Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Direct Access to Polycyclic Imidazolium Salts via Decarboxylative Condensation of α-Enaminones with Proline

Yuval Simha, Gil Daniels, Amalya Goldman, Elihay Kuniavsky and Dmitry Tsvelikhovsky

The Institute for Drug Research, Faculty of Medicine, The Hebrew University of Jerusalem, Jerusalem 91120, Israel

E-mail: dmitryt@ekmd.huji.ac.il

Table of contents:

General information

- Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60-F_{254} aluminum plates (Merck) and/or gas chromatography-mass spectrometry (GCMS). Visualization of compounds on TLC was accomplished by irradiation with UV light at 254 nm and/or vanillin stain. GCMS Analysis was performed with 'Agilent 7820A' gas chromatograph equipped with 'Agilent 5975' quadrupole mass selective detector, using Agilent HP-5MS capillary column (30 m, 0.25 mm, 0.25 μm film).
- Column chromatography was performed using silica gel 60 (particle size 0.040-0.063 mm) purchased from Sigma-Aldrich.
- Proton and Carbon NMR spectra were recorded on Varian Mercury 300 MHz spectrometer in deuterated solvent. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm). ^{13}C Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). Data is reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet), integration and coupling constants (Hz).
- High resolution mass spectra were determined on a ThermoScientific LTQ Orbitrap XL (FTMS).
- Infrared (IR) spectra were recorded on a ThermoFischer Scientific NICOLET iS10 spectrometer.

Thermal Analysis

- The thermal decomposition temperature was recorded in nitrogen atmosphere by thermogravimetric analysis (TGA) technique on Mettler Toledo TG50 Analyzer. The temperature, weight, and tau lag were calibrated using the Aluminum/Zinc standard sample. High-purity nitrogen (99.999%) was passed throughout the experiments to avoid contamination from the external atmosphere. Thermal stability was investigated by heating from 25 °C to 700 °C at a heating rate of 10 °C/min.
- The measurement of phase transition temperature was recorded by differential scanning calorimeter (DSC) using Mettler Toledo DSC1.

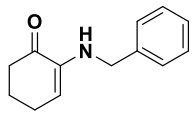
Preparation of α-enaminones

Procedure A: to a solution of 1,2-cyclohexadione (1.00 equiv.) in MeOH (0.3 M), was added corresponding primary amine (1.00 equiv.) in one portion. The solution was left to stir for 2-5 hours at 60-80 °C. The mixture was concentrated under high vacuum. The product was purified by flash chromatography (neutral aluminium oxide 90, diethyl ether\ethyl acetate in hexane, unless otherwise stated) to yield the corresponding α-enaminone.

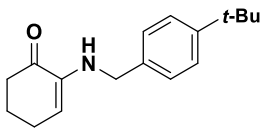
Preparation of desired product

Procedure B (from α-enaminone): a solution of α-enaminone (1.00 equiv.), proline (2.00 equiv.) and potassium iodide (1.00 equiv.) in MeOH (0.27 M) was left to stir for 8 hours at 100 °C. The mixture was concentrated under high vacuum. The product was purified by flash chromatography (silica gel, methanol, and ethyl acetate in DCM), to yield the corresponding desired product.

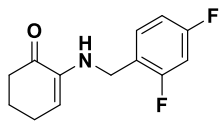
Procedure C (one-pot): a mixture of dione (1.00 equiv.), primary amine (1.00 equiv.), proline (2.00 equiv.) and KI (1.00 equiv.) in MeOH (0.27 M) was left to stir for 10-24 hours at 100 °C. The mixture was concentrated under high vacuum. The product was purified by flash chromatography (silica gel, methanol, and ethyl acetate in DCM), to yield the corresponding desired product.



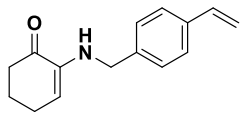
2-(benzylamino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.8 g, 7.00 mmol), phenylmethanamine (1.00 equiv., 0.77 ml, 7.00 mmol), in MeOH (0.3 M, 22.50 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (20% ethyl acetate in hexane) yielded α-enaminone (1.20 g, yellow solid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.37 – 7.27 (m, 6H), 5.44 (t, *J* = 4.7 Hz, 1H), 4.09 (s, 2H), 2.54 – 2.45 (m, 2H), 2.34 (q, *J* = 5.6 Hz, 2H), 1.95 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.82, 140.35, 139.03, 128.51, 127.38, 127.09, 111.78, 47.55, 37.92, 24.50, 23.49. **IR** (neat): 3406, 3029, 2928, 2834, 1658, 1618, 1486, 1207, 1129, 969, 868, 802, 740, 697 cm^{-1}.



2-((4-(tert-butyl)benzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.0 g, 8.90 mmol), (4-(tert-butyl)phenyl)methanamine (1.00 equiv., 1.57 ml, 8.90 mmol), in MeOH (0.3 M, 30.0 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (5% dichloromethane, 15% ethyl acetate in hexane) yielded α-enaminone (1.40 g, yellow crystals). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.23 (s, 2H), 5.61 (s, 1H), 4.05 (s, 2H), 2.54 – 2.45 (m, 2H), 2.36 (q, *J* = 5.6 Hz, 2H), 1.96 (p, *J* = 6.2 Hz, 2H), 1.32 (s, 10H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.86, 150.04, 140.51, 135.94, 127.24, 125.42, 111.64, 47.28, 37.94, 34.49, 31.39, 24.51, 23.49. **IR** (neat): 3406, 2953, 2865, 2830, 1662, 1625, 1486, 1352, 1264, 1179, 1158, 962, 866, 813, 703 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{17}H_{24}NO}$ ([M+H]$^{+}$): 258.1858; found: 258.1859.

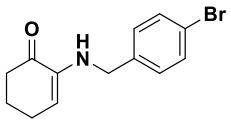


(2,4-difluorophenyl)methanamine: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.97 g, 8.65 mmol), (2,4-difluorophenyl)methanamine (1.00 equiv., 1.03 ml, 8.65 mmol), in MeOH (0.3 M, 29.00 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (15% ethyl acetate in hexane) yielded α-enaminone (1.19 g, yellow solid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.23 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.73 (m, 2H), 5.43 (t, *J* = 4.7 Hz, 1H), 4.10 (s, 2H), 2.53 – 2.44 (m, 2H), 2.34 (q, *J* = 5.6 Hz, 2H), 1.96 (q, *J* = 6.3 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.70, 163.76, 163.61, 162.30, 162.14, 160.48, 160.33, 159.01, 158.86, 139.95, 130.08, 130.00, 129.95, 129.87, 121.85, 121.81, 121.65, 121.61, 112.02, 111.29, 111.25, 111.02, 110.96, 104.01, 103.68, 103.34, 40.41, 40.36, 37.80, 24.41, 23.37. ^{19}F NMR (282 MHz, Chloroform-d) δ -112.05 (p, *J* = 7.6 Hz), -115.02 (q, *J* = 8.5 Hz). **IR** (neat): 3405, 2915, 2832, 1661, 1624, 1498, 1425, 1358, 1264, 1130, 1084, 961, 864, 806, 723 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{13}H_{14}F_2NO}$ ([M+H]$^{+}$): 238.1043; found: 238.1043.

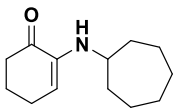


2-((4-vinylbenzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.83 g, 7.36 mmol), (4-vinylphenyl)methanamine (1.00 equiv., 1.00 ml, 7.36 mmol), in MeOH (0.3 M, 25.00 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (20% ethyl acetate in hexane) yielded

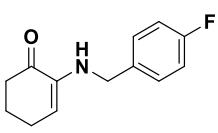
α-enaminone (0.15 g, orange-black oil). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 3H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.44 (t, *J* = 4.7 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.08 (s, 2H), 2.54 – 2.43 (m, 2H), 2.33 (q, *J* = 5.6 Hz, 2H), 1.95 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.88, 140.28, 138.69, 136.47, 127.99, 127.51, 126.35, 113.59, 111.92, 47.27, 37.90, 24.48, 23.46. **IR** (neat): 3405, 2924, 2856, 1664, 1624, 1490, 1351, 1156, 1126, 987, 917, 824, 792, 701 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{15}H_{18}NO}$ ([M+H]$^+$): 228.1388; found: 228.1388.



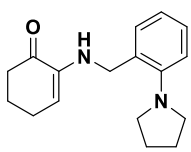
2-((4-bromobenzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.6 g, 5.40 mmol), (4-bromophenyl)methanamine (1.00 equiv., 0.68 ml, 5.40 mmol), in MeOH (0.3 M, 18.00 ml), 4 h, 80 °C, Yielded α-enaminone (1.23 g, dark orange solid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.38 (t, *J* = 4.7 Hz, 1H), 4.05 (s, 2H), 2.53 – 2.45 (m, 2H), 2.32 (q, *J* = 5.6 Hz, 2H), 1.94 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.83, 140.07, 138.10, 131.56, 128.94, 120.75, 112.13, 46.88, 37.85, 24.43, 23.41. **IR** (neat): 3398, 2946, 2920, 2855, 2825, 1664, 1623, 1485, 1335, 1157, 1126, 1067, 1009, 888, 868, 796, 722, 708 cm^{-1}.



2-(cycloheptylamino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.56 g, 5.00 mmol), cycloheptanamine (1.00 equiv., 0.64 ml, 5.00 mmol), in MeOH (0.3 M, 16.70 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (15% ethyl acetate, 20% diethyl ether in hexane) yielded α-enaminone (0.70 g, orange oil). **^{1}H NMR** (300 MHz, Chloroform-d) δ 5.31 (t, *J* = 4.8 Hz, 1H), 3.08 (dp, *J* = 8.3, 4.3 Hz, 1H), 2.49 – 2.41 (m, 2H), 2.36 (q, *J* = 5.6 Hz, 2H), 1.89 (ddt, *J* = 18.0, 11.4, 5.5 Hz, 4H), 1.68 – 1.32 (m, 10H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 196.17, 139.07, 110.79, 52.69, 38.00, 34.02, 28.34, 24.61, 24.48, 23.48. **IR** (neat): 3403, 2917, 2858, 2832, 1663, 1623, 1509, 1493, 1453, 1340,1245, 1178, 1125, 1031, 810, 796, 710 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{13}H_{21}NO}$ (M$^+$): 207.1623; found: 207.1623.

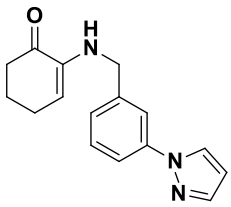


2-((4-fluorobenzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.00 g, 9.00 mmol), (4-fluorophenyl)methanamine (1.00 equiv., 1.13 ml, 9.00 mmol), in MeOH (0.3 M, 30.00 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (10% ethyl acetate in hexane) yielded α-enaminone (0.82 g, green solid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.29 – 7.20 (m, 2H), 7.06 – 6.93 (m, 2H), 5.39 (t, *J* = 4.7 Hz, 1H), 4.04 (s, 2H), 2.48 (dd, *J* = 7.3, 6.0 Hz, 2H), 2.33 (q, *J* = 5.6 Hz, 2H), 1.95 (q, *J* = 6.3 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.85, 163.55, 160.31, 140.21, 134.66, 134.62, 128.95, 128.84, 115.45, 115.17, 111.97, 46.86, 37.87, 24.45, 23.43. ^{19}F NMR (282 MHz, Chloroform-d) δ -115.72 – -115.91 (m). **IR** (neat): 3405, 3031, 2931, 2866, 1665, 1626, 1602, 1505, 1211, 1155, 813, 791, 744 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{13}H_{15}FNO}$ ([M+H]$^+$): 220.1138; found: 220.1141.

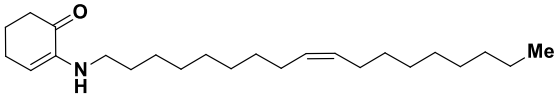


2-((2-(pyrrolidin-1-yl)benzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.64 g, 5.70 mmol), (2-(pyrrolidin-1-yl)phenyl)methanamine (1.00 equiv., 1.00 ml, 5.70 mmol), in MeOH (0.3 M, 20.00 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (5% ethyl acetate

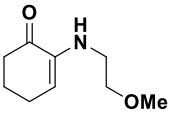
in hexane) yielded α-enaminone (0.27 g, brown solid). **^{1}H NMR** (300 MHz, Chloroform-d) *δ* 7.29 – 7.12 (m, 2H), 6.99 – 6.84 (m, 2H), 5.41 (t, *J* = 4.7 Hz, 1H), 4.06 (s, 2H), 3.20 – 3.11 (m, 4H), 2.53 – 2.43 (m, 2H), 2.35 (q, *J* = 5.6 Hz, 2H), 1.98 – 1.89 (m, 6H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.85, 148.70, 140.61, 129.75, 128.93, 127.69, 120.53, 116.47, 111.25, 51.25, 45.49, 38.01, 24.99, 24.58, 23.57. **IR** (neat): 3402, 2922, 2853, 1673, 1627, 1598, 1483, 1449, 1397, 1311, 1159, 1127, 865, 751 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{17}H_{22}N_2O}$ (M^+): 270.1732; found: 270.1734.



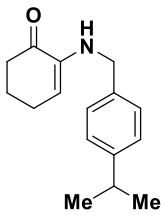
2-((3-(1H-pyrazol-1-yl)benzyl)amino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.64 g, 5.78 mmol), (3-(1H-pyrazol-1-yl)phenyl)methanamine (1.00 equiv., 1.00 g, 5.78 mmol), in MeOH (0.3 M, 20.00 ml). The setup was prepared under nitrogen atmosphere. 4 h, 80 °C, yielded α-enaminone (1.50 g, green solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.89-7.85 (d, *J* = 2.5 Hz, 1H), 7.68-7.63 (d, *J* = 1.8 Hz, 1H), 7.63-7.57 (q, *J* = 3.3, 1.8 Hz, 1H), 7.55-7.48 (ddd, *J* = 8.2, 2.2, 1.1Hz, 1H), 7.36-7.29 (t, *J* = 7.8 Hz, 1H), 7.18-7.12 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.42-6.35 (m, 1H), 5.38-5.29 (t, *J* = 4.7 Hz, 1H), 4.12-4.04 (s, 2H), 2.45-2.37 (dd, *J* = 7.4, 5.9 Hz, 2H), 2.29-2.18 (q, *J* = 5.6 Hz, 2H), 1.92-1.79 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.80, 145.98, 141.00, 140.32, 140.32, 140.12, 129.54, 126.83, 125.10, 117.90, 117.75, 112.18, 107.59, 47.29, 37.82, 24.40, 23.38. **IR** (neat): 3410, 3124, 3037, 2939, 1669, 1625, 1592, 1517, 1487, 1391, 1350, 1040, 936, 787, 749, 729, 702, 685 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{16}H_{18}N_3O}$ ($[M+H]^+$): 268.1450; found: 268.1450.



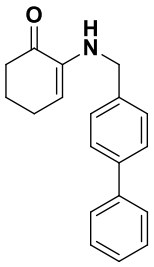
(Z)-2-(octadic-9-en-1-ylamino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.85 g, 7.60 mmol), oleylamine (1.00 equiv., 2.5 ml, 7.60 mmol), in MeOH (0.3 M, 25.00 ml), 3.5 h, 80 °C. Two phases was observed and separated. Purification of the main phase by flash column chromatography (5% ethyl acetate in hexane) yielded α-enaminone (0.89 g, dark blue oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.47-5.27 (m, 3H), 4.22-4.01 (s, 1H), 2.85-2.74 (t, *J* = 7.0 Hz, 2H), 2.51-2.42 (m, 2H), 2.40-2.32 (q, *J* = 5.6 Hz, 2H), 2.06-1.88 (m, 6H), 1.61-1.50 (t, *J* = 7.1 Hz, 2H), 1.39-1.20 (dt, *J* = 16.8, 5.1 Hz, 23H), 0.91-0.83(t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.92, 140.71, 129.89, 129.76, 110.80, 43.21, 37.93, 31.89, 29.75, 29.72, 29.68, 29.51, 29.45, 29.42, 29.31, 29.22, 28.97, 27.28, 27.18, 27.16, 24.53, 23.51, 22.67, 14.11. **IR** (neat): 3403, 2918, 2855, 2832, 1662, 1623, 1509, 1494, 1282, 1212, 1168, 1125, 1031, 975, 869, 810, 796, 721 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{24}H_{44}NO}$ ($[M+H]^+$): 362.3423; found: 362.3426.



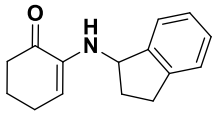
2-((2-methoxyethyl)amino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.29 g, 11.50 mmol), 2-methoxyethylamine (1.00 equiv., 1.00 ml, 11.50 mmol), in MeOH (0.3 M, 35.00 ml), 2 h, 60 °C. Purification of the crude product by flash column chromatography (20% diethyl ether in hexane) yielded α-enaminone (1.20 g, green oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.50-5.44 (t, *J* = 4.7 Hz, 1H), 4.53-4.28 (s, 1H), 3.59-3.51 (t, *J* = 5.3 Hz, 2H), 3.39-3.33 (s, 3H), 3.06-2.98 (t, *J* = 5.4 Hz, 2H), 2.51-2.44 (dd, *J* = 7.3, 6.0 Hz, 2H), 2.42-2.32 (q, *J* = 5.6 Hz, 2H), 2.01-1.89 (p, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.77, 140.64, 111.58, 70.73, 58.81, 42.88, 37.91, 24.50,23.43. **IR** (neat): 3405, 2930, 1668, 1453, 1194, 1115, 1018, 711 cm^{-1}. **HRMS** (m/z) calc. for $C_9H_{15}NNaO_2$ ($[M+Na]^+$): 192.0995; found: 192.0996.



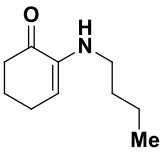
2-((4-isopropylbenzyl)amino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.00 g, 8.90 mmol), 4-isopropylbenzylamine (1.00 equiv., 1.33 g, 8.90 mmol), in MeOH (0.3 M, 30.00 ml), 3.5 h, 80 °C, yielded α-enaminone (2.10 g, brown solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.25-7.15 (m, 4H), 5.48-5.42 (t, *J* = 4.7 Hz, 1H), 4.07-3.99 (s, 2H), 2.97-2.81 (m, 1H), 2.53-2.44 (t, 2H), 2.39-2.30 (q, *J* = 5.6 Hz, 2H), 2.00-1.89 (p, *J* = 6.2 Hz, 2H), 1.27-1.21 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.67, 147.78, 140.48, 136.30, 127.49, 126.55, 111.67, 47.36, 37.93, 33.78, 24.51, 24.03, 23.48. **IR** (neat): 3405, 2953, 2864, 1663, 1623, 1494, 1336, 1157, 1127, 1051, 813, 796, 712 cm^{-1}. **HRMS** (m/z) calc. for $C_{16}H_{22}NO$ ($[M+H]^+$): 244.1695; found: 244.1701.



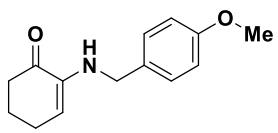
2-(([1,1'-biphenyl]-4-ylmethyl)amino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.61 g, 5.46 mmol), 4-phenylbenzylamine (1.00 equiv., 1.00 g, 5.46 mmol), in MeOH (0.3 M, 20.00 ml). The setup was prepared under nitrogen atmosphere. 5 h, 80 °C, yielded α-enaminone (1.40 g, yellow solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62-7.52 (td, *J* = 8.5 Hz, 4H), 7.47-7.40 (t, *J* = 7.4 Hz, 2H), 7.40-7.31 (m, 3H), 5.49-5.41 (t, *J* = 4.7Hz, 1H), 4.17-4.08 (s, 2H), 2.55-2.46 (t, 2H), 2.39-2.30 (q, *J* = 5.6 Hz, 2H), 2.01-1.90 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.92, 140.85, 140.35, 140.04, 138.11, 128.76, 127.80, 127.26, 127.22, 127.05, 111.96, 47.26, 37.93, 24.51, 23.48. **IR** (neat): 3406, 2953, 2915, 2832, 1662, 1625, 1490, 1426, 1357, 1265, 1206, 1130, 1085, 962, 865, 806, 759, 723, 692 cm^{-1}. **HRMS** (m/z) calc. for $C_{19}H_{20}NO$ ($[M+H]^+$): 278.1539; found: 278.1545.



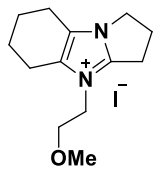
2-((2,3-dihydro-1H-inden-1-yl)amino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.01 g, 9.00 mmol), 1-aminoindane (1.00 equiv., 1.15 ml, 9.00 mmol), in MeOH (0.3 M, 30.00 ml), 4 h, 80 °C. Purification of the crude product by flash column chromatography (5% ethyl acetate in hexane) yielded α-enaminone (1.24 g, orange solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36-7.30 (m, 1H), 7.26-7.14 (m, 3H), 5.70-5.61 (t, *J* = 4.7 Hz, 1H), 4.70-4.61 (t, 1H), 4.59-4.40 (s, 1H), 3.07-2.92 (m, 1H), 2.90-2.78 (dt, *J* = 15.8, 7.7 Hz, 1H), 2.54-2.48 (dd, *J* = 7.6, 5.7 Hz, 2H), 2.48-2.37(h, *J* = 4.4 Hz, 3H), 2.06-1.94 (m, 2H), 1.90-1.74 (dq, *J* = 14.4, 7.7 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.82, 144.36, 143.47, 139.97, 127.82, 126.58, 124.76, 124.29, 111.21, 57.77, 38.02, 33.16, 30.35, 24.66, 23.54. **IR** (neat): 3405, 3022, 2934, 2858, 1665, 1624, 1476, 1356, 1165, 1127, 874, 814, 751, 714 cm^{-1}. **HRMS** (m/z) calc. for $C_{15}H_{17}NO$ (M^+): 227.1310; found: 227.1308.



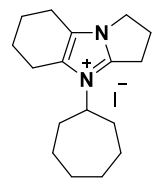
2-(butylamino)cyclohex-2-enone: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 1.68 g, 15.00 mmol), n-buthylamine (1.00 equiv., 1.50 ml, 15.00 mmol), in MeOH (0.3 M, 45.00 ml), 4 h, 80 °C, yielded α-enaminone (3.00 g, brown oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.45-5.39 (t, *J* = 4.7 Hz, 1H), 2.86-2.78 (t, *J* = 7.0 Hz, 2H), 2.50-2.42 (m, 2H), 2.41-2.32 (q, *J* = 5.6 Hz, 2H), 2.00-1.89 (p, *J* = 6.3 Hz, 2H), 1.61-1.49 (m, 2H), 1.45-1.31 (dq, *J* = 14.3, 7.2 Hz, 2H), 0.98-0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 195.98, 140.71, 110.90, 42.88, 37.93, 31.04, 24.52, 23.50, 20.38, 13.88. **IR** (neat): 3402, 2918, 2859, 2832, 1662, 1623, 1509, 1494, 1281, 1245, 1167, 1125, 1031, 809, 796, 721 cm^{-1}. **HRMS** (m/z) calc. for $C_{10}H_{18}NO$($[M+H]^+$): 168.1388; found: 168.1387.



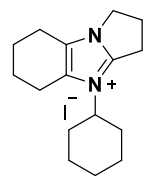
2-((4-methoxybenzyl)amino)cyclohex-2-en-1-one: general procedure **A** was applied using 1,2-cyclohexadione (1.00 equiv., 0.97 g, 8.65 mmol), (4-methoxyphenyl)methanamine (1.00 equiv., 1.11 ml, 8.65 mmol), in MeOH (0.3 M, 29.00 ml), 4 h, 80 °C, yielded α-enaminone (2.00 g, dark brown gelatinous solid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.25 – 7.18 (m, 2H), 6.90 – 6.83 (m, 2H), 5.45 (t, *J* = 4.7 Hz, 1H), 4.00 (s, 2H), 3.81 (s, 3H), 2.53 – 2.45 (m, 2H), 2.35 (q, *J* = 5.6 Hz, 2H), 1.95 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 195.90, 158.70, 140.40, 130.97, 128.68, 113.86, 111.76, 55.27, 47.03, 37.92, 24.50, 23.47. **IR** (neat): 3403, 2917, 2859, 2832, 1662, 1623, 1509, 1494, 1283, 1245, 1158, 1125, 1031, 810, 796, 710 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{14}H_{18}NO_2}$ ([M+H]$^+$): 232.1338; found: 232.1341.



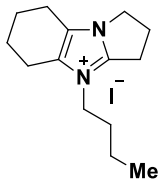
28: 4-(2-methoxyethyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.17 g, 1.00 mmol), proline (2.00 equiv., 0.23 g, 2.00 mmol), potassium iodide (1.00 equiv., 0.25 g, 1.00 mmol), in MeOH (0.27 M, 3.80 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.27 g, 76% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.30-4.48 (m, 4H), 3.69-3.63 (t, *J* = 5.0 Hz, 2H), 3.49-3.41 (t, *J* = 7.7 Hz, 2H), 3.36-3.32 (s, 3H), 2.92-2.79 (p, *J* = 7.5 Hz, 2H), 2.65-2.55 (d, *J* = 5.4 Hz, 4H), 1.93-1.85 (p, *J* = 2.9 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.24, 132.82, 125.74, 70.09, 59.03, 47.01, 46.62, 25.43, 24.37, 21.44, 21.22, 20.49, 20.06. **IR** (neat): 2932, 1631, 1555, 1424, 1305, 1199, 1115, 1088, 1019, 858, 829 cm^{-1}. **HRMS** (m/z) calc. for $C_{13}H_{21}N_2O$ (M^+): 221.1648; found: 221.1643.



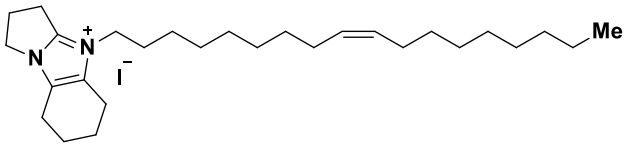
29: **4-cycloheptyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide:** general procedure **B** was applied using α-enaminone (1.00 equiv., 0.104 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 10% diethyl ether in DCM) yielded desired product (0.055 g, 28% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 4.26 (t, *J* = 7.3 Hz, 2H), 4.03 (tt, *J* = 11.2, 3.7 Hz, 1H), 3.41 (t, *J* = 7.6 Hz, 2H), 2.88 (p, *J* = 7.5 Hz, 2H), 2.65 – 2.52 (m, 4H), 2.18 (ddt, *J* = 13.9, 6.1, 3.5 Hz, 2H), 1.86 (qd, *J* = 12.1, 7.0 Hz, 9H), 1.60 (m, 8H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 148.02, 131.83, 126.20, 70.52, 60.37, 46.07, 34.72, 26.76, 25.94, 25.73, 24.85, 21.77, 21.27, 21.24, 20.15. **IR** (neat): 2924, 2855, 1629, 1538, 1444, 1427, 1115, 1017, 919, 724 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{17}H_{27}N_2}$ (M^+): 259.2174; found: 259.2169.



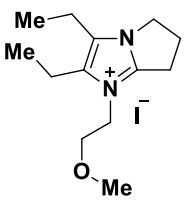
30: 4-cyclohexyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.06 g, 0.30 mmol), proline (2.00 equiv., 0.07 g, 0.60 mmol), potassium iodide (1.00 equiv., 0.05 g, 0.30 mmol), in MeOH (0.27 M, 1.15 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 10% diethyl ether in DCM) yielded desired product (0.09 g, 81% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 4.25 (t, *J* = 7.3 Hz, 2H), 3.92 (tt, *J* = 12.4, 3.8 Hz, 1H), 3.44 (t, *J* = 7.6 Hz, 2H), 2.88 (p, *J* = 7.5 Hz, 2H), 2.60 (q, *J* = 4.8 Hz, 4H), 2.18 – 2.10 (m, 2H), 1.98 – 1.83 (m, 6H), 1.72 (tt, *J* = 12.5, 6.3 Hz, 4H), 1.39 (qt, *J* = 12.9, 3.3 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.23, 126.21, 58.12, 45.89, 32.49, 26.34, 25.70, 25.46, 24.82, 21.77, 21.22, 20.13.



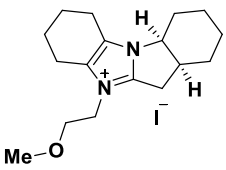
31: 4-butyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.08 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 25% ethyl acetate in DCM) yielded desired product (0.06 g, 34% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.24-4.15 (t, *J* = 7.3 Hz, 2H), 3.98-3.89 (t, *J* = 7.4 Hz, 2H), 3.37-3.29 (t, *J* = 7.6 Hz, 2H), 2.88-2.76 (p, *J* = 7.5 Hz, 2H), 2.57-2.45 (m, 4H), 1.86-1.74 (p, *J* = 3.6 Hz, 4H), 1.74-1.62 (m, 2H), 1.31-1.23 (h, *J* = 7.4 Hz, 2H), 0.92-0.83(p, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.51, 132.55, 126.16, 46.75, 46.55, 31.50, 25.62, 24.45, 21.57, 21.30, 20.53, 20.09, 19.86, 13.53. **IR** (neat): 2931, 2859, 1630, 1555, 1426, 1378, 1306, 1116, 1022, 919, 724 cm^{-1}. **HRMS** (m/z) calc. for $C_{14}H_{23}N_2$ (M^+): 219.1861; found: 219.1863.



