Supporting Information

Photochemical pincer catalyzed reductive cyclisation towards indolines and oxindoles

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1. General considerations

1.1 Materials

All operations were carried out in oven-dried glassware using N_2 gas filled glovebox or high-vacuum standard Schlenk techniques under nitrogen gas atmosphere until unless mentioned. THF was refluxed and freshly distilled over sodium/benzophenone and acetonitrile was refluxed and freshly distilled over calcium hydride. Both the solvents were degassed using three freeze-pump-thaw cycles and stored over molecular sieves (4 Å) inside the glovebox. Starting materials and reagents were purchased from commercial sources and used without further purification. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plate and visualized by short-wave ultraviolet light. Flash chromatography was performed with Silica Flash P60 silica gel (100–200 mesh).

1.2 Physical measurements

^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer at 400 and 101 MHz respectively. All chemical shifts are reported in part per million (ppm) with respect to the ^1H (residual) chemical shifts of the d-solvent. The residual solvent signals were taken as the reference ($CDCl_3$, 7.26 ppm for ^1H NMR spectra and $CDCl_3$, 77.16 ppm for ^{13}C NMR spectra). The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). All coupling constants were reported in hertz (Hz). High resolution mass spectroscopy was performed on Waters Synapt-G2S, analyser configuration Q-ToF with ion mobility and analysed using Masslynx41.

2. Experimental procedures with spectroscopic data

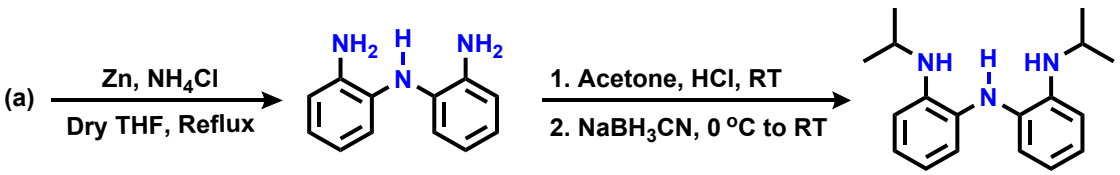
2a. Synthesis of $[NNN]H_3$ Pincer (1).[1]

(i) Synthesis of Bis(2-nitrophenyl) amine

(a)

In 100 mL round bottomed flask, 1-fluoro-2-nitrobenzene (0.9 g, 6.4 mmol), 2-nitroaniline (0.89 g, 6.4 mmol) and K_2CO_3 (1.09 g, 7.9 mmol) were dissolved in 10 mL of DMSO. The reaction mixture was stirred at a temperature of 120 °C for 36 h. The ice-chilled water (100 ml) was added to above reaction mixture and the mixture was extracted with dichloromethane (3 x 30 mL). The combined organic layer was washed with an aqueous solution of NaCl (4 x 20 mL, 15 %) and dried over anhydrous $MgSO_4$. The dichloromethane was removed under a rotary evaporator. Bis(2-nitrophenyl) amine was obtained as an orange solid (1.51 g, 90 %), which was used for the next step without further purification.

(ii) Synthesis of bis(2-isopropylaminophenyl) amine $[NNN]H_3$ pincer, 1:

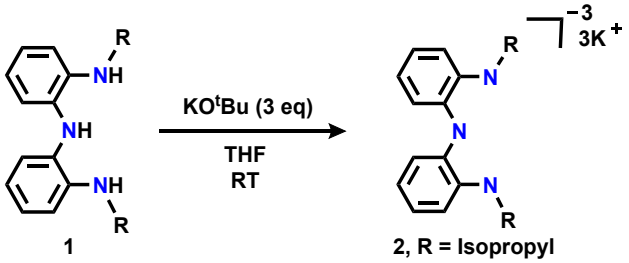


A 100 mL Schlenk flask equipped with a stir bar was charged with bis(2-nitrophenyl) amine (1.24 g, 4.3 mmol), Zn powder (3.712 g, 56.8 mmol) and NH_4Cl (2.78 g, 52 mmol). 40 mL of dry THF was added into the flask. A reflux condenser was attached to the Schlenk flask under N_2 flow. The reaction mixture was refluxed at a temperature of 65 °C for 16 h. At the completion of the reaction, the reaction mixture was filtered and the filtrate was removed under high vacuum to obtain yellow-brown oil. After that, yellow-brown oil was dissolved in 40 mL of degassed methanol under N_2 atmosphere. Acetone (0.64 mL, 8.6 mmol) and HCl (0.7 mL, 37%) were added to above reaction mixture. The reaction mixture immediately turned to green from brown on addition of HCl. It was stirred for 30 min at room temperature, followed by careful addition of $NaBH_3CN$ (1.14 g, 18.2 mmol) at a temperature of 0 °C. After complete addition of $NaBH_3CN$, the color of the reaction mixture turned to reddish-brown from green. It was stirred further for 12 h at room temperature. The solvent was removed under vacuum and

the resulting residue was dissolved in 40 mL of dichloromethane. It was washed with an aqueous sodium dithionite (2 x 40 mL, 1 M) and aqueous sodium bicarbonate (2 x 40 mL, 1 M) solution respectively. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum. Bis(2-isopropylaminophenyl) amine ($[NNN]H_3$ pincer) was obtained as brown oil in 75% yield, which was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, *J* = 7.6 Hz, 2H), 6.78 – 6.71 (m, 4H), 6.67 (t, *J* = 7.5 Hz, 2H), 4.93 (s, 1H), 3.65 (d, *J* = 6.3 Hz, 2H), 3.54 (s, 2H), 1.20 (d, *J* = 6.3 Hz, 13H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 131.5, 123.6, 120.5, 117.9, 112.7, 44.4, 23.2.

2b. The synthesis of trianoinic NNN_{imcat}^{3-} ligand (2):

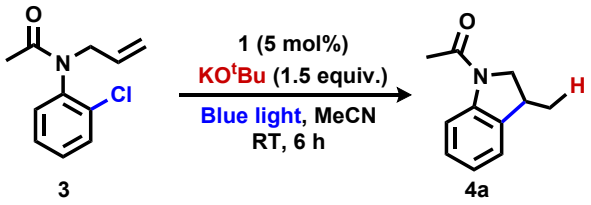


In a flame-dried Schlenk flask, bis(2-isopropylaminophenyl) amine (**1**) (57 mg, 0.2 mmol) was dissolved in 3 mL of dry THF. The above solution was cooled to a temperature of 0 °C and KO^{t}Bu (68 mg, 0.6 mmol) was added. The reaction mixture was stirred for 4 h at room temperature to obtain a yellow-colored solution. The reaction mixture was filtered through celite bed inside the glove box. The solvent was removed under vacuum. The potassium salt of trianoinic NNN_{imcat}^{3-} (**2**) was obtained as a yellow-colored solid in 88% yield.

3. Optimization of reaction conditions

An adequately dried Schlenk flask (overnight at 120 °C oven) with magnetic stirring bar was charged with *N*-allyl-*N*-(2-chlorophenyl)acetamide **3** (42 mg, 0.2 mmol) and catalyst **1** (3 mg, 5 mol%). 1 mL of dry acetonitrile was added to make a brown colored solution under N_2 atmosphere. The color of the reaction mixture instantly changed to yellowish brown upon the addition of KO^{t}Bu (34 mg, 0.3 mmol) into the reaction flask. The flask was kept under blue light (450 nm, 15 W) at room temperature, at a distance of 6-7 inch away from the light source. After 6 hours of stirring, the solvent was removed under vacuum. The crude reaction mixture was dissolved in DCM and organic layer was washed with water. The organic layer was collected and dried over anhydrous $MgSO_4$. DCM was removed using rotary evaporator. The yield of the desired product 1-(3-methylindolin-1-yl)ethan-1-one, **4a** was determined by NMR analysis.

Table S1. Reaction optimization.



Entry	Variation from standard conditions	Yield(%)[a]
1	None	98(93)[b]
2	2 mol% of **1**	59
3	1.0 equiv of KO^{t}Bu	68
4	0.5 equiv of KO^{t}Bu	38
5	Only NEt_3/DABCO/DIPEA	ND
6	K_2CO_3 instead of KO^{t}Bu	ND
7	DIPEA and KO^{t}Bu (20 mol%)	89
8	Only KO^{t}Bu	ND
9	Absence of light	ND
10	Absence of **1**	ND
11	Absence of KO^{t}Bu	ND

Standard conditions: (a) *N*-allyl-*N*-(2-chlorophenyl)acetamide (0.2 mmol), KO^{t}Bu (0.3 mmol), **1** (5 mol%), and dry MeCN (1 mL), room temperature under a N_2 atmosphere, blue LEDs (450 nm), 6 h. [a]NMR yields, [b]Isolated yield. ND = not detected.

4. General procedure for the reaction

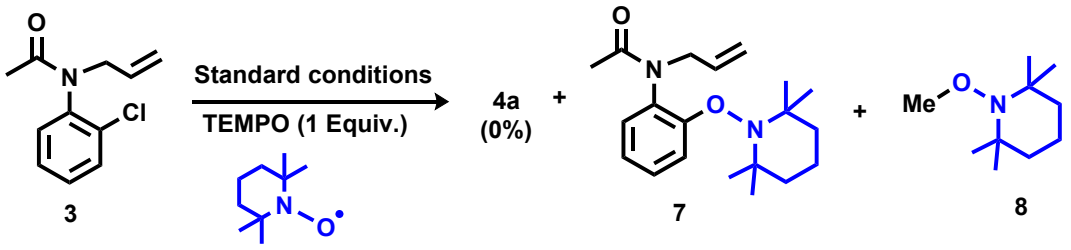
The oven-dried Schlenk flask with magnetic stirring bar was charged with 2-chloro-N,N-dialkylbenzamide (0.2 mmol), catalyst **1** (3 mg, 5 mol%) and KO^tBu (0.4 mmol) under N_2 atmosphere. 1 ml of dry acetonitrile was added to above reaction mixture. The reaction mixture was stirred under blue light at room temperature for 6 hours. After the completion of the reaction, the solvent was removed under rotary evaporator. The desired product was isolated by column chromatography using hexane/ethylacetate mixture. The isolated pure product was further analysed by ^1H and ^{13}C NMR spectroscopies.

5. Trapping of intermediates Using TEMPO radical

An overnight-dried Schlenk flask with magnetic stirring bar was charged with *N*-allyl-*N*-(2-chlorophenyl)acetamide **3** (42 mg, 0.2 mmol) and catalyst **1** (3 mg, 5 mol%). 1 mL of dry acetonitrile was added to make a brown colored solution under N_2 atmosphere. The color of the reaction mixture instantly changed to yellowish brown after the addition of KO^tBu (34 mg, 0.4 mmol) into the reaction flask. After that TEMPO (32 mg, 0.2 mmol) was added to the above reaction mixture. The flask was kept under blue light at room temperature. After 6 h of stirring, the reaction was ceased. The TEMPO adduct of *N*-allyl-*N*-(phenyl)acetamide radical was analysed by High-Resolution Mass Spectrometry (HRMS). Notably, methyl radical generates from the rearrangement of $^tBuO^{\cdot}$ radical, which is intercepted as **8**.

For **7**, HRMS (ESI, m/z) calcd. for $C_{20}H_{31}N_2O_2$ $[M + H]^+$: 331.2386; found: 331.2381.

For **8**, HRMS (ESI, m/z) calcd. for $C_{10}H_{22}NO$ $[M + H]^+$: 172.1701; found: 172.1691.



Scheme S1. Tapping of intermediates using TEMPO radical.

6. Control experiments

6.1 Synthesis of iminosemiquinonate form $[NNN_{imsq}]^{2-}$, 2_{imsq}, upon one-electron oxidation

In an overnight-dried vial, the trianionic $[NNN]K_3$ (40 mg, 0.1 mmol) was dissolved in THF solvent under N_2 atmosphere. The solid AgOTf (26 mg, 1 equiv.) was added to the above solution at room temperature. After 5 minutes, the color change from brownish yellow to green was observed. The reaction was allowed to stir for 1 hour at room temperature, while a metallic silver precipitation was observed on the wall of the vial. After completion of reaction, the reaction was filtered through celite pad and the filtrate was collected. The solvent was removed under high vacuum and a green colored solid was obtained in 88% yield.

6.2 Conversion of iminosemiquinone form $[NNN_{imsq}]^{2-}$, 2_{imsq} to iminocatecholate form $[NNN_{imcat}]^{3-}$, 2

This control reaction was performed to examine whether KO^tBu, a mild reductant can reduce the iminosemiquinone-form, $\mathbf{2}_{imsq}$ of the pincer backbone, without any photoexcitation. To test this, in an overnight-dried vial, the iminosemiquinonate form of the pincer $[NNN_{imsq}]^{2-}$ pincer (18 mg, 0.05 mmol) was dissolved in THF solvent to make a clear solution under N_2 atmosphere. Notably, the $[NNN_{imsq}]^{2-}$ was prepared by chemical oxidation by AgOTf. To the solution of $[NNN_{imsq}]^{2-}$, solid KO^tBu (12 mg, 1 equiv.) was added at room temperature, while the vial was covered with aluminum foil. The reaction mixture was allowed to stir for 6 hours at room temperature. After completion of the reaction, a brownish yellow color appeared which can be attributed to iminocatecholate, $[NNN_{imcat}]^{3-}$, **2**. This is evident from the following UV-Visible diagram (Figure S1).

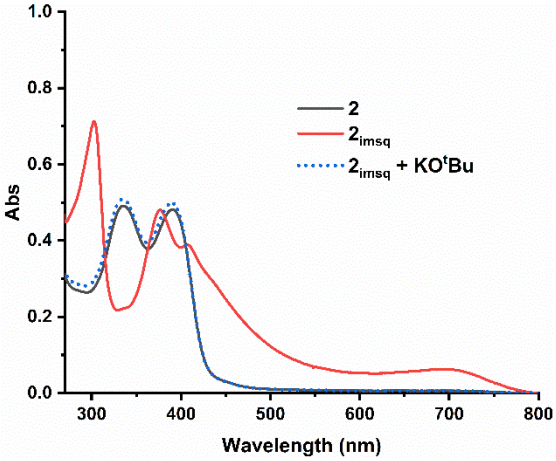
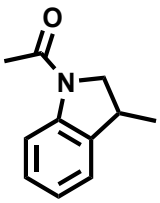


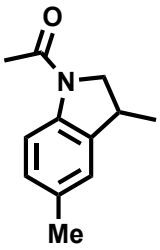
Figure S1. UV-Visible plot for $[NNN_{imcat}]^{3-}$, **2** (grey line) $[NNN_{imsq}]^{2-}$, $\mathbf{2_{imsq}}$ (Red line). The reaction mixture of $\mathbf{2_{imsq}}$ and KO^{t}Bu (blue dot line) shows the regeneration of **2**.

7. Spectroscopic characterization of isolated products



1-(3-methylindolin-1-yl)ethan-1-one (4a).[2]

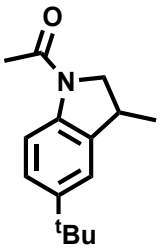
The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (86 mg, 98%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 3.57 (dd, *J* = 9.9, 6.7 Hz, 1H), 3.50 (dd, *J* = 15.9, 6.6 Hz, 1H), 2.22 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80, 142.48, 136.42, 127.85, 123.83, 123.48, 116.99, 57.06, 34.87, 24.38, 20.40.



1-(3,5-dimethylindolin-1-yl)ethan-1-one (4b).[2]

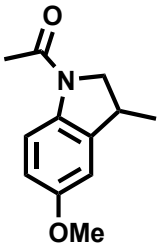
The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (84 mg, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 5.5 Hz, 1H), 6.96 (s, 1H), 4.18 (t, *J* = 9.7 Hz, 1H), 3.55 (dd, *J* = 10.0, 6.7 Hz, 1H), 3.45 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.31 (s, 3H), 2.20 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 140.17, 136.51, 133.41, 128.24, 124.11, 116.67, 57.17, 34.81, 24.23, 21.16, 20.35.



1-(5-(tert-butyl)-3-methylindolin-1-yl)ethan-1-one (4c).

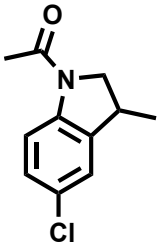
The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (97 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.17 (t, *J* = 1.5 Hz, 1H), 4.20 (t, *J* = 9.6 Hz, 1H), 3.56 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.48 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.20 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 147.04, 140.16, 136.12, 124.69, 120.30, 116.43, 57.27, 35.05, 34.63, 31.67, 24.21, 20.37.



1-(5-methoxy-3-methylindolin-1-yl)ethan-1-one (4d).

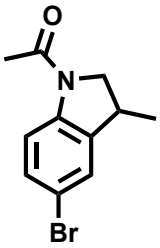
The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (85 mg, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 6.72 (ddd, *J* = 7.1, 2.7, 0.8 Hz, 2H), 4.20 (dd, *J* = 10.1, 9.3 Hz, 1H), 3.78 (s, 3H), 3.56 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.46 (dd, *J* = 15.9, 6.7 Hz, 1H), 2.19 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.05, 156.53, 138.08, 136.27, 117.60, 112.04, 109.95, 57.23, 55.74, 34.99, 24.07, 20.23.



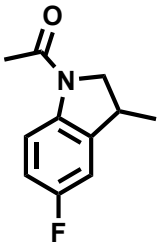
1-(5-chloro-3-methylindolin-1-yl)ethan-1-one (4e).[2]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (80 mg, 76%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.11 – 7.08 (m, 1H), 4.21 (t, *J* = 9.8 Hz, 1H), 3.58 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.47 (dq, *J* = 13.9, 7.0 Hz, 1H), 2.20 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 141.12, 138.33, 128.64, 127.72, 123.77, 117.87, 57.12, 34.74, 24.20, 20.23.



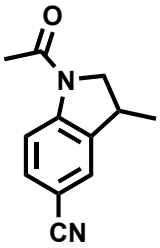
1-(5-bromo-3-methylindolin-1-yl)ethan-1-one (4f).[3]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (86 mg, 68%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (t, *J* = 1.6 Hz, 1H), 4.20 (t, *J* = 9.7 Hz, 1H), 3.57 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.48 (dt, *J* = 9.3, 6.7 Hz, 1H), 2.20 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.85, 141.60, 138.72, 130.66, 126.68, 118.35, 116.19, 57.08, 34.72, 24.24, 20.26.



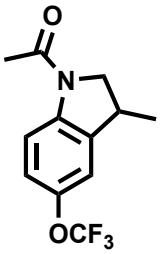
1-(5-fluoro-3-methylindolin-1-yl)ethan-1-one (4g).[2]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (77 mg, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.7, 4.9 Hz, 1H), 6.90 – 6.82 (m, 2H), 4.22 (t, *J* = 9.8 Hz, 1H), 3.59 (dd, *J* = 10.2, 6.8 Hz, 1H), 3.48 (dq, *J* = 14.3, 7.0 Hz, 1H), 2.20 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.49, 160.78(d, $^{1}J_{C\text{-}F}$= 242 Hz), 138.58(d, $^{3}J_{C\text{-}F}$= 8 Hz), 138.50(d, $^{3}J_{C\text{-}F}$= 8 Hz), 117.86(d, $^{3}J_{C\text{-}F}$= 8 Hz), 114.13(d, $^{3}J_{C\text{-}F}$= 23 Hz), 110.91(d, $^{3}J_{C\text{-}F}$= 24 Hz), 57.24, 34.85, 24.11, 20.17. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.20.



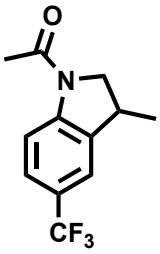
1-acetyl-3-methylindoline-5-carbonitrile (4h).[2]

The compound was purified by column chromatography (silica gel) with 15% mixture of ethyl acetate in hexane to give the product as a white solid (92 mg, 92%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.41 (s, 1H), 4.28 (t, *J* = 9.9 Hz, 1H), 3.65 (dd, *J* = 10.1, 6.7 Hz, 1H), 3.53 (h, *J* = 6.9 Hz, 1H), 2.25 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57, 146.17, 137.47, 133.08, 127.27, 119.47, 117.19, 106.61, 57.12, 34.54, 24.45, 20.33.



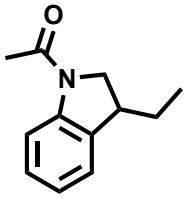
1-(3-methyl-5-(trifluoromethoxy)indolin-1-yl)ethan-1-one (4i).[3]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (115 mg, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 1H), 7.00 (s, 1H), 4.25 (t, *J* = 9.8 Hz, 1H), 3.62 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.51 (h, *J* = 7.0 Hz, 1H), 2.22 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 145.29, 145.27, 141.13, 138.22, 121.91, 120.65, 119.36, 117.55, 116.80, 57.25, 34.79, 29.82, 24.19, 20.17. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.13.



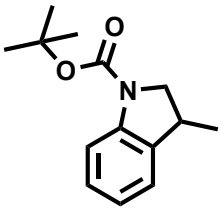
1-(3-methyl-5-(trifluoromethyl)indolin-1-yl)ethan-1-one(4j).[3]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (109 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 4.26 (t, *J* = 9.8 Hz, 1H), 3.64 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.53 (h, *J* = 6.9 Hz, 1H), 2.24 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.35, 145.27, 137.03, 125.58, 120.59, 116.68, 57.24, 34.67, 32.04, 29.82, 24.37, 20.29, 14.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.59.



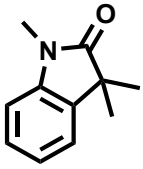
1-(3-ethylindolin-1-yl)ethan-1-one(4k).[2]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (86 mg, 91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 17.5, 8.0 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.67 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.33 (tt, *J* = 9.5, 5.3 Hz, 1H), 2.22 (s, 3H), 1.84 (td, *J* = 8.1, 7.3, 3.6 Hz, 1H), 1.64 – 1.54 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 142.81, 135.05, 127.87, 123.91, 123.66, 116.98, 54.80, 41.57, 28.22, 24.37, 11.27.



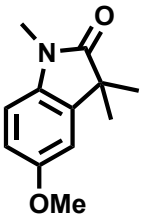
tert-butyl 3-methylindoline-1-carboxylate(4l).[4]

The compound was purified by column chromatography (silica gel) with 1% mixture of ethyl acetate in hexane to give the product as a white solid (108 mg, 93%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 18.5, 7.5 Hz, 3H), 6.95 (t, *J* = 7.4 Hz, 1H), 4.14 (t, *J* = 10.3 Hz, 1H), 3.50 (t, *J* = 9.9 Hz, 1H), 3.39 (dt, *J* = 9.4, 6.8 Hz, 1H), 1.57 (s, 9H), 1.32 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.66, 127.61, 123.64, 122.31, 114.68, 55.72, 34.13, 28.56, 20.37.



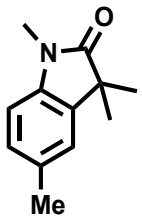
1,3,3-trimethylindolin-2-one (6a).[5]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a colorless oil (81 mg, 92%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.20 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.20, 142.49, 135.65, 127.58, 122.40, 122.15, 107.95, 44.02, 26.08, 24.28.



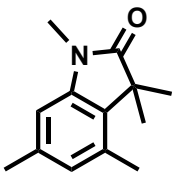
5-methoxy-1,3,3-trimethylindolin-2-one (6b).[5]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a colorless oil (90 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 2.3 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.10, 156.14, 137.30, 136.22, 111.61, 110.12, 108.31, 55.86, 44.68, 26.35, 24.47.



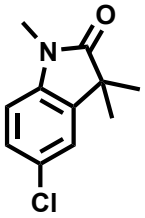
1,3,3,5-tetramethylindolin-2-one (6c).[5]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a yellow oil (80 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (ddd, *J* = 7.8, 1.7, 0.9 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 3H), 2.34 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.41, 140.29, 135.93, 132.05, 127.90, 123.22, 107.81, 44.29, 26.29, 24.48, 24.46, 21.18.



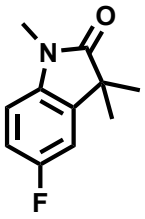
1,3,3,4,6-pentamethylindolin-2-one (6d).[6]

The compound was purified by column chromatography (silica gel) with 5 % mixture of ethyl acetate in hexane to give the product as a white solid (77 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 6.53 (s, 1H), 3.18 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.85, 143.16, 137.60, 133.88, 129.84, 125.64, 106.87, 44.85, 26.39, 22.64, 21.63, 18.13.



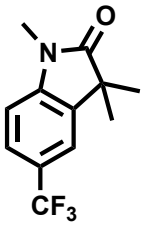
5-chloro-1,3,3-trimethylindolin-2-one (6e).[5]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a yellow solid (76 mg, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.19 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.93, 141.30, 137.57, 127.97, 127.67, 123.05, 109.07, 44.58, 26.45, 24.38.



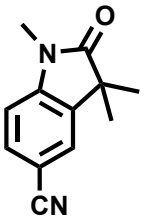
5-fluoro-1,3,3-trimethylindolin-2-one (6f).[5]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a yellow solid (82 mg, 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.89 (m, 2H), 6.74 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.20 (s, 3H), 1.36 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 181.10, 158.33 (d, $^{1}J_{C\text{-}F}$= 241 Hz), 138.64(d, $^{4}J_{C\text{-}F}$= 2 Hz), 137.55(d, $^{3}J_{C\text{-}F}$= 8 Hz), 113.74($^{2}J_{C\text{-}F}$= 24 Hz), 110.54($^{2}J_{C\text{-}F}$= 24 Hz), 108.50($^{3}J_{C\text{-}F}$= 8 Hz), 44.79, 26.48, 24.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.90.



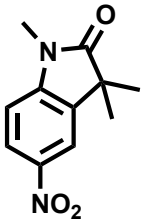
1,3,3-trimethyl-5-(trifluoromethyl)indolin-2-one (6g).[5]

The compound was purified by column chromatography (silica gel) with 5 % mixture of ethyl acetate in hexane to give the product as a white solid (100 mg, 82%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 9.0 Hz, 1H), 7.42 (s, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.24 (s, 3H), 1.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.36, 145.74, 136.41, 125.64(q, $^{3}J_{C\text{-}F}$= 4 Hz), 124.70(q, $^{2}J_{C\text{-}F}$= 32 Hz), 123.24(q, $^{1}J_{C\text{-}F}$= 272 Hz), 119.45(q, $^{3}J_{C\text{-}F}$= 4 Hz), 107.88, 44.31, 26.53, 24.34. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.34.



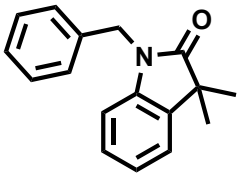
1,3,3-trimethyl-2-oxoindoline-5-carbonitrile (6h).[5]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a white solid (92 mg, 92%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 3.24 (s, 3H), 1.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.04, 146.69, 136.83, 133.31, 125.86, 119.44, 108.58, 105.71, 44.15, 26.59, 24.30.



