Supporting Information

Contents

1. General information

All solvents and reagents were purchased from the suppliers and used without further purification unless otherwise noted. The melting points (uncorrected) were taken on an X4 Electrothermal Micromelting point meter. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in solvents $CDCl_3$ or DMSO-d_6 at room temperature on Bruker Avance III 400 spectrometer. The chemical-shift scale is based on internal TMS. High-solution mass spectra were acquired on Waters UPLC/Xevo G2 quadrupole time-of-flight tandem mass spectrometry (Xevo G2 Q-TOF).

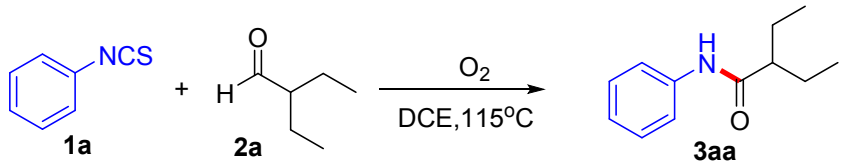
2. General procedure

Isothiocyanates **1** (0.2 mmol, 1.0 equiv)，aldehydes **2** (10 equiv)，1,2-dichloroethane (DCE) (0.25 mL, 0.8 M based on **1**) were placed in a 10 mL reaction tube, flushed with O_2, and sealed under O_2 atmosphere. The reaction system was moved to 115 °C (preheated oil bath) and stirred for 36 hours. Then the reaction mixture was concentrated and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:10, v/v) to give the products.

3. Screening parameters

3.1 Optimization of reactions with respect to aldehydes

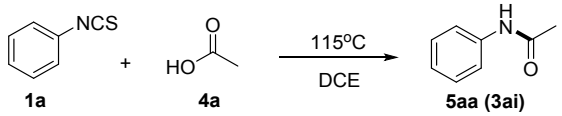
Table S1 Optimizing reaction conditions for autoxidation



Entry	**2a** (equiv)	Temp (°C)	Solvent	Conc.(M)	Time (h)	Yield (%)[c]
1	10	115	DCE	0.1	36h	49
2	10	115	DCE	0.3	36h	52
3	10	115	DCE	0.5	36h	75
4	10	115	DCE	0.8	36h	86
5	10	115	DCE	1	36h	71
6	10	115	EtOAc	0.8	36h	75
7	10	115	DCM	0.8	36h	77
8	10	115	CH_3OH	0.8	36h	27
9	10	115	CH_3CN	0.8	36h	Trace
10	10	115	H_2O	0.8	36h	15
11	10	115	DMF	0.8	36h	45
12	10	115	Toluene	0.8	36h	43
13	10	115	Chlorobenzene	0.8	36h	41
14	10	115	1,4-Dioxane	0.8	36h	43
15	6	115	DCE	0.8	36h	51
16	8	115	DCE	0.8	36h	75
17	12	115	DCE	0.8	36h	84
18	14	115	DCE	0.8	36h	84
19	10	80	DCE	0.8	36h	Trace
20	10	100	DCE	0.8	36h	Trace
21	10	110	DCE	0.8	36h	50
22	10	120	DCE	0.8	36h	83
23	10	140	DCE	0.8	36h	82
24[a]	10	115	DCE	0.8	36h	trace
25[b]	10	115	DCE	0.8	36h	71
26	10	115	DCE	0.8	24h	63
27	10	115	DCE	0.8	48h	85

Reaction condition: a solution of isothiocyanate **1a** (0.2 mmol), solvent (0.25 ml, 0.8 M) and isobutyraldehyde (**2a**) (2 mmol) sealed in a 10 mL tube flushed with O_2, stirred at 115 °C. [a] Under Ar. [b] Under air. [c] Isolated yield. DCE = 1,2-dichloroethane, DCM = dichloromethane.

3.2 Optimization of reactions with respect to carboxylic acids



1a **4a** **5aa (3ai)**

Table S2 Effect of substrate molar ratios

Entry	Molar ratio **(4a**:**1a)**	Isolated yield (%)
1	10	92
2	7	93
3	4	93
4	2	95
5	1	96

Reaction conditions：**1a** (0.2 mmol), **4a**, DCE (0.5 M), 115 °C, 36 h, under air.

Table S3 Effect of solvents

Entry	Solvent	Isolated yield (%)
1	DCE	96
2	EtOAc	30
3	DCM	89
4	CH_3OH	47
5	CH_3CN	70
6	H_2O	57
7	DMF	71
8	Toluene	45
9	Chlorobenzene	32
10	1,4-Dioxane	47
11	DMSO	36

Reaction conditions：**1a** (0.2 mmol), **4a** (0.2 mmol), solvent (0.5 M), 115 °C, 36 h, under air.

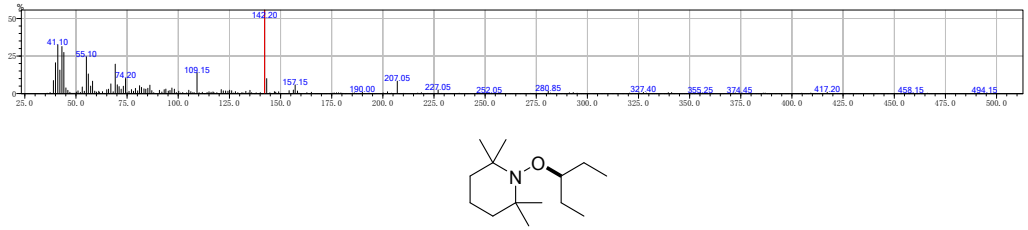
Table S4 Effect of reaction concentrations

Entry	Concentration (M)	Isolated yield (%)
1	0.10	50
2	0.25	96
3	0.50	96
4	0.75	91
5	1.00	89

Reaction conditions：**1a** (0.2 mmol), **4a** (0.2 mmol), 115 °C, 36 h, under air.

4. Control experiments

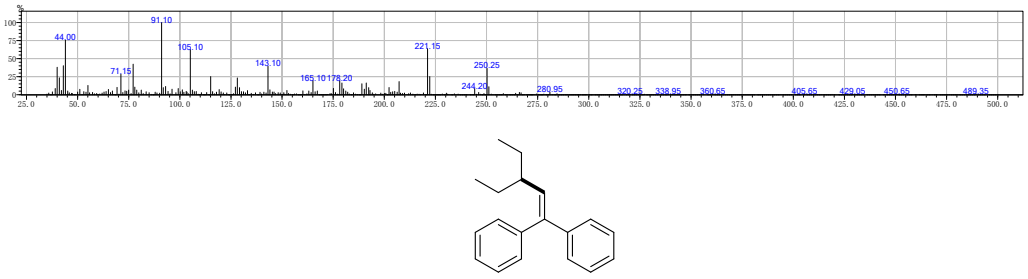
a) Use of TEMPO as trapper



m/e Found: 227.05, Calcd: 227.22

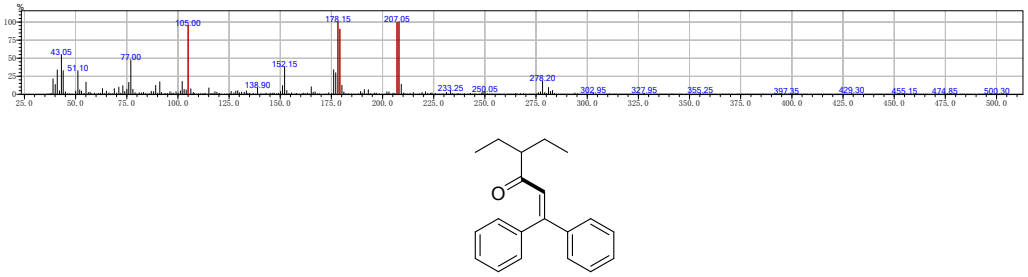
Figure S-1 Mass spectrum of the TEMPO-alkyl adduct

b) Use of DPE as trapper



m/e Found: 250.25, Calcd: 250.17

Figure S-2 Mass spectrum of the DPE-alkyl adduct

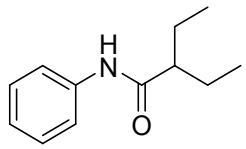


m/e Found: 278.20, Calcd: 278.17

Figure S-3 Mass spectrum of the DPE-acyl adduct

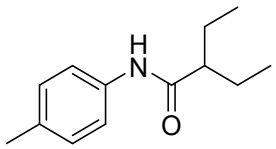
5.Characterization data

2-ethyl-*N*-phenylbutanamide (3aa)



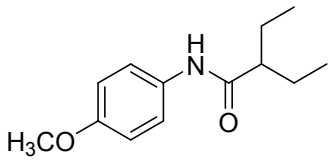
Yield 86%, white solid, mp 127-128 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.38 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.77– 1.66 (m, 2H), 1.61 – 1.50 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 138.0, 129.0, 124.2, 120.0, 52.4, 25.9, 12.1. HRMS (ESI): Calcd for $C_{12}H_{18}NO$ $[M+H]^+$: 192.13829; Found: 192.13796.

2-ethyl-*N*-(*p*-tolyl)butanamide (3ba)



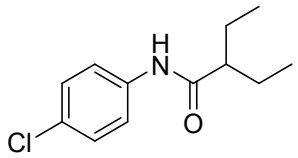
Yield 82%, white solid, mp 107-108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 3H), 2.05 – 1.97 (m, 1H), 1.77 – 1.66 (m, 2H), 1.60 – 1.50 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 135.4, 133.8, 129.4, 120.0, 52.4, 25.9, 20.8, 12.1. Calcd for $C_{13}H_{20}NO$ $[M+H]^+$: 256.15394; Found: 256.15338.

2-ethyl-*N*-(4-methoxyphenyl)butanamide (3ca)



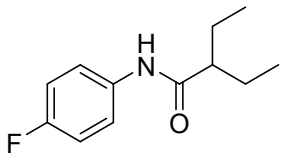
Yield 83%, white solid, mp 128-129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.25 (s, 1H), 6.87 – 6.83 (m, 2H) , 3.78 (s, 3H), 2.05 – 1.97 (m, 1H), 1.77 – 1.65 (m, 2H), 1.60 – 1.49 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 156.4, 131.1, 121.9, 114.1, 55.5, 52.2, 25.9, 12.1. Calcd for $C_{13}H_{20}NO_2$ $[M+H]^+$: 222.14886; Found: 222.14816.

***N*-(4-chlorophenyl)-2-ethylbutanamide (3da)**



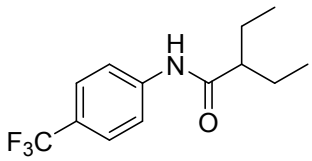
Yield 87%, white solid, mp 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 5.8 Hz, 2H), 7.32 (s, 1H), 7.27 (dd, *J* = 9.1, 2.6 Hz, 2H), 2.07 – 2.00 (m, 1H), 1.77 – 1.65 (m, 2H), 1.61 – 1.51 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 136. 5, 129.2, 128.9, 121.2, 52.3, 25.8, 12.1. Calcd for $C_{12}H_{17}ClNO$ $[M+H]^+$: 226.09932; Found: 226.09892.

2-ethyl-N-(4-fluorophenyl)butanamide (3ea)



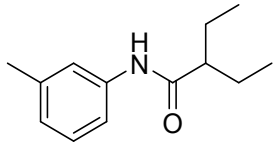
Yield 84%, white solid, mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.34 (s, 1H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.06 – 1.99 (m, 1H), 1.77 – 1.66 (m, 2H), 1.61 – 1.51 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 159.3(d, *J* = 242 Hz), 133.9(d, *J* = 2.7Hz), 121.9(d, *J* = 7.8 Hz), 115.5(d, *J* = 22.3 Hz), 52.2, 25.8, 12.1. Calcd for $C_{12}H_{17}FNO$ $[M+H]^+$: 210.12887; Found: 210.12872.

2-ethyl-*N*-(4-(trifluoromethyl)phenyl)butanamide (3fa)



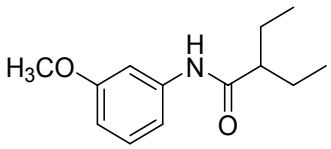
Yield 72%, white solid, mp 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.44 (s, 1H), 2.10 – 2.04 (m, 1H), 1.78 – 1.67 (m, 2H), 1.63 – 1.53 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 140.9, 126.2(q, *J* = 3.8 Hz), 124.1(q, *J* = 269.8 Hz), 119. 5, 52.4, 25.8, 12.0. Calcd for $C_{13}H_{17}F_3NO$ $[M+H]^+$: 260.12568; Found: 260.12506.

2-ethyl-*N*-(*m*-tolyl)butanamide (3ga)



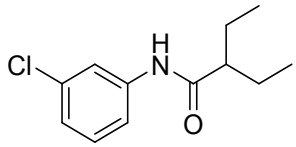
Yield 83%, white solid, mp 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.24 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 2.05 – 2.00 (m, 1H), 1.77 – 1.66 (m, 2H), 1.61 – 1.50 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 138.9, 137.9, 128.8, 125.0, 120.6, 117.0, 52.5, 25.9, 21.5, 12.1. Calcd for $C_{13}H_{20}NO$ $[M+H]^+$: 206.15394; Found: 206.15349.

2-ethyl-*N*-(3-methoxyphenyl)butanamide (3ha)



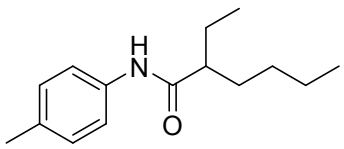
Yield 78%, white solid, mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 2.0 Hz, 1H), 7.24 (s, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.80 (s, 3H), 2.04 – 2.00 (m, 1H), 1.78 – 1.66 (m, 2H), 1.61 – 1.51 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 160.2, 139.2, 129.6, 111.81, 110.3, 105.4, 55.3, 52.6, 25.9, 12.1. Calcd for $C_{13}H_{20}NO_2$ $[M+H]^+$: 222.14886; Found: 222.14832.

***N*-(3-chlorophenyl)-2-ethylbutanamide (3ia)**



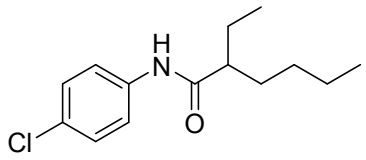
Yield 86%, white solid, mp 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.7 Hz, 1H), 7.52 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.78 – 1.65 (m, 2H), 1.61 – 1.50 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 139.1, 134.6, 129.9, 124.2, 120.1, 117.9, 52.3, 25.8, 12.1. Calcd for $C_{12}H_{17}ClNO$ $[M+H]^+$: 226.09932; Found: 226.09882.

2-ethyl-*N*-(*p*-tolyl)hexanamide (3bb)



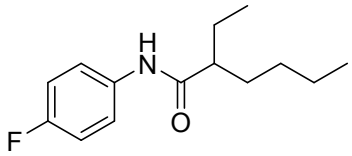
Yield 83%, white solid, mp 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 3H), 2.31 (s, 3H), 2.10 – 2.03 (m, 2H), 1.77 – 1.66 (m, 2H), 1.58 – 1.50 (m, 2H), 1.27 – 1.32 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 135.3, 133.8, 129.4, 120.0, 50.8, 32.6, 29.9, 26.2, 22.8, 20.8, 14.0, 12.1. Calcd for $C_{15}H_{24}NO$ $[M+H]^+$: 234.18524; Found: 234.18459.

***N*-(4-chlorophenyl)-2-ethylhexanamide (3db)**



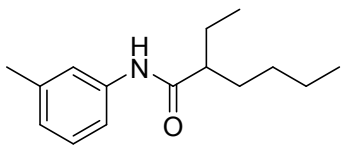
Yield 79%, white solid, mp 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.30 (s, 1H), 7.29 – 7.25 (m, 2H), 2.12 – 2.05 (m, 1H), 1.76 – 1.64 (m, 2H), 1.60 – 1.45 (m, 2H), 1.35 – 1.25 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 136.5, 129.2, 128.9, 121.2, 50.8, 32.5, 29.9, 26.2, 22.8, 14.0, 12.1. Calcd for $C_{14}H_{21}ClNO$ $[M+H]^+$: 254.13062; Found: 254.12991.

2-ethyl-*N*-(4-fluorophenyl)hexanamide (3eb)



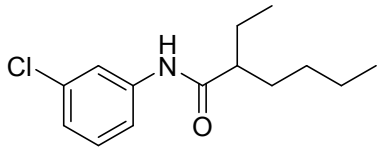
Yield 82%, white solid, mp 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.39 (s, 1H), 6.99 (t, *J* = 8.6 Hz, 2H), 2.13 – 2.06 (m, 1H), 1.76 – 1.65 (m, 2H), 1.60 – 1.47 (m, 2H), 1.38 – 1.22 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.5 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 159.3(d, *J* = 241.9 Hz), 133.9(d, *J* = 2.7 Hz), 121.9(d, *J* = 7.8 Hz), 115.5(d, *J* = 22.3 Hz), 50.6, 32.6, 29.9, 26.2, 22.8, 14.0, 12.1. Calcd for $C_{14}H_{21}FNO$ $[M+H]^+$: 238.16017; Found: 238.15958.

2-ethyl-*N*-(*m*-tolyl)hexanamide (3gb)



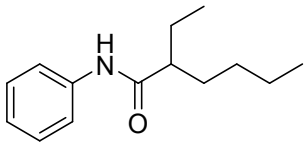
Yield 81%, white solid, mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 2.11 – 2.04 (m, 1H), 1.75 – 1.65 (m, 2H), 1.60 – 1.46 (m, 2H), 1.35 – 1.26 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 138.9, 137.9, 128.8, 125.0, 120.6, 116.9, 50.9, 32.7, 29.9, 26.3, 22.8, 21.5, 14.0, 12.1. Calcd for $C_{15}H_{24}NO$ $[M+H]^+$: 234.18524; Found: 234.18460.

_N_-(3-chlorophenyl)-2-ethylhexanamide (3ib)



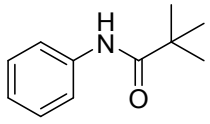
Yield 78%, white solid, mp 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.47 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 2.14 – 2.07 (m, 1H), 1.76 – 1.67 (m, 2H), 1.60 – 1.47 (m, 2H), 1.36 – 1.26 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 139.1, 134.6, 129.9, 124.2, 120.1, 117.9, 50.7, 32.5, 29.9, 26.2, 22.8, 14.0, 12.1. Calcd for $C_{14}H_{21}ClNO$ $[M+H]^+$: 254.13062; Found: 254.12985.

2-ethyl-_N_-phenylhexanamide (3ab)



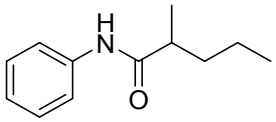
Yield 85%, white solid, mp 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.19 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.11 – 2.05 (m, 1H), 1.76 – 1.63 (m, 2H), 1.59 – 1.47 (m, 2H), 1.36 – 1.26 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 137.9, 129.0, 124.2, 119.9, 50.9, 32.6, 29.9, 26.2, 22.8, 14.0, 12.1. Calcd for $C_{14}H_{22}NO$ $[M+H]^+$: 220.16959; Found: 220.16911.

2,2-dimethyl-_N_-phenylpropanamide (3ac & 5ac)[1]



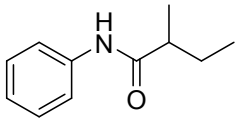
Yield 76%, white solid, mp 126-127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.34 (m, 3H), 7.30 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 1.32 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 138.0, 129.0, 124.2, 120.0, 39.6, 27.7. Calcd for $C_{11}H_{16}NO$ $[M+H]^+$: 178.12264; Found: 178.12228.

2-methyl-*N*-phenylpentanamide (3ad)[2]



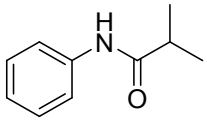
Yield 84%, white solid, mp 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H) , 2.40 – 2.31 (m, 1H), 1.77 – 1.69 (m, 1H), 1.48 – 1.32 (m, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 138.0, 128.9, 124.2, 119.9, 42.46, 36.61, 20.7, 17.9, 14.1. Calcd for $C_{12}H_{18}NO$ $[M+H]^+$: 192.13829; Found: 192.13774.

2-methyl-*N*-phenylbutanamide (3ae)



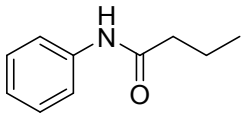
Yield 83%, white solid, mp 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.31 – 2.23 (m, 1H), 1.82 – 1.71 (m, 1H) , 1.57 – 1.46 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 138.0, 129.0, 124.2, 119.9, 44.2, 27.4, 17.5, 11.9. Calcd for $C_{11}H_{16}NO$ $[M+H]^+$: 178.12264; Found: 178.12228.

2-methyl-*N*-phenylpropanamide (3af)[3]



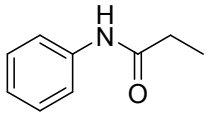
Yield 78%, white solid, mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.22 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.51 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 138.0, 129.0, 124.2, 119.8, 36.7, 19.6. Calcd for $C_{10}H_{14}NO$ $[M+H]^+$: 164.10699; Found:164.10660.

***N*-phenylbutanamide (3ag)[4]**



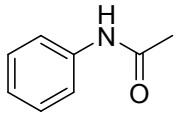
Yield 79%, white solid, mp 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.9 Hz, 2H), 7.36 (s, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 2.33 (t, J = 7.4 Hz, 2H), 1.76 (dd, J = 14.9, 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.0, 129.0, 124.2, 119.9, 39.7, 19.1, 13.8. Calcd for $C_{10}H_{14}NO$ $[M+H]^+$: 164.10699; Found: 164.10669.

***N*-phenylpropanamide (3ah & 5ab)[5]**



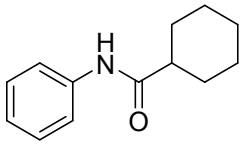
Yield 72%, white solid, mp 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.52 (d, J = 7.9 Hz, 2H), 7.29 (t, J = 7.9 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 2.37 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 138.1, 128.9, 124.2, 120.0, 30.7, 9.7. Calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.09134; Found: 150.09100.

***N*-phenylethanamide (3ai & 5aa)[6]**



Yield 70%, white solid, mp 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 138.0, 129.0, 124.3, 120.0, 24.5. Calcd for $C_8H_{10}NO$ $[M+H]^+$: 136.07569; Found: 136.07553.

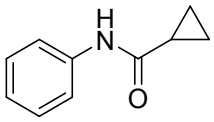
***N*-phenylcyclohexanecarboxamide (3aj)[7]**



Yield 87%, white solid, mp 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.09 (t, J = 7.4 Hz, 1H), 2.23 (tt, J = 11.6, 3.6 Hz, 1H), 1.93 – 1.97 (m, 2H), 1.82 – 1.85 (m, 2H), 1.69 – 1.71 (m, 1H), 1.59 – 1.49 (m,

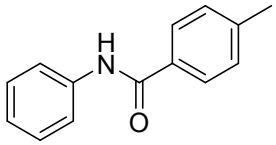
2H), 1.35 – 1.23 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 138.1, 129.0, 124.1, 119.8, 46.6, 29.7, 25.7. Calcd for $C_{13}H_{18}NO$ $[M+H]^+$: 204.13829; Found: 204.13783.

_N_-phenylcyclopropanecarboxamide (3ak)[8]



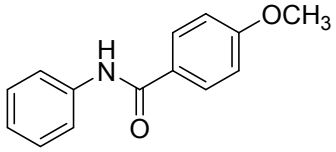
Yield 72%, white solid, mp 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 1.54 – 1.48(m, 1H), 1.10 – 1.06 (m, 2H), 0.85 – 0.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 138.1, 129.0, 124.0, 119.7, 15.7, 7.9. Calcd for $C_{10}H_{12}NO$ $[M+H]^+$: 162.09134; Found: 162.09094.

4-methyl-_N_-phenylbenzamide (3al)[9]



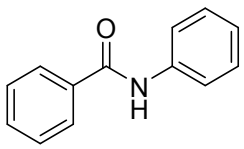
Yield 62%, white solid, mp 149-150 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.36 – 7.32 m, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 142.0, 139.7, 132.5, 129.4, 129.0, 128.1, 124.0, 120.8, 21.5.

4-methoxy-_N_-phenylbenzamide (3am)[10]



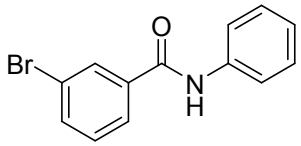
Yield 58%, white solid, mp 169-171 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.04 – 7.09 (m, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.3, 139.8, 130.1, 129.0, 127.4, 123.9, 120.8, 114.1, 55.9.

4-methoxy-_N_-phenylbenzamide (3an)[11]



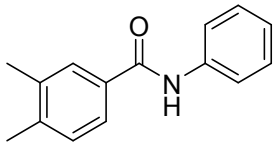
Yield 50%, white solid, mp 161-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (br s, 1H), 7.86 – 7.84 (m, 2H), 7.63 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.44 (m, 2H), 7.37 – 7.33 (m, 2H), 7.16 – 7.12 (m, 1H).

3-bromo-*N*-phenylbenzamide (3ao)[11]



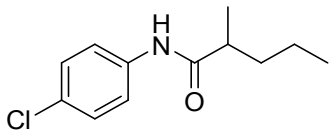
Yield 46%, white solid, mp 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.4 Hz, 1H), 7.80 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.75 (br s, 1H), 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H).

3,4-dimethyl-*N*-phenylbenzamide (3ap)[12]



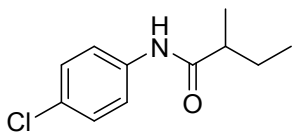
Yield 40%, white solid, mp 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 7.65 – 7.63 (m, 3H), 7.56 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H).

***N*-(4-chlorophenyl)-2-methylpentanamide (3dd)**



Yield 74%, white solid, mp 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.42 (s, 1H), 7.26 (d, 2H), 2.31 – 2.22 (m, 1H), 1.81 – 1.70 (m, 1H), 1.57 – 1.46 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 136.6, 129.1, 129.0, 121.1, 42.5, 36.6, 20.7, 17.8, 14.1. Calcd for $C_{12}H_{17}ClNO$ $[M+H]^+$: 226.09932; Found: 226.09869.

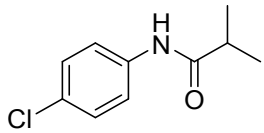
***N*-(4-chlorophenyl)-2-methylbutanamide (3de)**



Yield 75%, white solid, mp 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.42 (s, 1H), 7.27 – 7.25 (m, 2H), 2.31 – 2.22 (m, 1H), 1.81 – 1.70 (m, 1H), 1.56 – 1.46 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).^{13}C NMR

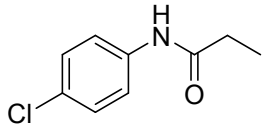
(100 MHz, $CDCl_3$) δ 175.0, 136.6, 129.1, 128.9, 121.2, 44.1, 27.4, 17.4, 11.9. Calcd for $C_{11}H_{15}ClNO$ $[M+H]^+$: 212.08367; Found: 212.08330.

***N*-(4-chlorophenyl)-2-methylpropanamide (3df)**



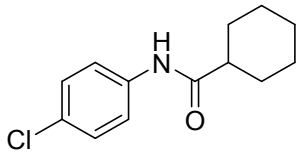
Yield 73%, white solid, mp 155-156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.7 Hz, 2H), 7.33 (s, 1H), 7.28 – 7.26 (m, 2H), 2.50 (hept, J = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 136.6, 129.1, 129.0, 121.1, 36.7, 19.6. Calcd for $C_{10}H_{13}ClNO$ $[M+H]^+$: 198.06802; Found: 198.06779.

***N*-(4-chlorophenyl)propanamide (3dh)[13]**



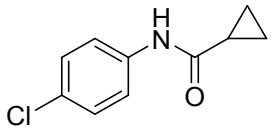
Yield 75%, white solid, mp 138-139 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.29 (t, J = 6.1 Hz, 2H), 2.41 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 136.6, 129.1, 128.9, 121.2, 30.6, 9.6. Calcd for $C_9H_{11}ClNO$ $[M+H]^+$: 184.05237; Found: 184.05212.

***N*-(4-chlorophenyl)cyclohexanecarboxamide (3dj)**



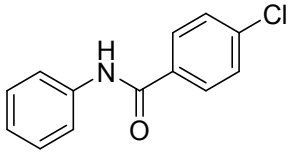
Yield 76%, white solid, mp 190-191 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.7 Hz, 2H), 7.32 (s, 1H), 7.27 – 7.25 (m, 2H), 2.22 (tt, J = 11.7, 3.4 Hz, 1H), 1.94 (d, J = 13.1 Hz, 2H), 1.85 – 1.82 (m, 2H), 1.70 (d, J = 9.8 Hz, 1H), 1.58 – 1.48 (m, 2H), 1.34 – 1.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 136.7, 129.0, 128.9, 121.0, 46.49, 29.6, 25.6. Calcd for $C_{13}H_{17}ClNO$ $[M+H]^+$: 238.09932; Found: 238.09877.

***N*-(4-chlorophenyl)cyclopropanecarboxamide (3dk)[14]**



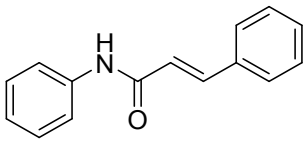
Yield 69%, white solid, mp 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 1.53 – 1.47 (m, 1H), 1.09– 1.05 (m, 2H), 0.86 – 0.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 136.7, 129.0, 121.0, 15.7, 8.1. Calcd for $C_{10}H_{11}ClNO$ $[M+H]^+$: 196.05237; Found: 196.05212.

