Supporting Information For

The synthesis of unsymmetric diamides through Rh-catalyzed selective C-H bond activation of amides with isocyanates

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1. General Information

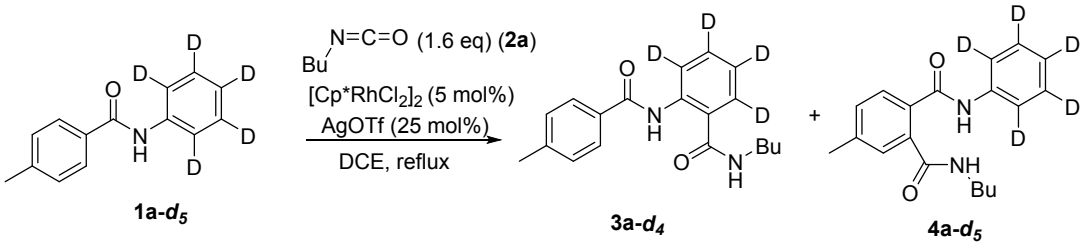
Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 400 MHz in DMSO or $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in DMSO or $CDCl_3$. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided.

2. Details of experimental procedures

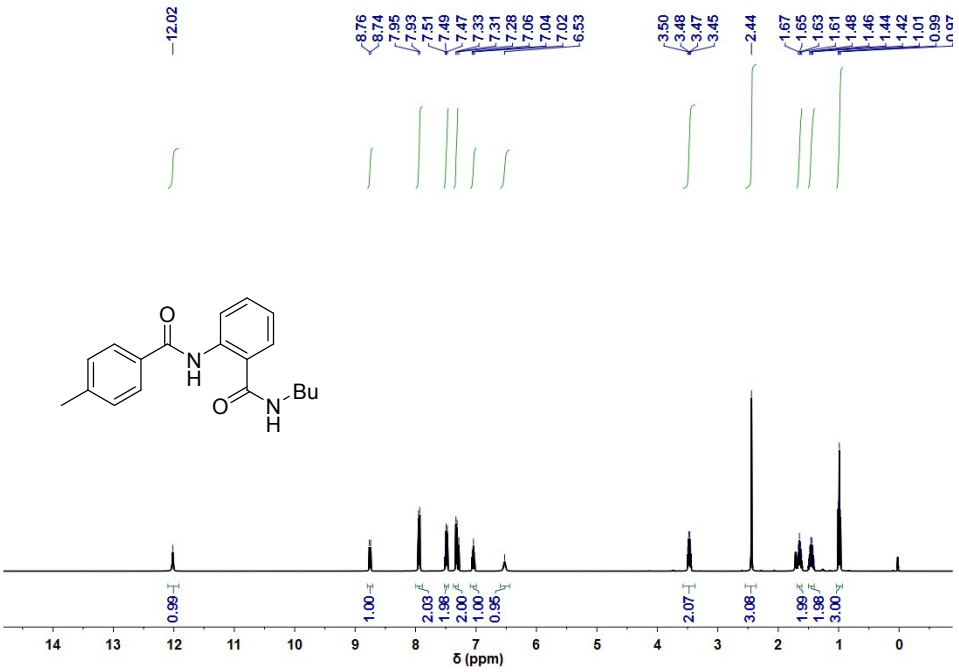
2.1. Typical procedure for the synthesis of anilides and isocyanates:

The mixture of anilide (**1a**) (0.50 mmol), isocyanate (**2a**) (0.80 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (25 mol%) in DCE (2.5 mL) was stirred at 90 °C for 24 h. Upon completion, the reaction mixture was removed the solvents to give the residue. The residue was then purified by column chromatography on silica gel (ethyl acetate / petroleum ether = 1:5) to provide the corresponding product as white solid **3a**.

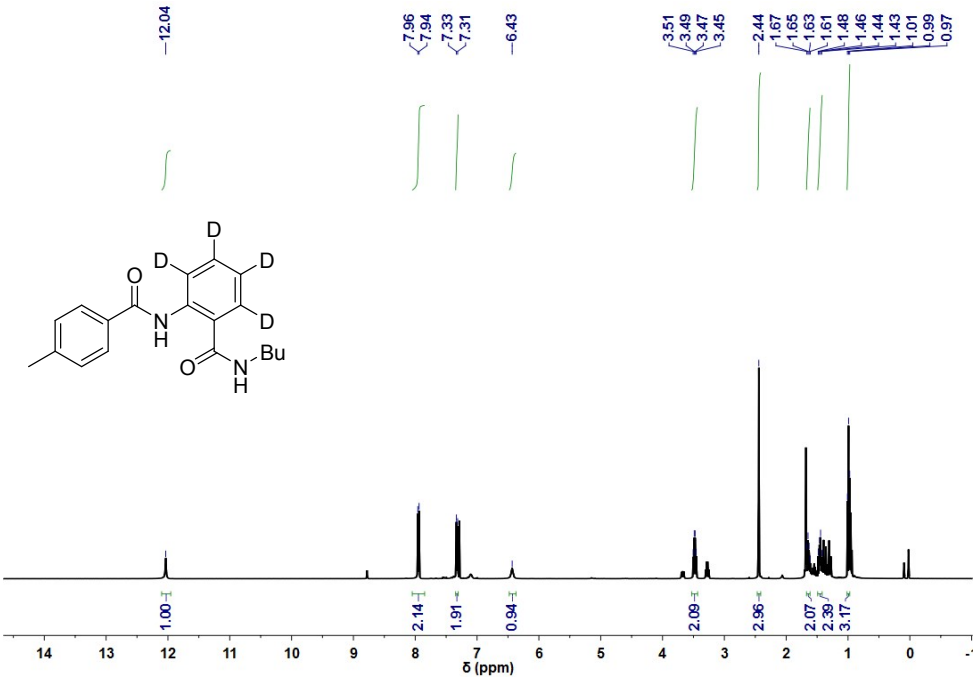
2.2. Deuteration experiment:



Experimental procedure: The mixture of 4-methyl-N-(phenyl-d5)benzamide (**1a-*d*$_5$**) (0.50 mmol), 1-isocyanatobutane (**2a**) (0.80 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) and AgOTf (25 mol%) in anhydrous DCE (2.5 mL) was stirred at 90 °C for 24 h. Upon completion, the reaction mixture was removed the solvents to give the residue. The residue was then purified by column chromatography on silica gel (ethyl acetate / petroleum ether = 1:5) to provide the corresponding product. The ^{1}H-NMR information showed that the **4a-*d*$_5$** was not found. **N-butyl-2-(4-methylbenzamido)benzamide-3,4,5,6-d$_4$ (3a-*d*$_4$).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.43 (s, 1H), 3.48 (dd, *J* = 13.0, 7.2 Hz, 2H), 2.44 (s, 3H), 1.67 – 1.61 (m, 2H), 1.45 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

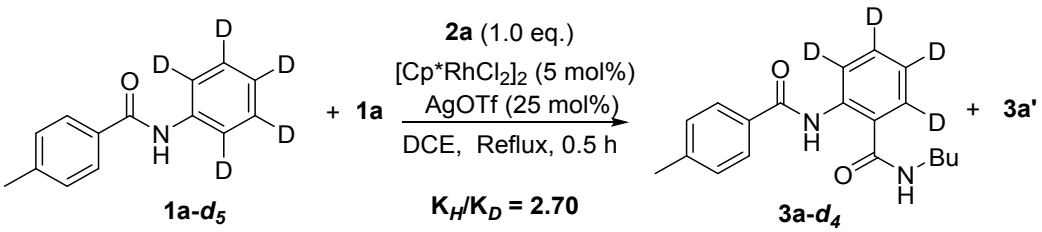


^{1}H-NMR spectrum of 3a

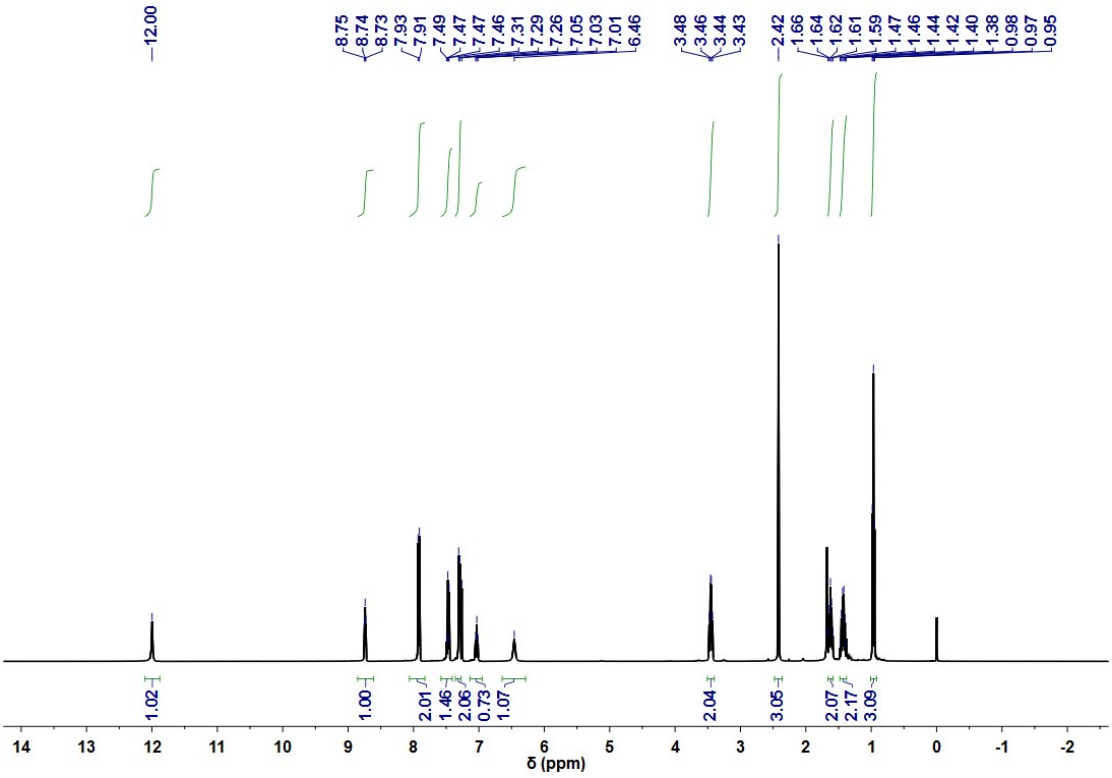


^{1}H-NMR spectrum of 3a-*d_4*

2.3. Isotope effect experiment:

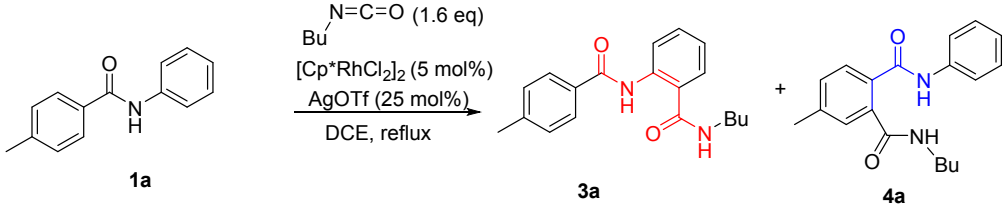


Experimental procedure: The mixture of 4-methyl-N-(phenyl-d_5)benzamide (**1a-d_5**) (0.50 mmol), 4-methyl-N-phenylbenzamide (**1a**) (0.50 mmol), 1-isocyanatobutane (**2a**) (0.50 mmol), [Cp*$RhCl_2$]$_2$ (5 mol%), AgOTf (25 mol%) in DCE (3.0 mL) was stirred at 90 °C for 0.5 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was then purified by column chromatography on silica gel (ethyl acetate / petroleum ether = 1:5) to provide the corresponding product.



^{1}H-NMR spectrum of isotope effect experiment

2.4. The "Silver Effect" test experiments (Table 4):



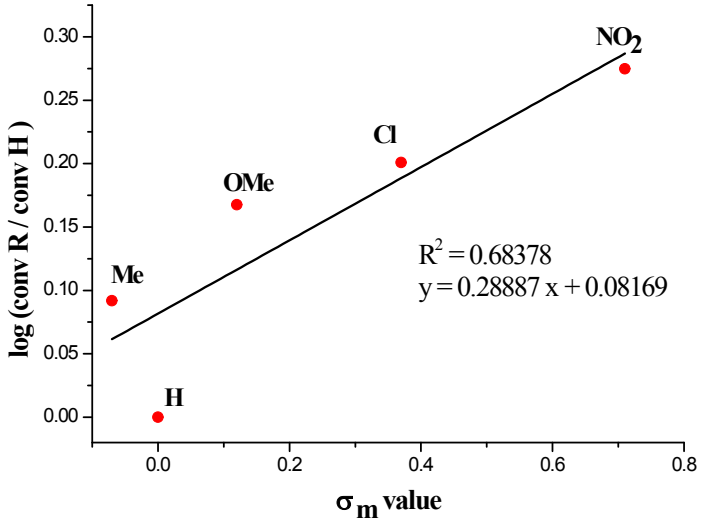
Experimental procedure: For entries 1,2,3,4,6,8, the experimental procedure is the same as typical procedure for the synthesis of anilides and isocyanates. For entries 5,7,9, a DCE solution of $[Cp^*RhCl_2]_2$ (5 mol%) and Ag salts (25 mol%) was firstly stirred for 5 min. After that, the mixture was filtrated to get rid of AgCl using paper pad. Then 4-methyl-N-phenylbenzamide (0.50 mmol) and 1-isocyanatobutane (0.80 mmol) was added into the filter liquor to begin the reaction. All the reactions were stirred for 24 h. The reaction mixture was removed the solvents to give the residue after cooling down to the room temperature. The residue was then purified by column chromatography on silica gel (ethyl acetate / petroleum ether = 1:5) to provide the corresponding product.

2.5. Hammett Pot of Various Anilide

Experimental procedure: The mixture of anilide (**1**) (0.50 mmol), isocyanate (**2a**) (0.80 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgOTf (25 mol%) in DCE (2.5 mL) was stirred at 90 °C for 0.5 h. Upon completion, the reaction mixture was removed the solvents to give the residue. The residue was then purified by column chromatography on silica gel (ethyl acetate / petroleum ether = 1:5) to provide the corresponding product **3**.

R	H	Me	OMe	Cl	NO_2
Yield	17 %	21 %	25 %	27 %	32 %

The yield was determined by ^1H NMR

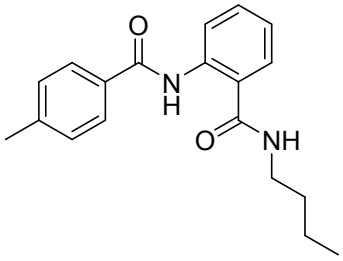


2.6. In Vitro Cytotoxicity Assays

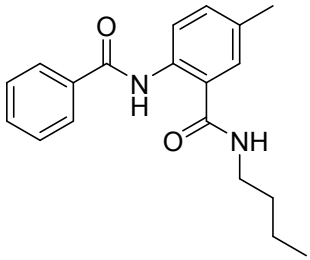
SF-268 (human central nervous system cancer cell line), NCI-H460 (human large cell lung cancer cell line) and MCF-7 (human breast adenocarcinoma cell line) cells

were seeded at 2.5×10^4 cells per well in 96-well plates and grown to subconfluence. After removal of the growth medium, all the six serial dilutions of tested compounds in 200 μL test medium were added. Plates were incubated at 37 °C in a humidified atmosphere with 5% carbon dioxide. After 72 h of exposure, we removed the culture medium and 30 mL of the MTT solution (5 mg/mL in PBS) was added to all the six wells. Then the plate was incubated for four hours to allow MTT formazan formation. To dissolve the resulting MTT formazan, DMSO (50 mL) was added to all the six wells, followed by mixing with a microplate shaker. Absorbance at 570 nm was measured on a microplate reader (Thermo Scientific, MK3). The data were analyzed with SPSS software, and the 50% inhibitory concentrations (IC_{50}) of all the compounds for the different cell lines were determined.

2.7. ^{1}H and ^{13}CNMR spectra of compounds

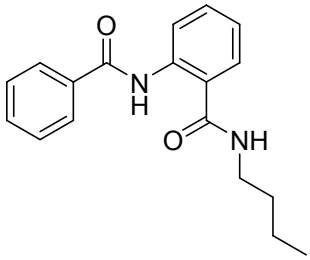


N-butyl-2-(4-methylbenzamido)benzamide (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.84 – 8.70 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.45 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.01 (m, 1H), 6.53 (s, 1H), 3.47 (dd, *J* = 13.0, 7.1 Hz, 2H), 2.44 (s, 3H), 1.65 (dt, *J* = 12.7, 7.5 Hz, 2H), 1.45 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24 (s), 165.65 (s), 142.30 (s), 139.79 (s), 132.39 (s), 132.05 (s), 129.44 (s), 127.40 (s), 126.52 (s), 122.68 (s), 121.58 (s), 120.91 (s), 39.83 (s), 31.51 (s), 21.52 (s), 20.19 (s), 13.76 (s). HRMS (ESI) Calculated for $C_{19}H_{23}N_2O_2$ $[M+H]^+$ 311.1760, found 311.1764.

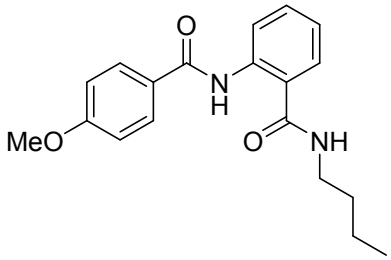


2-benzamido-N-butyl-5-methylbenzamide (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.59 – 7.47 (m, 3H), 7.31 – 7.26 (m, 2H), 6.63 (s, 1H), 3.54 – 3.39 (m, 2H), 2.25 (s, 3H), 1.66 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.46 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31 (s), 165.40 (s), 137.17 (s), 134.87 (s), 132.92 (s), 132.43

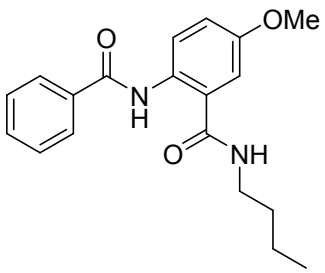
(s), 131.69 (s), 128.71 (s), 127.34 (s), 126.94 (s), 121.53 (s), 121.00 (s), 39.82 (s), 31.53 (s), 20.73 (s), 20.20 (s), 13.75 (s). HRMS (ESI) Calculated for $C_{19}H_{23}N_2O_2$ $[M+H]^+$ 311.1760, found 311.1763.



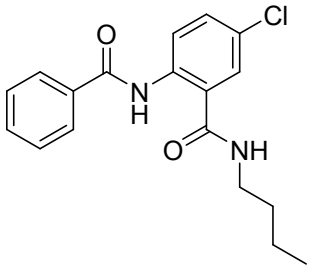
2-benzamido-N-butylbenzamide (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.81 – 8.73 (m, 1H), 8.10 – 7.98 (m, 2H), 7.62 – 7.47 (m, 5H), 7.12 – 7.00 (m, 1H), 6.54 (s, 1H), 3.53 – 3.42 (m, 2H), 1.65 (dt, *J* = 12.7, 7.5 Hz, 2H), 1.45 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.21 (s), 165.63 (s), 139.72 (s), 134.84 (s), 132.44 (s), 131.81 (s), 128.76 (s), 127.38 (s), 126.54 (s), 122.82 (s), 121.59 (s), 120.90 (s), 39.85 (s), 31.50 (s), 20.17 (s), 13.76 (s). HRMS (ESI) Calculated for $C_{18}H_{21}N_2O_2$ $[M+H]^+$ 297.1603, found 297.1601.



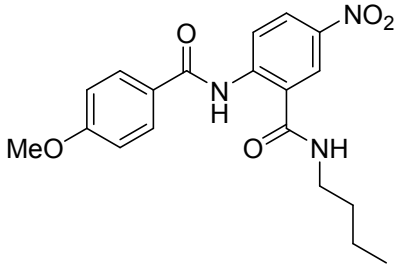
N-butyl-2-(4-methoxybenzamido)benzamide (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.01 (s, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.56 – 7.46 (m, 2H), 7.12 – 6.99 (m, 3H), 6.45 (s, 1H), 3.89 (s, 3H), 3.48 (dd, *J* = 13.0, 7.1 Hz, 2H), 1.69 – 1.59(m, 2H), 1.51 – 1.41 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29 (s), 165.20 (s), 162.49 (s), 140.00 (s), 132.47 (s), 129.30 (s), 127.20 (s), 126.45 (s), 122.54 (s), 121.54 (s), 120.71 (s), 113.97 (s), 55.43 (s), 39.84 (s), 31.51 (s), 20.18 (s), 13.76 (s). HRMS (ESI) Calculated for $C_{19}H_{23}N_2O_3$ $[M+H]^+$ 327.1709, found 327.1710.



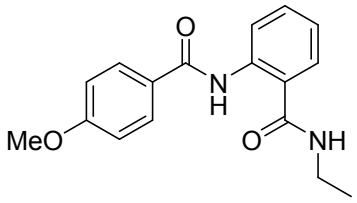
2-benzamido-N-butyl-5-methoxybenzamide (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.67 (d, *J* = 9.1 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.58 – 7.46 (m, 3H), 7.06 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.43 (s, 1H), 3.80 (s, 3H), 3.47 (dd, *J* = 13.0, 7.1 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.45 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87 (s), 165.26 (s), 154.92 (s), 134.87 (s), 132.78 (s), 131.64 (s), 128.70 (s), 127.29 (s), 123.21 (s), 122.64 (s), 116.64 (s), 112.79 (s), 55.67 (s), 39.87 (s), 31.48 (s), 20.17 (s), 13.75 (s). HRMS (ESI) Calculated for $C_{19}H_{23}N_2O_3$ $[M+H]^+$ 327.1709, found 327.1707.



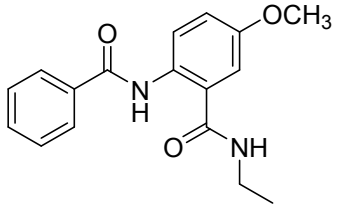
2-benzamido-N-butyl-5-chlorobenzamide(3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.80 – 8.72 (m, 1H), 8.08 – 7.98 (m, 2H), 7.59 – 7.50 (m, 3H), 7.46 (dd, *J* = 7.7, 2.2 Hz, 2H), 6.47 (s, 1H), 3.48 (td, *J* = 7.2, 5.8 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.45 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.00 (s), 165.58 (s), 138.33 (s), 134.43 (s), 132.25 (s), 132.01 (s), 128.80 (s), 127.84 (s), 127.39 (s), 126.43 (s), 122.98 (s), 122.23 (s), 40.00 (s), 31.43 (s), 20.17 (s), 13.74 (s). HRMS (ESI) Calculated for $C_{18}H_{20}ClN_2O_2$ $[M+H]^+$ 331.1213, found 331.1214.



