Supplementary Information

Transition metal/photocatalyst-free synthesis of geminal diamines *via* a sandwich-like photoactive donor-acceptor-donor complex

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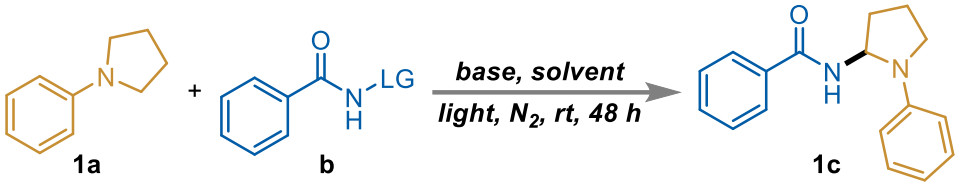
I. General Information

Magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruker Avance NEO 400 or Bruker Avance NEO 500 with $CDCl_3$ or DMSO-*d*6 as the solvent, and chemical shifts were internally referenced to TMS and residual portion solvent signals (note: TMS referenced at 0.00 ppm; $CDCl_3$ referenced at 7.26 and 77.16 ppm respectively; DMSO-*d*6 referenced at 2.50 and 39.52 ppm respectively). Data are shown as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, h = heptet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (*J* Hz). The HRMS analysis was performed on a Q Exactive plus mass spectrometer (Thermo Fisher Scientific, Germany) equipped with an electrospray ionization (ESI) source. Commercially available reagents and solvents were purchased from Energy Chemical, Bide Pharmatech and Shanghai Macklin Biochemical, and used as received unless otherwise specified. Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 100-200 mesh). Thin layer chromatography (TLC) was performed on Qingdao Haiyang 0.2 mm silica gel plates. Analytical balances Mettler Toledo ME204E /02 and MS205DU/A were used to weigh samples. UV-vis spectra were measured on a TU-1900 UV-visible spectrophotometer. Electron spin-resonance (ESR) spectra were measured on CIQTEK ESR200-plus (CIQTEK Co., Ltd.) with continuous-wave X band frequency.

II. Optimization of the reaction conditions

Table S1. Transition metal/photocatalyst-free synthesis of geminal diamines *via* a photoactive donor-acceptor-donor complex: optimization of the reaction conditions[a]



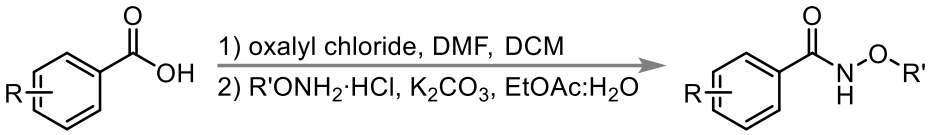
1a b 1c

Entry	Base	Solvent	Light	LG	Yield %[b]
1[c, d]	Cs_2CO_3	MeCN	405 nm	OMe	22
2[c, e]	Cs_2CO_3	MeCN	405 nm	OMe	17
3[c, f]	Cs_2CO_3	MeCN	405 nm	OMe	24
4[c]	Cs_2CO_3	MeCN	405 nm	OMe	26
5[c]	KO^{t}Bu	MeCN	405 nm	OMe	45
6[c]	KOH	MeCN	405 nm	OMe	50
7	KOH	MeCN	405 nm	OMe	76
8[c]	LiOH	MeCN	405 nm	OMe	40
9[c]	NaOH	MeCN	405 nm	OMe	38
10[c]	K_3PO_4	MeCN	405 nm	OMe	6
11[c]	DIPEA	MeCN	405 nm	OMe	14
12	KOH	DCE	405 nm	OMe	trace
13	KOH	acetone	405 nm	OMe	15
14	KOH	MeOH	405 nm	OMe	trace
15	KOH	DMSO	405 nm	OMe	42
16	KOH	MeCN	365 nm	OMe	68
17	**KOH**	**MeCN**	**395 nm**	**OMe**	**92**
18	KOH	MeCN	455 nm	OMe	N.D.
19	KOH	MeCN	395 nm	OEt	78 (90[g])
20	KOH	MeCN	395 nm	OPh	trace
21	KOH	MeCN	395 nm	OBz	N.R.
22[h]	KOH	MeCN	395 nm	OMe	78
23[i]	KOH	MeCN	395 nm	OMe	65
24	-	MeCN	395 nm	OMe	trace

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (3 equiv.), base (2 equiv.) and solvent (2 mL) under N_2 and 30 W LEDs for 48 h. [b]Isolated yield. [c]1 equiv. of base was added. [d]0.2 mol% of *fac*-Ir(ppy)$_3$ and 20 mol% of CuCl was added. [e]0.2 mol% of *fac*-Ir(ppy)$_3$ was added. [f]20 mol% of CuCl was added. [g]96 h. [h]100 μL of H_2O was added. [i]Under air. LG = Leaving group. N.D. = not detected. N.R. = no reaction.

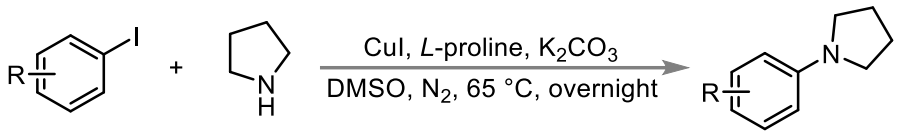
III. General procedure for the synthesis of starting materials and compounds

i. General procedure for the synthesis of amides[1]



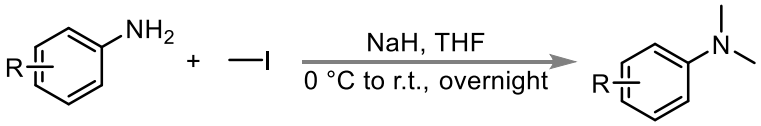
To a solution of the carboxylic acid (1.0 equiv.) in DCM (0.3 M) at 0 °C under N_2 was added dropwise oxalyl chloride (1.2 equiv.) followed by a catalytic amount of DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 4 h). The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Alkoxyamine hydrochloride (1.2 equiv.) was added to a biphasic mixture of K_2CO_3 (2 equiv.) in a 2: 1 mixture of EtOAc: H_2O (0.2 M). The resulting solution was cooled to 0 °C followed by the addition of a solution of unpurified acid chloride in a minimum amount of EtOAc dropwise. The flask containing the acid chloride was then rinsed with additional EtOAc. The mixture was allowed to stir for 4–8 hours (monitored by TLC) and slowly warmed up to room temperature. Upon completion, the mixture was extracted with EtOAc three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and removed under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.

ii. General procedure for the synthesis of arylpyrrolidines[2]



Aryl iodide (5 mmol), CuI (0.5 mmol, 0.1 equiv., 95 mg), *L*-proline (1 mmol, 0.2 equiv., 115 mg), K_2CO_3 (10 mmol, 2 equiv., 1.38 g), pyrrolidine (15 mmol, 3 equiv., 1.25 mL) and DMSO (3 mL) was added into a 10 mL Schlenk tube with a magnetic stir bar in sequence. The mixture was allowed to stir under N_2 at 65 ℃ overnight. Upon completion, the mixture was cooled to room temperature, and 30 mL of H_2O was added. The solution was extracted with EtOAc (10 mL ×3). The combined organic layer was washed with brine, dried over $MgSO_4$, and removed under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.

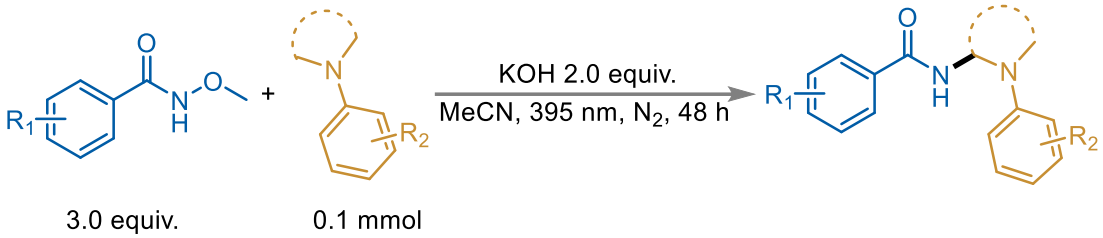
iii. General procedure for the synthesis of *N*, *N*-dimethylanilines



To a solution of arylamine (1.0 equiv.) in THF (0.2 M) at 0 °C, NaH (5 equiv.) was

added carefully and the mixture was stirred at 0 °C for 30 minutes, then iodomethane (3 equiv.) was added dropwise and the mixture was allowed to stir at room temperature overnight. Upon completion, H_2O was added and the solution was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and removed under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.

iv. General procedure I



Amine **b** (0.1 mmol), amide **a** (0.3 mmol, 3.0 equiv.), KOH (0.2 mmol, 2.0 equiv., 11.2 mg) and MeCN (1 mL) were added into a 10 mL reaction tube with a magnetic stir bar in sequence. The mixture was allowed to stir under N_2 with irradiation of a 30 W 395 nm LED (1 cm away, with circulating water to keep the reaction at room temperature) for 48 hours. Upon completion, the reaction solution was concentrated under reduced pressure, and the residue was purified by silica gel flash column chromatography to give the desired product.

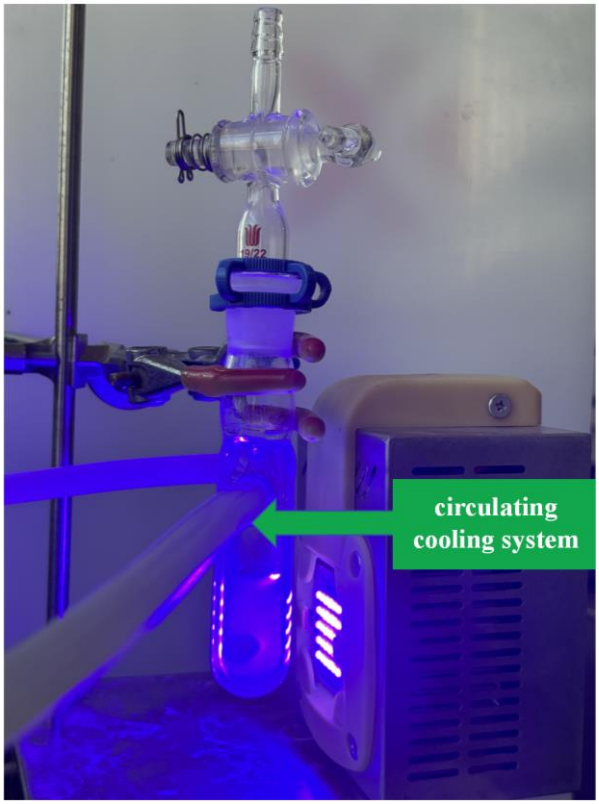


Figure S1. The photoreaction device.

IV. Mechanistic studies

i. Control experiments

Control experiments were performed to investigate the mechanism of the reaction further. 5 equiv. of 2, 2, 6, 6-tetramethylpiperidinooxy (TEMPO) or 2, 6-di-*tert*-butyl-4-methylphenol (BHT) or 1, 1-diphenylethylene was added to the reaction system, and the yields of **1c** obviously decreased. Some radical adducts were observed in HR-MS analyses, which suggested the reaction could undergo a radical process.

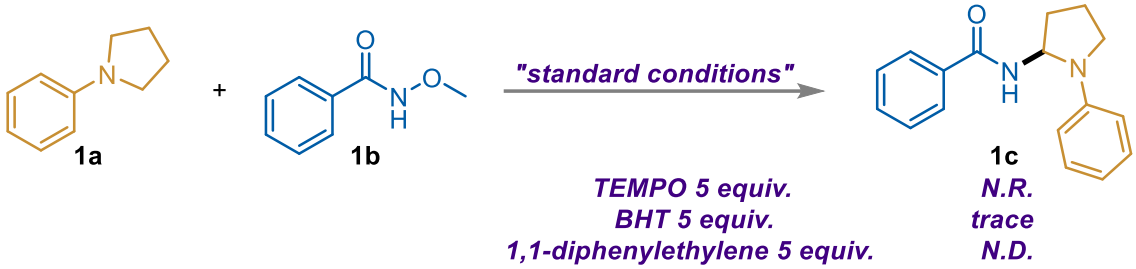
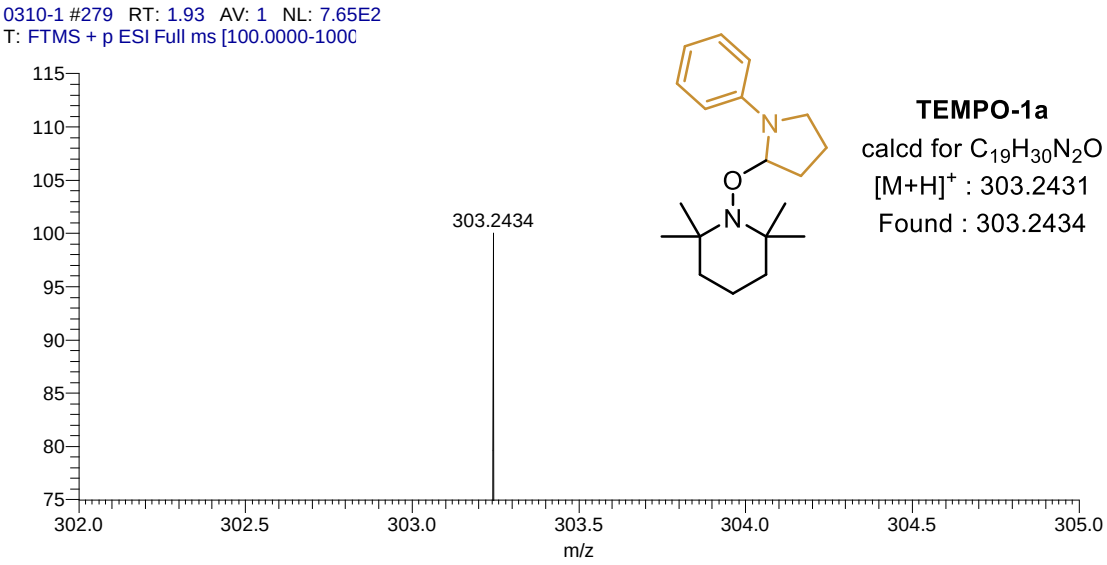
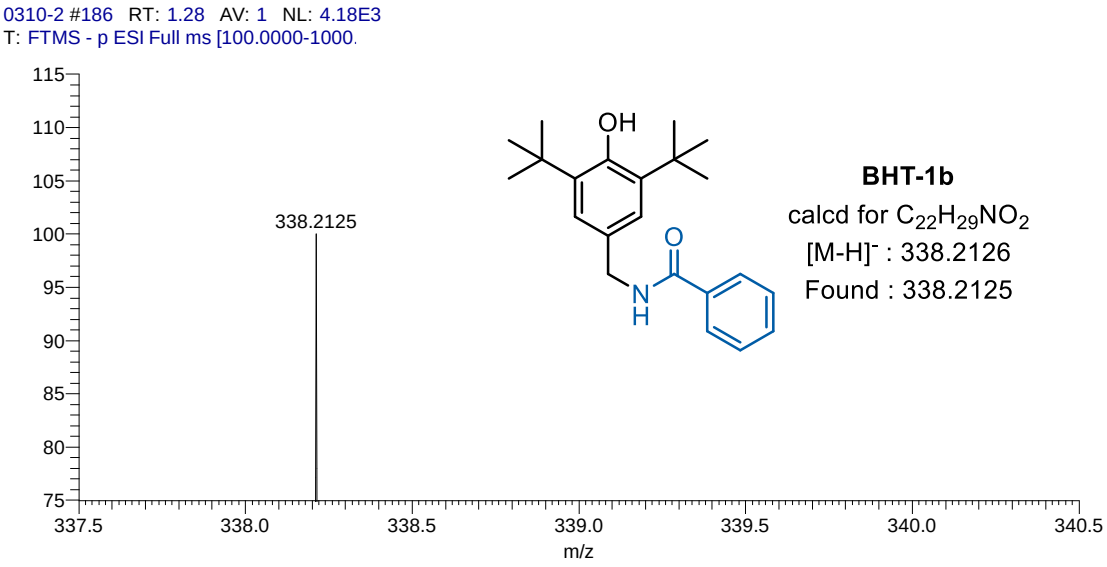


Figure S2. Control experiments with TEMPO, BHT, and 1, 1-diphenylethylene.





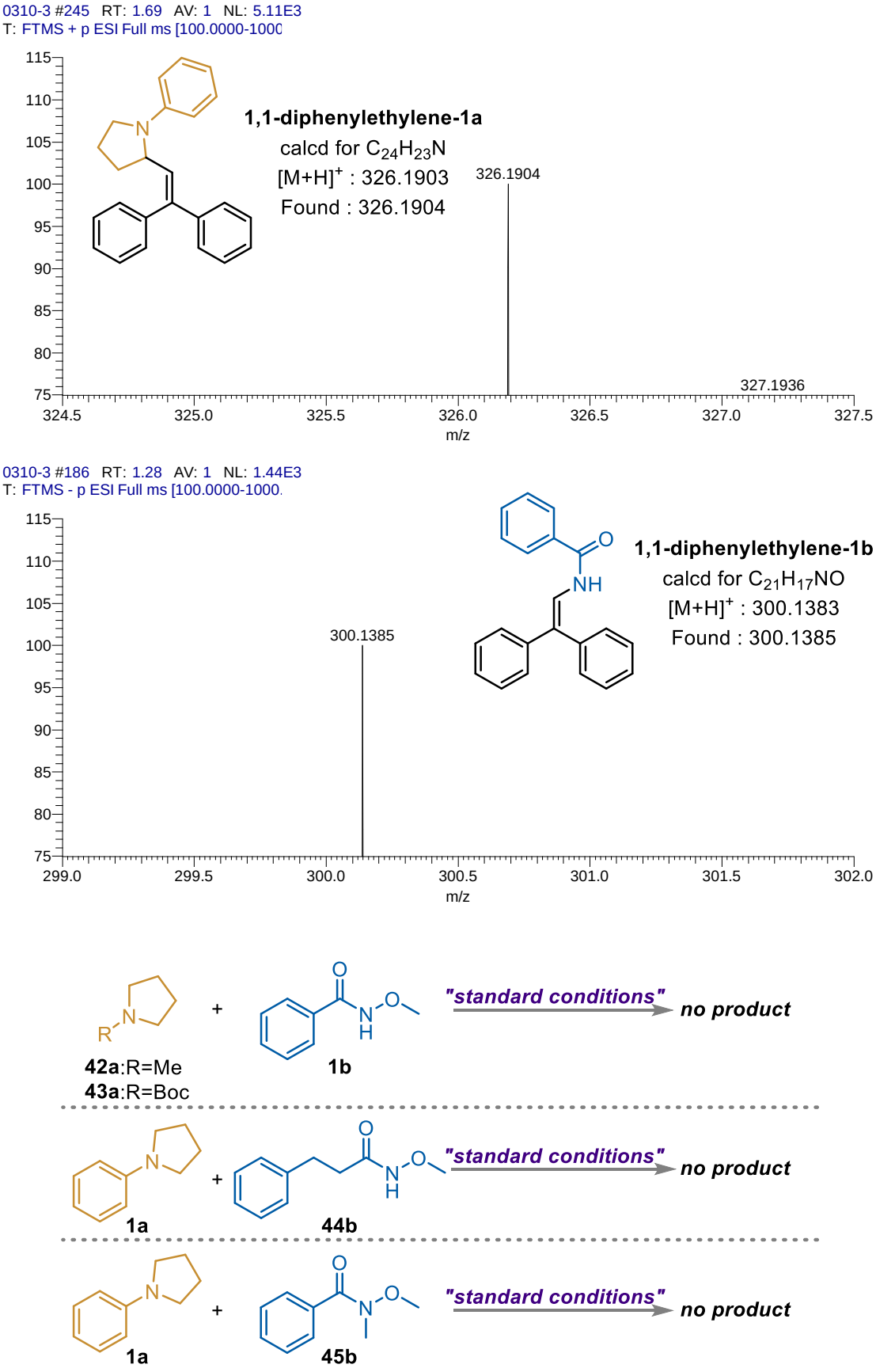


Figure S3. Control experiments with different types of substrates.

Different amines and amides such as 1-methylpyrrolidine (**42a**), *tert*-butyl pyrrolidine-1-carboxylate (**43a**), *N*-methoxy-3-phenylpropanamide (**44b**), and *N*-methoxy-*N*-methylbenzamide (**45b**) were employed as substrates respectively. The results showed that no product was observed, which suggested the interaction between the aromatic rings of the two substrates and the *in-situ* deprotonation of amide is important for the formation of photosensitive species.

ii. UV-VIS absorption spectroscopy experiments

The UV-visible absorption spectra of *N*-phenylpyrrolidine (**1a**) (10 mM) and *N*-methoxybenzamide (**1b**) (10 mM) were determined in the absence or presence of KOH (10 mM), and no absorption peak was observed in the visible light range. When KOH was added to the **1a** and **1b** mixture at the model equivalence ratio, a new absorption band between 350 and 500 nm was observed, implying the formation of the photosensitive species.

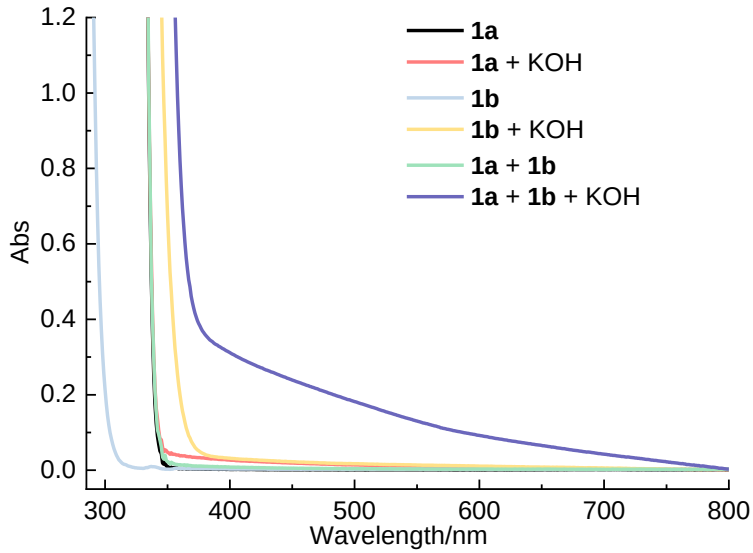


Figure S4. UV-VIS absorption spectra of the single **1a**, **1b**, and the mixture of **1a** and **1b** in the absence or presence of KOH. (Solvent: MeCN)

iii. Electron spin-resonance (ESR) spectroscopy experiments

Electron spin-resonance (ESR) spectra were recorded on a CIQTEK ESR200-plus. The reactions were performed in a 20 mL quartz tube under different conditions. Then small amount of the sample was transferred to a capillary, and ESR spectra were recorded.

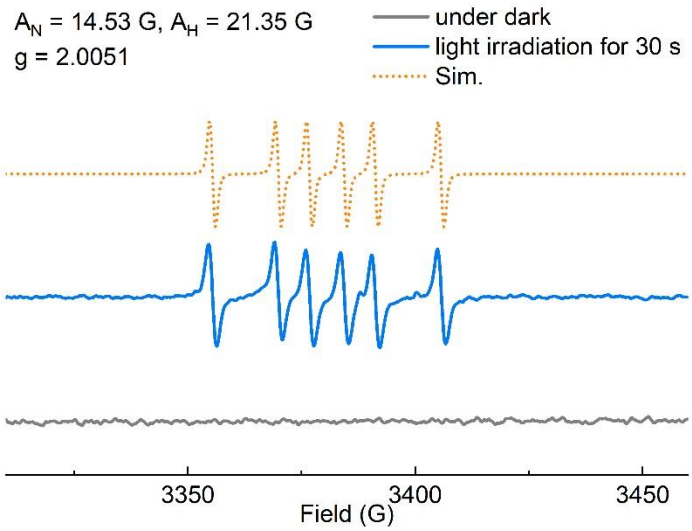


Figure S5. ESR spectrum of the mixture of DMPO (0.5 mmol), **11a** (0.1 mmol), **1b** (0.3 mmol) and KOH (0.2 mmol) in MeCN (1 mL) under dark and light irradiation (a 30 W 365 nm LED) at room temperature. ESR conditions: center field (3390.734 G), sweep width (200 G), frequency (9.487596 GHz), Attenuation (23 dB), MW Power (1.002374 mW), No. of Points (1024), No. of Sweeps (1), Modulation Amplitude (1.000 G), Modulation Frequency (100.00 kHz), Receiver Gain (0), Receiver Harmonic (1), Time Constant (100 ms), Convert Time (100 ms). Simulation software: CIQTEK ESR-ProPr.

iv. Competition experiments.

An experiment was carried out following procedure with **3a** (0.1 mmol, 1 equiv.) and **46a** (0.1 mmol, 1 equiv.), **1b** (0.6 mmol, 6 equiv.) under standard conditions. Upon completion, the reaction solution was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography, and only 62% of **3c** was observed. Another experiment was carried out following the procedure with **22b** (0.3 mmol, 3equiv.) and **37b** (0.3 mmol, 3 equiv.), **1a** (0.2 mmol, 2 equiv.) under standard conditions. Upon completion, the reaction solution was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography, and only 56% of **22c** was observed.

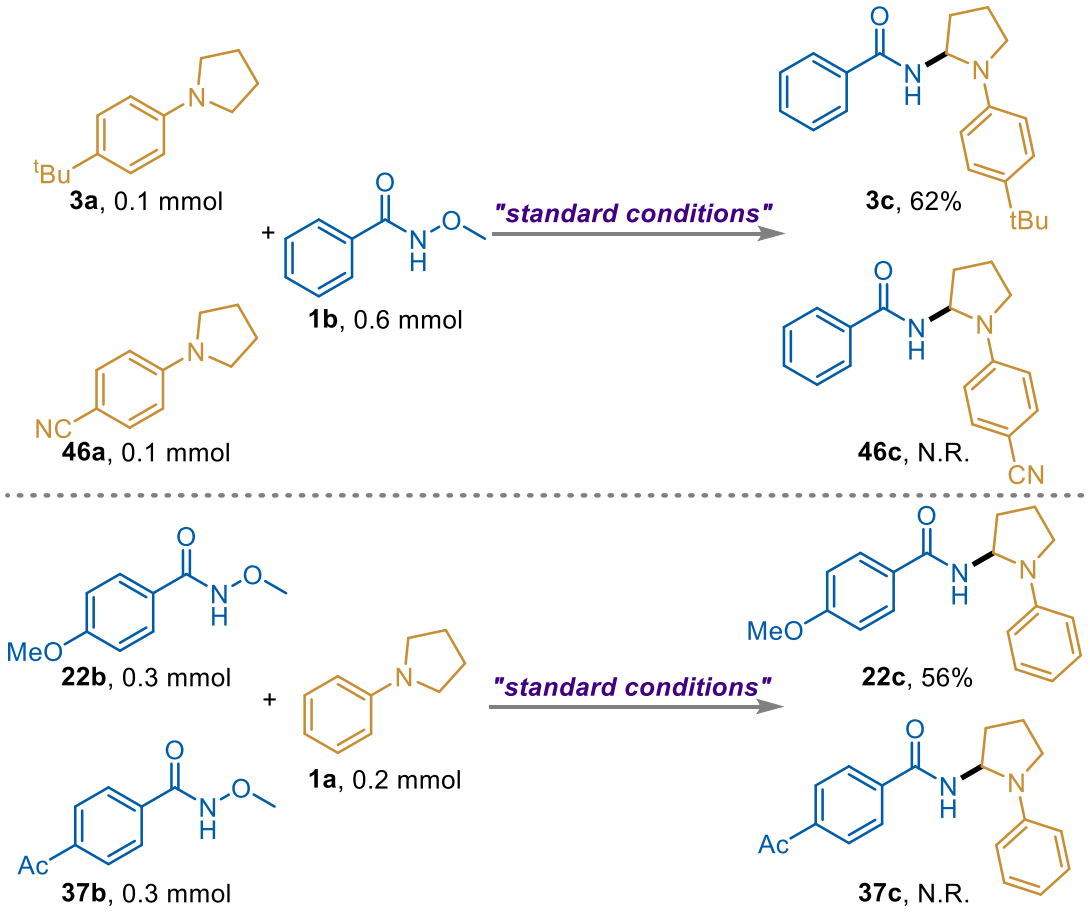
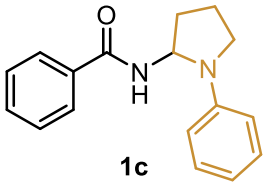


Figure S6. Competition experiments.

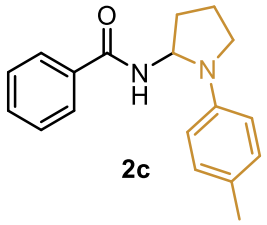
V. Characterization data of compounds 1c – 41c



1c

***N*-(1-phenylpyrrolidin-2-yl) benzamide (1c)**

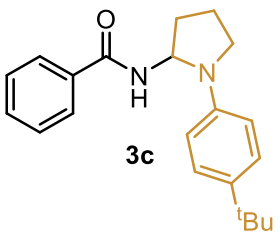
According to general procedure I, **1c** was obtained in 92% yield (24.5 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.77 (t, *J* = 7.1 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.26 (d, *J* = 6.8 Hz, 1H), 5.84 (t, *J* = 6.3 Hz, 1H), 3.63 – 3.54 (m, 1H), 3.23 (q, *J* = 8.9, 8.5 Hz, 1H), 2.25 – 2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.88, 145.89, 134.25, 131.80, 129.59, 128.72, 127.06, 117.72, 112.60, 67.29, 48.08, 34.39, 23.05. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{18}N_2O$ 265.1346, found 265.1346.



2c

***N*-(1-(*p*-tolyl)pyrrolidin-2-yl)benzamide (2c)**

According to general procedure I, **2c** was obtained in 75% yield (20.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 8.1 Hz, 2H), 6.34 (d, *J* = 6.6 Hz, 1H), 5.80 (t, *J* = 6.4 Hz, 1H), 3.60 – 3.52 (m, 1H), 3.19 (q, *J* = 8.4 Hz, 1H), 2.25 (s, 3H), 2.22 – 2.06 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.87, 143.74, 134.24, 131.71, 130.02, 128.65, 127.04, 126.79, 112.53, 67.45, 48.18, 34.33, 23.03, 20.39. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2O$ 279.1503, found 279.1505.

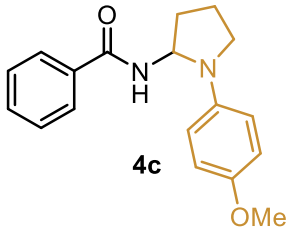


3c

***N*-(1-(4-(*tert*-butyl)phenyl)pyrrolidin-2-yl)benzamide (3c)**

According to general procedure I, **3c** was obtained in 80% yield (25.7 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 6.7 Hz, 1H), 5.83 (t, *J* = 6.1 Hz, 1H), 3.65 – 3.55 (m, 1H), 3.22

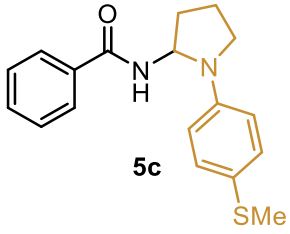
(q, *J* = 8.3 Hz, 1H), 2.24 – 2.08 (m, 4H), 1.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.77, 143.65, 140.32, 134.24, 131.66, 128.61, 127.05, 126.31, 112.18, 67.42, 48.12, 34.34, 33.90, 31.61, 23.04. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{26}N_2O$ 321.1972, found 321.1976.



4c

***N*-(1-(4-methoxyphenyl)pyrrolidin-2-yl)benzamide (4c)**

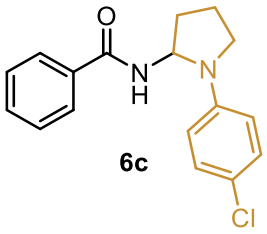
According to general procedure I, **4c** was obtained in 78% yield (23.1 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 7.3 Hz, 1H), 5.77 (t, *J* = 6.7 Hz, 1H), 3.73 (s, 3H), 3.57 – 3.50 (m, 1H), 3.16 (q, *J* = 8.3 Hz, 1H), 2.23 – 2.05 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.79, 152.04, 140.50, 134.24, 131.68, 128.63, 127.03, 115.13, 113.31, 67.66, 55.89, 48.46, 34.40, 23.10. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2O_2$ 295.1452, found 295.1455.



5c

***N*-(1-(4-(methylthio)phenyl)pyrrolidin-2-yl)benzamide (5c)**

According to general procedure I, **5c** was obtained in 72% yield (22.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 6.34 (s, 1H), 5.85 (t, *J* = 6.7 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.24 (q, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.26 – 2.12 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.88, 144.63, 134.12, 131.85, 131.45, 128.75, 128.72, 127.05, 113.31, 67.08, 48.15, 34.35, 23.02, 19.05. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2OS$ 311.1224, found 311.1225.

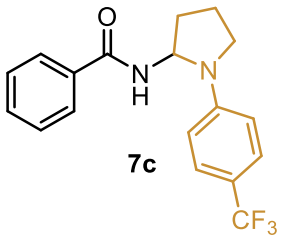


6c

***N*-(1-(4-chlorophenyl)pyrrolidin-2-yl)benzamide (6c)**

According to general procedure I, **6c** was obtained in 68% yield (20.4 mg). Eluent:

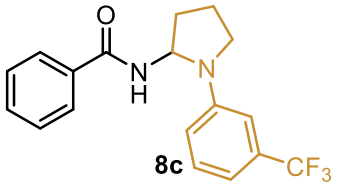
PE/EtOAc (4:1). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 1H), 5.81 (t, *J* = 6.7 Hz, 1H), 3.58 – 3.51 (m, 1H), 3.19 (q, *J* = 8.6, 8.1 Hz, 1H), 2.27 – 2.09 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.89, 144.42, 134.06, 131.90, 129.30, 128.75, 127.04, 122.57, 113.73, 66.99, 48.20, 34.40, 23.05. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{17}ClN_2O$ 299.0957, found 299.0958.



7c

***N*-(1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-yl)benzamide (7c)**

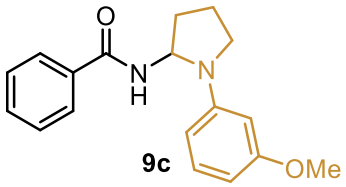
According to general procedure I, **7c** was obtained in 58% yield (19.3 mg). Eluent: PE/EtOAc (4:1). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.37 (m, 5H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.34 (d, *J* = 7.6 Hz, 1H), 5.91 (t, *J* = 6.8 Hz, 1H), 3.65 – 3.55 (m, 1H), 3.26 (q, *J* = 8.3 Hz, 1H), 2.28 – 2.10 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.95, 148.07, 133.97, 131.99, 128.78, 127.05, 126.77 (q, *J* = 3.8 Hz), 125.05 (q, *J* = 270.2 Hz), 119.34 (q, *J* = 32.6 Hz), 112.22, 66.56, 48.06, 34.34, 22.96. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{17}F_3N_2O$ 333.1220, found 333.1223.



8c

***N*-(1-(3-(trifluoromethyl)phenyl)pyrrolidin-2-yl)benzamide (8c)**

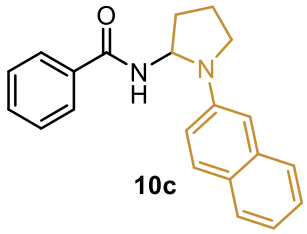
According to general procedure I, **8c** was obtained in 65% yield(21.7 mg). Eluent: PE/EtOAc (4:1). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.89 (t, *J* = 6.6 Hz, 1H), 3.63 – 3.55 (m, 1H), 3.26 (q, *J* = 7.9 Hz, 1H), 2.25 – 2.11 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.07, 145.93, 134.08, 131.83, 131.63 (q, *J* = 31.6 Hz), 129.89, 128.68, 127.03, 124.44 (q, *J* = 272.6 Hz), 115.80, 113.91 (q, *J* = 3.9 Hz), 108.86 (q, *J* = 4.1 Hz), 66.66, 48.04, 34.32, 22.89. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{17}F_3N_2O$ 333.1220, found 333.1224.



