Supporting Information

Tungsten-Catalyzed Transamidation of Tertiary Alkyl Amides

Fang-Fang Feng,[†] Xuan-Yu Liu,[†] Chi Wai Cheung,[†,‡,*] and Jun-An Ma[†,‡,*]

[†] Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Frontiers Science Center for Synthetic Biology (Ministry of Education), and Tianjin Collaborative Innovation Centre of Chemical Science & Engineering, Tianjin University, Tianjin 300072, P. R. of China

[‡] Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou 350207, P. R. of China

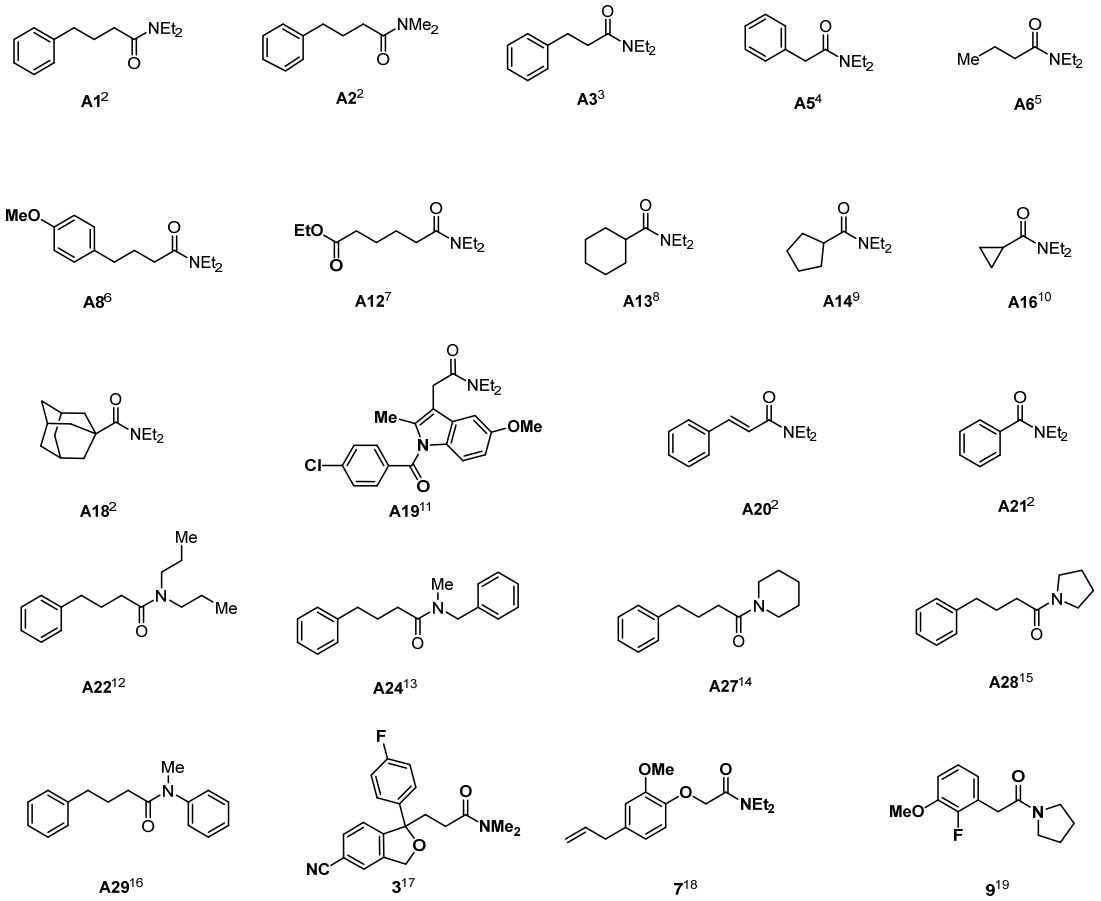
Table of contents

General Considerations

General Analytical Information. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR), or on JEOL AV 600 MHz instrument at 600 MHz (^{1}H NMR), 150 MHz (^{13}C NMR), 243 MHz (^{31}P NMR) or 565 MHz (^{19}F NMR). All ^{1}H NMR spectra were measured in parts per million (ppm) downfield from tetramethylsilane (TMS, 0 ppm), or were measured relative to the residual proton signals of d_1-chloroform ($CDCl_3$, 7.26 ppm), dimethyl sulfoxide-d_6 (DMSO-d_6, 2.50 ppm) or d_4-methanol (CD_3OD, 3.31 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual carbon signals of $CHCl_3$ (77.16 ppm), DMSO-d_6 (39.52 ppm) or CD_3OD (49.03 ppm) and were obtained with ^{1}H decoupling. Coupling constants (*J*) are reported in hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. GC-MS analyses were performed on a Thermo Scientific Model Trace 1300 instrument. X-ray structural analysis was conducted on a Bruker APEX-II CCD instrument. Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254 nm. Flash chromatography for purification of compounds were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.).

General Reagents Information. Unless otherwise noted, commerically available materials were used without prior purification. Anhydrous *N*-methylpyrrolidone (NMP) was purchased from HEOWNS and it was added with anhydrous 3Å molecular sieves for storage. Chlorotrimethylsilane (TMSCl, 98% purity) was purchased from HEOWNS and was stored in refrigerator for storage. Phenanthroline (phen, 99% purity) was purchased from Bidepharm. Tungsten(VI) chloride (WCl_6, 99% purity) was purchased from HEOWNS. Tungsten(VI) chloride (WCl_6, 99.99% purity) was purchased from Energy Chemical. A small amount (~1 g) of WCl_6 (99% purity) was taken from the original bulk bottle of WCl_6 each time for reaction study. The bulk original bottle and the small bottle of WCl_6 were stored in a decciator for storage (**Note:** The WCl_6 used for study is a deep purple amorphous solid. It turns yellow slowly upon

prolonged use under air conditions due to hydrolysis under air conditions. The pale yellow residue should be ignored and only the deep purple portion should always be used). WCl_5 was prepared according to the literature procedure.[1] The following teetiary amide substrates were prepared according to the literatture procedures.[2-19]

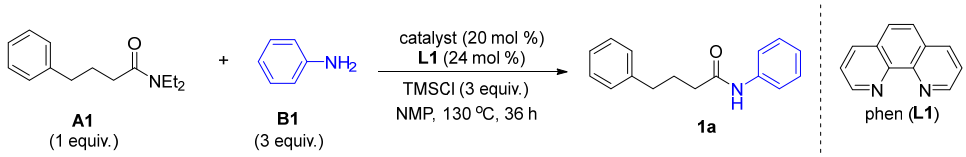


General Manipulation Considerations. All manipulations for transamidation reaction were performed in Teflon screw-capped Schlenk tubes. The eluents used for column chromatography were presented as ratios of solvent volumes. WCl_6 (99% purity) was used for scope study unless otherwise noted. Yields reported in the publication are isolated yields unless otherwise noted. All new starting materials and products were characterized by ^1H and ^{13}C NMR spectroscopies and high-resolution mass spectrometry (HRMS).

Optimization of Reaction Conditions

General procedure for optimizations of reaction conditions. An oven-dried 25 mL Teflon screw-capped Schlenk tube equipped with a stir bar was sequentially charged with tertiary amide **A1**, aniline **B1**, ligand, and catalyst. The tube was evacuated in vacuo and then backfilled with argon for three times. NMP solvent and TMSCl were transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the transamidated product **1a**.

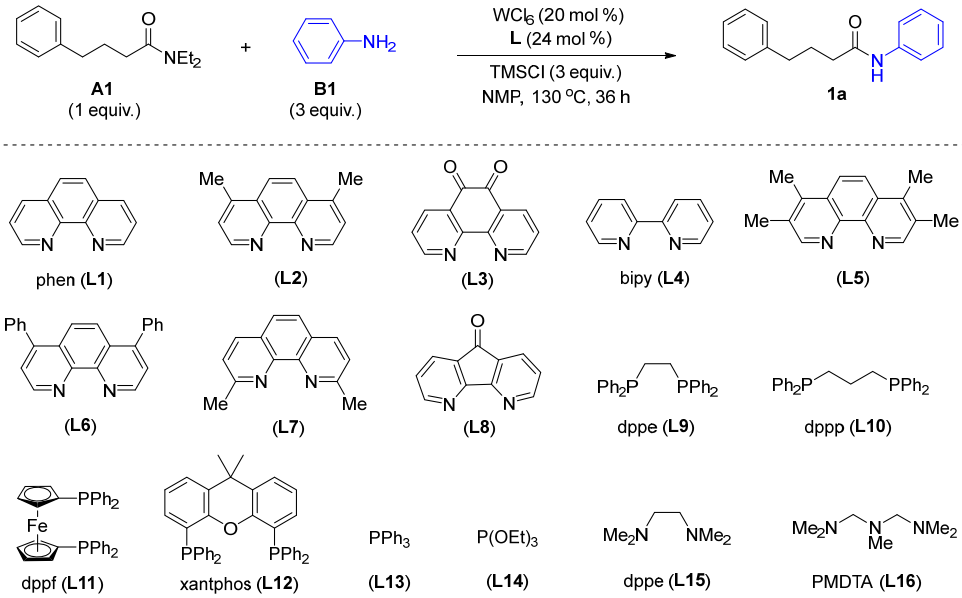
Table S1. Screening of catalyst and control experiments.



Entry	Catalyst	Yield/%
1	**WCl_6**	**68**
2	$AlCl_3$	12
3	$CrCl_2$	0
4	$FeCl_3$	Trace
5	$NiCl_2$	Trace
6	$ZnCl_2$	Trace
7	$ZrCl_2$	10
8	$MoCl_5$	11
9	$PdCl_2$	Trace
10	none	0
11	WCl_6 [a]	Trace
12	WCl_6 [b]	20

Reaction conditions: tertiary amide **A1** (0.2 mmol), aniline **B1** (0.6 mmol), catalyst (0.04 mmol), phen **L1** (0.048 mmol), TMSCl (0.6 mmol), NMP (2 mL), argon atmosphere, 130 °C, 36 h. [a] No phen. [b] No TMSCl.

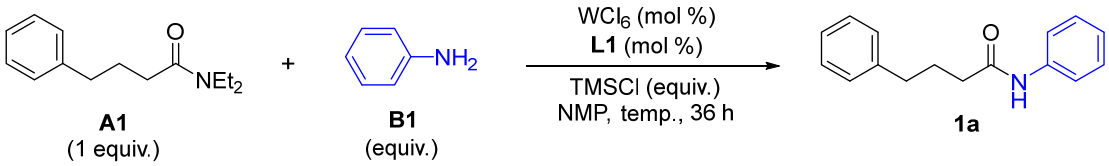
Table S2. Screening of ligands.



Entry	Ligand	Yield/%
1	**L1**	**68**
2	**L2**	59
3	**L3**	51
4	**L4**	48
5	**L5**	43
6	**L6**	40
7	**L7**	52
8	**L8**	42
9	**L9**	38
10	**L10**	33
11	**L11**	23
12	**L12**	24
13	**L13**	50
14	**L14**	18
15	**L15**	trace
16	**L16**	trace

Reaction conditions: tertiary amide **A1** (0.2 mmol), aniline **B1** (0.6 mmol), WCl_6 (0.04 mmol), ligand (0.048 mmol), TMSCl (0.6 mmol), NMP (2 mL), argon atmosphere, 130 °C, 36 h.

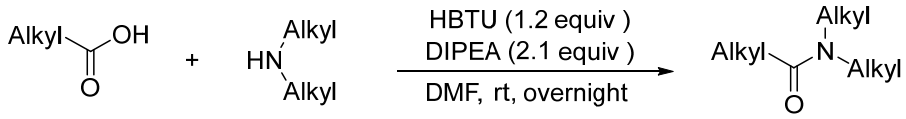
Table S3. Screening of loadings of catalyst, temperature, and additives.



Entry	WCl_6 (mol %)	**L1** (mol %)	Aniline **B1** (equiv.)	TMSCl (equiv.)	Temperature (°C)	Yield/%
1	20	24	3	3	130	68
2	20	24	2	2	130	70
3	20	24	1.5	1.5	130	80
4	20	40	1.5	1.5	130	86
5	20	60	1.5	1.5	130	88
6	20	80	1.5	1.5	130	70
7	10	20	1.5	1.5	130	71
8	15	30	1.5	1.5	130	86
9	**15**	**30**	**1.5**	**1.5**	**140**	**90**
10	15	30	1.5	1.2	140	80
11	15	30	1.5	0.5	140	41
12	15	30	1.5	1.5	120	30
13[a,b]	15	30	1.5	1.5	140	80
14[c]	15	30	1.5	1.5	140	30
15[c]	15	30	1.5	0	140	0

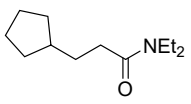
Reaction conditions: tertiary amide **A1** (0.2 mmol), aniline **B1** (0.3-0.6 mmol), WCl_6 (0.02-0.04 mmol), **L1** (0.04-0.16 mmol), TMSCl (0.1-0.6 mmol), NMP (2 mL), argon atmosphere, 130 °C, 36 h. [a] tertiary amide **A1** (0.5 mmol), aniline **B1** (0.75 mmol), WCl_6 (0.075 mmol), **L1** (0.15 mmol), TMSCl (0.75 mmol), NMP (5 mL), argon atmosphere, 140 °C, 36 h. [b] WCl_6 (99.99% purity) was used. [c] KOH (0.50 equiv.) was added.

Synthesis of starting materials[20]



To a 100 mL round bottom flask equipped with a magnetic stirrer bar was charged with the aliphatic carboxylic acid (10 mmol) and DMF solvent (20 mL). The aliphatic carboxylic acid was dissolved into DMF under an argon atmosphere. A solution of *O*-benzotriazol-1-yl-tetramethyluronium hexafluorophosphate (HBTU, 12 mmol) in DMF (10 mL) was added into the solution, followed by a solution of *N*,*N*-diisopropylethylamine (DIPEA, 21 mmol) in DMF (10 mL). The resulting reaction mixture was then stirred at room temperature for 15 min. At this point, dialkylamine (12 mmol) in DMF (10 mL) was added to the reaction mixture, and the resulting mixture was stirred at room temperature under the argon atmosphere for overnight. After the reaction, ethyl acetate (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of HCl (~1 M, ~30 mL; **note:** HCl was not added for pyridine/quinoline-containing amide products), water (3 × ~100 mL), and brine (30 mL). The organic fraction was concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to afford the tertiary amide substrate.

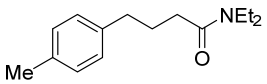
3-cyclopentyl-N,N-diethylpropanamide (A4).



A4

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.4), 1.70 g, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.39 – 3.10 (m, 4H), 2.32 – 2.11 (m, 2H), 1.82 – 1.63 (m, 3H), 1.65 – 1.49 (m, 4H), 1.51 – 1.35 (m, 2H), 1.18 – 0.94 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 42.0, 40.0, 39.9, 32.6, 32.5, 31.8, 25.2, 14.4, 13.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{24}NO^+$ 198.1858; Found 198.1867.

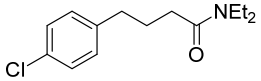
***N*,*N*-diethyl-4-(p-tolyl)butanamide (A7).**



A7

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.4), 1.86 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 1.2 Hz, 4H), 3.54 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H), 2.56 – 2.39 (m, 5H), 2.19 – 2.08 (m, 2H), 1.28 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 138.1, 135.0, 128.9, 128.3, 41.6, 39.9, 34.8, 32.0, 26.9, 20.9, 14.2, 13.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{24}NO^+$ 234.1858; Found 234.1867.

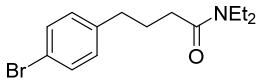
4-(4-chlorophenyl)-*N,N*-diethylbutanamide (A9).



A9

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.4), 2.08 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 2H), 7.03 (dd, *J* = 8.3, 1.5 Hz, 2H), 3.27 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.13 (qd, *J* = 7.2, 1.4 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.19 (td, *J* = 7.3, 1.3 Hz, 2H), 1.86 (pd, *J* = 7.4, 1.3 Hz, 2H), 1.01 (tdd, *J* = 7.2, 3.1, 1.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 140.3, 131.3, 129.7, 128.2, 41.7, 39.9, 34.4, 31.8, 26.5, 14.1, 12.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}NOCl^+$ 254.1312; Found 254.1322.

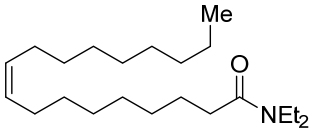
4-(4-bromophenyl)-*N,N*-diethylbutanamide (A10).



A10

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.4), 2.41 g, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.01 (dd, *J* = 8.3, 1.5 Hz, 2H), 3.25 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.12 (qd, *J* = 7.2, 1.3 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.18 (td, *J* = 7.4, 1.3 Hz, 2H), 1.84 (td, *J* = 7.5, 1.4 Hz, 2H), 0.99 (tdd, *J* = 7.2, 3.1, 1.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 140.3, 131.3, 129.7, 128.2, 41.7, 39.9, 34.4, 31.8, 26.5, 14.1, 12.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}NOBr^+$ 298.0807; Found 298.0805.

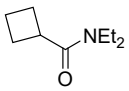
(Z)-N,N-diethyloleamide (A11).



A11

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 2.53 g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 5.27 (h, *J* = 2.5 Hz, 2H), 3.31 (qd, *J* = 7.1, 2.2 Hz, 2H), 3.24 (qd, *J* = 7.1, 2.1 Hz, 2H), 2.23 (ddd, *J* = 10.0, 7.5, 3.5 Hz, 2H), 1.95 (q, *J* = 6.7, 6.0 Hz, 3H), 1.58 (p, *J* = 6.8 Hz, 2H), 1.26 (dt, *J* = 13.4, 7.4 Hz, 11H), 1.20 (d, *J* = 8.3 Hz, 10H),1.11 (td, *J* = 7.1, 2.3 Hz, 3H), 1.04 (td, *J* = 7.1, 2.3 Hz, 3H), 0.82 (td, *J* = 6.9, 2.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 129.9, 129.8, 42.0, 40.1, 33.2, 31.9, 29.82, 29.80, 29.51, 29.52, 29.4, 29.3, 29.2, 27.23, 27.24, 25.5, 22.7, 14.4, 14.1, 13.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{42}NO^+$ 324.3266; Found 324.3270.

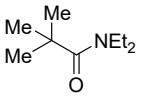
N,N-diethylcyclobutanecarboxamide (A15).



A15

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 1.13 g, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 – 3.23 (m, 2H), 3.23 – 3.07 (m, 3H), 2.38 – 2.14 (m, 2H), 2.14 – 1.98 (m, 2H), 1.97 – 1.69 (m, 2H), 1.19 – 0.91 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 41.2, 39.8, 37.3, 25.3, 18.0, 14.5, 13.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{18}NO^+$ 156.1388; Found 156.1394.

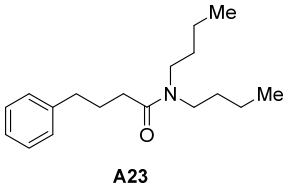
N,N-diethylpivalamide (A17).



A17

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 1.10 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (d, *J* = 7.3 Hz, 4H), 1.22 (q, *J* = 0.8 Hz, 9H), 1.10 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 41.7, 39.0, 28.6, 27.2, 13.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{20}NO^+$ 158.1545; Found 158.1549.

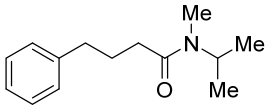
N,N-dibutyl-4-phenylbutanamide (A23).



A23

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 1.04 g, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.16 (dt, *J* = 8.1, 2.0 Hz, 3H), 3.37 – 3.14 (m, 2H), 3.17 – 2.94 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.36 – 2.13 (m, 2H), 2.09 – 1.82 (m, 2H), 1.59 – 1.35 (m, 4H), 1.36 – 1.10 (m, 4H), 0.88 (dt, *J* = 10.3, 7.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 141.8, 128.5, 128.2, 125.8, 47.6, 45.6, 35.3, 32.1, 31.2, 29.9, 26.9, 20.2, 20.0, 13.9, 13.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{30}NO^+$ 276.2327; Found 276.2336.

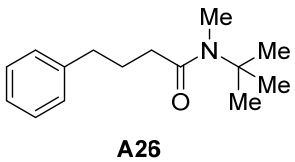
N-isopropyl-N-methyl-4-phenylbutanamide (A25).



A25

Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 1.93 g, 88% yield. The compound exists in two rotamers such that the NMR spectra became complex. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 2H), 7.14 – 7.03 (m, 3H), 4.82 (p, *J* = 6.8 Hz, 0.5H), 3.87 (p, *J* = 6.6 Hz, 0.4H), 2.68 (s, 1H), 2.62 (s, 2H), 2.61 – 2.55 (m, 2H), 2.26 (t, *J* = 7.5 Hz, 1H), 2.19 (t, *J* = 7.5 Hz, 1H), 1.90 (td, *J* = 7.6, 2.6 Hz, 2H), 1.08 – 0.90 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 171.4, 141.5, 141.4, 128.0, 127.9, 125.42, 125.43, 47.1, 43.1, 34.91, 34.92, 32.7, 32.0, 27.6, 26.5, 26.2, 25.2, 19.9, 19.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}NO^+$ 220.1701; Found 220.1708.

N-(tert-butyl)-N-methyl-4-phenylbutanamide (A26).



A26

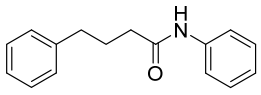
Obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 1.80 g, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (tt, *J* = 7.7, 1.7 Hz, 2H), 7.21 – 7.08 (m, 3H), 2.86 – 2.74 (m, 3H), 2.64 (td, *J* = 7.7, 2.0 Hz, 2H), 2.27 (tt, *J* = 7.8, 1.7 Hz, 2H), 1.93 (tt, *J* = 7.9, 1.4 Hz, 2H), 1.38 (d, *J* = 2.8 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 142.0, 128.5, 128.3, 125.9, 56.6,

35.8, 35.3, 31.9, 28.4, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{24}NO^+$ 234.1858; Found 234.1864.

W-catalyzed transamidation of tertiary alkyl amides

General Procedure: An oven-dried 25 mL Teflon screw-capped Schlenk tube equipped with a stir bar was sequentially charged with tertiary alkyl amide (0.5 mmol, 1 equiv.), amine (0.75 mmol, 1.5 equiv.), phen **L1** (0.15 mmol, 0.3 equiv.), and WCl_6 (0.075 mmol, 0.15 equiv.). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP solvent (5 mL) and TMSCl (0.75 mmol, 1.5 equiv.) were transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere in a preheated heat block at 140 °C for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (~0.1 M, 2 x 30 mL; **note:** water was used for washing instead of HCl (aq) for pyridine/quinoline-containing amide products) and saturated brine (~30 mL), dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the transamidated product.

N,4-diphenylbutanamide (1a).



1a

(i) Based on tertiary amide A1: Using the General Procedure, the title compound was obtained as a white solid after column chromatography based on 0.2 mmol of **A1** (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 43.1 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.30 (q, *J* = 7.1, 6.6 Hz, 4H), 7.20 (d, *J* = 7.5 Hz,

4H), 7.10 (t, J = 7.4 Hz, 1H), 2.72 (t, J = 7.4 Hz, 2H), 2.34 (t, J = 7.5 Hz, 2H), 2.08 (p, J = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 141.5, 138.0, 129.1, 128.7, 128.6, 126.2, 124.4, 119.9, 36.9, 35.2, 27.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1388; Found 240.1392.

(ii) Based on tertiary amide A2: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 133.7 mg, 95% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(iii) Based on tertiary amide A22: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 100.5 mg, 84% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(iv) Based on tertiary amide A23: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 95.7 mg, 80% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(v) Based on tertiary amide A24: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 89.7 mg, 75% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(vi) Based on tertiary amide A25: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 101.7 mg, 85% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(vii) Based on tertiary amide A26: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 63.4 mg, 53% yield. The spectra data were in agreement with that of the identical compound derived from (i).

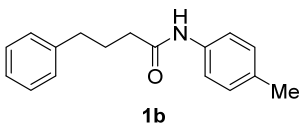
(viii) Based on tertiary amide A27: Using the General Procedure, the title compound

was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 99.3 mg, 83% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(ix) Based on tertiary amide A28: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 98.1 mg, 82% yield. The spectra data were in agreement with that of the identical compound derived from (i).

(x) Based on tertiary amide A29: Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 90.9 mg, 76% yield. The spectra data were in agreement with that of the identical compound derived from (i).

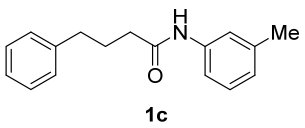
4-phenyl-N-(p-tolyl)butanamide (1b).



1b

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 103.3 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.35 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.69 (td, *J* = 7.6, 2.7 Hz, 2H), 2.42 – 2.28 (m, 5H), 2.05 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 141.5, 135.5, 133.9, 129.5, 128.6, 128.5, 126.1, 120.1, 36.8, 35.2, 27.0, 21.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; Found 254.1546.

4-phenyl-N-(m-tolyl)butanamide (1c).

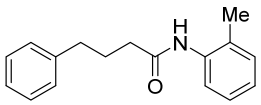


1c

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 96.2 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 7.24 – 7.14 (m, 4H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.43 – 2.25 (m, 5H), 2.06 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 141.5, 139.0 138.0,

128.9, 128.6, 128.5, 126.1, 125.1, 120.7, 117.1, 36.8, 35.2, 27.0, 21.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; Found 254.1545.

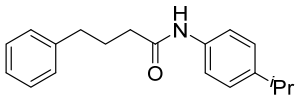
4-phenyl-N-(o-tolyl)butanamide (1d).



1d

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 107.6 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 3H), 7.19 – 7.12 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 2.06 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 141.5, 135.7, 130.5, 129.7, 128.6, 128.5, 126.7, 126.1, 125.4, 123.7, 36.6, 35.2, 27.2, 17.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; Found 254.1551.

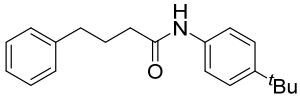
N-(4-isopropylphenyl)-4-phenylbutanamide (1e).



1e

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 121.2 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 (s, 1H), 7.30 (dd, *J* = 8.4, 6.2 Hz, 2H), 7.24 – 7.12 (m, 5H), 2.88 (p, *J* = 6.9 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.07 (q, *J* = 7.6 Hz, 2H), 1.23 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 145.1, 141.5, 135.7, 128.6, 128.5, 127.0, 126.1, 120.2, 36.8, 35.2 33.7, 27.1, 24.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{24}NO^+$ 282.1858; Found 282.1858.

N-(4-(tert-butyl)phenyl)-4-phenylbutanamide (1f).

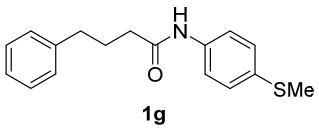


1f

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 110.8 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.6, 2.6 Hz, 2H), 7.38 – 7.24 (m,

5H), 7.19 (d, *J* = 7.7 Hz, 3H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.18 – 1.89 (m, 2H), 1.43 – 1.17 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 147.3, 141.5, 135.4, 128.6, 128.5, 126.1, 125.9, 119.8, 36.8, 35.2, 34.5, 31.5, 27.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}NO^+$ 296.2014; Found 296.2014.

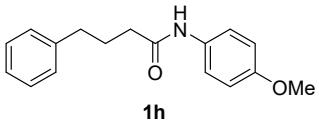
N-(4-(methylthio)phenyl)-4-phenylbutanamide (1g).



1g

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 115.6 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.11 (m, 5H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.06 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 141.4, 135.7, 133.6, 128.6, 128.5, 128.1, 126.1, 120.7, 36.8, 35.2, 27.0, 16.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NOS^+$ 286.1266; Found 286.1268.

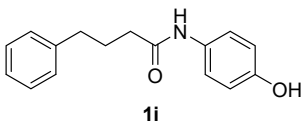
N-(4-methoxyphenyl)-4-phenylbutanamide (1h).



1h

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 87.5 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.32 (m, 3H), 7.34 – 7.24 (m, 2H), 7.20 (td, *J* = 7.5, 1.7 Hz, 3H), 6.92 – 6.68 (m, 2H), 3.77 (s, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.17 – 1.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 156.4, 141.5, 131.2, 128.6, 128.5, 126.1, 122.0, 114.2, 55.5, 36.6, 35.2, 27.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO_2^+$ 270.1494; Found 270.1496.

N-(4-hydroxyphenyl)-4-phenylbutanamide (1i).

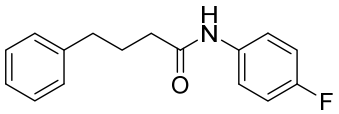


1i

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 96.9 mg, 76%

yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.61 (s, 1H), 9.15 (s, 1H), 7.42 – 7.32 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.08 (m, 3H), 6.76 – 6.57 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.87 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 170.3, 153.2, 141.8, 131.0, 128.4, 128.3, 125.8, 121.0, 115.0, 35.7, 34.7, 27.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1338; Found 256.1337.

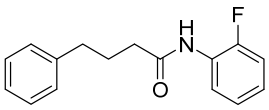
N-(4-fluorophenyl)-4-phenylbutanamide (1j).



1j

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 123.5 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.76 (s, 1H), 7.43 (ddd, *J* = 9.0, 4.8, 1.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.09 (m, 3H), 6.96 (t, *J* = 8.6 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.03 (p, *J* = 7.5 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.85. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 159.9 (d, *J* = 243.4 Hz), 141.8, 134.5, 129.0, 126.6, 122.5 (d, *J* = 8.9 Hz), 116.1 (d, *J* = 22.5 Hz), 37.1, 35.6, 27.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOF^+$ 258.1294; Found 258.1295.

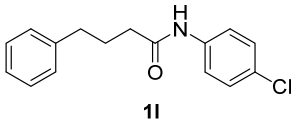
N-(2-fluorophenyl)-4-phenylbutanamide (1k).



1k

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 114.5 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (td, *J* = 8.1, 1.6 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.24 – 7.17 (m, 3H), 7.15 – 7.10 (m, 1H), 7.10 – 7.01 (m, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.09 (p, *J* = 7.5 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.30. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 152.4 (d, *J* = 242.7 Hz), 141.4, 128.64, 128.60, 126.5 (d, *J* = 10.0 Hz), 126.2, 124.7 (d, *J* = 3.7 Hz), 124.3 (d, *J* = 7.8 Hz), 121.9, 114.9 (d, *J* = 19.3 Hz), 36.9, 35.1, 26.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOF^+$ 258.1294; Found 258.1296.

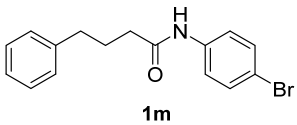
N-(4-chlorophenyl)-4-phenylbutanamide (1l).



1l

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 130.0 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.38 (s, 1H), 7.31 – 7.22 (m, 4H), 7.22 – 7.12 (m, 3H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.15 – 1.87 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 141.3, 136.6, 129.3, 129.1, 128.6, 126.2, 121.2, 36.8, 35.1, 26.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOCl^+$ 274.0999; Found 274.0995.

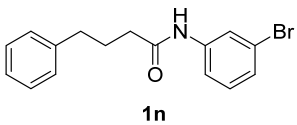
N-(4-bromophenyl)-4-phenylbutanamide (1m).



1m

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 135.2 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 4H), 7.37 – 7.26 (m, 3H), 7.27 – 7.11 (m, 3H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.07 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 141.3, 137.1, 132.1, 128.63, 128.60, 126.2, 121.5, 116.9, 36.8, 35.2, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOBr^+$ 318.0494; Found 318.0497.

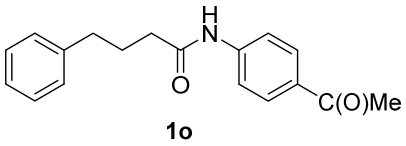
N-(3-bromophenyl)-4-phenylbutanamide (1n).



1n

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 128.9 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.52 – 7.34 (m, 2H), 7.33 – 7.25 (m, 2H), 7.24 – 7.10 (m, 5H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.05 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 141.3, 139.3, 130.4, 128.62, 128.59, 127.3, 126.2, 122.9, 122.7, 118.4, 36.8, 35.1, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOBr^+$ 318.0494; Found 318.0498.

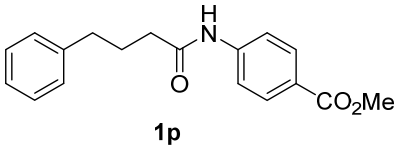
N-(4-acetylphenyl)-4-phenylbutanamide (1o).



1o

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 101.3 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.83 (m, 3H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.08 (m, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.09 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.3, 171.7, 142.7, 141.4, 132.8, 129.8, 128.6, 126.2, 119.0, 36.9, 35.1, 26.7, 26.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_2^+$ 282.1494; Found 282.1496.

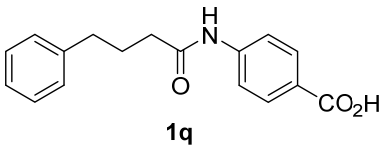
methyl 4-(4-phenylbutanamido)benzoate (1p).



1p

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 116.0 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.88 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.40 (s, 1H), 7.35 – 7.27 (m, 2H), 7.22 (td, *J* = 7.2, 6.7, 1.4 Hz, 3H), 3.91 (s, 3H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.27 – 1.98 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 166.7, 142.2, 141.3, 131.0, 128.64, 128.63, 126.3, 125.7, 118.9, 52.1, 36.9, 35.1, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_3^+$ 298.1443; Found 298.1440.

4-(4-phenylbutanamido)benzoic acid (1q).

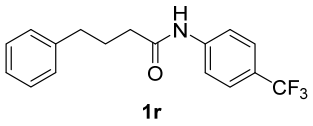


1q

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.1), 136.0 mg, 96% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.19 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.06 (m, 5H), 2.62 (t, *J* = 7.6 Hz,

2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.90 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 171.5, 166.9, 143.3, 141.6, 130.3, 128.32, 128.29, 125.8, 124.8, 118.3, 35.8, 34.6, 26.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_3^+$ 284.1287; Found 284.1296.

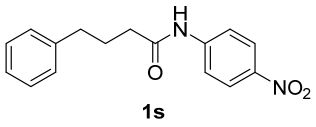
4-phenyl-N-(4-(trifluoromethyl)phenyl)butanamide (1r).



1r

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 122.9 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 6.7 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.25 – 7.11 (m, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.37 (dd, *J* = 8.0, 7.0 Hz, 2H), 2.16 – 1.98 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.2. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 141.2, 141.0, 128.6, 126.4 (q, *J* = 3.8 Hz), 126.3, 126.0, 124.2 (d, *J* = 271.4 Hz), 119.4, 36.8, 35.1, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}NOF_3^+$ 308.1262; Found 308.1257.

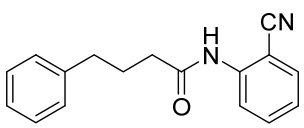
N-(4-nitrophenyl)-4-phenylbutanamide (1s).



1s

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 64.0 mg, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.09 (m, 2H), 7.97 (s, 1H), 7.79 – 7.61 (m, 2H), 7.26 (dd, *J* = 8.6, 6.7 Hz, 2H), 7.22 – 7.03 (m, 3H), 2.69 (td, *J* = 7.5, 1.8 Hz, 2H), 2.40 (td, *J* = 7.5, 1.9 Hz, 2H), 2.06 (pd, *J* = 7.6, 1.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 144.1, 143.3, 141.1, 128.58, 128.55, 126.3, 125.2, 119.1, 36.8, 35.0, 26.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2O_3^+$ 285.1239; Found 285.1246.

N-(2-cyanophenyl)-4-phenylbutanamide (1t).

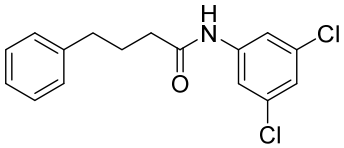


1t

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 85.9 mg, 65%

yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.65 (s, 1H), 7.61 – 7.53 (m, 2H), 7.35 – 7.27 (m, 2H), 7.21 (dt, *J* = 8.3, 2.3 Hz, 3H), 7.17 (qd, *J* = 7.5, 1.2 Hz, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.21 – 1.91 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 141.2, 140.6, 134.3, 132.4, 128.6, 126.2, 124.2, 121.5, 116.6, 101.9, 36.9, 35.1, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O^+$ 265.1341; Found 265.1349.

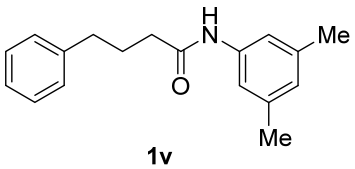
N-(3,5-dichlorophenyl)-4-phenylbutanamide (1u).



1u

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 124.7 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (d, *J* = 1.7 Hz, 2H), 7.33 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 7.06 (q, *J* = 1.6 Hz, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.02 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 141.2, 139.7, 135.2, 128.59, 128.56, 126.2, 124.3, 118.3, 36.7, 35.1, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NOCl_2^+$ 308.0609; Found 308.0610.

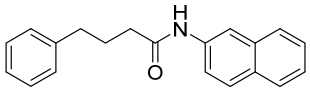
N-(3,5-dimethylphenyl)-4-phenylbutanamide (1v).



1v

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 96.2 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.4, 6.5 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.14 (s, 2H), 7.10 (s, 1H), 6.75 (s, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.29 (s, 6H), 2.06 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 141.5, 138.8, 137.8, 128.7, 128.6, 126.2, 126.1, 117.7, 36.9, 35.2, 27.0 21.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}NO^+$ 268.1701; Found 268.1698.

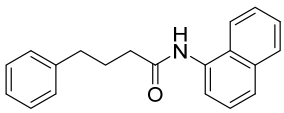
N-(naphthalen-2-yl)-4-phenylbutanamide (1w).



1w

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 131.6 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.2 Hz, 1H), 7.76 (dd, *J* = 8.1, 6.1 Hz, 3H), 7.58 (s, 1H), 7.51 – 7.34 (m, 3H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.14 (m, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.10 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 141.4, 135.5, 133.9, 130.7, 128.8, 128.62, 128.56, 127.7, 127.6, 126.6, 126.2, 125.1, 120.0, 116.8, 36.9, 35.2, 27.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO^+$ 290.1545; Found 290.1537.

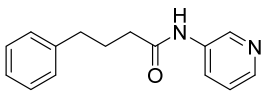
N-(naphthalen-1-yl)-4-phenylbutanamide (1x).



1x

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 112.8 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.74 (m, 3H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.54 – 7.41 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 3H), 2.86 – 2.62 (m, 2H), 2.62 – 2.32 (m, 2H), 2.28 – 1.93 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 141.5, 134.2, 132.4, 128.8, 128.7, 128.6, 127.5, 126.3, 126.2, 126.1, 126.0, 125.8, 121.5, 121.0, 36.6, 35.3, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO^+$ 290.1545; Found 290.1543.

4-phenyl-N-(pyridin-3-yl)butanamide (1y).

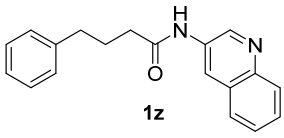


1y

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), 55.0 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.6 Hz, 1H), 8.32 (d, *J* = 4.8 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.38 – 7.26 (m, 3H), 7.25 – 7.10 (m, 3H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.10 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

171.8, 145.0, 141.3, 140.9, 135.2, 128.7, 128.6, 127.5, 126.3, 124.0, 36.7, 35.2, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O^+$ 241.1341; Found 241.1343.

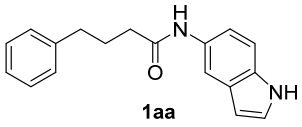
4-phenyl-N-(quinolin-3-yl)butanamide (1z).



1z

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3), 107.4 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 – 9.24 (m, 1H), 8.80 (d, *J* = 2.9 Hz, 1H), 8.70 (d, *J* = 2.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.16 – 6.98 (m, 3H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.19 – 1.88 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 144.6, 144.0, 141.2, 132.2, 128.40, 128.38, 128.31, 128.28, 127.8, 127.3, 126.0, 124.3, 36.5, 35.1, 26.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O^+$ 291.1497; Found 291.1497.

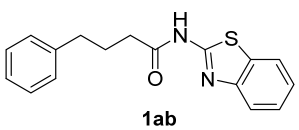
N-(1H-indol-5-yl)-4-phenylbutanamide (1aa).



1aa

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.3), 60.1 mg, 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.26 (m, 3H), 7.28 – 7.07 (m, 6H), 6.51 (s, 1H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.12 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 141.7, 133.4, 130.5, 128.7, 128.6, 128.2, 126.1, 125.3, 116.6, 112.9, 111.3, 102.9, 36.9, 35.3, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O^+$ 279.1497; Found 279.1506.

N-(benzo[d]thiazol-2-yl)-4-phenylbutanamide (1ab).

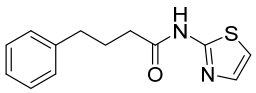


1ab

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3), 109.7 mg, 74% yield. ^{1}H

NMR (400 MHz, $CDCl_3$) δ11.58 – 10.82 (m, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.42 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.21 – 7.13 (m, 1H), 7.13 – 7.03 (m, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.07 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 159.7, 147.9, 140.9, 132.1, 128.6, 128.5, 126.5, 126.3, 124.2, 121.9, 120.5, 35.6, 34.9, 26.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2OS^+$ 297.1062; Found 297.1069.

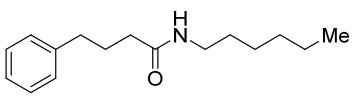
4-phenyl-N-(thiazol-2-yl)butanamide (1ac).



1ac

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3), 67.6 mg, 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.31 (dd, *J* = 8.5, 6.5 Hz, 2H), 7.26 – 7.16 (m, 3H), 7.07 (d, *J* = 3.6 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.29 – 1.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 160.3, 141.2, 136.1, 128.7, 128.6, 126.3, 113.4, 35.3, 35.2, 26.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2OS^+$ 247.0905; Found 247.0914.

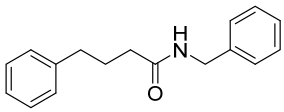
N-hexyl-4-phenylbutanamide (1ad).



1ad

Using the General Procedure, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 96.9 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.25 – 7.09 (m, 3H), 5.52 (s, 1H), 3.24 (td, *J* = 7.3, 5.8 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.99 (h, *J* = 7.5, 6.9 Hz, 2H), 1.48 (q, *J* = 7.1 Hz, 2H), 1.38 – 1.18 (m, 6H), 1.00 – 0.73 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 141.7, 128.6, 128.5, 126.1, 39.7, 36.1, 35.3, 31.6, 29.8, 27.3, 26.7, 22.7, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{26}NO^+$ 248.2014; Found 248.2017.

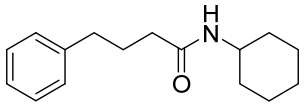
N-benzyl-4-phenylbutanamide (1ae).



1ae

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 95.0 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 7H), 7.22 – 7.10 (m, 3H), 5.87 (s, 1H), 4.40 (d, *J* = 5.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.09 – 1.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 141.6, 138.5, 128.8, 128.6, 128.5, 127.9, 127.6, 126.1, 43.6, 35.9, 35.3, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; Found 254.1548.

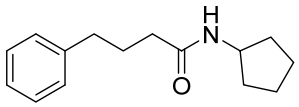
N-cyclohexyl-4-phenylbutanamide (1af).



1af

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 98.1 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 3H), 7.29 – 7.17 (m, 3H), 3.83 (dq, *J* = 10.7, 3.3 Hz, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 7.4 Hz, 2H), 2.11 – 1.88 (m, 4H), 1.88 – 1.60 (m, 4H), 1.53 – 1.31 (m, 2H), 1.25 – 1.11 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 141.7, 128.7, 128.5, 126.1, 48.2, 36.3, 35.3, 33.4, 27.4, 25.7, 25.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}NO^+$ 246.1858; Found 246.1859.

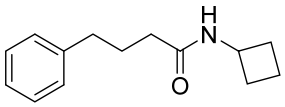
N-cyclopentyl-4-phenylbutanamide (1ag).



1ag

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 81.0 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 2H), 7.24 – 7.06 (m, 3H), 5.52 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.15 (t, *J* = 7.5 Hz, 2H), 2.06 – 1.90 (m, 4H), 1.80 – 1.49 (m, 4H), 1.37 (dt, *J* = 12.9, 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 141.7, 128.6, 128.5, 126.0, 51.2, 36.1, 35.3, 33.2, 27.3, 23.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}NO^+$ 232.1701; Found 232.1696.

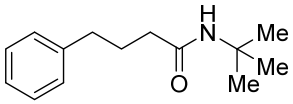
N-cyclobutyl-4-phenylbutanamide (1ah).



1ah

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 76.1 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.21 – 7.10 (m, 3H), 5.52 (s, 1H), 4.50 – 4.24 (m, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.39 – 2.25 (m, 2H), 2.11 (dd, *J* = 8.3, 6.8 Hz, 2H), 1.95 (tt, *J* = 8.5, 6.8 Hz, 2H), 1.86 – 1.73 (m, 2H), 1.72 – 1.62 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.9, 141.6, 128.6, 128.5, 126.1, 44.7, 35.9, 35.3, 31.4, 27.2, 15.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}NO^+$ 218.1545; Found 218.1554.

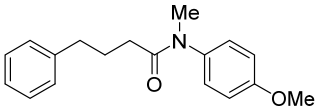
N-(tert-butyl)-4-phenylbutanamide (1ai).



1ai

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 43.9 mg, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 7.17 (dd, *J* = 8.6, 7.0 Hz, 3H), 5.27 (s, 1H), 2.68 – 2.59 (m, 2H), 2.08 (t, *J* = 7.5 Hz, 2H), 2.18 – 1.89 (m, 2H), 1.32 (d, *J* = 0.9 Hz, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.3, 141.7, 128.6, 128.5, 126.0, 51.2, 36.9, 35.2, 28.9, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}NO_3^+$ 220.1701; Found 220.1709.

N-(4-methoxyphenyl)-N-methyl-4-phenylbutanamide (1aj).

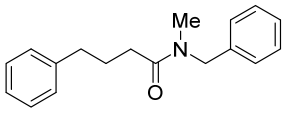


1aj

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol % of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 110.5 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.11 – 7.07 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.22 (s, 3H), 2.65 – 2.35 (m, 2H), 2.08 (t, *J* = 7.5 Hz, 2H), 1.94 – 1.79 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.3, 158.8, 141.9, 137.0, 128.5, 128.4, 128.3, 125.8, 114.9, 55.5, 37.5 35.3, 33.5, 27.1. **HRMS** (ESI) m/z:

$[M+H]^+$ Calcd for $C_{18}H_{22}NO_2^+$ 284.1651; Found 284.1657.

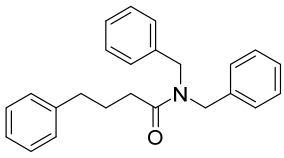
N-benzyl-N-methyl-4-phenylbutanamide (1ak).



1ak

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol % of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 94.9 mg, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.15 (m, 9H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.68 – 4.36 (m, 2H), 3.07 – 2.79 (m, 3H), 2.78 – 2.61 (m, 2H), 2.38 (td, *J* = 7.5, 2.6 Hz, 2H), 2.19 – 1.94 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.2, 172.8, 141.8, 141.7, 137.5, 136.7, 128.9, 128.6, 128.51, 128.46, 128.4, 128.3, 128.0, 127.5, 127.3, 126.3, 125.9, 125.8, 53.3, 50.7, 35.30, 35.25, 34.7, 33.9, 32.6, 32.2, 26.8, 26.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}NO^+$ 268.1701; Found 268.1708.

N,N-dibenzyl-4-phenylbutanamide (1al).

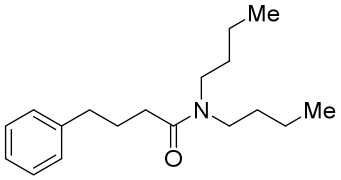


1al

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol % of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 127.1 mg, 74% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 5H), 7.33 – 7.25 (m, 5H), 7.21 (dd, *J* = 7.9, 5.1 Hz, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 4.67 (s, 2H), 4.41 (s, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.27 – 2.01 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.2, 141.7, 137.5, 136.6, 128.9, 128.6, 128.5, 128.4, 128.3, 127.6, 127.4, 126.4, 125.9, 49.9, 48.2, 35.2, 32.4, 26.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}NO^+$ 344.2014; Found 344.2017.

N,N-dibutyl-4-phenylbutanamide (1am).

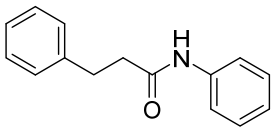
Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol % of **L1**,



1am

the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 52.0 mg, 38% yield. The spectra data are in agreements with that of the identical compound **A23**.

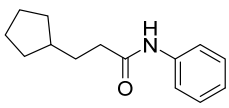
N,3-diphenylpropanamide (1an).



1an

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 99.1 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.5, 3.0 Hz, 3H), 7.28 (td, *J* = 7.1, 4.0 Hz, 4H), 7.22 (t, *J* = 7.1 Hz, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.19 – 2.88 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 140.7, 137.9, 129.0, 128.7, 128.5, 126.5, 124.4, 120.2, 39.4, 31.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}NO^+$ 226.1232; Found 226.1227.

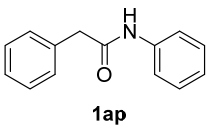
3-cyclopentyl-N-phenylpropanamide (1ao).



1ao

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 90.2 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.48 – 2.28 (m, 2H), 1.92 – 1.70 (m, 6H), 1.69 – 1.45 (m, 4H), 1.26 – 0.98 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 138.2, 129.0, 124.2, 120.1, 39.8, 37.2, 32.6, 32.0, 25.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}NO^+$ 218.1545; Found 218.1545.

N,2-diphenylacetamide (1ap).

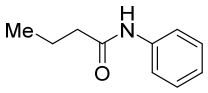


1ap

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 94.0 mg, 89% yield. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.46 – 7.22 (m, 10H), 7.14 – 7.02 (m, 1H), 3.71 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 137.8, 134.6, 129.6, 129.3, 129.0, 127.7, 124.6, 120.0, 44.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO^+$ 212.1075; Found 212.1073.

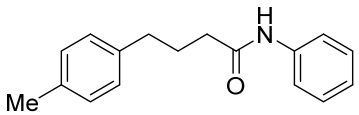
N-phenylbutyramide (1aq).



1aq

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 63.6 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.57 – 7.43 (m, 2H), 7.35 – 7.21 (m, 2H), 7.19 – 6.95 (m, 1H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.75 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 138.2, 129.0, 124.3, 120.1, 39.7, 19.2, 13.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{14}NO^+$ 164.1075; Found 164.1076.

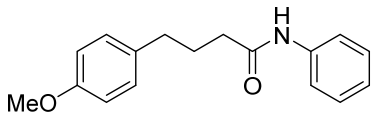
N-phenyl-4-(p-tolyl)butanamide (1ar).



1ar

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 95.0 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.40 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 3.8 Hz, 5H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.33 (d, *J* = 5.5 Hz, 5H), 2.05 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 138.3, 138.1, 135.6, 129.2, 129.1, 128.5, 124.3, 120.0, 36.9, 34.7, 27.1, 21.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; Found 254.1544.

4-(4-methoxyphenyl)-N-phenylbutanamide (1as).

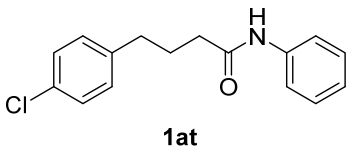


1as

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 94.3 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 3H), 7.17 – 7.00 (m, 3H), 6.96 – 6.71 (m, 2H), 3.78 (s,

3H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.03 (q, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 158.1, 138.1, 133.5, 129.5, 129.1, 124.3, 120.0, 114.0, 55.4, 36.9, 34.3, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO_2^+$ 270.1494; Found 270.1497.

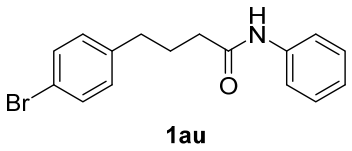
4-(4-chlorophenyl)-N-phenylbutanamide (1at).



1at

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 117.7 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.29 – 7.20 (m, 2H), 7.12 (dd, *J* = 7.8, 5.2 Hz, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.05 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 139.9, 138.0, 131.9, 130.0, 129.1, 128.7, 124.4, 120.0, 36.7, 34.5, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOCl^+$ 274.0999; Found 274.0999.

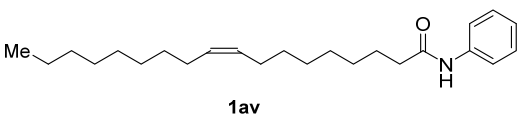
4-(4-bromophenyl)-N-phenylbutanamide (1au).



1au

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 132.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 3H), 7.30 (td, *J* = 7.9, 3.0 Hz, 2H), 7.39 (dd, J = 8.2, 4.0 Hz, 2H), 7.15 – 6.95 (m, 3H), 2.75 – 2.50 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.01 (q, *J* = 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 140.4, 138.0, 131.6, 130.3, 129.1, 124.4, 120.1, 119.9, 36.6, 34.5, 26.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NOBr^+$ 318.0494; Found 318.0500.

(Z)-1-phenyloctadec-9-en-1-one (1av).

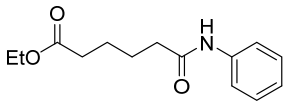


1av

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum

ether/ethyl acetate = 3:1, R_f = 0.5), 125.1 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.39 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.46 – 5.24 (m, 2H), 2.33 (t, *J* = 7.6 Hz, 2H), 2.00 (q, *J* = 6.6 Hz, 2H), 1.71 (q, *J* = 7.5 Hz, 2H), 1.45 – 1.15 (m, 22H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.7, 138.1, 130.1, 129.8, 129.1, 124.3, 120.0, 37.9, 32.0, 29.9, 29.82, 29.77, 29.6, 29.44, 29.42, 29.37, 29.3, 27.33, 27.28, 25.8, 22.8, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{40}NO^+$ 358.3110; Found 358.3114.

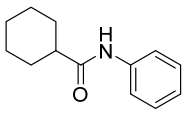
ethyl 6-oxo-6-(phenylamino)hexanoate (1aw).



1aw

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 72.3 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.32 (dt, *J* = 19.8, 7.0 Hz, 4H), 1.82 – 1.54 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.8, 171.4, 138.2, 128.9, 124.2 120.1, 60.5, 37.1, 34.0, 25.0, 24.4, 14.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}NO_3^+$ 250.1443; Found 250.1449.

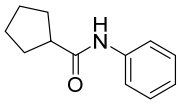
N-phenylcyclohexanecarboxamide (1ax).



1ax

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 88.4 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.3, 2.9 Hz, 3H), 7.38 – 7.22 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 2.33 – 2.13 (m, 1H), 2.04 – 1.87 (m, 2H), 1.86 – 1.73 (m, 2H), 1.69 (s, 1H), 1.62 – 1.45 (m, 2H), 1.38 – 1.11 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 138.3, 129.0, 124.1, 120.0, 46.6, 29.8, 25.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}NO^+$ 204.1388; Found 204.1386.

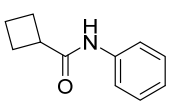
N-phenylcyclopentanecarboxamide (1ay).



1ay

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 83.3 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 3H), 7.39 – 7.19 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 2.67 (p, *J* = 8.1 Hz, 1H), 1.88 (qt, *J* = 7.1, 4.8 Hz, 4H), 1.82 – 1.68 (m, 2H), 1.68 – 1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 138.4, 129.0, 124.1, 119.9, 46.9, 30.7, 26.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}NO^+$ 190.1232; Found 190.1230.

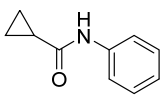
N-phenylcyclobutanecarboxamide (1az).



1az

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 83.2 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.39 (m, 3H), 7.35 – 7.17 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 3.16 (p, *J* = 8.5 Hz, 1H), 2.52 – 2.28 (m, 2H), 2.27 – 2.08 (m, 2H), 2.05 – 1.80 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 138.2, 129.0, 124.1, 119.9, 40.9, 25.4, 18.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO^+$ 176.1075; Found 176.1079.

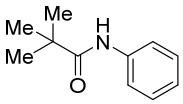
N-phenylcyclopropanecarboxamide (1ba).



1ba

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 56.4 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 1.52 (tt, *J* = 8.2, 4.5 Hz, 1H), 1.07 (p, *J* = 4.2 Hz, 2H), 0.81 (dq, *J* = 7.1, 3.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 138.3, 129.0, 124.1, 120.0, 15.8, 8.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO^+$ 162.0919; Found 162.0925.

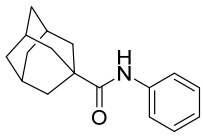
N-phenylpivalamide (1bb).



1bb

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 69.1 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.40 (s, 1H), 7.35 – 7.27 (m, 2H), 7.14 – 7.03 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 138.2, 129.0, 124.3, 120.1, 39.7, 27.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}NO^+$ 178.1232; Found 178.1237.

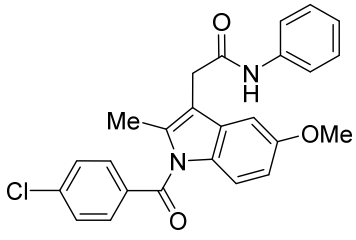
N-phenyladamantane-1-carboxamide (1bc).



1bc

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 120.0 mg, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.10 (s, 3H), 1.97 (d, *J* = 3.0 Hz, 6H), 1.90 – 1.65 (m, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 138.2, 129.0, 124.2, 120.1, 41.6, 39.4, 36.6, 28.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}NO^+$ 256.1701; Found 256.1699.

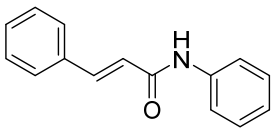
2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-phenylacetamide (1bd).



1bd

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 129.9 mg, 60% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 – 7.68 (m, 1H), 7.64 – 7.56 (m, 2H), 7.49 – 7.36 (m, 4H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 9.3 Hz, 1H), 3.98 – 3.52 (m, 5H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.5, 168.4, 156.4, 139.6, 137.5, 136.6, 133.6, 131.2, 131.0, 130.4, 129.2, 129.0, 124.7, 120.3, 115.2, 112.6, 112.3, 100.9, 55.8, 33.2, 13.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_2O_3Cl^+$ 433.1319; Found 433.1320.

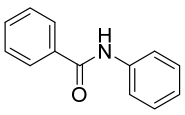
N-phenylcinnamamide (1be).



1be

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 56.9 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.57 (m, 4H), 7.48 (dq, *J* = 6.8, 4.2, 3.3 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.78 – 6.50 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 142.5, 138.2, 134.8, 130.1, 129.2, 129.0, 128.1, 124.6, 121.1, 120.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO^+$ 224.1075; Found 224.1084.

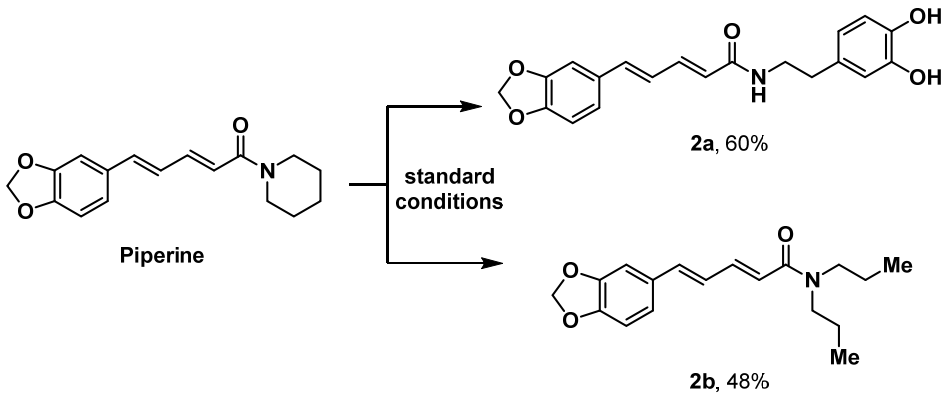
N-phenylbenzamide (1bf).



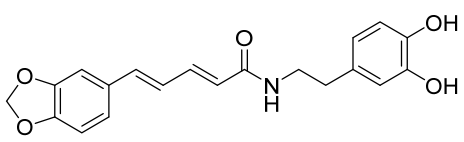
1bf

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 88.8 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.90 – 7.79 (m, 2H), 7.71 – 7.60 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 (ddt, *J* = 8.4, 6.6, 1.4 Hz, 2H), 7.41 – 7.31 (m, 2H), 7.20 – 7.10 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 138.1, 135.1, 132.0, 129.2, 128.9, 127.2, 124.7, 120.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}NO^+$ 198.0919; Found 198.0923.

Direct transformation of piperine to potential drug molecules



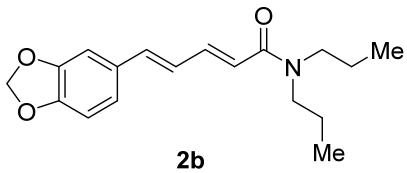
(2E,4E)-5-(benzo[d][1,3]dioxol-5-yl)-N-(3,4-dihydroxyphenethyl)penta-2,4-dienamide (2a).



2a

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 106.0 mg, 60% yield. ^{1}H NMR (600 MHz, CD_3OD) δ 7.33 – 7.13 (m, 1H), 7.03 – 6.93 (m, 1H), 6.93 – 6.80 (m, 1H), 6.76 – 6.69 (m, 3H), 6.69 – 6.58 (m, 2H), 6.49 (dt, *J* = 8.1, 2.4 Hz, 1H), 6.11 – 5.92 (m, 1H), 5.89 (d, *J* = 2.3 Hz, 2H), 3.44 – 3.33 (m, 2H), 2.72 – 2.49 (m, 2H). The proton signals of protic N-H and O-H groups were not observed due to the H/D exchange with CD_3OD. **^{13}C NMR** (150 MHz, CD_3OD) δ 169.0, 149.7, 146.3, 144.8, 142.2, 140.2, 132.3, 132.1, 125.9, 124.2, 123.8, 121.1, 116.9, 116.4, 109.4, 106.7, 102.7, 49.9, 42.5, 36.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_5^+$ 354.1341; Found 354.1349.

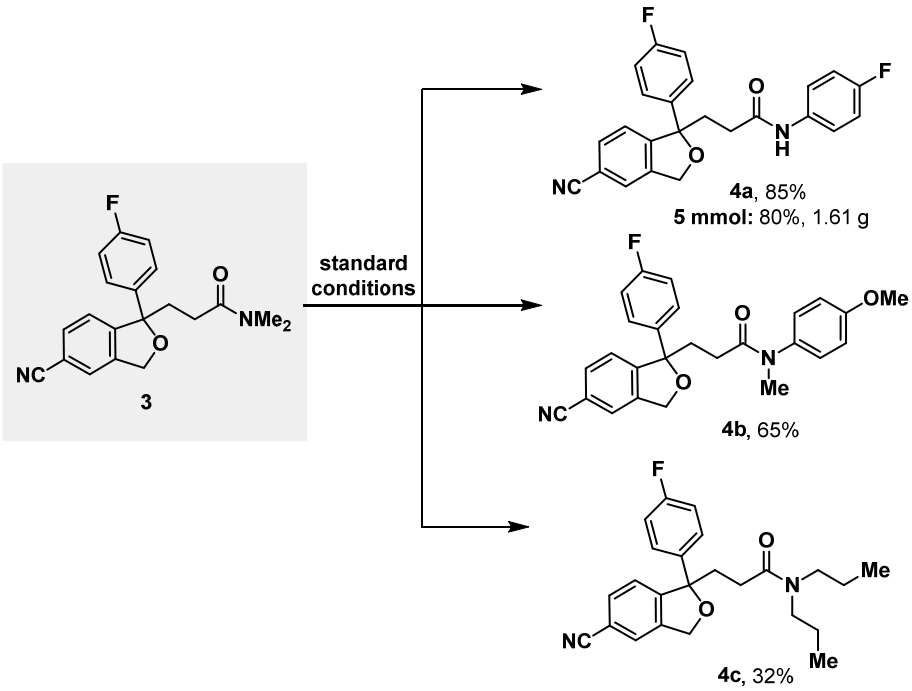
(2E,4E)-5-(benzo[d][1,3]dioxol-5-yl)-N-butyl-N-propylpenta-2,4-dienamide (2b).



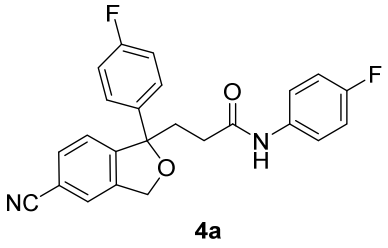
2b

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol% of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 72.3 mg, 48% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 1H), 6.96 (d, *J* = 1.7 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.80 – 6.68 (m, 3H), 6.33 (d, *J* = 14.6 Hz, 1H), 5.94 (s, 2H), 3.43 – 3.20 (m, 4H), 1.79 – 1.42 (m, 4H), 1.14 – 0.71 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.3, 148.2, 142.5, 138.4, 131.0, 125.4, 122.6, 120.3, 108.5, 105.7, 101.3, 49.9, 48.5, 23.0, 21.2, 11.5, 11.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}NO_3^+$ 302.1756; Found 302.1760.

Synthesis of Citalopram analogues



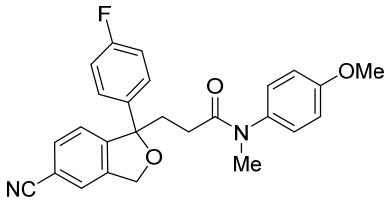
3-(5-cyano-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-1-yl)-N-(4-fluorophenyl) propanamide (4a).



(i) Based on 0.5 mmol of 3: Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 171.8 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.49 (s, 1H), 7.47 – 7.40 (m, 3H), 7.40 – 7.32 (m, 3H), 7.07 – 6.91 (m, 4H), 5.18 (q, *J* = 12.9 Hz, 2H), 2.73 – 2.46 (m, 2H), 2.30 (ddd, *J* = 8.7, 6.4, 4.8 Hz, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.52, -117.79. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 162.3 (d, *J* = 247.1 Hz), 159.4 (d, *J* = 243.6 Hz), 148.8, 140.2, 138.7, 133.9, 132.2, 126.9 (d, *J* = 8.2 Hz), 125.4, 123.0, 121.6 (d, *J* = 7.9 Hz), 118.6, 115.71 (dd, *J* = 22.0, 4.4 Hz), 115.71 (d, *J* = 17.6 Hz), 112.1, 90.8, 71.4, 36.3, 32.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}N_2O_2F_2^+$ 405.1415; Found 405.1413.

(ii) Based on 5 mmol of 3: Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2) using a 100 mL Schlenk flask, 1.61 g, 80% yield. The spectra data were in agreements with that of the identical compound above.

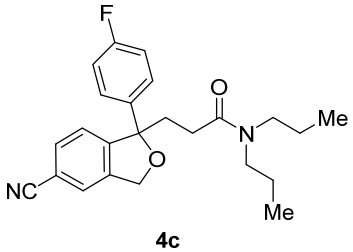
3-(5-cyano-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-1-yl)-N-(4-hydroxyphenyl)-N-methylpropanamide (4b).



4b

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol% of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 135.3 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.27 (d, *J* = 4.0 Hz, 1H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.87 – 6.77 (m, 2H), 5.18 – 4.86 (m, 2H), 3.81 (s, 3H), 3.13 (s, 3H), 2.67 – 2.30 (m, 2H), 2.23 – 1.76 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.07. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.7, 162.1 (d, *J* = 246.3 Hz), 158.9, 149.0, 140.1, 138.9 (d, *J* = 3.1 Hz), 136.6, 131.8, 128.2, 126.8 (d, *J* = 8.0 Hz), 125.1, 123.0, 118.7, 115.3 (d, *J* = 21.4 Hz), 114.8, 111.7, 90.7, 71.2, 55.6, 37.5, 36.5, 28.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_2O_3F^+$ 431.1771; Found 431.1773.

3-(5-cyano-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-1-yl)-N,N-dipropylpropanamide (4c).