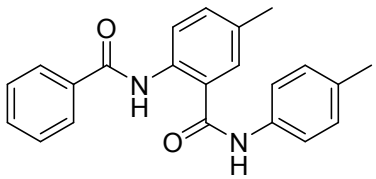
N-butyl-2-(4-methoxybenzamido)-5-nitrobenzamide(3g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 1H), 9.07 (d, *J* = 9.3 Hz, 1H), 8.45 (d, *J* = 2.6 Hz, 1H), 8.37 (dd, *J* = 9.3, 2.6 Hz, 1H), 8.06 – 8.00 (m, 2H), 7.09 – 6.99 (m, 2H), 6.58 (s, 1H), 3.91 (s, 3H), 3.54 (td, *J* = 7.2, 5.9 Hz, 2H), 1.70 (dt, *J* = 12.7, 7.5 Hz, 2H), 1.49 (dq, *J* = 14.6, 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.49 (s), 165.44 (s), 163.13 (s), 146.03 (s), 141.45 (s), 129.62 (s), 127.76 (s), 126.11 (s), 122.44 (s), 121.20 (s), 119.70 (s), 114.20 (s), 77.33 (s), 77.01 (s), 76.69 (s), 55.51 (s), 40.23 (s), 31.38 (s), 20.18 (s), 13.73 (s). HRMS (ESI) Calculated for $C_{19}H_{22}N_3O_5[M+H]^+$ 372.1559, found 372.1561.



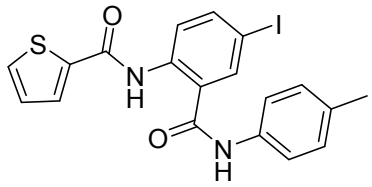
N-ethyl-2-(4-methoxybenzamido)benzamide (3h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.13 – 7.87 (d, *J* = 8.8 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.10 – 7.05 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 1H), 3.90 (s, 3H), 3.53 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.23 (s), 165.19 (s), 162.50 (s), 140.11 (s), 132.56 (s), 129.30 (s), 127.24 (s), 126.39 (s), 122.52 (s), 121.57 (s), 120.54 (s), 113.97 (s), 55.42 (s), 35.01 (s), 14.70 (s). HRMS (ESI) Calculated for $C_{17}H_{19}N_2O_3[M+H]^+$ 299.1396, found 299.1394.



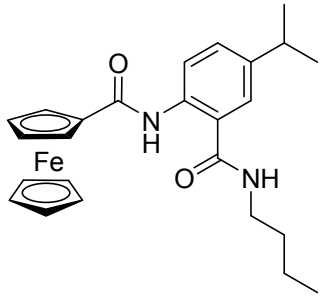
2-benzamido-N-ethyl-5-methoxybenzamide (3i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.68 (d, *J* = 9.1 Hz, 1H), 8.09 – 7.97 (m, 2H), 7.60 – 7.46 (m, 3H), 7.14 – 6.93 (m, 3H), 6.43 (s, 1H), 3.80 (s, 3H), 3.56 – 3.47 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82 (s), 165.26 (s), 154.95 (s), 134.91 (s), 132.88 (s), 131.62 (s), 128.70 (s), 127.28 (s), 123.23 (s), 122.49 (s), 116.82 (s), 112.71 (s), 55.68 (s), 35.04 (s), 14.64 (s). HRMS (ESI) Calculated for $C_{17}H_{19}N_2O_3[M+H]^+$ 299.1396, found 299.1397.



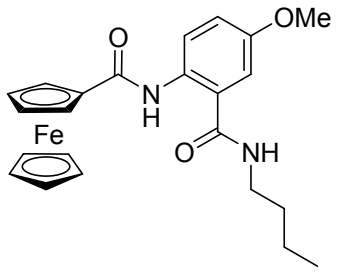
2-benzamido-5-methyl-N-(*p*-tolyl)benzamide(3j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 8.73 (s, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.10 – 8.00 (m, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 – 7.50 (m, 3H), 7.36 (d, J = 1.1 Hz, 1H), 7.26 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.5 Hz, 1H), 2.40 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.57 (s), 165.52 (s), 136.76 (s), 135.18 (s), 134.64 (s), 134.46 (s),132.92 (s), 132.83 (s), 131.91 (s), 129.66 (s), 128.76 (s), 127.51 (s), 127.43 (s), 121.85 (s), 121.83(s), 120.88 (s), 20.97 (s), 20.60 (s). HRMS (ESI) Calculated for $C_{22}H_{21}N_2O_2[M+H]^+$ 345.1603, found 345.1606.



N-(4-iodo-2-(*p*-tolylcarbamoyl)phenyl)thiophene-2-carboxamide(3k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 1H), 8.06 (s, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.80 – 7.69 (m, 2H), 7.60 – 7.47 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.99 (s), 160.36 (s), 141.52 (s), 139.84 (s), 139.42 (s), 135.42 (s), 135.29 (s), 134.30 (s), 131.59 (s), 129.78 (s), 128.97 (s), 128.02 (s), 123.45 (s), 122.86 (s), 121.20 (s), 85.46 (s), 20.99 (s). HRMS (ESI) Calculated for $C_{19}H_{16}IN_2O_2S$ $[M+H]^+$ 462.9977, found 462.9975.

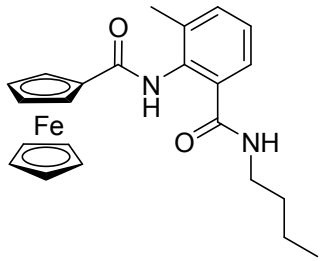


(5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 8.60 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 (s, 1H), 6.37 (s, 1H), 4.91 (s, 2H), 4.43 (s, 2H), 4.26 (s, 5H), 3.52 (dd, *J* = 13.0, 6.6 Hz, 2H), 2.91 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.76 – 1.60 (m, 2H), 1.47 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45 (s), 169.27(s), 142.87 (s), 137.72 (s), 130.47 (s), 124.18 (s), 121.50 (s), 120.46 (s), 70.88 (s), 69.91 (s), 68.61 (s), 39.84 (s), 33.66 (s), 31.70 (s), 23.98 (s), 20.20 (s), 13.79 (s). HRMS (ESI) Calculated for $C_{25}H_{30}FeN_2NaO_2$ $[M+Na]^+$ 469.1554, found 469.1553.

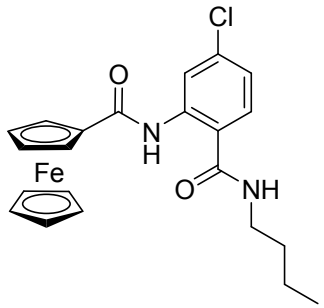


(5b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.57 (d, *J* = 8.8 Hz, 1H), 7.05 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.40 (s, 1H), 4.93 – 4.85 (m, 2H), 4.46 – 4.38 (m, 2H), 4.26 (s, 5H), 3.83 (s, 3H), 3.50 (dd, *J* = 13.0, 7.1 Hz, 2H), 1.71 – 1.59

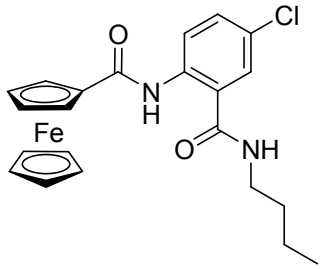
(m, 2H), 1.45 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.07 (s), 168.90 (s), 154.53 (s), 133.10 (s), 122.89 (s), 122.04 (s), 116.89 (s), 112.63 (s), 70.82 (s), 69.89 (s), 68.54 (s), 55.75 (s), 39.85 (s), 31.59 (s), 20.16 (s), 13.75 (s). HRMS (ESI) Calculated for $C_{23}H_{26}FeN_2NaO_3$ $[M+Na]^+$ 457.1191, found 457.1195.



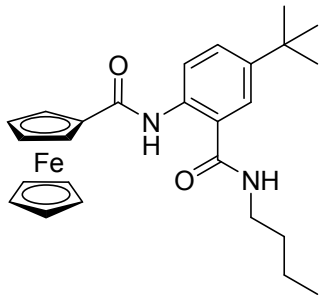
(5c).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.49 – 7.07 (m, 3H), 6.25 (s, 1H), 4.87 (s, 2H), 4.44 (s, 2H), 4.30 (s, 5H), 3.57 – 3.31 (m, 2H), 2.36 (s, 3H), 1.72 – 1.51 (m, 2H), 1.51 – 1.31 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.30 (s), 168.89 (s), 136.36 (s), 135.25 (s), 133.69 (s), 129.93 (s), 125.35 (s), 124.20 (s), 70.84 (s), 69.86 (s), 68.76 (s), 39.77 (s), 31.56 (s), 20.11 (s), 19.62 (s), 13.70 (s). HRMS (ESI) Calculated for $C_{23}H_{26}FeN_2NaO_2$ $[M+Na]^+$ 441.1241, found 441.1245.



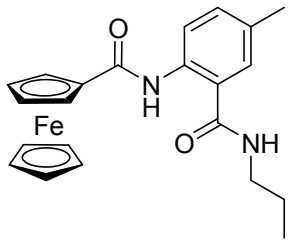
(5d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.78 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.49 (s, 1H), 4.90 (s, 2H), 4.46 (s, 2H), 4.26 (s, 5H), 3.51 (dd, *J* = 13.0, 7.1 Hz, 2H), 1.67 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.51 – 1.43 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.84 (s), 168.53 (s), 140.99 (s), 138.54 (s), 127.55 (s), 122.15 (s), 120.95 (s), 118.22 (s), 71.21 (s), 69.99 (s), 68.66 (s), 39.92 (s), 31.55 (s), 20.18 (s), 13.76 (s). HRMS (ESI) Calculated for $C_{22}H_{23}ClFeN_2NaO_2$ $[M+Na]^+$ 461.0695, found 461.0697.



(5e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 8.69 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 6.35 (s, 1H), 4.91 (s, 2H), 4.45 (s, 2H), 4.27 (s, 5H), 3.52 (dd, *J* = 13.0, 7.0 Hz, 2H), 1.67 (dt, *J* = 14.9, 7.3 Hz, 2H), 1.51 – 1.42 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59 (s), 168.03 (s), 138.58 (s), 132.30 (s), 127.07 (s), 126.27 (s), 122.67 (s), 121.55 (s), 71.11 (s), 69.96 (s), 68.64 (s), 39.97 (s), 31.54 (s), 20.16 (s), 13.75 (s). HRMS (ESI) Calculated for $C_{22}H_{23}ClFeN_2NaO_2$ $[M+Na]^+$ 461.0695, found 461.0698.

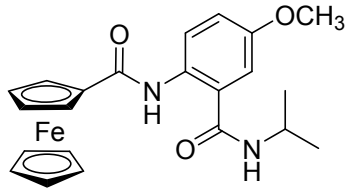


(5f).^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.60 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 6.31 (s, 1H), 4.97 – 4.86 (m, 2H), 4.48 – 4.38 (m, 2H), 4.26 (s, 5H), 3.53 (dd, *J* = 13.1, 7.1 Hz, 2H), 1.68 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.36 (s, 9H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.65 (s), 169.27 (s), 145.20 (s), 137.31 (s), 129.73 (s), 122.63 (s), 121.20 (s), 120.33 (s), 70.88 (s), 69.91 (s), 68.61 (s), 39.86 (s), 34.36 (s), 31.71 (s), 31.30 (s), 20.19 (s), 13.79 (s). HRMS (ESI) Calculated for $C_{26}H_{32}FeN_2NaO_2$ $[M+Na]^+$ 483.1711, found 483.1714.

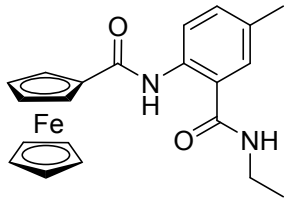


(5g). ^{1}H NMR (400 MHz, DMSO) δ 11.78 (s, 1H), 8.79 (t, *J* = 5.2 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 4.77 (s, 2H), 4.50 (s, 2H), 4.23 (s, 5H), 2.32 (s, 3H), 1.62 – 1.52 (m, 2H), 1.42 – 1.31 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.08 (s), 168.32 (s), 137.49 (s), 132.83 (s), 131.51 (s), 128.74 (s), 120.48 (s), 120.40 (s), 77.09 (s), 71.27 (s), 70.08 (s), 68.58 (s),

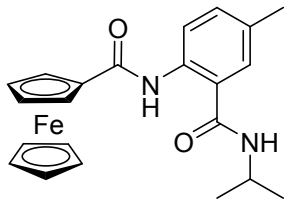
31.50 (s), 20.86 (s), 20.13 (s), 14.21 (s). HRMS (ESI) Calculated for $C_{22}H_{24}FeN_2NaO_2$ $[M+Na]^+$ 427.1085, found 427.1088.



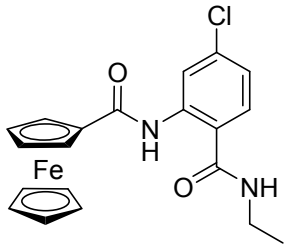
(5h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.58 (d, *J* = 9.1 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.12 (d, *J* = 7.2 Hz, 1H), 4.90 (s, 2H), 4.43 (s, 2H), 4.38 – 4.29 (m, 1H), 4.28 (s, 5H), 3.85 (s, 3H), 1.34 – 1.30 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.03 (s), 168.14 (s), 154.50 (s), 133.15 (s), 122.90 (s), 122.10 (s), 116.74 (s), 112.75 (s), 70.83 (s), 69.90 (s), 68.55 (s), 55.80 (s), 42.09 (s), 22.77 (s). HRMS (ESI) Calculated for $C_{22}H_{24}FeN_2NaO_3$ $[M+Na]^+$ 443.1034, found 443.1037.



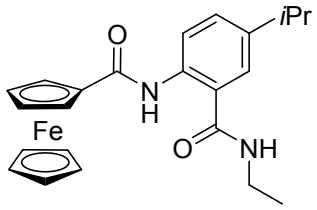
(5i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.30 (m, 1H), 6.66 (d, *J* = 4.9 Hz, 1H), 6.35 (s, 1H), 4.92 (s, 2H), 4.46 (s, 2H), 4.27 (s, 5H), 3.64 – 3.48 (m, 2H), 2.35 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31 (s), 169.26 (s), 155.74 (s), 137.48 (s), 133.15 (s), 131.72 (s), 126.76 (s), 121.31 (s), 120.25 (s), 70.89 (s), 69.91 (s), 68.60 (s), 34.97 (s), 22.90 (s), 14.84 (s). HRMS (ESI) Calculated for $C_{21}H_{22}FeN_2NaO_2$ $[M+Na]^+$ 413.0928, found 413.0926.



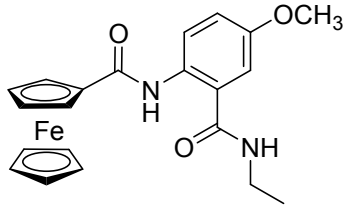
(5j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.24 (m, 2H), 6.18 (d, *J* = 7.3 Hz, 1H), 4.93 – 4.87 (m, *J* = 2.0 Hz, 2H), 4.46 – 4.40 (t, *J* = 2.0 Hz, 2H), 4.39 – 4.30 (m, 1H), 4.26 (s, 5H), 2.35 (s, 3H), 1.32 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24 (s), 168.57 (s), 137.49 (s), 133.10 (s), 131.70 (s), 126.70 (s), 121.29 (s), 120.41 (s), 70.88 (s), 69.91 (s), 68.61 (s), 41.99 (s), 22.80 (s), 20.80 (s). HRMS (ESI) Calculated for $C_{22}H_{24}FeN_2NaO_2$ $[M+Na]^+$ 427.1085, found 427.1083.



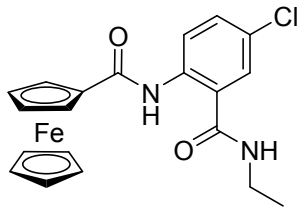
(5k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.83 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.25 (s, 1H), 4.96 (s, 2H), 4.50 (s, 2H), 4.32 (s, 5H), 3.62 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.65 (s), 168.53 (s), 141.09 (s), 138.76 (s), 127.35 (s), 122.15 (s), 121.10 (s), 117.96 (s), 71.35 (s), 70.13 (s), 68.80 (s), 35.11 (s), 14.78 (s). HRMS (ESI) Calculated for $C_{20}H_{19}ClFeN_2NaO_2$ $[M+Na]^+$ 433.0382, found 433.0384.



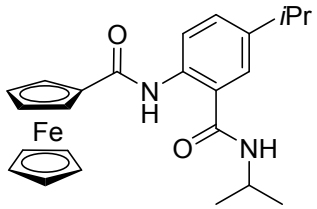
(5l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 7.37 (m, 2H), 6.24 (s, 1H), 5.01 (s, 2H), 4.52 (s, 2H), 4.37 (s, 5H), 3.63 – 3.48 (m, 2H), 3.02 – 2.82 (m, 1H), 1.35 – 1.31 (t, *J* = 7.8 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40(s), 169.27 (s), 142.88 (s), 137.76 (s), 130.59 (s), 124.08 (s), 121.57 (s), 120.34 (s), 70.91 (s), 69.94 (s), 68.64 (s), 35.00 (s), 33.68 (s), 23.99 (s), 14.89 (s). HRMS (ESI) Calculated for $C_{23}H_{26}FeN_2NaO_2$ $[M+Na]^+$ 441.1241, found 441.1243.



(5m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.40 (s, 1H), 4.87 (s, 2H), 4.40 (s, 2H), 4.24 (s, 5H), 3.81 (s, 3H), 3.58 – 3.43 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.10 (s), 168.87 (s), 154.55 (s), 133.09 (s), 122.93 (s), 121.97 (s), 117.01 (s), 112.57 (s), 70.83 (s), 69.89 (s), 68.54 (s), 55.75 (s), 35.47 (s), 14.98 (s). HRMS (ESI) Calculated for $C_{21}H_{22}FeN_2NaO_3$ $[M+Na]^+$ 429.0878, found 429.0876.

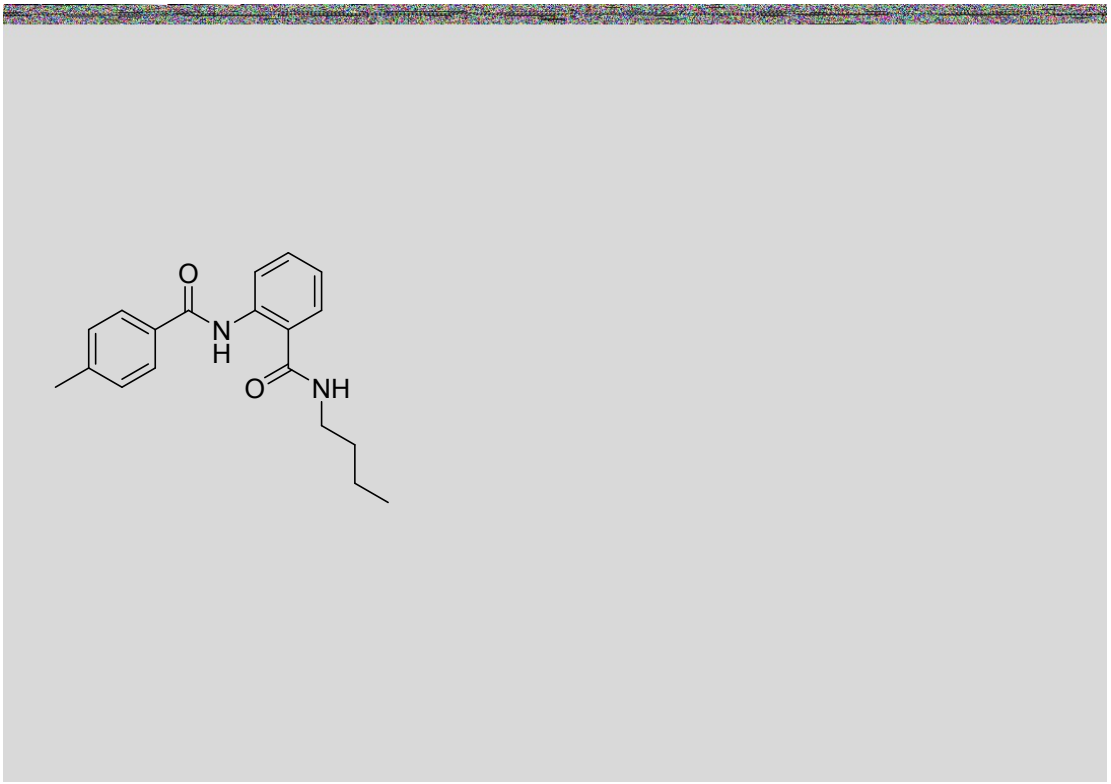


(5n). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 8.68 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.42 (m, 2H), 6.36 (s, 1H), 4.93 – 4.87 (m, 2H), 4.48 – 4.43 (m, 2H), 4.27 (s, 5H), 3.61 – 3.50 (m, 2H), 1.36 – 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63 (s), 167.99 (s), 138.58 (s), 132.33 (s), 127.10 (s), 126.32 (s), 122.68 (s), 121.46 (s), 76.15 (s), 71.13 (s), 69.97 (s), 68.64 (s), 35.17 (s), 14.75 (s). HRMS (ESI) Calculated for $C_{20}H_{19}ClFeN_2NaO_2$ $[M+Na]^+$ 433.0382, found 433.0380.

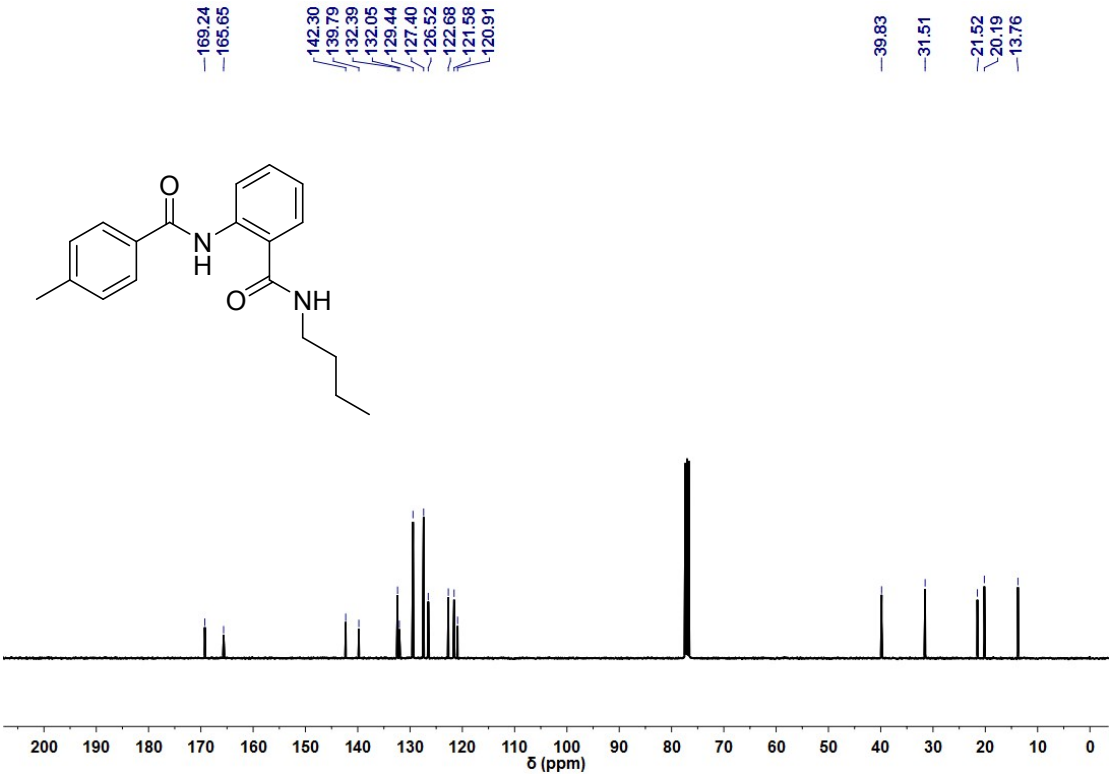


(5o). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 6.15 (d, *J* = 7.2 Hz, 1H), 4.95 – 4.87 (m, 2H), 4.44 – 4.41 (m, 2H), 4.36 (td, *J* = 13.3, 6.6 Hz, 1H), 4.26 (s, 5H), 2.98 – 2.83 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.23 (s), 168.72 (s), 142.88 (s), 137.72 (s), 130.36 (s), 124.21 (s), 121.53 (s), 120.53 (s), 70.89 (s), 69.91 (s), 68.61 (s), 42.02 (s), 33.69 (s), 24.00 (s), 22.81 (s). HRMS (ESI) Calculated for $C_{24}H_{28}FeN_2NaO_2$ $[M+Na]^+$ 455.1398, found 455.1399.

