Supporting Information

Efficient and regioselective nickel-catalyzed [2 + 2 + 2] cyclotrimerization of ynoates and related alkynes

Sanjeewa K. Rodrigo,[a] Israel V. Powell,[b] Michael G. Coleman,*[b] Jeanette A. Krause[a] and Hairong Guan*[a]

[a]*Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 45221-0172, United States*

[b]*School of Chemistry & Materials Science, Rochester Institute of Technology, Rochester, NY 14623, United States*

E-mails: mgcsch@rit.edu (M.G.C.); hairong.guan@uc.edu (H.G.)

General Experimental Methods. All reactions were carried out in flame-dried glassware under an argon atmosphere using standard glove box techniques. Dry and oxygen-free solvents for carrying out synthesis (THF and toluene) were collected from an Innovative Technology solvent purification system. CH_3CN was dried over CaH_2 and then degassed by freeze-pump-thaw cycles. Alkynes were purchased from Sigma-Aldrich and used without further purification except for phenylacetylene, which was freshly distilled prior to use. $Ni(COD)_2$ was purchased from Acros Organics, stored in a

–30 °C freezer of a glove box, and used without further purification. All other reagents were obtained from Sigma-Aldrich and used as received. NHC ligands were generated in situ by mixing equimolar amounts of imidazolidinium tetrafluoroborate and KO^{t}Bu in THF. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer. Chemical shift values were referenced internally to the residual solvent resonances. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory. High-resolution ESI-MS data for all the new compounds were obtained from either a Micromass Q-TOF-2^{TM} or a ThermoFinnigan LTQ Linear Ion-Trap FTMS instrument.

General Procedures for Catalytic [2+2+2] Cyclotrimerization of Alkynes (1 mol% Catalyst Loading). To a 10 mL scintillation vial under an argon atmosphere was added Ni(COD)$_2$ (4.1 mg, 0.015 mmol, 1 mol%), PPh$_3$ (11.8 mg, 0.045 mmol, 3 mol%) and 2 mL of toluene at 23 °C. The resulting mixture was stirred at the same temperature for 5 min, followed by the addition of the alkyne substrate (1.5 mmol). The reaction mixture was then stirred at appropriate temperature (see Tables 2 and 3 for details) until the starting material was fully converted. Upon completion of the reaction, the volatiles were removed under vacuum, and the residue was extracted by diethyl ether and filtered through a short plug of silica. The isomeric ratio was determined by analyzing either ^{1}H NMR (reactions of **1a-f** and **1k-p**) or GC/MS (reactions of **1g-j**) of the crude product. The desired 1,2,4-isomer was separated from the isomeric mixture using column chromatography (eluted with diethyl ether/hexanes). Reactions catalyzed by

$Ni(COD)_2$/NHC were carried out in the same fashion except that 0.045 mmol of PPh_3 was replaced with 0.015 mmol of NHC ligand and the solvent was switched to THF. Compounds **2a**,[1] **2b**,[2] **2c**,[3] **2e**,[4] **2f**,[5] **2g**,[5] **2j**,[6] **2k**,[7] **2l**,[8] **2m**,[9] **2n**[10] and **2p** + **3p**[11] have been reported in the literature, and the NMR data are consistent with the reported values. New compounds **2d** + **3d**, **2h**, **2i** and **2o** were further characterized using IR and high-resolution ESI-MS.

Procedures for Catalytic [2+2+2] Cyclotrimerization of Ethyl Propiolate (0.05 mol% Catalyst Loading). Under an argon atmosphere, $Ni(COD)_2$ (5.5 mg , 0.020 mmol) and PPh_3 (15.6 mg, 0.060 mmol) were mixed in 10 mL of toluene at 23 °C. The resulting mixture was stirred at this temperature for 5 min to produce a stock solution of the catalyst. A portion of the stock solution (375 μL) was added to a 10 mL scintillation vial under an argon atmosphere and the volume was brought up to 2 mL with toluene, followed by the addition of ethyl propiolate (152 μL, 1.5 mmol). The reaction was complete within 2 h, and the product was isolated in 92% yield.

Procedures for a Large-Scale Reaction of Methyl Propiolate. Under an argon atmosphere, 3.6 mL of the catalyst stock solution (as prepared above) was added to a 50 mL Schlenk flask. A solution of methyl propiolate (1.22 g, 1.29 mL, 14.5 mmol) in 2 mL of THF was then added to this flask at 23°C over a period of 30 min (best carried out using a syringe pump to avoid the evaporation of the alkyne due to high exothermicity of the reaction). The reaction mixture was stirred for additional 3 h before work up as described as above. The product **2b** was isolated in 86% yield.

Characterization Data for Compounds 2a-p, 3d and 3p

Compound 2a (colorless oil, 133 mg, 90%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 8.41 (1H, d, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H*), 8.20 (1H, dd, $^{3}J_{\text{H-H}}$ = 7.9 Hz, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H*), 7.76 (1H, d, $^{3}J_{\text{H-H}}$ = 7.9 Hz, Ar*H*), 4.50-4.35 (6H, m, C*H*$_2$), 1.50-1.35 (9H, m, C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 167.24, 166.70, 165.07, 136.36, 132.77, 132.17, 132.10, 130.19, 128.95, 62.09, 62.03, 61.78, 14.36, 14.20, 14.15.

Compound 2b (colorless oil, 115 mg, 91%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 8.43 (1H, d, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H*), 8.21 (1H, dd, $^{3}J_{\text{H-H}}$ = 8.2 Hz, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H*), 7.75 (1H, d, $^{3}J_{\text{H-H}}$ = 8.2 Hz, Ar*H*), 3.96 (3H, s, C*H*$_3$), 3.94 (6H, s, C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 167.76, 166.98, 165.52, 136.38, 132.59, 132.44, 131.75, 130.43, 129.03, 53.07, 53.00, 52.78.

Compound 2c (white solid, 167 mg, 88%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 8.23 (1H, d, $^{4}J_{\text{H-H}}$ = 1.8 Hz, Ar*H*), 8.05 (1H, dd, $^{3}J_{\text{H-H}}$ = 8.1 Hz, $^{4}J_{\text{H-H}}$ = 1.8 Hz, Ar*H*), 7.64 (1H, d, $^{3}J_{\text{H-H}}$ = 8.1 Hz, Ar*H*), 1.60 (27H, s, C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 166.54, 166.14, 164.48, 137.50, 133.78, 133.73, 131.39, 129.94, 128.76, 82.57, 82.43, 82.11, 28.27, 28.19, 28.17.

Compounds 2d + 3d (6.5: 1 ratio, white solid, 253 mg, 86% combined yield): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 9.36 (0.5H, s, Ar*H* of **3d**), 8.97 (1H, d, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H* of **2d**), 8.60 (1H, dd, $^{3}J_{\text{H-H}}$ = 8.0 Hz, $^{4}J_{\text{H-H}}$ = 1.7 Hz, Ar*H* of **2d**), 8.19 (1H, d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, Ar*H* of **2d**), 7.97-7.74 (14H, m, Ar*H* of **2d** and **3d**), 7.57-7.41 (10.5H, m, Ar*H* of **2d** and **3d**); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) of **2d** + **3d**: 165.71, 165.09, 163.73, 148.34, 136.73, 136.35, 133.91, 133.88, 133.66, 132.80, 131.99, 131.87, 131.51, 129.99, 129.88, 128.03, 127.95, 126.97, 126.85, 126.19, 126.14, 120.96, 120.89, 118.84; IR (neat, cm^{-1}) 3058, 1730 (ν_{CO}), 1630, 1600, 1582, 1511, 1463, 1442, 1356, 1297, 1277, 1256, 1236, 1204, 1148, 1136, 1120, 1073, 1038, 960, 928, 897, 853, 803, 780, 753, 725, 699, 631, 620; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{39}H_{24}O_6Na$ 611.1470, found 611.1478.

Compound 2e (yellow solid, 245 mg, 96%): ^1H NMR (400 MHz, $CDCl_3$, δ) 4.34 (12H, q, $^3J_{H\text{-}H}$ = 7.2 Hz, CH_2), 1.34 (18H, t, $^3J_{H\text{-}H}$ = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ) 164.77, 133.77, 62.64, 13.74.

Compound 2f (white solid, 240 mg, 92%): ^1H NMR (400 MHz, $CDCl_3$, δ) 7.35 (5H, s, ArH), 7.14-7.11 (6H, m, ArH), 7.04-7.00 (4H, m, ArH), 4.01-3.92 (4H, m, CH_2), 3.65 (2H, q, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_2), 0.92-0.85 (6H, m, CH_3), 0.67 (3H, t, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ) 167.84, 167.49, 167.45, 16, 140.89, 139.32, 137.72, 137.59, 137.45, 137.37, 134.24, 132.15, 130.00, 129.92, 129.22, 129.02, 128.15, 128.06, 127.61, 127.44, 127.30, 61.67, 61.06, 13.58, 13.46.

Compound 2g (colorless oil, 141 mg, 84%): ^1H NMR (400 MHz, $CDCl_3$, δ) 4.41 (2H, q, $^3J_{H\text{-}H}$ = 7.2 Hz, CH_2), 4.36-4.29 (4H, m, CH_2), 2.30 (3H, s, ArCH_3), 2.26 (3H, s, ArCH_3), 2.23 (3H, s, ArCH_3), 1.40-1.33 (9H, m, CH_2CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ) 169.48, 168.55, 167.86, 137.59, 135.90, 133.81, 132.68, 130.37, 129.97, 61.57, 61.54, 61.46, 17.38, 17.09, 16.63, 14.27, 14.13.

Compound 2h (colorless oil, 178 mg, 94%): ^1H NMR (400 MHz, $CDCl_3$, δ) 3.91 (3H, s, CO_2CH_3), 3.86 (3H, s, CO_2CH_3), 3.84 (3H, s, CO_2CH_3), 2.64-2.47 (6H, m, ArCH_2), 1.56-1.48 (6H, m, ArCH_2CH_2), 1.00-0.88 (9H, m, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ) 170.12, 169.23, 168.50, 140.56, 137.60, 137.43, 135.90, 134.10, 130.04, 52.56, 52.23, 33.81, 33.60, 32.10, 24.99, 24.74, 14.97, 14.83, 14.70; IR (neat, cm^{-1}) 2959, 2873, 1729 (ν_{CO}), 1438, 1305, 1267, 1240, 1200, 1146, 1114, 1087, 1014, 977, 743; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{30}O_6Na$ 401.19346, found 401.19357.

Compound 2i (colorless oil, 224 mg, 89%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 3.90 (3H, s, CO$_2$C*H*$_3$), 3.85 (3H, s, CO$_2$C*H*$_3$), 3.84 (3H, s, CO$_2$C*H*$_3$), 2.64-2.48 (6H, m, ArC*H*$_2$), 1.53-1.26 (24H, m, C*H*$_2$), 0.91-0.86 (9H, m, C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 170.11, 169.22, 168.50, 140.68, 137.49, 136.07, 134.08, 129.92, 52.54, 52.20, 31.79, 31.66, 31.60, 31.58, 31.51, 31.41, 31.27, 30.06, 30.02, 29.95, 29.83, 22.70, 22.65, 14.20; IR (neat, cm^{-1}) 2954, 2927, 2857, 2361, 2338, 1733 (ν_{CO}), 1437, 1210, 1146, 1099, 668; HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{30}H_{48}O_6Na$ 527.3348, found 527.3342.

Compound 2j (colorless oil, 234 mg, 92%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 4.35-4.25 (6H, m, C*H*$_2$), 1.40-1.32 (9H, m, CH$_2$C*H*$_3$), 0.37 (9H, s, Si(C*H*$_3$)$_3$), 0.33 (9H, s, Si(C*H*$_3$)$_3$), 0.28 (9H, s, Si(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 170.45, 169.71, 153.15, 151.02, 147.10, 139.05, 138.77, 138.54, 61.93, 61.88, 61.80, 14.09, 14.04, 4.32, 3.77, 1.72.

Compound 2k (white solid, 138 mg, 90%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.79-7.17 (18H, m, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 141.61, 141.24, 141.11, 140.72, 140.50, 139.67, 131.25, 130.05, 130.01, 129.57, 128.98, 128.07, 128.04, 127.58, 127.28, 126.74, 126.67, 126.27.

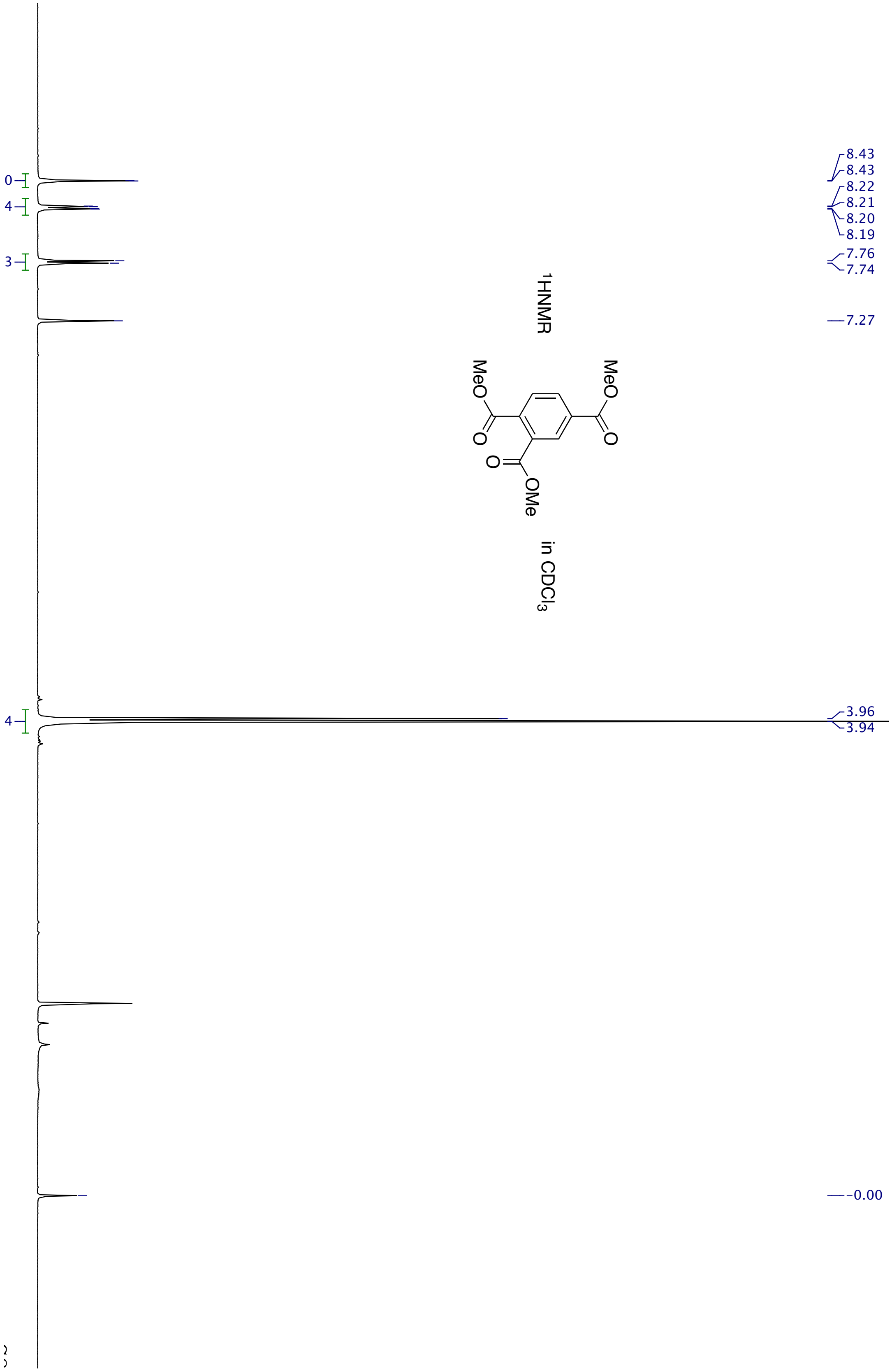
Compound 2l (yellow solid, 165 mg, 92%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.65-7.55 (4H, m, Ar*H*), 7.45-7.43 (1H, m, Ar*H*), 7.15-7.08 (6H, m, Ar*H*), 6.95-6.90 (4H, m, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ) 162.74 (d, $^1J_{C\text{-}F}$ = 247.4 Hz, *C*F), 162.00 (d, $^1J_{C\text{-}F}$ = 247.4 Hz, *C*F), 161.94 (d, $^1J_{C\text{-}F}$ = 247.4 Hz, *C*F), 140.14, 139.74, 138.62, 137.24 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 136.88 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 136.58 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.50 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 131.46 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 131.22, 129.30, 128.80 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 126.30, 115.90 (d, $^2J_{C\text{-}F}$ = 20.2 Hz), 115.19 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 115.15 (d, $^2J_{C\text{-}F}$ = 24.2 Hz).

Compound 2m (pale yellow solid, 216 mg, 90%): ^{1}H NMR (400 MHz, CDCl$_3$, δ) 8.16-8.12 (2H, m, Ar*H*), 7.92-7.89 (4H, m, Ar*H*), 7.76-7.68 (4H, m, Ar*H*), 7.55-7.52 (1H, m, Ar*H*), 7.24-7.20 (4H, m, Ar*H*), 3.94 (3H, s, CH_3), 3.89 (6H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, *δ*) 166.82, 145.53, 145.20, 144.43, 140.26, 139.90, 139.36, 131.22, 130.26, 129.87, 129.81, 129.49, 129.44, 129.36, 128.72, 128.64, 127.05, 126.97, 52.22, 52.15.

Compound 2n (white solid, 203 mg, 76%): ^1H NMR (400 MHz, $CDCl_3$, *δ*) 6.87-6.82 (30H, m, Ar*H*); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, *δ*) 140.75, 140.44, 131.56, 126.71, 125.32.

