Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Ionic Liquid Catalysed Aerobic Oxidative Amidation and Thioamidation of Benzylic Amines under Neat Conditions

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EXPERIMENTAL SECTION

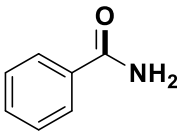
General. All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded at 600 and 150 MHz, respectively. The spectra were recorded in $CDCl_3$ and DMSO-d6 as solvent. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth, and coupling constants (J) are given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^{1}H NMR (7.26) and ^{13}C NMR (77.0) correspond to the deuterated solvent chloroform (water peak at 1.5 ppm) and ^{1}H NMR (2.50) and ^{13}C NMR (39.50) correspond to the deuterated solvent DMSO (water peak at 3.3 ppm), respectively. Mass spectra were obtained using the electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel with 100−200 mesh size using hexane/ethyl acetate as eluent unless otherwise indicated.

General procedure for 2a

A clean washed boiling tube equipped with a magnetic stir bar was charged with benzylamine **1a** (107.0 mg, 1.0 mmol), tetrabutylammonium hydroxide TBAOH ionic liquid (40% TBAOH+ 60% water) (100 µL, 0.15 mmol), the above mixture was stirred for 12h at 70°C temperature in open atmosphere. After completion of the reaction, the mixture was purified through column chromatography using silica gel (30% EtOAc/hexane) to obtain benzamide **2a** in 95 % yield (107.0 mg)

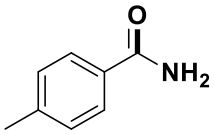
Charecterisation data:

benzamide (2a)[1]:



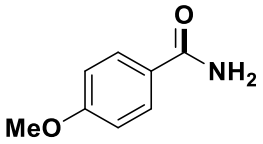
Yield (107 mg, 95% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.99 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.38 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.99, 134.28, 131.29, 128.27, 127.51.

4-methylbenzamide (2b)[1]



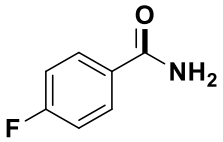
Yield (113.0 mg, 84% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.90 (s, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.25 (t, J = 9.1 Hz, 3H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.88, 141.12, 131.48, 128.77, 127.54, 20.98.

4-methoxybenzamide (2c)[1]



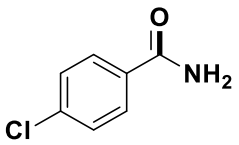
Yield (113.0 mg, 75% yield, white solid), eluent: 40% ethylacetate/hexane); ^{1}H NMR (600 MHz, DMSO-d6) δ 7.86 (d, J = 8.3 Hz, 3H), 7.21 (s, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.60, 161.65, 129.43, 126.52, 113.44, 55.34.

4-fluorobenzamide (2d)[1]



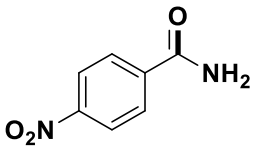
Yield (112.0 mg, 80% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.04 (s, 1H), 7.97 – 7.93 (m, 2H), 7.43 (s, 1H), 7.27 – 7.24 (m, 2H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.08, 164.89, 163.24, 130.81 (d, J = 2.1 Hz), 130.25 (d, J = 9.3 Hz), 115.29, 115.15.

4-chlorobenzamide (2e)[1]



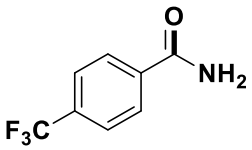
Yield (110.0 mg, 71% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.08 (s, 1H), 7.91 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.49 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.96, 136.17, 133.05, 129.46, 128.37.

4-nitrobenzamide (2f)[2]



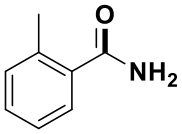
Yield (82.0 mg, 49% yield, yellow solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.28 (d, J = 7.3 Hz, 3H), 8.09 (d, J = 8.3 Hz, 2H), 7.73 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.24, 149.05, 139.99, 128.92, 123.44.

4-(trifluoromethyl)benzamide (2g)[1]



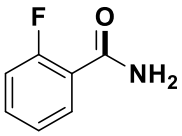
Yield (88.0 mg, 43% yield, white solid), eluent: 43% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.28 (s, 1H), 7.13 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.71 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.88, 138.15, 131.40, 131.19, 128.42, 125.33 (d, J = 3.4 Hz), 124.94, 123.14.

2-methylbenzamide (2h)[2]



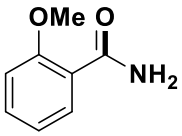
Yield (120.0 mg, 89% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.70 (s, 1H), 7.35 (d, J = 7.4 Hz, 2H), 7.30 (td, J = 7.5, 1.3 Hz, 1H), 7.21 (dd, J = 13.5, 7.2 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 171.17, 137.07, 135.16, 130.51, 129.24, 127.05, 125.46, 19.62.

2-fluorobenzamide (2i)[1]



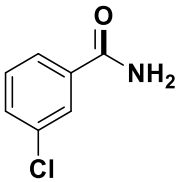
Yield (118.0 mg, 85% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 1H), 7.28 (s, 1H), 7.01 (t, J = 8.1 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 5.94 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.17, 157.77, 133.28, 132.41, 121.12, 120.76, 111.29.

2-methoxybenzamide (2j)[2]



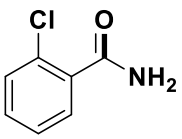
Yield (80.0 mg, 53% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.82 – 7.79 (m, 1H), 7.65 (s, 1H), 7.52 (s, 1H), 7.47 (dd, J = 11.4, 4.7 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.43, 157.29, 132.56, 130.79, 122.68, 120.46, 112.01, 55.84.

2-chlorobenzamide (2k)[1]



Yield (78.0 mg, 50% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.88 (s, 1H), 7.59 (s, 1H), 7.49 – 7.46 (m, 1H), 7.42 (ddd, J = 15.2, 7.5, 1.6 Hz, 2H), 7.37 (td, J = 7.4, 1.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 168.28, 137.14, 130.62, 129.65, 128.70, 127.07.

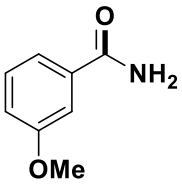
3-chlorobenzamide (2l)[2]



Yield (100.0 mg, 64% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.13 (s, 1H), 7.91 (t, J = 1.8 Hz, 1H), 7.85 –

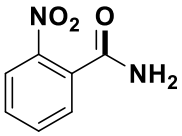
7.82 (m, 1H), 7.57 – 7.53 (m, 2H), 7.46 (t, J = 7.9 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.82, 136.35, 133.35, 131.25, 130.37, 127.48, 126.31.

3-methoxybenzamide (2m)[1]



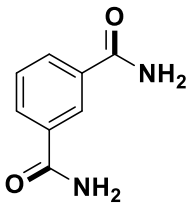
Yield (125.0 mg, 83% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.97 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.42 (s, 1H), 7.39 – 7.33 (m, 2H), 7.07 (dd, J = 8.0, 1.8 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.72, 159.16, 135.73, 129.38, 119.72, 117.11, 112.65, 55.25.

2-nitrobenzamide (2n)[3]



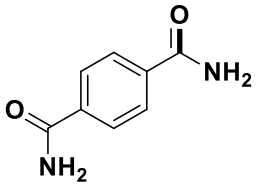
Yield (66.4 mg, 40% yield, yellow solid), eluent: 50% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.17 (d, J = 7.7 Hz, 1H), 7.99 (dd, J = 8.1, 0.8 Hz, 1H), 7.76 (td, J = 7.5, 1.1 Hz, 1H), 7.70 (s, 1H), 7.67 (td, J = 7.9, 1.4 Hz, 1H), 7.62 (dd, J = 7.6, 1.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.41, 147.30, 133.51, 132.65, 130.78, 128.95, 124.08.

Isophthalamide (2o)[4]



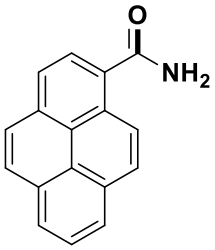
Yield (140.0 mg, 85% yield, white solid); ^{1}H NMR (600 MHz, DMSO-d6) δ 8.36 (t, J = 1.5 Hz, 1H), 8.05 (s, 2H), 7.99 (d, J = 1.7 Hz, 1H), 7.98 (d, J = 1.7 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.46 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.63, 134.47, 130.11, 128.32, 126.82.

Terephthalamide (2p)[4]



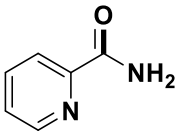
Yield (155.8 mg, 95% yield, white solid); ^{1}H NMR (600 MHz, DMSO-d6) δ 8.08 (s, 2H), 7.93 (s, 4H), 7.50 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.31, 136.58, 127.38, 126.68.

pyrene-1-carboxamide (2q)[5]



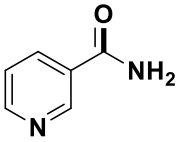
Yield (120.0 mg, 49% yield, yellow solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.62 (d, J = 9.2 Hz, 1H), 8.35 – 8.30 (m, 3H), 8.25 (dd, J = 12.3, 9.1 Hz, 3H), 8.22 – 8.17 (m, 2H), 8.10 (t, J = 7.6 Hz, 1H), 7.80 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 171.15, 131.78 (d, J = 18.7 Hz), 130.81, 130.28, 128.38, 128.14, 127.86, 127.31, 126.67, 125.89, 125.69, 125.37, 124.92, 124.50, 123.95, 123.76.

Picolinamide (2r)[1]



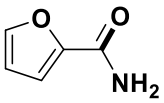
Yield (88.0 mg, 72% yield, white solid), eluent: 30% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 8.61 (d, J = 4.4 Hz, 1H), 8.14 (s, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.97 (t, J = 7.9 Hz, 1H), 7.66 (s, 1H), 7.57 (dd, J = 6.9, 5.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.24, 150.30, 148.56, 137.76, 126.58, 122.02.

Nicotinamide (2s)[2]



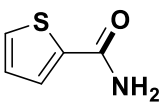
Yield (91.0 mg, 74% yield, white solid, eluent: ethylacetate; ^{1}H NMR (600 MHz, DMSO-d6) δ 9.04 (s, 1H), 8.68 (d, J = 3.7 Hz, 1H), 8.21 (d, J = 7.7 Hz, 2H), 7.64 (s, 1H), 7.47 (dd, J = 7.4, 5.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.82, 152.04, 148.79, 135.37, 129.80, 123.60.

furan-2-carboxamide (2t)[1]



Yield (89.0 mg, 80% yield, white solid), eluent: 50% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.80 (s, 1H), 7.77 (d, J = 0.9 Hz, 1H), 7.39 (s, 1H), 7.10 (d, J = 3.4 Hz, 1H), 6.58 (dd, J = 3.4, 1.7 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 159.76, 148.09, 145.21, 113.95, 112.00.

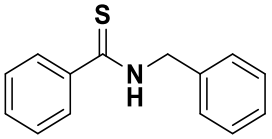
thiophene-2-carboxamide (2u)[2]



Yield (90.0 mg, 71% yield, white solid), eluent: 40% ethylacetate/hexane; ^{1}H NMR (600 MHz, DMSO-d6) δ 7.97 (s, 1H), 7.74 (d, J = 3.4 Hz, 1H), 7.72 (d, J

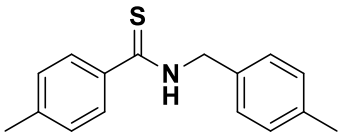
= 4.9 Hz, 1H), 7.39 (s, 1H), 7.18 – 7.07 (m, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 162.92, 140.31, 130.99, 128.69, 127.90.

N-benzylbenzothioamide (3a)[6]



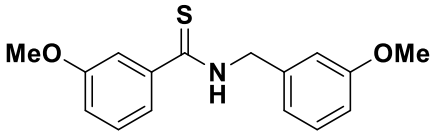
Yield (80.0 mg, 70 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 3H), 7.47 – 7.43 (m, 1H), 7.41 – 7.34 (m, 7H), 5.00 (d, J = 5.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.14, 141.60, 136.15, 131.14, 129.01, 128.50, 128.35, 128.22, 126.66, 51.06.

4-methyl-N-(4-methylbenzyl)benzothioamide (3b)[6]



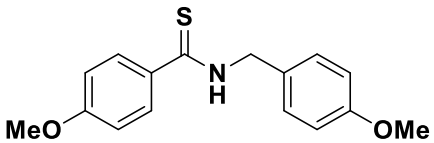
Yield (100.0 mg, 79 % yield, yellow solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 7.17 (d, J = 7.0 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 4.90 (d, J = 4.5 Hz, 2H), 2.35 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.43, 141.47, 137.69, 133.12, 129.43, 128.89, 128.13, 126.58, 50.49, 21.16, 21.00.

3-methoxy-N-(3-methoxybenzyl)benzothioamide (3c)[6]



Yield (100.0 mg, 70 % yield, yellow solid), eluent: 15% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$ δ 7.90 (s, 1H), 7.35 (s, 1H), 7.31 – 7.27 (m, 1H), 7.24 (t, J = 7.3 Hz, 2H), 7.00 – 6.94 (m, 2H), 6.91 (s, 1H), 6.87 (dd, J = 8.1, 2.1 Hz, 1H), 4.93 (d, J = 5.1 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.72, 159.86, 159.37, 142.84, 137.55, 129.92, 129.36, 120.33, 118.09, 116.96, 113.84, 113.39, 112.71, 55.32, 55.15, 50.74.

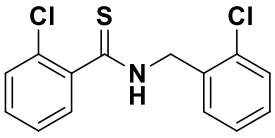
4-methoxy-N-(4-methoxybenzyl)benzothioamide (3d)[6]



Yield (120.0 mg, 83 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 4.86 (d, J = 5.4 Hz, 2H), 3.76 (s, 3H), 3.76

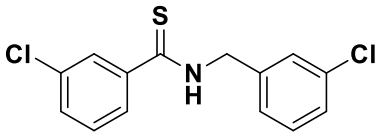
(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.32, 161.91, 159.14, 133.53, 129.49, 128.42, 128.29, 114.04, 113.32, 55.24, 55.10, 50.11.

2-chloro-N-(2-chlorobenzyl)benzothioamide (3e)[6]



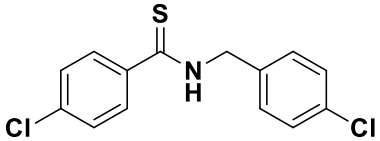
Yield (70.0 mg, 58 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (dd, J = 8.7, 4.8 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.34 (dd, J = 10.2, 3.4 Hz, 1H), 7.31 – 7.27 (m, 4H), 5.11 (d, J = 5.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.42, 141.74, 134.11, 133.23, 131.28, 130.43, 130.05, 129.95, 129.73, 129.72, 128.51, 127.20, 126.99, 48.16.

3-chloro-N-(3-chlorobenzyl)benzothioamide (3f)[7]



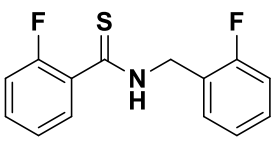
Yield (85.0 mg, 57 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.34 (s, 1H), 7.30 (d, J = 4.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.25 (dd, J = 9.1, 3.9 Hz, 1H), 4.93 (d, J = 5.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.65, 142.77, 137.83, 134.68, 134.47, 131.06, 130.21, 129.70, 128.31, 128.24, 126.96, 126.33, 124.67, 50.02.

4-chloro-N-(4-chlorobenzyl)benzothioamide (3g)[7]



Yield (90.5 mg, 61 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.71 – 7.62 (m, 2H), 7.40 – 7.27 (m, 6H), 4.94 (t, J = 4.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.79, 139.56, 137.46, 134.48, 134.02, 129.59, 129.08, 128.60, 128.01, 49.99.

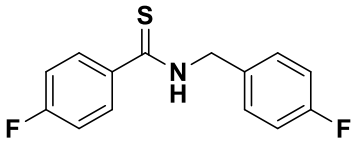
2-fluoro-N-(2-fluorobenzyl)benzothioamide (3h)[6]



Yield (68.3 mg, 52 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.14 (t, J = 8.1 Hz, 1H), 7.47 (dd, J = 8.0, 6.5 Hz, 1H), 7.40 (td, J = 6.5, 4.1 Hz, 1H), 7.33 (td, J =

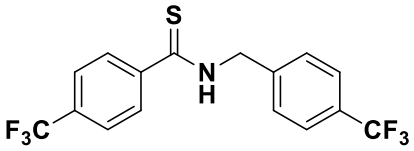
7.9, 1.8 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 9.2 Hz, 1H), 7.06 (dd, J = 11.9, 8.3 Hz, 1H), 5.11 (d, J = 5.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.60, 161.96, 160.32, 158.52, 156.87, 133.54, 132.46 (d, J = 8.9 Hz), 130.77 (d, J = 3.9 Hz), 130.00 (d, J = 8.4 Hz), 127.80, 124.58, 124.43 (d, J = 3.1 Hz), 122.88, 115.97, 115.75 (d, J = 18.9 Hz), 115.55, 44.84.

4-fluoro-N-(4-fluorobenzyl)benzothioamide (3i)[7]



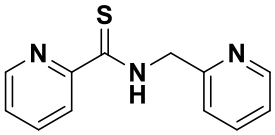
Yield (80.0 mg, 61 % yield, yellow solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.73 (dd, J = 8.1, 5.4 Hz, 2H), 7.35 (dd, J = 7.5, 5.8 Hz, 2H), 7.03 (dt, J = 21.8, 8.4 Hz, 4H), 4.93 (d, J = 5.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.65, 165.31, 163.63, 163.26, 161.62, 137.50, 131.85, 130.04 (d, J = 7.8 Hz), 128.88 (d, J = 8.8 Hz), 115.87, 115.73, 115.43, 115.29, 50.04.

4-(trifluoromethyl)-N-(4-(trifluoromethyl)benzyl)benzothioamide (3j)[7]



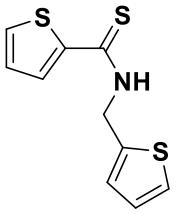
Yield (120.7 mg, 66 % yield, yellow solid), 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.80 (d, J = 5.8 Hz, 2H), 7.62 (dd, J = 15.9, 7.6 Hz, 4H), 7.49 (t, J = 8.6 Hz, 2H), 5.07 (d, J = 4.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.22, 144.37, 139.88, 128.41, 127.07, 125.90, 125.54, 49.99.

N-(pyridin-2-ylmethyl)pyridine-2-carbothioamide (3k)[6]



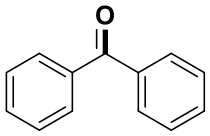
Yield (40.0 mg, 35 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.72 (d, J = 7.9 Hz, 1H), 8.66 (d, J = 4.7 Hz, 1H), 8.58 (d, J = 4.6 Hz, 1H), 7.84 (t, J = 7.4 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 5.1 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.29 – 7.20 (m, 1H), 5.15 (d, J = 4.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.01, 155.06, 151.44, 149.48, 147.38, 137.21, 136.94, 126.09, 124.87, 122.73, 122.34, 50.56.

N-(thiophen-2-ylmethyl)thiophene-2-carbothioamide (3l)[8]



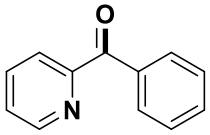
Yield (90.0 mg, 75 % yield, yellow solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.48 (d, J = 4.2 Hz, 1H), 7.41 (d, J = 3.7 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.11 (s, 1H), 7.06 – 6.97 (m, 2H), 5.14 (d, J = 4.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.14, 146.15, 138.09, 132.43, 127.79, 127.42, 127.00, 126.01, 124.65, 44.69.

benzophenone (5a)[9]



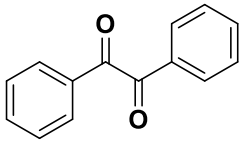
Yield (147.0 mg, 81 % yield, white solid), eluent: 2% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.65, 137.50, 132.33, 129.97, 128.19.

phenyl(pyridin-2-yl)methanone (5b)[9]



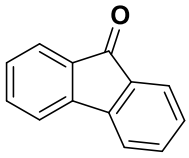
Yield (137.2 mg, 81 % yield, white solid), 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 4.3 Hz, 1H), 8.07 (d, J = 7.7 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.58 (t, J = 7.3 Hz, 1H), 7.47 (dd, J = 14.2, 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.71, 154.92, 148.40, 136.91, 136.12, 132.77, 130.83, 128.01, 126.03, 124.45.

benzil (5c)[9]



Yield (69.0 mg, 33 % yield, yellow solid), eluent: 1% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.9 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.55, 134.86, 132.93, 129.85, 128.98.

9H-fluoren-9-one (5d)[9]



Yield (149.0 mg, 83 % yield, yellow solid), eluent: 2% ethylacetate/hexane; δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, J = 7.2 Hz, 1H), 7.50 – 7.42 (m, 2H),

7.26 (t, J = 6.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.83, 144.33, 134.60, 134.05, 128.98, 124.20, 120.23.

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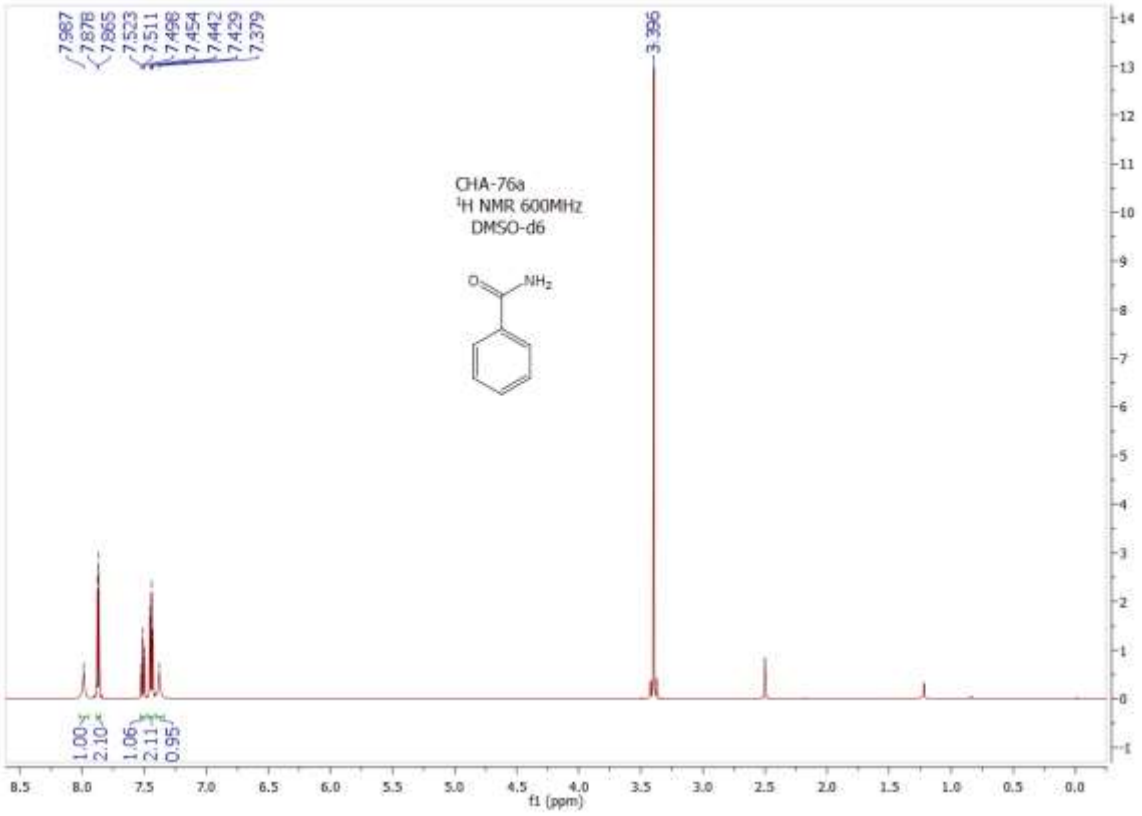
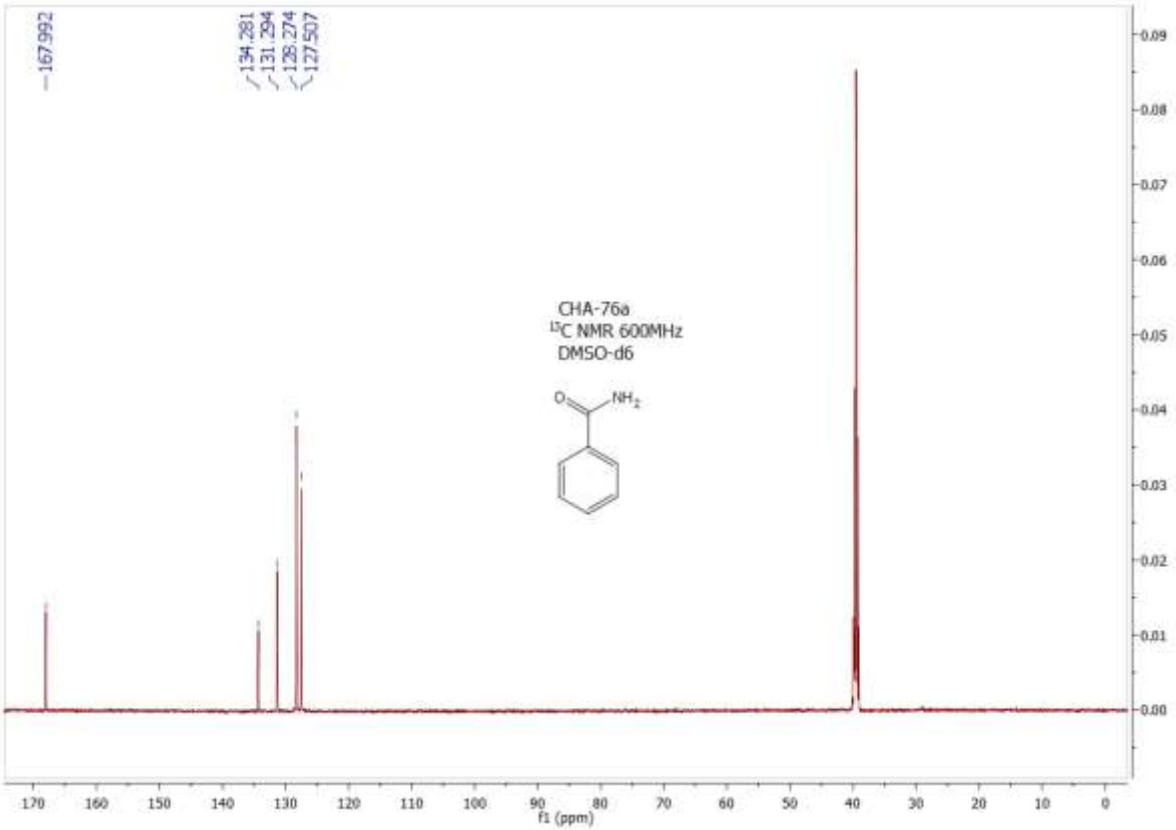
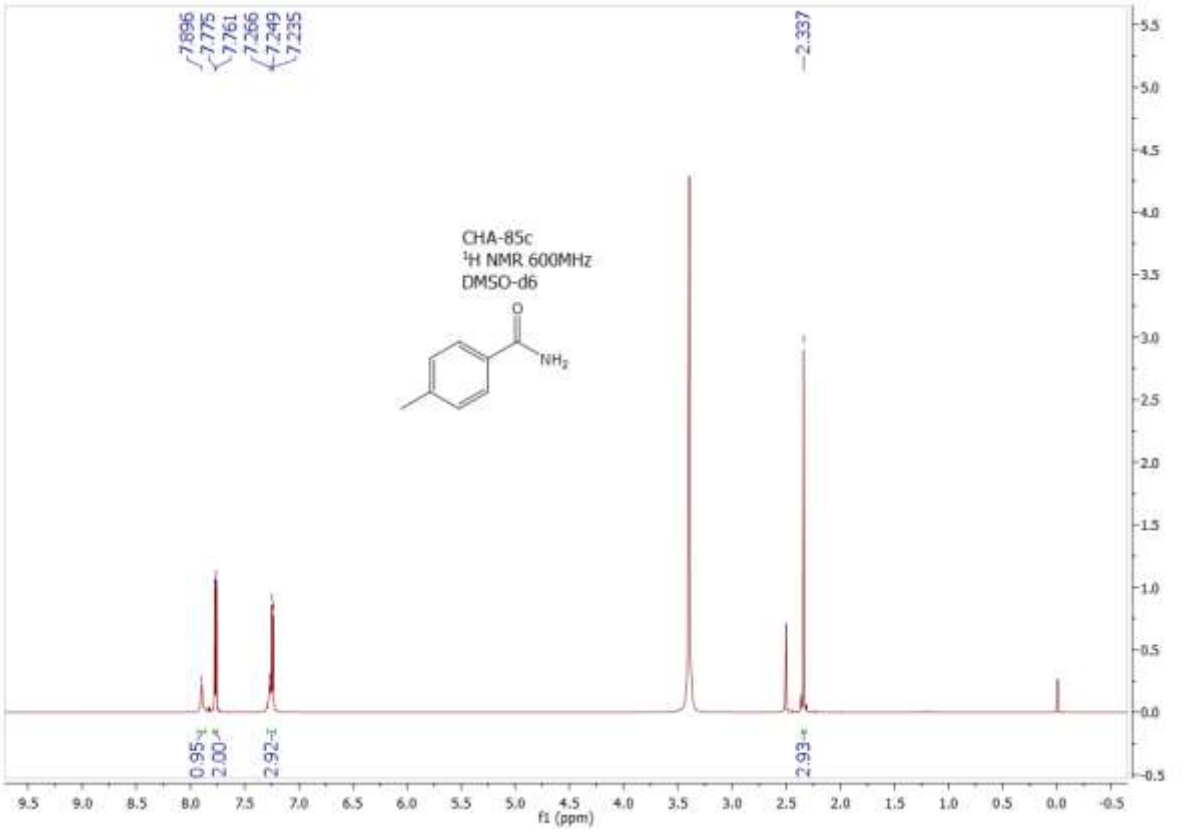
^{1}H ,^{13}C & HRMS spectra



