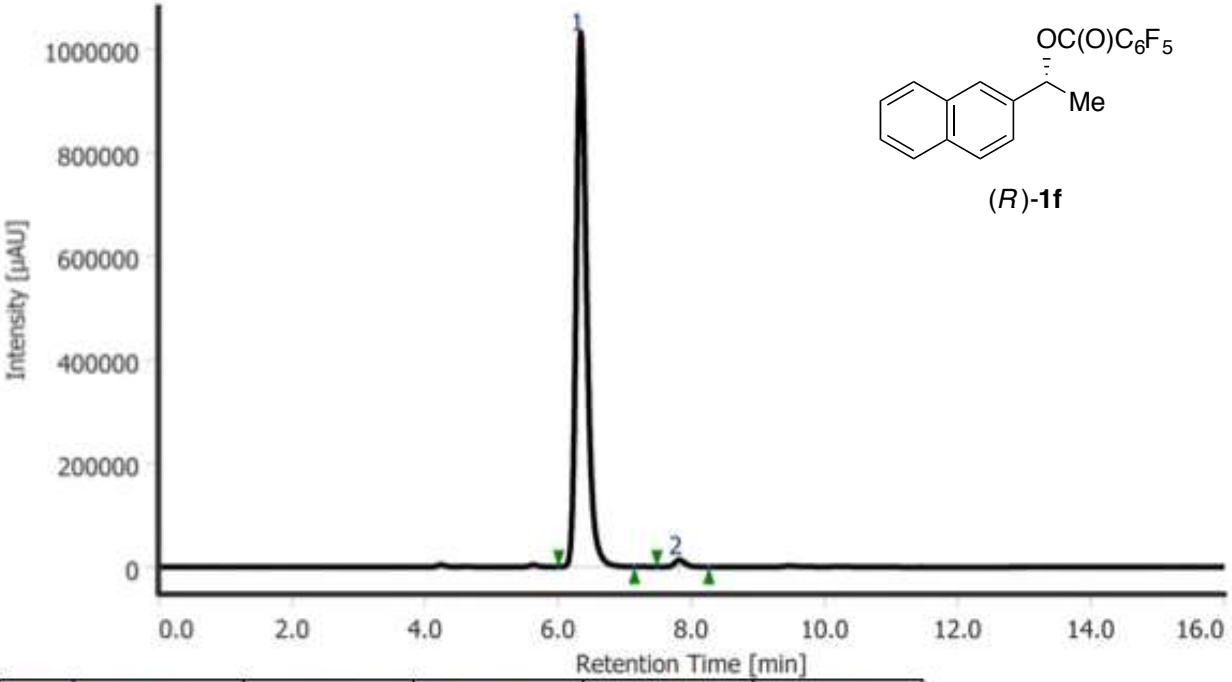
0114 7YT-433-Fr_004 2020/01/14 18:47:26



rac-**1f**

Number	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	6.337	5003425	470870	50.075	52.546
2	7.813	4988442	425239	49.925	47.454

