Electronic Supplementary Information

Multicomponent Benzannulation of Allylic P-ylides with Isocyanates or Aldehydes for Construction of Anilines and Biaryls

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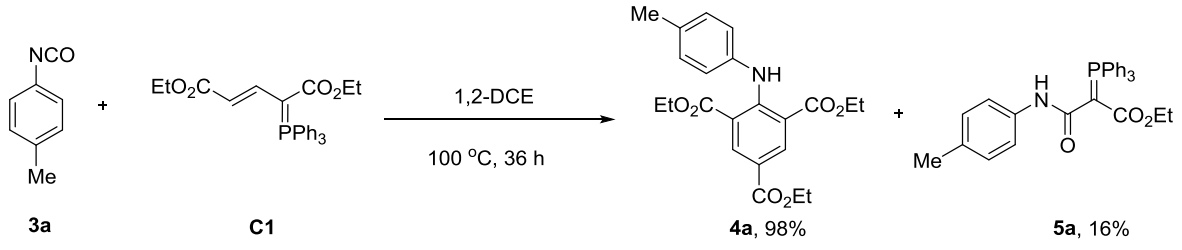
1. General Information

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere under anhydrous conditions using screw cap sealed tube. For all heating reactions, the heating source is the IKA heating Magnetic Stirrers with oil bath containing a temperature sensor. Solvents were purified prior to use according to standard procedures. All other reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz for ^{1}H, and 100 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm) with respect to tetramethylsilane (TMS, δ = 0). Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad signal. High-resolution ESI mass spectra were acquired with a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. IR data were obtained on a Nicolet iS10 FT-IR spectrometer. Melting points were measured on an SGW® X-4B apparatus and uncorrected. All reactions were monitored by thin layer chromatography (TLC) and visualized by UV irradiation or stained with potassium permanganate. X-ray crystallographic analysis was performed at Bruker D8 Quest. Column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether (b.p. 60–90 ºC)/ethyl acetate as eluent.

2. Initial Investigation

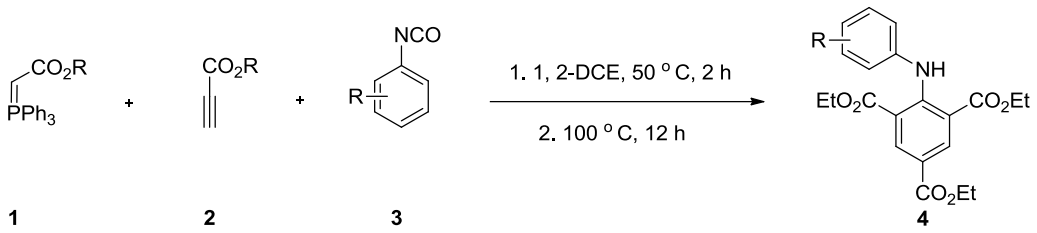


3a **C1** **4a**, 98% **5a**, 16%

Under N_2 atmosphere, to a solution of P-ylide **C1**[1] (223 mg, 0.50 mmol) in 1,2-dichloroethane (2.0 mL) was added isocyanate **3a** (66 mg, 0.50 mmol). The reaction mixture was stirred at 100 °C for 36 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure

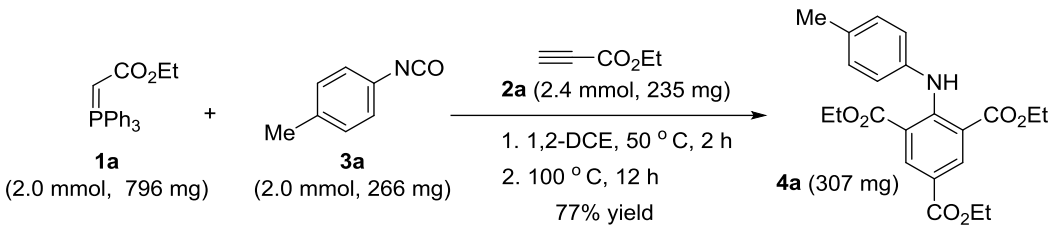
and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield compounds **4a** (98 mg, 98%) and **5a**[2] (20 mg, 16%).

3. Procedure for The Synthesis of Anilines **4**



Under N_2 atmosphere, to a solution of P-ylide **1** (0.50 mmol) in 1,2-dichloroethane (2.0 mL) was added alkyl propiolate **2** (0.60 mmol). The mixture was stirred at 50 ^{o}C for 2 h. The reaction mixture was cooled to room temperature, then isocyanate **3** (0.50 mmol) was added to the reaction mixture. The mixture was stirred at 100 °C for 12 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield **4**.

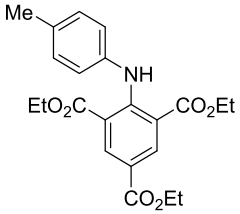
A scaled-up synthesis of compound 4a:



Under N_2 atmosphere and at rt, in a Schlenk tube (50 mL) was added P-ylide **1a** (2.0 mmol, 796 mg) and the solvent 1,2-DCE (10.0 mL), which was followed by the addition of ethyl propiolate (2.4 mmol, 235 mg, 243 μL) by syringe in one portion. The mixture was stirred at 50 ºC for 2 hours, at that time P-ylide **1a** was completed consumed as monitored by TLC. The reaction was cooled down to room temperature, and *p*-tolyl isocyanate (2.0 mmol, 266 mg) was added in one portion. The mixture was then stirred at 100 ºC for 12 hours. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (gradient elution: petroleum

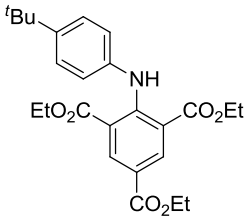
ether/ethyl acetate = 5/1 to 1/1) to afford the product **4a** as a pale yellow solid in 307 mg, 77% yield.

4. Analytical Data for Anilines **4**



4a

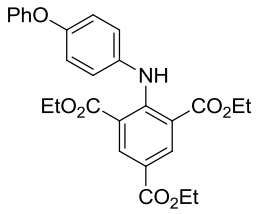
4a: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4a** as pale yellow solid, in 85 mg, 85% yield, m. p: 62–64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (br s, 1H), 8.55 (s, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 4H), 2.28 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.2, 149.1, 139.5, 137.0, 133.7, 129.8, 120.1, 118.8, 117.8, 61.3, 60.9, 20.7, 14.3, 13.9. IR v_{max} (neat): 3331, 2980, 2927, 1714, 1686, 1599, 1515, 1445, 1406, 1368, 1312, 1222, 1182, 1139, 1096, 1065, 1023, 862, 814, 768, 744, 719, 687, 637, 508 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_6$ 400.1755; Found 400.1754.



4b

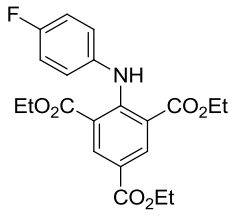
4b: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-(tert-butyl)-4-isocyanatobenzene **3b** (88 mg, 0.50 mmol) provided **4b** as pale yellow solid, in 89 mg, 80% yield, m. p: 94–96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br s, 1H), 8.56 (s, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.38

(q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 149.1, 147.1, 139.5, 137.0, 126.1, 119.9, 118.9, 117.9, 61.3, 60.9, 34.3, 31.3, 14.4, 14.0. IR ν_{max} (neat): 3237, 2958, 2923, 2867, 1713, 1682, 1598, 1518, 1465, 1366, 1268, 1235, 1220, 1174, 1142, 1067, 1025, 934, 882, 867, 836, 796, 763, 717, 686, 658, 553 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}NO_6$ 442.2225; Found 442.2220.



4c

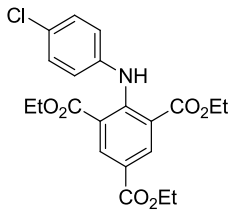
4c: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-phenoxybenzene **3c** (106 mg, 0.50 mmol) provided **4c** as pale yellow solid, in 117 mg, 98% yield, m. p: 64–66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (br s, 1H), 8.57 (s, 2H), 7.34–7.30 (m, 2H), 7.10–7.04 (m, 3H), 6.98–6.94 (m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.2, 157.5, 153.4, 149.2, 137.8, 137.0, 129.7, 123.0, 121.7, 120.1, 119.1, 118.2, 117.8, 61.4, 60.9, 14.3, 14.0. IR ν_{max} (neat): 3320, 2927, 2929, 1710, 1684, 1589, 1504, 1486, 1409, 1368, 1308, 1216, 1181, 1095, 1065, 1024, 935, 869, 849, 796, 763, 749, 690, 646, 555, 510 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_7$ 478.1861; Found 478.1855.



4d

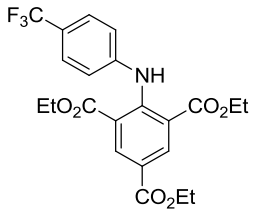
4d: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-fluoro-4-isocyanatobenzene **3d** (68 mg, 0.50 mmol) provided **4d**

as pale yellow solid, in 90 mg, 89% yield, m. p: 56–58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (br s, 1H), 8.57 (s, 2H), 7.06–6.96 (m, 4H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.1, 159.3 (d, J_{F-C} = 242.0 Hz), 149.1, 138.3 (d, J_{F-C} = 3.1 Hz), 137.0, 121.9 (d, J_{F-C} = 8.2 Hz), 119.3, 117.8, 116.0 (d, J_{F-C} = 23.1 Hz), 61.4, 61.0, 14.3, 14.0. IR ν_{max} (neat): 3244, 2981, 2935, 1711, 1672, 1589, 1506, 1488, 1444, 1409, 1367, 1309, 1218, 1182, 1141, 1095, 1066, 1025, 950, 854, 821, 798, 757, 723, 686, 629, 556, 513, 485, 453 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}FNO_6$ 404.1504; Found 404.1502.



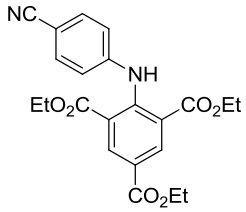
4e

4e: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-chloro-4-isocyanatobenzene **3e** (77 mg, 0.50 mmol) provided **4e** as pale yellow solid, in 94 mg, 89% yield, m. p: 84–86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br s, 1H), 8.59 (s, 2H), 7.26–7.23 (m, 2H), 7.00–6.98 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 165.1, 148.4, 140.9, 137.0, 129.3, 128.9, 128.8, 121.0, 119.9, 118.3, 61.5, 61.0, 14.3, 14.0. IR ν_{max} (neat): 3224, 2975, 2922, 2851, 1898, 1708, 1684, 1588, 1513, 1491, 1443, 1397, 1367, 1305, 1222, 1181, 1142, 1089, 1023, 934, 881, 852, 829, 809, 797, 762, 724, 679, 628, 591, 523, 504, 474, 436, 414 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}ClNO_6$ 420.1209; Found 420.1205.



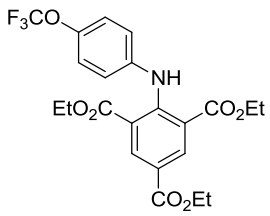
4f

4f: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-(trifluoromethyl)benzene **3f** (93 mg, 0.50 mmol) provided **4f** as pale yellow solid, in 76 mg, 67% yield, m. p: 62–64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (brs, 1H), 8.64 (s, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.9, 147.5, 145.6, 137.0, 125.9 (q, J_{F-C} = 62.1 Hz), 126.6 (q, J_{F-C} = 11.0 Hz), 124.6 (q, J_{F-C} = 270.3 Hz), 120.9, 119.1, 118.7, 117.9, 61.6, 61.2, 14.3, 13.9. IR v_{max} (neat): 3255, 2989, 2908, 1741, 1708, 1682, 1598, 1523, 1480, 1448, 1422, 1393, 1368, 1305, 1233, 1182, 1157, 1105, 1066, 1024, 945, 934, 849, 814, 798, 767, 756, 730, 715, 694, 665, 589, 548, 508, 447, 418 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}F_3NO_6$ 454.1472; Found 454.1464.



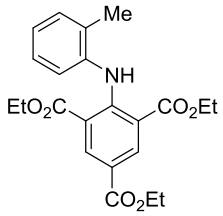
4g

4g: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 4-isocyanatobenzonitrile **3g** (72 mg, 0.50 mmol) provided **4g** as pale yellow solid, in 50 mg, 49% yield, m. p: 97–99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (br s, 1H), 8.66 (s, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.8, 146.6, 146.5, 137.0, 133.5, 121.9, 119.8, 118.9, 118.3, 105.6, 61.8, 61.3, 14.3, 14.0. IR v_{max} (neat): 3234, 2983, 2920, 2850, 2221, 1710, 1679, 1593, 1512, 1470, 1444, 1421, 1390, 1367, 1302, 1230, 1176, 1139, 1105, 1024, 935, 856, 814, 797, 761, 744, 715, 688, 597, 561, 545, 507, 460 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2O_6$ 411.1551; Found 411.1544.



4h

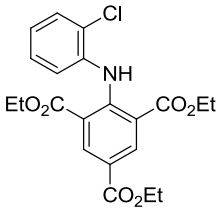
4h: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-(trifluoromethoxy)benzene **3h** (101 mg, 0.50 mmol) provided **4h** as pale yellow solid, in 94 mg, 80% yield, m. p: 36–38 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (br s, 1H), 8.52 (s, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.0, 148.5, 144.9 (q, J_{F-C} = 5.0 Hz), 141.2, 137.0, 122.5 (q, J_{F-C} = 255.0 Hz), 120.9, 120.0, 119.1, 118.3, 61.5, 61.1, 14.3, 13.9. IR v_{max} (neat): 3242, 2987, 1702, 1604, 1534, 1510, 1448, 1394, 1366, 1312, 1221, 1200, 1153, 1112, 1066, 1025, 939, 920, 856, 796, 760, 719, 695, 643, 584, 490, 431 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}F_3NO_7$ 470.1422; Found 470.1417.



4i

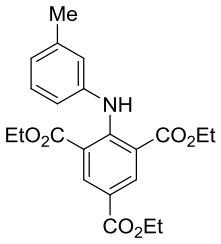
4i: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-2-methylbenzene **3i** (66 mg, 0.50 mmol) provided **4i** as pale yellow solid, in 88 mg, 88% yield, m. p: 98–100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (br s, 1H), 8.57 (s, 2H), 7.24-7.22 (m, 1H), 7.09-7.06 (m, 1H), 7.02-6.96 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 4H), 2.39 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 149.5, 140.7, 136.9, 130.9, 130.7, 126.5, 124.4, 118.8, 118.6, 117.7, 61.2, 60.9, 18.1, 14.3, 13.9. IR v_{max} (neat): 3241, 2979, 2917, 2849, 1707, 1682, 1611, 1592, 1513, 1460, 1411, 1389, 1366,

1310, 1225, 1178, 1104, 1029, 938, 887, 866, 797, 755, 715, 690, 657, 541, 513, 498, 451 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_6$ 400.1755; Found 400.1749.



4j

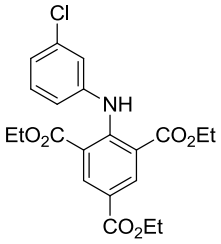
4j: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-chloro-2-isocyanatobenzene **3j** (77 mg, 0.50 mmol) provided **4j** as pale yellow solid, in 84 mg, 80% yield, m. p: 115–117 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.27 (br s, 1H), 8.61 (s, 2H), 7.42 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.13–7.09 (m, 1H), 7.03 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.97 (td, *J* = 7.8, 1.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.0, 147.7, 139.5, 137.0, 130.1, 127.2, 126.0, 124.2, 120.4, 118.9, 118.1, 61.5, 61.1, 14.3, 13.9. IR v_{max} (neat): 3368, 3235, 2980, 2922, 2851, 1706, 1683, 1589, 1512, 1470, 1444, 1410, 1390, 1368, 1310, 1278, 1224, 1180, 1114, 1049, 1022, 949, 886, 863, 793, 782, 751, 731, 715, 689, 638, 536, 500, 469, 452, 421 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}ClNO_6$ 420.1209; Found 420.1205.



4k

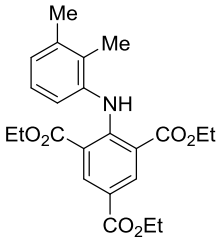
4k: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-3-methylbenzene **3k** (66 mg, 0.50 mmol) provided **4k** as pale yellow solid, in 91 mg, 91% yield, m. p: 87–89 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.28 (br s, 1H), 8.57 (s, 2H), 7.15 (dd, *J* = 10.8, 5.1 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 3H),

4.37 (q, *J* = 7.1 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 4H), 2.28 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.2, 148.7, 141.9, 139.2, 136.9, 129.1, 124.7, 120.3, 119.1, 118.1, 116.9, 61.32, 60.9, 21.3, 14.3, 13.9. IR ν_{max} (neat): 3243, 2961, 2920, 2851, 1707, 1681, 1633, 1600, 1581, 1541, 1487, 1443, 1406, 1367, 1315, 1225, 1180, 1164, 1114, 1025, 948, 934, 908, 885, 869, 829, 788, 774, 759, 718, 702, 679, 660, 631, 578, 549, 511, 455, 442 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_6$ 400.1755; Found 400.1749.



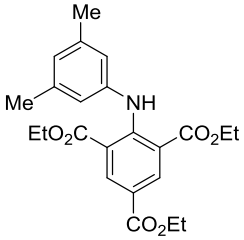
4l

4l: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-chloro-3-isocyanatobenzene **3l** (77 mg, 0.50 mmol) provided **4l** as pale yellow solid, in 85 mg, 81% yield, m. p: 94–96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br s, 1H), 8.59 (s, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.02–6.99 (m, 2H), 6.92 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.0, 147.9, 143.5, 136.9, 134.9, 130.4, 123.7, 120.2, 119.5, 118.7, 117.7, 61.5, 61.1, 14.3, 13.9. IR ν_{max} (neat): 3233, 3064, 2983, 2903, 1727, 1706, 1681, 1586, 1510, 1472, 1437, 1397, 1316, 1274, 1222, 1181, 1162, 1112, 1023, 945, 913, 882, 864, 796, 763, 722, 677, 655, 628, 580, 554, 518, 456, 444 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}ClNO_6$ 420.1209; Found 420.1205.



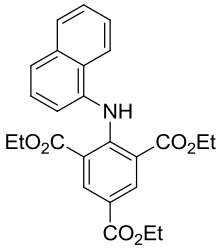
4m

4m: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-2,3-dimethylbenzene **3m** (73 mg, 0.50 mmol) provided **4m** as pale yellow solid, in 79 mg, 82% yield, m. p: 94–96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (br s, 1H), 8.66 (s, 2H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 5.4 Hz, 4H), 2.32 (s, 3H), 2.29 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.3, 149.9, 140.6, 137.9, 136.9, 129.6, 126.2, 125.8, 118.5, 117.6, 117.2, 61.2, 60.9, 20.5, 14.4, 13.9. IR v_{max} (neat): 3252, 2924, 2853, 1711, 1674, 1604, 1584, 1504, 1469, 1444, 1392, 1368, 1306, 1226, 1177, 1151, 1117, 1065, 1027, 948, 935, 868, 839, 799, 774, 761, 743, 715, 681, 633, 573, 508, 493 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_6$ 414.1912; Found 414.1904.



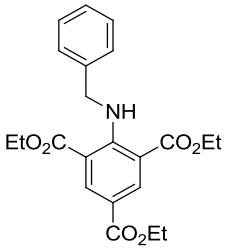
4n

4n: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-3,5-dimethylbenzene **3n** (73 mg, 0.50 mmol) provided **4n** as pale yellow solid, in 88 mg, 91% yield, m. p: 70–72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (br s, 1H), 8.56 (s, 2H), 6.67 (s, 3H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 4H), 2.24 (s, 6H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.2, 148.7, 141.8, 139.0, 136.9, 125.6, 119.0, 118.1, 117.4, 61.3, 60.9, 21.2, 14.3, 13.9. IR v_{max} (neat): 3252, 2983, 2917, 1708, 1682, 1592, 1512, 1467, 1445, 1408, 1366, 1321, 1290, 1247, 1227, 1181, 1116, 1094, 1024, 947, 935, 898, 869, 828, 798, 729, 712, 679, 619, 586, 550, 477 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_6$ 414.1912; Found 414.1909.



4o

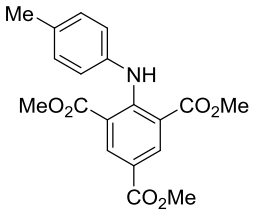
4o: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanatonaphthalene **3o** (84 mg, 0.50 mmol) provided **4o** as pale yellow solid, in 90 mg, 88% yield, m. p: 87–89 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (br s, 1H), 8.60 (s, 2H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.87–7.84 (m, 1H), 7.61–7.52 (m, 3H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.2, 149.9, 138.5, 137.0, 134.4, 128.2, 128.2, 126.6, 126.4, 125.5, 124.7, 122.2, 119.3, 118.2, 115.2, 61.3, 60.9, 14.4, 13.6. IR v_{max} (neat): 3281, 3229, 3057, 2977, 2920, 2850, 1708, 1678, 1629, 1592, 1518, 1469, 1387, 1309, 1269, 1234, 1185, 1108, 1023, 948, 932, 891, 796, 752, 690, 646, 590, 544, 491, 420 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_6$ 436.1755; Found 436.1753.



4p

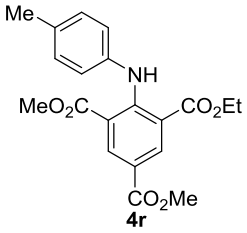
4p: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and (isocyanatomethyl)benzene **3p** (66 mg, 0.50 mmol) provided **4p** as pale yellow solid, in 45 mg, 45% yield, m. p: 34–36 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (t, *J* = 4.6 Hz, 1H), 8.55 (s, 2H), 7.36–7.26 (m, 5H), 4.39-4.31 (m, 6H), 4.29 (d, *J* = 4.6 Hz, 2H), 1.41-1.35 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.5, 152.8, 137.8, 137.2, 128.8, 127.7, 116.4, 115.3, 61.3, 60.7, 51.4, 14.4, 14.2. IR v_{max} (neat): 3242,

3062, 2980, 2932, 1705, 1683, 1599, 1511, 1464, 1393, 1367, 1317, 1221, 1170, 1150, 1096, 1082, 1028, 935, 866, 799, 762, 735, 700, 683, 594, 512, 491 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_6$ 400.1755; Found 400.1750.



4q

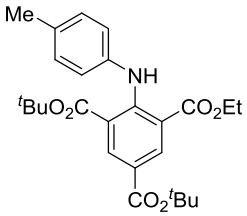
4q: Following the general procedure, the reaction of methyl 2-(triphenylphosphoranylidene)acetate **1b** (167 mg, 0.50 mmol), methyl propiolate **2b** (50 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4q** as pale yellow solid, in 63 mg, 70% yield, m. p: 139–141 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.23 (br s, 1H), 8.56 (s, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.59 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.6, 149.3, 139.3, 137.2, 133.9, 129.9, 120.4, 118.4, 117.3, 52.0, 20.8. IR v_{max} (neat): 3258, 2952, 2919, 2849, 1710, 1691, 1640, 1600, 1514, 1433, 1317, 1238, 1195, 1169, 1143, 1107, 1002, 936, 903, 888, 809, 780, 767, 757, 721, 686, 632, 529, 502, 475, 448 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_6$ 358.1286; Found 358.1284.



4r

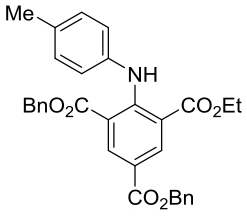
4r: Following the general procedure, the reaction of methyl 2-(triphenylphosphoranylidene)acetate **1b** (167 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4r** as pale yellow solid, in 83 mg, 89% yield, m. p: 92–94 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.26 (br s, 1H), 8.67–8.64 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.58 (s, 3H), 2.30 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.3, 165.6, 149.3, 137.1, 137.0, 133.8, 129.8,

120.3 118.4, 117.6, 117.4, 61.3, 52.0, 51.9, 20.8, 14.0. IR v_{max} (neat): 3247, 2948, 2922, 1714, 1692, 1604, 1579, 1517, 1431, 1365, 1322, 1279, 1239, 1194, 1174, 1025, 1004, 986, 934, 898, 867, 807, 797, 759, 721, 688, 657, 634, 561, 522, 506, 408 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_6$ 372.1442; Found 372.1443.



4s

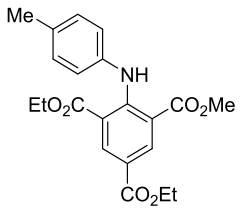
4s: Following the general procedure, the reaction of tert-butyl 2-(triphenylphosphoranylidene)acetate **1c** (188 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4s** as pale yellow liquid, in 91 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (br s, 1H), 8.63–8.46 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.60 (s, 9H), 1.42 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166.6, 164.6, 148.8, 140.1, 137.0, 136.7, 133.3, 129.9, 120.5, 119.8, 118.9, 118.4, 82.1, 81.0, 61.2, 28.2, 27.8, 20.7, 13.9. IR v_{max} (neat): 3252, 2977, 2931, 1708, 1681, 1599, 1515, 1476, 1451, 1417, 1392, 1367, 1315, 1238, 1144, 1023, 952, 912, 881, 845, 806, 765, 731, 686, 646, 522, 503, 488, 461 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}NO_6$ 456.2381; Found 456.2377.



4t

4t: Following the general procedure, the reaction of benzyl 2-(triphenylphosphoranylidene)acetate **1d** (205 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4t** as pale yellow liquid, in 107 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (br s, 1H), 8.63–8.58 (m, 2H), 7.45–7.25 (m, 10H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.1

Hz, 2H), 5.35 (s, 2H), 4.98 (s, 2H), 4.03–3.97 (m, 2H), 2.29 (s, 3H), 1.24-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.1, 165.0, 149.4, 139.3, 137.3, 137.2, 136.0, 135.3, 133.9, 129.8, 128.5, 128.3, 128.2, 128.1, 120.3, 120.2, 118.4, 117.9, 117.4, 66.8, 66.6, 61.3, 20.8, 13.9. IR v_{max} (neat): 3254, 3031, 2923, 1712, 1683, 1600, 1514, 1452, 1374, 1307, 1217, 1172, 1136, 1106, 1023, 967, 907, 865, 803, 779, 754, 730, 694, 637, 598, 508, 494 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{30}NO_6$ 524.2068; Found 524.2068.

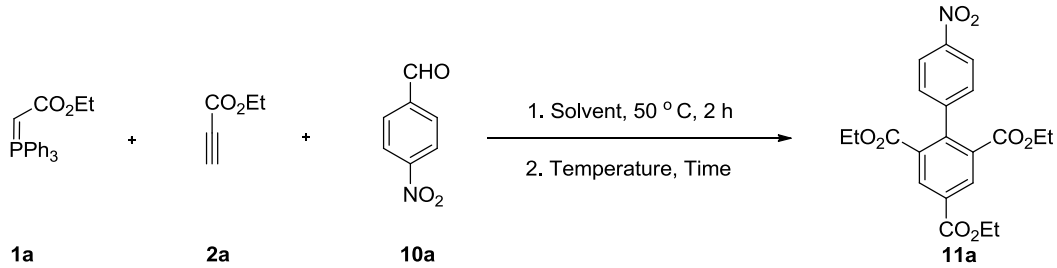


4u

4u: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), methyl propiolate **2b** (50 mg, 0.60 mmol) and 1-isocyanato-4-methylbenzene **3a** (66 mg, 0.50 mmol) provided **4u** as pale yellow solid, in 78 mg, 81% yield, m. p: 72–74 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (br s, 1H), 8.68– 8.54 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 3H), 2.30 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.3, 165.2, 149.2, 137.1, 137.0, 133.8, 129.8, 120.2, 118.8, 117.6, 117.4, 61.3, 60.9, 51.9, 20.8, 14.3, 14.0. IR v_{max} (neat): 3326, 3248, 3032, 2922, 2854, 1709, 1601, 1515, 1434, 1401, 1363, 1316, 1278, 1234, 1193, 1174, 1069, 1024, 990, 935, 881, 867, 839, 811, 797, 760, 720, 685, 634, 561, 522, 508 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_6$ 386.1599; Found 386.1596.

5. Optimization of Conditions for The Synthesis of Biaryls **11**

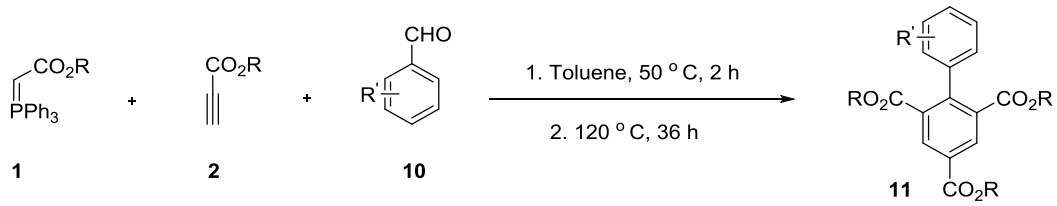
Table S1. Optimization of Reaction Conditions[a]



Entry	Solvent	Temp. (°C)	Time (h)	**11a** (%)[b]
1	1,2-DCE	100	12 h	44%
2 [c]	1,2-DCE	100	12 h	33%
3 [c]	1,2-DCE	100	24 h	38%
4	1,2-DCE	100	24 h	47%
5	Toluene	120	24 h	57%
6	***Toluene***	***120***	***36 h***	***74%***
7 [c]	Toluene	120	36 h	51%
8	Xylene	120	36 h	65%
9	DMSO	120	36 h	47%
10	DMF	140	36 h	53%

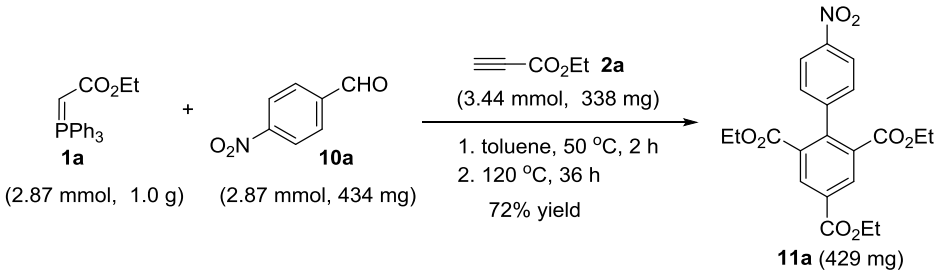
[a] Reaction conditions: P-ylide **1a** (0.50 mmol) and ethyl propiolate **2a** (0.60 mmol) were stirred for 2 h in the specified solvent (2.0 mL) at 50 ^{o}C under N_2 atmosphere, after cooling the reaction mixture to room temperature then aldehyde **10a** (0.50 mmol) was added to the reaction mixture under N_2 atmosphere and stirred for specified time at the indicated temperature. [b] Yield of isolated product. [c] Aldehyde **10a** (0.250 mmol) was used.

6. General Procedure for The Synthesis of Biaryls **11**



Under N_2 atmosphere, to a solution of P-ylide **1** (0.50 mmol) in toluene (2.0 mL) was added alkyl propiolate **2** (0.60 mmol). The mixture was stirred at 50 ^{o}C for 2 h. The reaction mixture was cooled to room temperature, then aldehyde **10** (0.50 mmol) was added to the reaction mixture. The mixture was stirred at 120 °C for 36 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and to the residue added water (5.0 mL) and the reaction mixture was extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo, and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield **11**.

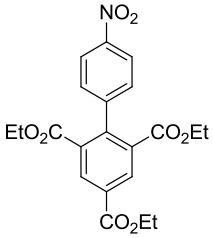
A scaled-up synthesis of compound 11a:



Under N_2 atmosphere and at rt, in a Schlenk tube (50 mL) was added P-ylide **1a** (2.87 mmol, 1.0 g) and toluene (10 mL), which was followed by the addition of ethyl propiolate **2a** (3.44 mmol, 338 mg) by syringe in one portion. The mixture was stirred at 50 ºC for 2 h, at that time P-ylide **1a** was completely consumed as monitored by TLC. The reaction was cooled down to room temperature, and 4-nitrobenzaldehyde (2.87 mmol, 434 mg) was added in one portion. The mixture was then stirred at 120 ºC for 36 h. The solvent was removed by rotary evaporation under reduced pressure and water (10.0 mL) was added. The mixture was extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo, and the residue was purified by column chromatography on

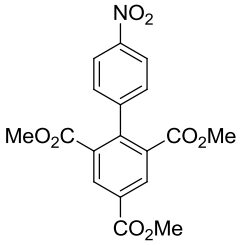
silica gel (ethyl acetate/ petroleum ether) to afford the product **11a** as colourless liquid in 429 mg, 72% yield.