9c

***N*-(1-(3-methoxyphenyl)pyrrolidin-2-yl)benzamide (9c)**

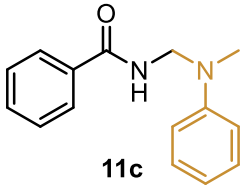
According to general procedure I, **9c** was obtained in 75% yield (22.2 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 7.1 Hz, 1H), 6.38 – 6.26 (m, 3H), 5.85 (t, *J* = 6.5 Hz, 1H), 3.75 (s, 3H), 3.59 – 3.50 (m, 1H), 3.27 – 3.16 (m, 1H), 2.25 – 2.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 160.9, 147.2, 134.3, 131.7, 130.2, 128.6, 127.0, 105.5, 103.1, 98.8, 67.0, 55.2, 48.1, 34.3, 22.9. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2O_2$ 295.1452, found 295.1454.



10c

***N*-(1-(naphthalen-2-yl)pyrrolidin-2-yl)benzamide (10c)**

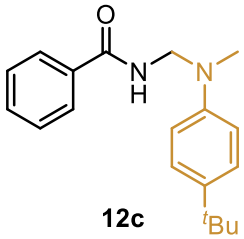
According to general procedure I, **10c** was obtained in 88% yield (27.7 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.93 (s, 1H), 6.45 (d, *J* = 7.1 Hz, 1H), 5.98 (t, *J* = 6.4 Hz, 1H), 3.81 – 3.63 (m, 1H), 3.32 (q, *J* = 8.2 Hz, 1H), 2.33 – 2.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.01, 143.69, 135.01, 134.29, 131.75, 129.33, 128.69, 127.65, 127.32, 127.06, 126.44, 126.35, 122.38, 115.78, 106.49, 67.23, 48.27, 34.38, 23.00. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{20}N_2O$ 315.1503, found 315.1505.



11c

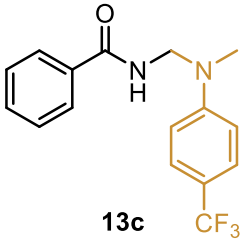
***N*-((methyl(phenyl)amino)methyl)benzamide (11c)[3]**

According to general procedure I, **11c** was obtained in 85% yield (20.5 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 5.14 (d, *J* = 5.5 Hz, 2H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.08, 147.92, 134.14, 131.70, 129.49, 128.57, 127.07, 118.16, 113.22, 58.17, 38.03. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{15}H_{16}N_2O$ 241.1335, found 241.1337.



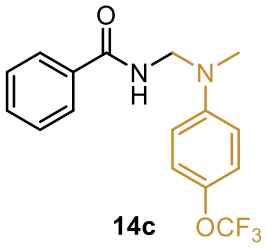
***N*-(((4-(*tert*-butyl)phenyl)(methyl)amino)methyl)benzamide (12c)**

According to general procedure I, **12c** was obtained in 82% yield (24.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.77 (s, 1H), 5.11 (d, *J* = 5.6 Hz, 2H), 3.07 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.03, 145.63, 141.03, 134.27, 131.70, 128.60, 127.10, 126.35, 113.12, 58.41, 38.07, 33.90, 31.56. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{19}H_{24}N_2O$ 295.1816, found 295.1818.



***N*-((methyl(4-(trifluoromethyl)phenyl)amino)methyl)benzamide (13c)**

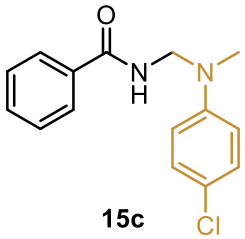
According to general procedure I, **13c** was obtained in 65% yield (20.1 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 1H), 5.13 (d, *J* = 5.7 Hz, 2H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.15, 150.24, 133.92, 132.04, 128.77, 127.12, 126.81 (q, *J* = 3.7 Hz), 124.97 (q, *J* = 270.6 Hz), 119.62 (q, *J* = 32.7 Hz), 112.22, 57.72, 38.33. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{16}H_{15}F_3N_2O$ 307.1064, found 307.1066.



***N*-((methyl(4-(trifluoromethoxy)phenyl)amino)methyl)benzamide (14c)**

According to general procedure I, **14c** was obtained in 75% yield (24.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 3H), 6.81 (d, *J* = 9.2 Hz, 2H), 5.03 (d, *J* = 5.7 Hz, 2H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.29, 146.76, 141.03 (q, *J* = 2.1 Hz), 134.03, 131.86, 128.63, 127.12, 122.40, 120.76 (q, *J* = 255.5 Hz), 113.68, 58.33, 38.28. HR-MS (ESI) $[M-H]^-$ m/z calcd for

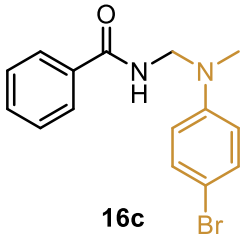
$C_{16}H_{15}F_3N_2O_2$ 323.1013, found 323.1016.



15c

***N*-(((4-chlorophenyl)(methyl)amino)methyl)benzamide (15c)[4]**

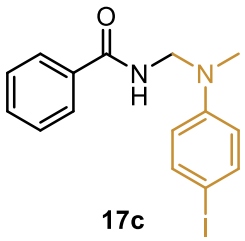
According to general procedure I, **15c** was obtained in 80% yield (21.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.74 (s, 1H), 5.04 (d, *J* = 5.7 Hz, 2H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.09, 146.60, 134.06, 131.91, 129.32, 128.71, 127.09, 123.22, 114.55, 58.29, 38.29. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{15}ClN_2O$ 273.0800, found 273.0802.



16c

***N*-(((4-bromophenyl)(methyl)amino)methyl)benzamide (16c)[4]**

According to general procedure I, **16c** was obtained in 78% yield (24.8 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.80 – 6.74 (m, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 5.04 (d, *J* = 5.7 Hz, 2H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.08, 147.00, 134.03, 132.20, 131.91, 128.71, 127.09, 114.98, 110.37, 58.16, 38.26. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{15}BrN_2O$ 317.0295, found 317.0297.

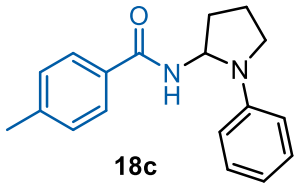


17c

***N*-(((4-iodophenyl)(methyl)amino)methyl)benzamide (17c)**

According to general procedure I, **17c** was obtained in 75% yield (27.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.47 (dd, *J* = 8.2, 3.8 Hz, 3H), 7.38 (dd, *J* = 8.3, 6.9 Hz, 2H), 6.85 (t, *J* = 5.7 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 2H), 5.02 (d, *J* = 5.6 Hz, 2H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.08, 147.54, 138.04, 133.98, 131.88, 128.67, 127.09, 115.50, 79.61, 57.95,

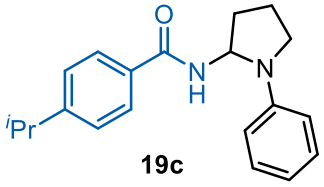
38.14. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{15}IN_2O$ 365.0156, found 365.0154.



18c

4-methyl-*N*-(1-phenylpyrrolidin-2-yl)benzamide (18c)

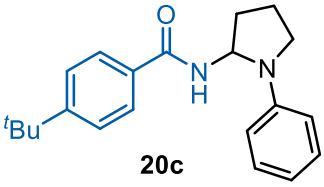
According to general procedure I, **18c** was obtained in 85% yield (22.6 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.79 – 6.75 (m, 1H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.22 (d, *J* = 6.8 Hz, 1H), 5.83 (t, *J* = 5.6 Hz, 1H), 3.58 (m, 1H), 3.23 (q, *J* = 8.9 Hz, 1H), 2.38 (s, 3H), 2.25 – 2.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 145.95, 142.25, 131.40, 129.57, 129.36, 127.07, 117.69, 112.62, 67.27, 48.09, 34.41, 23.06, 21.58. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{18}N_2O$ 265.1346, found 265.1348.



19c

4-isopropyl-*N*-(1-phenylpyrrolidin-2-yl) benzamide (19c)

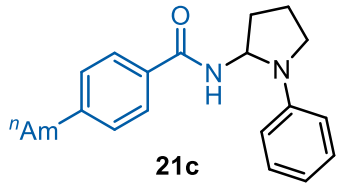
According to general procedure I, **19c** was obtained in 84% yield (25.6 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 7.9, 4.2 Hz, 4H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 6.9 Hz, 1H), 5.82 (t, *J* = 6.3 Hz, 1H), 3.57 (dt, *J* = 9.1, 4.0 Hz, 1H), 3.21 (q, *J* = 8.4 Hz, 1H), 2.93 (hept, *J* = 6.9 Hz, 1H), 2.25 – 2.07 (m, 4H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 153.05, 145.90, 131.70, 129.52, 127.17, 126.73, 117.60, 112.56, 67.17, 48.03, 34.38, 34.19, 23.88, 23.01. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{20}H_{24}N_2O$ 307.1816, found 307.1818.



20c

4-(*tert*-butyl)-*N*-(1-phenylpyrrolidin-2-yl)benzamide (20c)

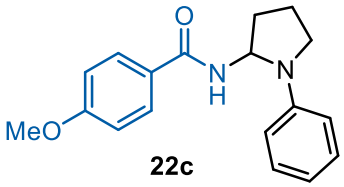
According to general procedure I, **20c** was obtained in 85% yield (27.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), 6.78 (m, 3H), 6.29 (s, 1H), 5.86 (t, *J* = 6.0 Hz, 1H), 3.61 (m, 1H), 3.25 (q, *J* = 8.9 Hz, 1H), 2.26 – 2.10 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 155.32, 145.94, 131.36, 129.54, 126.91, 125.62, 117.66, 112.62, 67.21, 48.07, 35.05, 34.41, 31.27, 23.04. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{26}N_2O$ 321.1972, found 321.1975.



21c

4-pentyl-*N*-(1-phenylpyrrolidin-2-yl)benzamide (21c)

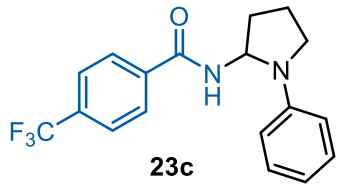
According to general procedure I, **21c** was obtained in 82% yield (27.5 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.21 (m, 4H), 6.81 – 6.74 (m, 3H), 6.26 (s, 1H), 5.86 (t, *J* = 6.4 Hz, 1H), 3.63 – 3.58 (m, 1H), 3.25 (q, *J* = 8.9 Hz, 1H), 2.68 – 2.62 (m, 2H), 2.26 – 2.09 (m, 4H), 1.66 – 1.59 (m, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.88, 147.24, 145.95, 131.61, 129.56, 128.73, 127.08, 117.66, 112.62, 67.23, 48.07, 35.91, 34.41, 31.50, 31.02, 23.05, 22.61, 14.12. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{22}H_{28}N_2O$ 335.2129, found 335.2133.



22c

4-methoxy-*N*-(1-phenylpyrrolidin-2-yl)benzamide (22c)

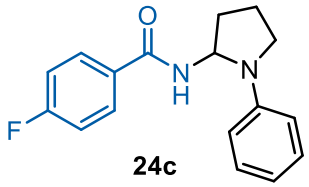
According to general procedure I, **22c** was obtained in 77% yield (22.7 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.81 – 6.72 (m, 3H), 6.31 (d, *J* = 6.1 Hz, 1H), 5.85 (t, *J* = 6.3 Hz, 1H), 3.85 (s, 3H), 3.64 – 3.56 (m, 1H), 3.24 (q, *J* = 8.2 Hz, 1H), 2.24 – 2.09 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.39, 162.39, 145.95, 129.50, 128.88, 126.50, 117.57, 113.82, 112.58, 67.16, 55.50, 48.03, 34.39, 22.99. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2O_2$ 295.1452, found 295.1455.



23c

***N*-(1-phenylpyrrolidin-2-yl)-4-(trifluoromethyl)benzamide (23c)**

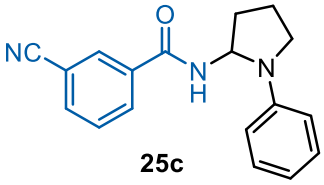
According to general procedure I, **23c** was obtained in 58% yield (19.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 9.0 Hz, 2H), 7.70 (t, *J* = 9.0 Hz, 2H), 7.33 – 7.25 (m, 2H), 6.86 – 6.72 (m, 3H), 6.47 – 6.34 (m, 1H), 5.88 (t, *J* = 5.4, 4.3 Hz, 1H), 3.68 – 3.56 (m, 1H), 3.29 (q, *J* = 8.8, 8.2 Hz, 1H), 2.30 – 2.11 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.48, 145.63, 137.36, 133.38 (q, *J* = 32.7 Hz), 129.53, 127.46, 125.65 (q, *J* = 3.7 Hz), 123.63 (q, *J* = 272.5 Hz), 117.81, 112.46, 67.37, 47.99, 34.20, 22.91. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{17}F_3N_2O$ 333.1220, found 333.1223.



24c

4-fluoro-*N*-(1-phenylpyrrolidin-2-yl)benzamide(24c)

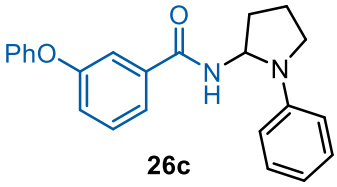
According to general procedure I, **24c** was obtained in 61% yield (17.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 2H), 7.27 – 7.20 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 6.9 Hz, 1H), 5.82 (t, *J* = 6.3 Hz, 1H), 3.64 – 3.55 (m, 1H), 3.23 (q, *J* = 8.7, 8.2 Hz, 1H), 2.26 – 2.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.83, 164.92 (d, *J* = 252.1 Hz), 145.82, 130.38 (d, *J* = 3.1 Hz), 129.59, 129.42 (d, *J* = 8.9 Hz), 117.75, 115.72 (d, *J* = 21.9 Hz), 112.56, 67.33, 48.06, 34.34, 23.01. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{17}FN_2O$ 283.1252, found 283.1256.



25c

3-cyano-*N*-(1-phenylpyrrolidin-2-yl)benzamide (25c)

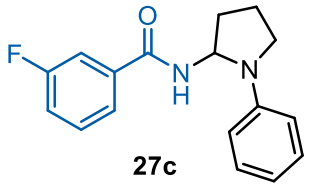
According to general procedure I, **25c** was obtained in 75% yield (21.8 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 6.8 Hz, 1H), 5.84 (t, *J* = 6.4 Hz, 1H), 3.64 – 3.55 (m, 1H), 3.24 (q, *J* = 8.9 Hz, 1H), 2.25 – 2.11 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.70, 145.67, 135.47, 134.92, 131.37, 130.90, 129.70, 129.65, 118.05, 117.96, 113.10, 112.57, 67.48, 48.08, 34.29, 22.99. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{17}N_3O$ 290.1299, found 290.1296.



26c

3-phenoxy-*N*-(1-phenylpyrrolidin-2-yl)benzamide (26c)

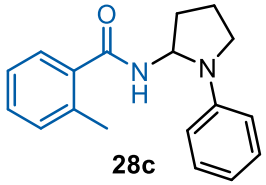
According to general procedure I, **26c** was obtained in 93% yield (33.2 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.15 – 7.08 (m, 2H), 7.01 – 6.98 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 2H), 6.31 (d, *J* = 6.9 Hz, 1H), 5.81 (t, *J* = 6.3 Hz, 1H), 3.62 – 3.50 (m, 1H), 3.20 (q, *J* = 8.7, 8.2 Hz, 1H), 2.24 – 2.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.22, 157.78, 156.70, 145.81, 136.16, 130.04, 129.55, 123.89, 121.87, 121.48, 119.34, 119.22, 117.70, 117.56, 112.56, 67.25, 48.03, 34.31, 22.99. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{23}H_{22}N_2O_2$ 357.1609, found 357.1606.



27c

3-fluoro-*N*-(1-phenylpyrrolidin-2-yl)benzamide (27c)

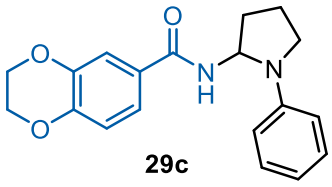
According to general procedure I, **27c** was obtained in 65% yield (18.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.39 – 7.33 (m, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.14 (m, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.32 (d, *J* = 8.7 Hz, 1H), 5.82 (t, *J* = 6.4 Hz, 1H), 3.63 – 3.53 (m, 1H), 3.23 (q, *J* = 8.7, 8.2 Hz, 1H), 2.26 – 2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.61, 162.88 (d, *J* = 247.9 Hz), 145.80, 136.53 (d, *J* = 6.6 Hz), 130.35 (d, *J* = 7.8 Hz), 129.60, 122.51 (d, *J* = 3.2 Hz), 118.77 (d, *J* = 21.2 Hz), 117.82, 114.51 (d, *J* = 22.9 Hz), 112.58, 67.37, 48.07, 34.32, 23.00. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{17}FN_2O$ 283.1252, found 283.1255.



28c

2-methyl-N-(1-phenylpyrrolidin-2-yl)benzamide (28c)

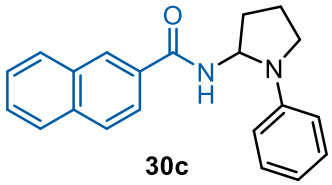
According to general procedure I, **28c** was obtained in 80% yield (22.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.24 – 7.15 (m, 2H), 6.84 – 6.77 (m, 3H), 5.98 (d, *J* = 7.6 Hz, 1H), 5.88 (t, *J* = 6.8 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.25 (q, *J* = 9.3 Hz, 1H), 2.49 (s, 3H), 2.28 – 2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.59, 145.64, 136.18, 136.15, 131.14, 130.09, 129.52, 126.76, 125.83, 117.59, 112.61, 66.34, 47.81, 34.45, 22.99, 19.96. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{18}H_{20}N_2O$ 279.1503, found 279.1503.



29c

***N*-(1-phenylpyrrolidin-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide (29c)**

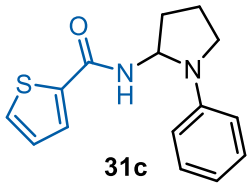
According to general procedure I, **29c** was obtained in 78% yield (25.2 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.20 (d, *J* = 6.9 Hz, 1H), 5.80 (t, *J* = 6.3 Hz, 1H), 4.27 – 4.22 (m, 4H), 3.59 – 3.51 (m, 1H), 3.20 (q, *J* = 8.6, 8.2 Hz, 1H), 2.20 – 2.06 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.09, 146.66, 145.88, 143.46, 129.50, 127.51, 120.45, 117.57, 117.30, 116.61, 112.55, 67.15, 64.63, 64.27, 48.00, 34.36, 22.99. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{19}H_{20}N_2O_3$ 323.1401, found 323.1404.



30c

***N*-(1-phenylpyrrolidin-2-yl)-2-naphthamide (30c)**

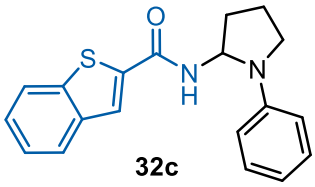
According to general procedure I, **30c** was obtained in 90% yield (28.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.92 – 7.83 (m, 4H), 7.58 – 7.51 (m, 2H), 7.27 – 7.24 (m, 2H), 6.80 – 6.75 (m, 3H), 6.42 (d, *J* = 6.9 Hz, 1H), 5.90 (t, *J* = 6.0 Hz, 1H), 3.66 – 3.60 (m, 1H), 3.26 (q, *J* = 8.4 Hz, 1H), 2.27 – 2.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 145.95, 134.94, 132.70, 131.39, 129.63, 129.06, 128.63, 127.89, 127.87, 127.54, 126.94, 123.65, 117.75, 112.62, 67.45, 48.14, 34.44, 23.10. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{20}N_2O$ 315.1503, found 315.1504.



31c

***N*-(1-phenylpyrrolidin-2-yl)thiophene-2-carboxamide (31c)**

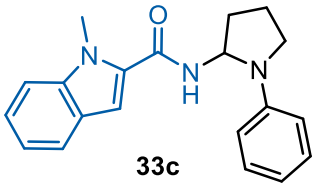
According to general procedure I, **31c** was obtained in 55% yield (14.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.26 – 7.22 (m, 2H), 7.07 – 7.02 (m, 1H), 6.80 – 6.71 (m, 3H), 6.11 (d, *J* = 6.8 Hz, 1H), 5.81 (t, *J* = 6.2 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.22 (q, *J* = 8.5 Hz, 1H), 2.22 – 2.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 145.83, 138.84, 130.35, 129.59, 128.26, 127.74, 117.79, 112.63, 67.24, 48.09, 34.40, 23.00. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{20}N_2O$ 271.0911, found 271.0912.



32c

***N*-(1-phenylpyrrolidin-2-yl)benzo[b]thiophene-2-carboxamide (32c)**

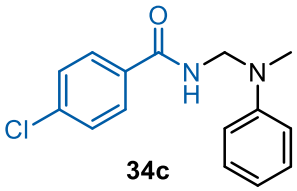
According to general procedure I, **32c** was obtained in 67% yield (21.6 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 4H), 7.46 – 7.30 (m, 3H), 7.26 – 7.19 (m, 2H), 6.81 – 6.70 (m, 3H), 6.46 (d, *J* = 6.9 Hz, 1H), 5.88 – 5.80 (m, 1H), 3.63 – 3.53 (m, 1H), 3.21 (q, *J* = 8.2, 7.7 Hz, 1H), 2.24 – 2.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 145.77, 141.04, 139.14, 138.39, 129.58, 126.47, 125.33, 125.14, 125.00, 122.81, 117.79, 112.61, 67.36, 48.07, 34.36, 22.97. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{19}H_{18}N_2OS$ 321.1067, found 321.1062.



33c

1-methyl-*N*-(1-phenylpyrrolidin-2-yl)-1H-indole-2-carboxamide (33c)

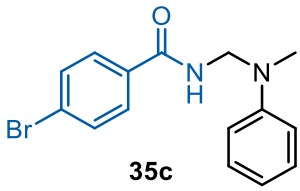
According to general procedure I, **33c** was obtained in 72% yield (22.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 9.3 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.83 – 6.76 (m, 4H), 6.37 (d, *J* = 7.1 Hz, 1H), 5.86 (t, *J* = 5.7 Hz, 1H), 4.13 (s, 3H), 3.66 – 3.59 (m, 1H), 3.27 (q, *J* = 8.8 Hz, 1H), 2.29 – 2.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.17, 145.86, 139.23, 131.63, 129.57, 126.05, 124.31, 121.92, 120.64, 117.75, 112.62, 110.25, 104.22, 66.77, 48.02, 34.44, 31.71, 23.04. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{20}H_{21}N_3O$ 318.1612, found 318.1614.



34c

4-chloro-*N*-((methyl(phenyl)amino)methyl)benzamide(34c)[3]

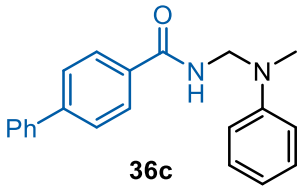
According to general procedure I, **34c** was obtained in 85% yield (23.3 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 5.10 (d, *J* = 5.5 Hz, 2H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.04, 147.87, 137.98, 132.54, 129.57, 128.85, 128.55, 118.36, 113.27, 58.37, 38.10. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{15}ClN_2O$ 273.0800, found 273.0802.



35c

4-bromo-*N*-((methyl(phenyl)amino)methyl)benzamide (35c)[3]

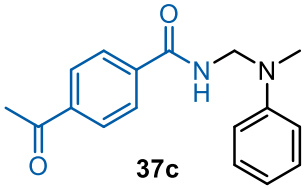
According to general procedure I, **35c** was obtained in 80% yield (25.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 5.4 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 5.07 (d, *J* = 5.9 Hz, 2H), 3.07 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 147.78, 132.92, 131.68, 129.46, 128.69, 126.31, 118.21, 113.17, 58.29, 38.04. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{15}BrN_2O$ 317.0295, found 317.0298.



36c

***N*-((methyl(phenyl)amino)methyl)-[1,1'-biphenyl]-4-carboxamide (36c)[3]**

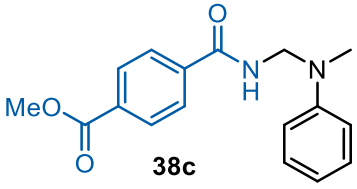
According to general procedure I, **36c** was obtained in 90% yield (28.4 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 5.7 Hz, 1H), 5.15 (d, *J* = 5.6 Hz, 2H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.76, 148.01, 144.54, 139.97, 132.83, 129.59, 128.99, 128.11, 127.65, 127.27, 127.25, 118.30, 113.33, 58.29, 38.11. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{20}N_2O$ 315.1503, found 315.1506.



37c

4-acetyl-*N*-((methyl(phenyl)amino)methyl)benzamide (37c)

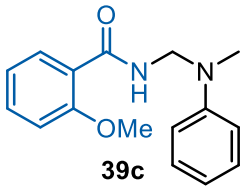
According to general procedure I, **37c** was obtained in 60% yield (16.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 5.4 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.09 (d, *J* = 5.6 Hz, 2H), 3.06 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.57, 167.19, 147.75, 139.04, 138.05, 129.38, 128.33, 127.39, 118.12, 113.12, 58.32, 38.03, 26.71. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{18}N_2O_2$ 281.1296, found 281.1298.



38c

methyl 4-(((methyl(phenyl)amino)methyl)carbamoyl)benzoate (38c)

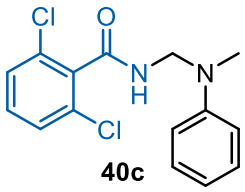
According to general procedure I, **38c** was obtained in 67% yield (19.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 5.14 (d, *J* = 5.3 Hz, 2H), 3.94 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.22, 166.32, 147.82, 138.10, 132.92, 129.90, 129.63, 127.17, 118.44, 113.29, 58.42, 52.52, 38.18. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{17}H_{18}N_2O_3$ 297.1245, found 297.1246.



39c

2-methoxy-*N*-((methyl(phenyl)amino)methyl)benzamide (39c)[3]

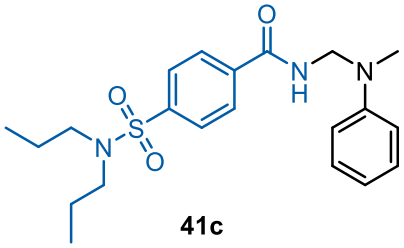
According to general procedure I, **39c** was obtained in 82% yield (22.1 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 – 6.86 (m, 3H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.13 (d, *J* = 5.6 Hz, 2H), 3.75 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.69, 157.47, 148.30, 132.99, 132.19, 129.36, 121.30, 121.28, 118.08, 113.50, 111.41, 57.77, 55.88, 38.18. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{16}H_{18}N_2O_2$ 269.1296, found 269.1299.



40c

2,6-dichloro-*N*-((methyl(phenyl)amino)methyl)benzamide (40c)

According to general procedure I, **40c** was obtained in 74% yield (22.7 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.22 – 7.16 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 5.04 (d, *J* = 3.9 Hz, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.80, 147.64, 135.51, 131.78, 130.36, 129.13, 127.75, 118.14, 113.42, 57.53, 37.84. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{15}H_{14}Cl_2N_2O$ 307.0410, found 307.0411.



41c

4-(*N*, *N*-dipropylsulfamoyl)-*N*-((methyl(phenyl)amino)methyl)benzamide (41c)

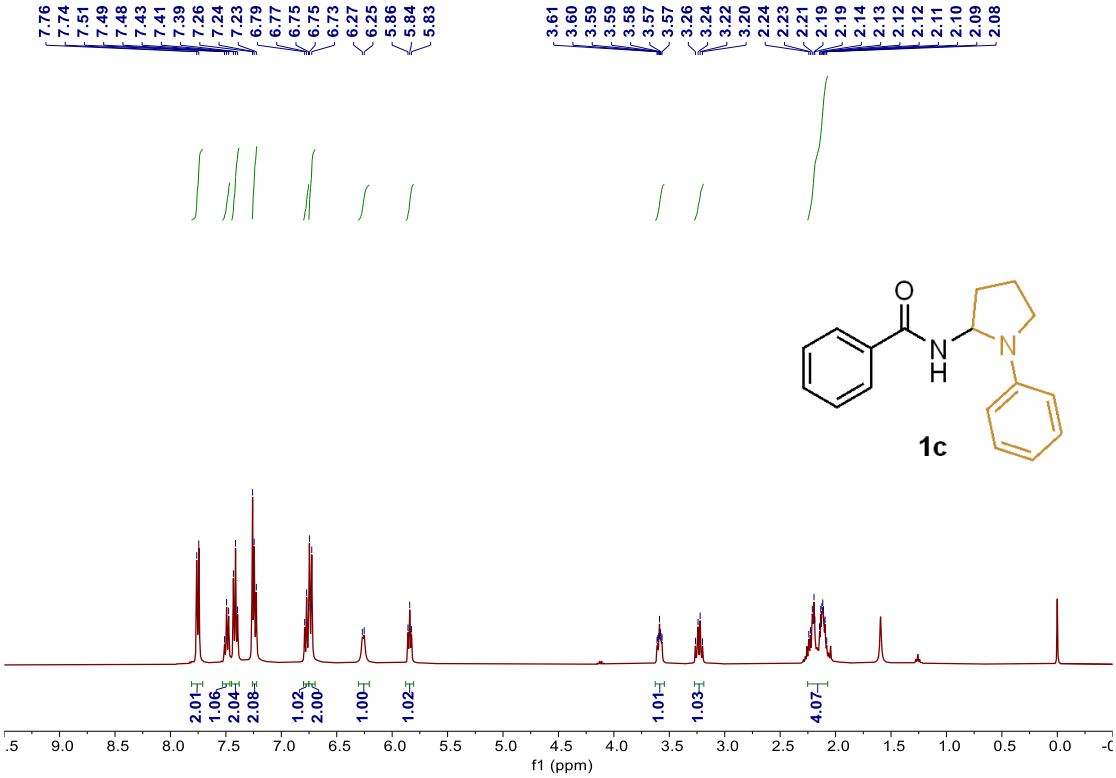
According to general procedure I, **41c** was obtained in 42% yield (16.9 mg). Eluent: PE/EtOAc (4:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 4H), 7.30 (t, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.56 (s, 1H), 5.15 (d, *J* = 5.4 Hz, 2H), 3.09 (s, 3H), 3.06 (t, *J* = 7.6 Hz, 4H), 1.55 – 1.50 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.70, 147.79, 143.31, 137.70, 129.75, 127.85, 127.44, 118.63, 113.36, 58.53, 50.06, 38.30, 22.06, 11.30. HR-MS (ESI) $[M-H]^-$ m/z calcd for $C_{21}H_{29}N_3O_3S$ 402.1857, found 402.1856.

VI. References

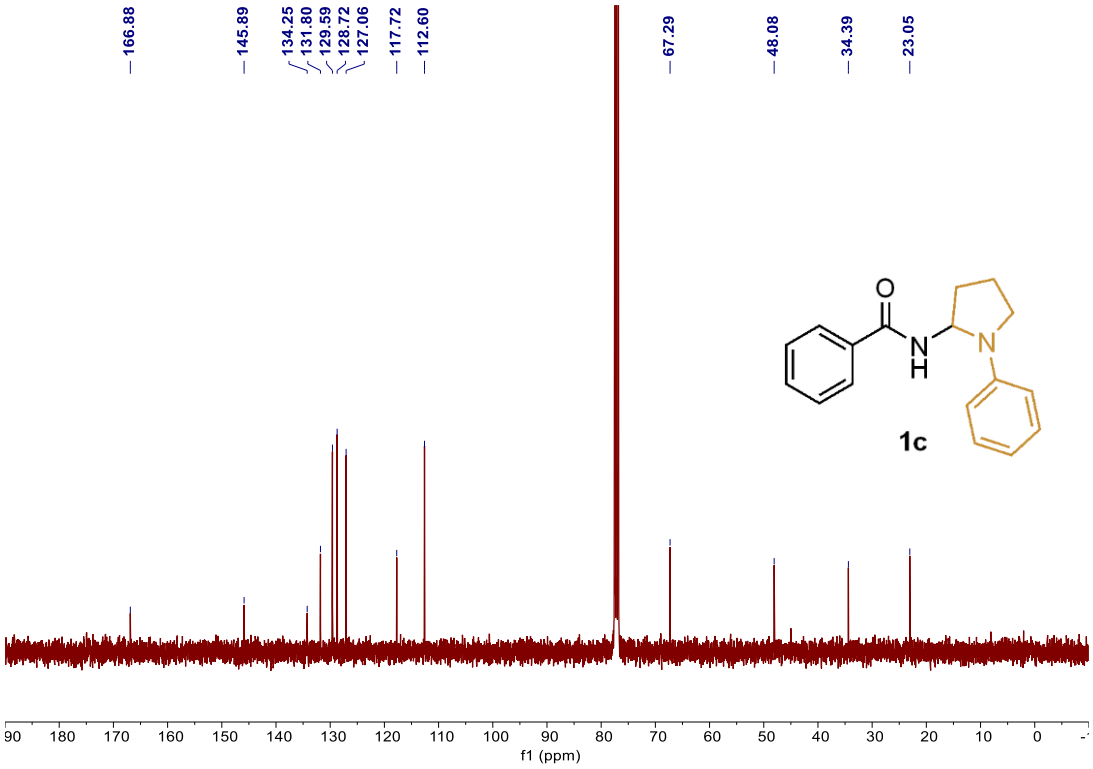
1. Lei, J.; Li, M.; Zhang, Q.; Liu, S.; Li, H.; Shi, L.; Jiang, W.-F.; Duan, C.; Jin, Y., Visible-Light-Induced Radical Cascade Cross-Coupling via C(sp^3)–H Activation and *C–N*/*N–O* Cleavage: Feasible Access to Methylenebisamide Derivatives. *Org. Lett.* **2023,** *25*, 2300-2305.
2. Zhang, H.; Cai, Q.; Ma, D., Amino Acid Promoted CuI-Catalyzed *C−N* Bond Formation between Aryl Halides and Amines or *N*-Containing Heterocycles. *J. Org. Chem.* **2005,** *70*, 5164-5173.
3. Lin, B.; Shi, S.; Cui, Y.; Liu, Y.; Tang, G.; Zhao, Y., Oxidative C(sp^3)–H amidation of *tert*iary arylamines with nitriles. *Organic Chemistry Frontiers* **2018,** *5*, 2860-2863.
4. Wusiman, A.; Hudabaierdi, R., Iron-catalyzed aerobic oxidative cross-coupling amidation of *N*, *N*-dimethylanilines. *Tetrahedron Lett.* **2019,** *60*, 681-683.

