Supporting Information for:

Ruthenium-Catalyzed Direct α-Alkylation of Amides Using Alcohols

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1. General Experimental Information :

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of nitrogen. All the alcohols and amides were purchased from Sigma-Aldrich or Alfa-Aesar and stored over molecular sieves. Deuterated solvents were used as received. All the solvents used were dry grade and stored over 4Å molecular sieves. Column chromatographic separations performed over 100-200 Silica-gel. Visualization was accomplished with UV light and/or PMA, CAM stain followed by heating. Ruthenium complexes **3**[1]and **5**[2] were prepared according to literature procedures. The complex **2** and **4** were purchased from Sigma-Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on 400 and 100 MHz respectively, using a Bruker 400 MHz or JEOL 400 MHz spectrometers. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Conversion of reactants was monitored using Gas Chromatography, with GC 2014, Shimadzu.

General experimental procedure for the α-Alkylation of unactivated amides (method A): To an oven dried 20 mL resealable pressure tube (equipped with rubber septum), complex **2** (0.005 mmol), KOtBu (6.5 mmol), alcohol (5 mmol) and *N,N*-dimethylacetamide (5 mL) were added under N_2 atmosphere using balloon. Then, the tube was purged with N_2 and quickly removed septum and sealed with cap using crimper. The reaction mixture was stirred at 140 ^{o}C for 16 hrs. After cooling to room temperature, mesitylene (1 mmole) was added and the products were analyzed by GC. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3 x 40 mL). The entire ethyl acetate layer was combined, washed with brine (50 mL) and then dried over Na_2SO_4. After concentration under reduced pressure, residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:4) to afford the pure product **1**. (In case of aliphatic alcohols and cyclic amides heated for 24 hours).

Experimental procedure for α-Alkylation-hydroxylation of 2-oxindole (method B): Complex **2** (0.0025 mmol), KO*t*Bu (1.95 mmol), alcohol (1.5 mmol), 2-oxindole (3 mmol) and toluene (2 mL) were added to 20 mL resealable pressure tube under N_2 atmosphere using balloon (equipped with rubber septum). Then, the tube was purged with N_2 and quickly removed septum and sealed with cap using crimper. The reaction mixture was

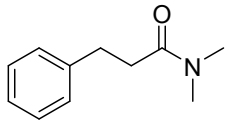
stirred at 140 °C for 16 hrs. After cooling to room temperature, mesitylene (1 mmole) was added and the products were analyzed by GC using an Rtx-5 column on a GC-2014 Shimadzu series GC system. The reaction mixture was concentrated under vacuum. DCM was added to the reaction mixture and passed through plug of celite. After concentrating the filtrate under reduced pressure, residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (3:7) to afford the pure product **7.**

Experimental procedure for α-hydroxylation of 3-benzylindolin-2-one: Complex **2** (0.01 mmol), KO*t*Bu (0.15 mmol), 3-benzylindolin-2-one (0.5 mmol), toluene (1 mL) were added to 20 mL glass tube (equipped with rubber septum) under N_2 atmosphere using balloon and reaction mixture was stirred at RT for 15 minutes under N_2 atmosphere and finally water (1 mmol) was added. Then, the tube was purged with N_2 and quickly removed septum and sealed with cap using crimper. The reaction mixture was stirred at 140 °C for 16 hrs. The reaction mixture was concentrated under vacuum and dichloromethane was added to the reaction mixture and passed through plug of celite. After concentrating the filtrate under reduced pressure, residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (3:7) to afford the pure product 7**a.**

Experimental procedure for control experiment:

KO*t*Bu (6.5 mmol), benzyl alcohol (5 mmol) and *N,N*-dimethylacetamide (5 mL) were added to 20 mL resealable pressure tube (equipped with rubber septum) under N_2 atmosphere using balloon. Then, the tube was purged with N_2 and quickly removed septum and sealed with cap using crimper. The reaction mixture was stirred at 140 °C for 16 hrs. After cooling to room temperature, mesitylene (1 mmole) was added and the products were analyzed by GC using an Rtx-5 column on a GC-2014 Shimadzu series GC system. This showed no reaction.

Experimental details and Characterization data:



(1a)

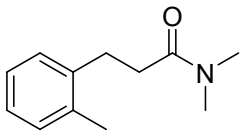
***N,N*-Dimethyl-3-phenylpropanamide (1a)[3]:** Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), benzyl alcohol (540 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1a** (495 mg, 56%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.34–7.21 (m, 5H), 3.02-2.96 (m, 8H), 2.64 (t, 2H).

^{13}C NMR (100 MHz ,$CDCl_3$) δ 172.33, 141.62, 128.58, 128.54, 128.45, 127.16, 126.21, 37.28, 35.56, 35.42, 31.51.

FTIR (neat) 1642 cm^{-1}

HRMS (ESI) m/z calculated for $C_{11}H_{15}NO$ (M+H)+: 178.1232, found: 178.1235.



(1b)

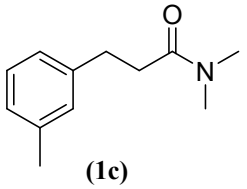
***N,N*-dimethyl-3-o-tolylpropanamide (1b)[4]:** Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 2-methylbenzylalcohol (610 mg , 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1b** (605 mg, 63%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.17-7.09 (m, 4H), 2.98-2.93 (m, 8H), 2.56 (t, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz ,$CDCl_3$) δ 172.48, 139.67, 136.1, 130.39, 128.89, 126.39, 126.22, 37.27, 35.57, 34.04, 28.82, 19.41.

FTIR (neat) 1641.9 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO$ (M+H)+: 192.1388, found: 192.1391.



(1c)

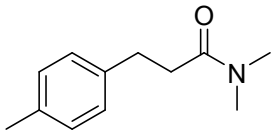
***N,N*-dimethyl-3-m-tolylpropanamide (1c)[4]:** Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 3-methylbenzylalcohol (610 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1c** (650 mg, 68%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, 1H), 7.03-7.01 (m, 3H), 2.95-2.90 (m, 8H), 2.60 (t, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.43, 141.57, 138.17, 129.36, 128.5, 126.96, 125.52, 37.31, 35.52, 35.57, 31.45, 21.51.

FTIR (neat) 1642.7 cm^{-1};

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO$ (M+H)+: 192.1388, found: 192.1390.



(1d)

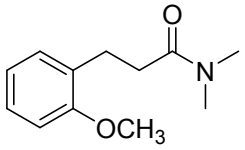
***N,N*-dimethyl-3-p-tolylpropanamide (1d)[5]:** Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 4-methylbenzylalcohol (610 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1d** (670 mg, 70%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 4H), 2.95-2.90 (m, 8H), 2.59 (t, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.42, 138.52, 135.69, 129.25, 128.41, 37.29, 35.61, 35.55, 31.06, 21.12.

FTIR (neat) 1641.04 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO$ (M+H)+: 192.1388, found: 192.1393.



(1e)

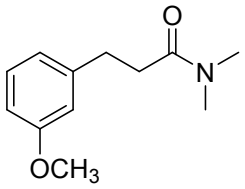
3-(2-methoxyphenyl)-*N,N*-dimethylpropanamide (1e)[4]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 2-methoxybenzylalcohol (690 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1e** (625 mg, 60%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 2H), 6.89-6.83 (m, 2H), 3.82 (s, 3H), 2.95-2.94 (m, 8H), 2.59 (t, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.04, 157.59, 130.3, 127.58, 120.63, 114.32, 110.29, 55.30, 37.28, 35.49, 33.84, 26.80.

FTIR (neat) 1643.9 cm^{-1};

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO_2$ (M+H)+: 208.1337, found: 208.1340.



(1f)

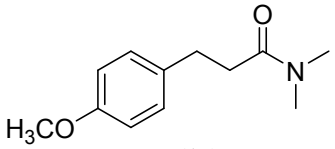
3-(3-methoxyphenyl)-*N,N*-dimethylpropanamide (1f)[6]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 3-methoxybenzylalcohol (690 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1f** (540 mg, 52%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 6.82-6.73 (m, 3H), 3.79 (s, 3H), 2.95-2.93 (m, 8H), 2.60 (t, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.30, 159.81, 143.26, 129.57, 120.89, 114.30, 111.50, 55.29, 37.30, 35.58, 35.35, 31.55.

FTIR (neat) 1640.4 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO_2$ (M+H)+: 208.1337, found: 208.1344.



(1g)

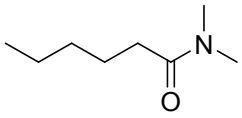
3-(4-methoxyphenyl)-*N,N*-dimethylpropanamide (1g)[7]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), 4-methoxybenzylalcohol (690 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1g** (566 mg, 55%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8 Hz, 2H), 6.82 (d, J = 8Hz, 2H), 3.78 (s, 3H), 2.94-2.92 (m, 8H), 2.58 (t, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.54, 158.08, 133.61, 129.48, 113.98, 55.38, 37.34, 35.69, 35.58, 30.62.

FTIR (neat) 1640.85 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{17}NO_2$ (M+H)+: 208.1337, found: 208.1339.



(1h)

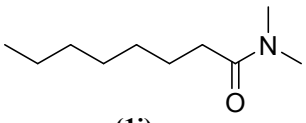
***N,N*-dimethylhexanamide (1h)[8]:** Complex **2** (4.88 mg, 0.01 mmol), KO*t*Bu (728 mg, 6.5 mmol), butanol (370 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1h** (393 mg, 55%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 3H), 2.93 (s, 3H), 2.29 (t, J = 8 Hz, 2H), 1.62 (quintet, J = 8 Hz, 2H), 1.30-1.33 (m, 4H), 0.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 173.55, 37.46, 35.51, 33.51, 31.81, 25.01, 22.62, 14.1.

FTIR (neat) 1643 cm^{-1}

HRMS (ESI) m/z calculated for $C_8H_{17}NO$ (M+H)+: 144.1388, found: 144.1390.



(1i)

***N,N*-dimethyloctanamide (1i)[9]:** Complex **2** (4.88 mg, 0.01 mmol), KO*t*Bu (728 mg, 6.5 mmol), hexanol (510 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1i** (513 mg, 60%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 3H),2.93 (s, 3H), 2.29 (t, J = 8 Hz, 2H), 1.61 (quintet, J = 8Hz, 2H), 1.30-1.27 (m, 8H), 0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 173.44, 37.44, 35.49, 33.57, 31.87, 29.62, 29.25, 22.76, 14.21.

FTIR (neat) 1642.8 cm^{-1}

HRMS (ESI) m/z calculated for $C_{10}H_{21}NO$ (M+H)+: 172.1701, found: 172.1701

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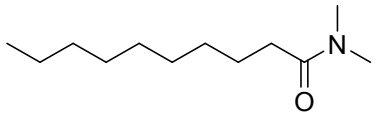


(1j)

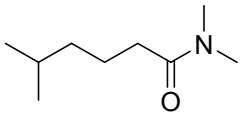
***N,N*-Dimethyldecanamide (1j)[10]:** Complex **2** (4.88 mg, 0.01 mmol), KO*t*Bu (728 mg, 6.5 mmol), octanol (650 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1j** (398 mg, 36%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 3H), 2.92 (s, 3H), 2.28 (t, J = 8 Hz, 2H), 1.60 (quintet, J = 8Hz, 2H), 1.28-1.24 (m, 12H), 0.86(m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 173.48, 37.43, 33.55, 31.99, 29.64, 29.6, 29.58, 29.4, 25.33, 22.77, 14.19.

FTIR (neat) 1645.6 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{25}NO$ (M+H)+: 200.2014, found: 200.2016.



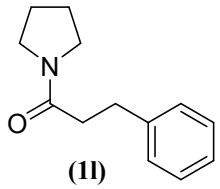
(1k)

***N,N*-Dimethyl-5-methylhexanamide (1k) [11]:** Complex **2** (4.88 mg, 0.01 mmol), KO*t*Bu (728 mg, 6.5 mmol), isoamyl alcohol (440 mg, 5 mmol) and *N,N*-dimethylacetamide (5 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford the amide **1k** (519 mg, 66%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (s, 3H), 2.94 (s, 3H), 2.28 (t, J=8Hz, 2H), 1.66-1.56 (m, 5H), 1.21 (m, 2H), 0.88(d, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.45, 38.88, 37.43, 35.49, 33.77, 28.03, 23.18, 22.67.

FTIR (neat) 1644.8 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{19}NO$ (M+H)+: 158.1545, found: 158.1548.



(1l)

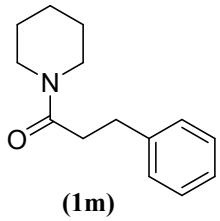
3-phenyl-1-(pyrrolidin-1-yl)propan-1-one (1l) [12]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), benzyl alcohol (440 mg, 5 mmol) and N-acetylpyrrolidine (1130 mg, 10 mmole) were allowed to react in 20 mL resealable pressure tube according to method A to afford the cyclic amide **1l** (450 mg, 44%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 5H), 3.46 (t, 2H), 3.28 (t, 2H), 2.98 (t, J = 8 Hz, 2H), 2.56 (t, J = 8.0 Hz, 2H), 1.89-1.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) 170.97, 141.64, 128.88, 128.57, 127.96,126.19, 46.71, 45.79, 36.89, 31.36, 26.18, 24.51.

FTIR (neat) 1641.8 cm^{-1}

HRMS (ESI) m/z calculated for $C_{13}H_{17}NO$ (M+H)+: 204.1388, found: 204.1389.



(1m)

3-phenyl-1-(piperidin-1-yl)propan-1-one (1m)[12]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), benzyl alcohol (440 mg, 5 mmol) and N-acetylpiperidine (1270

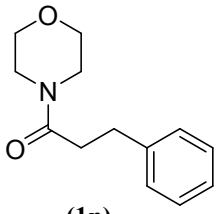
mg, 10 mmole) were allowed to react in 20 mL resealable pressure tube according to method A to afford the cyclic amide **1m** (585 mg, 54%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.05 (m, 5H), 3.43 (t, 2H), 3.20 (t, 2H), 2.84 (t, J = 8Hz, 2H), 2.49 (t, J = 8.0 Hz, 2H), 1.31-1.48 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) 170.58, 141.63, 128.6, 128.58, 126.93, 126.22, 46.77, 42.87, 35.33, 31.77, 26.54, 25.69, 24.76, 24.68.

FTIR (neat) 1633.9 cm^{-1}

HRMS (ESI) m/z calculated for $C_{14}H_{19}NO$ (M+H)+: 218.1545, found: 218.1547.



(1n)

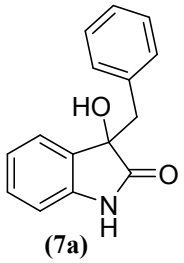
1-morpholino-3-phenylpropan-1-one (1n)[13]: Complex **2** (2.44 mg, 0.005 mmol), KO*t*Bu (728 mg, 6.5 mmol), benzyl alcohol (440 mg, 5 mmol) and N-acetyl piperidine (1290 mg, 10 mmole) were allowed to react in 20 mL resealable pressure tube according to method A to afford the cyclic amide **1n** (360 mg, 32%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.05 (m, 5H), 3.47 (s, 4H), 3.35 (t, J = 4 Hz, 2H), 3.2 (t, J = 4 Hz, 2H), 2.82 (t, J = 8 Hz, 2H), 2.46 (t, J = 8 Hz, 2H).

^{13}C NMR (100 Hz, $CDCl_3$) 171.05, 141.16, 128.68, 128.59, 127.21,126.41, 66.98, 66.59, 46.1, 42.07, 34.94, 31.61.

FTIR (neat)= 1639 cm^{-1}

HRMS (ESI) m/z calculated for $C_{13}H_{17}NO_2$ (M+H)+: 220.1337, found: 220.1343.



(7a)

3-benzyl-3-hydroxyindolin-2-one (7a) [14]: Complex 2 (1.22 mg, 0.0025 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), benzylalcohol (162 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7a** (223 mg, 62%) as a white solid.

Melting point: 165-168 ^{o}C.

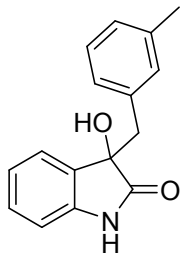
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (bs, 1H), 7.22-7.11 (m, 5H), 7.05-6.98 (m,3H), 6.71 (d, 1H), 3.31 (d, J = 13.2 Hz, 1H), 3.14 (d, J = 12.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 140.28, 133.92,130.57, 129.85, 128.06, 127.12, 125.11, 122.99, 110.19, 77.36, 44.79.

FTIR (neat) 3264.7, 1710.94 cm^{-1}

HRMS (ESI) m/z calculated for $C_{15}H_{13}NO_2$ (M+H)+: 240.1024, found: 240.1030.

Crystal data for the compound 7a: $C_{15}H_{13}NO_2$, *M = 239.26*, 0.22 x 0.20 x 0.18 mm^3, Monoclinic, space group P 21/c with a = 9.6173(5) Å, b = 9.7573(5) Å, c = 12.8363(7) Å, $\alpha = 90°$, $\beta = 100.175(2)°$, $\gamma = 90°$, V = 1185.60(11) $Å^3$, T = 296(2) K, R_1 = 0.0336, wR_2 = 0.1030 on observed data, z = 4, D_{calcd} = 1.340 g cm^{-3}, *F(000)* = 504, Absorption coefficient = 0.721 mm^{-1}, λ = 1.54178 Å, 12517 reflections were collected on a smart apex CCD single crystal diffractometer, 2174 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.267 and -0.168 e $Å^{-3}$, respectively.



(7b)

3-hydroxy-3-(3-methoxybenzyl)indolin-2-one (7b): Complex **2** (1.22 mg, 0.0025 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), 3-methoxybenzylalcohol (207 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7b** (195 mg, 48%) as a light brown solid.

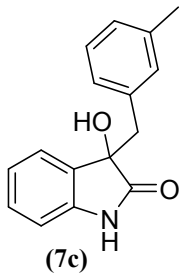
Melting point: 125-127 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.20-7.17 (m, 2H), 7.03(m, 2H), 6.70-6.68 (m, 2H), 6.57 (m, 1H), 6.48 (m, 1H), 3.61 (s, 3H), 3.43 (bs,1H), 3.28(d, J = 12.8 Hz, 1H), 3.11(d, J=13.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.34, 159.44, 140.74, 135.75, 130.25, 130.14, 129.3, 125.34, 123.35, 123.27, 115.96, 113.44, 110.70, 77.95, 55.51, 45.04.

FTIR (neat) 3228.8, 1704.7 cm^{-1}

HRMS (ESI) m/z calculated for $C_{16}H_{15}NO_3$ (M+Na)+: 292.0949, found: 292.0948.



(7c)

3-hydroxy-3-(3-methylbenzyl)indolin-2-one (7c): Complex **2** (1.22 mg, 0.0025 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), 3-methylbenzylalcohol (183 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7c** (206 mg, 54%) as a white solid.

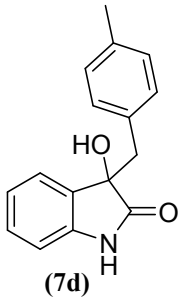
Melting point : 170-172 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (bs, 1H), 7.23-7.15 (m, 2H), 7.05-6.96 (m, 3H), 6.81-6.71 (m, 3H), 3.27 (d, J =12.8Hz, 1H), 3.19 (bs, 1H), 3.09 (d, J = 12.8 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.73, 140.31, 137.59, 133.79, 131.38, 129.88, 129.79, 127.90, 127.85, 127.58, 125.15, 122.91, 110.19, 44.72, 21.41.

FTIR (neat) 3267.7, 1713.5 cm^{-1}; HRMS (ESI) m/z calculated for $C_{16}H_{15}NO_2$ (M+Na)+ : 276.1000, found: 276.0999.

Crystal data for the compound 7c: $C_{16}H_{15}NO_2$, *M = 253.30*, 0.20 x 0.18 x 0.16 mm^3, Monoclinic, space group P21/c with *a* = 10.952(3) Å, *b* = 11.340(4) Å, *c* = 10.721(3) Å, α = 90°, β = 99.771(7)°, γ = 90°, *V* = 1312.3(7) $Å^3$, *T* = 296(2) K, R_1 = 0.0469, wR_2 = 0.1432 on observed data, z = 4, D_{calcd} = 1.282 g cm^{-3}, *F(000)* = 536, Absorption coefficient = 0.085 mm^{-1}, λ = 0.71073 Å, 20234 reflections were collected on a smart apex CCD single crystal diffractometer, 3311 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.305 and -0.264 e $Å^{-3}$, respectively.