7. Analytical Data for Biaryls **11**



11a

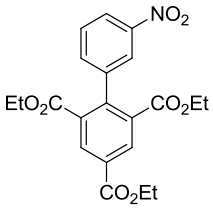
11a: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 4-nitrobenzaldehyde **10a** (75 mg, 0.50 mmol) provided **11a** as colourless liquid, in 77 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 4H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.5, 147.3, 145.9, 143.5, 133.3, 132.9, 130.8, 129.2, 122.7, 61.9, 61.7, 14.2, 13.7. IR ν_{max} (neat): 2982, 2938, 1719, 1598, 1519, 1448, 1391, 1367, 1344, 1234, 1189, 1142, 1105, 1021, 931, 853, 804, 768, 757, 698, 518 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}NO_8Na$ 438.1160; Found 438.1156.



11b

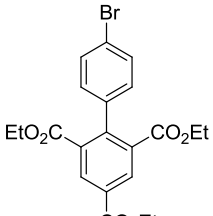
11b: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), methyl propiolate **2b** (50 mg, 0.60 mmol) and 4-nitrobenzaldehyde **10a** (75 mg, 0.50 mmol) provided **11b** as colourless liquid, in 56 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.7 (s, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 4.00 (s, 3H), 3.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 164.9, 147.3, 145.5, 144.3, 133.7, 132.6, 130.5, 129.1, 122.8, 52.7,

52.5. IR v_{max} (neat): 3010, 2956, 2849, 1724, 1599, 1575, 1511, 1436, 1337, 1287, 1233, 1203, 1139, 1108, 1001, 985, 943, 925, 890, 862, 854, 832, 808, 775, 755, 728, 704, 535, 506, 463 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO_8$ 374.0871; Found 374.0863.



11c

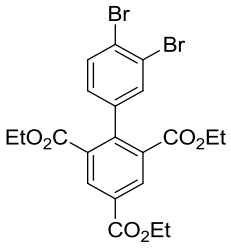
11c: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 3-nitrobenzaldehyde **10b** (75 mg, 0.50 mmol) provided **11c** as colourless liquid, in 74 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.0 Hz, 2H), 8.28–8.26 (m, 1H), 8.11 (d, *J* = 1.0 Hz, 1H), 7.60-7.54 (m, 1H), 4.47 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.09 (qd, *J* = 7.1, 1.2 Hz, 4H), 1.45 (td, *J* = 7.1, 1.5 Hz, 3H), 1.05 (td, *J* = 7.1, 1.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.7, 147.9, 144.3, 135.6, 134.4, 132.9, 131.4, 130.3, 129.8, 128.5, 124.1, 61.5, 14.3, 13.7. IR v_{max} (neat): 3084, 2982, 2936, 1719, 1609, 1576, 1529, 1447, 1414, 1348, 1326, 1233, 1188, 1113, 1093, 1020, 931, 875, 861, 806, 765, 735, 712, 687, 655 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}NO_8Na$ 438.1160; Found 438.1156.



11d

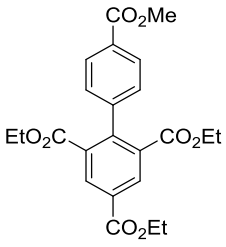
11d: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 4-bromobenzaldehyde **10c** (92 mg, 0.50 mmol) was conducted in sealed tube at 140 ^{o}C which provided **11d** as colourless liquid, in 57 mg, 52% yield; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 4H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.7, 143.9, 137.5, 133.7, 132.6, 130.8, 130.1, 129.9, 121.9, 61.7, 61.6, 14.3, 13.6. IR v_{max} (neat): 2981, 2919, 2850, 1720, 1632, 1607, 1491, 1448, 1416, 1391, 1367, 1326, 1236, 1186, 1095, 1071, 1022, 1001, 928, 862, 826, 802, 767, 712, 695, 630, 520 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}BrO_6Na$ 471.0414; Found 471.0412.



11e

11e: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and 3,4-dibromobenzaldehyde **10d** (132 mg, 0.50 mmol) provided **11e** as colourless liquid, in 65 mg, 49% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.6 (s, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.6, 142.6, 139.3, 133.4, 133.3, 132.9, 132.6, 130.5, 128.6, 124.1, 124.0, 61.8, 61.7, 14.2, 13.7. IR v_{max} (neat): 2980, 2918, 2850, 1718, 1606, 1544, 1448, 1414, 1390, 1367, 1325, 1232, 1187, 1141, 1109, 1020, 1009, 930, 861, 822, 766, 712, 658, 556, 436 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}Br_2O_6$ 528.9679; Found 528.9682.

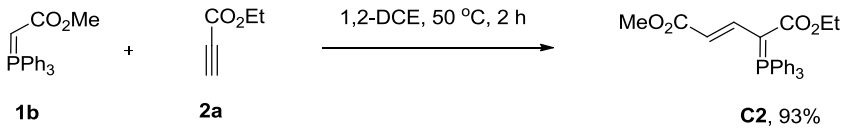


11f

11f: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol), ethyl propiolate **2a** (59 mg, 0.60 mmol) and methyl 4-formylbenzoate **10e** (82 mg, 0.50 mmol) provided **11f** as colourless liquid, in 42 mg, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 2H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 4H), 3.95 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.7, 164.6, 144.2, 143.6, 133.5, 132.7, 130.3, 129.3, 128.8, 128.3, 61.7, 61.5, 52.1, 14.2, 13.6. IR ν_{max} (neat): 2982, 1716, 1606, 1437, 1403, 1367, 1326, 1274, 1232, 1185, 1099, 1022, 929, 860, 826, 804, 765, 732, 706, 555, 474 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}O_8$ 429.1544; Found 429.1538.

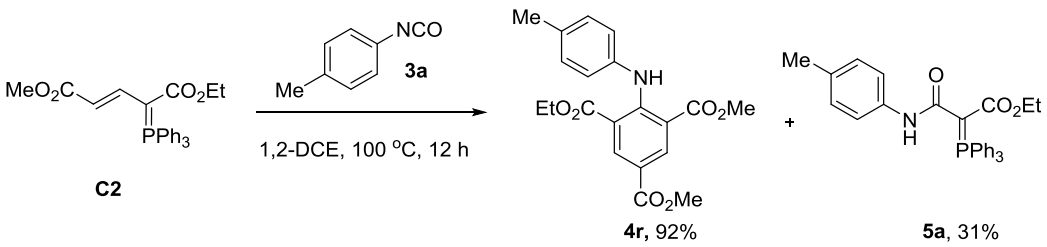
8. Control Experiment

A) Synthesis of P-ylide **C2**[1]



Under N_2 atmosphere, to a solution of P-ylide **1b** (167 mg, 0.50 mmol) in 1,2-dichloroethane (2.0 mL) was added ethyl propiolate **2a** (59 mg, 0.50 mmol). The reaction mixture was stirred at 50 °C for 2 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield compound **C2** (201 mg, 93%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.68 (m, 9H), 7.52 (dt, *J* = 7.6, 3.8 Hz, 6H), 7.03 (dd, *J* = 17.5, 14.6 Hz, 1H), 6.28 (d, *J* = 14.5 Hz, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 3.56 (s, 3H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 168.1 (d, $J_{c\text{-}p}$ = 15.4 Hz), 145.5 (d, $J_{c\text{-}p}$ = 15.8 Hz), 133.6 (d, $J_{c\text{-}p}$ = 9.7 Hz), 132.5 (d, $J_{c\text{-}p}$ = 2.9 Hz), 128.9 (d, $J_{c\text{-}p}$ = 12.4 Hz), 125.0 (d, $J_{c\text{-}p}$ = 92.1 Hz), 100.7 (d, $J_{c\text{-}p}$= 15.2 Hz), 58.7 (d, $J_{c\text{-}p}$ = 121.0 Hz), 58.7, 50.3, 14.1. **C2** is a known compound, the NMR data are consistent with those reported.[1]

B) Synthesis of Aniline Derivative **4r**



Under N_2 atmosphere, to a solution of P-ylide **C2** (173 mg, 0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added isocyanate **3a** (53 mg, 0.40 mmol). The reaction mixture was stirred at 100 °C for 12 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield compounds **4r** (68 mg, 92%) and **5a**[2] (30 mg, 31%).

9. X-ray Crystallographic Data

4a: Single crystal of compound **4a** was obtained by recrystallization from mixed solvents of dichloromethane and petroleum ether. The structure is shown in Figure S1. CIF file of **4a** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1974263.

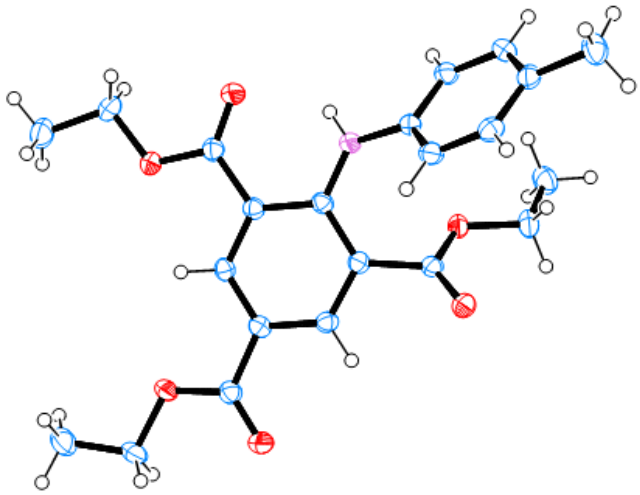


Figure S1. X-ray Single Crystal Structure of **4a**

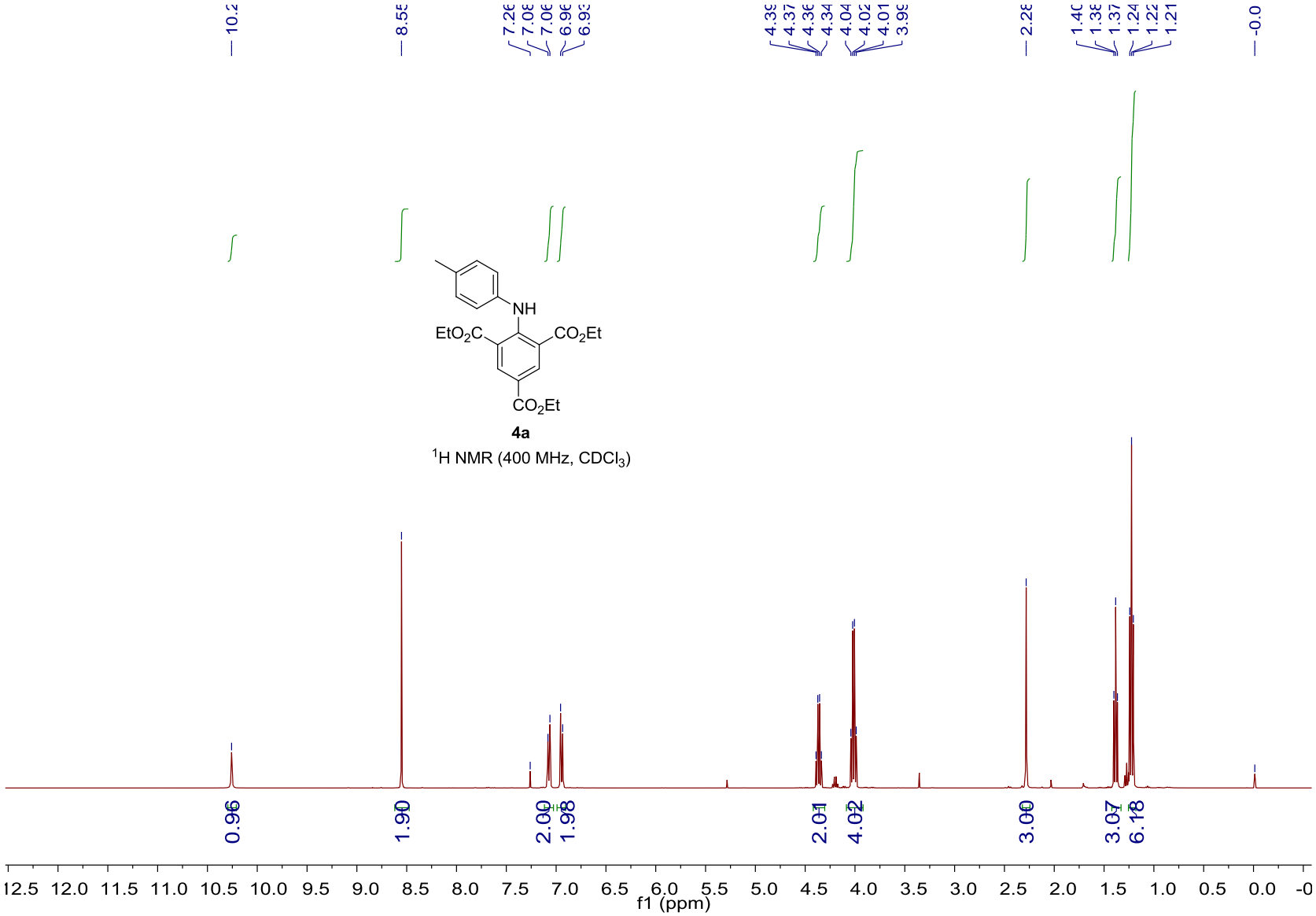
Table S1. Crystal Data and Structure Refinement for **4a**

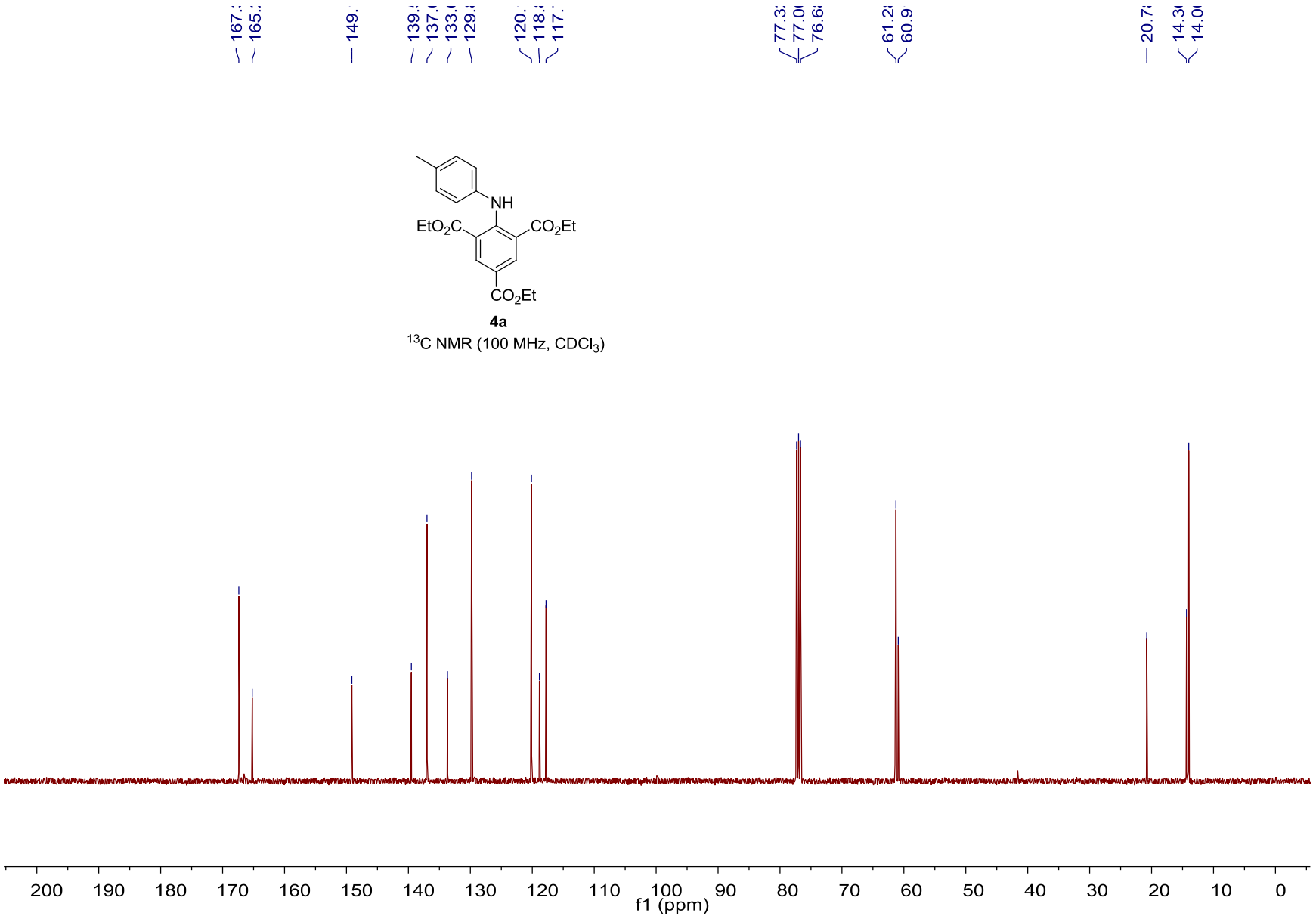
Identification code	**4a**
Empirical formula	$C_{22}H_{25}NO_6$
Formula weight	399.43
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.0462(17) Å, α = 90° b = 14.645(2) Å, β = 107.712(2)° c = 13.553(2) Å, γ = 90°
Volume	2088.6(6) $Å^3$
Z	4
Calculated density	1.270 Mg/m^3
Absorption coefficient	0.093 mm^{-1}
F(000)	848
Crystal size	0.130 × 0.120 × 0.100 mm^3
θ range for data collection	2.092 to 26.554 °
Limiting indices	-13<=h<=13, -18<=k<=18, -16<=l<=17
Reflections collected	22029
Independent reflections	4320 [R(int) = 0.0297]
Completeness to θ = 25.02°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.991 and 0.988
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4320 / 0 / 262
Goodness-of-fit on F^2	1.024
Final R indices [I>2σ(I)]	R1 = 0.0409, wR2 = 0.1034
R indices (all data)	R1 = 0.0547, wR2 = 0.1130
Extinction coefficient	n/a
Largest diff. peak and hole	0.399 and -0.222 e. $Å^{-3}$

10. References

1. Barluenga, J.; Lopez, F.; Palacios, F. *Tetrahedron Lett.* **1988**, *29*, 381–384.
2. Compound **5a** is a known compound, see: Kaki, R. B.; Han, W.; Chen, J.-B.; Li, Y.; Tang, Y.; Zhang, W.; Xu, W.; Xu, S., *Chem. Commun.* **2020**, *56*, 5909–5912.

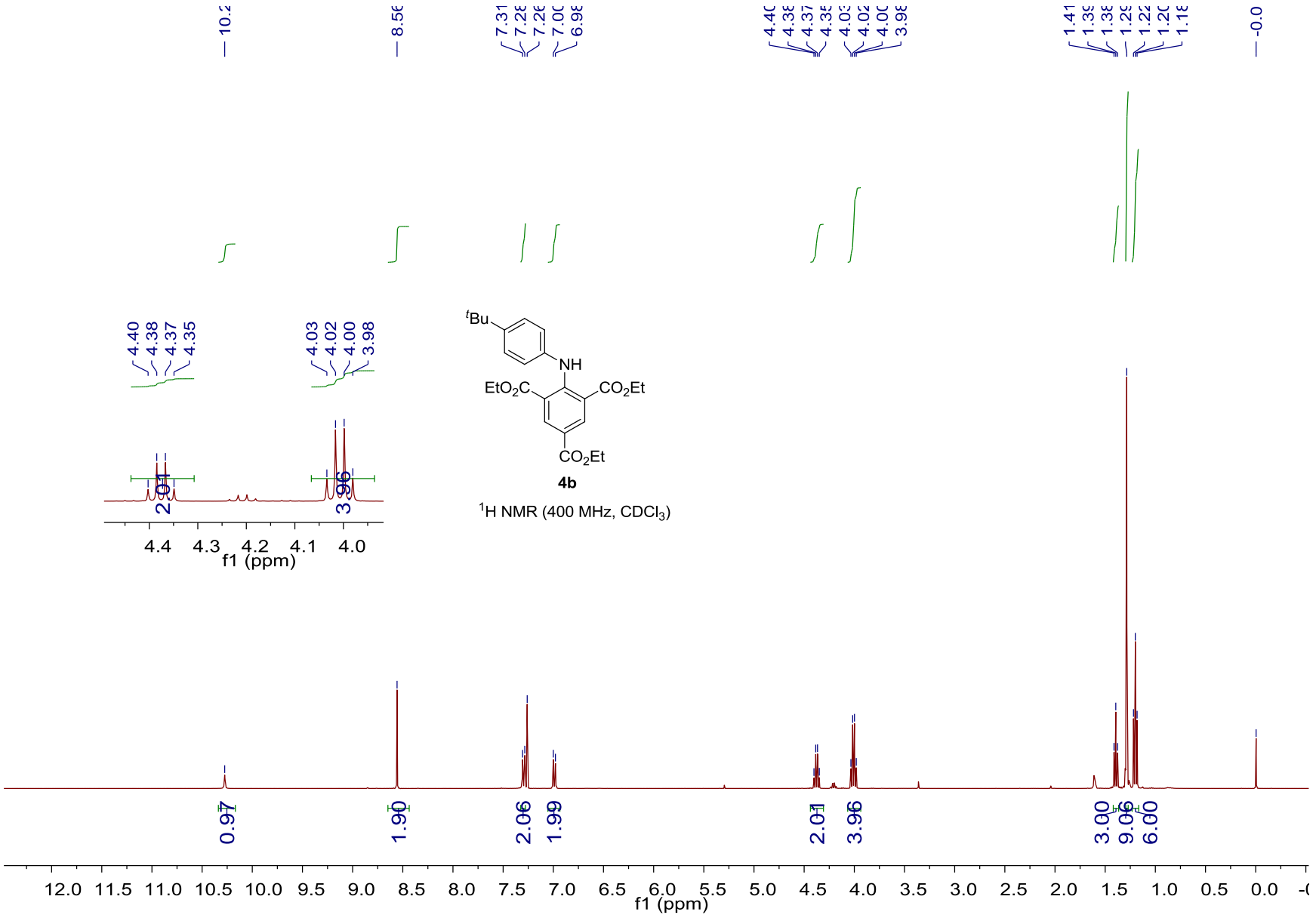
11. ^{1}H and ^{13}C NMR Spectra Copies

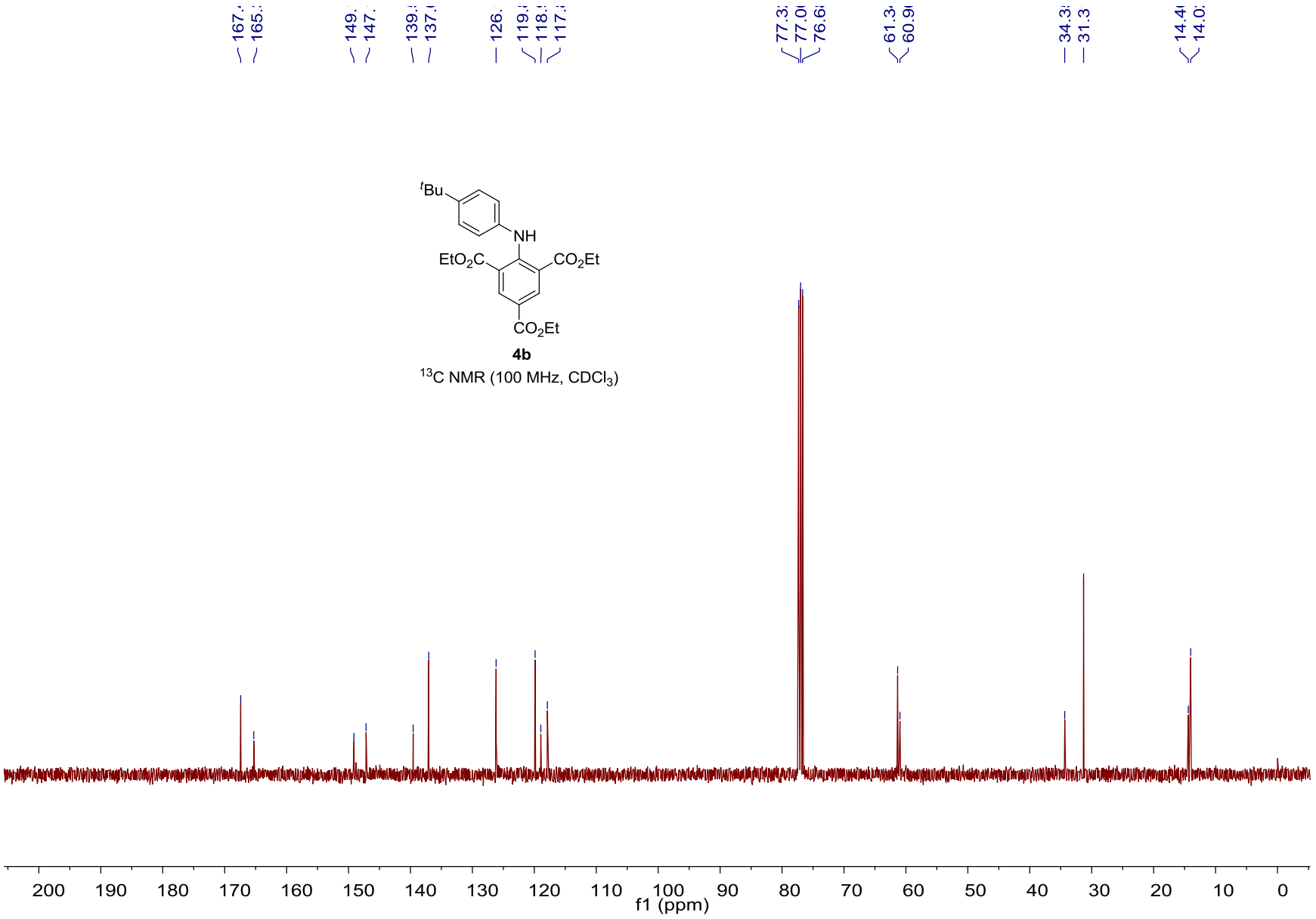


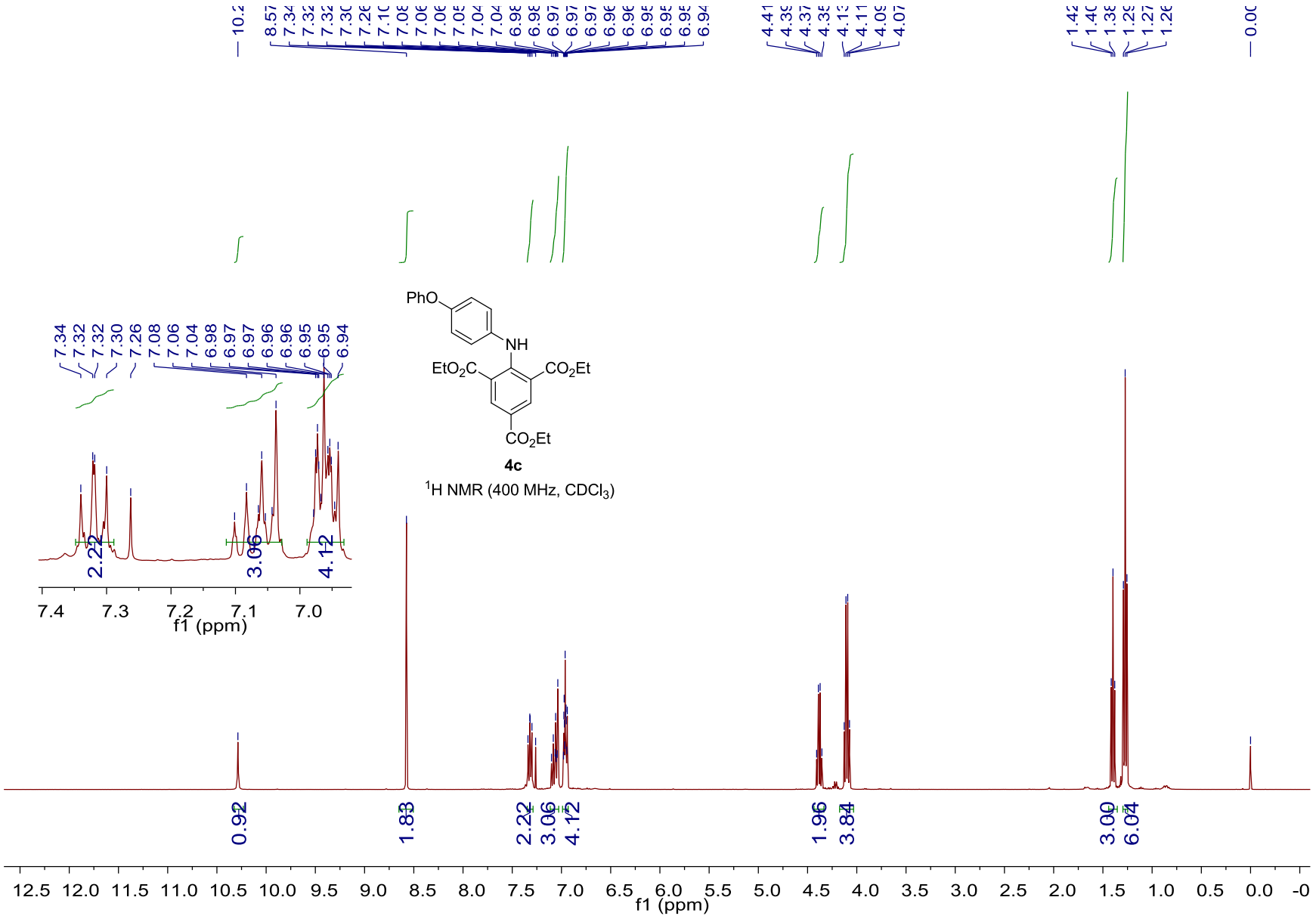


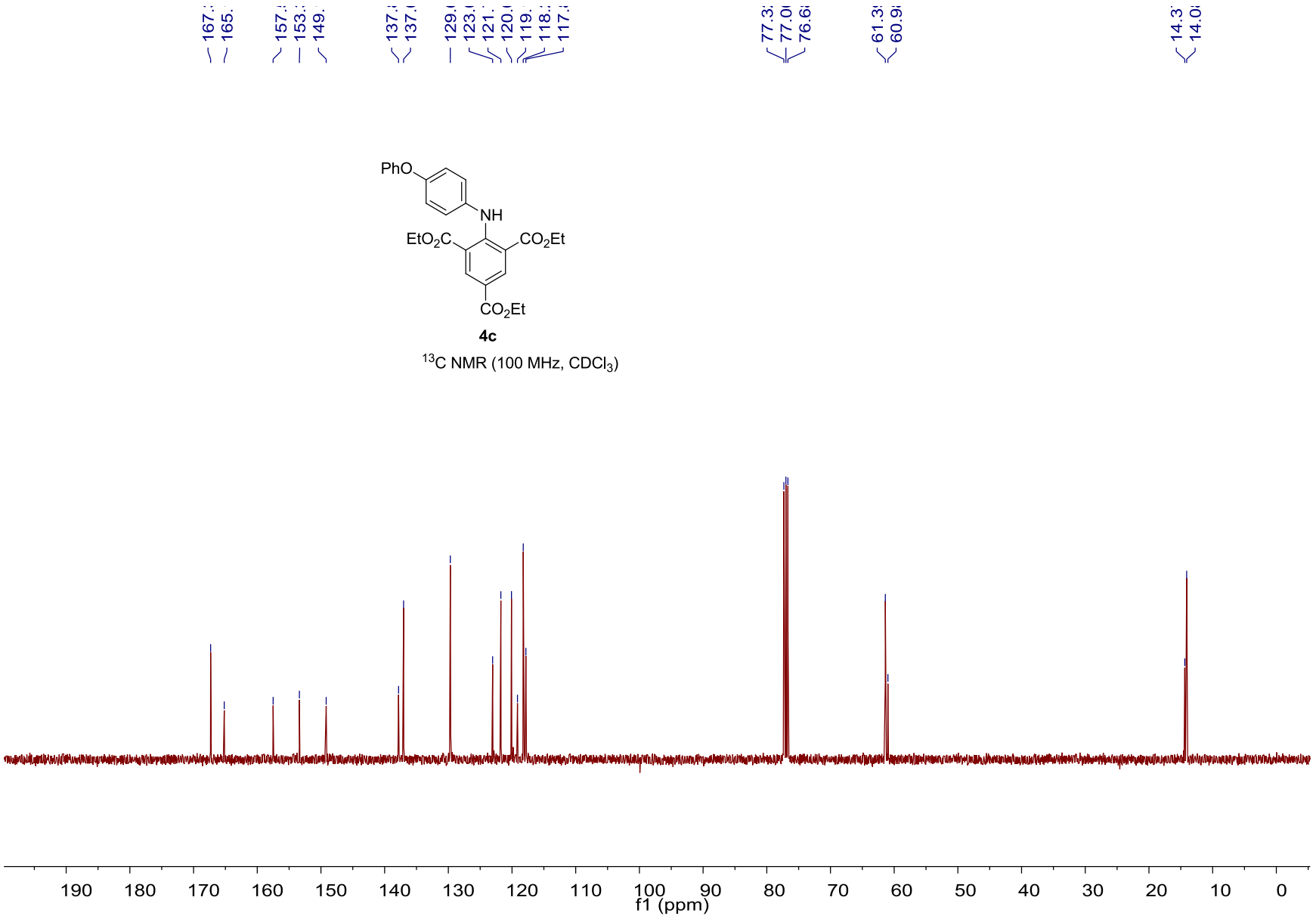
4a

^{13}C NMR (100 MHz, $CDCl_3$)


