Supporting Information

Rapid, in situ Synthesis of Bidentate Ligands: Chromatography-Free Generation of Catalyst Libraries

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General

All chemicals were obtained from commercial sources and used as received. NMR spectra were recorded in a Bruker DPX-400 Advance spectrometer, operating at 400.13 MHz for 1H-NMR, 100.61 MHz for 13C-NMR and 162.12 MHz for 31P-NMR. Shifts are referenced to the internal solvent signals (1H: δ 7.26 ppm, 13C: δ 77.0 ppm for $CDCl_3$). Analytical CSP-HPLC was performed using a Chiralpak IB (4.6 mm x 25 cm) column. Electrospray mass spectra were recorded on a Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector with methanol, water or ethanol as carrier solvents. Infrared spectra were recorded on a Mattson Genesis II FTIR spectrometer equipped with a Gateway 2000 4DX2-66 workstation and on a Perkin Elmer Spectrum One FT-IR Spectrometer equipped with Universal ATR sampling accessory. Toluene was distilled from calcium hydride.

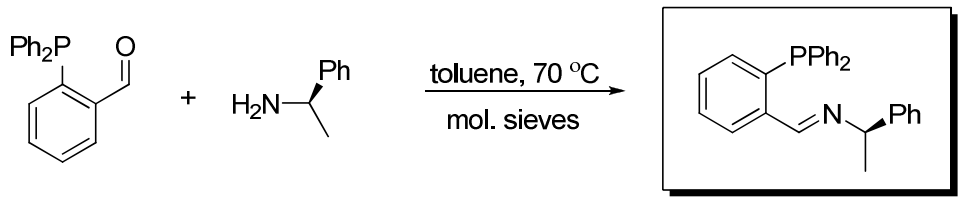
General Procedure A: Synthesis of imines, aminals and oxazolidines.

A vial was charged with aldehyde (0.085 mmol), amine, amino alcohol or diamine or (0.085 mmol) and anhydrous toluene (0.2 mL). To this was added 4Å molecular sieves and the vial was sealed. The reaction was then stirred at 70 °C overnight. Mixtures were then added directly to the catalytic reaction or the solvent was evaporated for NMR analysis.

General Procedure B: Synthesis of oxazolines, imidazolines and thiazolines.

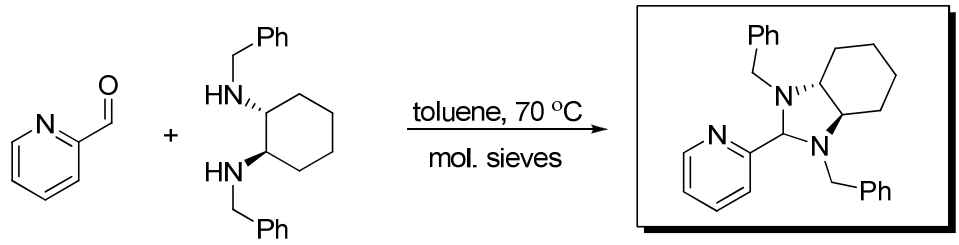
A vial was charged with imidate (0.085 mmol), amino alcohol, diamine or aminothiol (0.085 mmol) and anhydrous toluene (0.2 mL). To this was added 4Å molecular sieves and the vial was sealed. The reaction was then stirred at 70 °C overnight. Mixtures were then added directly to the catalytic reaction or the solvent was evaporated for NMR analysis.

Imine 1



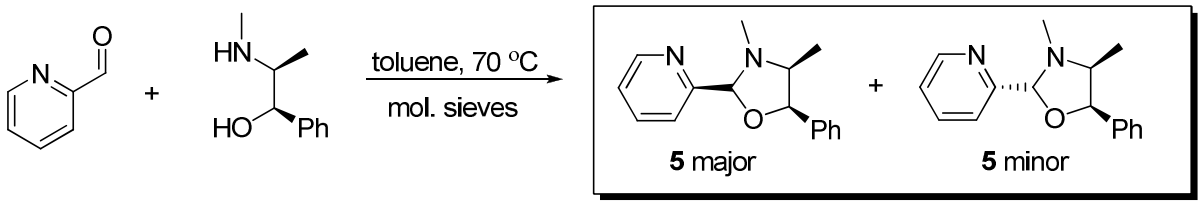
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.98 (d, 1H, *J* = 4.7 Hz), 8.05 (dd, 1H, *J* = 7.4, 3.8 Hz), 7.45-7.21 (m, 17H, Ar), 6.90 (dd, 1H, *J* = 7.4, 5.0 Hz), 4.45 (q, 1H, *J* = 6.6 Hz, NC*H*), 1.39 (d, 3H, *J* = 6.6 Hz, CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$) 157.8 (d, *J* = 20.3 Hz, *C*H=N), 144.3 (quat.), 139.1 (d, *J* = 16.9 Hz, quat.), 137.0 (d, *J* = 19.2 Hz, quat.), 136.1 (d, *J* = 21.2 Hz, quat.), 133.8 (d, *J* = 5.8 Hz), 133.6 (d, *J* = 5.7 Hz), 132.7, 129.7, 128.4, 128.2 (d, *J* = 7.1 Hz), 127.9, 127.6 (d, *J* = 4.0 Hz), 126.2, 69.3 (N-*C*H(CH_3)), 24.1 ((N-CH(*C*H_3)). ^{31}P-NMR δ (162MHz, $CDCl_3$) -11.9. HRMS calcd for $C_{27}H_{24}NP$ $[M + H]^+$ 394.1710, found 394.1725. Consistent with literature values.[1]

Aminal 4



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.40 (d, *J* = 4.5 Hz, 1H, Py-6-H), 7.53 (td, *J* = 7.6, 1.6 Hz, 1H, Ar), 7.37 (d, *J* = 7.8 Hz, 1H, Ar), 7.23-7.02 (m, 11H, Ar), 4.74 (s, 1H, N-C*H*-N), 3.85 (d, *J* = 13.8 Hz, Ph-C*H*H), 3.80 (d, *J* = 13.8 Hz, Ph-C*H*H), 3.53 (d, *J* = 14.5 Hz, Ph-C*H*H), 3.47 (d, *J* = 14.5 Hz, Ph-C*H*H), 3.05-2.91 (m, 1H, C*H*N), 2.59-2.45 (m, 1H, C*H*N), 1.90-1.61 (m, 4H, 2 x CH_2), 1.40-1.06 (m, 4H, 2 x CH_2). ^{13}C-NMR δ (100 MHz, $CDCl_3$) 161.2 (Py-6-C), 147.7, 140.5, 138.8, 134.9, 128.5, 127.6, 127.3, 127.2, 126.0, 125.8, 123.6, 121.6, 87.0 (N-*C*-N), 68.4 (benzyl), 67.0 (benzyl), 56.1 (*C*HN), 52.0 (*C*HN), 29.8, 29.5, 24.09, 24.08. IR (NaCl disk) ν/cm^{-1} 3027, 2929, 2857, 1637, 1588, 1452, 1434, 736. HRMS calcd for $C_{26}H_{29}N_3$ [M + H]$^{+}$ 384.2448, found 384.2440. Consistent with literature values.[2]

Oxazolidine 5



As reported previously[3] a mixture of two diastereomers were formed in a 5.6:1 ratio.

Major diastereomer: ^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.67 (d, 1H, *J* = 4.7 Hz, Py-6-H), 5.23 (d, 1H, *J* = 8.1 Hz, PhC*H*), 4.87 (s, 1H, N-C*H*-O), 3.10-3.01 (m, 1H, C*H*CH_3), 2.34 (s, 3H, NCH_3), 0.81 (d, 3H, *J* = 6.3 Hz, CHCH_3).

Minor diastereomer: ^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.64 (d, 1H, *J* = 4.8 Hz, Py-6-H), 5.65 (d, 1H, *J* = 5.1 Hz, PhC*H*), 5.44 (s, 1H, N-C*H*-O), 3.79-3.71 (m, 1H, C*H*CH_3), 2.37 (s, 3H, NCH_3), 0.76 (d, 3H, *J* = 6.6 Hz, CHCH_3).

Aromatic protons overlapped and could not be assigned to the diastereomers, as reported previously.[3] Combined aromatic region: 7.87-7.75 (m, Ar), 7.72-7.63 (m, Ar), 7.50 (d, *J* = 7.8 Hz, Ar), 7.38 (dd, *J* = 15.3, 7.0 Hz), 7.34-7.24 (m, Ar).

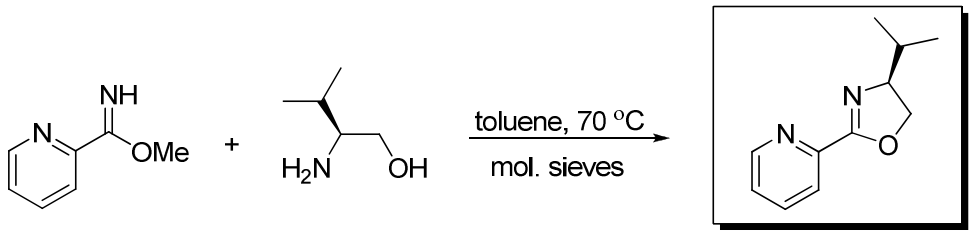
Major diastereomer: ^{13}C-NMR δ (100MHz, $CDCl_3$) 148.7, 139.3, 136.6, 127.7, 126.9, 125.9, 125.4, 123.0, 98.4 (N-*C*-O), 82.4 (Ph-*C*H), 63.8 (*C*HCH_3), 35.6 (N-*C*H_3), 14.4 (CH*C*H_3).

Minor diastereomer: ^{13}C-NMR δ (100MHz, $CDCl_3$) 157.7, 148.5, 136.4, 127.6, 127.5, 127.3, 123.4, 121.7, 95.1 (N-*C*-O), 82.3 (Ph-*C*H), 61.1 (*C*HCH_3), 31.1 (N-*C*H_3), 8.6 (CH*C*H_3).

IR (NaCl disk) v/cm^{-1} (mixture) 2969, 2846, 2795, 1713, 1591, 1502, 1456, 1437, 1059, 1038, 701.

HRMS calcd for $C_{16}H_{18}N_2O$ (mixture) $[M + H]^+$ 255.1502, found 255.1497.

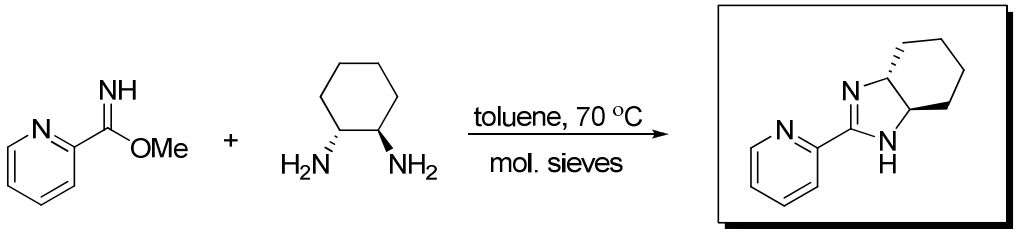
Oxazoline 7



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.71 (d, 1H, *J* = 4.7 Hz, Py-6-H), 8.06 (d, 1H, *J* = 7.8 Hz, Py-3-H), 7.81-7.74 (m, 1H, Py), 7.42-7.37 (m, 1H, Py), 4.54-4.48 (m, 1H, -C*H*N), 4.25-4.13 (m, 2H, -CH_2O), 1.95-1.89 (m, 1H,-C*H*(CH_3)$_2$), 1.06 (d, 3H, *J* = 6.8 Hz, CH_3), 0.95 (d, 3H, *J* = 6.8Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 162.1, 149.3, 146.4, 136.2, 125.0, 123.5, 72.5,

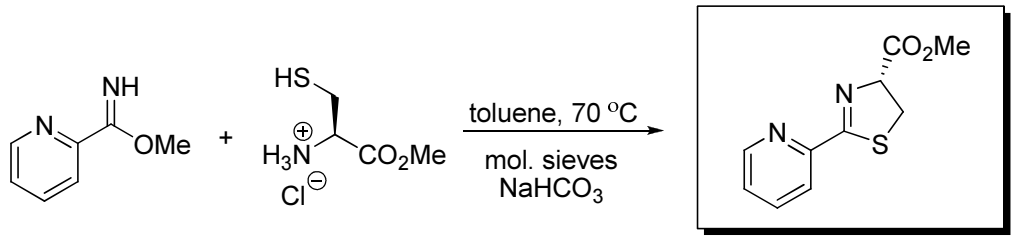
70.3, 32.3 (*C*H), 18.6 (*C*H_3), 17.7 (*C*H_3). IR (NaCl disk) v/cm^{-1} 3059, 2960, 2873, 1650, 1583, 1468, 1440, 1363, 1291, 1256, 746. HRMS calcd for $C_{11}H_{14}N_2O$ $[M + H]^+$ 119.1179, found 119.1183. Consistent with literature values.[4]

Imidazolidine 8



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.51 (d, 1H, *J* =4.6 Hz, Py-6-H), 8.13 (d, 1H, *J* = 7.8 Hz, Py-3-H), 7.83-7.75 (m, 1H, Py), 7.29 (m, 1H, Py), 3.20-3.09 (br m, 2H, 2 x CH) 2.31-2.19 (br m, 2H, CH_2), 1.83-1.72 (br m, 2H, CH_2), 1.58-1.45 (br m, 2H, CH_2), 1.36- 1.24 (br m, 2H, CH_2). ^{13}C-NMR δ (100 MHz, $CDCl_3$) 165.3, 148.8, 148.5, 136.7, 125.3, 122.2, 30.8 (CH_2), 25.0 (CH_2). Peak reported at 71.1 as broad[5] not observed. IR (NaCl disk) v/cm^{-1} 3944, 3690, 3054, 2987, 1594, 1265, 896. HRMS calcd for $C_{12}H_{16}N_3$ $[M + H]^+$ 202.1339, found 202.1344. Consistent with literature values.[5]

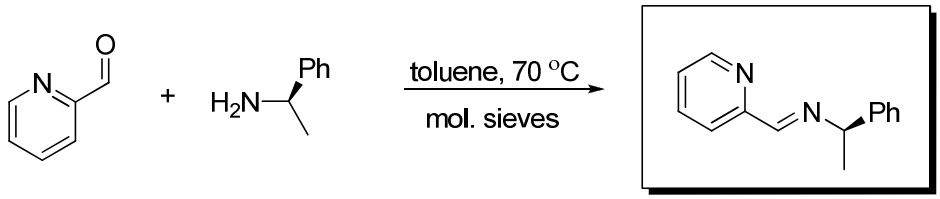
Thiazoline 9



Prepared as per Procedure B, except one equivalent of $NaHCO_3$ was charged to the vial at the start of the reaction.

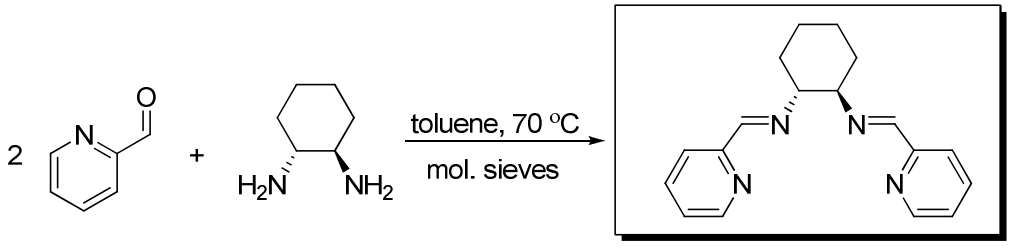
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.68 (d, 1H, *J* = 4.8 Hz, Py-6-H), 8.19 (d, 1H, *J* = 7.9 Hz, Py-3-H), 7.83-7.78 (m, 1H, Py), 7.43-7.40 (m, 1H, Py), 5.40 (t, 1H, *J* = 9.5 Hz, -C*H*CO_2Me), 3.87 (s, 3H, -C*H*$_3$), 3.72-3.61 (m, 2H, -C*H*$_2$CH). ^{13}C-NMR δ (100MHz, $CDCl_3$) 173.1, 170.8, 150.1, 148.9, 136.2, 125.4, 121.5, 78.5, 52.4, 33.9. IR (NaCl disk) v/cm^{-1} 3109, 2877, 1585, 1138, 887. HRMS calcd for $C_{10}H_{10}N_2O_2S$ $[M + H]^+$ 223.0536, found 223.0531. Consistent with literature values.[6]

Imine 10



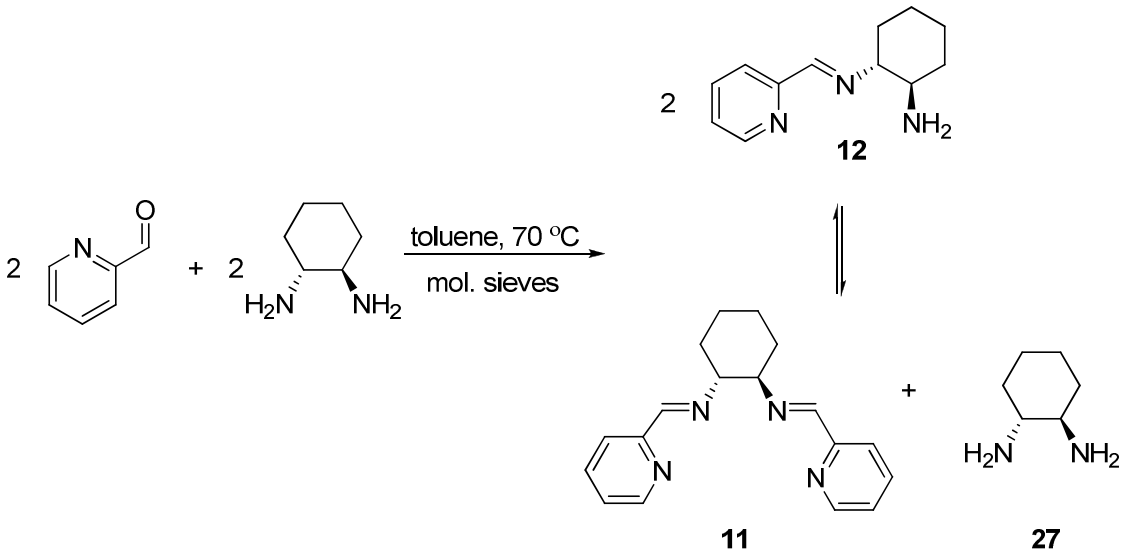
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.48 (d, 1H, *J* = 4.5 Hz, Py-6-H), 8.37 (s, 1H, CH=N), 7.95 (d, 1H, *J* = 7.2 Hz, Py-3-H), 7.49 (ap t, 1H), 7.39-7.29 (m, 2H), 7.27-7.17 (m, 2H), 7.17-6.98 (m, 2H), 4.51 (q, 1H, *J* = 6.6 Hz, CH), 1.49 (d, 3H, *J* = 6.6 Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 160.0, 154.3, 148.9, 144.1, 136.1, 128.1, 126.6, 126.3, 124.3, 121.0, 69.2 (CH), 24.2 (CH_3). IR (NaCl disk) v/cm^{-1} 3059, 2971, 2926, 2860, 1645, 1586, 1467, 1436, 1370, 761. HRMS calcd for $C_{14}H_{14}N_2$ $[M + H]^+$ 211.1235, found 211.1239. Consistent with literature values.[7]

Bisimine 11



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.52 (d, 2H, *J* = 4.8 Hz, Py-6-H), 8.29 (s, 2H, CH=N), 7.86 (d, 2H, *J* = 7.9 Hz, Py-3-H), 7.61 (ap t, 2H, Py), 7.23-7.16 (m, 2H, Py), 3.59-3.42 (m, 2H), 1.89-1.78 (m, 6H), 1.53-1.45 (m, 2H). ^{13}C-NMR δ (100MHz, $CDCl_3$) 161.4, 154.6 (q), 149.2, 136.4, 124.5, 121.3, 73.6 (CH), 32.7 (CH_2), 24.3 (CH_2). IR (NaCl disk) v/cm^{-1} 2928, 2842, 1714, 1644, 1587, 1467, 992. HRMS calcd for $C_{18}H_{20}N_4$ $[M + H]^+$ 293.1766, found 293.1759. Consistent with literature values.[8]

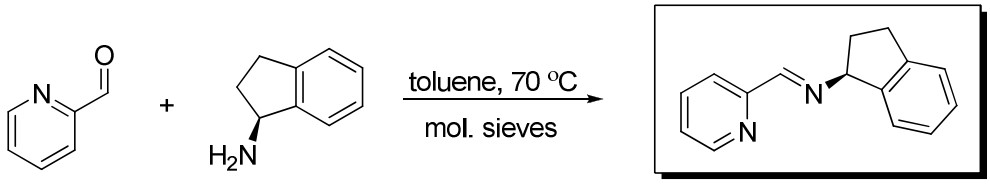
Equilibration mixture (12, 11 and 27)



The equilibrium mixture contained monoimine **12** and diamine **11** (with unreacted diamine **27**) in a 3:1 ratio as measured by ^{1}H-NMR.