VII. The ^{1}H and ^{13}C NMR spectra of compounds 1c – 41c

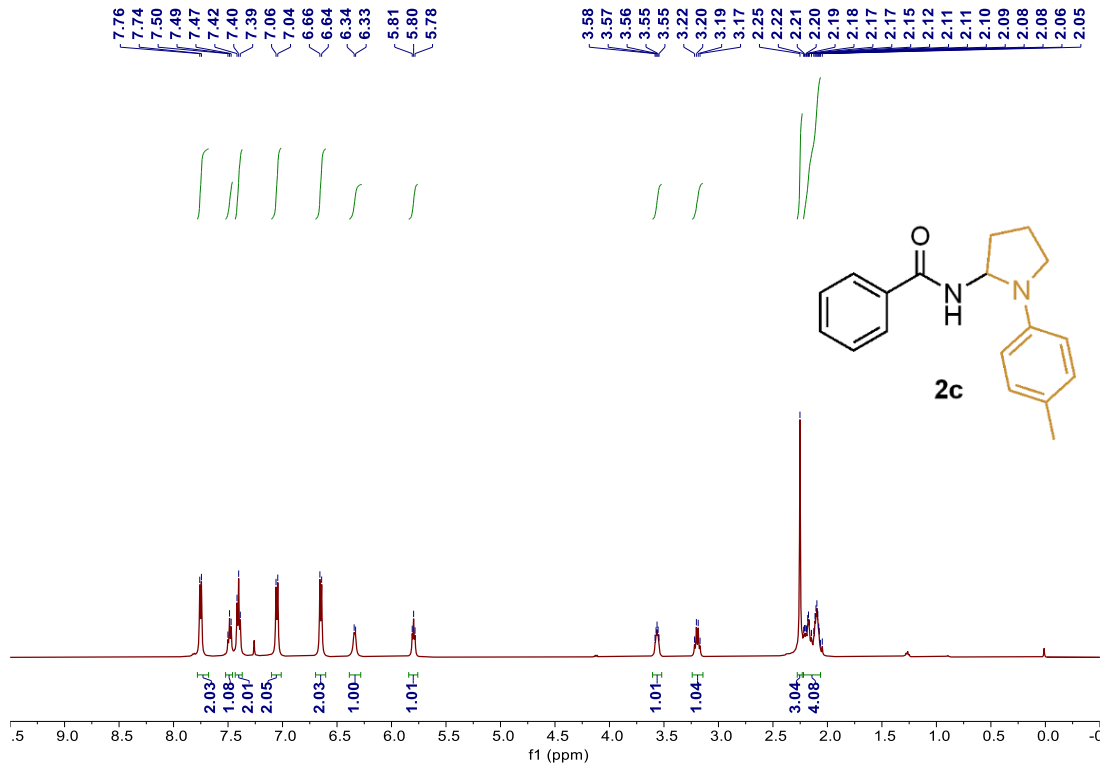
^{1}H NMR for **1c** (400 MHz, $CDCl_3$)



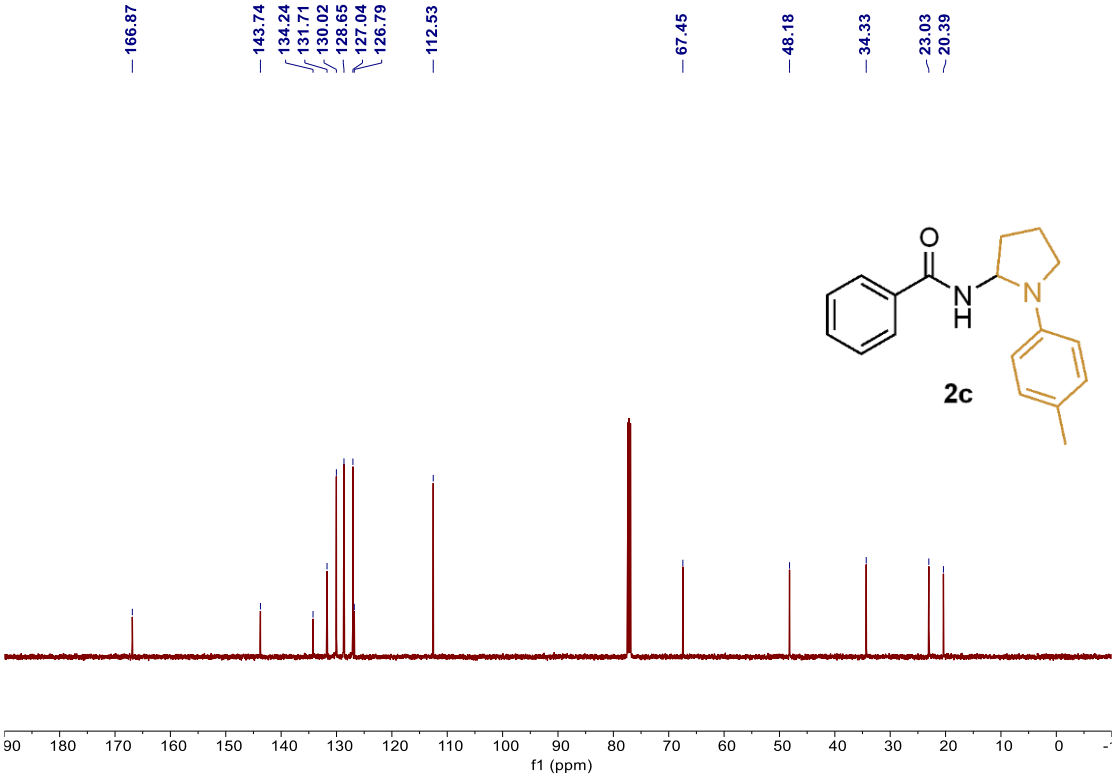
^{13}C NMR for **1c** (100 MHz, $CDCl_3$)



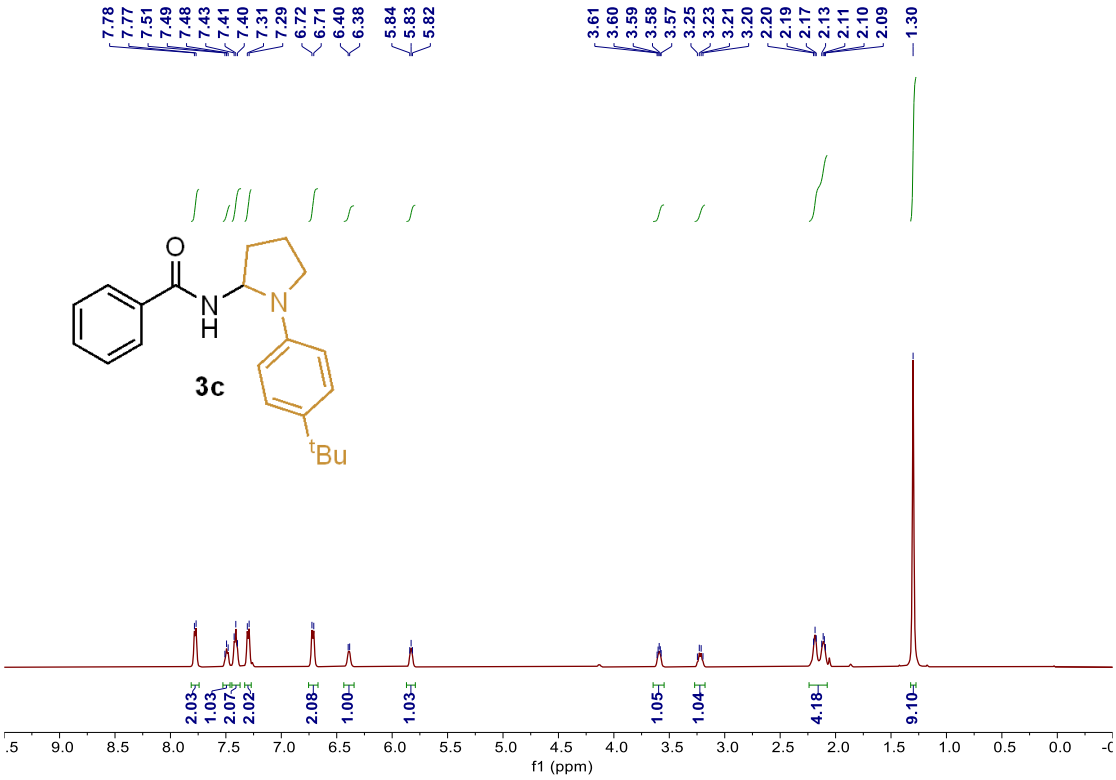
^{1}H NMR for **2c** (500 MHz, $CDCl_3$)



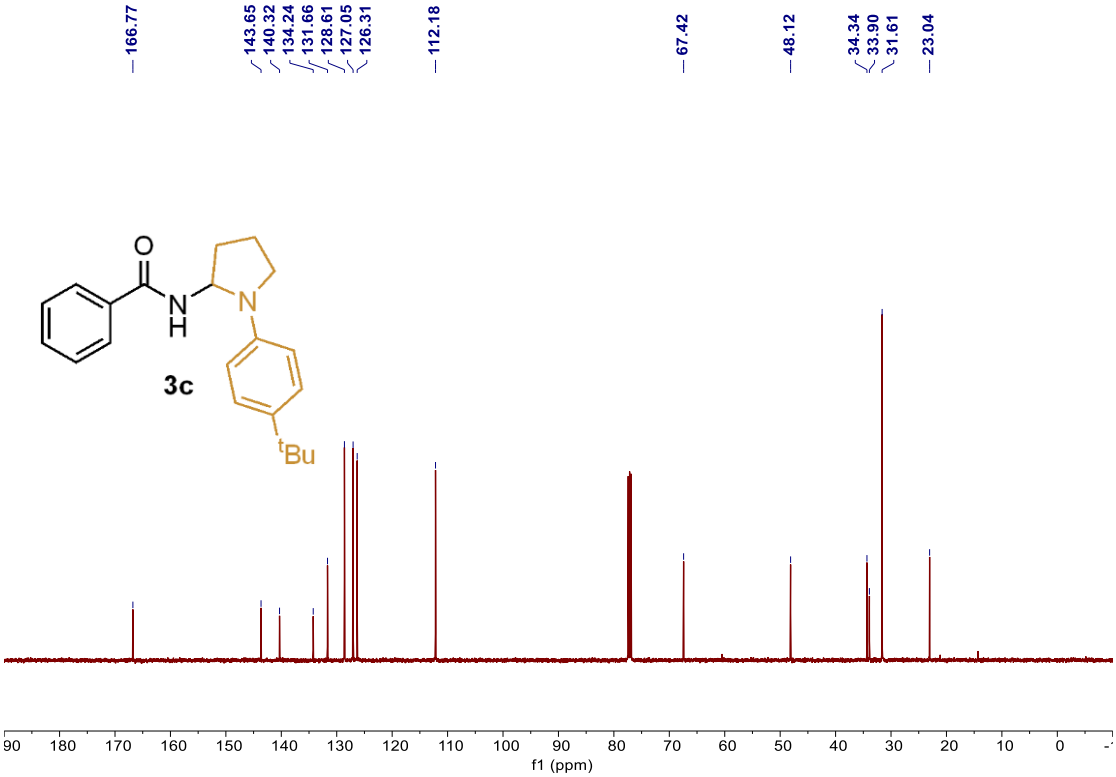
^{13}C NMR for **2c** (125 MHz, $CDCl_3$)



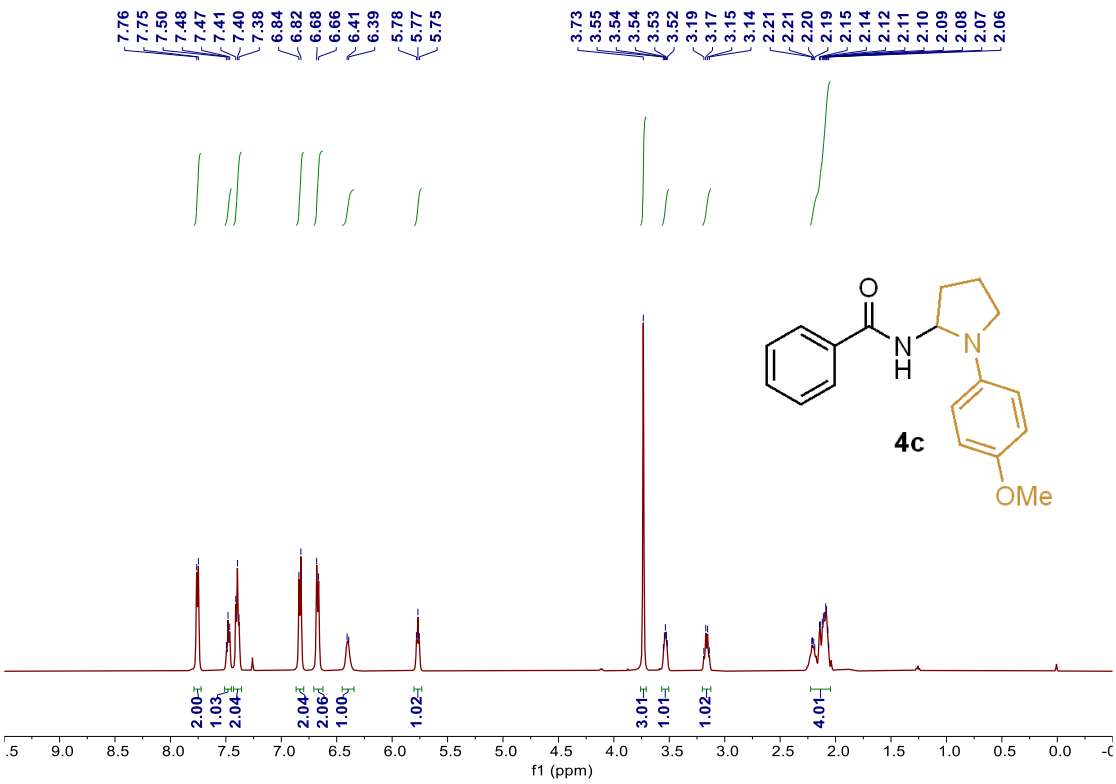
^{1}H NMR for **3c** (500 MHz, $CDCl_3$)



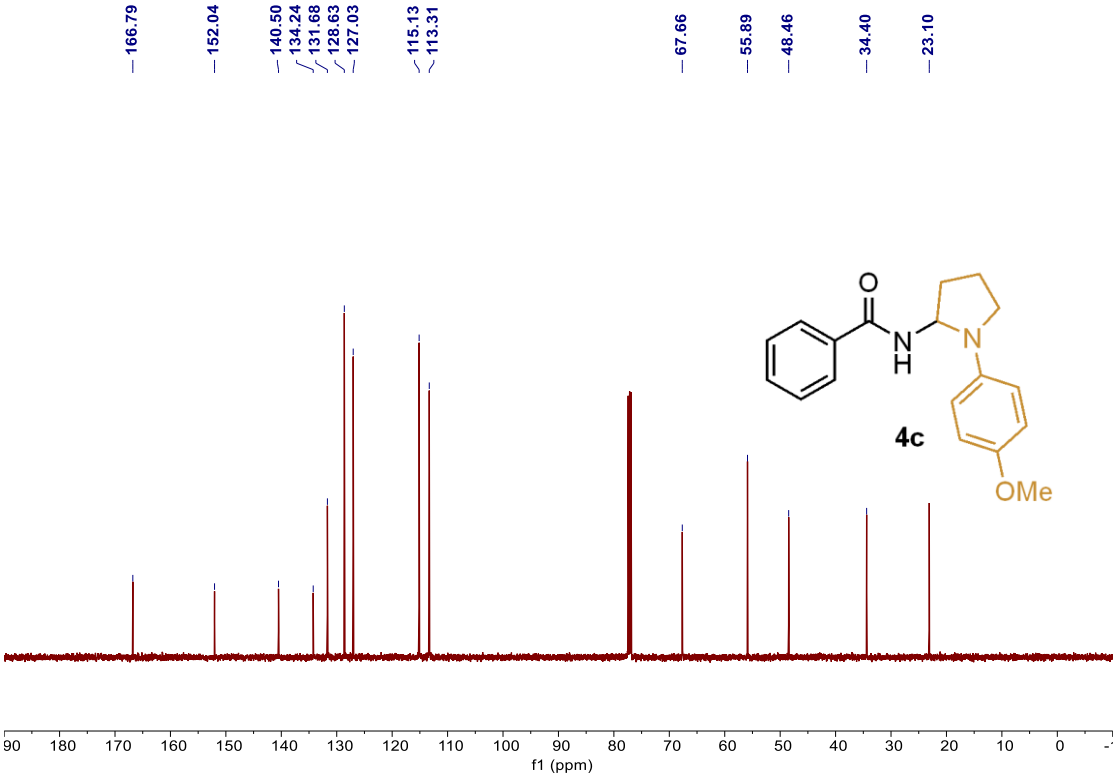
^{13}C NMR for **3c** (125 MHz, $CDCl_3$)



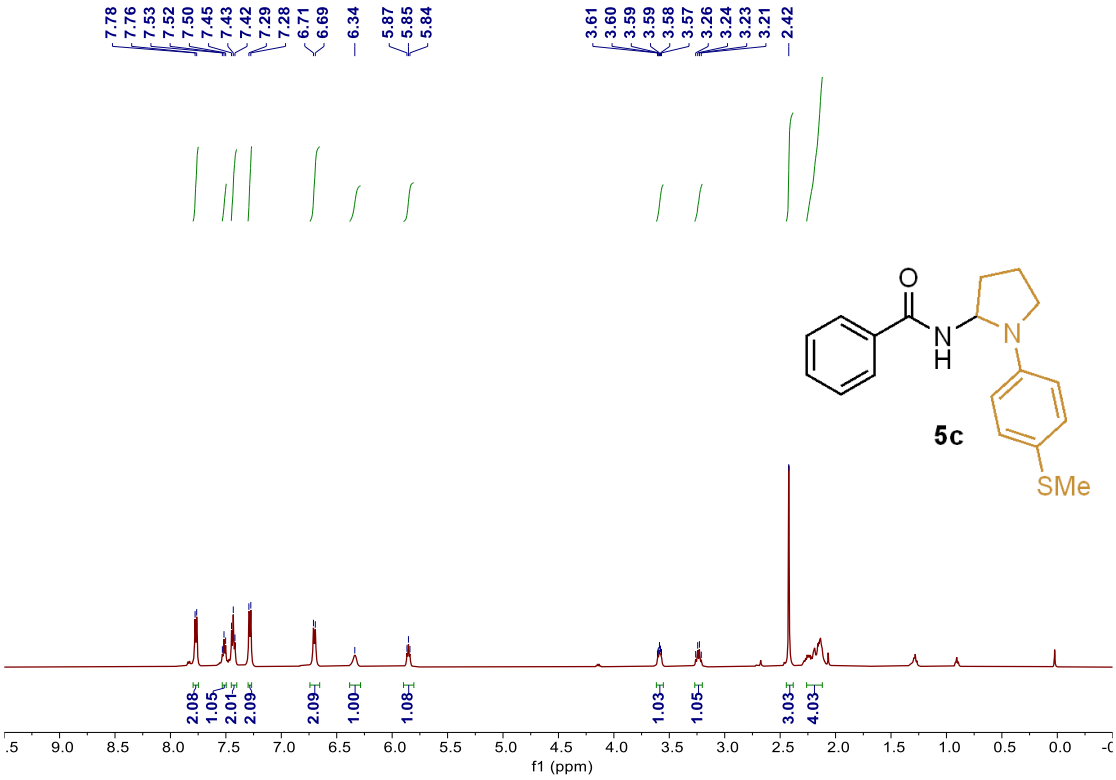
^{1}H NMR for **4c** (500 MHz, $CDCl_3$)



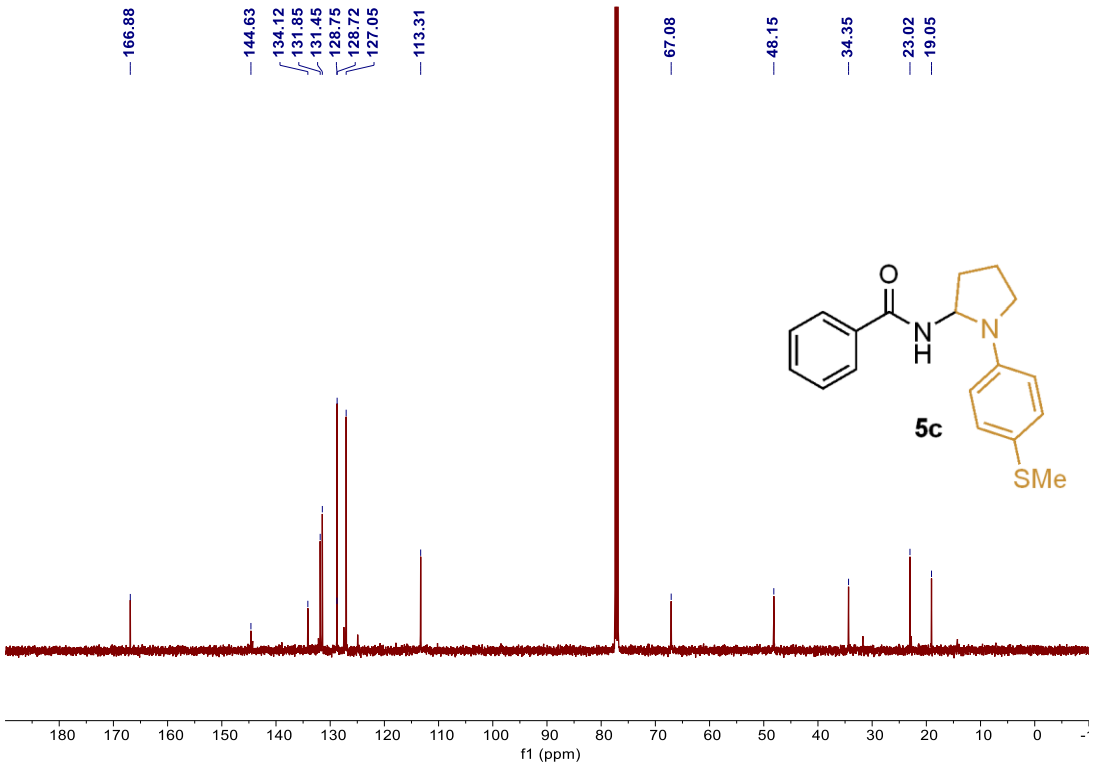
^{13}C NMR for **4c** (125 MHz, $CDCl_3$)



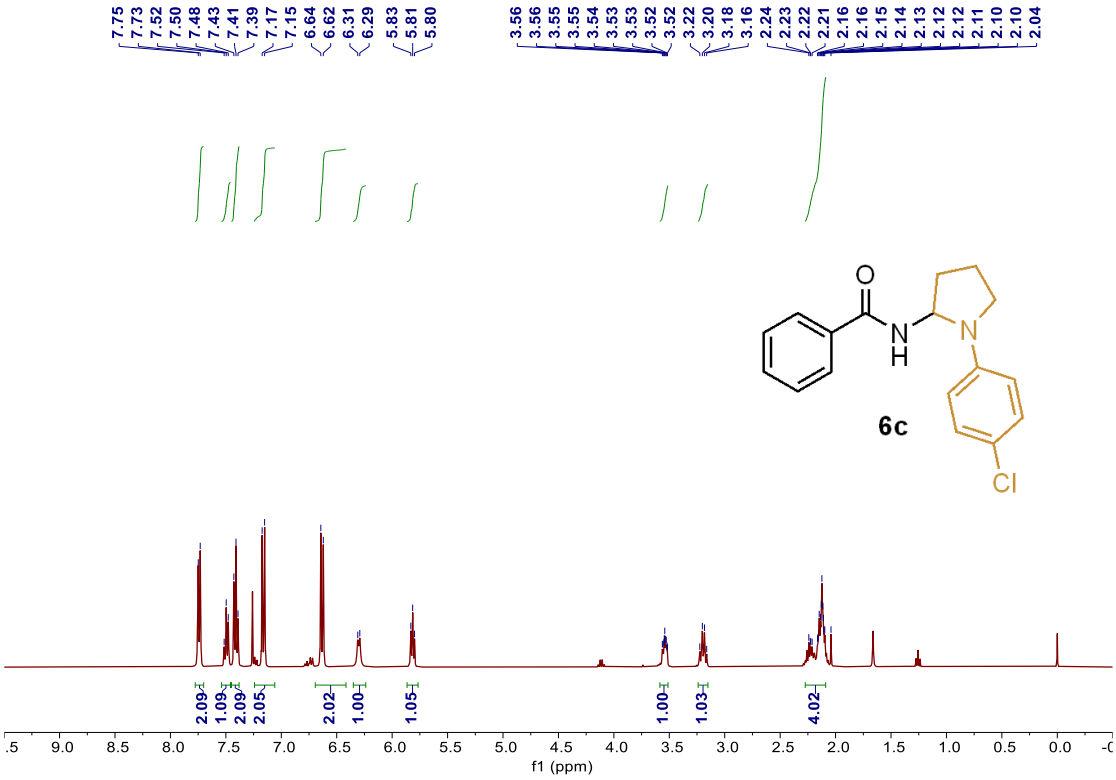
^{1}H NMR for **5c** (500 MHz, $CDCl_3$)



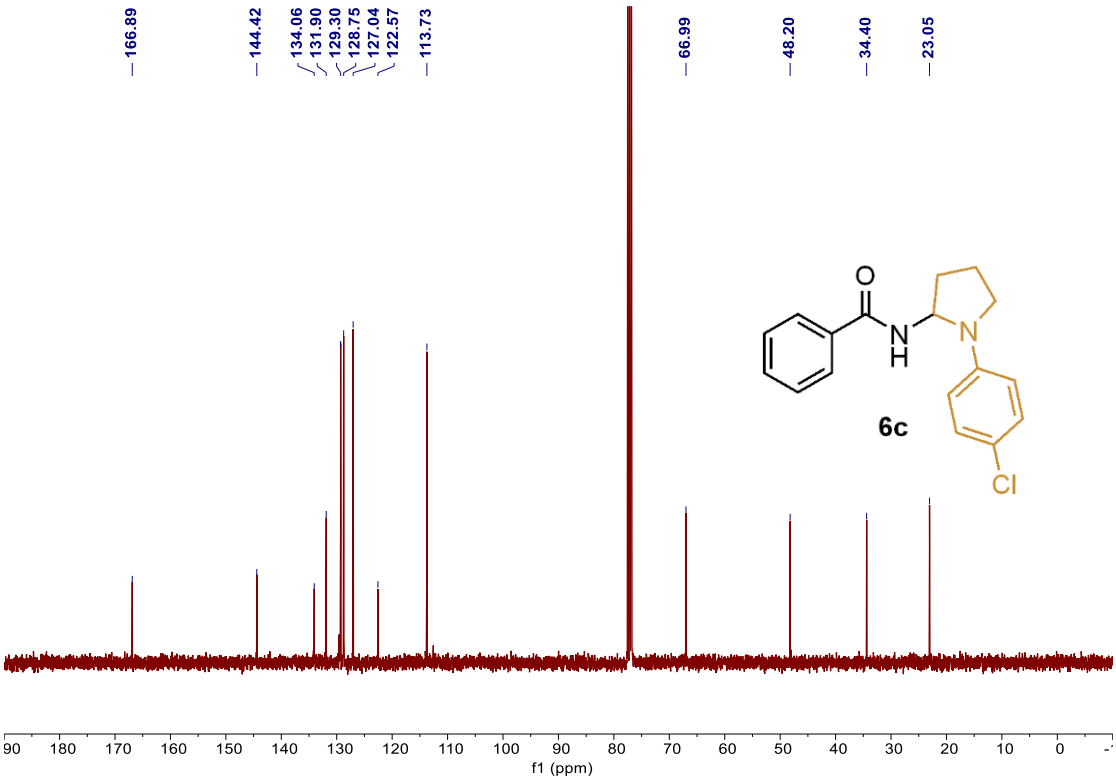
^{13}C NMR for **5c** (125 MHz, $CDCl_3$)



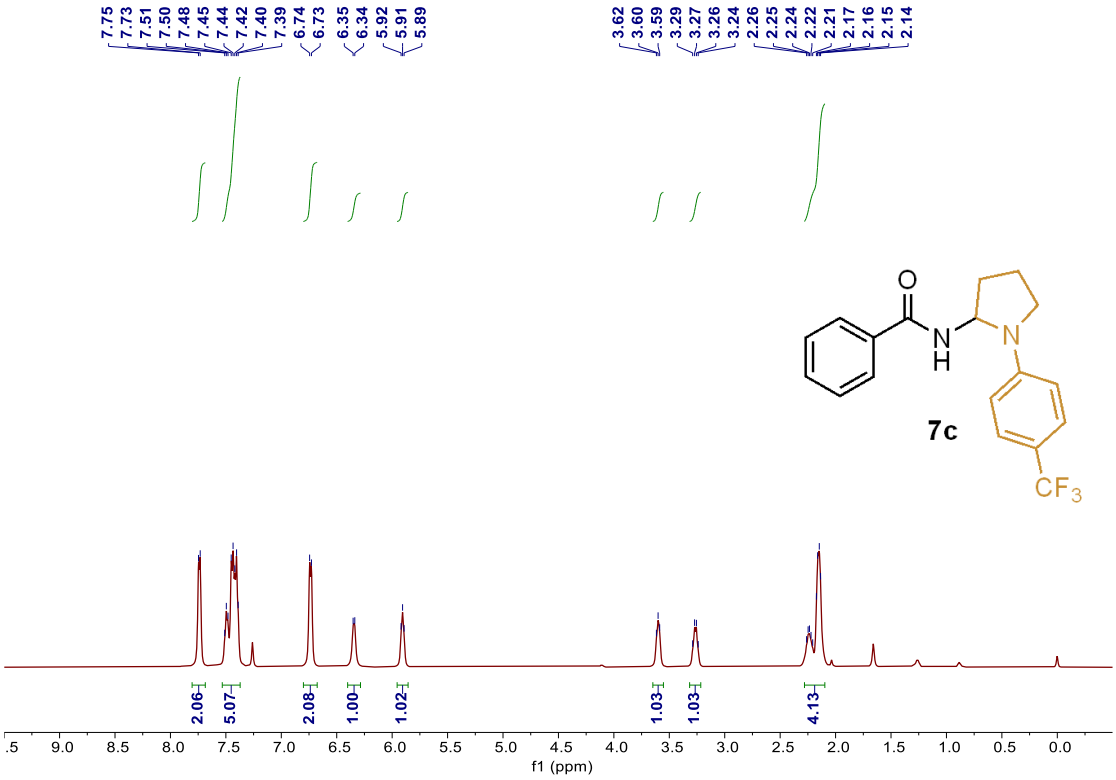
^{1}H NMR for **6c** (400 MHz, $CDCl_3$)



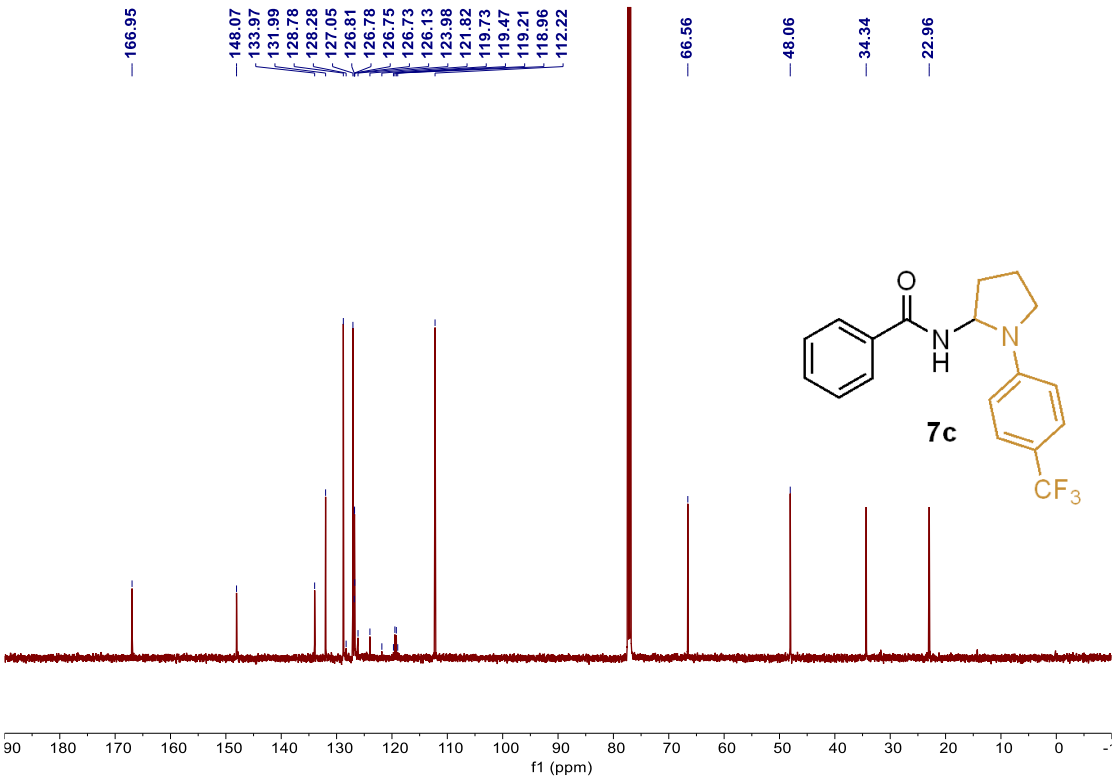
^{13}C NMR for **6c** (100 MHz, $CDCl_3$)



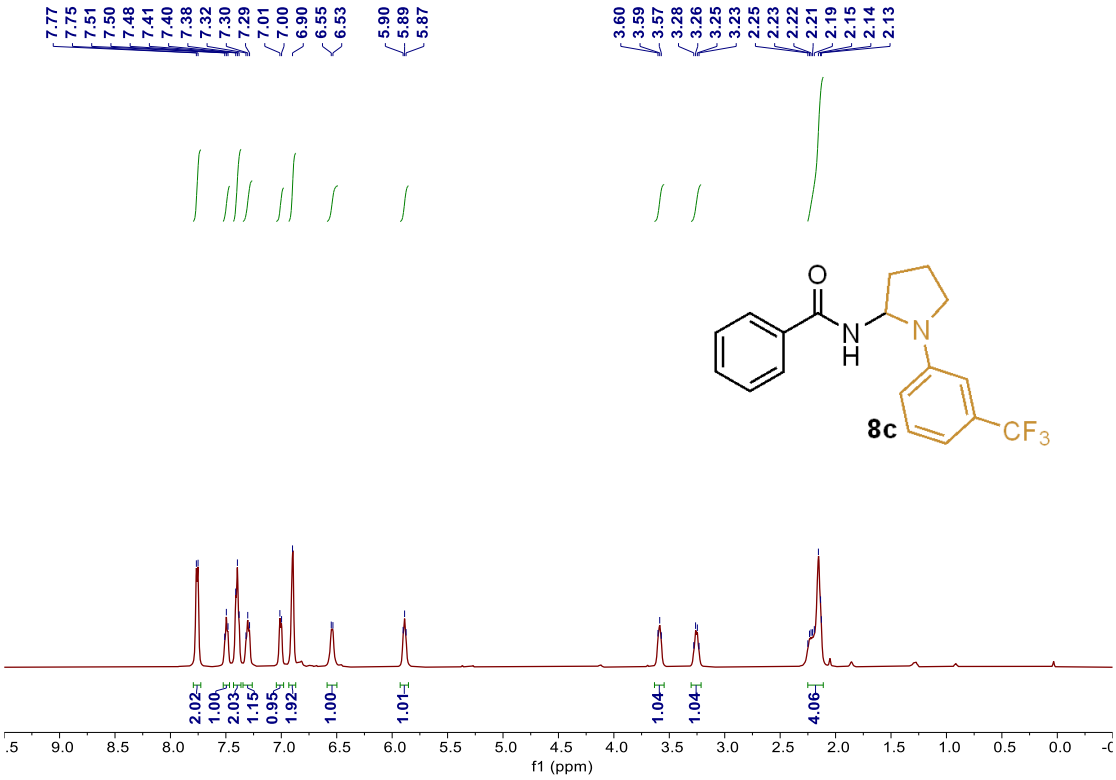
^{1}H NMR for **7c** (500 MHz, $CDCl_3$)



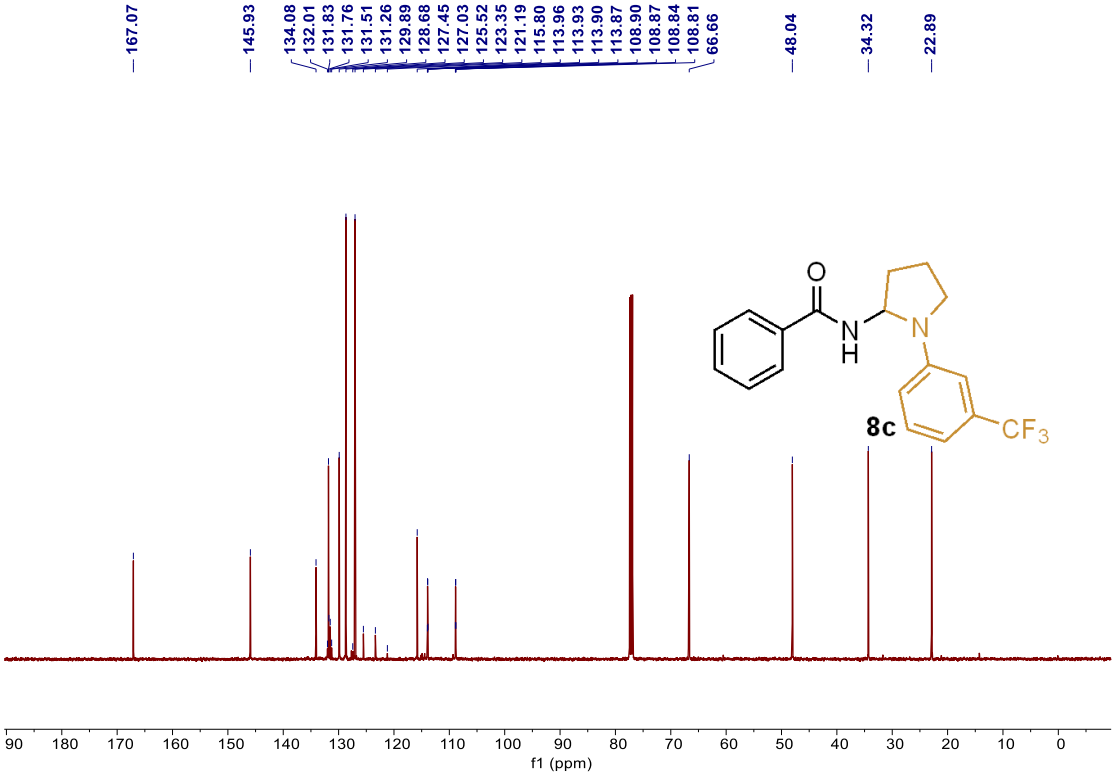
^{13}C NMR for **7c** (125 MHz, $CDCl_3$)