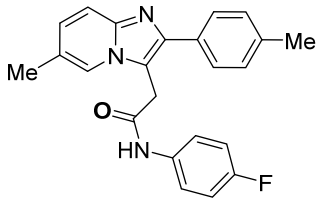


4c

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol% of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 63.1 mg, 32% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.45 (d, *J* = 3.1 Hz, 1H), 7.41 (tdd, *J* = 9.4, 6.6, 3.2 Hz, 3H), 6.96 (td,

J = 8.7, 3.2 Hz, 2H), 5.26 – 5.02 (m, 2H), 3.24 – 3.10 (m, 2H), 3.08 – 2.89 (m, 2H), 2.69 – 2.35 (m, 2H), 2.22 (td, *J* = 7.9, 3.1 Hz, 2H), 1.65 – 1.31 (m, 4H), 0.95 – 0.64 (m, 6H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.03. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.8, 162.1(d, *J* = 246.5 Hz), 149.2, 140.0, 138.9, 131.9, 126.8 (d, *J* = 8.0 Hz), 125.2, 123.0, 118.6, 115.4 (d, *J* = 21.5 Hz), 111.8, 90.7, 71.2, 49.5, 47.7, 36.4, 27.7, 22.1, 20.9, 11.3, 11.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}N_2O_2F^+$ 395.2135; Found 395.2133.

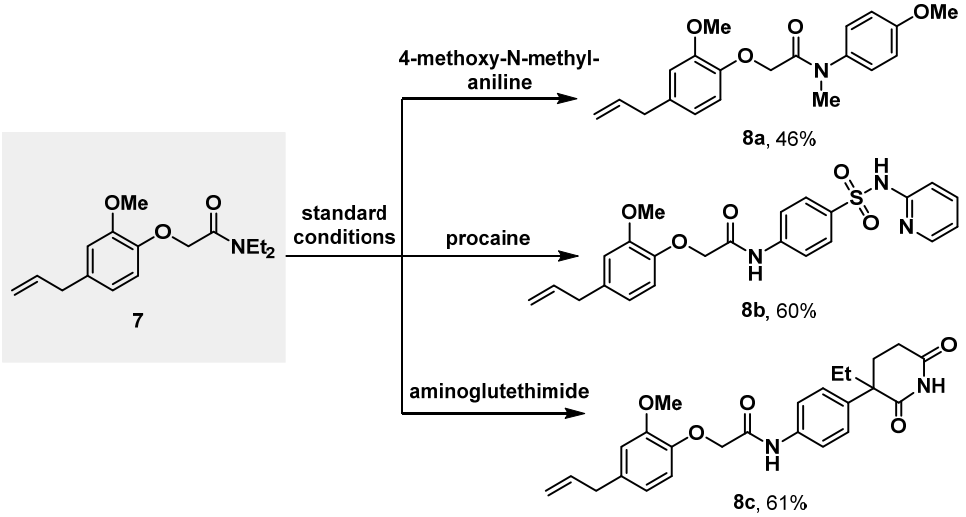
N-(4-fluorophenyl)-2-(6-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)acetamide (5)



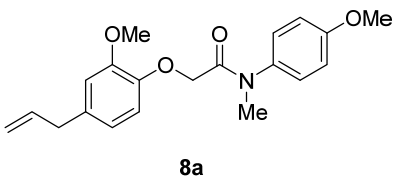
5

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 1:2, R_f = 0.5), 87.8 mg, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.80 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 9.0, 4.7 Hz, 2H), 7.33 (d, *J* = 9.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 10.7 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 4.09 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.10. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 159.5 (d, *J* = 244.1 Hz), 144.3, 143.9, 138.1, 133.6 (d, *J* = 2.7 Hz), 130.3, 129.5, 128.4, 127.9, 123.0, 122.1 (d, *J* = 7.9 Hz), 121.0, 116.2, 115.5 (d, *J* = 22.4 Hz), 112.6, 33.2, 21.2, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}N_3OF$ 374.1669; Found 374.1669.

Upcycling of less potent drugs to new amides for study



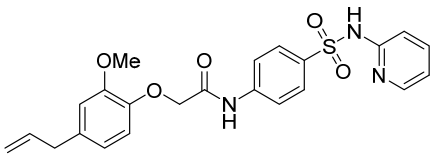
2-(4-allyl-2-methoxyphenoxy)-N-(4-methoxyphenyl)-N-methylacetamide (8a).



8a

Using the General Procedure as well as using 20 mol % of WCl_6 and 40 mol% of **L1**, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 78.5 mg, 46% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.64 (td, *J* = 7.4, 3.7 Hz, 3H), 6.04 – 5.73 (m, 1H), 5.17 – 4.90 (m, 2H), 4.41 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.28 (d, *J* = 6.8 Hz, 2H), 3.25 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.0, 159.3, 149.5, 145.9, 137.6, 134.9, 133.9, 128.2, 120.3, 115.6, 115.1, 114.4, 112.5, 67.3, 55.8, 55.5, 39.8, 37.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_4^+$ 342.1705; Found 342.1709.

2-(4-allyl-2-methoxyphenoxy)-N-(4-(N-(pyridin-2-yl)sulfamoyl)phenyl)acetamide (8b).

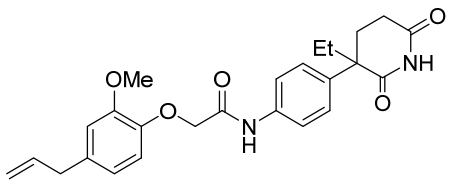


8b

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 136.0 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.36 (dd, *J* = 6.0, 1.9 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H),

7.75 – 7.59 (m, 4H), 7.42 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.85 – 6.71 (m, 3H), 6.11 – 5.73 (m, 1H), 5.20 – 5.01 (m, 2H), 4.60 (s, 2H), 3.91 (s, 3H), 3.34 (d, J = 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 155.2, 149.9, 145.8, 142.3, 140.9, 137.2, 136.4, 129.0, 128.3, 121.4, 119.7, 117.4, 116.3, 115.2, 114.6, 114.2, 112.9, 71.2, 56.2, 40.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}N_3O_5S^+$ 454.1437; Found 454.1439.

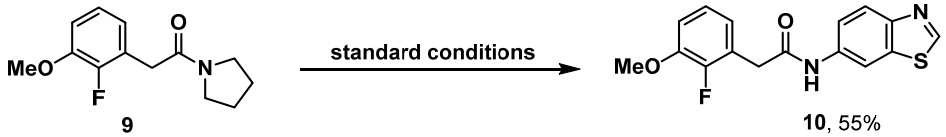
2-(4-allyl-2-methoxyphenoxy)-N-(4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl) acetamide (8c).



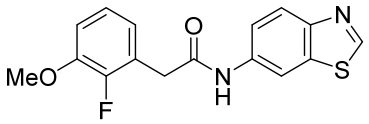
8c

Using the General Procedure, the title compound was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 133.1 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.23 (d, J = 9.3 Hz, 1H), 7.62 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.0 Hz, 1H), 6.85 – 6.74 (m, 2H), 6.13 – 5.83 (m, 1H), 5.26 – 4.99 (m, 2H), 4.65 (s, 2H), 3.94 (s, 3H), 3.37 (d, J = 6.6 Hz, 2H), 2.70 – 2.56 (m, 1H), 2.51 – 2.33 (m, 2H), 2.30 – 2.19 (m, 1H), 2.16 – 2.02 (m, 1H), 1.97 – 1.84 (m, 1H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 172.4, 167.4, 149.9, 145.8, 137.2, 136.8, 136.1, 134.8, 127.1, 121.3, 120.4, 117.1, 116.2, 112.8, 71.1, 56.1, 50.8, 40.0, 33.0, 29.4, 27.2, 9.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}N_2O_5^+$ 437.2076; Found 437.2078.

Direct transformation of tertiary amide intermediate to amide agrochemical



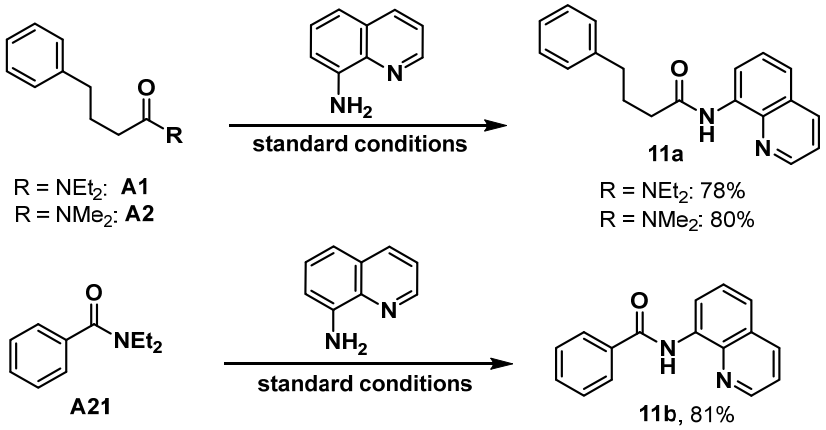
N-(benzo[d]thiazol-6-yl)-2-(2-fluoro-3-methoxyphenyl)acetamide (10).



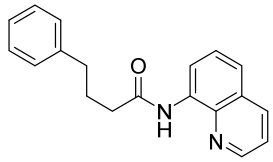
10

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 1:1, R_f = 0.2), 87.0 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.48 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 1H), 7.25 (ddd, *J* = 7.2, 3.4, 1.7 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.92 (q, *J* = 8.2, 7.3 Hz, 2H), 3.87 (s, 3H), 3.77 (s, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -139.43. **^{13}C NMR** (150 MHz, $CDCl_3$) 168.3, 153.7 , 150.8 (d, *J* = 244.7 Hz), 150.1, 148.1 (d, *J* = 10.8 Hz), 135.6, 134.8, 124.7 (d, *J* = 4.7 Hz), 123.6, 122.7 (d, *J* = 2.0 Hz), 122.5 (d, *J* = 13.0 Hz), 119.2, 112.9, 112.8, 56.3, 38.0 . **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}N_2O_2SF^+$ 317.0760; Found 317.0761.

Installation of 8-aminoquinolyl directing group to tertiary amides for direct functionalization



4-phenyl-N-(quinolin-8-yl)butanamide (11a).

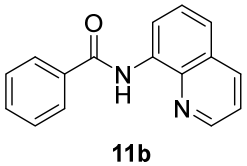


11a

(i) From A1: Using the General Procedure, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.6), 113.2 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.96 – 8.68 (m, 2H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.49 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.24 (dt, *J* = 7.9, 1.1 Hz, 2H), 7.22 – 7.15 (m, 1H), 2.82 – 2.72 (m, 2H), 2.57 (dd, *J* = 8.0, 7.0 Hz, 2H), 2.26 – 2.09 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.6, 148.2, 141.6, 138.5, 136.5, 134.6, 128.7, 128.5, 128.1, 127.6, 126.1, 121.7, 121.5, 116.6, 37.4, 35.3, 27.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O^+$ 291.1497; Found 291.1504.

(ii) From A2: Using the General Procedure, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.6), 116.1 mg, 80% yield. Spectra data are in agreements with that of the identical compound from (i).

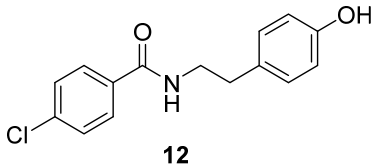
N-(quinolin-8-yl)benzamide (11b).



11b

Using the General Procedure, the title compound was obtained as a yellow liquid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.6), 100.5 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 8.95 (dd, *J* = 7.5, 1.4 Hz, 1H), 8.84 (dt, *J* = 5.1, 2.5 Hz, 1H), 8.23 – 8.13 (m, 1H), 8.09 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.70 – 7.49 (m, 5H), 7.46 (dt, *J* = 8.6, 4.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 148.4, 138.9, 136.5, 135.3, 134.7, 131.9, 128.9, 128.1, 127.6, 127.4, 121.8, 116.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}N_2O^+$ 249.1028; Found 249.1036.

4-chloro-N-(4-hydroxyphenethyl)benzamide (12)



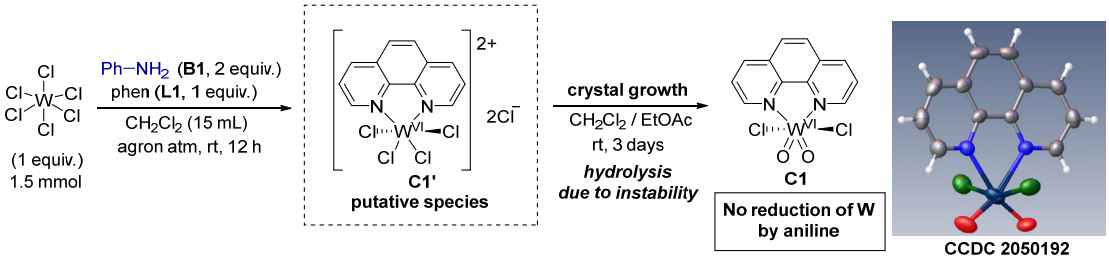
12

Using the General Procedure, the title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.5), 89.6 mg, 65% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.75 (d, *J* = 9.8 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 7.4 Hz, 2H), 3.55-3.49 (m, 2H), 2.80 (t, J=7.5 Hz, 2H) (The proton signal of NH and OH groups could not be observed owing to the rapid exchange with methanol-d_4). **^{13}C NMR** (100 MHz, CD_3OD) δ 169.0, 157.0, 138.7, 134.5, 131.3, 130.8, 130.0, 129.7, 116.3, 43.1, 35.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}ClNO_2^+$ 276.0791; Found 276.0789.

Mechanistic study of transamidation of tertiary amides

(i) Study of the tungsten complex formation in the stoichiometric reactions of WCl_6 with L1 and substrates (Figures S1 and S2).

Figure S1. Formation of $W^{VI}(phen)(O)_2Cl_2$ (C1).

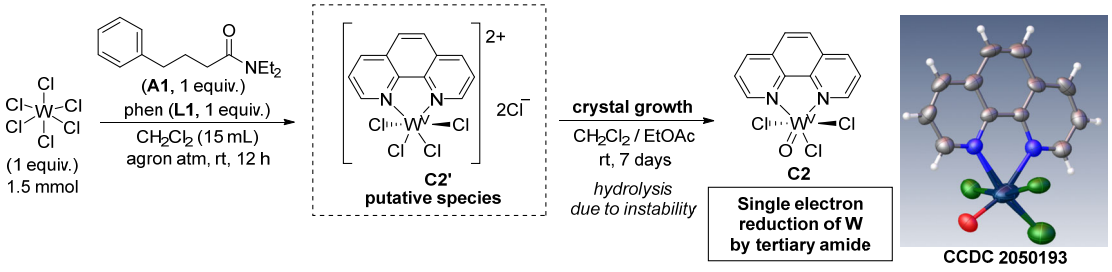


Empirical formula	$C_{13}H_{10}Cl_4N_2O_2W$ (**C1**)
CCDC number	2050192
Formula weight	551.88
Temperature	293 (2) K
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 9.0393 (5) Å alpha = 90 deg. b = 13.5853 (9) Å beta = 95.465 (5) deg. c = 13.4735 (8) Å gamma = 90 deg.
Volume	1647.1 (17) $Å^3$
Z, Calculated density	4, 2.226 g/m^3
Absorption coefficient	7.668 mm^{-1}
F (000)	1040.0
Crystal size	0.26 x 0.19 x 0.15 mm
Radiation	MoK^a (λ = 0.71073)
Theta range for data collection	4.268 to 50.052 deg.
Limiting indices	-10<=h<=10, -12<=k<=16, -15<=l<=16
Reflections collected / unique	10185 / 2091 [R(int) = 0.0384]
Data / restraints / parameters	2901 / 0 / 199
Goodness-of-fit on F^2	1.145
Final R indices [I>2sigma(I)]	R_1 = 0.0433, wR_2 = 0.0782
R indices (all data)	R_1 = 0.0567, wR_2 = 0.0816
Largest diff. peak and hole	2.88 and -1.28 $e.Å^{-3}$

An oven-dried 25 mL round bottom flask equipped with a stir bar and capped with a rubber septum was charged with aniline (2 equiv., 3 mmol), phenanthroline (**L1**, 1 equiv., 1.5 mmol), and WCl_6 (1 equiv., 1.5 mmol). The flask was evacuated in vacuo and then backfilled with argon for three times. Pre-dried CH_2Cl_2 (12 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at room temperature for 12 h. After filtration, pre-dried EtOAc (5 mL) was added into the flask, and the reaction mixture was left at room temperature for slow evaporation. A deep purple crystal was formed after 3 days. $W^{VI}(phen)(O)_2Cl_2$ (**C1**) was formed according to the X-ray crystallographic analysis, with ORTEP representation with 50% probability thermal ellipsoids. The dichloromethane (CH_2Cl_2) molecule in the original crystallographic data was omitted for clarity.

Presumably, WCl_6 reacts with **L1** to form $W^{VI}(phen)Cl_6$ (**C1'**), which is not stable and undergoes hydrolysis with residual water to form **C1**. The result also suggested that aniline does not reduce the complex to lower-valent W species.

Figure S2. Formation of $W^{V}(phen)(O)Cl_3$ (C2).



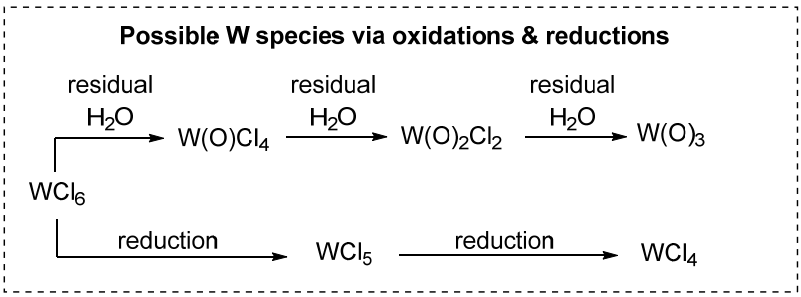
Empirical formula	$C_{12}H_8Cl_3N_2OW$ C(**C2**)
CCDC number	2050193
Formula weight	486.40
Temperature	293 (2) K
Crystal system, space group	monoclinic, $P2_1$ / c
Unit cell dimensions	a = 7.8945 (5) Å alpha = 90 deg. b = 17.8773 (9) Å beta = 106.957 (6) deg. c = 10.1868 (5) Å gamma = 90 deg.

Volume	1375.18 (14) $Å^3$
Z, Calculated density	4, 2.349 g/m^3
Absorption coefficient	8.973 mm^{-1}
F (000)	908.0
Crystal size	0.28 x 0.19 x 0.15 mm
Radiation	MoK^a (λ = 0.71073)
Theta range for data collection	4.556 to 58.722 deg.
Limiting indices	-10<=h<=9, -23<=k<=19, -13<=l<=12
Reflections collected / unique	12431 / 3229 [R(int) = 0.0729]
Data / restraints / parameters	3229 /66 / 182
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R_1 = 0.0542, wR_2 = 0.1228
R indices (all data)	R_1 = 0.0978, wR_2 = 0.1312
Largest diff. peak and hole	1.60 and -1.58 $e.Å^{-3}$

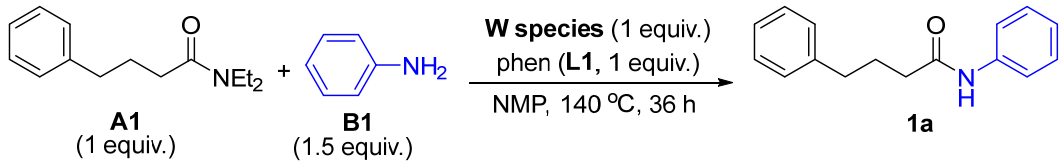
An oven-dried 25 mL round bottom flask equipped with a stir bar and capped with a rubber septum was charged with WCl_6 (1 equiv., 1.5 mmol), phenanthroline (**L1**, 1 equiv., 1.5 mmol), and tertiary alkyl amide **A1** (1 equiv., 1 mmol). The flask was evacuated in vacuo and then backfilled with argon for three times. Pre-dried CH_2Cl_2 (15 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at room temperature for 12 h. After filtration, pre-dried EtOAc (5 mL) was added into the flask, and the reaction mixture was left at room temperature for slow evaporation. A deep purple crystal was formed after 7 days. $W^V(phen)(O)Cl_3$ (**C2**) was formed according to the X-ray crystallographic analysis, with ORTEP representation with 50% probability thermal ellipsoids.

Presumably, WCl_6 reacts with **L1** to form $W^{VI}(phen)Cl_6$ (**C1'**) and is futher reduced by tertiary alkyl amide **A1** to form $W^V(phen)Cl_5$ (**C2**'), which is not stable and undergoes hydrolysis with residual water to form $W^V(phen)(O)Cl_3$ (**C2**).

(ii) Probing the reactivity of viable W species (Scheme 5(b)).



W-mediated transamidation



A1 (1 equiv.) **B1** (1.5 equiv.) **1a**

W species	WCl_6	$W(O)Cl_4$	$W(O)_2Cl_2$	$W(O)_3$	WCl_5	WCl_4
yield of **1** (%)	87	58	30	trace	84	65

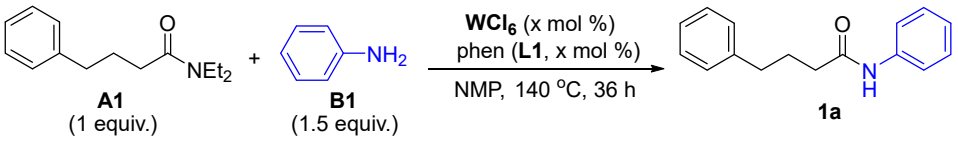
An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (1 equiv., 0.5 mmol), aniline **B1** (1.5 equiv., 0.75 mmol), phenanthroline **L1** (1 equiv., 0.5 mmol), and W species (1 equiv., 0.5 mmol). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the transamidated product **1a**.

Experimental results suggested that the reactivity of transamidation is generally consistent with the Lewis acidity of W species: $WCl_6 > W(O)Cl_4 > W(O)_2Cl_2 > W(O)_3$; $WCl_6 > WCl_5 > WCl_4$.

(iii) Probing the reactivity of viable W species using catalytic loadings of W (Figure S3).

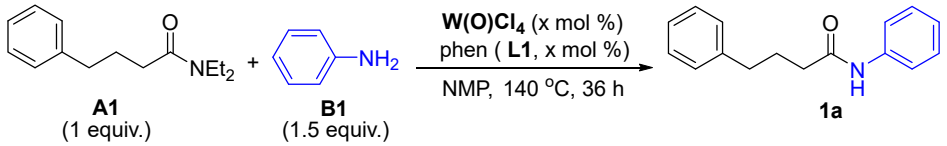
Figure S3. Probing the reactivity of viable W species using catalytic loadings of W.

Effect of loading of W on transamidation



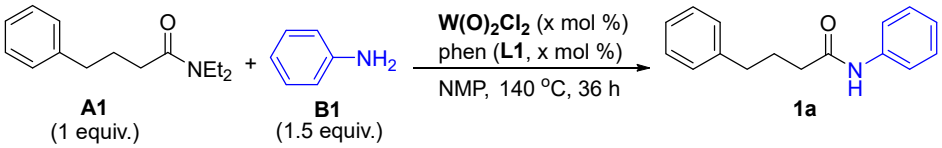
A1 (1 equiv.) **B1** (1.5 equiv.) **1a**

Loading of WCl_6 / phen (x mol %)	100	25
yield of **1** (%):	87	52



A1 (1 equiv.) **B1** (1.5 equiv.) **1a**

Loading of $W(O)Cl_4$ / phen (x mol %)	100	25
yield of **1** (%):	58	35



A1 (1 equiv.) **B1** (1.5 equiv.) **1a**

Loading of $W(O)_2Cl_2$ / phen (x mol %)	100	25
yield of **1** (%):	30	27

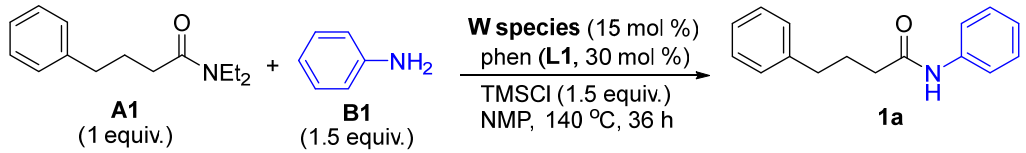
An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (0.5 mmol, 1 equiv), aniline **B1** (0.75 mmol, 1.5 equiv), phenanthroline **L1** (0.125 mmol, 25 mol %), and W salt (0.125 mmol, 25 mol%). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to

give the transamidated product **1a**.

Experimental results suggested that the reactivity of transamidation is consistent with the Lewis acidity of W species: WCl_6 > $W(O)Cl_4$ > $W(O)_2Cl_2$ even when catalytic amounts of W salts are employed.

(iv) Probing the catalytic reactivity of viable W species under otherwise identical conditions (Scheme 5(c)).

W-catalyzed transamidation



A1 (1 equiv.) **B1** (1.5 equiv.) **1a**

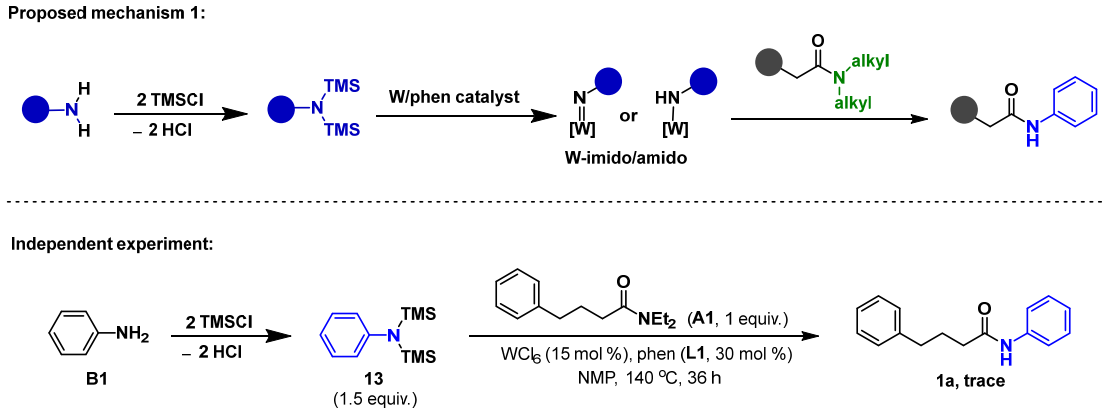
W species	WCl_6	$W(O)Cl_4$	$W(O)_2Cl_2$	$W(O)_3$	WCl_5	WCl_4
yield of **1** (%)	90	57	56	52	74	65

An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (0.5 mmol, 1 equiv.), aniline **B1** (0.75 mmol, 1.5 equiv.), phenanthroline **L1** (0.15 mmol, 30 mol %), and W salt (0.075 mmol, 15 mol %). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the transamidated product **1a**.

Experimental results suggested that: (1) W-oxo speices are likely converted to the most reactive WCl_6 or other polychlorinated W species to maintain the high catalytic reactivity; (2) the catalytic activity is consistent with the Lewis activity of W: WCl_6 > WCl_5 and WCl_4.

(v) Probing the proposed mechanism (1): transamidation with N-trimethylsilylated amine (Figure S4).

Figure S4. Transamidation via the intermediacy of N-trimethylsilylated amine.

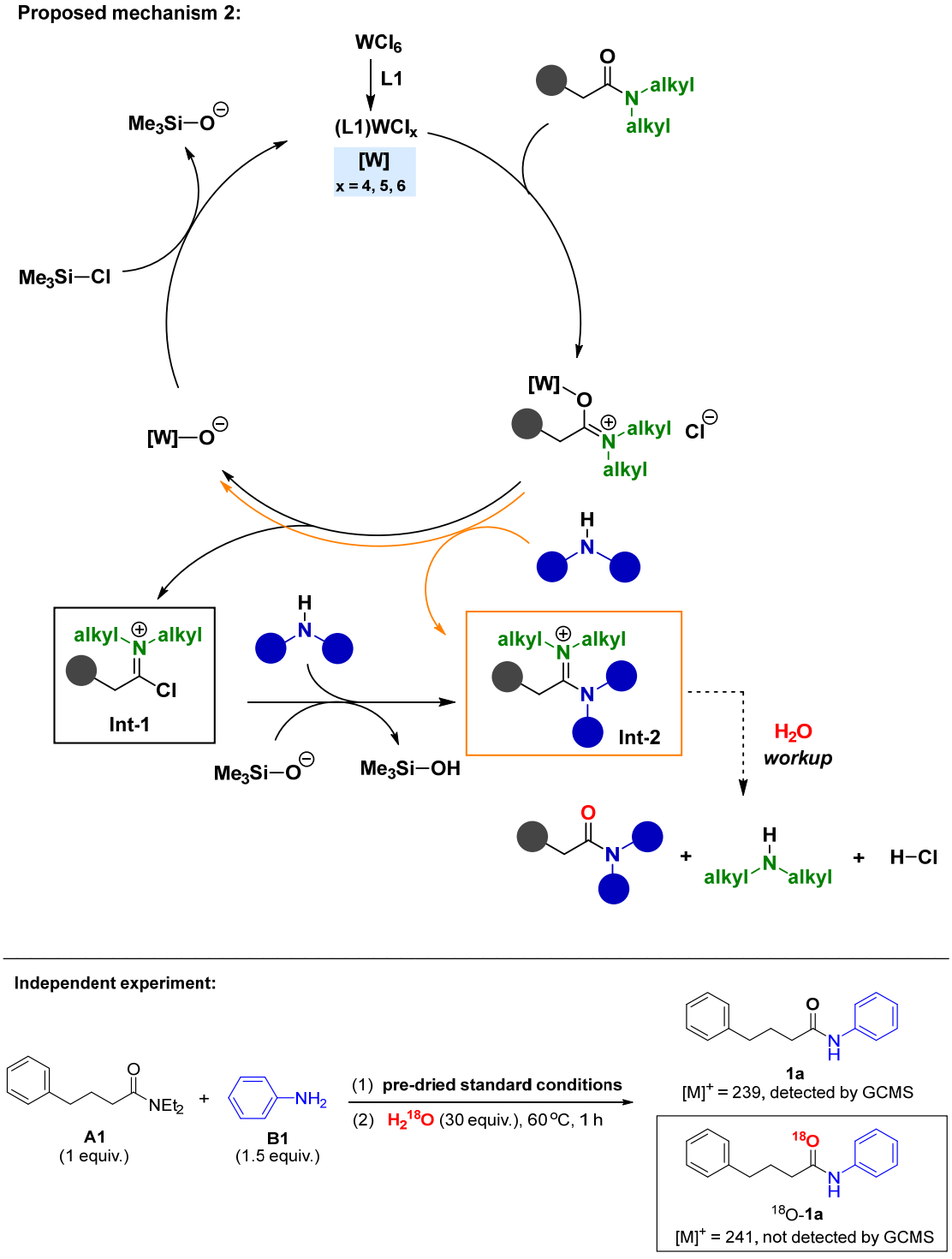


An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (0. 5 mmol, 1 equiv.), N,N-bis(trimethylsilyl)aniline **13**[21] (0.75 mmol, 1.5 equiv.), phenanthroline (**L1**, 0.075 mmol, 15 mol %), and WCl_6 (0.075 mmol, 15 mol %). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. A trace of transamidated product **1a** was formed while most of **A1** remained unreacted.

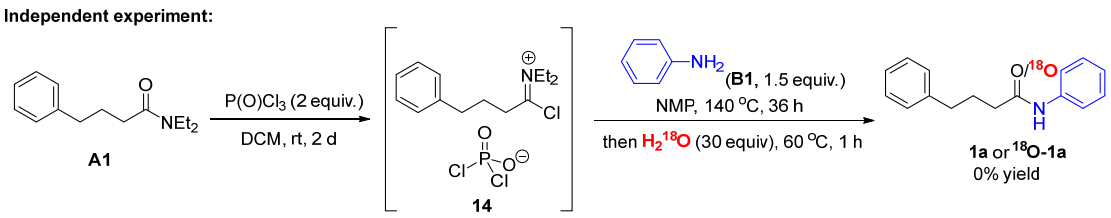
Therefore, the mechanism of transamidation via the intermediacy of N-trimethylsilylated amine is precluded.

(vi) Probing the proposed mechanism (2): transamidation via W-catalyzed amide C=O bond cleavage (Figure S5).

Figure S5. Transamidation via W-catalyzed amide C=O bond cleavage.



An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (0.5 mmol, 1 equiv.), aniline **B1** (0.75 mmol, 1.5 equiv.), phenanthroline **L1** (0.15 mmol, 30 mol %), and WCl_6 (0.075 mmol, 15 mol %). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) and TMSCl (0.75 mmol, 1.5 equiv.) were transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. ^{18}O-water (30 equiv., 15 mmol) was then added into the reaction under the positive argon pressure, and the resulting mixture was further heated at 60 °C for 1 h to conduct the hydrolysis with ^{18}O-water. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The crude product was analyzed by GC-MS analysis. Only unlabeled **1a** was detected ($[M]^+ = 239$) without the formation of ^{18}O-labelled **1a** ($[M]^+ = 241$). Therefore, the mechanism involving the W-mediated amide C=O bond cleavage is precluded.



(a) Synthesis of Vilsmeier salt 14. Vilsmeier salt **14** was prepared according to the typical literature procedure.[22] An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (1 equiv., 2 mmol) and $P(O)Cl_3$ (2 equiv., 4 mmol). The tube was evacuated in vacuo and then backfilled with argon for three times. Pre-dried CH_2Cl_2 (10 mL) was transferred into the tube via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at room temperature for 2 d. At this point, TLC analysis indicated that an exceedingly

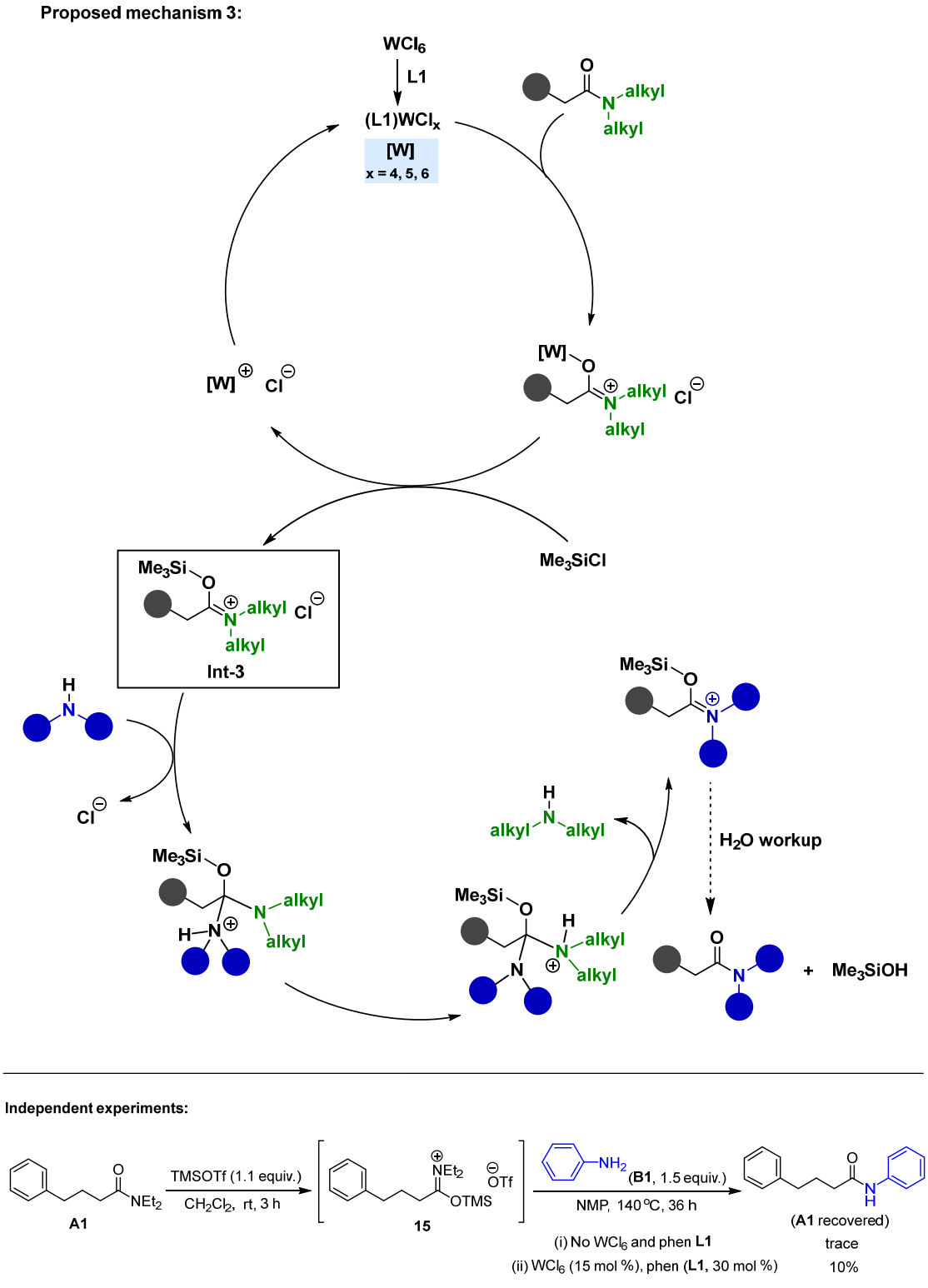
polar product was formed while a small amount of **A1** remained unreacted. The reaction mixture was concentrated in vacuo with the aid of rotary evaporator. Diethyl ether was added to precipitate the product. The residue was filtered and washed with diethyl ether to obtain **14** as a white crystalline solid. ^{1}H NMR spectroscopy indicated that **14** was in ~85% purity in association with ~15% unreacted **A1**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.33 – 3.90 (m, 2H), 3.48 – 3.05 (m, 3H), 2.89 – 2.72 (m, 2H), 2.71 – 2.59 (m, 1H), 2.20 (p, *J* = 7.6 Hz, 1H), 2.13 – 1.95 (m, 1H), 1.54 – 1.35 (m, 3H), 1.18 (td, *J* = 7.2, 4.9 Hz, 3H). ^{31}P NMR (243 MHz, $CDCl_3$) δ -2.66. ^{13}C NMR was not performed due to the impurity of **14** and the multiplicity of signals brought by the splitting effect of P.

(b) Transamidation with Vilsmeier salt 14. An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with Vilsmeier salt **14** (~85% purity, ~0.2 mmol, ~1 equiv.) and aniline **B1** (0.3 mmol, 1.5 equiv.). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (2 mL) was transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. ^{18}O-water (30 equiv., 6 mmol) was then added into the reaction under the positive argon pressure, and the resulting mixture was further heated at 60 °C for 1 h. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x). The crude product in the organic layer was analyzed by TLC analysis, indicating that no transamidated product (**1a** or **^{18}O-1a**) was formed.

Therefore, transamidation via the intermediacy of Vilsmeier salt **Int-1** derived from tertiary alkyl amides is precluded.

(vii) Probing the proposed mechanism (3): transamidation with trimethylsilyoxy-substituted imine intermediate (Figure S6).

Figure S6. Transamidation via the intermediacy of trimethylsilyoxy imine species.



(a) Preparation of trimethylsilyoxy imine 15. Trimethylsilyoxy imine **15** was prepared according to the typical literature procedure.[23,24] An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (1 equiv., 0.5 mmol). The tube was evacuated in vacuo and then backfilled with argon for three times. CH_2Cl_2 (0.2 mL) and TMSOTf (1 equiv., 0.5 mmol) were sequentially transferred into the tube via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at room temperature for 3 h. At this point, **A1** was consumed and trimethylsilyoxy imine **15** was formed in situ as an exceedingly polar compound as determined by TLC analysis. **15** decomposed to complex species after the crystallization as identified by ^{1}H NMR spectroscopy. Therefore, **15** was prepared in situ for subsequent study.

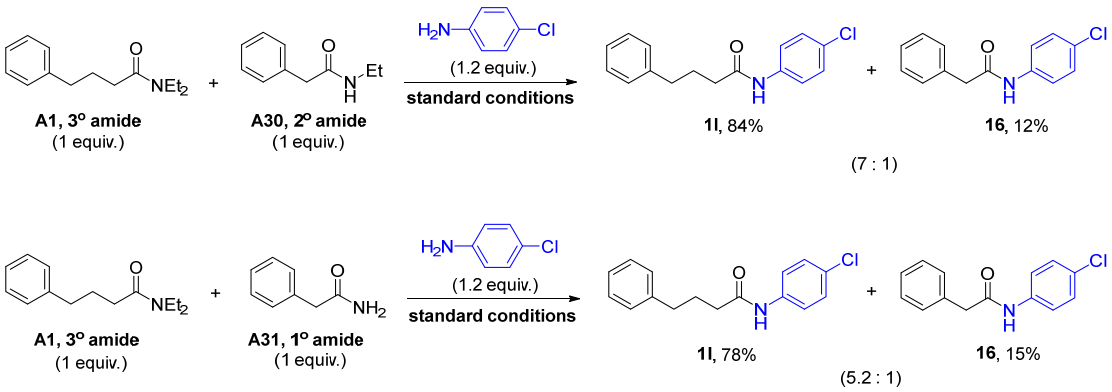
(b) Transamidation of trimethylsilyoxy imine 15 without WCl_6. Based on the in situ formed trimethylsilyoxy imine **15** from the procedure (a), aniline **B1** (1.5 equiv, 0.75 mmol) and NMP (5 mL) were added into the tube under the positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 ^{o}C in a preheated heat block for 36 h. The reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x). The crude product in the organic layer was analyzed by TLC analysis, indicating that a trace of transamidated product **1a** was formed.

(c) Transamidation of trimethylsilyoxy imine 15 with WCl_6. Based on the in situ formed trimethylsilyoxy imine **15** from the procedure (a), aniline **B1** (1.5 equiv, 0.5 mmol), phenanthroline (**L1**, 27.1 mg, 0.15 mmol), WCl_6 (29.8 mg, 0.075 mmol), phen **L1** (27.0 mg, 0.15 mmol) and NMP (5 mL) were sequentially added into the tube under the positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 ^{o}C in a preheated heat block for 36 h. The reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by column chromatography to give the transamidated product

1a in 10% yield.

Owing to the low productivity of transamidation with trimethylsilyoxy imine **15**, transamidation via the intermediacy of Vilsmeier salt can be ruled out.

(viii) Competition experiments among tertiary, secondary and primary Amides (Scheme 7(b)).



An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with tertiary alkyl amide **A1** (1 equiv., 0.5 mmol), secondary alkyl amide **A30** (or primary alkyl amide **A31**, 1 equiv., 0.5 mmol), 4-chloroaniline (1.2 equiv, 0.6 mmol), phenanthroline **L1** (0.15 mmol), and WCl_6 (0.075 mmol). The tube was evacuated in vacuo and then backfilled with argon for three times. NMP (5 mL) and TMSCl (1.5 equiv., 0.75 mmol) were transferred into the flask via a syringe under a positive argon pressure. The resulting mixture was stirred under an argon atmosphere at 140 °C in a preheated heat block for 36 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with dilute aqueous HCl solution (2x) and saturated brine, dried with anhydrous Na_2SO_4, and finally concentrated in vacuo with the aid of rotary evaporator. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the mixture of transamidated products. The ratios of the isolated amides **1l** and **16** derived from the equimolar mixture of amide substrates were identified by ^{1}H NMR spectroscopy.

References

1 Sundermeyer, J.; Hamel, L.; Mueller, R. R.; Rivas-Nass, A.; Doppiu, A.; Woerner, E.; Karch, R. Method for the reductions of metal halides. US Patent US/ 2020/0031684 (2020).

2 Li, Z. H.; Liu, L.; Xu, K. Q.; Huang, T. Z.; Li, X. Y.; Song, B.; Chen, T. Q. Palladium-Catalyzed *N*-Acylation of Tertiary Amines by Carboxylic Acids: A Method for the Synthesis of Amides. *Org. Lett*. **2020**, *22*, 5517-5521.

3 Yamada, K.; Kota, M.; Takahashi, K.; Fujita, H.; Kitamura, M; Kunishima, M. Development of Triazinone-Based Condensing Reagents for Amide Formation. *J. Org. Chem*. **2019**, *84*, 15042-15051.

4 Zhang, H. Q.; Riomet, M.; Roller, A.; Maulide, N. Synthesis of Novel Heterocycles by Amide Activation and Umpolung Cyclization. *Org. Lett*. **2020**, *22*, 2376-2380.

5 Tona, V.; Torre, A. D. L.; Padmanaban, M.; Ruider, S.; Gonzalez, L; Maulide, N. Chemo- and Stereoselective Transition-Metal-Free Amination of Amides with Azides. *J. Am. Chem. Soc*. **2016**, *138*, 8348-8351.

6 Wang, S. M.; Zhao, C.; Zhang, X; Qin, H. L. Clickable coupling of carboxylic acids and amines at room temperature mediated by SO_2F_2: a significant breakthrough for the construction of amides and peptide linkages. *Org. Biomol. Chem*. **2019**, *17*, 4087-4101.

7 Jeong, K. S.; Cho, Y. L.; Chang, S. Y.; Park, T. Y; Song, J. U. Assembly and Binding Properties of Osmate Ester-Bridged Binuclear Macrocycles. *J. Org. Chem*. **1999**, *64*, 9459-9466.

8 Muhammad, A. I.; Lee, S. Transamidation via C–N bond cleavage of amides and tertiary amines. *Org. Chem. Front*. **2020**, *7*, 2737-2743.

9 Akhrem, I. S.; Avetisyan, D. V.; Lyudmila, A. E.; Sergei, V. V.; Pavel, V. P.; Alexander, O. The first one-pot amidation of alkanes and cycloalkanes. *Tetrahedron Lett.* **2008**, *49*, 1399-1404.

10 Liu, Q. S.; Wang, D. Y.; Yang, Z. J.; Luan, Y. X.; Yang, J. F.; Li, J. F.; Pu, Y. G.; Ye, M. C. Ni−Al Bimetallic Catalyzed Enantioselective Cycloaddition of Cyclopropyl Carboxamide with Alkyne. *J. Am. Chem. Soc*. **2017**, *139*, 18150-18153.

11 Kalgutkar, A. S.; Marnett, A. B.; Crews, B. C.; Remmel, R. P.; Marnett, L. J. Ester

and Amide Derivatives of the Nonsteroidal Antiinflammatory Drug, Indomethacin, as Selective Cyclooxygenase-2 Inhibitors. *J. Med. Chem*. **2000**, *43*, 2860-2870.

12 Hlkmat, N. A. J.; Hussain, A. A.; Mansoor, H. B.; Sameh, A. A.; Slnan, K. A. S. Synthesis and Properties off Some *N, N*- Dialkylamides as New Extractants. *J. Chem. Eng. Date*. **1984**, *29*, 479-481.

13 Maki, T.; Ishihara, K.; Yamamoto, H. New boron(III)-catalyzed amide and ester condensation Reactions. *Tetrahedron*. **2007**, *63*, 8645-8657.

14 Li, X. W.; Lin, F. G.; Huang, K. M.; Wei, J. L.; Li, X. Y.; Wang, X. Y.; Geng, X. Y.; Jiao, N. Selective a-Oxyamination and Hydroxylation of Aliphatic Amides. *Angew. Chem. Int. Ed*. **2017**, *56*, 12307-12311.

15 Goncalves, C. R.; Lemmerer, M.; Teskey, C. J.; Adler, P.; Kaiser, D.; Maryasin B.; Gonzalez, L.; Maulide, N. Unified Approach to the Chemoselective α-Functionalization of Amides with Heteroatom Nucleophiles. *J. Am. Chem. Soc*. **2019**, *141*, 18437-18443.

16 Li, J.-S.; Da, Y.-D.; Chen, G.-Q.; Yang, Q.; Li, Z.-W.; Yang, F.; Huang, P.-M. Solvent-, and Catalyst–free Acylation of Anilines with Meldrum's Acids: A Neat Access to Anilides. *ChemistrySelect*. **2017**, *2*, 1770-1733.

17 Adler, P.; Teskey, C. J.; Kaiser, D.; Holy, M.; Harald, S.; Maulide, N. α-Fluorination of carbonyls with nucleophilic Fluorine. *Nat. Chem*. **2019**, *11*, 329-334.

18 Hernández, D.; Bernal, P.; Cruz, A.; Garciafigueroa, Y.; Garduño, L.; Salazar, M.; Díaz, F.; Chamorro, G.; Tamariz, J. Potent Hypolipidemic Activity of Mimetic Amides of Fibrates Based on the 2-Methoxy-4-(2-propenyl) phenoxyacetic Scaffold. *Drug Develop. Res*. **2004**, *61*, 19-36.

19 Sakaguchi, H. Preparation of N-benzothiazolyl amides for controlling a plant disease. WO Patent WO/2010/024365 (2010).

20 Pintori, D. G.; Greaney, M. F. Oxidative C–H Homodimerization of Phenylacetamides. *Org. Lett*. **2011**, *13,* 5713-5715.

21 Keck, C.; Maichle-Mossmerb, C.; Bettinger, H. F. Photo electron transfer induced desilylation of N,N-bis(trimethylsilyl)aminodibenzoborole to aminodibenzoborole. *Chem. Commun*. **2019**, *55*, 7470-7473.

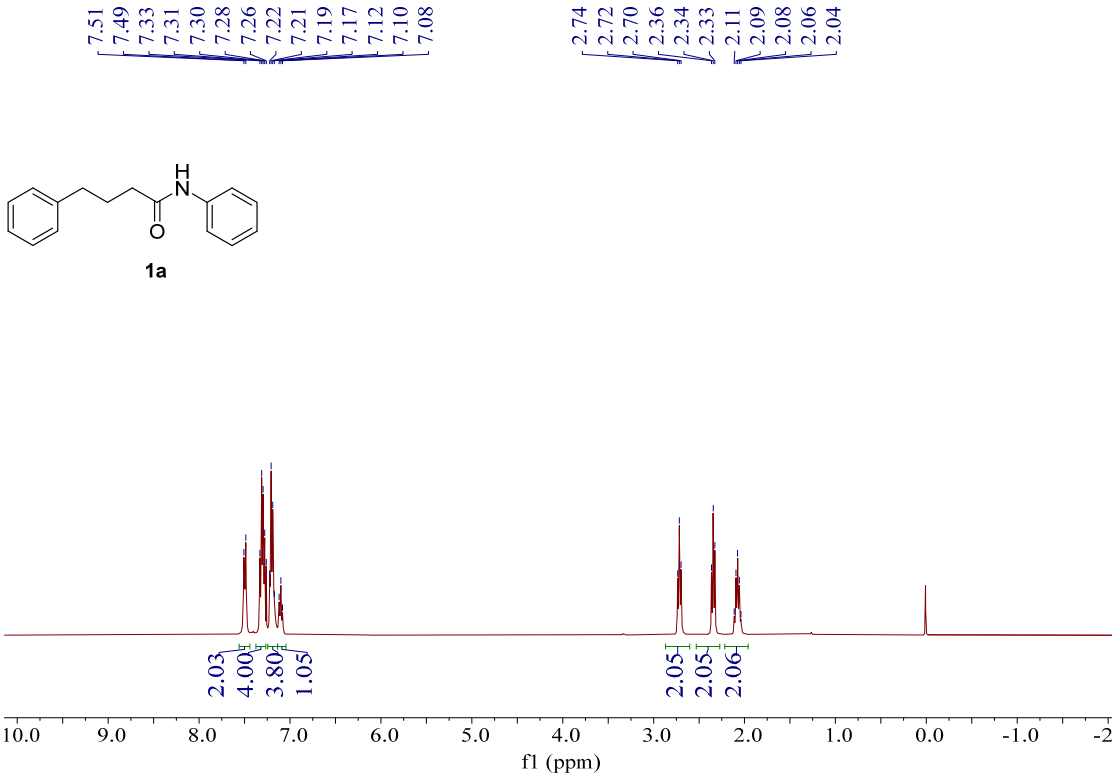
22 Qiu, Z. G. Synthetic method of 1-ethyl-2-nitromethylenepyrrolidine. CN Patent CN 106854171 (2017).

23 Stevan, W. D. A Mild and Convenient Procedure for the *N*-Formylation of

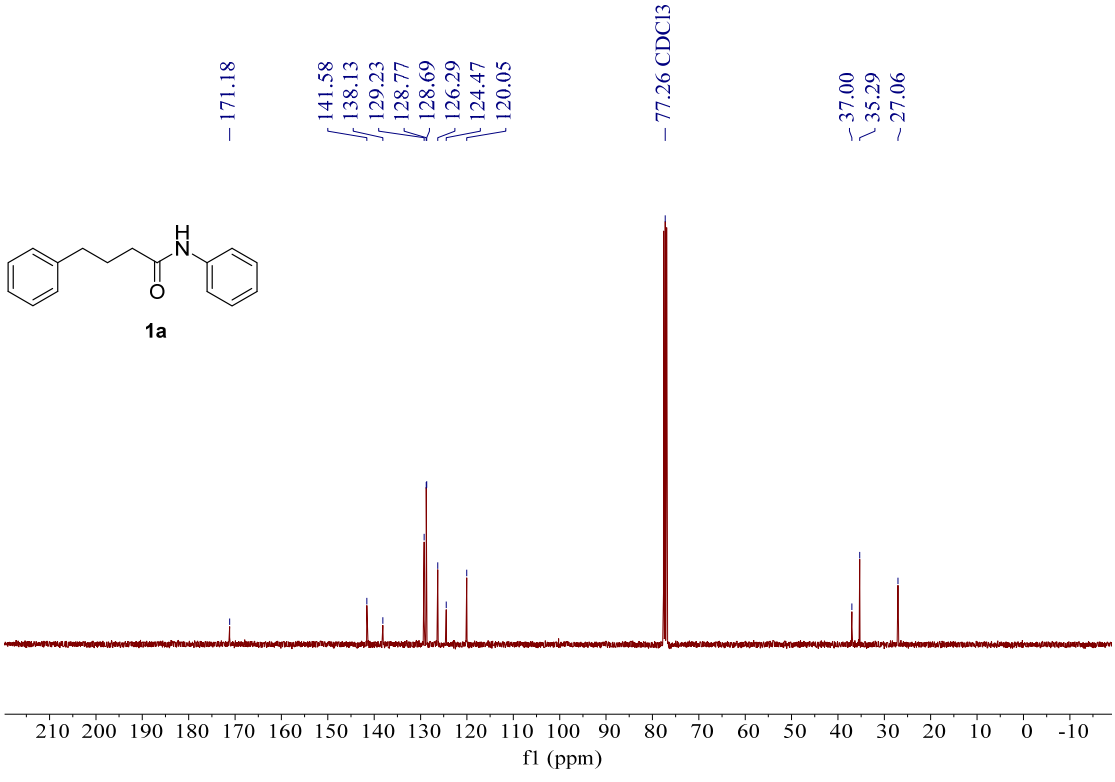
Secondary Amines Using Organosilicon Chemistry. *J. Org. Chem*. **1984**, *49*, 1311-1312.

24 Kobayashi, S.; Kiyohara, H.; Yamaguchi, M. Catalytic Silicon-Mediated Carbon-Carbon Bond-Forming Reactions of Unactivated Amides. *J. Am. Chem. Soc.* **2011**, *133*, 708-711.