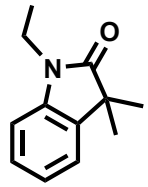
1,3,3-trimethyl-5-nitroindolin-2-one (6i).[5]

The compound was purified by column chromatography (silica gel) with 10% mixture of ethyl acetate in hexane to give the product as a yellow solid (82 mg, 75%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.05 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.26 (d, *J* = 1.1 Hz, 3H), 1.39 (d, *J* = 1.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.28, 148.44, 143.44, 136.46, 125.20, 118.29, 107.68, 44.22, 26.67, 24.15.



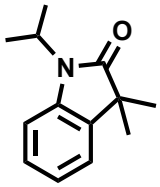
1-benzyl-3,3-dimethylindolin-2-one (6j).[5]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a white solid (93 mg, 74%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 13.8, 6.7 Hz, 5H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.92 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.60, 141.79, 136.21, 135.92, 128.90, 127.70, 127.66, 127.29, 122.63, 122.46, 109.21, 44.33, 43.65, 24.68.



1-ethyl-3,3-dimethylindolin-2-one (6k).[7]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a white solid (73 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.8, 0.8 Hz, 1H), 3.76 (q, *J* = 7.2 Hz, 2H), 1.36 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 145.29, 145.27, 141.13, 138.22, 121.91, 120.65, 119.36, 117.55, 116.80, 57.25, 34.79, 29.82, 24.19, 20.17.



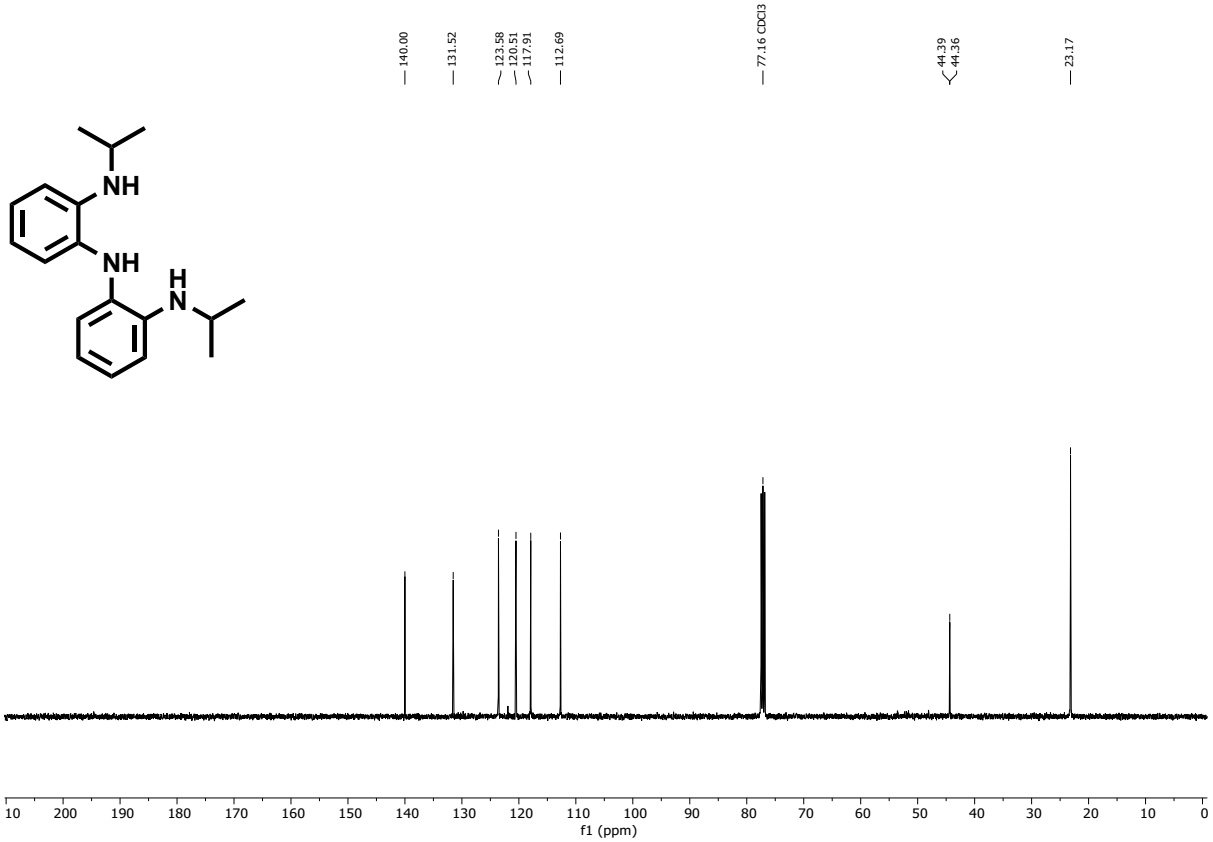
1-isopropyl-3,3-dimethylindolin-2-one (6l).[7]

The compound was purified by column chromatography (silica gel) with 5% mixture of ethyl acetate in hexane to give the product as a white solid (82 mg, 81%).

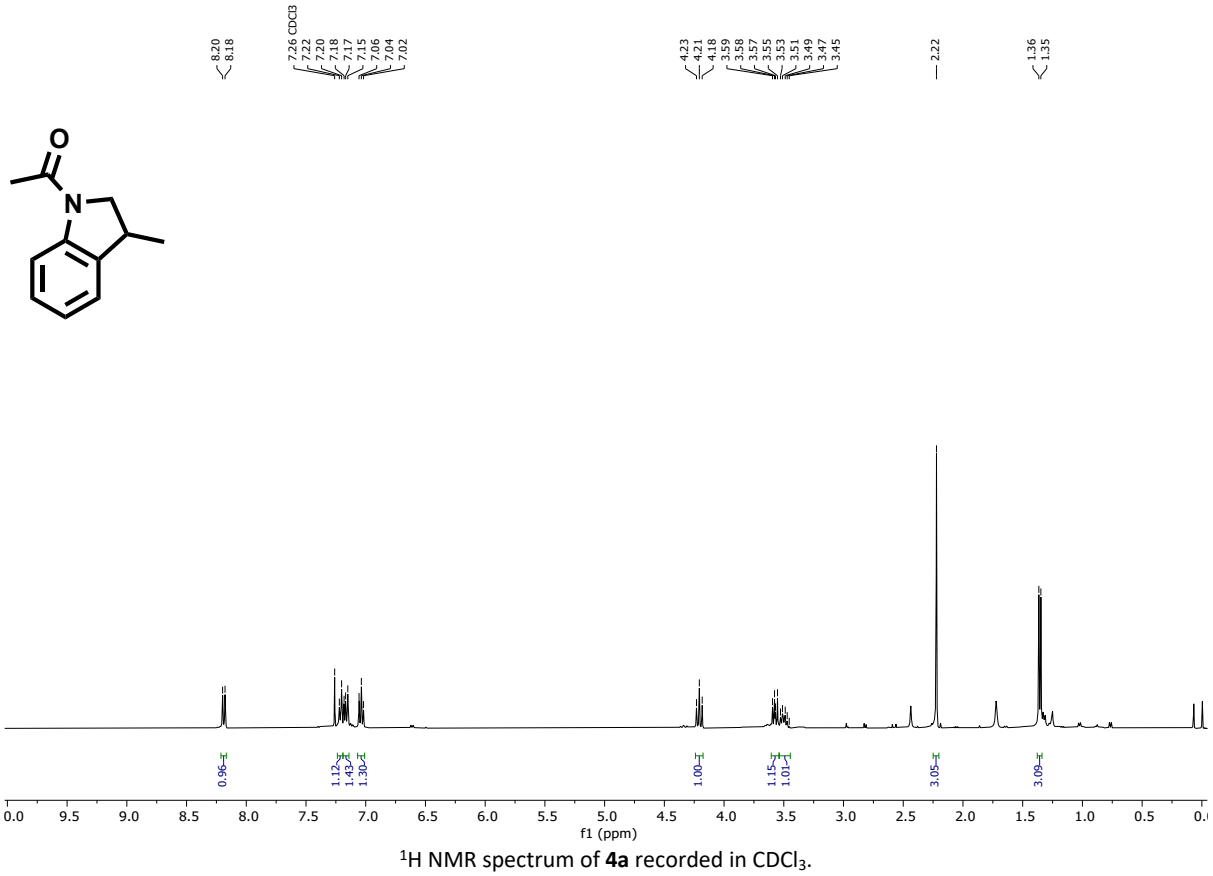
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (ddd, *J* = 8.5, 7.5, 1.2 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 2H), 4.66 (hept, *J* = 7.1 Hz, 1H), 1.48 (d, *J* = 7.1 Hz, 6H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.17, 141.29, 136.53, 127.44, 122.66, 121.99, 110.01, 43.97, 43.53, 24.63, 19.56.

8. Spectral data

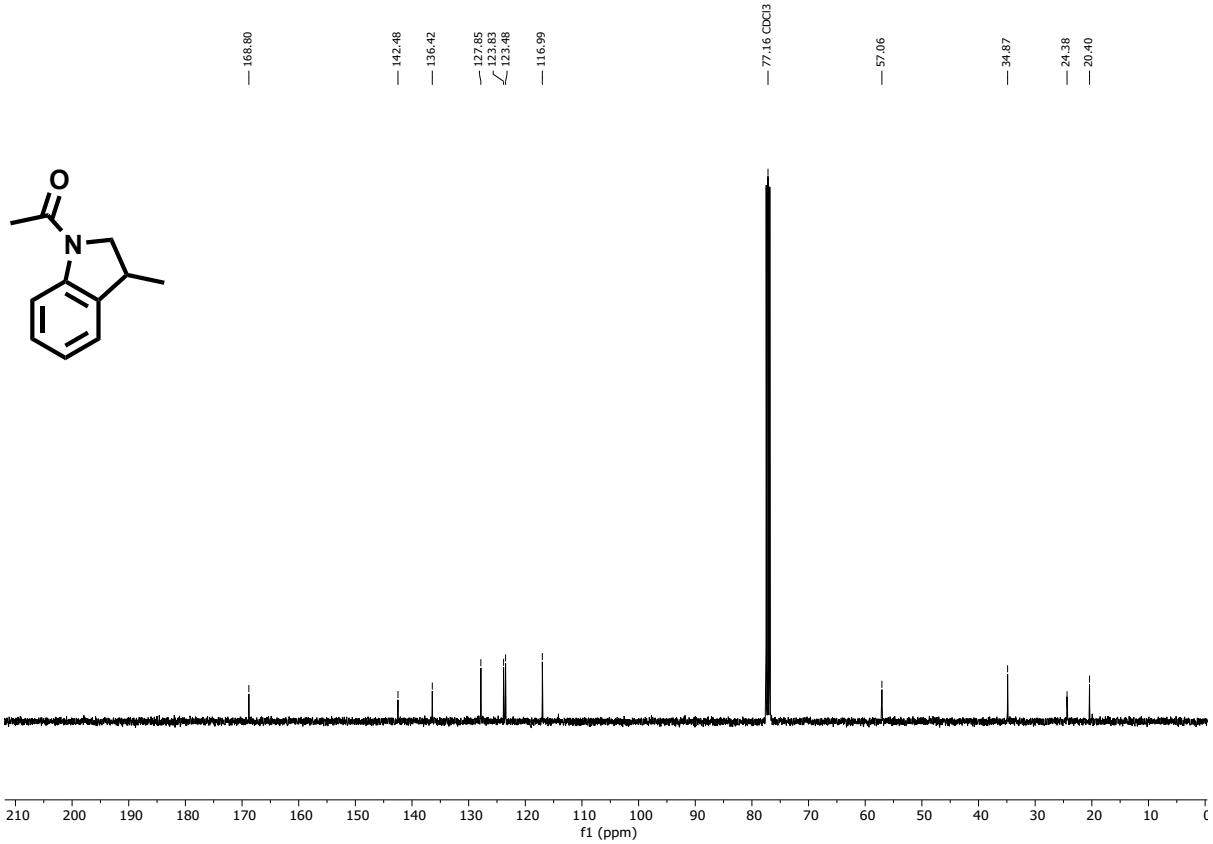
^{1}H NMR spectrum of **1** recorded in $CDCl_3$.



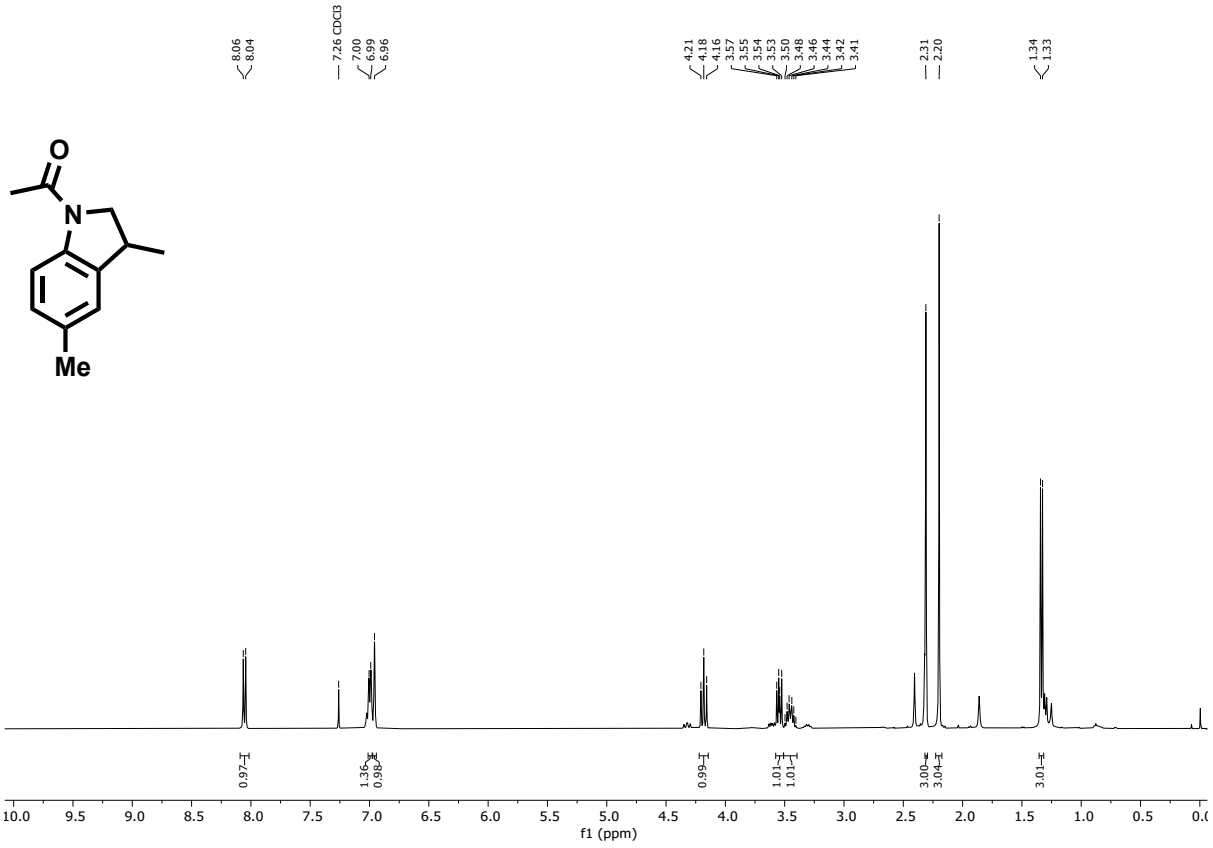
^{13}C NMR spectrum of **1** recorded in $CDCl_3$.



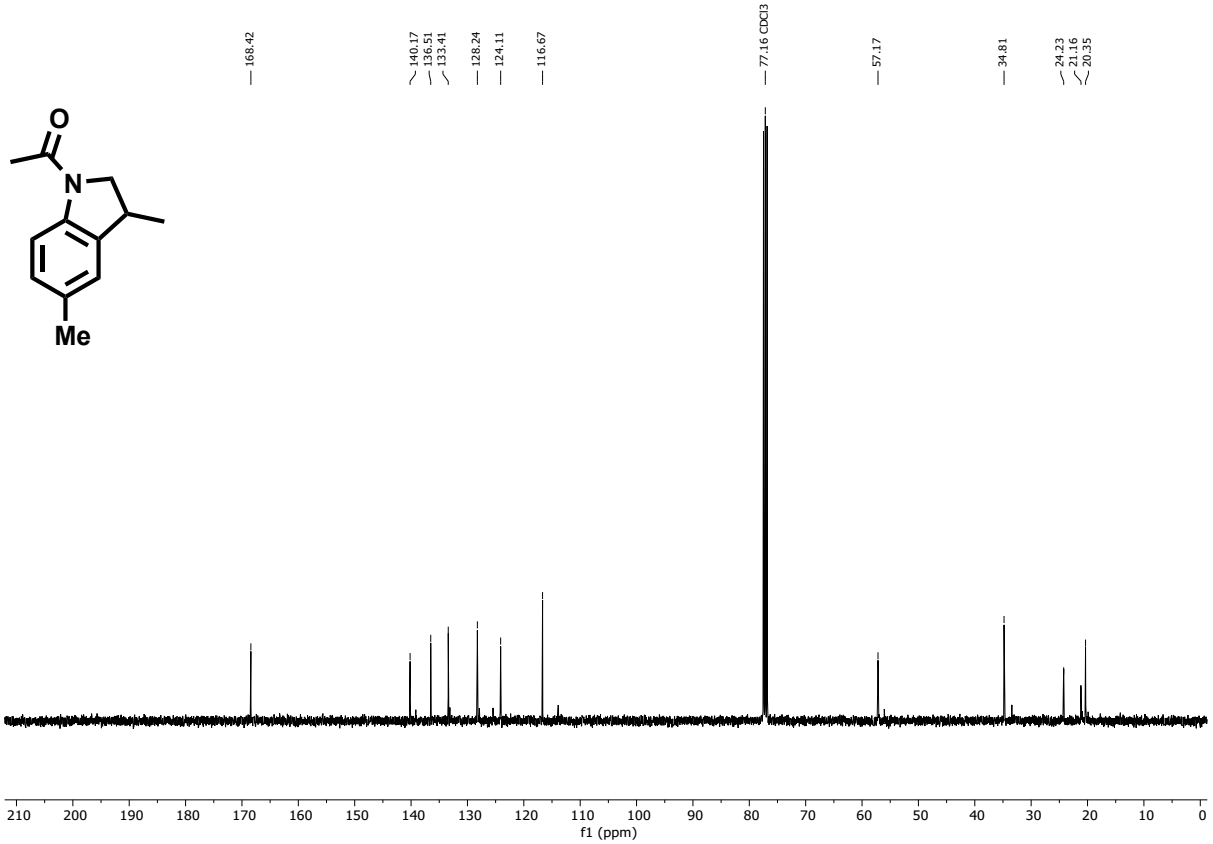
^{1}H NMR spectrum of **4a** recorded in $CDCl_3$.



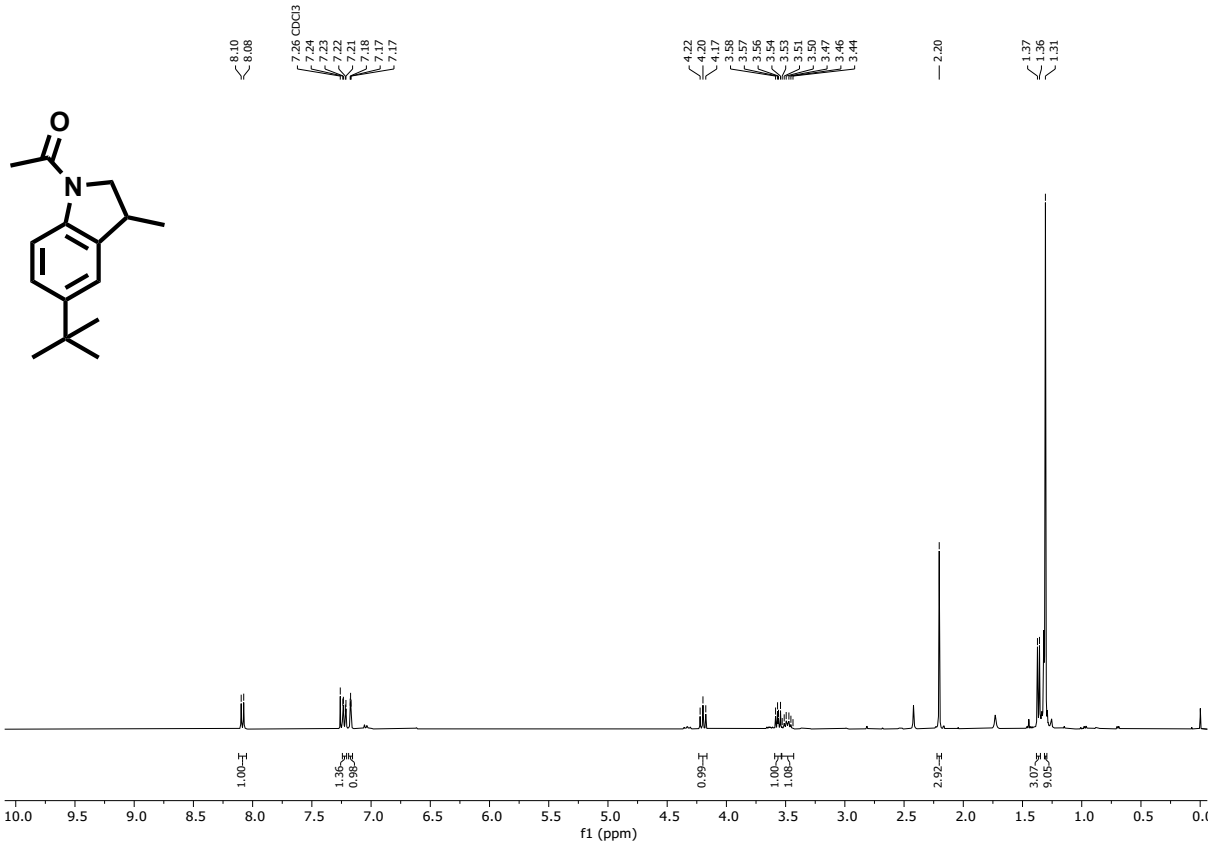
^{13}C NMR spectrum of **4a** recorded in $CDCl_3$.



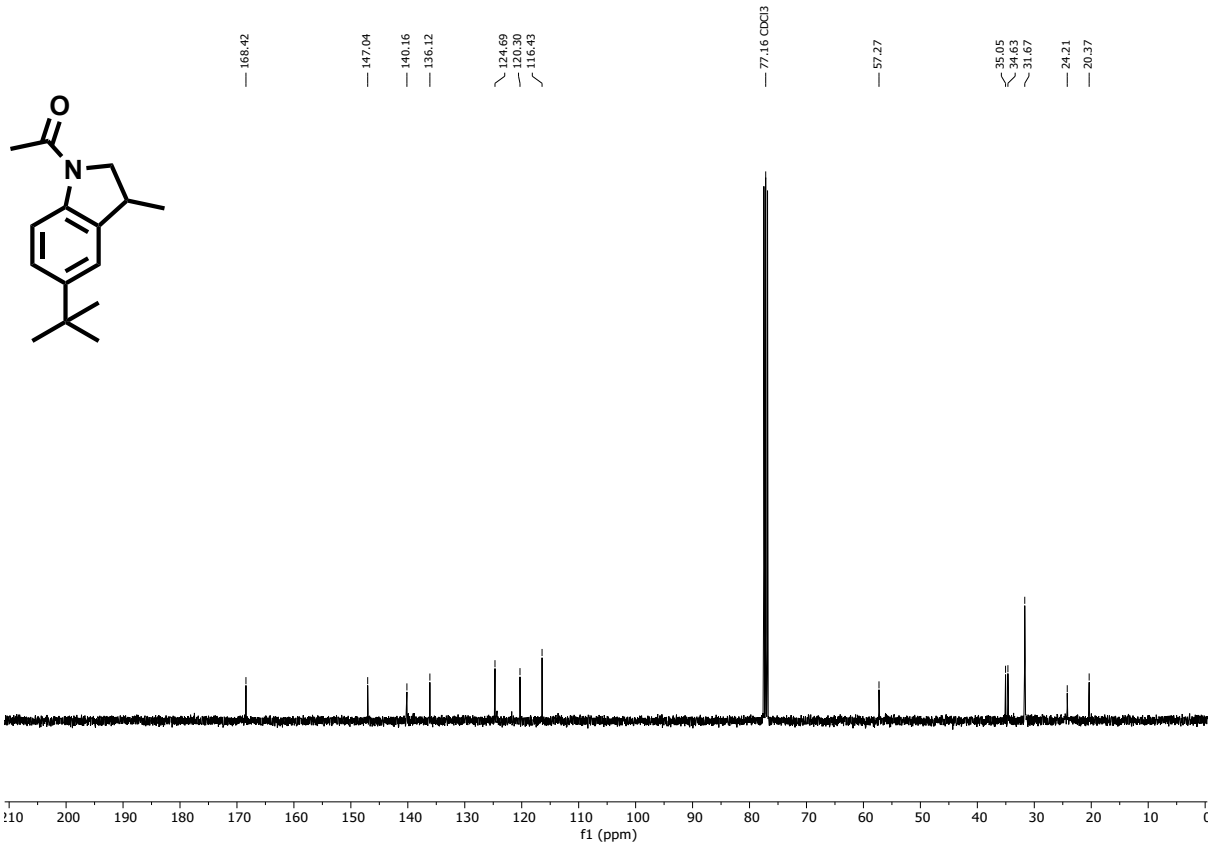
^{1}H NMR spectrum of **4b** recorded in $CDCl_3$.