4.40
4.38
4.37
4.35
4.03
4.02
4.00
3.98
2.01
3.96
4.4
4.3
4.2
4.1
4.0
f1 (ppm)
tBu
NH
EtO2C
CO2Et
CO2Et
4b
1H NMR (400 MHz, CDCl3)
0.97
1.90
2.06
1.99
2.01
3.96
3.00
9.06
6.00
12.0 11.5 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
f1 (ppm)

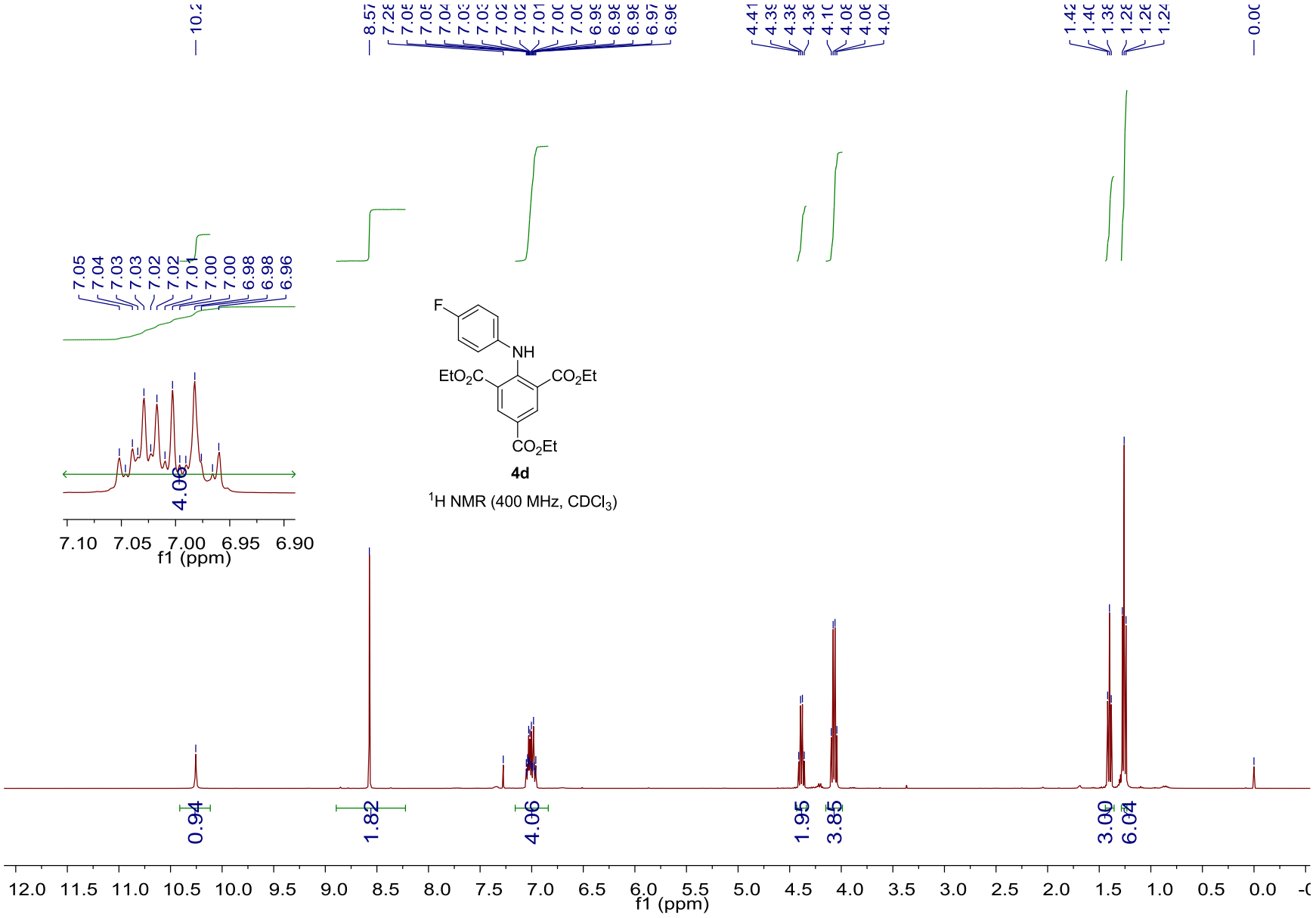

167.
165.
149.
147.
139.
137.
126.
119.
118.
117.
77.3
77.0
76.6
61.3
60.9
34.3
31.3
14.4
14.0
tBu
NH
EtO2C
CO2Et
CO2Et
4b
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PhO
NH
EtO2C
CO2Et
CO2Et
4c
1H NMR (400 MHz, CDCl3)
f1 (ppm)



4c

^{13}C NMR (100 MHz, $CDCl_3$)


F
NH
EtO2C
CO2Et
CO2Et
4d
1H NMR (400 MHz, CDCl3)
f1 (ppm)
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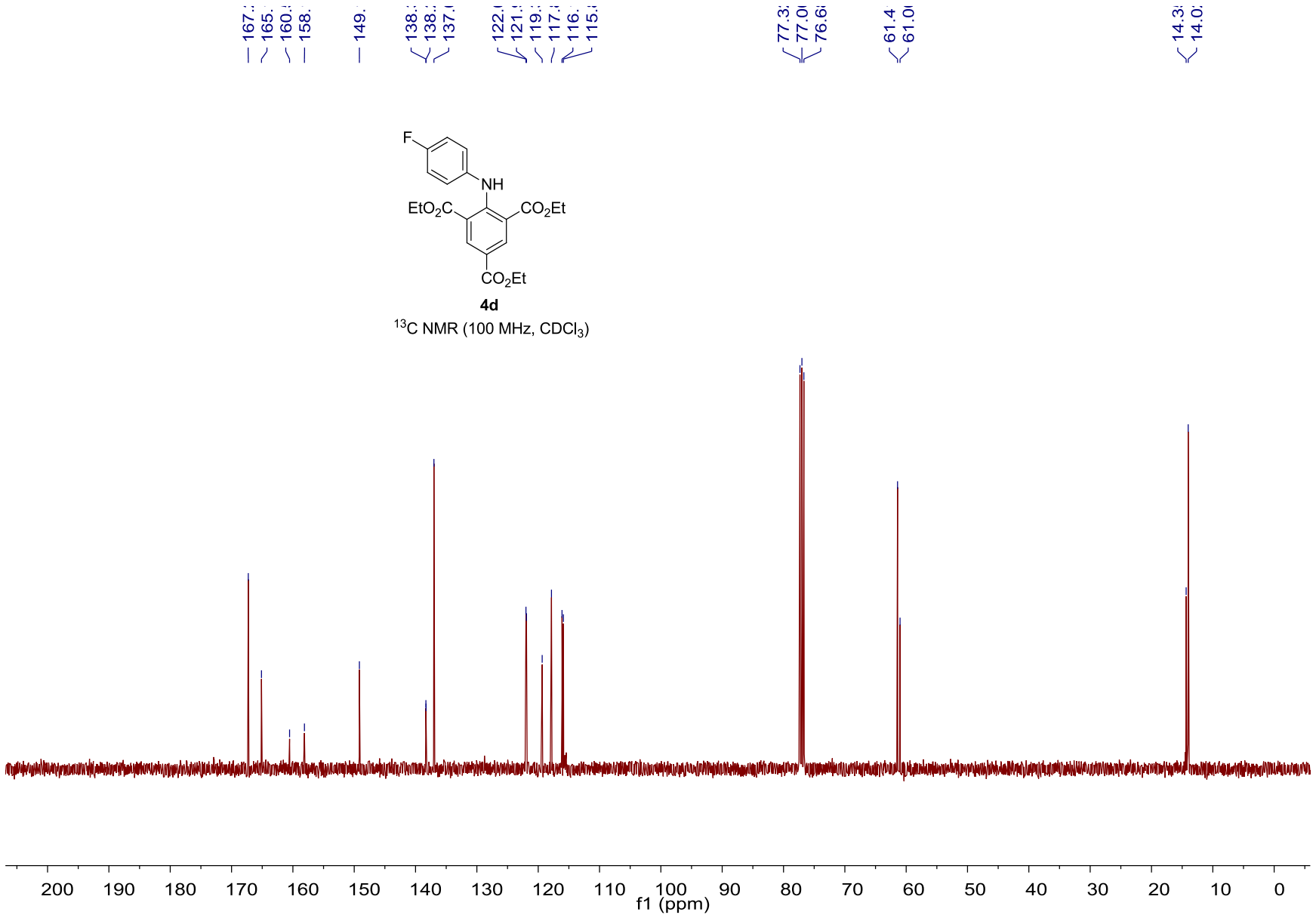
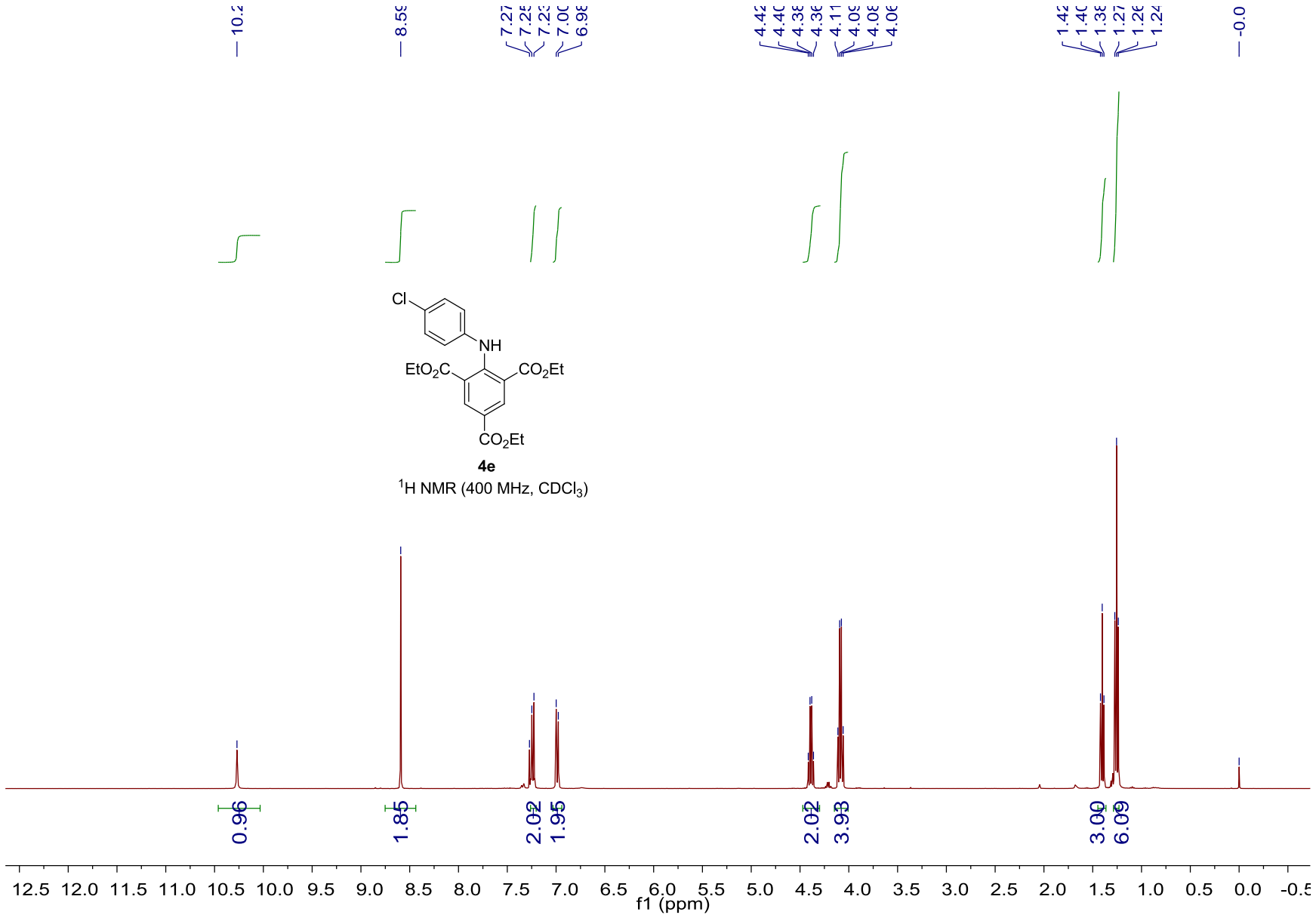
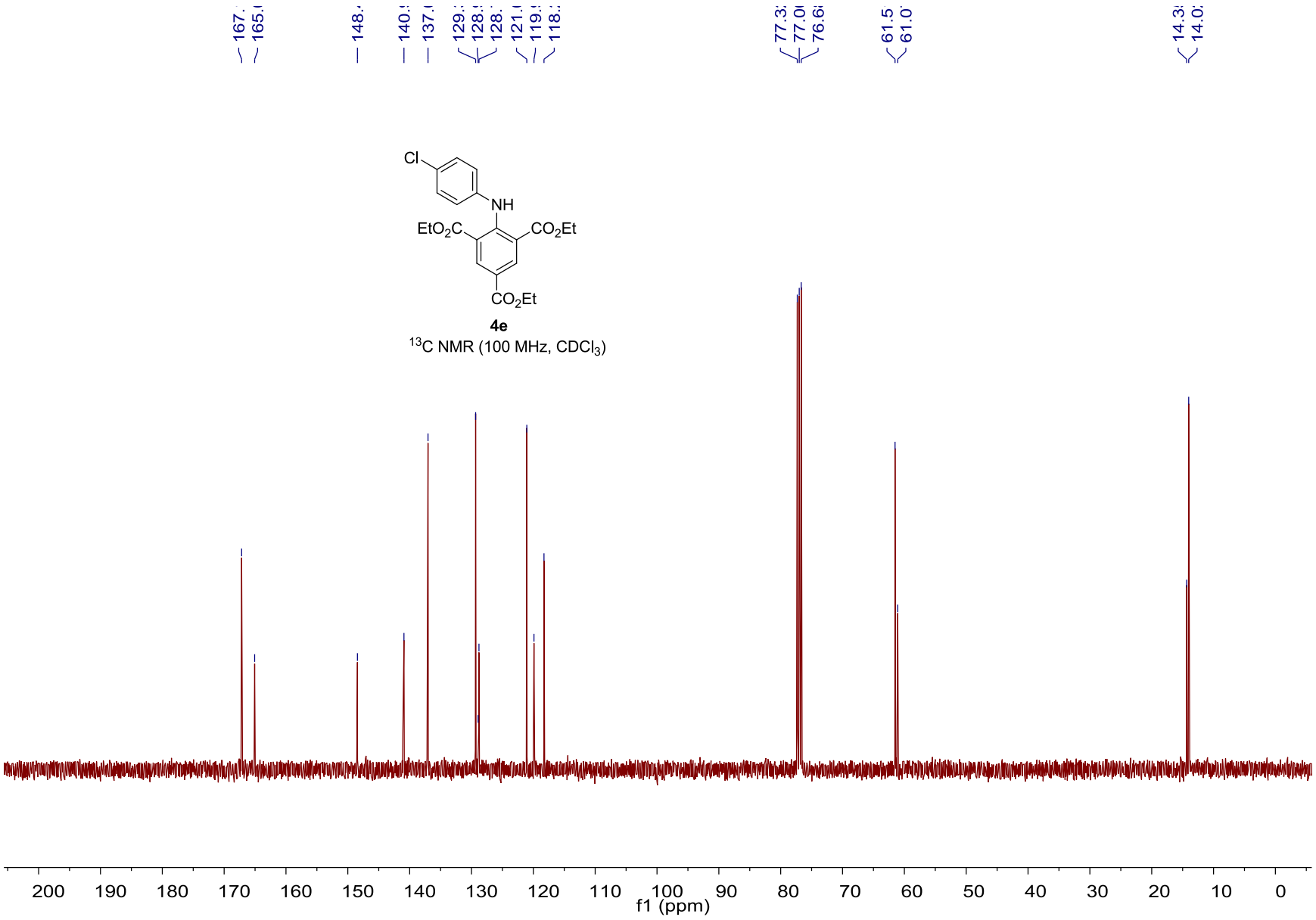
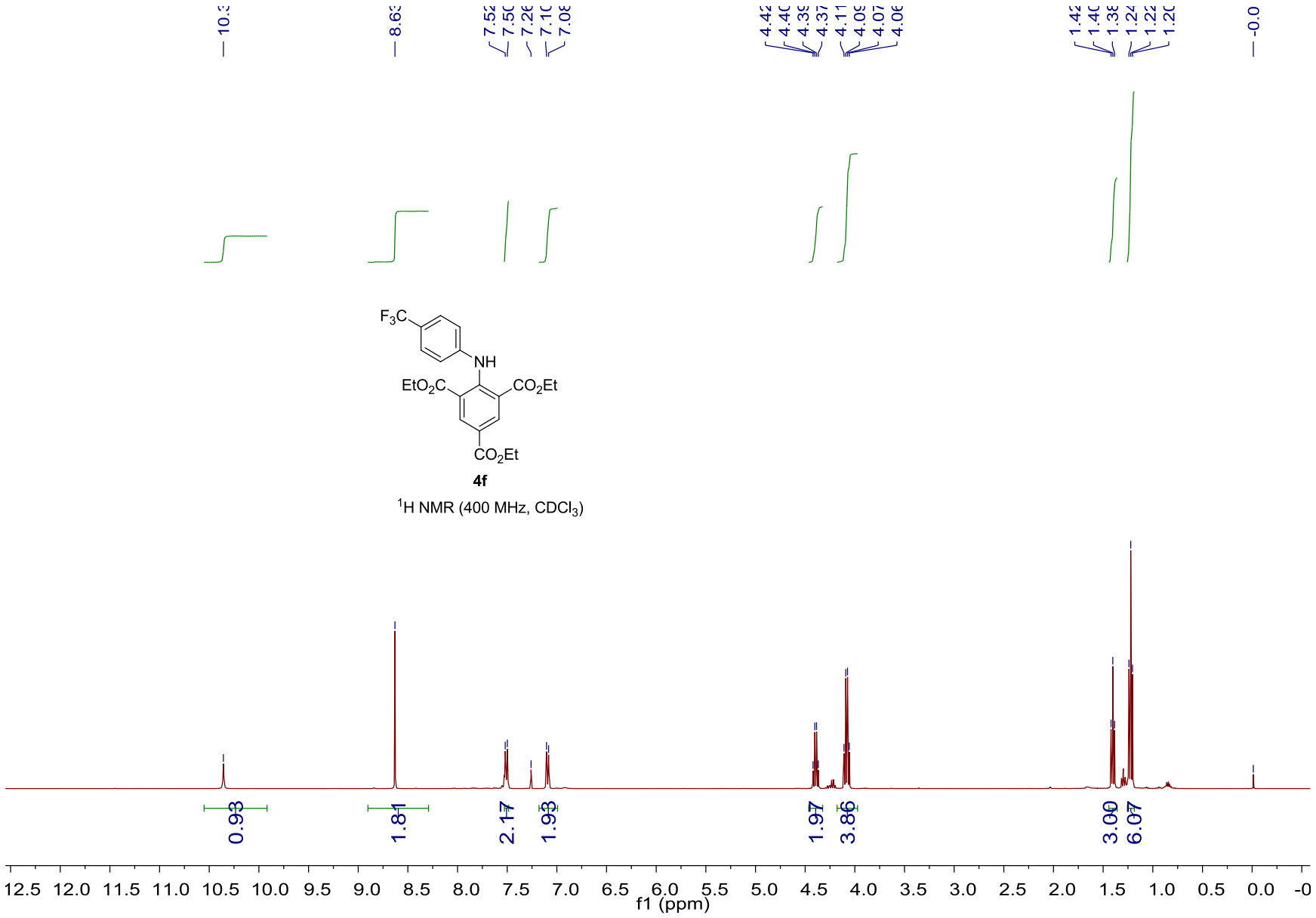
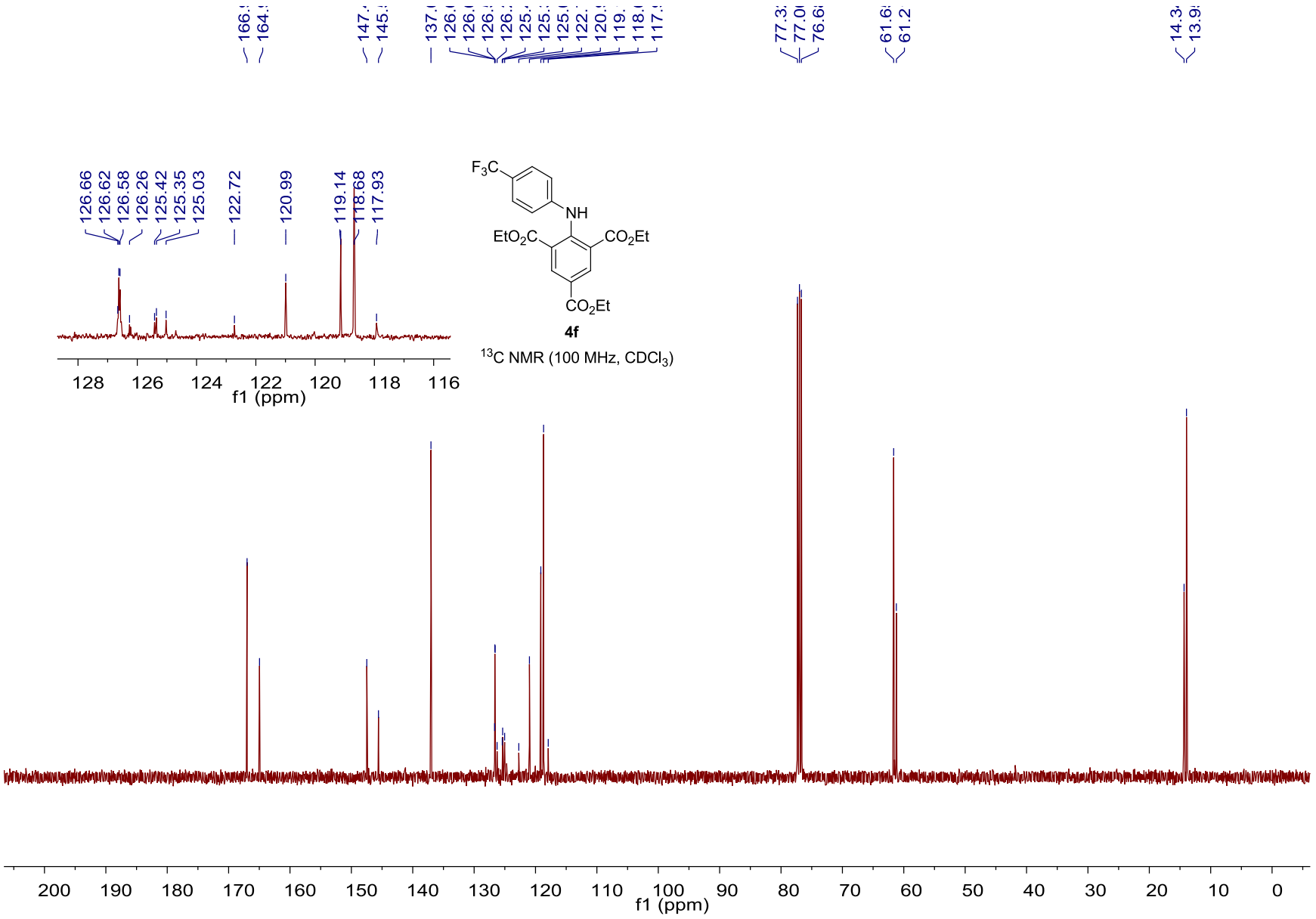
1.82
4.06
1.95
3.85
3.00
6.04

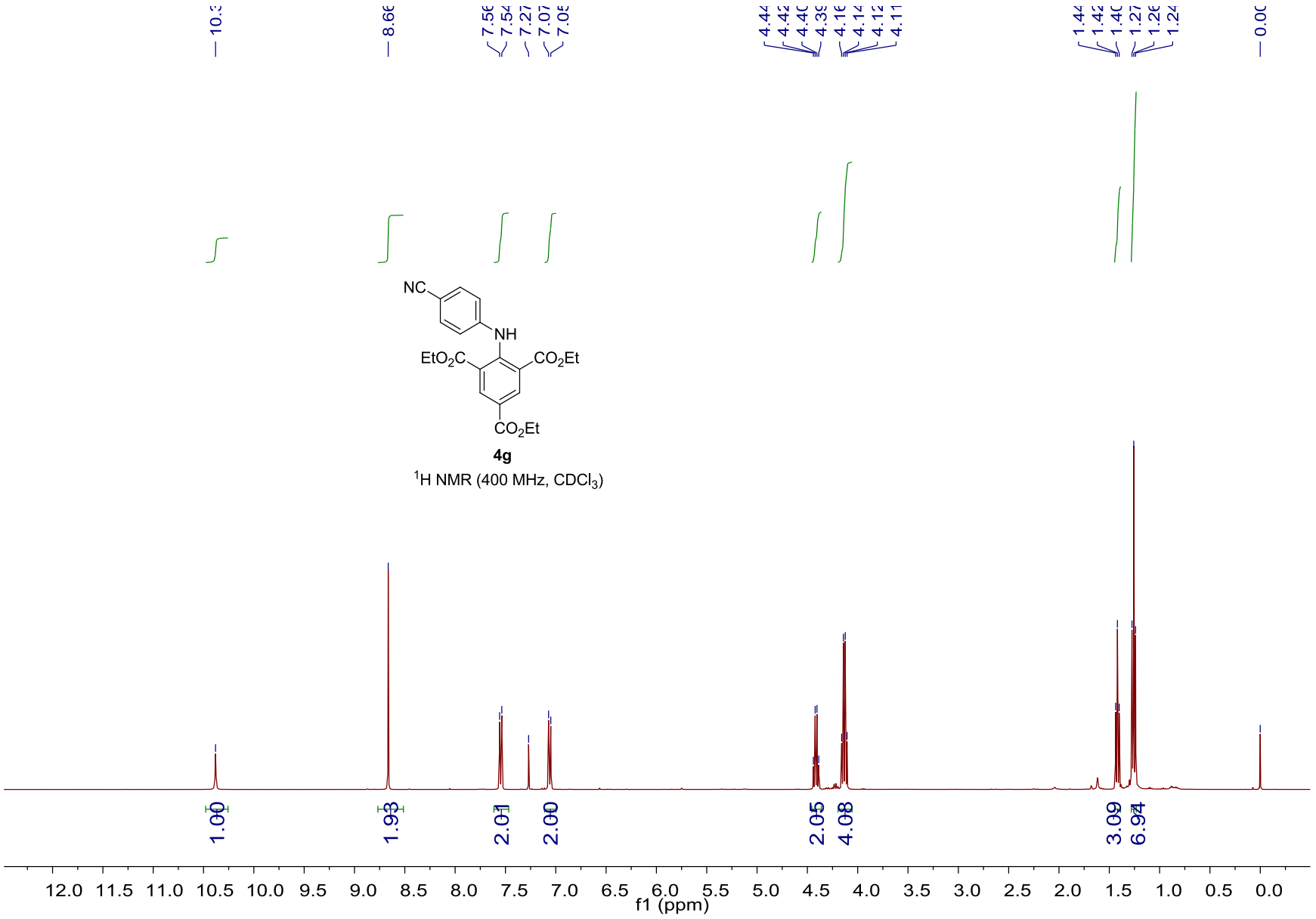

F
NH
EtO2C
CO2Et
CO2Et
4d
13C NMR (100 MHz, CDCl3)
f1 (ppm)

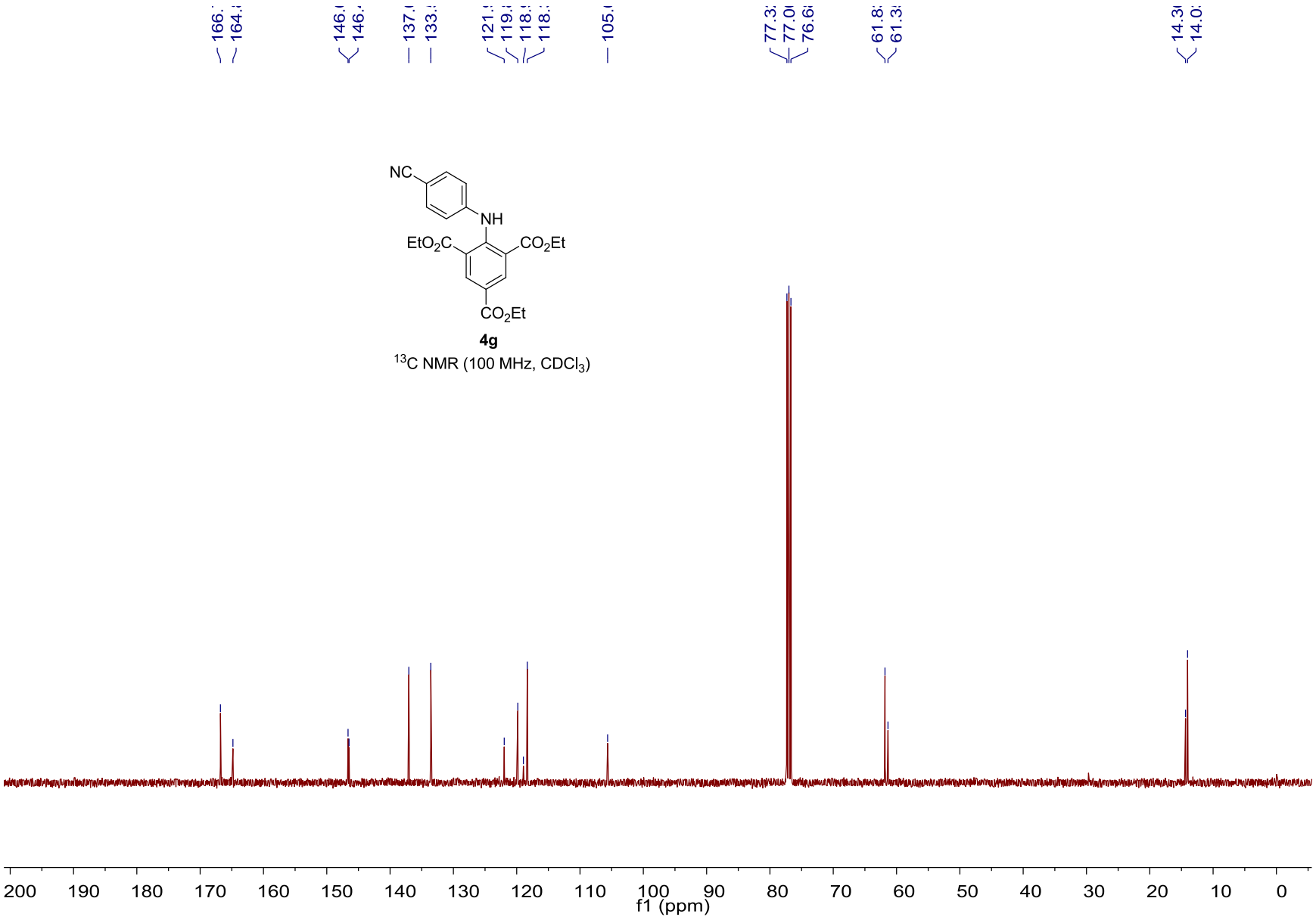

Cl
NH
EtO2C
CO2Et
CO2Et
4e
1H NMR (400 MHz, CDCl3)
0.96
1.85
2.02
1.95
2.02
3.93
3.00
6.09
f1 (ppm)