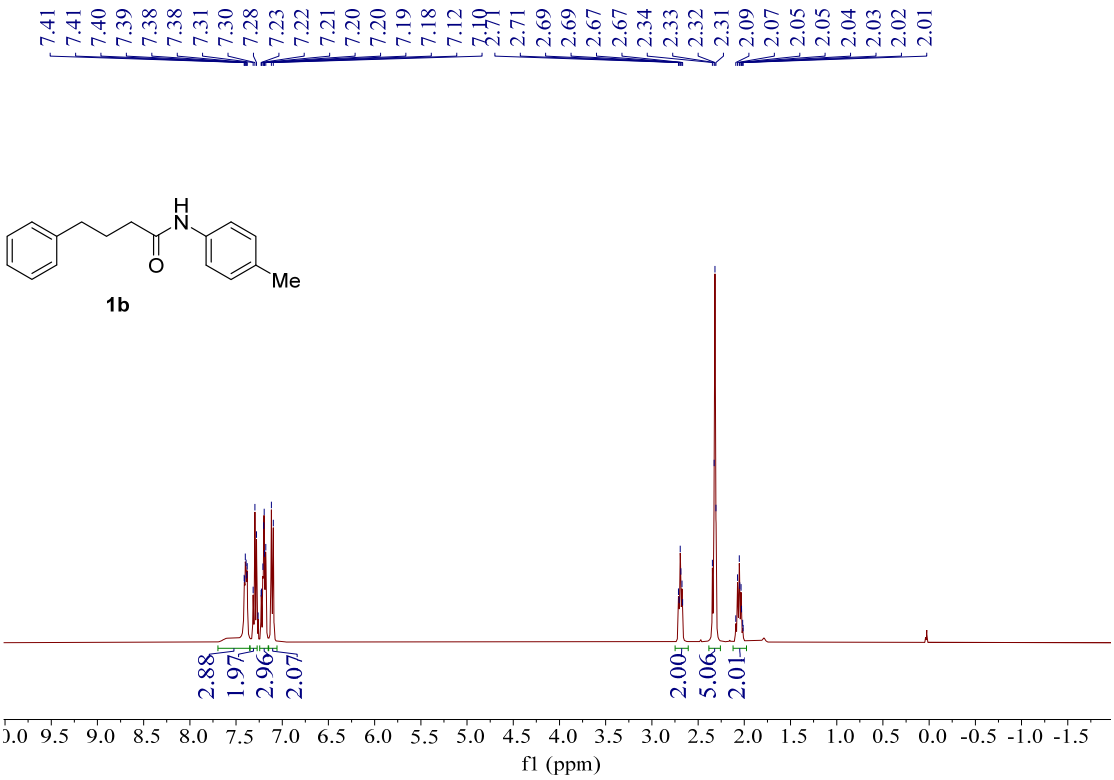
NMR spectra



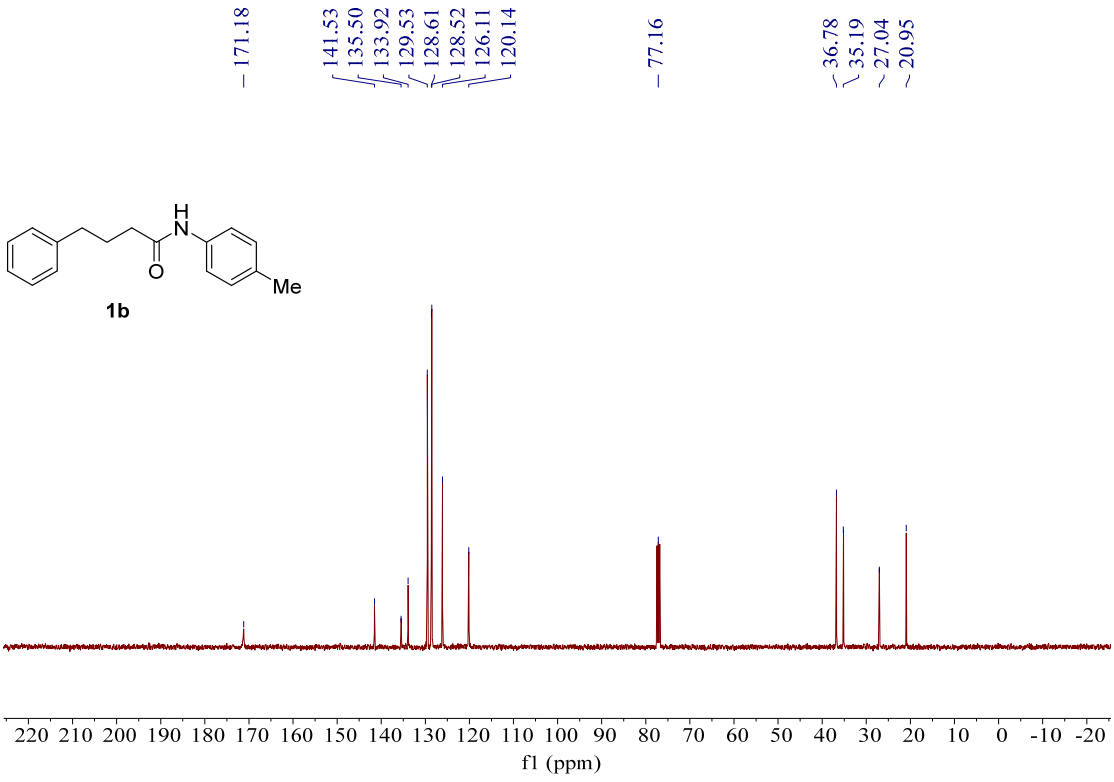
^{1}H NMR spectrum of **1a**



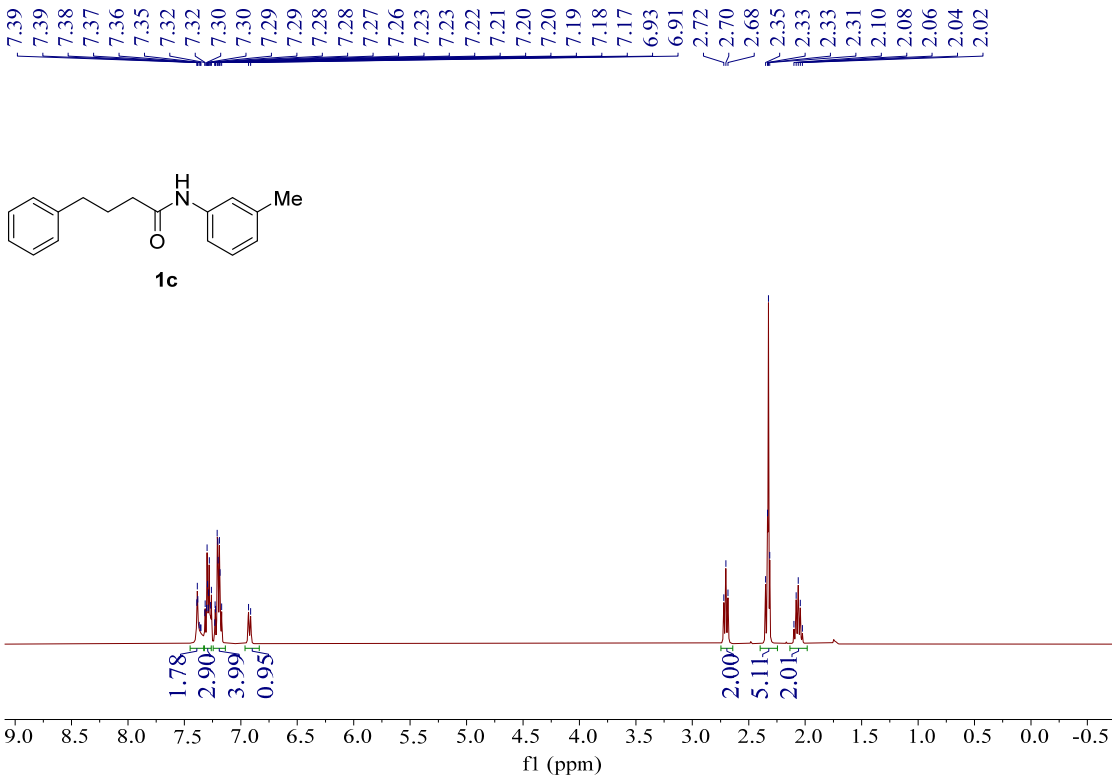
^{13}C NMR spectrum of **1a**



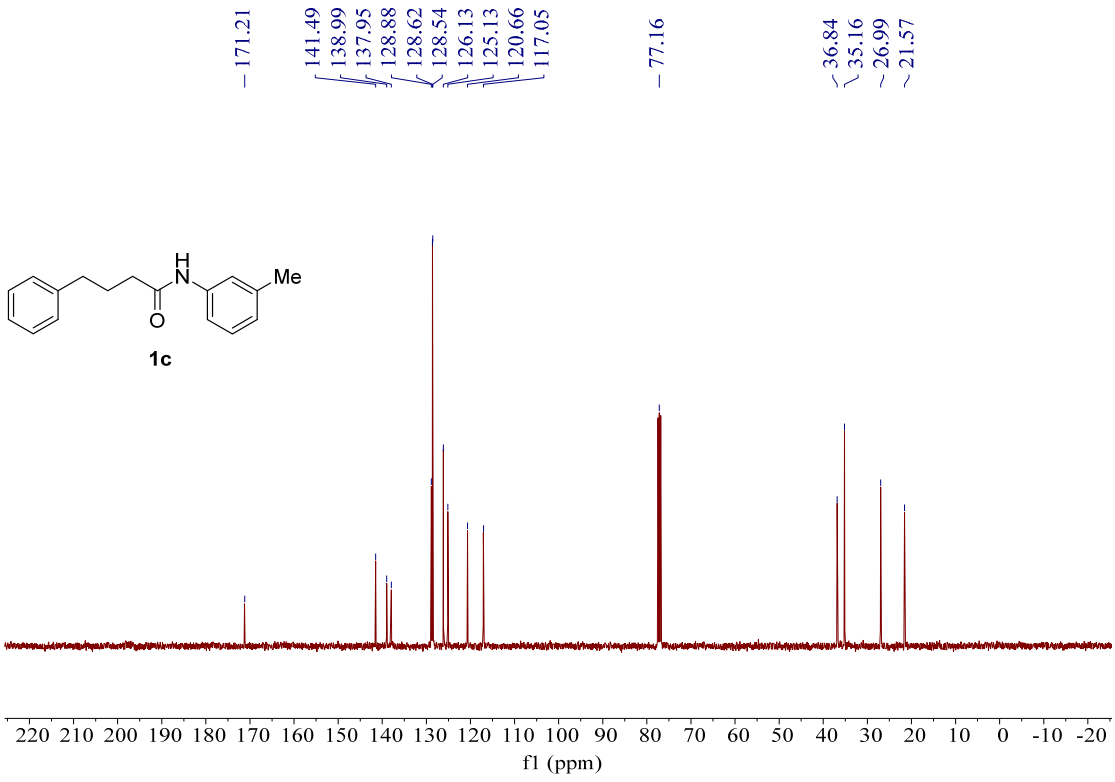
^{1}H NMR spectrum of **1b**



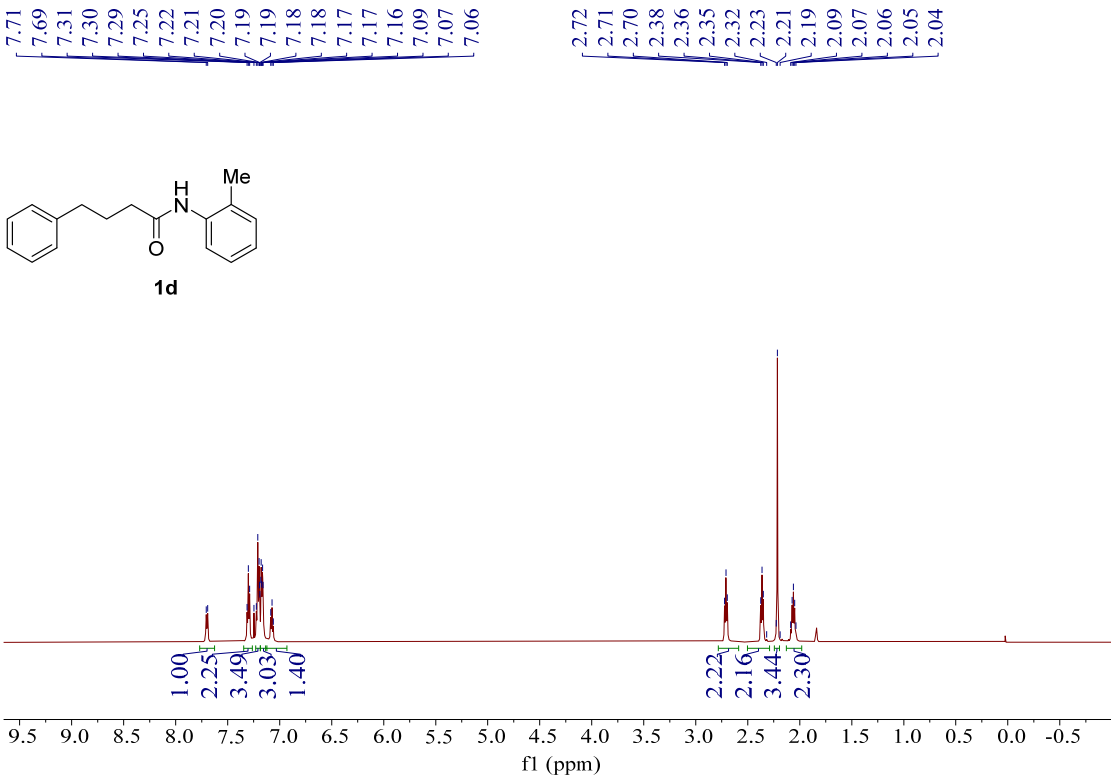
^{13}C NMR spectrum of **1b**



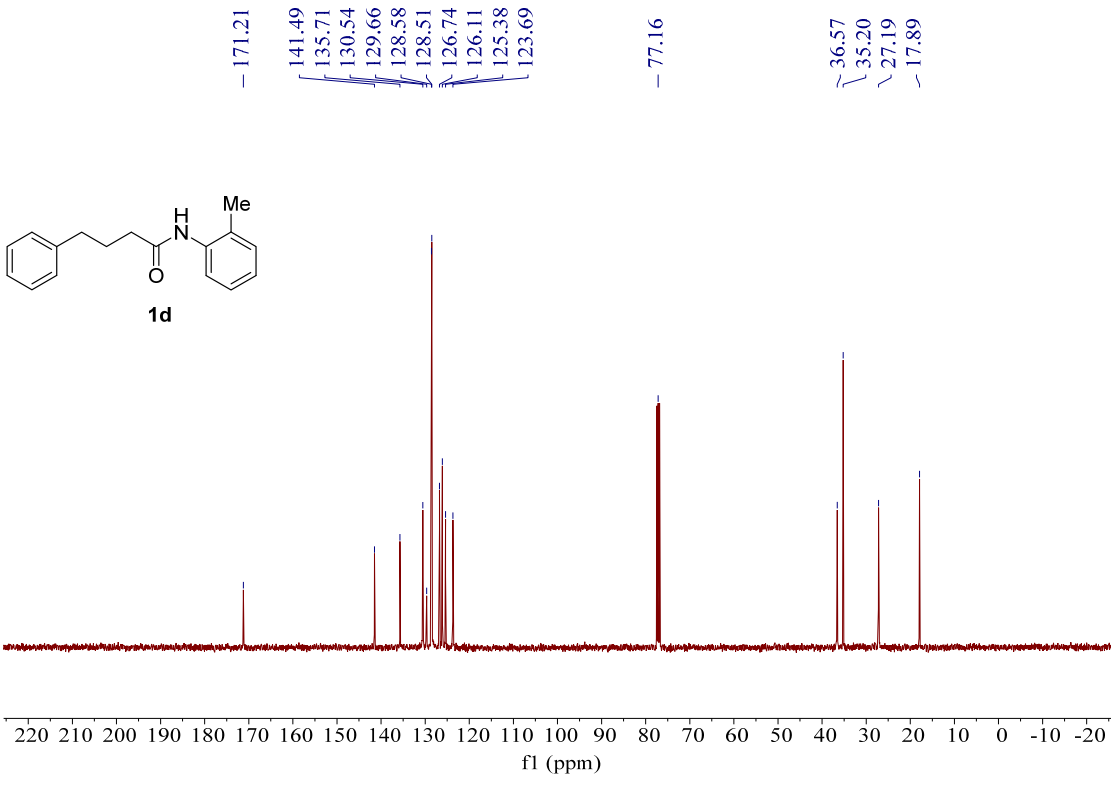
^{1}H NMR spectrum of **1c**



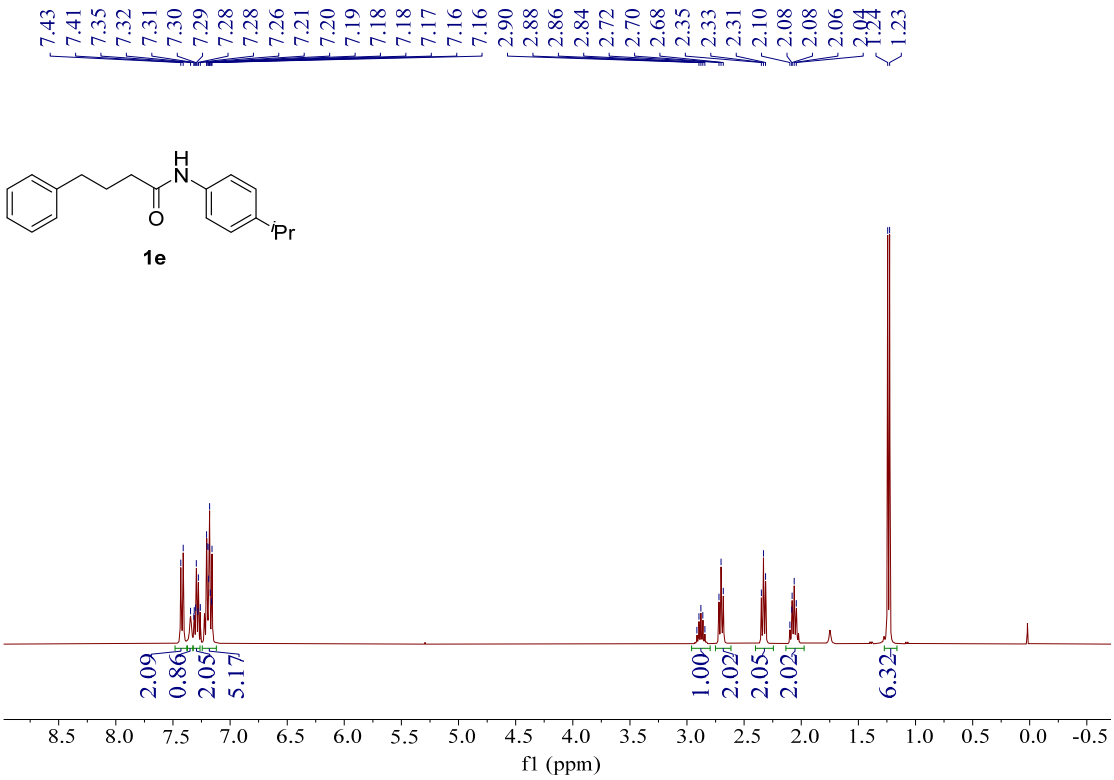
^{13}C NMR spectrum of **1c**



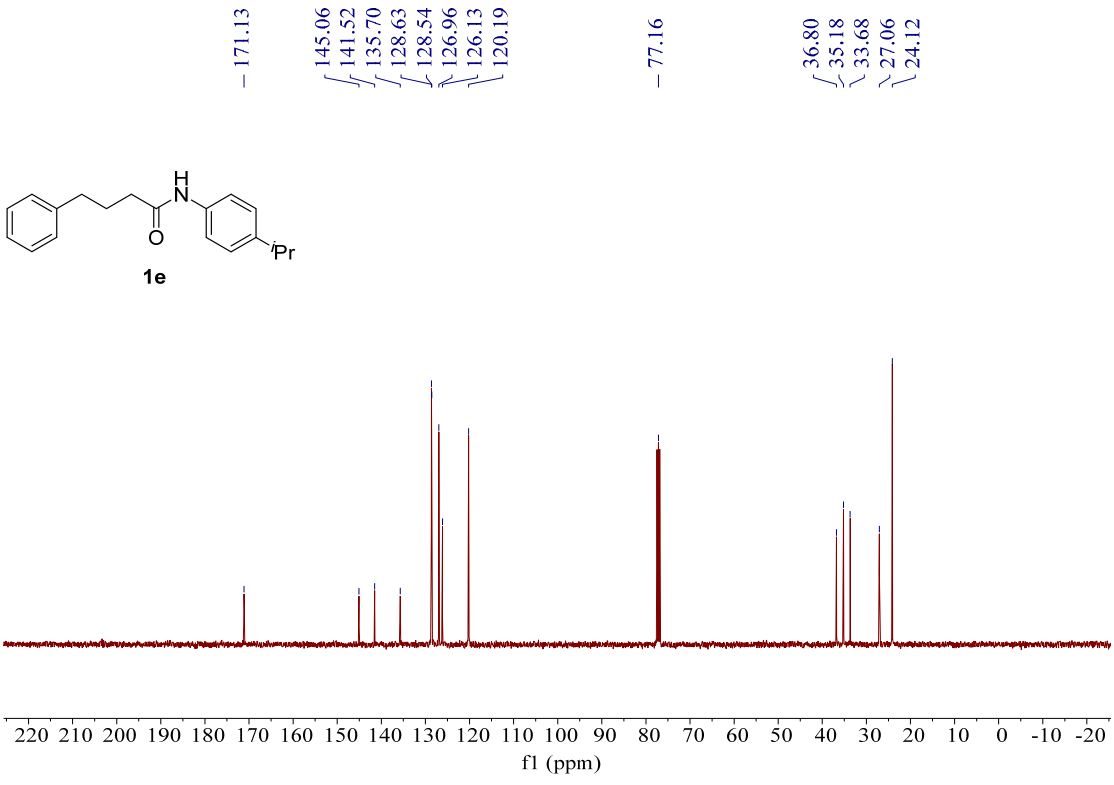
^{1}H NMR spectrum of **1d**



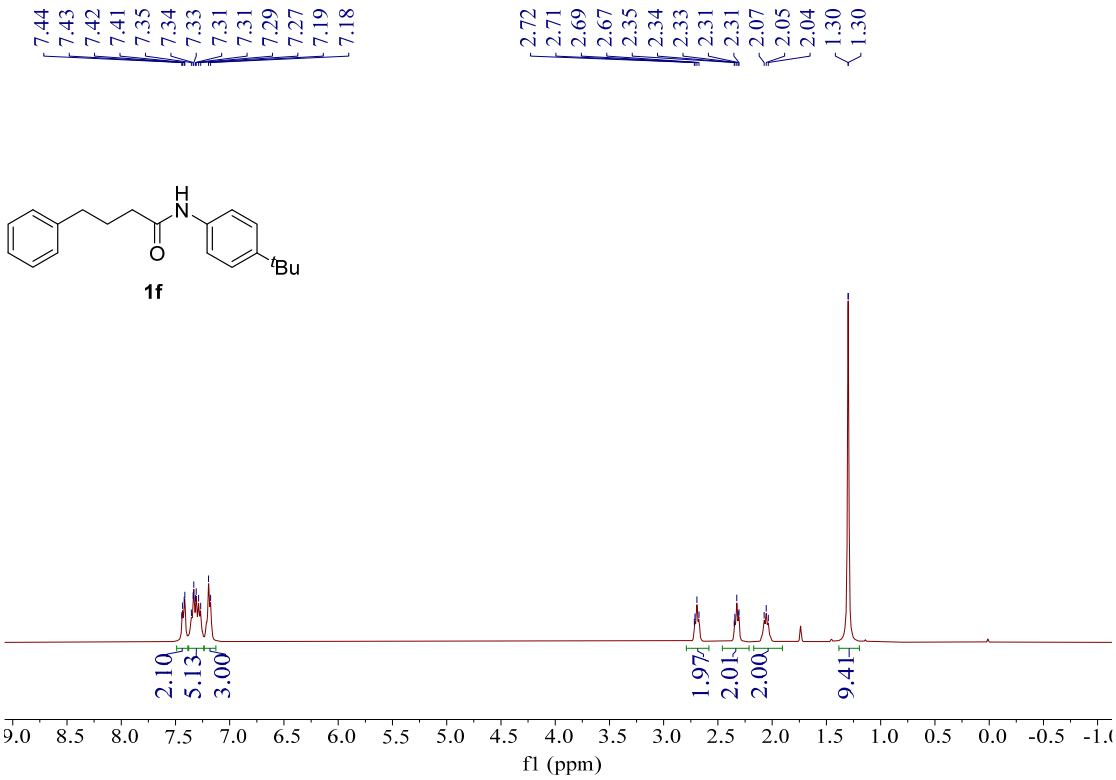
^{13}C NMR spectrum of **1d**



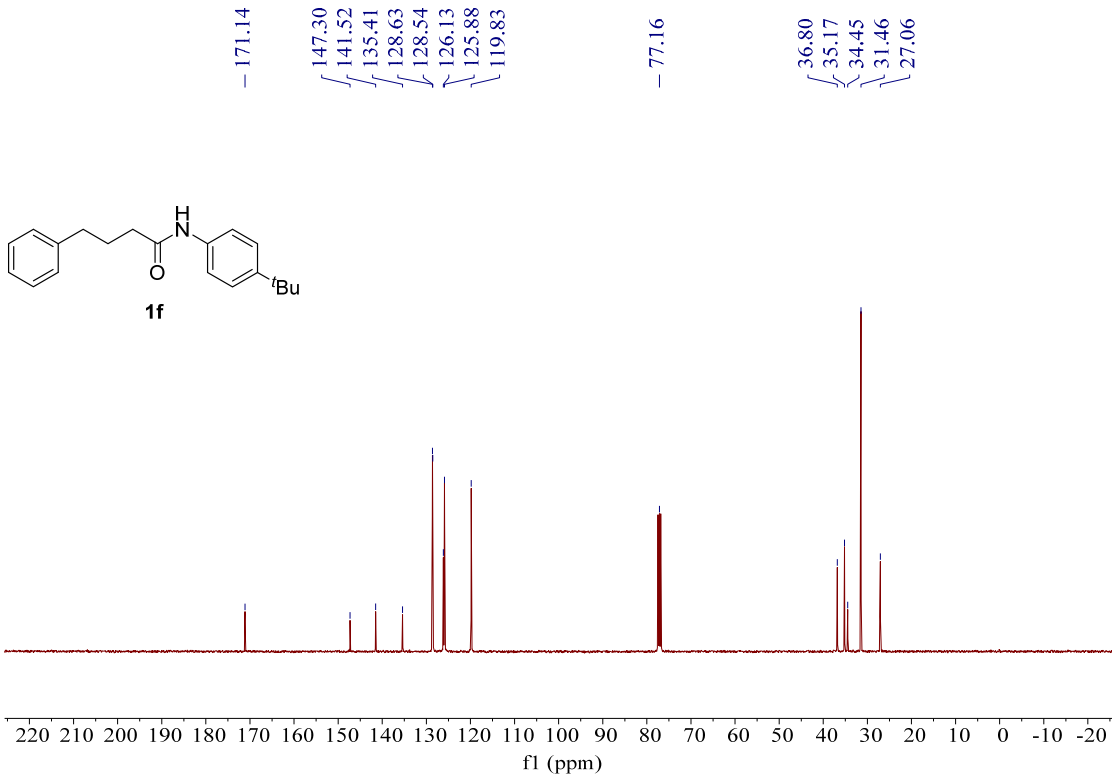
^{1}H NMR spectrum of **1e**



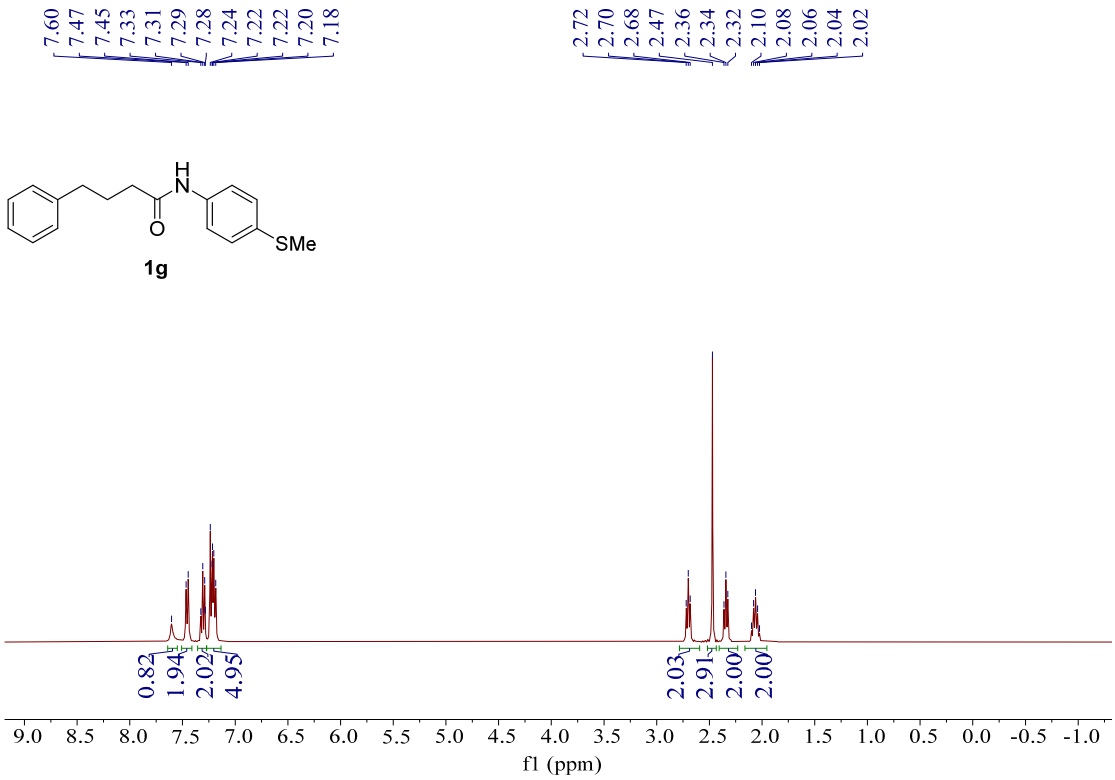
^{13}C NMR spectrum of **1e**



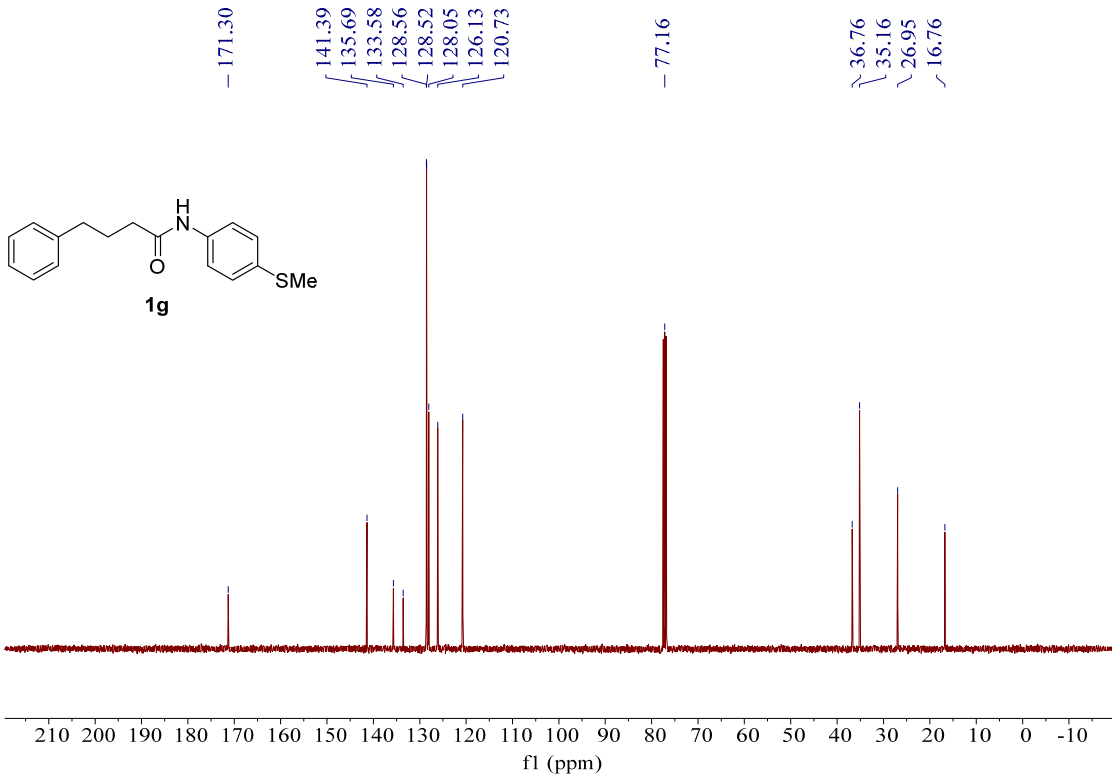
^{1}H NMR spectrum of **1f**



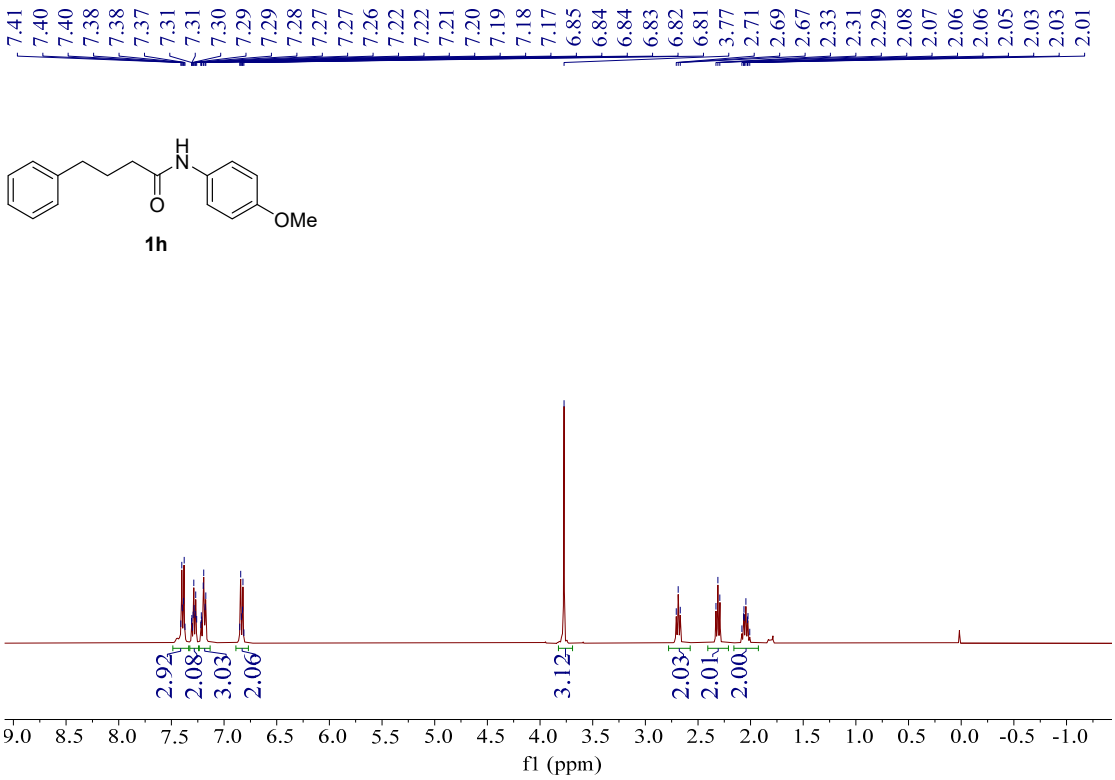
^{13}C NMR spectrum of **1f**



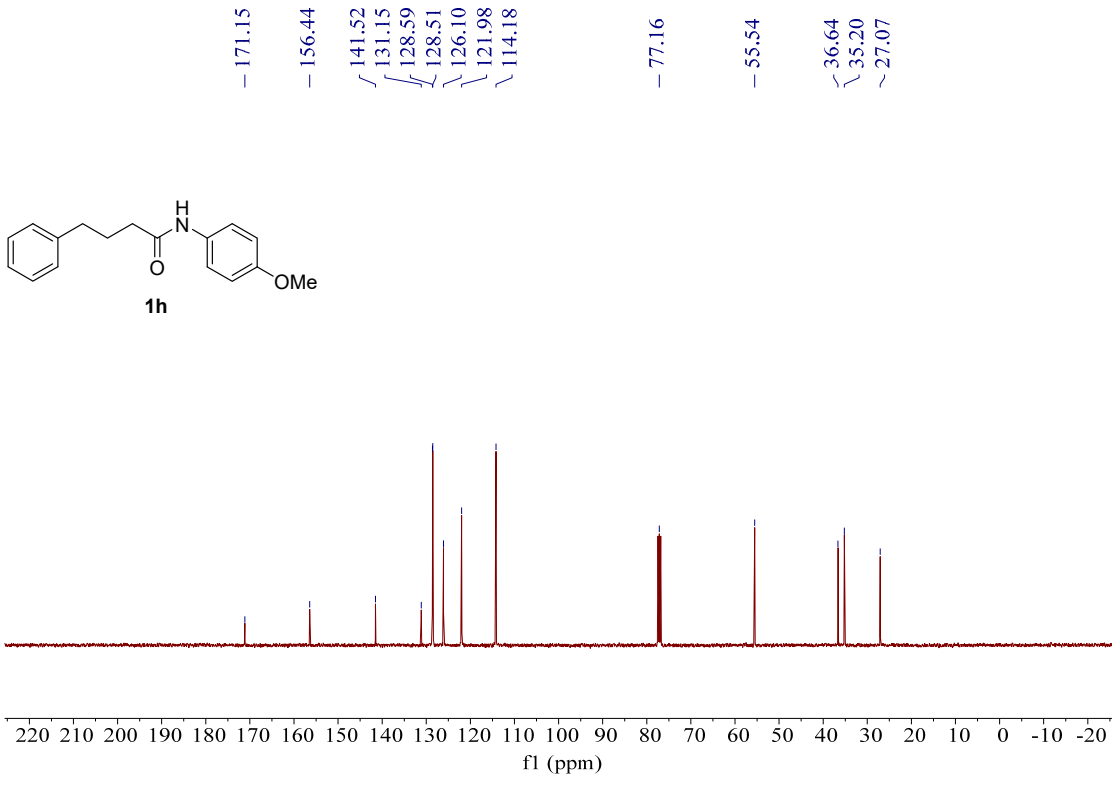
^{1}H NMR spectrum of **1g**



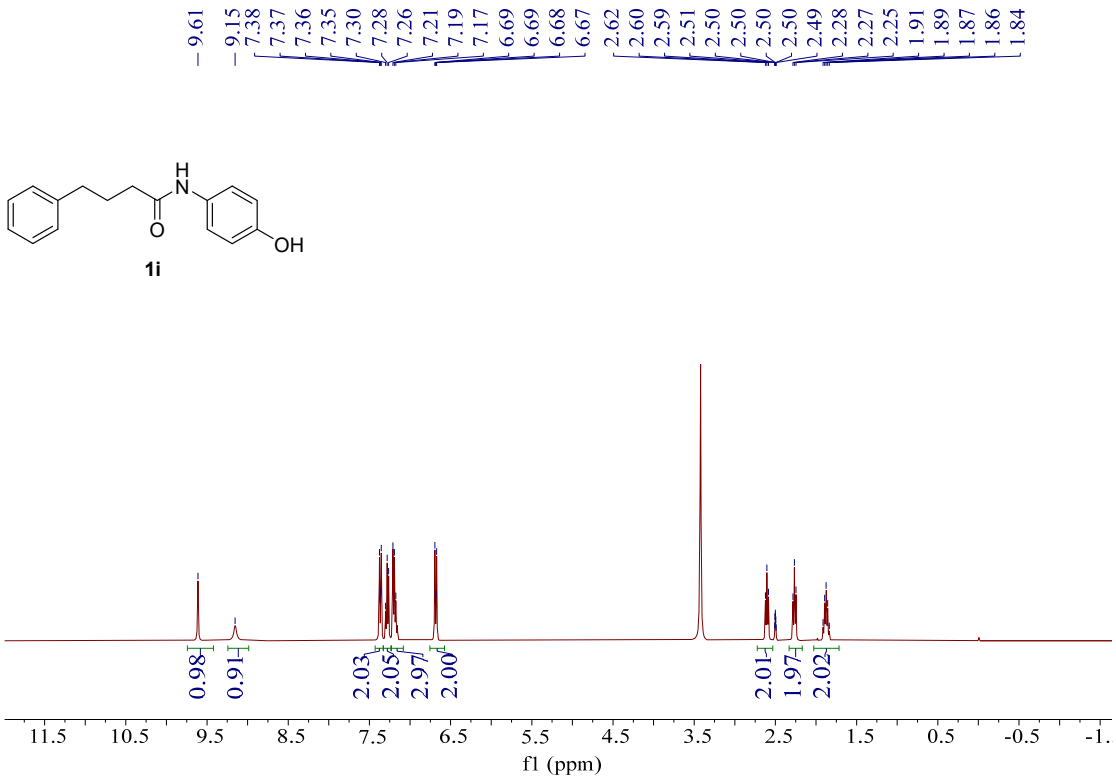
^{13}C NMR spectrum of **1g**



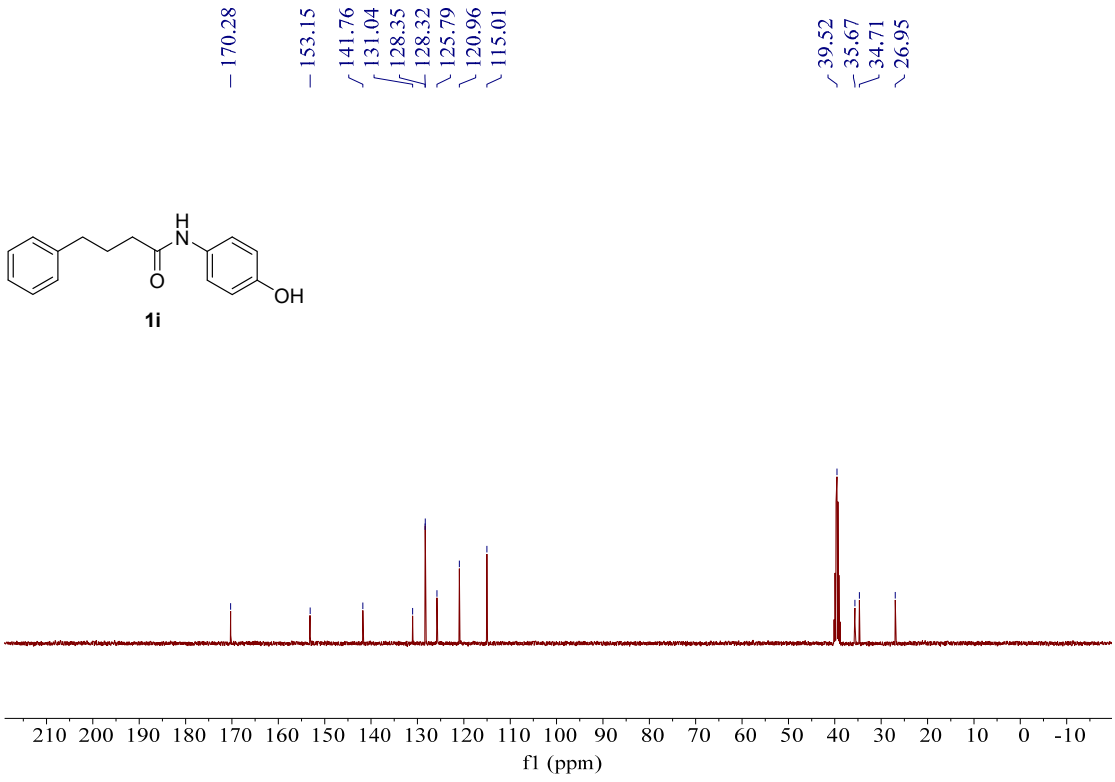
^{1}H NMR spectrum of **1h**



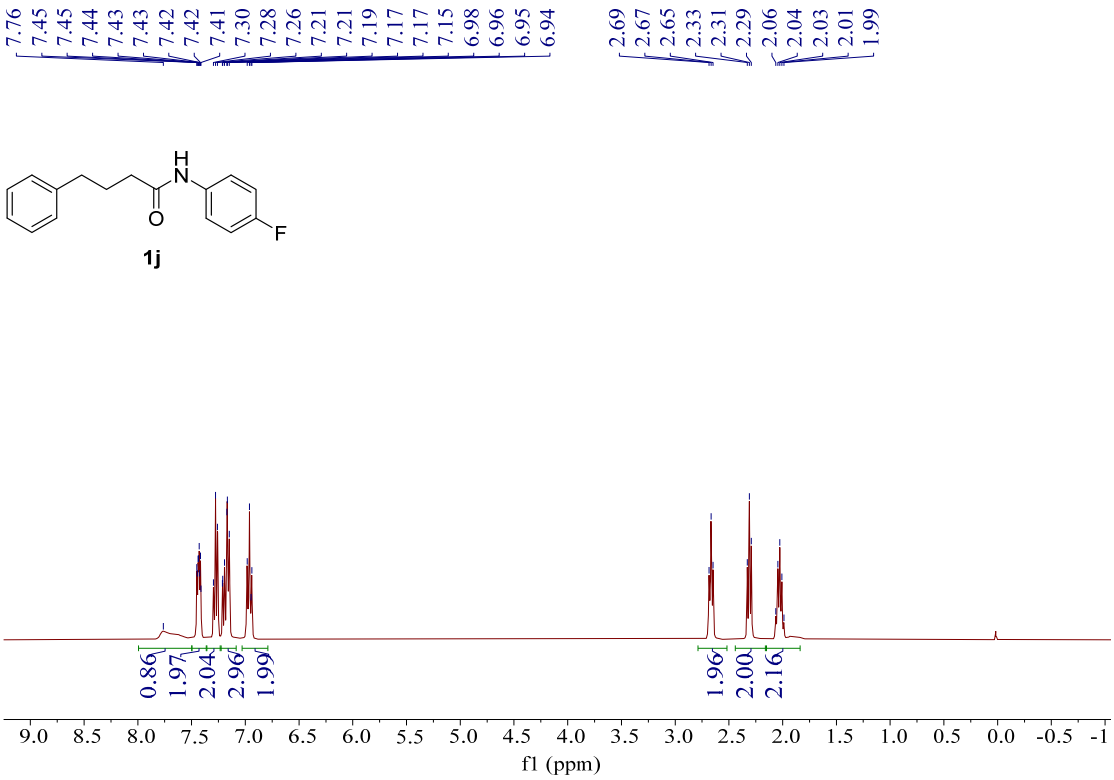
^{13}C NMR spectrum of **1h**



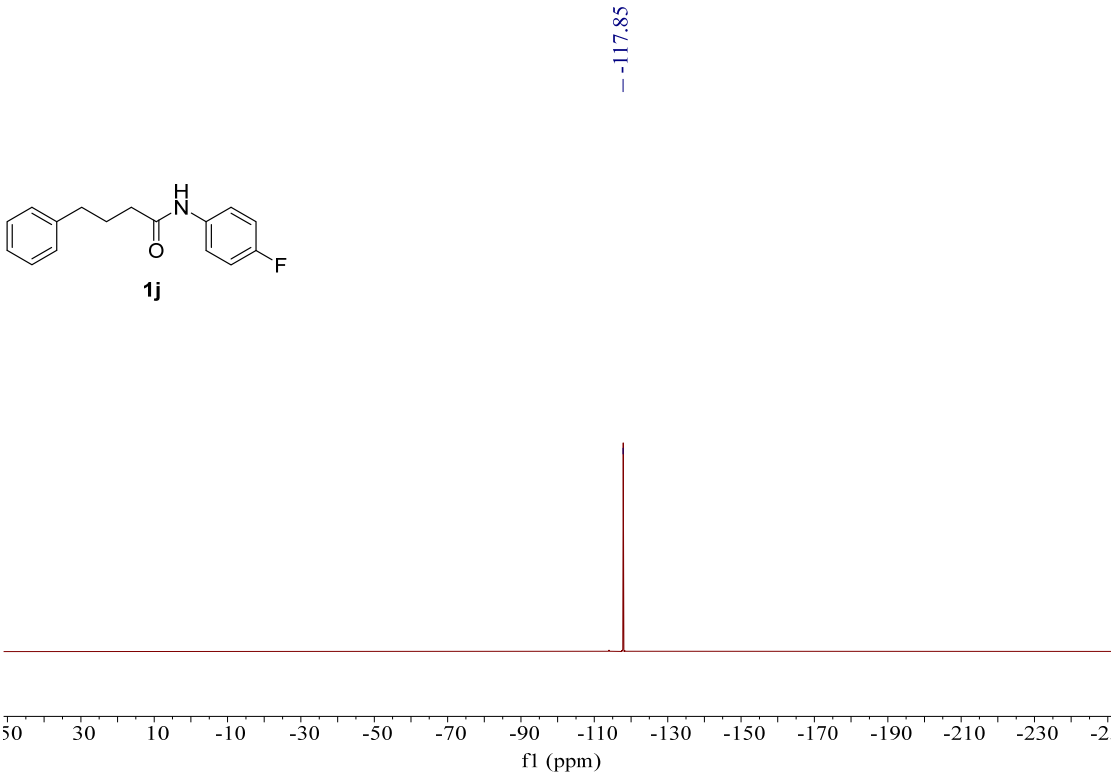
^{1}H NMR spectrum of **1i**



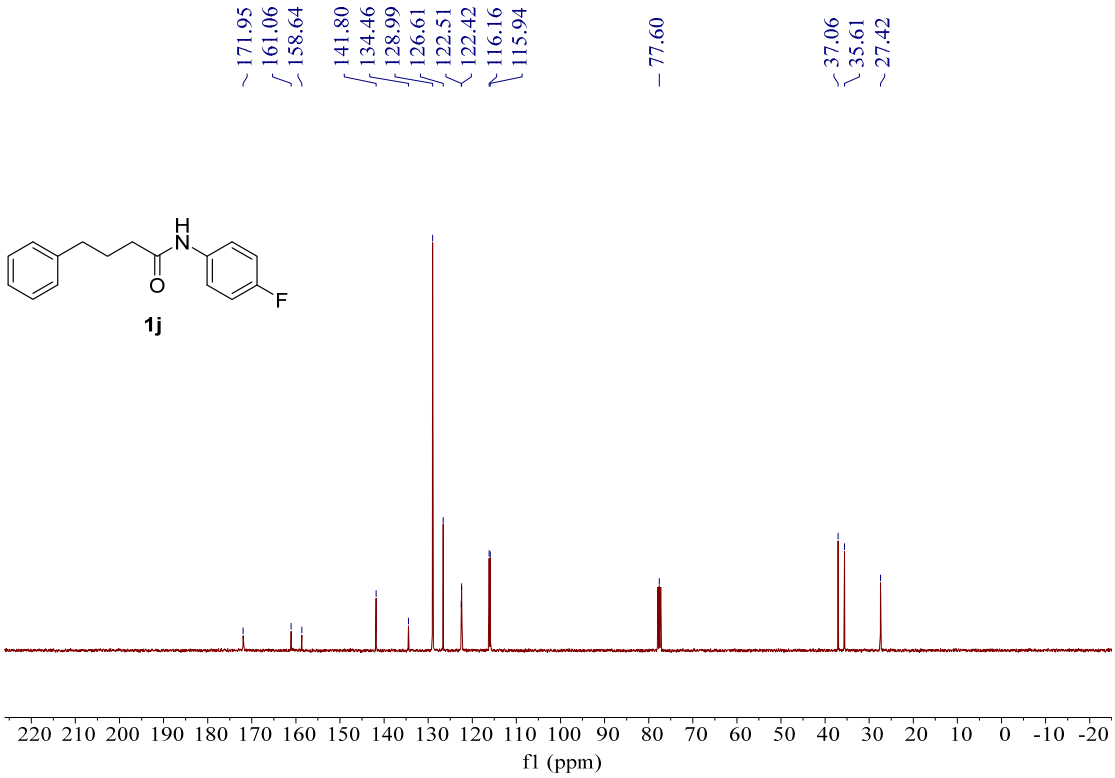
^{13}C NMR spectrum of **1i**



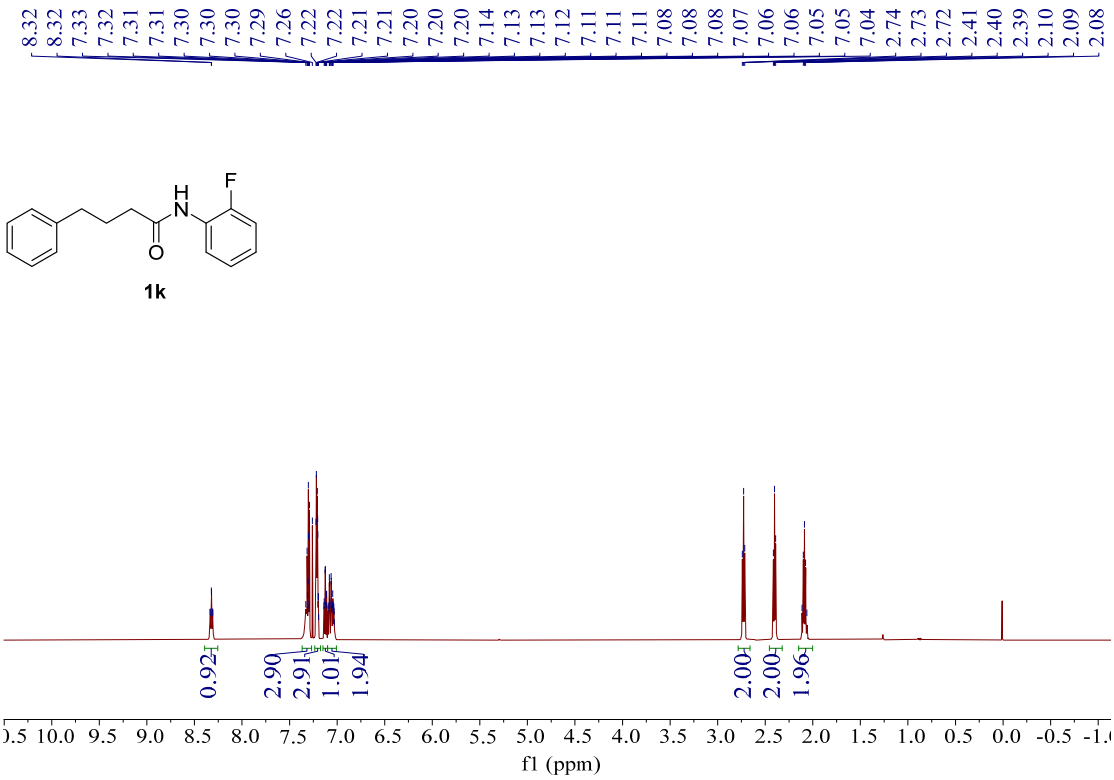
^{1}H NMR spectrum of **1j**



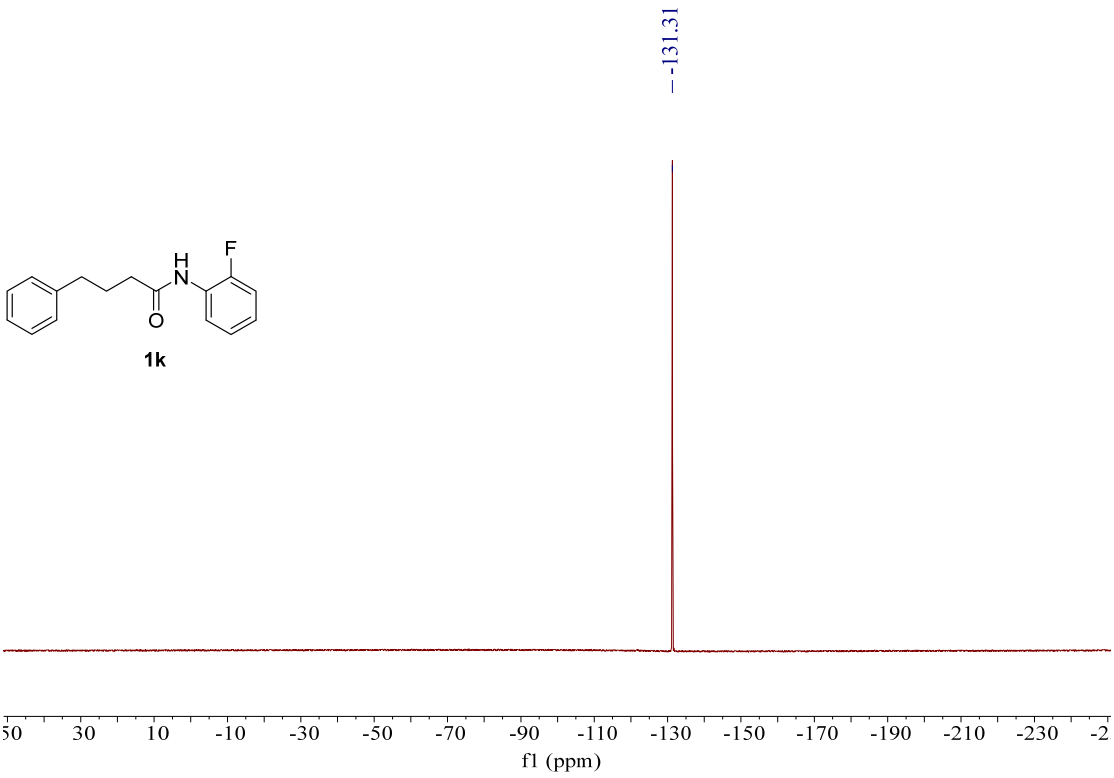
^{19}F NMR spectrum of **1j**



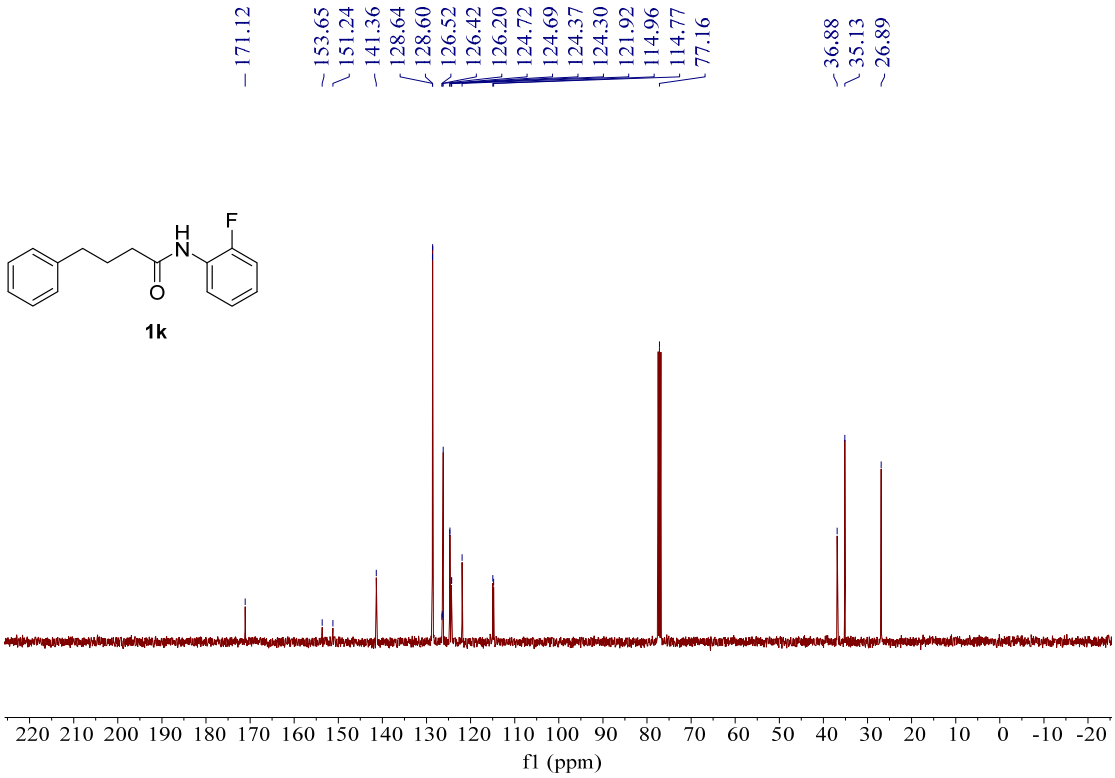
^{13}C NMR spectrum of **1j**



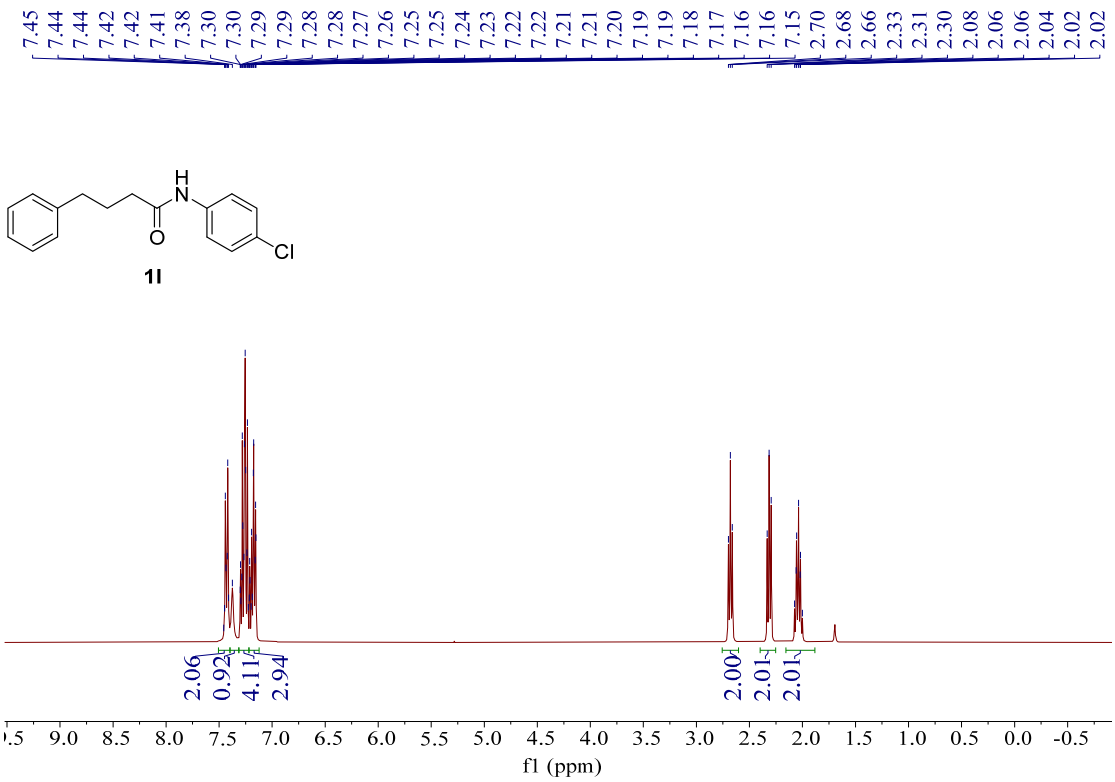
^{1}H NMR spectrum of **1k**



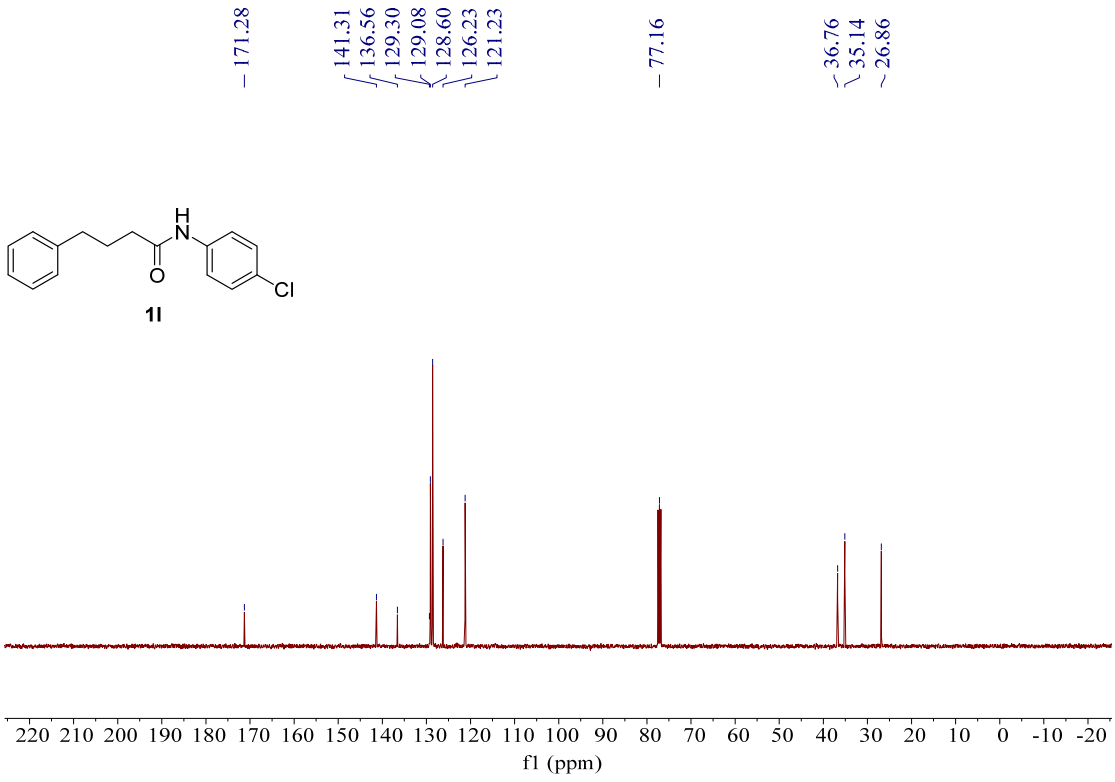
^{19}F NMR spectrum of **1k**



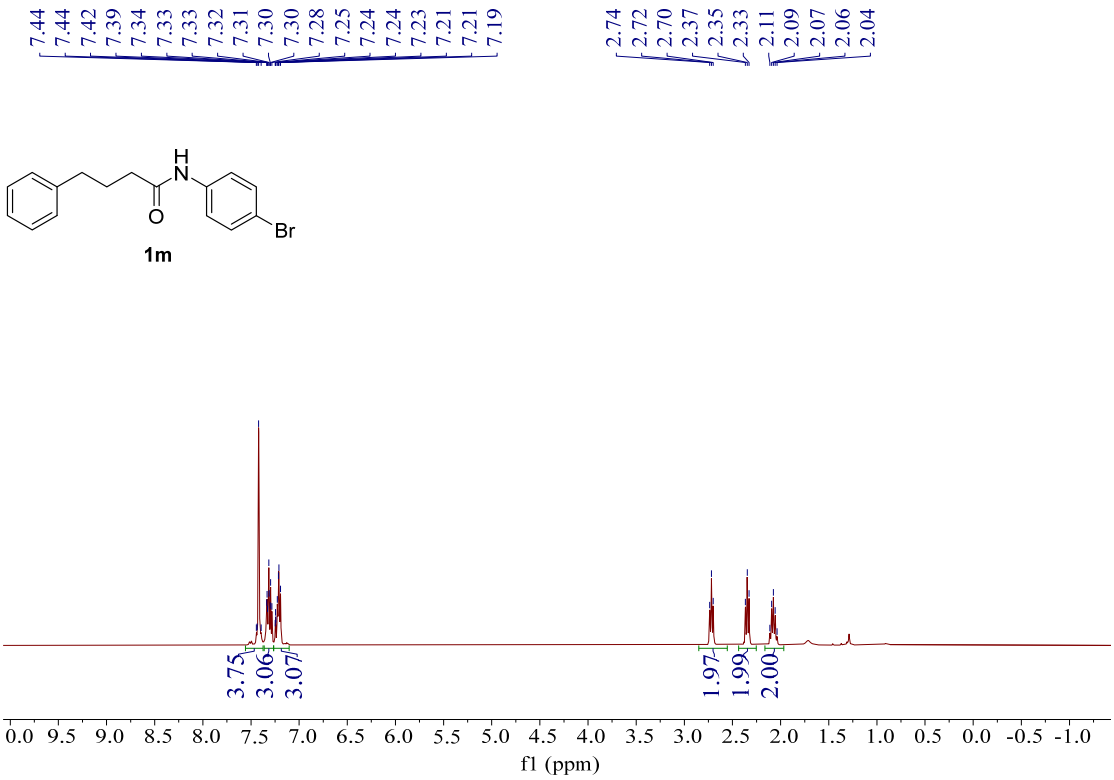
^{13}C NMR spectrum of **1k**



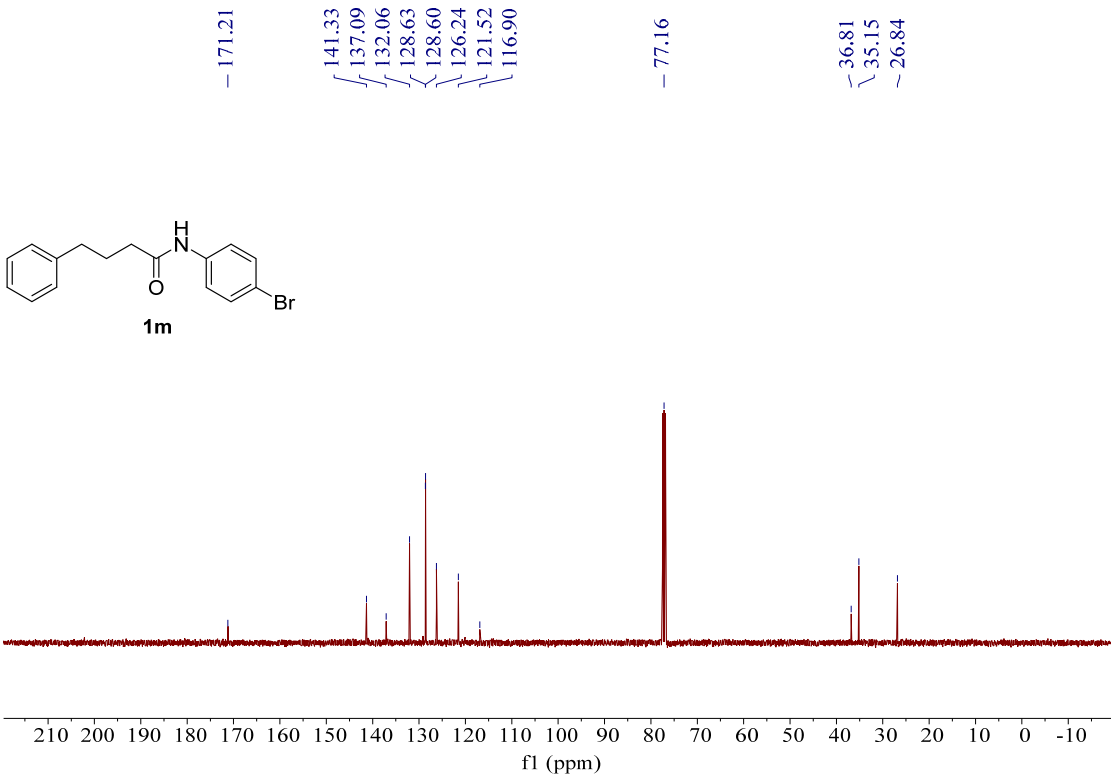
^{1}H NMR spectrum of **1l**