***N*-(4-chlorophenyl)benzamide (5ad)[10]**



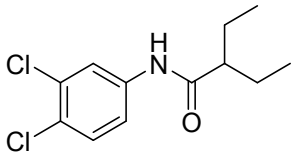
Yield 92%, white solid, mp 197-198 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.95 – 7.92 (m, 2H), 7.72 – 7.70 (m, 2H), 7.58 – 7.54 (m, 2H), 7.31 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.9, 139.4, 136.8, 134.1, 130.1, 129.1, 128.9, 124.3, 120.9.

***N*-Phenylamide of 3-phenylpropenoic acid (5ae)[15]**



Yield 78%, colorless solid, mp 171–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.65 (d, *J* = 6.9 Hz, 2H), 7.45 (dd, *J* = 4.9, 2.6 Hz, 2H), 7.33 – 7.29 (m, 5H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.62 (dd, *J* = 15.5, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 142.3, 138.1, 134.6, 129.9, 129.1, 128.9, 128.0, 124.5, 121.0, 120.2. Calcd for $C_{15}H_{14}NO$ $[M+H]^+$ 224.10699, Found 224.10705.

***N*-(3,4-dichlorophenyl)-2-ethylbutanamide (7aa)**



Yield 69%, white solid, mp 96-97 °C. ^{1}H NMR (48600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.36 (s, 2H), 7.25 (s, 1H), 2.05 – 2.00 (m, 1H), 1.75 – 1.65 (m, 2H), 1.62 – 1.52 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 137.3, 132.8, 130.5, 127.4, 121.6, 119.0, 52.4, 25.8, 12.1. Calcd for $C_{12}H_{16}Cl_2NO$ $[M+H]^+$: 260.06035; Found: 260.05994.

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6. Copies of NMR spectra of some compounds

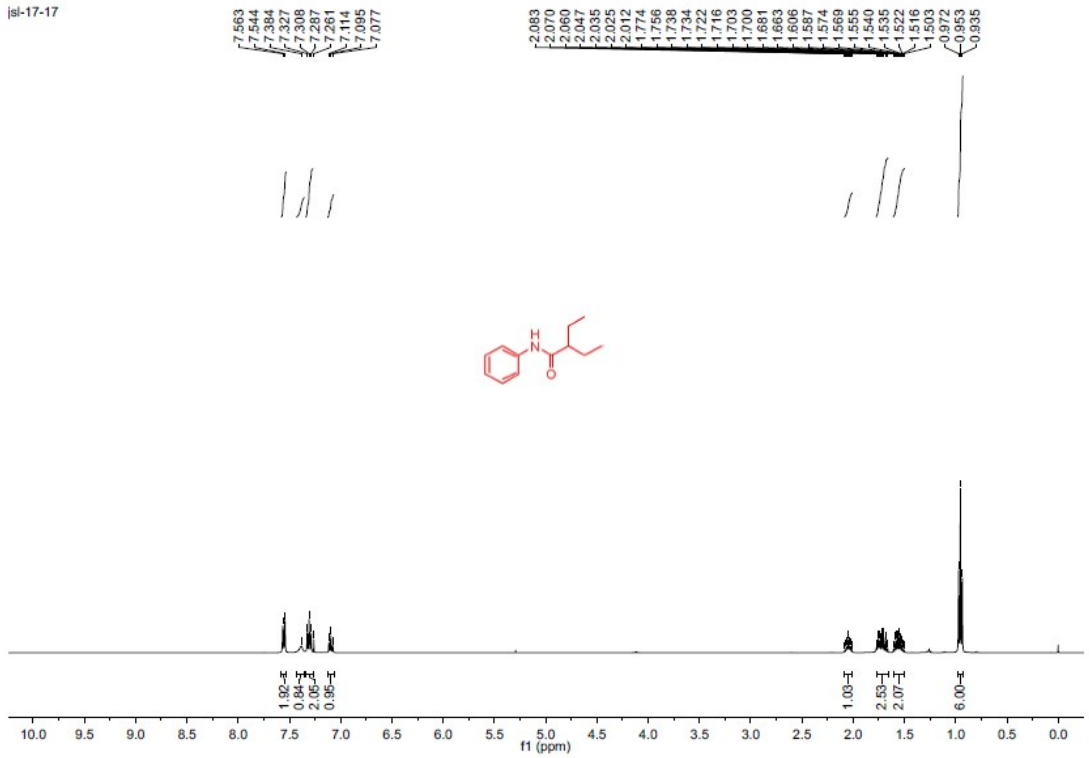

Figure S-4 ^{1}H NMR spectrum of **3aa** ($CDCl_3$)

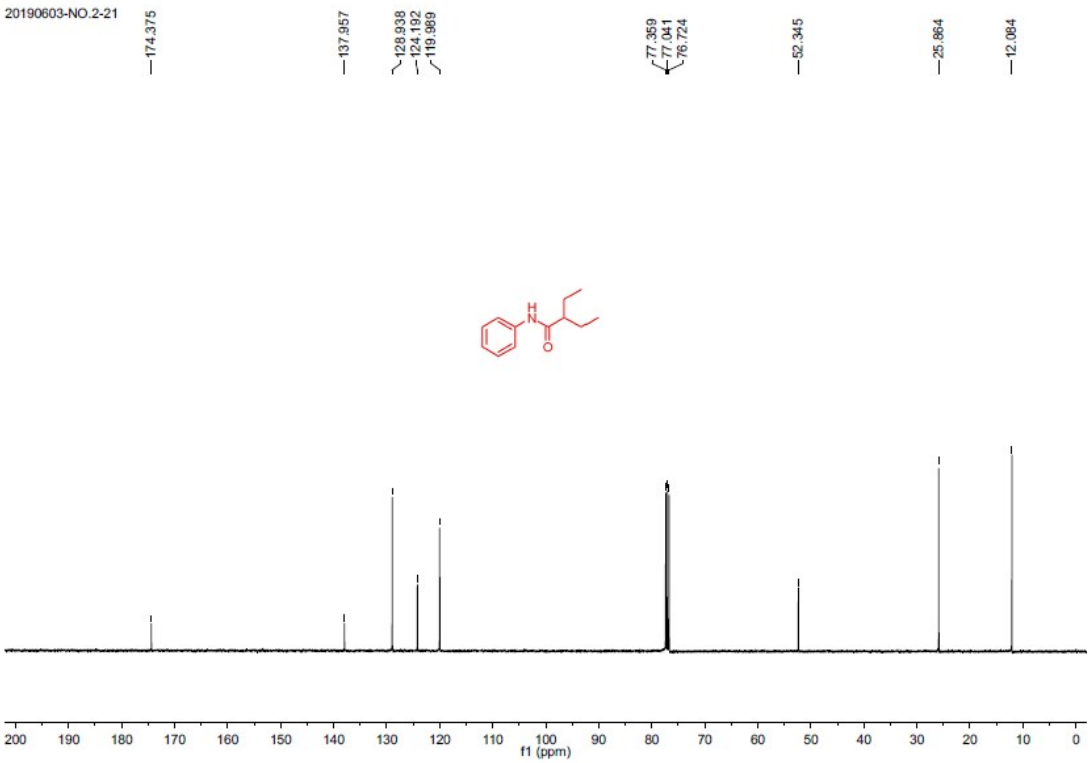

Figure S-5 ^{13}C NMR spectrum of **3aa** ($CDCl_3$)

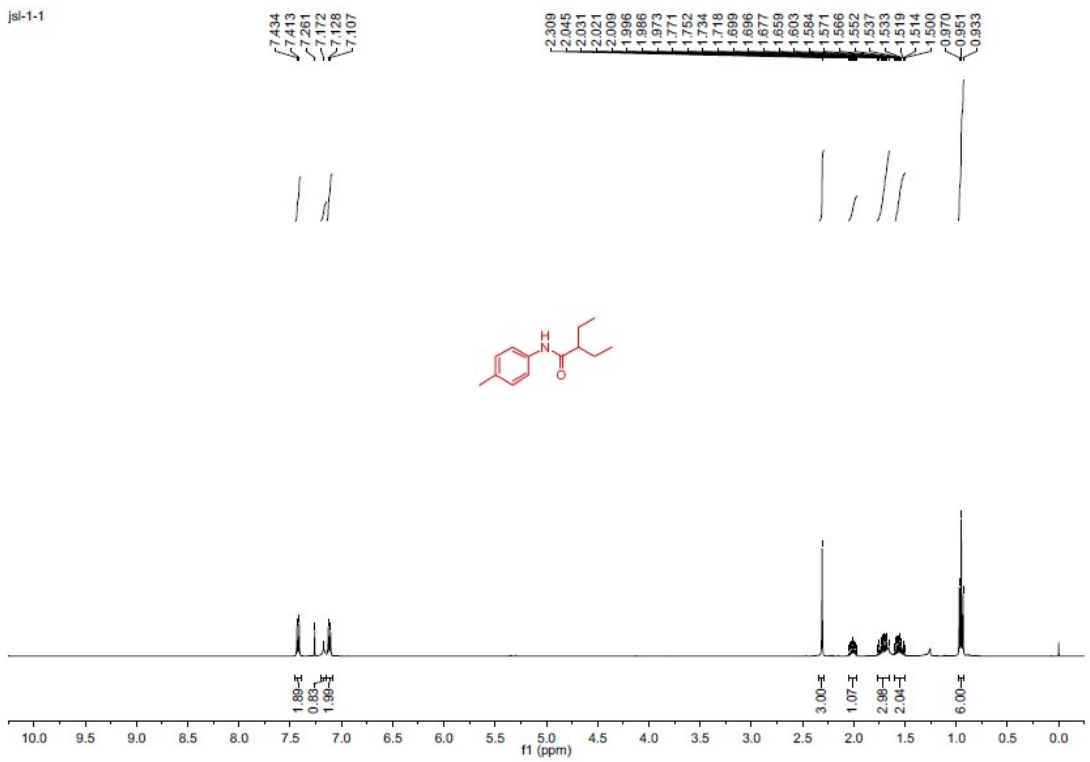

Figure S-6 ^{1}H NMR spectrum of **3ba** ($CDCl_3$)

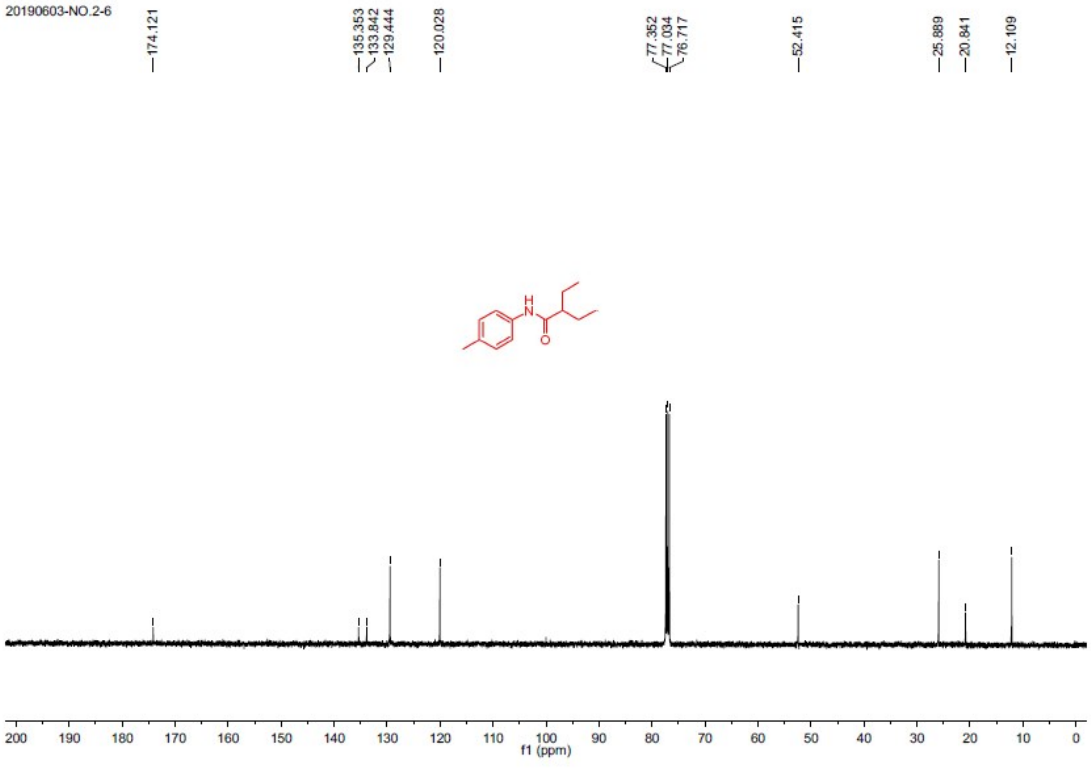

Figure S-7 ^{13}C NMR spectrum of **3ba** ($CDCl_3$)

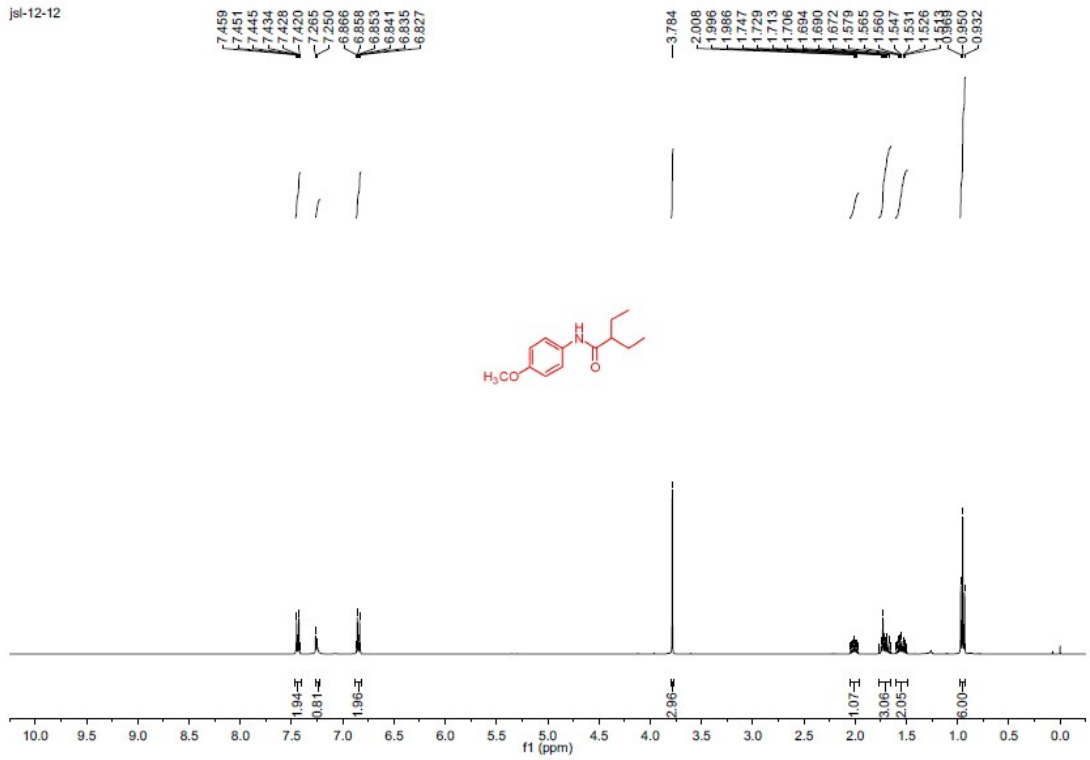

Figure S-8 ^{1}H NMR spectrum of **3ca** ($CDCl_3$)

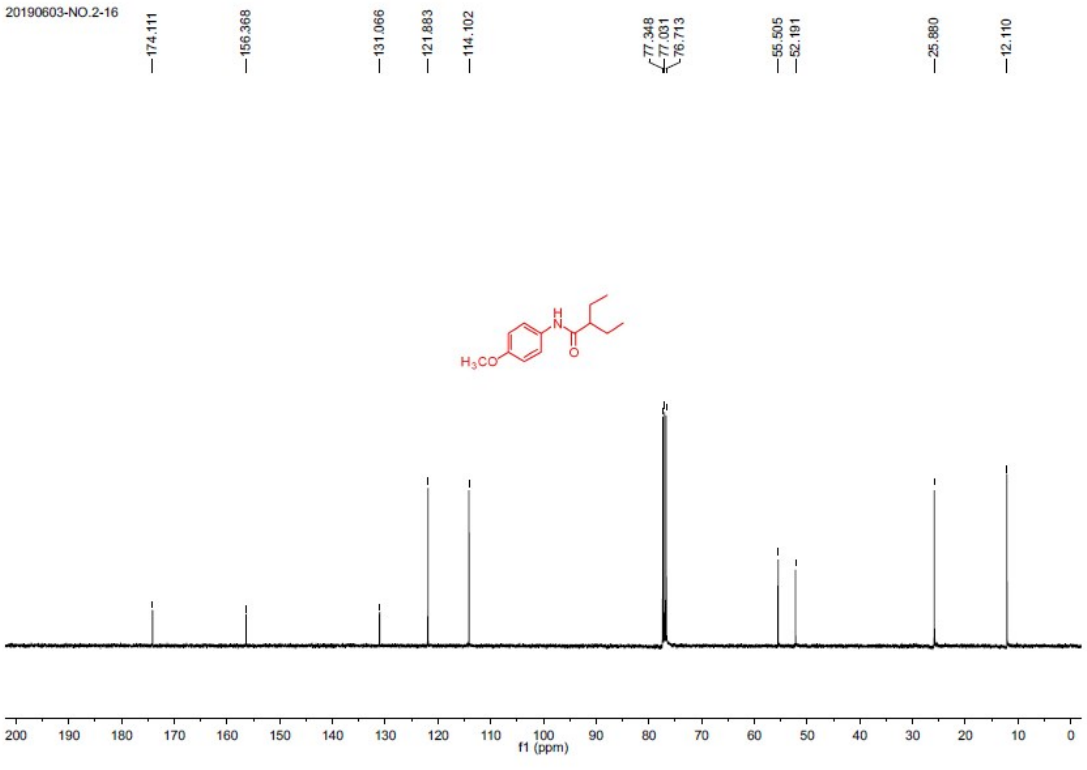

Figure S-9 ^{13}C NMR spectrum of **3ca** ($CDCl_3$)

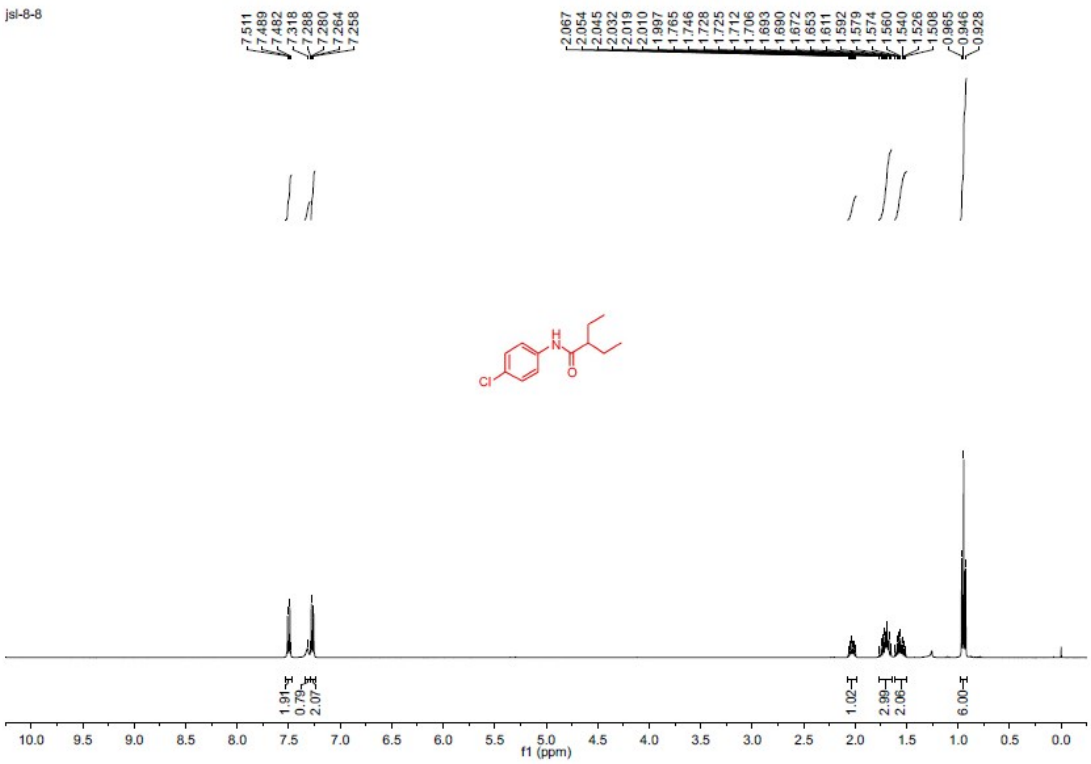

Figure S-10 ^{1}H NMR spectrum of **3da** ($CDCl_3$)

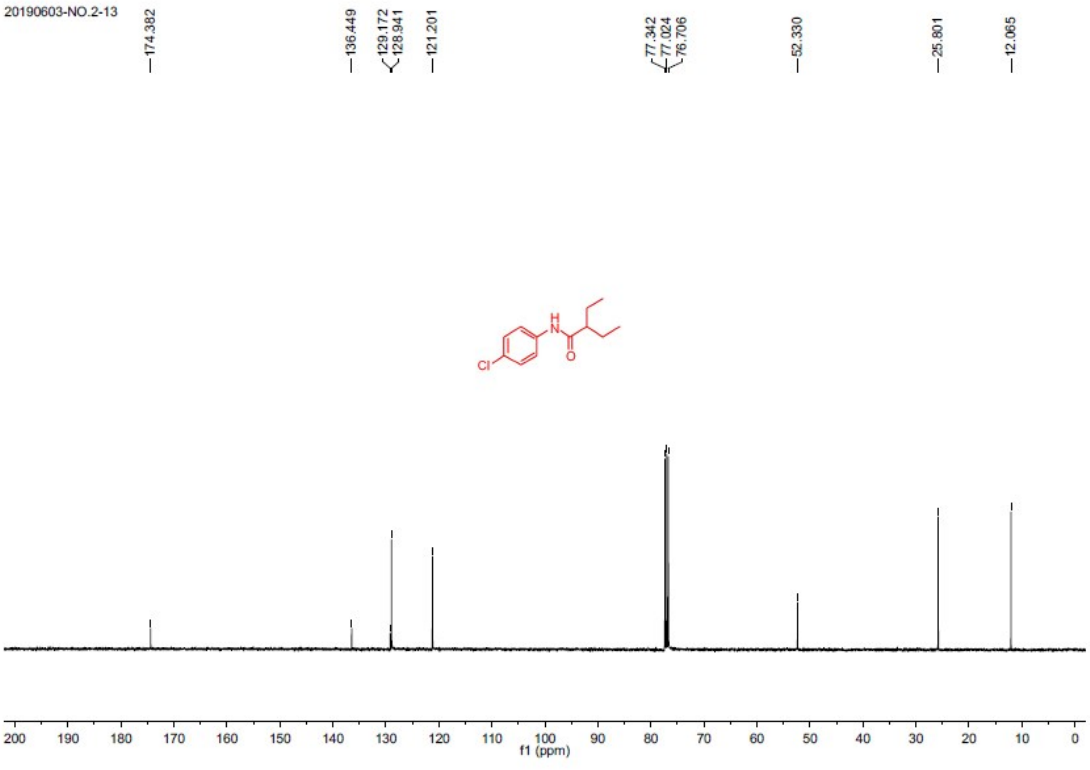

Figure S-11 ^{13}C NMR spectrum of **3da** ($CDCl_3$)

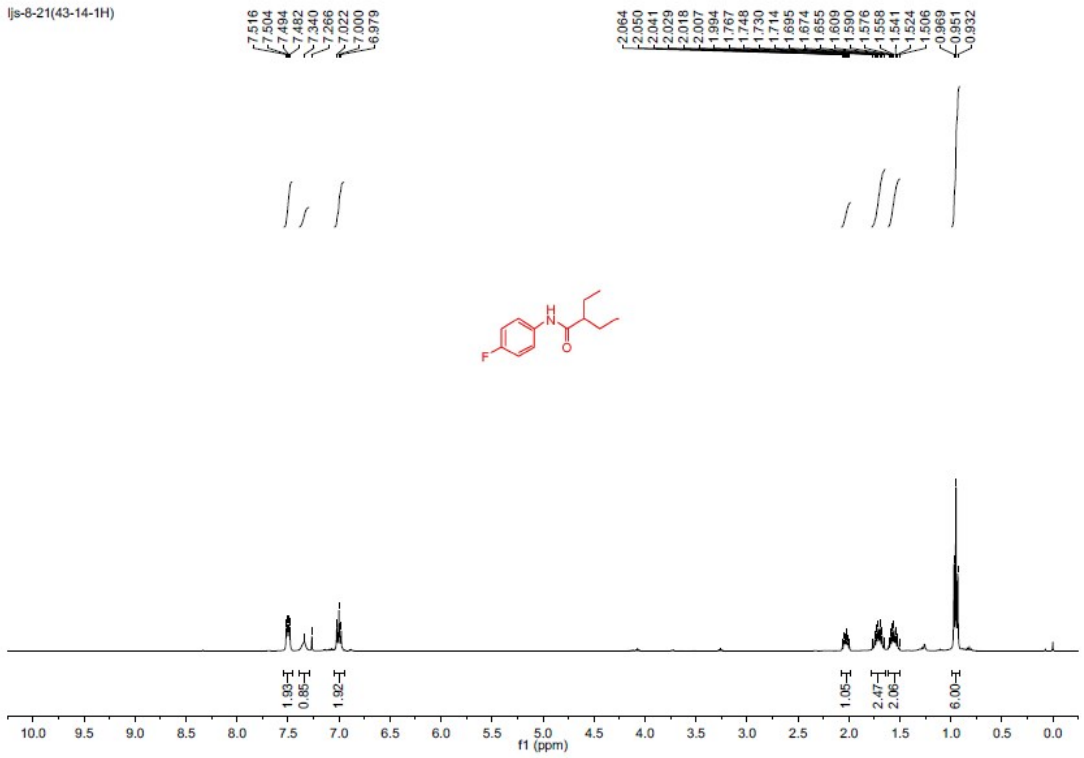

Figure S-12 ^{1}H NMR spectrum of **3ea** ($CDCl_3$)

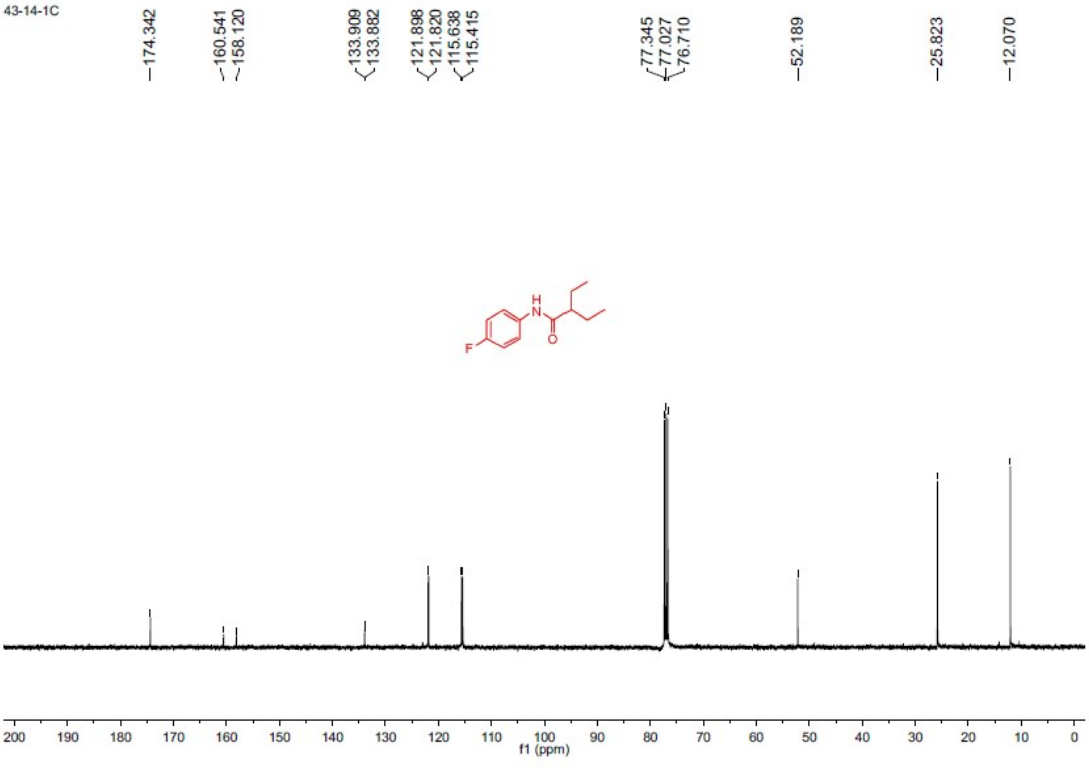

Figure S-13 ^{13}C NMR spectrum of **3ea** ($CDCl_3$)