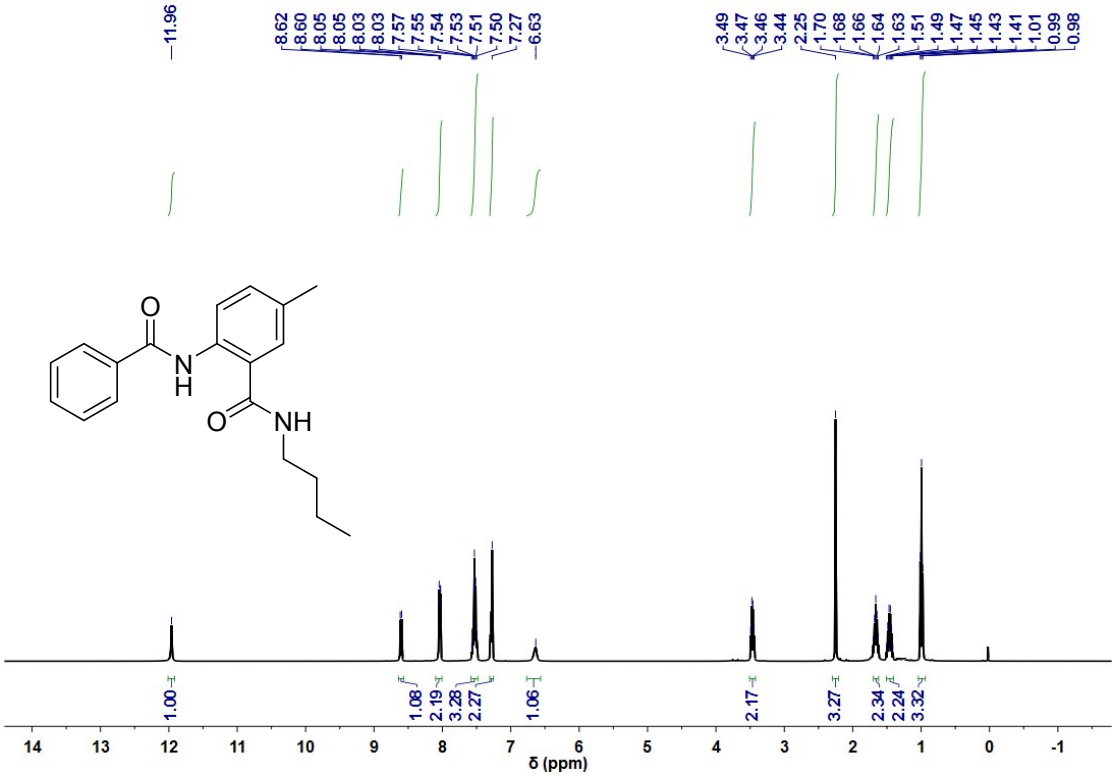
3. Copies of NMR spectra



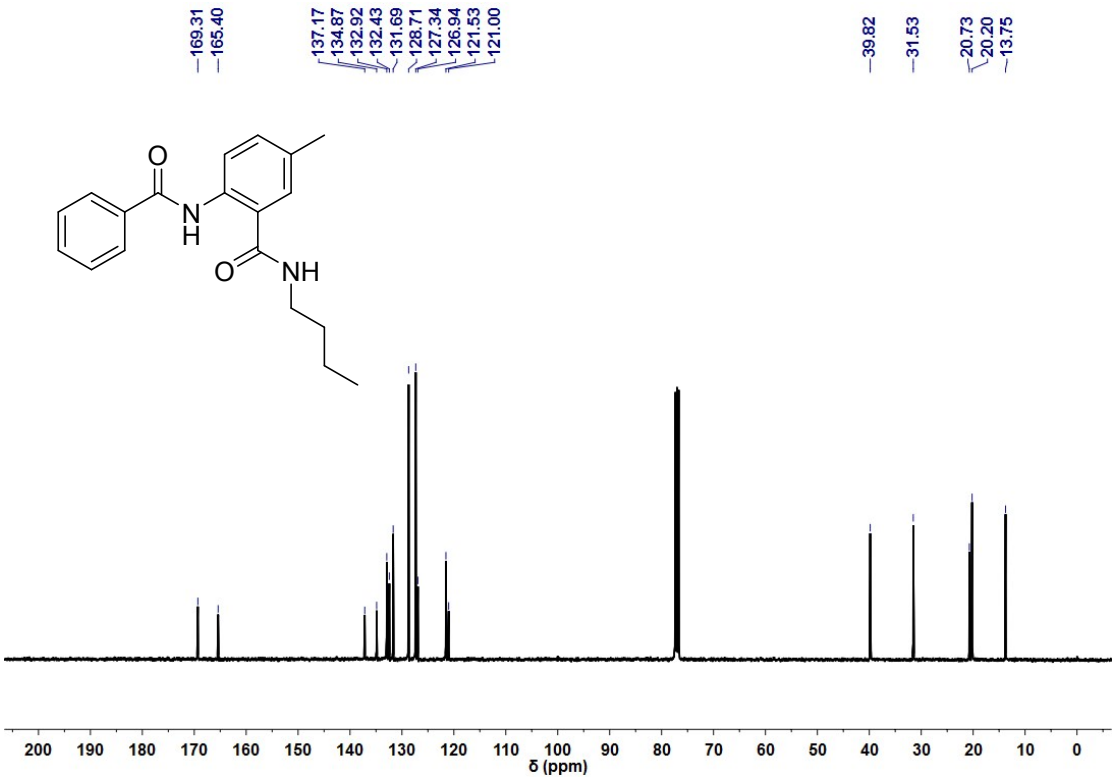
^{1}H-NMR spectrum of 3a



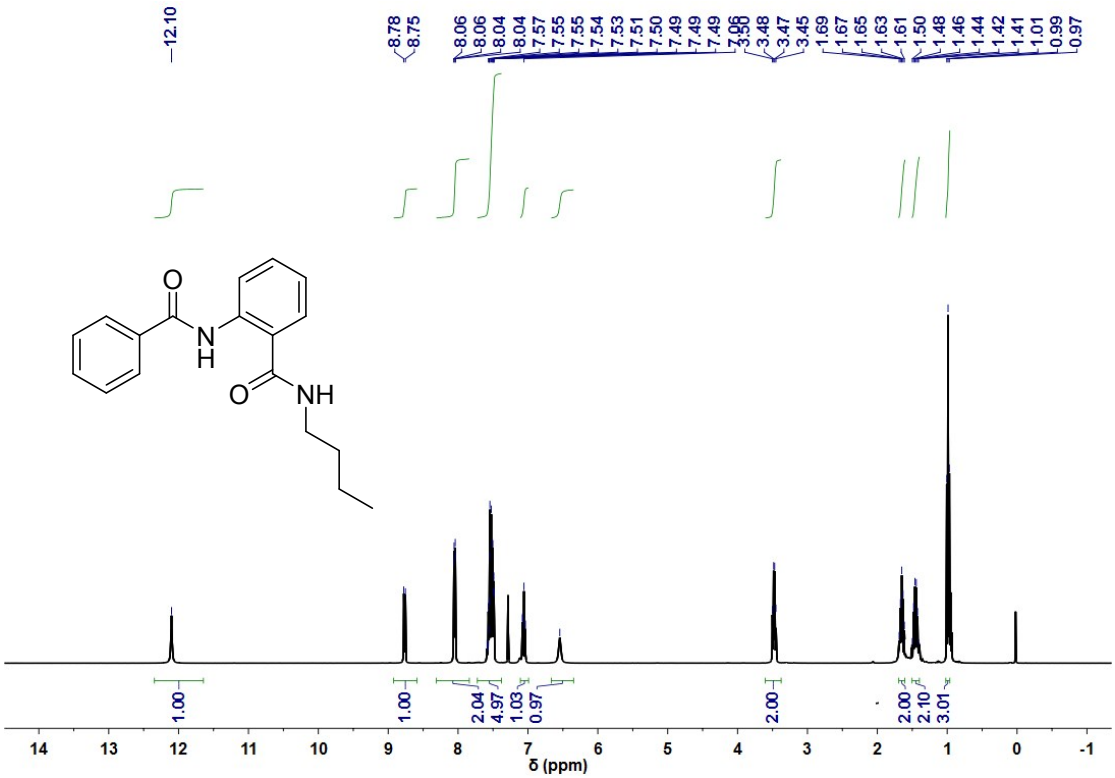
^{13}C-NMR spectrum of 3a



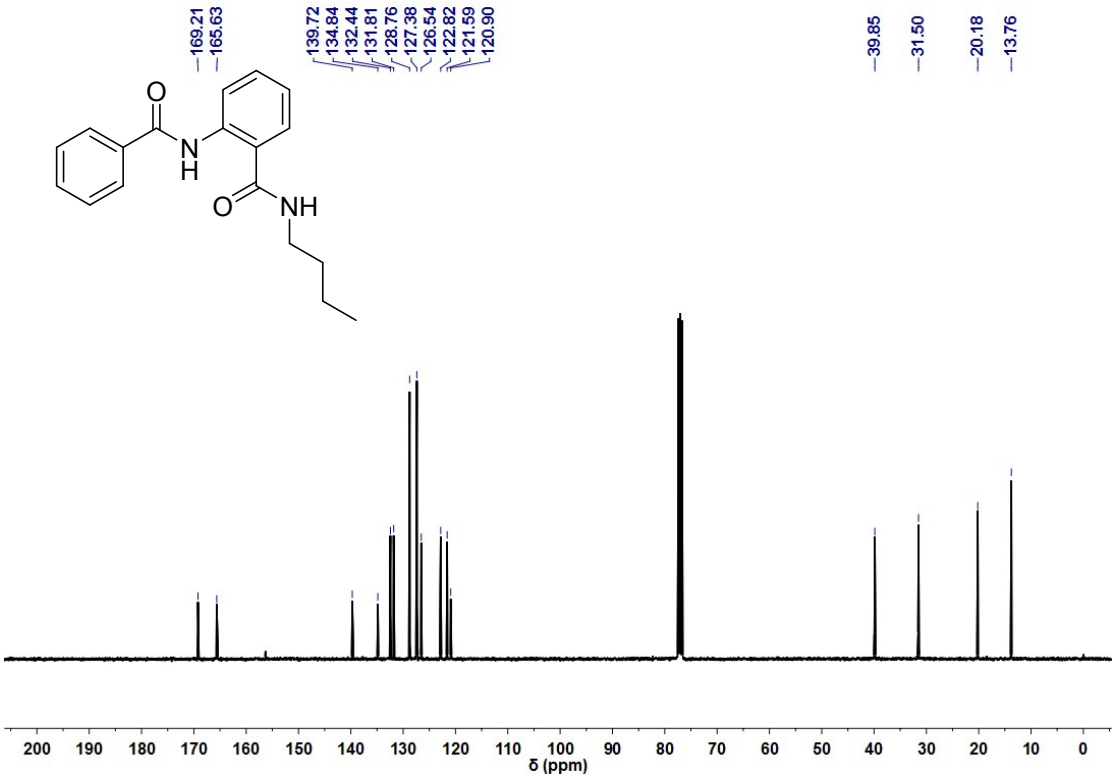
^{1}H-NMR spectrum of 3b



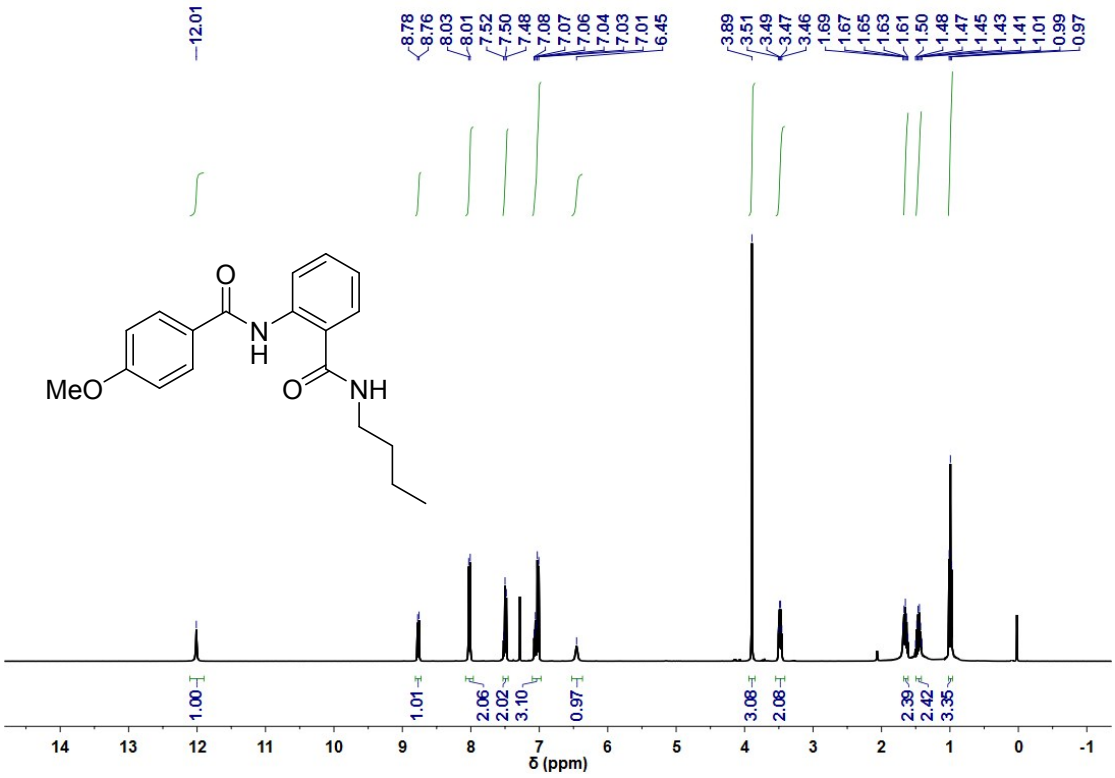
^{13}C-NMR spectrum of 3b



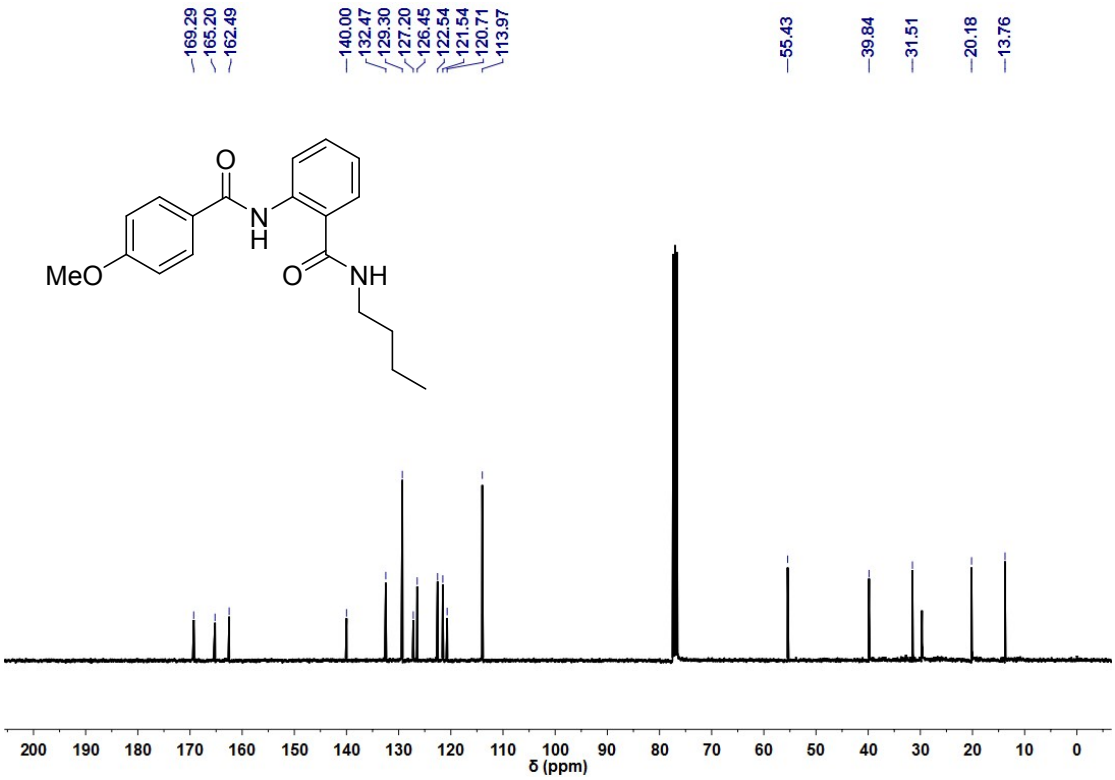
^{1}H-NMR spectrum of 3c



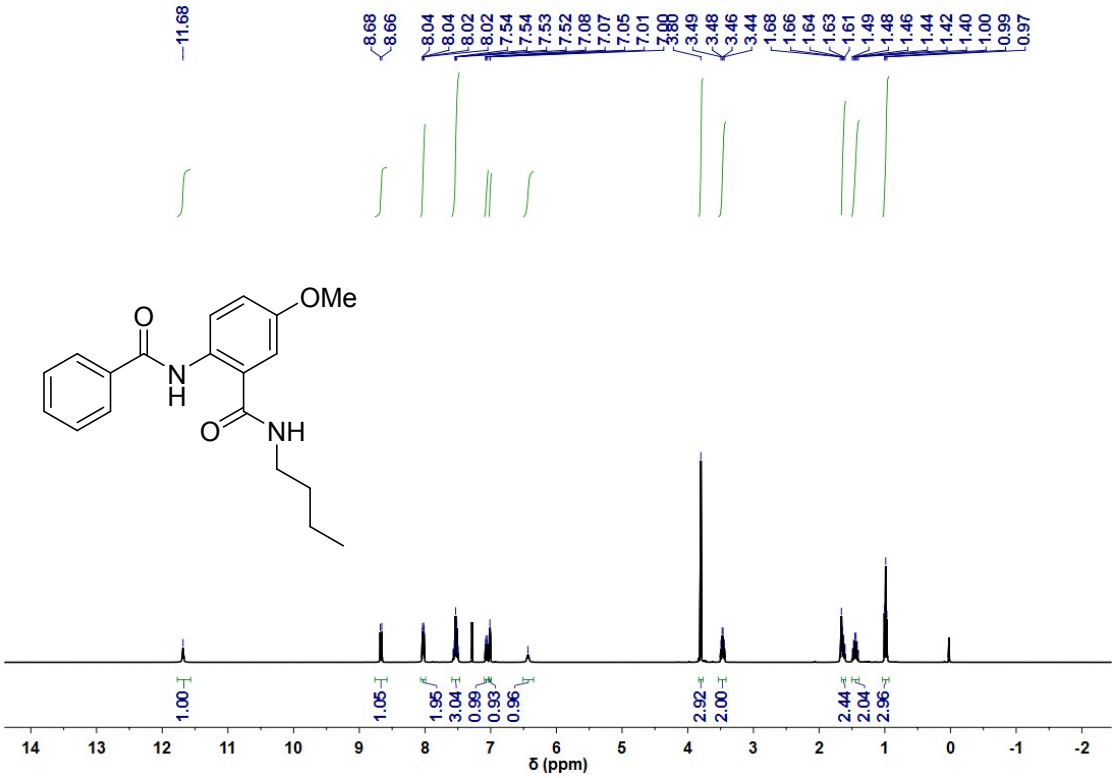
^{13}C-NMR spectrum of 3c



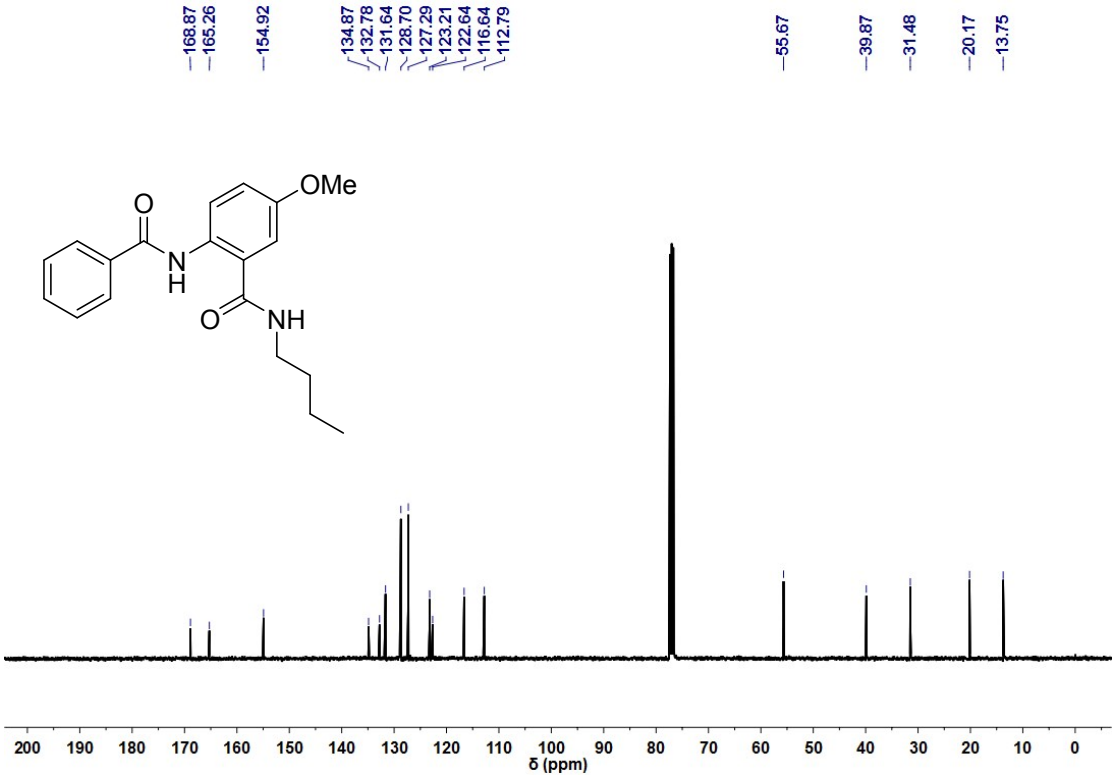
^{1}H-NMR spectrum of 3d



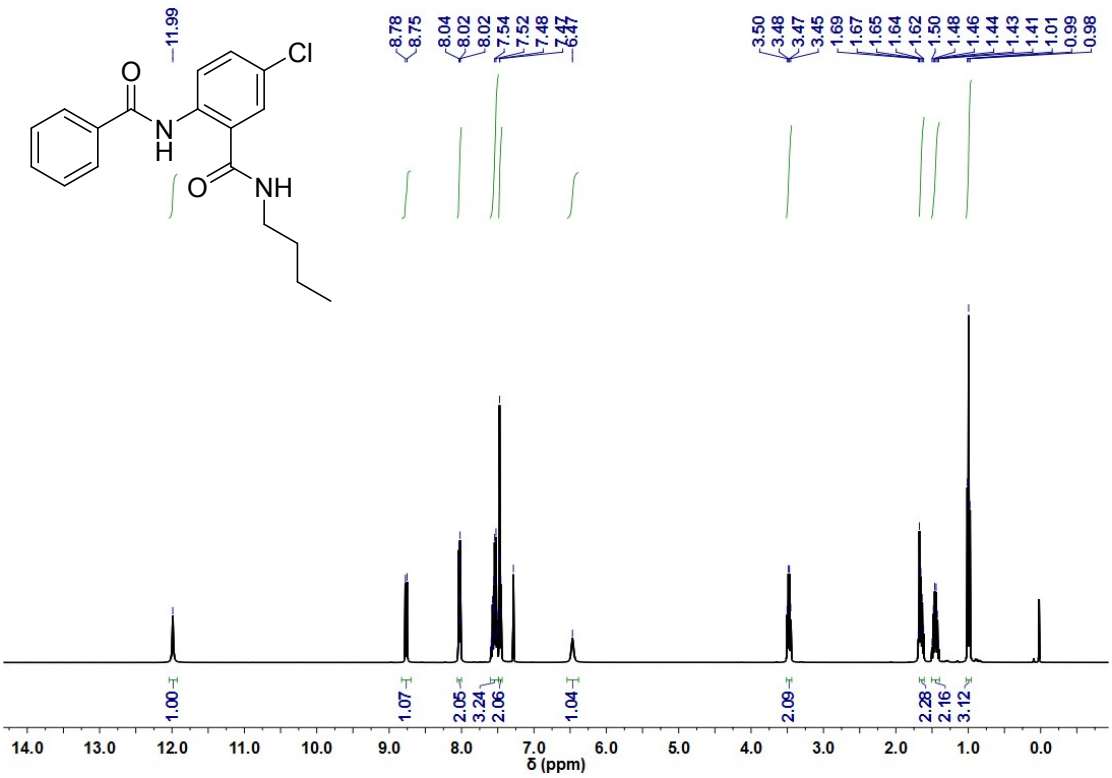
