Supporting Information

Photoinduced Halogen-Bonding Enabled Synthesis of Oxindoles and Isoindolinones from Aryl Iodides

Wen-Xin Tang, [†a] Kun-Quan Chen,[†b] De-Qun Sun*[a] and Xiang-Yu Chen*[b]

[a] School of Life Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, P. R. China. dqsun@swust.edu.cn,

[b] School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049 P. R. China. chenxiangyu20@ucas.ac.cn.

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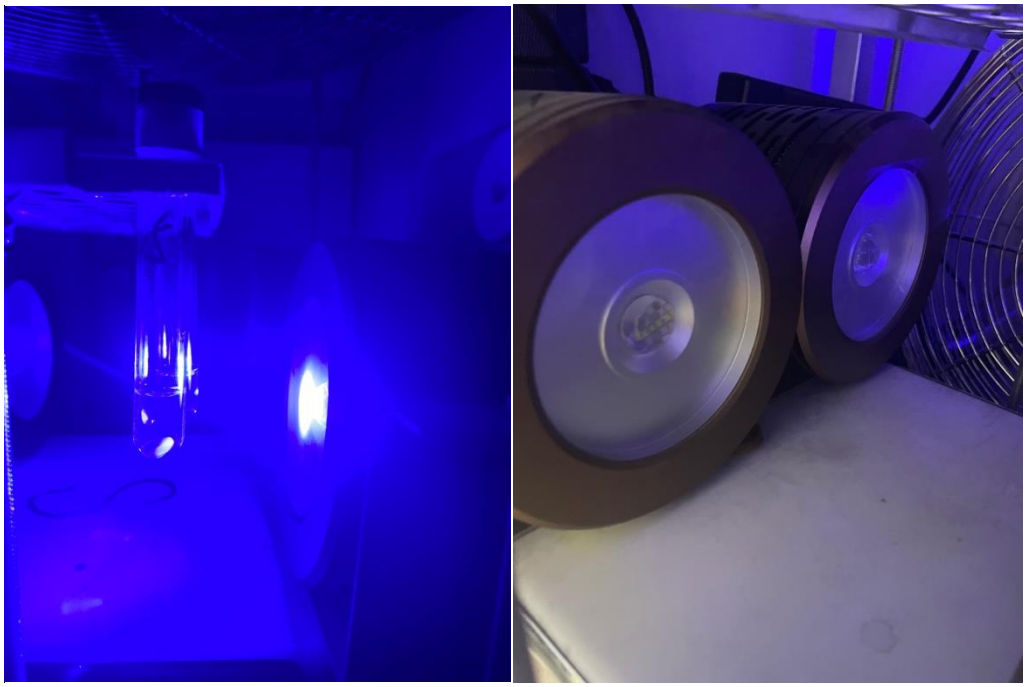
1. General Information

- Chemicals were purchased from Heowns, Innochem and Bidepharm, and they were used without further purification unless otherwise noted. The starting materials aryl iodides were readily prepared according to the related literatures.[1] Solvents were purified using a solvent-purification system (VSPS-8, Vigor).
- Chromatographic purification of the products was performed on 200-300 mesh silica gel.
- IR spectra were taken on a Vertex 70 spectrophotometer and reported as wave numbers (cm^{-1}).
- UV/vis absorption spectra were acquired on a UV-5 spectrophotometer (METTLER TOLEDO).
- The GC-MS TQ8040 was used in the detection of the reaction mixture.
- The SGW X-4 was used to measure the melting point of solids.
- HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. The mass analysis mode of the HRMS was orbitrap.
- **^{1}H-, ^{19}F-** and **^{13}C- NMR** spectra were recorded at ambient temperature on a Shimadzu Avance 400 Spectrometer and Shimadzu Avance 500 Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as the internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).
- Photochemical experiments were performed magnetically stirred in 10 mL glass tubes, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm) using a LED lamp (kelo-A0100s blue LED). The distance from the light source to the irradiation vessel was 2 cm and a fan was used to keep the reaction temperature at 50 ± 5 °C. （The purchase link for LED lamp is https://item.jd.com/52714507033.html）