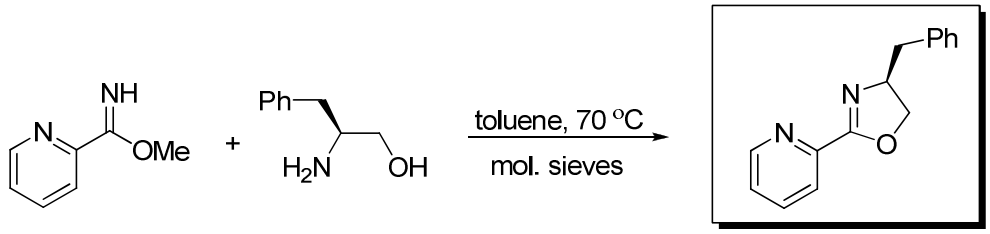
Compound **12**: ^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.67 (d, 1H, *J* = 4.8 Hz, Py-6-H), 8.46 (s, 1H, C*H*=N), 7.99 (d, 1H, *J* = 7.9 Hz, Py-3-H), 7.75 (ap t, 1H, Py), 7.36-7.30 (m, 1H, Py), 3.00-2.85 (m, 2H, 2 x C*H*-N), 2.0-1.1 (m, overlapping with compounds **11** and **27**, 4 x CH_2). The presence of compounds **12**, **11** and **27** was confirmed by mass spectroscopy.

Imine 13



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.66 (m, 1H, Py-6-H), 8.55 (s, 1H, C*H*=N), 8.07 (dt, 1H, *J* = 8.0, 1.0 Hz, Py-3-H), 7.77-7.68 (m, 1H, Ar), 7.36-7.26 (m, 2H, Ar), 7.26-7.10 (m, 3H, Ar), 5.03 (ap t, 1H, C*H*N), 3.16 (ddd, 1H, *J* = 15.8, 8.7, 4.2 Hz, C*H*H), 3.05-2.91 (m, 1H, C*H*H), 2.60-2.43 (m, 1H, C*H*H), 2.29 (dddd, 1H, *J* = 12.8, 8.7, 8.0, 6.6 Hz, C*H*H). ^{13}C-NMR δ (100MHz, $CDCl_3$) 161.4, 154.7 (q), 149.4, 144.0 (q), 143.8 (q), 136.6, 127.8, 126.5, 124.9, 124.8, 124.4, 121.5, 74.7 (CH), 34.1 (CH_2), 31.1 (CH_2). IR (NaCl disk) v/cm^{-1} 2934, 2851, 1641, 1587, 1567, 1467, 1436. $[\alpha]^{20}_{D}$ = +64.4 (c 0.7, $CHCl_3$). HRMS calcd for $C_{15}H_{14}N_2$ [M + H]$^{+}$ 245.1055, found 245.1067.

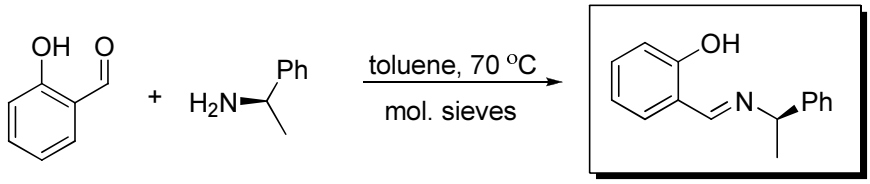
Oxazoline 14



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.71 (d, 1H, *J* = 4.7 Hz, Py-6-H), 8.06 (d, 1H, *J* = 7.9 Hz, Py-3-H), 7.82-7.72 (m, 1H, Py-4-H), 7.40 (dd, 1H *J* = 7.5, 4.7 Hz, Py-5-H), 7.35-7.27 (m, 2H, Ph), 7.28-7.20 (m, 3H, Ph), 4.71-4.61 (m, 1H, C*H*, 4-H), 4.45 (ap t, 1H, C*H*, 5-H), 4.23 (ap t, 1H, C*H*, 5-H), 3.30 (dd, 1H, *J* = 13.8, 5.0 Hz, CH_2), 2.76 (dd, 1H, *J* = 13.8, 9.1 Hz, CH_2). ^{13}C-NMR δ (100MHz, $CDCl_3$) 162.7 (q), 149.3, 146.3 (q), 137.3 (q), 136.21, 128. 8, 128.2, 126.1, 125.2, 123.5, 72.1 (CH_2), 67.7 (CH), 41.2 (CH_2). IR (NaCl disk) v/cm^{-1} 3084, 2980,

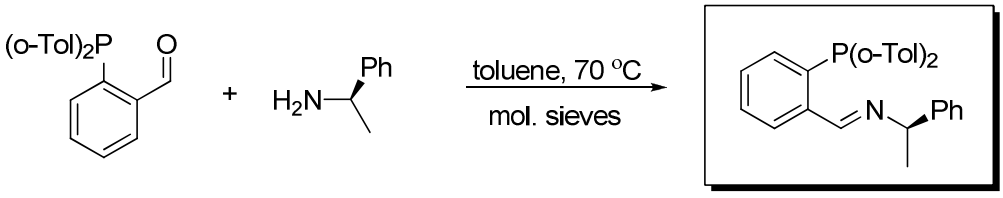
2860, 1641, 1469, 1440, 1363, 1099. HRMS calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1184, found 239.1189. Consistent with literature values.[4]

Imine 15



^{1}H-NMR δ (400 MHz, $CDCl_3$) 13.58 (s, 1H, OH), 8.40 (s, 1H, C*H*=N), 7.41-7.25 (m, 6H, Ar), 7.24-7.17 (m, 1H, Ar), 6.98 (d, 1H, *J* = 8.3 Hz, Ar), 6.87 (ap t, 1H), 4.54 (q, 1H, *J* = 6.7 Hz, CH), 1.63 (d, 3H, *J* = 6.7 Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 163.5 (*C*H=N), 161.1 (q), 143.9 (q), 132.4, 131.5, 128.7, 127.3, 126.5, 118.9 (q), 118.7, 117.0, 68.6 (*C*H), 25.0 (CH_3). IR (NaCl disk) v/cm^{-1} 3062, 3032, 2980, 2880, 1664, 1622, 1578, 1454. HRMS calcd for $C_{15}H_{15}NO$ $[M + H]^+$ 226.1232, found 226.1234. Consistent with literature values.[9]

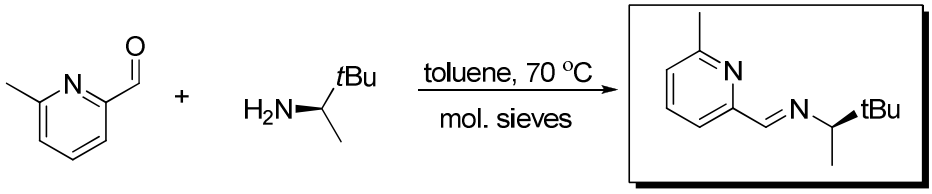
Imine 16



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.98 (d, 1H, *J* = 5.1Hz, 1H, CH=N), 8.15-8.07 (m, 1H, Ar), 7.43 (apt t, 1H, Ar), 7.34-7.17 (m, 9H, Ar), 7.16-7.05 (m, 3H, Ar), 6.87 (dd, 1H *J* = 6.8, 4.6 Hz, Ar), 6.81 (dd, 2H *J* = 11.1, 6.6 Hz), 4.46 (q, 1H, *J* = 6.6 Hz, NC*H*(CH_3)), 2.44 (d, 6H, *J* = 13.8Hz, ArCH_3), 1.42 (d, 3H, *J* = 6.6 Hz, NCH(C*H*$_3$)). ^{13}C-NMR δ (100MHz, $CDCl_3$) 158.3 (d, *J* = 22.8 Hz, *C*H=N), 144.7 (q), 142.6 (d, *J* = 7.2 Hz, tolyl *C*-CH_3), 142.3 (d, *J* = 7.5 Hz, tolyl' *C*-CH_3), 140.0 (d, *J* = 17.6 Hz, *C*-CH=N), 136.0 (d, *J* = 17.5 Hz, P-*C*), 134.5 (d, *J* = 9.9

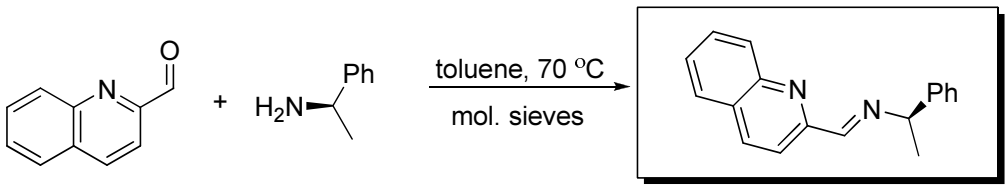
Hz, tolyl P-*C*), 134.3 (d, *J* = 10.3 Hz, tolyl' P-*C*), 133.7, 133.5, 133.3, 130.3, 130.1 (d, *J* = 1.9 Hz, tolyl *C*-C-CH_3), 130.07 (d, *J* = 1.7 Hz, tolyl' *C*-C-CH_3), 128.9, 128.86, 128.82, 128.3 (Ph-3-C), 127.8 (d, *J* = 4.2 Hz), 126.6 (Ph-4-C), 126.3 (Ph-2-C), 69.5 (N-*C*H), 24.4 (NCH(*C*H_3)), 21.3 (d, *J* = 21.7 Hz, tolyl *C*H_3). ^{31}P-NMR δ (162MHz, $CDCl_3$) -28.5. IR (NaCl disk) v/cm^{-1} 2967, 2923, 1634, 1451, 1376, 908. HRMS calcd for $C_{29}H_{28}NP$ $[M + H]^+$ 422.2038, found 422.2031.

Imine 17



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.30 (s, 1H, CH=N), 7.87 (d, 1H, *J* = 7.8Hz, Py), 7.60 (ap t, 1H, Py-4-H), 7.14 (d, 1H, *J* = 7.6 Hz, Py), 3.04 (q, 1H *J* = 6.5Hz, CH), 2.58 (s, 3H, ArCH_3), 1.15 (d, 3H, *J* = 6.5Hz, CH_3), 0.91 (s, 9H, C(CH_3)$_3$). ^{13}C-NMR δ (100MHz, $CDCl_3$) 159.5, 157.4, 154.1, 136.3, 123.6, 117.6, 74.8, 33.8, 26.2, 23.9, 16.8. IR (NaCl disk) v/cm^{-1} 2964, 2868, 1653, 1647, 1591, 1575, 1457, 1363, 1120, 783. $[\alpha]^{20}_D$ = +51.1 (c 0.6, $CHCl_3$). HRMS calcd for $C_{13}H_{20}N_2$ $[M + Na]^+$ 227.1524, found 227.1517.

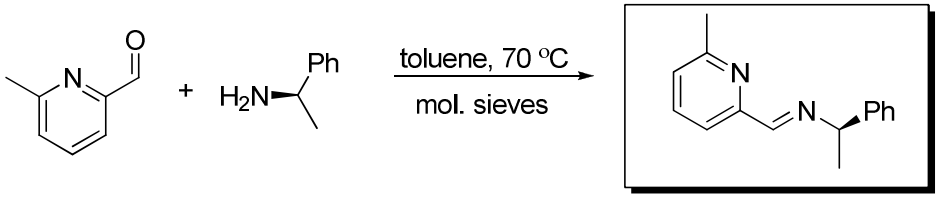
Imine 18



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.66 (s, 1H, CH=N), 8.27 (d, 1H, *J* = 8.6 Hz, Ar), 8.21 (d, 1H, *J* = 8.6 Hz, Ar), 8.14 (d, 1H, *J* = 8.5 Hz, Ar), 7.83 (d, 1H, *J* = 8.1Hz, Ar), 7.74 (dd, 1H, *J* = 8.3, 7.1 Hz, Ar), 7.57 (dd, 1H, *J* = 8.0, 7.0 Hz, Ar), 7.49 (d, 1H, *J* = 7.9 Hz, Ar), 7.38 (dd, 2H,

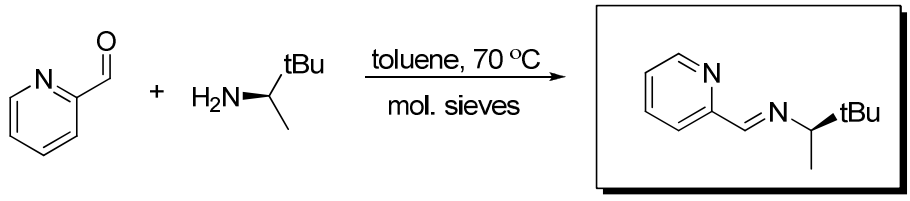
J = 8.1, 7.0 Hz , Ar), 7.30-7.25 (m, 1H, Ar), 4.73 (q, 1H, *J* = 6.6 Hz, C*H*), 1.66 (d, 3H, *J* = 6.6 Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 160.5, 154.6, 147.3, 144.1, 136.0, 129.3, 129.1, 128.3, 128.1, 127.3, 127.0, 126.6, 126.3, 118.2, 69.2, 24.2. IR (NaCl disk) v/cm^{-1} 3053, 2967, 2861, 1633, 1595, 1560, 1505, 1364. HRMS calcd for $C_{18}H_{16}N_2$ $[M + H]^+$ 261.1392, found 261.1388. Consistent with literature values.[10]

Imine 19



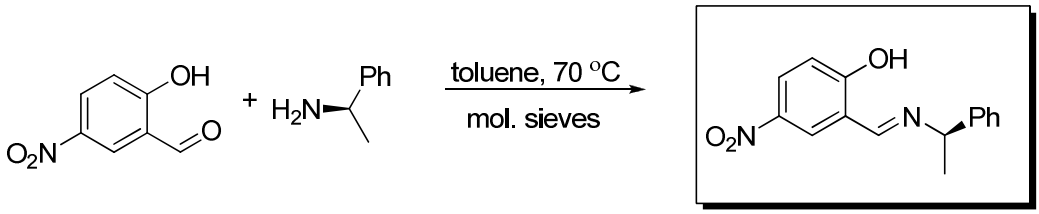
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.48 (s, 1H, CH=N), 7.95 (d, 1H, *J* = 7.7 Hz, Ar), 7.62-7.68 (m, 1H, Ar), 7.42-7.51 (m, 2H, Ar), 7.33-7.40 (m, 2H, Ar), 7.20 (d, 1H, *J* = 7.7 Hz, Ar), 4.65 (q, 1H, *J* = 6.7 Hz, C*H*CH_3), 2.61 (s, 3H, PyrCH_3), 1.63 (d, 3H, *J* = 6.7 Hz, CHC*H*$_3$). ^{13}C-NMR δ (100MHz, $CDCl_3$) 160.4 (CH=N), 157.5, 153.8, 144.1, 136.3, 128.0, 126.5, 126.3, 125.4, 123.9, 117.9, 69.1 (CH), 24.1 (CH_3), 23.9 (CH_3). IR (NaCl disk) v/cm^{-1} 3388, 3061, 2971, 2926, 2861, 1711, 1645, 1591, 1453. HRMS calcd for $C_{15}H_{16}N_2$ $[M + H]^+$ 225.1392, found 225.1395. Consistent with literature values.[12]

Imine 20



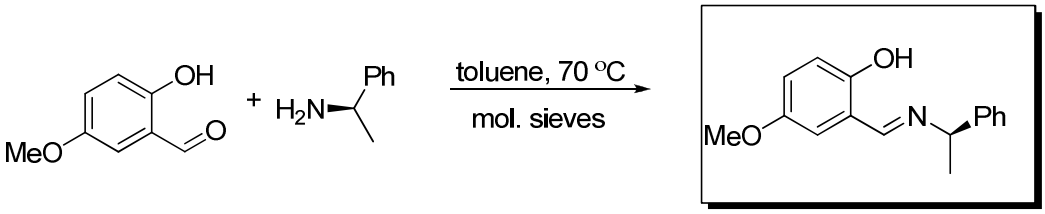
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.63 (d, 1H, *J* = 4.8 Hz, Py-6-H), 8.34 (s, 1H, CH=N), 8.06 (d, 1H, *J* = 7.9 Hz, Py), 7.73 (apt t, 1H, Py), 7.30 (dd, 1H, *J* = 7.4 Hz, 4.8 Hz, Py-5-H), 3.08 (q, 1H, *J* = 6.5 Hz, CH), 1.18 (d, 3H, *J* = 6.5 Hz, CHC*H*$_3$), 0.94 (s, 9H, tBu). ^{13}C-NMR δ (100MHz, $CDCl_3$) 159.1 (CH=N), 154.6, 148.8, 136.0, 124.0, 120.7, 74.8, 33.8 (*C*HCH$_3$), 26.1 (tBu), 16.8 (CH*C*H$_3$). IR (NaCl disk) v/cm^{-1} 2964, 2905, 2869, 1648, 1588, 1568, 1436, 1364. HRMS calcd for $C_{12}H_{18}N_2$ [M + H]+ 191.1548, found 191.1550. Consistent with literature values.[12]

Imine 21



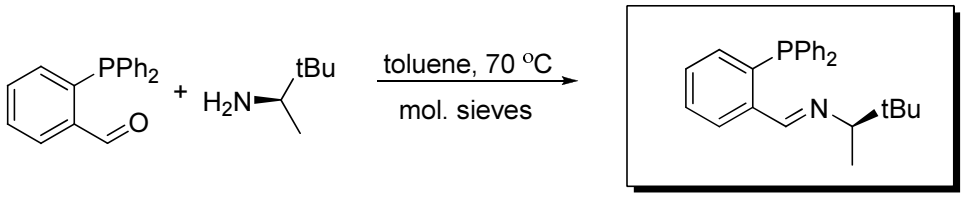
^{1}H-NMR δ (400 MHz, $CDCl_3$) 14.93 (s, 1H, OH), 8.43 (s, 1H, CH=N), 8.18-8.30 (m, 2H, Ar), 7.31-7.51 (m, 6H, Ar), 7.01 (d, 1H, *J* = 9.1 Hz, Ar), 4.72 (q, 1H, *J* = 6.6 Hz, CH), 1.73 (d, 3H, *J* = 6.6 Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 168.4, 161.9, 141.5, 138.5, 128.6, 127.80, 127.75, 127.5, 126.0, 118.4, 116.5, 66.7 (CH), 23.7 (CH_3). IR (NaCl disk) v/cm^{-1} 2971, 1739, 1633, 1481, 1353. HRMS calcd for $C_{15}H_{14}N_2O_3$ [M - O + H]$^{+}$ 255.1134, found 255.1143. Consistent with literature values.[9]

Imine 22



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.40 (s, 1H, CH=N), 7.35-7.43 (m, 4H, Ar), 7.26-7.34 (m, 1H, Ar), 6.92-6.99 (m, 2H, Ar), 6.80 (d, 1H, *J* = 2.6 Hz, Ar), 4.58 (q, 1H, *J* = 6.7 Hz, C*H*CH_3), 3.80 (s, 3H, $ArOCH_3$), 1.66 (d, 3H, *J* = 6.7 Hz, $CHCH_3$). ^{13}C-NMR δ (100MHz, $CDCl_3$) 162.7, 154.7 (q), 151.5 (q), 143.3 (q), 128.2, 126.8, 126.0, 118.8, 118.0 (q), 117.2, 114.5, 68.2 (*C*HCH_3), 55.5 ($ArOCH_3$), 24.6 ($CHCH_3$). IR (NaCl disk) v/cm^{-1} 3032, 2973, 2930, 2899, 1630, 1584, 1490. HRMS calcd for $C_{16}H_{17}O_2N$ $[M + H]^+$ 256.1338, found 256.1346.Consistent with literature values.[13]

Imine 23



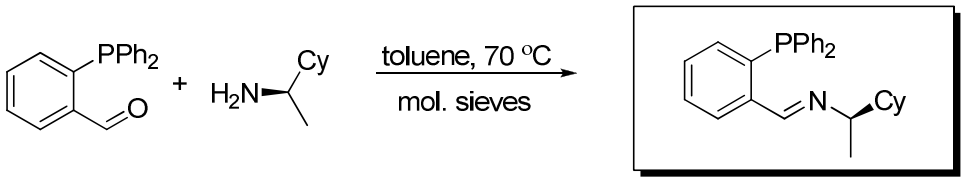
^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.83 (d, 1H, *J* = 4.8Hz, CH=N), 8.03 (ddd, 1H, *J* = 7.6 Hz, 4.0 Hz, 1.4 Hz, Ar), 7.42 (apt t, 1H, Ar), 7.24-7.39 (m, 10H, Ar), 6.88 (ddd, 1H, *J* = 7.6 Hz, 4.8 Hz, 1.4 Hz, Ar), 2.87 (q, 1H, *J* = 6.5 Hz, CH), 0.91 (d, 3H, *J* = 6.5 Hz, CH_3), 0.85 (s, 9H, tBu). ^{13}C-NMR δ (100MHz, $CDCl_3$) 157.3 (d, *J* = 20.5 Hz, CH=N), 139.8 (d, *J* = 16.9 Hz, Ar, quat.), 137.1 (d, *J* = 19.3 Hz, Ar, quat.), 136.7 (d, *J* = 9.8 Hz, Ar, quat.), 136.5 (d, *J* = 9.5 Hz, Ar, quat.), 134.3, 134.2, 134.1, 134.0, 133.0, 129.8, 128.9, 128.6, 128.5, 127.8 (d, *J* = 4.2

Hz, Ar), 75.7 (CH), 34.2 (*C*(CH_3)$_3$), 126.6 (tBu), 17.1 (CH_3). ^{31}P-NMR δ (162MHz, $CDCl_3$) -12.9. IR (NaCl disk) v/cm^{-1} 3053, 2968, 2864, 1739, 1637, 1433, 1368. HRMS calcd for $C_{25}H_{28}NP$ [M + H]+ 374.2038, found 374.2033.