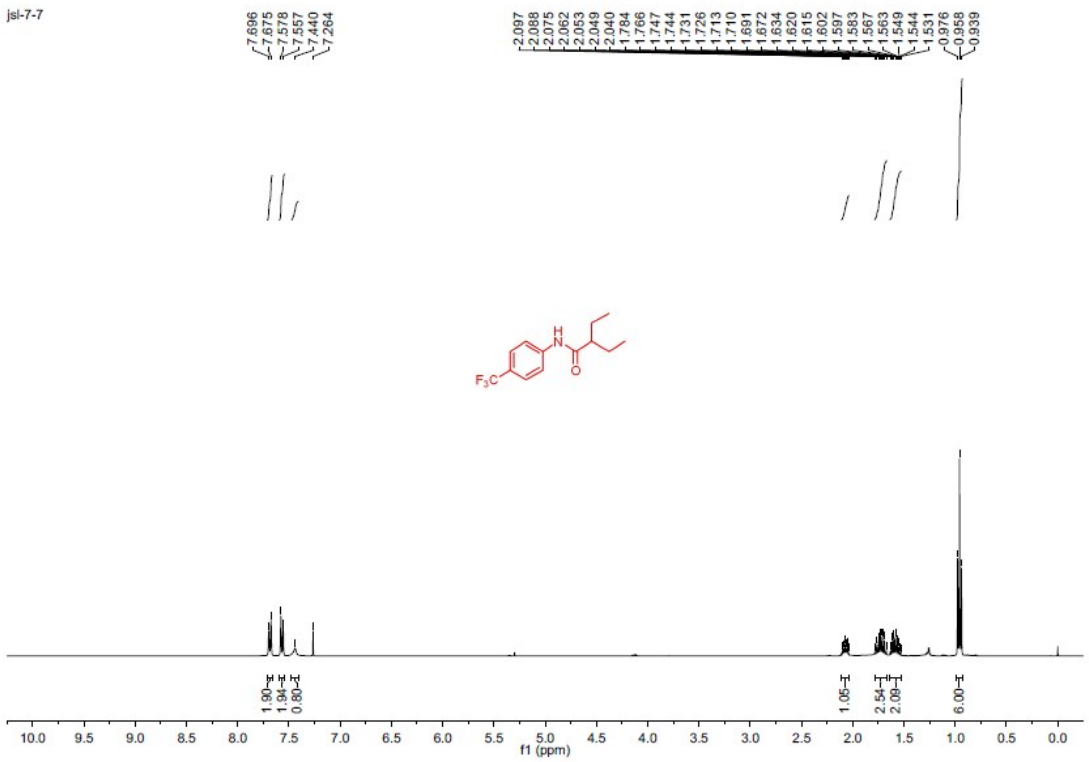

Figure S-14 ^{1}H NMR spectrum of **3fa** ($CDCl_3$)

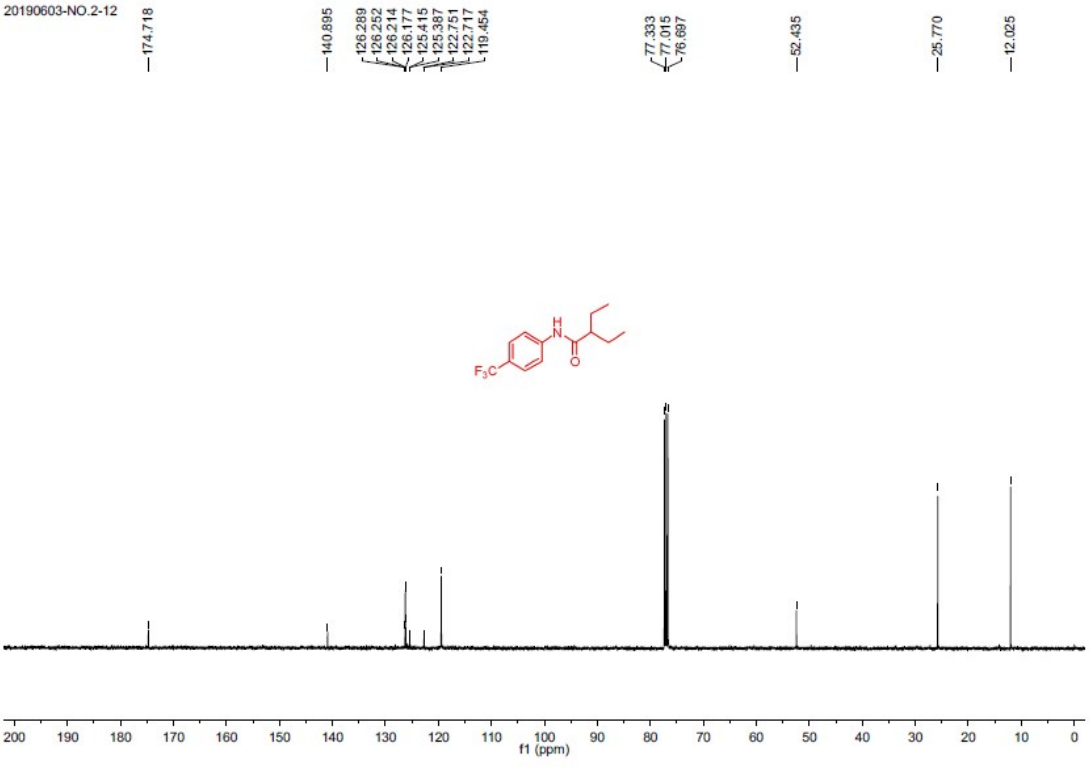

Figure S-15 ^{13}C NMR spectrum of **3fa** ($CDCl_3$)

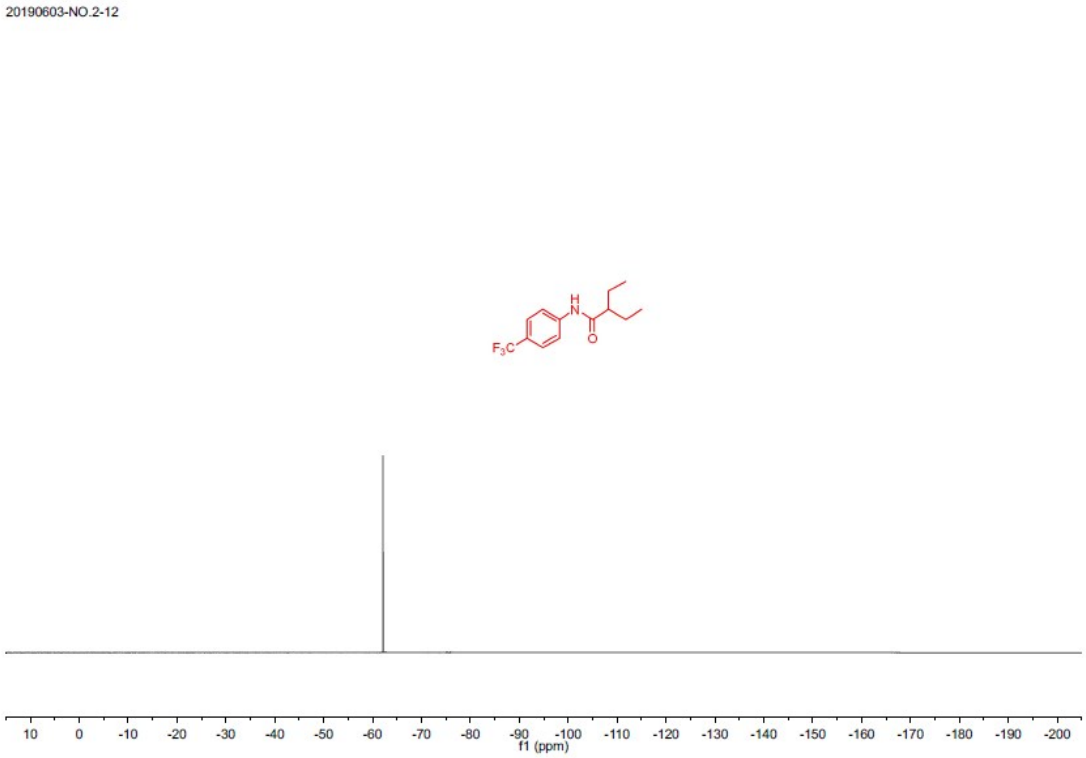

Figure S-16 ^{19}F NMR spectrum of **3fa** ($CDCl_3$)

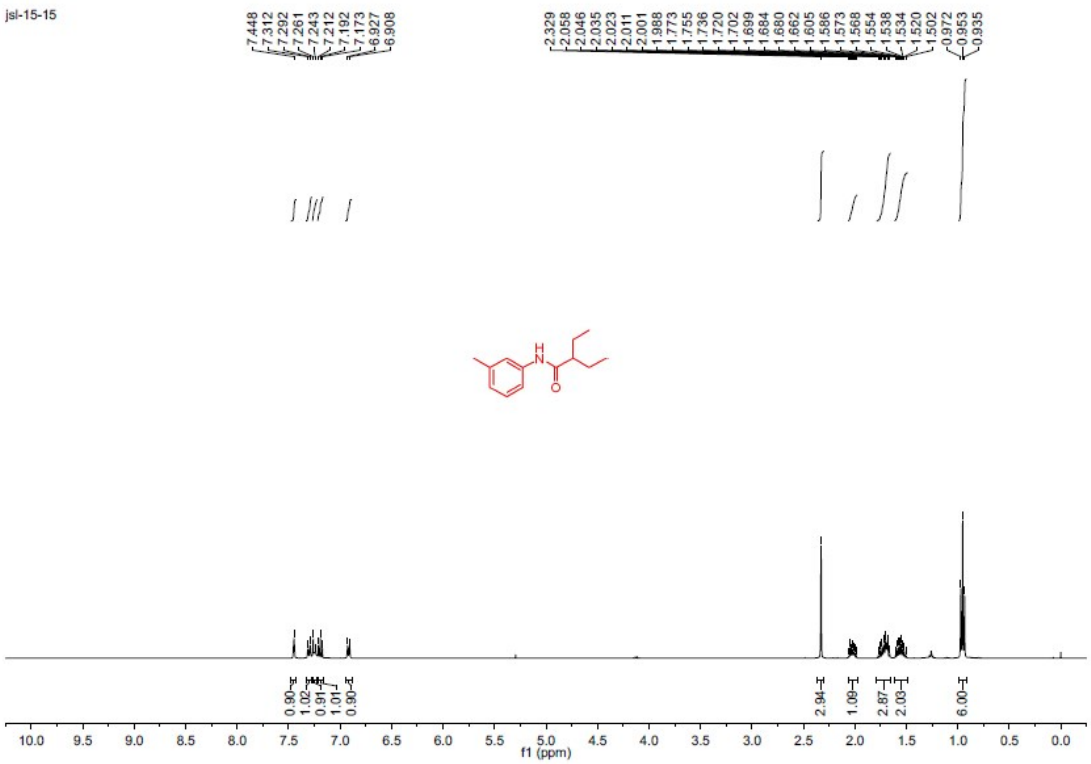

Figure S-17 ^{1}H NMR spectrum of **3ga** ($CDCl_3$)

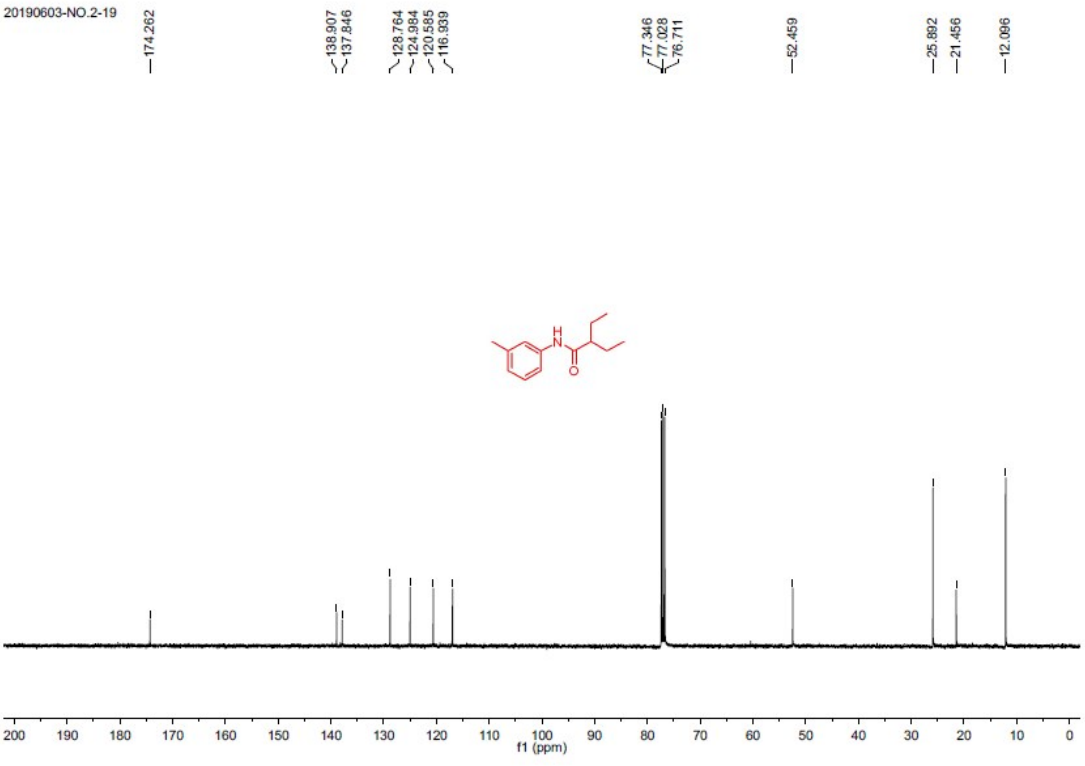

Figure S-18 ^{13}C NMR spectrum of **3ga** ($CDCl_3$)

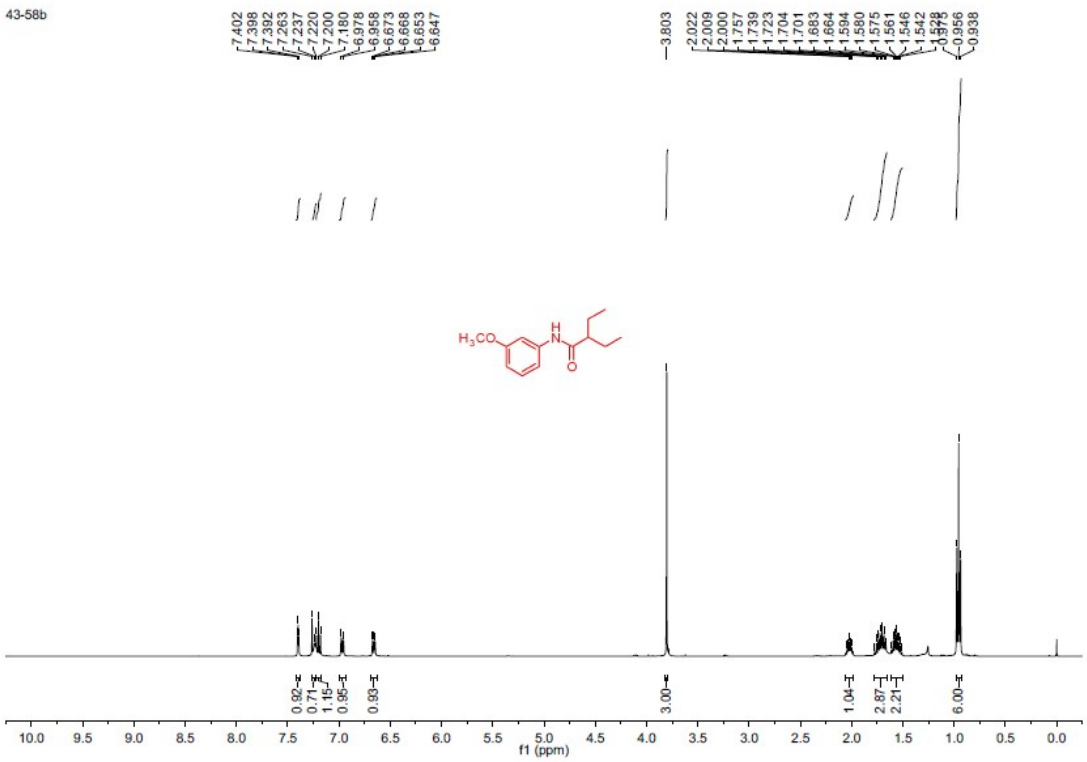

Figure S-19 ^{1}H NMR spectrum of **3ha** ($CDCl_3$)

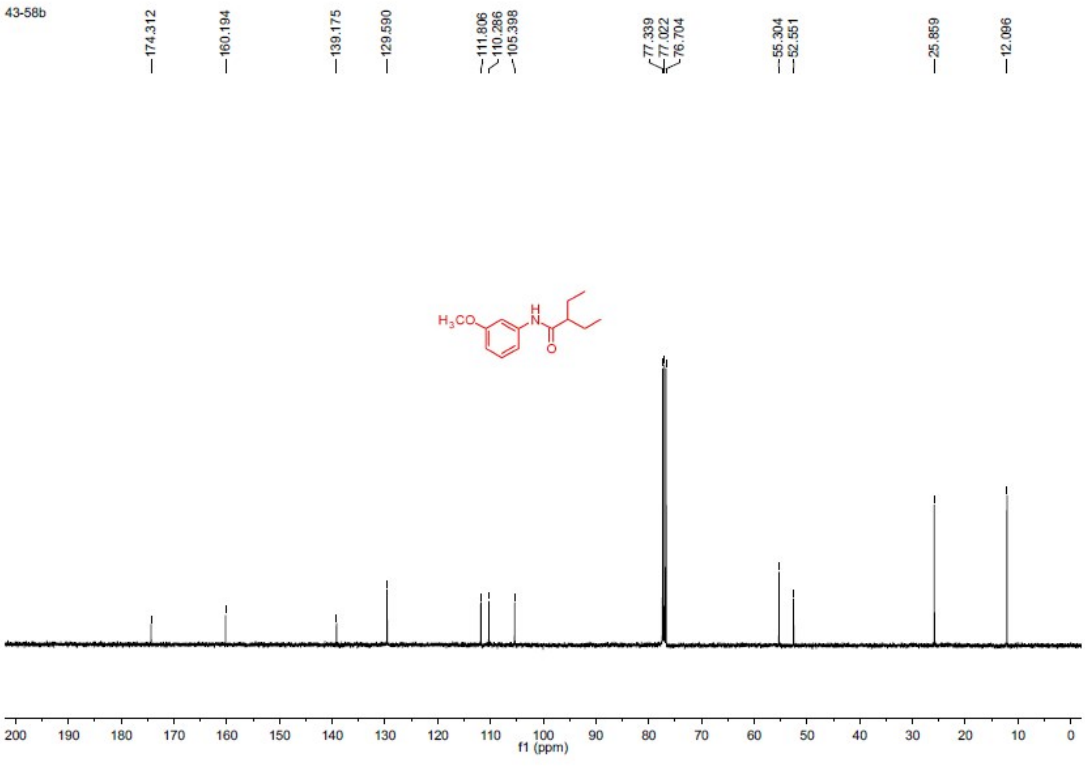

Figure S-20 ^{13}C NMR spectrum of **3ha** ($CDCl_3$)

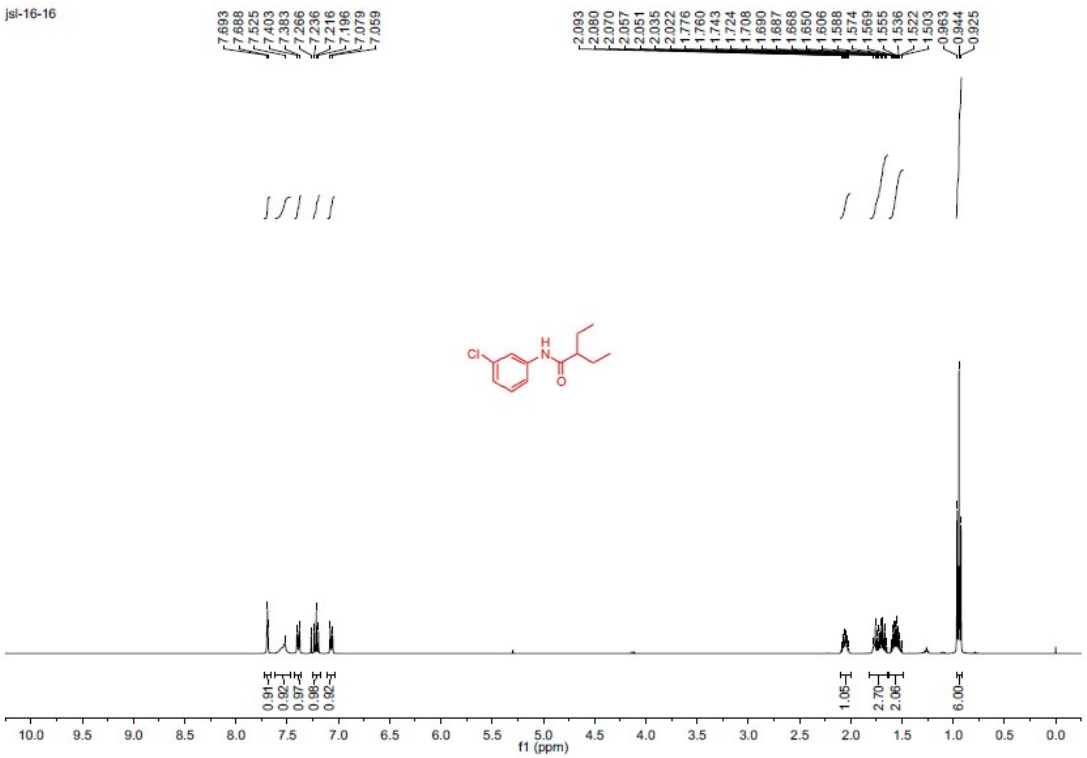

Figure S-21 ^{1}H NMR spectrum of **3ia** ($CDCl_3$)

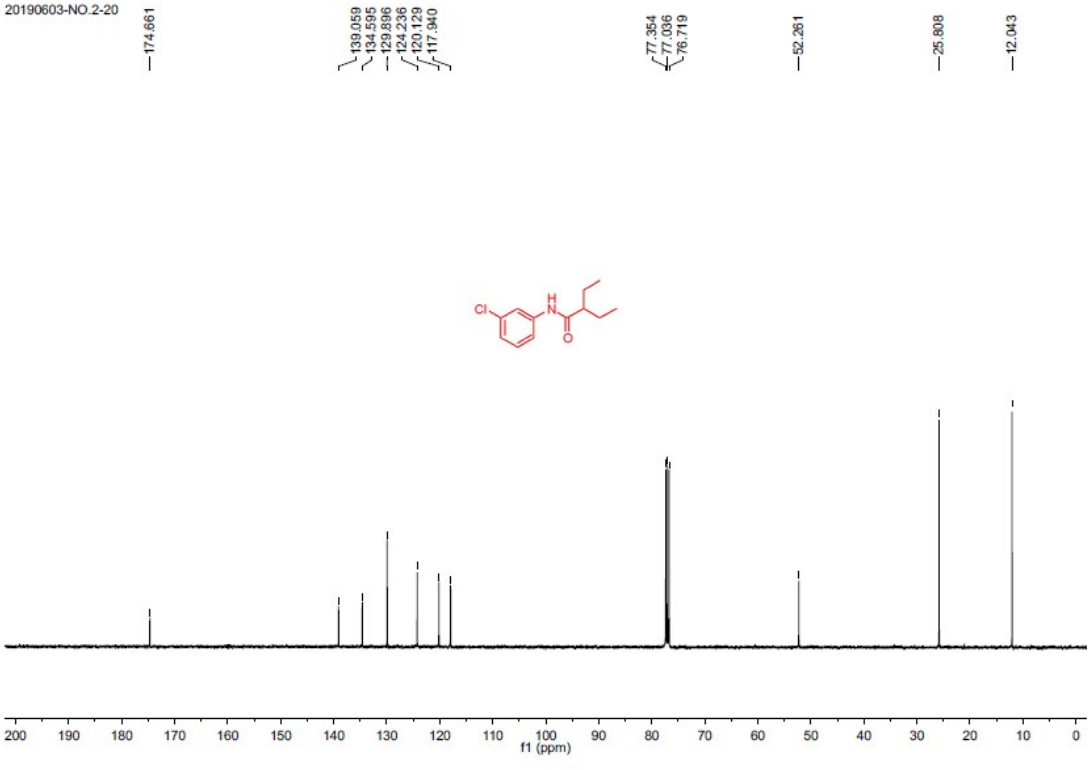

Figure S-22 ^{13}C NMR spectrum of **3ia** ($CDCl_3$)

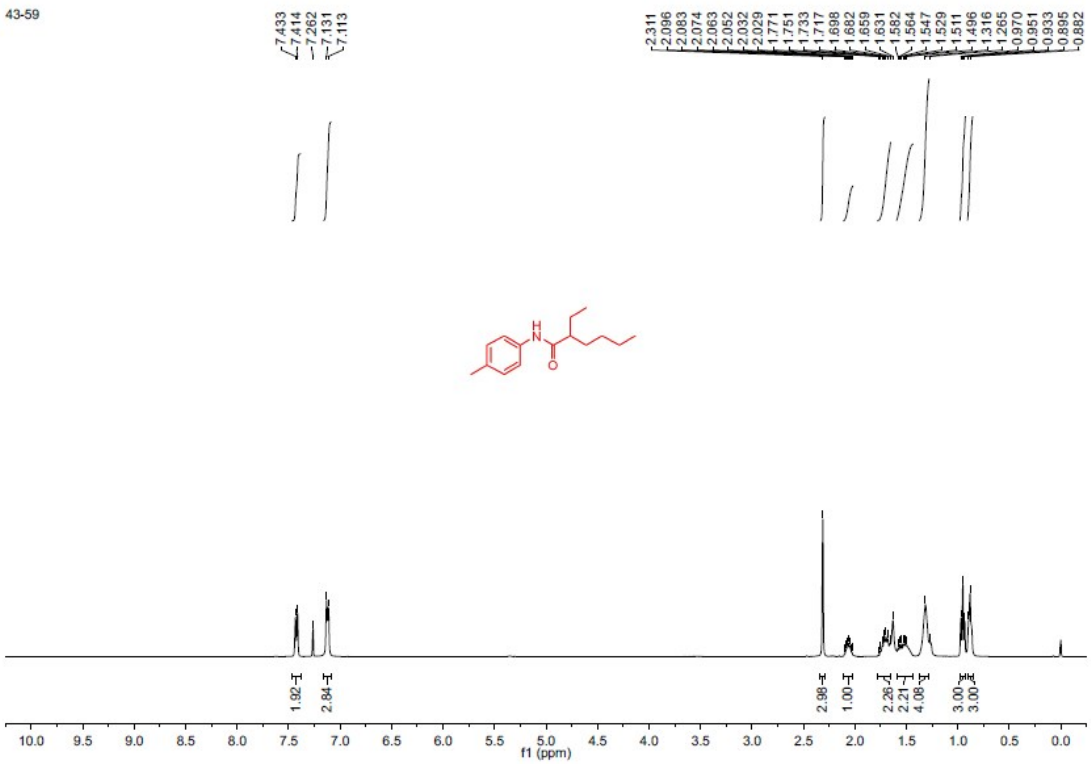

Figure S-23 ^{1}H NMR spectrum of **3bb** ($CDCl_3$)

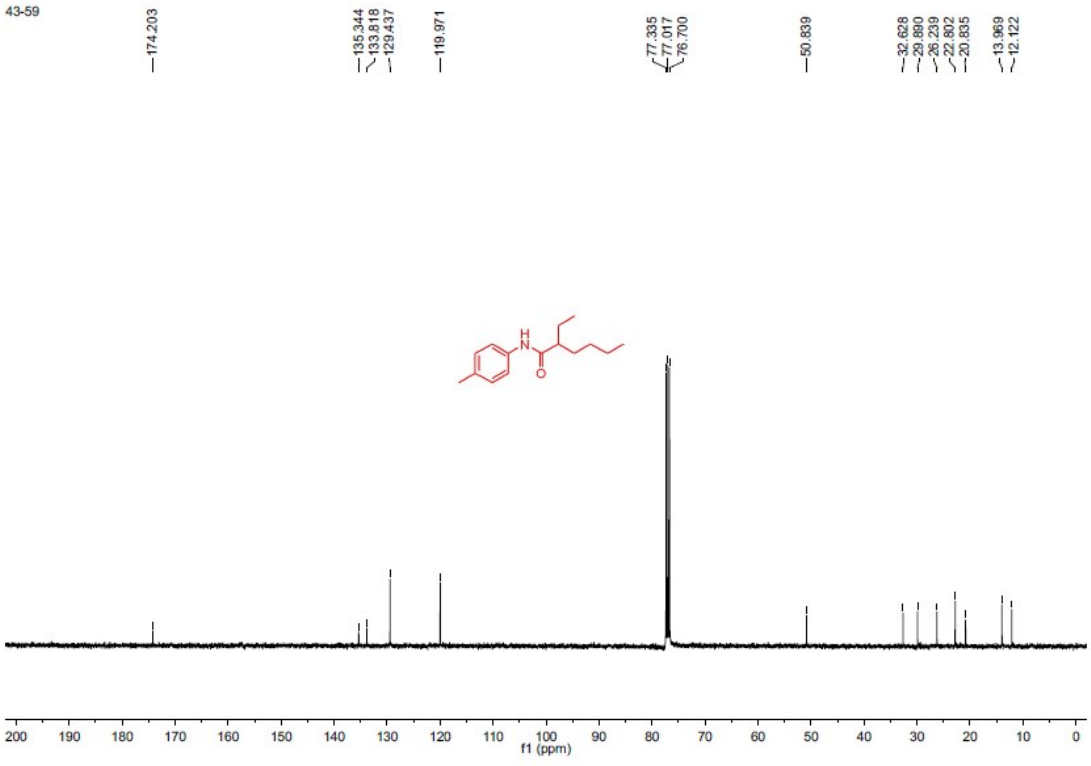

Figure S-24 ^{13}C NMR spectrum of **3bb** ($CDCl_3$)

