Electronic Supporting Information

Rh(III)-Catalyzed Diamidation of Olefins via Amidorhodation and Further Amidation

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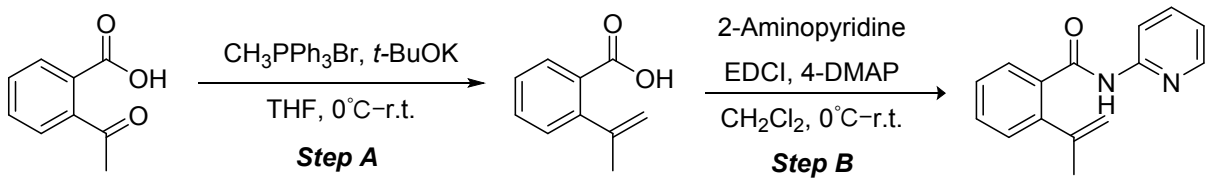
Contents

1. General Considerations

All the reactions were carried out using standard Schlenk technique. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). The chemical shifts were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), dt (doublets of triplet), and m (multiplet). The coupling constants *J* were given in Hz. HRMS data were obtained using a ESI mode. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized under UV light (254 and 365 nm). Column chromatography was performed on silica gel 200-300 mesh. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification.

2. Synthesis and Characterization of starting materials

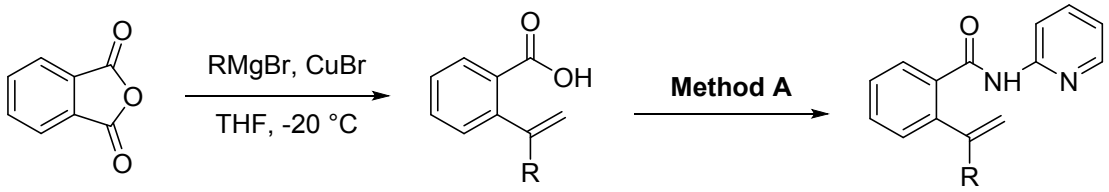
a. Method A: Preparation of the Substrates 1 (Synthesis of 1a is representative)



Step A.[1] To a stirred suspension of methyltriphenylphosphonium bromide (3.0 equiv) in THF (1.0 M), potassium *tert*-butoxide (3.0 equiv) was added at 0 °C and stirred for 0.5 hour under Ar. A solution of 2-ketobenzoic acid (1.0 equiv) in THF (3 M) was added dropwise. Until the reaction was completed, as monitored by TLC, the resulting mixture was quenched with water, basified with aqueous NaOH (3.0 M) and washed with diethyl ether. The resulting aqueous phase was acidified with aqueous HCl (2.0 M) until pH 1-2 and extracted twice with ethyl acetate. The combined organic layers were washed with water, brine, dried over with Na_2SO_4, filtered and concentrated in vacuo. The resulting crude product was purified by flash column chromatography to afford the desired unsaturated benzoic acid derivatives.

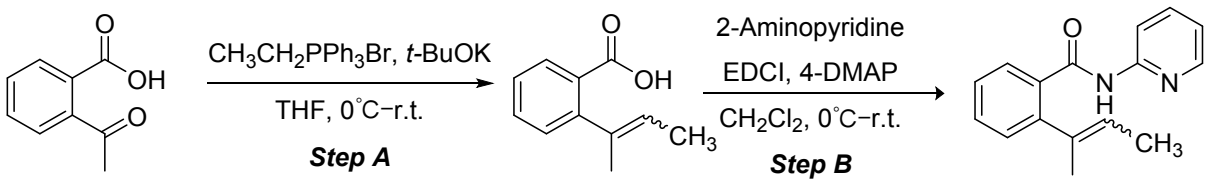
Step B.[2] To a solution of unsaturated benzoic acid derivative (1.0 equiv) in anhydrous DCM (0.25 M) were added 2-aminopyridine (1.1 equiv), *N*,*N*-dimethyl-4-aminopyridine (DMAP, 0.1 equiv) at 0℃. Then 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 1.2 equiv) in DCM (20 mL) was dropwise added to the solution under an argon atmosphere. After the addition, the reaction was then warmed to room temperature, stirred for 10 hours and quenched with water (30 mL). The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic solvent was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give pure **1a** as a white solid.

b. Method B: Preparation of the Substrate 1j and 1k.[3]



Phthalicacidanhydrid (1.0 equiv), copper bromide (5 mmol%) and anhydrous THF were added to a flame-dried flask and cooled to -20 °C under N_2 atmosphere. RMgBr (1.1 equiv) was added dropwise to the mixture over 1 h. The reaction mixture was stirred overnight at -20 °C, then allowed to warm to room temperature, quenched with water, basified with aqueous NaOH (3.0 M) until pH = 12-14 and washed with diethyl ether. The resulting aqueous phase was acidified with aqueous HCl (2.0 M) until pH 1-2 and extracted twice with ethyl acetate. The combined organic layers were washed with water, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was dissolved in DCM and the solid was filtered off. The crude benzoic acid derivative was used for the next step without further purification. From benzoic acid derivative, the corresponding benzamide derivate was synthesized by the same **method A**.

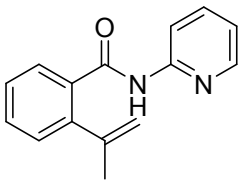
c. Method C: Preparation of the Substrate 1m.



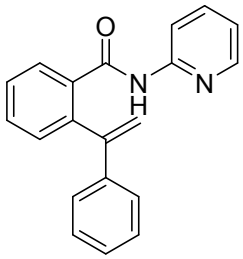
d. Preparation of the Substrate 2.[4]

To a solution of hydroxamic acid derivatives (5.0 mmol) in anhydrous DCM (50 mL), 1,1′-carbonyldiimidazole (CDI) (0.85 g, 5.25 mmol) was added slowly at room temperature and stirred for 30 min. The reaction mixture was quenched with 1 N HCl (30 mL) and extracted with anhydrous DCM (50 mL) for 3 times. The combined organic layer was evaporated under reduced pressure and purified by flash column chromatography on a silica gel column by using hexane/ethylacetate eluent to afford 3- substituted-1,4,2-dioxazol-5-one derivatives **2**. The compound **2** decomposes in column on performing the column chromatography over a prolonged time period (> 20 min).

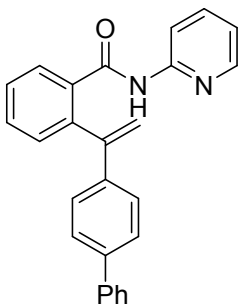
c. Characterization of Starting Substrates 1



2-(prop-1-en-2-yl)-N-(pyridin-2-yl)benzamide (1a). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.60 – 7.54 (m, 1H), 7.46 – 7.43 (m, 1H), 7.36 – 7.34 (m, 1H), 7.27 (d, J = 7.7 Hz, 1H), 6.89 – 6.87 (m, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 151.9, 147.6, 145.0, 142.1, 138.4, 134.5, 130.6, 129.0, 128.3, 127.5, 119.6, 116.5, 114.1, 23.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{15}H_{14}N_2NaO$: 261.0998, found: 221.1006.

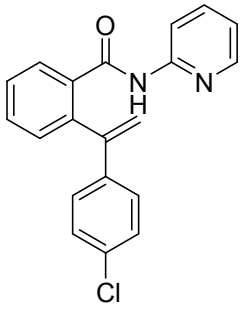


2-(1-phenylvinyl)-N-(pyridin-2-yl)benzamide (1b). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.97 – 7.84 (m, 2H), 7.71 (d, J = 6.8 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.49 – 7.39 (m, 2H), 7.20 – 7.10 (m, 5H), 6.93 – 6.86 (m, 1H), 5.75 (s, 1H), 5.43 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 151.4, 149.2, 147.5, 140.2, 138.1, 135.6, 131.0, 130.9, 128.7, 128.3, 128.1, 128.1, 128.0, 127.1, 119.6, 116.4, 113.8. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO$: 323.1155, found: 323.1152.

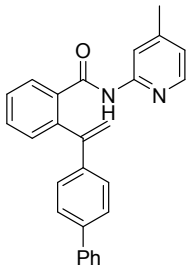


2-(1-([1,1'-biphenyl]-4-yl)vinyl)-N-(pyridin-2-yl)benzamide (1c). off white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 4.9 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.44 (t, J = 7.4 Hz, 4H), 7.38 – 7.33 (m, 4H), 7.28 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 6.83 (t, J = 6.1 Hz, 1H), 5.77 (s, 1H), 5.40

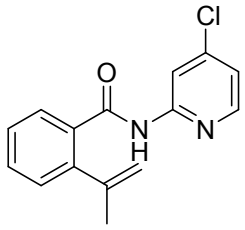
(s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 151.6, 148.7, 147.5, 140.7, 140.6, 140.2, 139.2, 138.1, 135.8, 131.0, 130.9, 128.7, 128.6, 128.3, 127.6, 127.3, 127.0, 126.9, 119.6, 116.4, 113.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{26}H_{20}N_2NaO$: 399.1468, found: 399.1466.



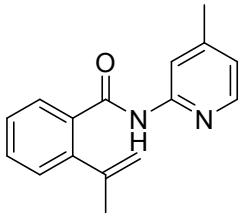
2-(1-(4-chlorophenyl)vinyl)-N-(pyridin-2-yl)benzamide (1d). yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 3.3 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.53 – 7.51 (m, 1H), 7.46 – 7.43 (m, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.11 – 7.04 (m, 4H), 6.90 – 6.85 (m, 1H), 5.68 (s, 1H), 5.38 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 151.5, 148.1, 147.5, 139.8, 138.8, 138.2, 135.7, 133.8, 130.9, 129.0, 128.5, 128.5, 128.3, 128.2, 119.7, 116.8, 113.8. HRMS (ESI): m/z: $[M + Na]^+$ $C_{20}H_{15}ClN_2NaO$: 357.0765, found: 357.0763.



2-(1-([1,1'-biphenyl]-4-yl)vinyl)-N-(4-methylpyridin-2-yl)benzamide (1e). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 – 8.51 (m, 1H), 7.92 – 7.89 (m, 1H), 7.77 – 7.70 (m, 2H), 7.56 – 7.53 (m, 1H), 7.49 – 7.44 (m, 4H), 7.40 – 7.35 (m, 4H), 7.29 – 7.23 (m, 3H), 6.75 (d, J = 5.0 Hz, 1H), 5.83 (s, 1H), 5.47 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 151.3, 149.5, 148.7, 147.2, 140.7, 140.5, 140.1, 139.1, 135.6, 131.0, 131.0, 128.7, 128.4, 128.0, 127.5, 127.3, 126.9, 126.8, 120.9, 116.4, 114.2, 21.2. HRMS (ESI): m/z: $[M + Na]^+$ $C_{27}H_{22}N_2NaO$: 413.1624, found: 413.1625.

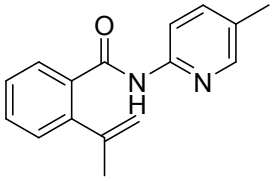


N-(4-chloropyridin-2-yl)-2-(prop-1-en-2-yl)benzamide (1f). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.47 (s, 1H), 7.71 – 7.64 (m, 2H), 7.49 – 7.46 (m, 1H), 7.39 – 7.37 (m, 1H), 7.29 (d, J = 7.6 Hz, 1H), 6.96-6.94 (m, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168, 152.6, 148.4, 146, 145.1, 142.2, 133.7, 131.0, 129.1, 128.5, 127.6, 120.2, 116.7, 114.2, 24.1. HRMS (ESI): m/z: $[M + Na]^+$ $C_{15}H_{13}ClN_2NaO$: 295.0609, found: 295.0609.

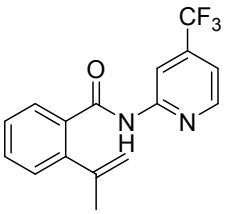


N-(4-methylpyridin-2-yl)-2-(prop-1-en-2-yl)benzamide (1g). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.26 (s, 1H), 7.63 – 7.50 (m, 1H), 7.42 – 7.39 (m, 1H), 7.35 – 7.20 (m, 2H), 6.94 – 6.81 (m,

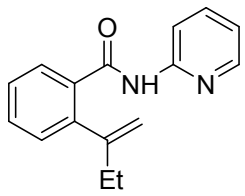
1H), 6.56 (s, 1H), 5.16 (s, 1H), 4.95 (s, 1H), 2.30 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 152.3, 149.8, 146.8, 144.4, 142.0, 135.4, 130.1, 128.71, 128.0, 127.3, 120.6, 116.1, 114.7, 23.7, 21.3. HRMS (ESI): m/z: $[M + Na]^+$ $C_{16}H_{16}N_2NaO$: 275.1155, found: 275.1153.



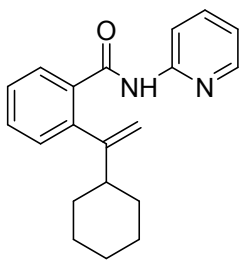
N-(5-methylpyridin-2-yl)-2-(prop-1-en-2-yl)benzamide (1h). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.40 – 7.30 (m, 1H), 7.26 (t, J = 7.1 Hz, 1H), 6.86 (s, 1H), 5.15 (s, 1H), 4.93 (s, 1H), 2.07 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 150.1, 147.3, 144.5, 142.1, 138.9, 135.4, 130.1, 128.7, 128.7, 128.1, 127.3, 116.2, 113.7, 23.7, 17.7. HRMS (ESI): m/z: $[M + Na]^+$ $C_{16}H_{16}N_2NaO$: 275.1155, found: 275.1156.



2-(prop-1-en-2-yl)-N-(4-(trifluoromethyl)pyridin-2-yl)benzamide (1i). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.69 (s, 1H), 7.75 – 7.64 (m, 2H), 7.50 – 7.47 (m, 1H), 7.40 – 7.37 (m, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 4.9 Hz, 1H), 5.27 (s, 1H), 5.07 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 152.7, 148.7, 144.9, 142.3, 140.6 (q, J = 33.9 Hz), 133.8, 131.1, 129.1, 128.5, 127.7, 122.7 (q, J = 273.5 Hz), 116.7, 115.3 (q, J = 3.4 Hz), 110.1 (q, J = 3.9 Hz), 24.0. HRMS (ESI): m/z: $[M + Na]^+$ $C_{16}H_{13}F_3N_2NaO$: 329.0872, found: 329.0873.

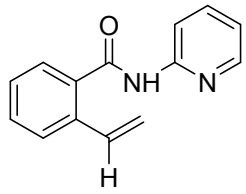


2-(but-1-en-2-yl)-N-(pyridin-2-yl)benzamide (1j). white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 – 8.89 (m, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.98 – 7.83 (m, 1H), 7.77 – 7.64 (m, 2H), 7.46 – 7.43(m, 1H), 7.38 – 7.36 (m, 1H), 7.30 – 7.20 (m, 1H), 7.06 – 6.88 (m, 1H), 5.49 – 5.14 (m, 1H), 5.15 – 5.13(m, 1H), 2.41 – 2.37(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 151.8, 151.5, 147.8, 141.8, 138.3, 134.2, 130.7, 129.6, 128.6, 127.5, 119.7, 114.5, 114.0, 30.6, 12.6. HRMS (ESI): m/z: m/z: $[M + Na]^+$ $C_{16}H_{16}N_2NaO$: 275.1155, found: 275.1152.

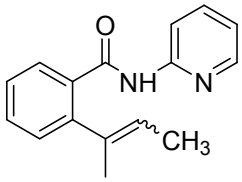


2-(1-cyclohexylvinyl)-N-(pyridin-2-yl)benzamide (1k). white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.22 – 8.21(m, 1H), 7.83 – 7.81 (m, 1H), 7.75 – 7.64 (m, 1H), 7.48 – 7.34 (m, 2H), 7.19 (dd, J = 7.4, 1.4 Hz, 1H), 7.03 – 7.00 (m, 1H), 5.32 – 5.31 (m, 1H), 5.20 (s, 1H), 2.17 – 2.10 (m, 1H), 1.78 – 1.74 (m, 2H), 1.66 – 1.65

(m, 2H), 1.61 – 1.59 (m, 1H), 1.15 – 1.08 (m, 5H). ^{13}C NMR (100MHz, $CDCl_3$) δ 167.4, 156.2, 151.6, 148.1, 142.1, 138.4, 133.4, 130.9, 130.4, 129.3, 127.7, 119.9, 113.9, 113.6, 45.3, 32.2, 26.6, 26.2. HRMS (ESI): m/z: m/z: $[M + Na]^+$ $C_{20}H_{22}N_2NaO$: 329.1624, found: 392.1624.



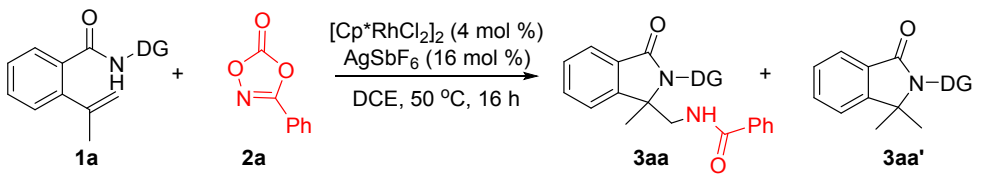
N-(pyridin-2-yl)-2-vinylbenzamide (1l). white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.78 (s, 1H), 7.73 – 7.67 (m, 1H), 7.59 – 7.55 (m, 2H), 7.46 – 7.42 (m, 1Hz), 7.33 – 7.29 (m, 1H), 7.09 (dd, J = 17.4, 11.0 Hz, 1H), 6.95 – 6.92 (m, 1H), 5.70 (dd, J = 17.4, 0.8 Hz, 1H), 5.37 (dd, J = 11.0, 0.9 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ168.1, 151.7, 147.7, 138.5, 136.4, 135.1, 134.2, 130.8, 127.9, 127.6, 126.7, 119.9, 117.4, 114.3. HRMS (ESI): m/z: m/z: $[M + Na]^+$ $C_{14}H_{12}N_2NaO$: 247.0842, found:247.0844.



2-(but-2-en-2-yl)-N-(pyridin-2-yl)benzamide (1m). white solid (*E*:*Z* = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.36 (d, J = 8.3 Hz, 1H), 8.07 – 8.06 (m, 1H), 7.89 (dd, J = 7.8, 1.4 Hz, 1H), 7.72 – 7.68 (m, J = 8 1H), 7.49 – 7.46 (m, 1H), 7.38 – 7.36 (m, 1H), 7.16 – 7.15 (m, 1H), 6.99 – 6.97 (m, 1H), 5.78 (dddd, J = 8.4, 6.9, 5.3, 1.6 Hz, 1H), 2.09 – 2.00 (m, 3H), 1.55 – 1.54 (m, 3H). ^{13}C NMR (150MHz, $CDCl_3$) δ 166.9, 151.9, 148.0, 140.5, 138.2, 136.9, 133.7, 131.2, 129.8, 129.2, 127.3, 124.5, 119.7, 114.1, 25.7, 14.9. HRMS (ESI): m/z: m/z: $[M + Na]^+$ $C_{16}H_{16}N_2NaO$: 275.1155, found: 275.1157.

3. General procedure for the catalysis

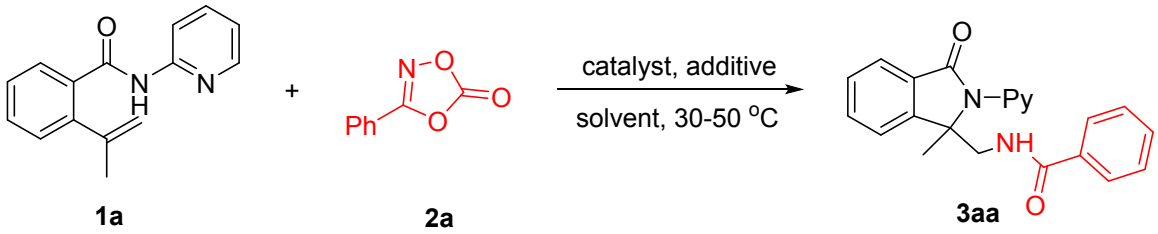
a. Table S1. Modification of the Directing Group.[a]



Entry	DG	additive	*T* (°C)	Yield (%)[b](**3aa**/**3aa'**)
1	OMe	PivOH	50	-/74
2	OMe	AgOAc	50	-/54
3	OMe	-	50	-/84
4	NHPh	-	100	-/37
5	NHPh	$Zn(OAc)_2$	100	-/24
6	2-Py	PivOH	100	40/18
7	2-Py	$Zn(OAc)_2$	100	35/24
8	2-Py	-	100	44/-

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), Acid (2.0 equiv), DCE (1.5 mL), *T* °C, 16 h under air in a sealed tube. [b]Yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Optimization Studies on Rh-Catalyzed Amidation With Dioxazolones [a].



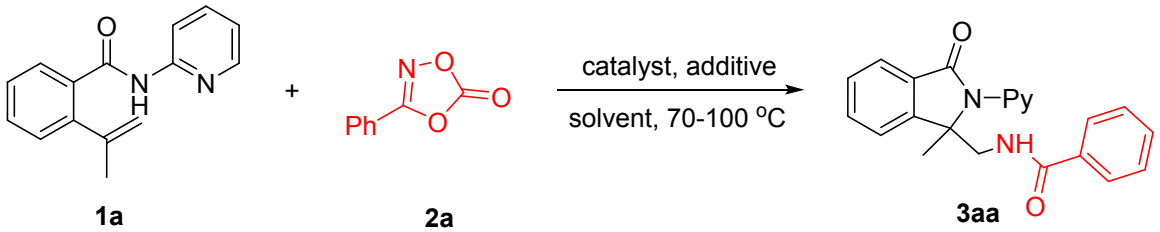
1a **2a** **3aa**

entry	catalyst (mol%)	solvent	*T* (°C)	yield (%)[b]
1	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8)	DCE[d]	30	-.
2	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8)	DCE[d]	40	-.
3	$AgSbF_6$ (16)	DCE[d]	30	-
4	$[Cp^*RhCl_2]_2$ (4)	DCE[d]	30	-.
5	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	DCE[d]	30	47
6	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	DCE	30	62
7	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	DCE	50	90 (83[c])
8	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	DCE	70	52
9	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	DCM	50	80

10	[Cp*RhCl$_2$]$_2$ (4)/AgSbF$_6$ (16)	DCM[d]	50	80
11	[Cp*RhCl$_2$]$_2$ (4)/AgSbF$_6$ (16)	DMF	50	76
12	[Cp*RhCl$_2$]$_2$ (4)/AgSbF$_6$ (16)	MeOH	50	-
13	[Cp*RhCl$_2$]$_2$ (4)/AgSbF$_6$ (16)	THF	50	58
14	[Cp*RhCl$_2$]$_2$ (4)/AgSbF$_6$ (16)	MeCN	50	-
15	[Cp*RhCl$_2$]$_2$ (4)/AgBF$_4$ (16)	DCE	50	67
16	[Cp*RhCl$_2$]$_2$ (4)/AgPF$_6$ (16)	DCE	50	-
17	[Cp*RhCl$_2$]$_2$ (4)/AgOTf (16)	DCE	50	83
18	[Cp*RhCl$_2$]$_2$ (4)/AgNTf$_2$ (16)	DCE	50	-

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.1 mmol), and **2a** (0.2 mmol) in a solvent (1.5 mL) for 16 h under air. [b]Yield was determined by ^{1}H NMR spectroscopy. [c]Isolated yield in parenthesis. [d]Under N_2.

Table S3. Optimization Studies on Co-Catalyzed Amidation With Dioxazolones [a].



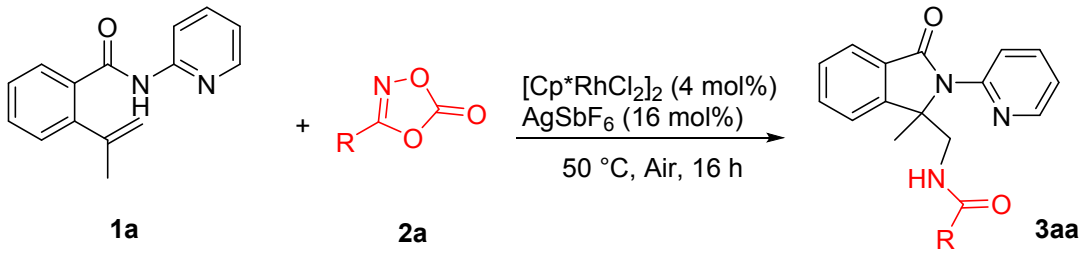
1a **2a** **3aa**

entry	catalyst (mol%)	Additive (equiv)	solvent	*T* (℃)	yield(%)[b]
1	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	AgOAc (0.2)	DCE	70	32
2	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	PivOH (0.5)	DCE	70	22
3	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	AgOAc (1.0)	DCE	70	23
4	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	AgOAc (1.0)	DCE	100	43
5	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	PivOH (1.0)	DCE	100	27
6	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	PivOH (2.0)	DCE	100	42
7	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	Zn(OAc)$_2$ (2.0)	DCE	100	52
8	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	PivOH (2.0)	TFE	100	78
9	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	Zn(OAc)$_2$ (2.0)	TFE	100	84(76[c])
10	Cp*Co(CO)I$_2$ (8) + AgSbF$_6$ (16)	Zn(OAc)$_2$ (2.0)	MeCN	100	73
11	Cp*Co(CO)I$_2$ (8) + AgBF$_4$ (16)	Zn(OAc)$_2$ (2.0)	TFE	100	-

12	Cp*Co(CO)I_2 (8)+ $AgPF_6$ (16)	$Zn(OAc)_2$ (2.0)	TFE	100	-
13	Cp*Co(CO)I_2 (8) + AgOTf (16)	$Zn(OAc)_2$ (2.0)	TFE	100	-

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.1 mmol), and **2a** (0.2 mmol) in a solvent (1.5 mL) for 16 h. [b]Yield was determined by ^{1}H NMR spectroscopy. [c]Isolated yield.

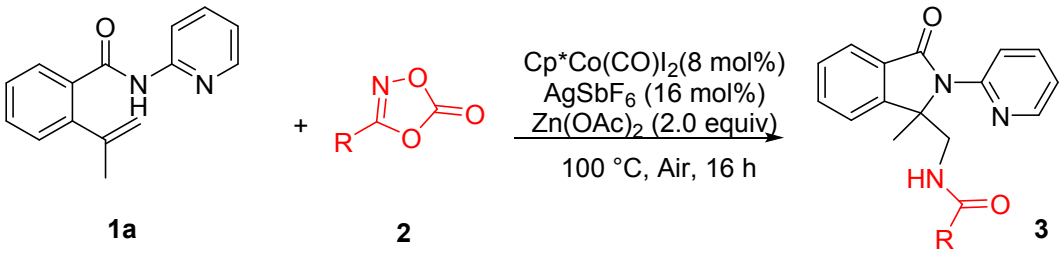
b. Cp*Rh(III)-Catalyzed Pyridine-Directed Amidation With Dioxazolones



1a **2a** **3aa**

An oven-dried 35 mL round bottom pressure tube was equipped with a magnetic stir bar and was charged with the substrate **1** (0.1 mmol, 1.0 equiv), substrate **2** (0.2 mmol, 2.0 equiv), catalyst $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol, 4.0 mol %), and $AgSbF_6$ (5.5 mg, 0.016 mmol, 16.0 mol %) under air atmosphere, then the mixture was dissolved in dry 1,2-dichloroethane (DCE, 1.5 mL). Then the mixture was heated to 50 °C under air atmosphere. After stirring for 16 hours, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to give the desired product.

c. Cp*Co(III)-Catalyzed Pyridine-Directed Amidation With Dioxazolones (3c)

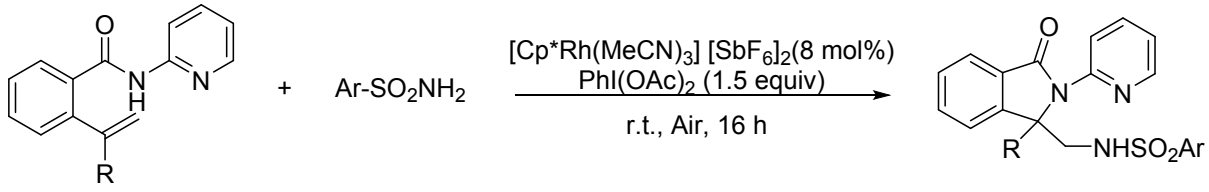


1a **2** **3**

An oven-dried 35 mL round bottom pressure tube was equipped with a magnetic stir bar and was charged with olefin **1** (0.1 mmol, 1.0 equiv), substrate **2** (0.2 mmol, 2.0 equiv), catalyst Cp*Co(CO)I_2 (3.8 mg, 0.008 mmol, 8.0 mol %), $AgSbF_6$ (5.5 mg, 0.016 mmol, 16.0 mol %), and $Zn(OAc)_2$ (36.7mg, 0.2 mmol, 2.0 equiv) under air atmosphere. The mixture was dissolved in dry 2,2,2-trifluoroethanol (TFE, 1.5 mL). Then the mixture was heated to 100 °C under air

atmosphere. After stirring for 16 hours, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to give the desired product.

d. Cp*Rh(III)-Catalyzed Pyridine-Directed Amidation With Sulfonamide (3d)

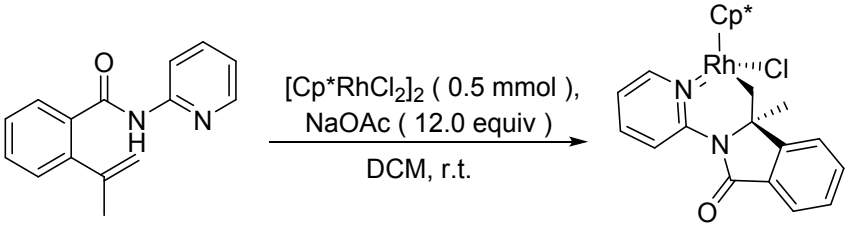


1 **4**

An oven-dried 35 mL round bottom pressure tube was equipped with a magnetic stir bar and was charged with the substrate **1** (0.1 mmol, 1.0 equiv), sulfonamide (0.1 mmol, 1.0 equiv), $PhI(OAc)_2$ (0.15 mmol, 1.5 equiv), and catalyst $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (6.7 mg, 0.008 mmol, 8.0 mol %) under air atmosphere. Then the mixture was dissolved in dry 1,2-dichloromethane (DCM, 1.5 mL). Then the mixture was stirred at room temperature under air atmosphere. After stirring for 16 hours, the solvent of the reaction mixture was removed by rotary evaporation. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to give the desired product.

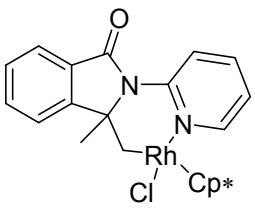
4. Mechanistic Studies.

a. Preparation of the Rh(III)-Complex 5



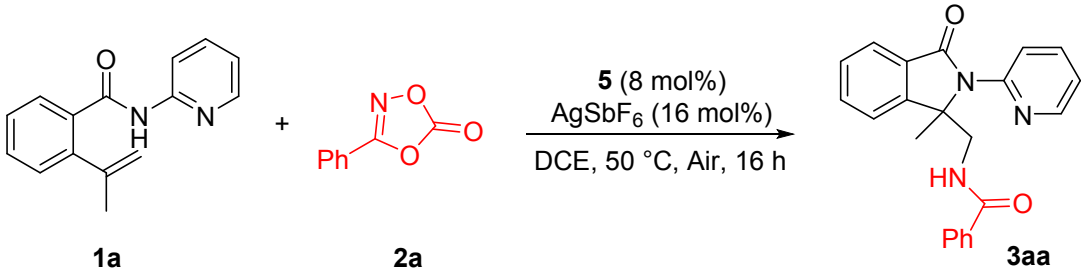
5 90% yield

To an oven-dried 35 mL round bottom pressure tube was equipped with a magnetic stir bar was added substrate **1** (0.1 mmol, 1.0 equiv), catalyst $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05mmol, 0.5 equiv), and NaOAc (98.4 mg, 12.0 equiv) in dichloromethane (DCM, 3 mL). After the addition, the reaction was then stirred at r.t. until the reaction was completed, as monitored by TLC. Then the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to afford the Rh(III)-complex as a red solid (92 mg, 90% yield).



Rh(III) Complex 5. red solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17 (d, J = 5.6 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.22 – 7.17 (m, 1H), 2.84 (dd, J = 9.2, 3.0 Hz, 1H), 2.70 (dd, J = 9.1, 3.5 Hz, 1H), 1.33 (s, 15H), 1.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 155.3, 154.2, 152.4, 138.2, 133.7, 128.1, 127.5, 124.2, 122.1, 120.9, 119.9, 94.5 (d, J = 6.6 Hz), 67.1, 30.9 (d, J = 26.6 Hz), 25.7, 8.6. HRMS (ESI): m/z: $[M-Cl]^+$ calculated for $C_{25}H_{28}N_2ORh$: 475.1251, found: 475.1257.

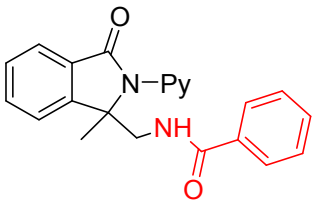
b. Catalytic activity of complex 5



1a **2a** **3aa**

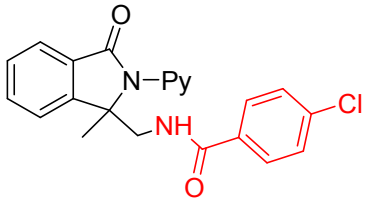
An oven-dried 35 mL round bottom pressure tube, which was equipped with a magnetic stir bar and charged with the substrate **1a** (0.1 mmol, 1.0 equiv), the substrate **2a** (0.2 mmol, 2.0 equiv), Complex **5** (4.1 mg, 0.008 mmol, 8.0 mol %), and $AgSbF_6$ (5.5 mg, 0.016 mmol, 16.0 mol %) under air atmosphere. To the mixture was added dry 1,2-dichloroethane (DCE, 1.5 mL). Then the mixture was heated to 50 °C under air atmosphere. After stirring for 16 hours, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to give the desired product (22.8 mg, 64% yield).

5. NMR Analytical data for new compounds



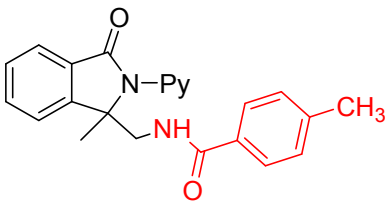
N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3aa)

The title compound **3aa** was synthesized according to the **3b** and **3c**. The product **3aa** was isolated as white solid. Yield: **3b**: 83% (29.1 mg); and **3c**: 76% (26.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 3.8 Hz, 1H), 8.15 (s, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.85 (t, J = 7.1 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 4.42 (dd, J = 14.1, 6.2 Hz, 1H), 4.06 (dd, J = 14.1, 6.0 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 167.4, 150.9, 149.1, 147.8, 138.5, 134.8, 133.3, 131.3, 130.3, 128.9, 128.5, 126.9, 124.0, 122.1, 121.2, 120.5, 68.9, 47.4, 21.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{19}NaN_3O_2$:380.1369,found:380.1375.



4-chloro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ab)

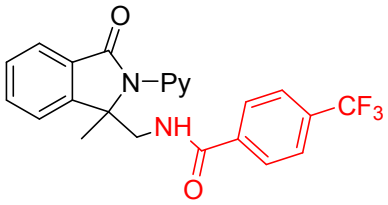
The title compound **3ab** was synthesized according to the **3b** and **3c**. The product **3ab** was isolated as white solid. Yield: **3b**: 90% (35.3 mg); and **3c**: 47% (18.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 3.4 Hz, 1H), 8.24 (s, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.67 (d, J = 4.2 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.34 (d, J = 8.9 Hz, 2H), 7.25 – 7.23 (m, 1H), 4.38 (dd, J = 14.1, 6.1 Hz, 1H), 4.04 (dd, J = 14.1, 6.0 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 166.344, 150.844, 149.0, 147.8, 138.6, 137.5, 133.4, 133.1, 130.3, 128.9, 128.8, 128.3, 124.0, 122.1, 121.4, 120.7, 68.8, 47.4, 21.8. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}ClNaN_3O_2$: 414.0980, found: 414.0988.



4-methyl-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ac)

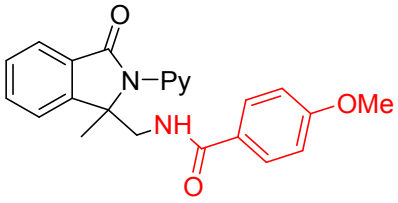
The title compound **3ac** was synthesized according to the **3b** and **3c**. The product **3ac** was isolated as white solid. Yield: **3b**: 71% (26.4 mg); and **3c**: 65% (24.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 – 8.50 (M, 1H), 8.11 (s, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.71 – 7.65 (m, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 (d, J = 7.9 Hz, 2H), 4.42 (dd, J = 14.1, 6.2 Hz, 1H), 4.04 (dd, J = 14.1, 5.9 Hz, 1H), 2.36 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 167.3, 151.0, 149.2, 147.8, 141.7, 138.5, 133.3, 131.9, 130.3, 129.2, 128.8, 126.9, 123.9, 122.1, 121.2, 120.4, 68.9, 47.3, 21.9, 21.4. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_2$: 394.1526, found: 394.1532



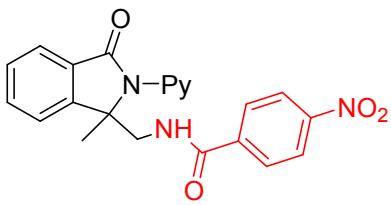
N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)-4-(trifluoromethyl)benzamide (3ad)

The title compound **3ad** was synthesized according to the **3b** and **3c**. The product **3ad** was isolated as white solid. Yield: **3b**: 71% (30.2 mg); and **3c**: 28% (11.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 3.1 Hz, 1H), 8.38 (s, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.69 – 7.67 (m, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.52 – 7.50 (m, 1H), 7.27 – 7.23 (m, 1H), 4.40 (dd, J = 14.1, 6.1 Hz, 1H), 4.06 (dd, J = 14.1, 6.0 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 166.1, 150.8, 148.9, 147.7, 138.6, 138.1, 133.4, 133.1 (q, J = 32.6 Hz), 130.3, 128.9, 127.3, 125.5 (q, J = 3.1 Hz), 124.0, 123.6 (q, J = 272.5 Hz), 122.1, 121.4, 120.8, 68.7, 47.5, 21.8. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{18}F_3N_3NaO_2$: 448.1243, found: 448.1252



4-methoxy-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ae)

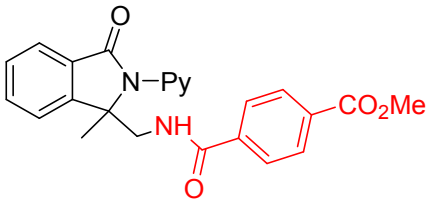
The title compound **3ae** was synthesized according to the **3b** and **3c**. The product **3ae** was isolated as white solid. Yield: **3b**: 84% (32.5 mg); and **3c**: 28% (14.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 – 8.49 (m, 1H), 8.05 (d, J = 8.1 Hz, 1H), 8.00 (s, 1H), 7.88 (d, J = 7.3 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.70 – 7.65 (m, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.24 – 7.21 (m, 1H), 6.87 (d, J = 8.8 Hz, 2H), 4.40 (dd, J = 14.1, 6.2 Hz, 1H), 4.05 (dd, J = 14.1, 6.0 Hz, 1H), 3.81 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 166.8, 162.1, 151.0, 149.2, 147.8, 138.5, 133.3, 130.3, 128.8, 128.6, 127.1, 123.9, 122.1, 121.2, 120.5, 113.7, 68.9, 55.4, 47.3, 21.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_3$: 410.1475, found: 410.1481.



N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)-4-nitrobenzamide (3af)

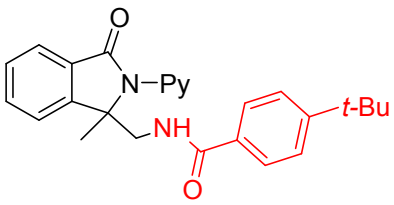
The title compound **3af** was synthesized according to the **3b** and **3c**. The product **3af** was isolated as white solid.

Yield: **3b**: 32% (13.0 mg); and **3c**: <5% (trace). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 – 8.46 (m, 2H), 8.24 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.2 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.54 – 7.49 (m, 1H), 7.29 – 7.25 (m, 2H), 4.38 (dd, J = 14.1, 6.1 Hz, 1H), 4.06 (dd, J = 14.1, 6.0 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 165.3, 150.8, 148.8, 147.7, 140.4, 138.7, 133.4, 130.2, 129.1, 128.0, 124.1, 123.8, 122.1, 121.5, 121.0, 68.6, 47.7, 21.8. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}N_4NaO_4$: 425.1220, found: 425.1228.



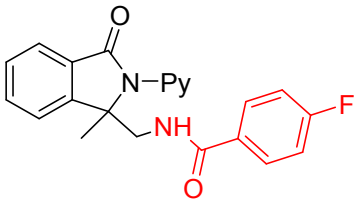
methyl-4-(((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)carbamoyl)benzoate (3ag)

The title compound **3ag** was synthesized according to the **3b** and **3c**. The product **3ag** was isolated as white solid. Yield: **3b**: 72% (30.0 mg); and **3c**: 34% (14.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 3.3 Hz, 1H), 8.45 (s, 1H), 8.06 – 8.04 (m, 3H), 7.89 (d, J = 7.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 4.4 Hz, 2H), 7.52 – 7.50 (m, 1H), 7.25-7.23 (m, 1H), 4.44 (dd, J = 14.1, 6.3 Hz, 1H), 4.00 (dd, J = 14.1, 5.6 Hz, 1H), 3.92 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 166.5, 166.3, 150.9, 149.0, 147.7, 138.8, 138.6, 133.4, 132.6, 130.3, 129.8, 128.9, 126.1, 124.1, 122.1, 121.3, 120.6, 68.7, 52.3, 47.6, 21.7. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{24}H_{21}N_3NaO_4$: 438.1424, found: 438.1432.



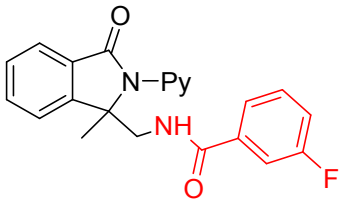
4-(tert-butyl)-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ah)

The title compound **3ah** was synthesized according to the **3b** and **3c**. The product **3ah** was isolated as white solid. Yield: **3b**: 65% (27.0 mg); and **3c**: 64% (26.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 – 8.53 (m, 1H), 8.06 – 8.03 (m, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.71 – 7.65 (m, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.50 – 7.48 (m, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.25 – 7.23 (m, 1H), 4.41 (dd, J = 14.1, 6.1 Hz, 1H), 4.07 (dd, J = 14.1, 6.1 Hz, 1H), 1.62 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 167.2, 154.8, 150.9, 149.2, 147.9, 138.5, 133.3, 131.8, 130.3, 128.8, 126.7, 125.4, 124.0, 122.1, 121.2, 120.5, 68.9, 47.2, 34.9, 31.2, 21.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{26}H_{27}N_3NaO_2$: 436.1995, found: 436.2000.