Compound 2o (pale yellow solid, 146 mg, 95%): ^1H NMR (400 MHz, $CDCl_3$, *δ*) 8.72 (1H, d, $^3J_{H-H}$ = 8.0 Hz, Ar*H*), 8.62 (2H, d, $^3J_{H-H}$ = 8.0 Hz, Ar*H*), 8.32 (1H, s, Ar*H*), 8.19 (1H, d, $^3J_{H-H}$ = 8.0 Hz, Ar*H*), 7.88-7.75 (3H, m, Ar*H*), 7.51-7.45 (2H, m, Ar*H*), 7.27-7.24 (1H, m, Ar*H*), 7.17-7.03 (4H, m, Ar*H*); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, *δ*) 159.26, 158.85, 156.67, 149.79, 149.56, 149.54, 140.21, 140.17, 139.58, 136.83, 135.69, 135.63, 131.05, 129.08, 127.02, 125.12, 122.46, 121.70, 120.82; IR (neat, cm^{-1}) 3005, 1583, 1562, 1466, 1458, 1442, 1423, 1386, 1306, 1288, 1249, 1141, 1096, 1047, 1030, 1019, 988, 962, 929, 900, 857, 847, 802, 793, 781, 773, 753, 718, 646, 634, 622, 612, 579, 541, 524, 498, 445; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{21}H_{16}N_3$ 310.1344, found 310.1341.

Compounds 2p + 3p (6:1 ratio, colorless oil, 87 mg, 88% combined yield): ^1H NMR (400 MHz, $CDCl_3$, *δ*) 6.86 (1H, d, $^3J_{H-H}$ = 8.0 Hz, Ar*H* of **2p**), 6.79 (1H, d, $^3J_{H-H}$ = 8.0 Hz, Ar*H* of **2p**), 6.70 (1H, s, Ar*H* of **2p**), 6.57 (0.5H, s, Ar*H* of **3p**), 2.26-2.05 (2H, m, C*H* of **2p**), 1.85-1.78 (1.5H, m, C*H* of **2p** and **3p**), 1.02-0.78 (7H, m, CH_2 of **2p** and **3p**), 0.75-0.53 (7H, m, CH_2 of **2p** and **3p**); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, *δ*) of **2p**: 142.43, 141.28, 139.74, 125.37, 122.91, 122.69, 15.22, 13.22, 12.92, 9.04, 7.33, 7.21; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, *δ*) of **3p**: 143.98, 120.39, 15.47, 9.09; IR (neat, cm^{-1}) 3080, 3002, 1612, 1565, 1502, 1461, 1426, 1348, 1217, 1173, 1099, 1045, 1015, 945, 895, 812, 743, 702, 660, 626, 518, 455; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{15}H_{19}$ 199.1487, found 199.1483.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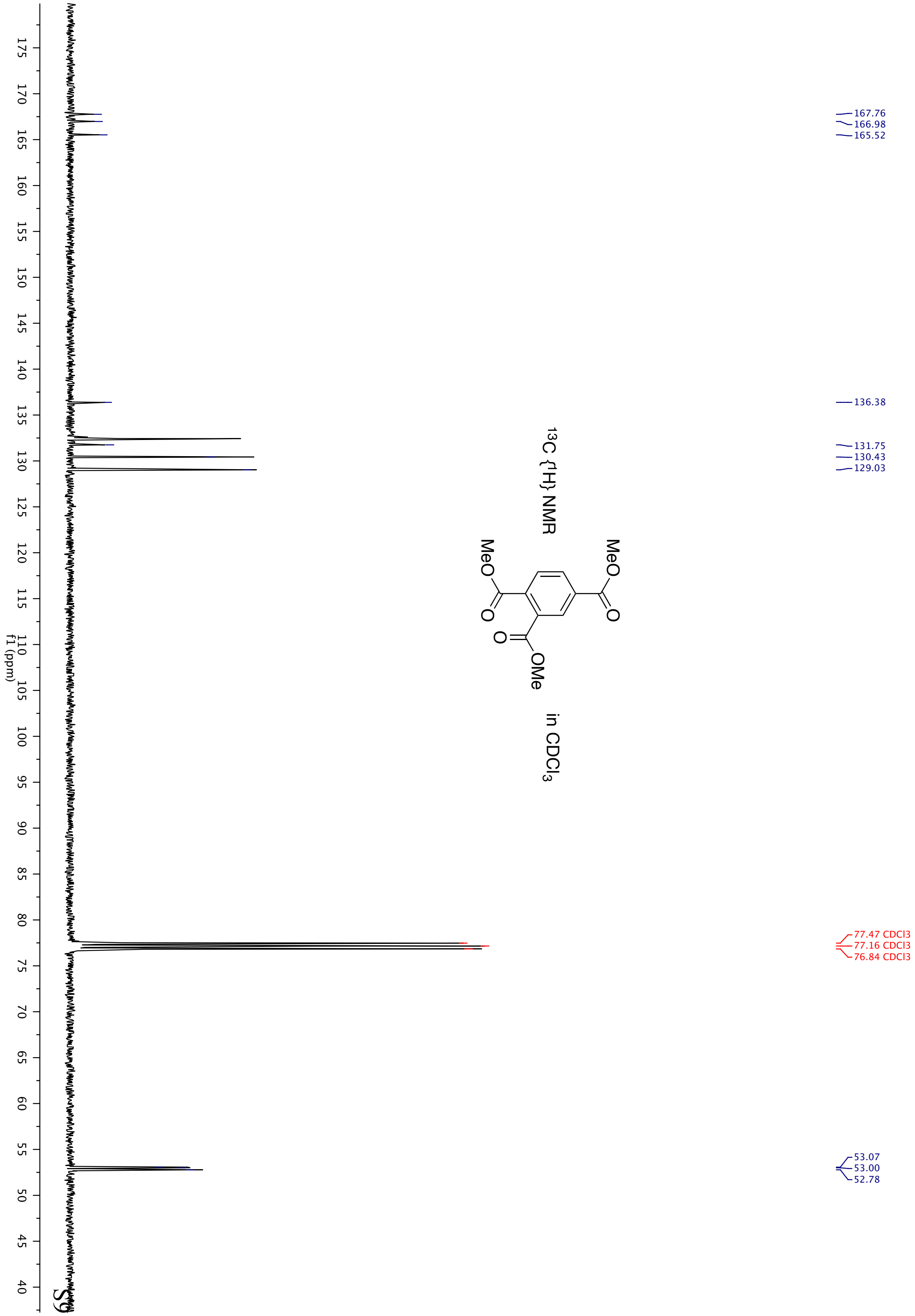
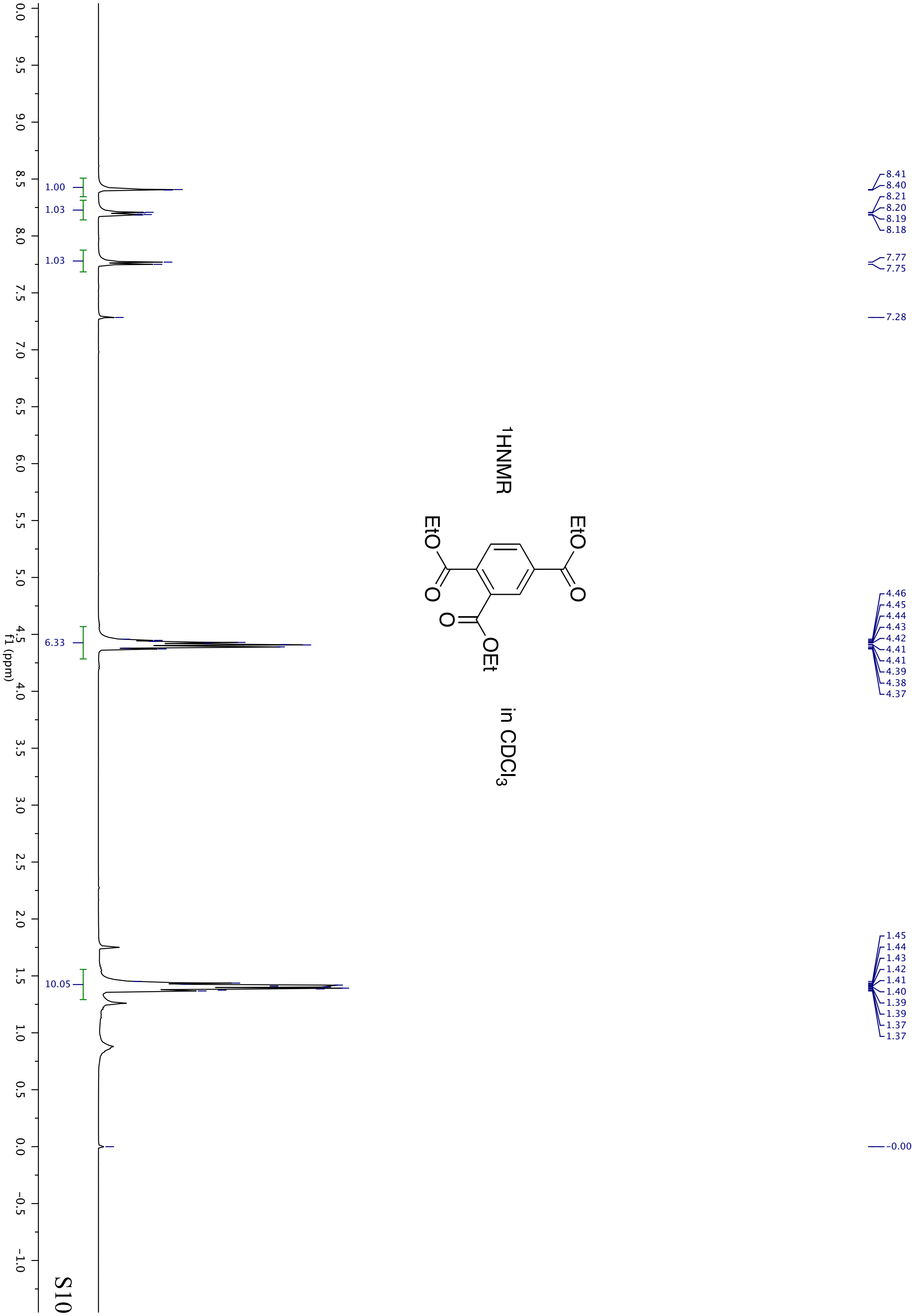


