

Cooperative Metal-Ligand Catalyzed Intramolecular Hydroamination and Hydroalkoxylation of Allenes using a Stable Iron Catalyst

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I- General Information

All reactions were carried out under an argon atmosphere using oven-dried glassware. The dry and degassed toluene was obtained from MBRAUN Solvent Purification System. All other chemicals were used as purchased without further purification. ^1H and ^{13}C spectra were recorded in CDCl_3 using Varian VNMR 600 or Inova 400 MHz spectrometer. The signals were referenced to residual chloroform (7.26 ppm, ^1H , 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra (EI-MS, 70 eV) were conducted on a Finnigan SSQ 7000 spectrometer. HRMS were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 pre-coated aluminium plates (Macherey-Nagel 0.20 mm thickness) with a fluorescent indicator UV254. Visualization was performed with standard phosphomolybdic acid stain (10g in 100 mL EtOH) or UV light. Column chromatography was performed using Macherey-Nagel Aluminium oxide 90 neutral (50–200 μm) and Macherey-Nagel Silica Gel (0.040–0.063 mm).

II- Catalyst optimization

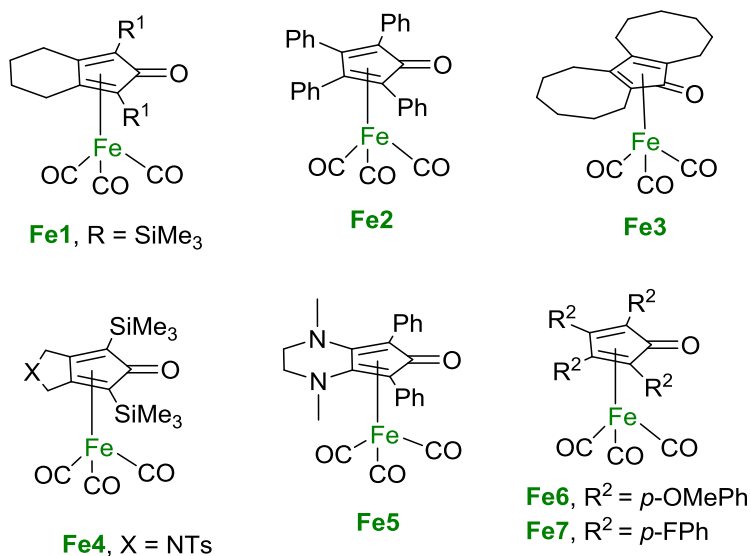


Table 1. Optimization of the reaction conditions.^[a]

10 mol% **[Fe]**
 12 mol% Me₃NO
 70 °C, 16 h

Entry	Cat.	Yield (%) ^[b]
1	Fe1	2
2	Fe2	98
3	Fe3	12
4	Fe4	12
5	Fe5	0
6	Fe6	43
7	Fe7	99

[a] The reactions were performed on 0.1 mmol scale with an iron complex and additive in 0.5 mL of toluene at 70 °C in a Schlenk tube under an inert atmosphere for 16h. [b] Yields were determined by the ¹H NMR analysis of the crude reaction mixture using mesitylen as an internal standard.

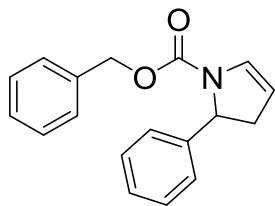
III - Experimental Procedures and Characterizations of the Products

General methodology for transformation of α -allenic amines into 2,3-dihydropyrroles.

A 10 mL Schlenk tube equipped with a stir bar was charged with the allenic-amine **1** (0.5 mmol), **Fe1** (5 mol %), Me₃NO (6 mol %) and 1 mL of THF under argon. The reaction mixture was stirred at 70°C for 24 h. The reaction mixture was then purified by column chromatography on silica gel with hexane/ether as eluent to give the pure 2,3-dihydropyrroles **2a-k**.

General methodology for transformation of α -allenic alcohols into 2,3-dihydrofuranes.

A 10 mL Schlenk tube equipped with a stir bar was charged with the allenic alcohols **3** (1 mmol), **Fe1** (2.5 mol %), Me₃NO (4 mol %) and 1 mL of toluene under argon. The reaction mixture was stirred for 2 h at 70°C. The reaction mixture was then purified using a short chromatography column and neutral alumina with pentane/ether mixtures as eluent to give pure 2,3-dihydrofuranes **4a-r**.

Benzyl 2-phenyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2a)

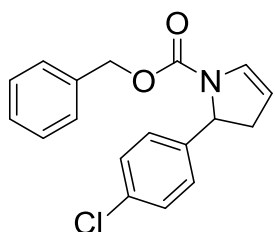
Yield: (114 mg, 82% yield), colorless oil.

^1H NMR (600 MHz, Acetone- d_6) (rotamers): ^1H NMR (600 MHz, Acetone- d_6) δ 7.39 – 7.18 (m, 9H), 6.92 (s, 1H), 6.79 – 6.78 (m, 1H), 5.23 – 5.22 (m, 1H), 5.15 – 4.93 (m, 3H), 3.36 – 3.25 (m, 1H), 2.50 – 2.42 (m, 1H).

^{13}C NMR (151 MHz, Acetone- d_6) (rotamers): δ 153.2, 152.5, 145.7, 145.1, 137.9, 137.7, 130.9, 130.3, 129.5, 129.3, 129.0, 128.7, 128.4, 128.0, 126.3, 126.2, 107.4, 107.3, 67.3, 67.0, 61.0, 41.5, 40.2.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{NNa}$ [$\text{M} + \text{Na}$] $^+$: 302.1152, found 302.1146

IR (ATR): ν = 3035, 2938, 2328, 2096, 1881, 1701, 1614, 1498, 1410, 1326, 1207, 1124, 961, 903, 748, 701 cm^{-1} .

Benzyl 2-(4-chlorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2b)

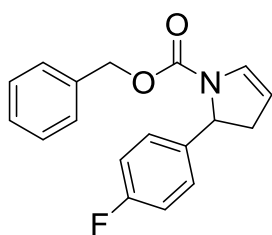
Yield: (123 mg, 78% yield), colorless oil.

^1H NMR (600 MHz, Acetone- d_6) (rotamers) δ 7.31 – 7.20 (m, 8H), 6.94 (s, 1H), 6.78 – 6.76 (m, 1H), 5.24 – 4.91 (m, 4H), 3.36 – 3.29 (m, 1H), 2.50 – 2.42 (m, 1H).

^{13}C NMR (151 MHz, Acetone- d_6) (rotamers) δ 144.6, 144.1, 137.9, 137.6, 133.1, 130.9, 130.3, 129.6, 129.4, 129.0, 128.8, 128.5, 128.2, 107.5, 107.3, 67.5, 67.2, 60.5, 41.3, 40.0.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{NClNa}$ [$\text{M} + \text{Na}$] $^+$: 336.0762, found 336.0757

IR (ATR): ν = 3035, 2942, 2860, 2327, 2092, 1995, 1895, 1703, 1619, 1491, 1409, 1324, 1208, 1125, 1090, 1013, 961, 904, 824, 750, 699 cm^{-1} .



Benzyl 2-(4-fluorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2c)

Yield: (128 mg, 86% yield), colorless oil.

¹H NMR (600 MHz, CDCl₃) (rotamers) δ = 7.36-7.16 (m, 6H), 7.03-6.92 (m, 3H), 6.83-6.72 (m, 1H), 5.20-4.93 (m, 4H), 3.30 – 3.21 (m,

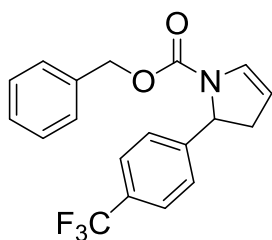
1H), 2.54 – 2.50 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) (rotamers) δ = 163.3, 160.9, 152.8, 140.2, 139.5, 136.5, 136.2, 132.0, 130.4, 130.2, 129.5, 128.6, 128.4, 128.2, 128.0, 127.7, 127.3, 115.6, 115.4, 106.9, 106.7, 67.3, 67.1, 60.0, 59.9, 40.8, 39.5.

¹⁹F NMR (376 MHz, CDCl₃) (rotamers) δ = -115.45, -115.58.

HRMS (ESI): calc. for C₁₈H₁₆O₂NFNa [M + Na]⁺: 320.1057, found 320.1050

IR (ATR): ν = 3375, 3105, 2939, 2326, 2108, 1892, 1692, 1607, 1504, 1461, 1414, 1345, 1318, 1214, 1126, 1008, 974, 918, 892, 828, 739, 697 cm⁻¹.



Benzyl 2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2d)

Yield: (141 mg, 81% yield), colorless oil.

¹H NMR (600 MHz, C₆D₆) (rotamers) δ = 7.32-7.17 (m, 3H), 7.08-6.51 (m, 7H), 5.06 – 5.01 (m, 1H), 4.96 – 4.94 (m, 1H), 4.75 – 4.60 (m, 1H), 4.54 – 4.49 (m, 1H), 2.64 – 2.59 (m, 1H), 1.97 – 1.94 (m, 1H).

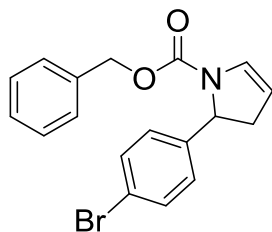
¹³C NMR (151 MHz, C₆D₆) (rotamers) δ = 152.4, 152.0, 148.6, 148.0, 136.9, 136.5, 130.7, 129.7, 128.7, 128.6, 128.4, 128.4, 126.4, 126.0, 125.8 (q, J = 3.7 Hz), 124.1, 122.3, 106.2, 105.7, 67.5, 67.0, 60.3, 60.0, 40.4, 39.1.

¹⁹F NMR (376 MHz, C₆D₆) δ = -62.09.

HRMS (ESI): calc. for C₁₉H₁₆F₃O₂NNa [M + Na]⁺: 370.1025, found 370.1017

IR (ATR): ν = 3316, 3103, 2922, 1959, 1696, 1616, 1541, 1466, 1413, 1320, 1260, 1208, 1158, 1122, 1062, 1014, 969, 927, 835, 800, 734, 693 cm⁻¹.

Benzyl 2-(4-bromophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2e)



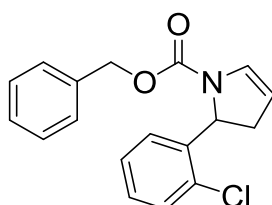
Yield: (107 mg, 60% yield), colorless oil.

¹H NMR (600 MHz, CDCl₃) (rotamers) δ = 7.47-7.34 (m, 4H), 7.25-7.19 (m, 3H), 7.09 – 7.08 (m, 1H), 6.90 – 6.89 (m, 1H), 6.86-6.73 (m, 1H), 5.20-5.16 (m, 1H), 5.11-4.92 (m, 3H), 3.30 – 3.22 (m, 1H), 2.54 – 2.48 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) (rotamers) δ = 152.8, 152.2, 143.3, 142.7, 136.4, 136.1, 131.9, 131.7, 130.3, 129.6, 128.7, 128.4, 128.3, 128.3, 128.0, 127.7, 127.6, 127.5, 121.3, 121.1, 107.0, 106.7, 67.4, 67.1, 60.1, 60.0, 40.7, 39.5.

IR (ATR): ν = 3033, 2938, 2858, 2330, 2183, 2115, 1993, 1803, 1703, 1621, 1488, 1448, 1409, 1322, 1209, 1126, 1009, 959, 913, 820, 755, 699 cm⁻¹.

Benzyl 2-(2-chlorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2f)



Yield: (116 mg, 74% yield), colorless oil.

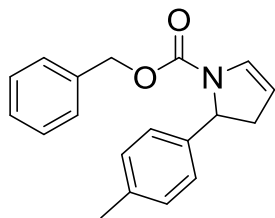
¹H NMR (600 MHz, CDCl₃) (rotamers) δ = 7.38 (m, 3H), 7.19 (m, 5H), 6.93-6.76 (m, 2H), 5.62 – 5.60 (m, 1H), 5.21-4.97 (m, 3H), 3.39 – 3.32 (m, 1H), 2.45-2.37 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) (rotamers) δ = 152.8, 152.1, 141.4, 140.6, 136.5, 136.2, 131.9, 131.6, 130.1, 129.9, 129.6, 129.4, 129.1, 128.6, 128.3, 127.8, 127.4, 127.2, 126.8, 126.7, 125.9, 125.6, 107.2, 106.9, 67.4, 66.9, 57.9, 57.4, 39.6, 38.5.

HRMS (ESI): calc. for C₁₈H₁₆O₂N³⁵Cl [M + H]⁺: 313.0864, found 313.0857

Benzyl 2-(p-tolyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2g)

Yield: (101 mg, 69% yield), colorless oil.



¹H NMR (600 MHz, Acetone-d₆) (rotamers) ¹H NMR (600 MHz, Acetone-d₆) δ 7.38 – 7.11 (m, 8H), 6.92 (s, 1H), 6.78 – 6.76 (m, 1H), 5.20 – 4.92 (m, 4H), 3.33 – 3.23 (m, 1H), 2.49 – 2.40 (m, 1H), 2.32 – 2.29 (m, 3H).

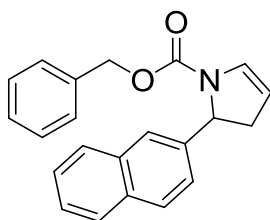
¹³C NMR (151 MHz, Acetone-d₆) (rotamers) δ 153.2, 152.4, 142.8, 142.2, 137.7, 137.4, 130.9, 130.3, 130.0, 129.3, 128.9, 128.8, 128.7, 128.3, 128.0, 126.2, 107.3, 67.3, 67.0, 60.9, 41.5, 40.2, 21.1.

HRMS (ESI): calc. for C₁₉H₁₉O₂NNa [M + Na]⁺: 316.1308, found 316.1308

IR (ATR): ν = 3028, 2938, 1702, 1618, 1512, 1410, 1325, 1208, 1123, 962, 907, 808, 744, 700 cm⁻¹.

Benzyl 2-(naphthalen-2-yl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2h)

Yield: (133 mg, 81% yield), colorless oil.

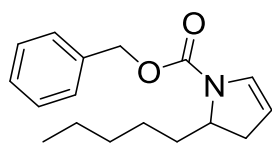


¹H NMR (600 MHz, CDCl₃) (rotamers) δ = 7.86-7.66 (m, 4H), 7.52-7.37 (m, 5H), 7.15-6.84 (m, 3H), 6.79 – 6.77 (m, 1H), 5.43-4.95 (m, 4H), 3.39 – 3.31 (m, 1H), 2.69 – 2.62 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) (rotamers) δ = 153.0, 152.2, 141.5, 140.8, 136.5, 136.0, 133.4, 133.0, 132.9, 132.7, 132.6, 130.4, 129.7, 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 127.7, 127.5, 127.4, 126.2, 126.1, 125.8, 124.4, 124.3, 123.8, 123.7, 107.1, 106.8, 67.2, 67.0, 60.8, 60.6, 40.7, 39.5.

HRMS (ESI): calc. for C₂₂H₁₉O₂NNa [M + Na]⁺: 352.1308, found 352.1309

Benzyl 2-pentyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2i)



Yield: (78 mg, 57% yield), colorless oil.

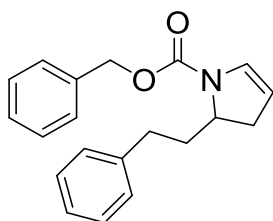
¹H NMR (600 MHz, Acetone-d₆) (rotamers) δ 7.42 – 7.31 (m, 5H), 6.72 – 6.45 (m, 1H), 5.23 – 4.98 (m, 4H), 4.17 – 4.14 (m, 1H), 2.34 – 2.28 (m, 1H), 1.81 – 1.65 (m, 1H), 1.55 – 1.52 (m, 1H), 1.30 – 1.25 (m, 6H), 0.89 – 0.84 (m, 3H).

¹³C NMR (151 MHz, Acetone-d₆) (rotamers) δ 153.3, 152.5, 138.1, 138.0, 130.3, 129.6, 129.3, 128.8, 128.7, 108.0, 70.1, 67.1, 58.3, 57.8, 36.4, 35.3, 34.5, 32.5, 24.9, 24.7, 23.3, 14.4.

HRMS (ESI): calc. for C₁₇H₂₃O₂NNa [M + Na]⁺: 296.1621, found 296.1618

IR (ATR): ν = 2929, 2860, 2323, 2100, 1897, 1701, 1618, 1412, 1329, 1211, 1123, 976, 894, 746, 701 cm⁻¹.

Benzyl 2-phenethyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2j)



Yield: (125 mg, 82% yield), colorless oil.

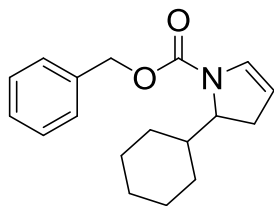
¹H NMR (600 MHz, Acetone-d₆) (rotamers) δ 7.41 – 7.32 (m, 5H), 7.28 – 7.21 (m, 3H), 7.17 – 7.11 (m, 2H), 6.57 – 6.56 (m, 1H), 5.23 – 4.03 (m, 4H), 4.22 (s, 1H), 2.63 – 2.60 (m, 2H), 2.50 – 2.42 (m, 1H), 2.15 – 2.12 (m, 1H), 1.87 – 1.85 (m, 1H).

¹³C NMR (151 MHz, Acetone-d₆) (rotamers) δ 130.3, 129.7, 129.3, 129.2, 129.2, 129.0, 128.7, 126.6, 108.1, 67.3, 67.2, 58.0, 57.4, 37.1, 36.4, 36.2, 35.2, 31.4, 31.3.

HRMS (ESI): calc. for C₂₀H₂₁O₂NNa [M + Na]⁺: 330.1465, found 330.1460

IR (ATR): ν = 3062, 3028, 2930, 2858, 2329, 2114, 1994, 1806, 1700, 1620, 1495, 1448, 1411, 1329, 1213, 1124, 1092, 1031, 999, 952, 909, 815, 750, 698 cm⁻¹

Benzyl 2-cyclohexyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2k)



Yield: (96 mg, 67% yield), colorless oil.

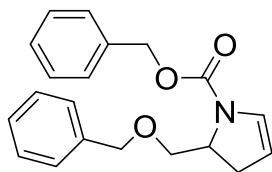
¹H NMR (600 MHz, C₆D₆) (rotamers) δ = 7.26-7.21 (m, 2H), 7.11-7.09 (m, 2H), 7.06-7.03 (m, 1H), 6.86-6.52 (m, 1H), 5.22-5.12 (m, 1H), 5.08-5.06 (m, 1H), 4.65-4.60 (m, 1H), 4.16-3.91 (m, 1H), 2.29-2.24 (m, 1H), 2.08-2.03 (m, 1H), 1.62-1.43 (m, 5H), 1.15-0.76 (m, 6H).

¹³C NMR (151 MHz, C₆D₆) (rotamers) δ = 156.0, 152.5, 137.6, 137.4, 131.1, 130.0, 128.7, 128.6, 128.4, 107.7, 77.5, 67.1, 66.8, 62.2, 61.6, 54.5, 42.9, 41.4, 40.4, 31.9, 30.9, 29.5, 28.8, 27.0, 26.6, 26.4, 26.3, 25.8, 25.5.

HRMS (ESI): calc. for C₁₈H₂₃O₂NNa [M + Na]⁺: 308.1621, found 308.1621

IR (ATR): ν = 2919, 2339, 2094, 1700, 1409, 1332, 1114, 951, 722 cm⁻¹.

Benzyl 2-((benzyloxy)methyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2l)



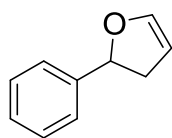
Yield: (97 mg, 60% yield), colorless oil.

¹H NMR (600 MHz, CDCl₃) (rotamers) δ = 7.39-7.31 (m, 10H), 6.64-6.55 (m, 1H), 5.20-5.02 (m, 3H), 4.59-4.38 (m, 3H), 3.77-3.47 (m, 2H), 2.86-2.83 (m, 1H), 2.68-2.65 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) (rotamers) δ = 152.6, 152.2, 138.5, 138.3, 136.6, 136.5, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 108.0, 73.3, 70.5, 70.0, 67.1, 56.7, 56.3, 34.0, 32.9, 26.3, 25.3.

HRMS (ESI): calc. for C₂₀H₂₁O₃N [M + H]⁺: 323.1516, found 323.1517

2-Phenyl-2,3-dihydrofuran (4a)



Yield: (131 mg, 90%), colorless oil.

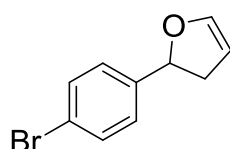
¹H NMR (600 MHz, CDCl₃) δ = 7.40-7.36 (m, 4H), 7.32-7.31 (m, 1H), 6.48 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 5.54 (dd, apparent m, 1H), 4.99-4.97 (m, 1H), 3.12 – 3.08 (m, 1H), 2.66 – 2.61 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ = 145.3, 143.1, 128.5, 127.6, 125.6, 99.1, 82.4, 37.9.

MS: (EI) m/z: 146([M⁺], 10), 117 (34), 115 (65), 105 (34), 91 (47), 78 (24), 77 (77), 65 (23), 63 (44), 51 (100), 50 (61).

IR (ATR): ν = 3033, 2924, 2860, 2331, 2101, 1615, 1452, 1137, 1048, 930, 749, 700 cm⁻¹.

2-(4-Bromophenyl)-2,3-dihydrofuran (4b)



Yield: (203 mg, 91% yield), colorless oil.

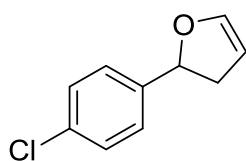
¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.43 (ddd, apparent q $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 5.47 (dd, J_1 = 10.8, J_2 = 8.1 Hz, 1H), 4.95 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 3.08 (dddd, apparent ddt, J_1 = 15.4, J_2 = 10.8, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.55 (dddd, apparent ddt, J_1 = 15.2, J_2 = 8.2, $J_3 \approx J_4 \approx 2.4$ Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 145.2, 142.1, 131.6, 127.3, 121.4, 99.0, 81.6, 37.8.

MS: (EI) m/z: 226 ([M+H⁺], 53), 197 (23), 195 (25), 145 (32), 117 (26), 116 (100), 115 (56), 89 (13).

IR (ATR): ν = 3099, 2925, 2858, 1619, 1487, 1135, 1049, 932, 818, 706 cm⁻¹.

2-(4-Chlorophenyl)-2,3-dihydrofuran (4c)



Yield: (155 mg, 86% yield), colorless oil.

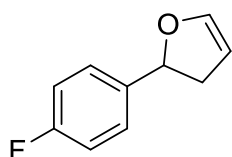
^1H NMR (600 MHz, CDCl_3) δ = 7.34 – 7.28 (m, 4H), 6.44 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 5.49 (dd, $J_1 = 10.8$, $J_2 = 8.2$ Hz, 1H), 4.96 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 3.11-3.05 (m, 1H), 2.58-2.53 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 145.3, 141.6, 133.3, 128.7, 127.0, 99.0, 81.6, 37.9

MS: (EI) m/z : 180 ($[\text{M}^+]$, 83), 179 (14), 153 (24), 151 (72), 145 (38), 117 (32), 116 (57), 115 (100), 89 (21).

IR (ATR): ν = 2925, 2860, 2325, 2096, 1909, 1734, 1615, 1489, 1342, 1138, 1047, 931, 824, 707 cm^{-1} .

2-(4-Fluorophenyl)-2,3-dihydrofuran (4d)



Yield: (149 mg, 91% yield), colorless oil.

^1H NMR (400 MHz, CDCl_3) δ = 7.34 – 7.30 (m, 2H), 7.05 – 6.99 (m, 2H), 6.42 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 5.47 (dd, $J_1 = 10.7$, $J_2 = 8.3$ Hz, 1H), 4.94 (q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 3.05 (dddd, apparent ddt, $J_1 = 15.3$, $J_2 = 10.7$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.56 (dddd, apparent ddt, $J_1 = 15.2$, $J_2 = 8.3$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H).

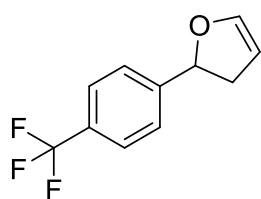
^{13}C NMR (101 MHz, CDCl_3) δ = 163.5, 145.2, 138.8 (d, $J = 2.6$ Hz), 127.3 (d, $J = 8.1$ Hz), 115.3 (d, $J = 21.6$ Hz), 99.0, 81.7, 37.9.

^{19}F NMR (376 MHz, CDCl_3) δ = -115.0.

MS: (EI) m/z : 165 (23), 164($[\text{M}^+]$, 100), 163 (30), 135 (91), 115 (25), 109 (28).

IR (ATR): ν = 2927, 2860, 2111, 1615, 1509, 1339, 1224, 1136, 1049, 935, 834, 705 cm^{-1} .

2-(4-(Trifluoromethyl)phenyl)-2,3-dihydrofuran (4e)



Yield: (161 mg, 75% yield), colorless oil.

¹H NMR (600 MHz, CDCl₃) δ = 7.62 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 6.47 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 5.57 (dd, J_1 = 10.9, $J_2 \approx 8.0$ Hz, 1H), 4.97 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx$

2.6 Hz, 1H), 3.14 (dddd, apparent ddt, J_1 = 15.5, J_2 = 10.9, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.57 (dddd, apparent ddt, J_1 = 15.2, J_2 = 8.0, $J_3 \approx J_4 \approx 2.4$ Hz, 1H).

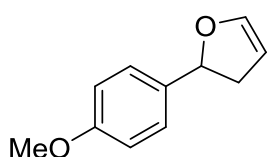
¹³C NMR (151 MHz, CDCl₃) δ = 147.1, 145.3, 129.7 (q, J = 31 Hz), 125.7, 125.5 (q, J = 3.8 Hz), 123.5 (q, J = 272 Hz), 99.0, 81.4, 37.9.