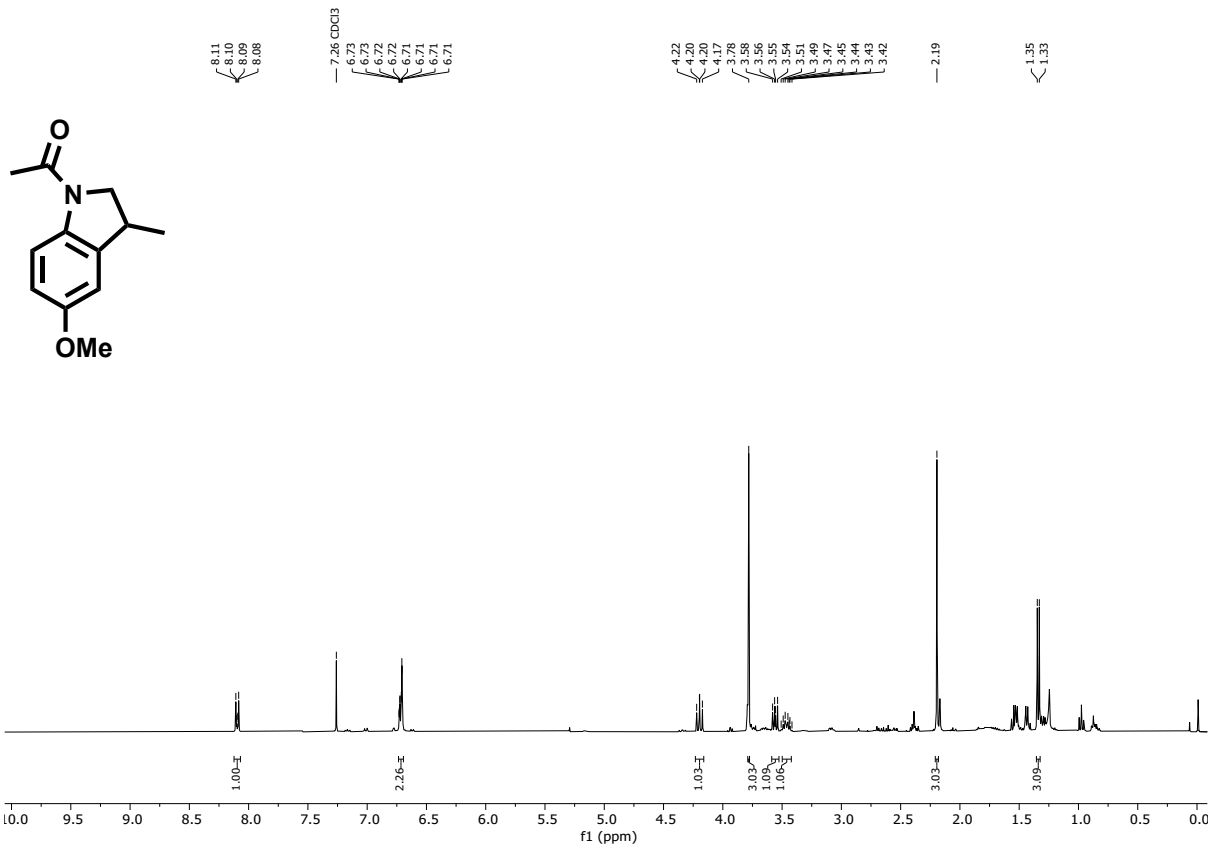
^{13}C NMR spectrum of **4b** recorded in $CDCl_3$.



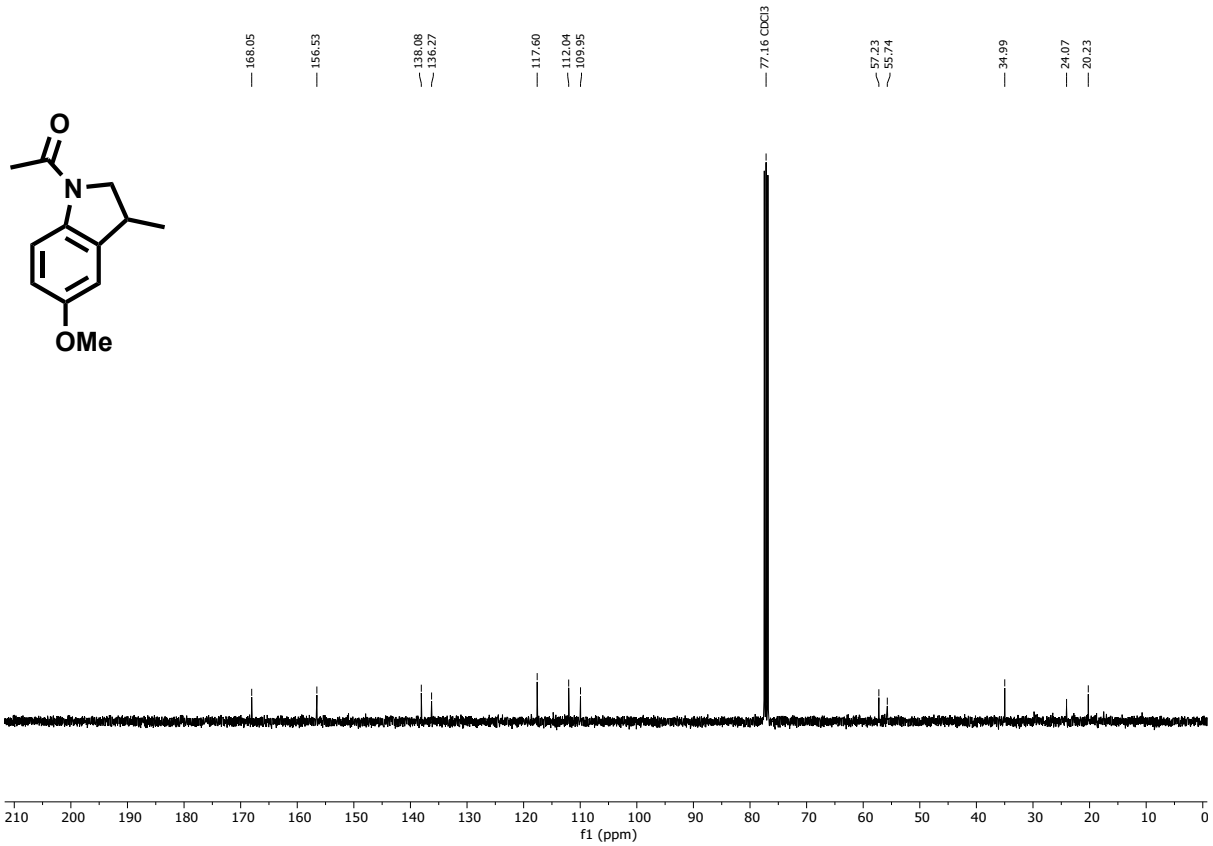
^{1}H NMR spectrum of **4c** recorded in $CDCl_3$.



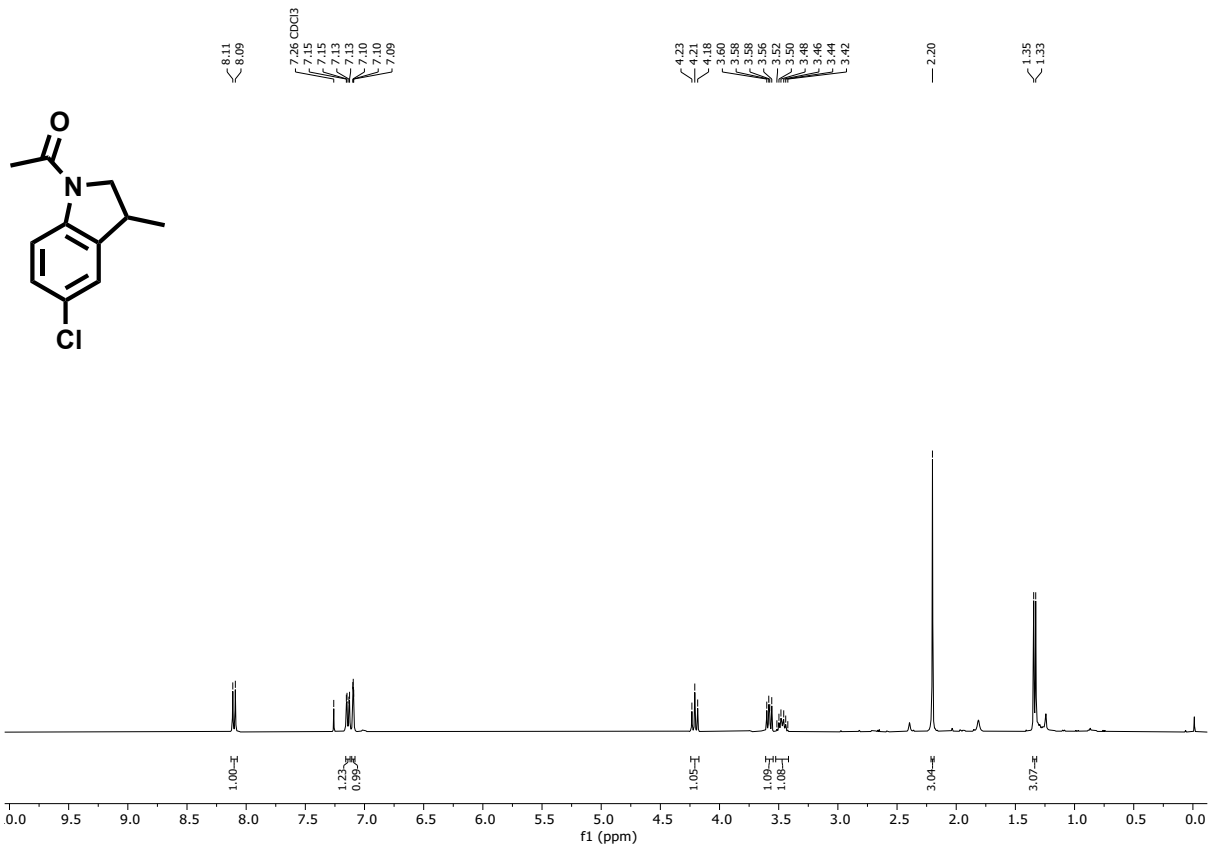
^{13}C NMR spectrum of **4c** recorded in $CDCl_3$.



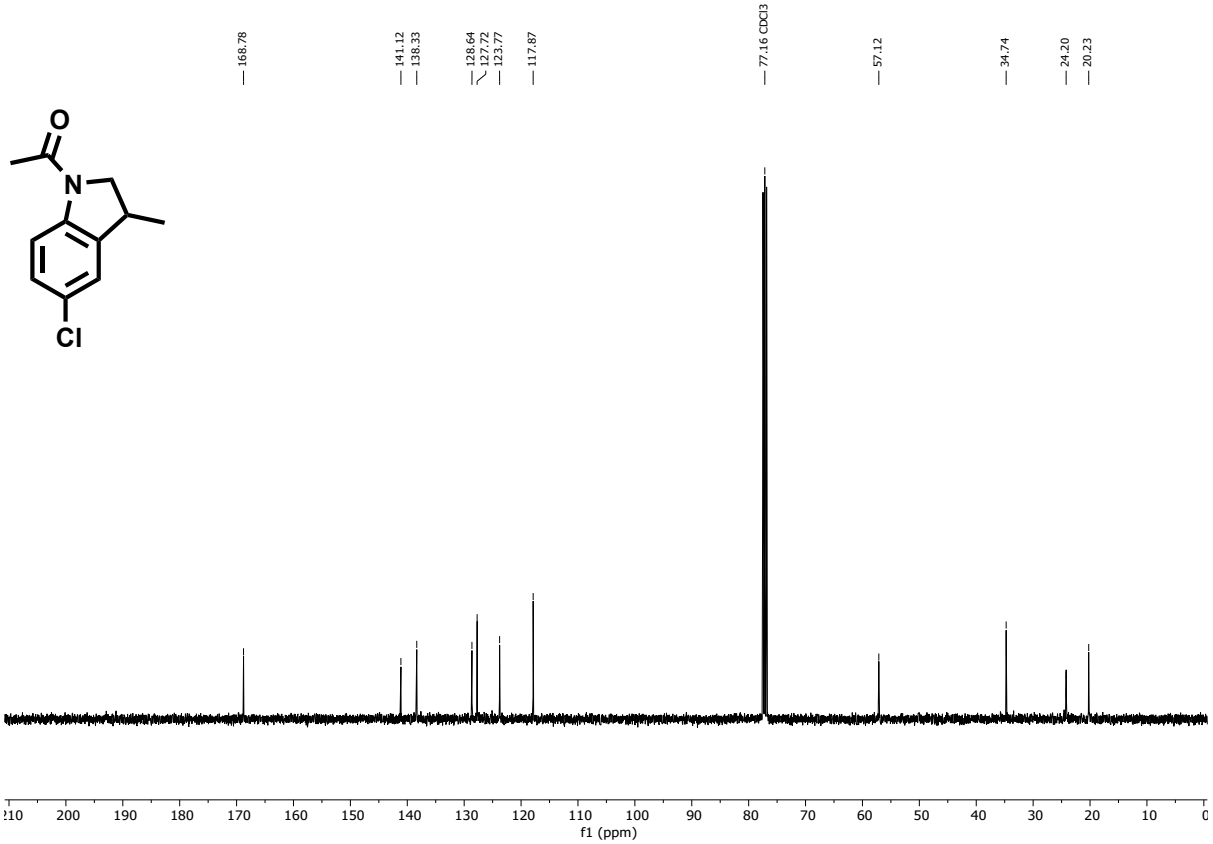
^{1}H NMR spectrum of **4d** recorded in $CDCl_3$.



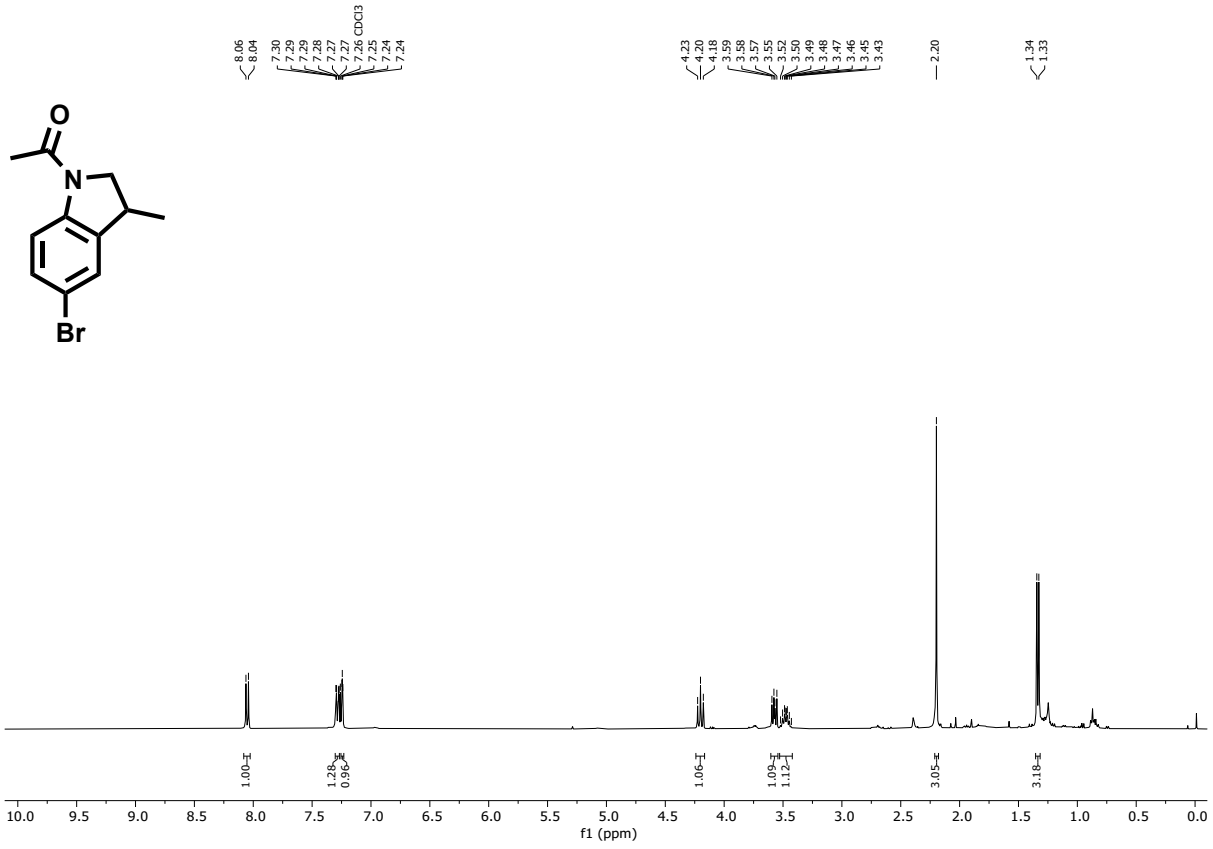
^{13}C NMR spectrum of **4d** recorded in $CDCl_3$.



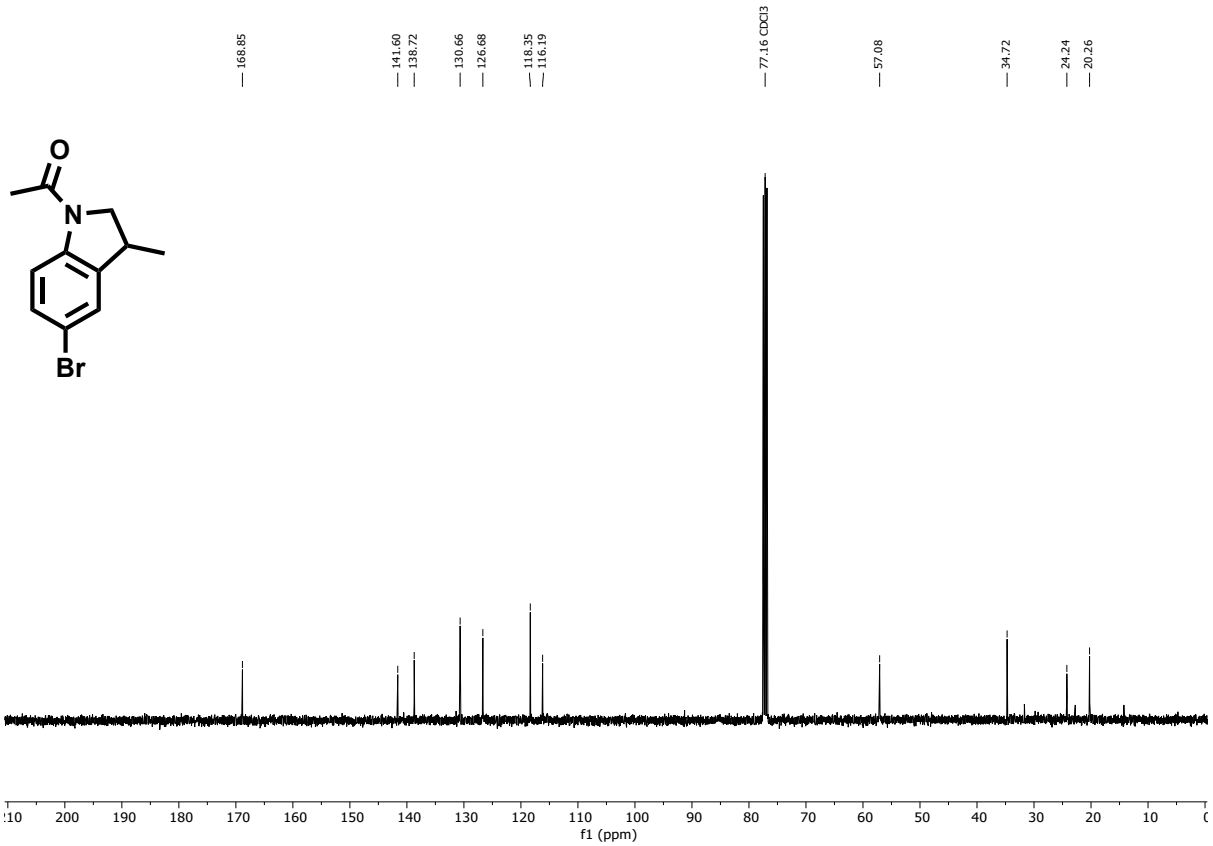
^{1}H NMR spectrum of **4e** recorded in $CDCl_3$.



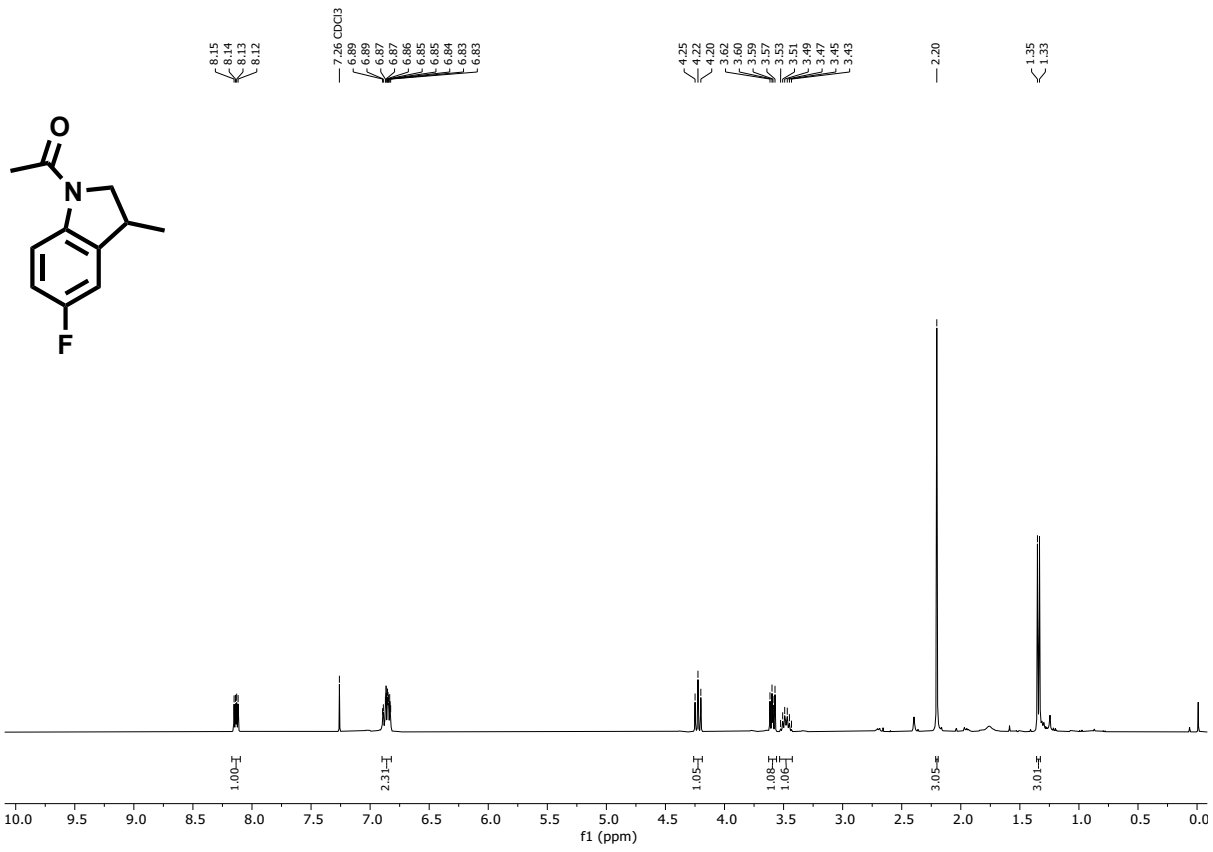
^{13}C NMR spectrum of **4e** recorded in $CDCl_3$.



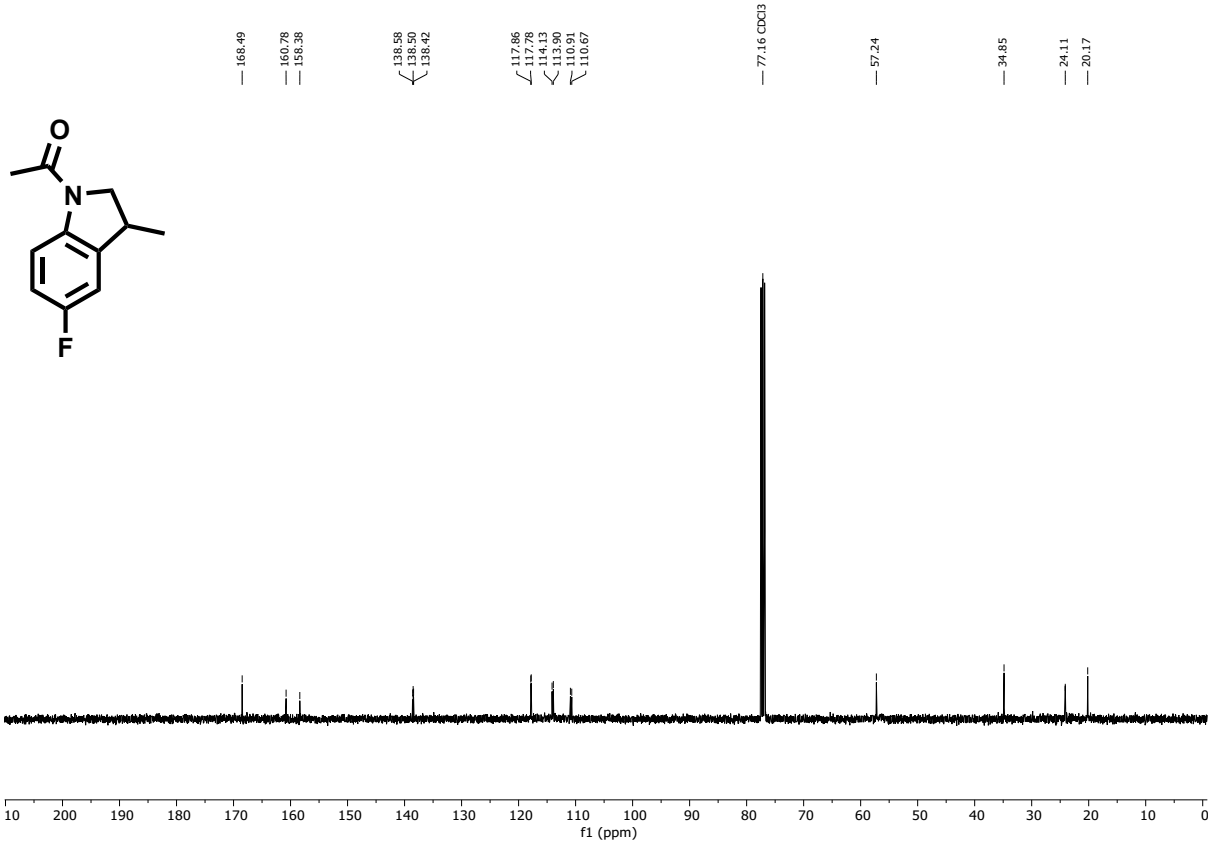
^{1}H NMR spectrum of **4f** recorded in $CDCl_3$.