$^{13}C\ \{^1H\}$ NMR

in $CDCl_3$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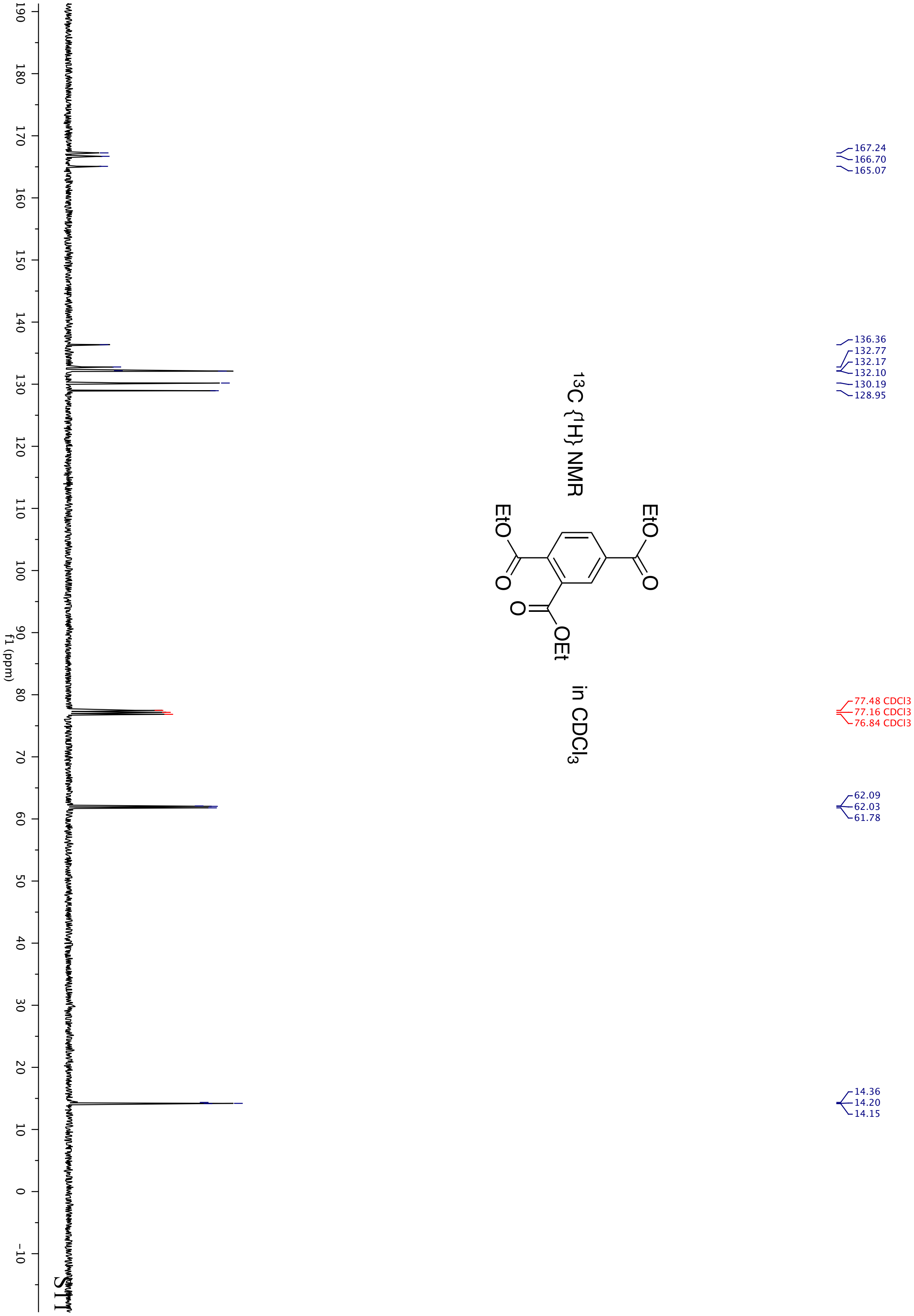
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77.16 CDCl3
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62.03
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14.20
14.15
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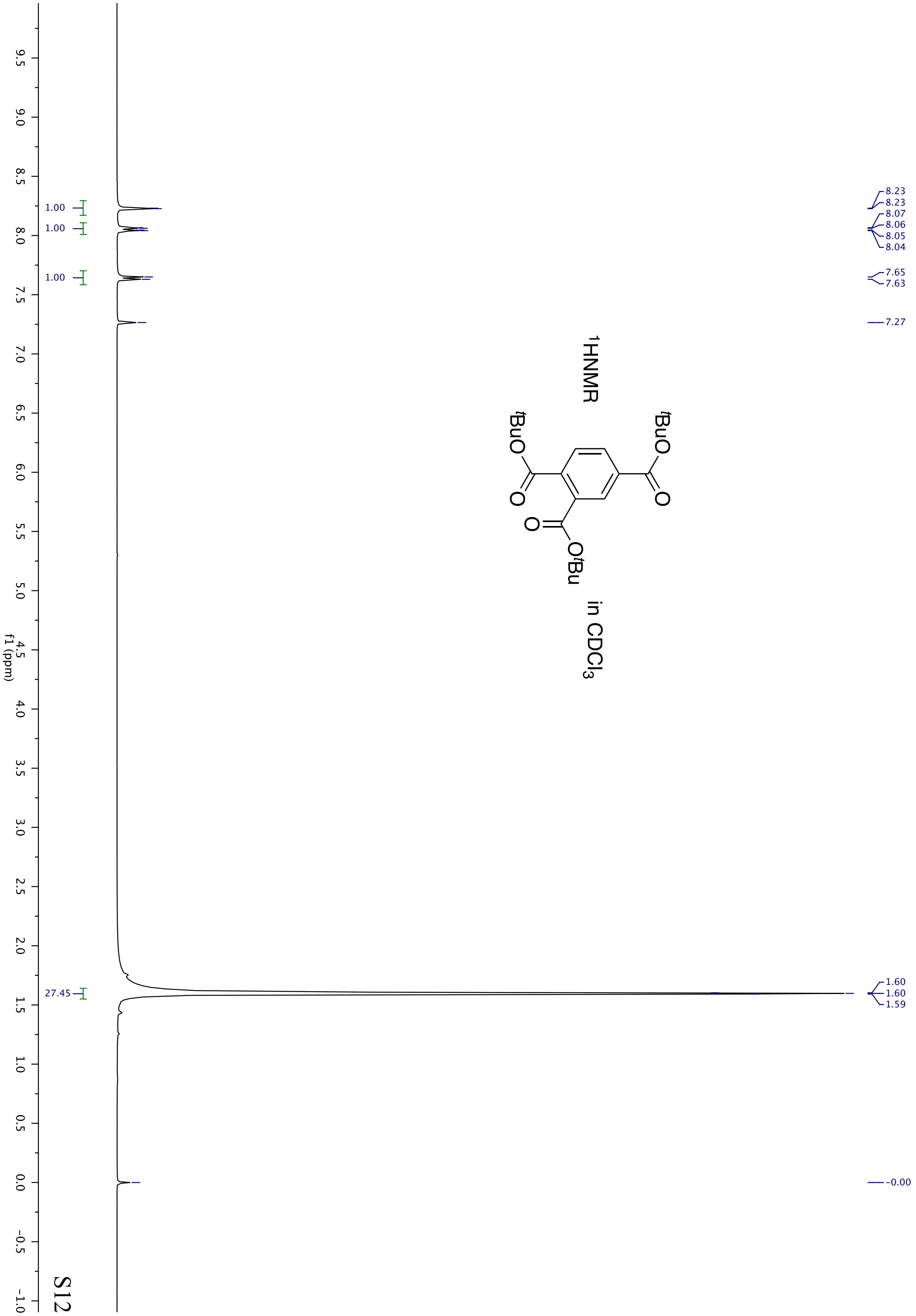
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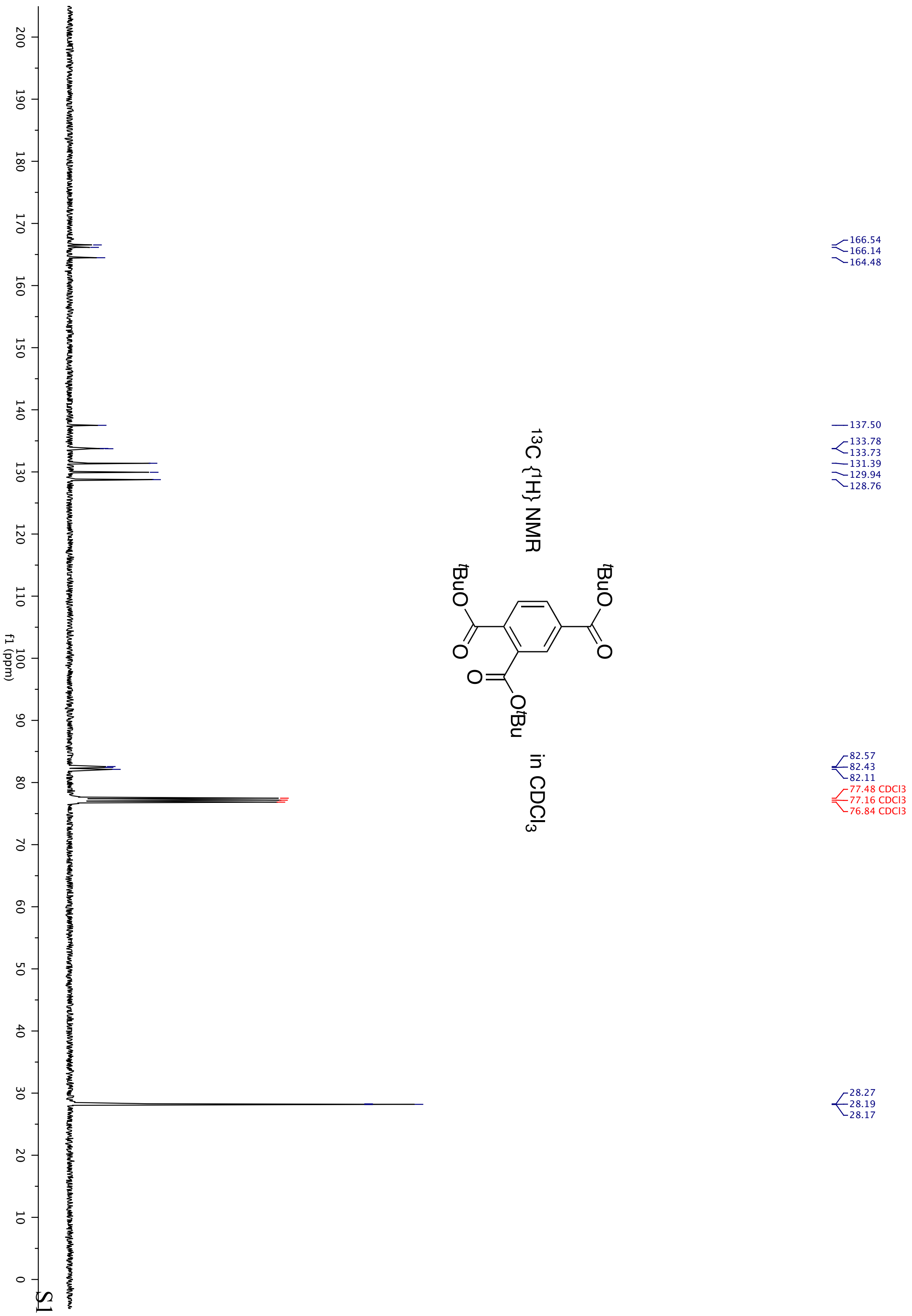
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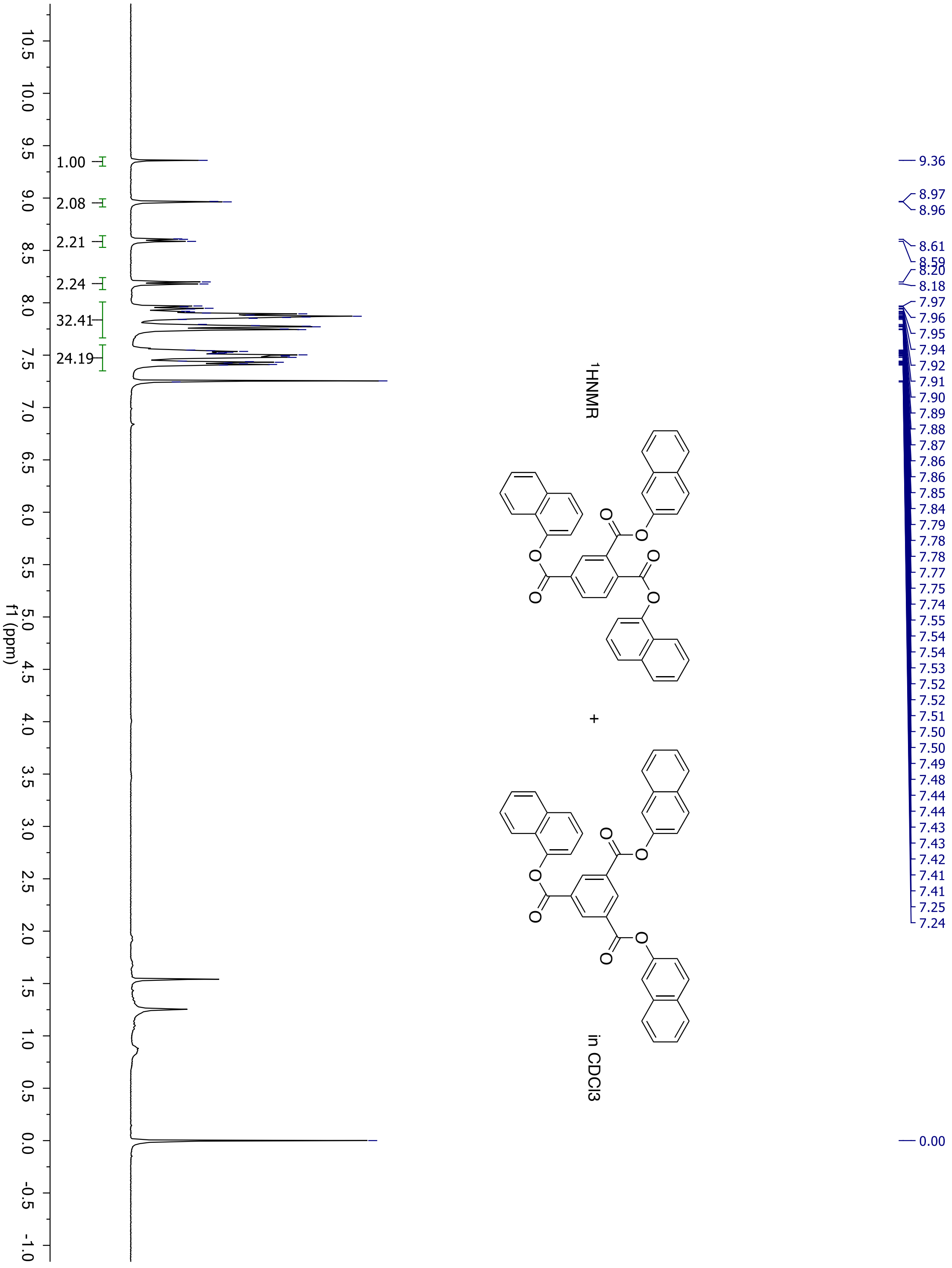
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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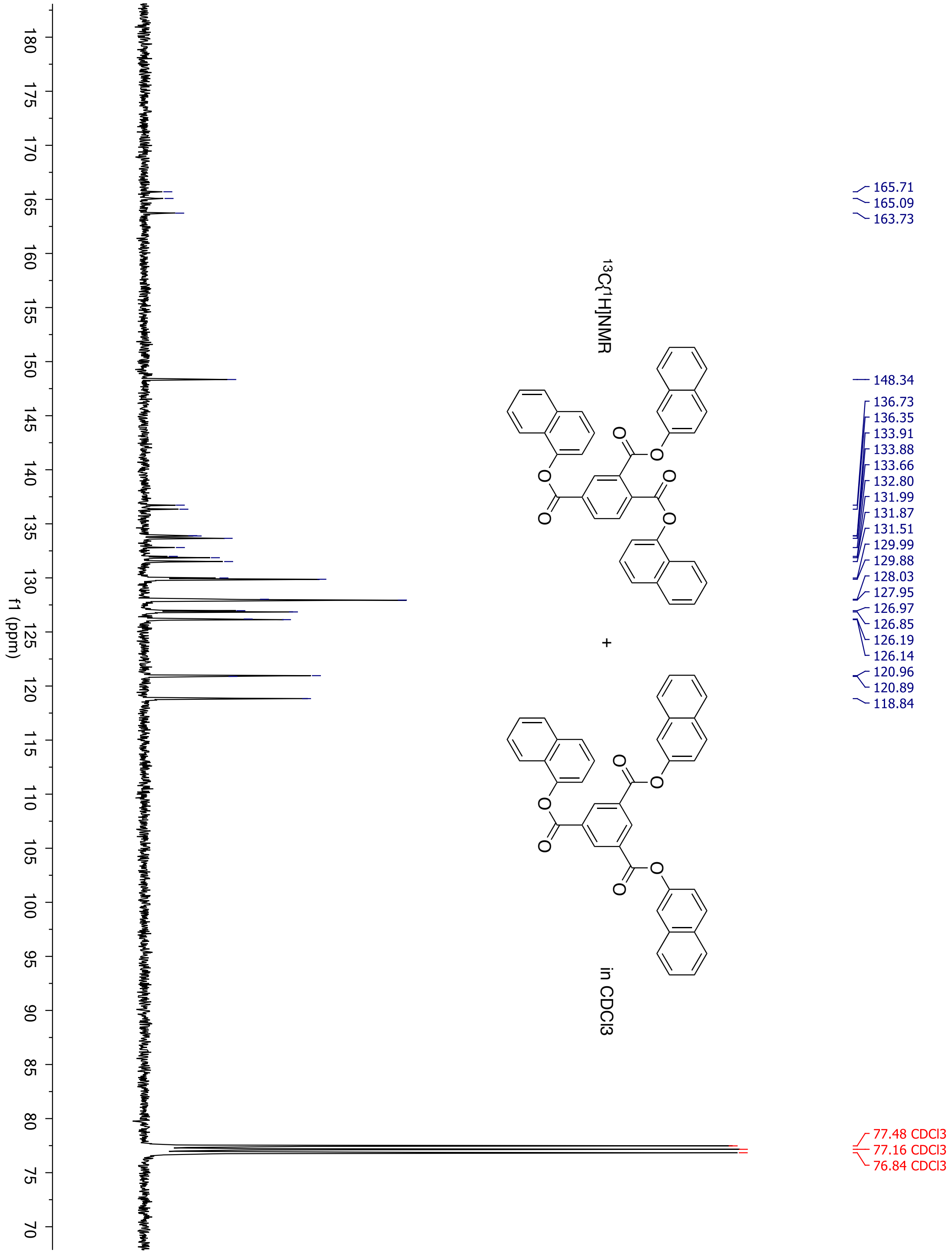
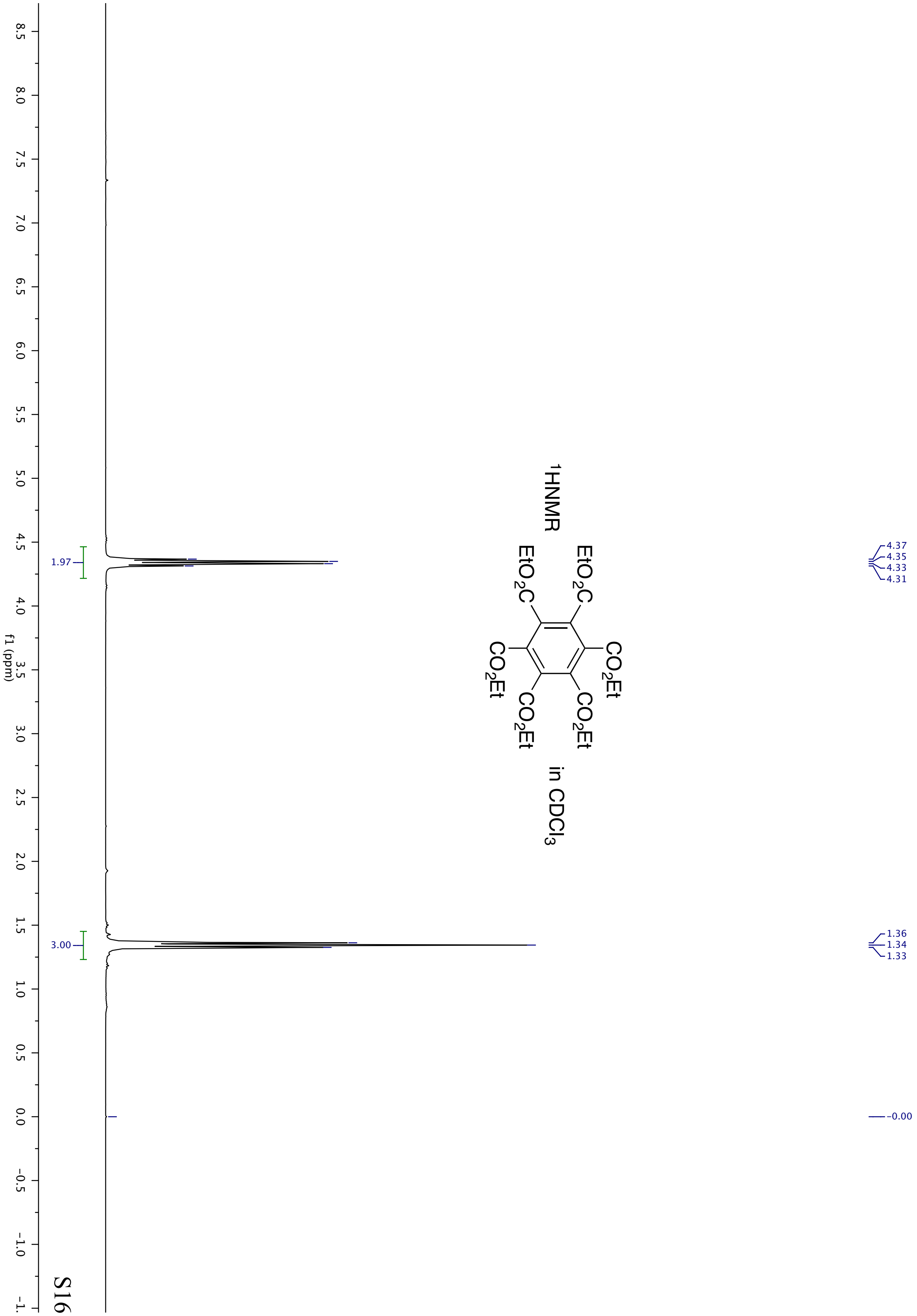
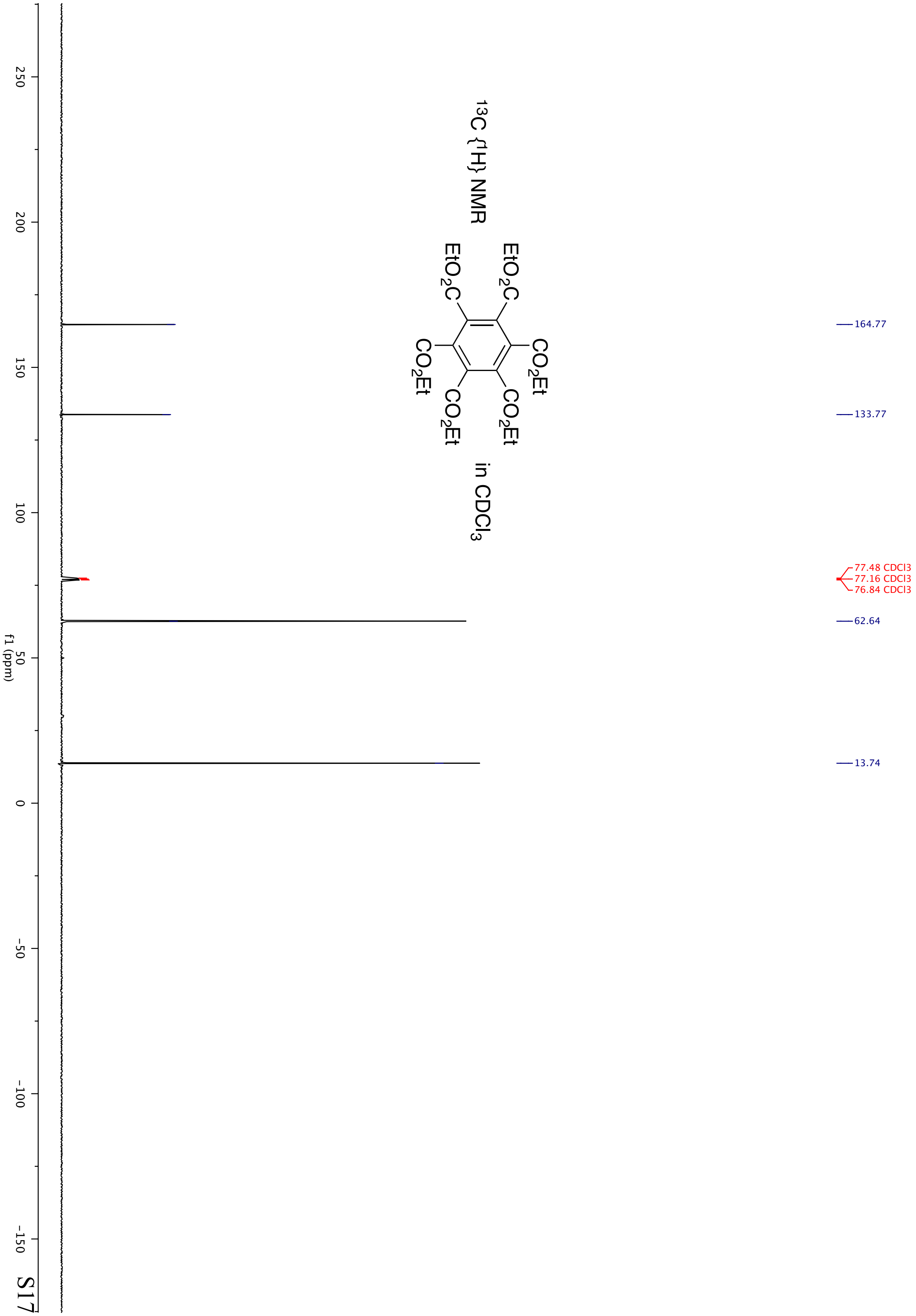
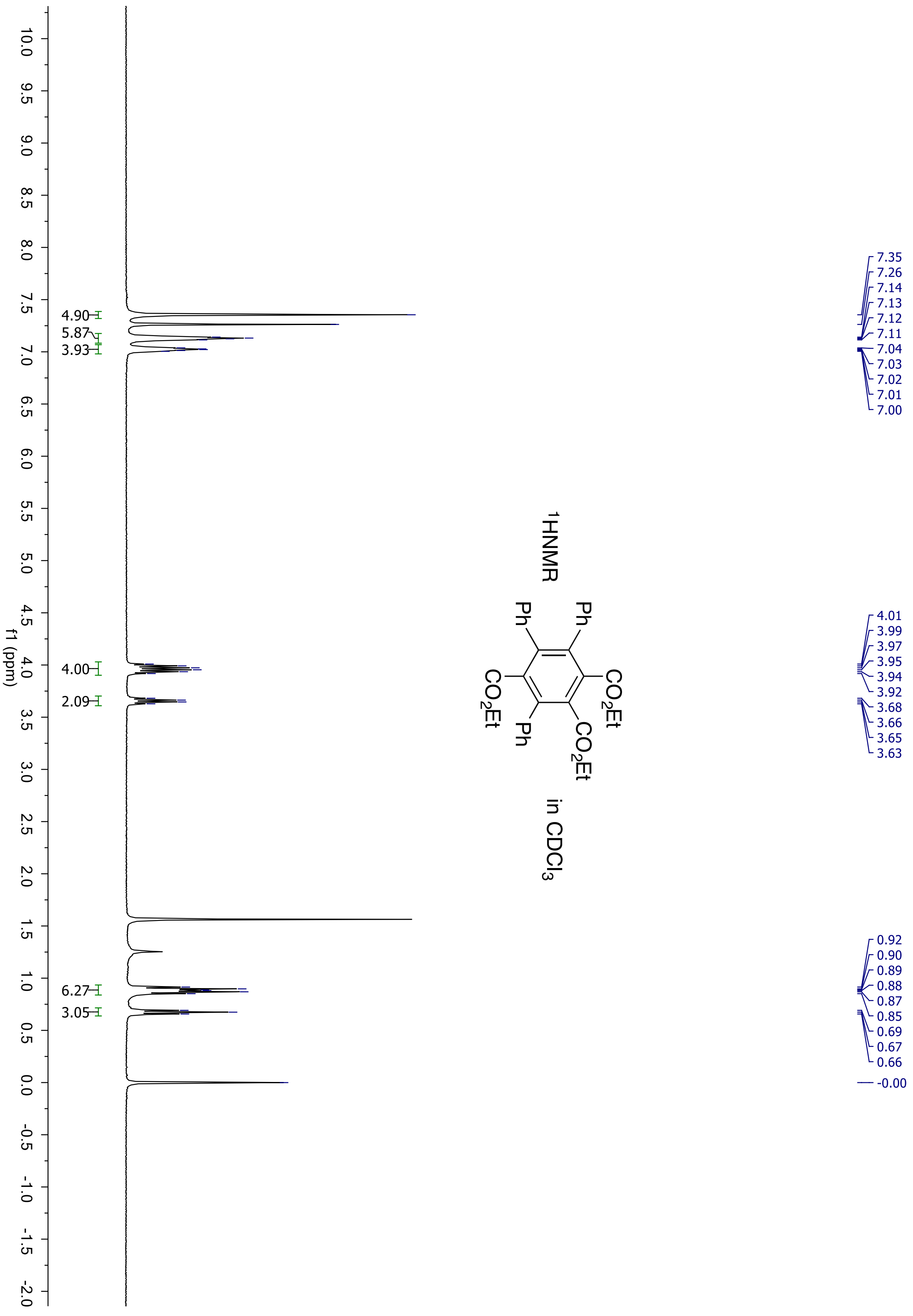
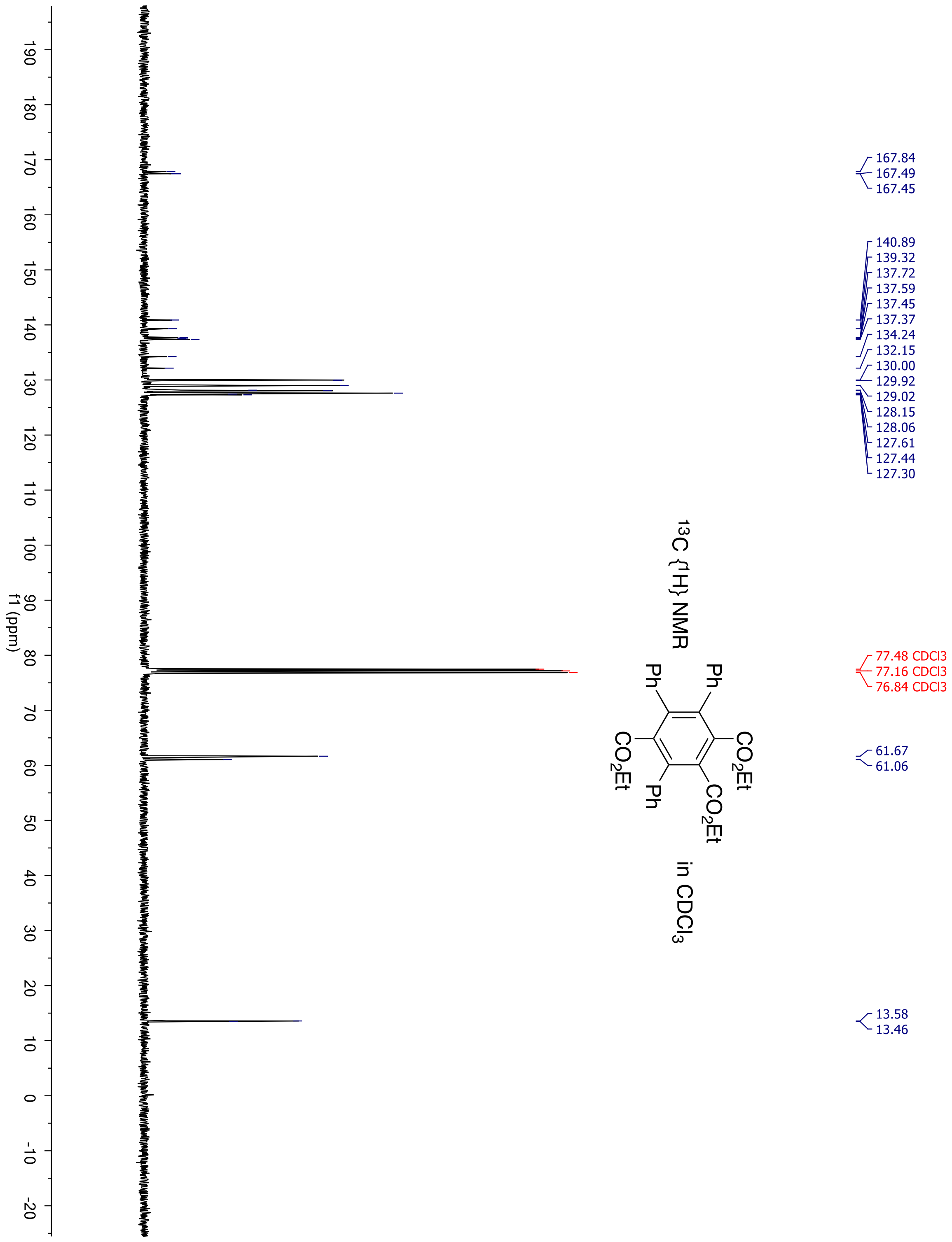
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.25
7.24
0.00
O
O
O
O
O
O
O
O
O
O
O
O

