SUPPORTING INFORMATION

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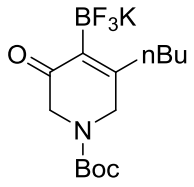
General. Otherwise noted, all reactions were carried out in flame-dried glassware under dry nitrogen atmosphere. The solvents were purified with the solvent purification system Pure Solv MD-6 (THF, Et_2O, CH_2Cl_2); toluene and dioxane were purchased from Acros (>99%, Extra Dry over Molecular Sieve, AcroSeal™). Oxetanone **3** was purchased from Fluorochem. Compound **12** was purchased from Aldrich. Compounds **1**,[1] **2**,[1] **4**,[2] **5**,[3] **6**,[4] **7**,[2] **8**,[2] **9**,[3] **10**,[5] **11**[6] and **13**[3] were prepared according to the literature.[1,2] Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DRX 500 in the indicated solvent; chemical shifts (δ) are given in ppm. The solvent signals were used as references and the chemical shifts converted to the TMS scale (MeCN-d_3: δC = 118.2 ppm; δH = 1.96 ppm / DMSO-d_6: δC = 39.5 ppm; δH = 2.50 ppm;); apparent splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintuplet), sept. (septuplet), m (multiplet), br (broad), and the appropriate combinations. In ^{19}F NMR, 1,3,5-trifluorobenzene was used as internal standard (δF = -110.6 ppm). Note that the rapid quadrupolar relaxation of ^{11}B prevented the observation of the quaternary carbon atom that bears the boron atom in ^{13}C NMR spectra. IR: PerkinElmer Spectrum 100 FT-IR spectrometer, wavenumbers in cm^{-1}. HRMS determined at the University of Liverpool on micromass LCT mass spectrometer (ES) and Trio-1000 or Agilent QTOF 7200 mass spectrometers (CI). Melting points: Griffin melting point apparatus (not corrected). All commercially available compounds were used as received.

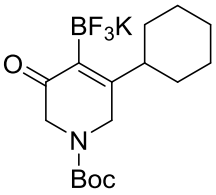
Synthesis of compounds 14–26

Compound 14. Inside an argon-filled glovebox, a J-Young flame-dried Schlenk flask equipped with a small stirrer bar was charged with $Ni(cod)_2$ (48 mg, 0.18 mmol, 0.1 equiv) and PPh_3 (142 mg, 0.54 mmol, 0.3 equiv). Then, outside the glovebox and under N_2, dioxane (1.5 mL) was added. The mixture was stirred at room temperature for 10 minutes, then **1** (431 mg, 2.52 mmol, 1.4 equiv), potassium trifluoro(hex-1-yn-1-yl)borate **4** (339 mg, 1.80 mmol, 1 equiv) and dioxane (4.5 mL) were added in that order. The tube was sealed and the mixture was stirred at 60 °C for 18 h. At room temperature, MeCN (30 mL) was added and all volatiles were removed *in vacuo*. The resulting brown residue was dissolved in acetone (15 mL) and Et_2O (60 mL) was added to induce precipitation. The resulting solid was filtrated through a sintered funnel followed by trituration with Et_2O (3 x 15 mL) at room temperature to afford **14** as a white solid (457 mg, 70%); m.p.: 155–157 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 4.02 (s, 2H), 3.83 (s, 2H), 2.49-2.41 (m, 2H), 1.56-1.47 (m, 2H), 1.48 (s, 9H), 1.45-1.33 (m, 2H), 0.953 (t, *J* = 7.4 Hz); ^{13}C NMR (126 MHz, MeCN-d_3): δ 201.7 (br), 165.5, 155.2, 80.7, 52.4 (br), 47.9 (br), 34.6, 32.4, 28.7 (3C), 23.8, 14.4; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -136.7 – -137.5 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 2.29 (q, *J* = 50.5 Hz); IR (neat): $\tilde{\nu}$ = 2960, 2969, 2871, 1675, 1665, 1609, 1479, 1418, 1377, 1366, 1315, 1293, 1245, 1160, 1140, 1098, 1065, 1015, 984, 958, 898 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 320.1645; found: 320.1655



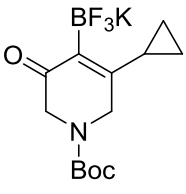
14

Compound 15. This compound was obtained from **1** (431 mg, 2.52 mmol) and potassium (cyclohexylethynyl)trifluoroborate **5** (385 mg, 1.80 mmol) by the procedure described for the preparation of **14**. White solid, 430 mg, 62%; m.p.: 145–147 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 4.00 (s, 2H), 3.81 (s, 2H), 3.21-3.10 (m, 1H), 1.80–1.72 (m, 2H), 1.72–1.65 (m, 1H), 1.65–1.58 (m, 2H), 1.43 (s, 9H), 1.40-1.15 (m, 5H); ^{13}C NMR (126 MHz, MeCN-d_3): δ 202.8 (br), 169.4, 155.2, 80.7, 53.0 (br), 44.1 (br), 43.6, 31.7, 28.7 (3C), 27.3, 27.0; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -136.3 – -137.0 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 2.23 (q, *J* = 53.3 Hz); IR (neat): $\tilde{\nu}$ = 2978, 2928, 2850, 1686, 1656, 1594, 1424, 1391, 1376, 1367, 1303, 1285, 1250, 1162, 1141, 1120, 1078, 1013, 986, 962, 934, 898 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 345.1843; found: 345.1844.



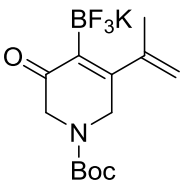
15

Compound 16. This compound was obtained from **1** (288 mg, 1.68 mmol) and potassium (cyclopropylethynyl)trifluoroborate **6** (206 mg, 1.20 mmol) by the procedure described for the preparation of **14**, except that the precipitation was induced by a mixture of acetone and petroleum ether. White solid, 206 mg, 56%; m.p. > 105 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.70 (s, 2H), 3.46 (s, 2H), 2.62–2.50 (m, 1H), 1.39 (s, 9H), 0.79–0.64 (m, 4H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 197.3 (br), 161.3 (br), 153.2, 79.2, 52.00 (br), 28.0 (3C), 14.4, 5.8 (the signal of one methylene of the heterocycle is overlapped with the NMR solvent); ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.6 – -134.4 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 2.49 (q, *J* = 52.2 Hz); IR (neat): $\tilde{\nu}$ = 2974, 1691, 1641, 1612, 1582, 1418, 1378, 1365, 1310, 1249, 1168, 1127, 1083, 1028, 1003, 974, 900 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 303.1374; found: 303.1378.



16

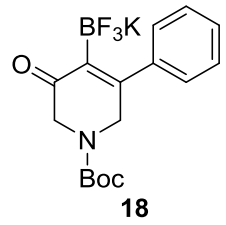
Compound 17. This compound was obtained from **1** (288 mg, 1.68 mmol) and potassium (3-methylbut-3-en-1-yn-1-yl)trifluoroborate **7** (206 mg, 1.20 mmol) by the procedure described for the preparation of **14**. White solid, 365 mg, 89%; m.p.: 168–170 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.83 (s, 1H), 4.66 (s, 1H), 3.94 (s, 2H), 3.77 (s, 2H) 1.89 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 198.8 (br), 160.5, 153.4, 145.7, 139.2 (br), 111.3, 79.3, 51.2 (br), {46.9 (br) & 46.2 (br), two signals for one of the methylene of the heterocycle are visible, corresponding to two rotamers}, 27.9 (3C), 22.5; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -136.2 – -136.9 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 1.89 (q, *J* = 51.6 Hz); IR (neat): $\tilde{\nu}$ = 2976,



17

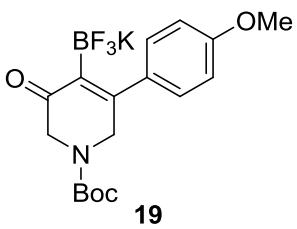
2911, 2819, 1702, 1658, 1604, 1476, 1431, 1415, 1366, 1311, 1265, 1239, 1161, 1139, 1087, 1022, 1006, 982, 950 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 303.1374; found: 303.1385.

Compound 18. This compound was obtained from **1** (288 mg, 1.68 mmol) and potassium (phenylethynyl)trifluoroborate **8** (250 mg, 1.20 mmol) by the procedure described for the preparation of **14**. White solid, 359 mg, 79%; m.p.: 150–153 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 7.45–7.26 (m, 5H), 4.35–4.16 (s (br), 2H), 4.06–3.89 (s (br), 2H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, MeCN-d_3): δ 202.3 (br), 161.5 (br), 155.3, 142.3, 129.1 (2C), 128.6, 128.4 (2C), 81.0, 52.5 (br), 49.6 (br), 28.6 (3C); ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.9 – -134.8 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 3.09–0.90 (m); IR (neat): $\tilde{\nu}$ = 2976, 1694, 1656, 1585, 1441, 122, 1394, 1359, 1305, 1276, 1241, 1160, 1128, 1081, 1031, 978, 959, 929, 906, 858 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 339.1374; found: 339.1374.



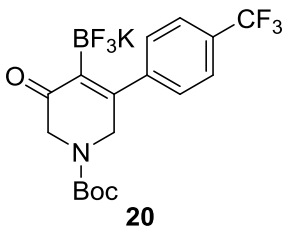
18

Compound 19. This compound was obtained from **1** (288 mg, 1.68 mmol) and potassium ((4-methoxyphenyl)ethynyl)trifluoroborate **9** (286 mg, 1.20 mmol) by the procedure described for the preparation of **14**, except that the precipitation was induced by a mixture of acetone and petroleum ether. White solid, 395 mg, 80%; m.p.: 151–153 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.24 (s, 2H), 3.96 (s, 2H), 3.83 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, MeCN-d_3): δ 202.6 (br), 161.5 (br), 160.9, 155.4, 134.3, 130.9 (2C), 113.9 (2C), 81.0, 56.0, 52.8 (br), 49.6 (br), 28.7 (3C); ^{19}F NMR (376 MHz, MeCN-d_3): δ = -135.5 – -136.4 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 3.09–0.90 (m); IR (neat): $\tilde{\nu}$ = 2977, 2836, 1694, 1643, 1606, 1509, 1434, 1415, 1363, 1305, 1285, 1243, 1162, 1130, 1087, 1030, 968, 907, 890 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 369.1479; found: 369.1489.



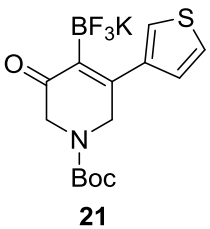
19

Compound 20. This compound was obtained from **1** (144 mg, 0.84 mmol) and potassium (((4-trifluoromethyl)phenyl)ethynyl)trifluoroborate **10** (166 mg, 0.60 mmol) by the procedure described for the preparation of **14**. White solid, 141 mg, 57%; m.p.: 152–155 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 4.23 (s, 2H), 4.00 (s, 2H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, MeCN-d_3): δ 201.8 (br), 159.5 (br), 155.3, 146.7, 129.9 (2C), 129.8 (q, *J* = 32.1 Hz), 125.7 (q, *J* = 271.1 Hz), 125.3 (q, *J* = 4.1 Hz, 2C), 81.1, 52.7 (br), 49.6 (br), 28.7 (3C); ^{19}F NMR (376 MHz, MeCN-d_3): δ = -64.2, -135.5 – -136.3 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 1.68 (q, *J* = 46.8 Hz); IR (neat): $\tilde{\nu}$ = 1701, 1665, 1604, 1419, 1368, 1325, 1303, 1247, 1223, 1180, 1135, 1114, 1105, 1066, 1015, 968 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 408.1211; found: 408.1196.



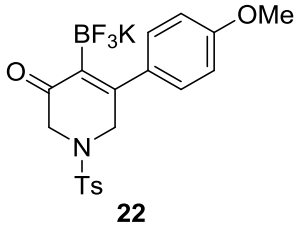
20

Compound 21. This compound was obtained from **1** (144 mg, 0.84 mmol) and potassium (thiophen-3-yl)ethynyl)trifluoroborate **11** (128 mg, 0.60 mmol) by the procedure described for the preparation of **14**. White solid, 183 mg, 79%; m.p.: 162–164 °C; ^{1}H NMR (500 MHz, MeCN-d_3): δ 7.58–7.49 (s (br), 1H), 7.33 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.30 (d, *J* = 4.7 Hz, 1H), 4.29 (s, 2H), 3.96 (s, 2H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, MeCN-d_3): δ 202.5 (br), 155.4, 155.3 (br), 142.2, 130.4, 125, 7, 124.9, 81.0, 52.7 (br), 49.9 (br), 28.6 (3C); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 3.13–1.09 (m); IR (neat): $\tilde{\nu}$ = 2985, 1686, 1644, 1596, 1424, 1366, 1299, 1248, 1159, 1125, 1076, 999, 975, 91, 896, 852, 841 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 345.0938; found: 345.0941.



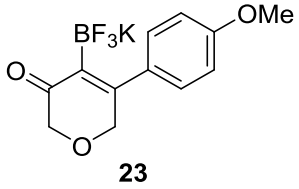
21

Compound 22. Inside an argon-filled glovebox, a Teflon-screw flame-dried Schlenk flask equipped with a small stirrer bar was charged with $Ni(cod)_2$ (16 mg, 0.06 mmol, 0.1 equiv) and PPh_3 (48 mg, 0.18 mmol, 0.3 equiv). Then, outside the glovebox and under N_2, dioxane (0.5 mL) was added. The mixture was stirred at room temperature for 10 minutes, then a solution of **2** (182 mg, 0.84 mmol, 1.4 equiv) in dioxane (0.5 mL) was added, followed by **9** (143 mg, 0.60 mmol, 1 equiv) and finally dioxane (1 mL). The tube was sealed and the mixture was stirred at 60 °C for 18 h. At room temperature, MeCN (15 mL) was added and all volatiles were removed *in vacuo*. The resulting brown residue was dissolved in acetone (5 mL) and Et_2O (30 mL) was added to induce precipitation. The resulting solid was filtrated through a sintered funnel followed by trituration with Et_2O (2 x 15 mL) at room temperature to afford **22** as a cream-coloured solid (275 mg, 98%); m.p.> 155 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.76 (s, 2H), 3.43 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 196.1, 159.0, 155.8, 143.8, 132.7, 132.1, 130.0 (2C), 129.6 (2C), 127.6 (2C), 112.6 (2C), 55.0, 52.5, 49.4, 21.0; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -135.8 – -136.6 (m); ^{11}B NMR (160 MHz, DMSO-d_6): δ = 4.06 – -0.39 (m); IR (neat): $\tilde{\nu}$ = 1651, 1604, 1509, 1440, 1348, 1306, 1289, 1249, 1162, 1120, 1091, 1028, 962 cm^{-1}; HRMS (ES+): calcd for $[M + K]^+$: 502.0276; found: 502.0266.



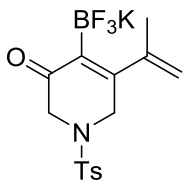
22

Compound 23. Inside an argon-filled glovebox, a Teflon-screw flame-dried Schlenk flask equipped with a small stirrer bar was charged with $Ni(cod)_2$ (16 mg, 0.06 mmol,, 0.1 equiv) and PPh_3 (48 mg, 0.18 mmol, 0.3 equiv). Then, outside the glovebox and under N_2, dioxane (0.5 mL) was added. The mixture was stirred at room temperature for 10 minutes, then **3** (54 μL, 0.84 mmol, 1.4 equiv), **9** (143 mg, 0.60 mmol, 1 equiv) and dioxane (1.5 mL) were added in that order. The tube was sealed and the mixture was stirred at 90 °C for 18 h. At room temperature, MeCN (15 mL) was added and all volatiles were removed *in vacuo*. The resulting brown residue was dissolved in acetone (5 mL) and Et_2O (30 mL) was added to induce precipitation. The resulting solid was filtrated through a sintered funnel followed by trituration with Et_2O (2 x 10 mL) at room temperature to afford **23** as a cream-coloured solid (93 mg, 55%); m.p.> 145 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.33 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.30 (s, 2H), 3.87 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 199.4, 158.9, 158.6, 131.6, 129.7 (2C), 112.4 (2C), 71.5, 68.7, 54.9; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -135.6 – -136.4 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 1.97 (q, *J* = 51.1 Hz); IR (neat): $\tilde{\nu}$ = 1642, 1602, 1589, 1564, 1506, 1470, 1435, 1416, 1387, 1313, 1287, 1249, 1223, 1178, 1134, 1118, 1104, 1050, 955, 944, 927, 888, 870, 826, 814 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 271.0753; found: 271.0754.



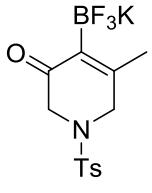
23

Compound 24. This compound was obtained from **2** (### mg, 0.84 mmol) and potassium ((4-methoxyphenyl)ethynyl)trifluoroborate **9** (103 mg, 0.60 mmol) by the procedure described for the preparation of **22**. Pale brown solid, 216 mg, 92%; m.p.: 112–115 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.80 (s, 1H), 4.59 (s, 1H), 3.56 (s, 2H), 3.37 (s, 2H), 2.39 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 195.7, 158.2, 145.6, 143.8, 132.1, 129.9 (2C), 111.7 (2C), 52.2, 48.1, 22.6, 20.1; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -137.6 – -138.4 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 3.87 – -0.57 (m); IR (neat): $\tilde{\nu}$ = 2981, 2889, 1653, 1596, 1462, 1382, 1349, 1263, 1160, 1088, 955 cm^{-1}; HRMS (ES+): calcd for $[M + K]^+$: 436.0170; found: 436.0171.



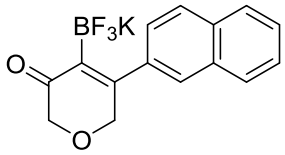
24

Compound 25. This compound was obtained from **2** (113 mg, 0.50 mmol) and propyn-1-yl-trifluoroborate **12** (70 mg, 0.36 mmol) by the procedure described for the preparation of **22**. Pale brown solid, 94 mg, 70%; ^{1}H NMR (500 MHz, MeCN-d_3): δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 2H), 3.44 (s, 2H), 2.42 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 194.6, 155.5, 143.5, 131.9, 129.6 (2C), 127.3 (2C), 51.9, 49.1, 20.7, 19.9; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -136.5 – -137.4 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 2.92 – 1.22 (m); IR (neat): $\tilde{\nu}$ = 1658, 1603, 1437, 1342, 1303, 1187, 1161, 1141, 1122, 1096, 1035, 962, 919, 896, 835, 813 cm^{-1}; HRMS (ES+): calcd for $[M + K]^+$: 410.0014; found: 410.0017.



25

Compound 26. This compound was obtained from **3** (35 μL, 0.50 mmol) and potassium ((2-naphthyl)ethynyl)trifluoroborate **13** (93 mg, 0.36 mmol) by the procedure described for the preparation of **22**. Pale yellow solid, 83 mg, 70%; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.92–7.84 (m, 3H), 7.83–7.76 (m, 1H), 7.55–7.44 (m, 3H), 4.44 (s, 2H), 3.97 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 199.3, 158.9, 137.4, 132.4, 132.3, 127.9, 127.4, 127.1, 126.4, 126.0, 125.7, 125.6, 71.4, 68.9; ^{19}F NMR (376 MHz, MeCN-d_3): δ = -135.8 – -136.6 (m); ^{11}B NMR (160 MHz, MeCN-d_3): δ = 1.92 (q, *J* = 48.5 Hz); IR (neat): $\tilde{\nu}$ = 1647, 1634, 1603, 1585, 1428, 1377, 1310, 1258, 1126, 1107, 107, 997, 943 cm^{-1}; HRMS (ES-): calcd for $[M - K]^-$: 291.0804; found: 291.0797.



26

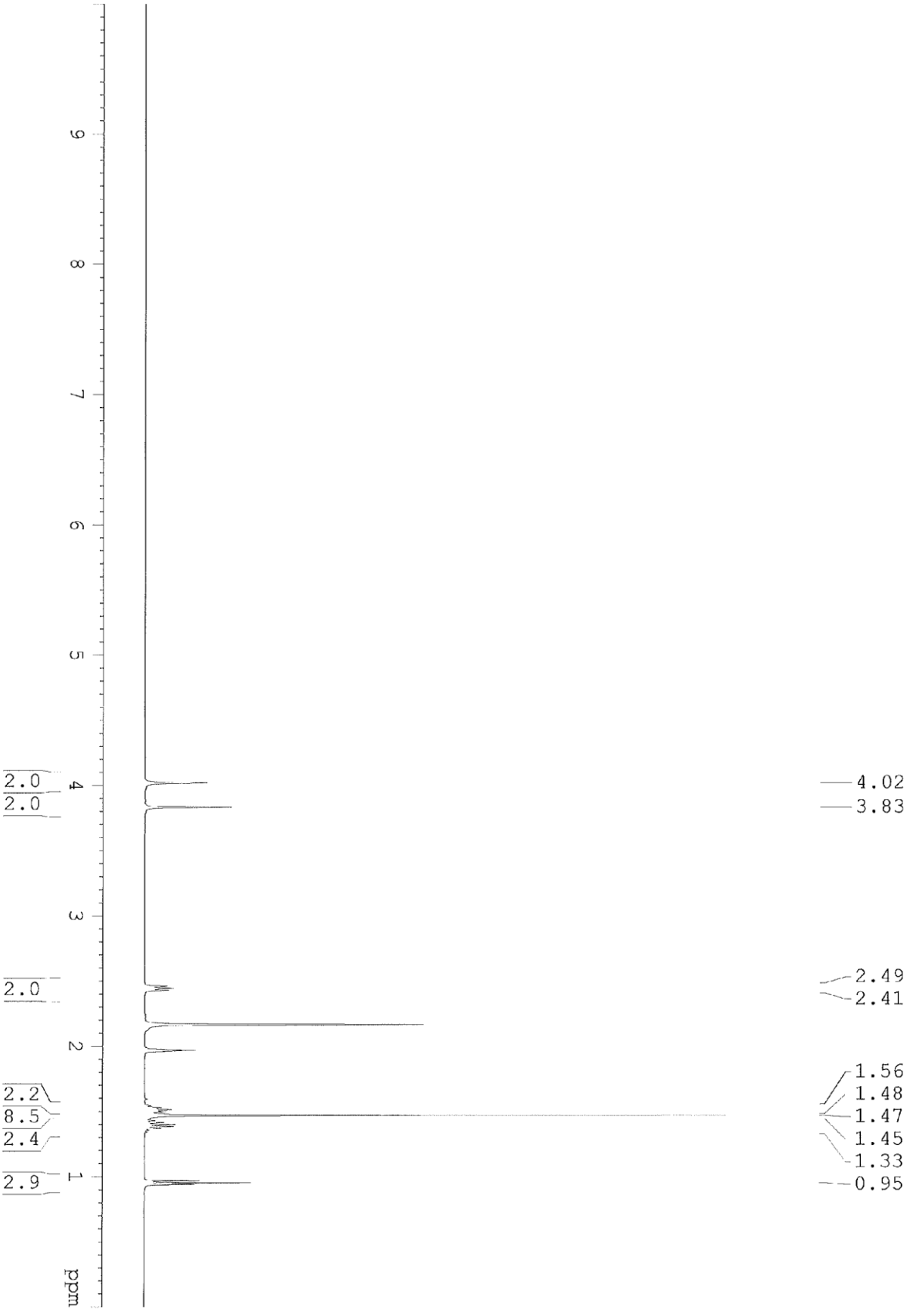
Synthesis of compound 27

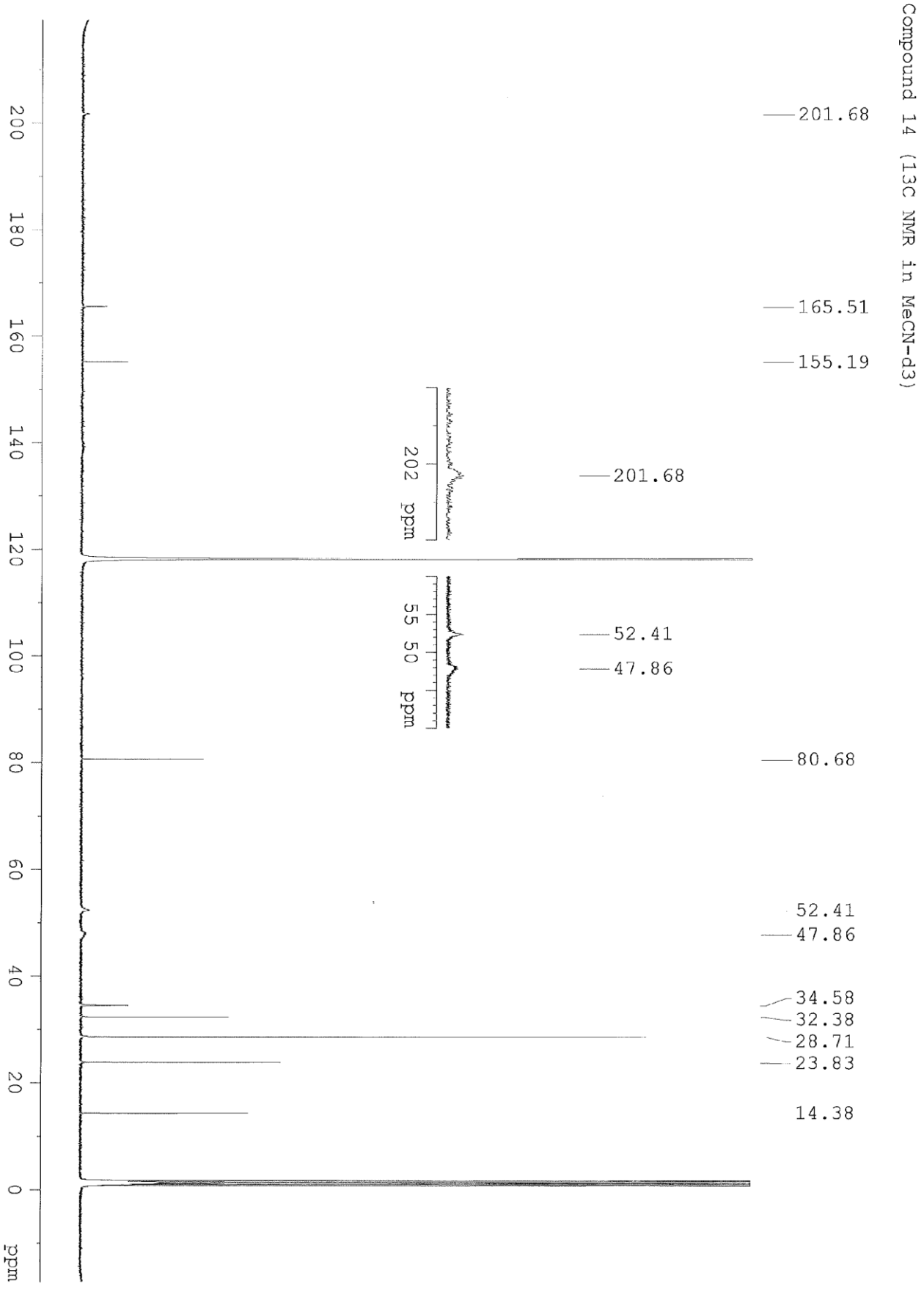
Compound 27. To a solution of **14** (245 mg, 0.68 mmol, 1 equiv) in THF/Water 1:1 (6 mL) was added tetrabutylammonium tribromide (329 mg , 0.68 mmol, 1 equiv). The mixture was stirred at r.t for 1 h until the disappearance of the orange colour. The mixture was quenched with water, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuo*. The residue was purified by flash chromatography (Hexane/EtOAc 4:1) to give a colourless oil (192 mg, 85%). This material was not entirely pure but used in the next step without further purification. Thus, a small amount of this material (42 mg, 0.126 mmol, 1 equiv) was placed in a J-Young schlenck tube, and the tube was evacuated. Under N2, 4-Methoxyphenylboronic acid (58 mg, 0.379 mmol, 3 equiv), K_3PO_4 (81 mg, 0.379 mmol, 3 equiv) and toluene (0.5 mL) were added, and this mixture was degassed by gently bubbling argon through the solution for 1 minute. Then, SPhos (8 mg, 0.020 mmol, 0.016 equiv) and $Pd_2(dba)_3$ (9 mg, 0.010 mmol, 0.08 equiv) were added and the schlenck was sealed. After heating at 80 C for 3 h, the mixture was diluted with EtOAc and washed with water. The organic layer was dried over $MgSO_4$, filtered and concentrated under *vacuo*. The residue was purified by flash chromatography (Hexane to Hexane/EtOAc (95/5)) to give 27 as colourless oil (37 mg, 81%). The spectroscopic data for this compound was identical to that described in the literature.[1a]

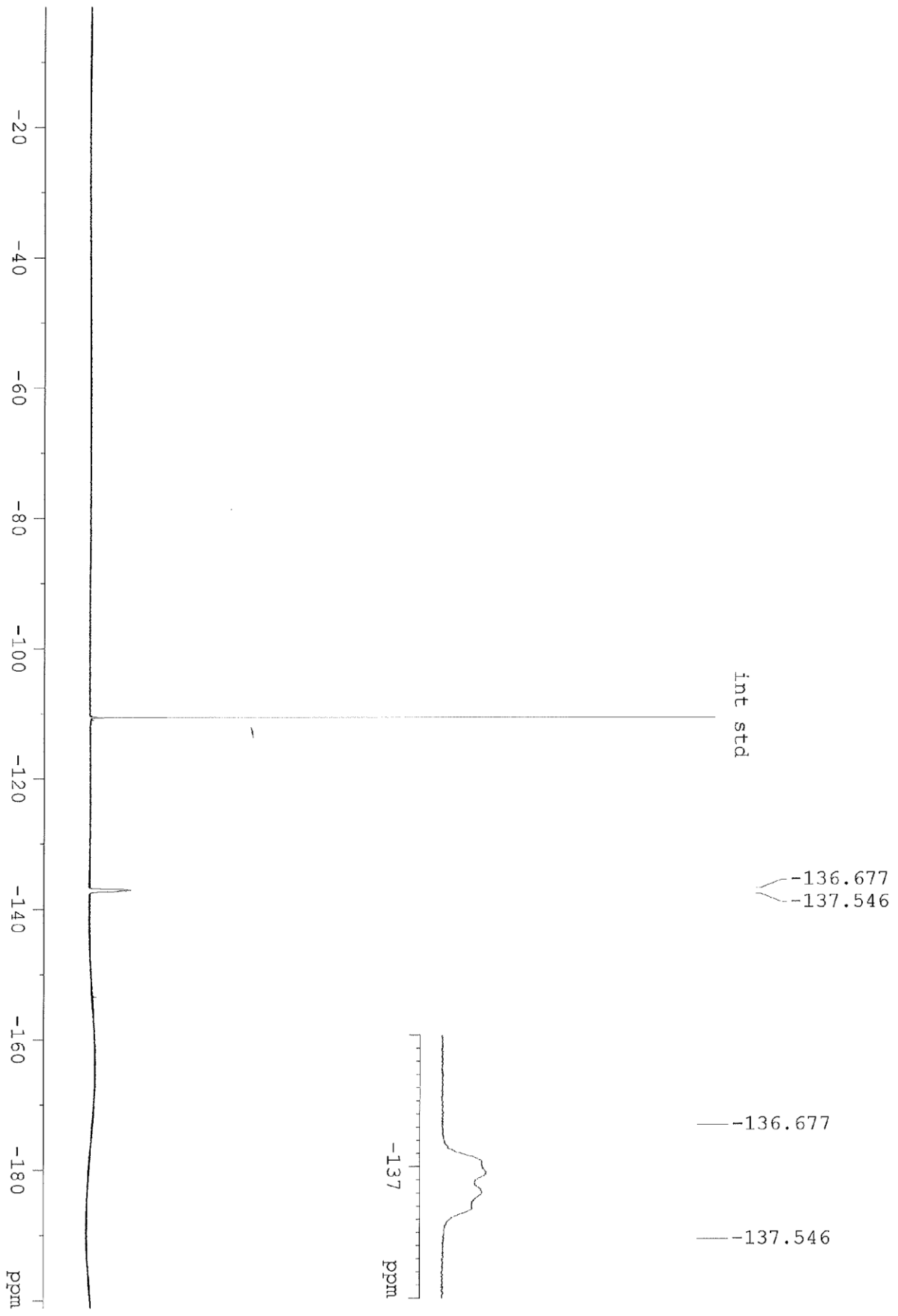
References

1. a) K. Y. T. Ho, C. Aïssa, *Chem. Eur. J.* **2012**, *18*, 3486; b) M. Barday, K. Y. T. Ho, C. T. Halsall, C. Aïssa, *Org. Lett.* 2016, **8**, 1756.
2. G. A. Molander, B. W. Katona, F. Machrouhi, *J. Org. Chem.* **2002**, *67*, 8416.
3. D. A. Mundal, K. E. Lutz, R. J. Thomson, *J. Am. Chem. Soc.* **2012**, *134*, 5782.
4. K. Jouvin, F. Couty, G. Evano, *Org. Lett.* **2010**, *12*, 3272.
5. J. H. Song, P. Choi, S. E. Lee, K. H. Jeong, T. Kim, K. S. Kang, Y. S. Choi, J. Ham, *Eur. J. Org. Chem.* **2013**, 6249.
6. J. Y. Hamilton, D. Sarlah, E. M. Carreira, *Angew. Chem. Int. Ed.* **2013**, *52*, 7532.