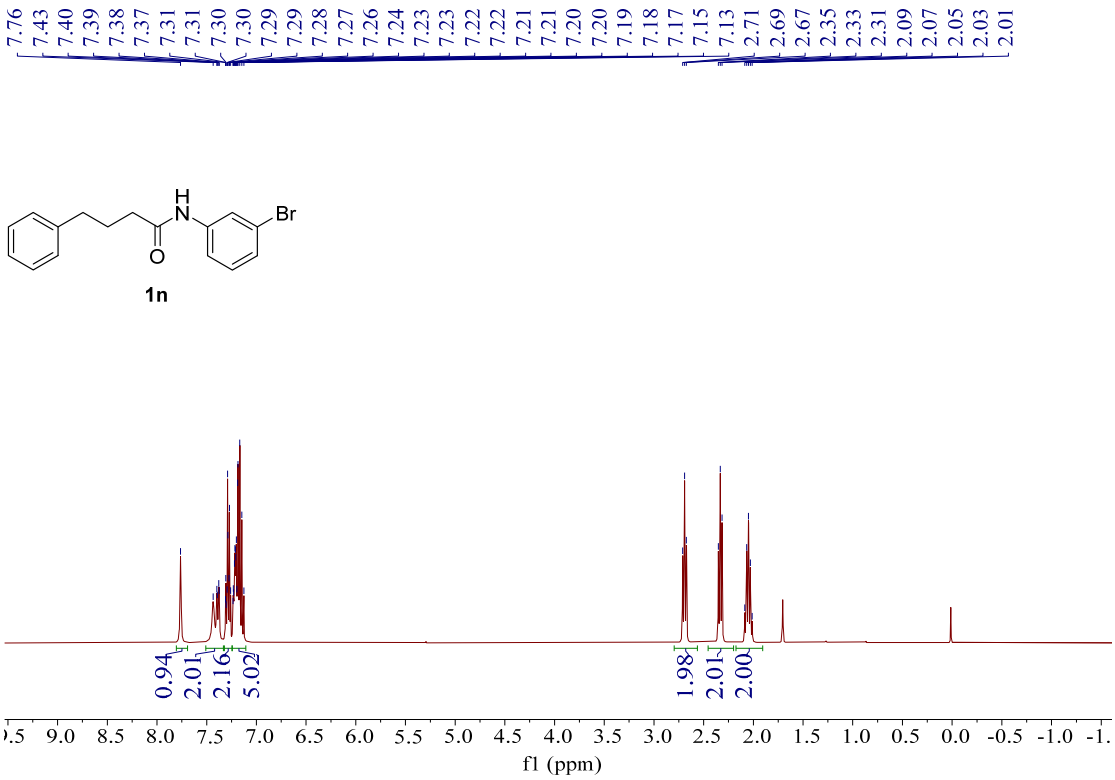
^{13}C NMR spectrum of **1l**



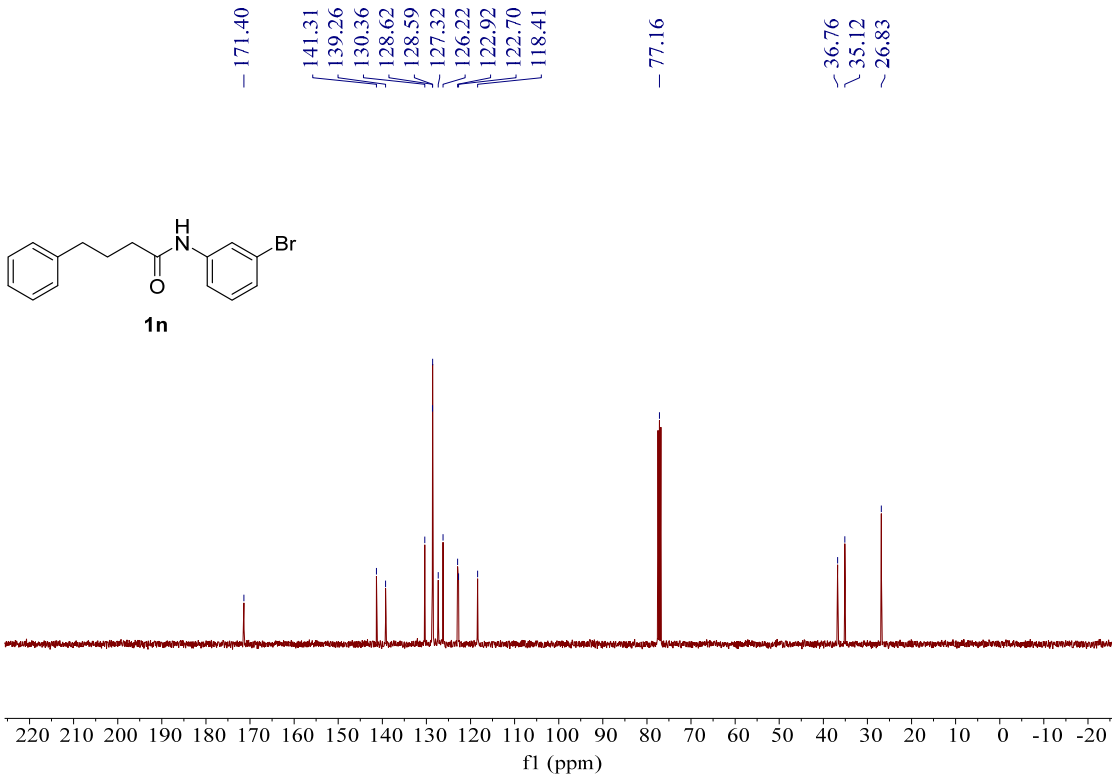
^{1}H NMR spectrum of **1m**



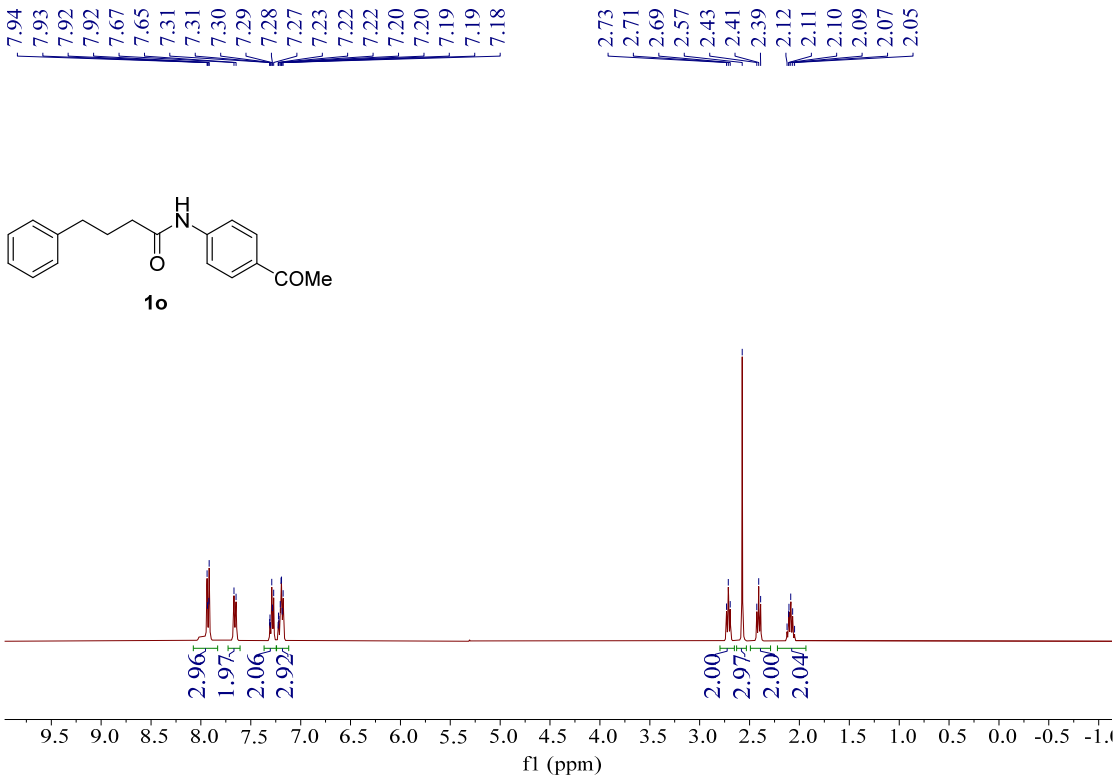
^{13}C NMR spectrum of **1m**



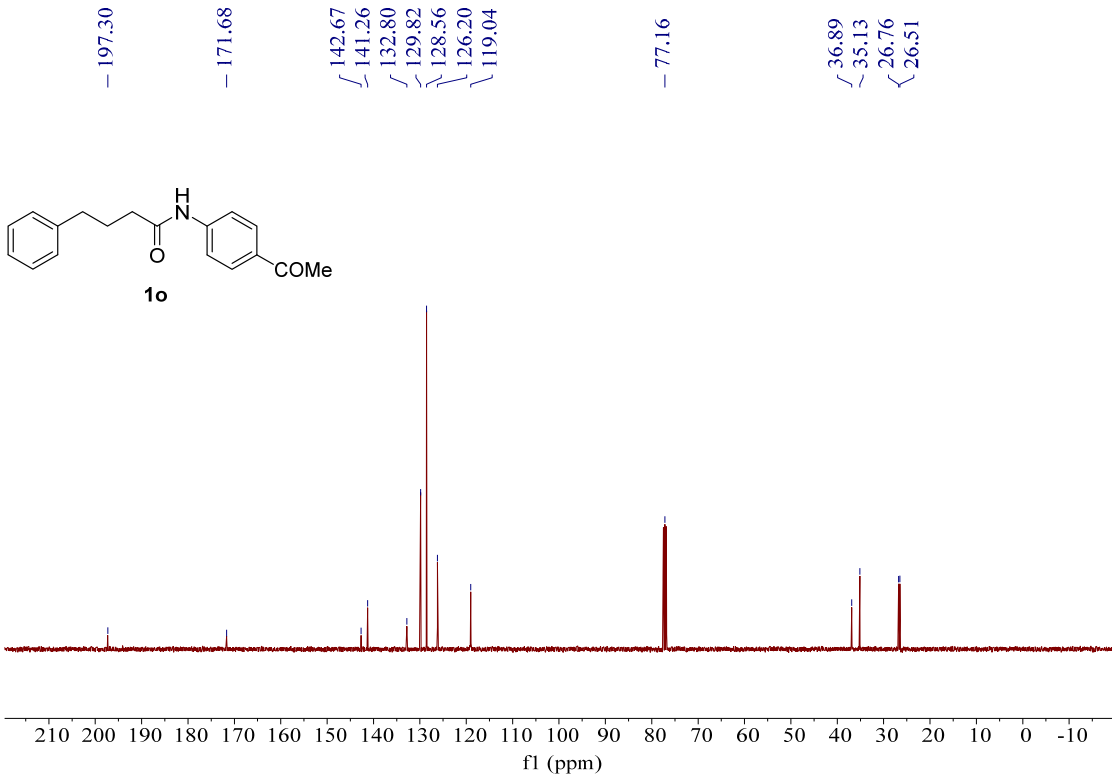
^{1}H NMR spectrum of **1n**



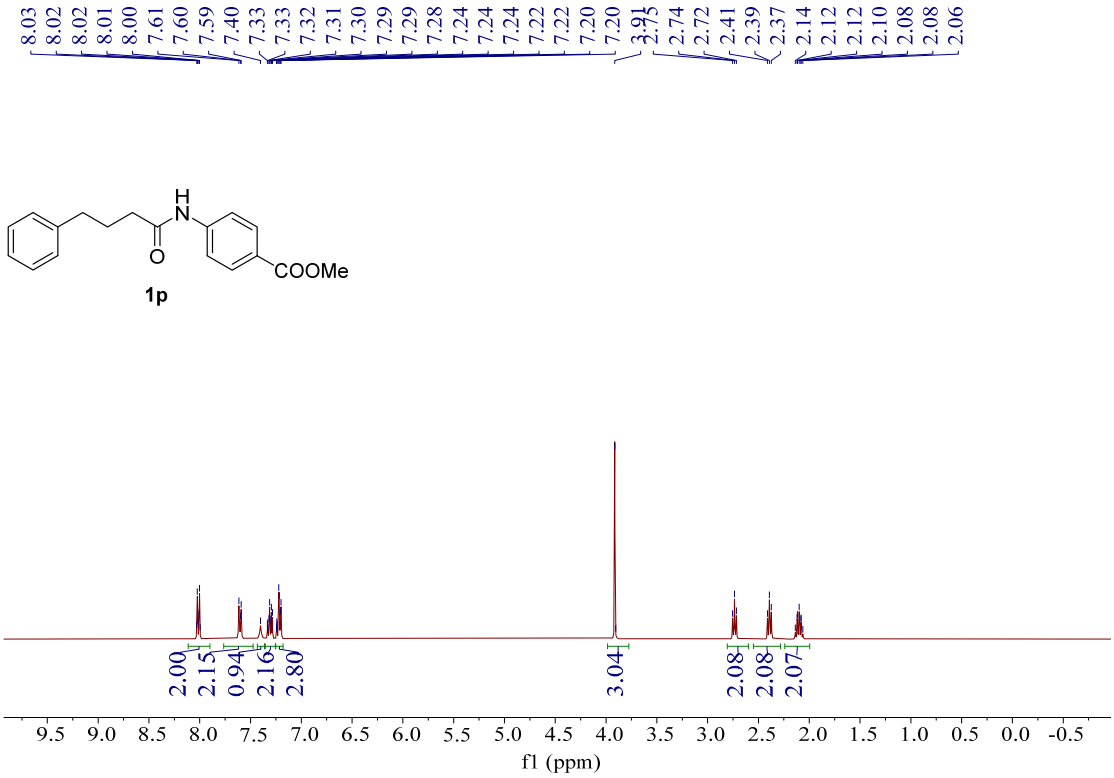
^{13}C NMR spectrum of **1n**



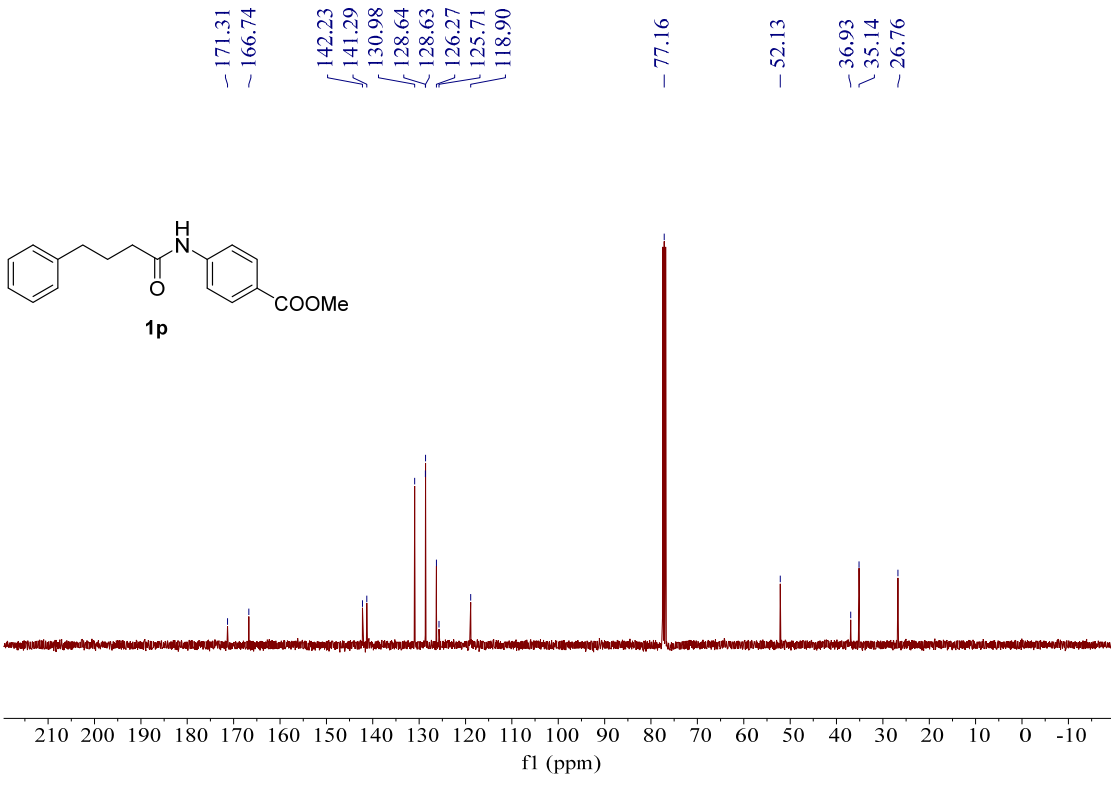
^{1}H NMR spectrum of **1o**



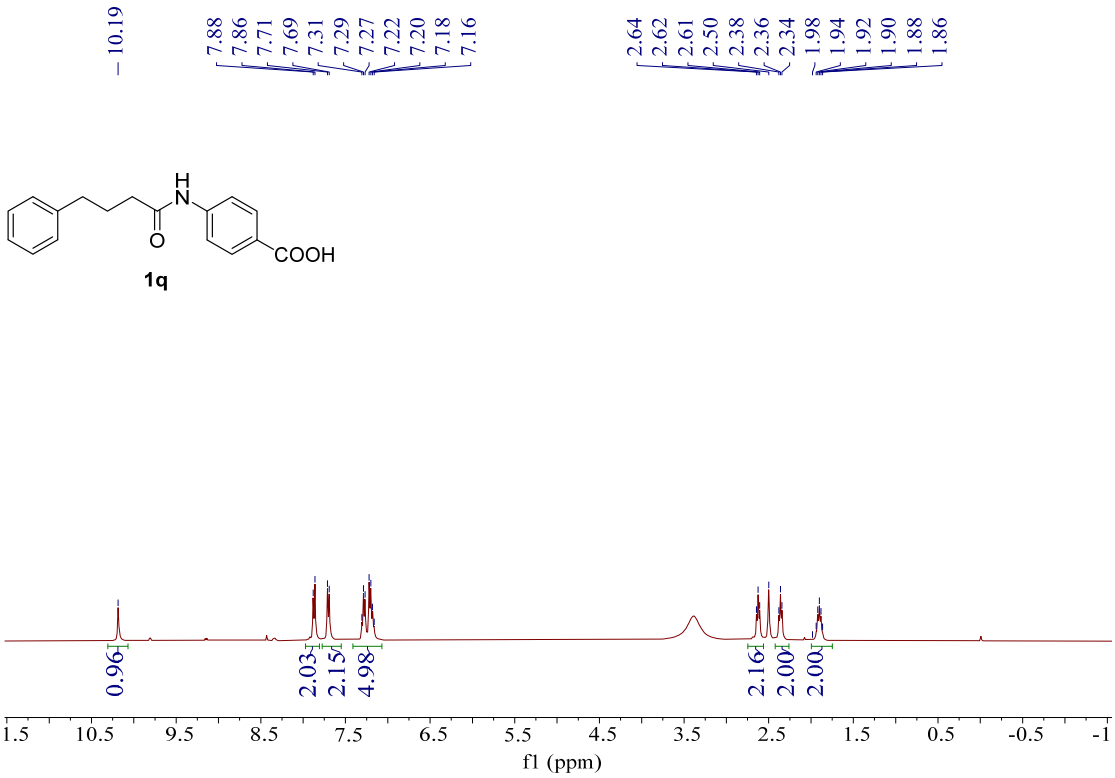
^{13}C NMR spectrum of **1o**



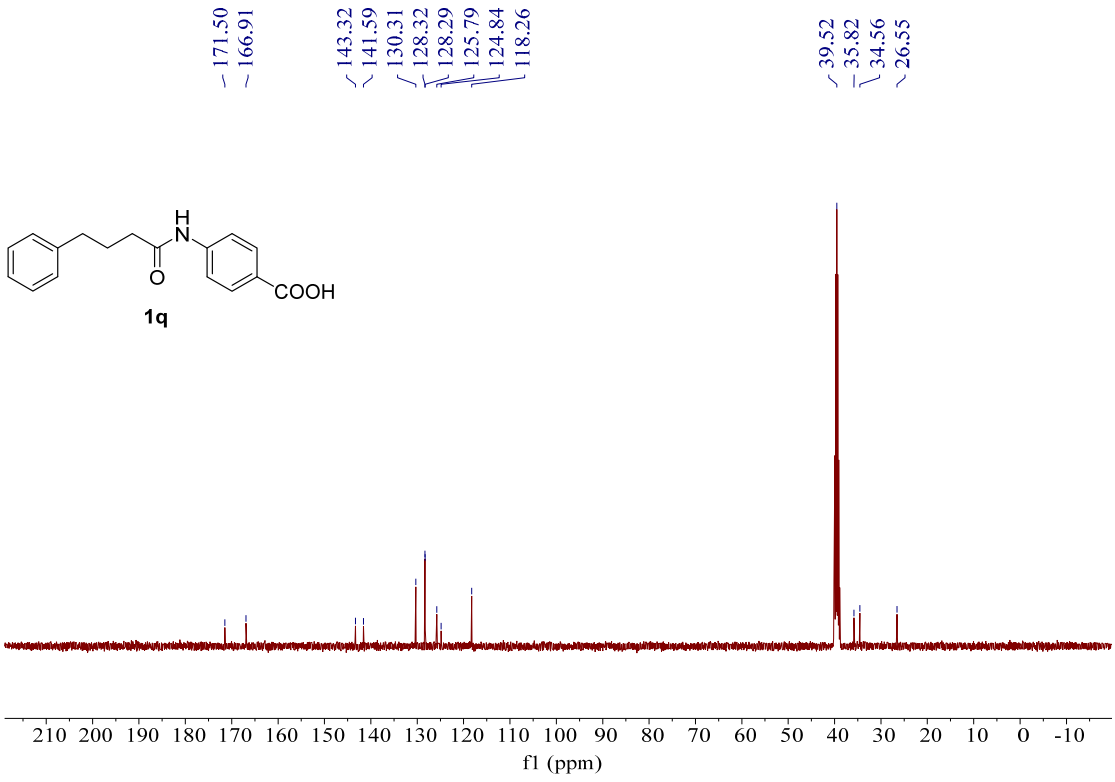
^{1}H NMR spectrum of **1p**



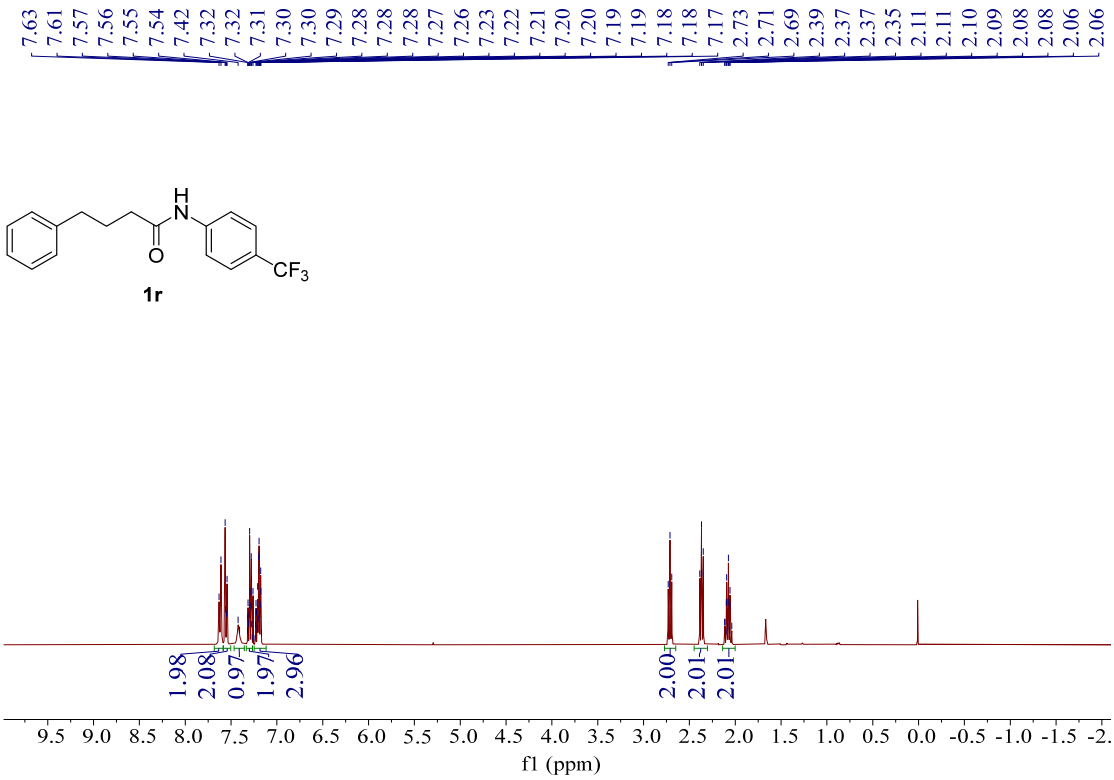
^{13}C NMR spectrum of **1p**



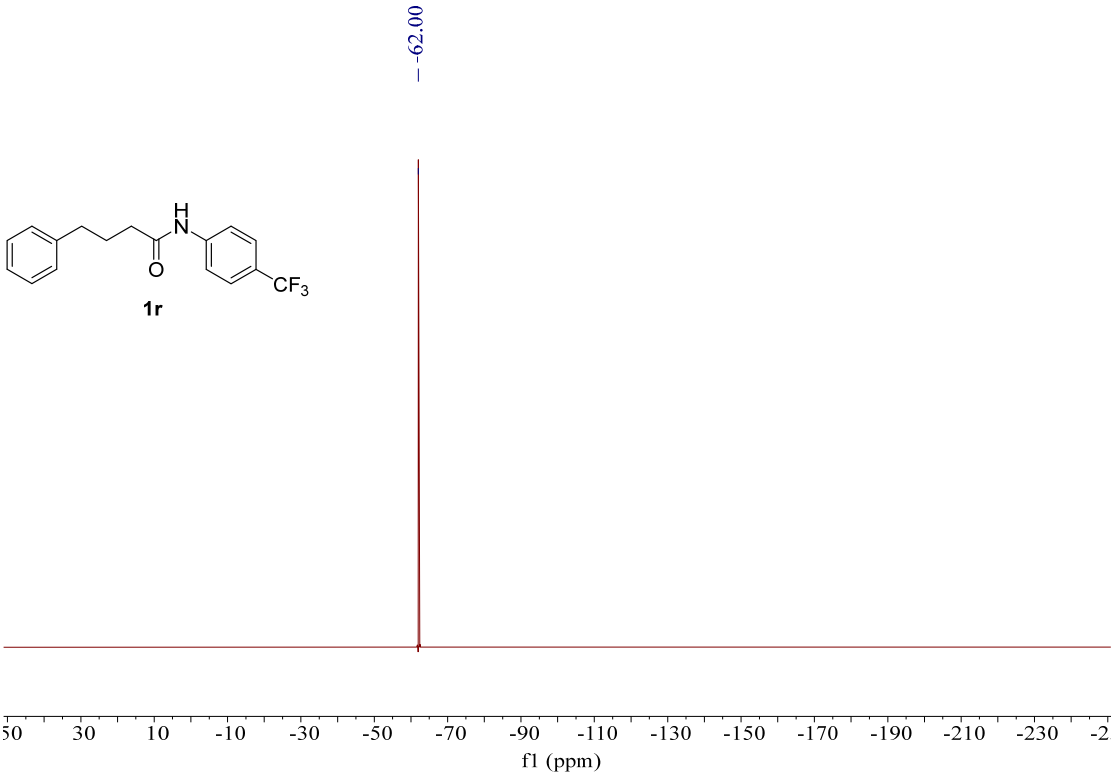
^{1}H NMR spectrum of **1q**



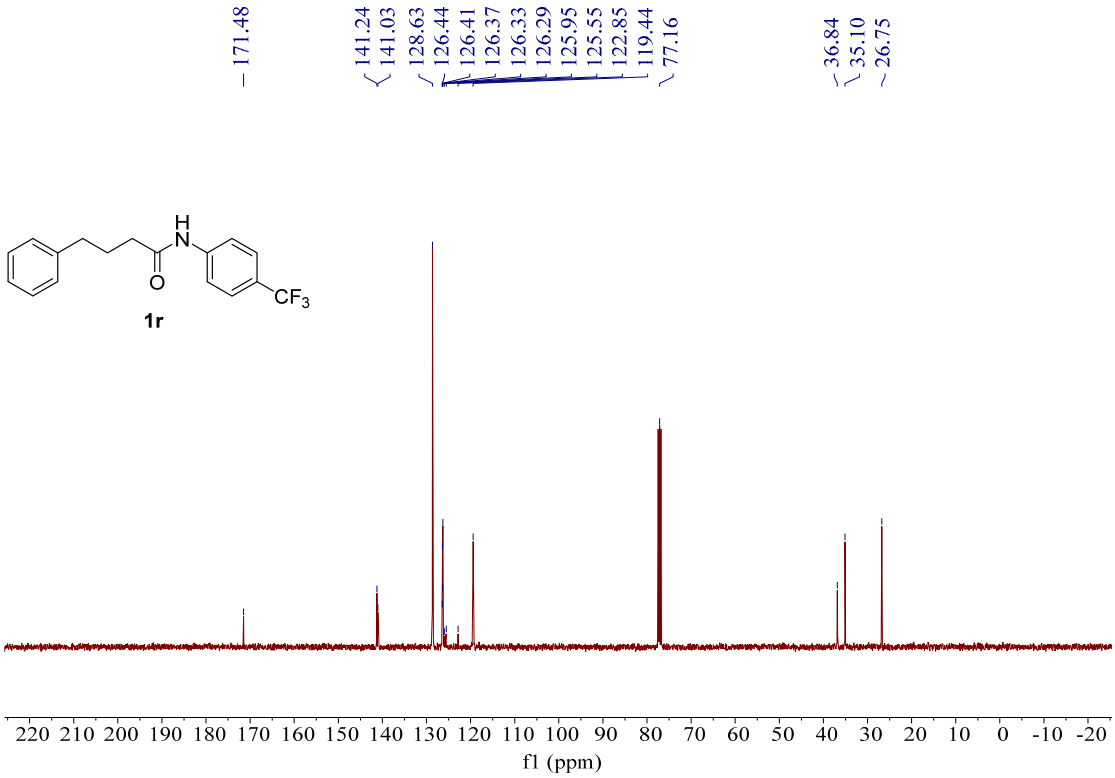
^{13}C NMR spectrum of **1q**



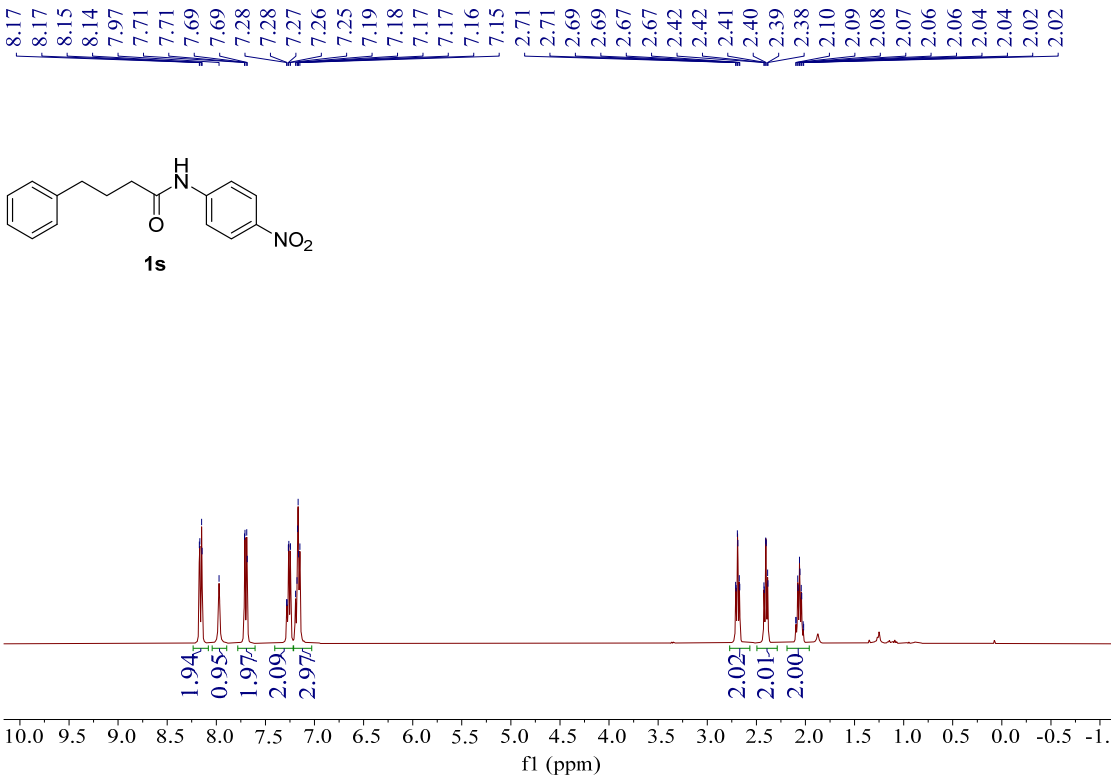
^{1}H NMR spectrum of **1r**



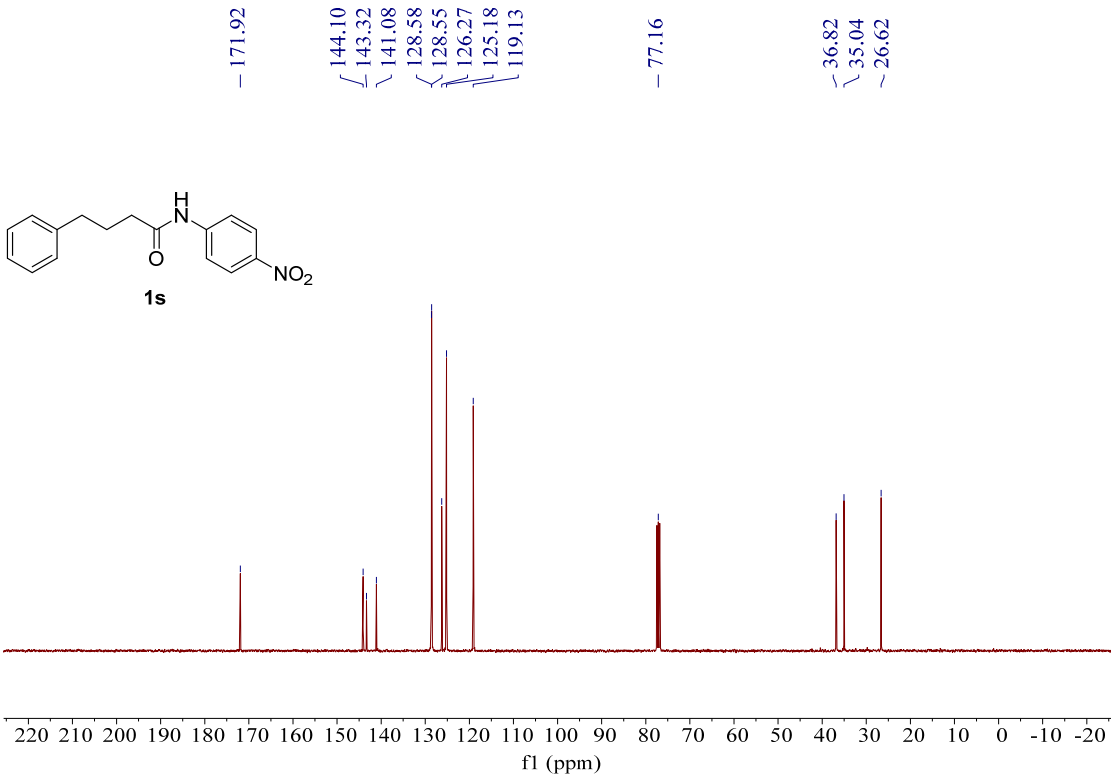
^{19}F NMR spectrum of **1r**



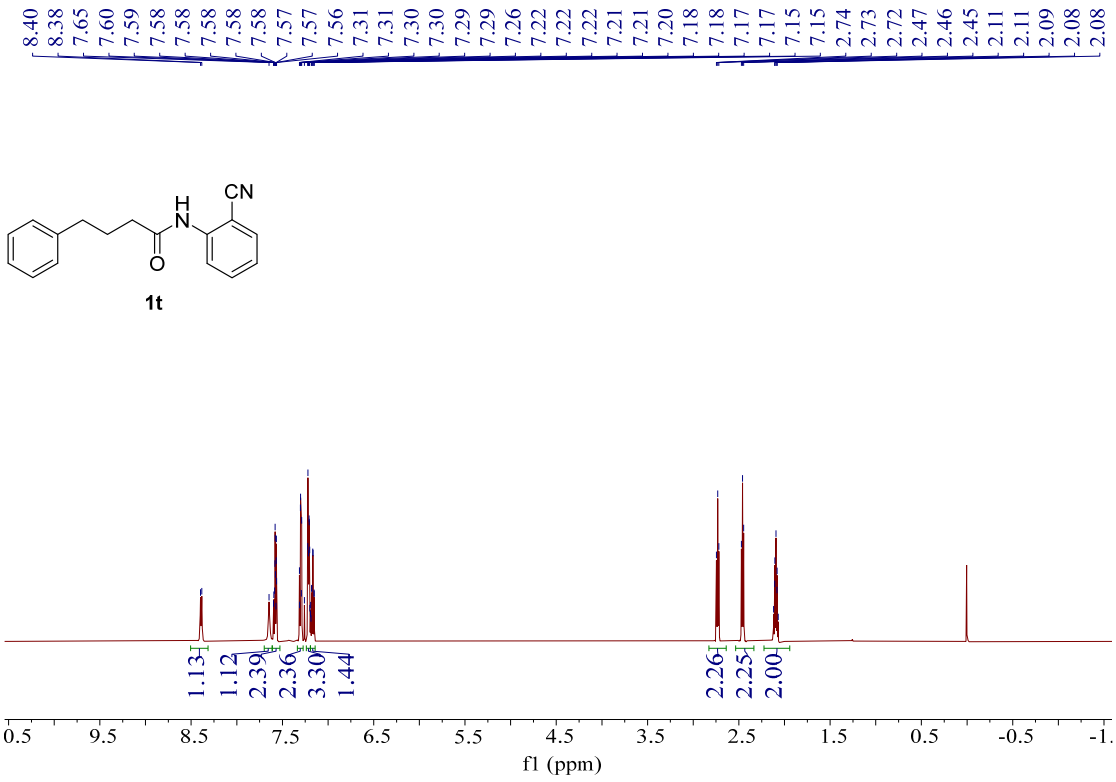
^{13}C NMR spectrum of **1r**



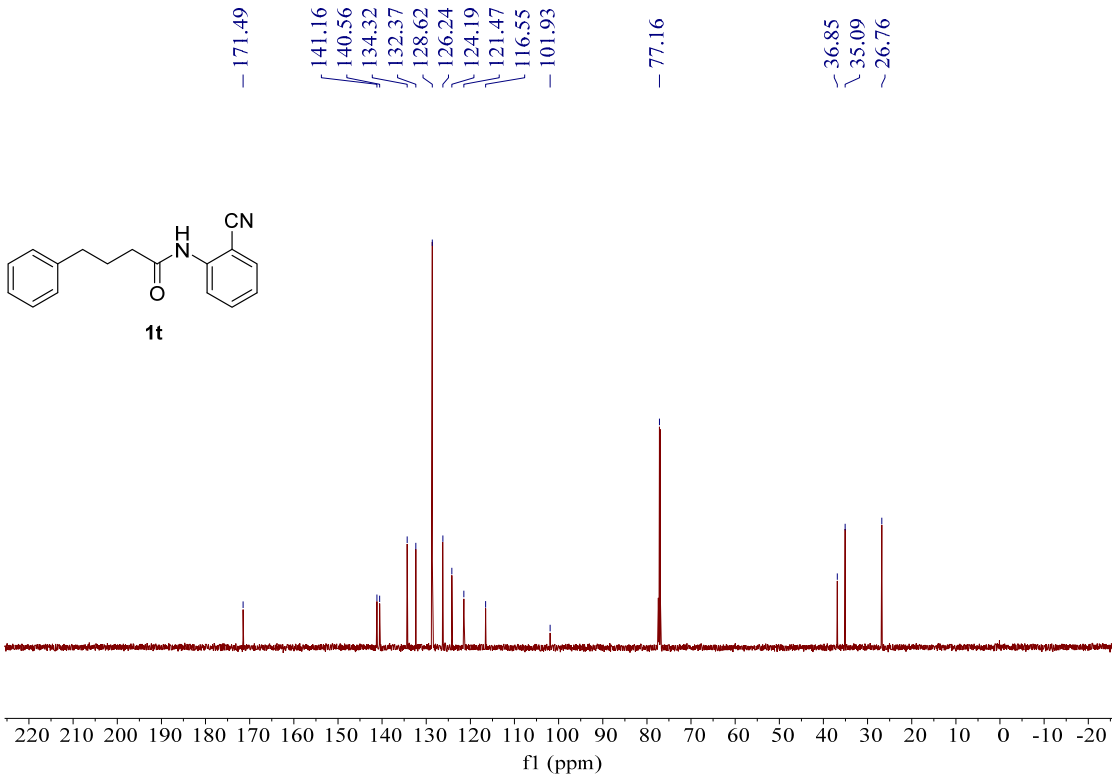
^{1}H NMR spectrum of **1s**



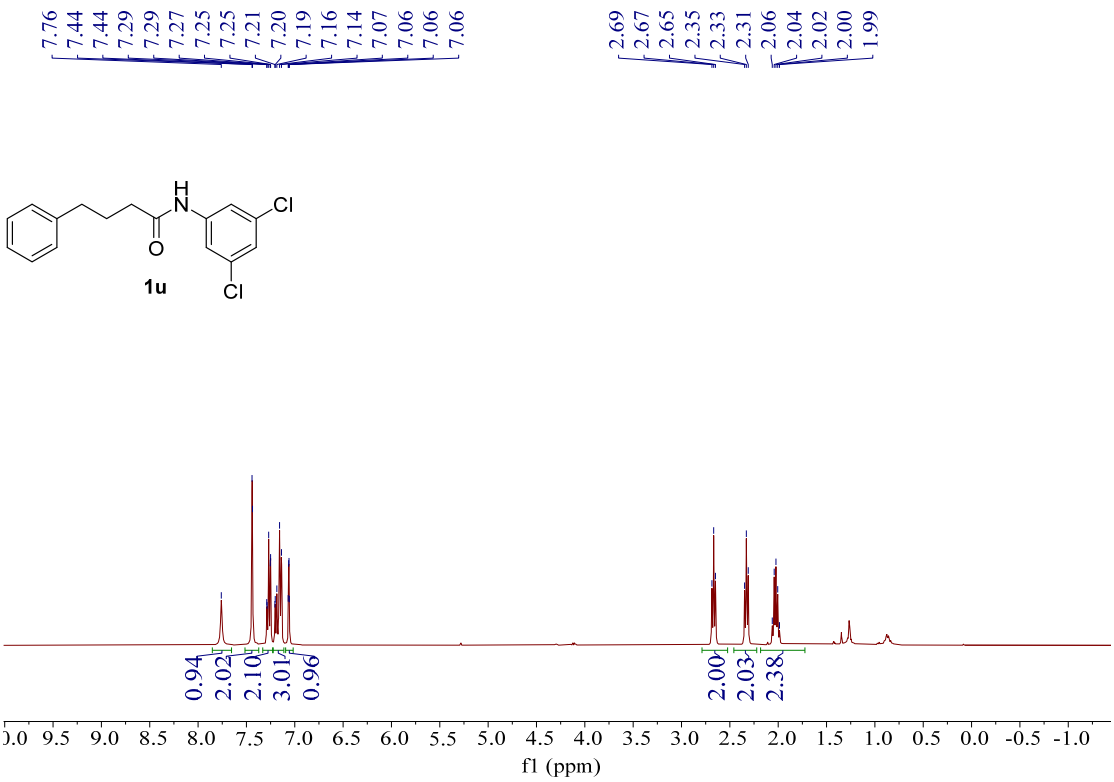
^{13}C NMR spectrum of **1s**



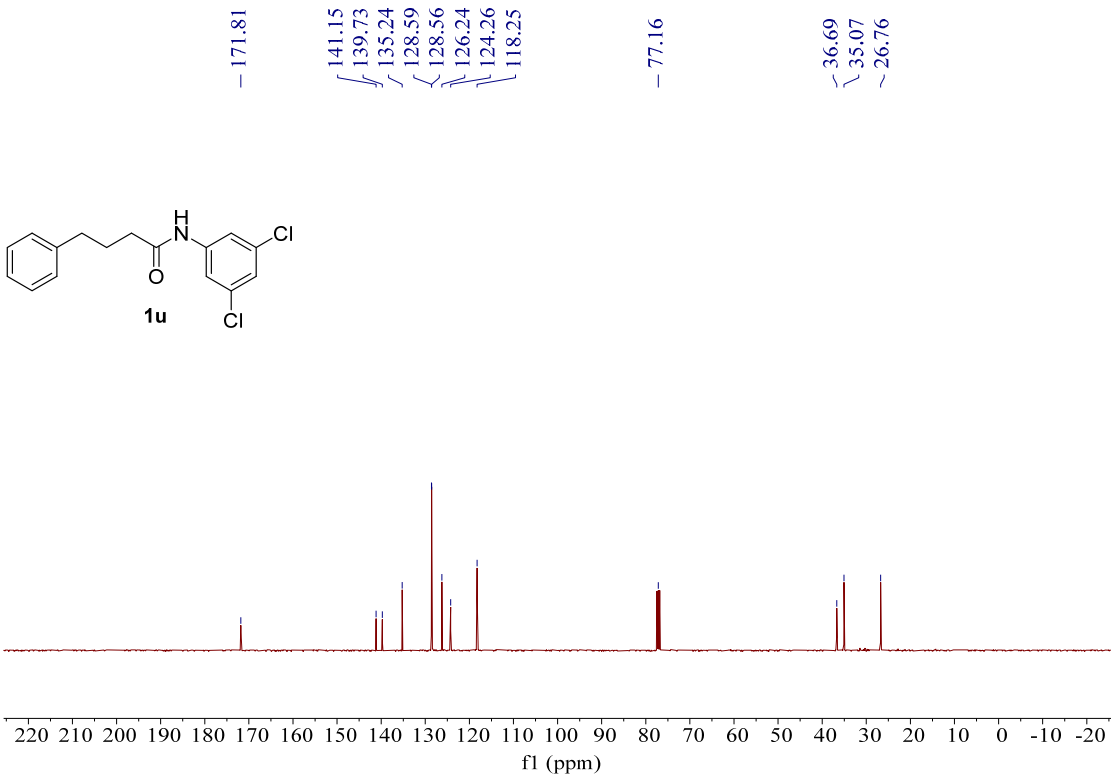
^{1}H NMR spectrum of **1t**



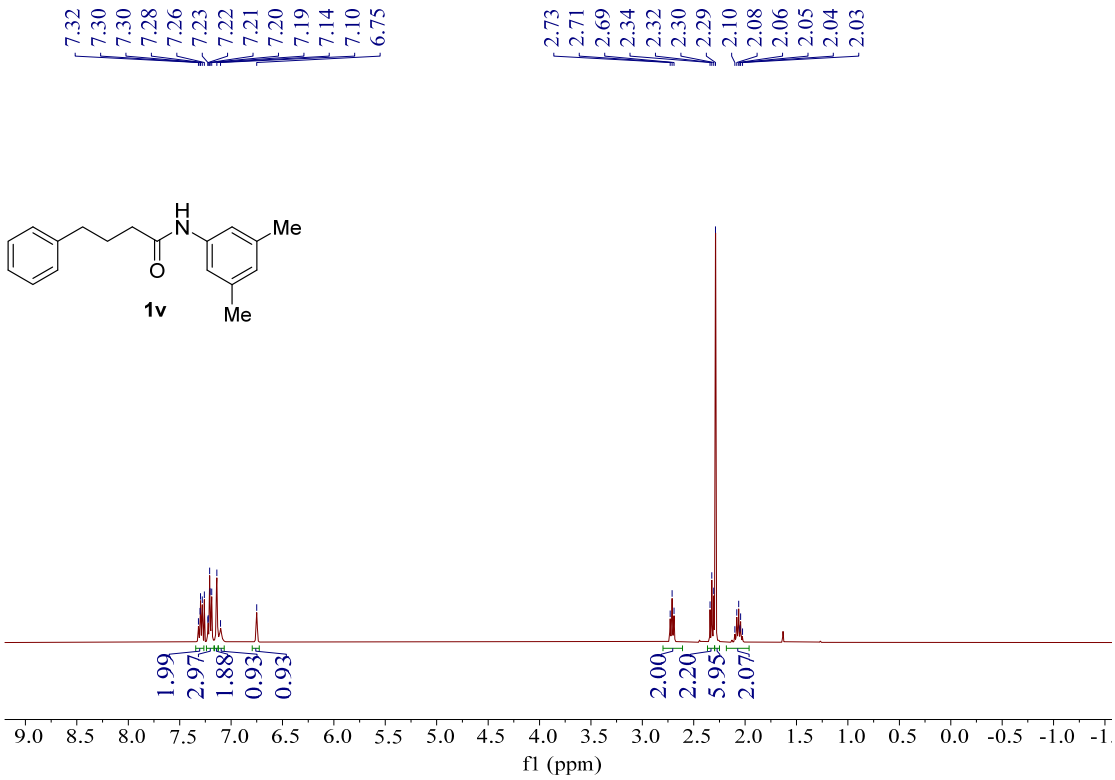
^{13}C NMR spectrum of **1t**



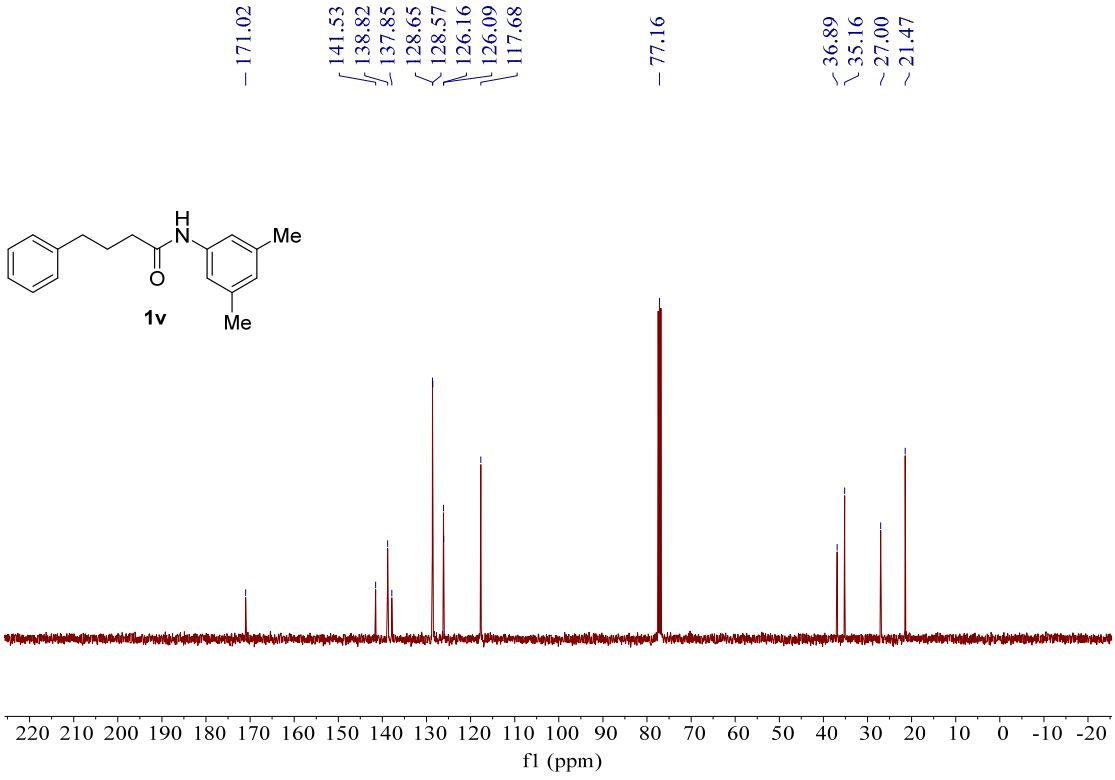
^{1}H NMR spectrum of **1u**



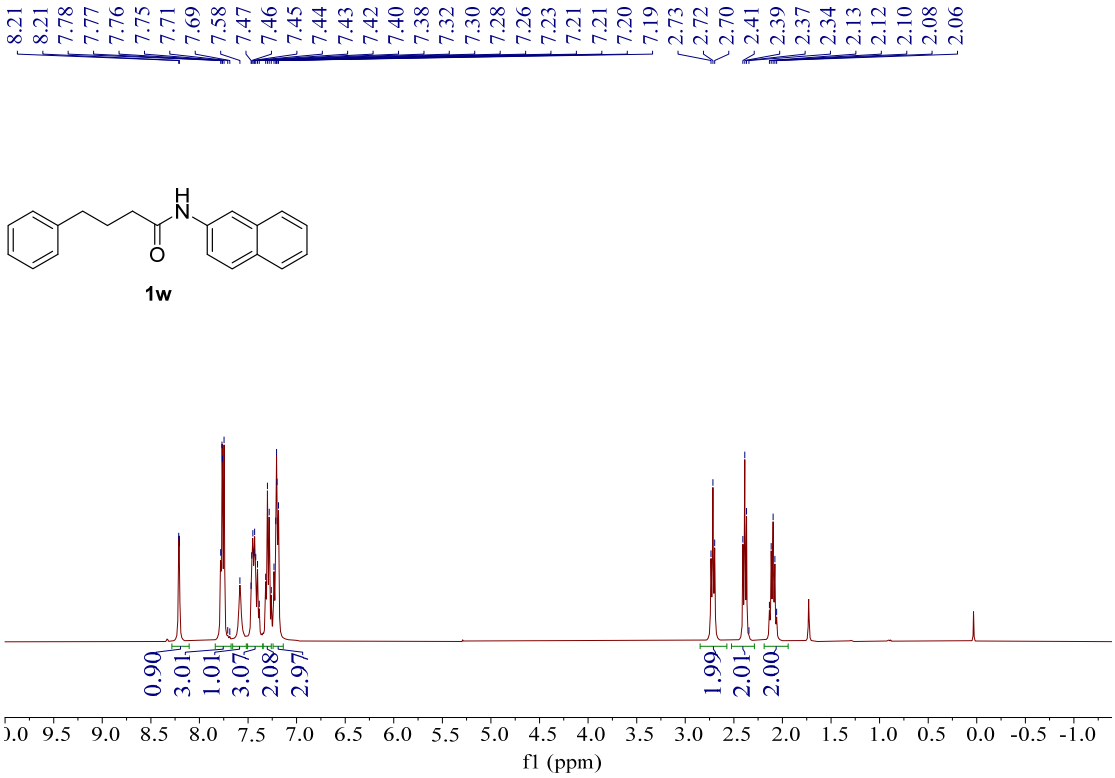
^{13}C NMR spectrum of **1u**



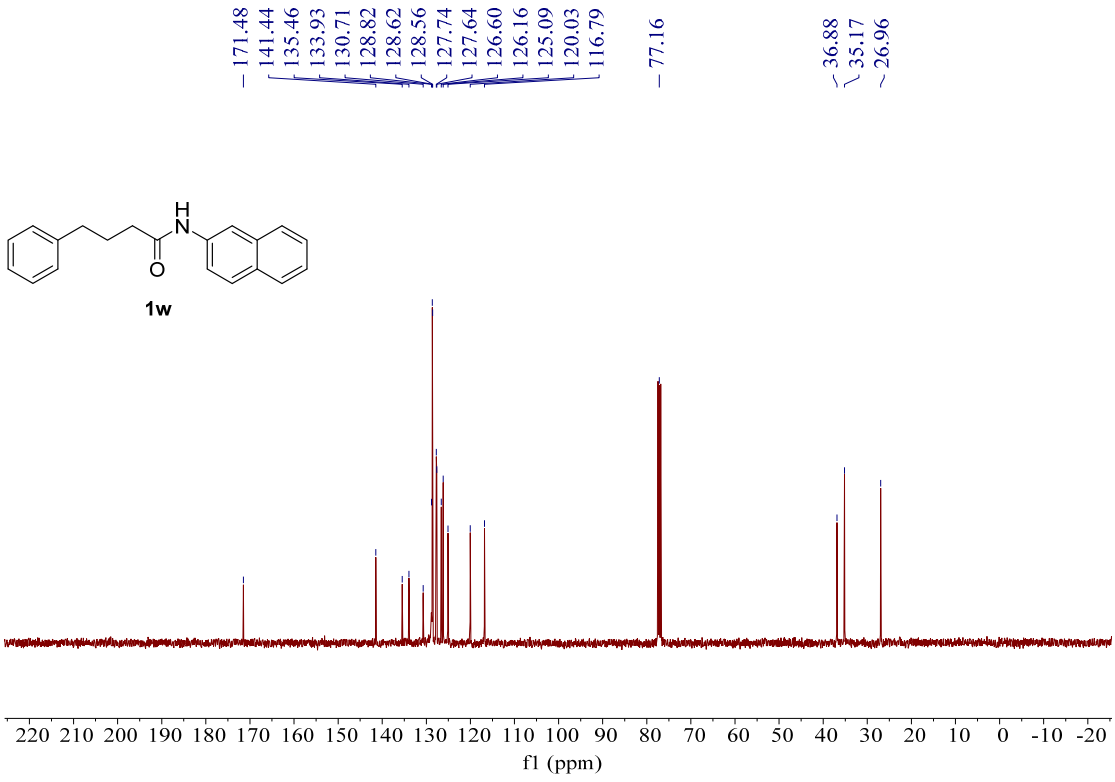
^{1}H NMR spectrum of **1v**



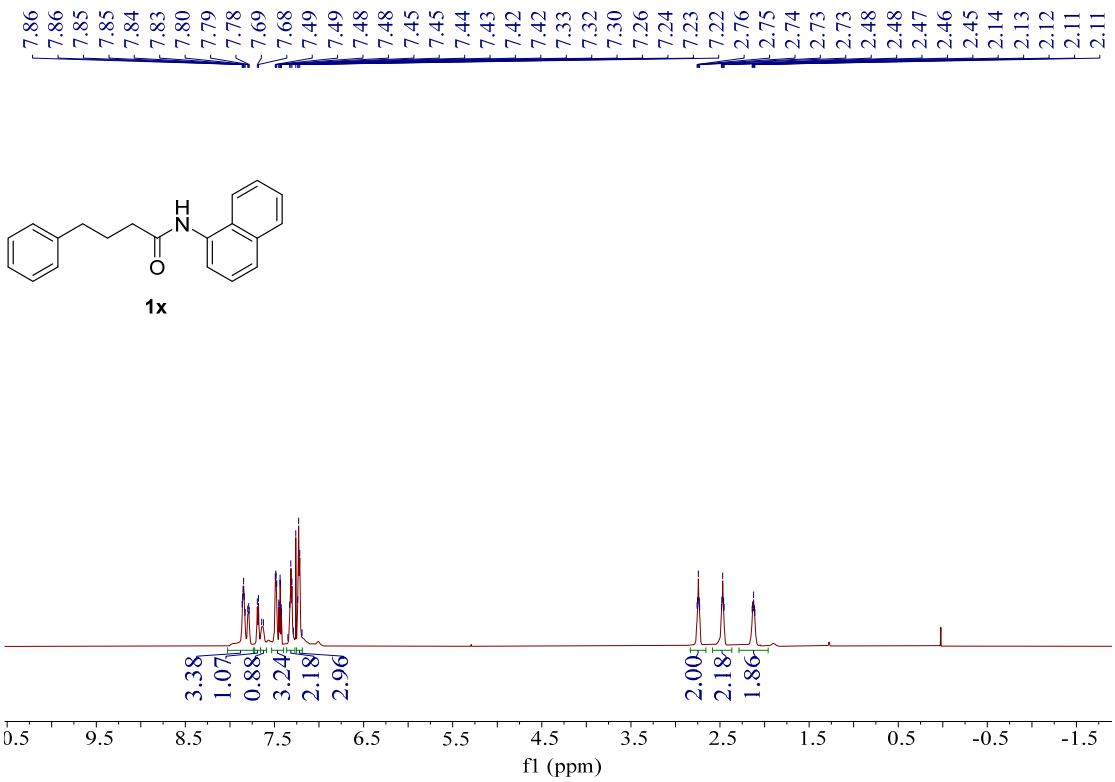
^{13}C NMR spectrum of **1v**



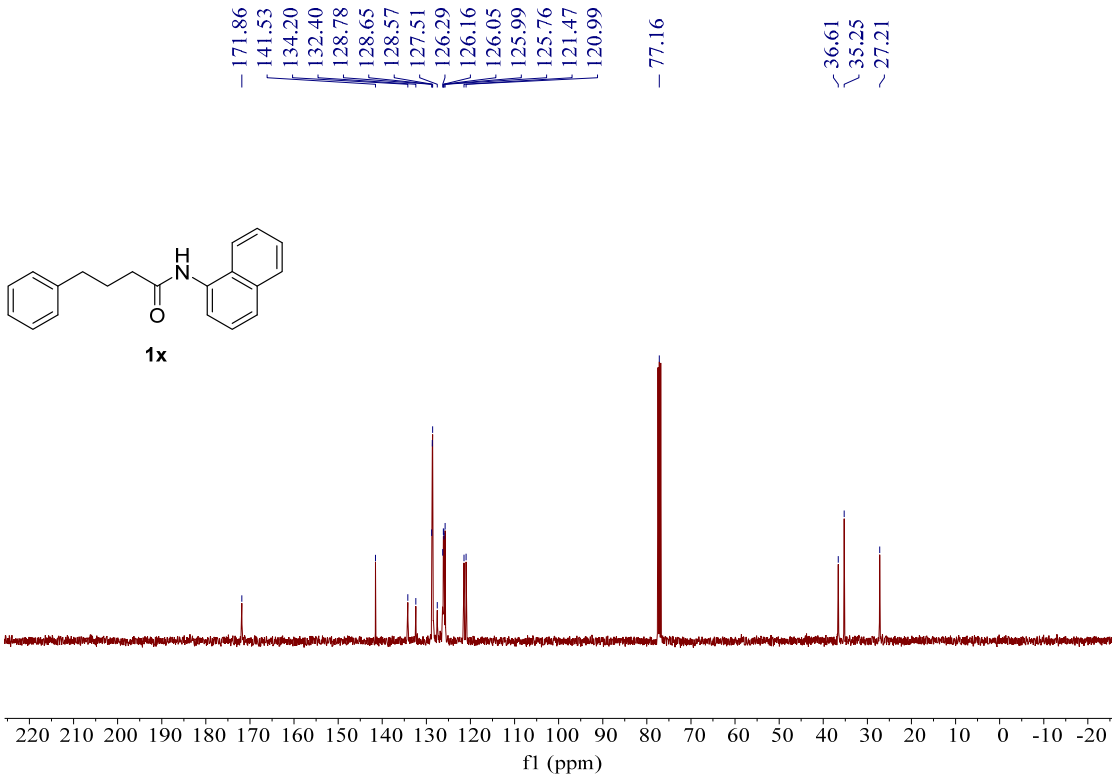
^{1}H NMR spectrum of **1w**



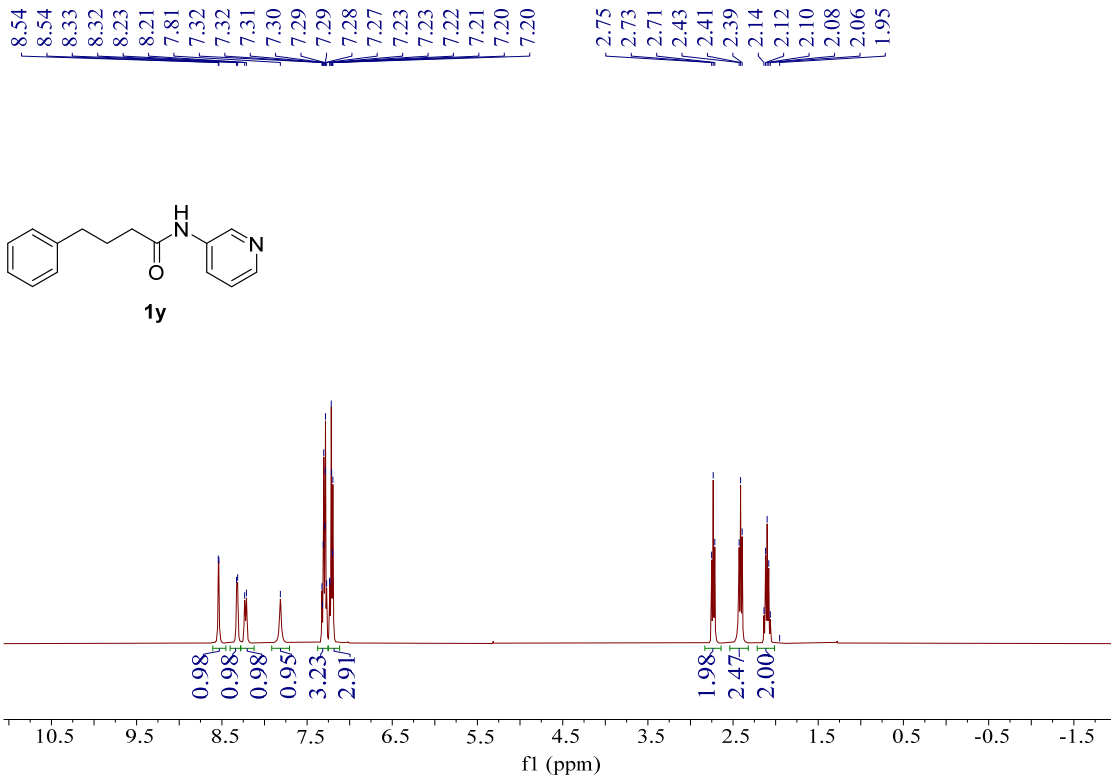
^{13}C NMR spectrum of **1w**



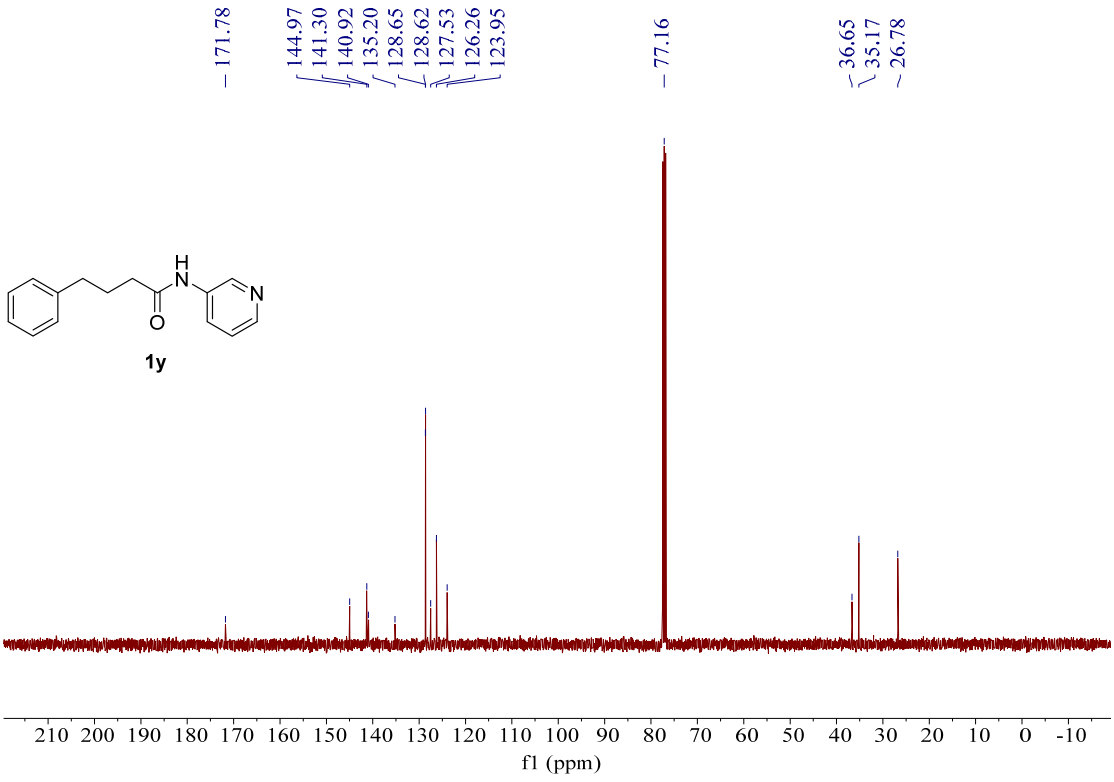
^{1}H NMR spectrum of **1x**



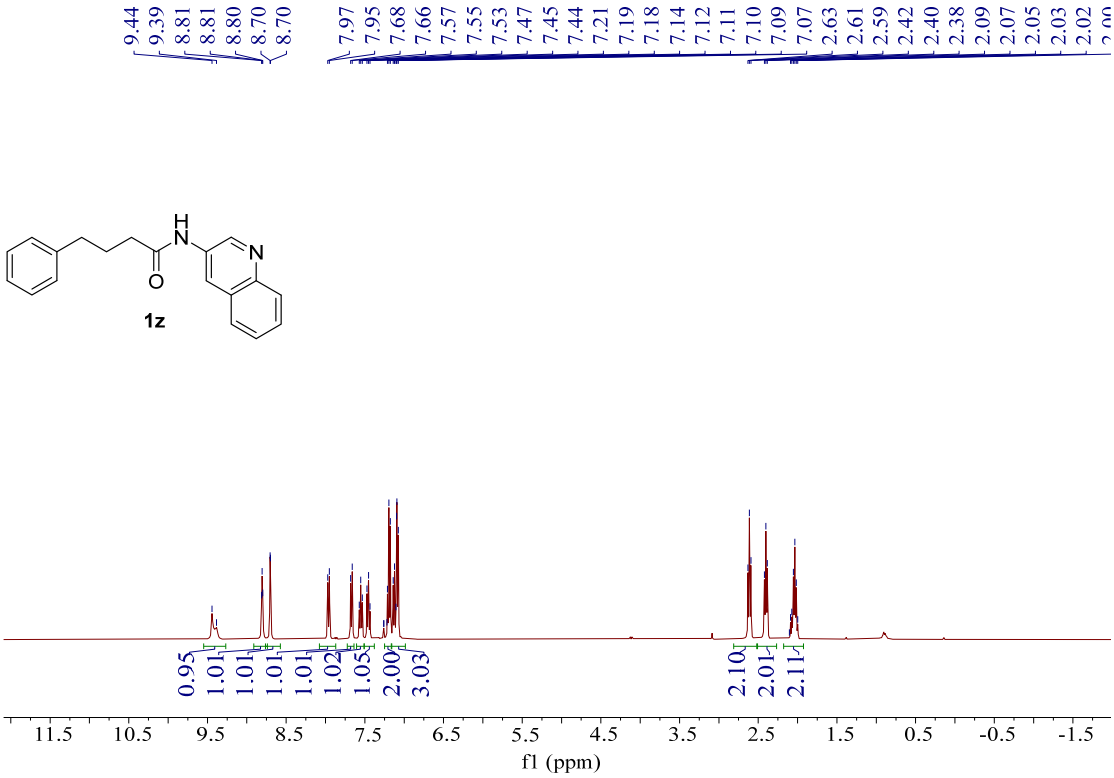
^{13}C NMR spectrum of **1x**