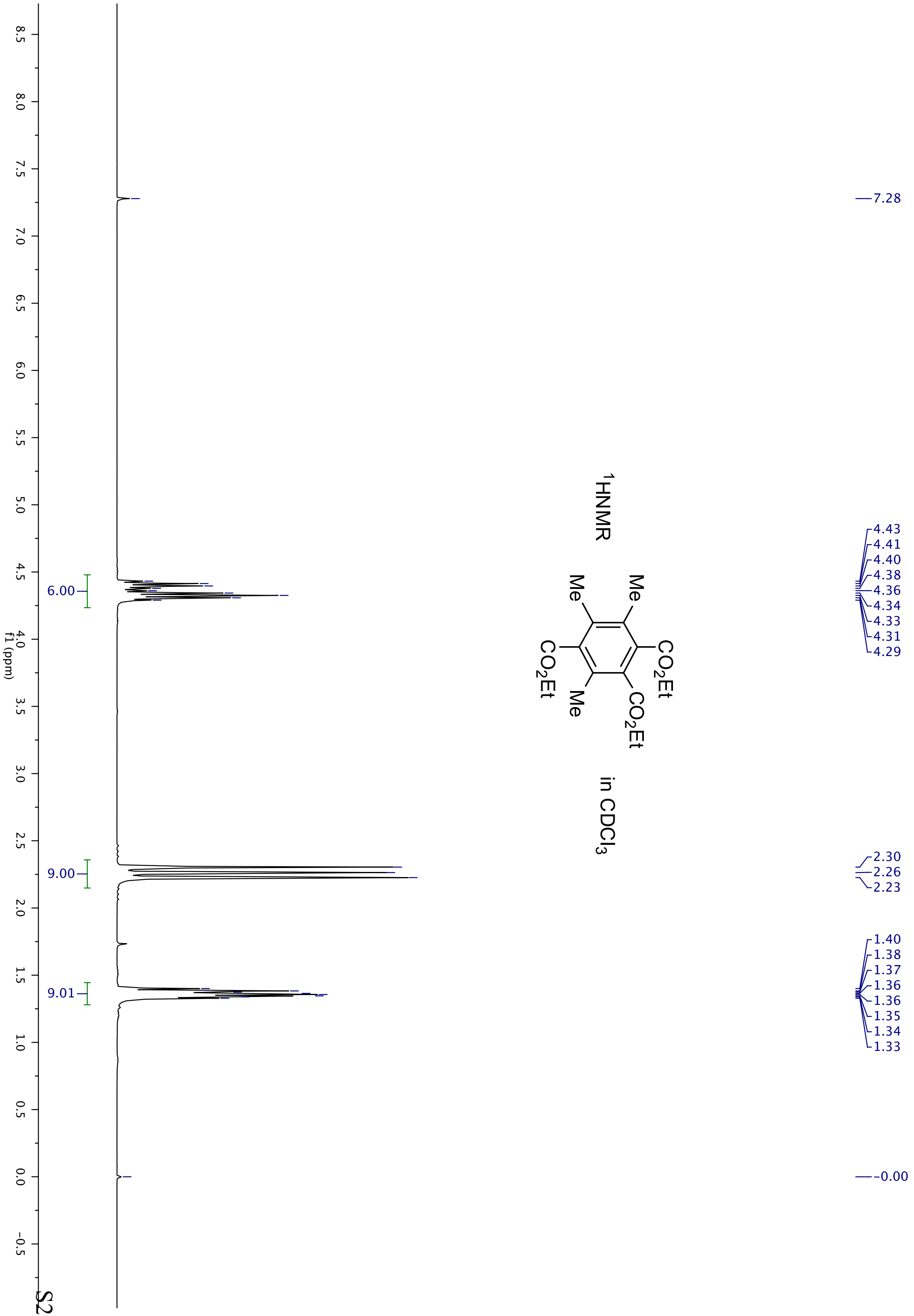

$^{13}C\{^1H\}NMR$
+
in CDCl3
O
165.71
165.09
163.73
148.34
136.73
136.35
133.91
133.88
133.66
132.80
131.99
131.87
131.51
129.99
129.88
128.03
127.95
126.97
126.85
126.19
126.14
120.96
120.89
118.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
f1 (ppm)


1HNMR
in CDCl3
EtO2C
EtO2C
CO2Et
CO2Et
CO2Et
CO2Et
4.37
4.35
4.33
4.31
1.36
1.34
1.33
-0.00
1.97
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.
f1 (ppm)

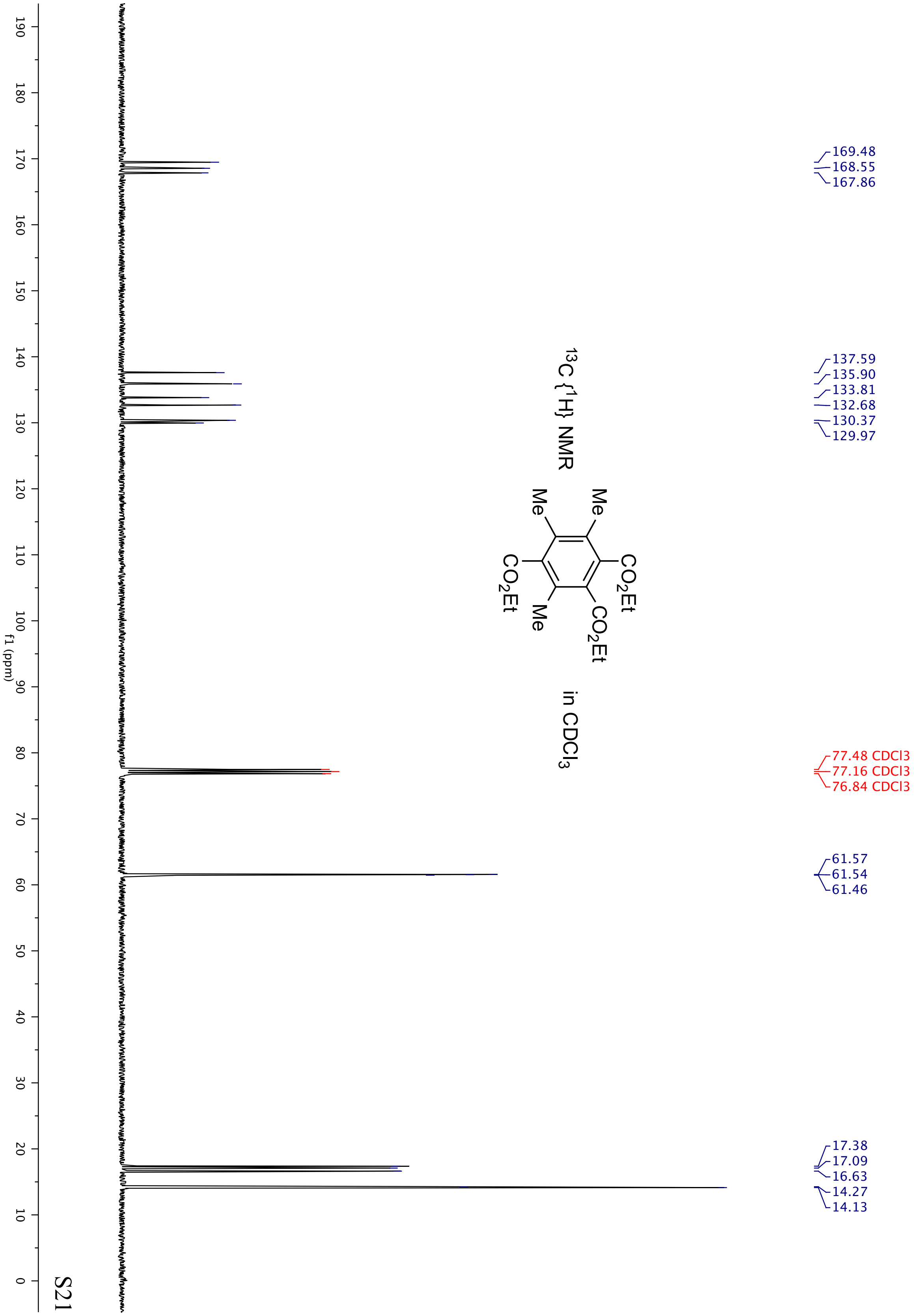

^{13}C {^{1}H} NMR
EtO$_2$C
EtO$_2$C
CO$_2$Et
CO$_2$Et
CO$_2$Et
CO$_2$Et
in CDCl$_3$
164.77
133.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.64
13.74
250
200
150
100
50
0
−50
−100
−150
f1 (ppm)

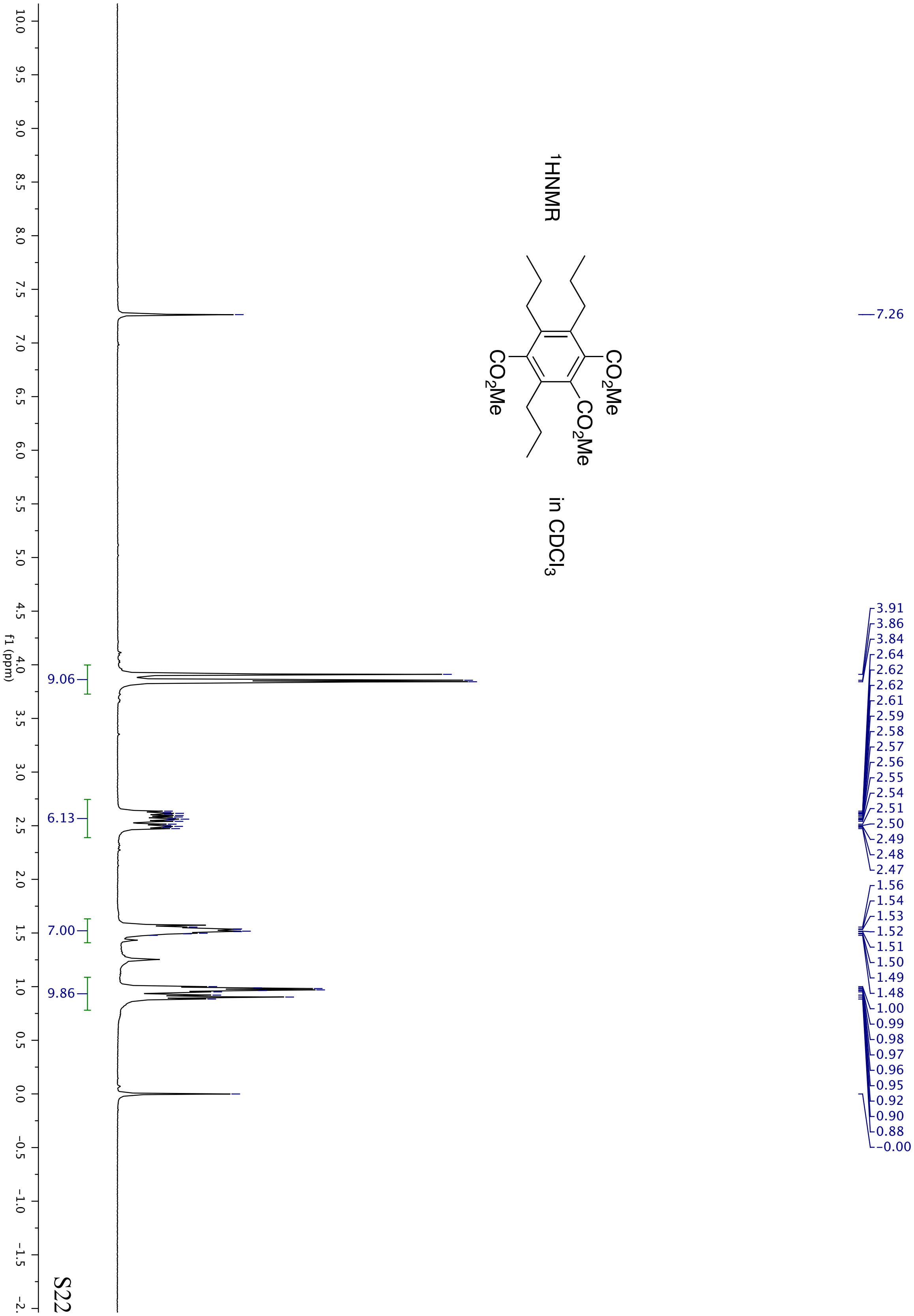

1HNMR
Ph
Ph
Ph
CO2Et
CO2Et
CO2Et
in CDCl3
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
4.90
5.87
3.93
4.00
2.09
6.27
3.05
7.35
7.26
7.14
7.13
7.12
7.11
7.04
7.03
7.02
7.01
7.00
4.01
3.99
3.97
3.95
3.94
3.92
3.68
3.66
3.65
3.63
0.92
0.90
0.89
0.88
0.87
0.85
0.69
0.67
0.66
-0.00