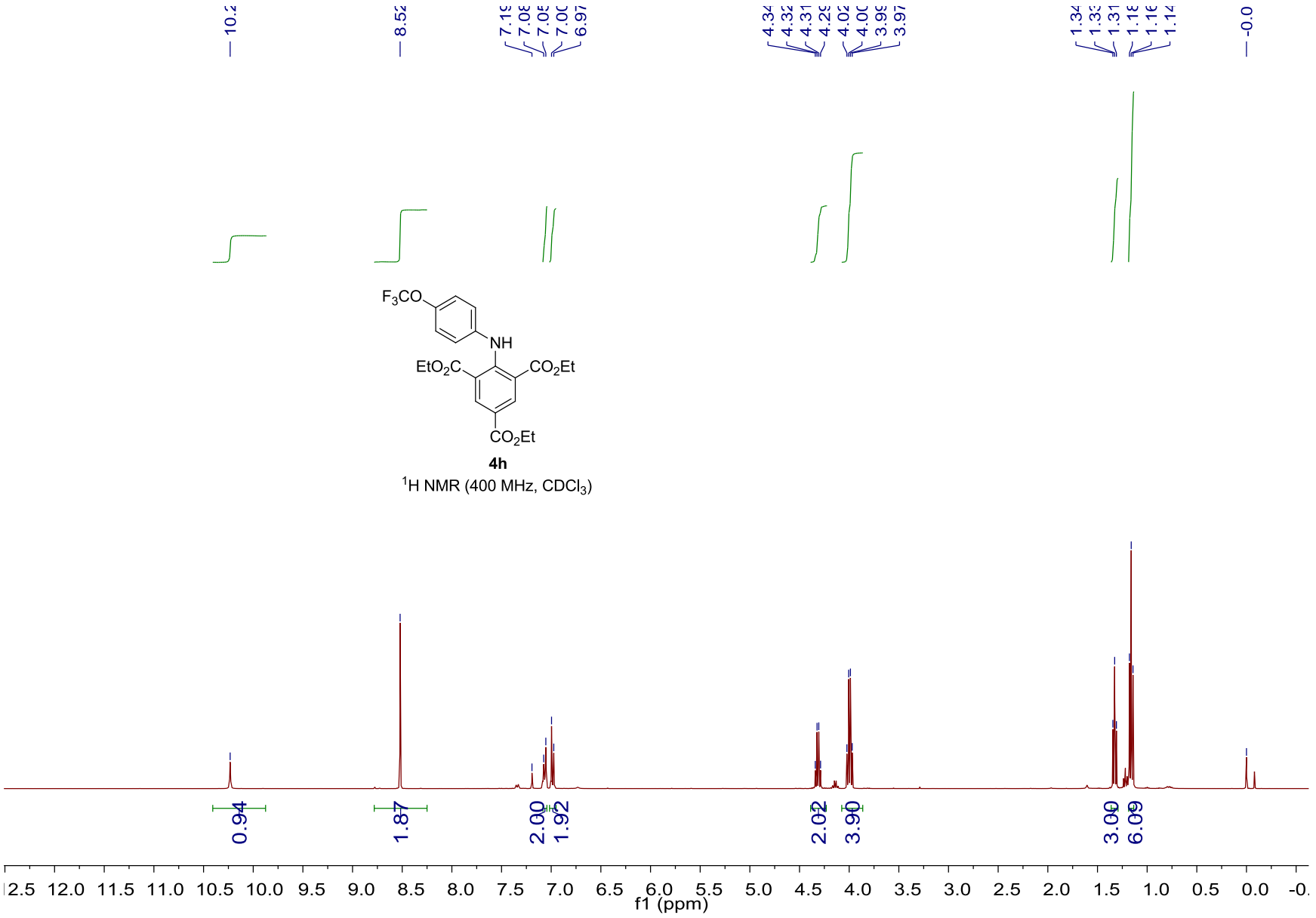

167.
165.
148.
140.
137.
129.
128.
128.
121.
119.
118.
77.3
77.0
76.6
61.5
61.0
14.3
14.0
Cl
NH
EtO2C
CO2Et
CO2Et
4e
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

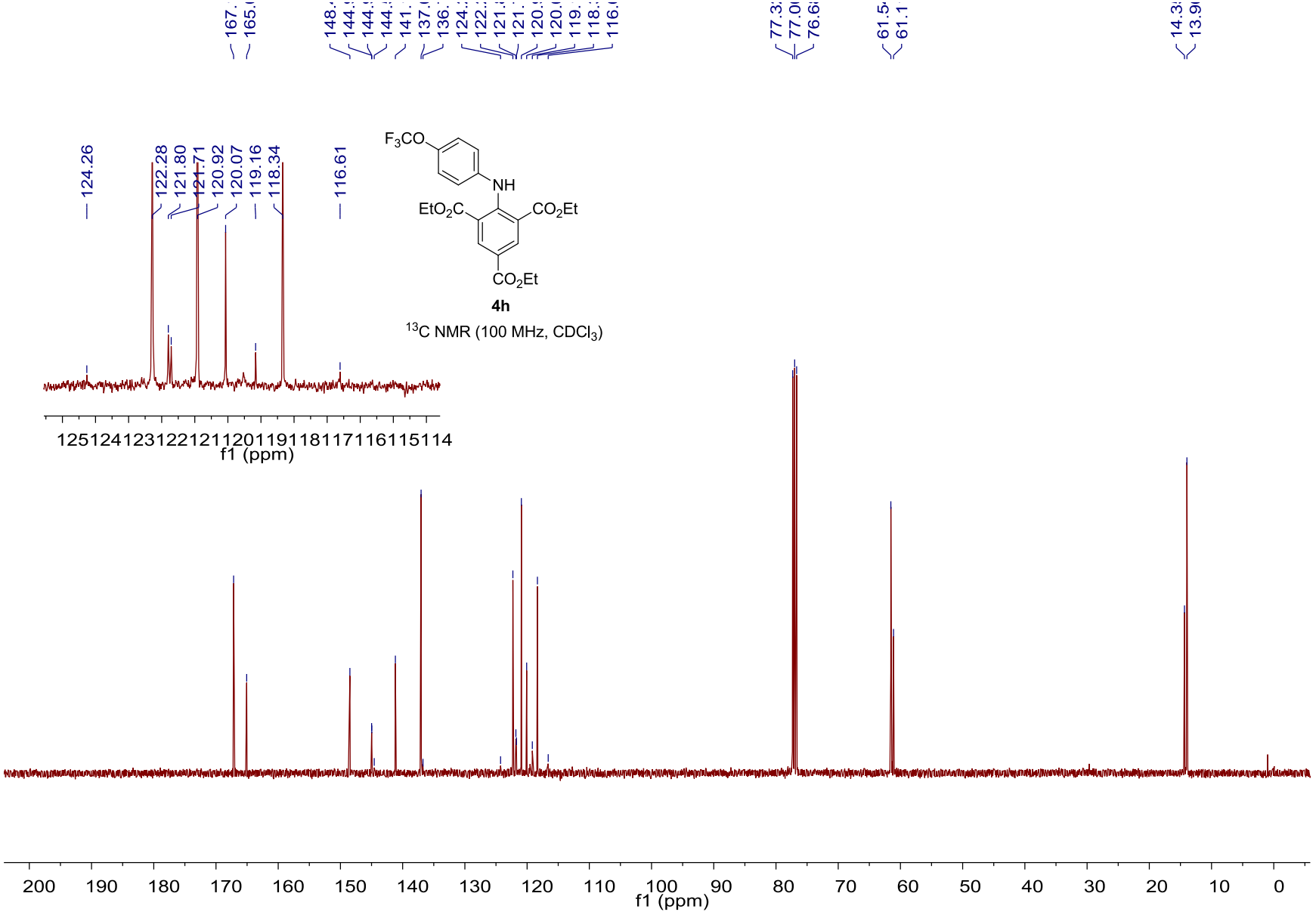

F3C
NH
EtO2C
CO2Et
CO2Et
4f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

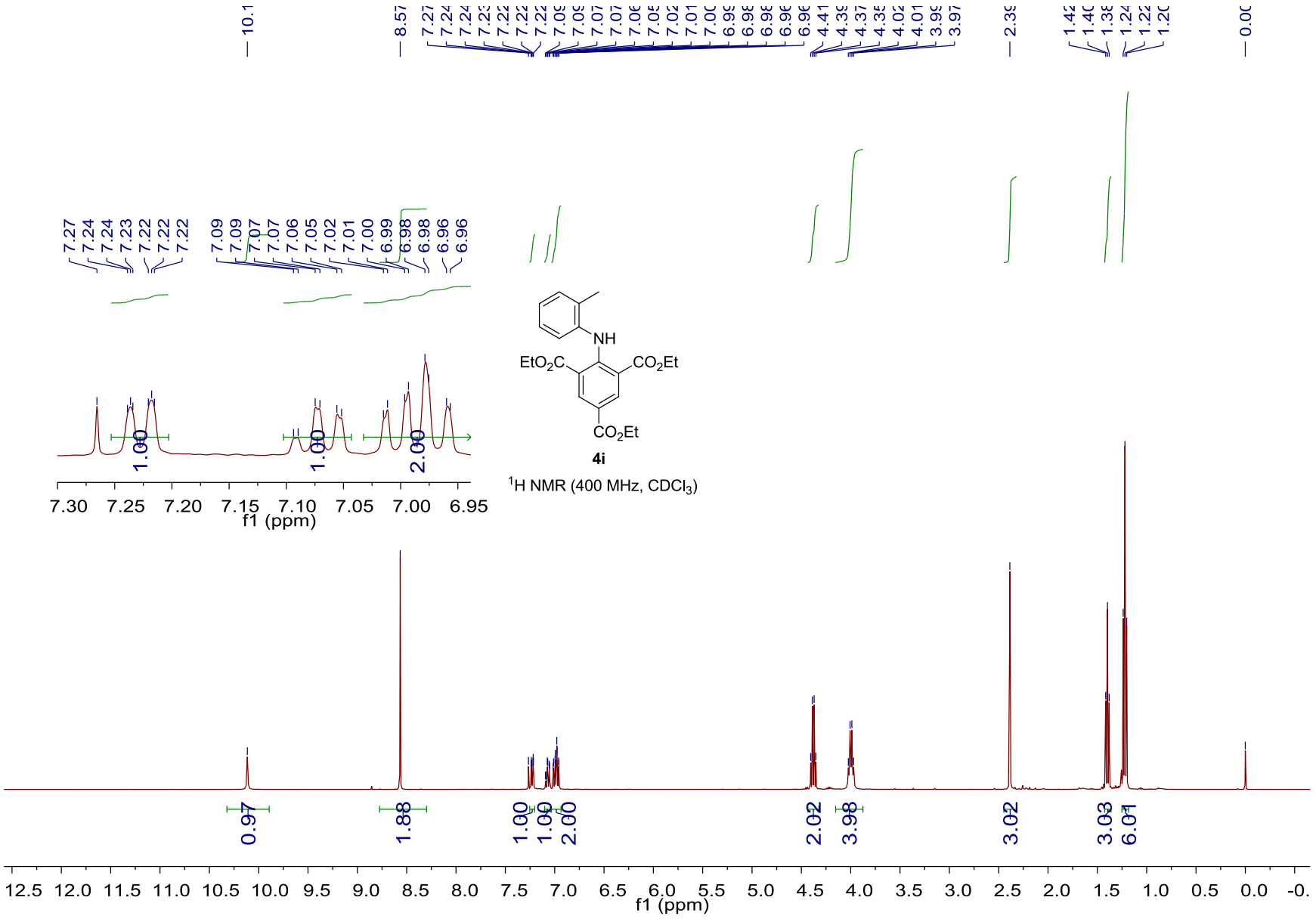

166.
164.
147.
145.
137.
126.
126.
126.
126.
125.
125.
125.
122.
120.
119.
118.
117.
77.3
77.0
76.6
61.6
61.2
14.3
13.9
126.66
126.62
126.58
126.26
125.42
125.35
125.03
122.72
120.99
119.14
118.68
117.93
128
126
124
122
120
118
116
f1 (ppm)
F3C
NH
EtO2C
CO2Et
CO2Et
4f
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

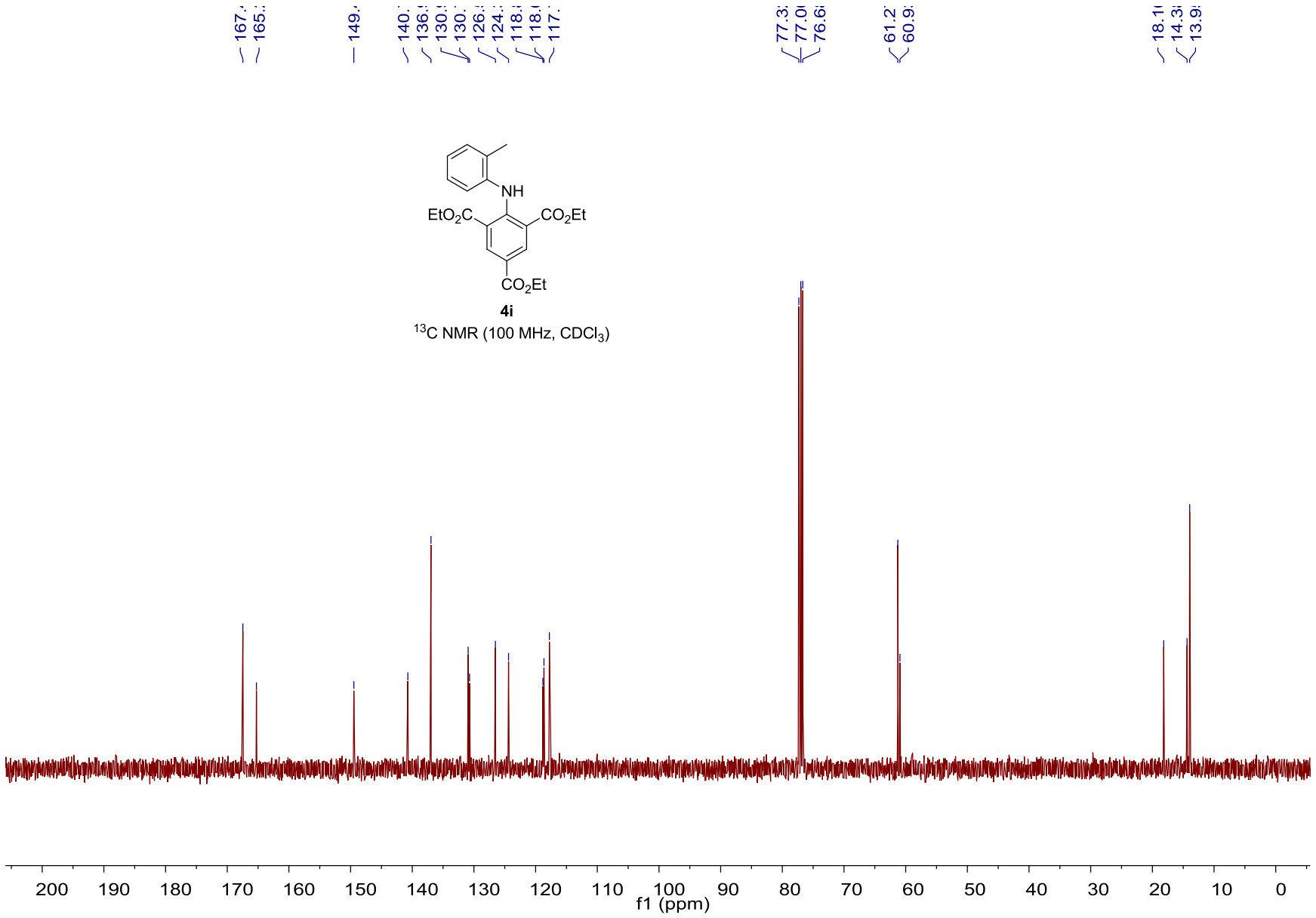

NC
NH
EtO2C
CO2Et
CO2Et
4g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

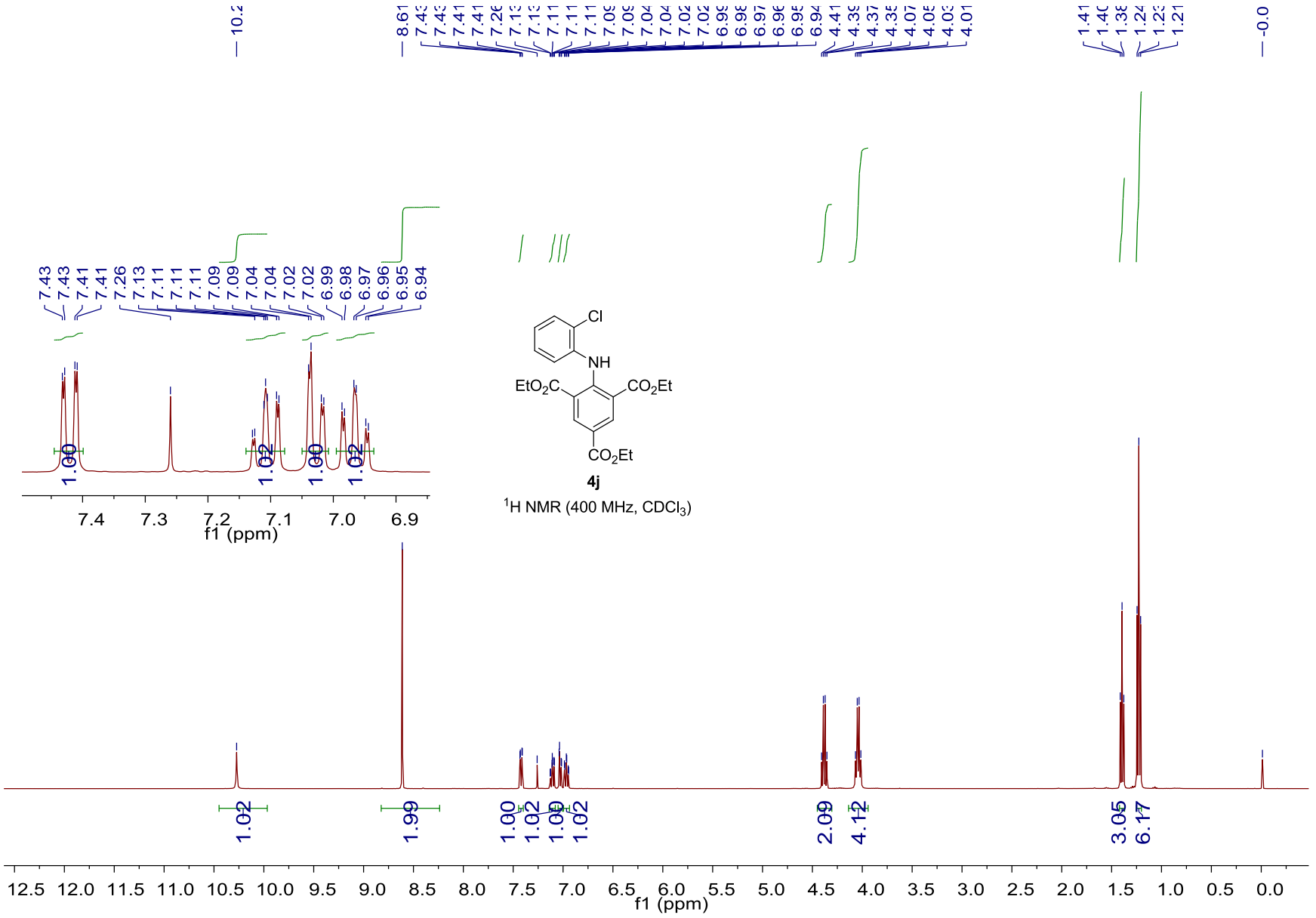

NC
NH
EtO2C
CO2Et
CO2Et
4g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

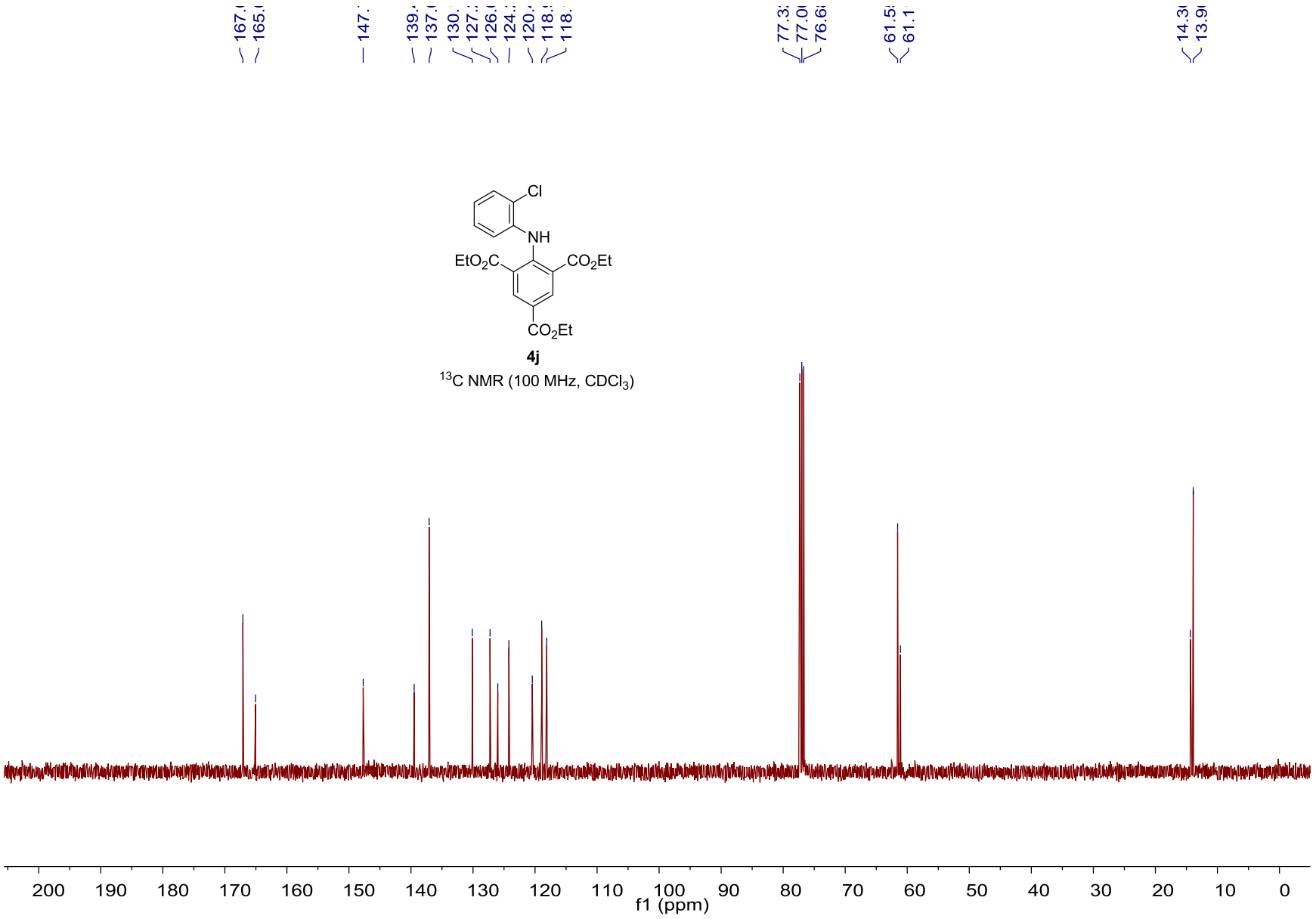

F3CO
NH
EtO2C
CO2Et
CO2Et
4h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

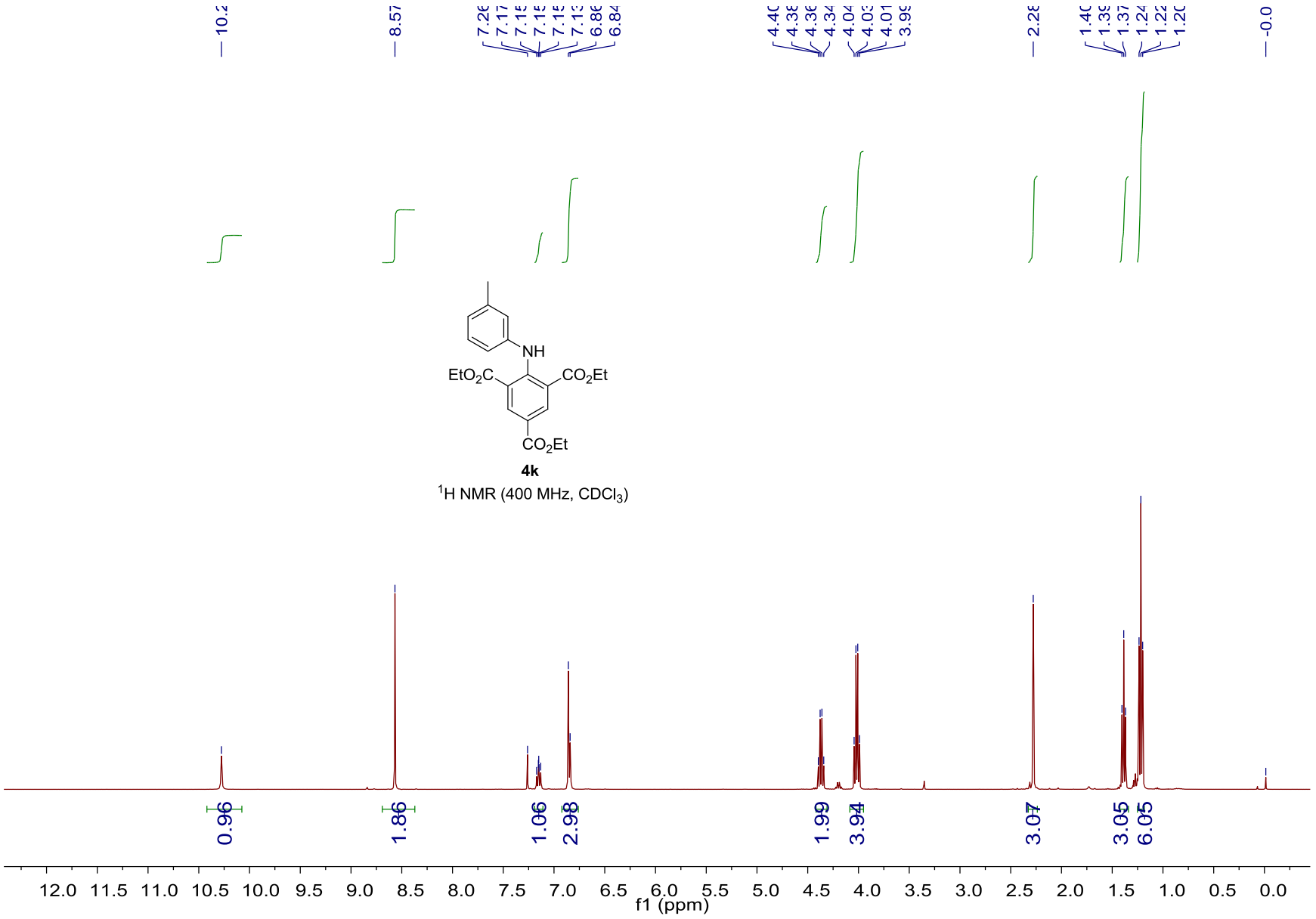

124.26
122.28
121.80
121.71
120.92
120.07
119.16
118.34
116.61
F3CO
NH
EtO2C
CO2Et
CO2Et
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

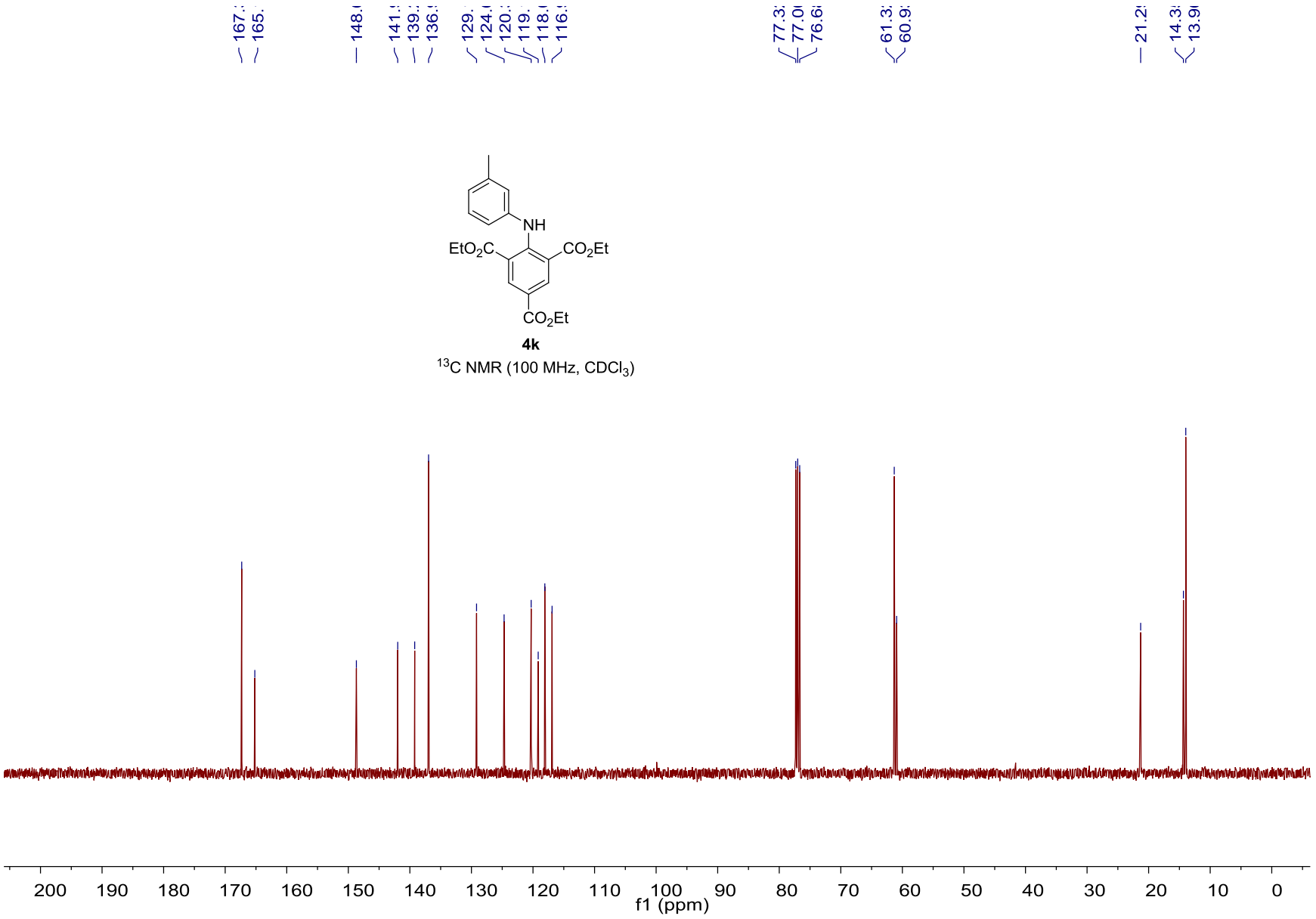

NH
EtO2C
CO2Et
CO2Et
4i
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NH
EtO2C
CO2Et
CO2Et
4i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