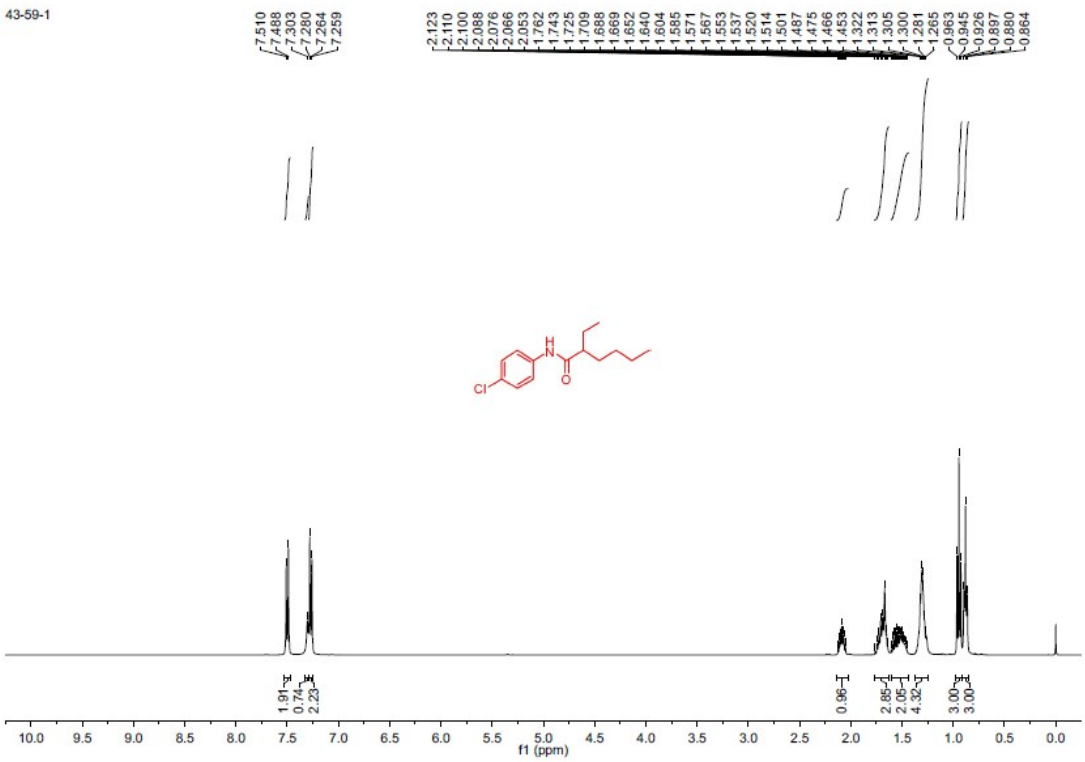

Figure S-25 ^{1}H NMR spectrum of **3db** ($CDCl_3$)

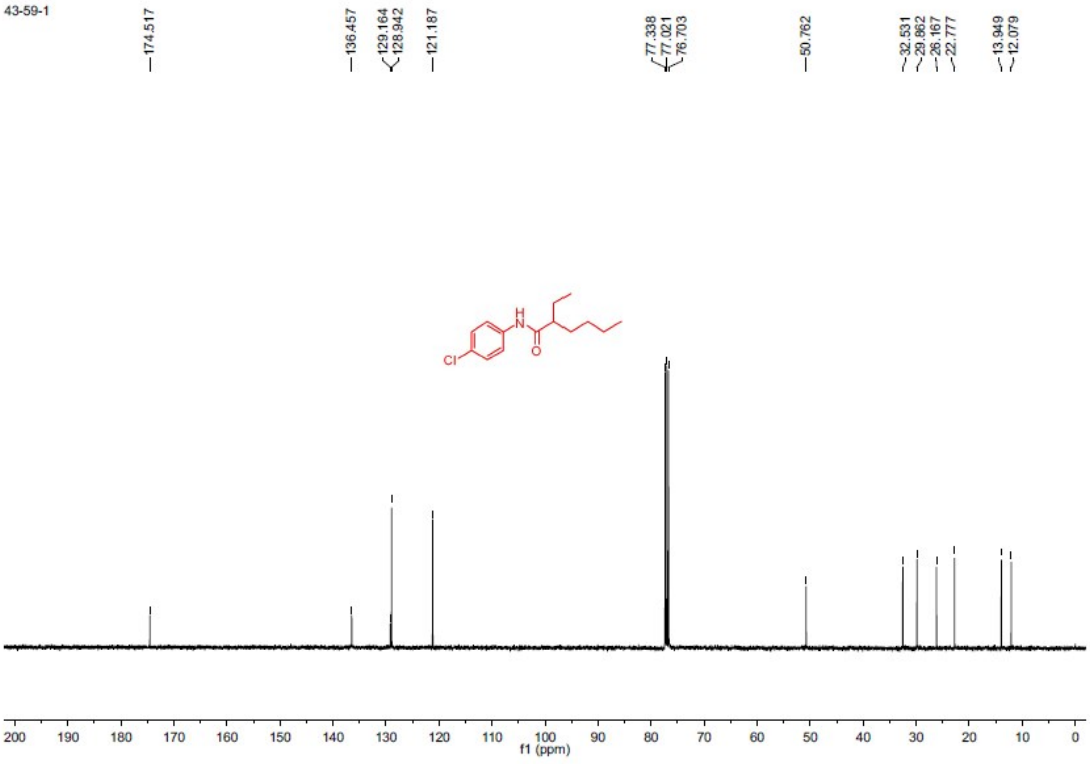

Figure S-26 ^{13}C NMR spectrum of **3db** ($CDCl_3$)

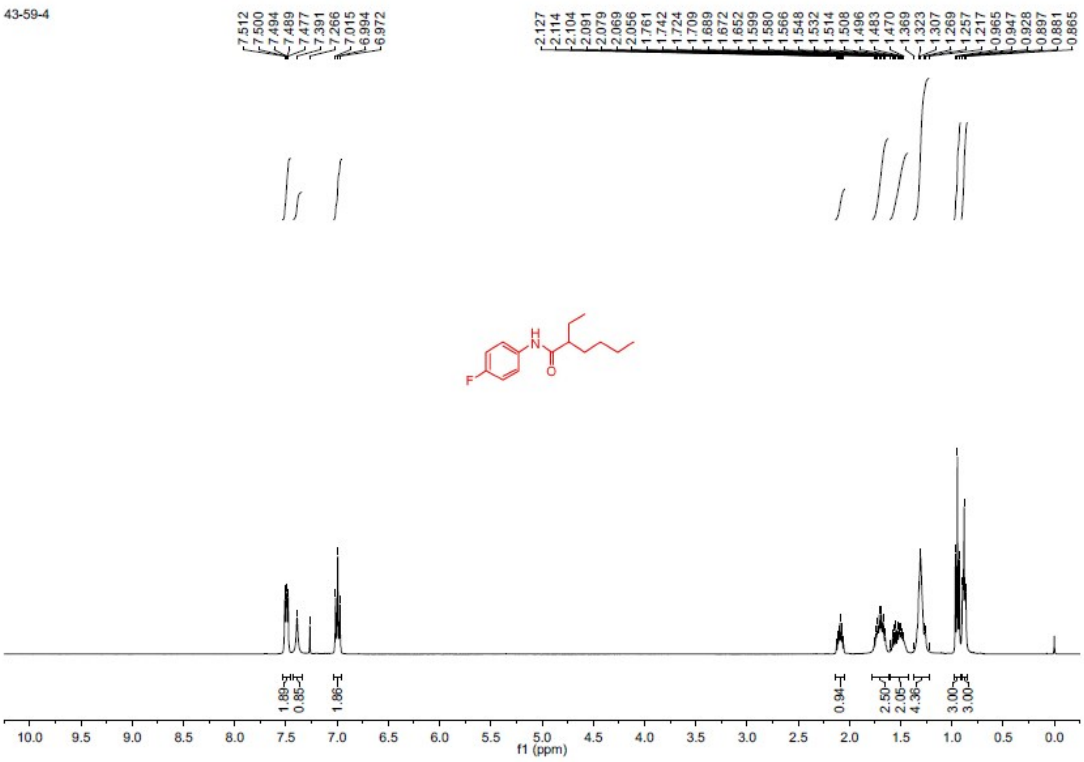

Figure S-27 ^{1}H NMR spectrum of **3eb** ($CDCl_3$)

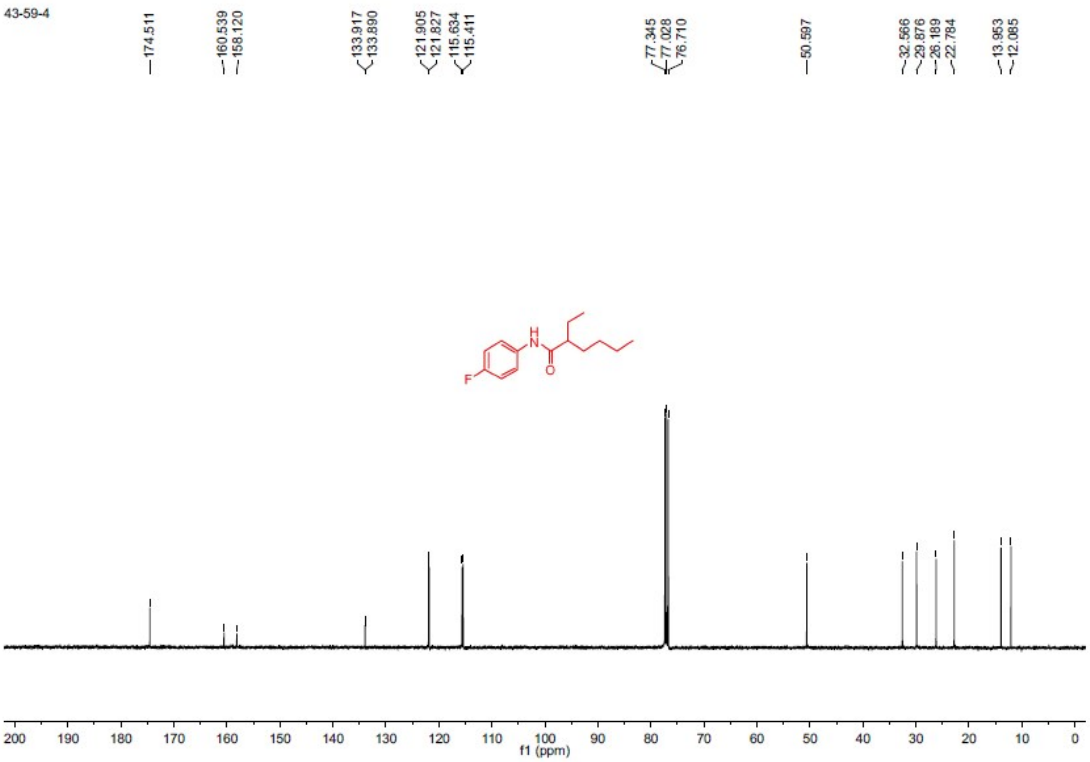

Figure S-28 ^{13}C NMR spectrum of **3eb** ($CDCl_3$)

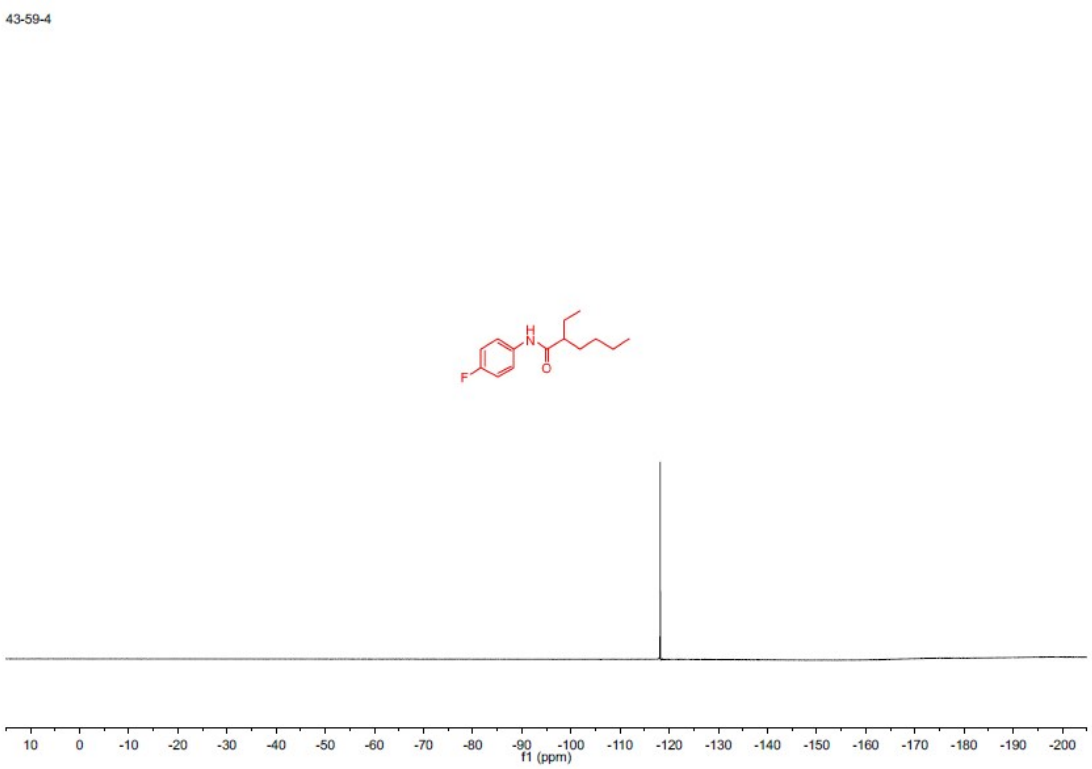

Figure S-29 ^{19}F NMR spectrum of **3eb** ($CDCl_3$)

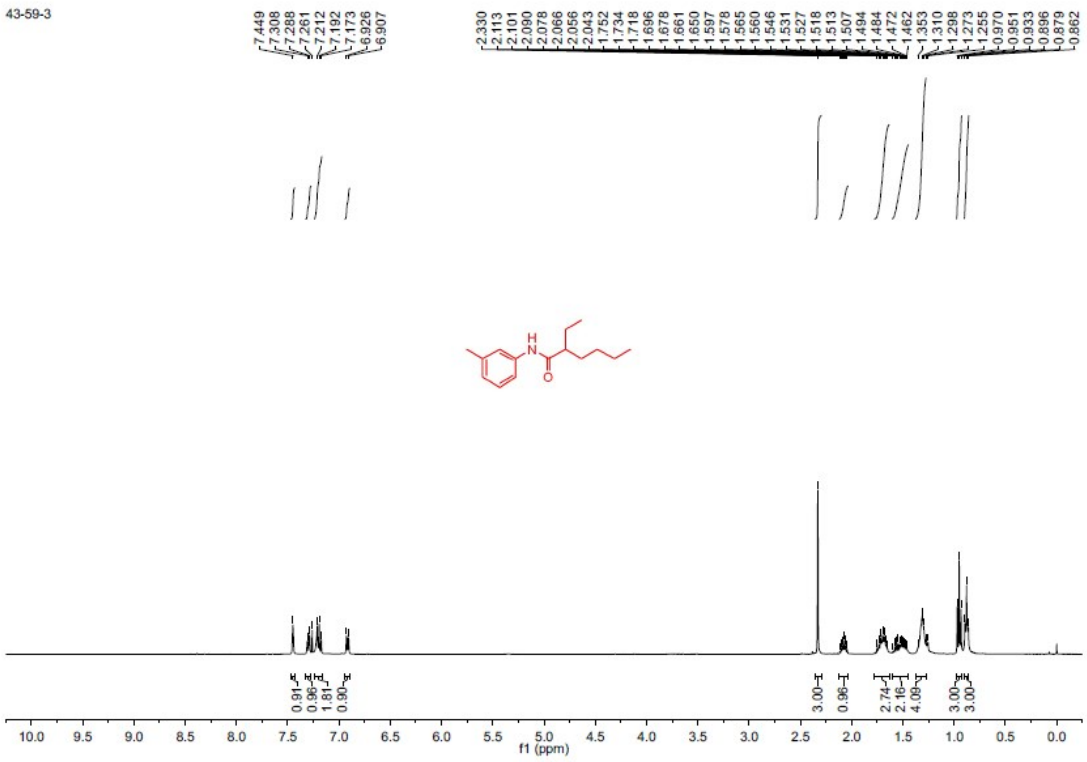

Figure S-30 ^{1}H NMR spectrum of **3gb** ($CDCl_3$)

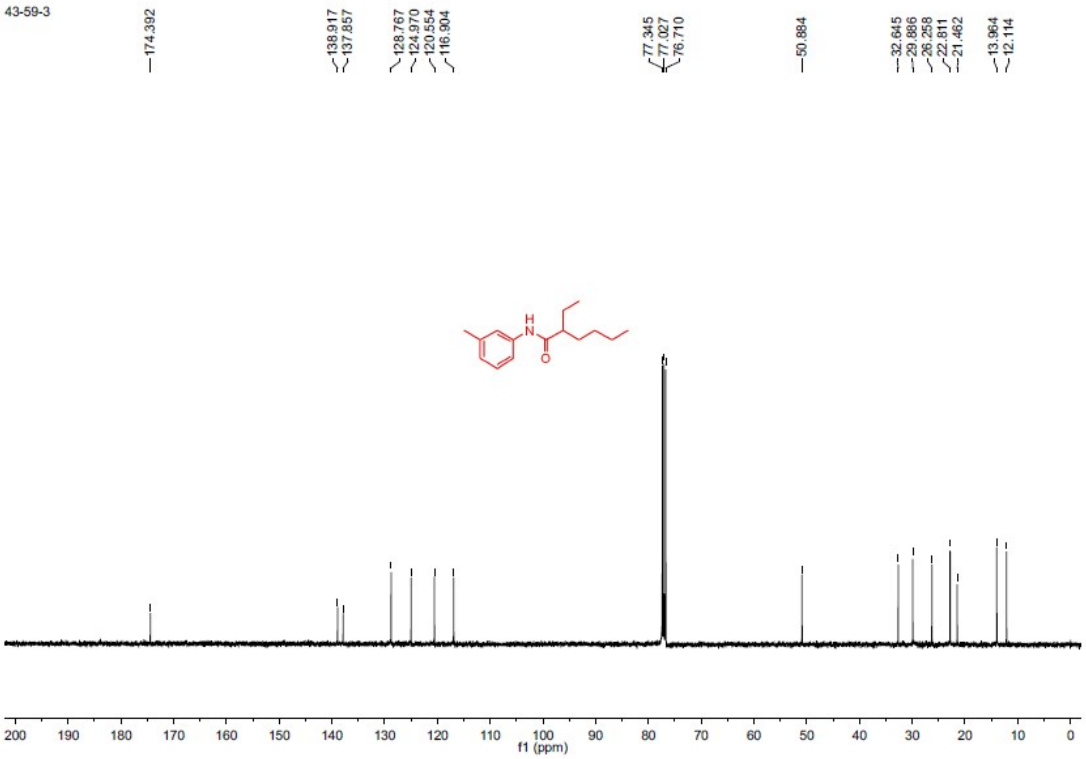

Figure S-31 ^{13}C NMR spectrum of **3gb** ($CDCl_3$)

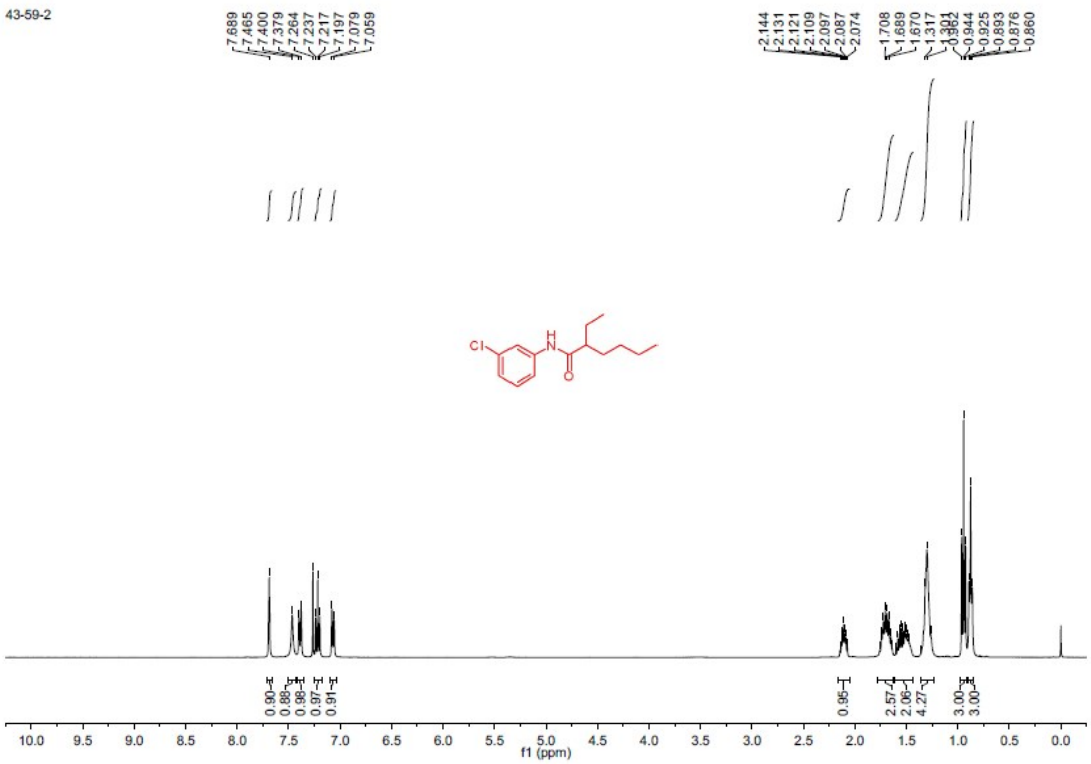

Figure S-32 ^{1}H NMR spectrum of **3ib** ($CDCl_3$)

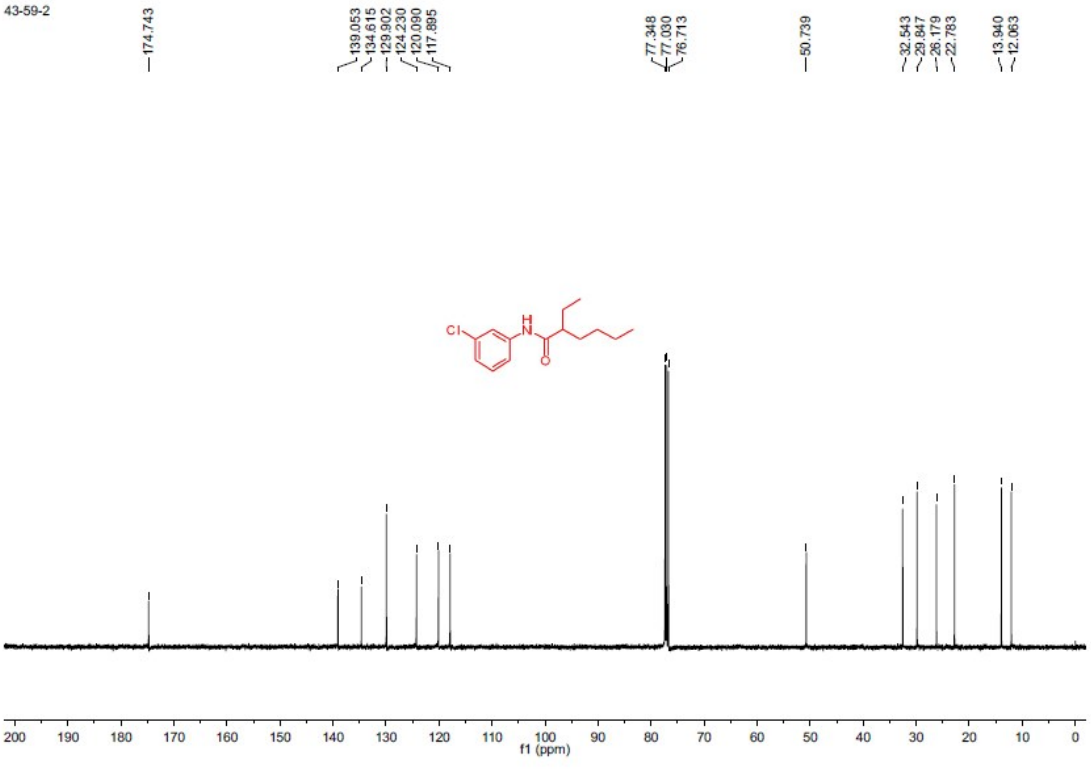

Figure S-33 ^{13}C NMR spectrum of **3ib** ($CDCl_3$)

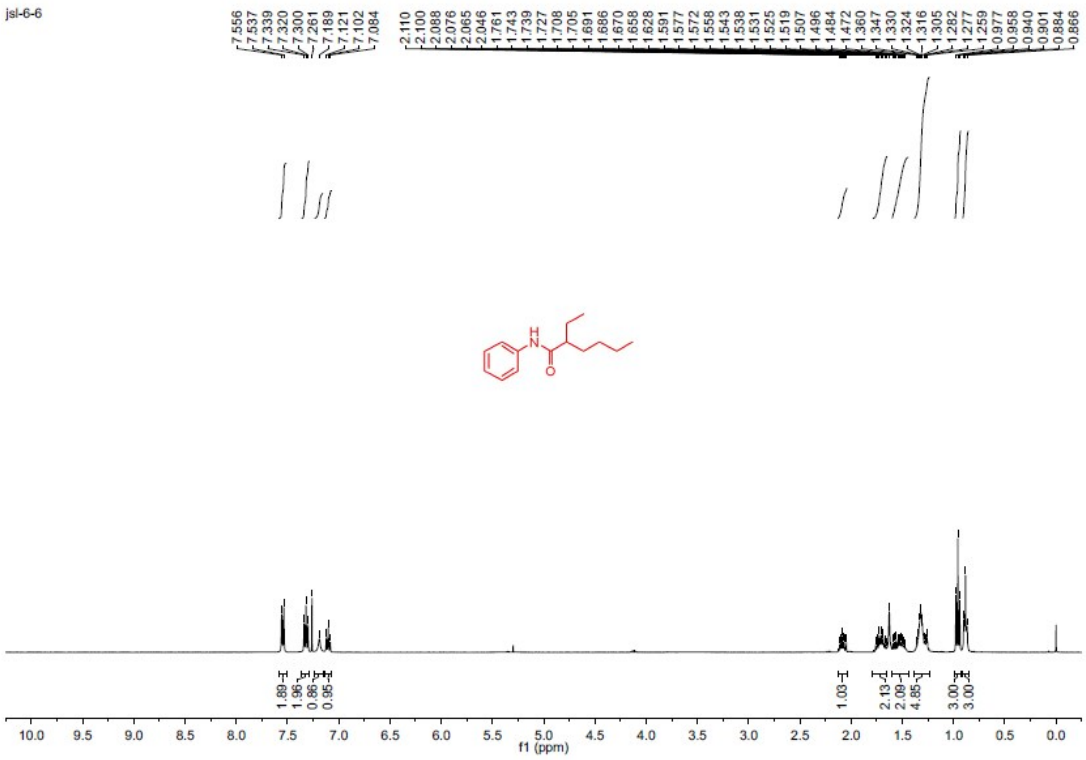

Figure S-34 ^{1}H NMR spectrum of **3ab** ($CDCl_3$)

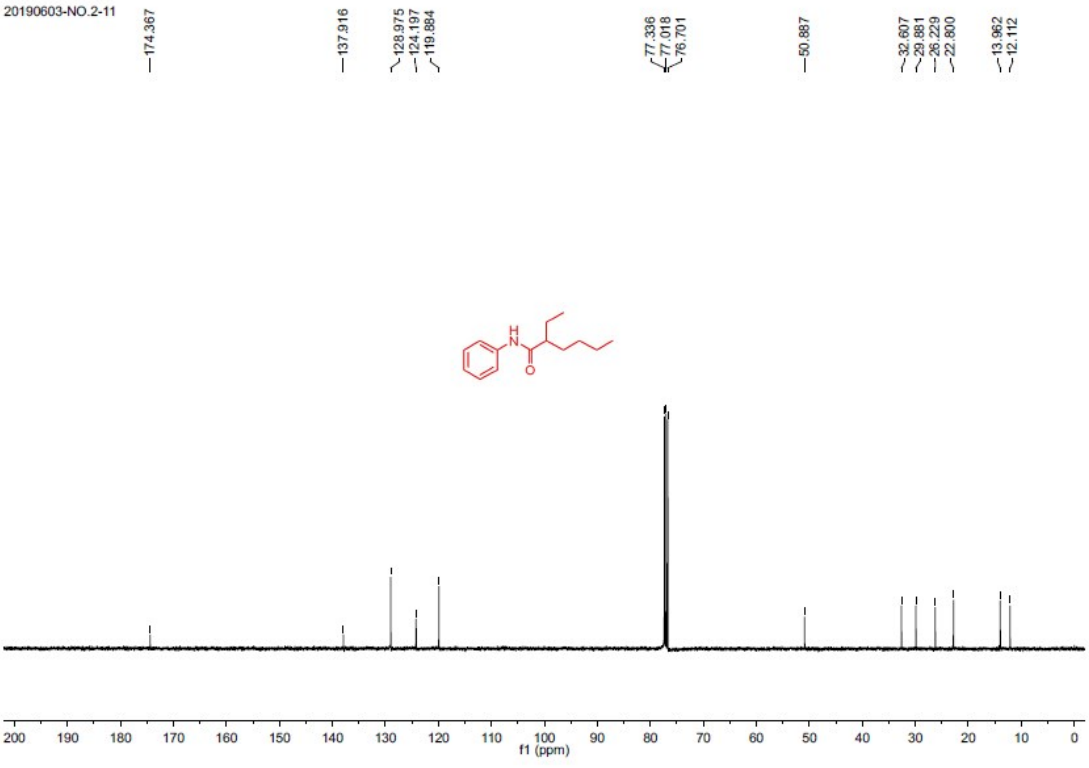

Figure S-35 ^{13}C NMR spectrum of **3ab** ($CDCl_3$)