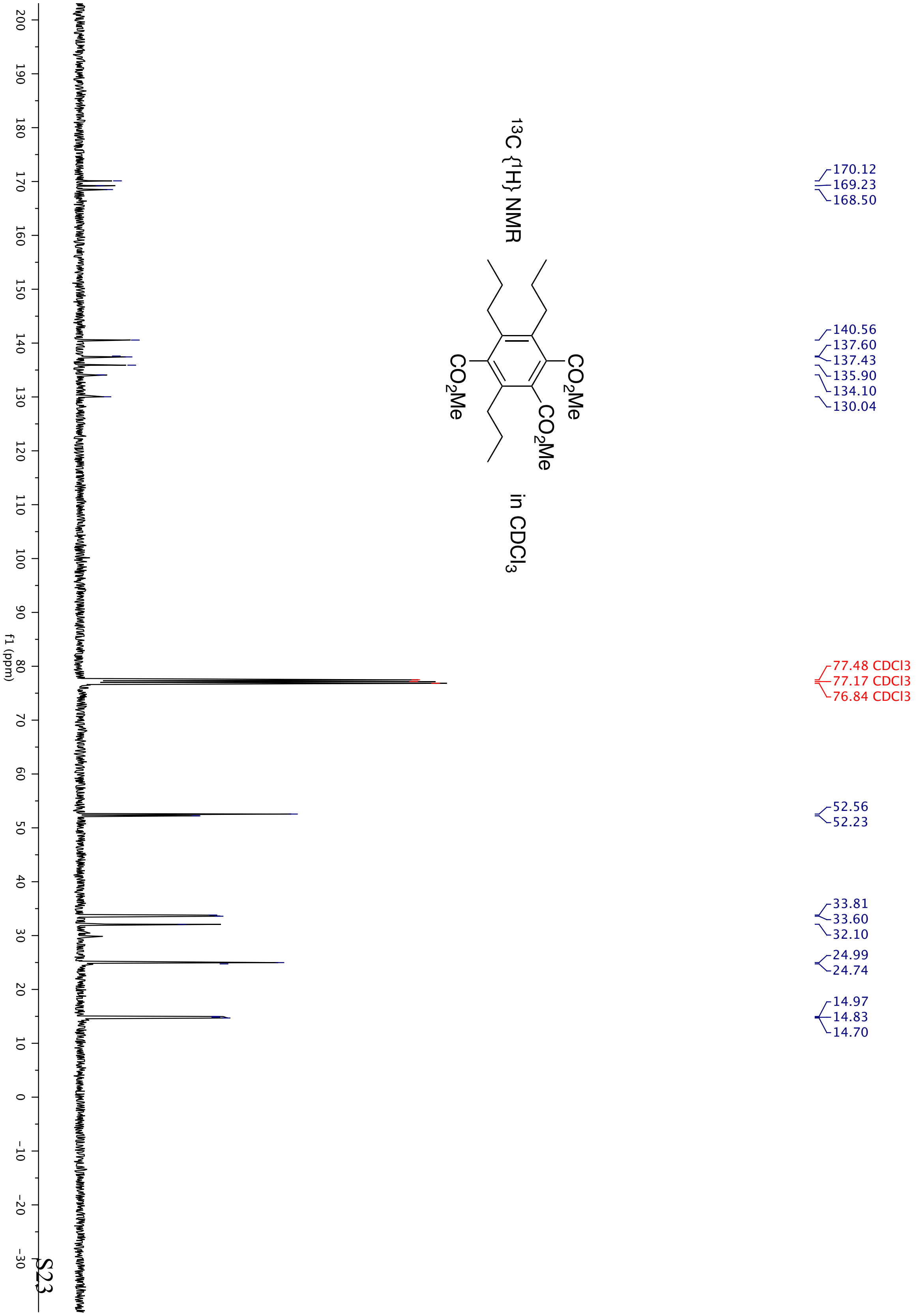

^{13}C {^{1}H} NMR
in CDCl$_3$
Ph
Ph
Ph
CO$_2$Et
CO$_2$Et
CO$_2$Et
167.84
167.49
167.45
140.89
139.32
137.72
137.59
137.45
137.37
134.24
132.15
130.00
129.92
129.02
128.15
128.06
127.61
127.44
127.30
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.67
61.06
13.58
13.46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

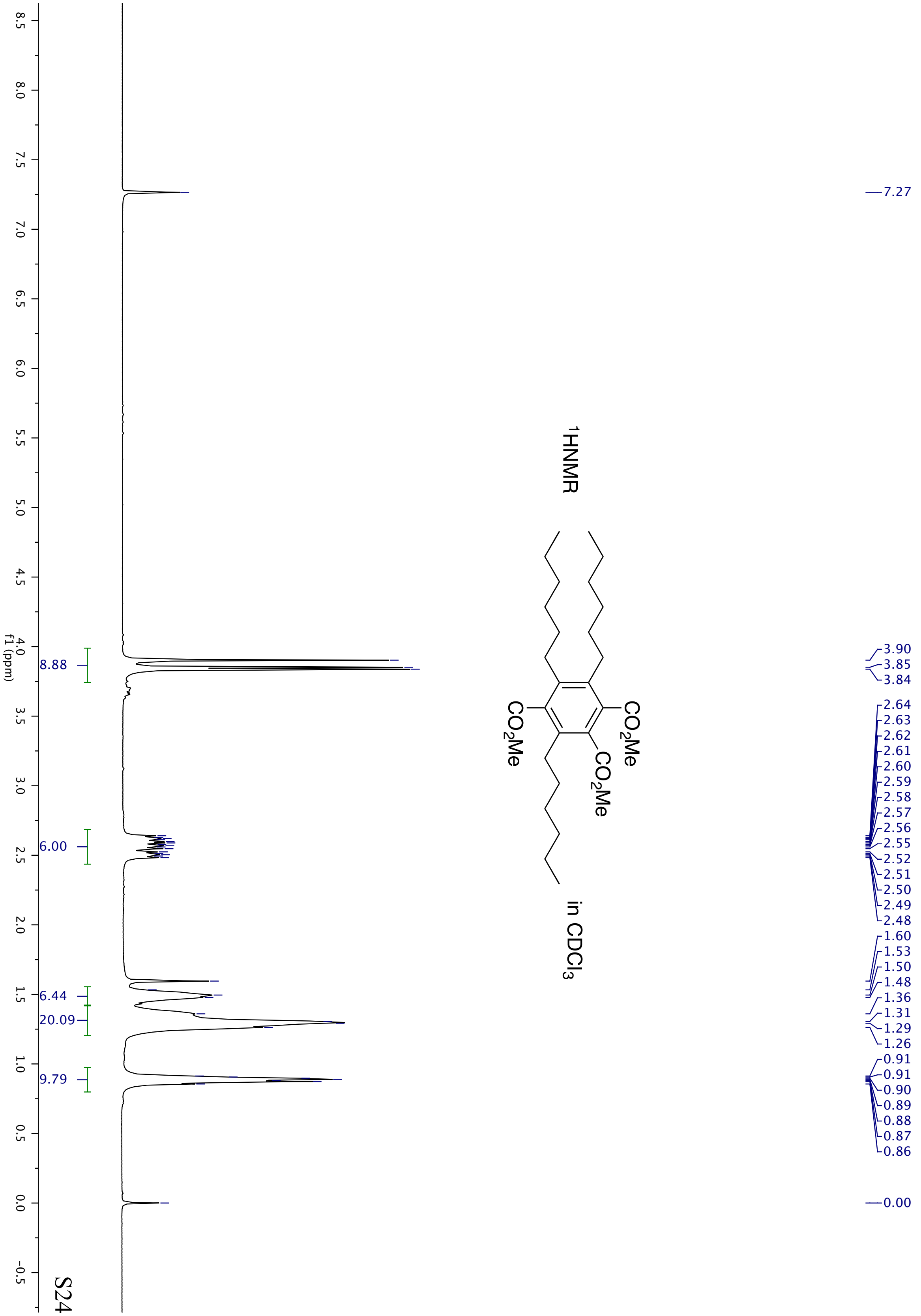


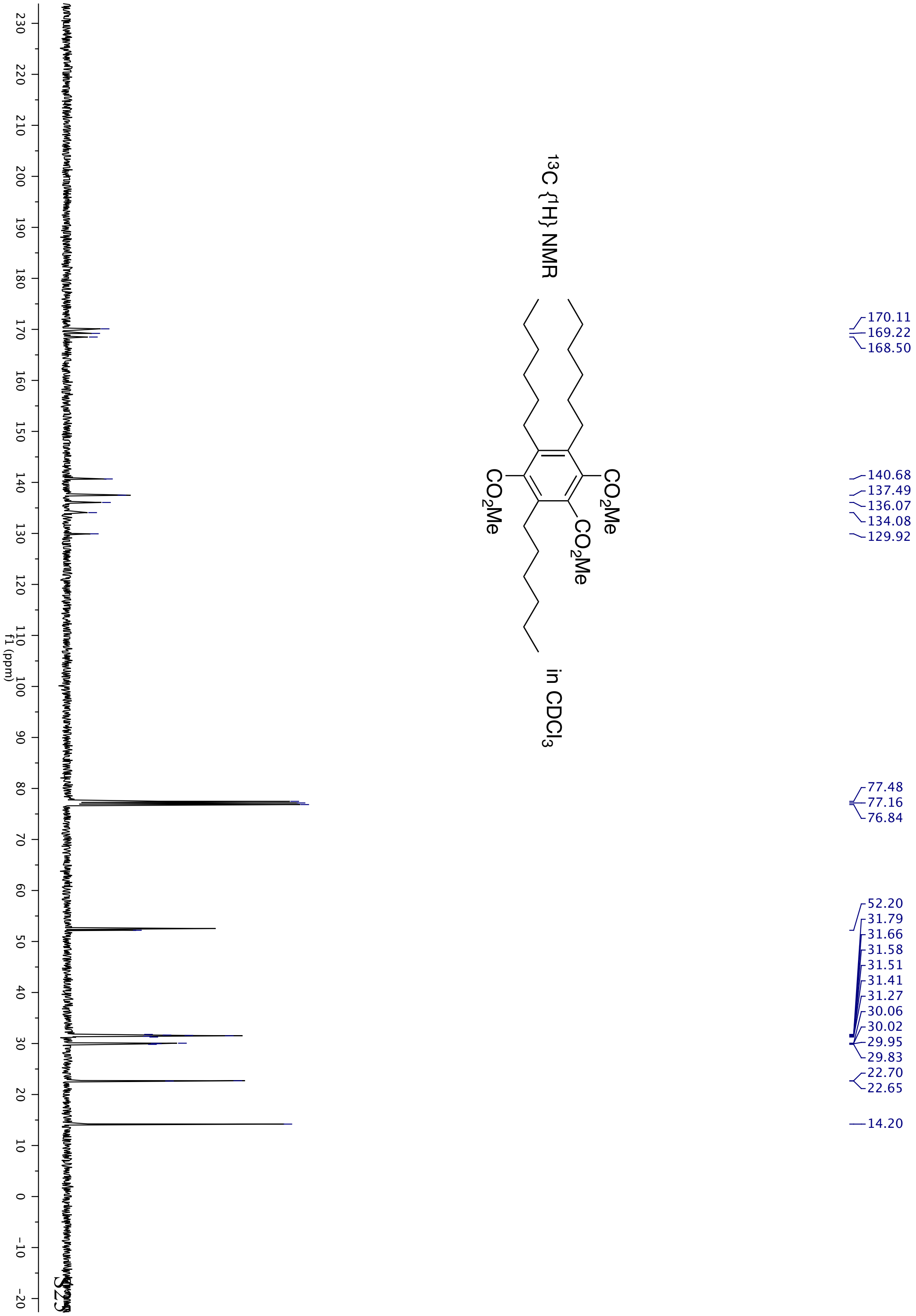
1HNMR
in CDCl3
Me
Me
Me
CO2Et
CO2Et
CO2Et
7.28
4.43
4.41
4.40
4.38
4.36
4.34
4.33
4.31
4.29
2.30
2.26
2.23
1.40
1.38
1.37
1.36
1.36
1.35
1.34
1.33
-0.00
6.00
9.00
9.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

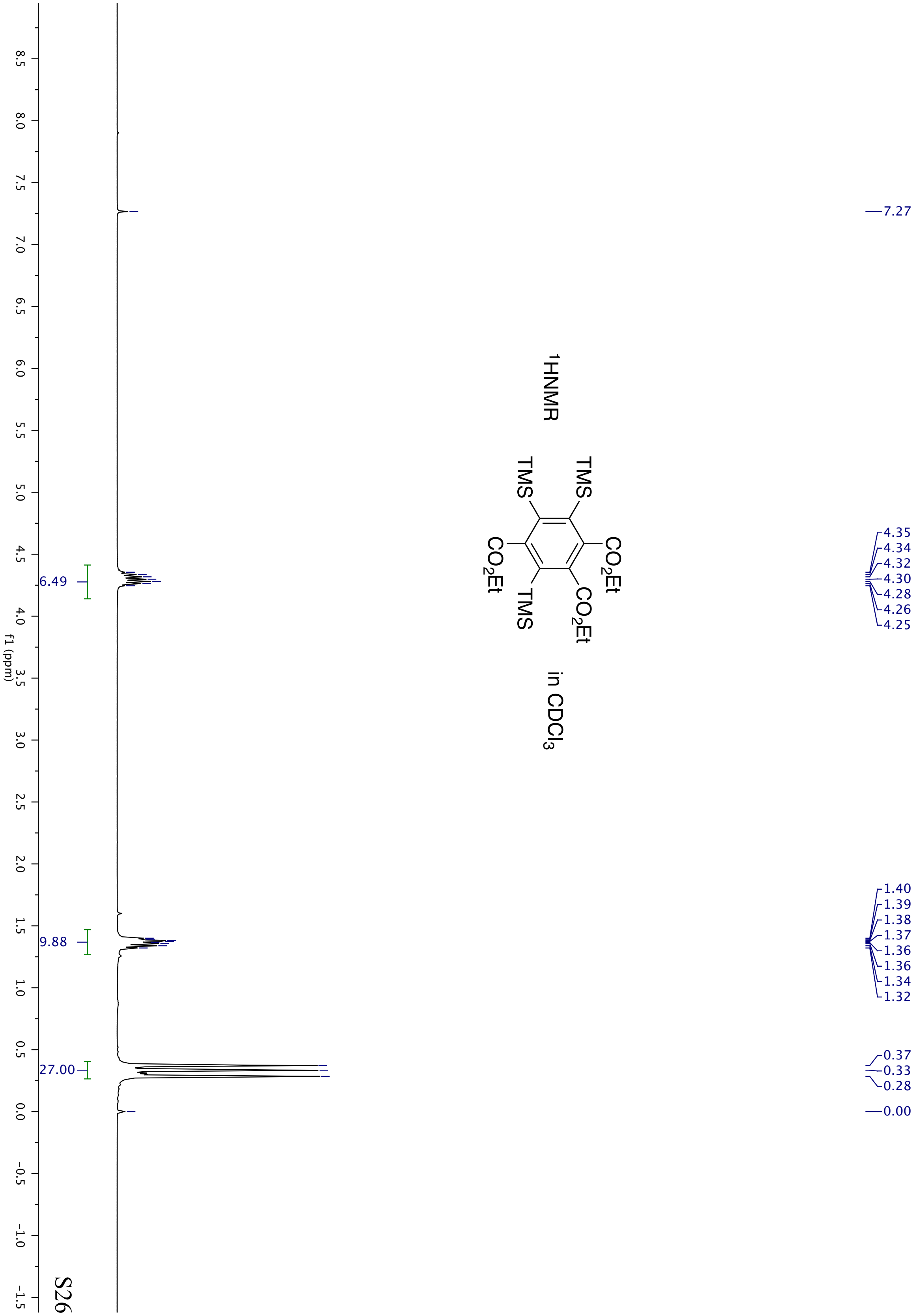

$^{13}C\{^1H\}$ NMR
Me
Me
Me
CO_2Et
CO_2Et
CO_2Et
in $CDCl_3$
169.48
168.55
167.86
137.59
135.90
133.81
132.68
130.37
129.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.57
61.54
61.46
17.38
17.09
16.63
14.27
14.13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