^{13}C-NMR spectrum of 3d



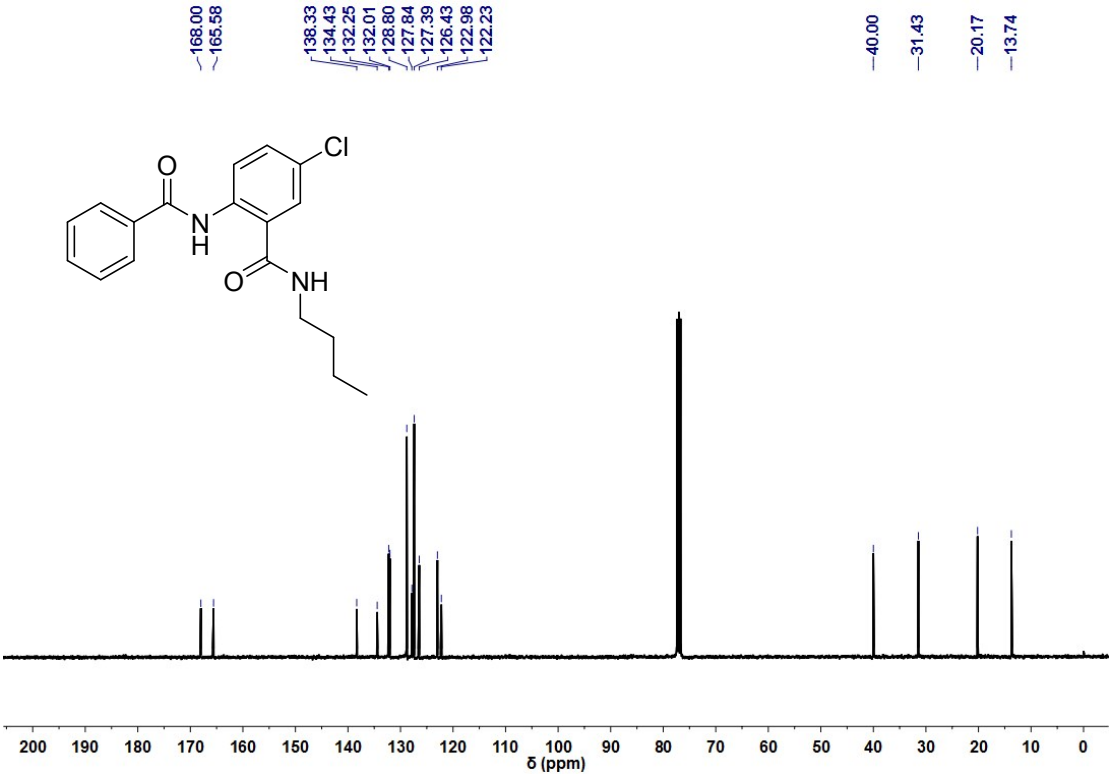
^{1}H-NMR spectrum of 3e



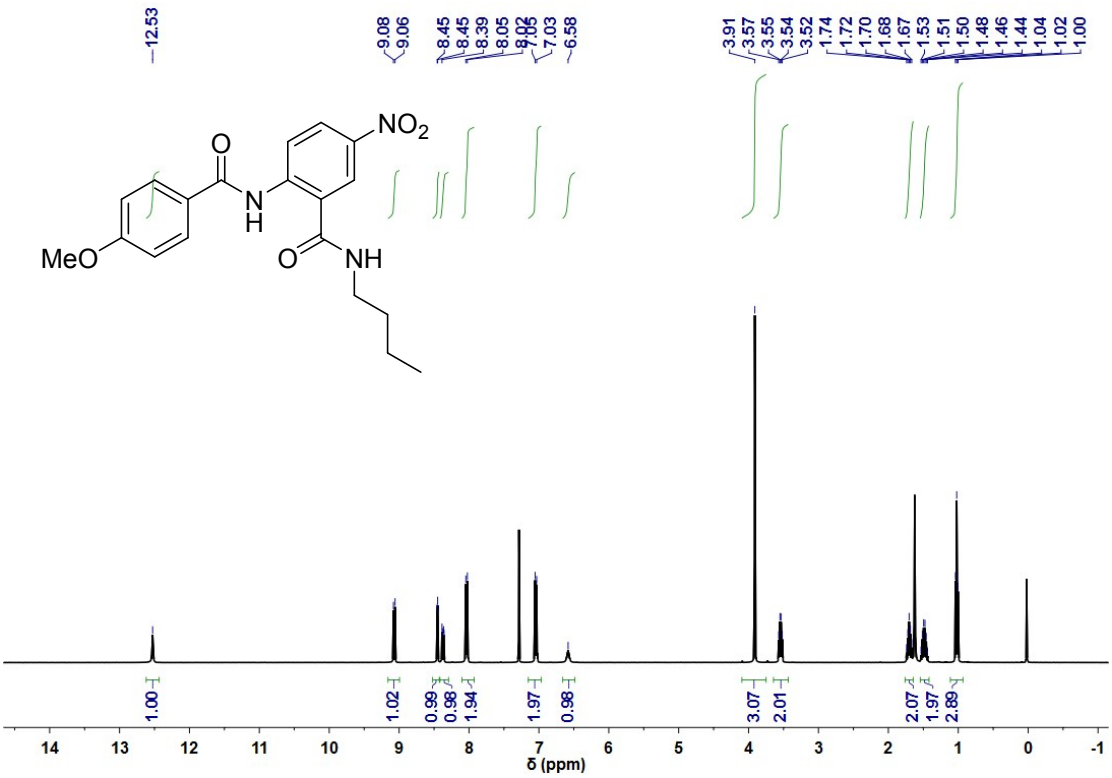
^{13}C-NMR spectrum of 3e



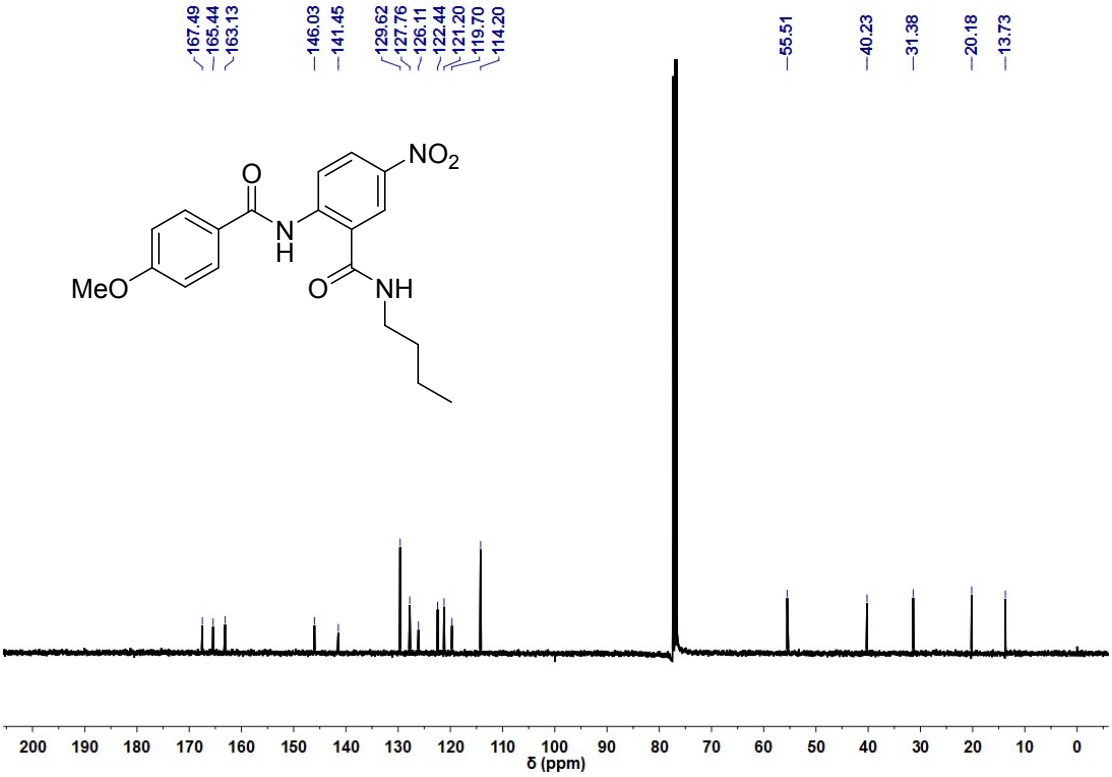
^{1}H-NMR spectrum of 3f



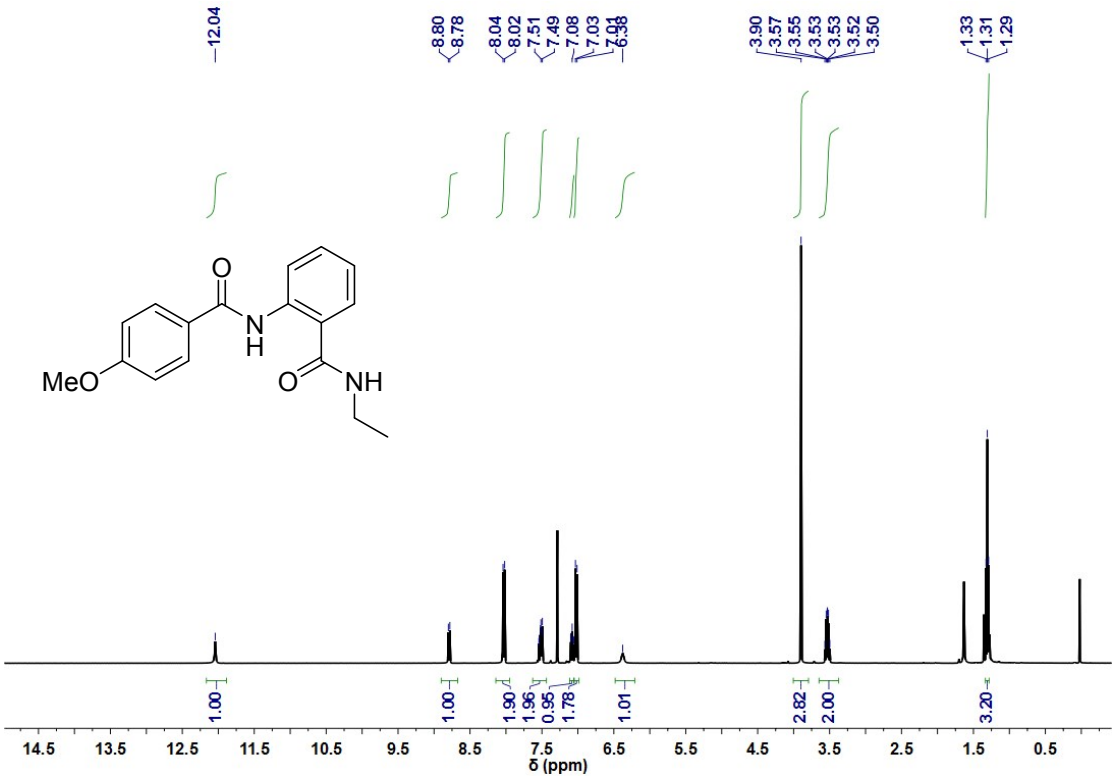
^{13}C-NMR spectrum of 3f



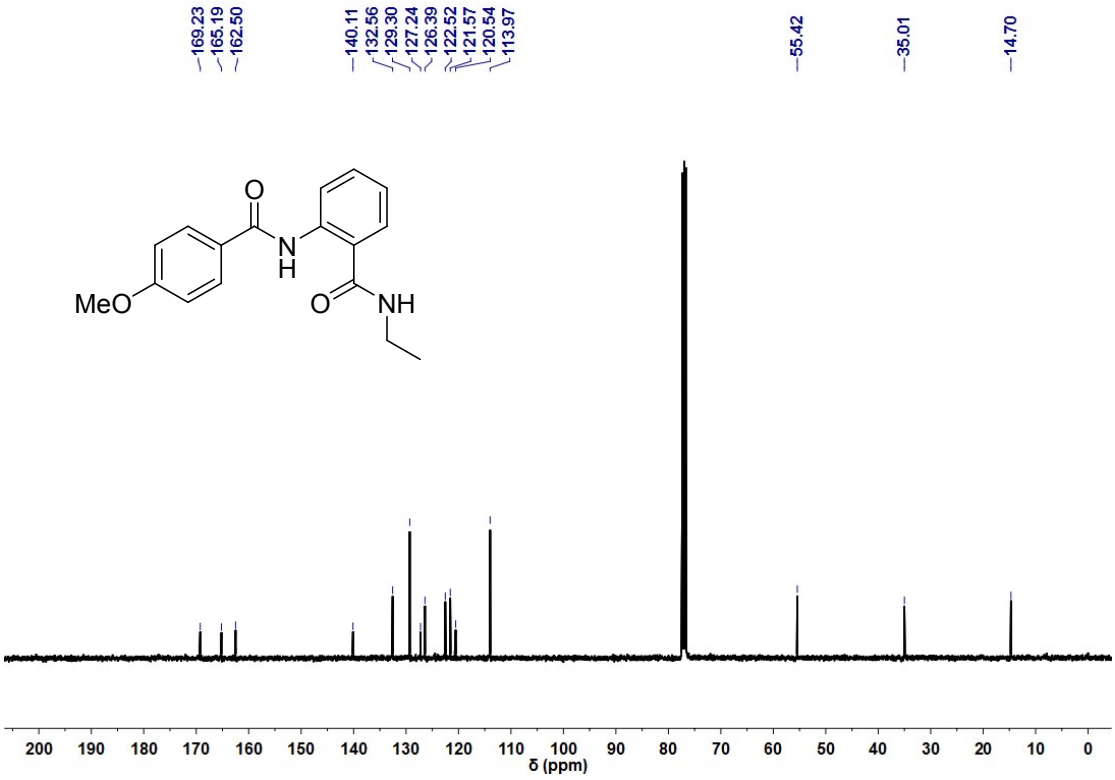
^{1}H-NMR spectrum of 3g



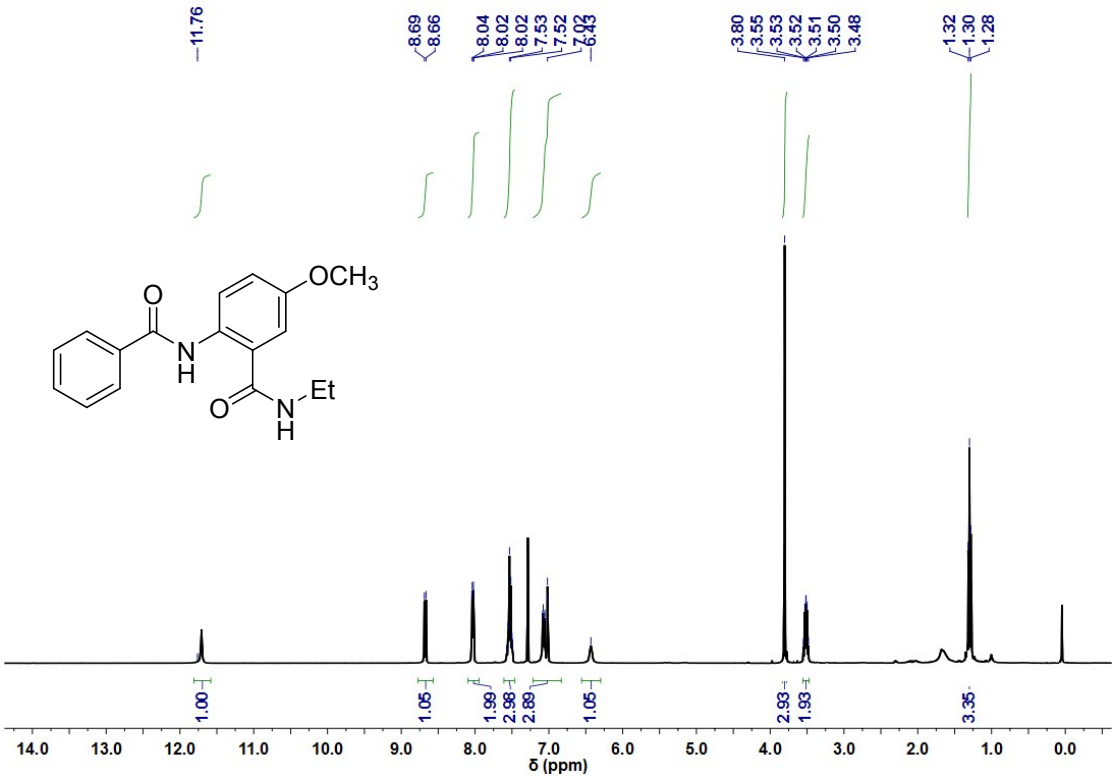
^{13}C-NMR spectrum of 3g



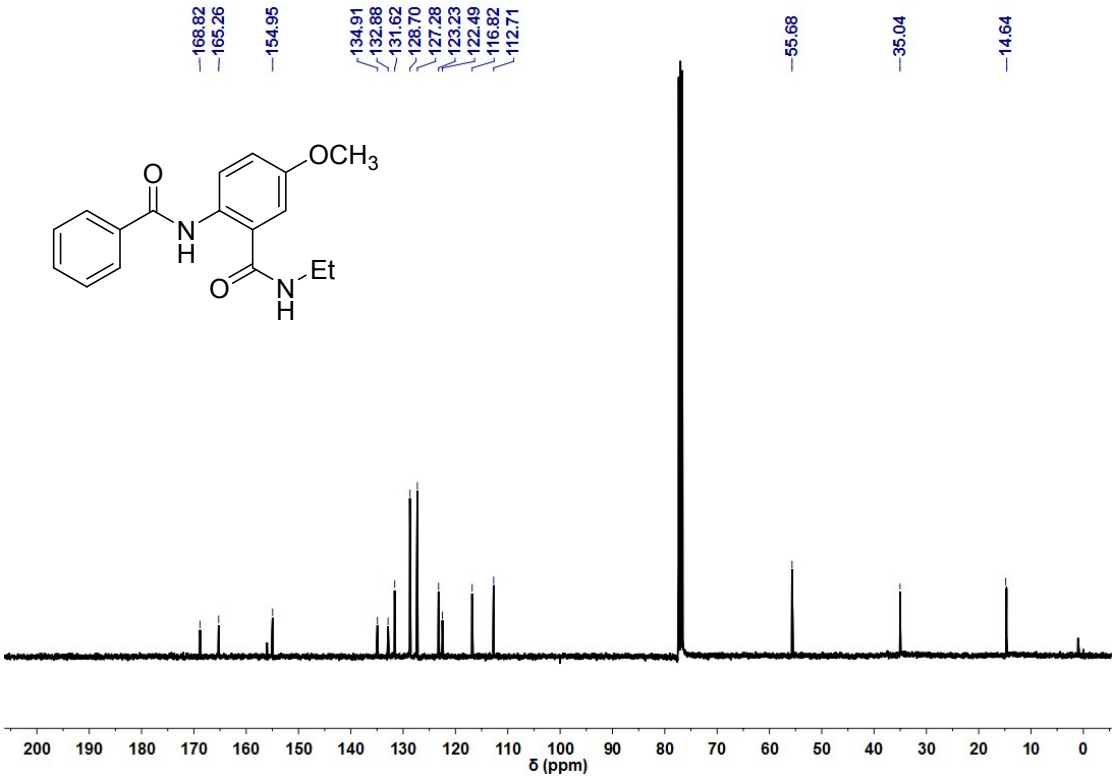
^{1}H-NMR spectrum of 3h



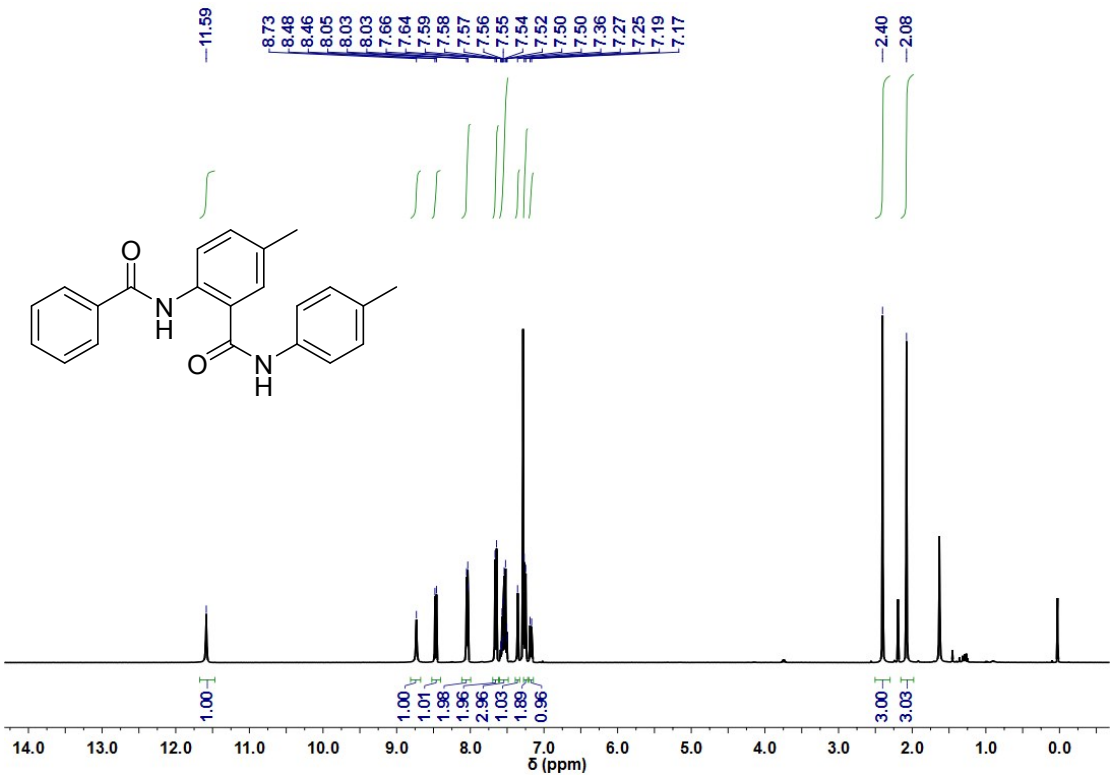
^{13}C-NMR spectrum of 3h