Cl
NH
EtO2C
CO2Et
CO2Et
4j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

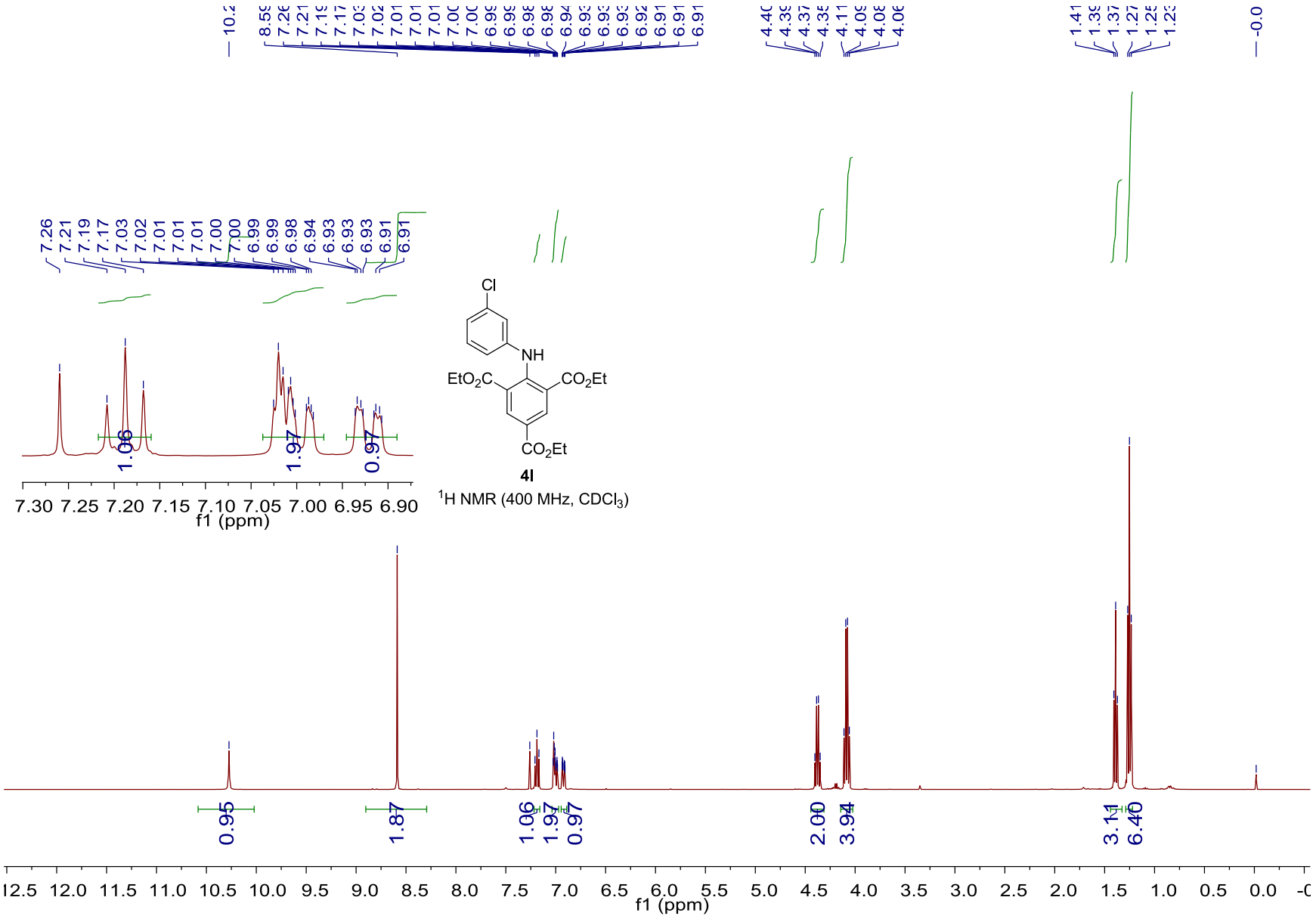

Cl
NH
EtO2C
CO2Et
CO2Et
4j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

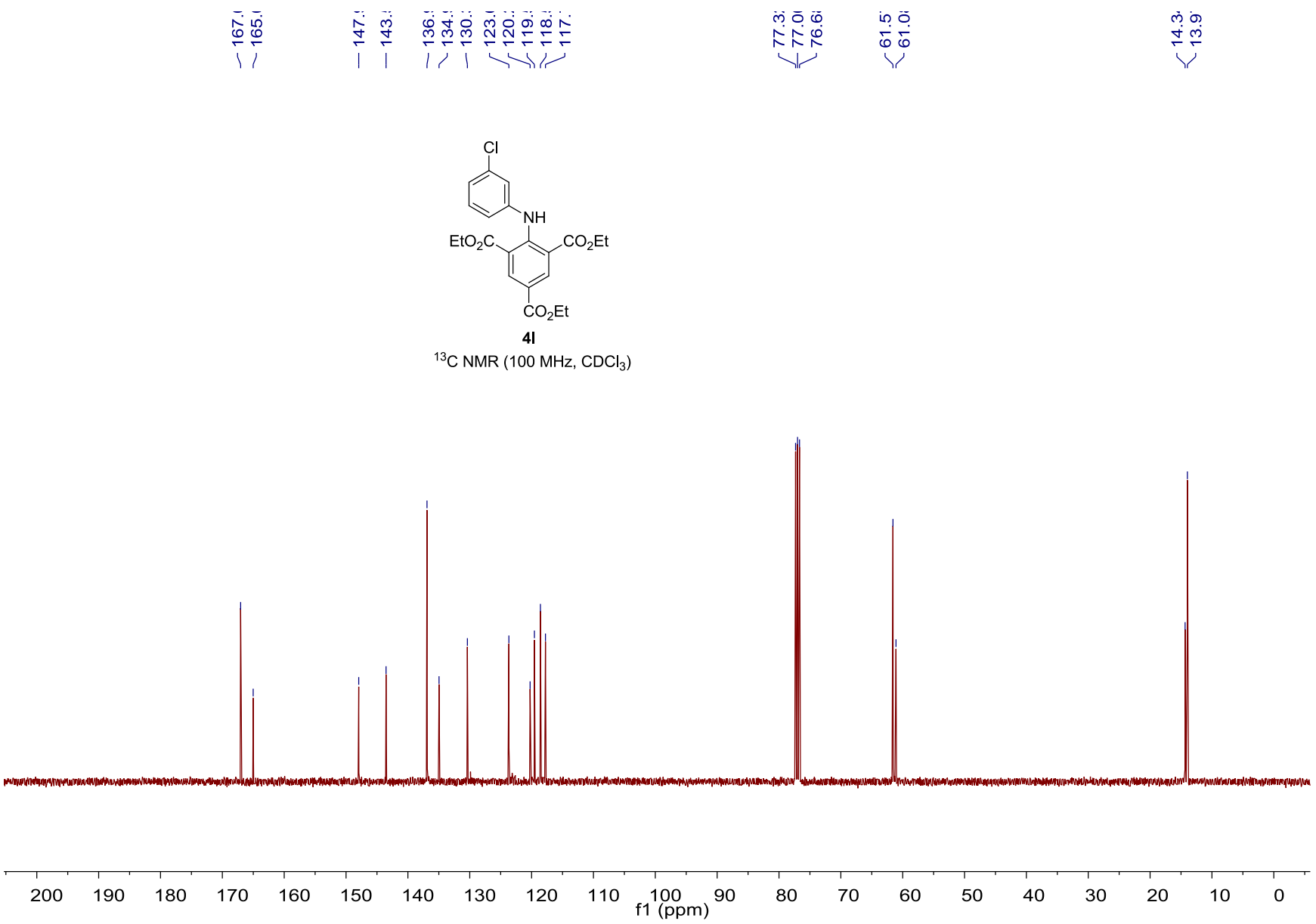

NH
EtO2C
CO2Et
CO2Et
4k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

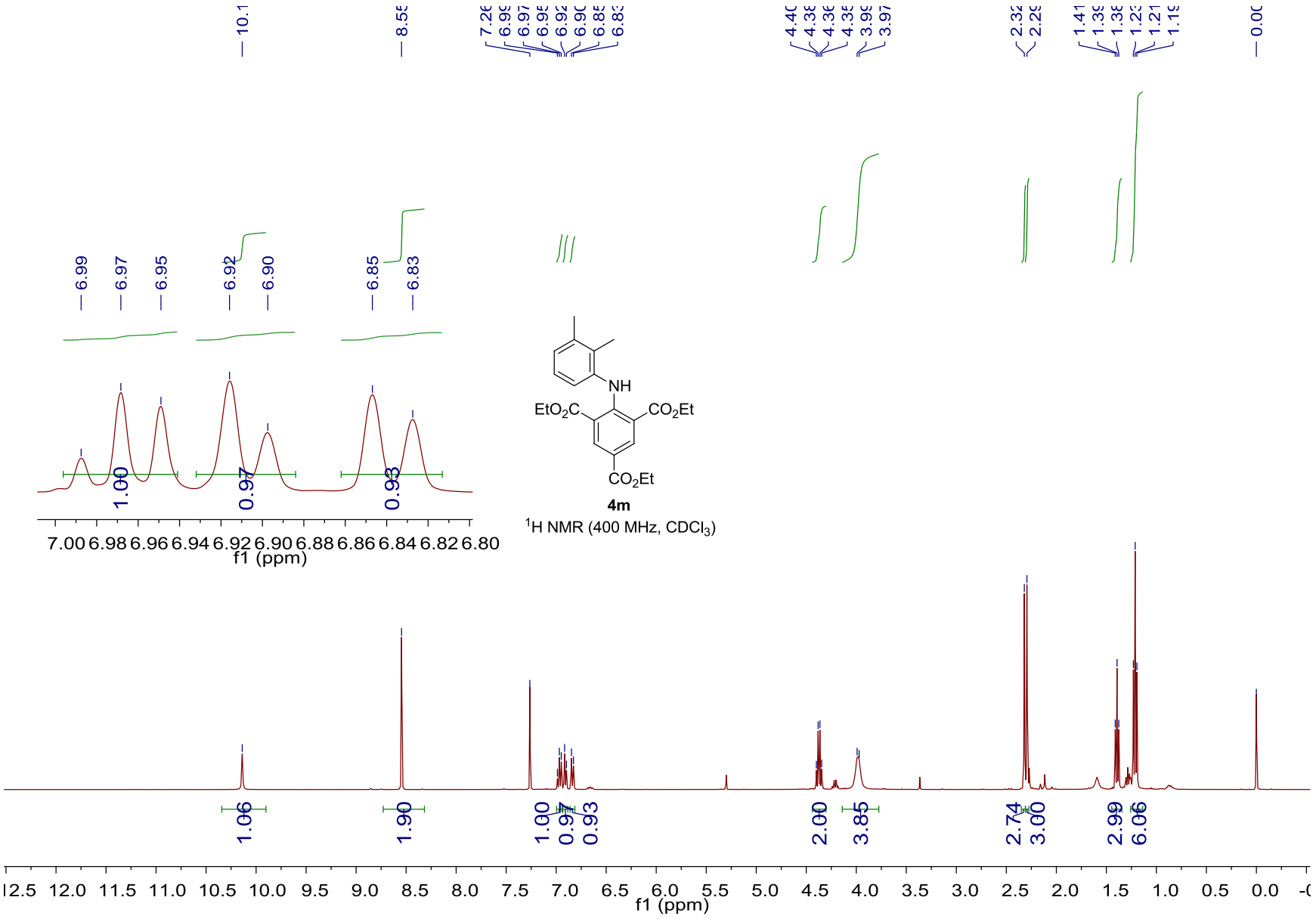


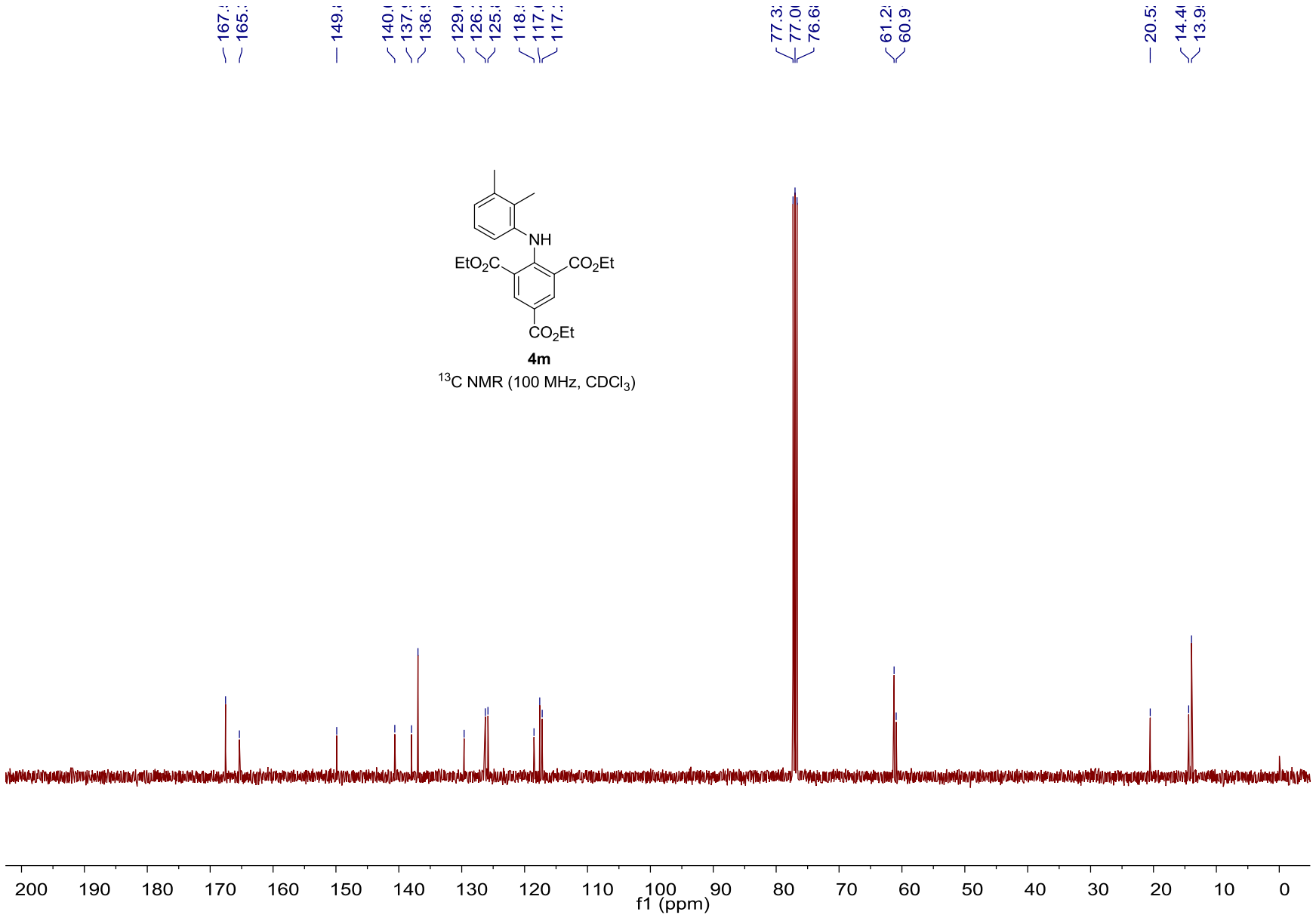
4k

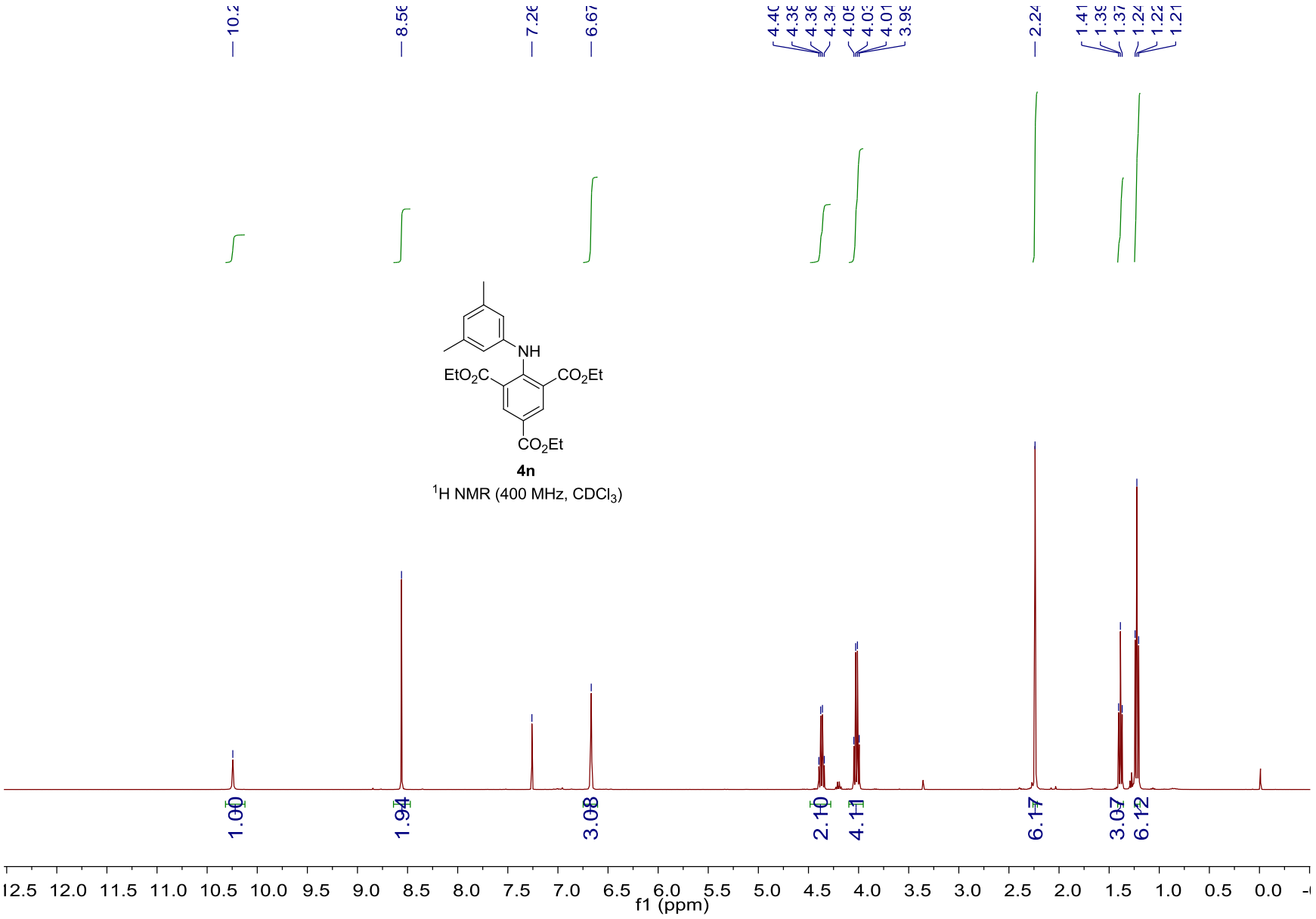
^{13}C NMR (100 MHz, $CDCl_3$)

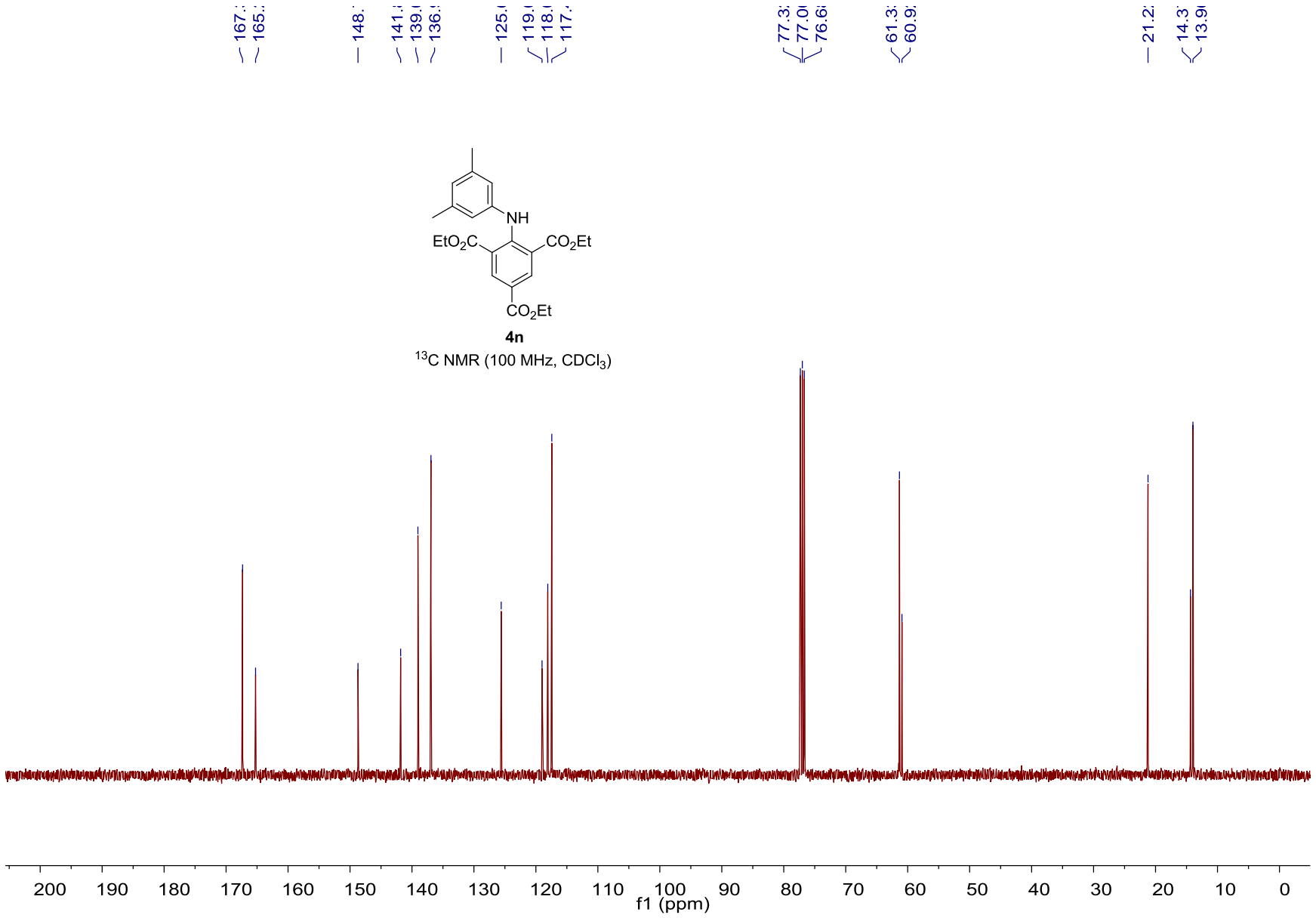

Cl
NH
EtO2C
CO2Et
CO2Et
4l
1H NMR (400 MHz, CDCl3)
f1 (ppm)

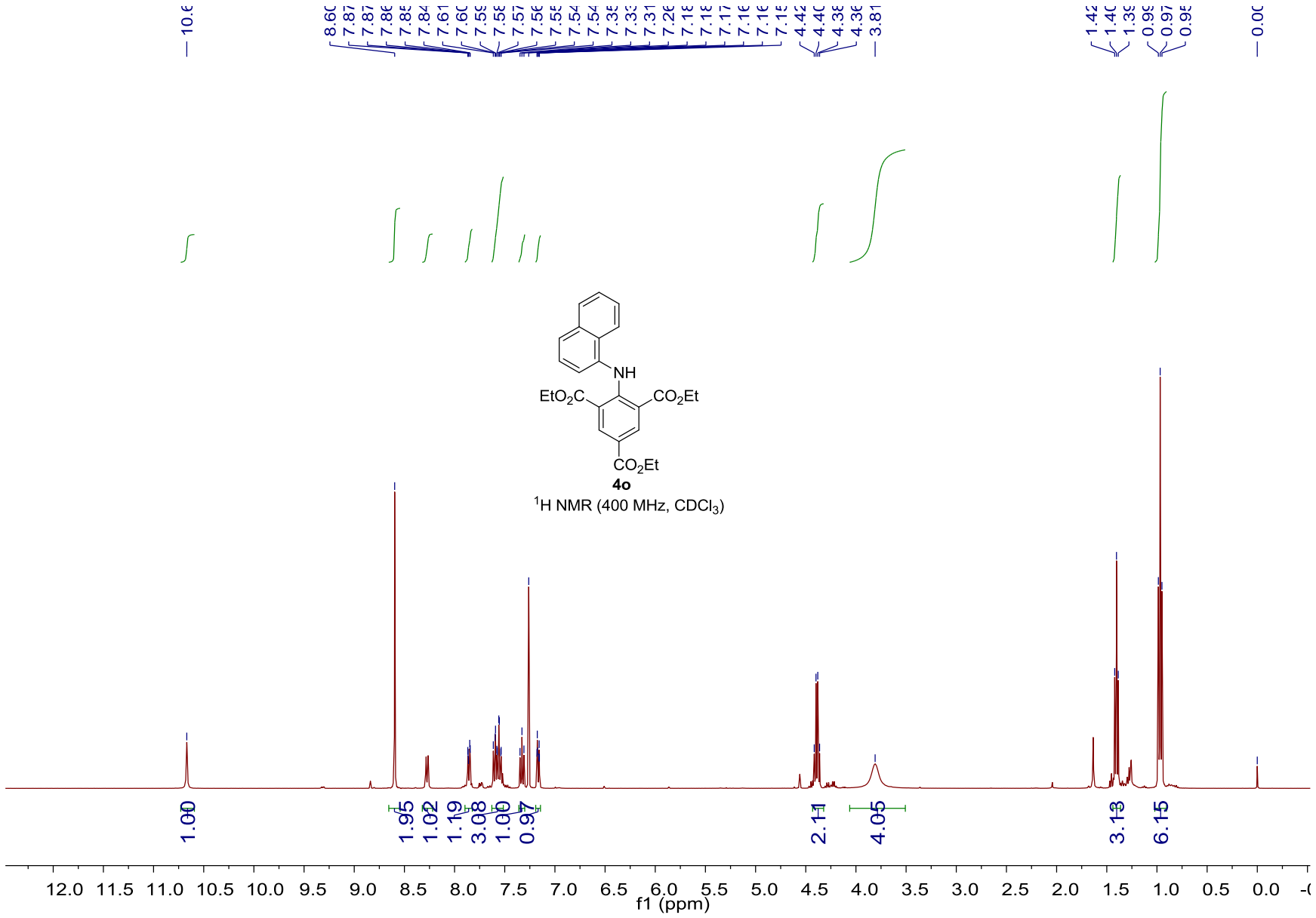

Cl
NH
EtO2C
CO2Et
CO2Et
4l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

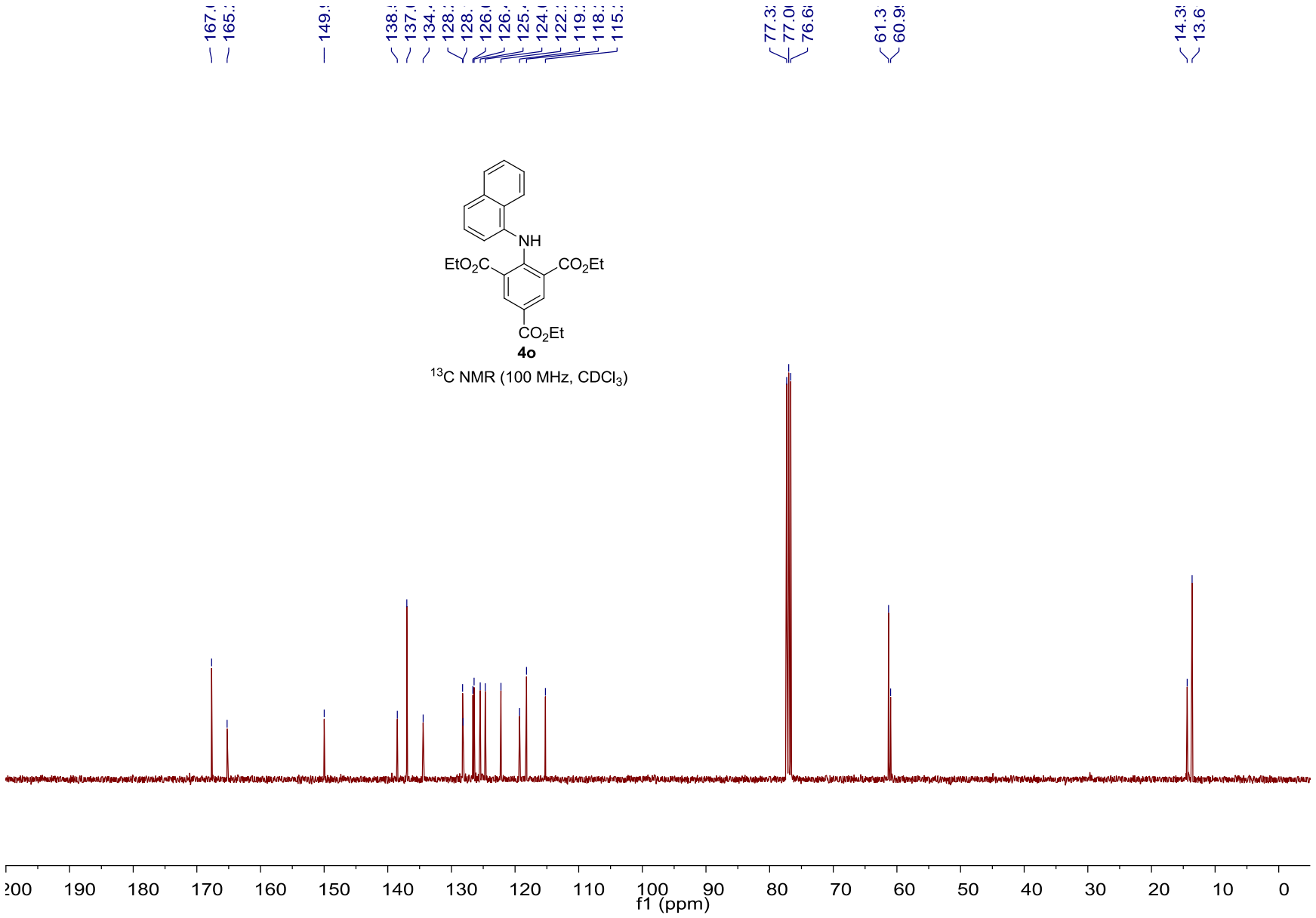

NH
EtO2C
CO2Et
CO2Et
4m
1H NMR (400 MHz, CDCl3)
f1 (ppm)

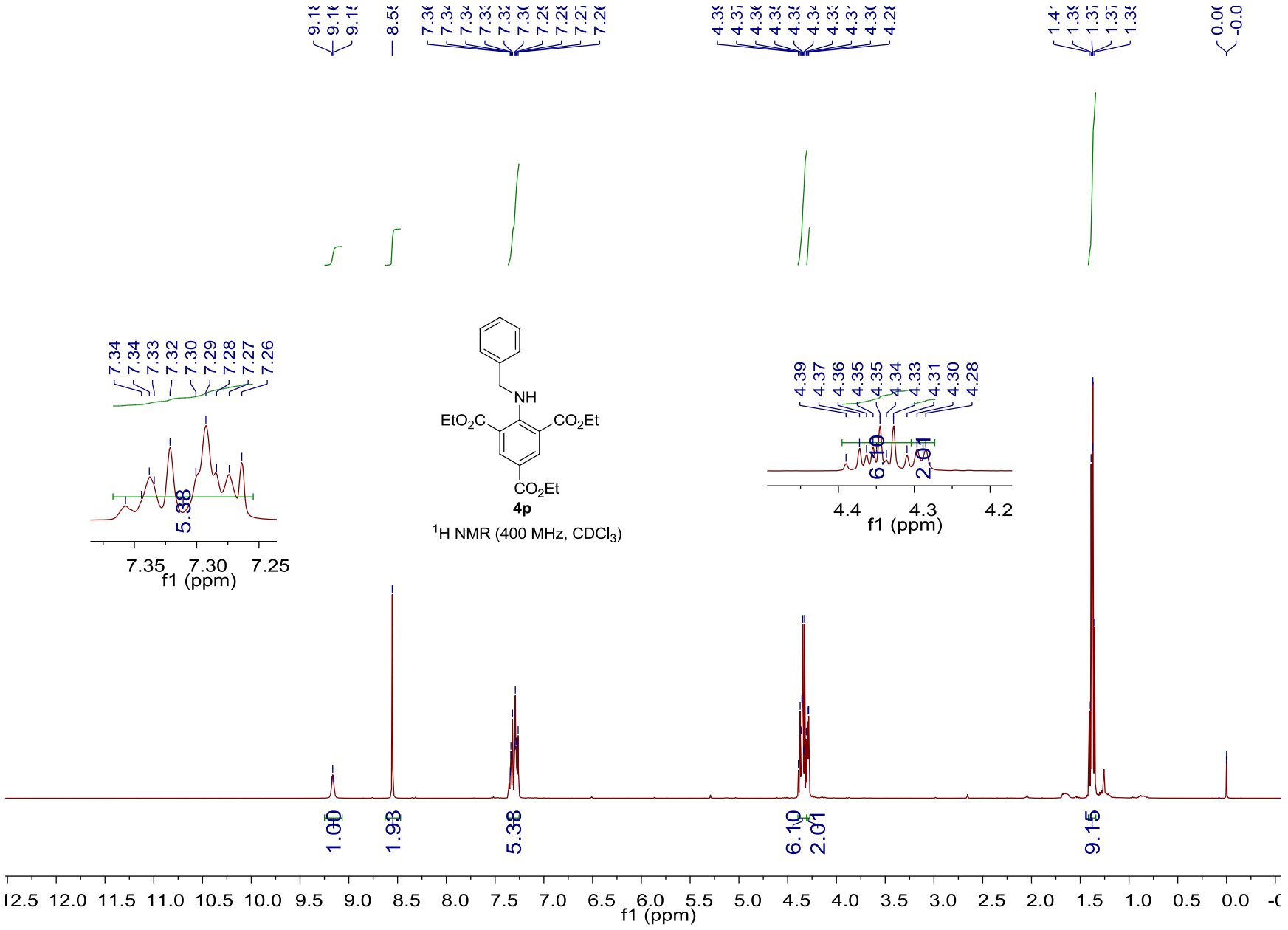

NH
EtO2C
CO2Et
CO2Et
4m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

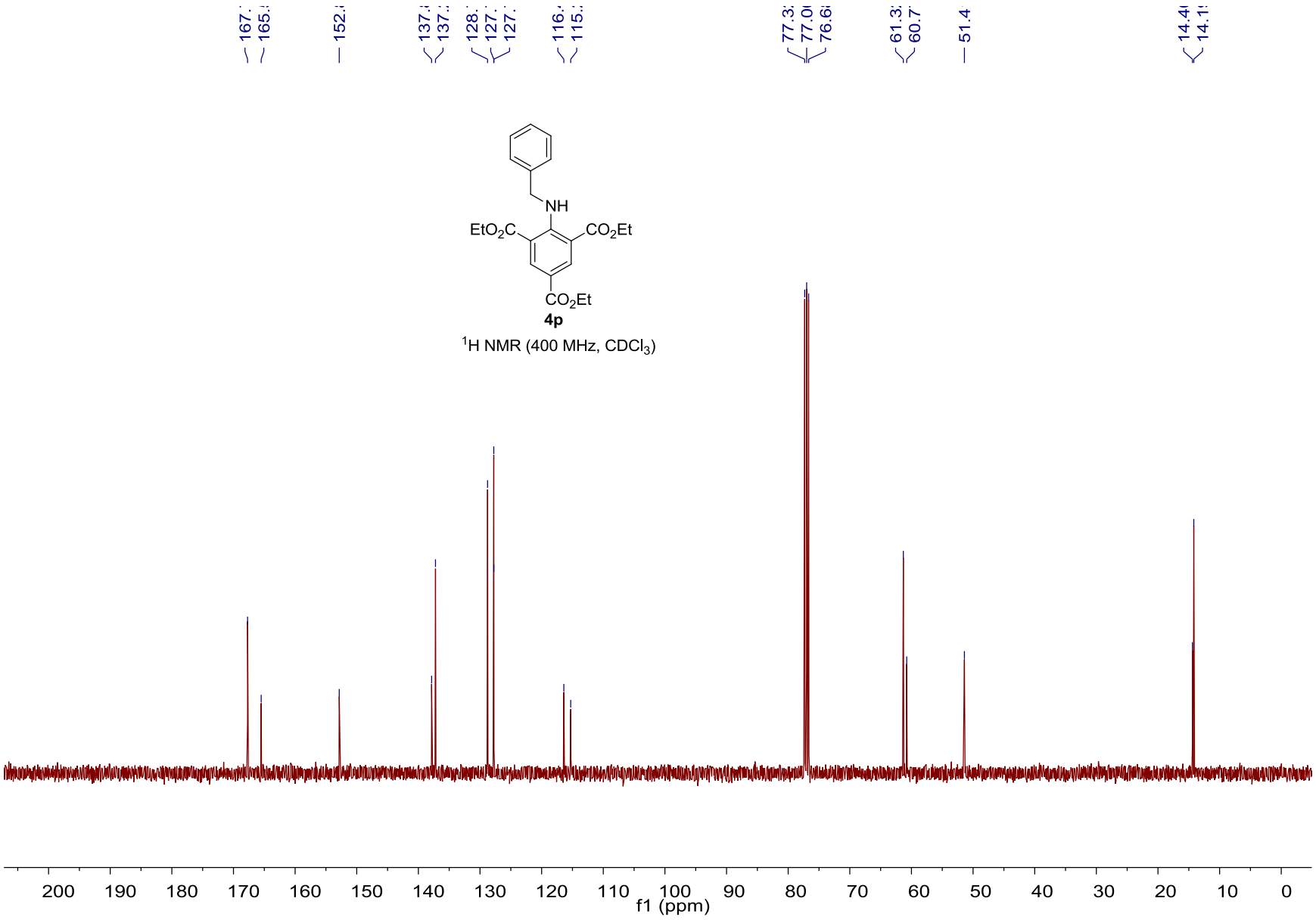

NH
EtO2C
CO2Et
CO2Et
4n
1H NMR (400 MHz, CDCl3)
1.00
1.94
3.08
2.10
4.11
6.17
3.07
6.12
f1 (ppm)