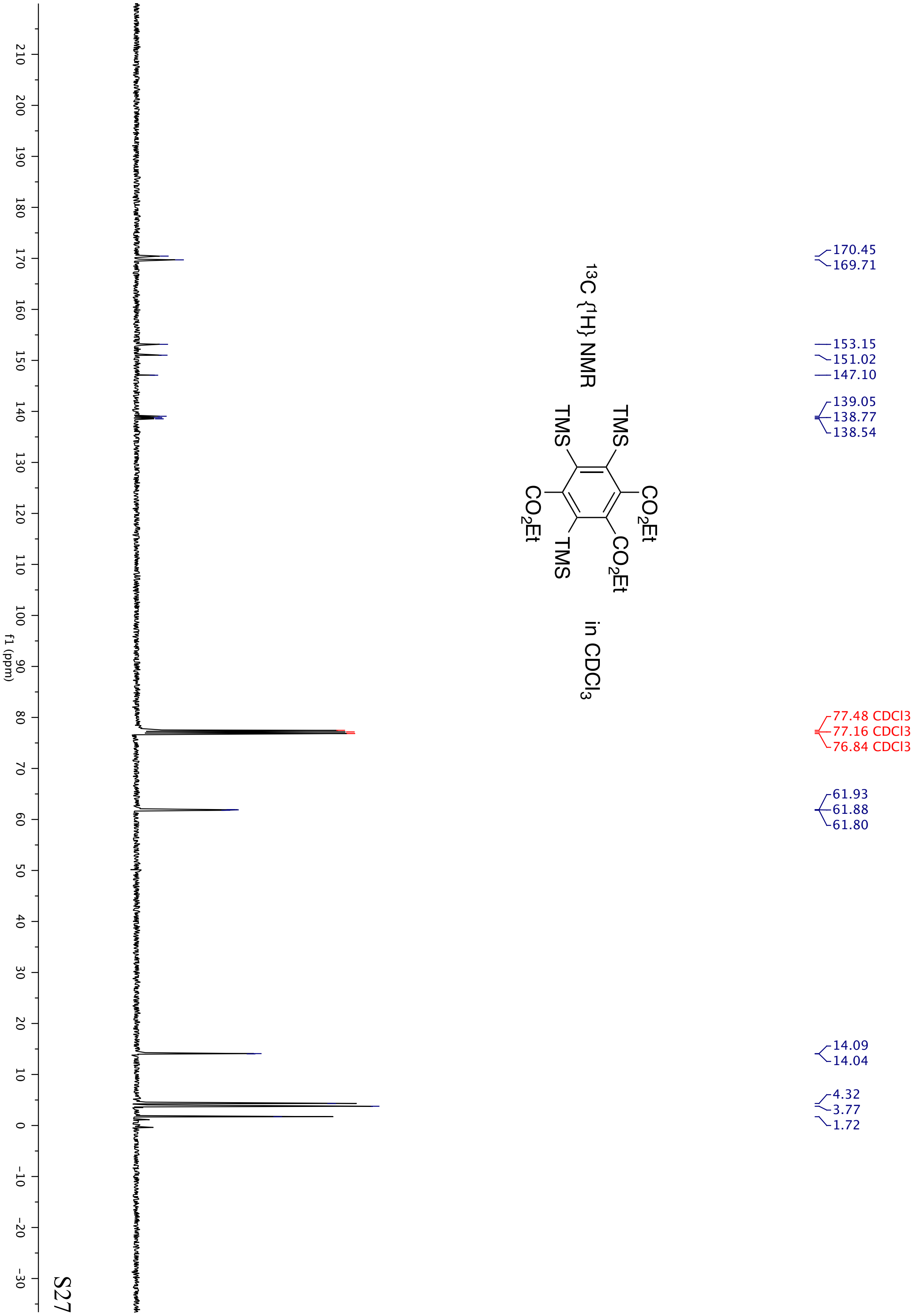

1HNMR
CO2Me
CO2Me
CO2Me
in CDCl3
7.26
3.91
3.86
3.84
2.64
2.62
2.62
2.61
2.59
2.58
2.57
2.56
2.55
2.54
2.51
2.50
2.49
2.48
2.47
1.56
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.00
0.99
0.98
0.97
0.96
0.95
0.92
0.90
0.88
−0.00
9.06
6.13
7.00
9.86
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.

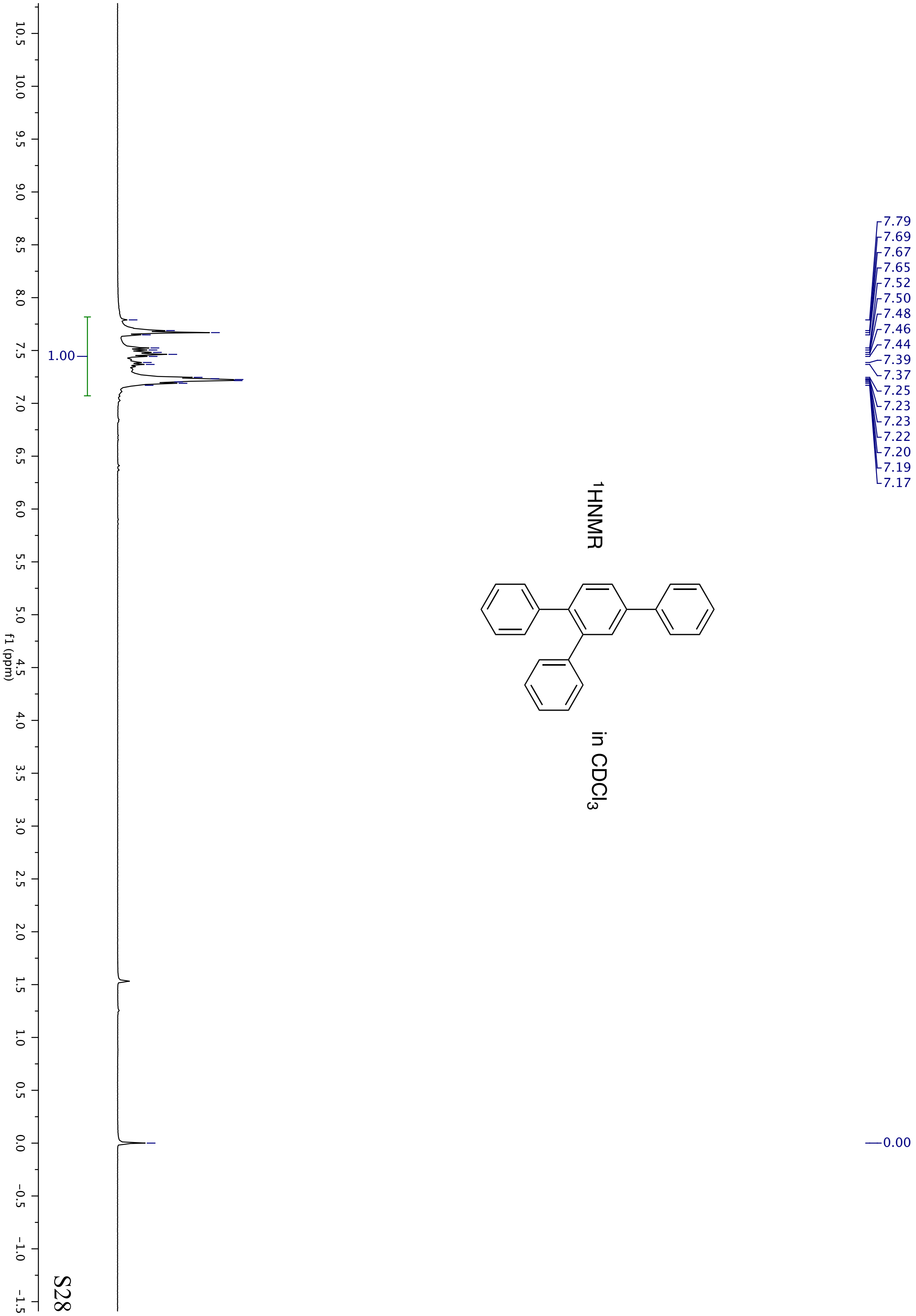

^{13}C {^{1}H} NMR
in CDCl$_3$
CO$_2$Me
CO$_2$Me
CO$_2$Me
170.12
169.23
168.50
140.56
137.60
137.43
135.90
134.10
130.04
77.48 CDCl3
77.17 CDCl3
76.84 CDCl3
52.56
52.23
33.81
33.60
32.10
24.99
24.74
14.97
14.83
14.70
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30

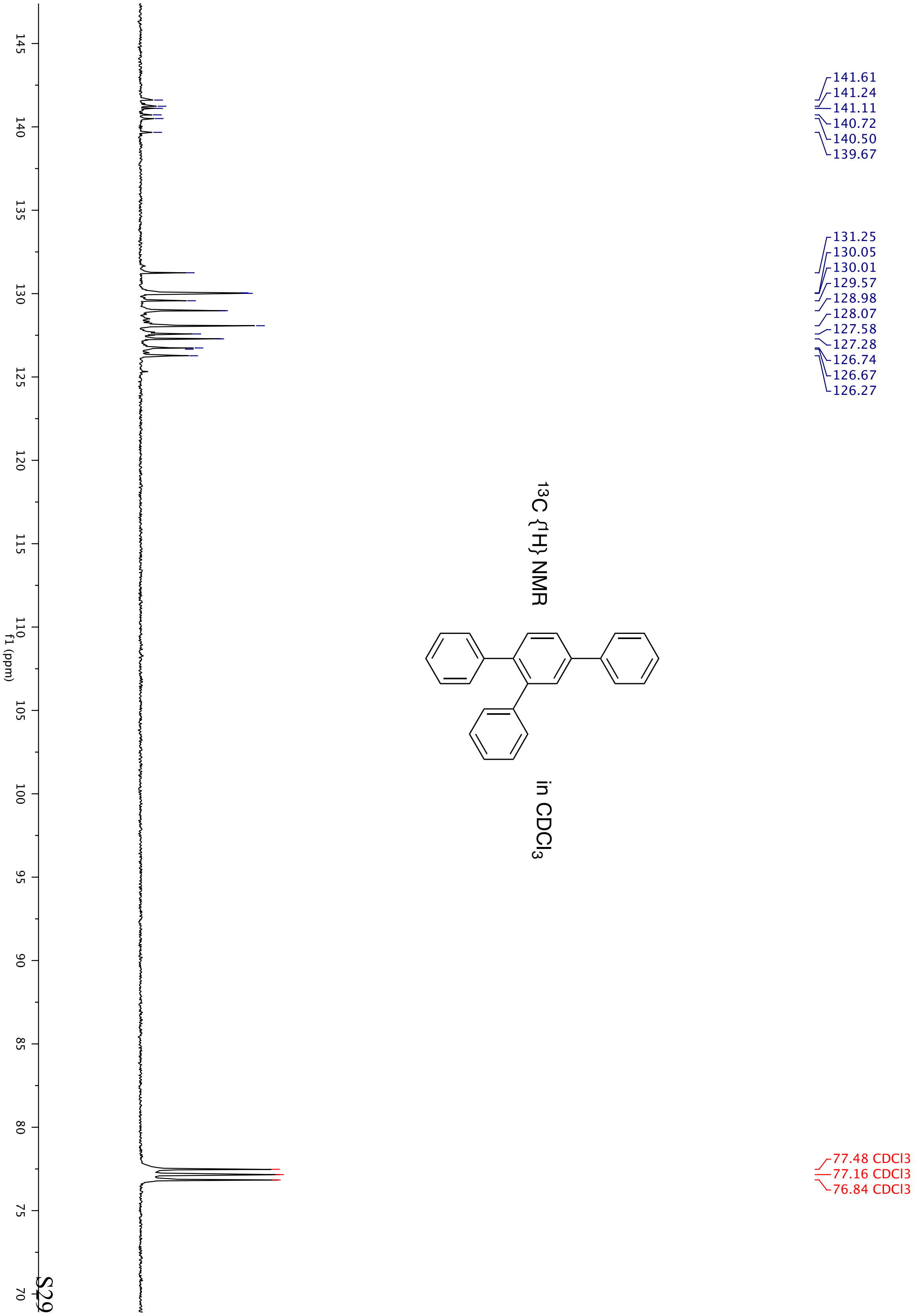

^{1}HNMR
CO_2Me
CO_2Me
CO_2Me
in $CDCl_3$
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
8.88
6.00
6.44
20.09
9.79
7.27
3.90
3.85
3.84
2.64
2.63
2.62
2.61
2.60
2.59
2.58
2.57
2.56
2.55
2.52
2.51
2.50
2.49
2.48
1.60
1.53
1.50
1.48
1.36
1.31
1.29
1.26
0.91
0.91
0.90
0.89
0.88
0.87
0.86
0.00

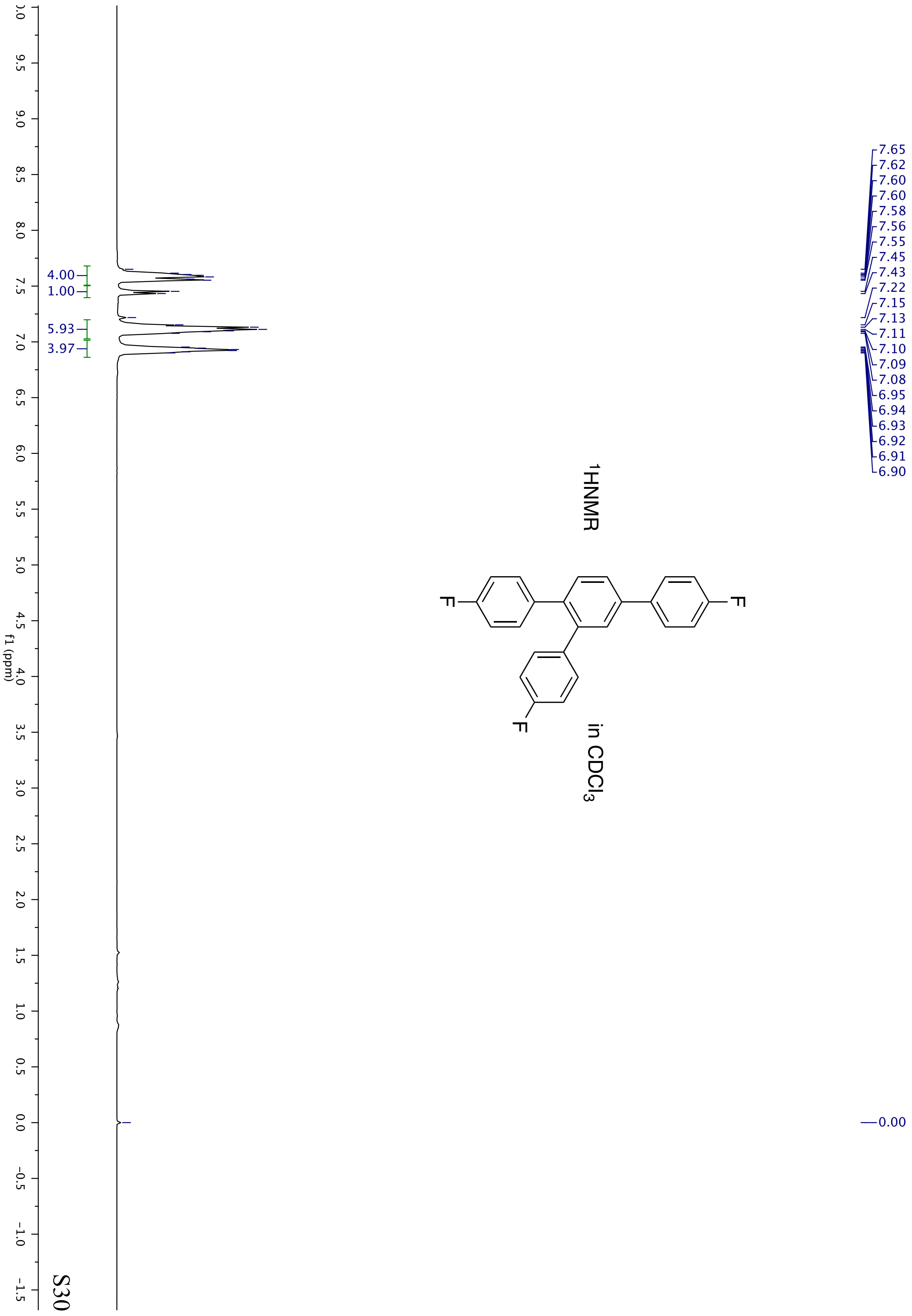

$^{13}C\ \{^1H\}$ NMR
in $CDCl_3$
CO_2Me
CO_2Me
CO_2Me
170.11
169.22
168.50
140.68
137.49
136.07
134.08
129.92
77.48
77.16
76.84
52.20
31.79
31.66
31.58
31.51
31.41
31.27
30.06
30.02
29.95
29.83
22.70
22.65
14.20
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20