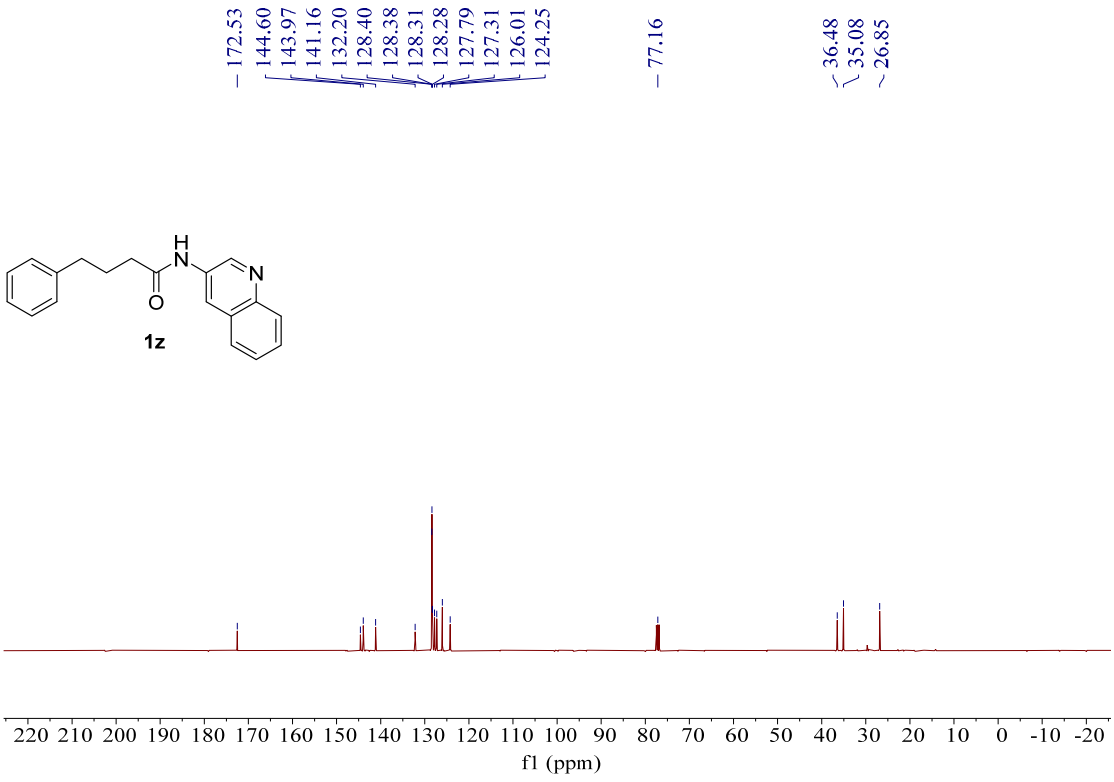
^{1}H NMR spectrum of **1y**



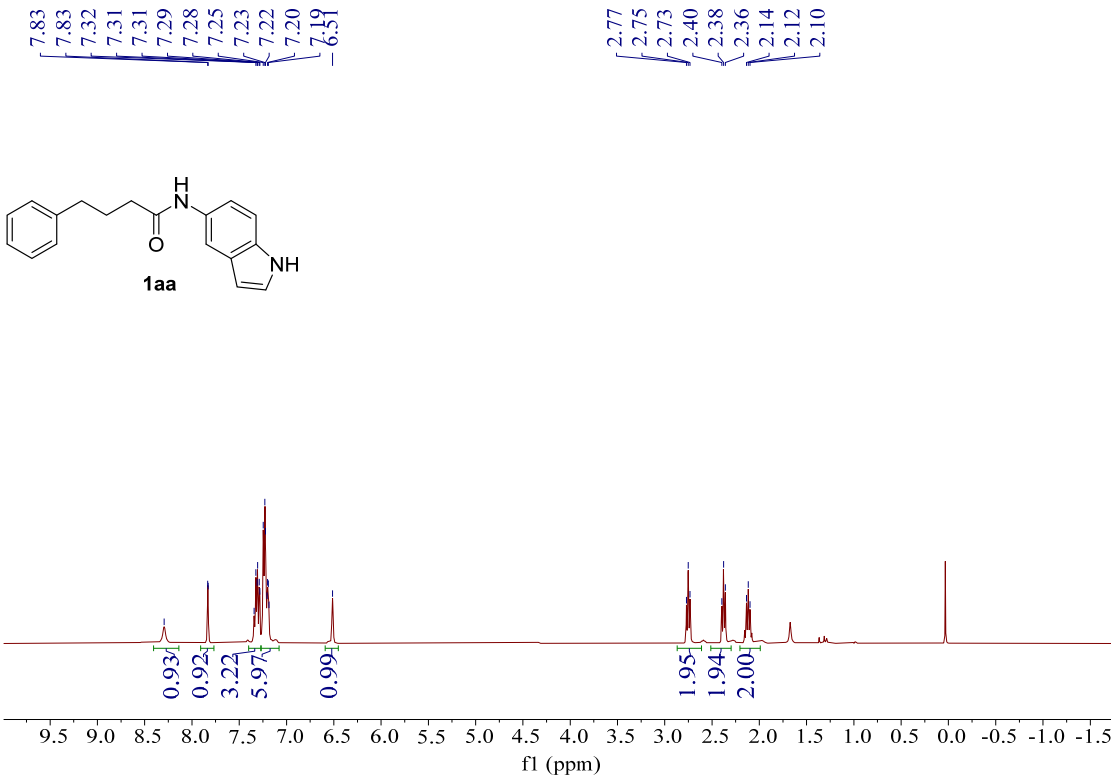
^{13}C NMR spectrum of **1y**



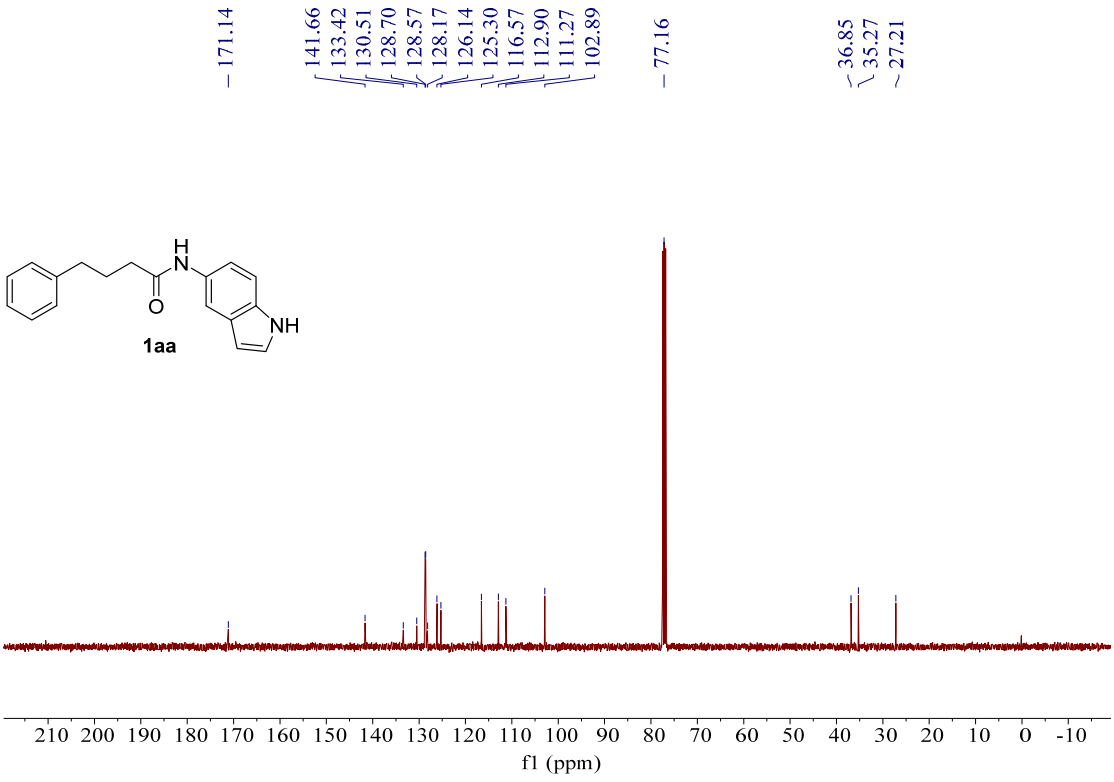
^{1}H NMR spectrum of **1z**



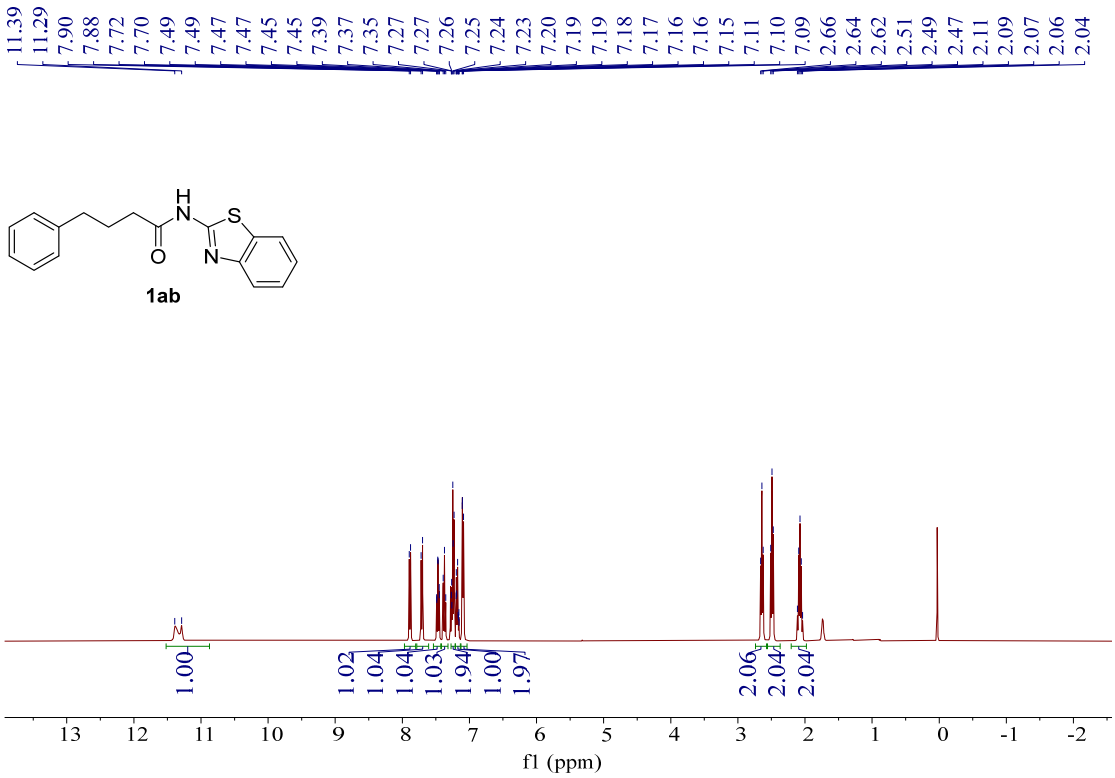
^{13}C NMR spectrum of **1z**



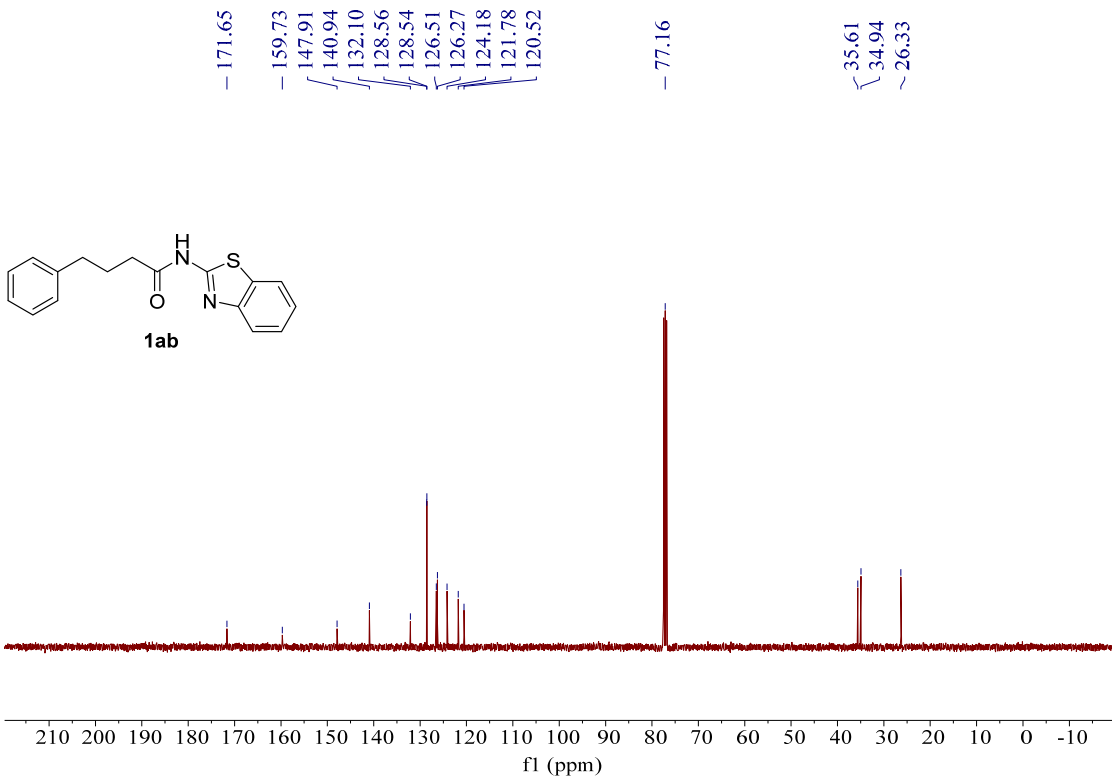
^{1}H NMR spectrum of **1aa**



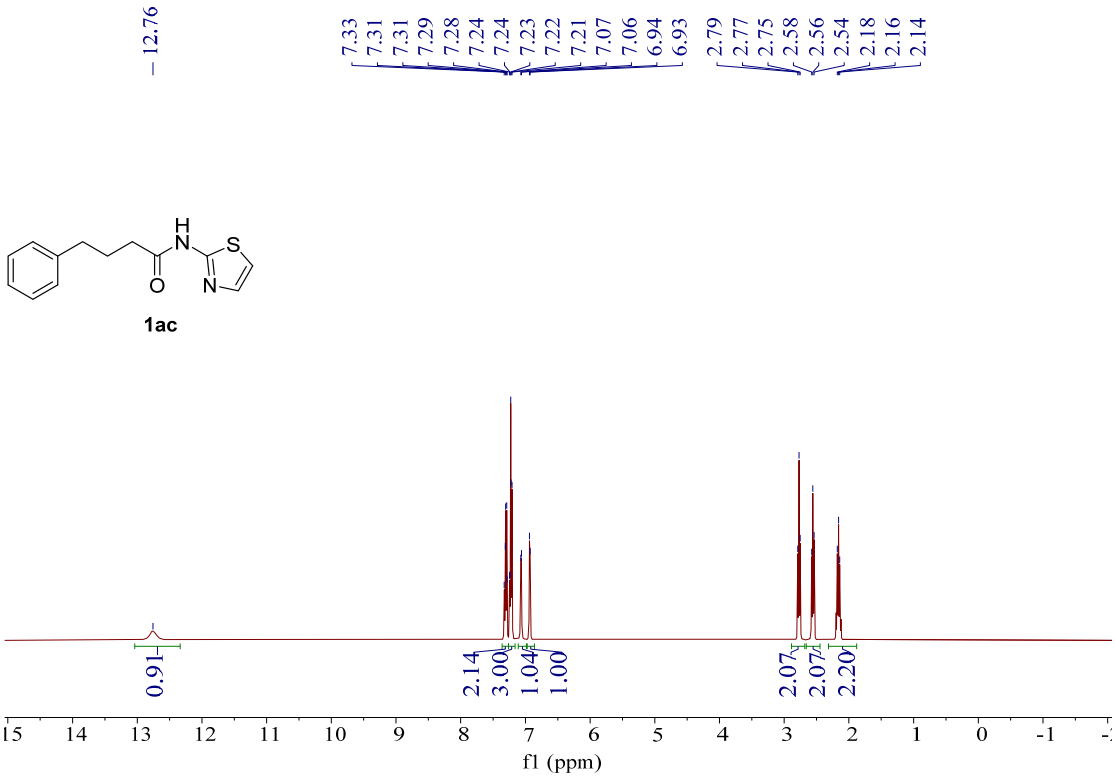
^{13}C NMR spectrum of **1aa**



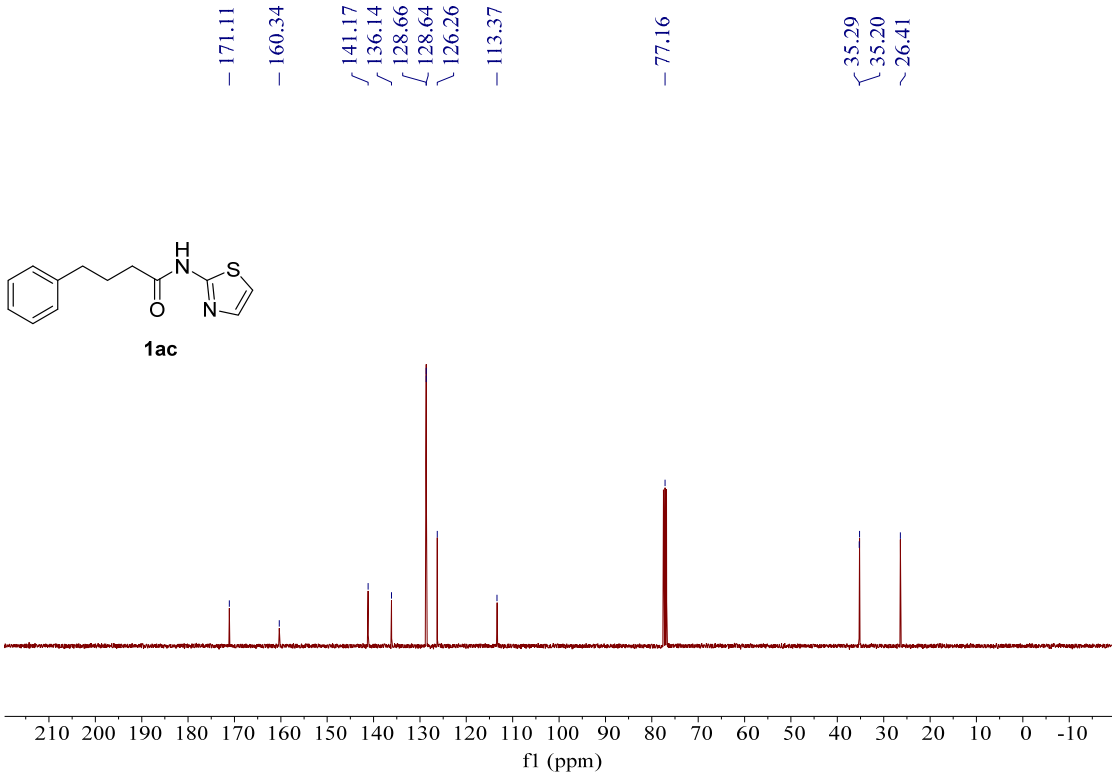
^{1}H NMR spectrum of **1ab**



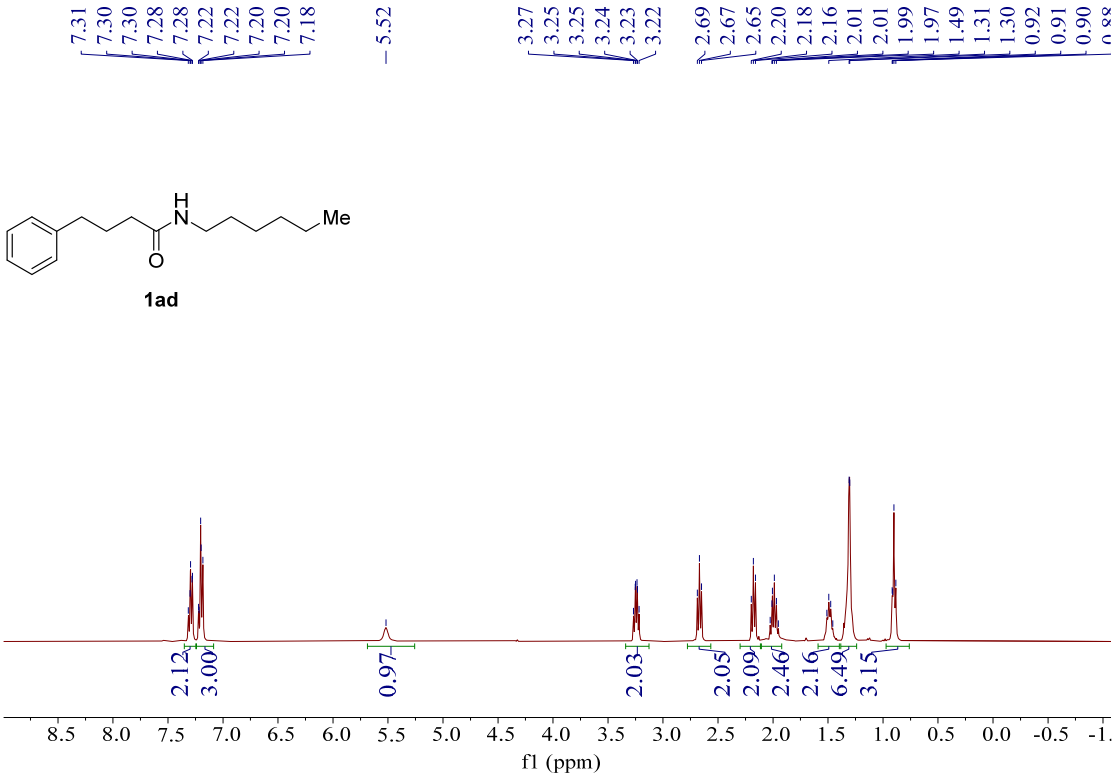
^{13}C NMR spectrum of **1ab**



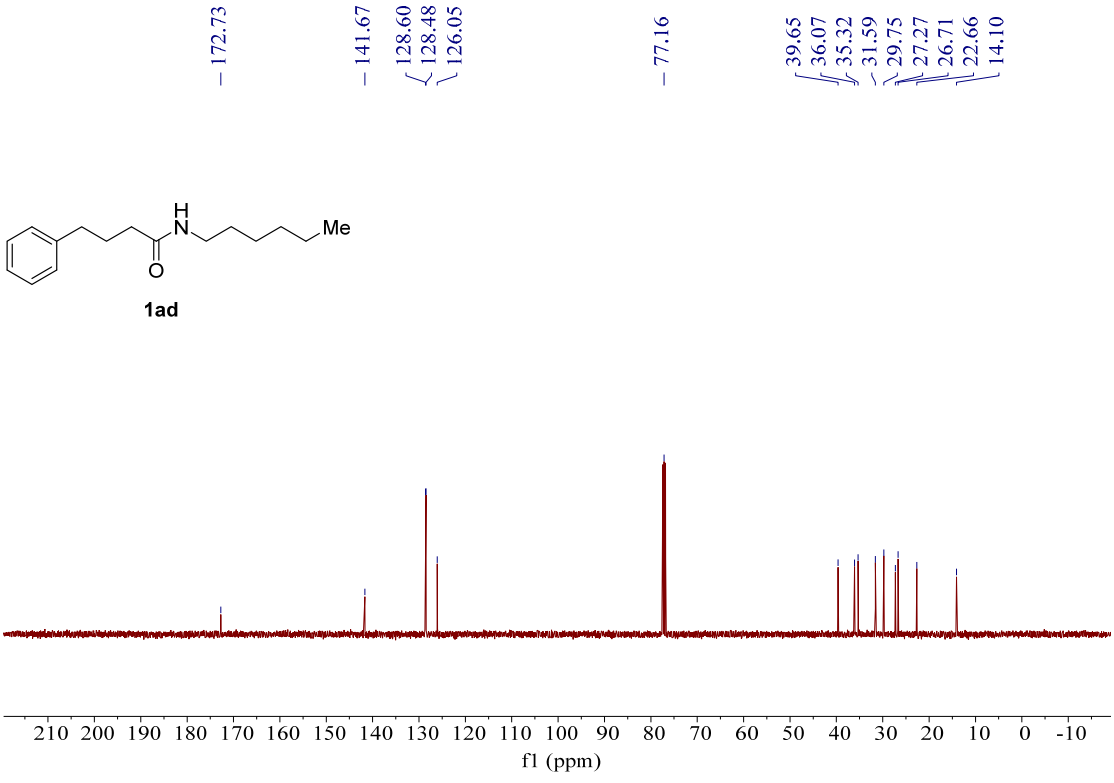
^{1}H NMR spectrum of **1ac**



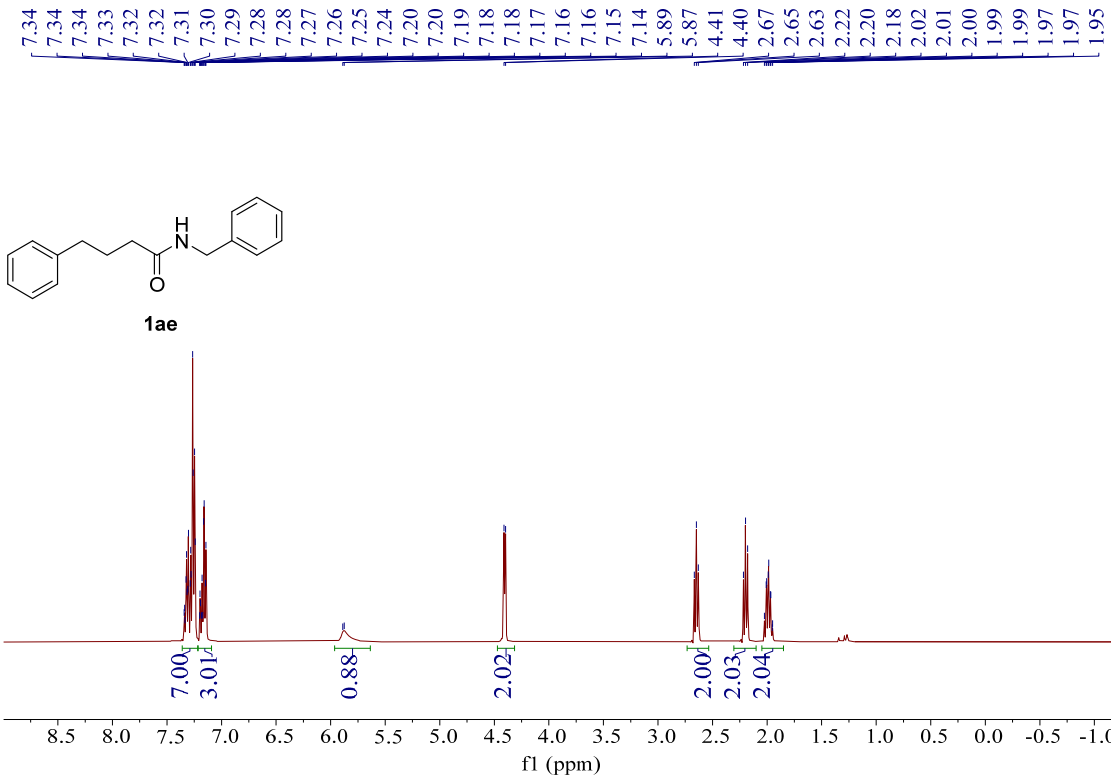
^{13}C NMR spectrum of **1ac**



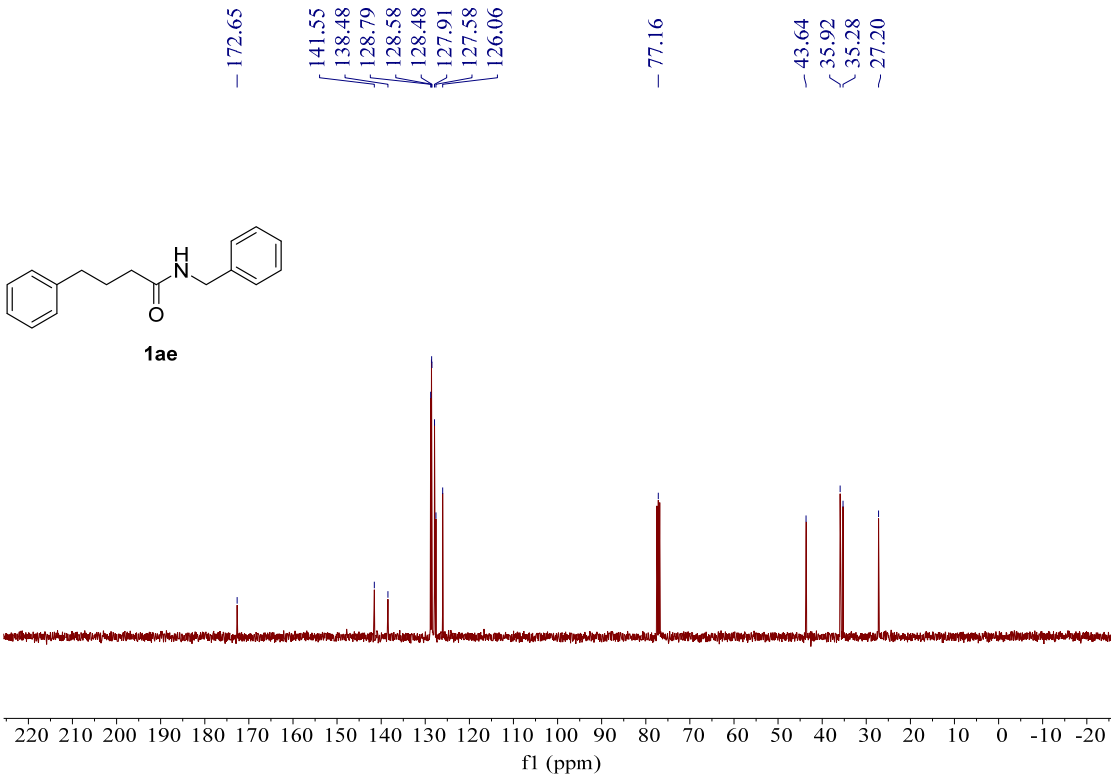
^{1}H NMR spectrum of **1ad**



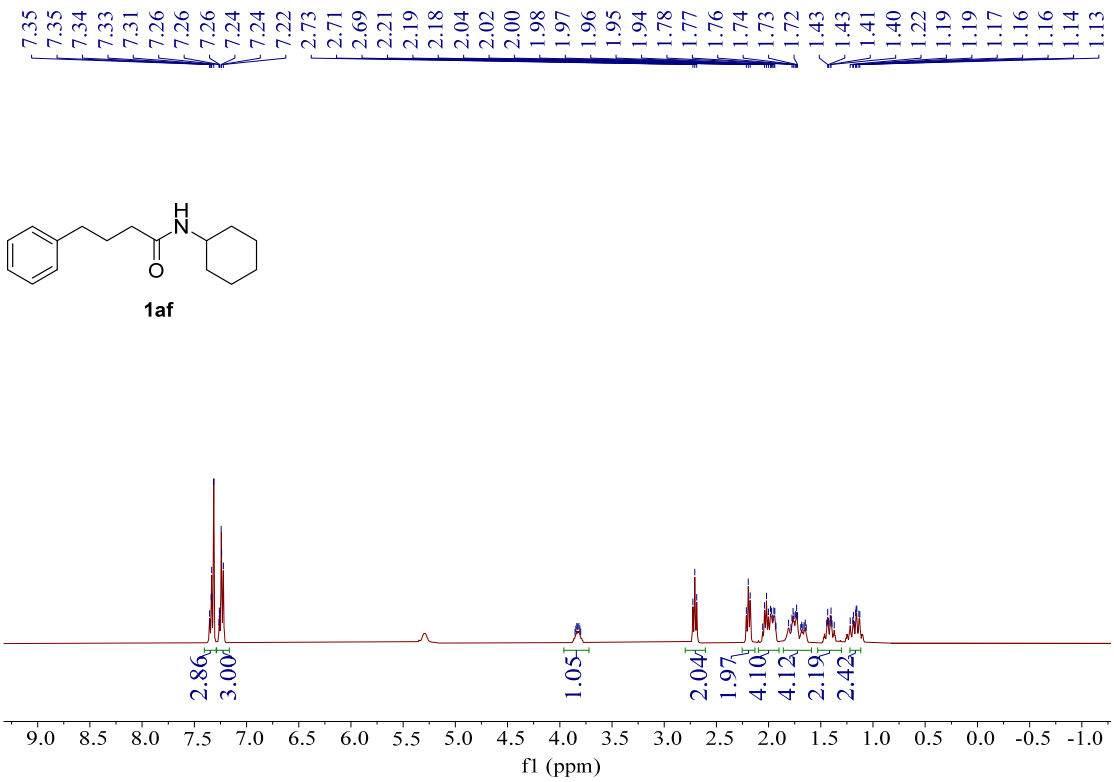
^{13}C NMR spectrum of **1ad**



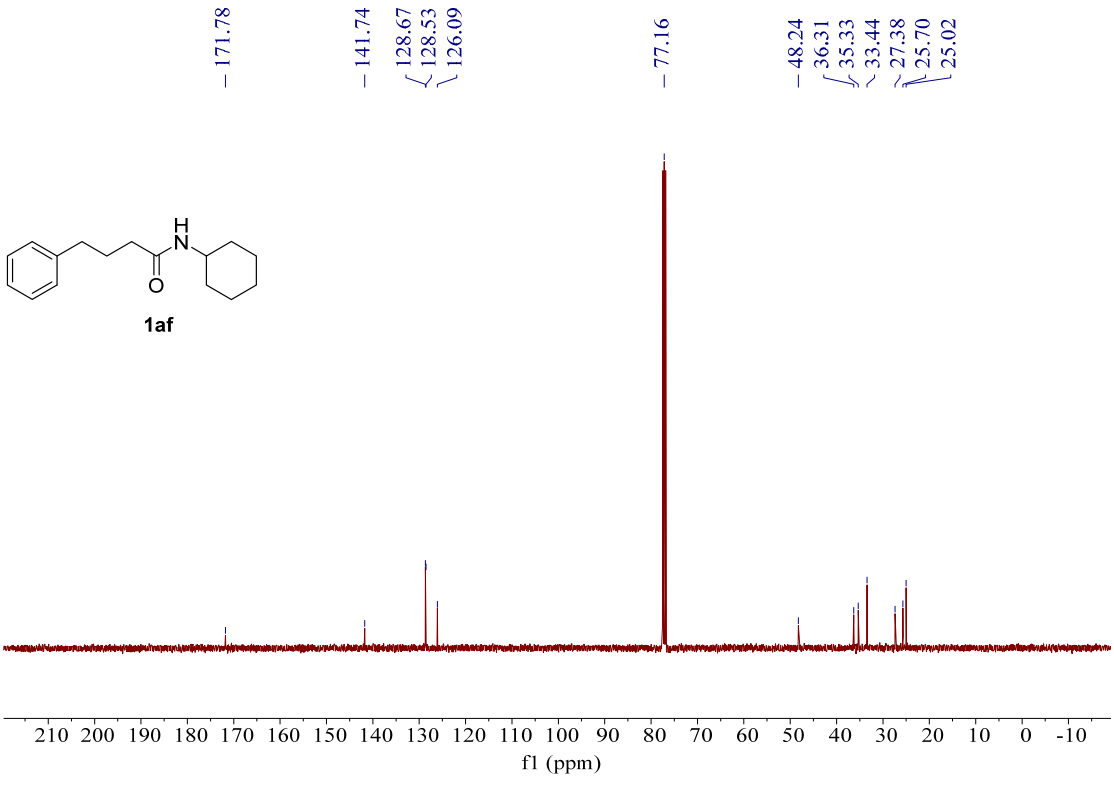
^{1}H NMR spectrum of **1ae**



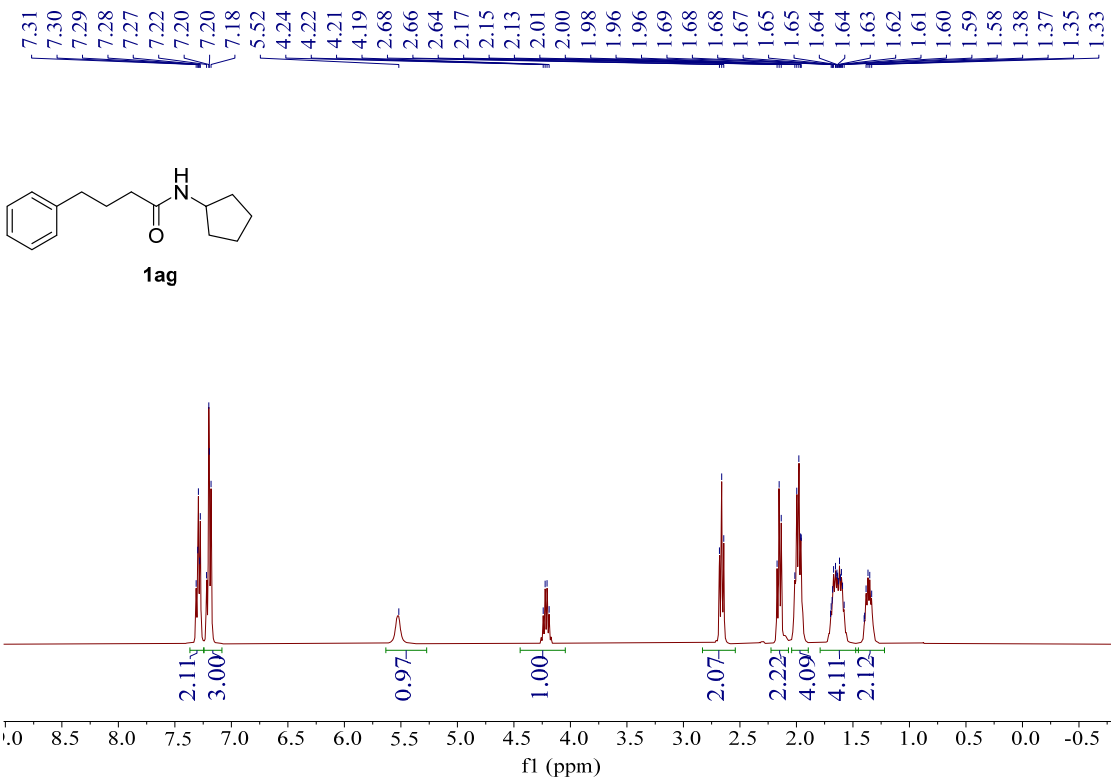
^{13}C NMR spectrum of **1ae**



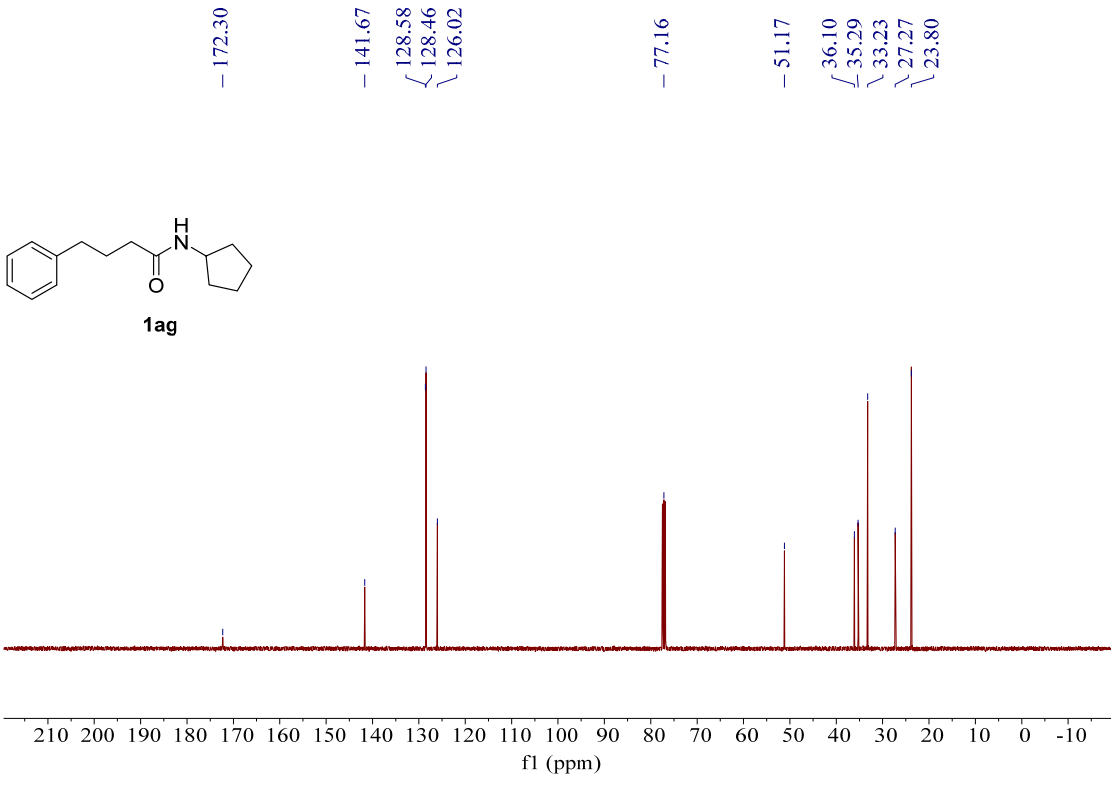
^{1}H NMR spectrum of **1af**



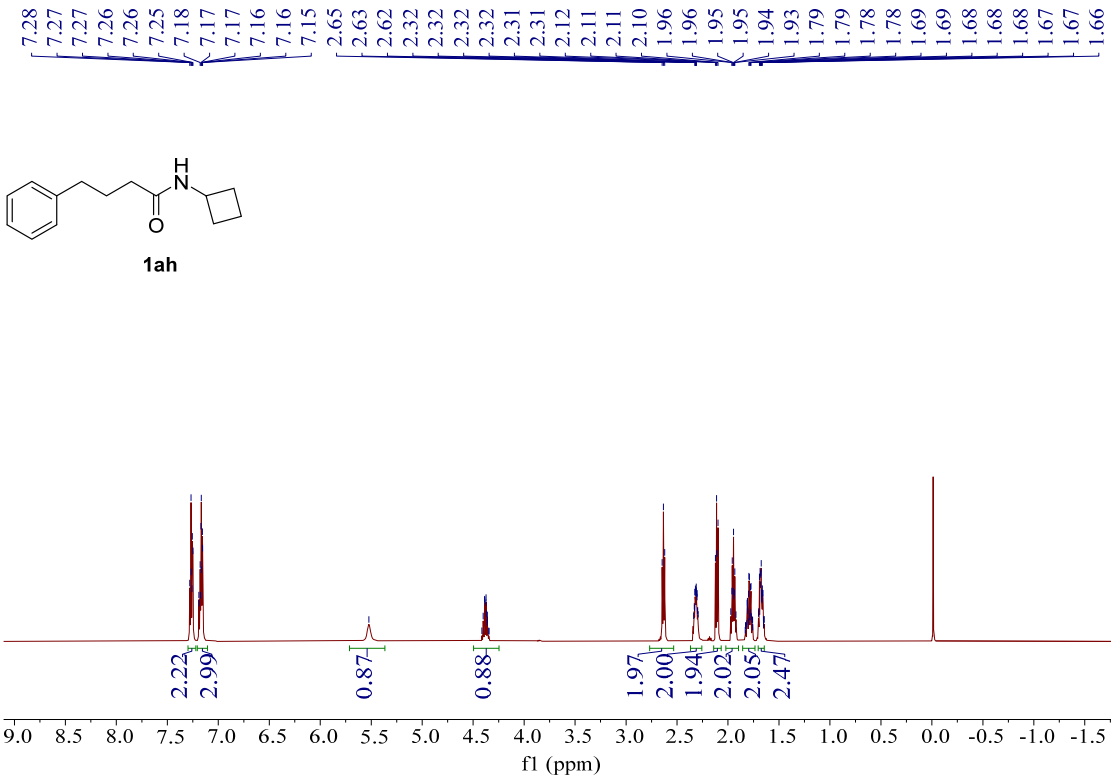
^{13}C NMR spectrum of **1af**



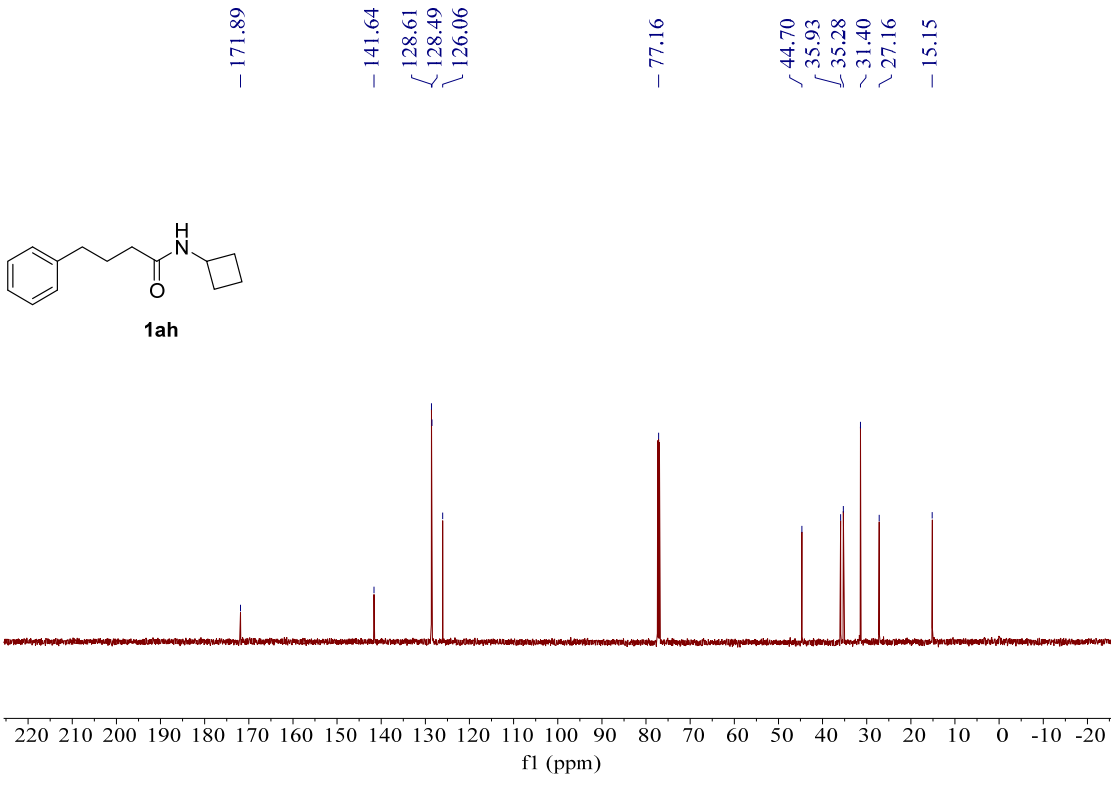
^{1}H NMR spectrum of **1ag**



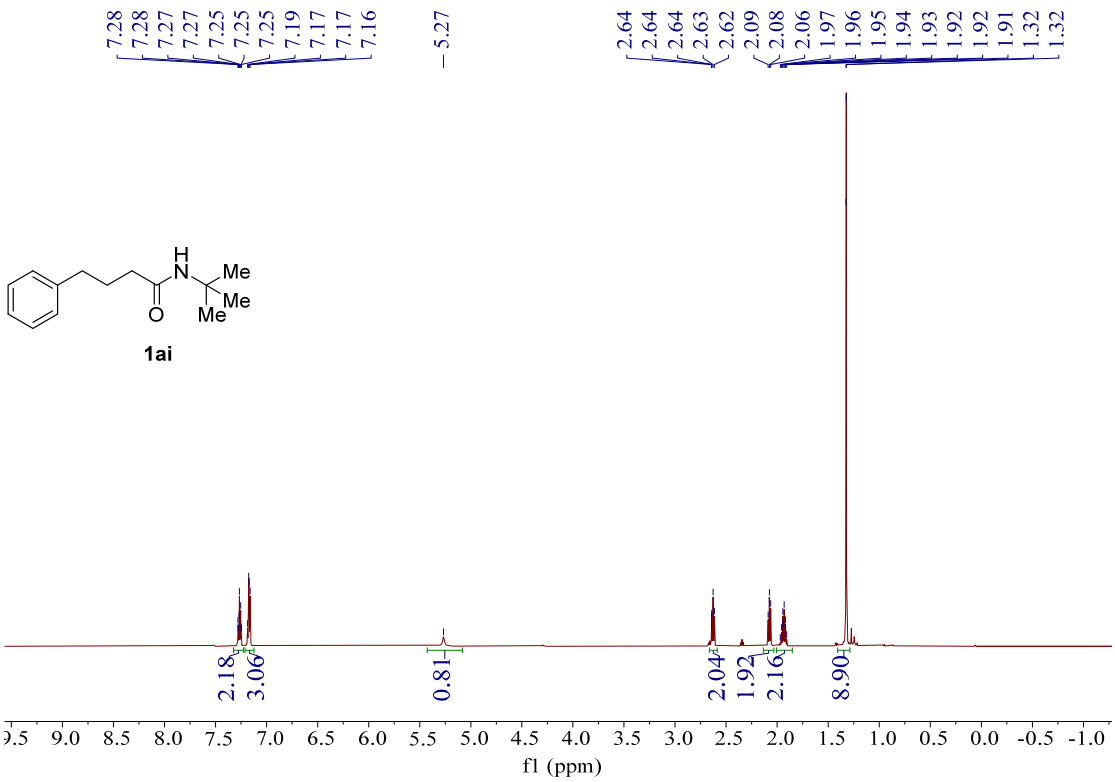
^{13}C NMR spectrum of **1ag**



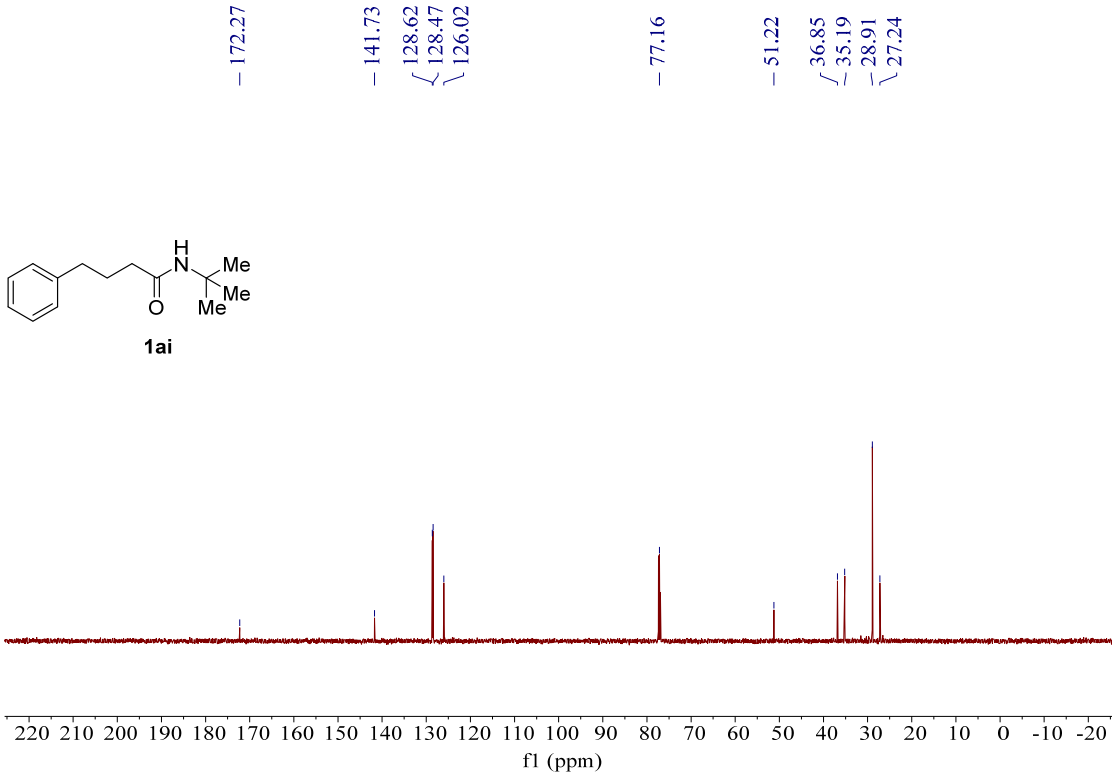
^{1}H NMR spectrum of **1ah**



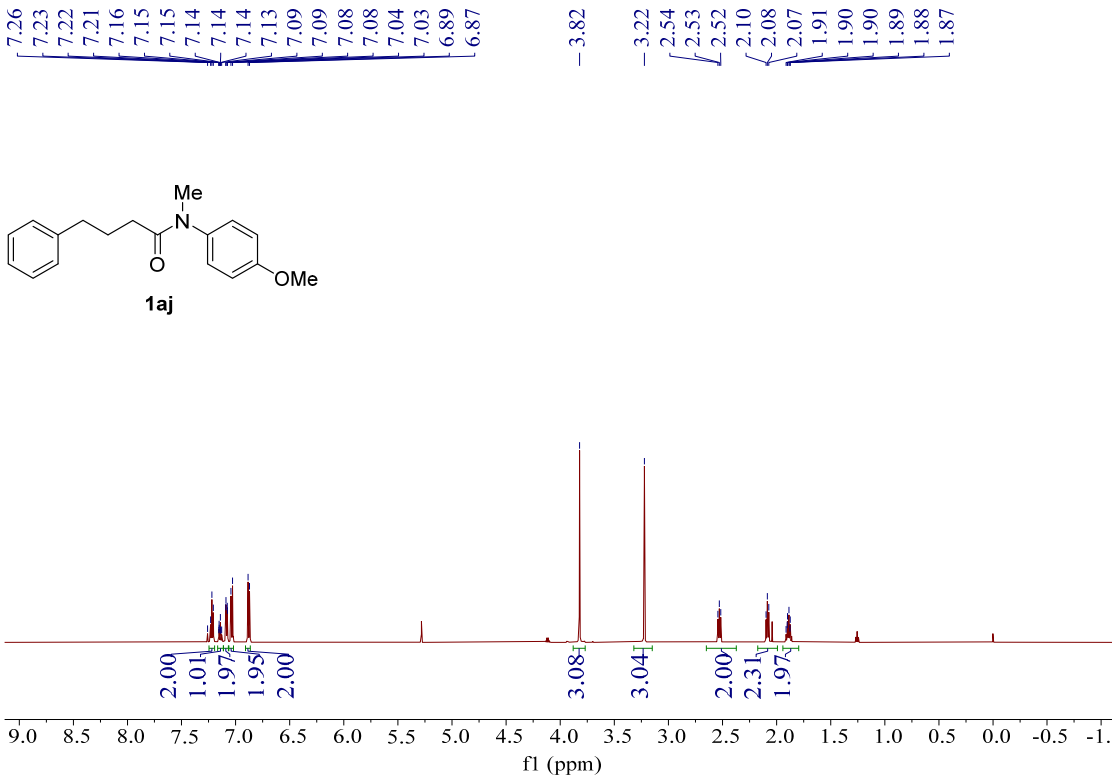
^{13}C NMR spectrum of **1ah**



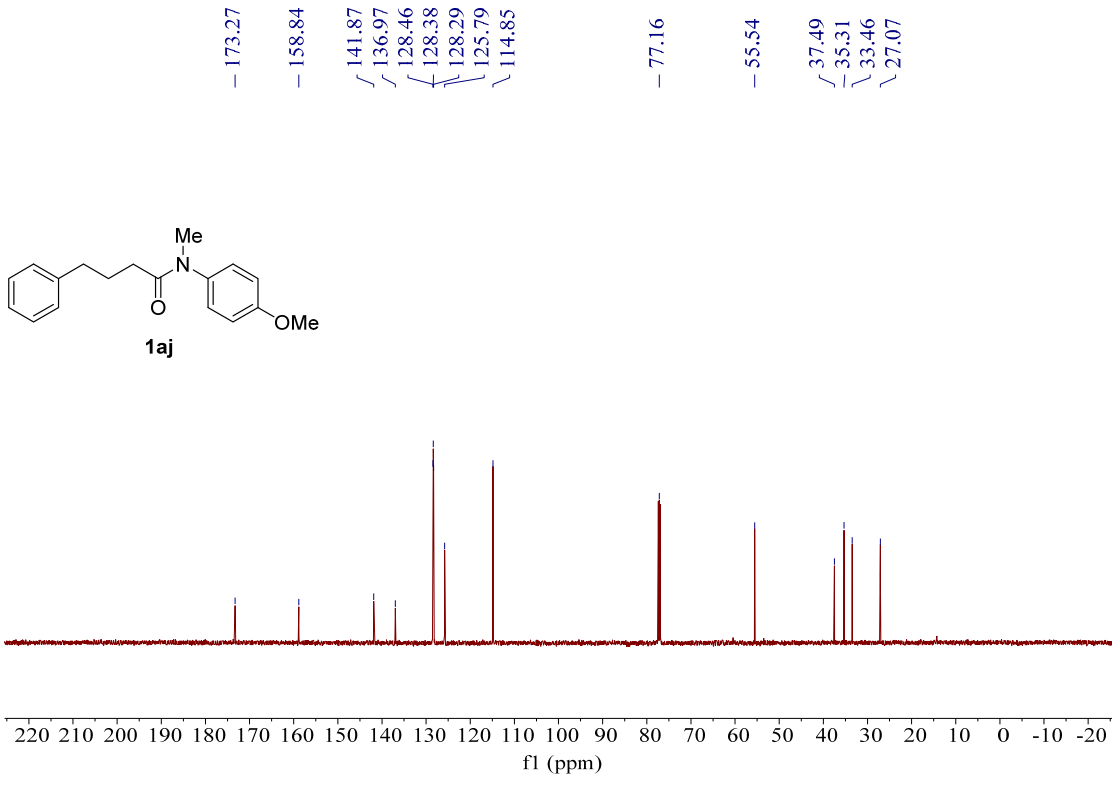
^{1}H NMR spectrum of **1ai**



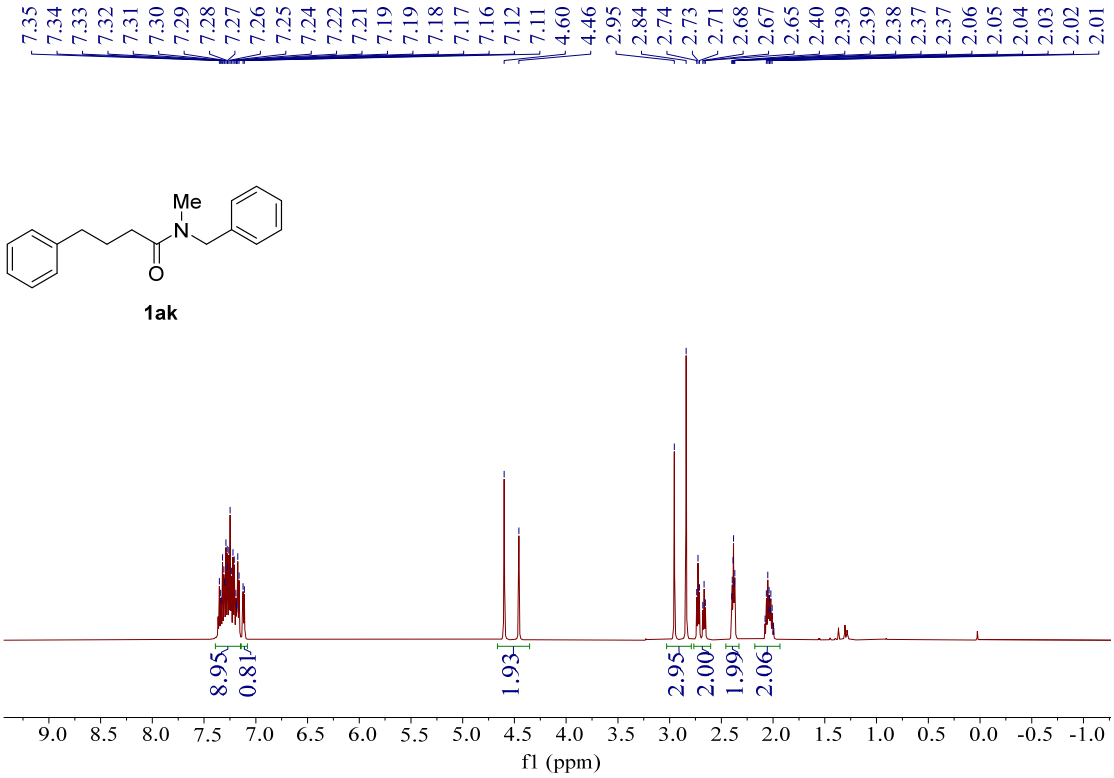
^{13}C NMR spectrum of **1ai**



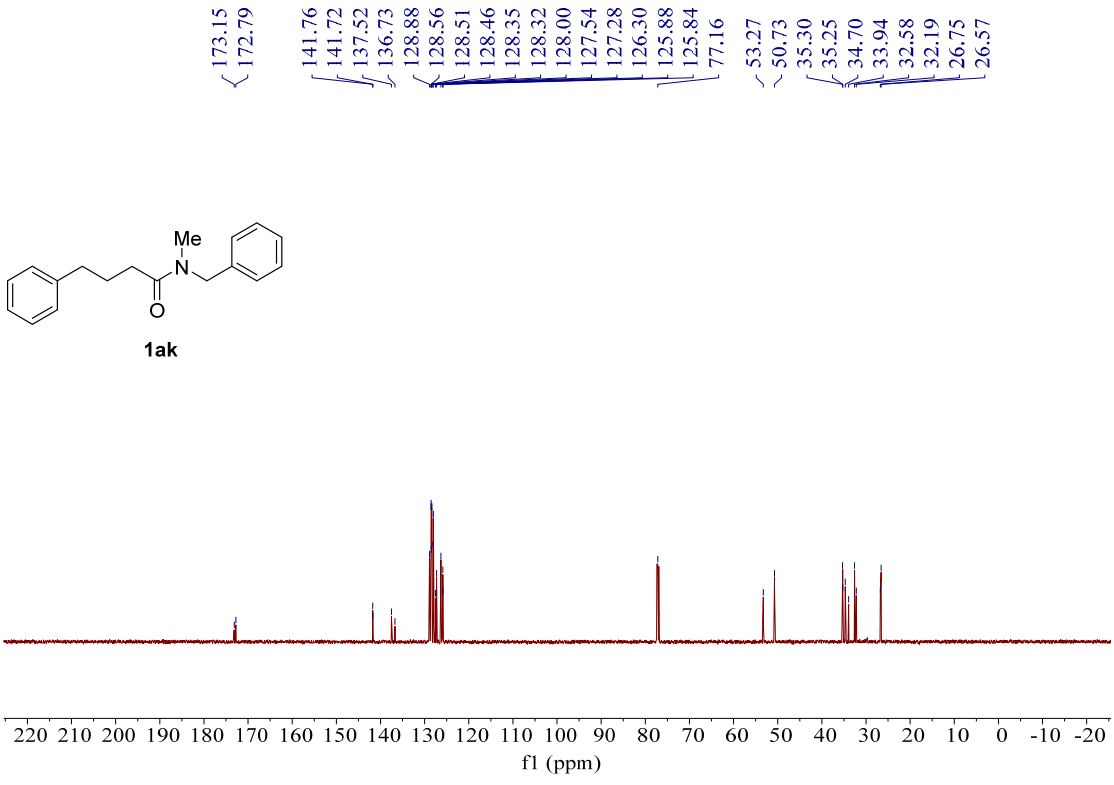
^{1}H NMR spectrum of **1aj**



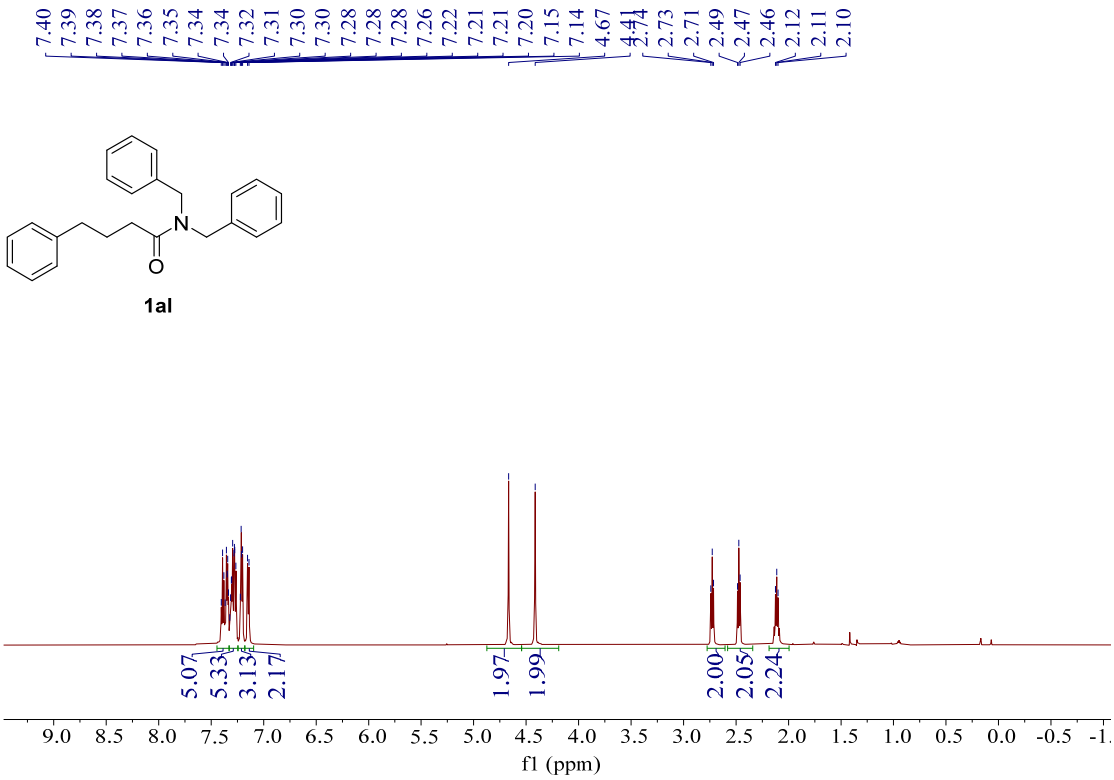
^{13}C NMR spectrum of **1aj**



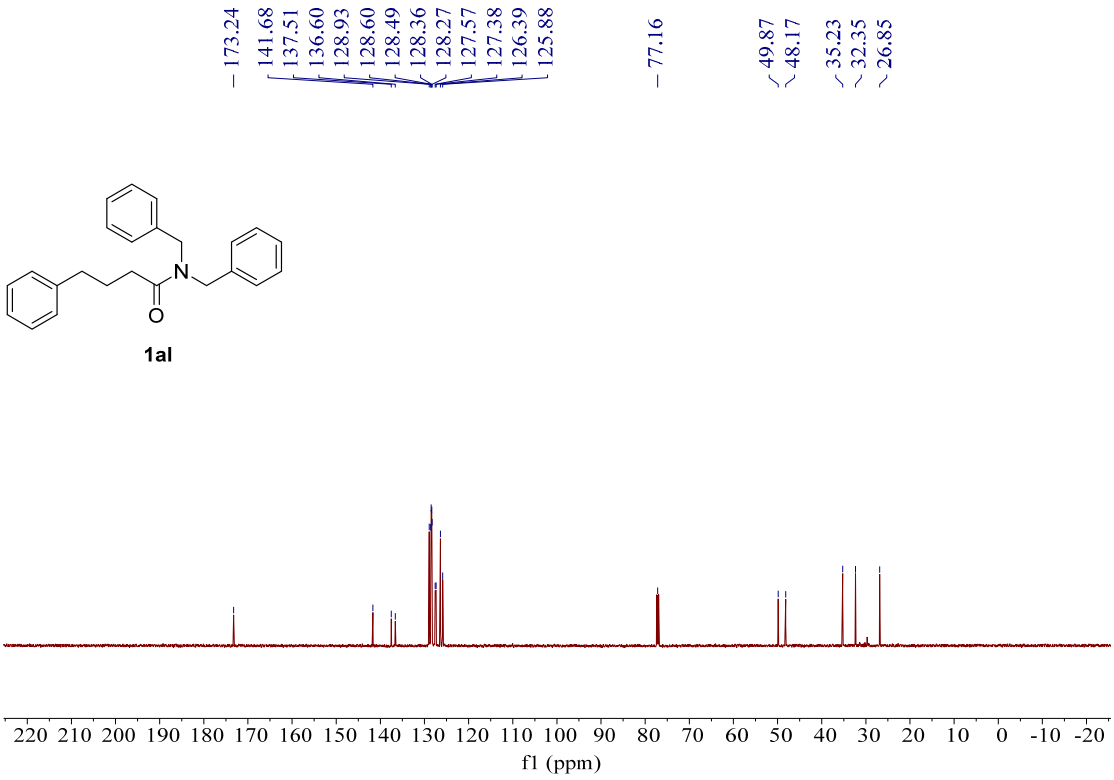
^{1}H NMR spectrum of **1ak**



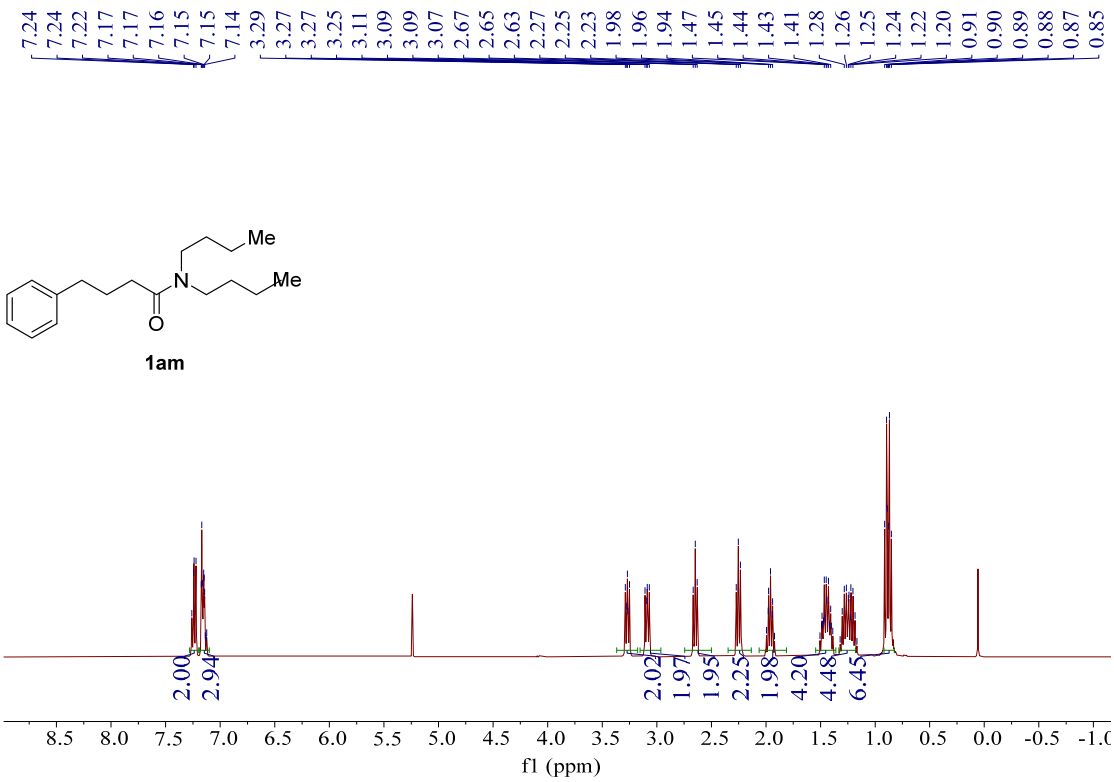
^{13}C NMR spectrum of **1ak**