(7d)

3-hydroxy-3-(4-methylbenzyl)indolin-2-one (7d) [14]: Complex **2** (1.22 mg, 0.0025 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), 4-methylbenzylalcohol (183 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7d** (196 mg, 51%) as a light brown solid.

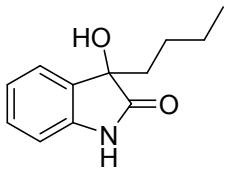
Melting point : 185-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (bs, 1H), 7.23-7.18 (m, 2H), 7.04 (dt, J=8Hz, 1H), 6.96 (d, J=8Hz, 2H), 6.88 (d, J=8Hz, 2H), 6.71 (d, J=8Hz, 1H), 3.26 (d, J =13.2 Hz, 1H), 3.10 (d, J = 12.8 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.09, 140.11, 138.63, 136.57, 130.55, 130.27, 129.67, 128.66, 124.96, 122.82, 109.96, 44.29, 21.06.

FTIR (neat) 3261.79, 1693 cm^{-1}

HRMS (ESI) m/z calculated for $C_{16}H_{15}NO_2$ (M+Na)+ : 276.1000, found: 276.0998.



(7e)

3-butyl-3-hydroxyindolin-2-one (7e): Complex **2** (4.88 mg, 0.01 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), butanol (111 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7e** (238 mg, 77%) as a light yellow solid.

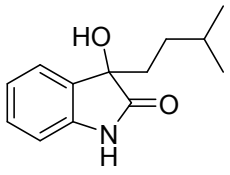
Melting point: 95-98 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (bs, 1H), 7.28-7.24 (m, 1H), 7.10-7.06 (dd, 1H), 6.89 (d, 1H), 3.18 (bs, 1H), 1.99-1.93 (m, 2H), 1.29 - 1.04 (m, 4H), 0.82 (3H, t).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.74, 140.60, 130.69, 129.72, 124.43, 123.27, 110.40, 38.44, 25.32, 22.86, 13.95.

FTIR (neat) 3678, 3183, 1710 cm^{-1}

HRMS (ESI) m/z calculated for $C_{12}H_{15}NO_2$ (M+Na)+ : 228.1000, found: 228.1010.



(7f)

3-hydroxy-3-isopentylindolin-2-one (7f): Complex 2 (4.88 mg,0.01 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), isoamyl alcohol (132 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7f** (237 mg, 72%) as a light yellow solid.

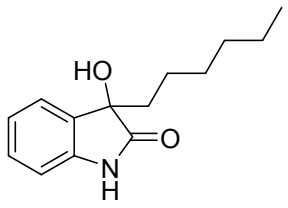
Melting point : 117-119 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (bs, 1H), 7.34 (d, 1H), 7.26-7.22 (m, 1H), 7.07 (dd, 1H), 6.88 (d, 1H), 3.49 (bs, 1H), 1.99-1.89 (m, 2H), 1.49-1.43 (septet, 1H), 1.15-0.95 (m, 2H), 0.8 (d, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.33, 140.69, 130.79, 129.64, 124.32, 123.24, 110.61, 77.01, 36.43, 31.82, 28.21, 22.52, 22.41.

FTIR (neat) 3389, 3680, 1711 cm^{-1}

HRMS (ESI) m/z calculated for $C_{13}H_{17}NO_2$ $(M+Na)^+$: 242.1157, found : 242.1164.



(7g)

3-hexyl-3-hydroxyindolin-2-one (7g)[16]: Complex 2 (4.88 mg, 0.01 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), hexanol (153 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7g** (228 mg, 65%) as a white solid.

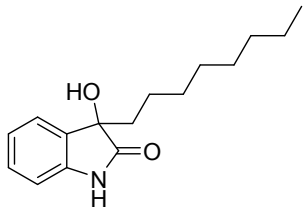
Melting point: 90-92 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (bs, 1H), 7.35 (d, 1H), 7.27-7.25 (m, 1H), 7.07 (dd, 1H), 6.88 (d, 1H), 3.15 (bs, 1H), 1.96-1.93 (m, 2H), 1.22-1.19 (m, 8H), 0.82 (t, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.01, 140.62, 130.72, 129.68, 124.37, 123.25, 110.49, 77.25, 38.60, 31.63, 29.40, 23.14, 22.63, 14.14.

FTIR (neat) 3678, 3324, 1711 cm^{-1}

HRMS (ESI) m/z calculated for $C_{14}H_{19}NO_2$ (M+Na)+ : 256.1313, found: 256.1319.



(7h)

3-hydroxy-3-octylindolin-2-one (7h): Complex 2 (4.88 mg,0.01 mmol), KO*t*Bu (218.4 mg, 1.95 mmol), octanol (195 mg, 1.5 mmol), oxindole (399 mg, 3 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford the C3-hydroxy 2-oxindole **7h** (254 mg, 65%) as a light yellow solid.

Melting point: 102-105 ^oC.

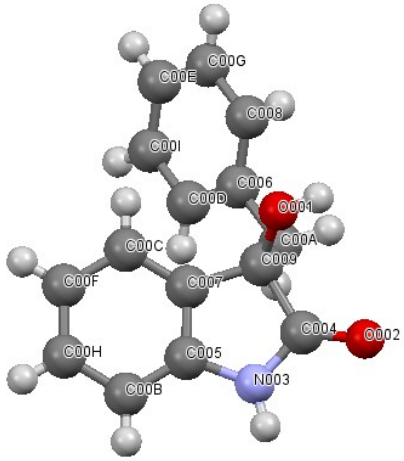
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (bs, 1H), 7.36 (d, 1H), 7.29-7.25 (m, 1H), 7.08 (dd, 1H), 6.87 (d, 1H), 2.76 (bs, 1H), 1.96-1.94 (m, 2H), 1.25-1.19 (m, 12H), 0.85 (t, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.31, 140.51, 130.56, 129.75, 124.46, 123.28, 110.29, 77.07, 38.72, 31.91, 29.74, 29.41, 29.28, 23.20, 22.75, 14.23.

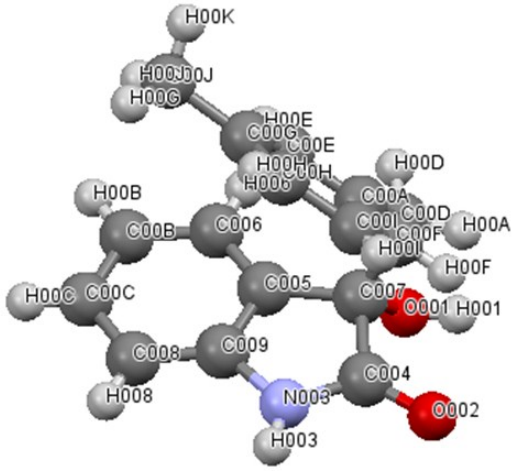
FTIR (neat) 3267.7, 1713.5 cm^{-1}

HRMS (ESI) m/z calculated for $C_{16}H_{23}NO_2$ (M+Na)+ : 284.1626, found: 284.1632.

2. X-ray structure for entry (7a):



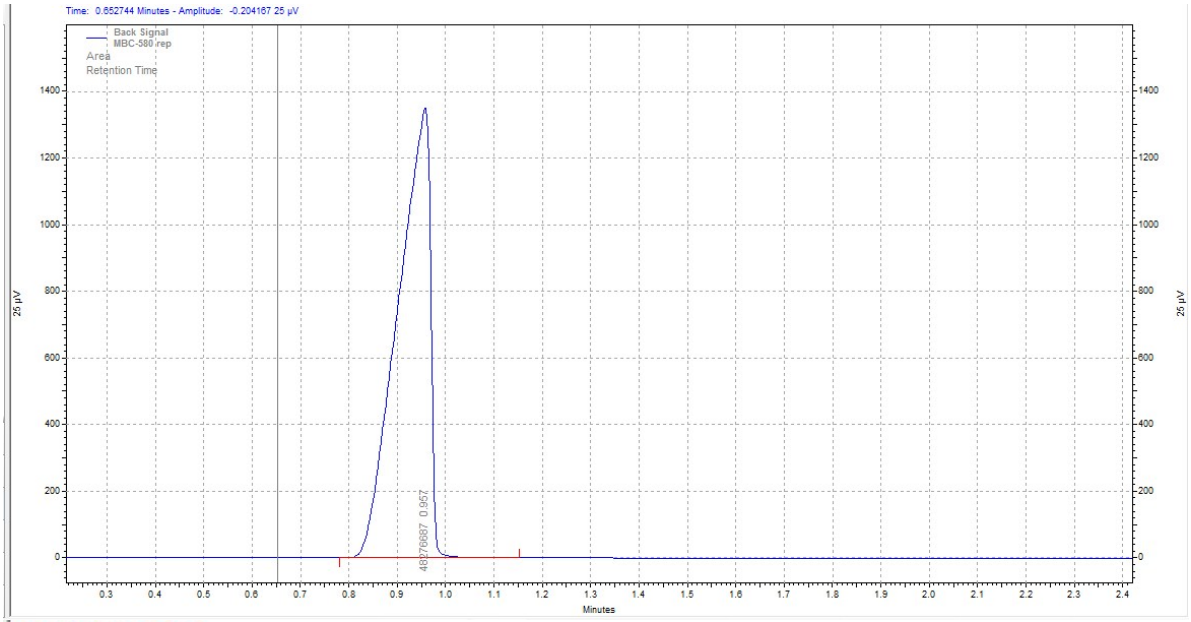
X-ray structure for entry (7c):



GC Experiment for detection of H2 gas liberation:

Two different runs-

1)



Area % Report

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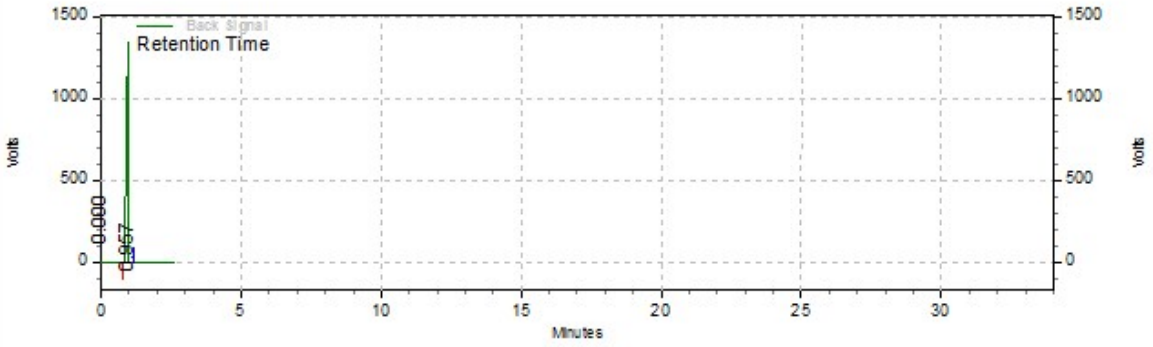
Printed: 8/29/2016 4:01:34 PM



Back Signal
Results

Retention Time	Area	Area %	Height	Height %
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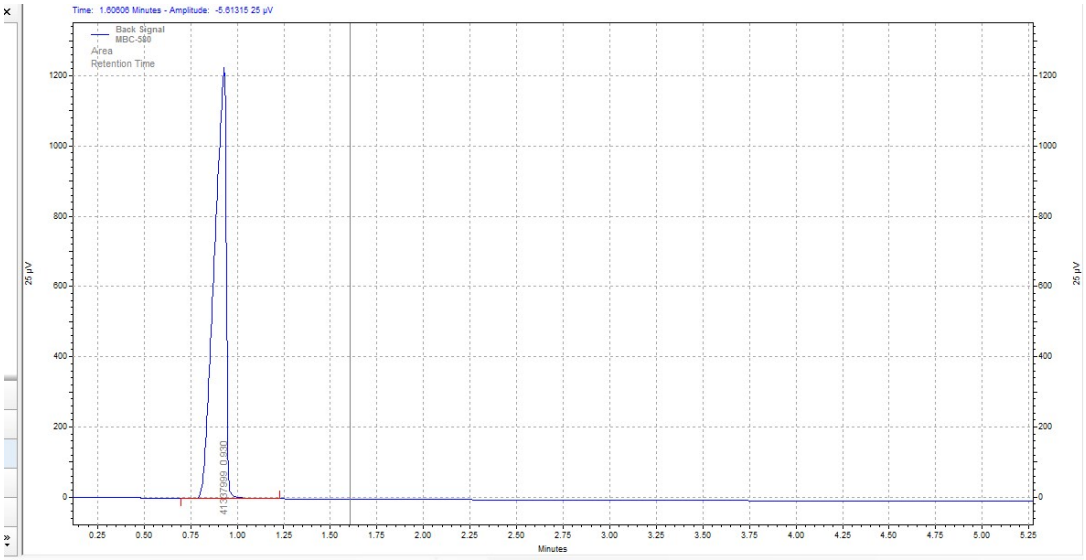
Totals				
	48276687	100.00	10363178	100.00

2)



Area % Report

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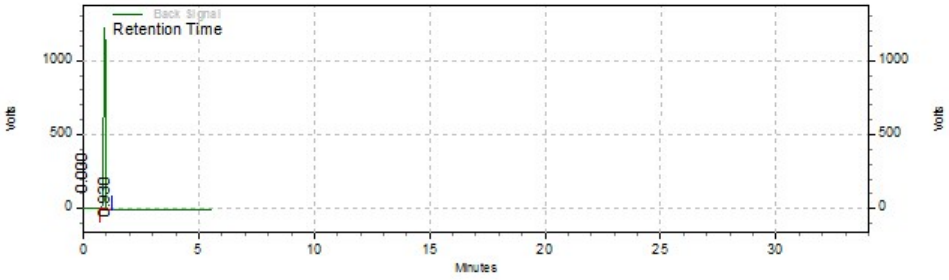

Back Signal
Results

Retention Time	Area	Area %	Height	Height %
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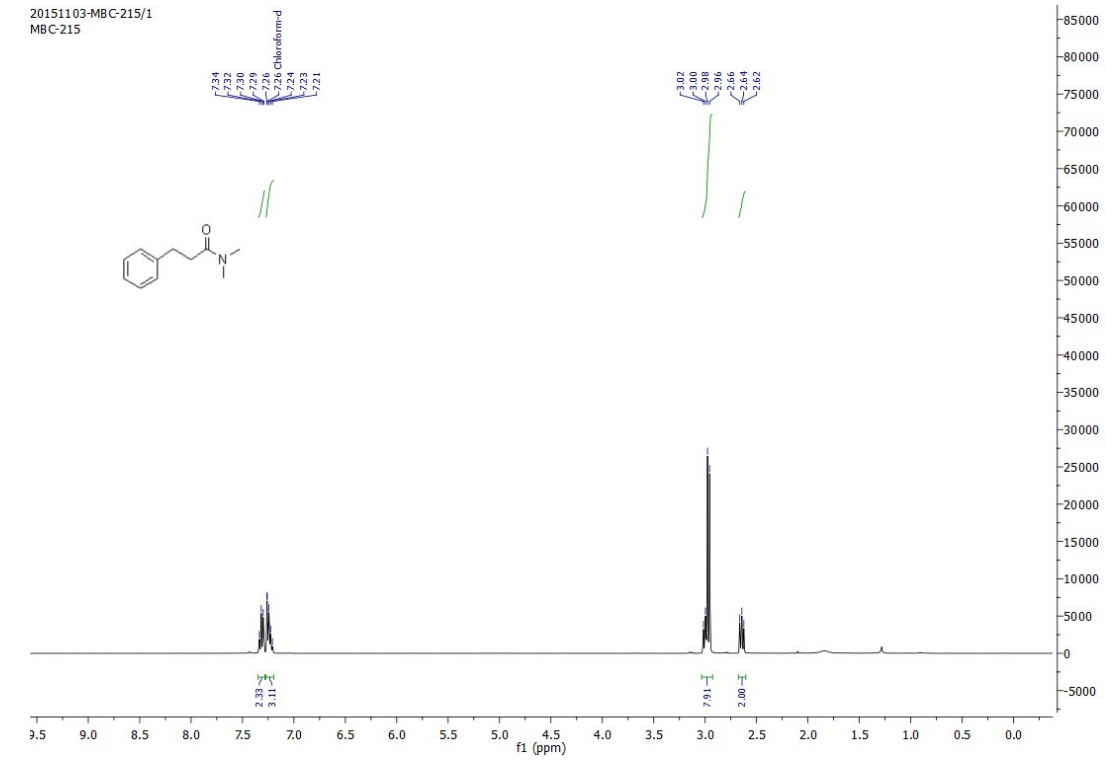
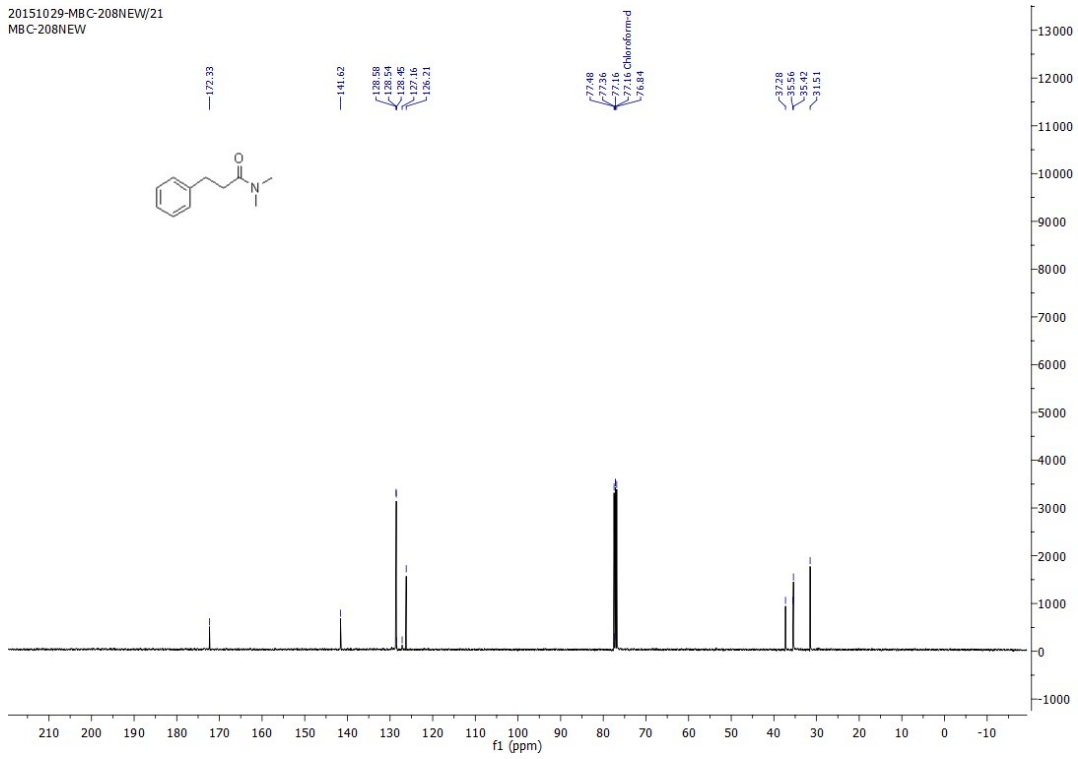
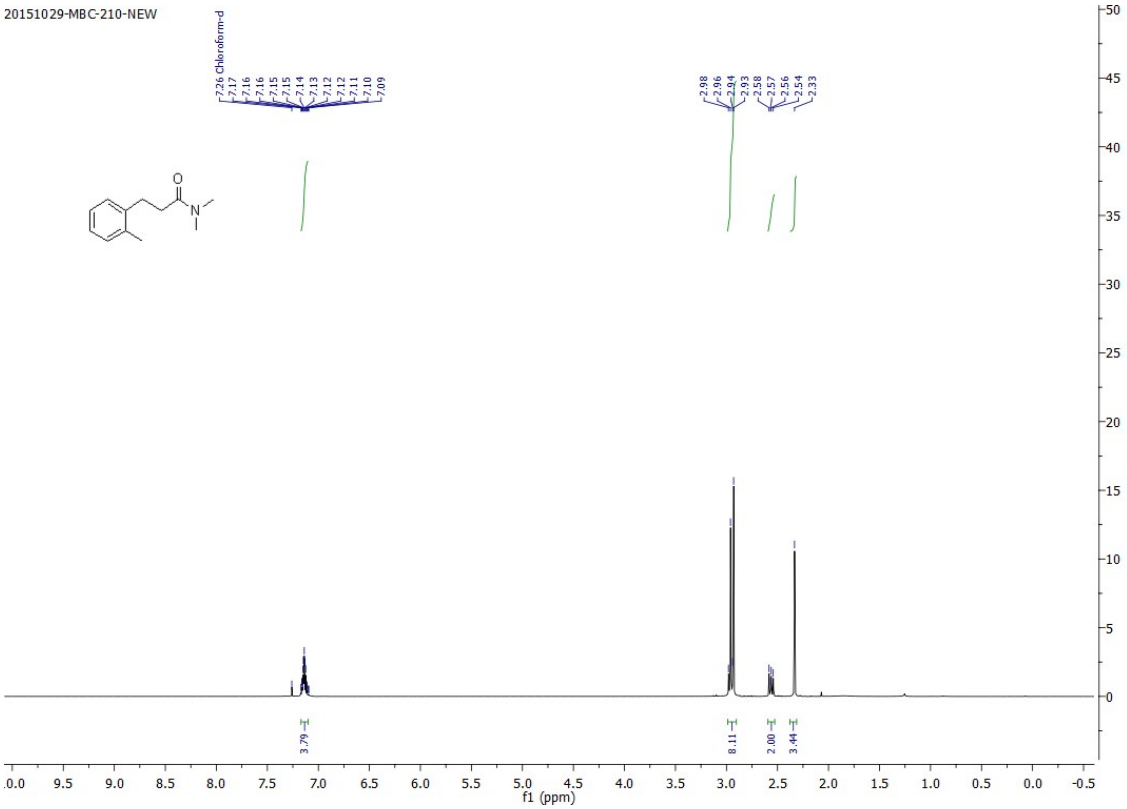
3. Copies of NMR Spectra:



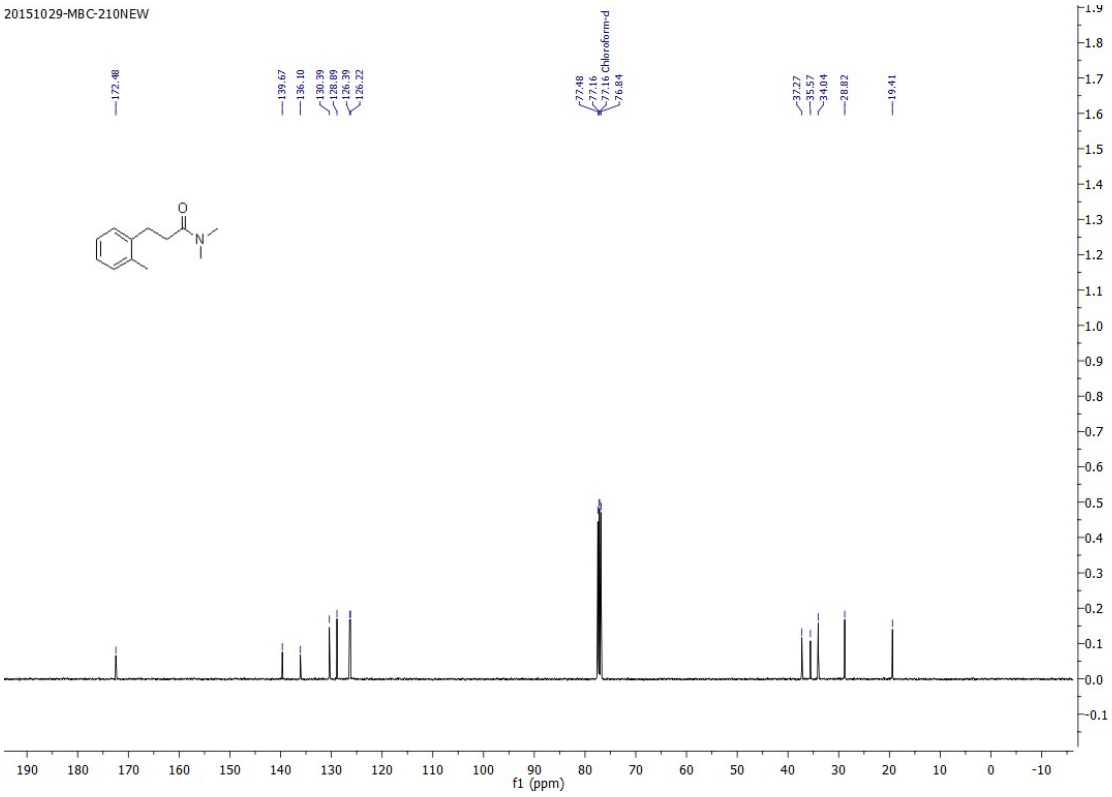
^{1}H NMR of Compound **1a**



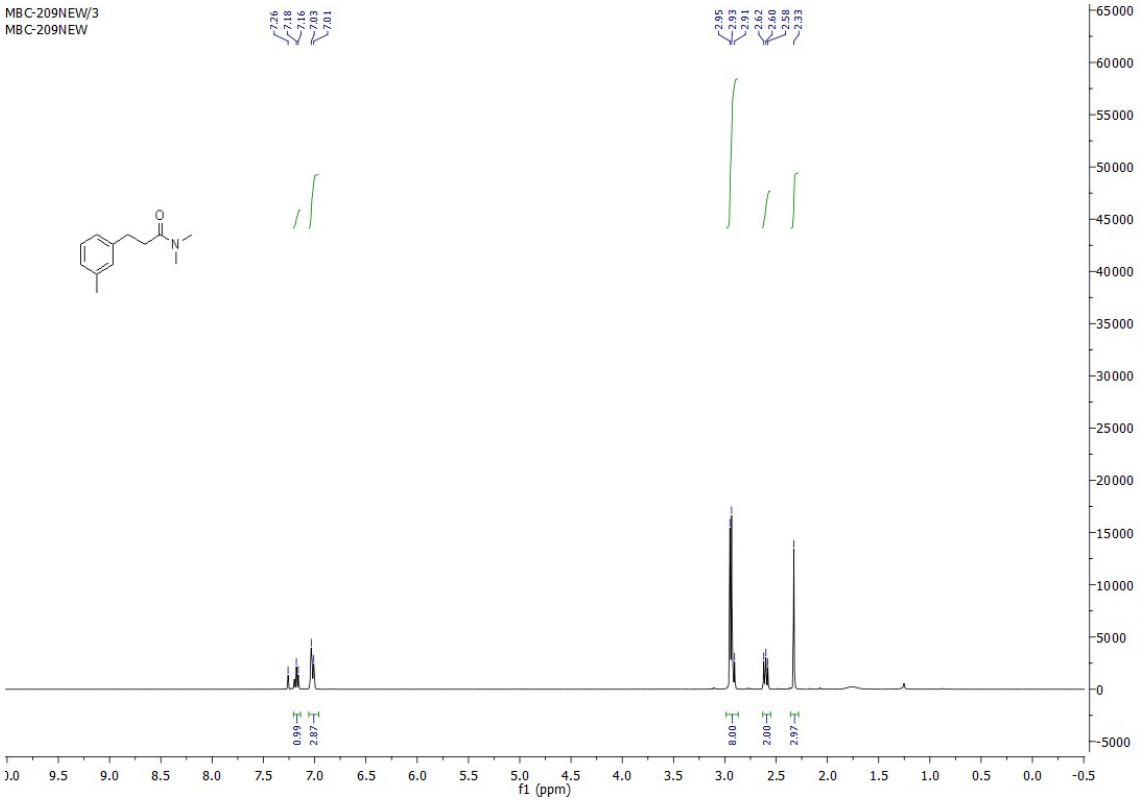
^{13}C NMR of Compound **1a**



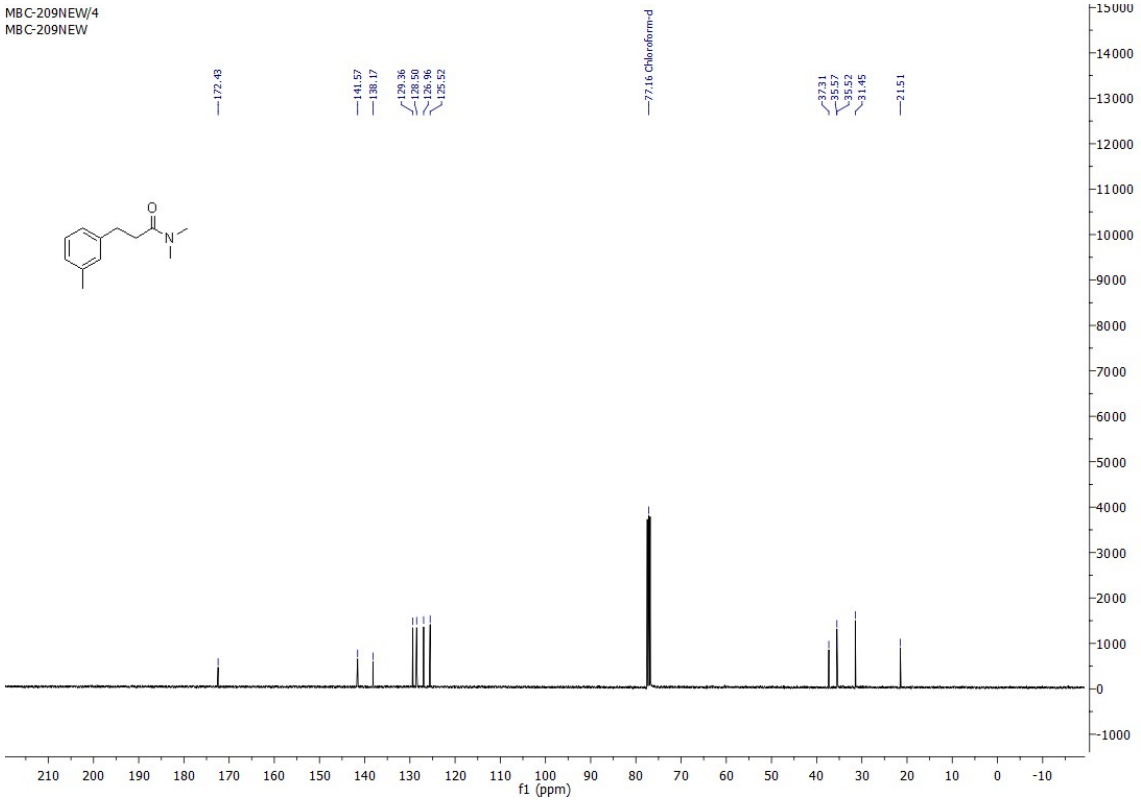
^{1}H NMR of Compound **1b**



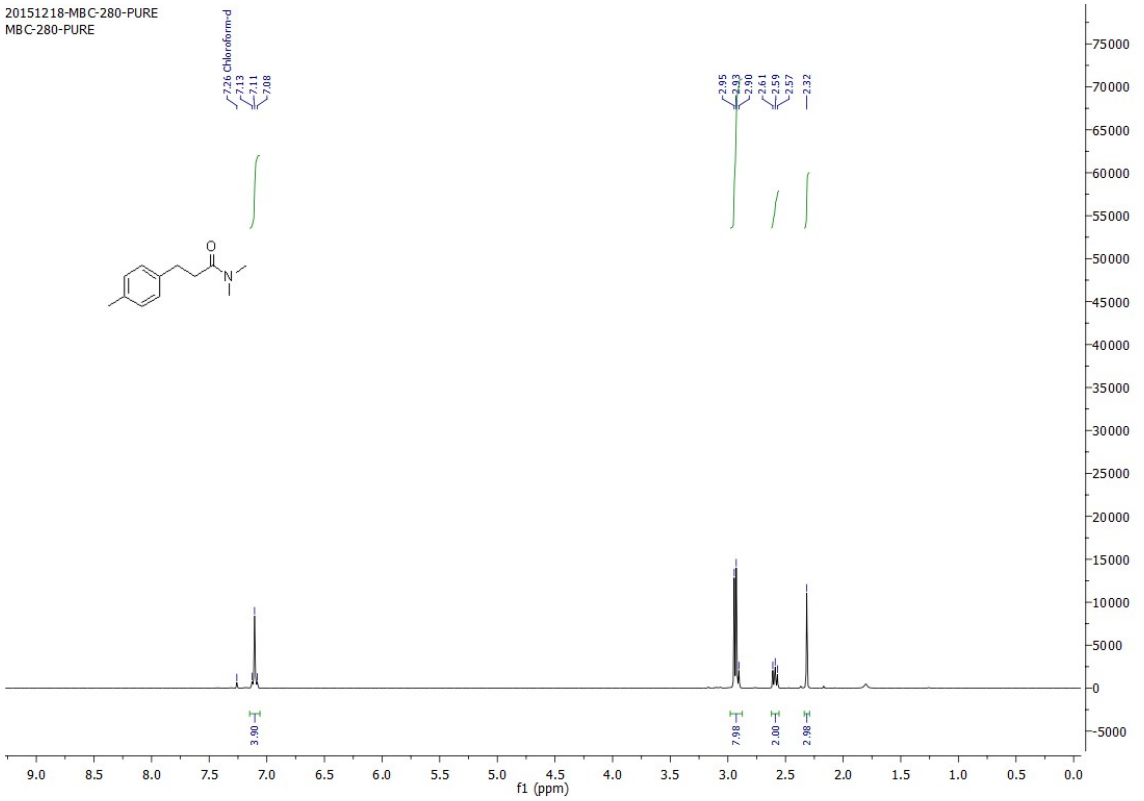
^{13}C NMR of Compound **1b**



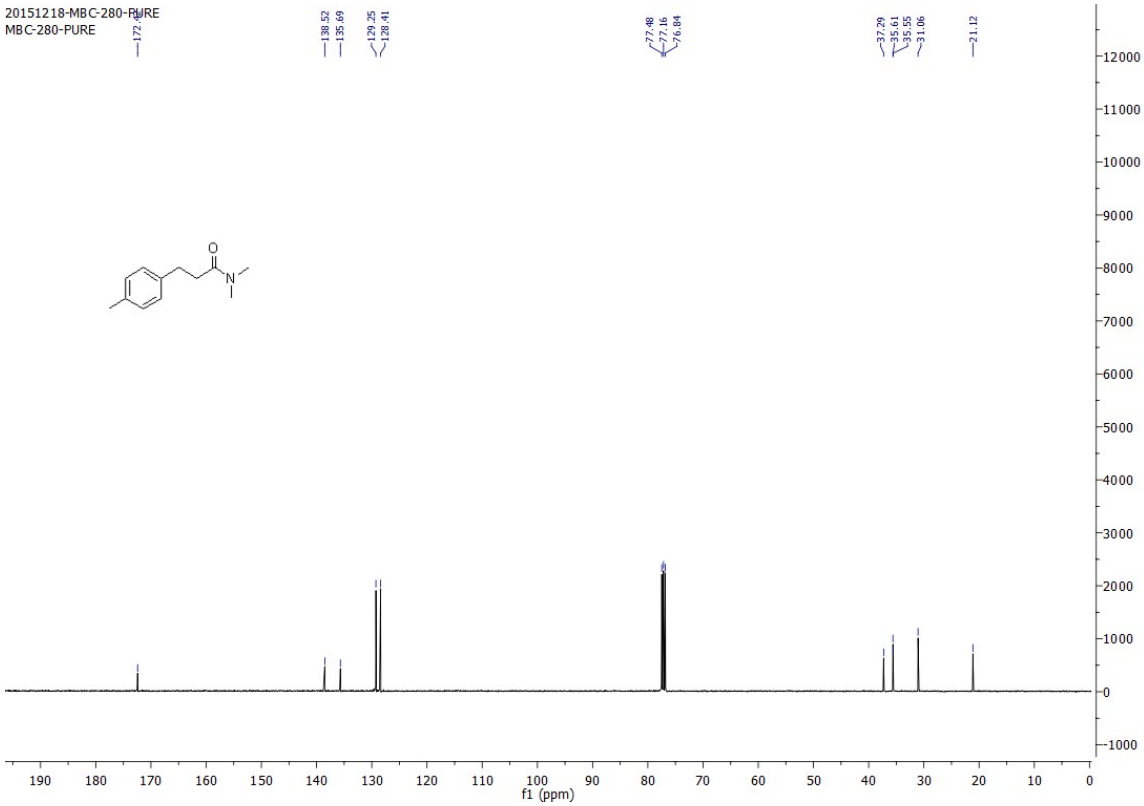
^{1}H NMR of Compound **1c**



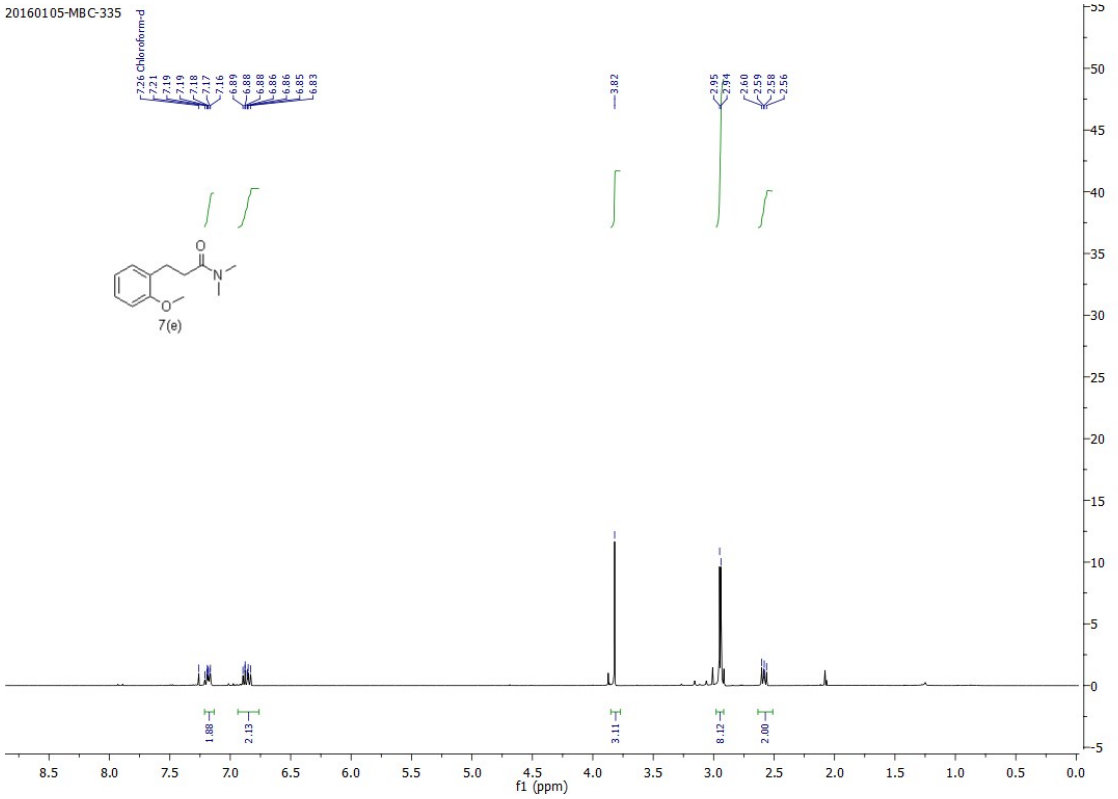
^{13}C NMR of Compound **1c**



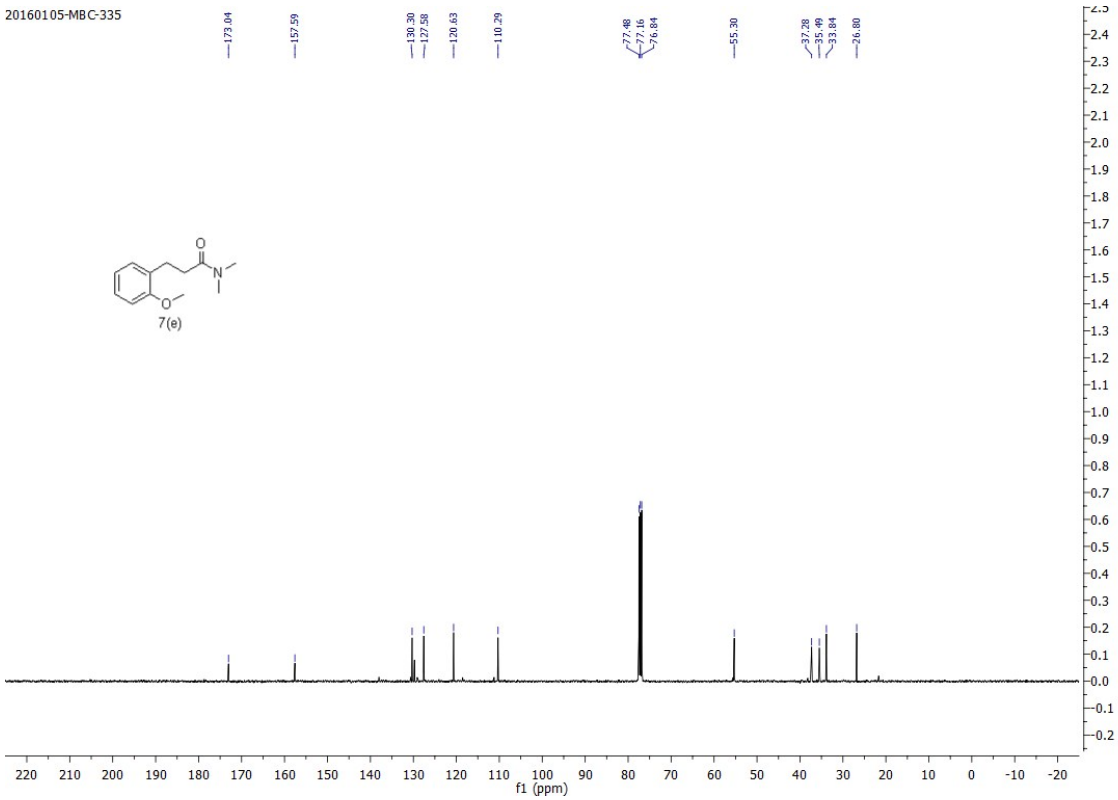
^{1}H NMR of Compound **1d**



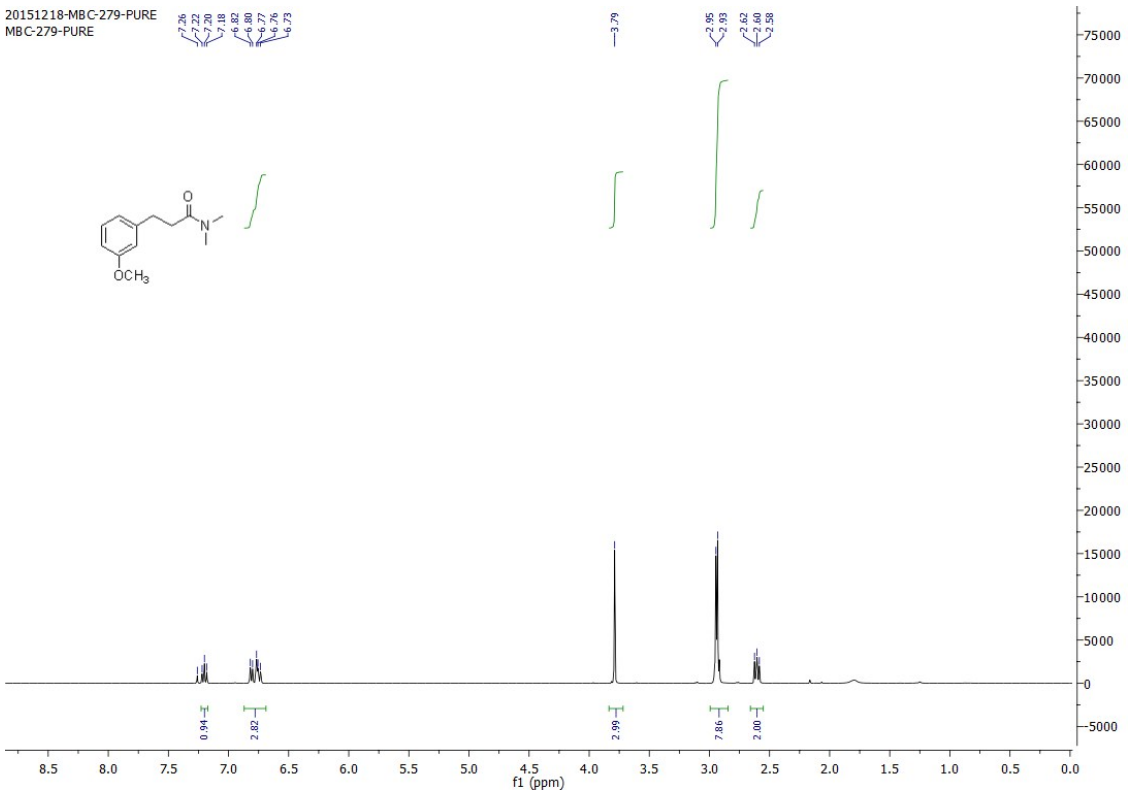