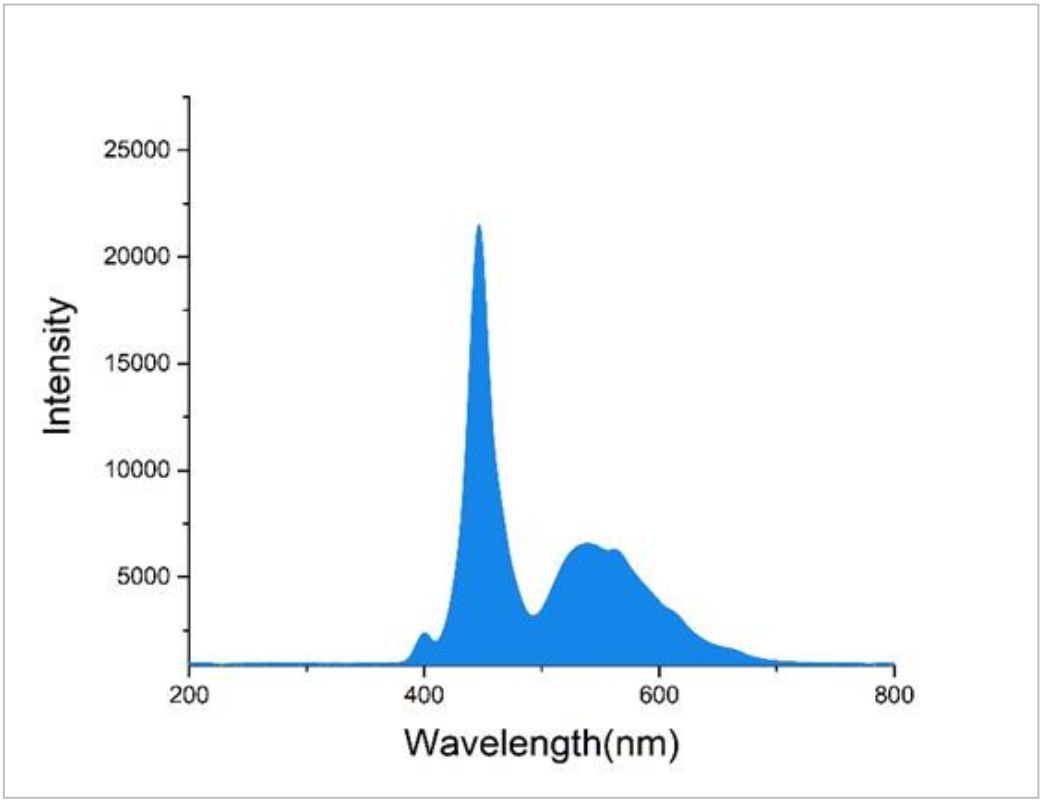
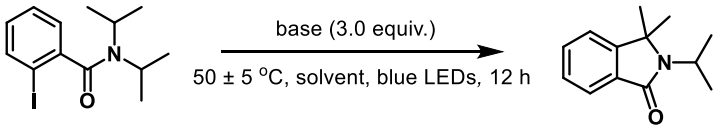


Figure S1. The spectra of blue LEDs employed in the reaction.

2. Experimental Procedures

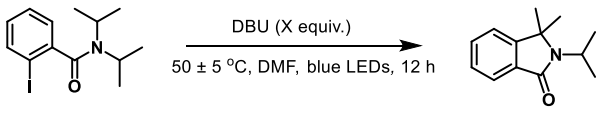
Scheme S1. Optimization of the reaction conditions.



Entry	Base	Solvent	Yield/%[a]
1	DBU	DMF	88
2	DBU	THF	85
3	DBU	MeCN	75
4	DBU	DMA	81
5	DBU	Et_2O	31
6	DBU	toluene	17
7	DBU	acetone	trace
8	DBU	DCE	28
9	TMEDA	DMF	trace
10	DIPEA	DMF	20
11	NEt_3	DMF	trace
12	DABCO	DMF	trace
13	K_2CO_3	DMF	trace
14	Na_2CO_3	DMF	trace
15	Cs_2CO_3	DMF	trace
16	K_3PO_4	DMF	trace
17	K_2HPO_4	DMF	trace
18	None	DMF	NR
19[b]	DBU/Cs_2CO_3	DMF	79
20	1,2-diphenyldisulfane	DMF	trace
21	triphenylphosphine	DMF	trace
22	triphenylphosphine oxide	DMF	trace
23	sodium benzenethiolate	DMF	74