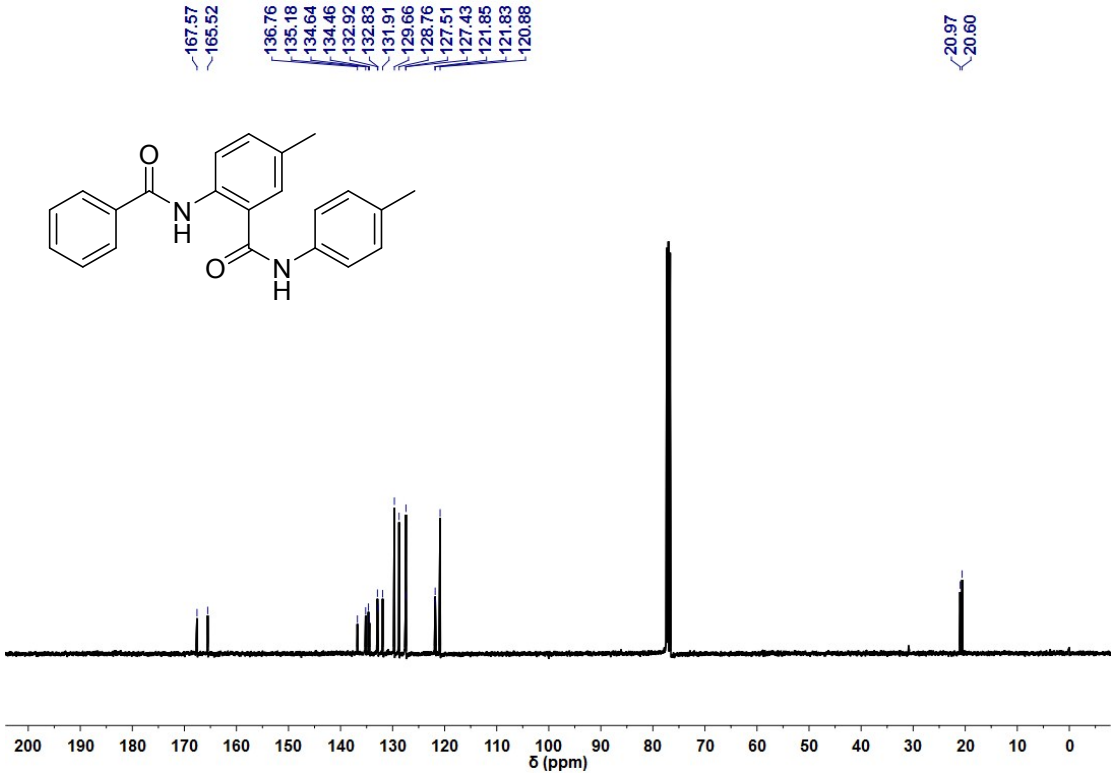
^{1}H-NMR spectrum of 3i



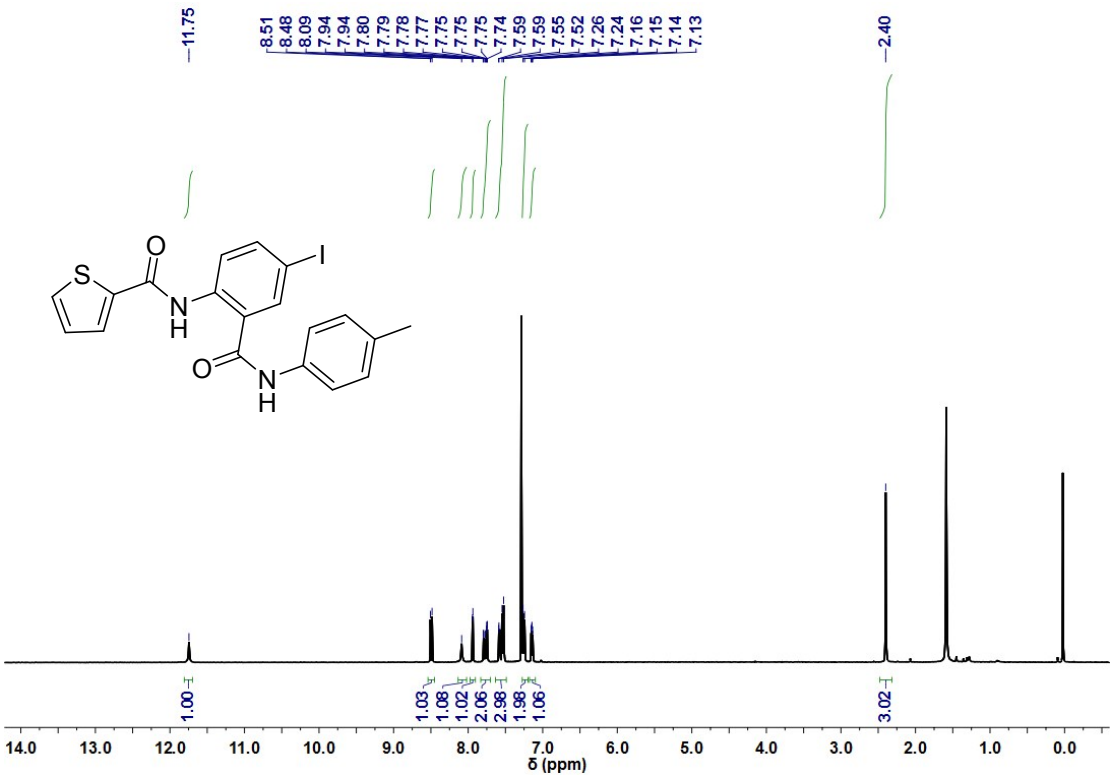
^{13}C-NMR spectrum of 3i



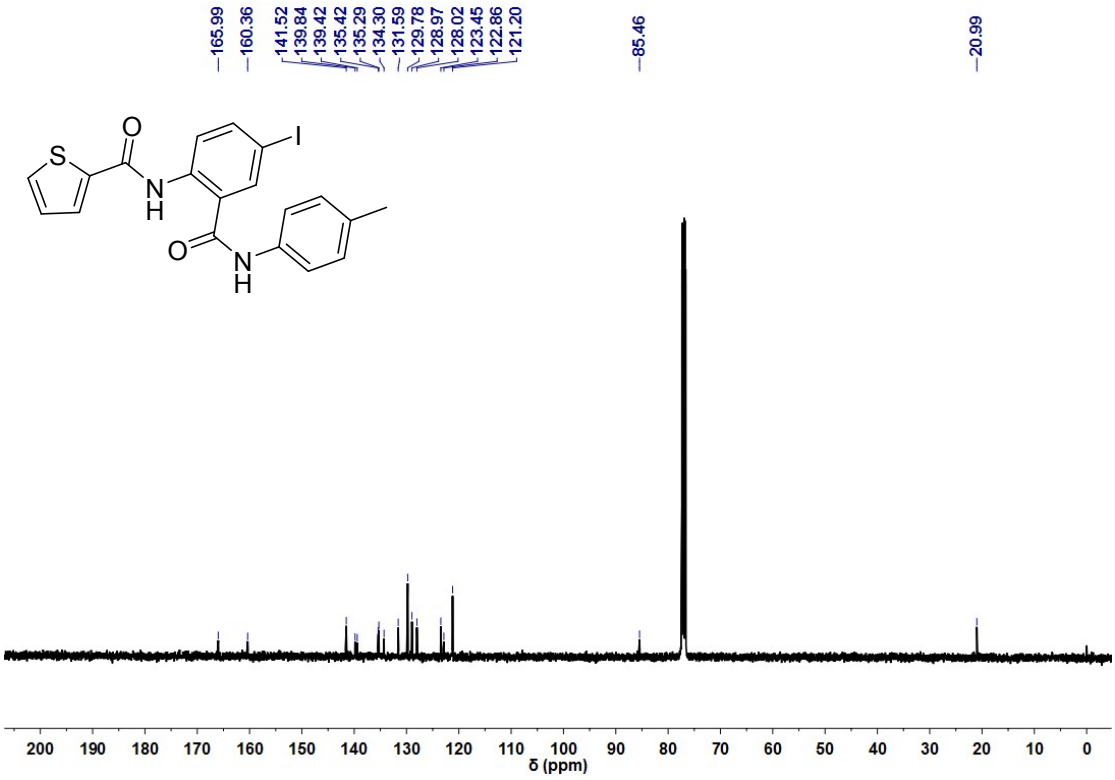
^{1}H-NMR spectrum of 3j



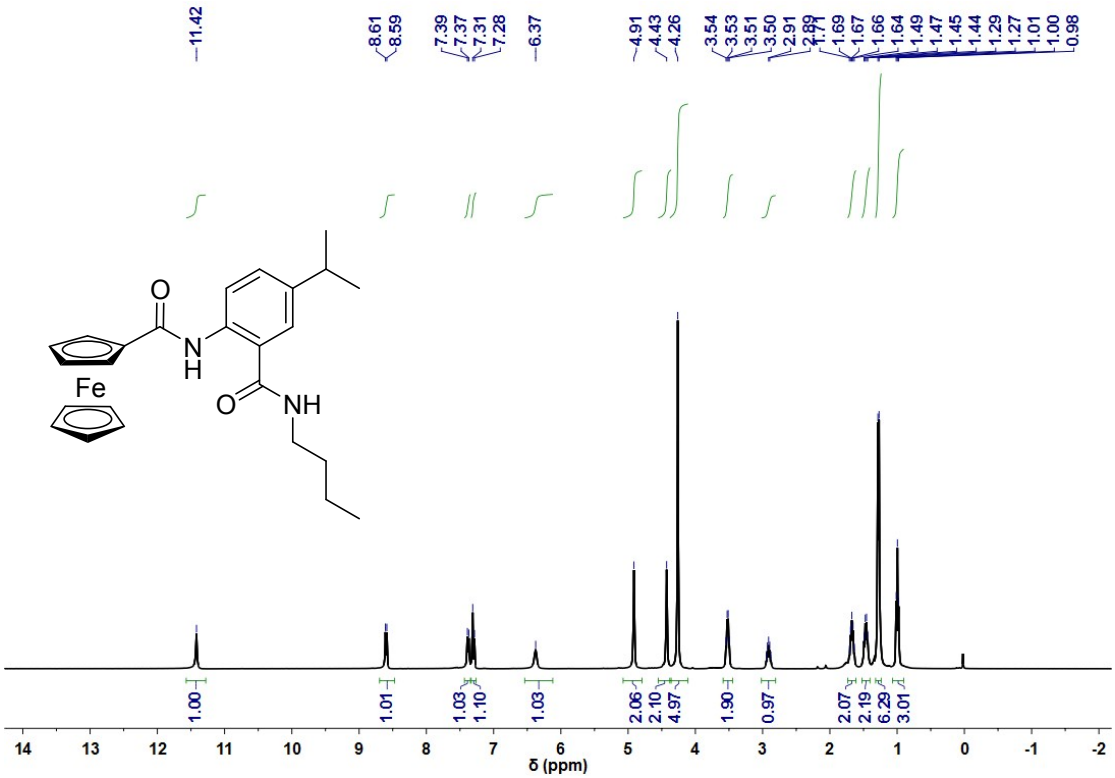
^{13}C-NMR spectrum of 3j



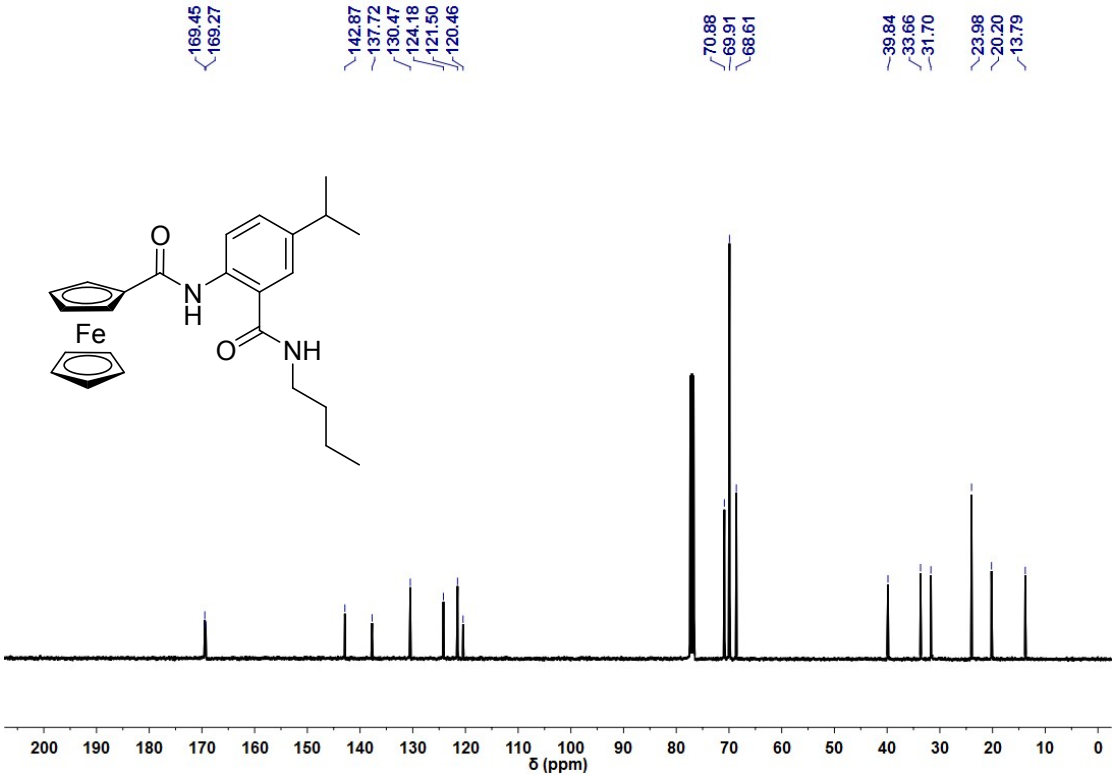
^{1}H-NMR spectrum of 3k



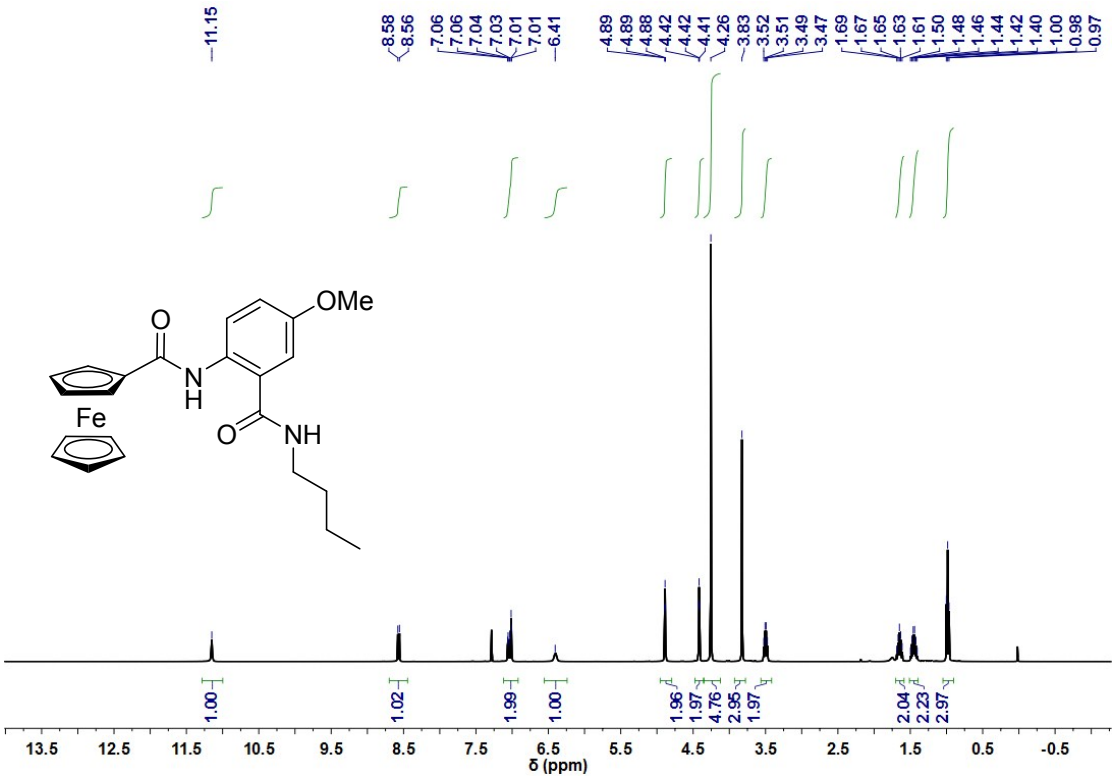
^{13}C-NMR spectrum of 3k



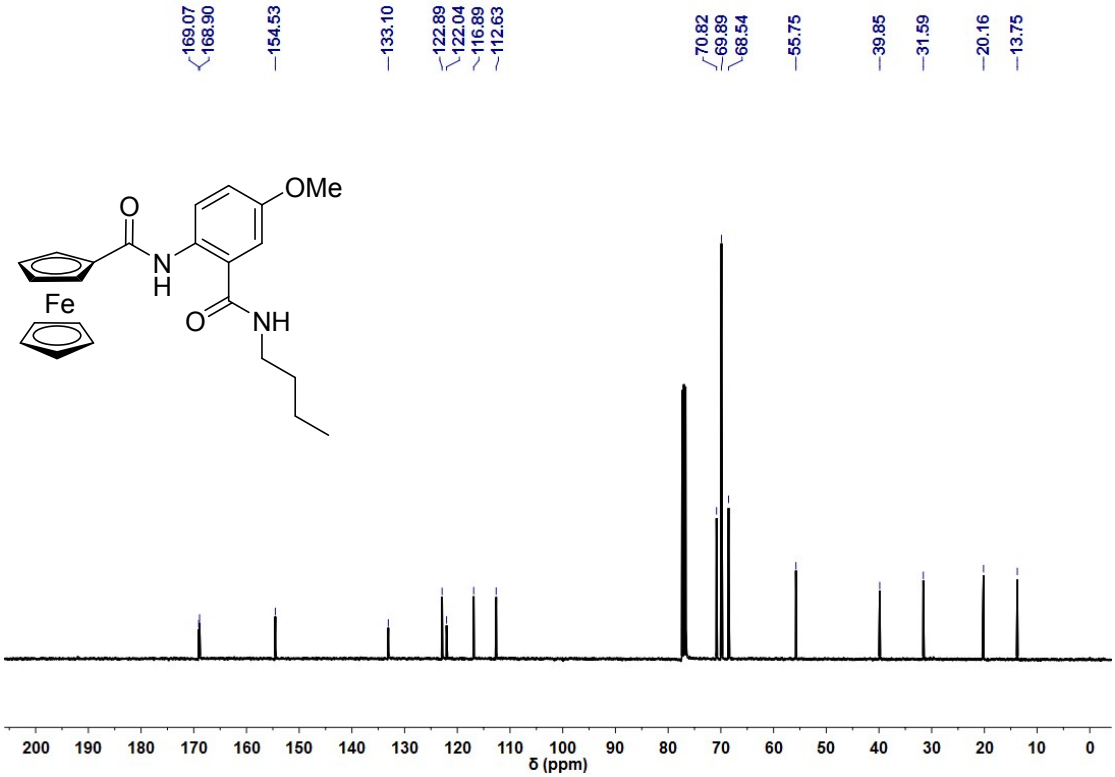
^{1}H-NMR spectrum of 5a



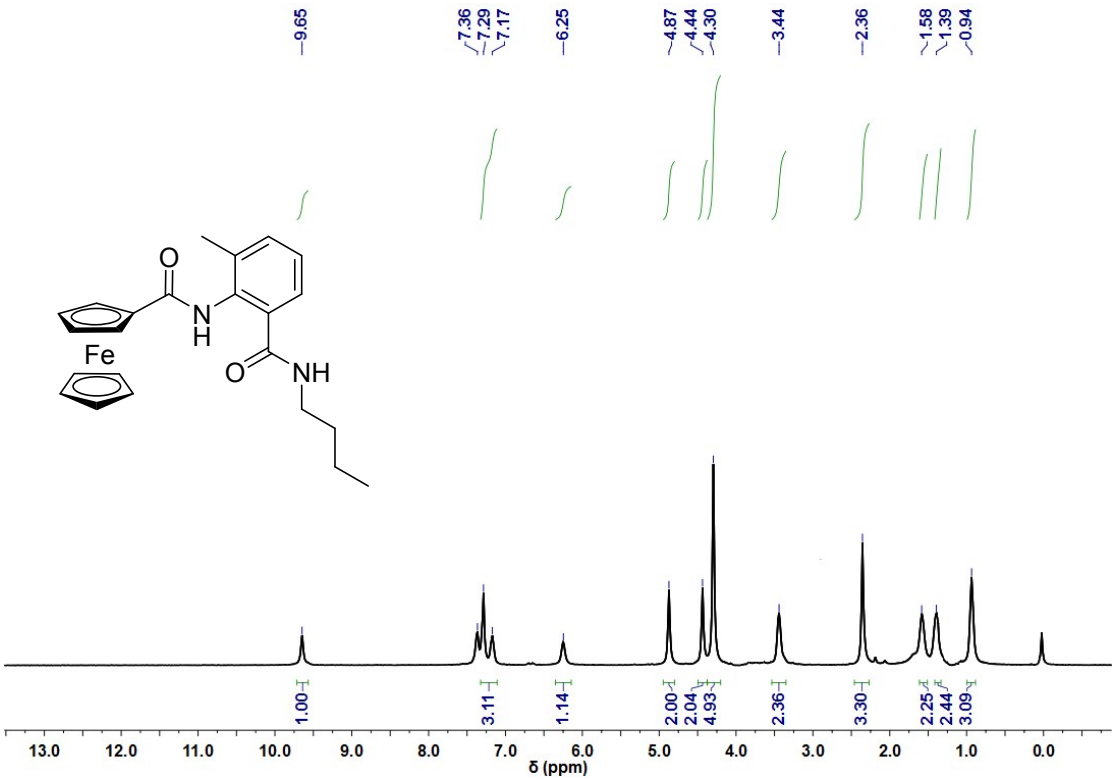
^{13}C-NMR spectrum of 5a



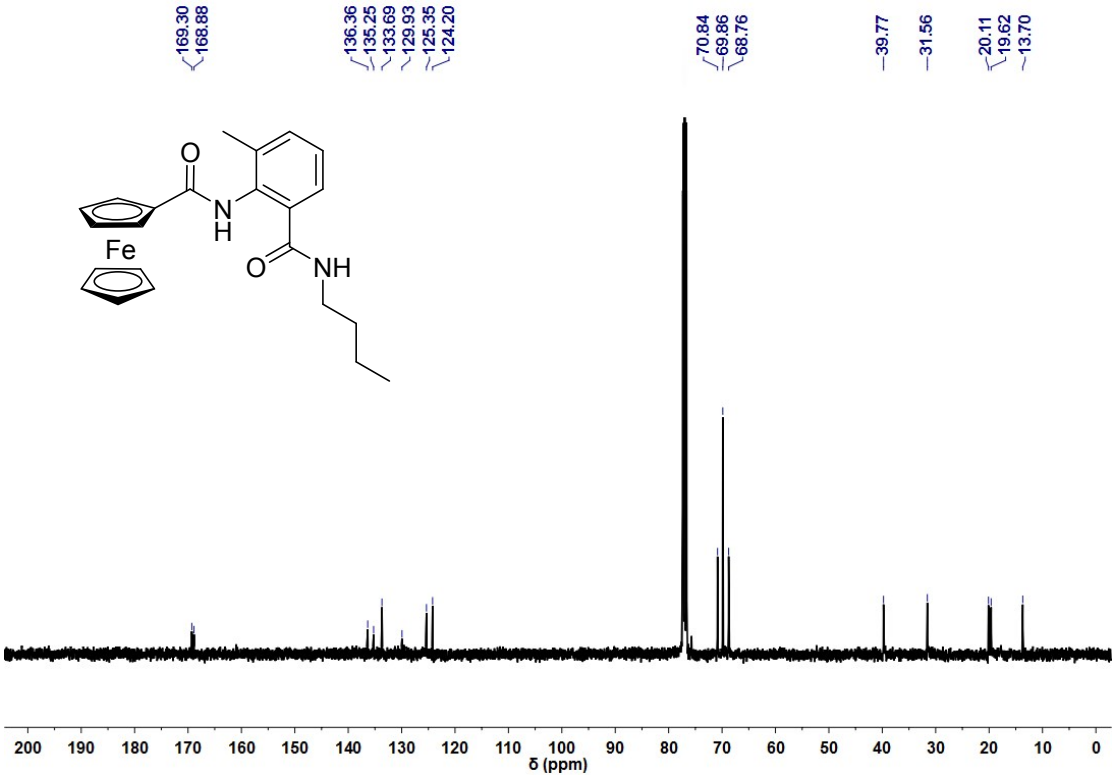