¹⁹F NMR (376 MHz, CDCl₃) δ = -62.6.

MS: (EI) m/z : 214 ([M⁺], 100), 195 (60), 185 (83). 165 (86), 145 (88), 127 (69), 115 (44), 83 (16).

IR (ATR): ν = 2929, 2864, 1732, 1617, 1417, 1321, 1122, 1054, 934, 838, 709 cm⁻¹.

2-(4-Methoxyphenyl)-2,3-dihydrofuran (4f)



Yield: (162 mg, 92% yield), colorless oil.

¹H NMR (400 MHz, CDCl₃) δ = 7.28 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.41 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 5.45 (dd, J_1 = 10.6, J_2 = 8.5 Hz, 1H), 4.94 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 3.79 (s, 3H),

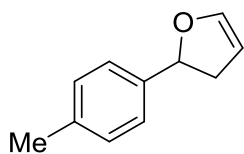
3.02 (dddd, apparent ddt, J_1 = 15.2, J_2 = 10.6, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.60 (dddd, J = 15.1, 8.5, 2.6, 1.9 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 159.2, 145.2, 135.0, 127.0, 113.9, 99.0, 82.2, 55.3, 37.6.

MS: (EI) m/z : 177(20), 176([M⁺], 100), 159 (16), 147 (75), 115 (13), 91 (15).

IR (ATR): ν = 3020, 2924, 2861, 1617, 1514, 1451, 1136, 1049, 930, 810, 705 cm⁻¹.

2-(*p*-Tolyl)-2,3-dihydrofuran (4g)



Yield: (131 mg, 82% yield), colorless oil.

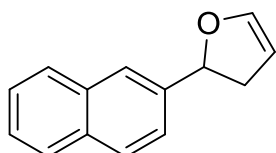
¹H NMR (300 MHz, CDCl₃) δ = 7.28 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.45 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 5.50 (dd, $J_1 = 10.7$, $J_2 = 8.4$ Hz, 1H), 4.97 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 3.07 (dddd, apparent ddt, $J_1 = 15.3$, $J_2 = 10.7$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.62 (dddd, apparent ddt, $J_1 = 15.2$, $J_2 = 8.4$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.36 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 145.3, 140.0, 137.3, 129.2, 125.6, 99.0, 82.3, 37.8, 21.2.

MS: (EI) m/z : 161 (26), 160([M⁺], 100), 159 (38), 145 (39), 131 (100), 115 (28), 91 (31).

IR (ATR): ν = 2925, 2850, 2326, 2098, 1612, 1510, 1456, 1297, 1245, 1136, 1041, 930, 825, 705 cm⁻¹.

2-(Naphthalen-2-yl)-2,3-dihydrofuran (4h)



Yield: (186 mg, 95% yield), white solid.

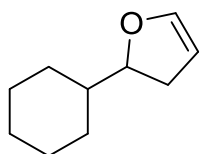
¹H NMR (400 MHz, CDCl₃) δ = 7.85 – 7.78 (m, 4H), 7.49 – 7.43 (m, 3H), 6.50 (m, 1H), 5.68 (dd, $J_1 = 10.8$, $J_2 = 8.3$ Hz, 1H), 4.99 (m, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 3.14 (dddd, apparent ddt, $J_1 = 15.4$, $J_2 = 10.8$, $J_3 \approx J_4 \approx 2.4$, 1H), 2.68 (dddd, $J_1 = 15.1$, $J_2 = 8.3$, $J_3 \approx J_4 \approx 2.8$ Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 145.4, 140.2, 133.2, 132.9, 128.5, 128.0, 127.6, 126.2, 125.8, 124.3, 123.7, 99.1, 82.5, 37.9.

MS: (EI) m/z : 197 (22), 196 ([M⁺], 100), 195 (26), 167 (88), 165 (37), 152 (17).

IR (ATR): ν = 3058, 2924, 2856, 2093, 1619, 1599, 1506, 1266, 1133, 1047, 932, 818, 742, 707 cm⁻¹.

2-Cyclohexyl-2,3-dihydrofuran (4i)



Yield: (106 mg, 70% yield), colorless oil.

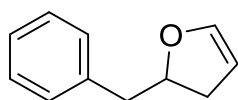
¹H NMR (400 MHz, CDCl₃) δ = 6.28 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 4.84 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 4.24 (ddd, $J_1 = 10.3$, $J_2 = 9.1$, $J_3 = 6.9$ Hz, 1H), 2.56 (dddd, apparent ddt, $J_1 = 15.1$, $J_2 = 10.2$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.35 (dddd, apparent ddt, $J_1 = 15.2$, $J_2 = 9.1$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 1.89-1.85 (m, 1H), 1.77-1.73 (m, 2H), 1.69-1.62 (m, 2H), 1.53 – 1.46 (m, 1H), 1.28 – 1.13 (m, 3H), 1.05 – 0.97 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ = 145.2, 99.1, 85.9, 43.0, 32.2, 28.6, 28.3, 26.5, 26.0, 25.8.

MS: (EI) m/z : 205 (16), 152([M⁺], 52), 95 (31), 83 (95), 81 (54), 69 (39), 60 (34), 58 (60), 49 (48).

IR (ATR): ν = 2921, 2854, 2328, 2104, 1617, 1449, 1266, 1139, 1055, 944, 703 cm⁻¹.

2-Benzyl-2,3-dihydrofuran (4j)



Yield: (120 mg, 75% yield), colorless oil.

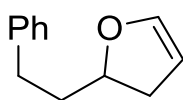
¹H NMR (600 MHz, CDCl₃) δ = 7.32-7.30 (m, 3H), 7.26 – 7.22 (m, 2H), 6.29 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 4.87 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 4.82 – 4.77 (m, 1H), 3.05 (dd, $J_1 = 13.8$, $J_2 = 7.1$ Hz, 1H), 2.84 (dd, $J_1 = 13.8$, $J_2 = 6.3$ Hz, 1H), 2.66 (dddd, apparent ddt, $J_1 = 14.9$, $J_2 = 10.0$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H), 2.37 (dddd, apparent ddt, $J_1 = 15.1$, $J_2 = 7.5$, $J_3 \approx J_4 \approx 2.4$ Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ = 144.9, 138.0, 129.3, 128.4, 126.4, 99.0, 81.8, 42.0, 34.2.

MS: (EI) m/z : 161 (26), 160 ([M⁺], 100), 91 (42), 69 (46).

IR (ATR): ν = 3029, 2925, 2856, 1617, 1452, 1138, 1052, 952, 698 cm⁻¹.

2-Phenethyl-2,3-dihydrofuran (4k)



Yield: (138 mg, 79% yield), colorless oil.

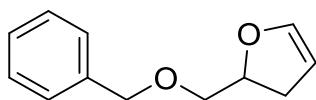
¹H NMR (400 MHz, CDCl₃) δ = 7.30 – 7.16 (m, 5H), 6.29 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 4.86 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 4.57-4.49 (m, 1H), 2.81-2.66 (m, 3H), 2.31-2.24 (m, 1H), 2.07-1.98 (m, 1H), 1.88-1.80 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 145.0, 141.8, 128.4(3), 128.3(5), 125.8, 98.9, 80.6, 37.9, 34.7, 31.8.

MS: (EI) *m/z*: 175 (21), 174([M⁺], 77), 157 (11), 131 (18), 130 (100), 117 (43), 91 (74).

IR (ATR): ν = 3027, 2927, 2856, 2663, 2326, 2104, 1887, 1615, 1451, 1268, 1139, 1052, 906, 701 cm⁻¹.

2-((Benzyloxy)methyl)-2,3-dihydrofuran (4l)



Yield: (141 mg, 74% yield), colorless oil.

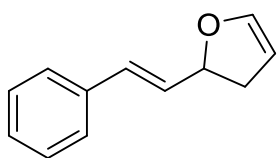
¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.21 (m, 5H), 6.28 (q, J = 2.5 Hz, 1H), 4.86 (q, J = 2.6 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 3.58 (dd, J = 10.3, 6.8 Hz, 1H), 3.49 (dd, J = 10.3, 4.3 Hz, 1H), 2.70-2.62 (m, 1H), 2.39-2.32 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ = 145.1, 138.1, 128.4, 127.7, 127.6, 99.0, 79.8, 73.4, 72.3, 31.6.

MS: (EI) *m/z*: 191 ([M+H⁺], 28), 91 (100).

IR (ATR): ν = 3435, 3030, 2863, 2324, 2095, 1904, 1615, 1453, 1360, 1199, 1103, 973, 737 cm⁻¹.

(E)-2-styryl-2,3-dihydrofuran (4m)



Yield: (107 mg, 62% yield), colorless oil.

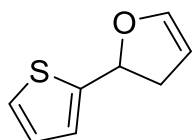
^1H NMR (600 MHz, CDCl_3) δ = 7.41-7.39 (m, 2H), 7.33-7.31 (m, 2H), 7.26-7.24 (m, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.36 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.4$ Hz, 1H), 6.31 (dd, J_1 = 15.8, J_2 = 7.1 Hz, 1H), 5.16 – 5.12 (m, 1H), 4.94 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 2.90 – 2.85 (m, 1H), 2.52 – 2.47 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ = 145.1, 136.5, 131.1, 129.1, 128.5, 127.8, 126.6, 99.2, 81.7, 35.6.

MS: (EI) m/z : 172 ($[\text{M}^+]$, 53), 144 (56), 143 (76), 129 (35), 128 (100), 116 (19), 115 (68), 104 (21).

IR (ATR): ν = 3028, 2922, 2857, 2331, 2097, 1887, 1614, 1449, 1136, 1046, 963, 743, 698 cm^{-1} .

2-(Thiophen-2-yl)-2,3-dihydrofuran (4n)



Yield: (94 mg, 62% yield), colorless oil.

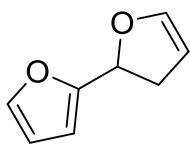
^1H NMR (400 MHz, CDCl_3) δ = 7.26-7.24 (m, 1H), 7.04-7.02 (m, 1H), 6.97-6.95 (m, 1H), 6.37 (q, J = 2.5 Hz, 1H), 5.72 (dd, J = 10.4, 7.9 Hz, 1H), 4.98 (q, J = 2.6 Hz, 1H), 3.11-3.03 (m, 1H), 2.80-2.72 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ = 145.8, 144.8, 126.6, 125.0, 124.5, 99.2, 78.2, 37.8.

MS: (EI) m/z : 153 ($[\text{M}+\text{H}^+]$, 100), 123 (28), 111 (74), 110 (33), 97 (42), 85 (18).

IR (ATR): ν = 3433, 2942, 1722, 1660, 1420, 1243, 1168, 1015, 838, 703 cm^{-1} .

2,3-Dihydro-2,2'-bifuran (4o)



Yield: (118 mg, 86% yield), colorless oil.

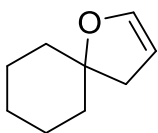
¹H NMR (600 MHz, CDCl₃) δ = 7.42 (t, J =1.3 Hz, 1H), 6.36 – 6.34 (m, 3H), 5.50 (dd, J_1 = 10.5, J_2 = 8.8 Hz, 1H), 5.00 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx$ 2.6 Hz, 1H), 2.94-2.86 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ = 153.9, 144.8, 142.8, 110.2, 107.4, 99.2, 75.4, 33.6.

MS: (EI) m/z : 136 ($[M^+]$, 24), 107 (21), 85 (63), 83 (100), 79 (32), 77 (26), 52 (33).

IR (ATR): ν = 3448, 2924, 2860, 2642, 2105, 1740, 1455, 1365, 1217, 684 cm⁻¹.

1-Oxaspiro[4.5]dec-2-ene (4p)



Yield: (105 mg, 76% yield), colorless oil.

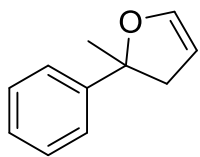
¹H NMR (400 MHz, CDCl₃) δ = 6.21 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx$ 2.5 Hz, 1H), 4.74 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx$ 2.6 Hz, 1H), 2.33 (dd, apparent t, $J_1 \approx J_2 \approx$ 2.4 Hz, 2H), 1.71-1.65 (m, 4H), 1.56 – 1.50 (m, 2H), 1.45-1.37 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ = 144.0, 98.0, 86.4, 40.4, 37.1, 25.2, 23.0.

MS: (EI) m/z : 139 ($[M+H^+]$, 33), 121 (26), 97 (28), 95 (31), 85 (28), 83 (33), 81 (33), 71 (45), 69 (48), 67 (33), 57 (100), 55 (96).

IR (ATR): ν = 2926, 2856, 2326, 2099, 1726, 1618, 1447, 1148, 1055, 702 cm⁻¹.

2-Methyl-2-phenyl-2,3-dihydrofuran (4q)



Yield: (147 mg, 92% yield), colorless oil.

¹H NMR (400 MHz, CDCl₃) δ = 7.43-7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 6.40 (ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.5$ Hz, 1H), 4.86

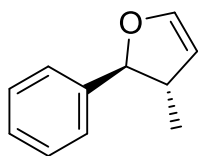
(ddd, apparent q, $J_1 \approx J_2 \approx J_3 \approx 2.6$ Hz, 1H), 2.87 – 2.75 (m, 2H), 1.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 147.7, 144.2, 128.2, 126.7, 124.4, 98.5, 87.2, 44.2, 29.1.

MS: (EI) m/z: 161 ([M+H⁺], 10), 143 (13), 128 (15), 117 (35), 105 (100), 91 (38), 77 (62), 57 (32).

IR (ATR): ν = 1970, 1923, 2859, 2328, 2100, 1616, 1445, 1283, 1161, 1054, 913, 755, 700 cm⁻¹.

(2S,3S)-3-methyl-2-phenyl-2,3-dihydrofuran (4r)



Yield: (109 mg, 68% yield), colorless oil, obtained with *cis*-isomer in the ratio 4:1.

¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.24 (m, 5H), 6.43 (m, 1H), 4.93-4.91 (m, 2H), 2.98-2.91 (m, 1H), 1.21 (d, J = 6.7 Hz, 3H).

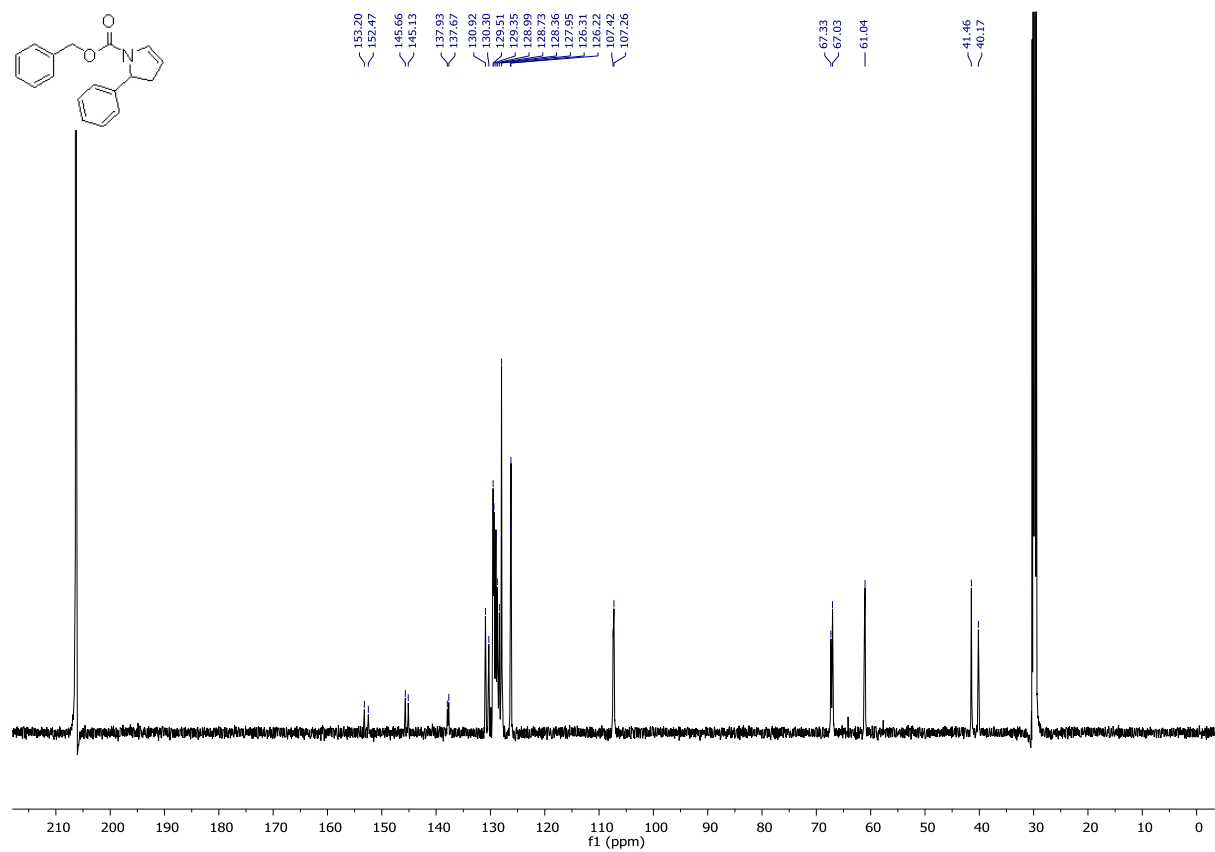
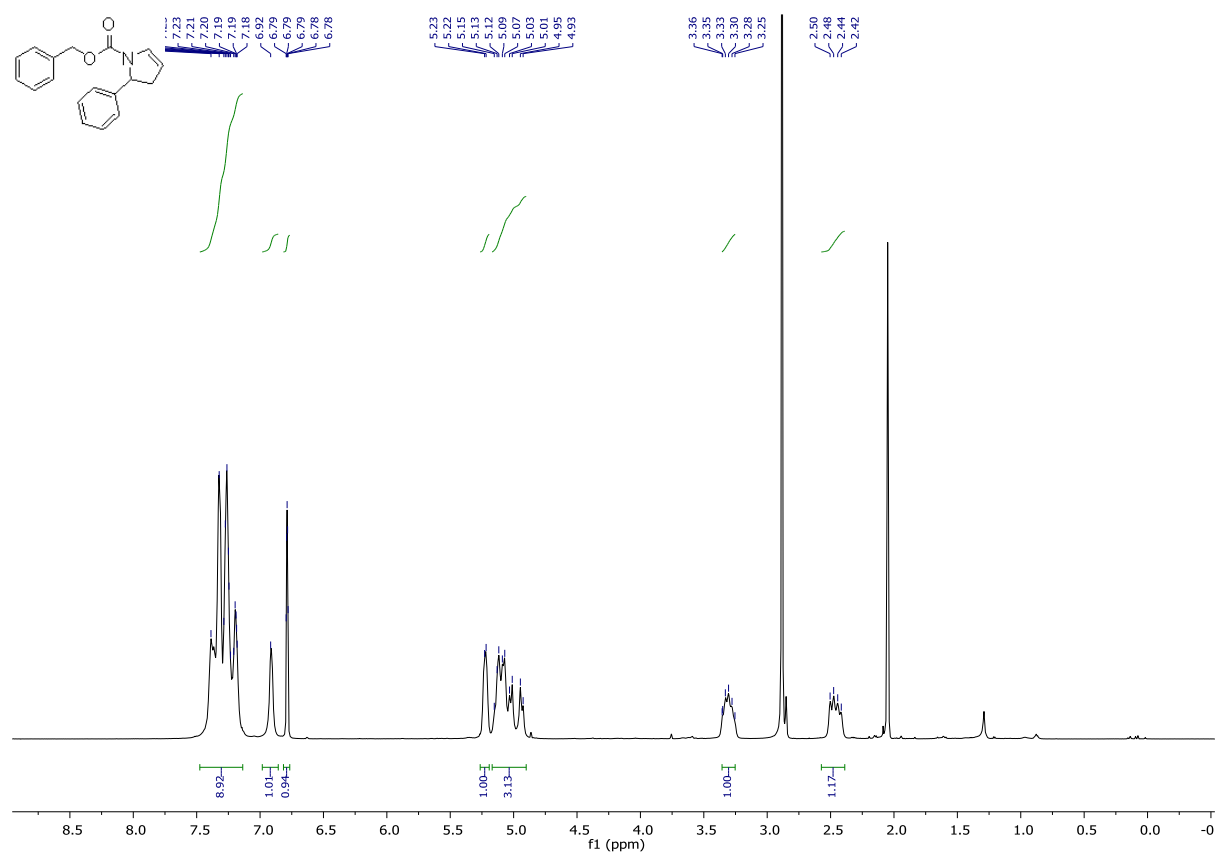
¹³C NMR (101 MHz, CDCl₃) δ = 144.7, 142.4, 128.5, 127.7, 125.4, 105.8, 90.1, 45.9, 20.8.

MS: (EI, 70) m/z: 161 ([M+H⁺], 70), 143 (30), 131,2 (30), 105 (100), 91 (58), 77 (40).

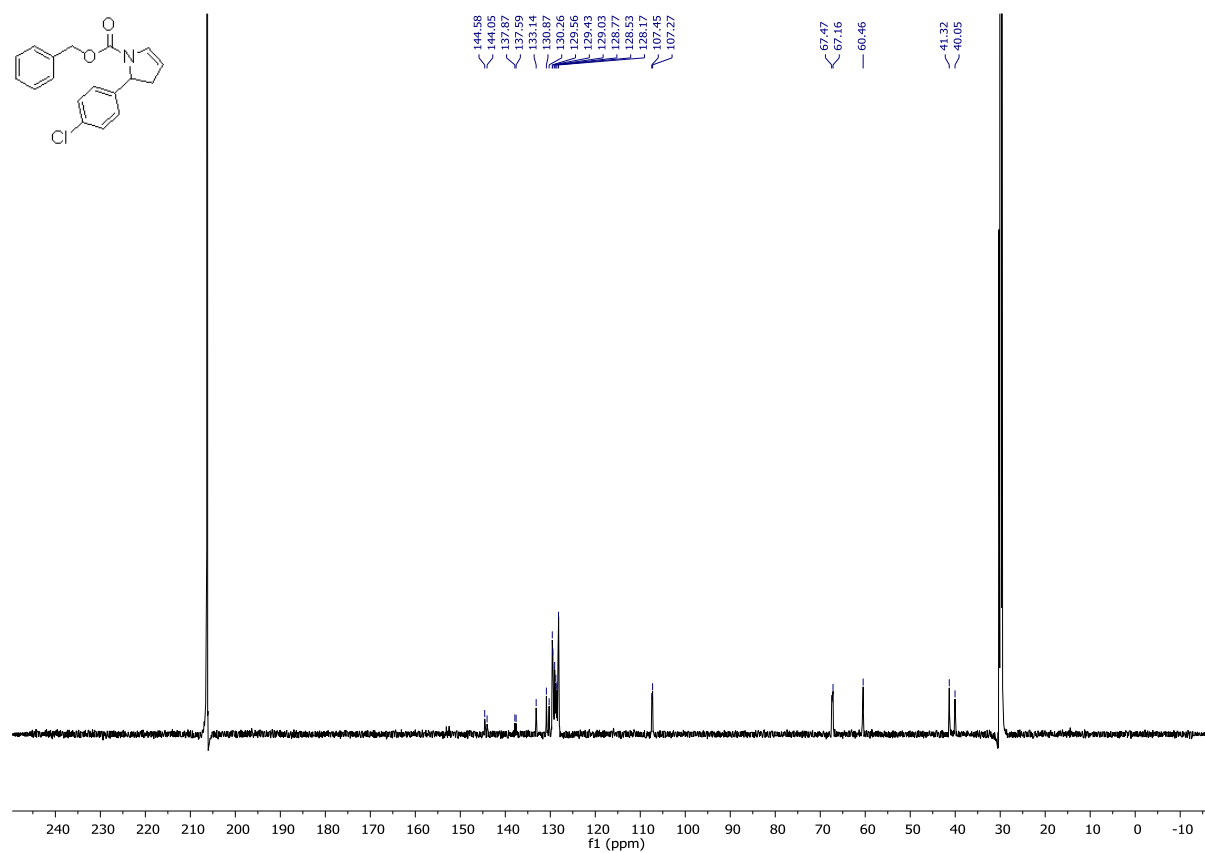
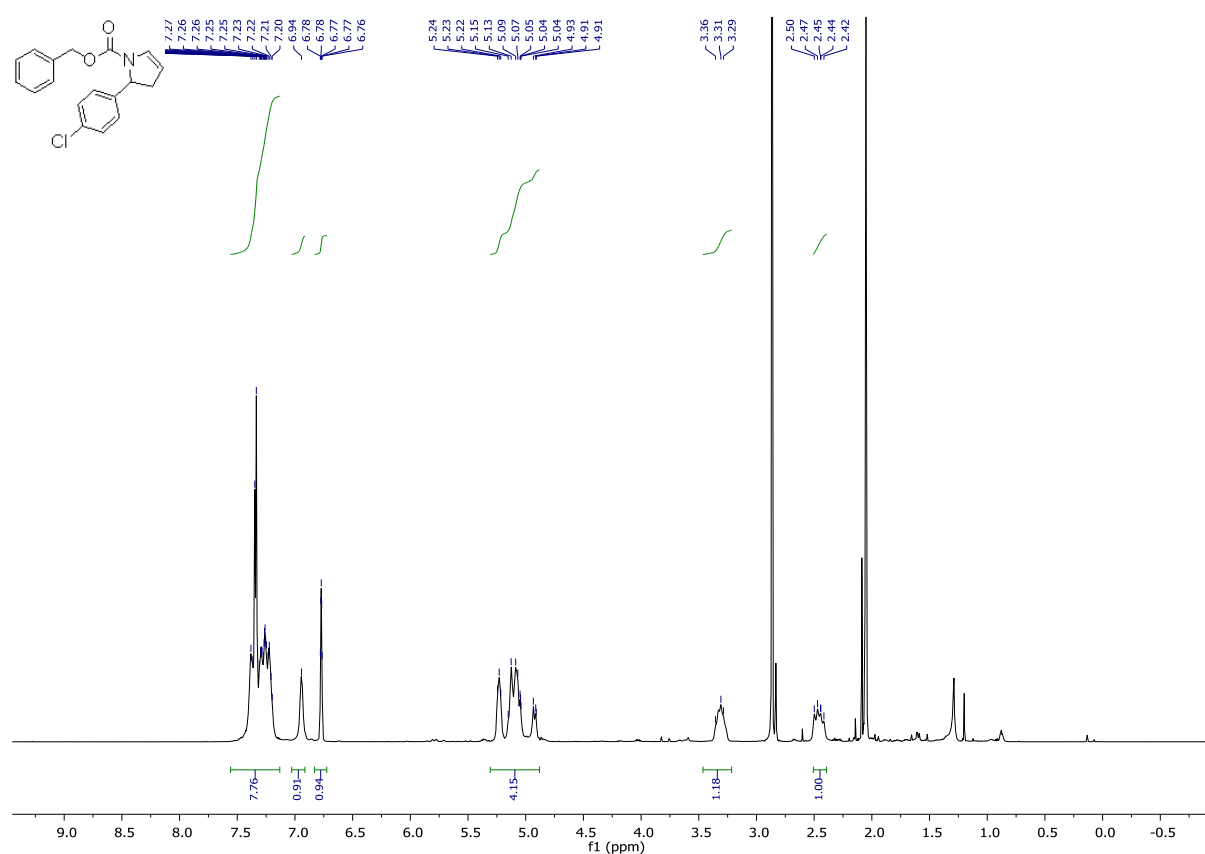
IR (ATR): ν = 3441, 3035, 2937, 1723, 1452, 1371, 1261, 985, 756, 700 cm⁻¹.