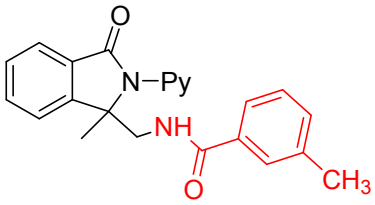
4-fluoro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ai).

The title compound **3ai** was synthesized according to the **3b** and **3c**. The product **3ai** was isolated as white solid. Yield: **3b**: 85% (31.7 mg); and **3c**: 74% (27.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.49 (m, 1H), 8.14 (s, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.68 (d, J = 4.1 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.51 – 7.47 (m, 1H), 7.25 – 7.23 (m, 1H), 7.05 (t, J = 8.6 Hz, 2H), 4.37 (dd, J = 14.1, 6.1 Hz, 1H), 4.07 (dd, J = 14.1, 6.2 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 166.3, 164.1 (d, J = 251.6 Hz), 150.9, 149.0, 147.8, 138.6, 133.3, 130.9 (d, J = 3.1 Hz), 130.3, 129.1 (d, J = 8.9 Hz), 128.9, 124.0, 122.1, 121.3, 120.7, 115.5 (d, J = 21.9 Hz), 68.83, 47.39, 21.85. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}FN_3NaO_2$: 398.1275, found: 398.1284.



3-fluoro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3aj)

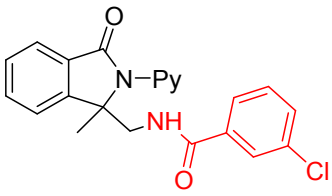
The title compound **3aj** was synthesized according to the **3b** and **3c**. The product **3aj** was isolated as white solid. Yield: **3b**: 97% (36.5 mg); and **3c**: 52% (19.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 3.7 Hz, 1H), 8.39 (s, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.71 – 7.66 (m, 2H), 7.52 – 7.49 (m, 2H), 7.44 – 7.39 (m, 1H), 7.26 – 7.24 (m, 2H), 7.17 – 7.13 (m, 1H), 4.44 (dd, J = 14.1, 6.2 Hz, 1H), 4.02 (dd, J = 14.1, 5.7 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 166.1, 162.7 (d, J = 247.5 Hz), 150.8, 149.0, 147.7, 138.6, 137.1 (d, J = 6.8 Hz), 133.4, 130.2 (d, J = 5.2 Hz), 130.1, 128.9, 124.1, 122.3 (d, J = 3.0 Hz), 122.1, 121.3, 120.6, 118.3 (d, J = 21.3 Hz), 114.3 (d, J = 22.8 Hz), 68.7, 47.6, 21.7. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}FN_3NaO_2$: 398.1275, found: 398.1275.



3-methyl-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3ak)

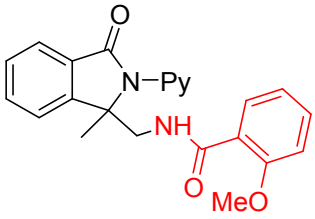
The title compound **3ak** was synthesized according to the **3b** and **3c**. The product **3ak** was isolated as white solid. Yield: **3b**: 82% (30.5 mg); and **3c**: 57% (21.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 3.2 Hz, 1H), 8.15 (s, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.71 – 7.66

(m, 2H), 7.51 – 7.48 (m, 2H), 7.44 – 7.39 (m, 1H), 7.28 – 7.24 (m, 2H), 7.24 – 7.21 (m, 1H), 4.44 (dd, J = 14.1, 6.2 Hz, 1H), 4.02 (dd, J = 14.1, 5.7 Hz, 1H), 2.36 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 167.5, 151.0, 149.2, 147.7, 138.5, 138.3, 134.8, 133.3, 132.0, 130.3, 128.9, 128.4, 127.7, 124.0, 123.7, 122.1, 121.1, 120.4, 68.9, 47.4, 21.9, 21.4. HRMS (ESI): m/z: $[M + Na]^+$ calculated for : $C_{23}H_{21}NNaO_2$: 394.1526, found: 394.1525.



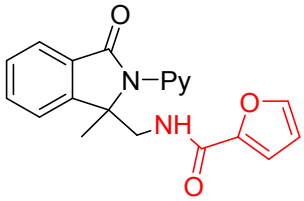
3-chloro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3al)

The title compound **3al** was synthesized according to the **3b** and **3c**. The product **3al** was isolated as white solid. Yield: **3b**: 74% (29.1 mg); and **3c**: 36% (14.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 – 8.52 (m, 2H), 8.05 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.72 – 7.65 (m, 3H), 7.55 – 7.49 (m, 2H), 7.45 – 7.41 (m, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 4.43 (dd, J = 14.2, 6.5 Hz, 1H), 3.92 (dd, J = 14.2, 5.3 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 166.0, 150.8, 149.0, 147.7, 138.6, 136.6, 134.7, 133.4, 131.3, 130.2, 129.8, 129.0, 127.3, 124.9, 124.1, 122.1, 121.3, 120.6, 68.7, 47.8, 21.6. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}ClN_3NaO_2$: 414.0980, found: 414.0976.



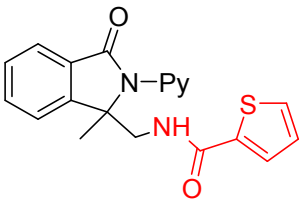
2-methoxy-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3am)

The title compound **3am** was synthesized according to the **3b** and **3c**. The product **3am** was isolated as white solid. Yield: **3b**: 74% (29.1 mg); and **3c**: 36% (14.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.49 (m, 1H), 8.20 (d, J = 8.3 Hz, 1H), 7.99 (s, 1H), 7.93 (dd, J = 7.8, 1.9 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.65 – 7.64 (m, 2H), 7.49 – 7.42 (m, 1H), 7.32 – 7.29 (m, 1H), 7.18 – 7.15 (m, 1H), 6.95 – 6.88 (m, 1H), 6.79 (d, J = 8.3 Hz, 1H), 4.53 – 4.48 (m, 2H), 3.61 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.80 , 157.38 , 149.22 , 147.99 , 137.87 , 133.17 , 132.47 , 131.96 , 130.72 , 128.64 , 123.66 , 121.81 , 121.27 , 120.89 , 120.58 , 118.91 , 111.18 , 68.75 , 55.55 , 46.35 , 23.30 . HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_3$: 410.1475, found: 410.1475.



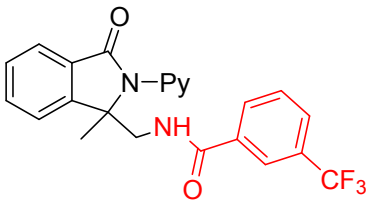
N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)furan-2-carboxamide (3an)

The title compound **3an** was synthesized according to the **3b** and **3c**. The product **3an** was isolated as white solid. Yield: **3b**: 87% (30.1 mg); and **3c**: 30% (10.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 – 8.58 (m, 1H), 8.42 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.68 (d, J = 6.9 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.42 (s, 1H), 7.23 – 7.21 (m, 1H), 7.01 (d, J = 3.4 Hz, 1H), 6.45 – 6.44 (m, 1H), 4.49 (dd, J = 14.2, 6.8 Hz, 1H), 3.94 (dd, J = 14.2, 5.7 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 158.2, 150.9, 149.1, 148.1, 147.6, 143.8, 138.4, 133.3, 130.3, 128.8, 124.1, 122.0, 120.9, 119.8, 114.1, 112.0, 68.7, 46.8, 21.9. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{20}H_{17}N_3NaO_3$: 370.1162, found: 370.1163.



N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)thiophene-2-carboxamide (3ao)

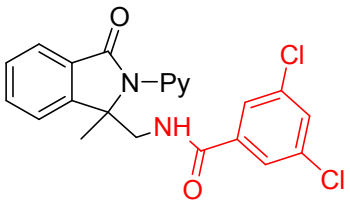
The title compound **3ao** was synthesized according to the **3b** and **3c**. The product **3ao** was isolated as white solid. Yield: **3b**: 93% (33.9 mg); and **3c**: 25% (9.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, J = 3.1 Hz, 1H), 8.28 (s, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.71 – 7.64 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 (d, J = 3.2 Hz, 1H), 7.42 (d, J = 4.9 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.06 – 7.01 (m, 1H), 4.44 (dd, J = 14.2, 6.7 Hz, 1H), 3.89 (dd, J = 14.2, 5.2 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 161.7, 150.9, 149.2, 147.7, 139.0, 138.5, 133.4, 130.2, 129.5, 128.9, 128.2, 127.5, 124.1, 122.1, 121.1, 120.3, 68.7, 47.6, 21.7. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{20}H_{17}N_3NaO_2S$: 386.0934, found: 386.0936.



N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)-3-(trifluoromethyl)benzamide (3ap)

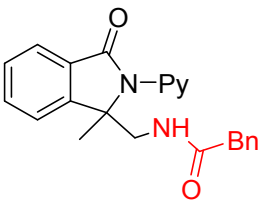
The title compound **3ap** was synthesized according to the **3b** and **3c**. The product **3ap** was isolated as white solid. Yield: **3b**: 59% (25.0 mg); and **3c**: <5% (trace). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.50 – 8.49 (m, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.99 (s, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.73 (d, J = 7.8 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.57 – 7.51 (m, 2H), 7.26 – 7.24 (m, 1H), 4.46 (dd, J = 14.2, 6.6 Hz, 1H), 3.92 (dd, J = 14.2, 5.2 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 165.9, 150.8, 149.0, 147.6, 138.7, 135.7, 133.4, 131.1 (q, J = 32.7 Hz), 130.2, 130.1, 129.2, 129.0, 127.9 (q, J = 3.5 Hz), 124.1, 124.0 (q, J = 3.8 Hz), 123.7(q, J = 272.5 Hz),

122.1, 121.3, 120.7, 68.67, 47.92, 21.57. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{18}F_3N_3NaO_2$: 448.1243, found: 448.1244.



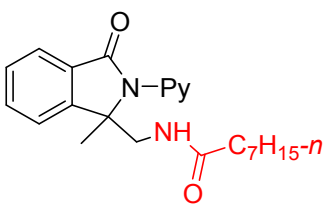
3,5-dichloro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (3aq)

The title compound **3aq** was synthesized according to the **3b** and **3c**. The product **3aq** was isolated as white solid. Yield: **3b**: 66% (28.2 mg); and **3c**: 42% (17.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.54 – 8.53 (m, 1H), 8.05 – 8.04(m, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.72 – 7.70 (m, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 2.0 Hz, 2H), 7.55 – 7.53 (m, 1H), 7.46 (t, J = 1.9 Hz, 1H), 7.28 – 7.25 (m, 2H), 4.45 (dd, J = 14.2, 7.1 Hz, 1H), 3.76 (dd, J = 14.2, 4.6 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 164.7, 150.7, 148.9, 147.5, 138.8, 137.7, 135.4, 133.5, 131.2, 130.1, 129.1, 125.6, 124.2, 122.1, 121.4, 120.7, 68.6, 48.3, 21.3. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{17}Cl_2N_3NaO_2$: 448.0590, found: 448.0589.



N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)-3-phenylpropanamide (3ar)

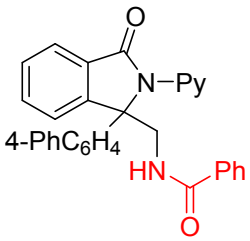
The title compound **3ar** was synthesized according to the **3b** and **3c**. The product **3ar** was isolated as white solid. Yield: **3b**: 47% (17.5 mg); and **3c**: 39% (14.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.11 (m, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.10 – 7.08 (m, 1H), 6.98 – 6.92 (m, 2H), 6.49 (s, 1H), 4.15 (dd, J = 14.0, 5.4 Hz, 1H), 4.03 (dd, J = 14.0, 7.3 Hz, 1H), 3.38 – 3.31 (m, 2H), 1.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.68, 167.98, 150.82, 148.96, 147.69, 138.05, 134.64, 133.12, 130.39, 129.22, 128.88, 128.67, 127.07, 123.79, 122.03, 120.69, 119.54, 68.62, 46.06, 43.71, 22.55. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_2$: 394.1526, found: 394.1528.



N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)octanamide (3as)

The title compound **3as** was synthesized according to the **3b** and **3c**. The product **3as** was isolated as white solid. Yield: **3b**: 88% (33.4 mg); and **3c**: 71% (26.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.49 (m, 1H), 8.03 (d,

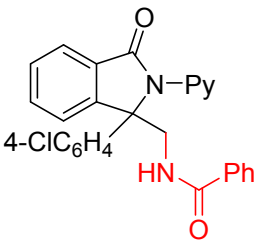
J = 8.2 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.83 – 7.81 (m, 1H), 7.67 – 7.64 (m, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.22 – 7.19 (m, 1H), 6.54 (s, 1H), 4.21 – 4.13 (m, 2H), 2.00 – 1.95 (m, 1H), 1.92 – 1.87 (m, 1H), 1.59 (s, 3H), 1.31 (m, 2H), 1.28 – 1.20 (m, 2H), 1.18 – 1.12 (m, 4H), 1.06 – 0.96 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 168.4, 151.1, 148.9, 147.9, 138.2, 133.1, 130.5, 128.7, 123.7, 122.2, 121.0, 120.1, 68.9, 45.9, 36.8, 31.6, 28.9, 28.8, 25.7, 22.6, 22.4, 14.1. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{29}N_3NaO_2$: 402.2152, found: 402.2152.



N-((1-([1,1'-biphenyl]-4-yl)-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ba)

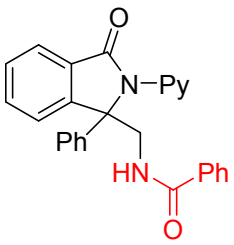
The title compound **4ba** was synthesized according to the **3b** and **3c**. The product **4ba** was isolated as white solid. Yield: **3b**: 64% (31.8 mg); and **3c**: 24% (11.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.30 – 8.29 (m, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.77 – 7.80 (m, 1H), 7.61 – 7.56 (m, 3H), 7.50 – 7.41 (m, 7H), 7.39 – 7.28 (m, 7H), 7.11 – 7.09 (m, 1H), 4.98 (dd, J = 14.0, 5.5 Hz, 1H), 4.65 (dd, J = 14.0, 6.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 167.7, 150.9, 149.1, 147.7, 140.5, 134.0, 138.5, 137.3, 134.9, 133.6, 131.3, 129.7, 128.9, 128.8, 128.7, 128.5, 127.5, 127.4, 126.9, 126.5, 124.3, 123.2, 121.2, 120.3, 73.4, 45.7.

HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{33}H_{25}N_3NaO_2$: 518.1839, Found: 518.1842.



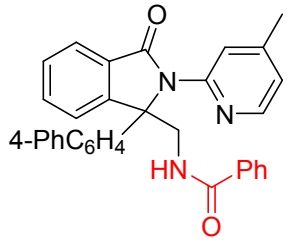
N-((1-(4-chlorophenyl)-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ca)

The title compound **4ca** was synthesized according to the **3b** and **3c**. The product **4ca** was isolated as white solid. Yield: **3b**: 81% (36.7 mg); and **3c**: 35% (15.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.27 – 8.25 (m, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.59 – 7.54 (m, 3H), 7.47 – 7.41 (m, 2H), 7.39 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.19 (s, 4H), 7.11 – 7.09 (m, 1H), 4.96 (dd, J = 14.0, 5.6 Hz, 1H), 4.56 (dd, J = 14.0, 5.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 167.6, 150.7, 148.7, 147.6, 138.6, 137.0, 134.7, 133.8, 133.7, 131.4, 129.6, 129.1, 129.0, 128.5, 127.5, 126.9, 124.1, 123.1, 121.1, 119.8, 72.9, 45.7. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{27}H_{20}ClN_3NaO_2$: 476.1136, Found: 476.1146.



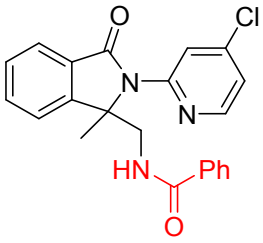
N-((1-([1,1'-biphenyl]-4-yl)-2-(4-methylpyridin-2-yl)-3-oxoisoindolin-1-yl)methyl)benzamide (4da)

The title compound **4da** was synthesized according to the **3b** and **3c**. The product **4da** was isolated as white solid. Yield: **3b**: 94% (47.7 mg); and **3c**: 41% (20.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.14 (d, J = 5.1 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.62 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.50 – 7.40 (m, 7H), 7.38 – 7.27 (m, 7H), 6.92 (d, J = 5.1 Hz, 1H), 4.96 (dd, J = 14.0, 5.6 Hz, 1H), 4.59 (dd, J = 14.0, 5.9 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 167.6, 150.8, 150.0, 149.2, 147.3, 140.4, 140.0, 137.3, 135.0, 133.6, 131.3, 129.7, 128.9, 128.8, 128.5, 127.5, 127.4, 126.9, 126.9, 126.5, 124.0, 123.2, 122.5, 120.9, 73.4, 45.9, 21.4. HRMS (ESI): m/z: [M + Na]$^+$ calculated for $C_{34}H_{27}N_3NaO_2$: 532.1995, found: 532.2002.



N-((3-oxo-1-phenyl-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ea)

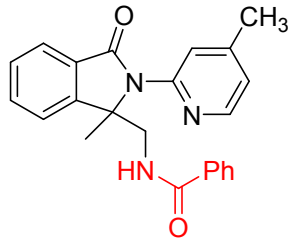
The title compound **4ea** was synthesized according to the **3b** and **3c**. The product **4ea** was isolated as white solid. Yield: **3b**: 84% (35.0 mg); and **3c**: 22% (9.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.27 – 8.26 (m, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.58 – 7.54 (m, 3H), 7.46 – 7.39 (m, 3H), 7.34 (t, J = 7.6 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.20 – 7.16 (m, 1H), 7.10 – 7.07 (m, 1H), 4.94 (dd, J = 13.9, 5.4 Hz, 1H), 4.65 (dd, J = 13.9, 6.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 167.6, 150.9, 149.2, 147.7, 138.4, 138.4, 134.9, 133.6, 131.3, 129.7, 128.9, 128.9, 128.5, 127.8, 126.9, 126.1, 124.0, 123.2, 121.1, 120.3, 73.5, 45.6. HRMS (ESI): m/z: [M + Na]$^+$ calculated for $C_{27}H_{21}N_3NaO_2$: 442.1526, found: 442.1533.



N-((2-(4-chloropyridin-2-yl)-1-methyl-3-oxoisoindolin-1-yl)methyl)benzamide (4fa)

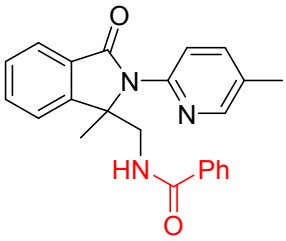
The title compound **4fa** was synthesized according to the **3b** and **3c**. The product **4fa** was isolated as white solid. Yield: **3b**: 84% (33.0 mg); and **3c**: 42% (16.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, J = 5.4 Hz, 1H), 8.29 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.57 (d, J = 7.3 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.20 – 7.19 (m, 1H), 4.53 (dd, J = 14.1, 6.0 Hz, 1H), 4.09 (dd, J = 14.1, 6.1 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$)

δ 168.3, 167.5, 152.1, 149.1, 148.1, 145.9, 134.6, 133.7, 131.4, 129.9, 129.0, 128.5, 126.8, 124.1, 122.1, 121.3, 119.4, 69.3, 47.1, 22.1. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}ClN_3NaO_2$: 414.0980, found: 414.0985.



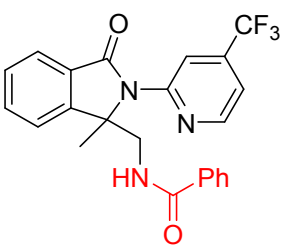
N-((1-methyl-2-(4-methylpyridin-2-yl)-3-oxoisoindolin-1-yl)methyl)benzamide (4ga)

The title compound **4ga** was synthesized according to the **3b** and **3c**. The product **4ga** was isolated as white solid. Yield: **3b**: 44% (16.4 mg); and **3c**: 20% (7.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.36 (d, J = 5.1 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.80 (s, 1H), 7.71 – 7.65 (m, 4H), 7.51 – 7.44 (m, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 5.0 Hz, 1H), 4.36 (dd, J = 14.1, 6.3 Hz, 1H), 4.02 (dd, J = 14.1, 5.9 Hz, 1H), 2.44 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 167.3, 150.8, 150.1, 149.1, 147.5, 134.8, 133.2, 131.3, 130.4, 128.8, 128.5, 126.9, 123.9, 122.6, 122.1, 121.4, 68.8, 47.5, 21.8, 21.3. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_2$: 394.1526, found: 394.1531.



N-((1-methyl-2-(5-methylpyridin-2-yl)-3-oxoisoindolin-1-yl)methyl)benzamide (4ha)

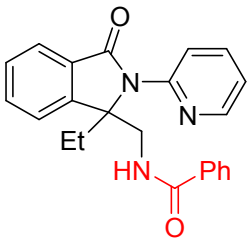
The title compound **4ha** was synthesized according to the **3b** and **3c**. The product **4ha** was isolated as white solid. Yield: **3b**: 86% (32.0 mg); and **3c**: 36% (13.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, J = 2.4 Hz, 1H), 8.23 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.71 – 7.61 (m, 5H), 7.47 – 7.49 (m, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 4.30 (dd, J = 14.1, 6.0 Hz, 1H), 4.08 (dd, J = 14.0, 6.3 Hz, 1H), 2.38 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 167.3, 149.0, 148.4, 148.1, 139.2, 134.8, 133.1, 131.3, 131.2, 130.5, 128.8, 128.5, 126.9, 123.9, 122.1, 120.5, 68.6, 47.2, 21.9, 18.0. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_2$: 394.1526, found: 394.1531.



N-((1-methyl-3-oxo-2-(4-(trifluoromethyl)pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ia)

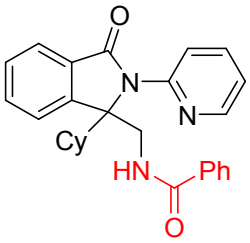
The title compound **4ia** was synthesized according to the **3b** and **3c**. The product **4ia** was isolated as white solid. Yield: **3b**: 86% (32.0 mg); and **3c**: 36% (13.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 – 8.60 (m,

2H), 7.90 (d, J = 7.6 Hz, 1H), 7.67-7.71 (m, 2H), 7.50-7.52 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 3.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.19 (s, 1H), 4.63 (dd, J = 14.1, 6.0 Hz, 1H), 4.17 (dd, J = 14.1, 6.5 Hz, 1H), 1.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 167.4, 152.3, 149.0, 148.5, 140.5 (q, J = 33.9 Hz), 134.5, 133.8, 131.4, 129.8, 129.1, 128.5, 126.7, 125.3, 124.1, 122.6 (q, J = 273.5 Hz), 115.9 (q, J = 3.2 Hz), 114.7 (q, J = 3.9 Hz), 69.4, 46.8, 22.2. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{18}F_3N_3NaO_2$: 448.1243, found: 448.1249.



N-((1-ethyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ja).

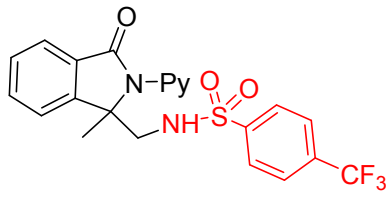
The title compound **4ja** was synthesized according to the **3b** and **3c**. The product **4ja** was isolated as white solid. Yield: **3b**: 84% (31.2 mg); and **3c**: 37% (13.4 mg) .^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.49 (m, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.98 (s, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.73 – 7.58 (m, 4H), 7.50 – 748 (m, 1H), 7.46 – 7.40 (m, 1H), 7.37 – 7.35 (m, 2H), 7.23 – 7.21 (m, 1H), 4.44 (dd, J = 14.0, 6.0 Hz, 1H), 4.15 (dd, J = 14.0, 6.3 Hz, 1H), 2.28 (dd, J = 14.6, 7.3 Hz, 1H), 2.02 (dd, J = 14.6, 7.3 Hz, 1H), 0.42 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 167.3, 151.0, 147.8, 147.0, 138.5, 134.8, 133.3, 131.4, 131.3, 128.8, 128.5, 126.8, 123.9, 122.2, 121.1, 120.3, 72.9, 47.2, 26.4, 7.1. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{23}H_{21}N_3NaO_2$: 394.1526, found: 394.1527.



N-((1-cyclohexyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzamide (4ka)

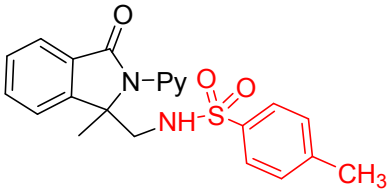
The title compound **4ka** was synthesized according to the **3b** and **3c**. The product **4ka** was isolated as white solid. Yield: **3b**: 67% (28.5 mg); and **3c**: <5% .^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 – 8.51 (m, 1H), 8.07 (s, 0H), 7.92 – 7.82 (m, 3H), 7.73 (d, J = 7.8 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.58 – 7.53 (m, 2H), 7.48 – 7.45 (m, 1H), 7.43 – 7.37 (m, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.24 (m, 2H), 4.52 (dd, J = 13.8, 7.5 Hz, 1H), 4.26 (dd, J = 13.8, 4.9 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.96 – 1.91 (m, 1H), 1.83 – 1.72 (m, 1H), 1.61 – 1.44 (m, 3H), 1.43 – 1.35 (m, 1H), 1.20 – 1.05 (m, 1H), 1.03 – 0.75 (m, 2H), 0.34 – 0.27 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 167.2, 151.1, 148.3, 145.8, 138.6, 135.0, 132.6, 131.7, 131.2, 128.7, 128.4, 126.8, 123.8, 123.7, 121.9, 121.7, 75.4, 44.8,

42.6, 27.7, 26.8, 26.6, 26.1, 26.0. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{27}H_{27}N_3NaO_2$: 448.1995, found: 448.1995.



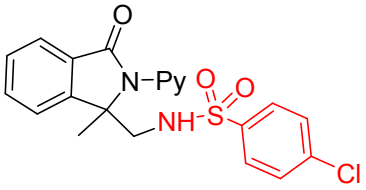
N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)-4-(trifluoromethyl)benzenesulfonamide (4aa)

The title compound **4aa** was synthesized according to the **3d**. The product **4aa** was isolated as white solid. Yield: 88% (40.7 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 8.41 – 8.37 (m, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.58 – 7.53 (m, 3H), 7.45 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.67 (t, J = 6.5 Hz, 1H), 4.18 (dd, J = 13.4, 6.8 Hz, 1H), 3.51 (dd, J = 13.4, 6.3 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 150.5, 148.3, 147.5, 144.0, 138.5, 133.7(q, J = 32.8 Hz), 133.3, 130.5, 129.1, 127.1, 126.0(q, J = 3.7 Hz), 124.4, 123.2(q, J = 272.7 Hz), 121.1, 121.0, 119.7, 67.8, 51.1, 22.1. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}F_3N_3NaSO_3$: 484.0913, found: 484.0915.



4-methyl-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzenesulfonamide (4ab)

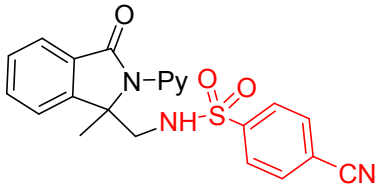
The title compound **4ab** was synthesized according to the **3d**. The product **4ab** was isolated as white solid. Yield: 95% (38.7 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 8.33 – 8.24 (m, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.50 (t, J = 7.1 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.51 (s, 1H), 3.94 (d, J = 13.1 Hz, 1H), 3.32 (d, J = 13.1 Hz, 1H), 2.29 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 150.5, 148.6, 147.4, 142.9, 138.4, 133.3, 130.5, 129.5, 128.9, 126.8, 126.4, 124.3, 121.3, 120.8, 119.6, 67.9, 51.1, 22.2, 21.5. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{21}N_3NaSO_3$: 430.1196, found: 430.1197.



4-chloro-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzenesulfonamide (4ac)

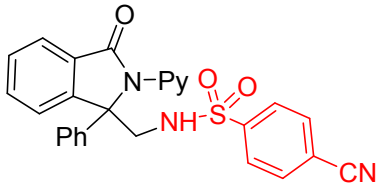
The title compound **4ac** was synthesized according to the **3d**. The product **4ac** was isolated as white solid. Yield: 98% (41.8 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 8.38 – 8.36 (m, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.86 – 7.76 (m, 3H), 7.59 – 7.56 (m, 1H), 7.52 – 7.48 (m, 3H), 7.38 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.18 – 7.16 (m, 1H), 6.54 (t, J = 6.6 Hz, 1H), 4.13 (dd, J = 13.2, 6.9 Hz, 1H), 3.46 (dd, J

= 13.3, 6.3 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 148.4, 147.5, 138.6, 138.4, 133.4, 130.5, 129.3, 129.1, 129.0, 128.2, 127.9, 124.4, 121.1, 121.0, 119.6, 67.8, 51.0, 22.2. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{21}H_{18}ClN_3NaSO_3$: 450.0650, found: 450.0654.



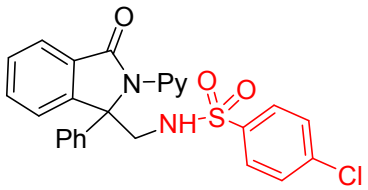
4-cyano-N-((1-methyl-3-oxo-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzenesulfonamide (4ad)

The title compound **4ad** was synthesized according to the **3d**. The product **4ad** was isolated as white solid. Yield: 71% (29.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 – 8.38 (m, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.62 – 7.56 (m, 3H), 7.51 – 7.48 (m, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.21 – 7.18 (m, 1H), 6.85 (t, J = 6.4 Hz, 1H), 4.18 (dd, J = 13.5, 7.0 Hz, 1H), 3.50 (dd, J = 13.4, 5.9 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 150.4, 148.2, 147.4, 144.7, 138.6, 133.4, 132.6, 130.5, 129.2, 127.2, 124.4, 121.2, 121.1, 119.7, 117.3, 115.8, 67.8, 51.2, 22.0. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{22}H_{18}N_4NaSO_3$: 441.0992, found: 441.0995.



4-cyano-N-((3-oxo-1-phenyl-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzenesulfonamide (4ae)

The title compound **4ae** was synthesized according to the **3d**. The product **4ae** was isolated as white solid. Yield: 88% (40.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 – 8.17 (m, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.76 – 7.73 (m, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.24 – 7.13 (m, 6H), 7.10 – 7.05 (m, 1H), 6.70 (t, J = 6.4 Hz, 1H), 4.90 (dd, J = 13.0, 6.2 Hz, 1H), 4.14 (dd, J = 13.0, 6.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 150.4, 148.4, 147.5, 144.5, 138.4, 137.9, 133.6, 132.6, 130.0, 129.1, 128.9, 128.0, 127.3, 125.8, 124.4, 122.2, 121.0, 119.6, 117.3, 115.8, 72.1, 49.3. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{27}H_{20}N_4NaSO_3$: 503.1148, found: 503.1151.



4-chloro-N-((3-oxo-1-phenyl-2-(pyridin-2-yl)isoindolin-1-yl)methyl)benzenesulfonamide (4af)

The title compound **4af** was synthesized according to the **3d**. The product **4af** was isolated as white solid. Yield: 88% (40.7

mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.78 – 7.70 (m, 1H), 7.54 – 7.49 (m, 2H), 7.49 – 7.43 (m, 2H), 7.29 (d, J = 2.7 Hz, 2H), 7.24 – 7.15 (m, 5H), 7.14 – 7.11 (m, 1H), 7.06 – 7.04 (m, 1H), 6.36 (t, J = 6.6 Hz, 1H), 4.84 (dd, J = 12.8, 6.0 Hz, 1H), 4.12 (dd, J = 12.8, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 156.8, 150.4, 148.5, 147.5, 138.7, 138.5, 138.2, 133.5, 130.0, 129.1, 128.9, 128.8, 128.3, 127.9, 125.8, 124.4, 122.1, 120.9, 119.5, 72.1, 49.0. HRMS (ESI): m/z: $[M + Na]^+$ calculated for $C_{26}H_{20}ClN_3NaSO_3$: 512.0806, found: 512.0803.

6. X-Ray Crystallographic Data of the Complex 5

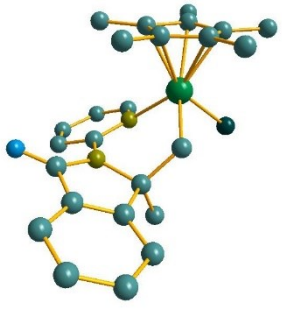


Table S2 Crystal data and structure refinement for CCDC 1957959.

Identification code	CCDC 1957959
Empirical formula	$C_{25}H_{28}ClN_2ORh$
Formula weight	510.85

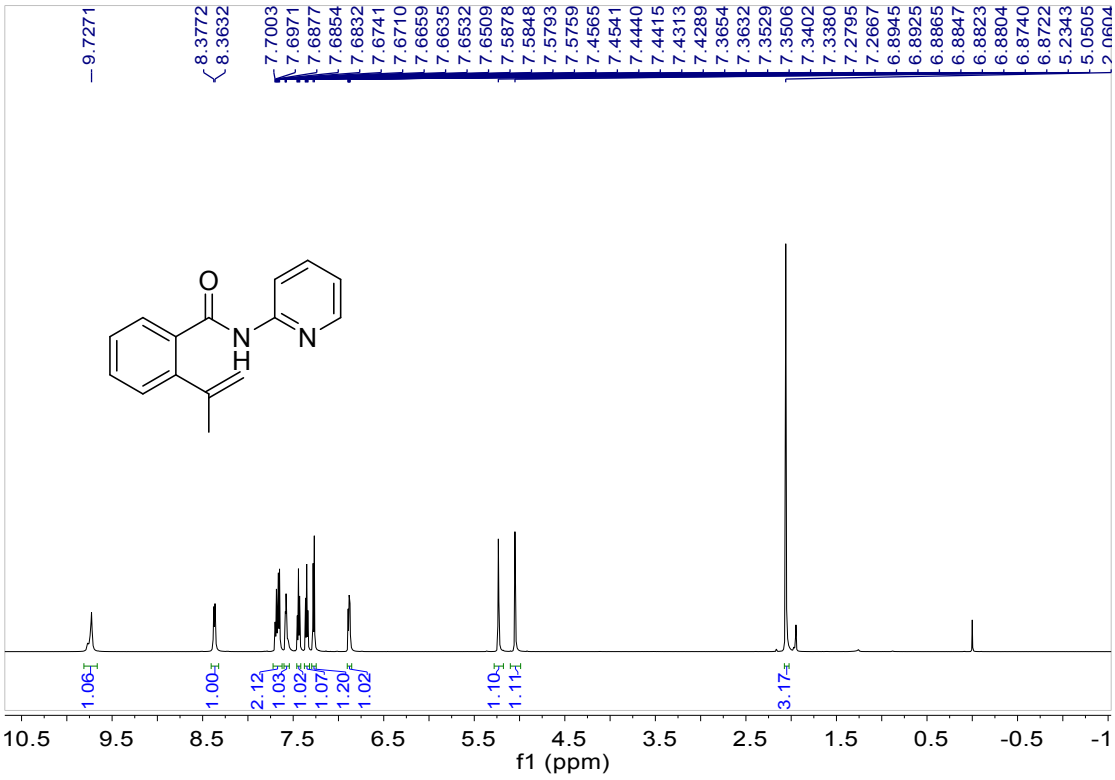
Temperature/K	153.02
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.9749(4)
b/Å	15.7608(5)
c/Å	23.8262(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4496.8(2)
Z	8
ρ_{calc}g/cm^3	1.509
μ/mm^{-1}	7.375
F(000)	2096.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.42 to 136.596
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28
Reflections collected	76351
Independent reflections	4120 [R_{int} = 0.0405, R_{sigma} = 0.0133]
Data/restraints/parameters	4120/41/373
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0237, wR_2 = 0.0577
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0580
Largest diff. peak/hole / e Å^{-3}	0.40/-0.71

7. References

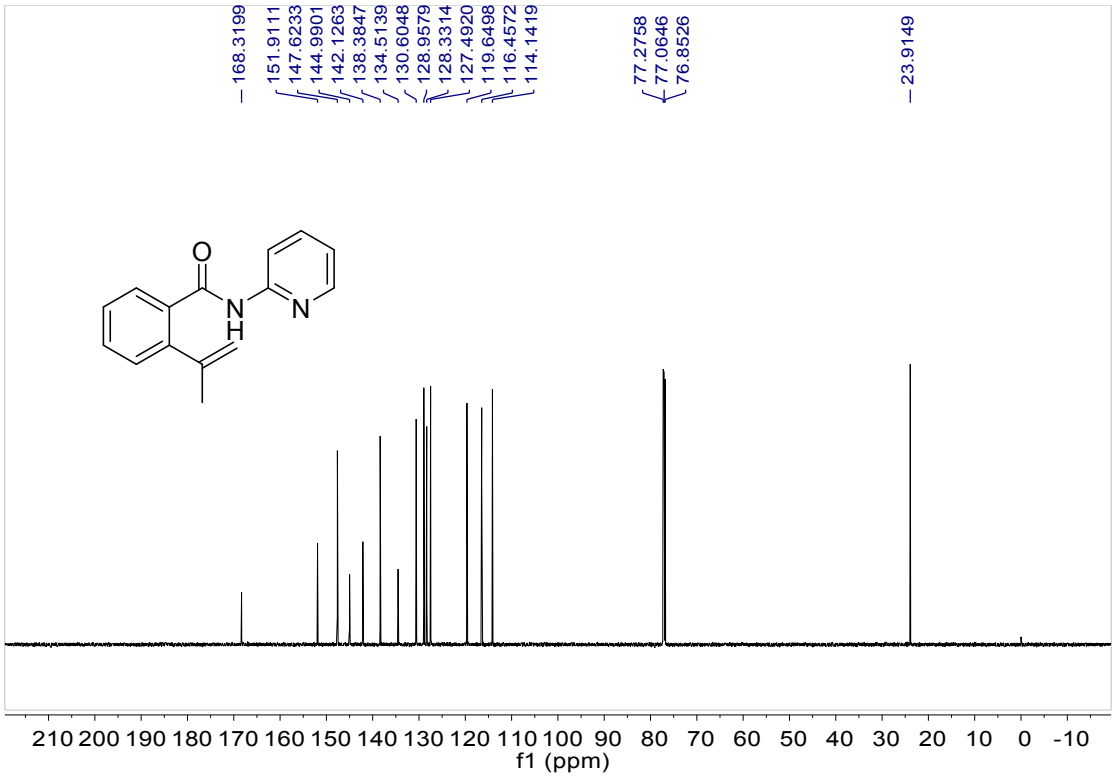
1. X. Kou, Y. Li, L. Wu, X. Zhang, G. Yang and W. Zhang, *Org. Lett.* 2015, **17**, 5566.
2. X. Hao, B. Chen, L. Ren, L. Li, X. Yang, J. Gong, J. Niu and M. Song, *Org. Lett*. 2014, **16**, 1104.
3. a) Yang, G.; Shen, C.; Zhang, W. *Angew. Chem. Int. Ed*. 2012, **51**, 9141. b) Bunescu, A.; Wang, Q.; Zhu, J. *Chem.-Eur. J.* 2014, **20**, 14633.
4. J. Park, J. Lee and S. Chang, *Angew. Chem., Int. Ed.* 2017, **56**, 4256.