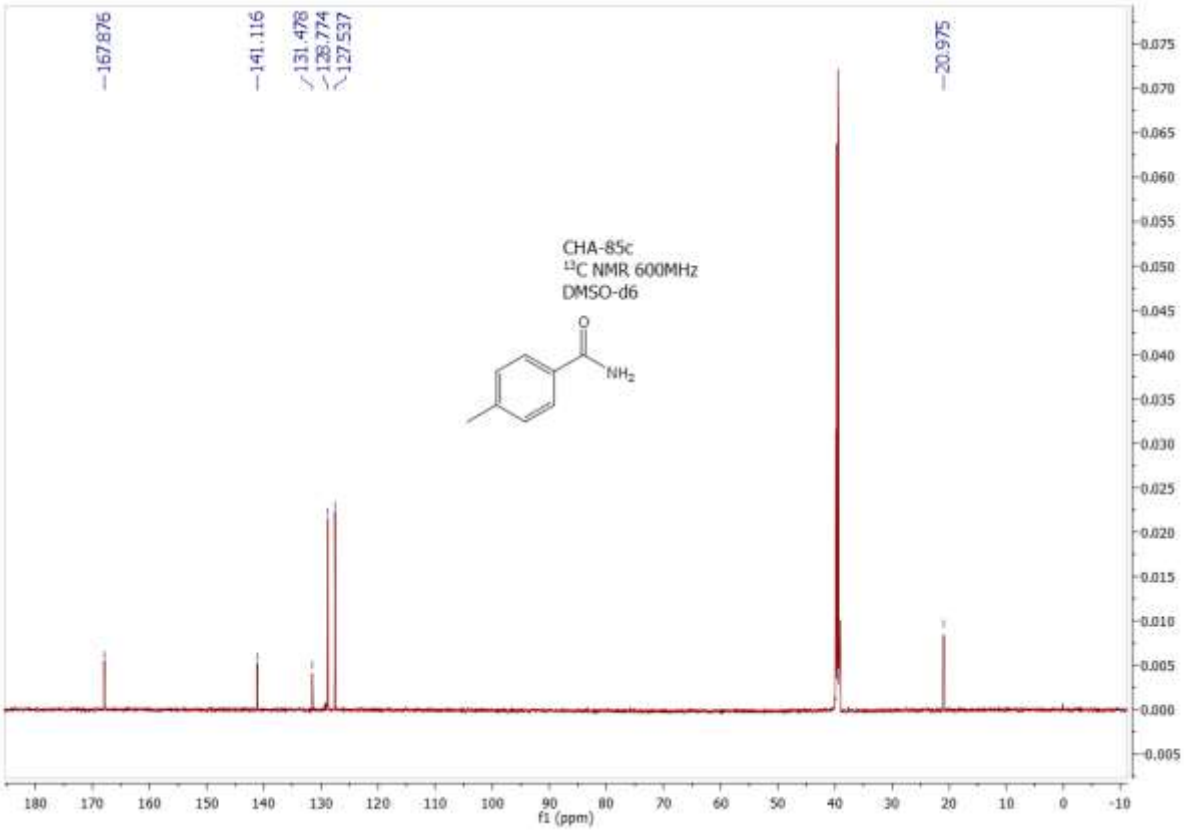
^{1}H NMR of 2a



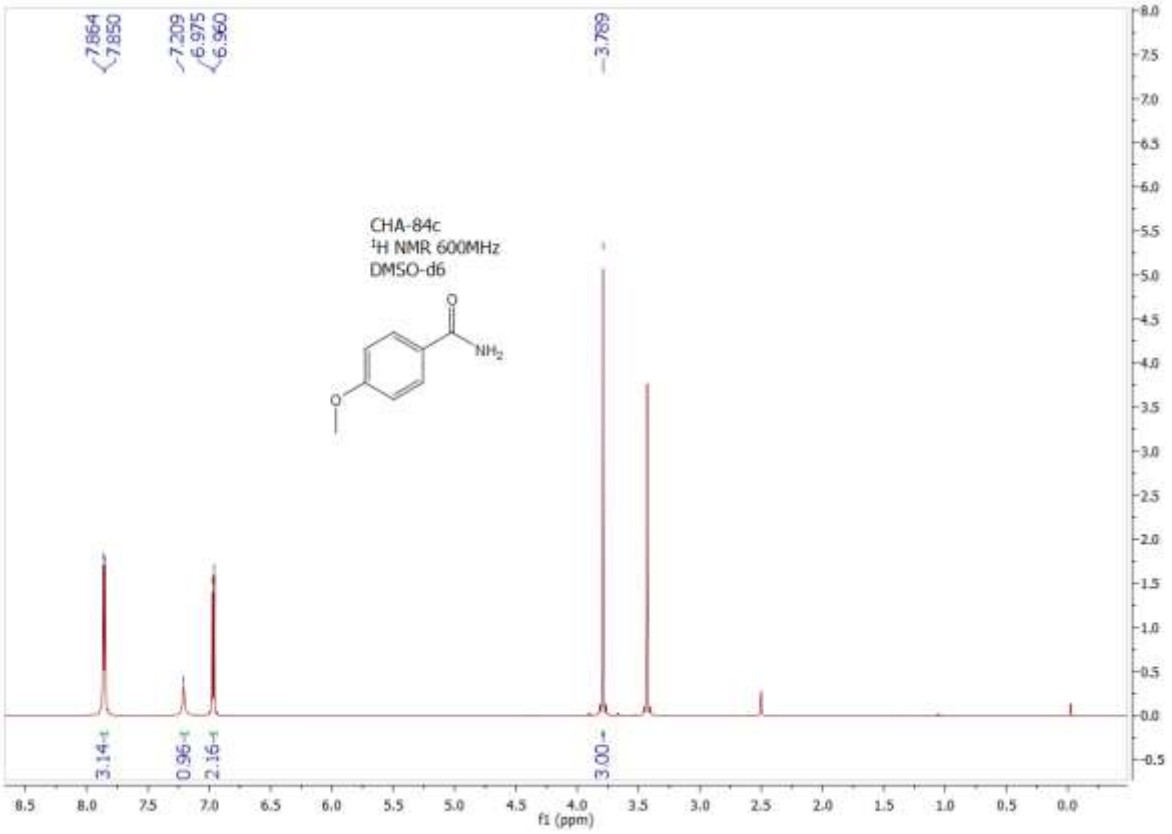
^{13}C NMR of 2a



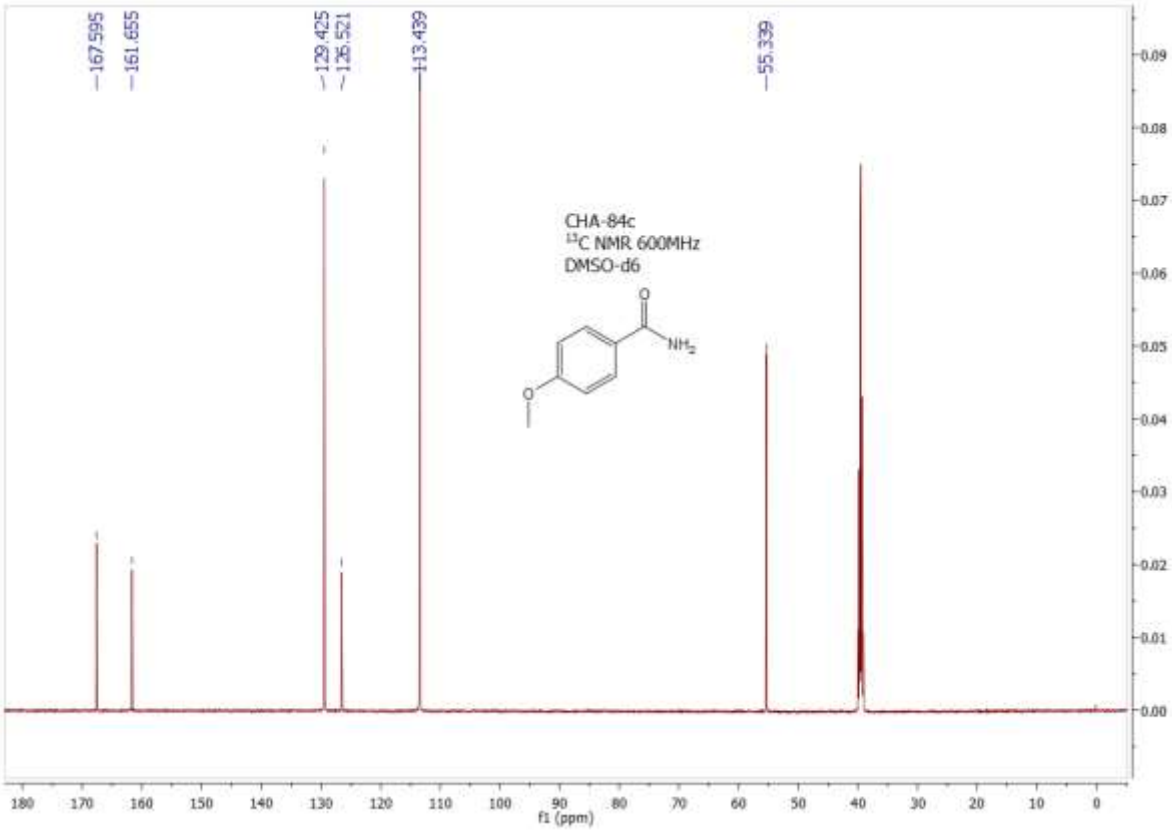
^{1}H NMR of 2b



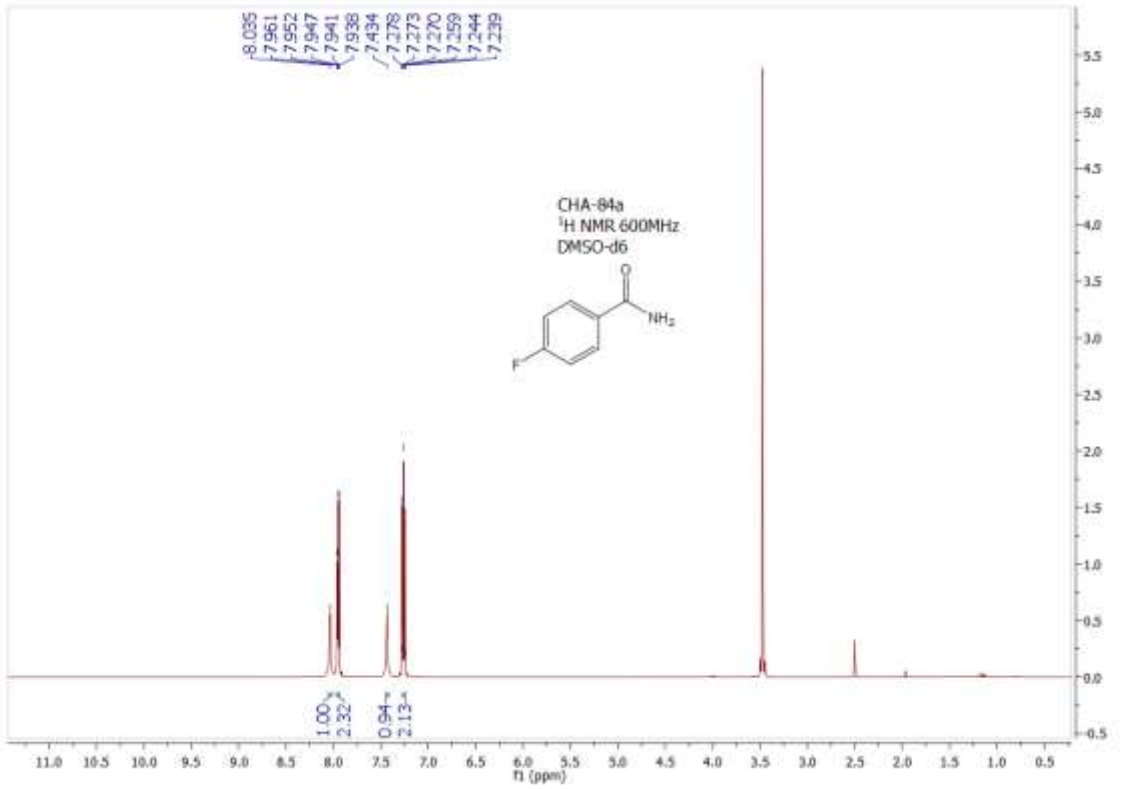
^{13}C NMR of 2b



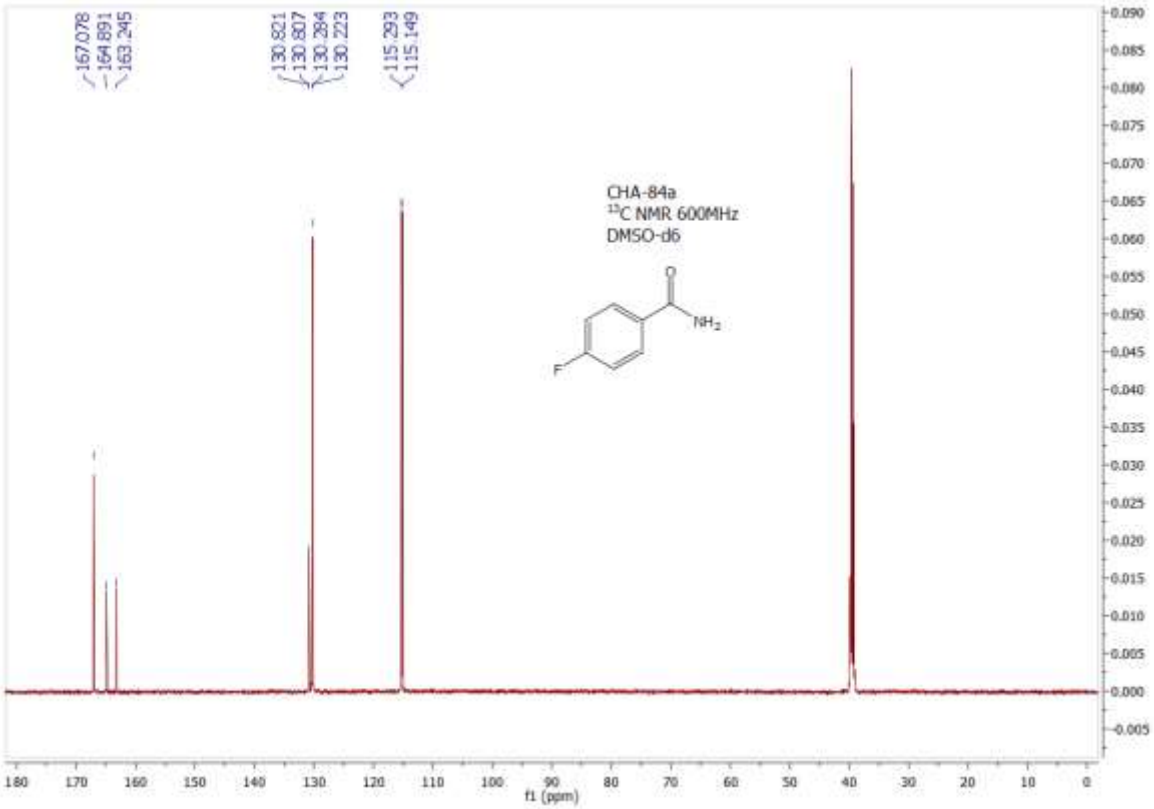
^{1}H NMR of 2c



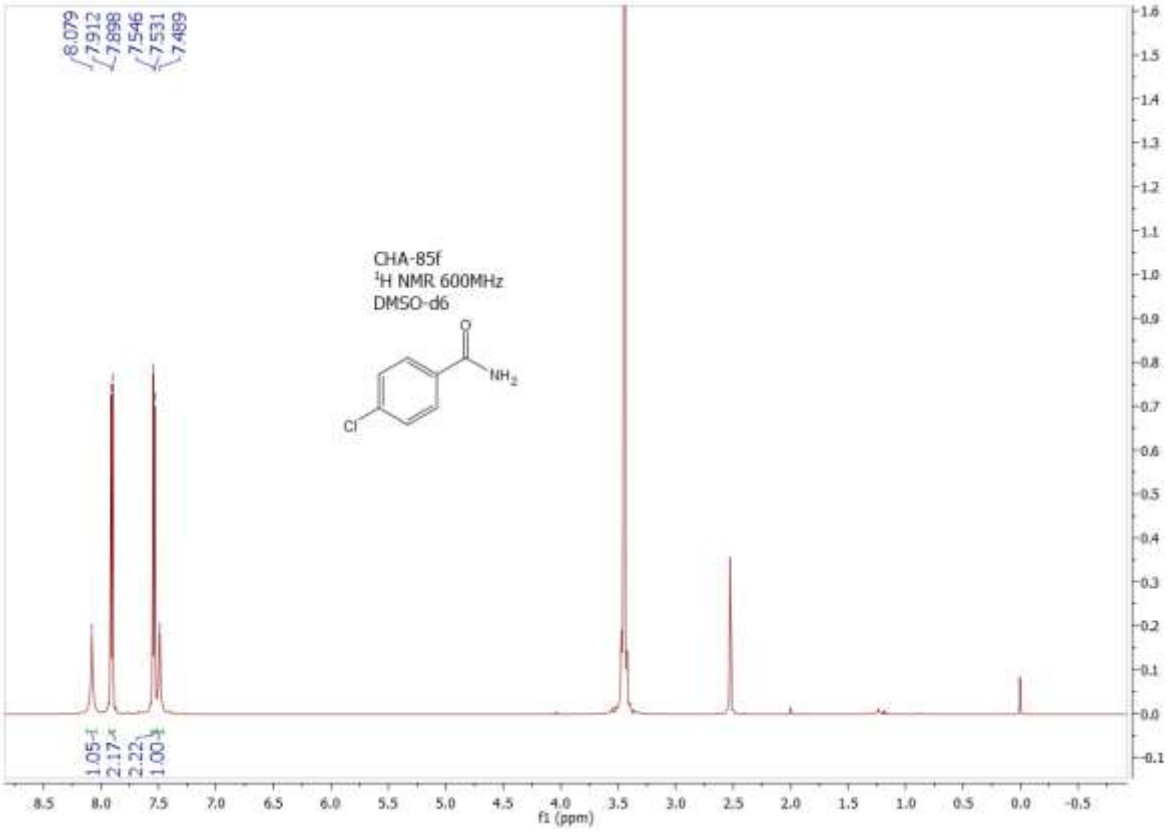
^{13}C NMR of 2c



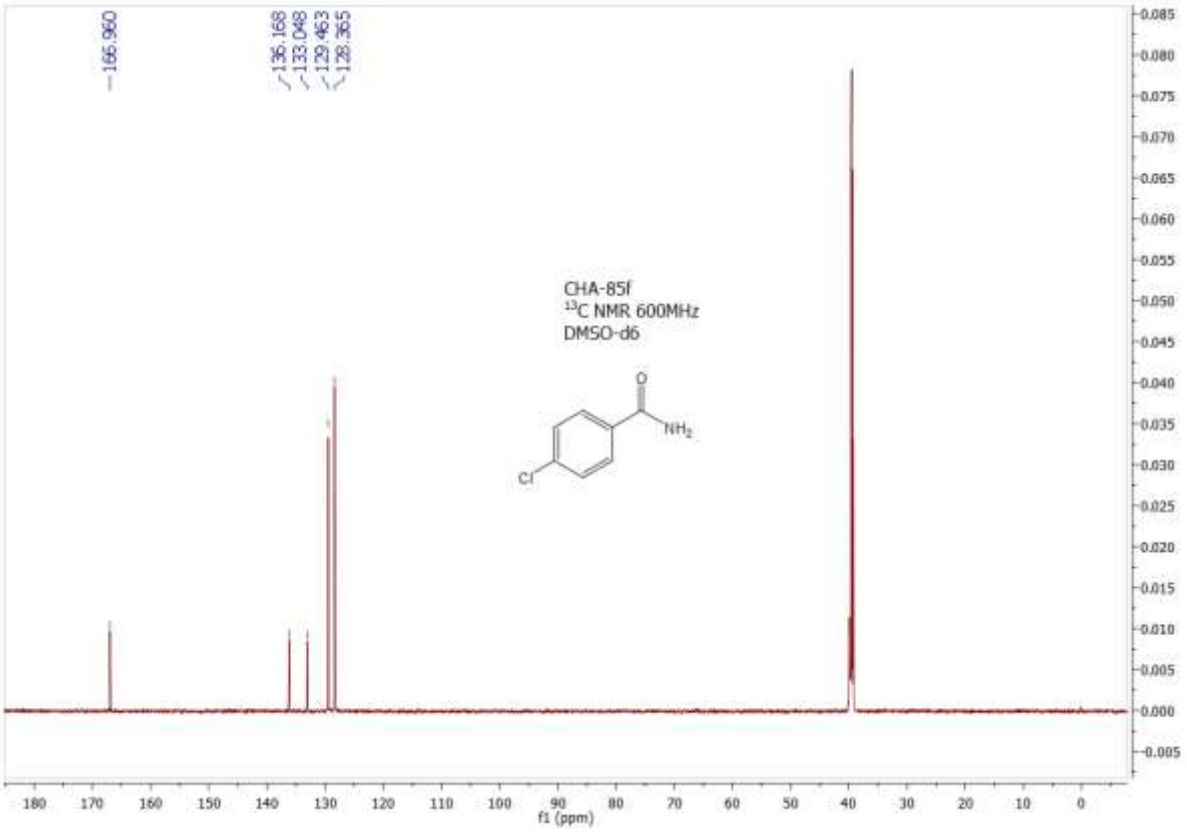
^{1}H NMR of 2d



^{13}C NMR of 2d



^{1}H NMR of 2e



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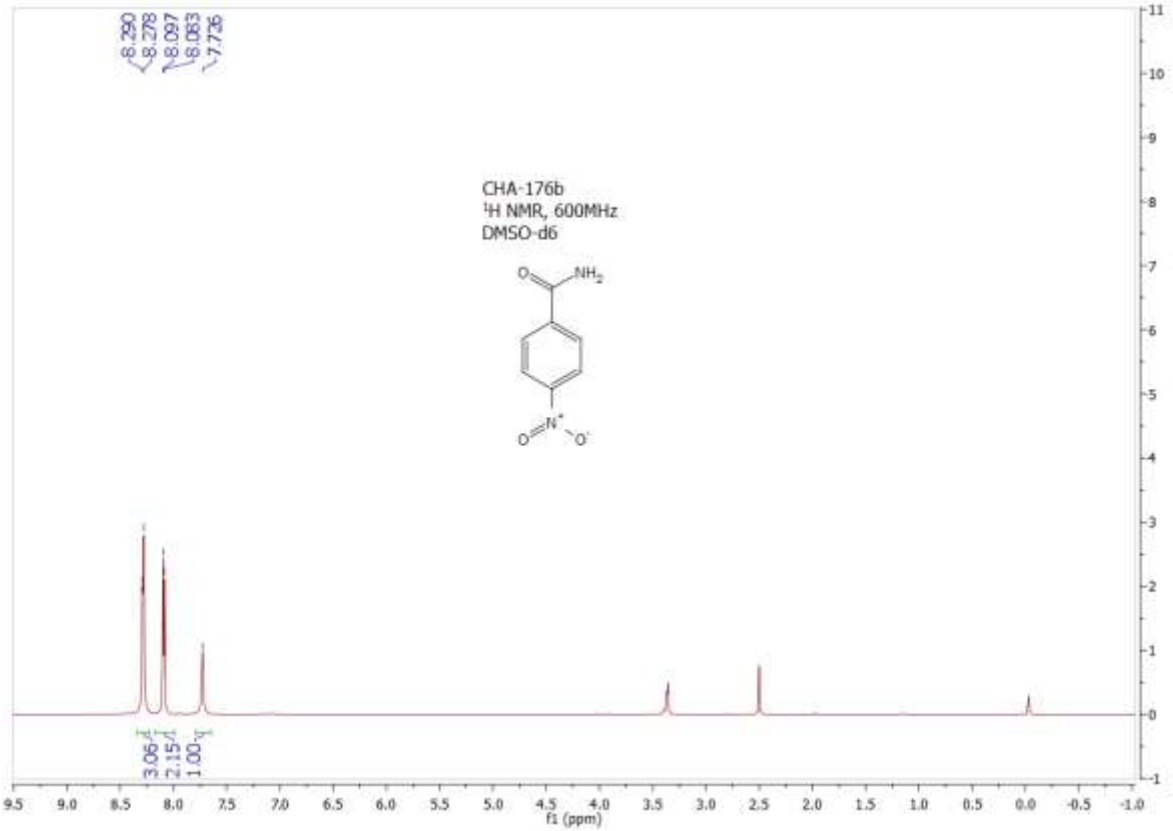
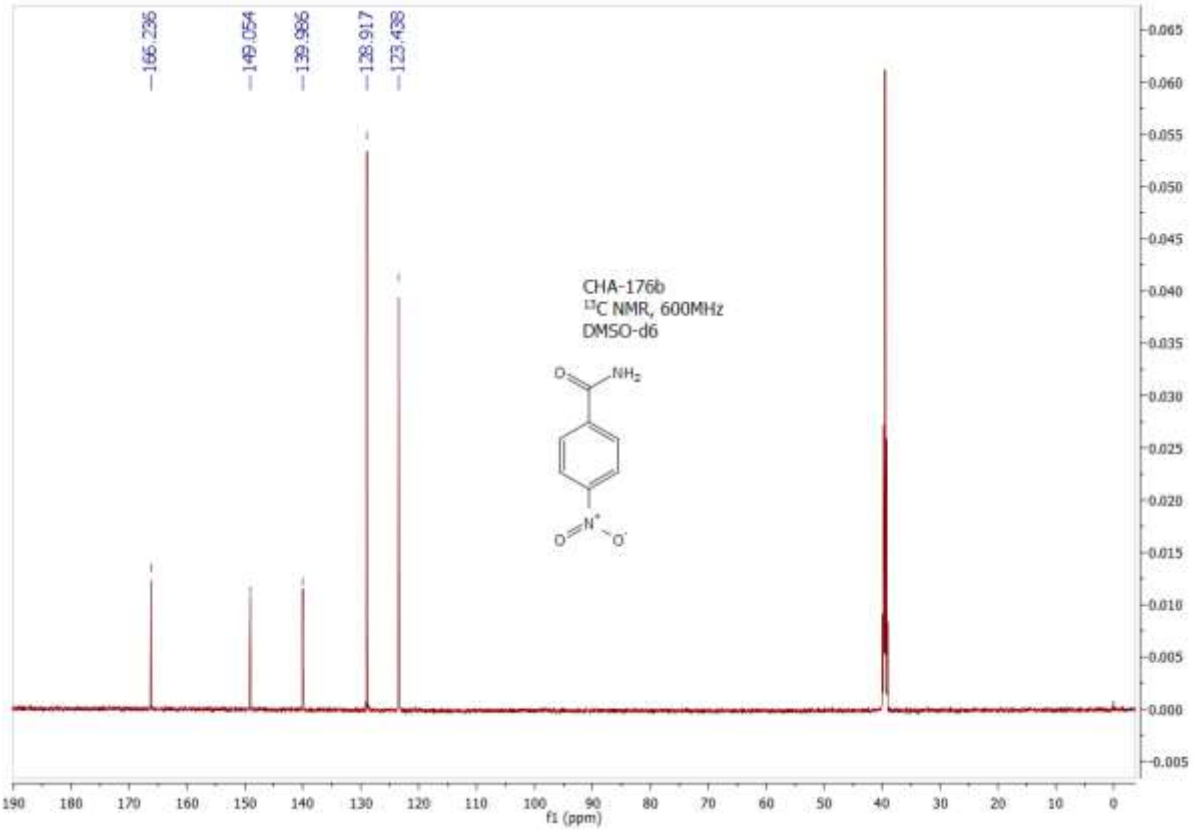
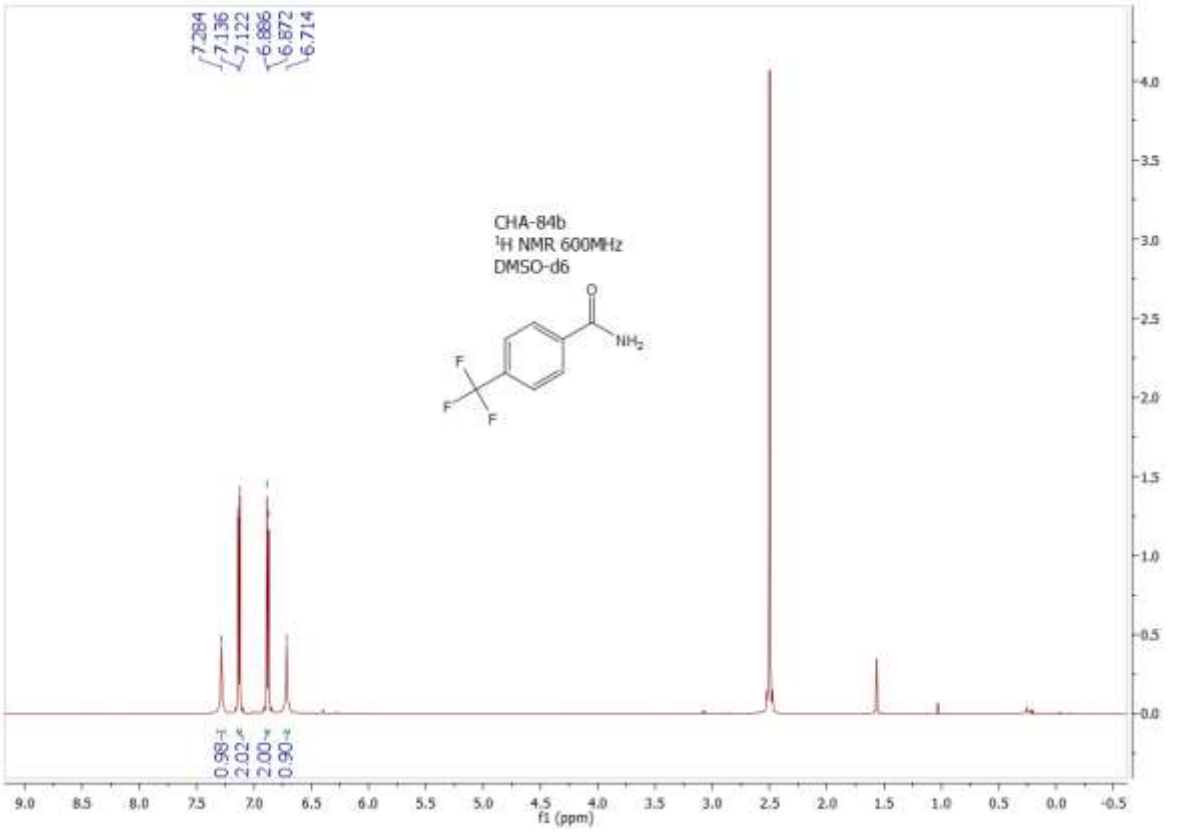