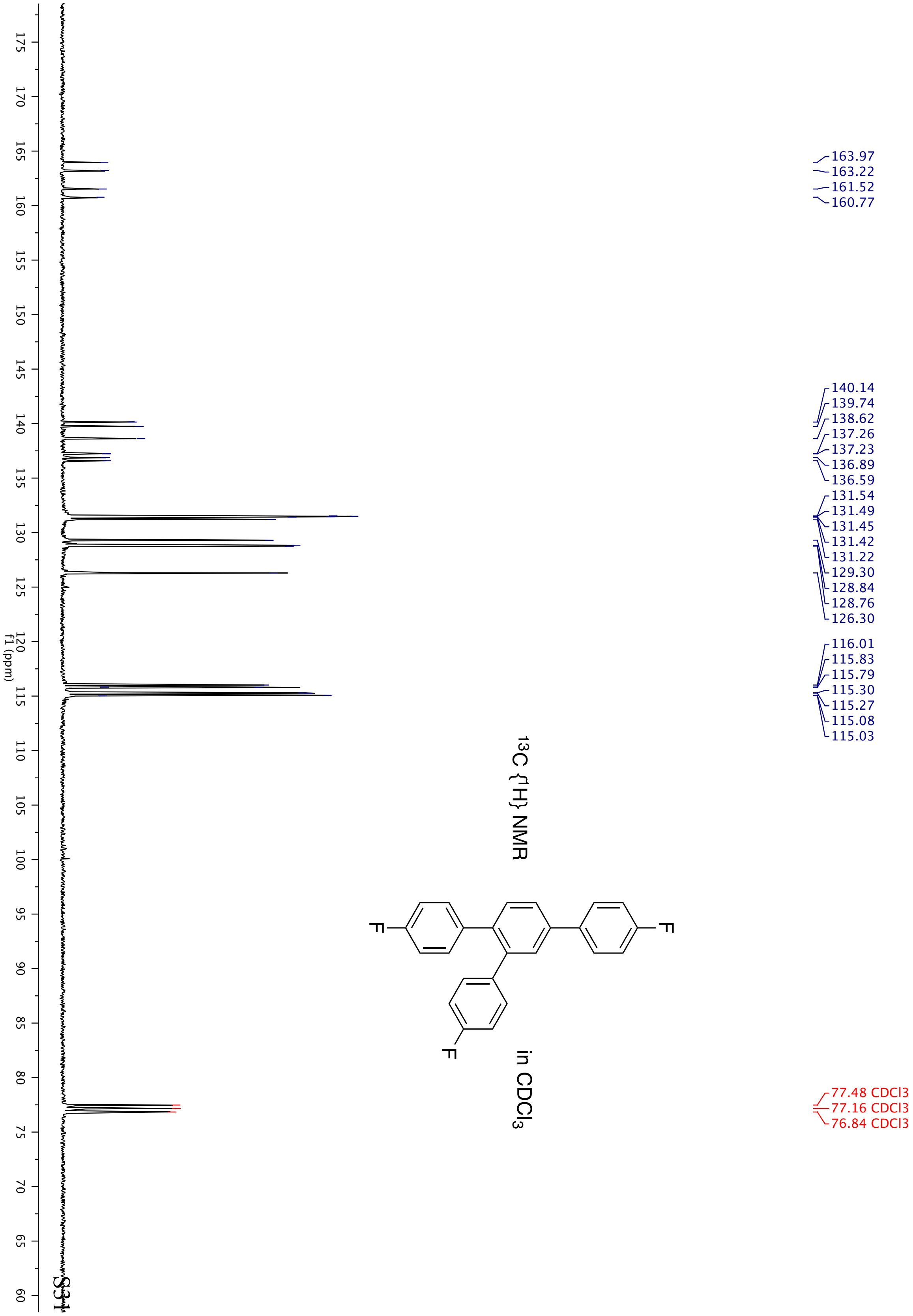

¹HNMR
TMS
TMS
TMS
CO2Et
CO2Et
CO2Et
in CDCl3
7.27
4.35
4.34
4.32
4.30
4.28
4.26
4.25
1.40
1.39
1.38
1.37
1.36
1.36
1.34
1.32
0.37
0.33
0.28
0.00
6.49
9.88
27.00
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

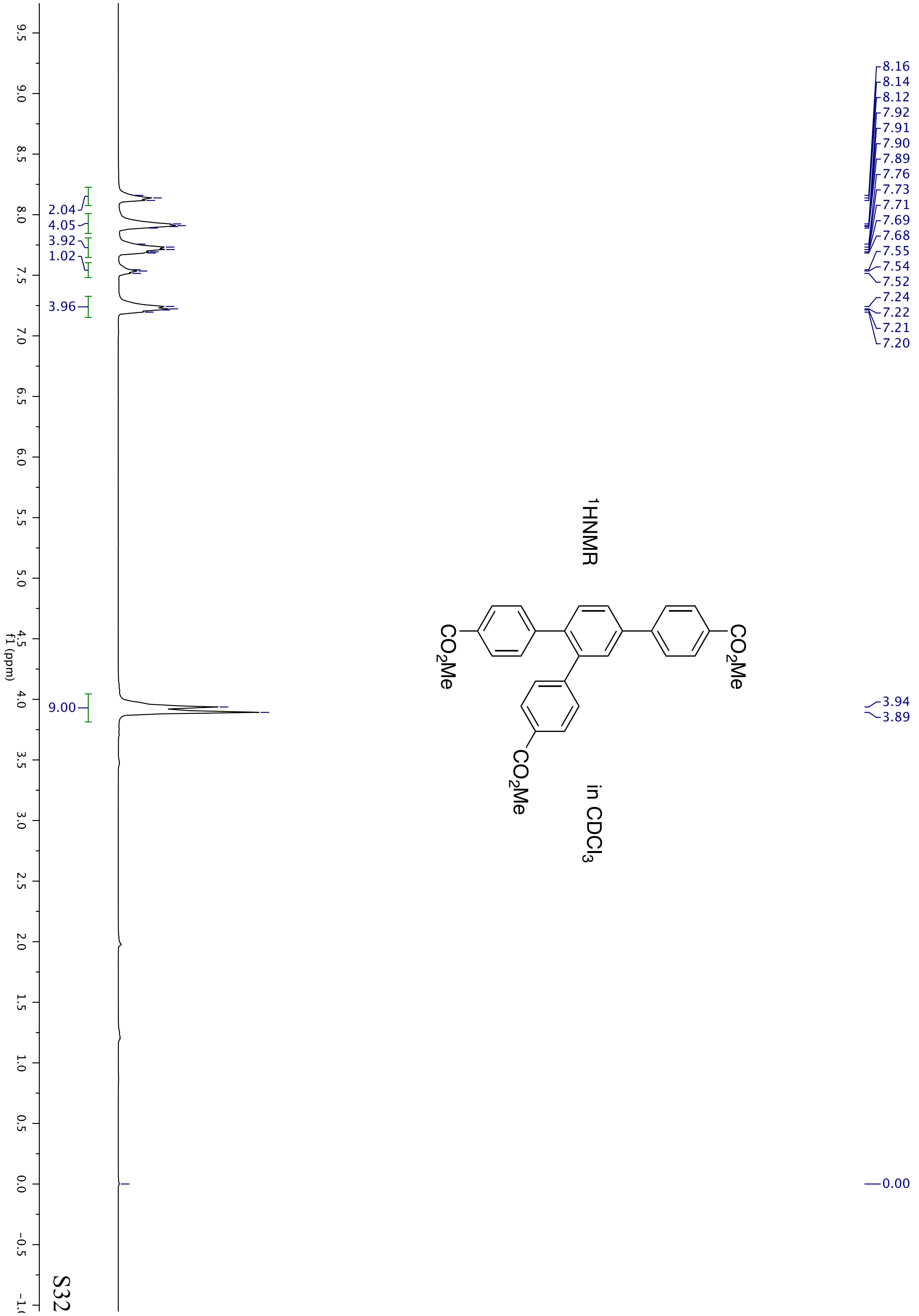

^{13}C {^{1}H} NMR
in CDCl$_3$
TMS
TMS
TMS
CO$_2$Et
CO$_2$Et
CO$_2$Et
170.45
169.71
153.15
151.02
147.10
139.05
138.77
138.54
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.93
61.88
61.80
14.09
14.04
4.32
3.77
1.72
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30

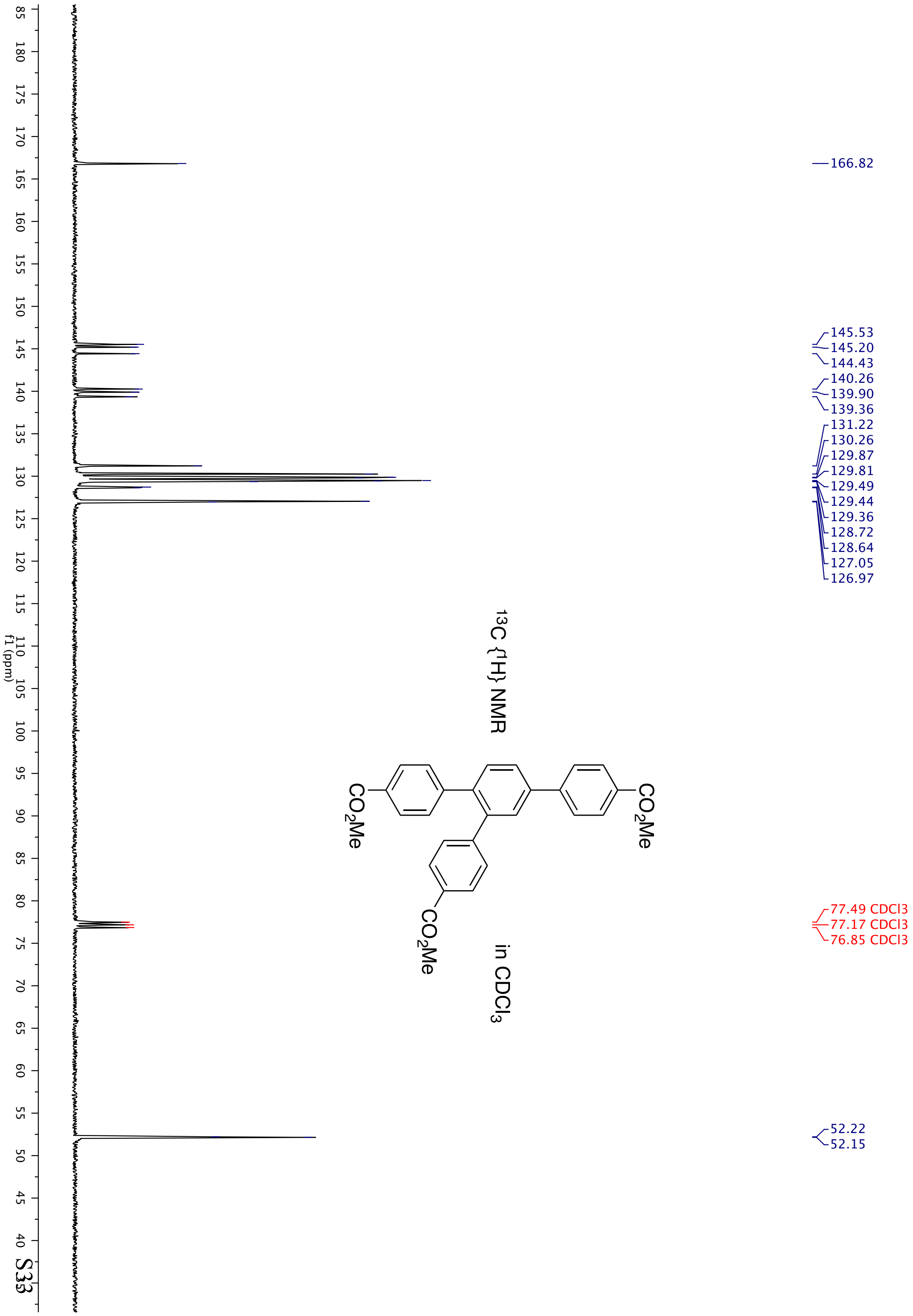

7.79
7.69
7.67
7.65
7.52
7.50
7.48
7.46
7.44
7.39
7.37
7.25
7.23
7.23
7.22
7.20
7.19
7.17
0.00
1.00
¹HNMR
in CDCl₃
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
f1 (ppm)


13C {1H} NMR
in CDCl3
141.61
141.24
141.11
140.72
140.50
139.67
131.25
130.05
130.01
129.57
128.98
128.07
127.58
127.28
126.74
126.67
126.27
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
f1 (ppm)


1HNMR
in CDCl3
F
F
F
7.65
7.62
7.60
7.60
7.58
7.56
7.55
7.45
7.43
7.22
7.15
7.13
7.11
7.10
7.09
7.08
6.95
6.94
6.93
6.92
6.91
6.90
0.00
4.00
1.00
5.93
3.97
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5


175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)
163.97
163.22
161.52
160.77
140.14
139.74
138.62
137.26
137.23
136.89
136.59
131.54
131.49
131.45
131.42
131.22
129.30
128.84
128.76
126.30
116.01
115.83
115.79
115.30
115.27
115.08
115.03
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
^{13}C {^{1}H} NMR
F
F
F
in CDCl$_3$


¹HNMR
in CDCl₃
CO₂Me
CO₂Me
CO₂Me
8.16
8.14
8.12
7.92
7.91
7.90
7.89
7.76
7.73
7.71
7.69
7.68
7.55
7.54
7.52
7.24
7.22
7.21
7.20
3.94
3.89
0.00
2.04
4.05
3.92
1.02
3.96
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)