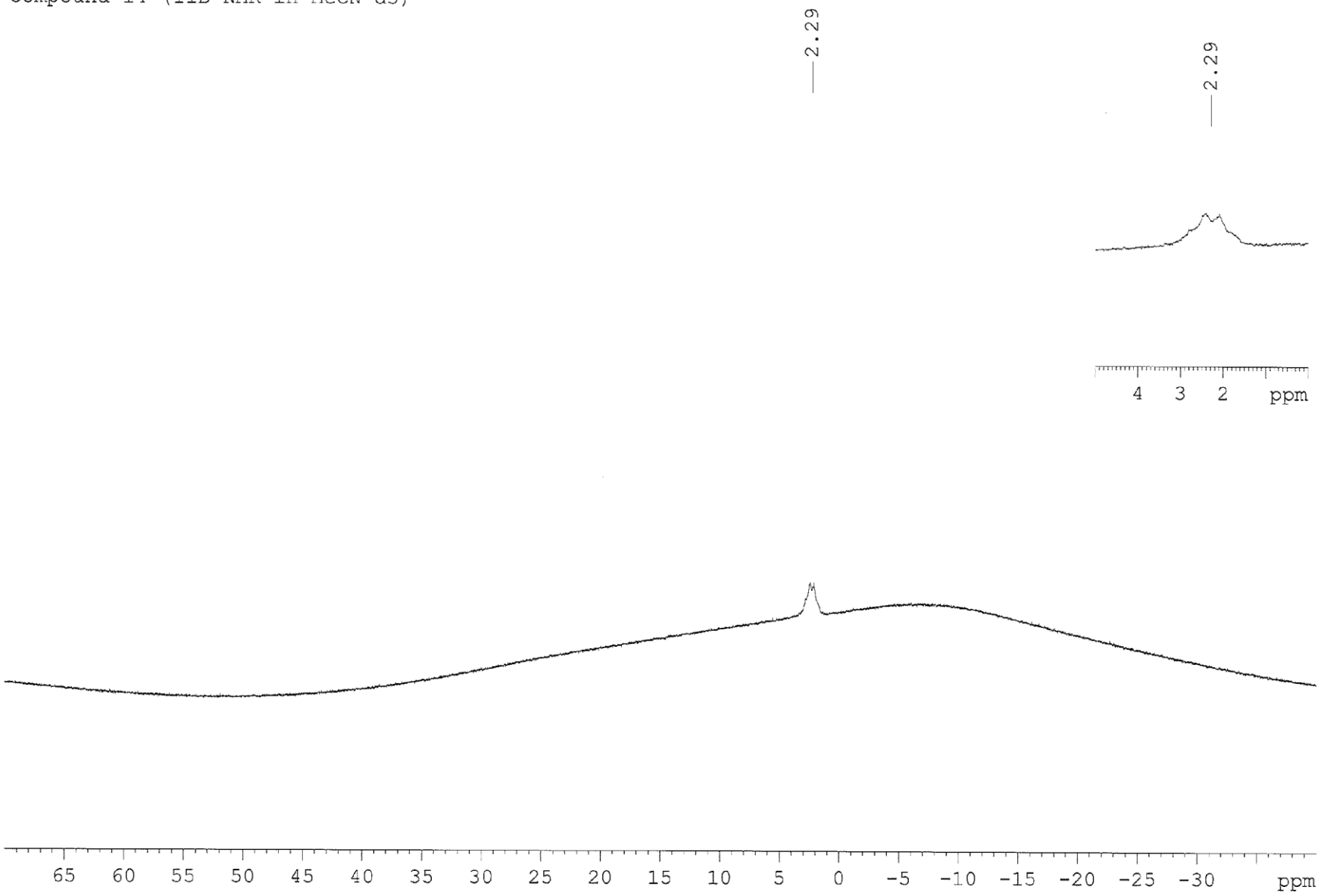
Compound 14 (1H NMR in MeCN-d3)

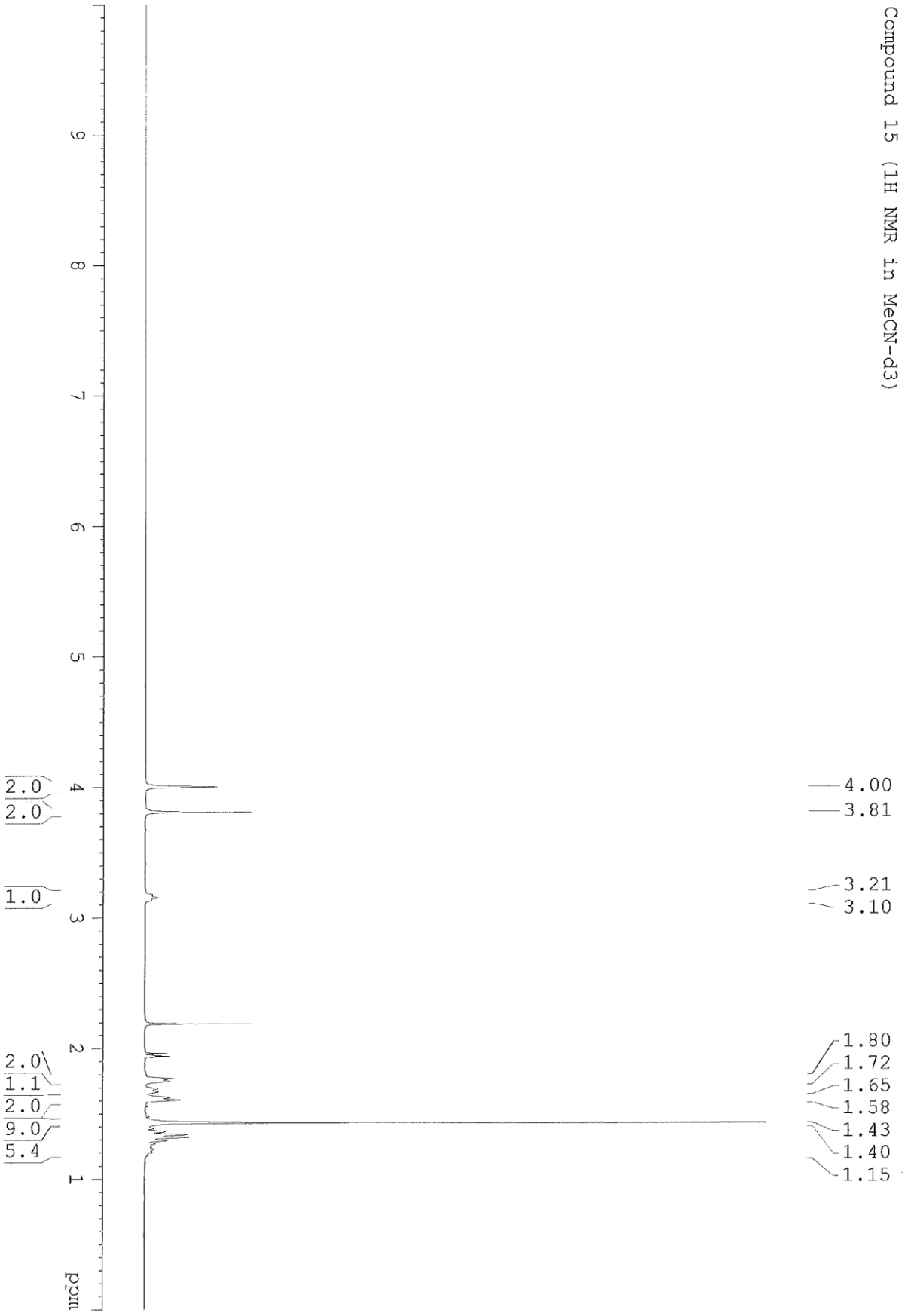


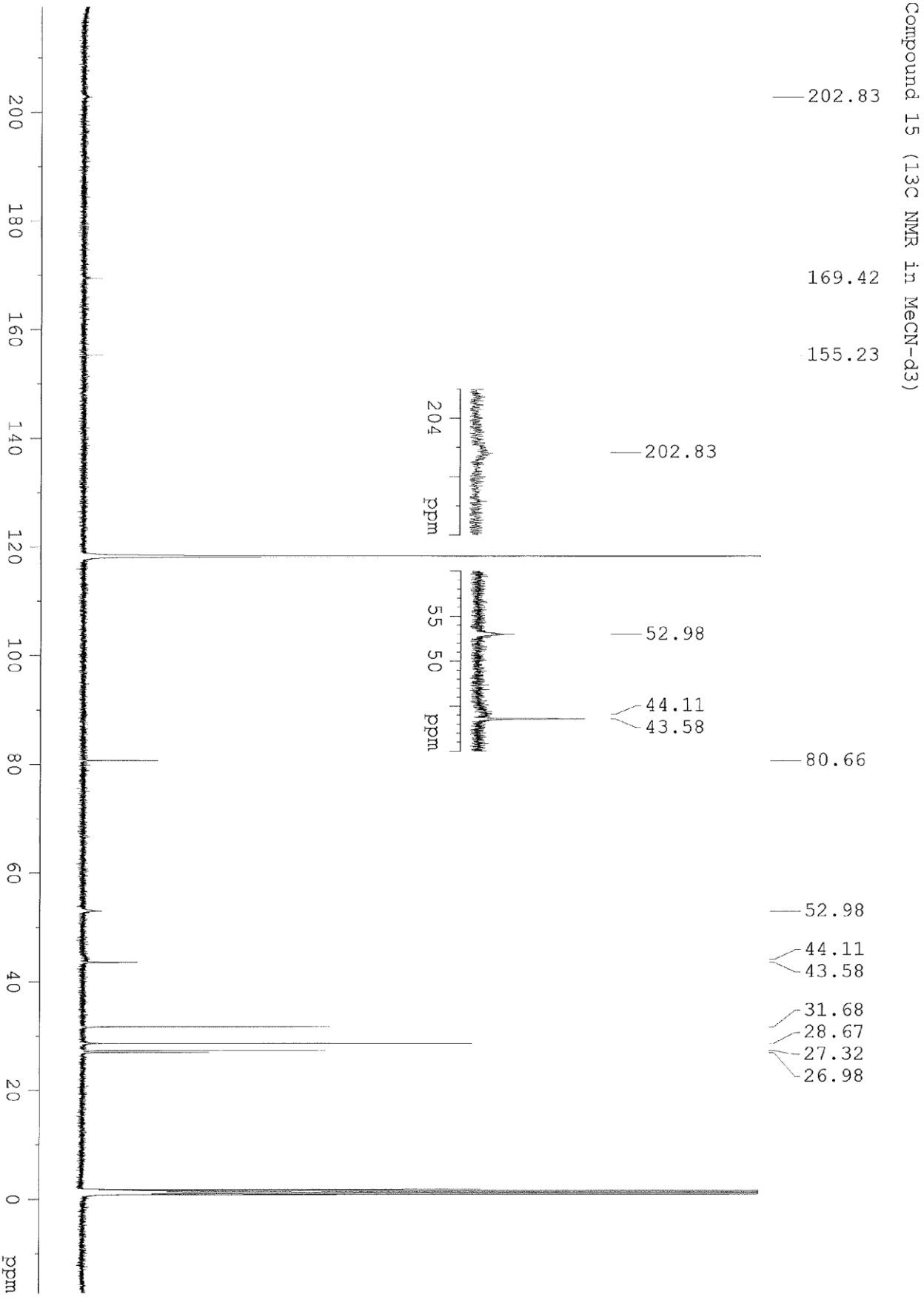

Compound 14 (13C NMR in MeCN-d3)
201.68
165.51
155.19
201.68
202 ppm
52.41
47.86
55 50 ppm
80.68
52.41
47.86
34.58
32.38
28.71
23.83
14.38
200
180
160
140
120
100
80
60
40
20
0
ppm


Compound 14 (19F NMR in MeCN-d3)
int std
-136.677
-137.546
-136.677
-137.546
-137
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

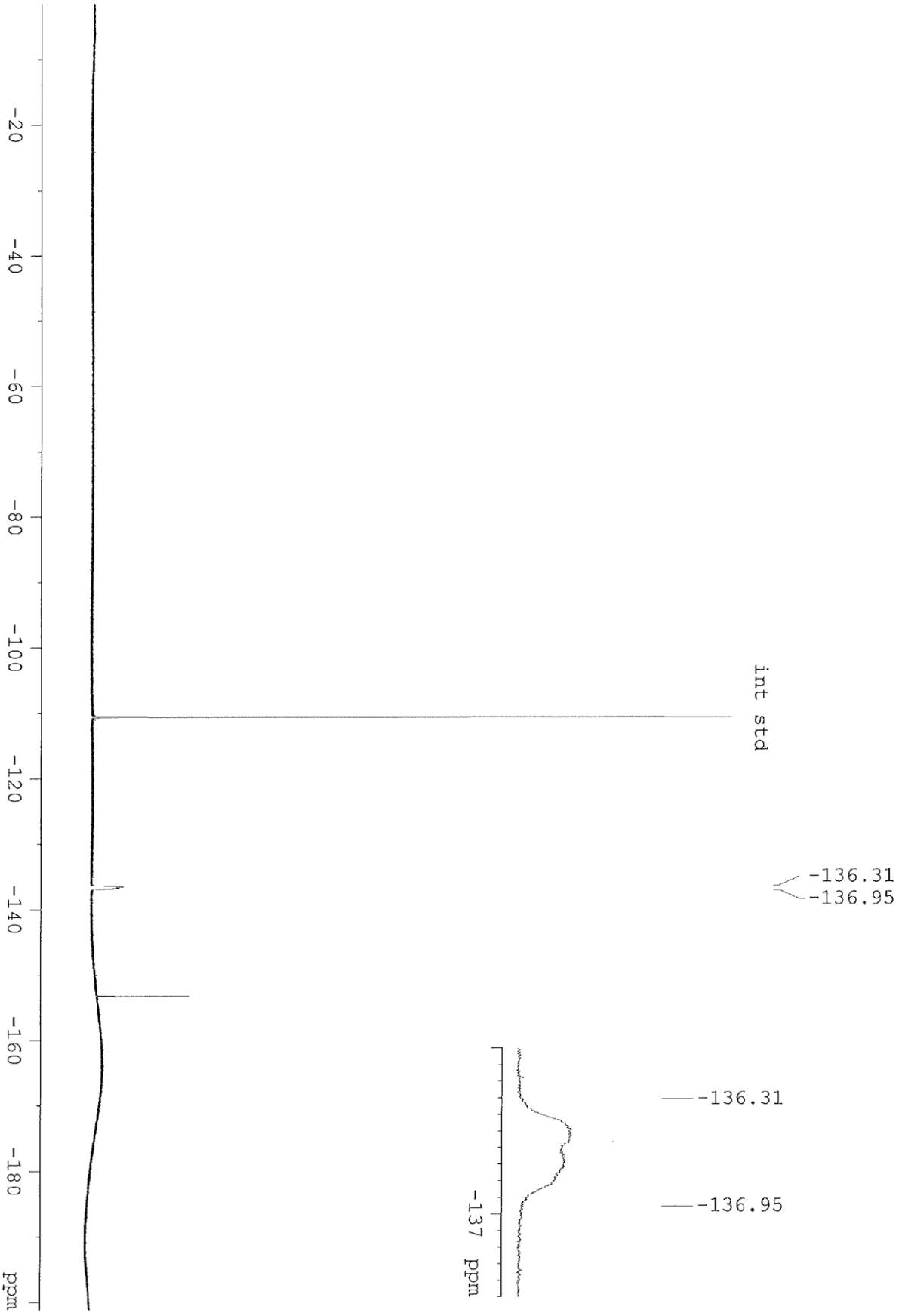
Compound 14 (11B NMR in MeCN-d3)



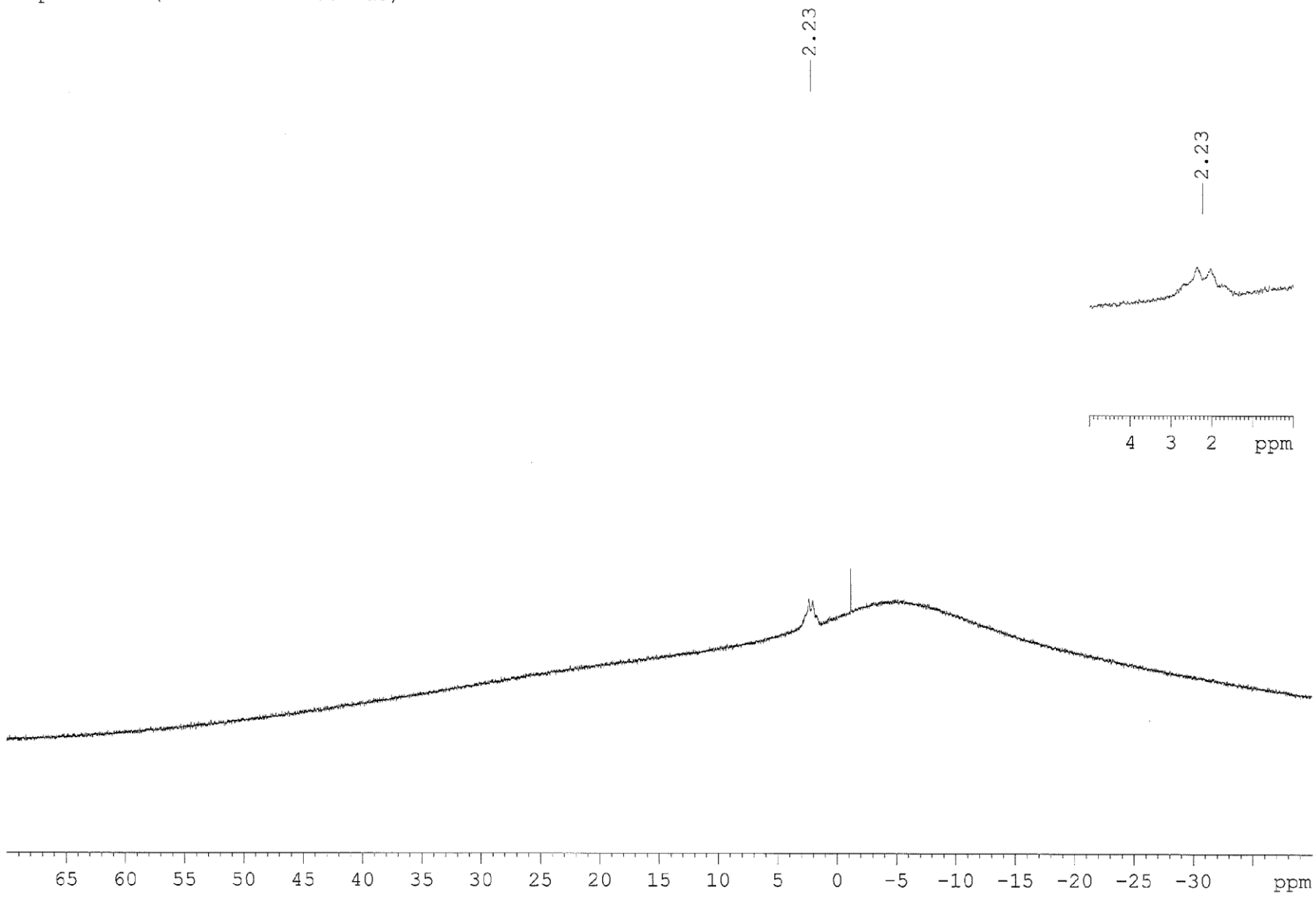

Compound 15 (1H NMR in MeCN-d3)
4.00
3.81
3.21
3.10
1.80
1.72
1.65
1.58
1.43
1.40
1.15
2.0
2.0
1.0
2.0
1.1
2.0
9.0
5.4
ppm


Compound 15 (13C NMR in MeCN-d3)
202.83
169.42
155.23
80.66
52.98
44.11
43.58
31.68
28.67
27.32
26.98
ppm
200
180
160
140
120
100
80
60
40
20
0
204
ppm
202.83
55
50
ppm
52.98
44.11
43.58

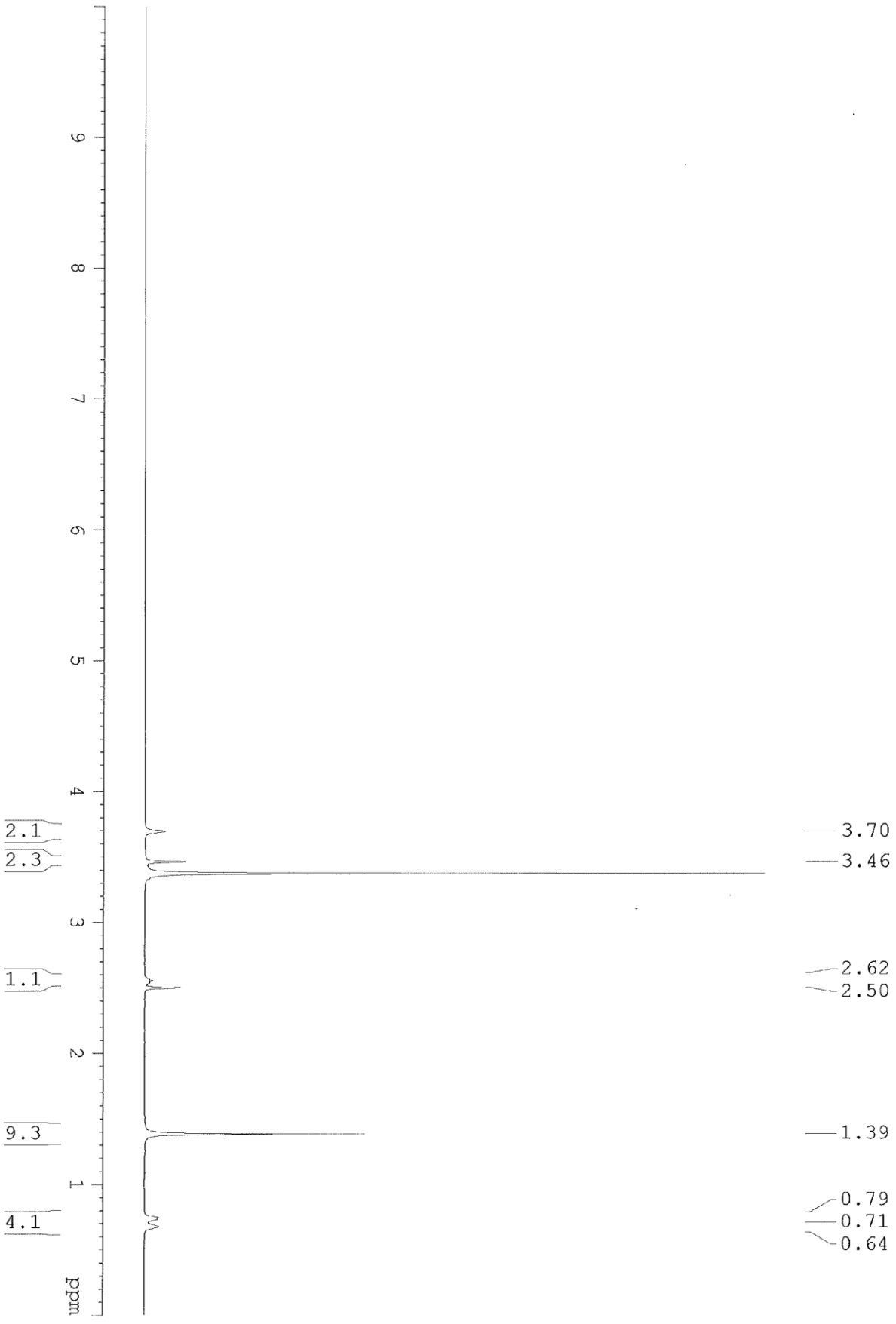
Compound 15 (19F NMR in MeCN-d3)

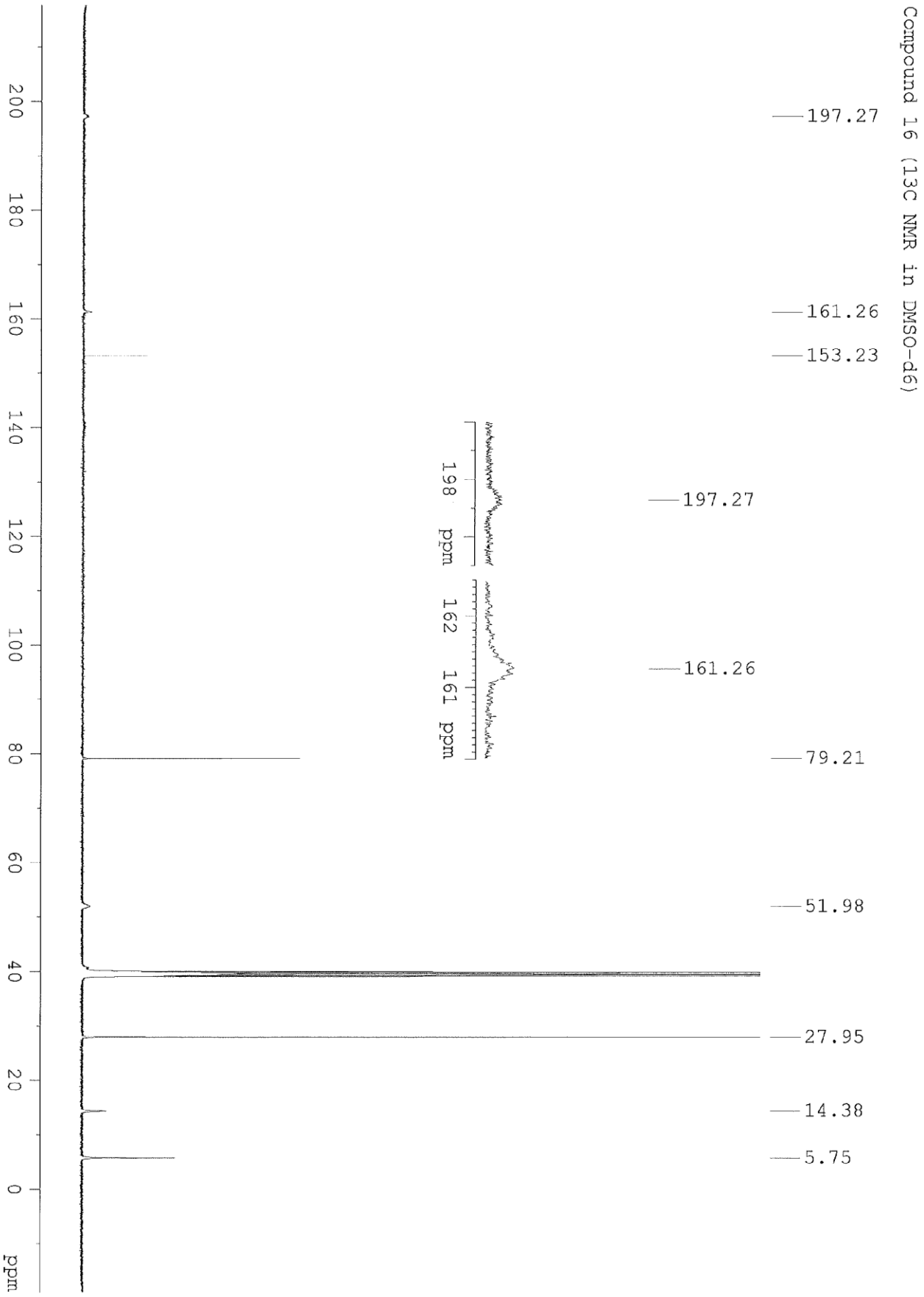


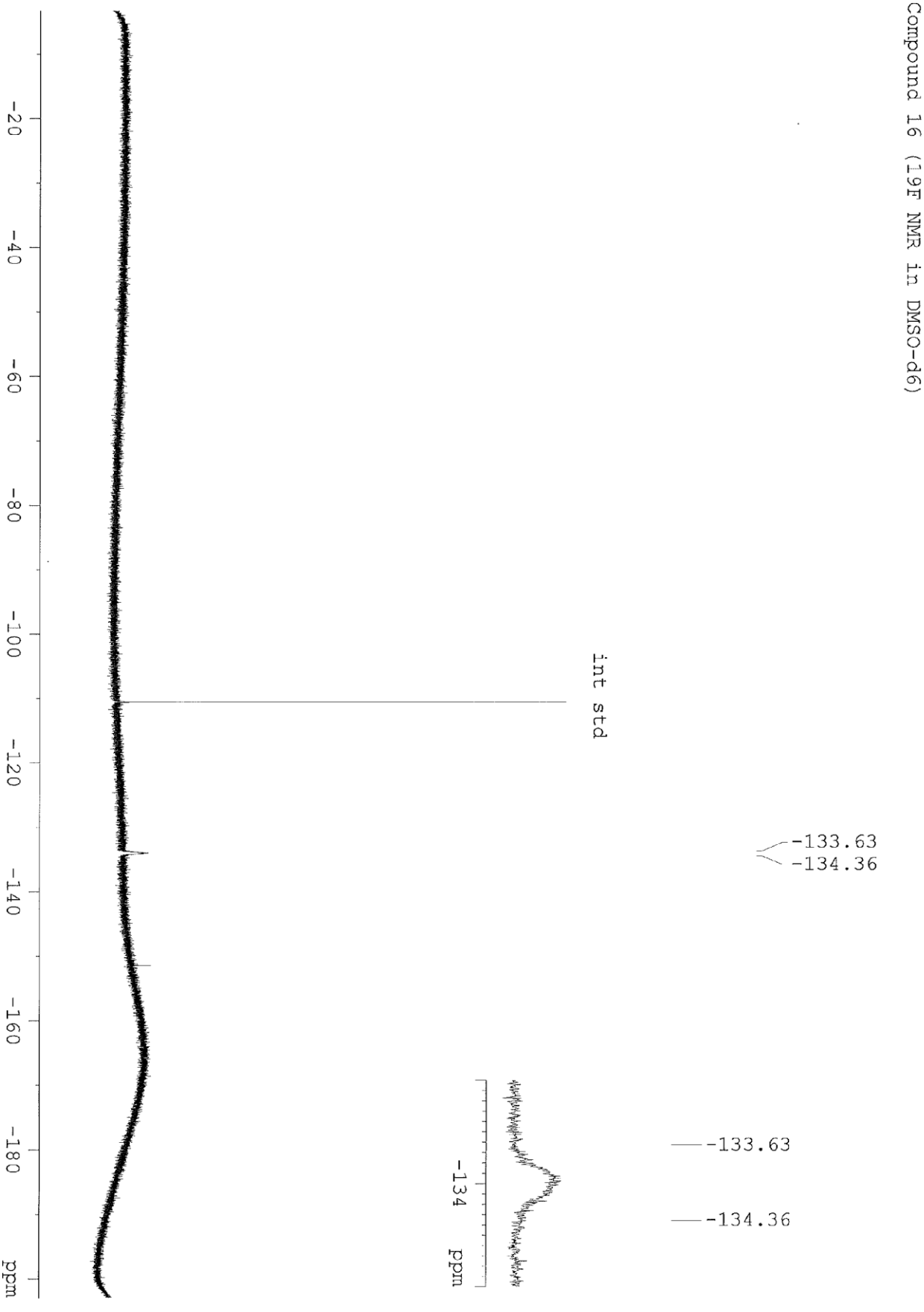
Compound 15 (11B NMR in MeCN-d3)



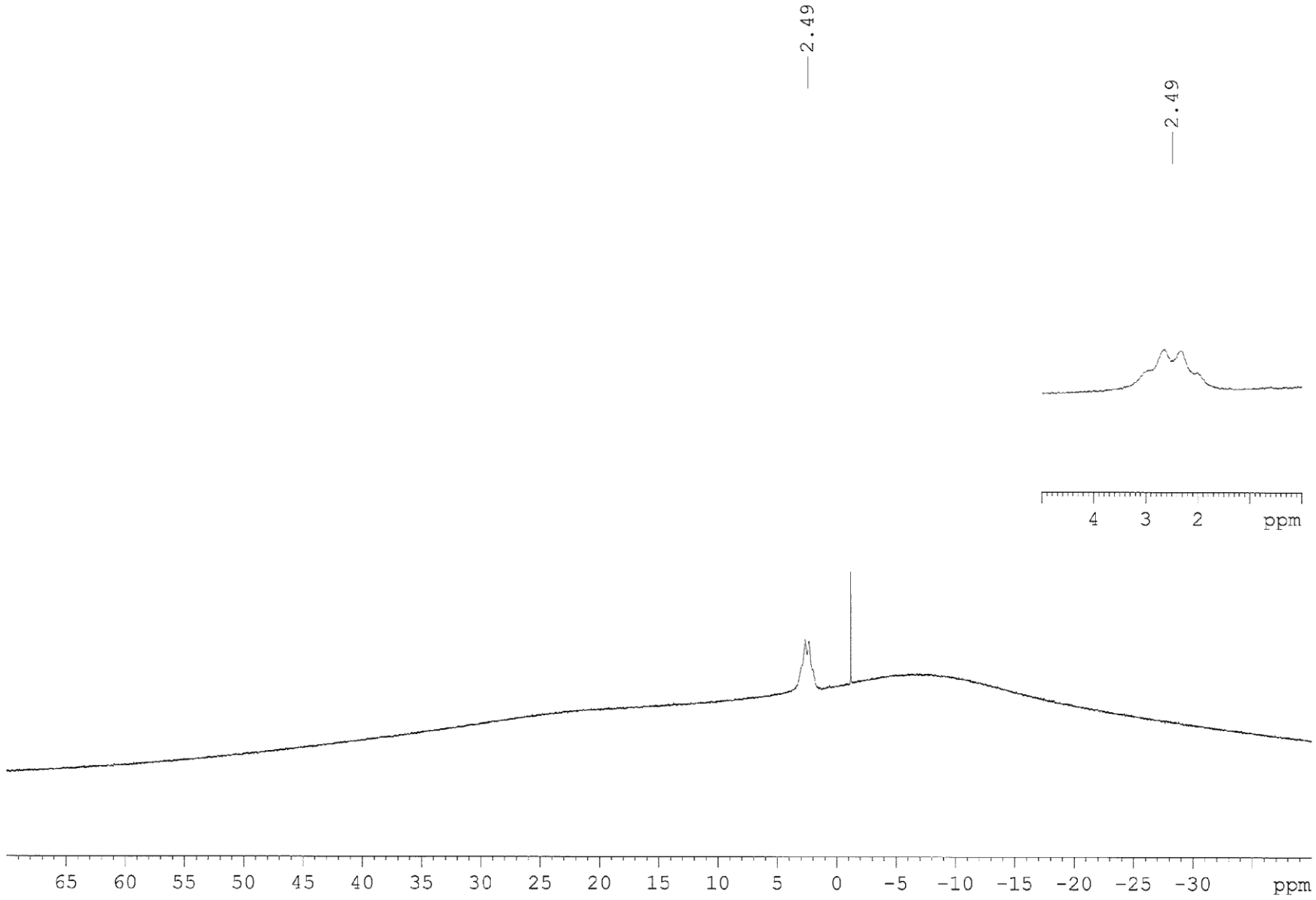
Compound 16 (1H NMR in DMSO-d6)