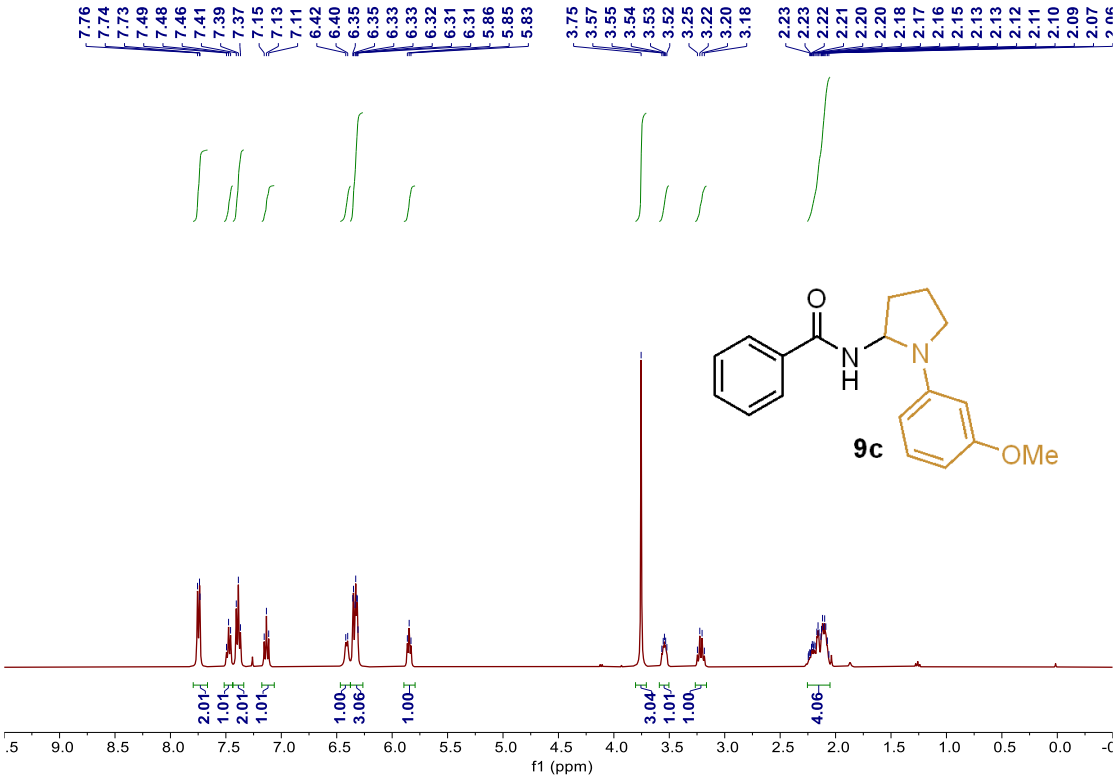
^{1}H NMR for **8c** (500 MHz, $CDCl_3$)



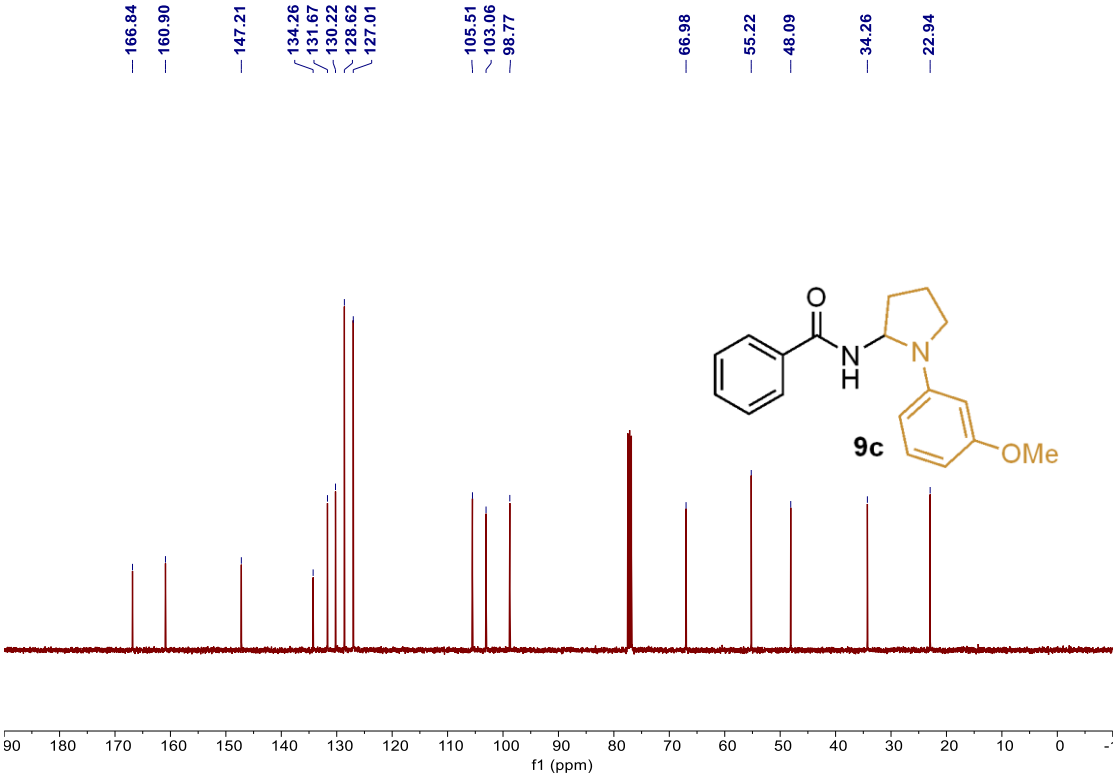
^{13}C NMR for **8c** (125 MHz, $CDCl_3$)



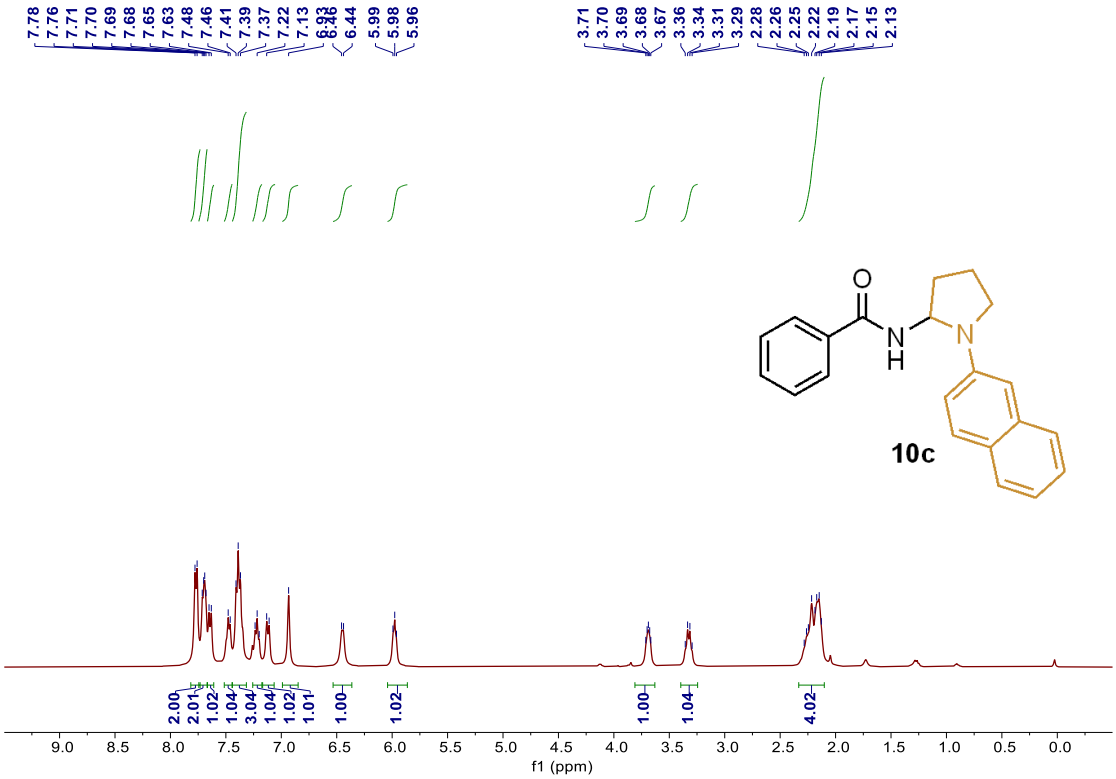
^{1}H NMR for **9c** (400 MHz, $CDCl_3$)



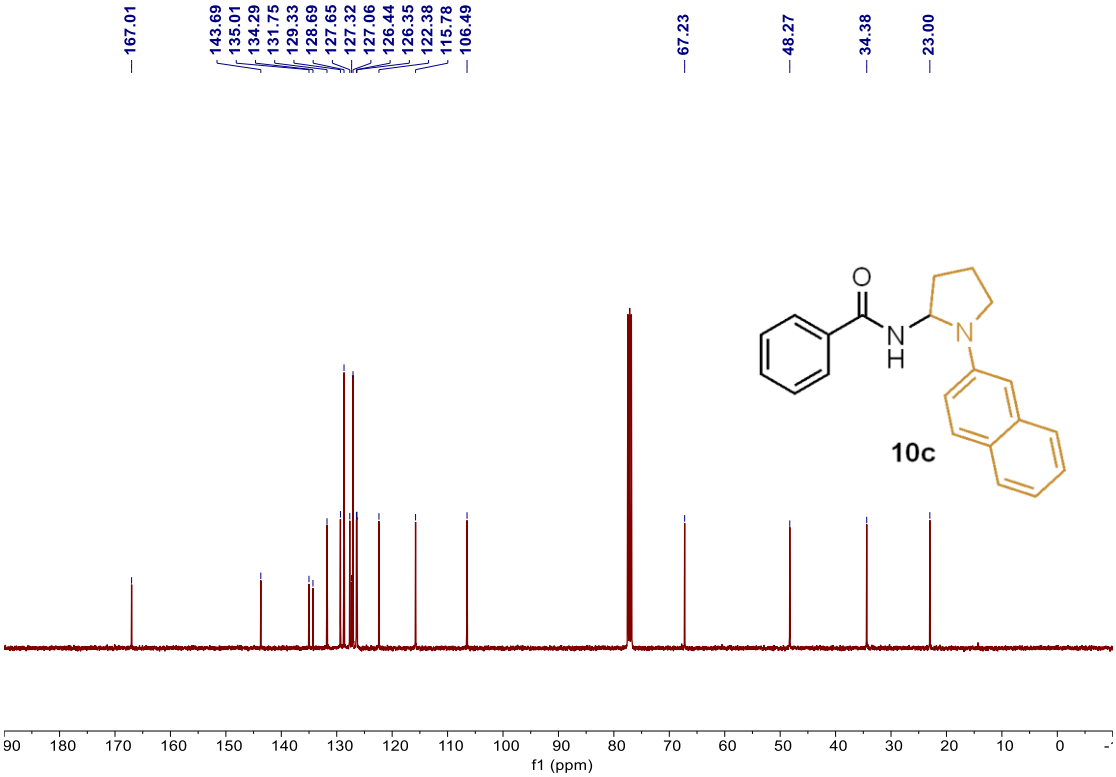
^{13}C NMR for **9c** (100 MHz, $CDCl_3$)



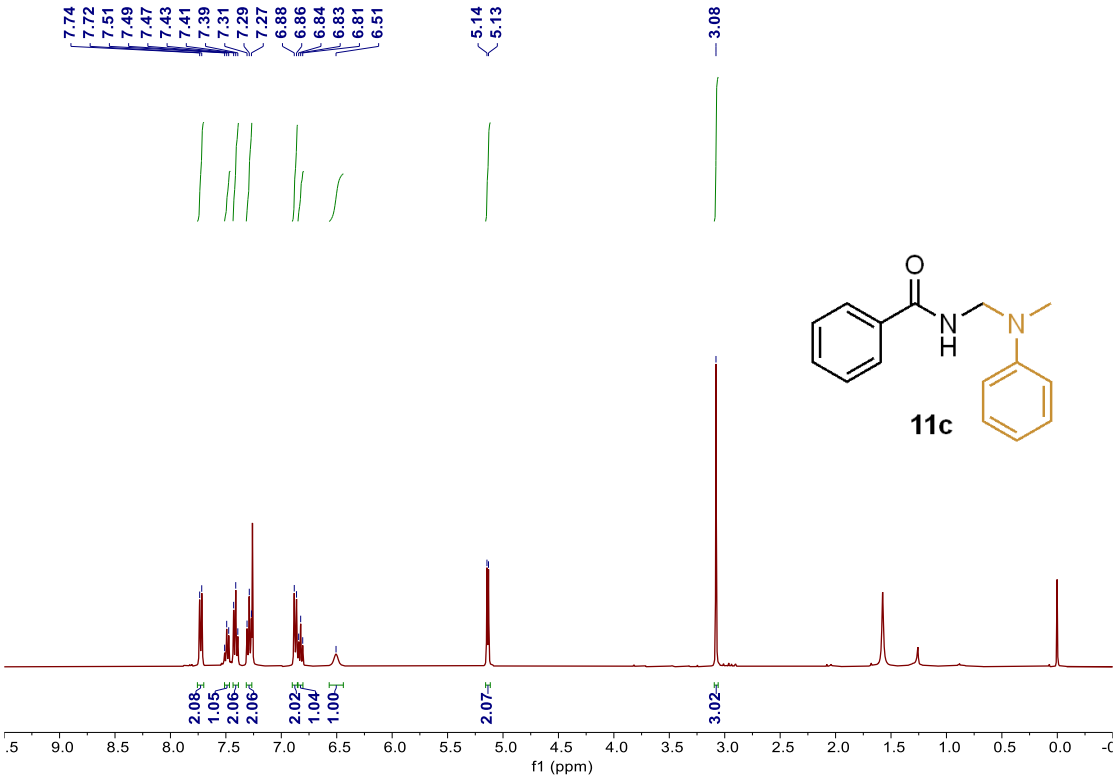
^{1}H NMR for **10c** (400 MHz, $CDCl_3$)



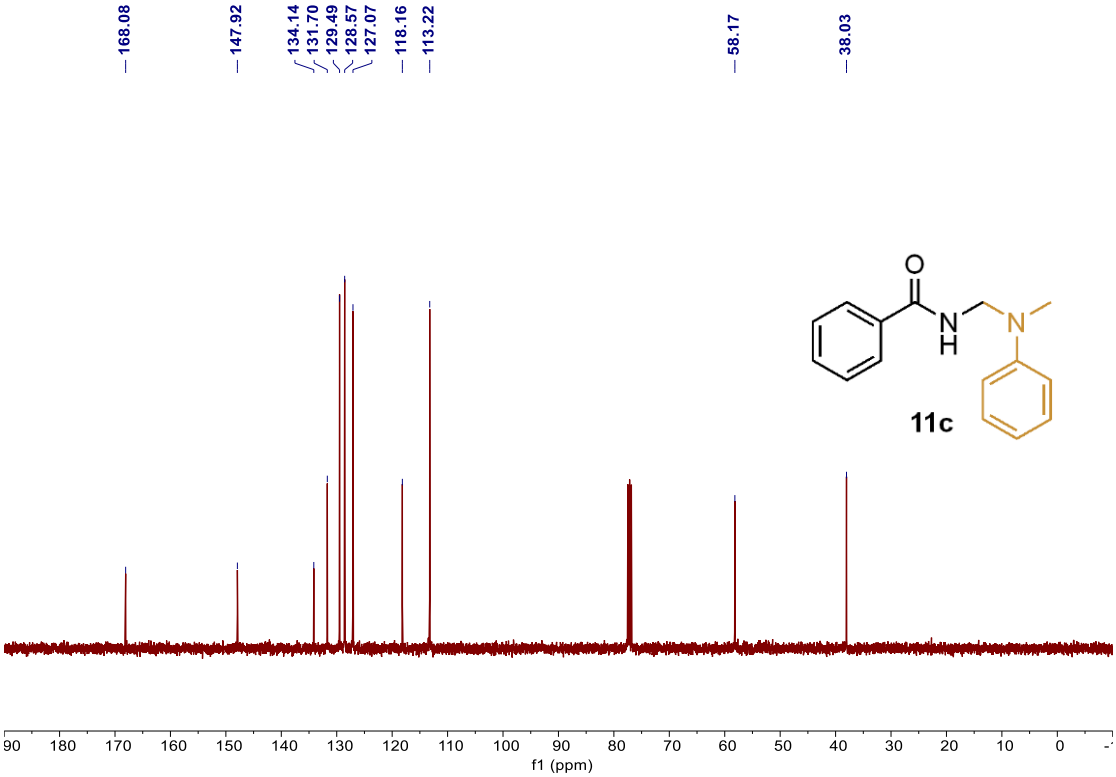
^{13}C NMR for **10c** (100 MHz, $CDCl_3$)



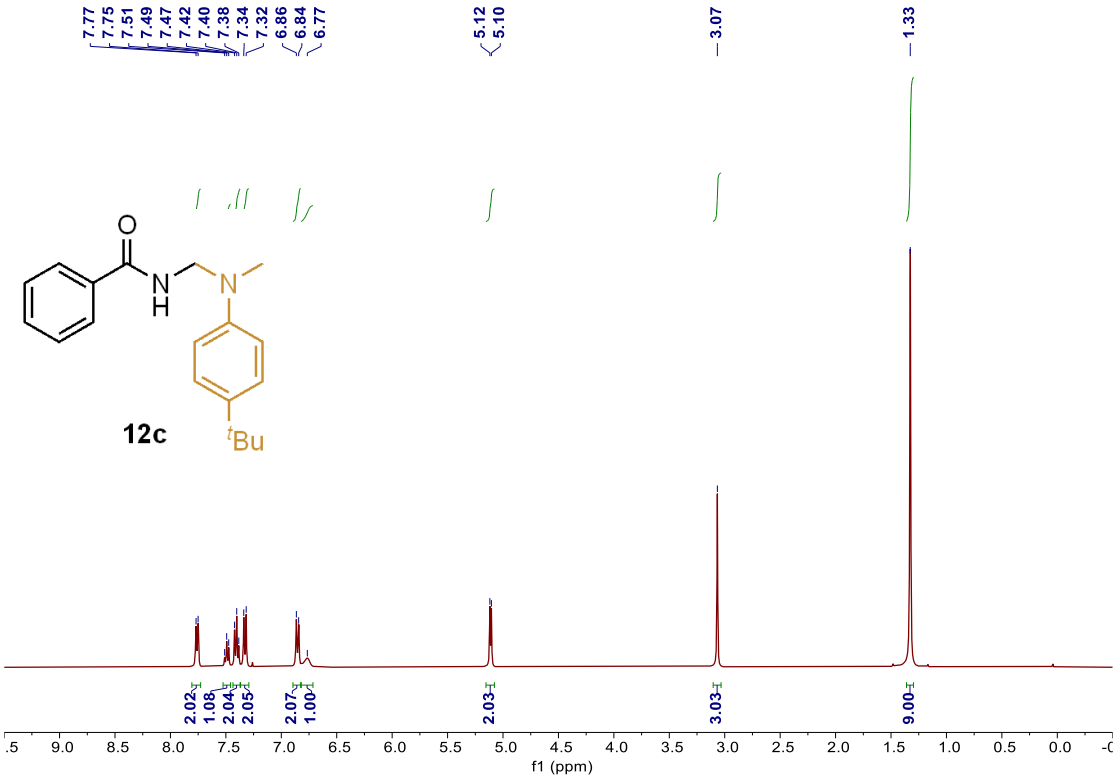
^{1}H NMR for **11c** (400 MHz, $CDCl_3$)



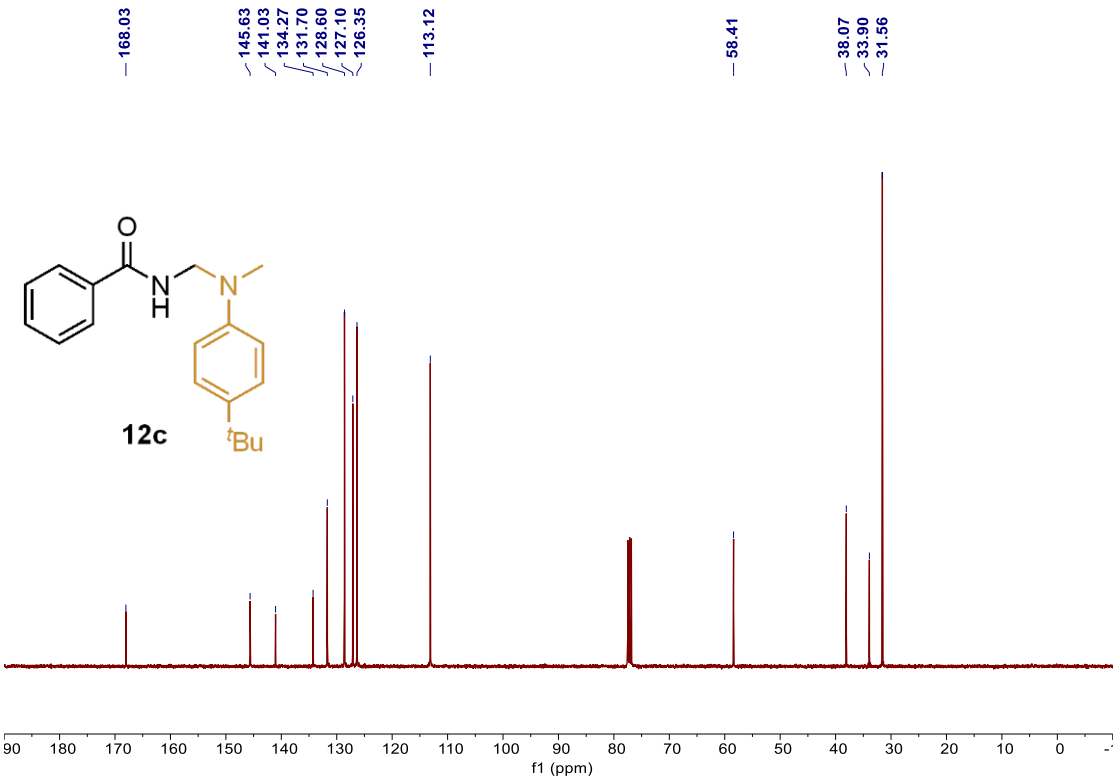
^{13}C NMR for **11c** (100 MHz, $CDCl_3$)



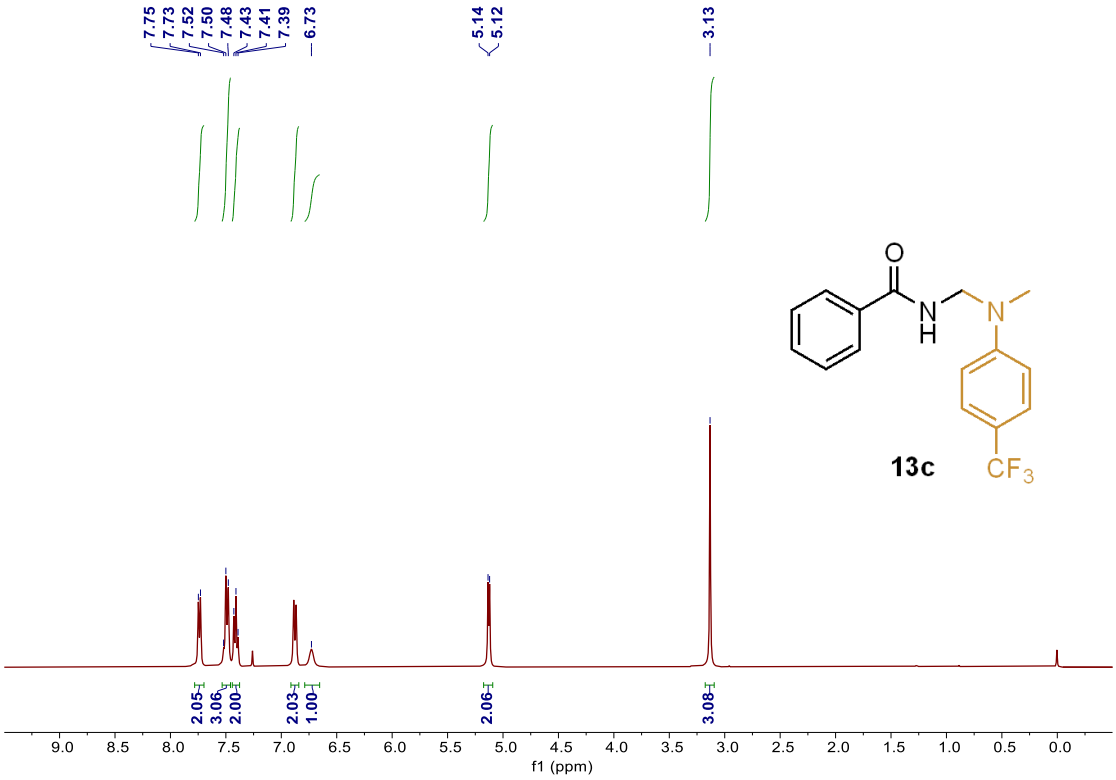
^{1}H NMR for **12c** (400 MHz, $CDCl_3$)



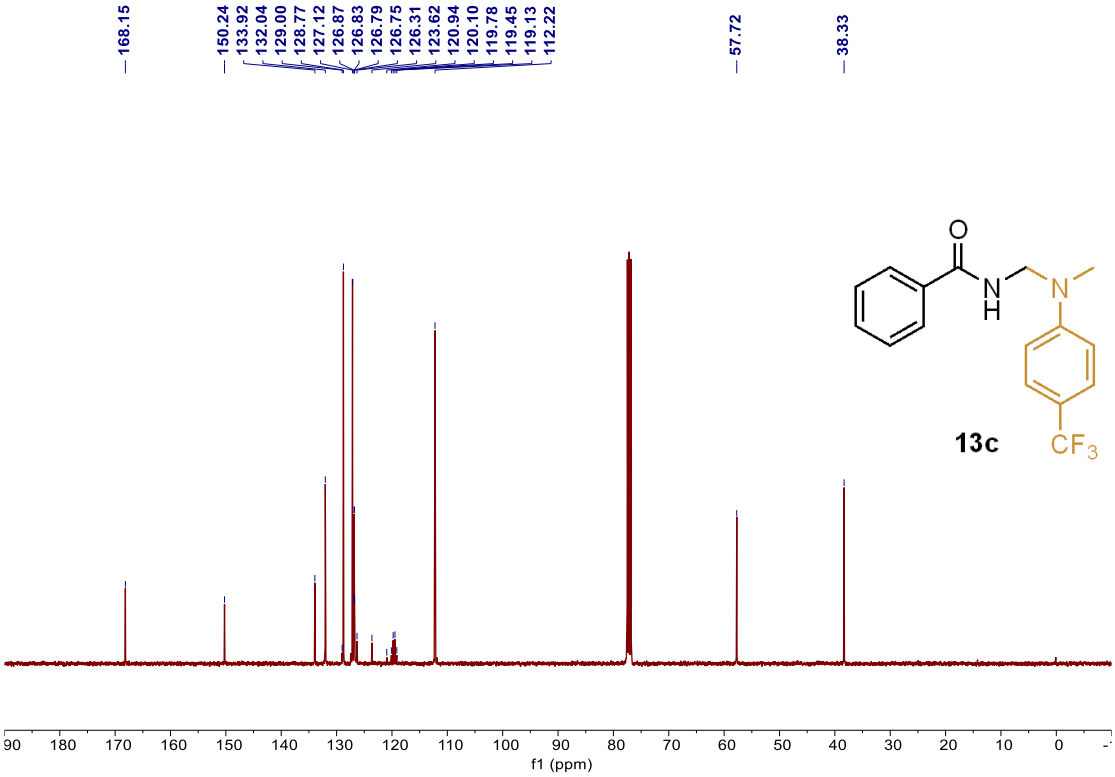
^{13}C NMR for **12c** (100 MHz, $CDCl_3$)



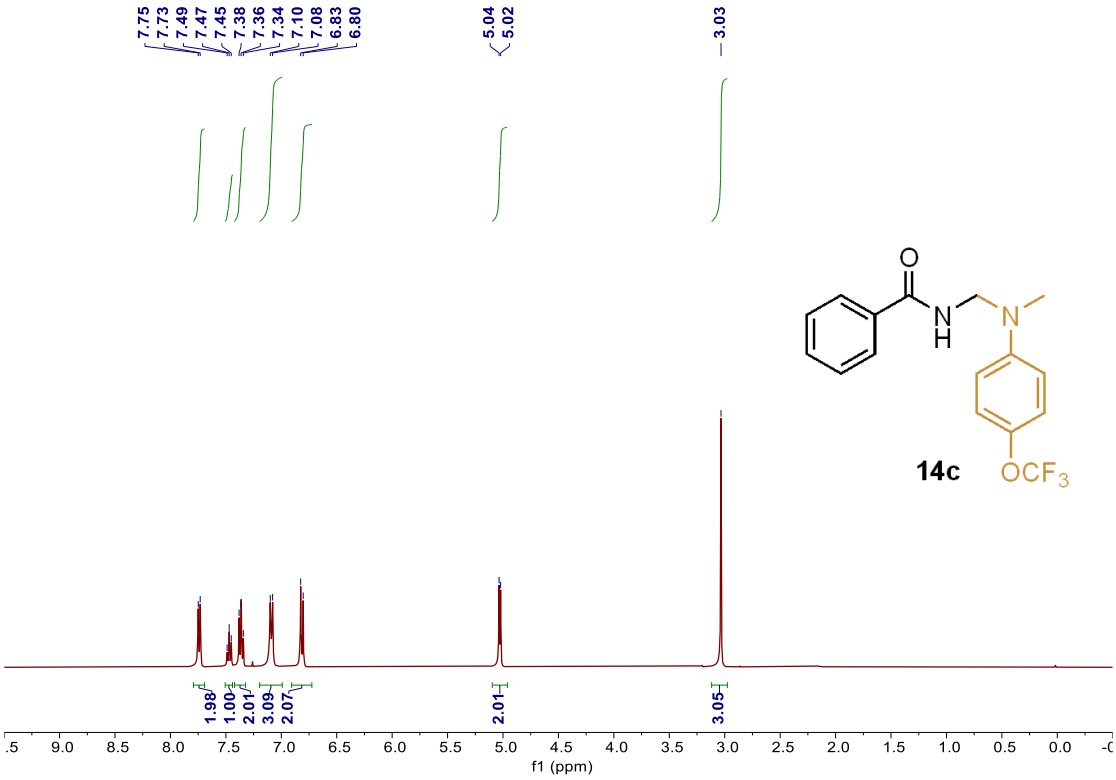
^{1}H NMR for **13c** (400 MHz, $CDCl_3$)



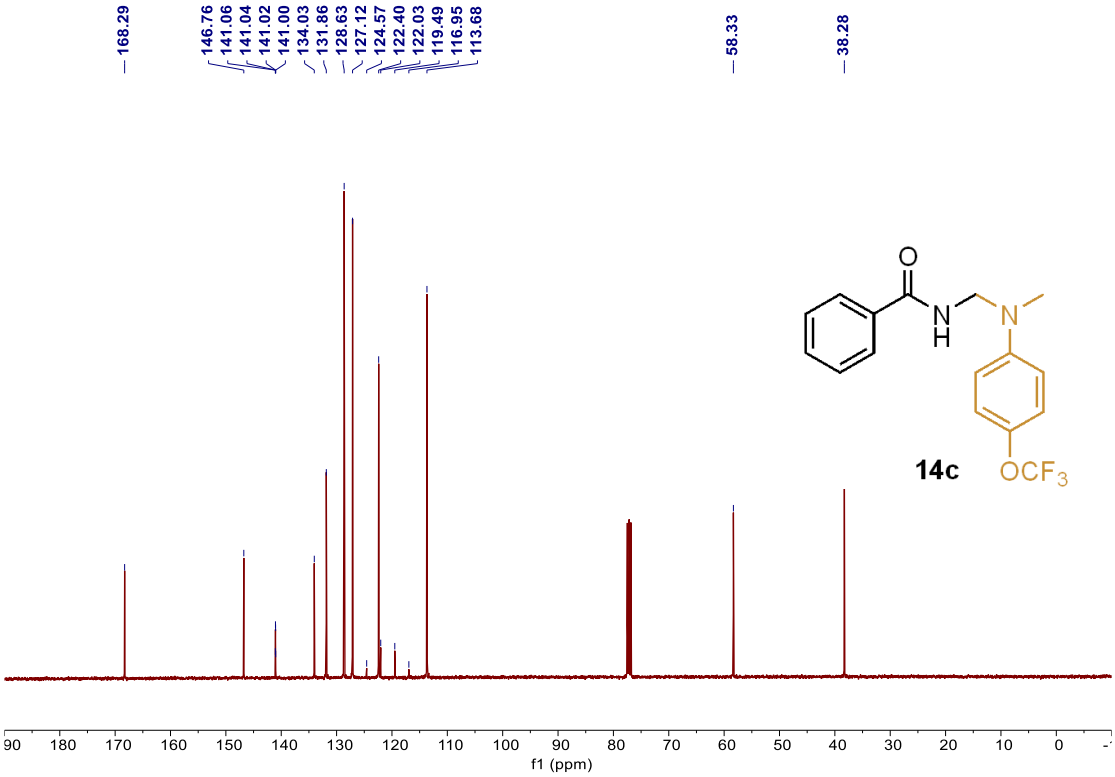
^{13}C NMR for **13c** (100 MHz, $CDCl_3$)



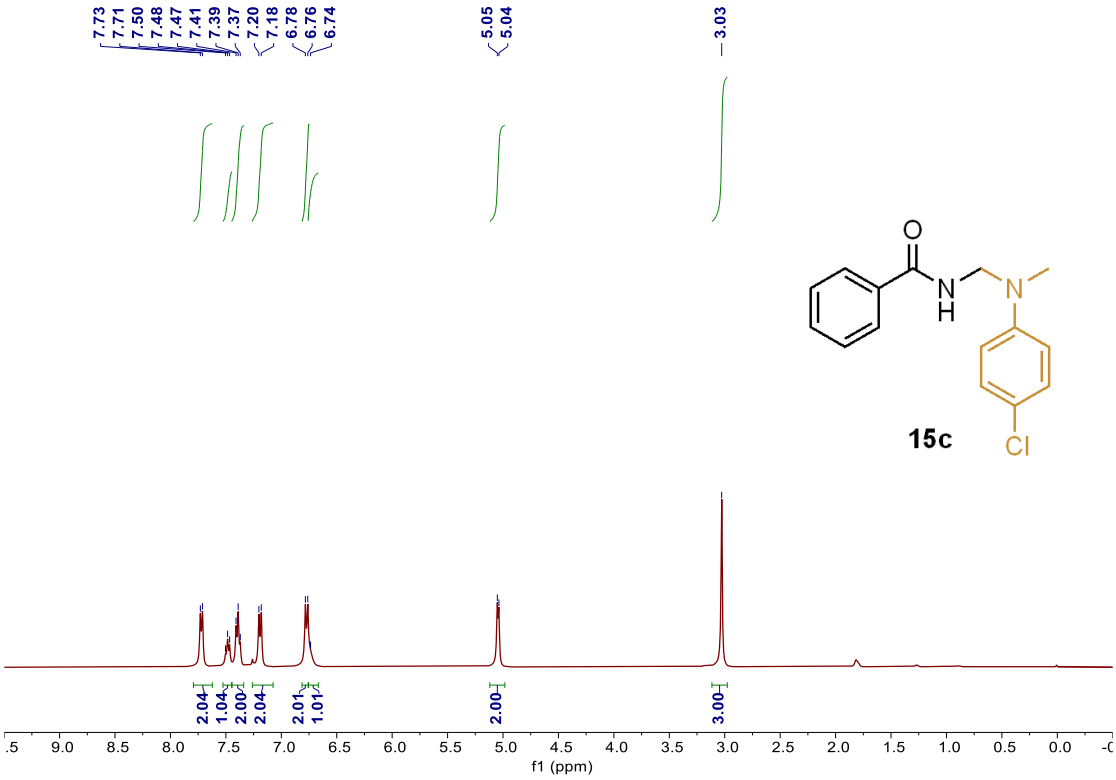
^{1}H NMR for **14c** (400 MHz, $CDCl_3$)