8. NMR Spectral for new compounds

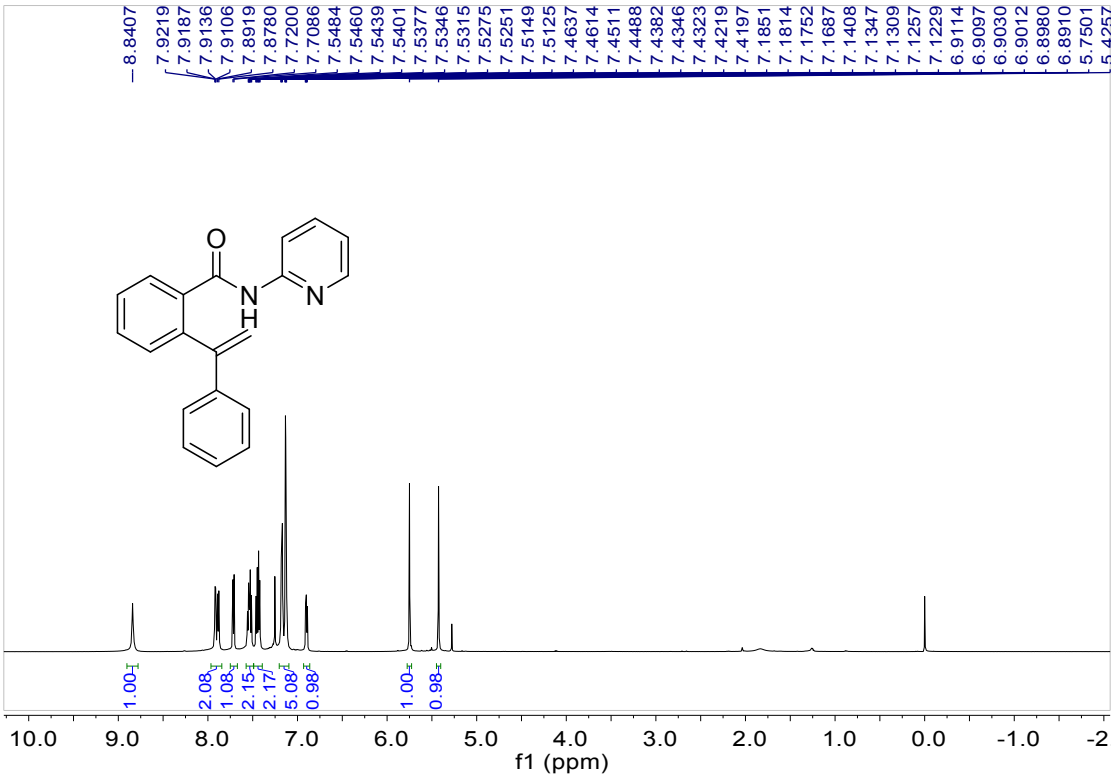
^{1}H NMR Spectra of Compound **1a**



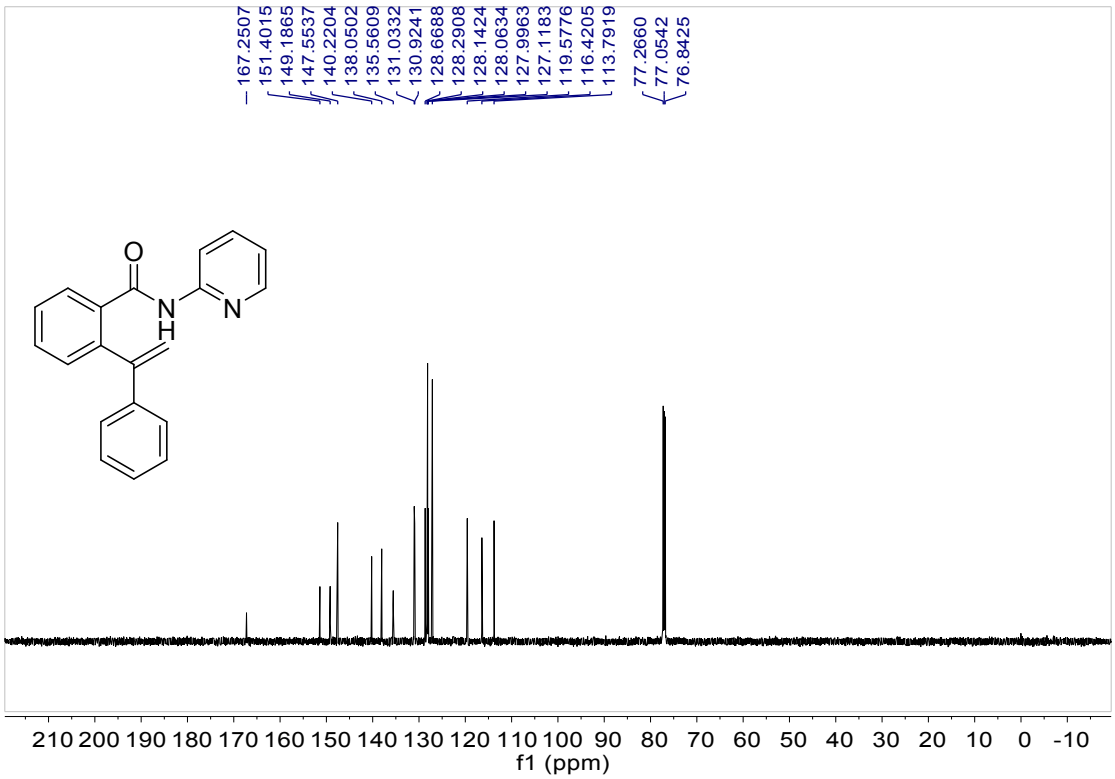
^{13}C NMR Spectra of Compound **1a**



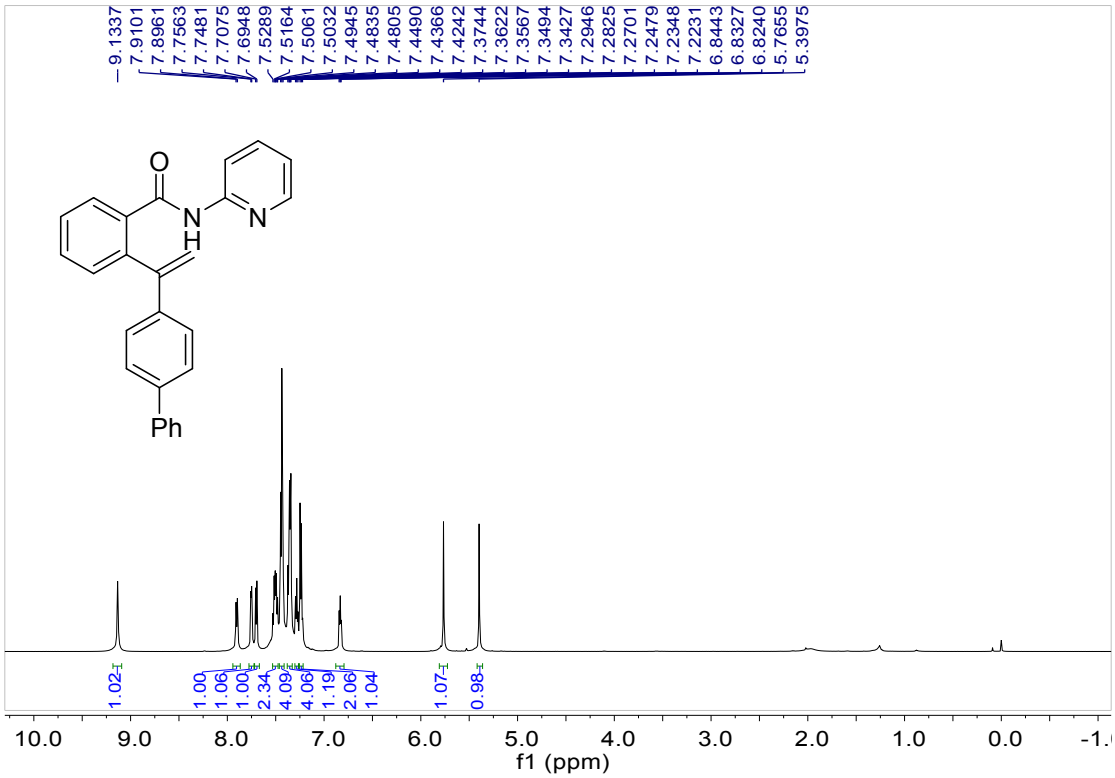
^{1}H NMR Spectra of Compound **1b**



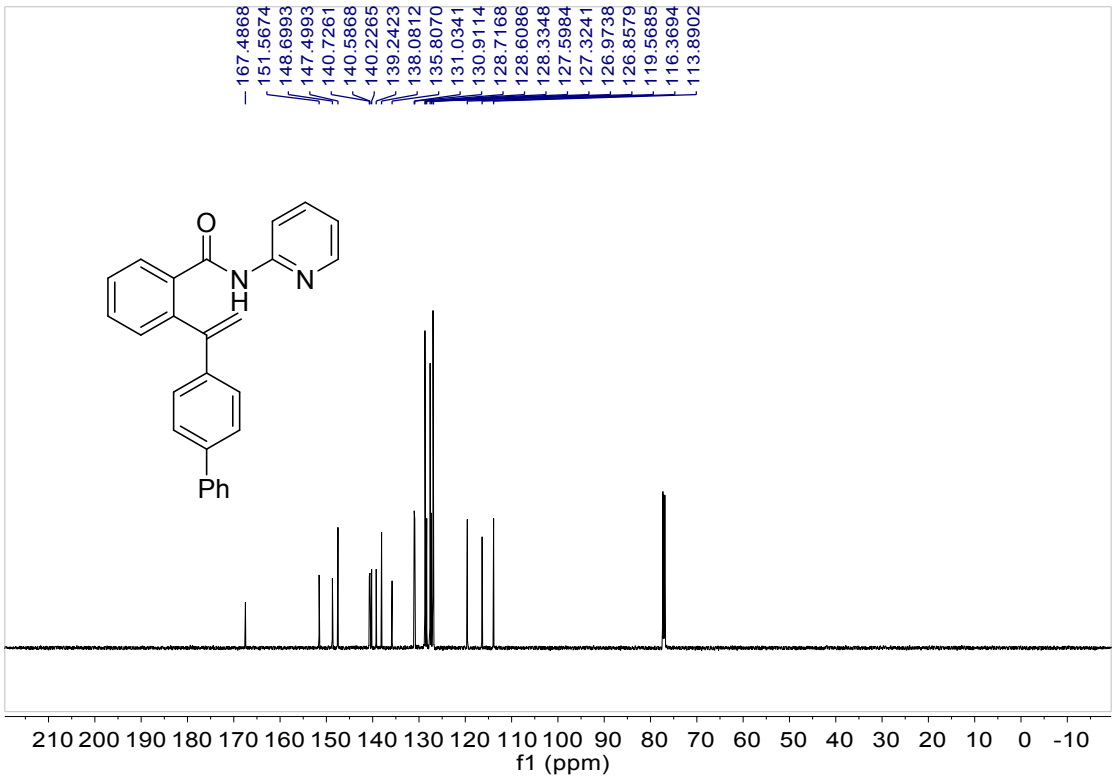
^{13}C NMR Spectra of Compound **1b**



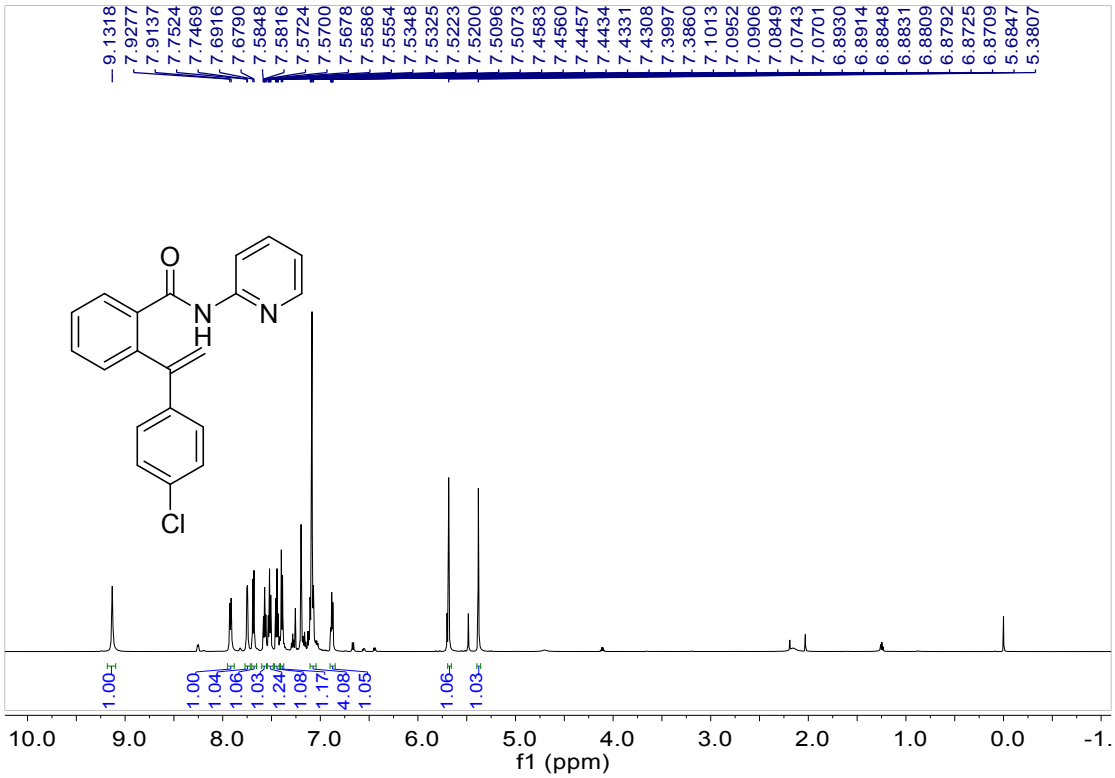
^{1}H NMR Spectra of Compound **1c**



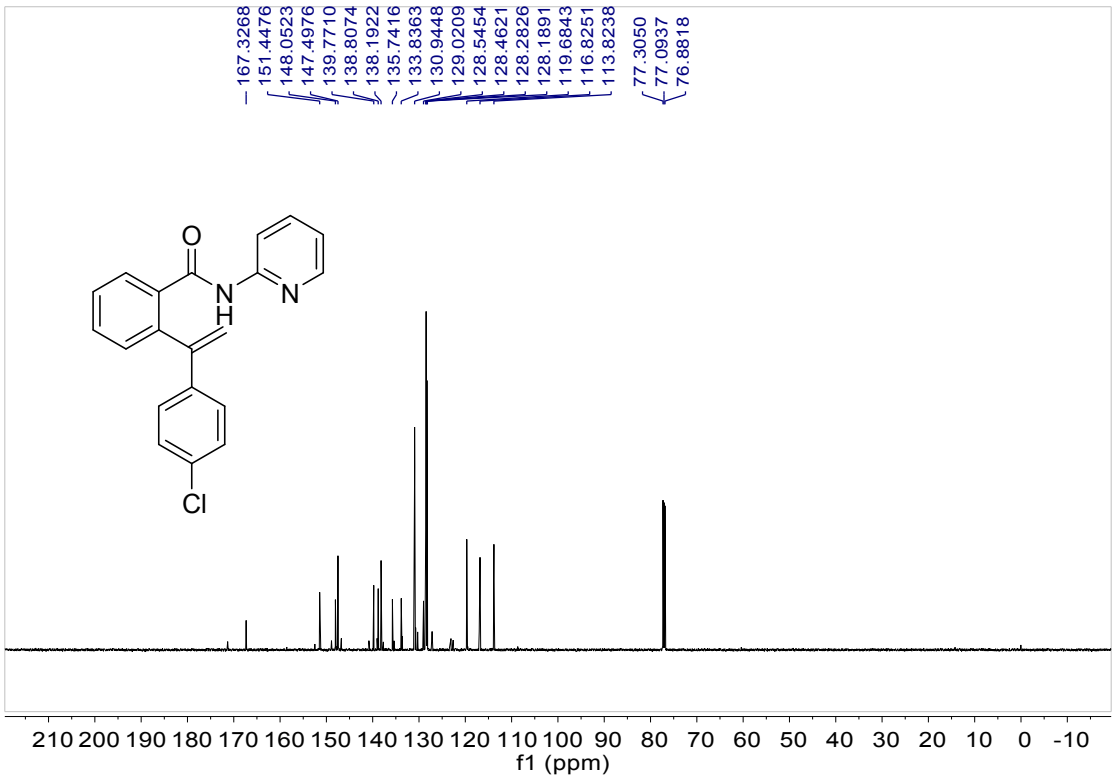
^{13}C NMR Spectra of Compound **1c**



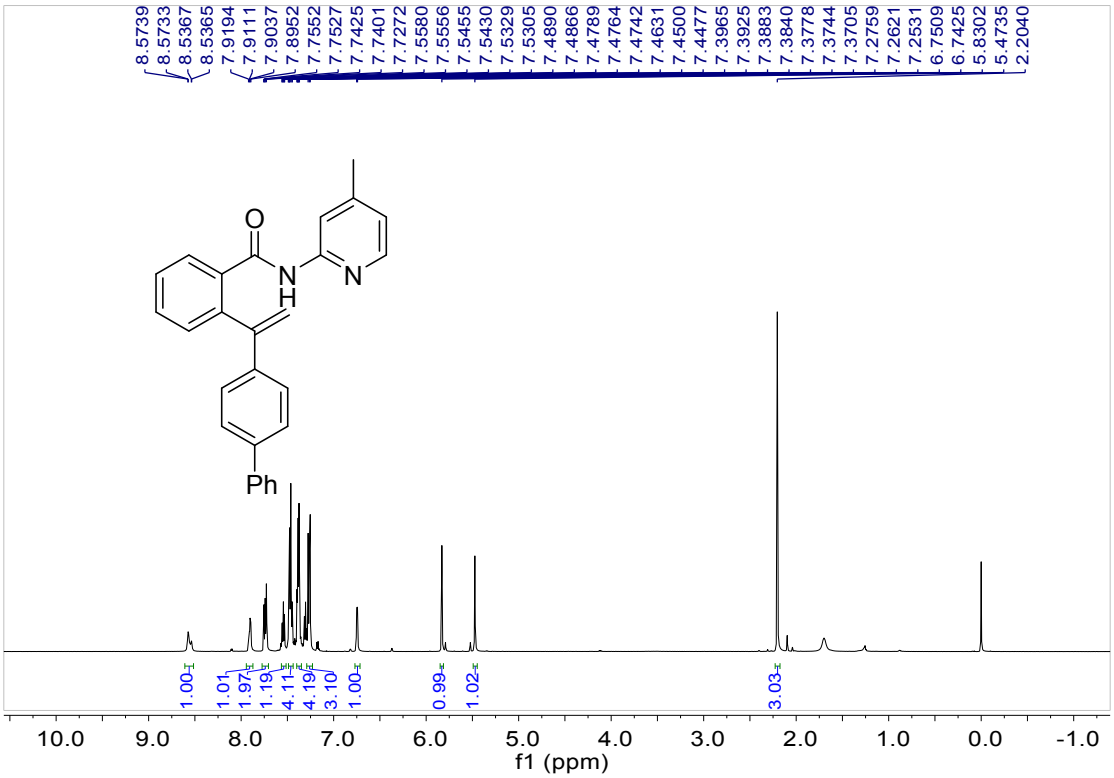
^{1}H NMR Spectra of Compound **1d**



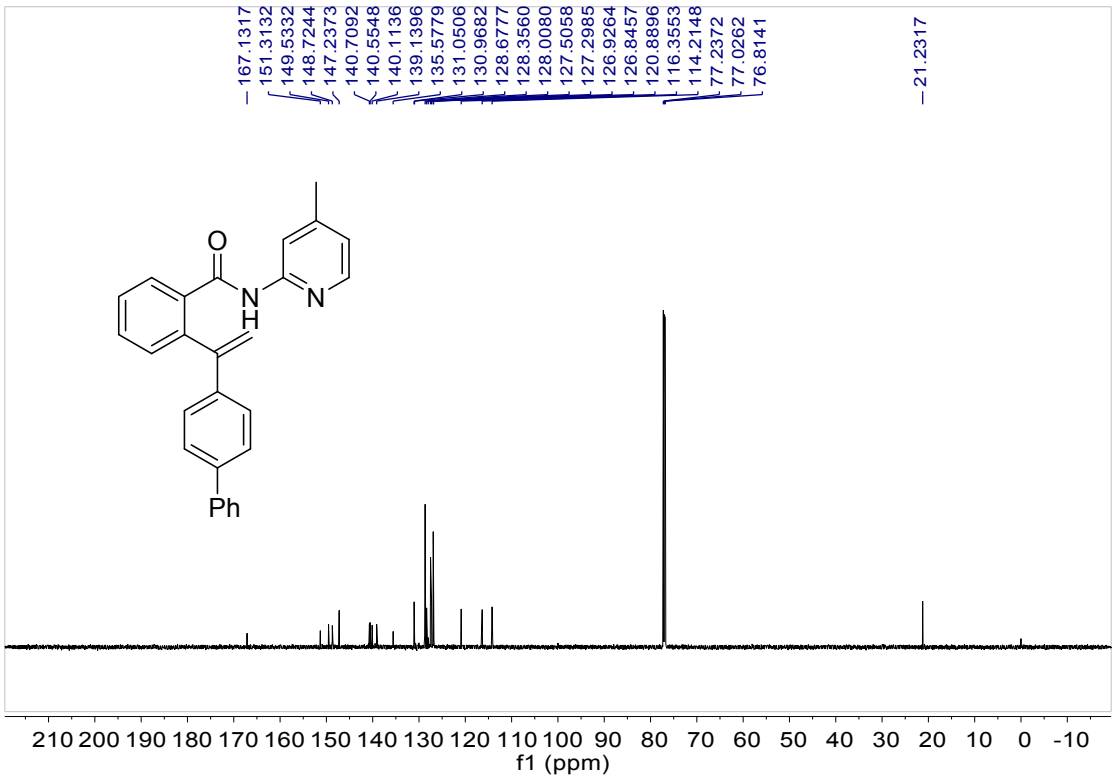
^{13}C NMR Spectra of Compound **1d**



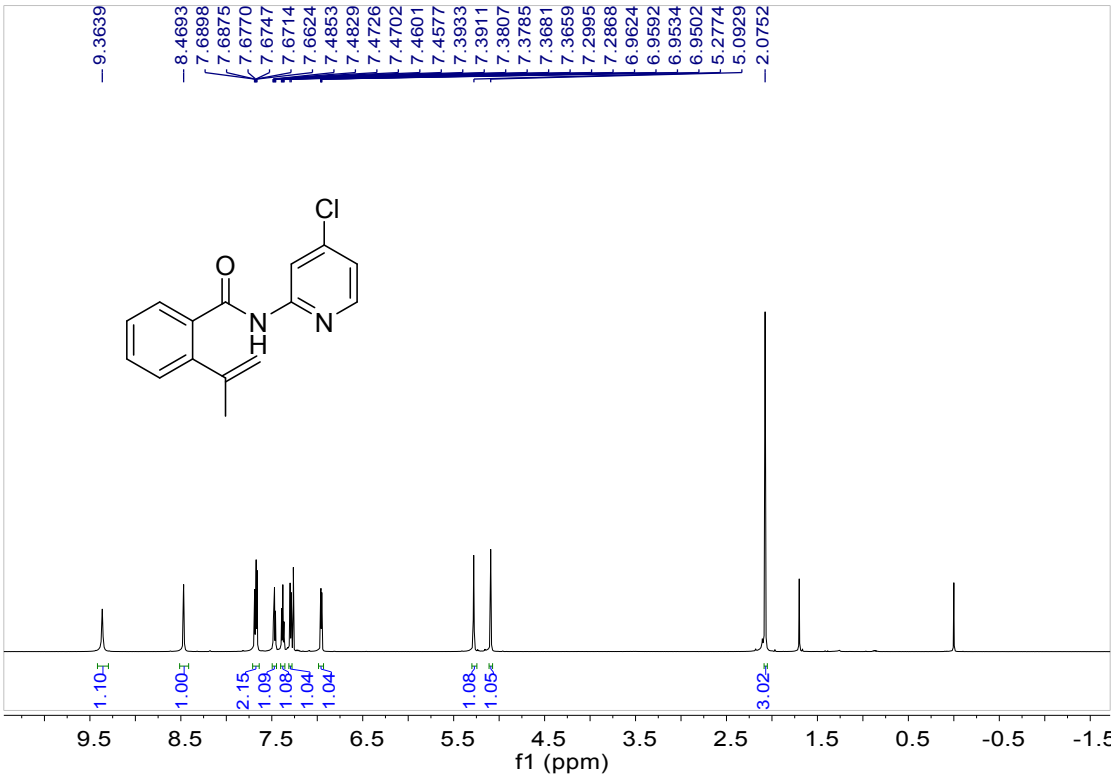
^{1}H NMR Spectra of Compound **1e**



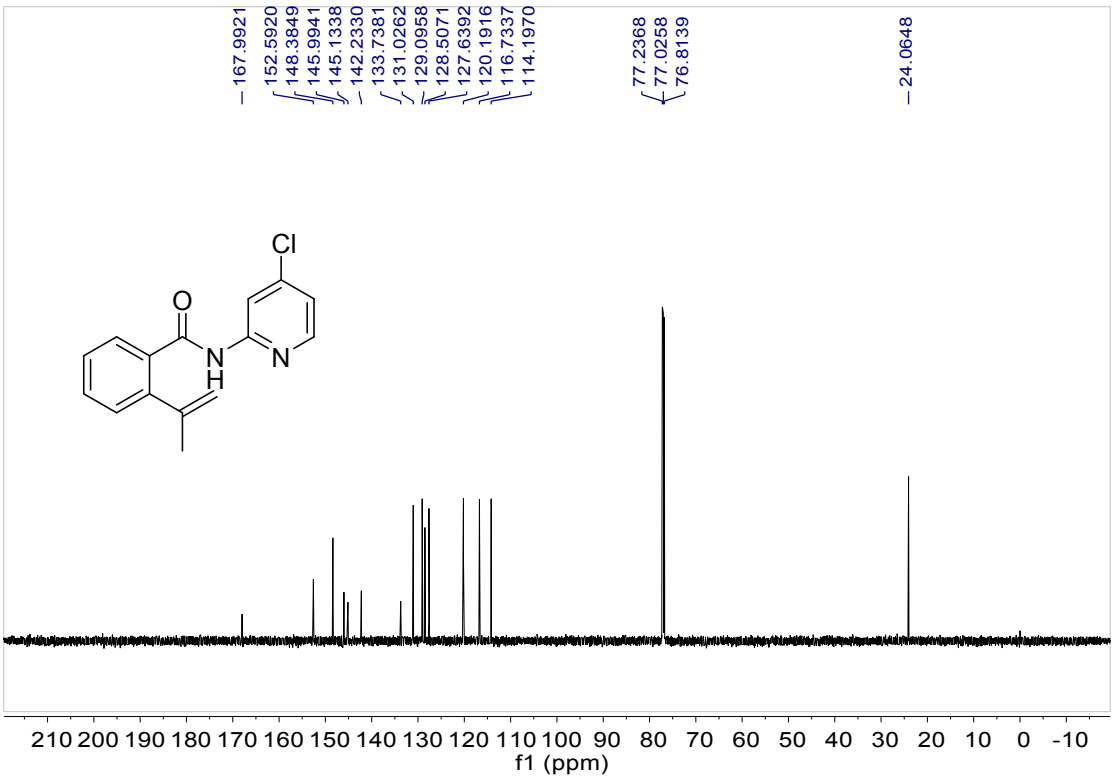
^{13}C NMR Spectra of Compound **1e**



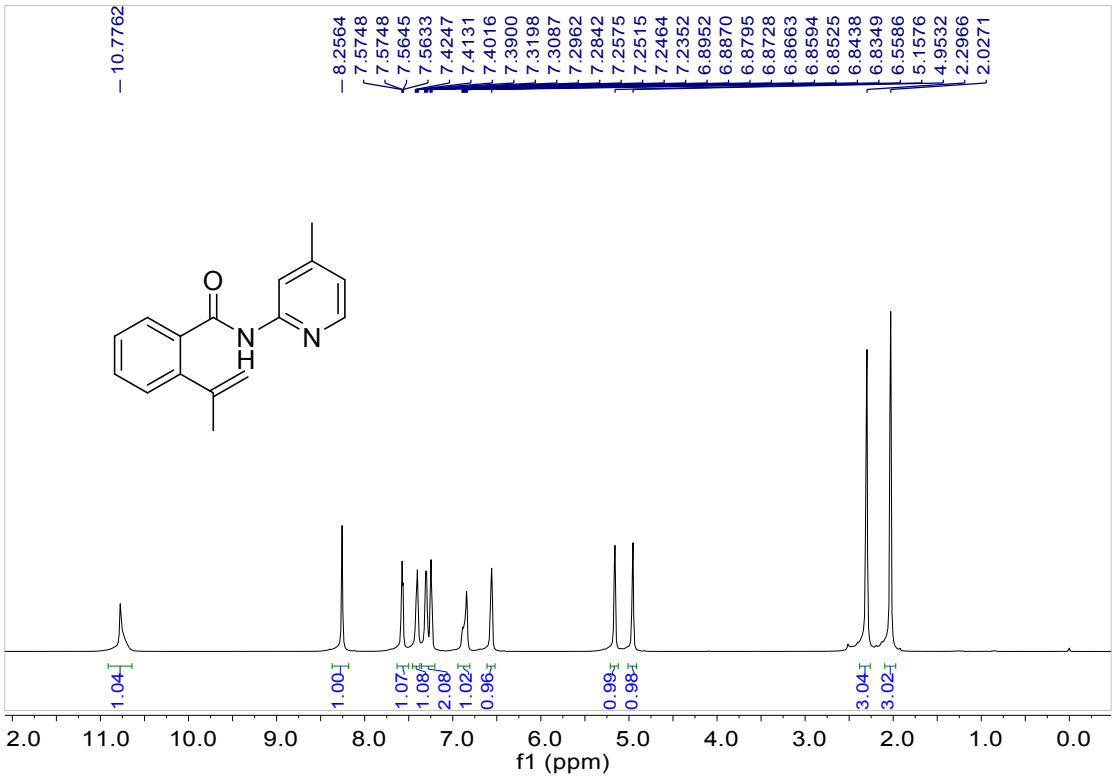
^{1}H NMR Spectra of Compound **1f**



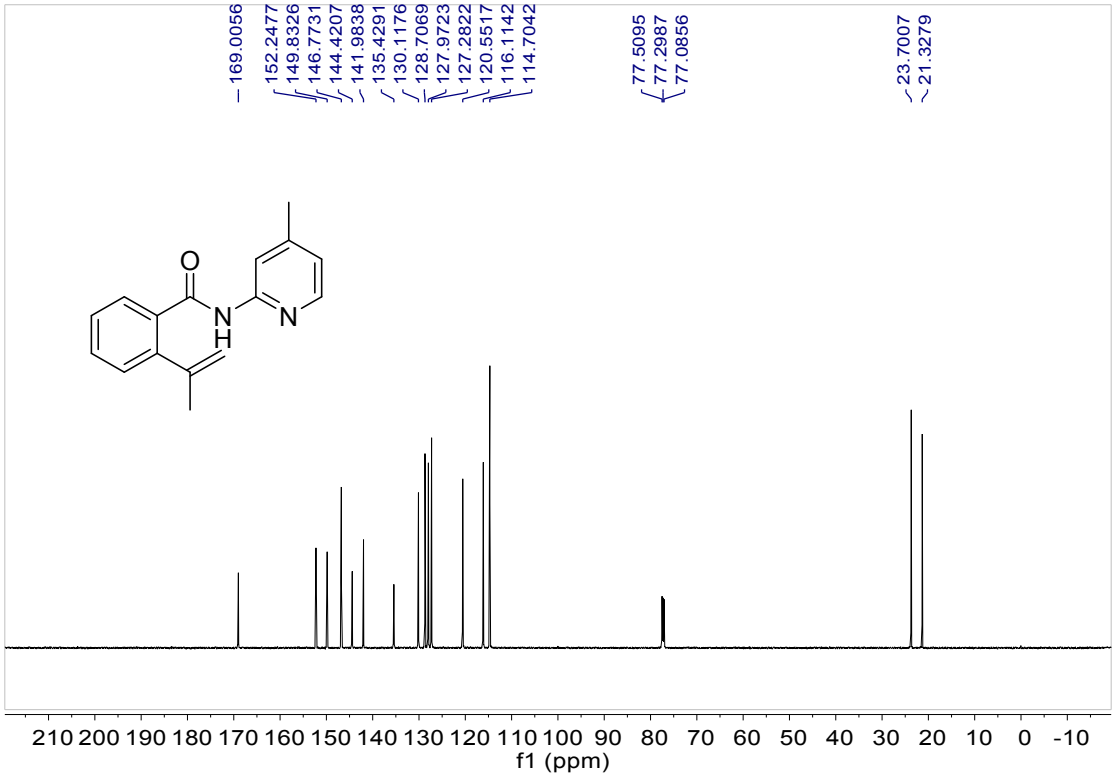
^{13}C NMR Spectra of Compound **1f**



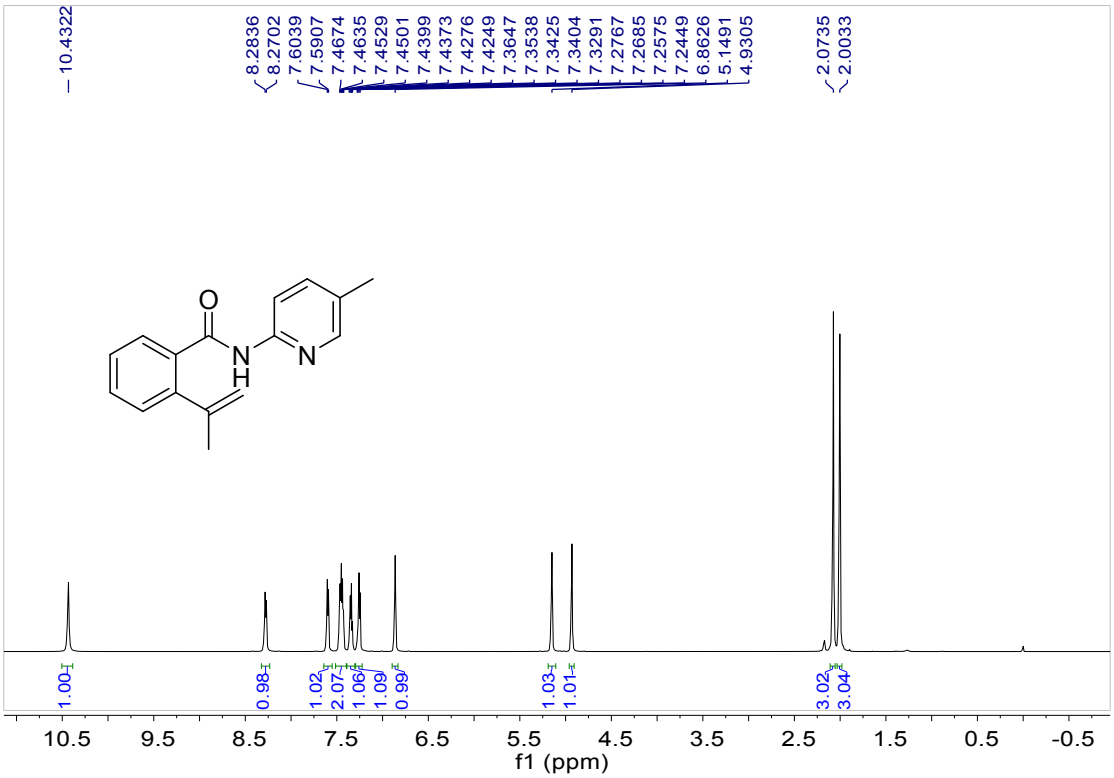
^{1}H NMR Spectra of Compound **1g**



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



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



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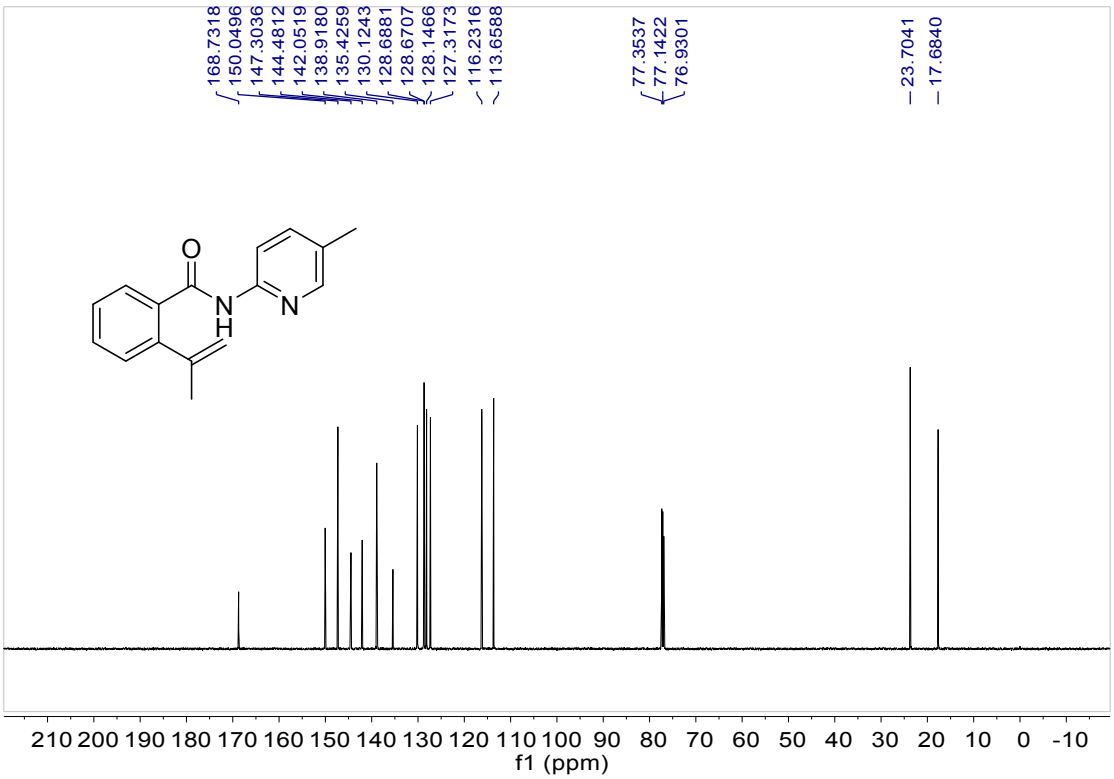
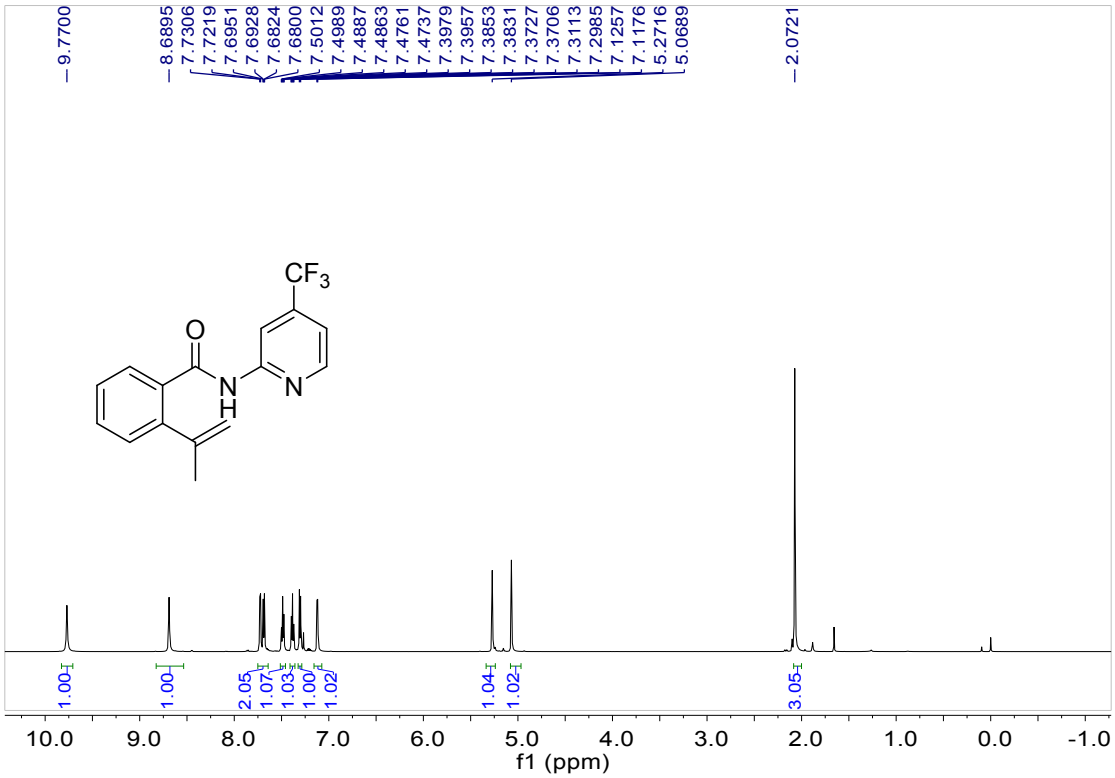
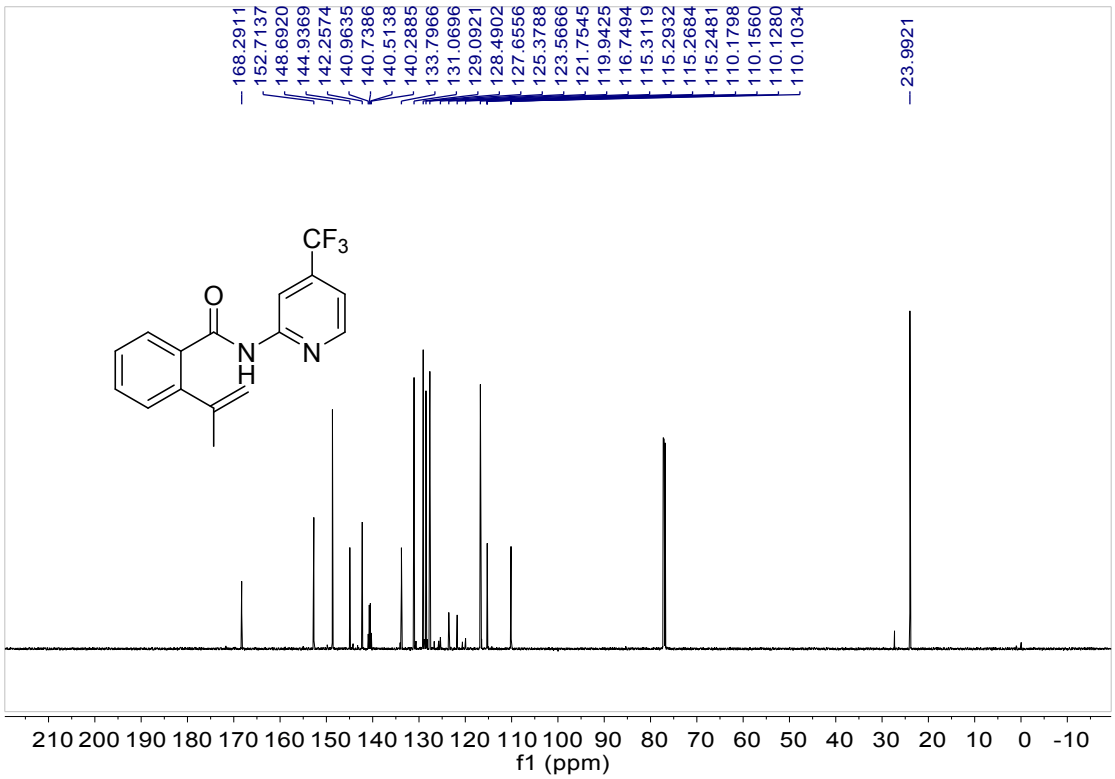