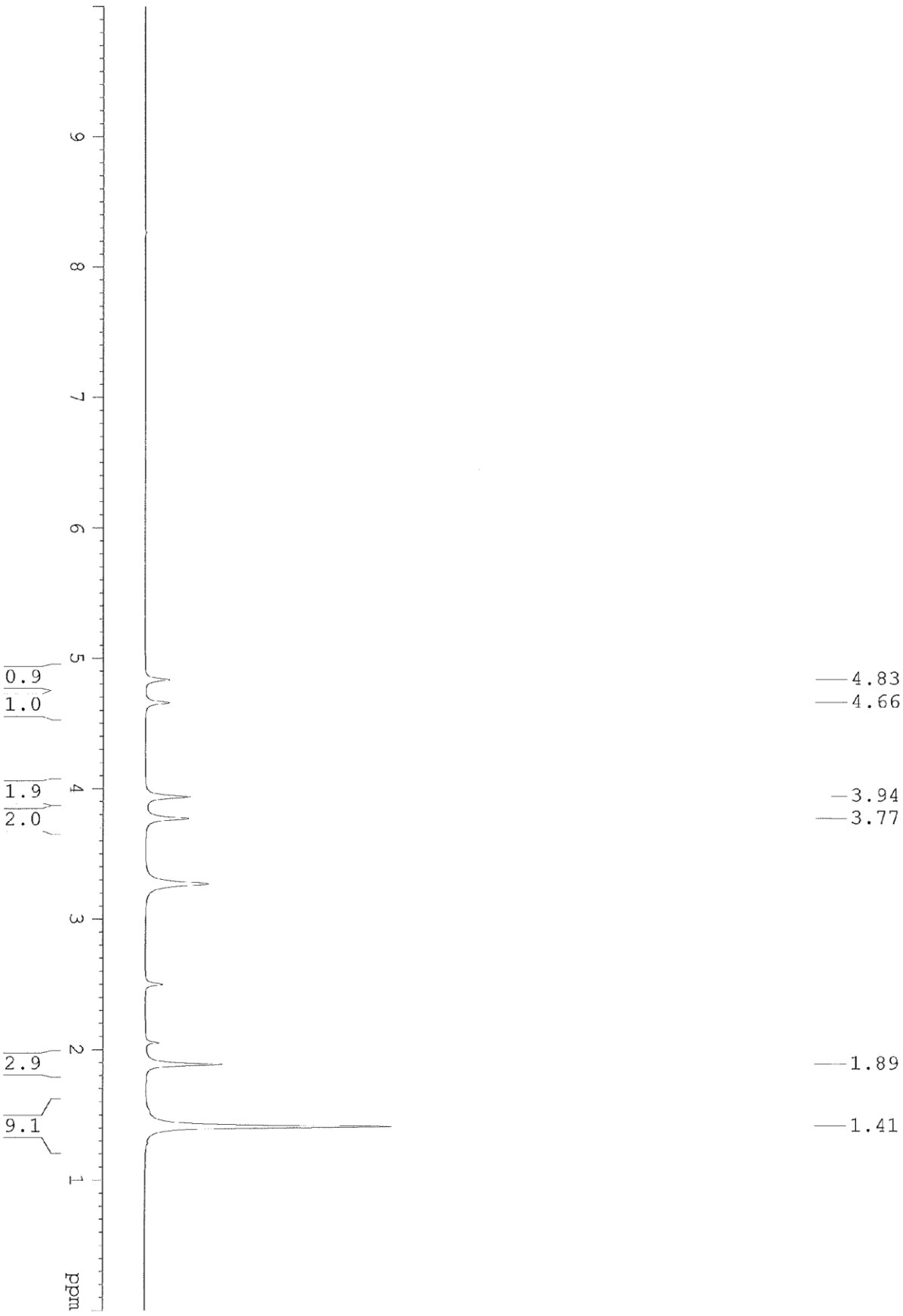

Compound 16 (13C NMR in DMSO-d6)
197.27
161.26
153.23
197.27
161.26
79.21
51.98
27.95
14.38
5.75
198 ppm
162 161 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

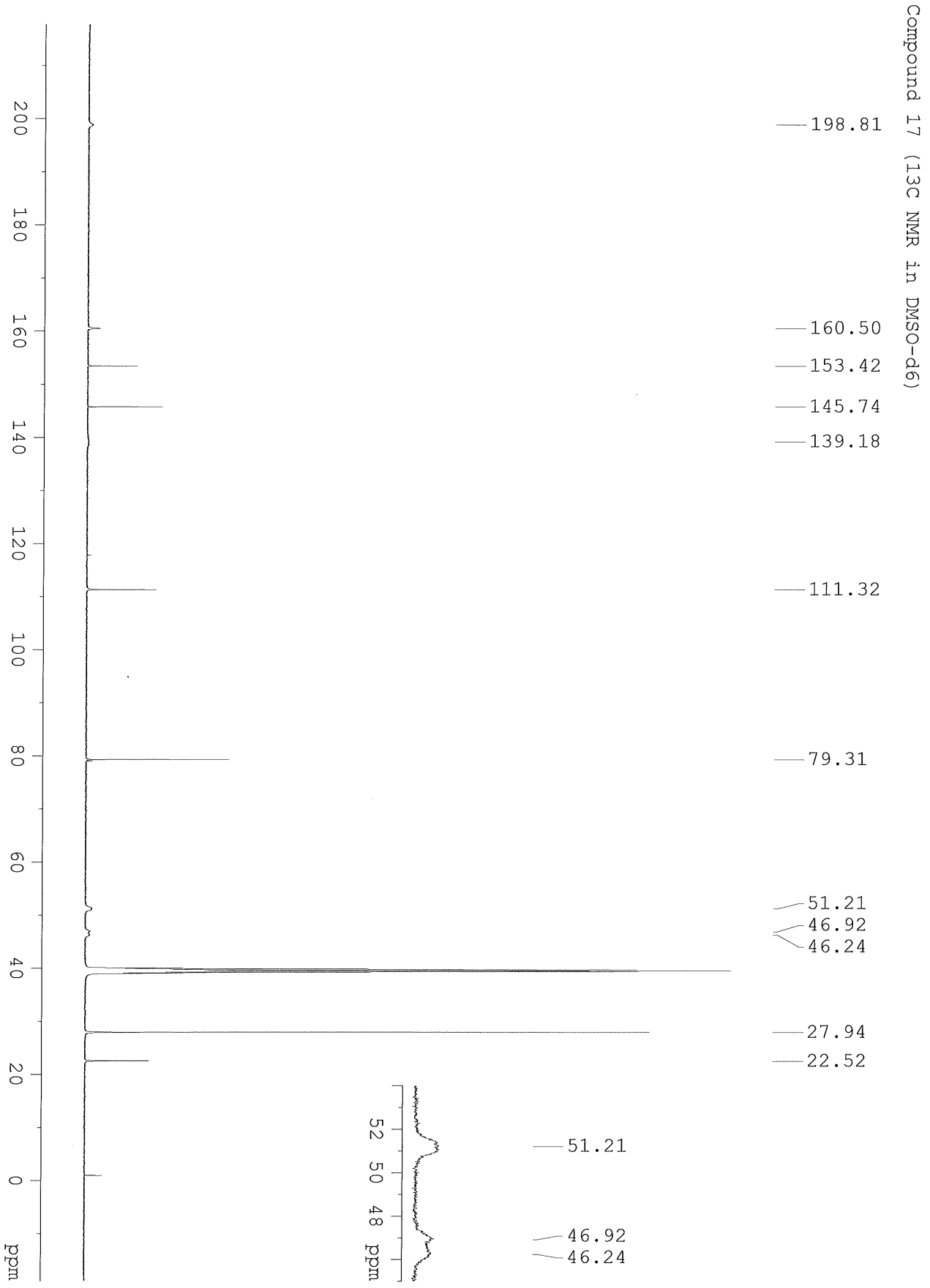

Compound 16 (19F NMR in DMSO-d6)
-133.63
-134.36
int std
-133.63
-134.36
-134 ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

Compound 16 (11B NMR in MeCN-d3)

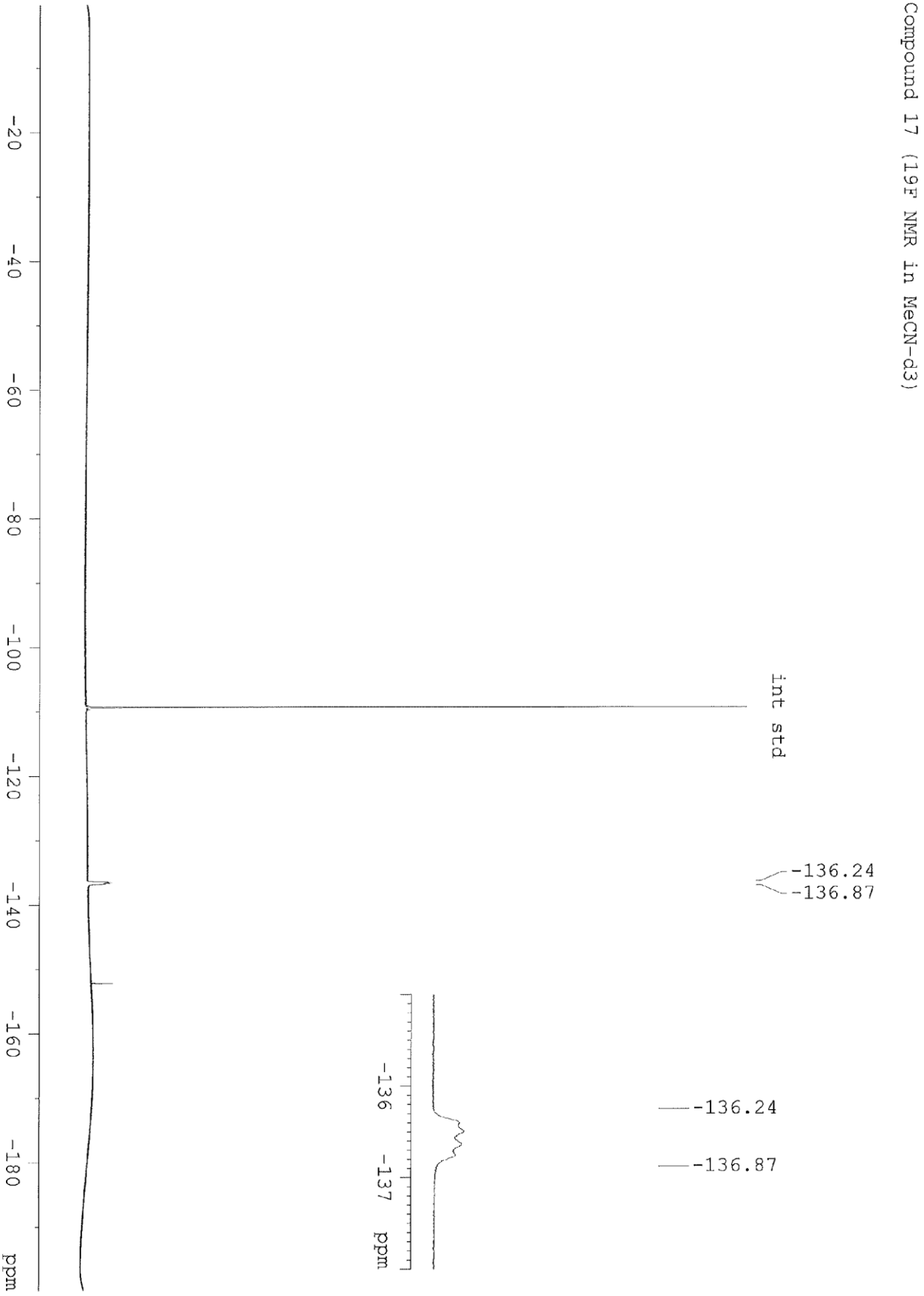


Compound 17 (1H NMR in DMSO-d6)

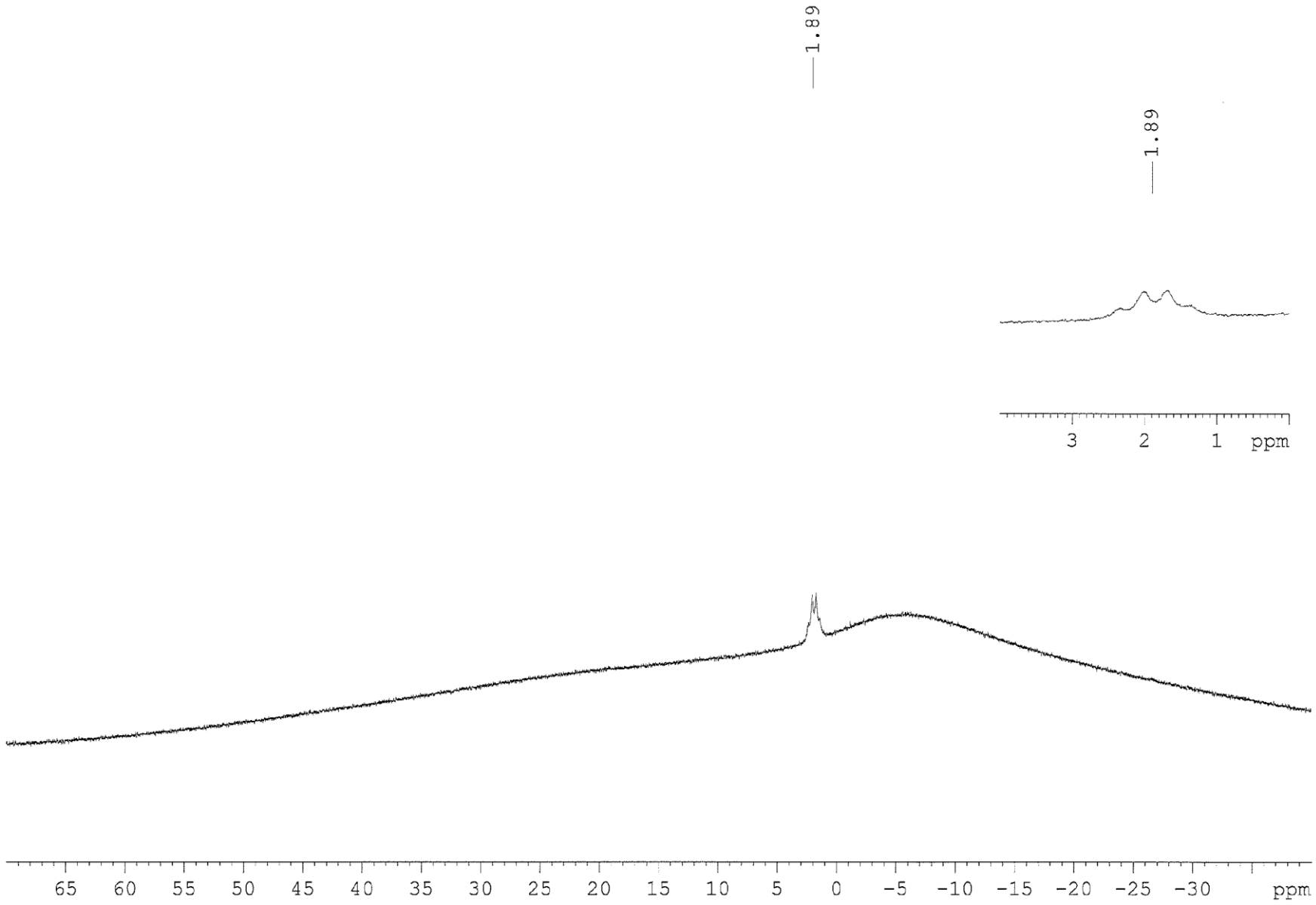


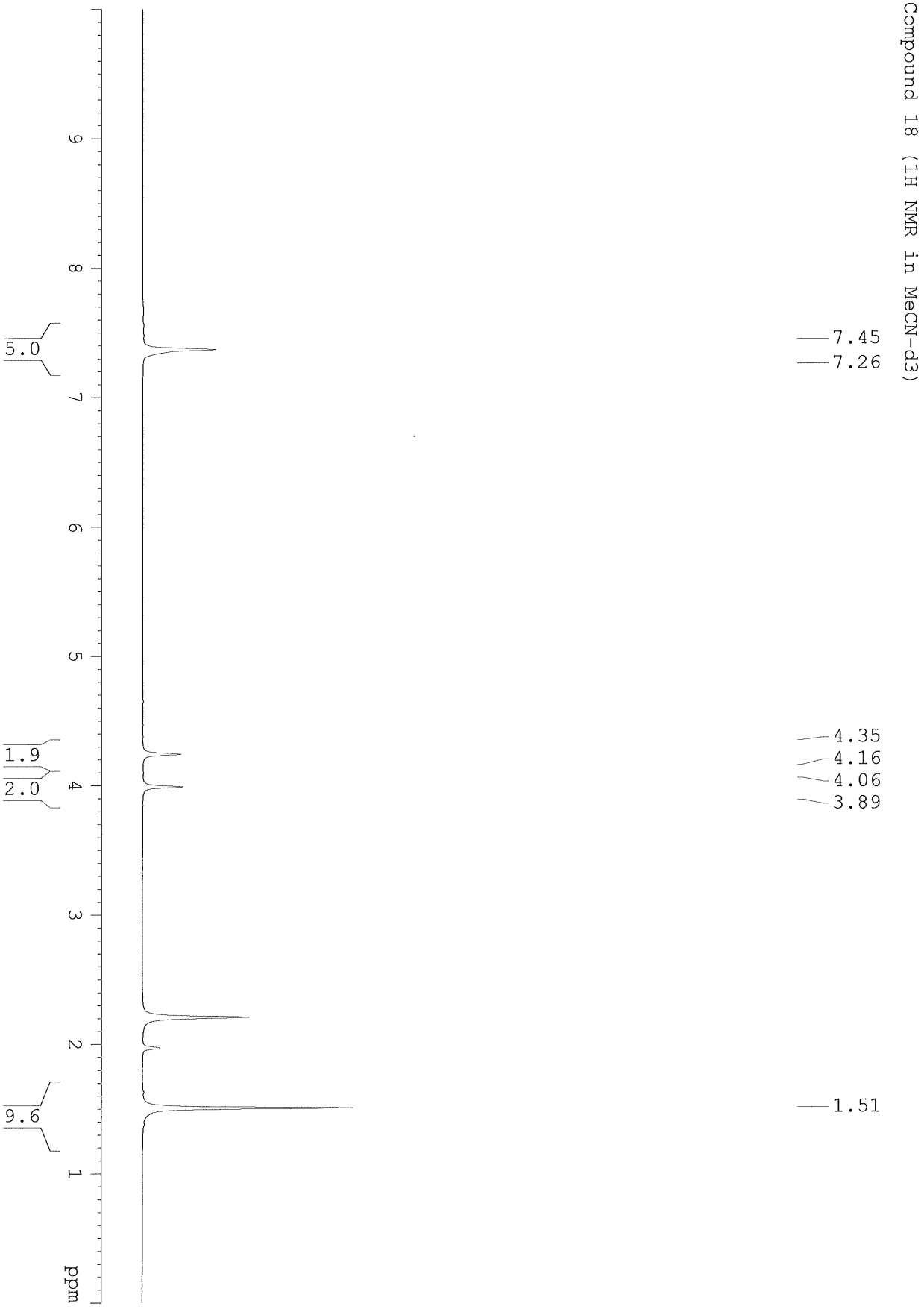

Compound 17 (13C NMR in DMSO-d6)
198.81
160.50
153.42
145.74
139.18
111.32
79.31
51.21
46.92
46.24
27.94
22.52
200
180
160
140
120
100
80
60
40
20
0
ppm
52
50
48
ppm
51.21
46.92
46.24

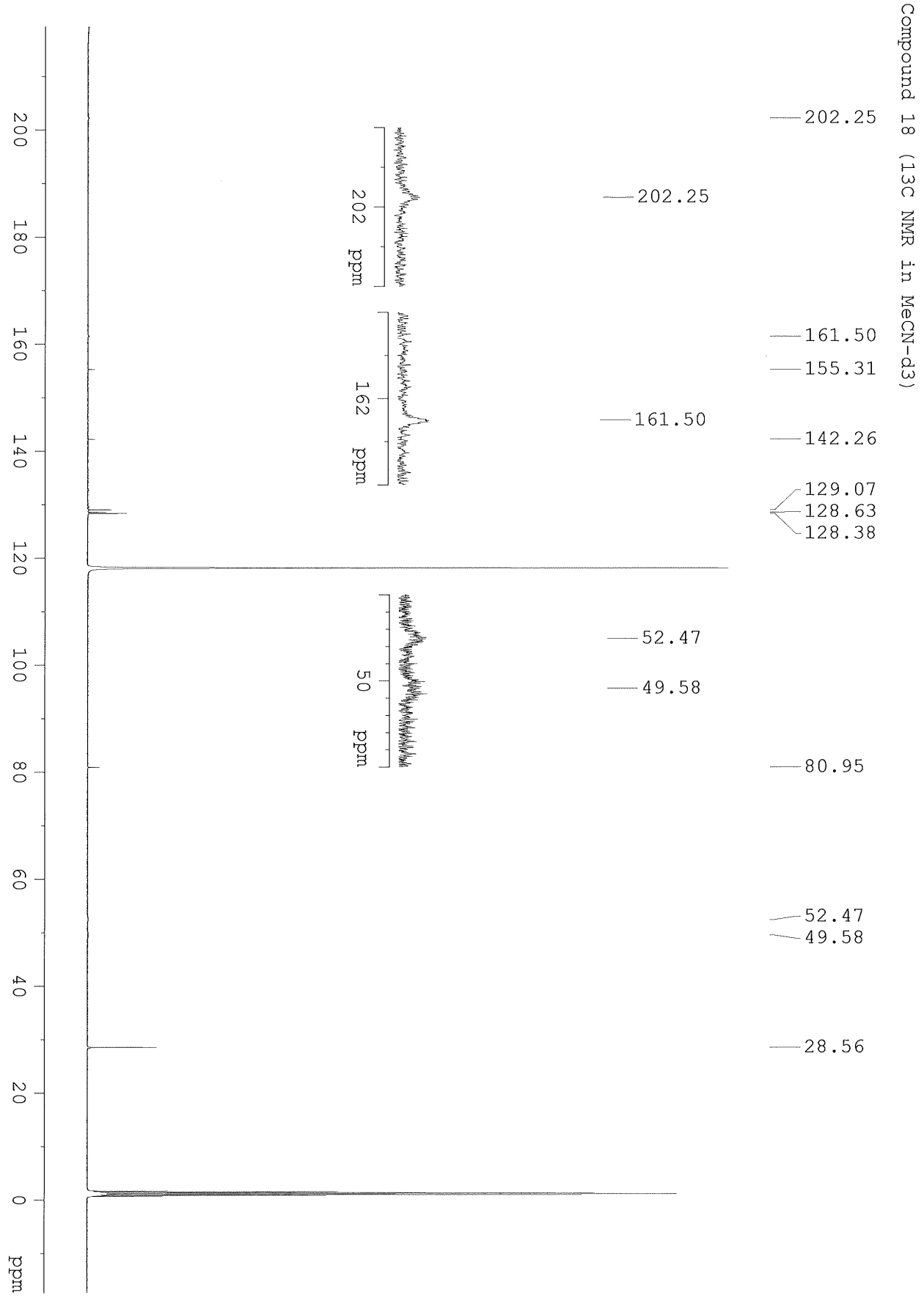
Compound 17 (19F NMR in MeCN-d3)



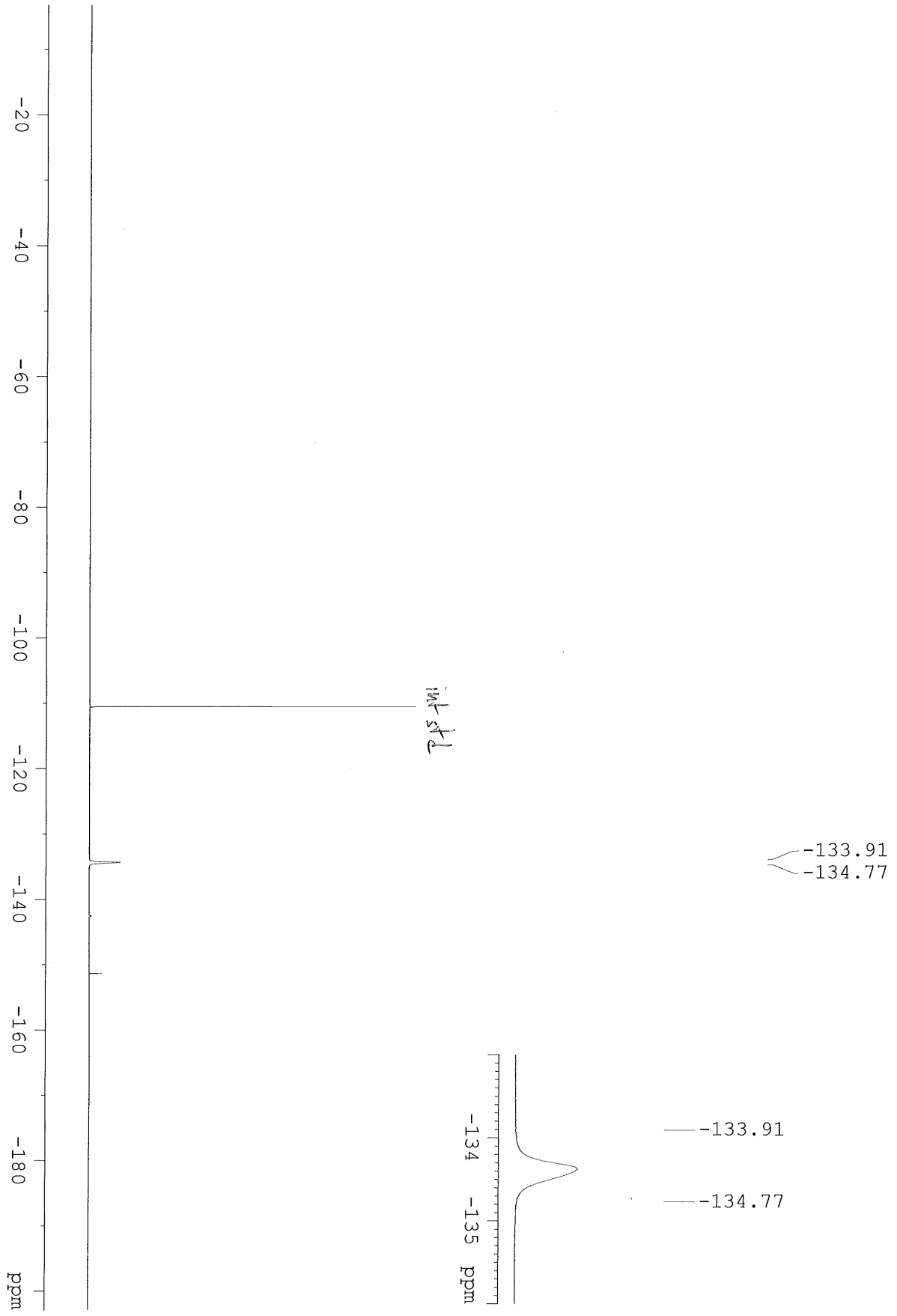
Compound 17 (11B NMR in MeCN-d3)



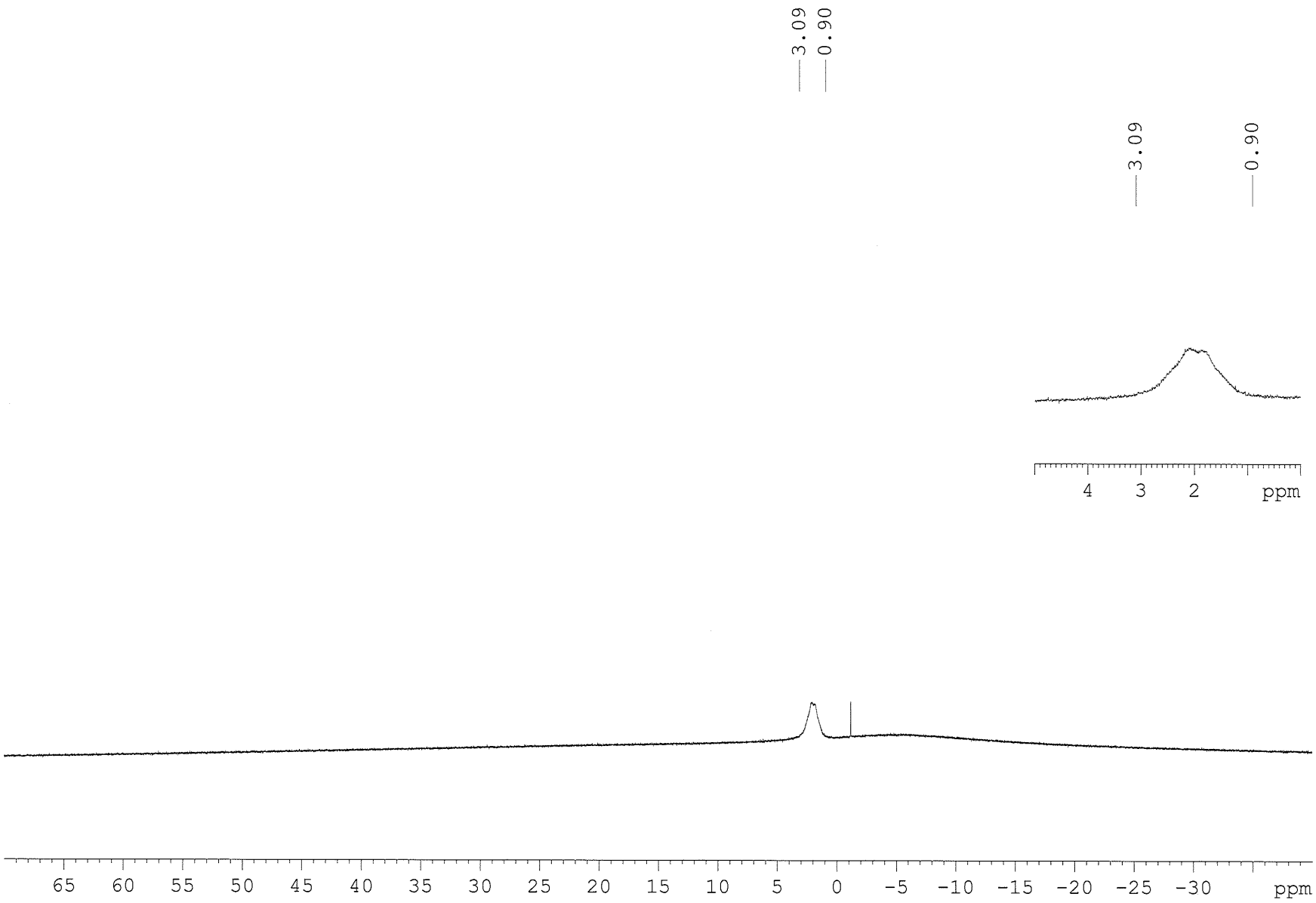

Compound 18 (1H NMR in MeCN-d3)
7.45
7.26
4.35
4.16
4.06
3.89
1.51
5.0
1.9
2.0
9.6
ppm

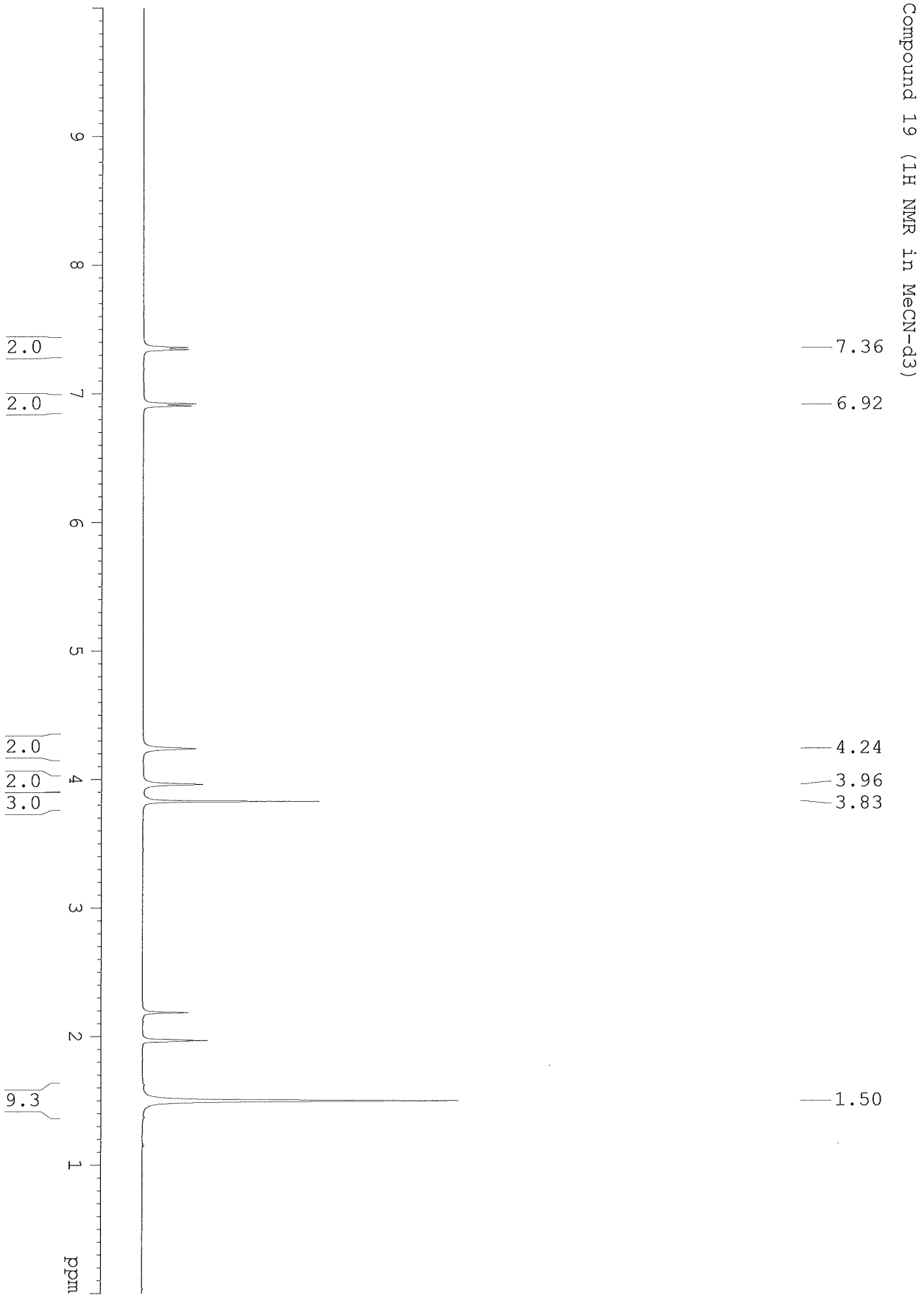

Compound 18 (13C NMR in MeCN-d3)
202.25
161.50
155.31
142.26
129.07
128.63
128.38
80.95
52.47
49.58
28.56
202.25
161.50
52.47
49.58
202 ppm
162 ppm
50 ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