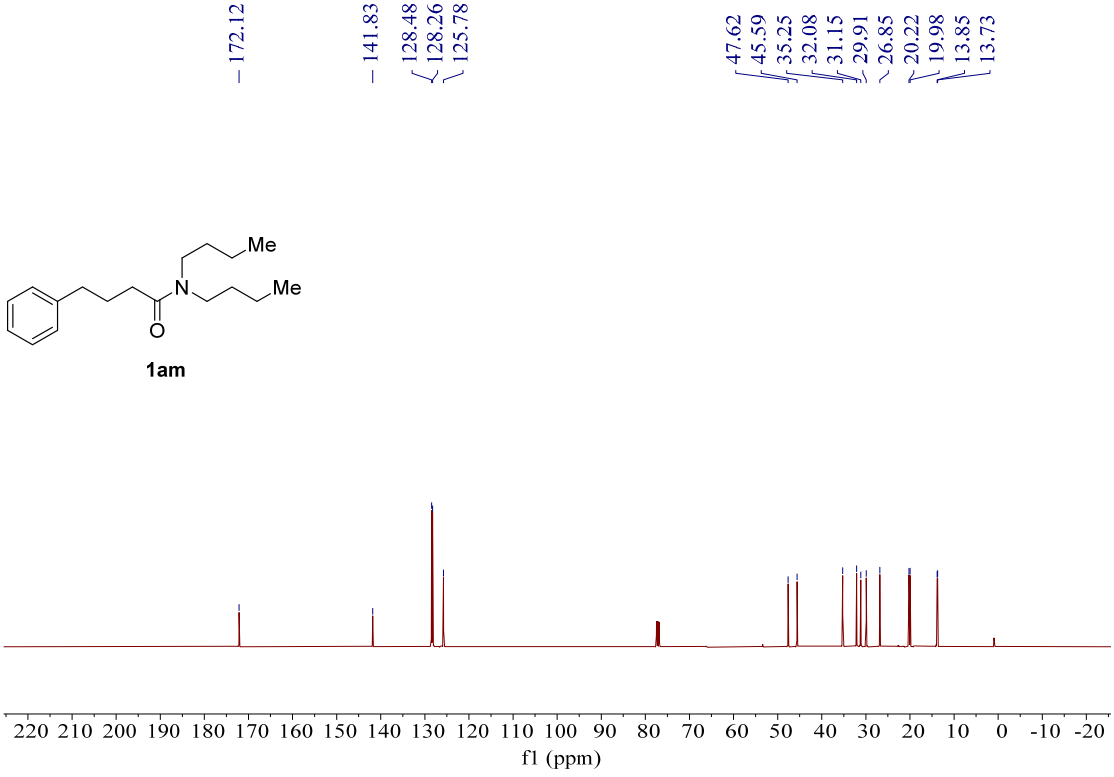
^{1}H NMR spectrum of **1al**



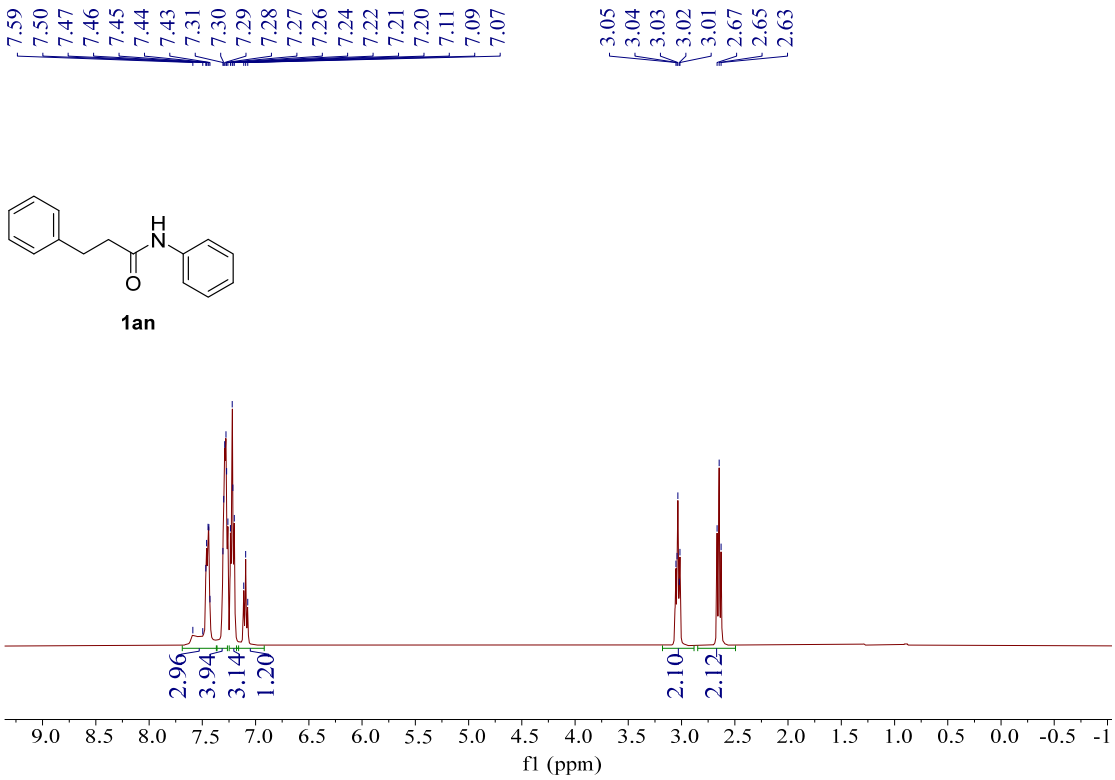
^{13}C NMR spectrum of **1al**



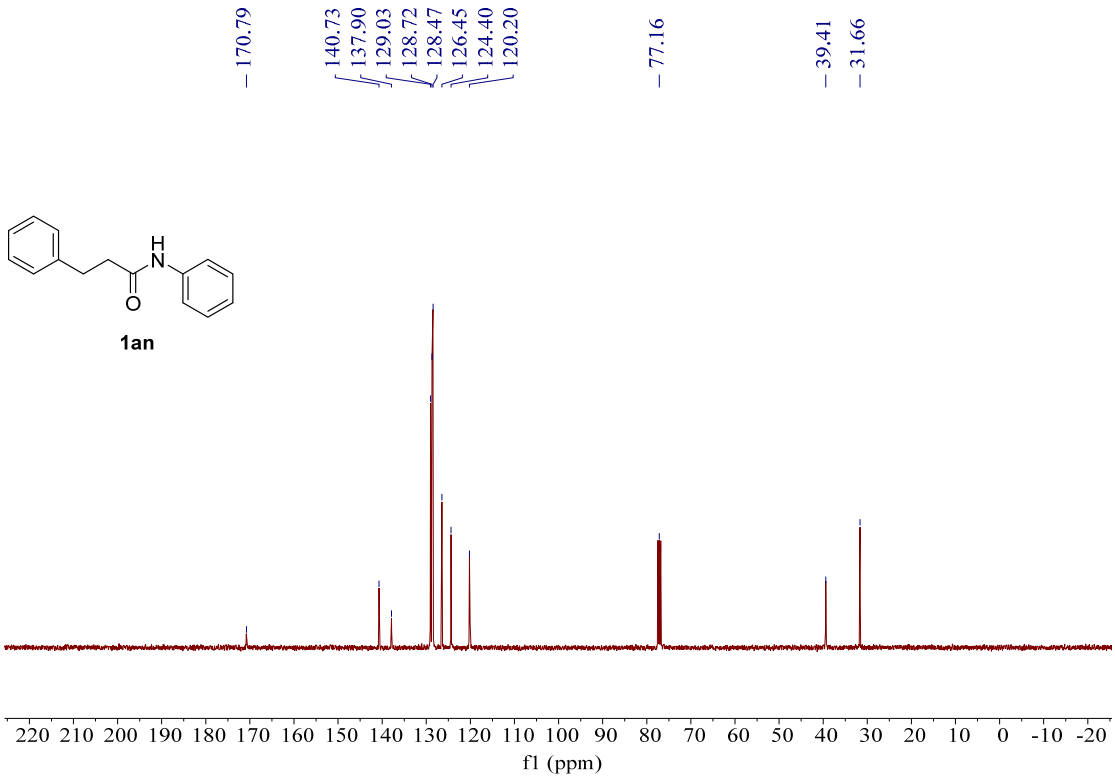
^{1}H NMR spectrum of **1am**



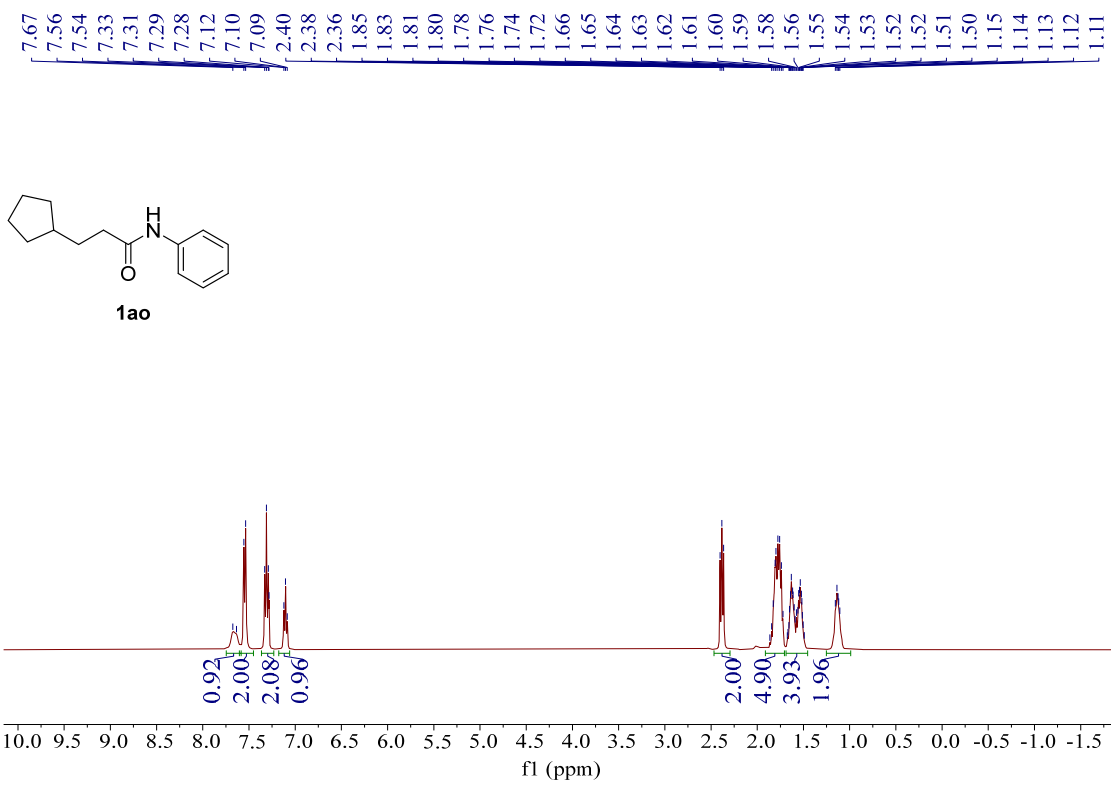
^{13}C NMR spectrum of **1am**



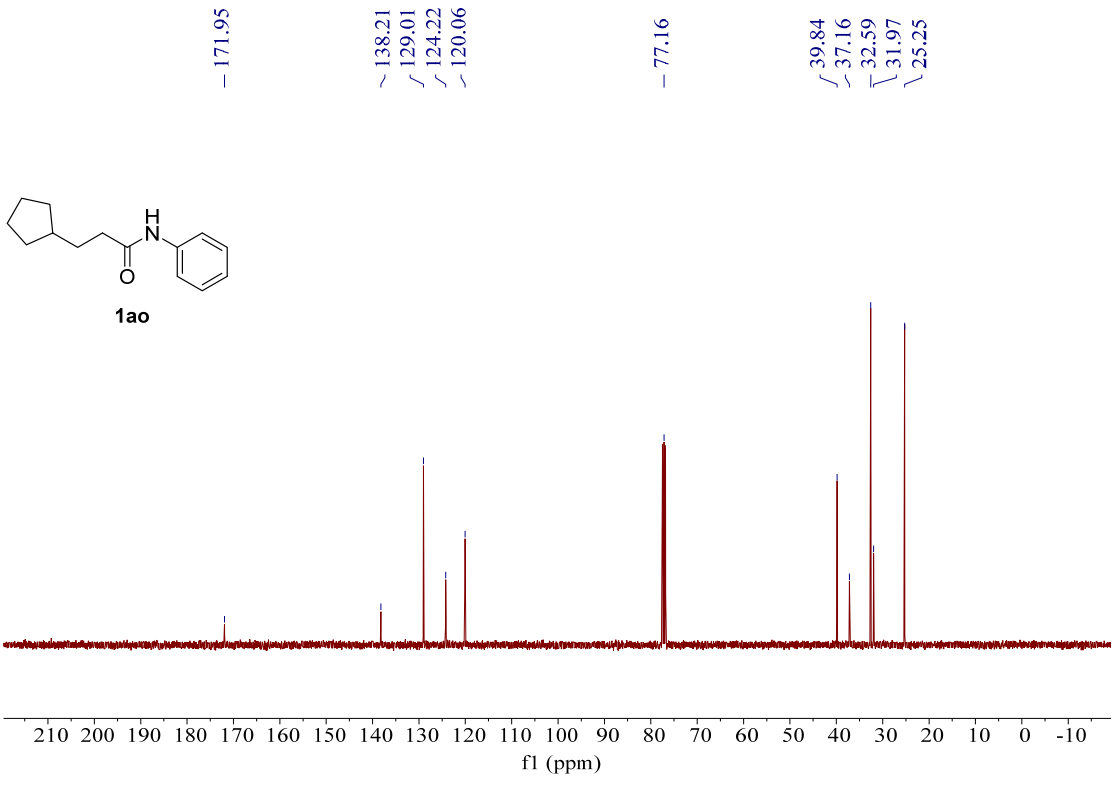
^{1}H NMR spectrum of **1an**



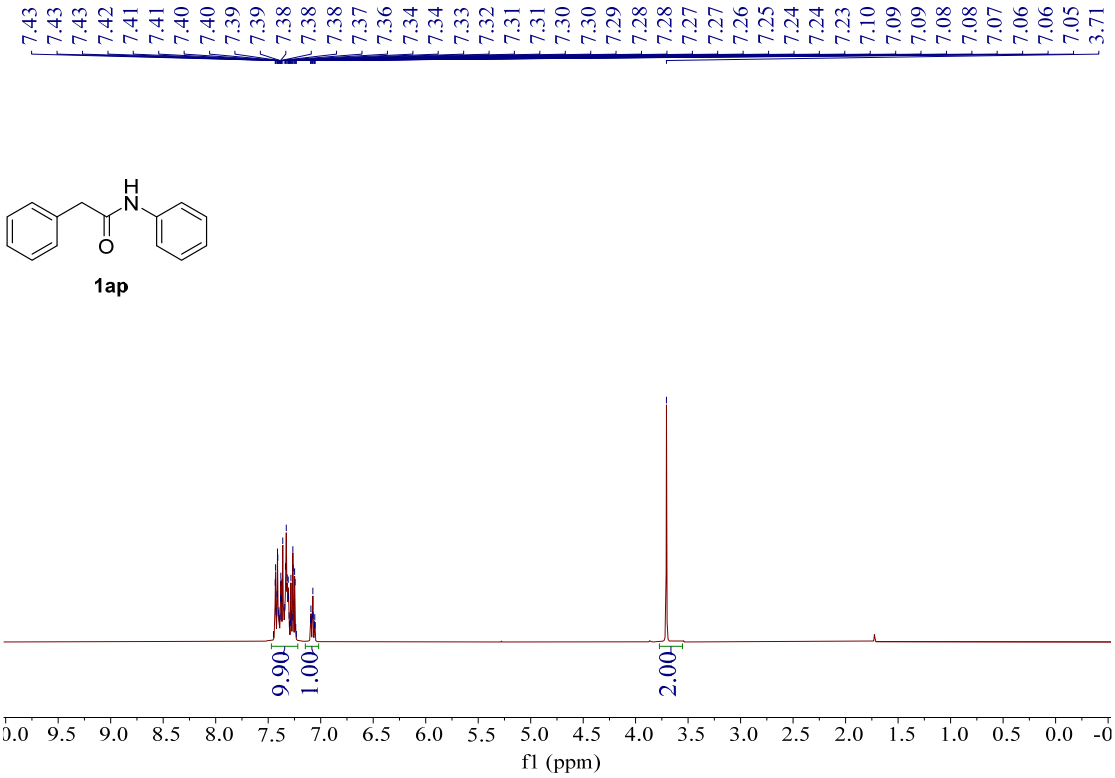
^{13}C NMR spectrum of **1an**



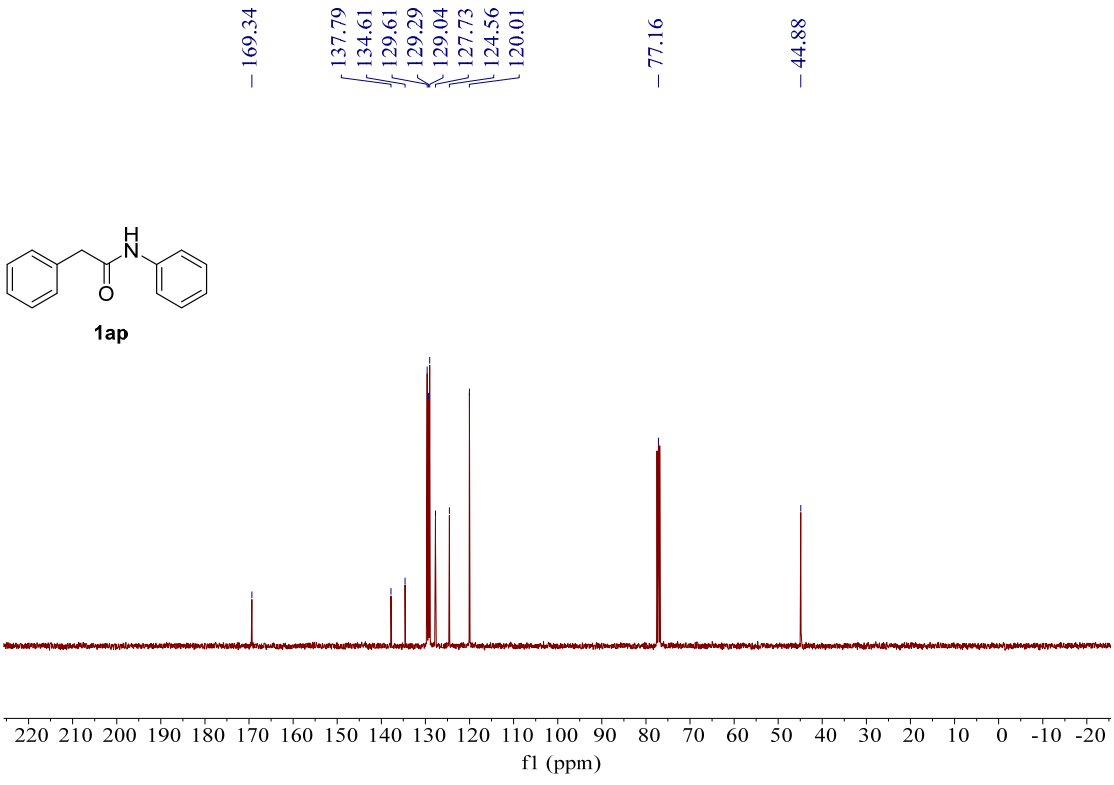
^{1}H NMR spectrum of **1ao**



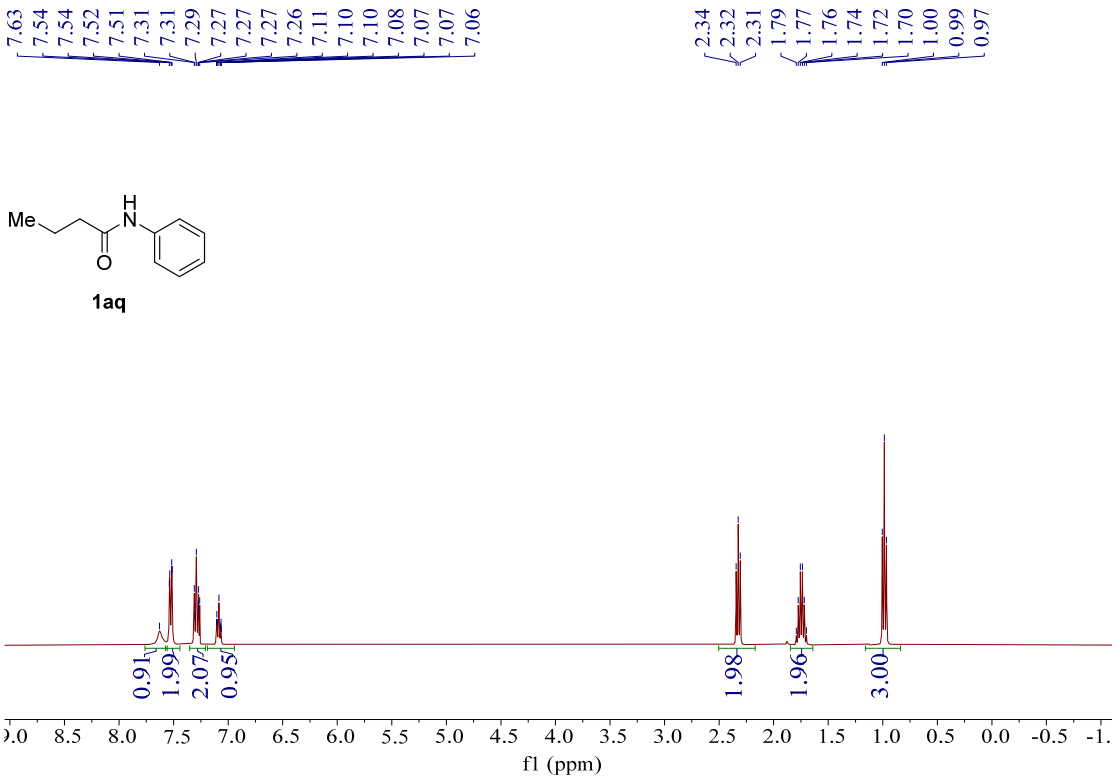
^{13}C NMR spectrum of **1ao**



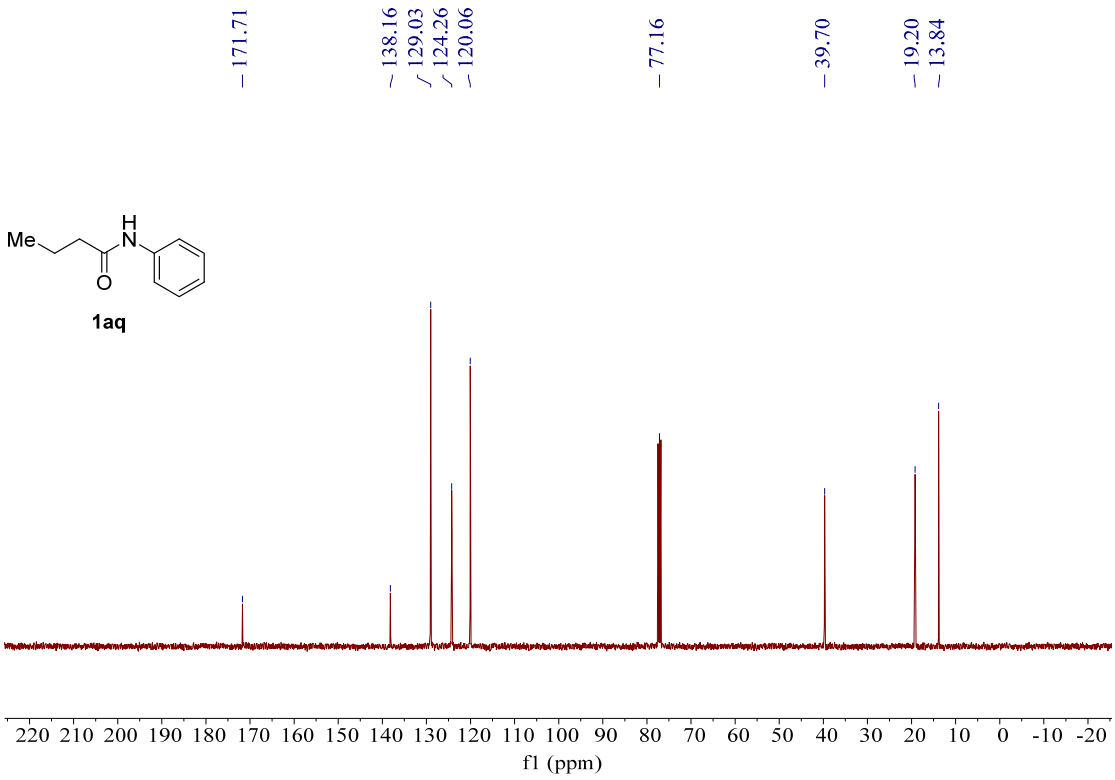
^{1}H NMR spectrum of **1ap**



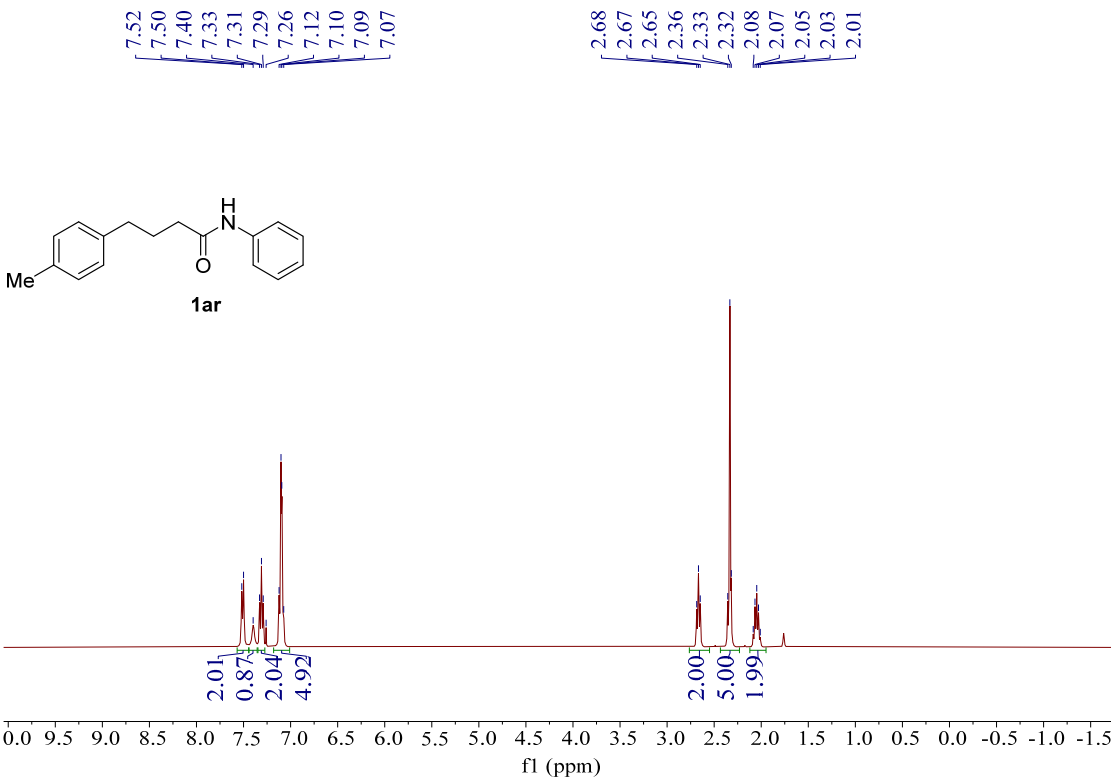
^{13}C NMR spectrum of **1ap**



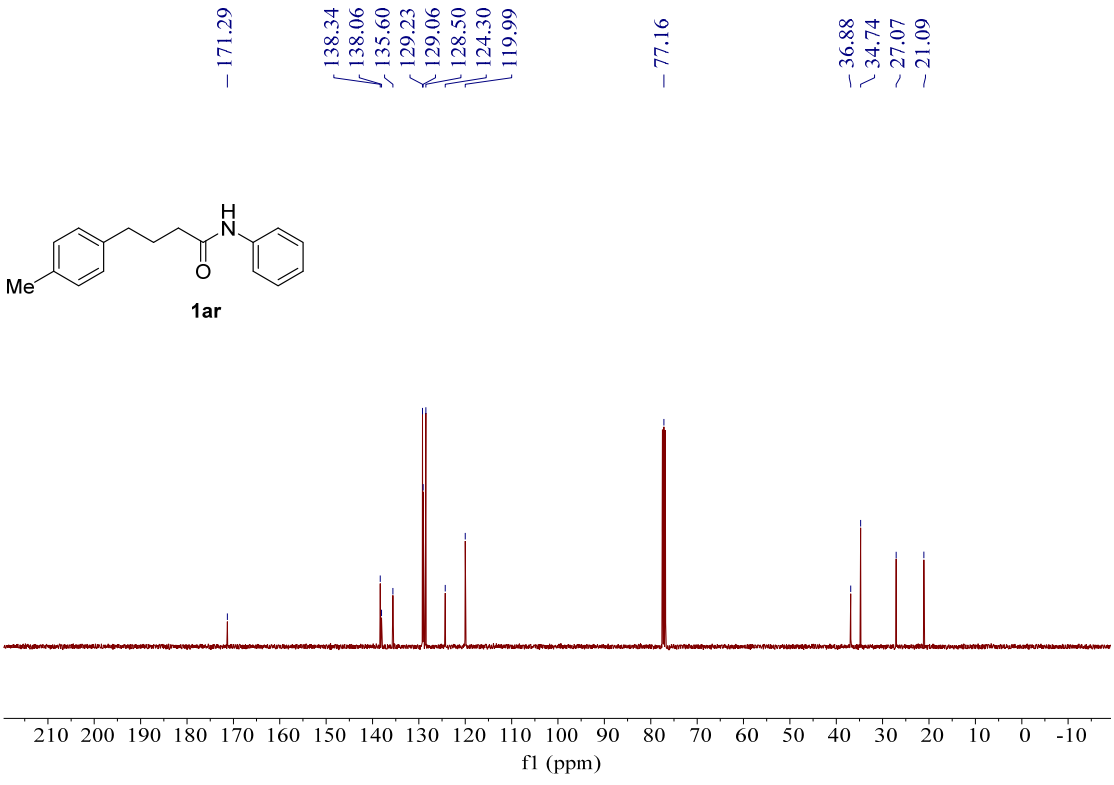
^{1}H NMR spectrum of **1aq**



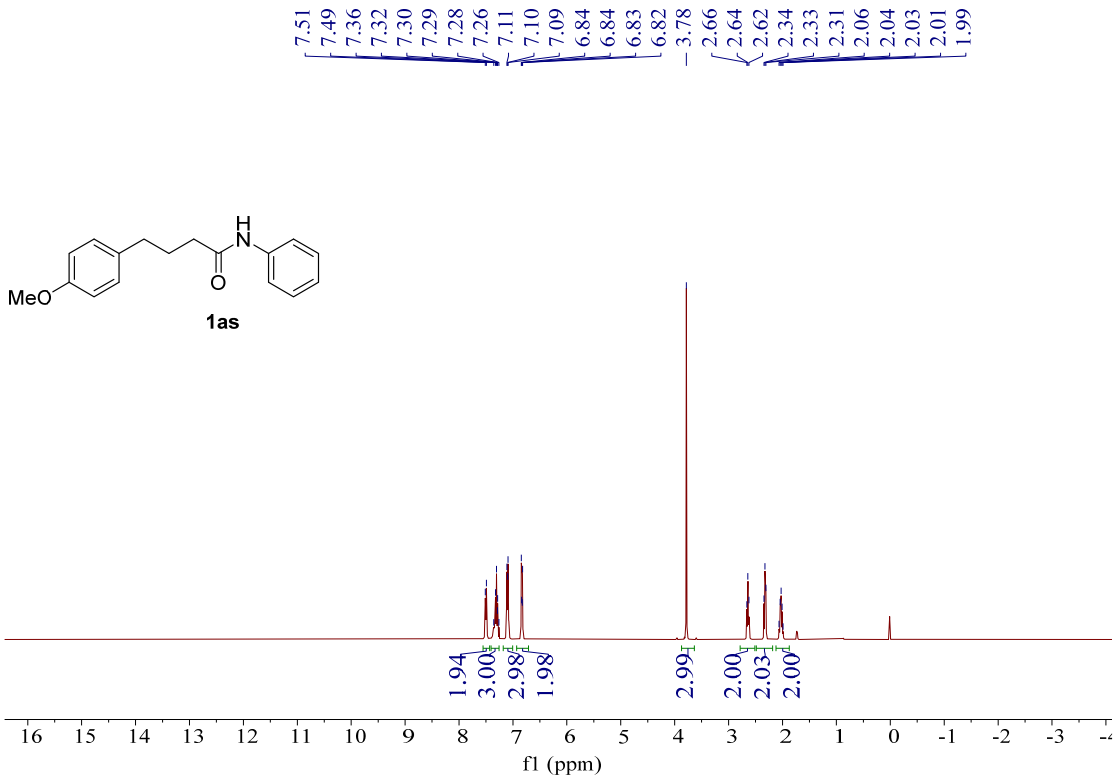
^{13}C NMR spectrum of **1aq**



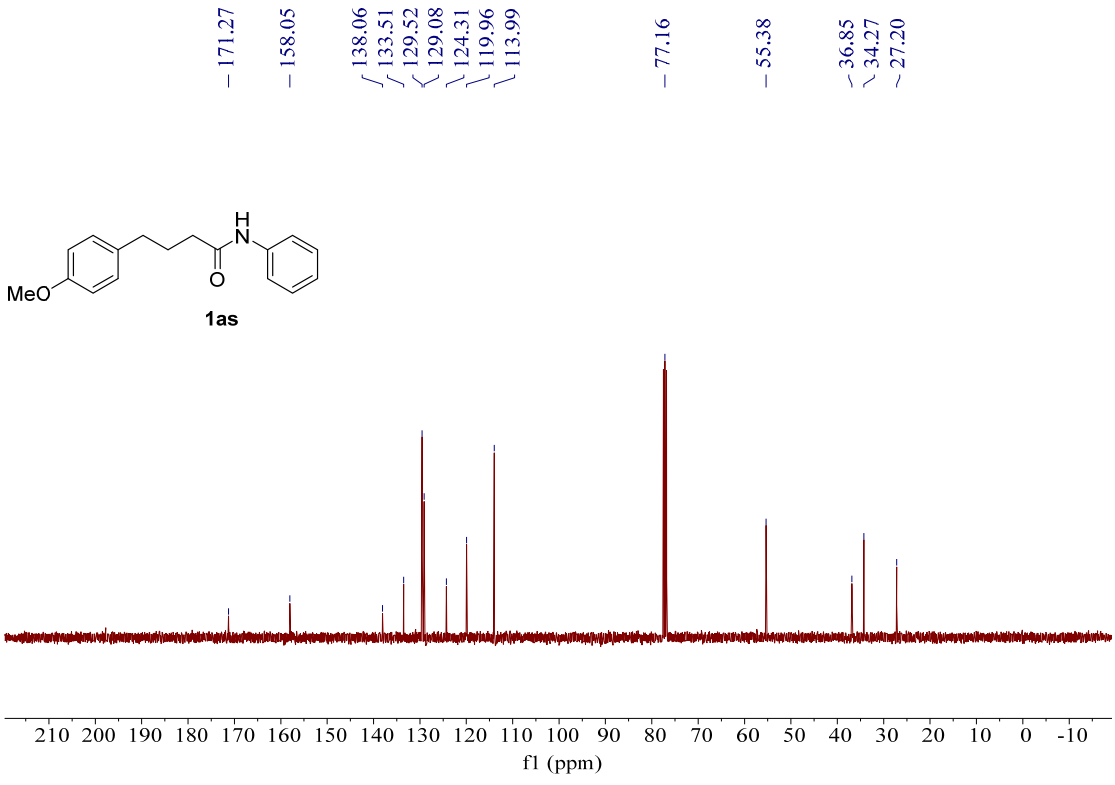
^{1}H NMR spectrum of **1ar**



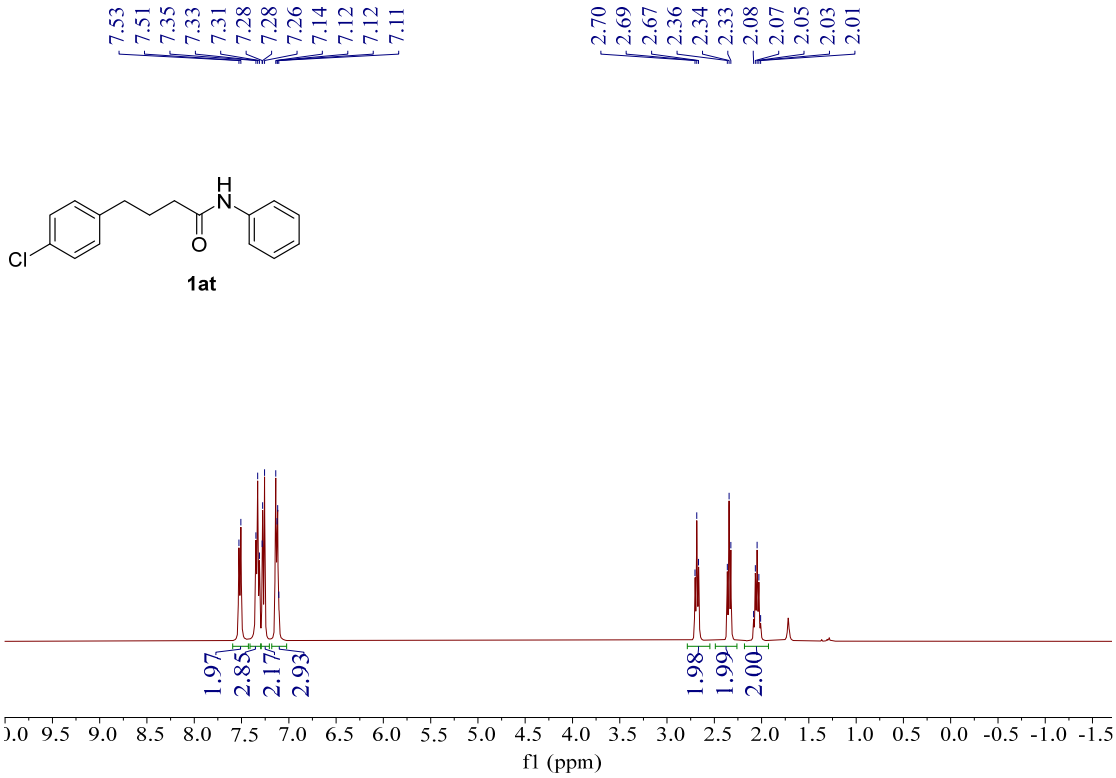
^{13}C NMR spectrum of **1ar**



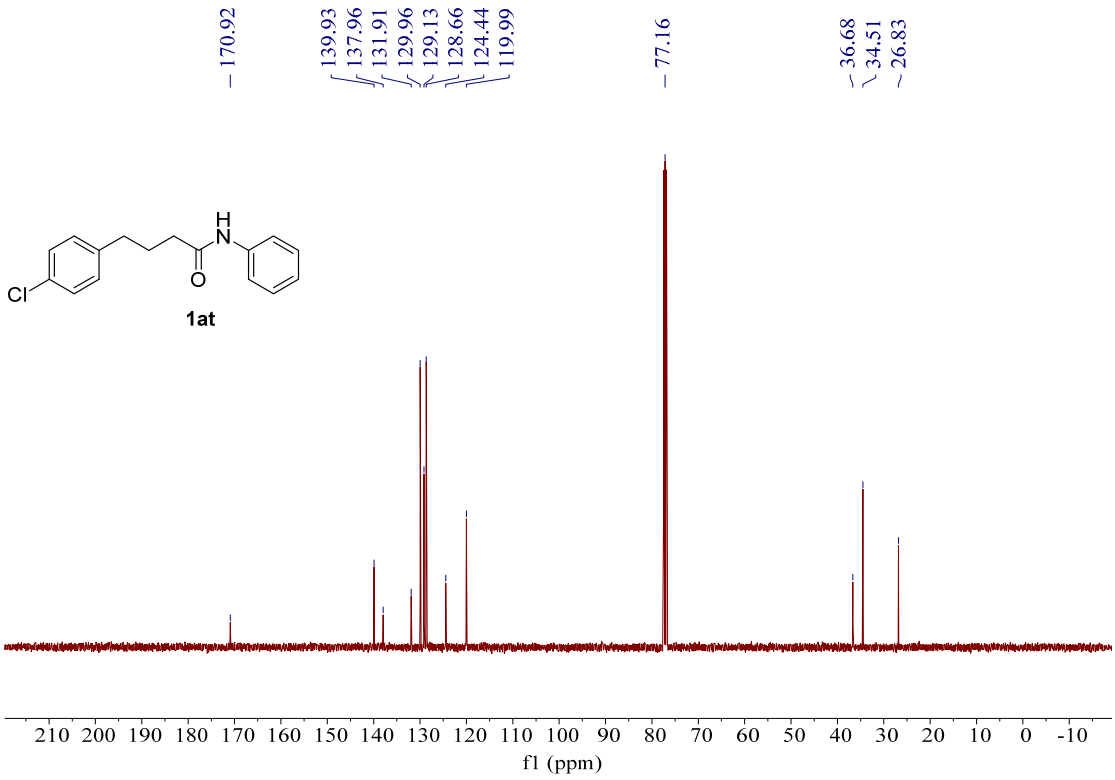
^{1}H NMR spectrum of **1as**



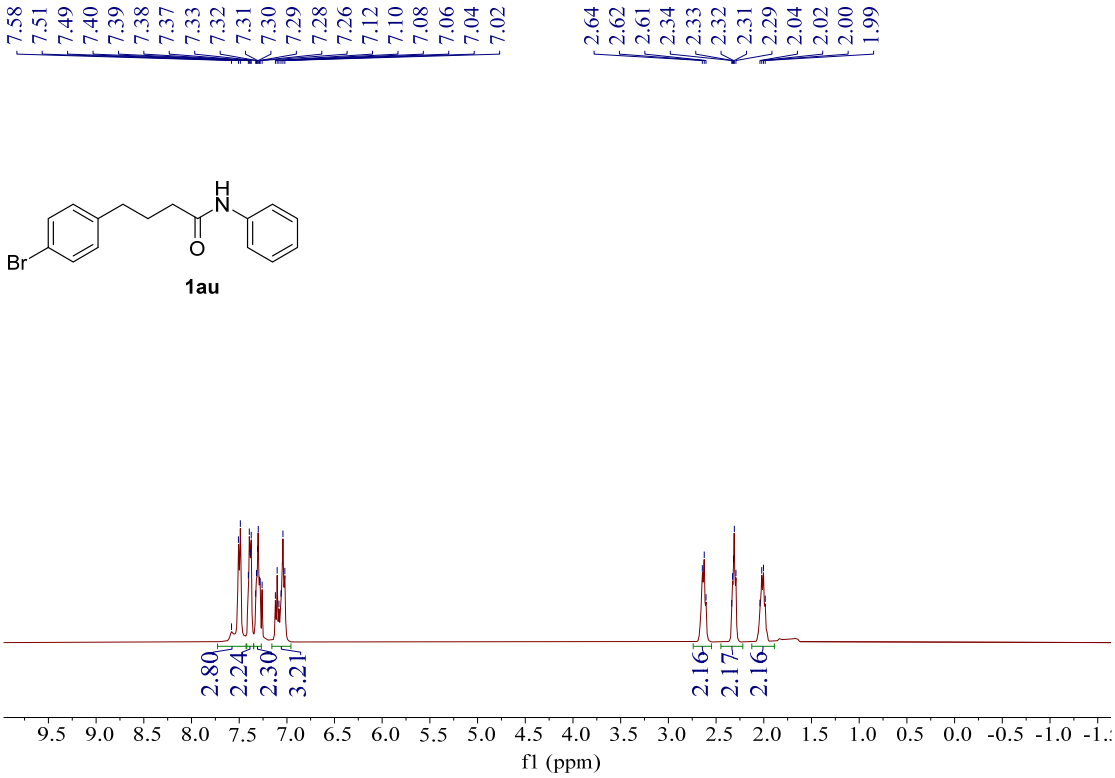
^{13}C NMR spectrum of **1as**



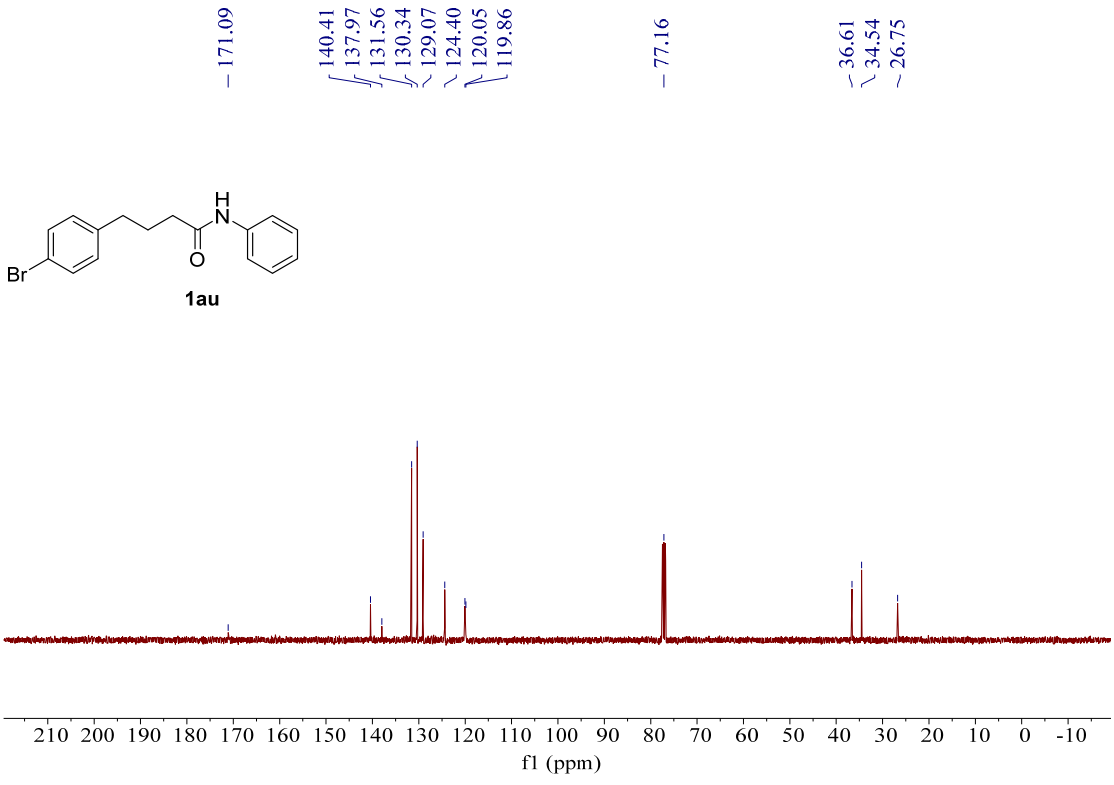
^{1}H NMR spectrum of **1at**



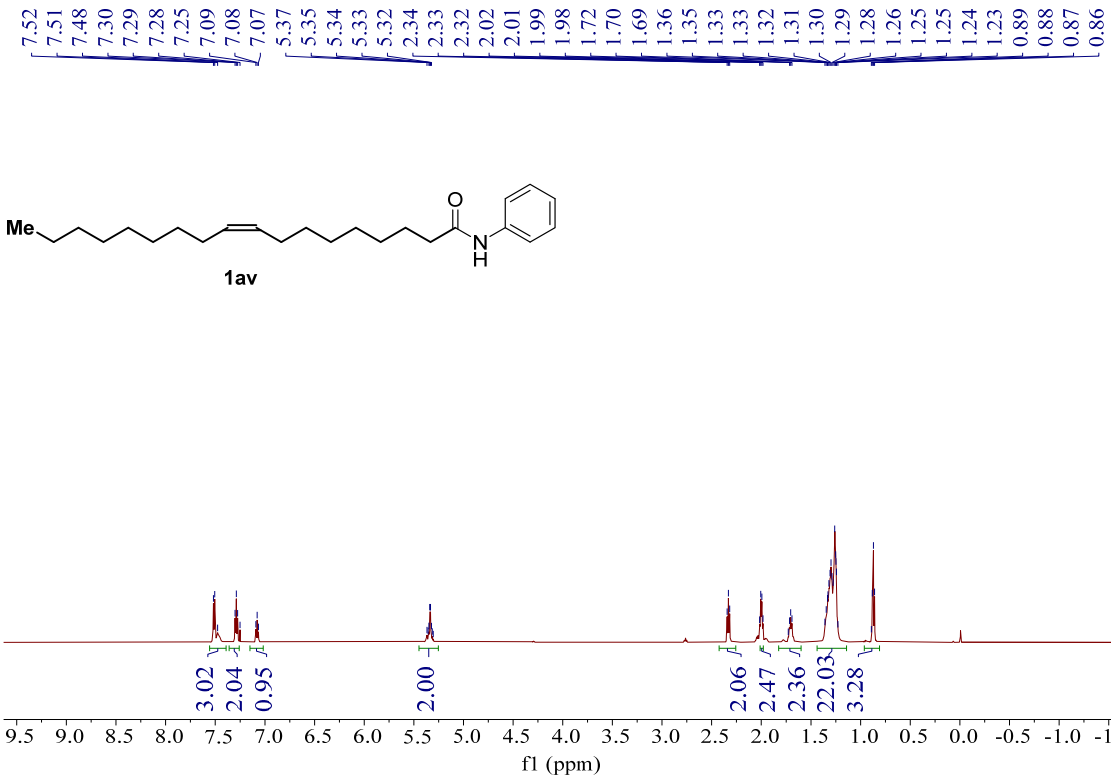
^{13}C NMR spectrum of **1at**



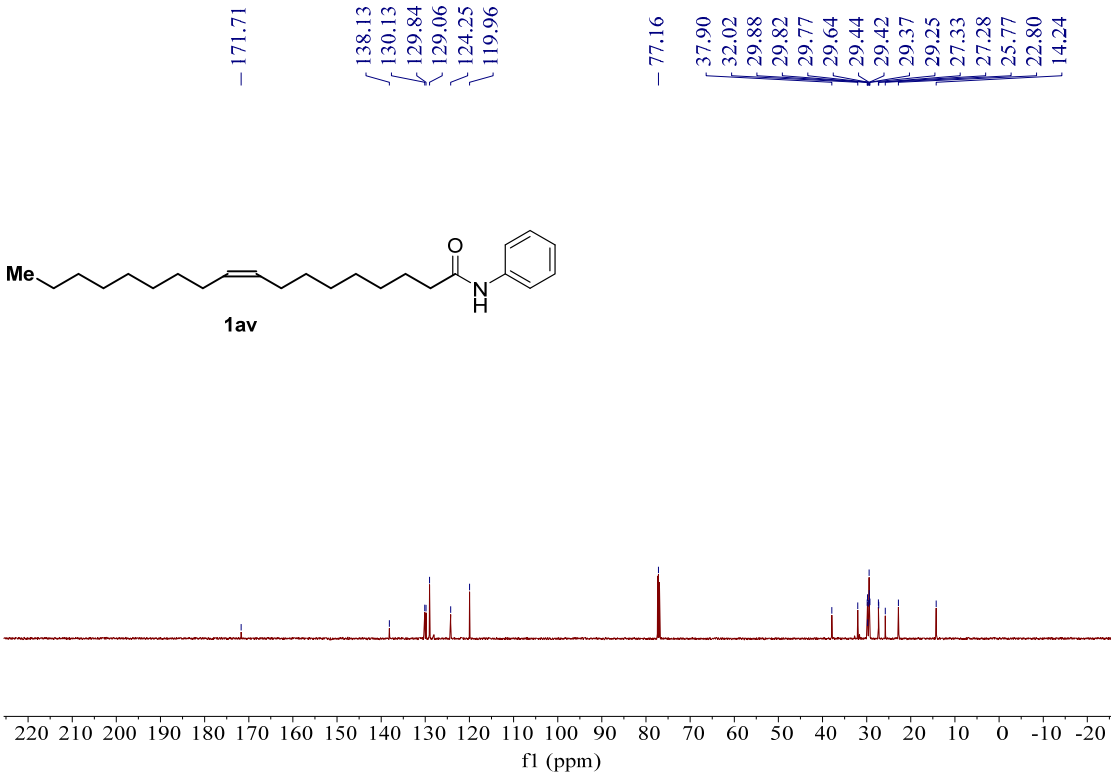
^{1}H NMR spectrum of **1au**



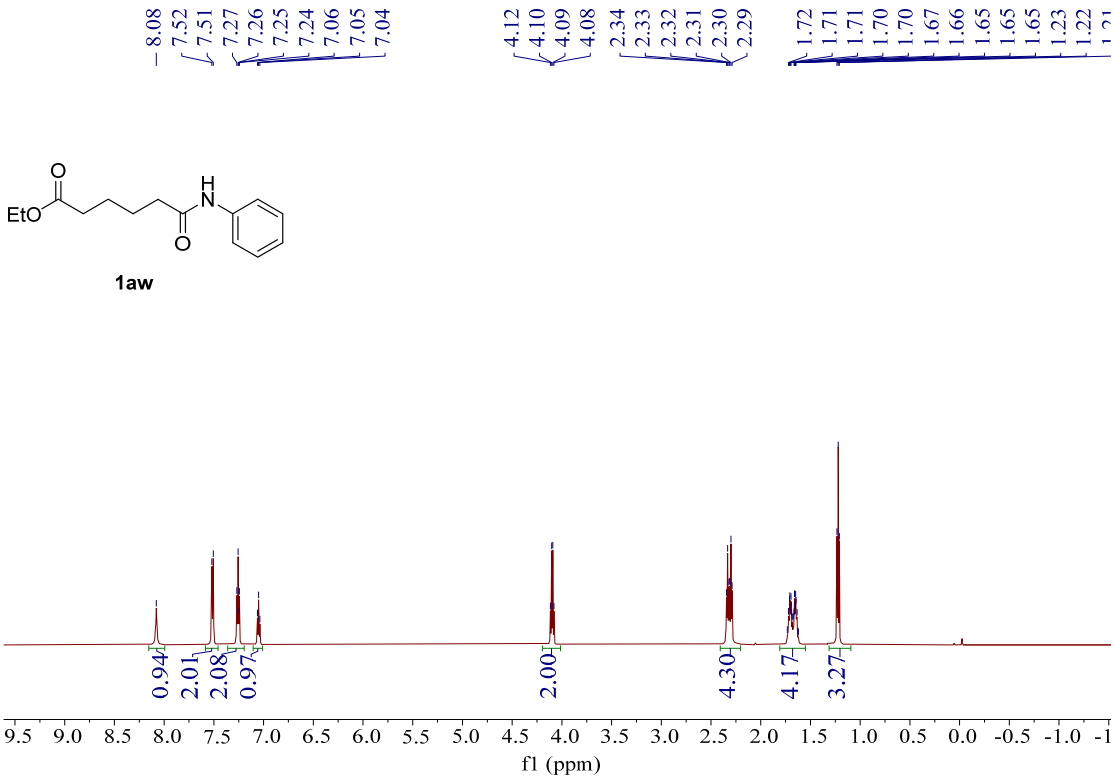
^{13}C NMR spectrum of **1au**



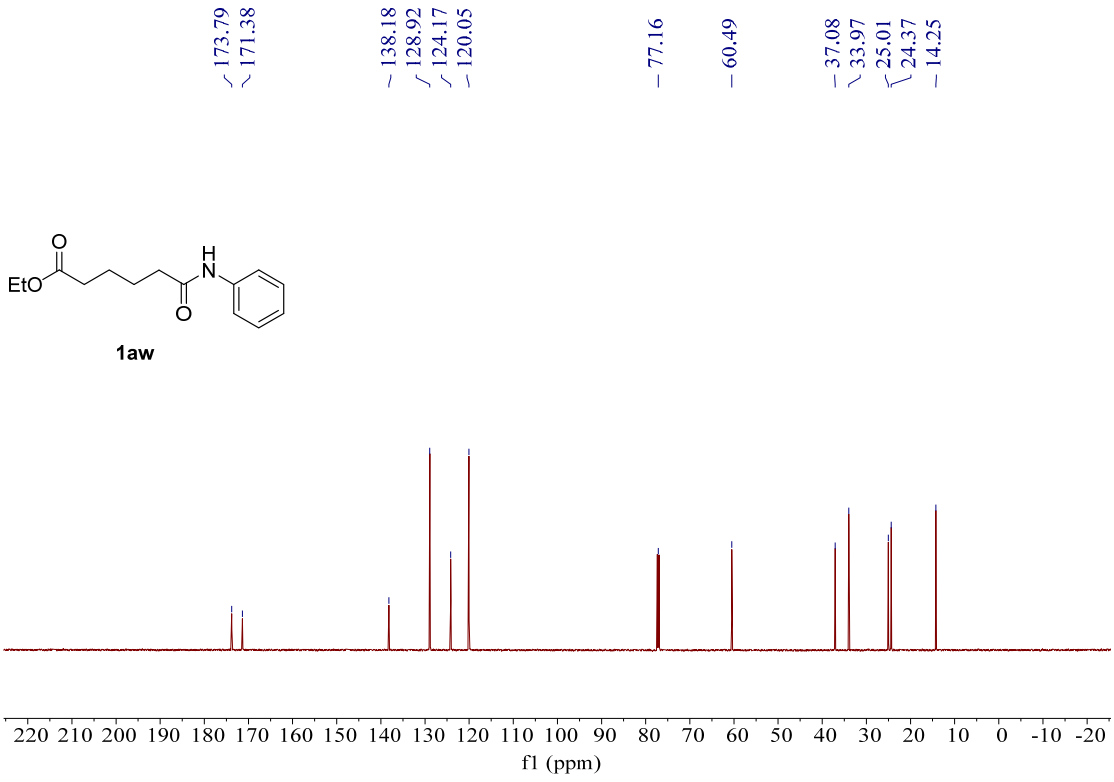
^{1}H NMR spectrum of **1av**



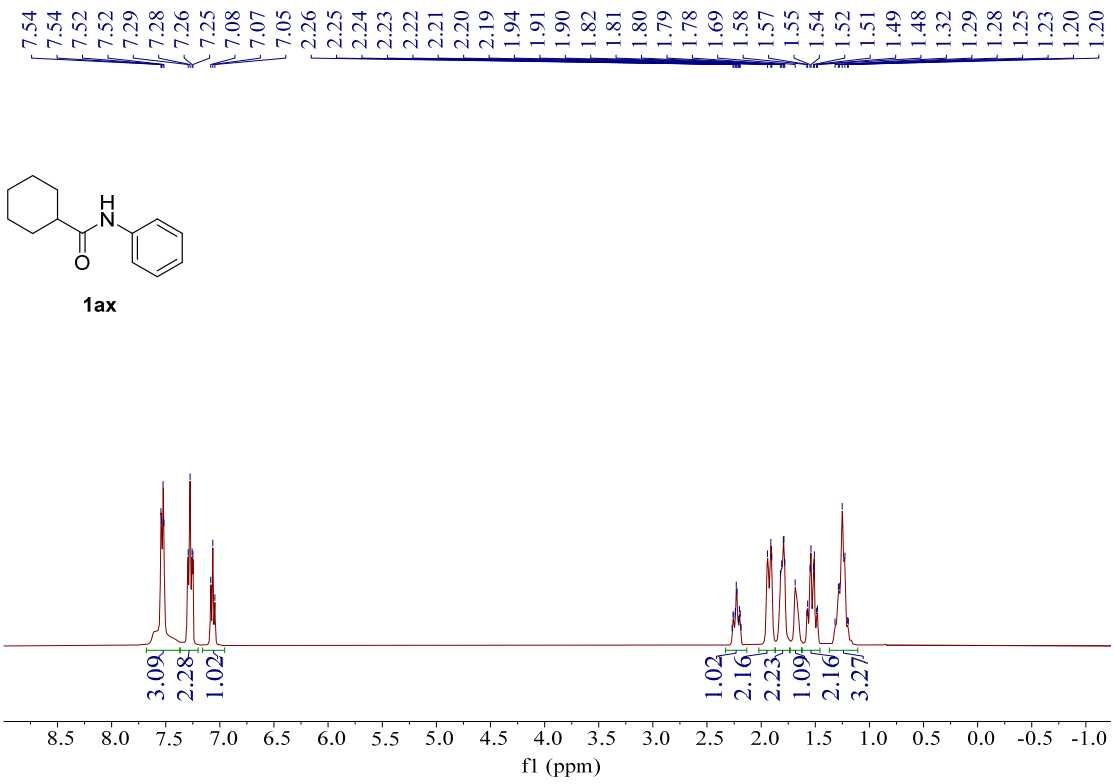
^{13}C NMR spectrum of **1av**



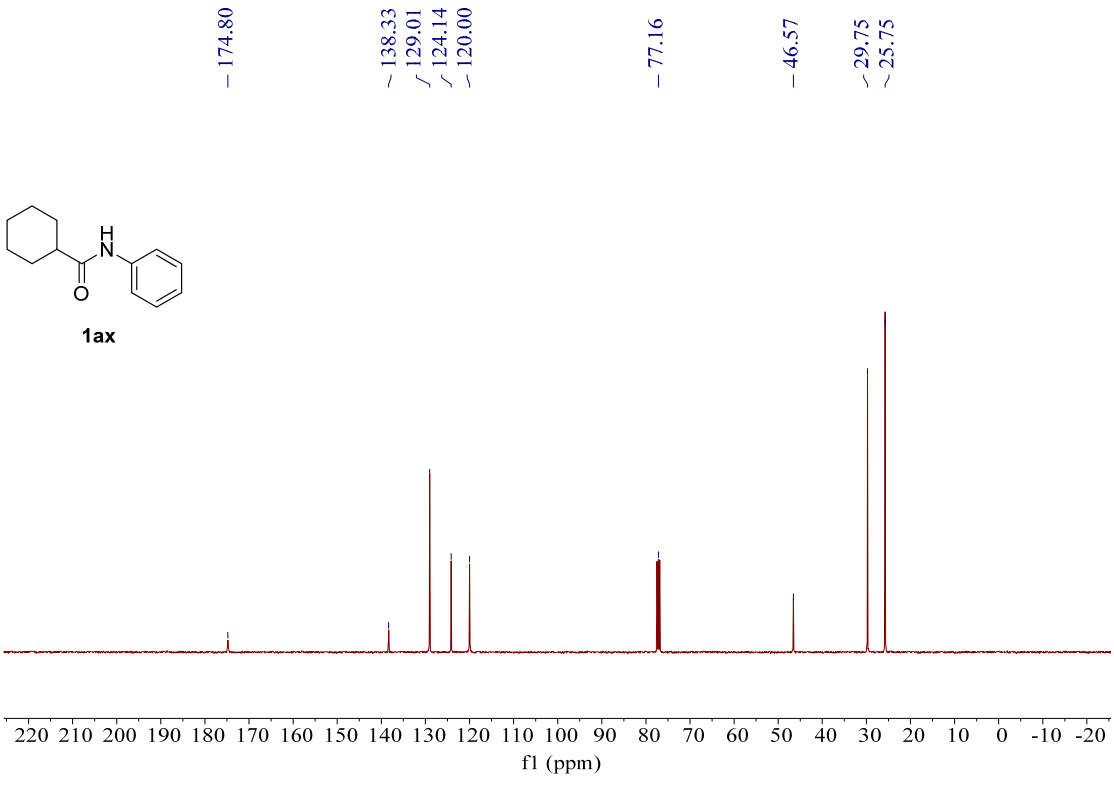
^{1}H NMR spectrum of **1aw**



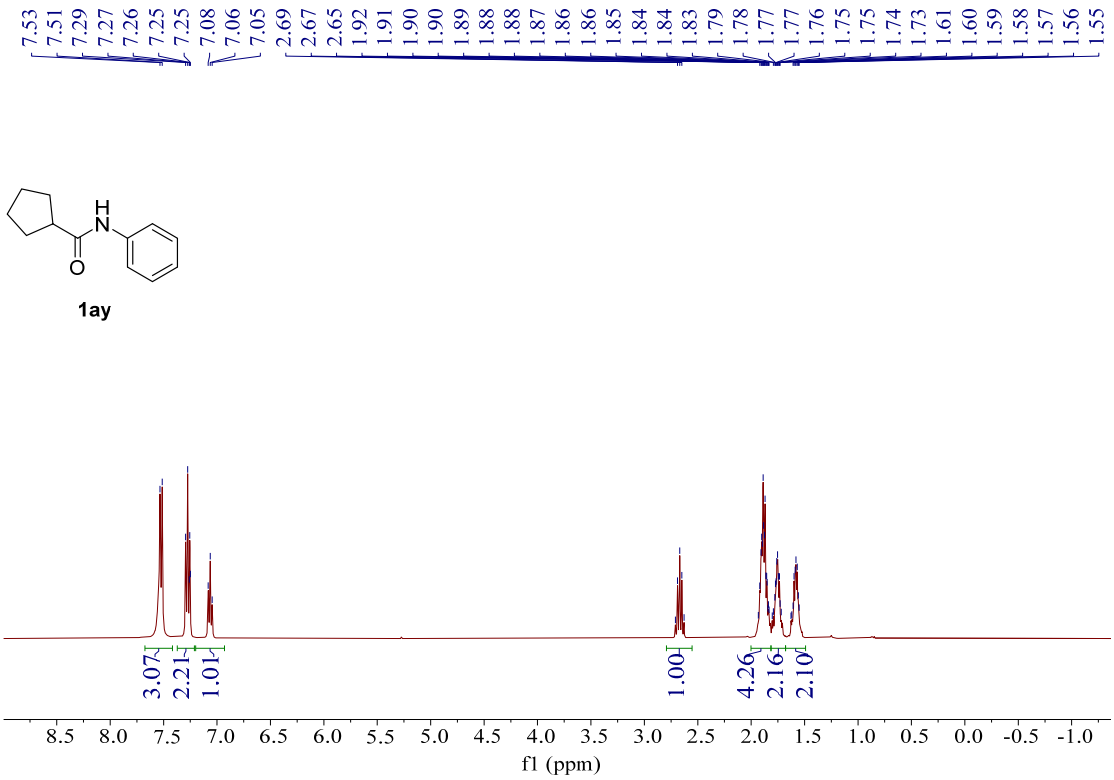
^{13}C NMR spectrum of **1aw**



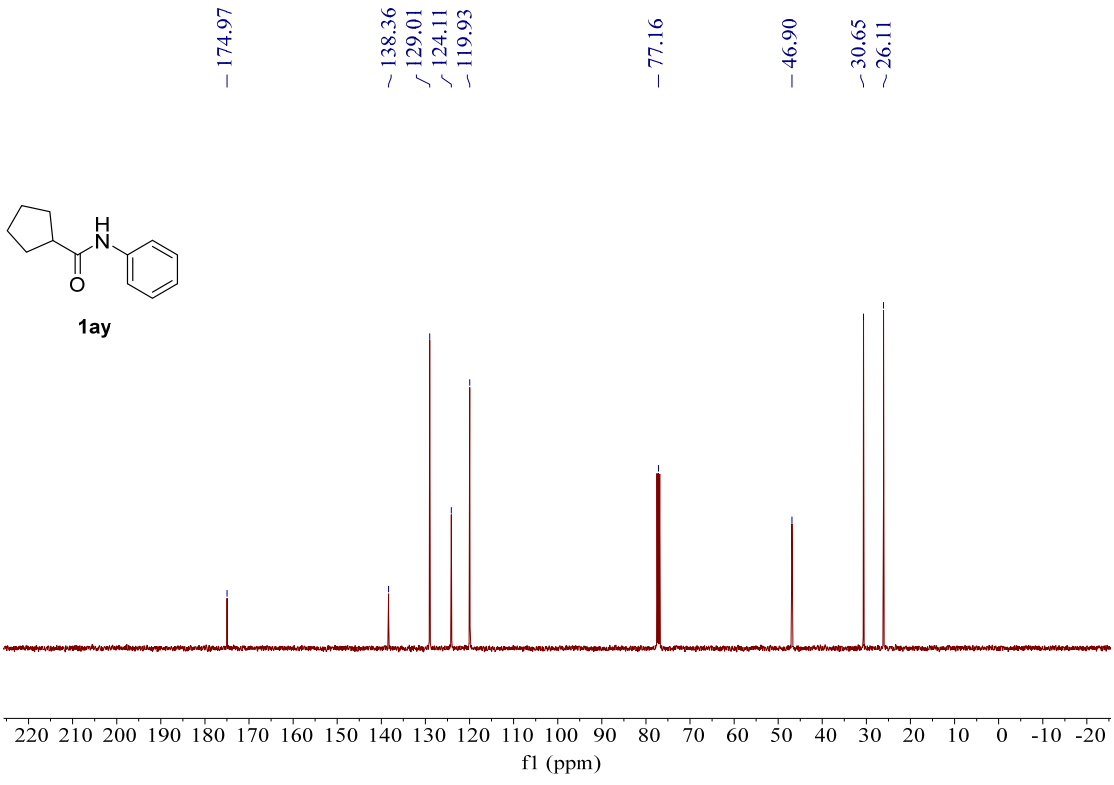
^{1}H NMR spectrum of **1ax**



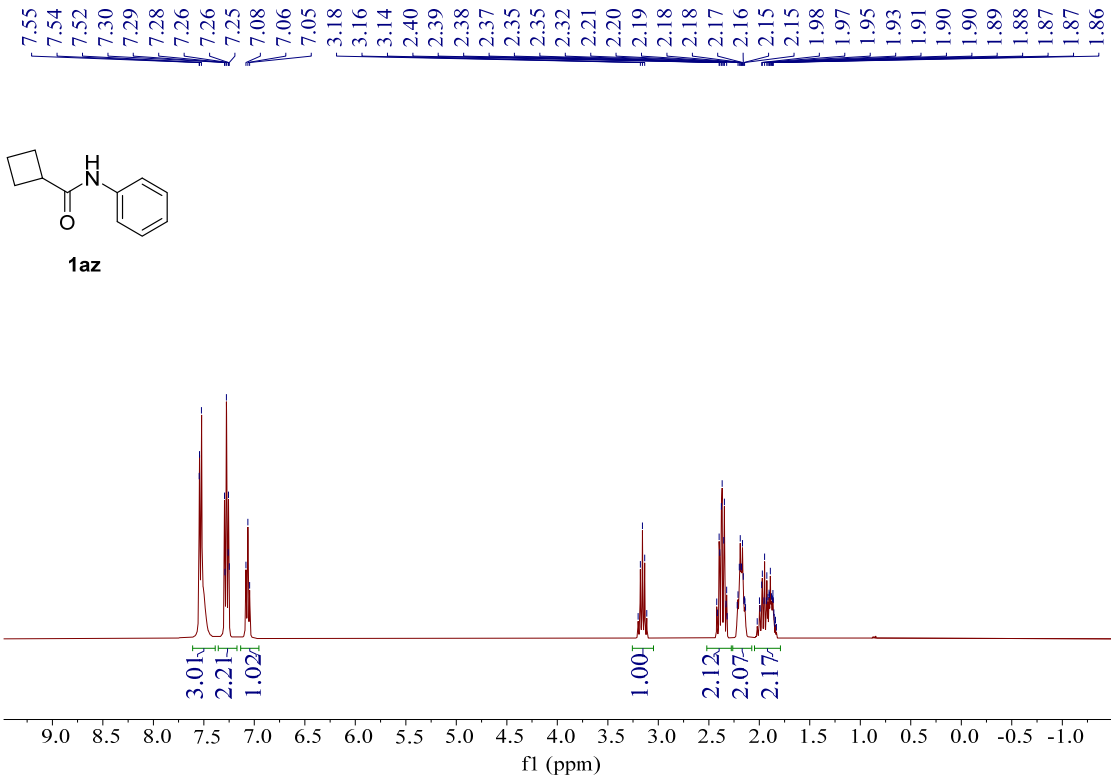