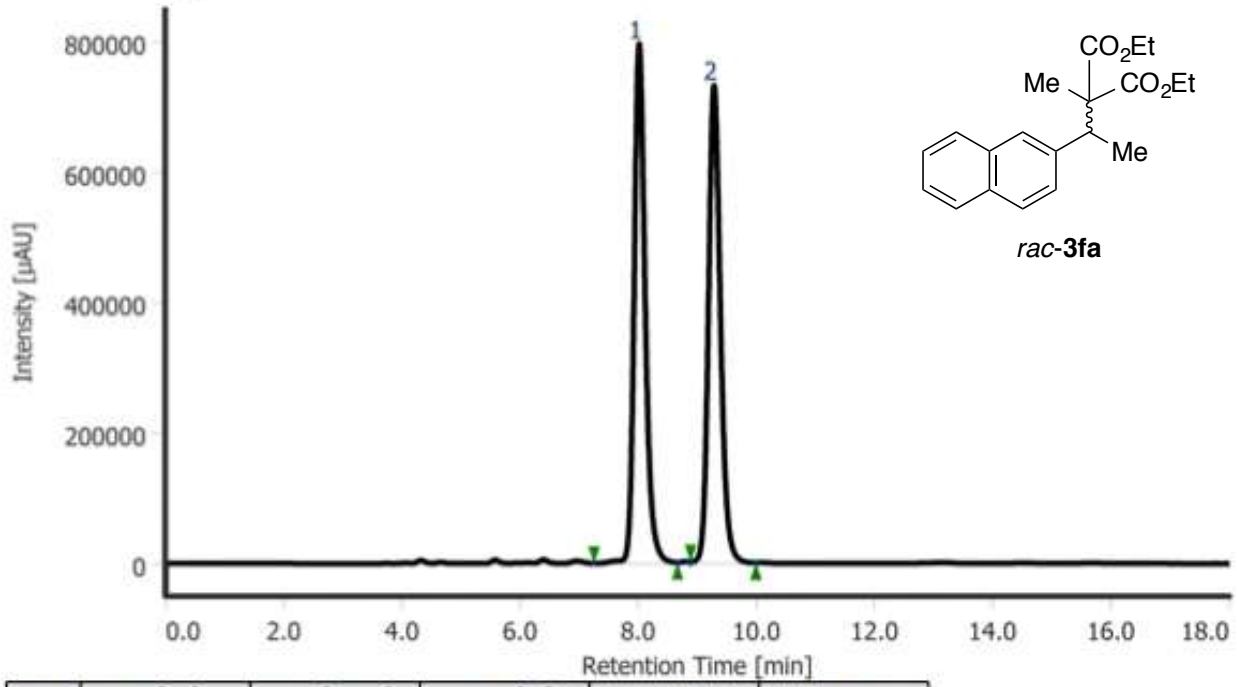
0114 7YT-460-Fr_005 2020/01/14 18:46:41



(*R*)-**1f**

Number	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	6.337	11328426	1029996	98.621	98.707
2	7.817	158445	13488	1.379	1.293

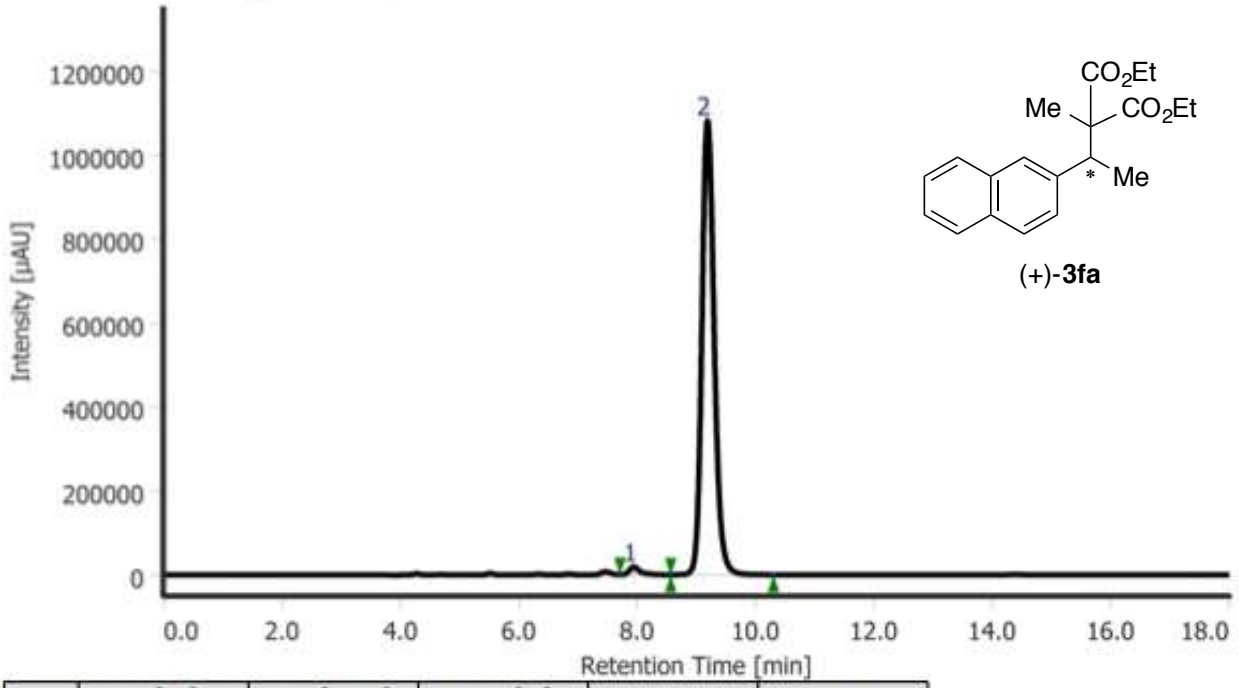
0114 7KS-238-Fr_001 2020/01/14 18:54:51



rac-**3fa**

Number	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	8.010	10367853	796055	50.041	52.076
2	9.280	10350841	732586	49.959	47.924

0114 HT-1299-Fr-PTLC_003 2020/01/16 12:30:18



(+)-**3fa**

Number	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	7.940	265181	19213	1.656	1.746
2	9.187	15743580	1081455	98.344	98.254