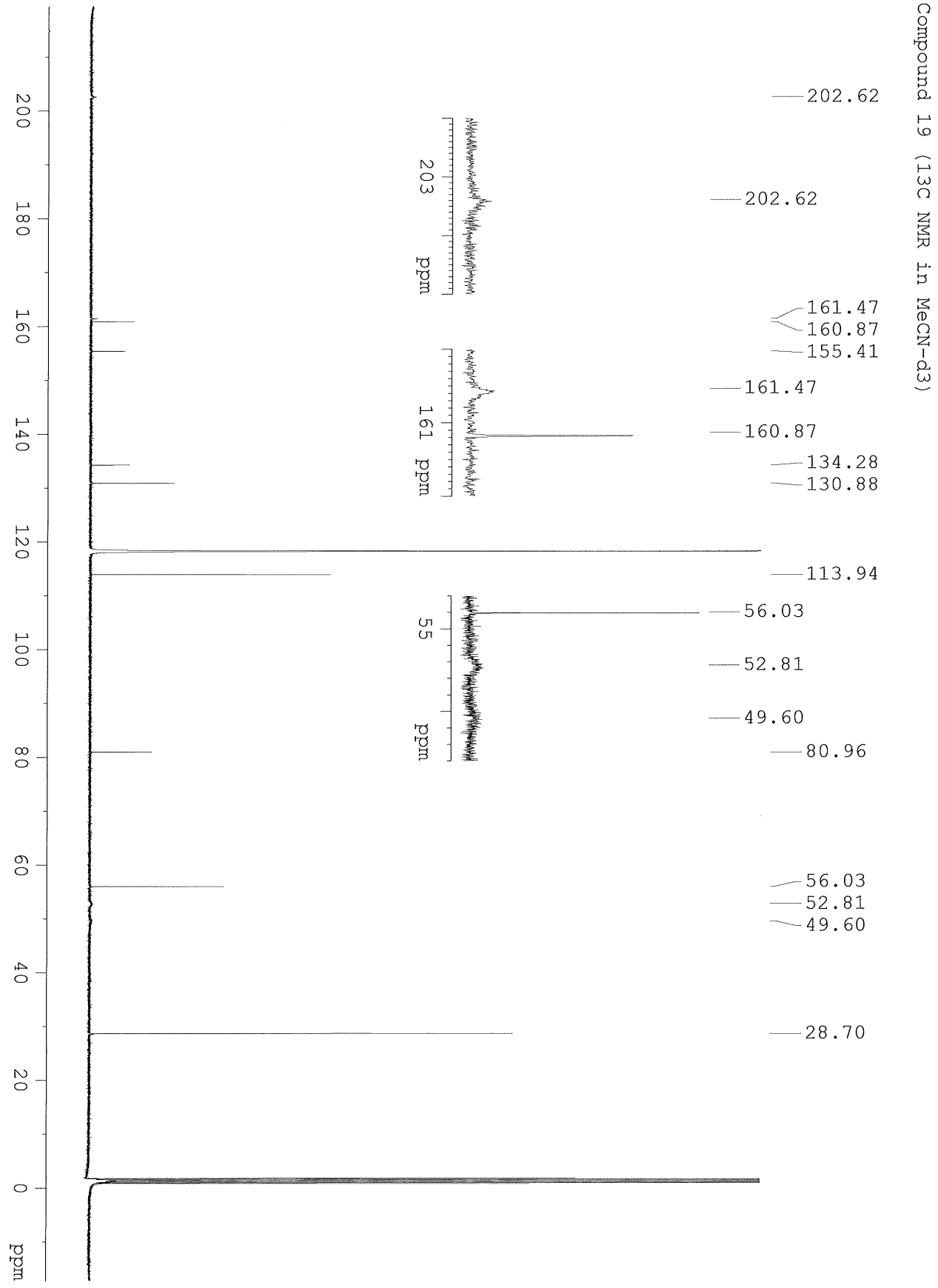
Compound 18 (19F NMR in DMSO-d6)



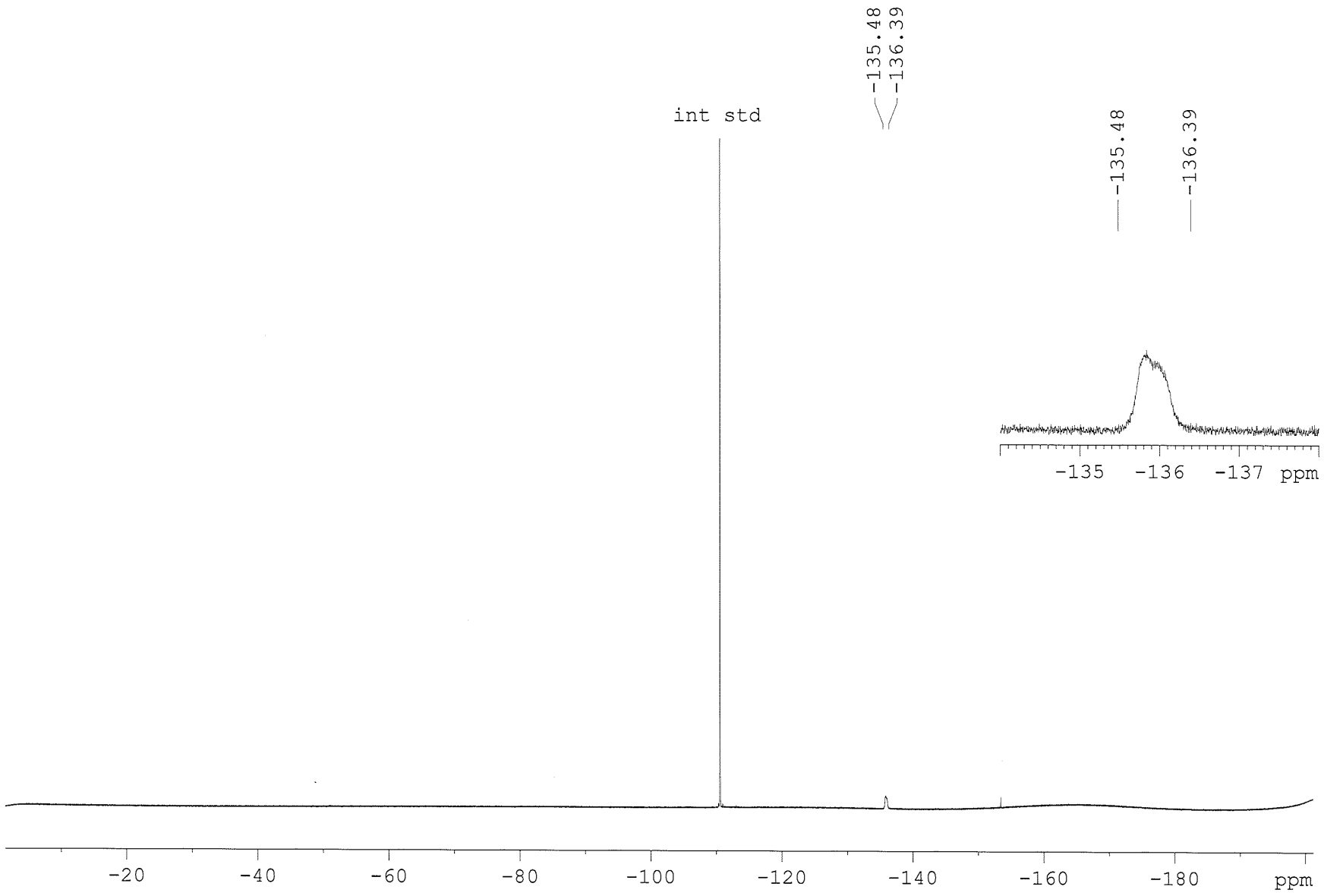
Compound 18 (11B NMR in MeCN-d3)



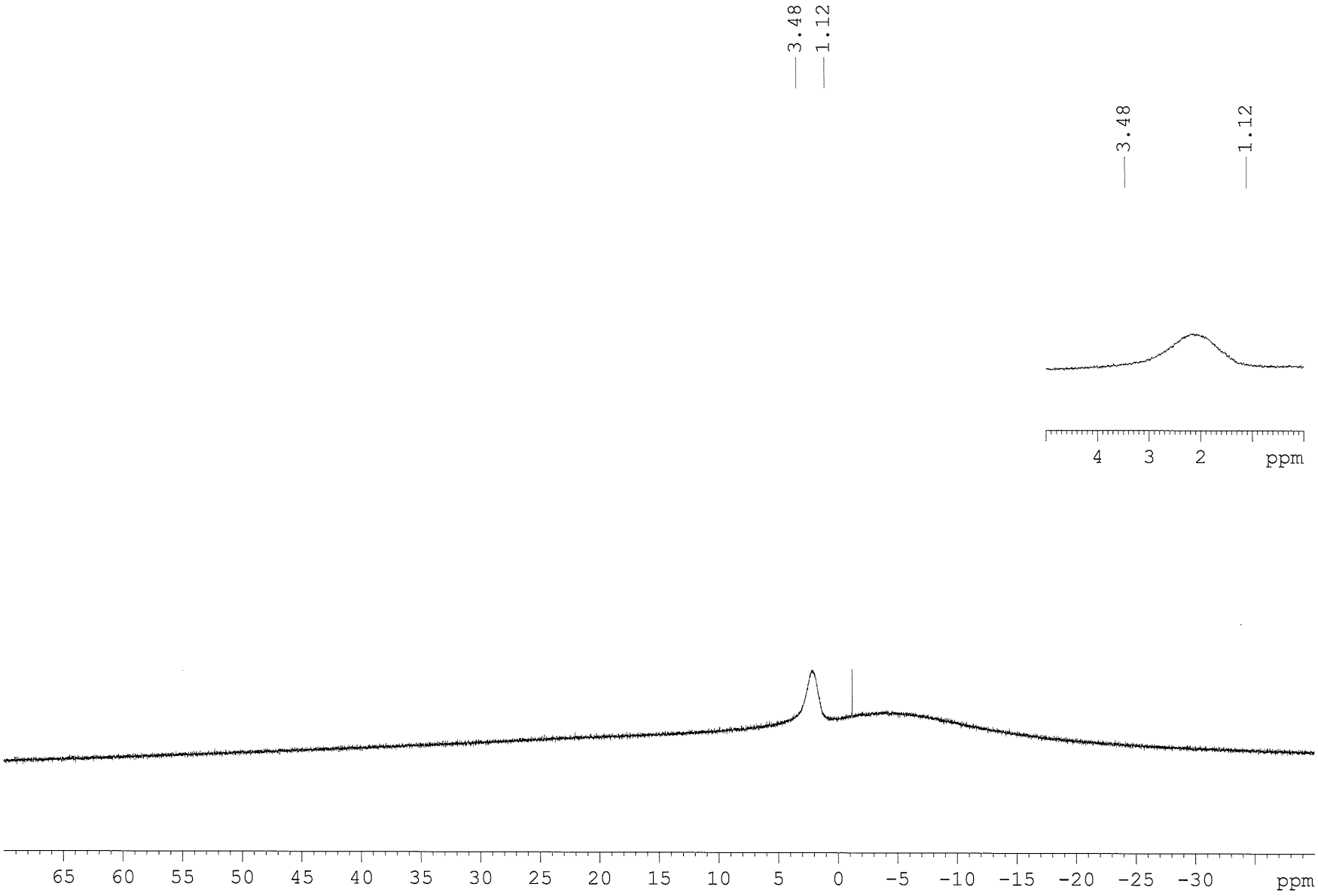

Compound 19 (1H NMR in MeCN-d3)
7.36
6.92
4.24
3.96
3.83
1.50
2.0
2.0
2.0
2.0
3.0
9.3
ppm

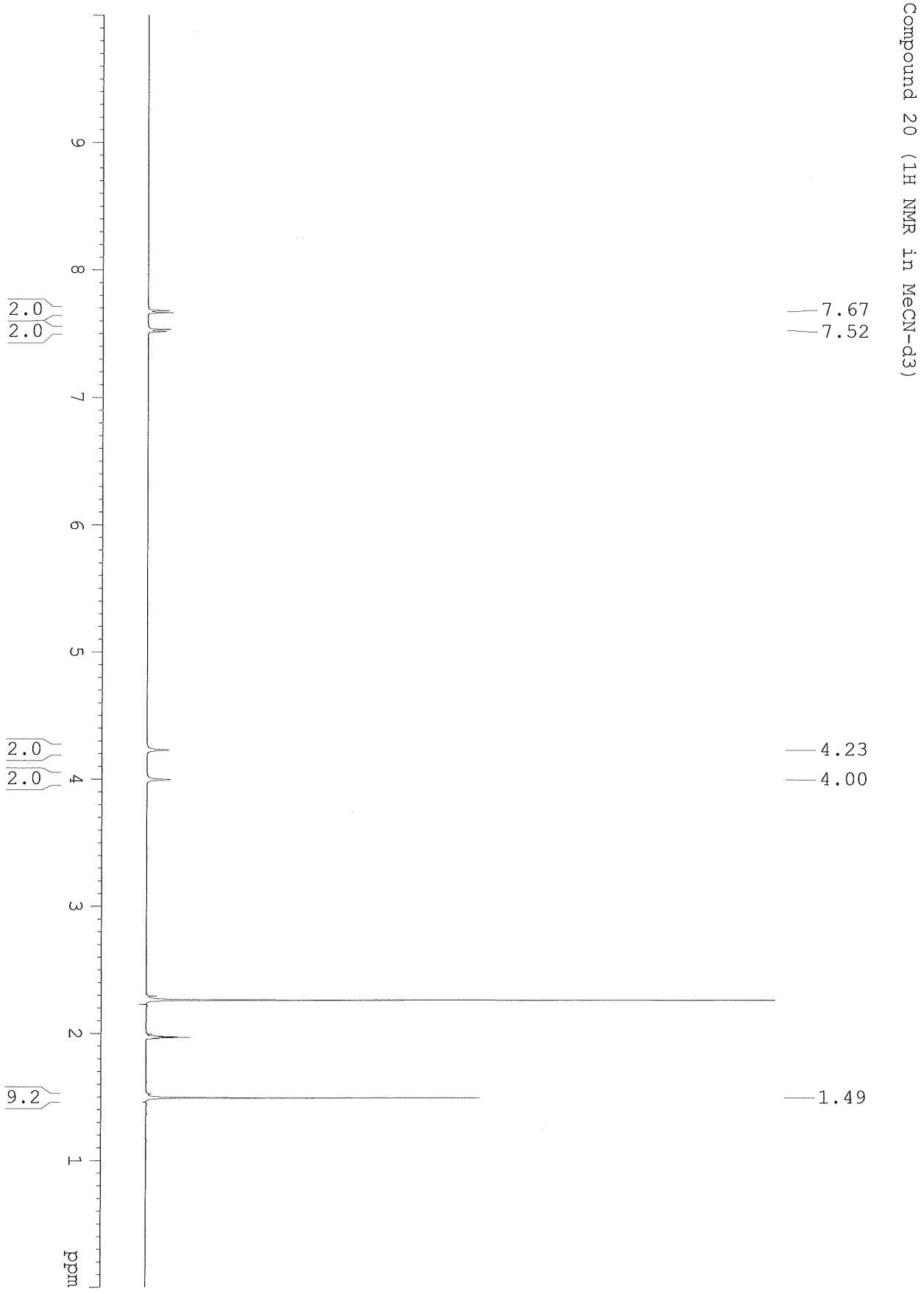

Compound 19 (13C NMR in MeCN-d3)
202.62
202.62
161.47
160.87
155.41
161.47
160.87
134.28
130.88
113.94
56.03
52.81
49.60
80.96
56.03
52.81
49.60
28.70
203 ppm
161 ppm
55 ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

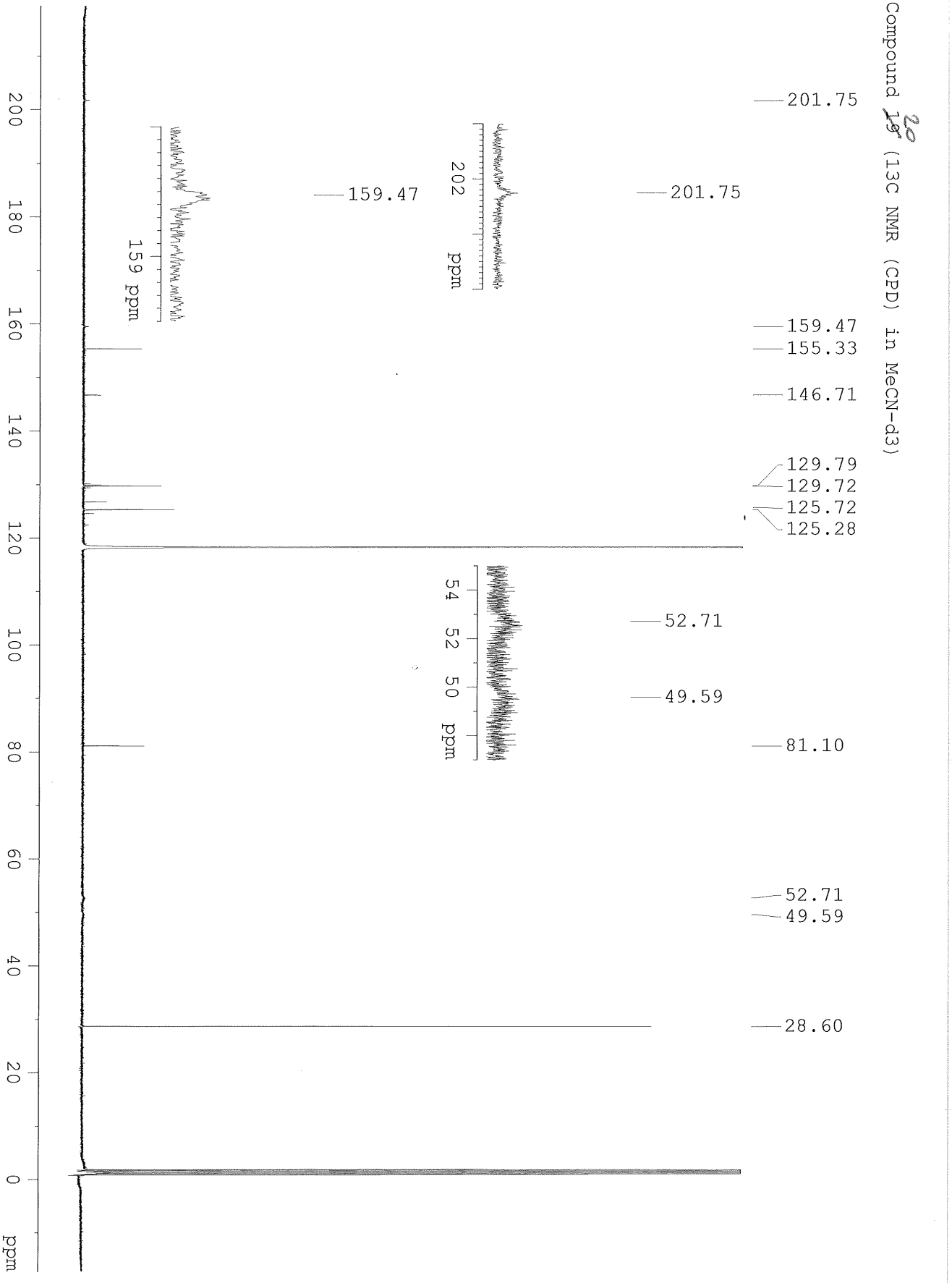
Compound 19 (19F NMR in MeCN-d3)

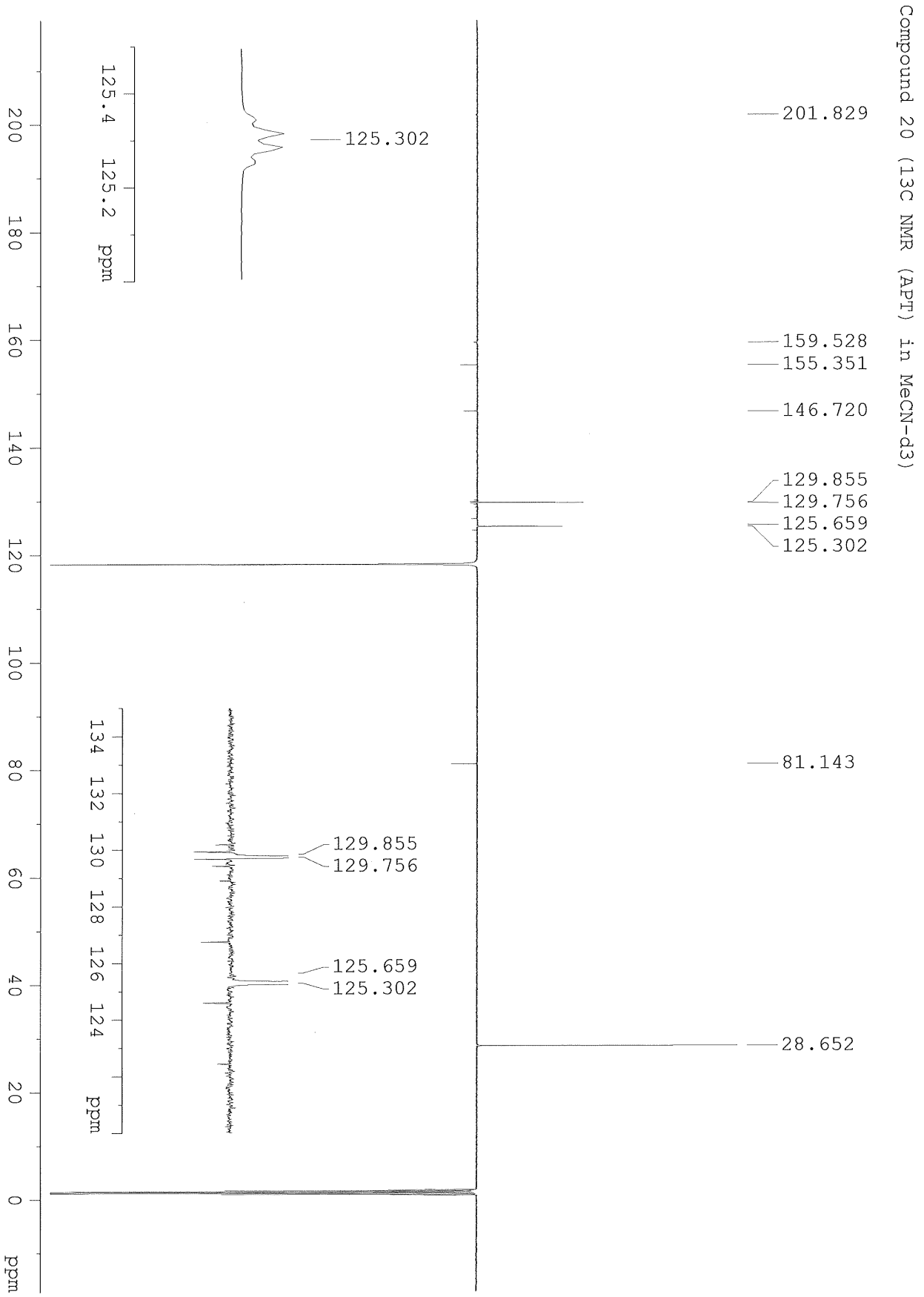


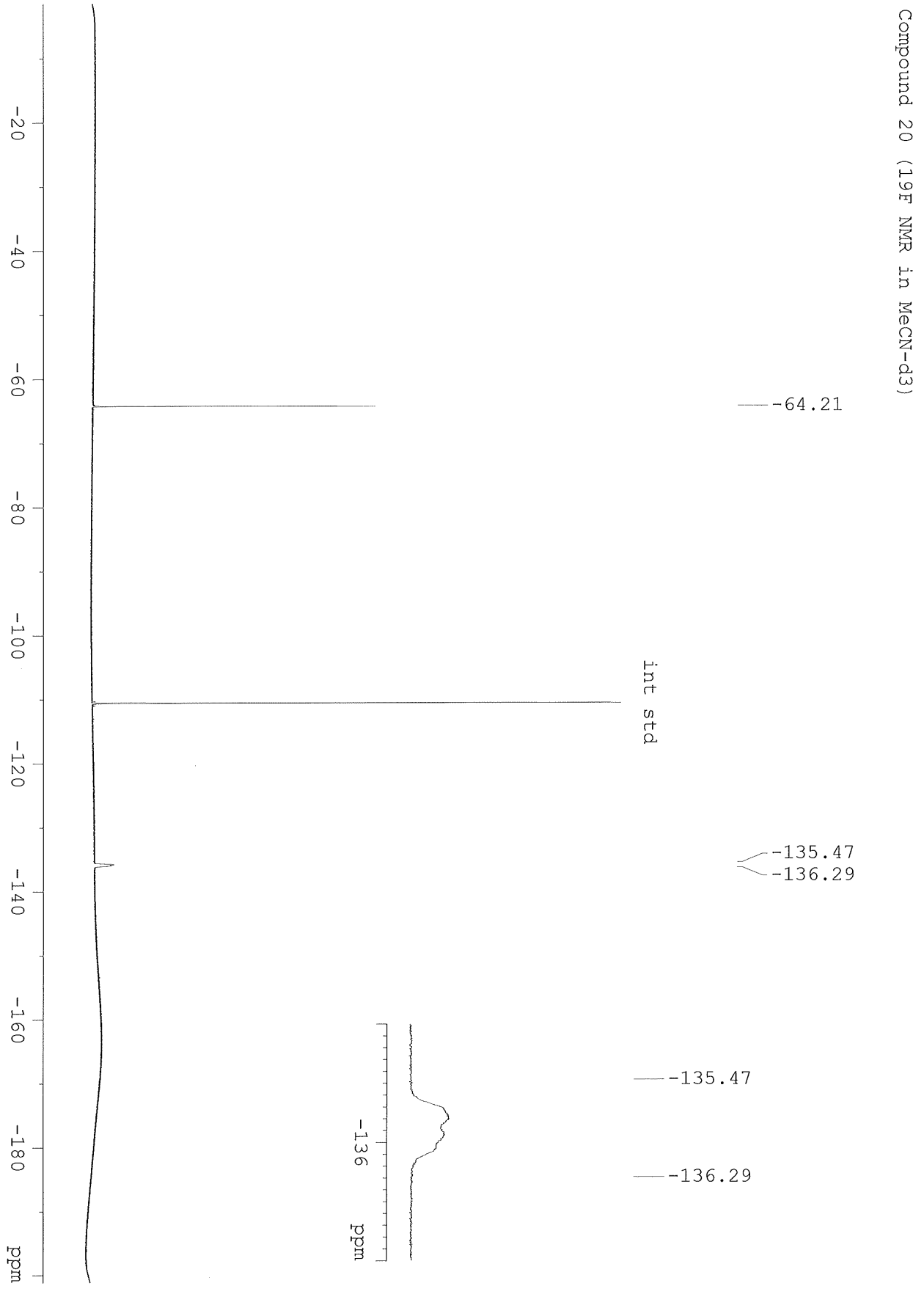
Compound 19 (11B NMR in MeCN-d3)

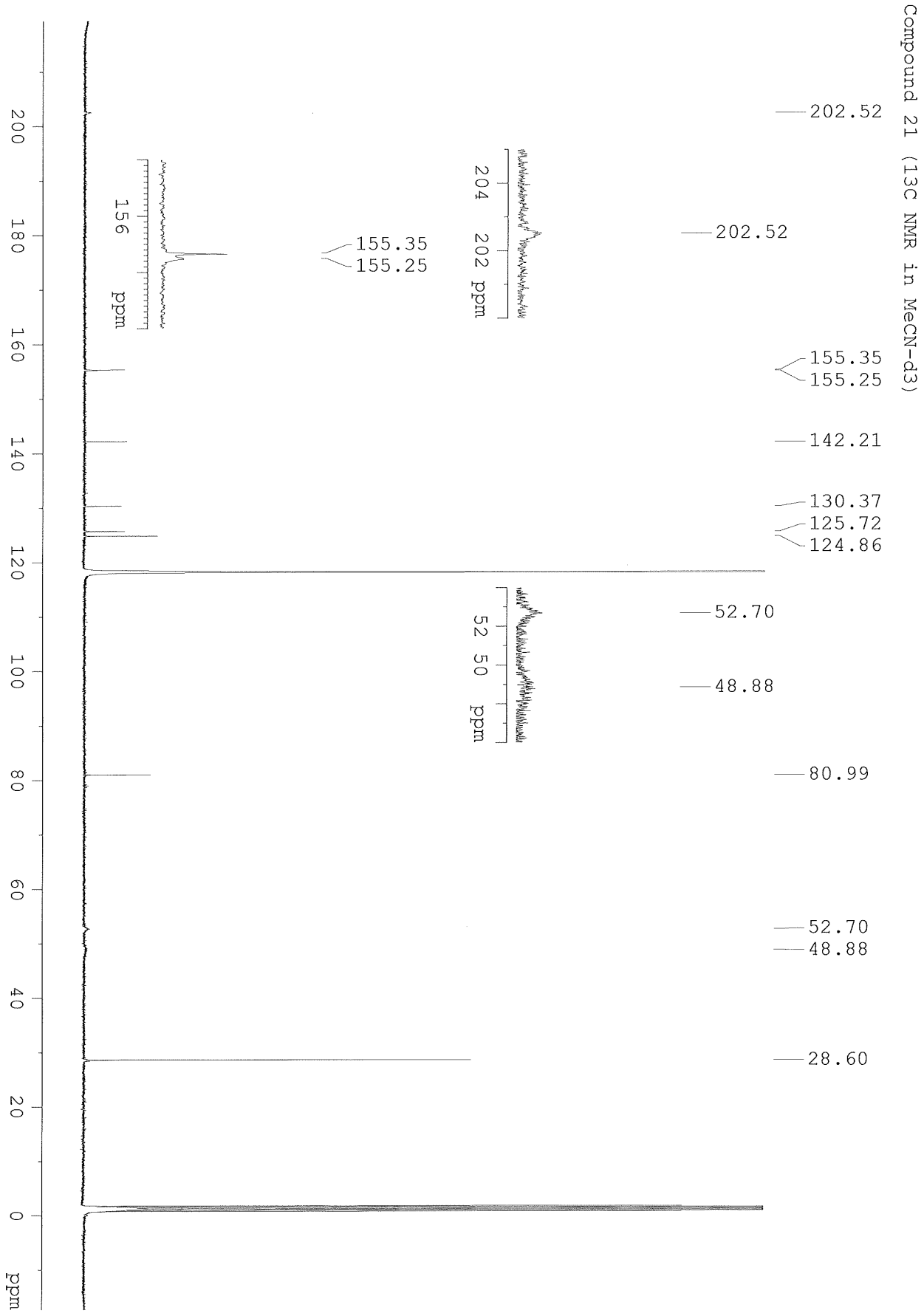



Compound 20 (1H NMR in MeCN-d3)
7.67
7.52
4.23
4.00
1.49
2.0
2.0
2.0
2.0
9.2
ppm

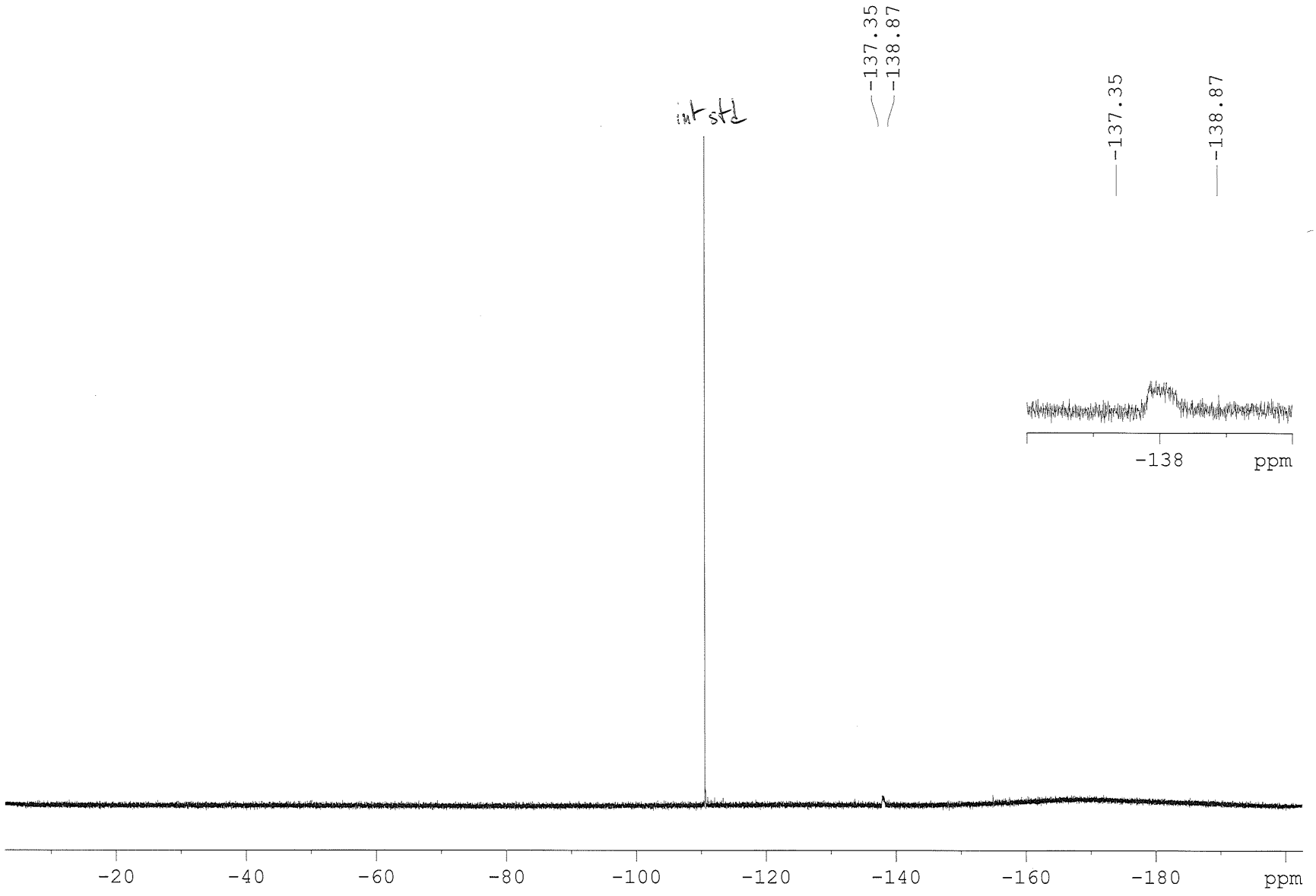

Compound 20 (13C NMR (CPD) in MeCN-d3)
201.75
159.47
155.33
146.71
129.79
129.72
125.72
125.28
52.71
49.59
81.10
52.71
49.59
28.60
159.47
201.75
159 ppm
202 ppm
54 52 50 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm


Compound 20 (13C NMR (APT) in MeCN-d3)
201.829
159.528
155.351
146.720
129.855
129.756
125.659
125.302
81.143
28.652
125.302
125.4 125.2 ppm
129.855
129.756
125.659
125.302
134 132 130 128 126 124 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