Imine 24

^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.68 (d, 1H *J* = 3.6 Hz, Py-6-H), 8.56 (s, 1H, CH=N), 8.16 (d, 1H, *J* = 7.8 Hz), 7.81-7.95 (m, 4H, Ar), 7.78 (apt t, 1H, Ar), 7.63 (d, 1H, *J* = 8.4 Hz, Ar), 7.41-7.55 (m, 2H, Ar), 7.31-7.40 (m, 1H, Ar), 4.85 (q, 1H, *J* = 6.5 Hz, CH), 1.74 (d, 3H, *J* = 6.5 Hz, CH_3). ^{13}C-NMR δ (100MHz, $CDCl_3$) 160.2, 154.3, 149.0, 141.5, 136.1, 133.0, 132.2, 127.7, 127.5, 127.2, 126.1, 124.8, 124.6, 124.3, 121.1, 69.2 (CH), 24.1 (CH_3). IR (NaCl disk) v/cm^{-1} 3048, 3009, 2979, 2966, 2924, 2858, 1648, 1599, 1567, 1436. $[\alpha]^{20}_D$ = +68.9 (c 1.6, $CHCl_3$). HRMS calcd for $C_{18}H_{16}N_2$ $[M + H]^+$ 261.1392, found 261.1397.

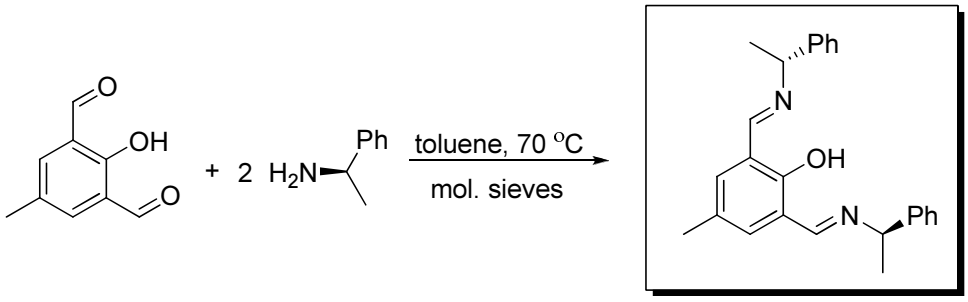
Imine 25



^{1}H-NMR δ (400 MHz, $CDCl_3$) 8.82 (d, 1H, *J* = 4.6 Hz, CH=N), 7.99 (dd, 1H, *J* = 7.5 Hz, 3.9 Hz, Ar), 7.21-7.47 (m, 12H, Ar), 6.86 (apt t, 2H, Ar), 2.89 (apt quint, 1H, *J* = 6.0 Hz, CH),

1.64-1.79 (m, 2H, Cy), 1.51-1.64 (m, 2H, Cy), 1.06-1.49 (m, 5H, Cy), 1.03 (d, 3H, *J* = 6.0 Hz, CH_3), 0.73-0.90 (m, 1H, Cy), 0.53-0.70 (m, 1H, Cy). ^{13}C-NMR δ (100MHz, $CDCl_3$) 156.9 (d, *J* = 21.6 Hz, CH=N), 139.3 (d, *J* = 16.7 Hz, Ar, quat.), 136.6 (d, *J* = 18.3 Hz, Ar, quat.), 135.99 (d, *J* = 9.6 Hz, Ar, quat.), 135.95 (d, *J* = 9.4 Hz, Ar, quat.), 133. 6 (d, *J* = 3.8Hz, Ar), 133.6 (d, *J* = 3.8 Hz, Ar), 132.4, 129.4, 128.38, 128.35, 128.1 (d, *J* = 7.3 Hz, Ar), 127.2 (d, *J* = 4.1 Hz, Ar), 71.5 (NCH), 43.0 (CH), 29.2 (CH_2), 26.1 (CH), 25.9 (CH), 25.7 (CH), 19.3 (CH_3). ^{31}P-NMR δ (162MHz, $CDCl_3$) -12.4. IR (NaCl disk) v/cm^{-1} 3052, 2921, 2849, 1635, 1448, 1434. HRMS calcd for $C_{27}H_{30}NP$ $[M + H]^+$ 400.2194, found 400.2183.

Imine 26



^{1}H-NMR δ (400 MHz, $CDCl_3$) 14.13 (s, 1H, OH), 8.69 (br s, 2H, CH=N), 7.23-7.53 (m, 12H, Ar), 4.62 (q, 2H, *J* = 6.7 Hz, C*H*CH_3), 2.33 (s, 3H, Ar-CH_3), 1.67 (d, 6H, *J* = 6.7 Hz, CHC*H*$_3$). ^{13}C-NMR δ (100MHz, $CDCl_3$) 159.0, 132.2, 131.5, 128.6, 127.7, 127.1, 126.6, 118.6, 116.8, 72.7 (*C*HCH_3), 24.8 (ArCH_3), 20.3 (CH*C*H_3). IR (NaCl disk) v/cm^{-1} 3027, 2970, 2923, 2865, 1634, 1599, 1450. HRMS calcd for $C_{25}H_{26}N_2O$ $[M + H]^+$ 371.2123, found 371.2127. Consistent with literature values.[14]

Asymmetric Transfer Hydrogenation

Ligands synthesised as above were either analyzed by NMR or used directly in catalytic reactions. The ligand solution in toluene could be used directly in the reaction or the toluene could be evaporated without affecting the results.

Transfer Hydrogenation Protocol as per that reported by Himeda.[11]

A mixture of chiral ligand (21 μmol) and $[Cp^*RhCl_2]_2$ (10 μmol) in methanol (10 mL) was stirred at 40 °C for 12 hours. At this time the solvent was removed under vacuum and sodium formate/formic acid buffer (20 mL, 1.0M, pH 3.5) was added along with acetophenone (2.0 mmol). This was stirred at 40 °C for 24 hours, at which point the reaction was extracted with ethyl acetate (2 x 15 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum. The product was isolated by vacuum distillation and analysed by chiral HPLC. CHIRALPAK IB (4.6 mm x 25 cm), hexane/IPA, 97:3, 1.5 mL min-1, RT, UV detection at 254 nm, retention times: 17.0 min (*S*) and 20.0 min (*R*).

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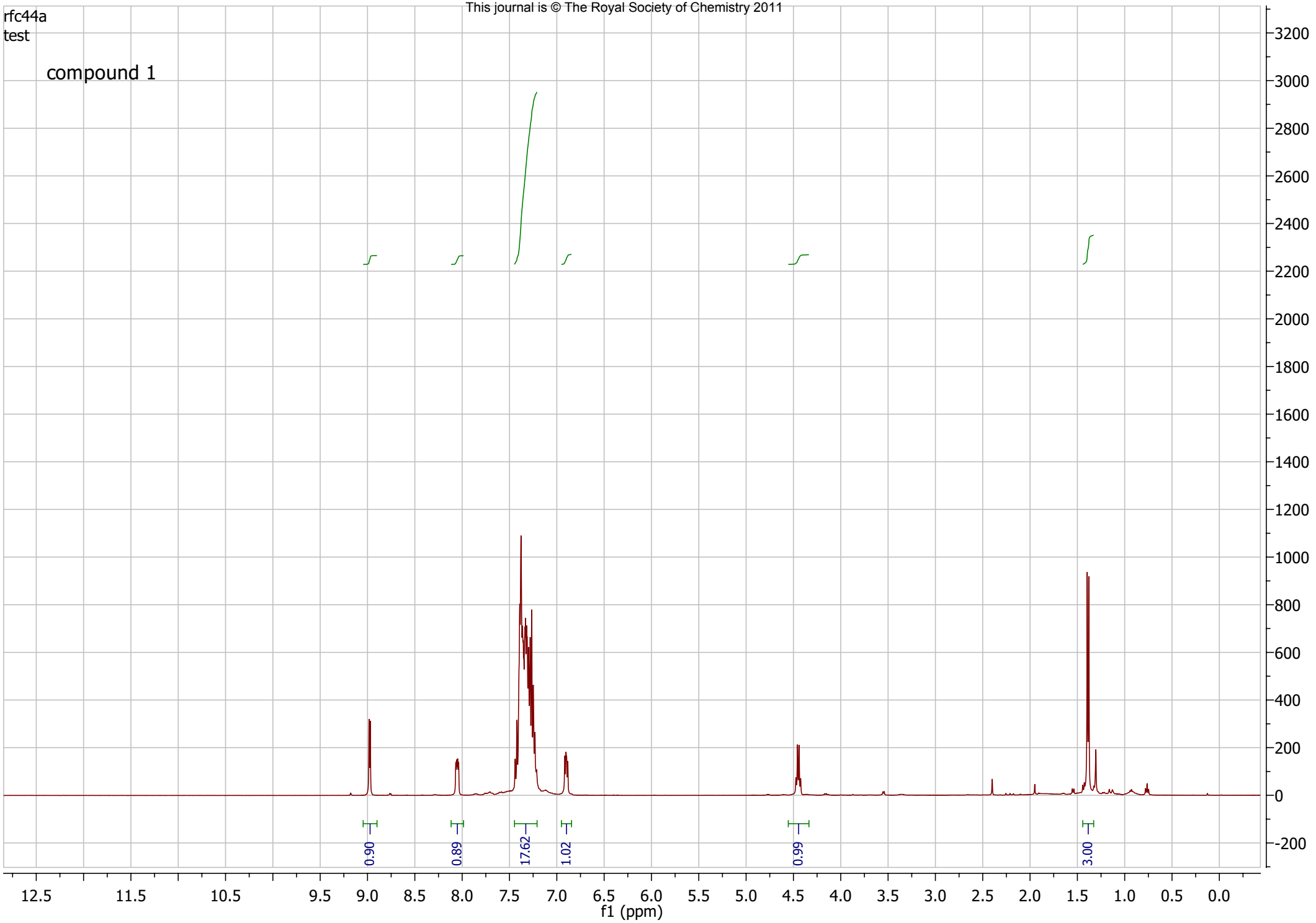