^{13}C NMR spectrum of **1ax**



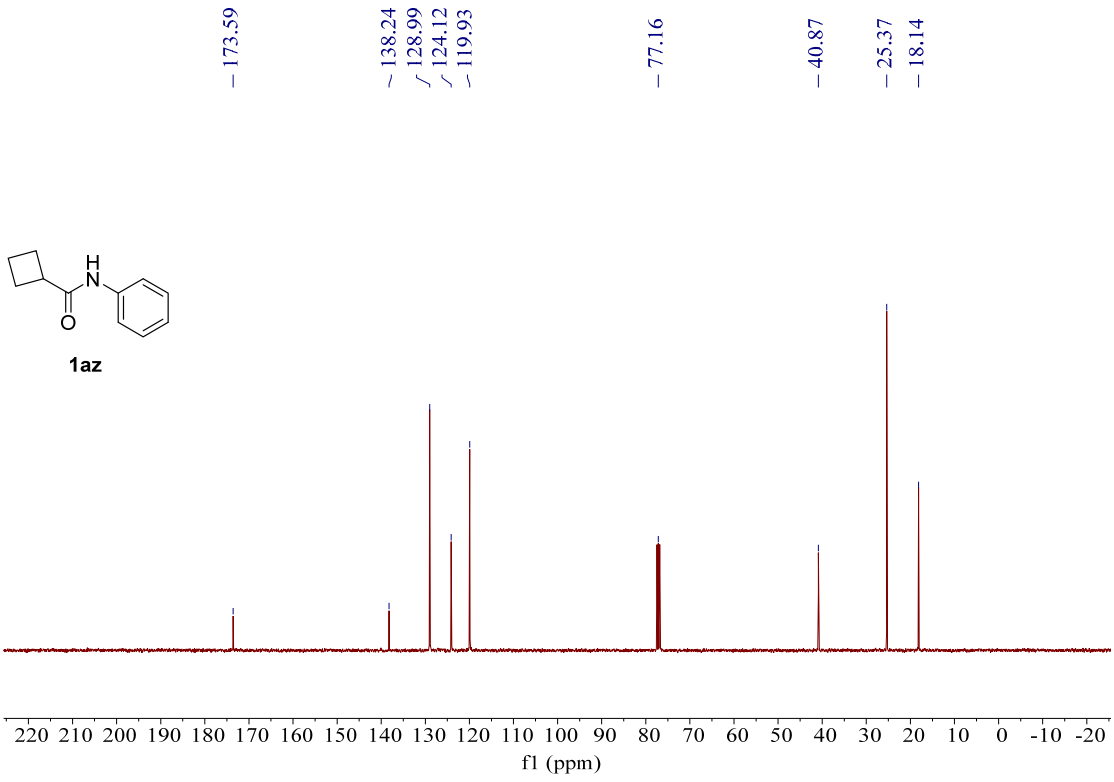
^{1}H NMR spectrum of **1ay**



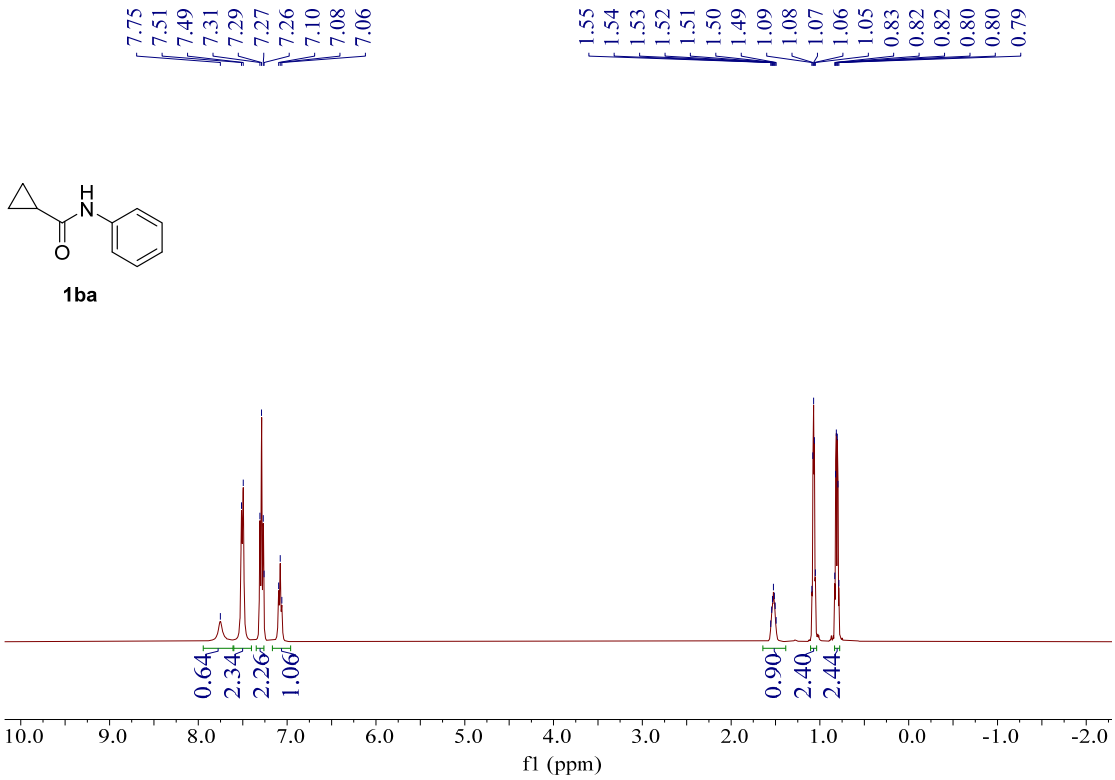
^{13}C NMR spectrum of **1ay**



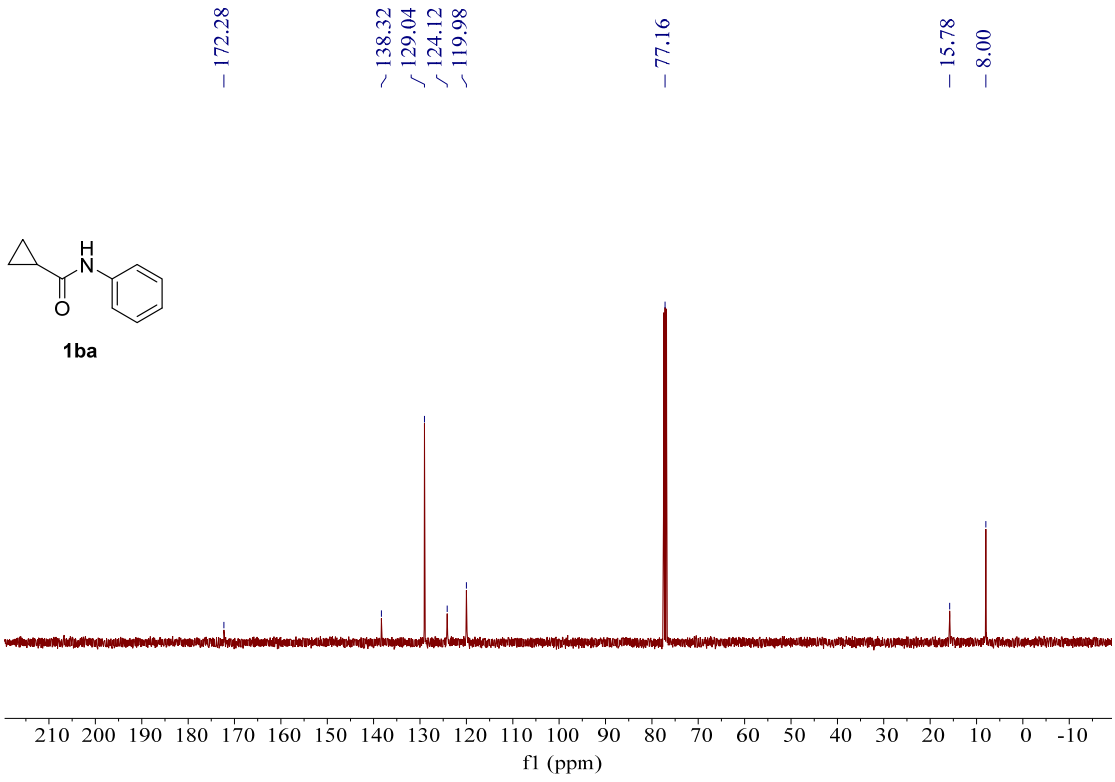
^{1}H NMR spectrum of **1az**



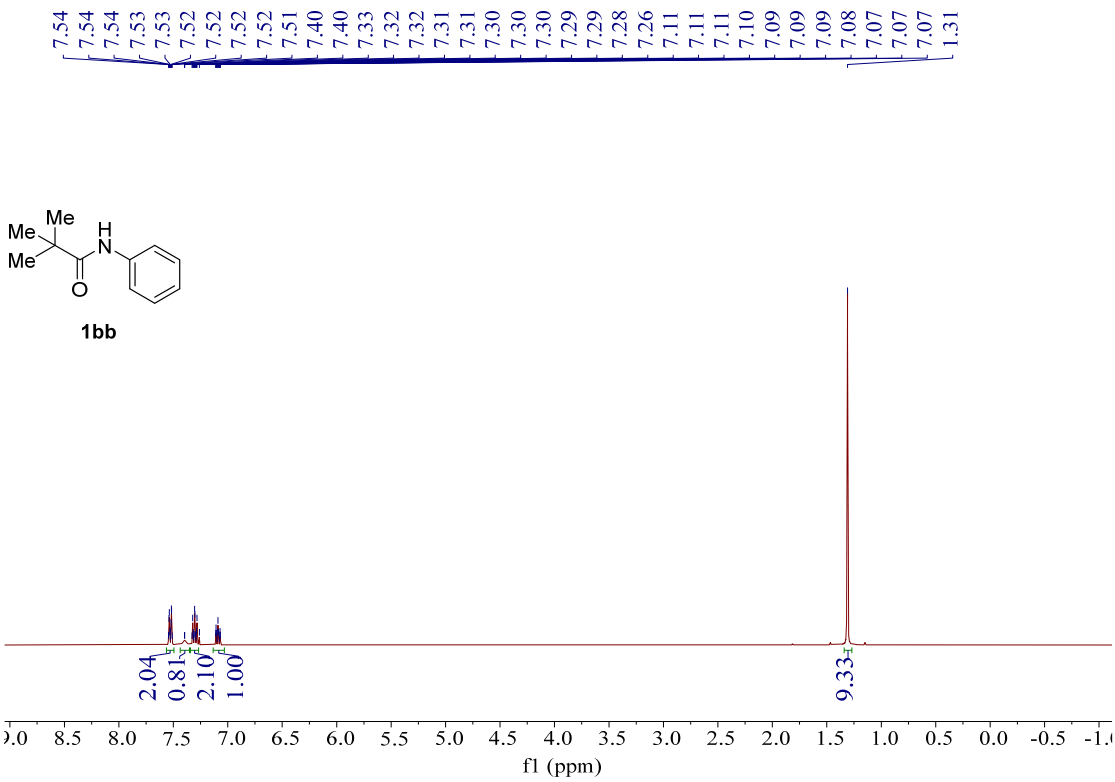
^{13}C NMR spectrum of **1az**



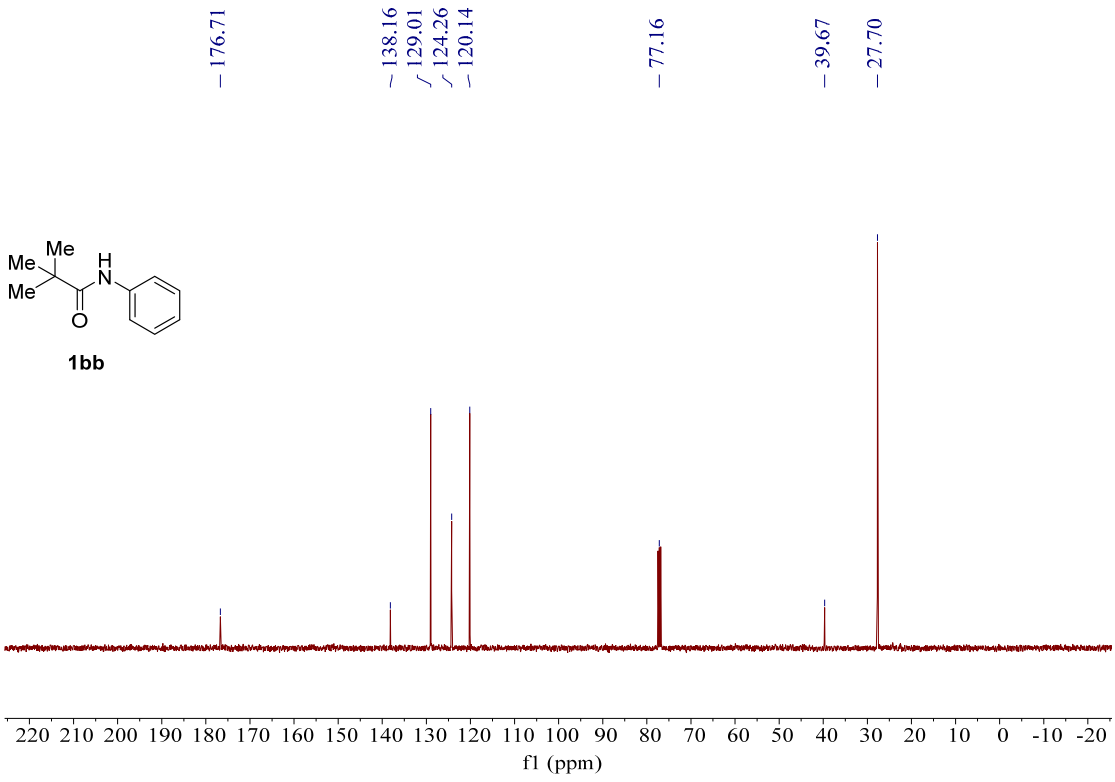
^{1}H NMR spectrum of **1ba**



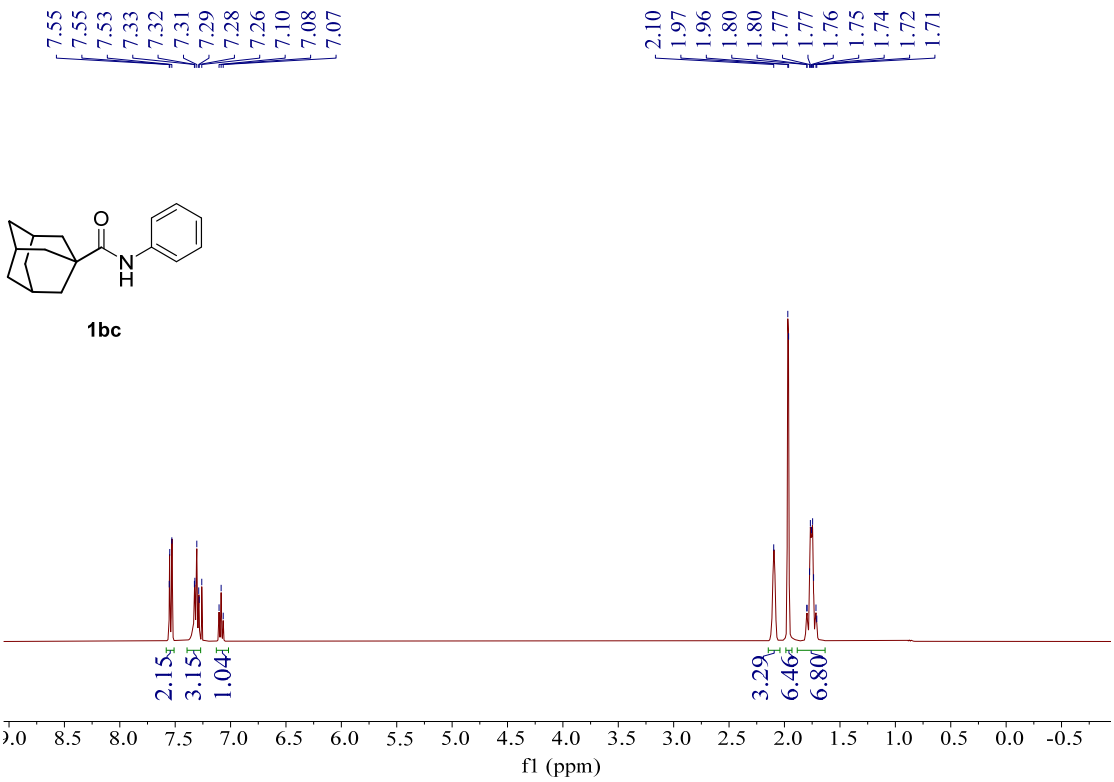
^{13}C NMR spectrum of **1ba**



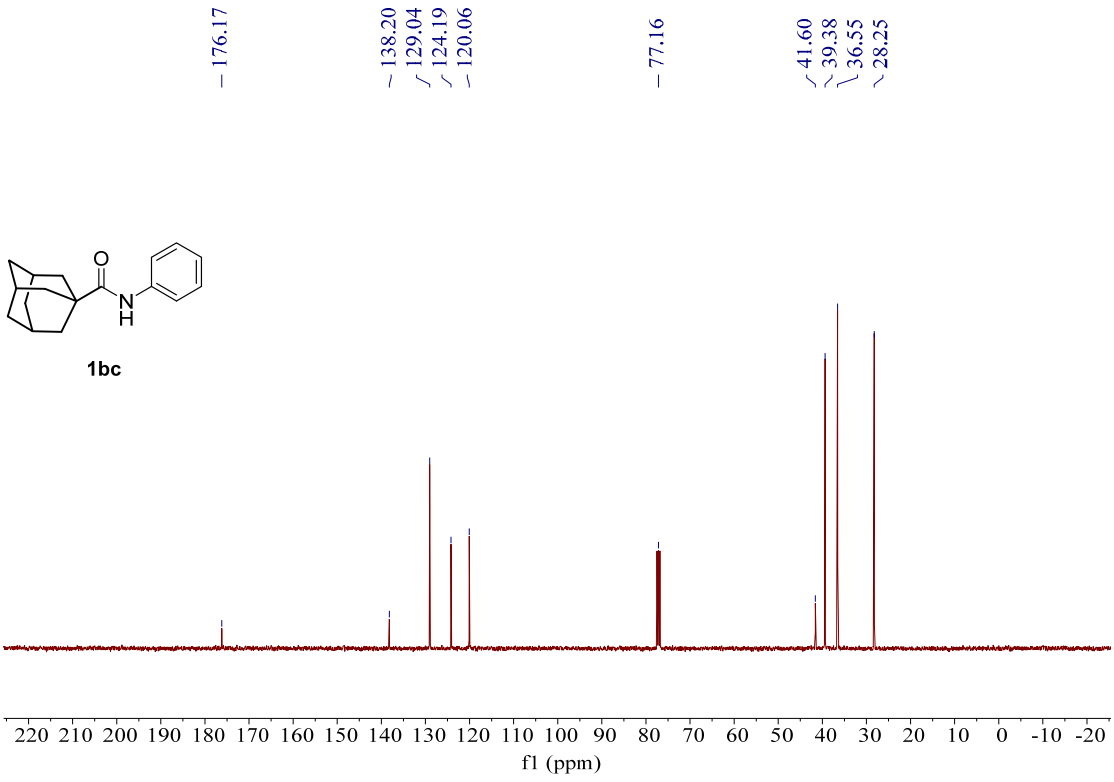
^{1}H NMR spectrum of **1bb**



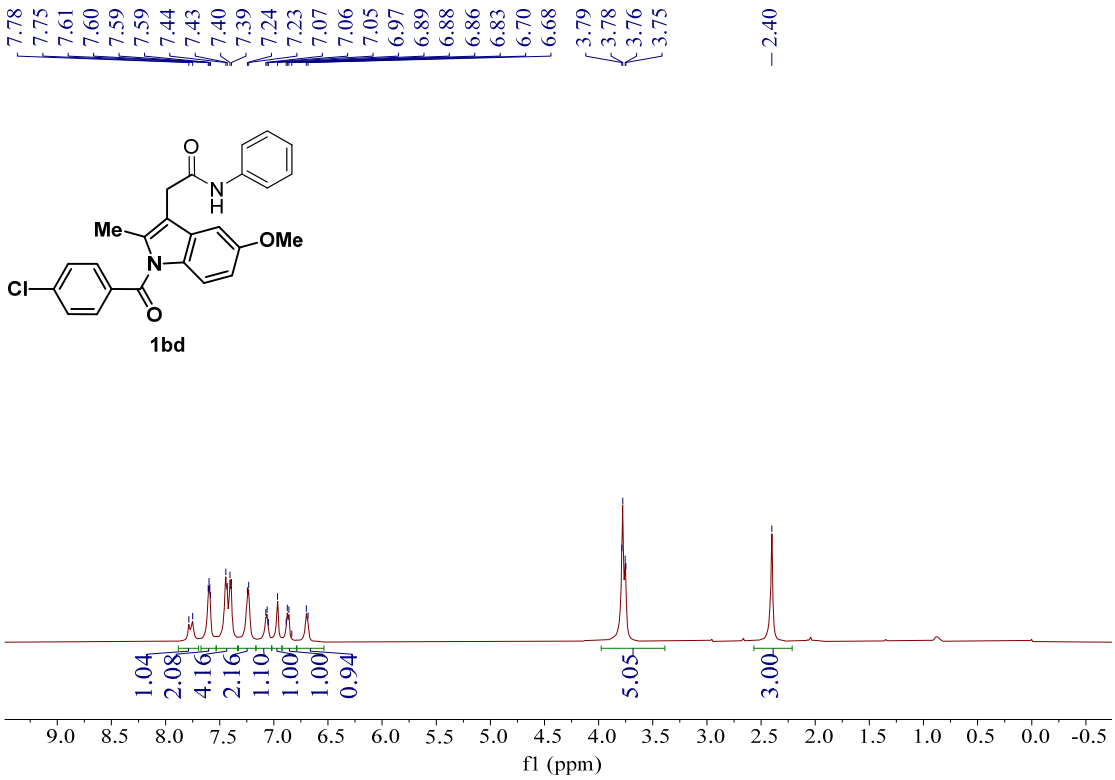
^{13}C NMR spectrum of **1bb**



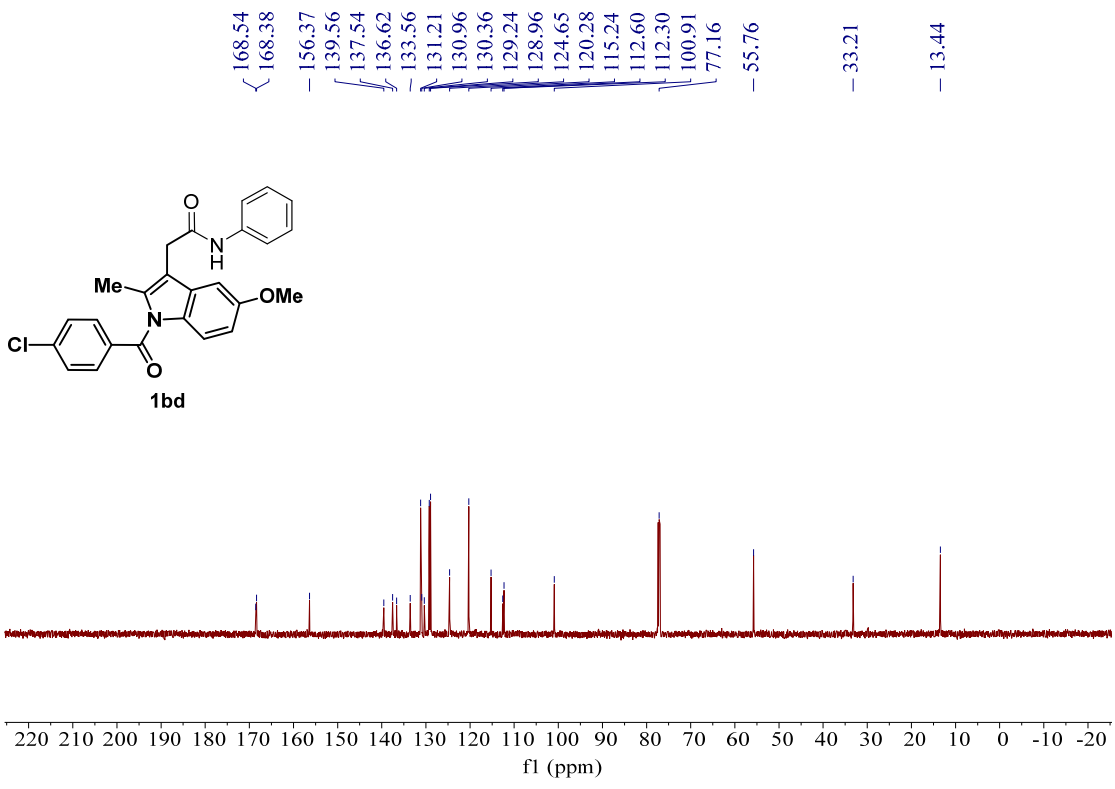
^{1}H NMR spectrum of **1bc**



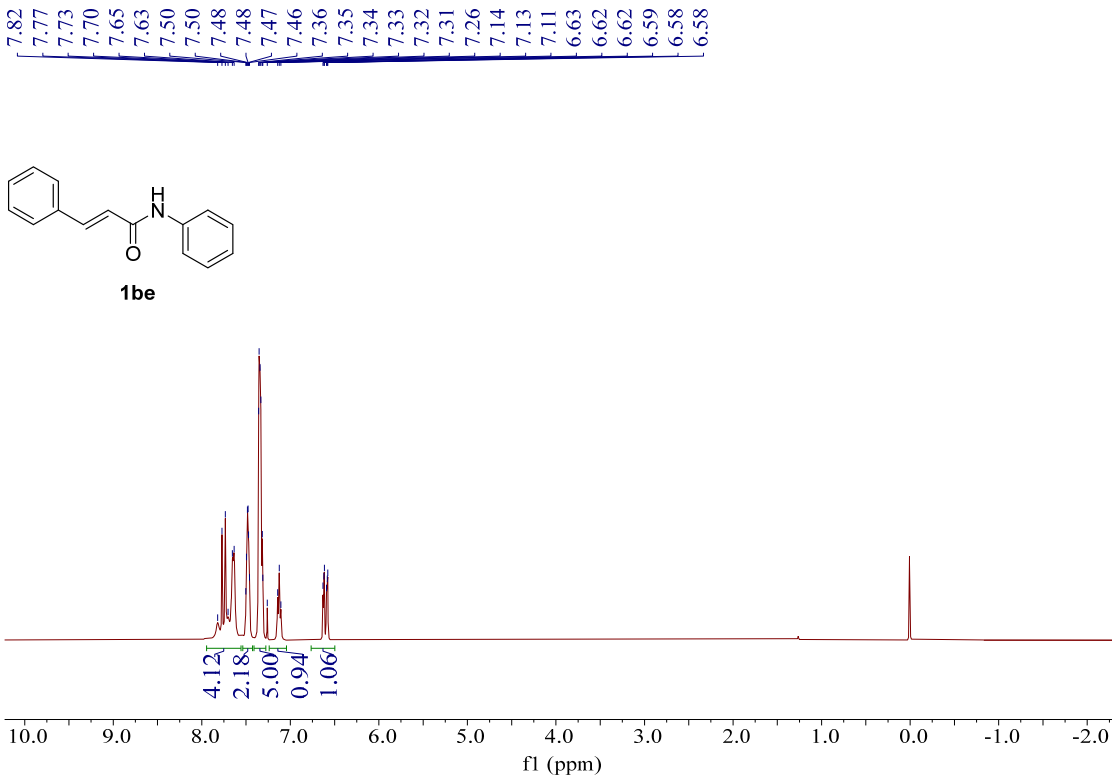
^{13}C NMR spectrum of **1bc**



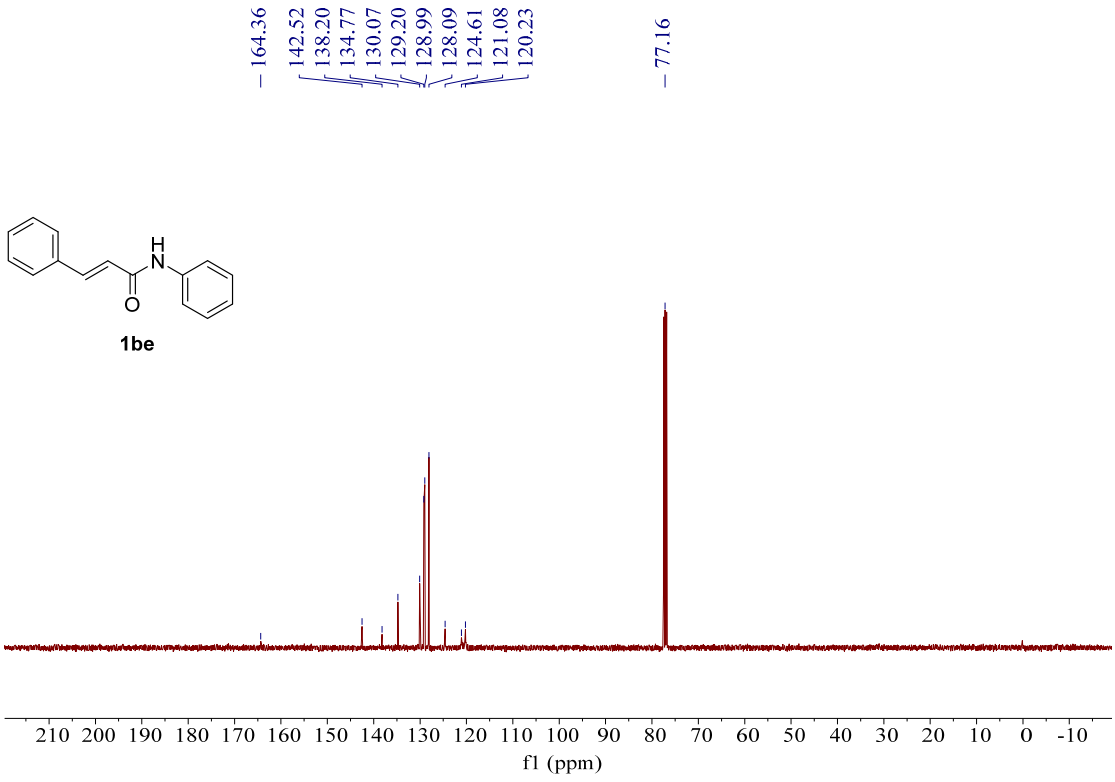
^{1}H NMR spectrum of **1bd**



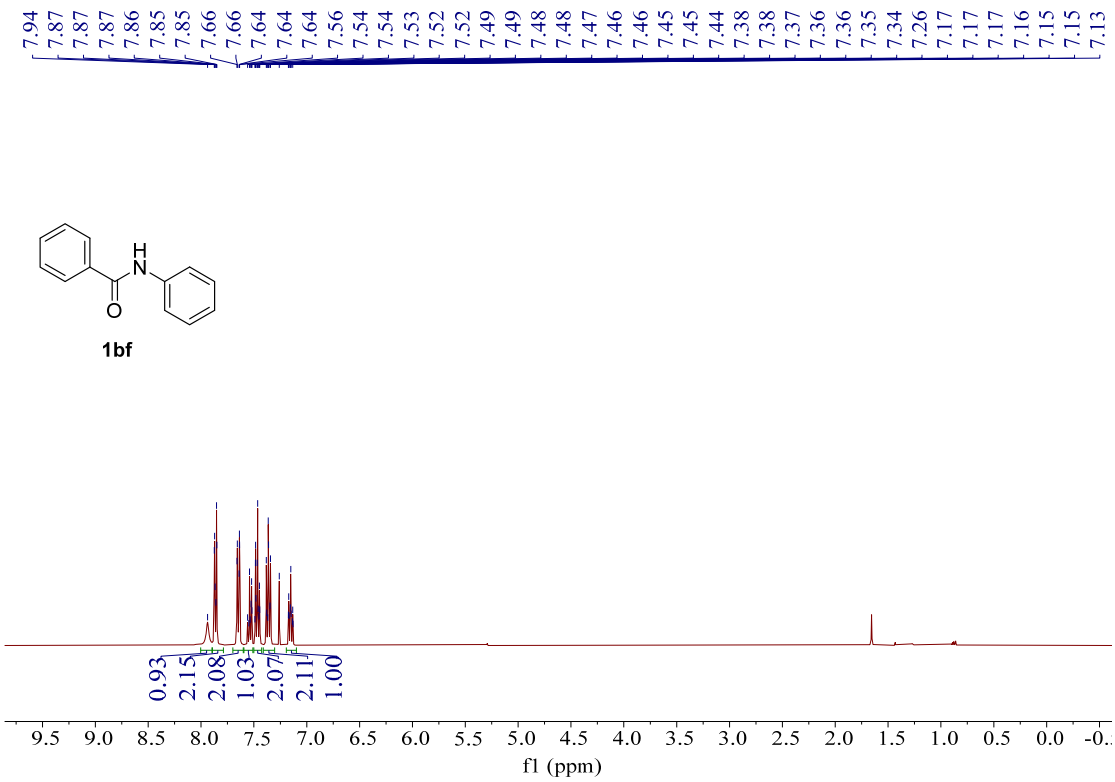
^{13}C NMR spectrum of **1bd**



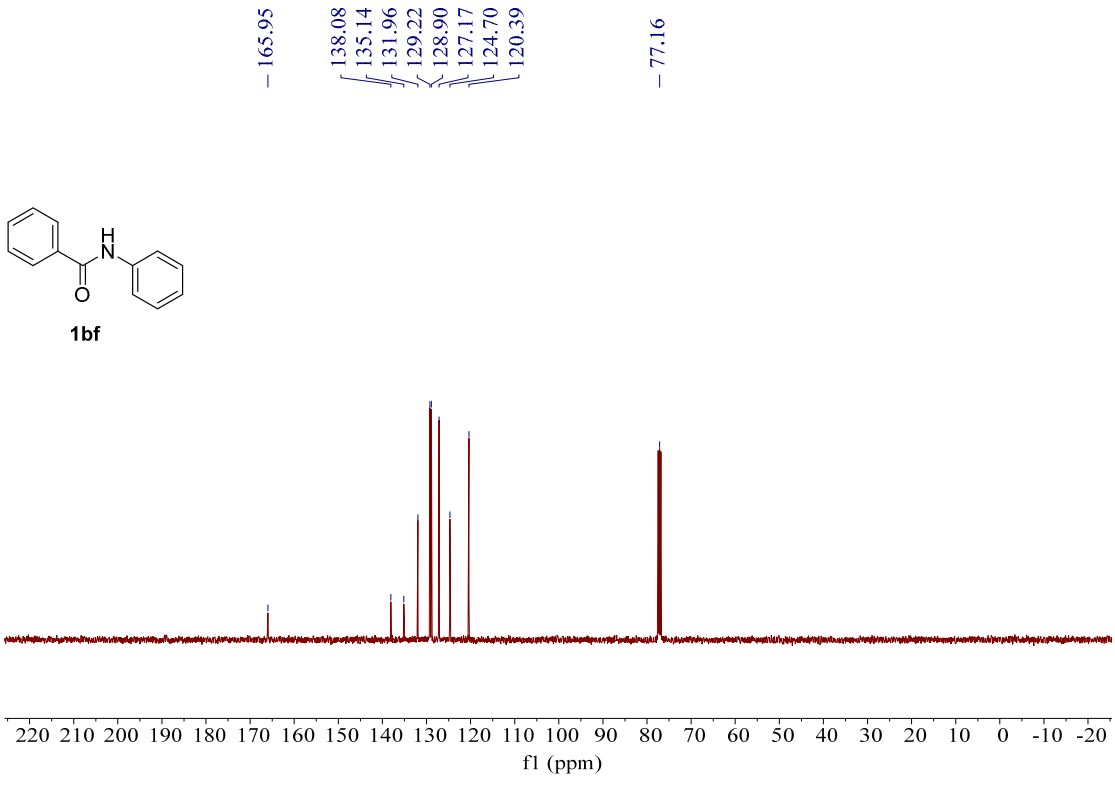
^{1}H NMR spectrum of **1be**



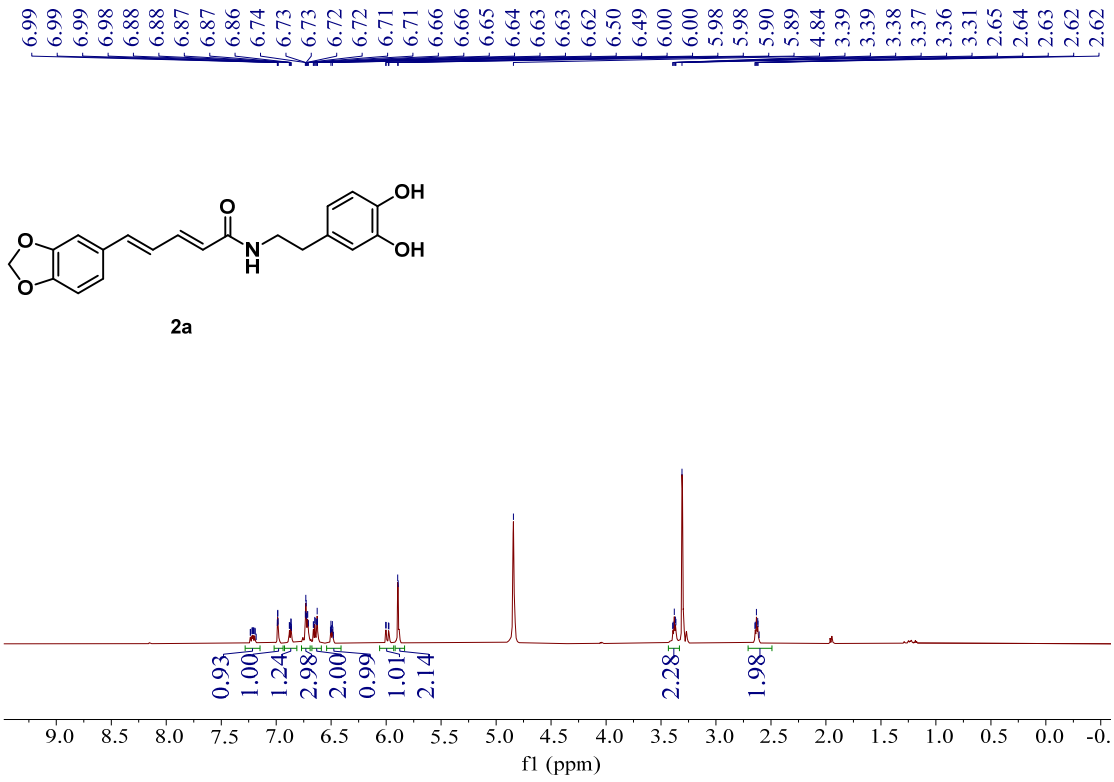
^{13}C NMR spectrum of **1be**



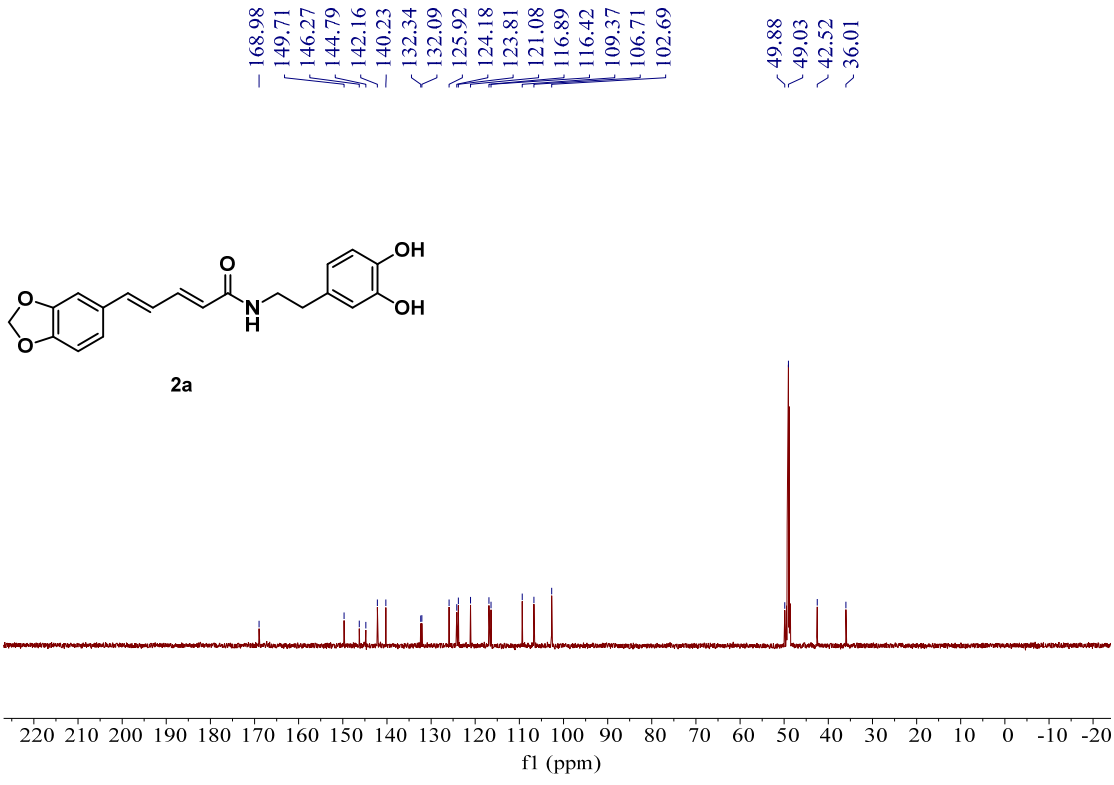
^{1}H NMR spectrum of **1bf**



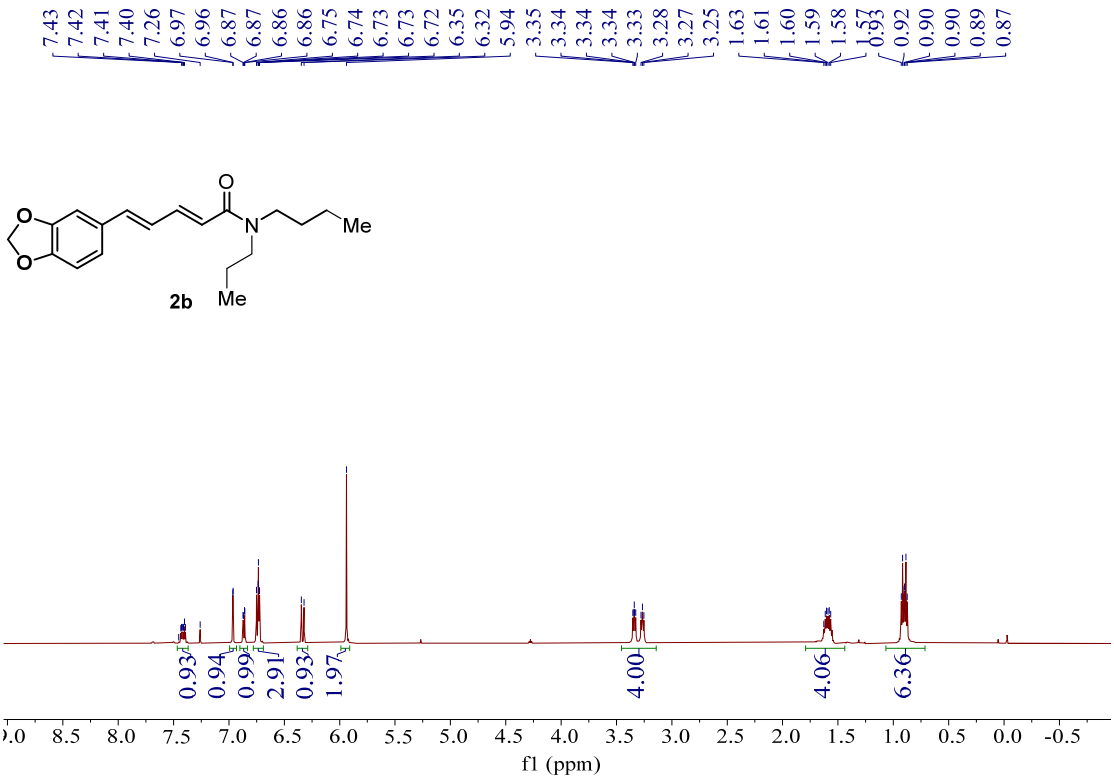
^{13}C NMR spectrum of **1bf**



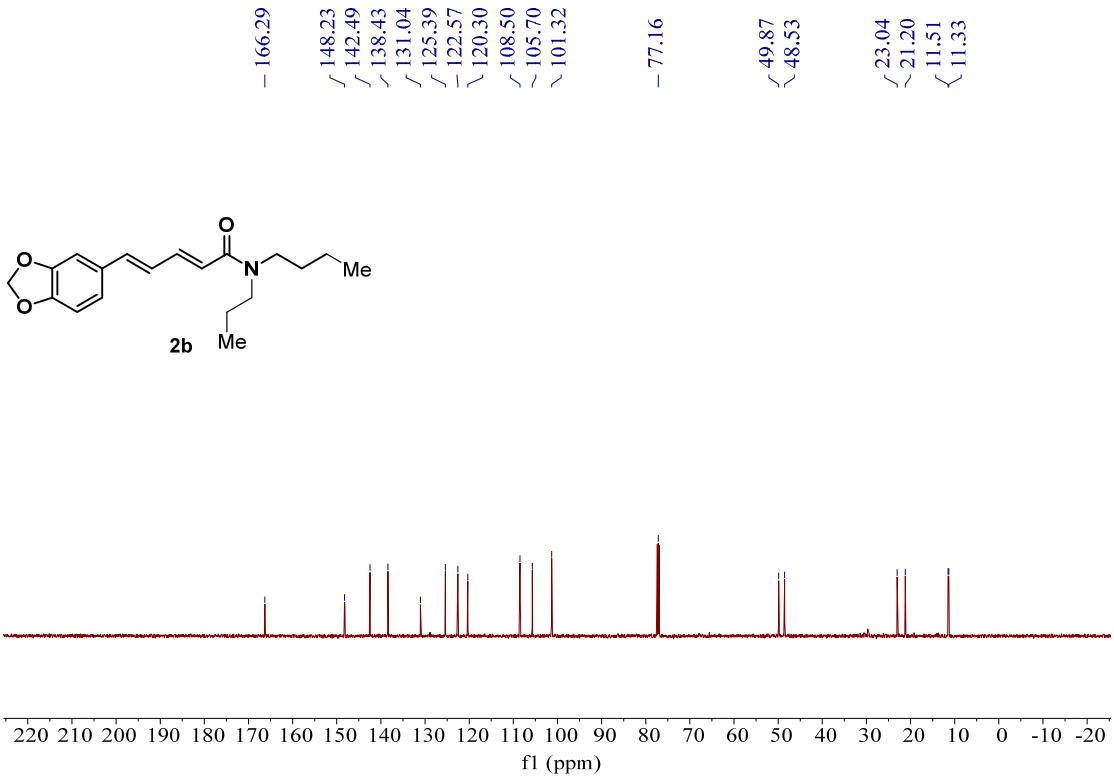
^{1}H NMR spectrum of **2a**



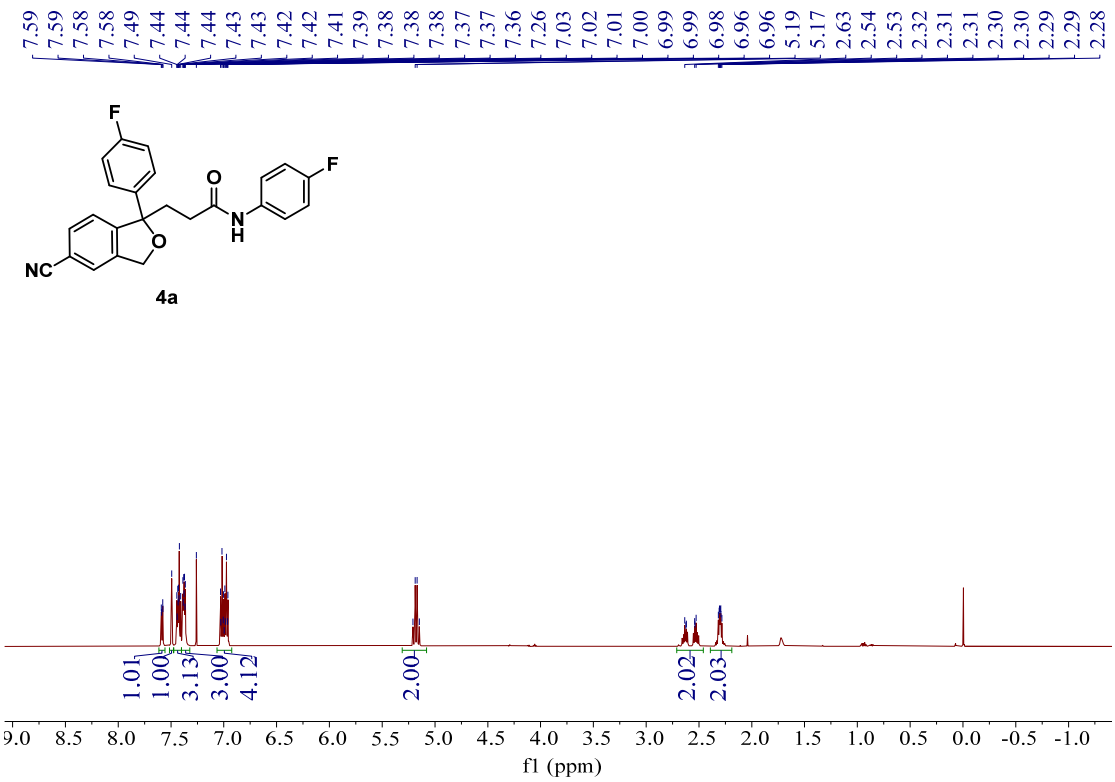
^{13}C NMR spectrum of **2a**



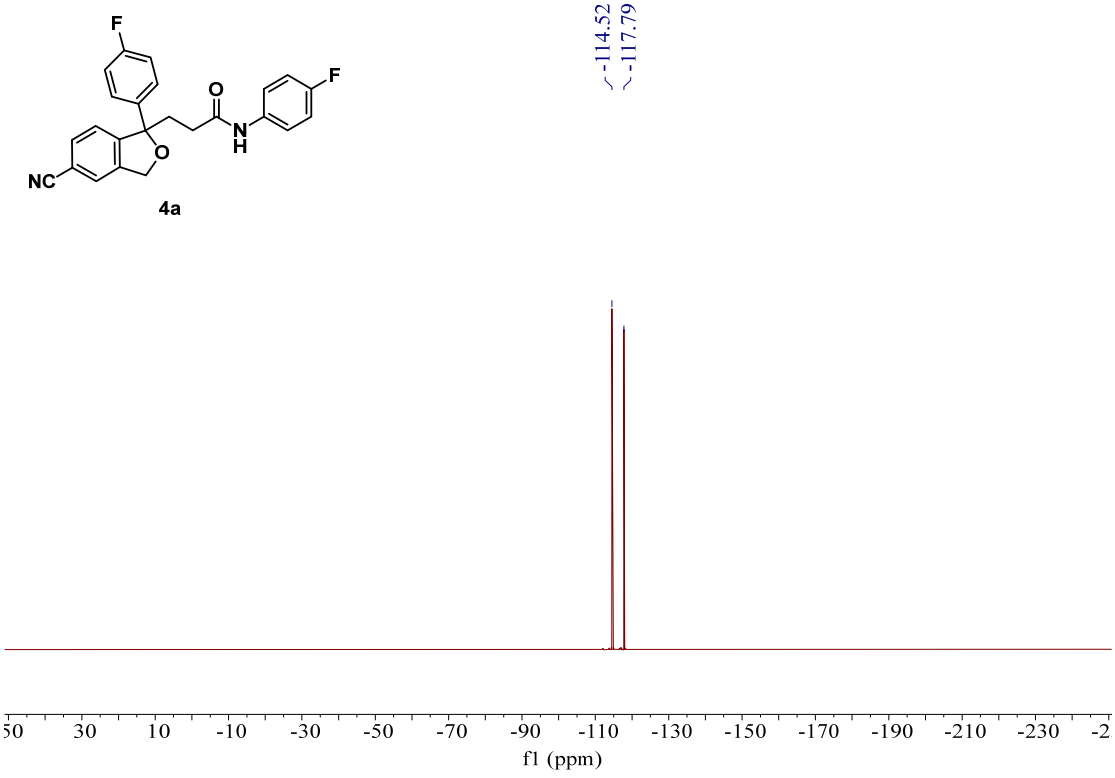
^{1}H NMR spectrum of **2b**



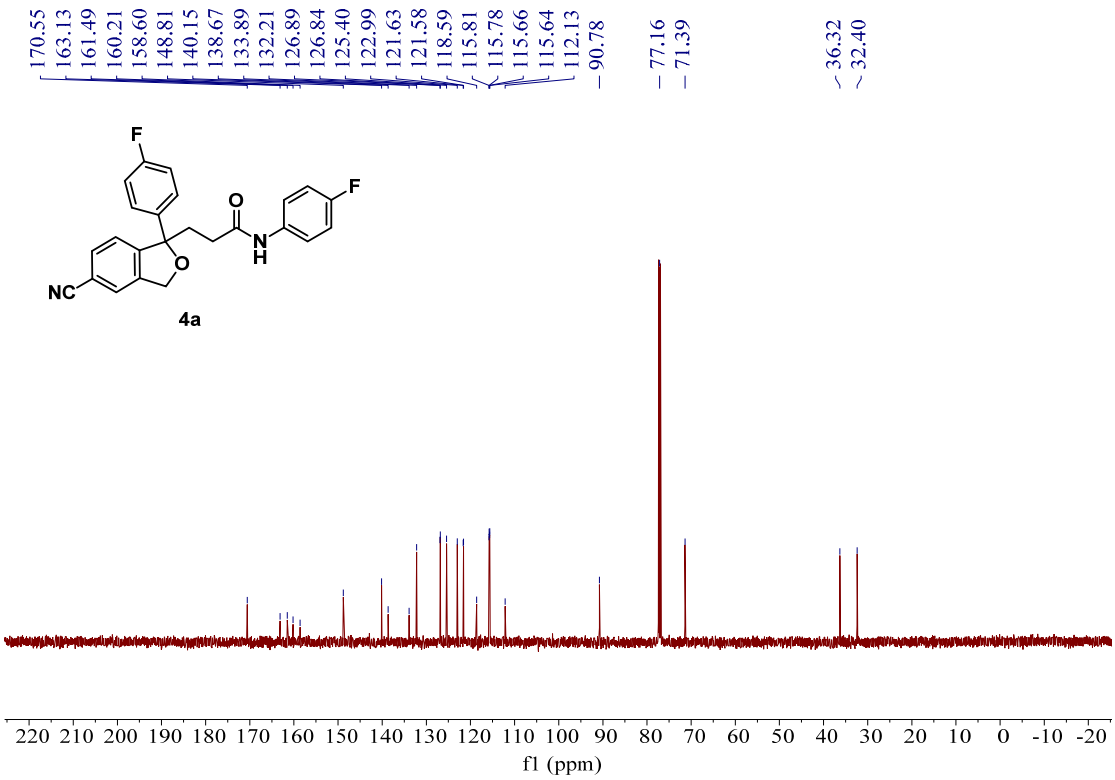
^{13}C NMR spectrum of **2b**



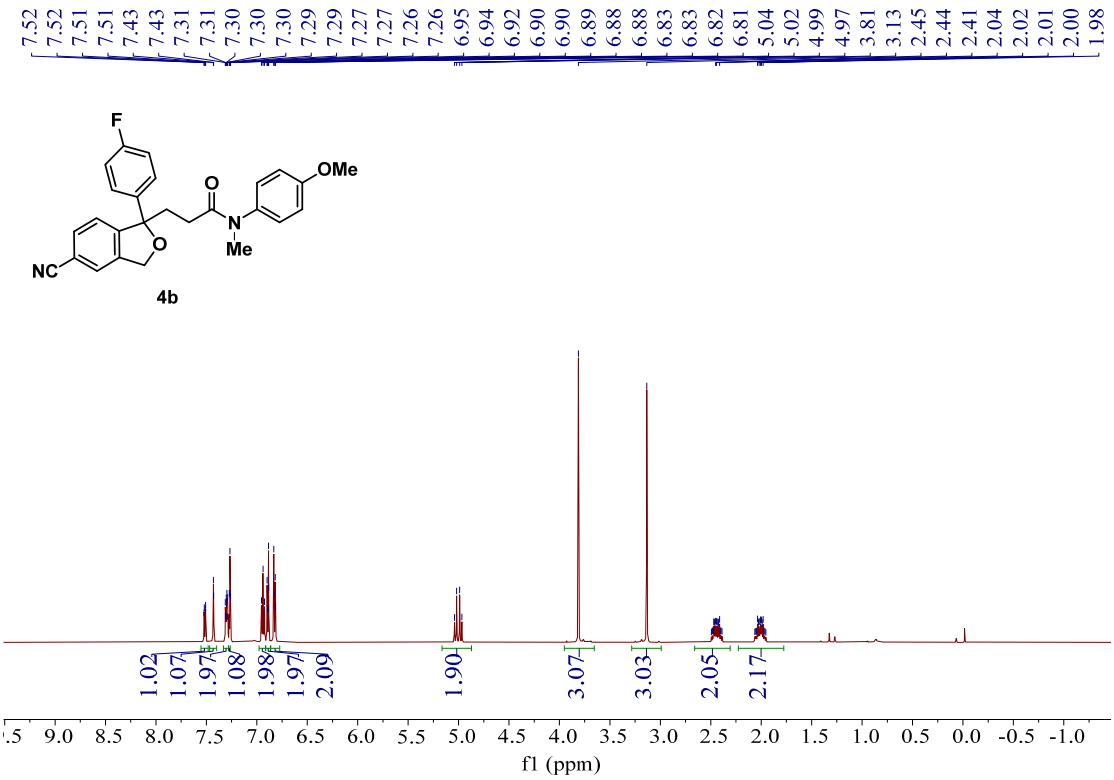
^{1}H NMR spectrum of **4a**



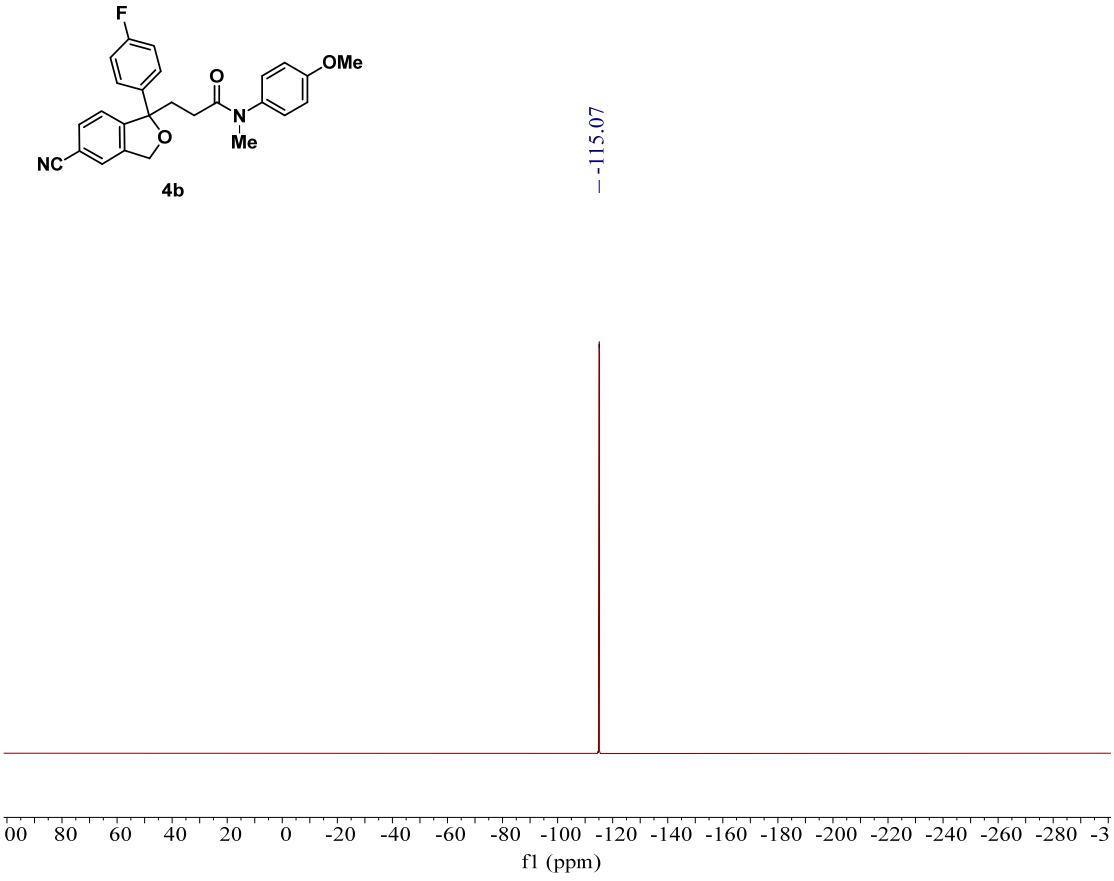
^{19}F NMR spectrum of **4a**



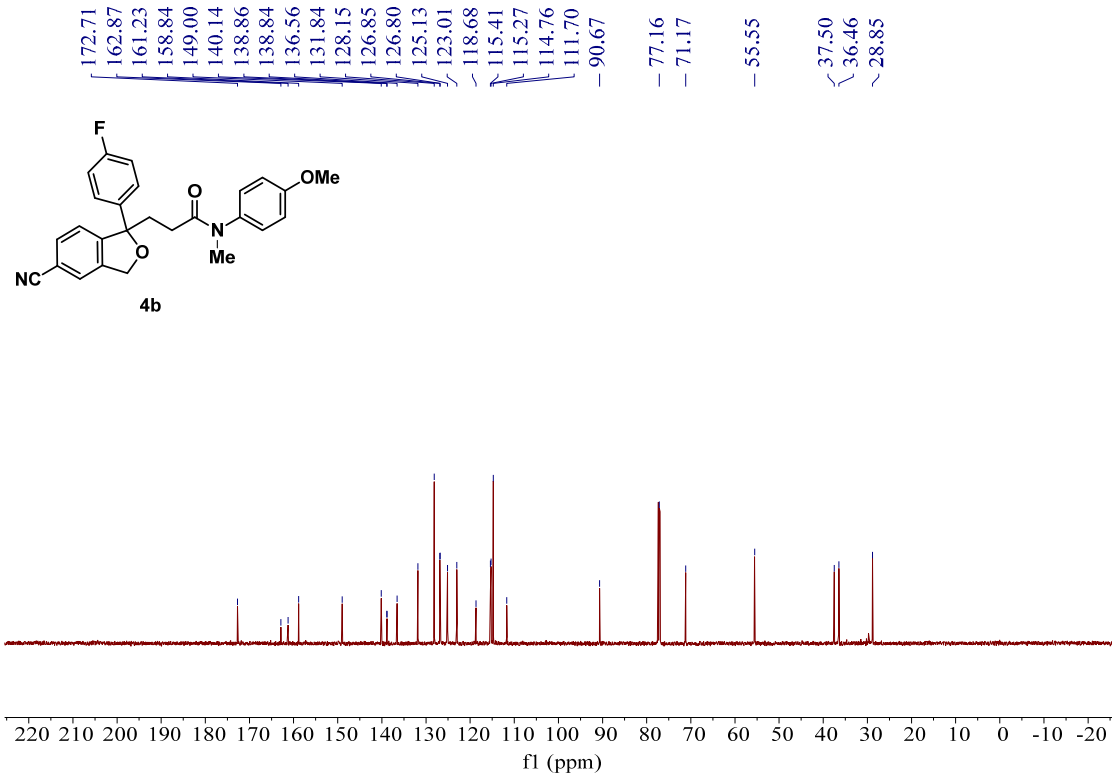
^{13}C NMR spectrum of **4a**



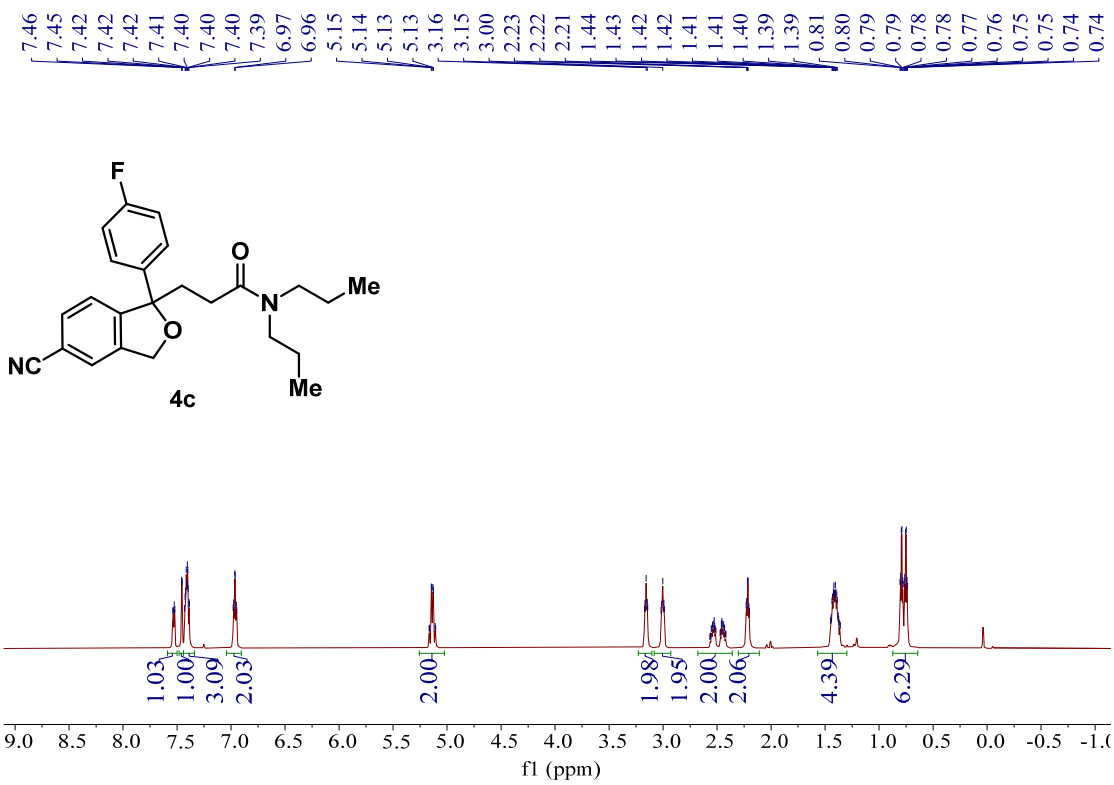
^{1}H NMR spectrum of **4b**



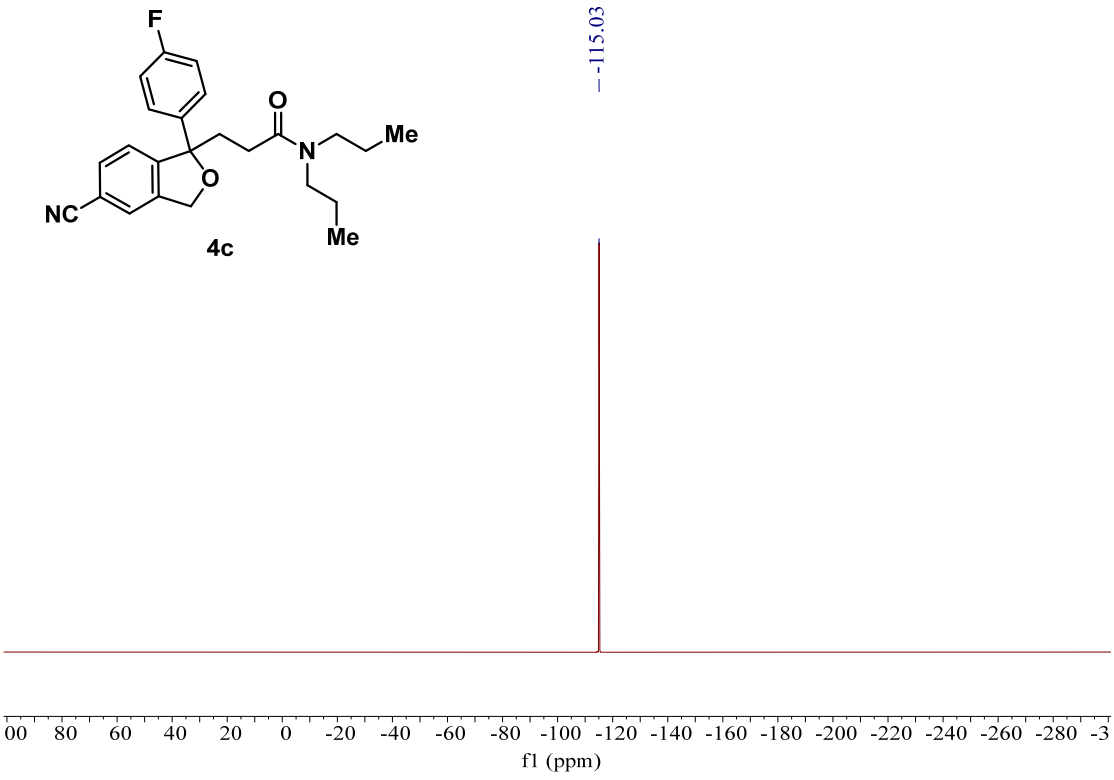
^{19}F NMR spectrum of **4b**