^{13}C NMR of Compound **1d**



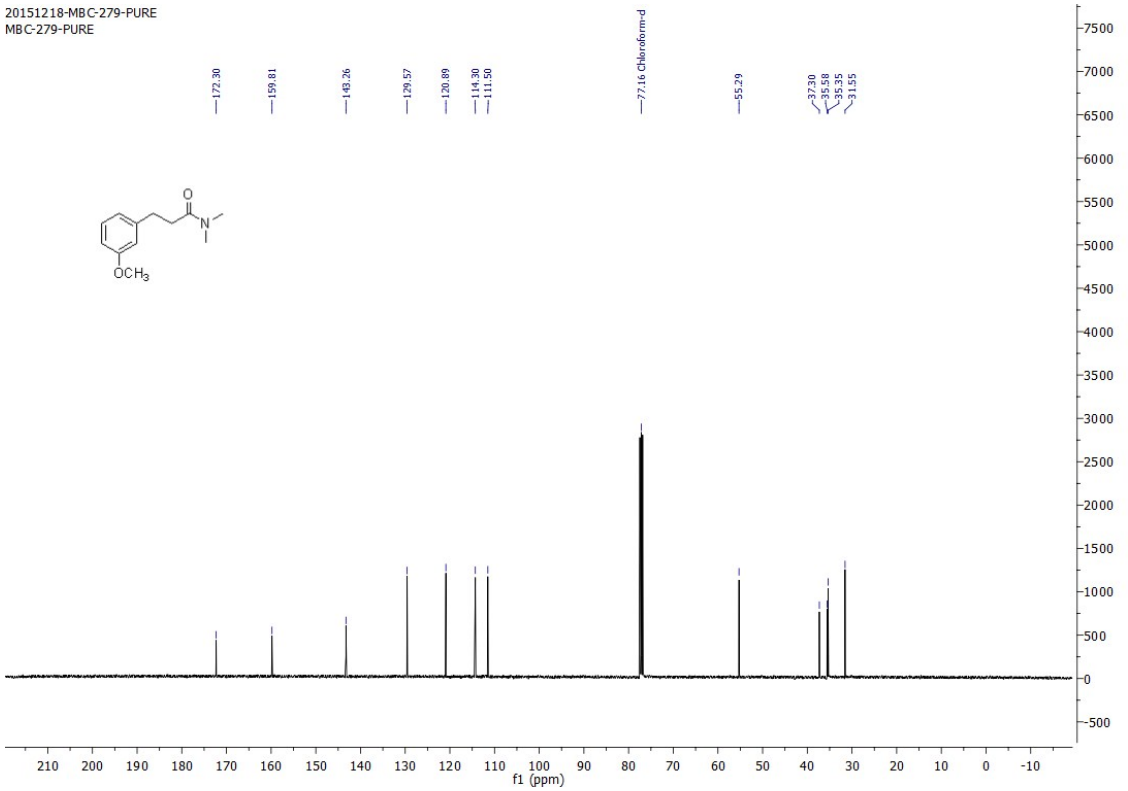
^{1}H NMR of Compound **1e**



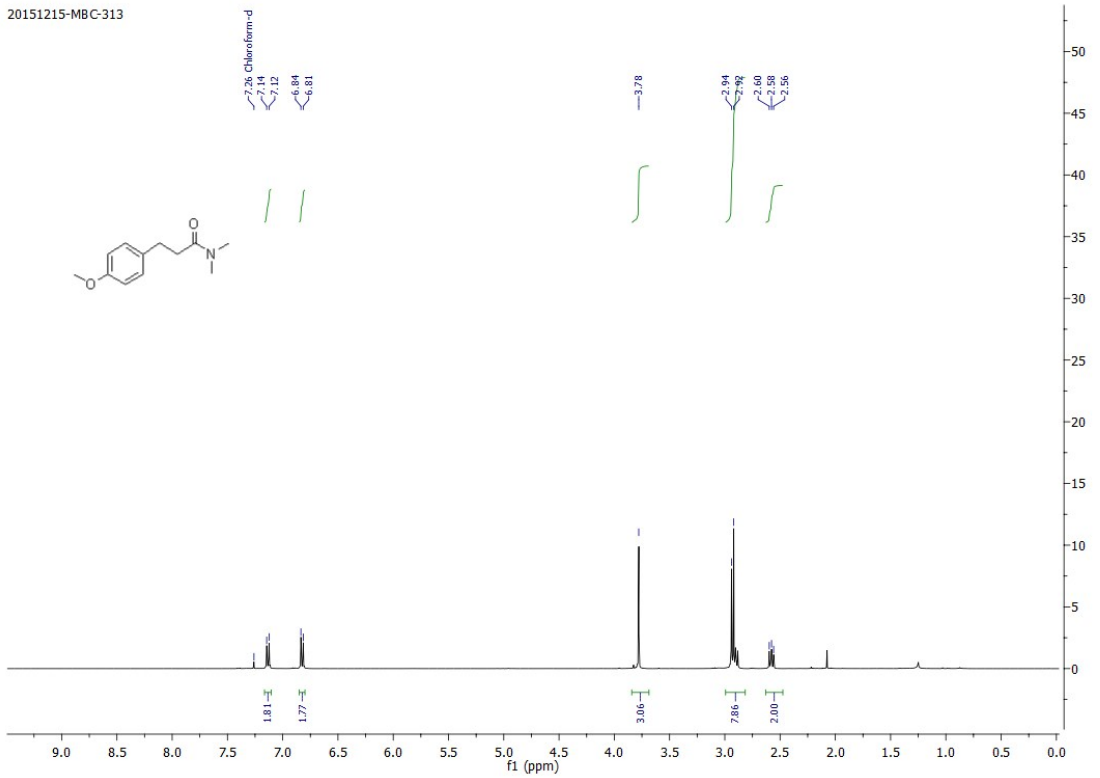
^{13}C NMR of Compound **1e**



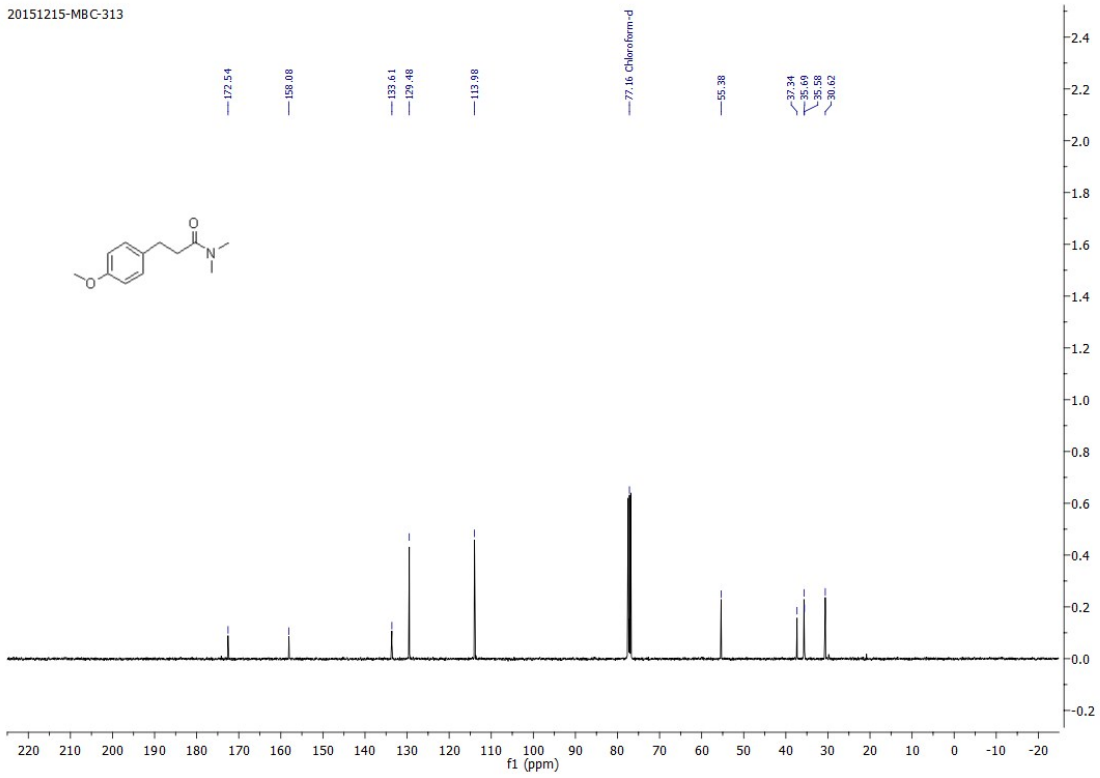
^{1}H NMR of Compound **1f**



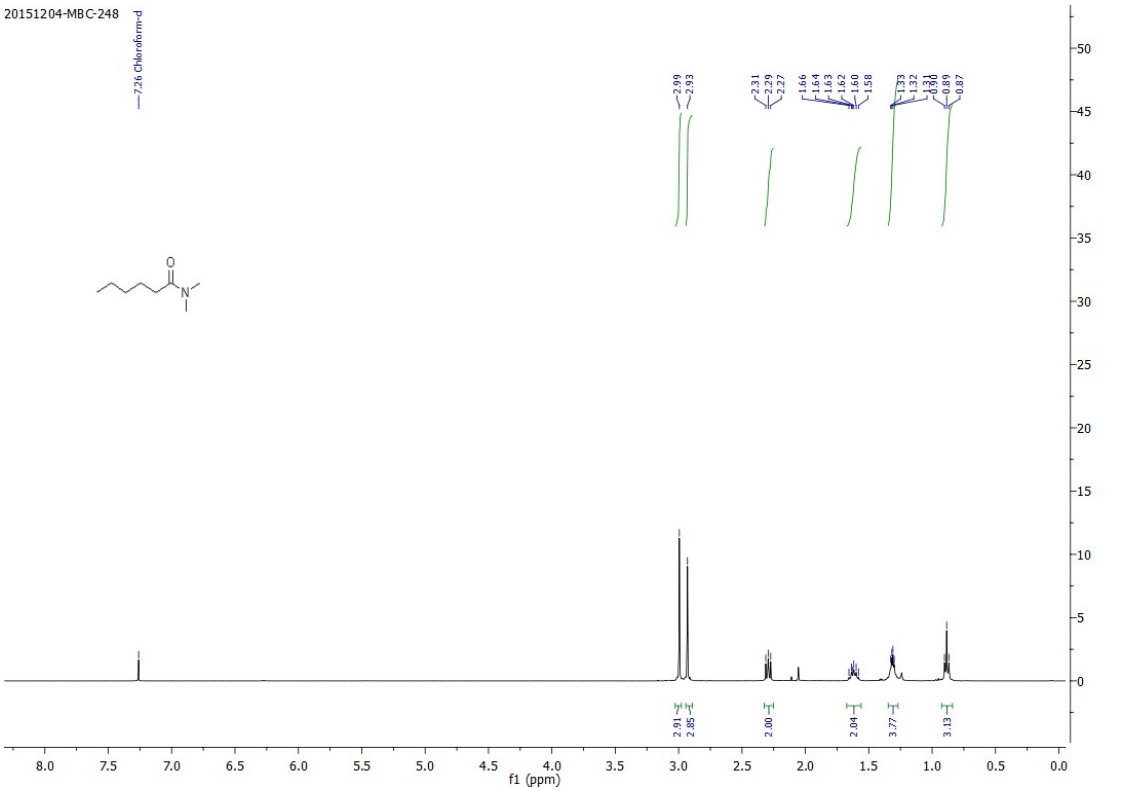
^{13}C NMR of Compound **1f**



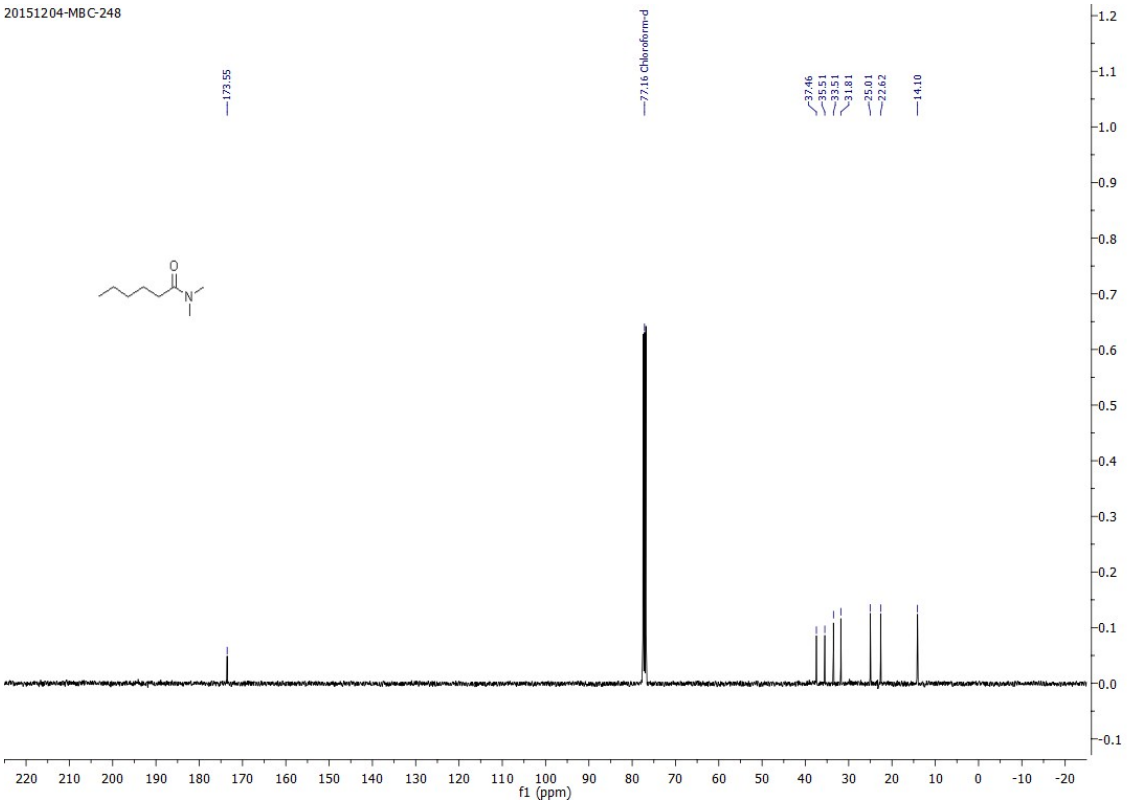
^{1}H NMR of Compound **1g**



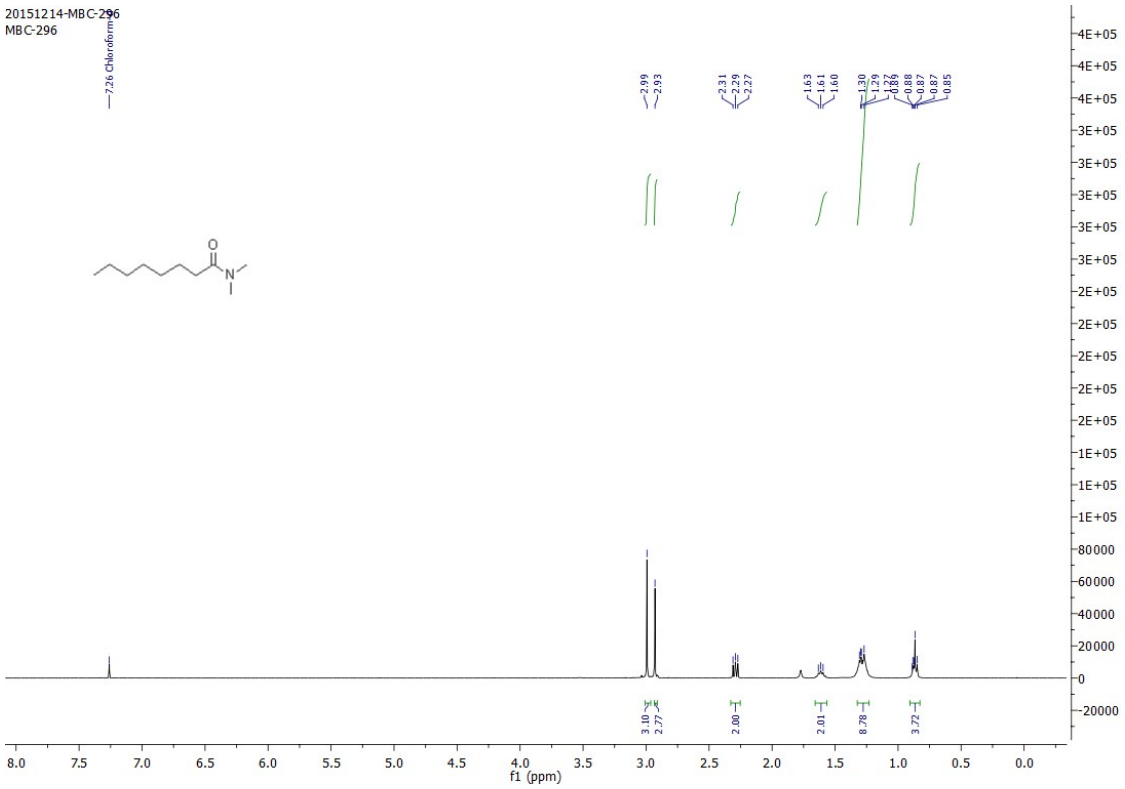
^{13}C NMR of Compound **1g**



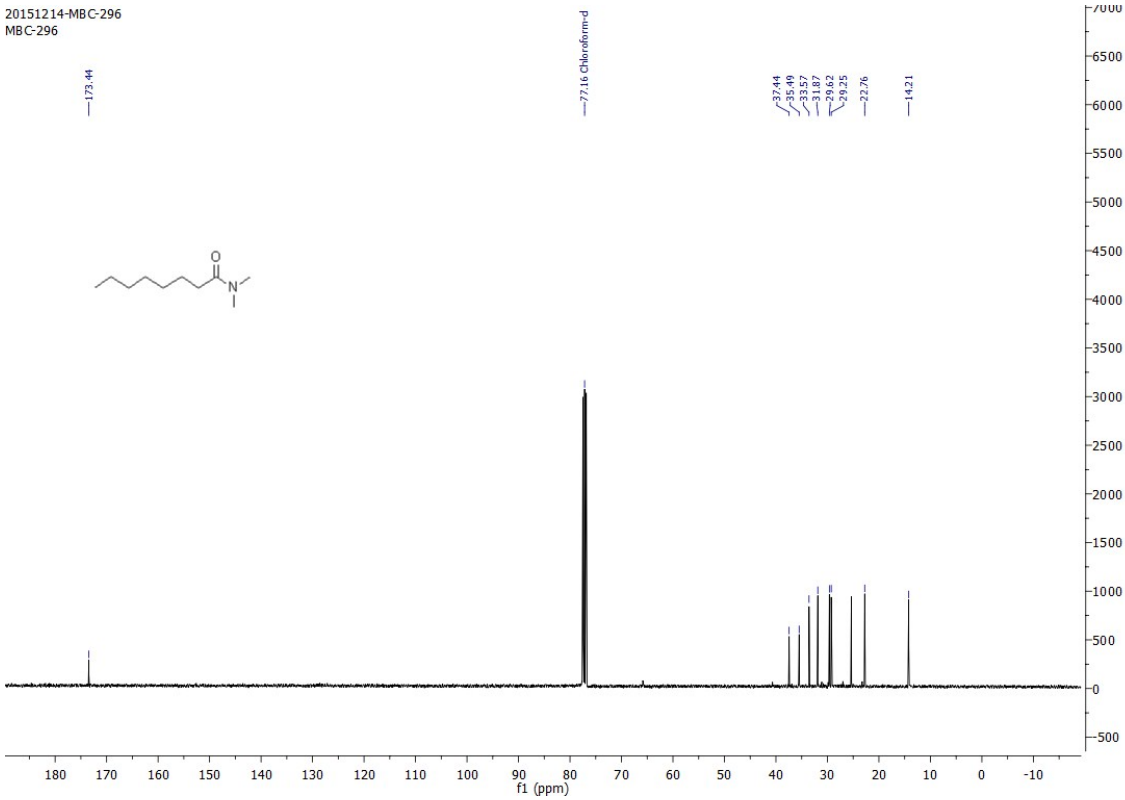
^{1}H NMR of Compound **1h**