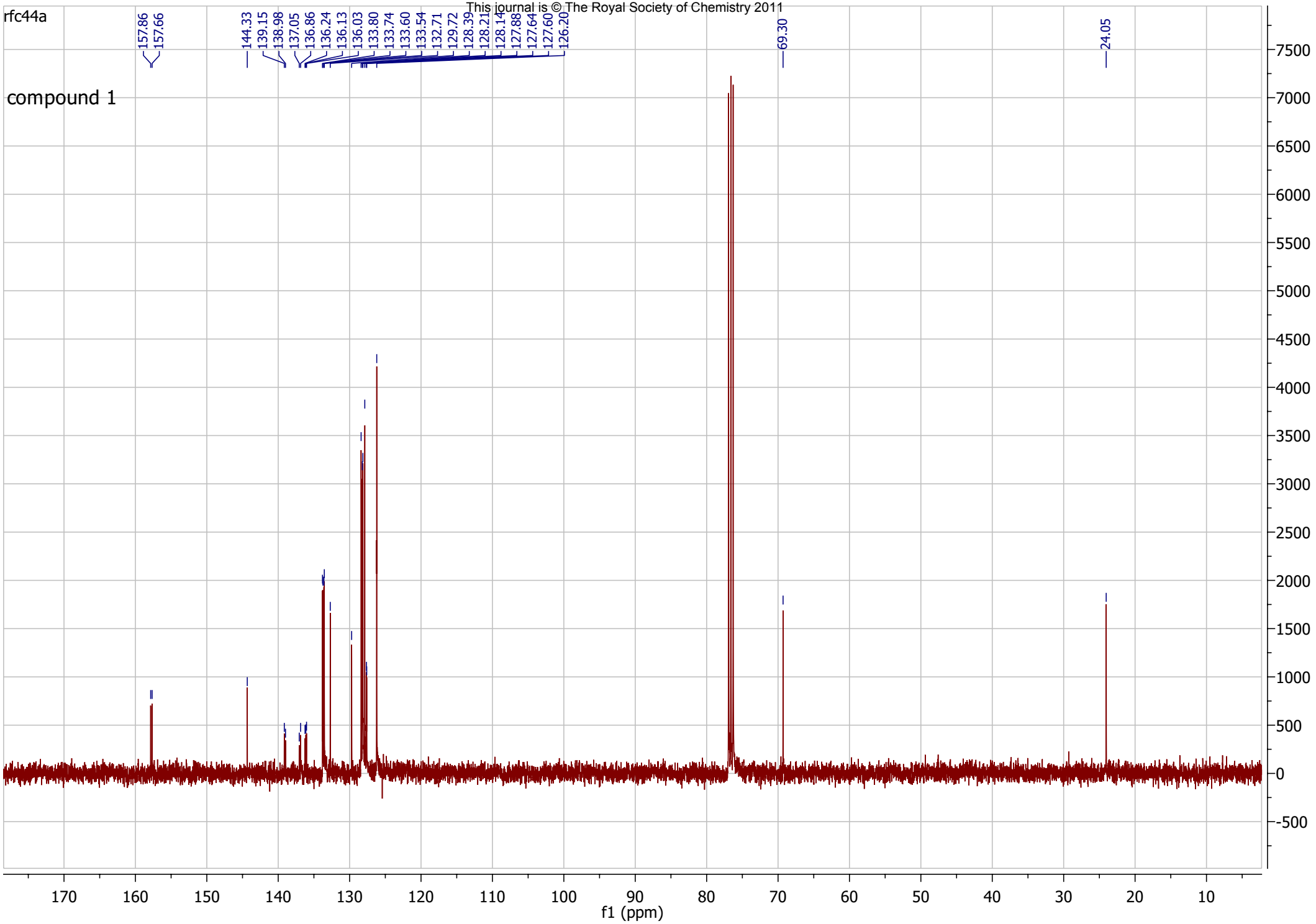

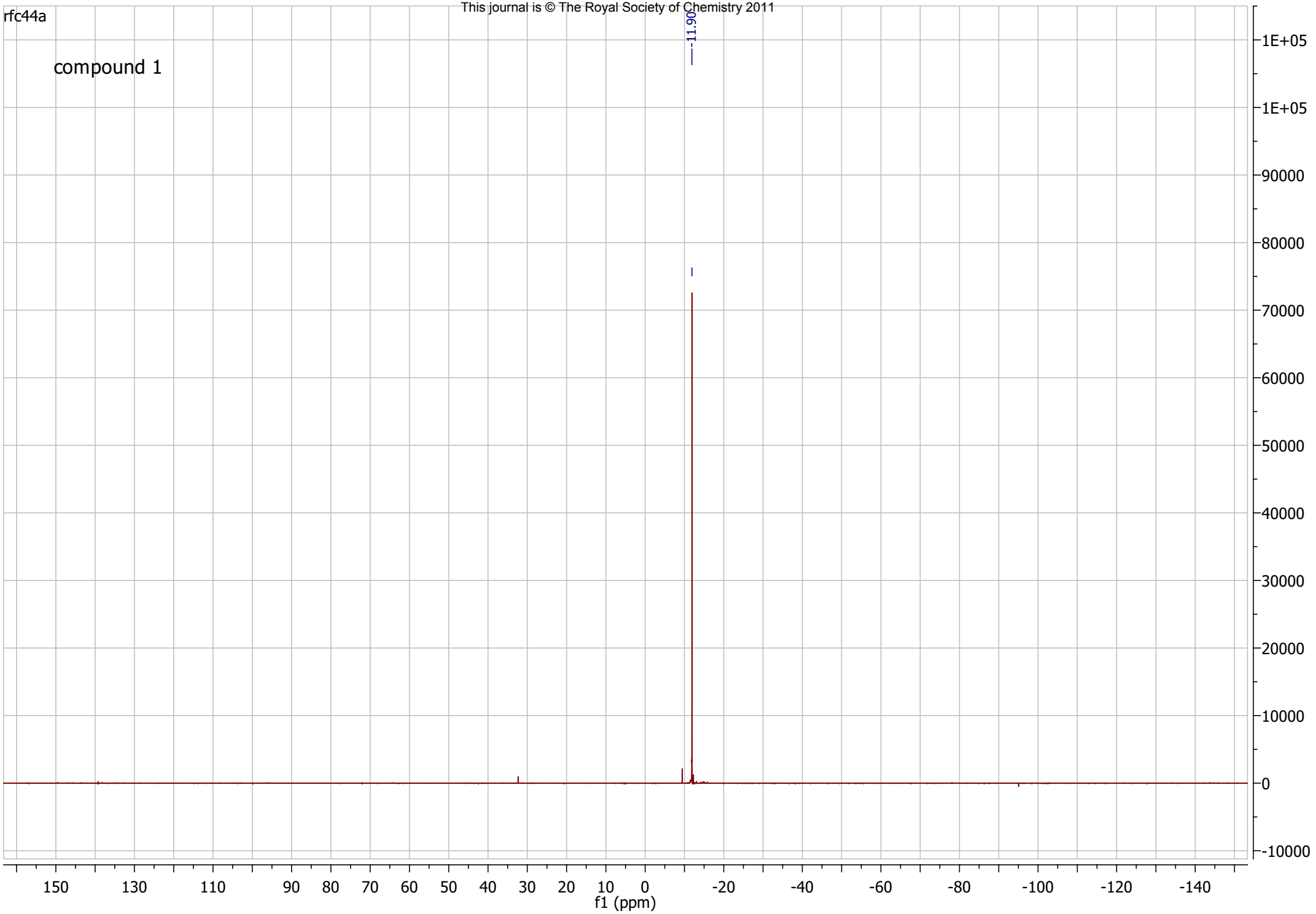

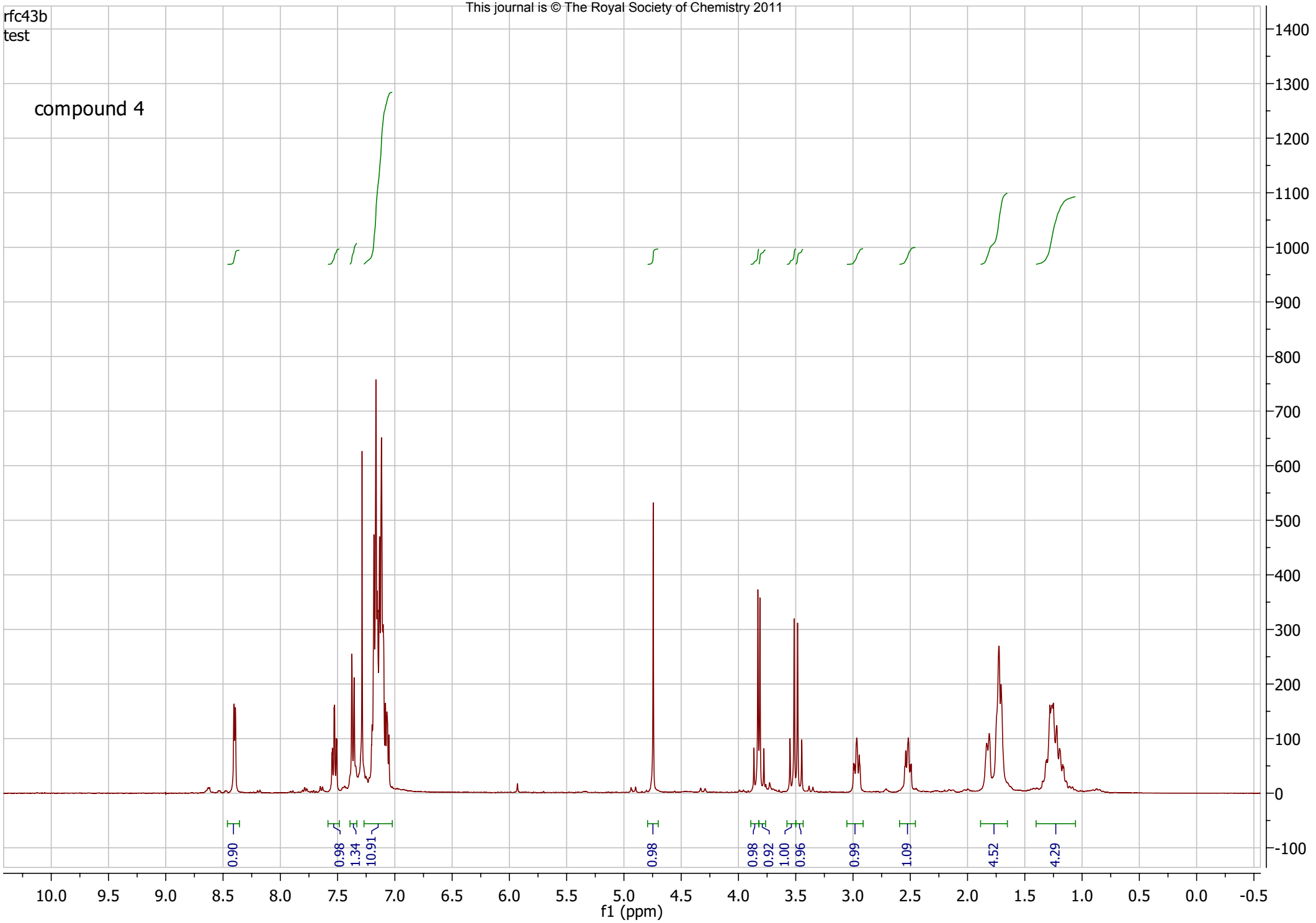

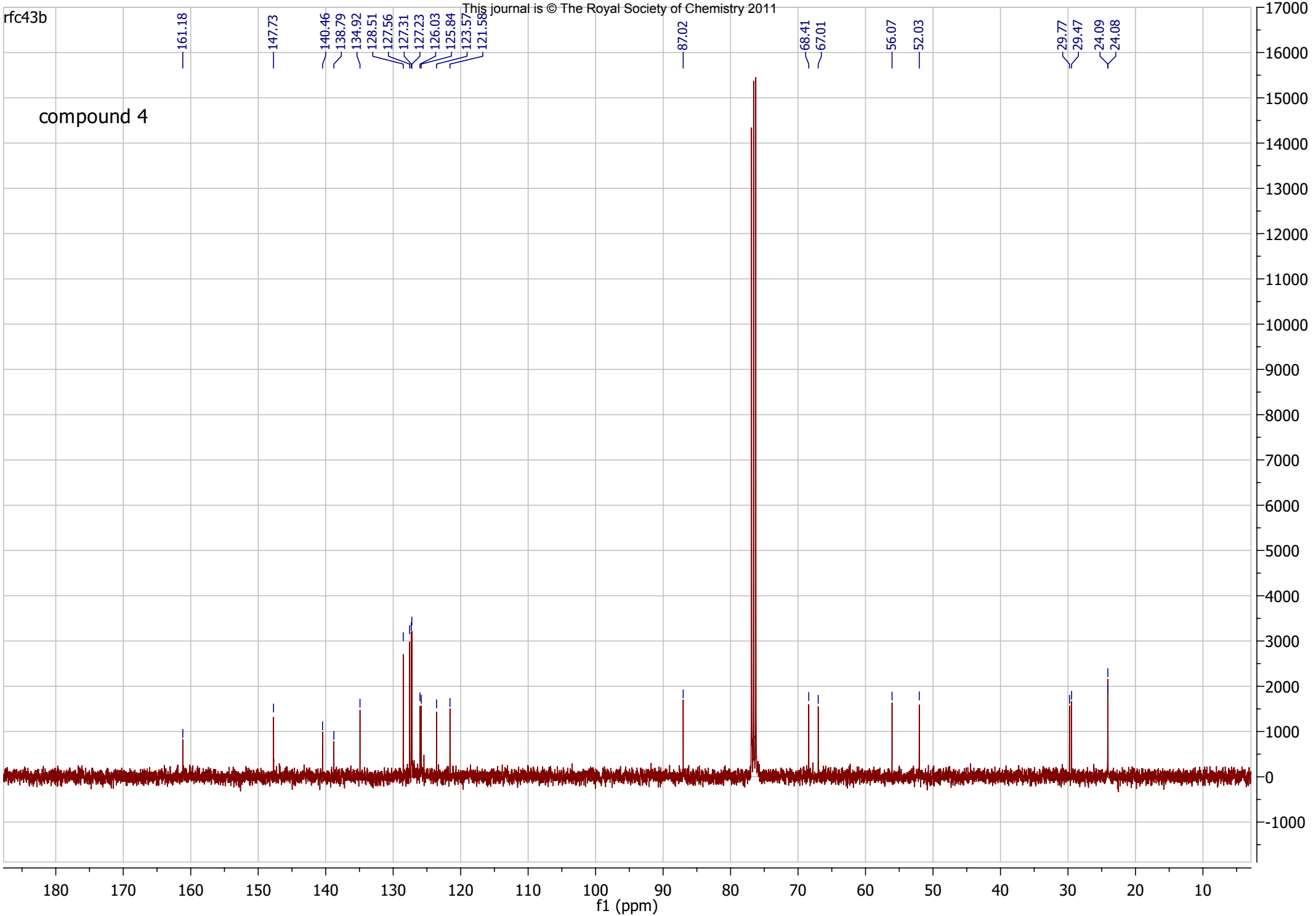

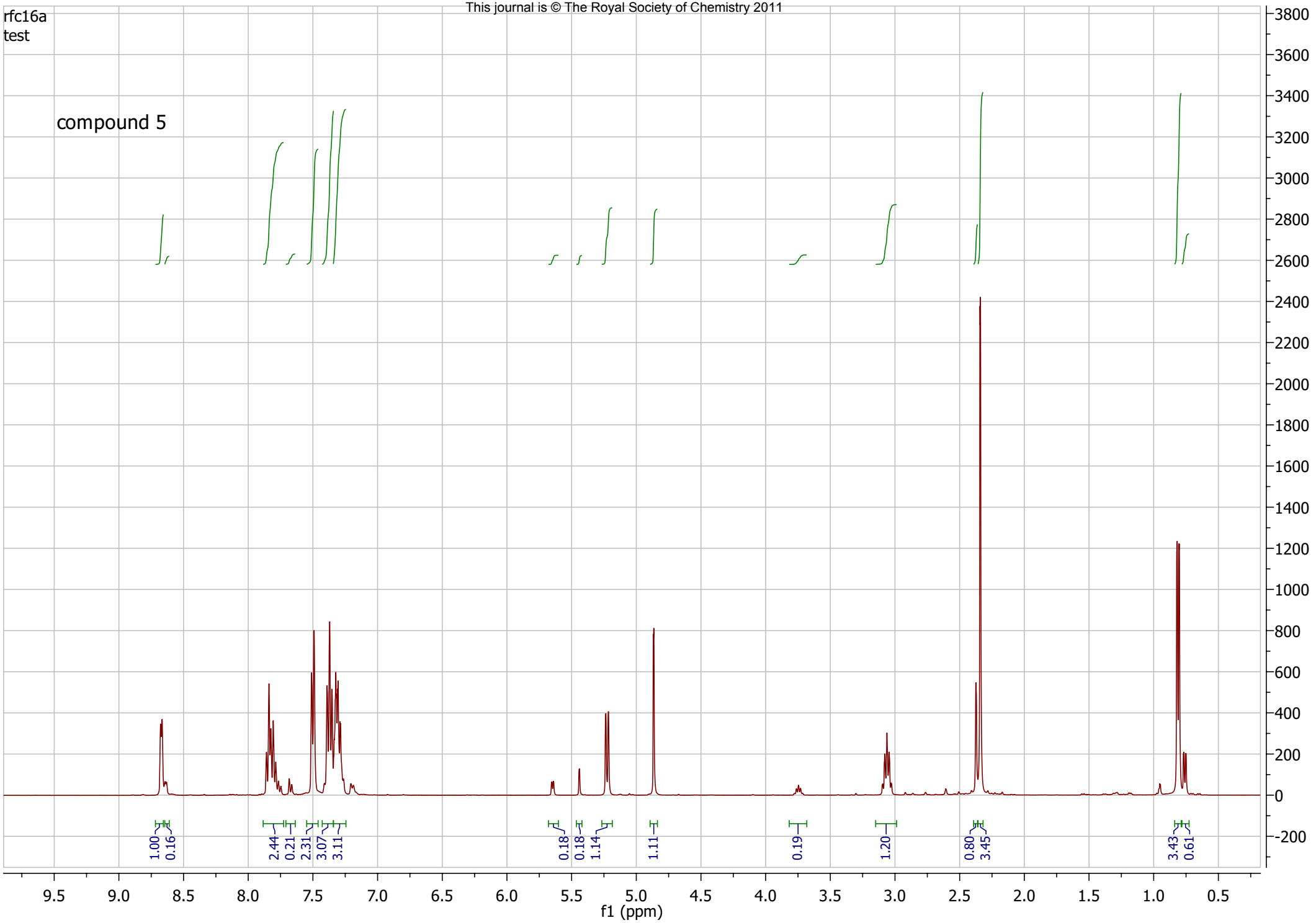

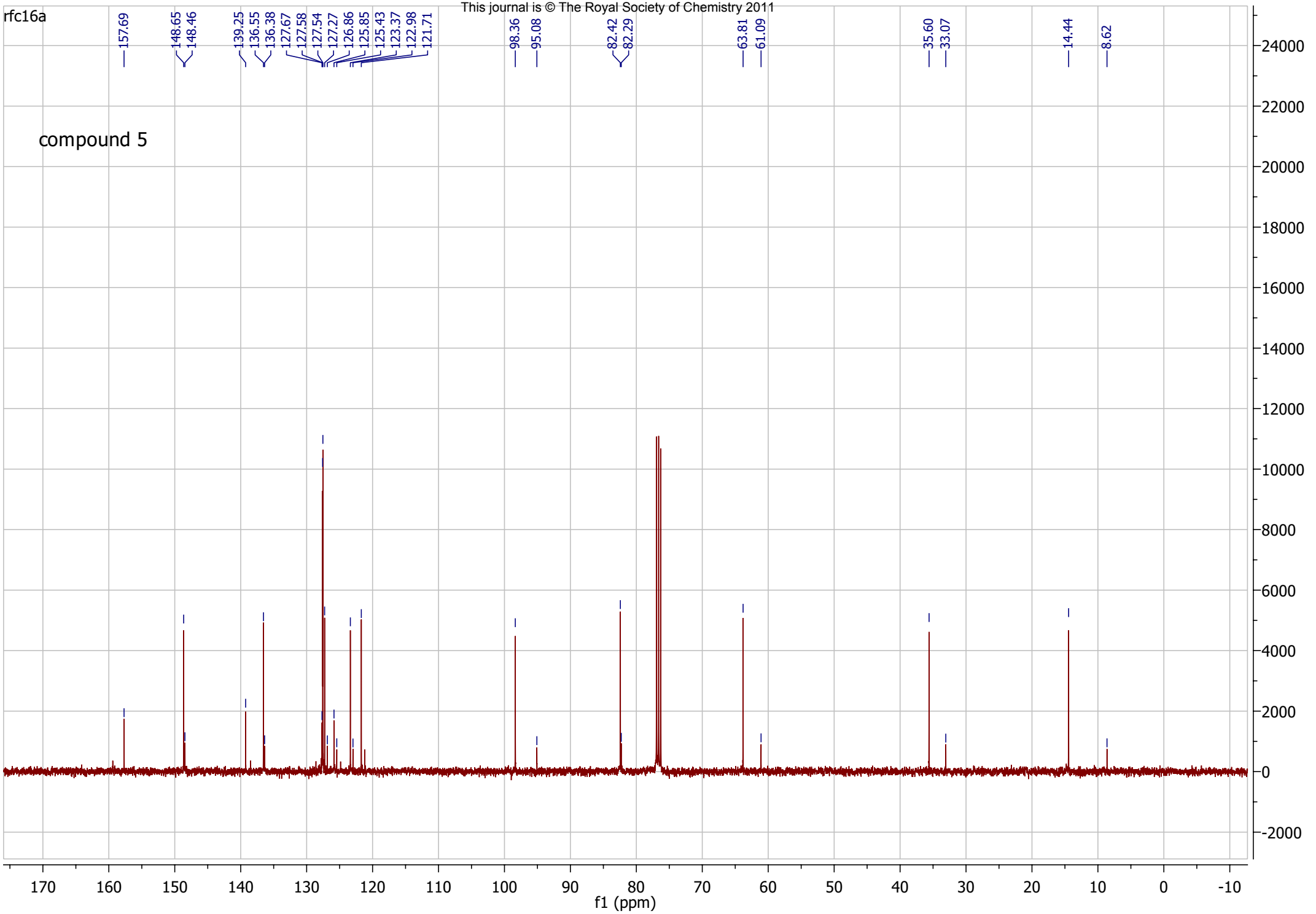