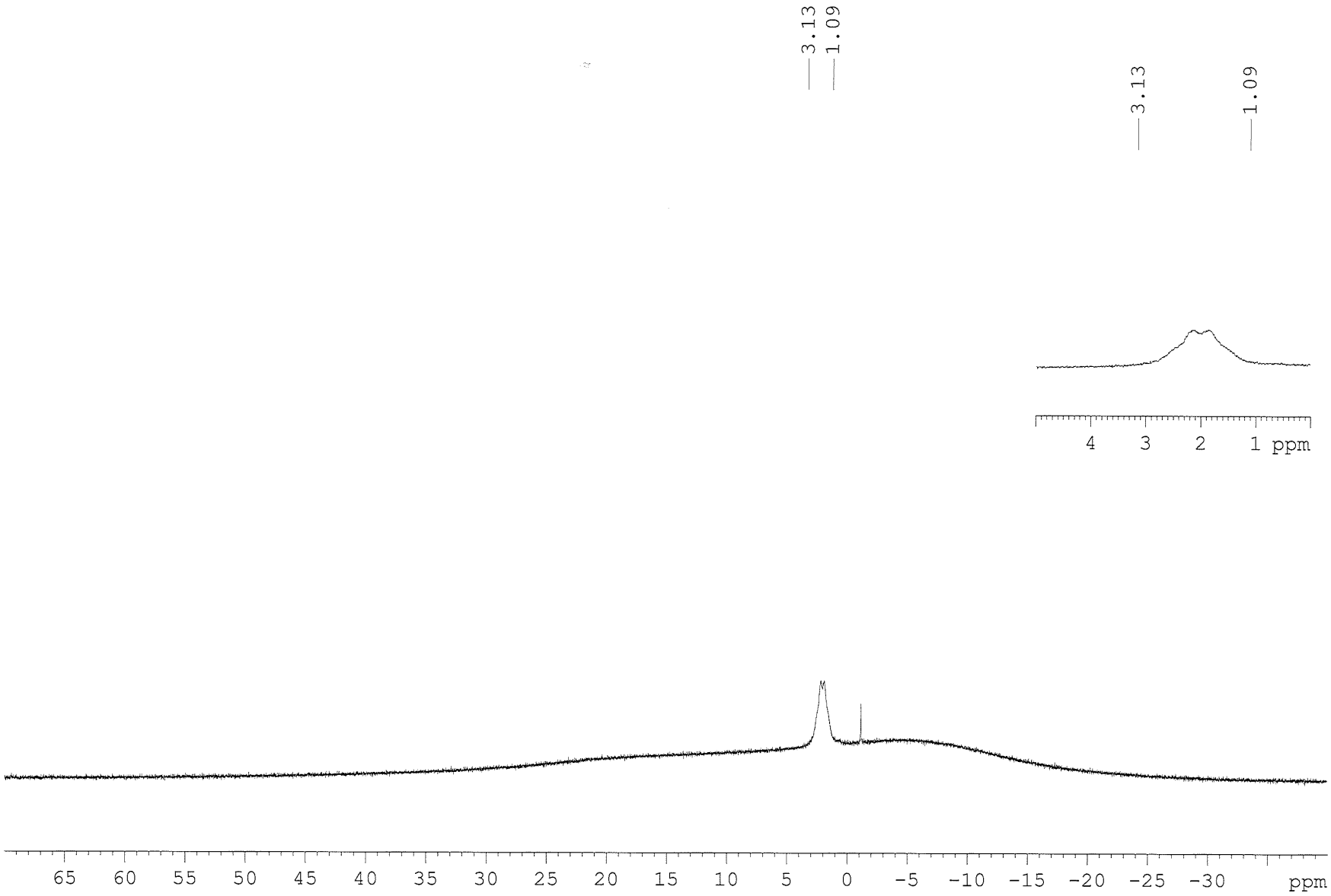

Compound 20 (19F NMR in MeCN-d3)
-64.21
int std
-135.47
-136.29
-135.47
-136.29
-136
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


Compound 21 (13C NMR in MeCN-d3)
202.52
155.35
155.25
142.21
130.37
125.72
124.86
80.99
52.70
48.88
28.60
156 ppm
204 202 ppm
52 50 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

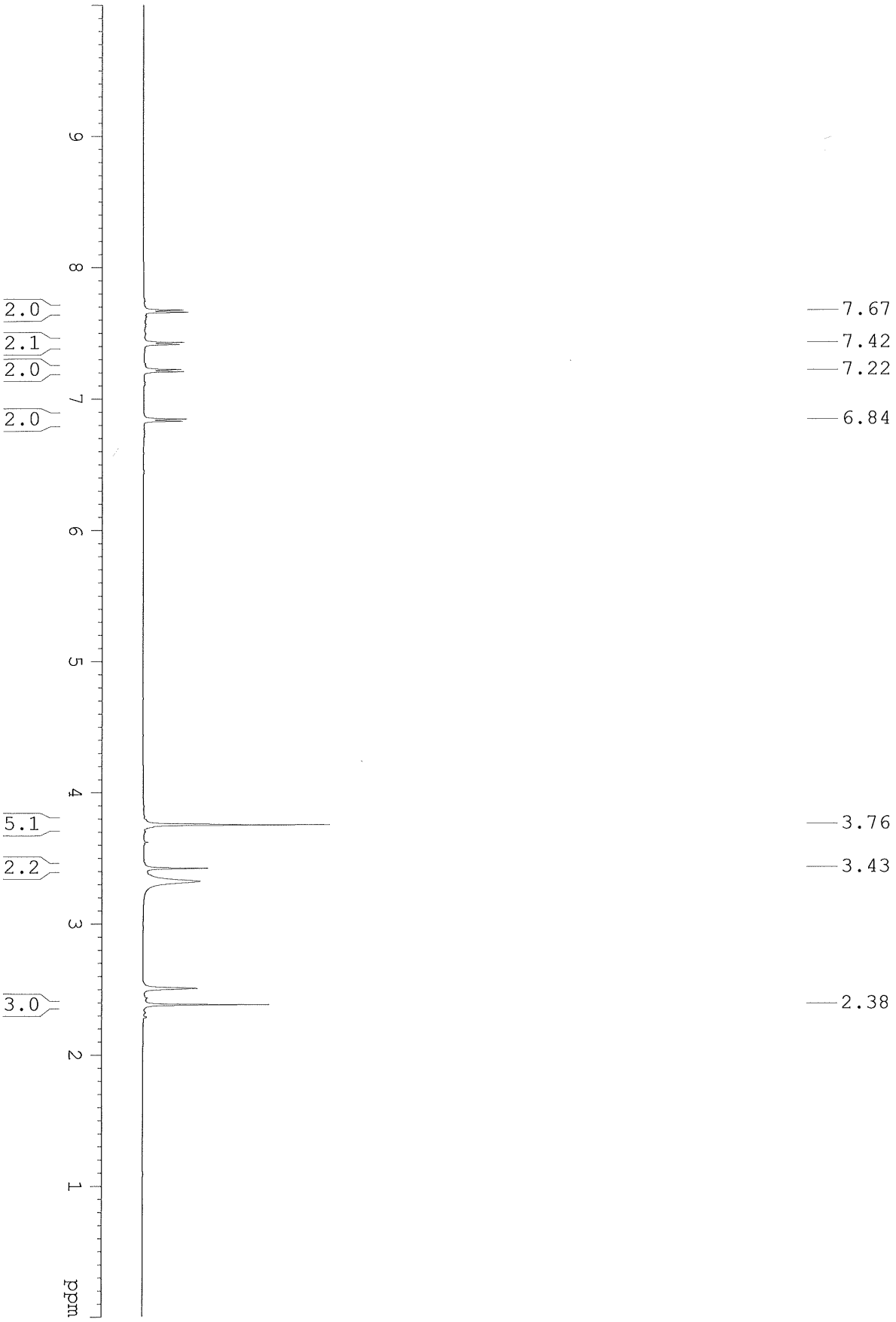
:ompound 21 (19F NMR in MeCN-d3

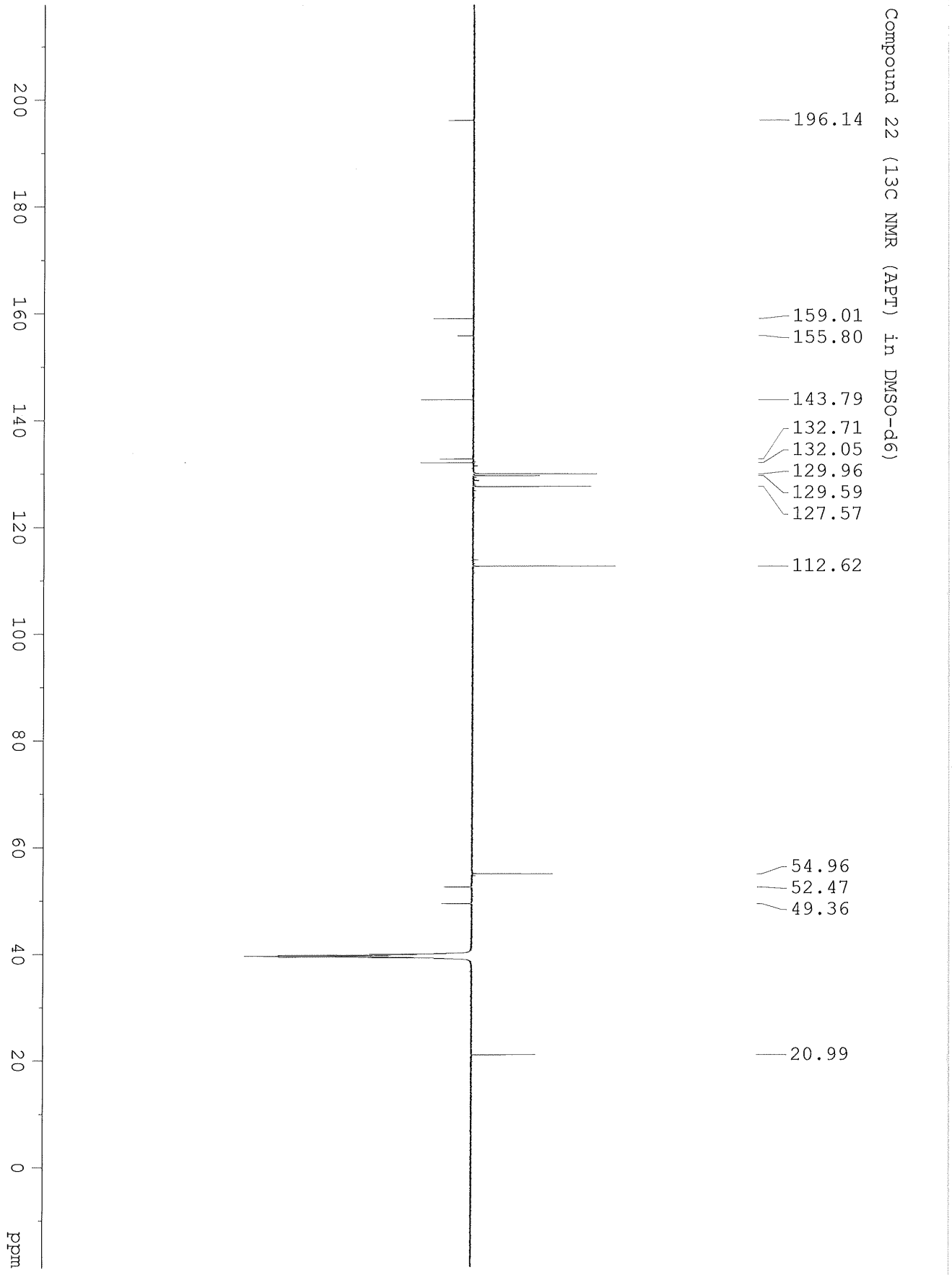


Compound 21 (11B NMR in MeCN-d3)

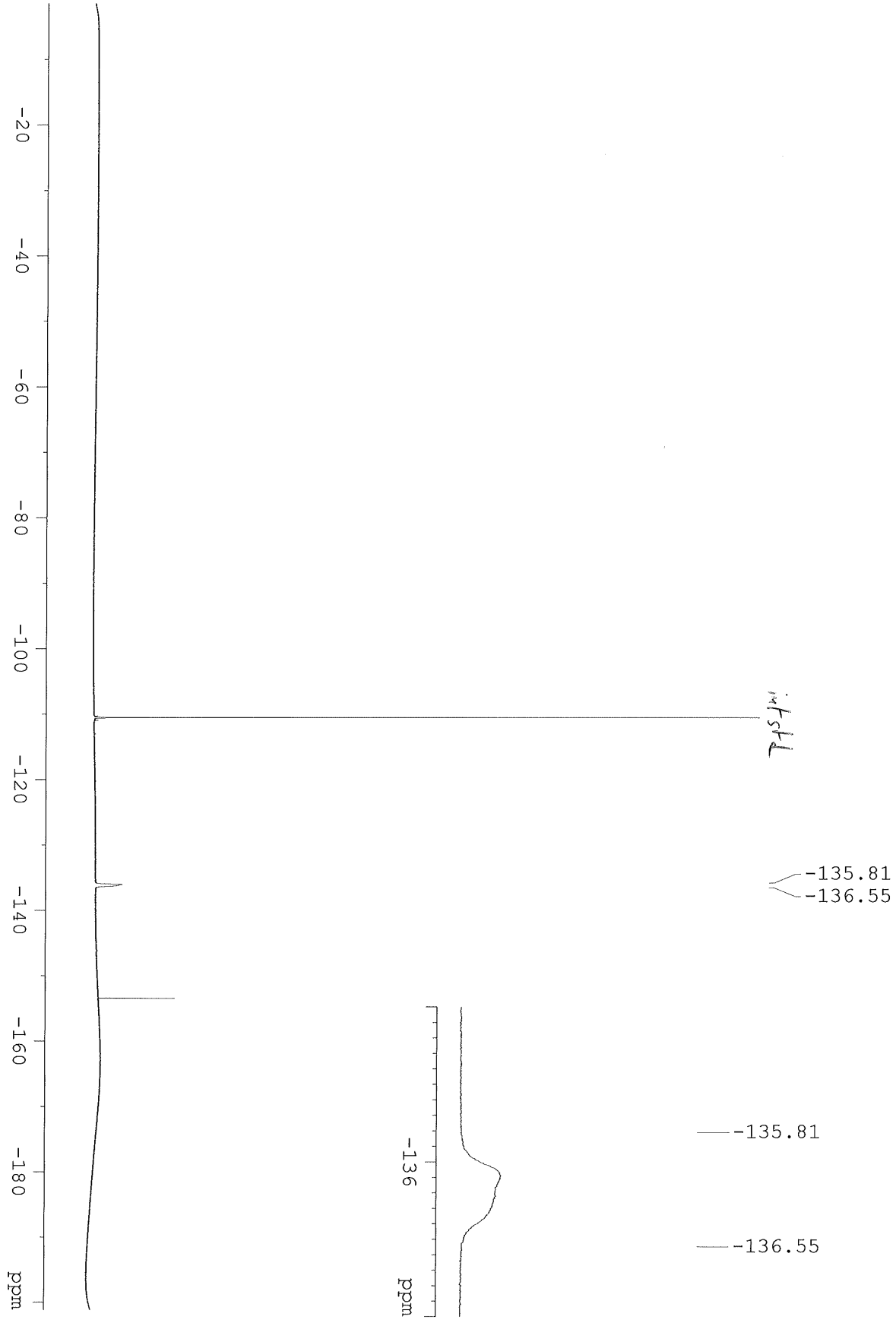


Compound 22 (1H NMR in DMSO-d6)

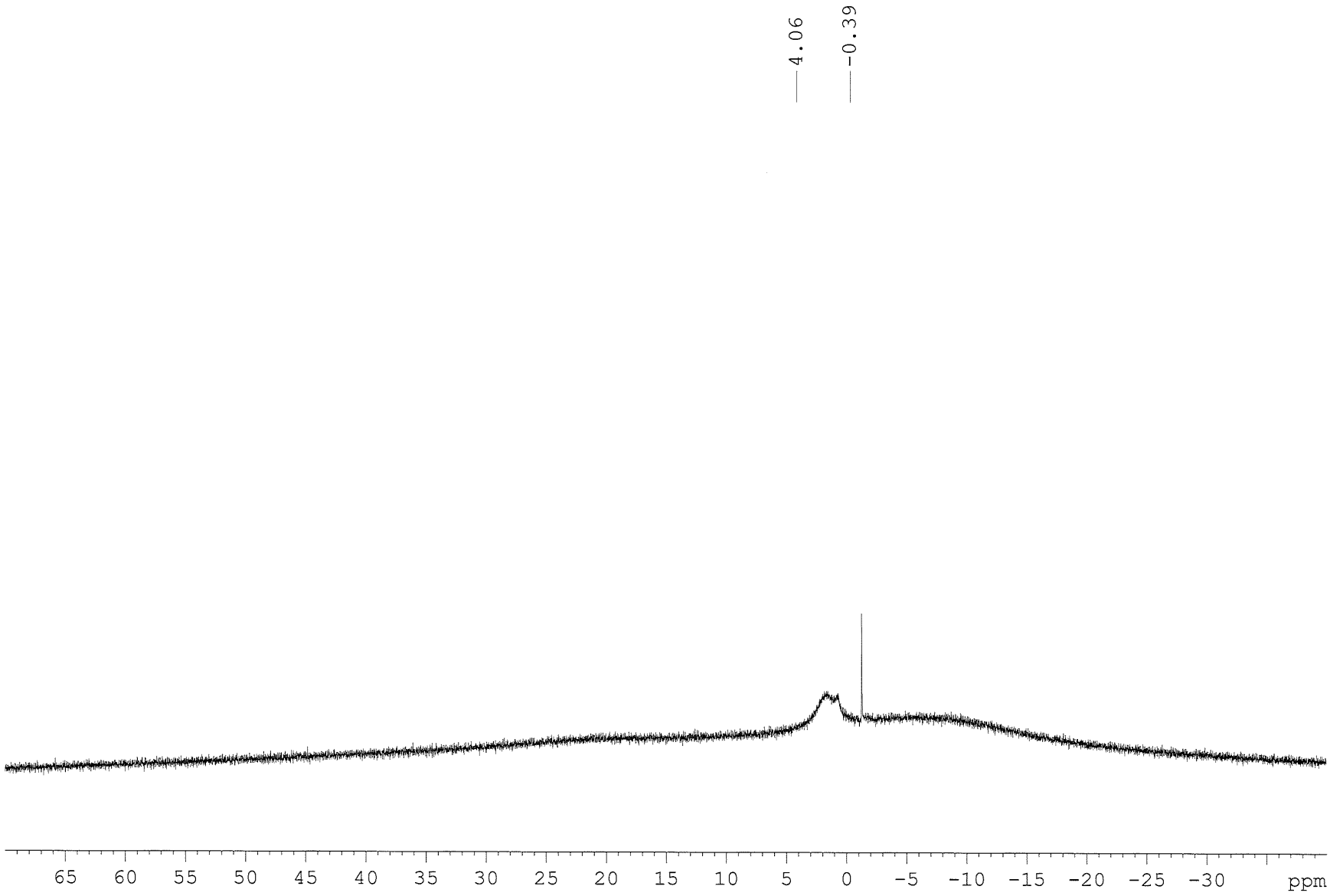


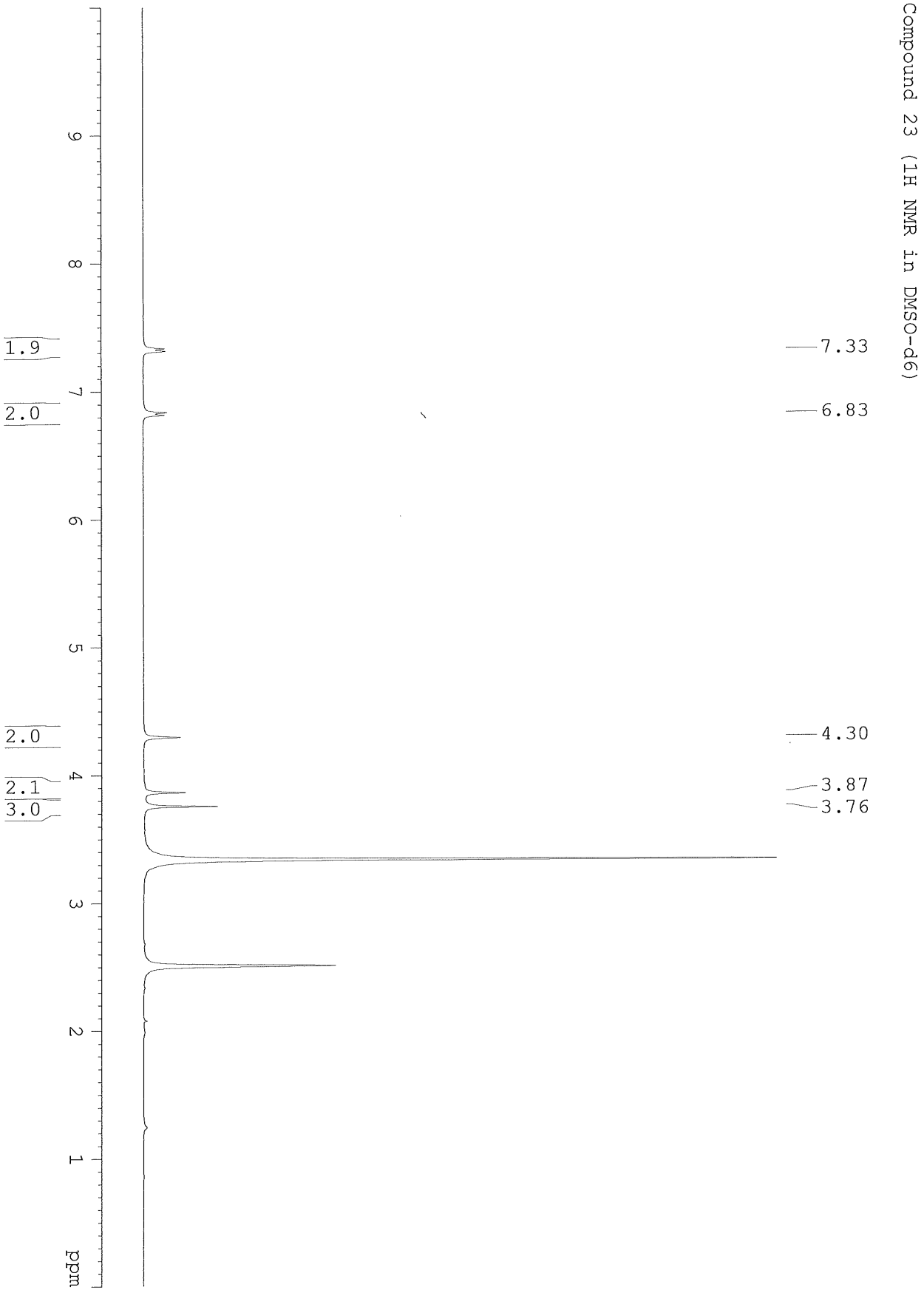

Compound 22 (13C NMR (APT) in DMSO-d6)
196.14
159.01
155.80
143.79
132.71
132.05
129.96
129.59
127.57
112.62
54.96
52.47
49.36
20.99
200
180
160
140
120
100
80
60
40
20
0
ppm

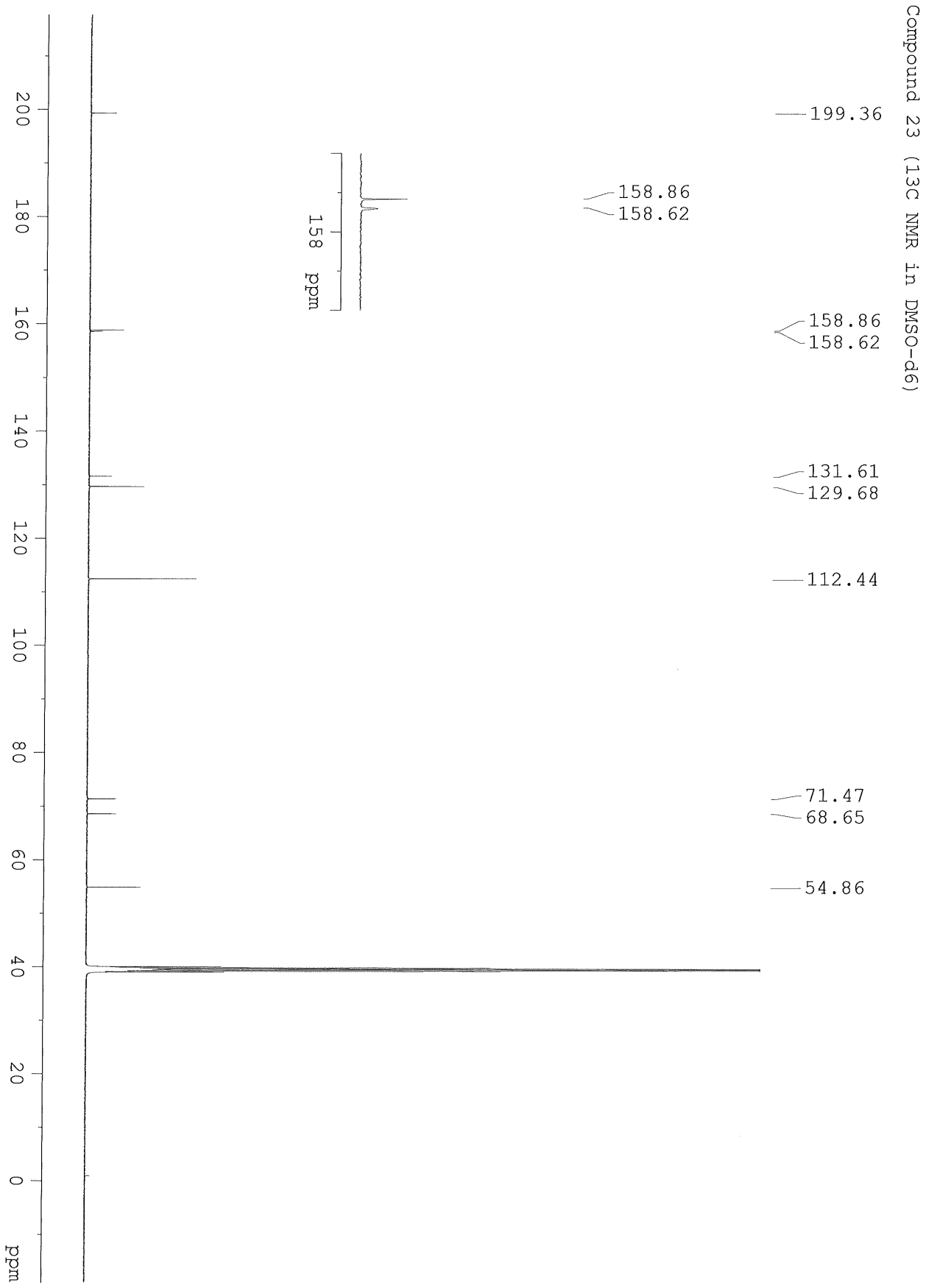
Compound 22 (19F NMR in MeCN-d3)



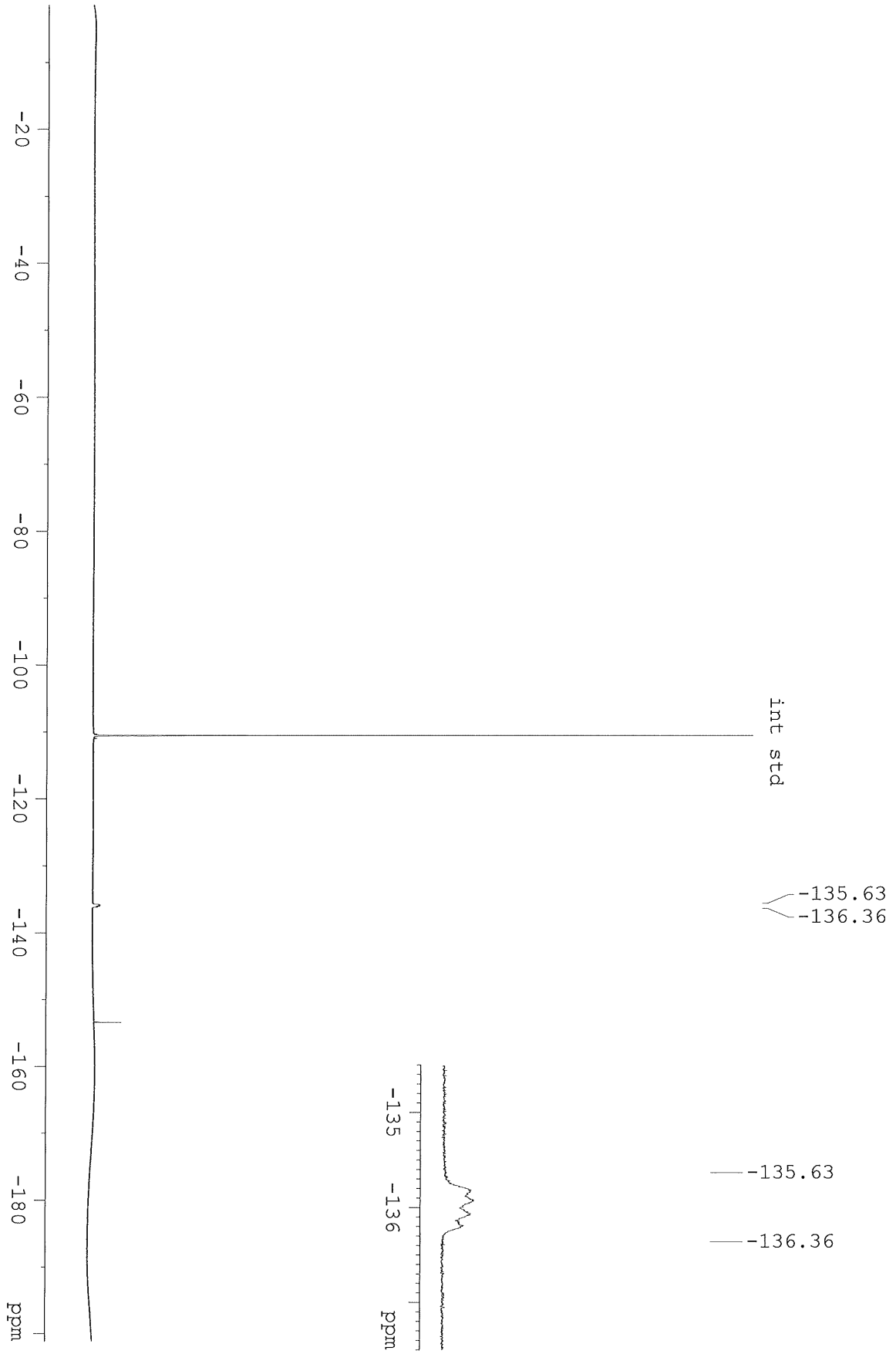
Compound 22 (11B NMR in DMSO-d6)



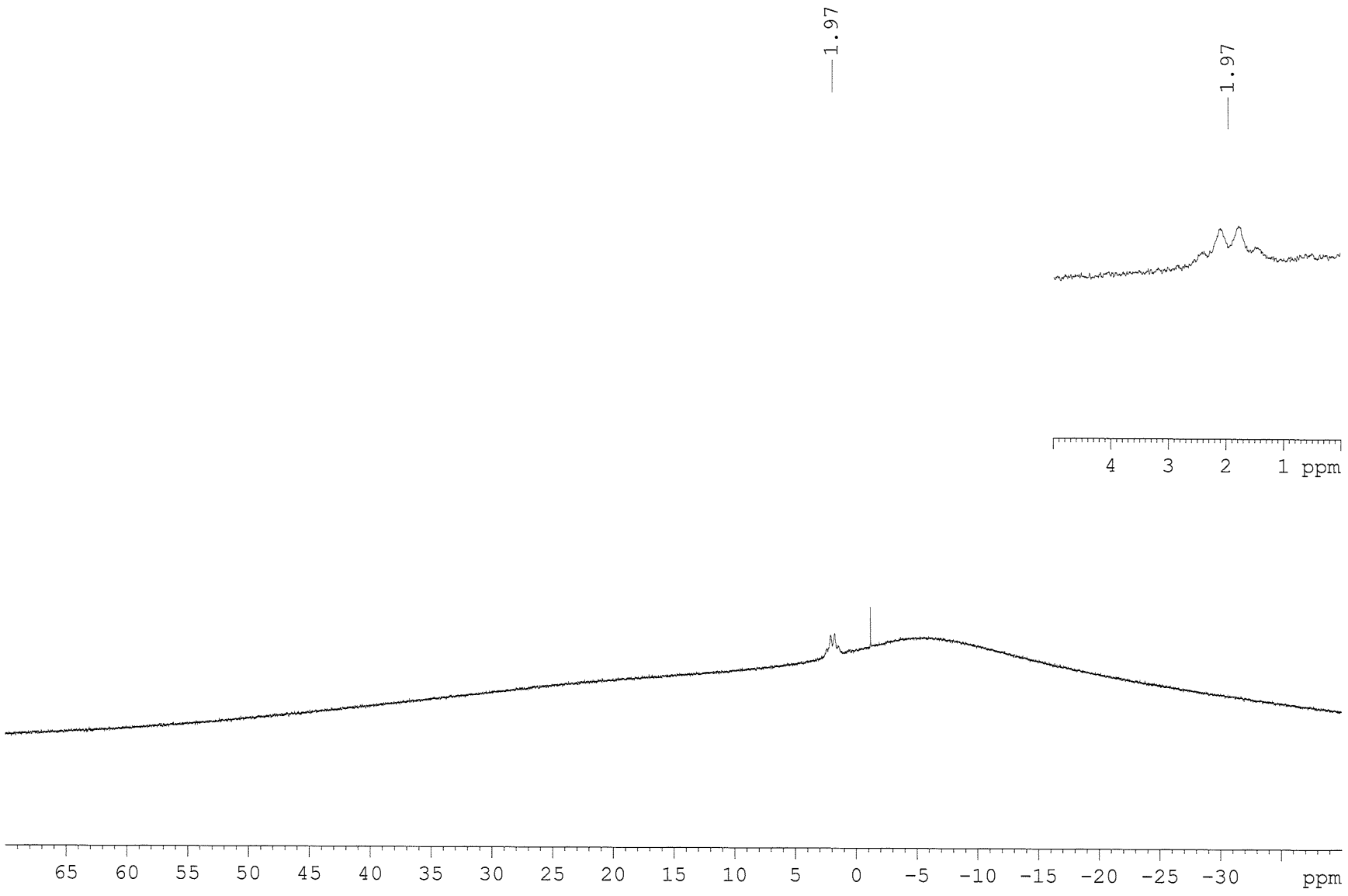

Compound 23 (1H NMR in DMSO-d6)
7.33
6.83
4.30
3.87
3.76
1.9
2.0
2.0
2.1
3.0
9
8
7
6
5
4
3
2
1
ppm