IV – NMR Spectra

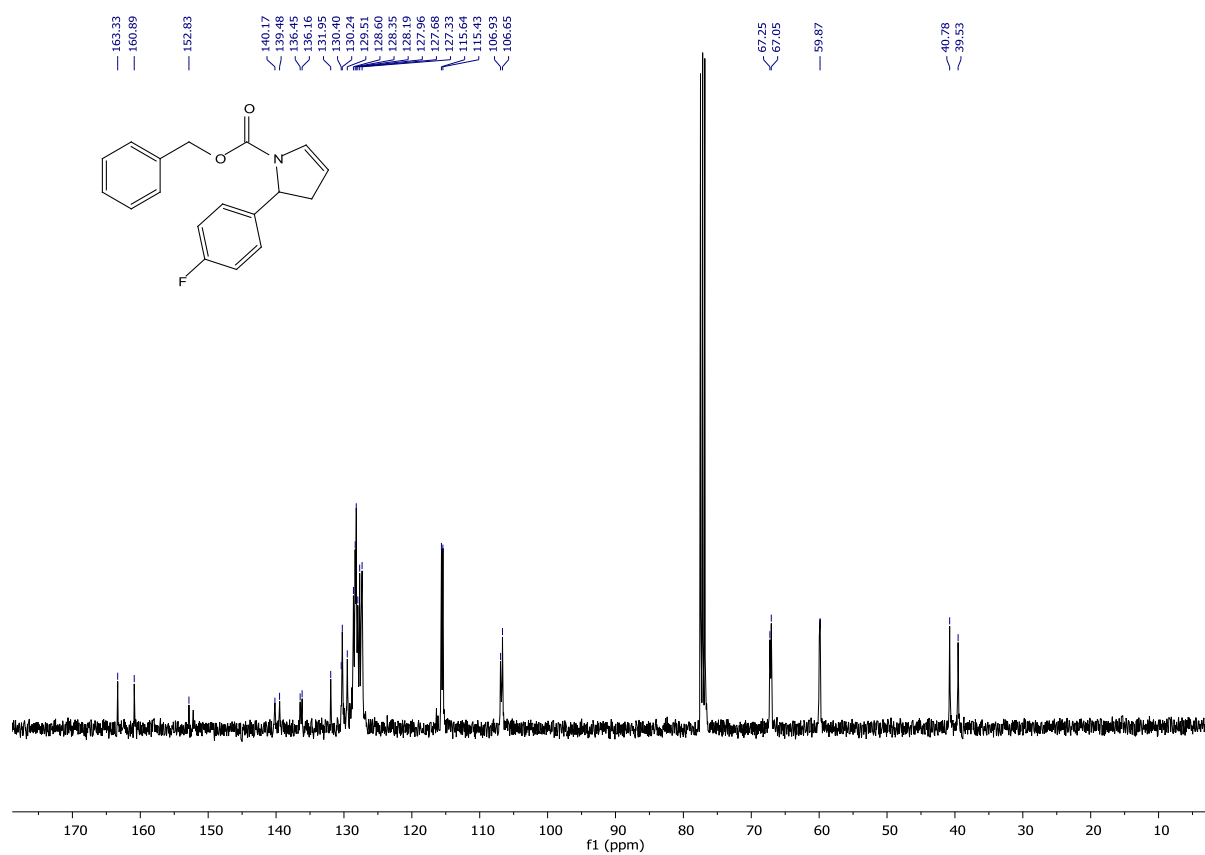
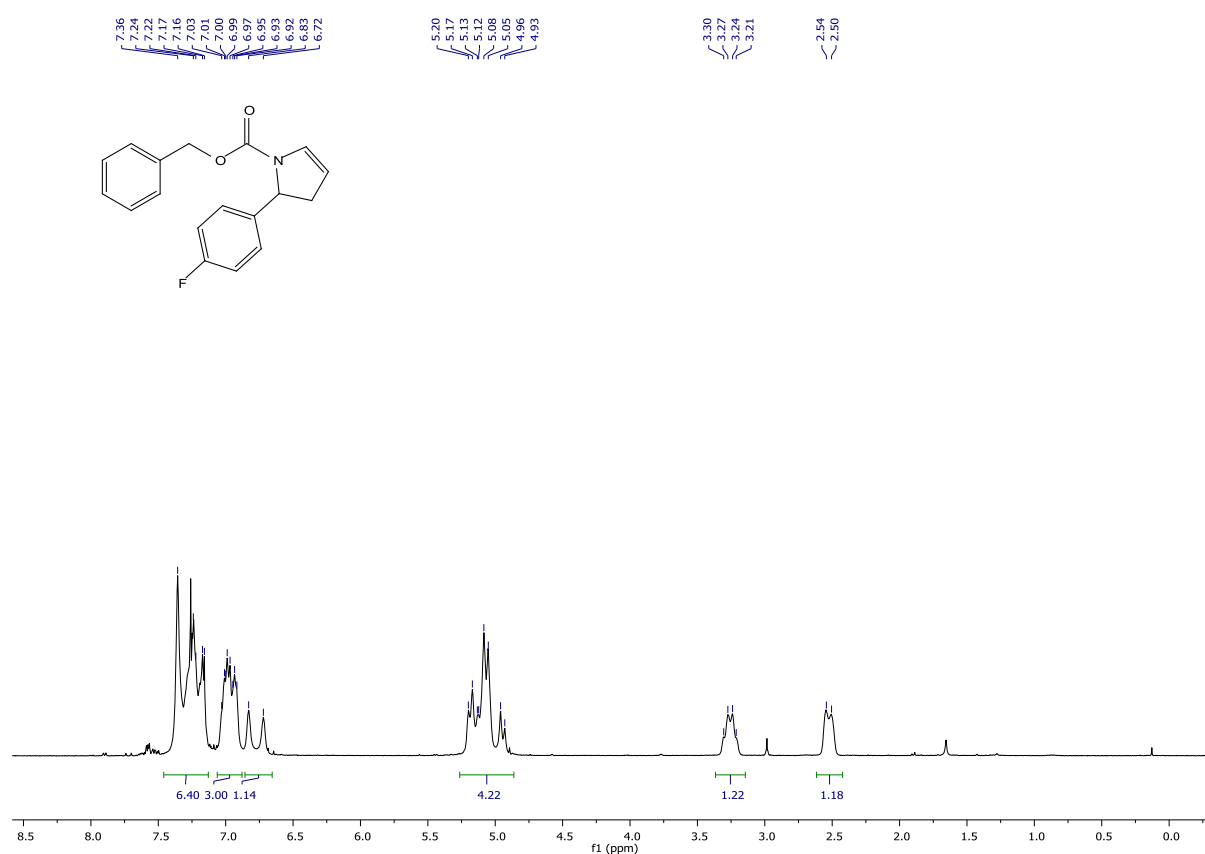
Benzyl 2-phenyl-2,3-dihydro-1*H*-pyrrole-1-carboxylate (2a)

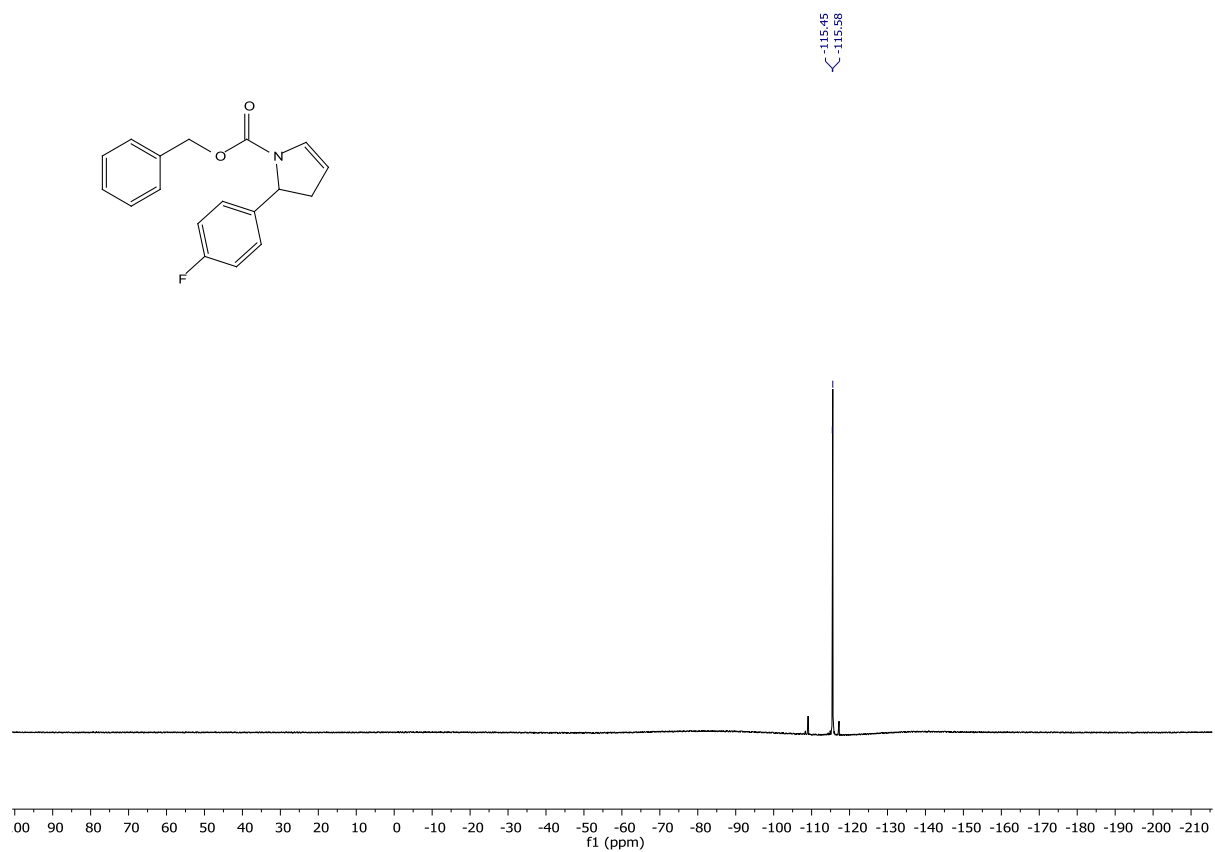


Benzyl 2-(4-chlorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2b)

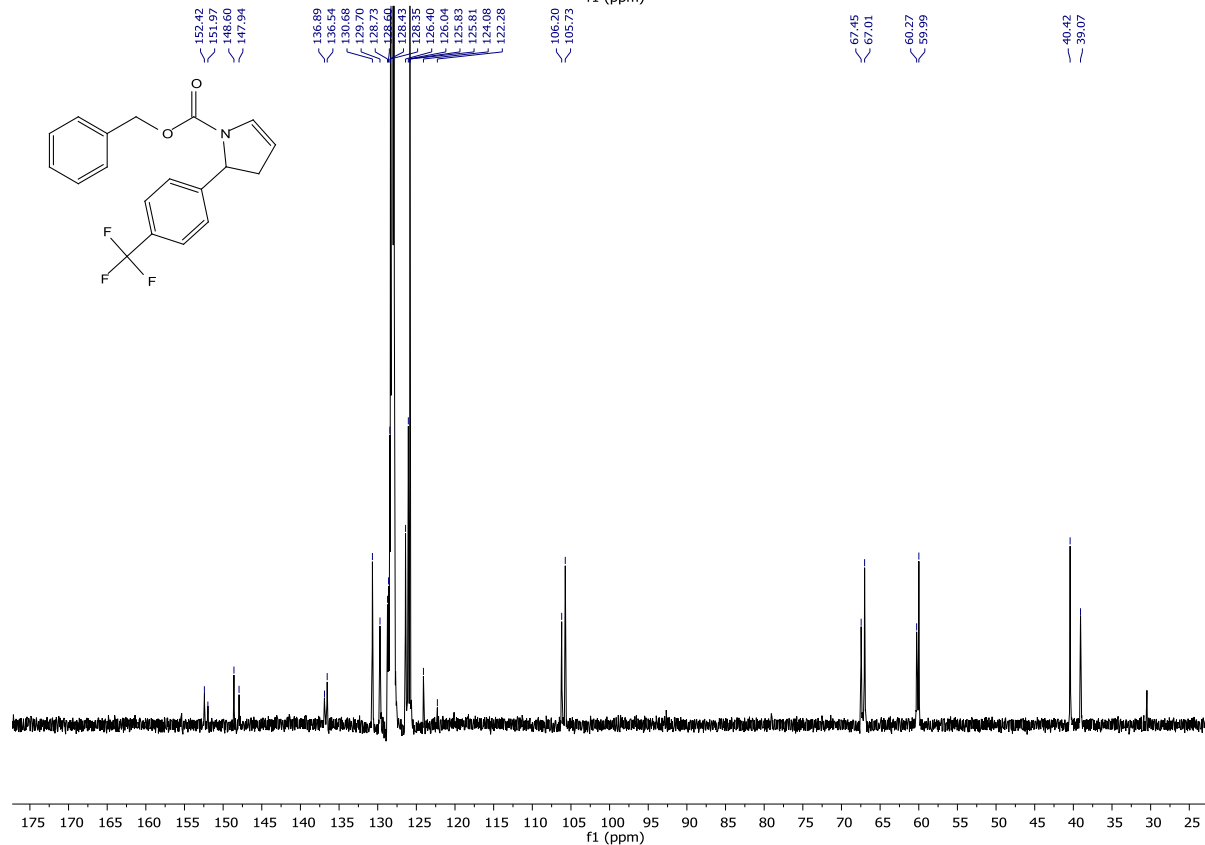
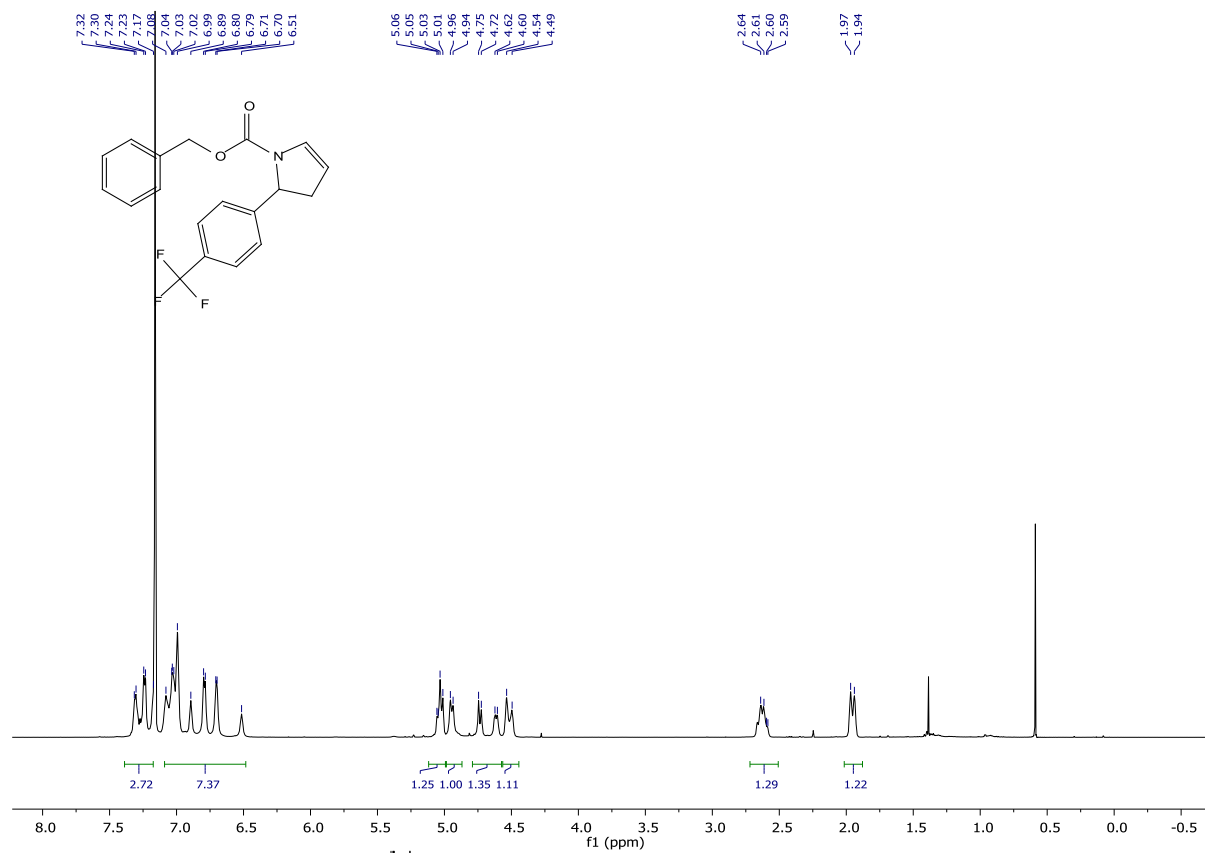


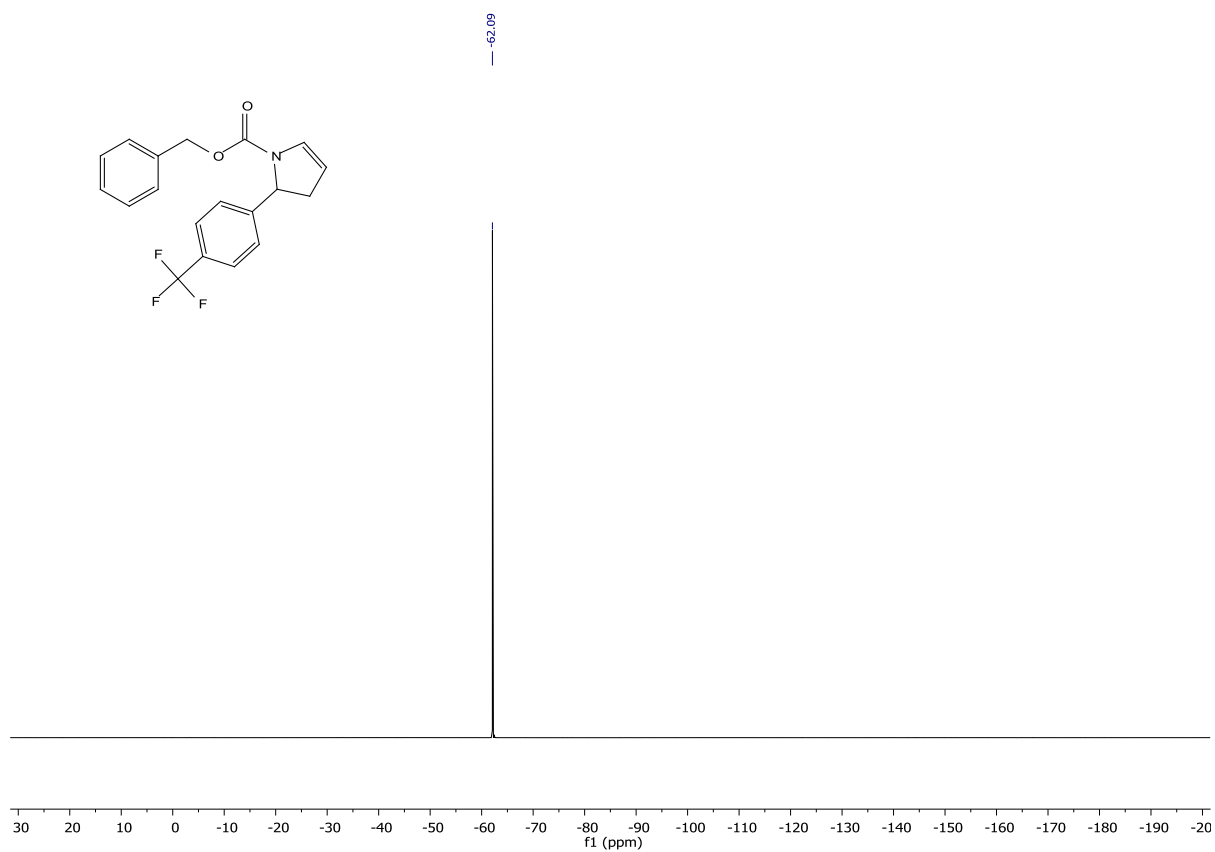
Benzyl 2-(4-fluorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2c)



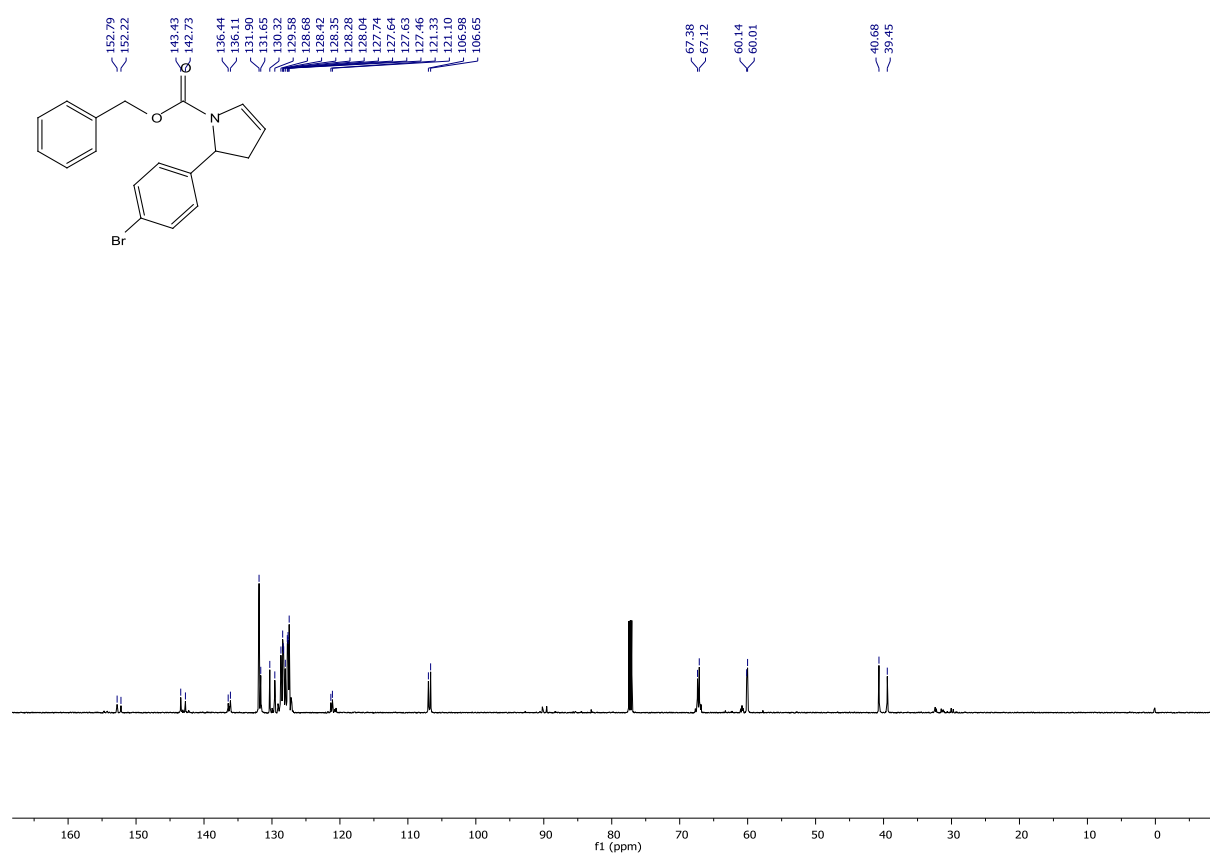
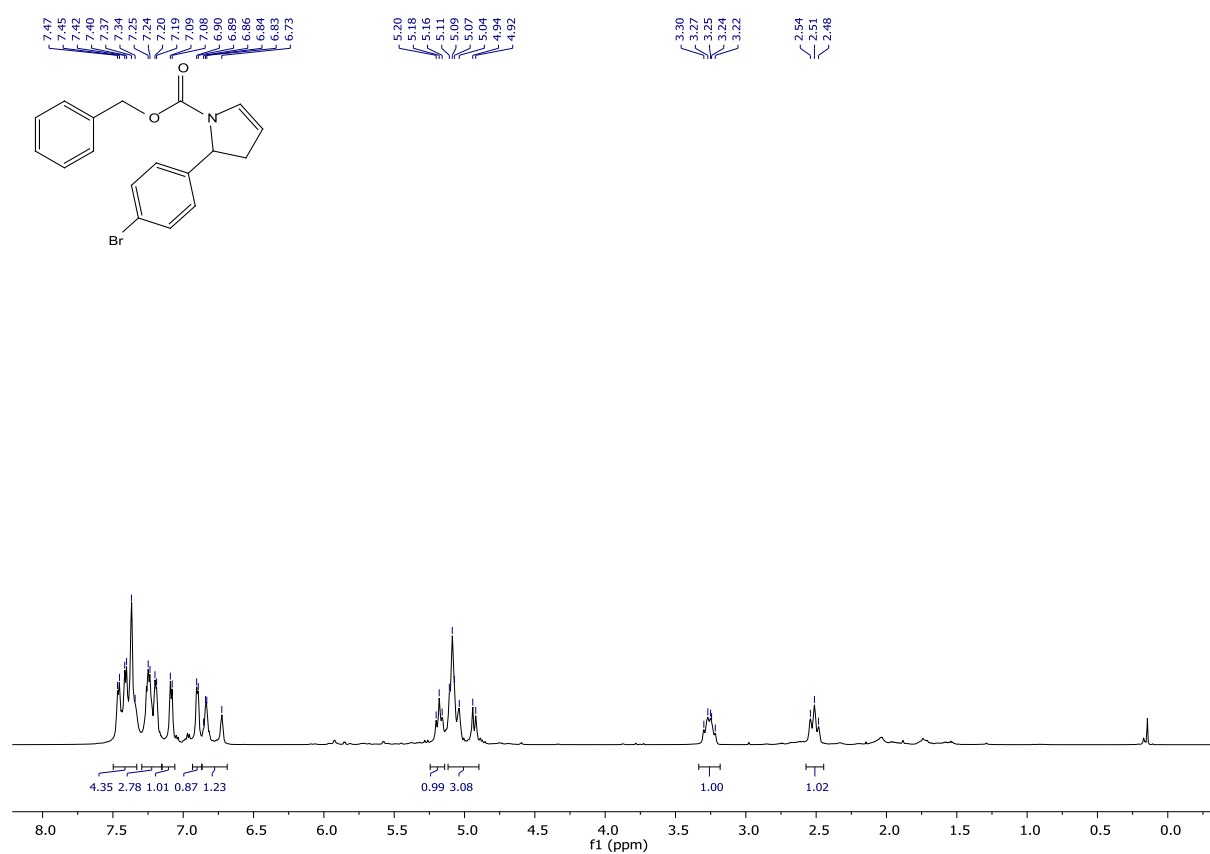