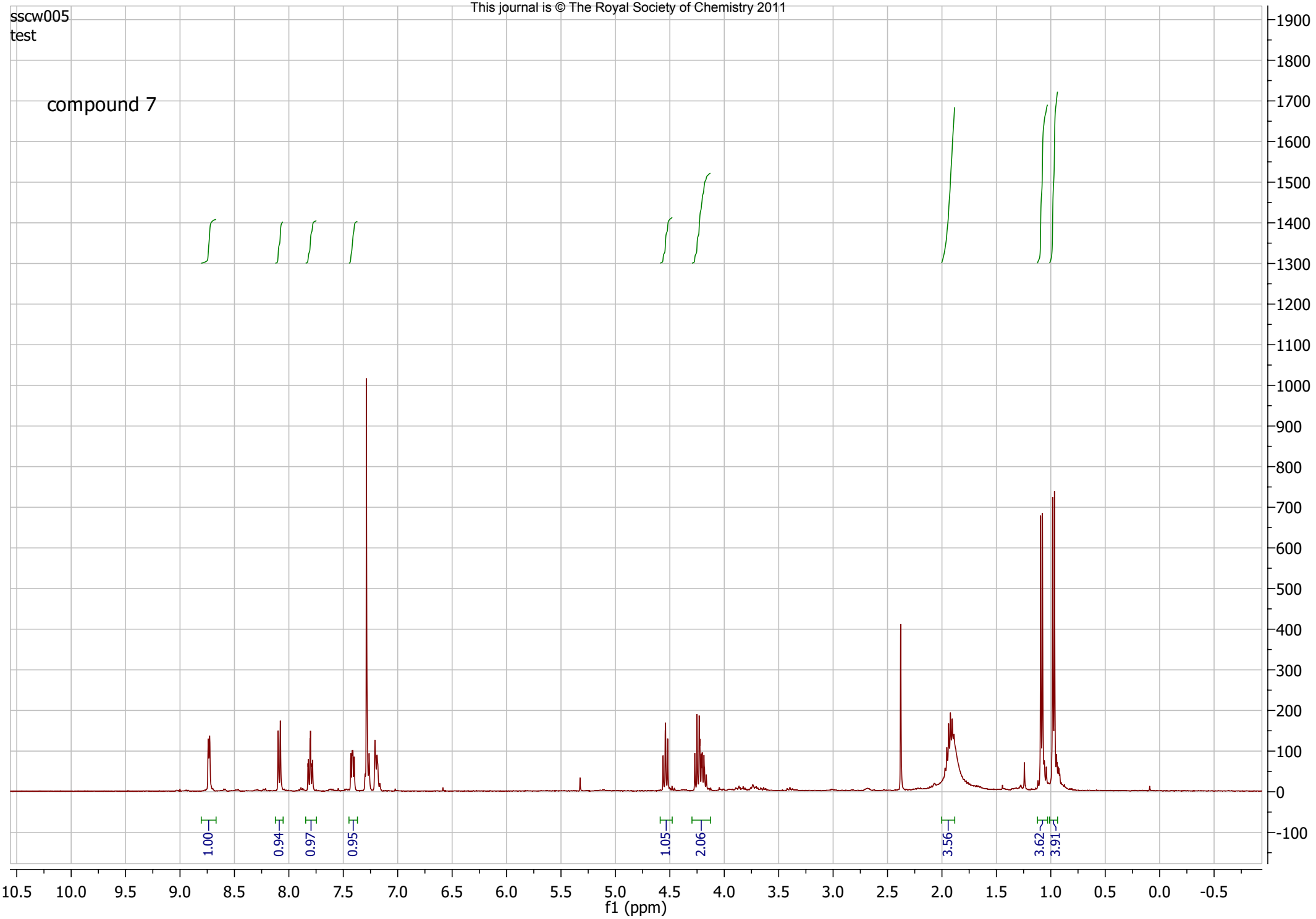

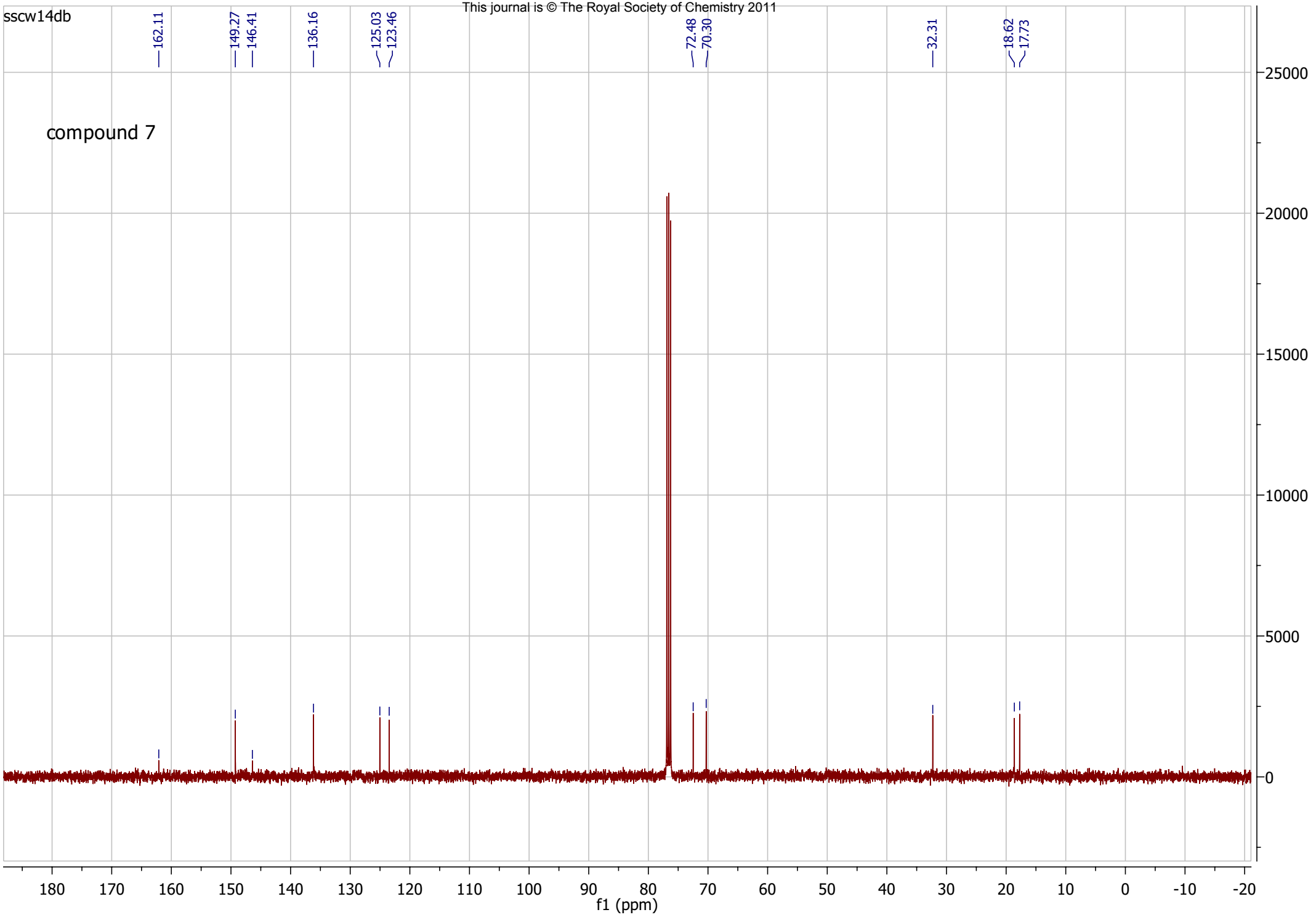

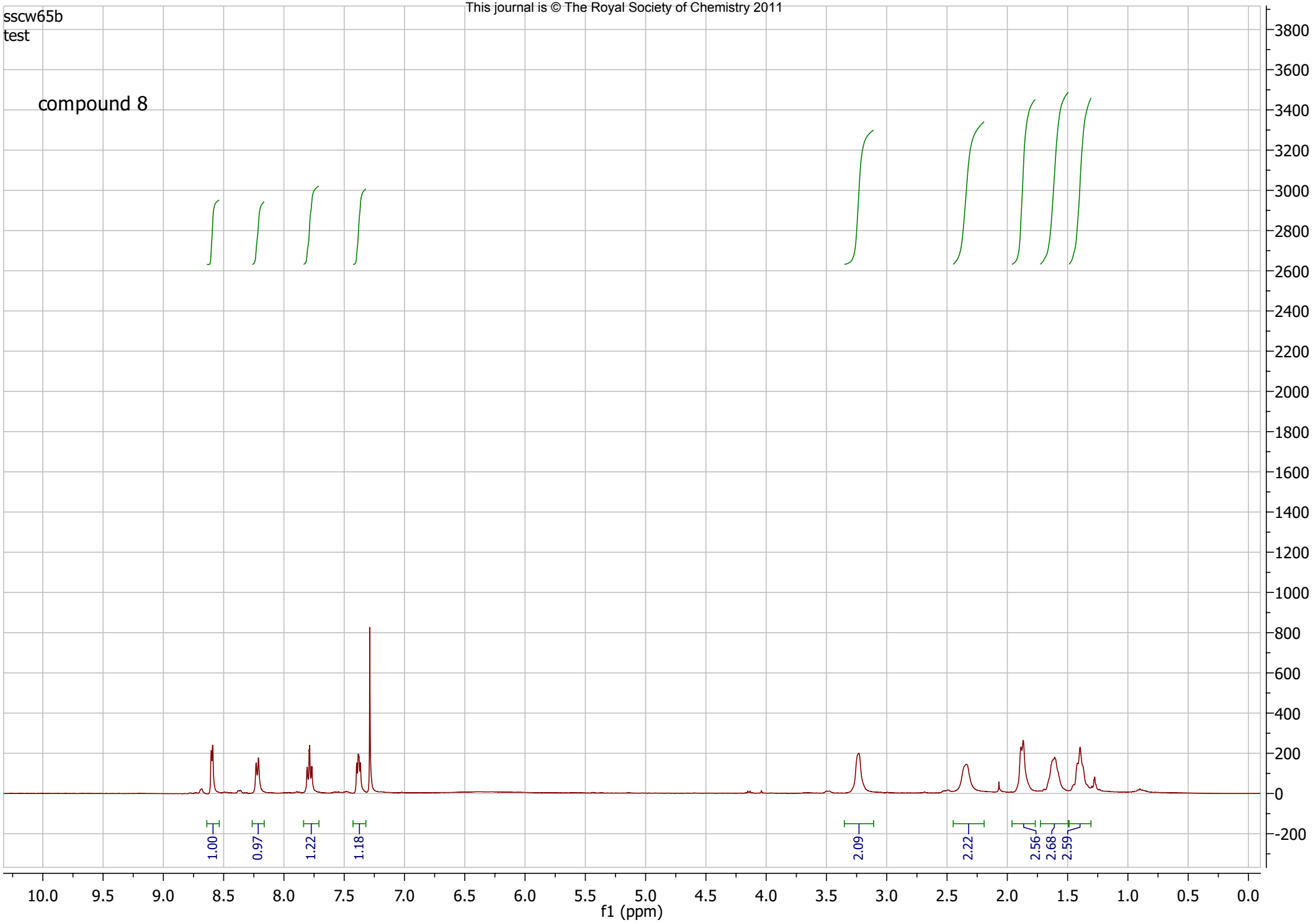

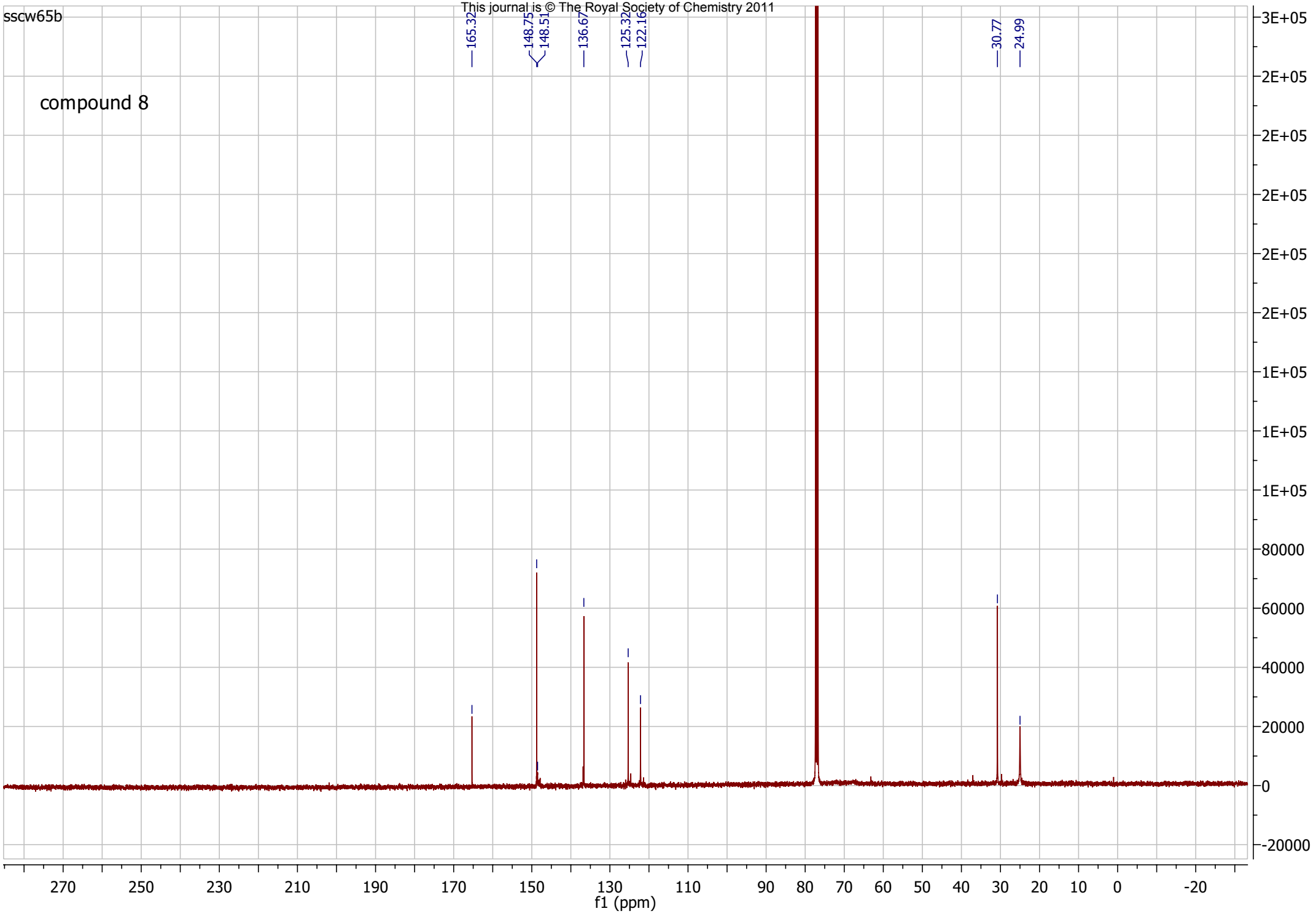

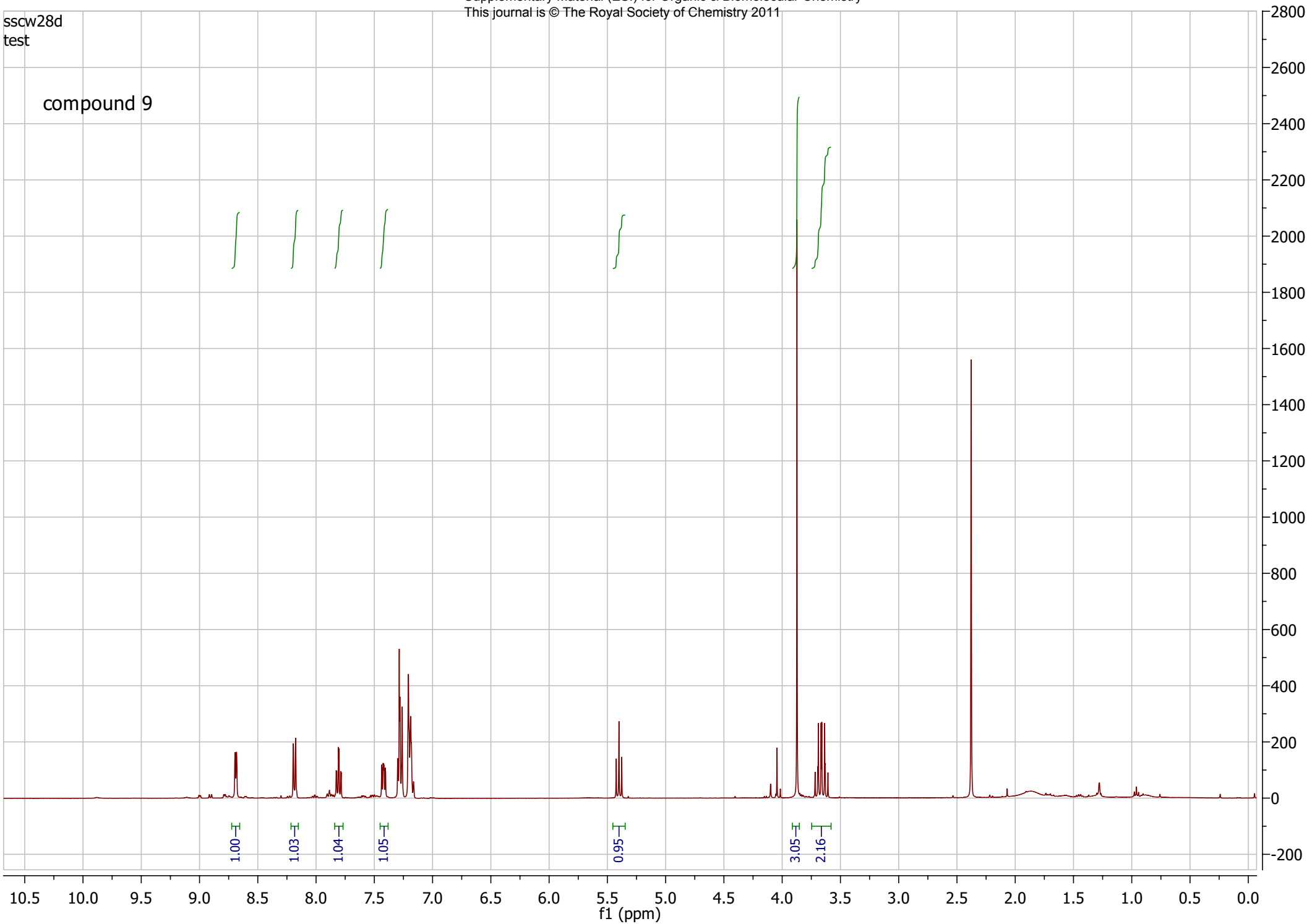

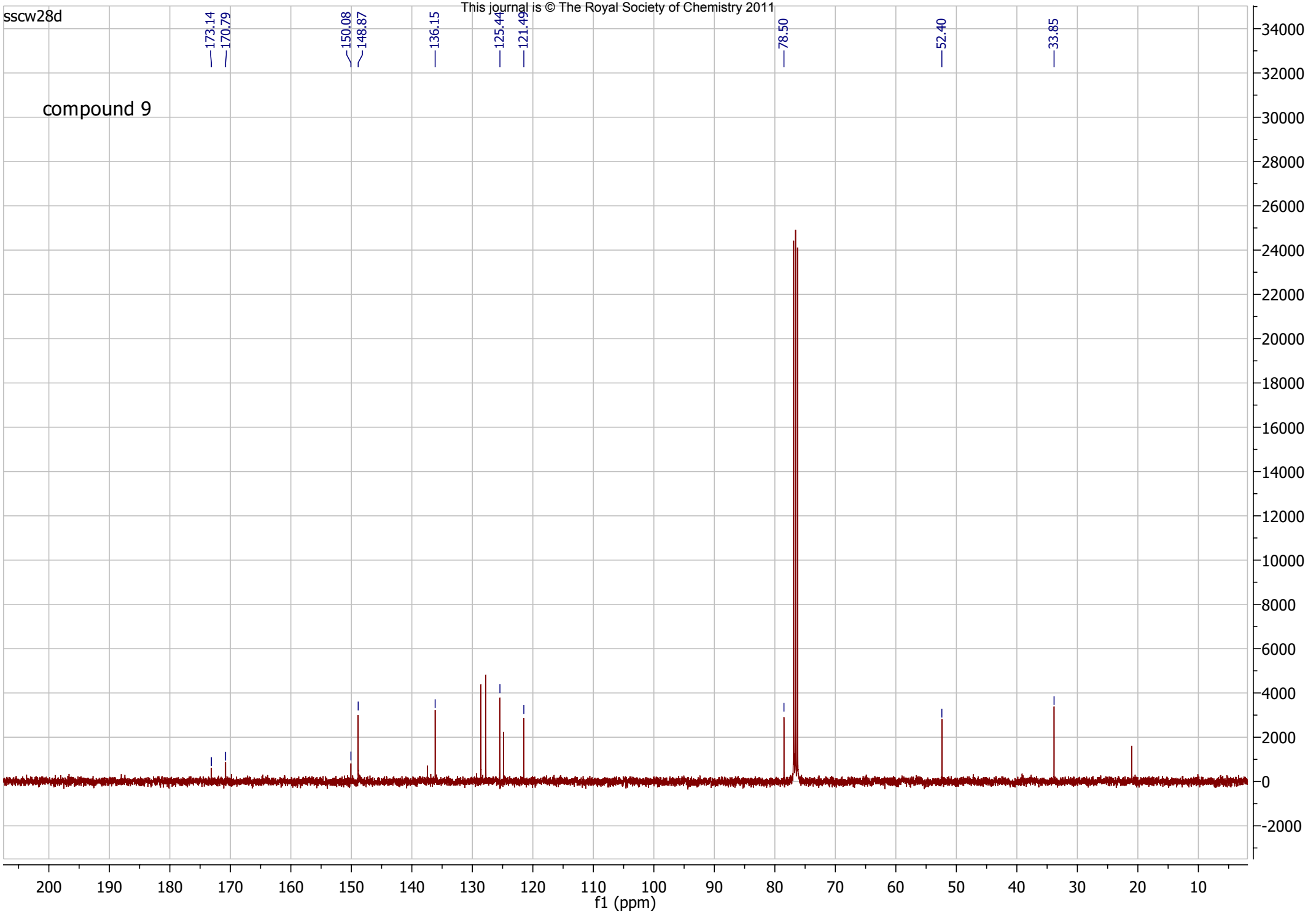

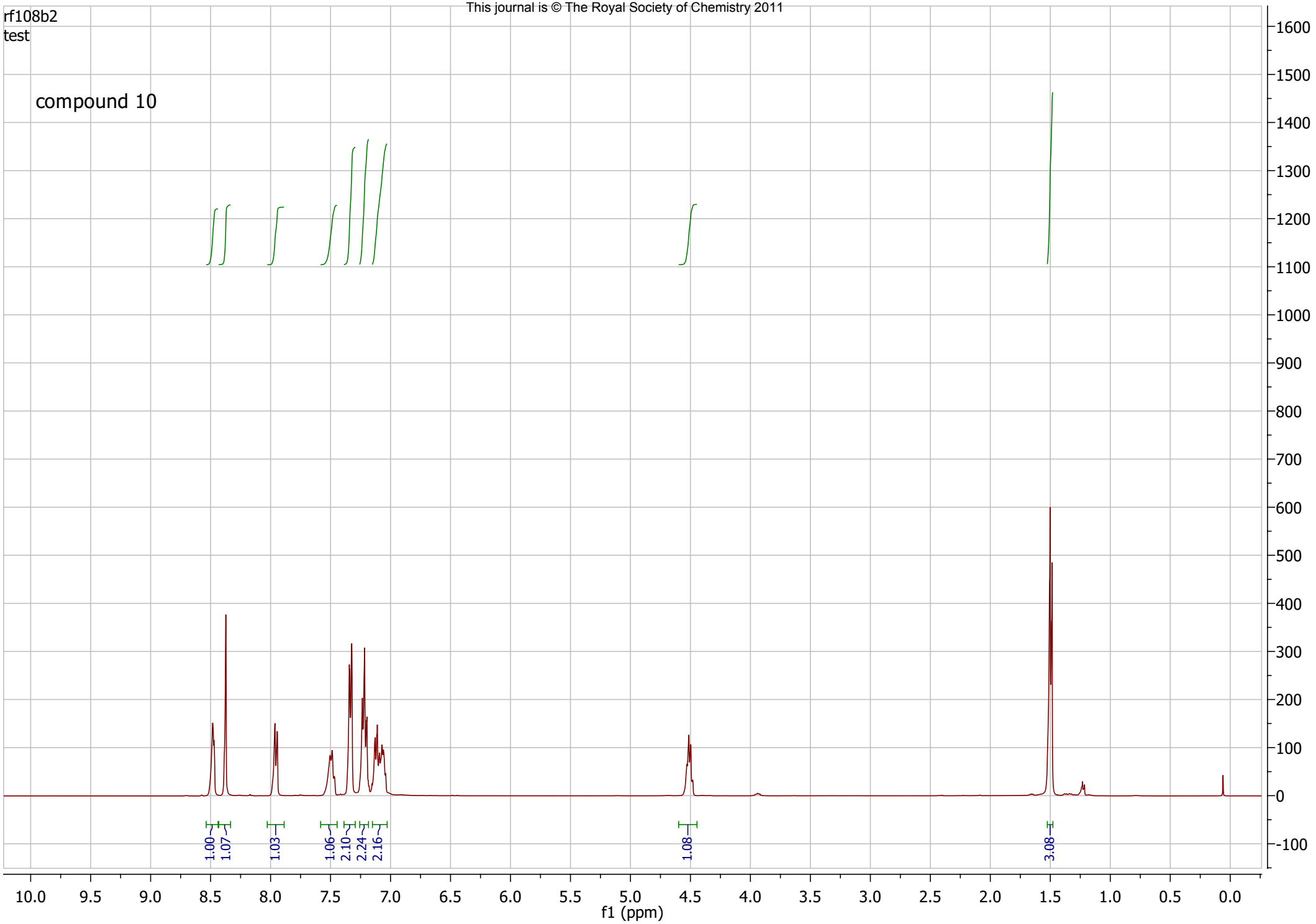