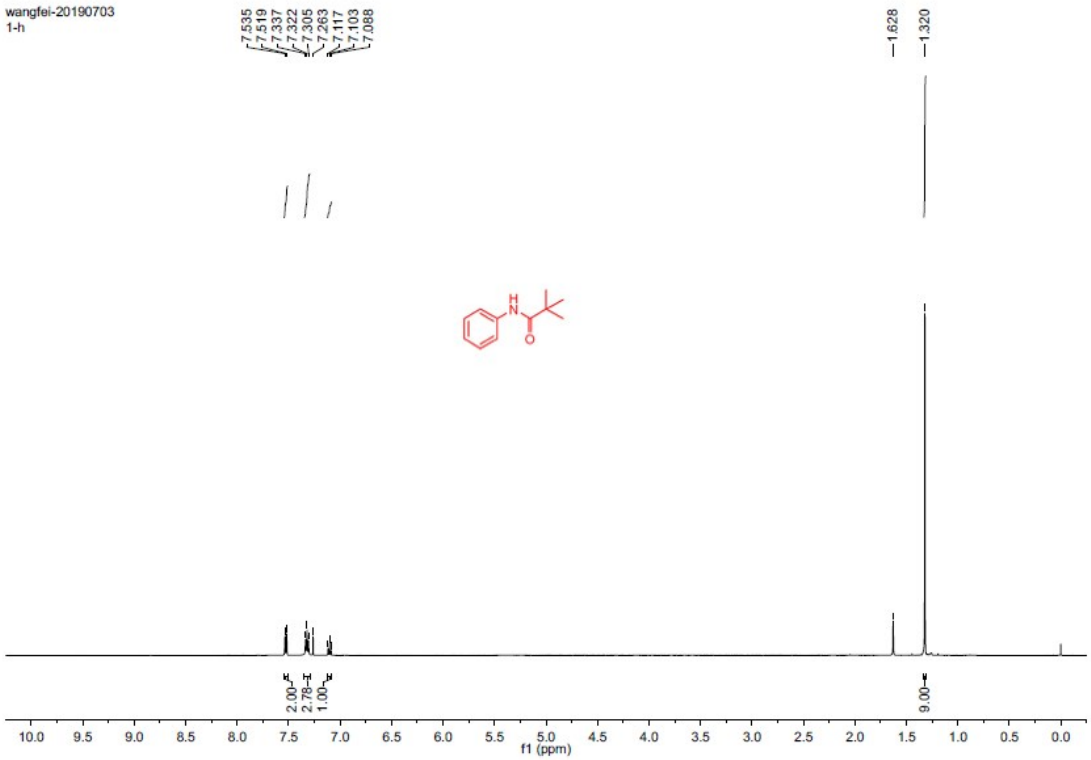

Figure S-36 ^{1}H NMR spectrum of **3ac** ($CDCl_3$)

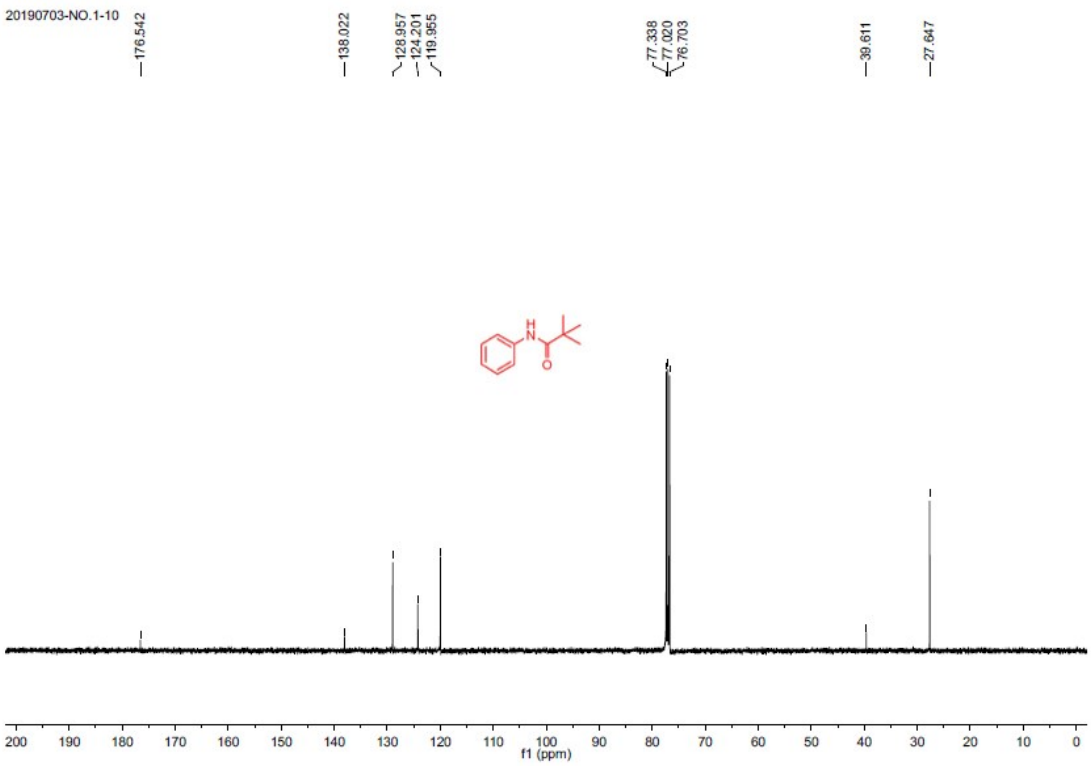

Figure S-37 ^{13}C NMR spectrum of **3ac** ($CDCl_3$)

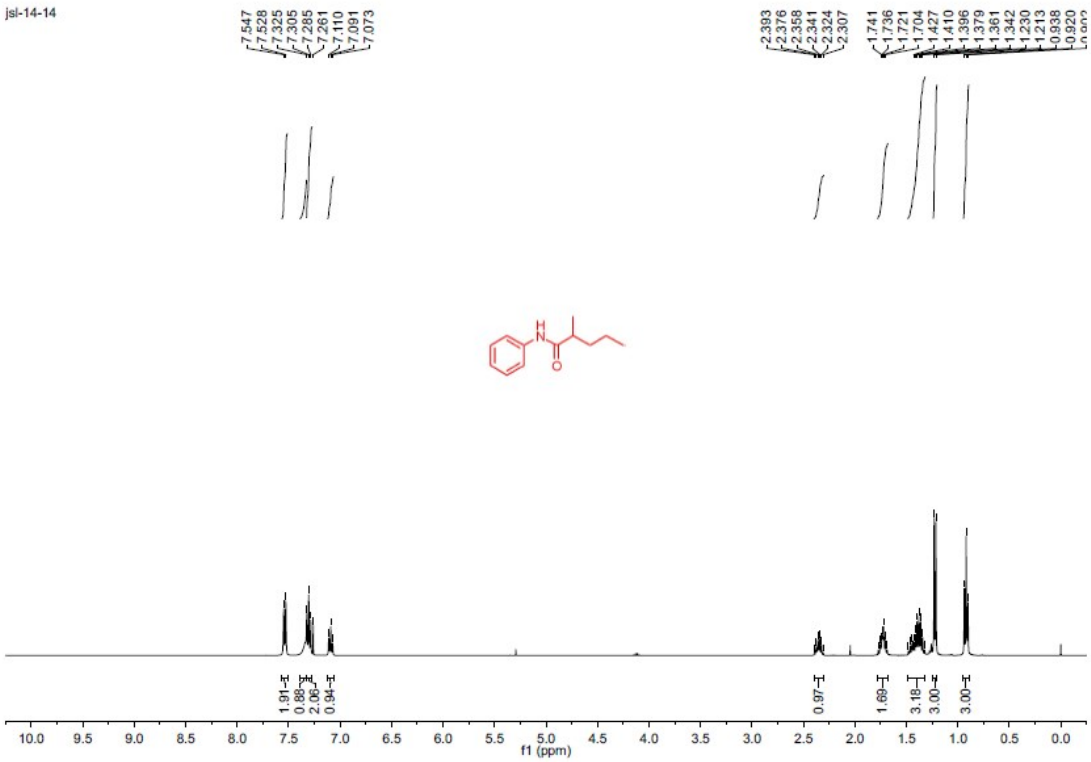

Figure S-38 ^{1}H NMR spectrum of **3ad** ($CDCl_3$)

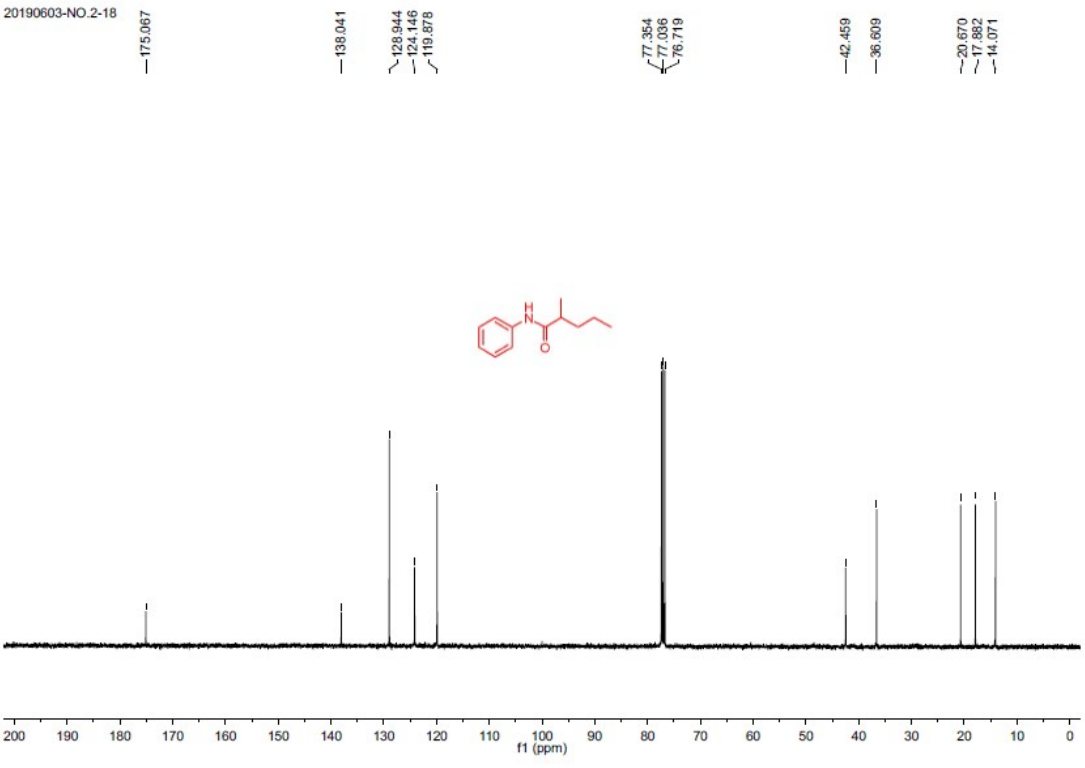

Figure S-39 ^{13}C NMR spectrum of **3ad** ($CDCl_3$)

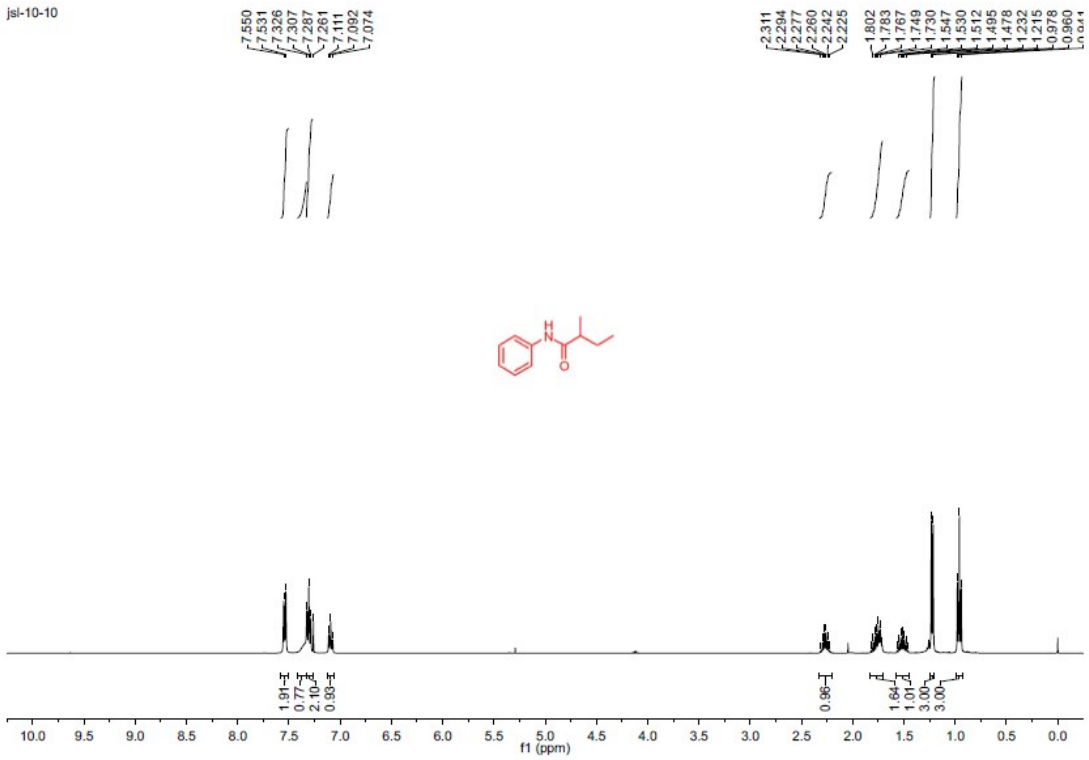

Figure S-40 ^{1}H NMR spectrum of **3ae** ($CDCl_3$)

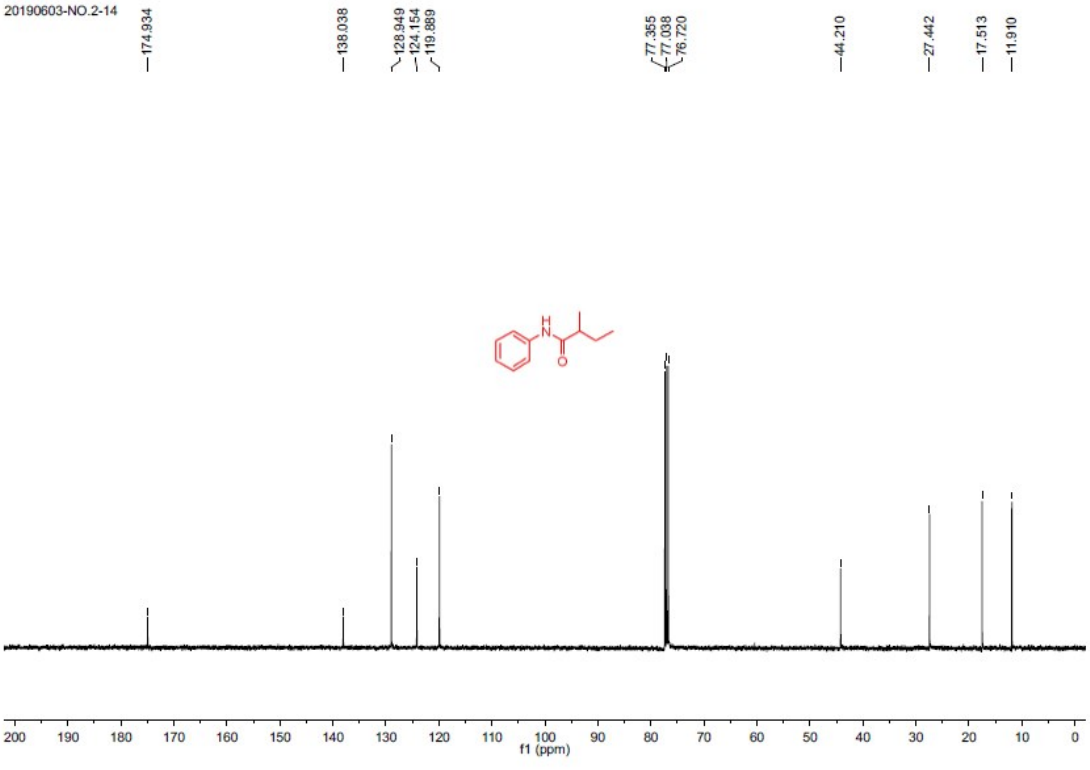

Figure S-41 ^{13}C NMR spectrum of **3ae** ($CDCl_3$)

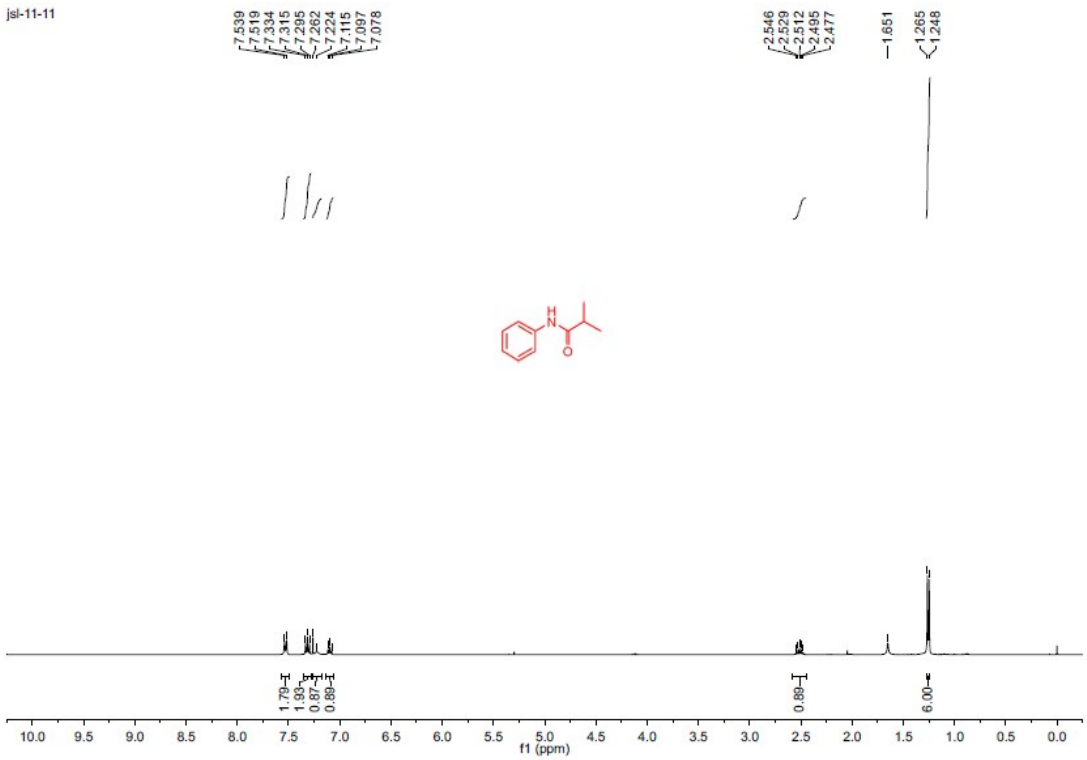

Figure S-42 ^{1}H NMR spectrum of **3af** ($CDCl_3$)

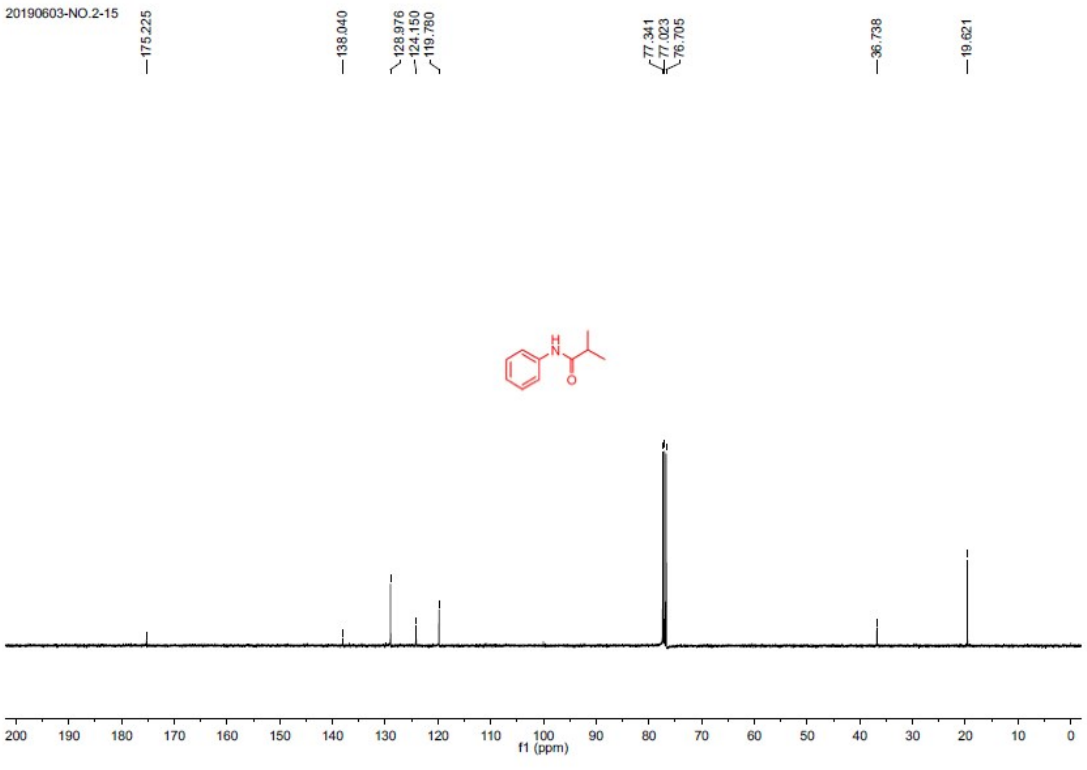

Figure S-43 ^{13}C NMR spectrum of **3af** ($CDCl_3$)

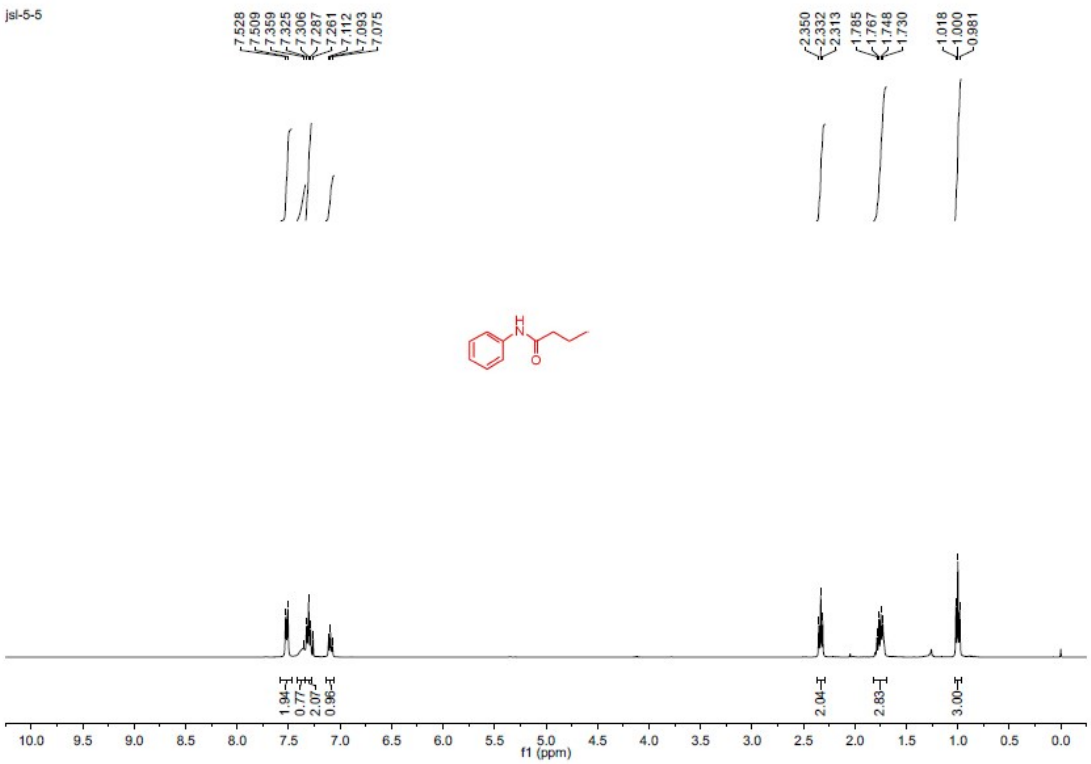

Figure S-44 ^{1}H NMR spectrum of **3ag** ($CDCl_3$)

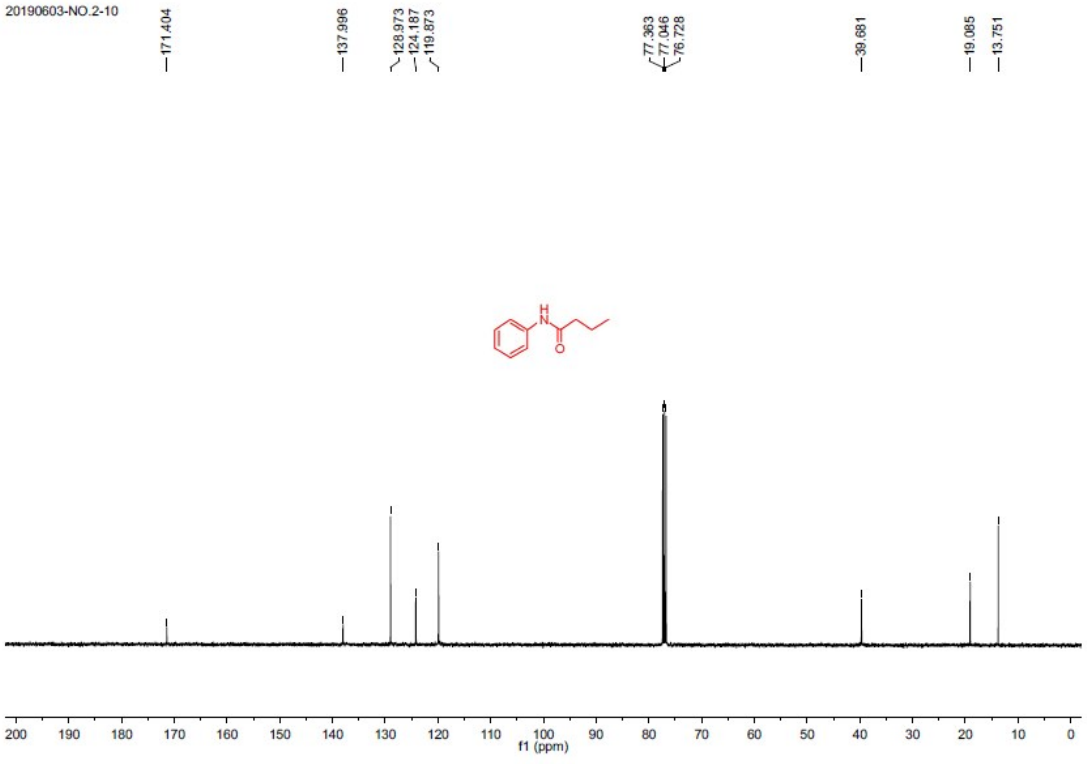

Figure S-45 ^{13}C NMR spectrum of **3ag** ($CDCl_3$)

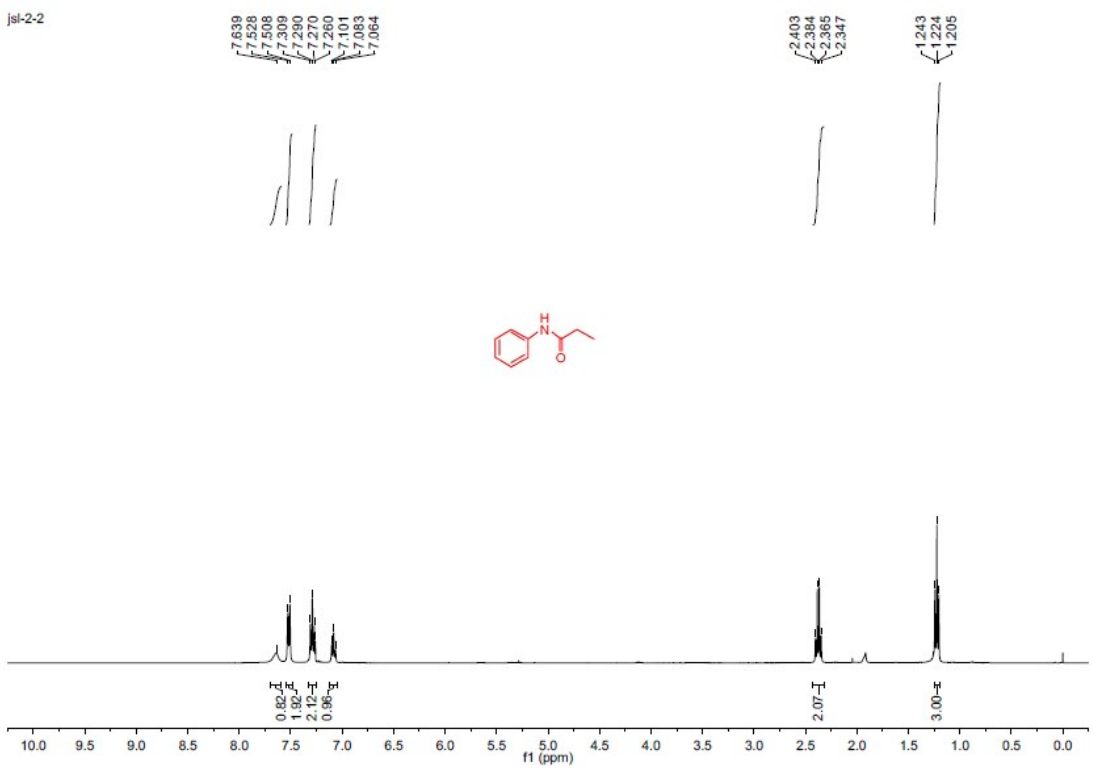

Figure S-46 ^{1}H NMR spectrum of **3ah** ($CDCl_3$)