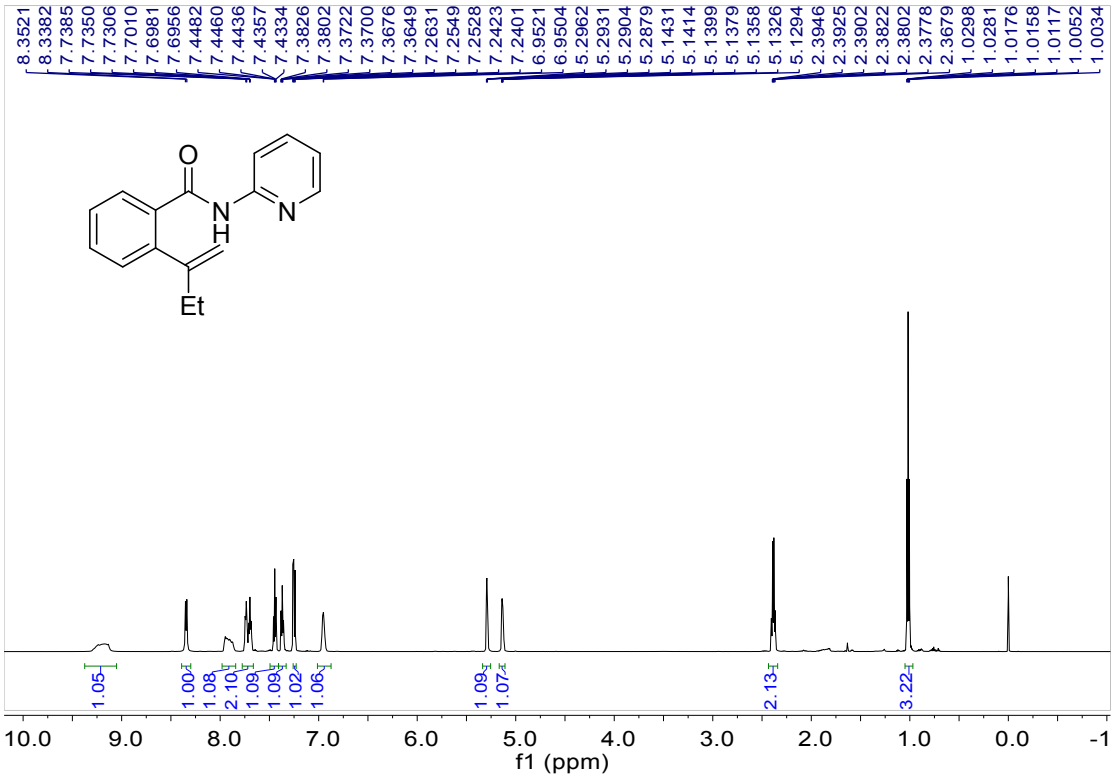
^{1}H NMR Spectra of Compound **1i**



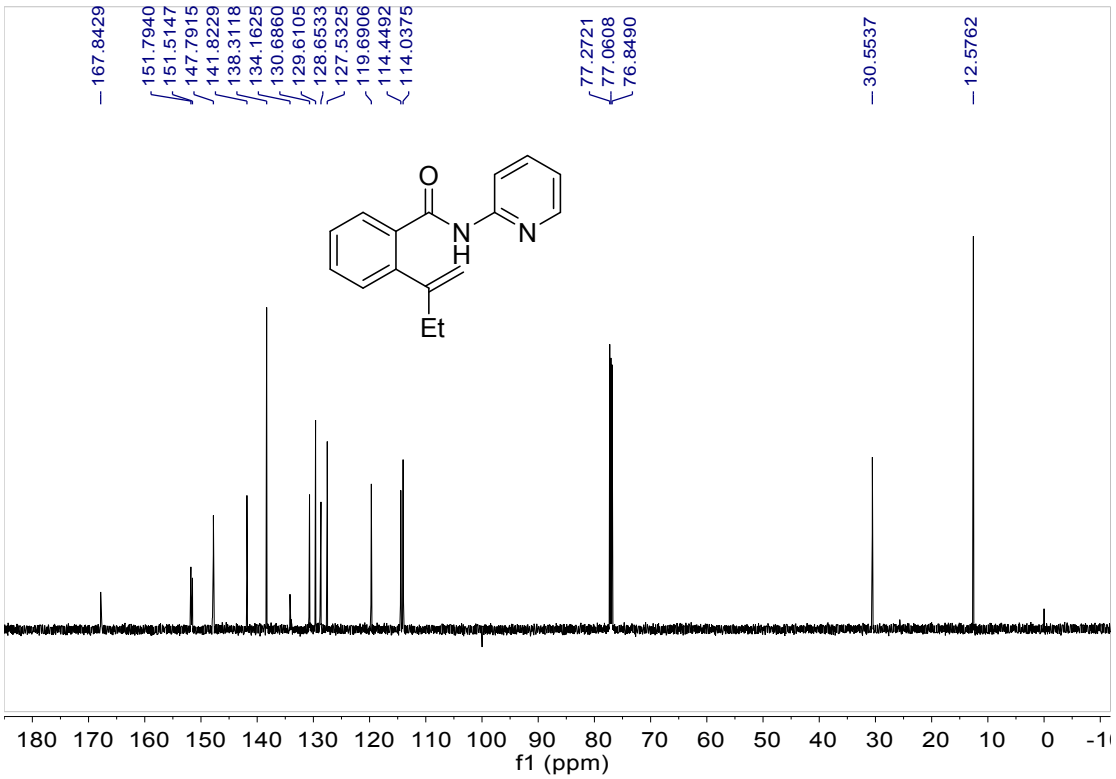
^{13}C NMR Spectra of Compound **1i**



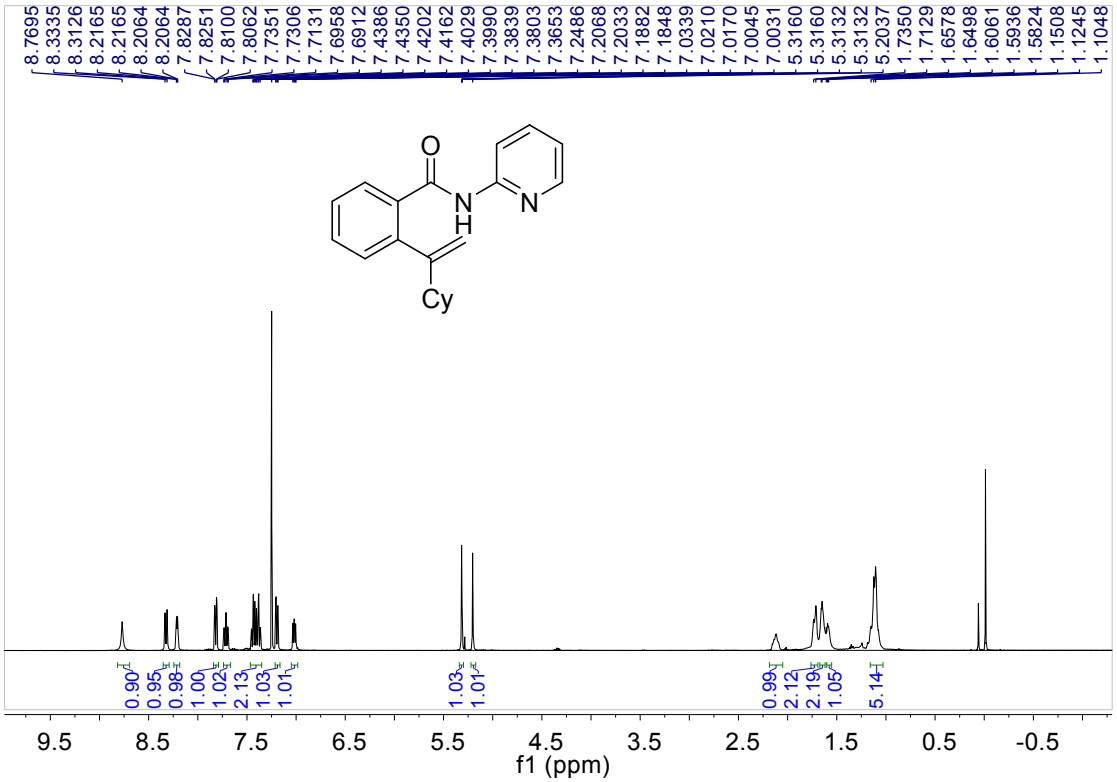
^{1}H NMR Spectra of Compound **1j**



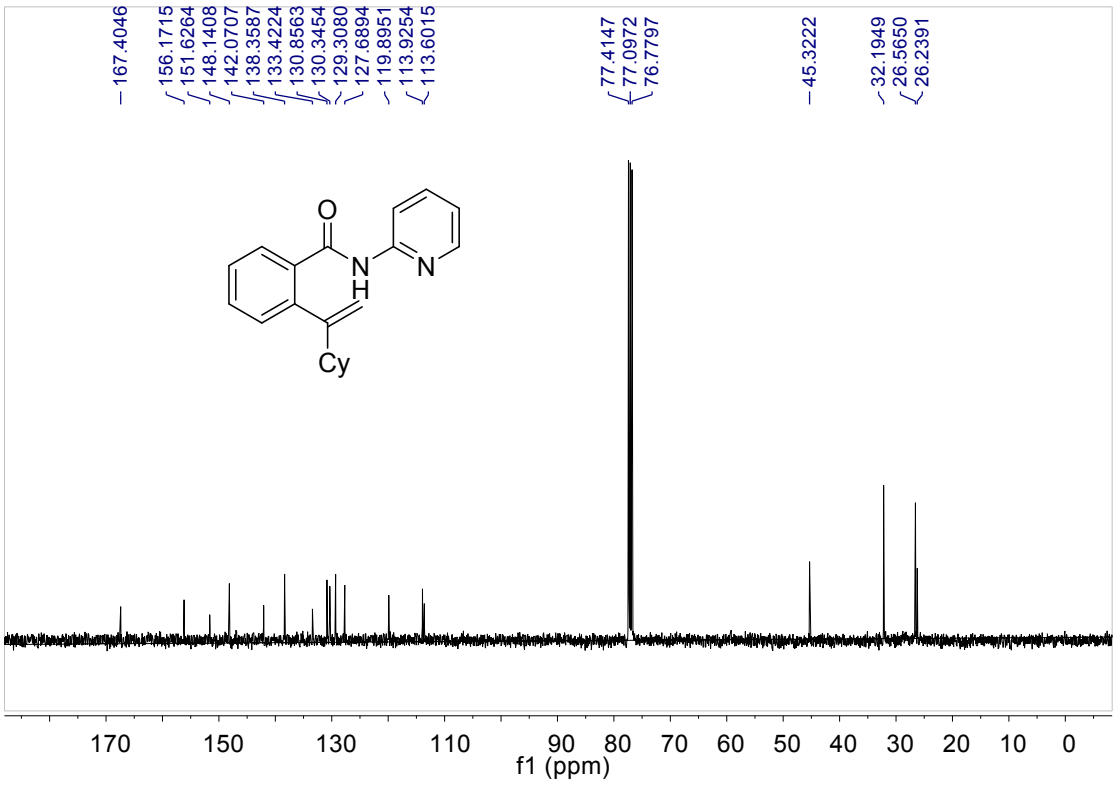
^{13}C NMR Spectra of Compound **1j**



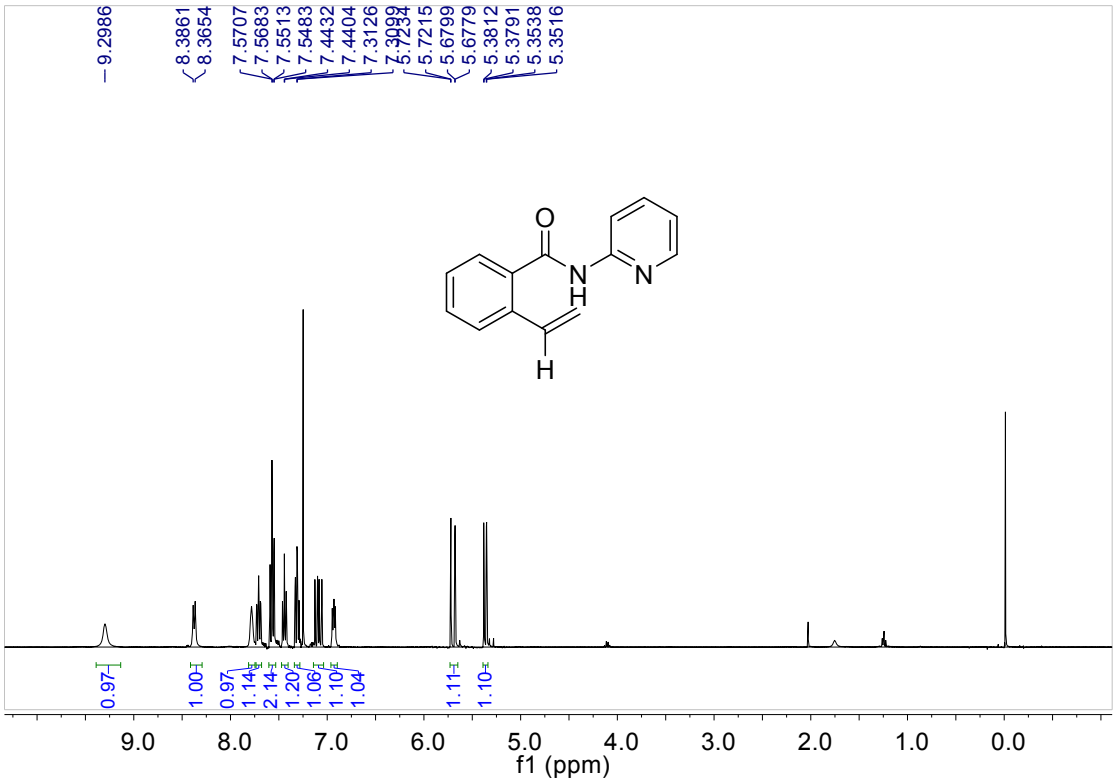
^{1}H NMR Spectra of Compound **1k**



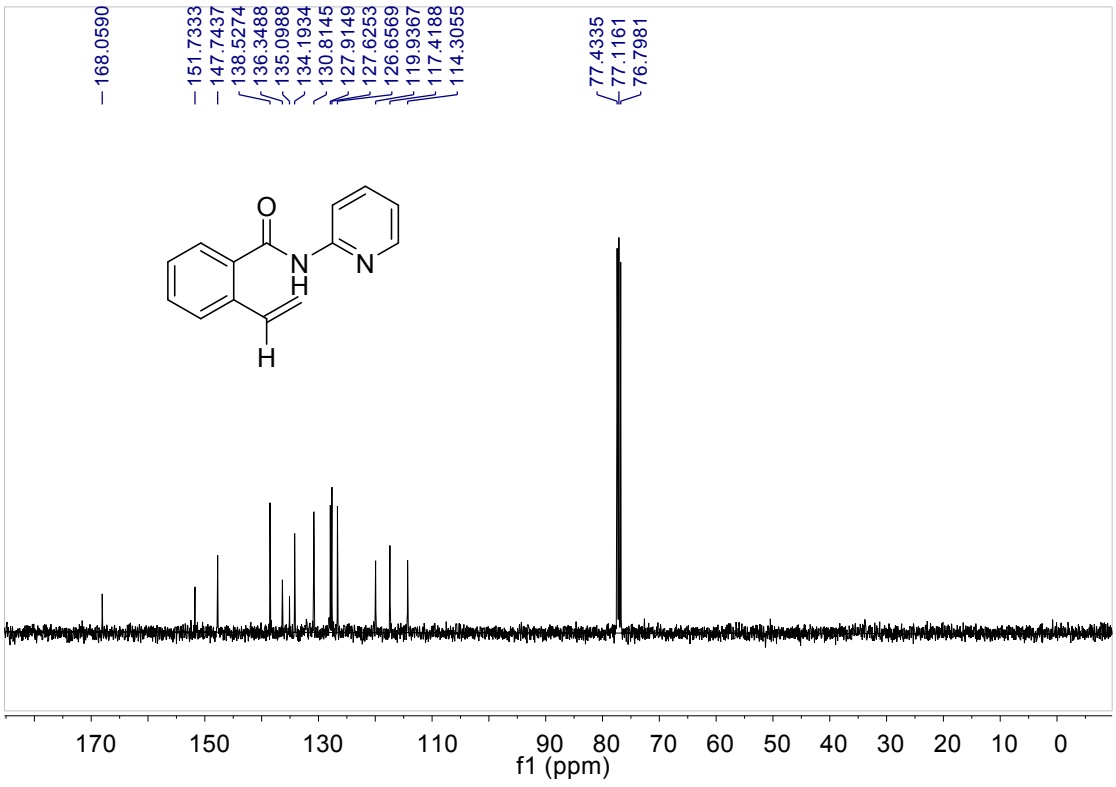
^{13}C NMR Spectra of Compound **1k**



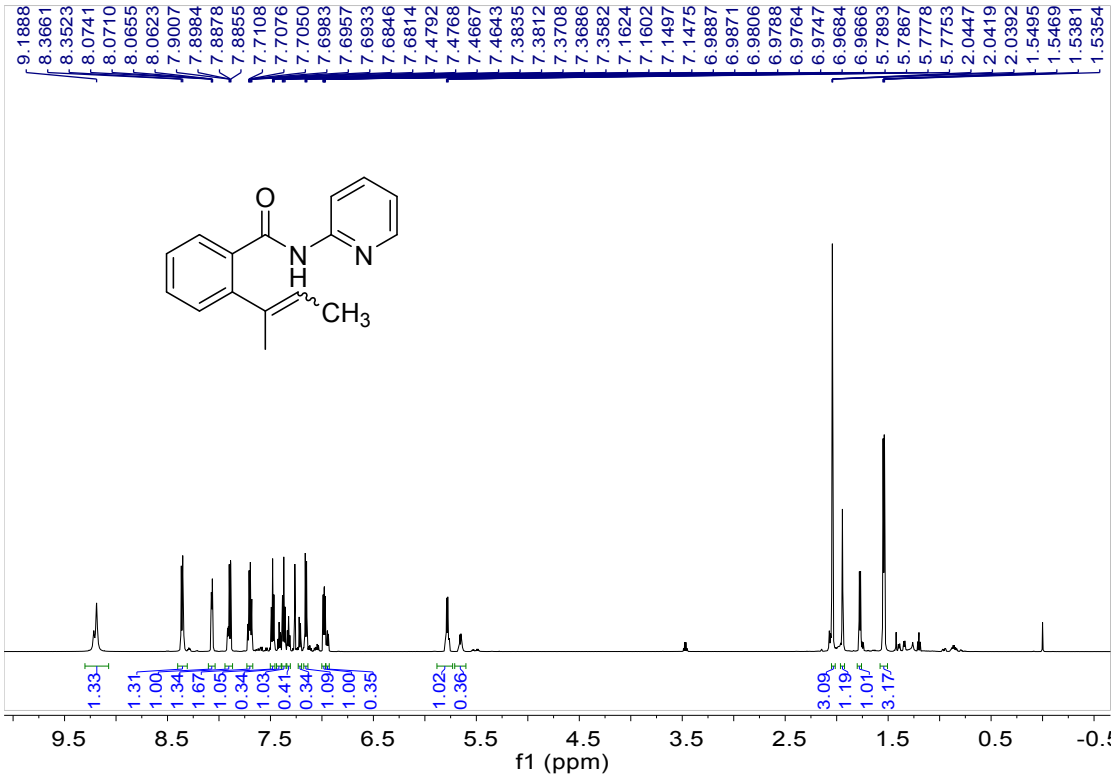
^{1}H NMR Spectra of Compound **1l**



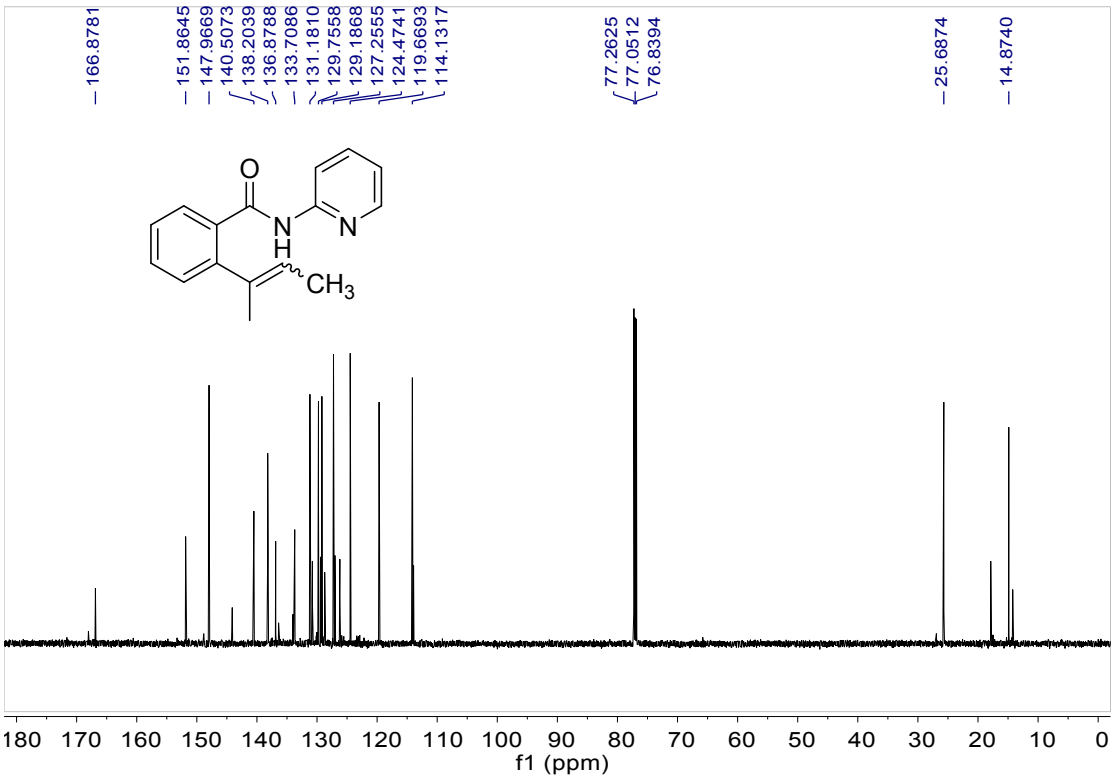
^{13}C NMR Spectra of Compound **1l**



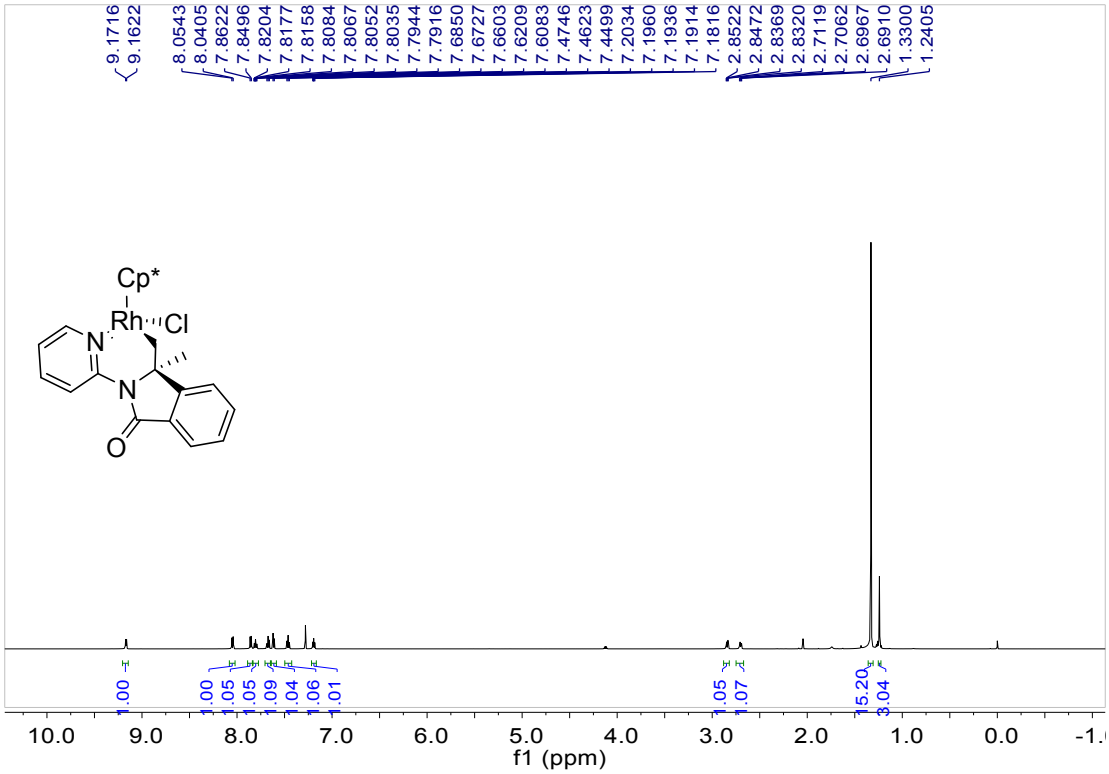
^{1}H NMR Spectra of Compound **1m**



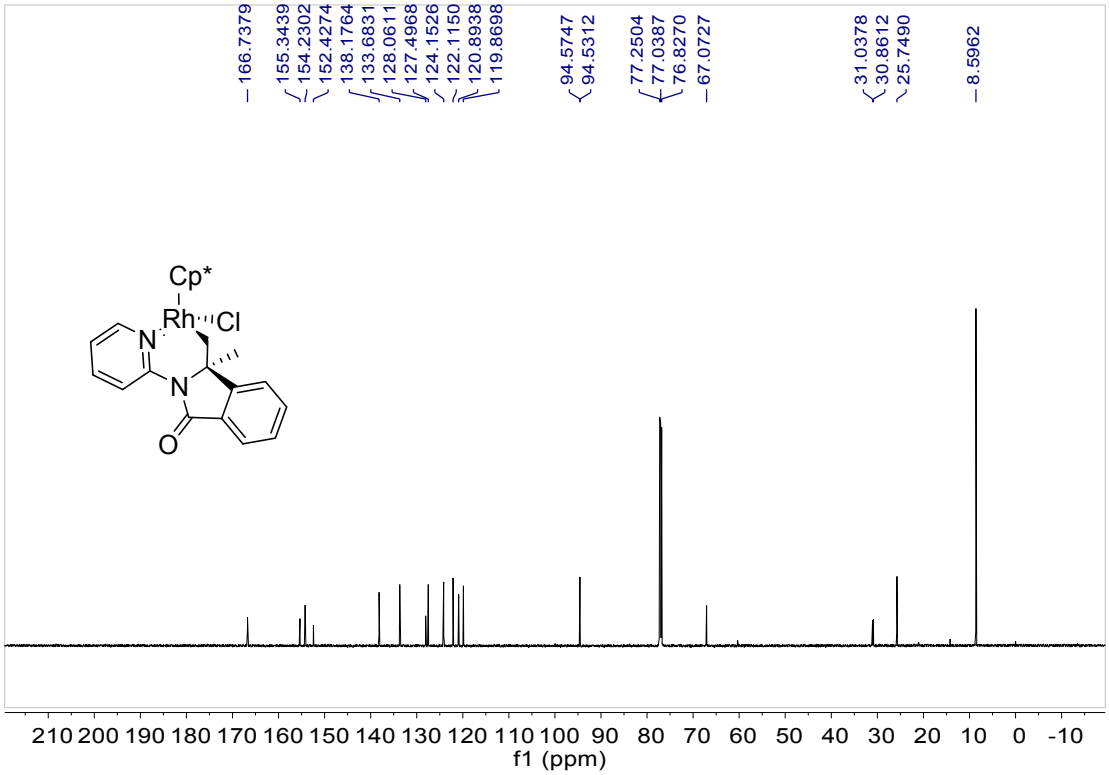
^{13}C NMR Spectra of Compound **1m**



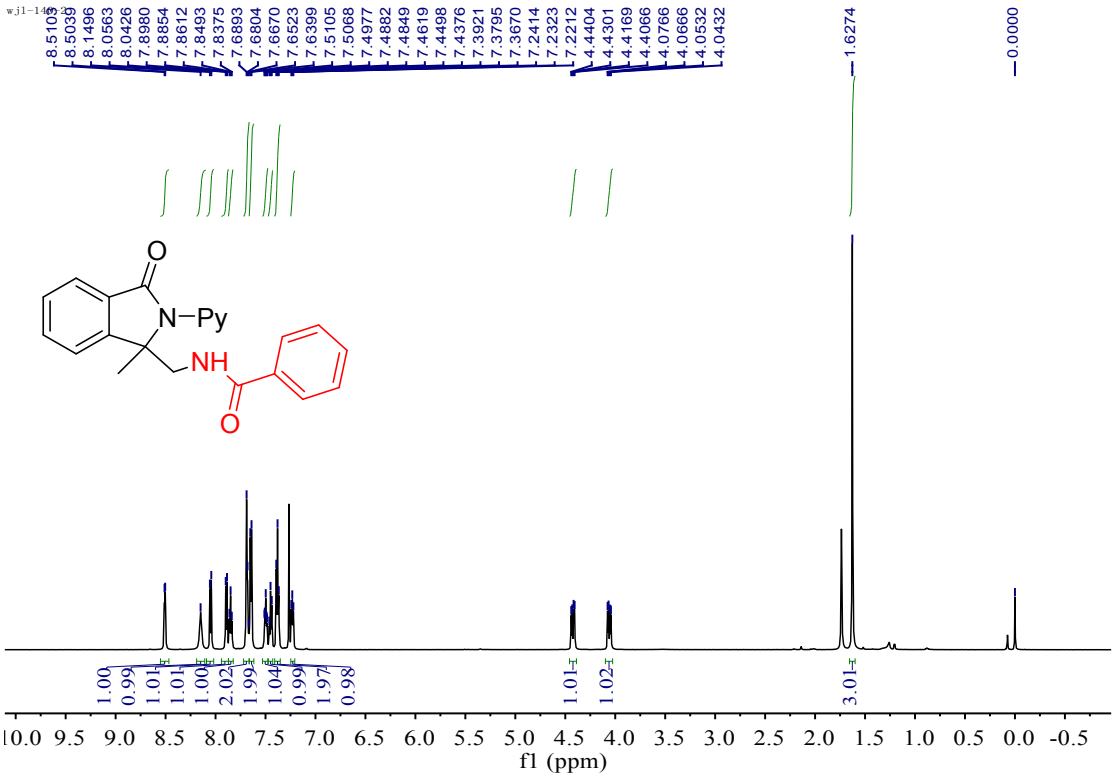
^{1}H NMR Spectra of Rh(III)-Complex 5



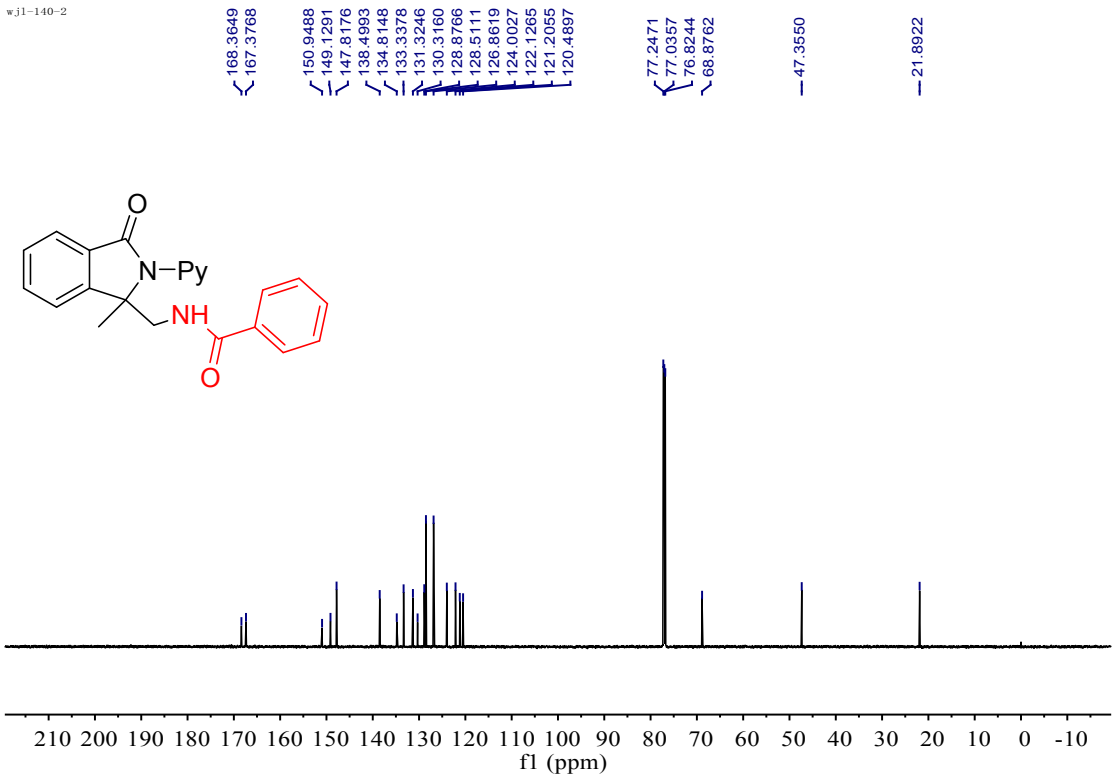
^{13}C NMR Spectra of Rh(III)-Complex 5



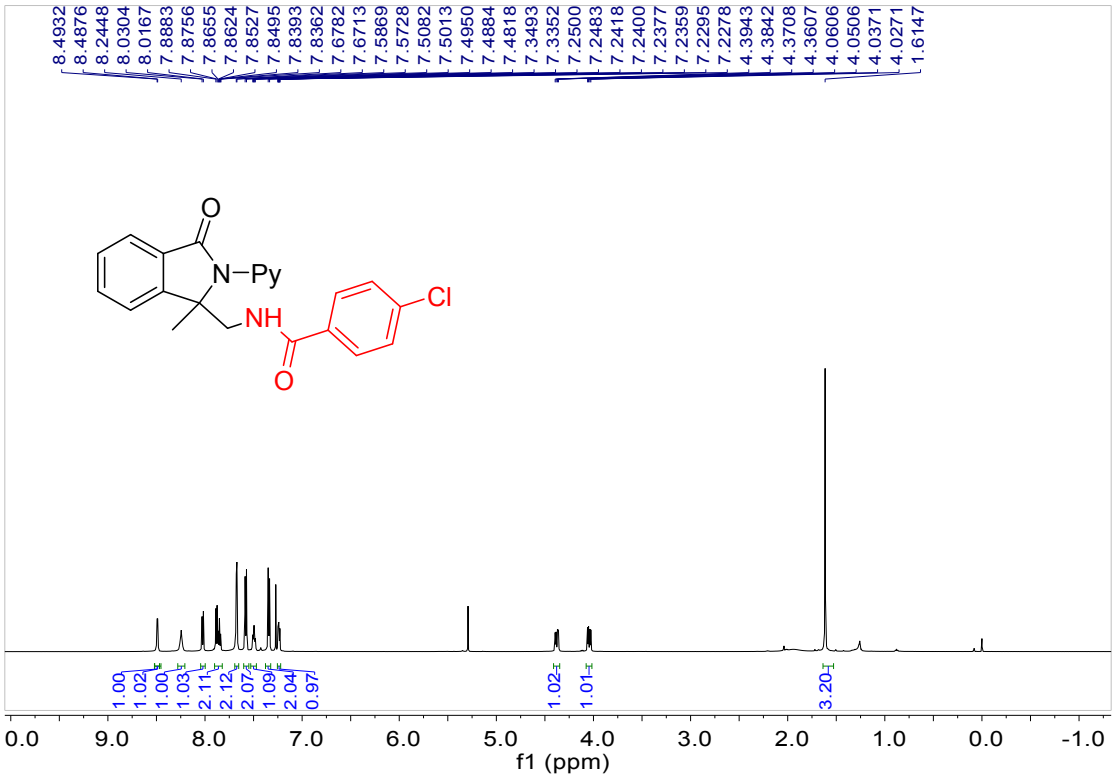
^{1}H NMR Spectra of Compound **3aa**



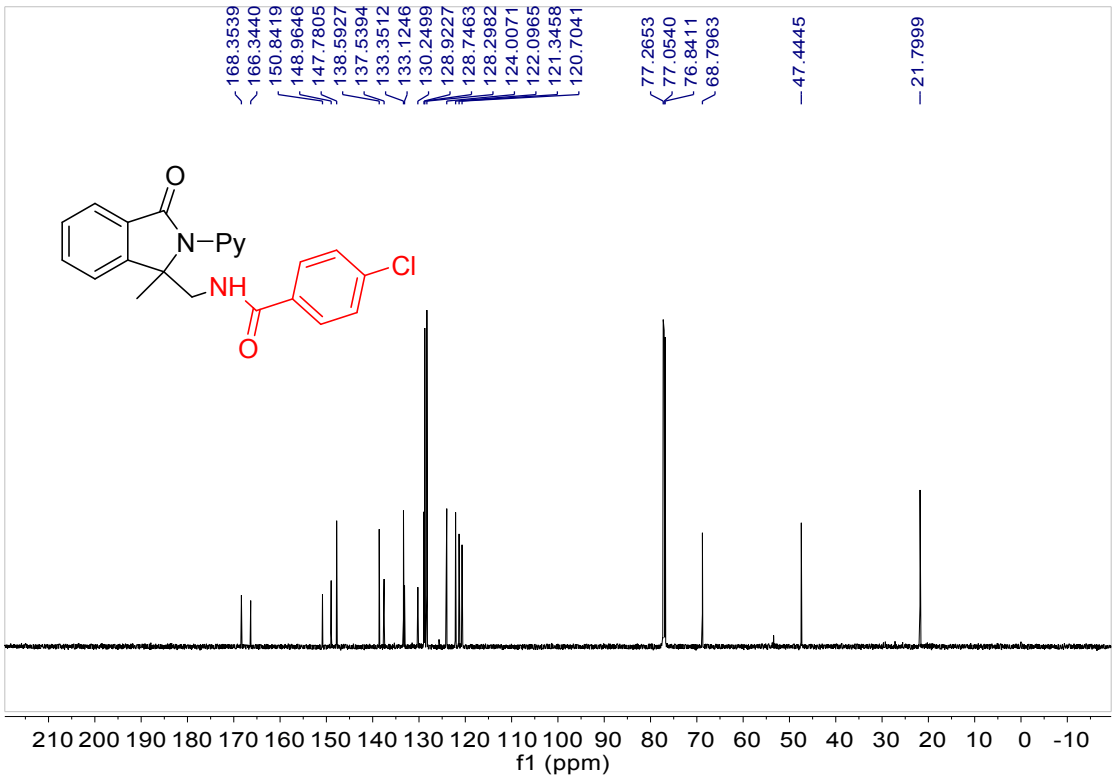
^{13}C NMR Spectra of Compound **3aa**



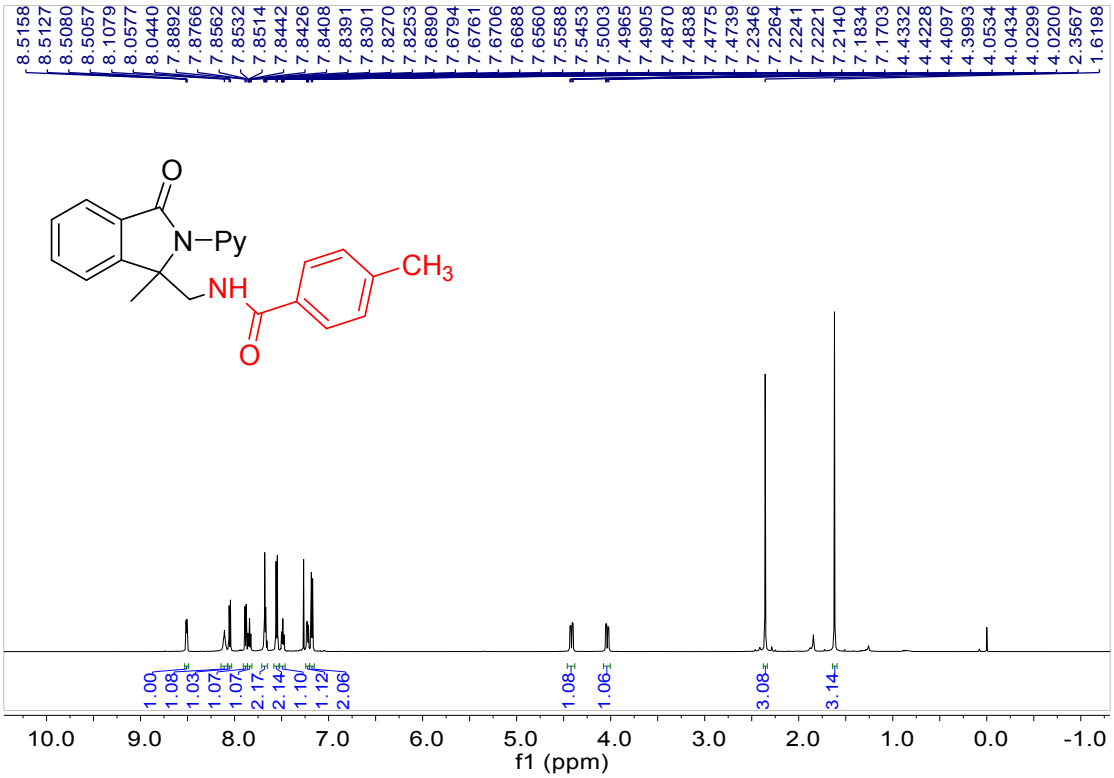
^{1}H NMR Spectra of Compound **3ab**



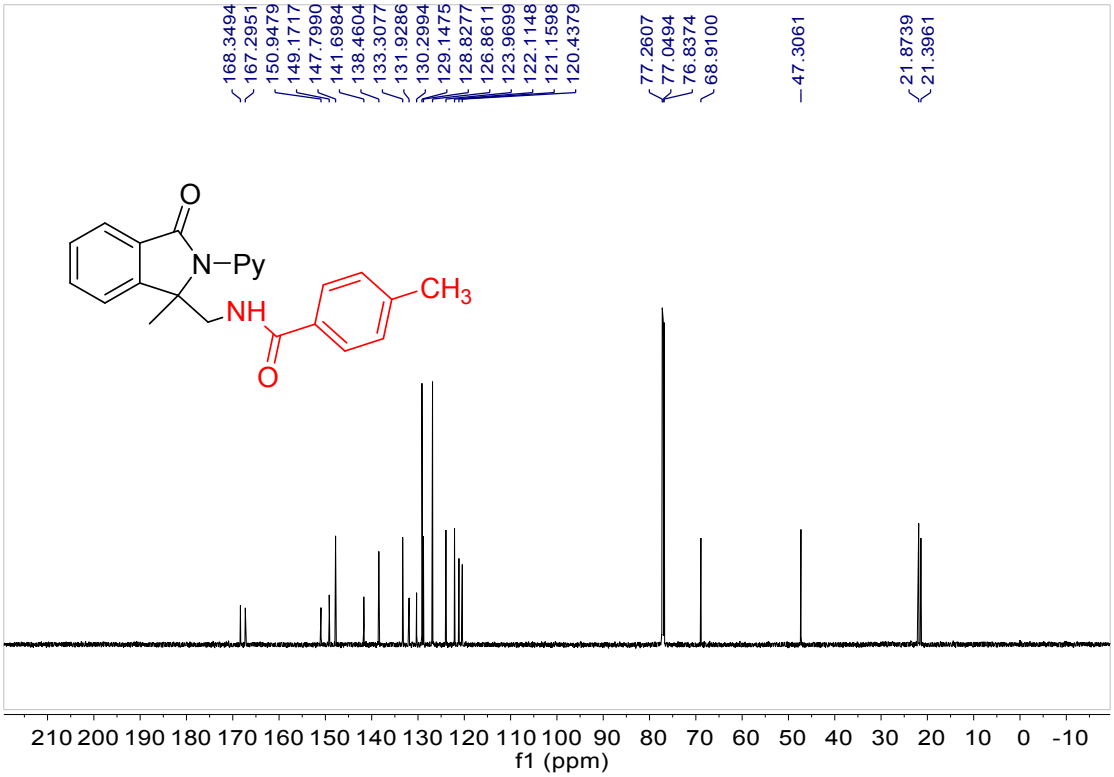
^{13}C NMR Spectra of Compound **3ab**



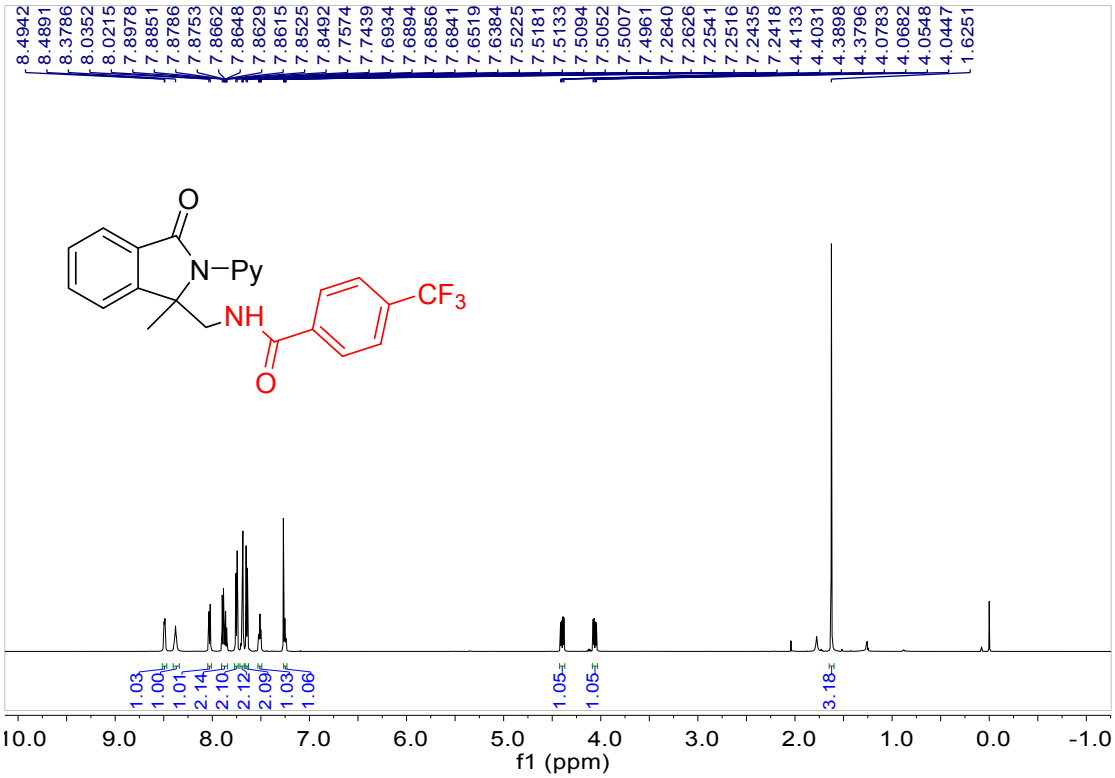
^{1}H NMR Spectra of Compound **3ac**



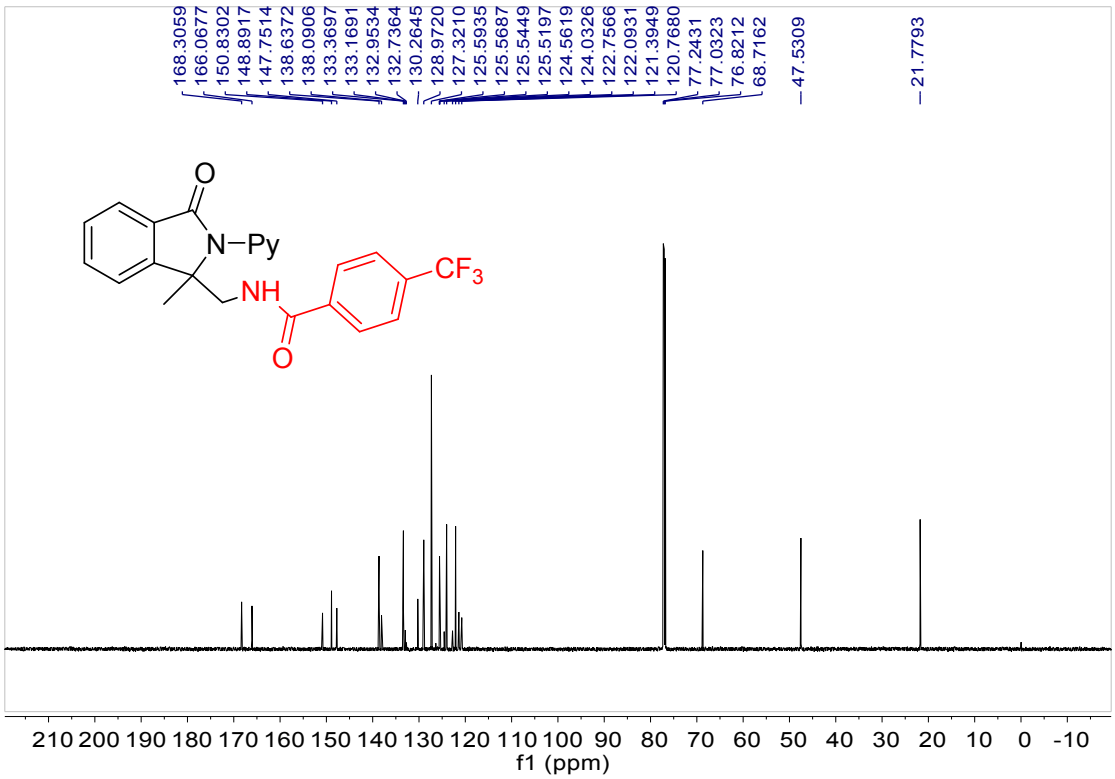
^{13}C NMR Spectra of Compound **3ac**



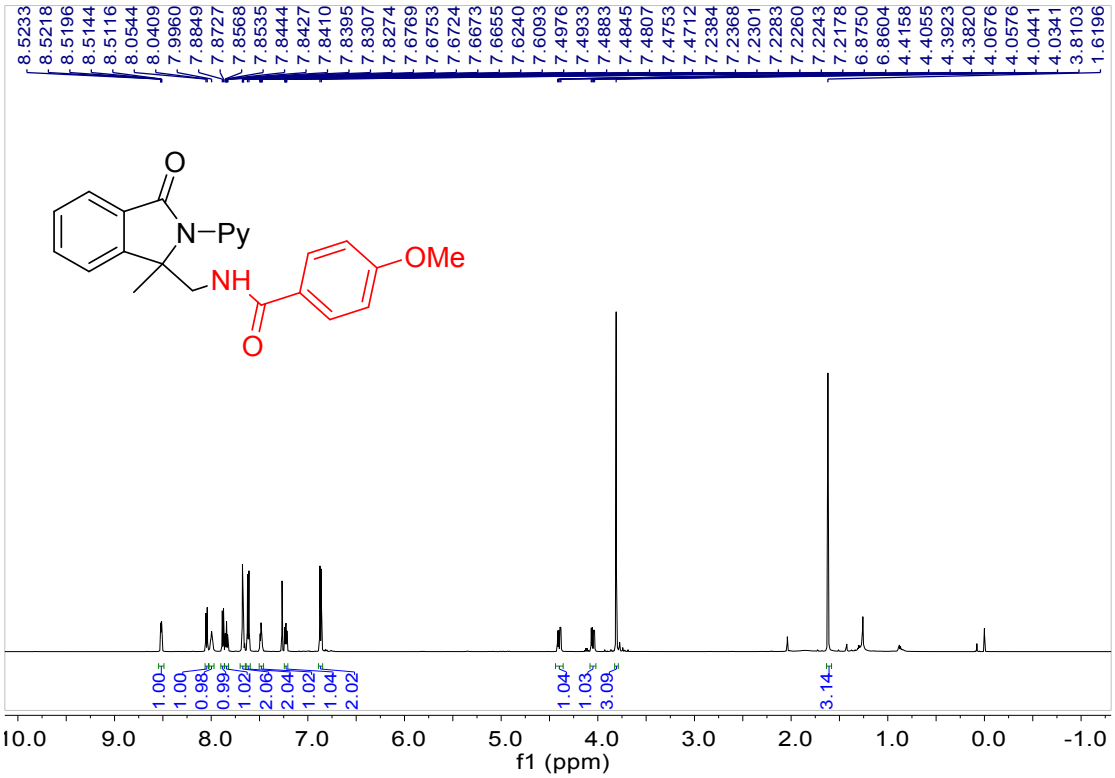