[a] *Yield of isolated product.* [b] *0.2 equiv. of DBU and 3 equiv. of Cs_2CO_3 were added.*

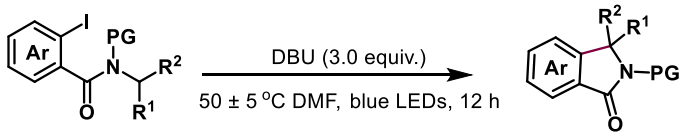
Scheme S2. Controlled experiments



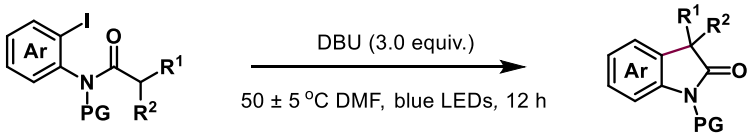
Entry	X equiv.	Yield/%[a]
1	0	NR
2	0.2	trace
3	1.5	61
4	2.0	76

[a] Yield of isolated product.

3. General Procedures



General procedure A: In a nitrogen atmosphere, to a dry tube equipped with a stirring bar, the 2-iodo-benzamide derivates (0.2 mmol， 66.2 mg), DBU (0.6 mmol, 69.6 mg, 90.3 uL) and DMF (2.0 mL) were added, the mixture was stirred under a 100 W blue LED (450 nm) lamp with an interval of 2 cm from the lamp and a fan was used to keep the reaction temperature at 50 ± 5 °C. After 12 hours, the reaction mixture was subjected to silica gel chromatography to afford the desired product (PE/EA = 10:1 – 30:1).



General procedure B: In a nitrogen atmosphere, to a dry tube equipped with a stirring bar, the *o*-iodoaniline derivates (0.2 mmol, 66.2 mg), DBU (0.6 mmol, 69.6 mg, 90.3 uL) and DMF (2.0 mL) were added, the mixture was stirred under a 100 W blue LED (450 nm) lamp with an interval of 2 cm from the lamp and a fan was used to keep the reaction temperature at 50 ± 5 °C. After 12 hours, the reaction mixture was subjected to silica gel chromatography to afford the desired product (PE/EA = 10:1 – 30:1).

4. Mechanism Studies

4.1 UV/Vis absorption spectrometry

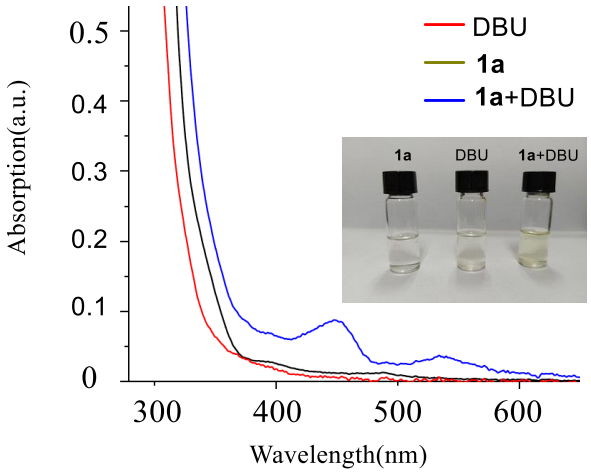


Figure S2: Absorption spectra of substrate **1a**, DBU and their mixture. The UV/vis spectra of *N*-(2-iodophenyl)-*N*-isopropylisobutyramide **1a** (0.1 M in DMF), DBU (0.3 M in DMF).