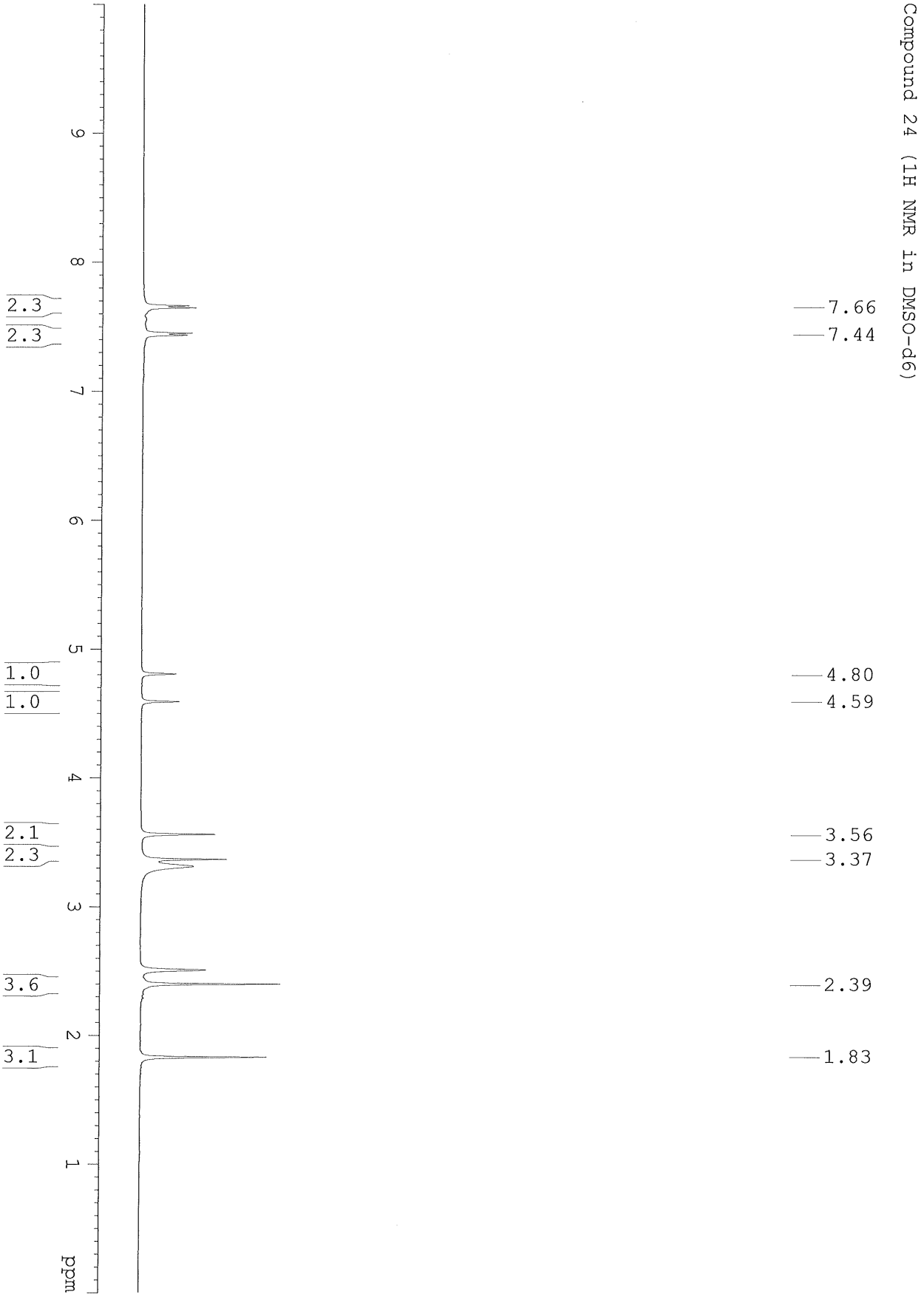

Compound 23 (13C NMR in DMSO-d6)
199.36
158.86
158.62
158.86
158.62
131.61
129.68
112.44
71.47
68.65
54.86
158 ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

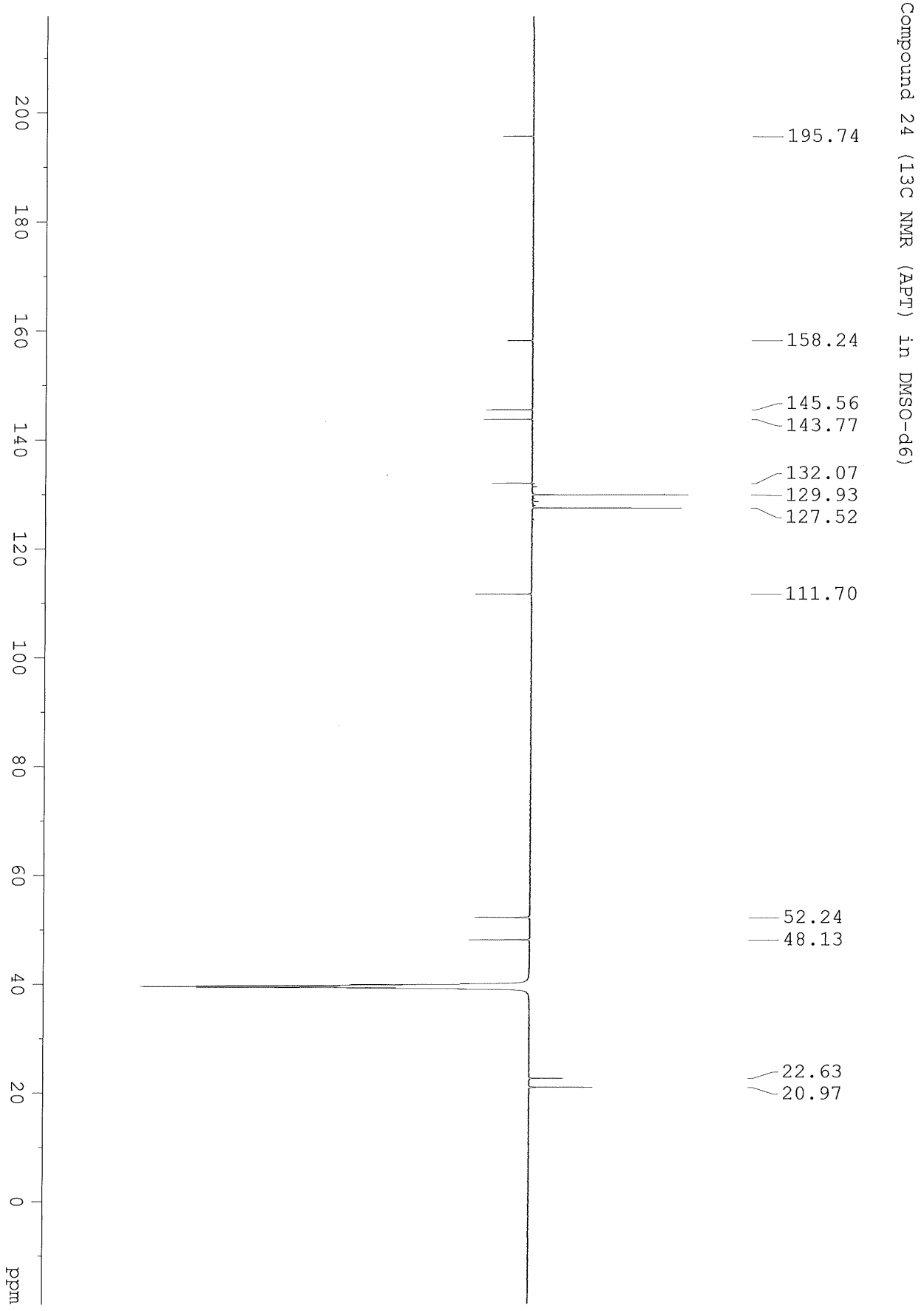
Compound 23 (19F NMR in MeCN-d3)

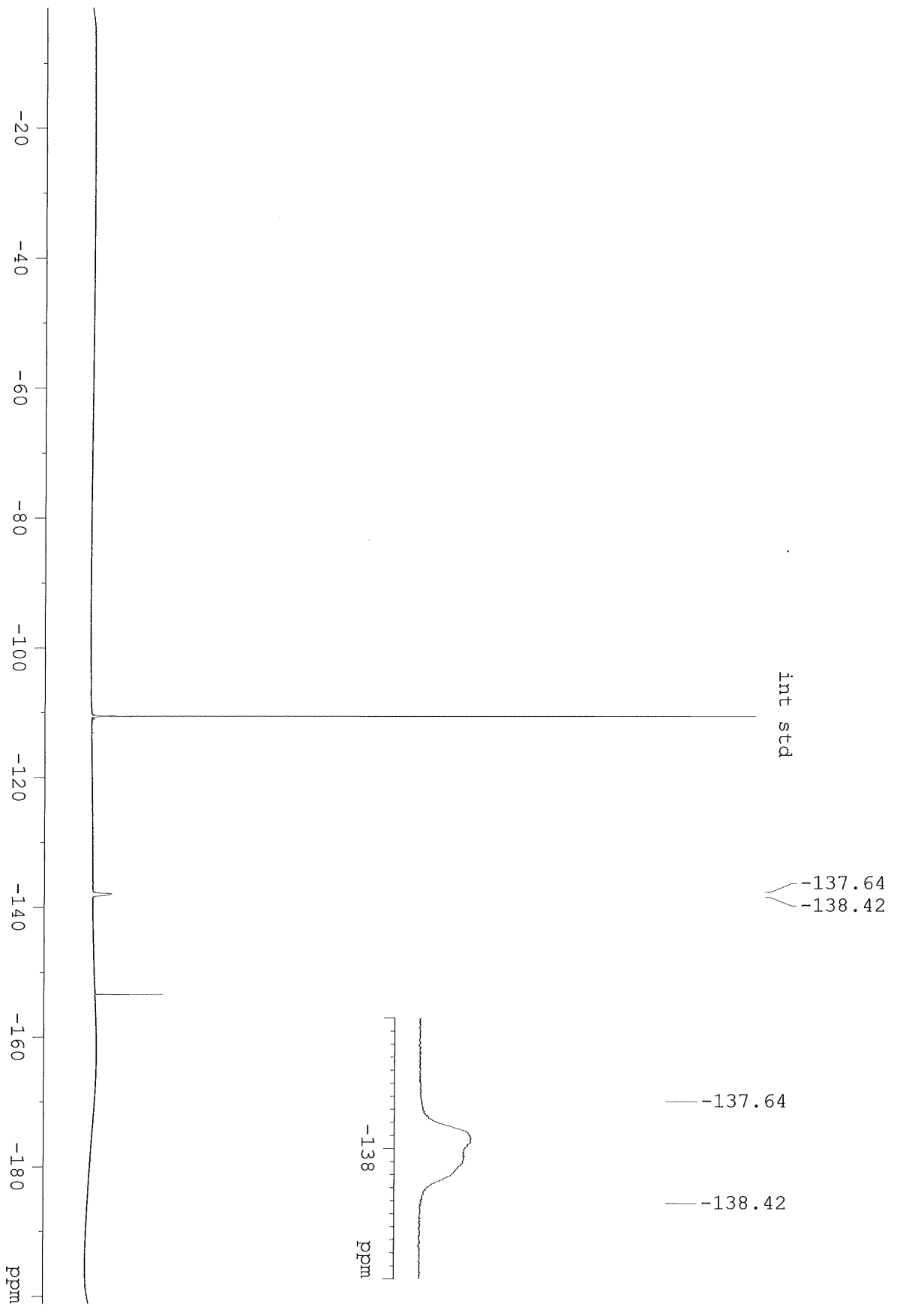


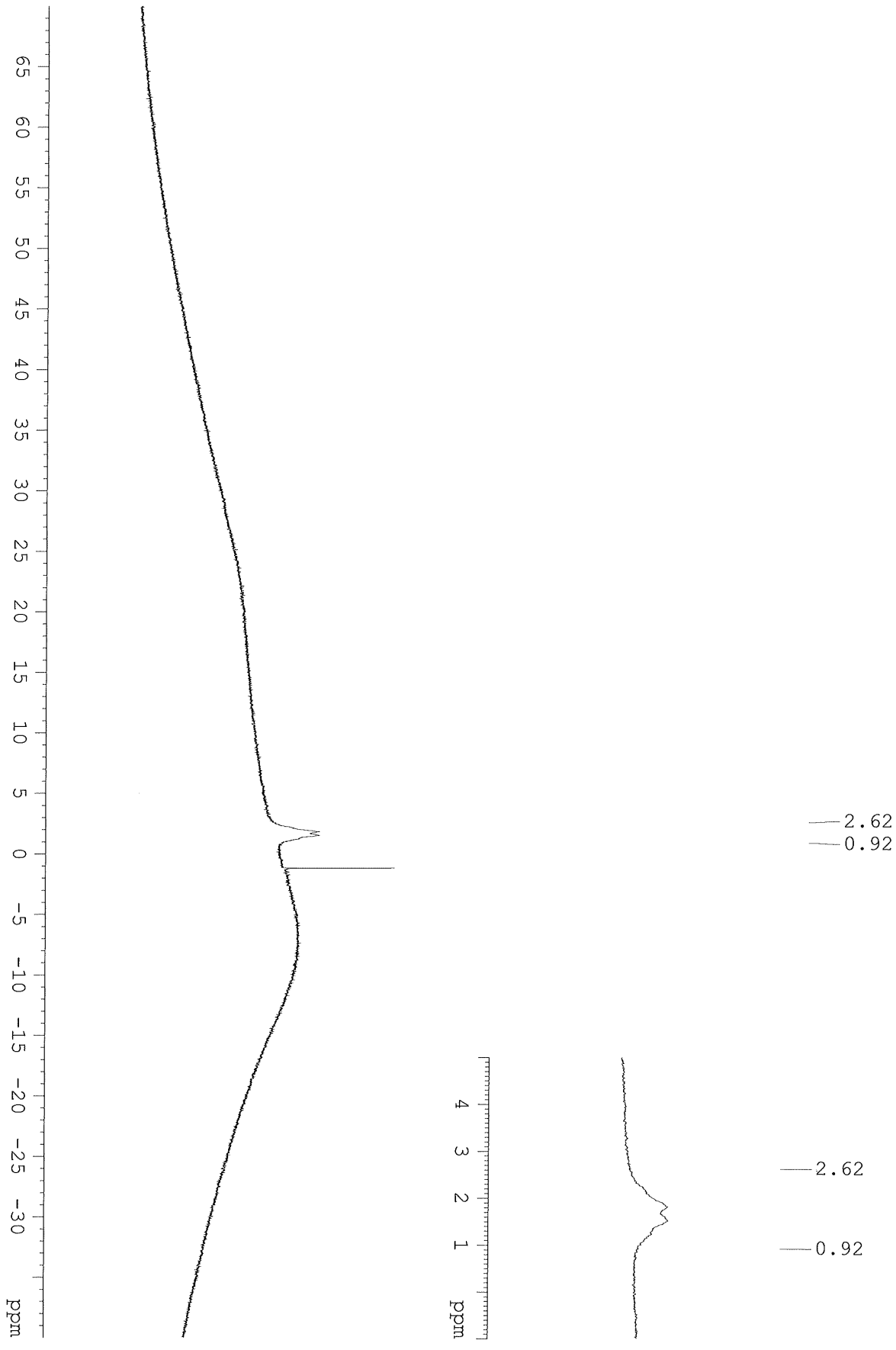
Compound 23 (11B NMR in MeCN-d3)

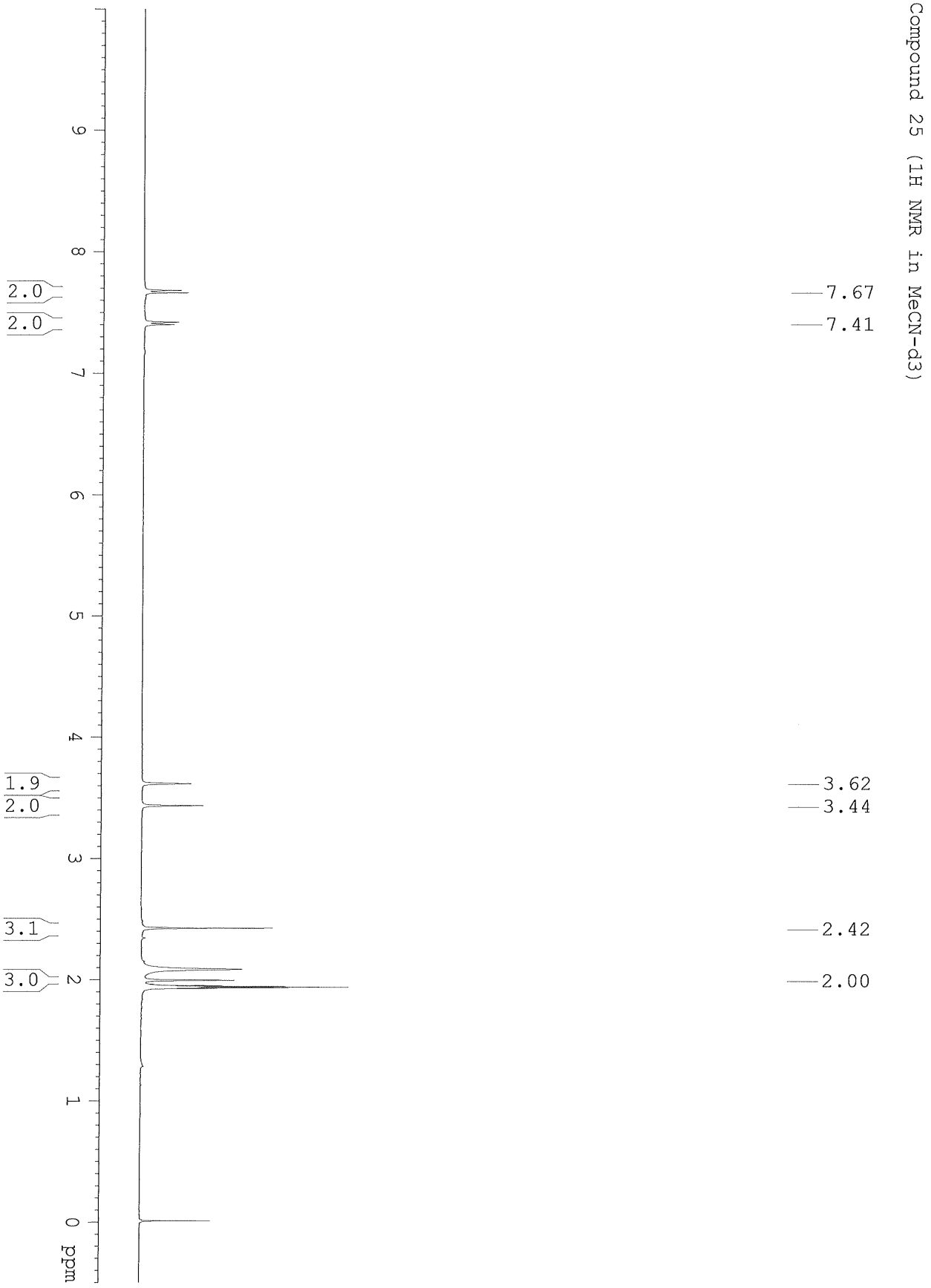


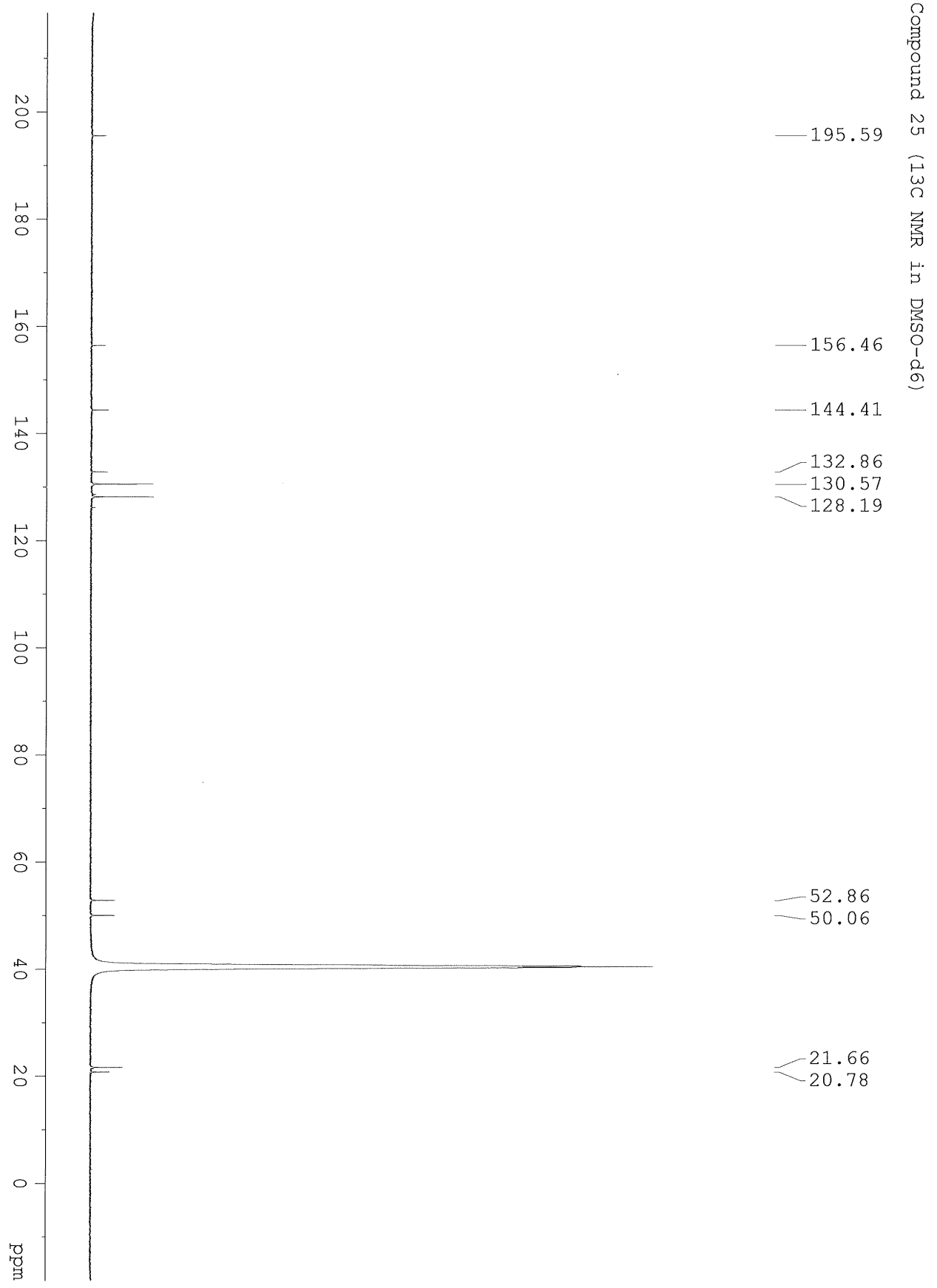

Compound 24 (1H NMR in DMSO-d6)
7.66
7.44
4.80
4.59
3.56
3.37
2.39
1.83
2.3
2.3
1.0
1.0
2.1
2.3
3.6
3.1
ppm


Compound 24 (13C NMR (APT) in DMSO-d6)
195.74
158.24
145.56
143.77
132.07
129.93
127.52
111.70
52.24
48.13
22.63
20.97
200
180
160
140
120
100
80
60
40
20
0
ppm

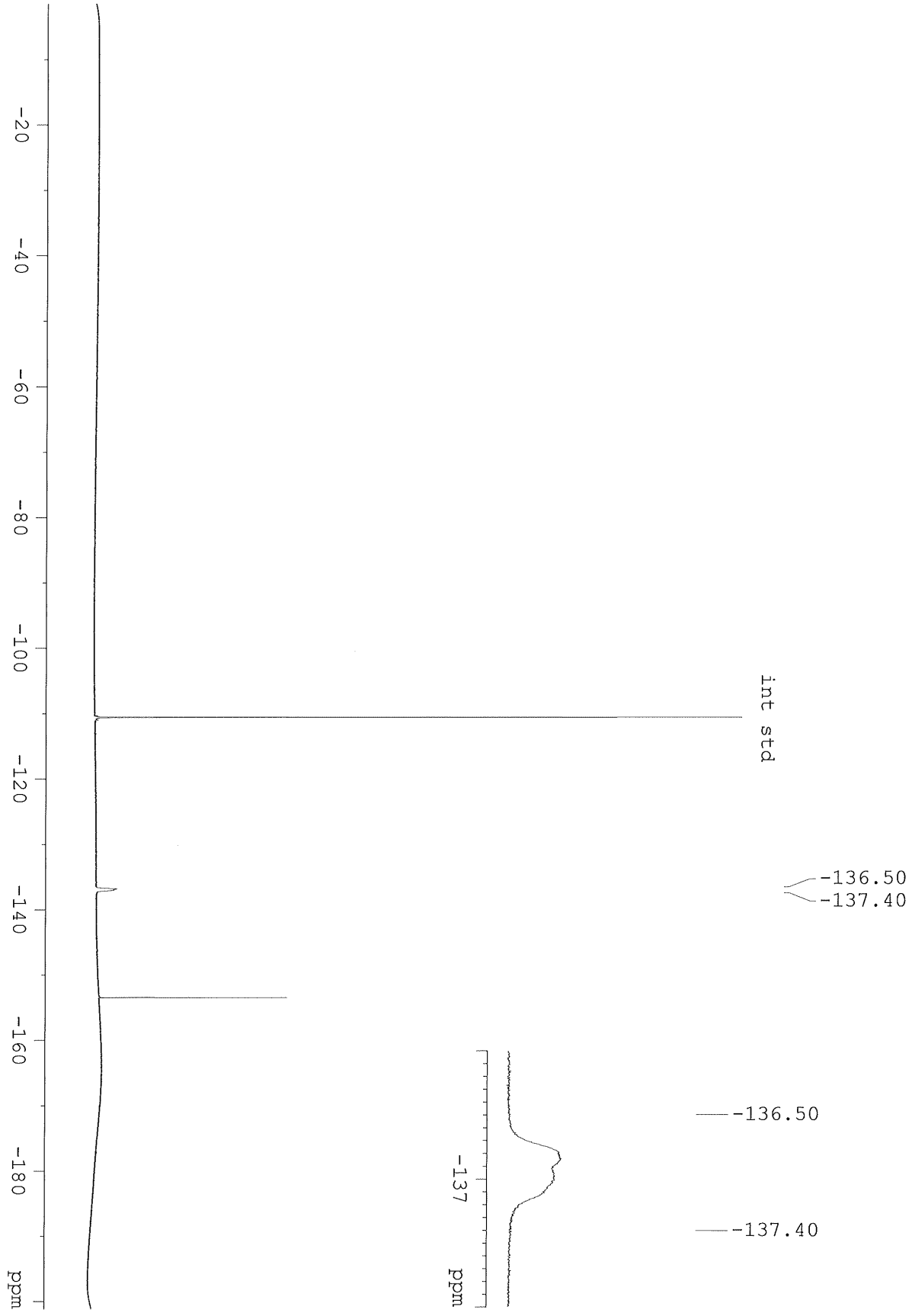

Compound 24 (19F NMR in MeCN-d3)
int std
-137.64
-138.42
-137.64
-138.42
-138
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


Compound 24 (11B NMR in MeCN-d3)
2.62
0.92
2.62
0.92
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
ppm
4 3 2 1
ppm

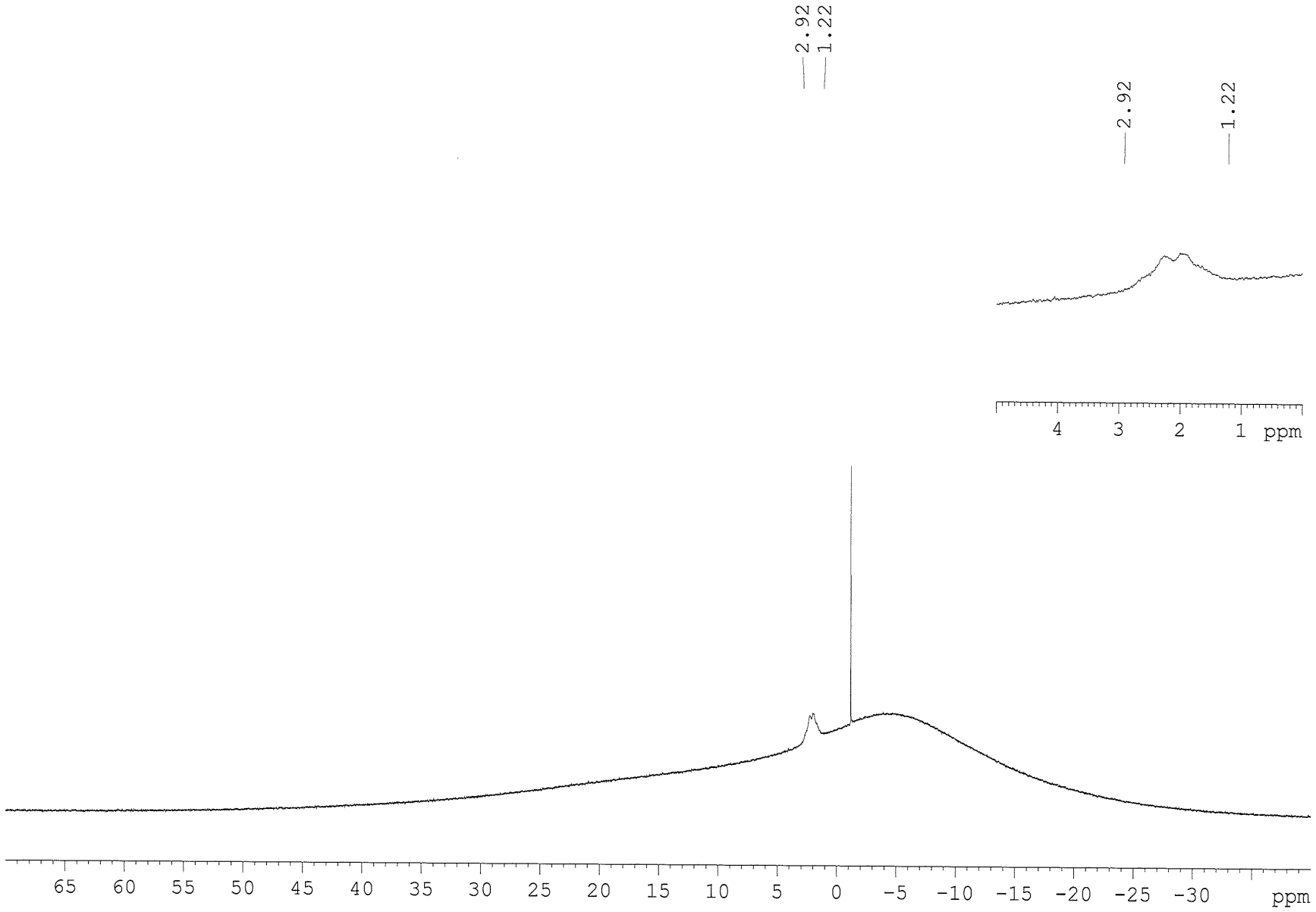

Compound 25 (1H NMR in MeCN-d3)
7.67
7.41
3.62
3.44
2.42
2.00
2.0
2.0
1.9
2.0
3.1
3.0
9
8
7
6
5
4
3
2
1
0 ppm


Compound 25 (13C NMR in DMSO-d6)
195.59
156.46
144.41
132.86
130.57
128.19
52.86
50.06
21.66
20.78
200
180
160
140
120
100
80
60
40
20
0
ppm

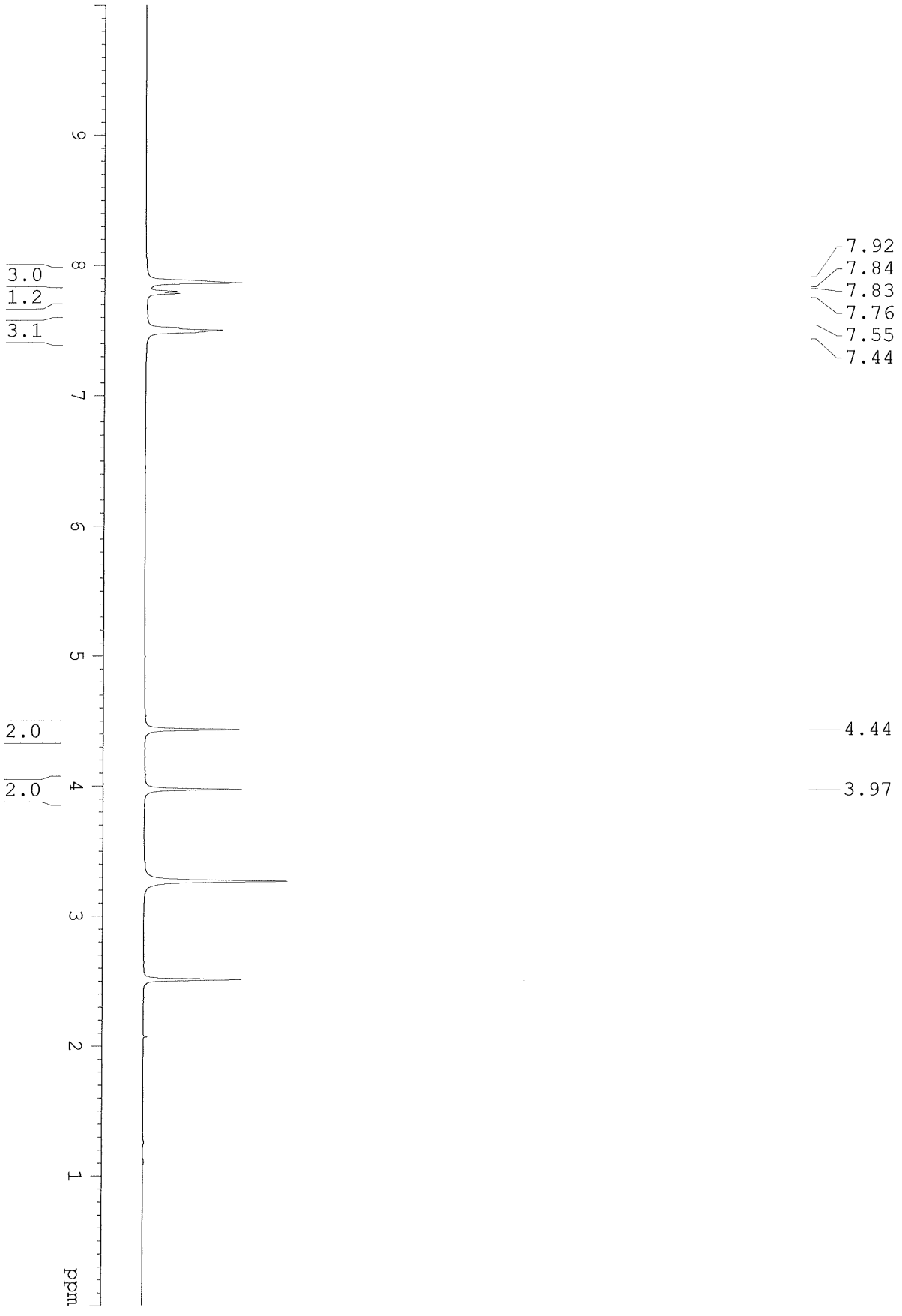
Compound 25 (19F NMR in MeCN-d3)