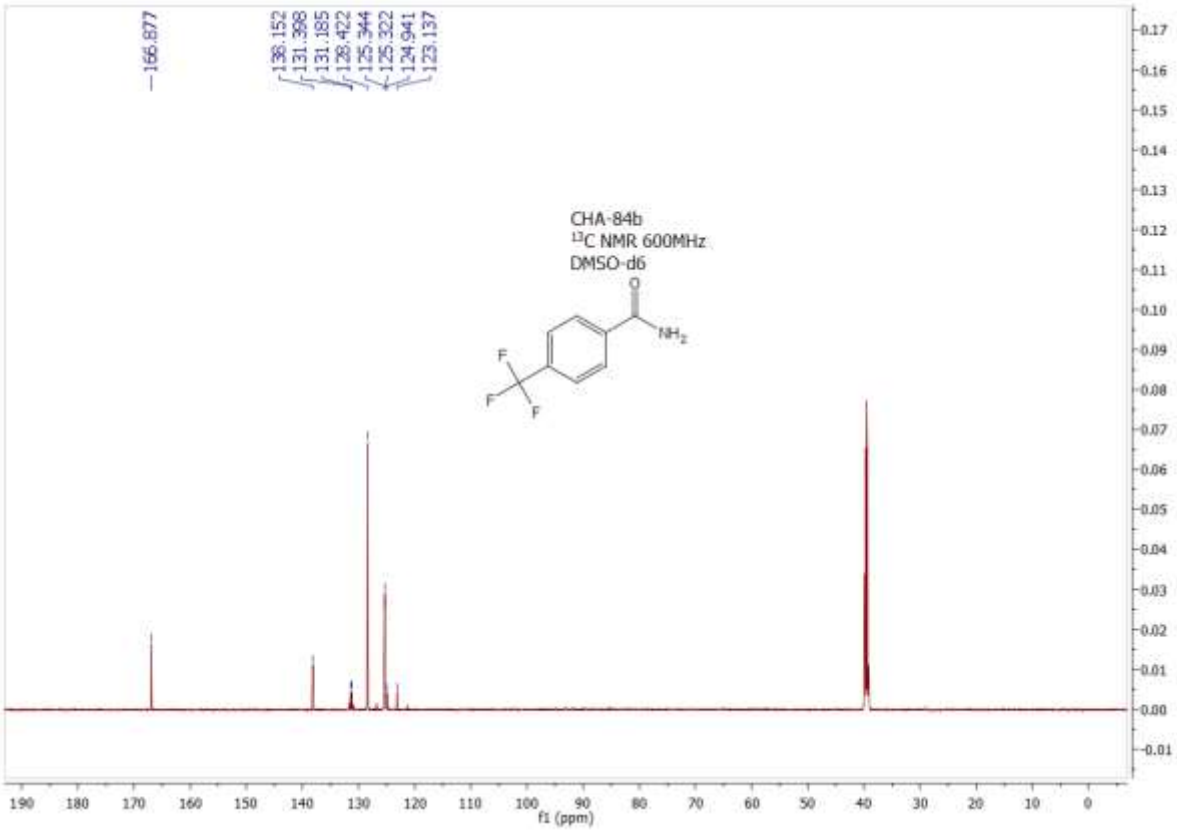
^{1}H NMR of 2f



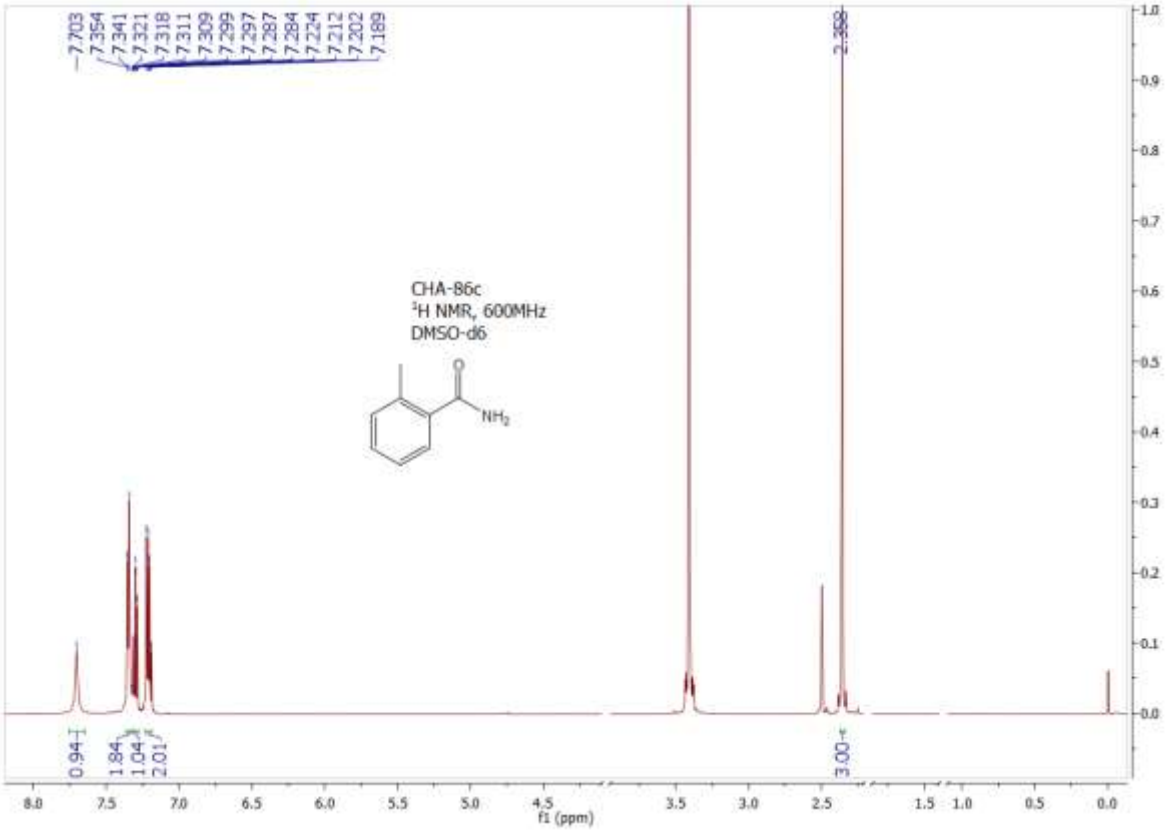
^{13}C NMR of 2f



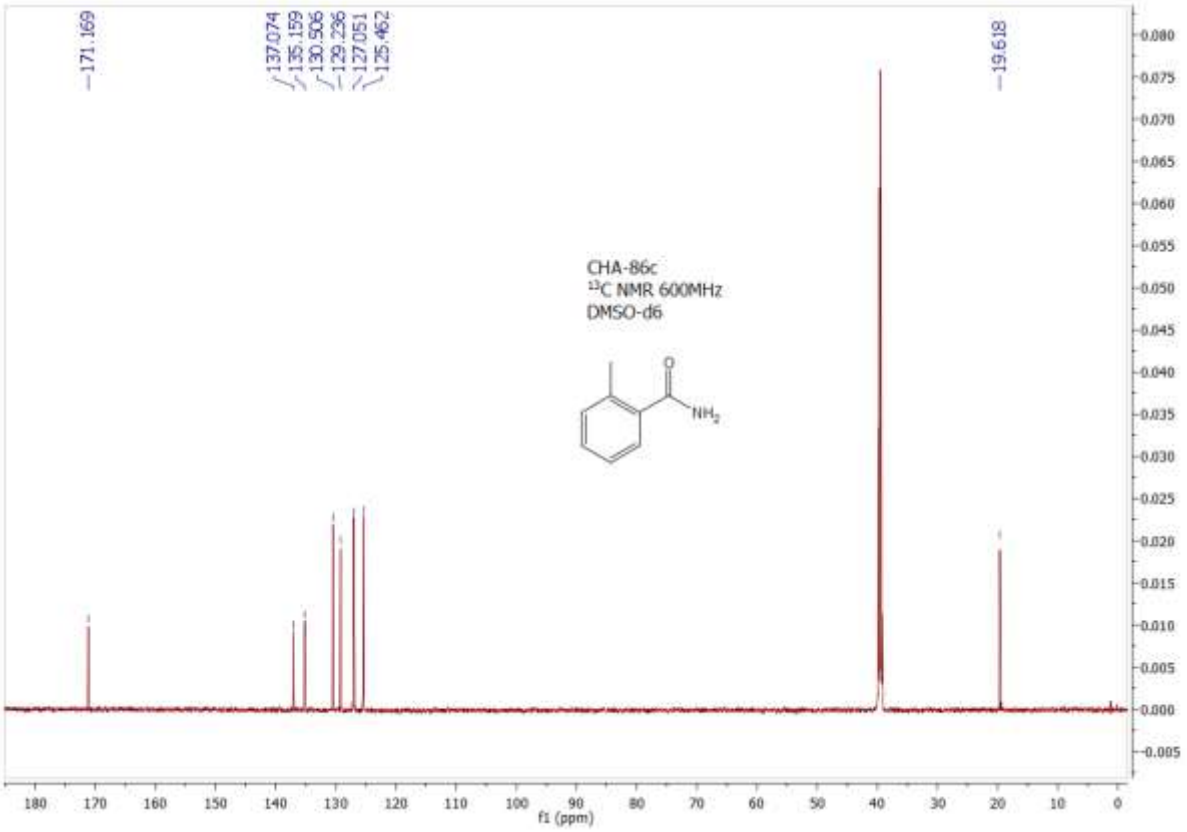
^{1}H NMR of 2g



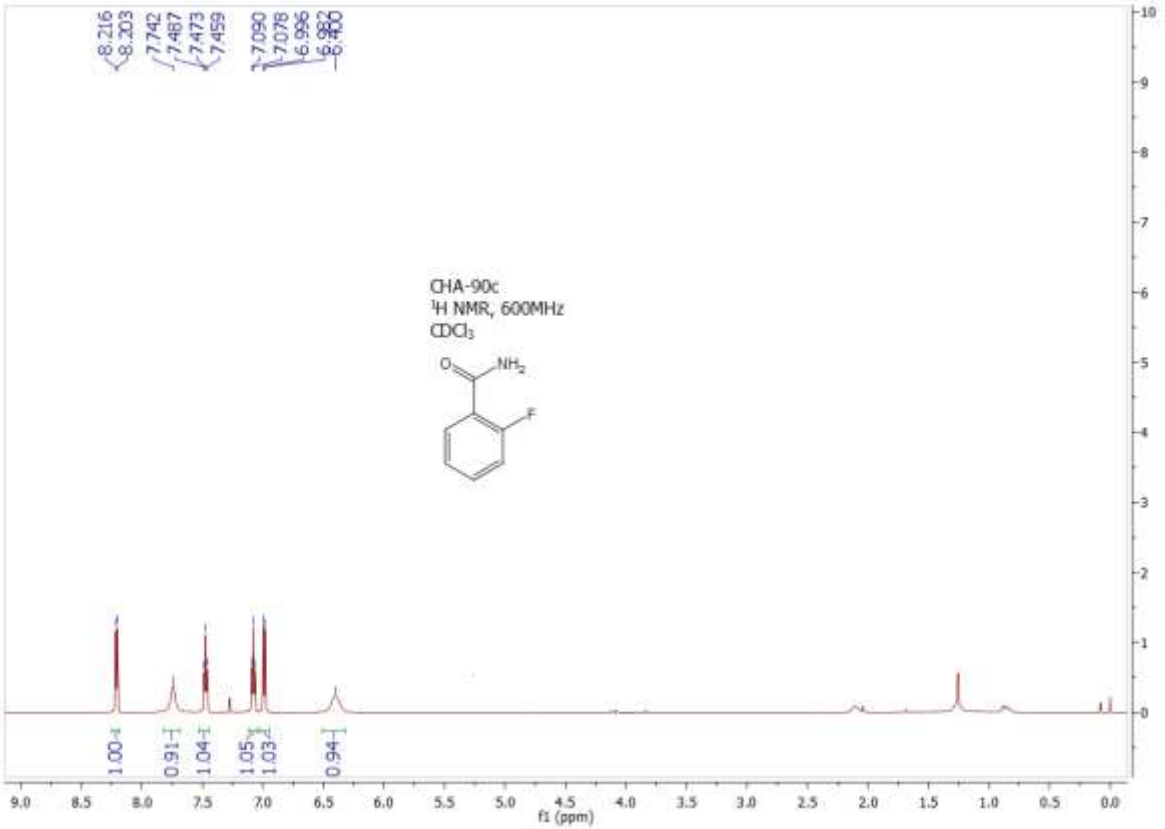
^{13}C NMR of 2g



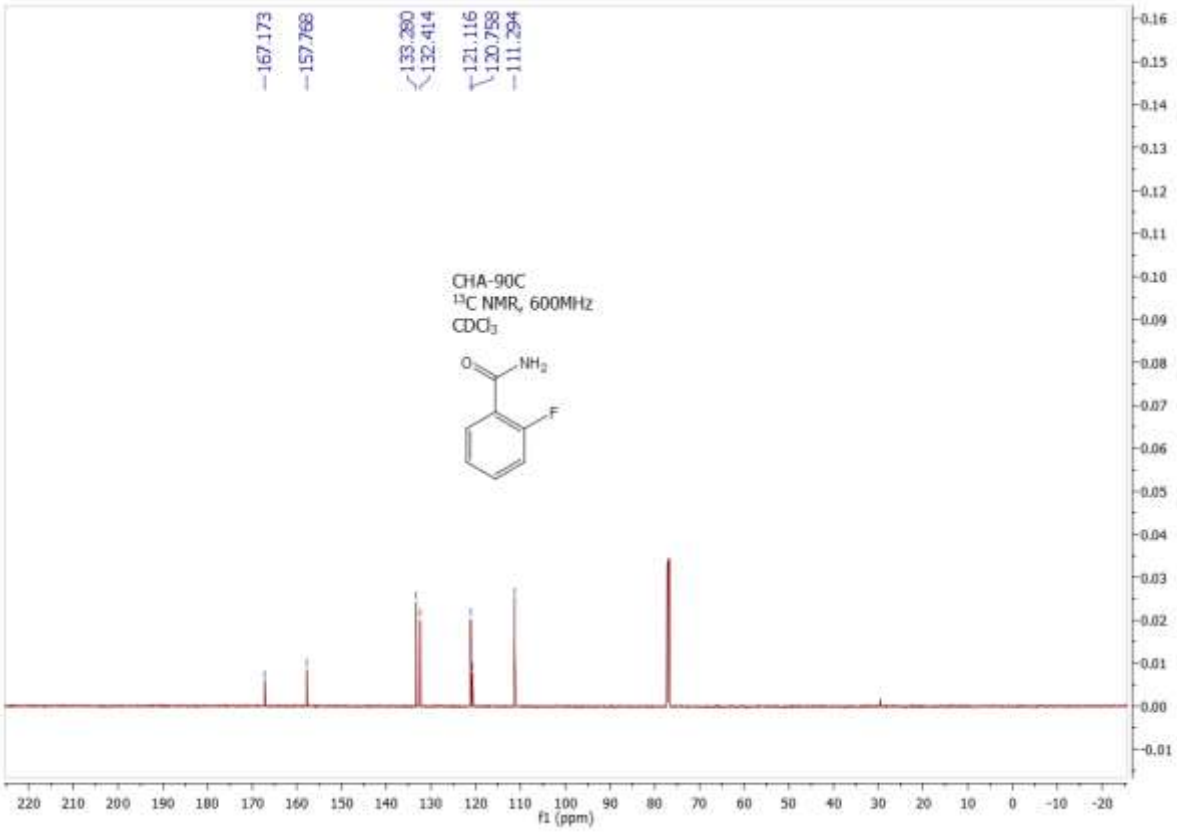
^{1}H NMR of 2h



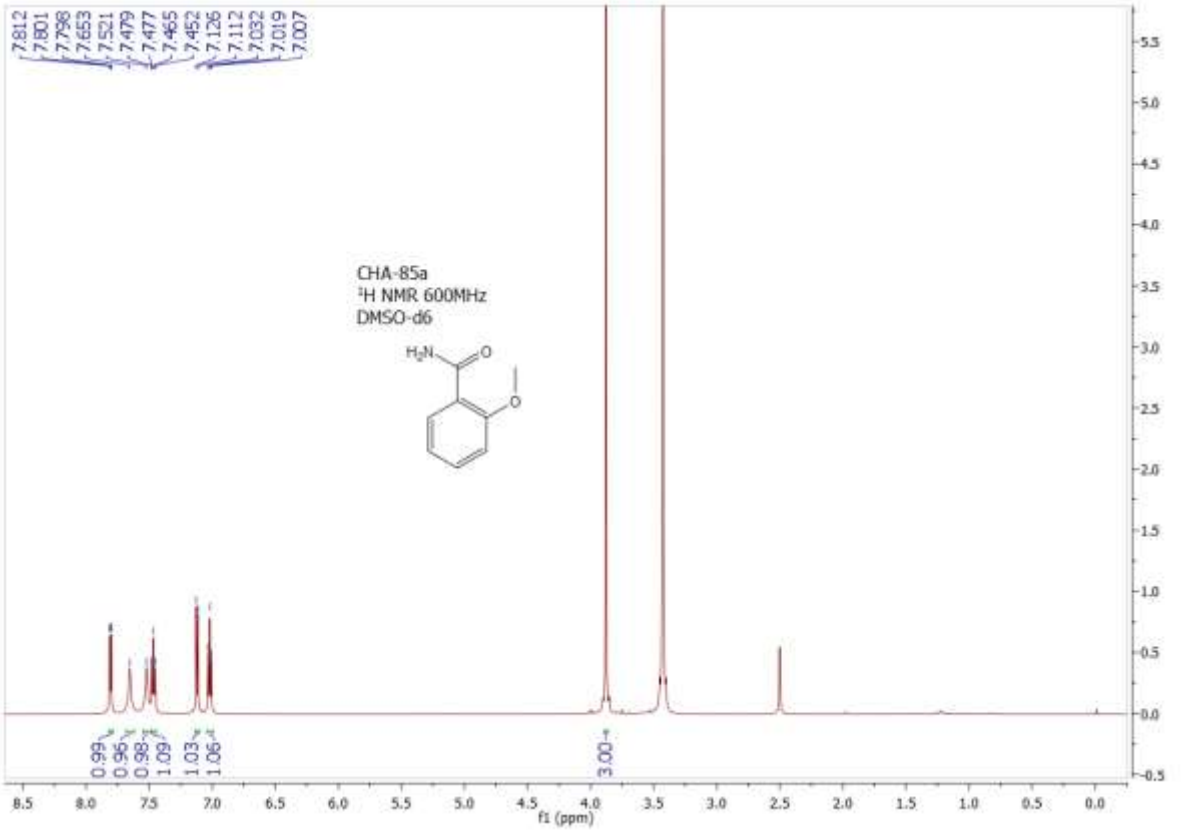
^{13}C NMR of 2h



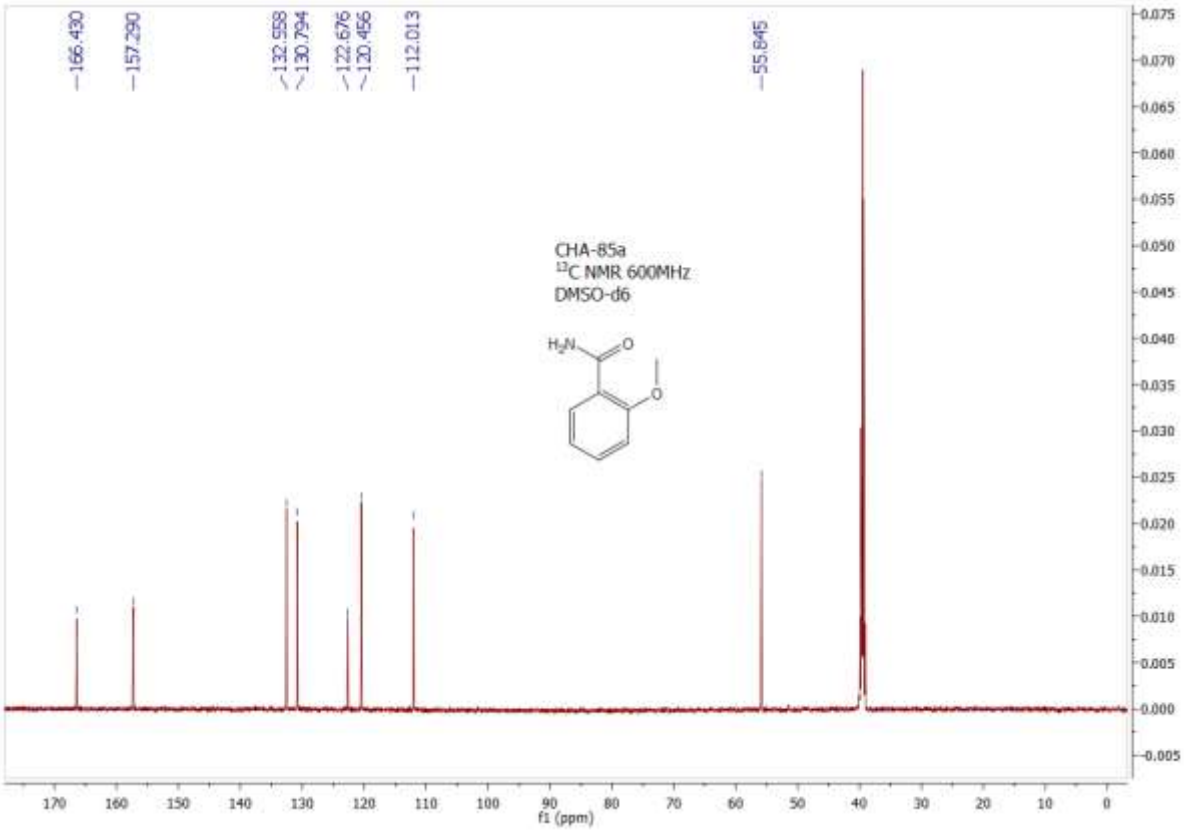
^{1}H NMR of 2i



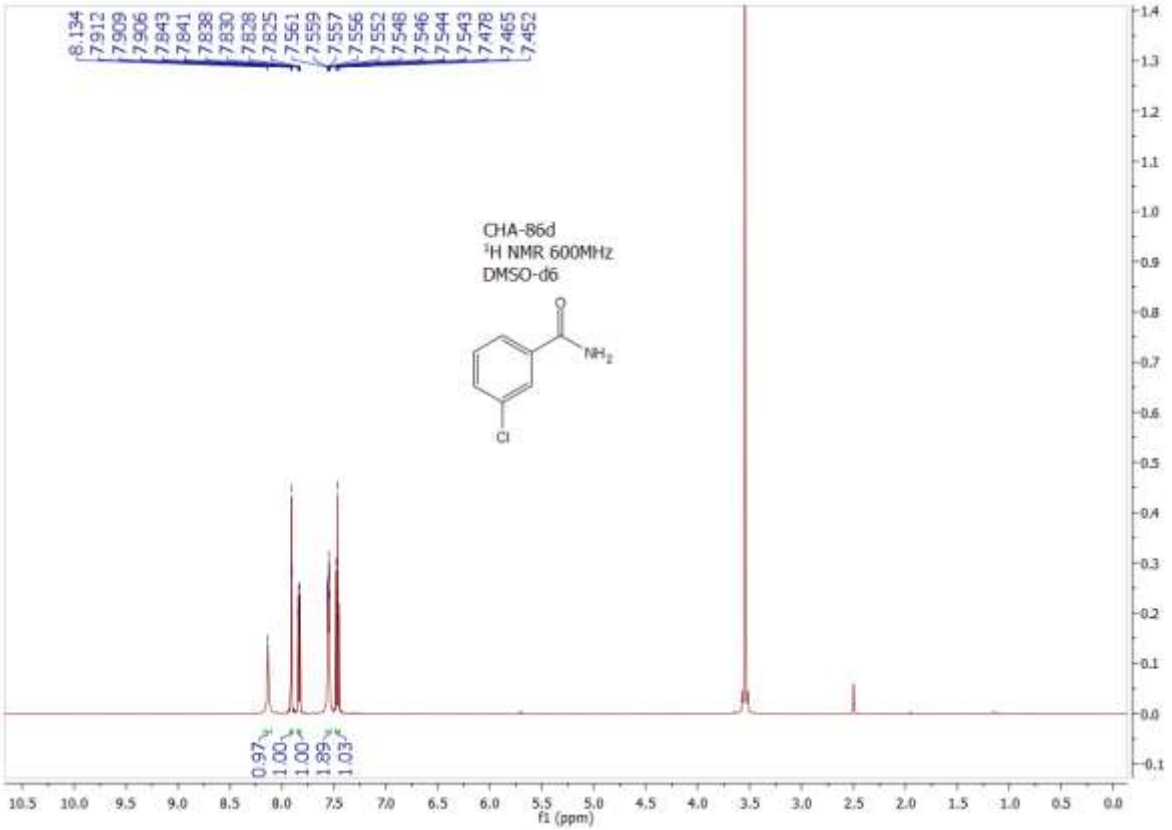
^{13}C NMR of 2i



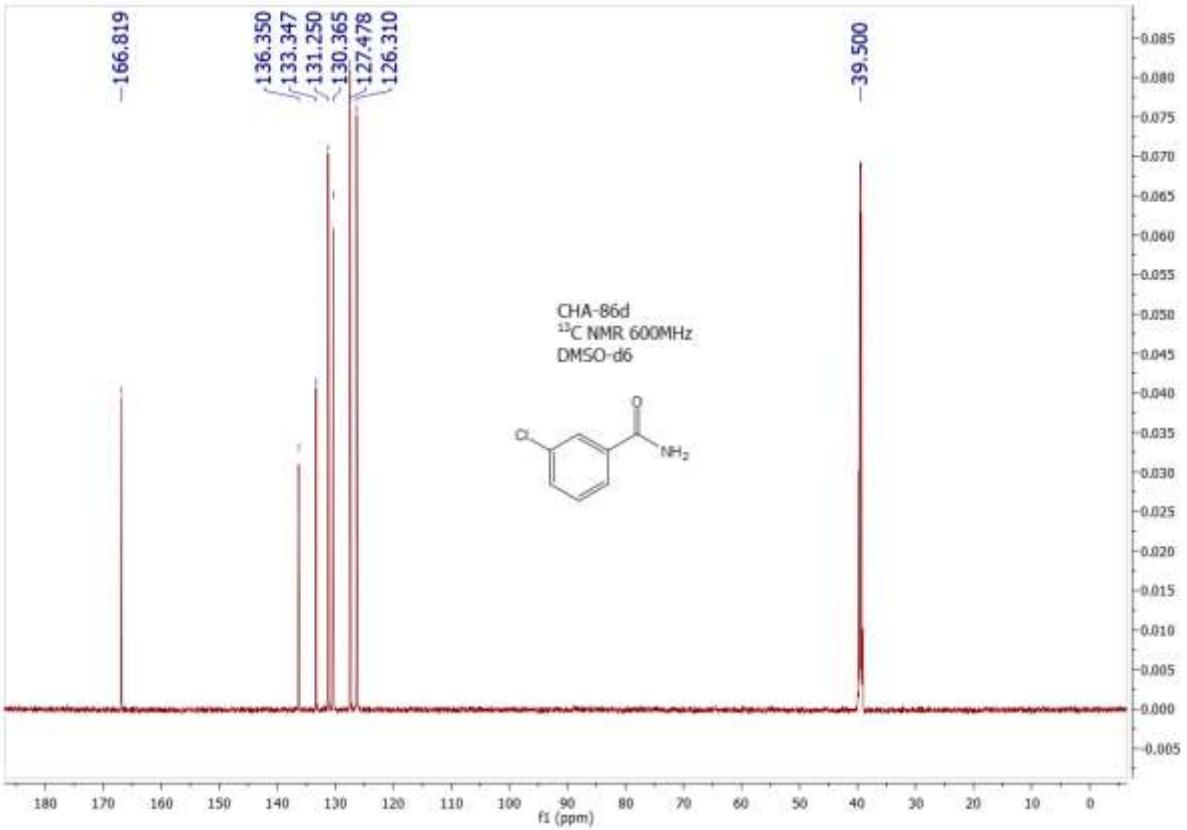
^{1}H NMR of 2j



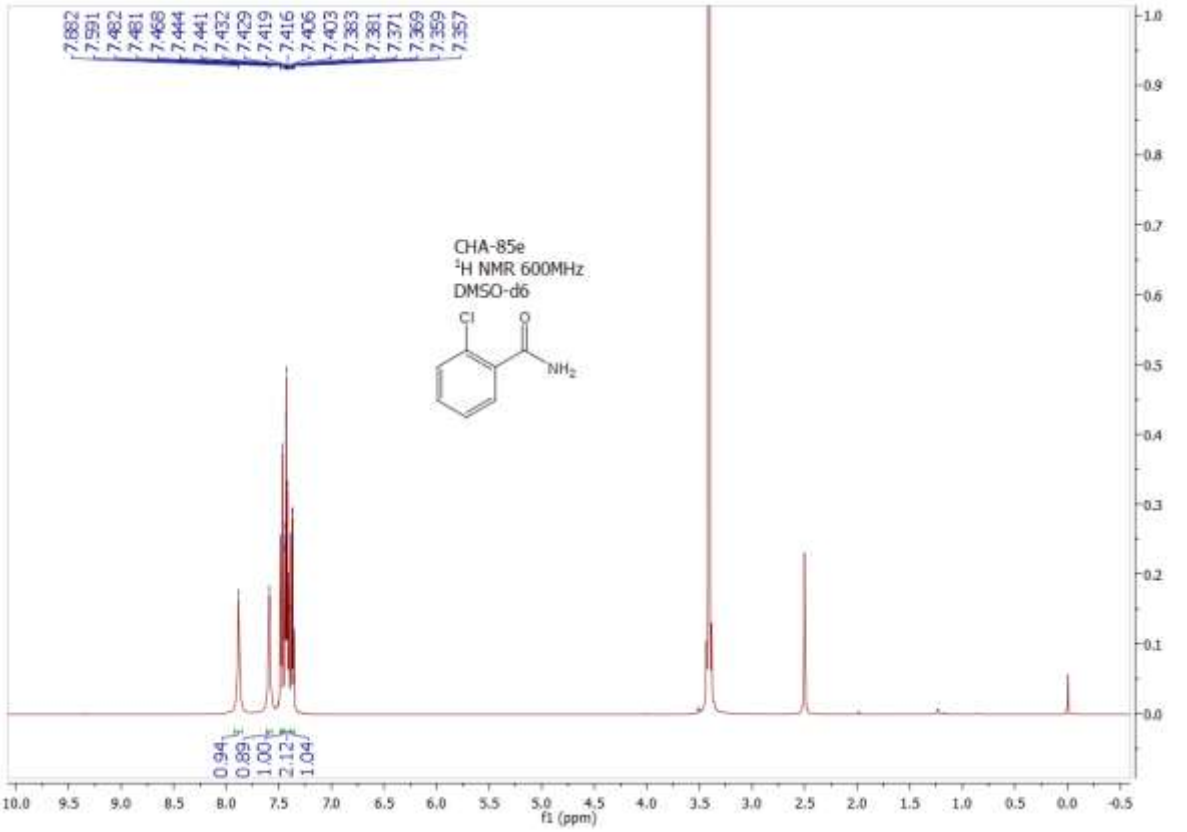
^{13}C NMR of 2j



^{1}H NMR of 2k



^{13}C NMR of 2k



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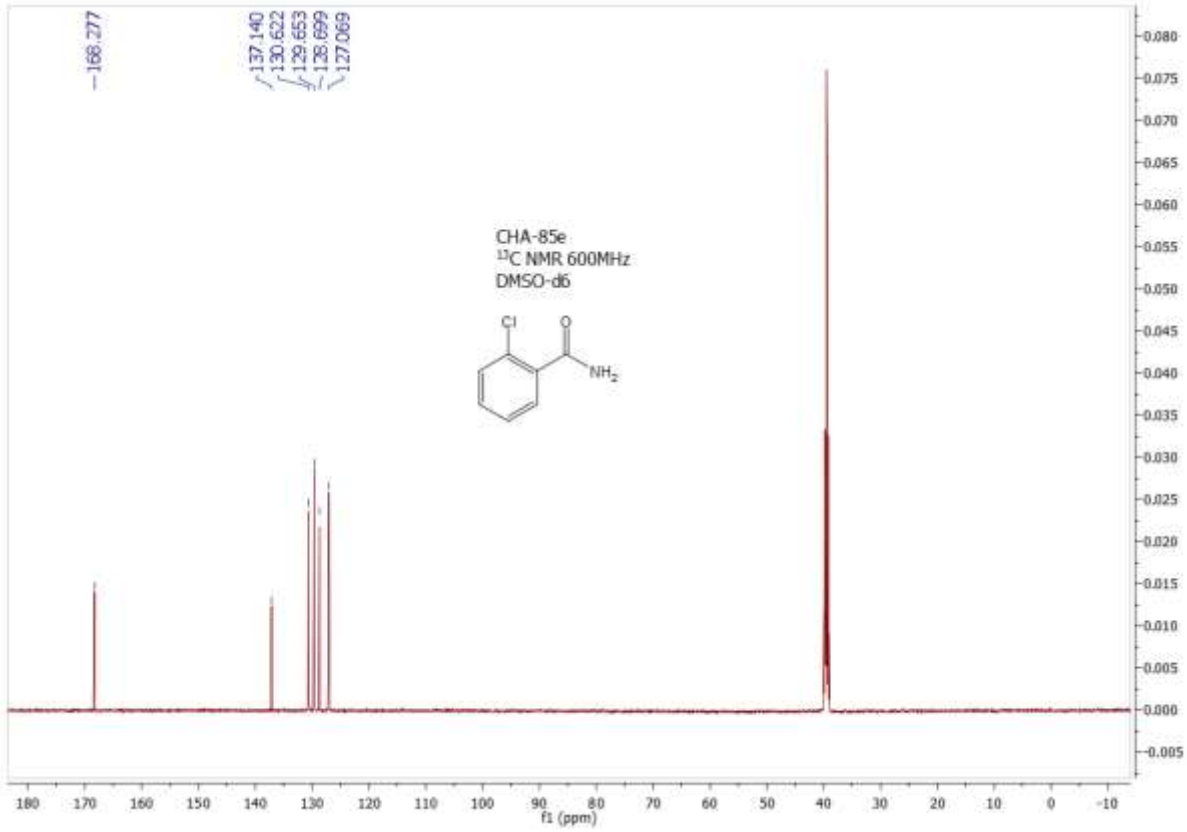
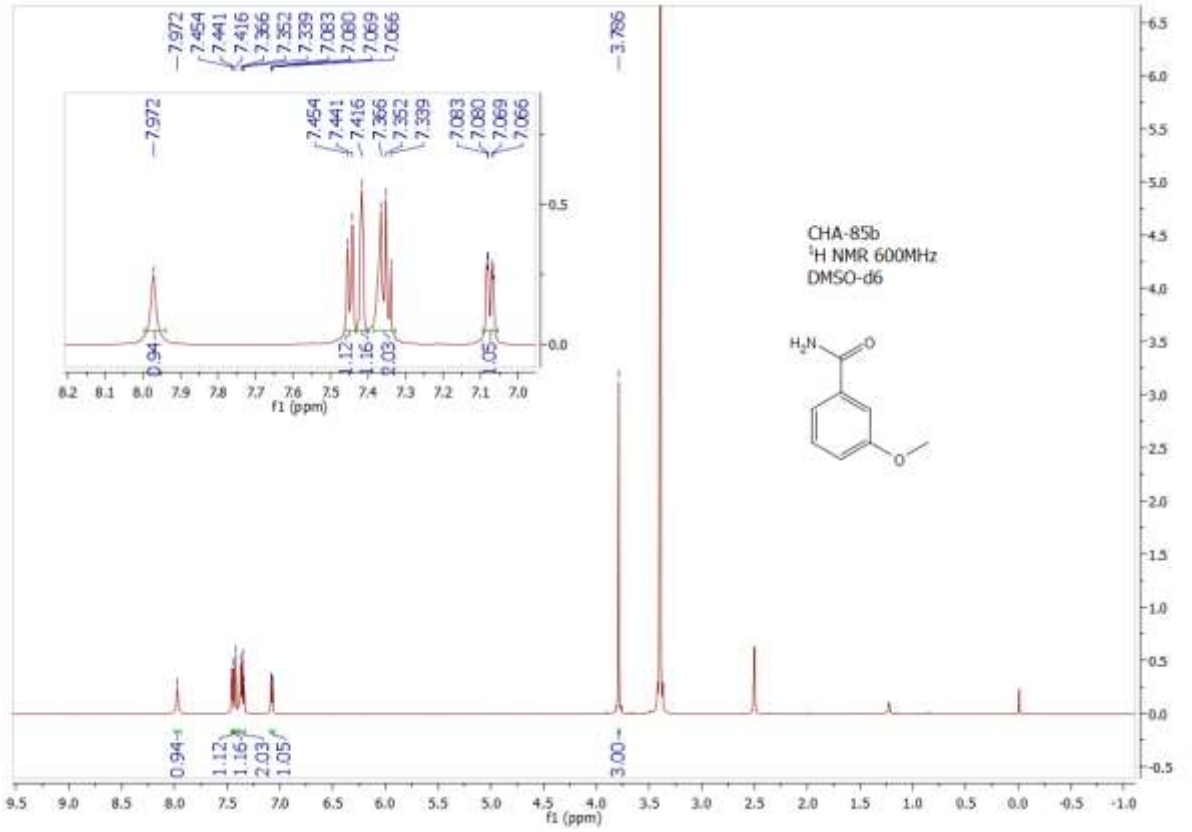
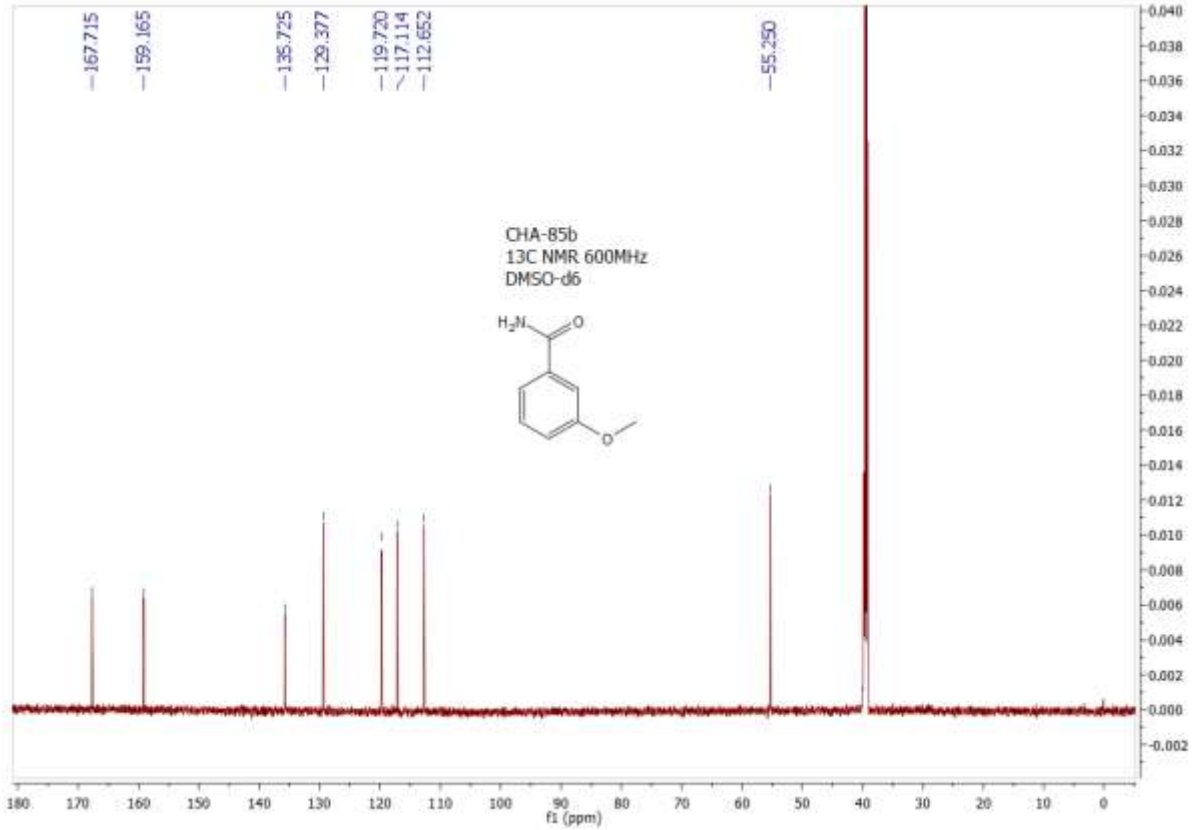