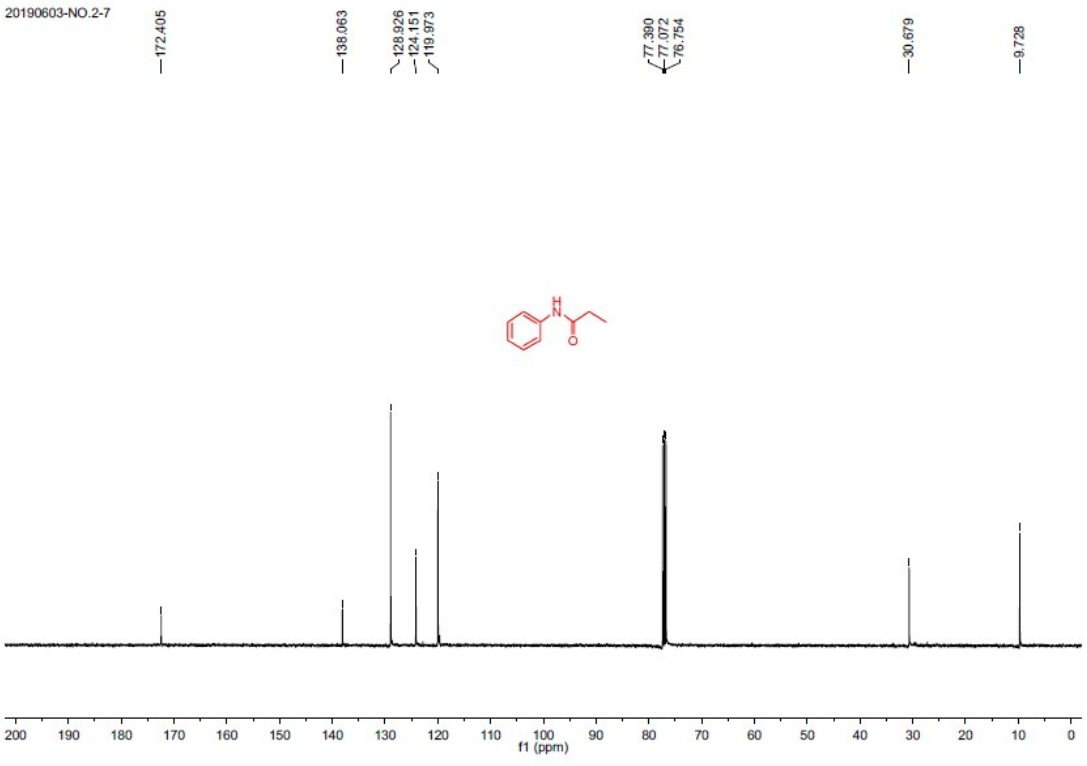

Figure S-47 ^{13}C NMR spectrum of **3ah** ($CDCl_3$)

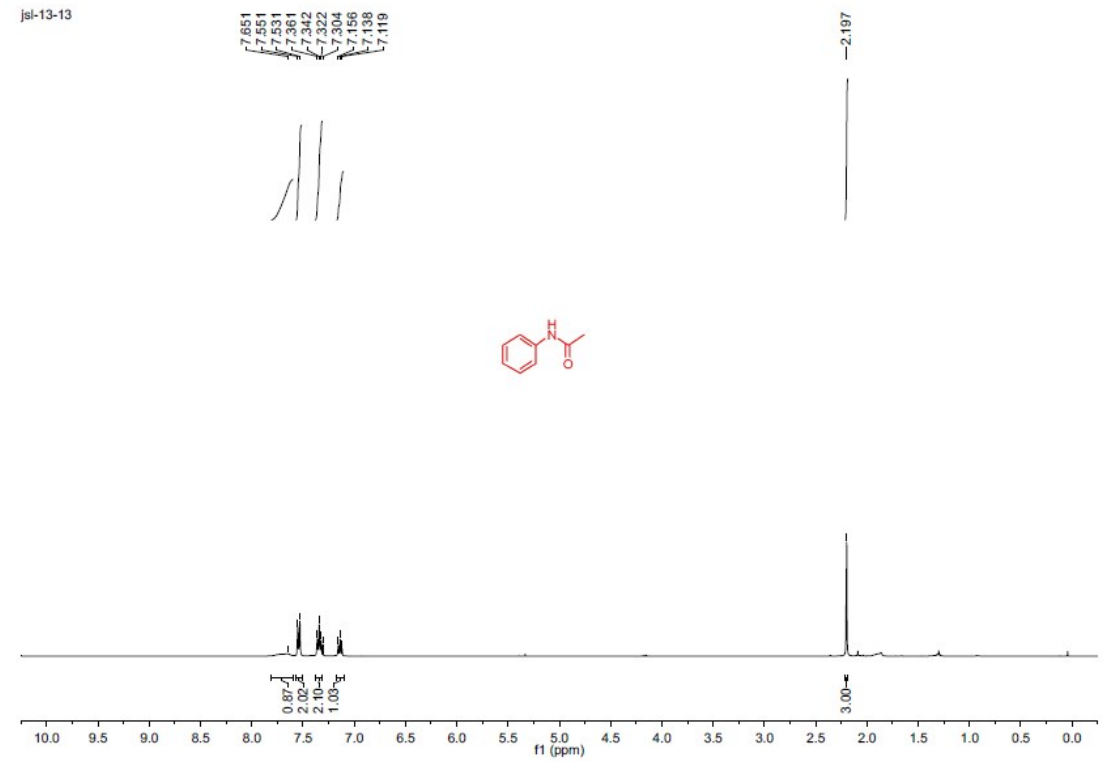

Figure S-48 ^{1}H NMR spectrum of **3ai** ($CDCl_3$)

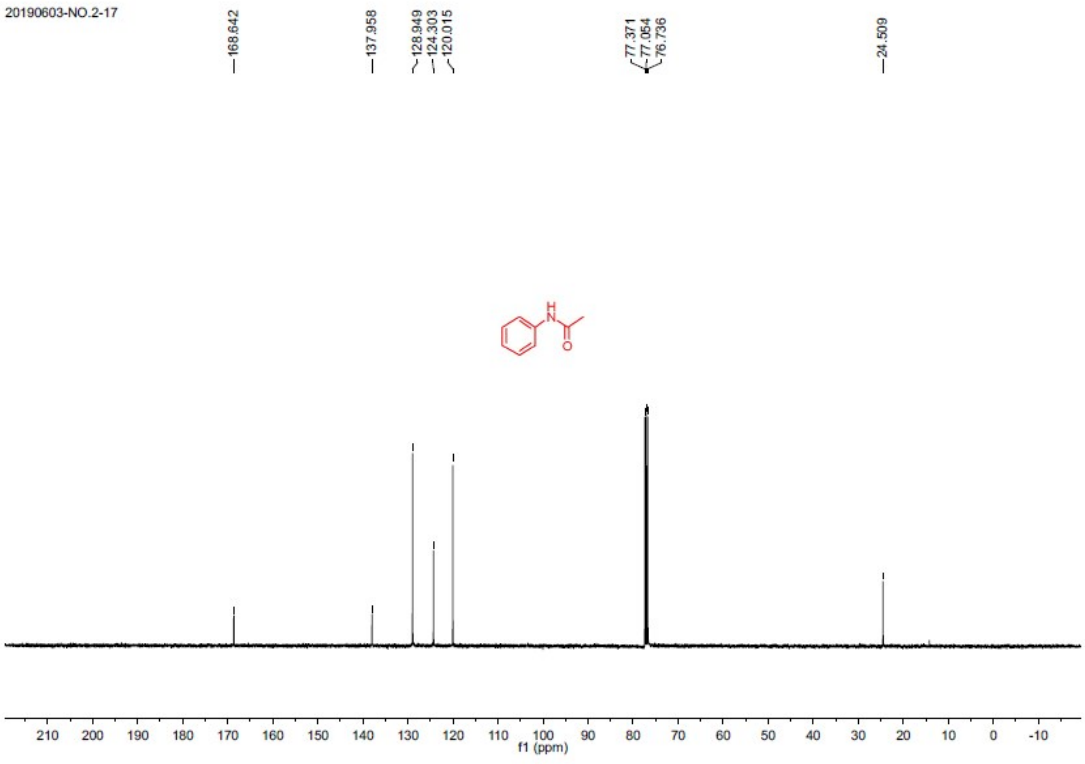

Figure S-49 ^{13}C NMR spectrum of **3ai** ($CDCl_3$)

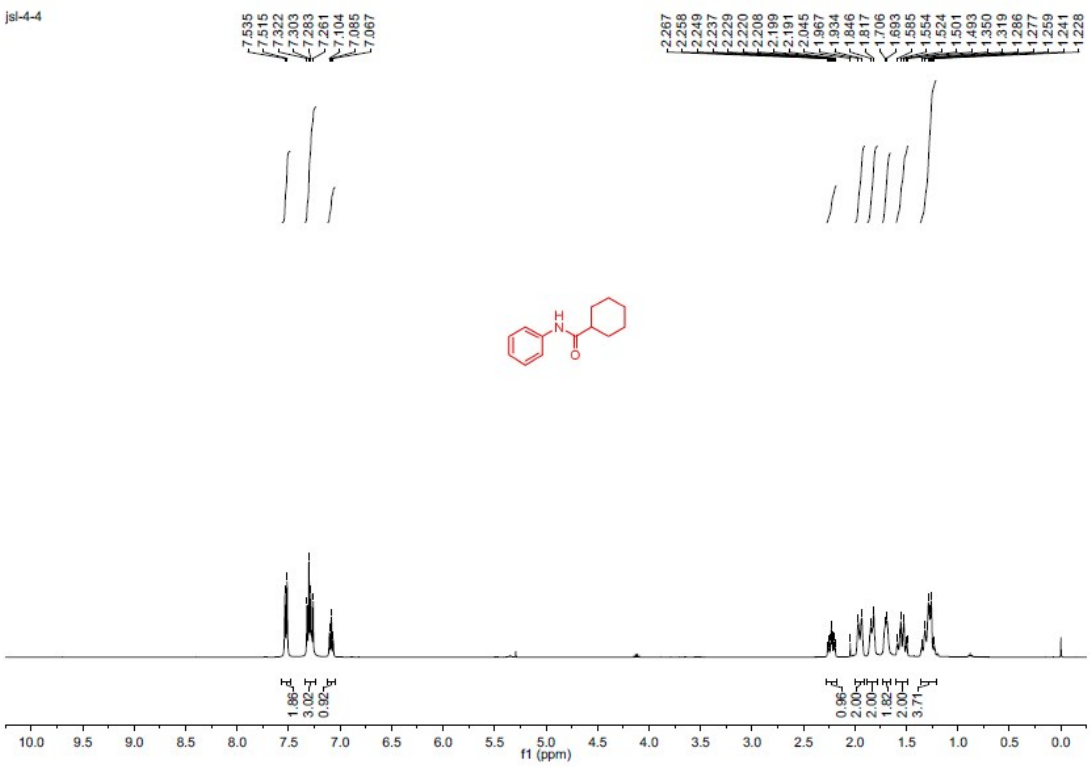

Figure S-50 ^{1}H NMR spectrum of **3aj** ($CDCl_3$)

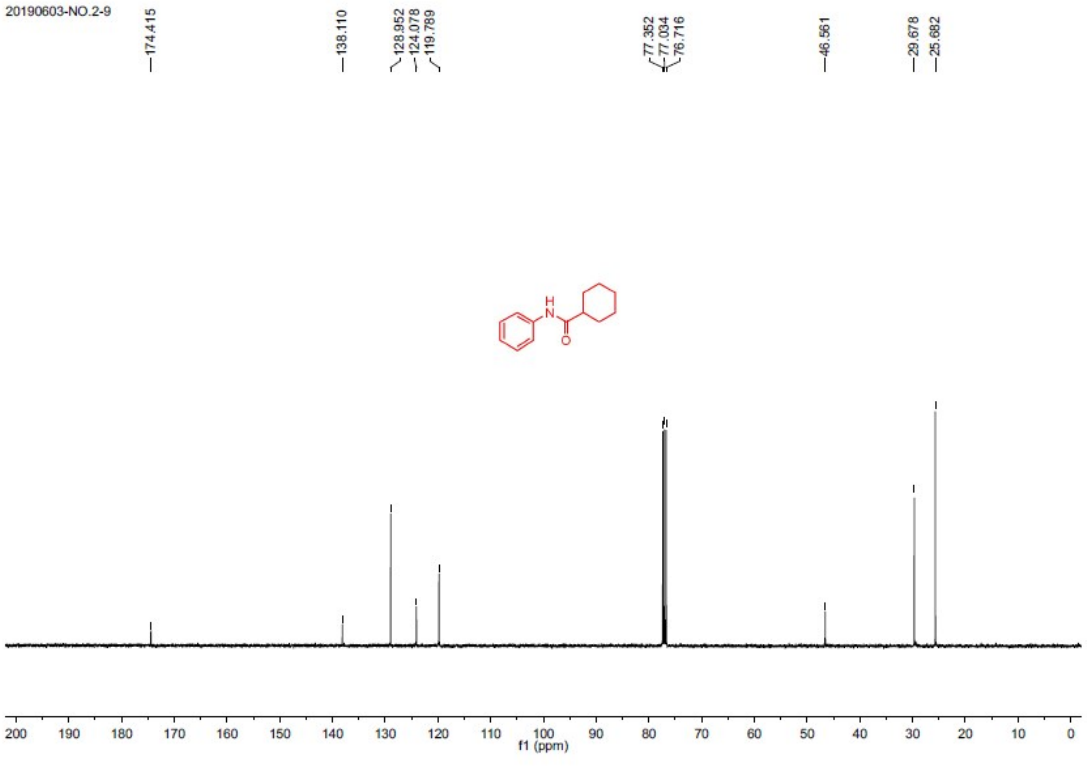

Figure S-51 ^{13}C NMR spectrum of **3aj** ($CDCl_3$)

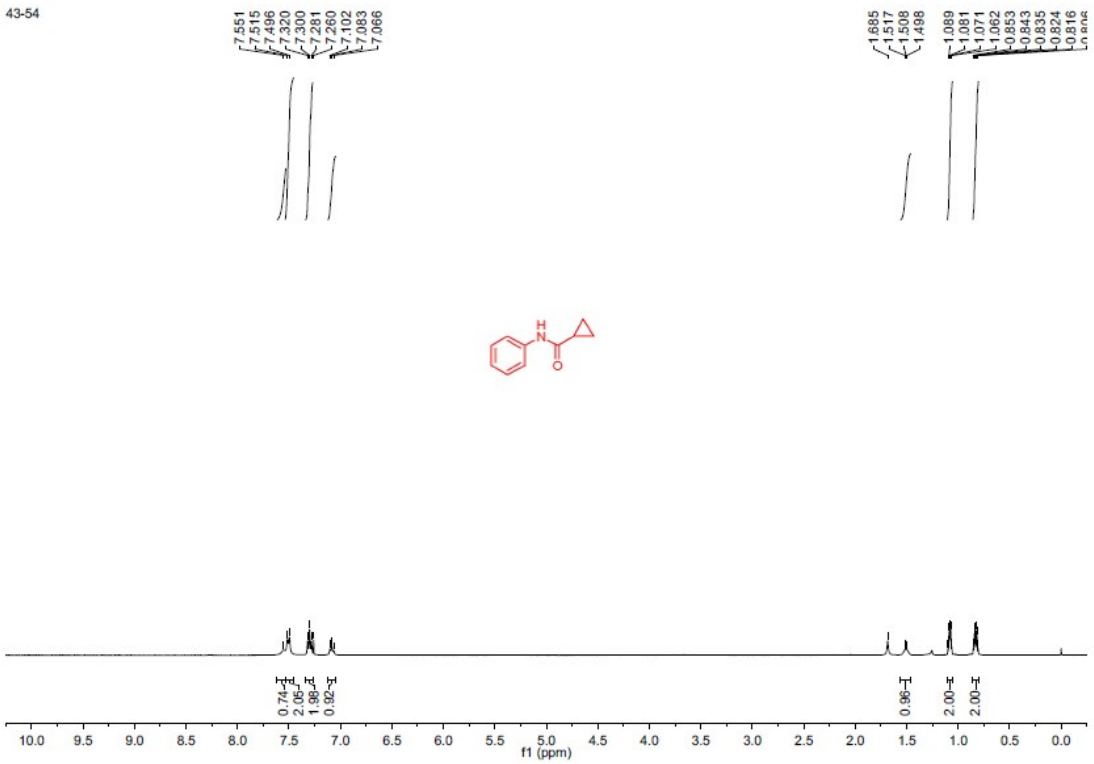

Figure S-52 ^{1}H NMR spectrum of **3ak** ($CDCl_3$)

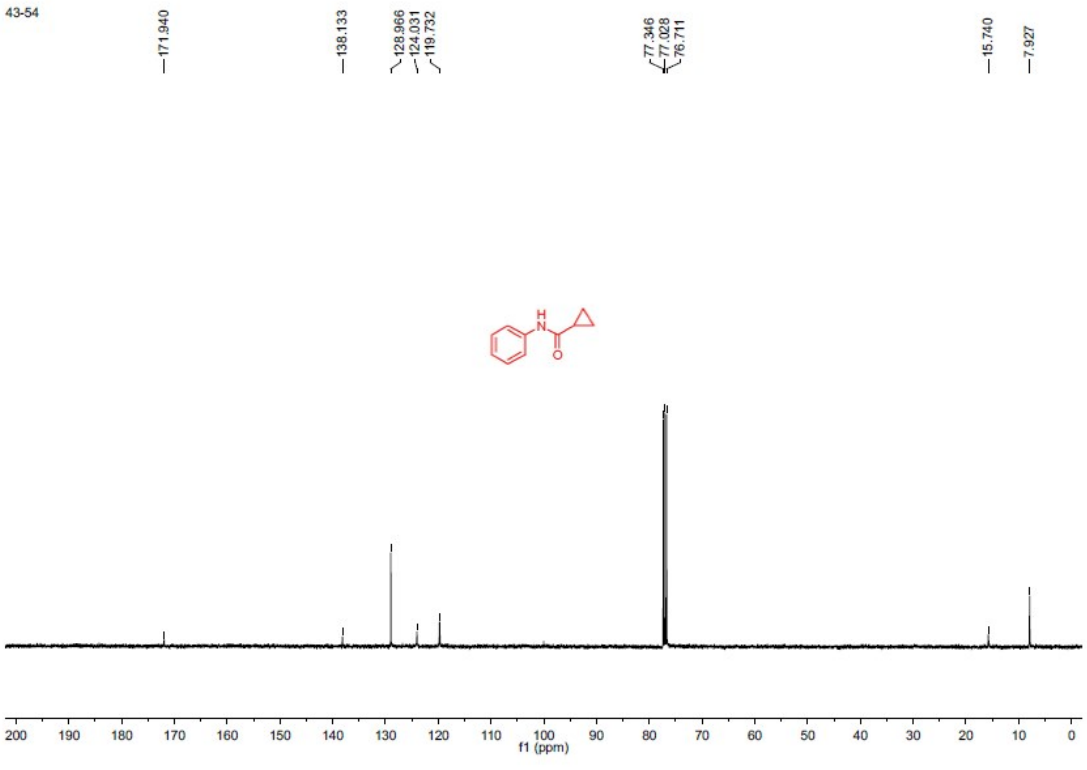

Figure S-53 ^{13}C NMR spectrum of **3ak** ($CDCl_3$)

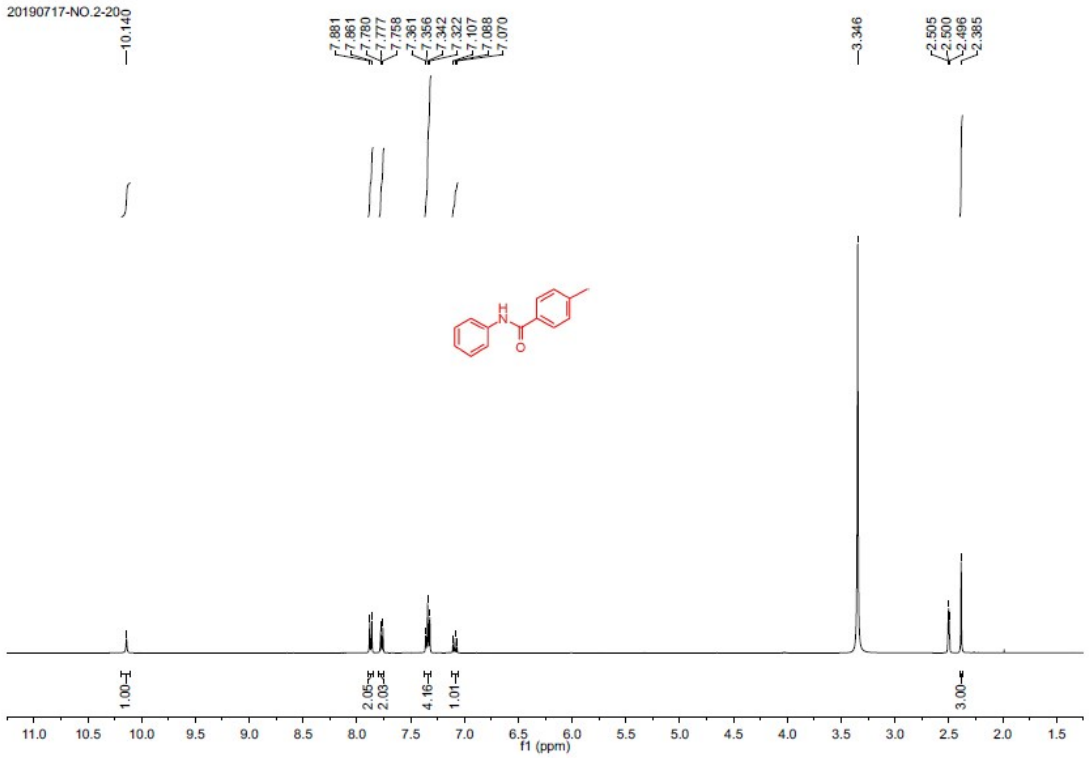

Figure S-54 ^{1}H NMR spectrum of **3al** (DMSO-d_6)

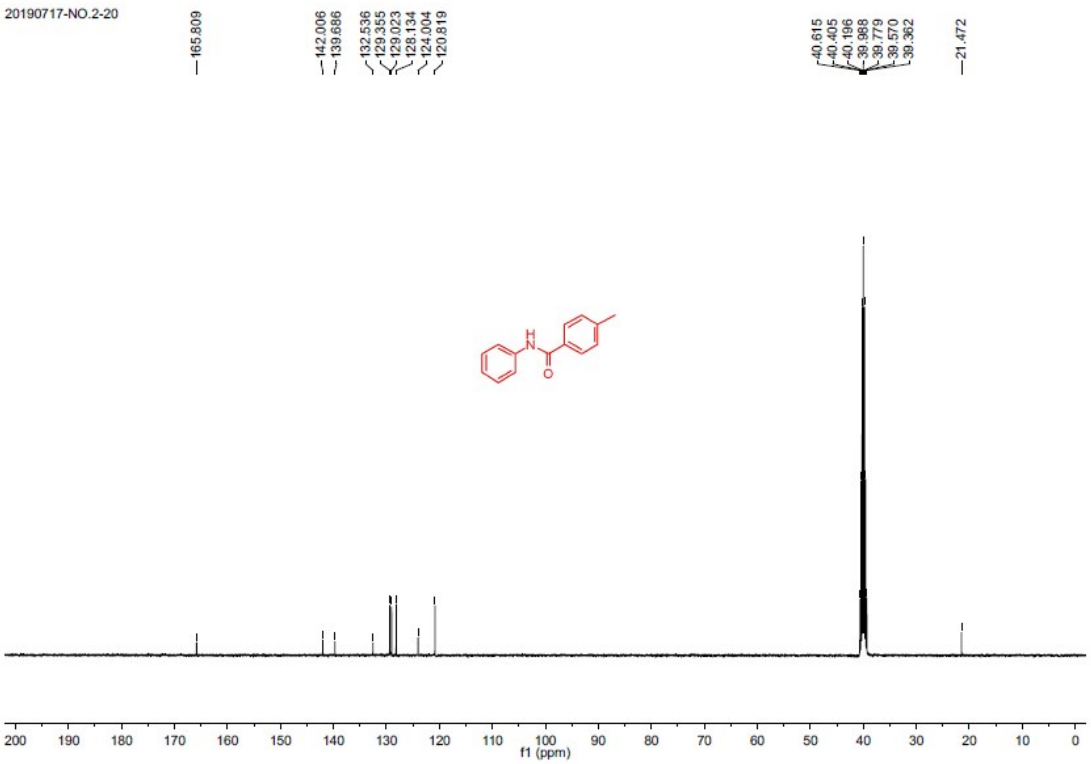

Figure S-55 ^{13}C NMR spectrum of **3al** (DMSO-d_6)

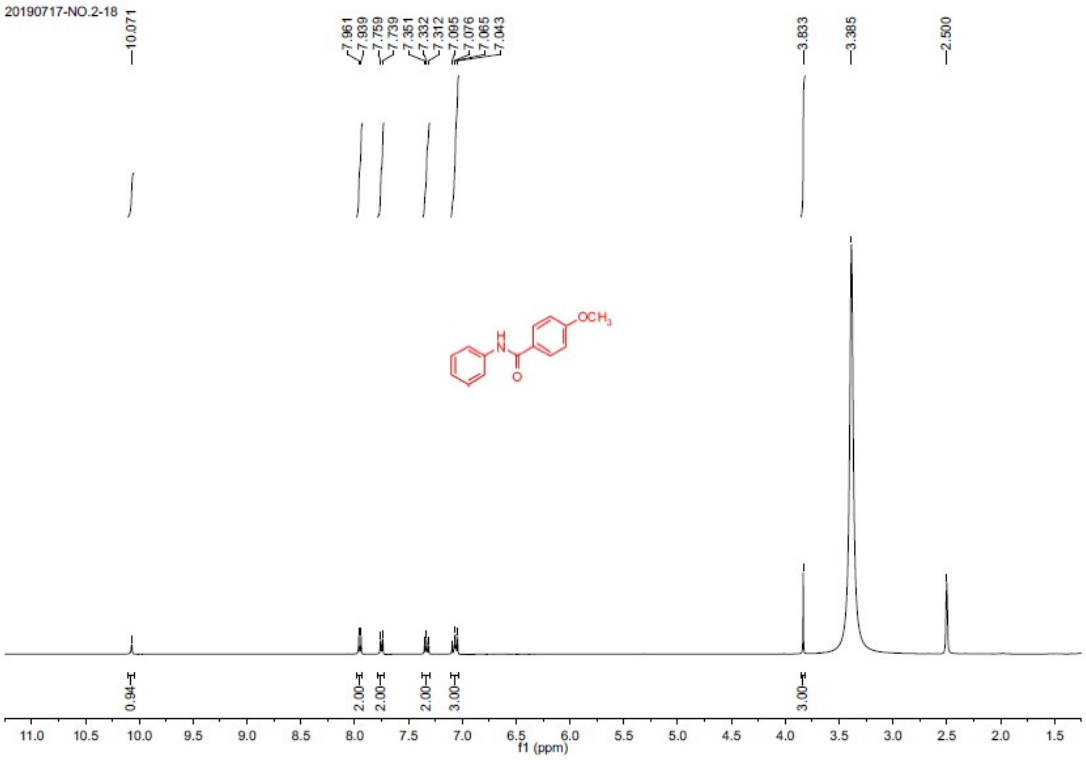

Figure S-56 ^{1}H NMR spectrum of **3am** (DMSO-d_6)

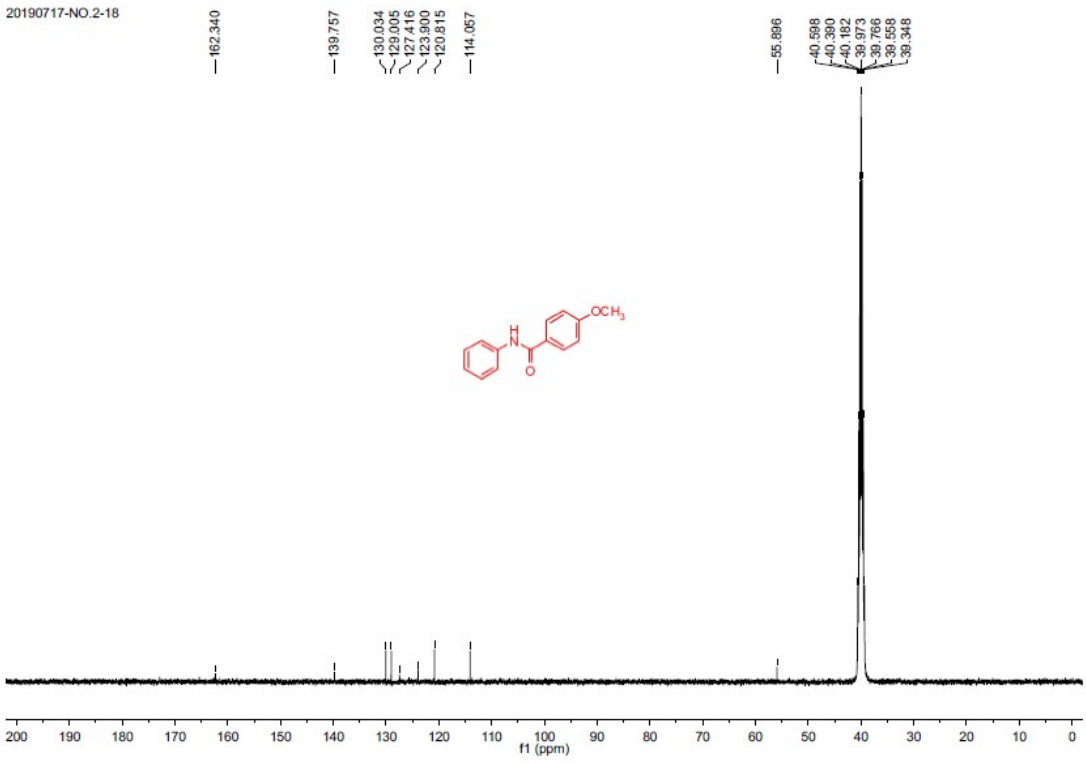

Figure S-57 ^{13}C NMR spectrum of **3am** (DMSO-d_6)