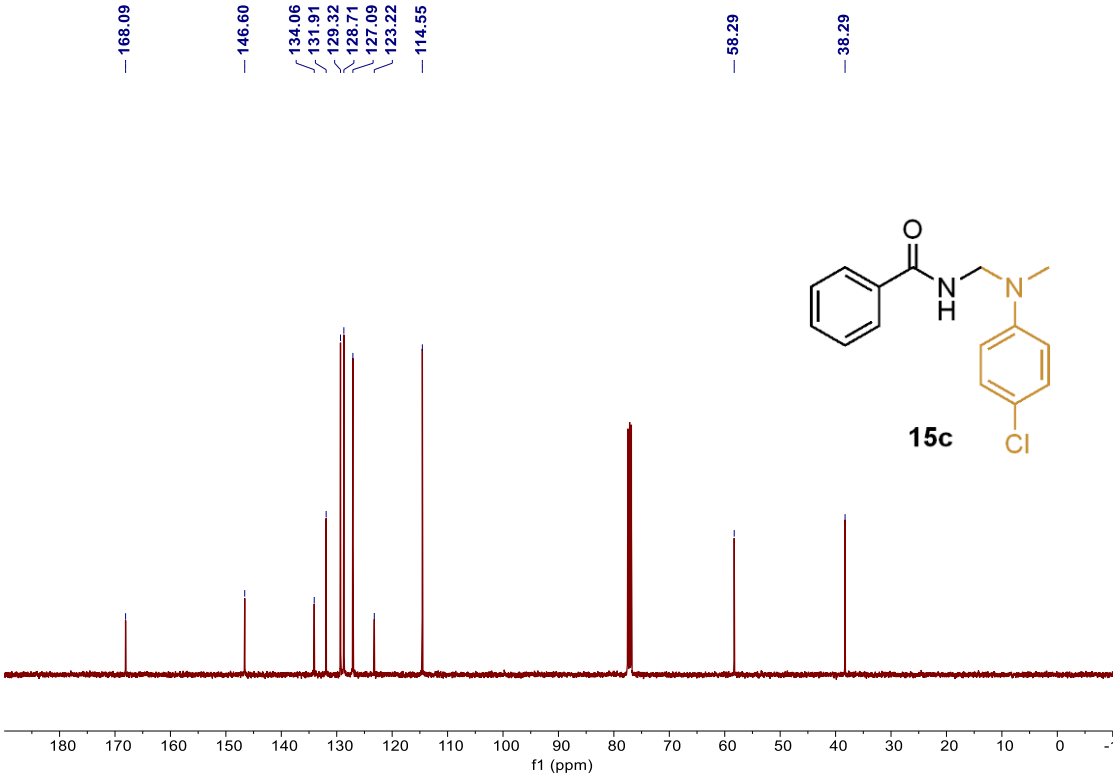
^{13}C NMR for **14c** (100 MHz, $CDCl_3$)



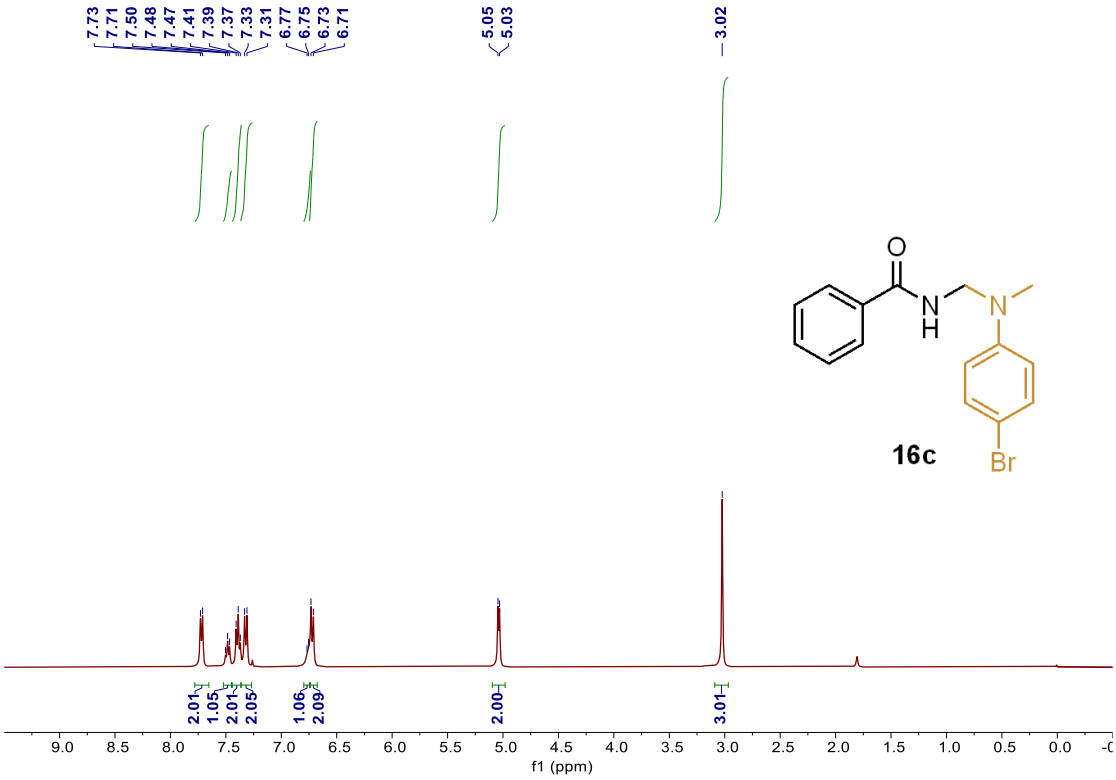
^{1}H NMR for **15c** (400 MHz, $CDCl_3$)



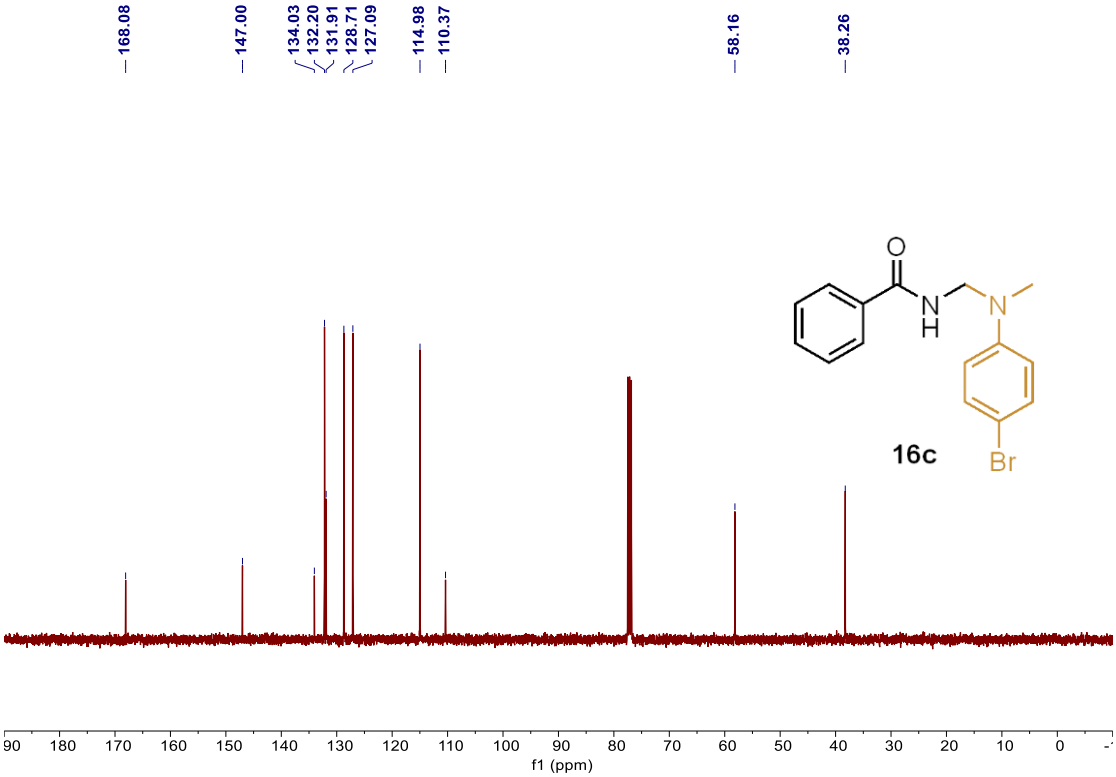
^{13}C NMR for **15c** (100 MHz, $CDCl_3$)



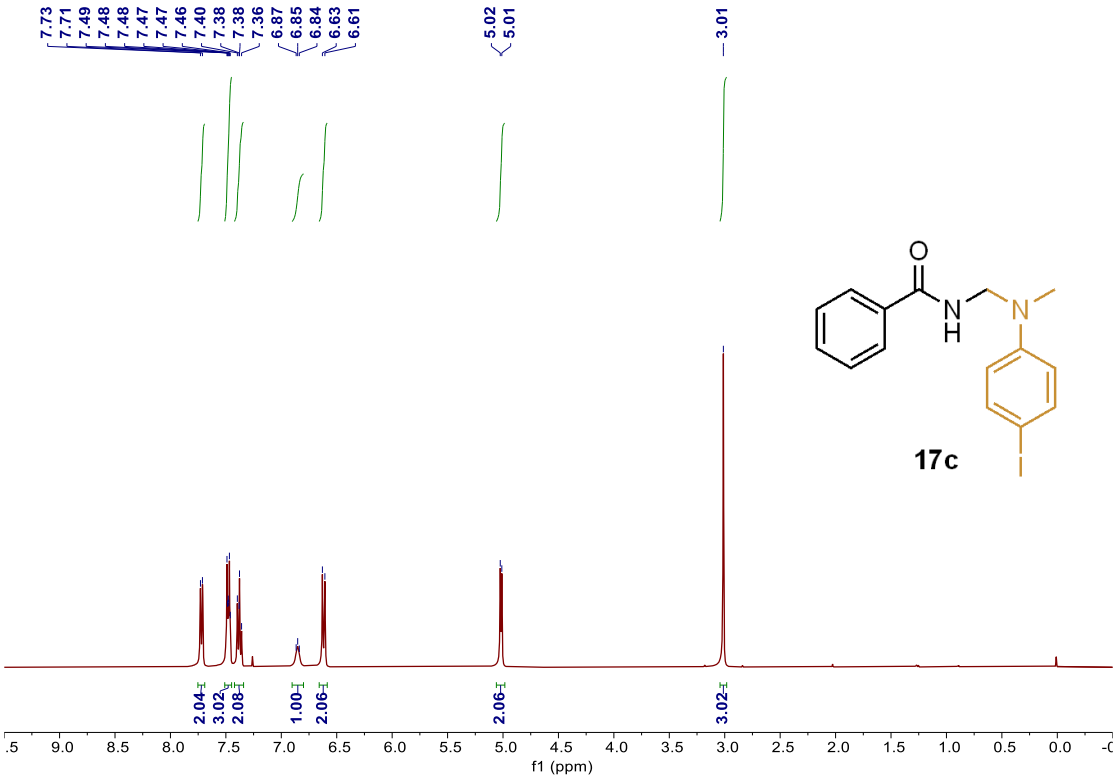
^{1}H NMR for **16c** (400 MHz, $CDCl_3$)



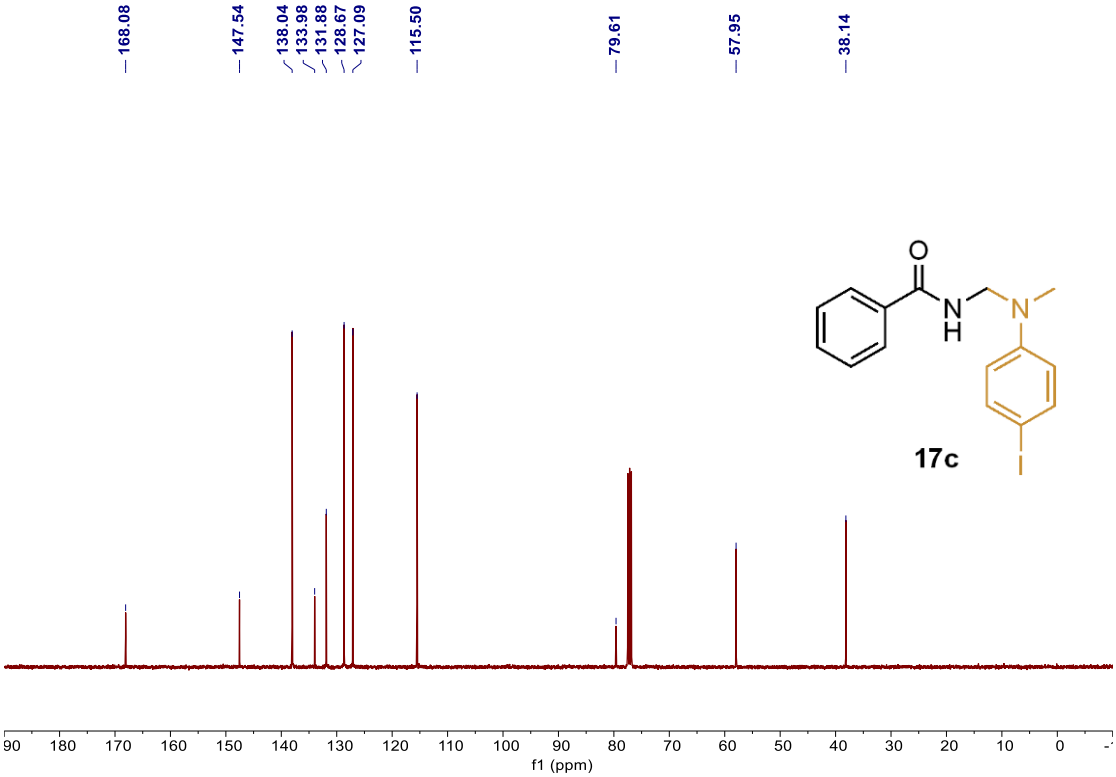
^{13}C NMR for **16c** (100 MHz, $CDCl_3$)



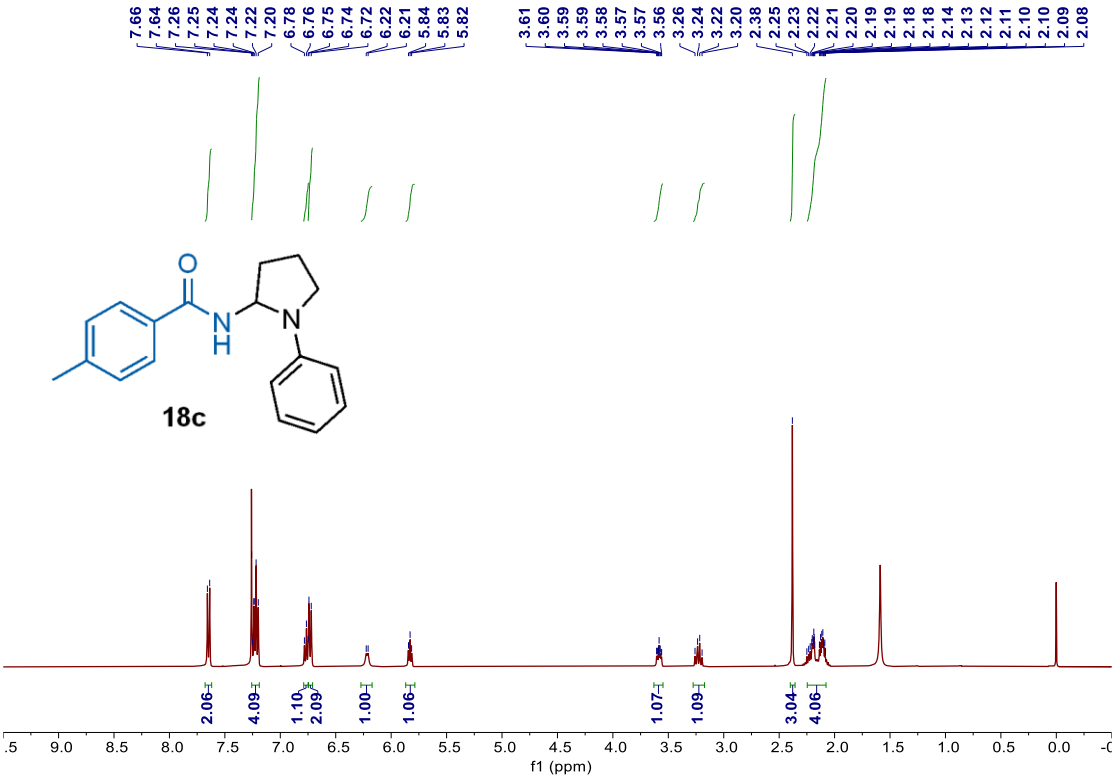
^{1}H NMR for **17c** (400 MHz, $CDCl_3$)



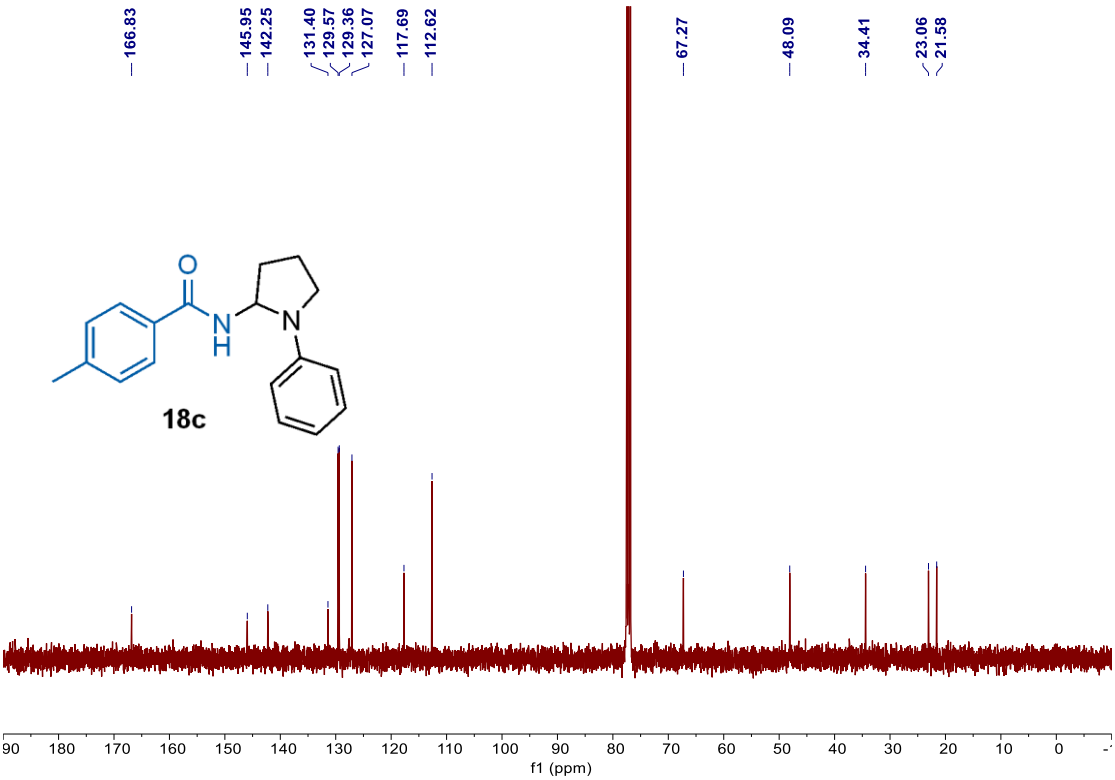
^{13}C NMR for **17c** (100 MHz, $CDCl_3$)



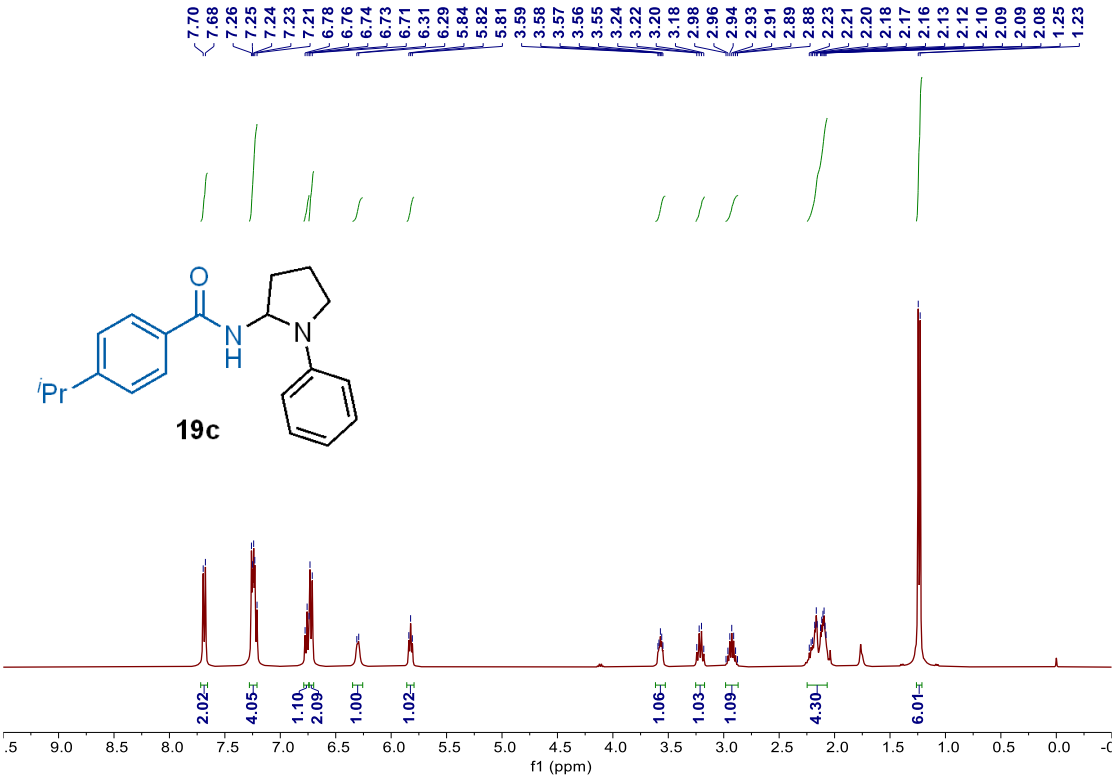
^{1}H NMR for **18c** (400 MHz, $CDCl_3$)



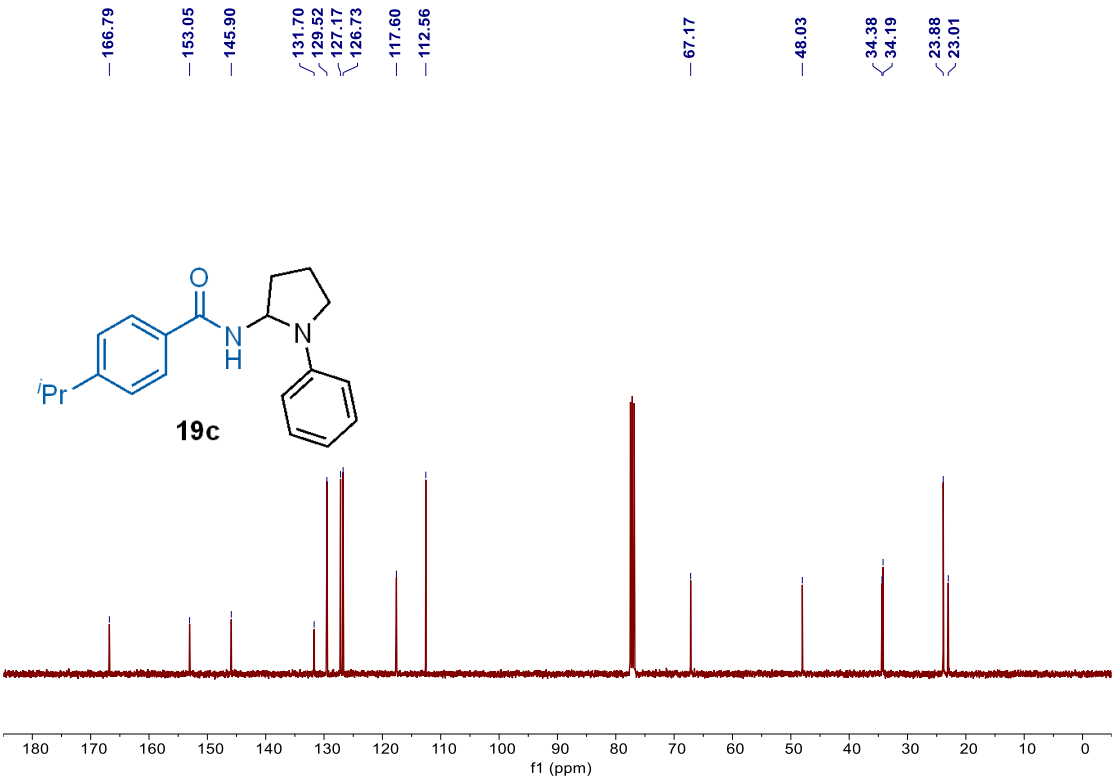
^{13}C NMR for **18c** (100 MHz, $CDCl_3$)



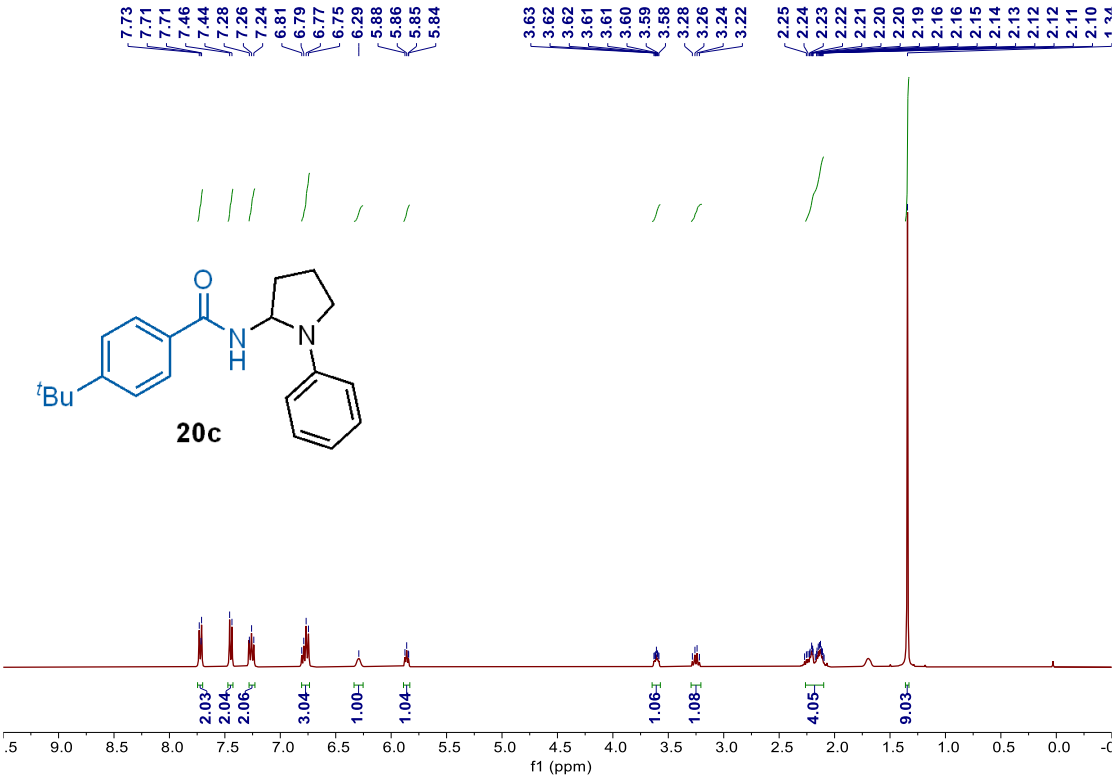
^{1}H NMR for **19c** (400 MHz, $CDCl_3$)



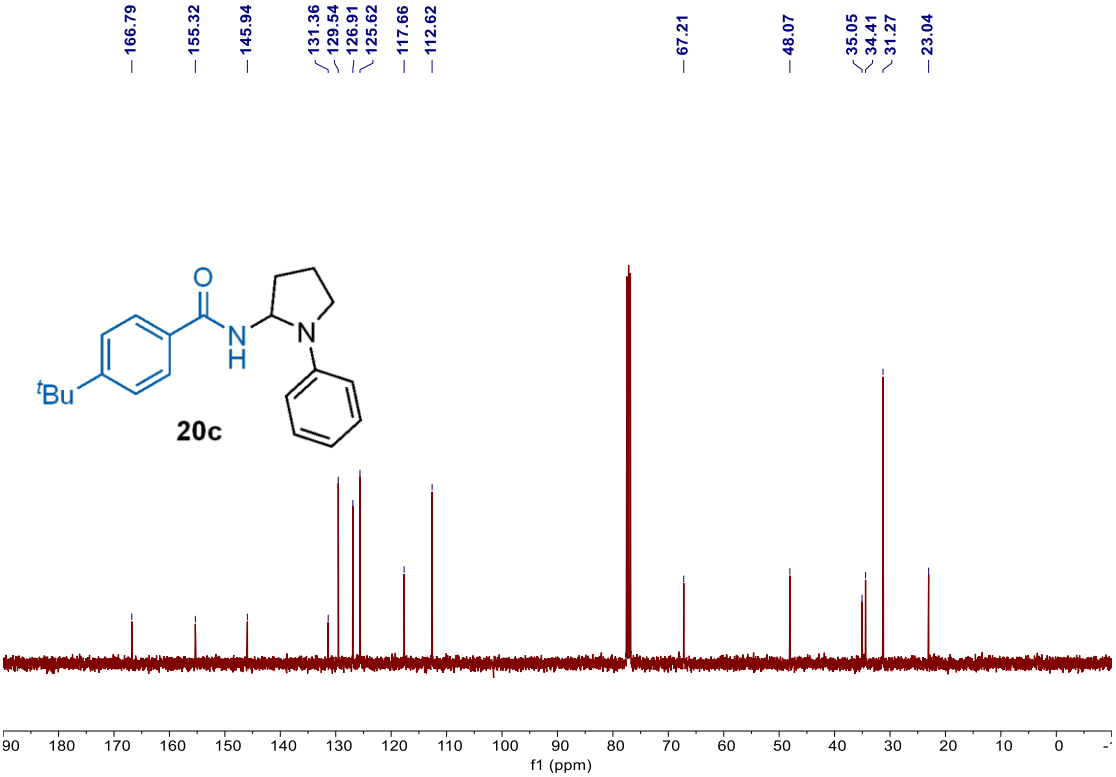
^{13}C NMR for **19c** (100 MHz, $CDCl_3$)



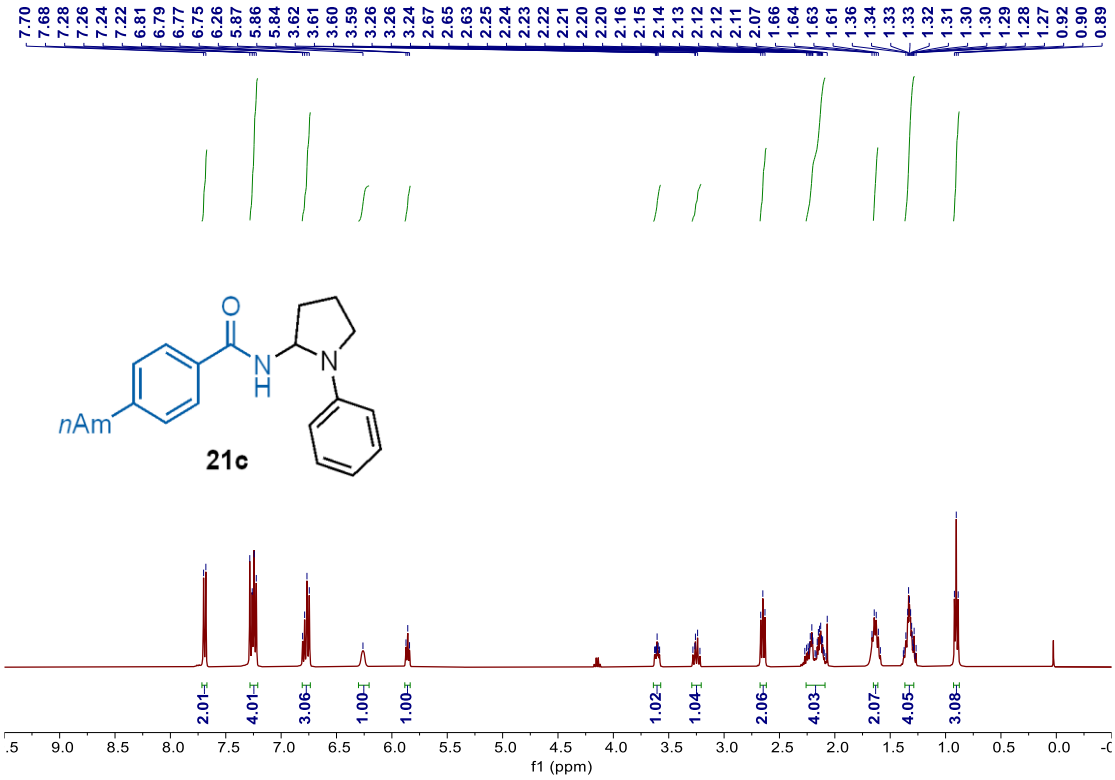
^{1}H NMR for **20c** (400 MHz, $CDCl_3$)



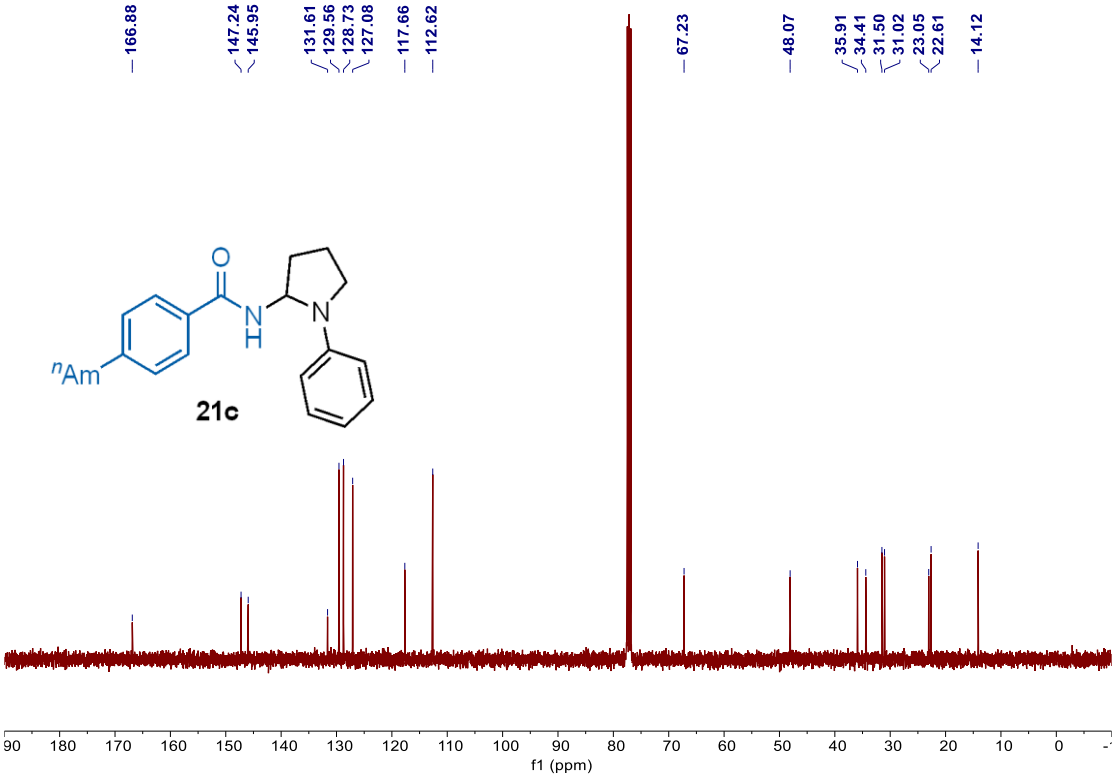
^{13}C NMR for **20c** (100 MHz, $CDCl_3$)