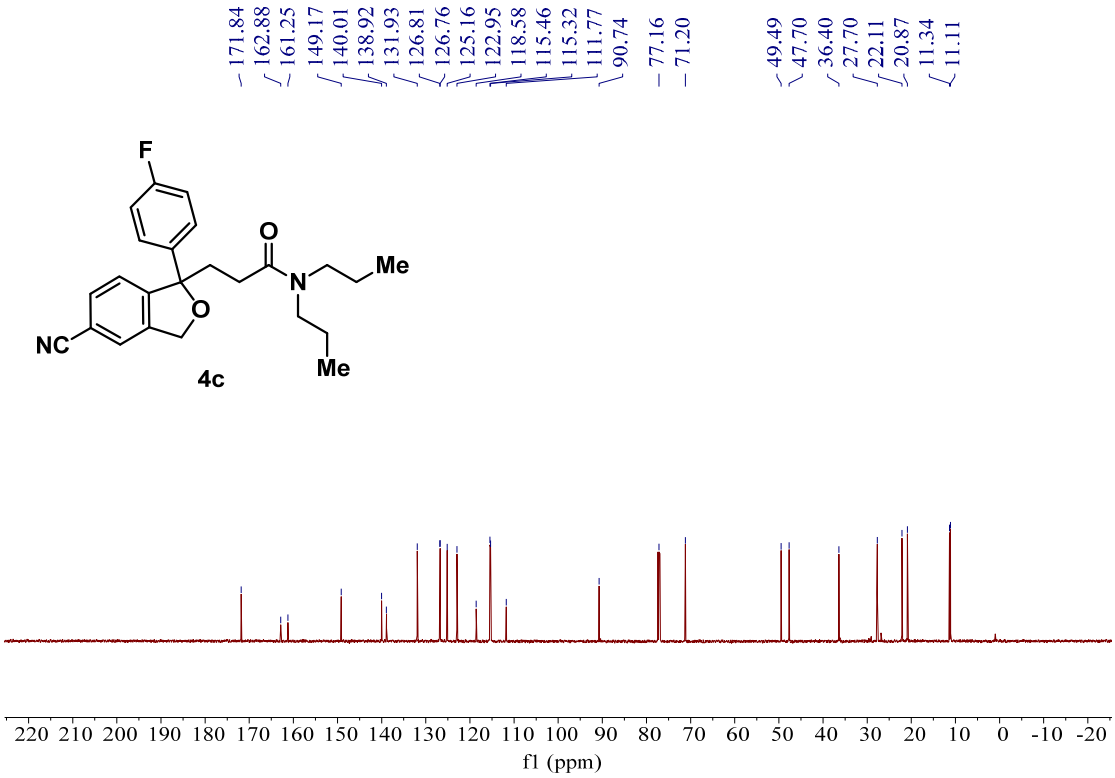
^{13}C NMR spectrum of **4b**



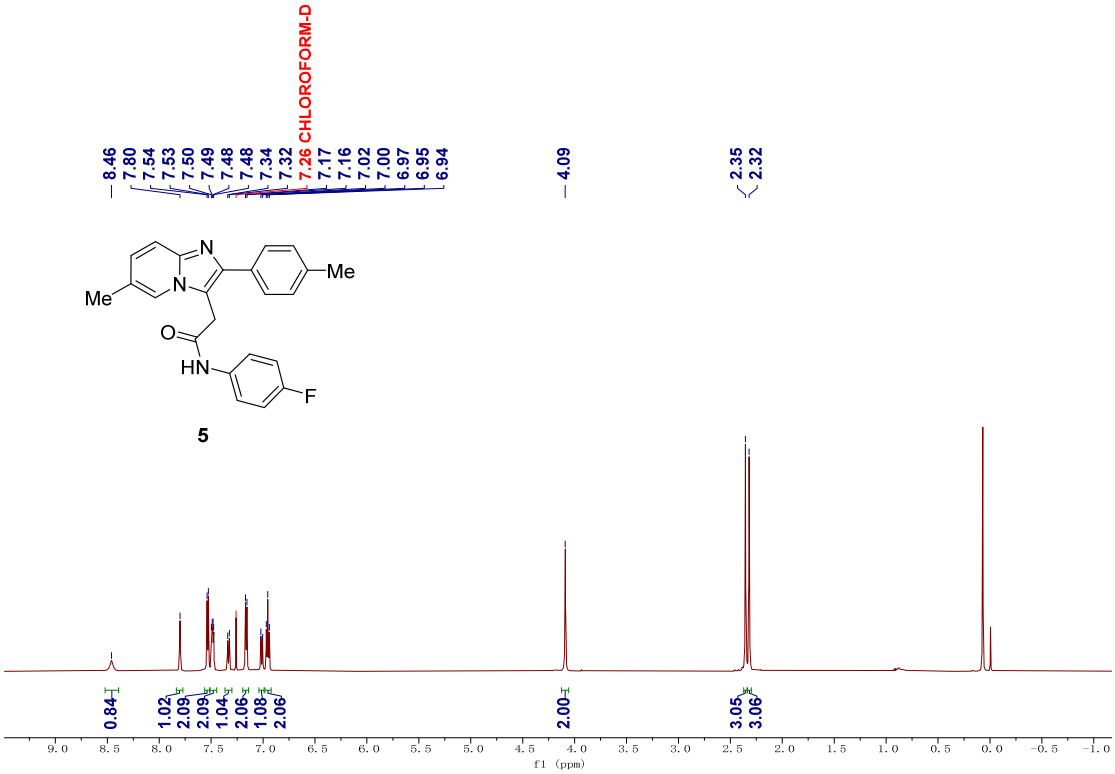
^{1}H NMR spectrum of **4c**



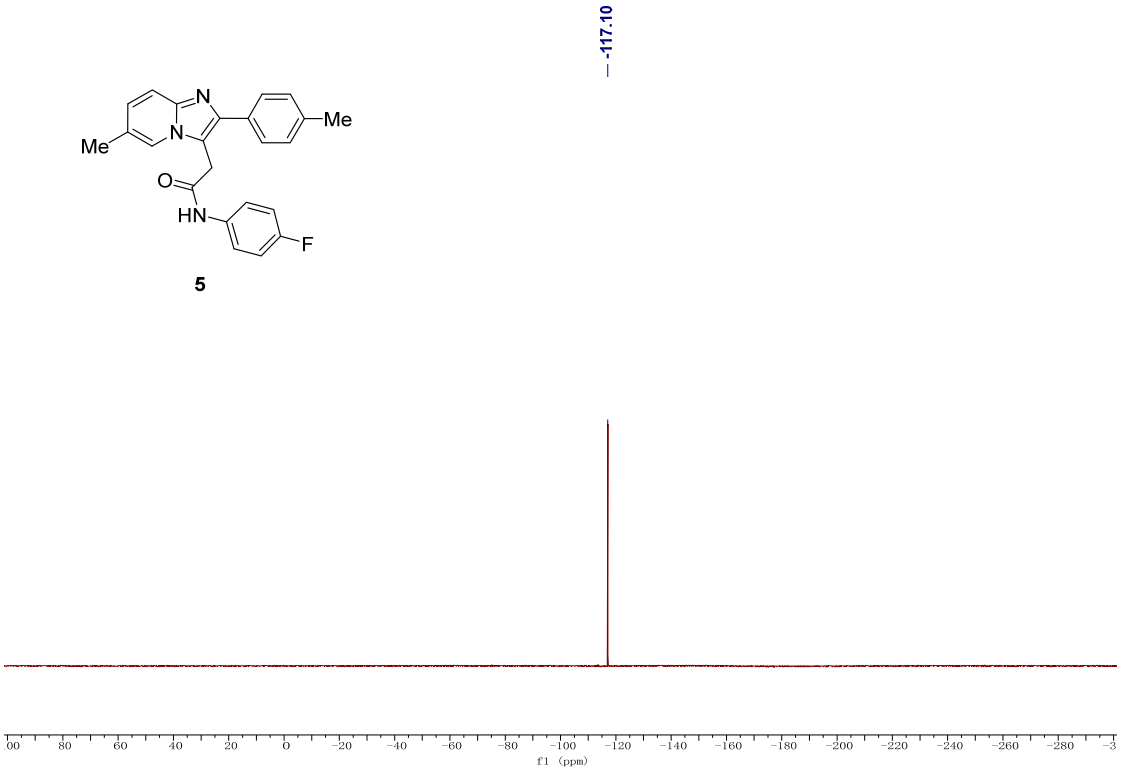
^{19}F NMR spectrum of **4c**



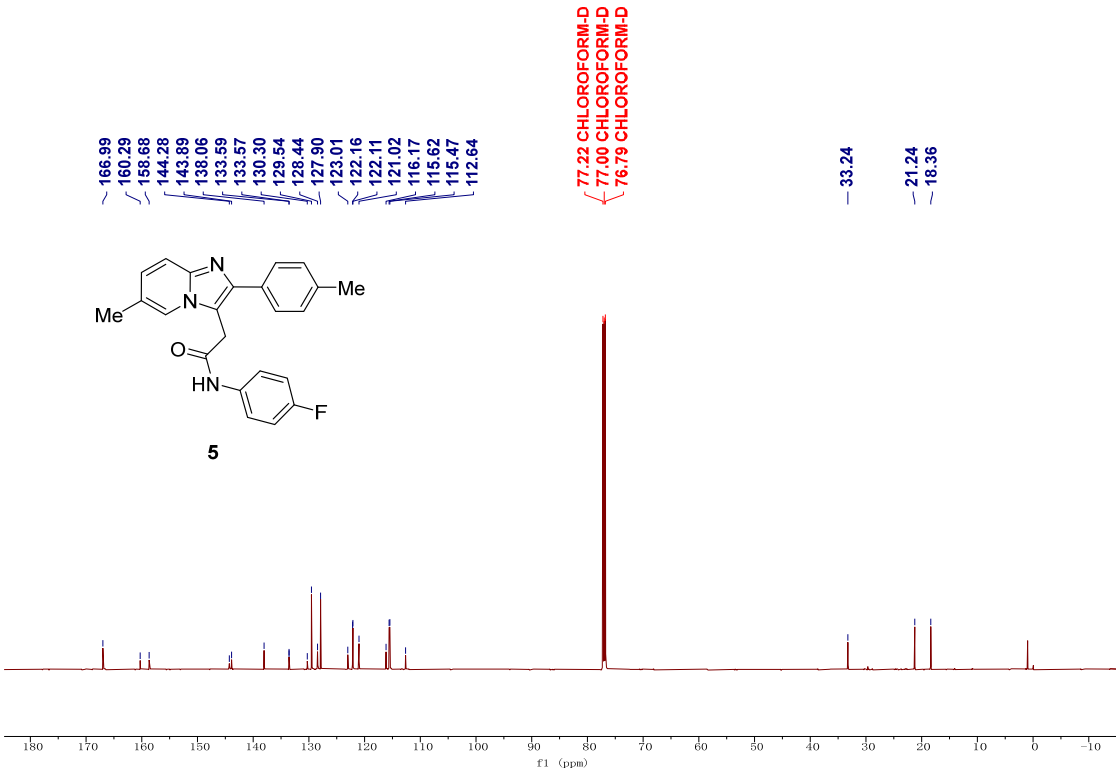
^{13}C NMR spectrum of **4c**



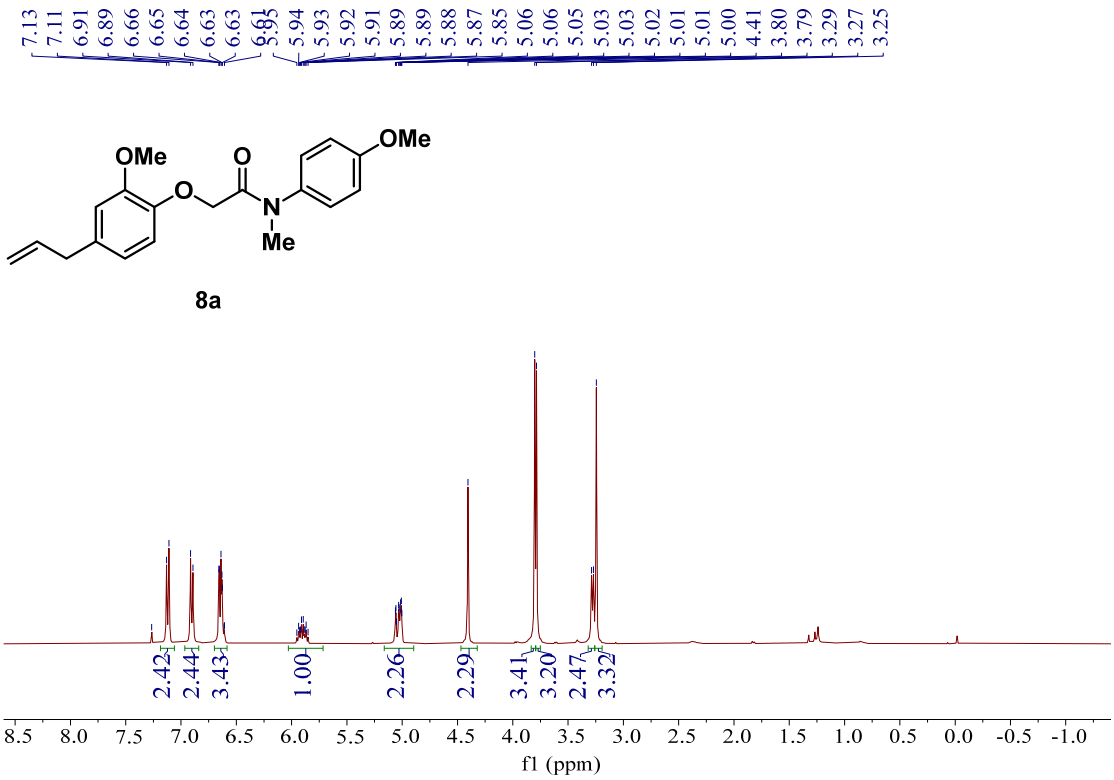
^{1}H NMR spectrum of **5**



^{19}F NMR spectrum of **5**

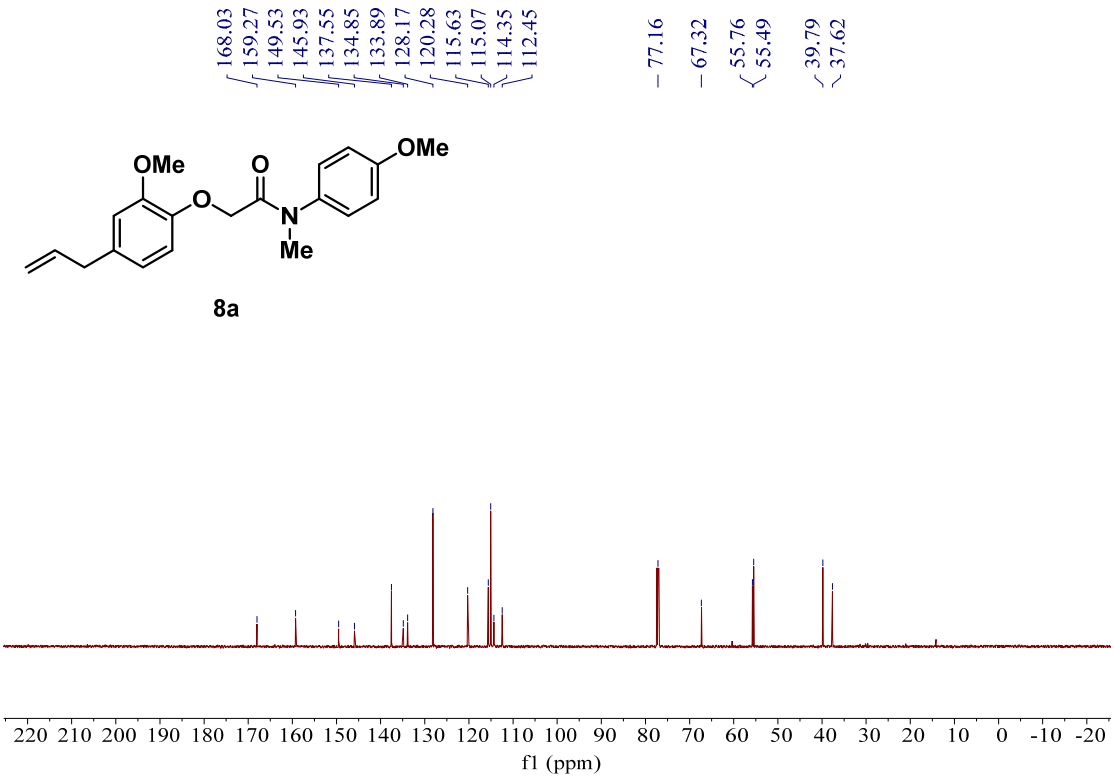


^{13}C NMR spectrum of **5**



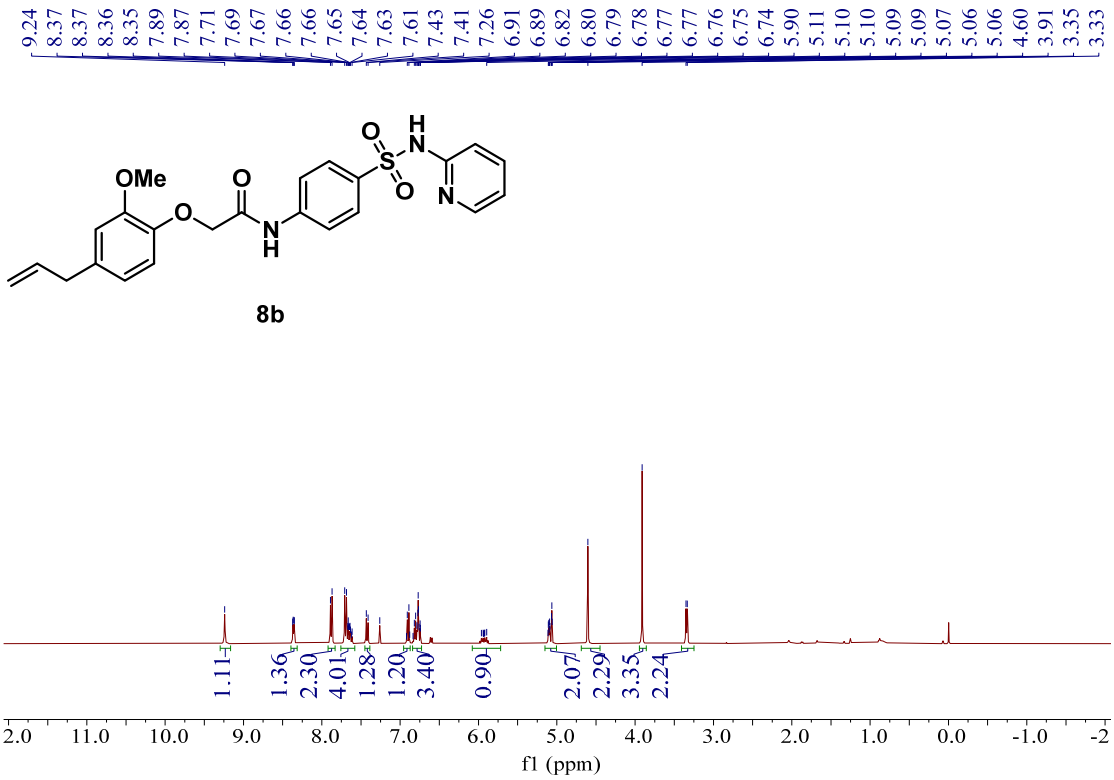
8a

^{1}H NMR spectrum of **8a**

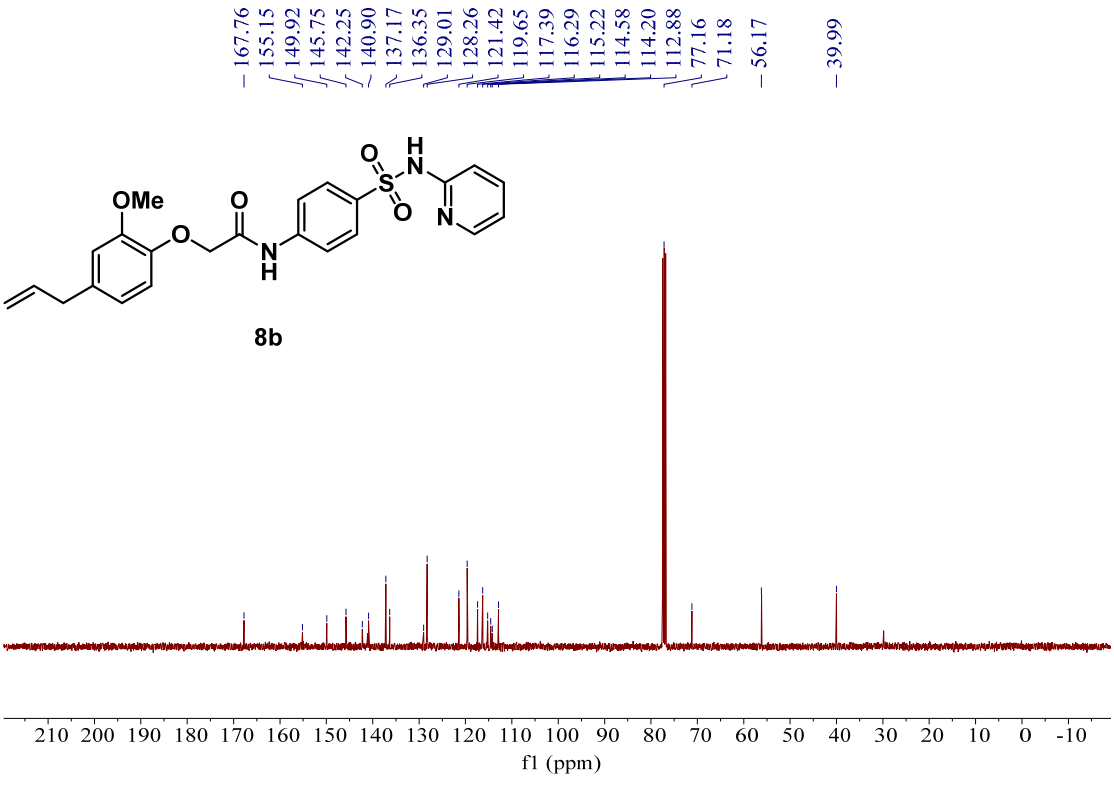


8a

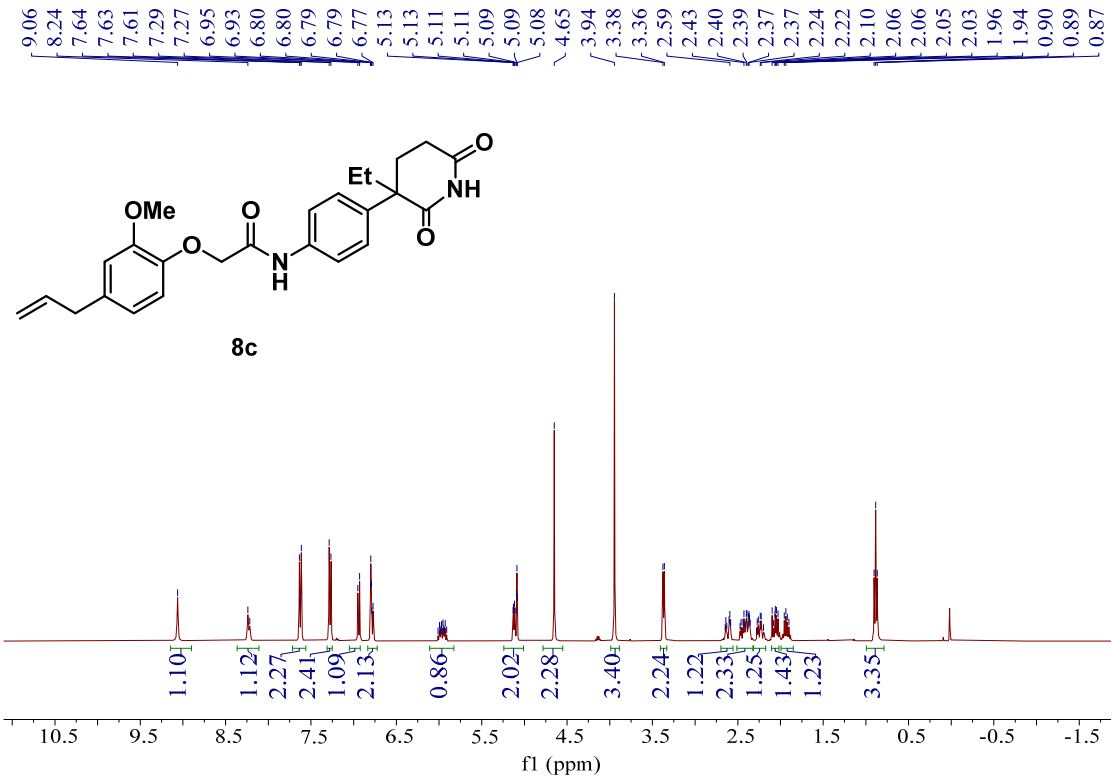
^{13}C NMR spectrum of **8a**



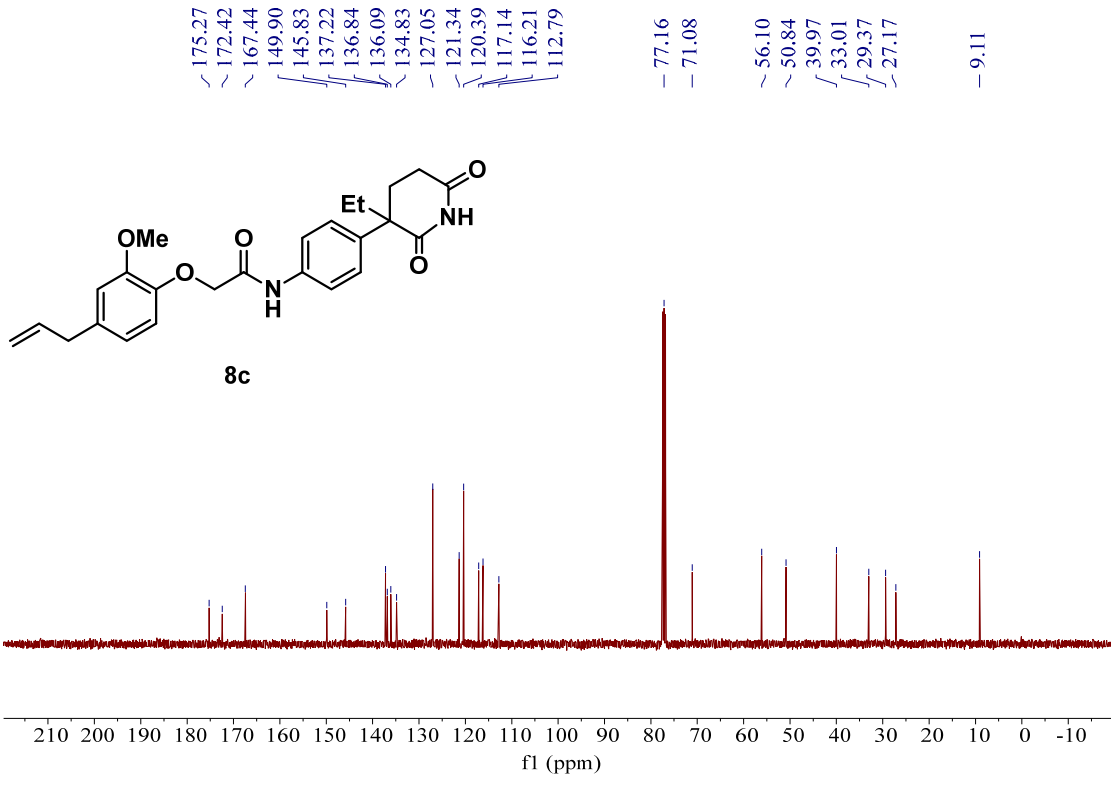
^{1}H NMR spectrum of **8b**



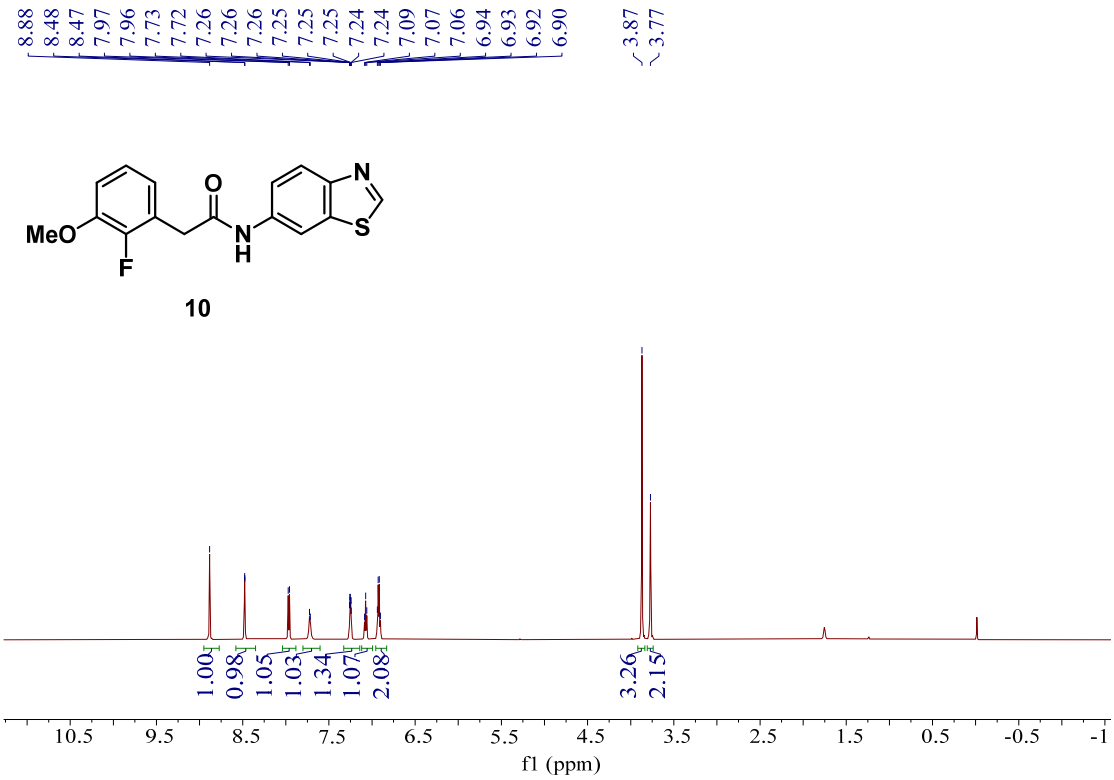
^{13}C NMR spectrum of **8b**



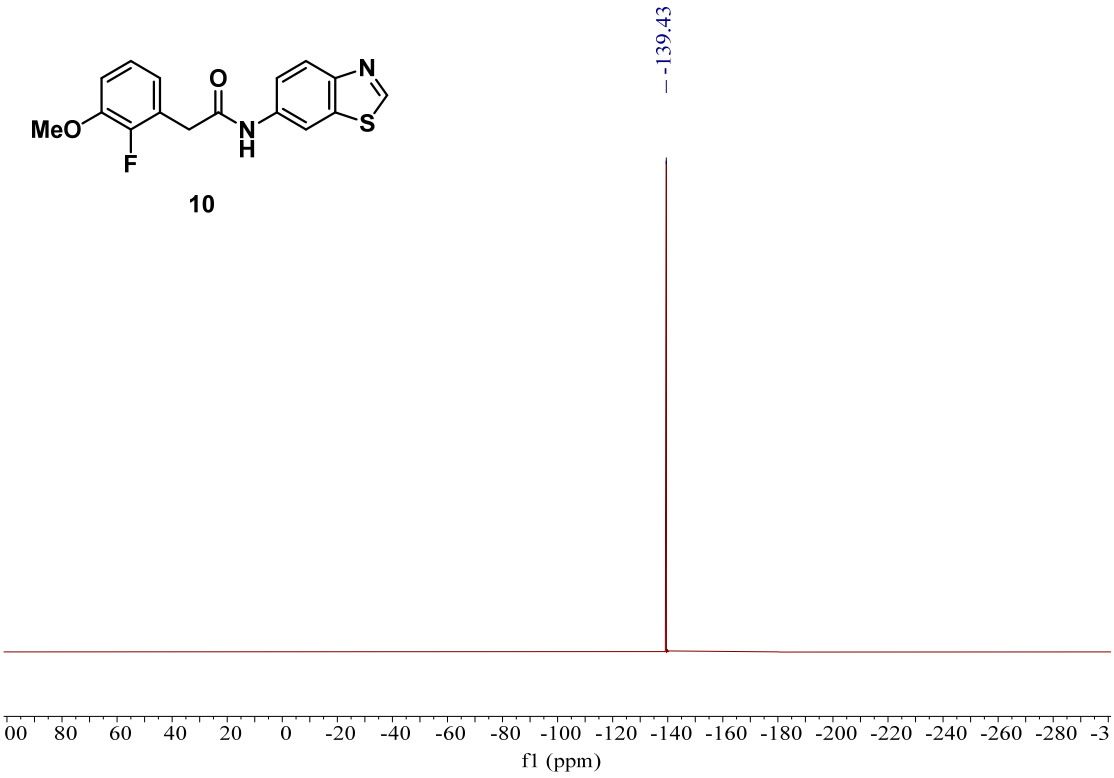
^{1}H NMR spectrum of **8c**



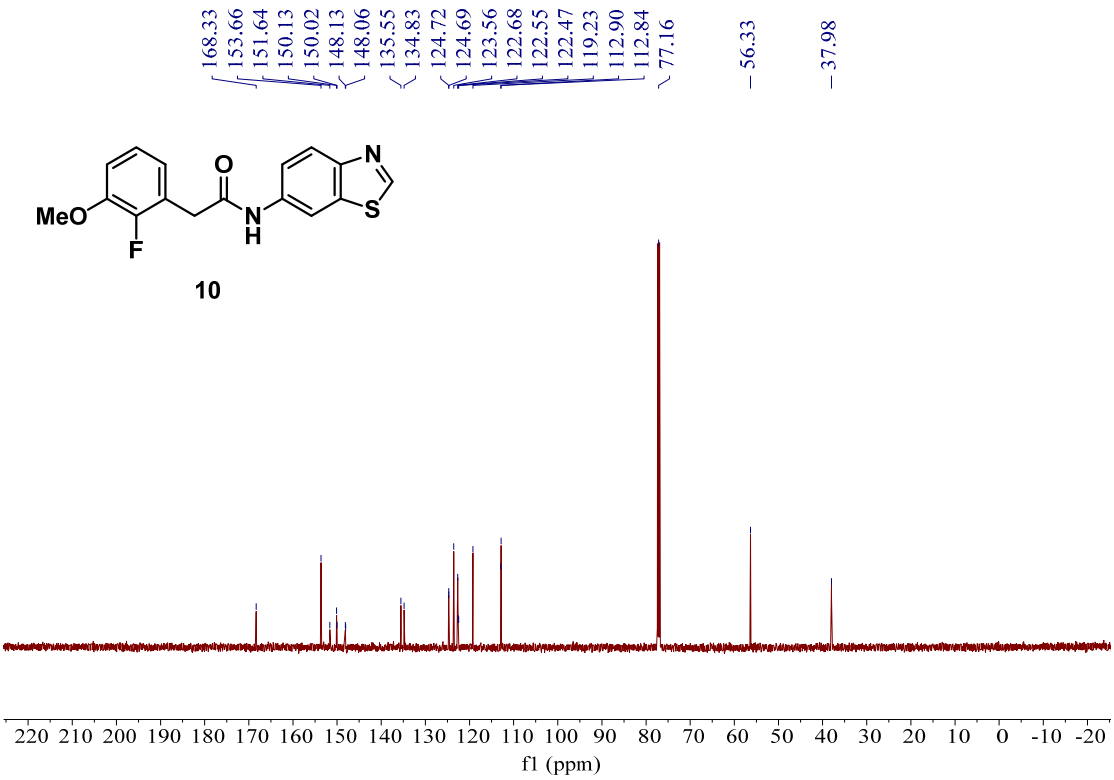
^{13}C NMR spectrum of **8c**



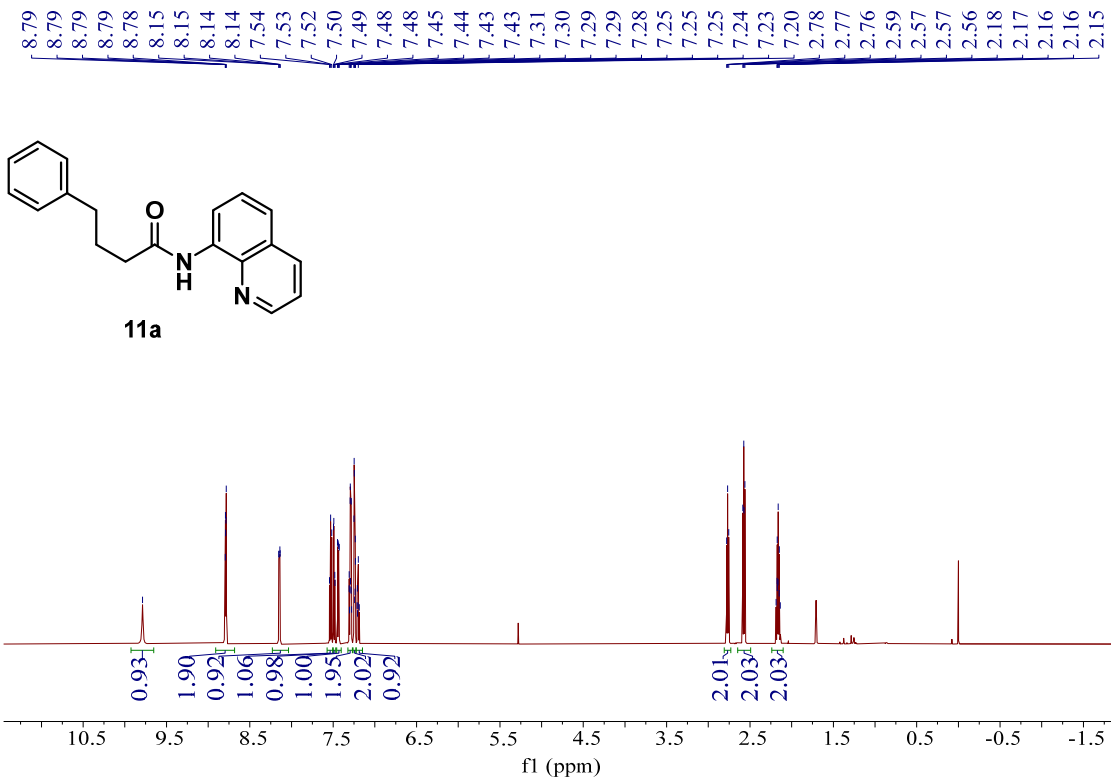
^{1}H NMR spectrum of **10**



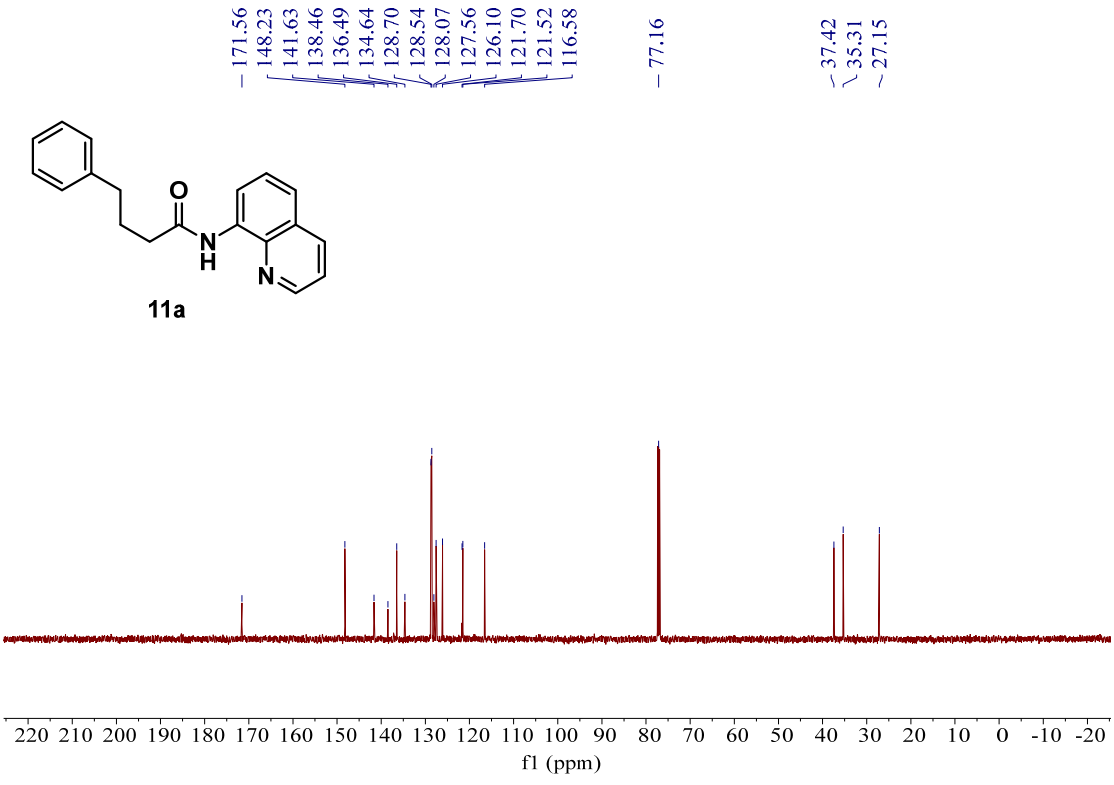
^{19}F NMR spectrum of **10**



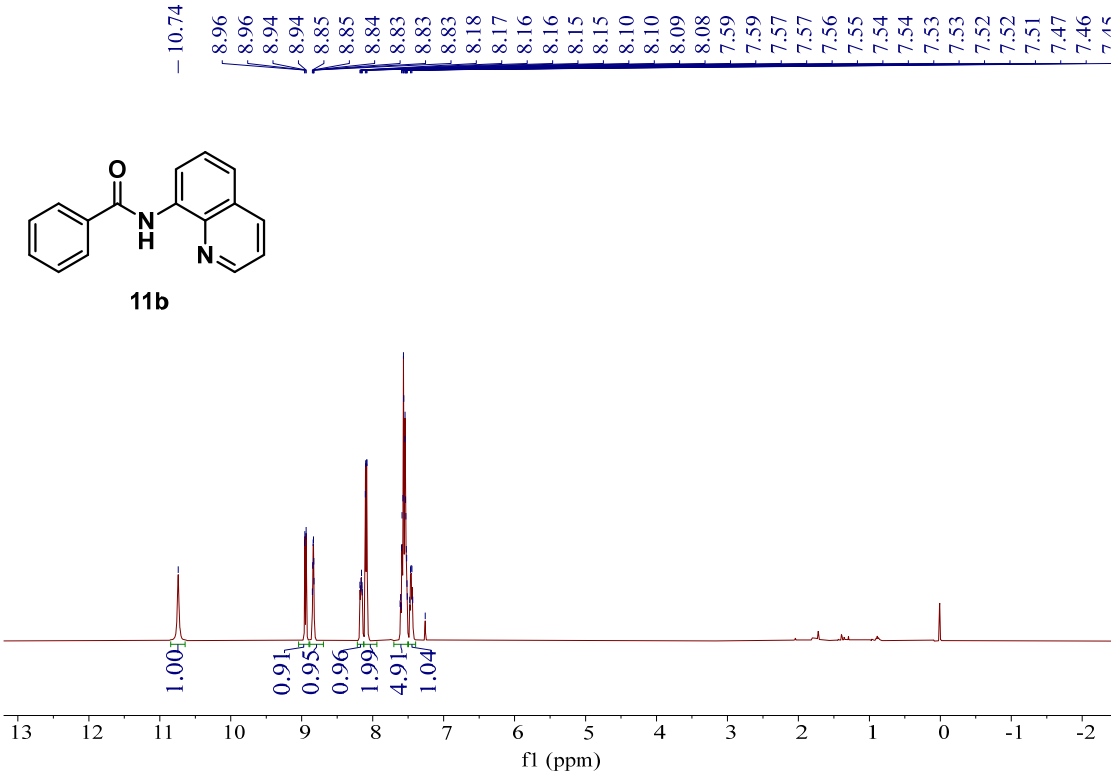
^{13}C NMR spectrum of **10**



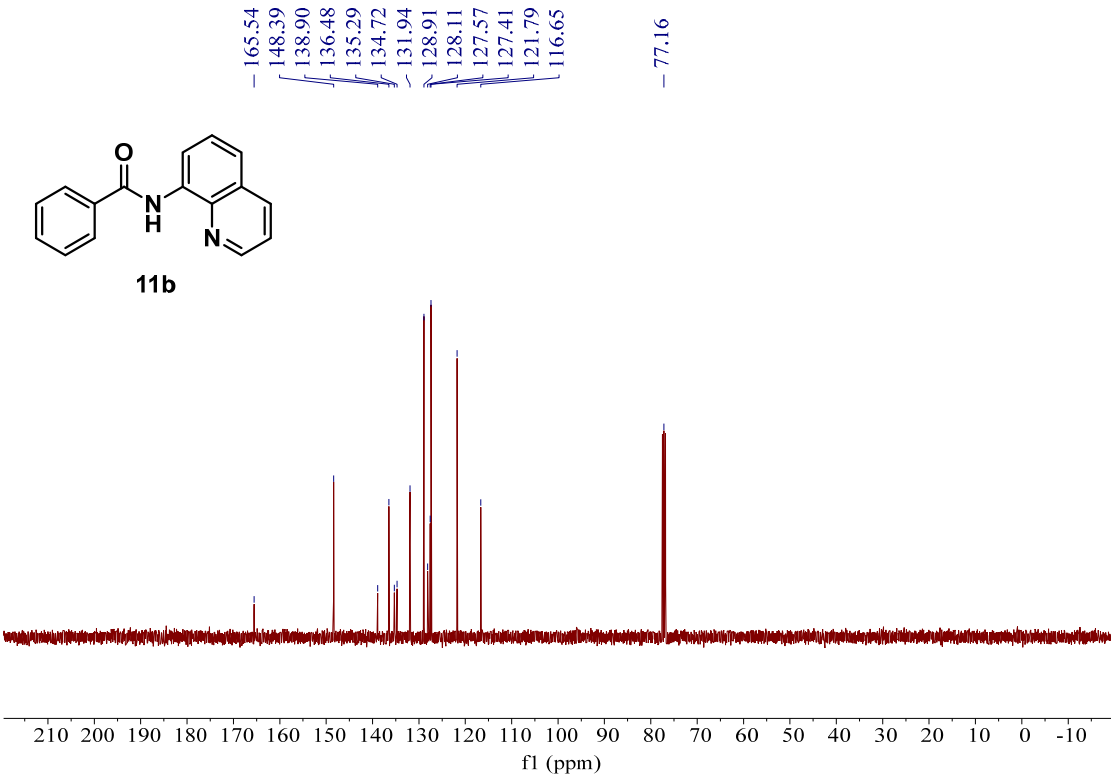
^{1}H NMR spectrum of **11a**



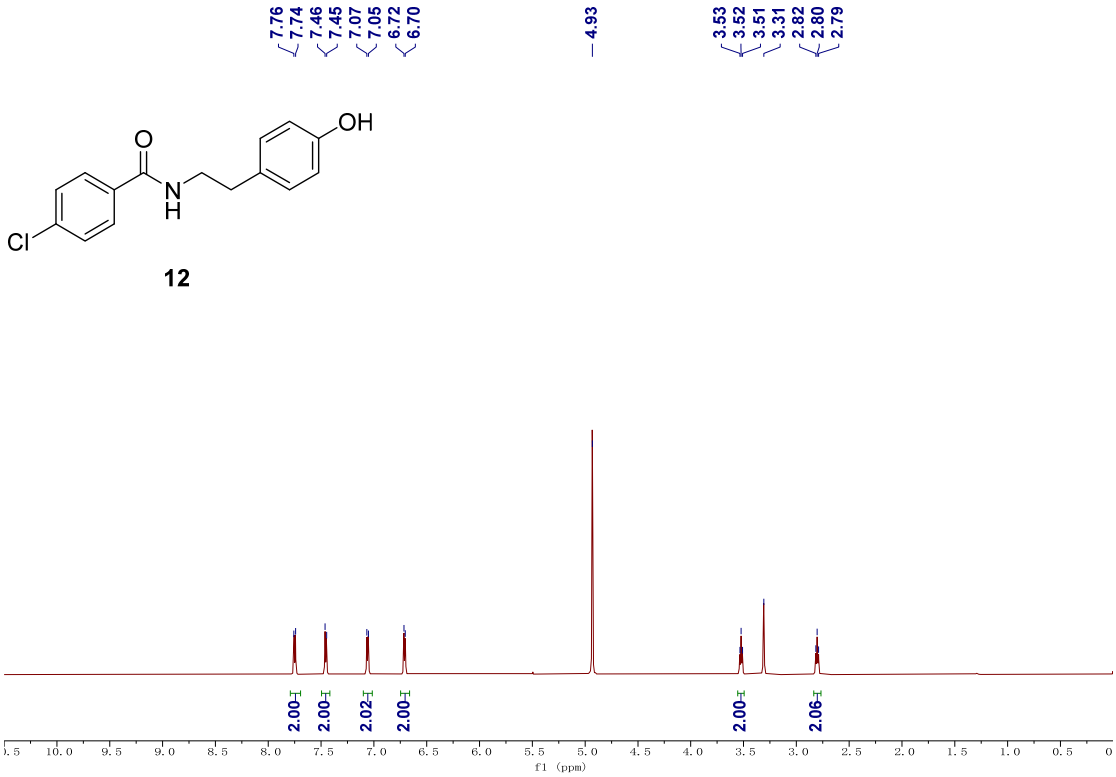
^{13}C NMR spectrum of **11a**



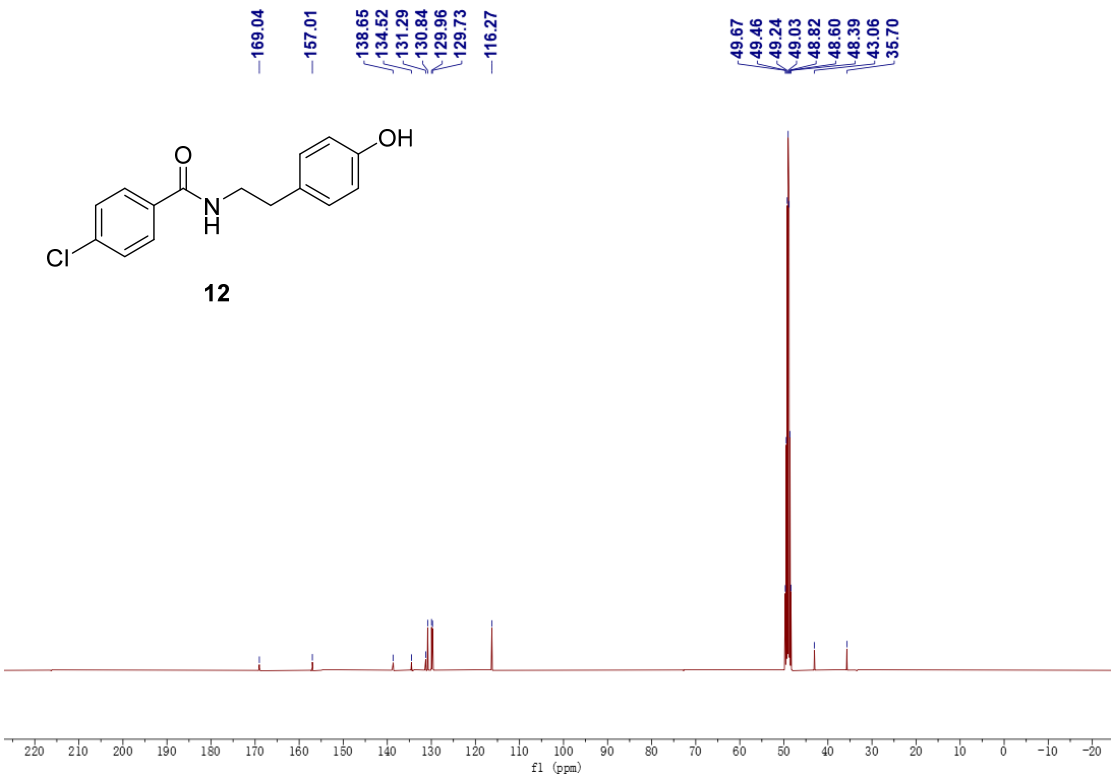
^{1}H NMR spectrum of **11b**



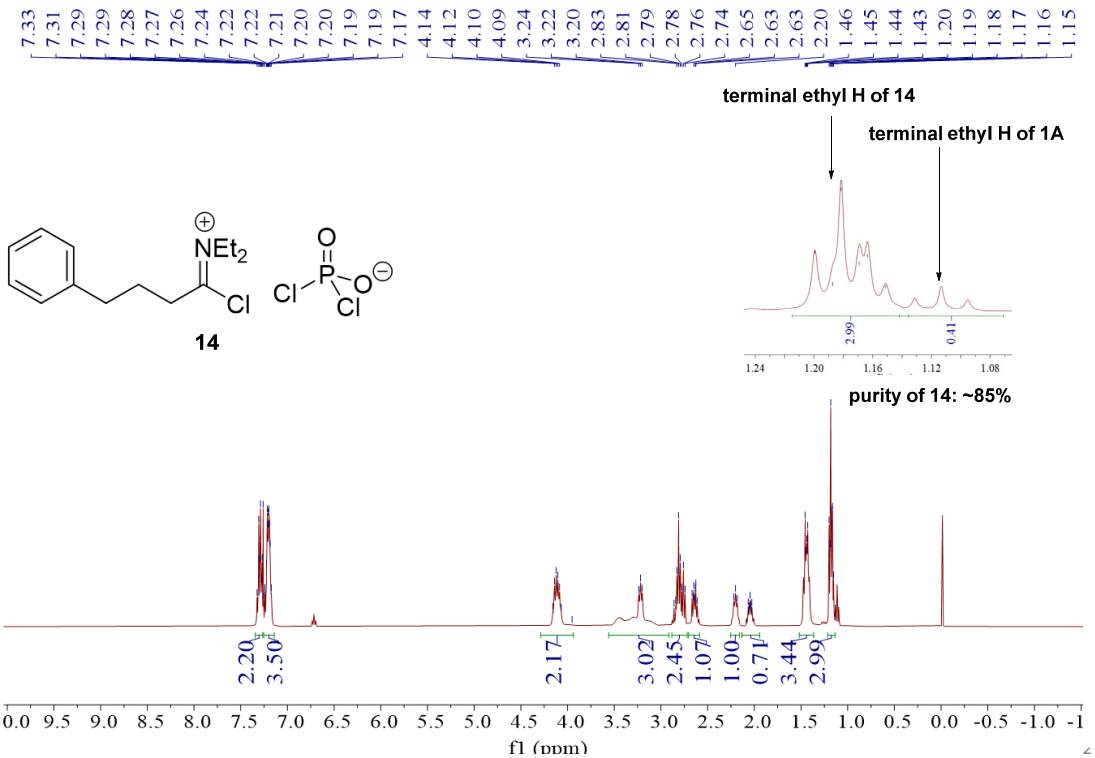
^{13}C NMR spectrum of **11b**



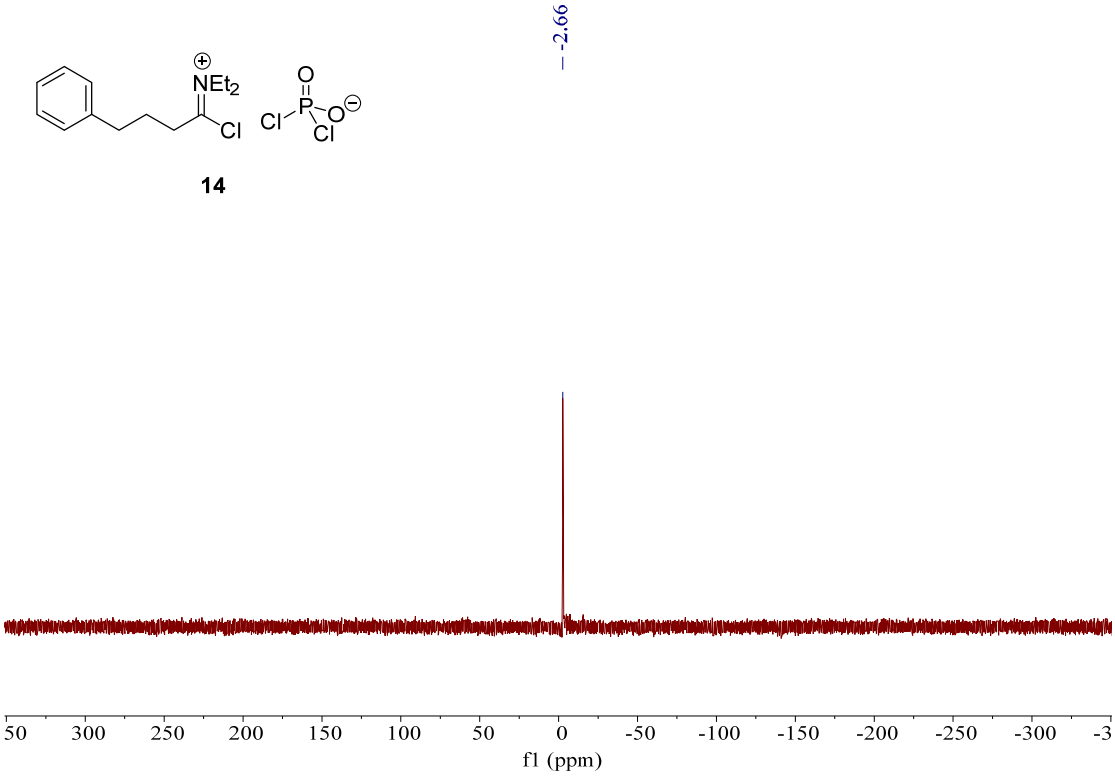
^{1}H NMR spectrum of **12**



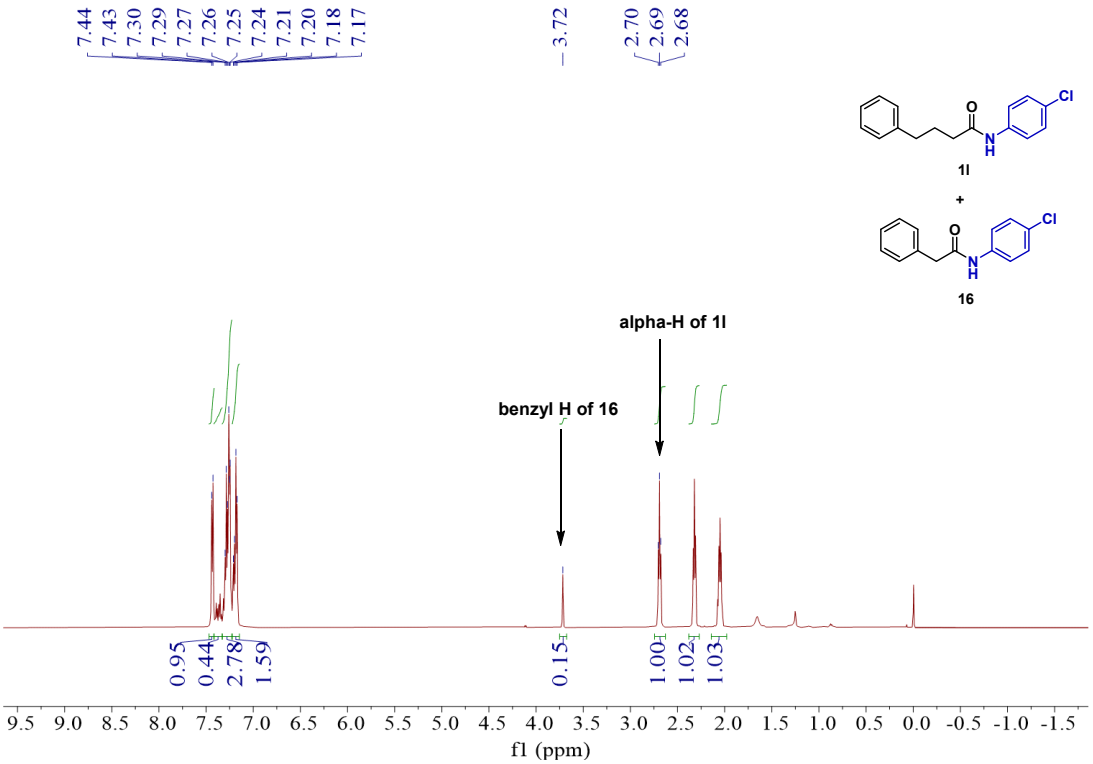
^{13}C NMR spectrum of **12**



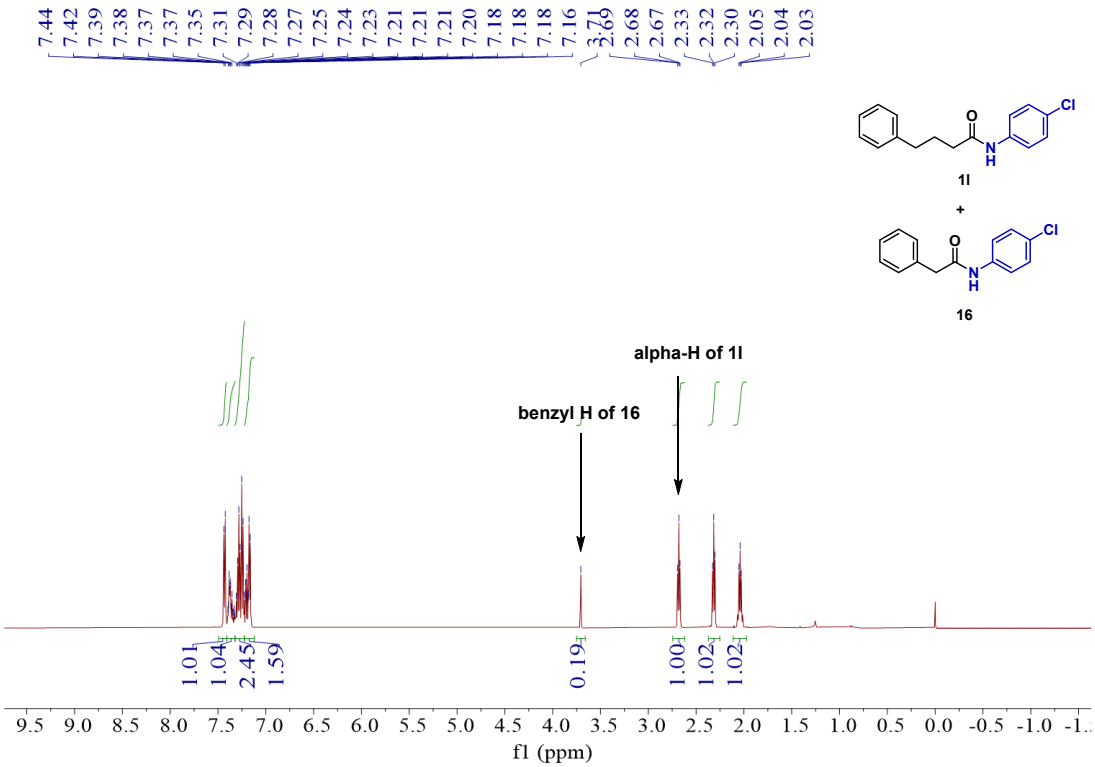
^{1}H NMR spectrum of **14**



^{31}P NMR spectrum of **14**



^{1}H NMR spectrum of competition experiment for transamidation between **A1** and **A30.**



^{1}H NMR spectrum of competition experiment for transamidation between **A1** and **A31**