4.2 Control experiments

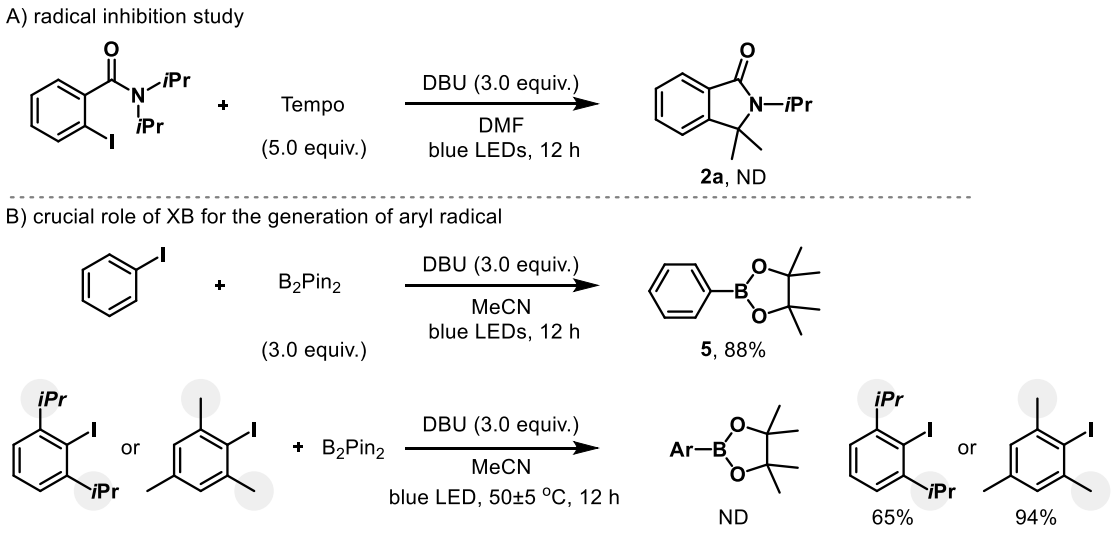
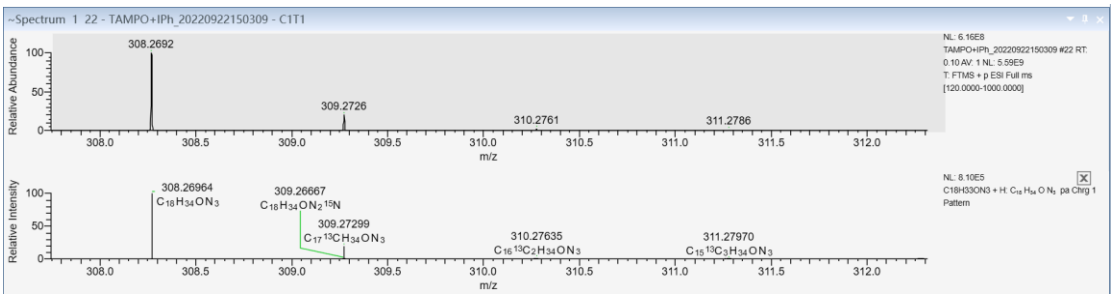


Figure S3. A) radical inhibition study; B) control experiment.

In a nitrogen-filled glove box, a 10-mL vial equipped with a magnetic stirring bar was charged the 2-iodo-benzamide (0.2 mmol, 1.0 equiv.), TEMPO (1.0 mmol, 5.0 equiv.) and DMF (2.0 mL). The vial was closed and removed from the glove box. The resulting mixture was allowed to stir at 50 ± 5 ℃under blue LED (100 W) irradiation for overnight. The trapped radical species was detected by HRMS (Figure S3A).

HRMS (ESI): m/z [M+H]+ calcd for $C_{18}H_{34}ON_3$+: 308.2696; found 308.2692.



In a nitrogen-filled glove box, a 10-mL vial equipped with a magnetic stirring bar was charged sequentially with iodobenzene (0.2 mmol, 1.0 equiv.), DBU (0.6 mmol, 3.0 equiv.), B_2pin_2 (0.6 mmol, 3.0 equiv.) and DMF (2.0 mL).The vial was closed and removed from the glove box. The resulting mixture was allowed to stir at 50 ± 5 ℃under blue LED (100 W) irradiation for overnight. Their products were obtained in 88% yield by H NMR spectroscopy. In a nitrogen-filled glove box, a 10-mL vial equipped with a magnetic stirring bar was charged sequentially with

2-iodo-1,3-diisopropylbenzene or 2-iodo-1,3,5-trimethylbenzene (0.2 mmol, 1.0 equiv.), DBU (0.6 mmol, 3.0 equiv.), B_2pin_2 (0.6 mmol, 3.0 equiv.) and DMF (2.0 mL).The vial was closed and removed from the glove box. The resulting mixture was allowed to stir at 50 ± 5 ℃under blue LED (100 W) irradiation for overnight. The starting material 2-iodo-1,3-diisopropylbenzene or 2-iodo-1,3,5-trimethylbenzene were recovered in 65% and 94% yield respectively.(Figure S3B).