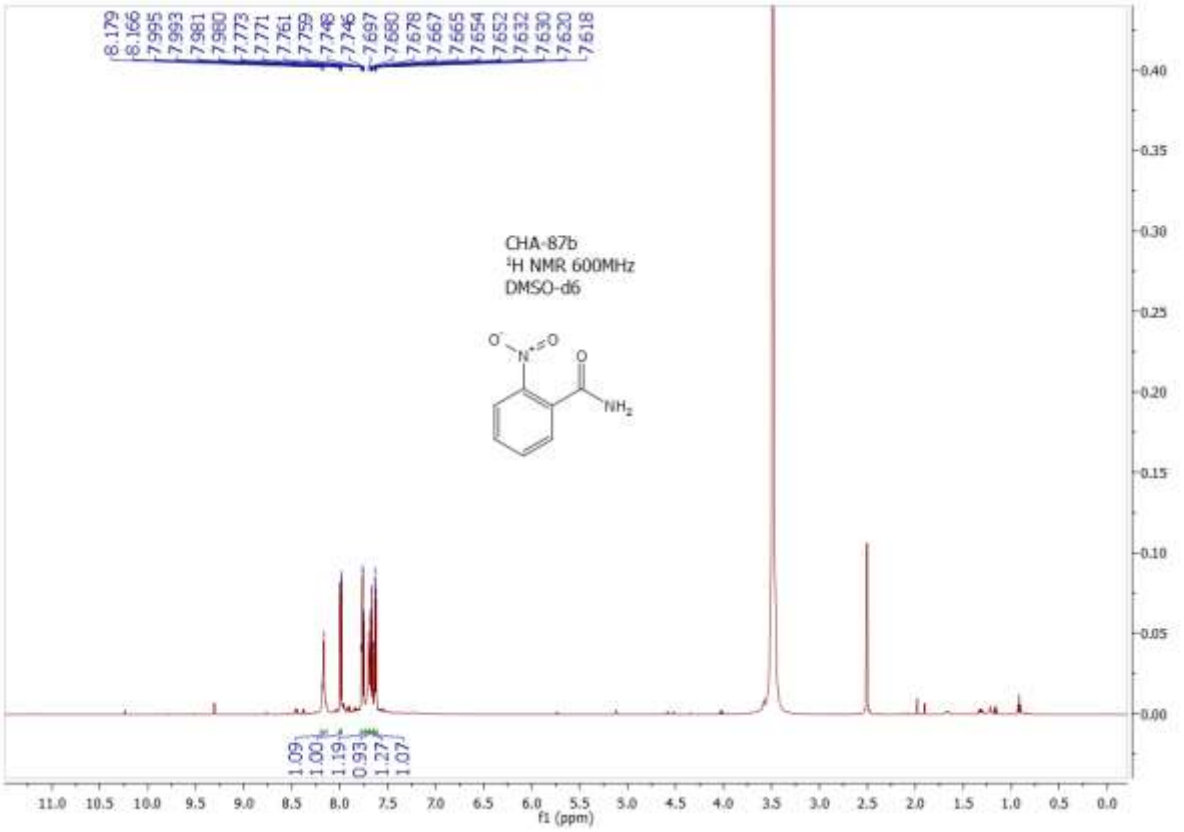
^{13}C NMR of 2l



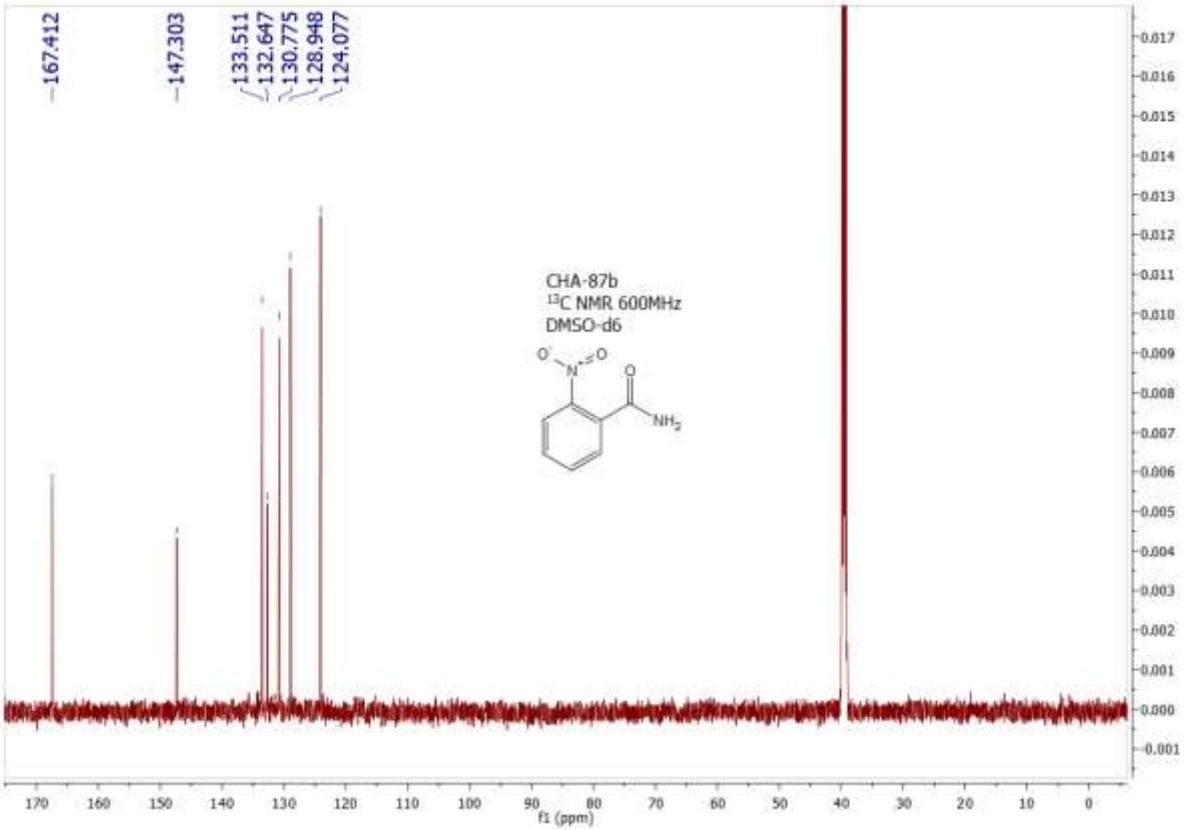
^{1}H NMR of 2m



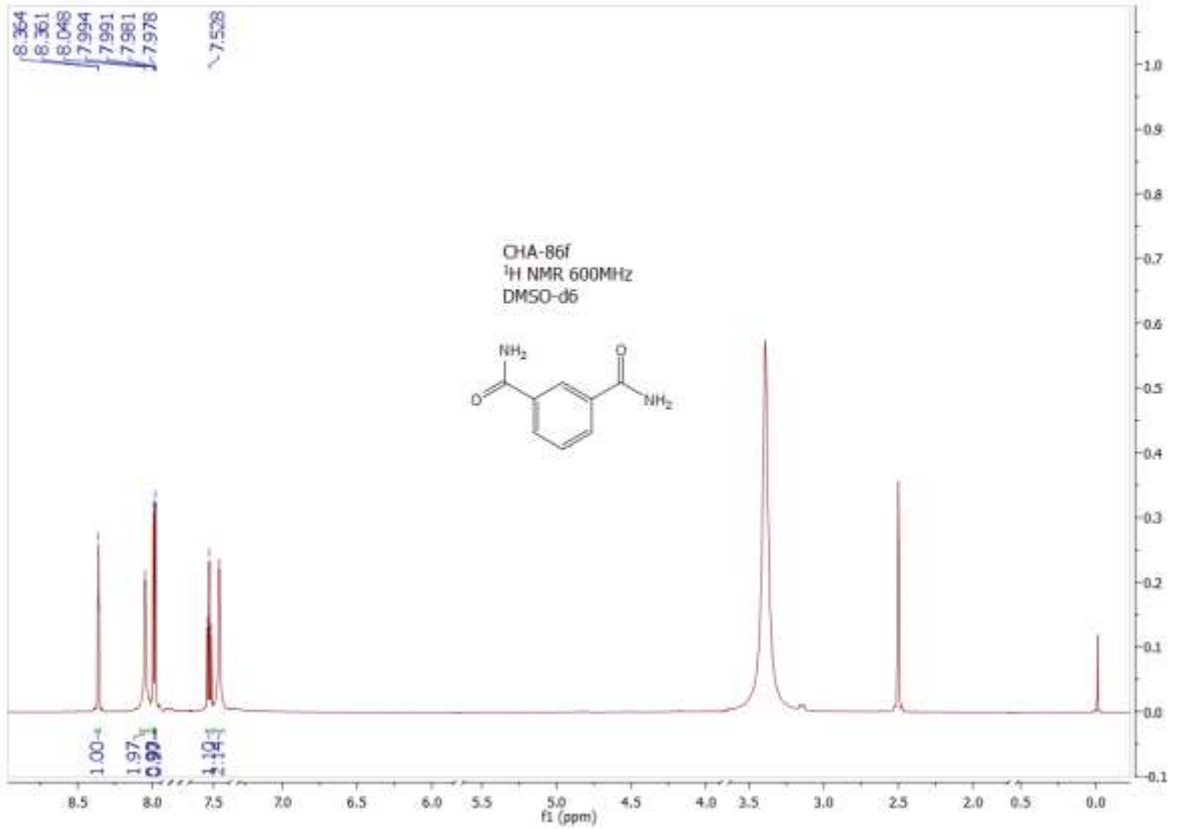
^{13}C NMR of 2m



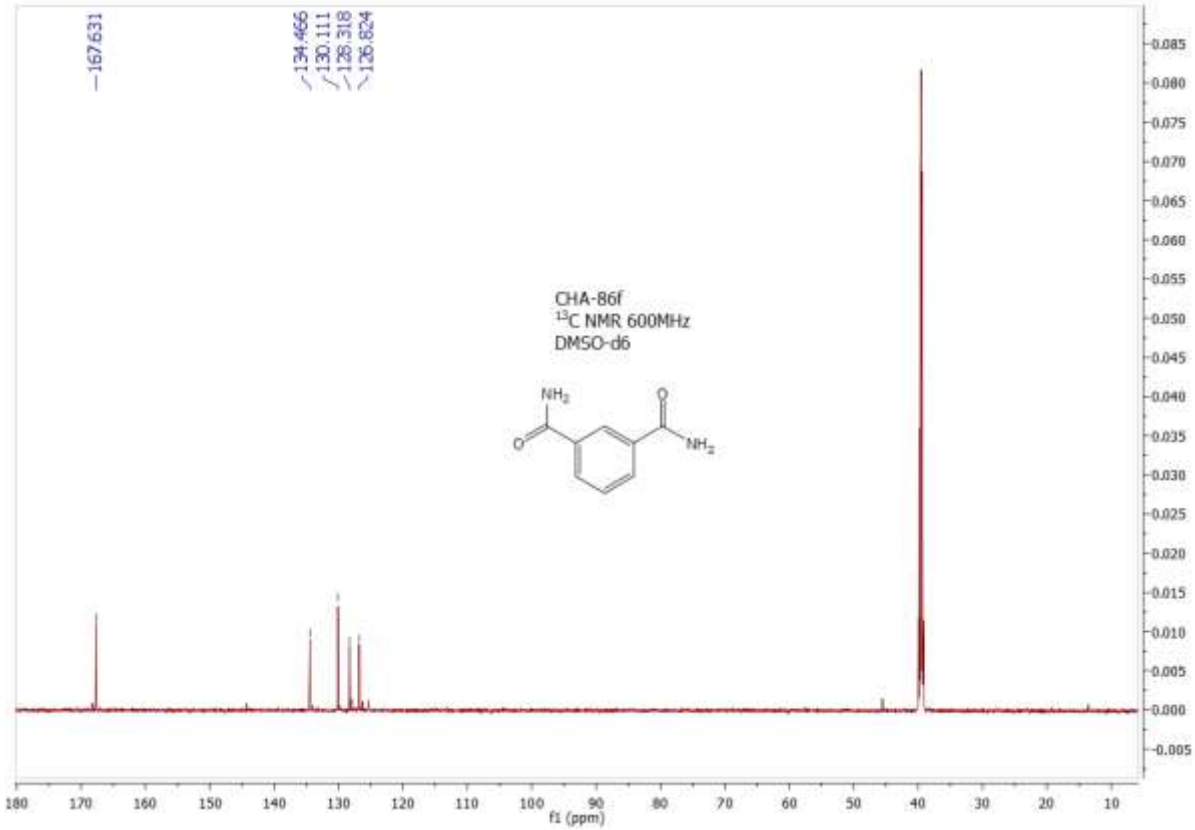
^{1}H NMR of 2n



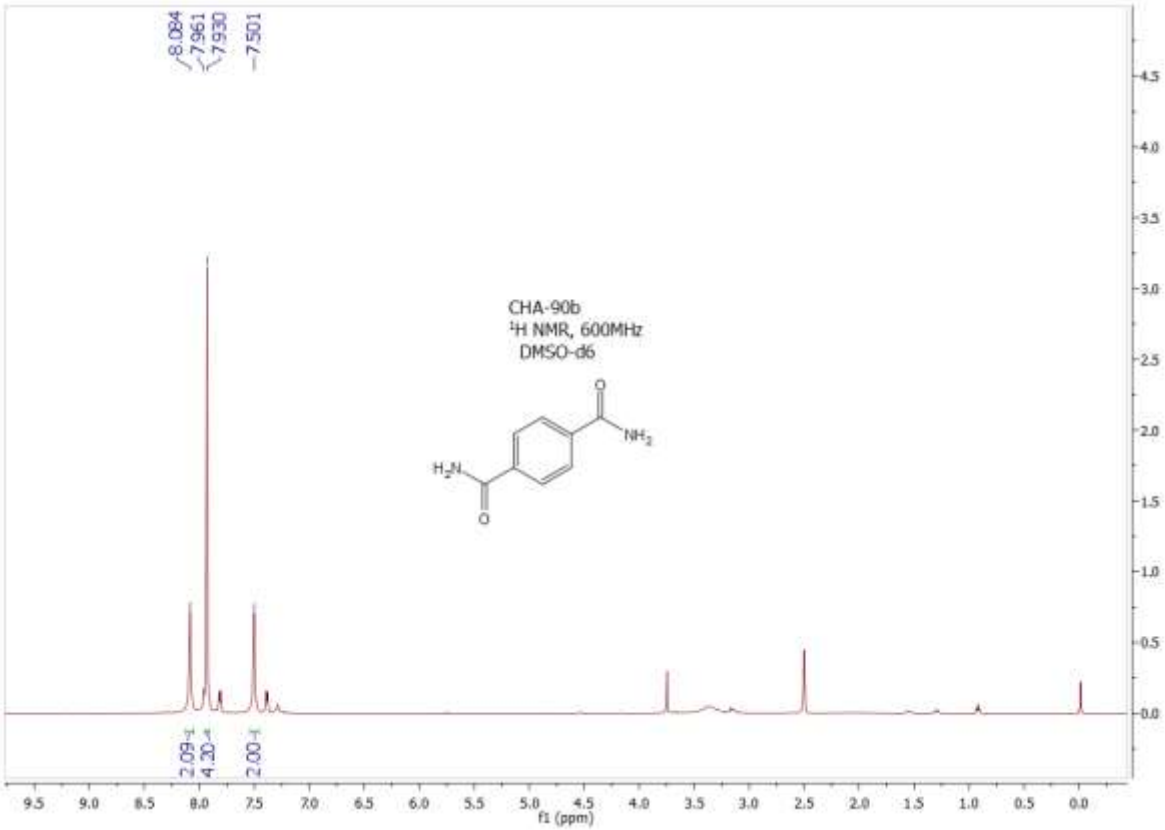
^{13}C NMR of 2n



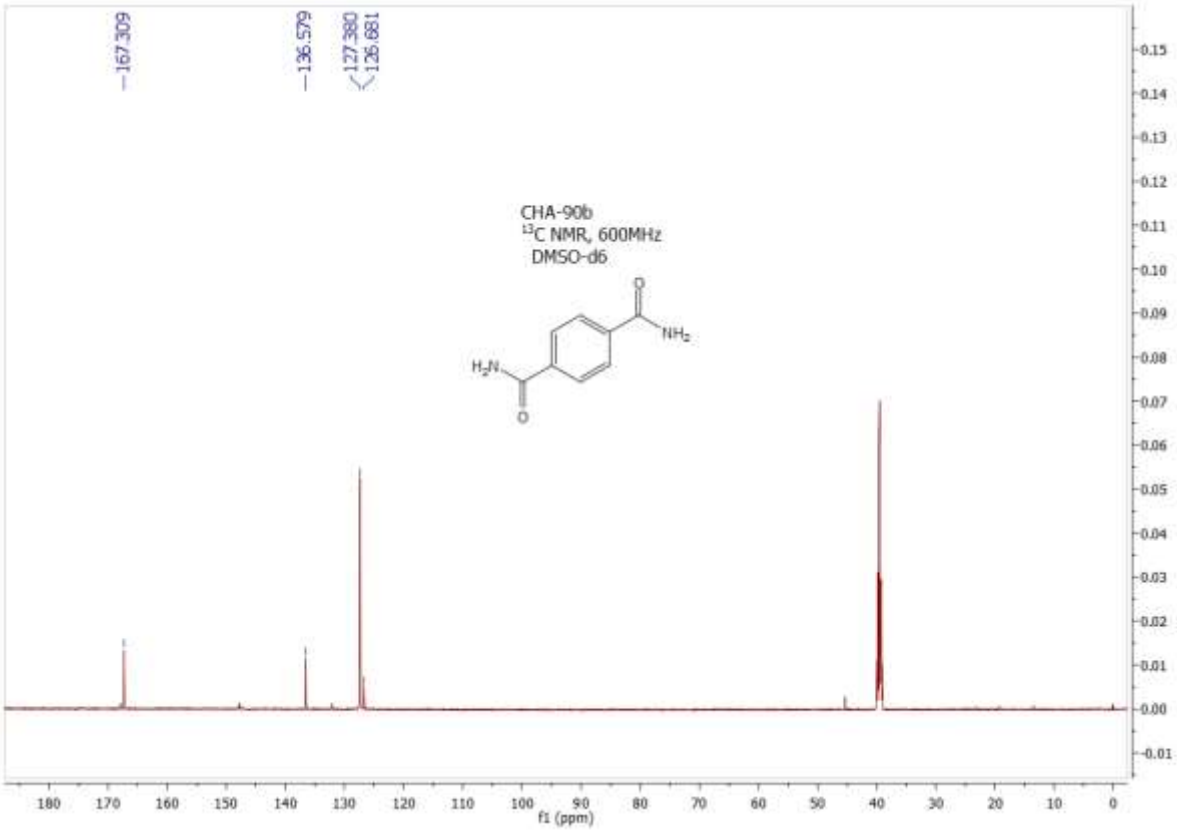
^{1}H NMR of 2o



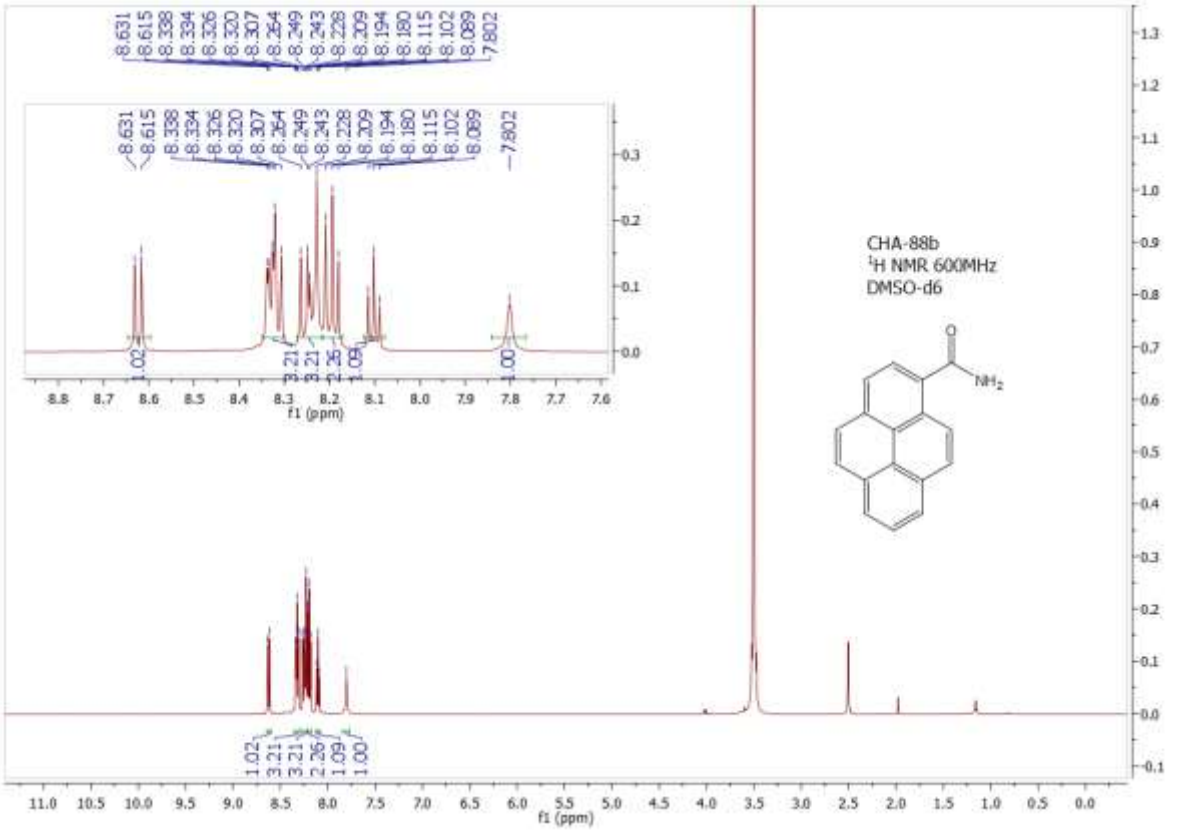
^{13}C NMR of 2o



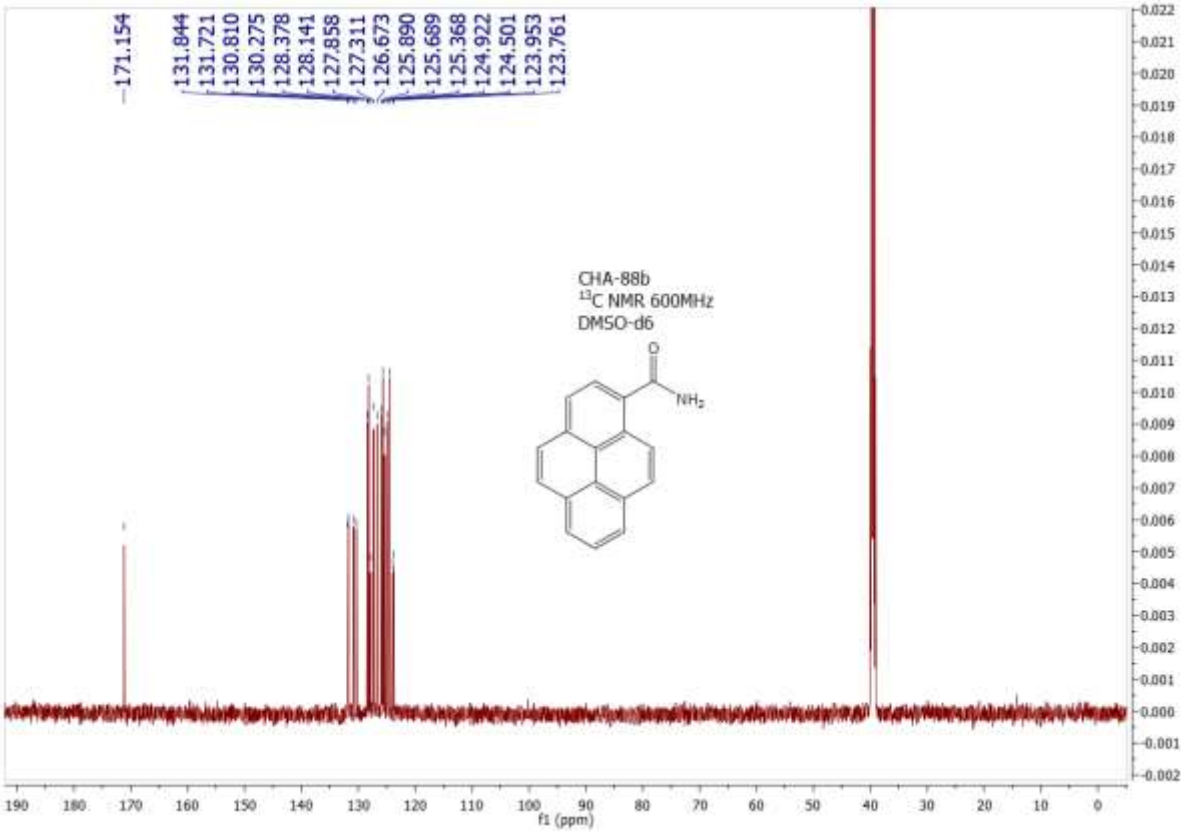