Benzyl 2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2d)

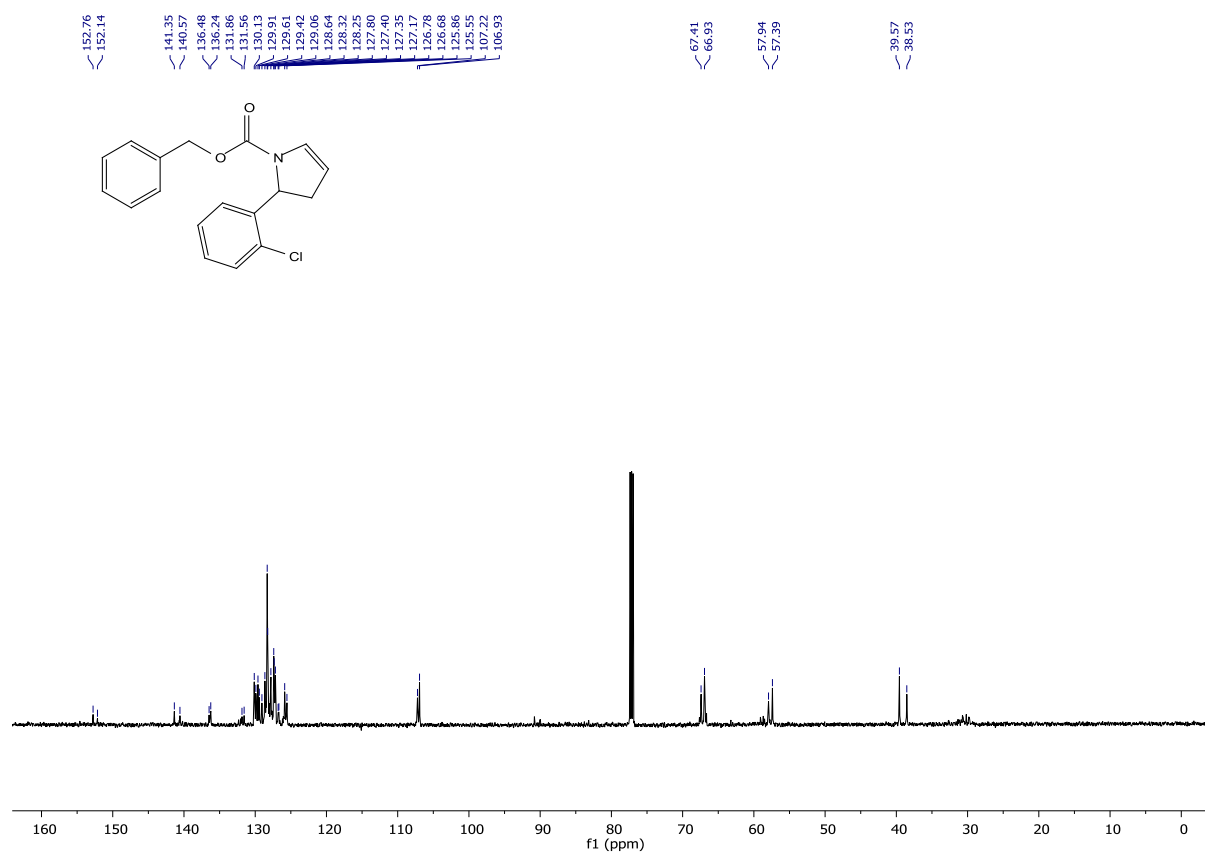
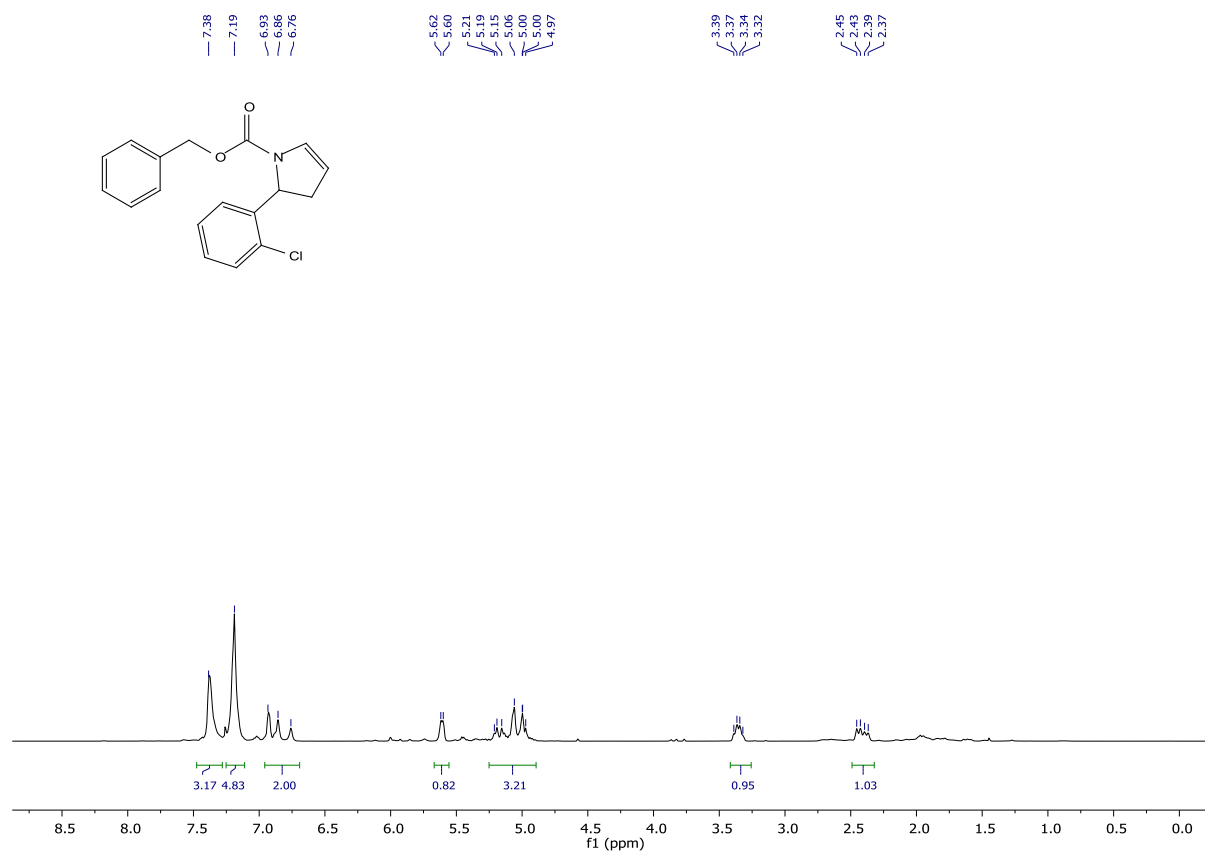




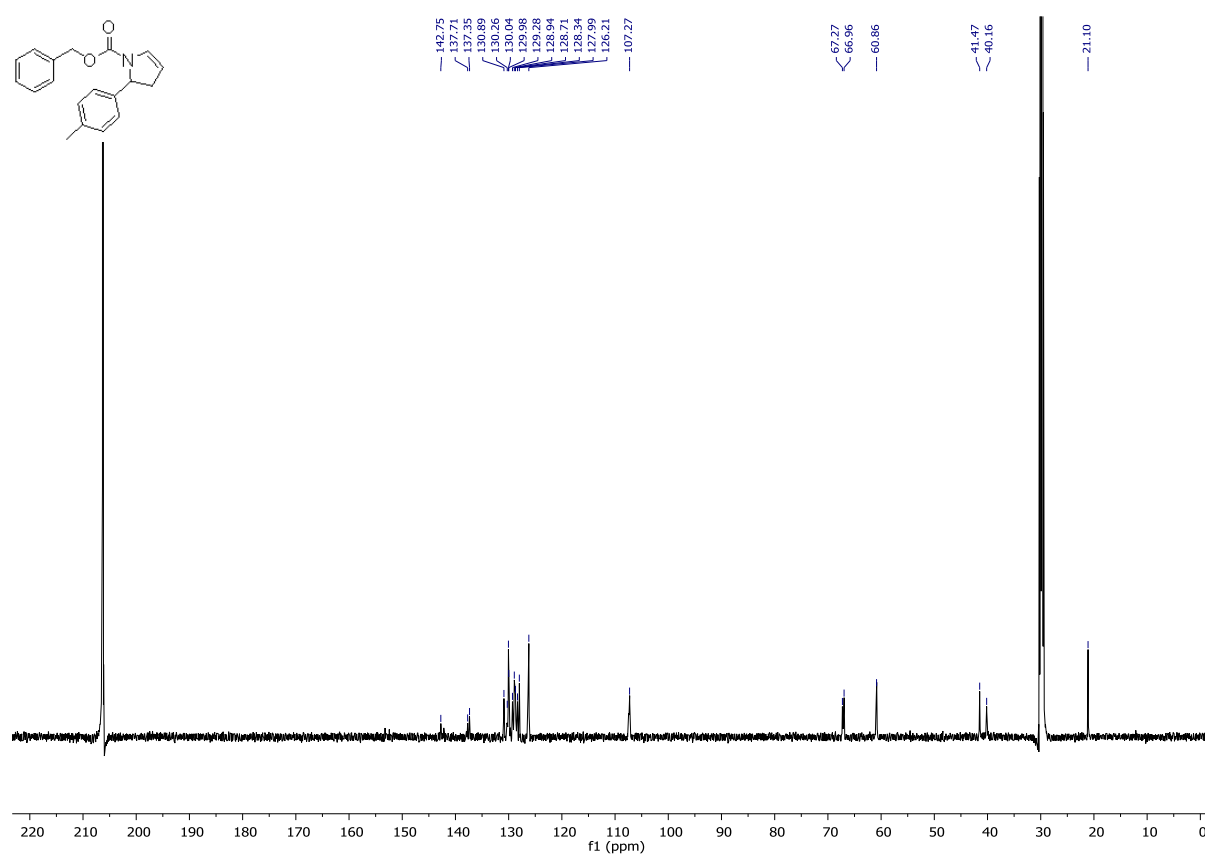
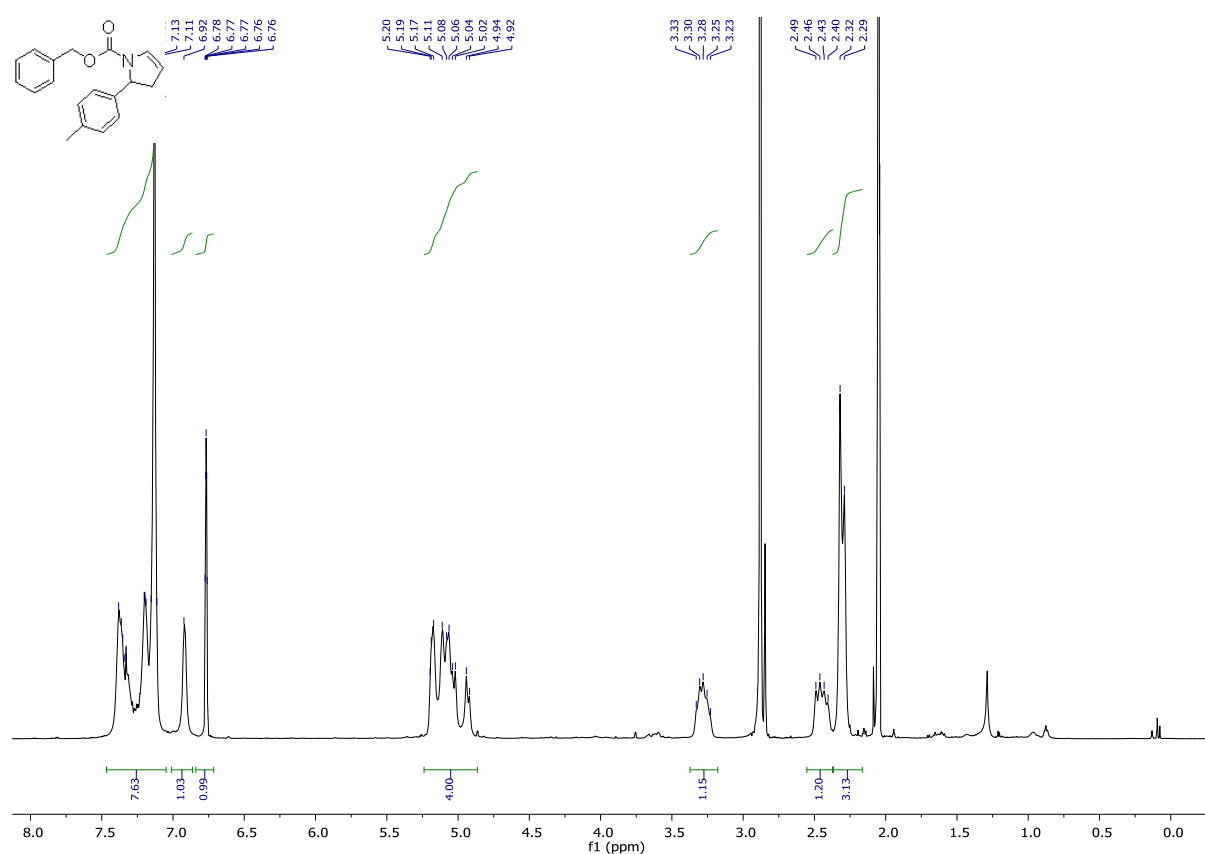
Benzyl 2-(4-bromophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2e)



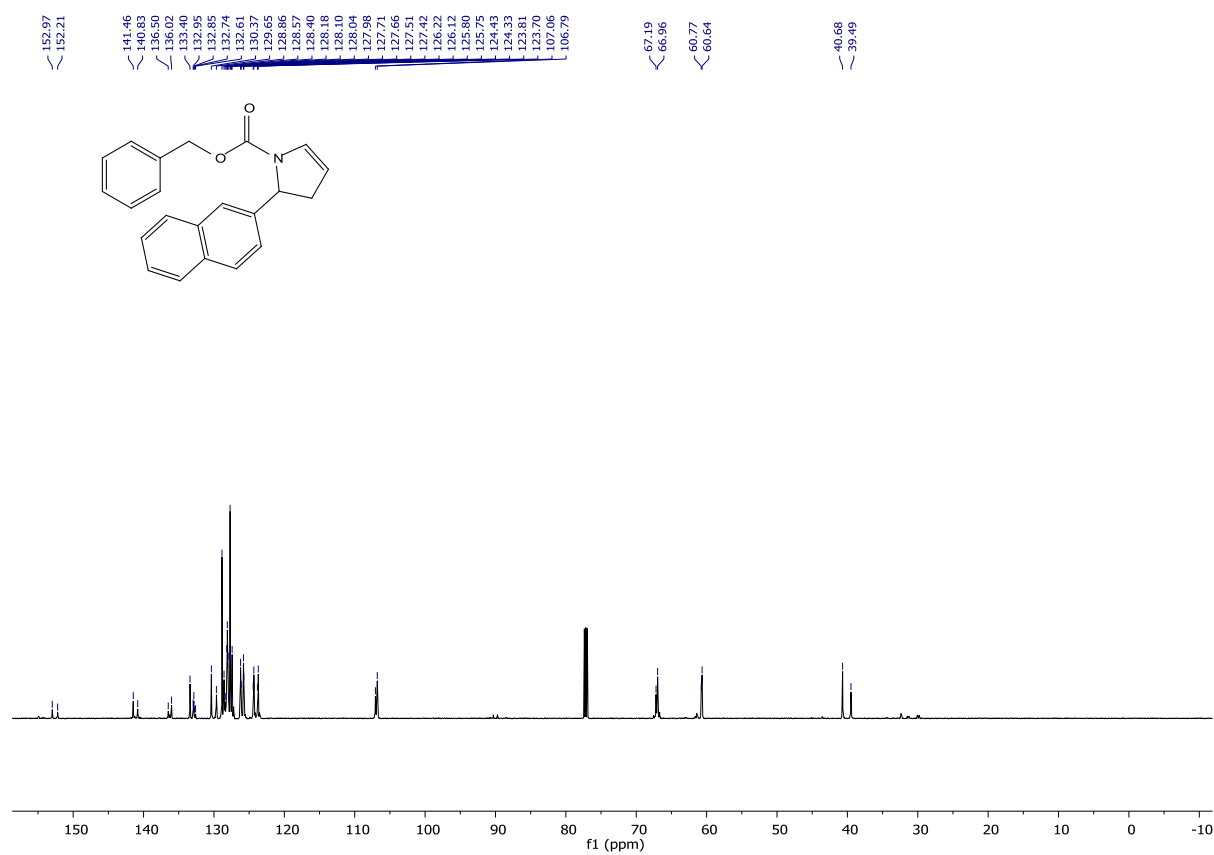
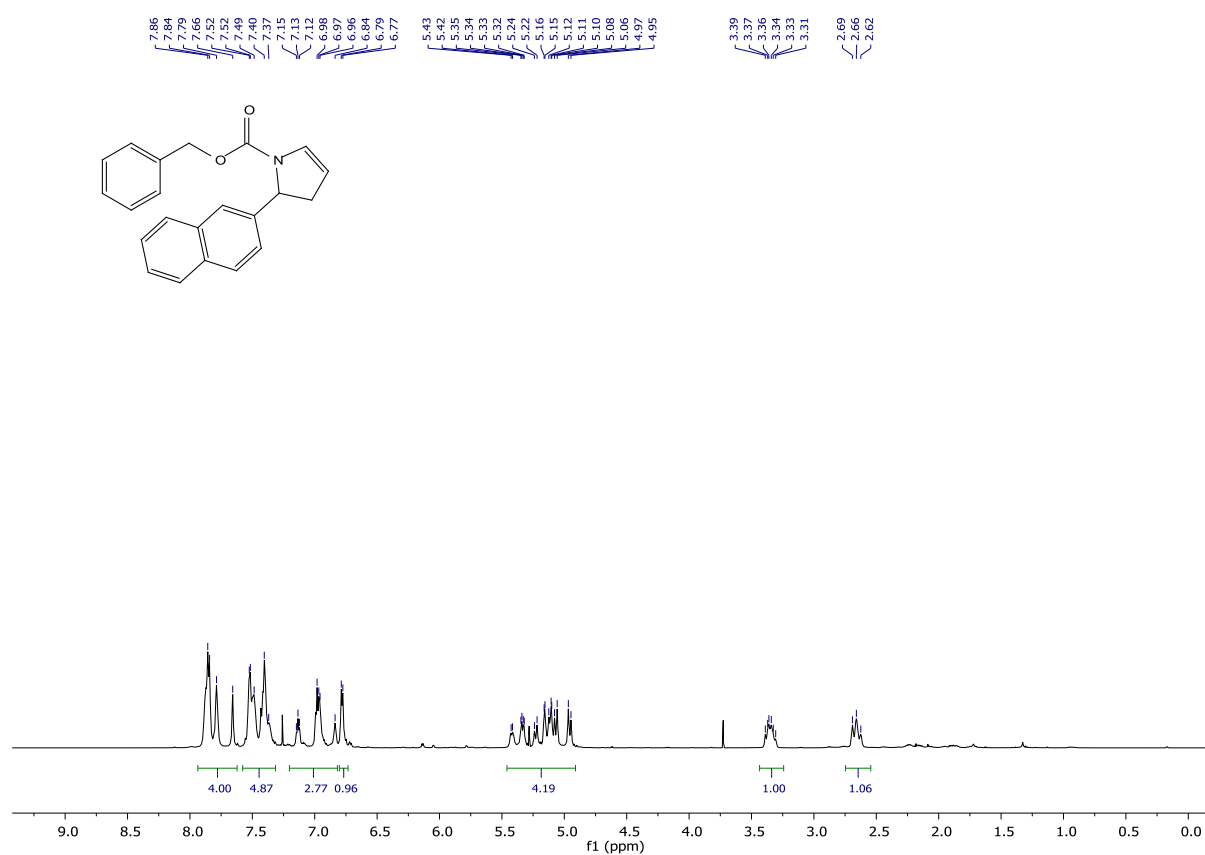
Benzyl 2-(2-chlorophenyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2f)