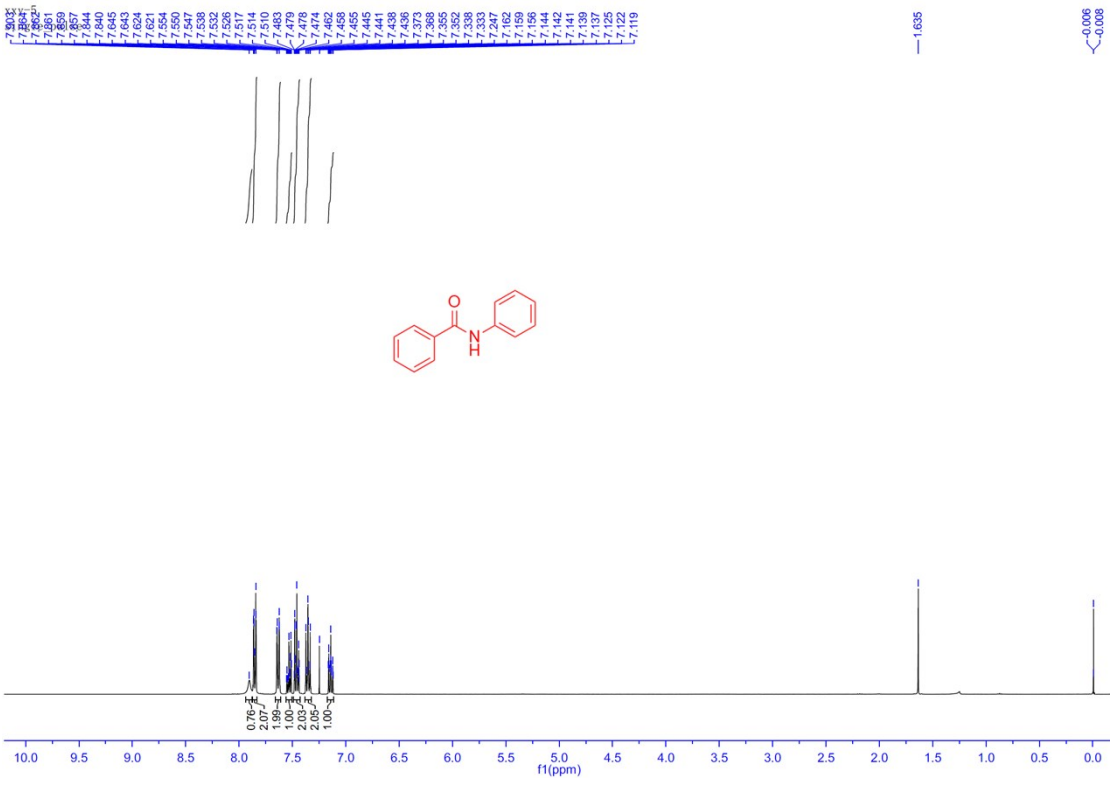

Figure S-58 ^{13}C NMR spectrum of **3an** ($CDCl_3$)

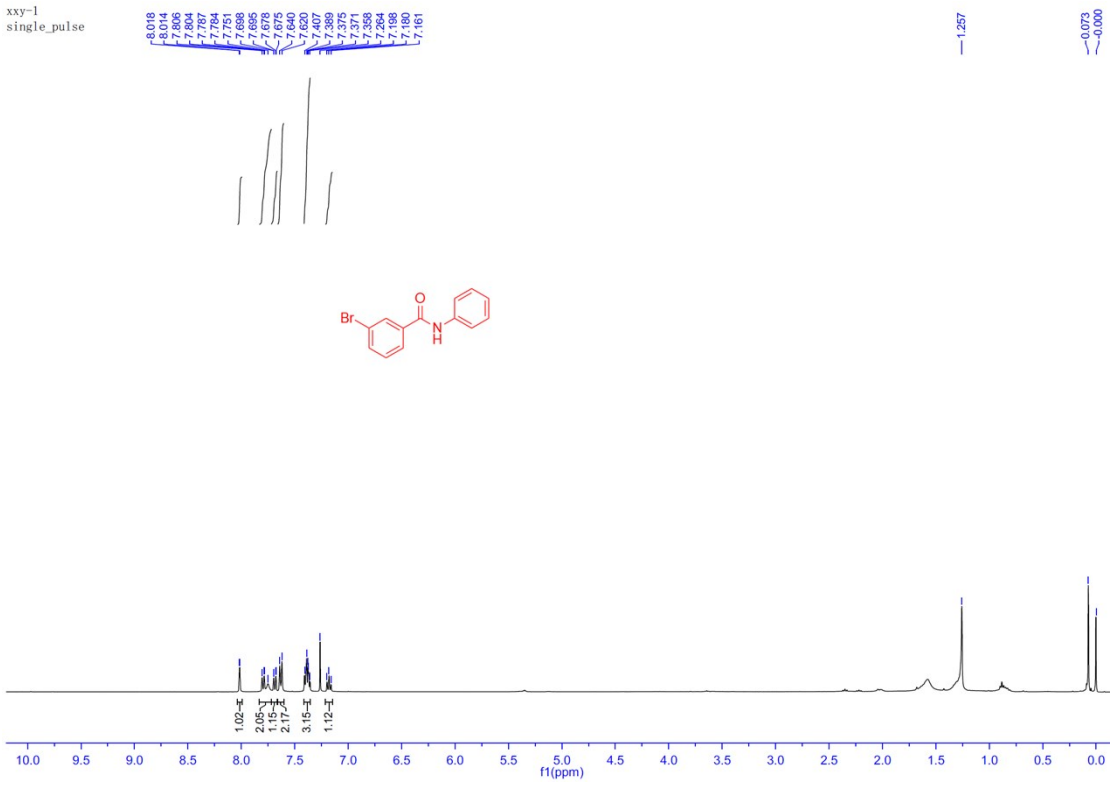

Figure S-59 ^{13}C NMR spectrum of **3ao** ($CDCl_3$)

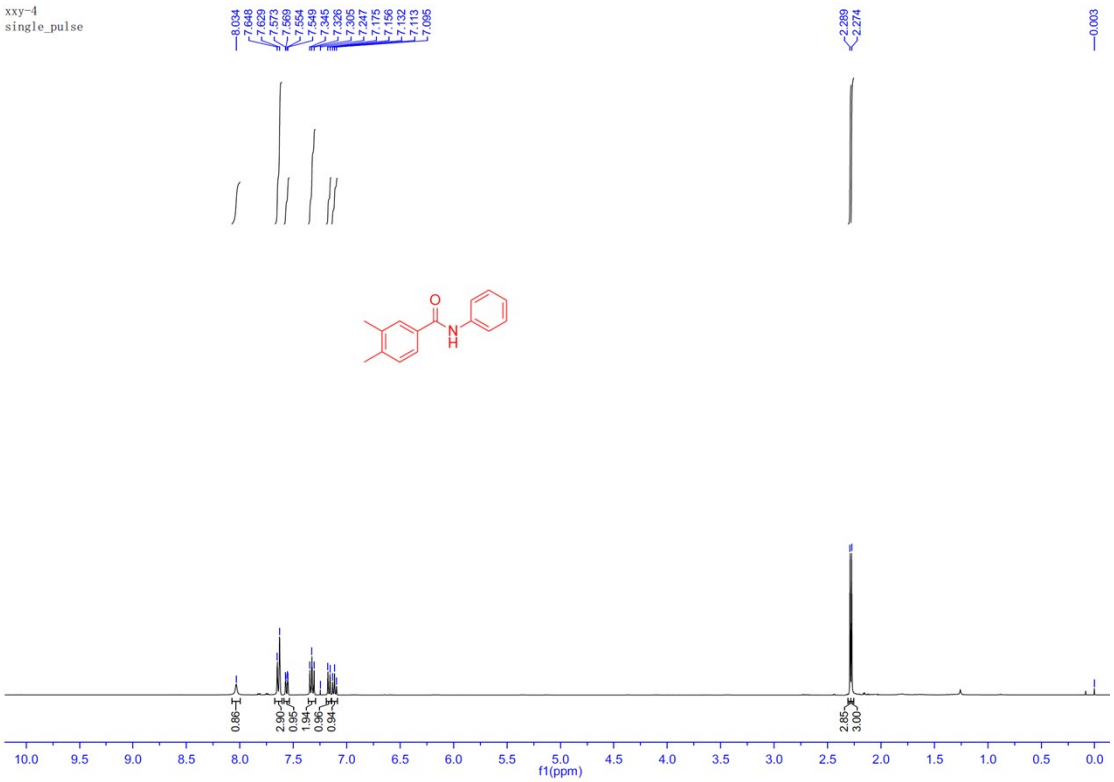

Figure S-60 ^{13}C NMR spectrum of **3ap** ($CDCl_3$)

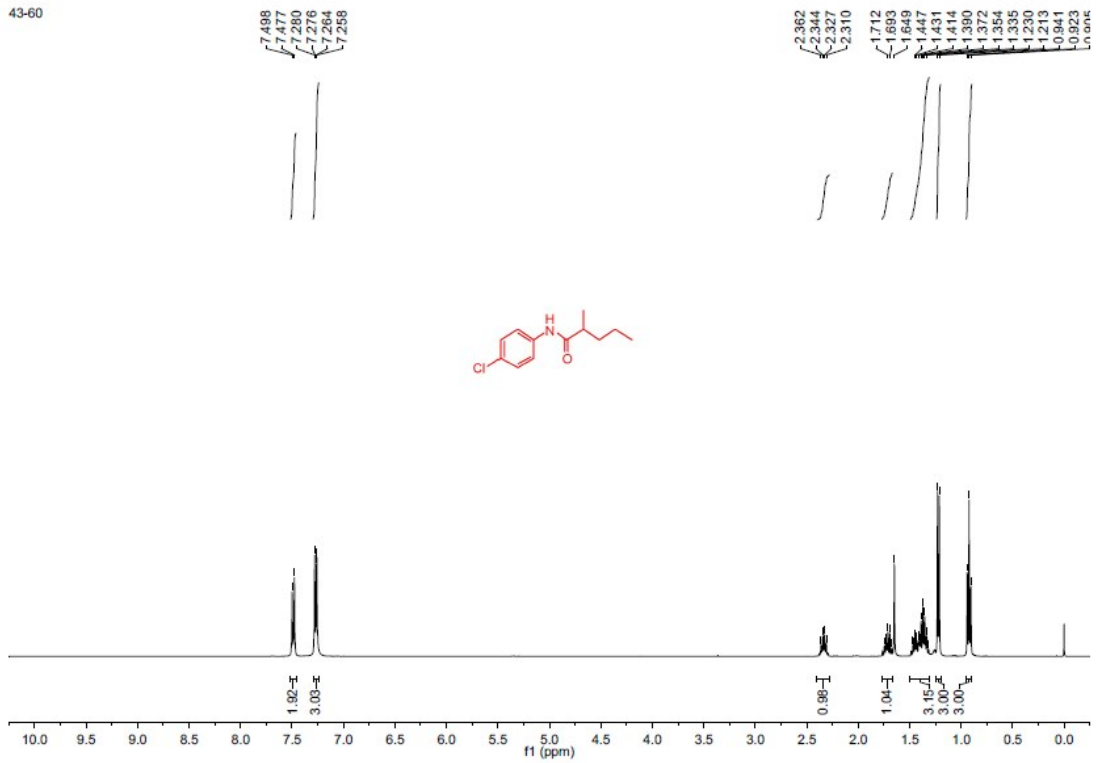

Figure S-61 ^{1}H NMR spectrum of **3dd** ($CDCl_3$)

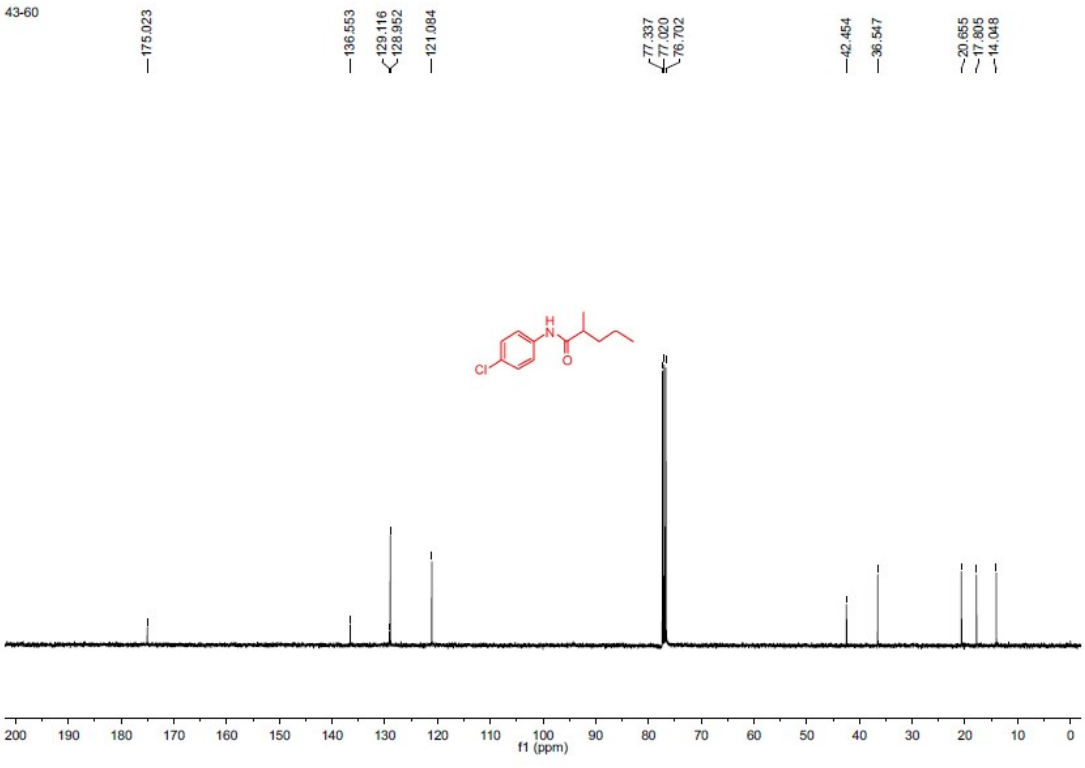

Figure S-62 ^{13}C NMR spectrum of **3dd** ($CDCl_3$)

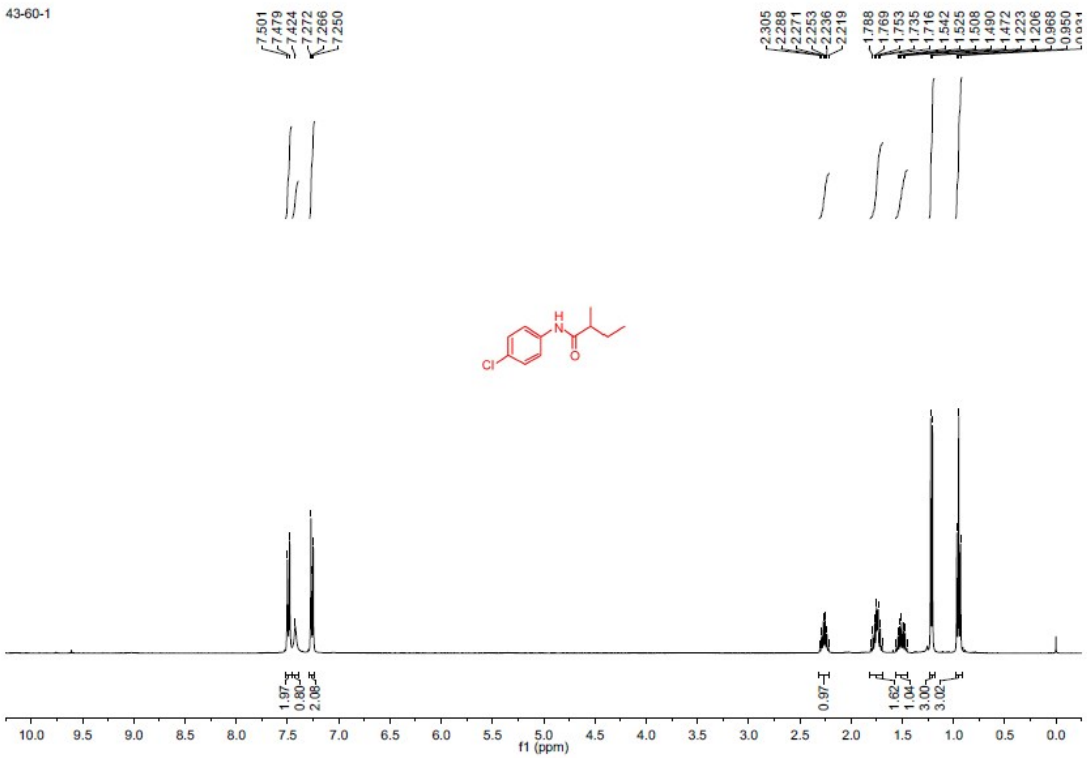

Figure S-63 ^{1}H NMR spectrum of **3de** ($CDCl_3$)

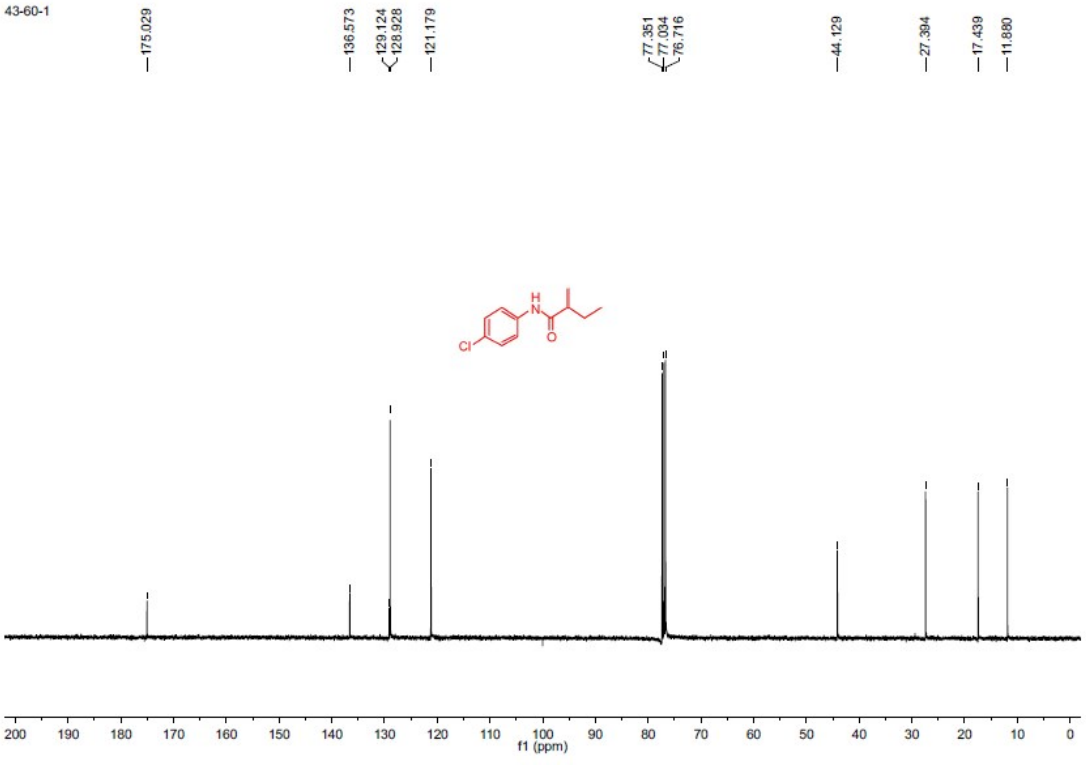

Figure S-64 ^{13}C NMR spectrum of **3de** ($CDCl_3$)

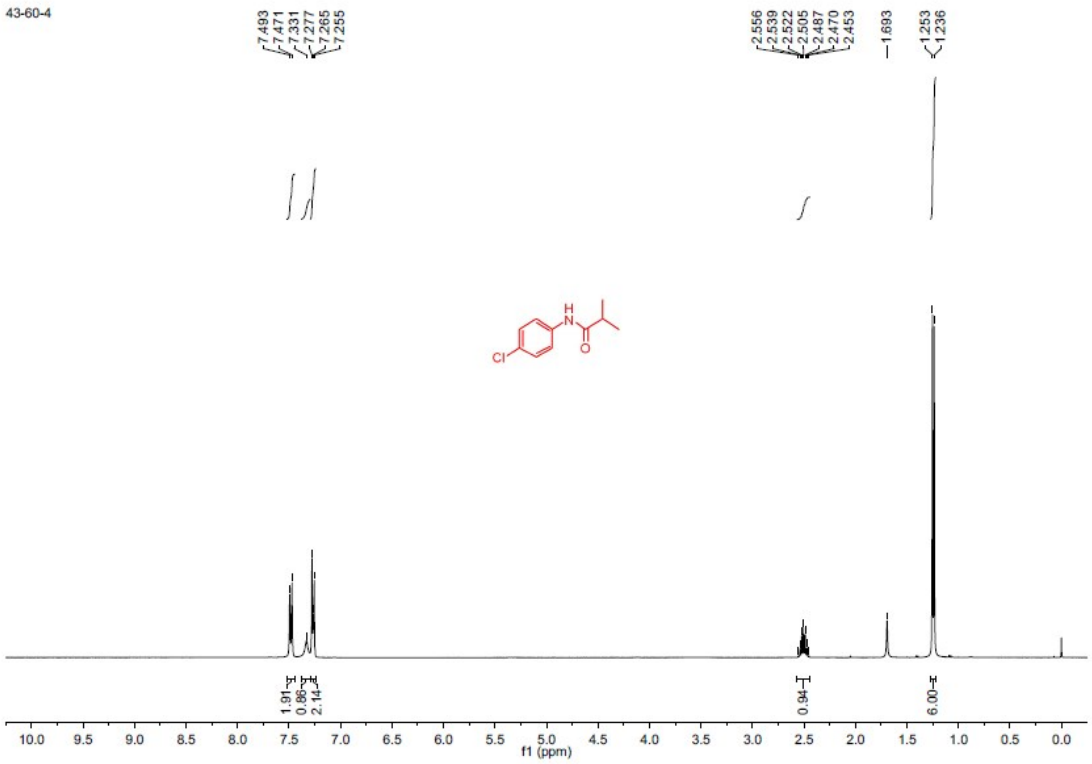

Figure S-65 ^{1}H NMR spectrum of **3df** ($CDCl_3$)

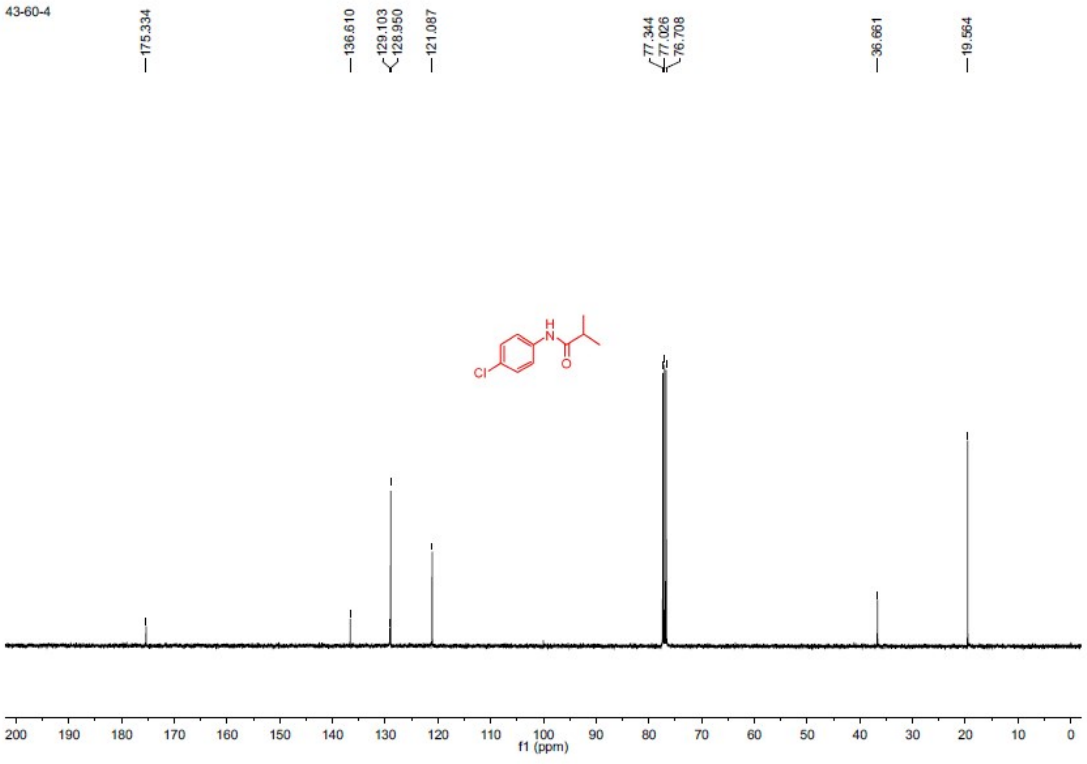

Figure S-66 ^{13}C NMR spectrum of **3df** ($CDCl_3$)

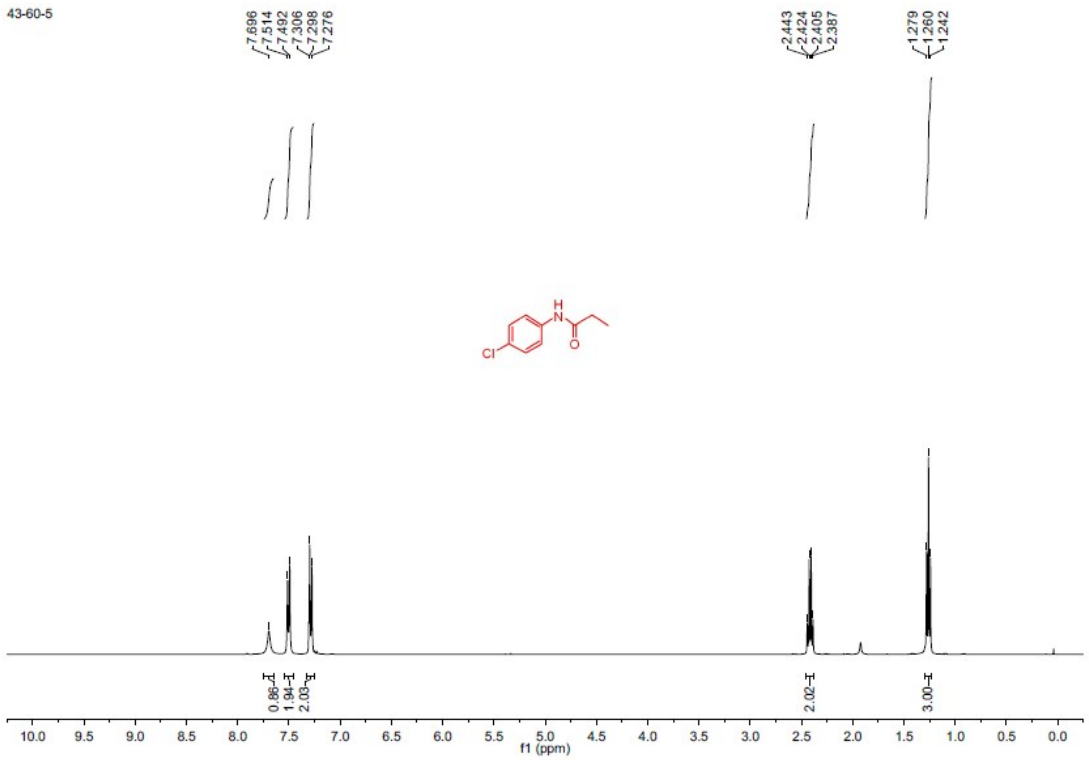

Figure S-67 ^{1}H NMR spectrum of **3dh** ($CDCl_3$)