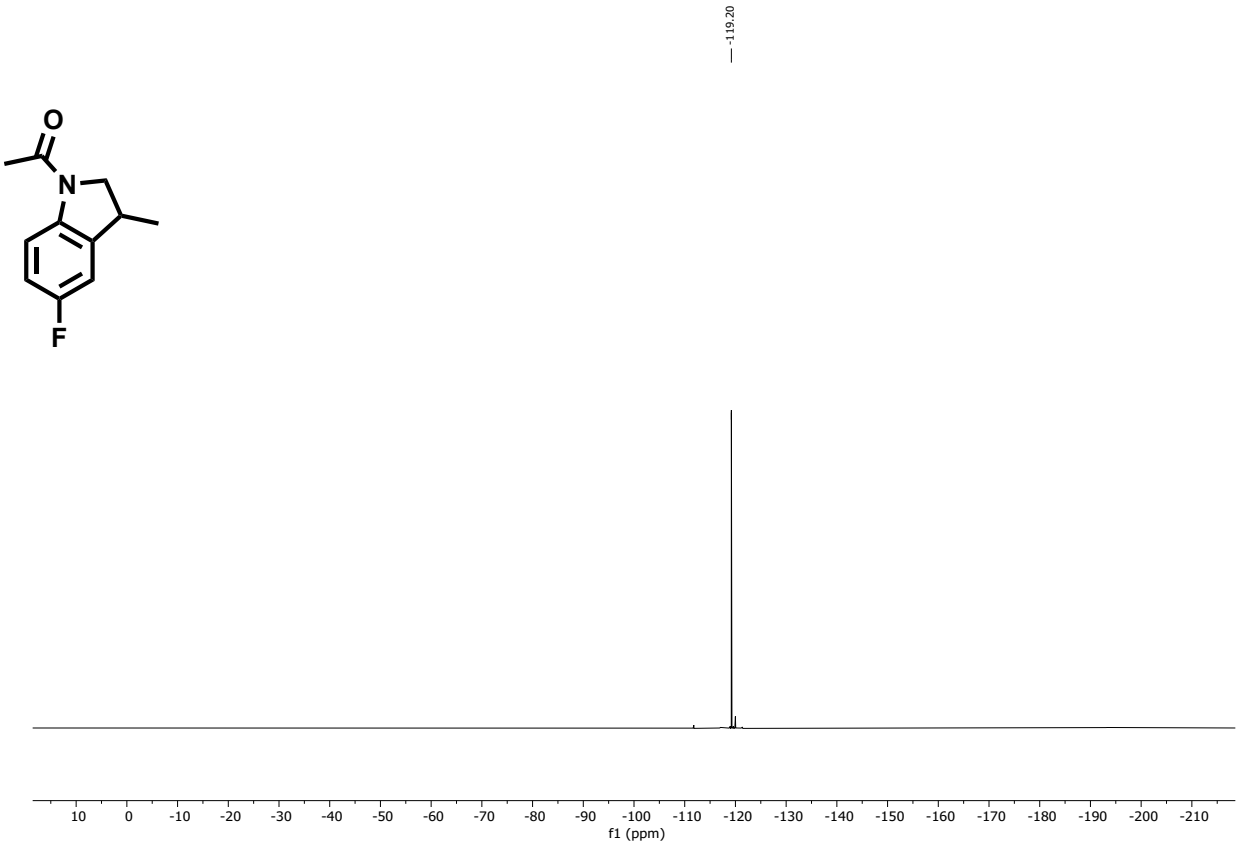
^{13}C NMR spectrum of **4f** recorded in $CDCl_3$.



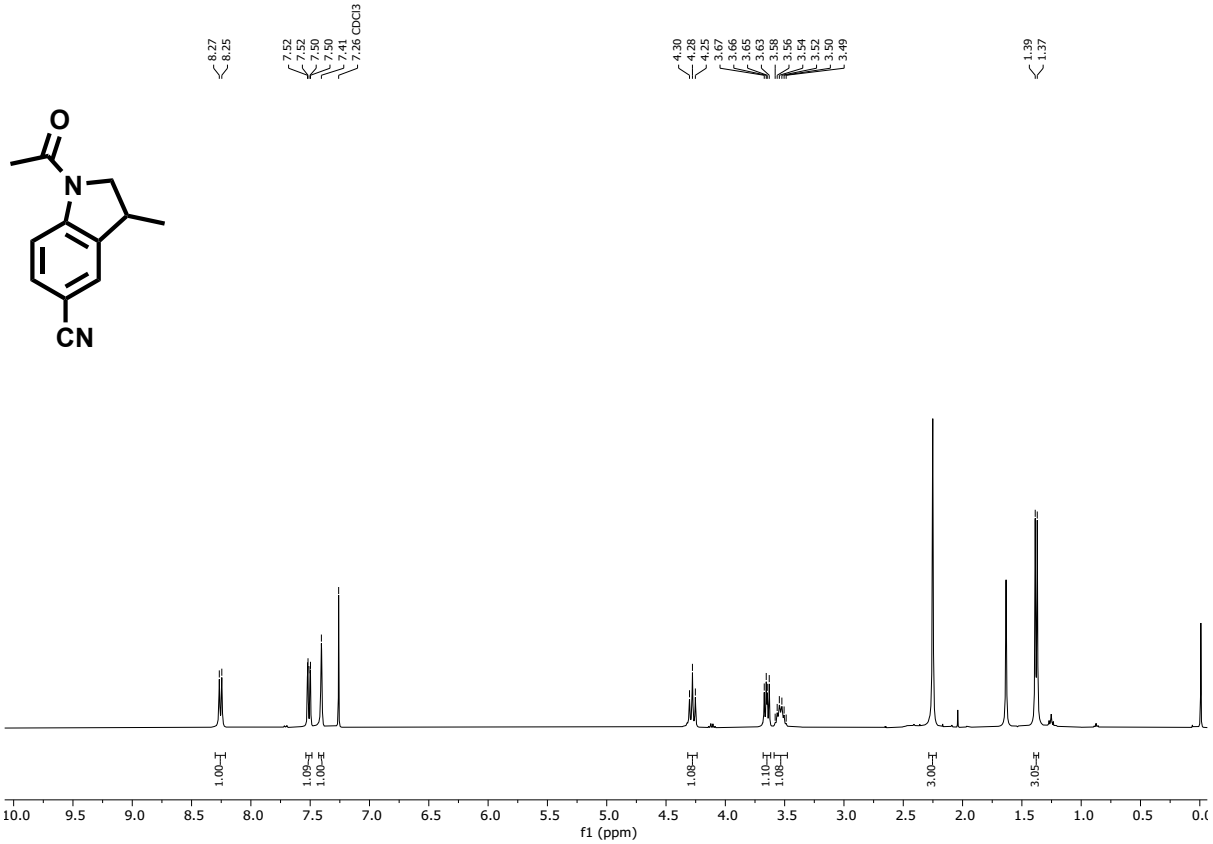
^{1}H NMR spectrum of **4g** recorded in $CDCl_3$.



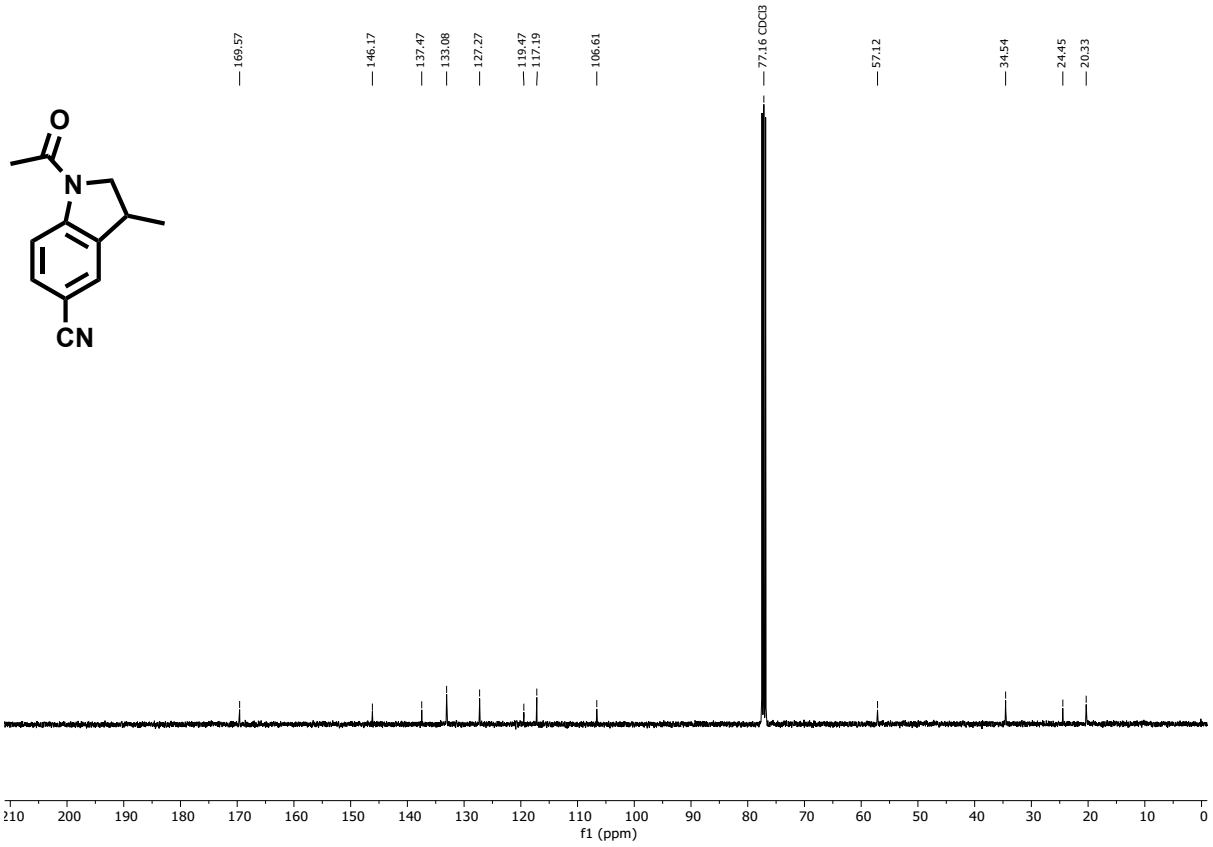
^{13}C NMR spectrum of **4g** recorded in $CDCl_3$.



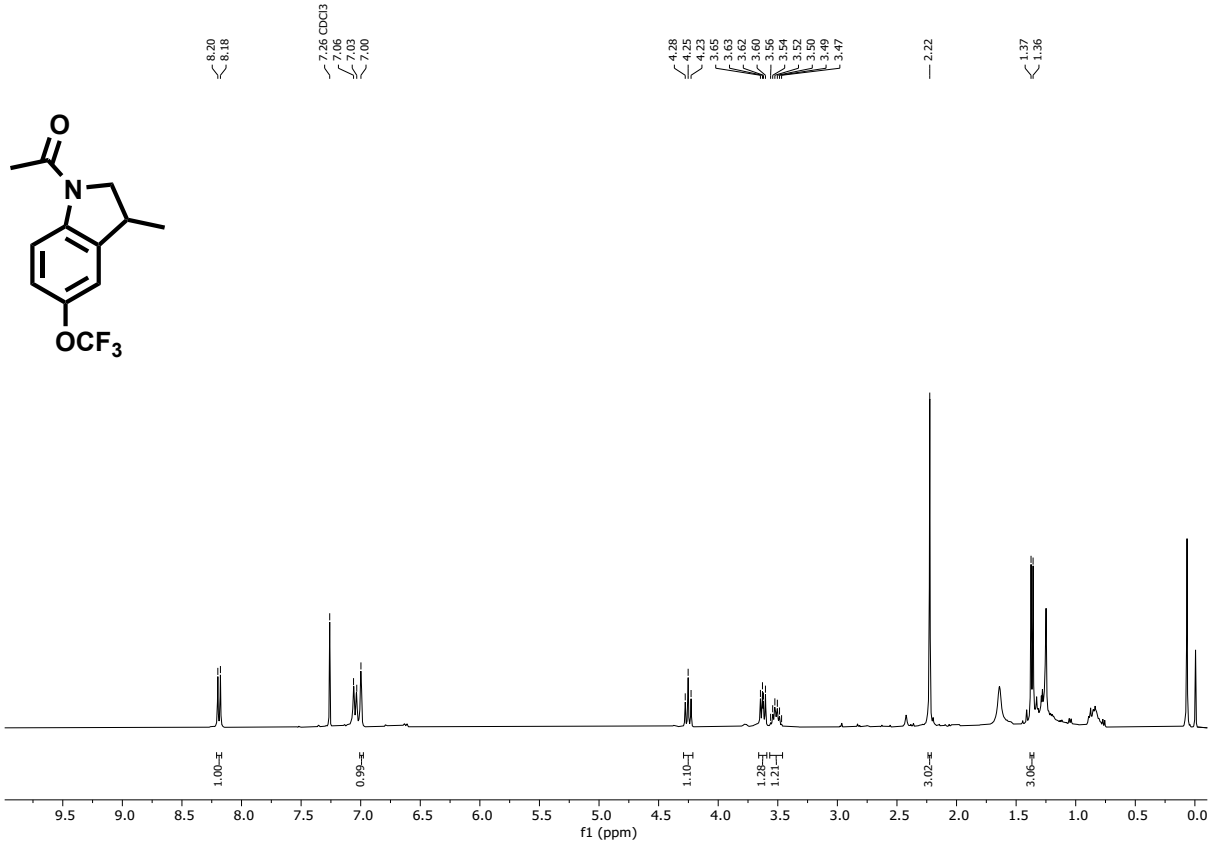
^{19}F NMR spectrum of **4g** recorded in $CDCl_3$.



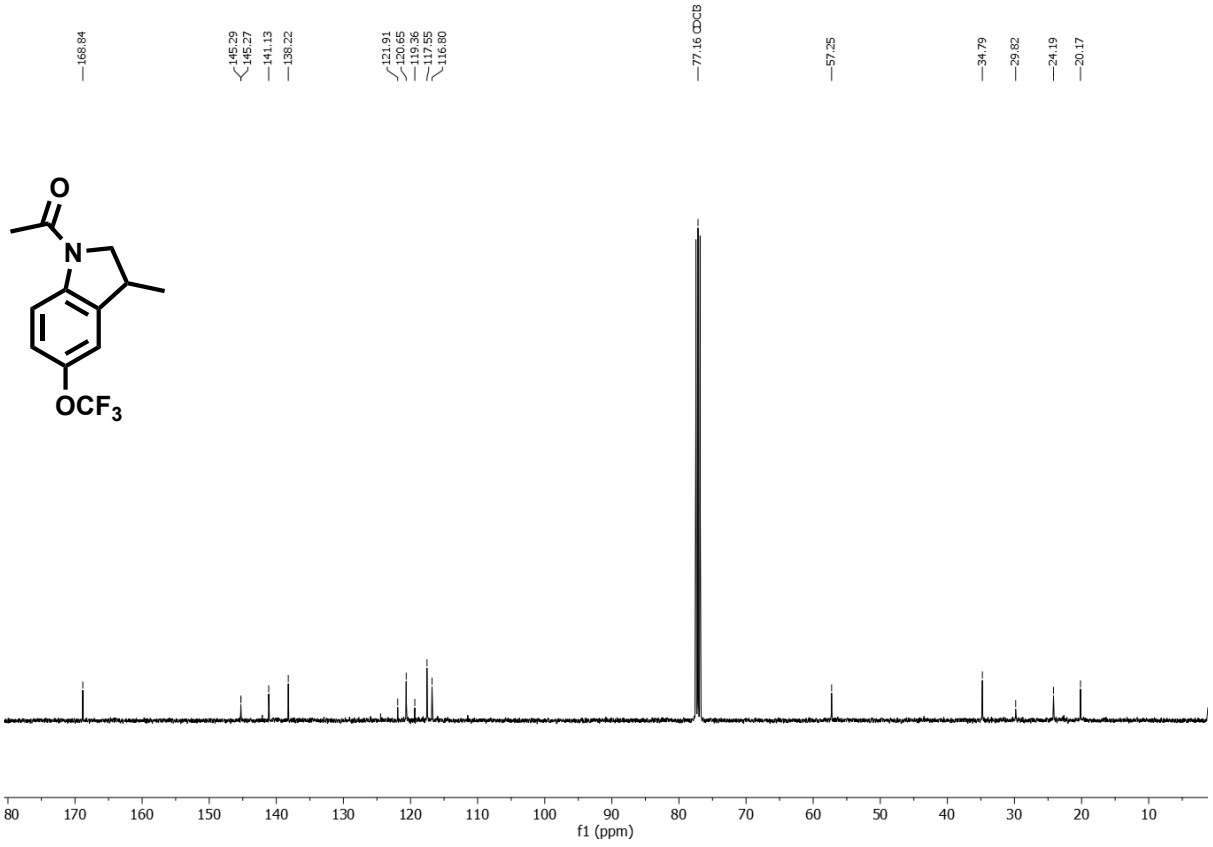
^{1}H NMR spectrum of **4h** recorded in $CDCl_3$.



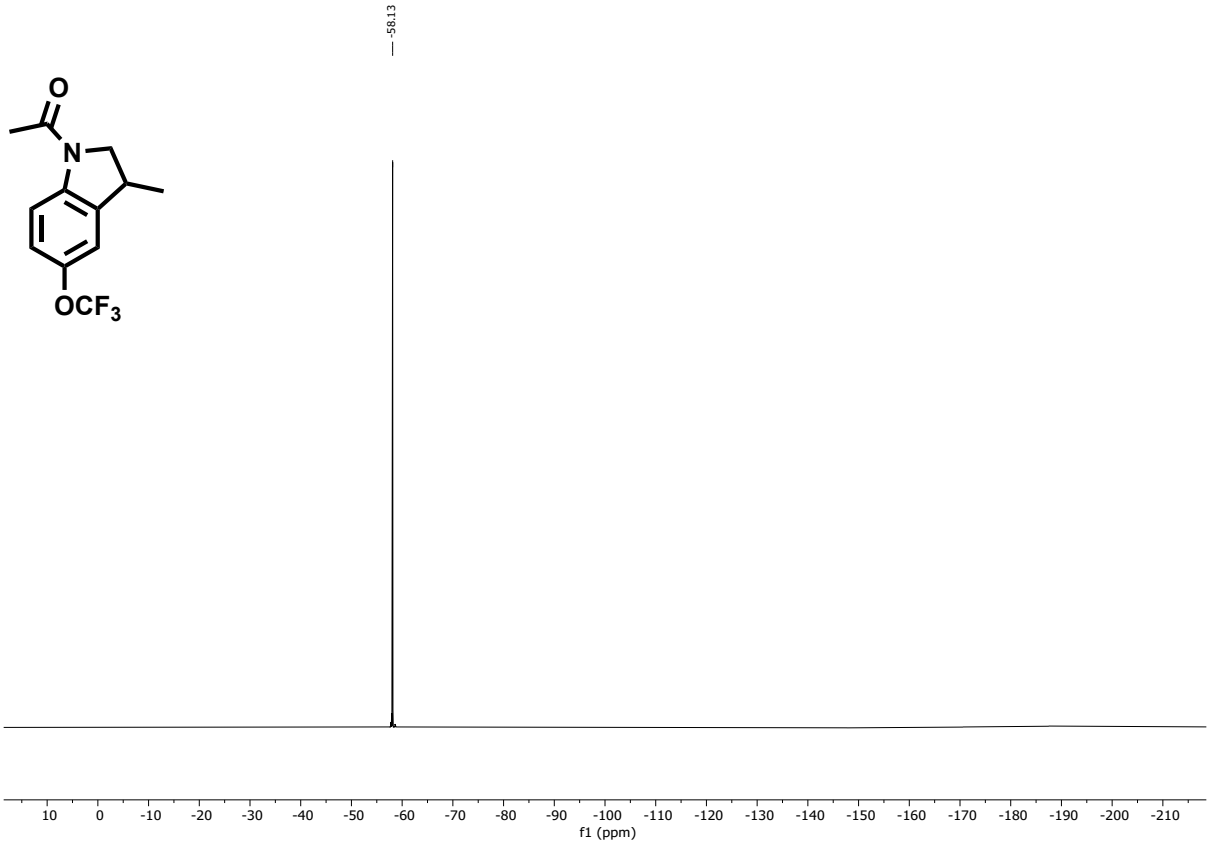
^{13}C NMR spectrum of **4h** recorded in $CDCl_3$.



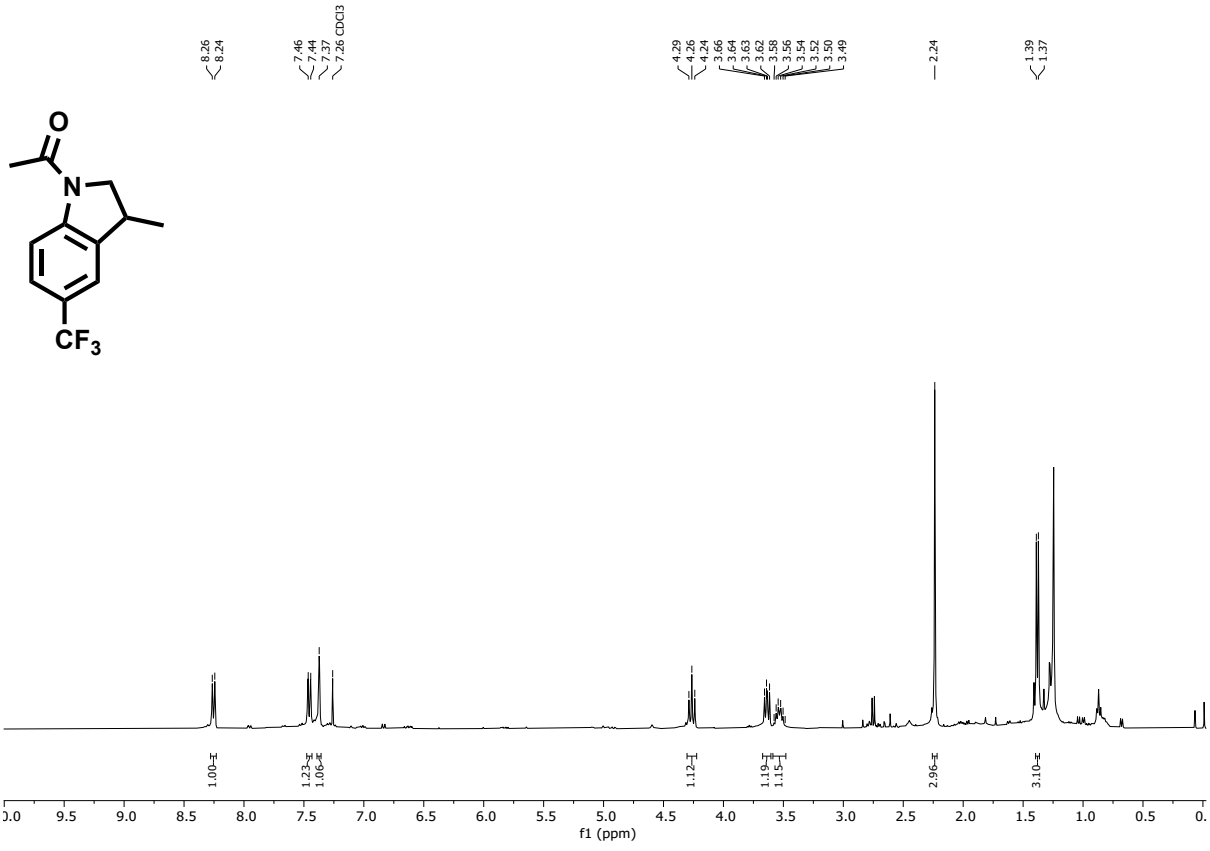
^{1}H NMR spectrum of **4i** recorded in $CDCl_3$.



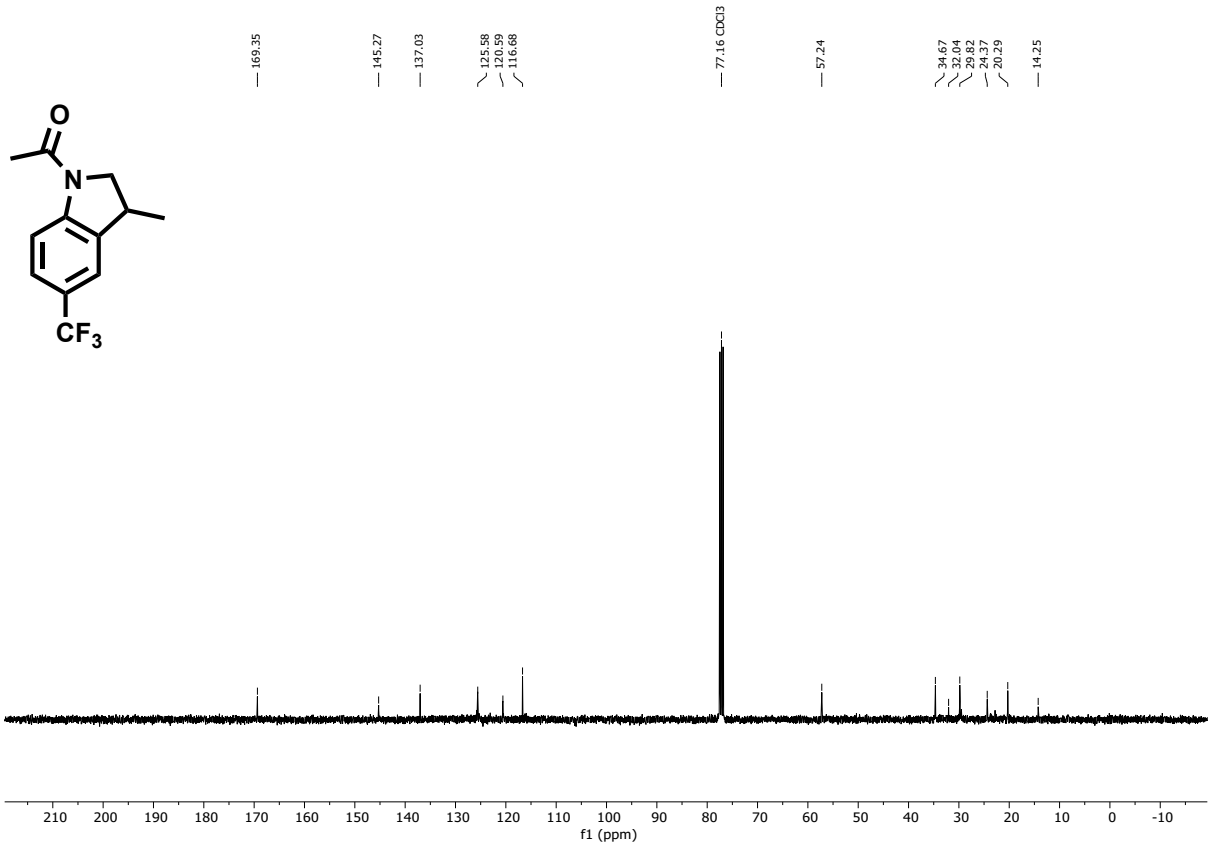
^{13}C NMR spectrum of **4i** recorded in $CDCl_3$.