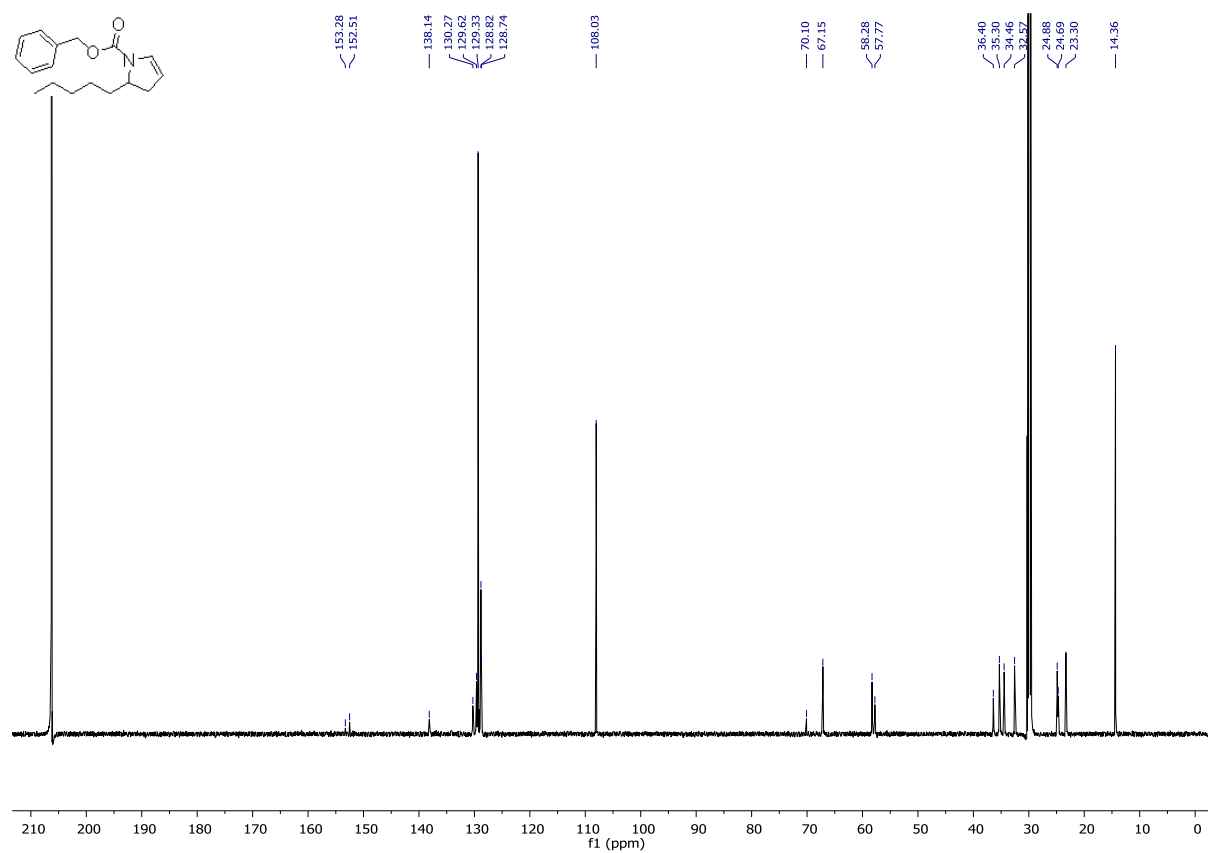
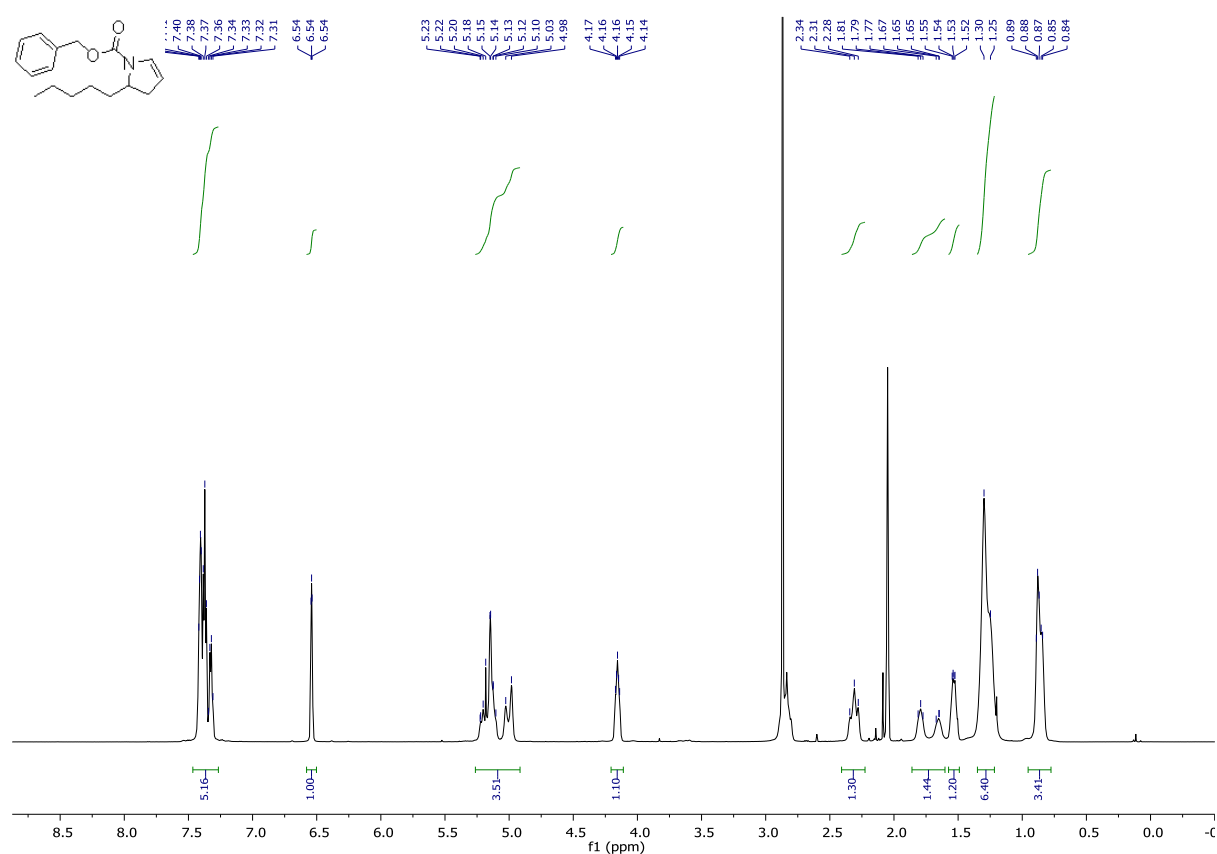
Benzyl 2-(p-tolyl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2g)



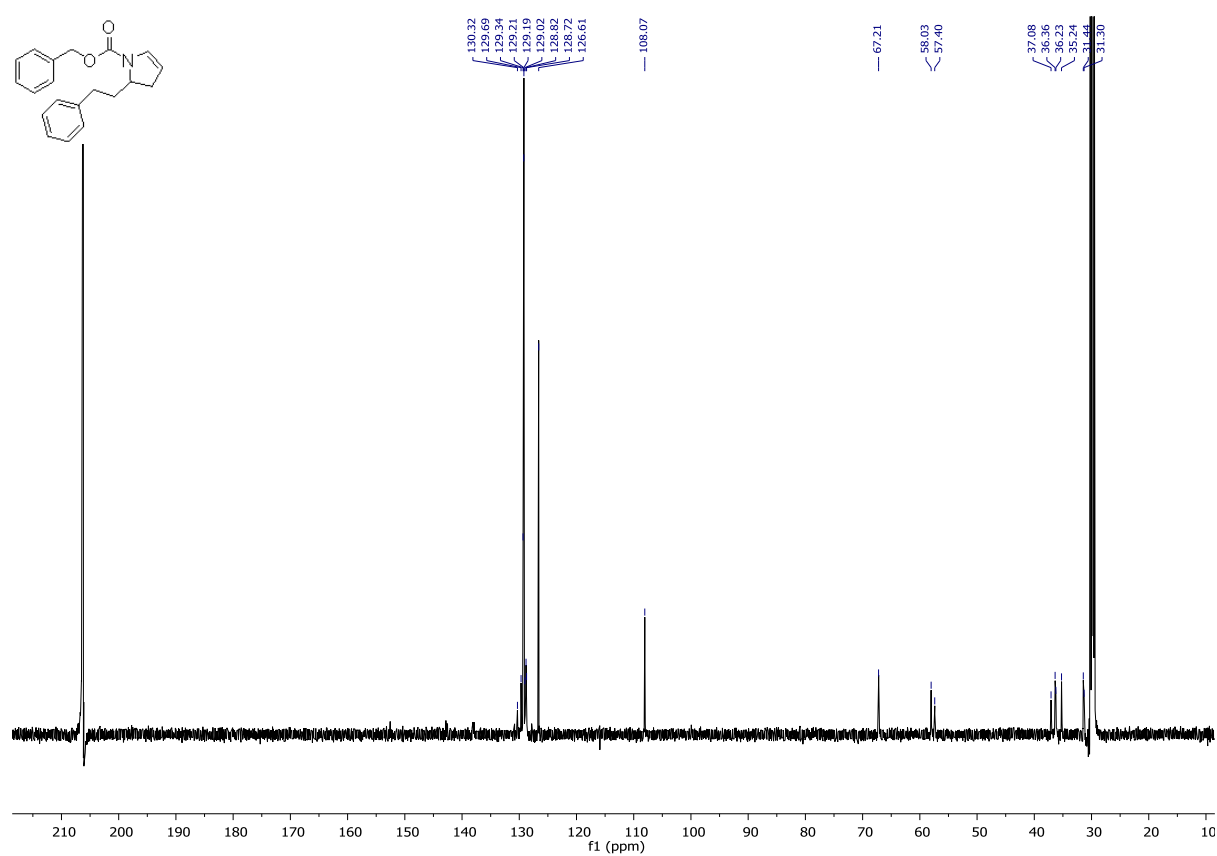
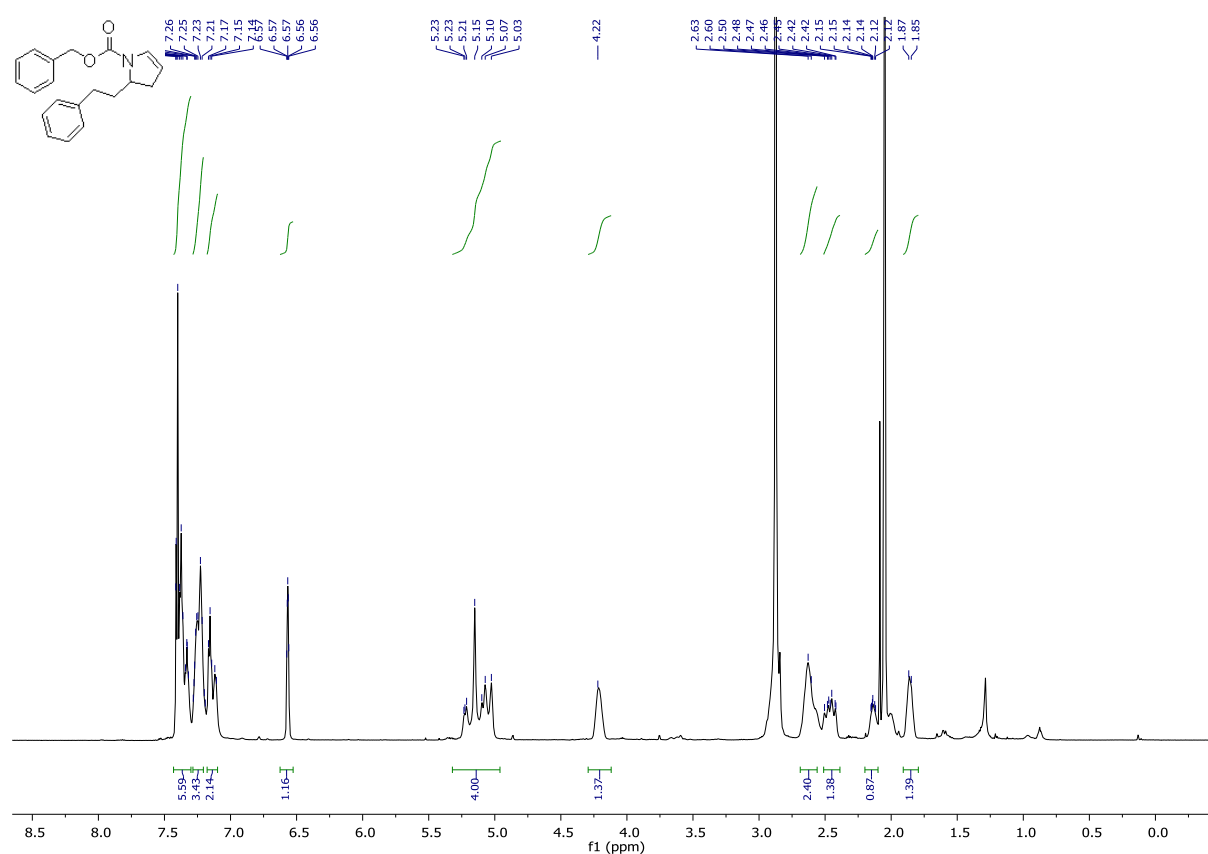
Benzyl 2-(naphthalen-2-yl)-2,3-dihydro-1H-pyrrole-1-carboxylate (2h)



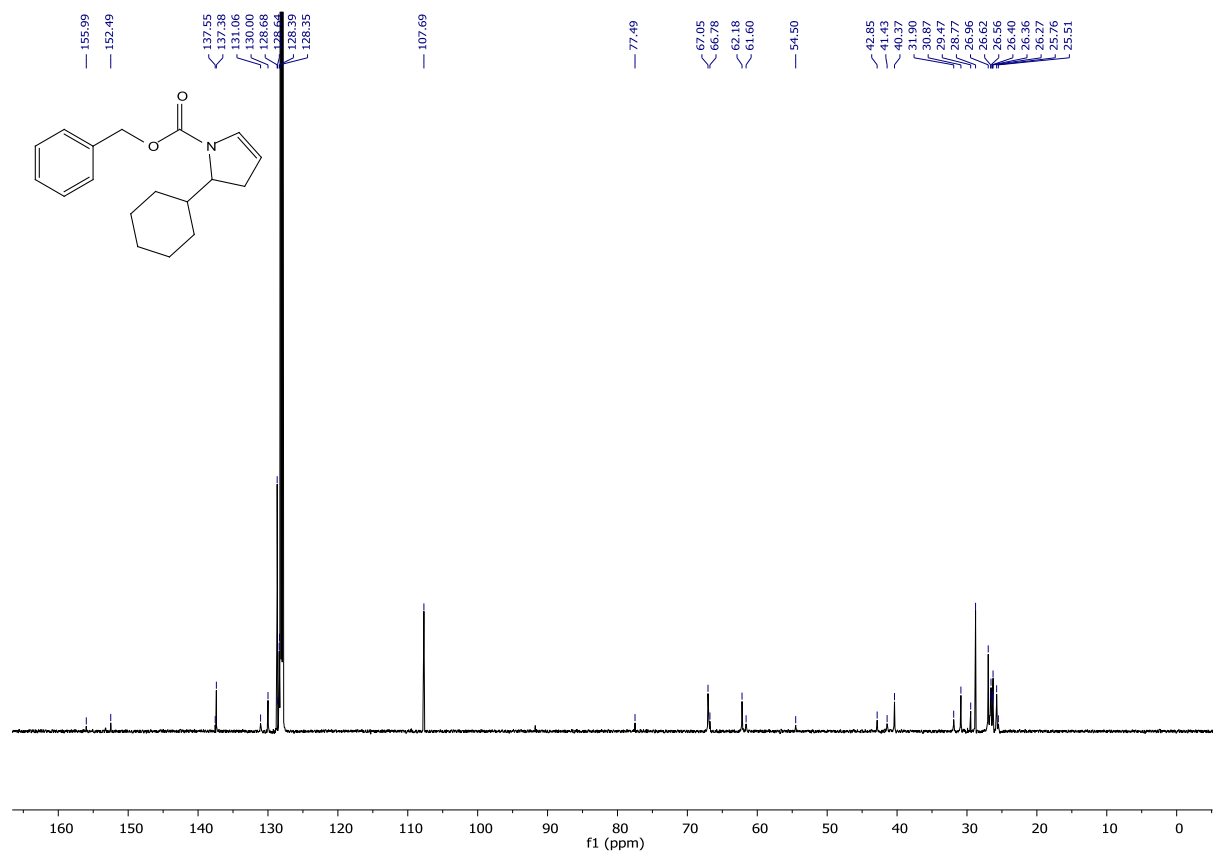
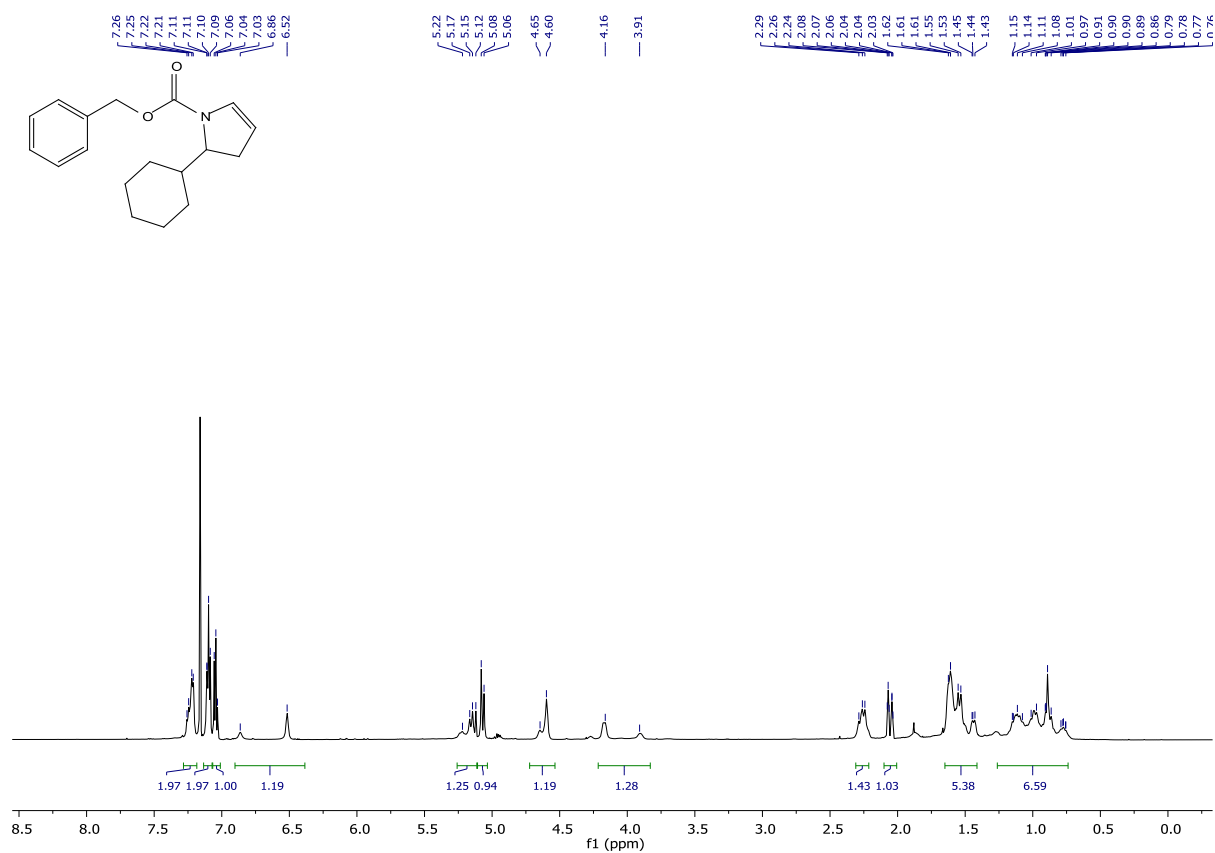
Benzyl 2-pentyl-2,3-dihydro-1*H*-pyrrole-1-carboxylate (2i)



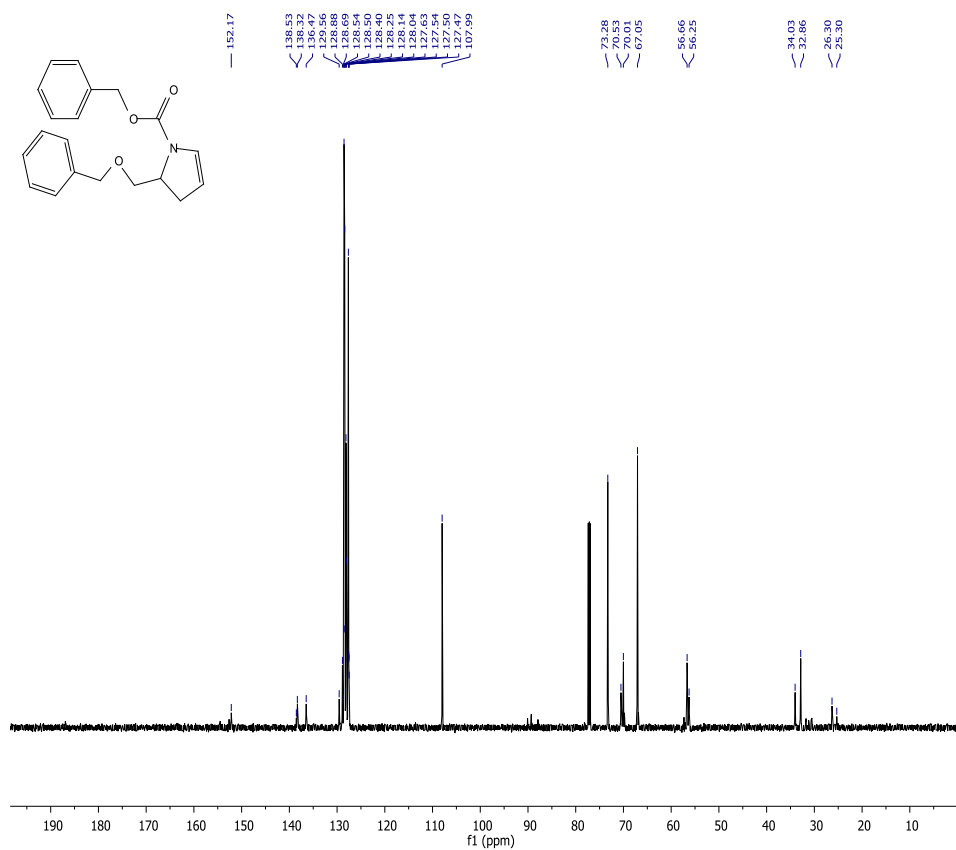
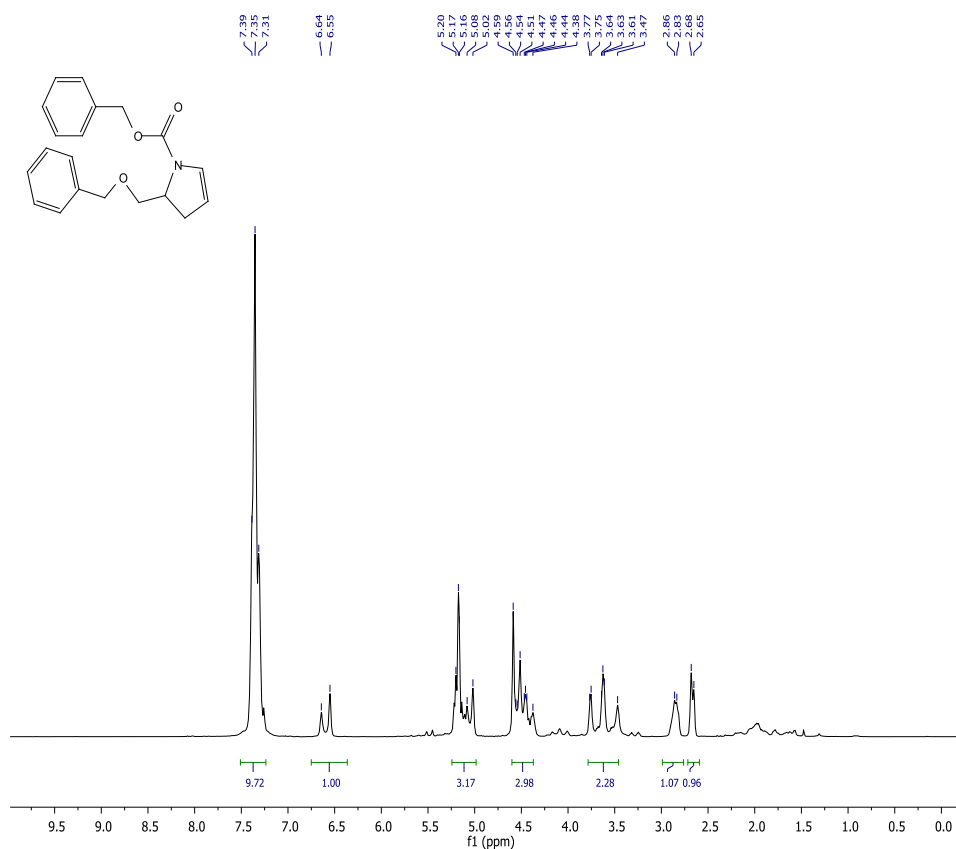
Benzyl 2-phenethyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2j)



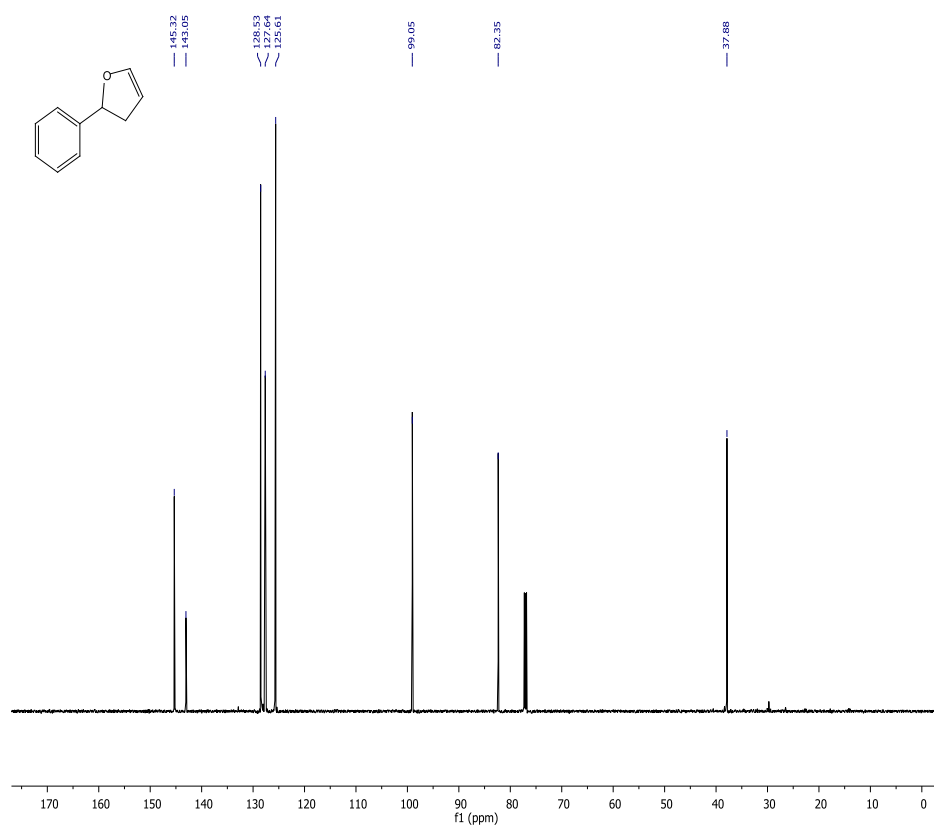
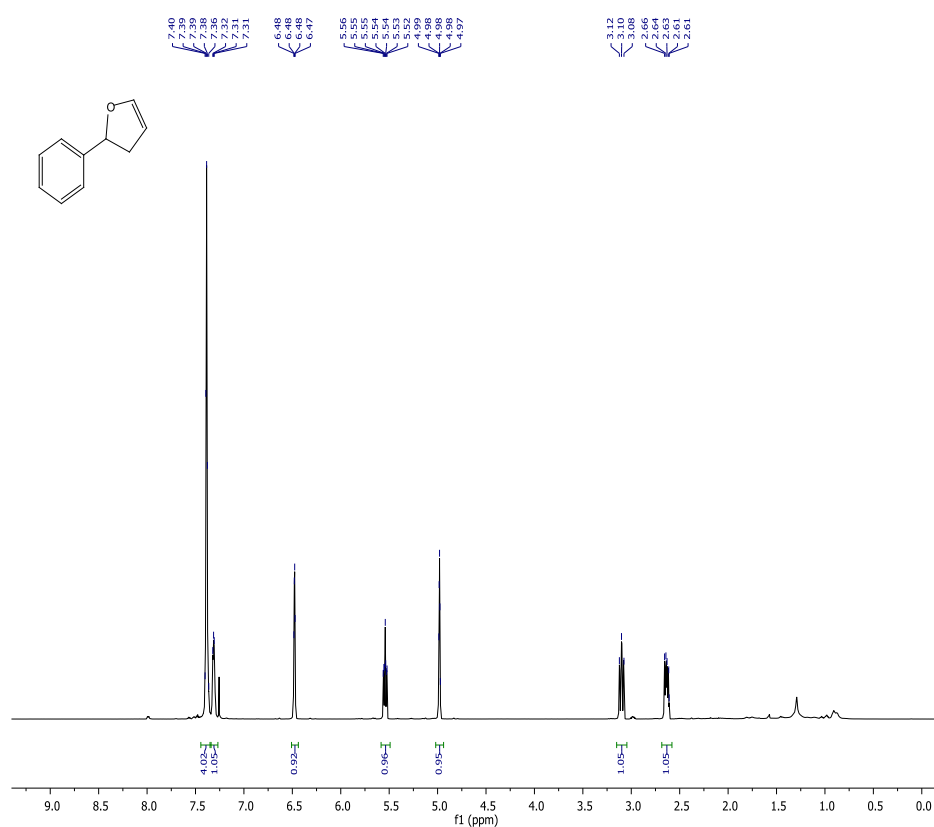
Benzyl 2-cyclohexyl-2,3-dihydro-1H-pyrrole-1-carboxylate (2k)