^{1}H NMR Spectra of Compound **3ad**



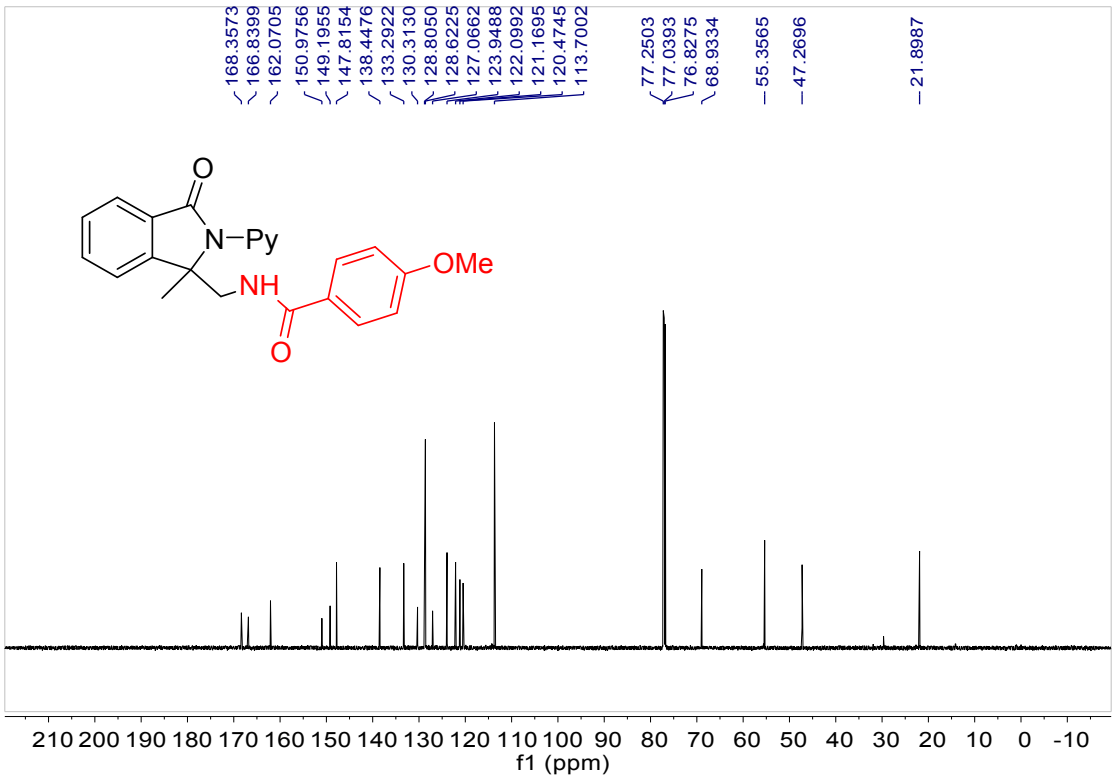
^{13}C NMR Spectra of Compound **3ad**



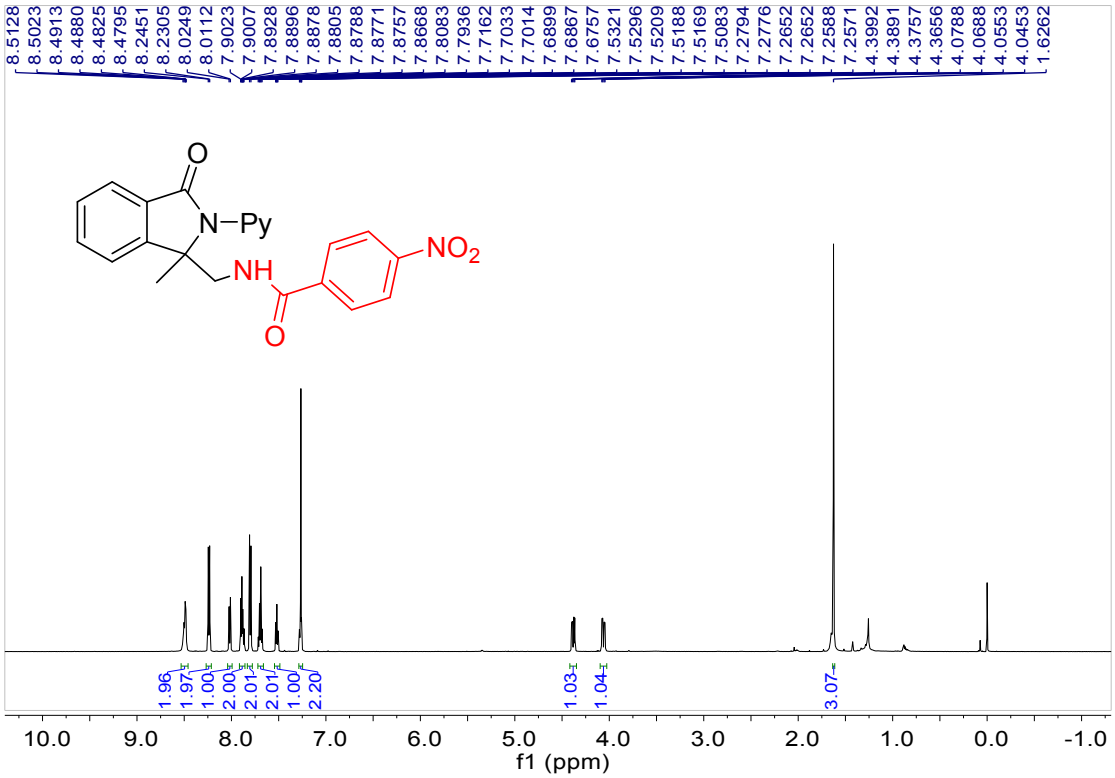
^{1}H NMR Spectra of Compound **3ae**



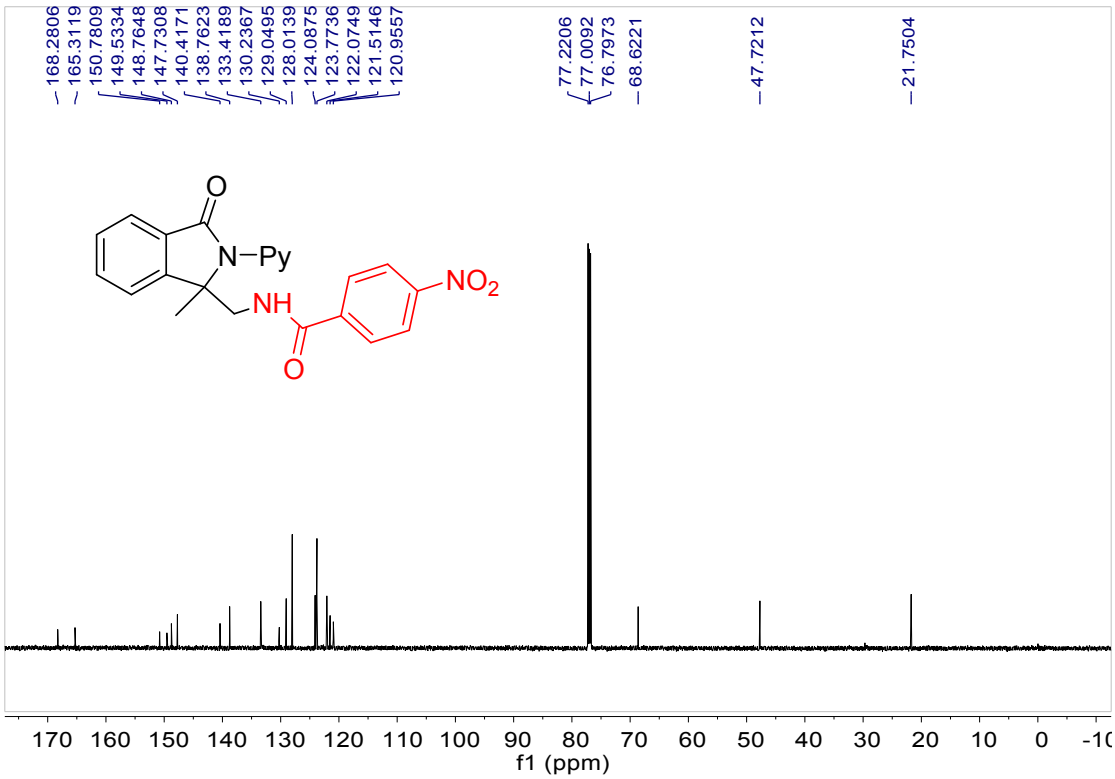
^{13}C NMR Spectra of Compound **3ae**



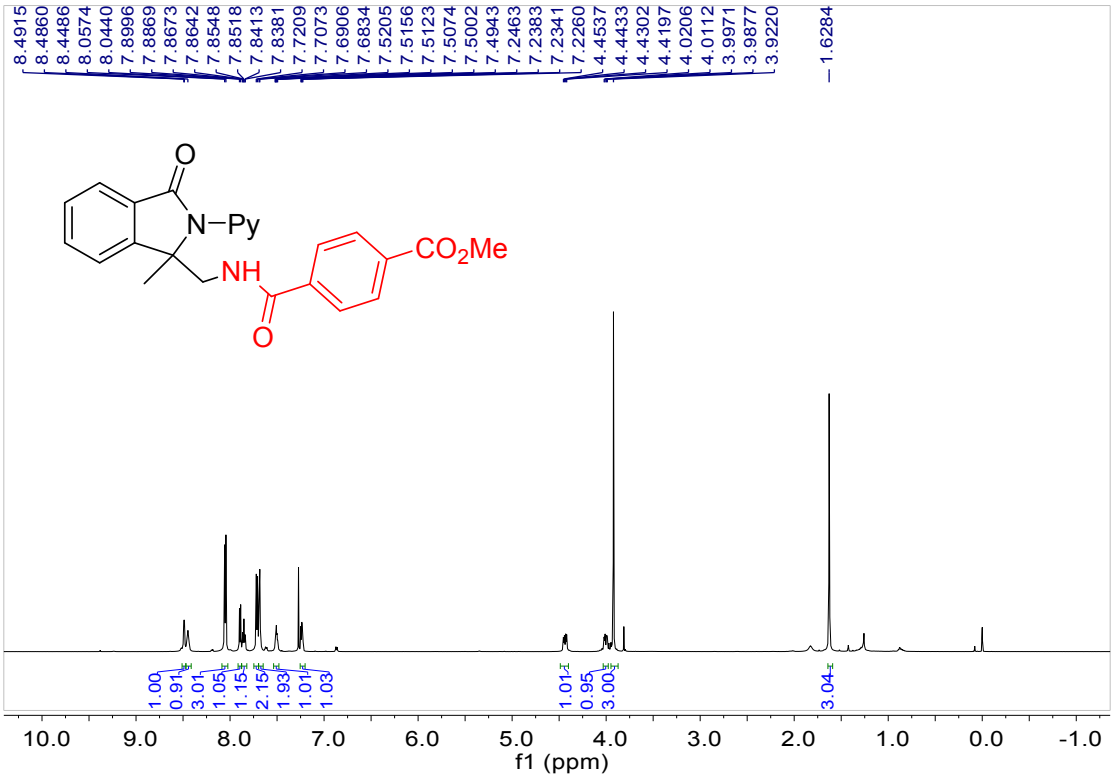
^{1}H NMR Spectra of Compound **3af**



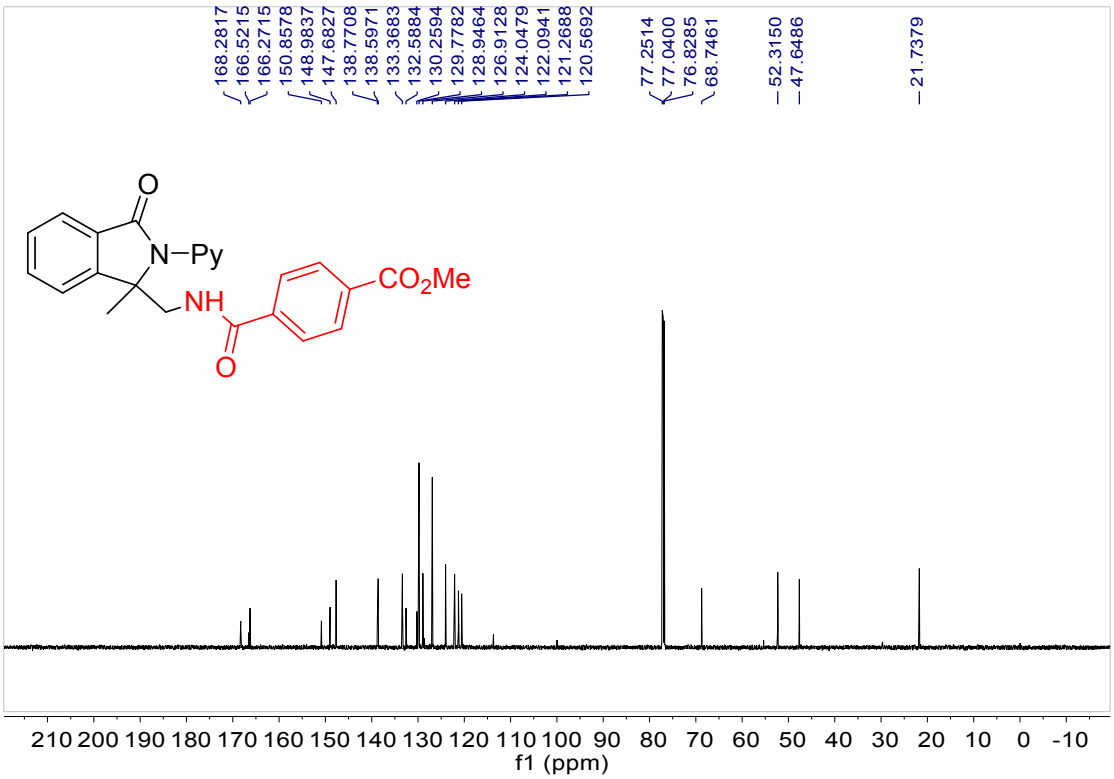
^{13}C NMR Spectra of Compound **3af**



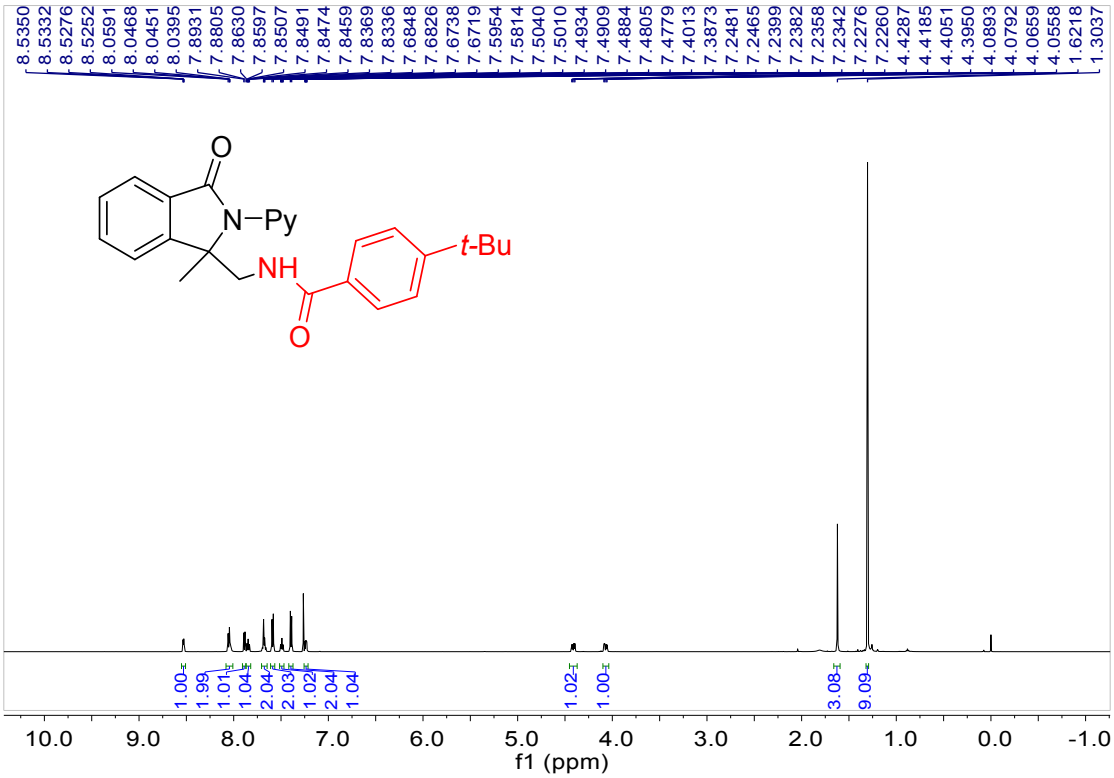
^{1}H NMR Spectra of Compound **3ag**



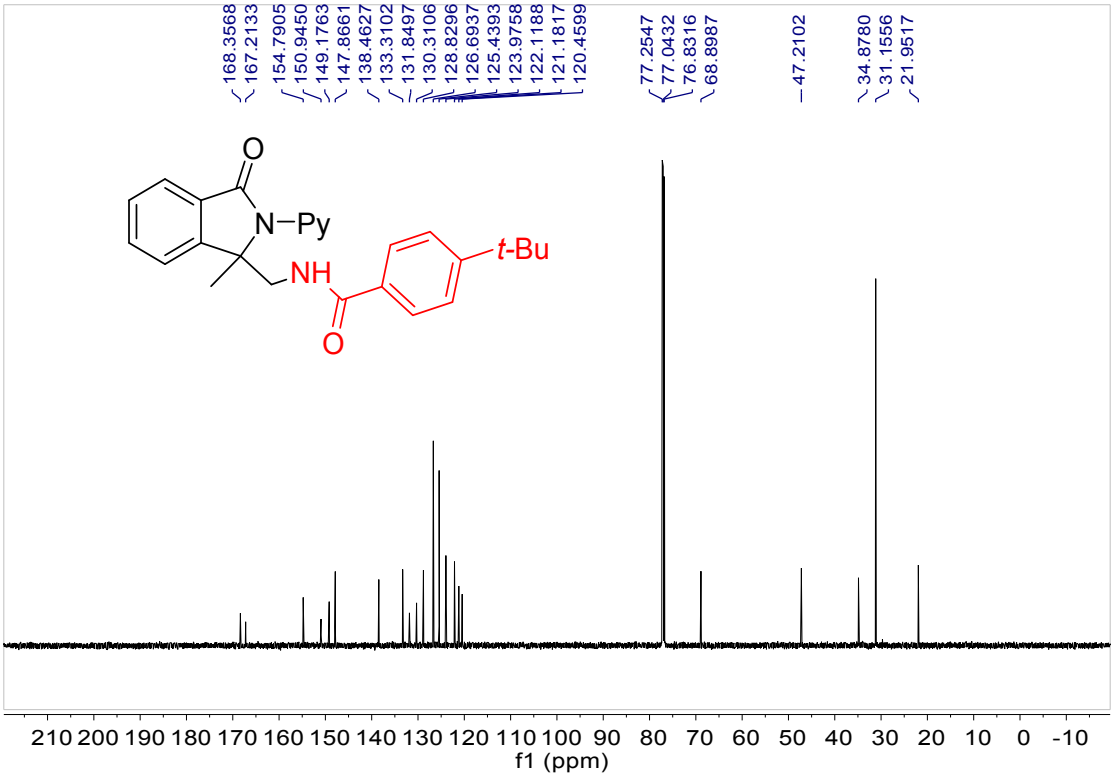
^{13}C NMR Spectra of Compound **3ag**



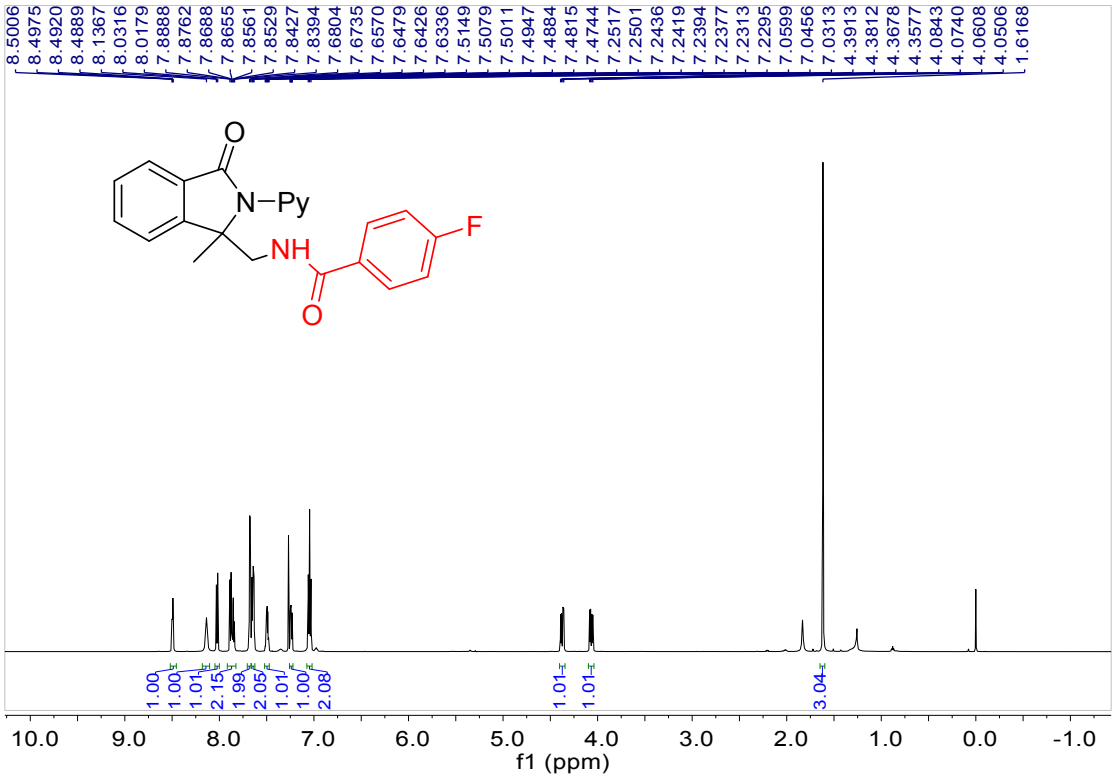
^{1}H NMR Spectra of Compound **3ah**



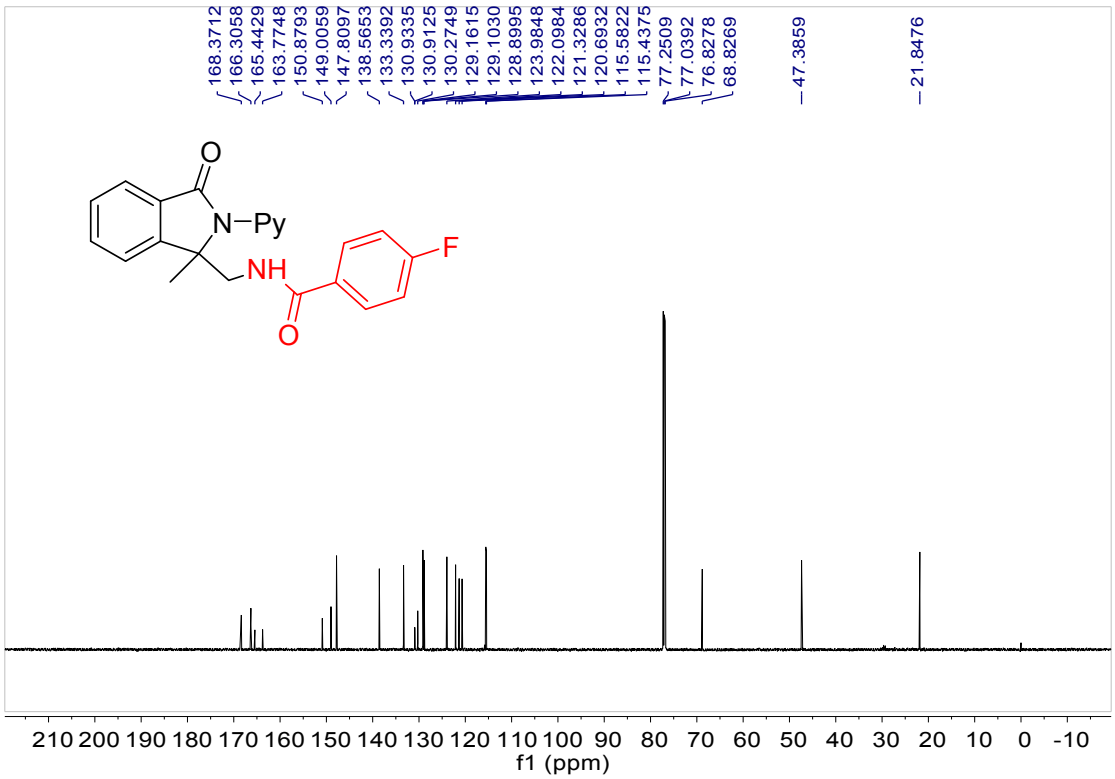
^{13}C NMR Spectra of Compound **3ah**



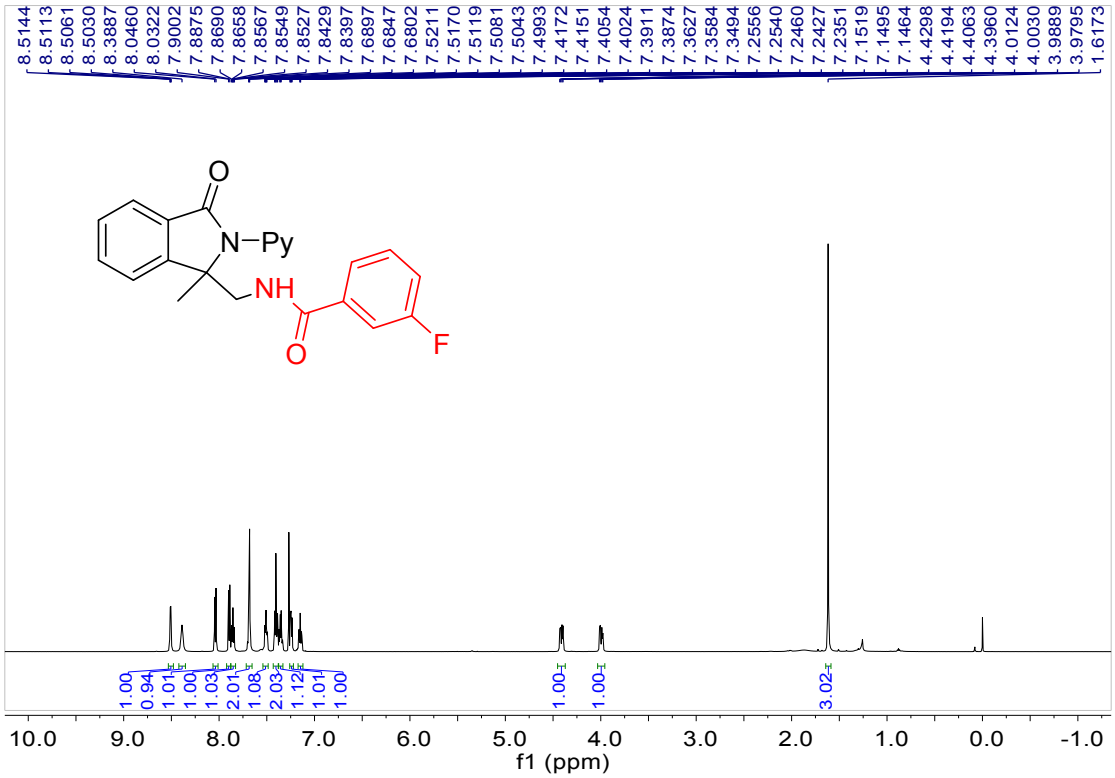
^{1}H NMR Spectra of Compound **3ai**



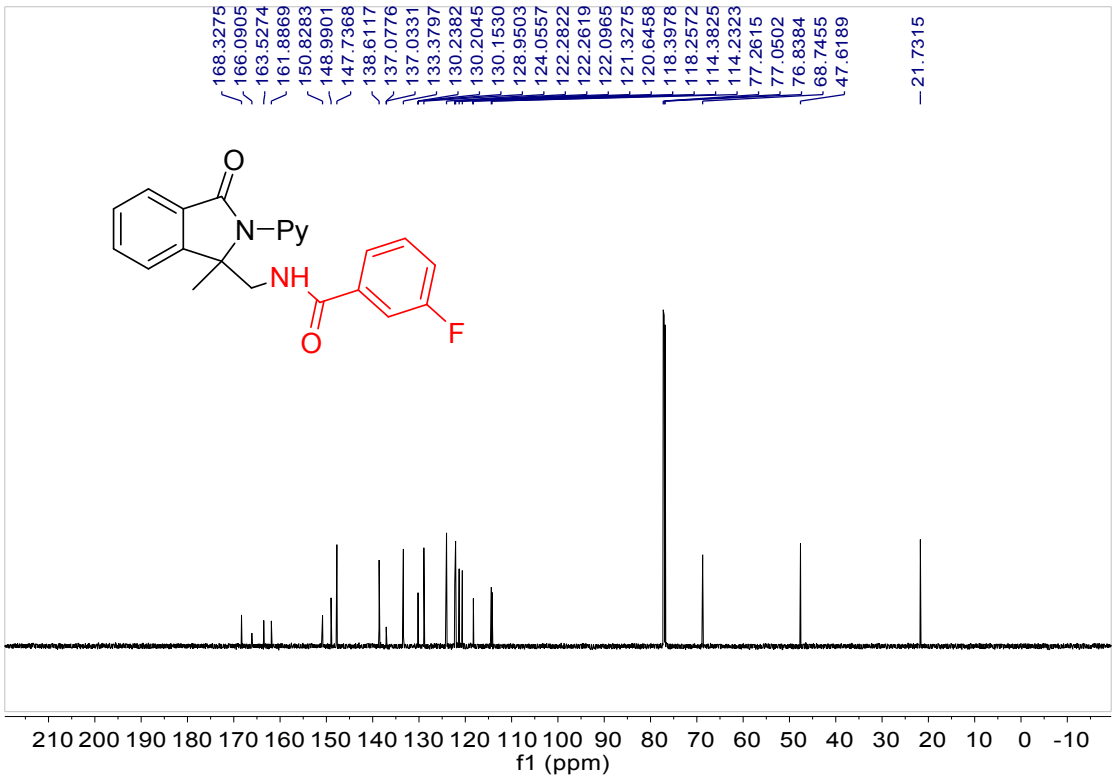
^{13}C NMR Spectra of Compound **3ai**



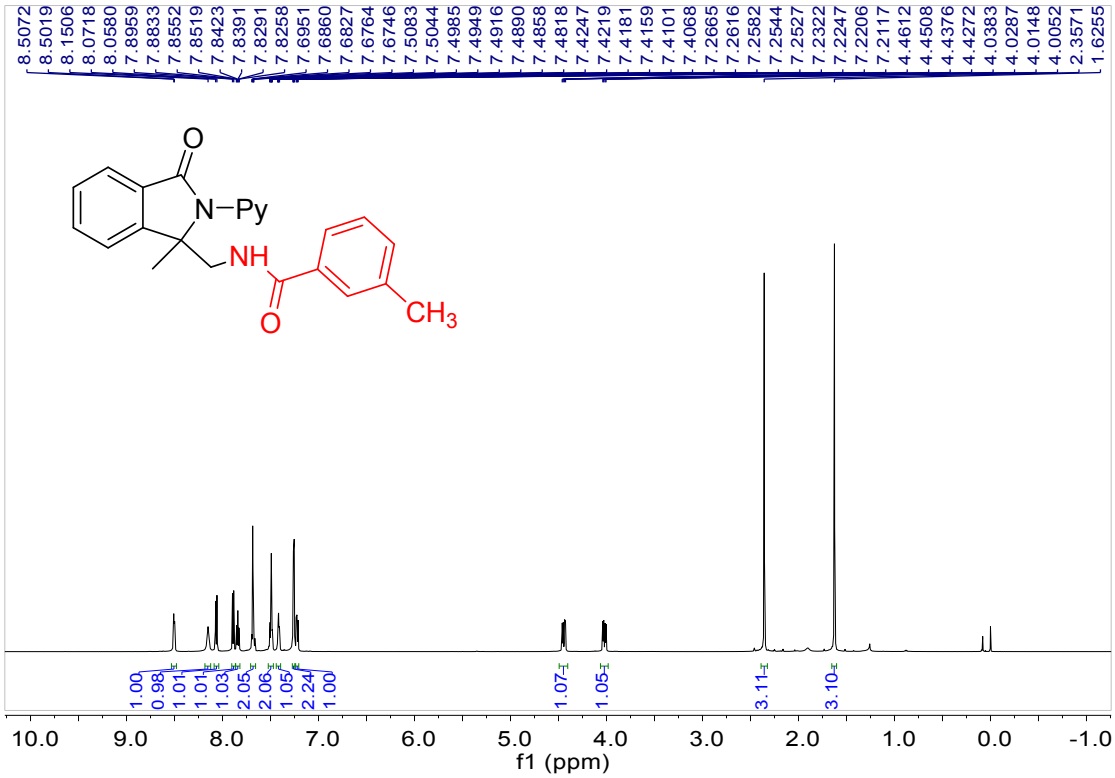
^{1}H NMR Spectra of Compound **3aj**



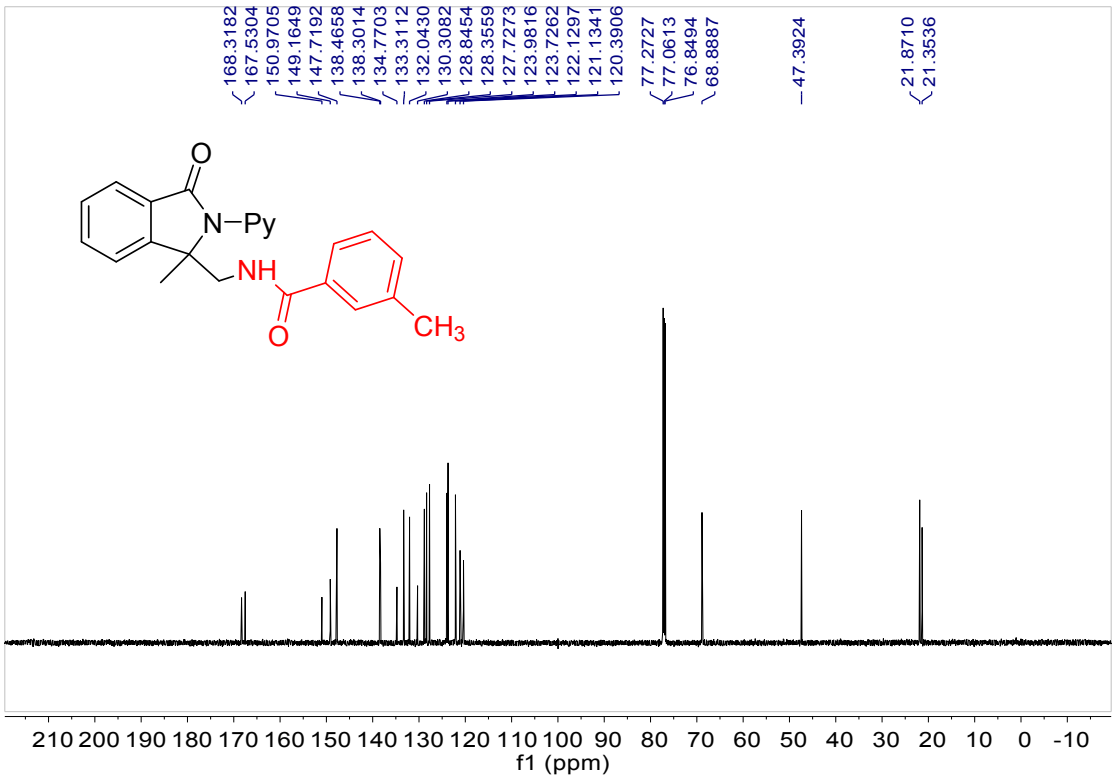
^{13}C NMR Spectra of Compound **3aj**



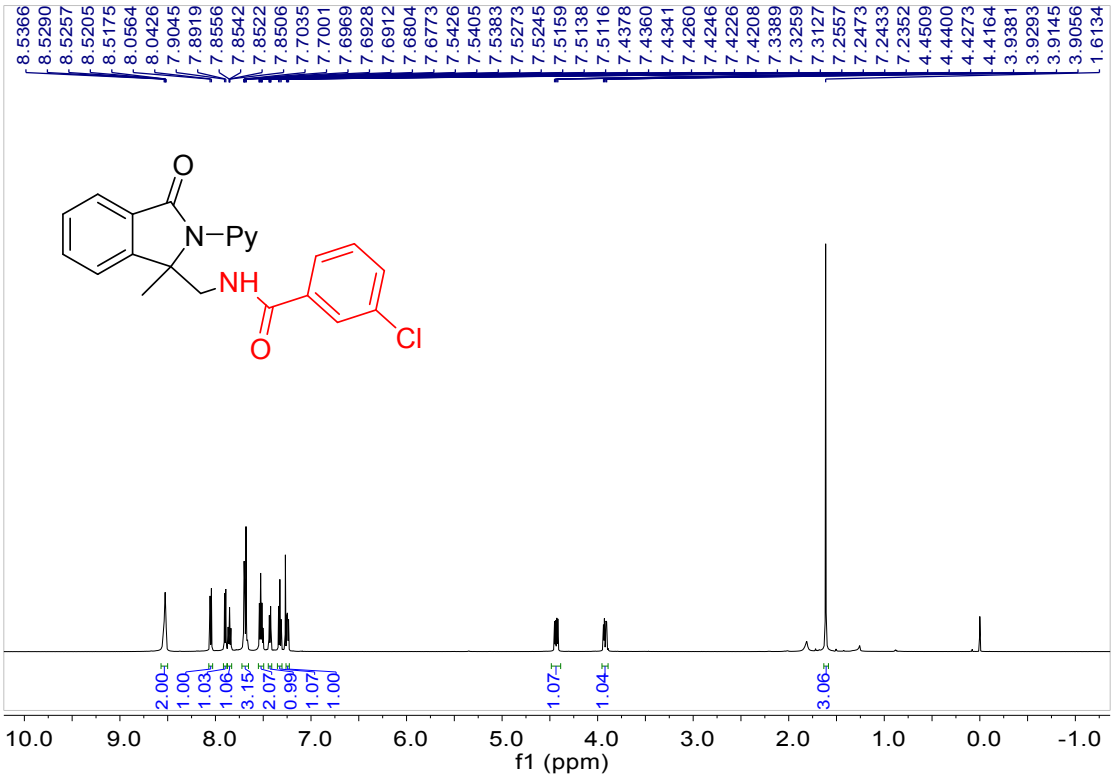
^{1}H NMR Spectra of Compound **3ak**



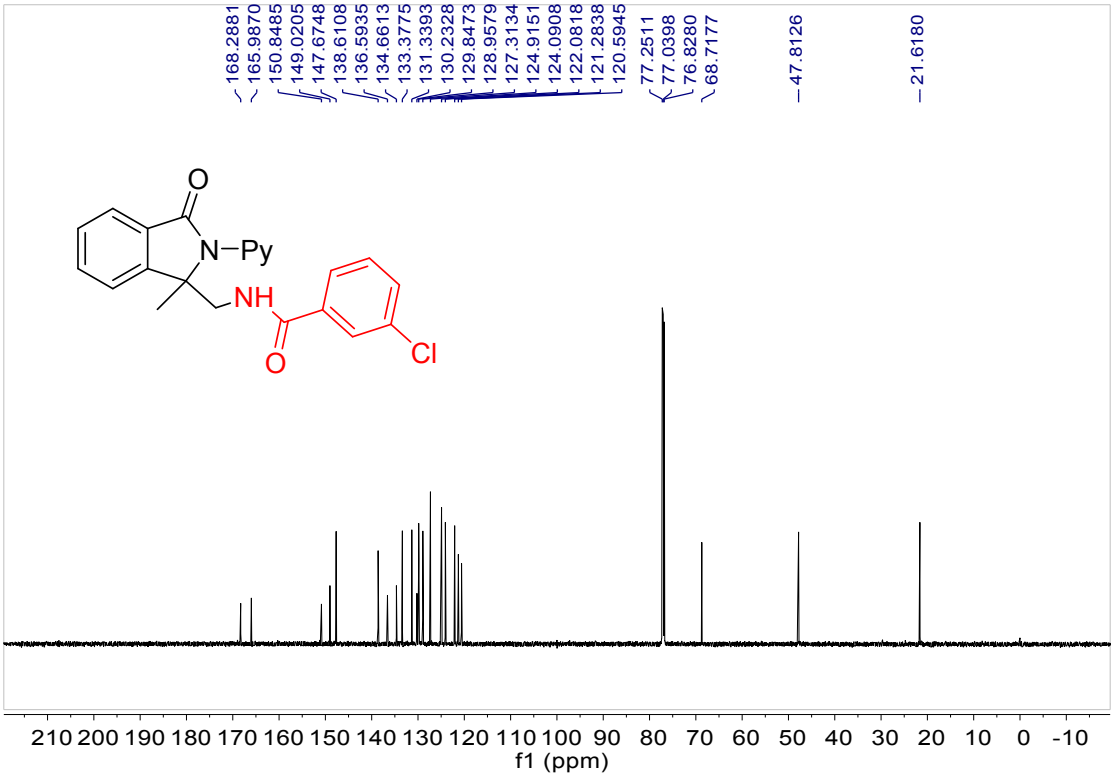
^{13}C NMR Spectra of Compound **3ak**



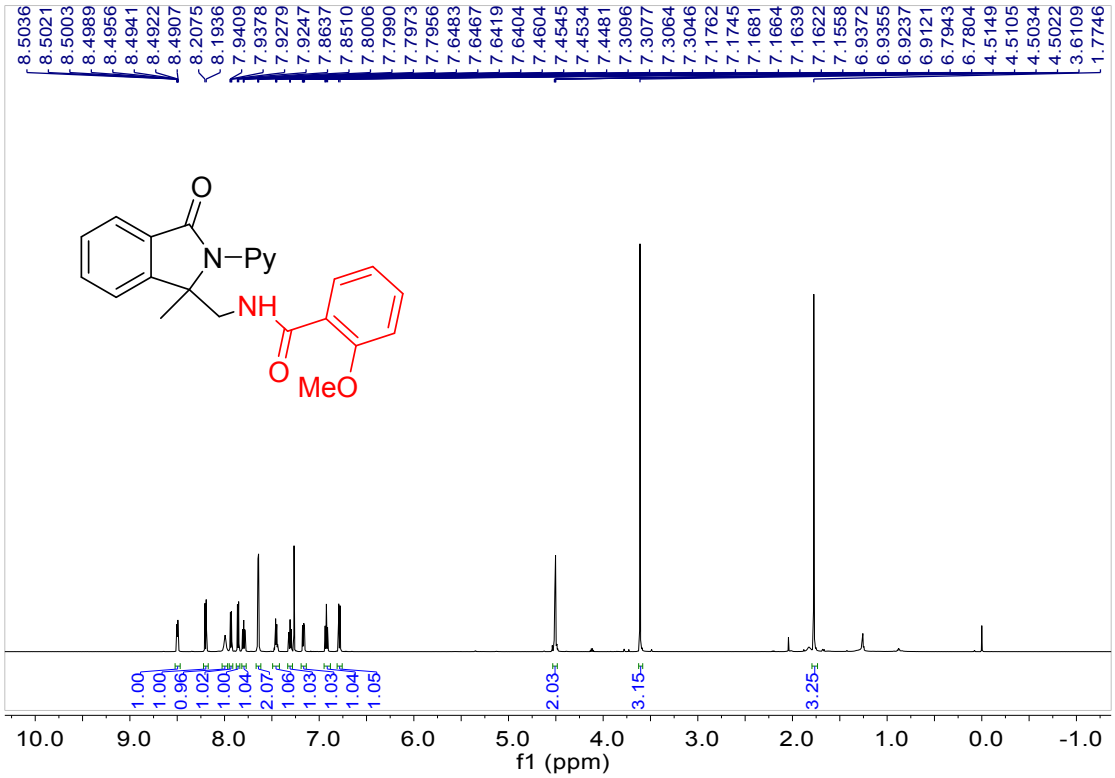
^{1}H NMR Spectra of Compound **3al**



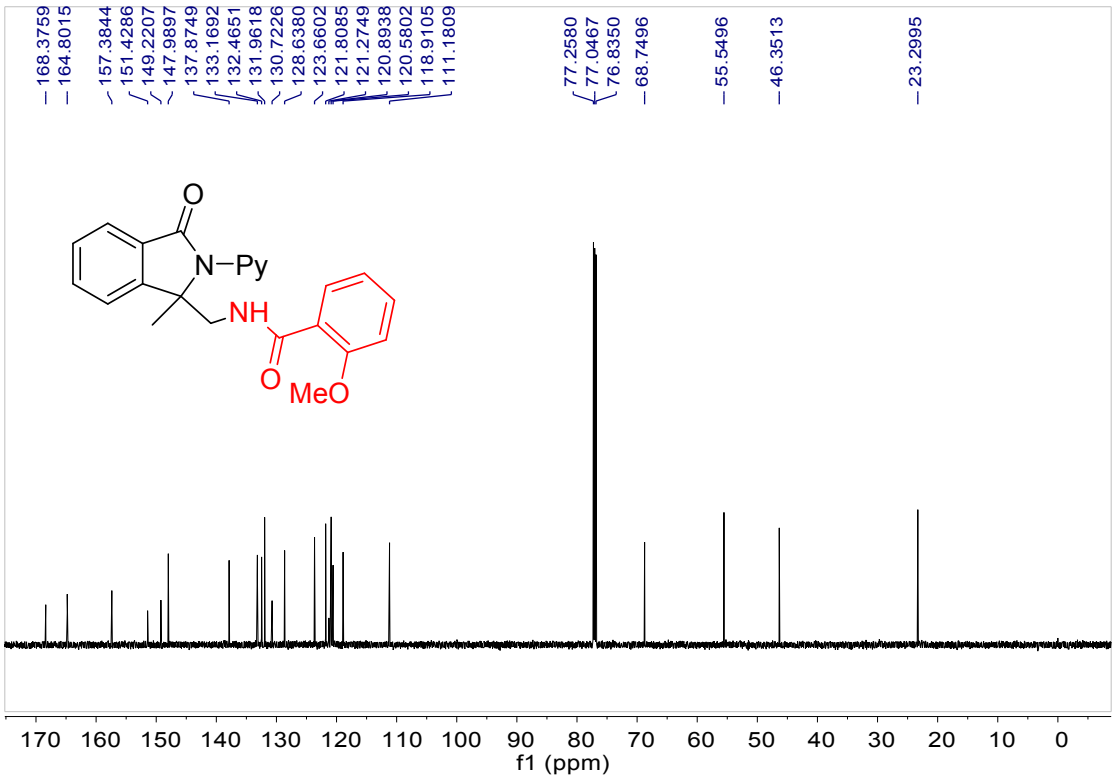
^{13}C NMR Spectra of Compound **3al**



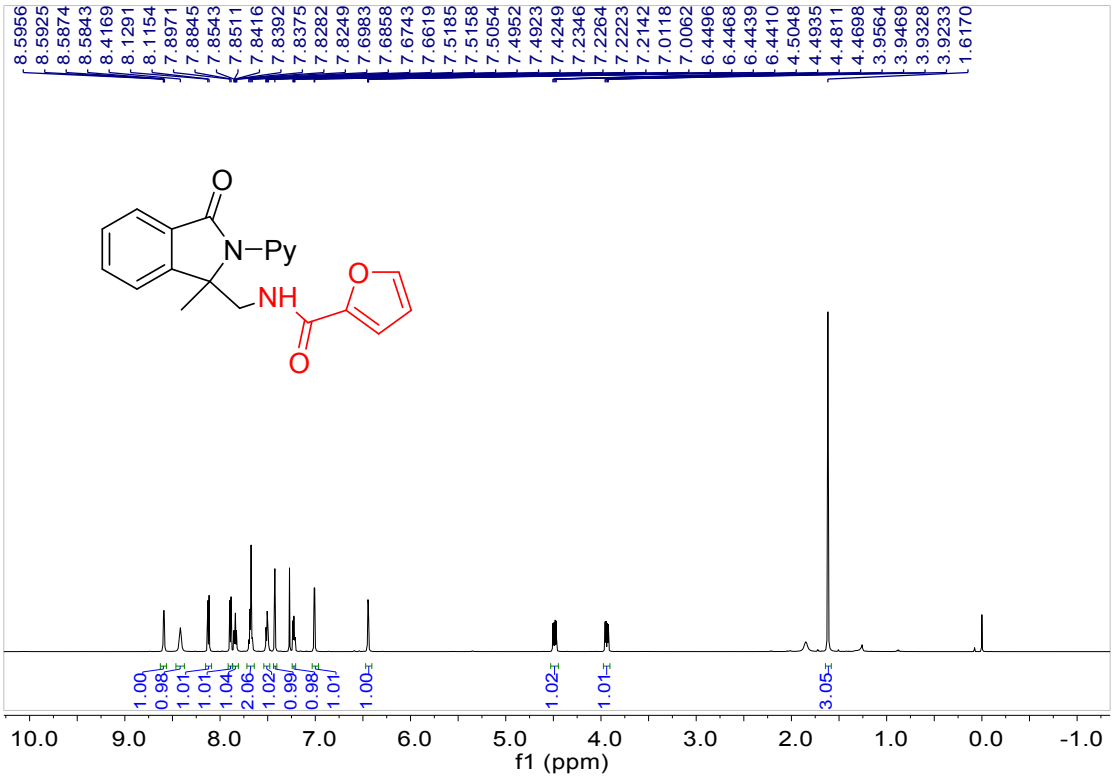
^{1}H NMR Spectra of Compound **3am**