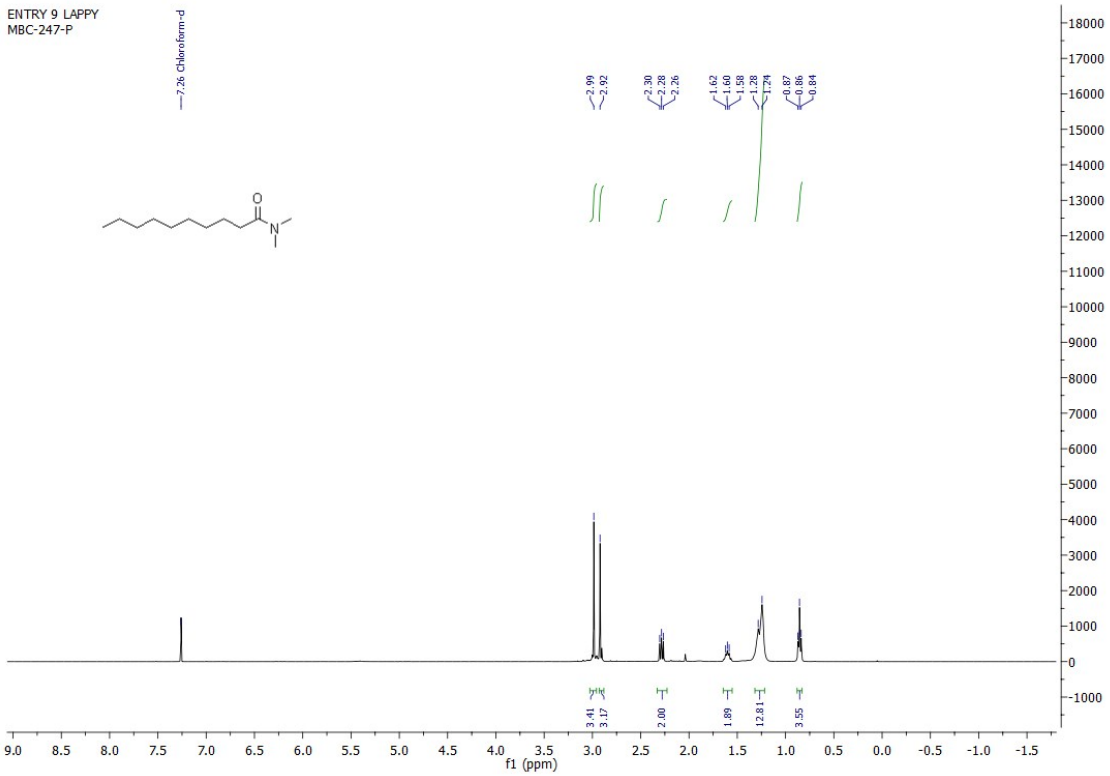
^{13}C NMR of Compound **1h**



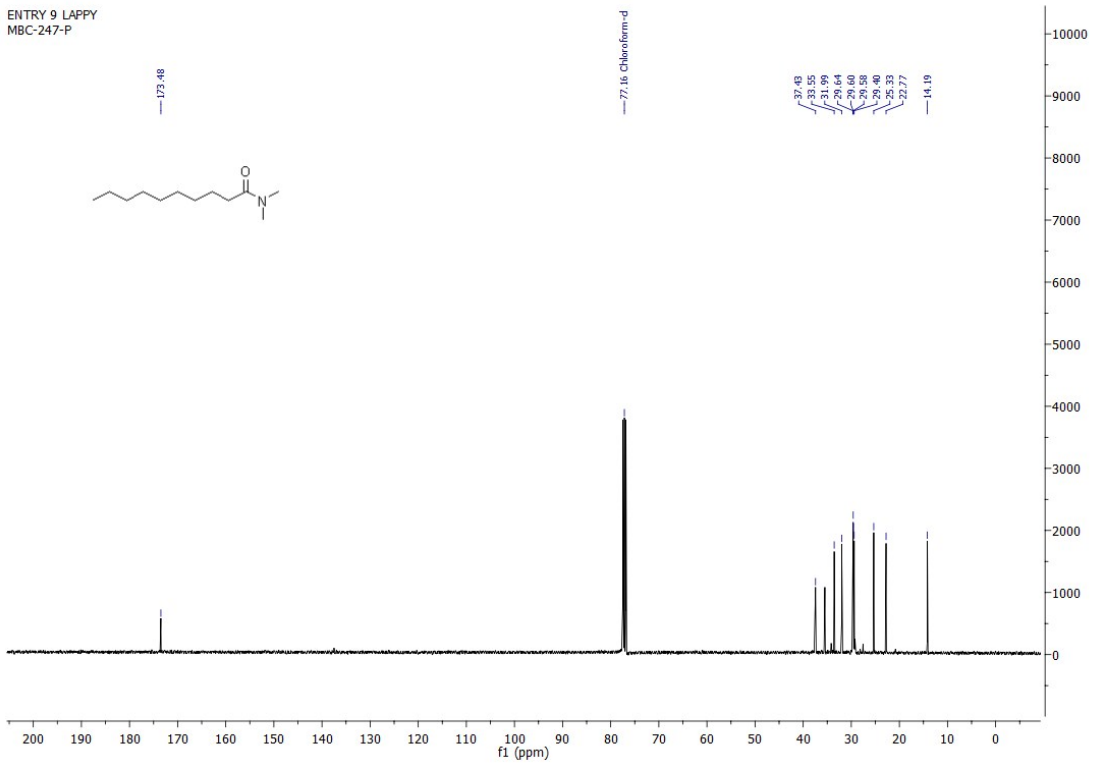
^{1}H NMR of Compound **1i**



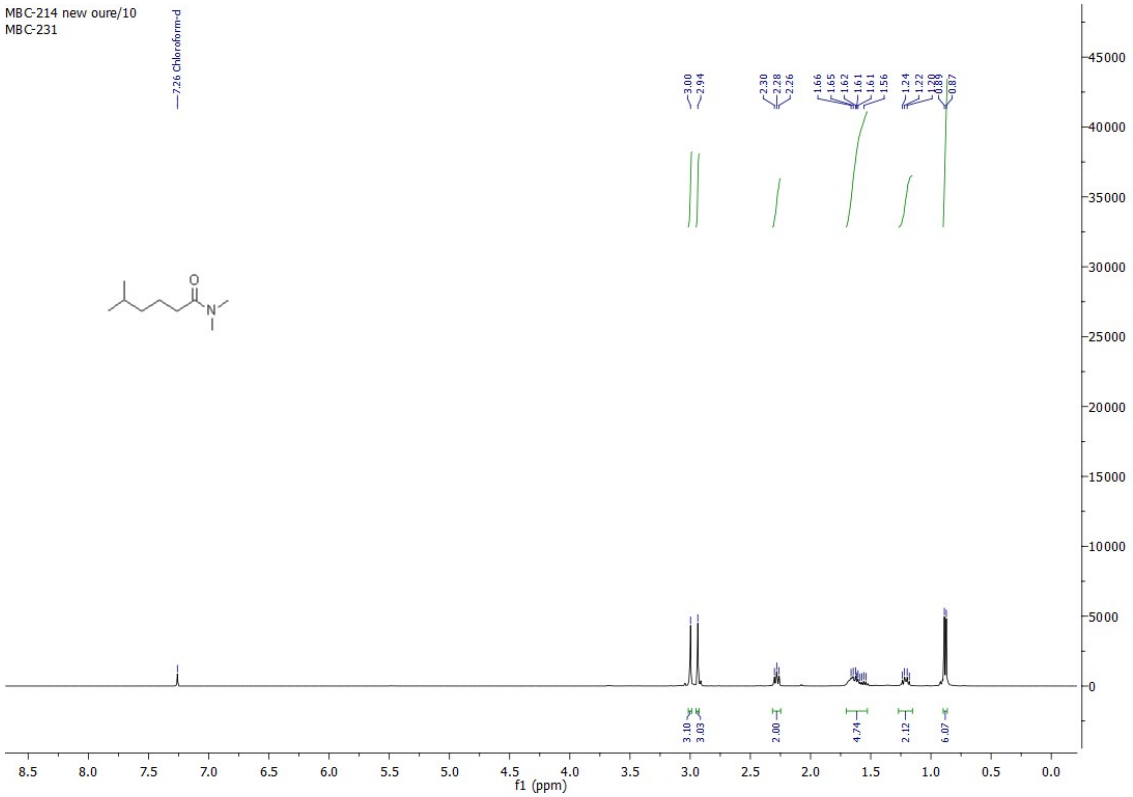
^{13}C NMR of Compound **1i**



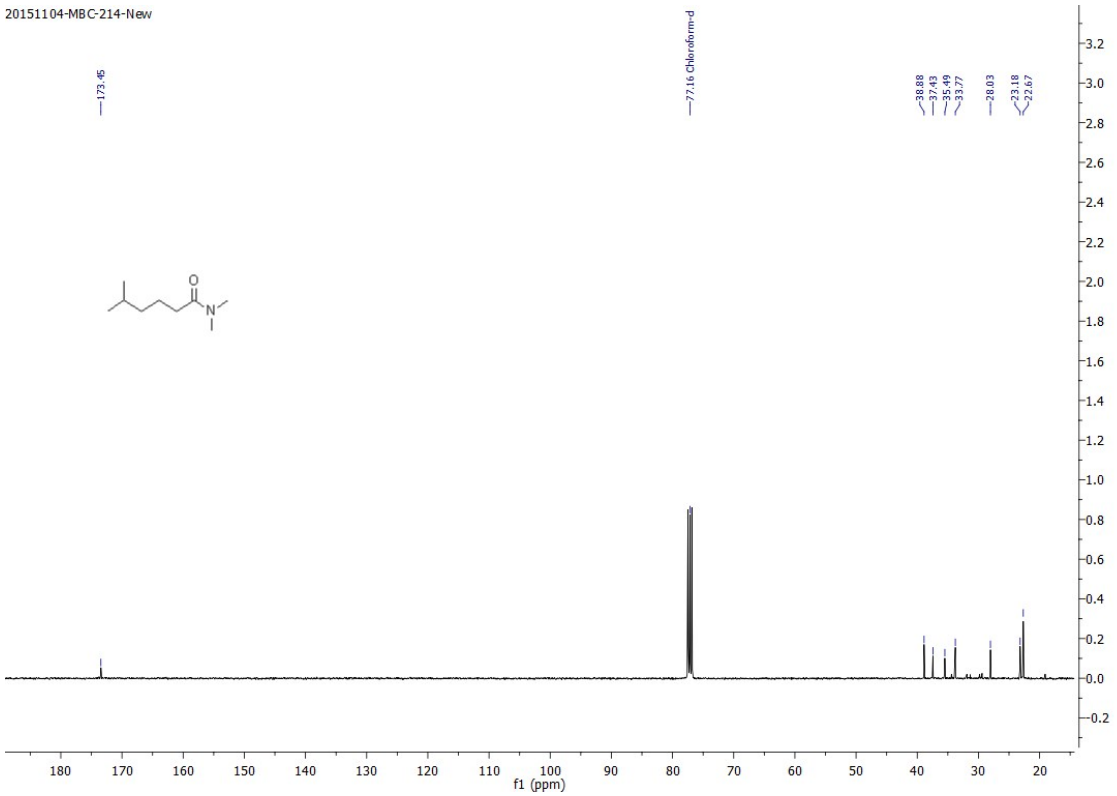
^{1}H NMR of Compound **1j**



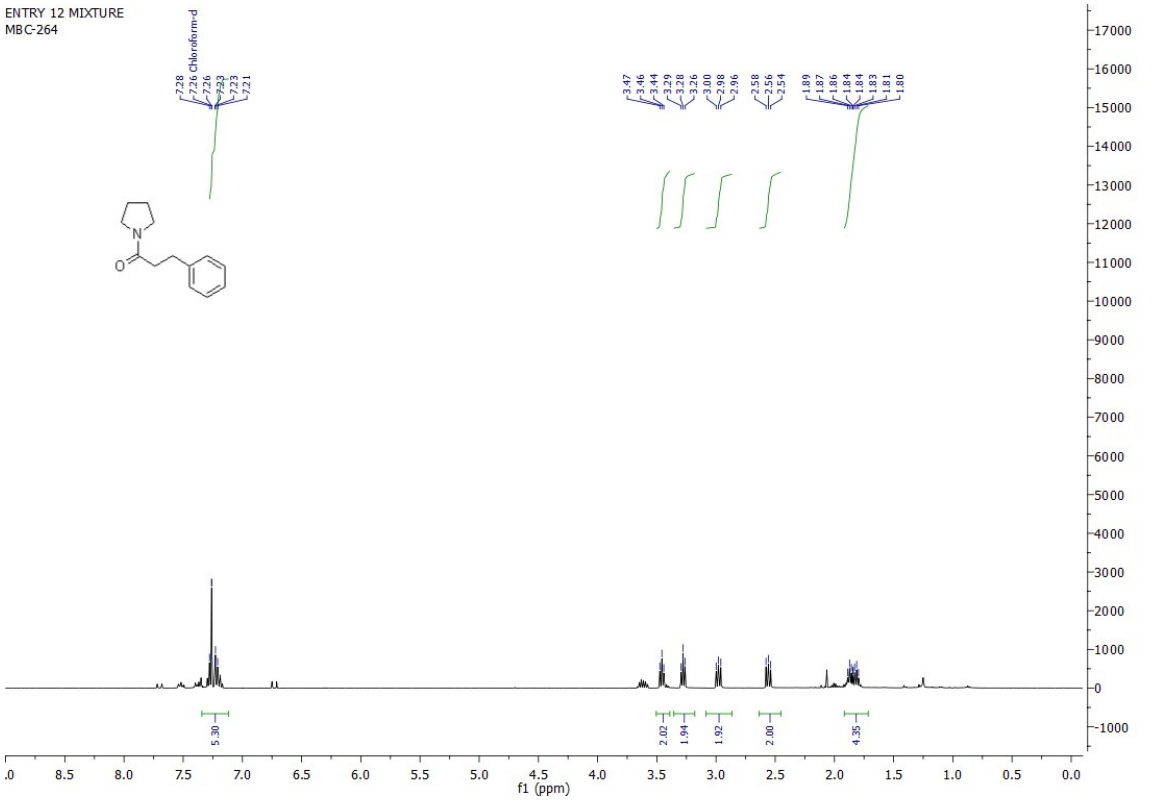
^{13}C NMR of Compound **1j**



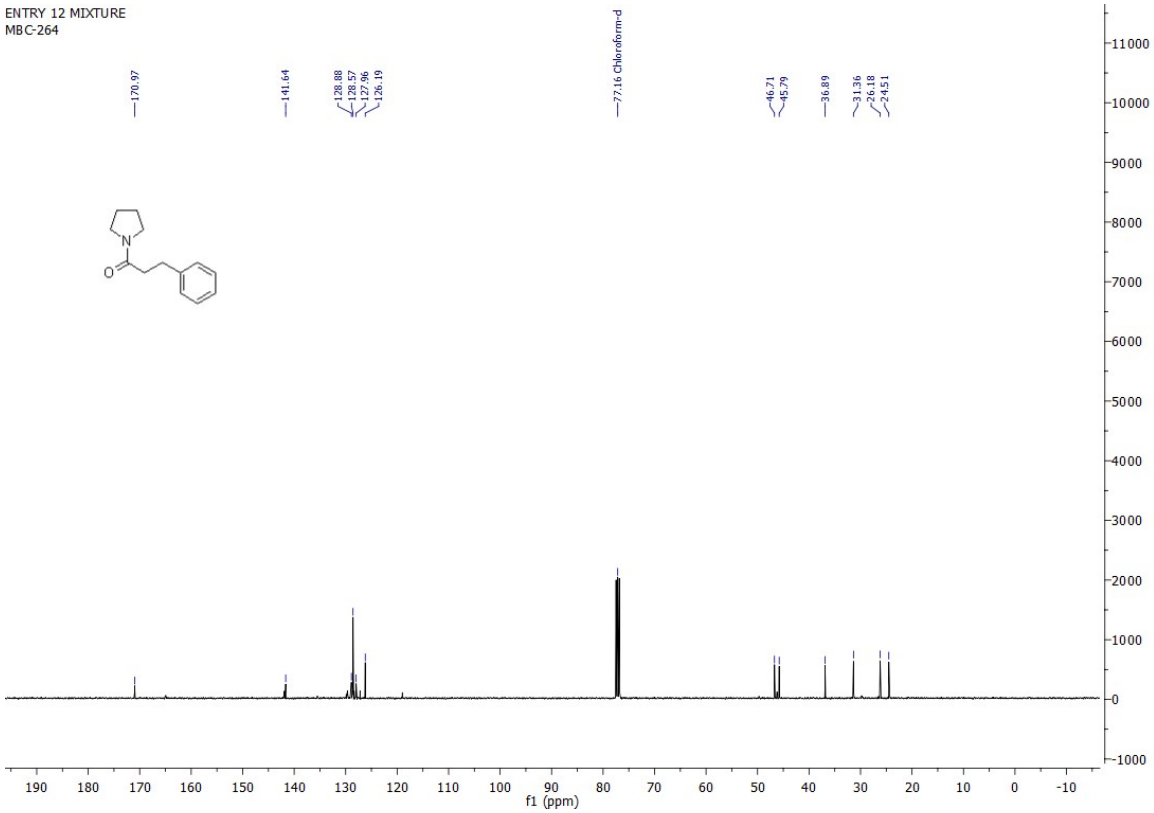
^{1}H NMR of Compound **1k**



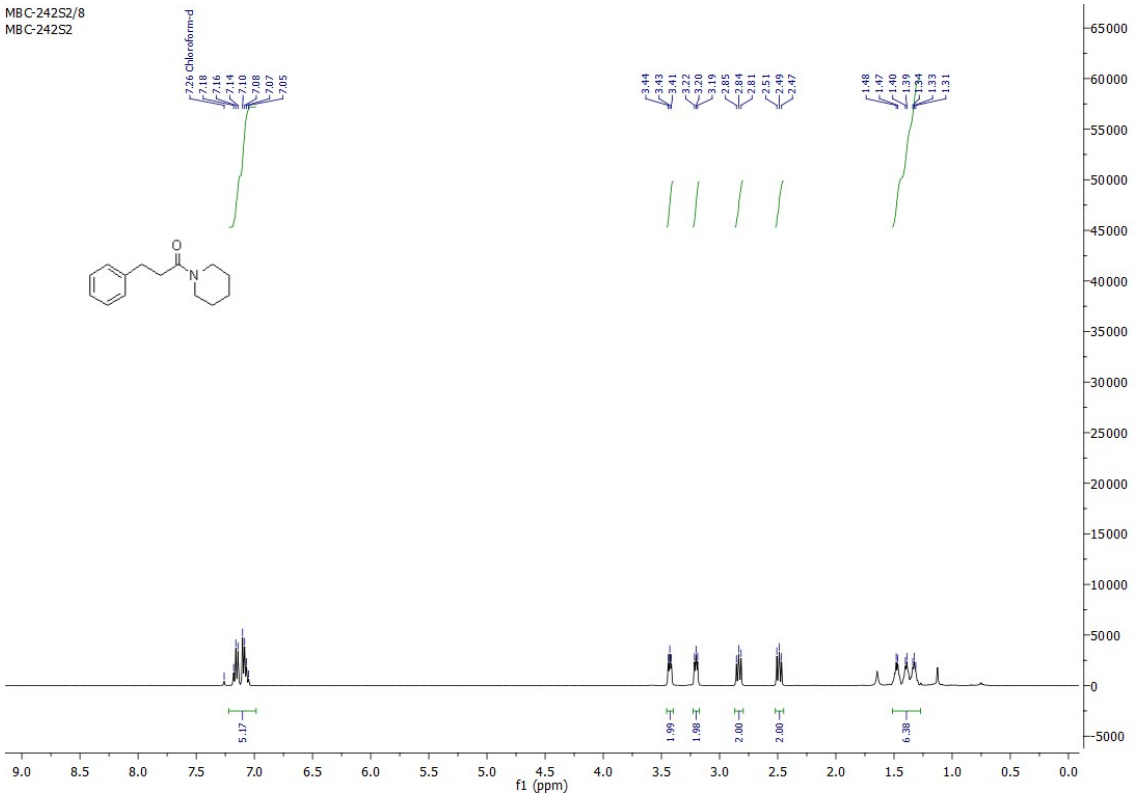
^{13}C NMR of Compound **1k**