4.3 Determination of the Binding Ratio by Job's Plot.

The binding stoichiometry between **1a** and DBU was evaluated using Job's plot analysis[5]: **^{1}H NMR** spectra of ten samples of mixtures of **1a** and DBU acceptor in $CDCl_3$ were recorded at 298 K. The total volume of the mixture was 0.5 mL, and the total amount of **1a** and DBU was kept constant at 0.1 mmol (0.2 M), while the amount of DBU varied from 0 to 0.1 mmol (0-0.2 M). The molar ratios of DBU / (**1a** + DBU) were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.8, 0.9, 1.0. **^{1}H NMR** for each sample was recorded and the chemical shifts differences (Δδ) for **1a** were used to draw the plot. The stoichiometry was determined by plotting ratios of [**1a**] × Δδ against ratios of [**1a**] / [**1a** + DBU] to afford a maximum at ratio [**1a**] / [**1a** + DBU] = 0.5, which meant a 1:1 complex ratio between **1a** and DBU. (Figure S3).

	[1a] (M)	Δδ (ppm)	**[1a]/[1a** + DBU**]**	[**1a**]×Δδ (M.ppm)
1	0.10	0	1.00	0
2	0.09	0.0072	0.90	0.001296
3	0.08	0.0089	0.80	0.001424
4	0.07	0.0133	0.70	0.001862
5	0.05	0.0197	0.50	0.001970
6	0.04	0.0200	0.40	0.001600
7	0.03	0.0213	0.30	0.001278
8	0.02	0.0266	0.20	0.001064
9	0.01	0.0279	0.10	0.000558
10	0	0	0	0

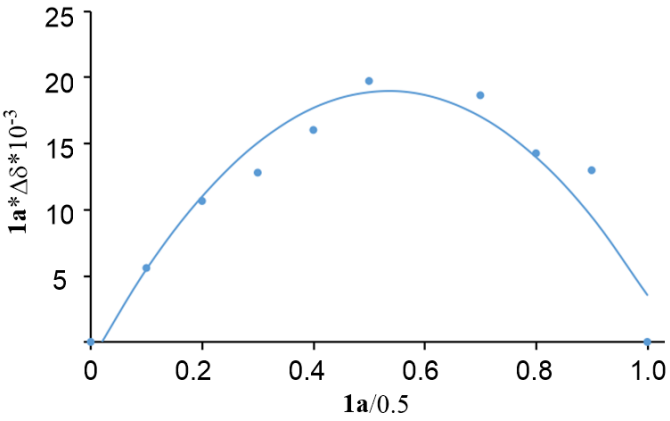


Figure S3. Job plot was used to determine binding stoichiometry between **1a** and DBU.

4.4 Determination of the association constant (K_{EDA})

The association constant (K_{EDA}) was calculated using Hanna and Ashbaugh's[2-5]. **^{1}H NMR** spectra of ten samples of mixtures of **1a** and DBU in $CDCl_3$ were recorded at 298 K. The total volume of the mixture was 0.5 mL, the amount of **1a** was kept constant at 0.02 mmol (6.62 mg), while that of DBU varied from 0.04 to 0.4 mmol. **^{1}H NMR** for each sample was recorded and the chemical shifts differences (Δδ) for **1a** were used to draw the plot. While TMEDA and DIPEA made the curves according to the above method.