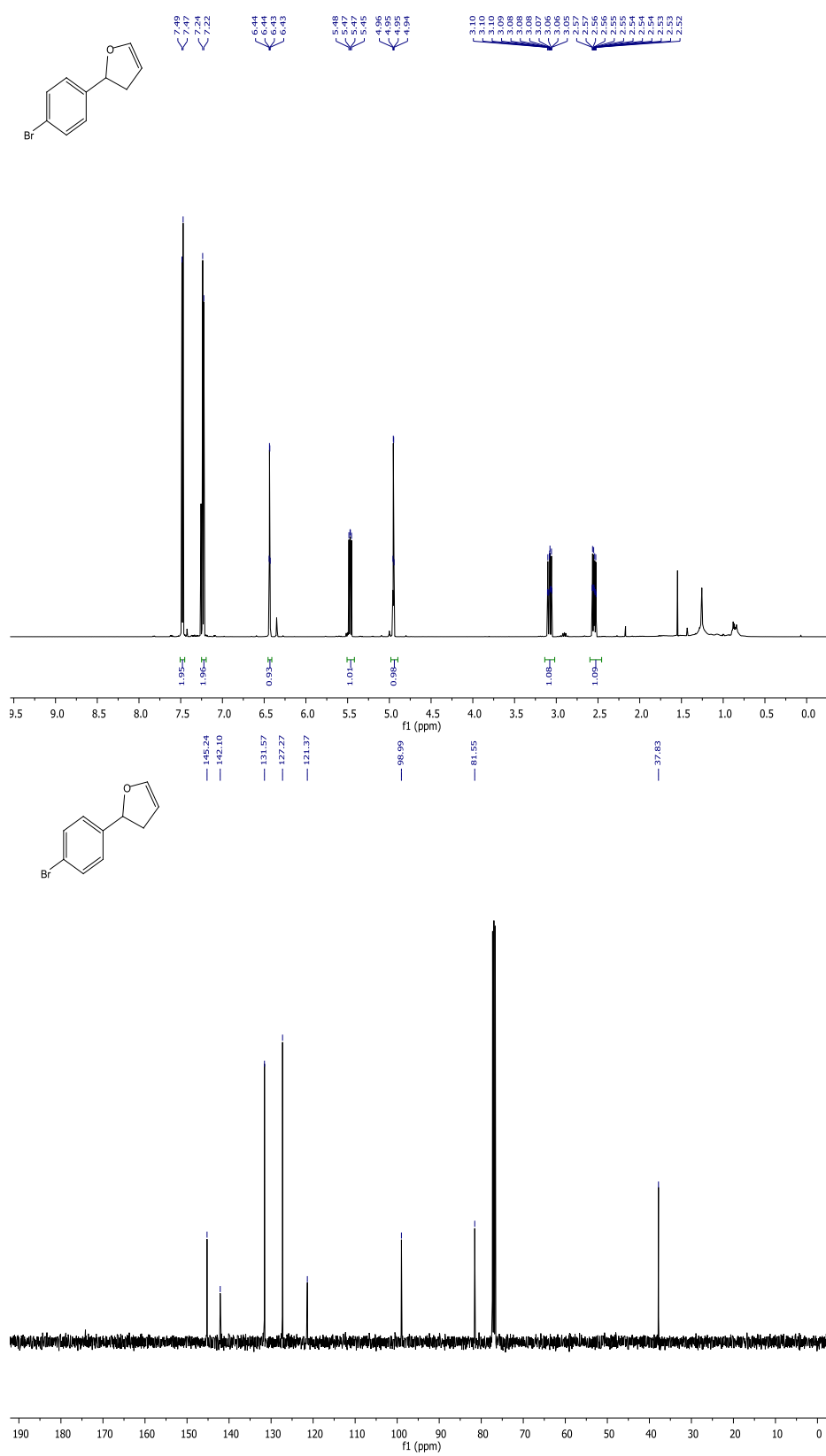
Benzyl 2-((benzyloxy)methyl)-2,3-dihydro-1*H*-pyrrole-1-carboxylate (2l)



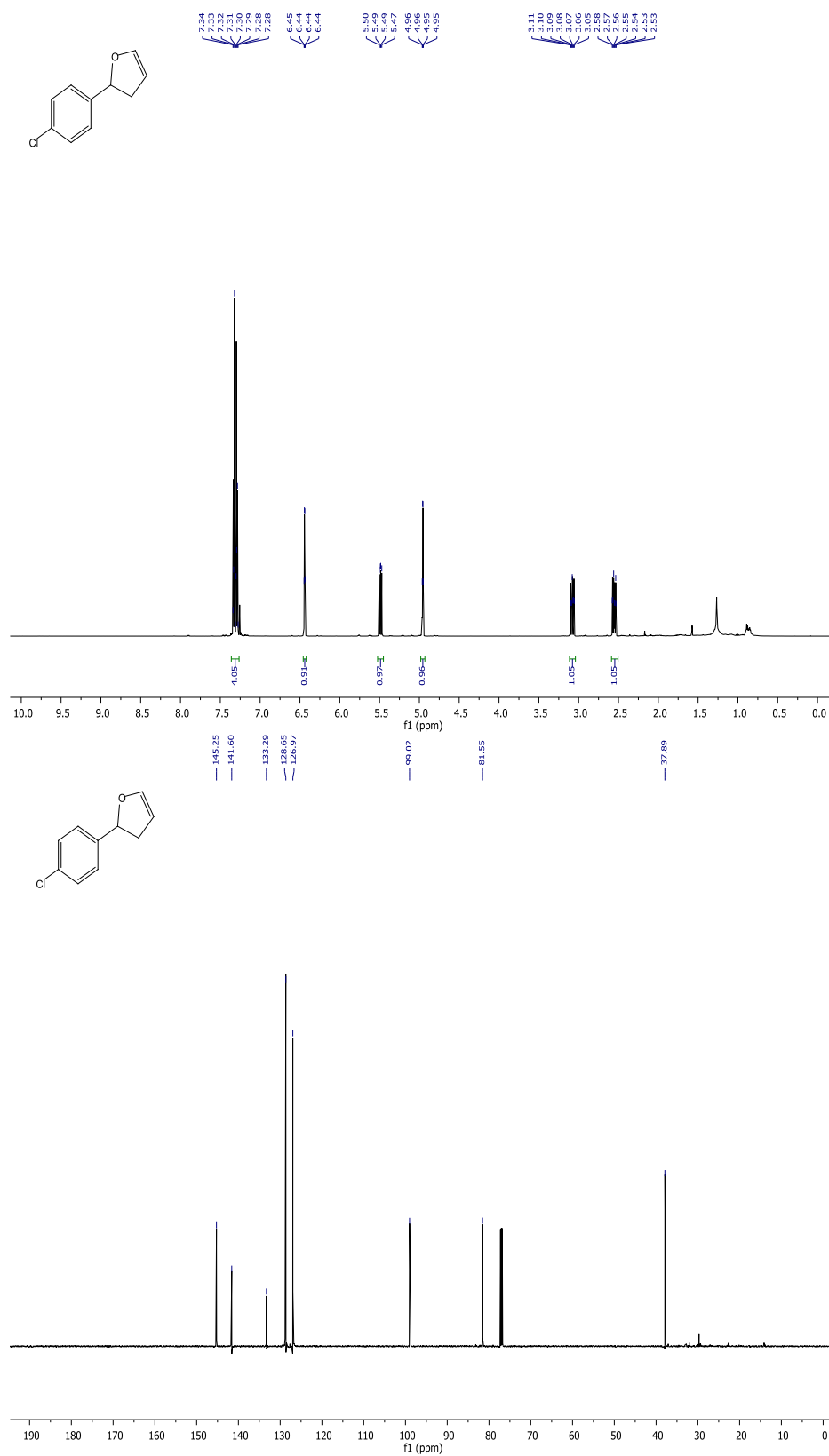
2-Phenyl-2,3-dihydrofuran (4a)



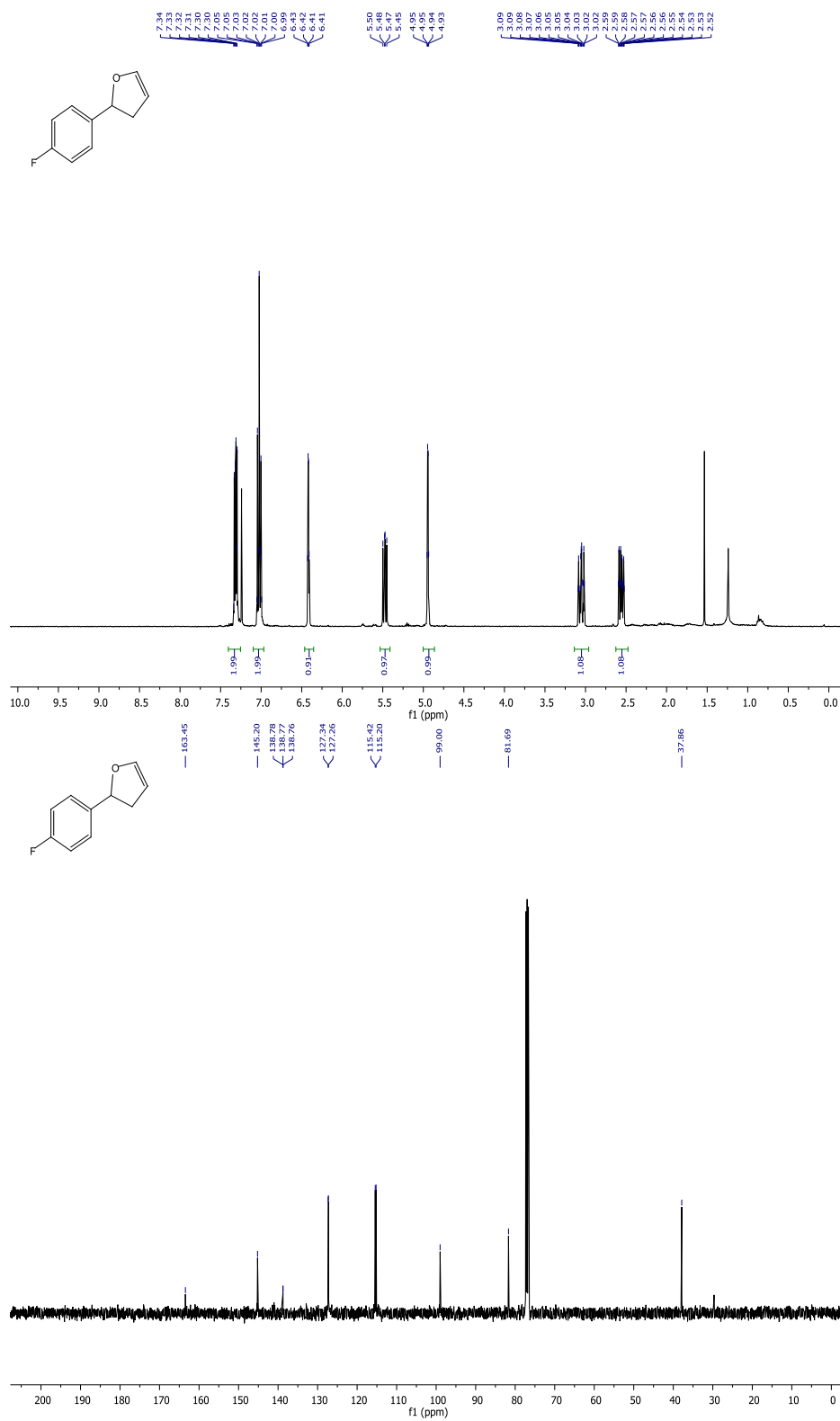
2-(4-Bromophenyl)-2,3-dihydrofuran (4b)

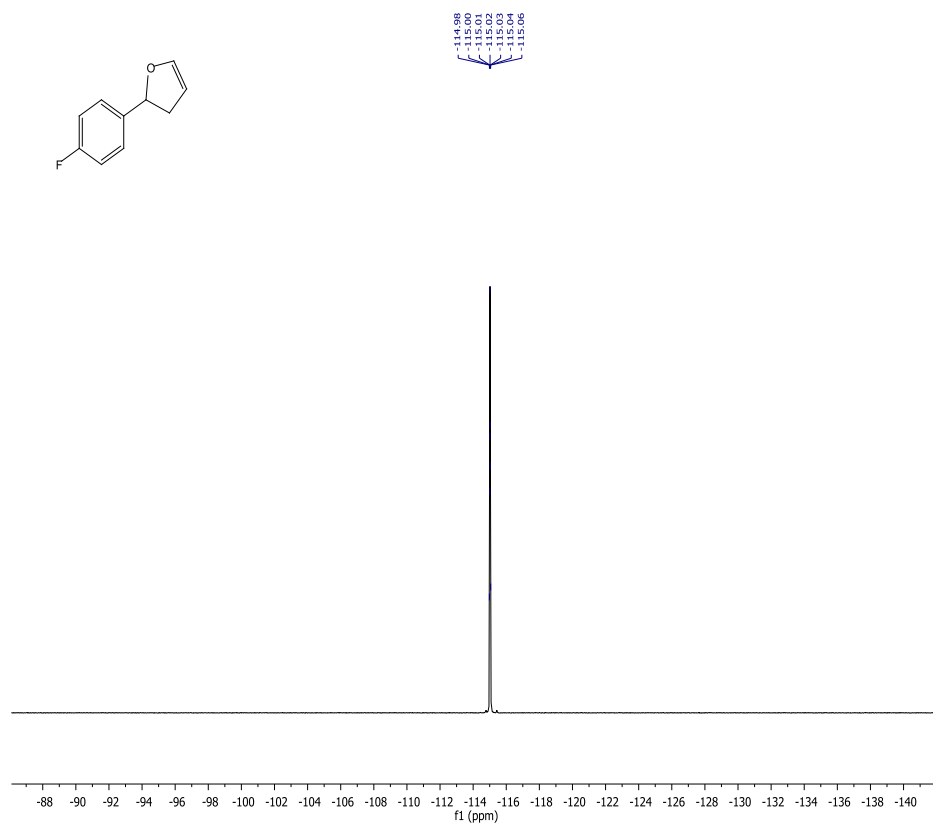


2-(4-Chlorophenyl)-2,3-dihydrofuran (4c)

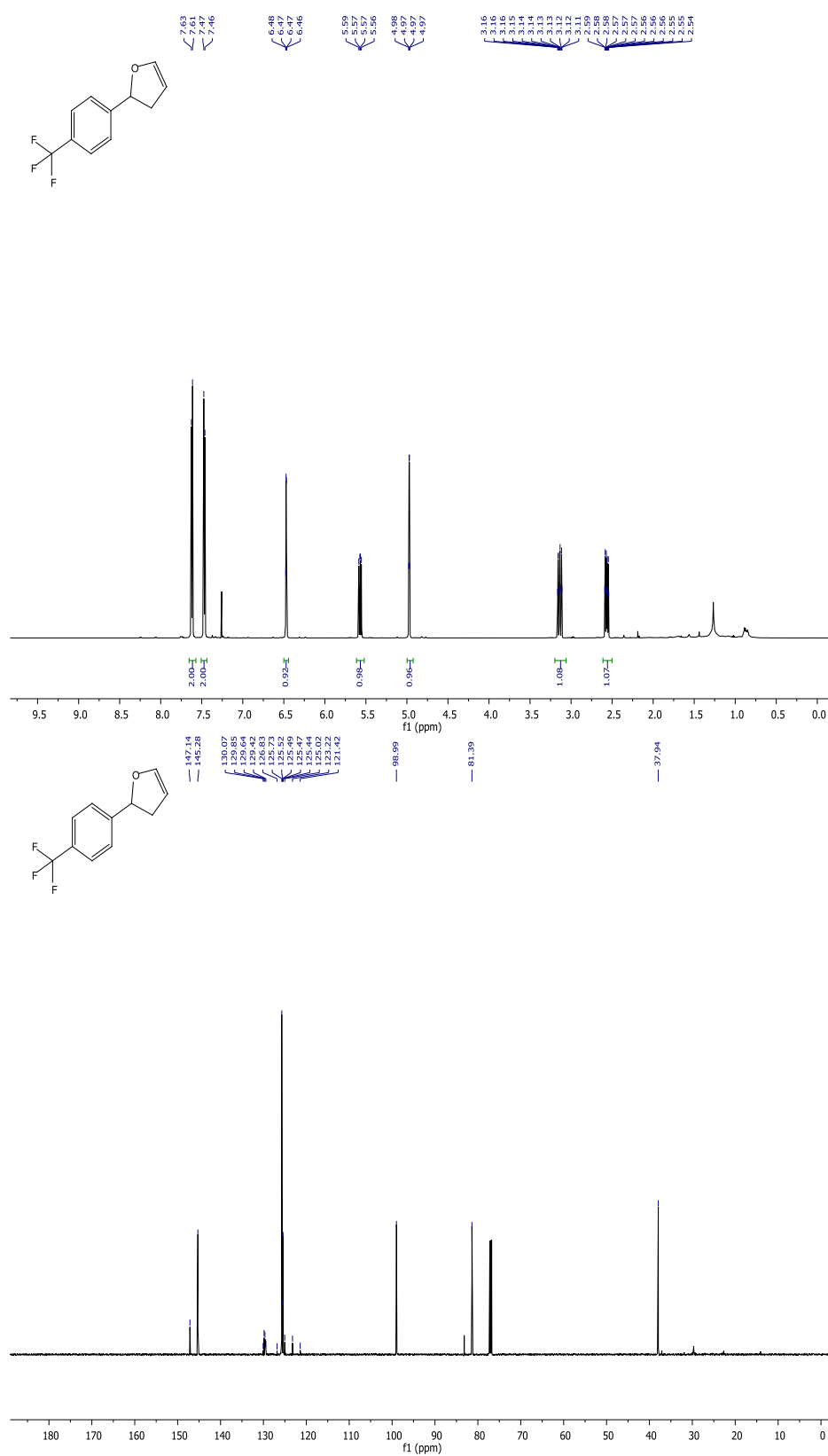


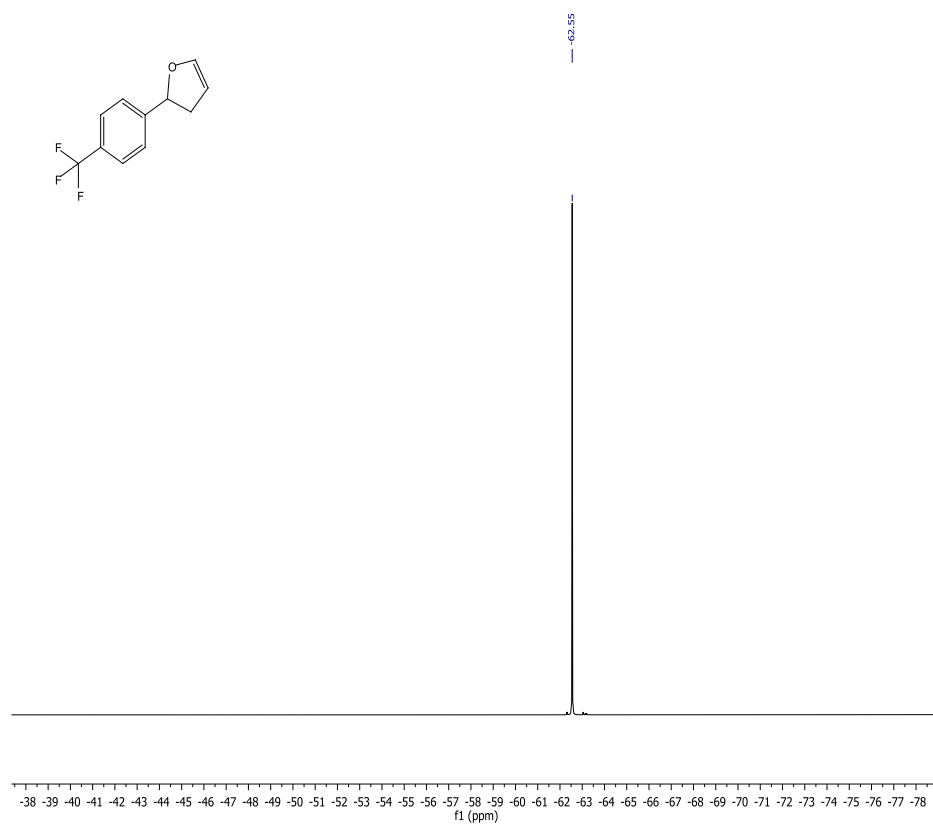
2-(4-Fluorophenyl)-2,3-dihydrofuran (4d)



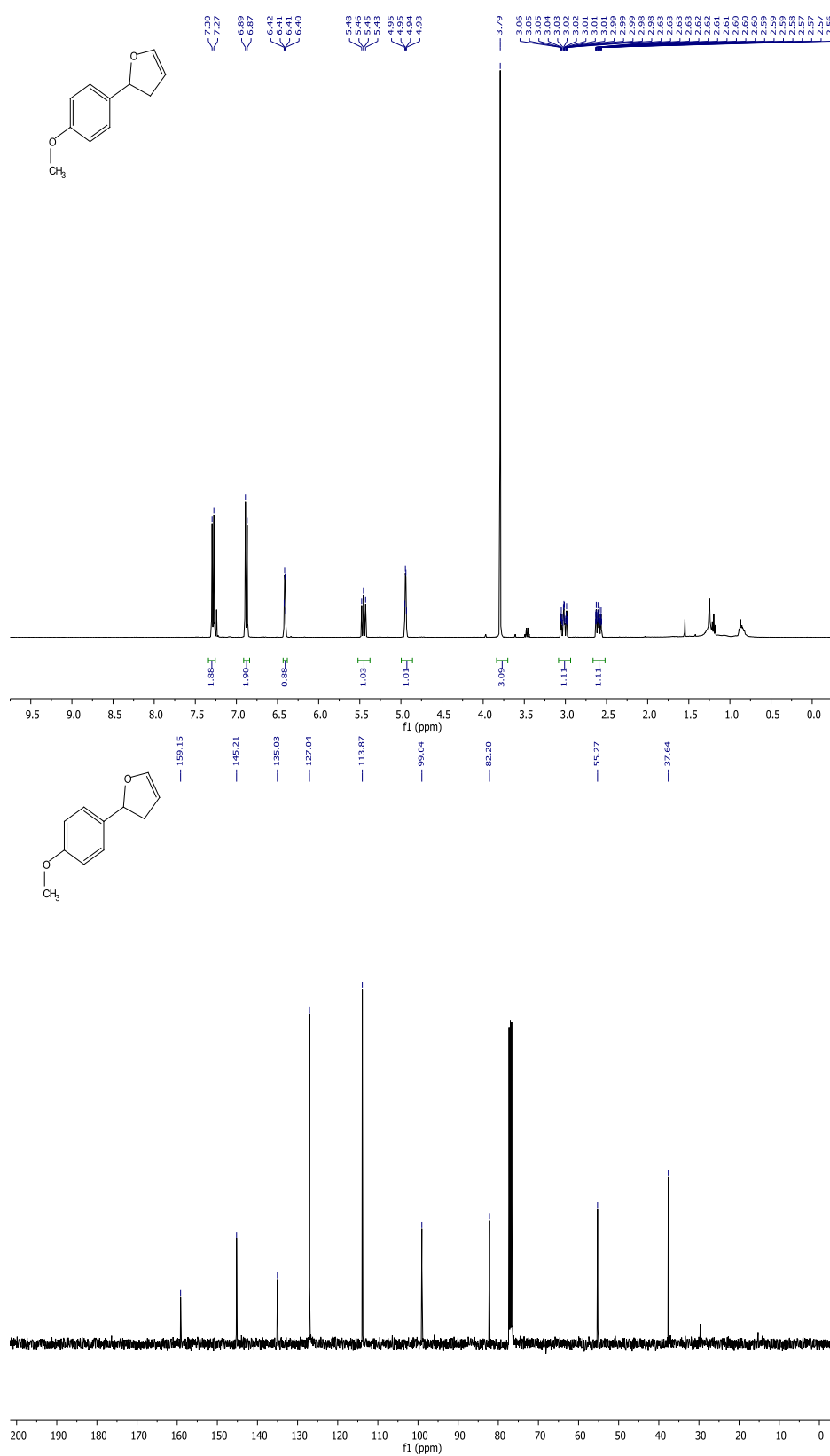


2-(4-(Trifluoromethyl)phenyl)-2,3-dihydrofuran (4e)