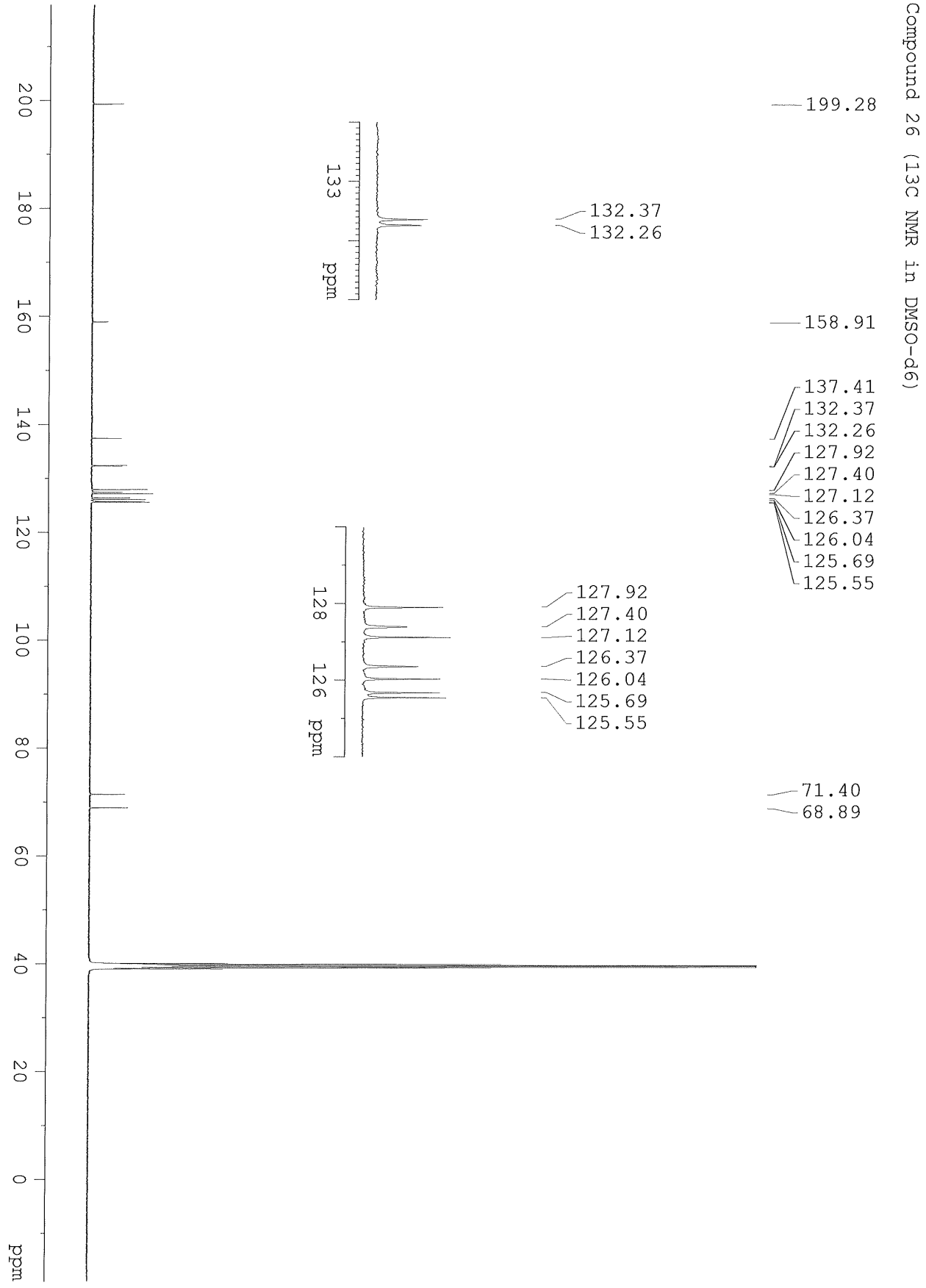


Compound 25 (11B NMR in MeCN-d3)

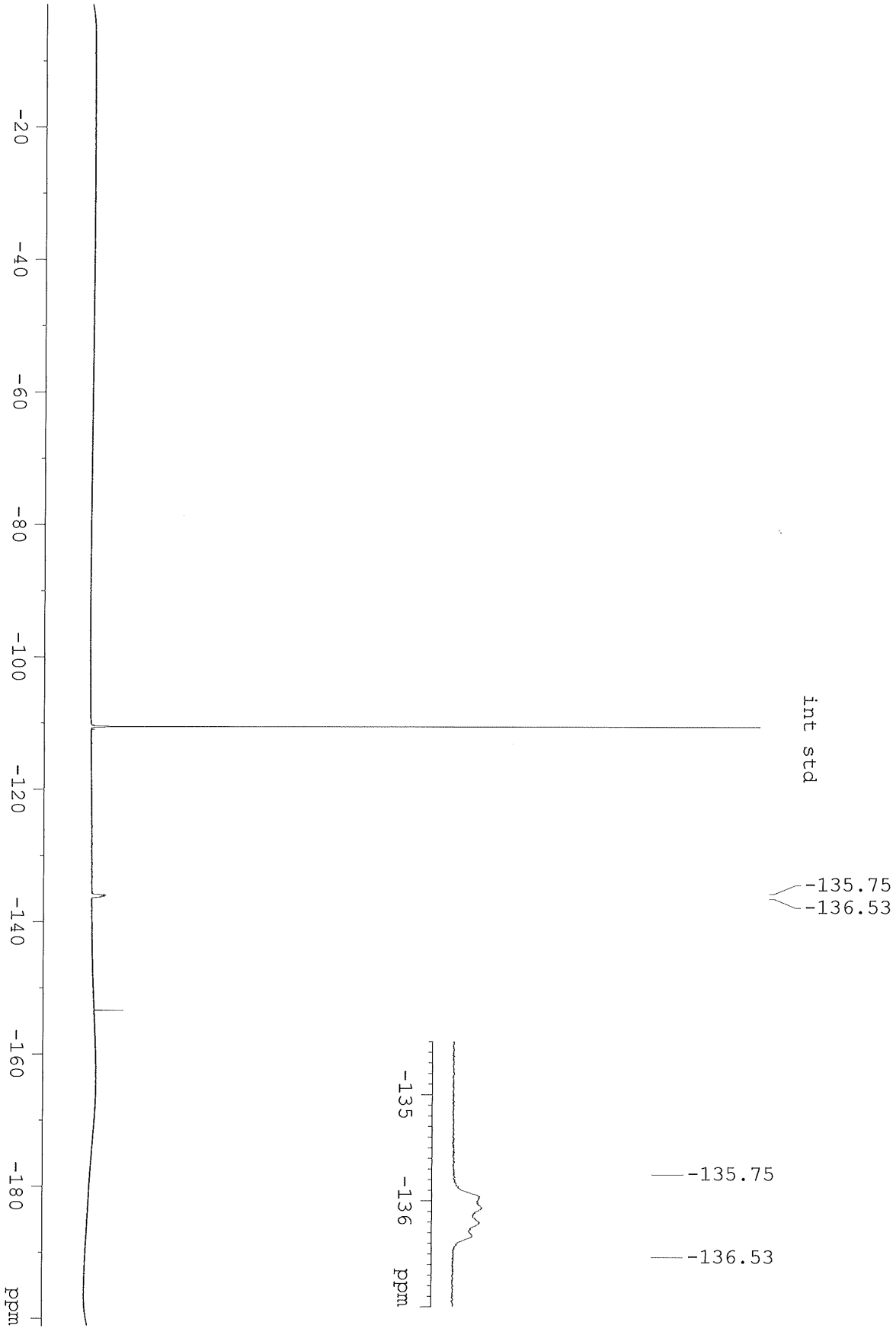


Compound 26 (1H NMR in DMSO-d6)

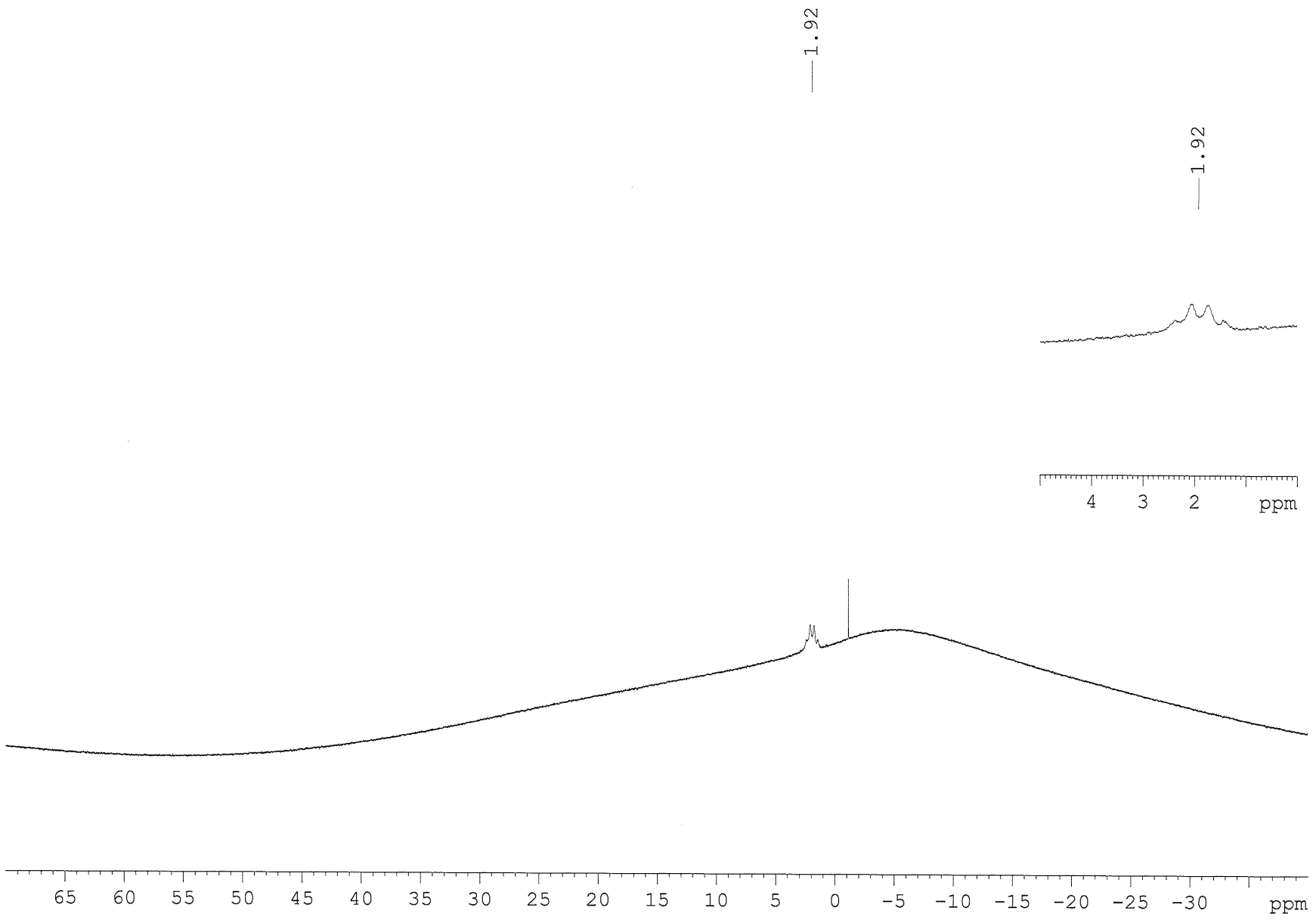


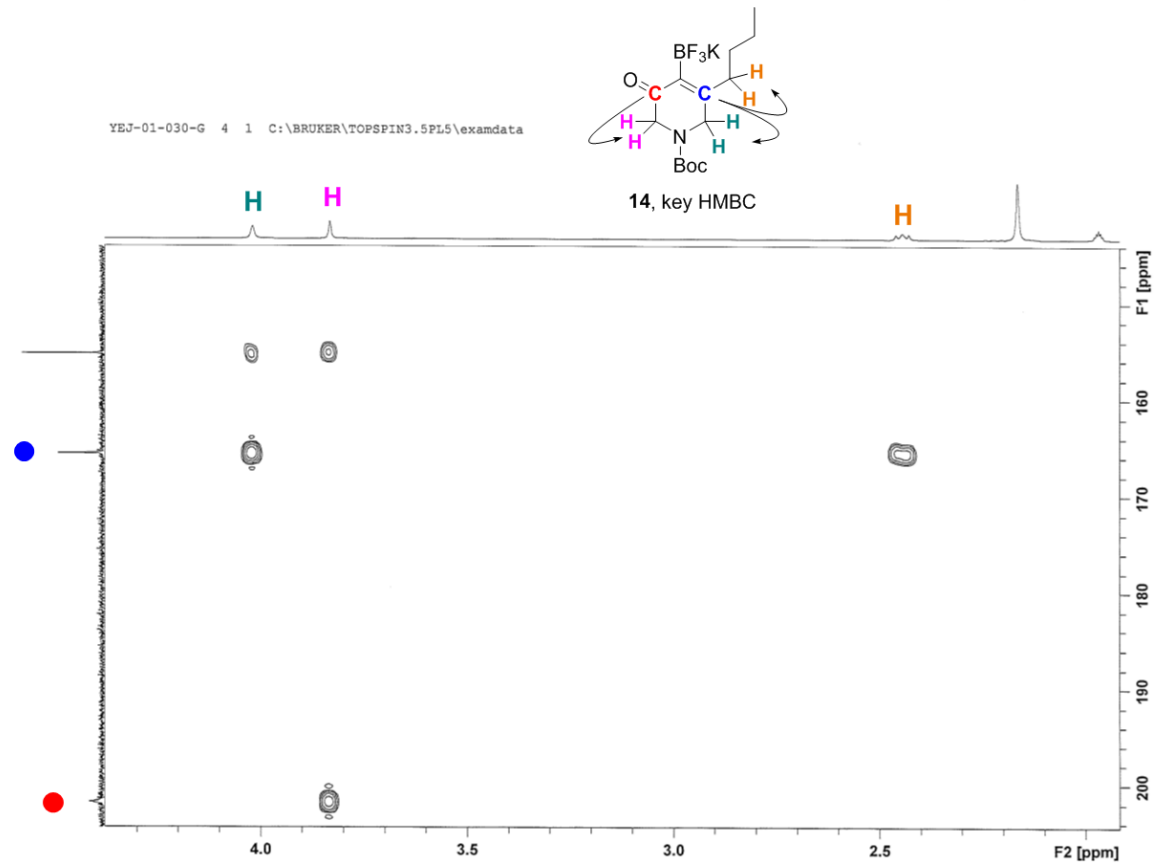

Compound 26 (13C NMR in DMSO-d6)
199.28
158.91
137.41
132.37
132.26
127.92
127.40
127.12
126.37
126.04
125.69
125.55
71.40
68.89
133 ppm
128 126 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

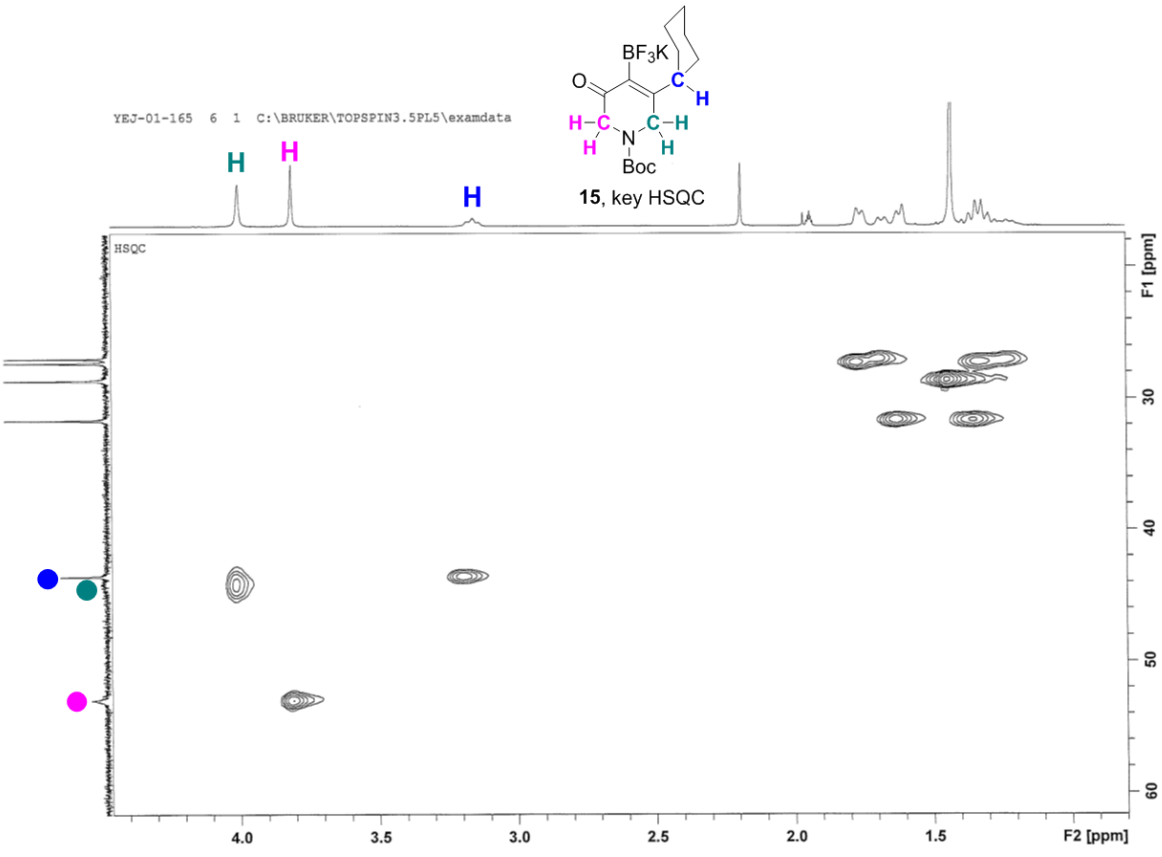
Compound 26 (19F NMR in MeCN-d3)

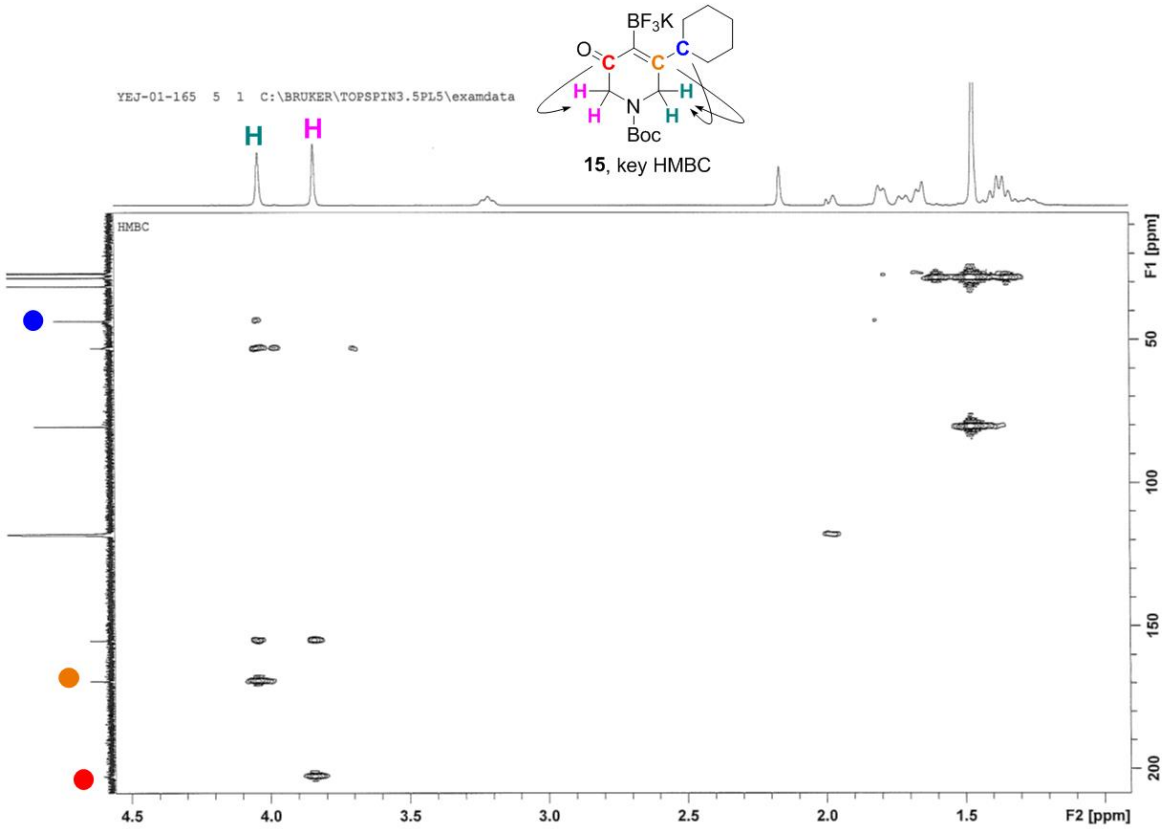


Compound 26 (11B NMR in MeCN-d3)

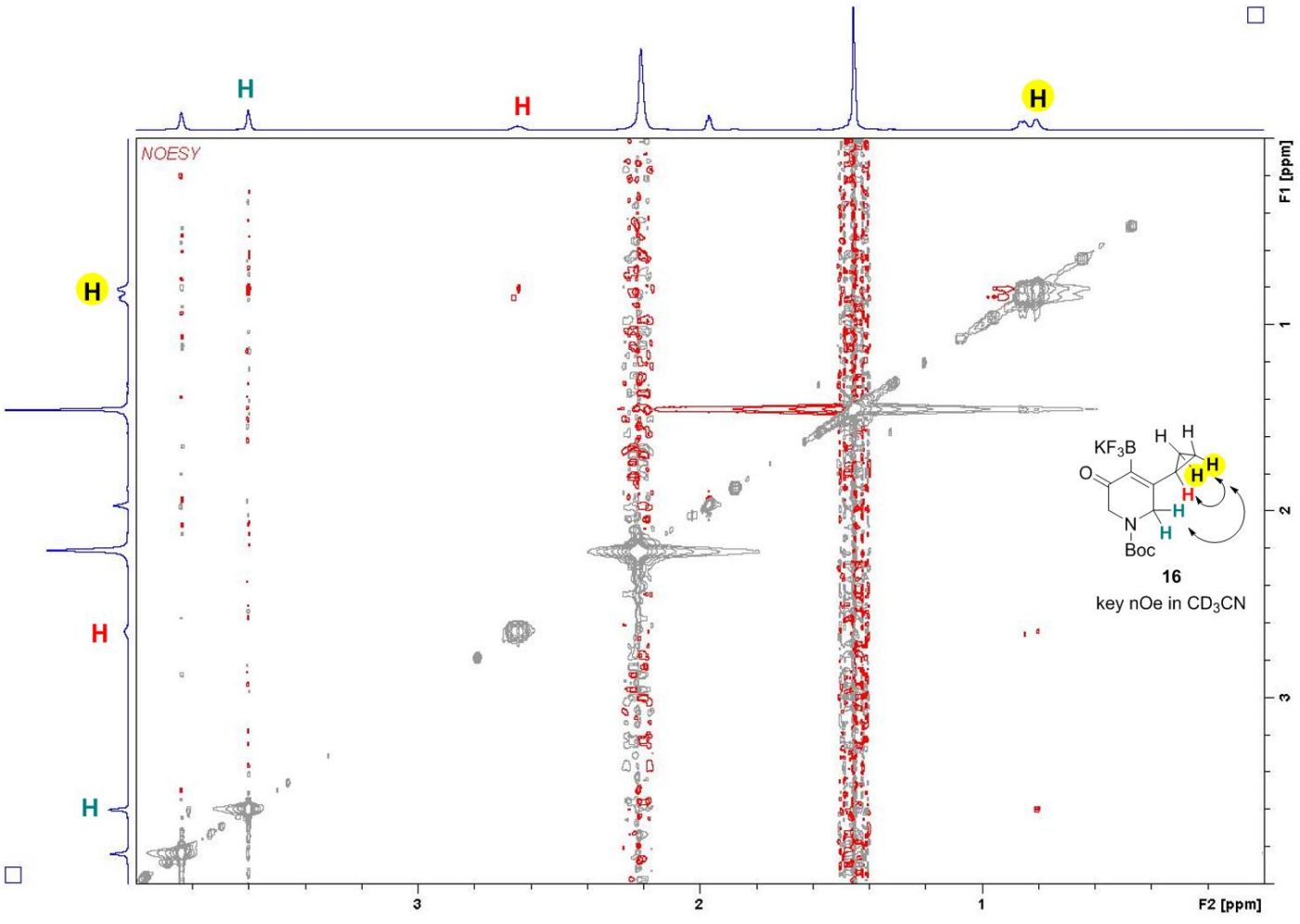



YEJ-01-030-G 4 1 C:\BRUKER\TOPSPIN3.5PL5\examdata
BF3K
O
C
C
H
H
H
H
H
H
N
H
Boc
14, key HMBC
H
H
H
F1 [ppm]
160
170
180
190
200
4.0
3.5
3.0
2.5
F2 [ppm]

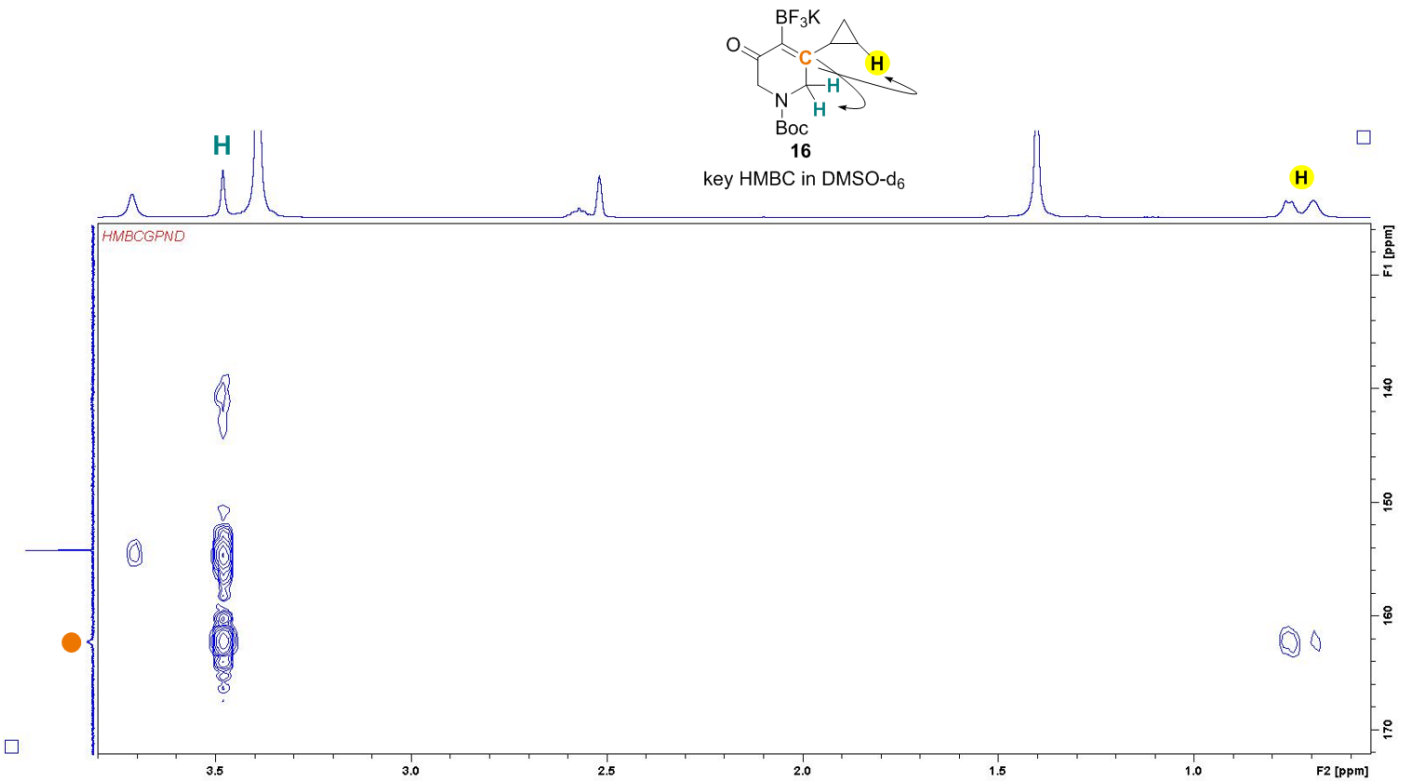

YEJ-01-165 6 1 C:\BRUKER\TOPSPIN3.5PL5\examdata
BF3K
O
C
H
H
C
C
H
H
N
H
Boc
15, key HSQC
H
H
H
HSQC
F1 [ppm]
30
40
50
60
4.0
3.5
3.0
2.5
2.0
1.5
F2 [ppm]

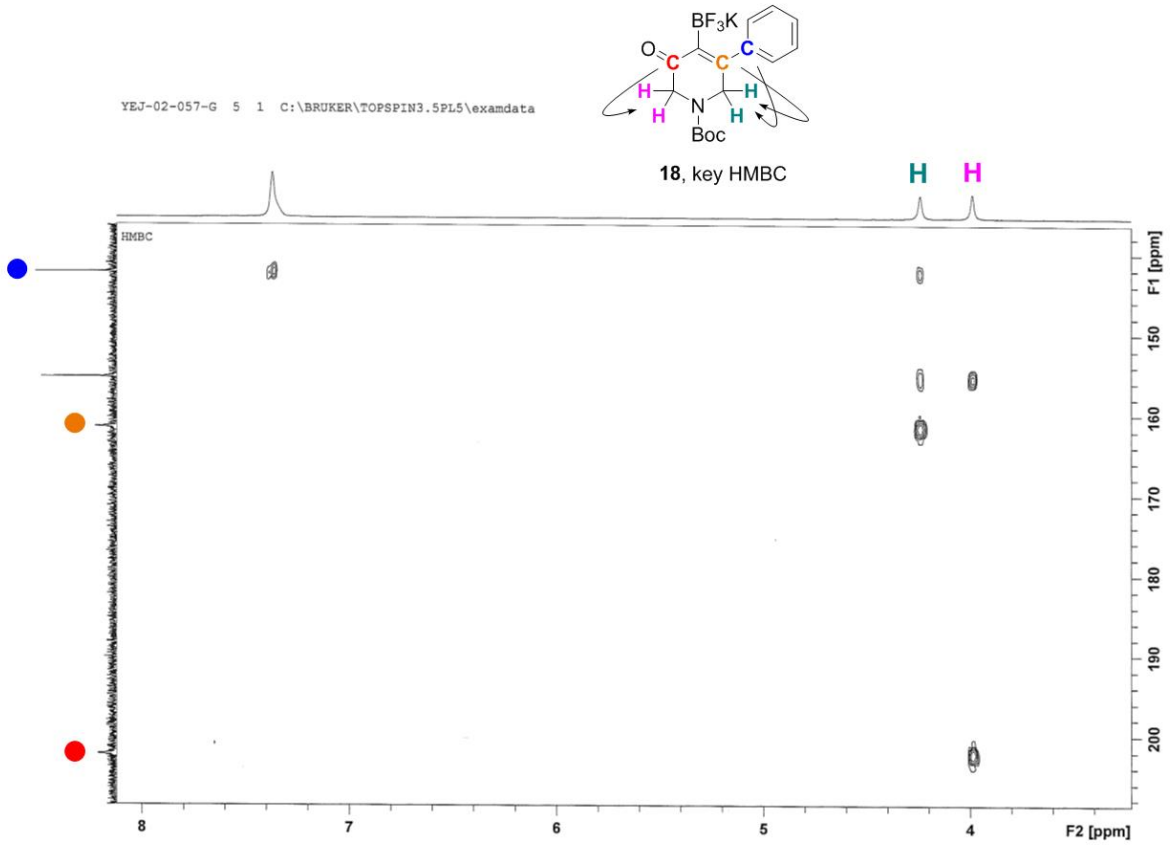


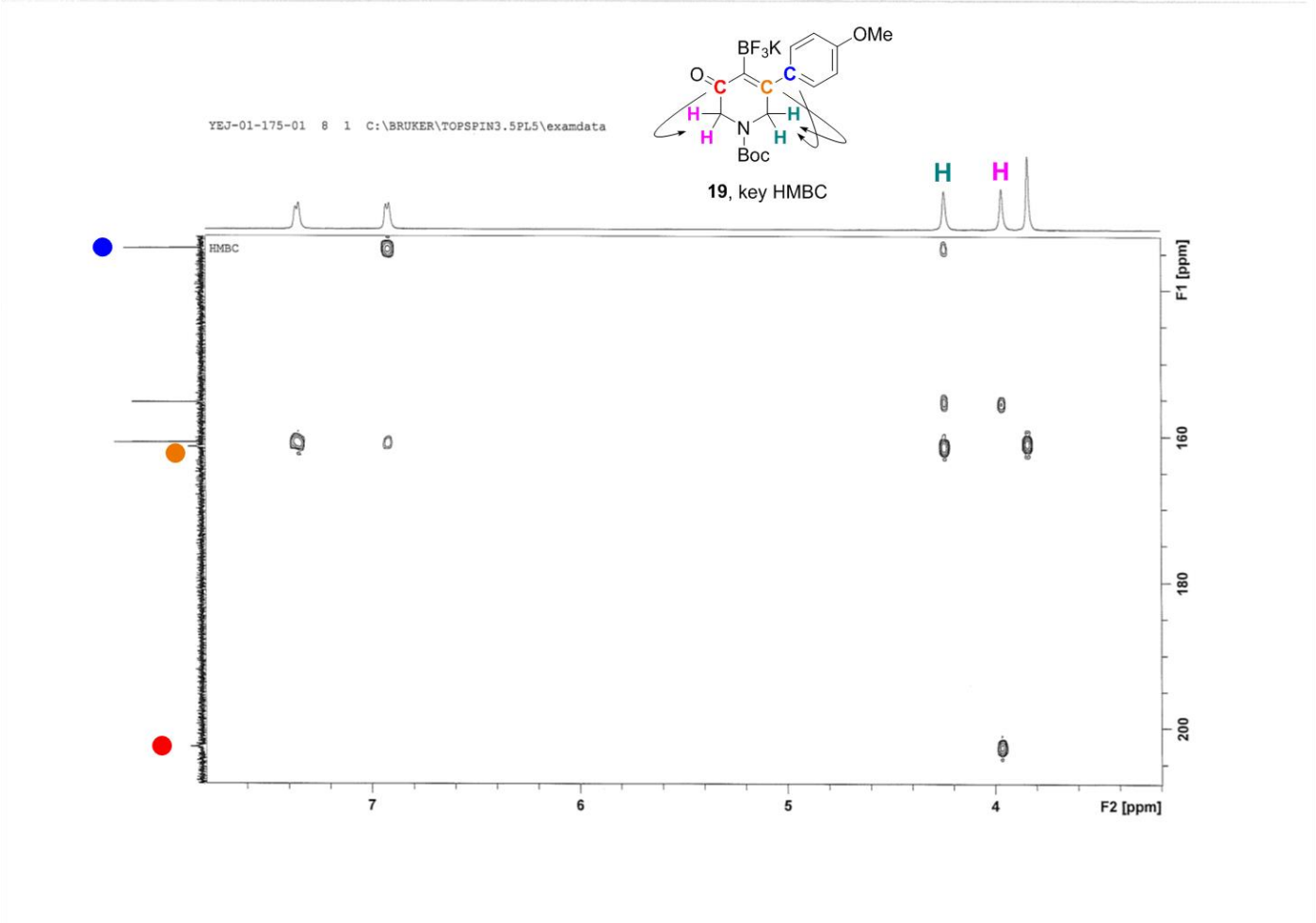
15, key HMBC



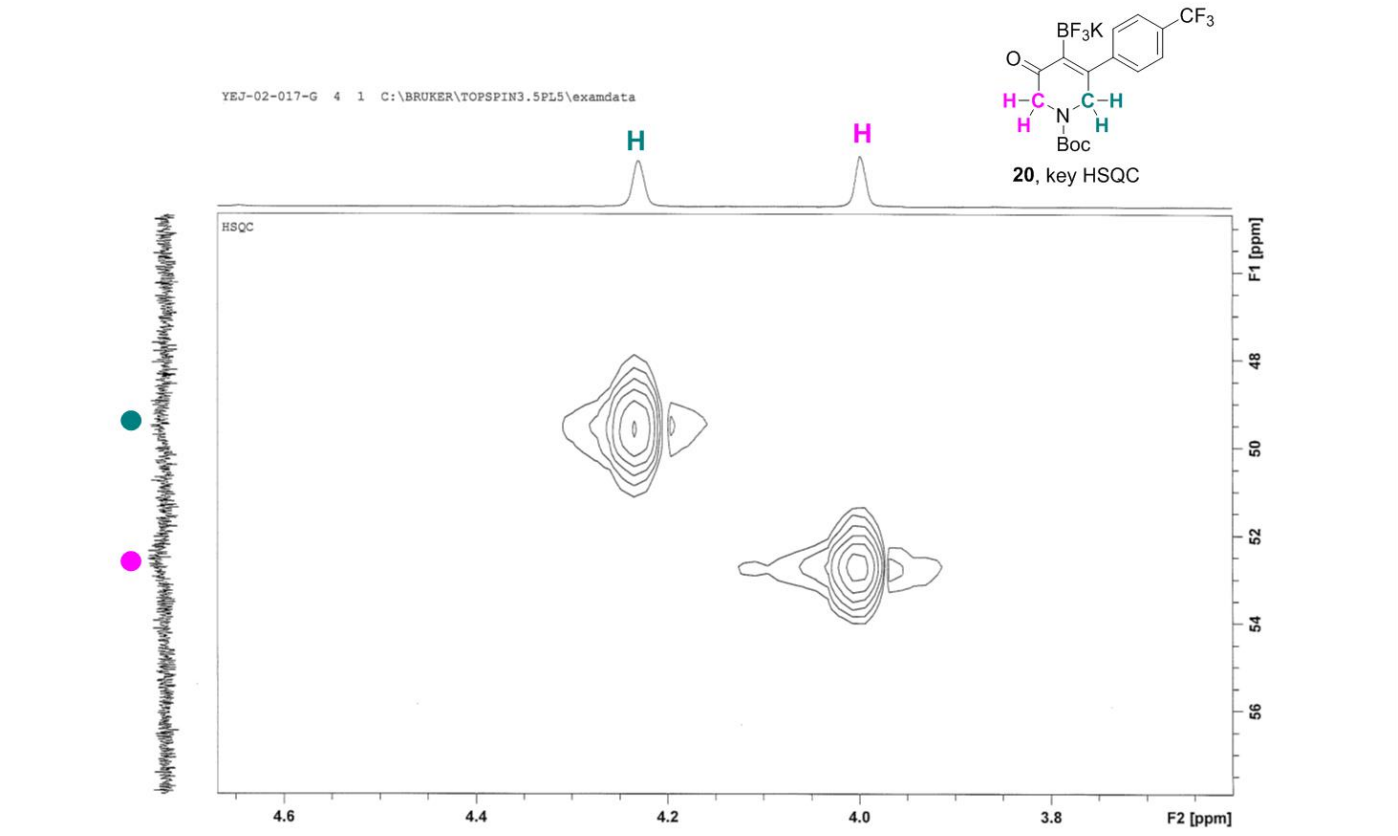
16
key nOe in CD_3CN


BF3K
O
C
H
H
N
H
Boc
16
key HMBC in DMSO-d6
H
H
HMBCGPND
F1 [ppm]
140
150
160
170
3.5
3.0
2.5
2.0
1.5
1.0
F2 [ppm]