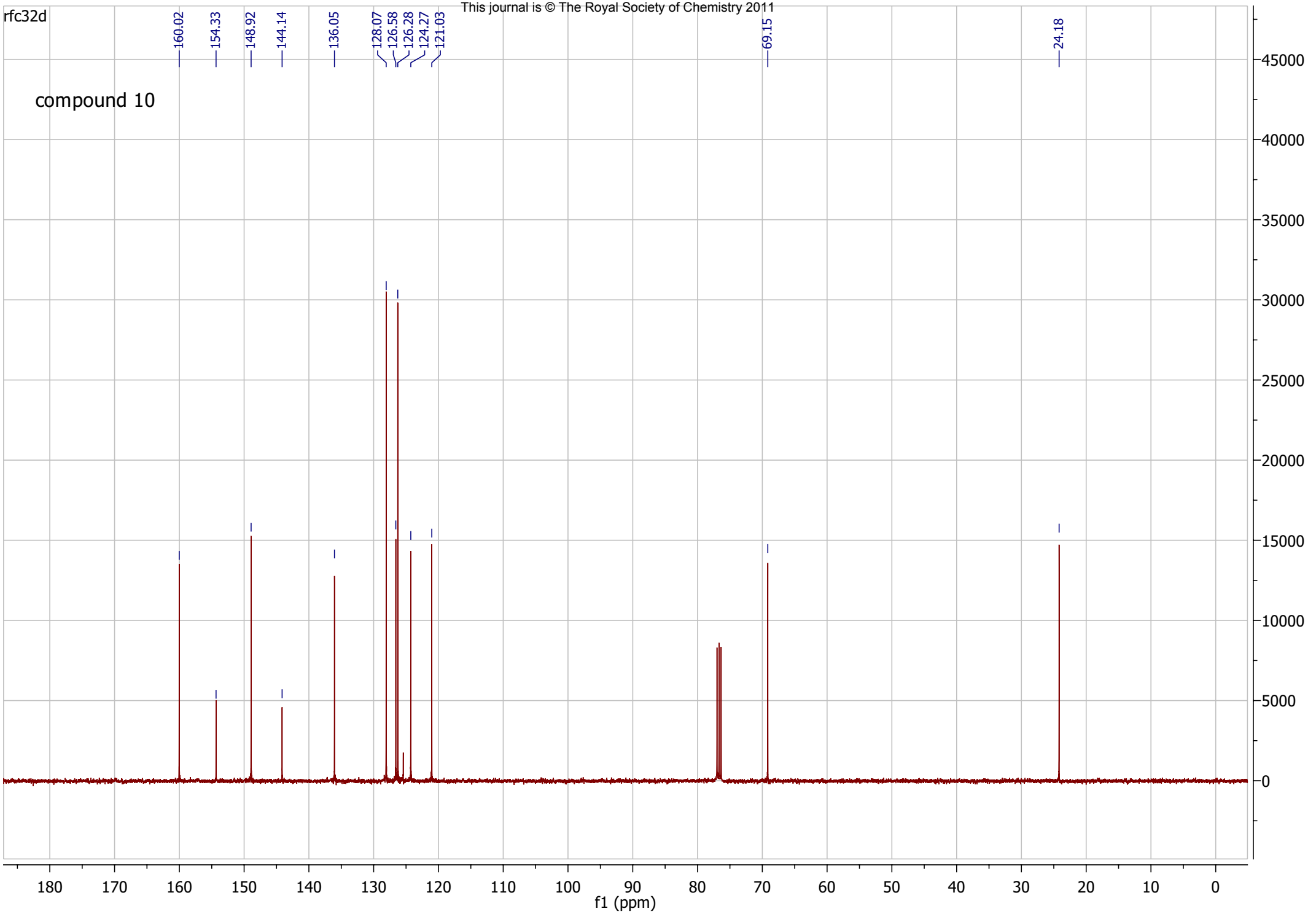

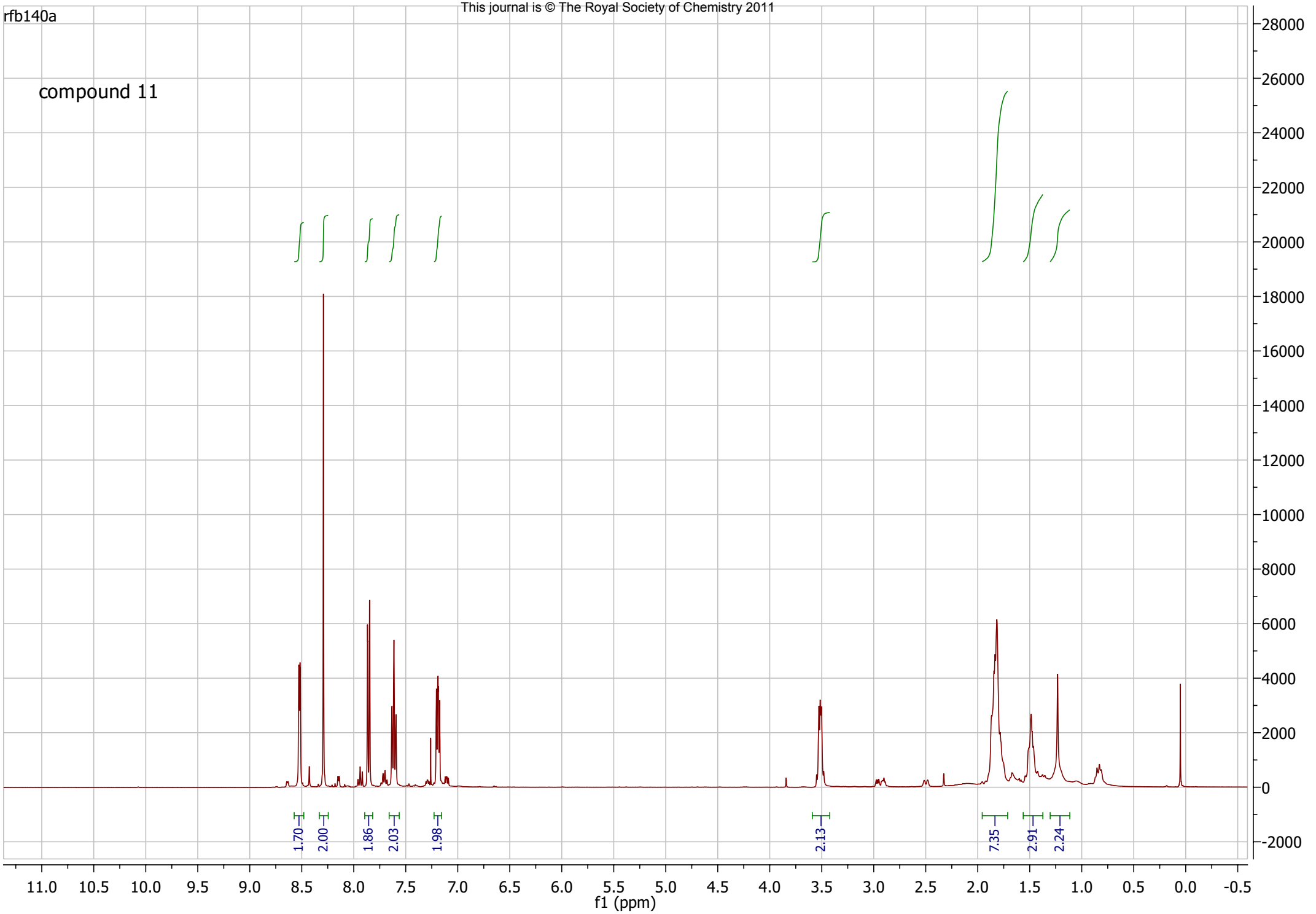

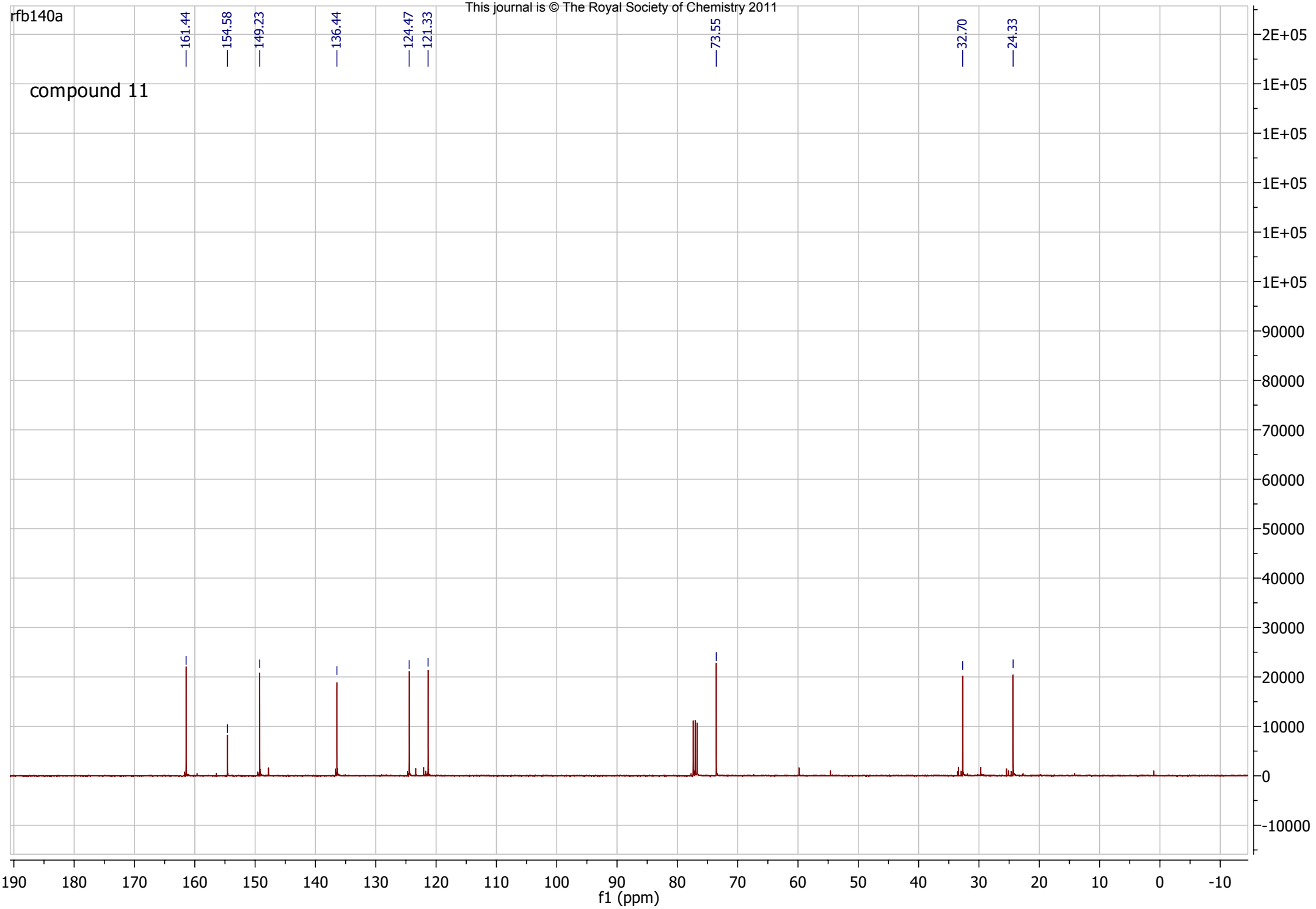

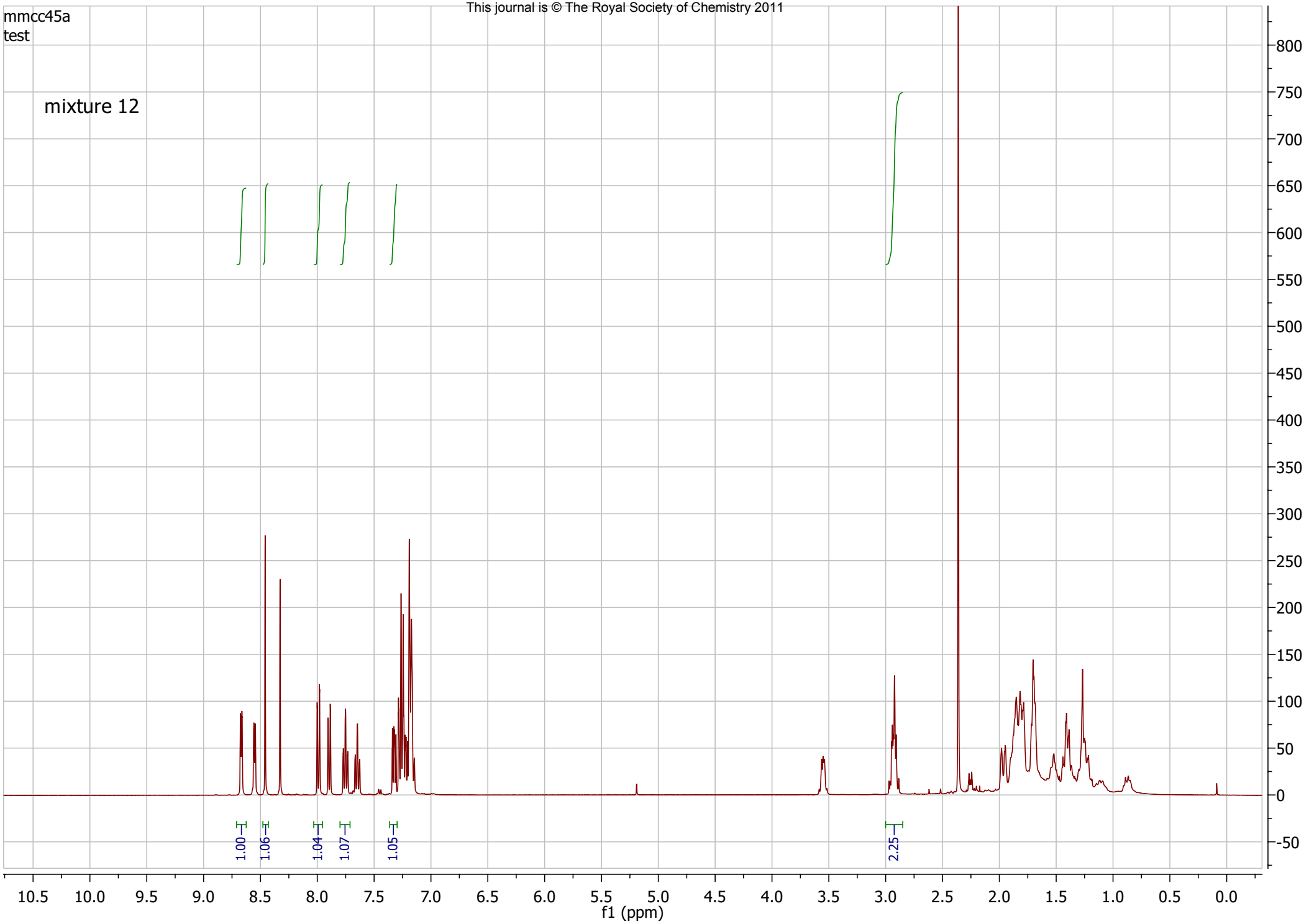

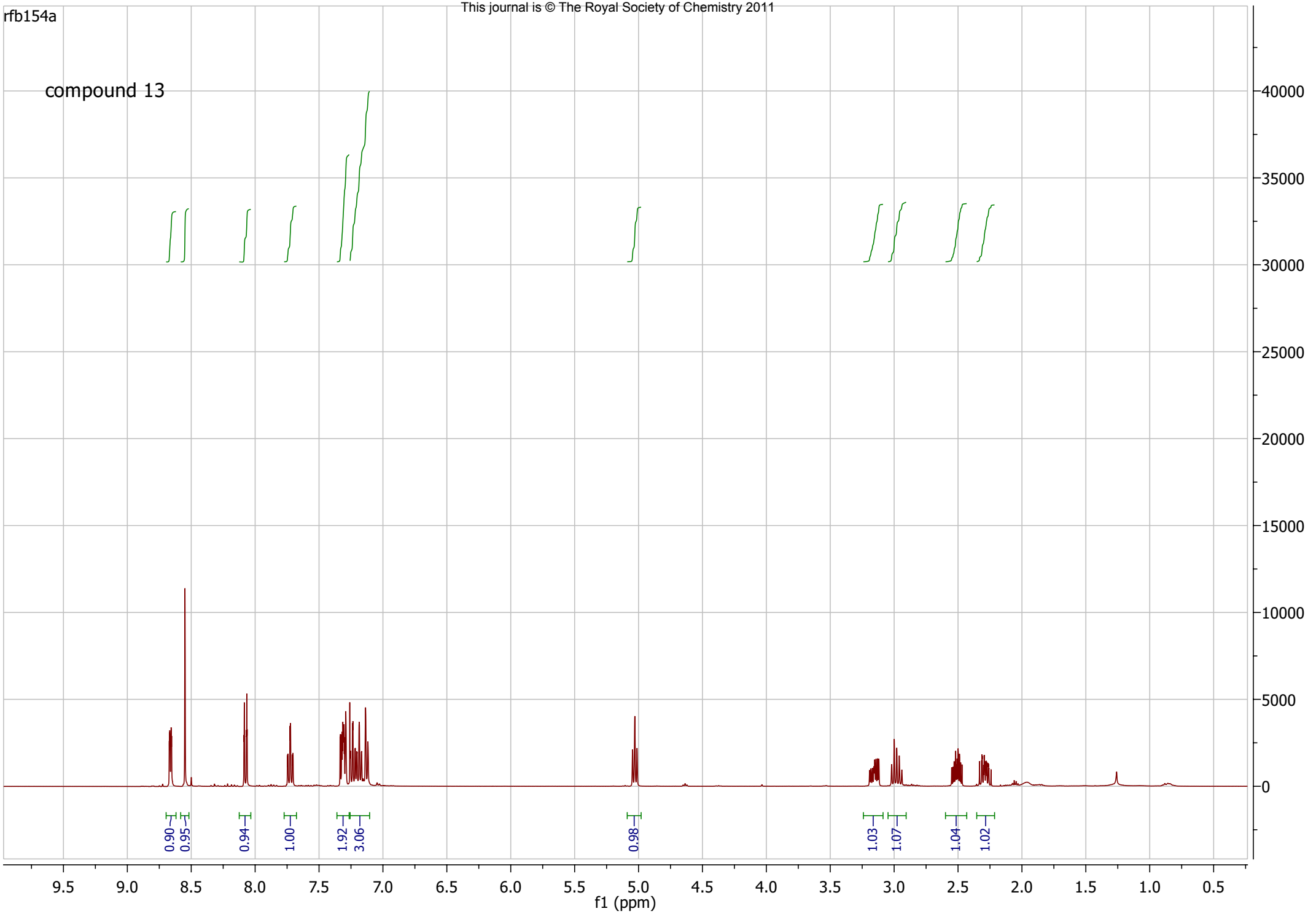

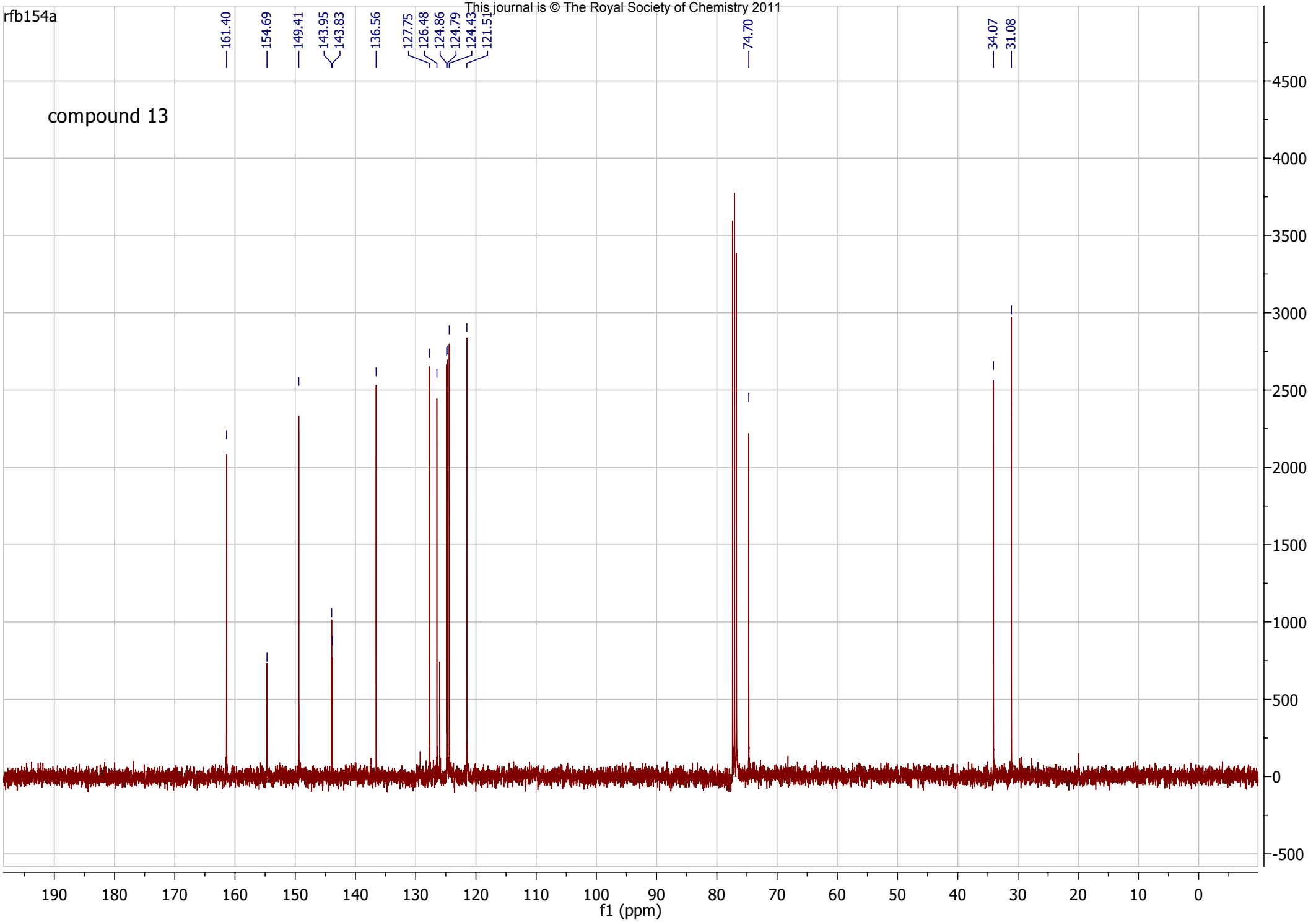