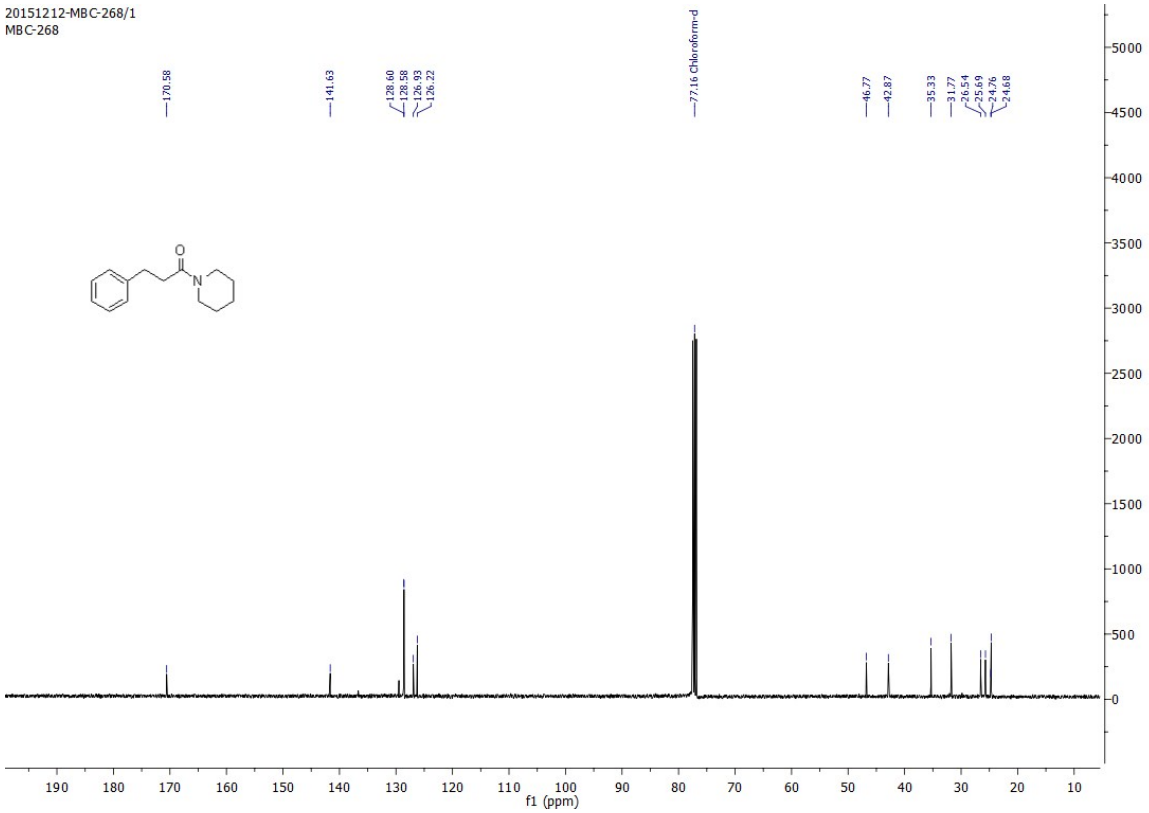
^{1}H NMR of Compound **1l**



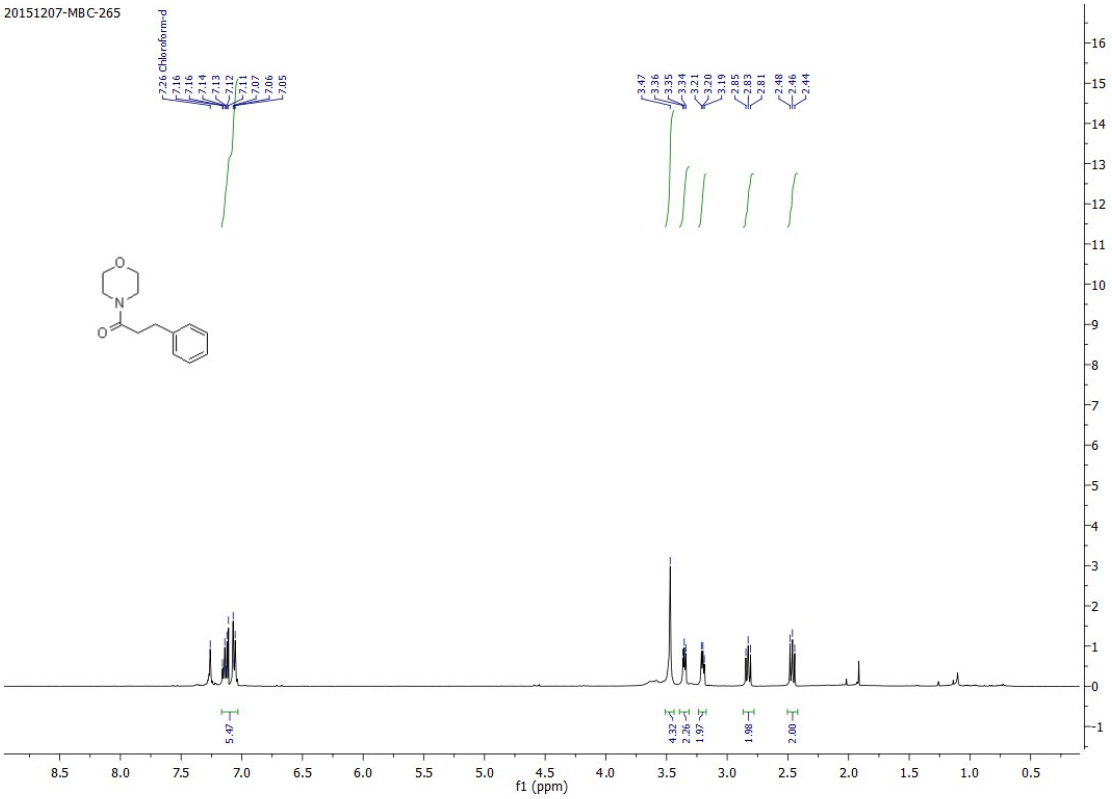
^{13}C NMR of Compound **1l**



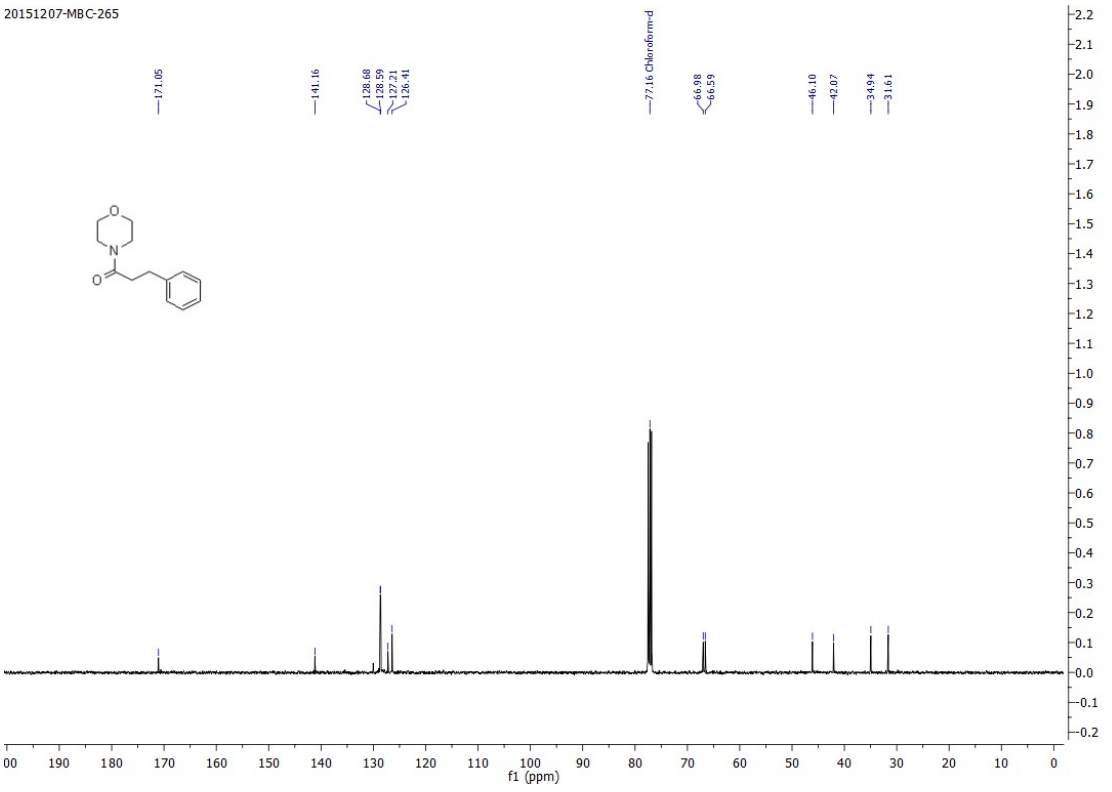
^{1}H NMR of Compound **1m**



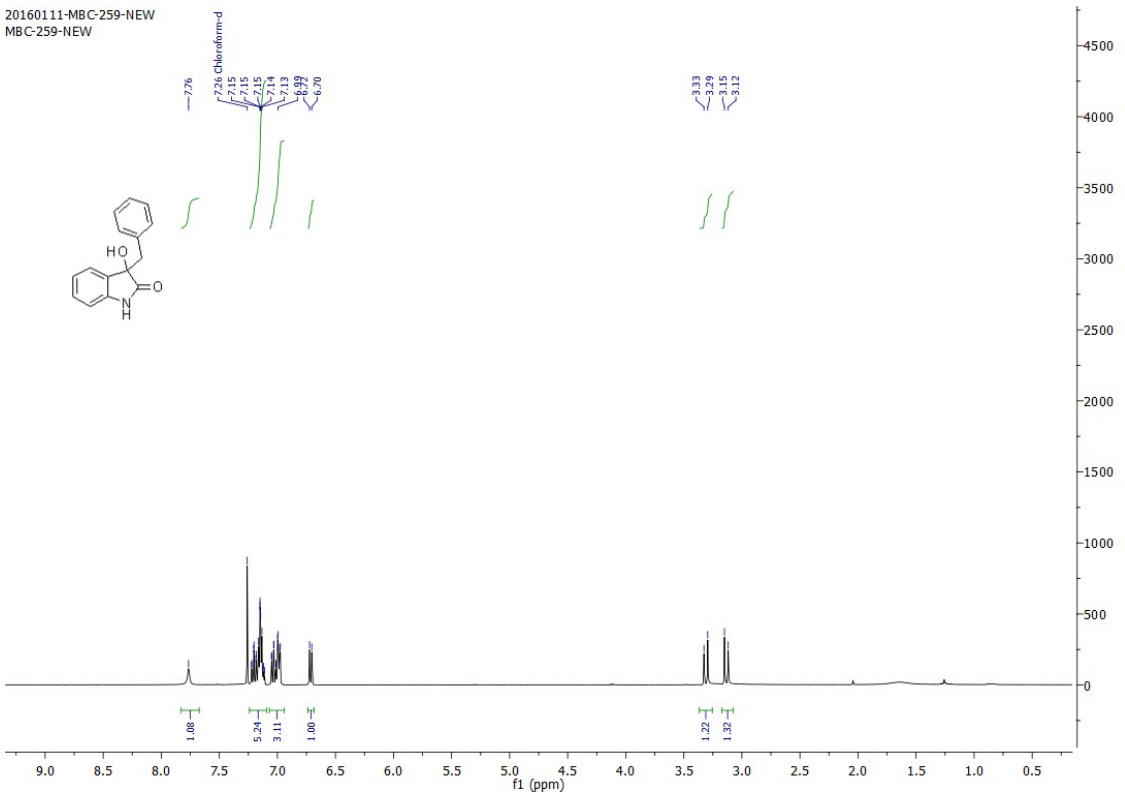
^{13}C NMR of Compound **1m**



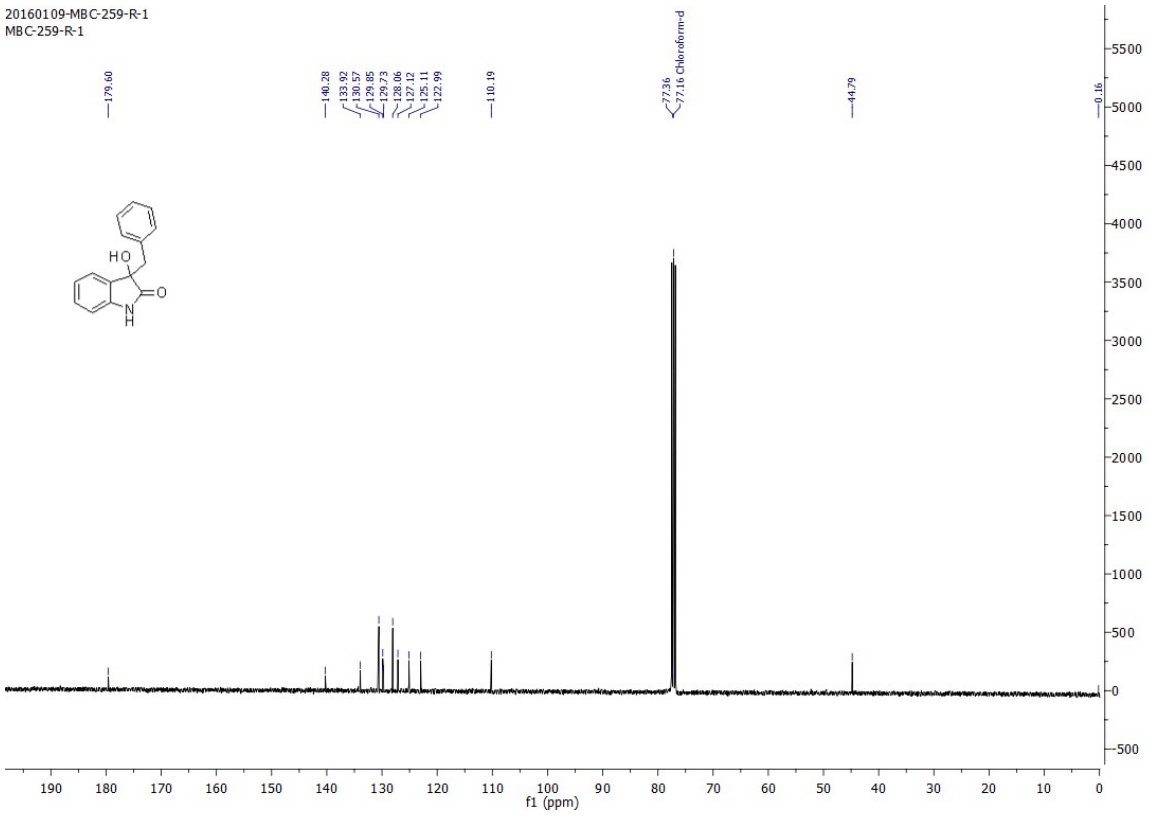
^{1}H NMR of Compound **1n**



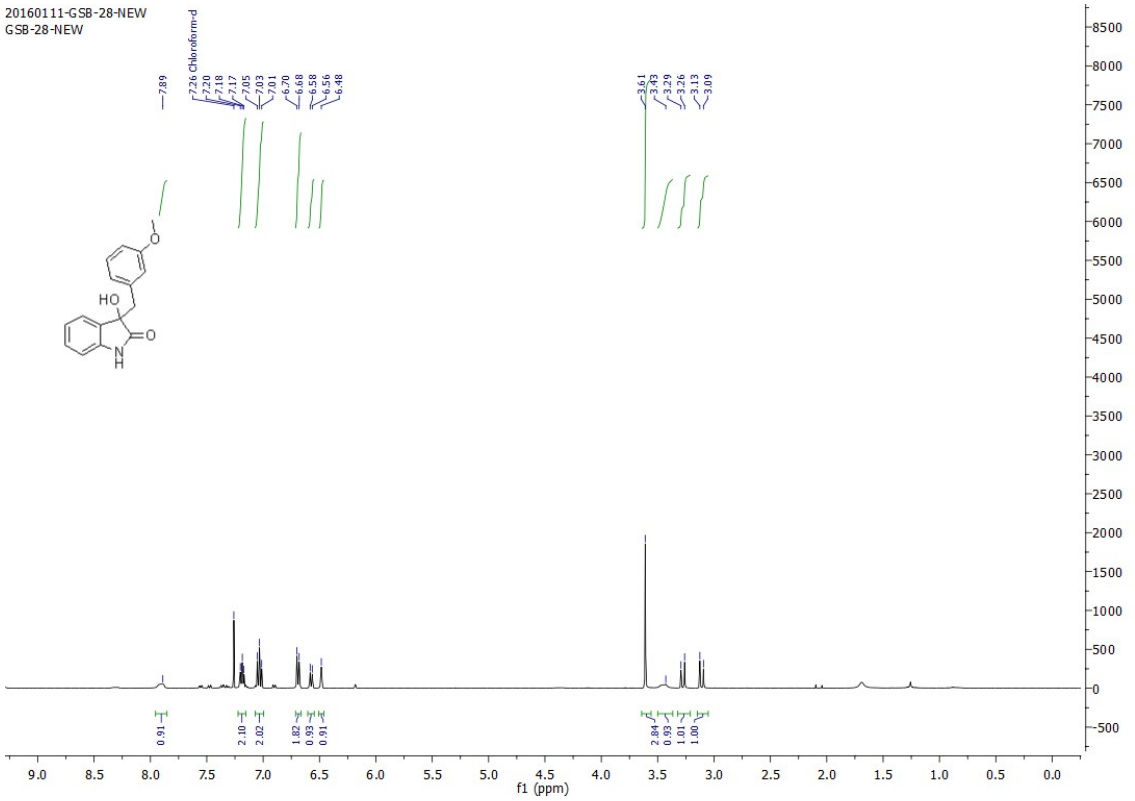
^{13}C NMR of Compound **1n**



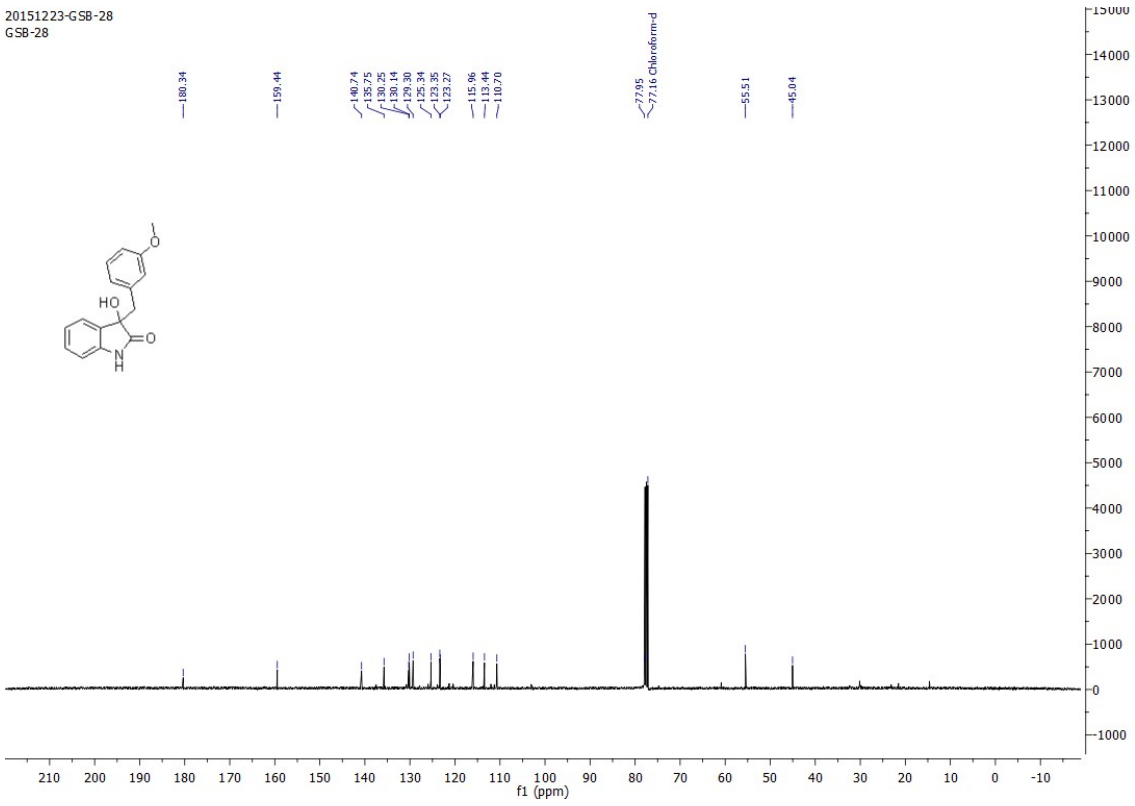
^{1}H NMR of Compound **7a**



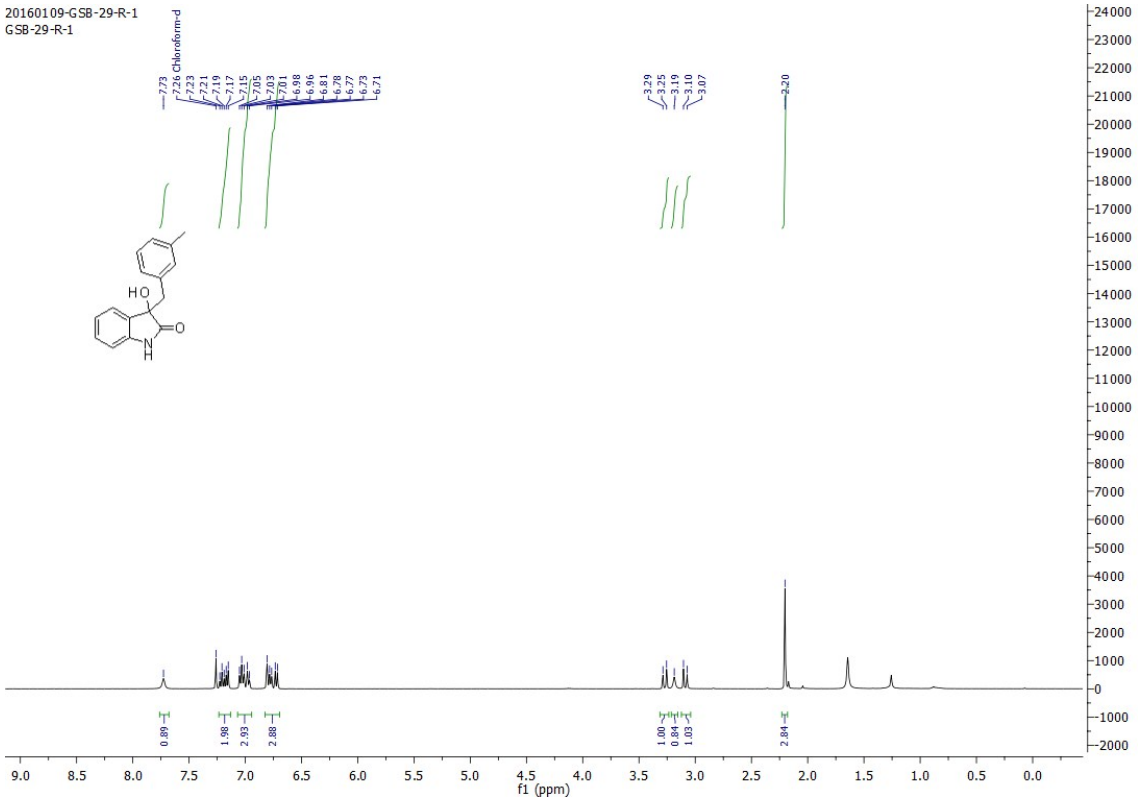