^{1}H-NMR spectrum of 5b



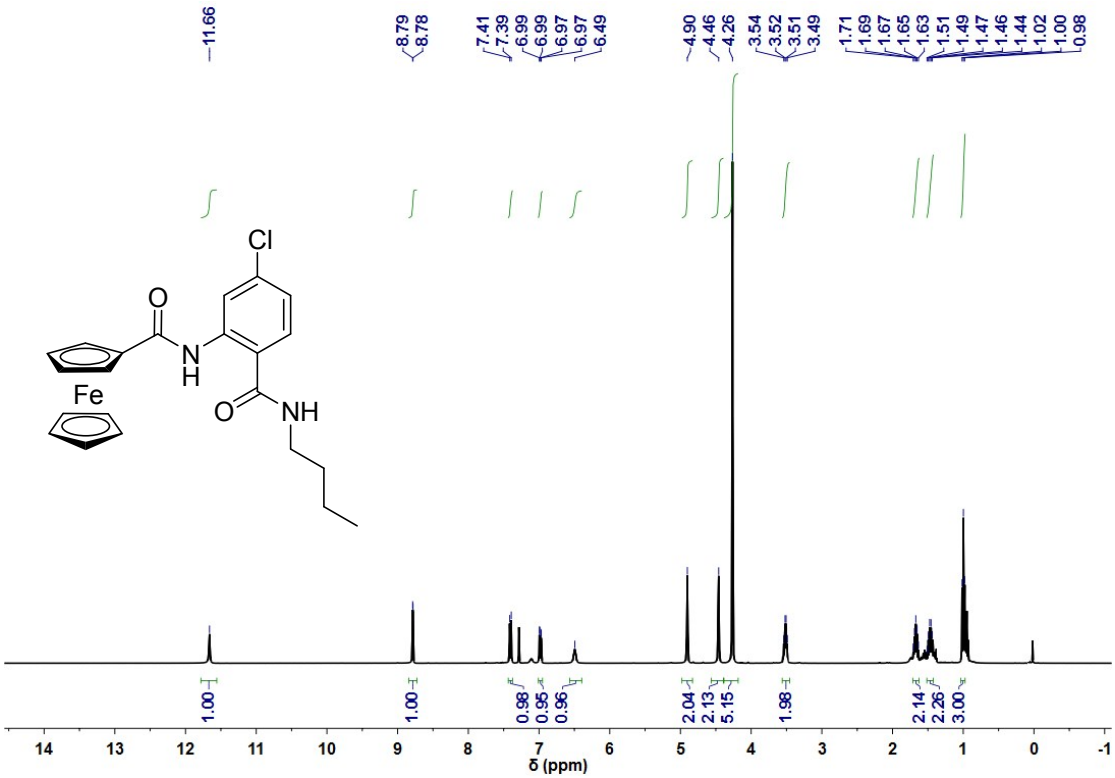
^{13}C-NMR spectrum of 5b



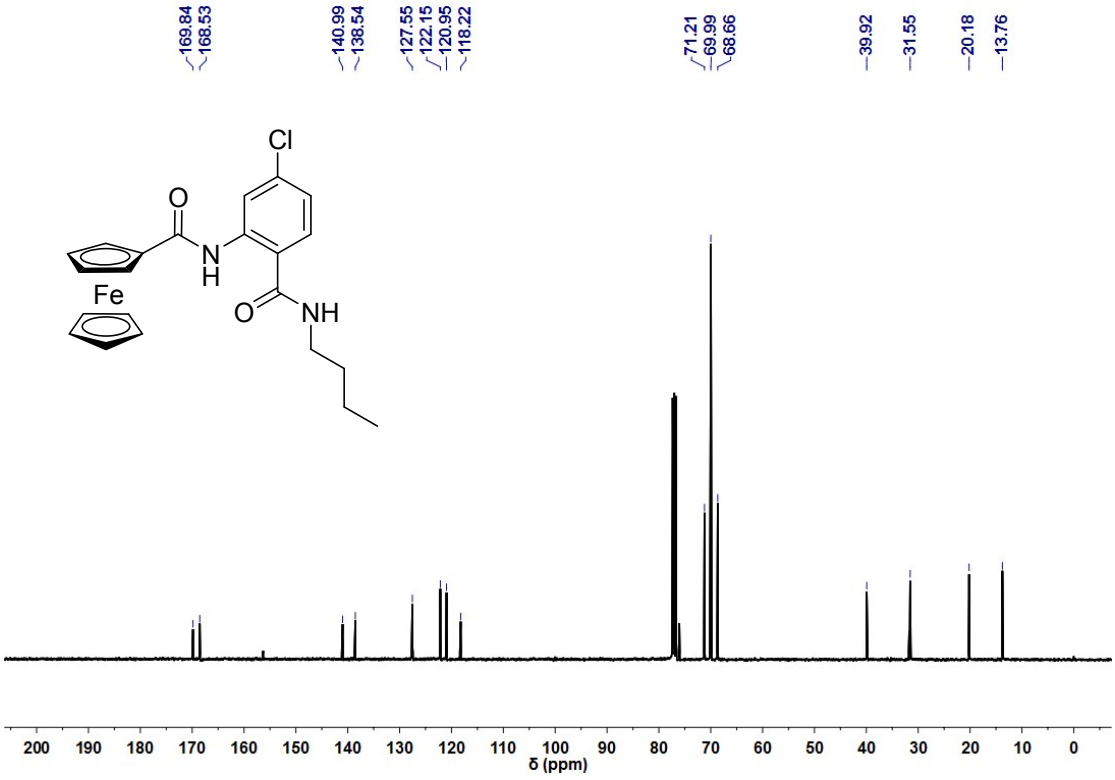
^{1}H-NMR spectrum of 5c



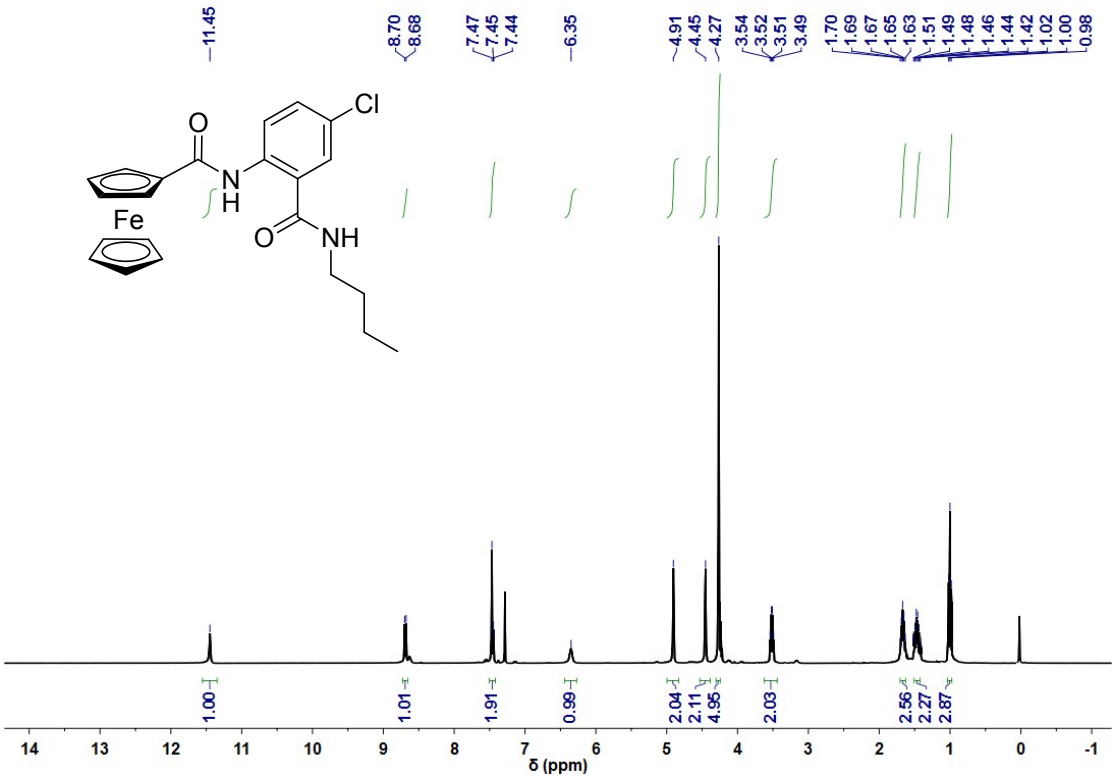
^{13}C-NMR spectrum of 5c



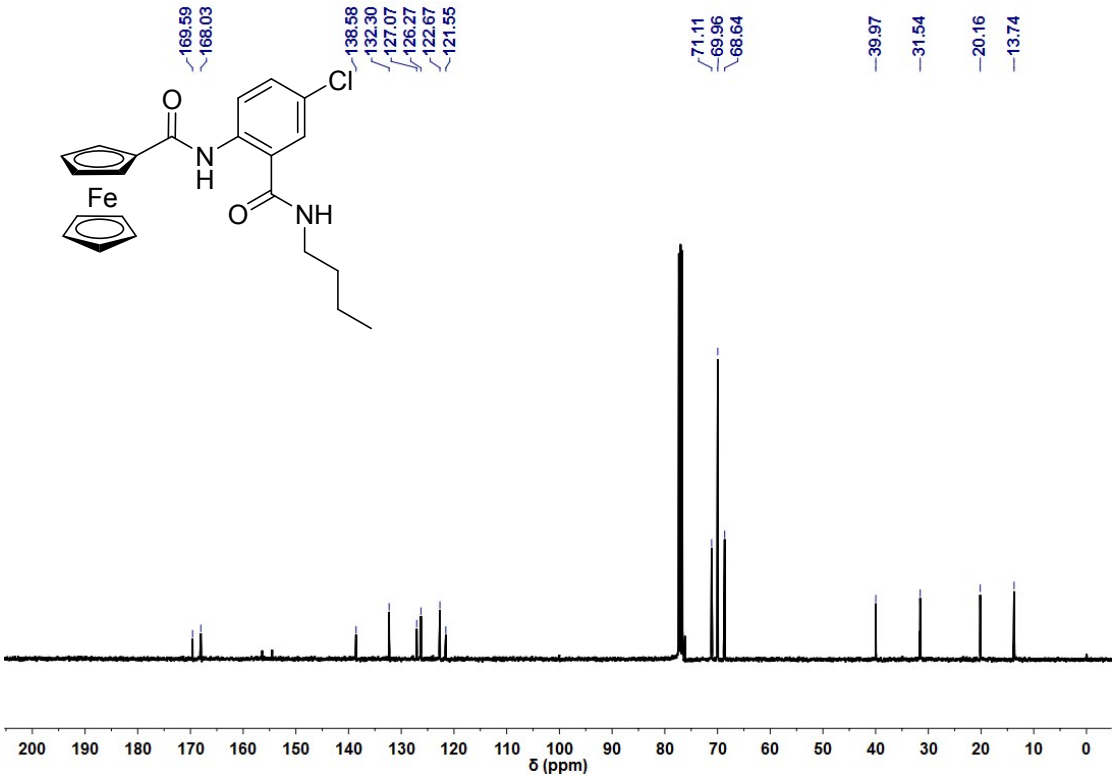
^{1}H-NMR spectrum of 5d



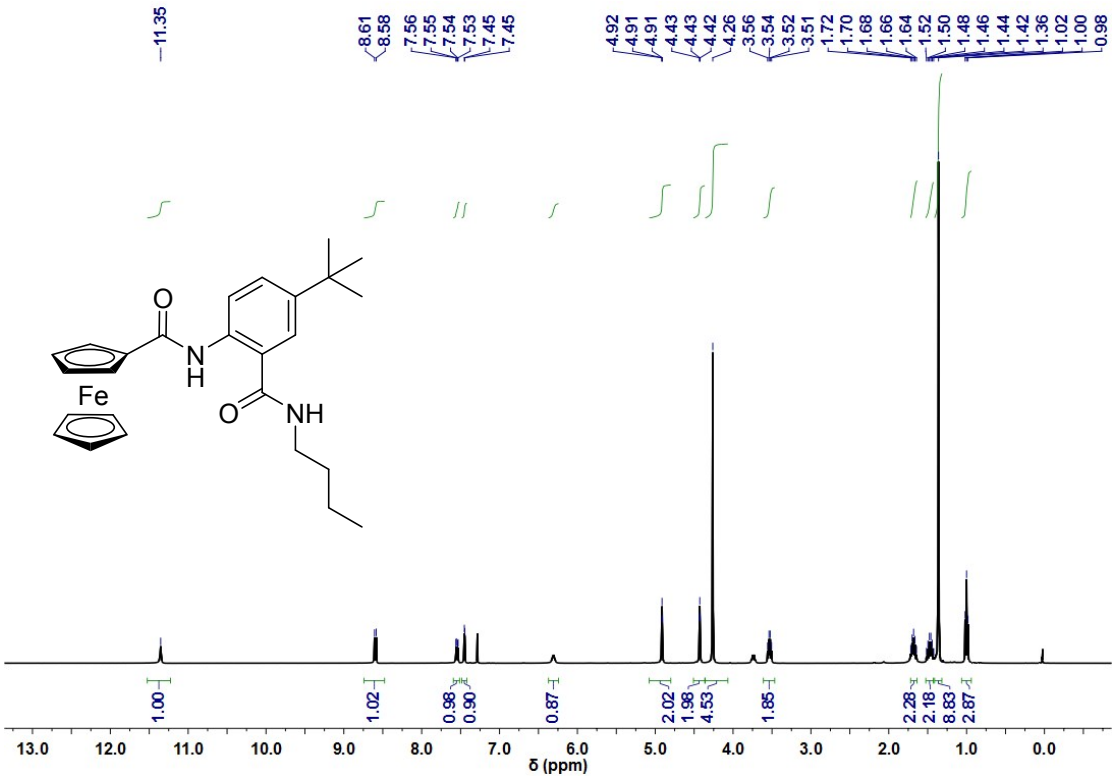
^{13}C-NMR spectrum of 5d



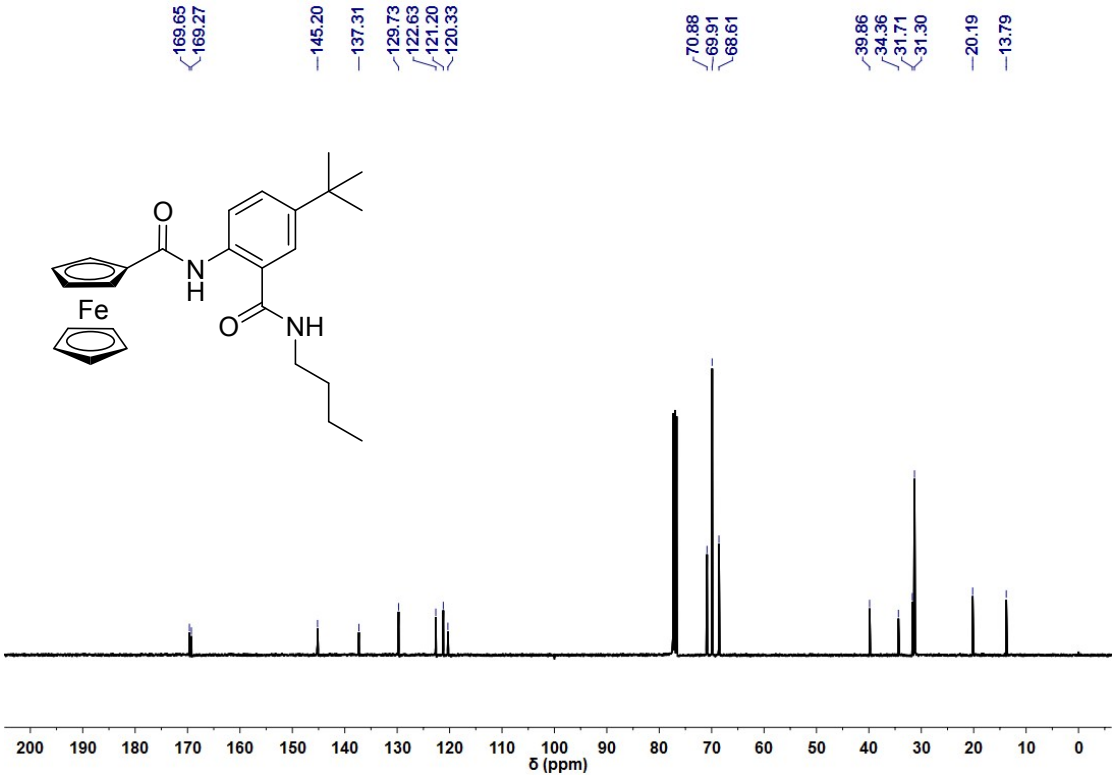
^{1}H-NMR spectrum of 5e



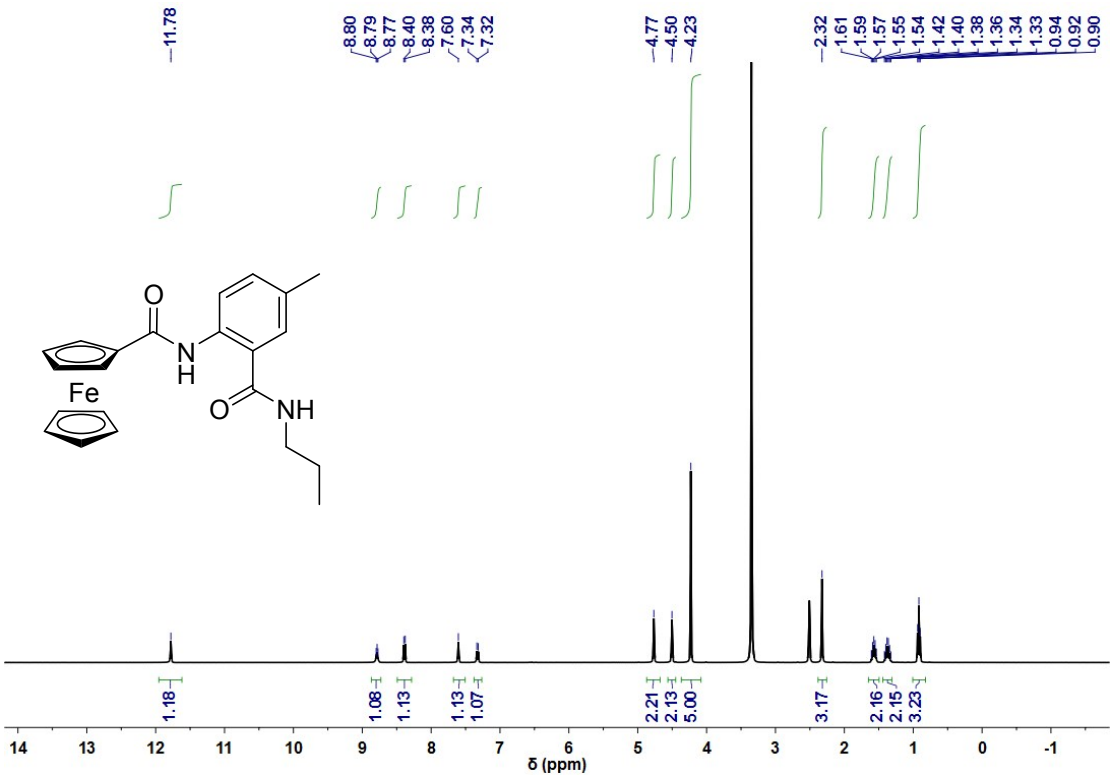
^{13}C-NMR spectrum of 5e



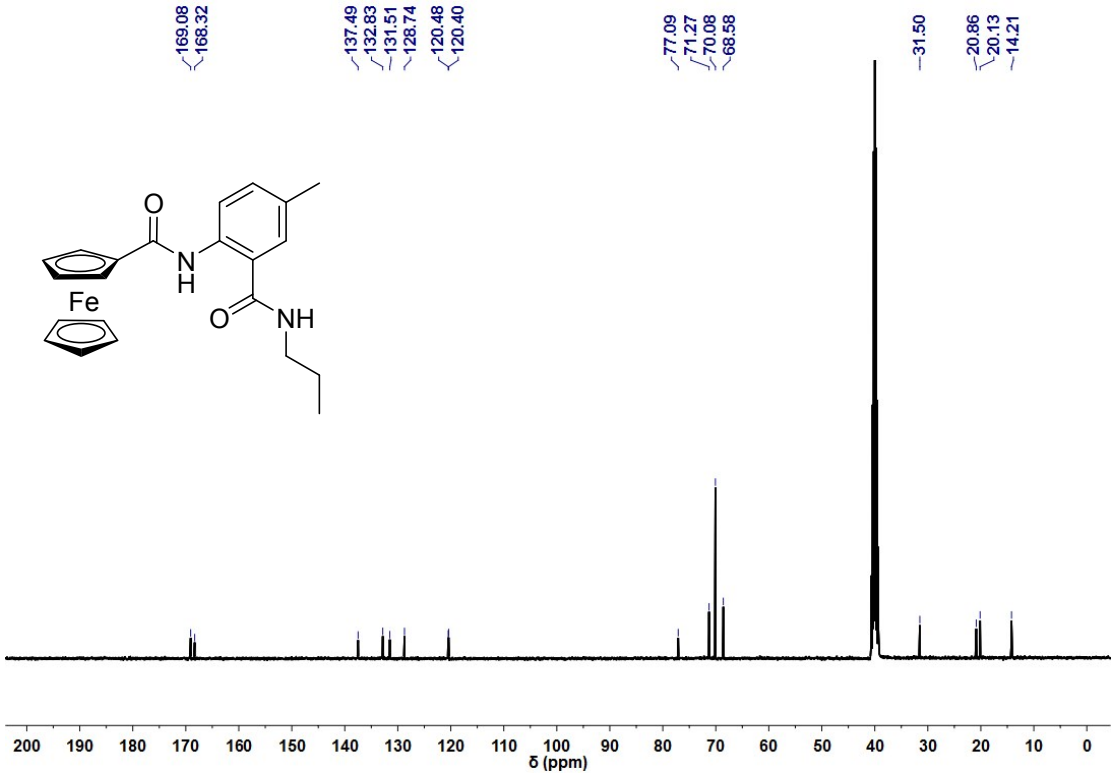
^{1}H-NMR spectrum of 5f