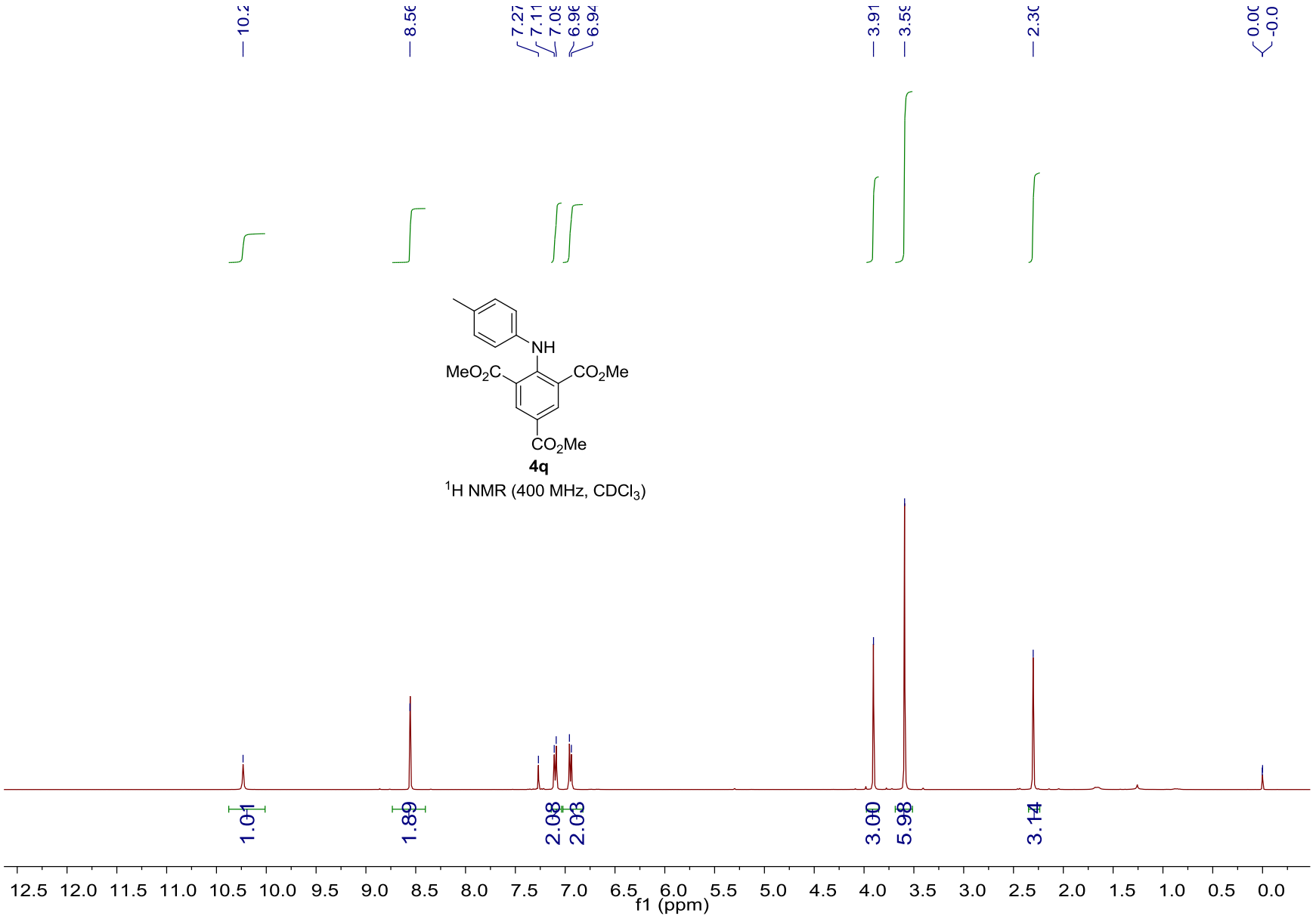

NH
EtO2C
CO2Et
CO2Et
4n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

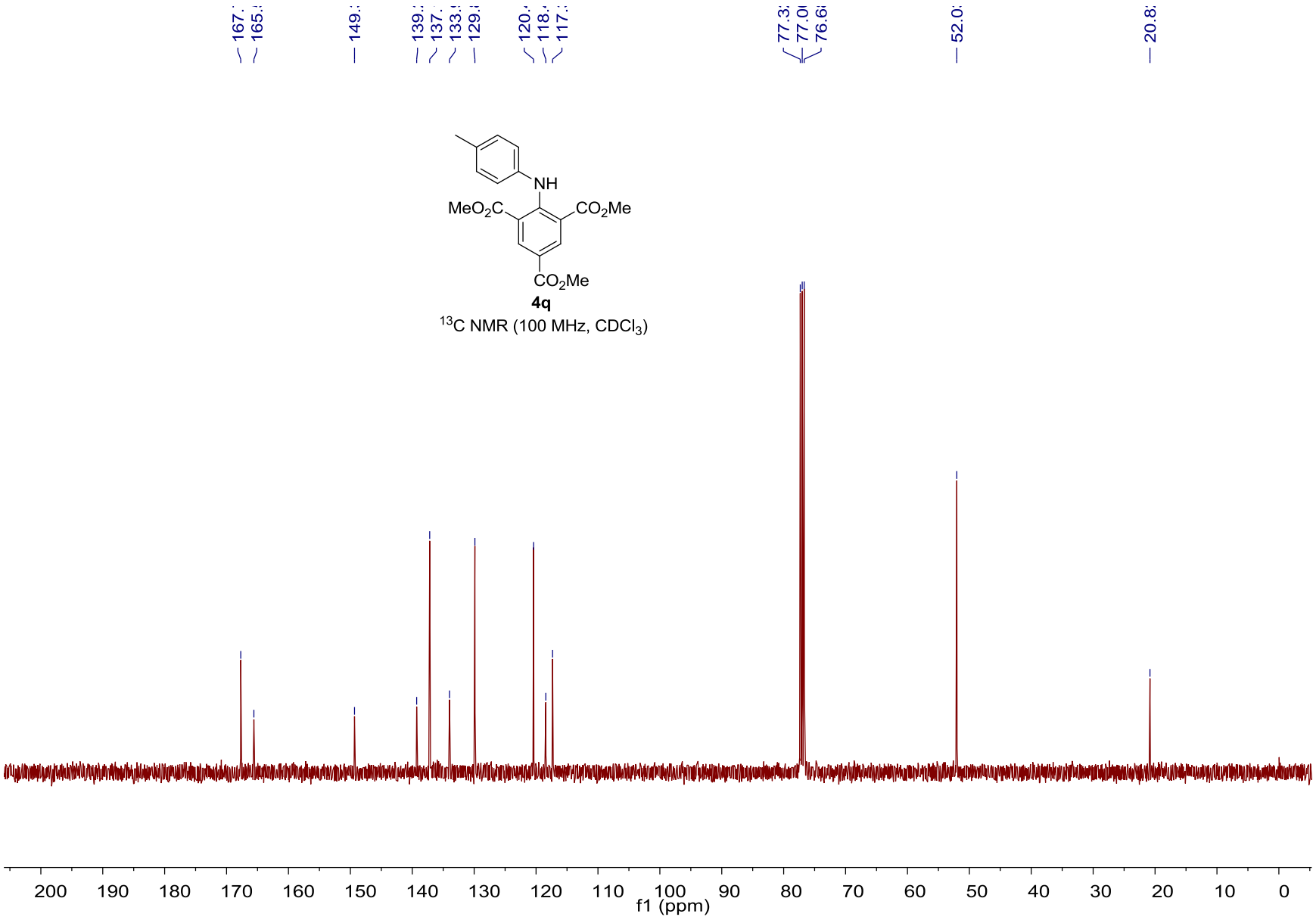

NH
EtO2C
CO2Et
CO2Et
4o
1H NMR (400 MHz, CDCl3)
f1 (ppm)

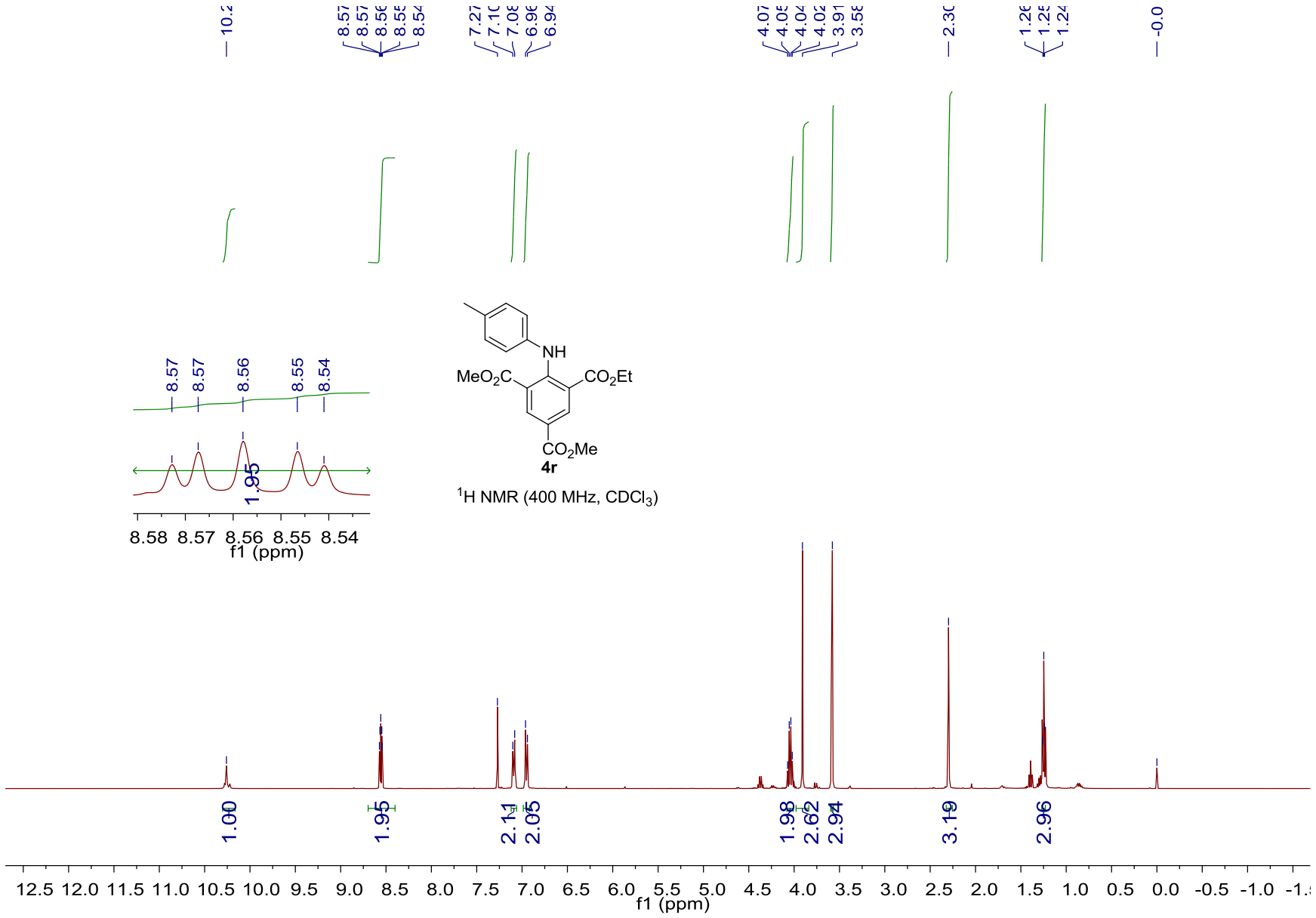

NH
EtO2C
CO2Et
CO2Et
4o
13C NMR (100 MHz, CDCl3)
f1 (ppm)

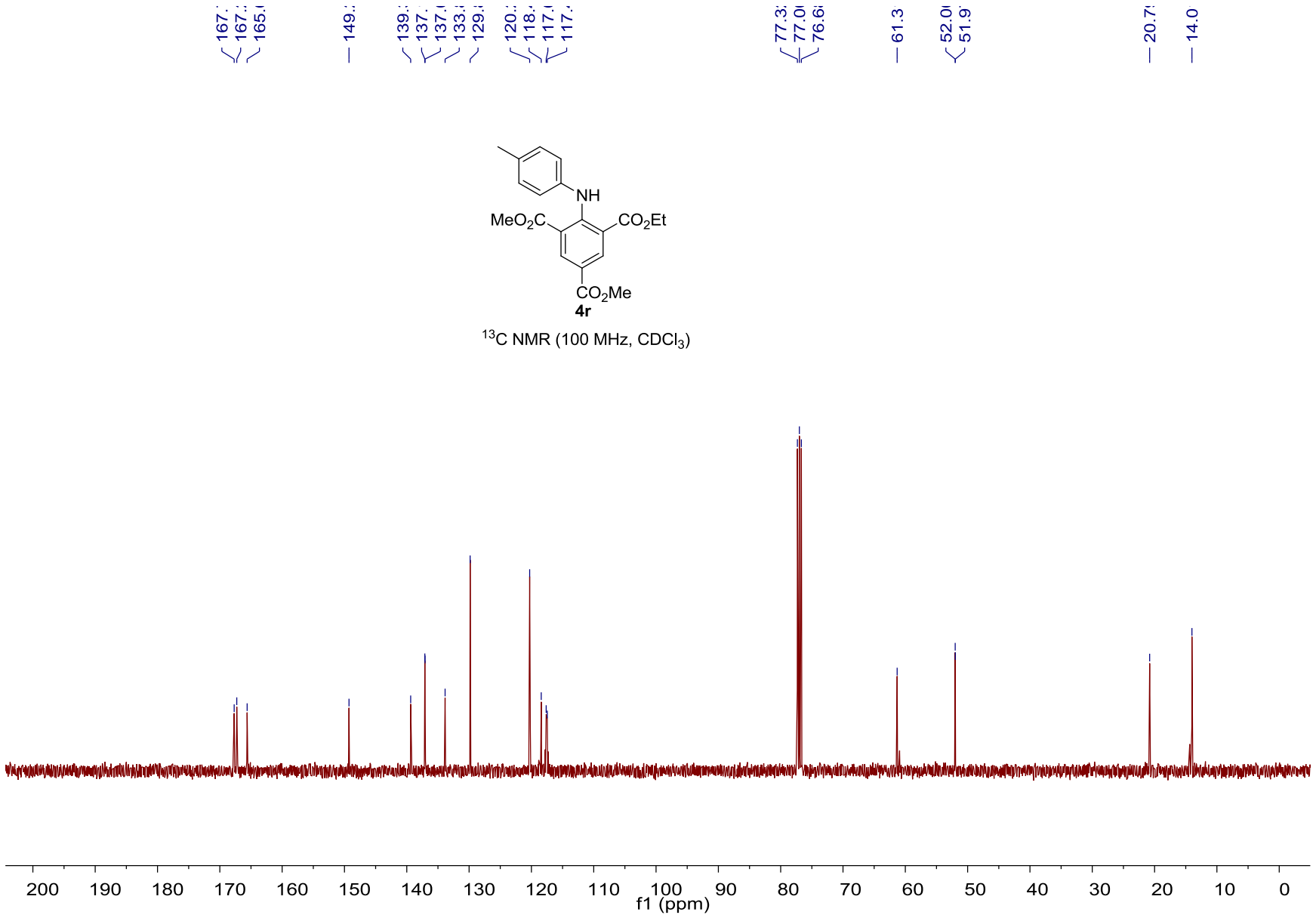

NH
EtO2C
CO2Et
CO2Et
4p
1H NMR (400 MHz, CDCl3)
f1 (ppm)
1.00
1.93
5.38
6.10
2.01
9.15

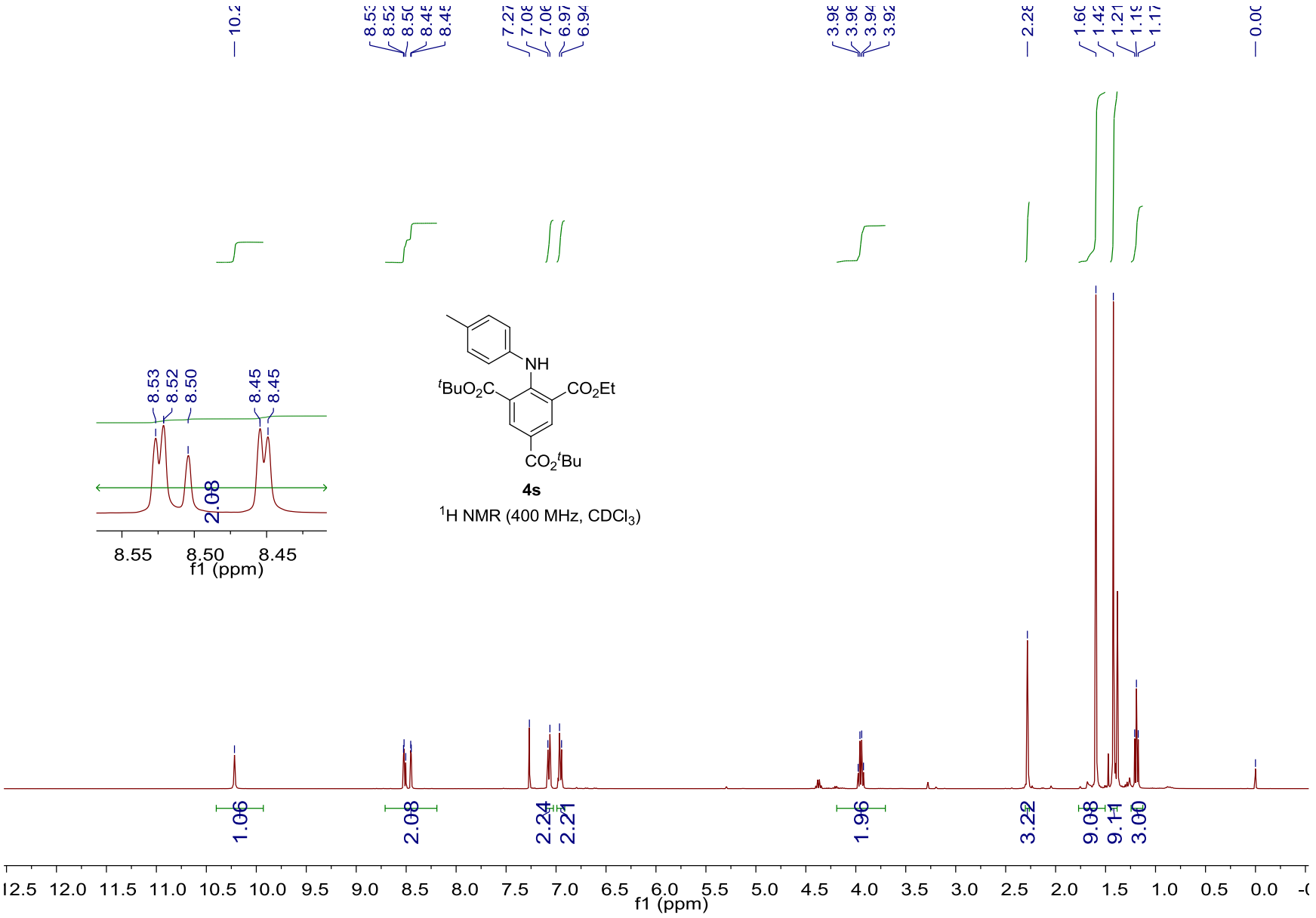

NH
EtO2C
CO2Et
CO2Et
4p
1H NMR (400 MHz, CDCl3)
f1 (ppm)

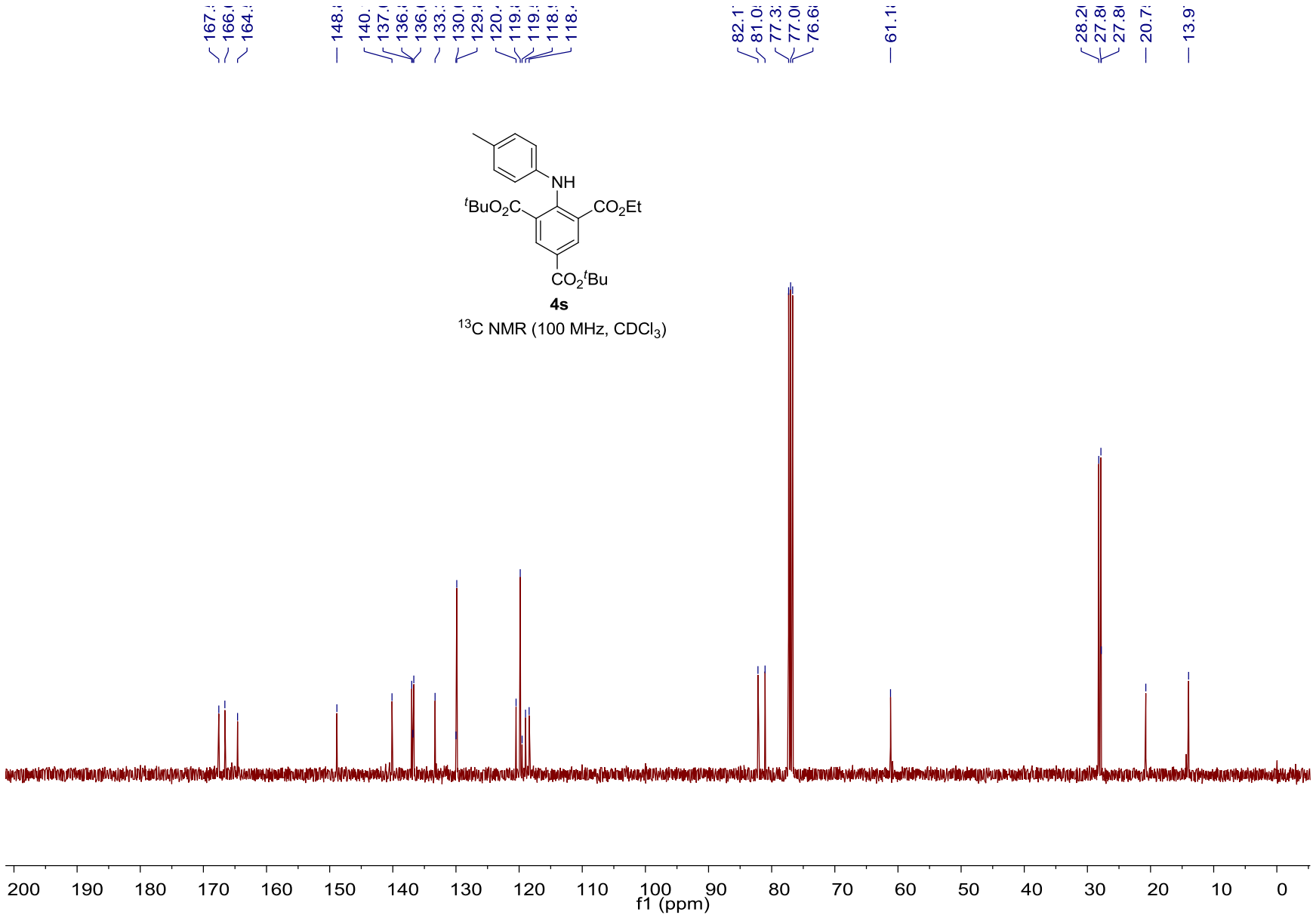

NH
MeO2C
CO2Me
CO2Me
4q
1H NMR (400 MHz, CDCl3)
f1 (ppm)

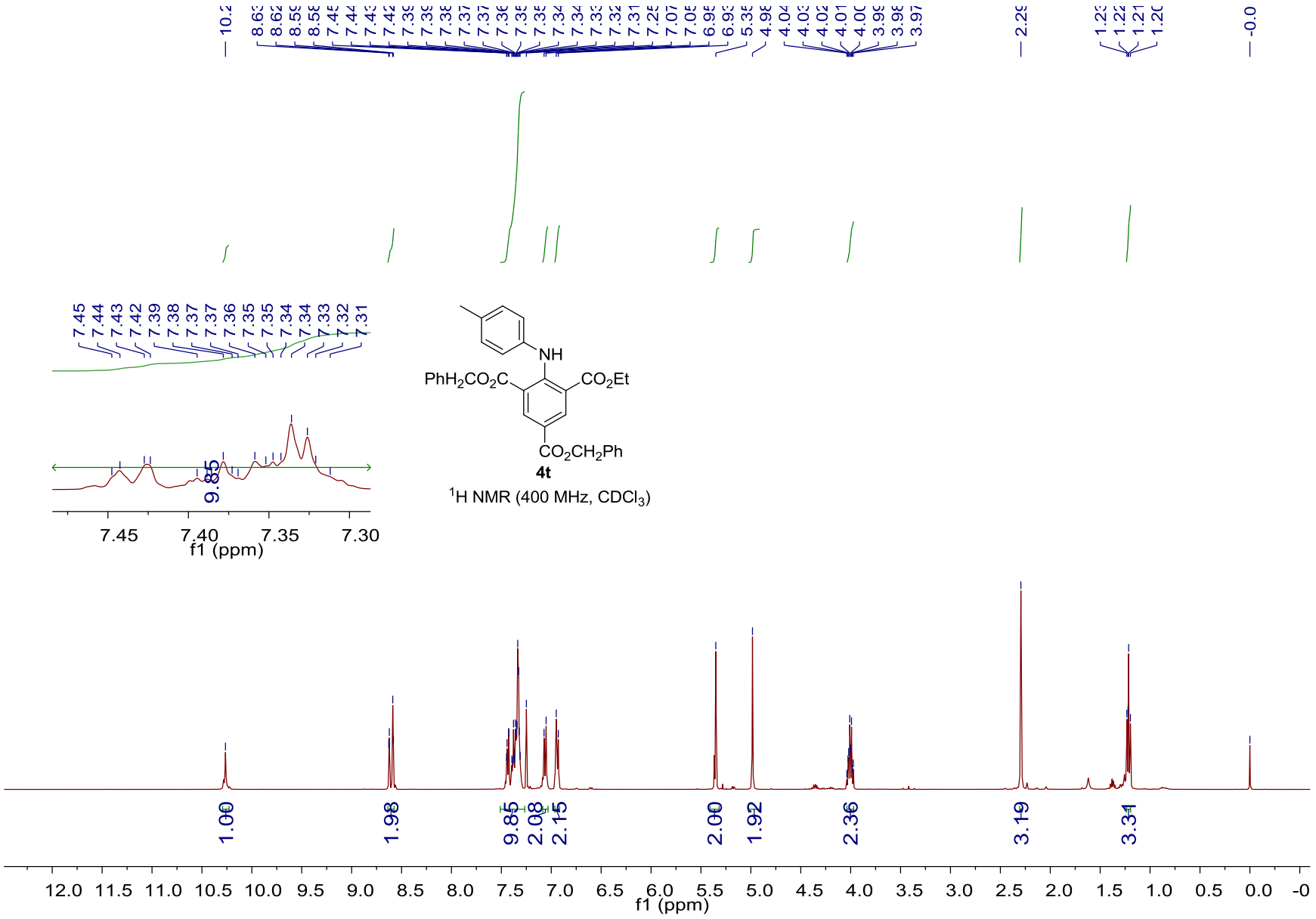

NH
MeO2C
CO2Me
CO2Me
4q
13C NMR (100 MHz, CDCl3)
f1 (ppm)

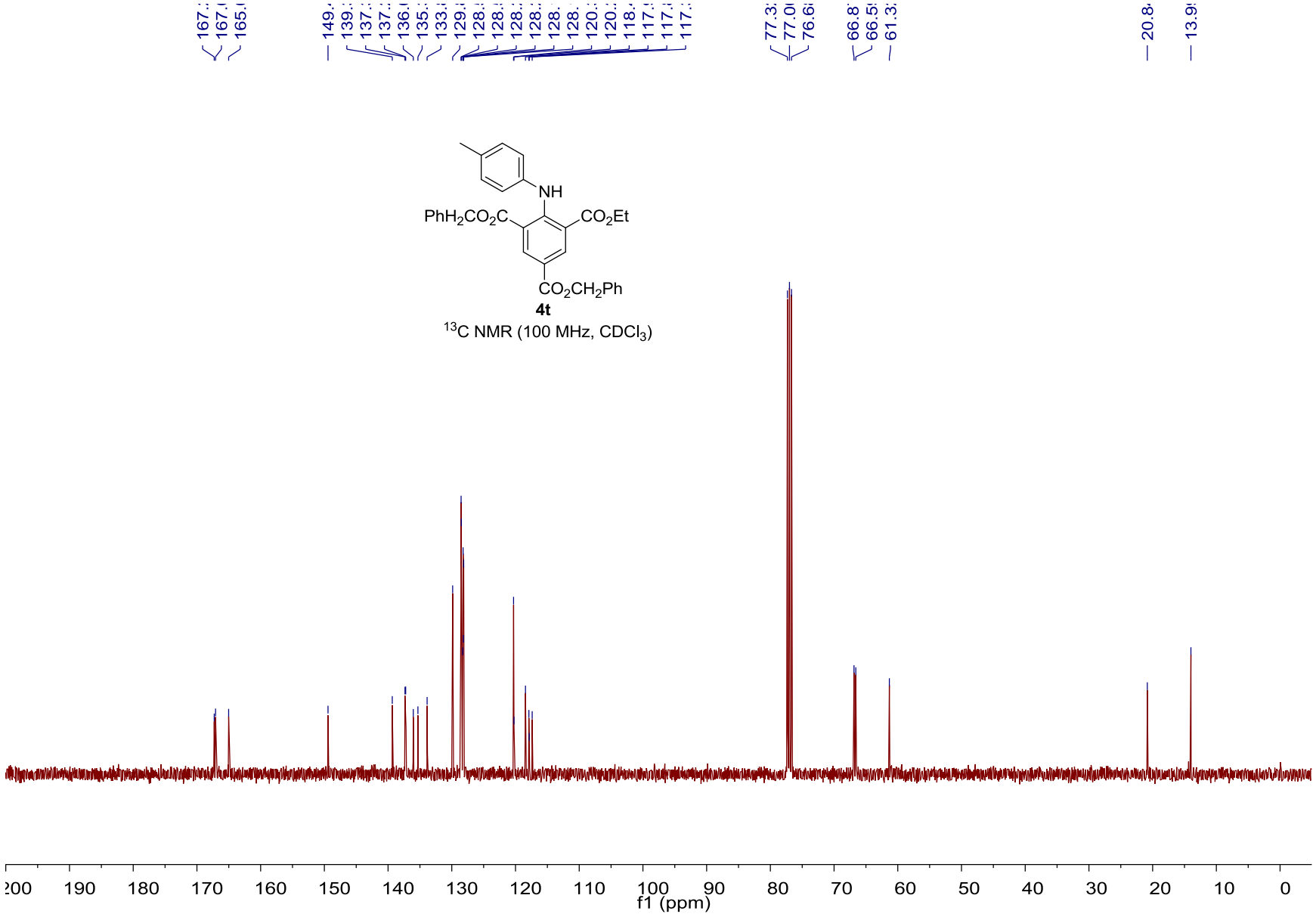

8.57
8.57
8.56
8.55
8.54
1.95
8.58 8.57 8.56 8.55 8.54
f1 (ppm)
NH
MeO2C
CO2Et
CO2Me
4r
1H NMR (400 MHz, CDCl3)
1.00
1.95
2.11
2.05
1.98
2.62
2.94
3.19
2.96
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