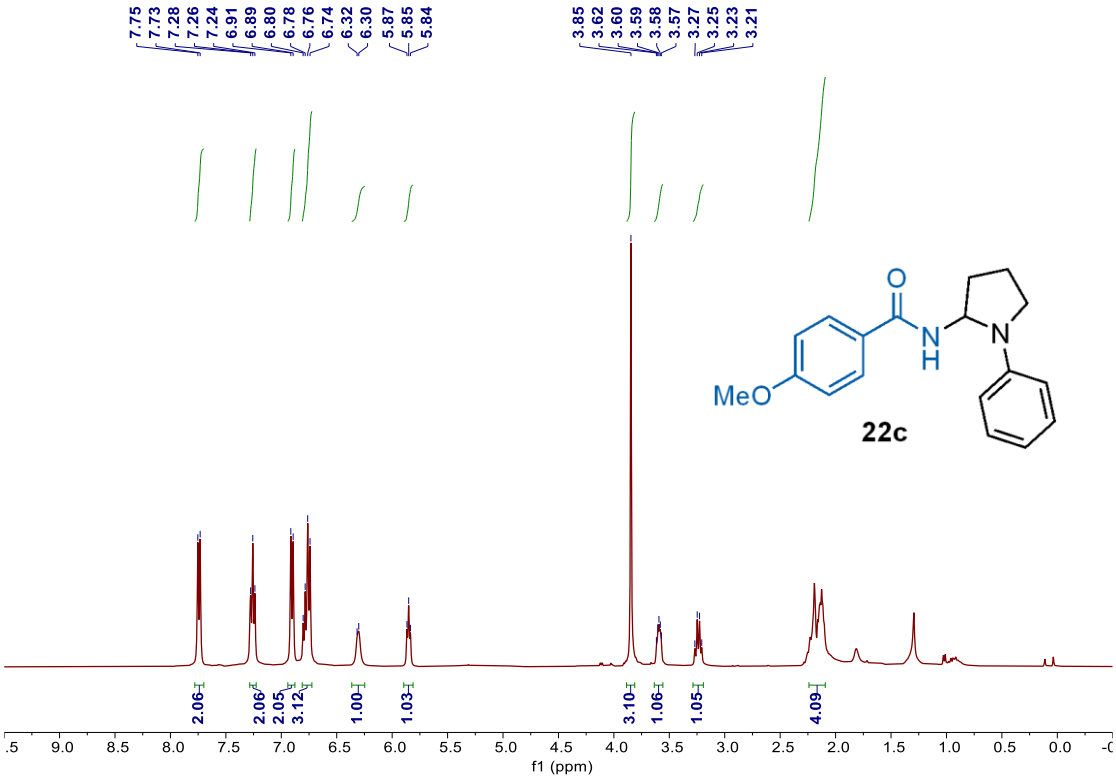
^{1}H NMR for **21c** (400 MHz, $CDCl_3$)



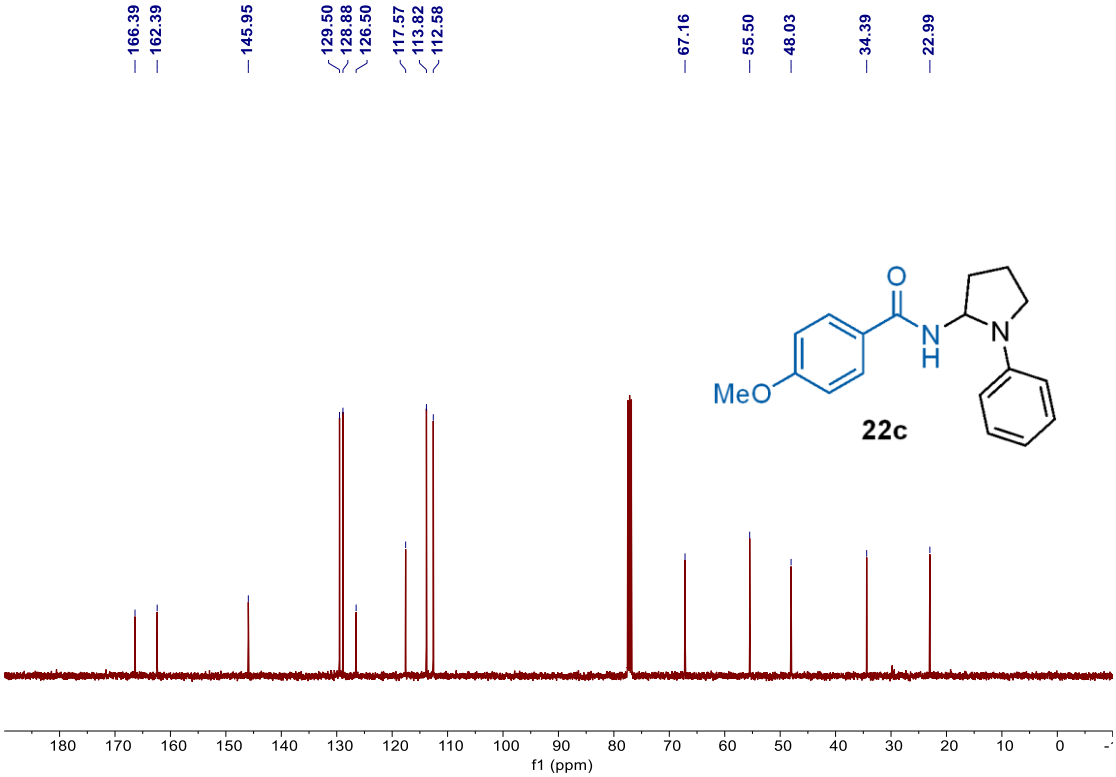
^{13}C NMR for **21c** (100 MHz, $CDCl_3$)



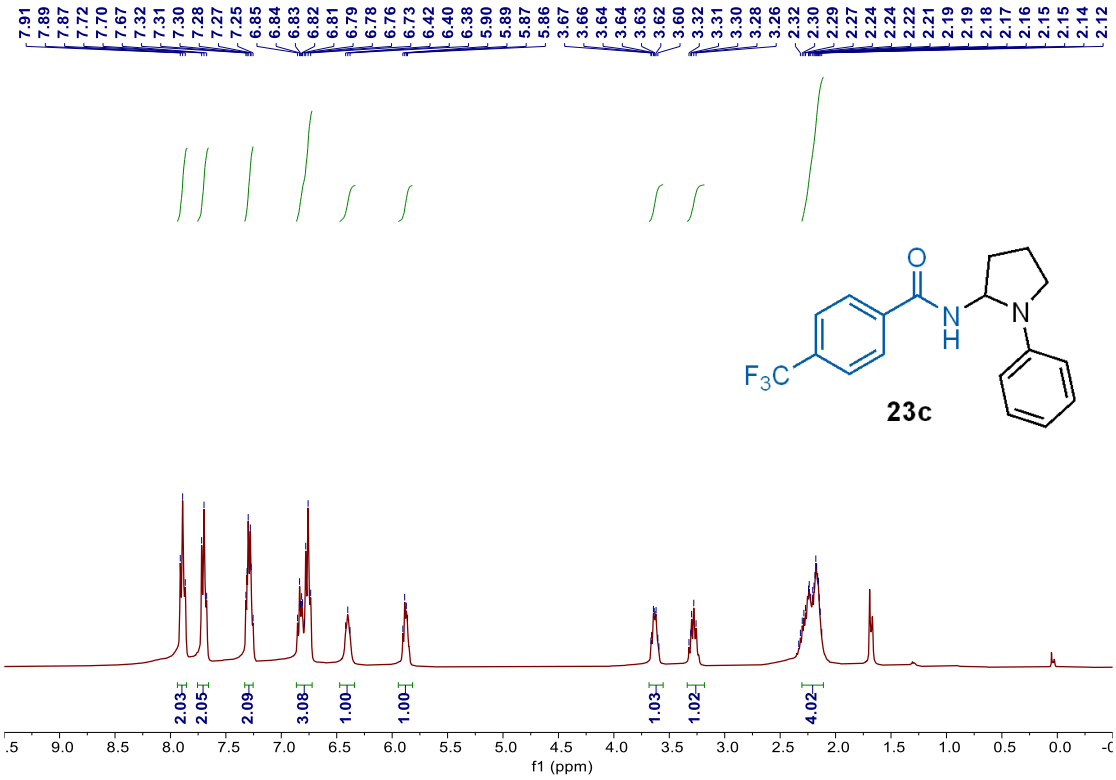
^{1}H NMR for **22c** (400 MHz, $CDCl_3$)



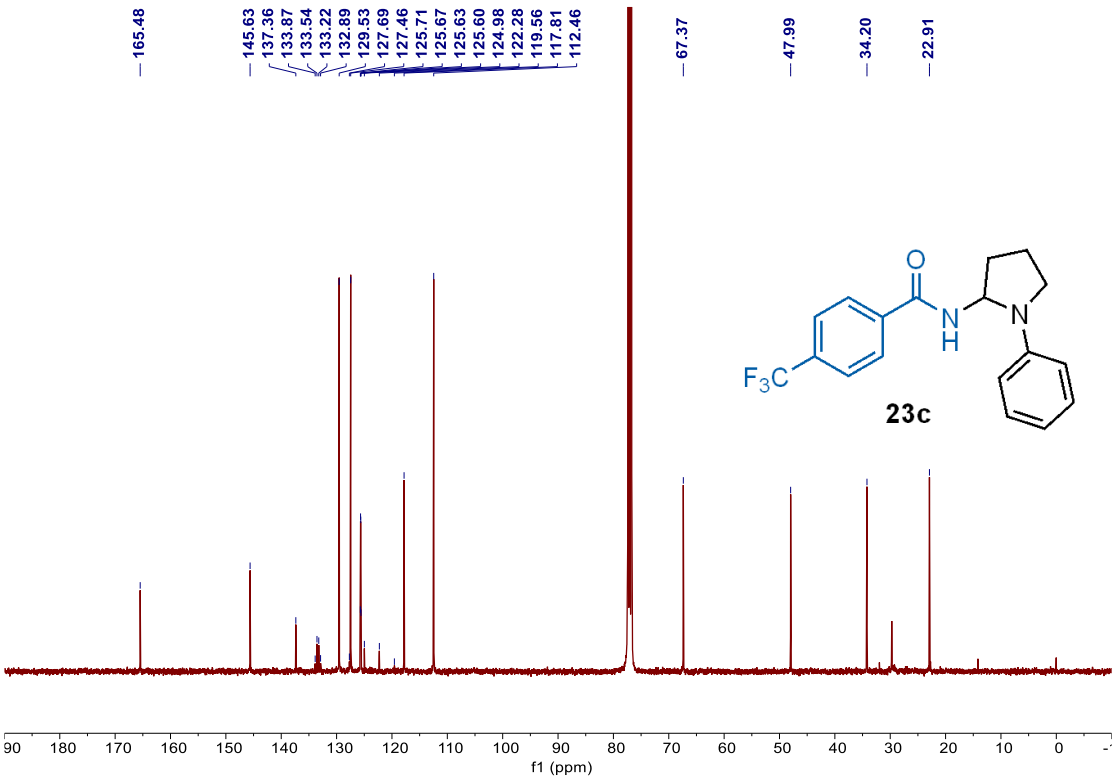
^{13}C NMR for **22c** (100 MHz, $CDCl_3$)



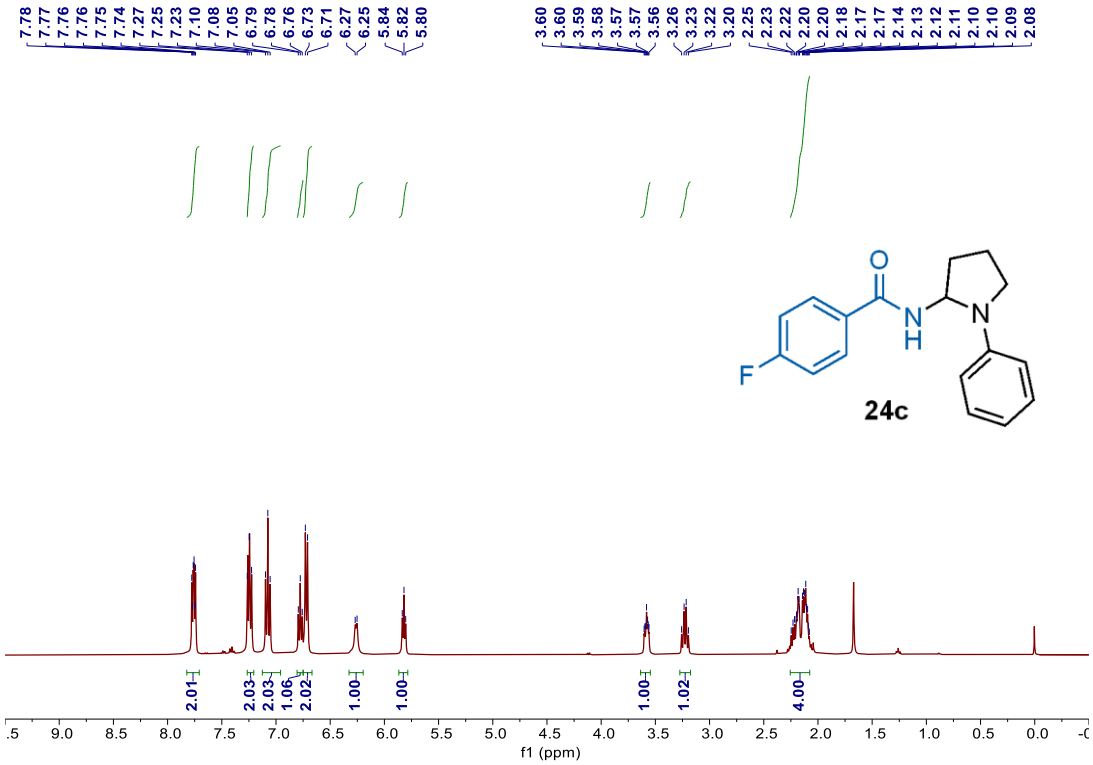
^{1}H NMR for **23c** (400 MHz, $CDCl_3$)



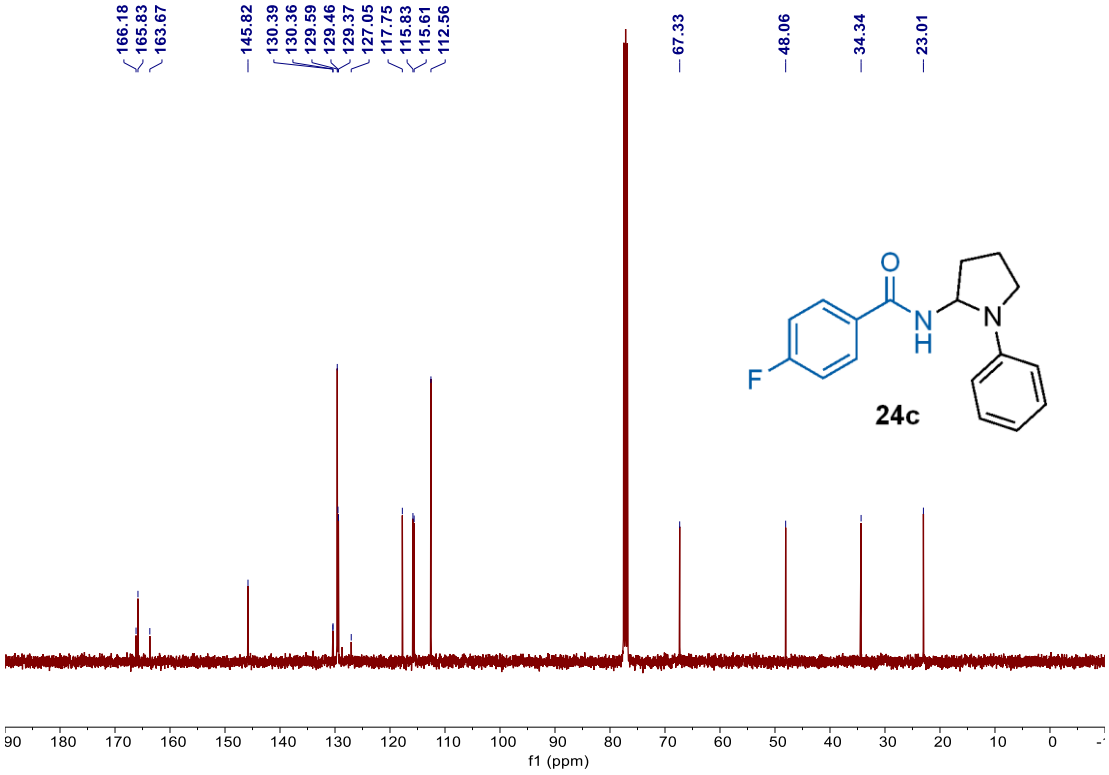
^{13}C NMR for **23c** (100 MHz, $CDCl_3$)



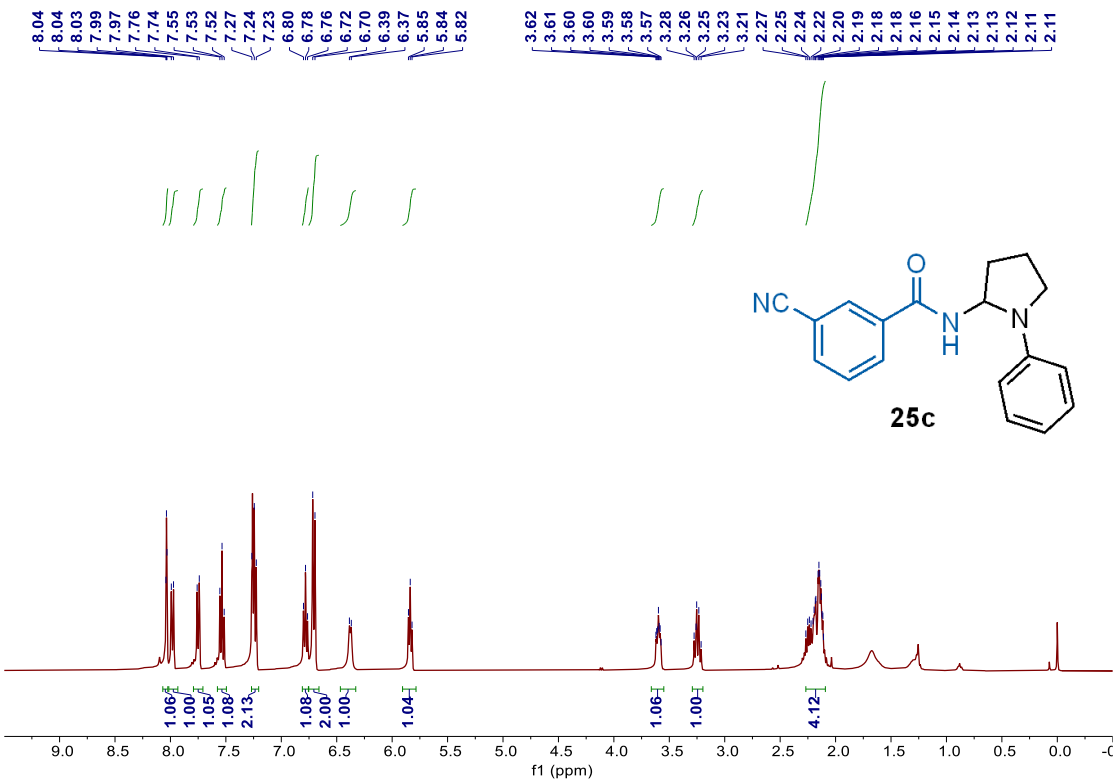
^{1}H NMR for **24c** (400 MHz, $CDCl_3$)



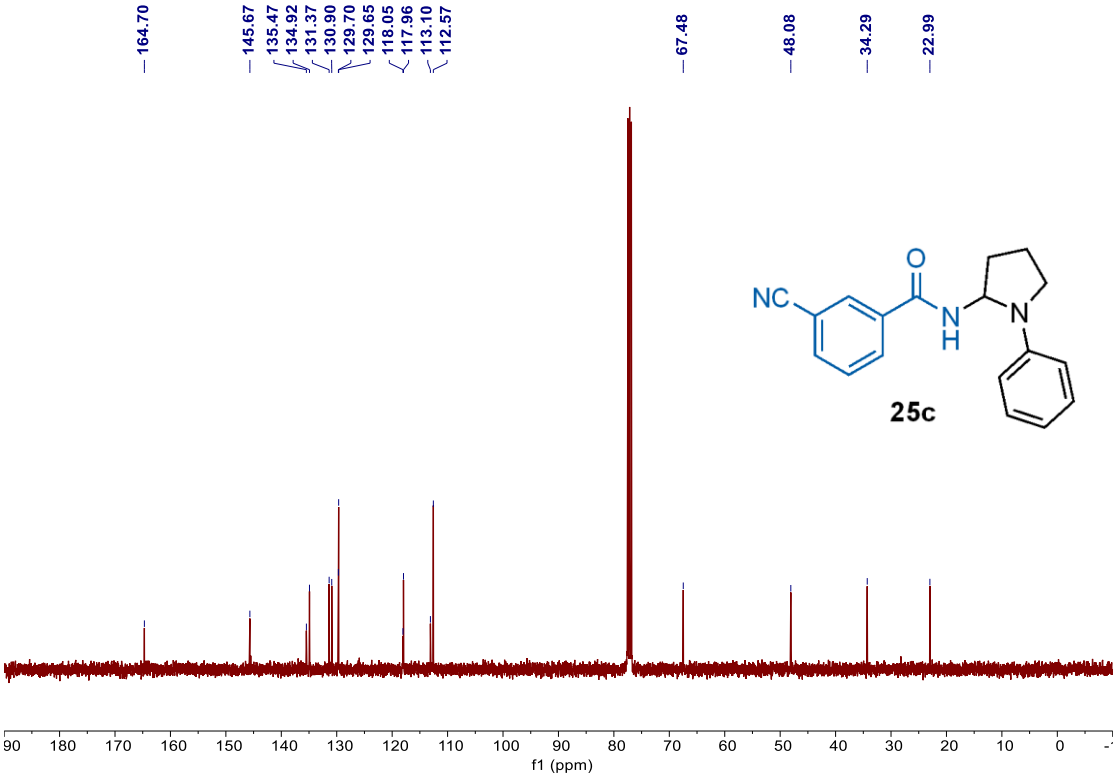
^{13}C NMR for **24c** (100 MHz, $CDCl_3$)



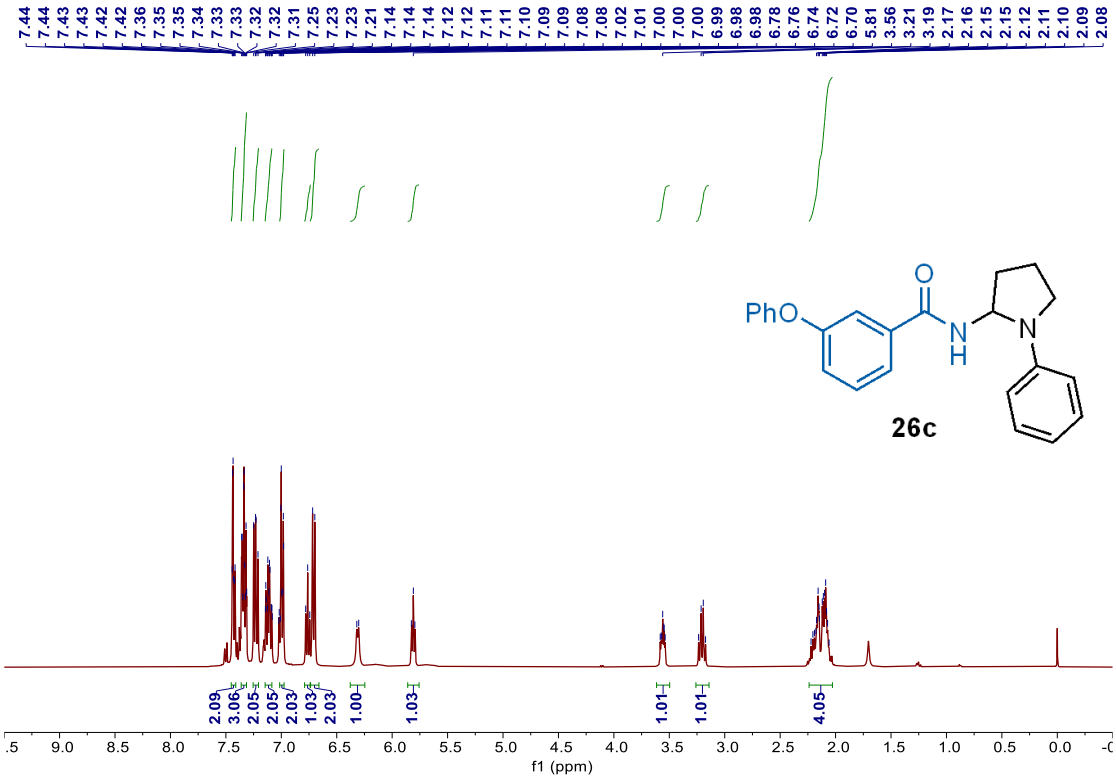
^{1}H NMR for **25c** (400 MHz, $CDCl_3$)



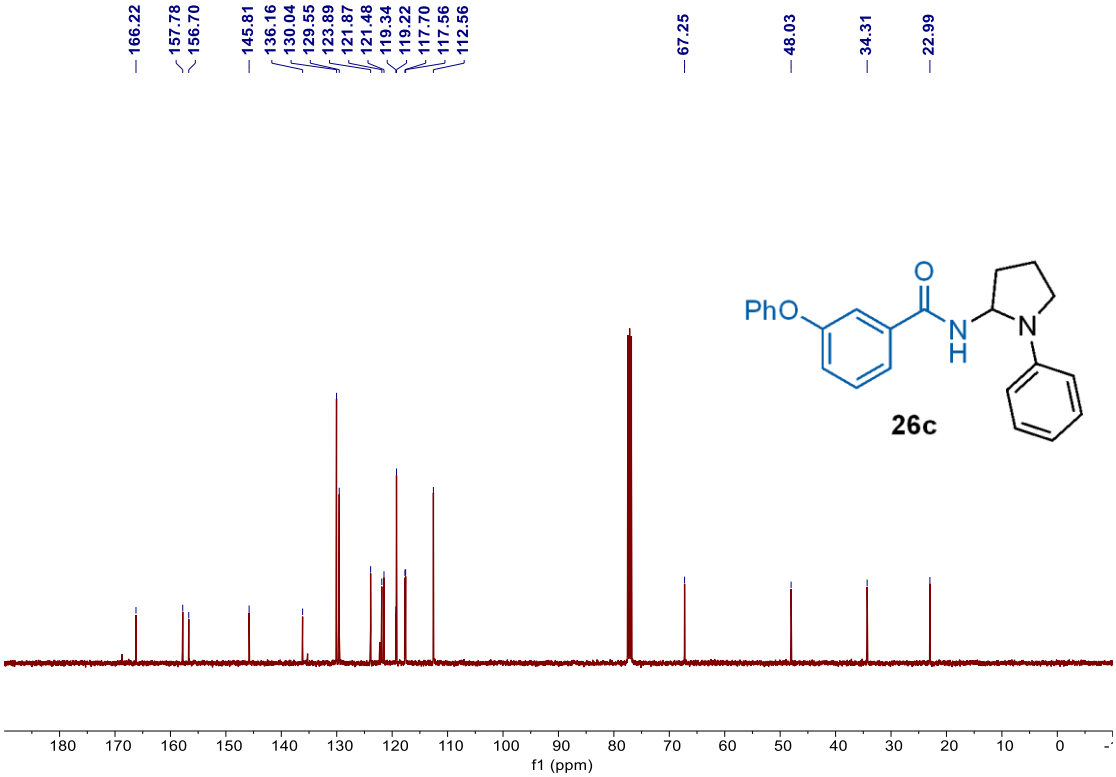
^{13}C NMR for **25c** (100 MHz, $CDCl_3$)



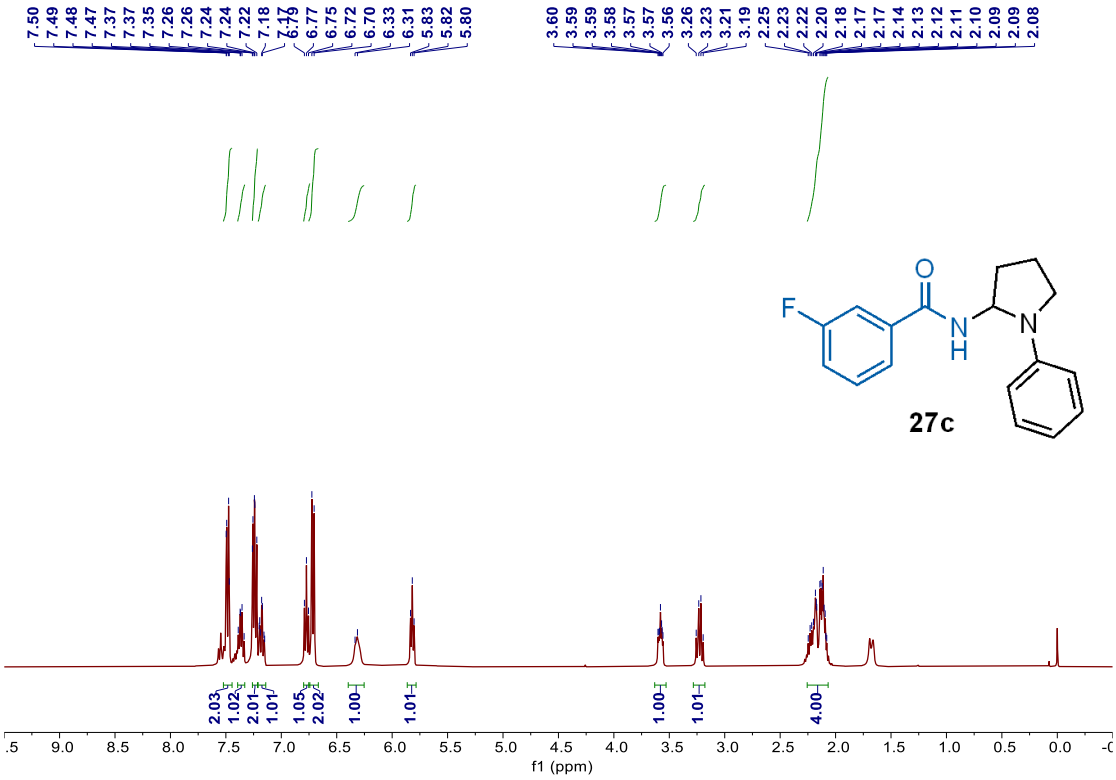
^{1}H NMR for **26c** (400 MHz, $CDCl_3$)



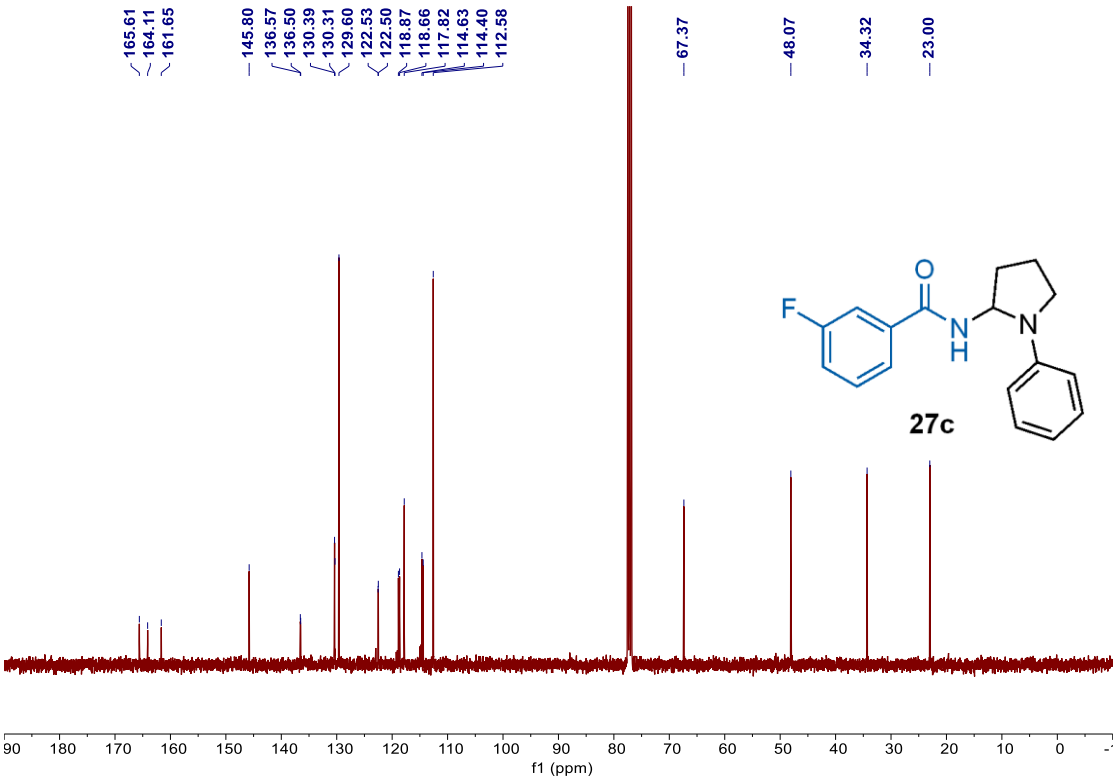
^{13}C NMR for **26c** (100 MHz, $CDCl_3$)



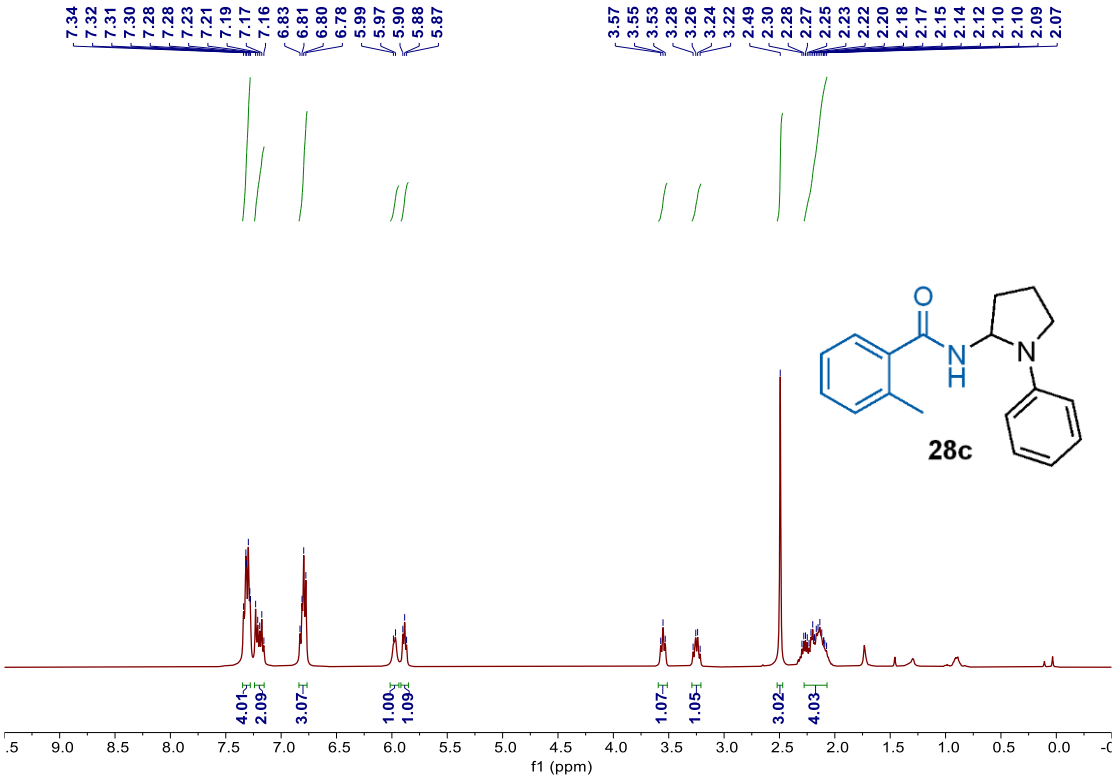
^{1}H NMR for **27c** (400 MHz, $CDCl_3$)