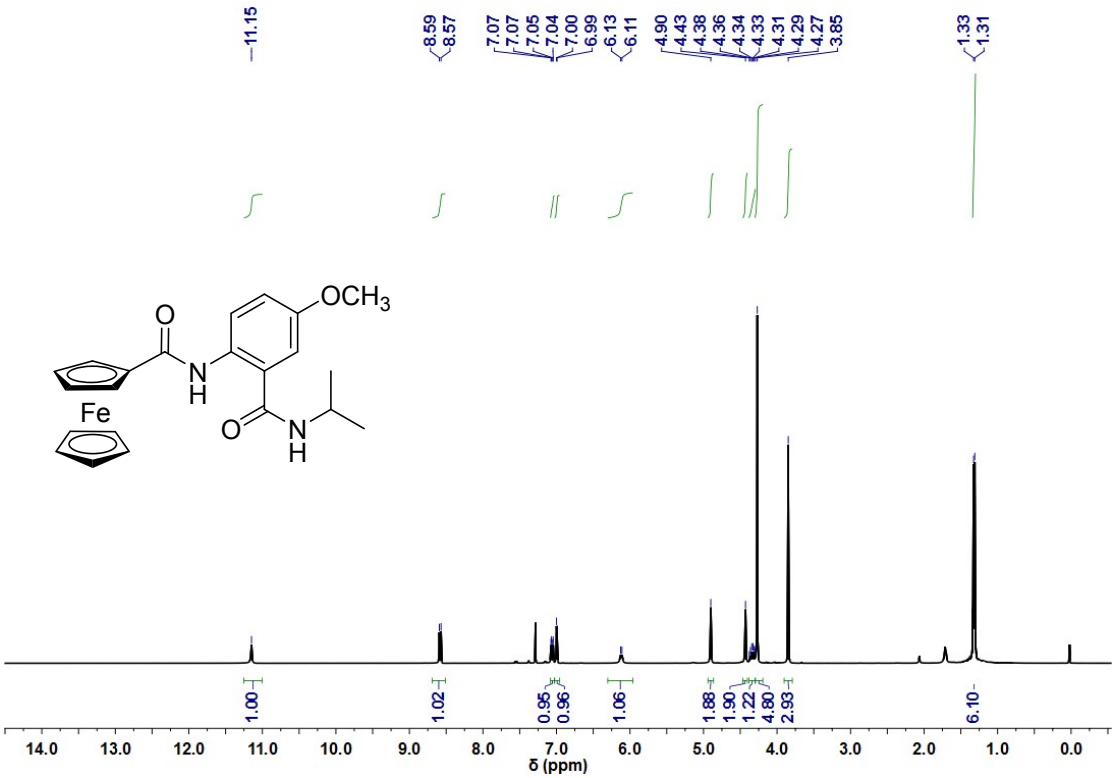
^{13}C-NMR spectrum of 5f



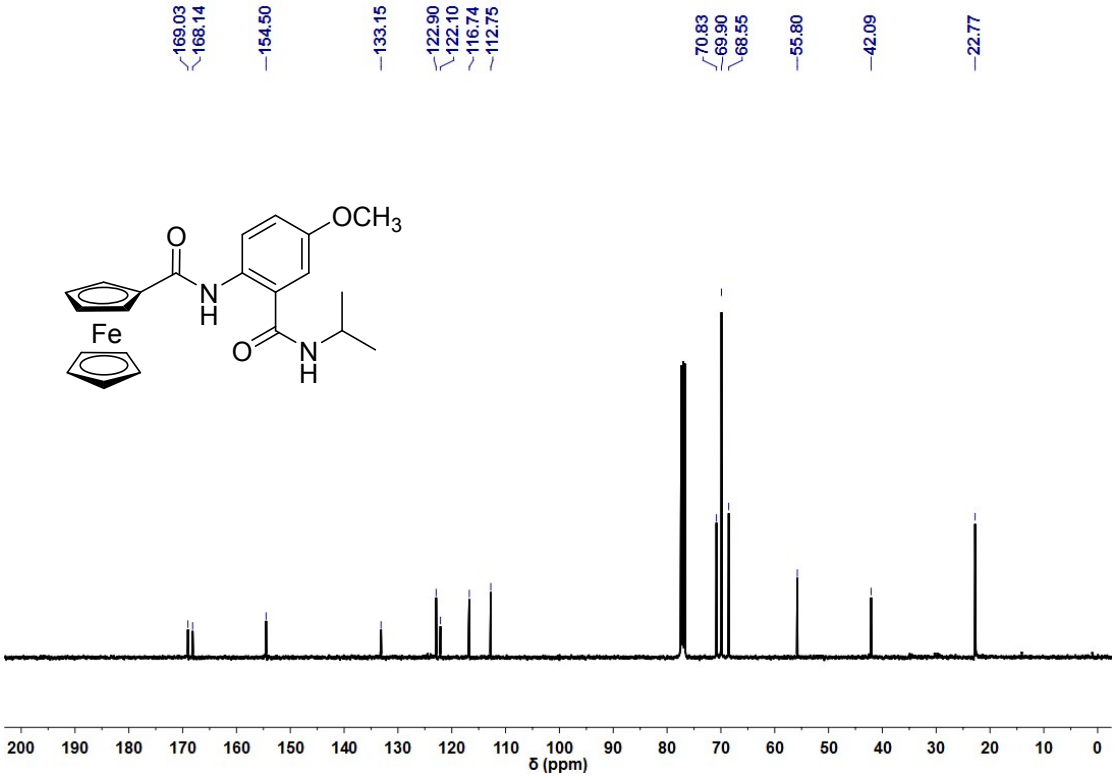
^{1}H-NMR spectrum of 5g



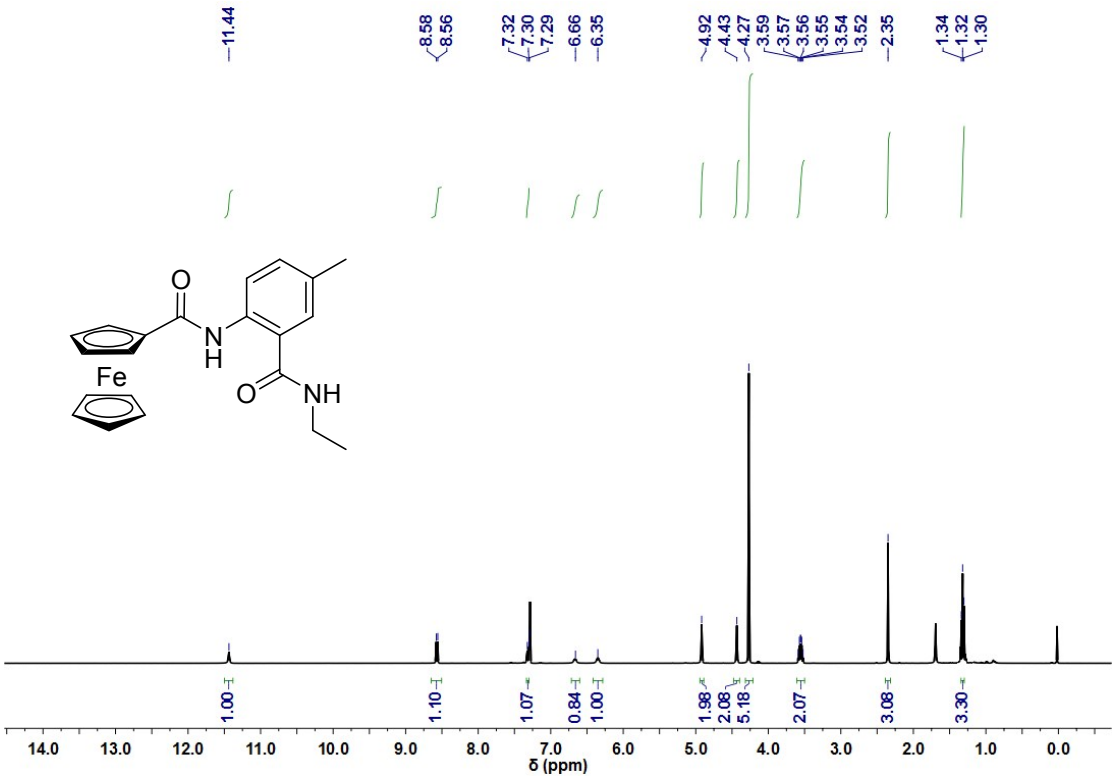
^{13}C-NMR spectrum of 5g



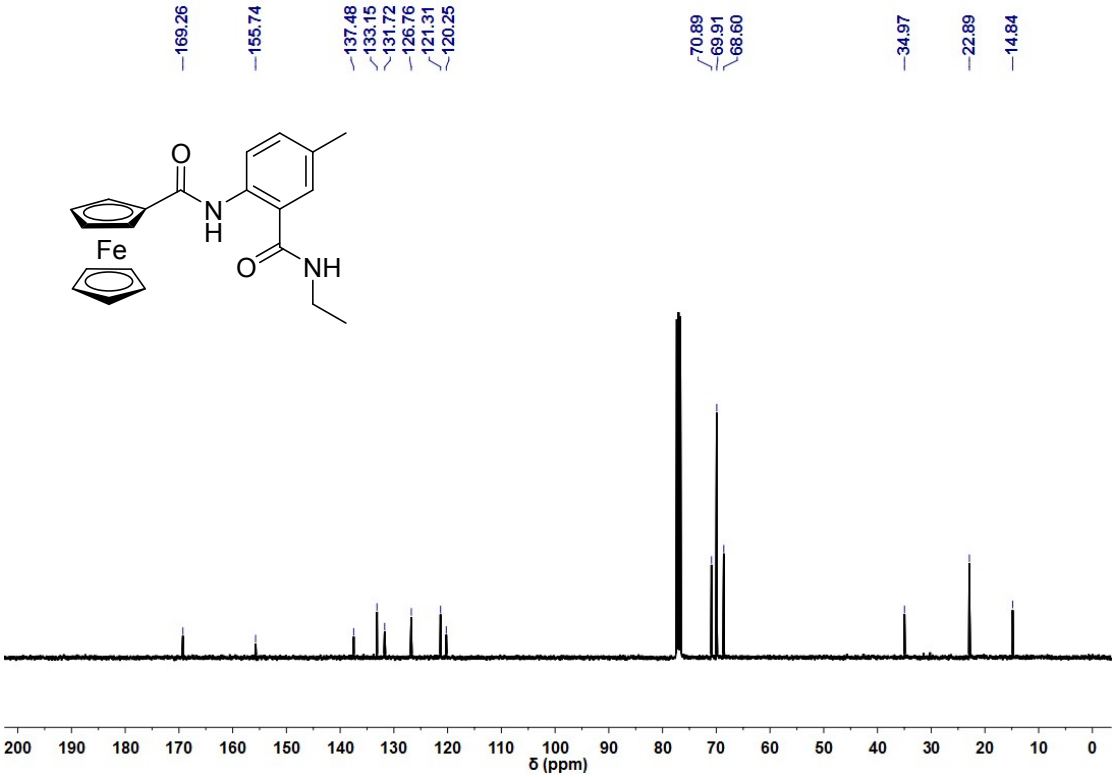
^{1}H-NMR spectrum of 5h



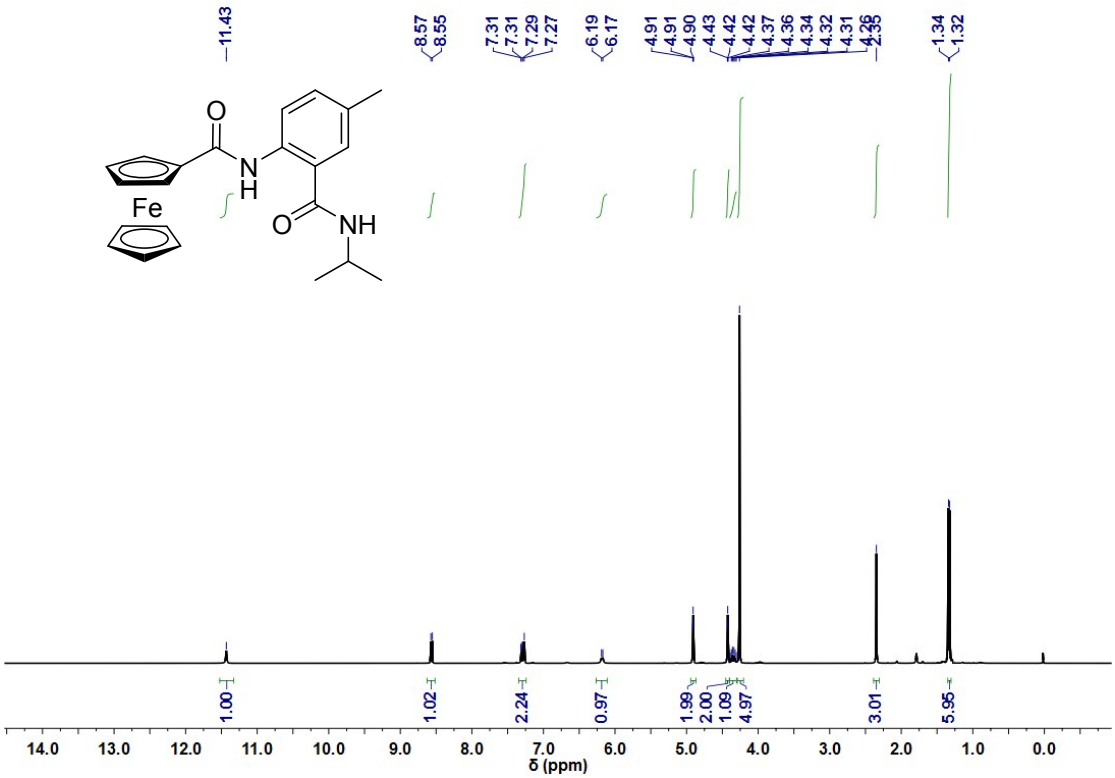
^{13}C-NMR spectrum of 5h



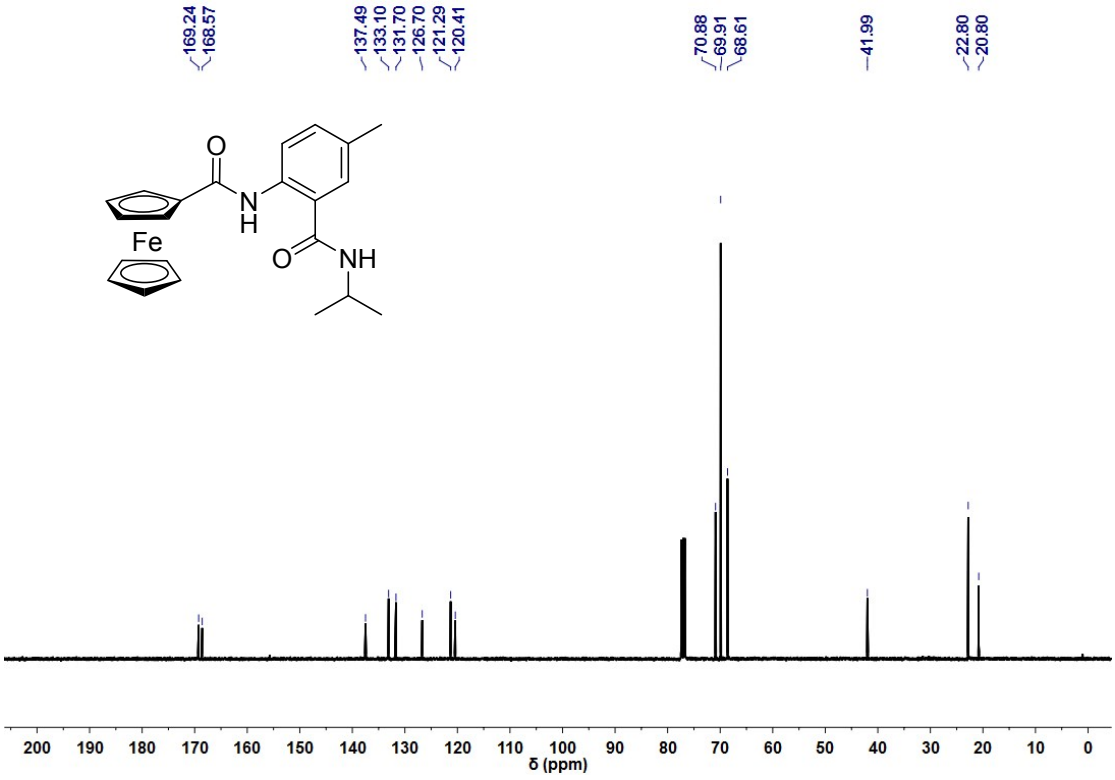
^{1}H-NMR spectrum of 5i



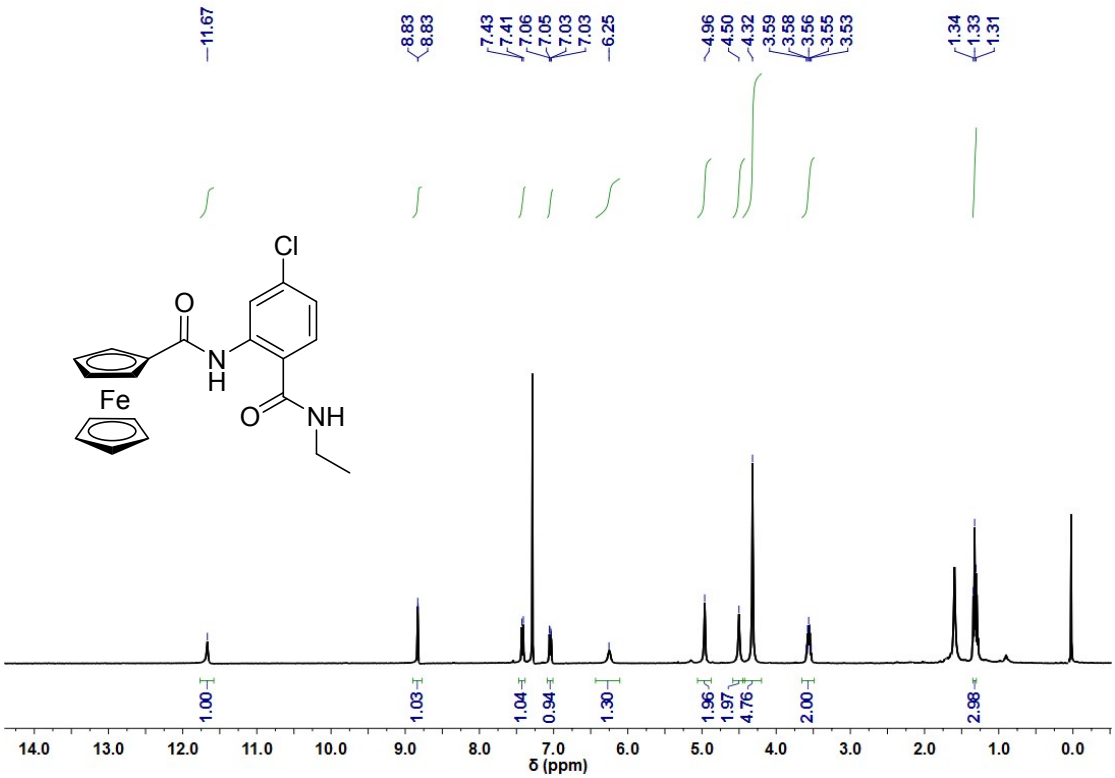
^{13}C-NMR spectrum of 5i



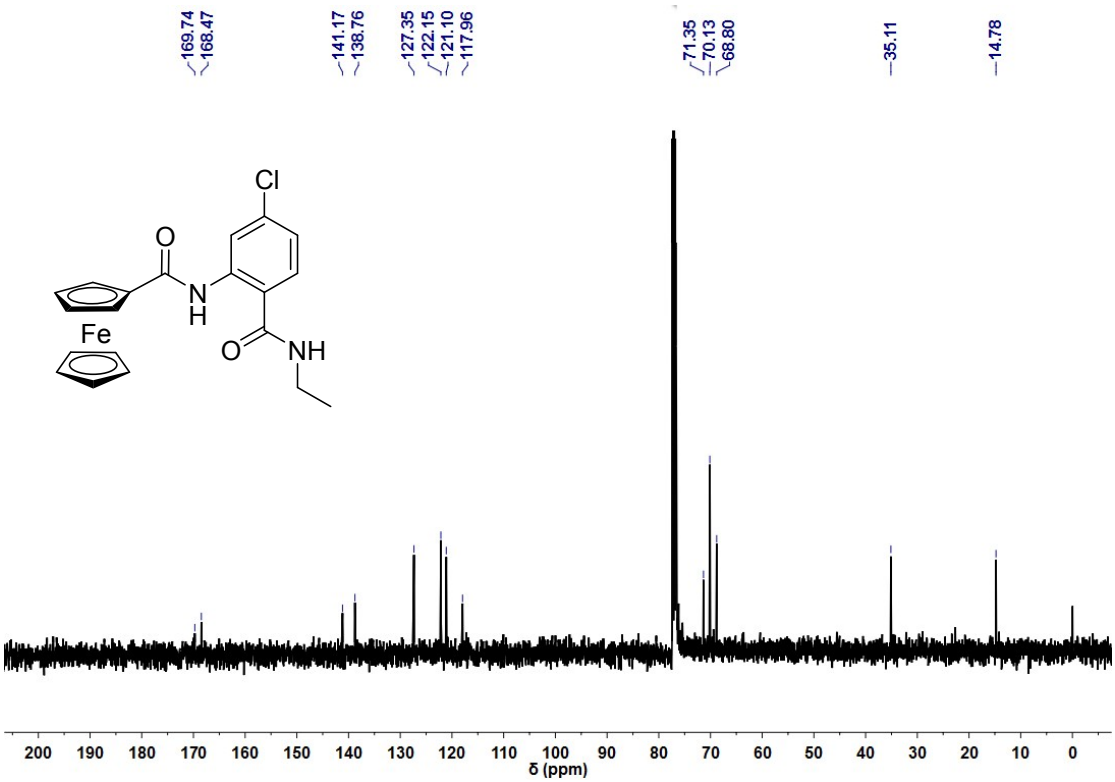
^{1}H-NMR spectrum of 5j



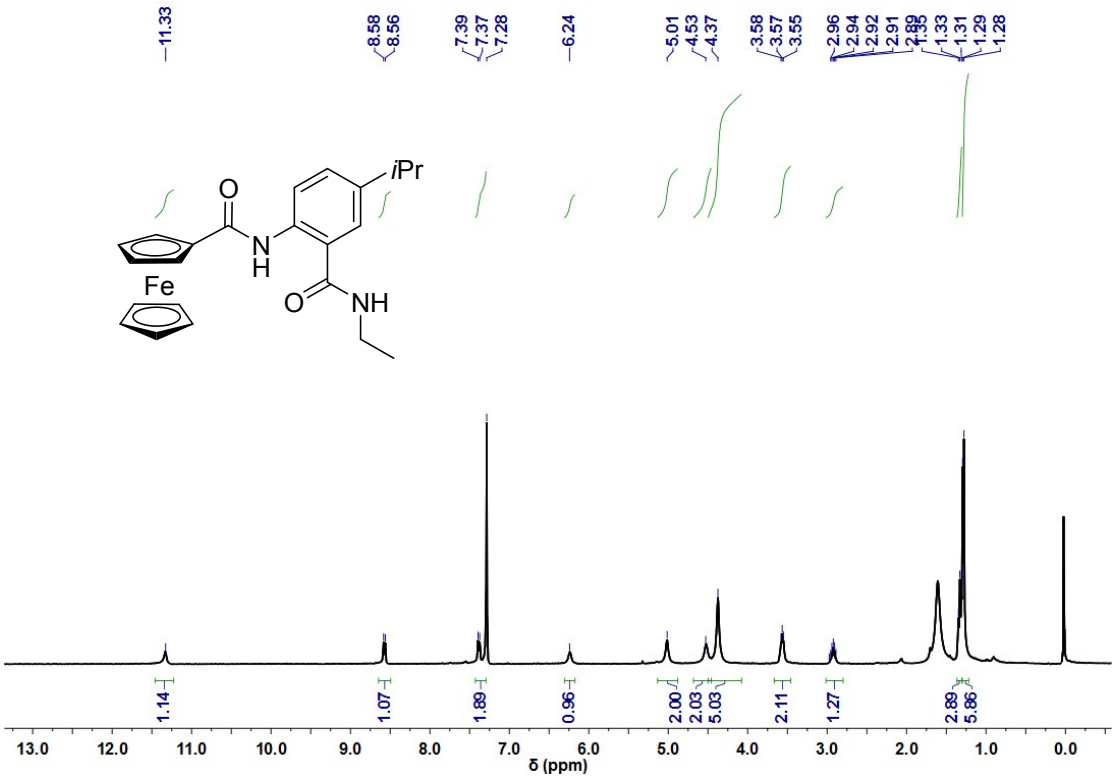