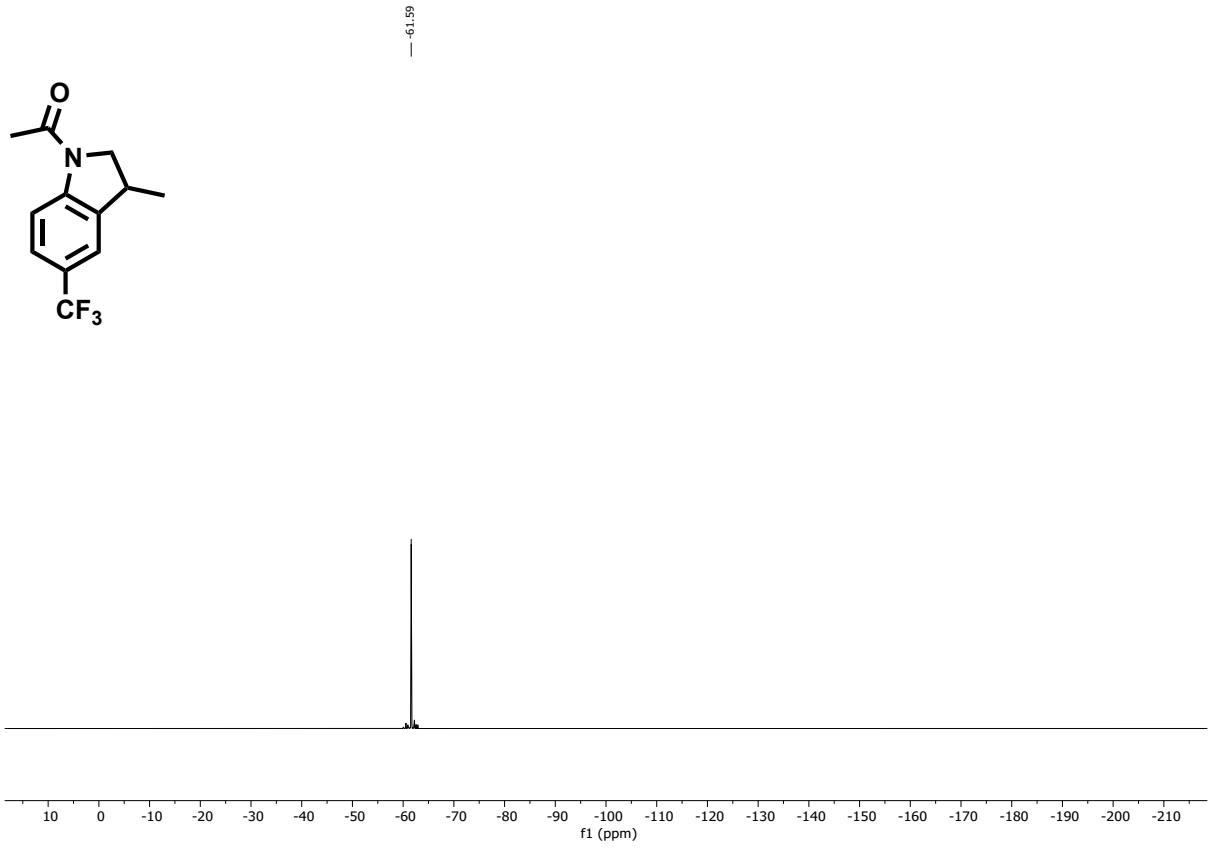
^{19}F NMR spectrum of **4i** recorded in $CDCl_3$.



^{1}H NMR spectrum of **4j** recorded in $CDCl_3$.



^{13}C NMR spectrum of **4j** recorded in $CDCl_3$.



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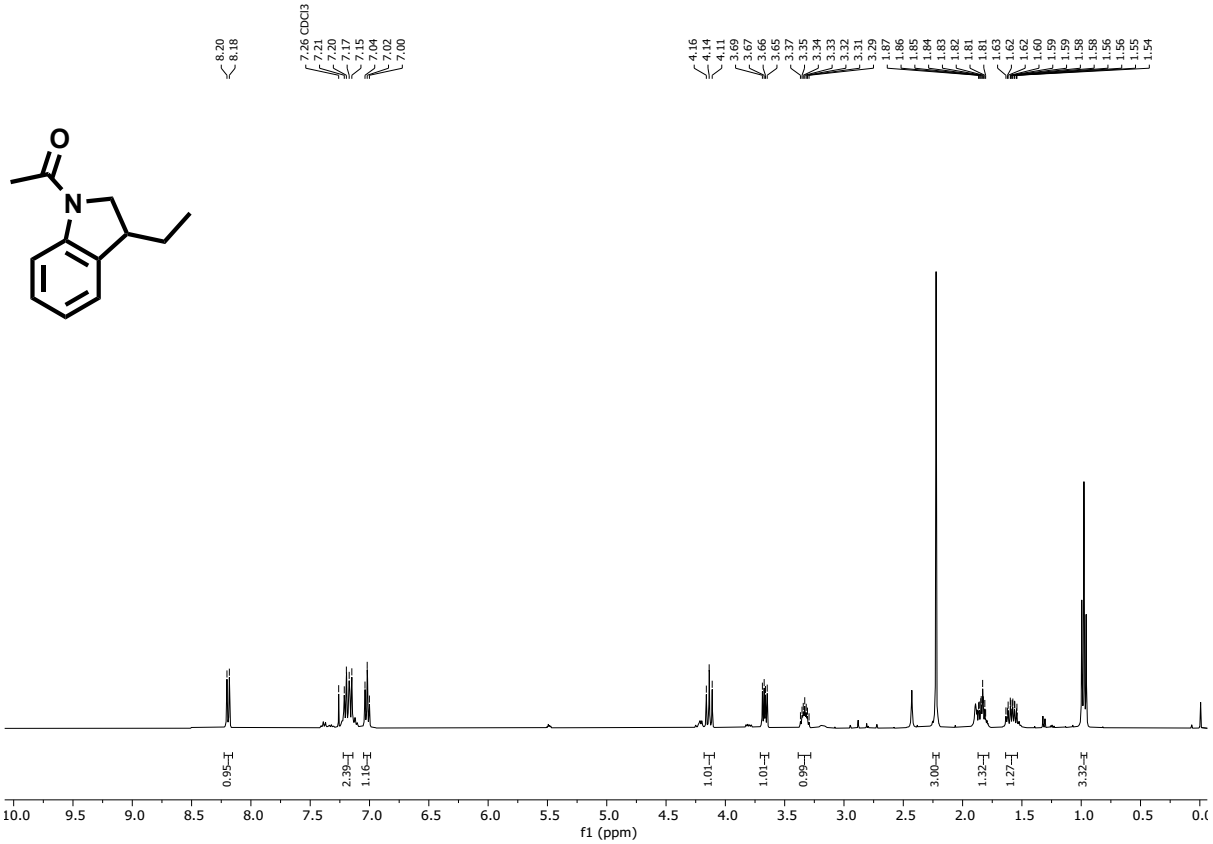
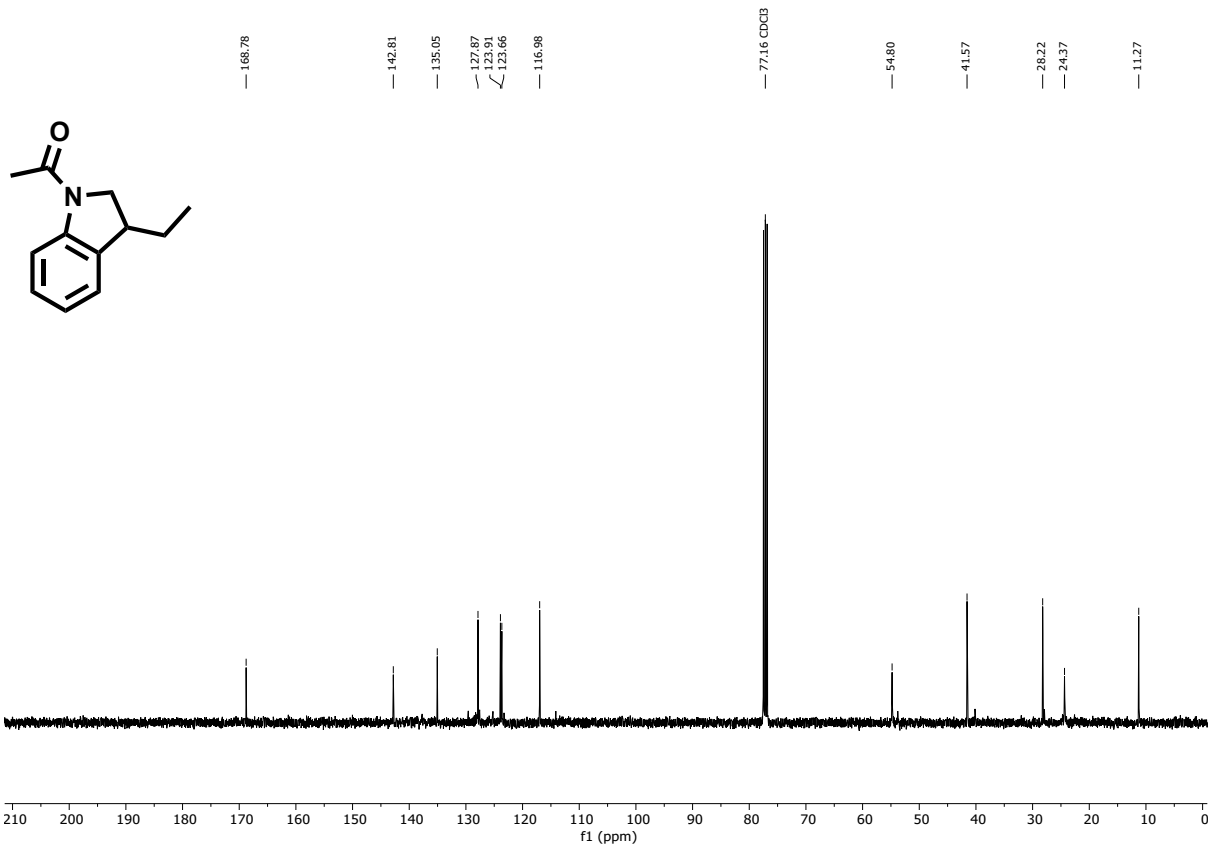
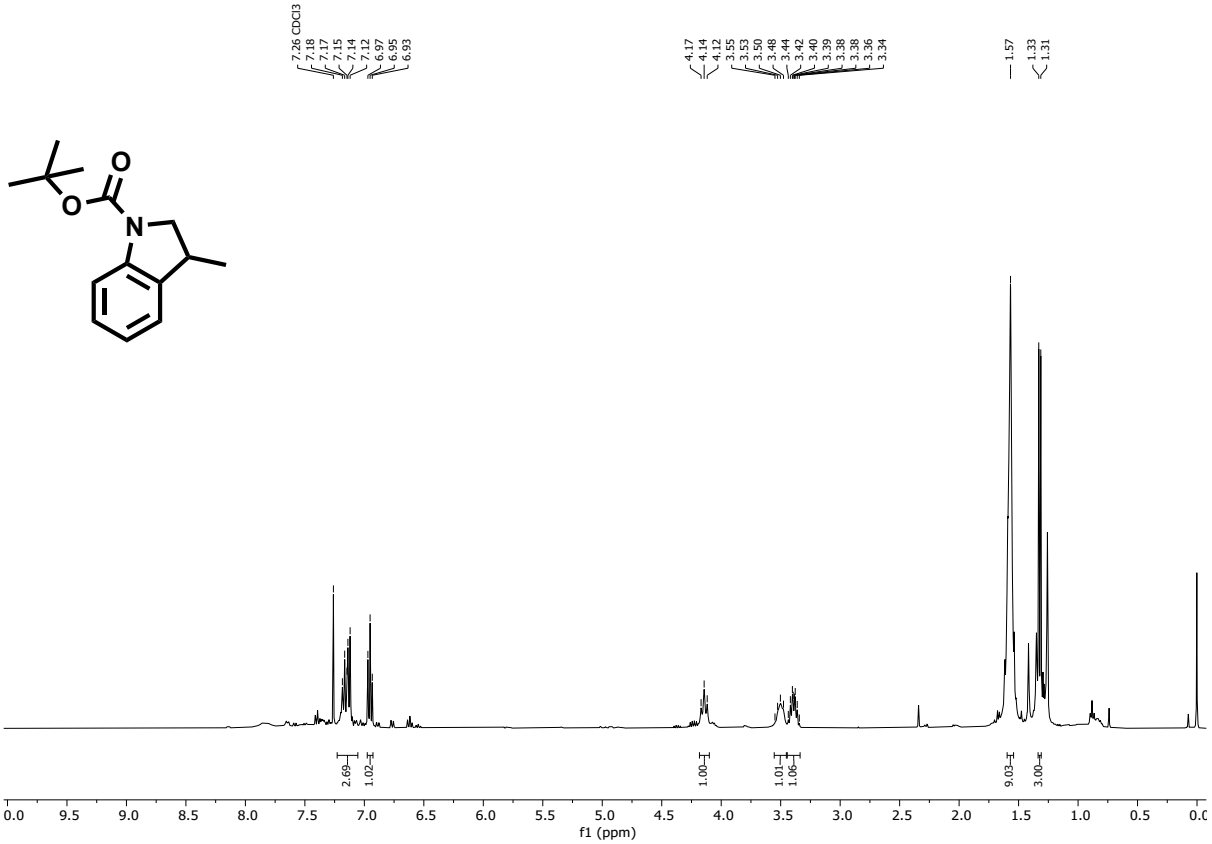


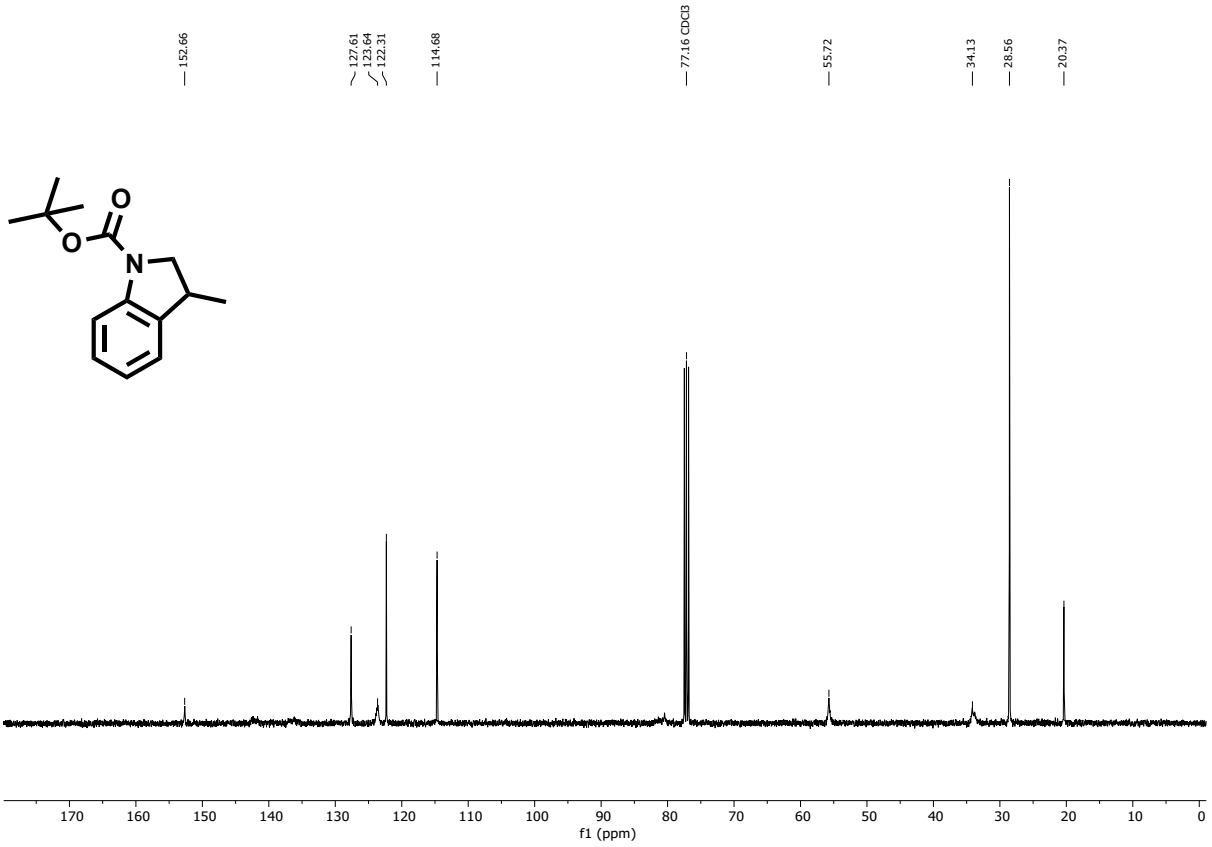
^{1}H NMR spectrum of **4k** recorded in $CDCl_3$.



^{13}C NMR spectrum of **4k** recorded in $CDCl_3$.



^{1}H NMR spectrum of **4l** recorded in $CDCl_3$.



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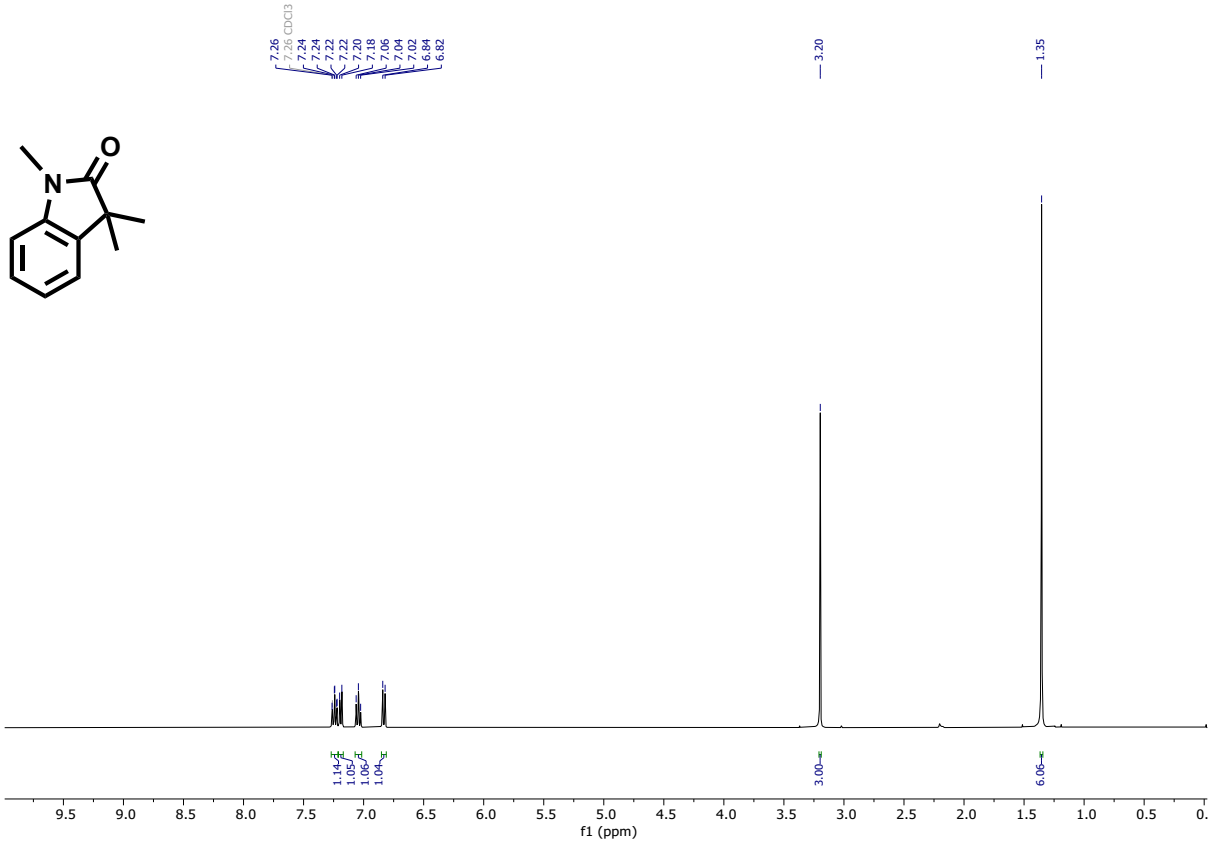
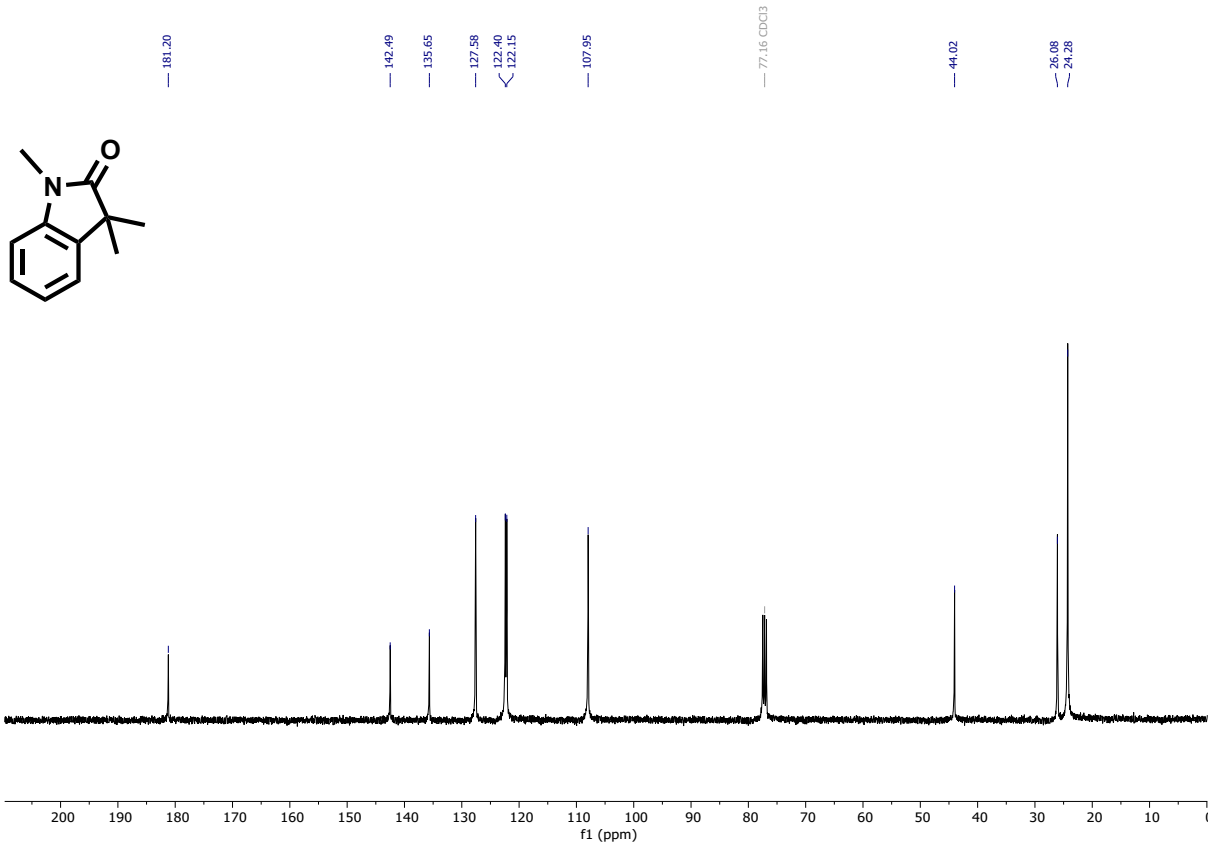
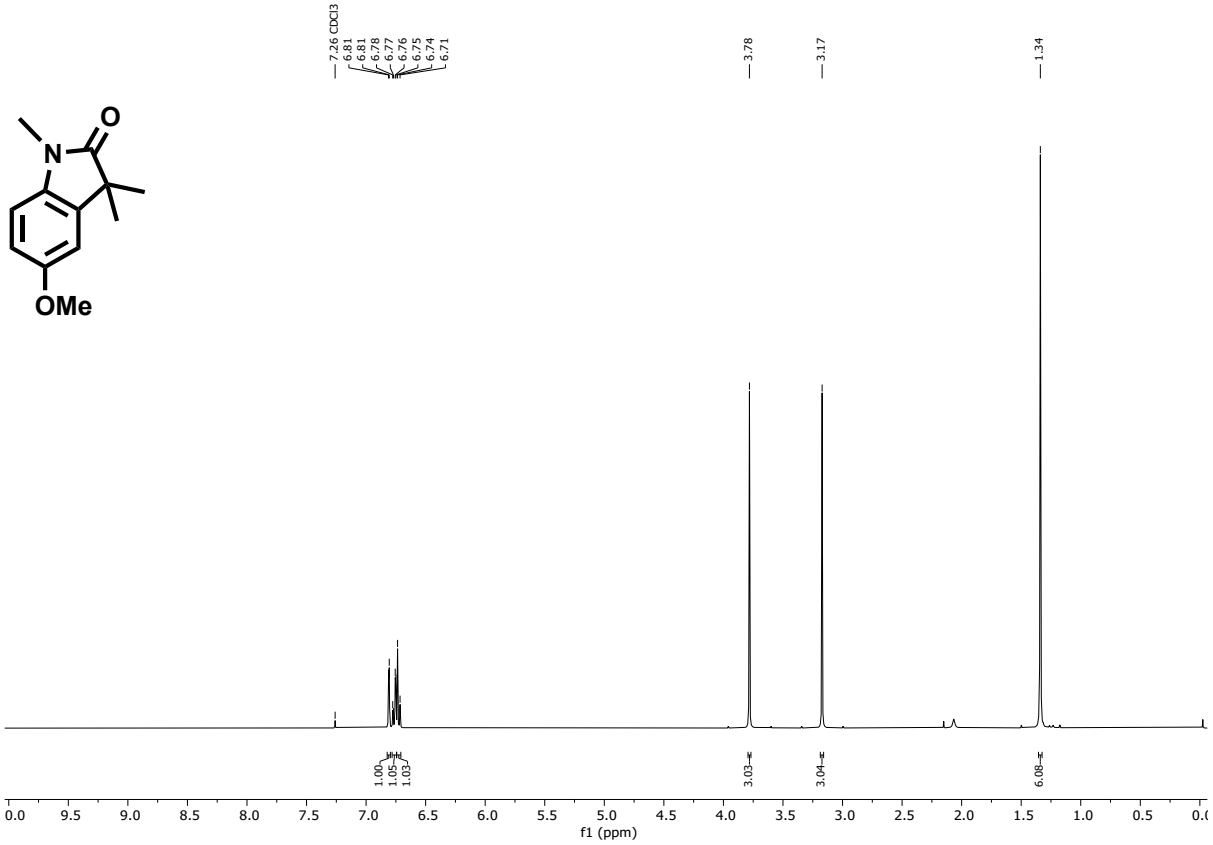


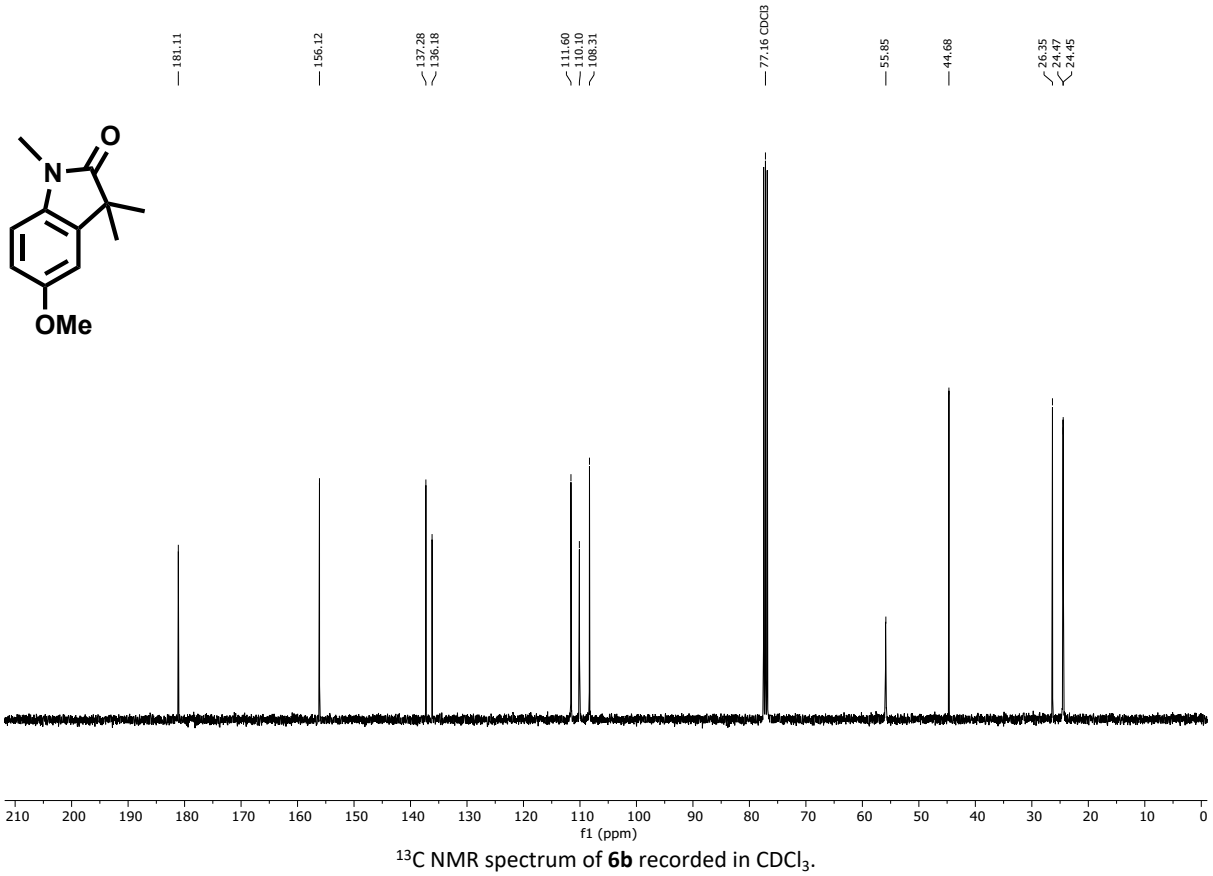
^{1}H NMR spectrum of **6a** recorded in $CDCl_3$.