^{1}H NMR of 2p



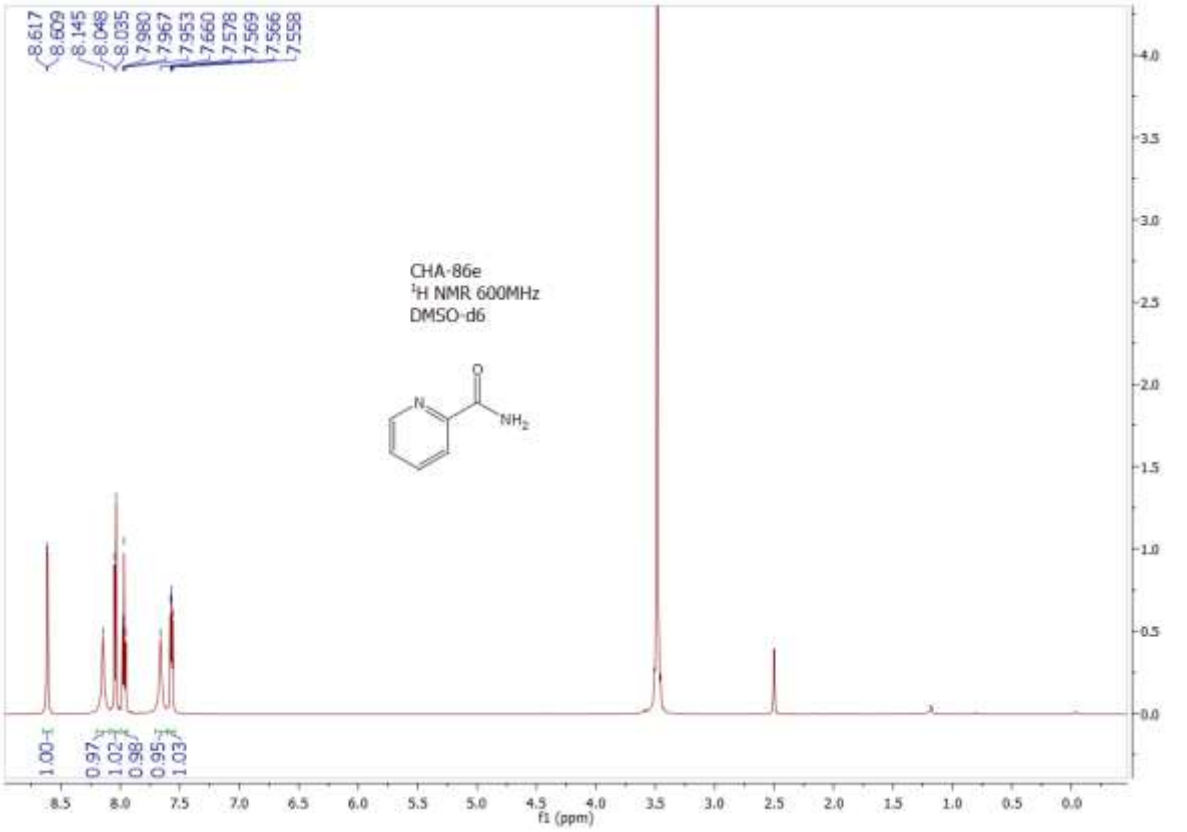
^{13}C NMR of 2p



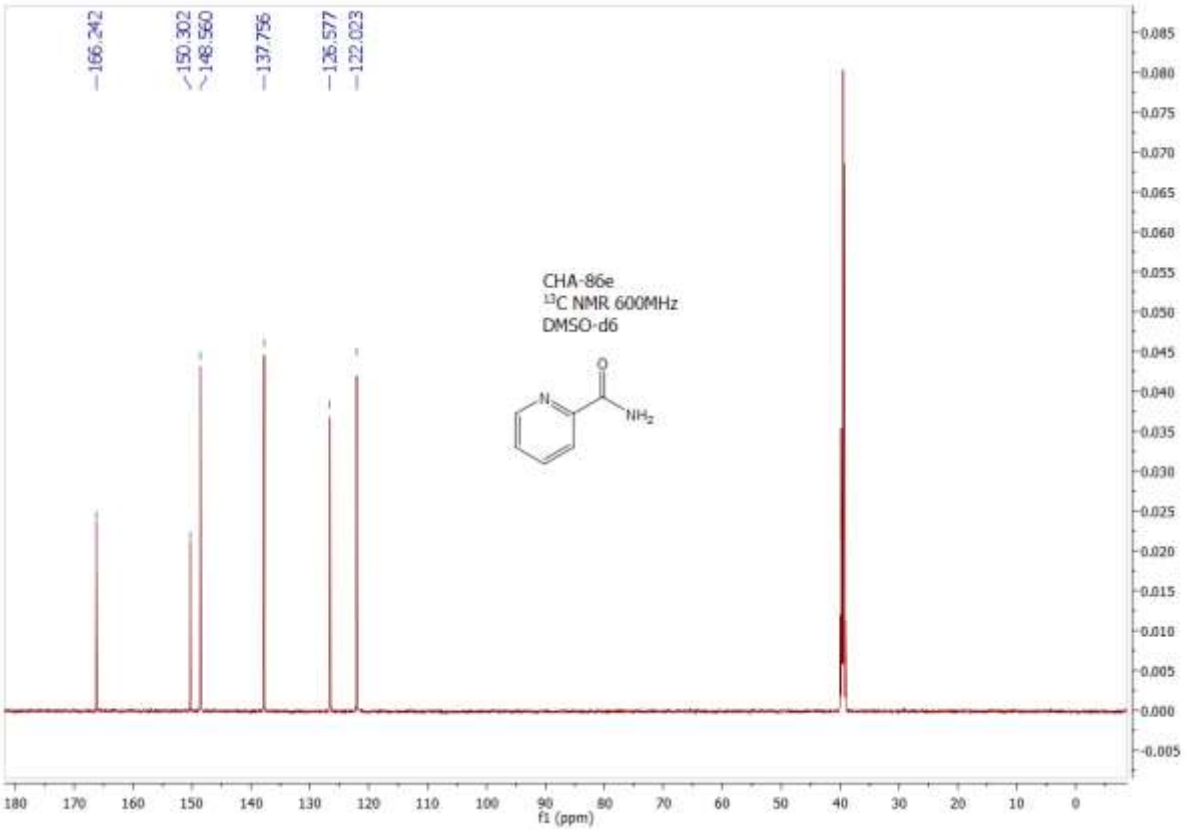
^{1}H NMR of 2q



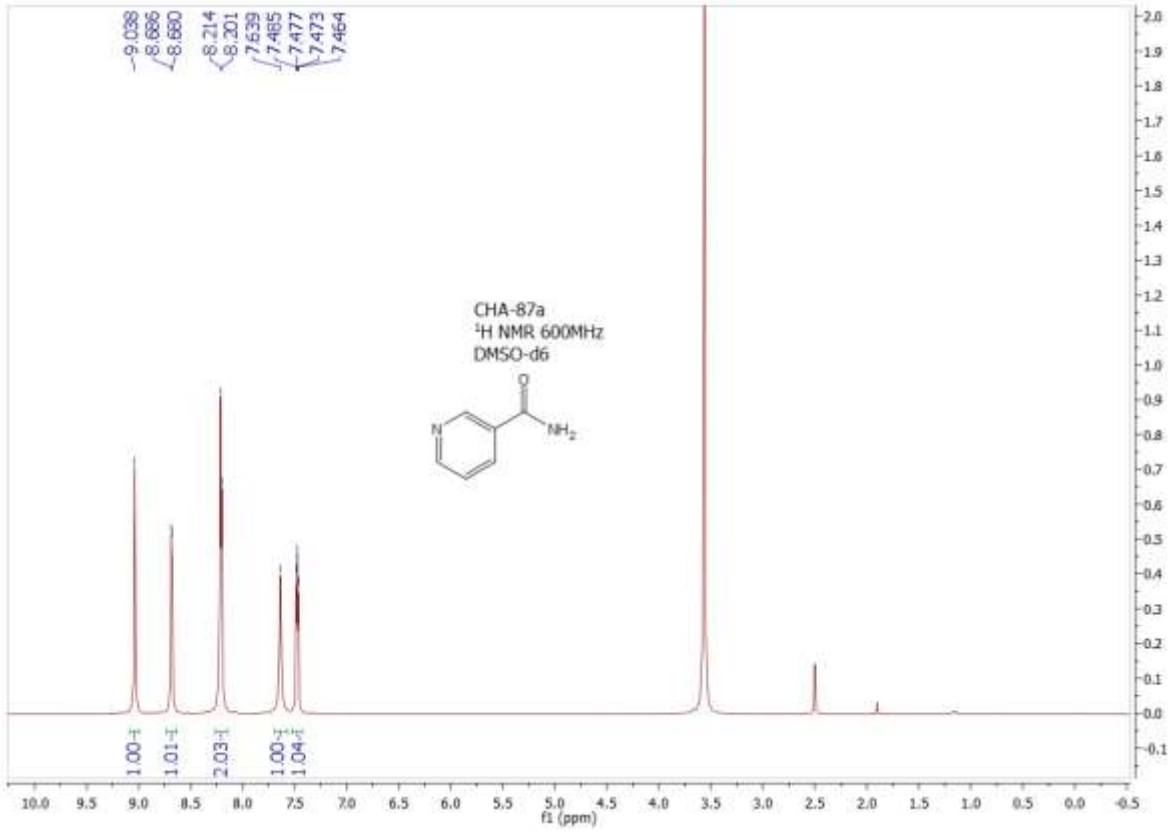
^{13}C NMR of 2q



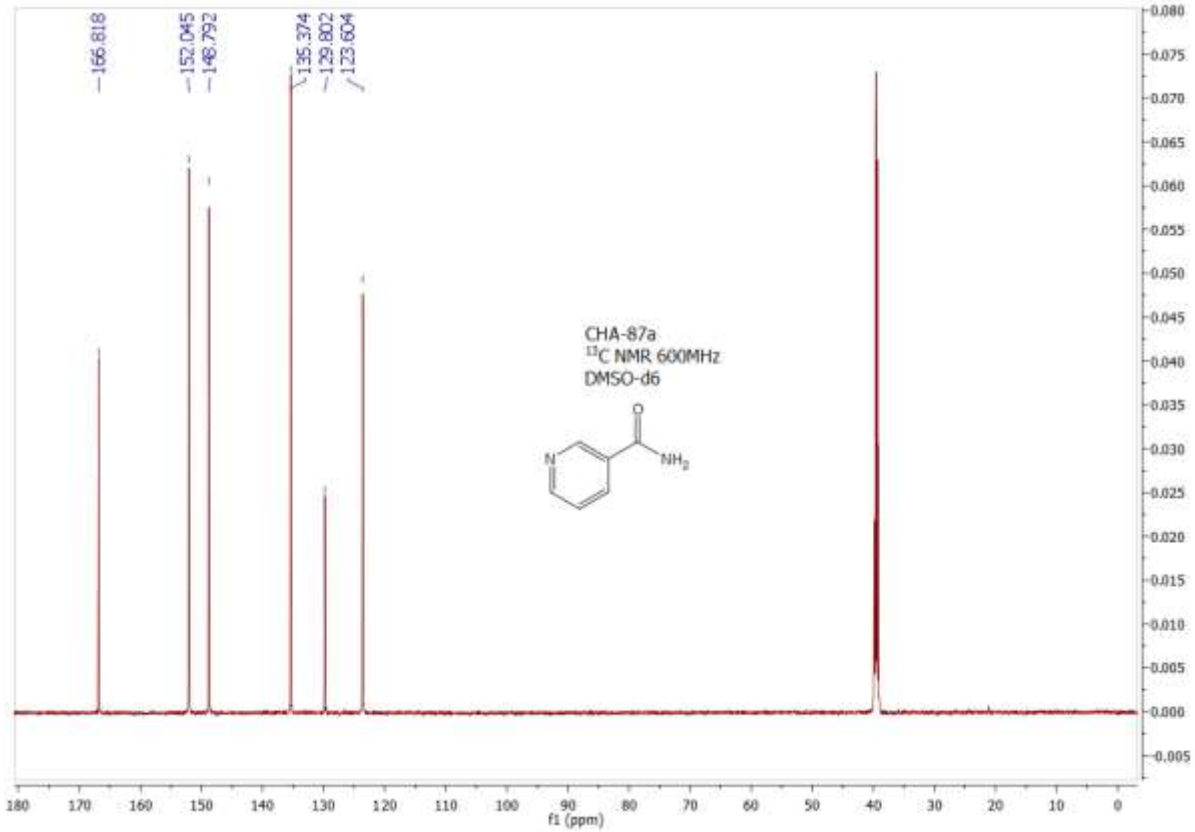
^{1}H NMR of 2r



^{13}C NMR of 2r



^{1}H NMR of 2s



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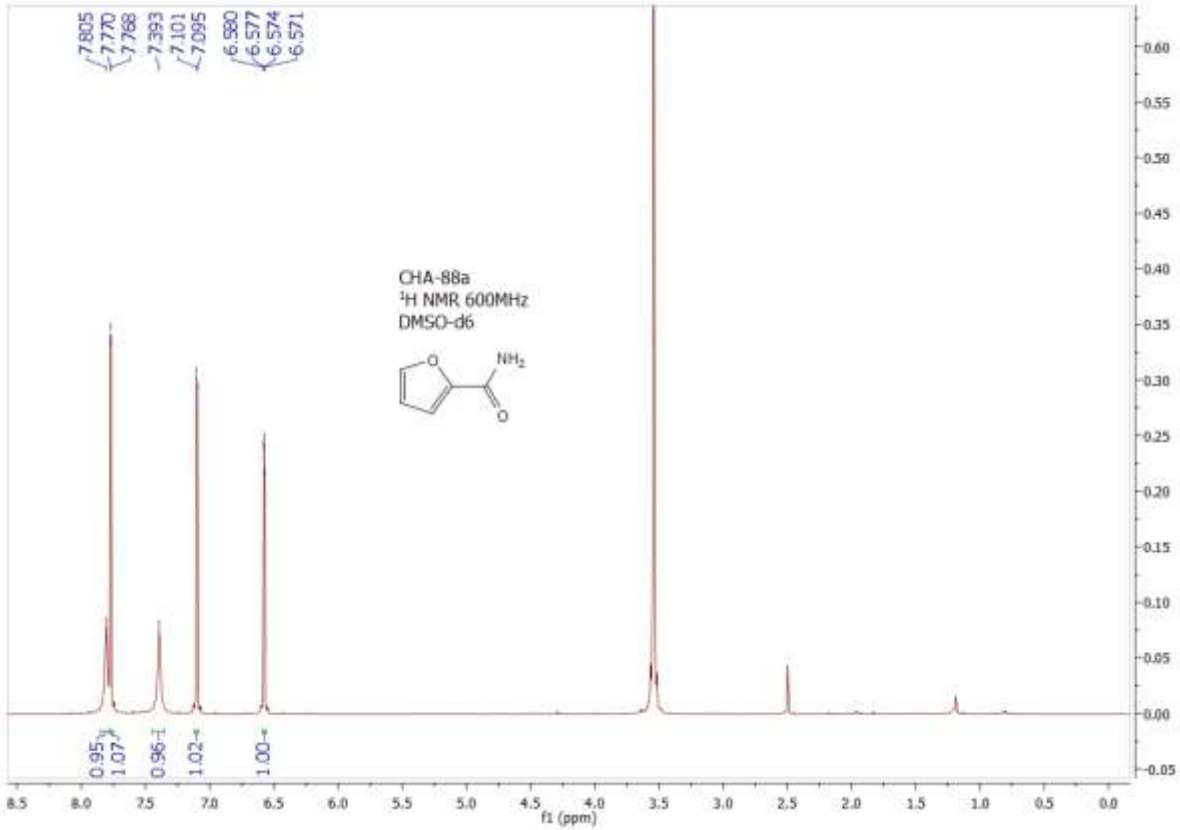
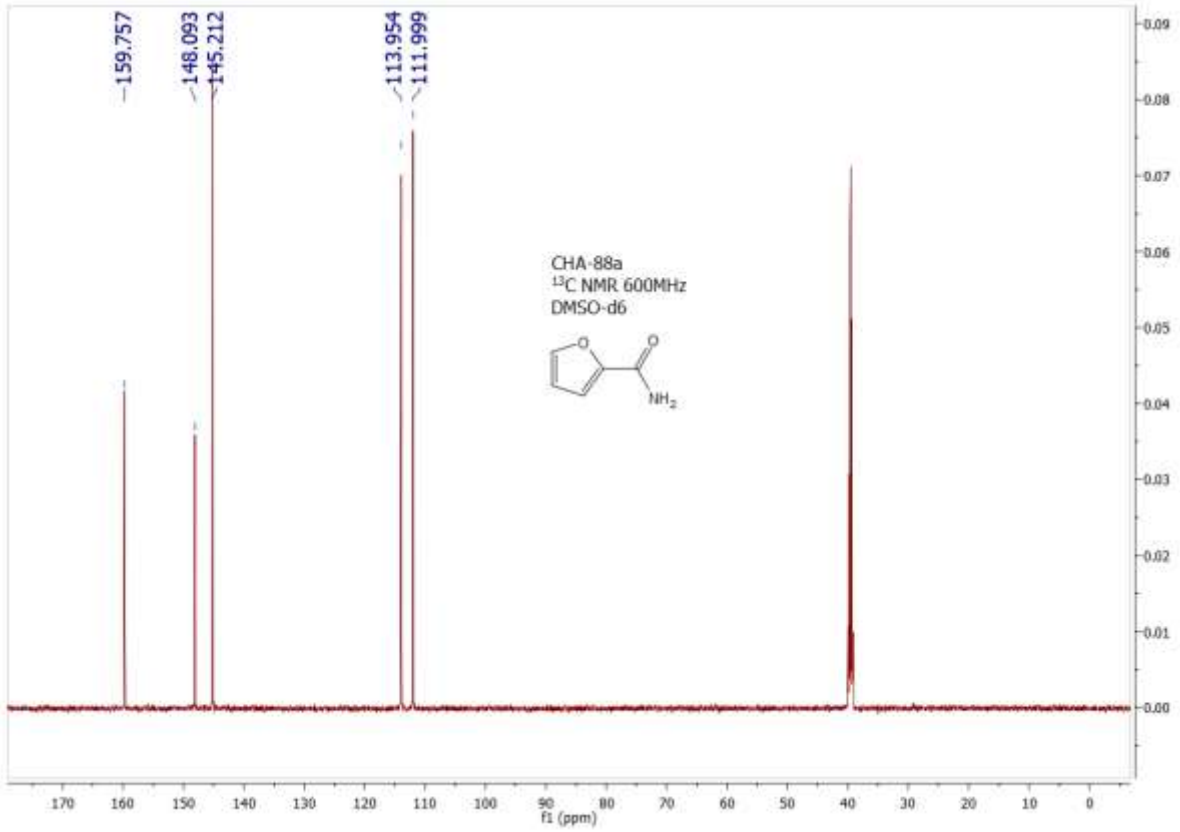
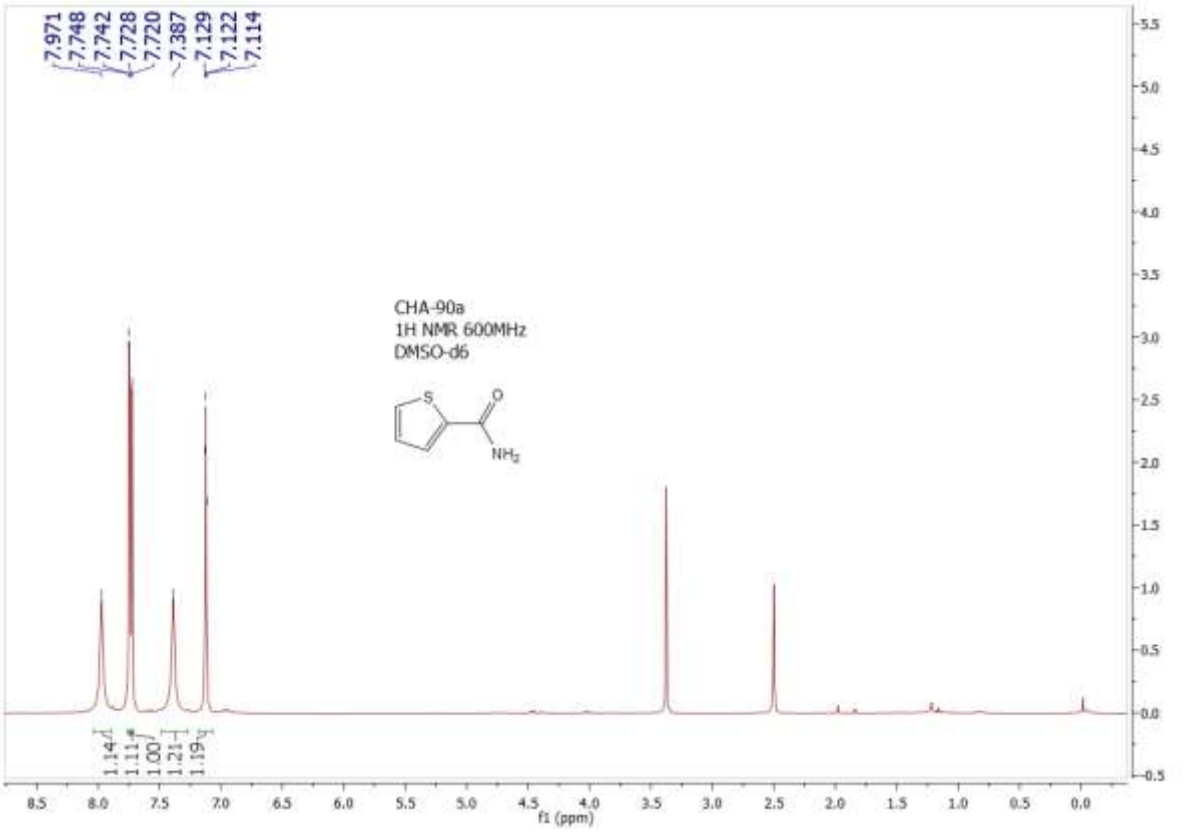