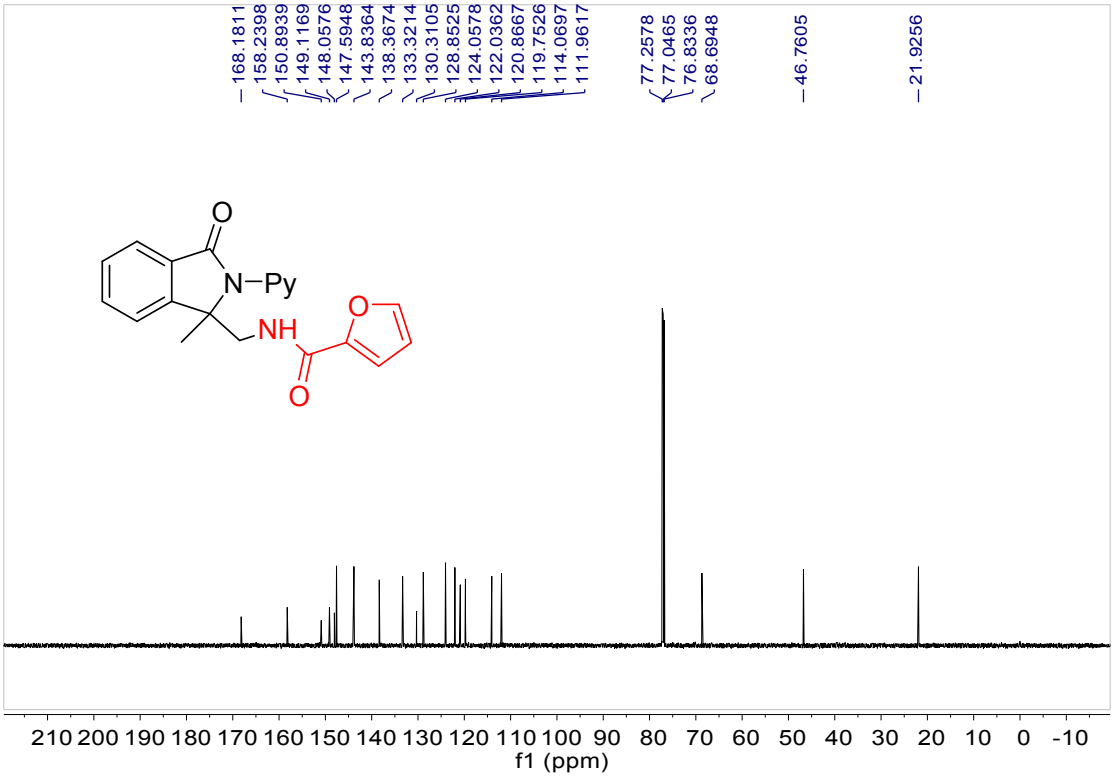
^{13}C NMR Spectra of Compound **3am**



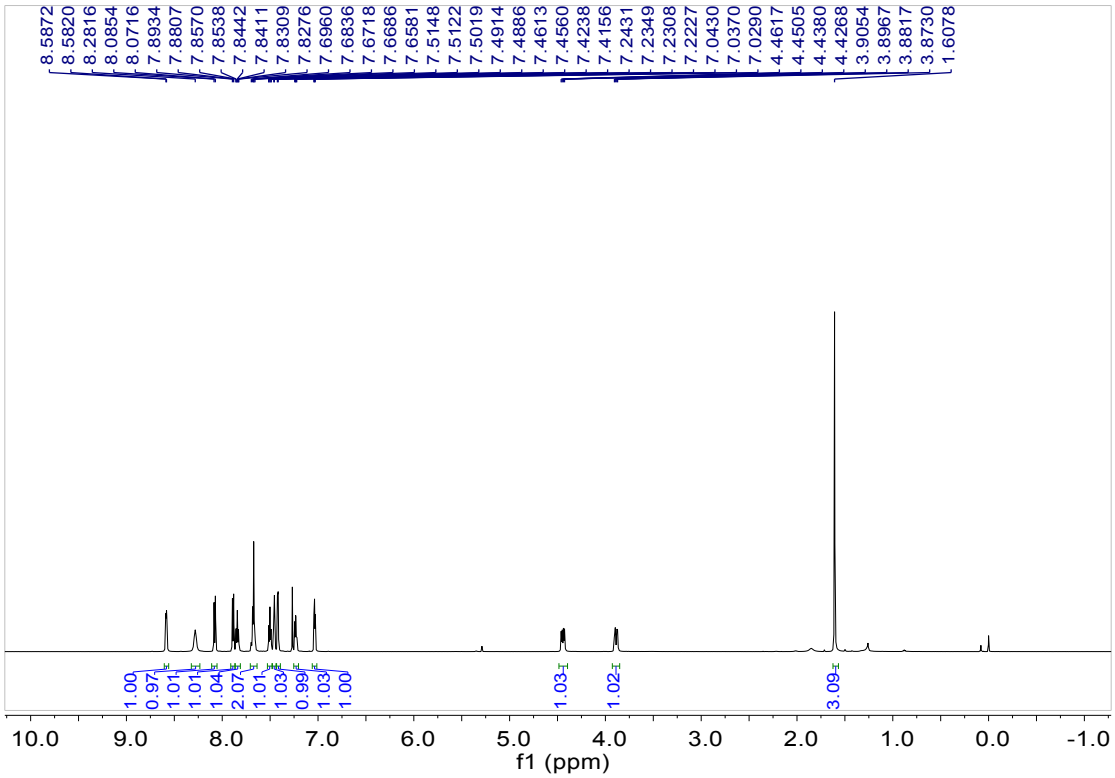
^{1}H NMR Spectra of Compound **3an**



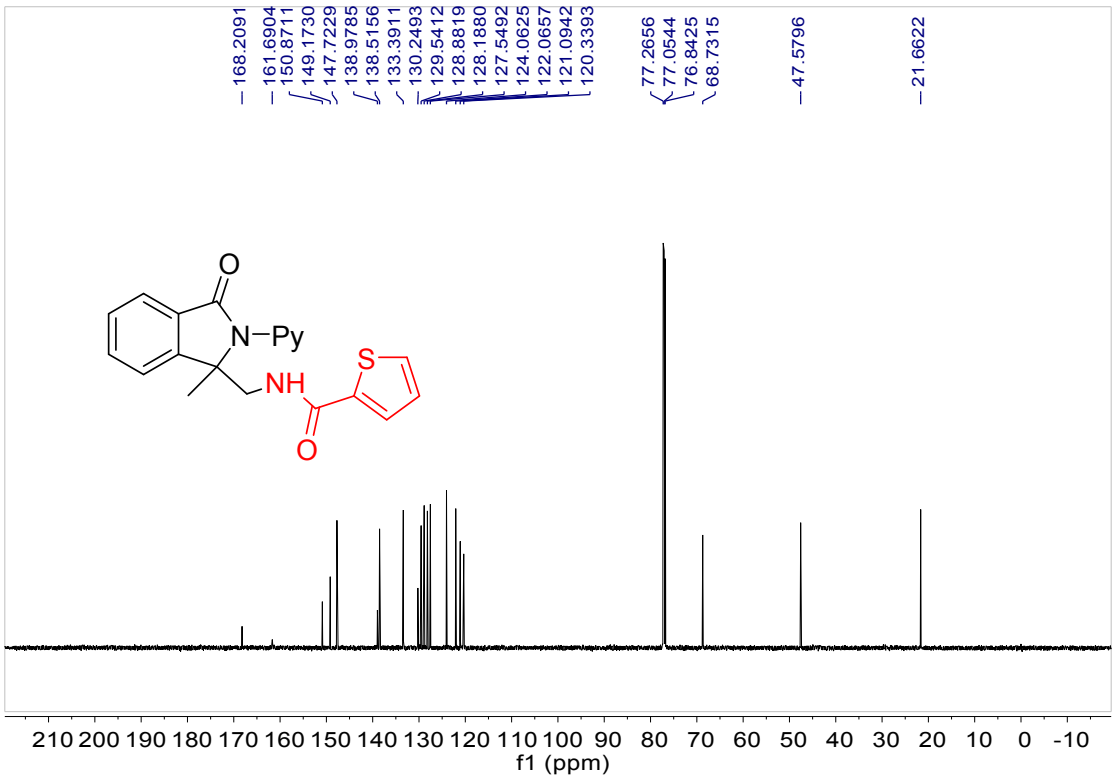
^{13}C NMR Spectra of Compound **3an**



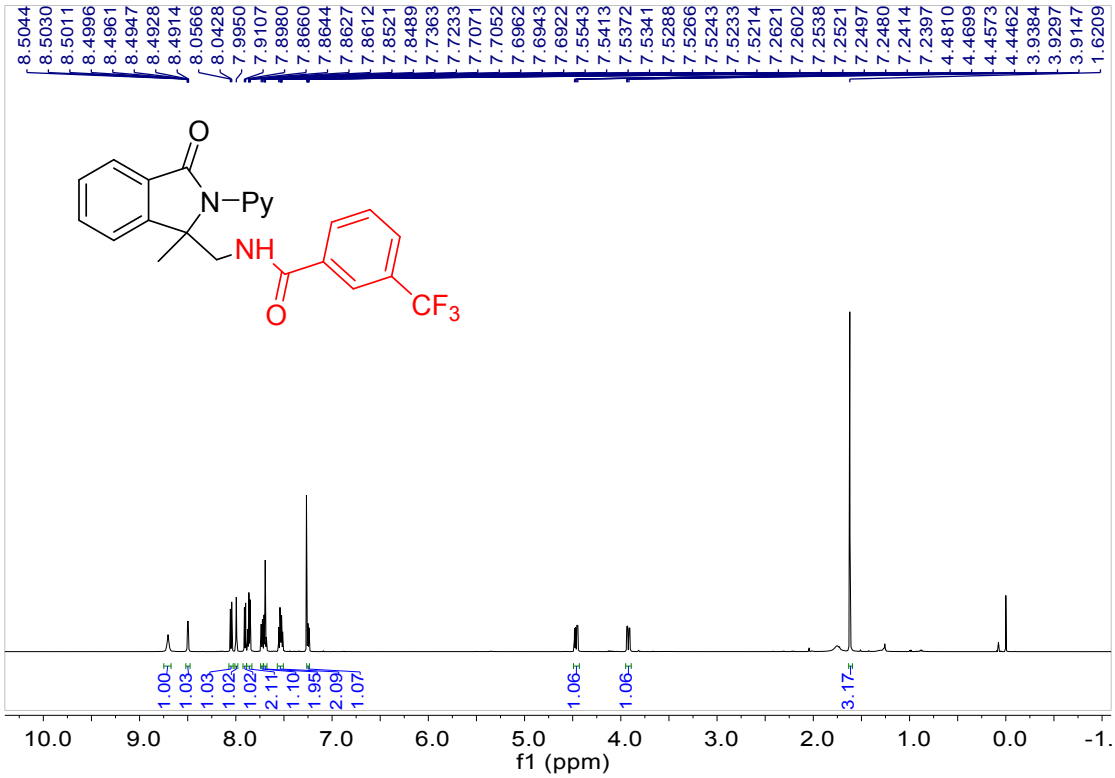
^{1}H NMR Spectra of Compound **3ao**



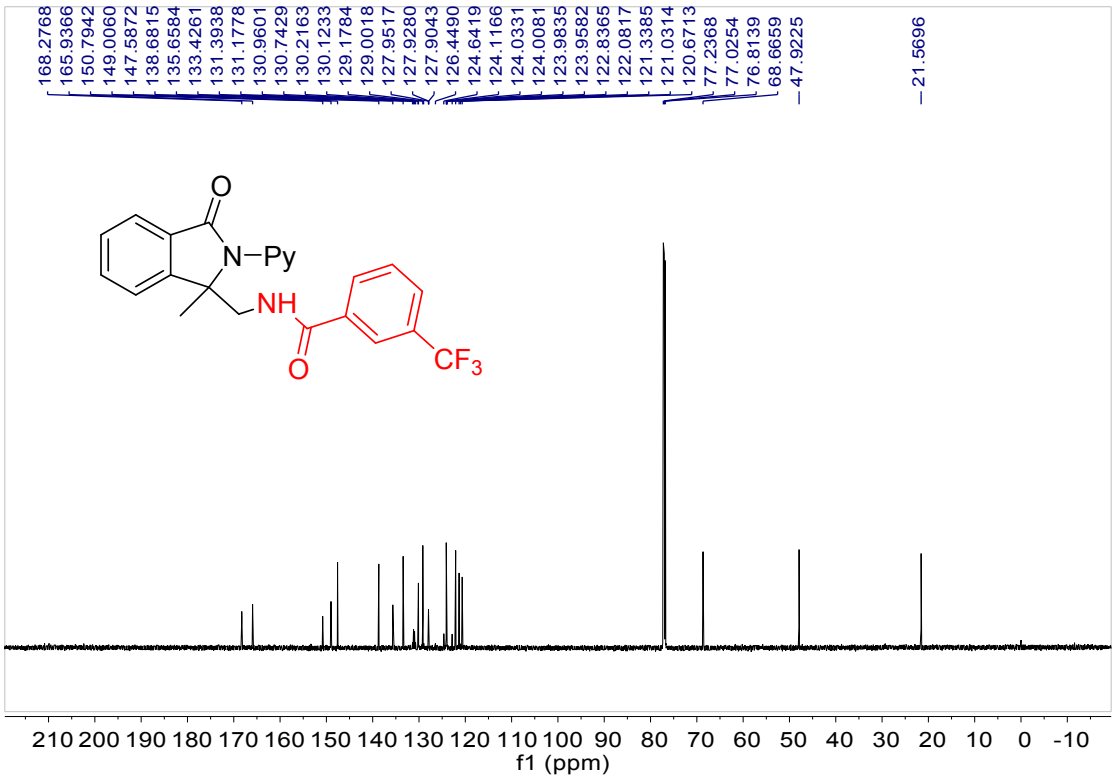
^{13}C NMR Spectra of Compound **3ao**



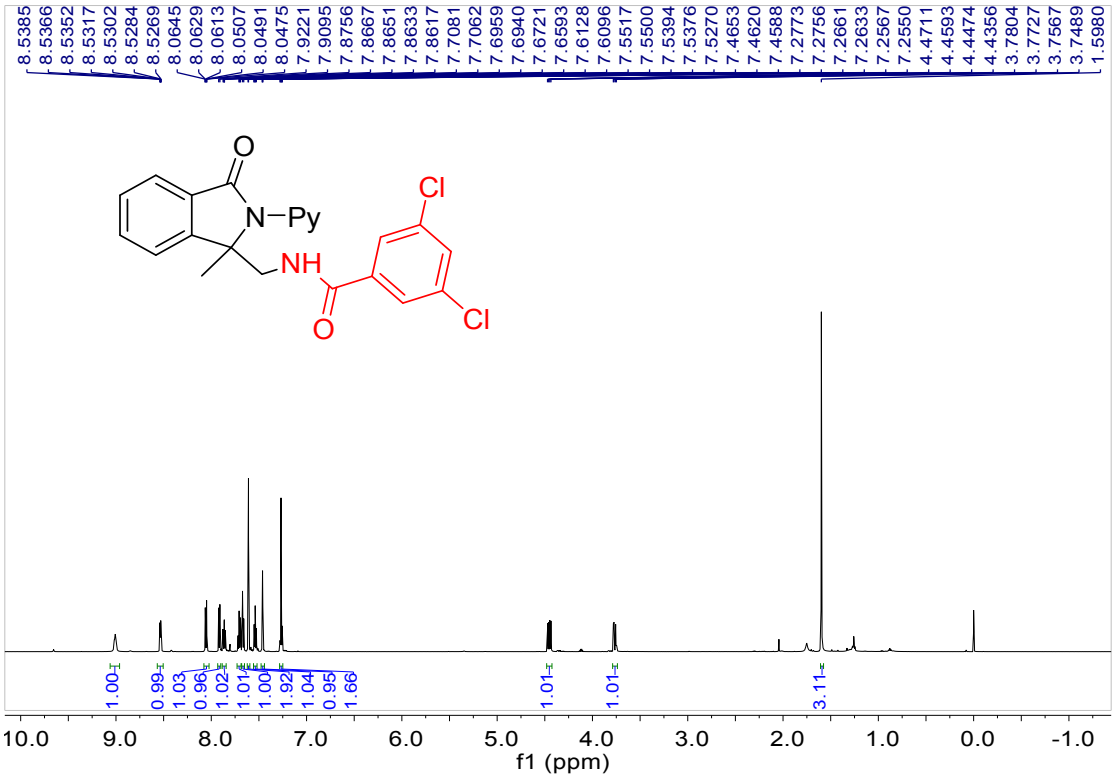
^{1}H NMR Spectra of Compound **3ap**



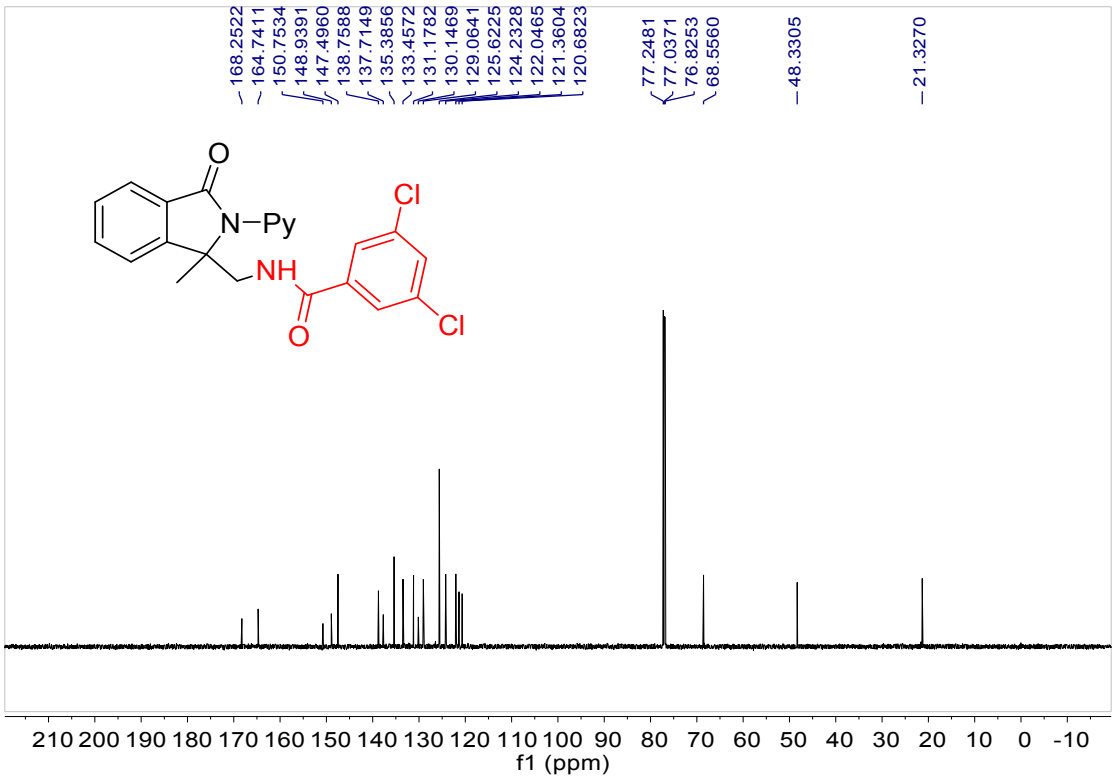
^{13}C NMR Spectra of Compound **3ap**



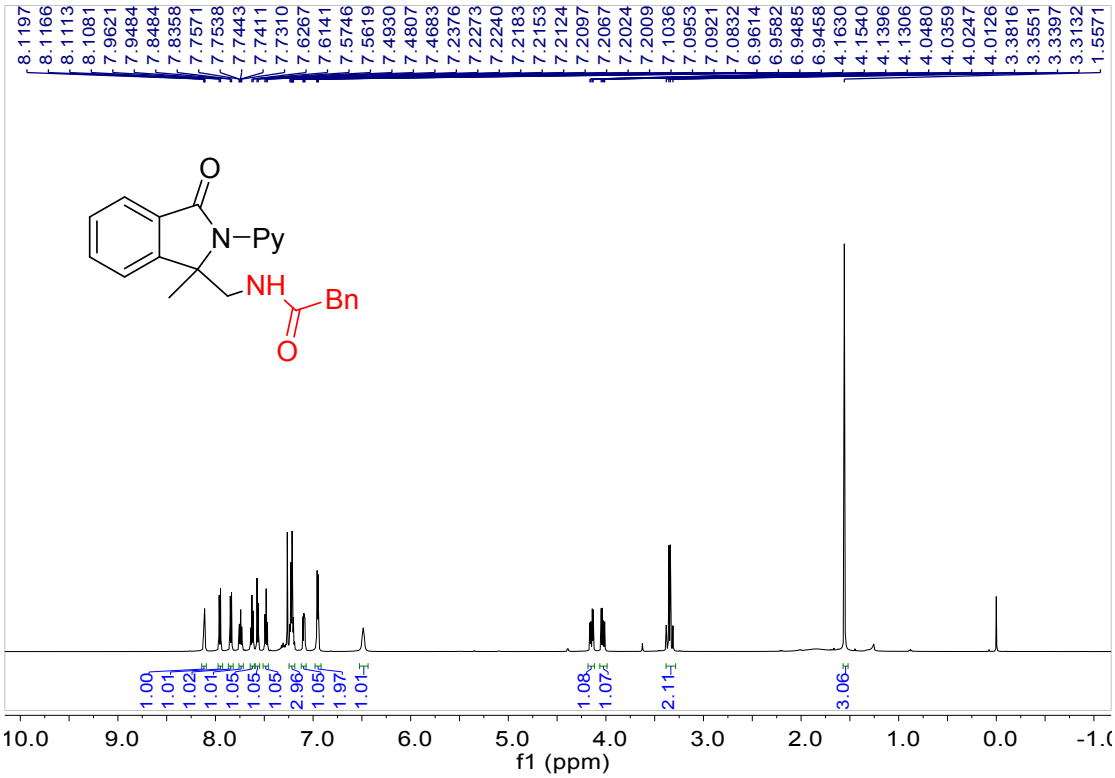
^{1}H NMR Spectra of Compound **3aq**



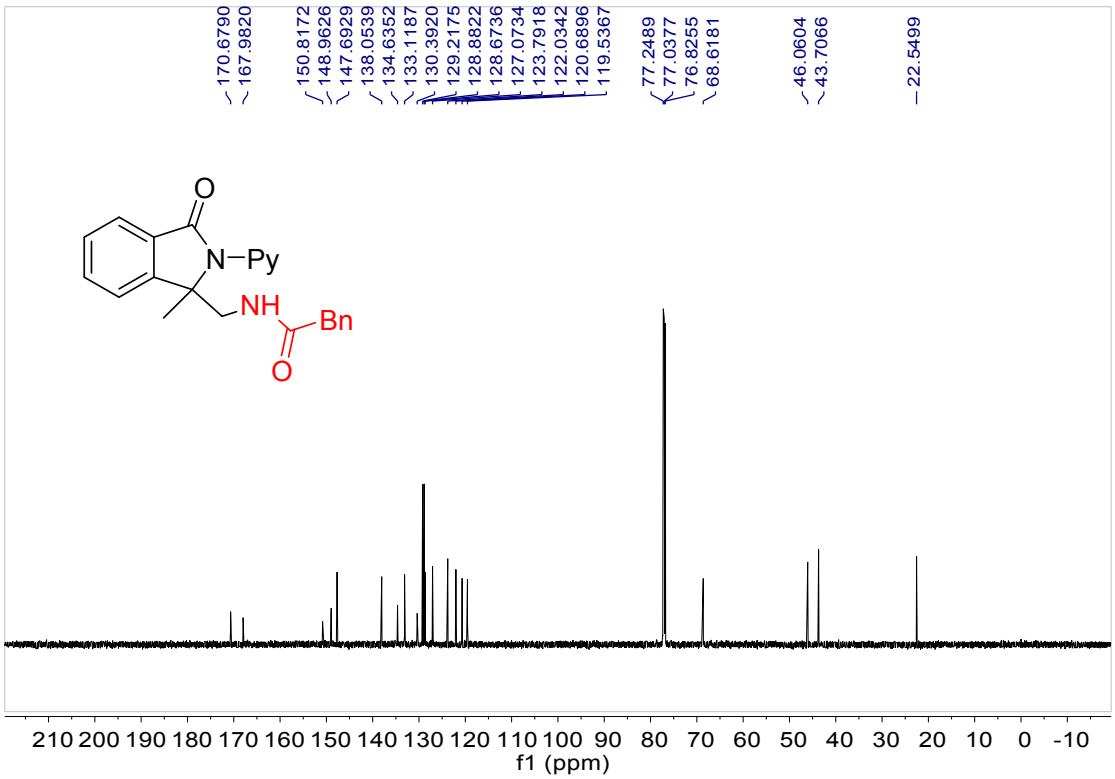
^{13}C NMR Spectra of Compound **3aq**



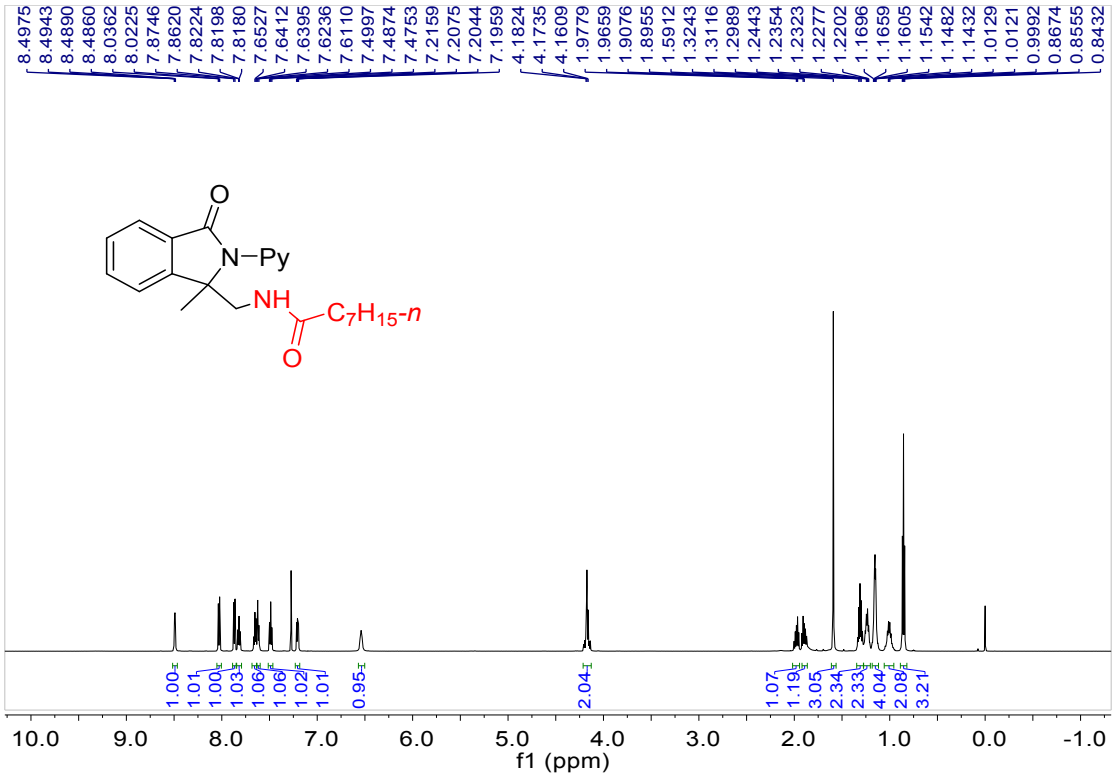
^{1}H NMR Spectra of Compound **3ar**



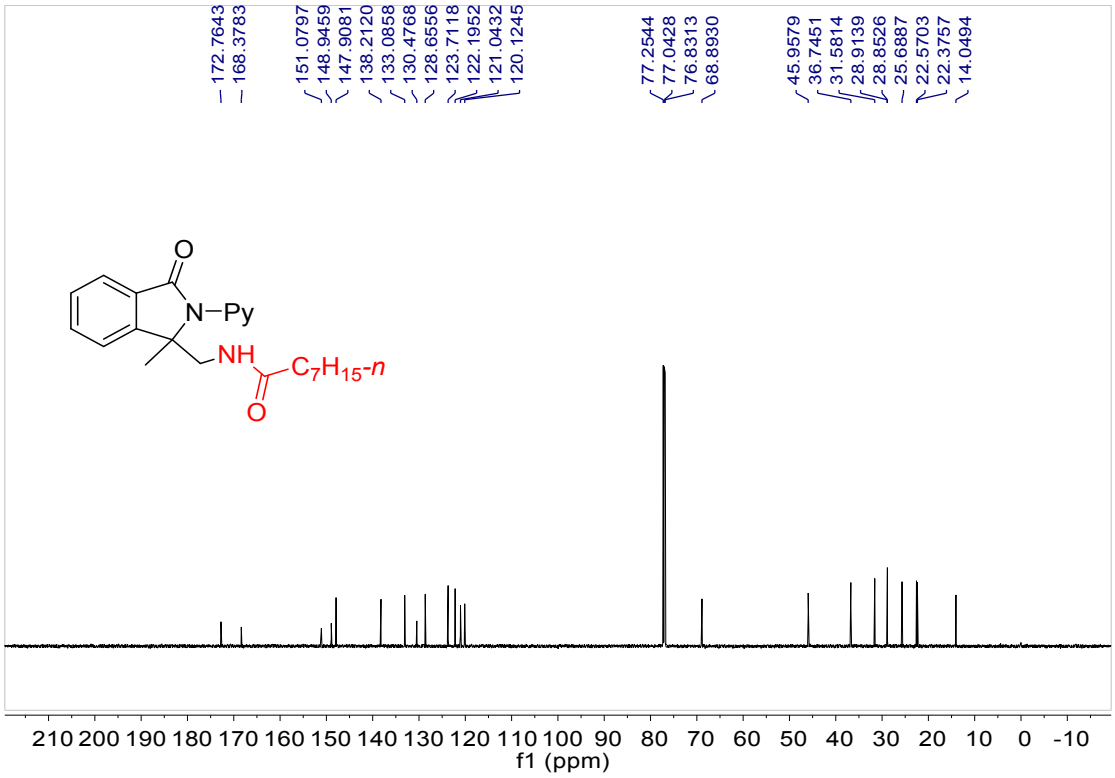
^{13}C NMR Spectra of Compound **3ar**



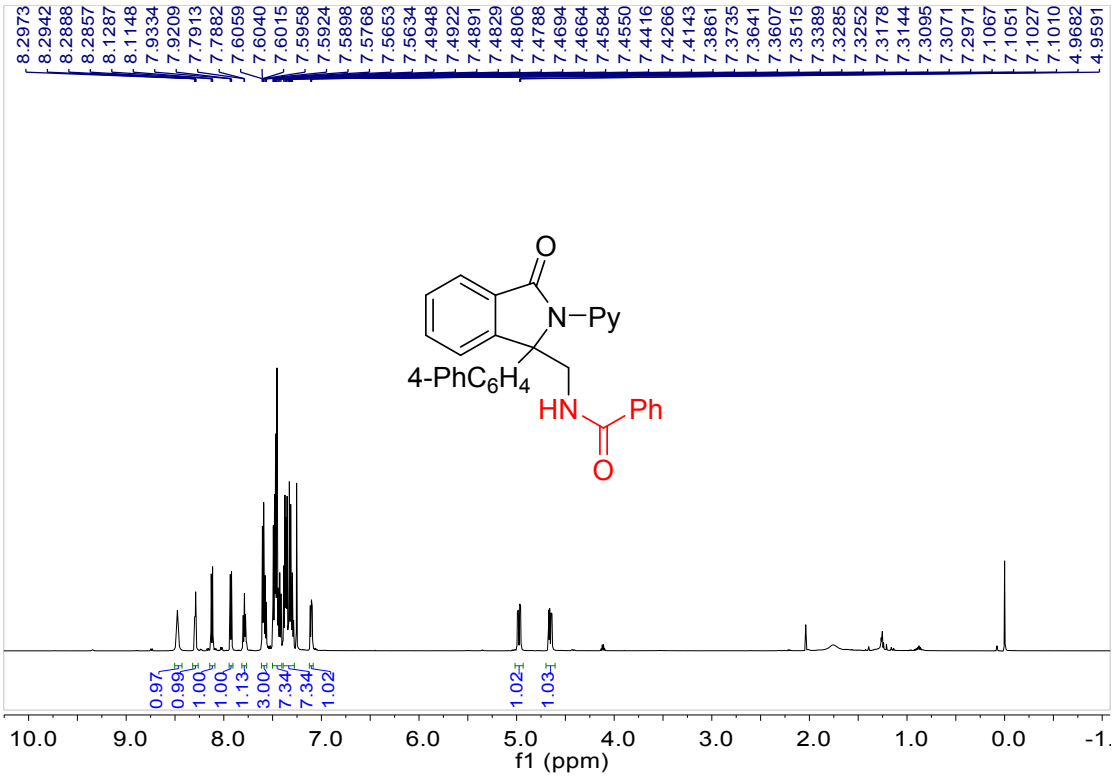
^{1}H NMR Spectra of Compound **3as**



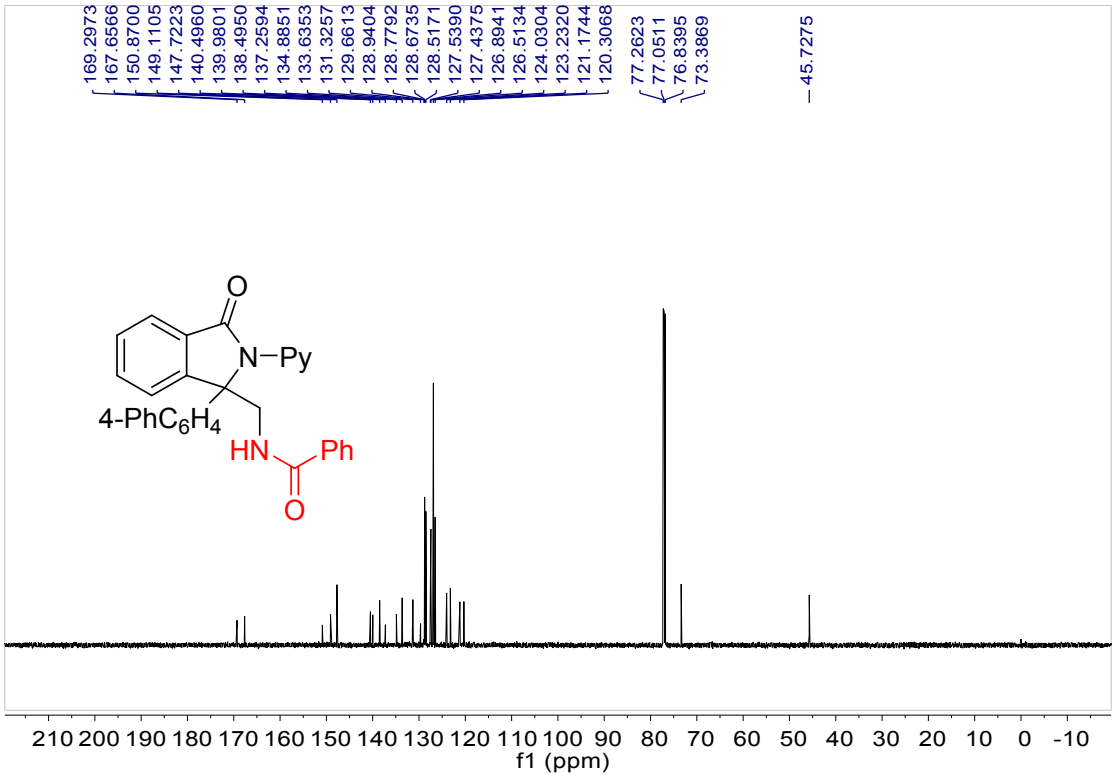
^{13}C NMR Spectra of Compound **3as**



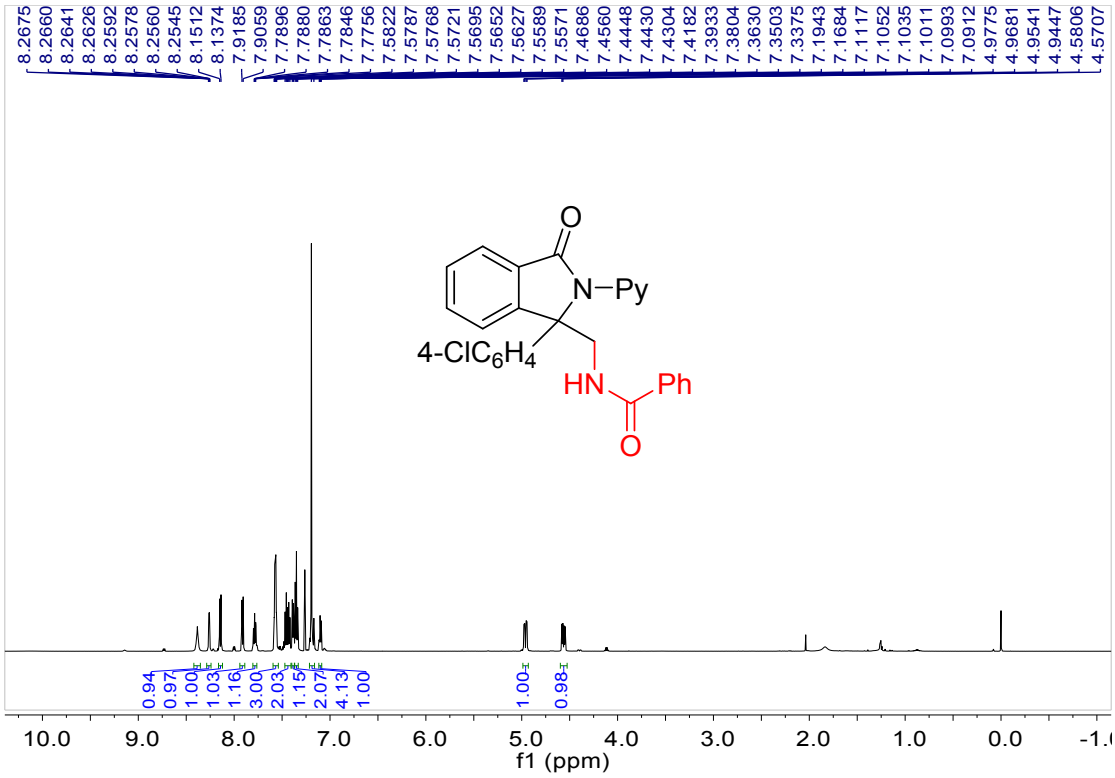
^{1}H NMR Spectra of Compound **4ba**



^{13}C NMR Spectra of Compound **4ba**



^{1}H NMR Spectra of Compound **4ca**



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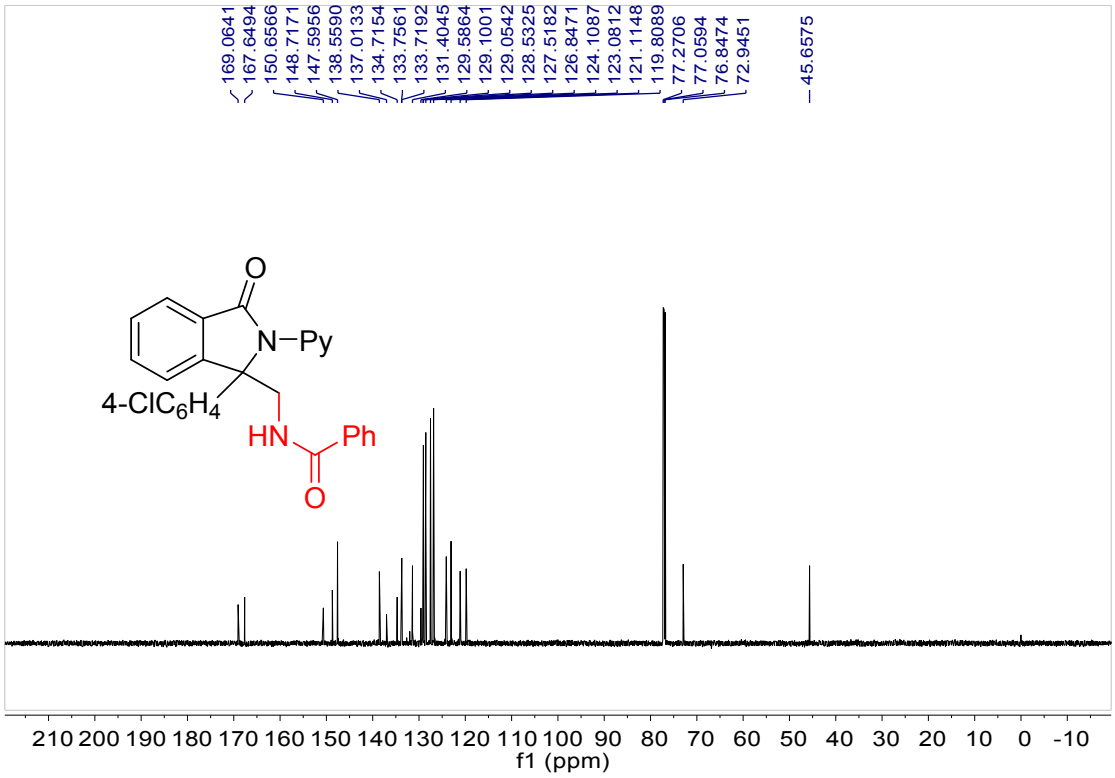

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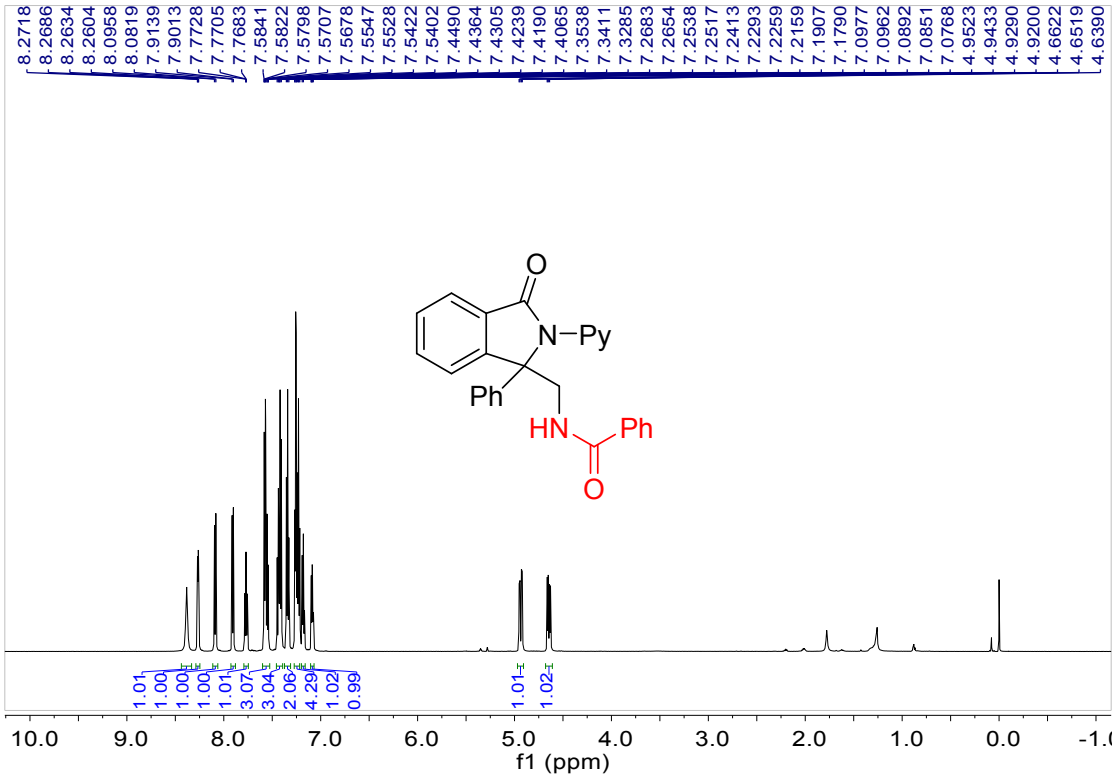
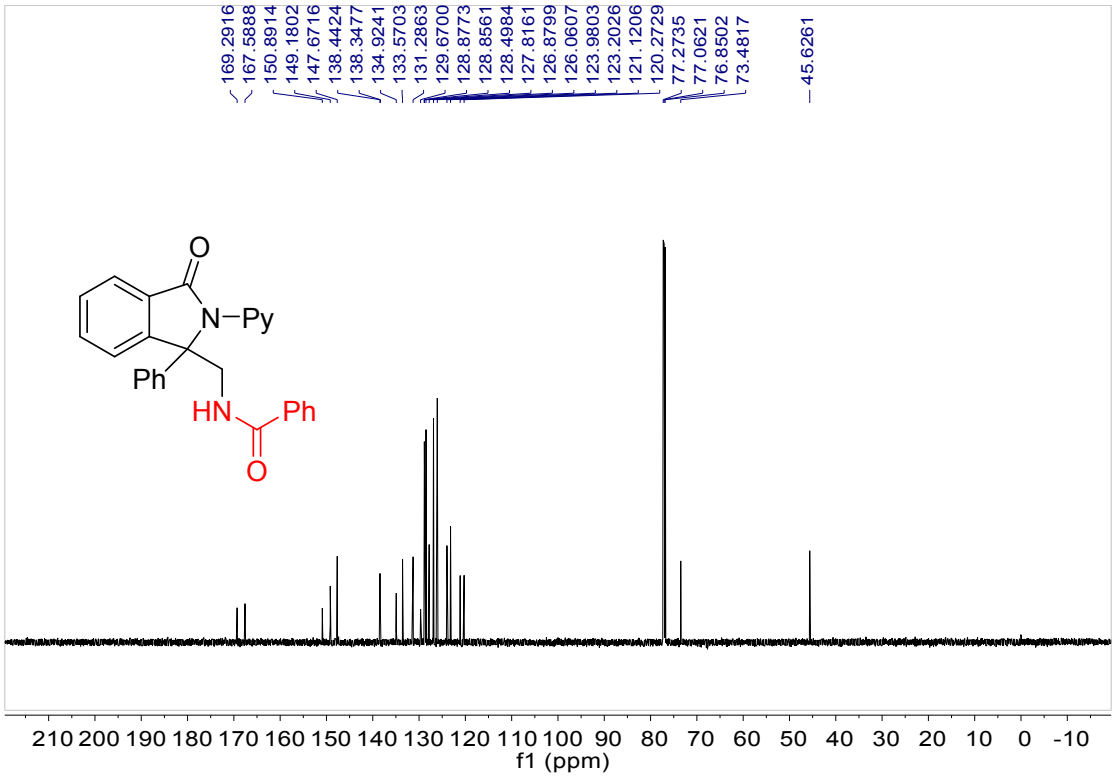
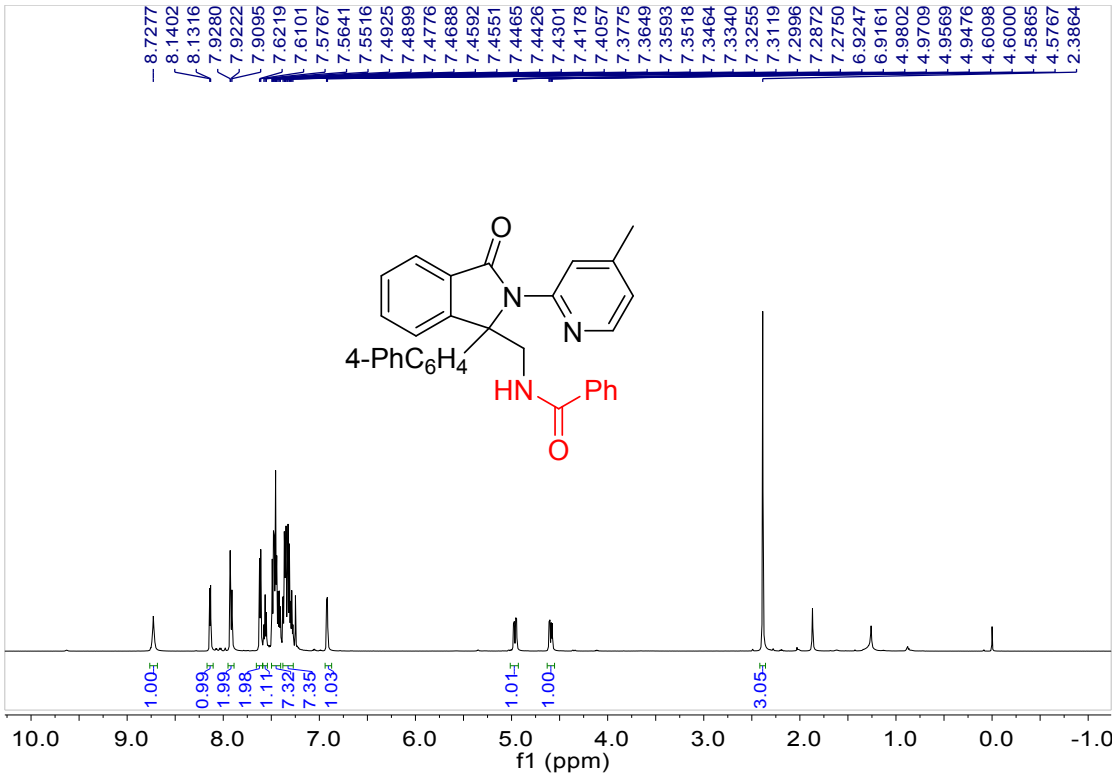