^{13}C NMR of Compound **7a**



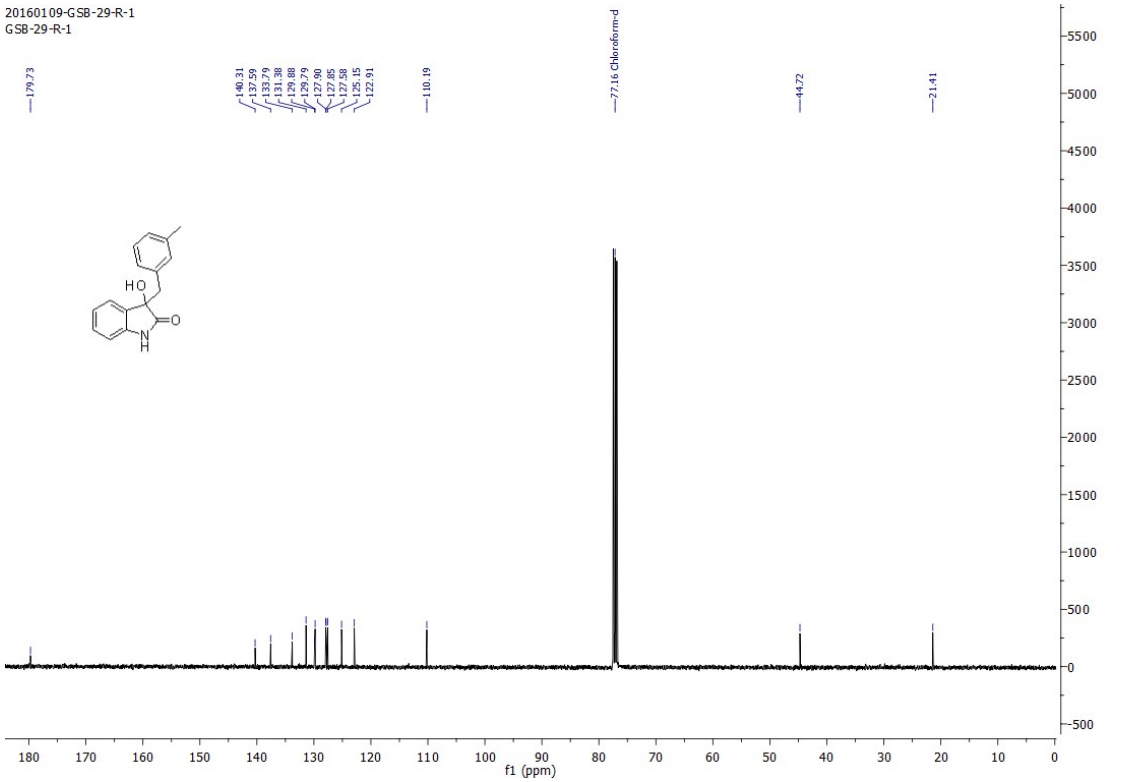
^{1}H NMR of Compound **7b**



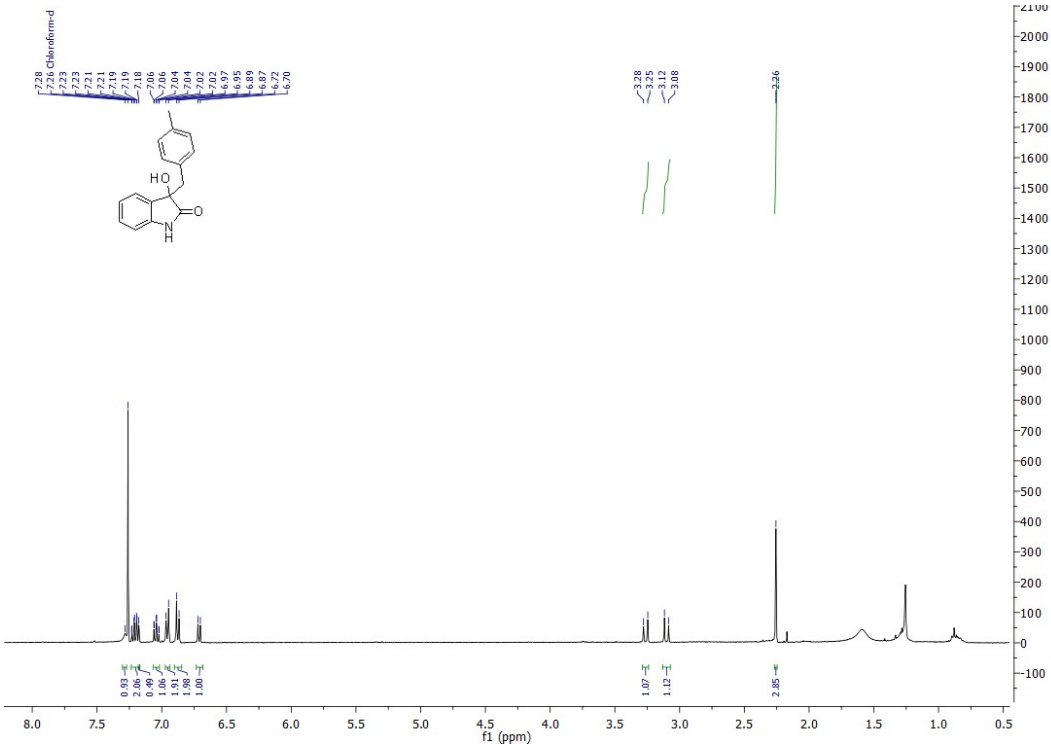
^{13}C NMR of Compound **7b**



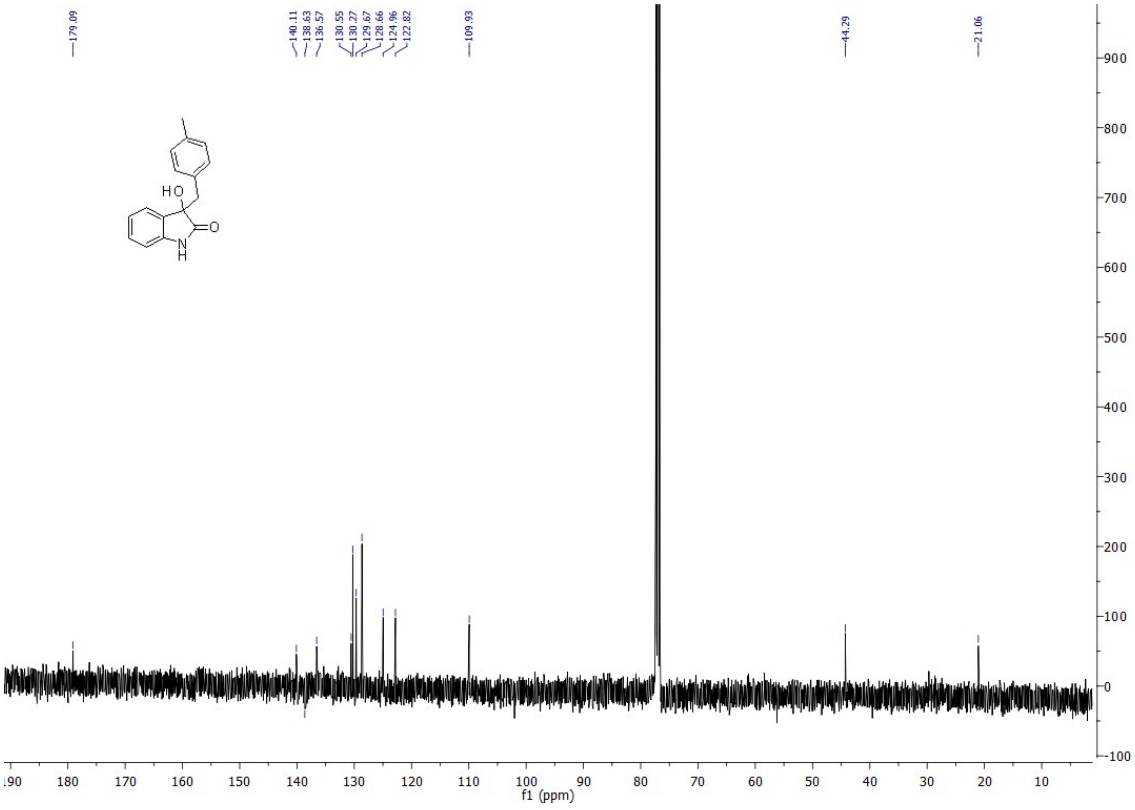
^{1}H NMR of Compound **7c**



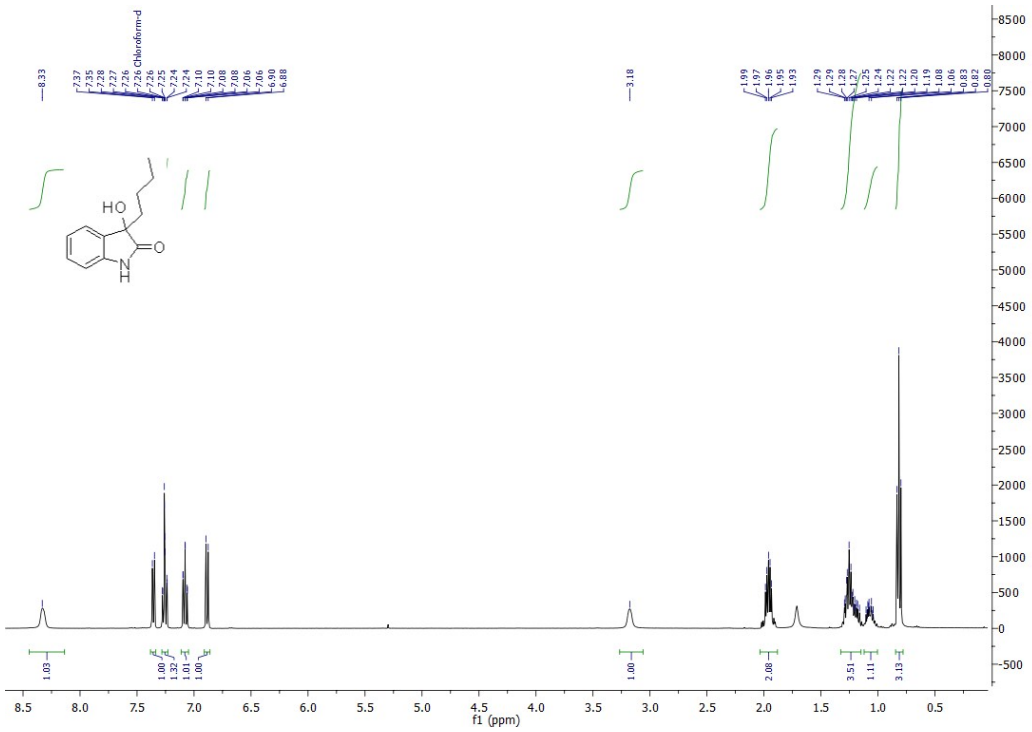
^{13}C NMR of Compound **7c**



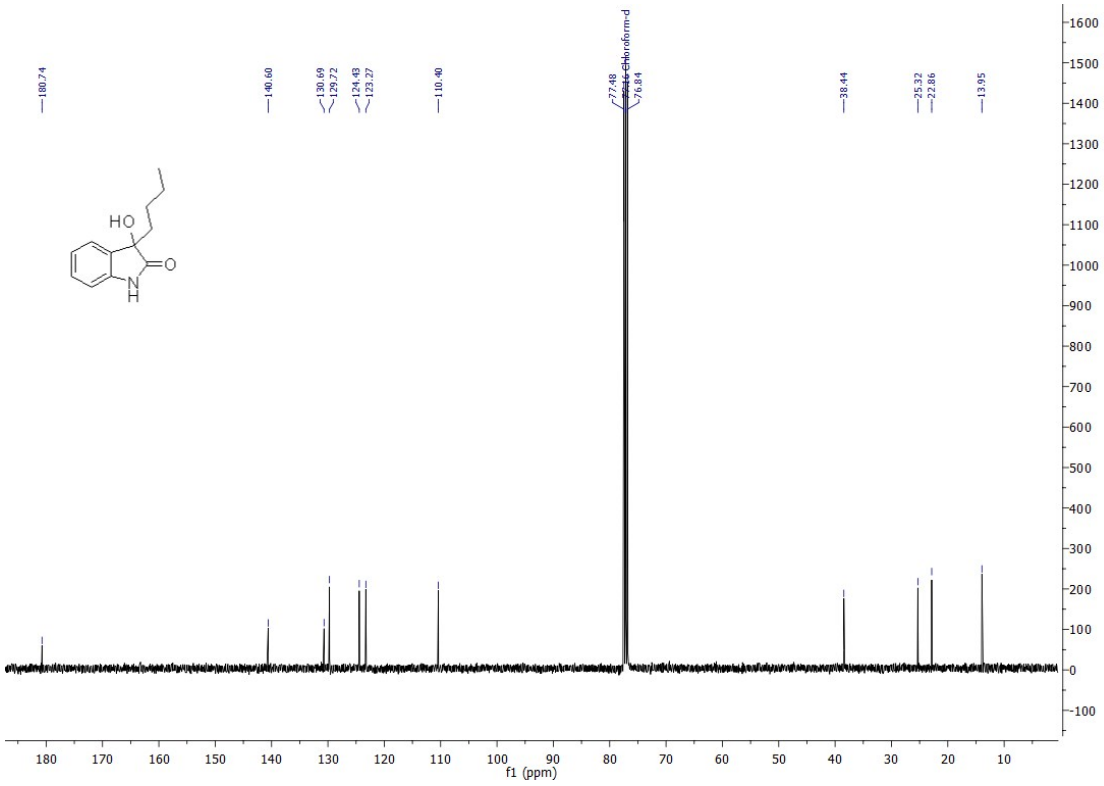
^{1}H NMR of Compound **7d**



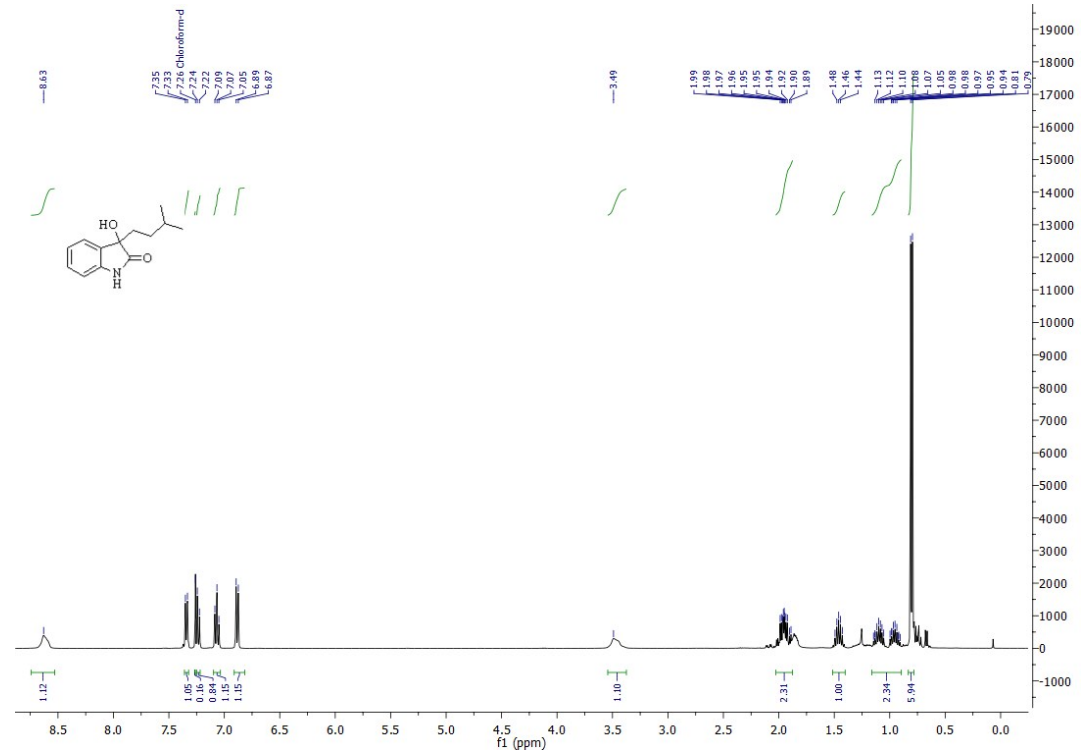
^{13}C NMR of Compound **7d**



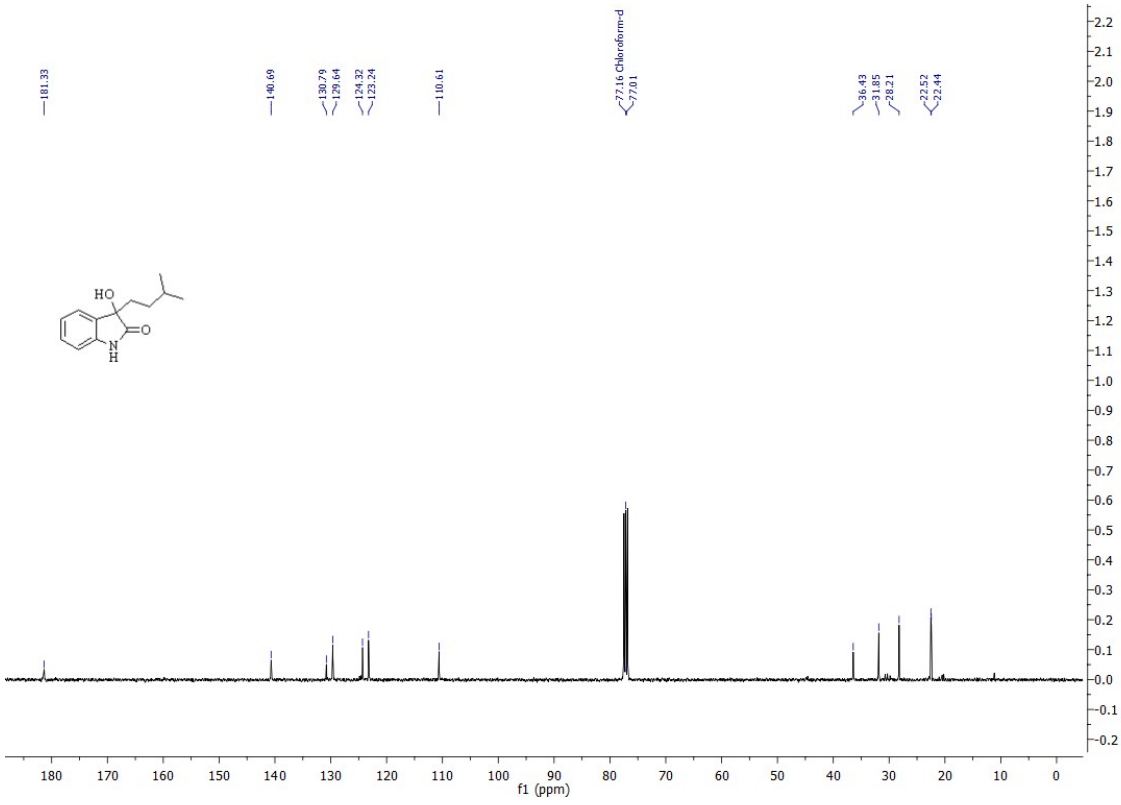
^{1}H NMR of Compound **7e**