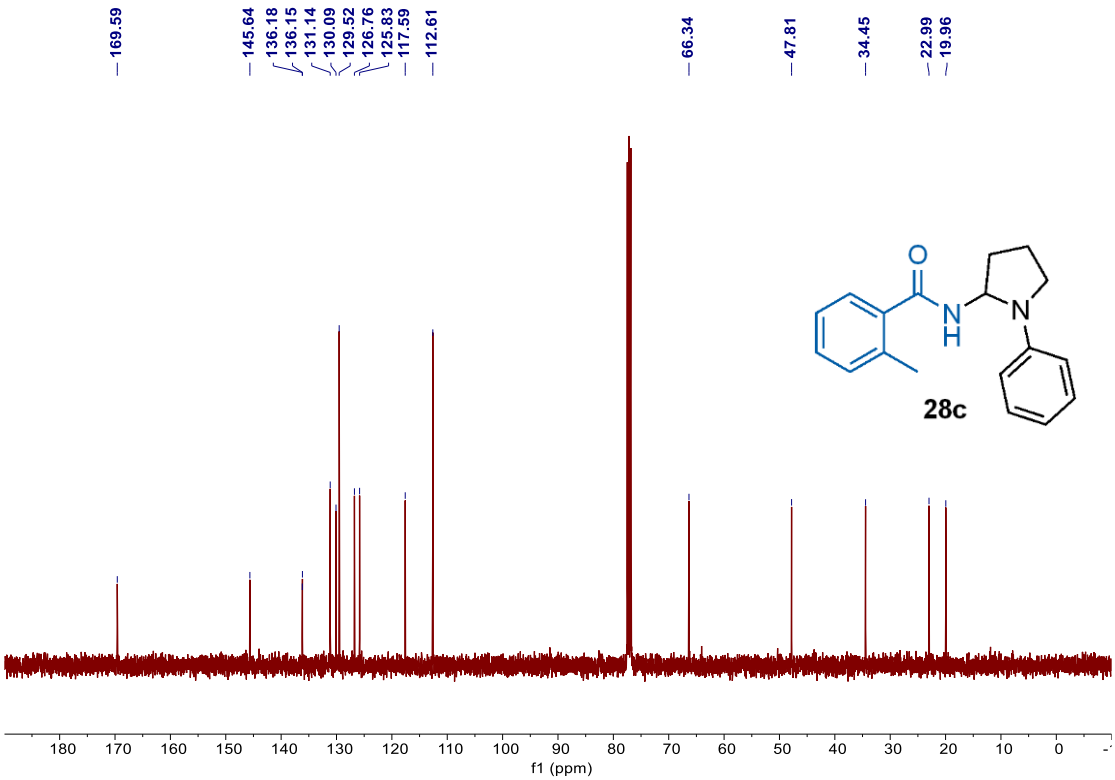
^{13}C NMR for **27c** (100 MHz, $CDCl_3$)



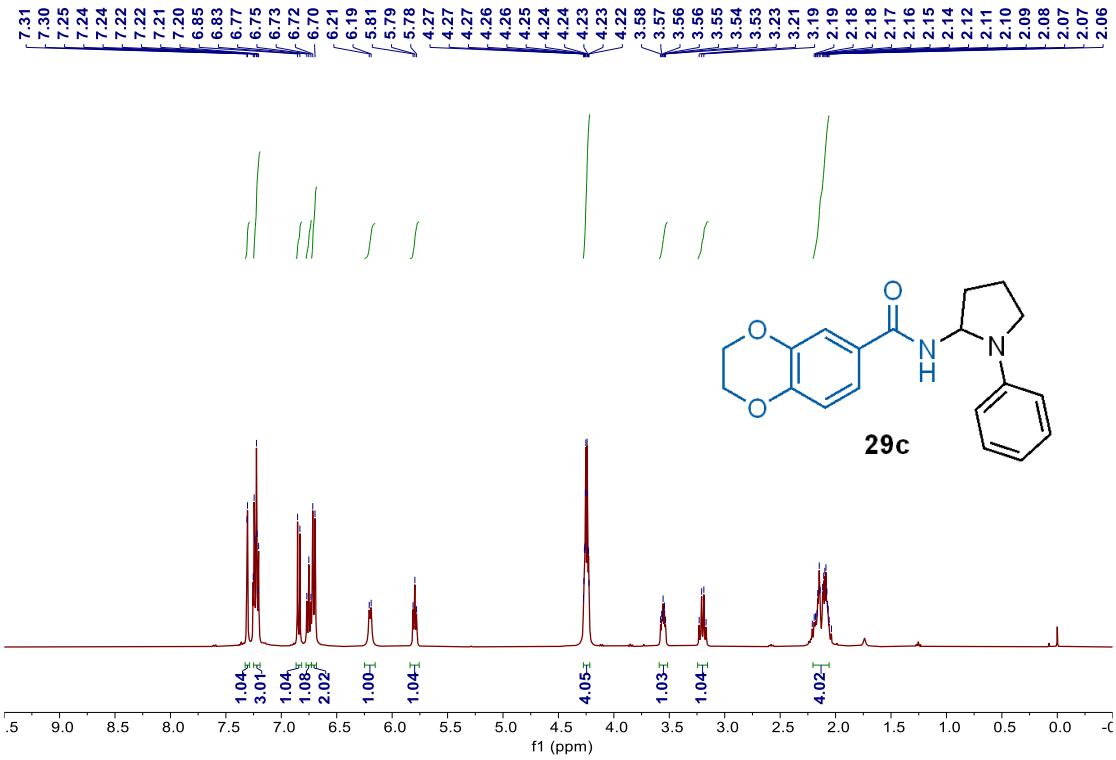
^{1}H NMR for **28c** (400 MHz, $CDCl_3$)



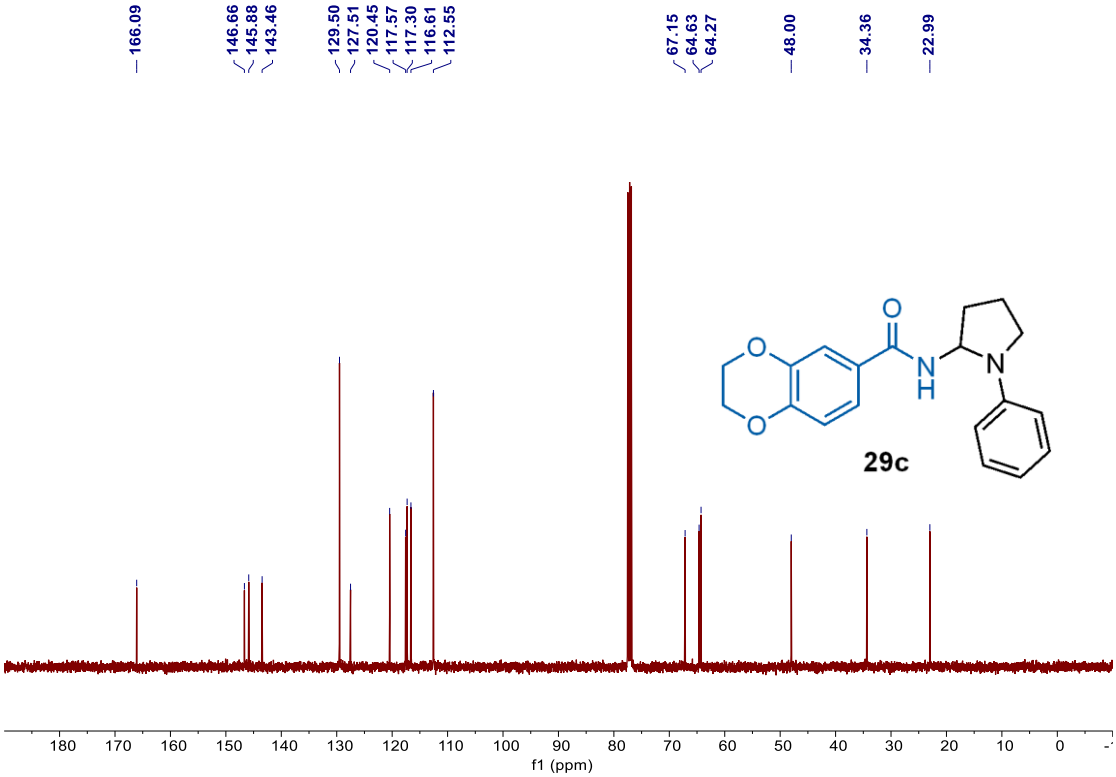
^{13}C NMR for **28c** (100 MHz, $CDCl_3$)



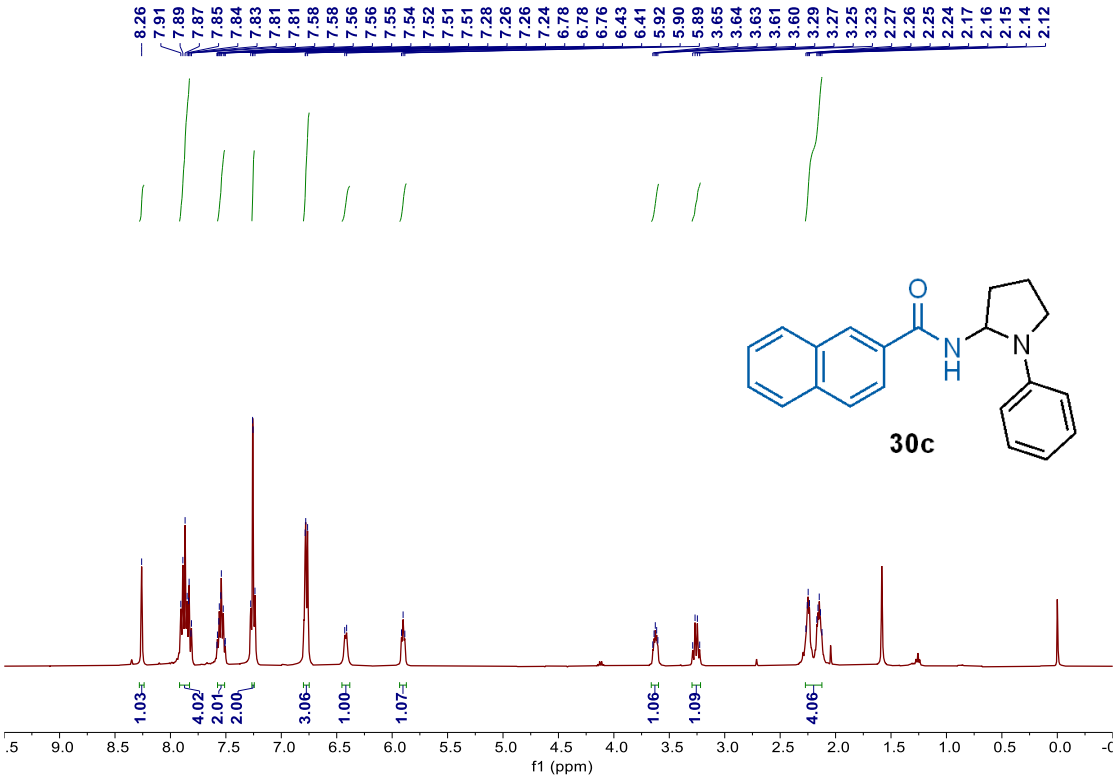
^{1}H NMR for **29c** (400 MHz, $CDCl_3$)



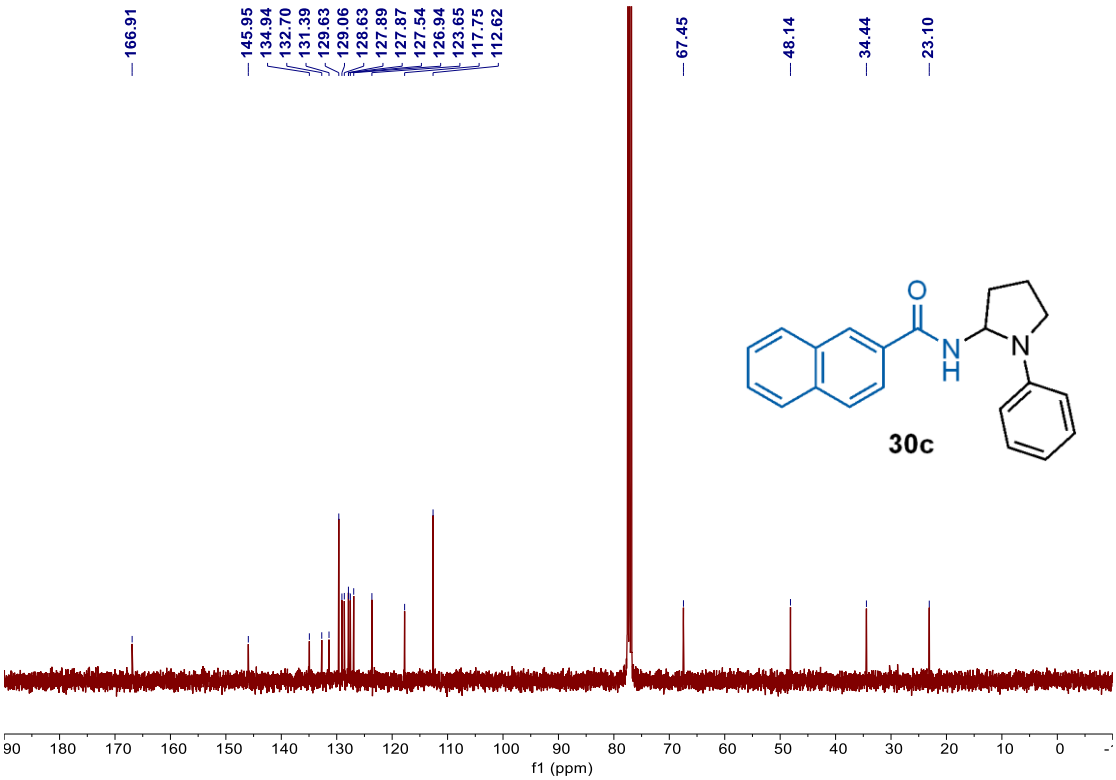
^{13}C NMR for **29c** (100 MHz, $CDCl_3$)



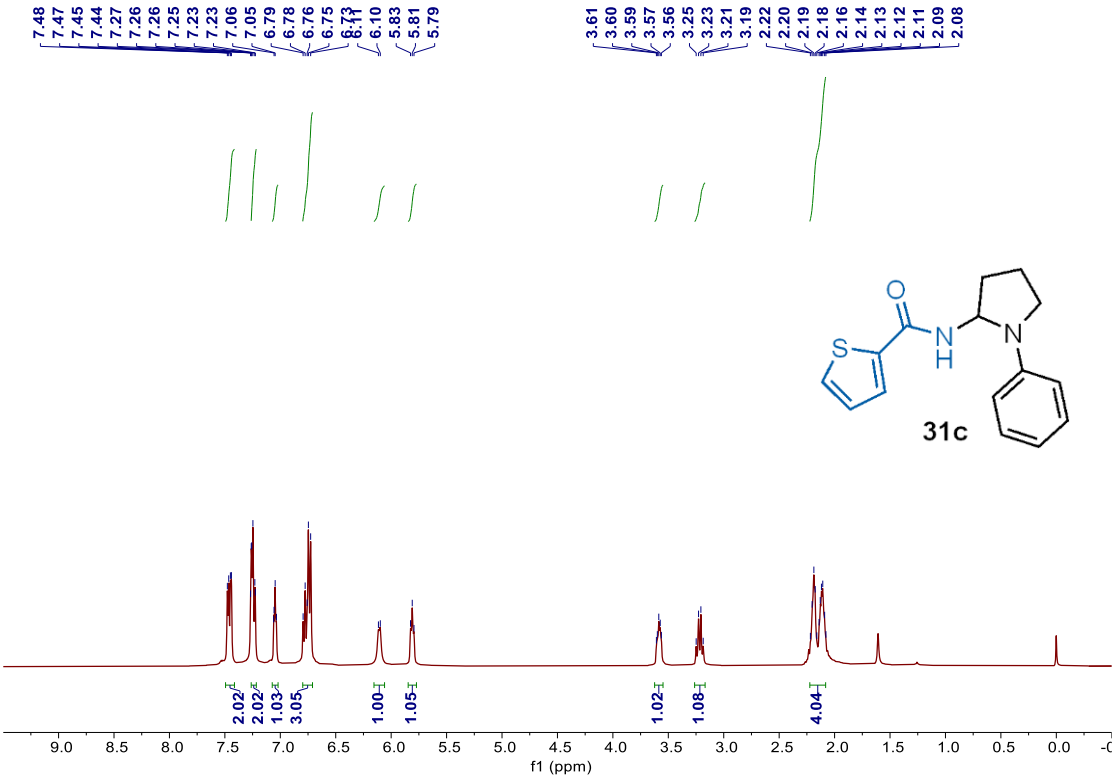
^{1}H NMR for **30c** (400 MHz, $CDCl_3$)



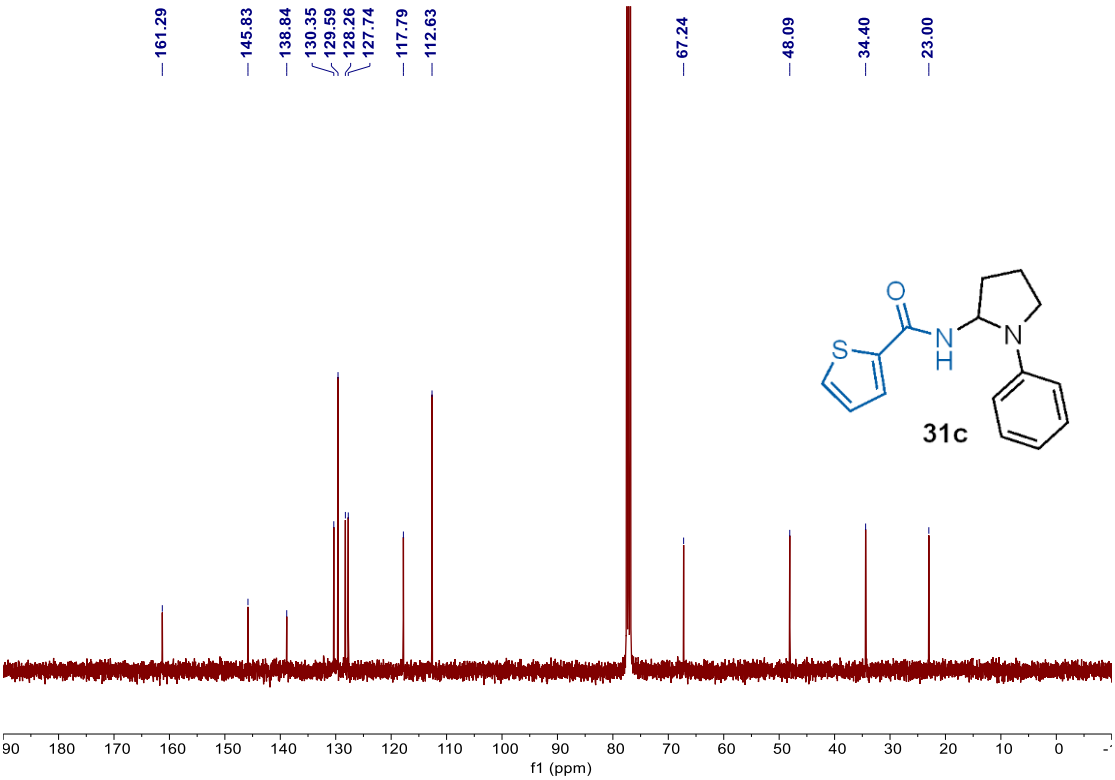
^{13}C NMR for **30c** (100 MHz, $CDCl_3$)



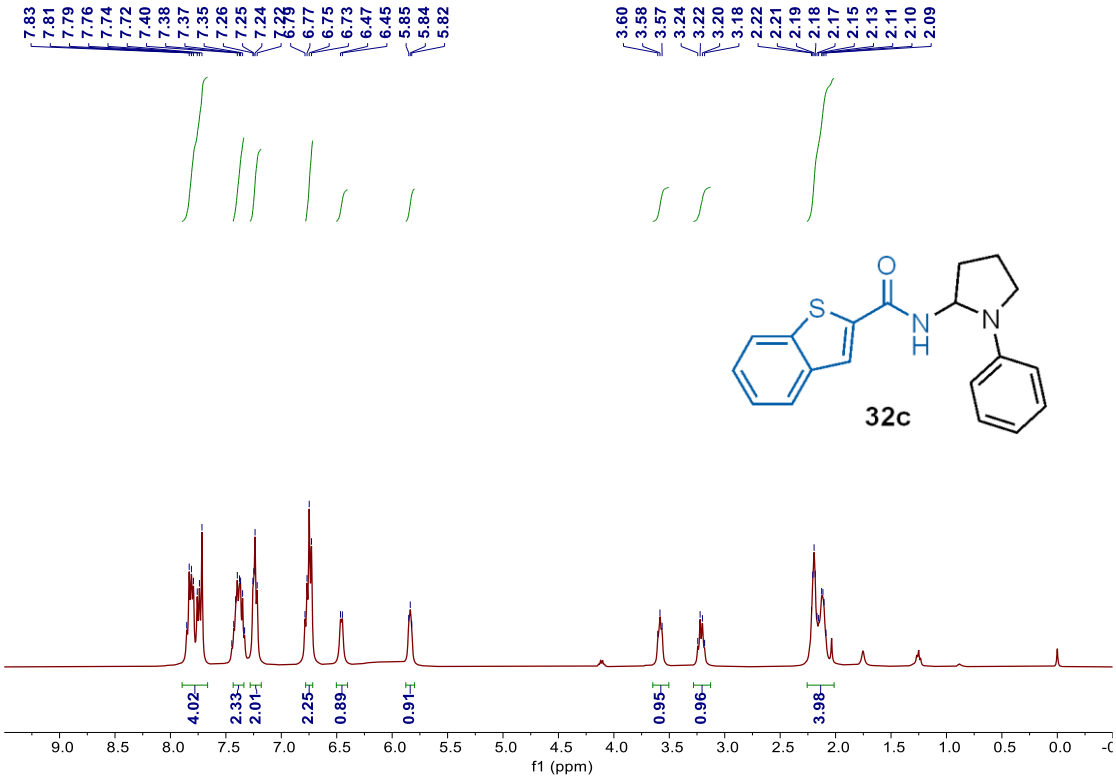
^{1}H NMR for **31c** (400 MHz, $CDCl_3$)



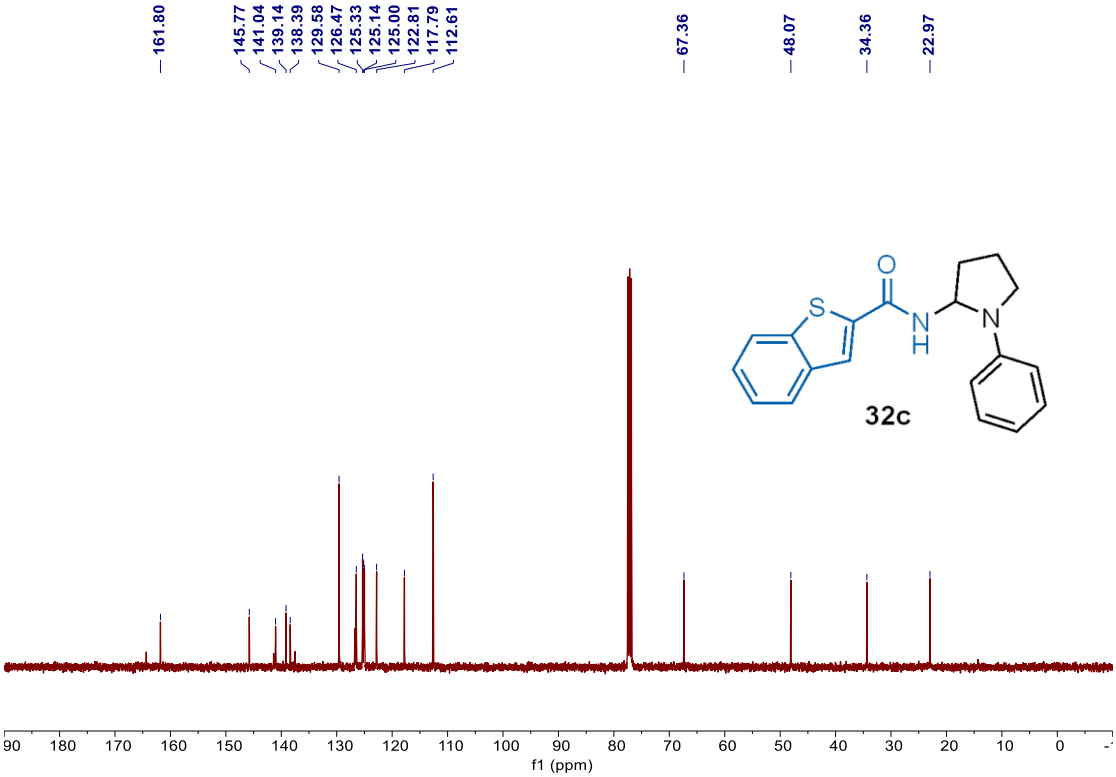
^{13}C NMR for **31c** (100 MHz, $CDCl_3$)



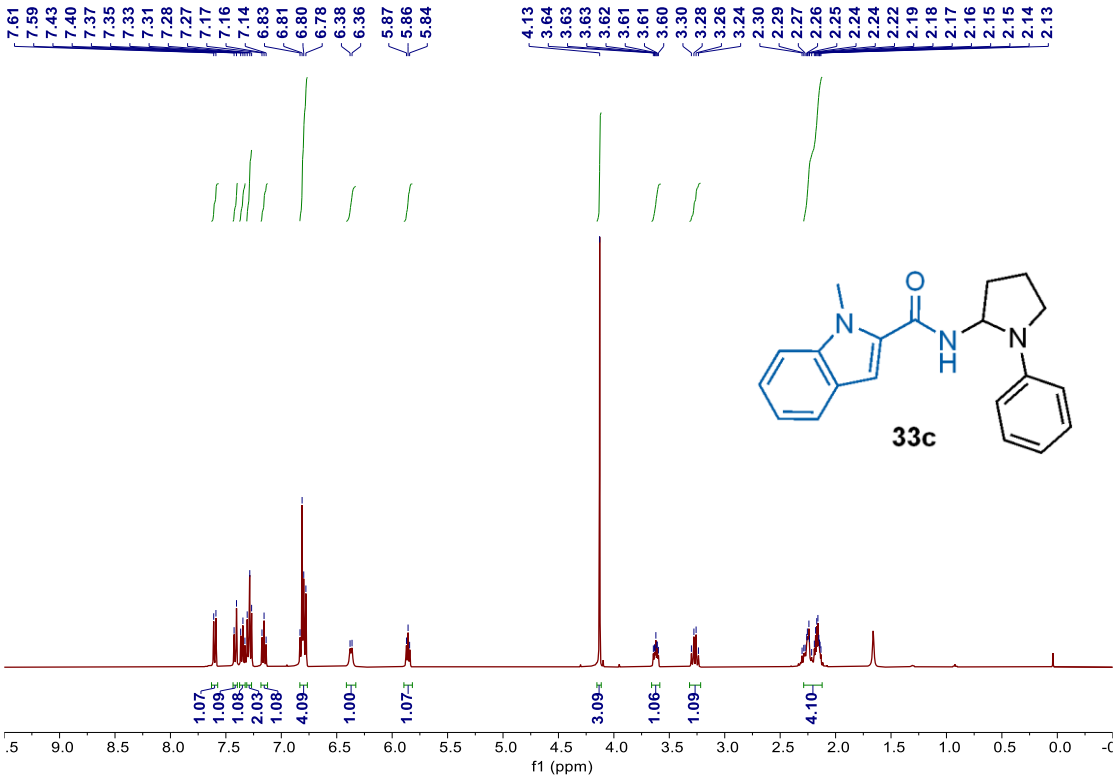
^{1}H NMR for **32c** (400 MHz, $CDCl_3$)



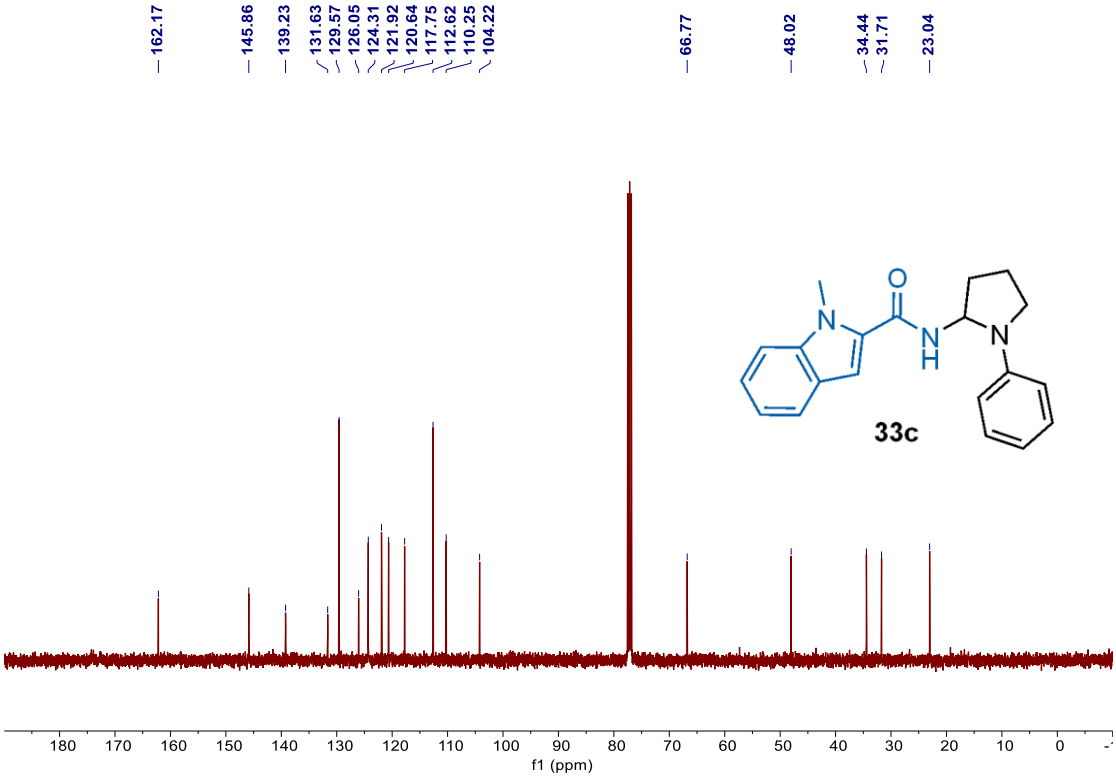
^{13}C NMR for **32c** (100 MHz, $CDCl_3$)



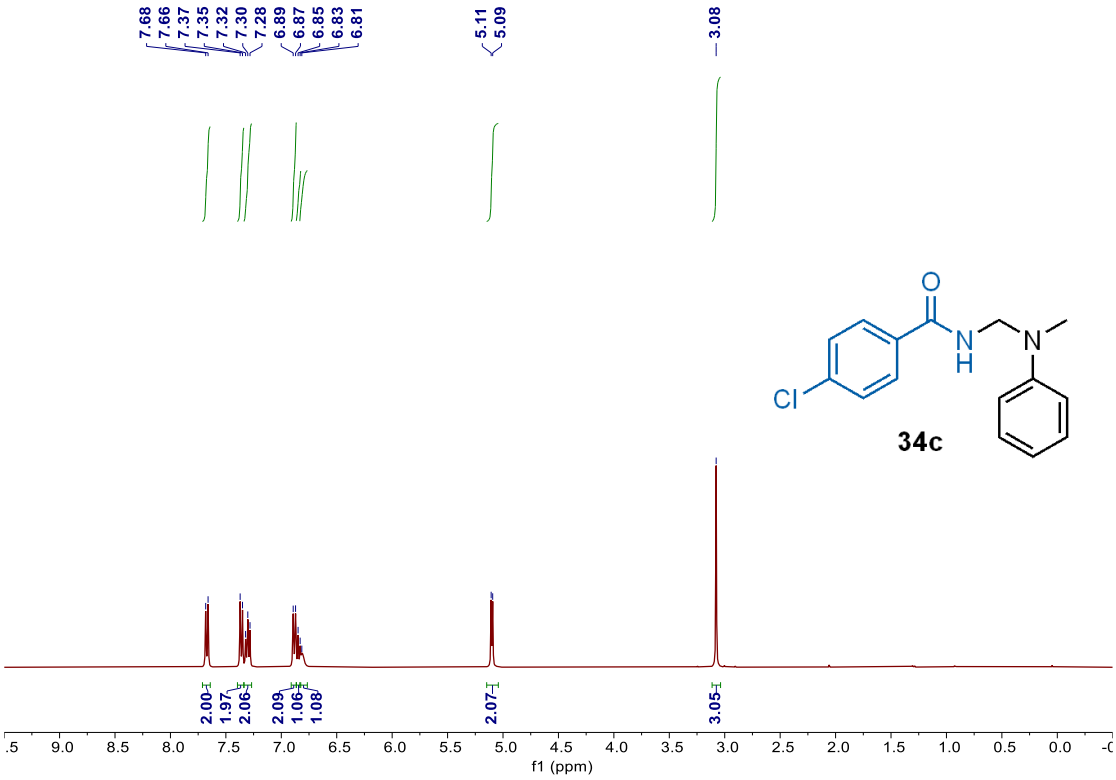
^{1}H NMR for **33c** (400 MHz, $CDCl_3$)



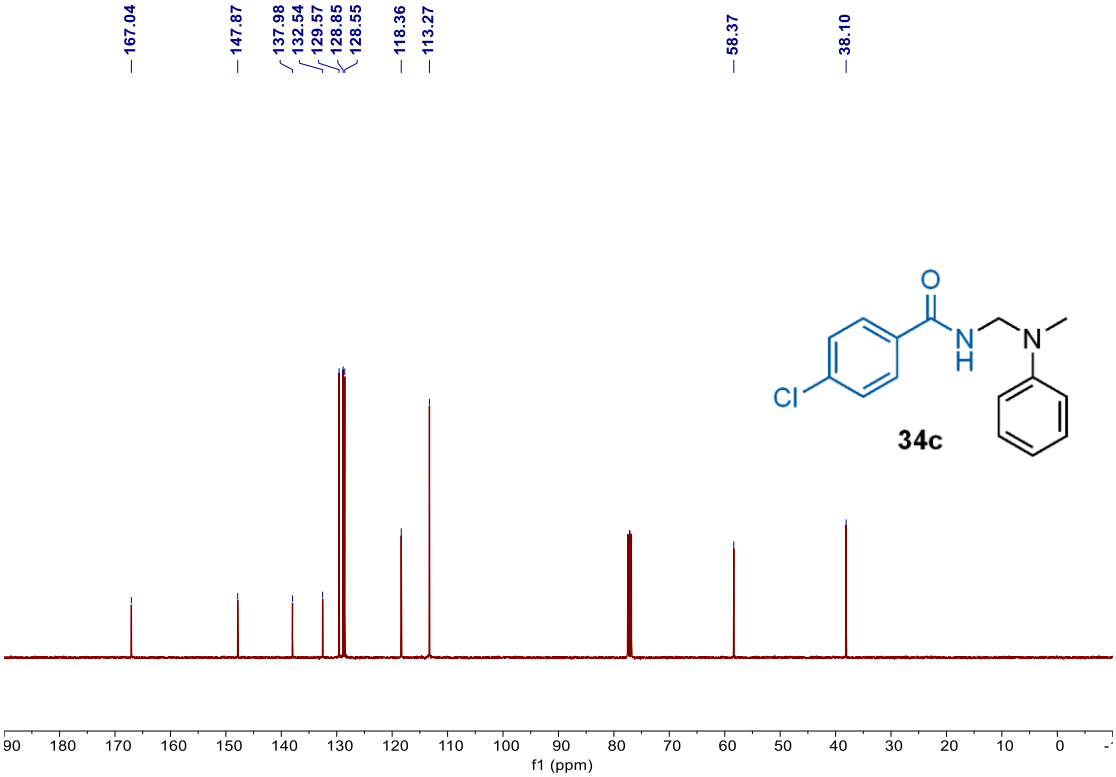
^{13}C NMR for **33c** (100 MHz, $CDCl_3$)