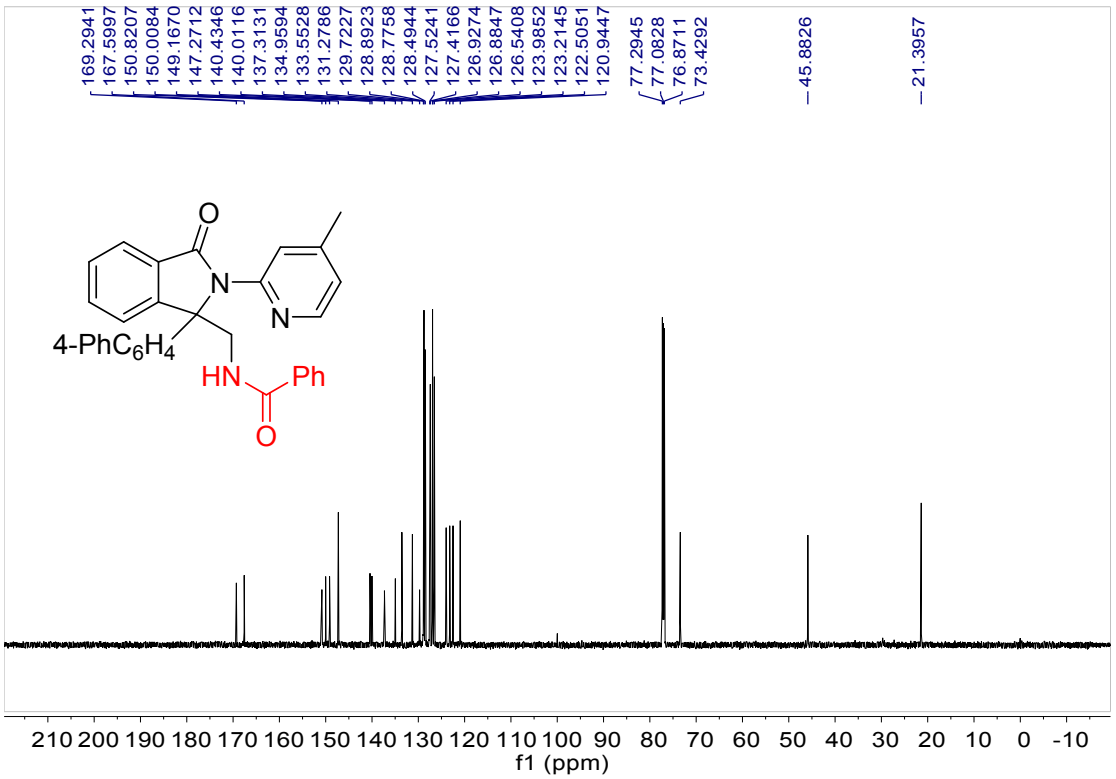
^{13}C NMR Spectra of Compound **4da**



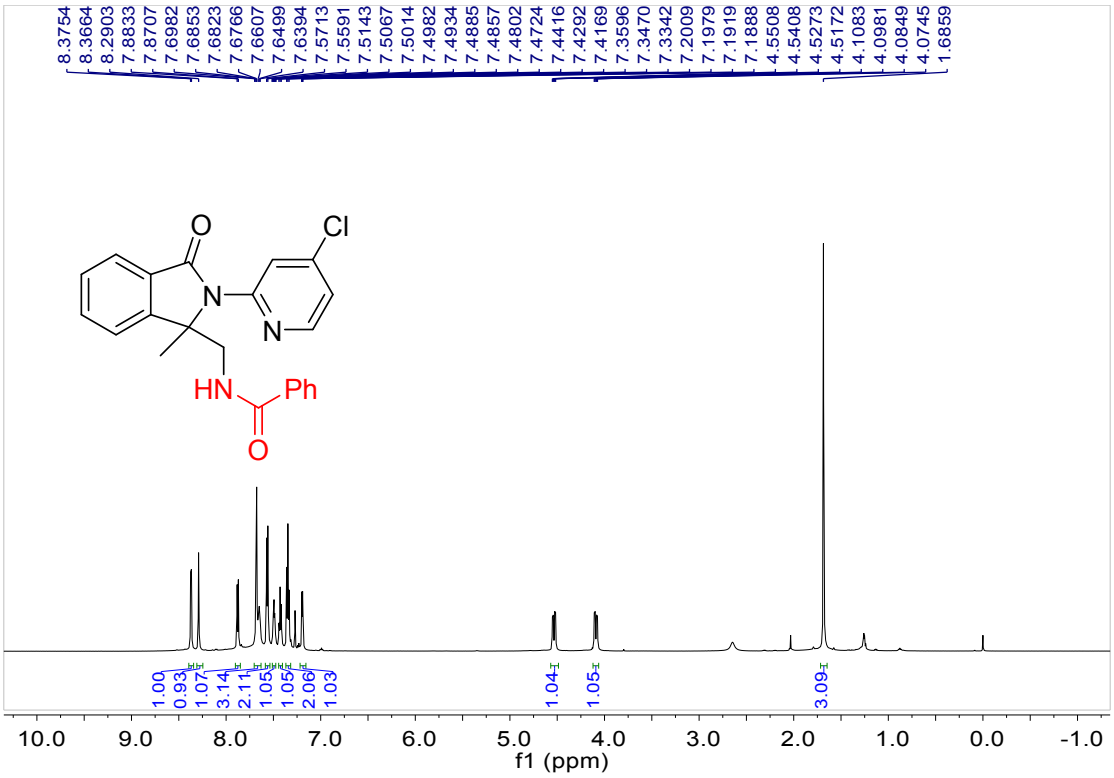
^{1}H NMR Spectra of Compound **4ea**



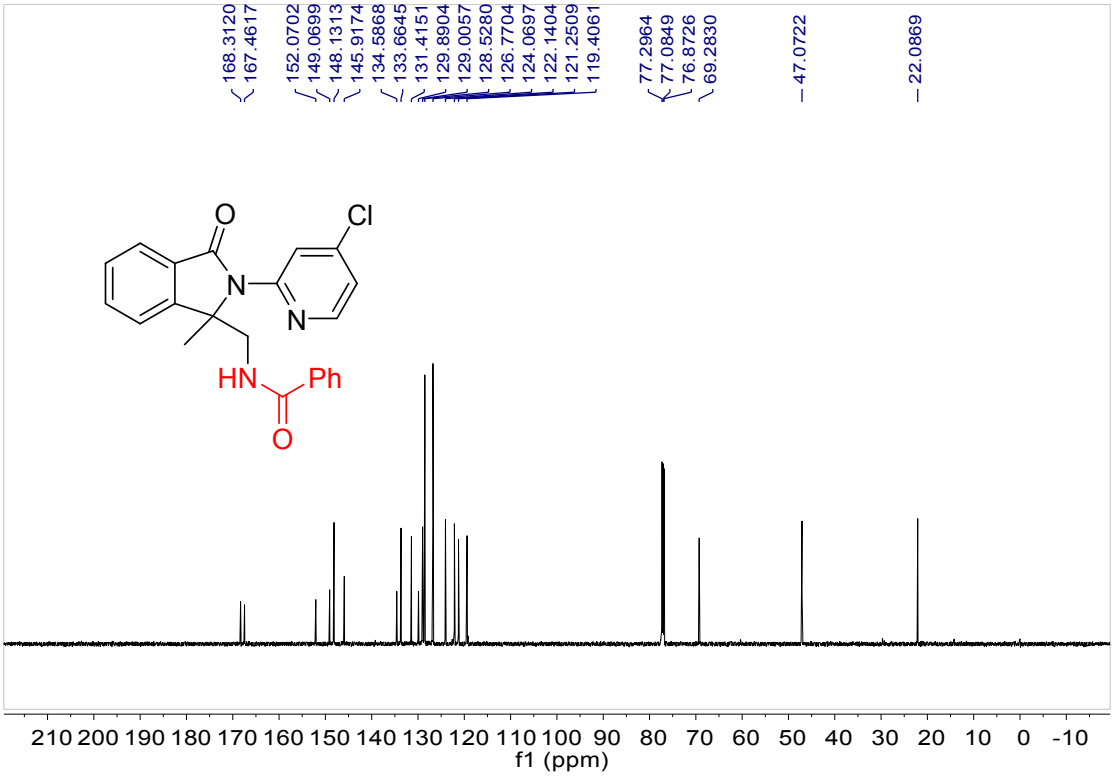
^{13}C NMR Spectra of Compound **4ea**



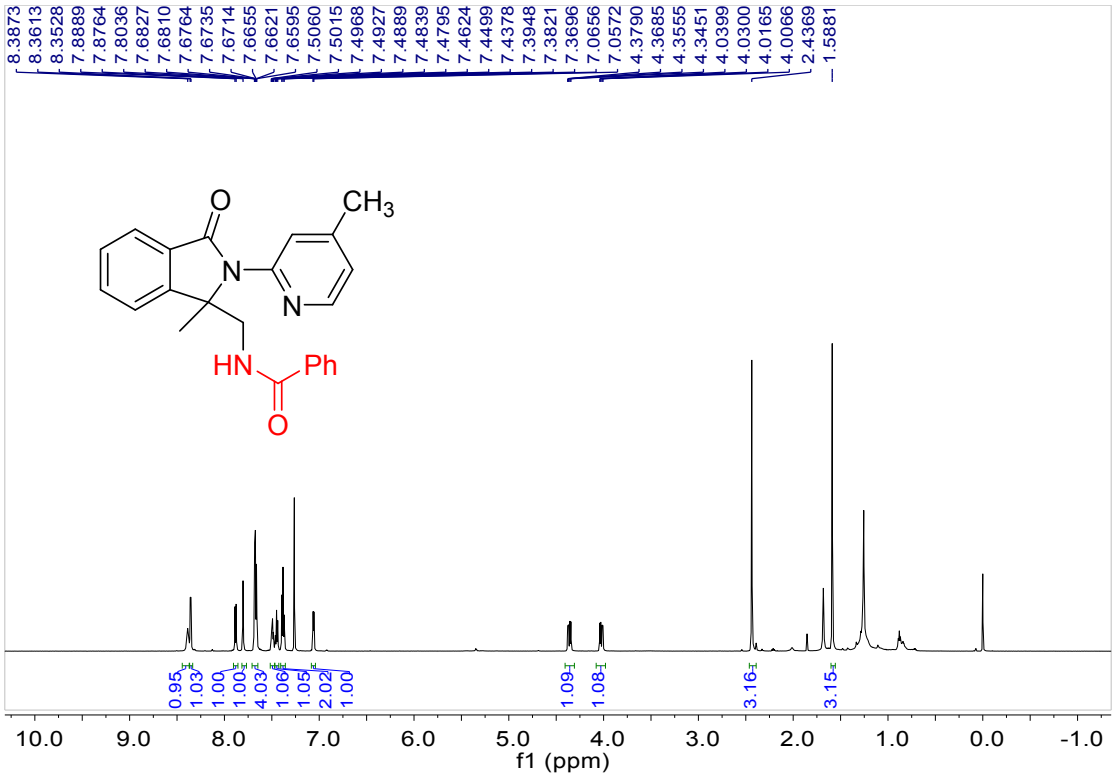
^{1}H NMR Spectra of Compound **4fa**



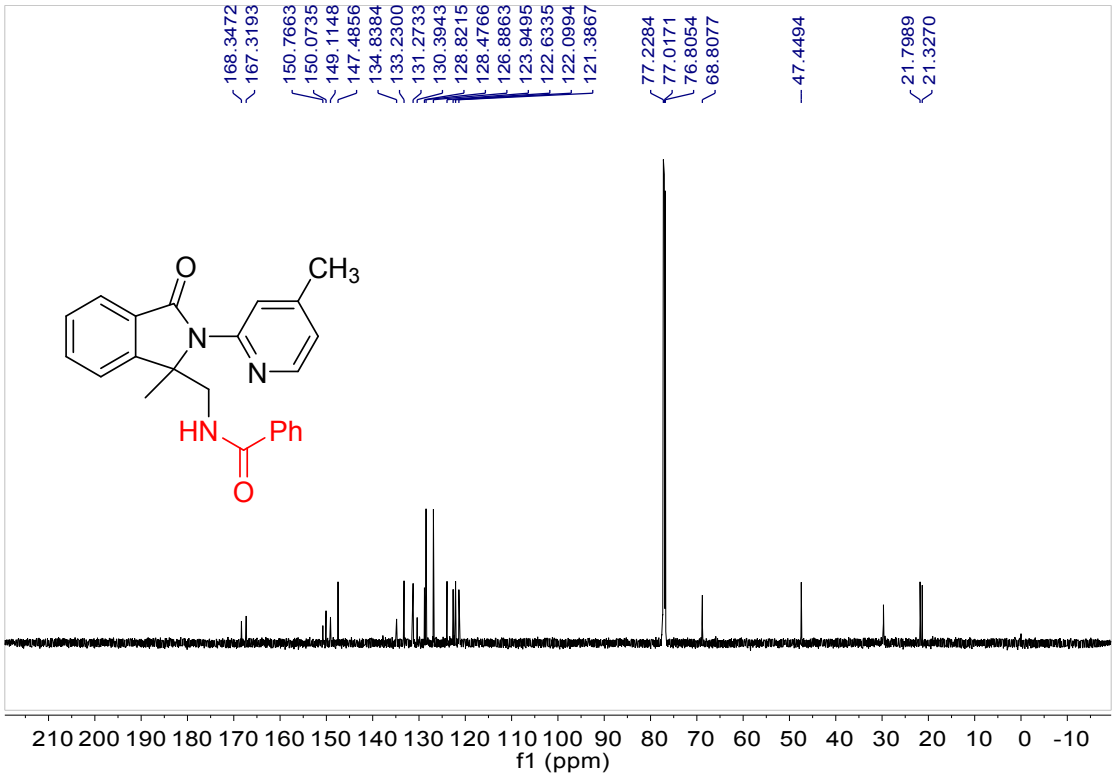
^{13}C NMR Spectra of Compound **4fa**



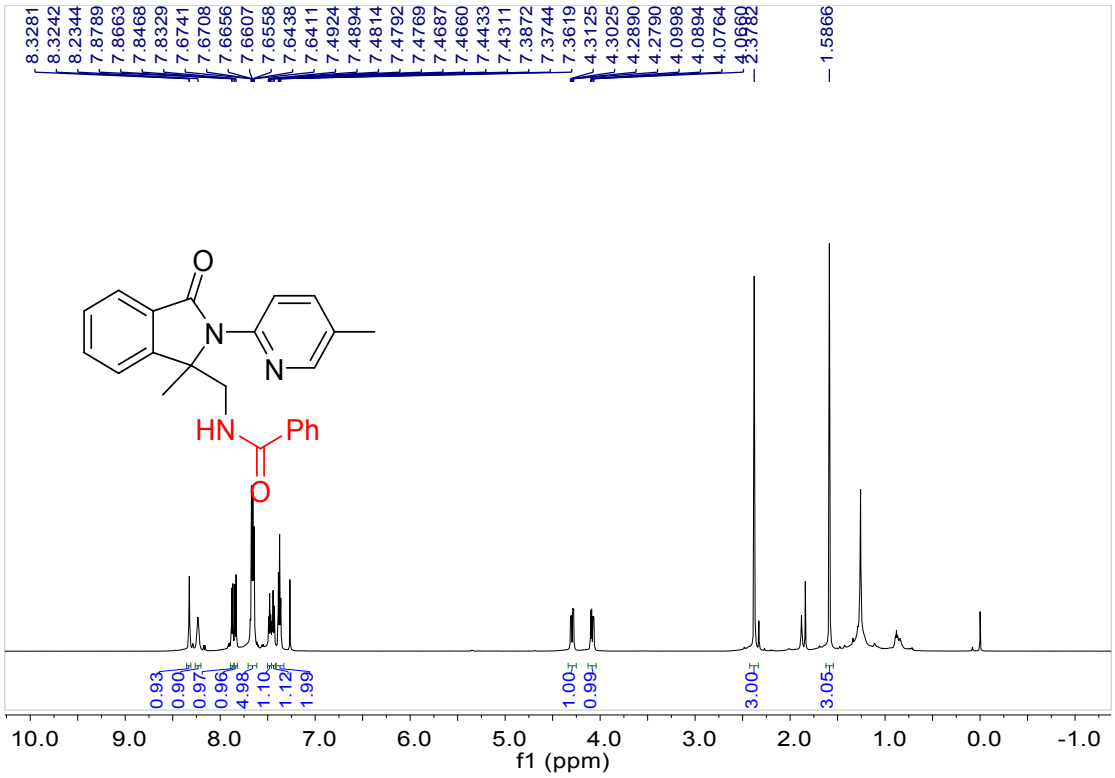
^{1}H NMR Spectra of Compound **4ga**



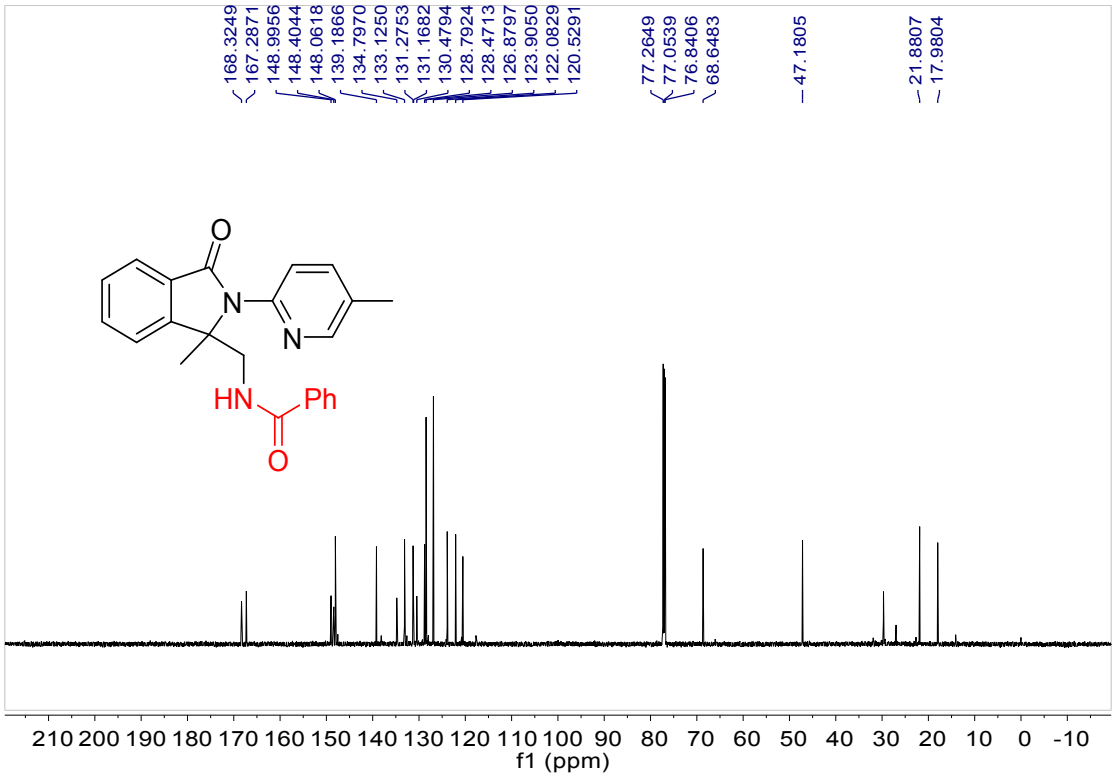
^{13}C NMR Spectra of Compound **4ga**



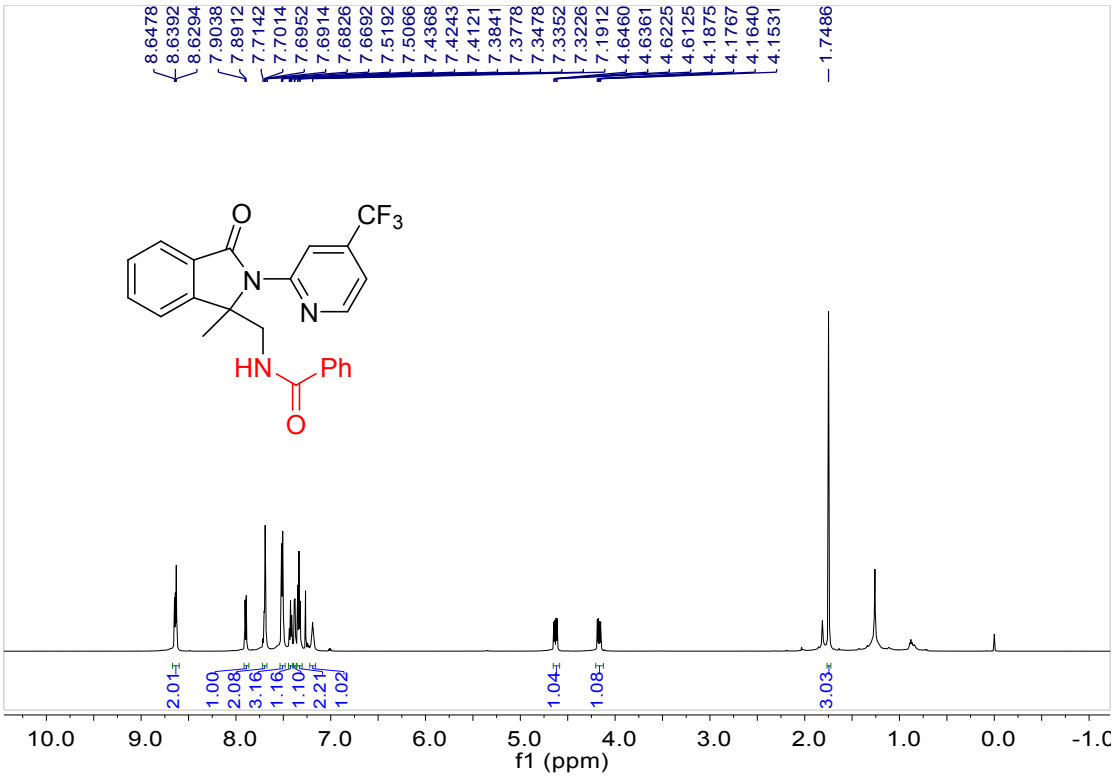
^{1}H NMR Spectra of Compound **4ha**



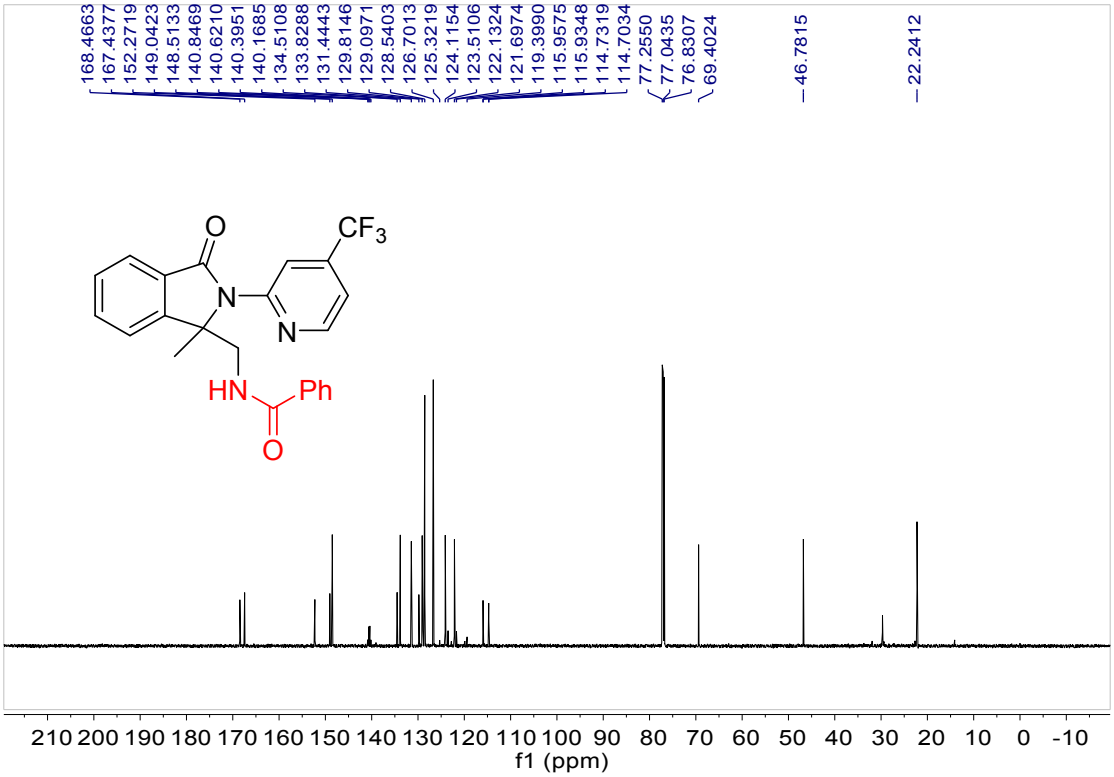
^{13}C NMR Spectra of Compound **4ha**



^{1}H NMR Spectra of Compound **4ia**



^{13}C NMR Spectra of Compound **4ia**



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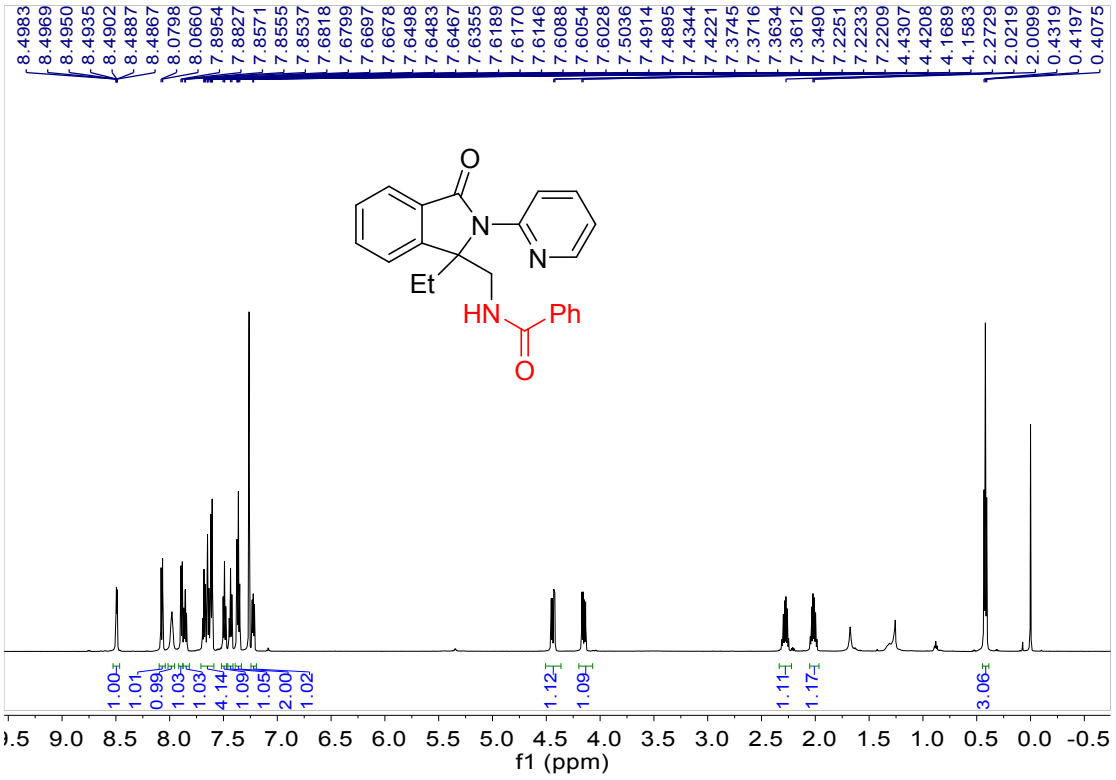
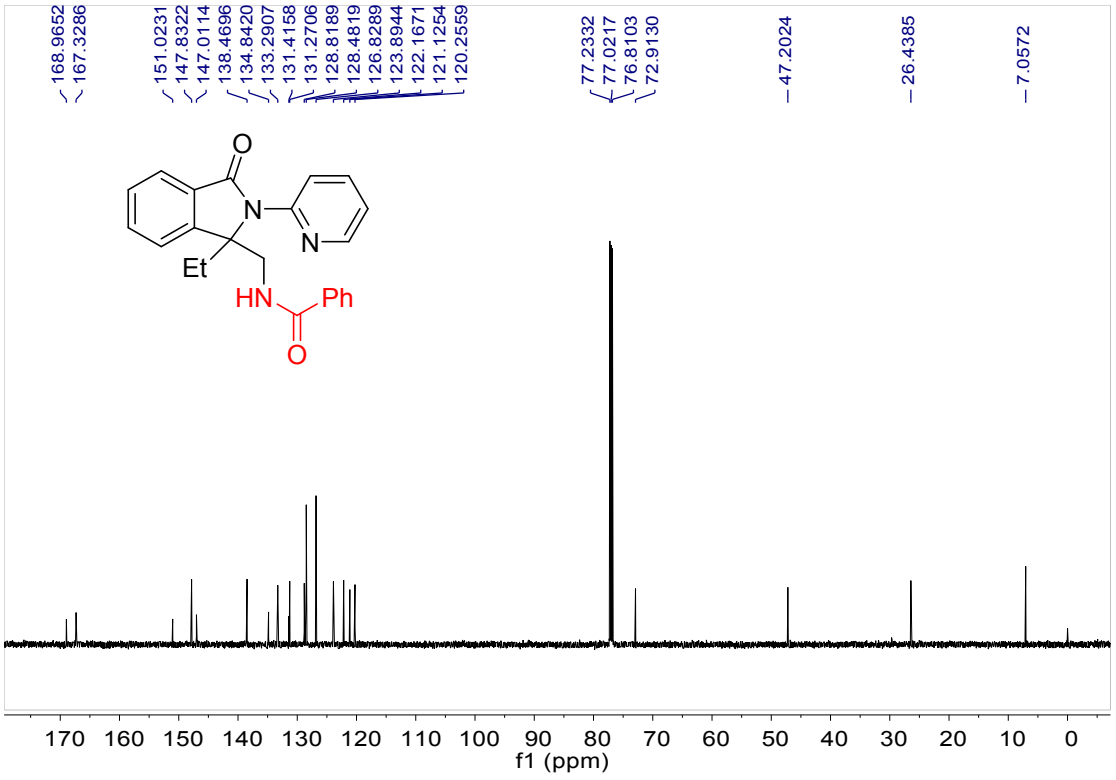
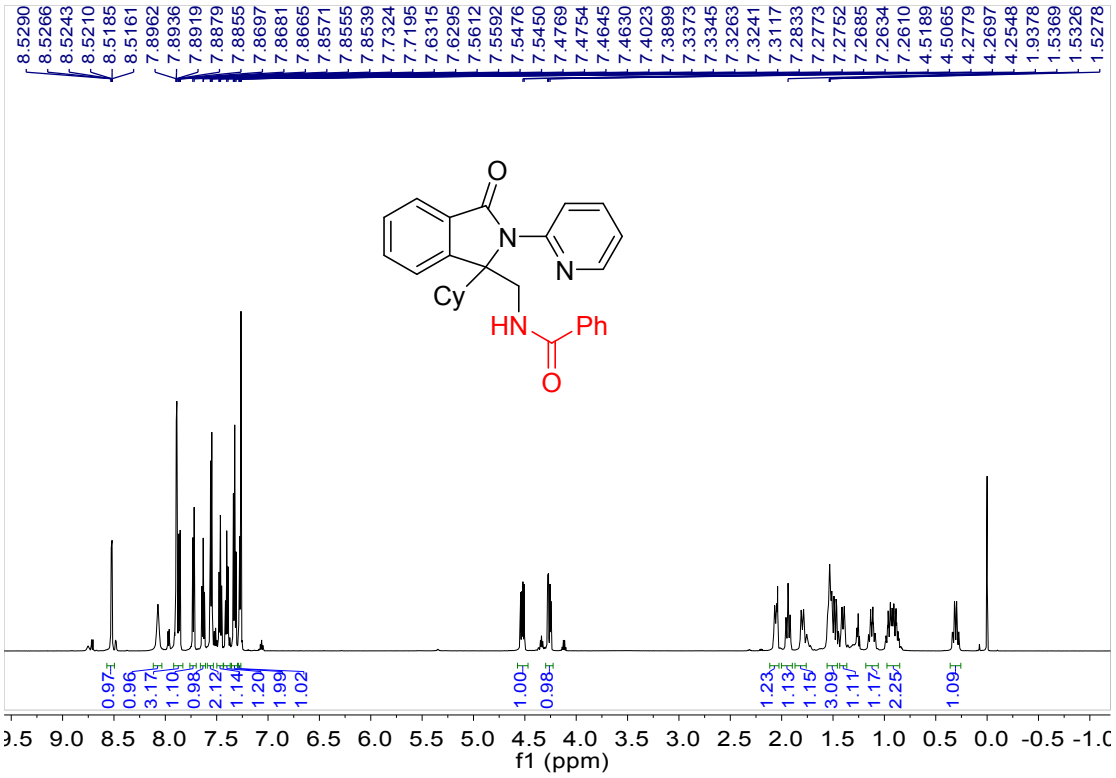


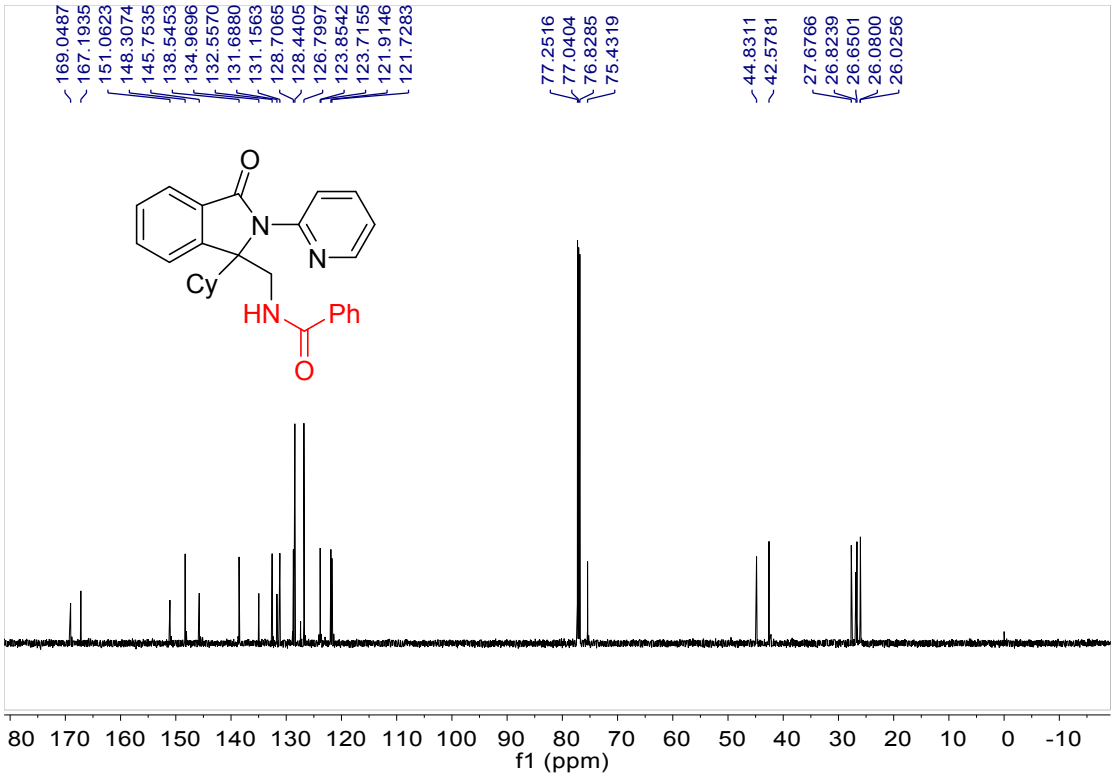