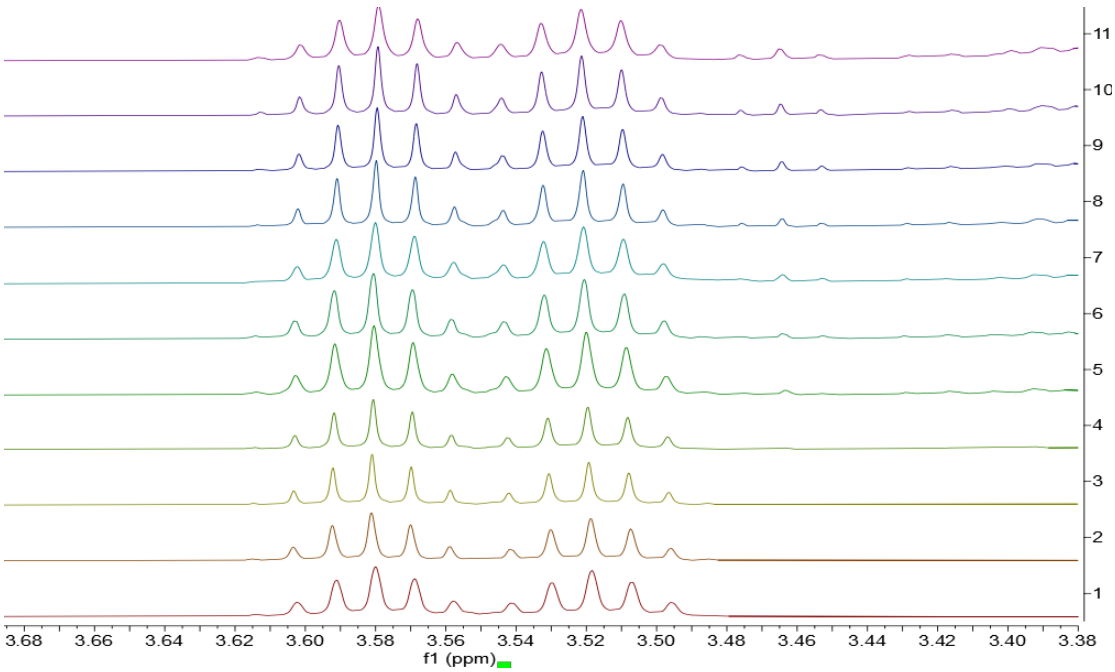
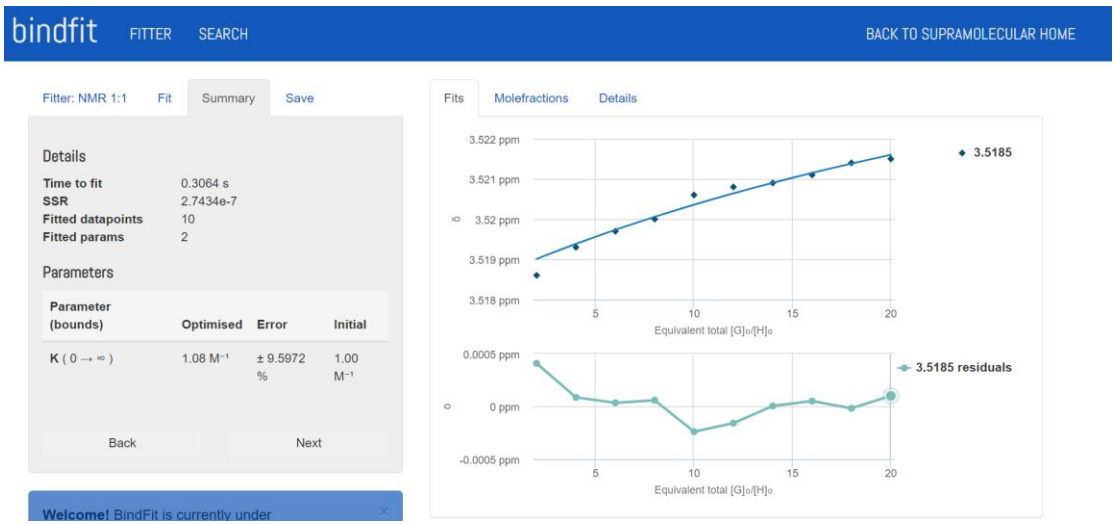