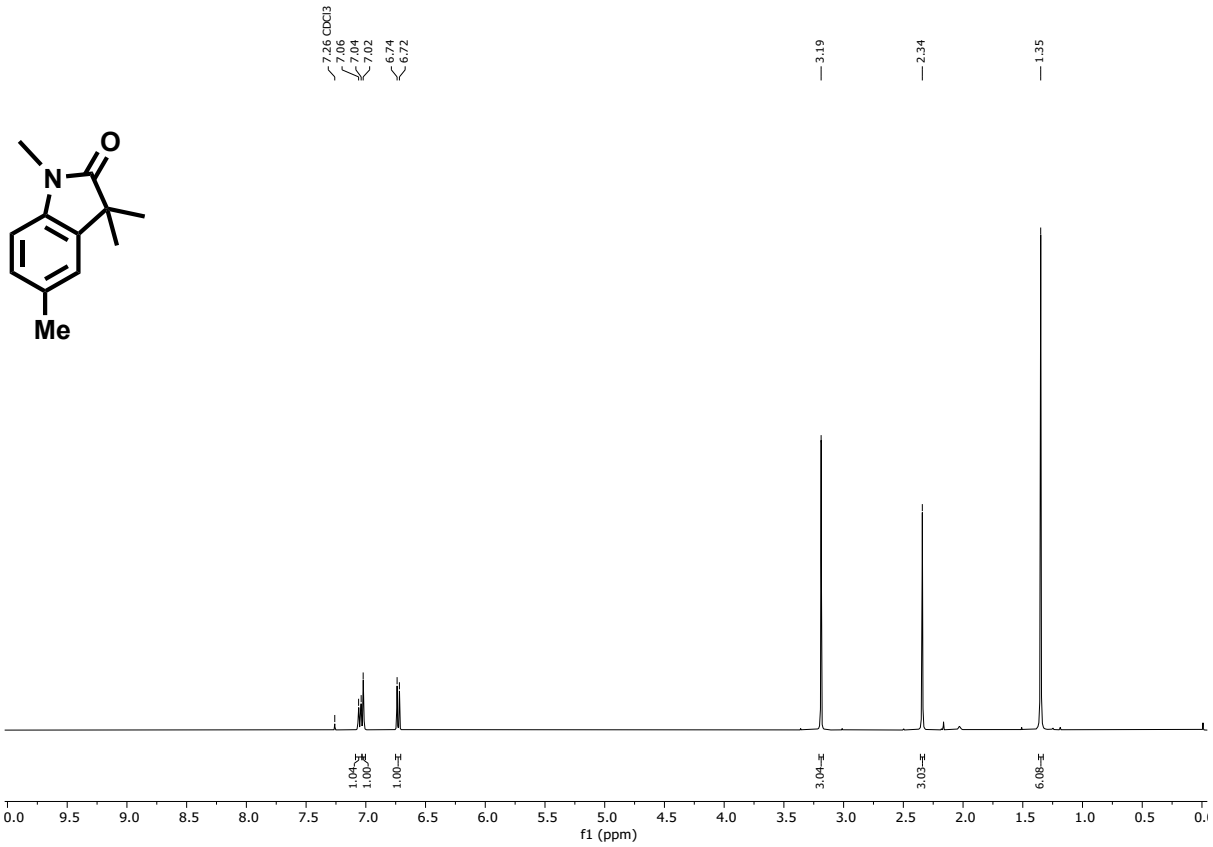
^{13}C NMR spectrum of **6a** recorded in $CDCl_3$.



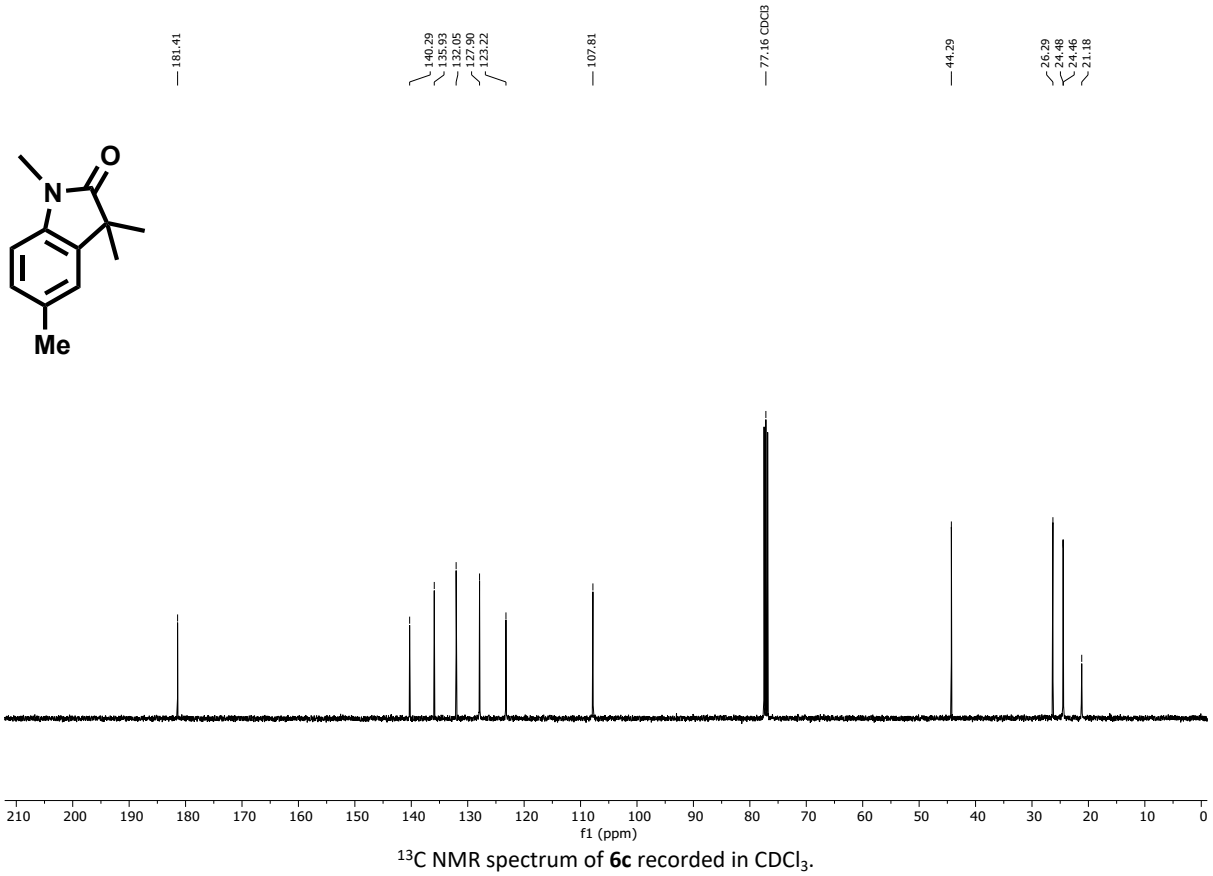
^{1}H NMR spectrum of **6b** recorded in $CDCl_3$.



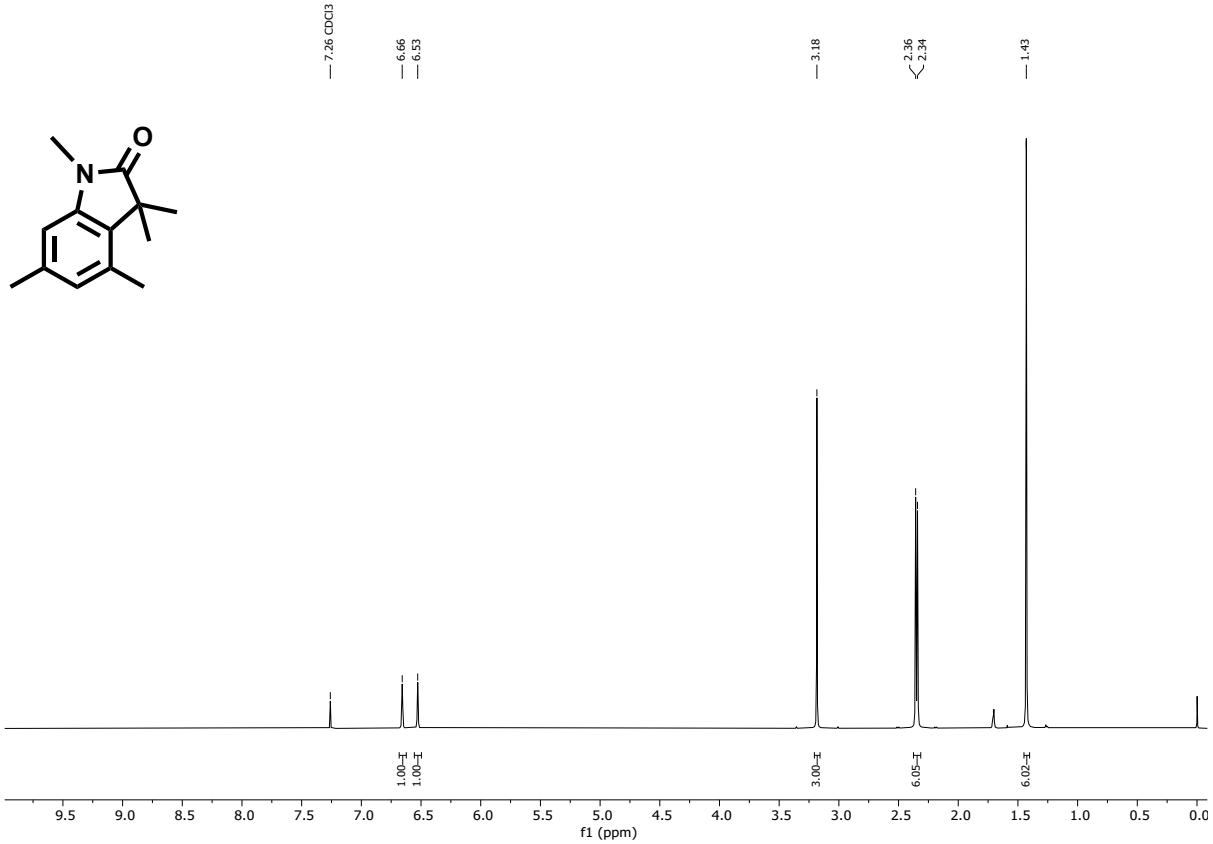
^{13}C NMR spectrum of **6b** recorded in $CDCl_3$.



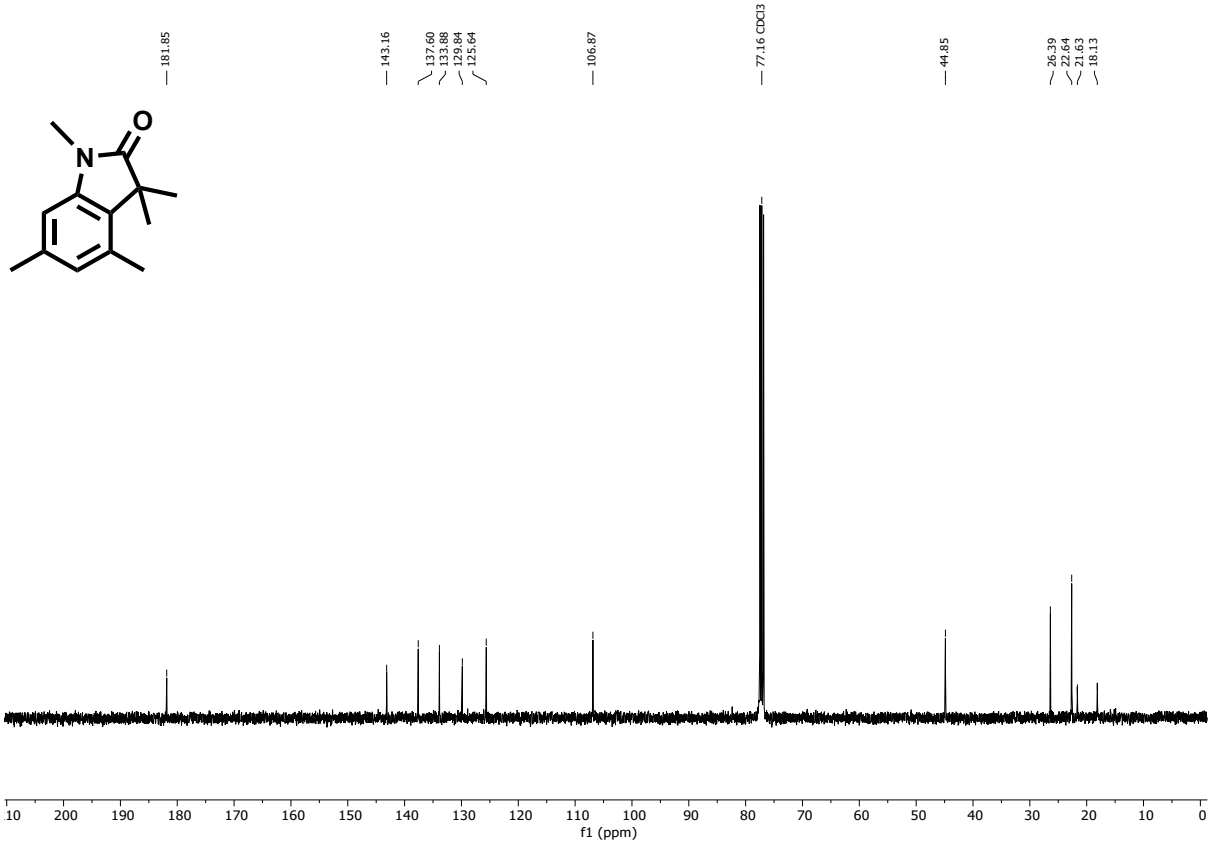
^{1}H NMR spectrum of **6c** recorded in $CDCl_3$.



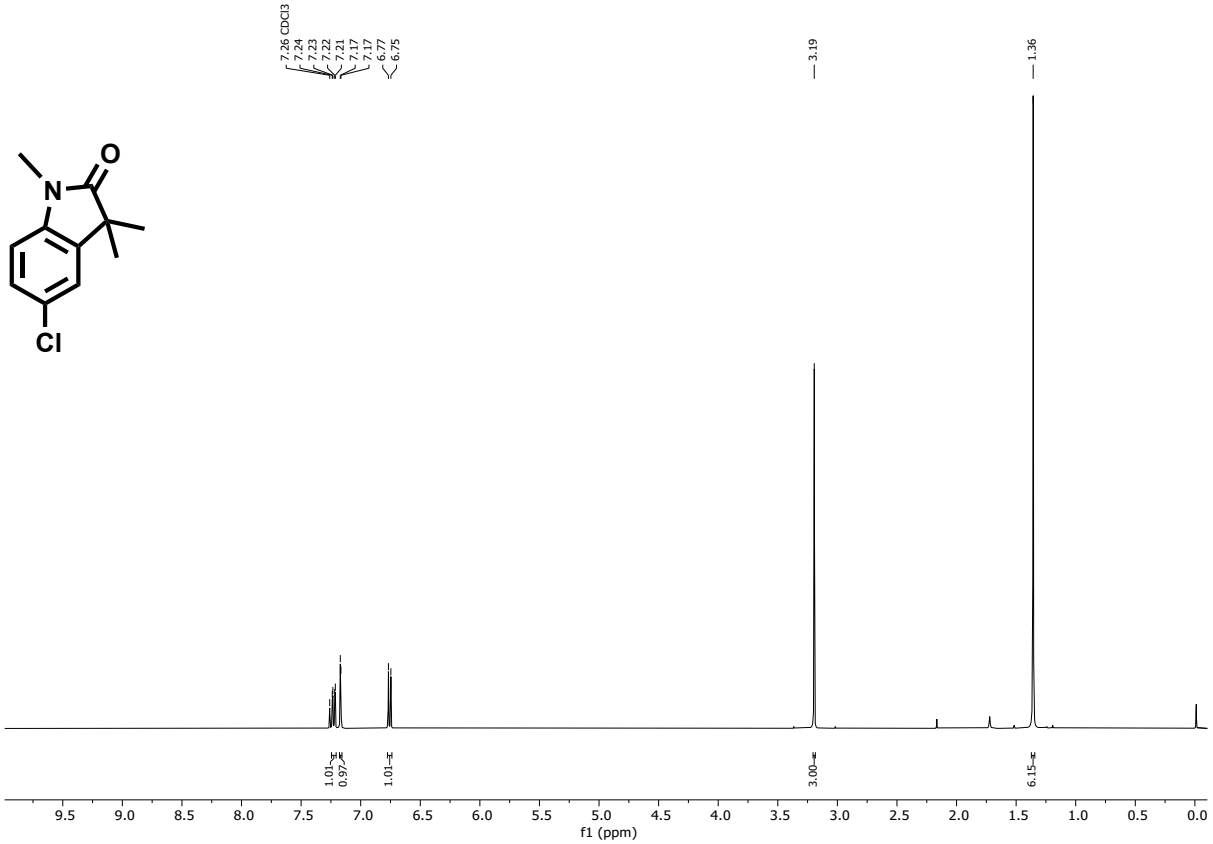
^{13}C NMR spectrum of **6c** recorded in $CDCl_3$.



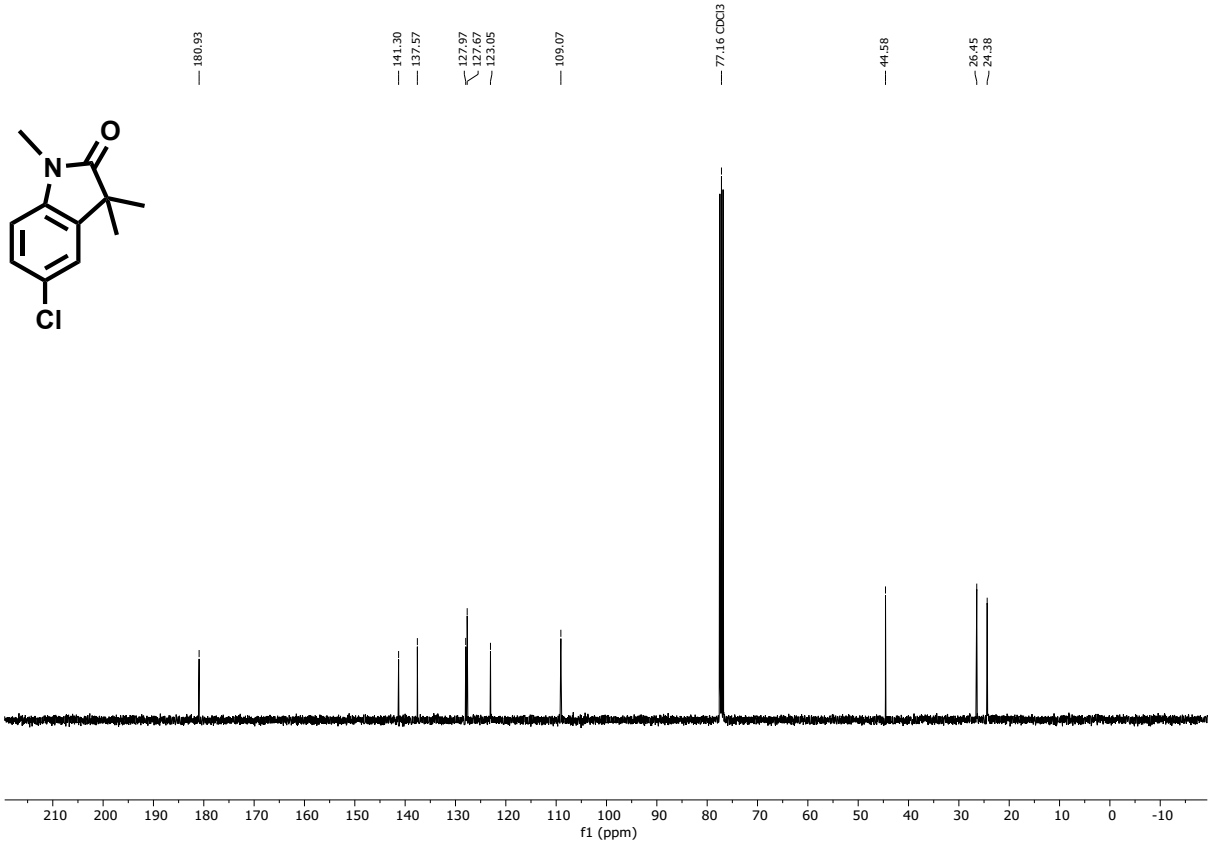
^{1}H NMR spectrum of **6d** recorded in $CDCl_3$.



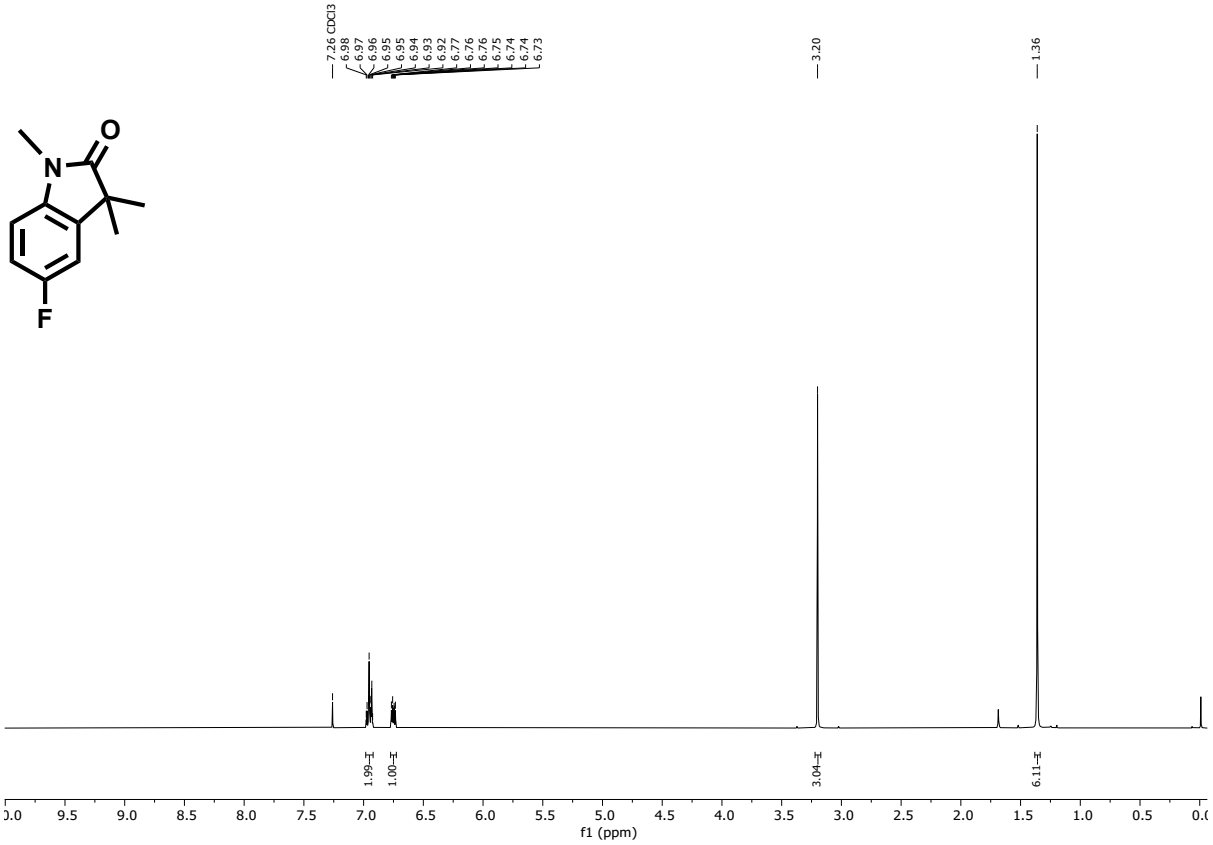
^{13}C NMR spectrum of **6d** recorded in $CDCl_3$.