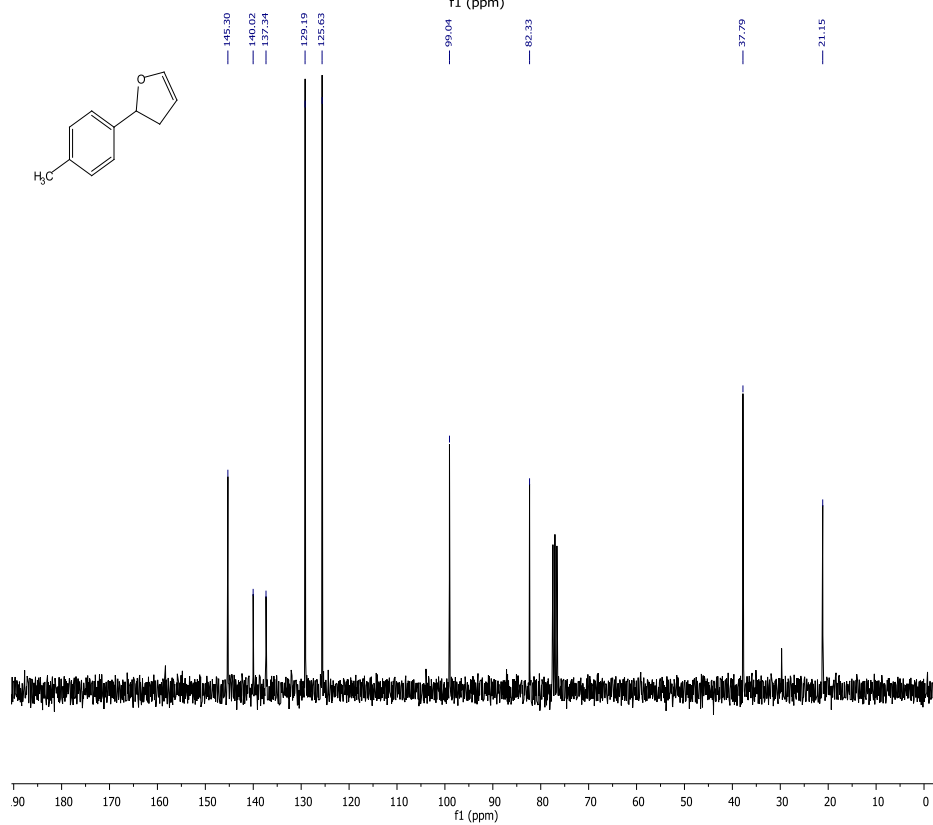
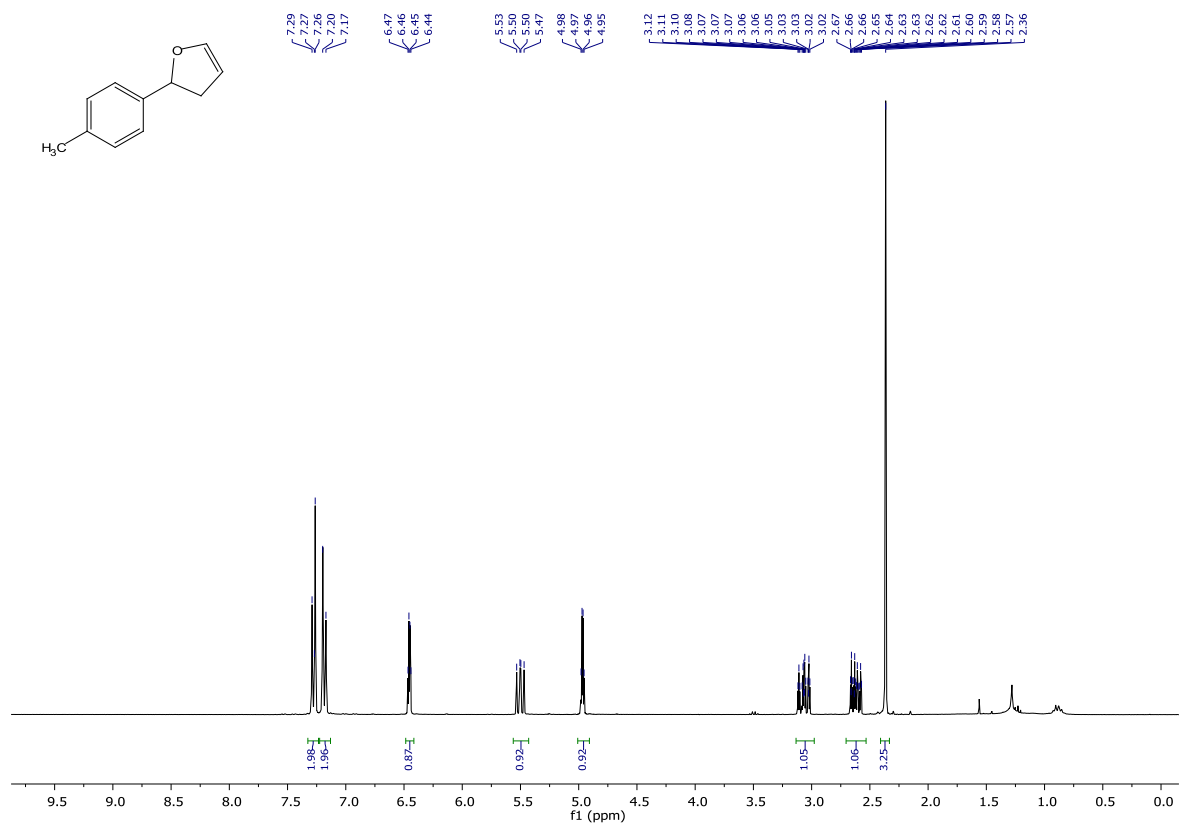




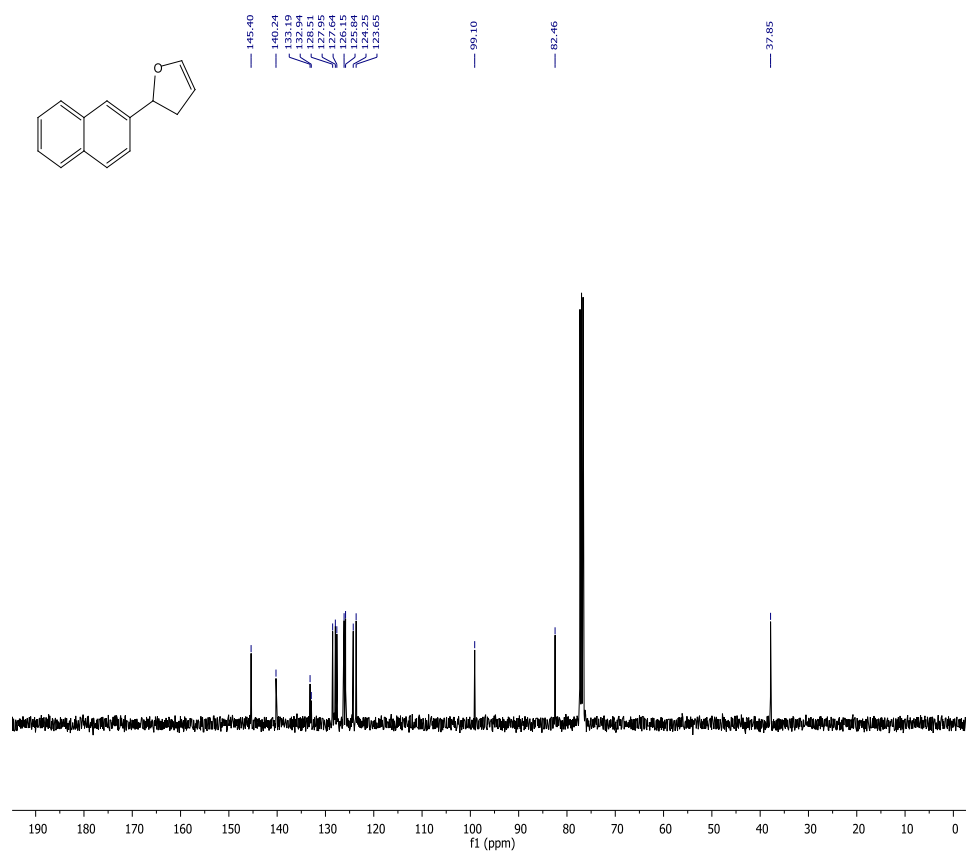
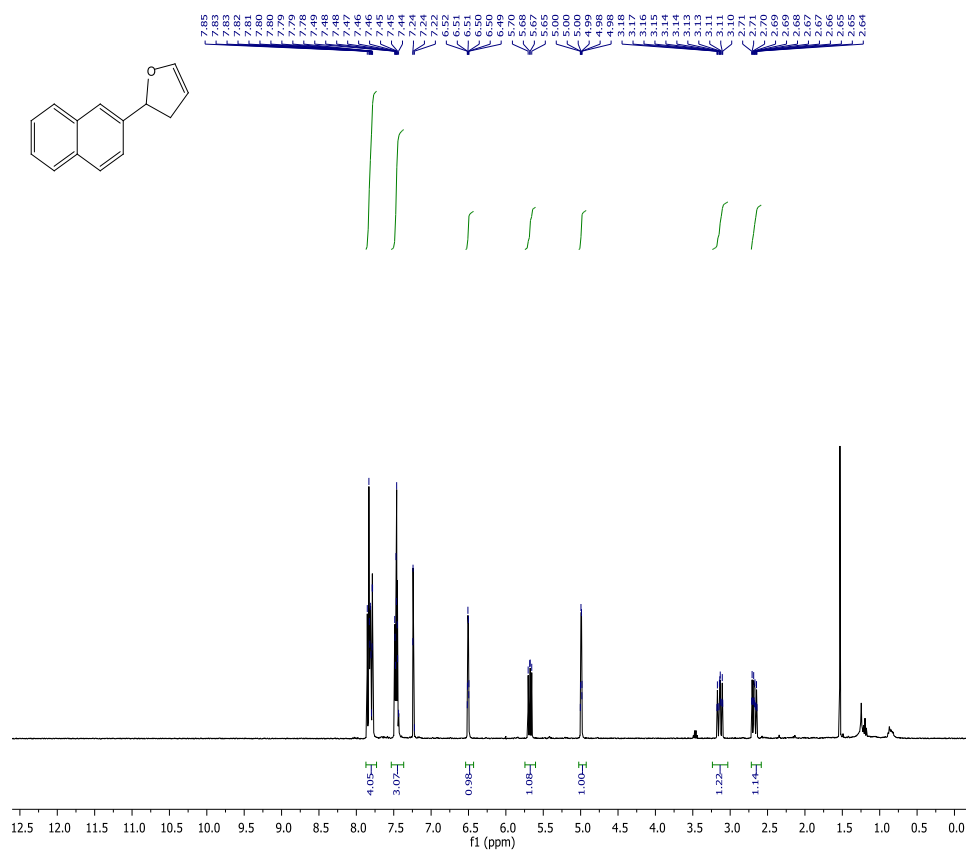
2-(4-Methoxyphenyl)-2,3-dihydrofuran (4f)



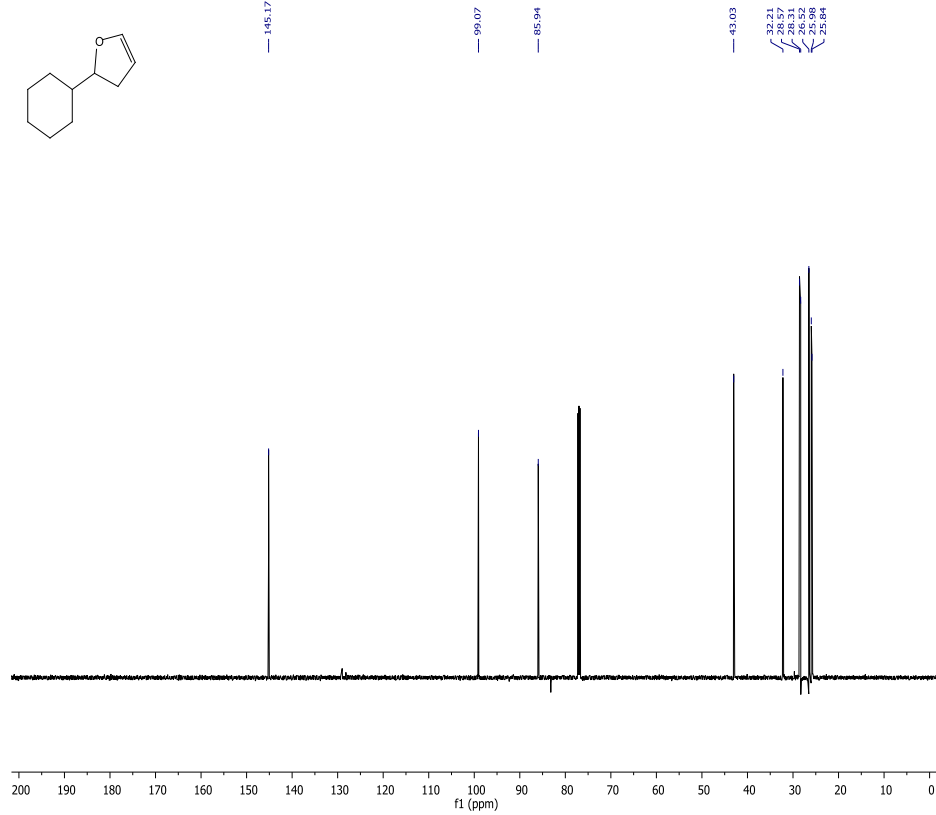
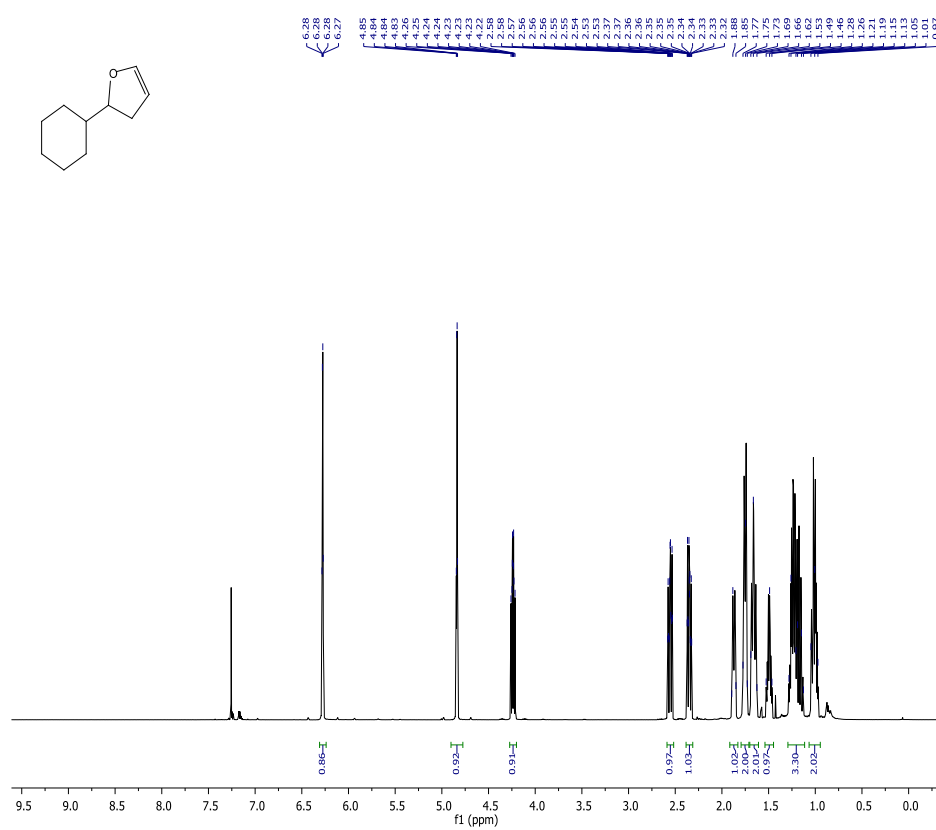
2-(p-Tolyl)-2,3-dihydrofuran (4g)



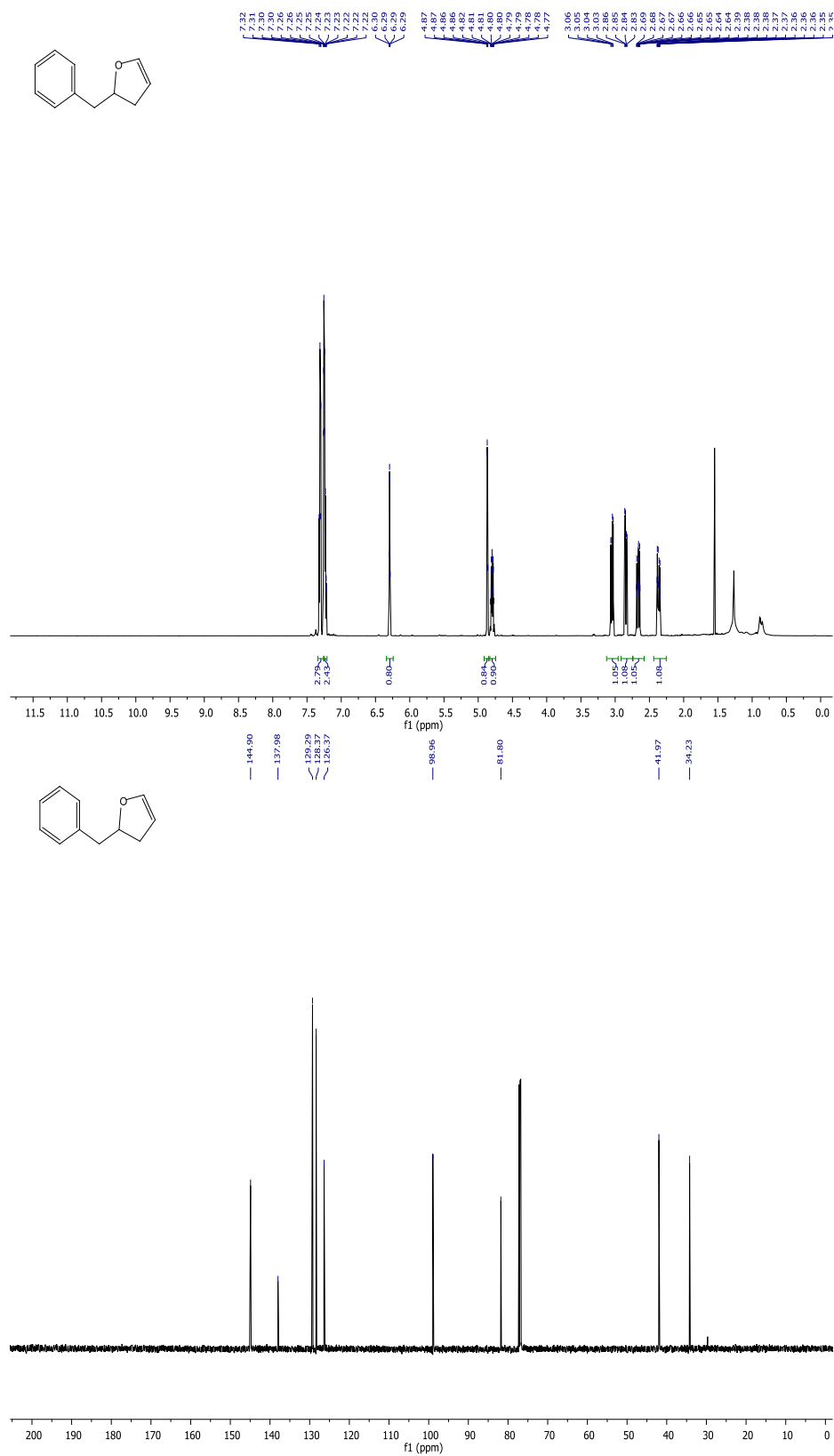
2-(Naphthalen-2-yl)-2,3-dihydrofuran (4h)



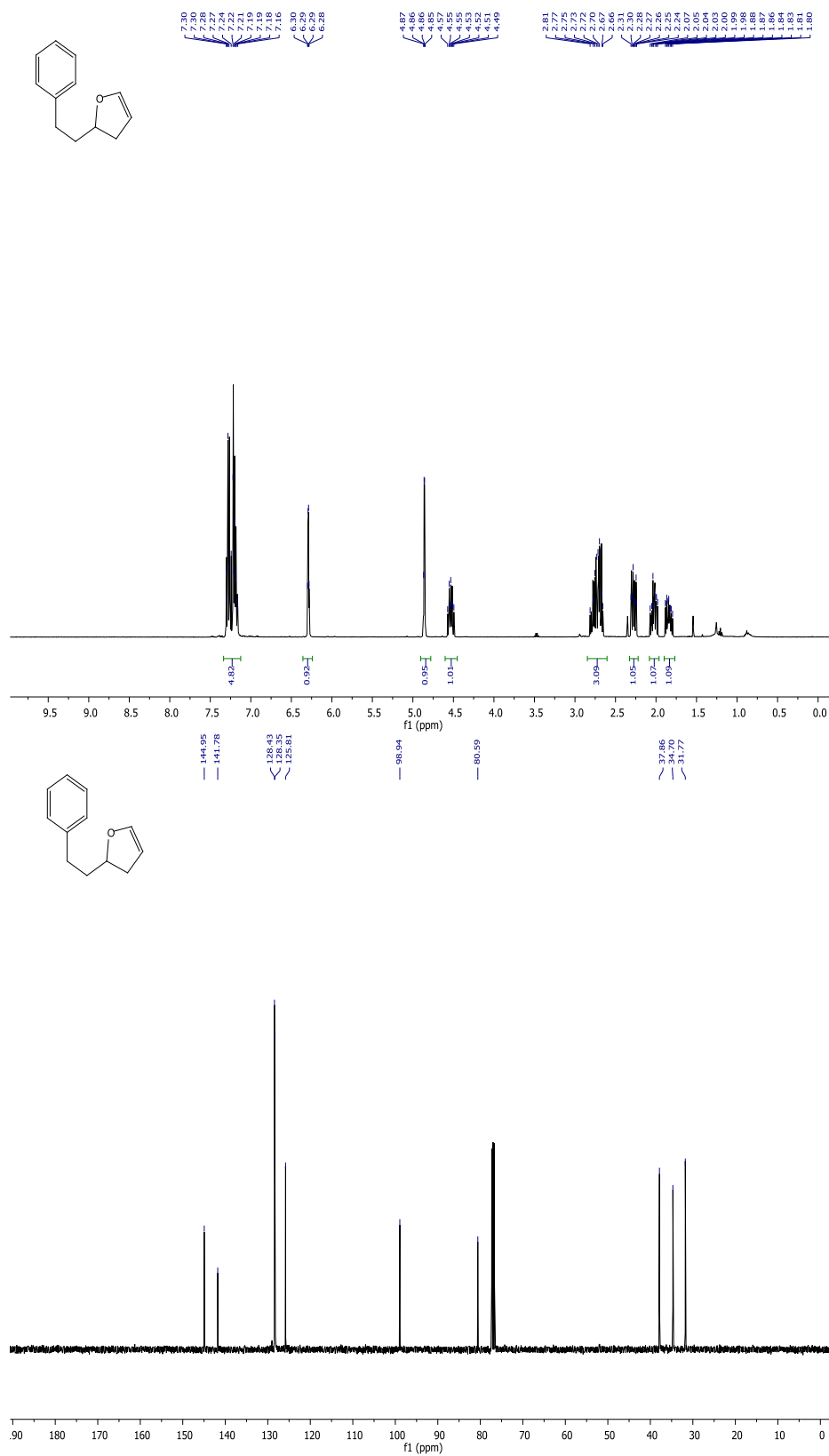
2-Cyclohexyl-2,3-dihydrofuran (4i)