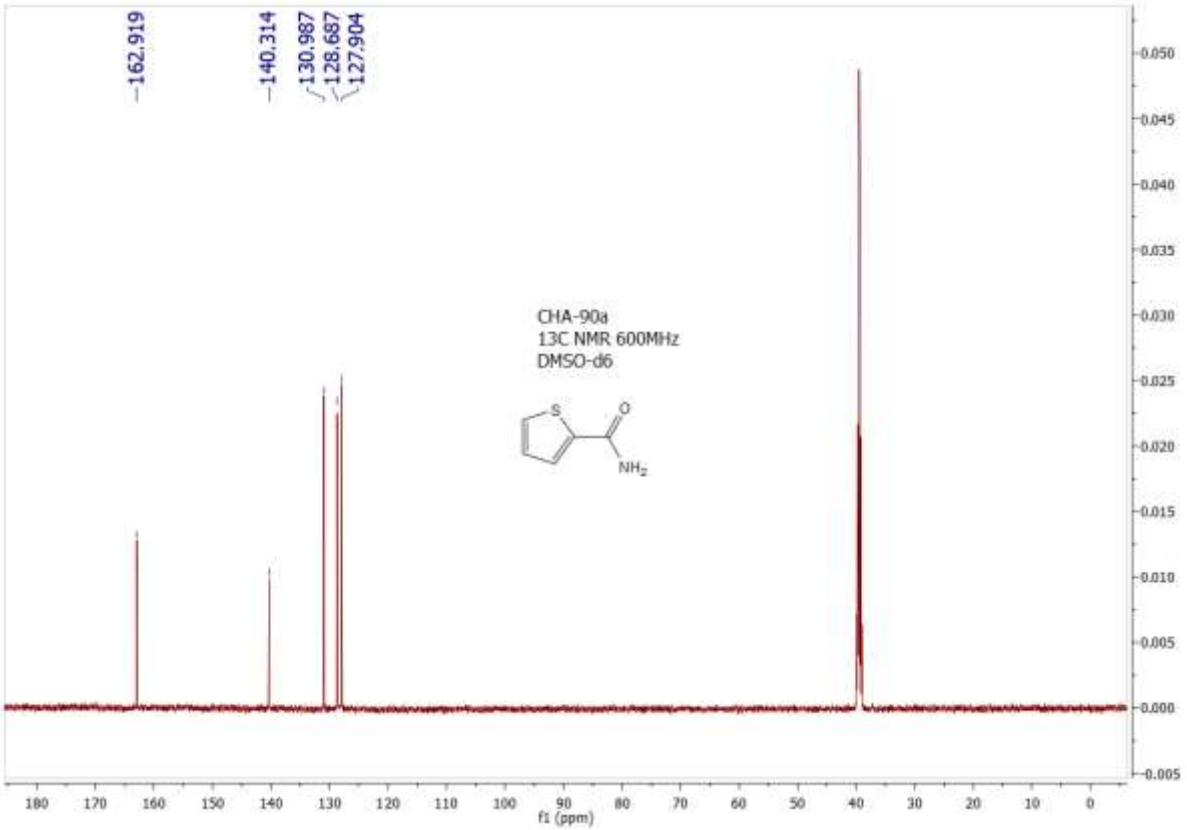
^{1}H NMR of 2t



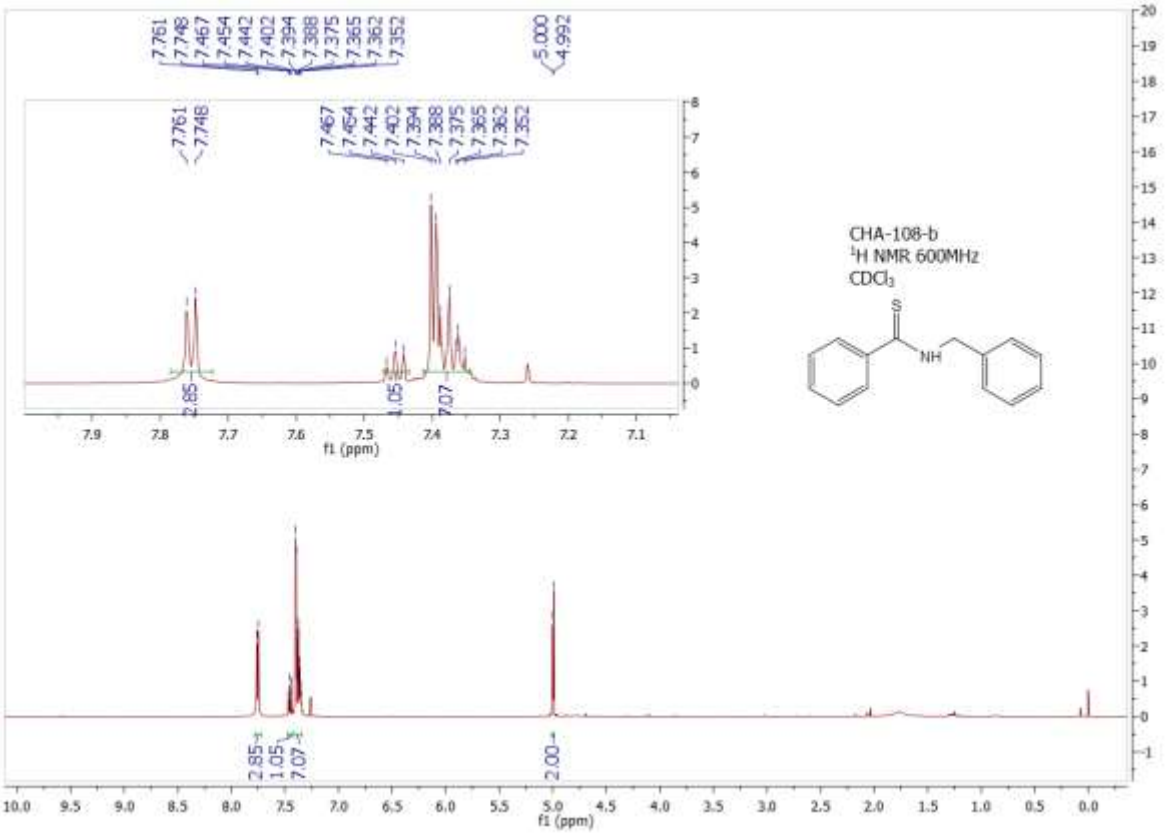
^{13}C NMR of 2t



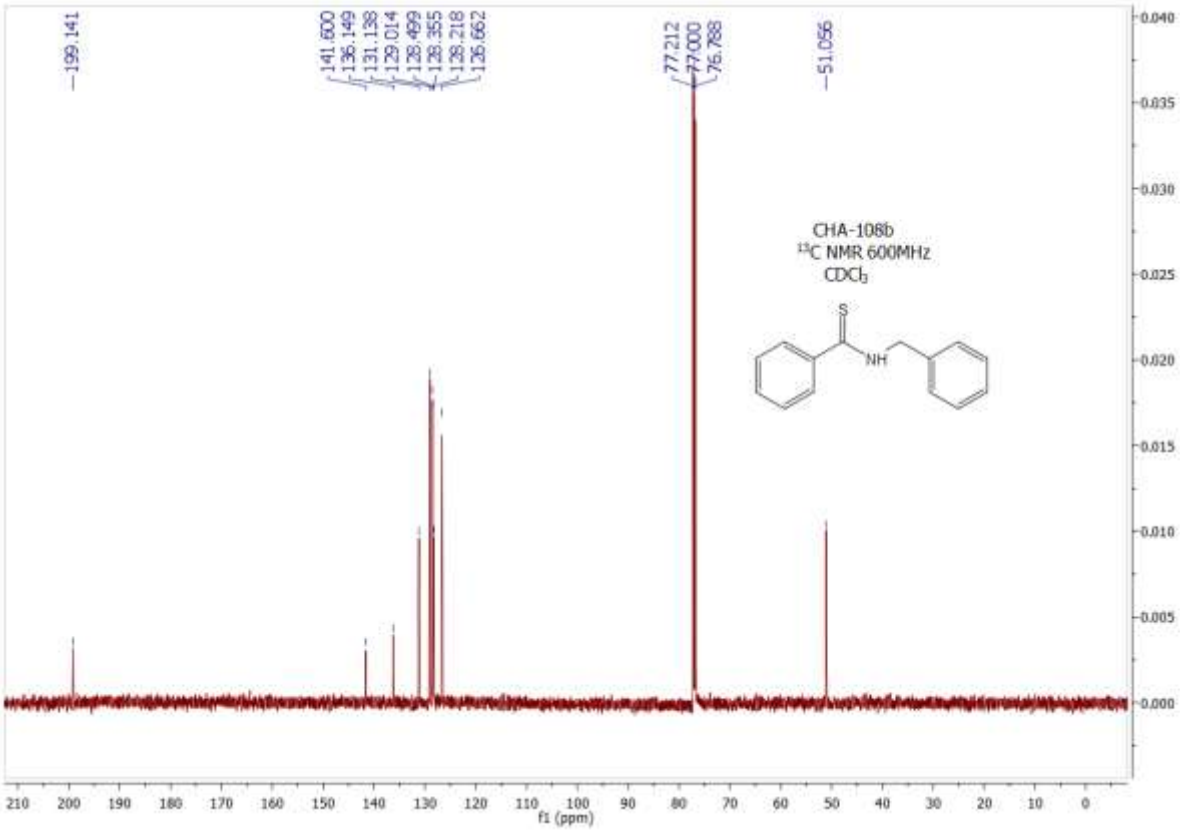
^{1}H NMR of 2u



^{13}C NMR of 2u

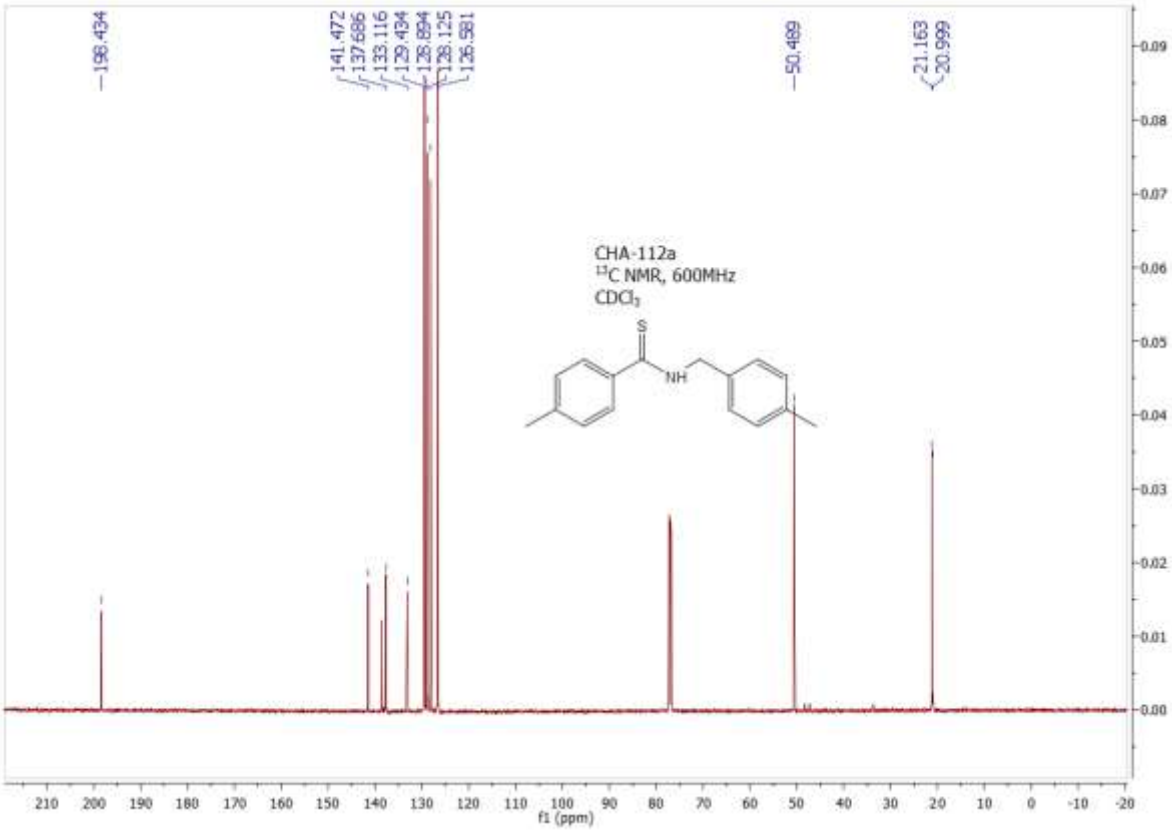


^{1}H NMR of 3a



^{13}C NMR of 3a

^{1}H NMR of 3b



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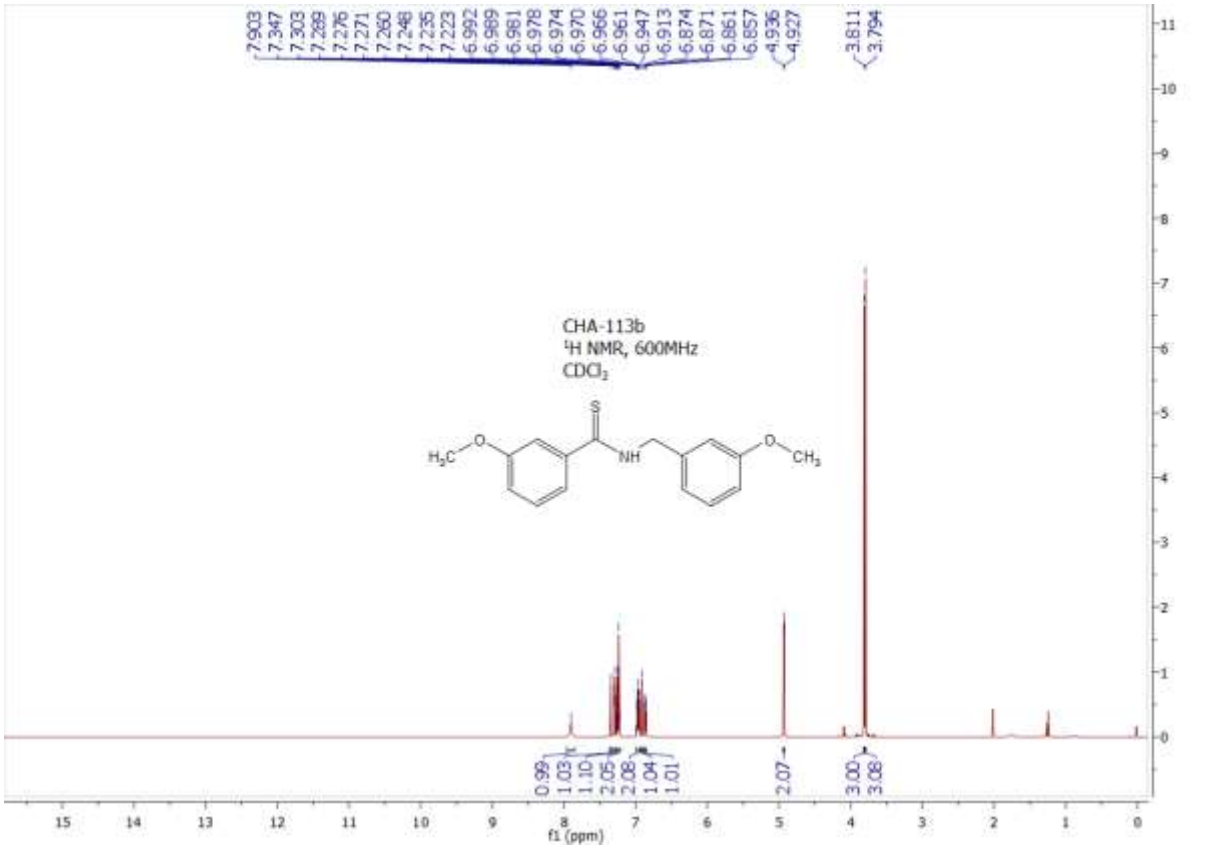
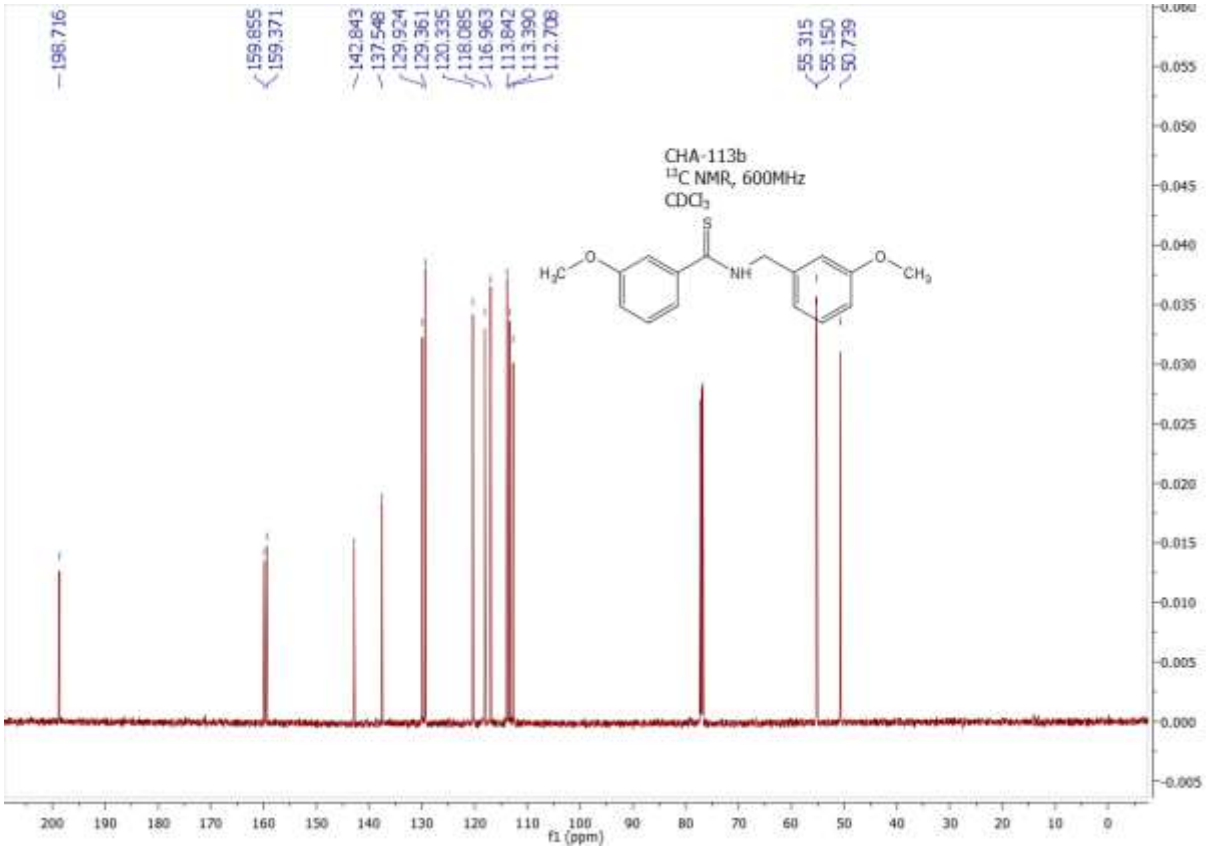
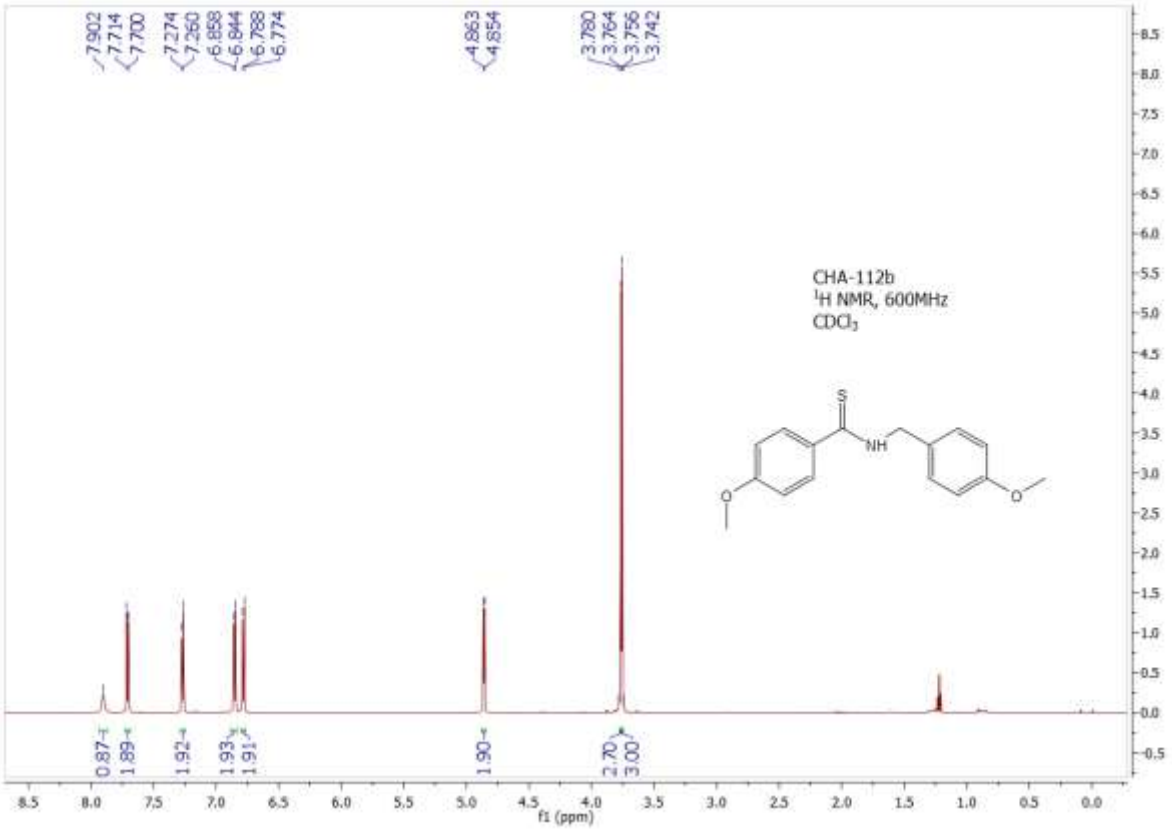


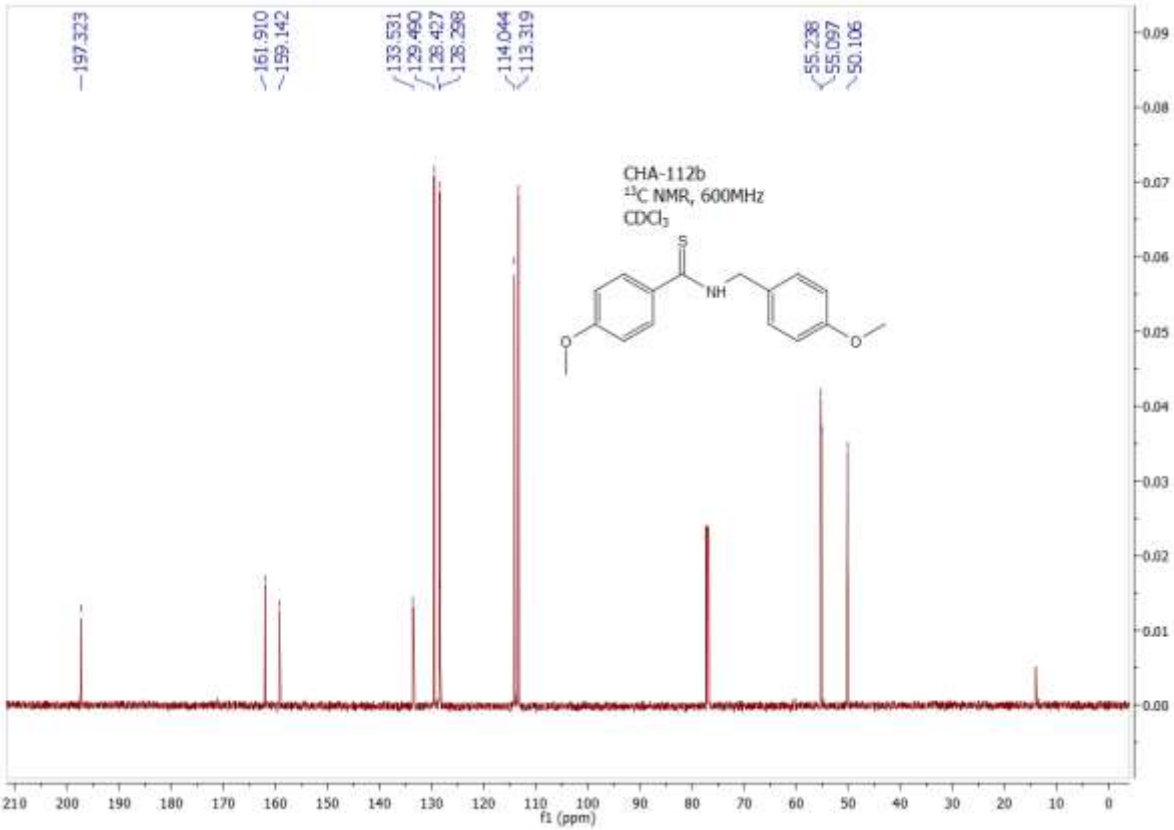
^{1}H NMR of 3c



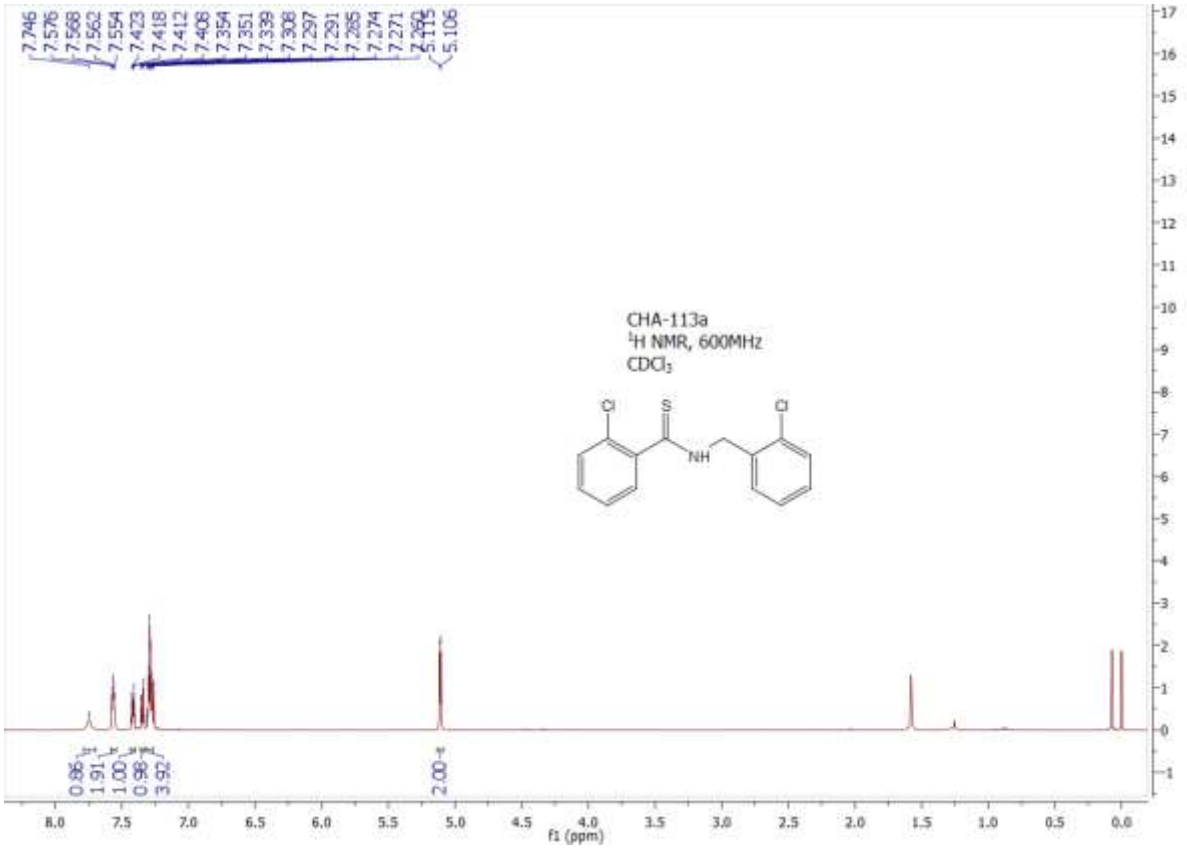
^{13}C NMR of 3c



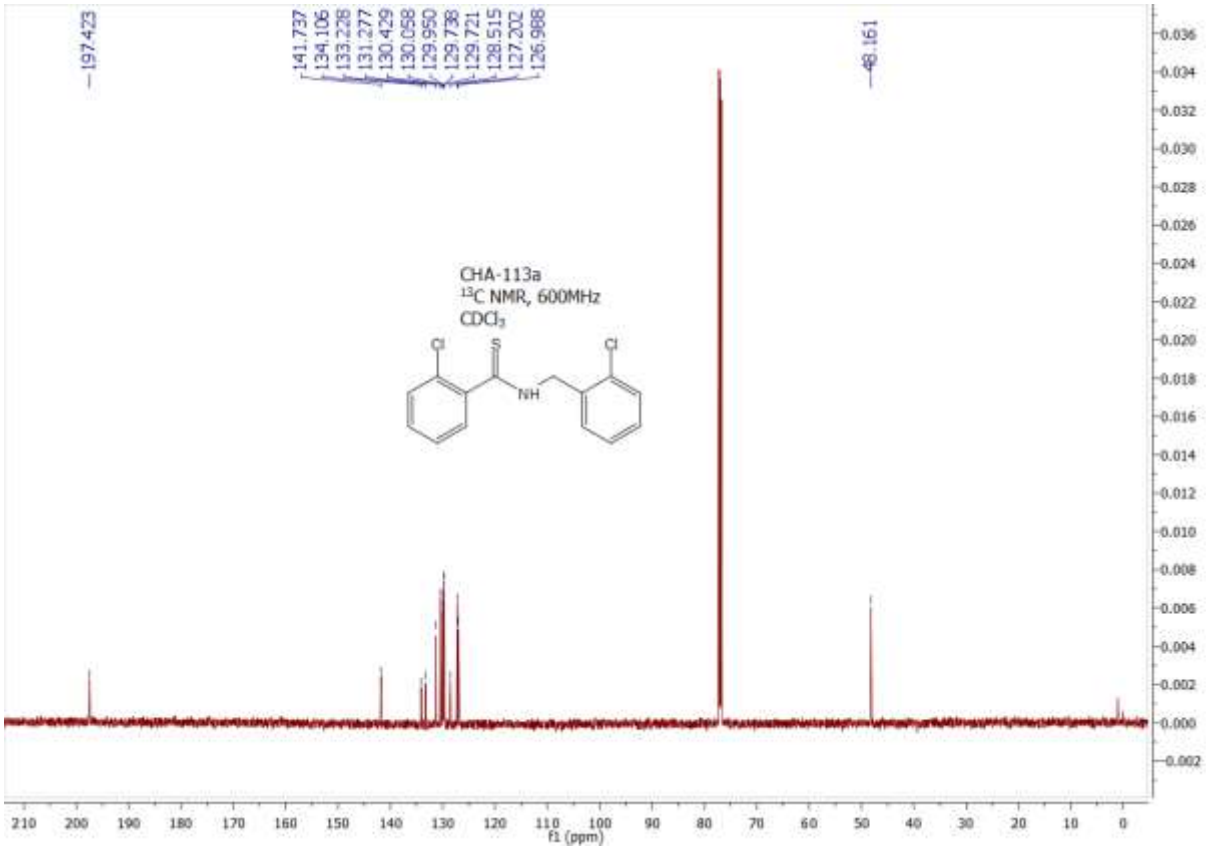
^{1}H NMR of 3d



^{13}C NMR of 3d



^{1}H NMR of 3e



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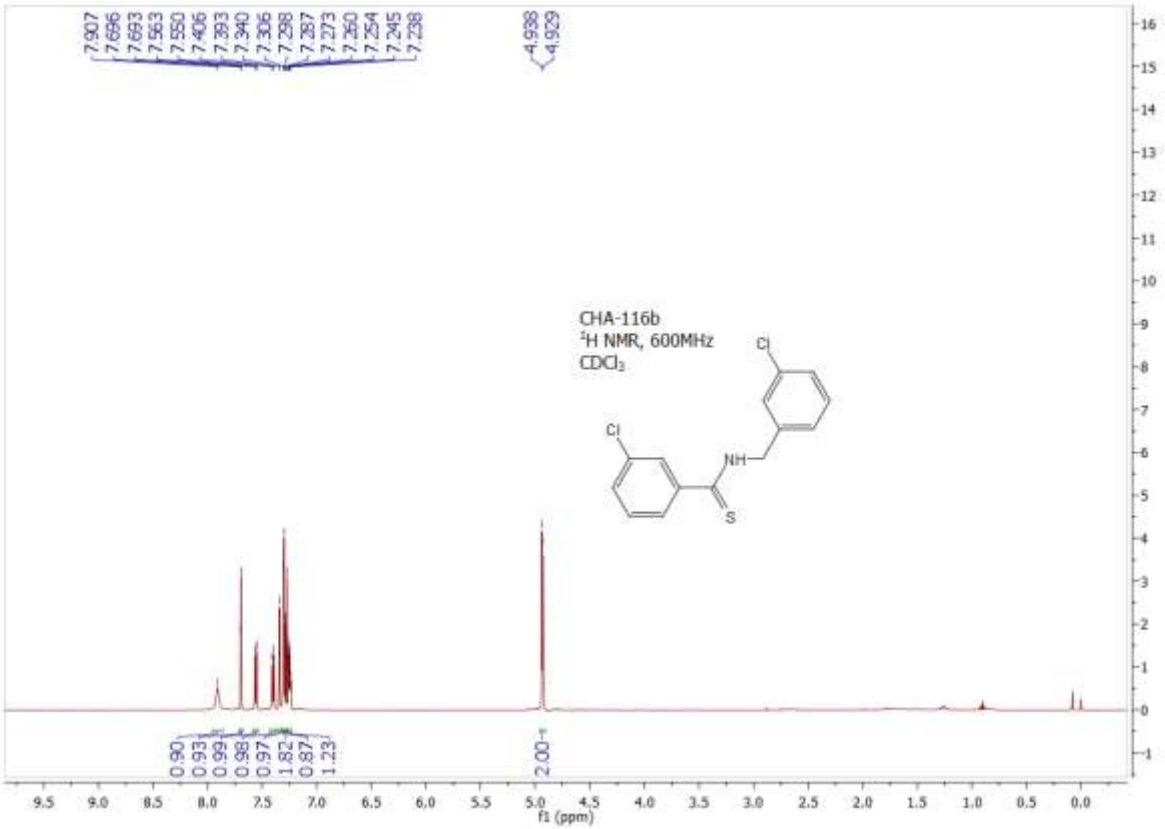
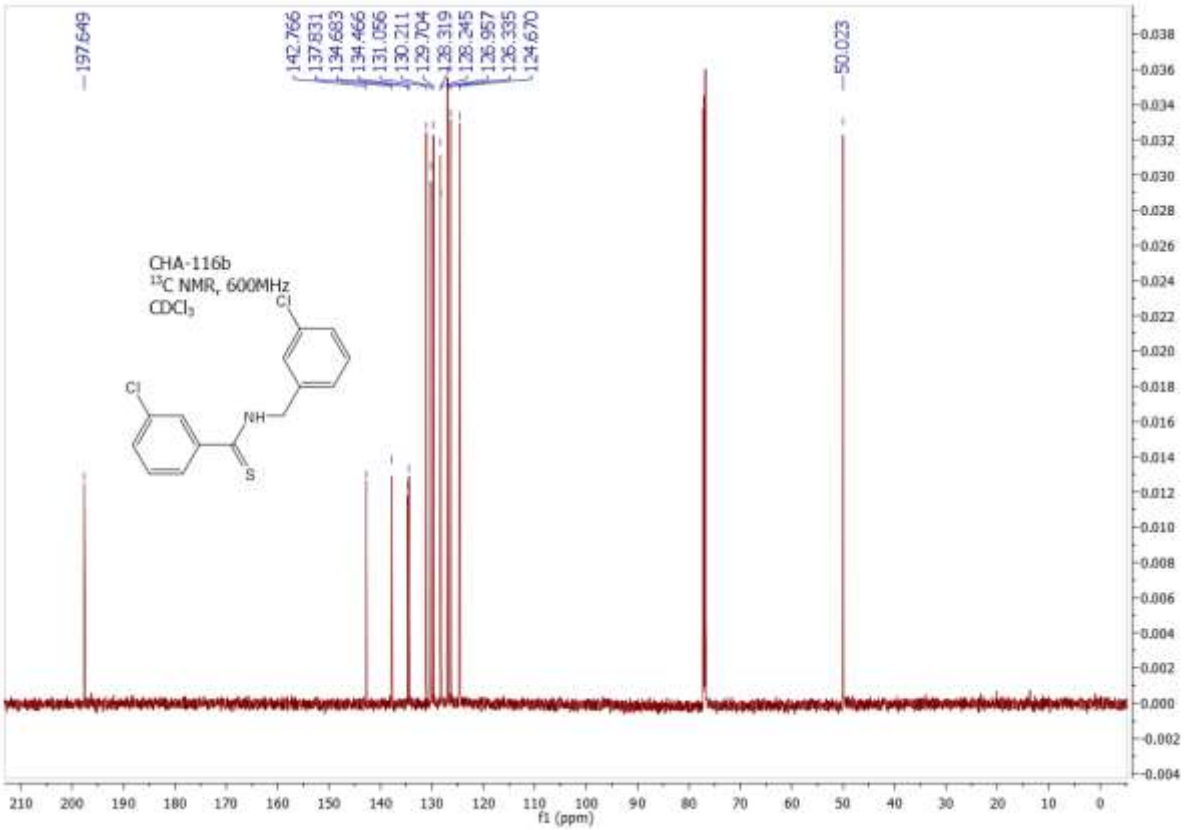
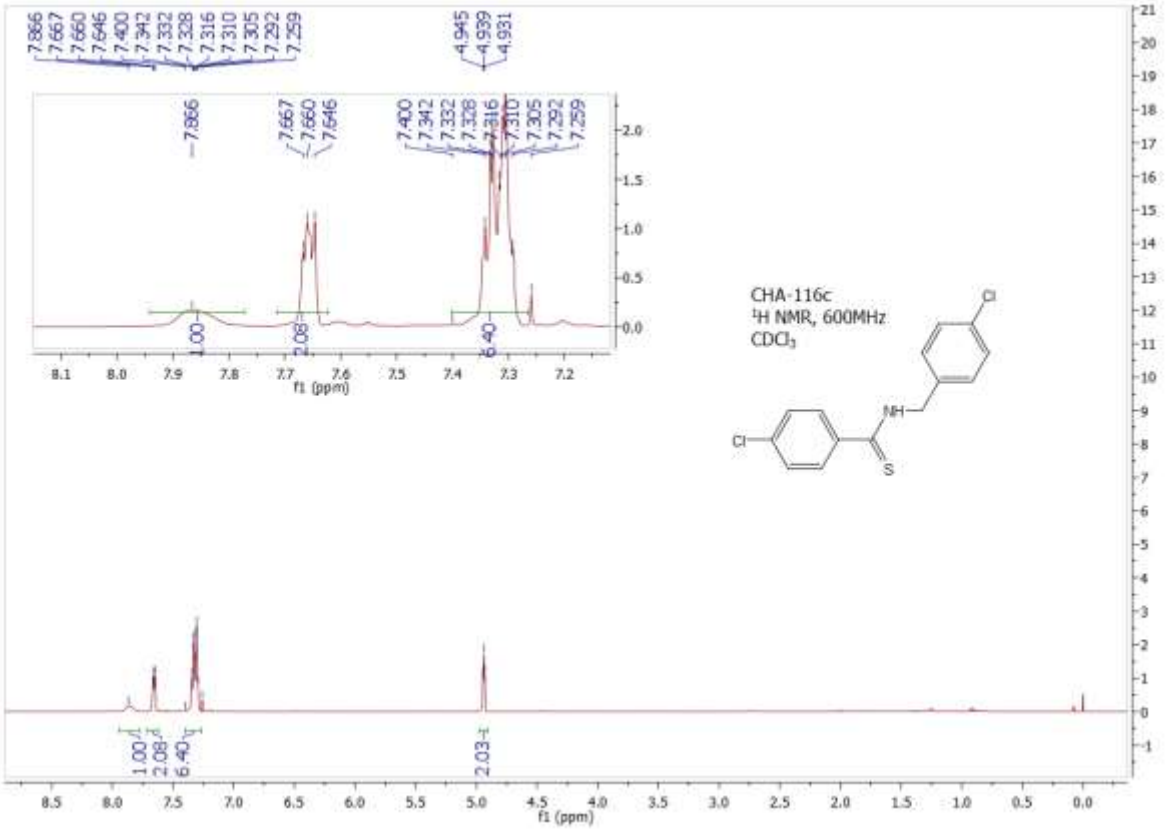