32: (Z)-4-(octadic-9-en-1-yl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.18 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (5% methanol, 25% ethyl acetate in DCM) yielded desired product (0.08 g, 30% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.4-5.24 (m, 2H), 4.30-4.18 (t, *J* = 7.3 Hz, 2H), 4.02-3.90 (t, *J* = 7.6 Hz, 2H), 3.44-3.32 (t, *J* = 7.6 Hz, 2H), 2.93-2.80 (m, 2H), 2.62-2.48 (m, 4H), 2.04-1.65 (m, 10H), 1.38-1.13 (m, 22H), 0.89-0.77 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.57, 132.57, 130.02, 129.62, 126.23, 47.04, 46.58, 31.87, 29.73, 29.66, 29.59, 29.50, 29.34, 29.30, 29.14, 29.01, 28.98, 27.20, 27.13, 26.63, 25.64, 24.57, 22.67, 21.61, 21.35, 20.57, 20.13, 14.13. **IR** (neat): 2921, 2851, 1630, 1556, 1457, 1377, 1306, 1020, 721 cm^{-1}. **HRMS** (m/z) calc. for $C_{28}H_{49}N_2$ (M^+): 413.3896; found: 413.3900.

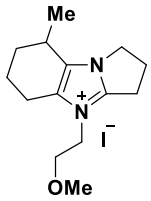


33: 2,3-diethyl-1-(2-methoxyethyl)-6,7-dihydro-5H-pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **C** was applied using 3,4-hexanedione (1.00 equiv., 0.36 ml, 3.00 mmol), 2-methoxyethylamine (1.00 equiv., 0.26 ml, 3.00 mmol), proline (2.00 equiv., 0.69 g, 6.00 mmol), potassium iodide (1.00 equiv., 0.49 g, 3.00 mmol), in MeOH (0.27 M, 12.00 ml), 24 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 30% ethyl acetate in DCM) yielded desired product (0.22 g, 21% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.34-4.22 (m, 4H), 3.73-3.65 (t, *J* = 4.9 Hz, 2H), 3.51-3.43 (t, *J* = 7.7 Hz, 2H), 3.36-3.31(s, 3H), 2.94-2.80 (m, 2H), 2.69-2.55 (m, 4H), 1.27-1.16 (q, *J* = 7.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.83, 134.98, 128.14, 70.38, 59.14, 47.14, 47.09, 25.34, 25.03, 17.13, 16.74, 14.53, 13.79. **IR** (neat): 2970, 2932, 1619, 1560, 1453, 1301, 1359, 1310, 1197, 1115, 1017, 918, 835, 729 cm^{-1} . **HRMS** (m/z) calc. for $C_{13}H_{24}N_2O$ ($[M+H]^+$): 224.1889; found: 224.1889.

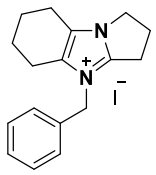


34: (4aS,11aS)10-(2-methoxyethyl)-2,3,4,4a,6,7,8,9,11,11a-decahydro-1H-benzo[4,5]imidazo[1,2-a]indol-10-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.08 g, 0.50 mmol), L-octahydroindol-2-carboxylic acid (2.00 equiv., 0.17 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH

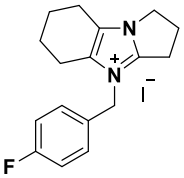
(0.27 M, 1.90 ml), 25 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.07 g, 37% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.56-4.46 (m, 1H), 4.24-4.13 (t, *J* = 4.9 Hz, 2H), 3.57-3.49 (t, *J* = 4.9 Hz, 2H), 3.33-3.24 (dd, *J* = 16.1, 6.9 Hz, 1H), 3.23-3.19 (s, 3H), 3.11-3.01 (dt, *J* = 12.8, 6.3 Hz, 1H), 3.00-2.88 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.65-2.35 (m, 4H), 2.02-1.58 (m, 8H), 1.52-1.30 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.01, 132.26, 125.44, 70.08, 59.63, 59.04, 47.19, 39.81, 29.72, 27.50, 26.58, 21.40, 21.32, 20.68, 20.55, 20.22. **IR** (neat): 2928, 2855, 1626, 1552, 1508, 1444, 1199, 1116, 1017, 919, 854, 725 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{27}N_2O$ (M^+): 275.2123; found: 275.2122.



35: 4-(2-methoxyethyl)-8-methyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.09 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 15% ethyl acetate, 15% diethyl ether in DCM) yielded desired product (0.113 g, 62% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 4.21 (dt, *J* = 13.7, 6.7 Hz, 4H), 3.65 (t, *J* = 4.9 Hz, 2H), 3.35 (dq, *J* = 5.8, 3.5, 3.0 Hz, 2H), 3.29 (s, 3H), 2.97 (dt, *J* = 7.2, 3.7 Hz, 1H), 2.79 (p, *J* = 7.6 Hz, 2H), 2.54 (p, *J* = 5.1, 4.7 Hz, 2H), 1.86 – 1.65 (m, 4H), 1.19 (d, *J* = 3.1 Hz, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.04, 137.06, 125.46, 70.35, 59.14, 47.19, 46.62, 29.86, 29.63, 25.48, 25.37, 25.05, 20.32, 19.96, 17.26.

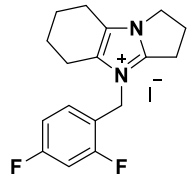


36: 4-benzyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.10 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.07 g, 50% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.34 – 7.17 (m, 5H), 5.19 (s, 2H), 4.17 (t, *J* = 7.3 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.72 (p, *J* = 7.5 Hz, 2H), 2.52 (s, 2H), 2.42 (s, 2H), 1.81 – 1.68 (m, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 149.95, 133.02, 132.62, 129.31, 128.98, 128.09, 126.29, 50.56, 46.56, 25.52, 24.67, 21.50, 21.23, 20.71, 20.11. **IR** (neat): 2921, 2852, 1635, 1555, 1496, 1453, 1364, 1019, 751, 700 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{21}N_2$ (M^+): 253.1705; found: 253.1707.

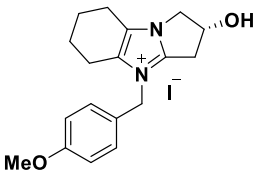


37: 4-(4-fluorobenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.11 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% diethyl ether in DCM) yielded desired product (0.07 g, 35% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.35 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 5.26 (s, 2H), 4.20 (t, *J* = 7.3 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H), 2.78 (p, *J* = 7.5 Hz, 2H), 2.61 – 2.42 (m, 4H), 1.82 (p, *J* = 2.7 Hz, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 162.77 (d, *J* = 248.8 Hz), 149.97, 132.99, 130.40 (d, *J* = 8.5 Hz), 128.51 (d, *J* = 3.4 Hz), 126.39, 116.32 (d, *J* = 21.9 Hz), 49.90, 46.50, 25.51, 24.82, 21.51, 21.22, 20.78, 20.09. **^{19}F NMR** (282 MHz, Chloroform-d) δ -111.89 – -112.15 (m). **IR** (neat): 2922, 2854, 1636, 1603, 1555,

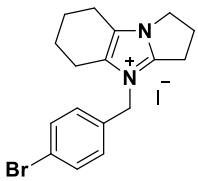
1509, 1444, 1421, 1221, 1160, 1016, 917, 823, 726 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{20}N_2F$ (M^+): 271.1611; found: 271.1616.



38: 4-(2,4-difluorobenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.12 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 10% ethyl acetate, 10% diethyl ether in DCM) yielded desired product (0.11 g, 51% yield, dark orange-brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.61 (td, *J* = 8.6, 6.1 Hz, 1H), 6.92 – 6.71 (m, 2H), 5.25 (s, 2H), 4.15 (t, *J* = 7.3 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.74 (p, *J* = 7.5 Hz, 2H), 2.48 (dt, *J* = 11.0, 5.4 Hz, 4H), 1.75 (h, *J* = 5.1, 3.9 Hz, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 163.87 (dd, *J* = 185.4, 12.1 Hz), 160.54 (dd, *J* = 183.4, 12.1 Hz), 161.83, 161.67, 159.40, 159.24, 150.08, 145.98, 133.07, 132.81 (dd, *J* = 9.9, 4.8 Hz), 126.23, 116.15 (dd, *J* = 14.6, 3.8 Hz), 112.28 (dd, *J* = 21.3, 3.6 Hz), 104.54 (t, *J* = 25.3 Hz), 60.33, 46.51, 44.65, 44.62, 37.75, 29.58, 25.49, 24.72, 24.69, 22.69, 21.87, 21.49, 21.16, 20.64, 20.06, 14.12. **^{19}F NMR** (282 MHz, Chloroform-d) δ -106.69 (h, *J* = 8.4, 7.9 Hz), -112.33 (q, *J* = 9.1 Hz). **IR** (neat): 2932, 1662, 1617, 1603, 1551, 1505, 1426, 1274, 1140, 1096, 964, 918, 849, 724 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{19}N_2F_2$ (M^+): 289.1516; found: 289.1514.

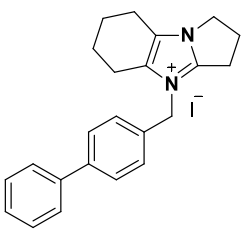


39: (R)-2-hydroxy-4-(4-methoxybenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide (7p): general procedure **B** was applied using α-enaminone (1.00 equiv., 0.069 g, 0.30 mmol), trans-4-Hydroxy-L-proline (2.00 equiv., 0.079 g, 0.60 mmol), potassium iodide (1.00 equiv., 0.050 g, 0.30 mmol), in MeOH (0.27 M, 1.15 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 15% ethyl acetate, 15% diethyl ether in DCM) yielded desired product (0.040 g, 34% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.92 – 6.87 (m, 2H), 5.10 (s, 2H), 4.41 (dd, *J* = 12.1, 5.6 Hz, 1H), 4.18 (dd, *J* = 12.0, 1.9 Hz, 1H), 3.79 (s, 4H), 3.71 – 3.66 (m, 1H), 3.44 (dd, *J* = 17.8, 6.4 Hz, 1H), 3.15 (d, *J* = 17.9 Hz, 1H), 2.61 – 2.54 (m, 2H), 2.50 (s, 2H), 1.84 (p, *J* = 2.9 Hz, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 160.3, 147.98, 132.71, 129.92, 126.53, 124.1, 114.78, 72.08, 55.45, 55.40, 50.22, 34.95, 29.68, 21.59, 21.29, 20.80, 20.12. IR (neat): 3297, 2929, 1732, 1631, 1611, 1553, 1513, 1441, 1422, 1359, 1303, 1249, 1177, 1080, 945, 820, 736, 726 cm^{-1}.

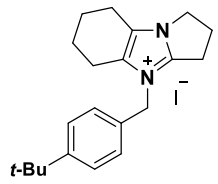


40: 4-(4-bromobenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.14 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% ethyl acetate, 20% isopropanol in DCM) yielded desired product (0.11 g, 47% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.45 (d, *J* = 8.0 Hz, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.23 (s, 2H), 4.18 (t, *J* = 7.3 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H), 2.76 (p, *J* = 7.5 Hz, 2H), 2.53 (s, 2H), 2.42 (s, 2H), 1.77 (q, *J* = 2.9, 2.5 Hz, 5H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 150.04, 133.02, 132.42, 131.73, 129.99, 126.46, 123.05, 49.97, 46.58, 25.52, 24.82, 21.50, 21.22, 20.77, 20.10. **IR** (neat): 2923, 2852, 1643,

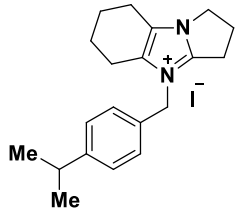
1550, 1488, 1439, 1421, 1409, 1307, 1070, 1009, 916, 798, 725 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{20}N_2Br$ (M^+): 331.0810; found: 331.0810.



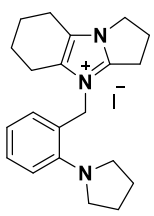
41: 4-([1,1'-biphenyl]-4-ylmethyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.13 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.07 g, 30% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.57-7.45 (dd, *J* = 15.6, 7.5 Hz 4H), 7.39-7.28 (m, 5H), 5.28-5.21 (s, 2H), 4.23-4.11 (t, *J* = 7.3 Hz, 2H) 3.23-3.15 (t, *J* = 7.6 Hz, 2H), 2.81-2.66 (p, *J* = 7.5 Hz, 2H), 2.57-2.42 (d, *J* = 20.5 Hz, 4H), 1.81-1.72 (q, *J* = 2.9 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ150.00, 141.71, 139.80, 133.05, 131.62, 128.86, 128.65, 127.86, 127.74, 126.97, 126.33, 50.30, 46.56, 25.54, 24.74, 21.53, 21.25, 20.76, 20.12. **IR** (neat): 2932, 1631, 1550, 1486, 1443, 1424, 1305, 1017, 1006, 918, 852, 767, 724, 699 cm^{-1}. **HRMS** (m/z) calc. for $C_{23}H_{25}N_2$ (M^+): 329.2012; found: 329.2060.



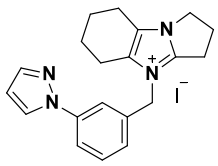
42: 4-(4-(tert-butyl)benzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.12 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (5% ethyl acetate, 10% methanol, 25% diethyl ether in DCM) yielded desired product (0.125 g, 57% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 4.19 (t, *J* = 7.3 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.75 (p, *J* = 7.5 Hz, 2H), 2.51 (d, *J* = 35.5 Hz, 4H), 1.78 (p, *J* = 2.8 Hz, 4H), 1.22 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 152.07, 149.76, 132.96, 129.60, 127.79, 126.18, 50.19, 46.55, 34.58, 31.15, 29.56, 25.53, 24.52, 21.51, 21.23, 20.69, 20.12. **IR** (neat): 2922, 2851, 1628, 1547, 1512, 1443, 1425, 1360, 1298, 1255, 1212, 1178, 1117, 1013, 919, 864, 827, 725 cm^{-1}. **HRMS** (m/z) calc. for $C_{21}H_{29}N_2$ (M^+): 309.2331; found: 309.2336.



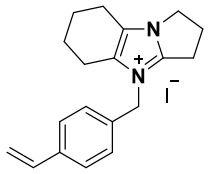
43: 4-(4-isopropylbenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.12 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.07 g, 32% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.25-7.16 (m, 4H), 5.23-5.14 (s, 2H), 4.27-4.18 (t, *J* = 7.3 Hz, 2H), 3.26-3.16 (t, *J* = 7.6 Hz, 2H), 2.94-2.74 (m, 3H), 2.63-2.47 (d, *J* = 19.6 Hz, 4H), 1.91-1.79 (p, *J* = 2.8 Hz, 4H), 1.24-1.17 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.94, 149.92, 133.01, 129.99, 128.10, 127.38, 126.23, 50.34, 46.51, 33.76, 25.53, 24.66, 23.83, 21.55, 21.28, 20.71, 20.12. **IR** (neat): 2955, 2865, 1631, 1552, 1422, 1017, 919, 819, 726 cm^{-1}.



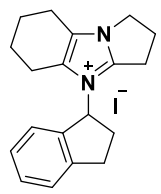
44: 4-(2-(pyrrolidin-1-yl)benzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.135 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 30% ethyl acetate in DCM) yielded desired product (0.067 g, 30% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.25 – 7.15 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 4.4 Hz, 2H), 5.16 (s, 2H), 4.22 (t, *J* = 7.3 Hz, 2H), 3.11 – 2.95 (m, 7H), 2.74 (p, *J* = 7.5 Hz, 2H), 2.55 (q, *J* = 3.8 Hz, 2H), 2.34 (d, *J* = 6.3 Hz, 2H), 1.90 – 1.84 (m, 4H), 1.75 (p, *J* = 3.2 Hz, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 149.98, 149.30, 133.09, 129.58, 128.88, 126.19, 124.74, 122.13, 118.20, 52.52, 47.62, 46.57, 25.57, 24.94, 24.36, 21.52, 21.33, 20.40, 20.16. **IR** (neat): 2937, 2856, 1632, 1598, 1555, 1490, 1448, 1306, 918, 759, 723 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{21}H_{28}N_3}$ (M^+): 322.2283; found: 322.2282.



45: 4-(3-(1H-pyrazol-1-yl)benzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.13 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.12 g, 54% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.17-8.12 (d, *J* = 2.5 Hz, 1H), 7.78-7.73 (d, *J* = 2.0 Hz, 1H), 7.66-7.55 (m, 2H), 7.42-7.34 (t, *J* = 7.9 Hz, 1H), 7.19-7.14 (d, *J* = 7.7 Hz, 1H), 6.38-6.34 (t, *J* = 2.2 Hz, 1H), 5.31-5.23 (s, 2H), 4.17-4.09 (t, *J* = 7.3 Hz, 2H), 3.21-3.12 (t, *J* = 7.6 Hz, 2H), 2.75-2.64 (m, 2H), 2.53-2.39 (m, 4H), 1.77-1.68 (dq, *J* = 7.9, 5.4, 4.0 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.06, 141.32, 140.57, 134.24, 133.14, 130.55, 127.77, 126.36, 126.08, 119.24, 118.61, 108.15, 50.27, 46.48, 25.46, 24.83, 21.49, 21.18, 20.83, 20.06. **IR** (neat): 2924, 1851, 1632, 1609, 1594, 1552, 1519, 1450, 1392, 1305, 1046, 945, 915, 792, 759, 724, 691 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{20}H_{23}N_4}$ (M^+): 319.1923; found: 319.1920.

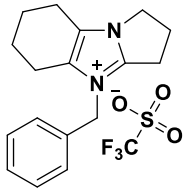


46: 4-(4-vinylbenzyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.114 g, 0.50 mmol), proline (2.00 equiv., 0.115 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.083 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.08 g, 40% yield, brown liquid). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.61 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.20 (s, 2H), 4.18 (t, *J* = 7.3 Hz, 2H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.74 (p, *J* = 7.5 Hz, 2H), 2.59 – 2.35 (m, 4H), 1.77 (h, *J* = 5.4 Hz, 4H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 149.95, 138.21, 135.74, 133.04, 131.93, 128.46, 127.02, 126.33, 115.22, 50.39, 46.55, 25.53, 24.75, 21.52, 21.25, 20.76, 20.13. **IR** (neat): 2923, 2852, 1729, 1628, 1547, 1443, 1425, 1360, 1304, 1212, 1118, 1014, 918, 864, 827, 772, 724 cm^{-1}. **HRMS** (m/z) calc. for $\mathrm{C_{19}H_{23}N_2}$ (M^+): 279.1877; found: 279.1855.

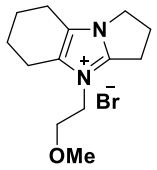


47: 4-(2,3-dihydro-1H-inden-1-yl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium iodide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.11 g, 0.50 mmol), proline (2.00 equiv., 0.11 g, 1.00 mmol), potassium iodide (1.00 equiv., 0.08 g, 0.50 mmol), in MeOH (0.27 M, 1.90 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.11 g,

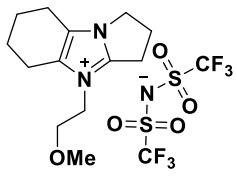
56% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45-7.22 (m, 4H), 5.78-5.68 (dd, *J* = 8.3 Hz, 1H), 4.32-4.19 (m, 1H), 4.19-4.04 (ddd, *J* = 14.4, 8.5, 3.7 Hz, 1H), 3.31-3.17 (ddd, *J* = 15.5, 8.8, 6.0 Hz, 1H), 3.07-2.93 (ddd, *J* = 16.5, 8.9, 5.4 Hz, 1H), 2.87-2.68 (m, 3H), 2.68-2.46 (m, 4H), 2.46-2.21 (m, 3H), 1.92-1.78 (p, *J* = 2.7 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 148.92, 144.81, 136.80, 132.43, 130.11, 127.58, 126.67, 125.83, 125.51, 62.36, 46.08, 33.40, 30.73, 25.38, 24.86, 21.72, 21.28, 21.11, 20.17. **IR** (neat): 2928, 2853, 1630, 1538, 1425, 1305, 1024, 918, 759, 723 cm^{-1}. **HRMS** (m/z) calc. for $C_{19}H_{23}N_2$ (M^+): 279.1861; found: 279.1862.



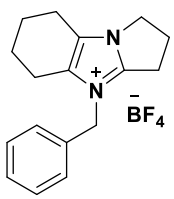
48: 4-benzyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium trifluoromethanesulfonate: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.060 g, 0.3 mmol), proline (2.00 equiv., 0.069 g, 0.6 mmol), and scandium triflate (0.3 equiv., 0.049 g, 0.1 mmol) instead of KI, in MeOH (0.27 M, 1.15 ml), 17 h, 100 °C. The crude was purified at first through a silica plug using an eluent composed of 10% methanol, 20% ethyl acetate in DCM. Then, flushed with DCM, EtOAc, Hexane and finally with DCM/Hexane 50/50% (0.050g, 42% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 3H), 7.21 (dd, *J* = 7.4, 2.2 Hz, 2H), 5.13 (s, 2H), 4.14 (t, *J* = 7.3 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.74 (p, *J* = 7.5 Hz, 2H), 2.56 (dp, *J* = 5.8, 3.0 Hz, 2H), 2.47 (t, *J* = 4.3 Hz, 2H), 1.83 (t, *J* = 3.1 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.16, 132.95 (d, *J* = 7.3 Hz), 129.37, 129.02, 127.86, 126.20, 49.89, 45.83, 25.30, 23.46, 21.52, 21.25, 20.50, 19.77. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.50. **IR** (neat): 2950, 1632, 1556, 1455, 1426, 1258, 1221, 1155, 1026, 739, 698 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{21}N_2$ $(M+H)^+$: 253.16993; found: 253.16988.



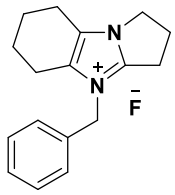
49: 4-(2-methoxyethyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium bromide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.051 g, 0.3 mmol), proline (2.00 equiv., 0.069 g, 0.6 mmol), and potassium bromide (1.00 equiv., 0.036 g, 0.3 mmol) instead of KI, in MeOH (0.27 M, 1.15 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.03 g, 19% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.36 (t, *J* = 5.0 Hz, 2H), 4.21 (t, *J* = 7.3 Hz, 2H), 3.68 – 3.63 (m, 2H), 3.52 (t, *J* = 7.6 Hz, 2H), 3.33 (s, 3H), 2.85 (p, *J* = 7.5 Hz, 2H), 2.60 (d, *J* = 6.2 Hz, 4H), 1.87 (p, *J* = 2.9 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.09, 133.06, 125.56, 70.78, 70.17, 59.09, 59.06, 46.99, 46.93, 46.28, 25.55, 24.50, 21.61, 21.52, 21.39, 20.49, 20.03, 19.99. **IR** (H_2O): 2917, 2848, 2360, 1560, 1459, 1361, 1201, 1115, 1084, 1014 cm^{-1}. **HRMS** (m/z) calc. for $C_{13}H_{21}N_2O$ $(M+H)^+$: 221.16484; found: 221.16469.



50: 4-(2-methoxyethyl)-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium bis((trifluoromethyl)sulfonyl)amide: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.051 g, 0.3 mmol), proline (2.00 equiv., 0.069 g, 0.6 mmol), and lithium bis(trifluoromethanesulfonyl)imide (1.00 equiv., 0.086 g, 0.3 mmol) instead of KI, in MeOH (0.27 M, 1.15 ml), 8 h, 100 °C. Purification of the crude product by flash column chromatography (10% methanol, 20% ethyl acetate in DCM) yielded desired product (0.087 g, 58% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.17 – 3.95 (m, 4H), 3.56 (t, *J* = 4.9 Hz, 2H), 3.28 (s, 3H), 3.14 (t, *J* = 7.7 Hz, 2H), 2.74 (p, *J* = 7.5 Hz, 2H), 2.52 (d, *J* = 5.4 Hz, 4H), 1.83 (p, *J* = 3.0 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.45, 132.84, 125.79, 121.90, 117.63, 69.95, 58.89, 46.31, 45.82, 25.10, 23.31, 21.46, 21.24, 20.16, 19.65. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.03. **IR** (neat): 2922, 2851, 1635, 1555, 1457, 1350, 1332, 1225, 1177, 1133, 1052, 787, 739 cm^{-1}. **HRMS** (m/z) calc. for $C_{13}H_{21}N_2O$ $(M+H)^+$: 221.16484; found: 221.16467.

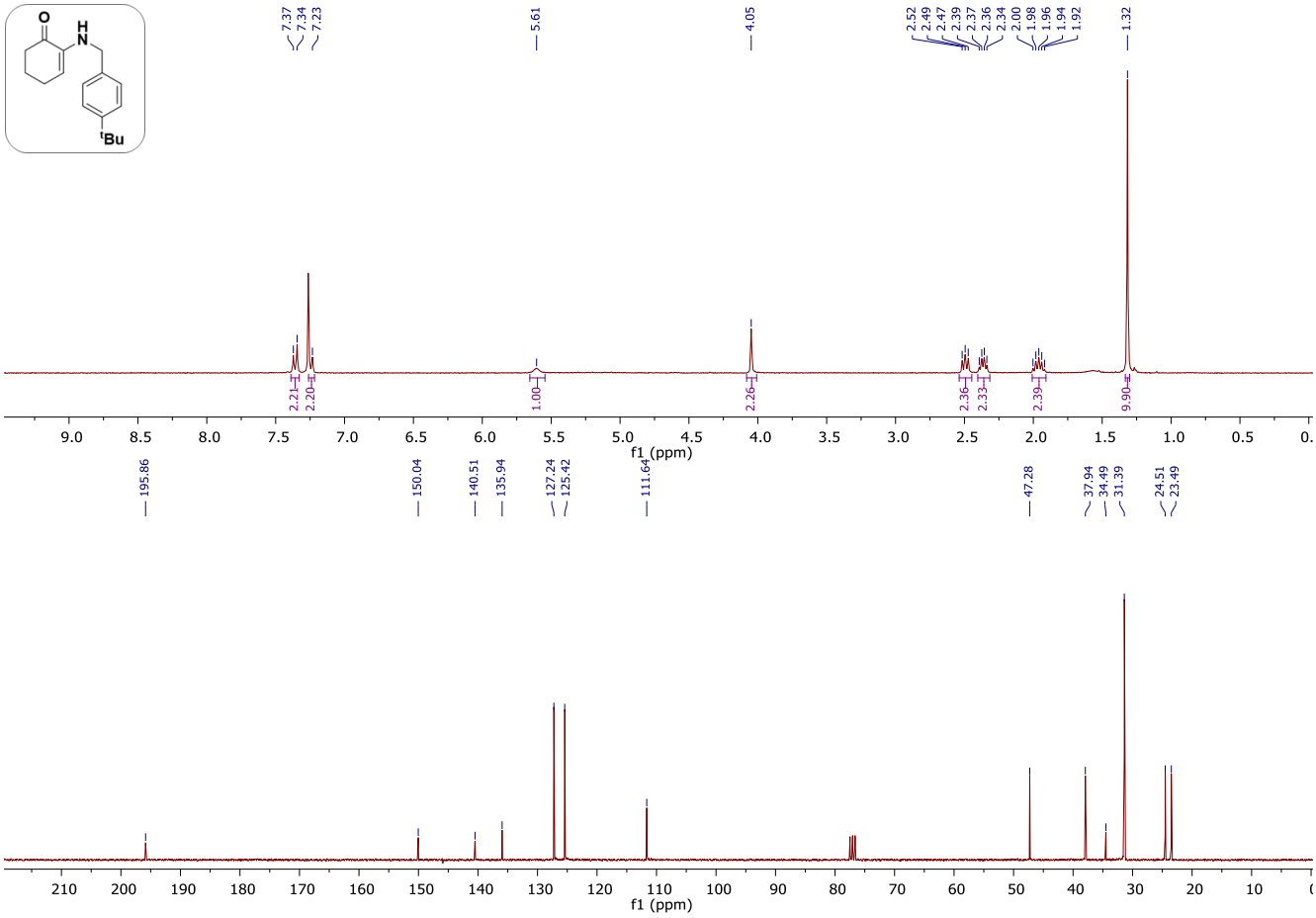


51: 4-benzyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium tetrafluoroborate: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.033 g, 0.16 mmol), proline (2.00 equiv., 0.037 g, 0.32 mmol), and copper(II) tetrafluoroborate hexahydrate (1.00 equiv., 0.056 g, 0.16 mmol) instead of KI, in MeOH (0.27 M, 0.65 ml), 17 h, 100 °C. The crude was purified by flushing the crude compound through a silica plug using DCM and eluent composed of 10% methanol, 20% ethyl acetate in DCM (0.026 g, 47% yield, brown liquid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 3H), 7.21 (dd, *J* = 7.4, 1.9 Hz, 2H), 5.11 (s, 2H), 4.12 (t, *J* = 7.3 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.73 (p, *J* = 7.5 Hz, 2H), 2.54 (h, *J* = 3.0 Hz, 2H), 2.45 (t, *J* = 4.1 Hz, 2H), 1.81 (t, *J* = 3.3 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.15, 132.98, 132.91, 129.34, 128.95, 127.87, 126.19, 77.50, 77.08, 76.65, 49.73, 45.80, 25.32, 23.22, 21.54, 21.27, 20.47, 19.72. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -153.86, -153.91. **IR** (neat): 2949, 1741, 1637, 1558, 1455, 1309, 1285, 1047, 1035, 917, 750, 700 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{21}N_2$ (M+H) $^{+}$: 253.16993; found: 253.16931.