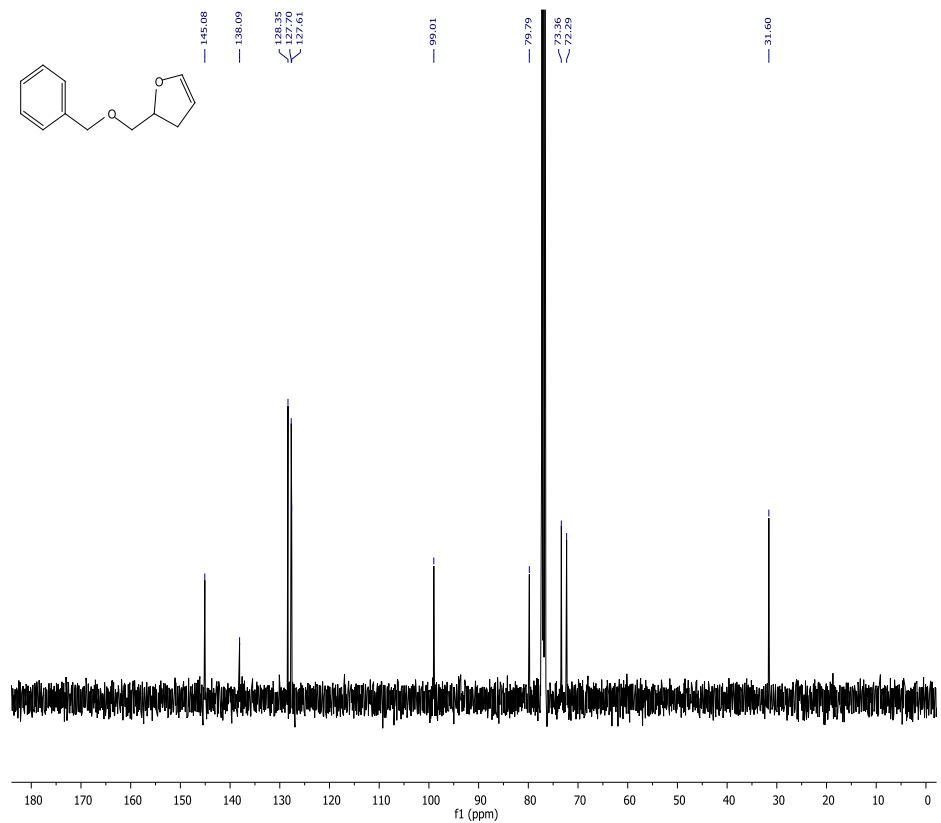
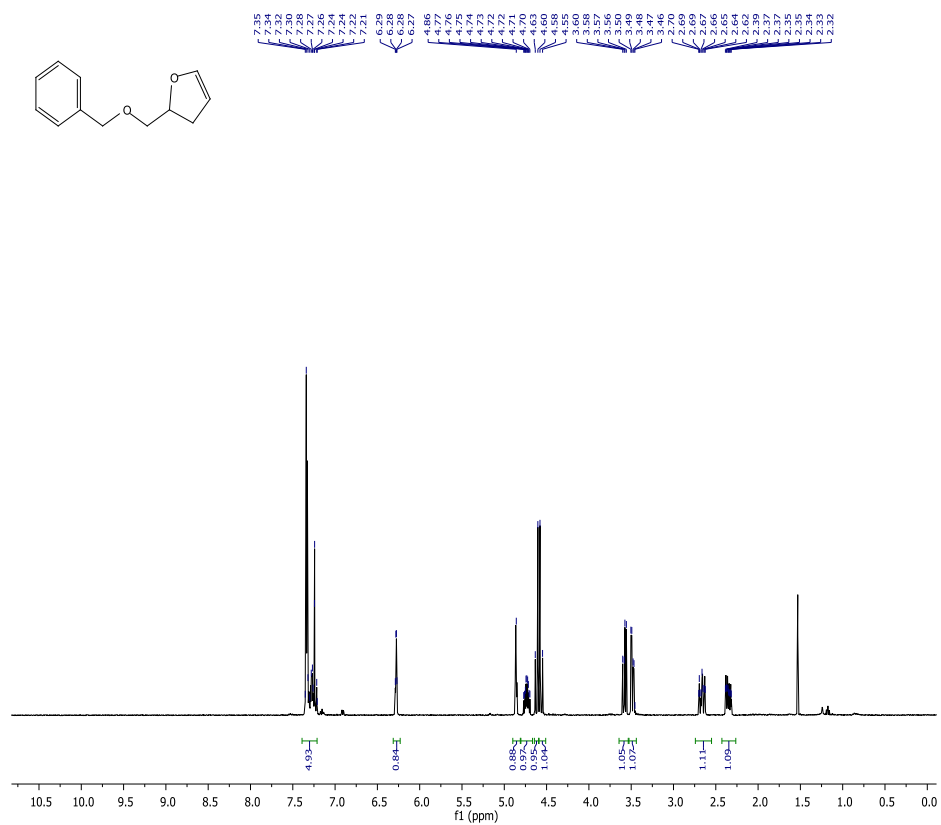
2-Benzyl-2,3-dihydrofuran (4j)



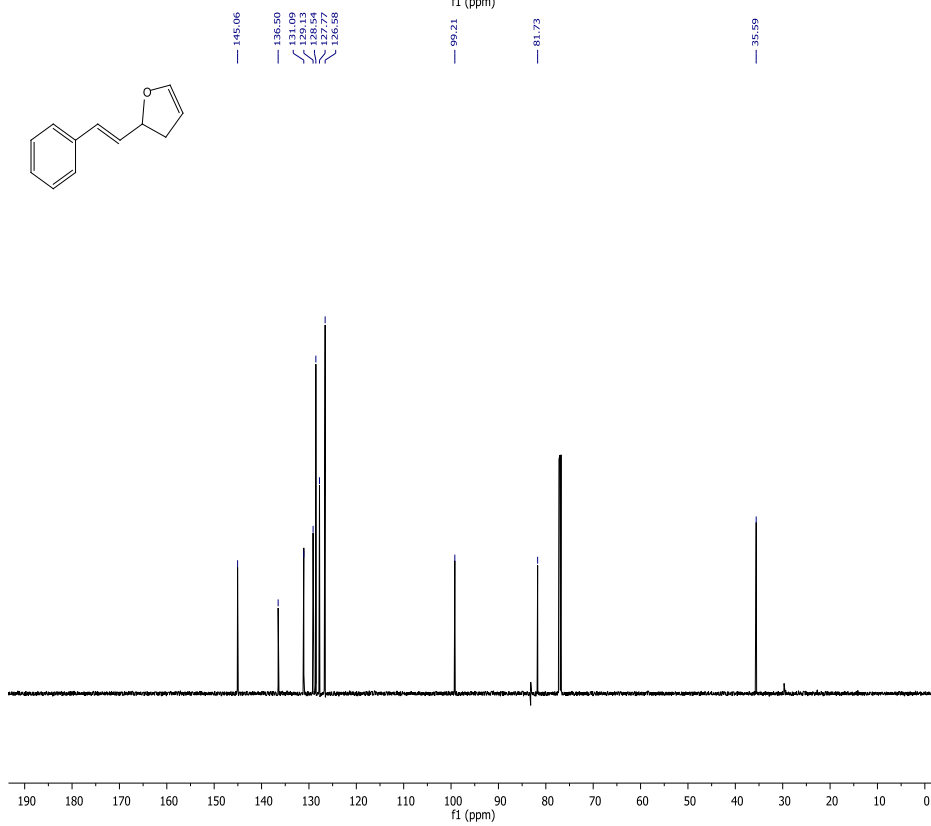
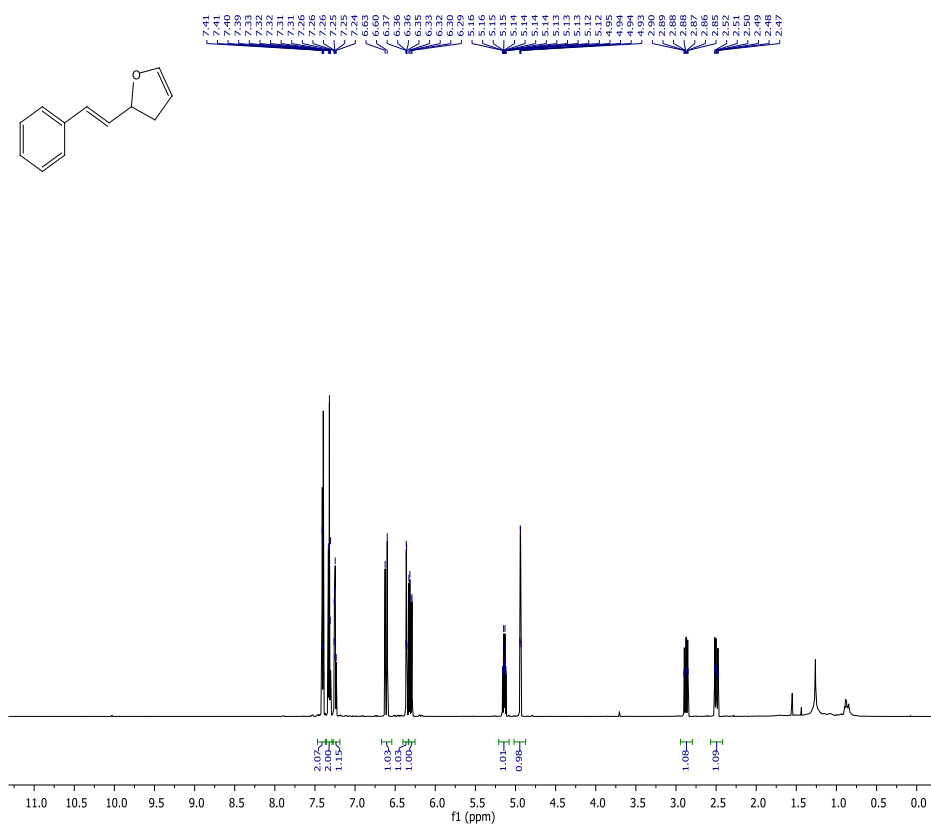
2-Phenethyl-2,3-dihydrofuran (4k)



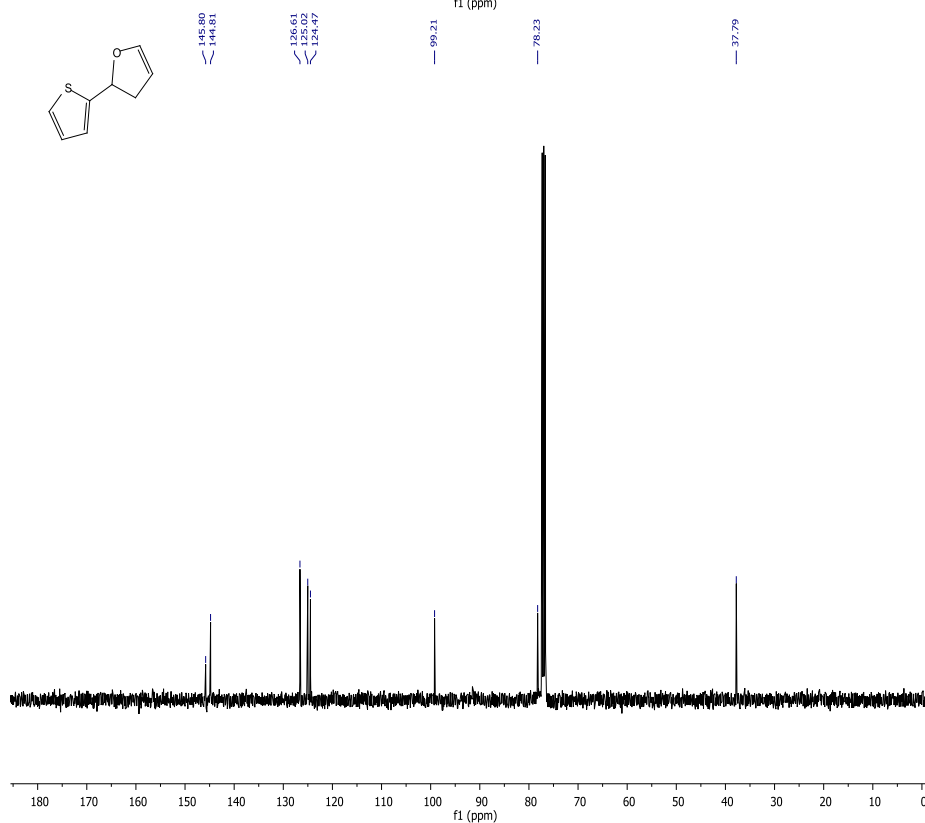
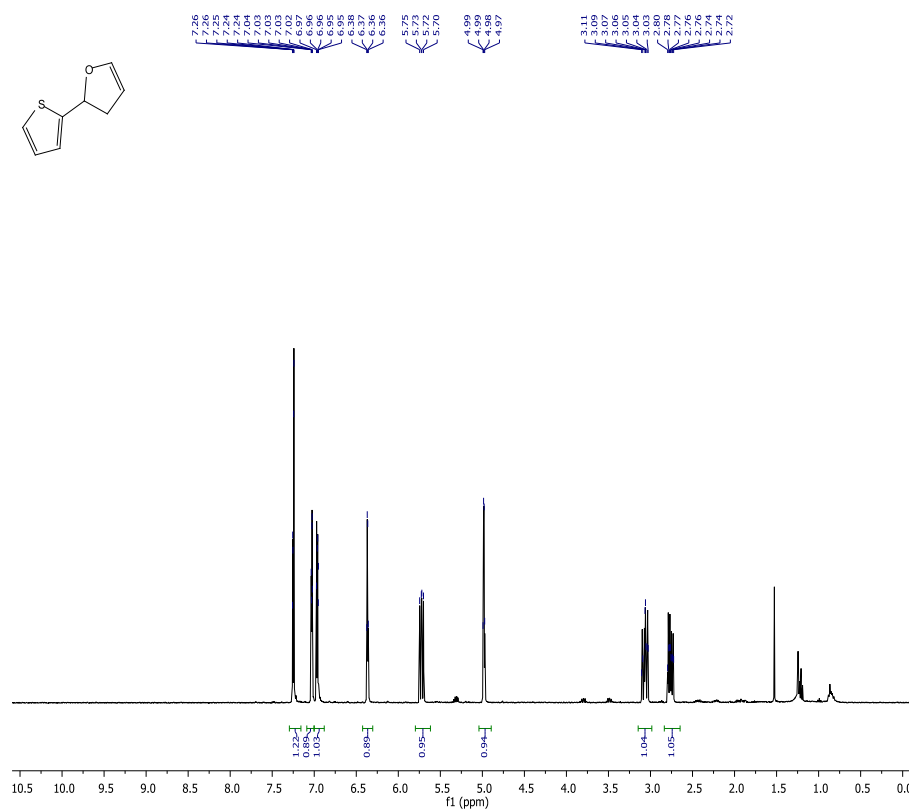
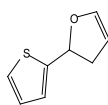
2-((Benzyloxy)methyl)-2,3-dihydrofuran (4l)



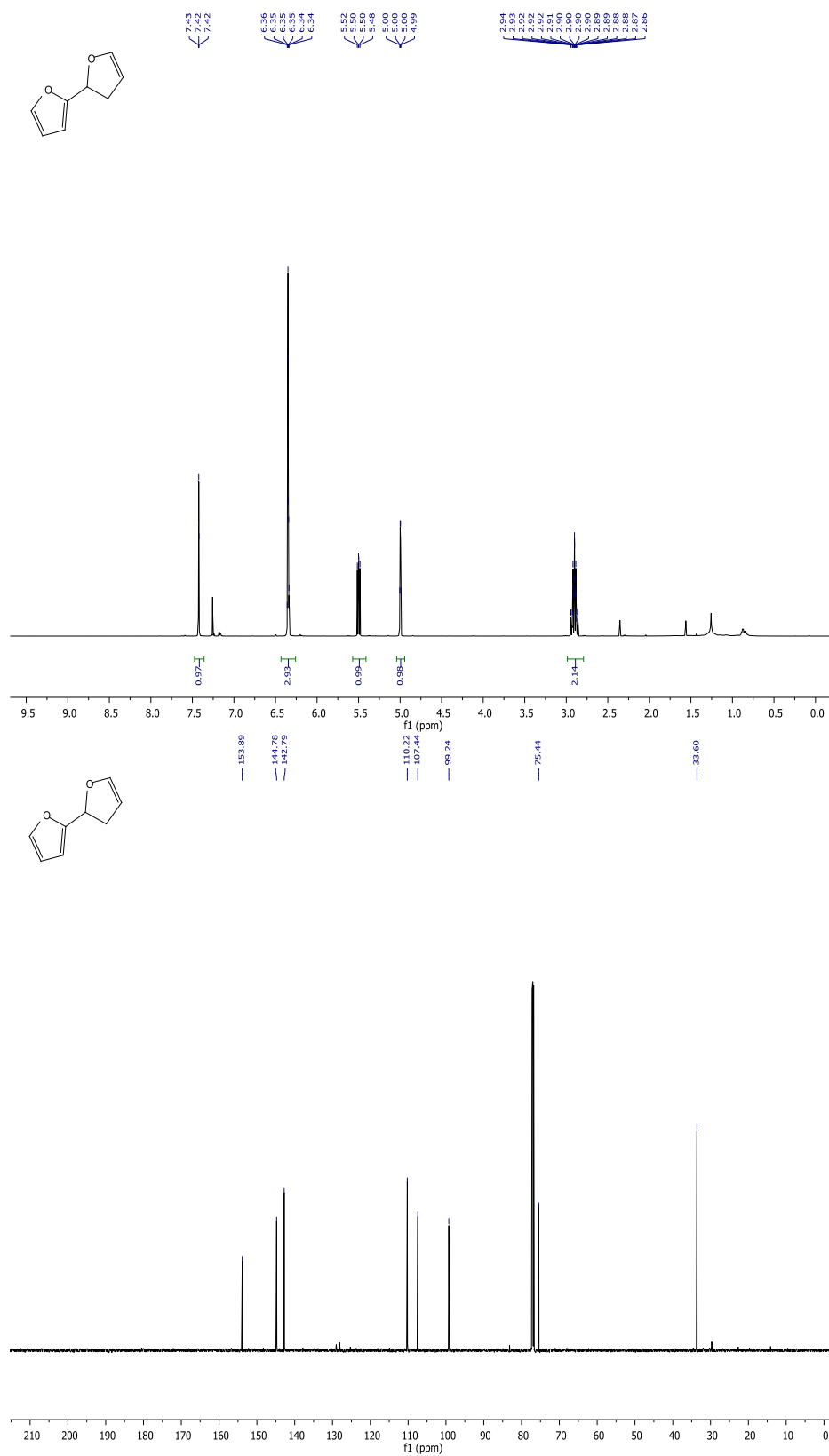
(E)-2-styryl-2,3-dihydrofuran (4m)



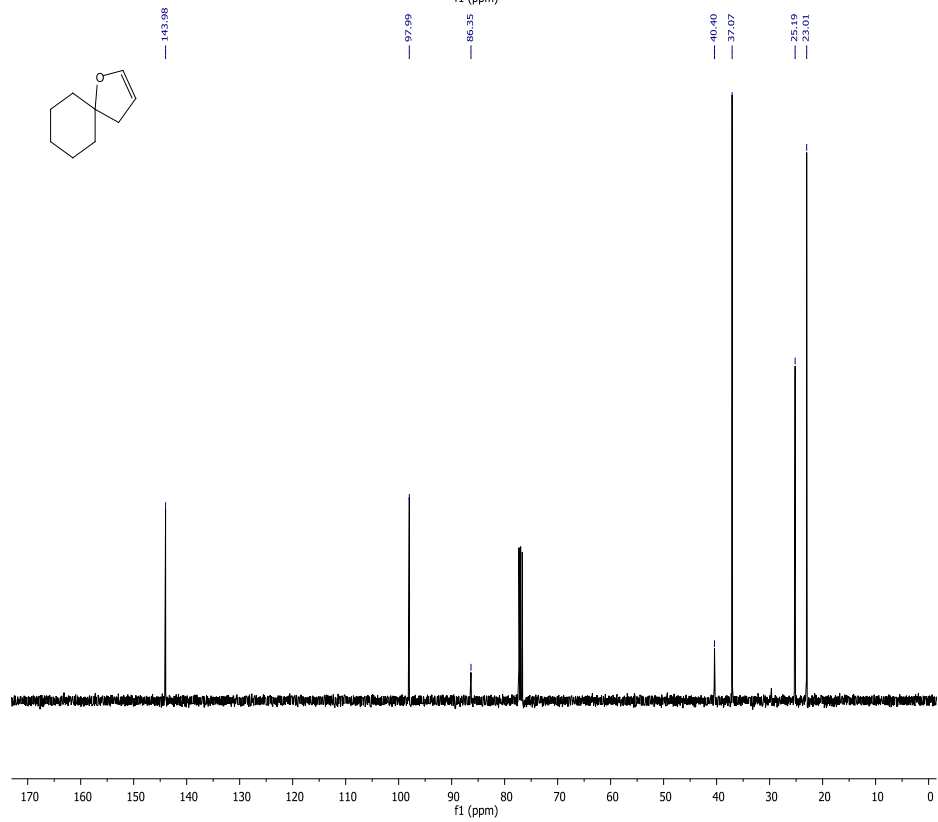
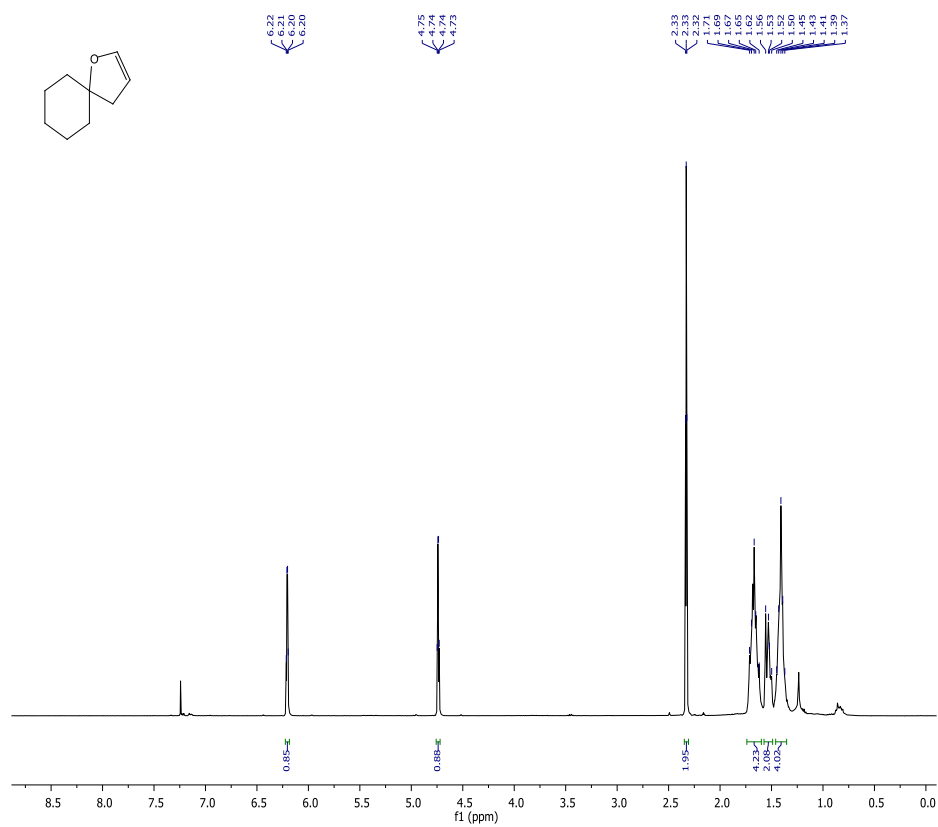
2-(Thiophen-2-yl)-2,3-dihydrofuran (4n)



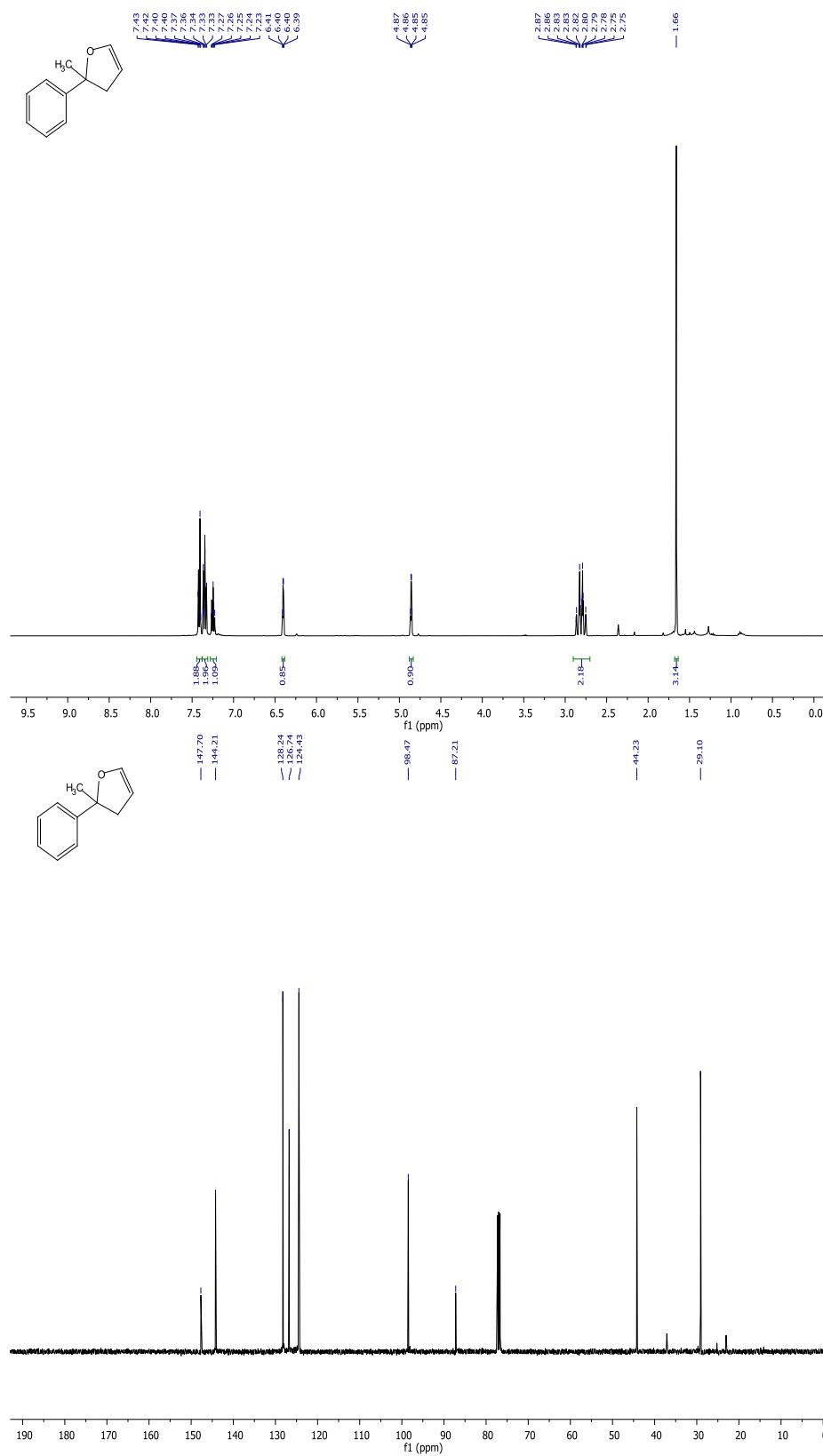
2,3-Dihydro-2,2'-bifuran (4o)



1-Oxaspiro[4.5]dec-2-ene (4p)



2-Methyl-2-phenyl-2,3-dihydrofuran (4q)



(2S,3S)-3-methyl-2-phenyl-2,3-dihydrofuran (4r)