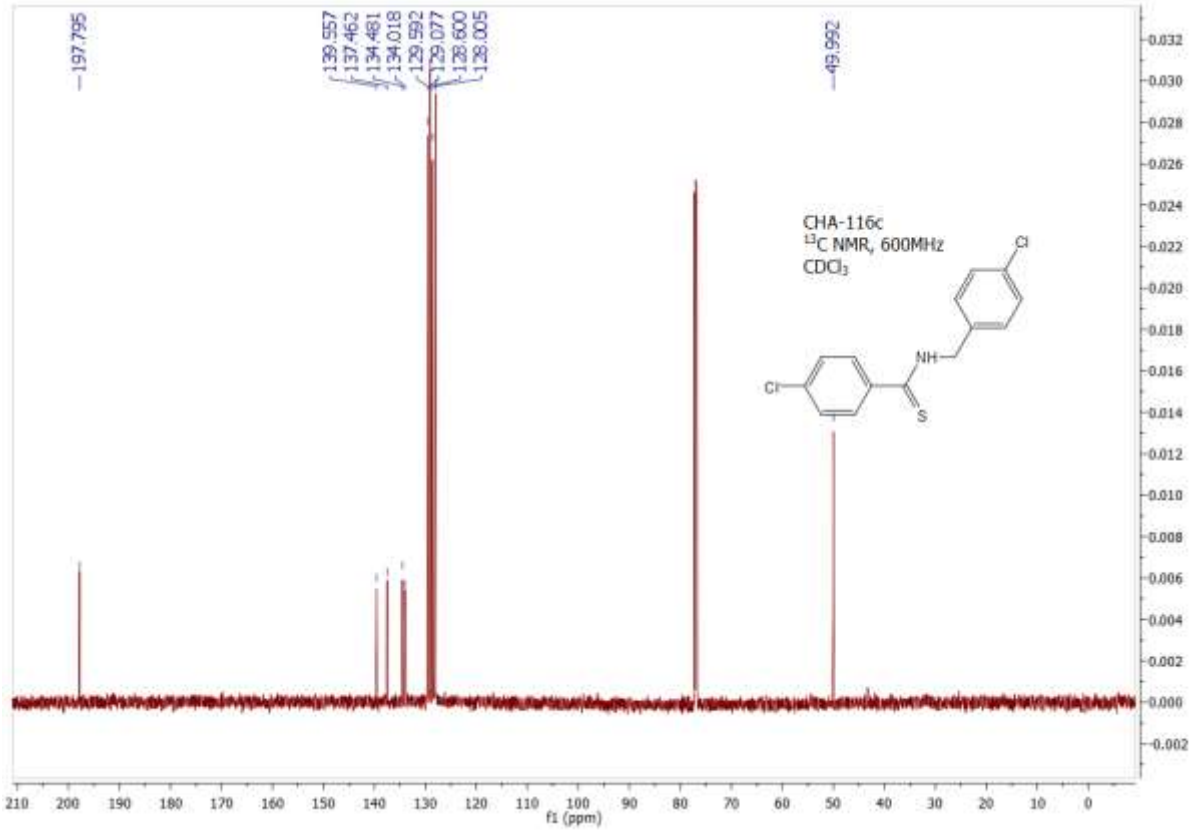
^{1}H NMR of 3f



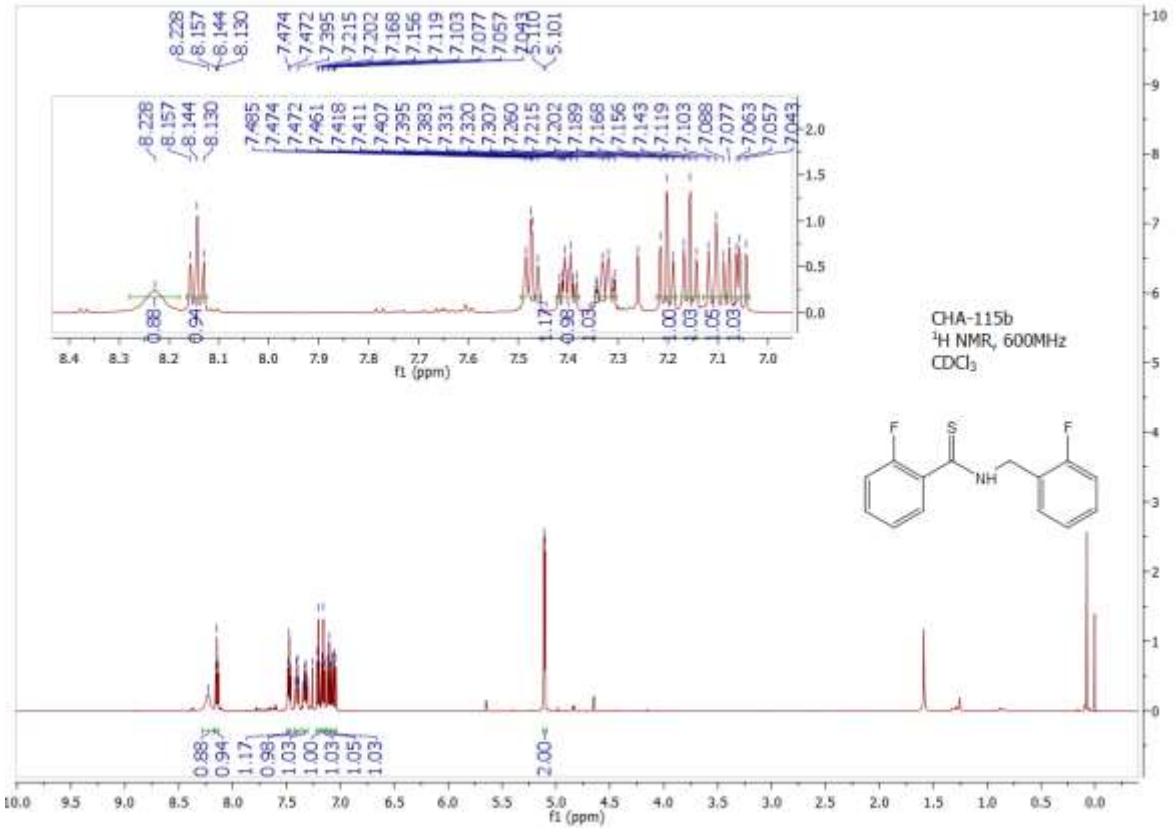
^{13}C NMR of 3f



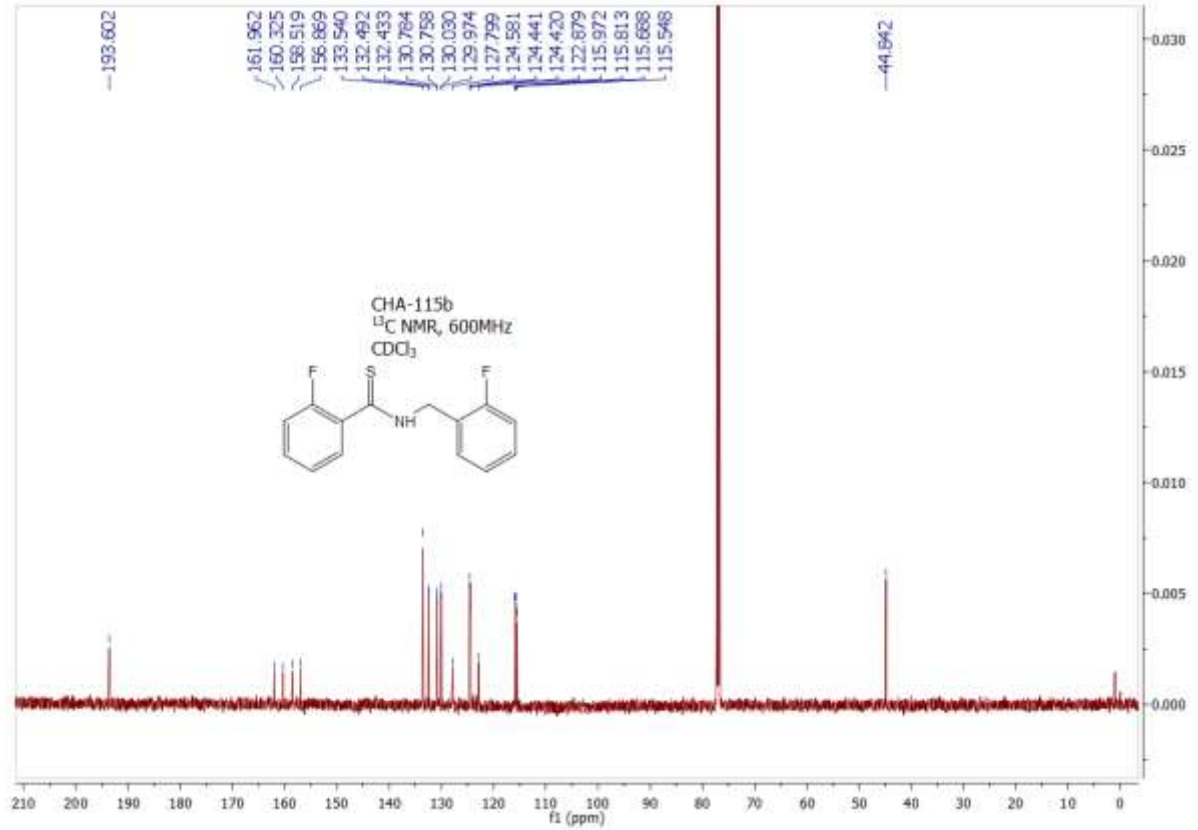
^{1}H NMR of 3g



^{13}C NMR of 3g



^{1}H NMR of 3h



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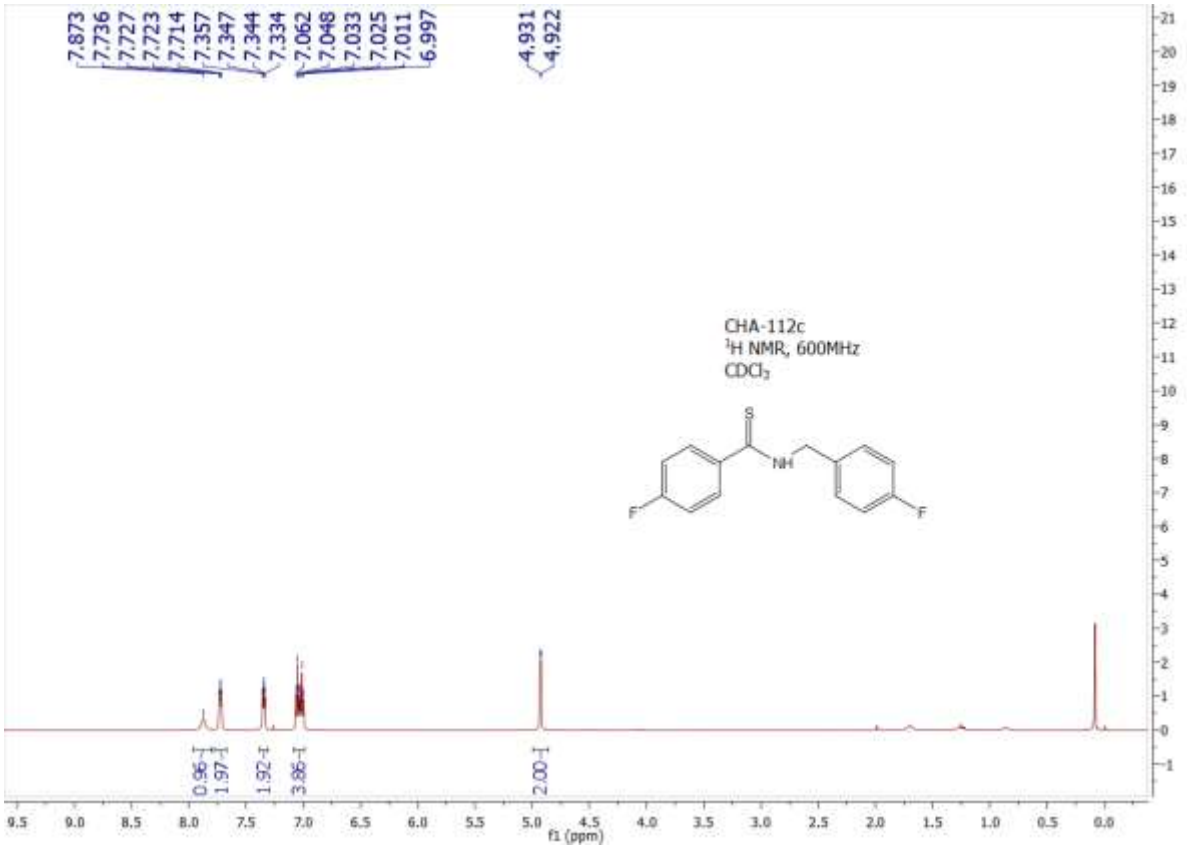
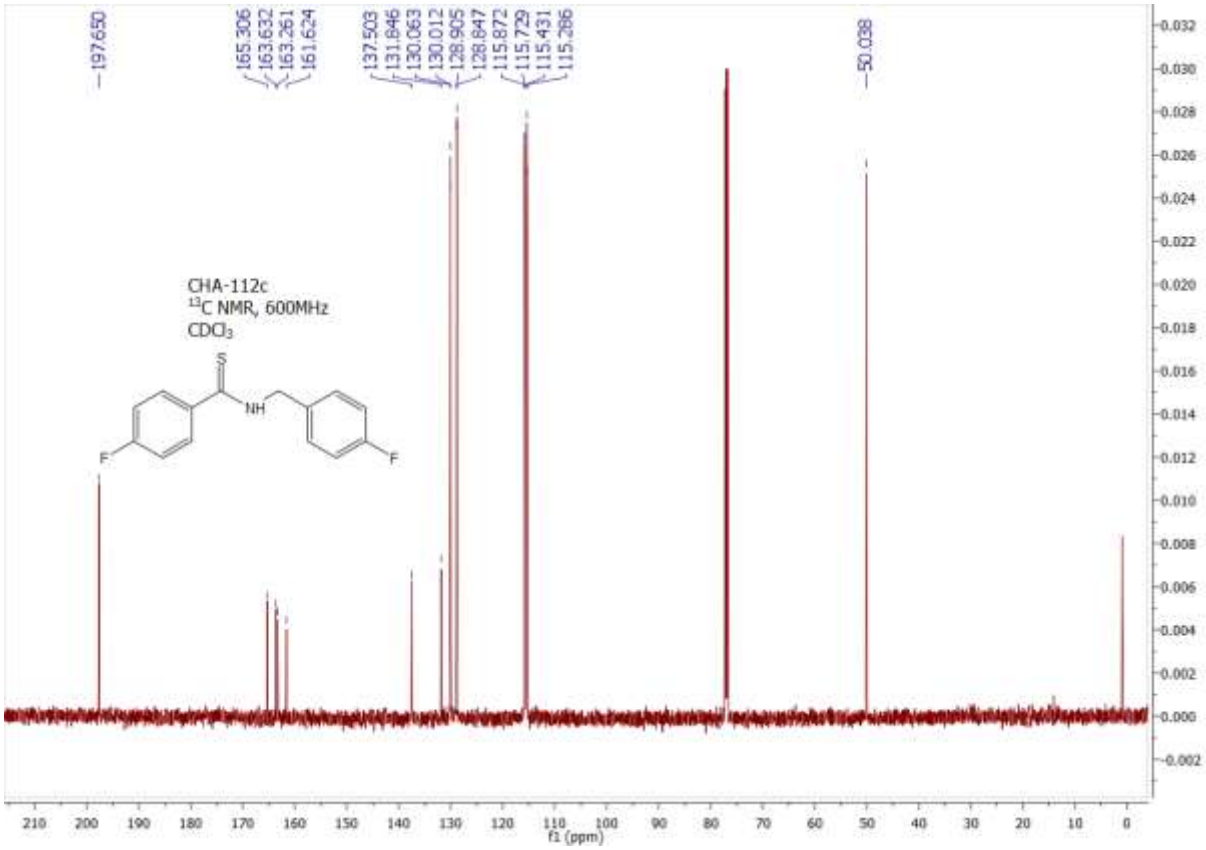
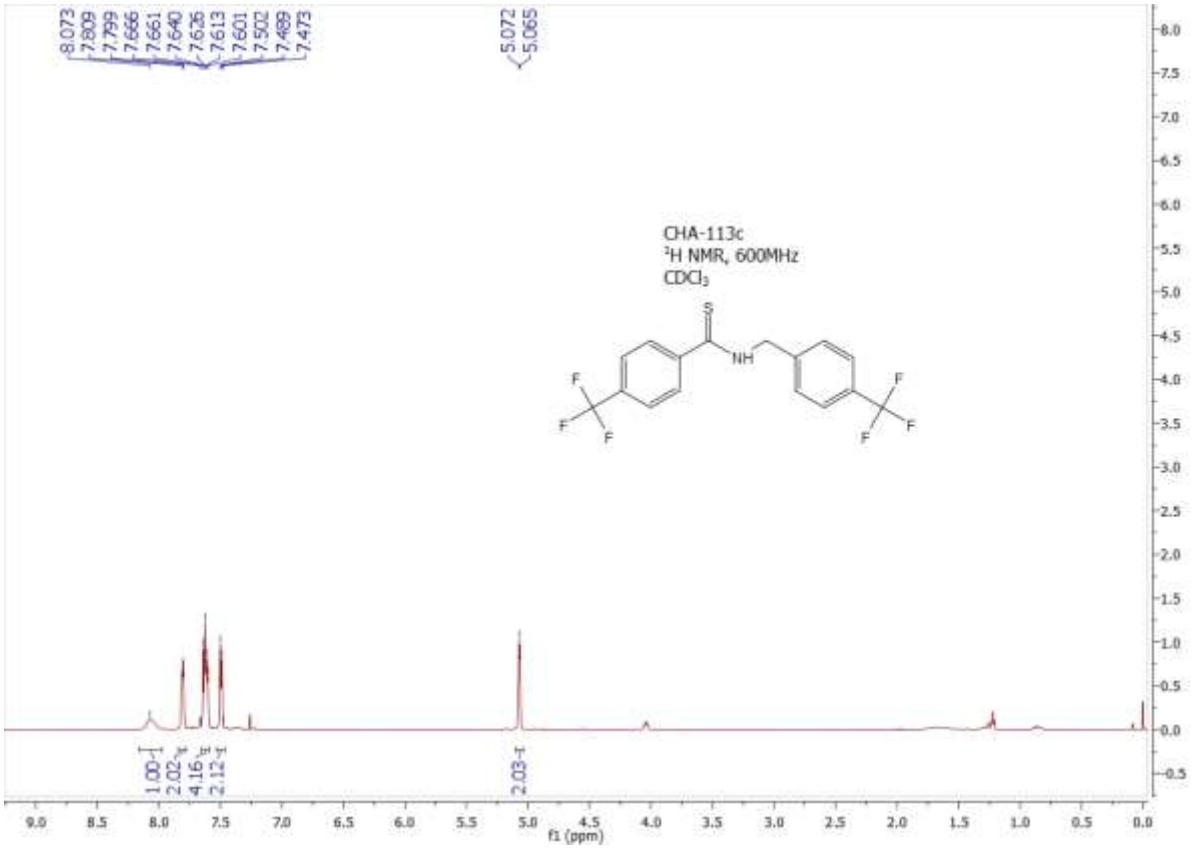