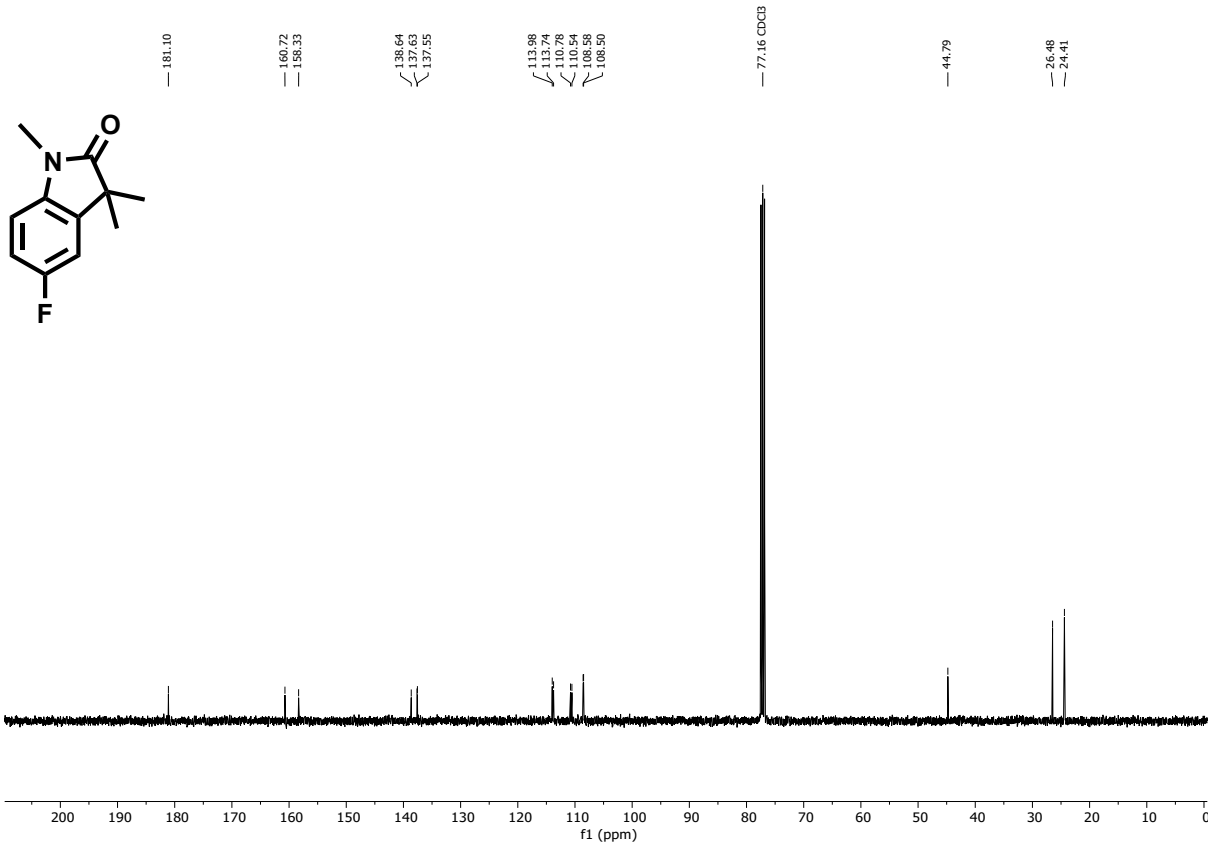
^{1}H NMR spectrum of **6e** recorded in $CDCl_3$.



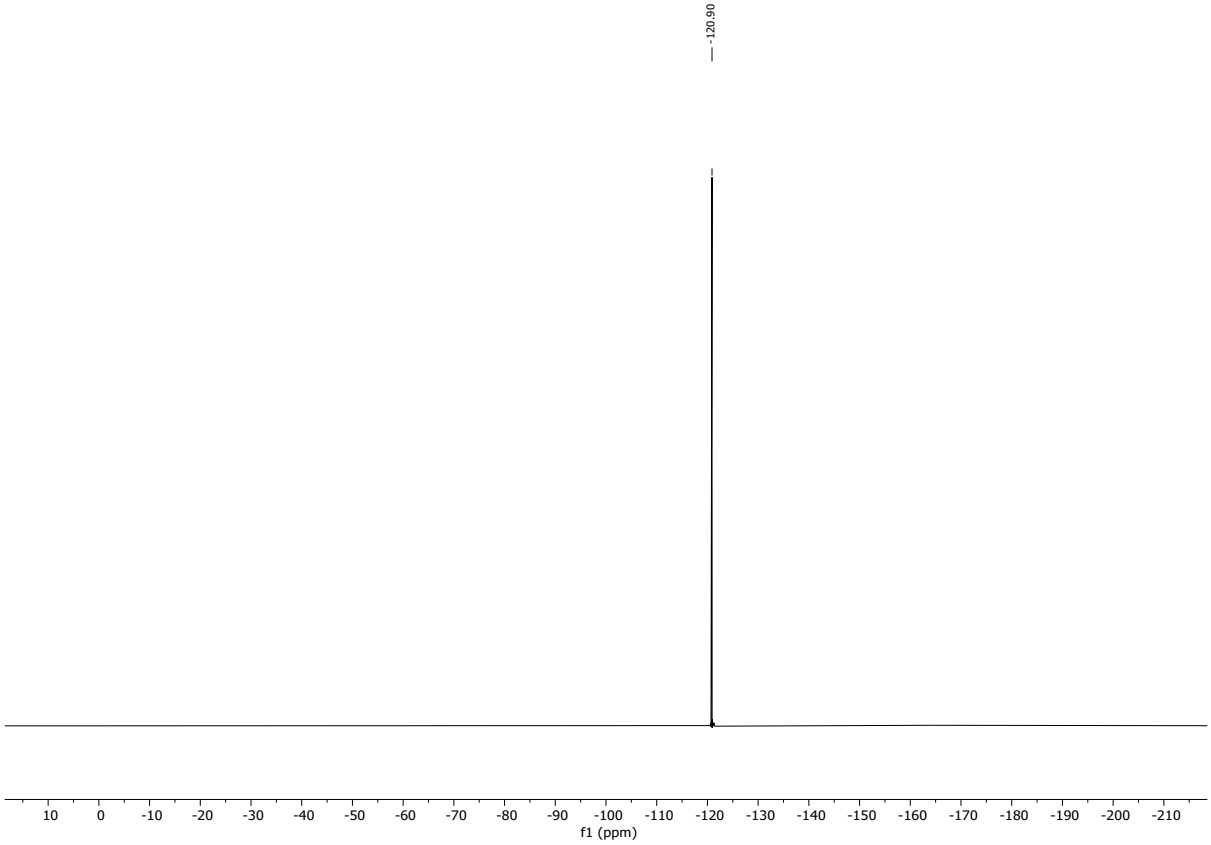
^{13}C NMR spectrum of **6e** recorded in $CDCl_3$.



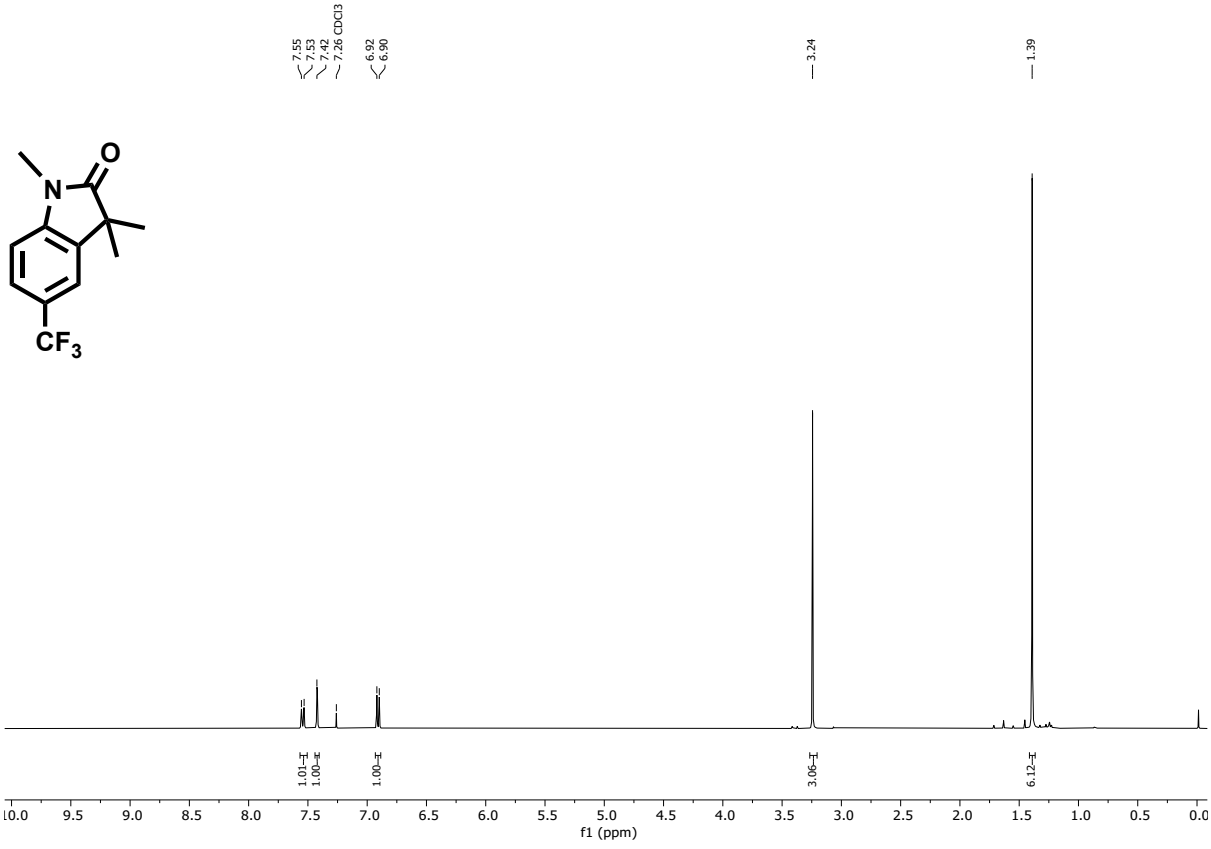
^{1}H NMR spectrum of **6f** recorded in $CDCl_3$.



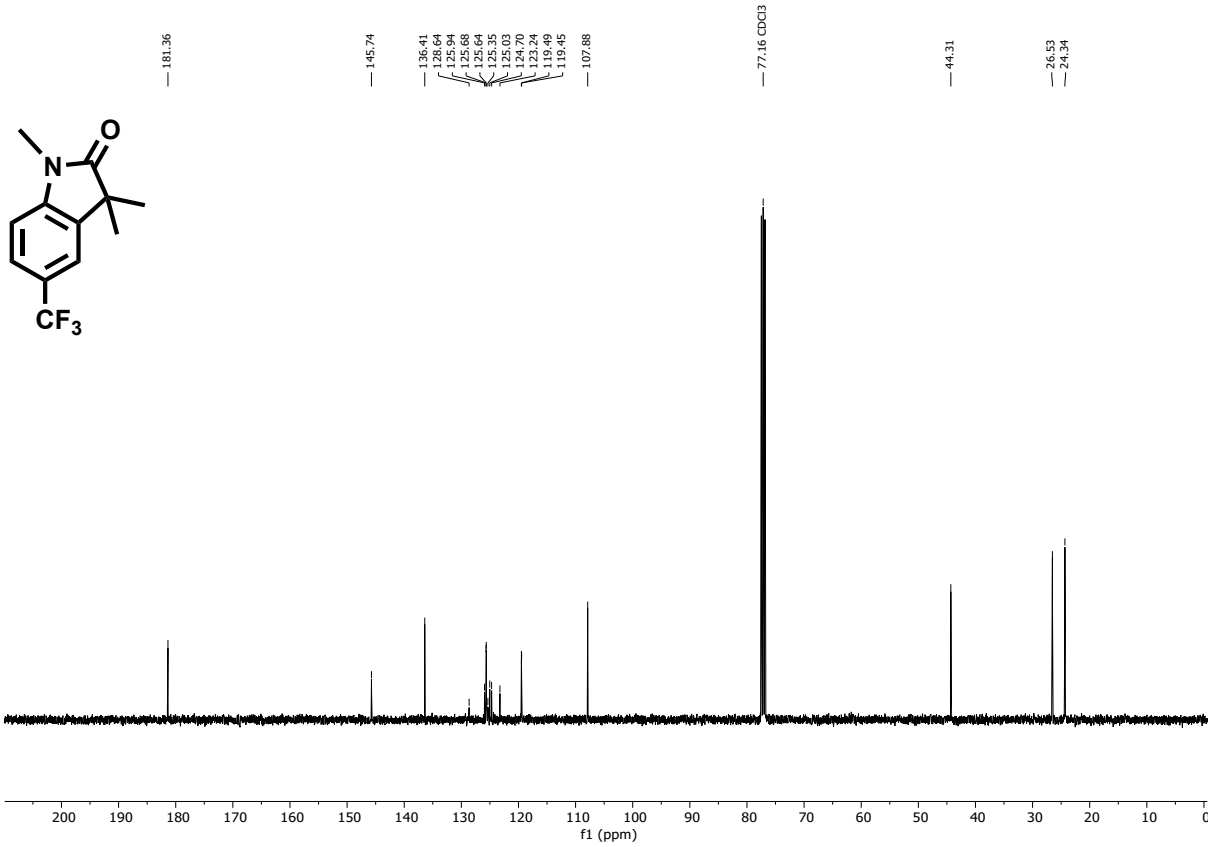
^{13}C NMR spectrum of **6f** recorded in $CDCl_3$.



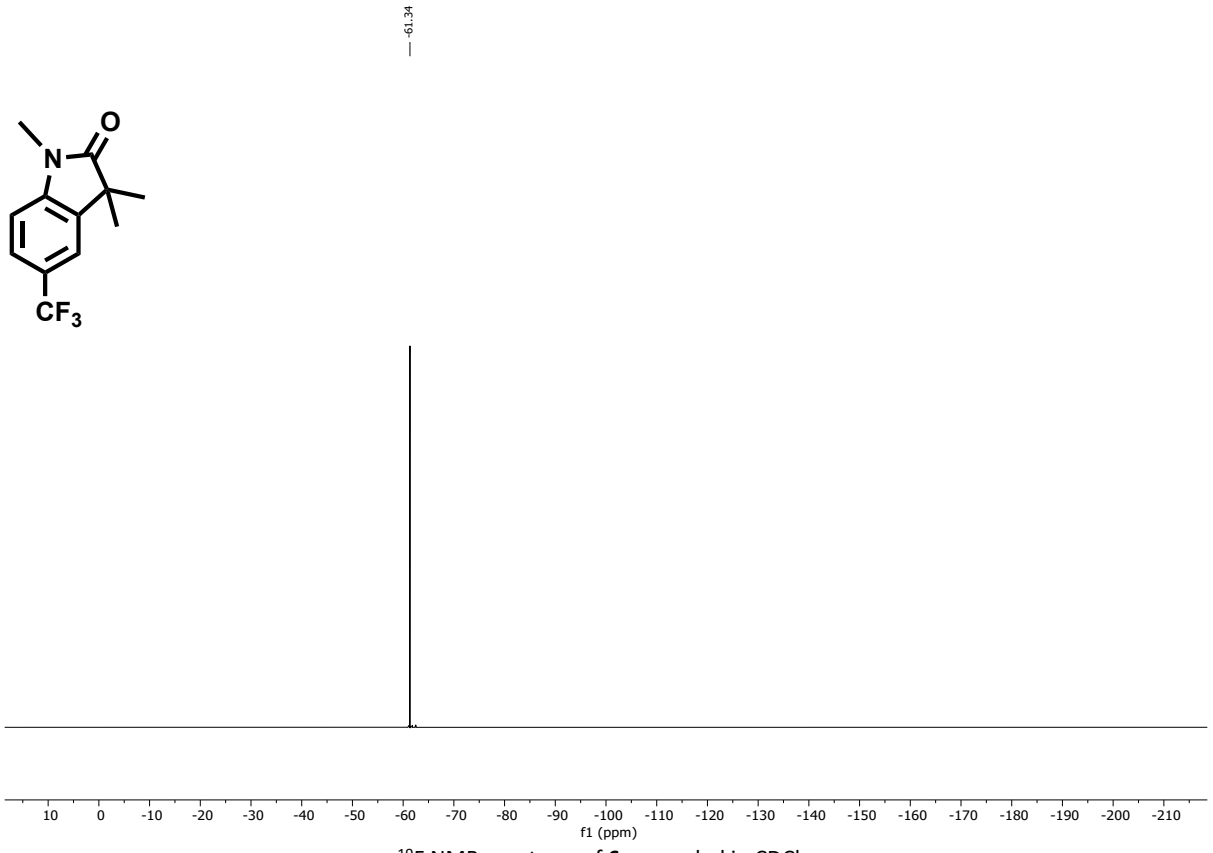
^{19}F NMR spectrum of **6f** recorded in $CDCl_3$.



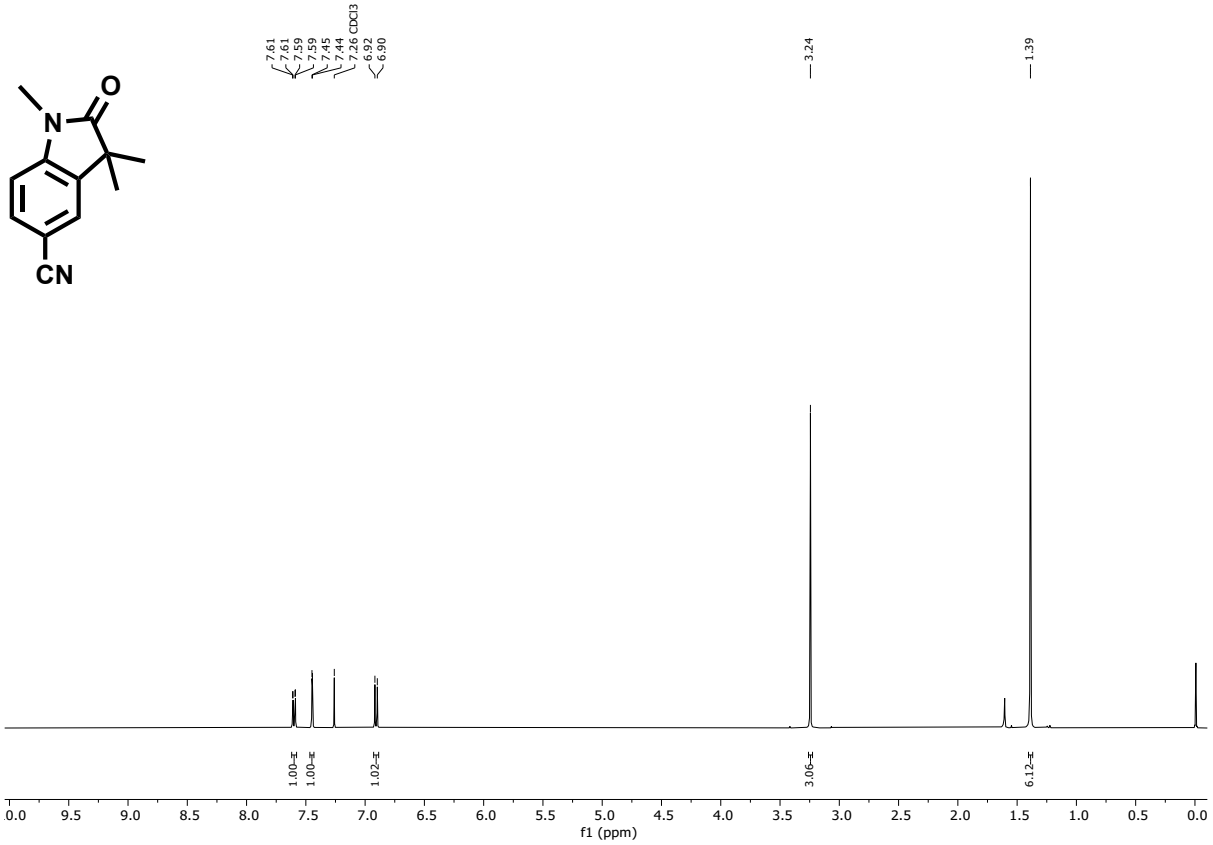
^{1}H NMR spectrum of **6g** recorded in $CDCl_3$.



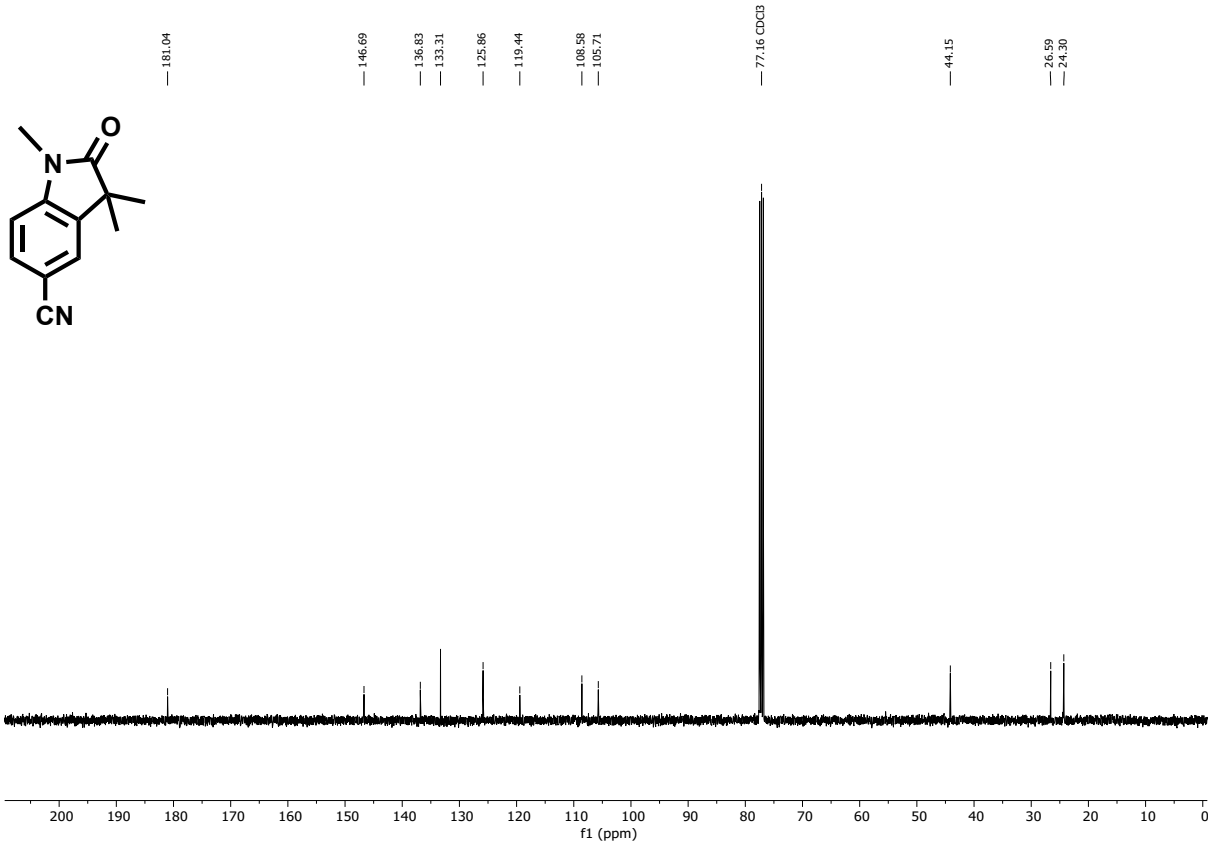
^{13}C NMR spectrum of **6g** recorded in $CDCl_3$.



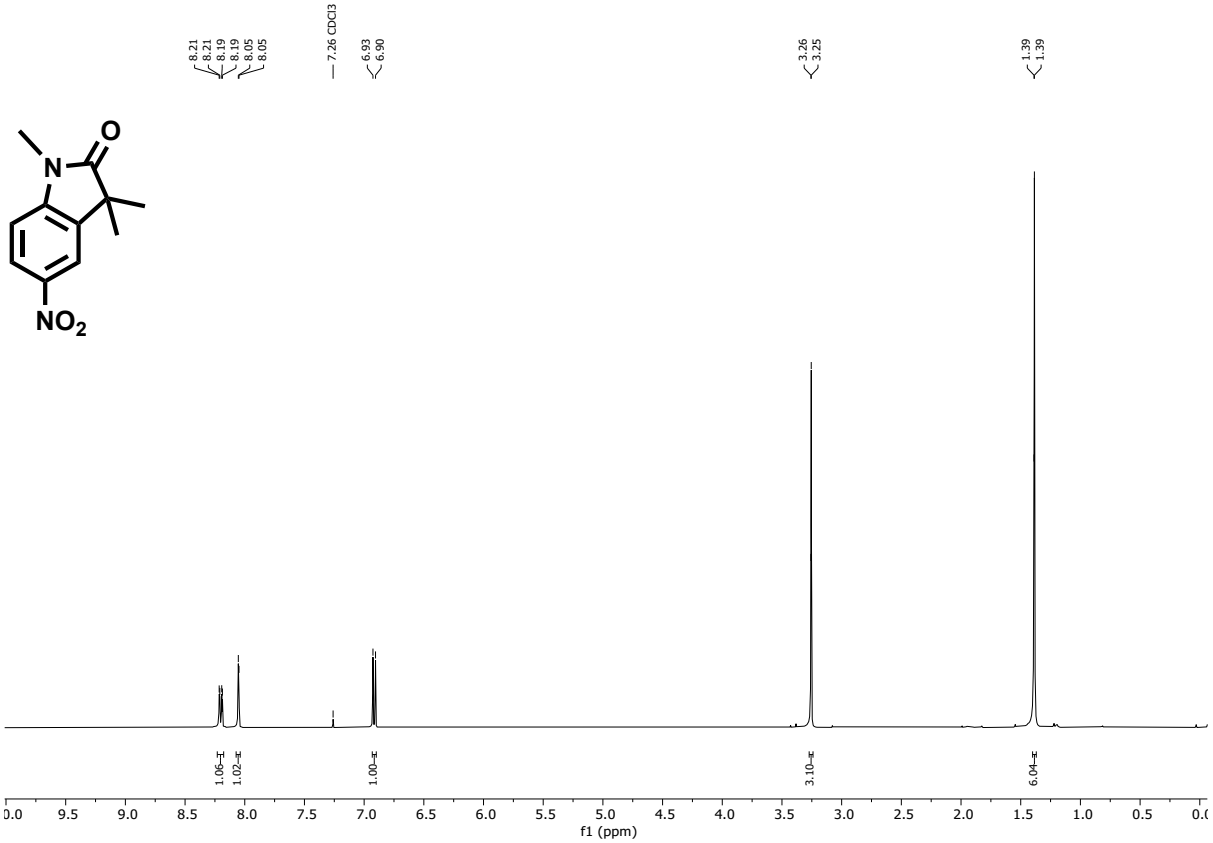
^{19}F NMR spectrum of **6g** recorded in $CDCl_3$.