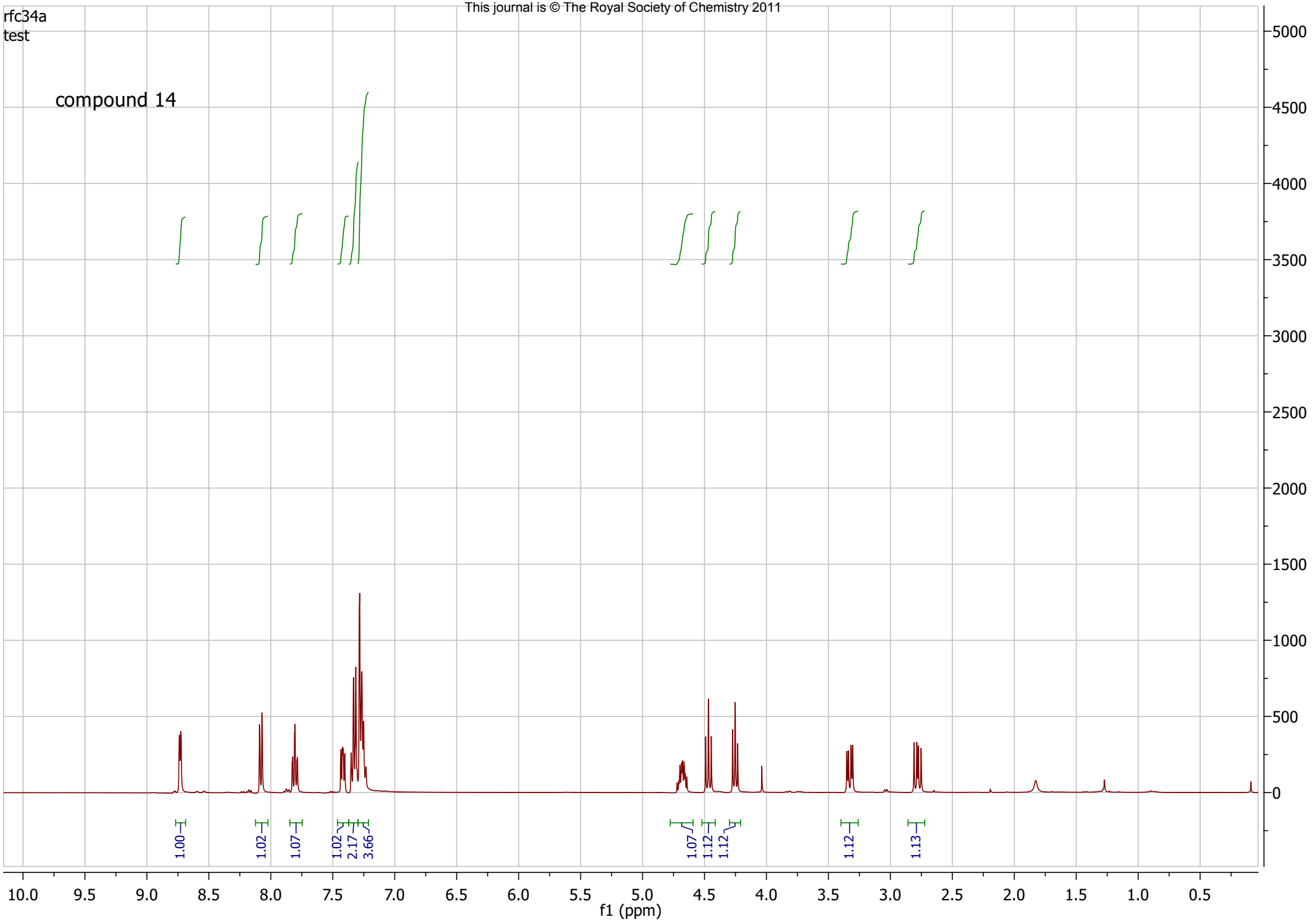

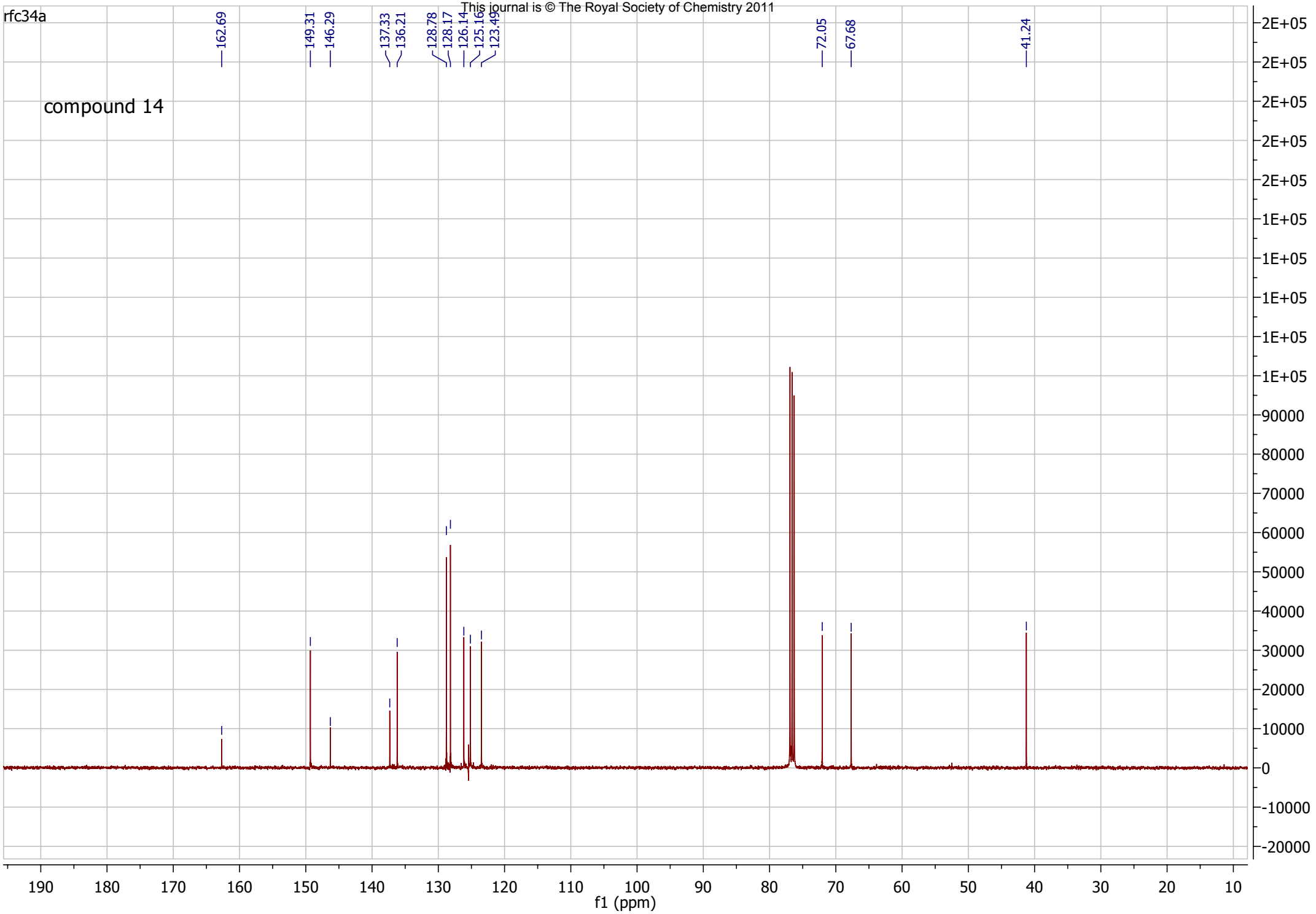

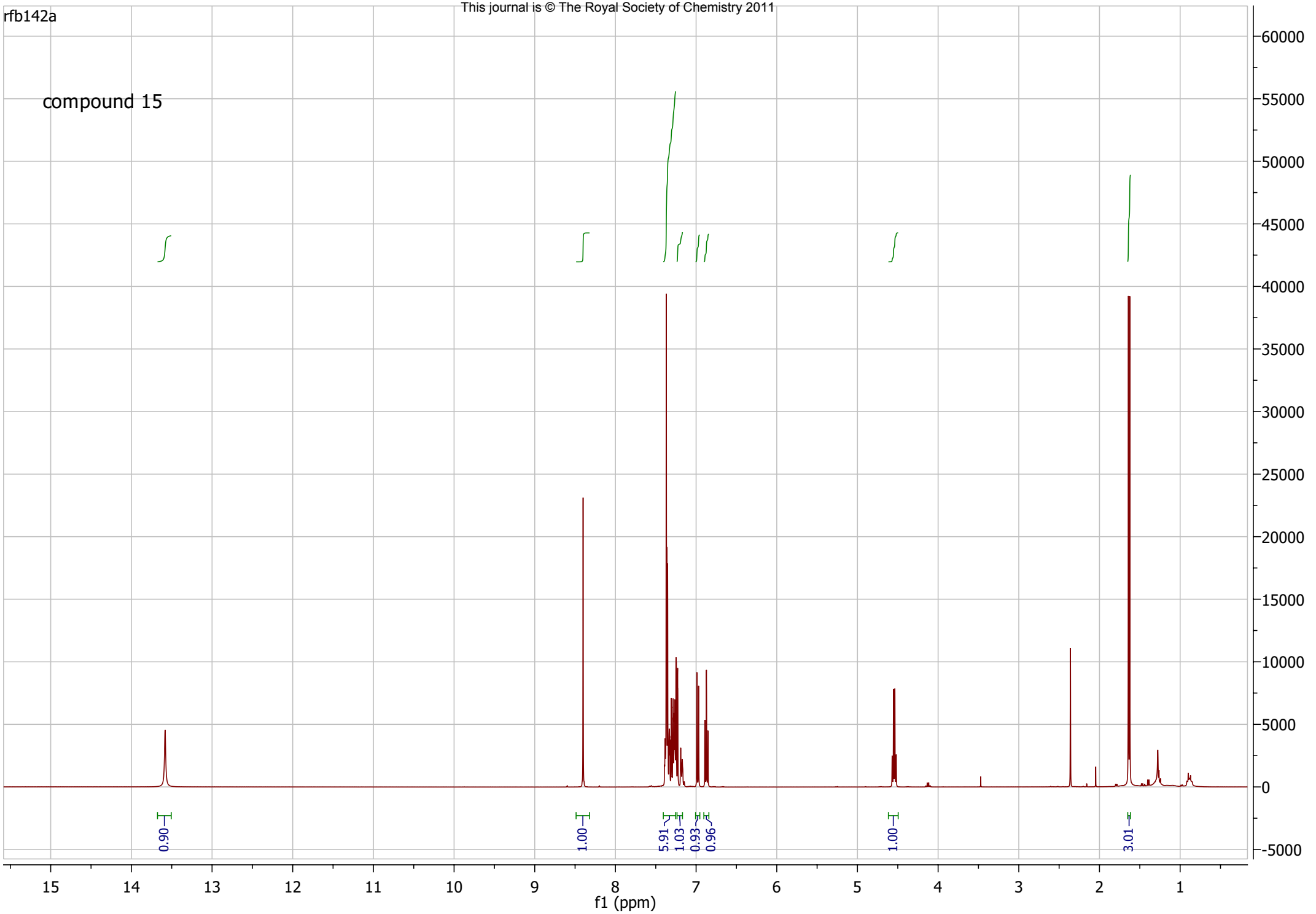

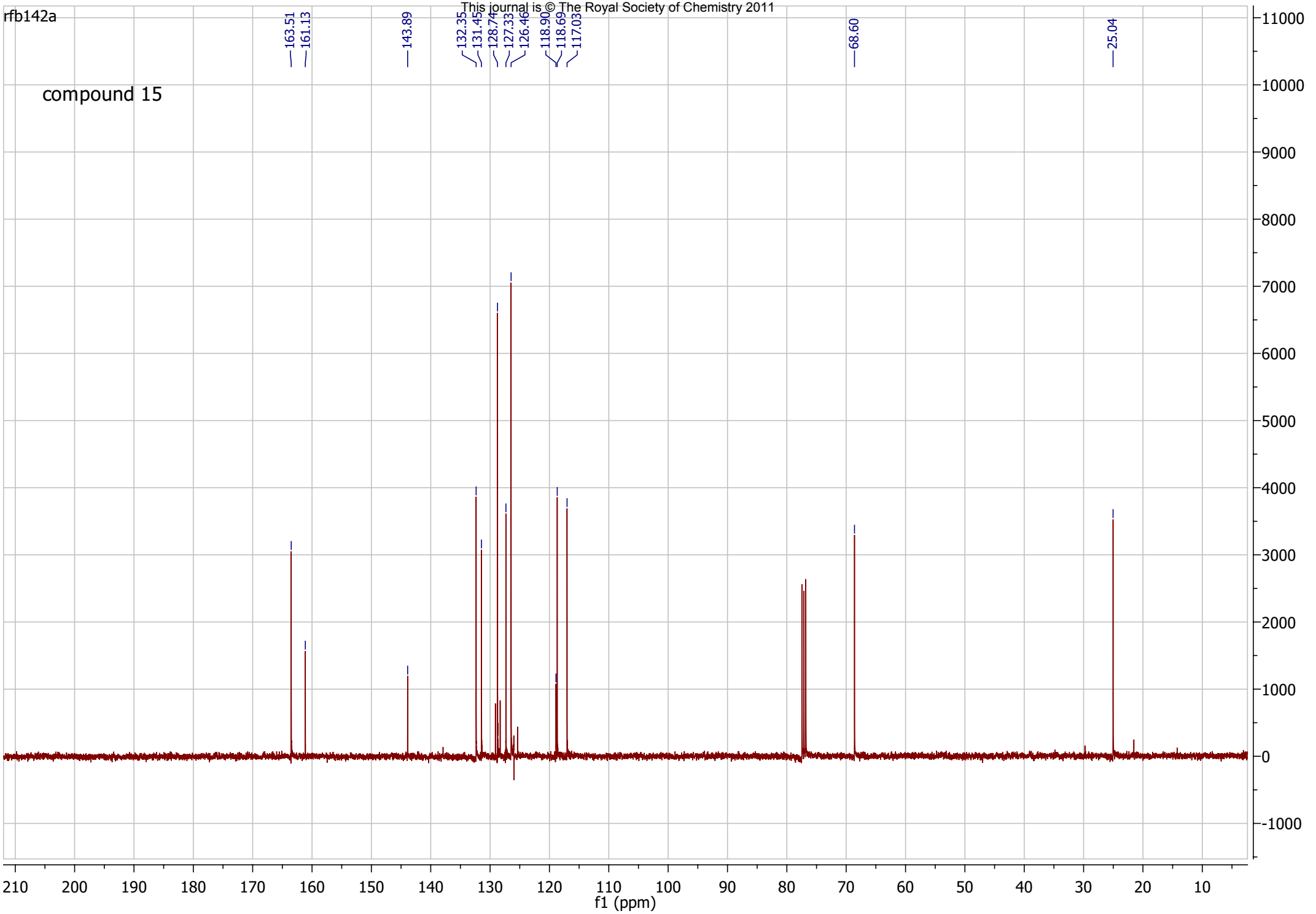

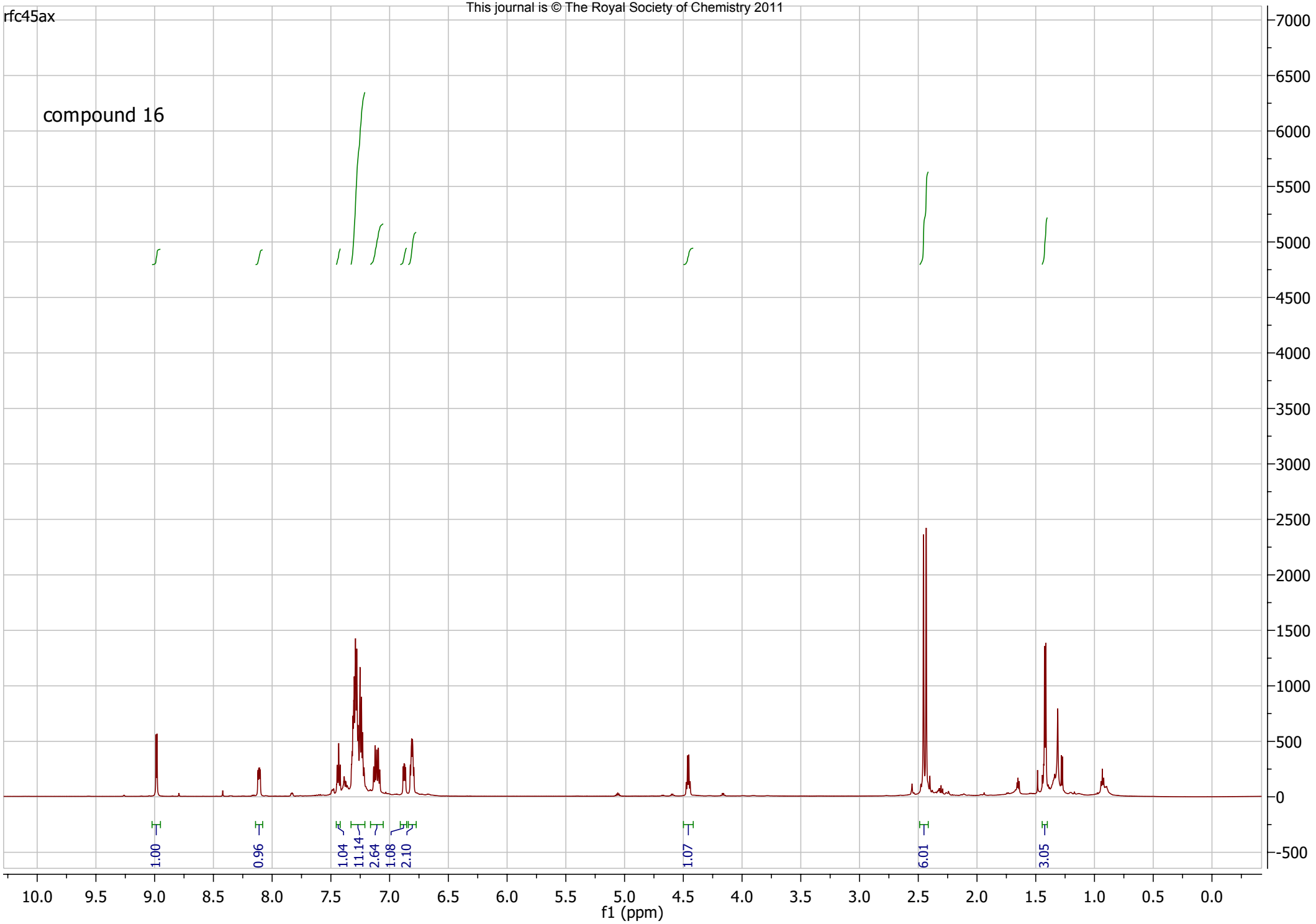

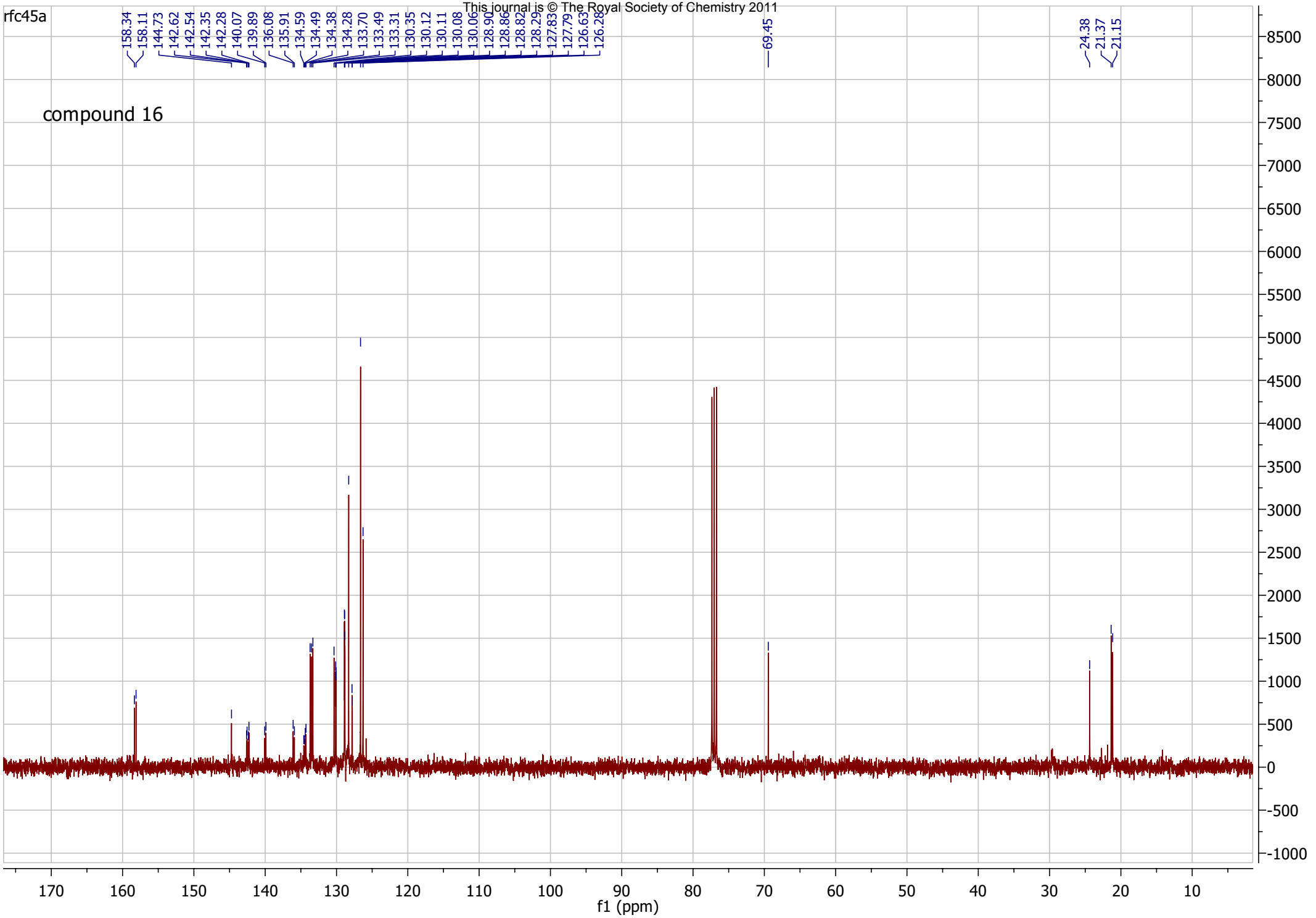