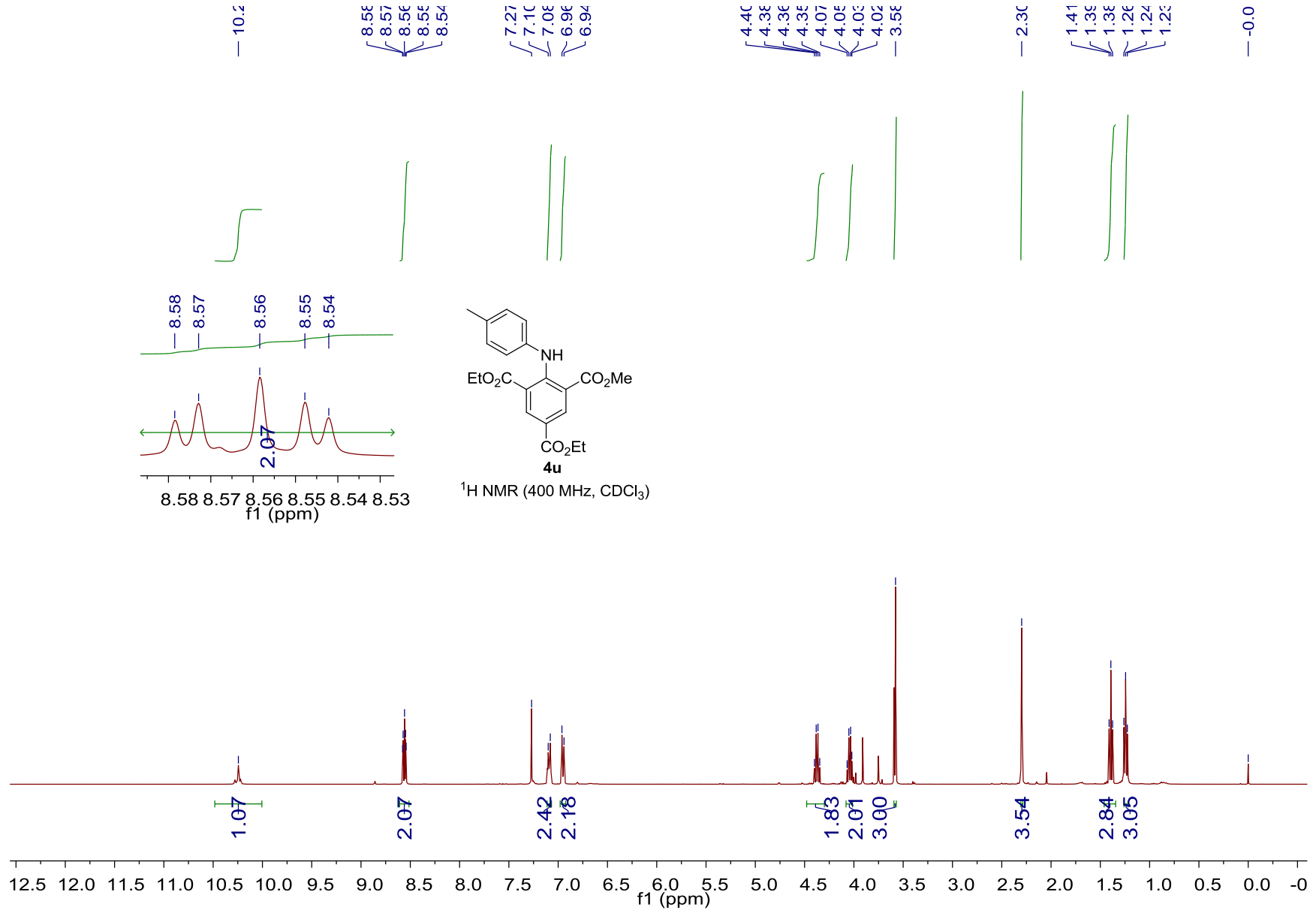

167.
167.
165.
149.
139.
137.
137.
133.
129.
120.
118.
117.
117.
77.3
77.0
76.6
61.3
52.0
51.9
20.7
14.0
NH
MeO2C
CO2Et
CO2Me
4r
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

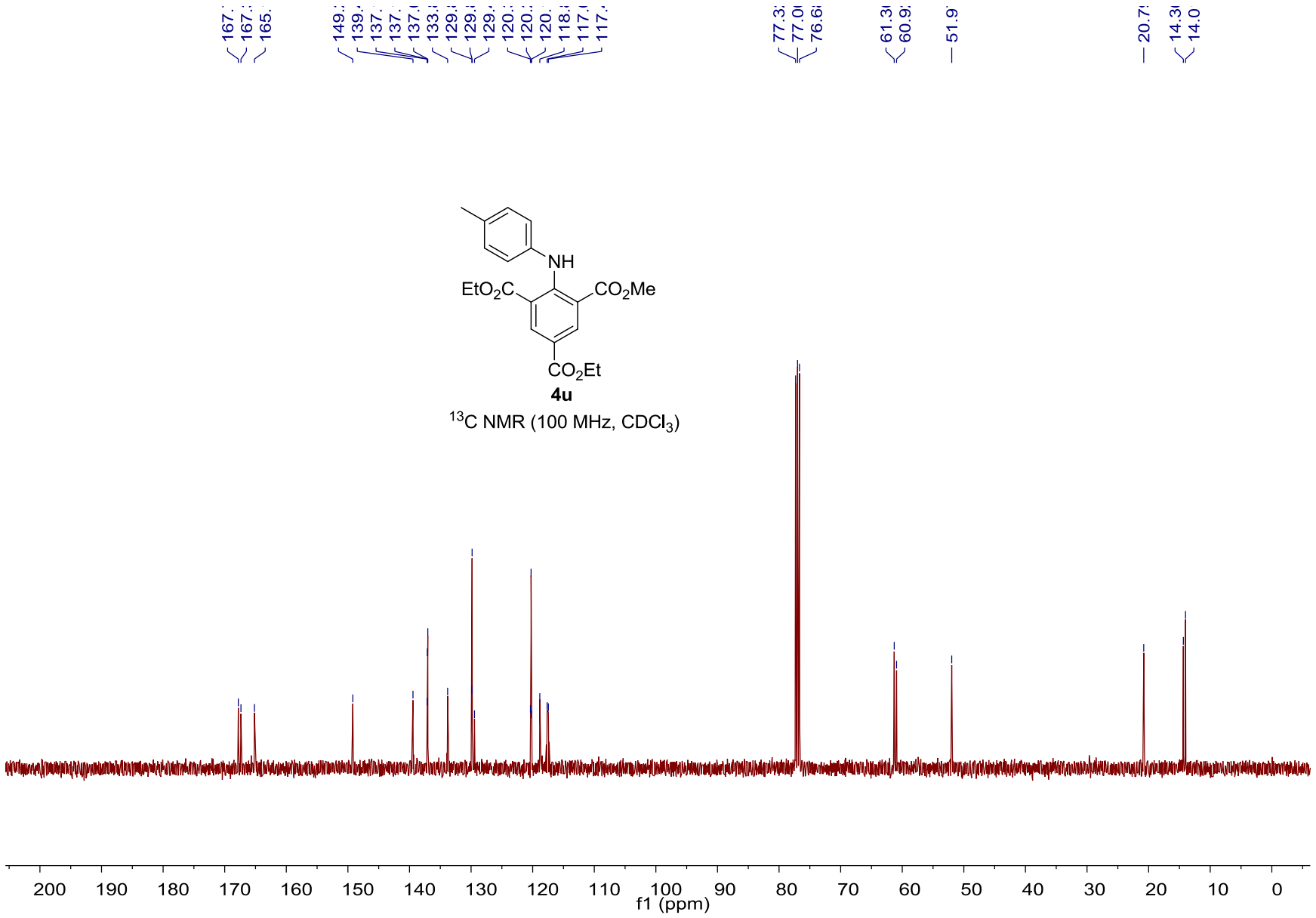

8.53
8.52
8.50
8.45
8.45
2.08
8.55
8.50
8.45
f1 (ppm)
NH
tBuO2C
CO2Et
CO2tBu
4s
1H NMR (400 MHz, CDCl3)
1.06
2.08
2.24
2.21
1.96
3.22
9.08
9.11
3.00
f1 (ppm)

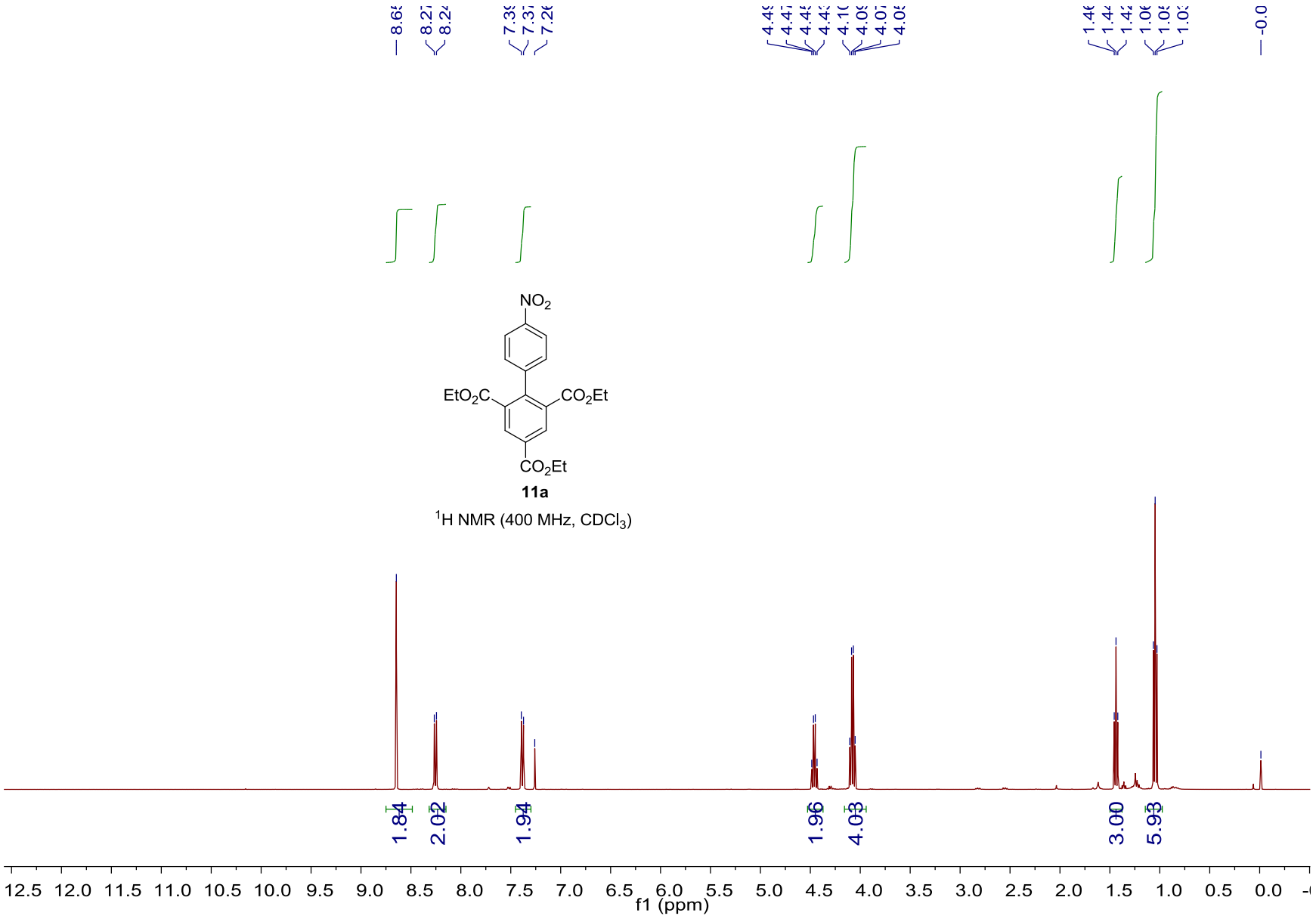

NH
^{t}BuO$_2$C
CO$_2$Et
CO$_2$^{t}Bu
4s
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

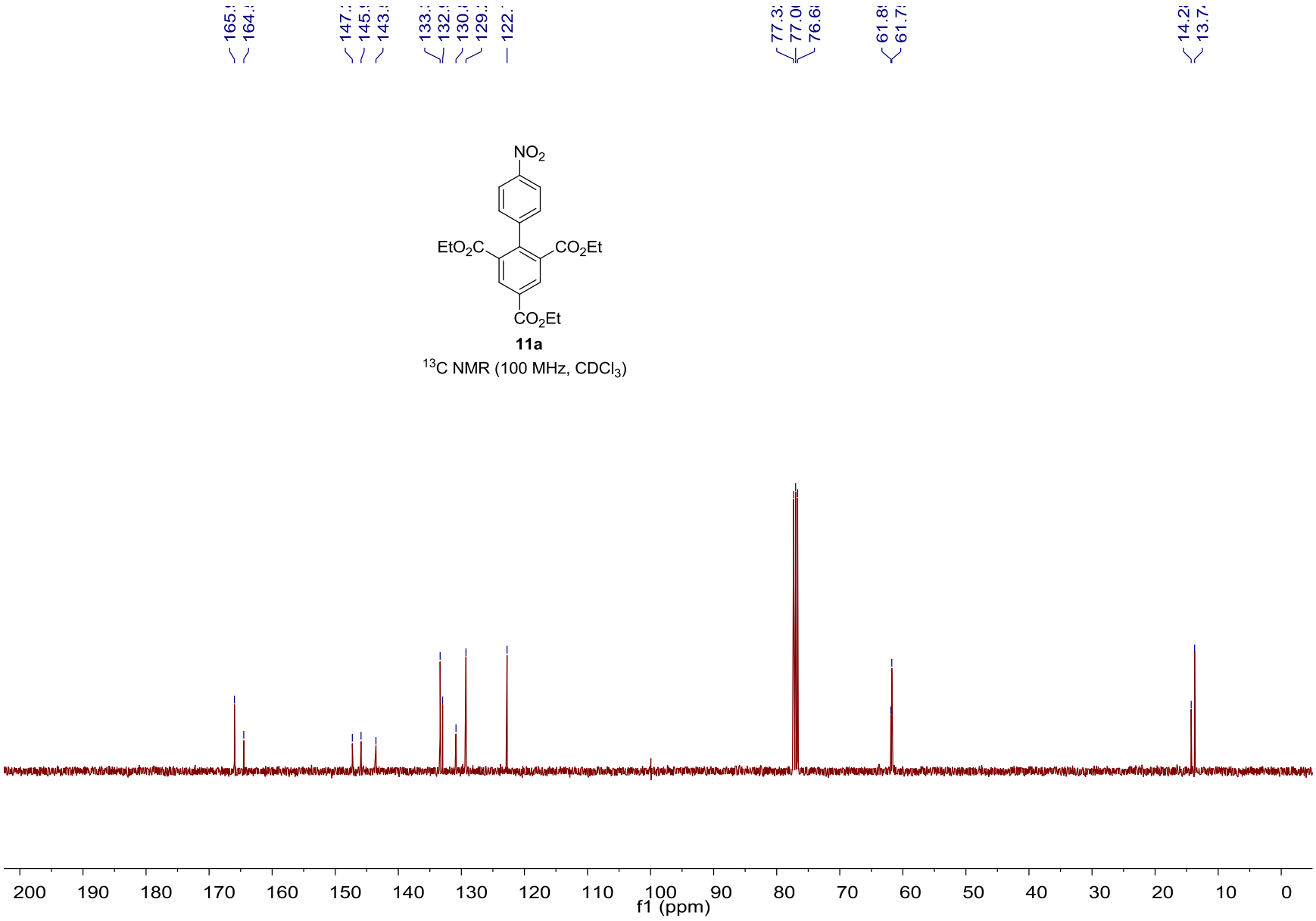

NH
PhH2CO2C
CO2Et
CO2CH2Ph
4t
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NH
PhH2CO2C
CO2Et
CO2CH2Ph
4t
13C NMR (100 MHz, CDCl3)
f1 (ppm)


8.58
8.57
8.56
8.55
8.54
2.07
8.58 8.57 8.56 8.55 8.54 8.53
f1 (ppm)
NH
EtO2C
CO2Me
CO2Et
4u
1H NMR (400 MHz, CDCl3)
1.07
2.07
2.42
2.18
1.83
2.01
3.00
3.54
2.84
3.05
12.5 12.0 11.5 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
f1 (ppm)

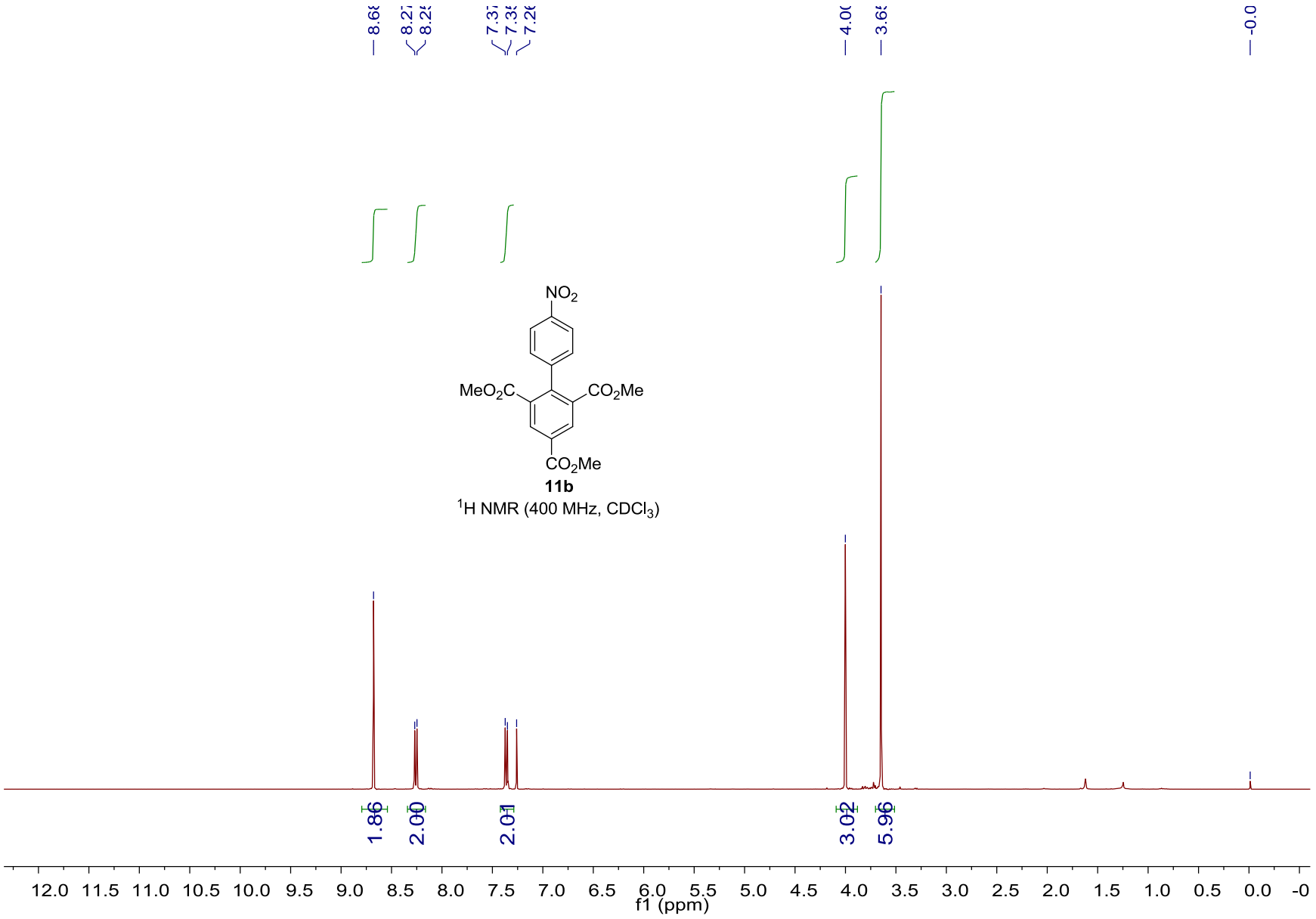

NH
EtO2C
CO2Me
CO2Et
4u
13C NMR (100 MHz, CDCl3)
f1 (ppm)

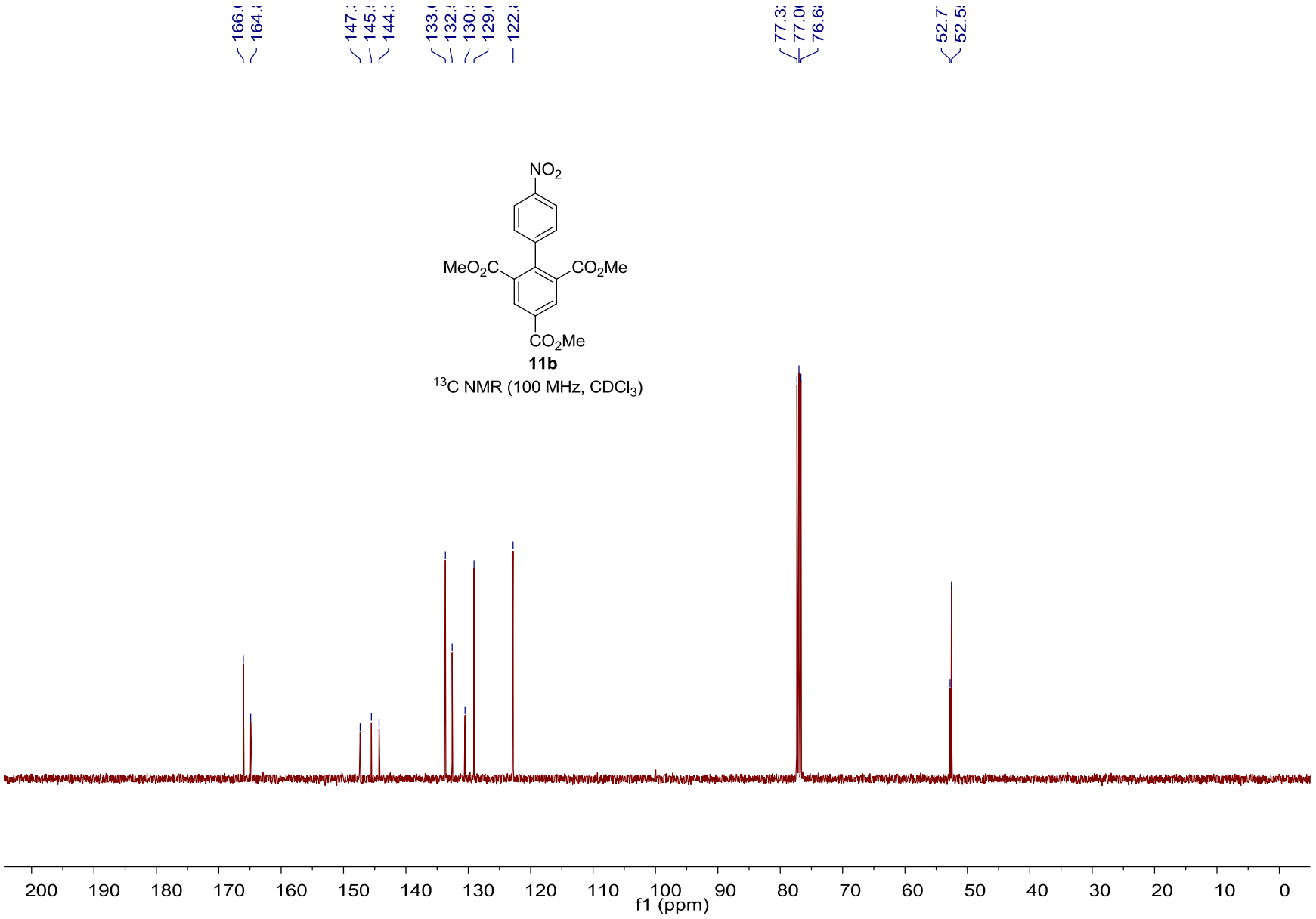

NO2
EtO2C
CO2Et
CO2Et
11a
1H NMR (400 MHz, CDCl3)
1.84
2.02
1.94
1.96
4.03
3.00
5.93
f1 (ppm)

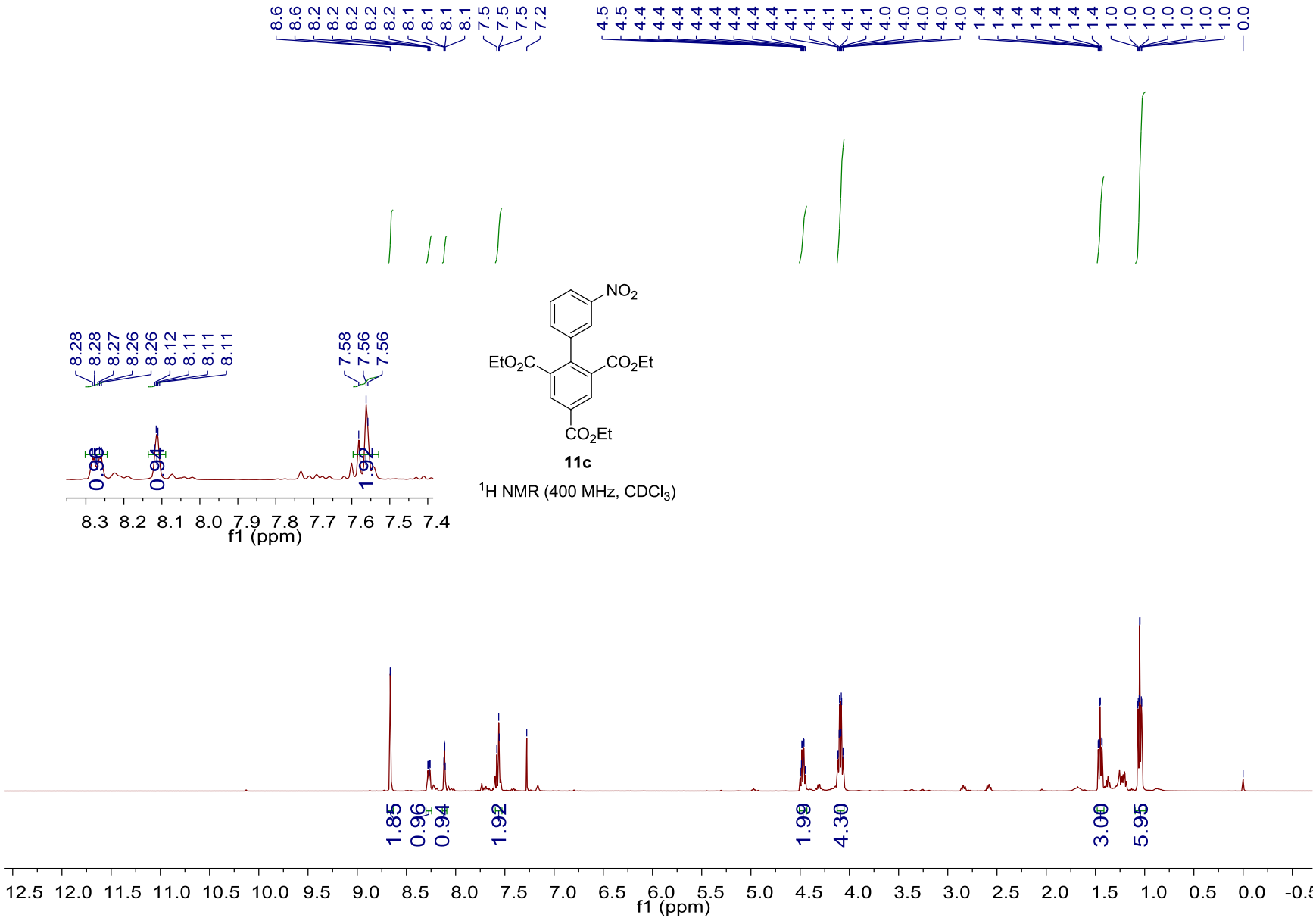


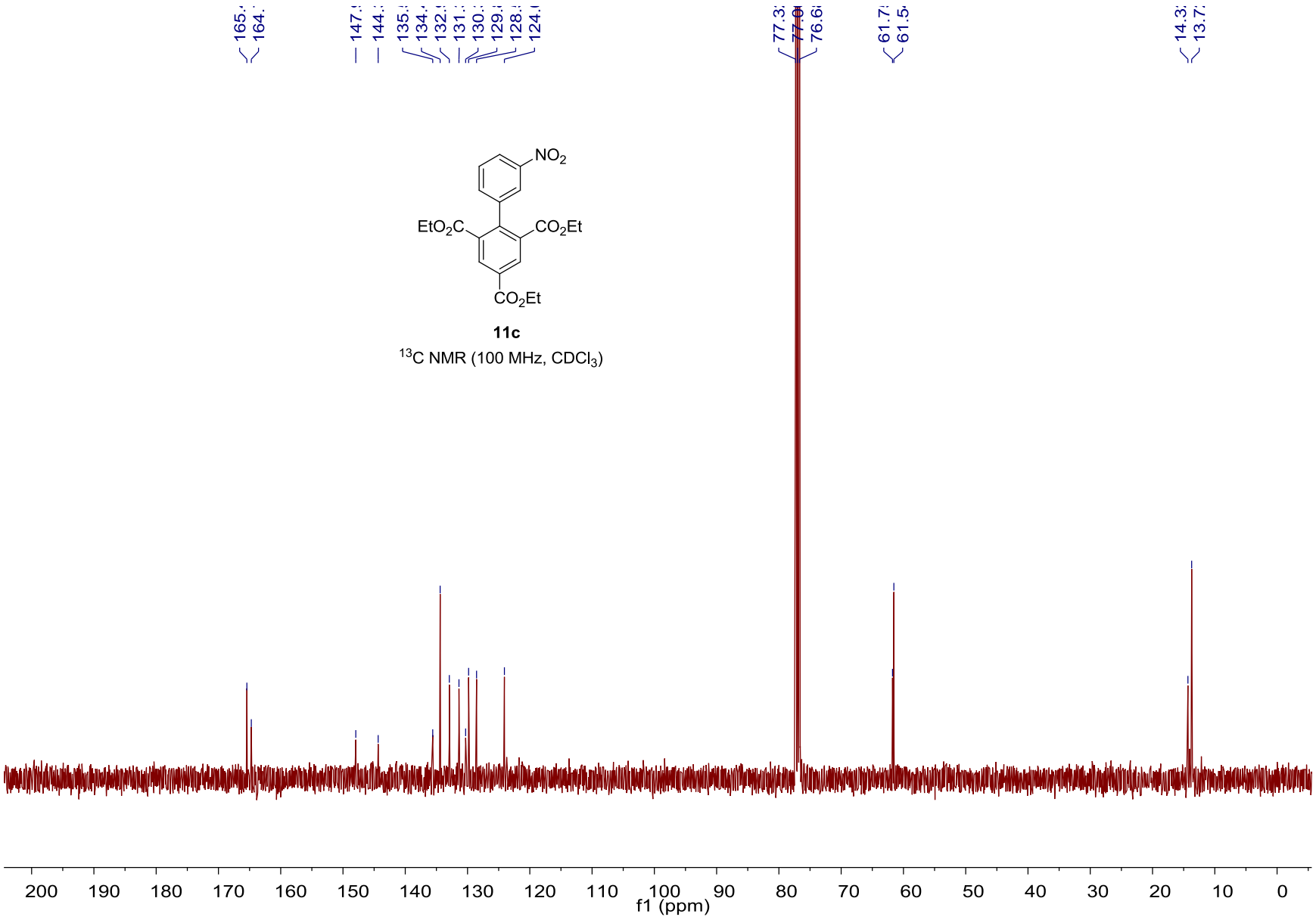
11a

^{13}C NMR (100 MHz, $CDCl_3$)