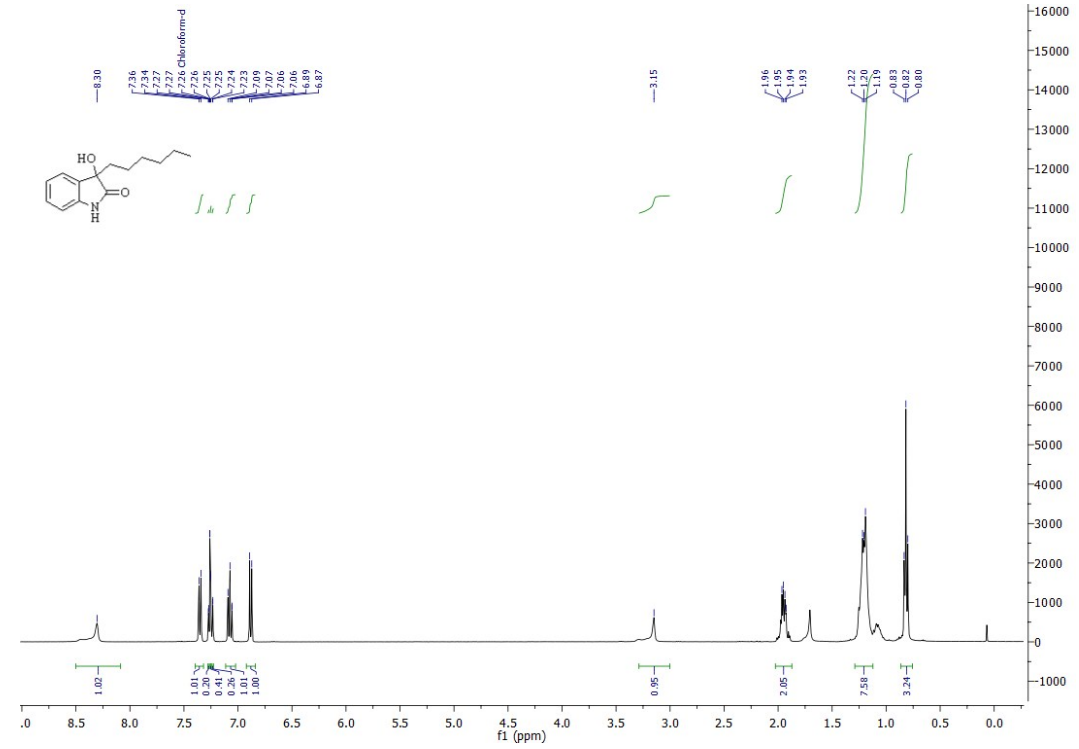
^{13}C NMR of Compound **7e**



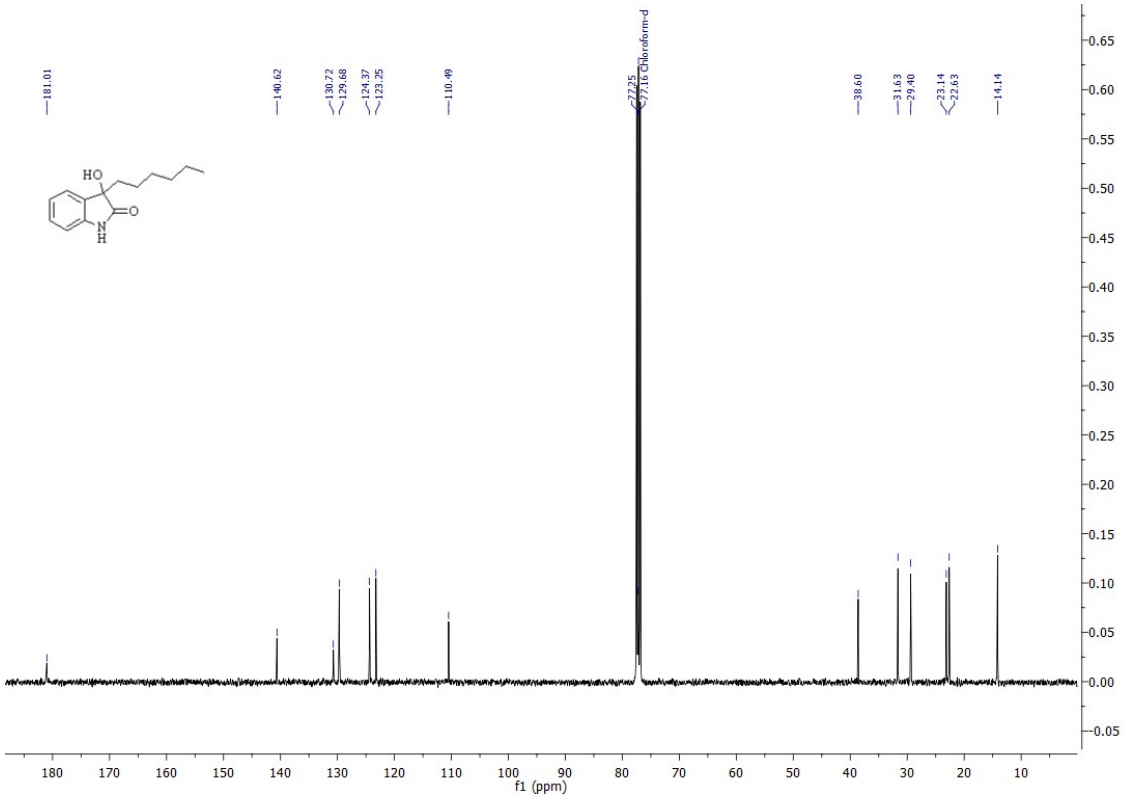
^{1}H NMR of Compound **7f**



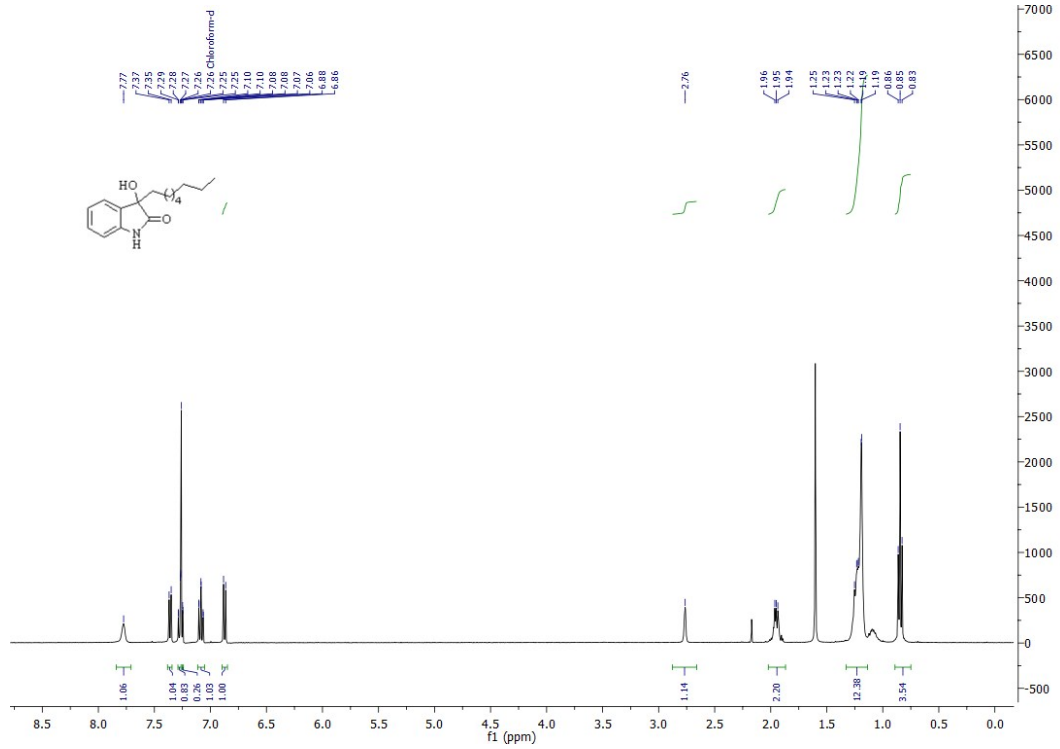
^{13}C NMR of Compound **7f**



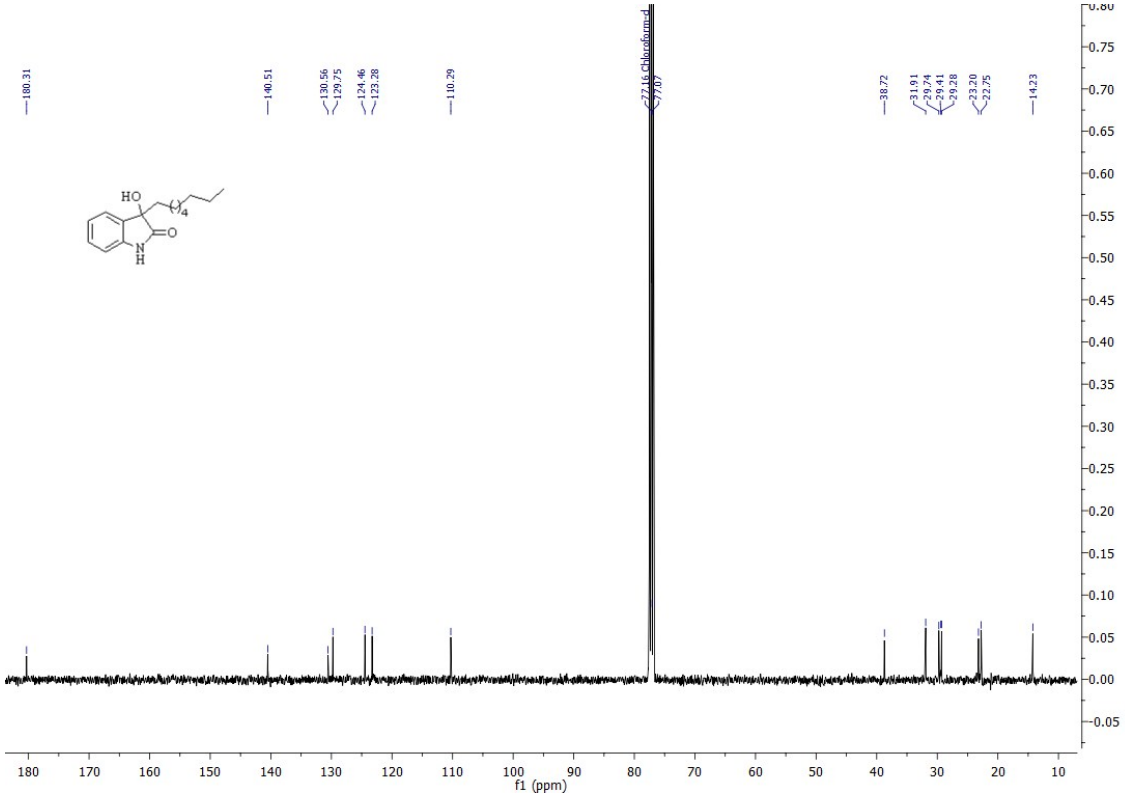
^{1}H NMR of Compound **7g**



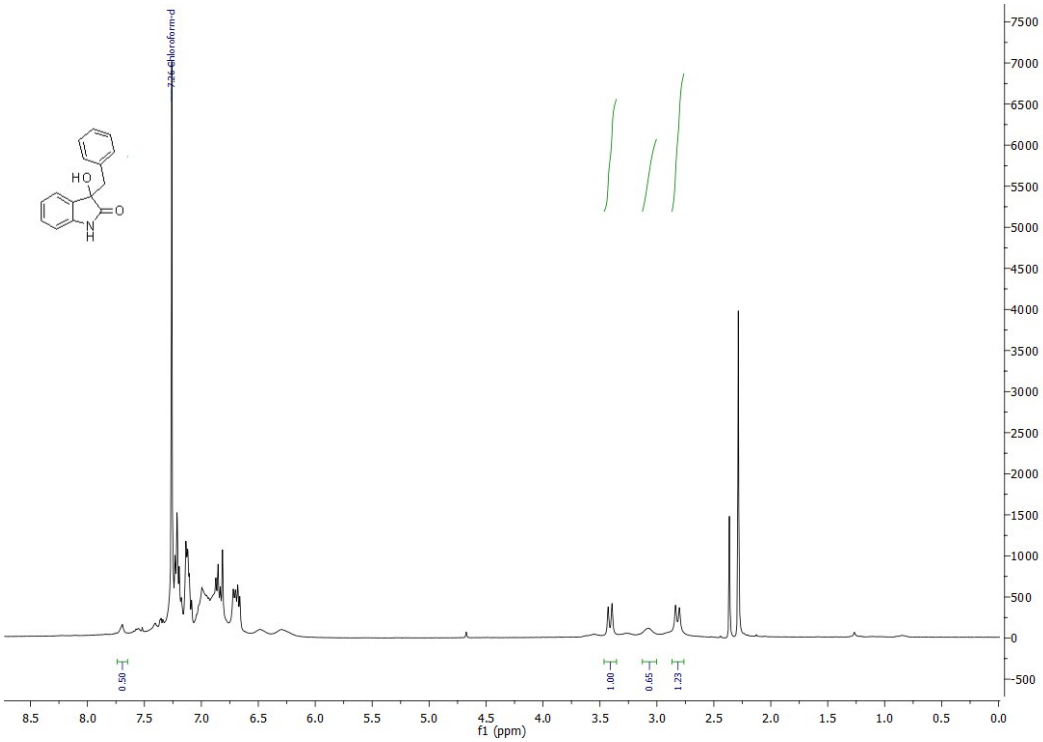
^{13}C NMR of Compound **7g**



^{1}H NMR of Compound **7h**



^{13}C NMR of Compound**7h**



^{1}H-NMR of crude reaction mixture (Compound **7a)**

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