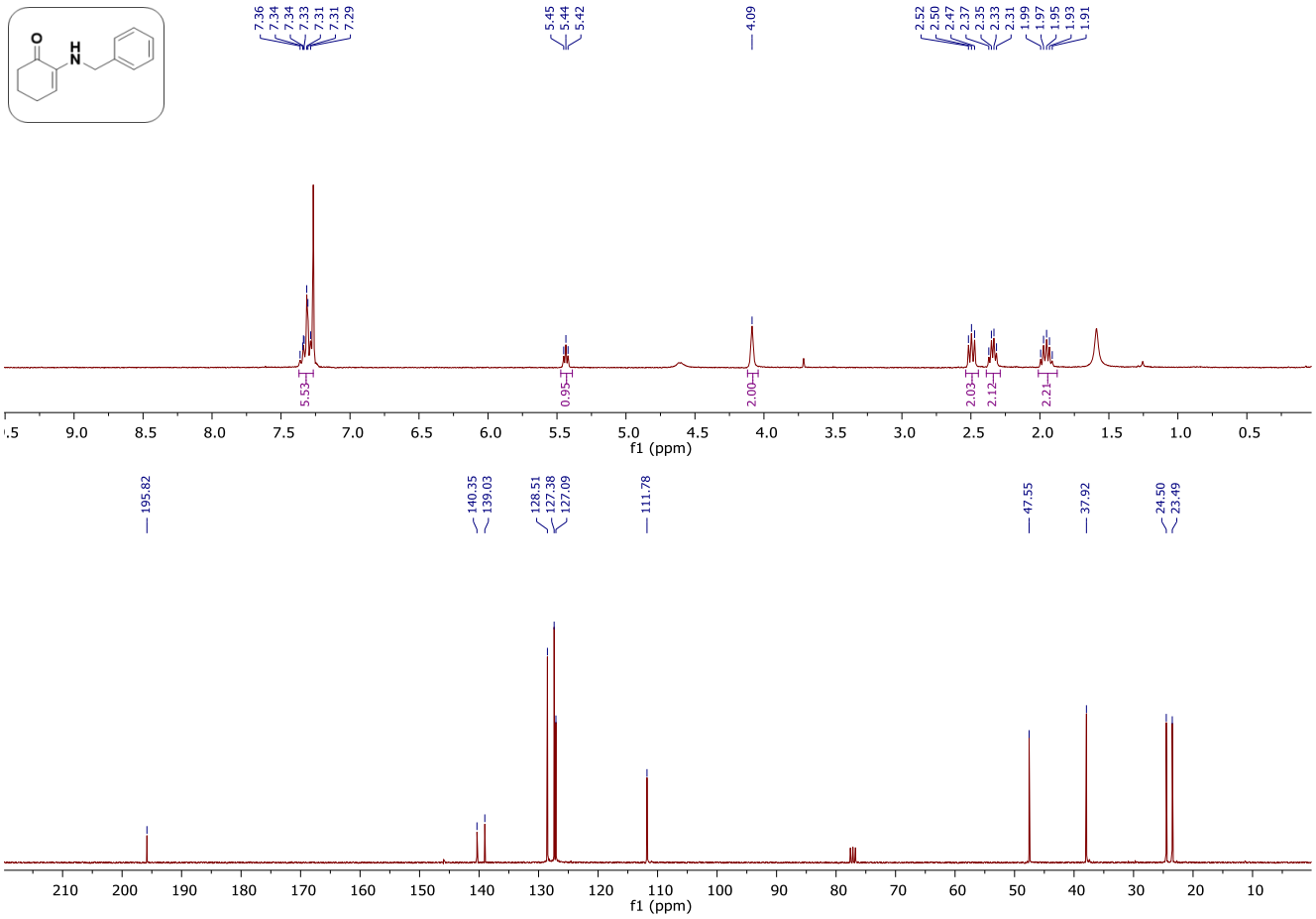


52: 4-benzyl-2,3,5,6,7,8-hexahydro-1H-benzo[d]pyrrolo[1,2-a]imidazol-4-ium fluoride: general procedure **B** was applied using α-enaminone (1.00 equiv., 0.028 g, 0.14 mmol), proline (2.00 equiv., 0.032 g, 0.28 mmol), and sodium fluoride (1.00 equiv., 0.006 g, 0.14 mmol) instead of KI, in MeOH (0.27 M, 0.55 ml), 17 h, 100 °C. The crude was purified by flushing the crude compound twice through a silica plug using DCM and eluent composed of 10% methanol, 20% ethyl acetate in DCM (0.004 g, 11% yield, yellow liquid). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 6.7 Hz, 6H), 5.36 (s, 3H), 4.21 (t, *J* = 7.2 Hz, 3H), 3.33 (t, *J* = 7.7 Hz, 3H), 2.88 – 2.76 (m, 3H), 2.59 (s, 3H), 2.53 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) 150.78, 133.29, 132.98, 129.32, 128.96, 127.96, 125.94, 77.45, 77.02, 76.60, 50.13, 46.17, 25.59, 24.14, 21.60, 21.34, 20.62, 19.93. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -142.54. **IR** (H_2O): 2923, 2852, 2359, 1723, 1556, 1455, 698 cm^{-1}. **HRMS** (m/z) calc. for $C_{17}H_{21}N_2$ (M+H) $^{+}$: 253.16993; found: 253.16937.

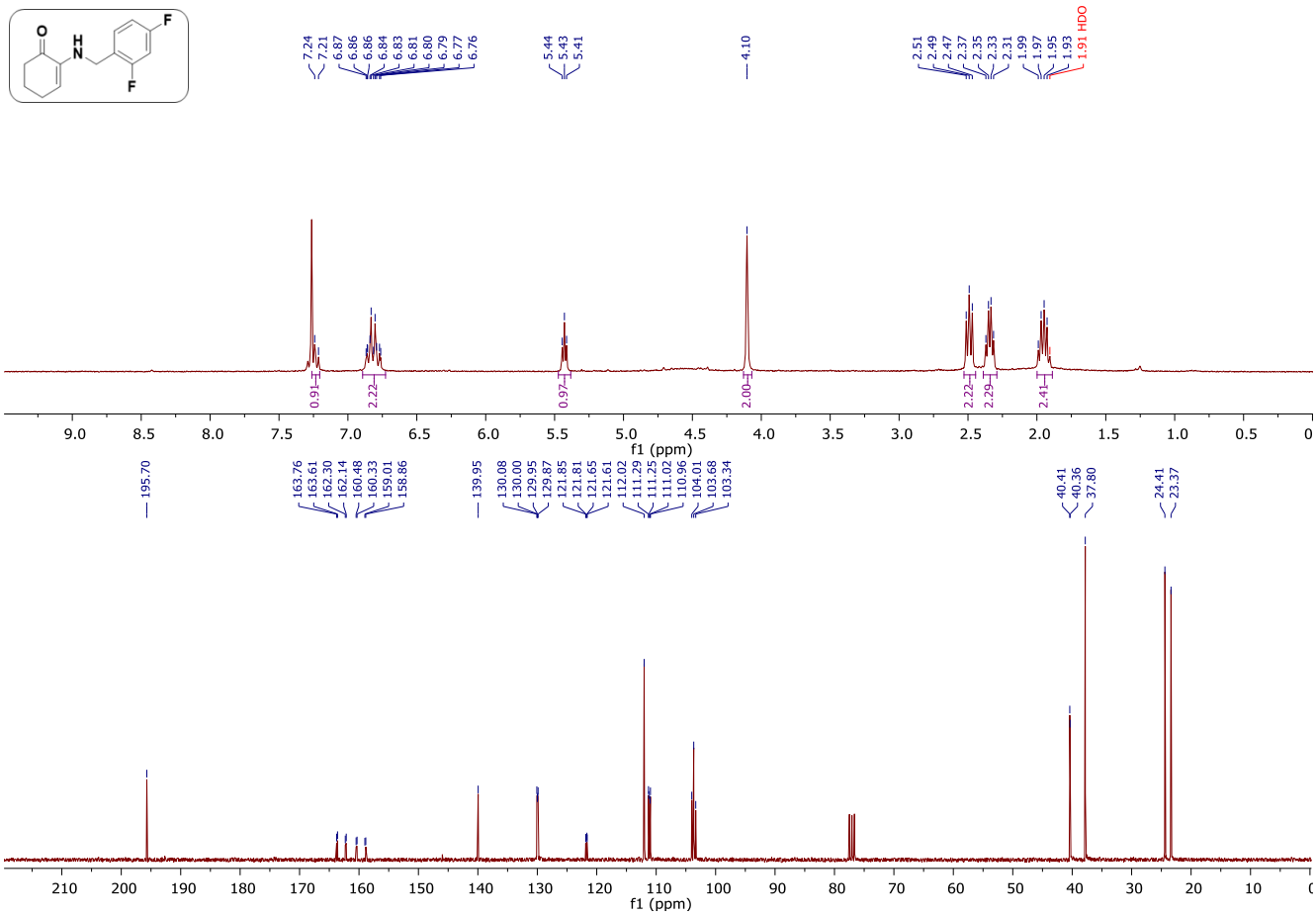
2-((4-(tert-butyl)benzyl)amino)cyclohex-2-en-1-one



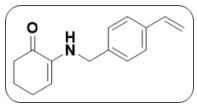
2-(benzylamino)cyclohex-2-en-1-one



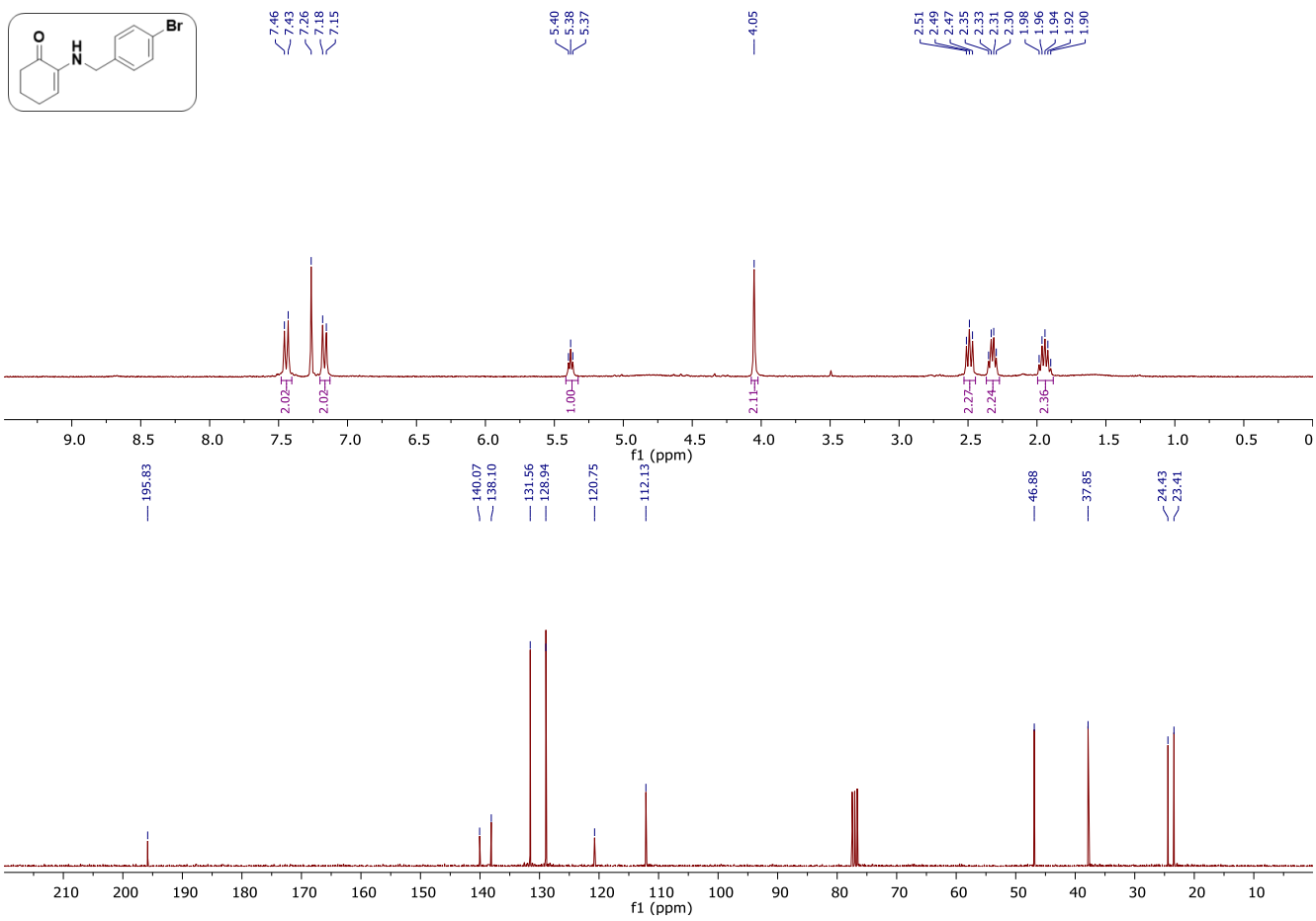
2-((2,4-difluorobenzyl)amino)cyclohex-2-en-1-one



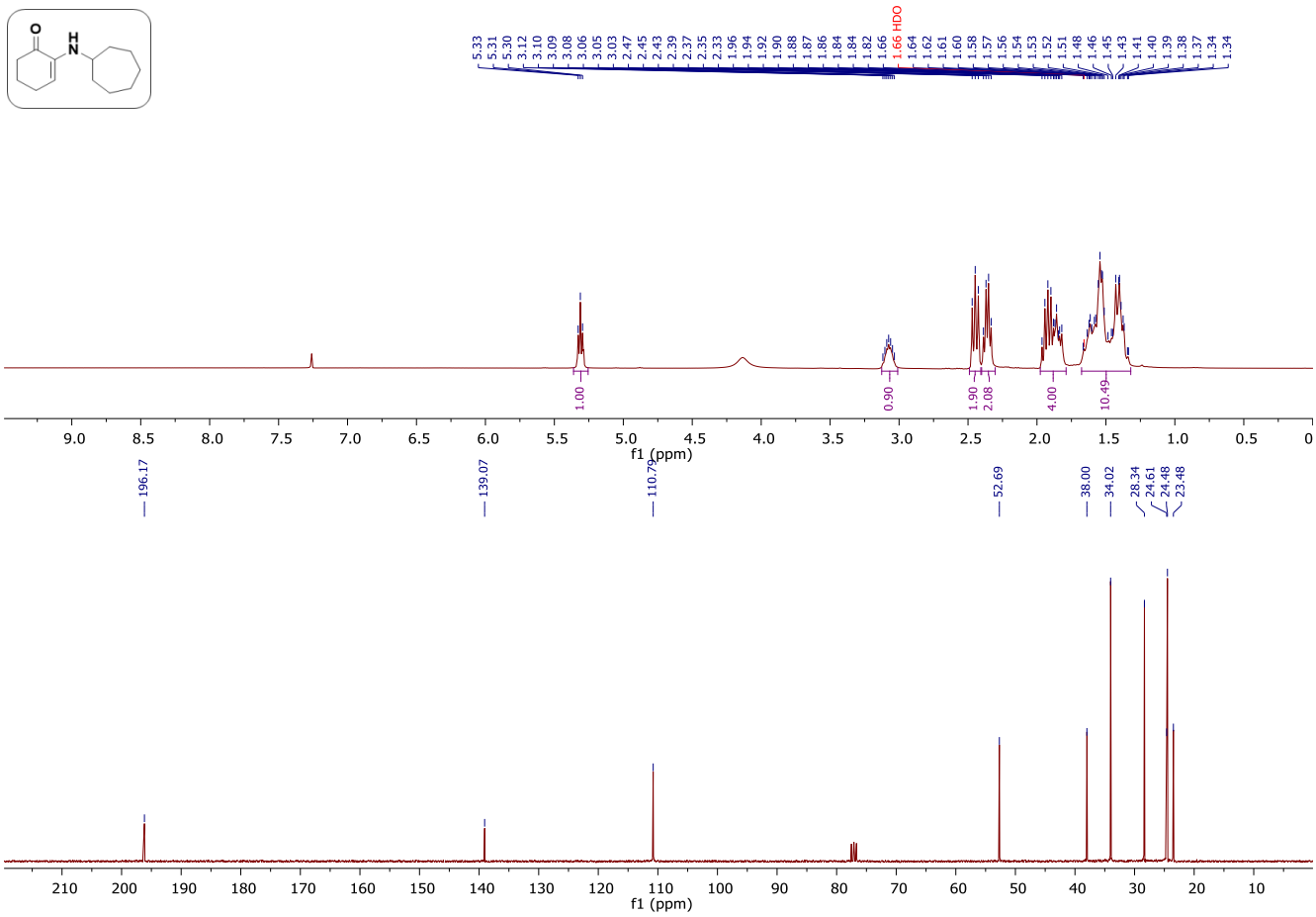
2-((4-vinylbenzyl)amino)cyclohex-2-en-1-one



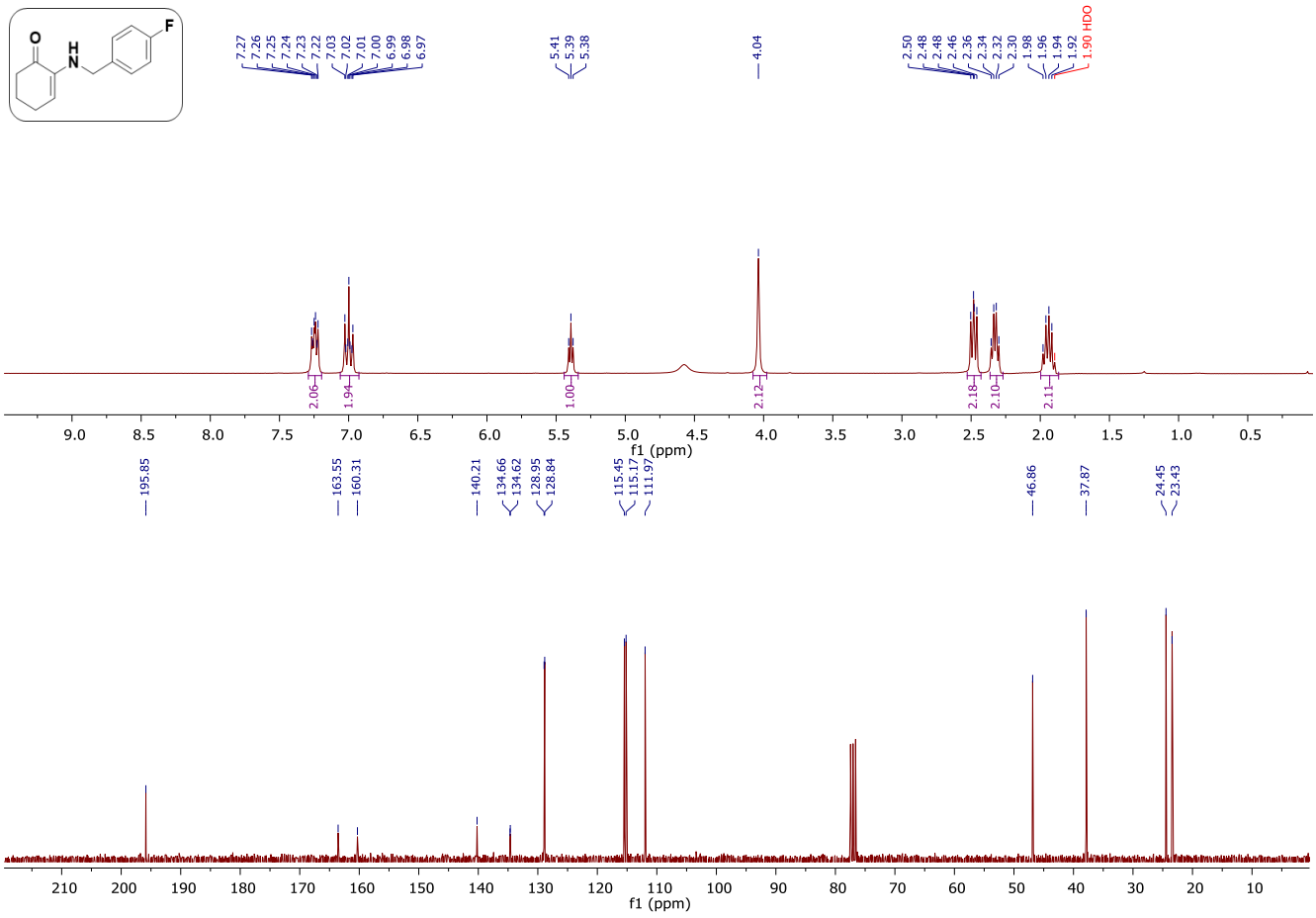
2-((4-bromobenzyl)amino)cyclohex-2-en-1-one



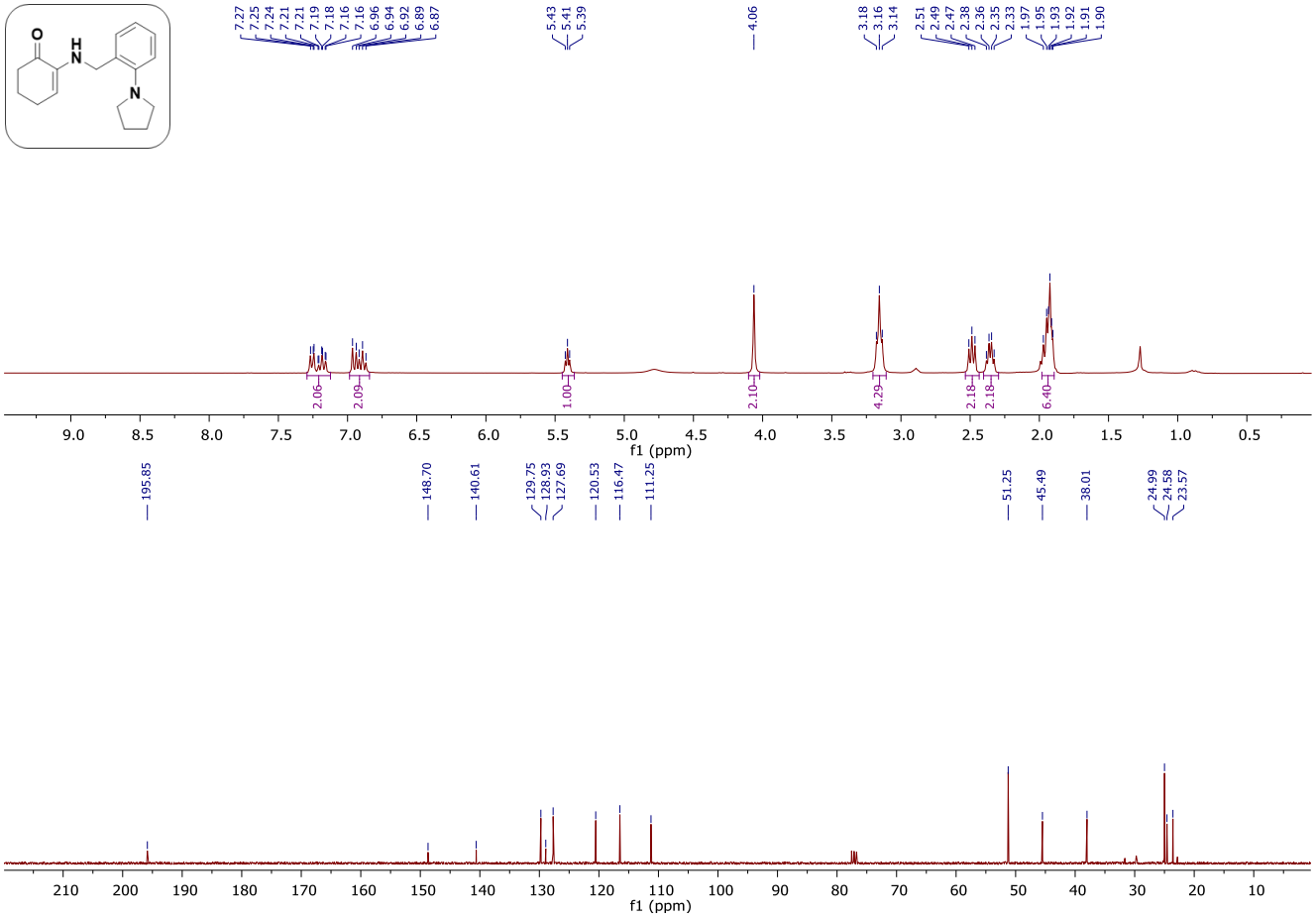
2-(cycloheptylamino)cyclohex-2-en-1-one



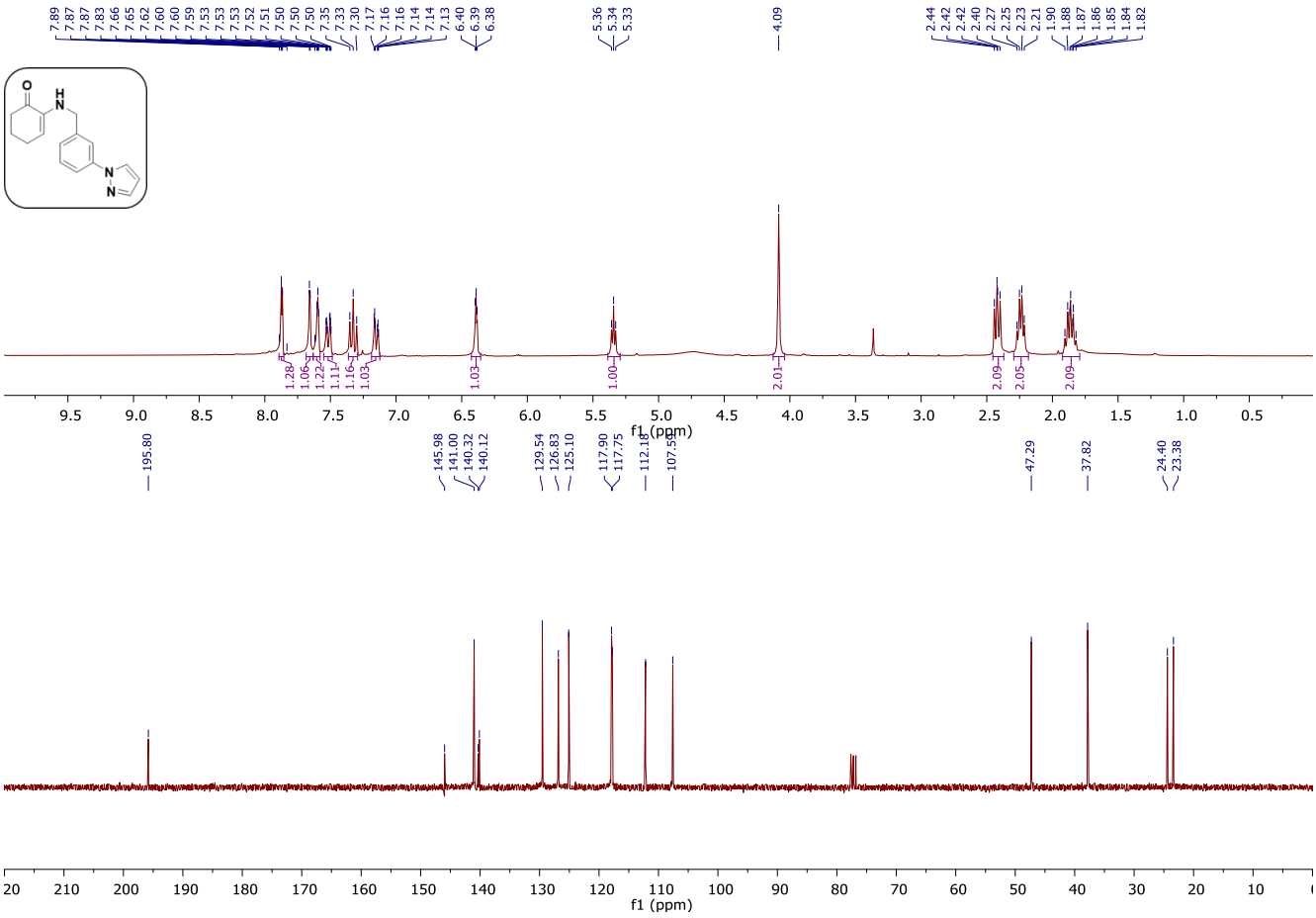
2-((4-fluorobenzyl)amino)cyclohex-2-en-1-one