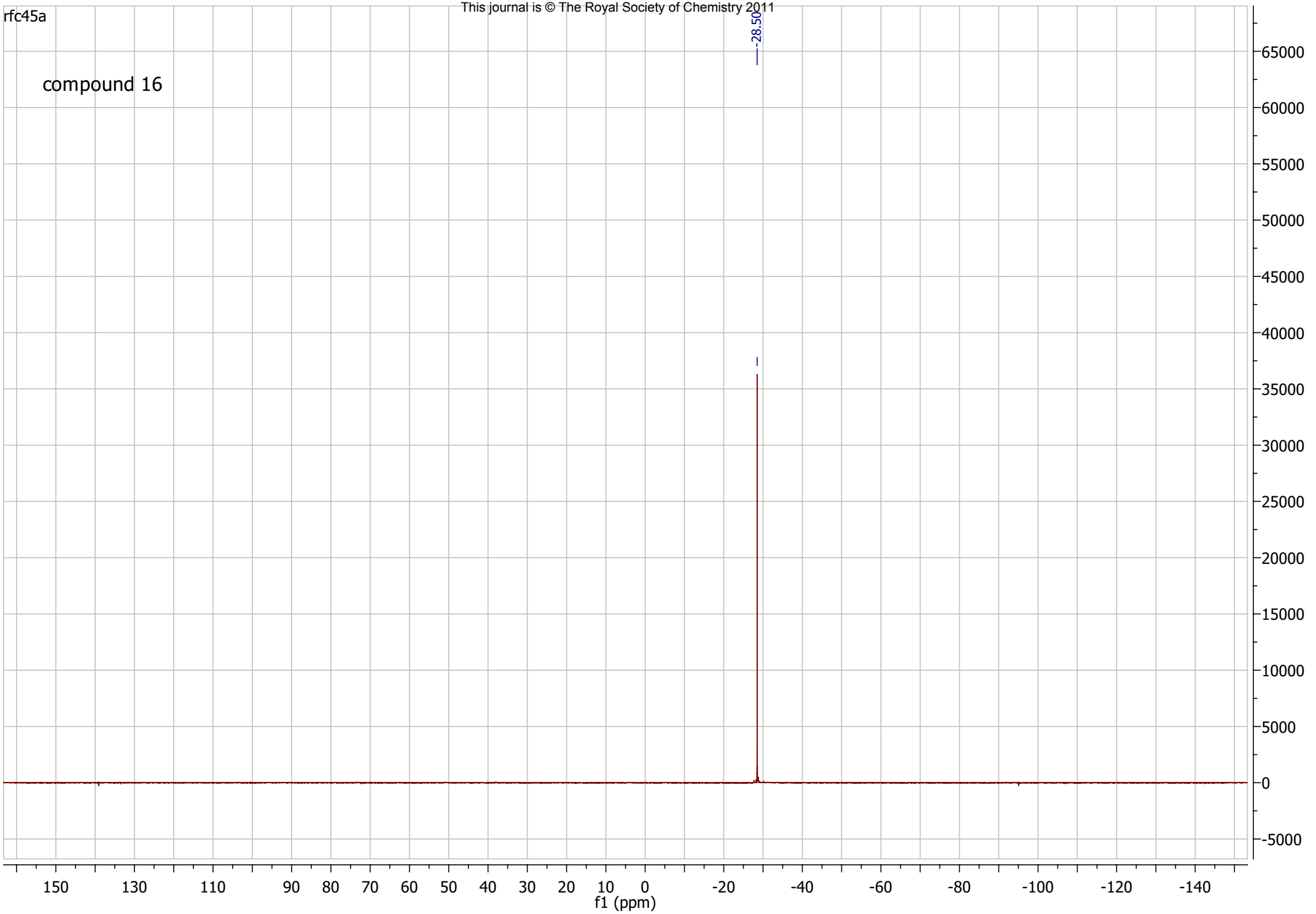

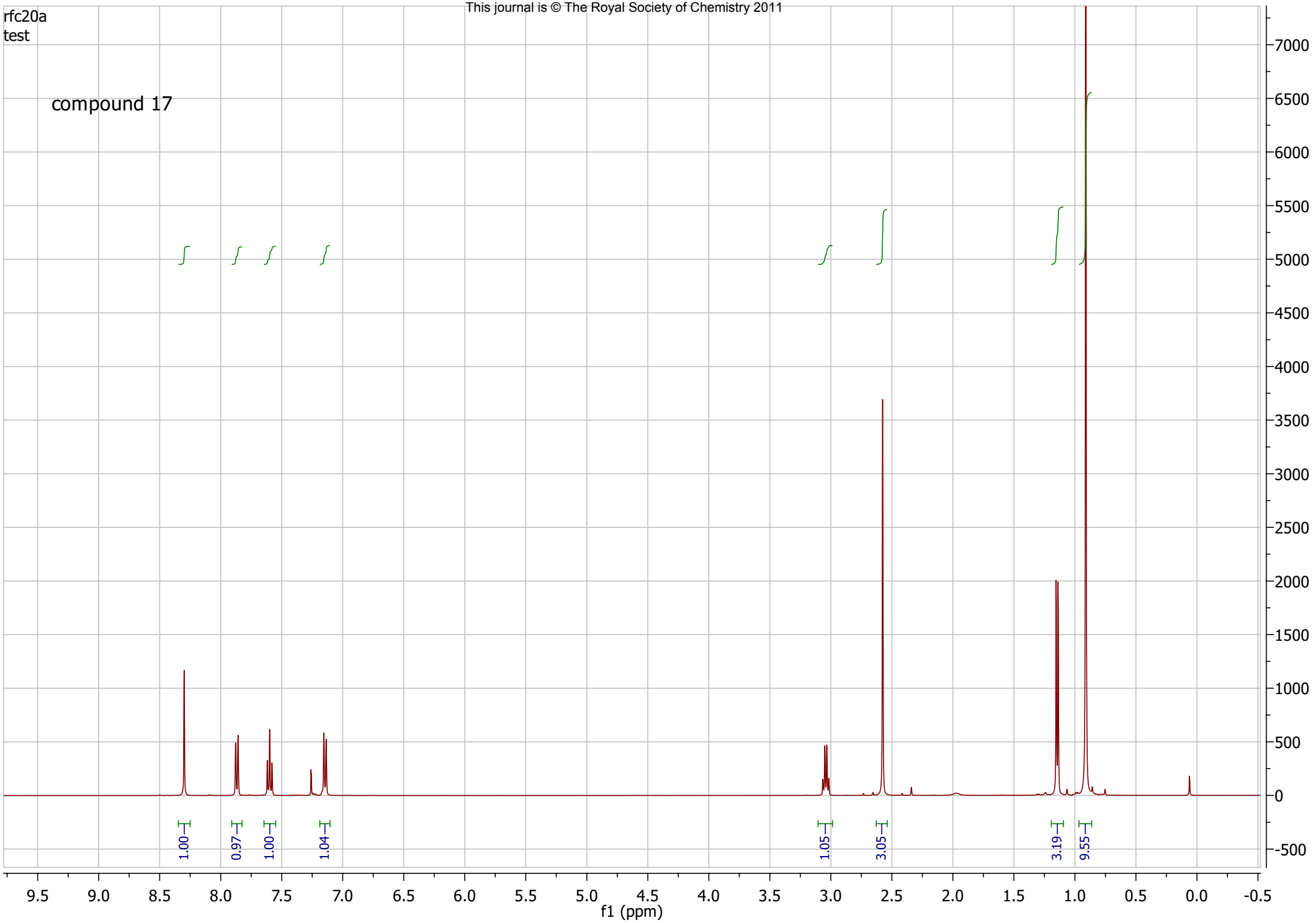

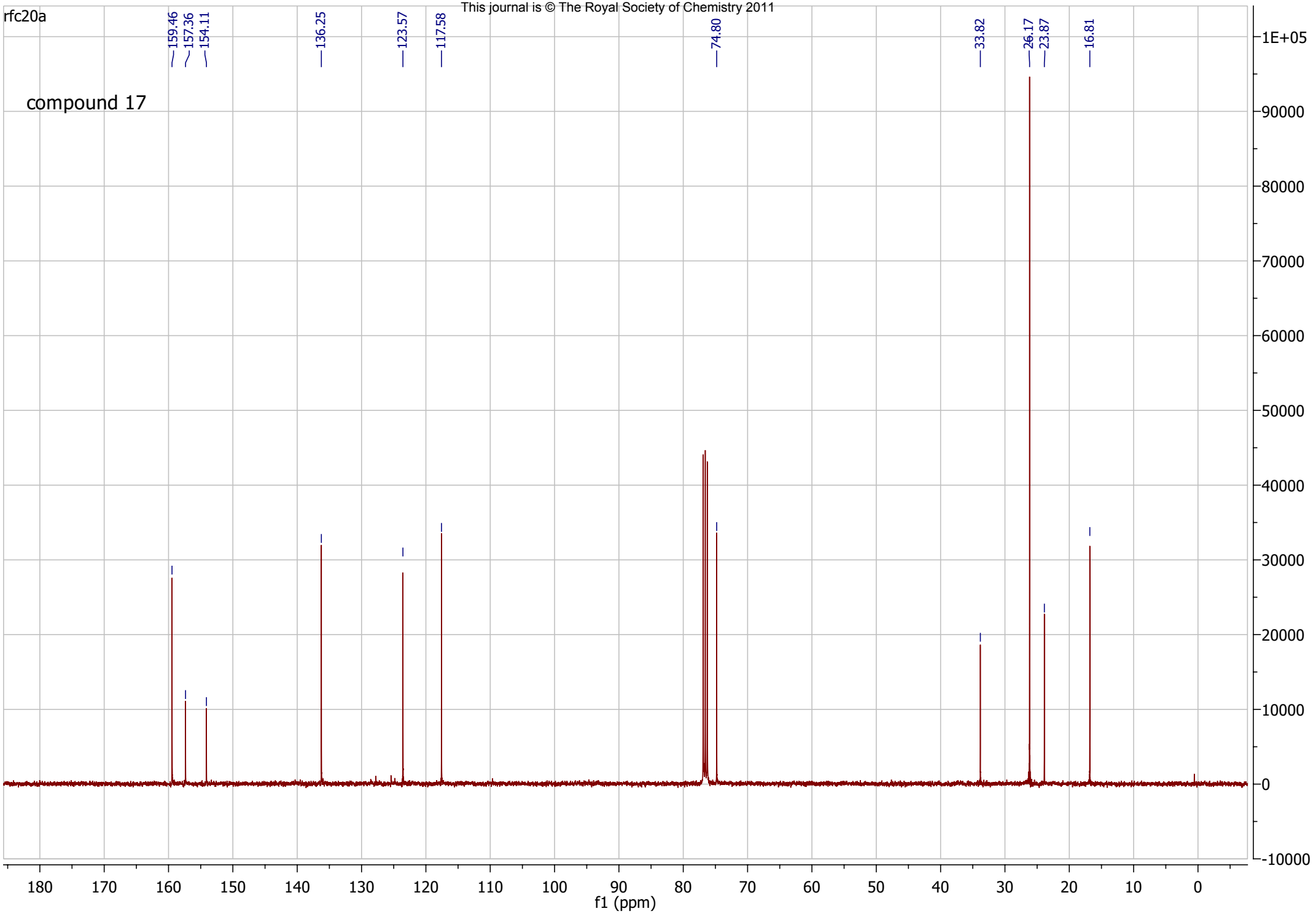

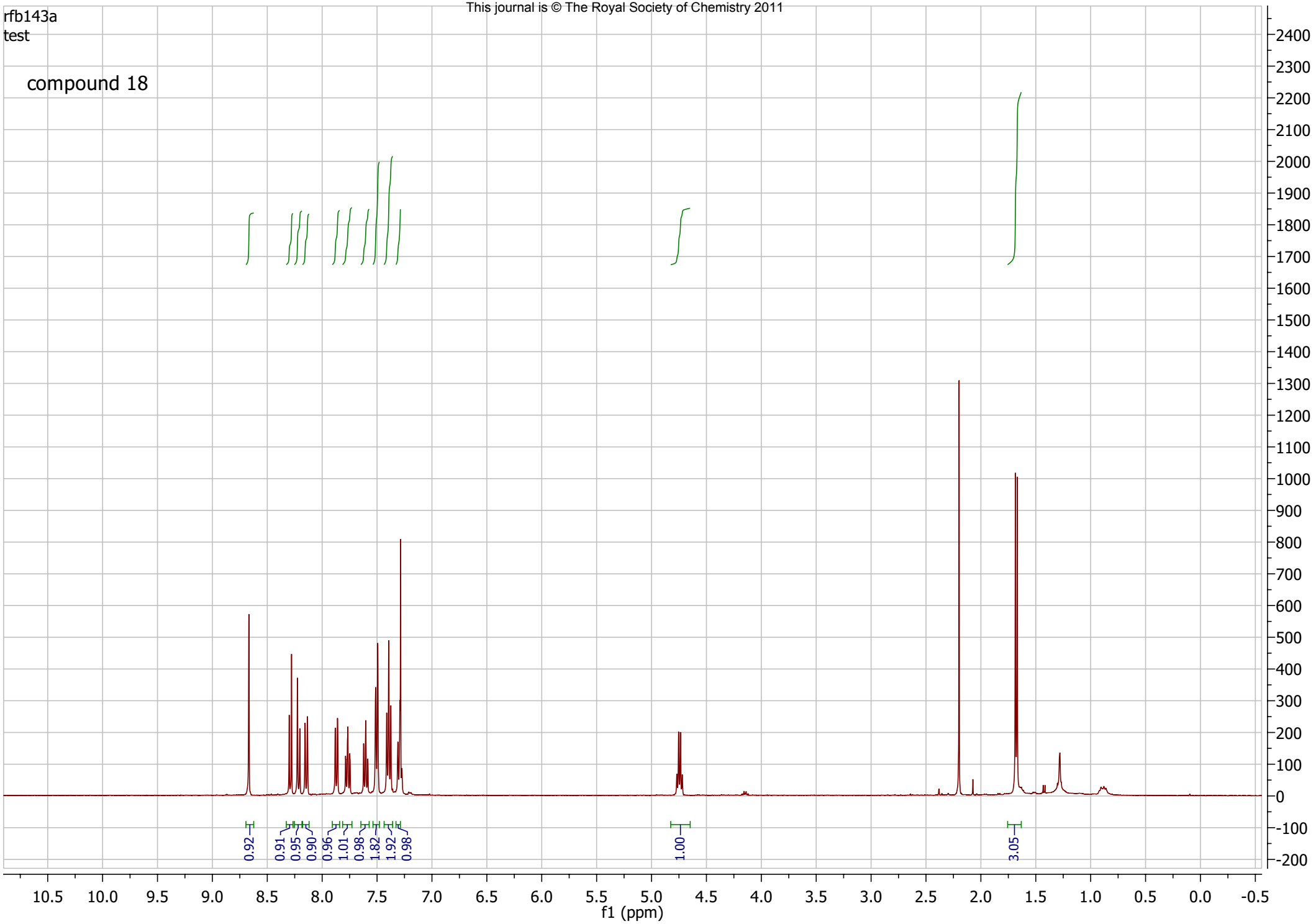

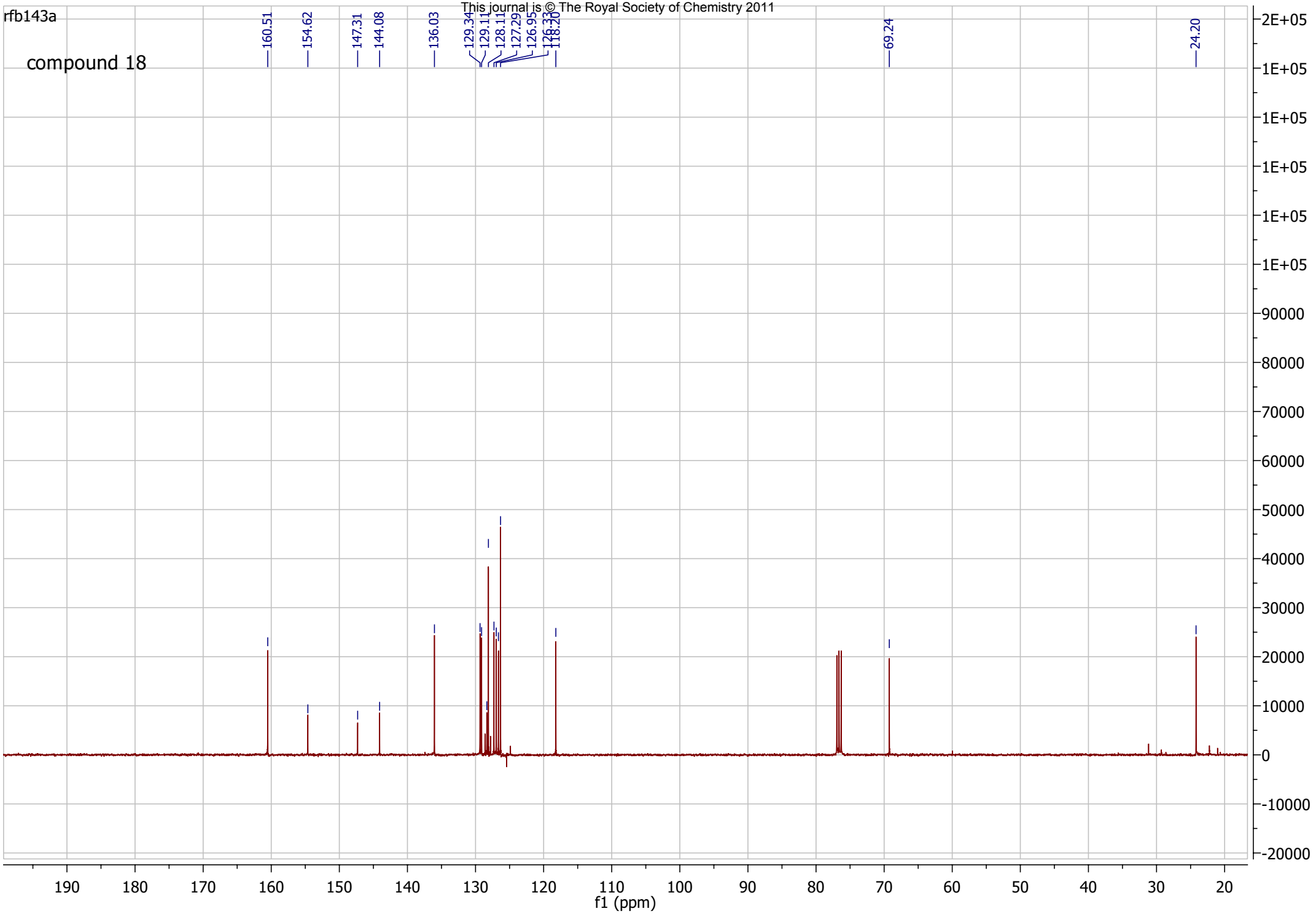

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compound 19