^{13}C NMR Spectra of Compound **4ja**



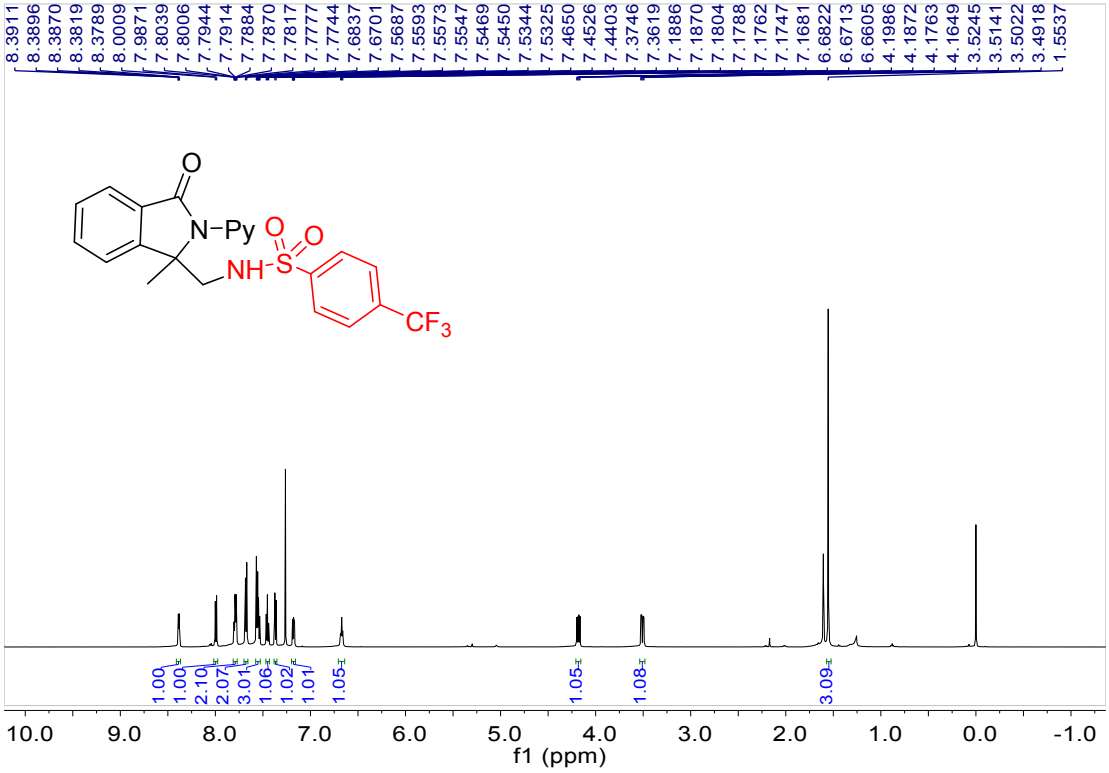
^{1}H NMR Spectra of Compound **4ka**



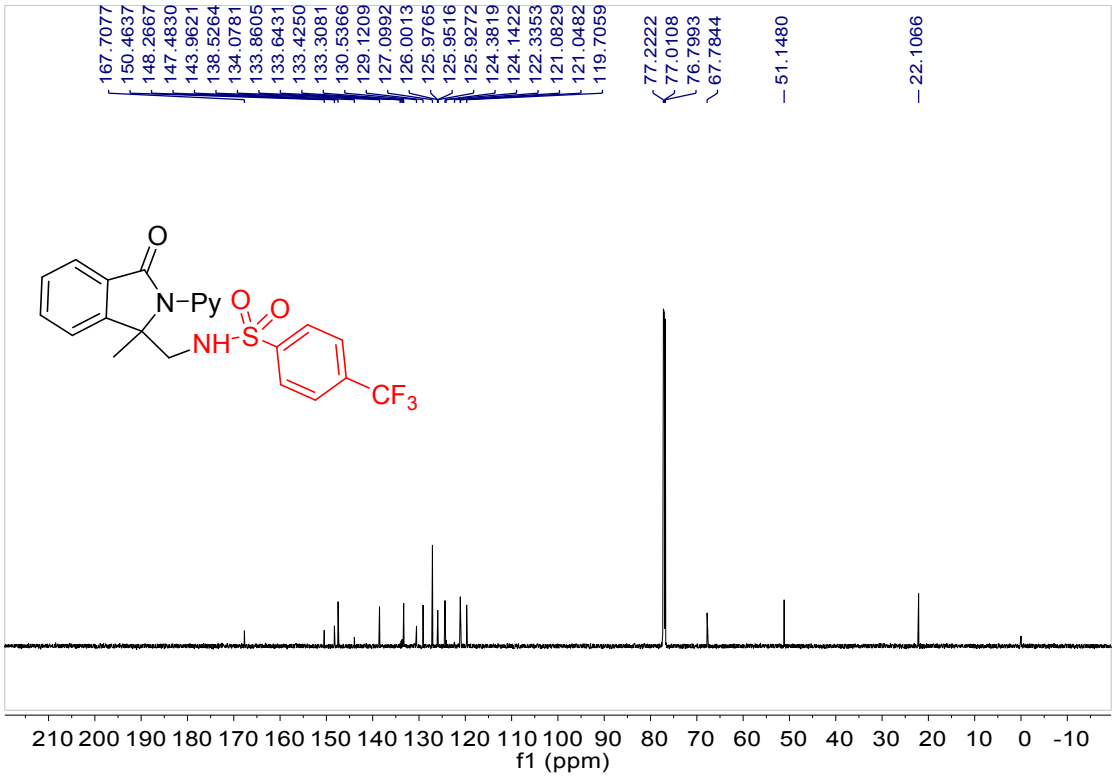
^{13}C NMR Spectra of Compound **4ka**



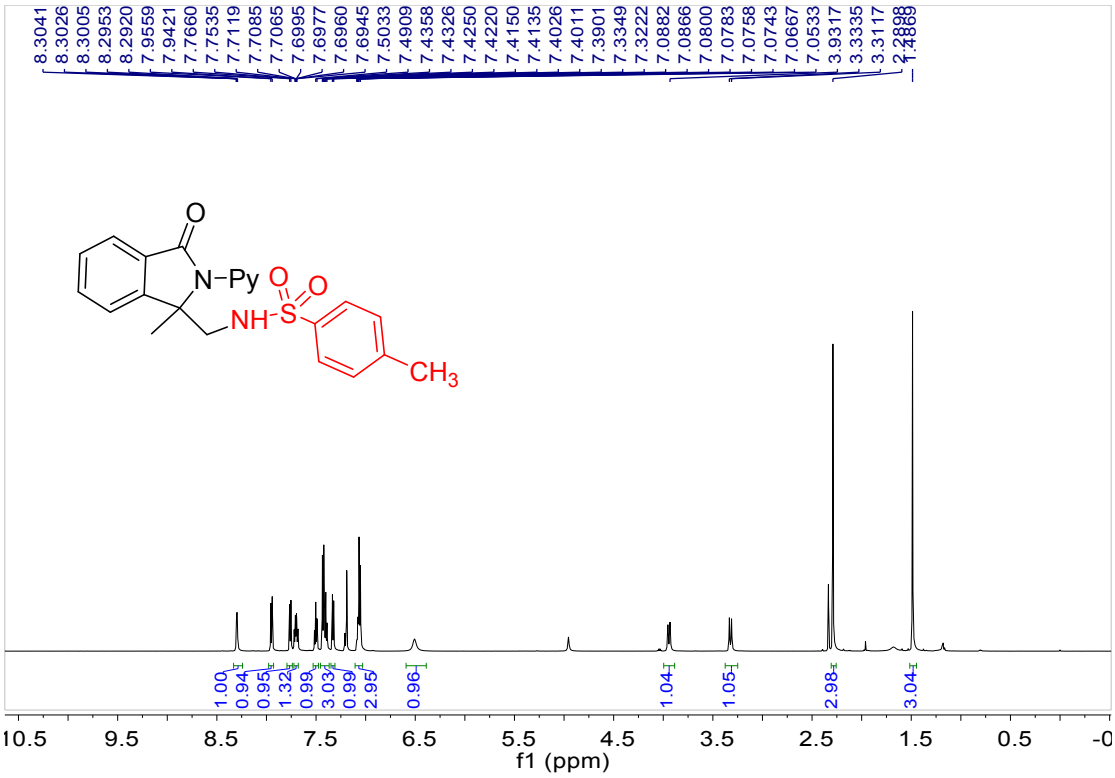
^{1}H NMR Spectra of Compound **4aa**



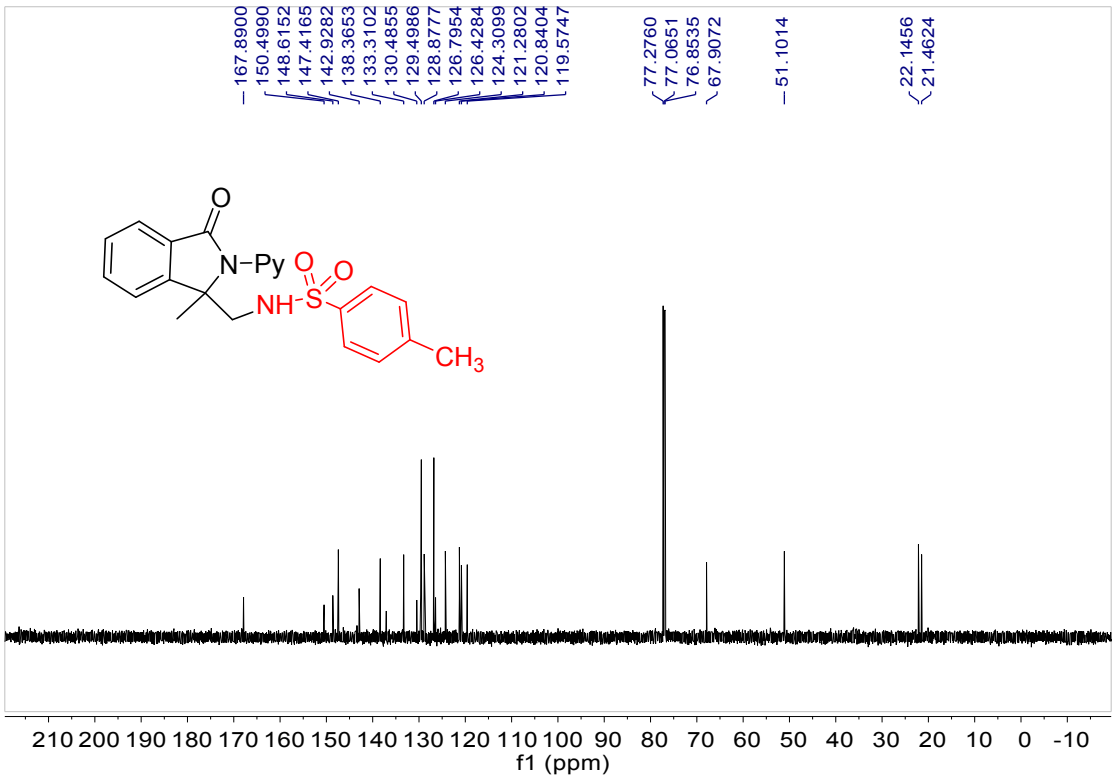
^{13}C NMR Spectra of Compound **4aa**



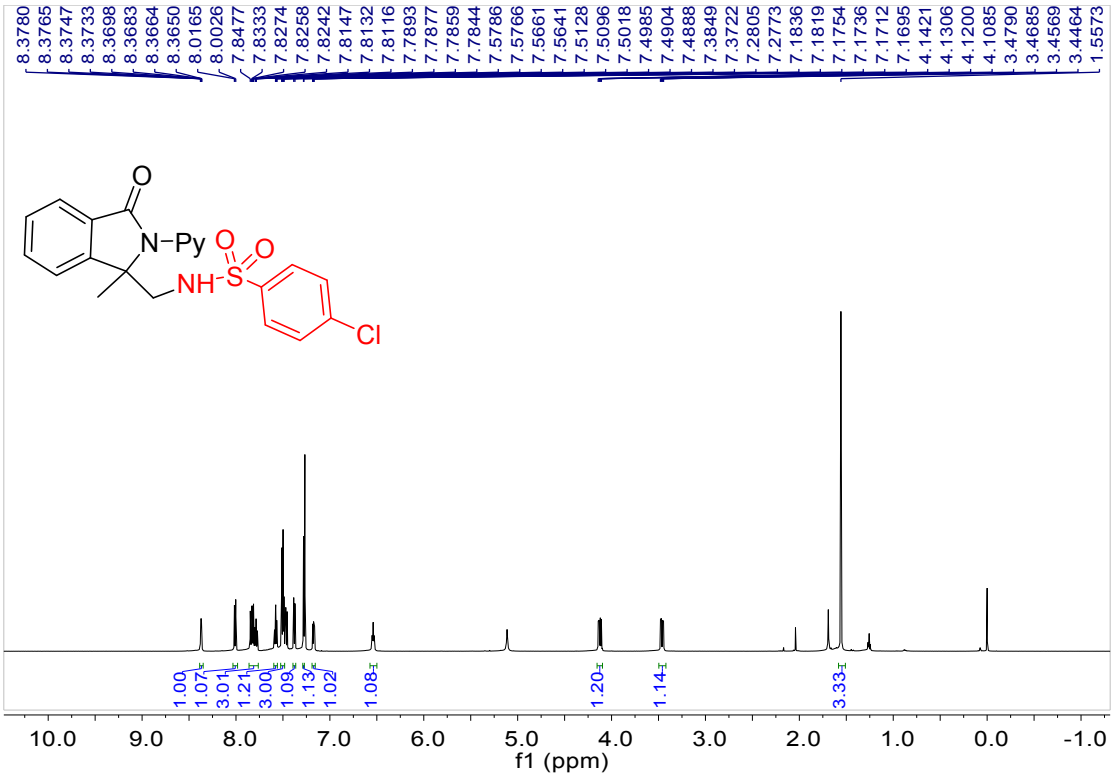
^{1}H NMR Spectra of Compound **4ab**



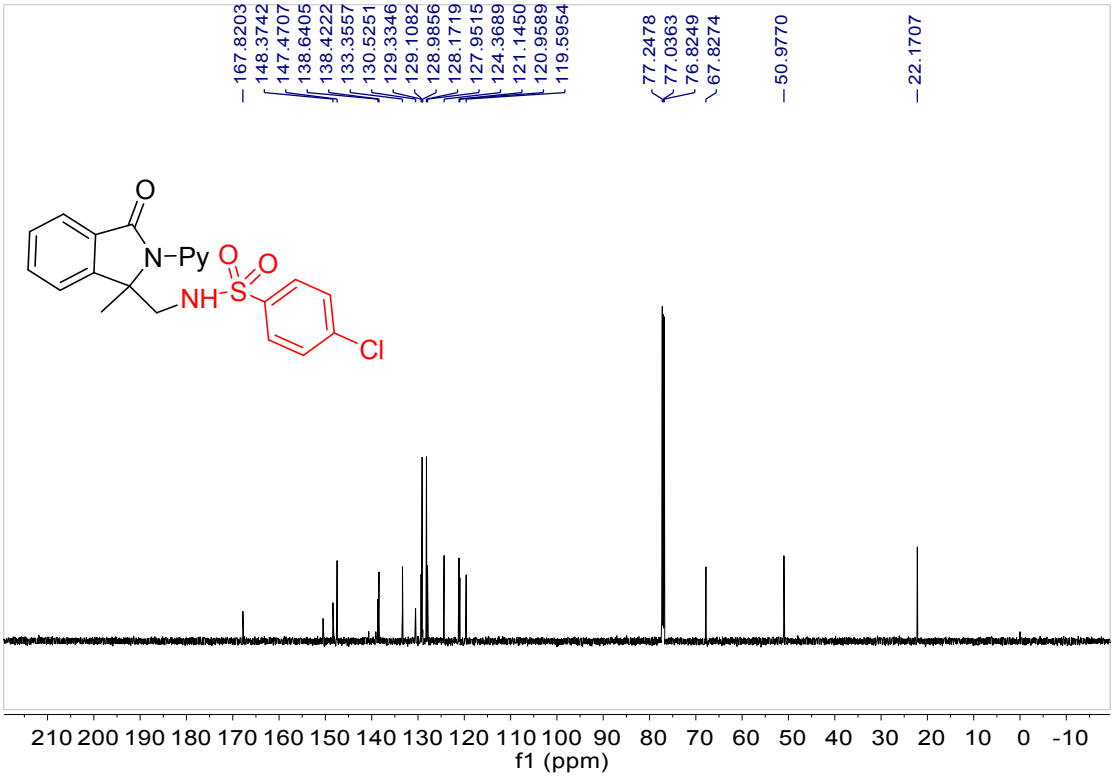
^{13}C NMR Spectra of Compound **4ab**



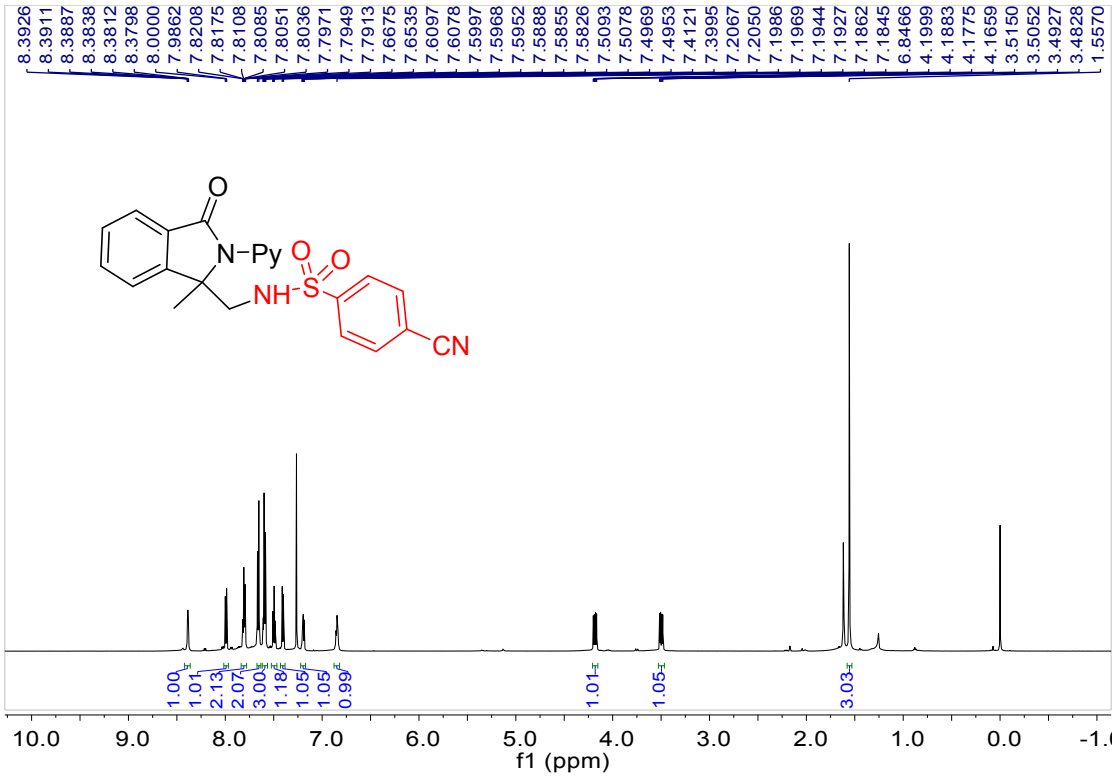
^{1}H NMR Spectra of Compound **4ac**



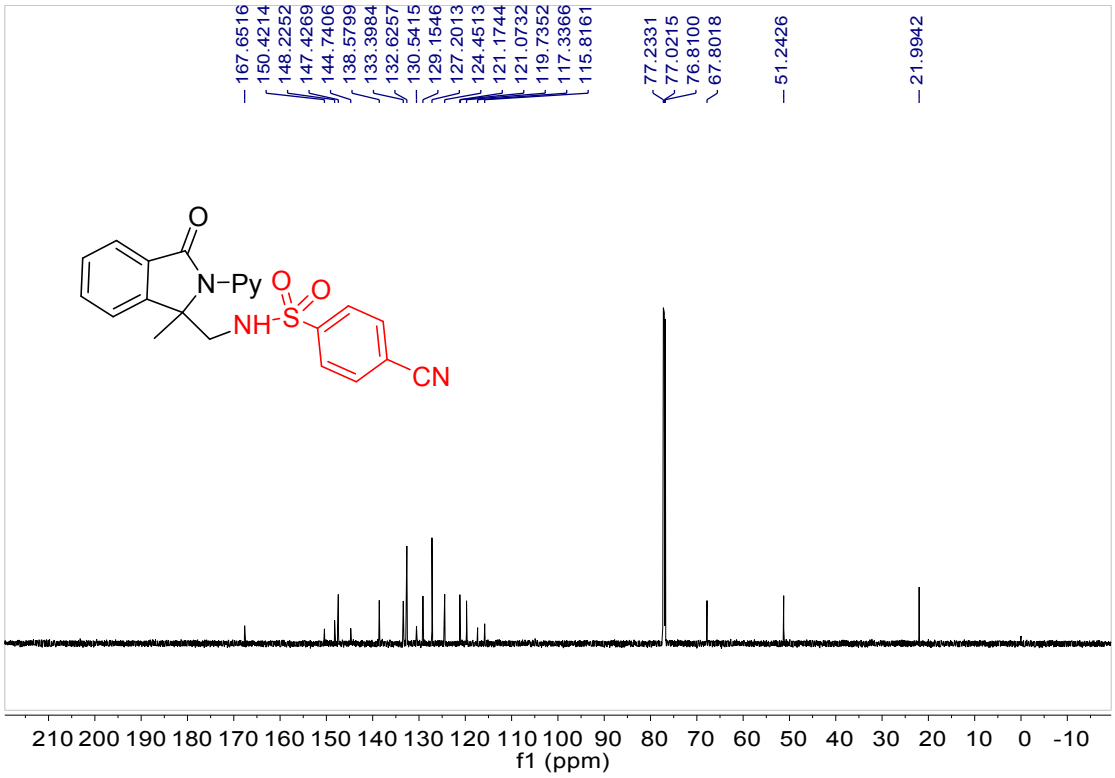
^{13}C NMR Spectra of Compound **4ac**



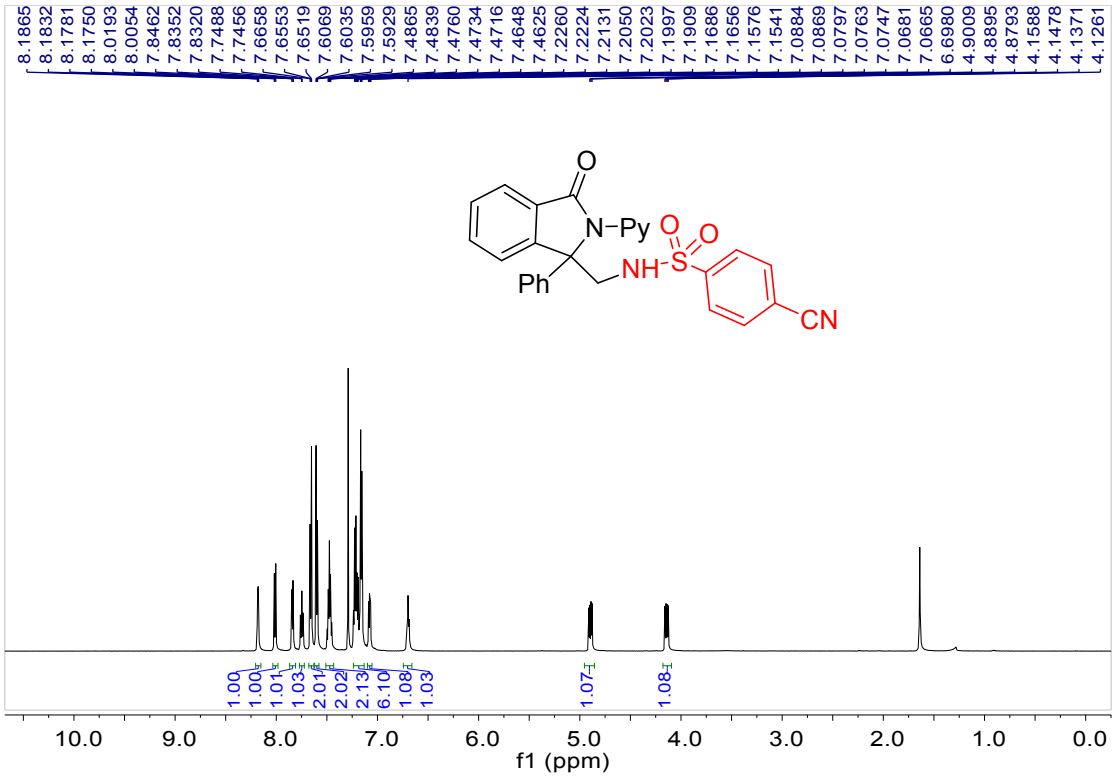
^{1}H NMR Spectra of Compound **4ad**



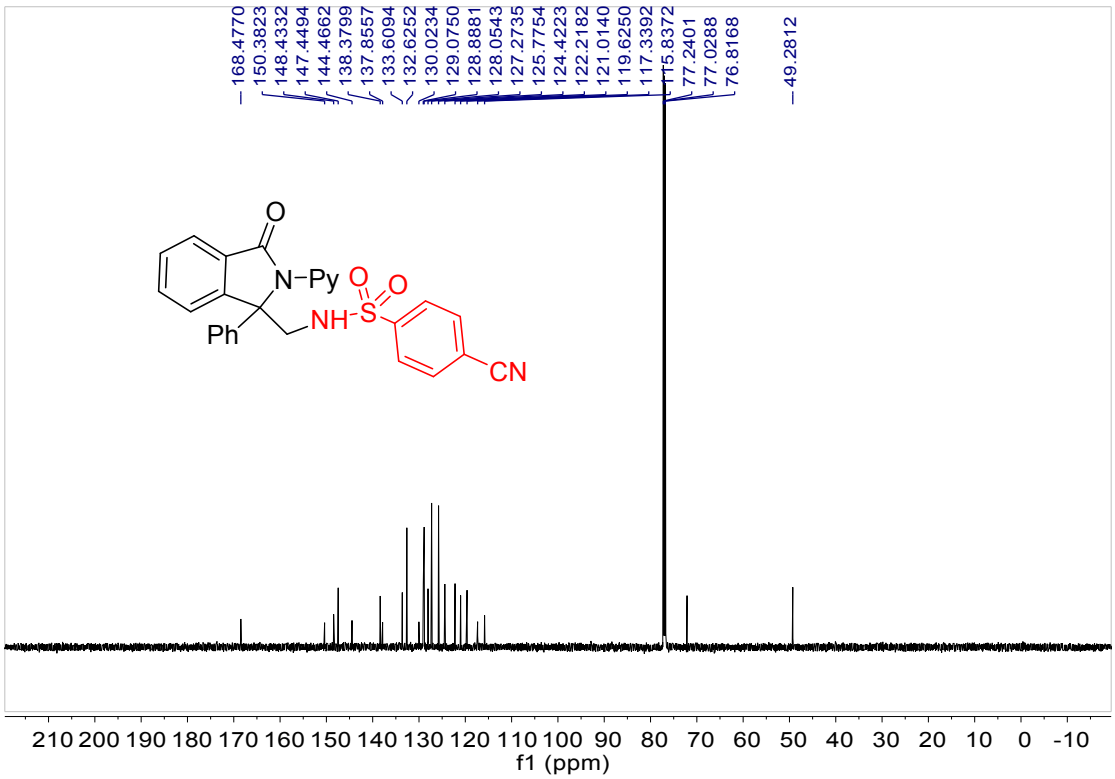
^{13}C NMR Spectra of Compound **4ad**



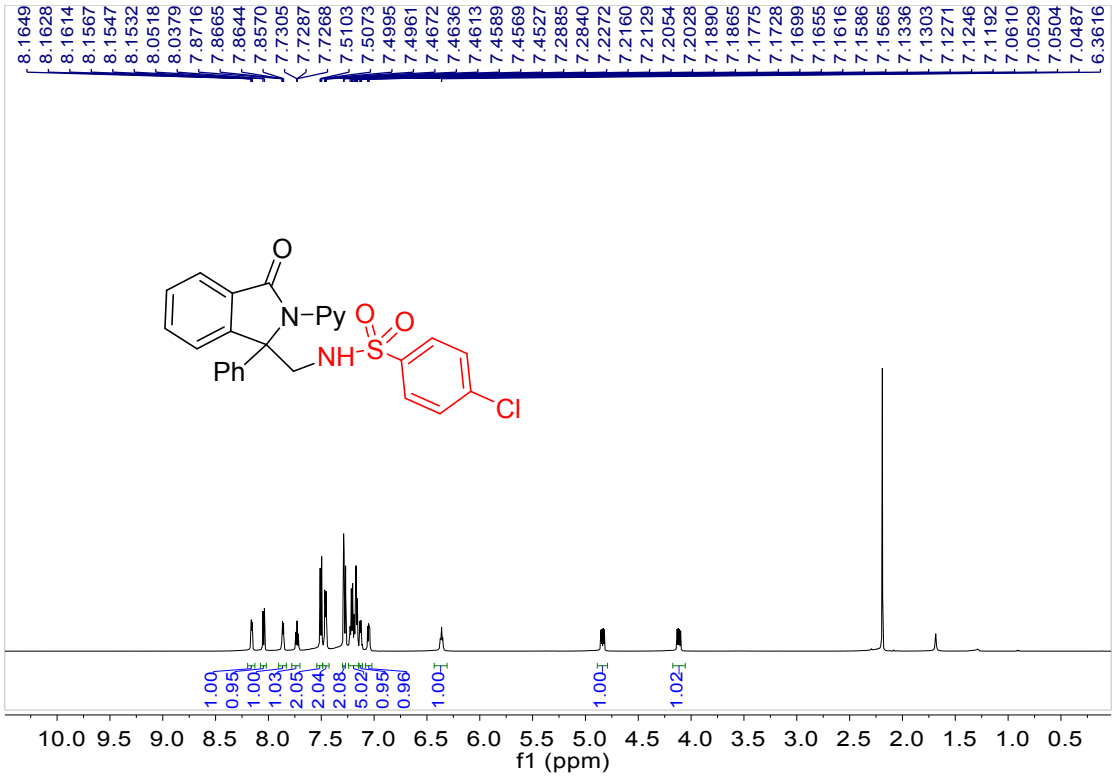
^{1}H NMR Spectra of Compound **4ae**



^{13}C NMR Spectra of Compound **4ae**



^{1}H NMR Spectra of Compound **4af**



^{13}C NMR Spectra of Compound **4af**