^{13}C-NMR spectrum of 5j



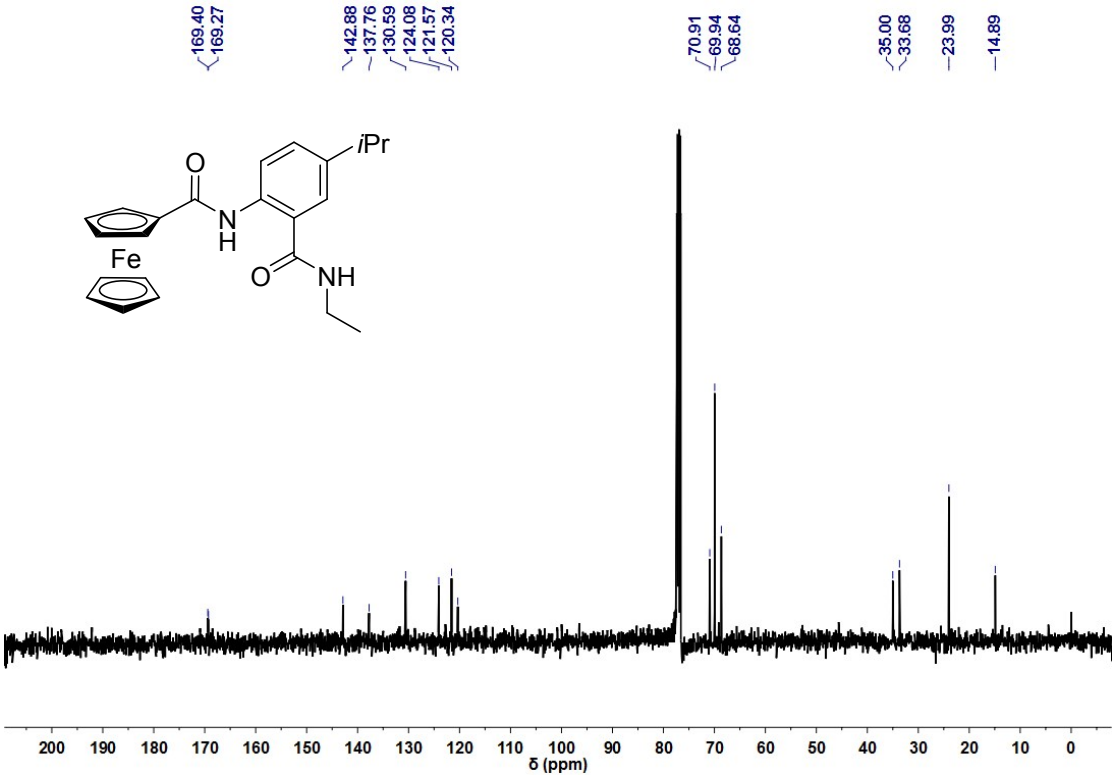
^{1}H-NMR spectrum of 5k



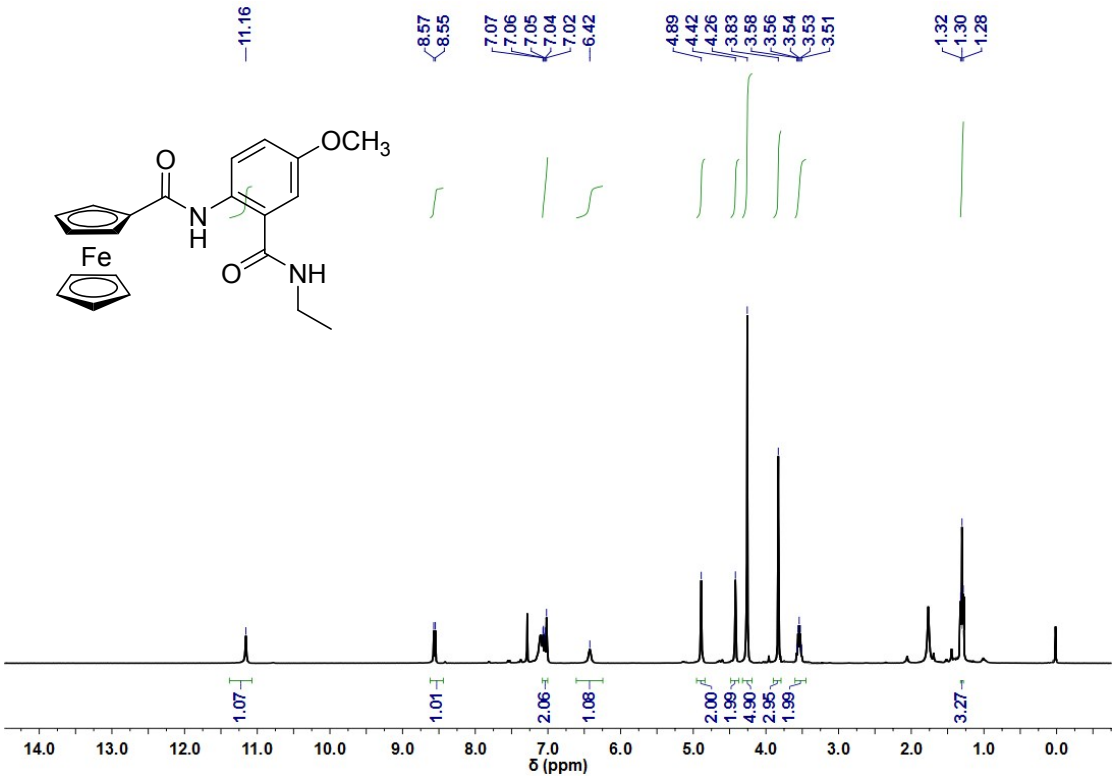
^{13}C-NMR spectrum of 5k



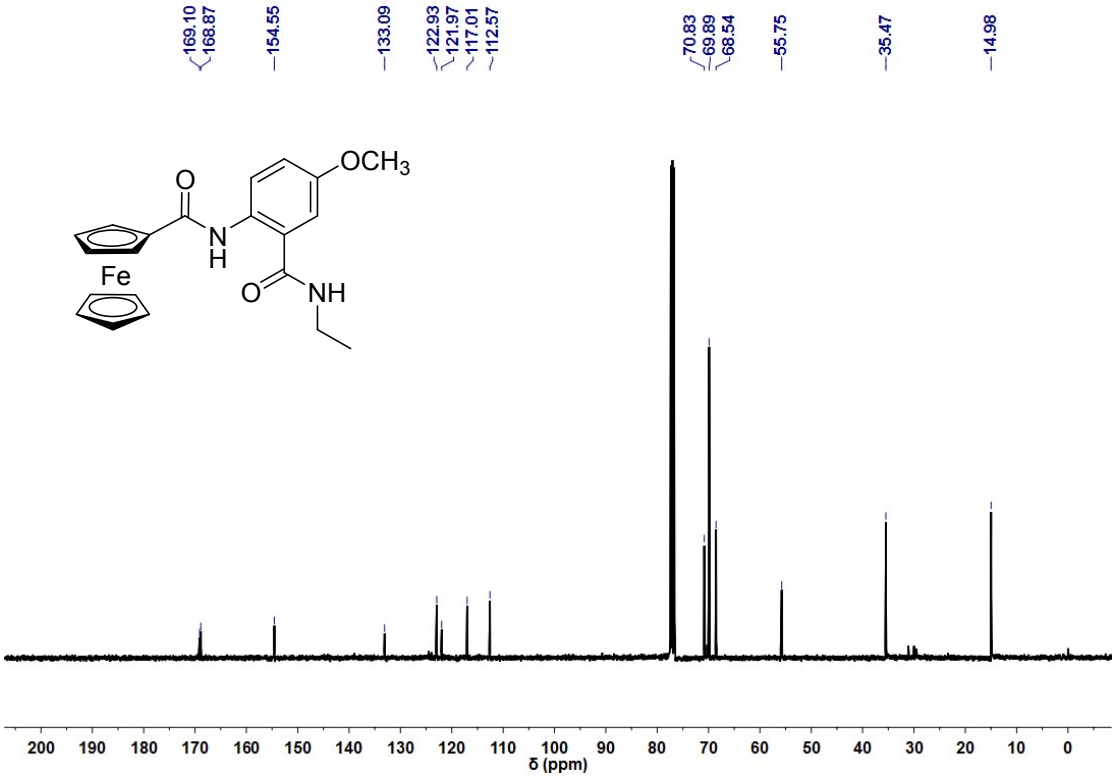
^{1}H-NMR spectrum of 5l



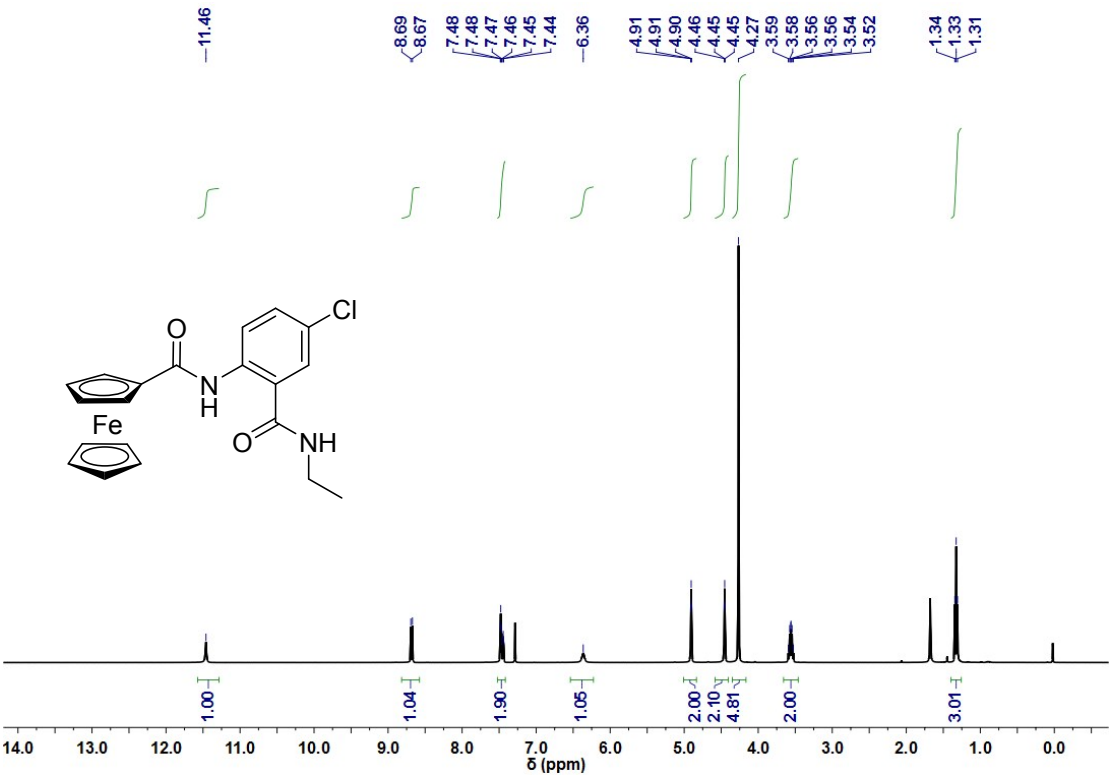
^{13}C-NMR spectrum of 5l



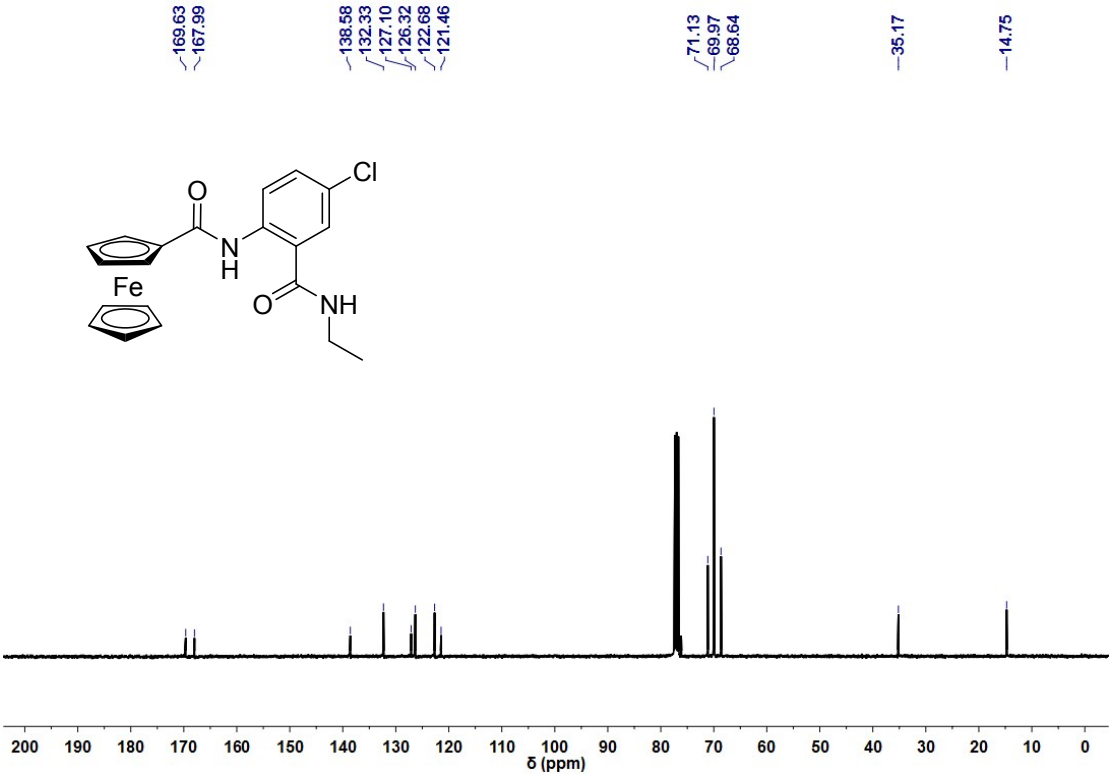
^{1}H-NMR spectrum of 5m



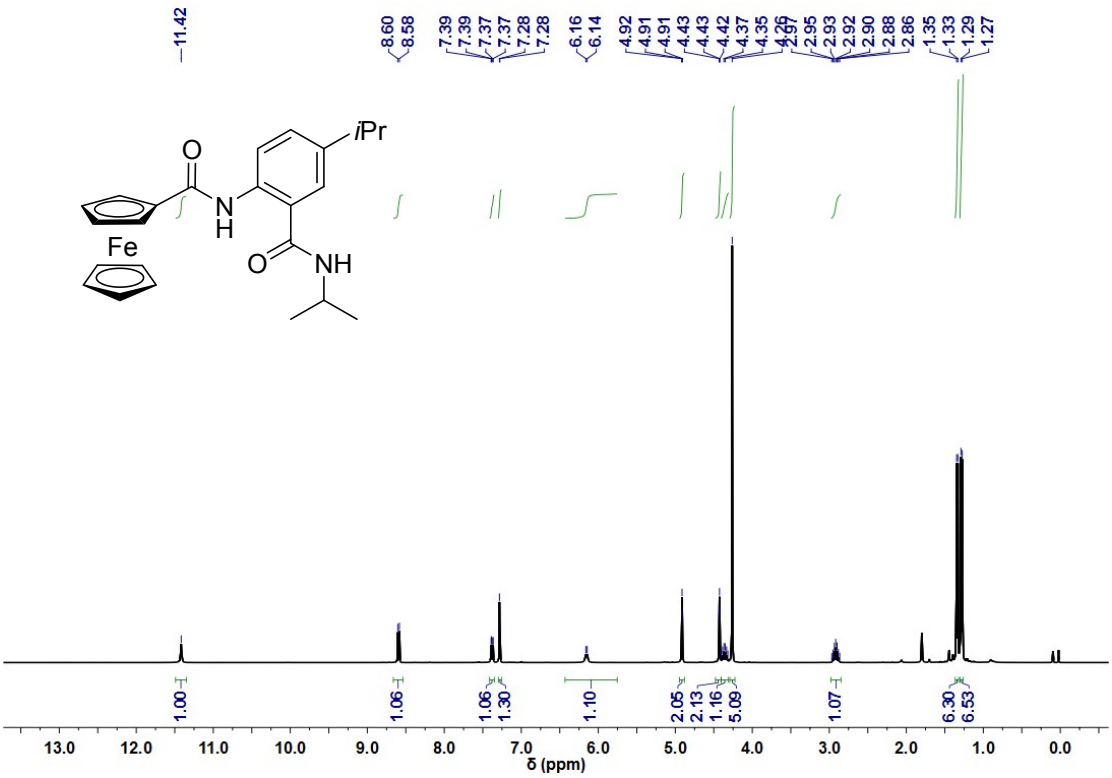
^{13}C-NMR spectrum of 5m



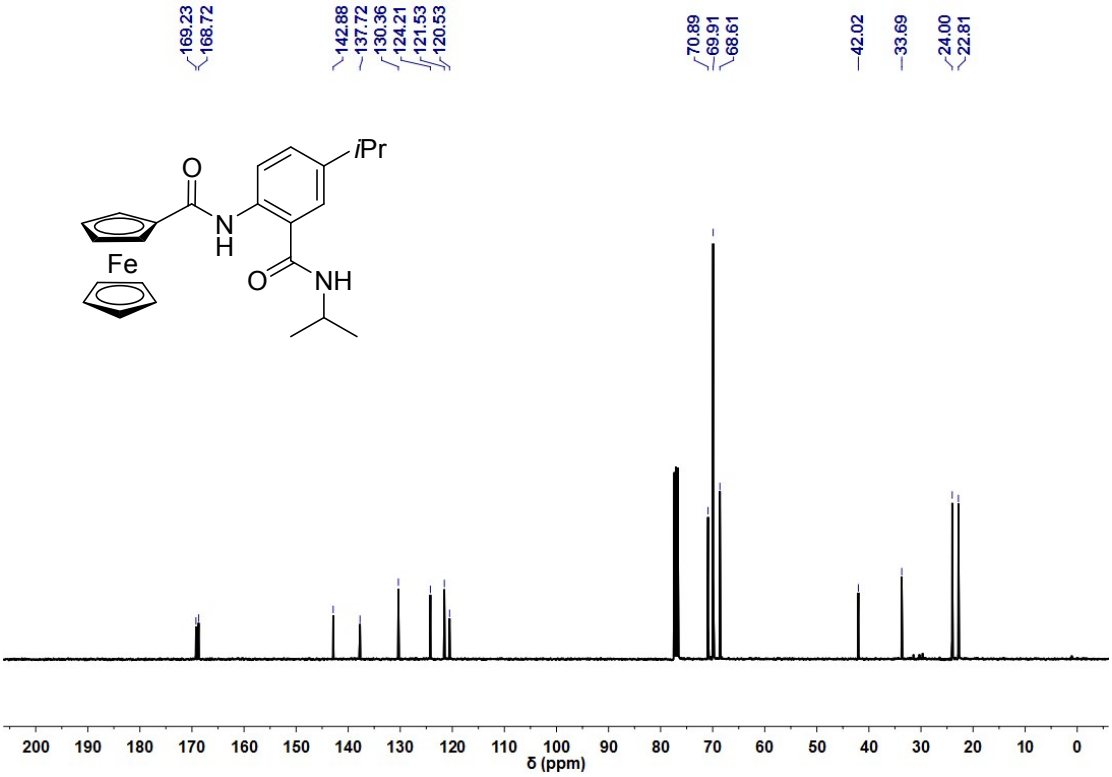
^{1}H-NMR spectrum of 5n



^{13}C-NMR spectrum of 5n



^{1}H-NMR spectrum of 5o



^{13}C-NMR spectrum of 5o