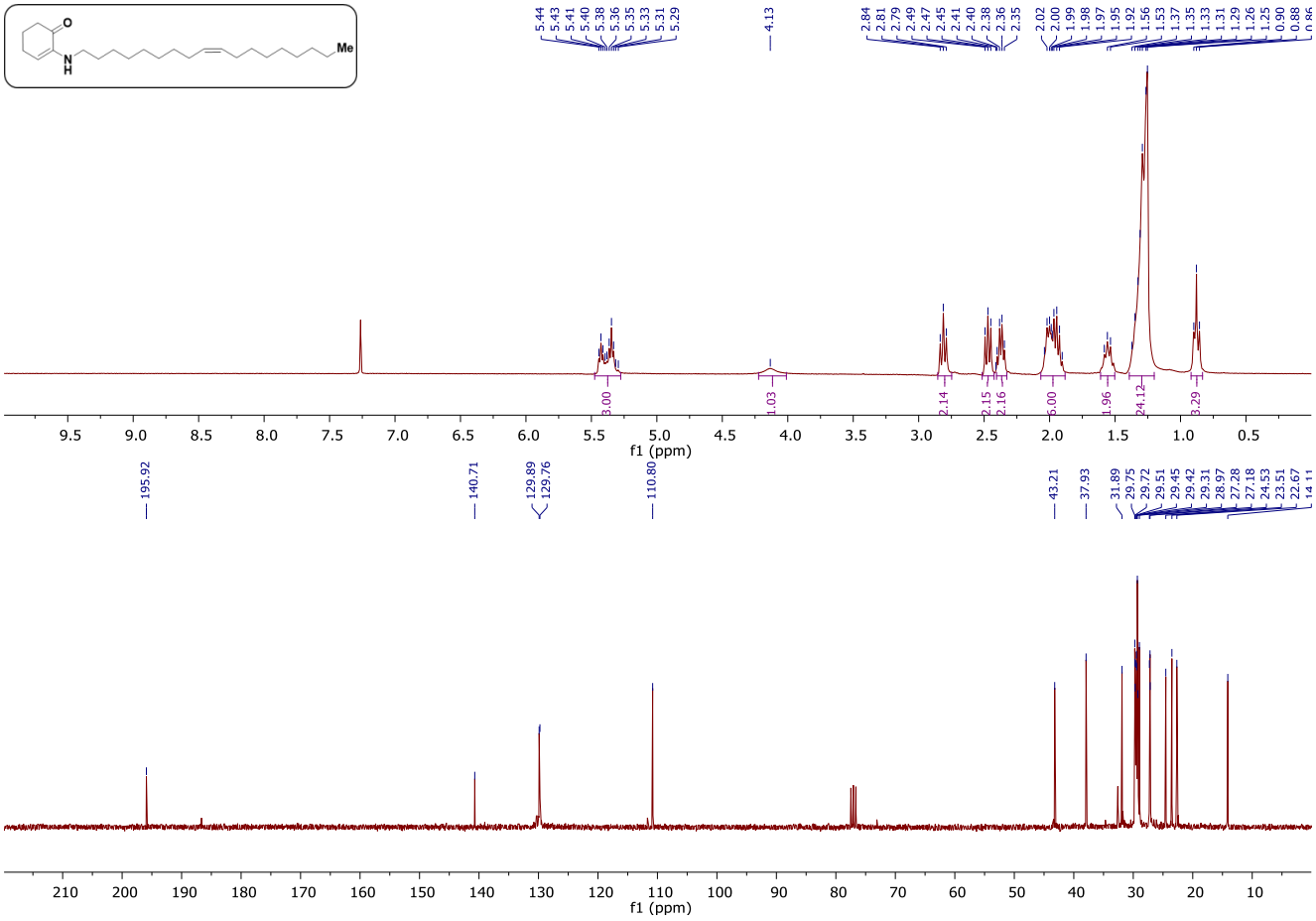
2-((2-(pyrrolidin-1-yl)benzyl)amino)cyclohex-2-en-1-one



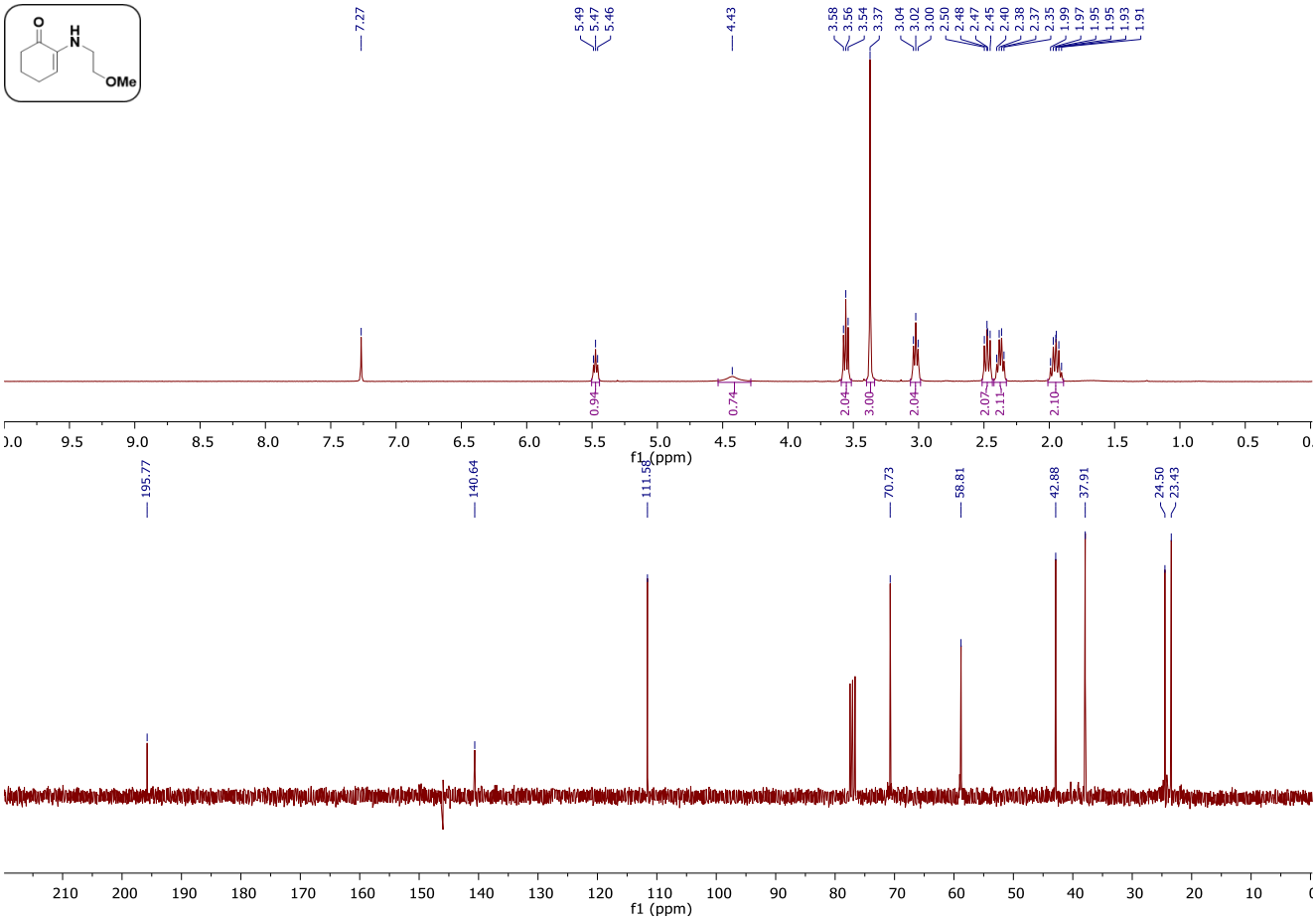
2-((3-(1H-pyrazol-1-yl)benzyl)amino)cyclohex-2-enone



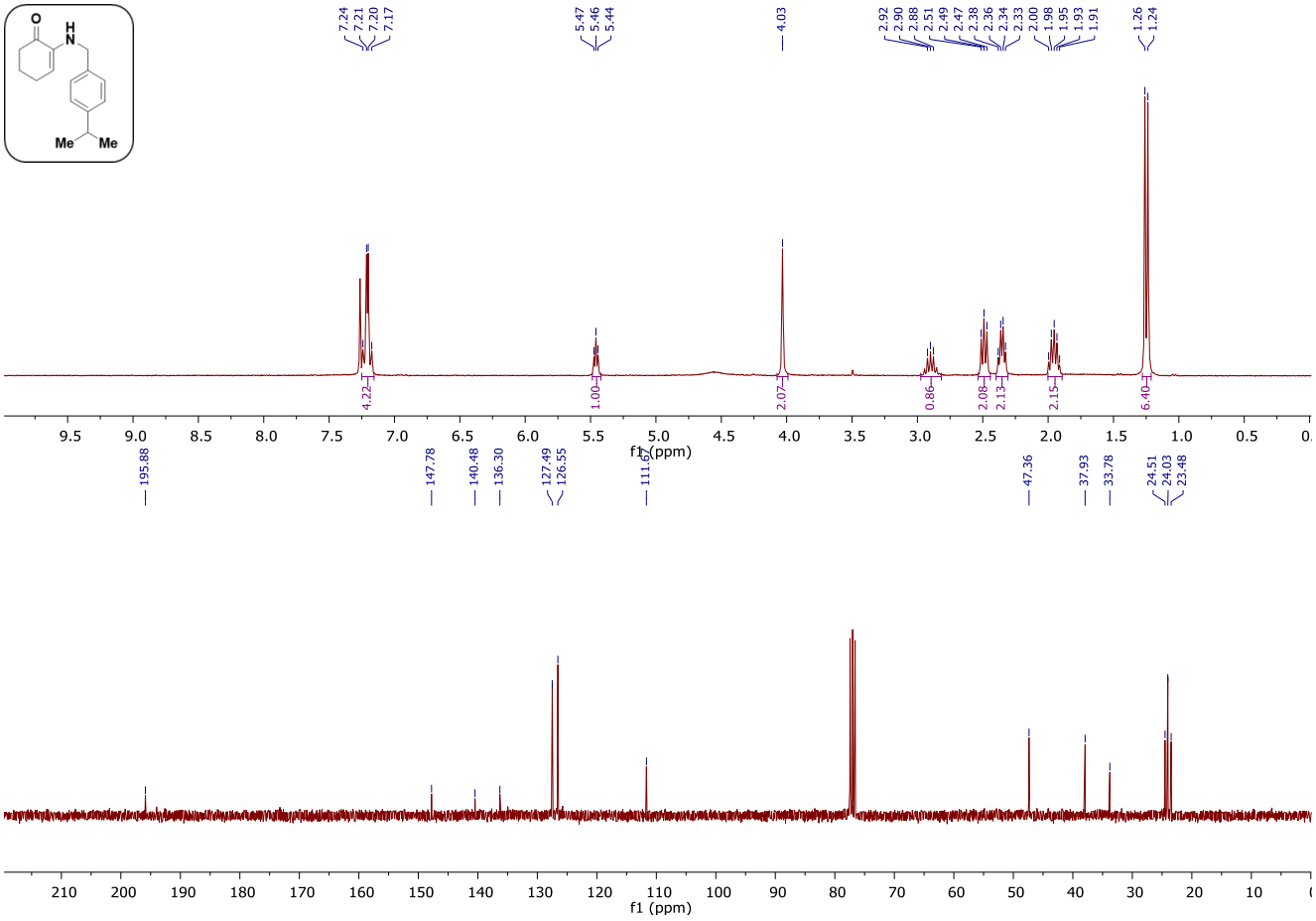
(Z)-2-(octadic-9-en-1-ylamino)cyclohex-2-enone



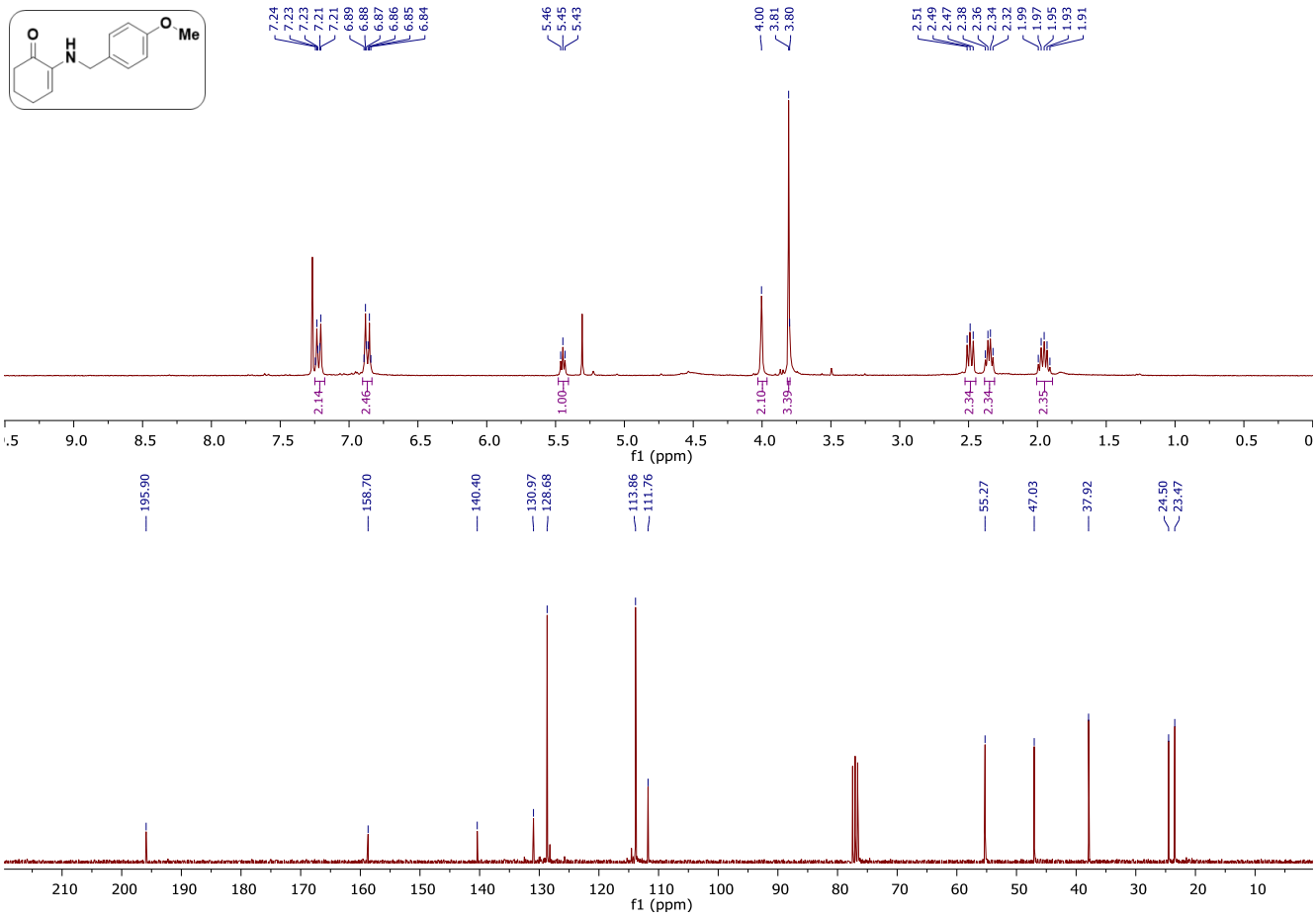
2-((2-methoxyethyl)amino)cyclohex-2-enone



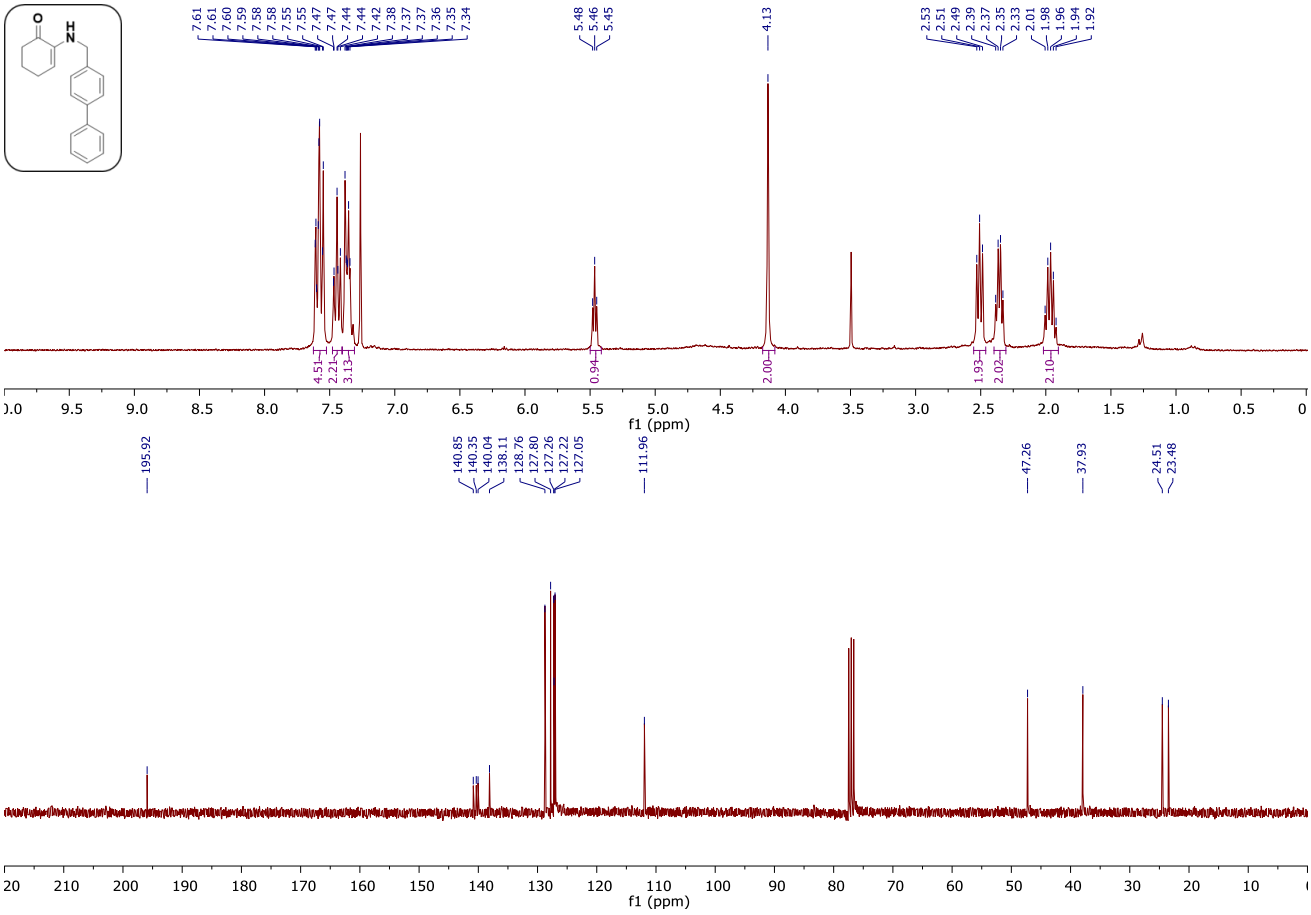
2-((4-isopropylbenzyl)amino)cyclohex-2-enone



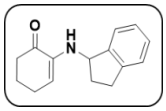
2-((4-methoxybenzyl)amino)cyclohex-2-en-1-one



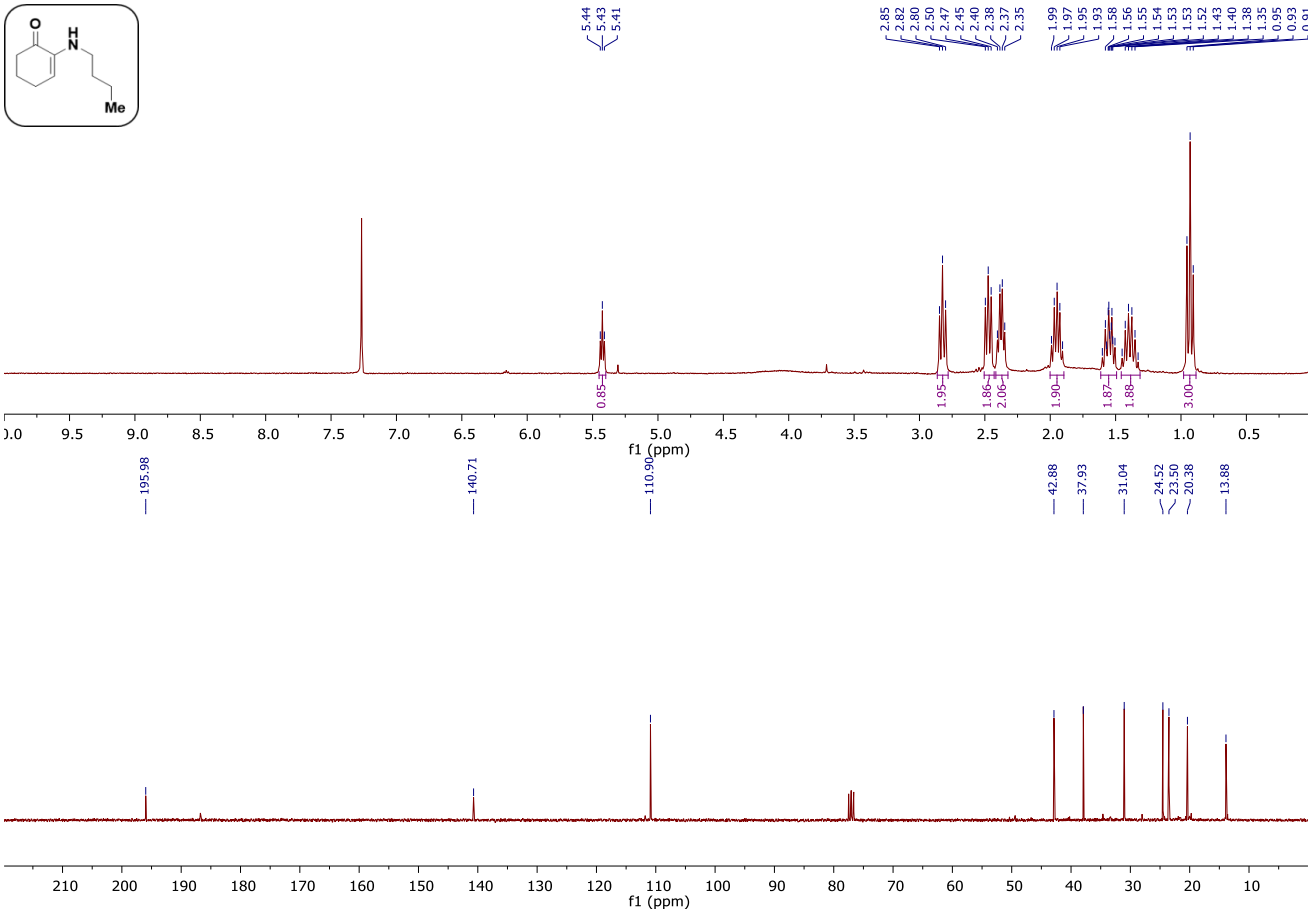
2-(([1,1’-biphenyl]-4-ylmethyl)amino)cyclohex-2-enone



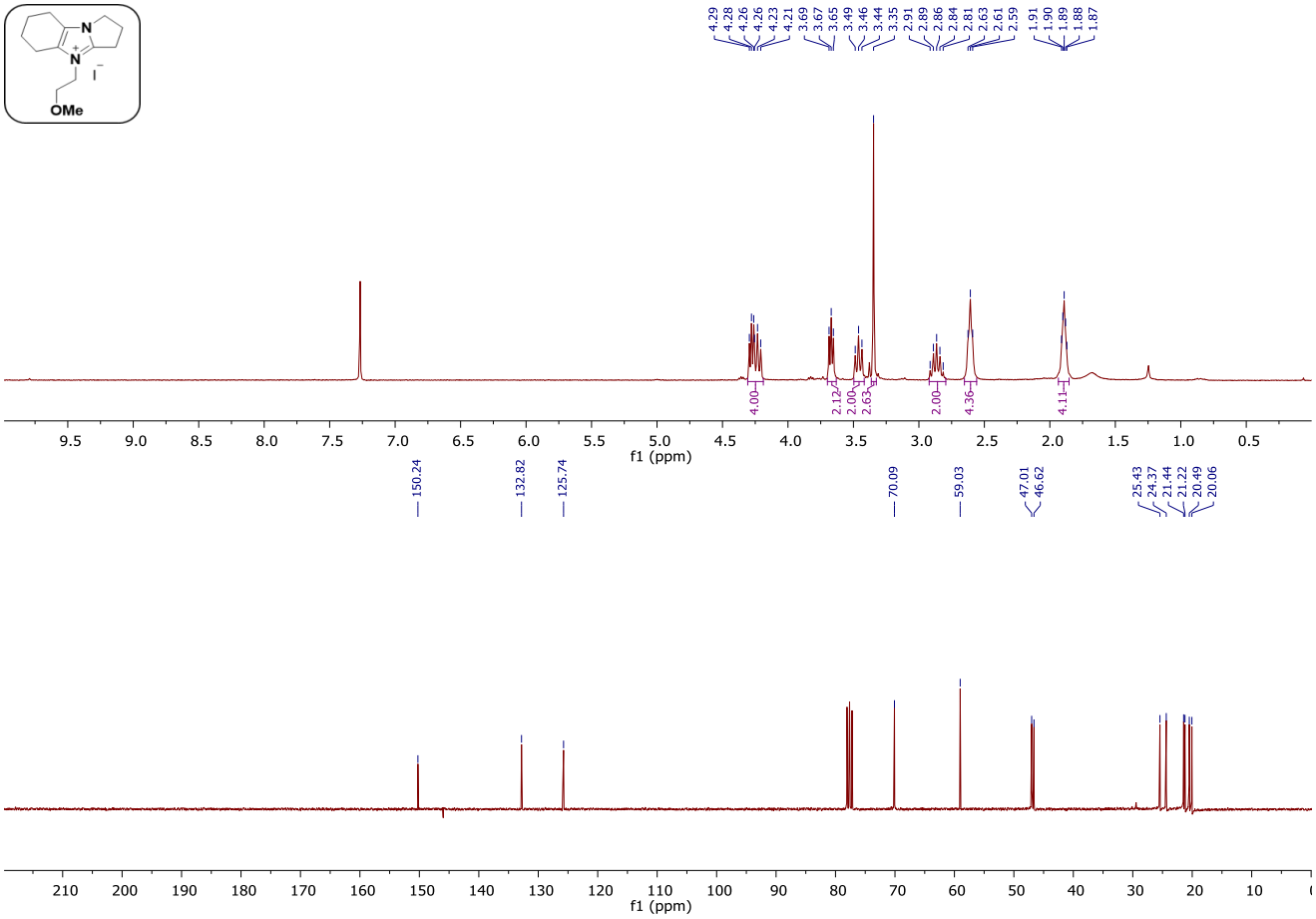
2-((2,3-dihydro-1H-inden-1-yl)amino)cyclohex-2-enone