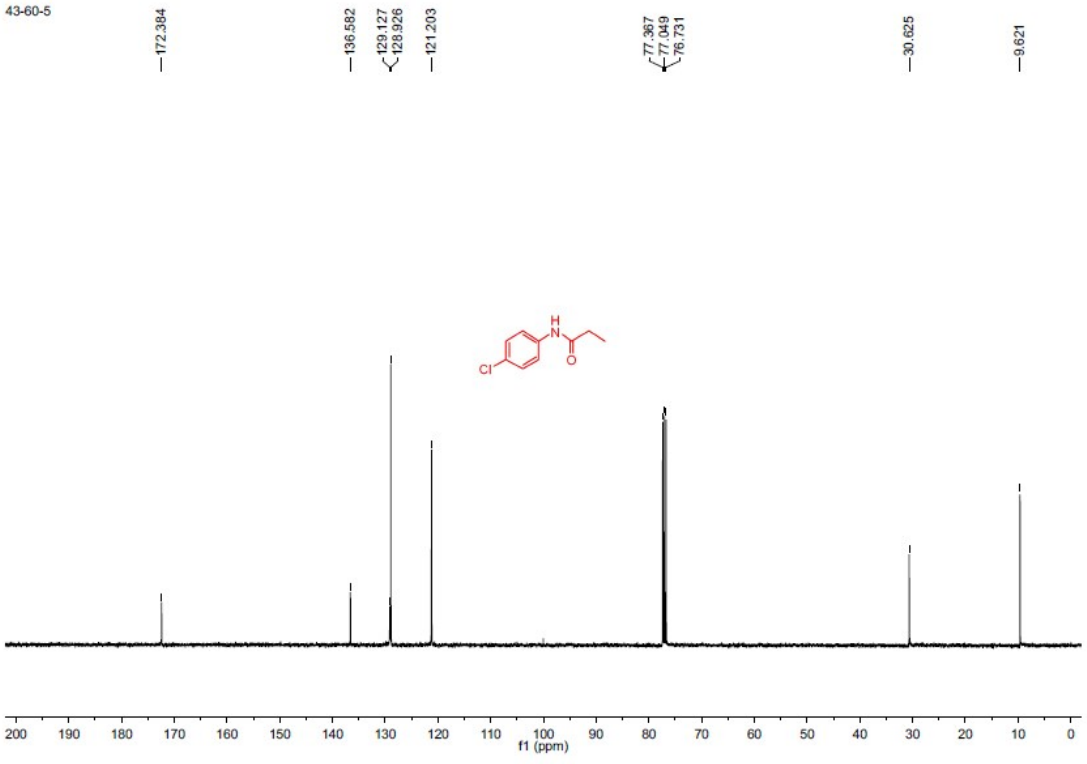

Figure S-68 ^{13}C NMR spectrum of **3dh** ($CDCl_3$)

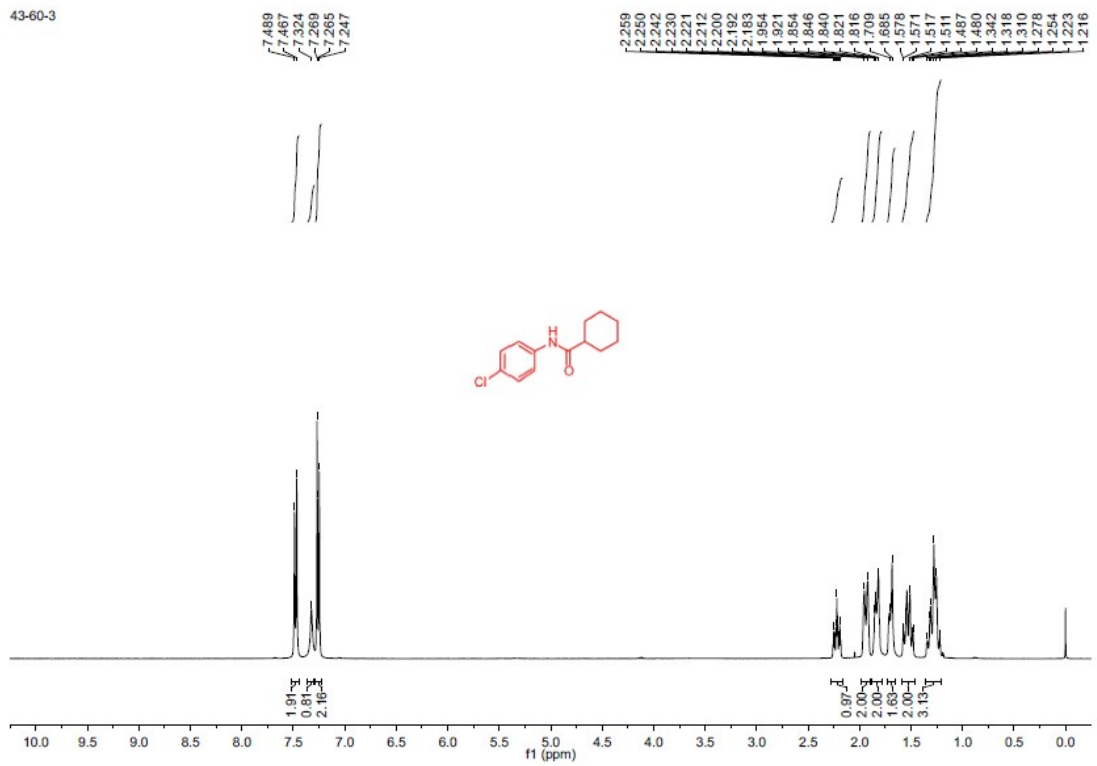

Figure S-69 ^{1}H NMR spectrum of **3dj** ($CDCl_3$)

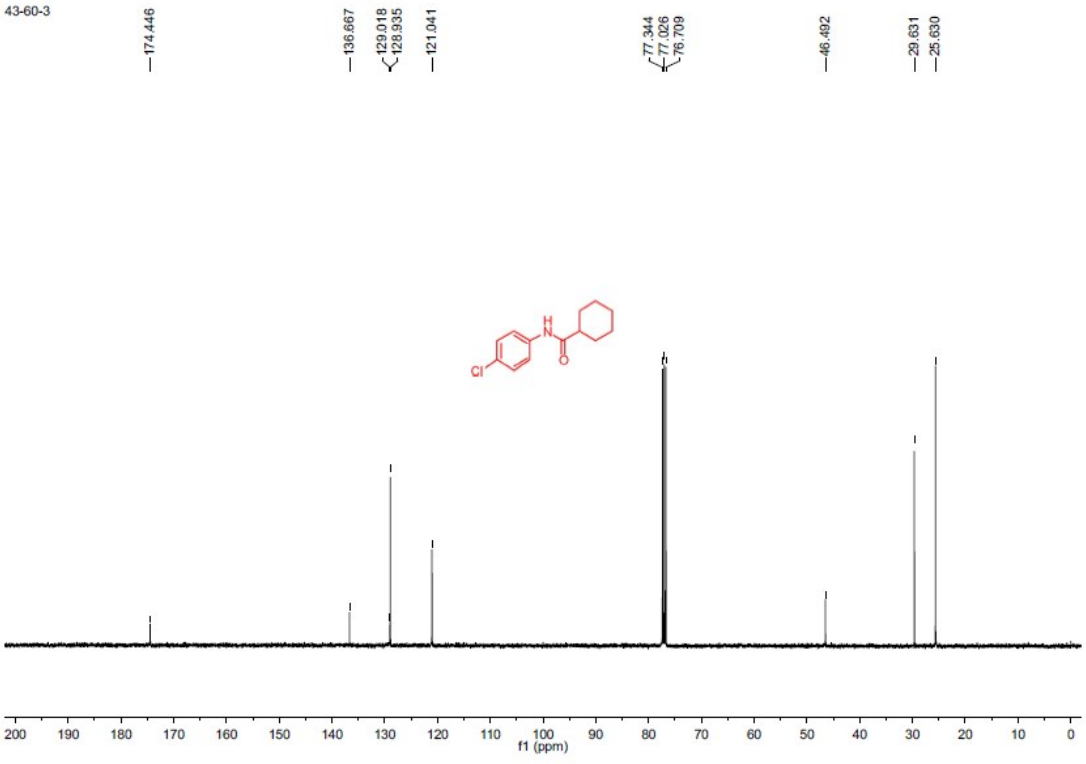

Figure S-70 ^{13}C NMR spectrum of **3dj** ($CDCl_3$)

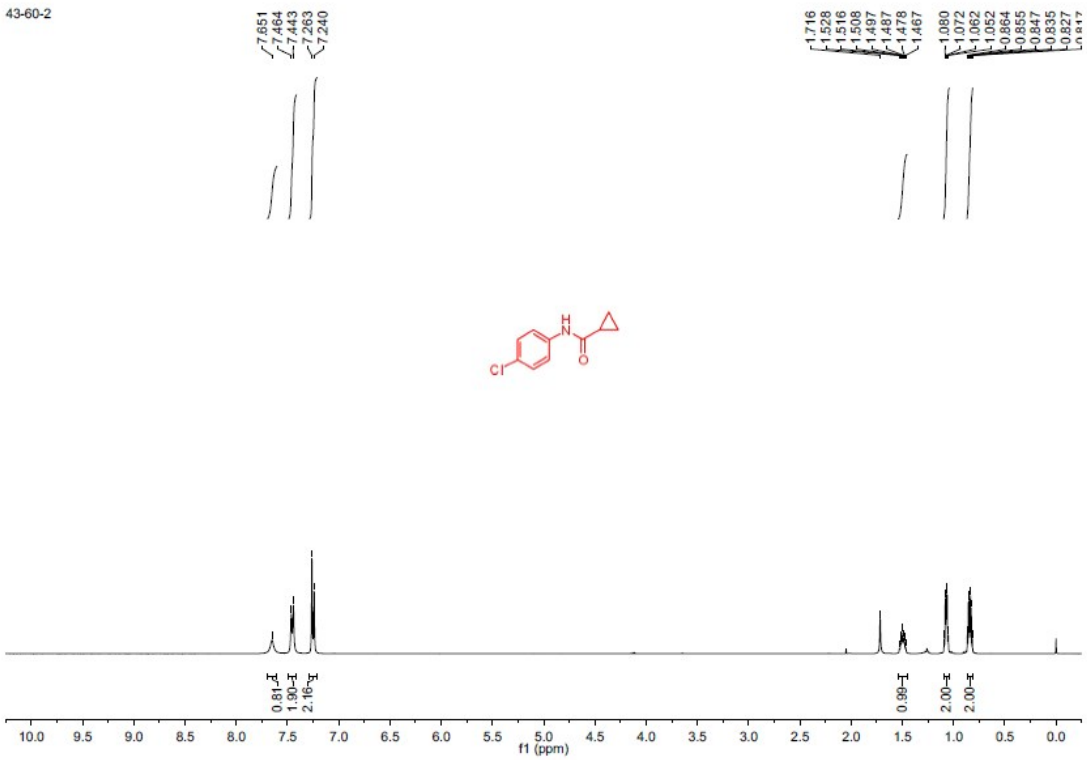

Figure S-71 ^{1}H NMR spectrum of **3dk** ($CDCl_3$)

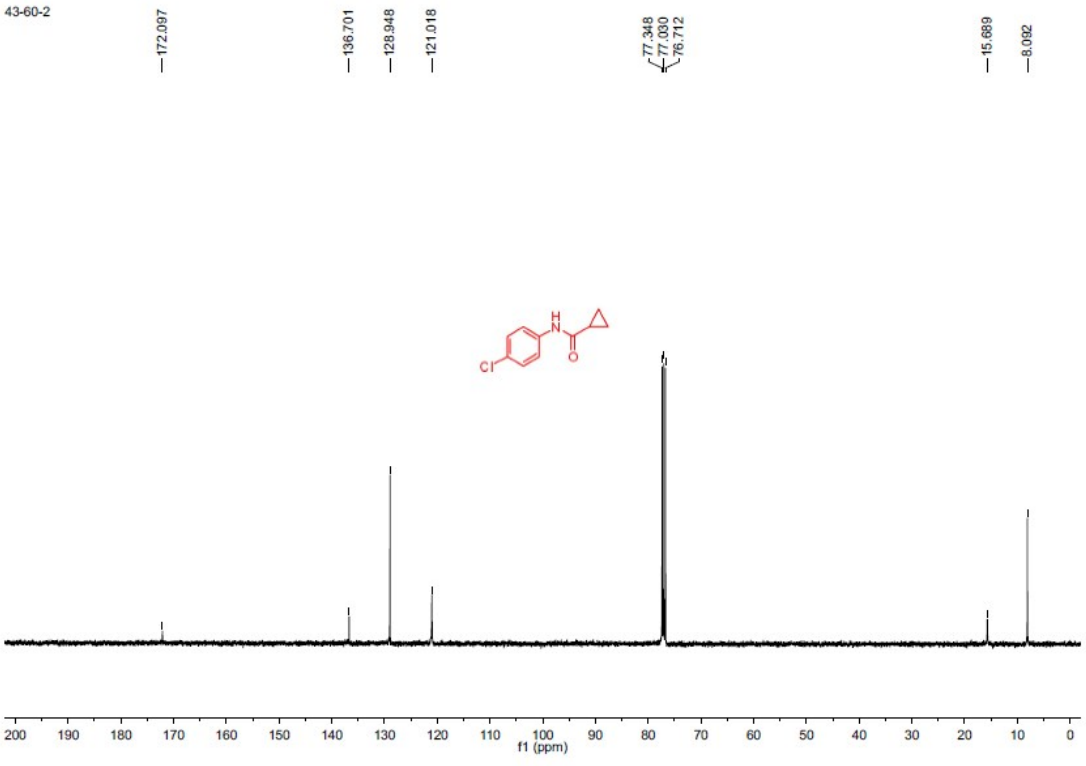

Figure S-72 ^{13}C NMR spectrum of **3dk** ($CDCl_3$)

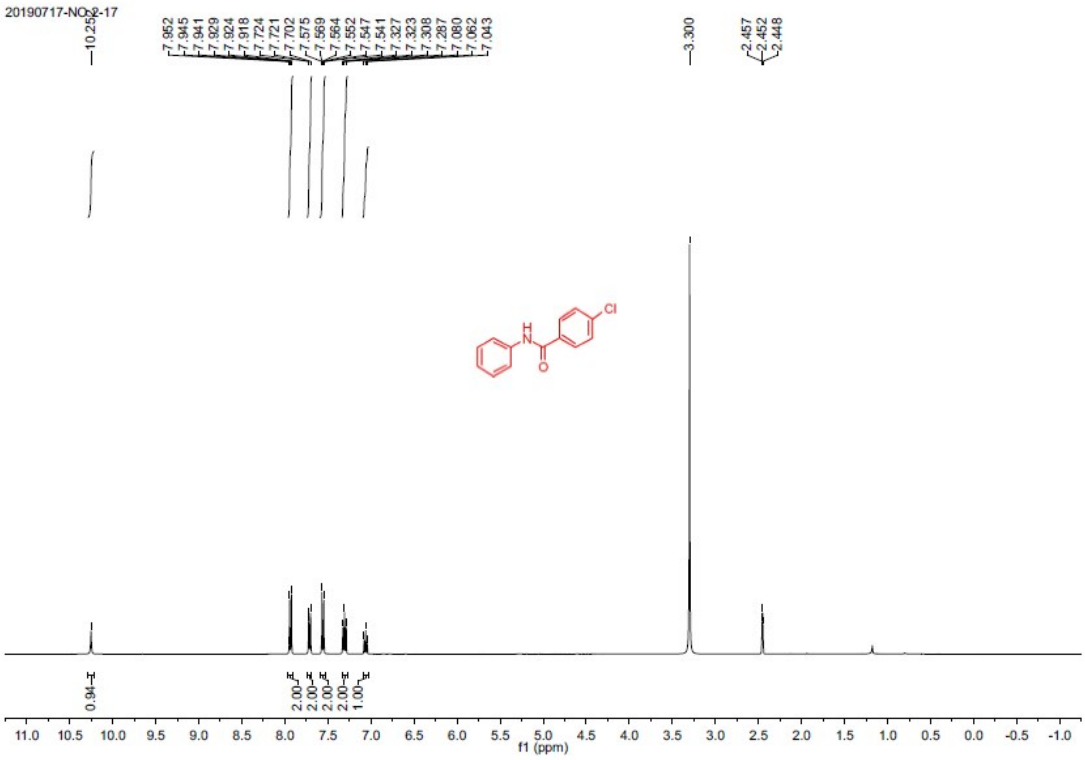

Figure S-73 ^{1}H NMR spectrum of **5ad** (DMSO-d_6)

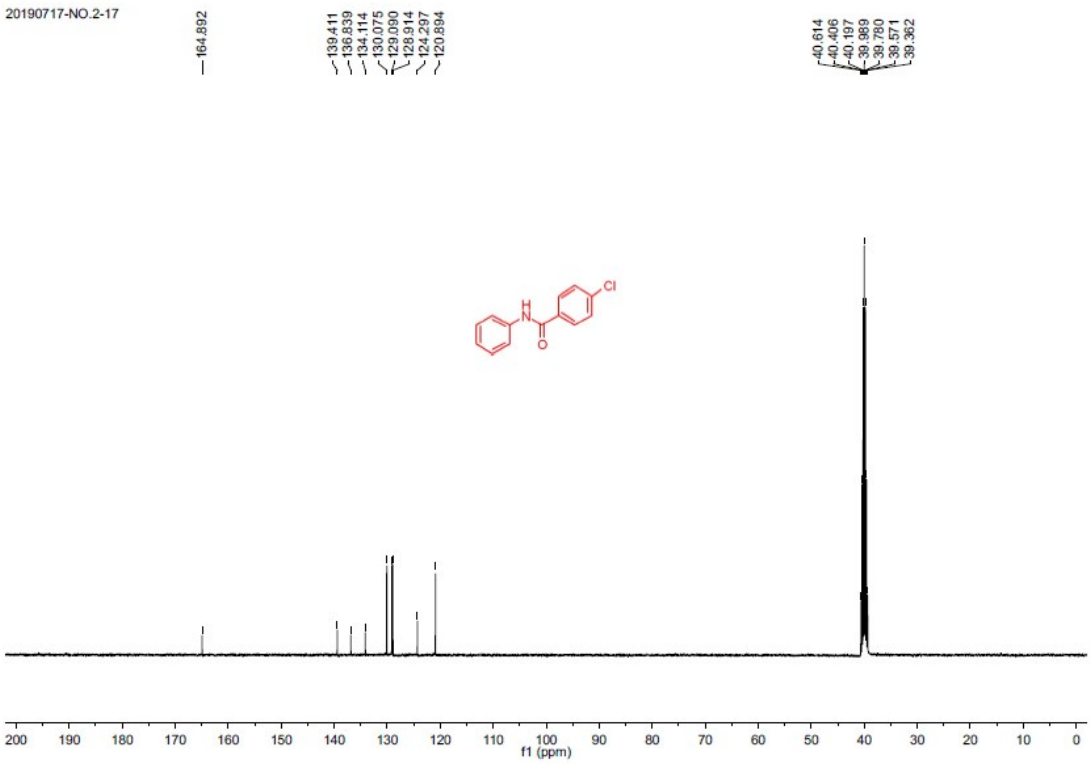

Figure S-74 ^{13}C NMR spectrum of **5ad** (DMSO-d_6)

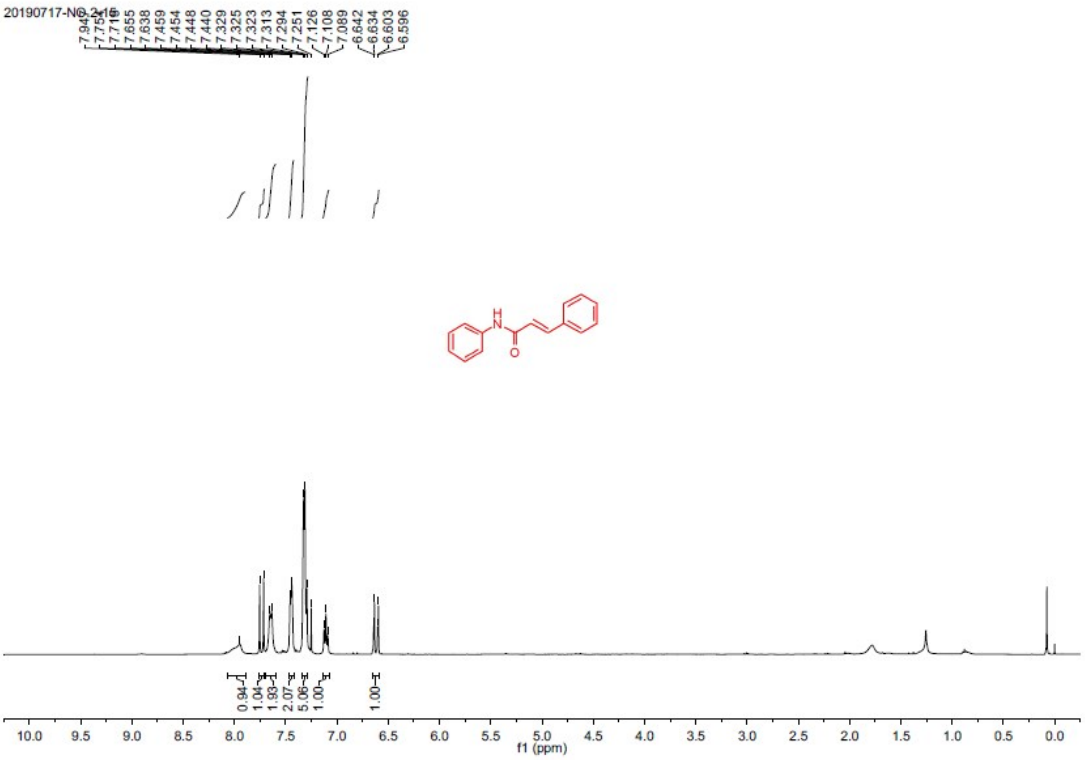

Figure S-75 ^{1}H NMR spectrum of **5ae** ($CDCl_3$)

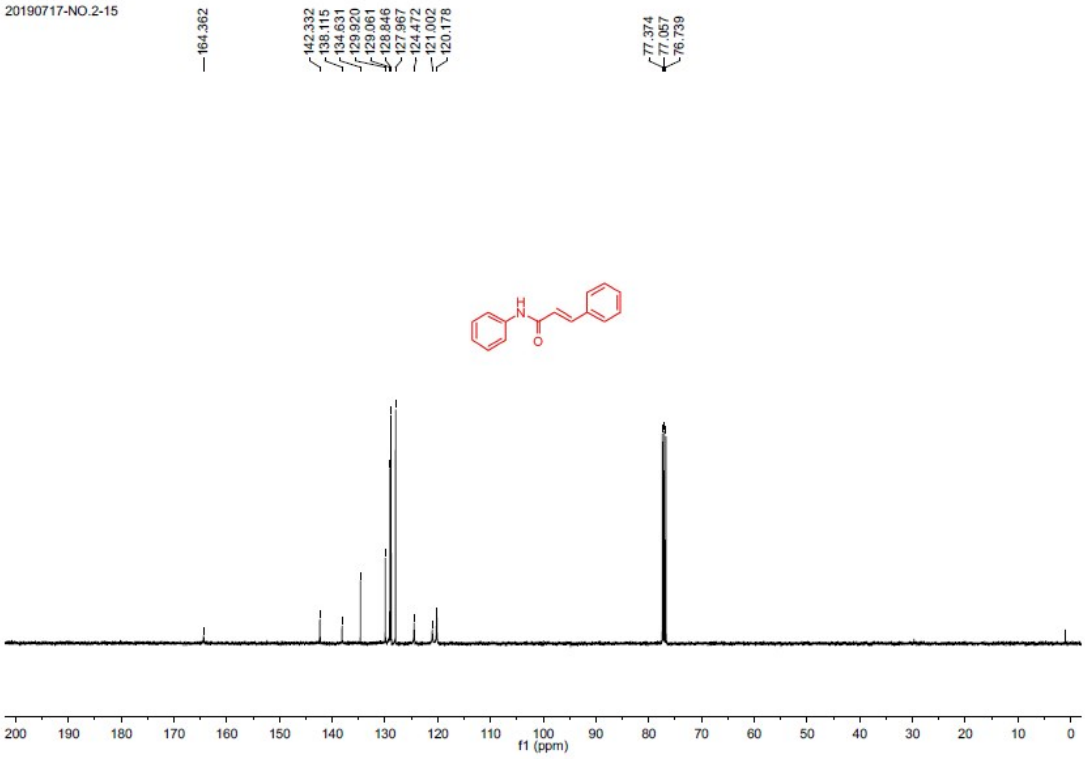

Figure S-76 ^{13}C NMR spectrum of **5ae** ($CDCl_3$)

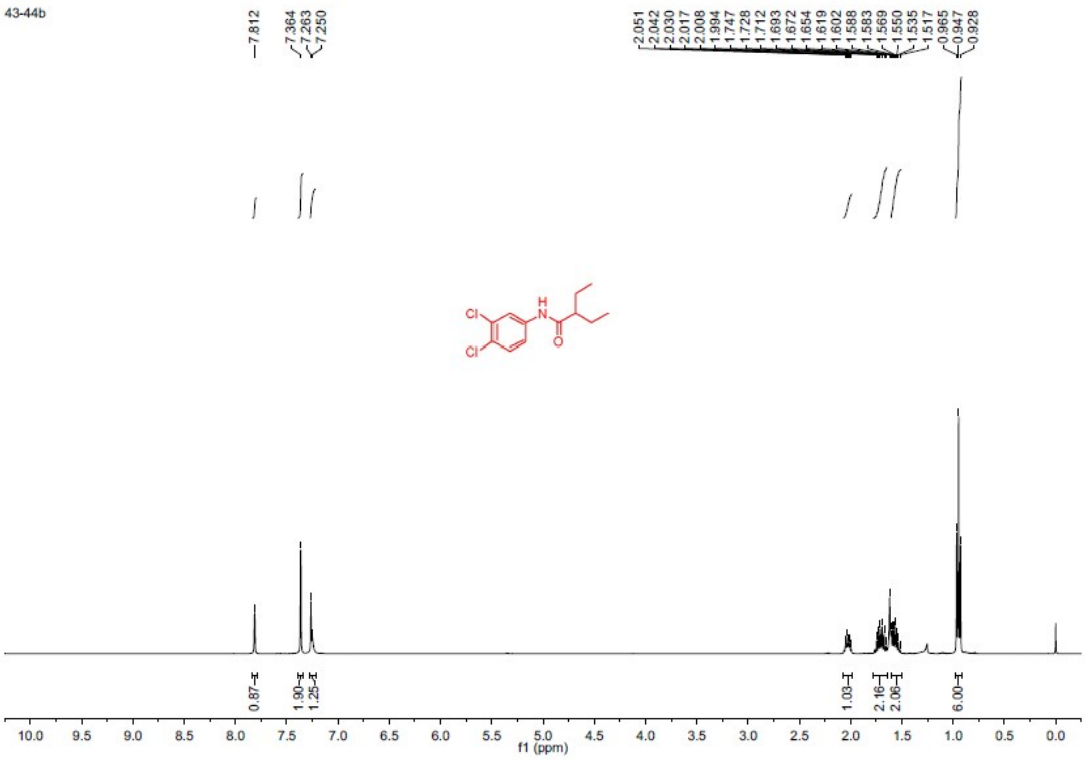

Figure S-77 ^{1}H NMR spectrum of **7aa** ($CDCl_3$)

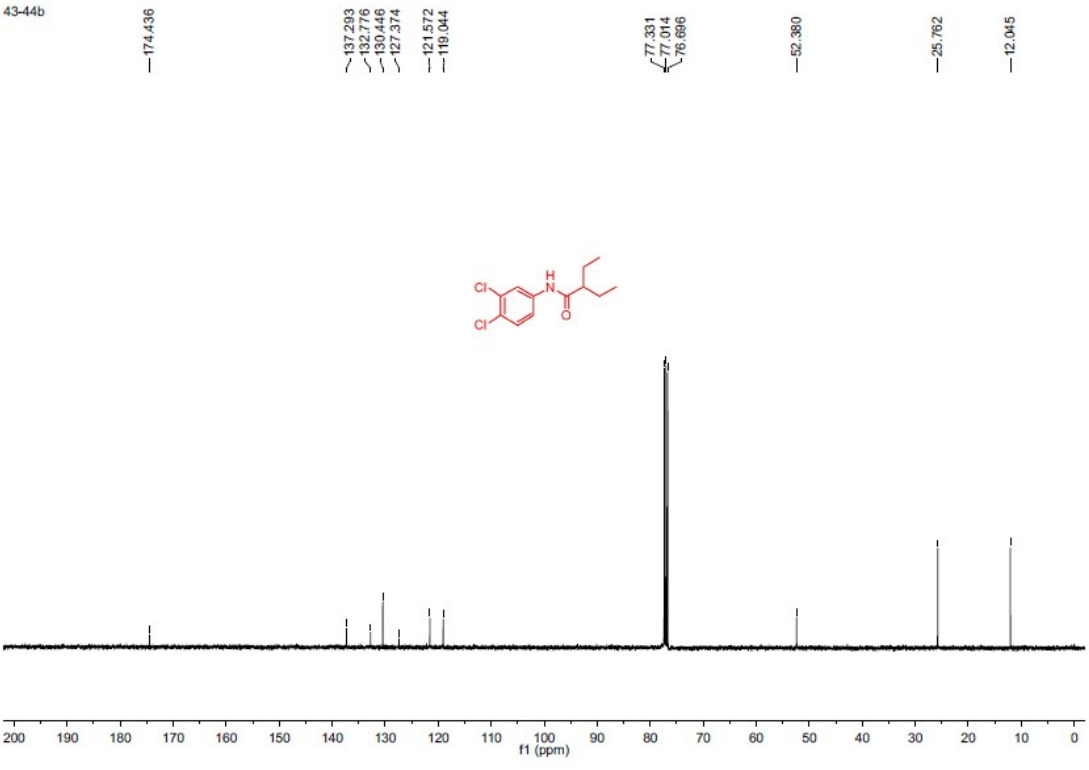

Figure S-78 ^{13}C NMR spectrum of **7aa** ($CDCl_3$)