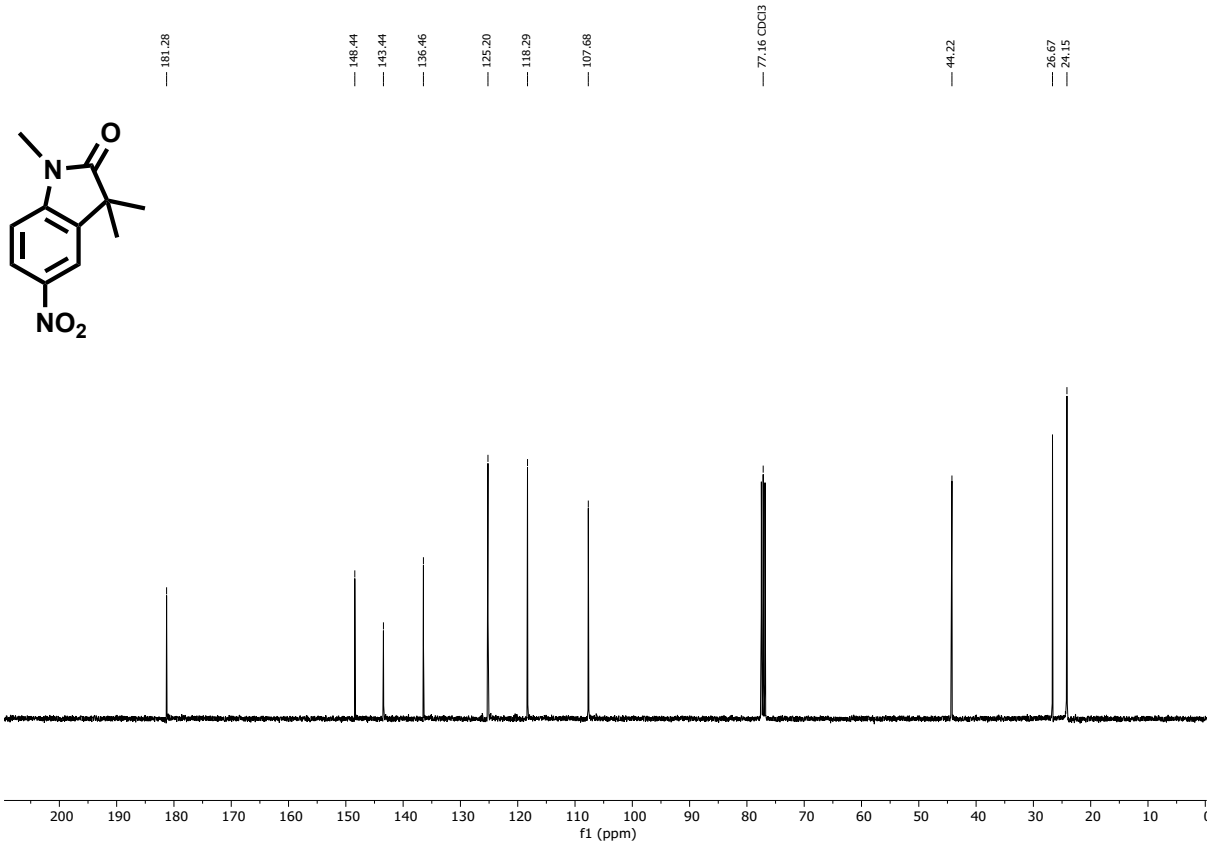
^{1}H NMR spectrum of **6h** recorded in $CDCl_3$.



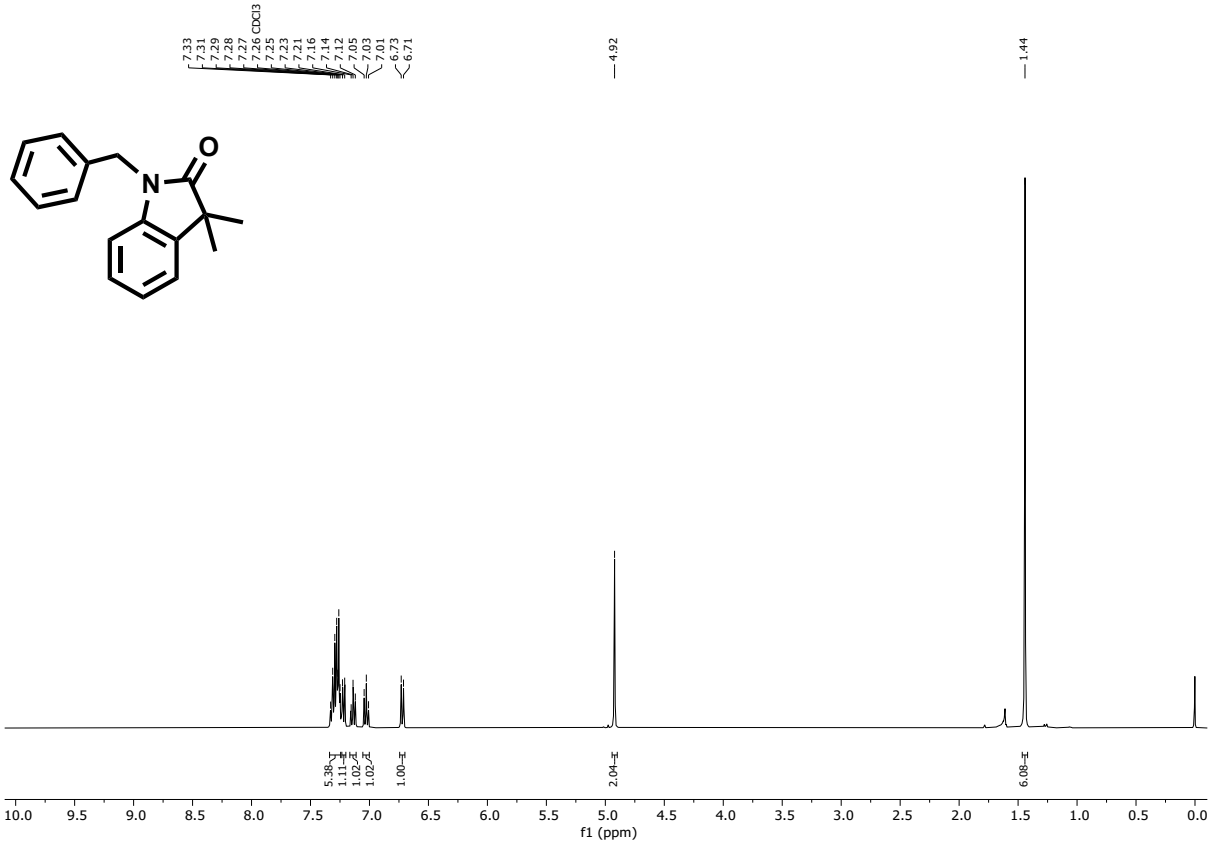
^{13}C NMR spectrum of **6h** recorded in $CDCl_3$.



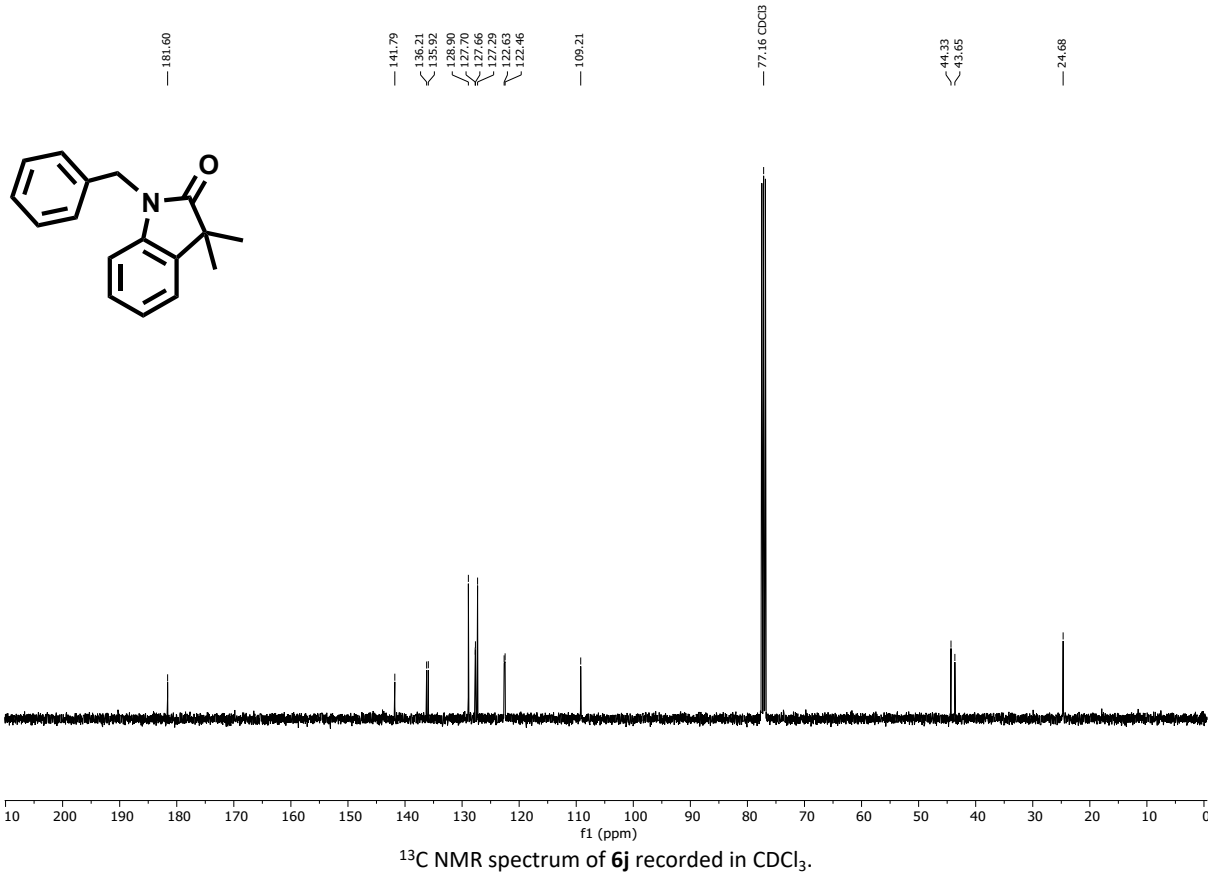
^{1}H NMR spectrum of **6i** recorded in $CDCl_3$.



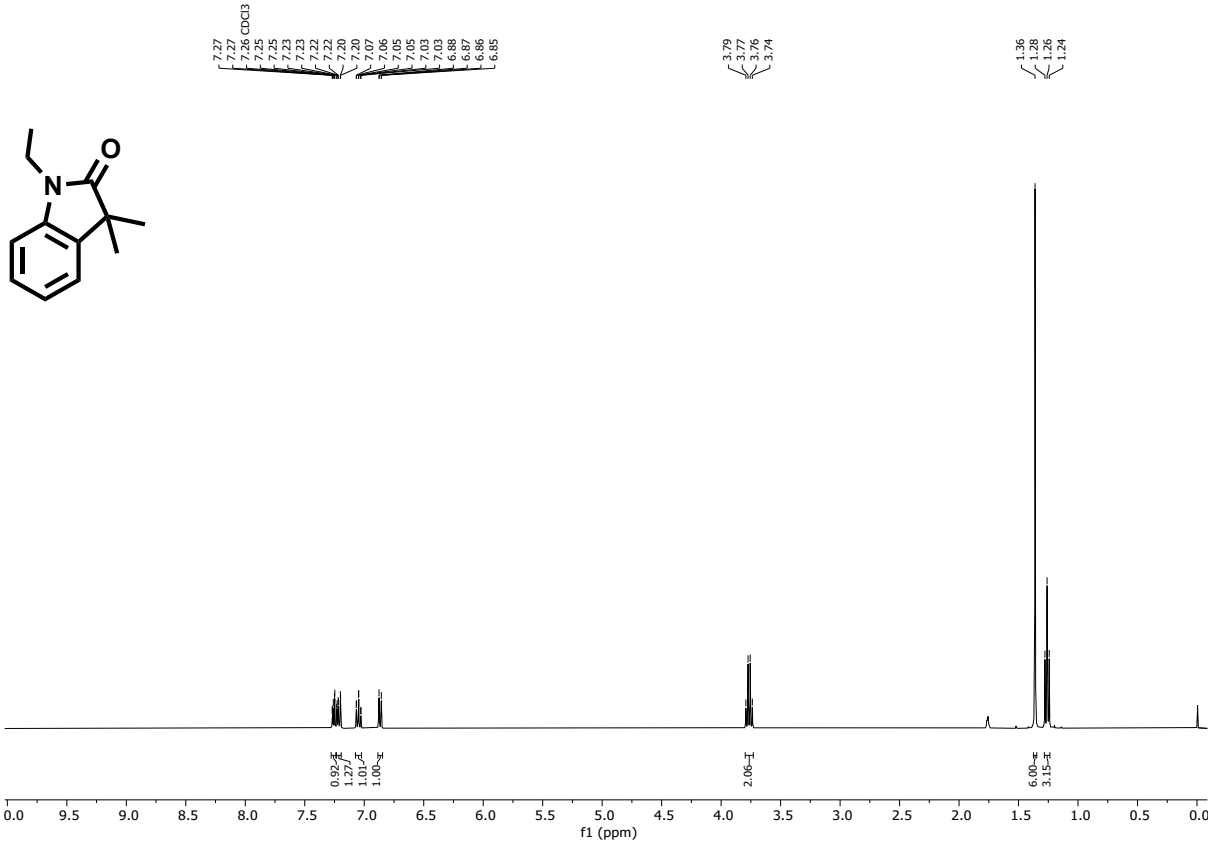
^{13}C NMR spectrum of **6i** recorded in $CDCl_3$.



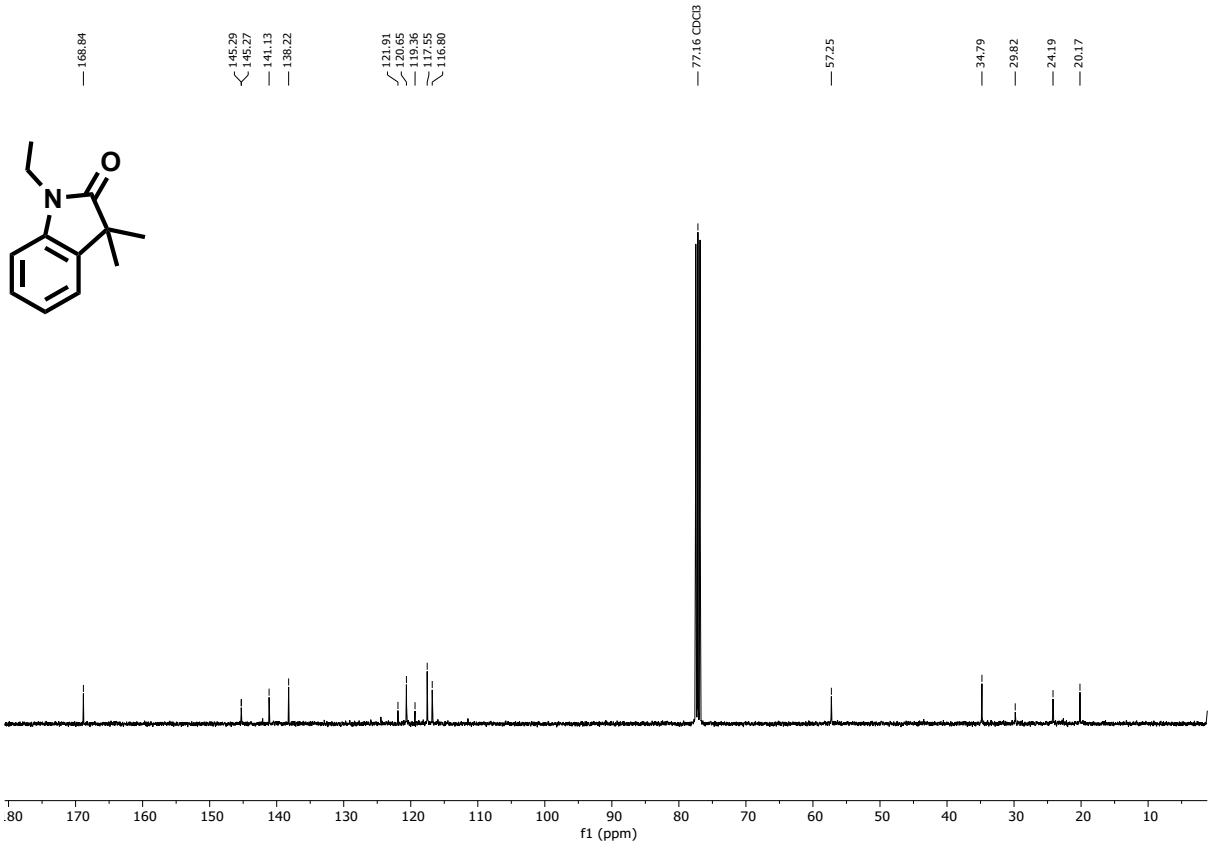
^{1}H NMR spectrum of **6j** recorded in $CDCl_3$.



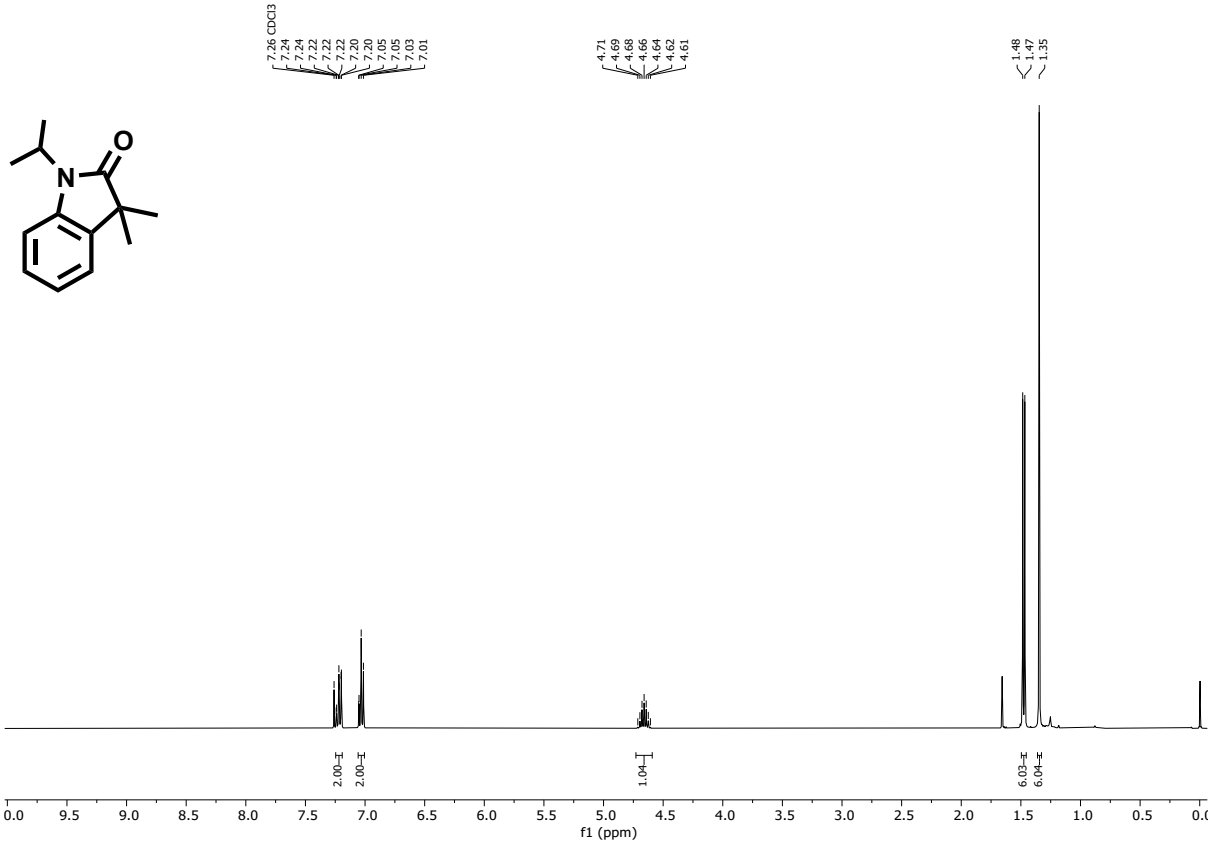
^{13}C NMR spectrum of **6j** recorded in $CDCl_3$.



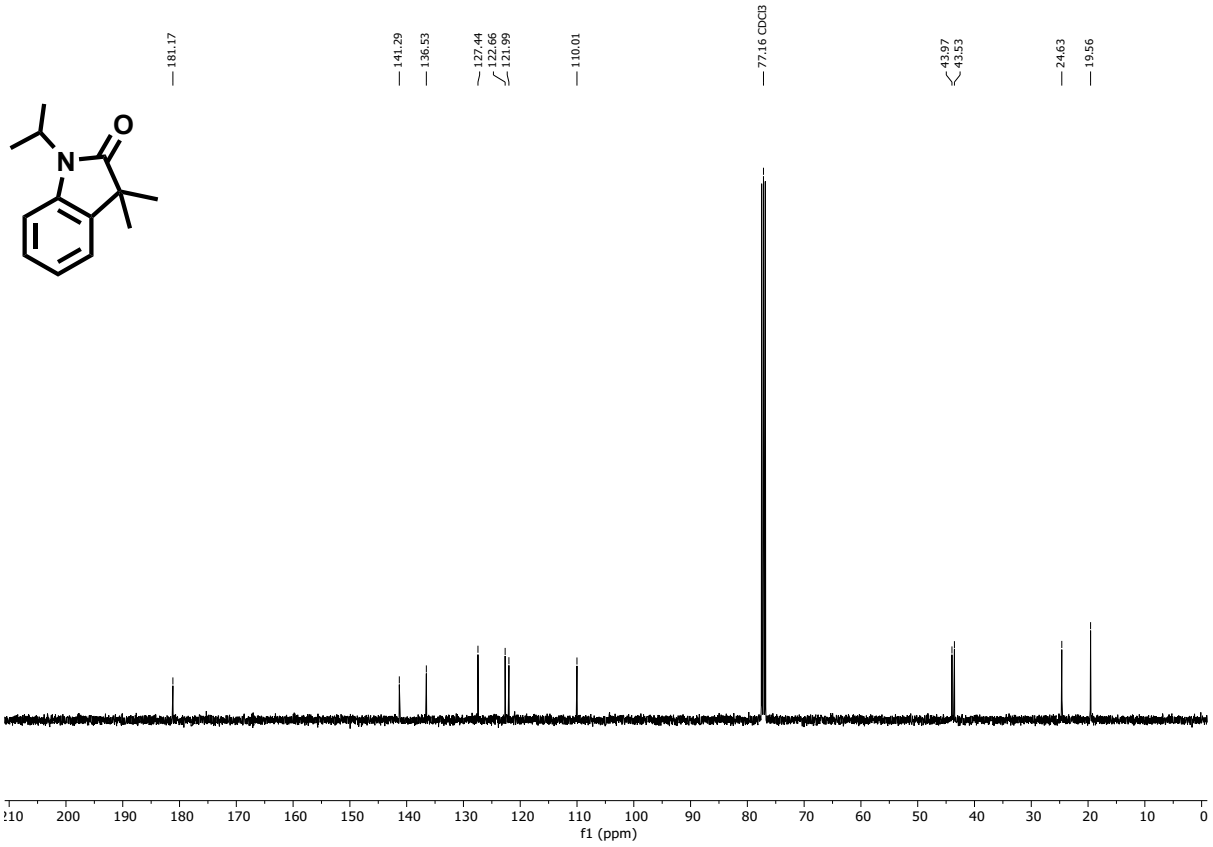
^{1}H NMR spectrum of **6k** recorded in $CDCl_3$.



^{13}C NMR spectrum of **6k** recorded in $CDCl_3$.



^{1}H NMR spectrum of **6l** recorded in $CDCl_3$.



^{13}C NMR spectrum of **6l** recorded in $CDCl_3$.

9. References

1. R. F. Munhá, R. A. Zarkesh and A. F. Heyduk, *Inorg. Chem.*, 2013, **52**, 11244 -11255.
2. C. A. D. Caiuby, A. Ali, V. T. Santana, F. W. S. De Lucas, M. S. Santos, A. G. Corrêa, O. R. Nascimento, H. Jiang and M. W. Paixão, *RSC Adv.*, 2018, **8**, 12879 -12886.
3. M. Cao, H. Wang, Y. Ma, C.-H. Tung, L. Liu, *J. Am. Chem. Soc.* 2022, **144**, 15383-15390.
4. B. Michelet, C. Deldaele , S. Kajouj , C. Moucheron and G. Evano , *Org. Lett.*, 2017, **19** , 3576 -3579.
5. S. Wu, Q. Zhao, C. Wu, C. Wang, H. Lei, *Org. Chem. Front.* 2022, **9**, 2593–2599.
6. V. Singh, R. Singh, A. S. Hazari, D. Adhikari, *JACS Au* 2023, **3**, 1213– 1220.
7. Y. Z. Ren, C. Z. Fang, B. B. Zhang, L. He, Y. L. Tu, X. Y. Chen, *Org. Lett.* 2023, **25**, 3585– 3589.