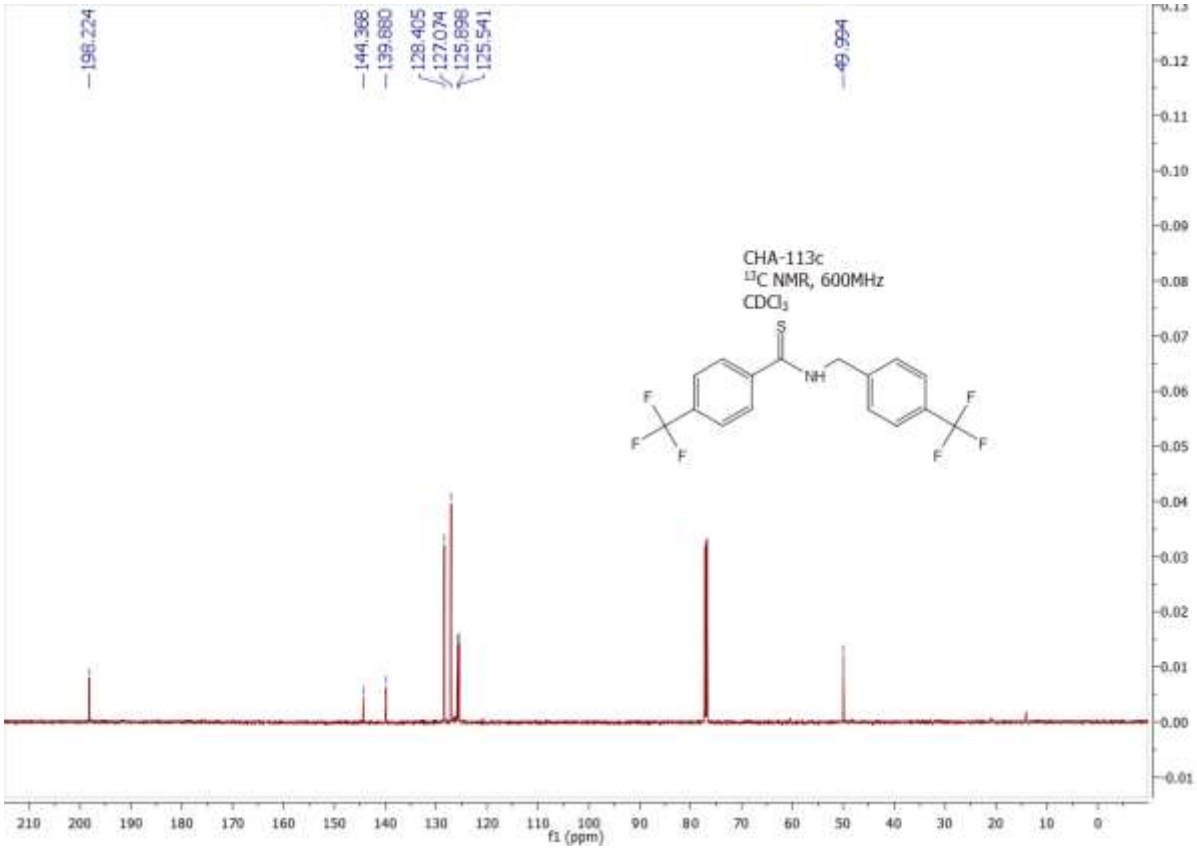
^{1}H NMR of 3i



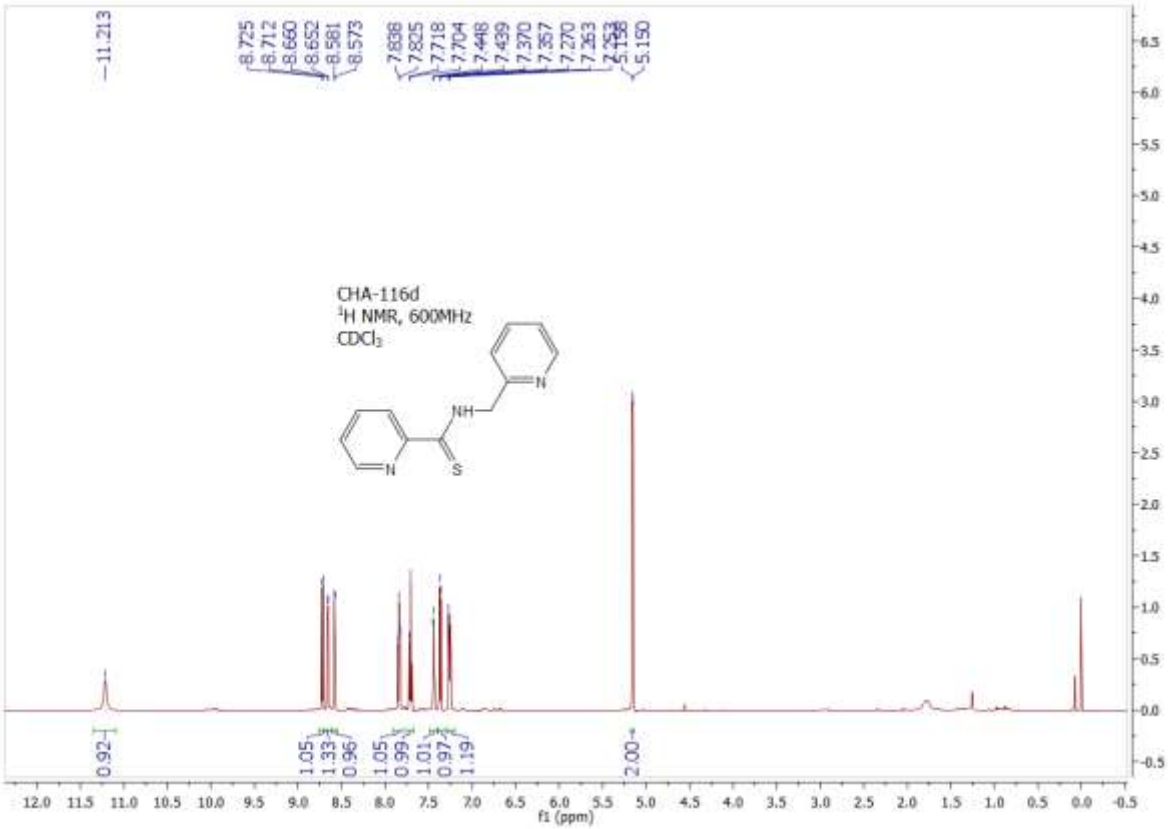
^{13}C NMR of 3i



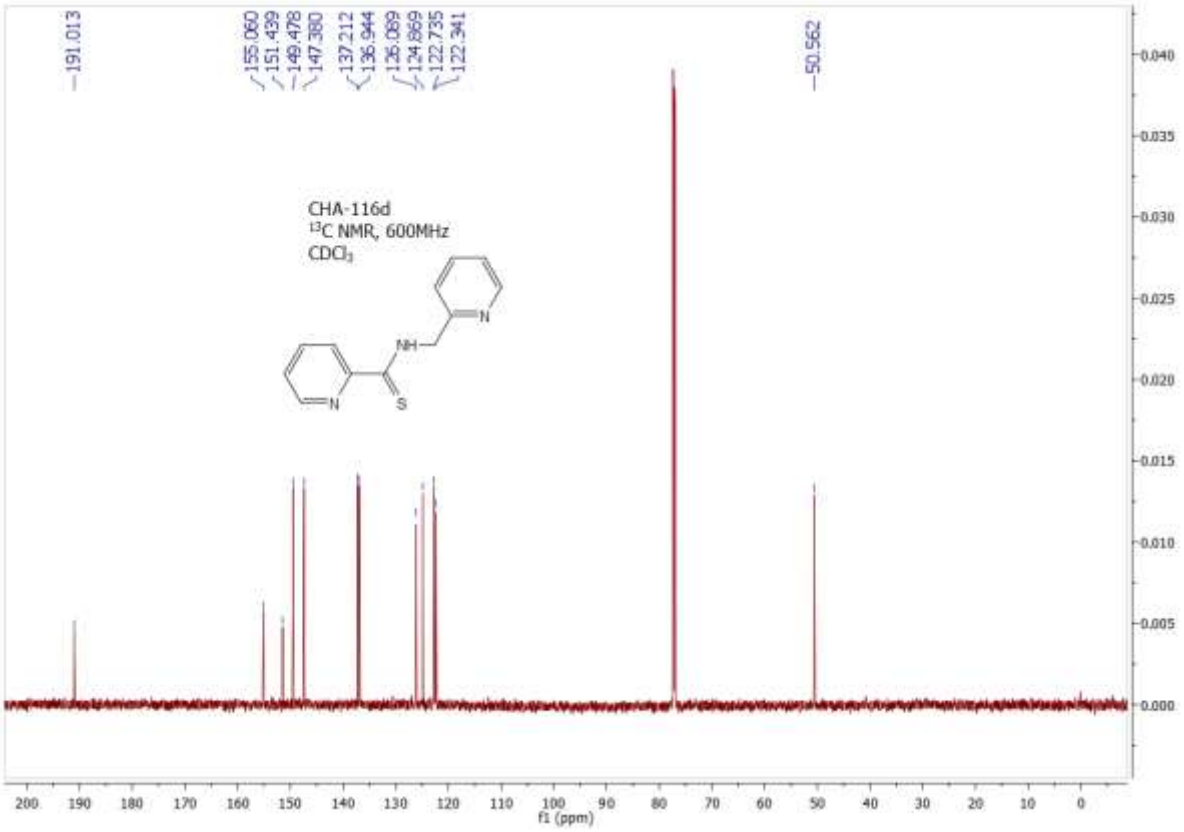
^{1}H NMR of 3j



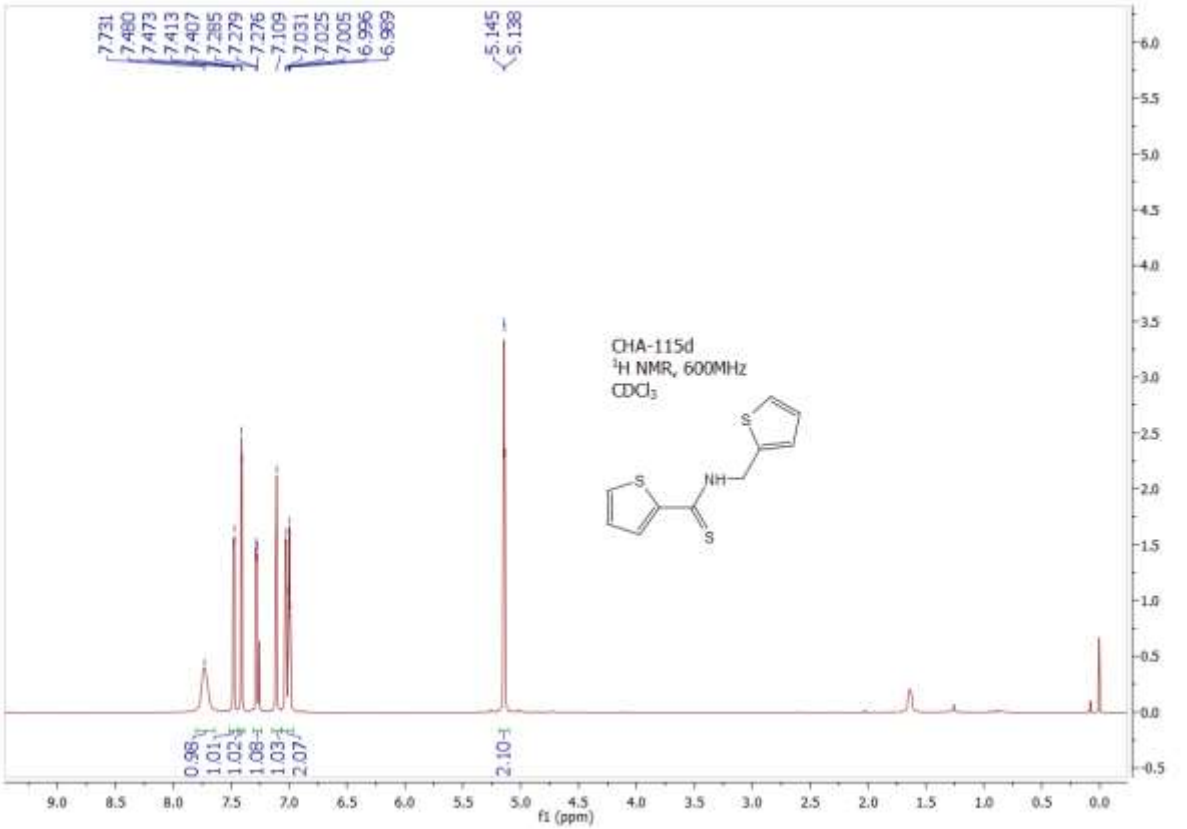
^{13}C NMR of 3j



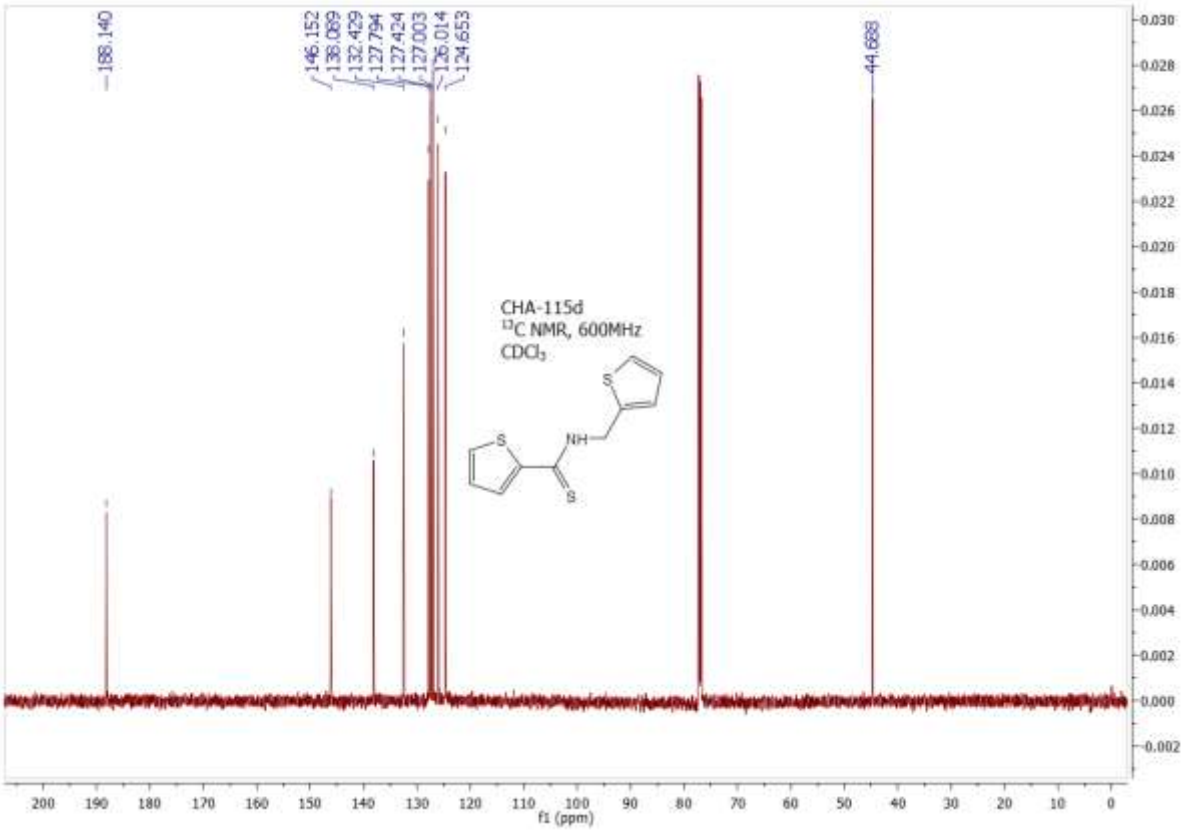
^{1}H NMR of 3k



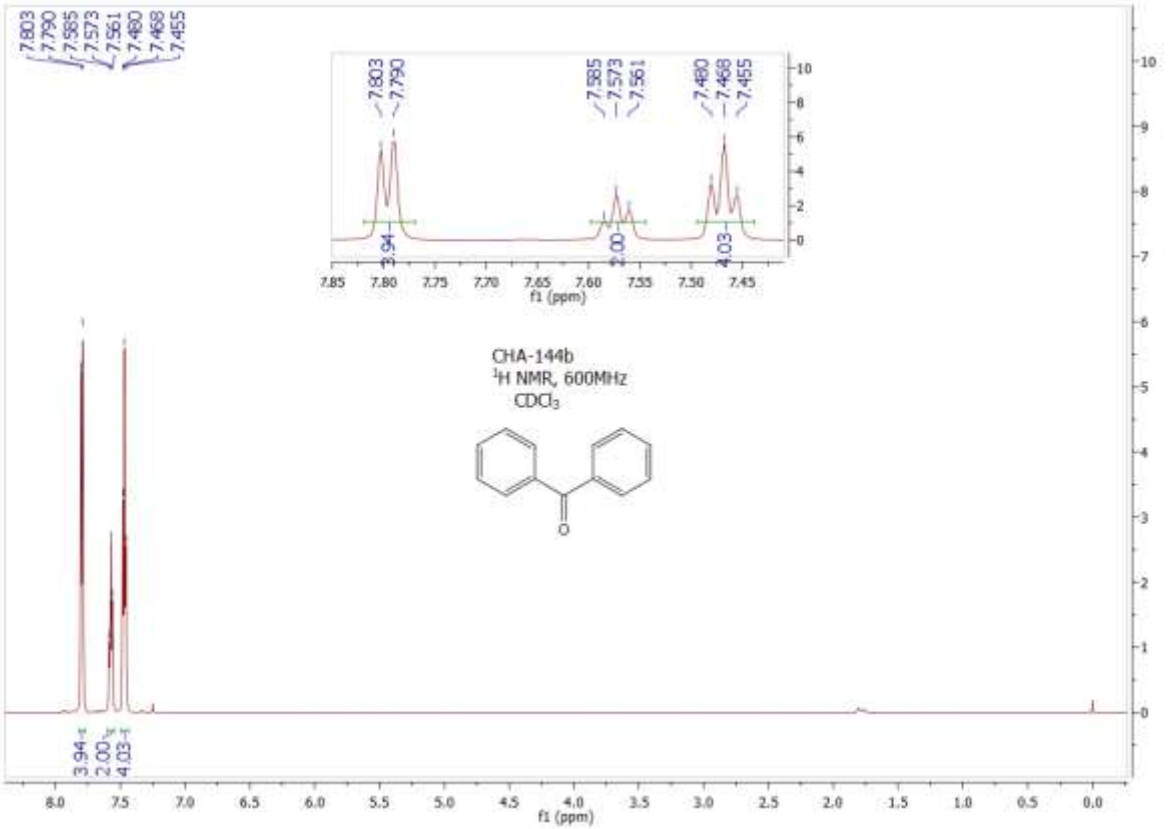
^{13}C NMR of 3k



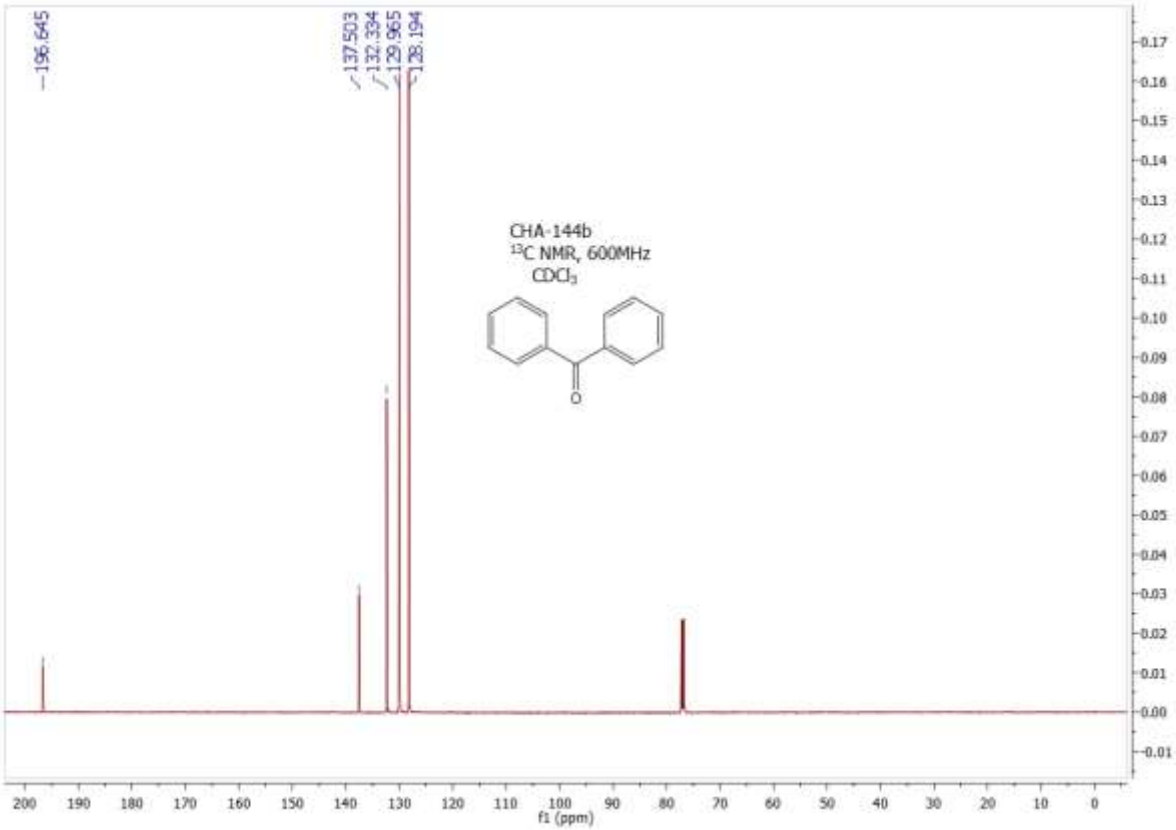
^{1}H NMR of 3l



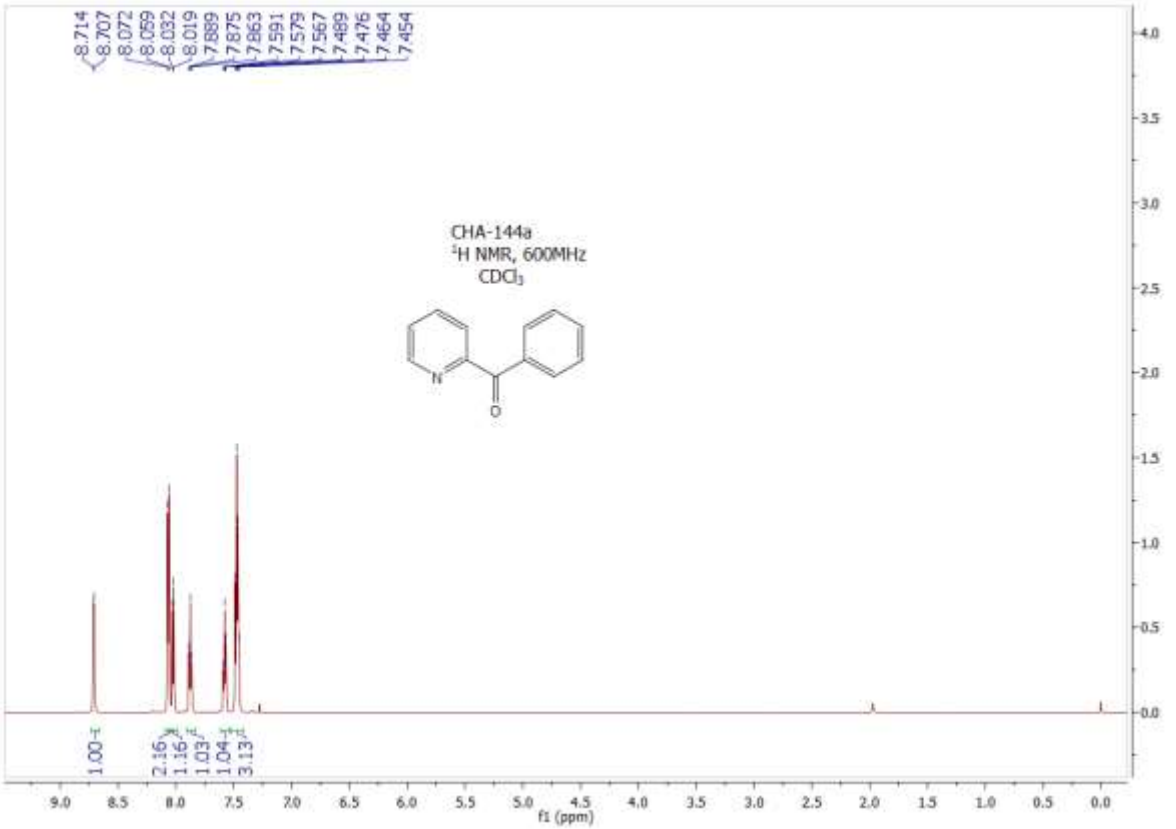
^{13}C NMR of 3l



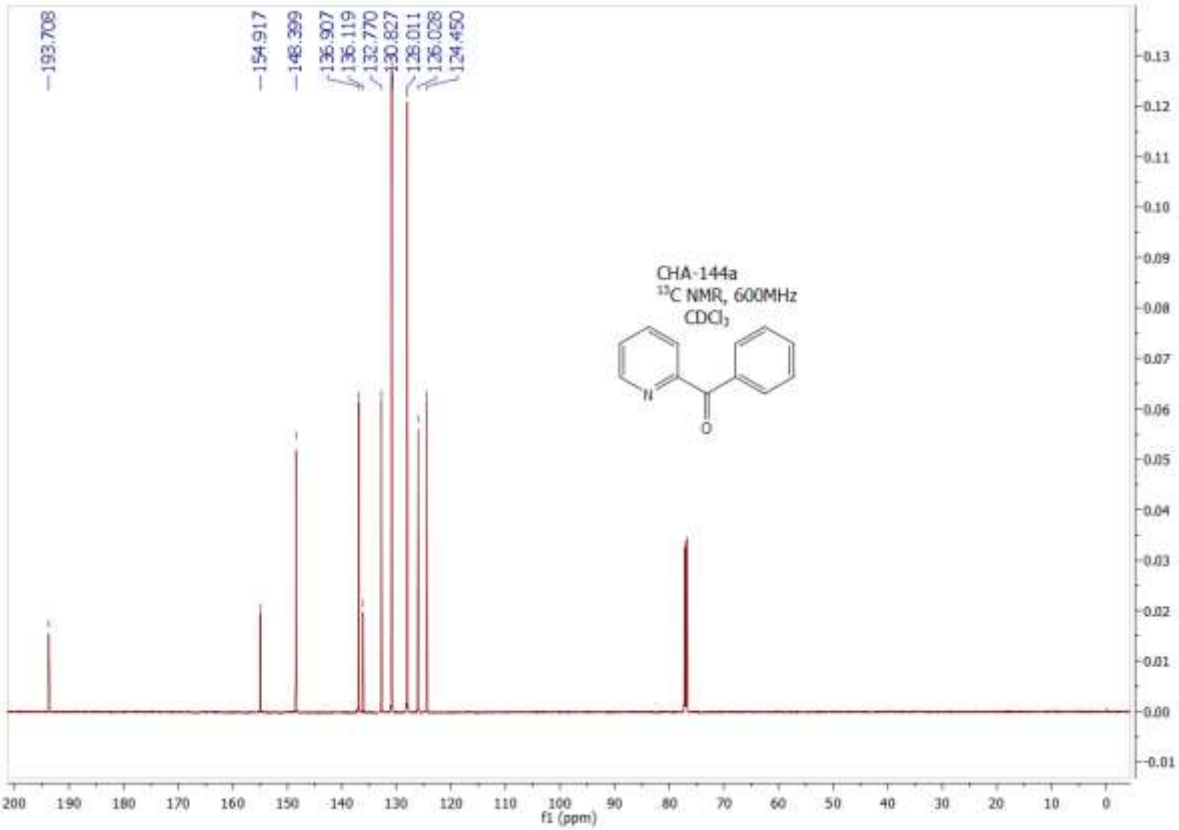
^{1}H NMR of 5a



^{13}C NMR of 5a



^{1}H NMR of 5b



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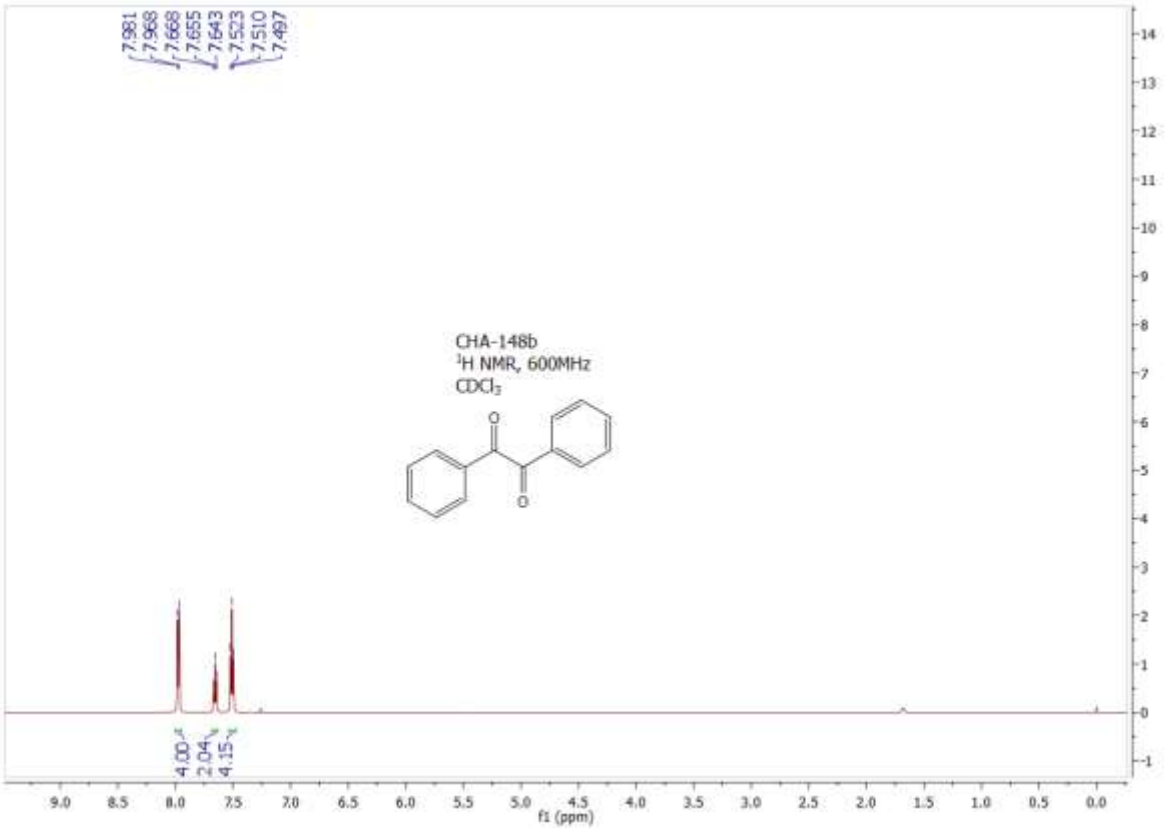

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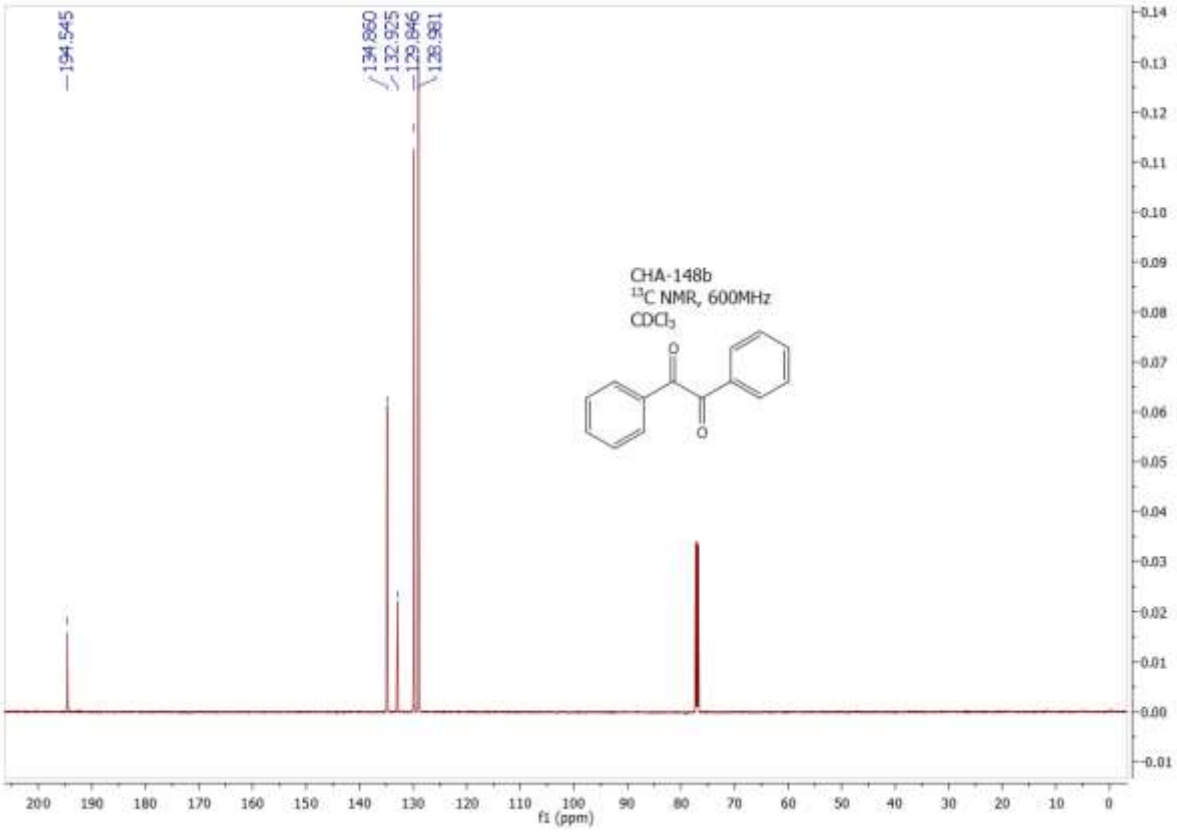

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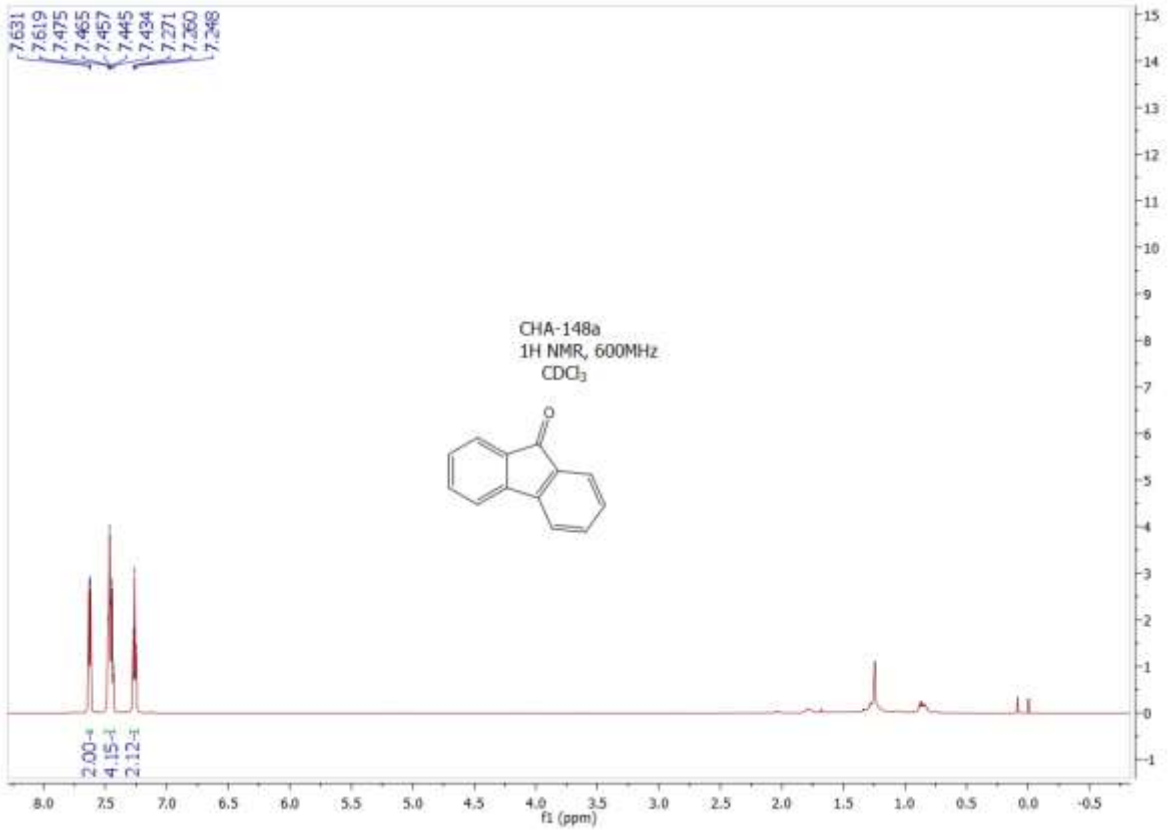

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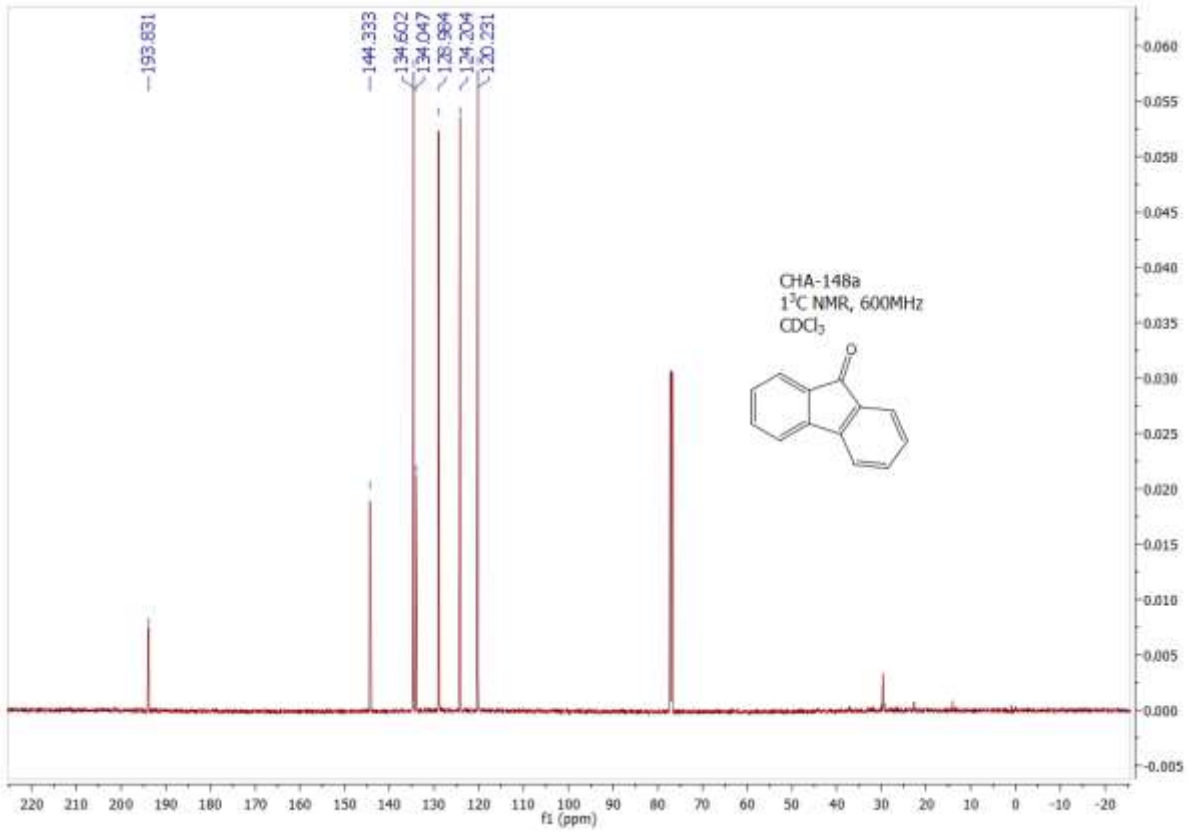
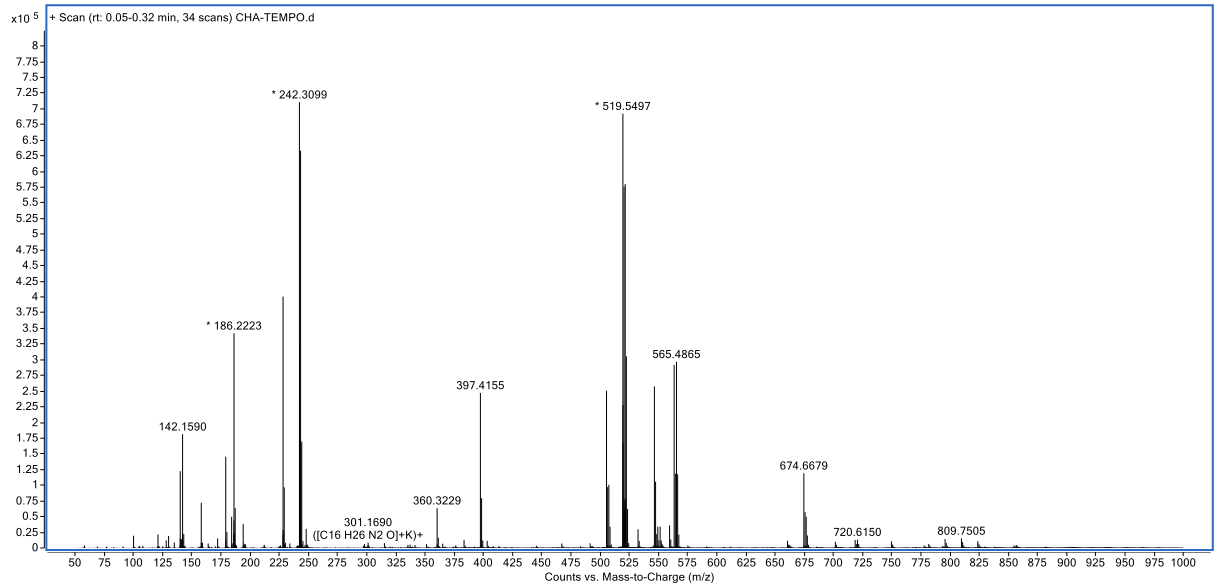
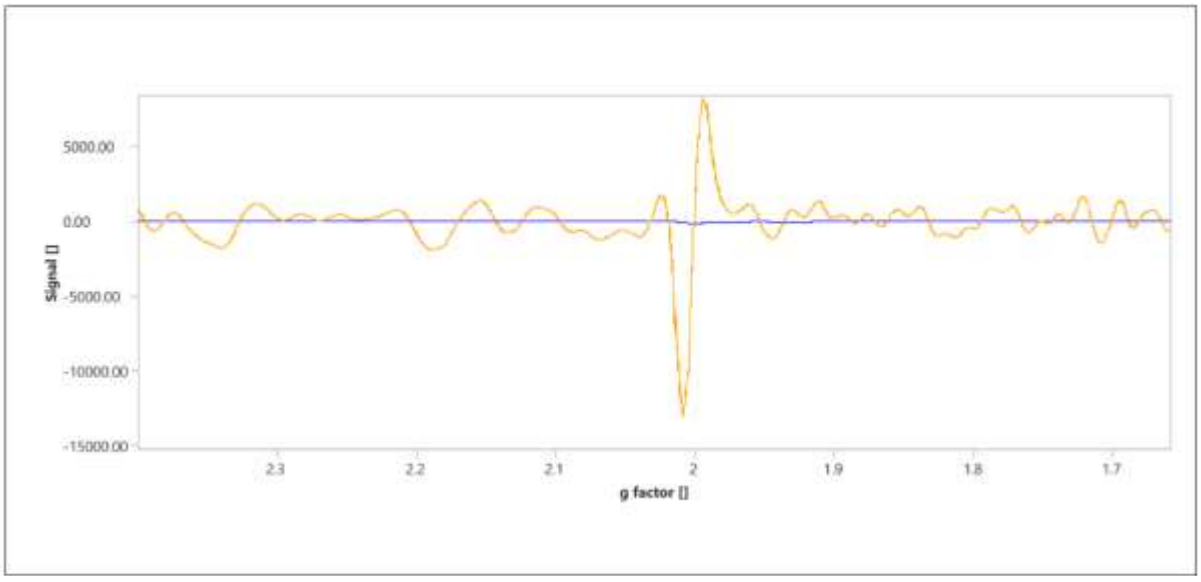


^{13}C NMR of 5d



HRMS Spectra of TEMPO adduct



EPR spectra recorded at −160°C in acetonitrile solution.