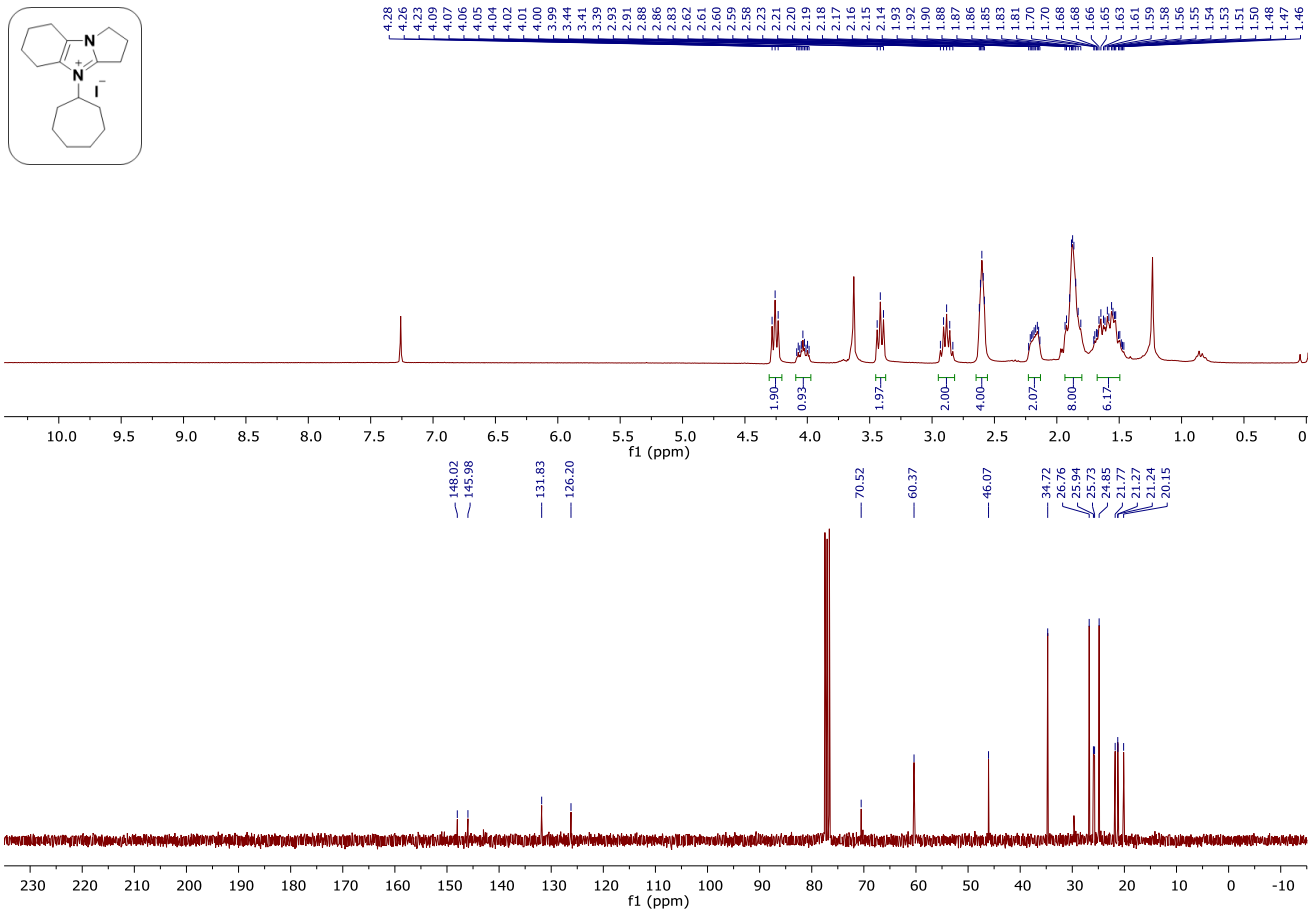
2-(butylamino)cyclohex-2-enone



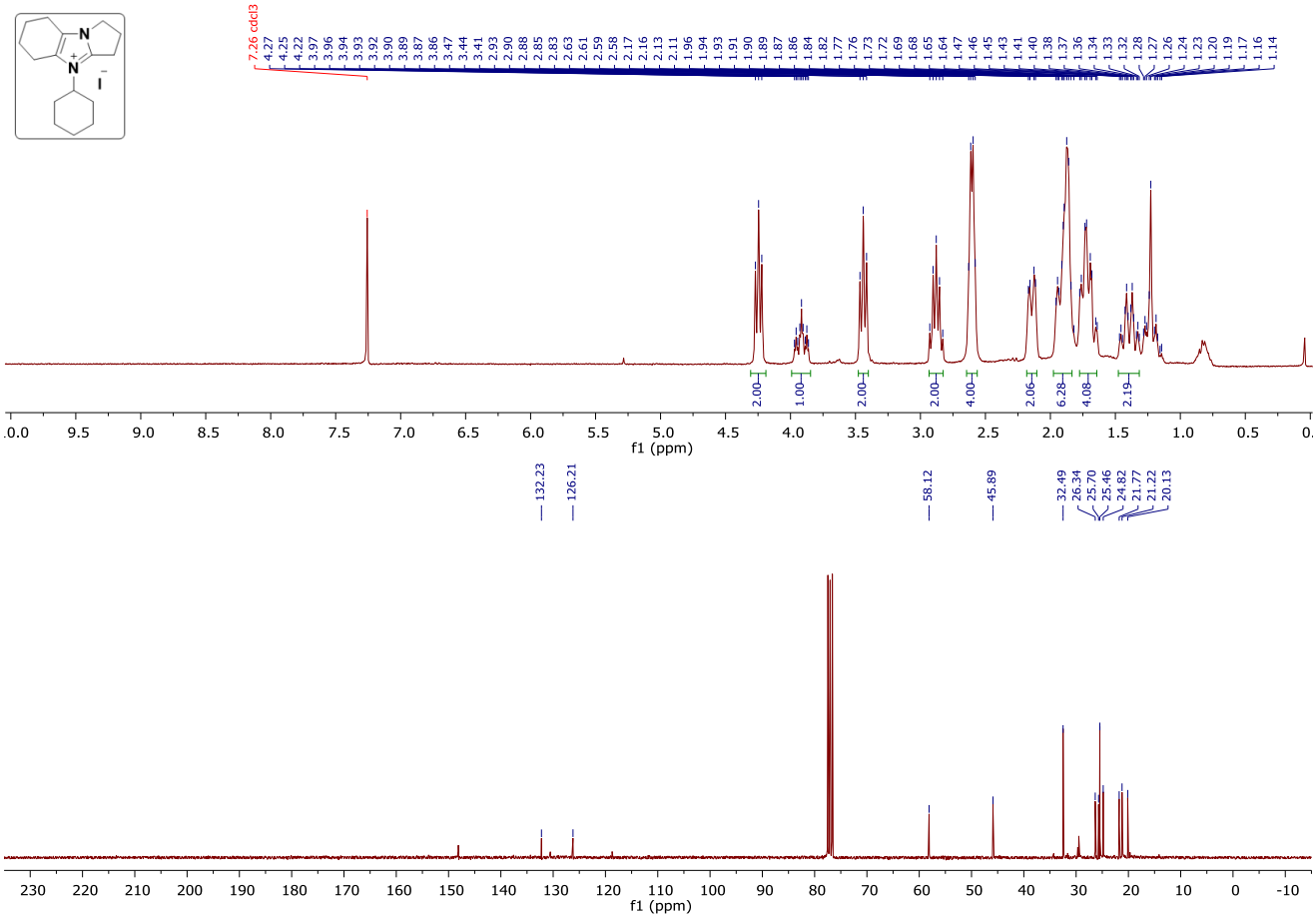
(28)


N
N
I
OMe
4.29
4.28
4.26
4.26
4.23
4.21
3.69
3.67
3.65
3.49
3.46
3.44
3.35
2.91
2.89
2.86
2.84
2.81
2.63
2.61
2.59
1.91
1.90
1.89
1.88
1.87
4.00
2.12
2.00
2.63
2.00
4.36
4.11
f1 (ppm)
150.24
132.82
125.74
70.09
59.03
47.01
46.62
25.43
24.37
21.44
21.22
20.49
20.06
f1 (ppm)

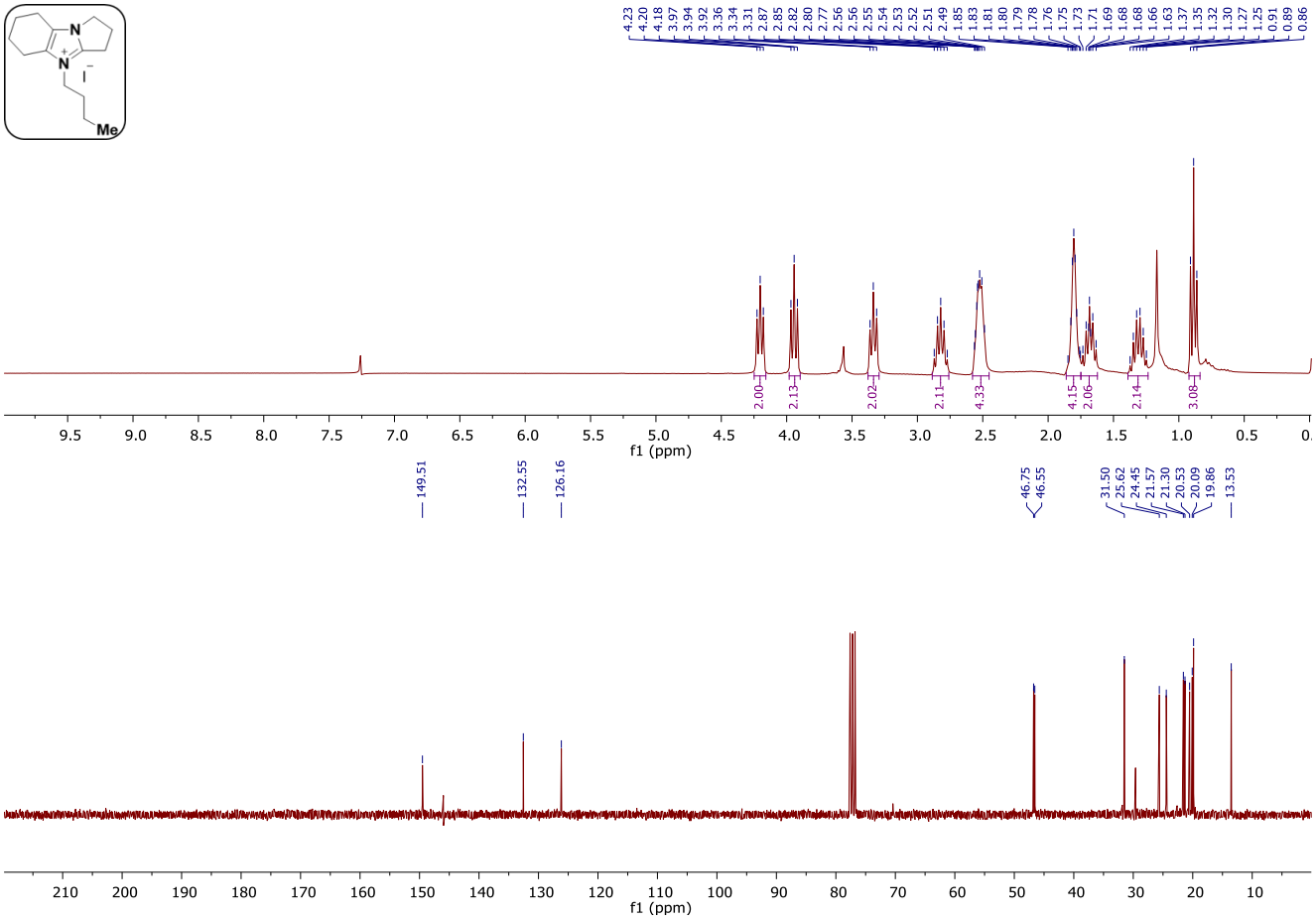
(29)


4.28 4.26 4.23 4.09 4.07 4.06 4.05 4.04 4.02 4.01 4.00 3.99 3.44 3.41 3.39 2.93 2.91 2.88 2.86 2.83 2.62 2.61 2.60 2.59 2.58 2.23 2.21 2.20 2.19 2.18 2.17 2.16 2.15 2.14 1.93 1.92 1.90 1.88 1.87 1.86 1.85 1.83 1.81 1.70 1.70 1.68 1.68 1.66 1.65 1.63 1.61 1.59 1.58 1.56 1.55 1.54 1.53 1.51 1.50 1.48 1.47 1.46
1.90 0.93 1.97 2.00 4.00 2.07 8.00 6.17
f1 (ppm)
148.02 145.98 131.83 126.20 70.52 60.37 46.07 34.72 26.76 25.94 25.73 24.85 21.77 21.27 21.24 20.15
f1 (ppm)

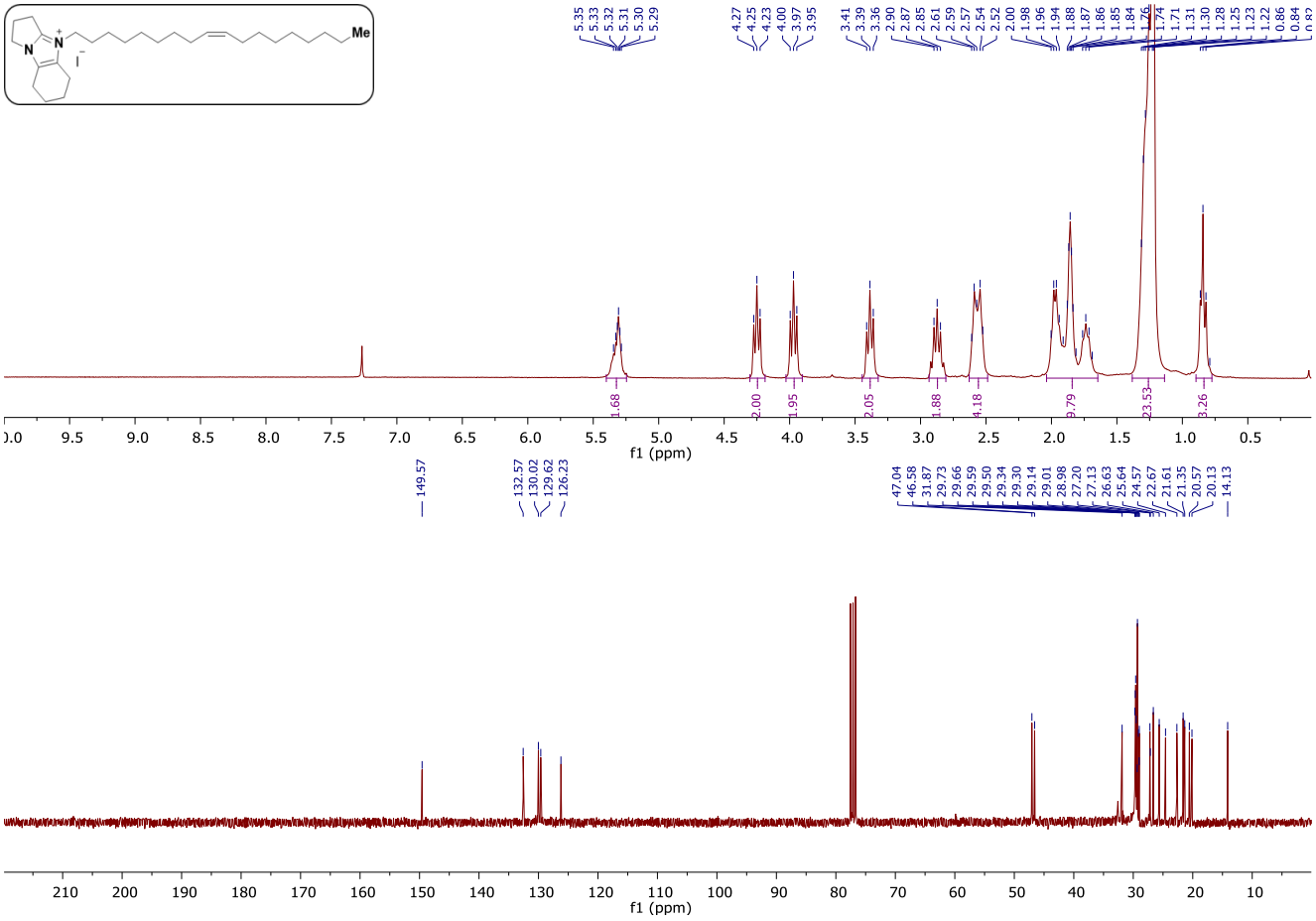
(30)


7.26 cdcl3
2.00
1.00
2.00
2.00
4.00
2.06
6.28
4.08
2.19
f1 (ppm)
132.23
126.21
58.12
45.89
32.49
26.34
25.70
25.46
24.82
21.77
21.22
20.13
f1 (ppm)

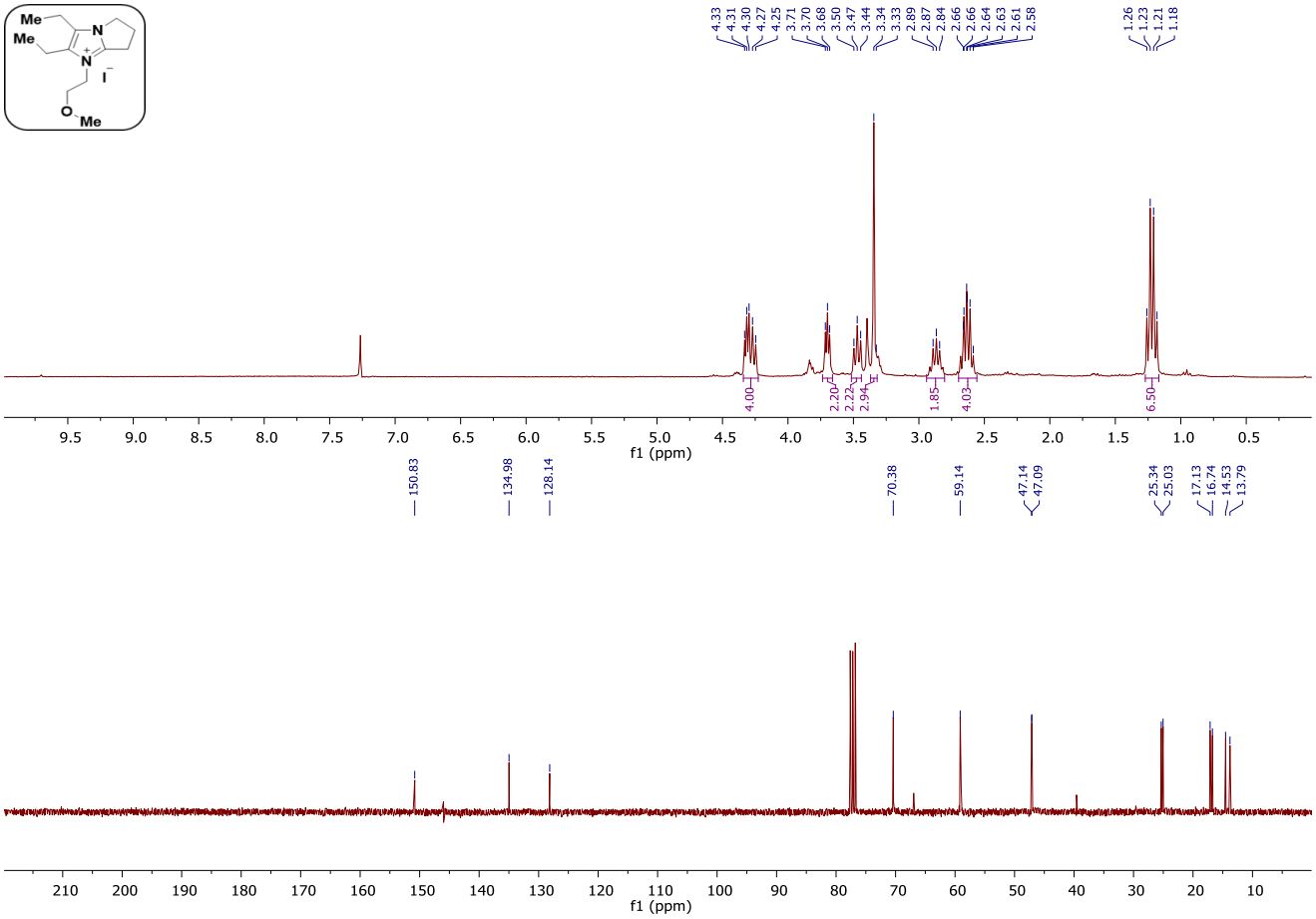
(31)


4.23 4.20 4.18 3.97 3.94 3.92 3.36 3.34 3.31 2.87 2.85 2.82 2.80 2.77 2.56 2.56 2.55 2.54 2.53 2.52 2.51 2.49 1.85 1.83 1.81 1.80 1.79 1.78 1.76 1.75 1.73 1.71 1.69 1.68 1.68 1.66 1.63 1.37 1.35 1.32 1.30 1.27 1.25 0.91 0.89 0.86
2.00 2.13 2.02 2.11 4.33 4.15 2.06 2.14 3.08
f1 (ppm)
149.51 132.55 126.16 46.75 46.55 31.50 25.62 24.45 21.57 21.30 20.53 20.09 19.86 13.53
f1 (ppm)

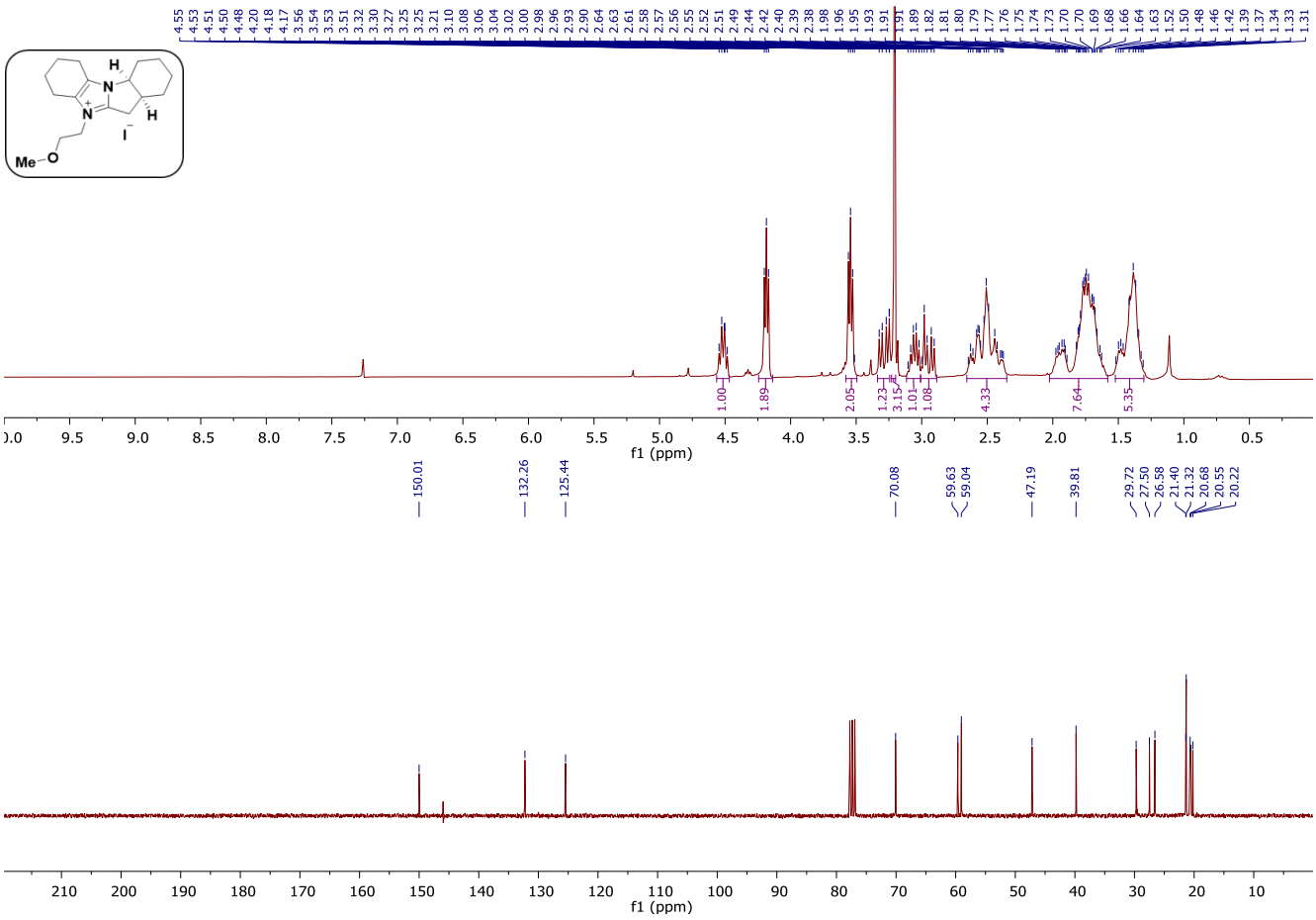
(32)



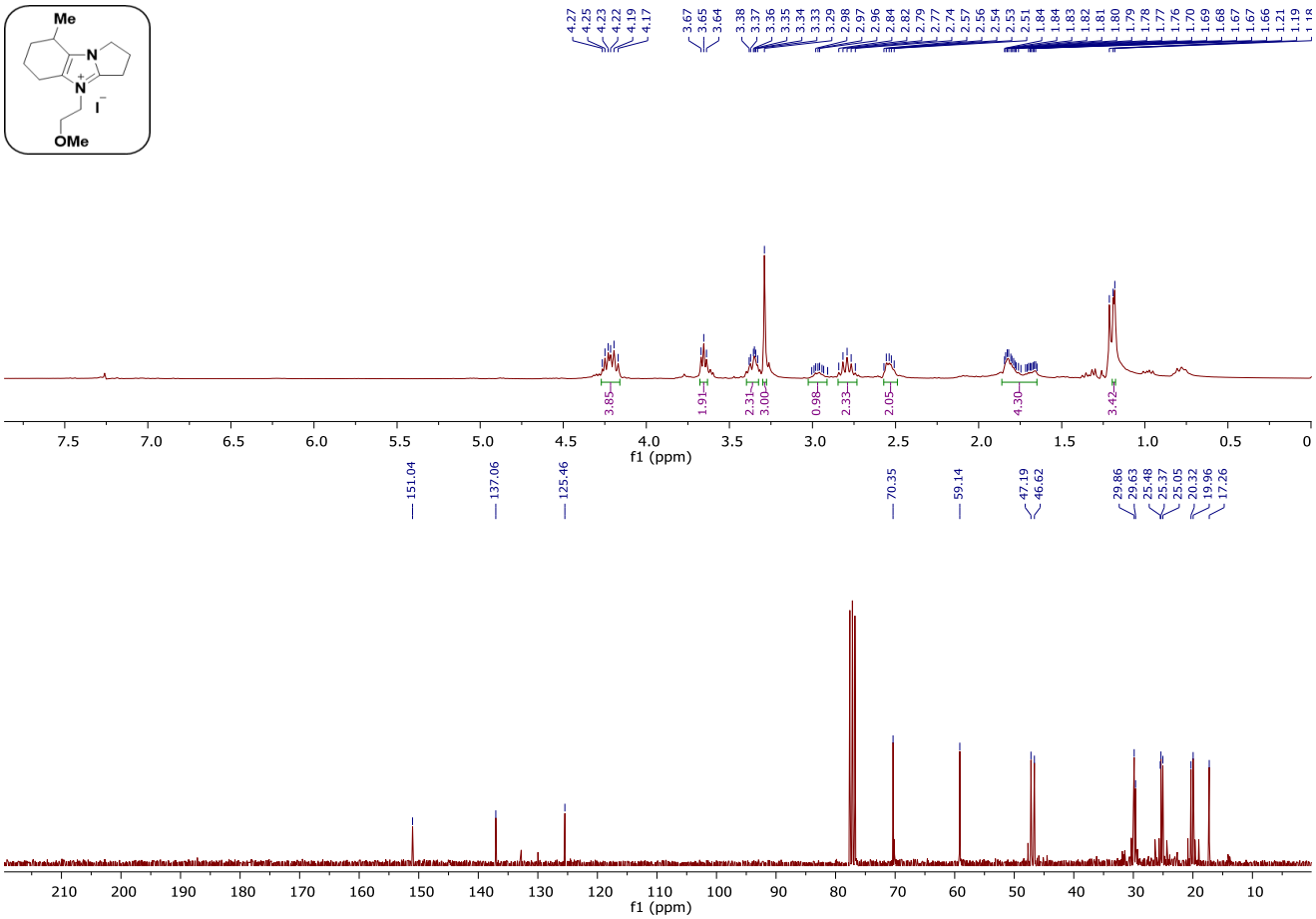
(33)


Me
Me
N
N
I
O
Me
4.33
4.31
4.30
4.27
4.25
3.71
3.70
3.68
3.50
3.47
3.44
3.34
3.33
2.89
2.87
2.84
2.66
2.66
2.64
2.63
2.61
2.58
1.26
1.23
1.21
1.18
4.00
2.20
2.22
2.94
1.85
4.03
6.50
f1 (ppm)
150.83
134.98
128.14
70.38
59.14
47.14
47.09
25.34
25.03
17.13
16.74
14.53
13.79
f1 (ppm)