$^{13}C\ \{^1H\}$ NMR
in $CDCl_3$
CO_2Me
CO_2Me
CO_2Me
166.82
145.53
145.20
144.43
140.26
139.90
139.36
131.22
130.26
129.87
129.81
129.49
129.44
129.36
128.72
128.64
127.05
126.97
77.49 CDCl3
77.17 CDCl3
76.85 CDCl3
52.22
52.15
f1 (ppm)
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
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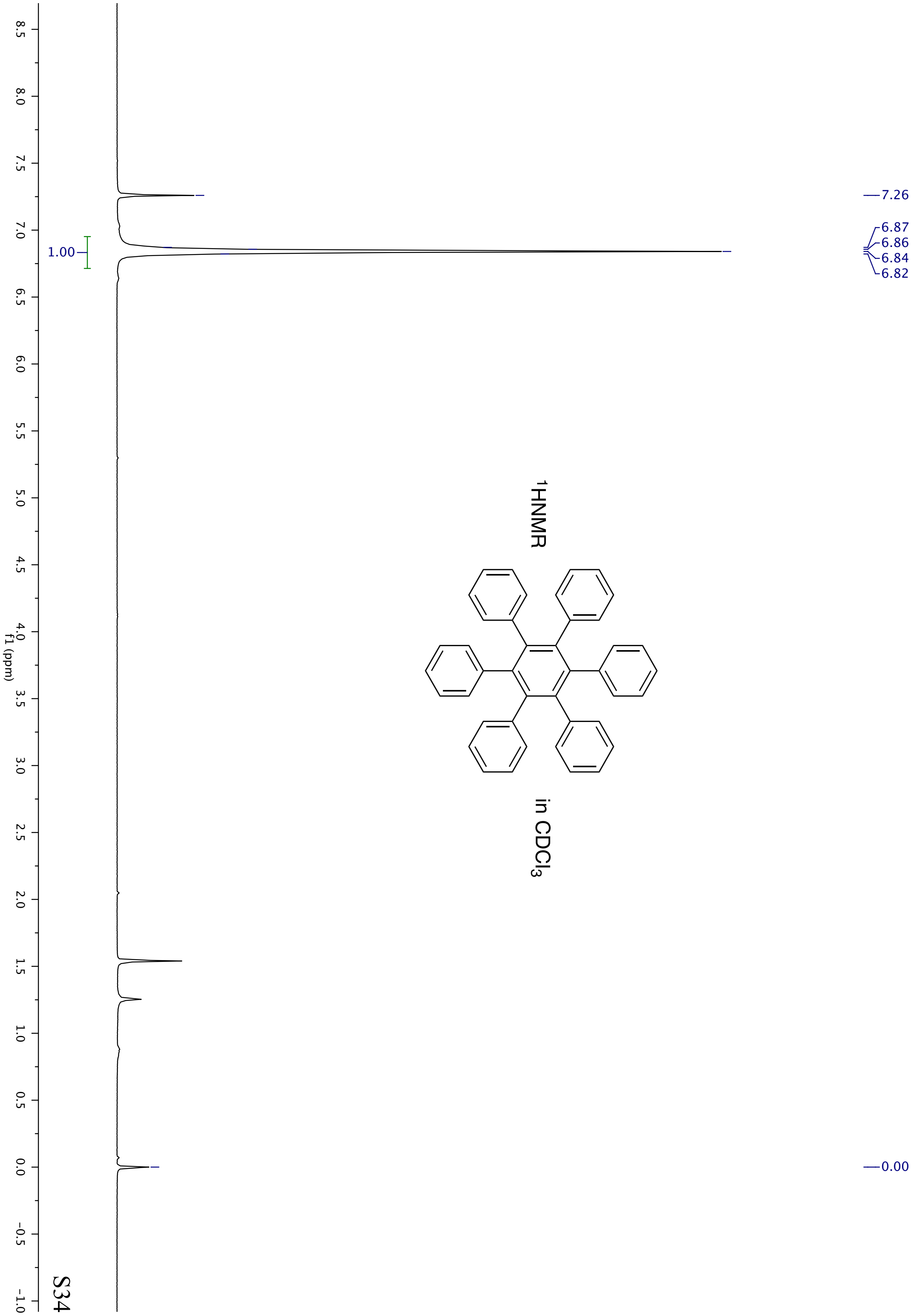
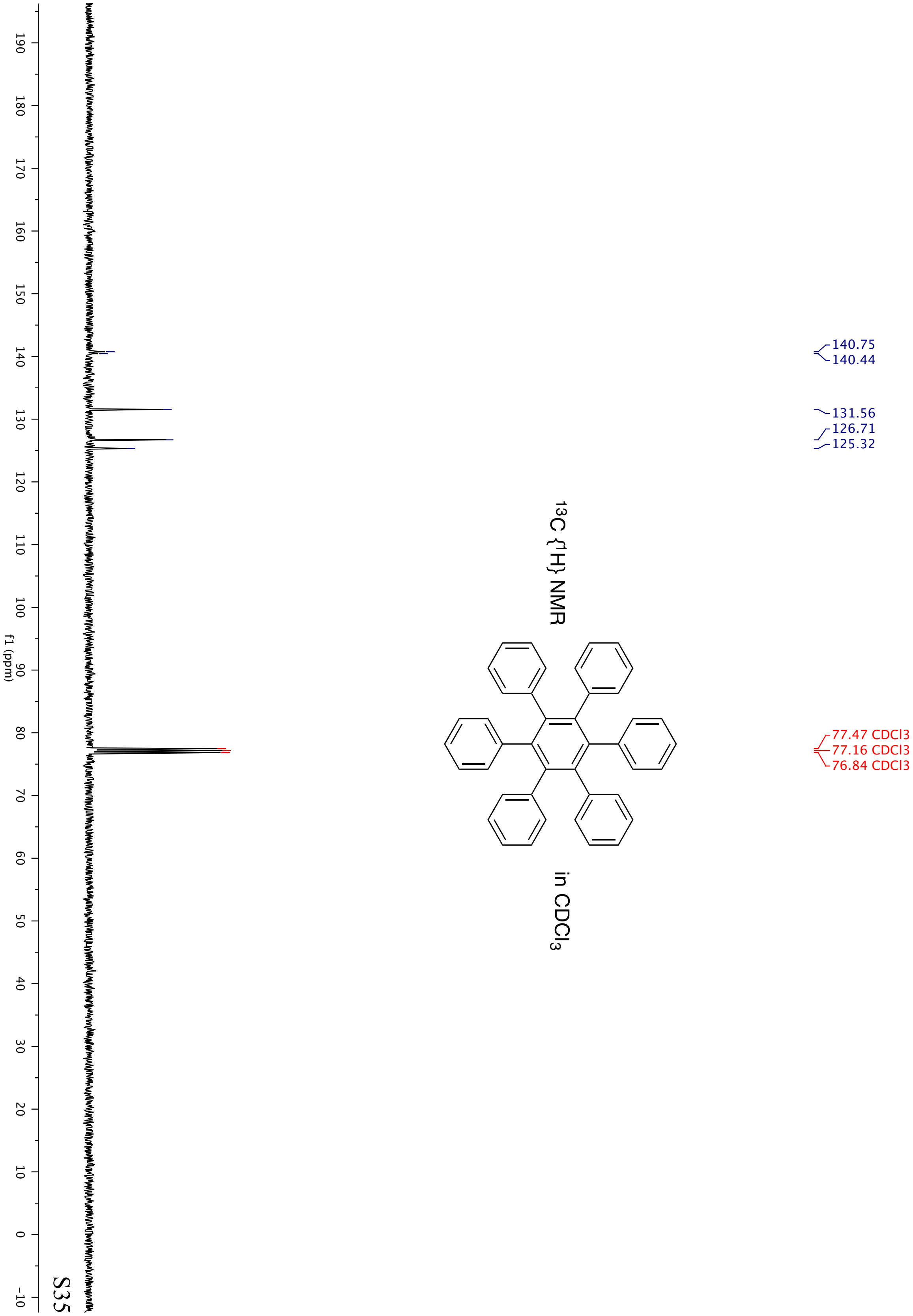
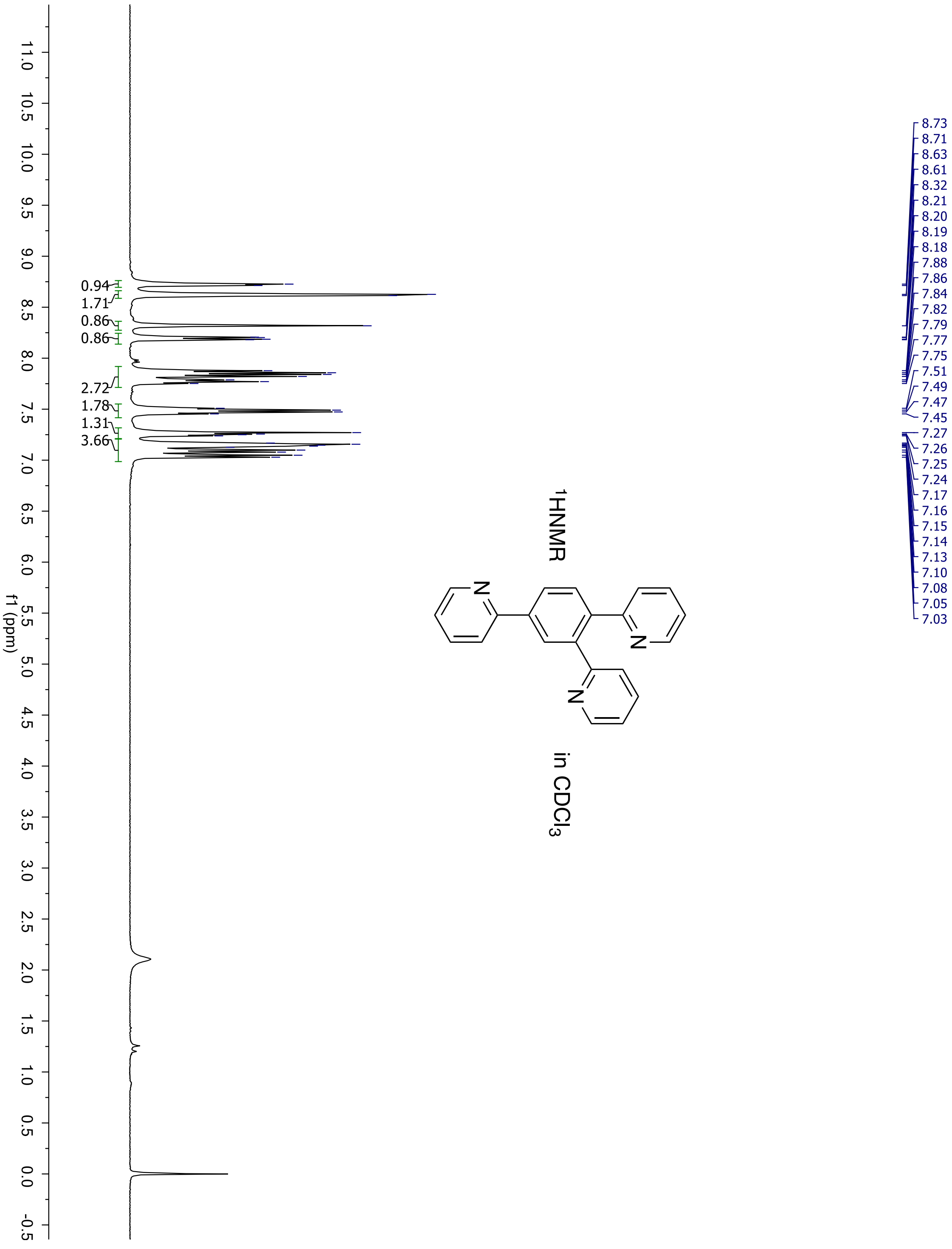
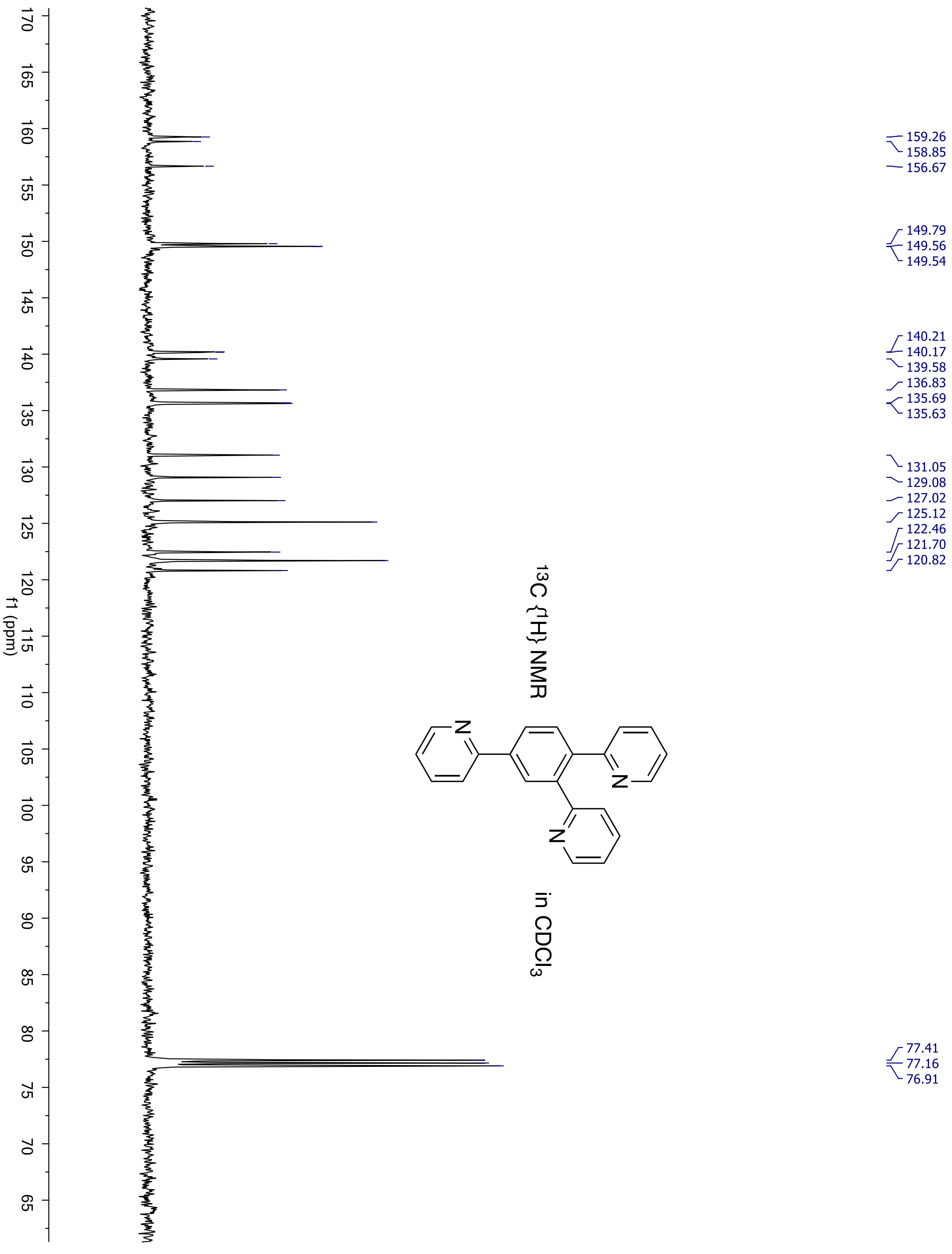
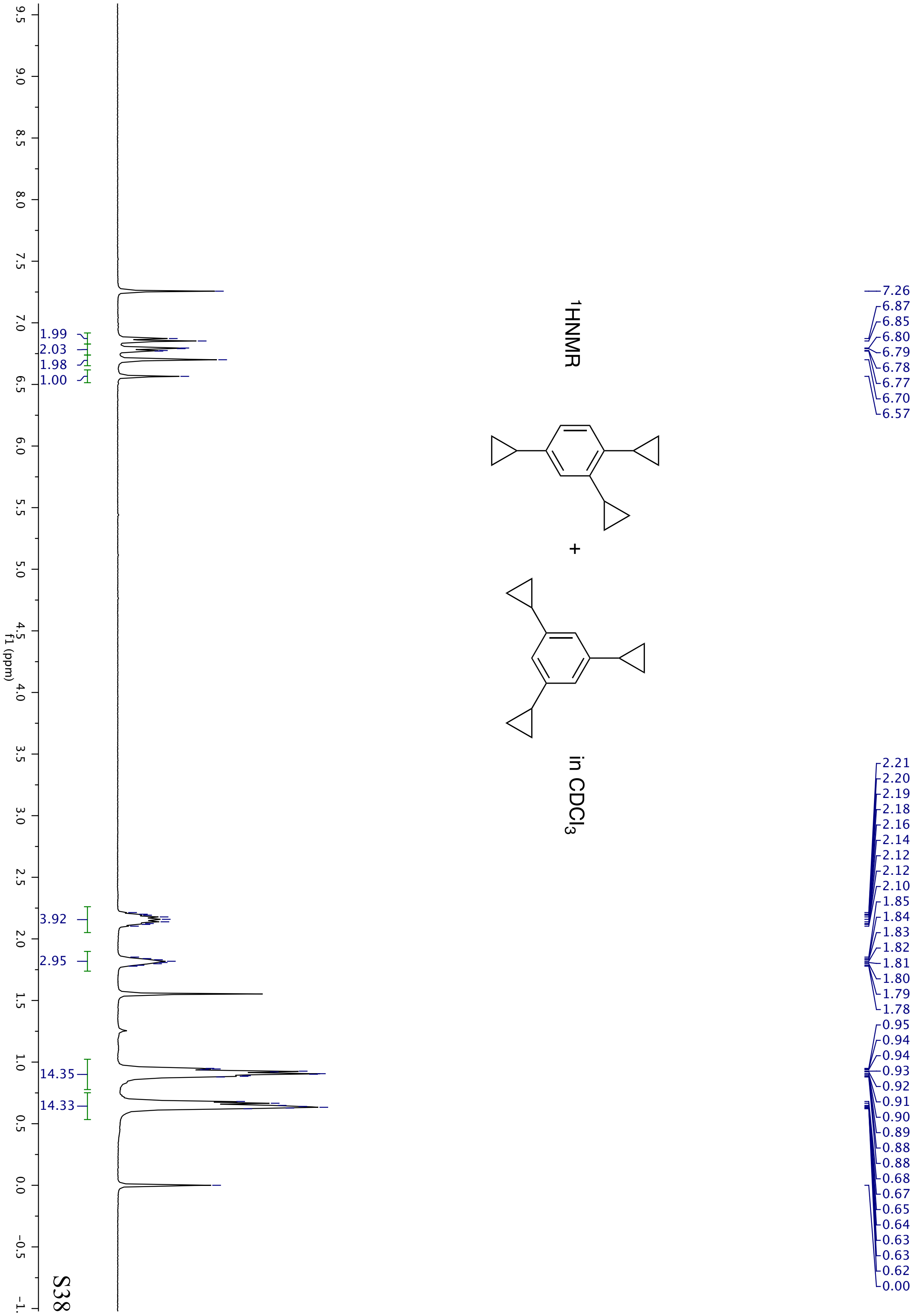
60
55
50
45
40
35

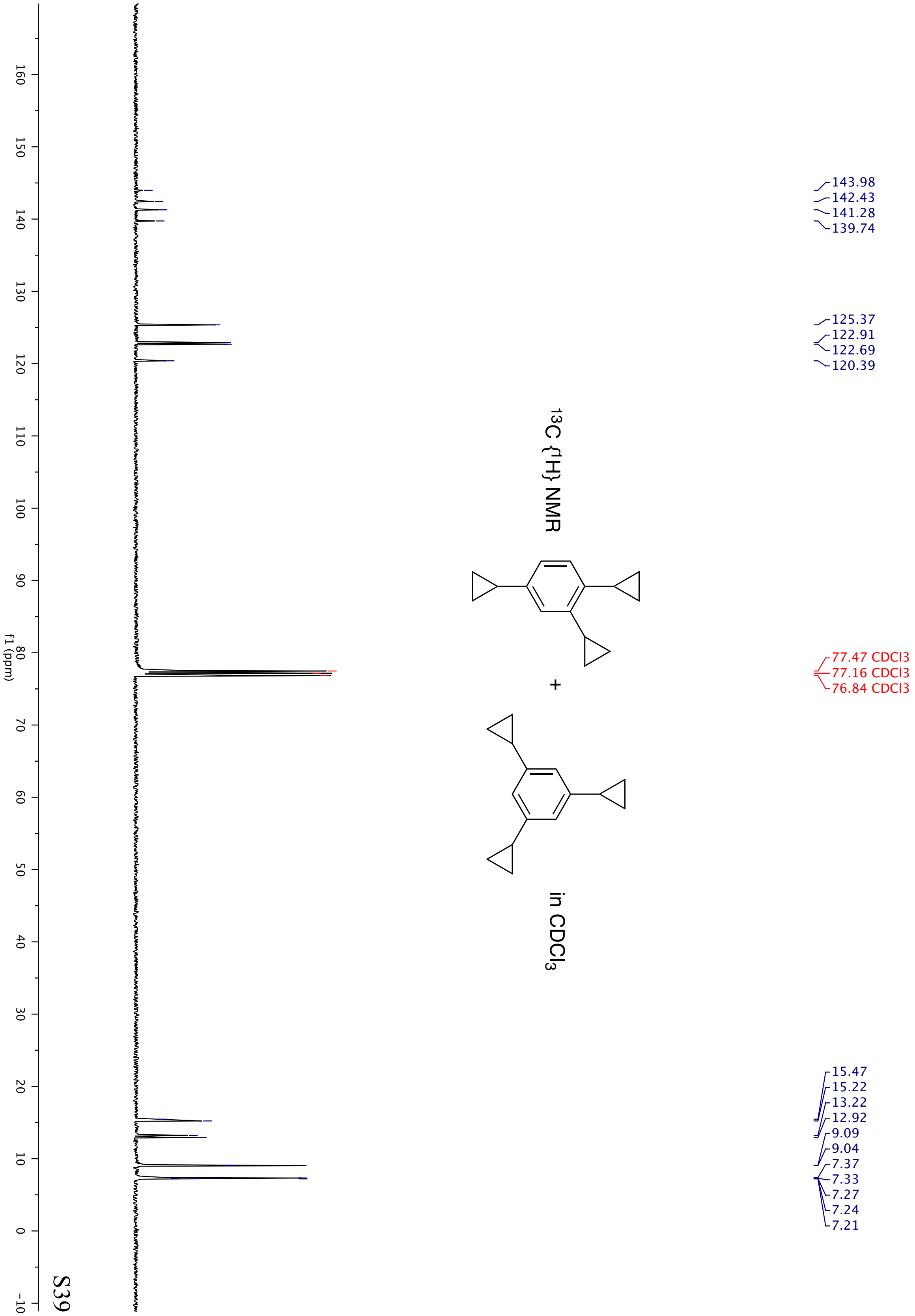

^{1}HNMR
in $CDCl_3$
7.26
6.87
6.86
6.84
6.82
0.00
1.00
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0


^{13}C {^{1}H} NMR
in CDCl$_3$
140.75
140.44
131.56
126.71
125.32
77.47 CDCl3
77.16 CDCl3
76.84 CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.73
8.71
8.63
8.61
8.32
8.21
8.20
8.19
8.18
7.88
7.86
7.84
7.82
7.79
7.77
7.75
7.51
7.49
7.47
7.45
7.27
7.26
7.25
7.24
7.17
7.16
7.15
7.14
7.13
7.10
7.08
7.05
7.03
0.94
1.71
0.86
0.86
2.72
1.78
1.31
3.66
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
^{1}HNMR
N
N
N
in $CDCl_3$


^{13}C {^{1}H} NMR
in CDCl$_3$
N
N
N
159.26
158.85
156.67
149.79
149.56
149.54
140.21
140.17
139.58
136.83
135.69
135.63
131.05
129.08
127.02
125.12
122.46
121.70
120.82
77.41
77.16
76.91
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


1HNMR
+
in CDCl3
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
1.99
2.03
1.98
1.00
3.92
2.95
14.35
14.33
7.26
6.87
6.85
6.80
6.79
6.78
6.77
6.70
6.57
2.21
2.20
2.19
2.18
2.16
2.14
2.12
2.12
2.10
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.78
0.95
0.94
0.94
0.93
0.92
0.91
0.90
0.89
0.88
0.88
0.68
0.67
0.65
0.64
0.63
0.63
0.62
0.00


^{13}C {^{1}H} NMR
+
in CDCl$_3$
143.98
142.43
141.28
139.74
125.37
122.91
122.69
120.39
77.47 CDCl3
77.16 CDCl3
76.84 CDCl3
15.47
15.22
13.22
12.92
9.09
9.04
7.37
7.33
7.27
7.24
7.21
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

References

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