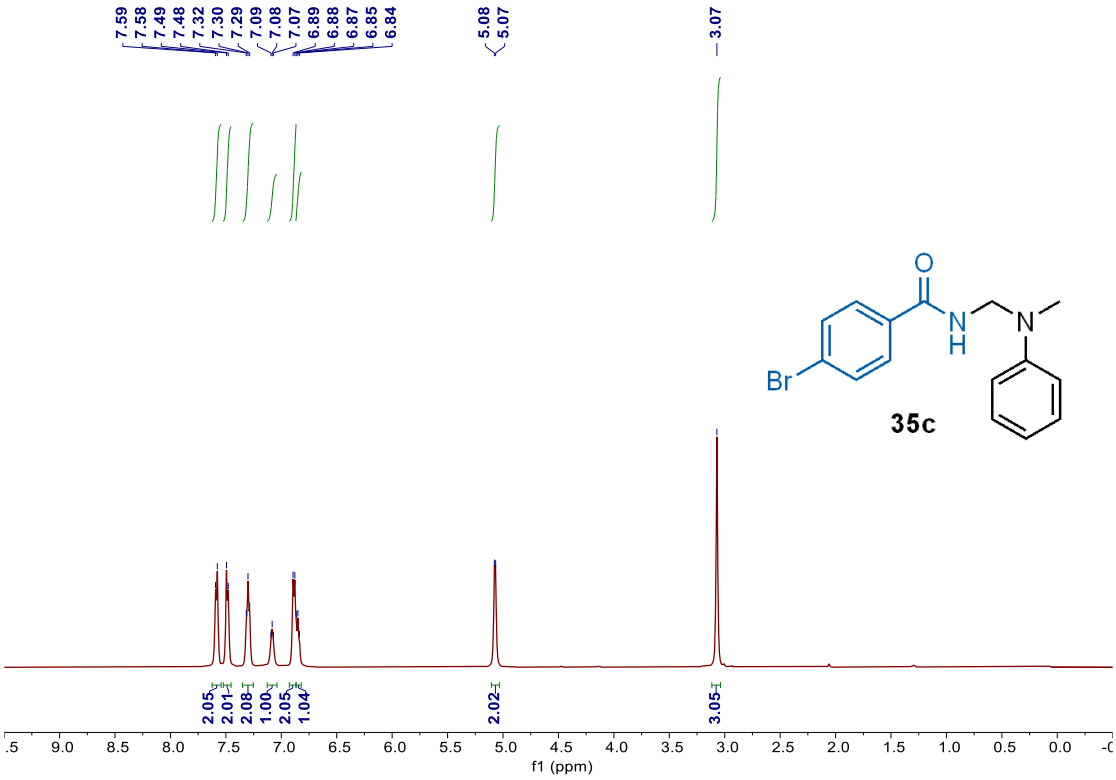
^{1}H NMR for **34c** (400 MHz, $CDCl_3$)



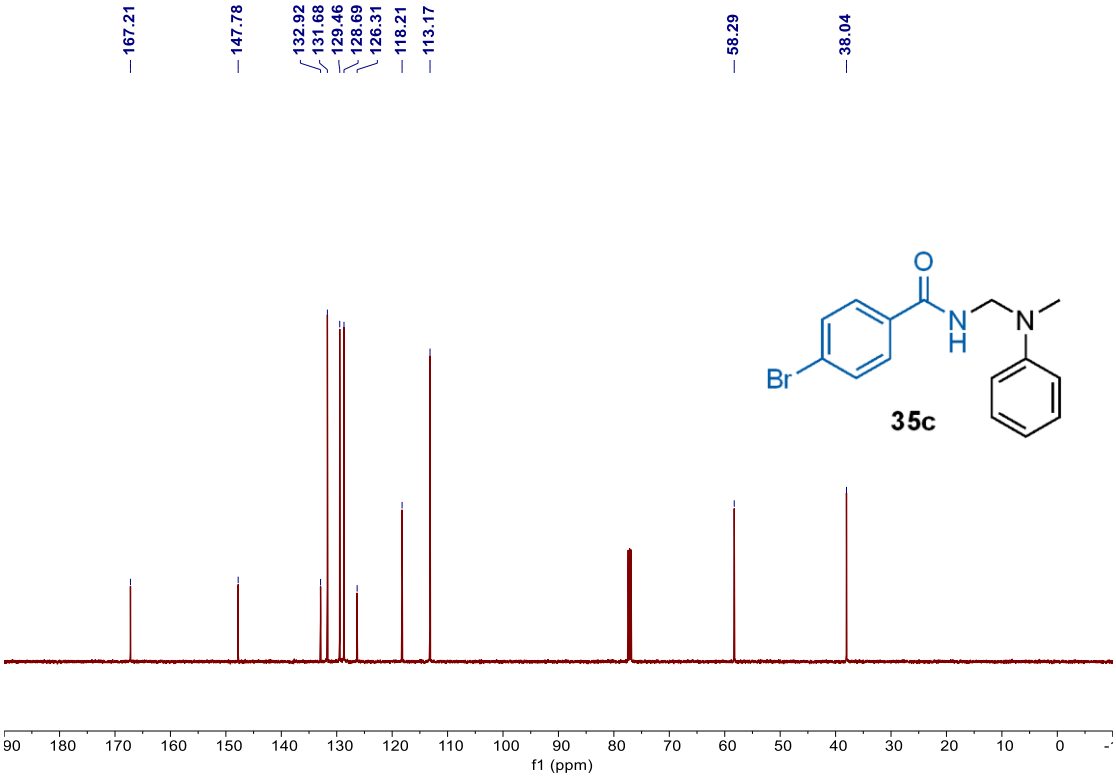
^{13}C NMR for **34c** (100 MHz, $CDCl_3$)



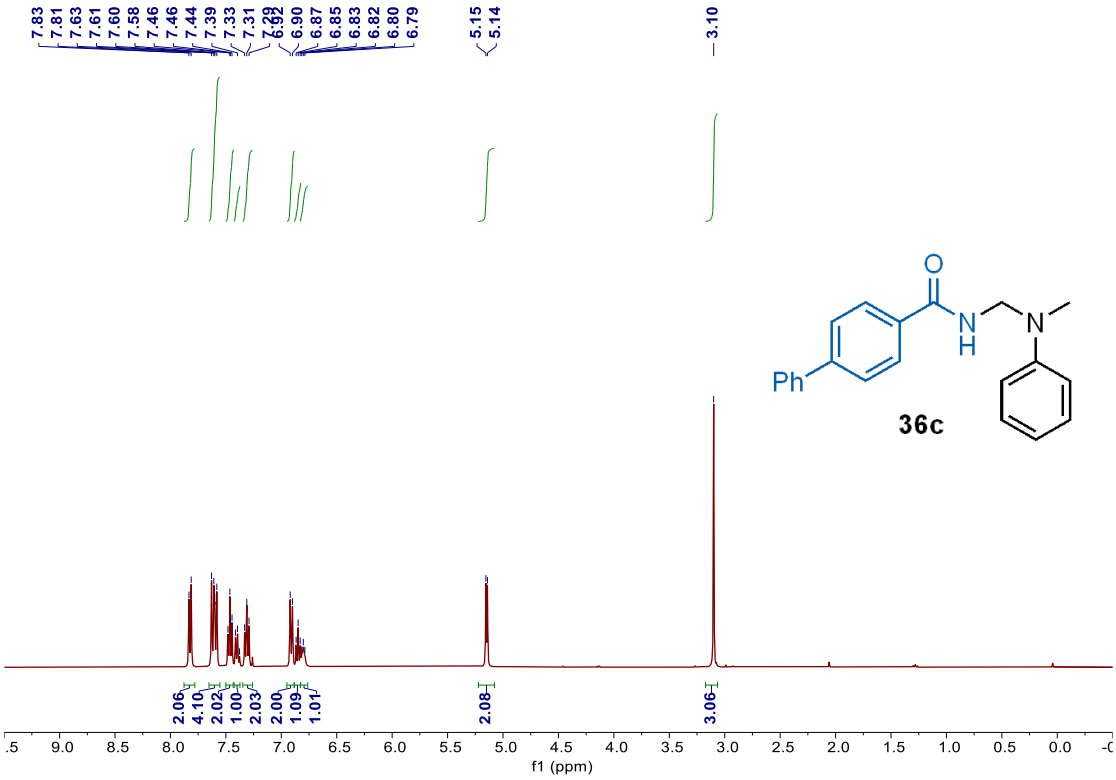
^{1}H NMR for **35c** (500 MHz, $CDCl_3$)



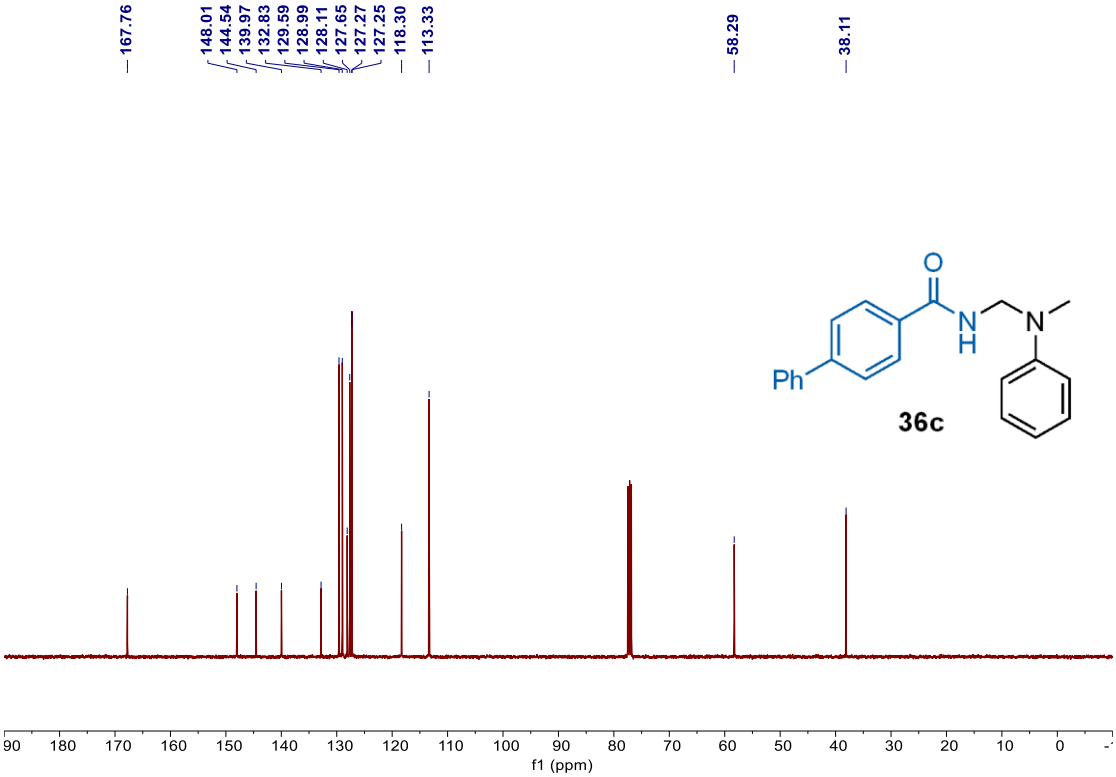
^{13}C NMR for **35c** (125 MHz, $CDCl_3$)



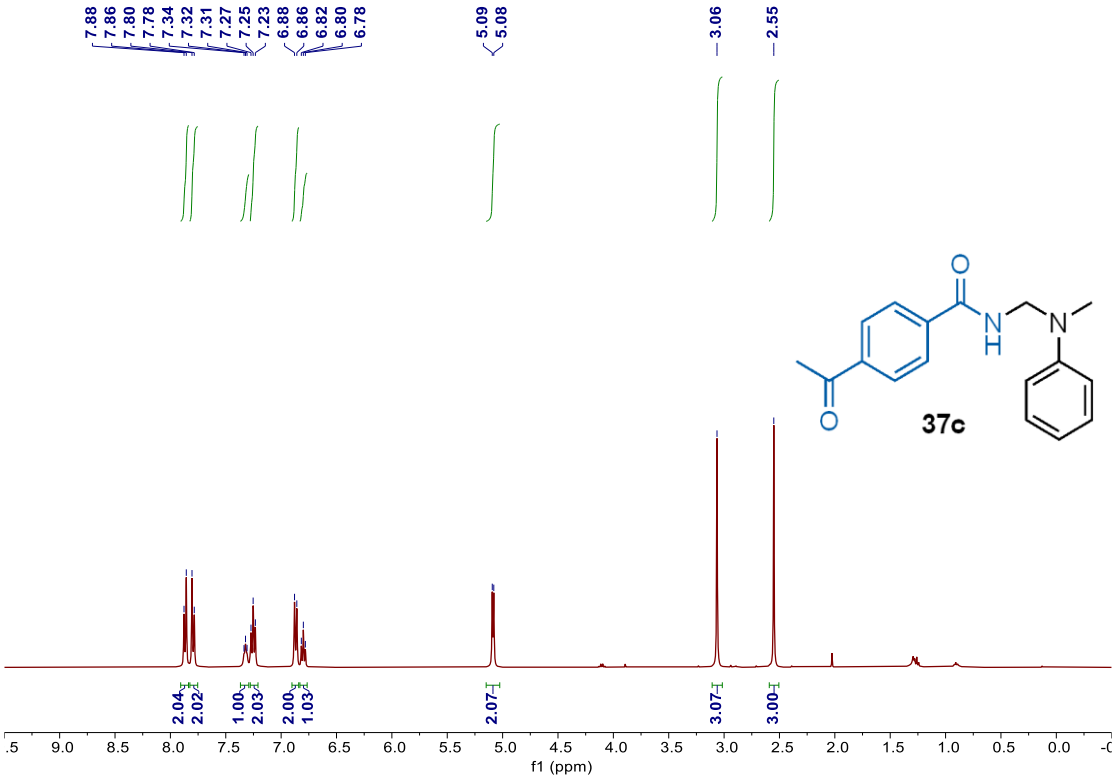
^{1}H NMR for **36c** (400 MHz, $CDCl_3$)



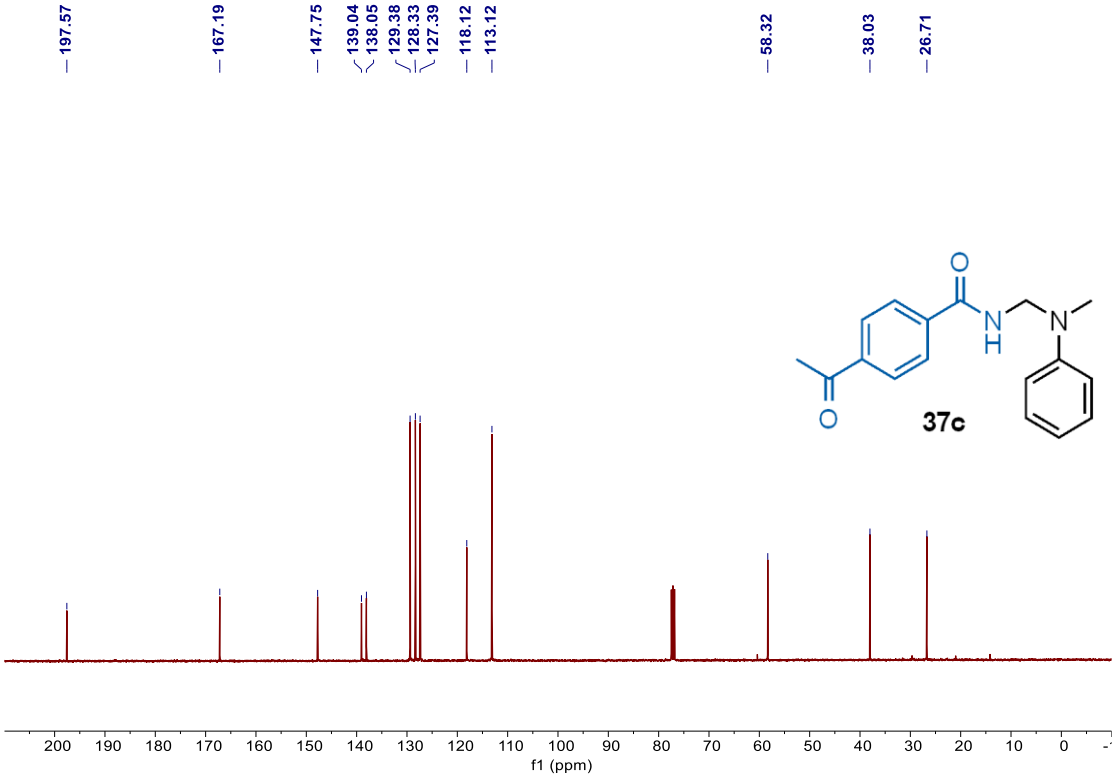
^{13}C NMR for **36c** (100 MHz, $CDCl_3$)



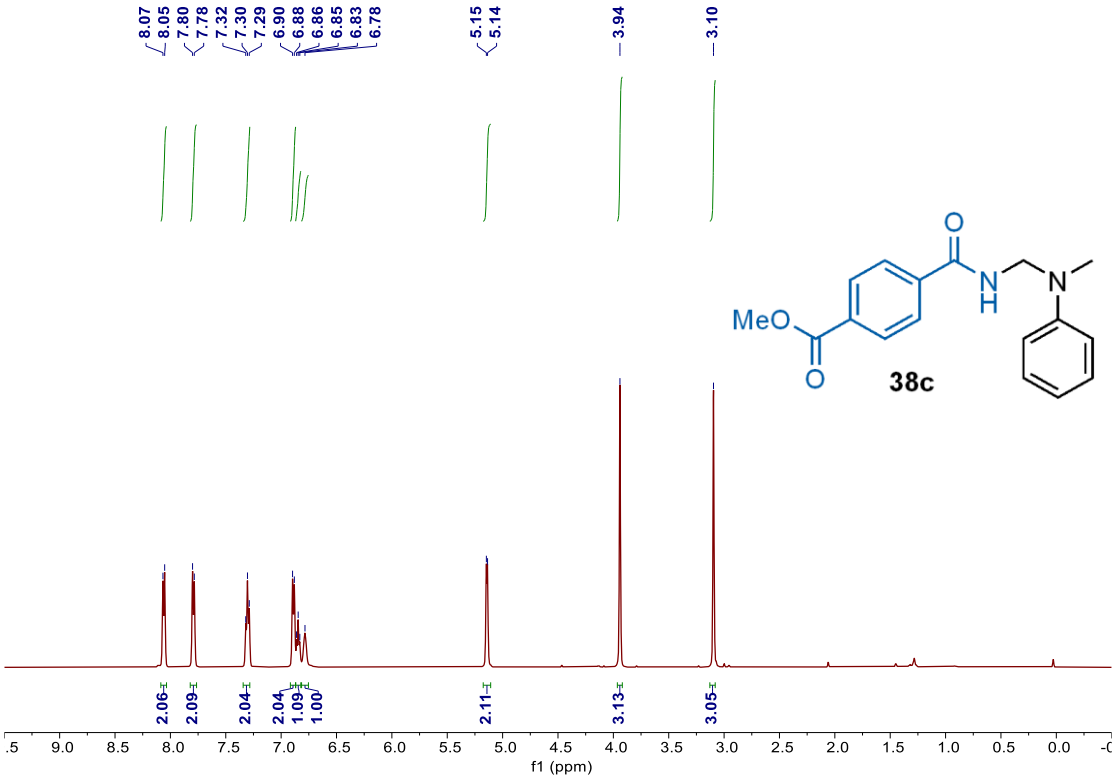
^{1}H NMR for **37c** (400 MHz, $CDCl_3$)



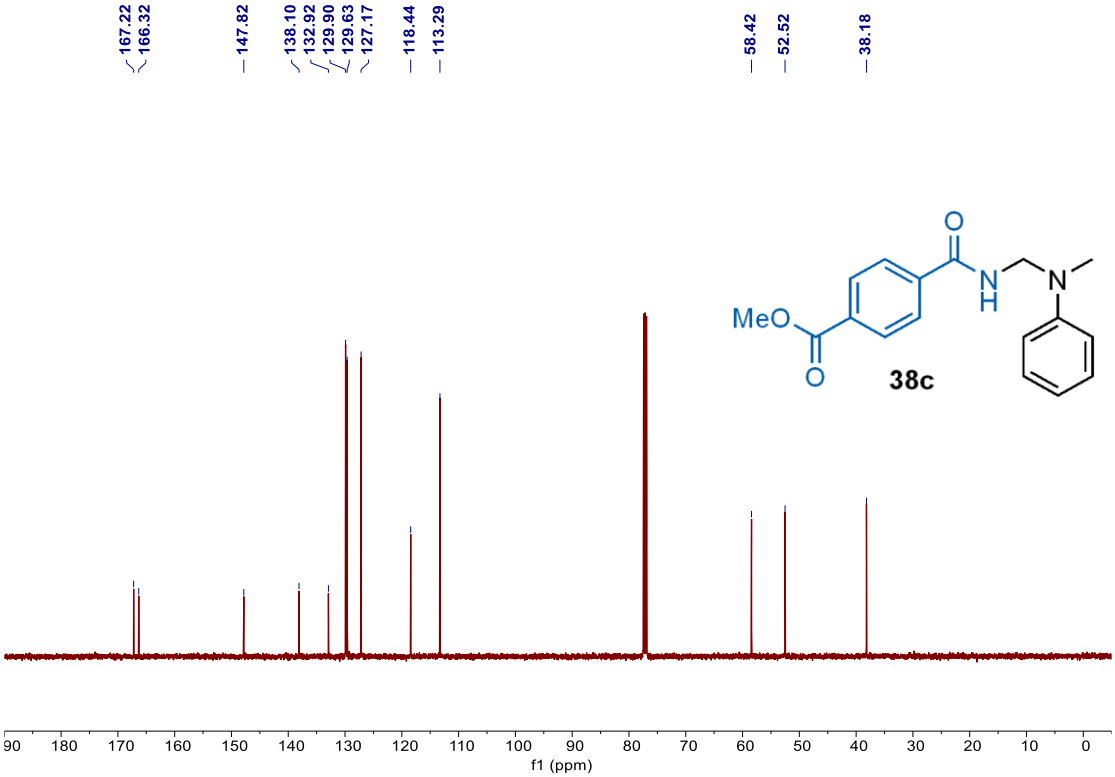
^{13}C NMR for **37c** (100 MHz, $CDCl_3$)



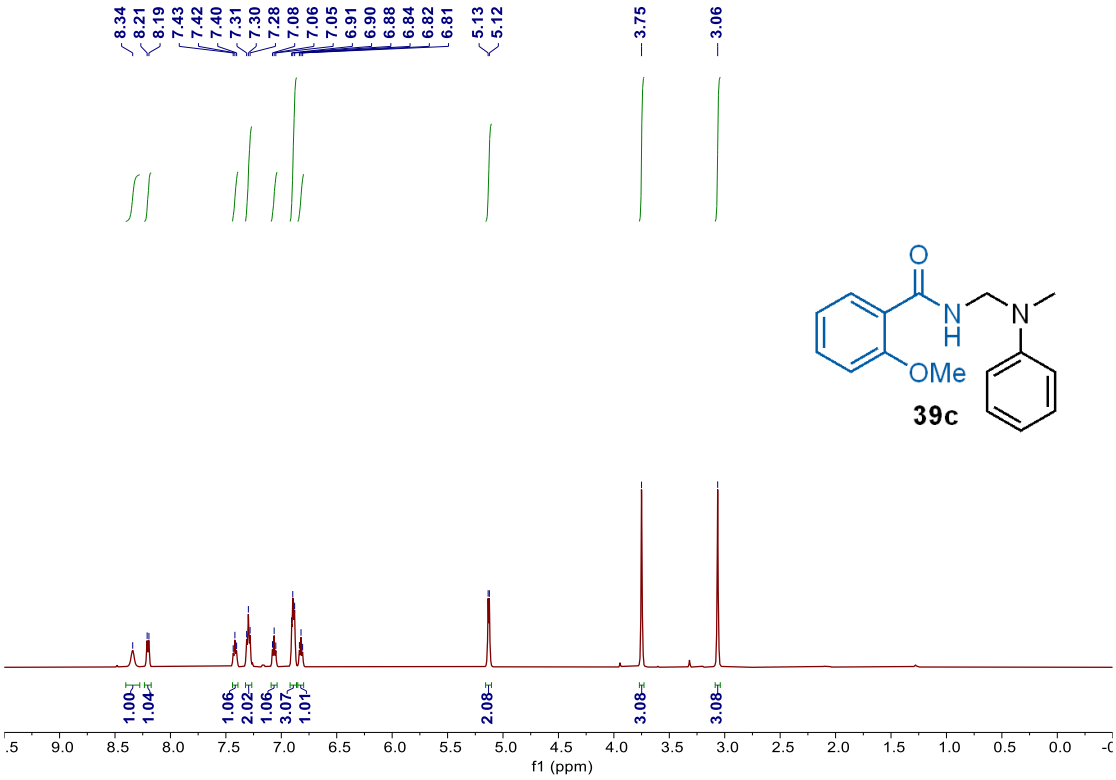
^{1}H NMR for **38c** (500 MHz, $CDCl_3$)



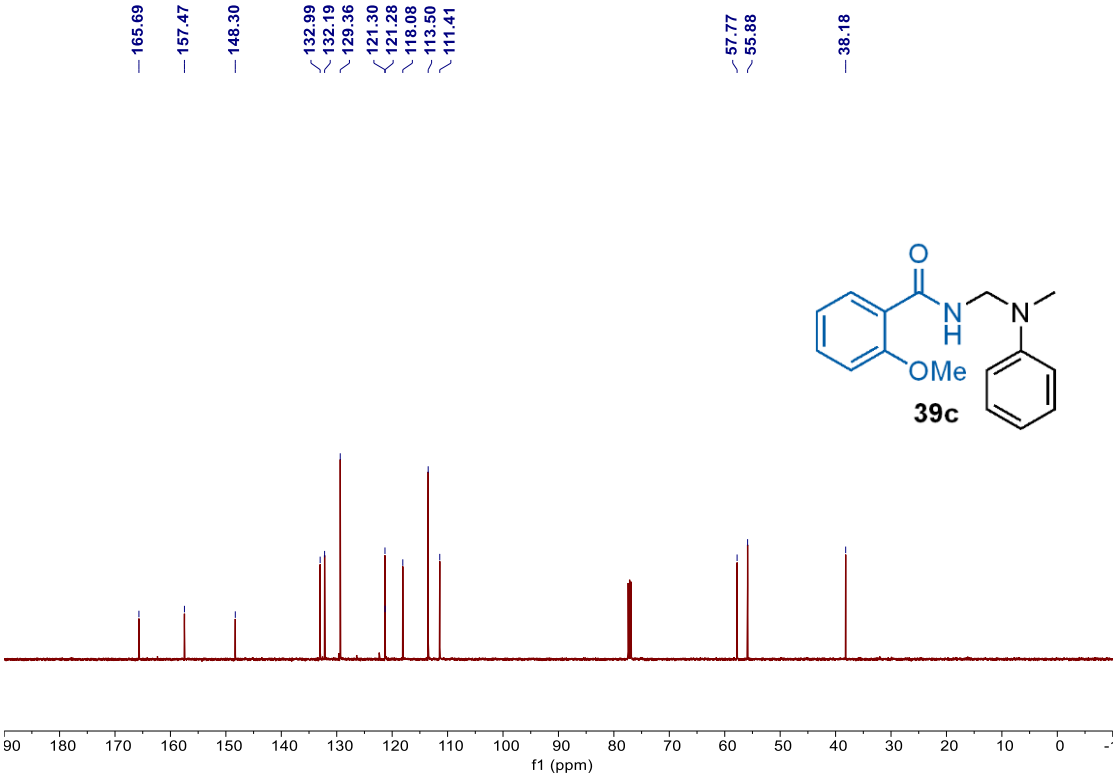
^{13}C NMR for **38c** (125 MHz, $CDCl_3$)



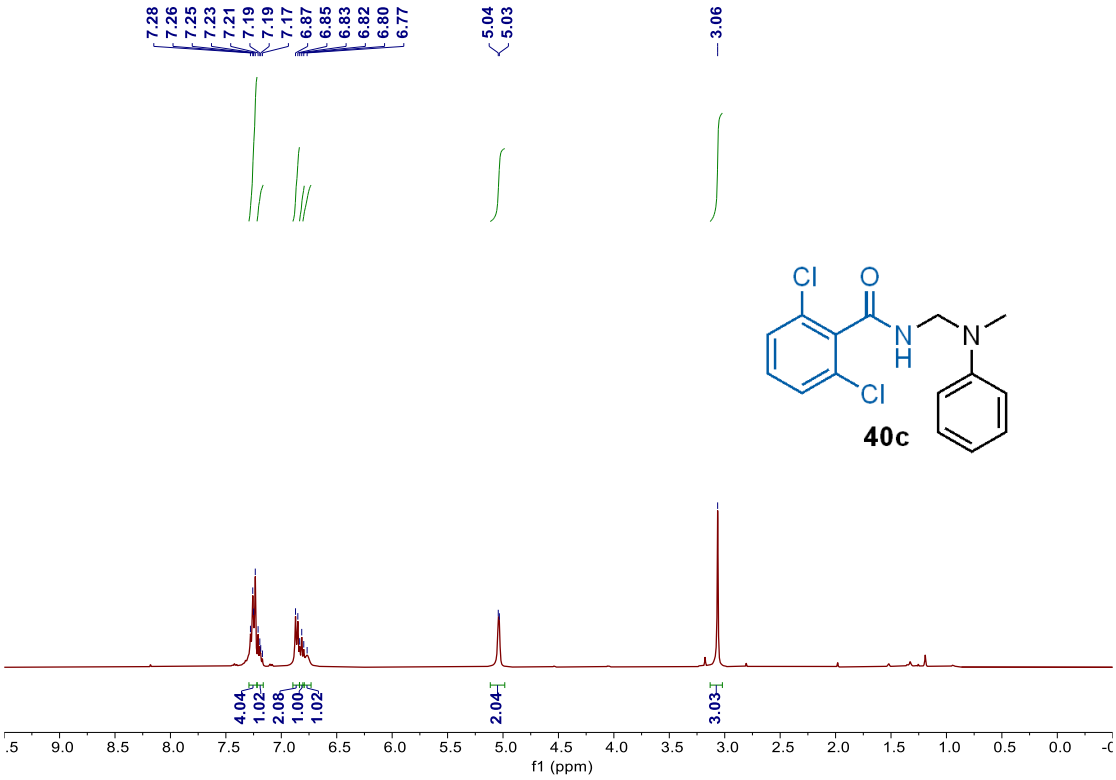
^{1}H NMR for **39c** (500 MHz, $CDCl_3$)



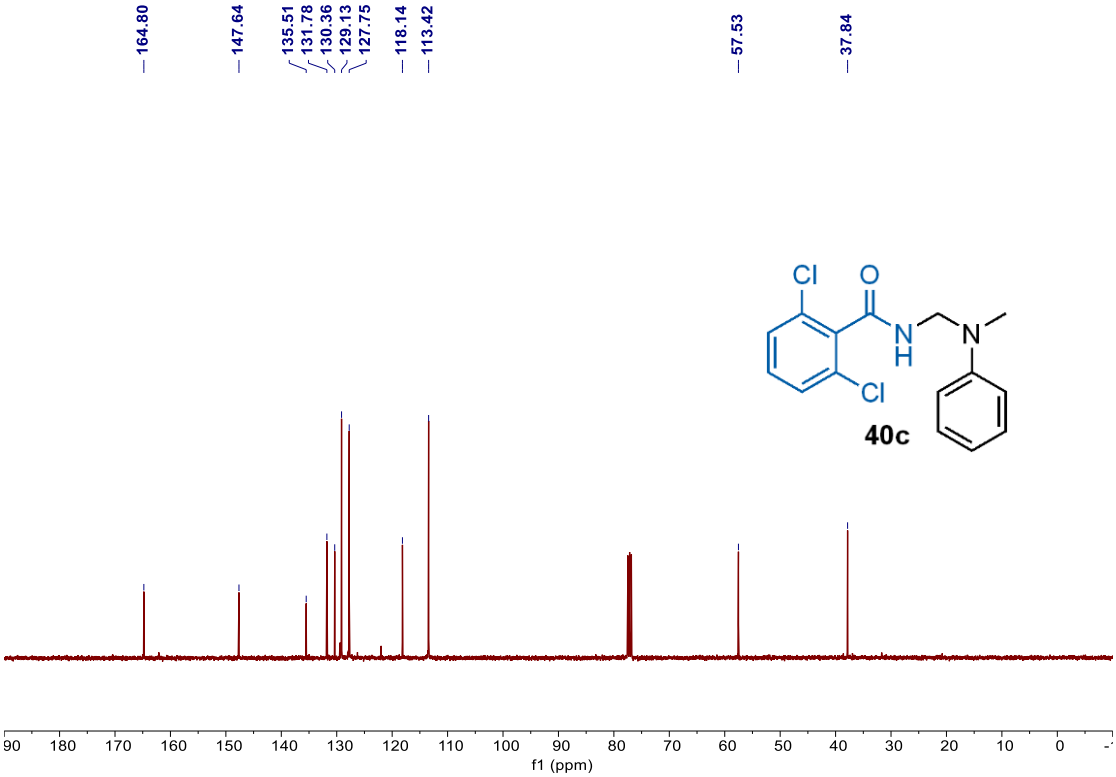
^{13}C NMR for **39c** (125 MHz, $CDCl_3$)



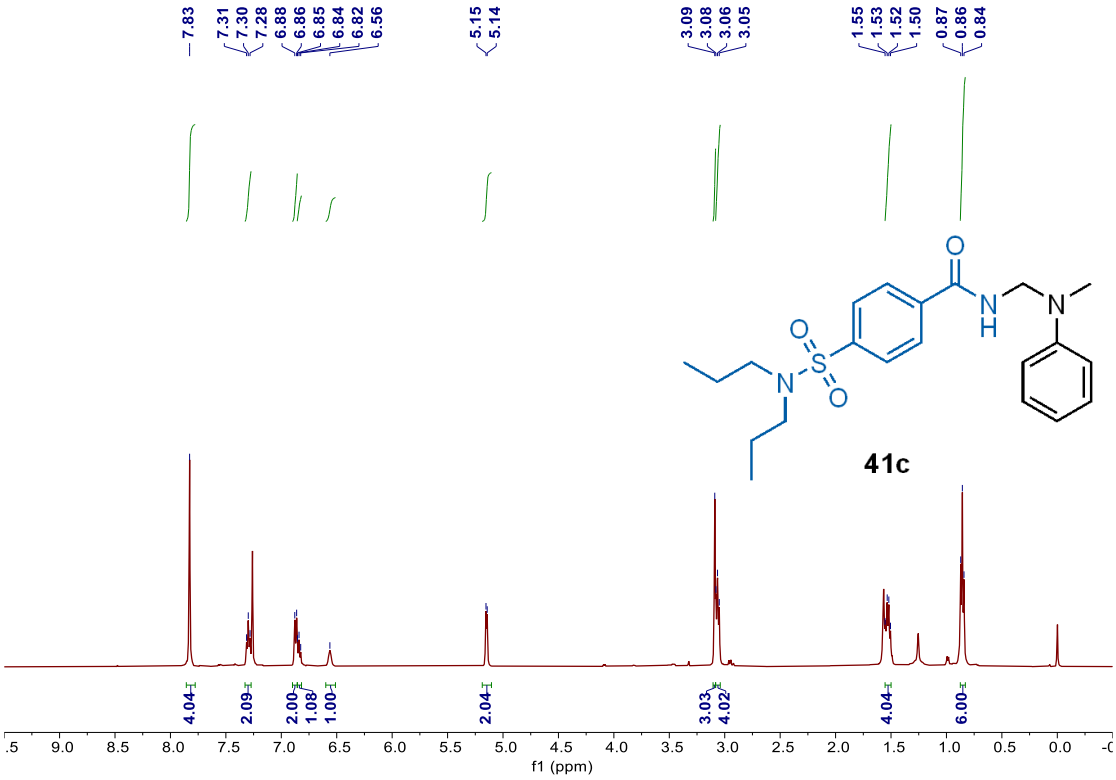
^{1}H NMR for **40c** (400 MHz, $CDCl_3$)



^{13}C NMR for **40c** (100 MHz, $CDCl_3$)



^{1}H NMR for **41c** (500 MHz, $CDCl_3$)



^{13}C NMR for **41c** (125 MHz, $CDCl_3$)