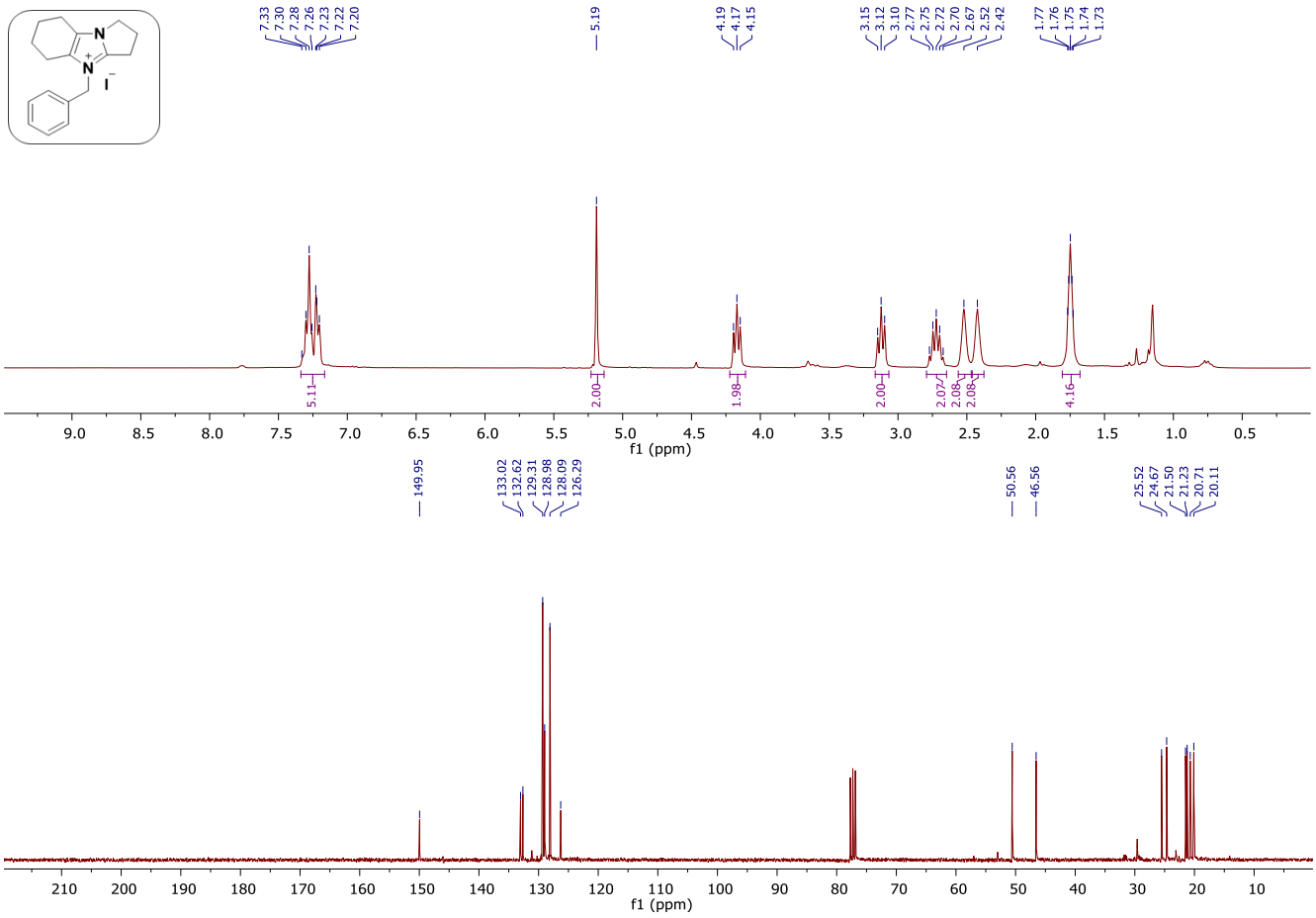
(34)


f1 (ppm)
150.01
132.26
125.44
70.08
59.63
59.04
47.19
39.81
29.72
27.50
26.58
21.40
21.32
20.68
20.55
20.22
f1 (ppm)

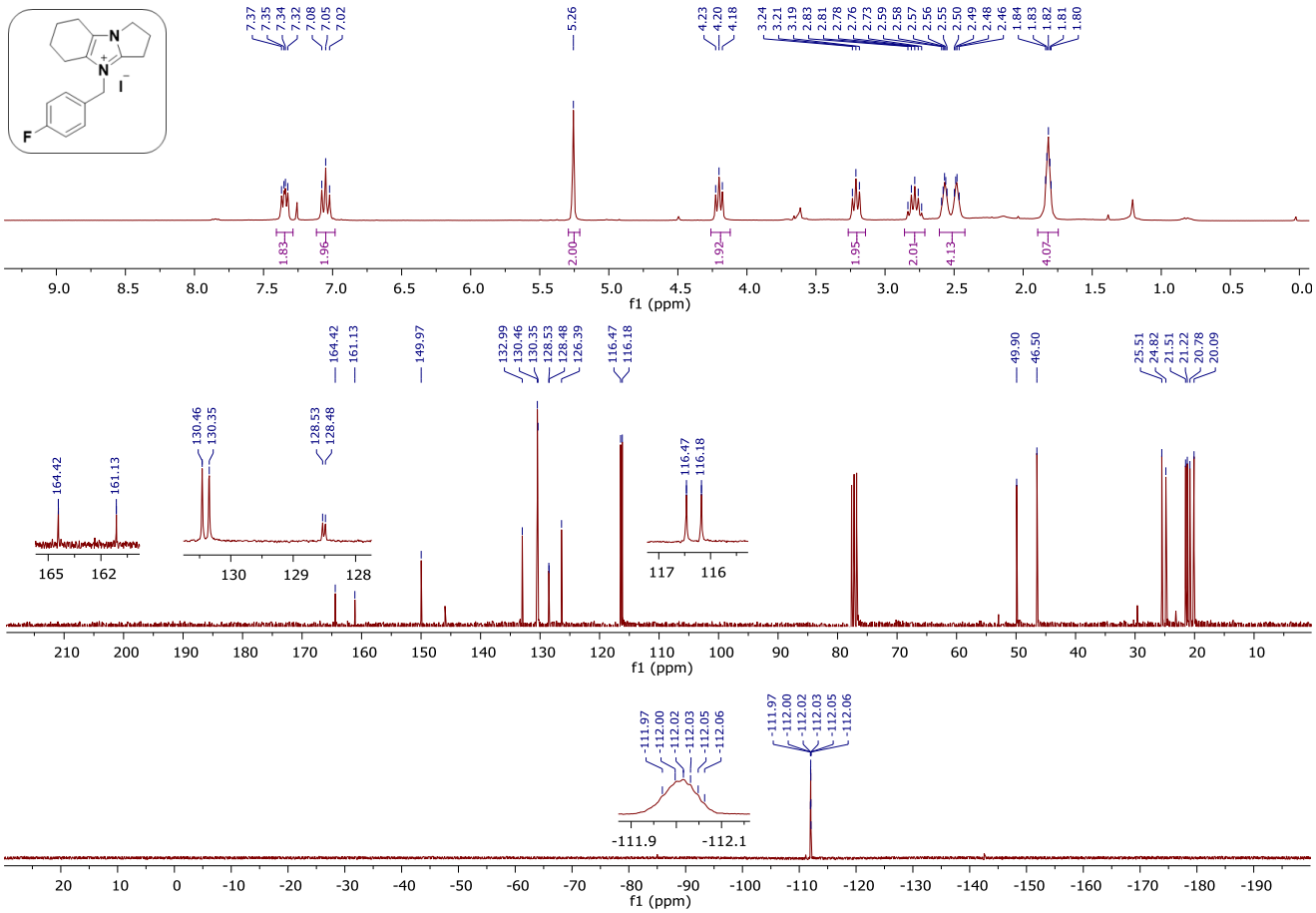
(35)


Me
N
N
I
OMe
4.27 4.25 4.23 4.22 4.19 4.17 3.67 3.65 3.64 3.38 3.37 3.36 3.35 3.34 3.33 3.29 2.98 2.97 2.96 2.84 2.82 2.79 2.77 2.74 2.57 2.56 2.54 2.53 2.51 1.84 1.84 1.83 1.82 1.81 1.80 1.79 1.78 1.77 1.76 1.70 1.69 1.68 1.67 1.67 1.66 1.21 1.19
3.85 1.91 2.31 3.00 0.98 2.33 2.05 4.30 3.42
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)
151.04 137.06 125.46 70.35 59.14 47.19 46.62 29.86 29.63 25.48 25.37 25.05 20.32 19.96 17.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

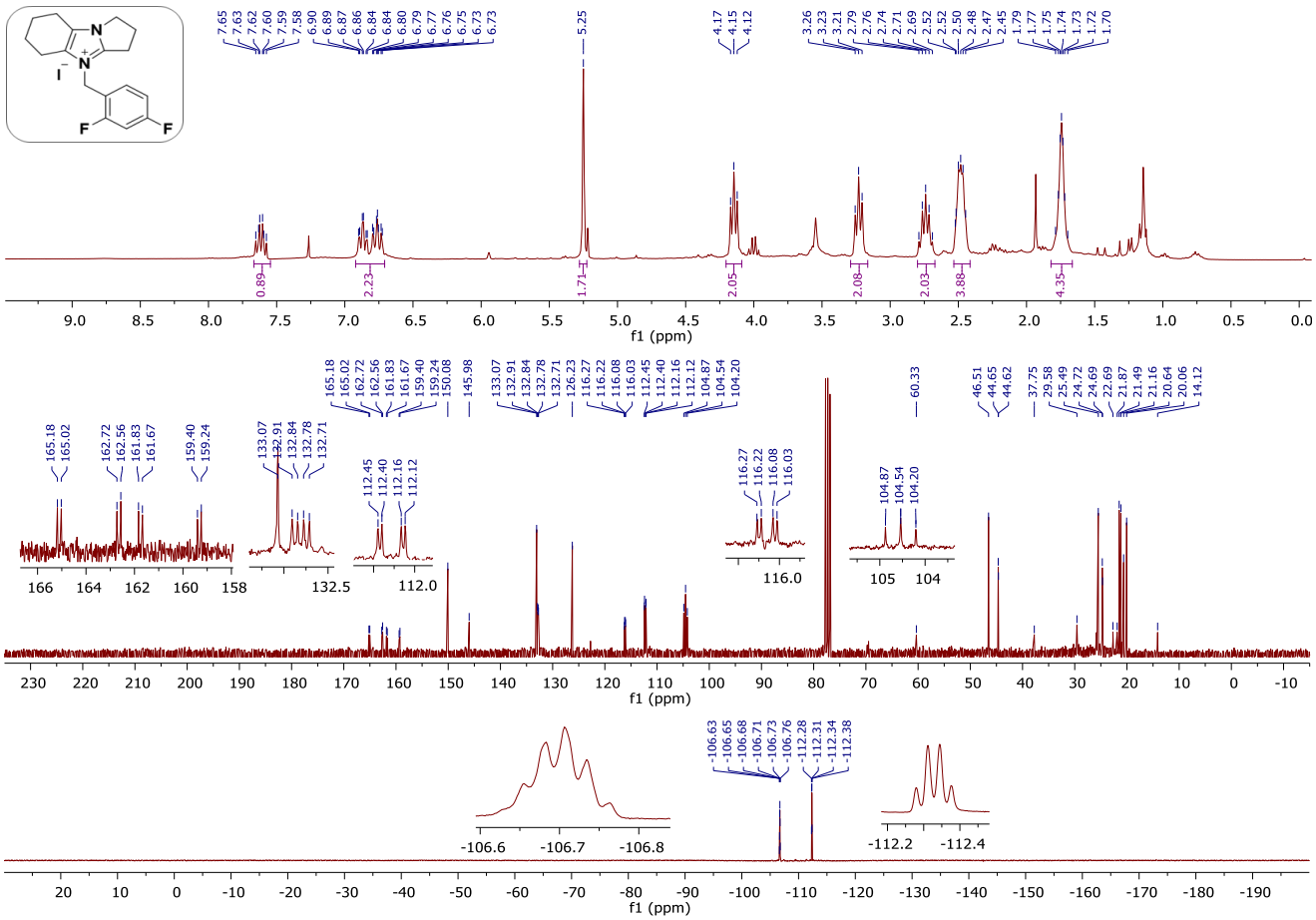
(36)


7.33
7.30
7.28
7.26
7.23
7.22
7.20
5.19
4.19
4.17
4.15
3.15
3.12
3.10
2.77
2.75
2.72
2.70
2.67
2.52
2.42
1.77
1.76
1.75
1.74
1.73
5.11
2.00
1.98
2.00
2.07
2.08
2.08
4.16
f1 (ppm)
149.95
133.02
132.62
129.31
128.98
128.09
126.29
50.56
46.56
25.52
24.67
21.50
21.23
20.71
20.11
f1 (ppm)

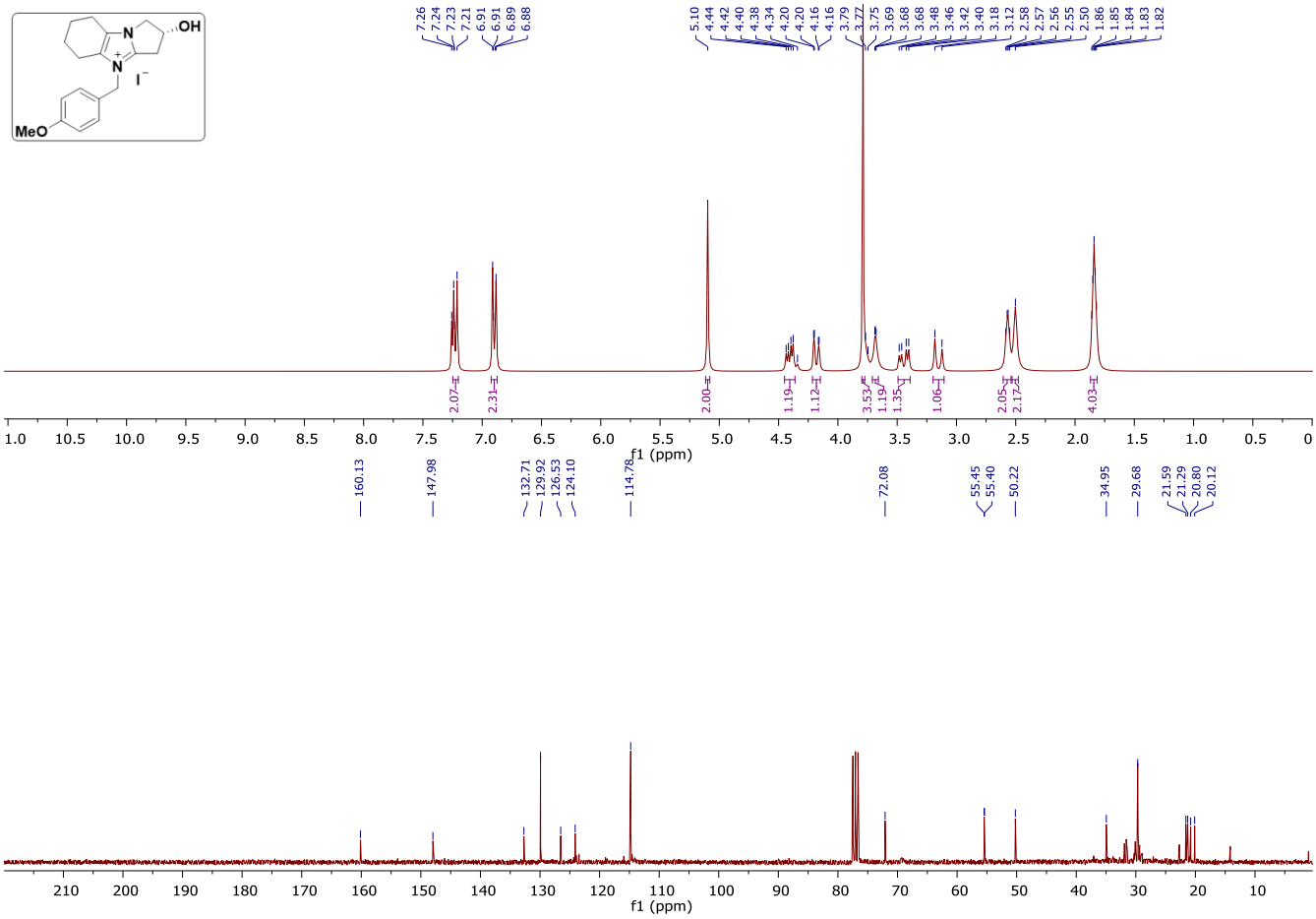
(37)


7.37
7.35
7.34
7.32
7.08
7.05
7.02
5.26
4.23
4.20
4.18
3.24
3.21
3.19
2.83
2.81
2.78
2.76
2.73
2.59
2.58
2.57
2.56
2.55
2.50
2.49
2.48
2.46
1.84
1.83
1.82
1.81
1.80
1.83
1.96
2.00
1.92
1.95
2.01
4.13
4.07
f1 (ppm)
164.42
161.13
149.97
132.99
130.46
130.35
128.53
128.48
126.39
116.47
116.18
49.90
46.50
25.51
24.82
21.51
21.22
20.78
20.09
-111.97
-112.00
-112.02
-112.03
-112.05
-112.06
-111.9
-112.1

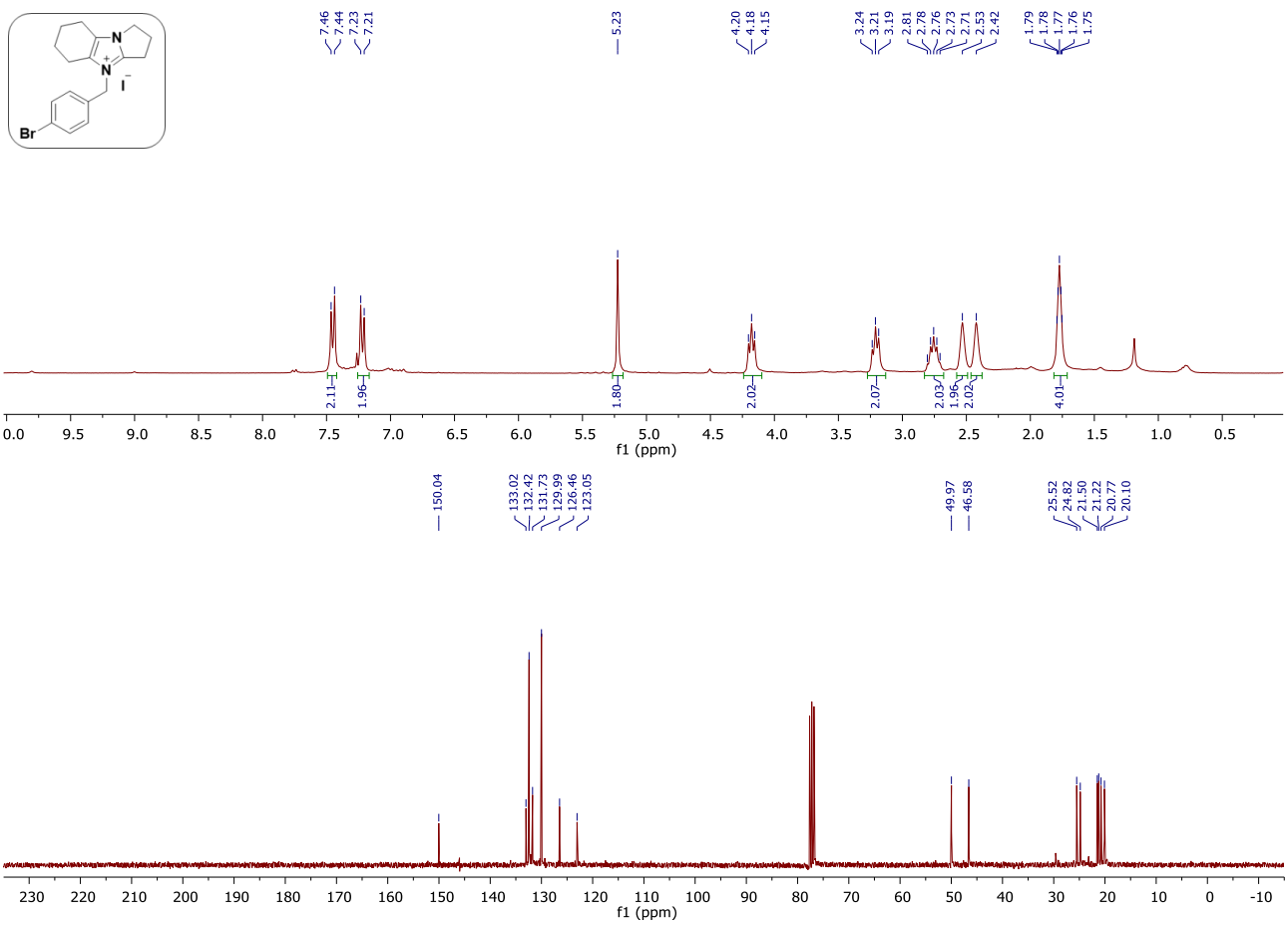
(38)



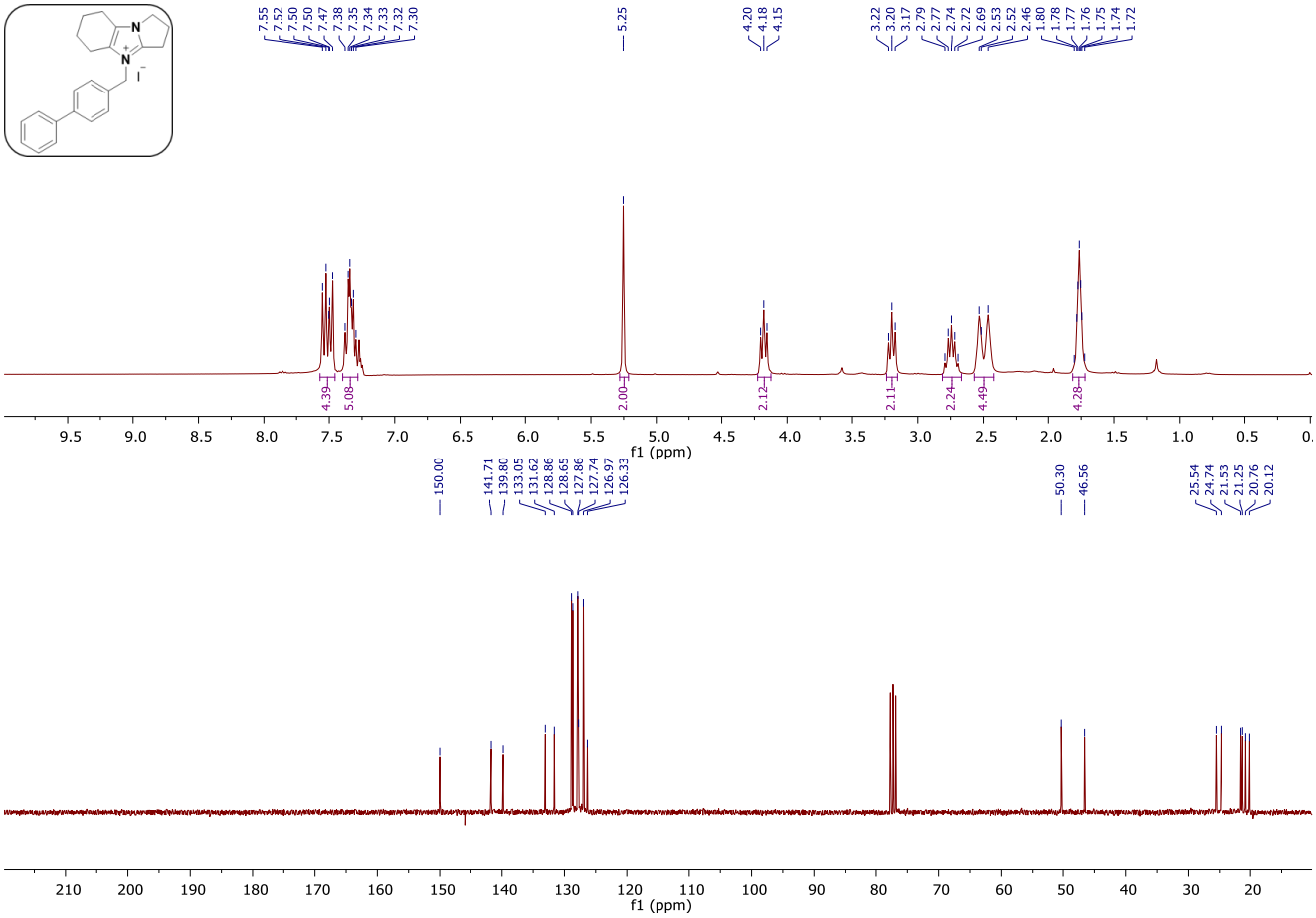
(39)


OH
N
N
I⁻
MeO
7.26
7.24
7.23
7.21
6.91
6.91
6.89
6.88
5.10
4.44
4.42
4.40
4.38
4.34
4.20
4.20
4.16
4.16
3.79
3.77
3.75
3.69
3.68
3.68
3.48
3.46
3.42
3.40
3.18
3.12
2.58
2.57
2.56
2.55
2.50
1.86
1.85
1.84
1.83
1.82
2.07
2.31
2.00
1.19
1.12
3.53
1.19
1.35
1.06
2.05
2.17
4.03
f1 (ppm)
160.13
147.98
132.71
129.92
126.53
124.10
114.78
72.08
55.45
55.40
50.22
34.95
29.68
21.59
21.29
20.80
20.12
f1 (ppm)

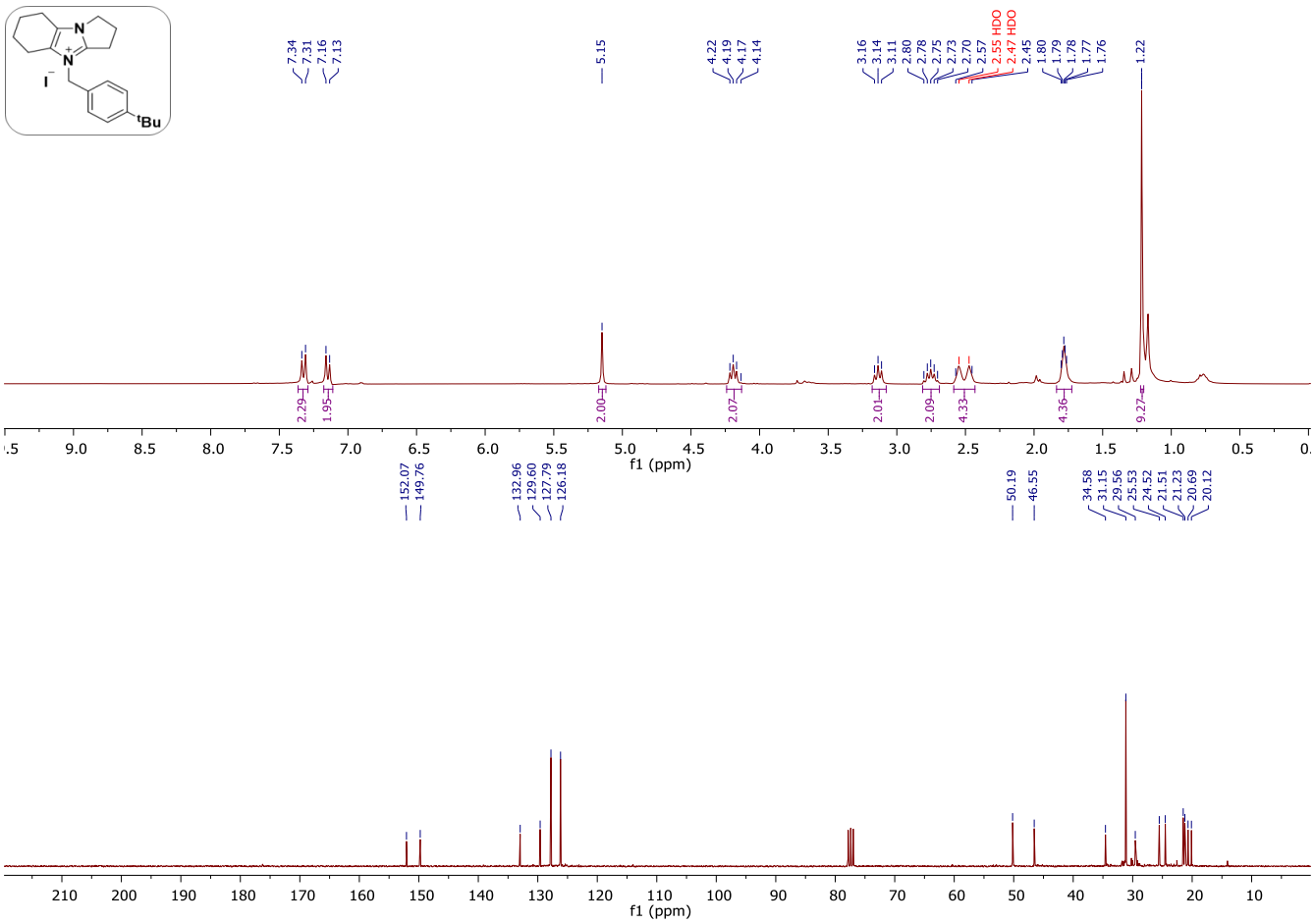
(40)