NO2
MeO2C
CO2Me
CO2Me
11b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

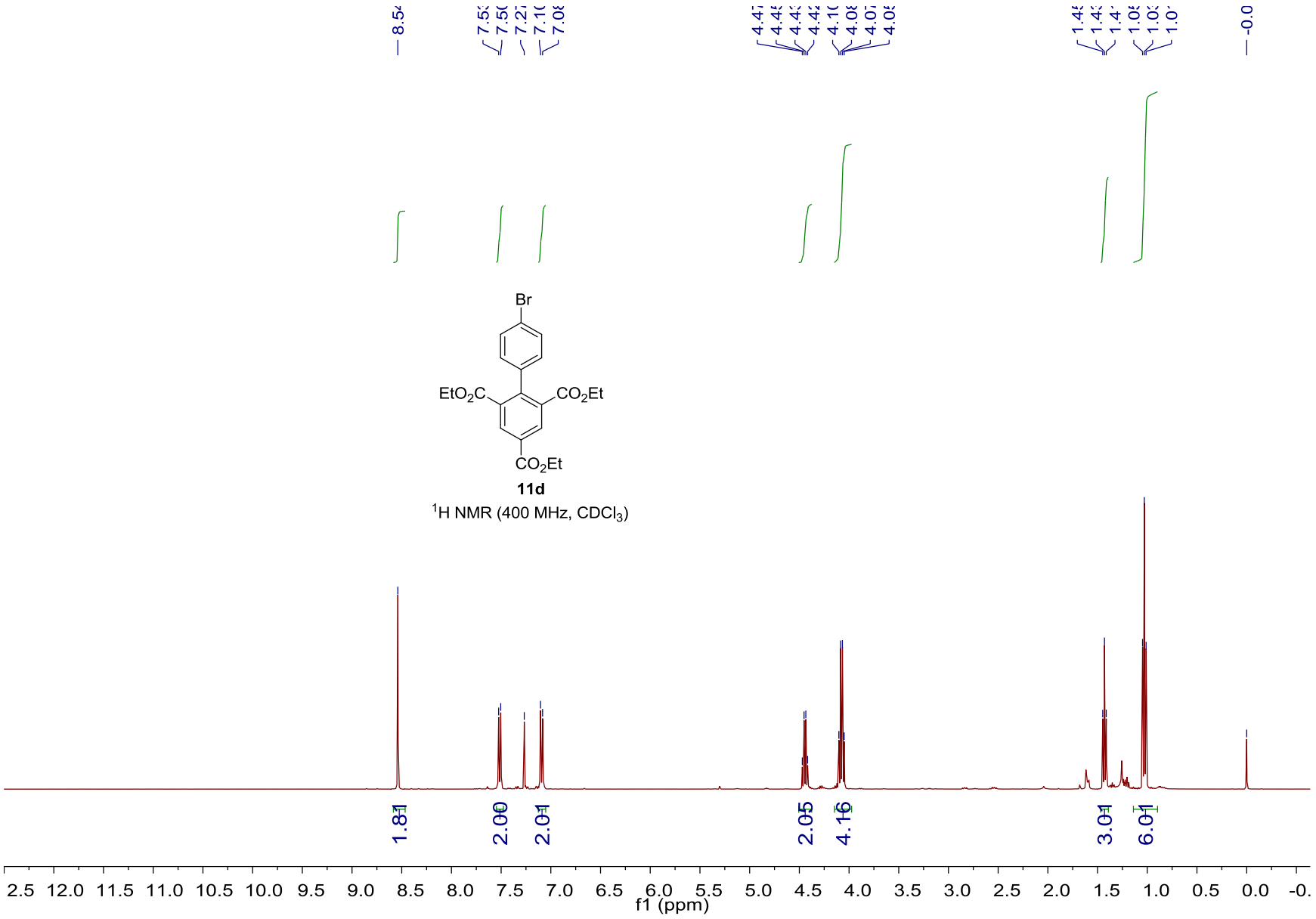

166.
164.
147.
145.
144.
133.
132.
130.
129.
122.
77.3
77.0
76.6
52.7
52.5
NO2
MeO2C
CO2Me
CO2Me
11b
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

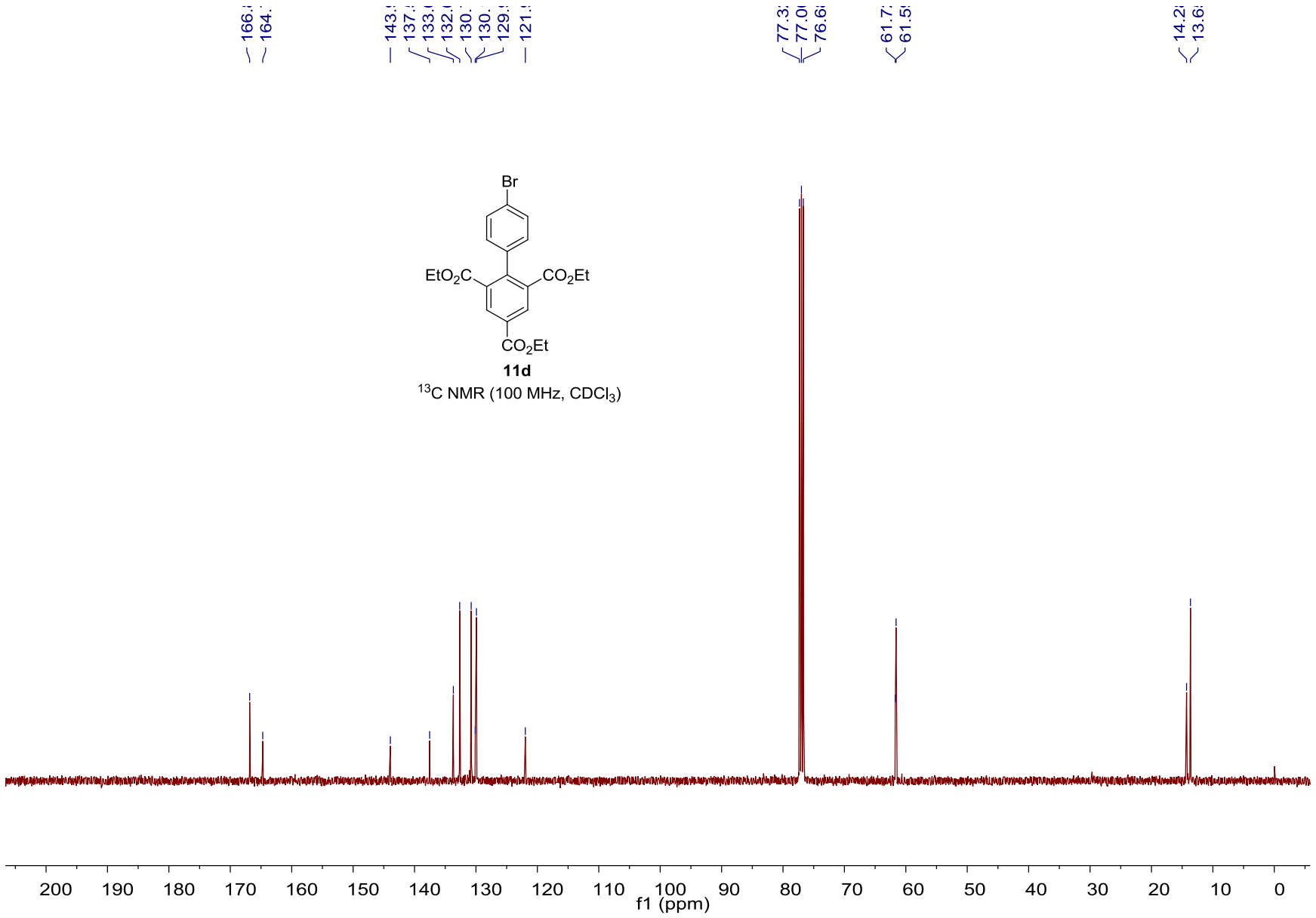

NO2
EtO2C
CO2Et
CO2Et
11c
1H NMR (400 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

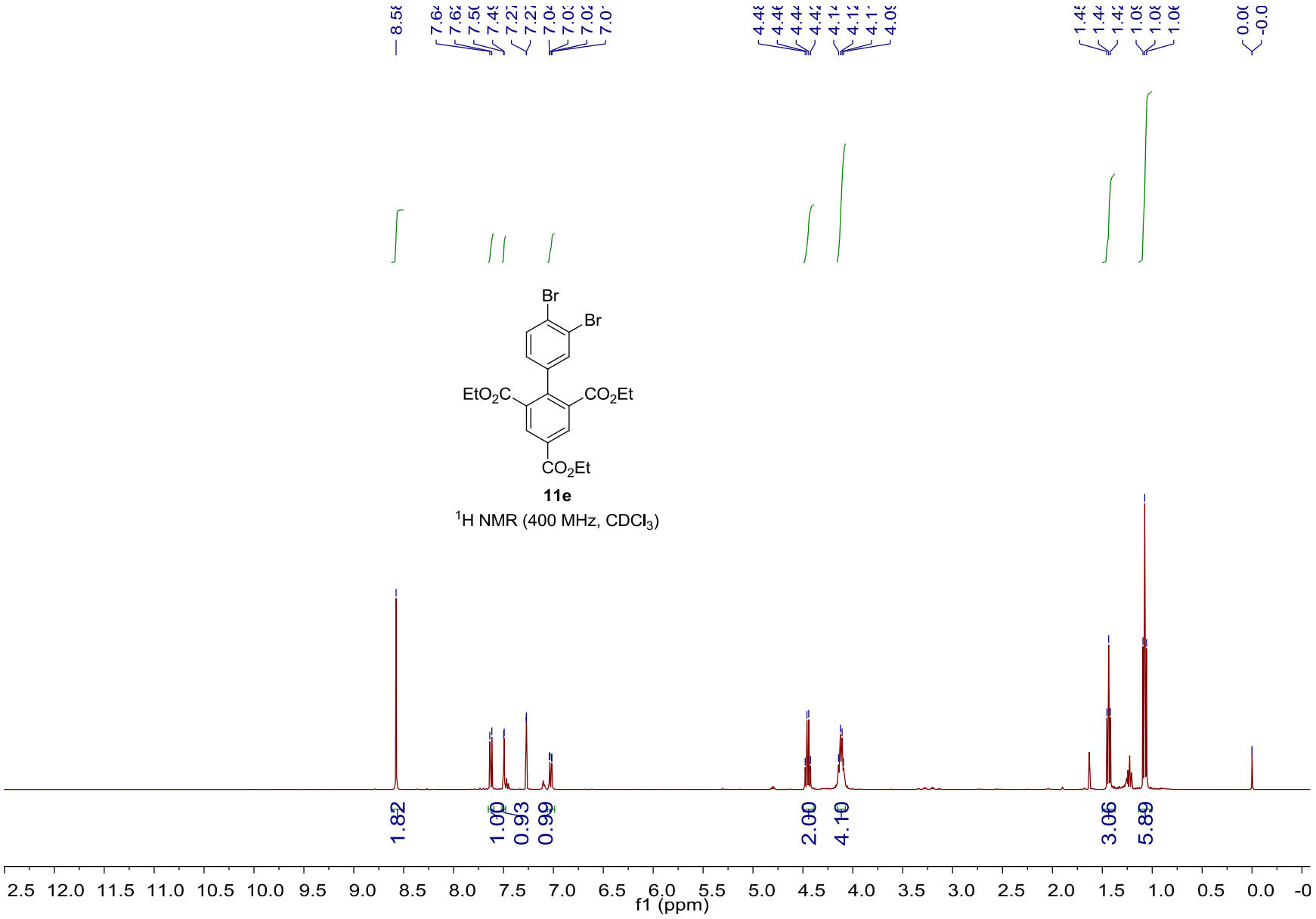


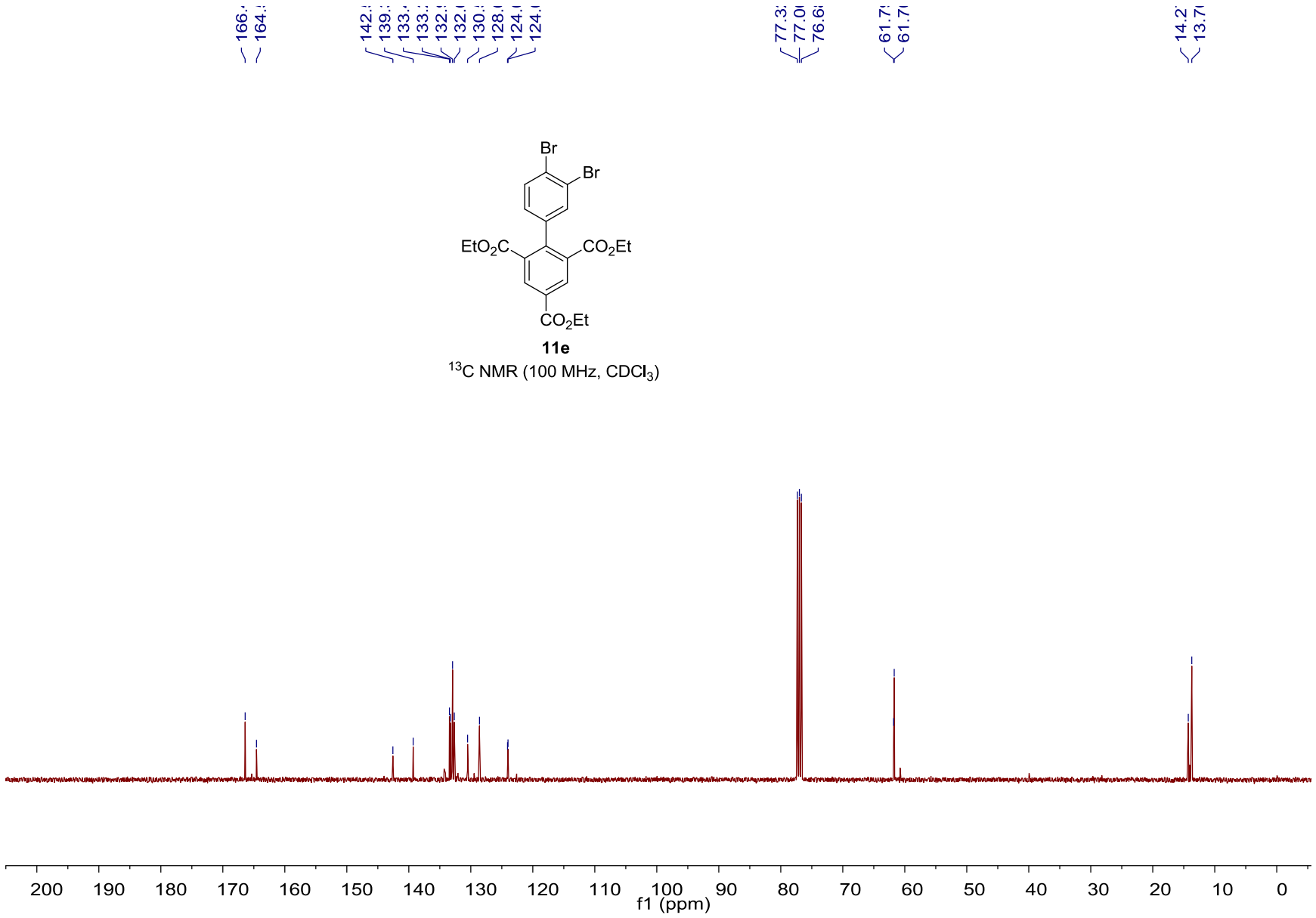
11c

^{13}C NMR (100 MHz, $CDCl_3$)


Br
EtO2C
CO2Et
CO2Et
11d
1H NMR (400 MHz, CDCl3)
1.81
2.00
2.01
2.05
4.15
3.01
6.01
f1 (ppm)

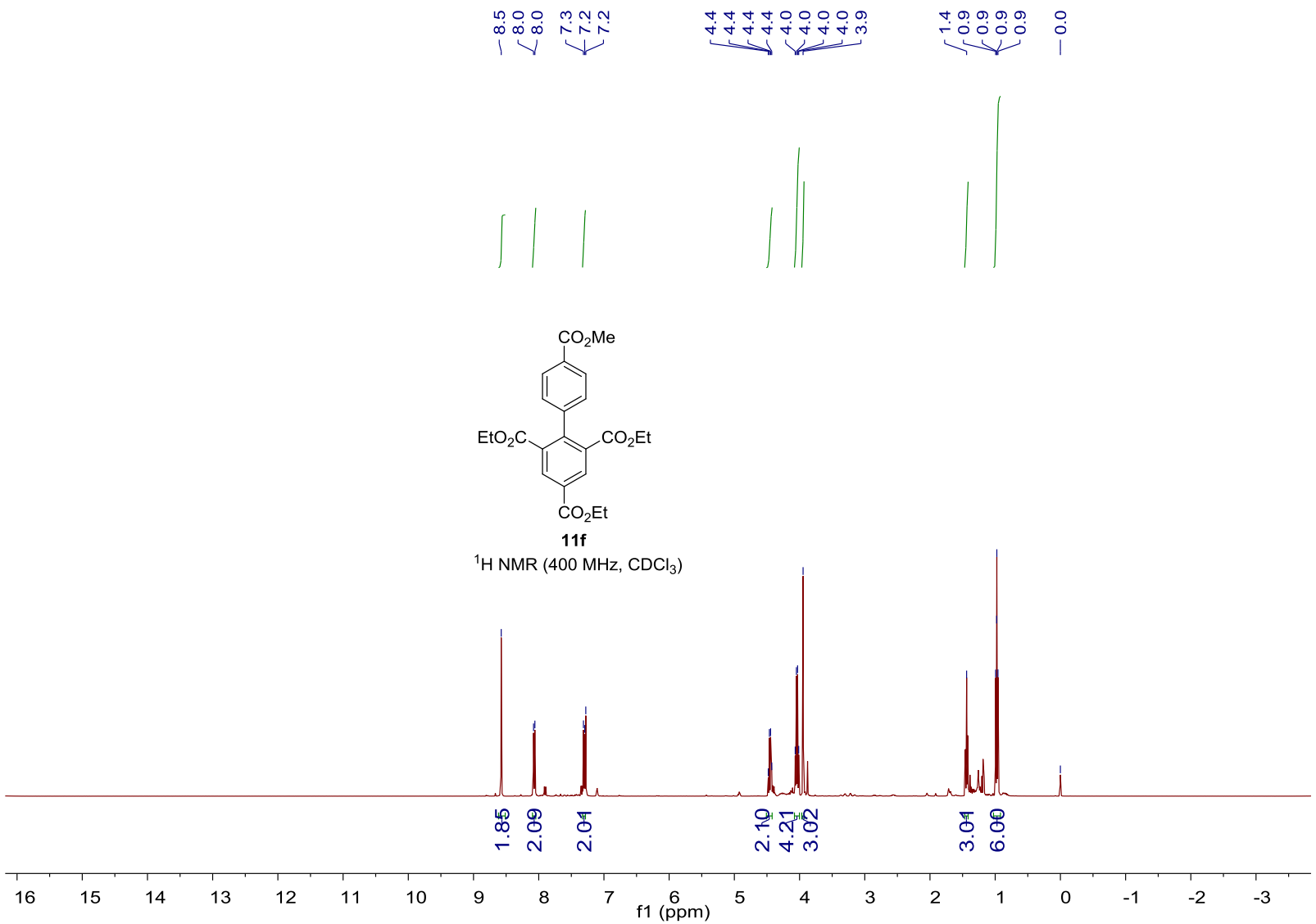

Br
EtO2C
CO2Et
CO2Et
11d
13C NMR (100 MHz, CDCl3)
f1 (ppm)

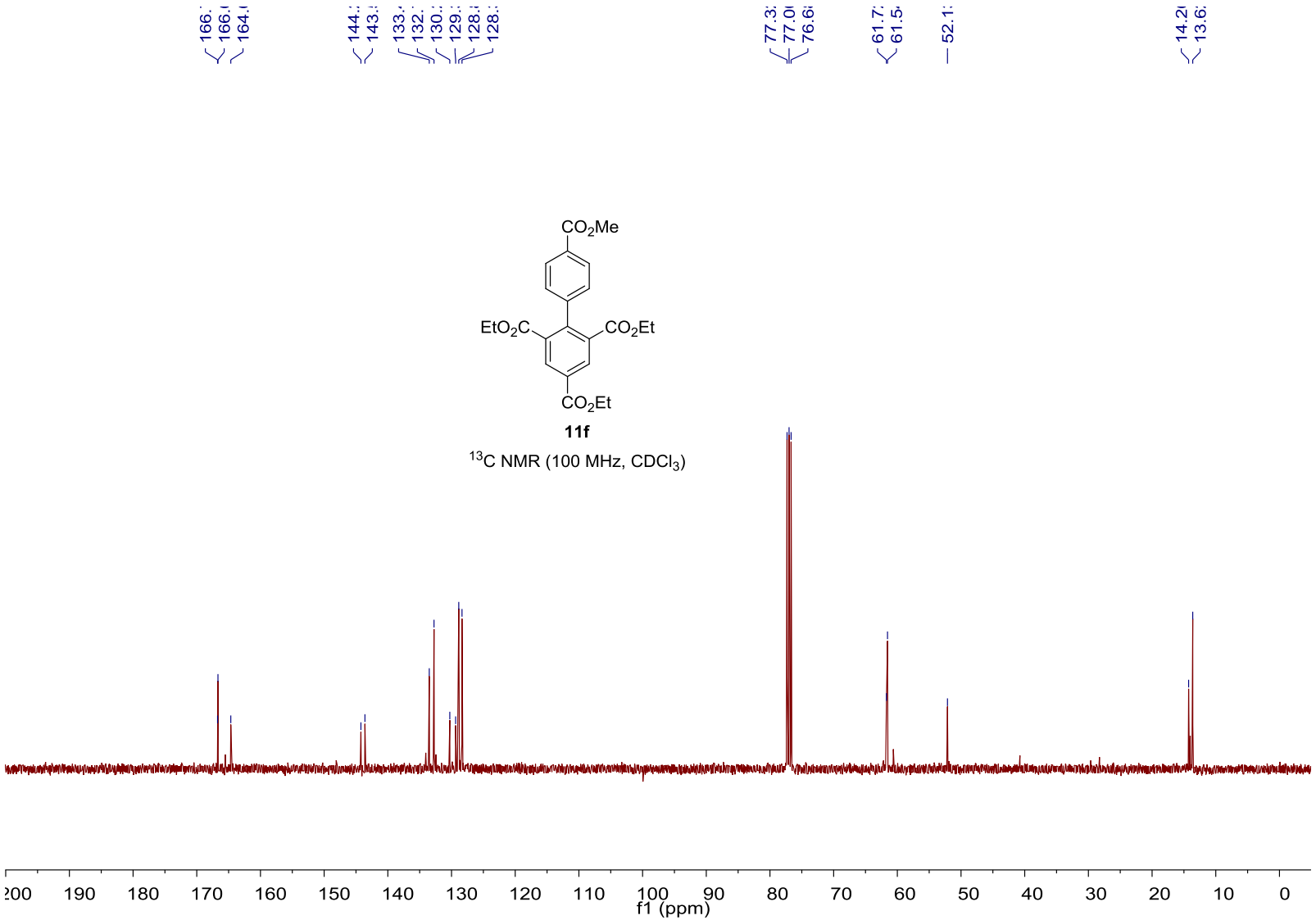

Br
Br
EtO2C
CO2Et
CO2Et
11e
1H NMR (400 MHz, CDCl3)
f1 (ppm)

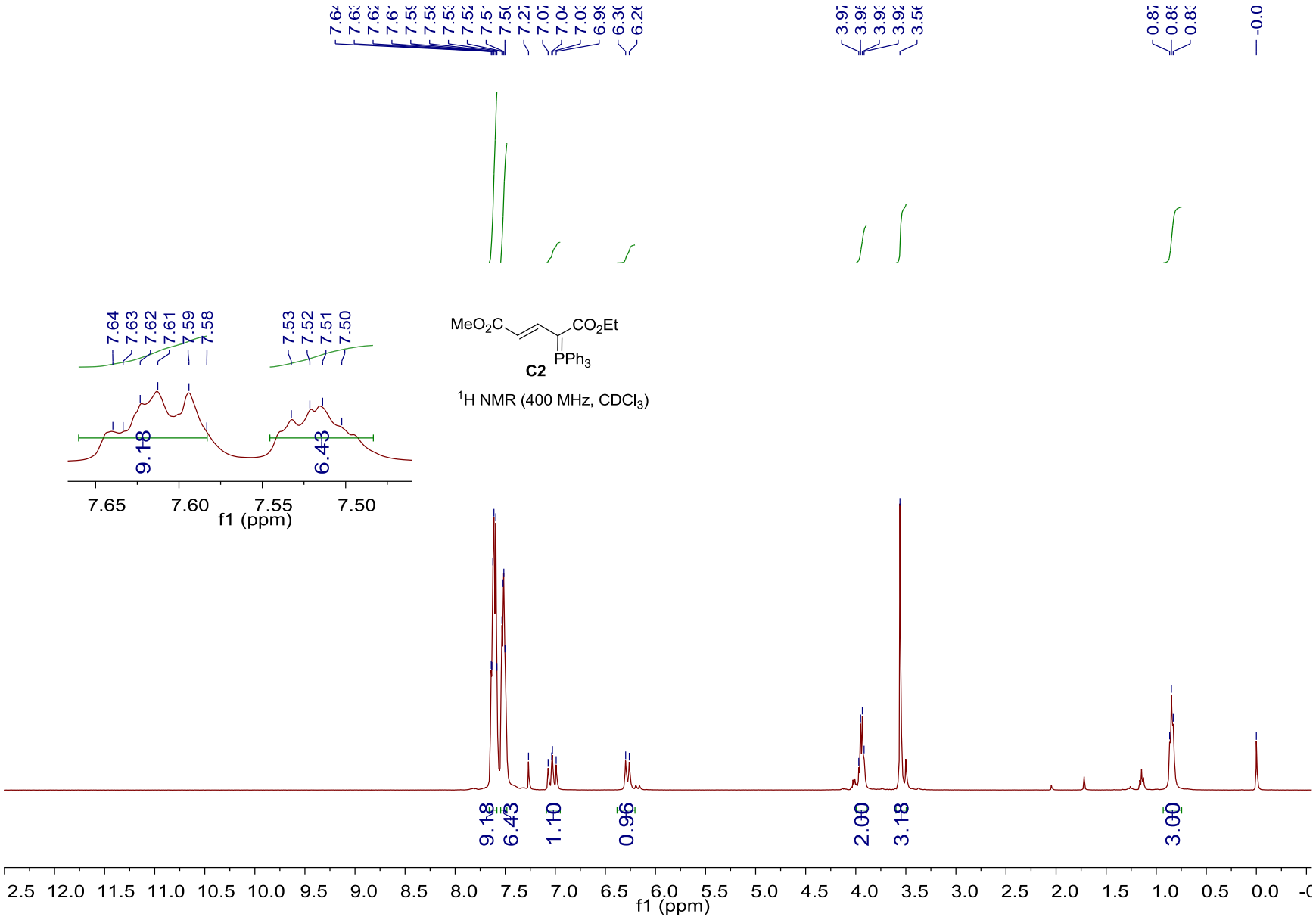


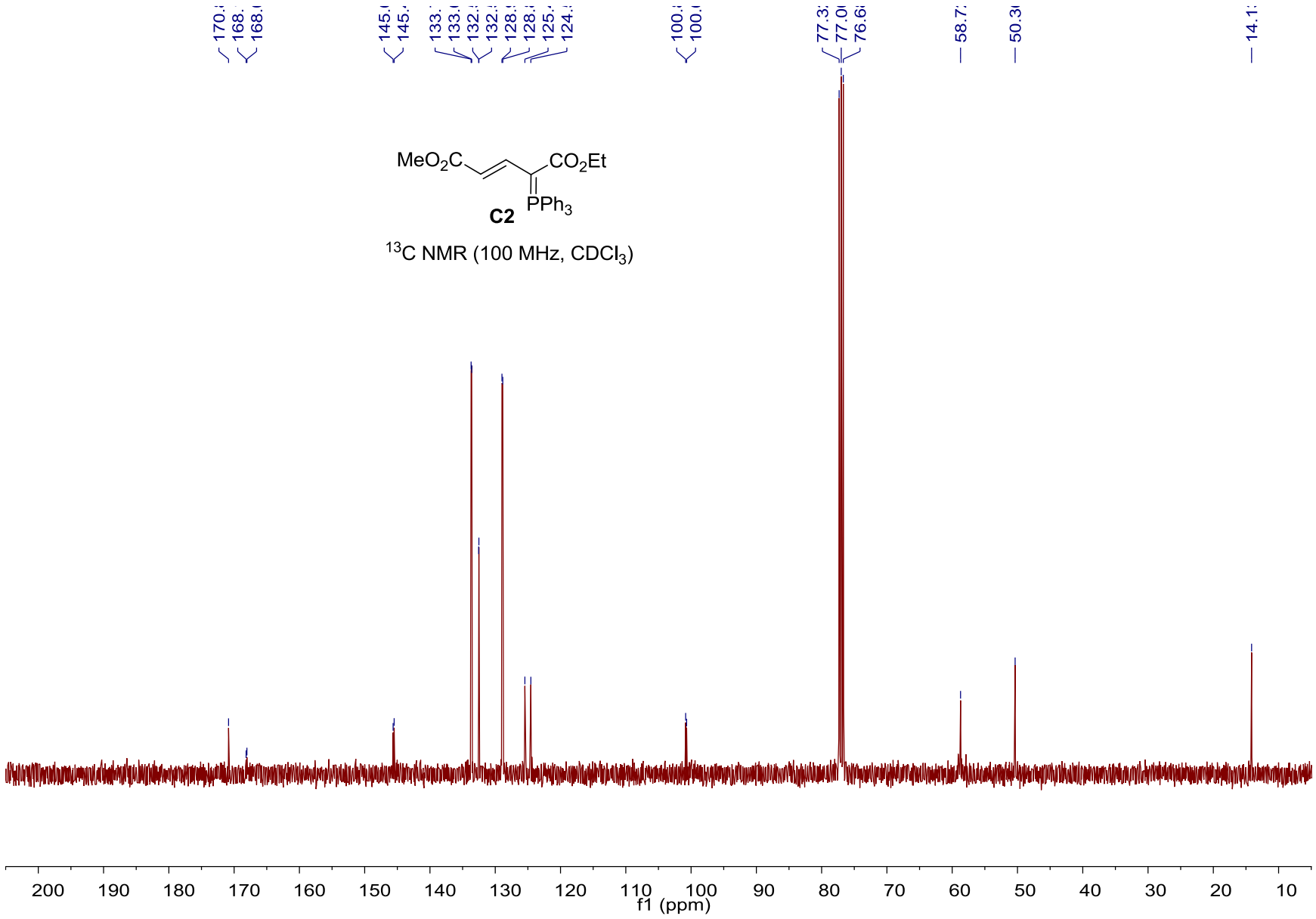
11e

^{13}C NMR (100 MHz, $CDCl_3$)


8.5
8.0
8.0
7.3
7.2
7.2
4.4
4.4
4.4
4.4
4.0
4.0
4.0
4.0
3.9
1.4
0.9
0.9
0.9
0.9
0.0
CO2Me
EtO2C
CO2Et
CO2Et
11f
1H NMR (400 MHz, CDCl3)
1.85
2.00
2.04
2.10
4.21
3.02
3.04
6.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


166.
166.
164.
144.
143.
133.
132.
130.
129.
128.
128.
77.3
77.0
76.6
61.7
61.5
52.1
14.2
13.6
CO2Me
EtO2C
CO2Et
CO2Et
11f
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO2C
CO2Et
PPh3
C2
1H NMR (400 MHz, CDCl3)
f1 (ppm)


MeO2C
CO2Et
PPh3
C2
13C NMR (100 MHz, CDCl3)
f1 (ppm)