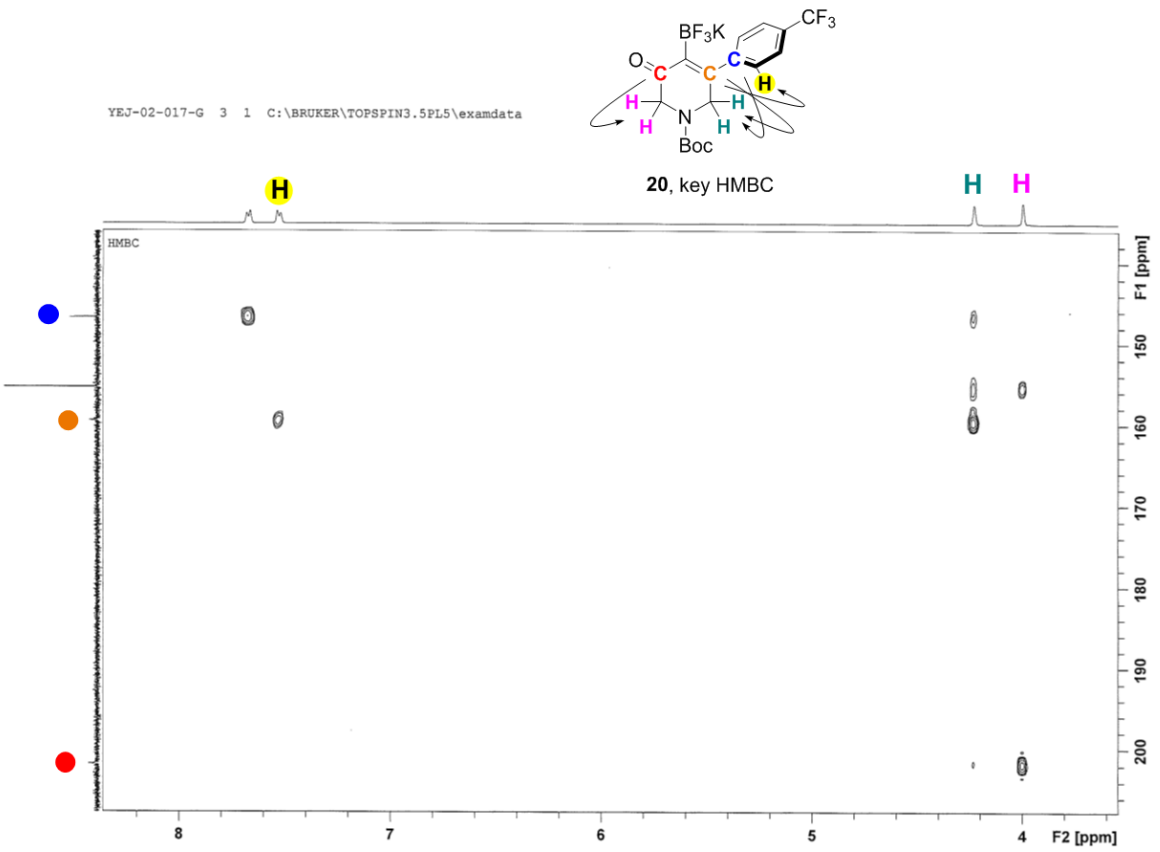

YEJ-02-057-G 5 1 C:\BRUKER\TOPSPIN3.5PL5\examdata
BF3K
O
C
C
C
H
H
H
H
N
Boc
18, key HMBC
H
H
HMBC
F1 [ppm]
150
160
170
180
190
200
8
7
6
5
4
F2 [ppm]



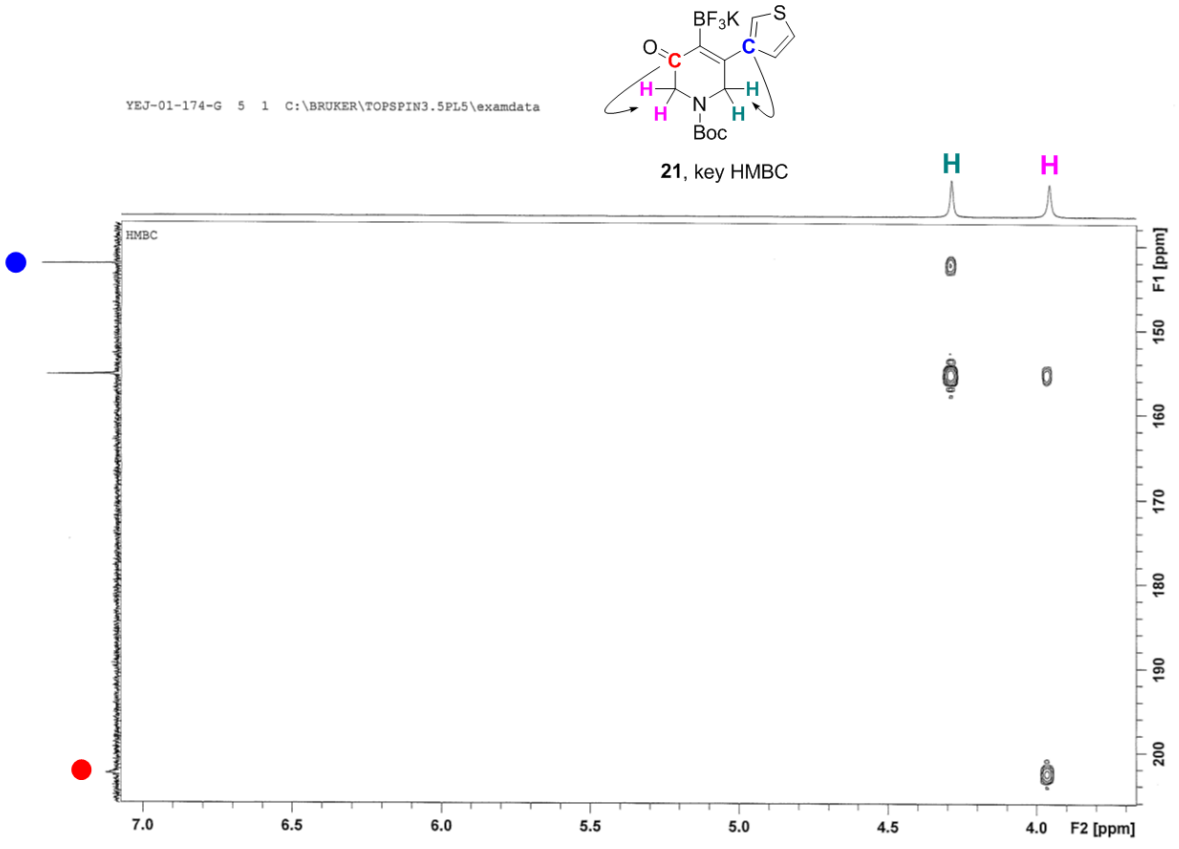
19, key HMBC



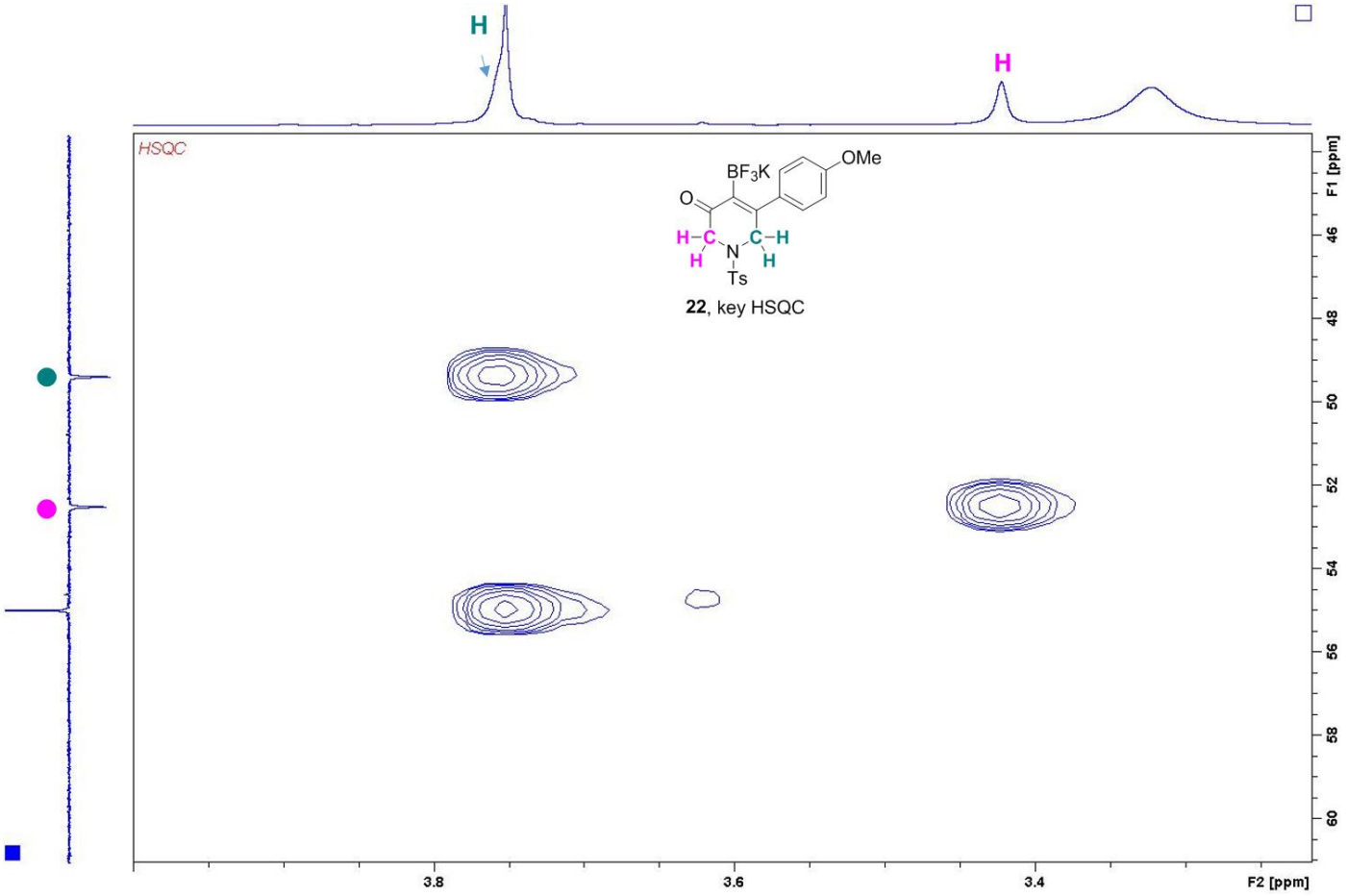
20, key HSQC



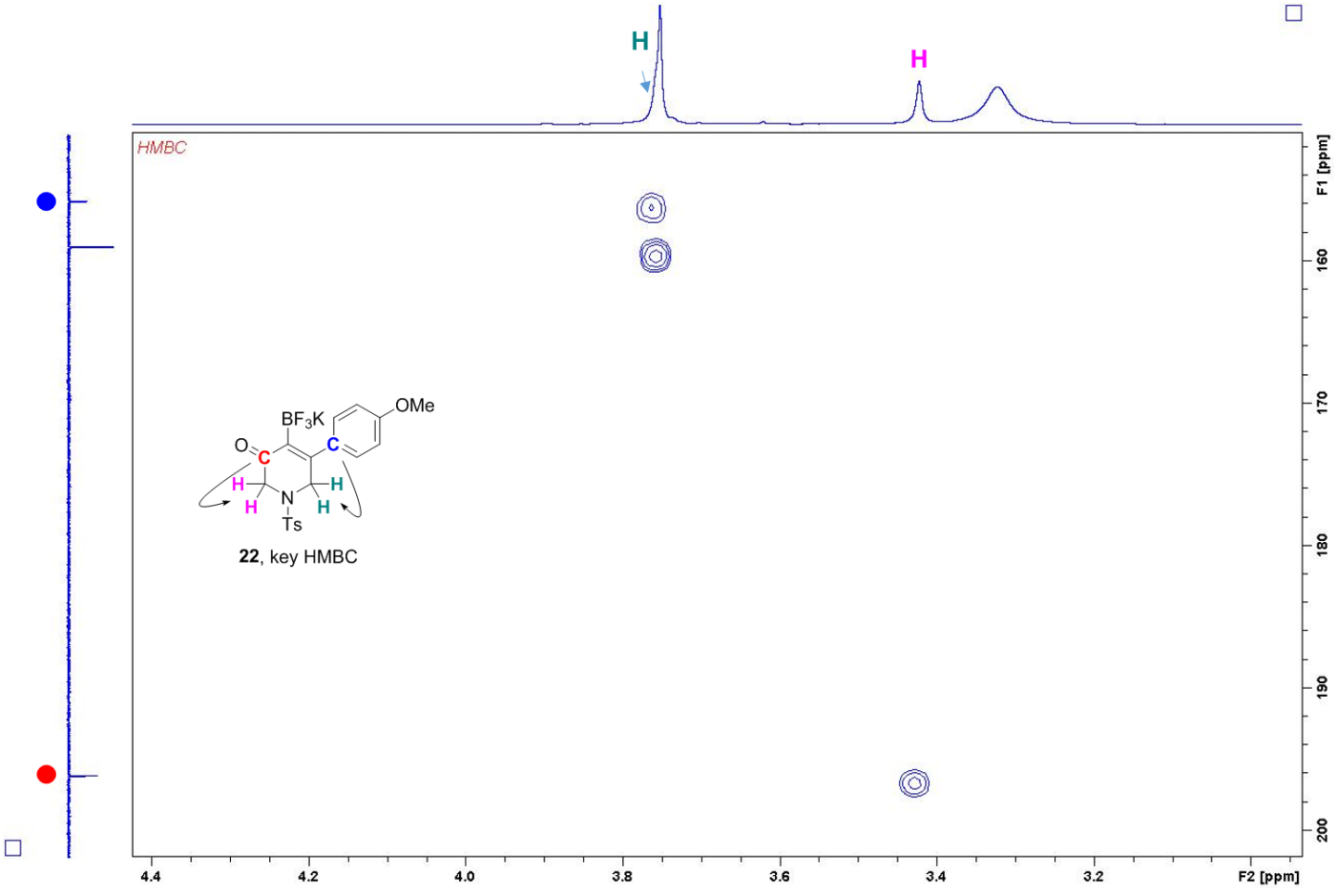
20, key HMBC



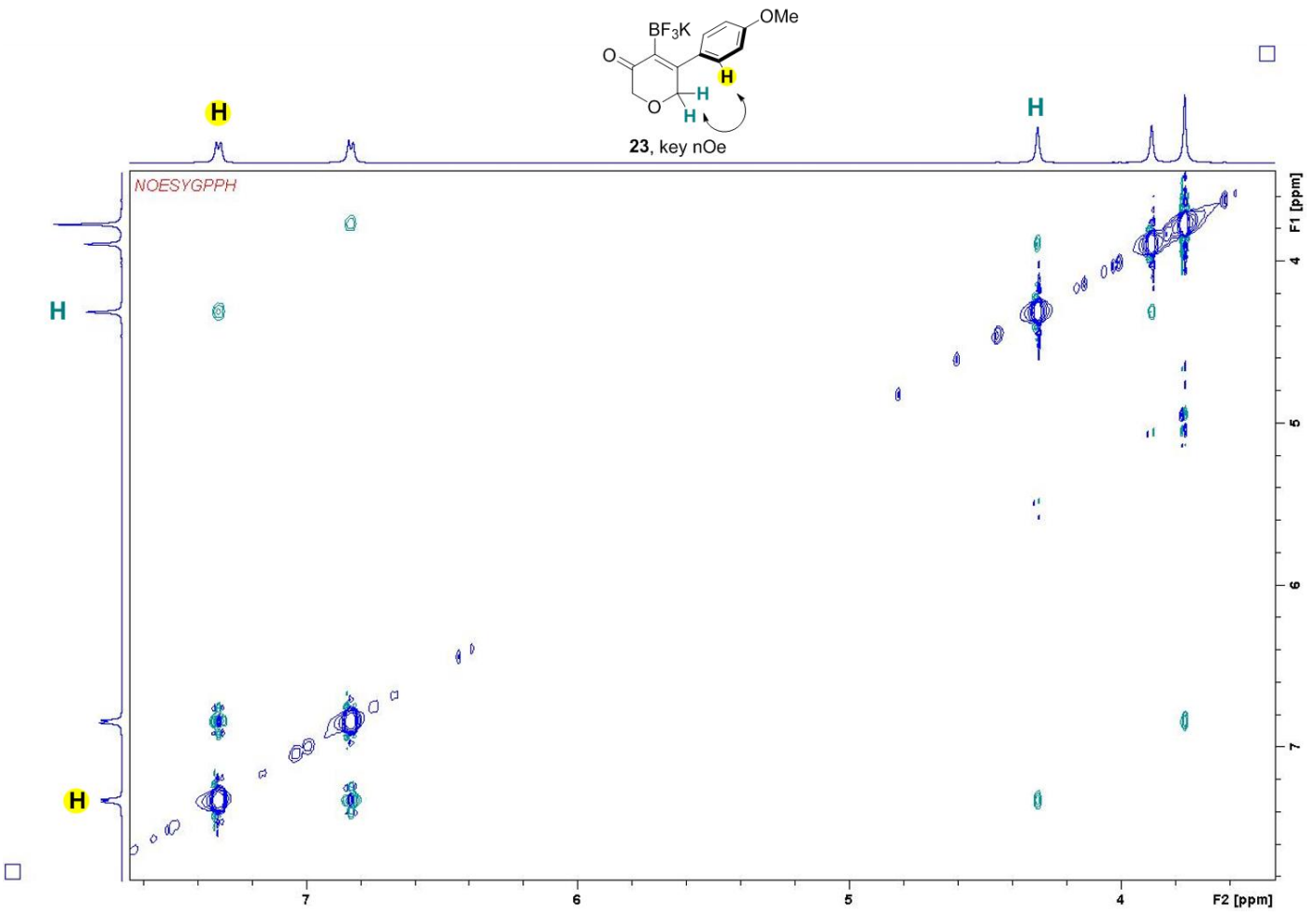
21, key HMBC

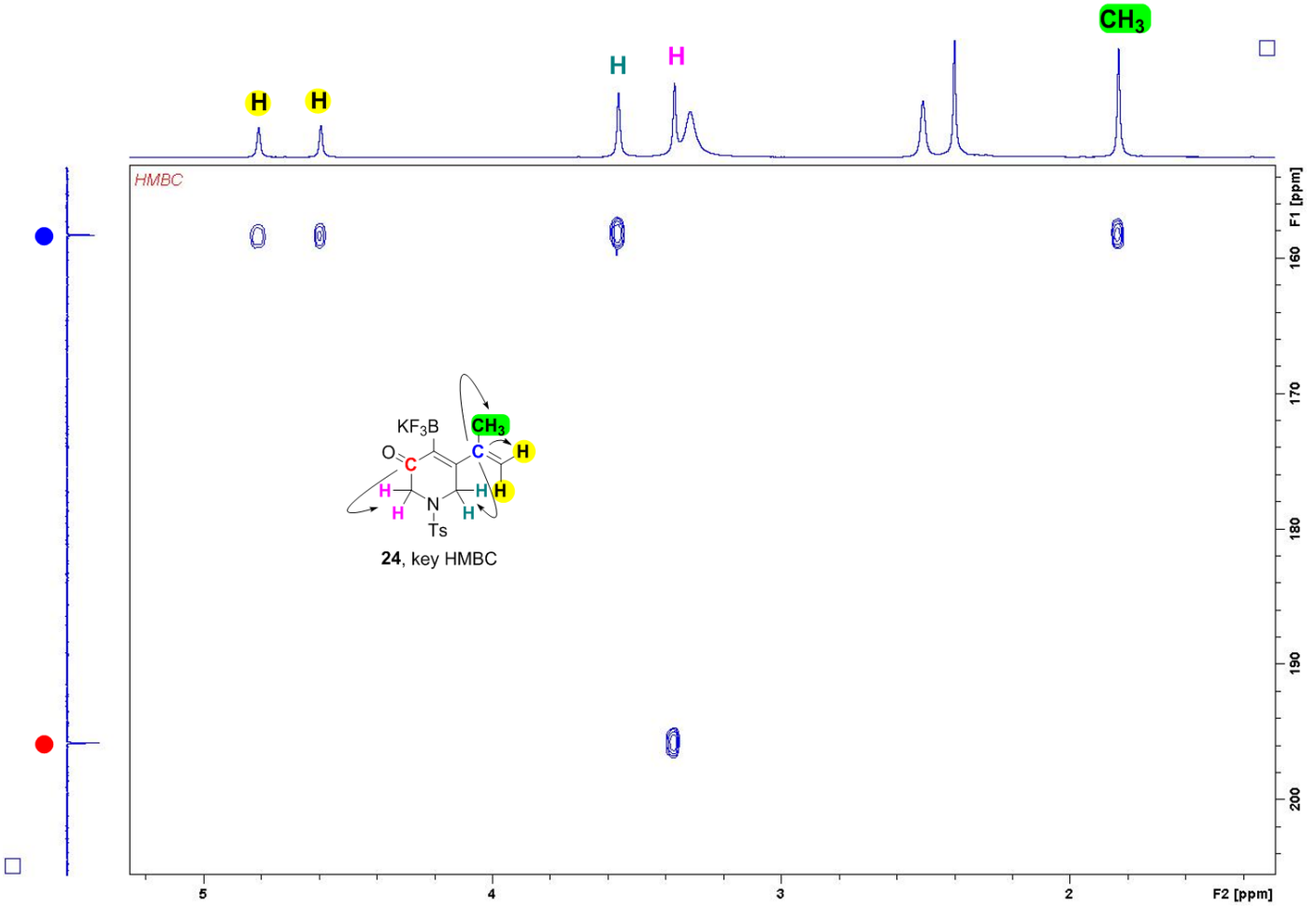


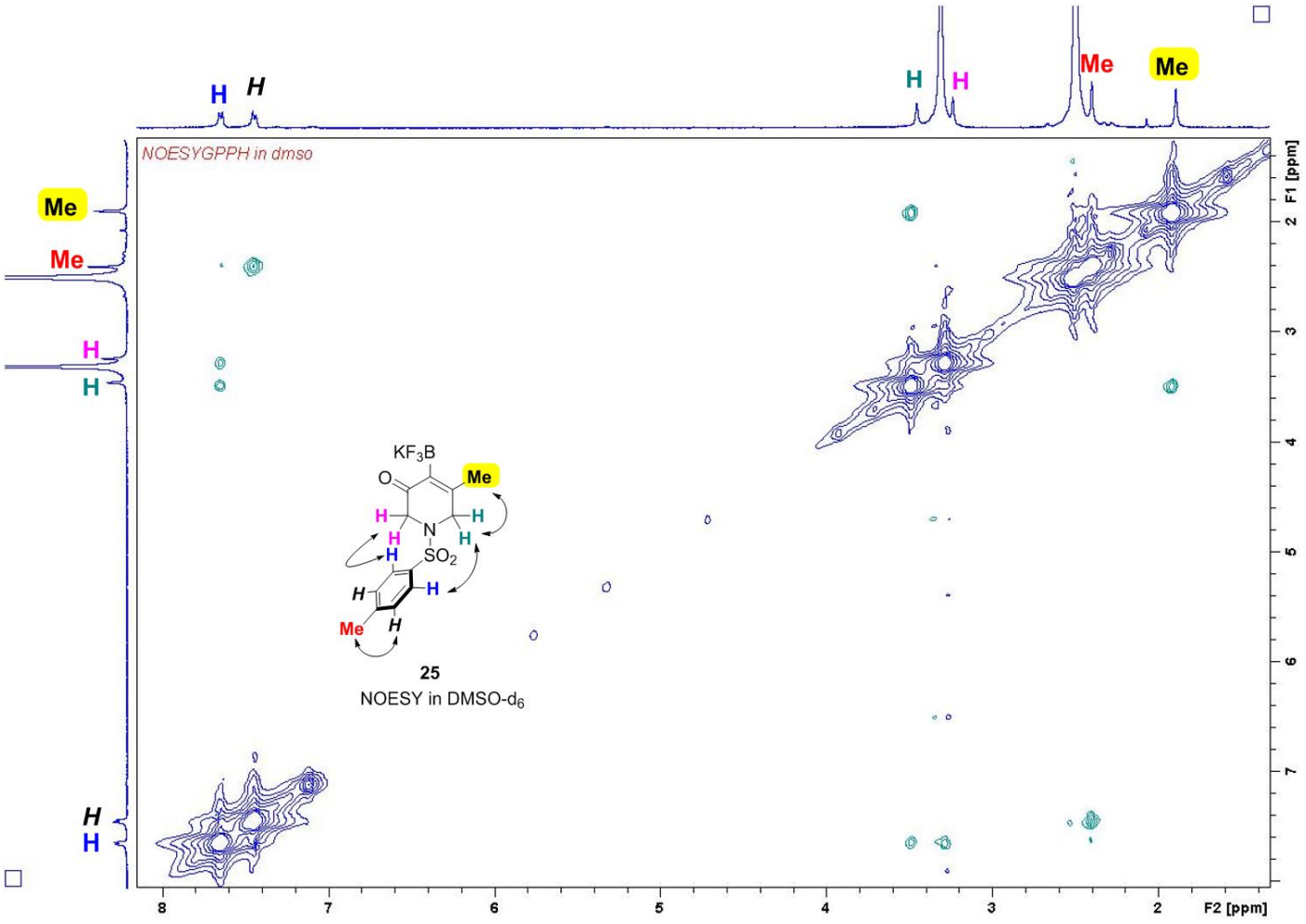
22, key HSQC



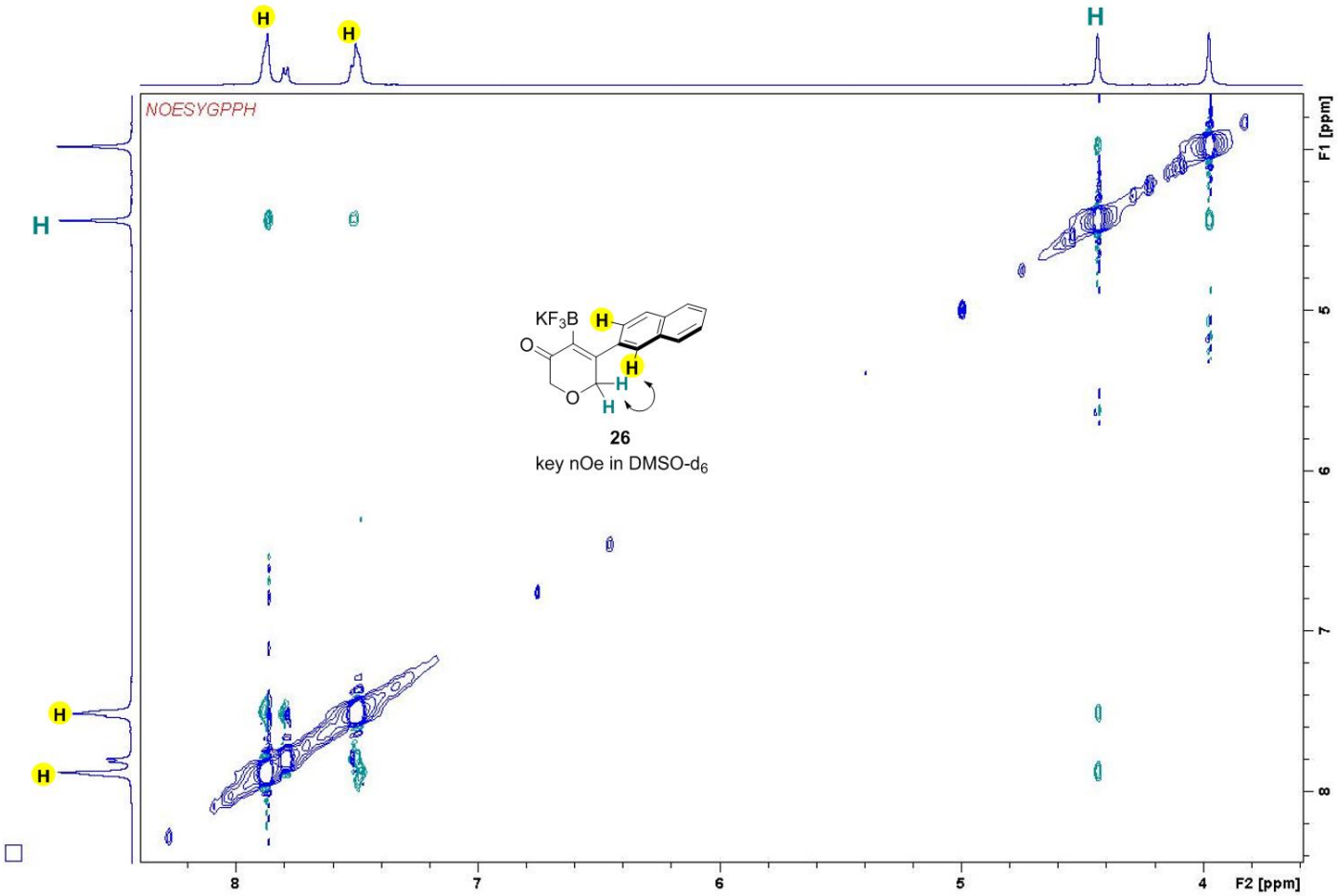
22, key HMBC


BF3K
OMe
O
O
H
H
H
23, key nOe
NOESYGPPH
H
H
H
H
F1 [ppm]
F2 [ppm]
7
6
5
4


CH3
H
H
H
H
HMBC
KF3B
CH3
O
C
C
H
H
H
H
H
N
Ts
24, key HMBC
F1 [ppm]
F2 [ppm]
160
170
180
190
200
5
4
3
2



25
NOESY in DMSO-d_6



26
key nOe in DMSO-d_6