7.46
7.44
7.23
7.21
5.23
4.20
4.18
4.15
3.24
3.21
3.19
2.81
2.78
2.76
2.73
2.71
2.53
2.42
1.79
1.78
1.77
1.76
1.75
2.11
1.96
1.80
2.02
2.07
2.03
1.96
2.02
4.01
f1 (ppm)
150.04
133.02
132.42
131.73
129.99
126.46
123.05
49.97
46.58
25.52
24.82
21.50
21.22
20.77
20.10
f1 (ppm)

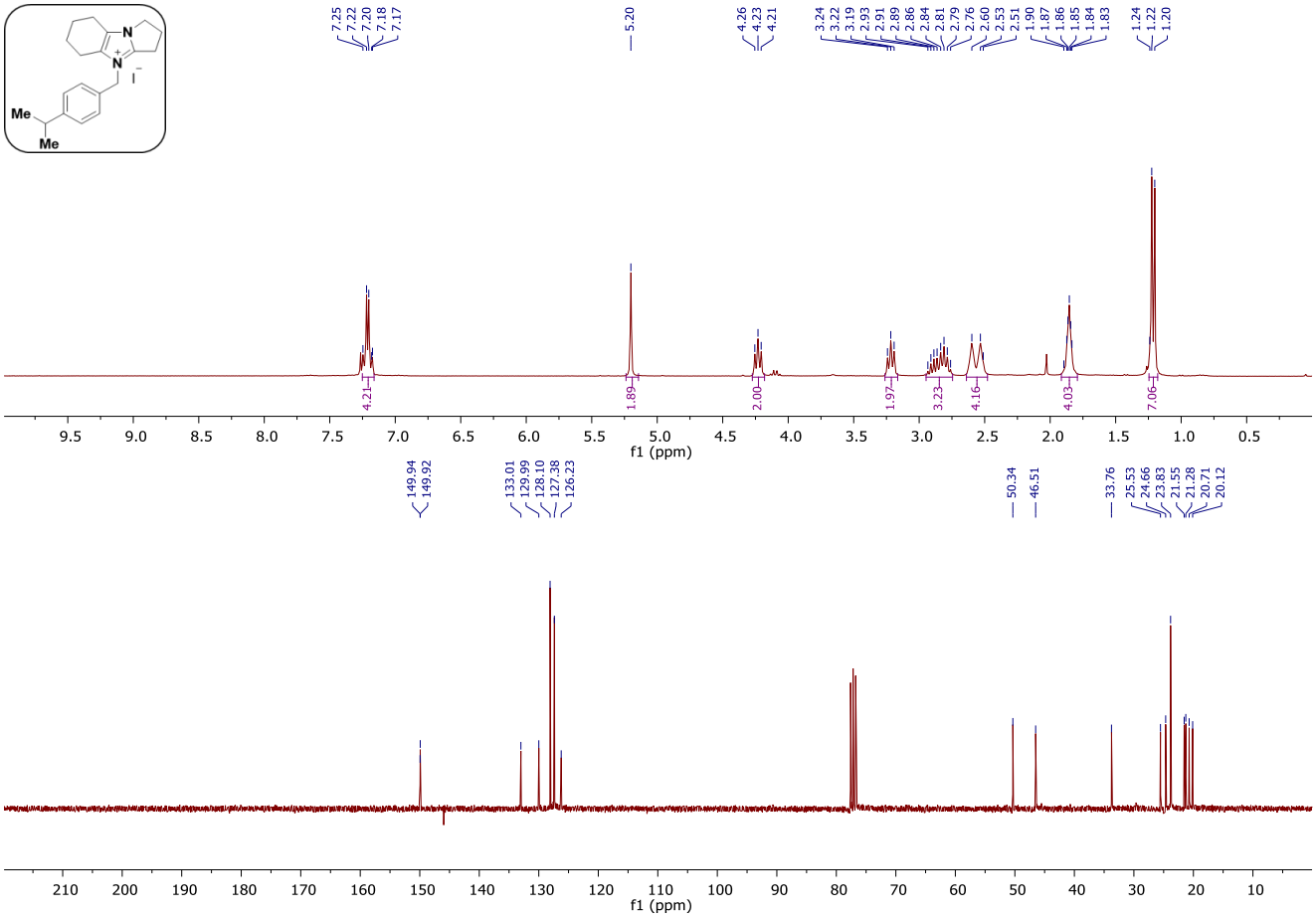
(41)


7.55
7.52
7.50
7.50
7.47
7.38
7.35
7.34
7.33
7.32
7.30
5.25
4.20
4.18
4.15
3.22
3.20
3.17
2.79
2.77
2.74
2.72
2.69
2.53
2.52
2.46
1.80
1.78
1.77
1.76
1.75
1.74
1.72
4.39
5.08
2.00
2.12
2.11
2.24
4.49
4.28
f1 (ppm)
150.00
141.71
139.80
133.05
131.62
128.86
128.65
127.86
127.74
126.97
126.33
50.30
46.56
25.54
24.74
21.53
21.25
20.76
20.12
f1 (ppm)

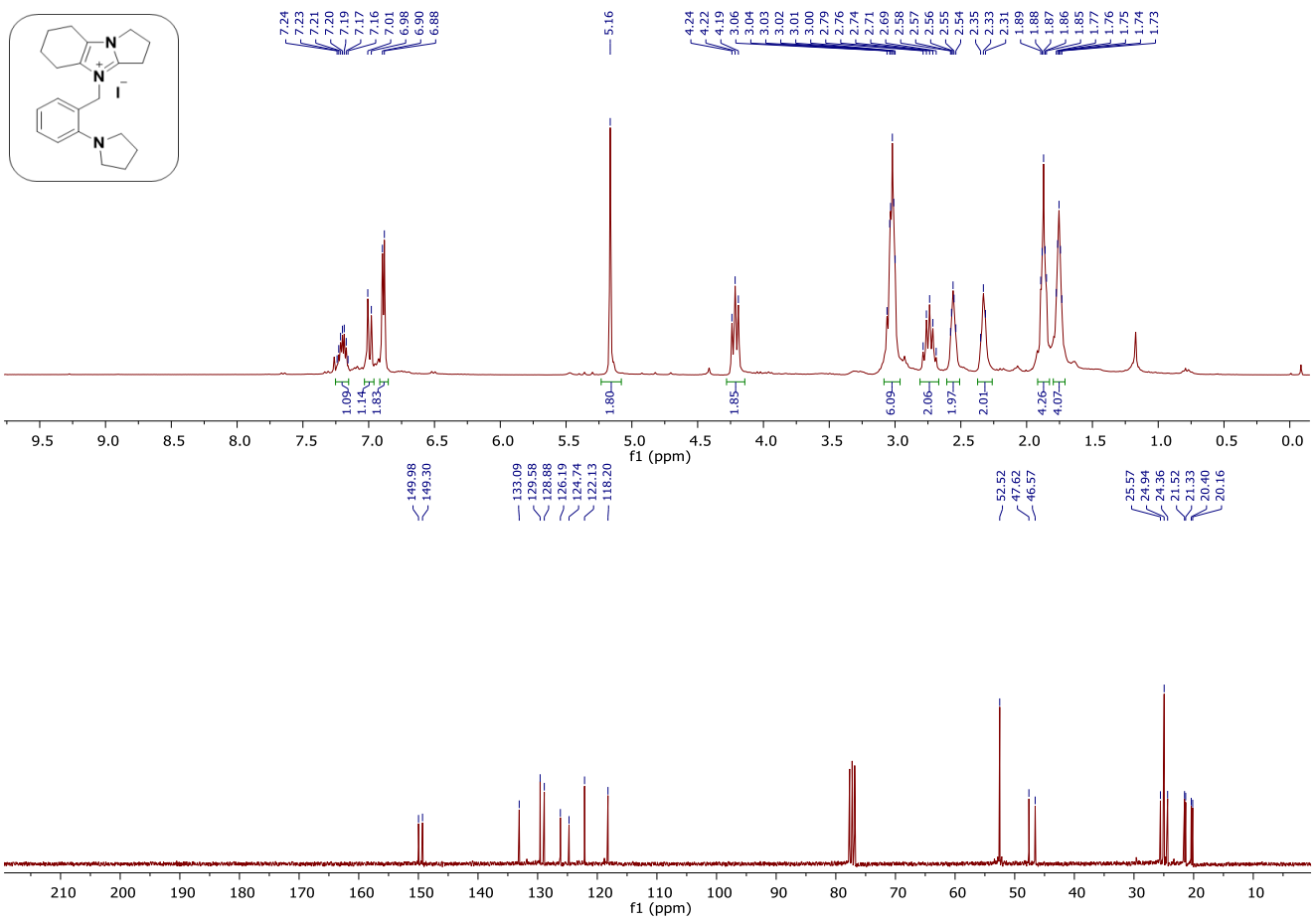
(42)


7.34
7.31
7.16
7.13
5.15
4.22
4.19
4.17
4.14
3.16
3.14
3.11
2.80
2.78
2.75
2.73
2.70
2.57
2.55 HDO
2.47 HDO
2.45
1.80
1.79
1.78
1.77
1.76
1.22
2.29
1.95
2.00
2.07
2.01
2.09
4.33
4.36
9.27
f1 (ppm)
152.07
149.76
132.96
129.60
127.79
126.18
50.19
46.55
34.58
31.15
29.56
25.53
24.52
21.51
21.23
20.69
20.12
f1 (ppm)

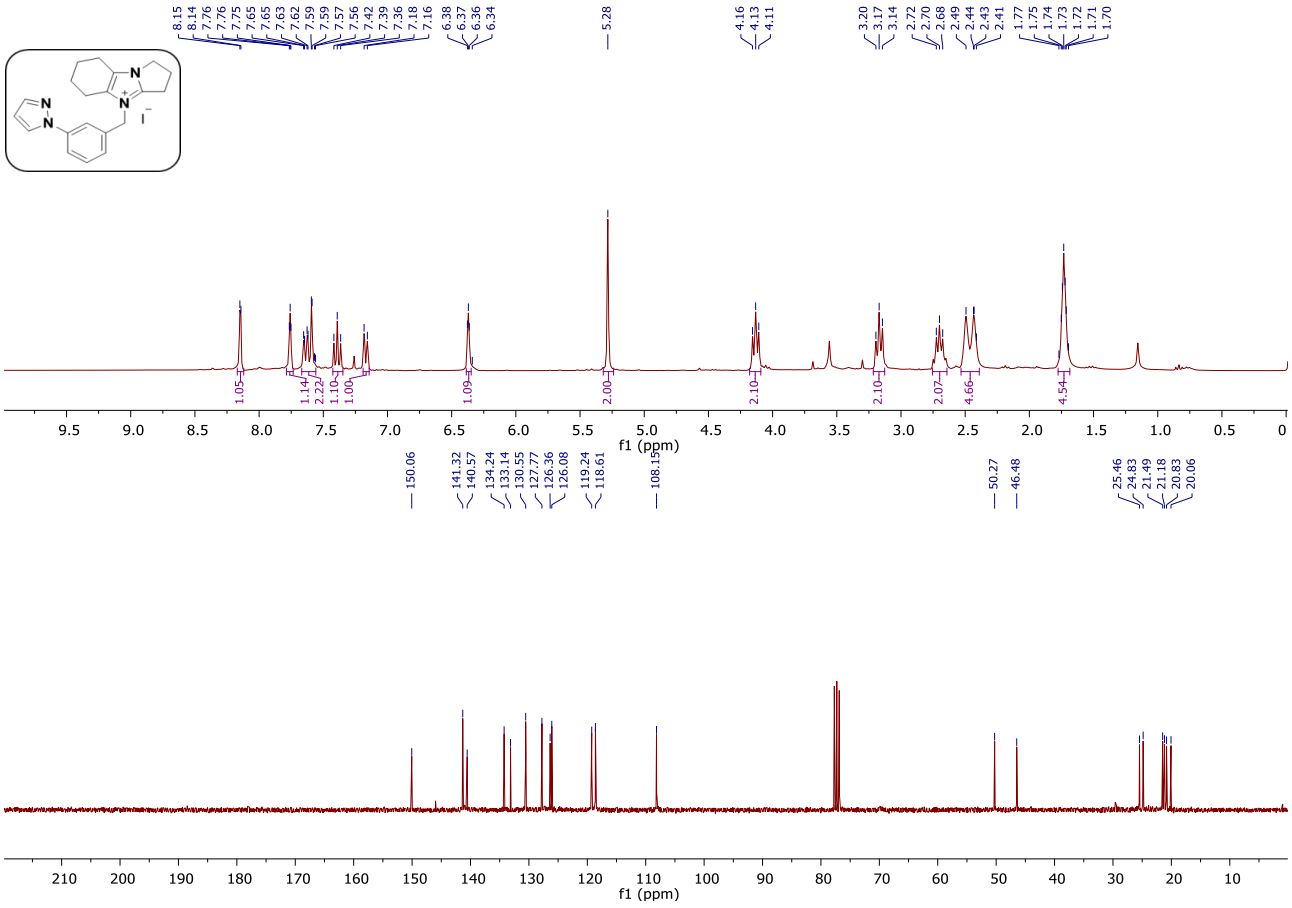
(43)


Me
Me
7.25
7.22
7.20
7.18
7.17
5.20
4.26
4.23
4.21
3.24
3.22
3.19
2.93
2.91
2.89
2.86
2.84
2.81
2.79
2.76
2.60
2.53
2.51
1.90
1.87
1.86
1.85
1.84
1.83
1.24
1.22
1.20
4.21
1.89
2.00
1.97
3.23
4.16
4.03
7.06
f1 (ppm)
149.94
149.92
133.01
129.99
128.10
127.38
126.23
50.34
46.51
33.76
25.53
24.66
23.83
21.55
21.28
20.71
20.12
f1 (ppm)

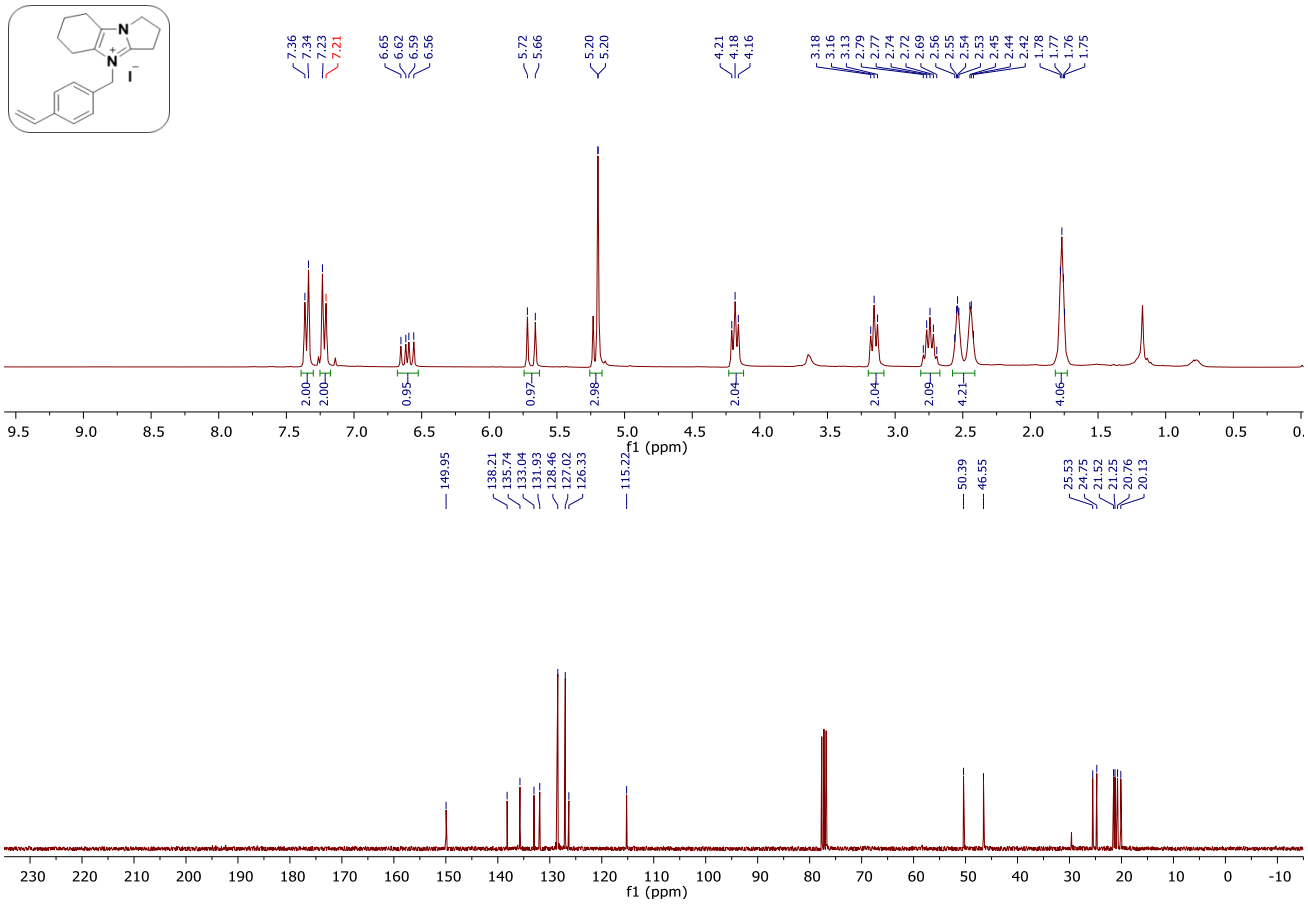
(44)


7.24
7.23
7.21
7.20
7.19
7.17
7.16
7.01
6.98
6.90
6.88
5.16
4.24
4.22
4.19
3.06
3.04
3.03
3.02
3.01
3.00
2.79
2.76
2.74
2.71
2.69
2.58
2.57
2.56
2.55
2.54
2.35
2.33
2.31
1.89
1.88
1.87
1.86
1.85
1.77
1.76
1.75
1.74
1.73
1.09
1.14
1.83
1.80
1.85
6.09
2.06
1.97
2.01
4.26
4.07
f1 (ppm)
149.98
149.30
133.09
129.58
128.88
126.19
124.74
122.13
118.20
52.52
47.62
46.57
25.57
24.94
24.36
21.52
21.33
20.40
20.16
f1 (ppm)

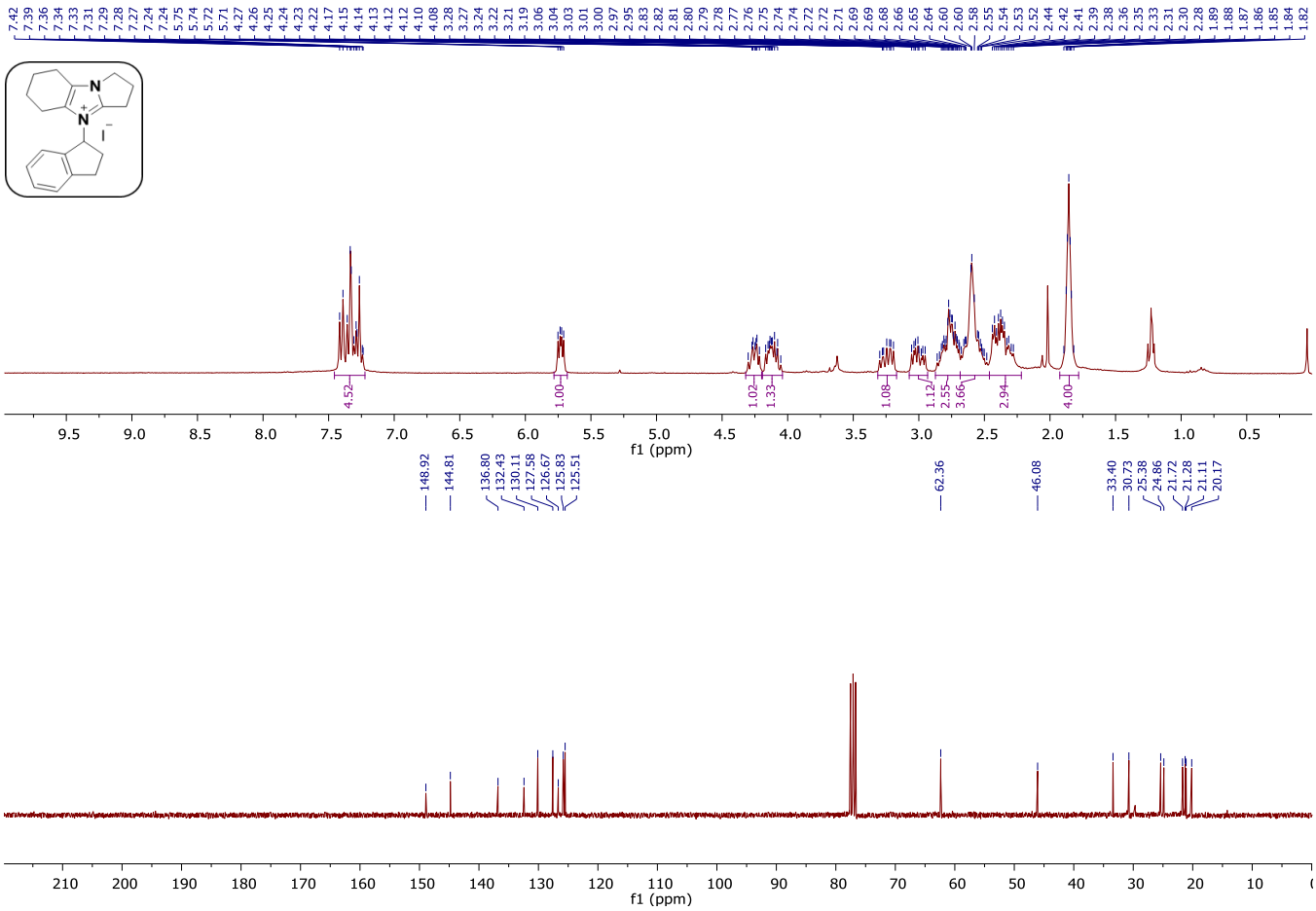
(45)


8.15
8.14
7.76
7.76
7.75
7.65
7.63
7.62
7.59
7.59
7.57
7.56
7.42
7.39
7.36
7.18
7.16
6.38
6.37
6.36
6.34
5.28
4.16
4.13
4.11
3.20
3.17
3.14
2.72
2.70
2.68
2.49
2.44
2.43
2.41
1.77
1.75
1.74
1.73
1.72
1.71
1.70
1.05
1.14
2.22
1.10
1.00
1.09
2.00
2.10
2.10
2.07
4.66
4.54
f1 (ppm)
150.06
141.32
140.57
134.24
133.14
130.55
127.77
126.36
126.08
119.24
118.61
108.15
50.27
46.48
25.46
24.83
21.49
21.18
20.83
20.06
f1 (ppm)

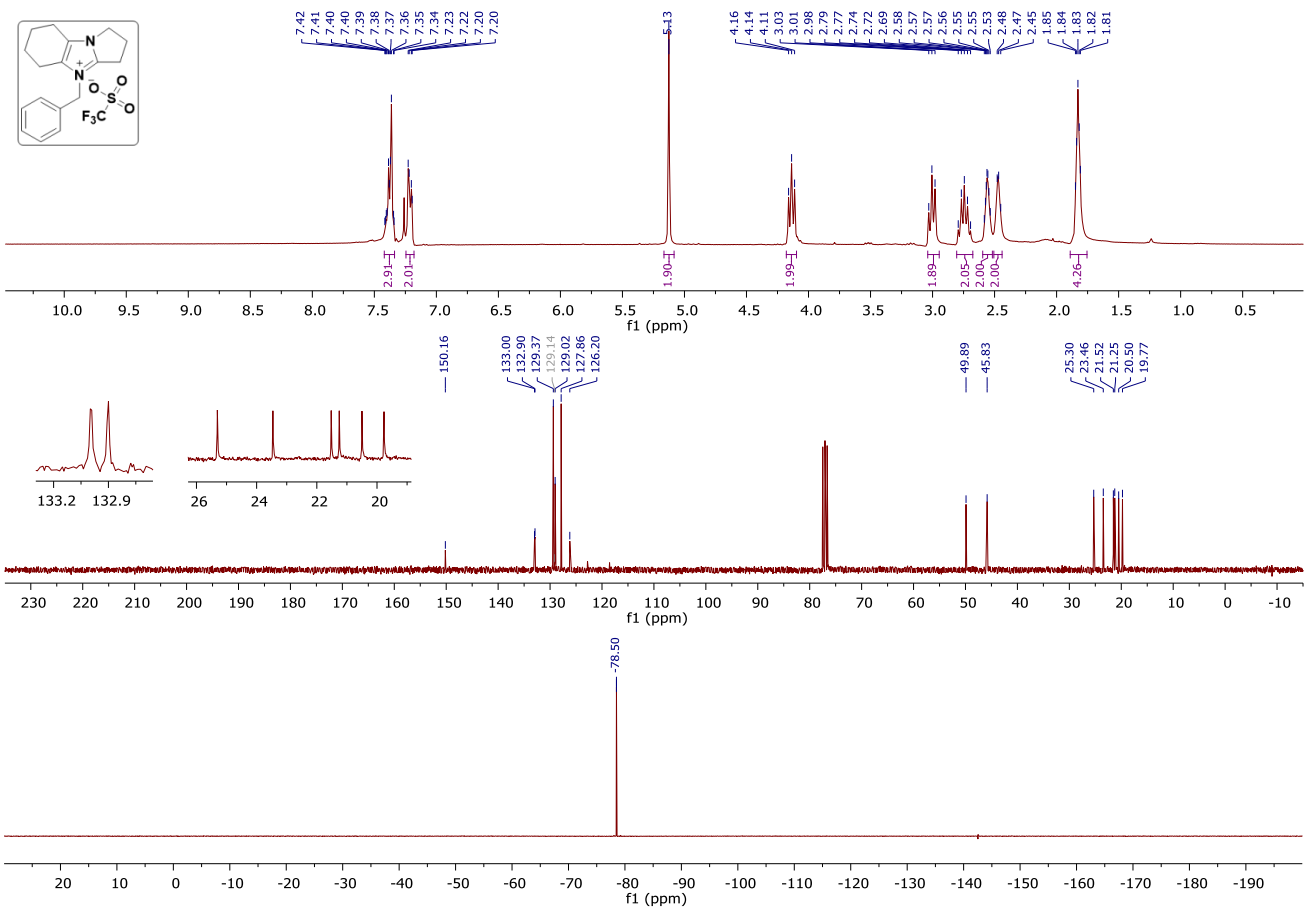
(46)


7.36
7.34
7.23
7.21
6.65
6.62
6.59
6.56
5.72
5.66
5.20
5.20
4.21
4.18
4.16
3.18
3.16
3.13
2.79
2.77
2.74
2.72
2.69
2.56
2.55
2.54
2.53
2.45
2.44
2.42
1.78
1.77
1.76
1.75
2.00
2.00
0.95
0.97
2.98
2.04
2.04
2.09
4.21
4.06
f1 (ppm)
149.95
138.21
135.74
133.04
131.93
128.46
127.02
126.33
115.22
50.39
46.55
25.53
24.75
21.52
21.25
20.76
20.13
f1 (ppm)

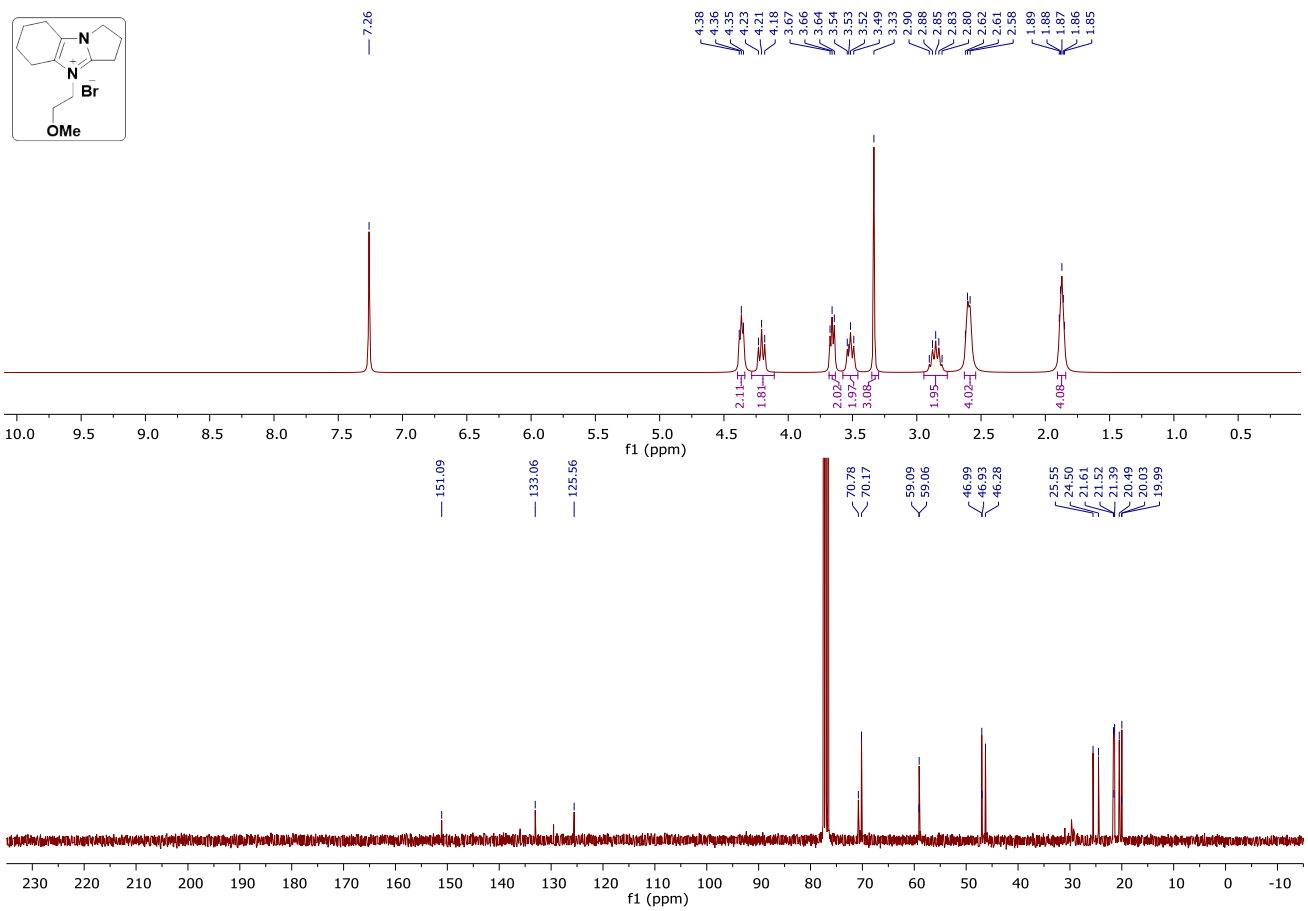
(47)


7.42 7.39 7.36 7.34 7.33 7.31 7.29 7.28 7.27 7.24 7.24 5.75 5.74 5.72 5.71 4.27 4.26 4.25 4.24 4.23 4.22 4.17 4.15 4.14 4.13 4.12 4.12 4.10 4.08 3.28 3.27 3.24 3.22 3.21 3.19 3.06 3.04 3.03 3.01 3.00 2.97 2.95 2.83 2.82 2.81 2.80 2.79 2.78 2.77 2.76 2.75 2.74 2.74 2.72 2.72 2.71 2.69 2.69 2.68 2.66 2.65 2.64 2.60 2.60 2.58 2.55 2.54 2.53 2.52 2.44 2.42 2.41 2.39 2.38 2.36 2.35 2.33 2.31 2.30 2.28 1.89 1.88 1.87 1.86 1.85 1.84 1.82
N
N
I
4.52
1.00
1.02
1.33
1.08
1.12
2.55
3.66
2.94
4.00
f1 (ppm)
148.92
144.81
136.80
132.43
130.11
127.58
126.67
125.83
125.51
62.36
46.08
33.40
30.73
25.38
24.86
21.72
21.28
21.11
20.17
f1 (ppm)

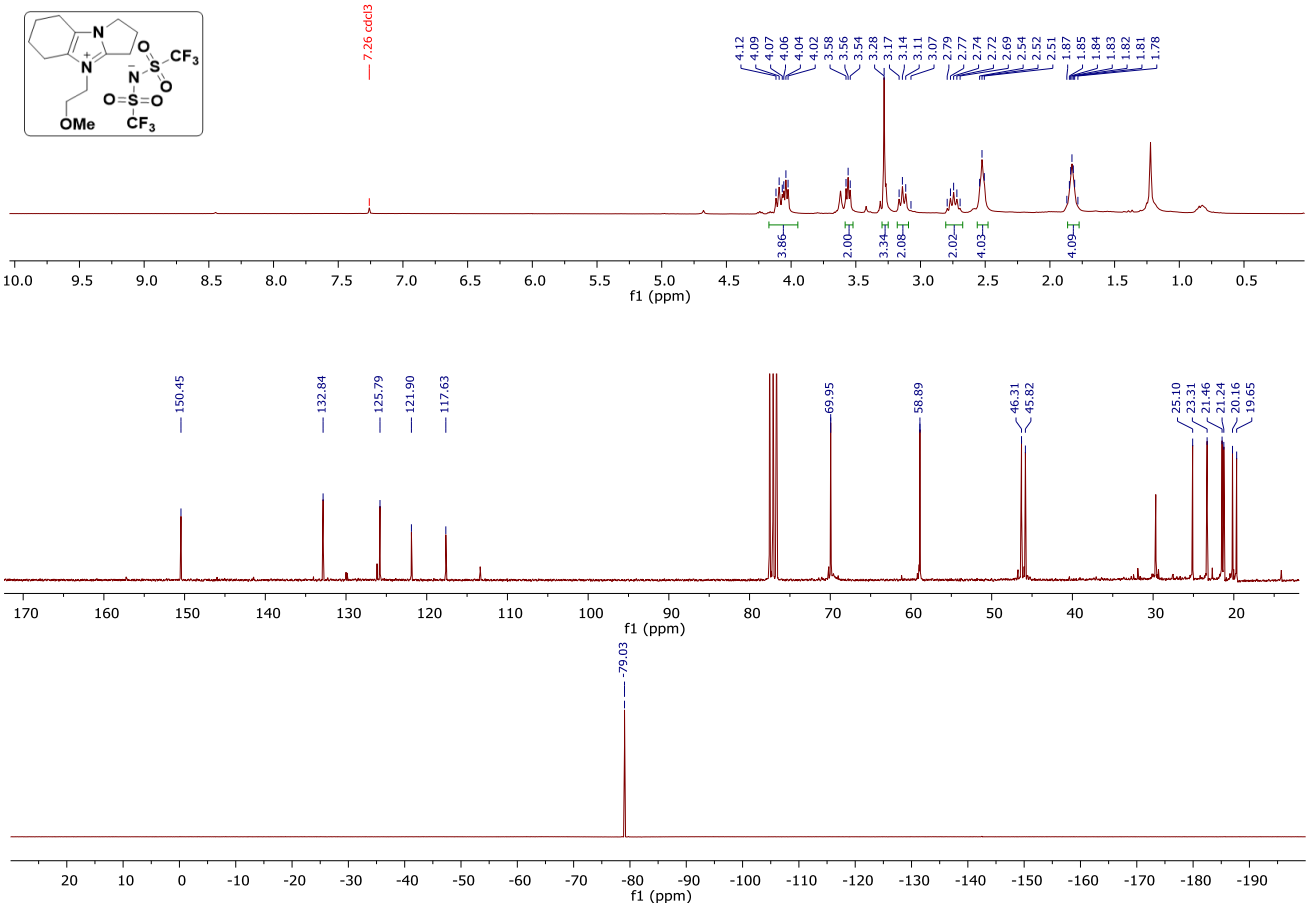
(48)


7.42 7.41 7.40 7.40 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.23 7.22 7.20 7.20
5.13
4.16 4.14 4.11 3.03 3.01 2.98 2.79 2.77 2.74 2.72 2.69 2.58 2.57 2.57 2.56 2.55 2.55 2.53 2.48 2.47 2.45 1.85 1.84 1.83 1.82 1.81
2.91 2.01 1.90 1.99 1.89 2.05 2.00 2.00 4.26
f1 (ppm)
150.16
133.00 132.90 129.37 129.14 129.02 127.86 126.20
49.89 45.83
25.30 23.46 21.52 21.25 20.50 19.77
133.2 132.9
26 24 22 20
f1 (ppm)
-78.50
f1 (ppm)

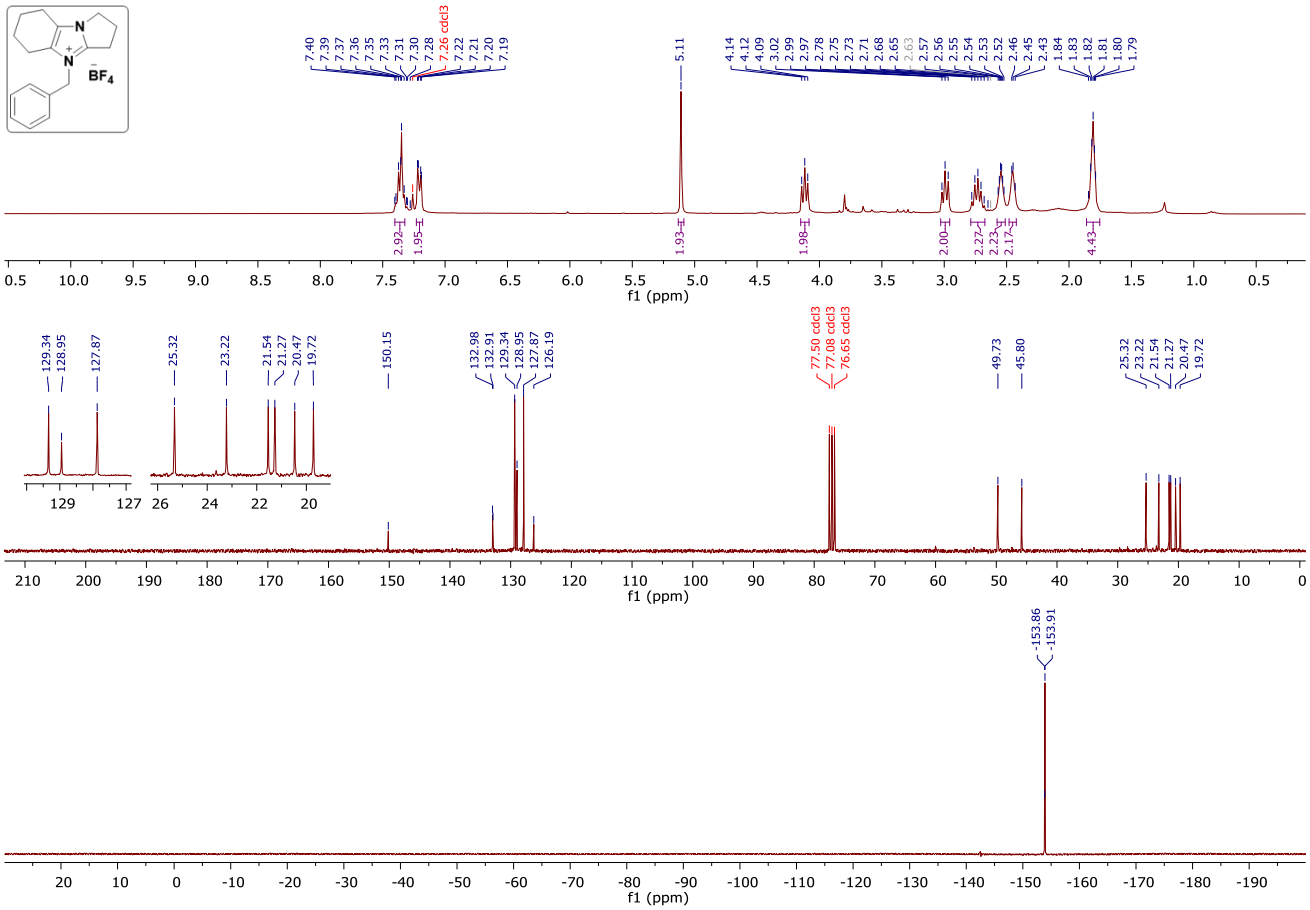
(49)


N
N
Br
OMe
7.26
4.38
4.36
4.35
4.23
4.21
4.18
3.67
3.66
3.64
3.54
3.53
3.52
3.49
3.33
2.90
2.88
2.85
2.83
2.80
2.62
2.61
2.58
1.89
1.88
1.87
1.86
1.85
2.11
1.81
2.02
1.97
3.08
1.95
4.02
4.08
f1 (ppm)
151.09
133.06
125.56
70.78
70.17
59.09
59.06
46.99
46.93
46.28
25.55
24.50
21.61
21.52
21.39
20.49
20.03
19.99
f1 (ppm)

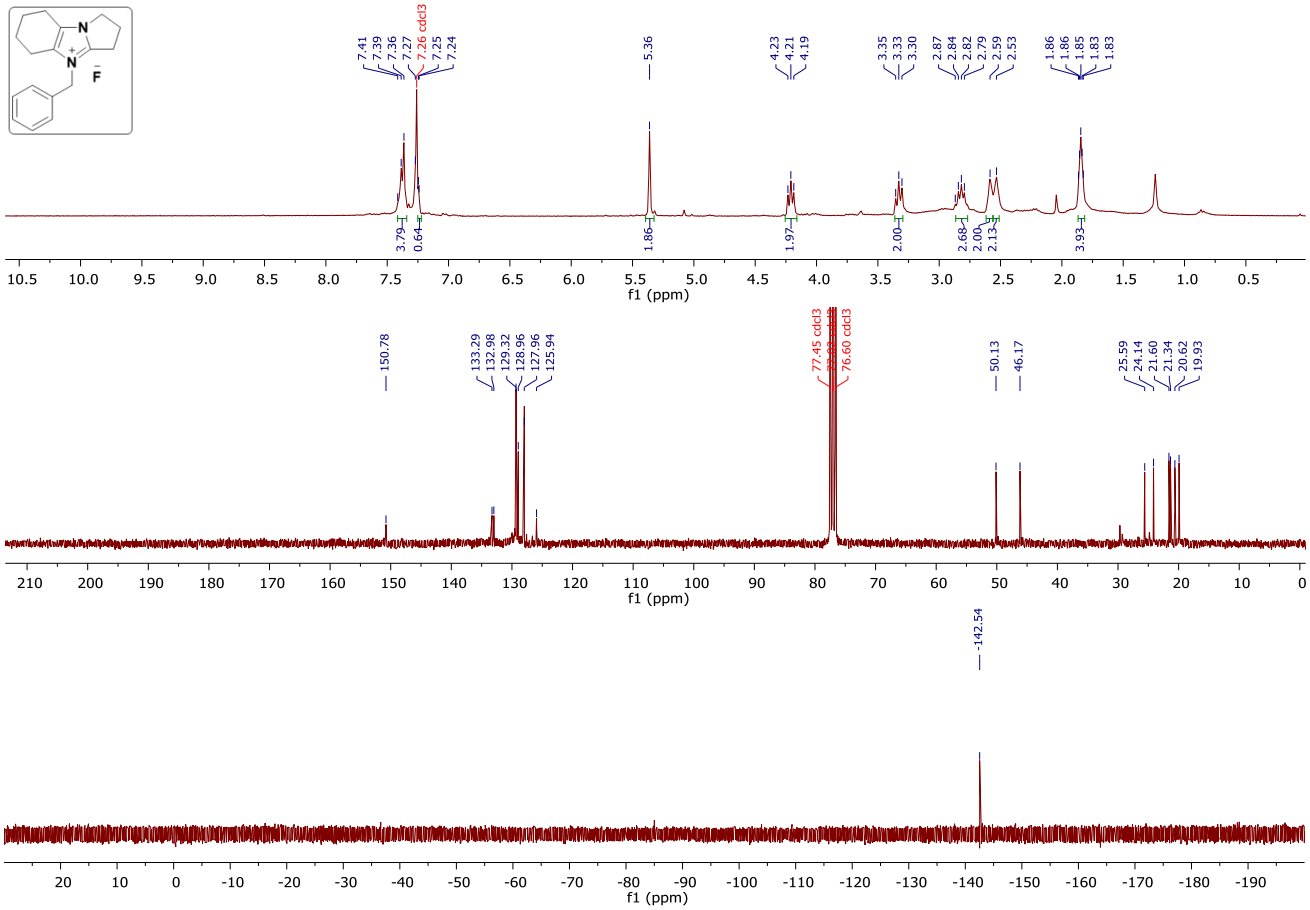
(50)


7.26 cdcl3
4.12
4.09
4.07
4.06
4.04
4.02
3.58
3.56
3.54
3.28
3.17
3.14
3.11
3.07
2.79
2.77
2.74
2.72
2.69
2.54
2.52
2.51
1.87
1.85
1.84
1.83
1.82
1.81
1.78
3.86
2.00
3.34
2.08
2.02
4.03
4.09
f1 (ppm)
150.45
132.84
125.79
121.90
117.63
69.95
58.89
46.31
45.82
25.10
23.31
21.46
21.24
20.16
19.65
f1 (ppm)
-79.03
f1 (ppm)

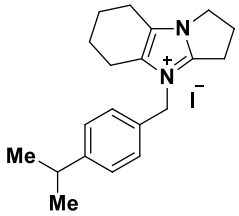
(51)


N
N
BF4
7.40 7.39 7.37 7.36 7.35 7.33 7.31 7.30 7.28 7.26 cdcl3 7.22 7.21 7.20 7.19
5.11
4.14 4.12 4.09 3.02 2.99 2.97 2.78 2.75 2.73 2.71 2.68 2.65 2.63 2.57 2.56 2.55 2.54 2.53 2.52 2.46 2.45 2.43 1.84 1.83 1.82 1.81 1.80 1.79
2.92 1.95 1.93 1.98 2.00 2.22 2.23 2.17 4.43
f1 (ppm)
129.34 128.95 127.87 25.32 23.22 21.54 21.27 20.47 19.72 150.15 132.98 132.91 129.34 128.95 127.87 126.19 77.50 cdcl3 77.08 cdcl3 76.65 cdcl3 49.73 45.80 25.32 23.22 21.54 21.27 20.47 19.72
f1 (ppm)
-153.86 -153.91
f1 (ppm)

(52)


7.41
7.39
7.36
7.27
7.26 cdcl3
7.25
7.24
5.36
4.23
4.21
4.19
3.35
3.33
3.30
2.87
2.84
2.82
2.79
2.59
2.53
1.86
1.86
1.85
1.83
1.83
3.79
0.64
1.86
1.97
2.00
2.68
2.00
2.13
3.93
f1 (ppm)
150.78
133.29
132.98
129.32
128.96
127.96
125.94
77.45 cdcl3
76.60 cdcl3
50.13
46.17
25.59
24.14
21.60
21.34
20.62
19.93
f1 (ppm)
-142.54
f1 (ppm)

Thermal Analysis for Imidazolium salt **(43)**



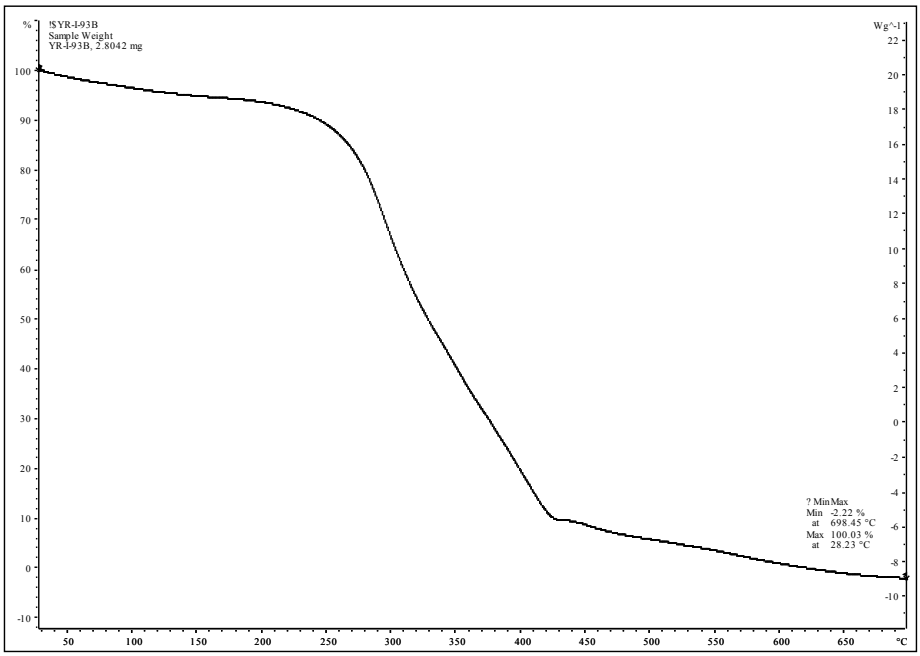


Figure 1. Decomposition of **43** through TGA plots analysis. 10 °C min^{-1} ramping experiment.

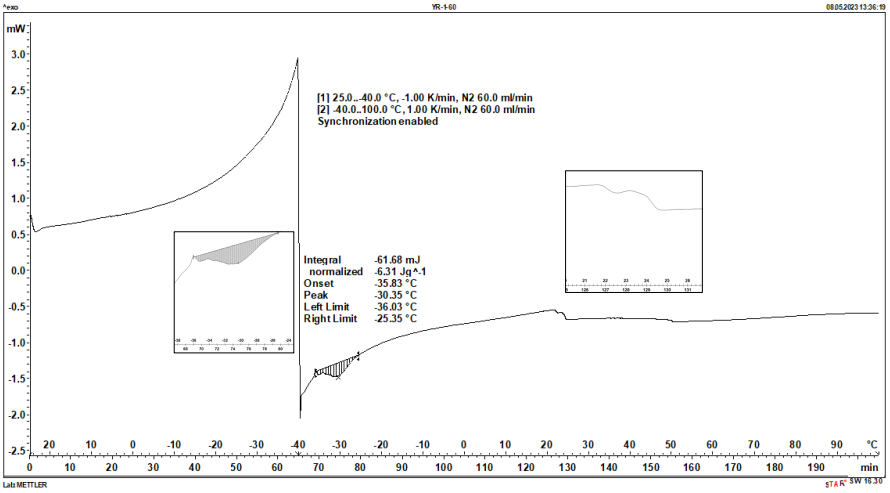
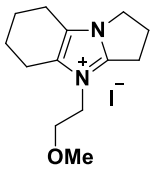


Figure 2. DSC thermograph of Imidazolium salt **(43)**

Thermal Analysis for Imidazolium salt **(28)**



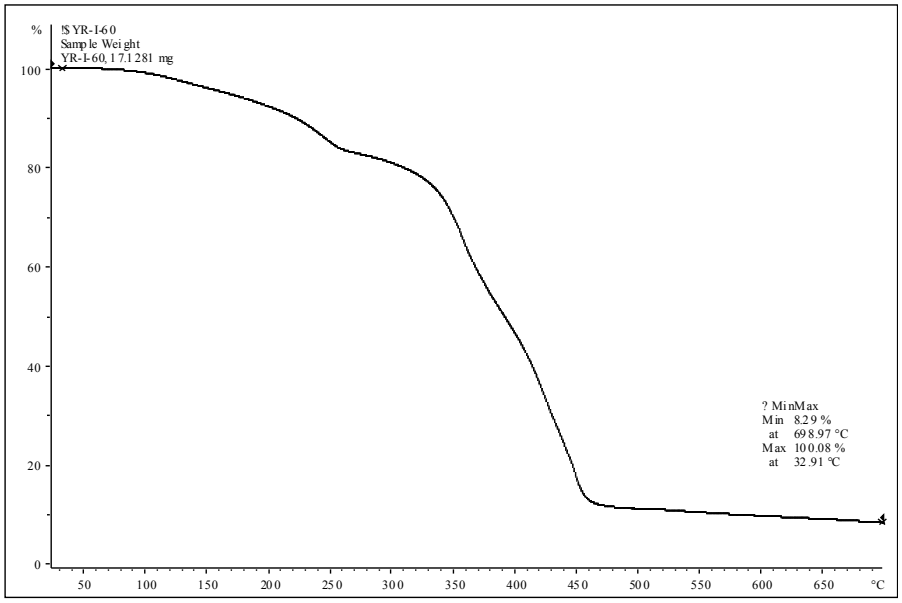


Figure 3. Decomposition of **28** through TGA plots analysis. 10 °C min^{-1} ramping experiment.

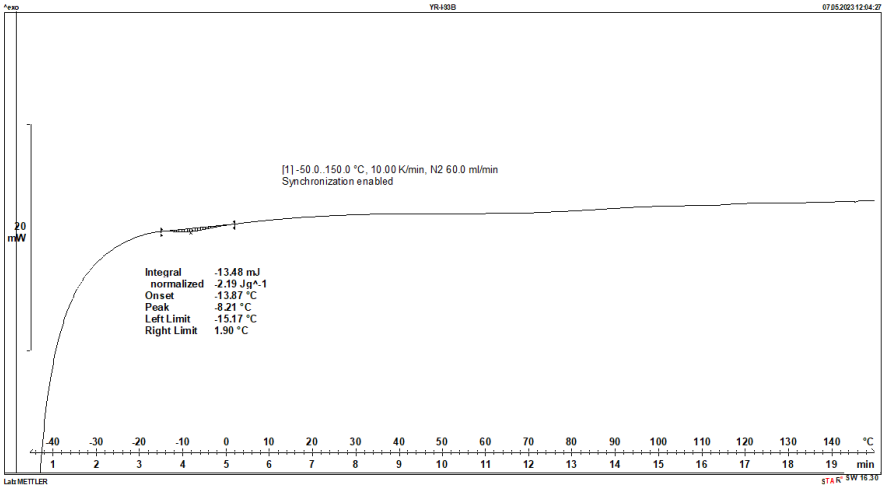
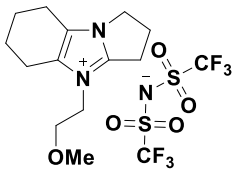


Figure 4. DSC thermograph of Imidazolium salt **(28)**

Thermal Analysis for Imidazolium salt **(50)**



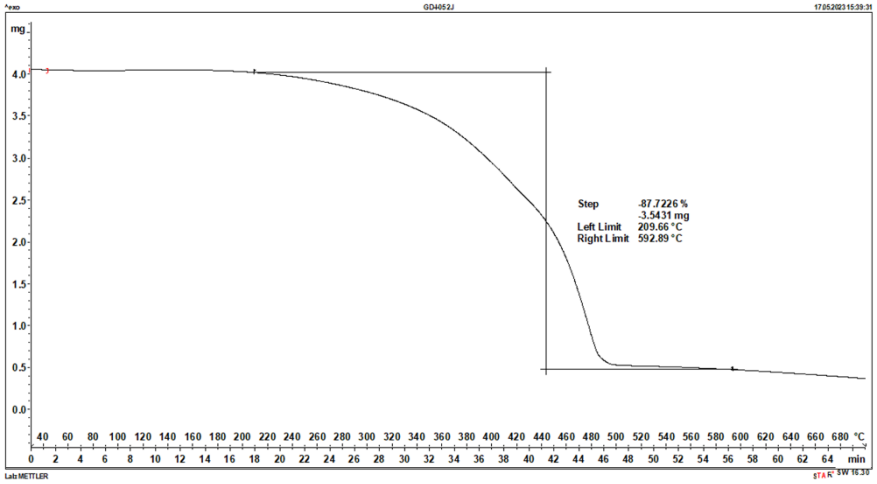


Figure 5. Decomposition of **50** through TGA plots analysis. 10 °C min^{-1} ramping experiment.

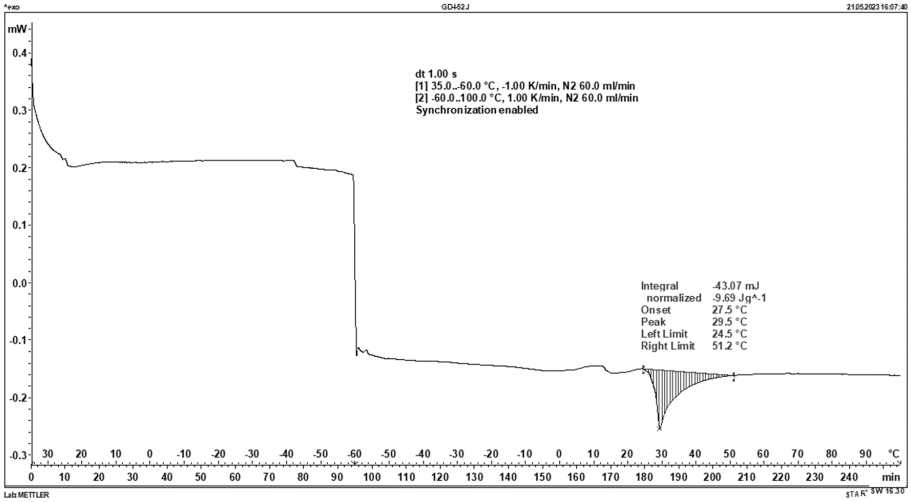


Figure 6. DSC thermograph of Imidazolium salt **(50)**