Figure S4. **^{1}H NMR** spectra recorded during the titration of **1a** (4×10^{-2} M) with variable concentrations (0-10 equiv.) of DBU in Chloroform-*d*.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Save
Details
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Fitted datapoints 10
Fitted params 2
Parameters
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Error
Initial
K (0 → ∞)
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± 9.5972 %
1.00 M⁻¹
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Next
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Details
3.522 ppm
3.521 ppm
3.52 ppm
3.519 ppm
3.518 ppm
δ
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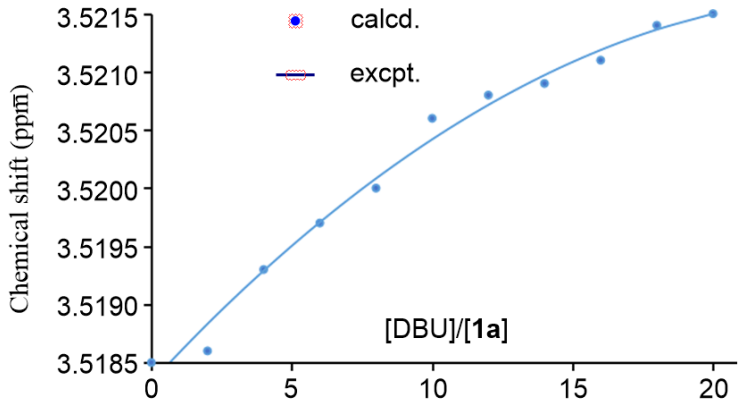
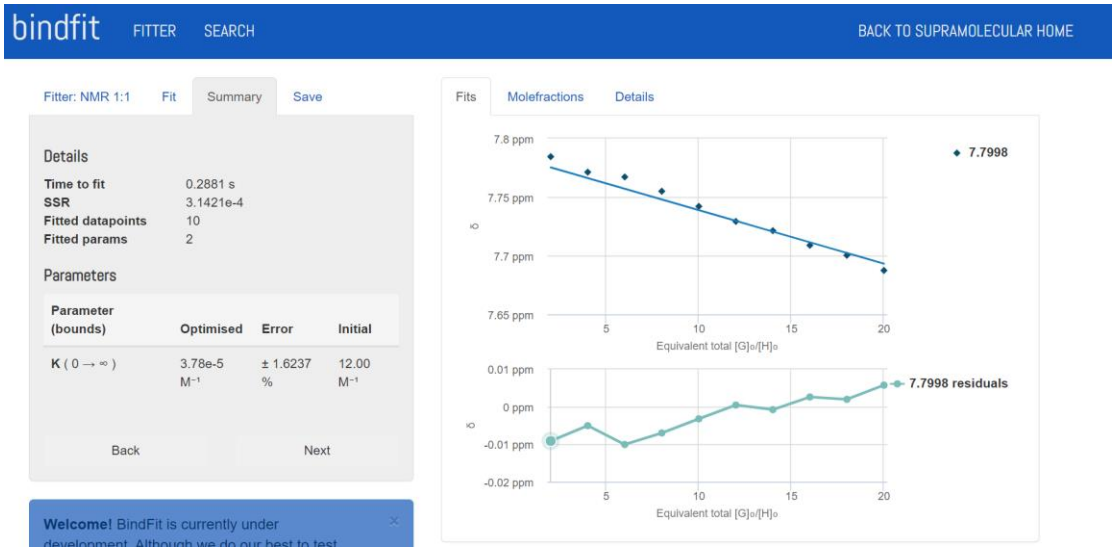
-0.0005 ppm
3.5185 residuals


3.5215
3.5210
3.5205
3.5200
3.5195
3.5190
3.5185
Chemical shift (ppm)
calcd.
excpt.
[DBU]/[1a]
0
5
10
15
20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Fit
Summary
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Details
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SSR 3.1421e-4
Fitted datapoints 10
Fitted params 2
Parameters
Parameter (bounds)
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Error
Initial
K (0 → ∞)
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± 1.6237 %
12.00 M⁻¹
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Fits
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Details
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7.75 ppm
7.7 ppm
7.65 ppm
δ
7.7998
Equivalent total [G]₀/[H]₀
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0 ppm
-0.01 ppm
-0.02 ppm
7.7998 residuals

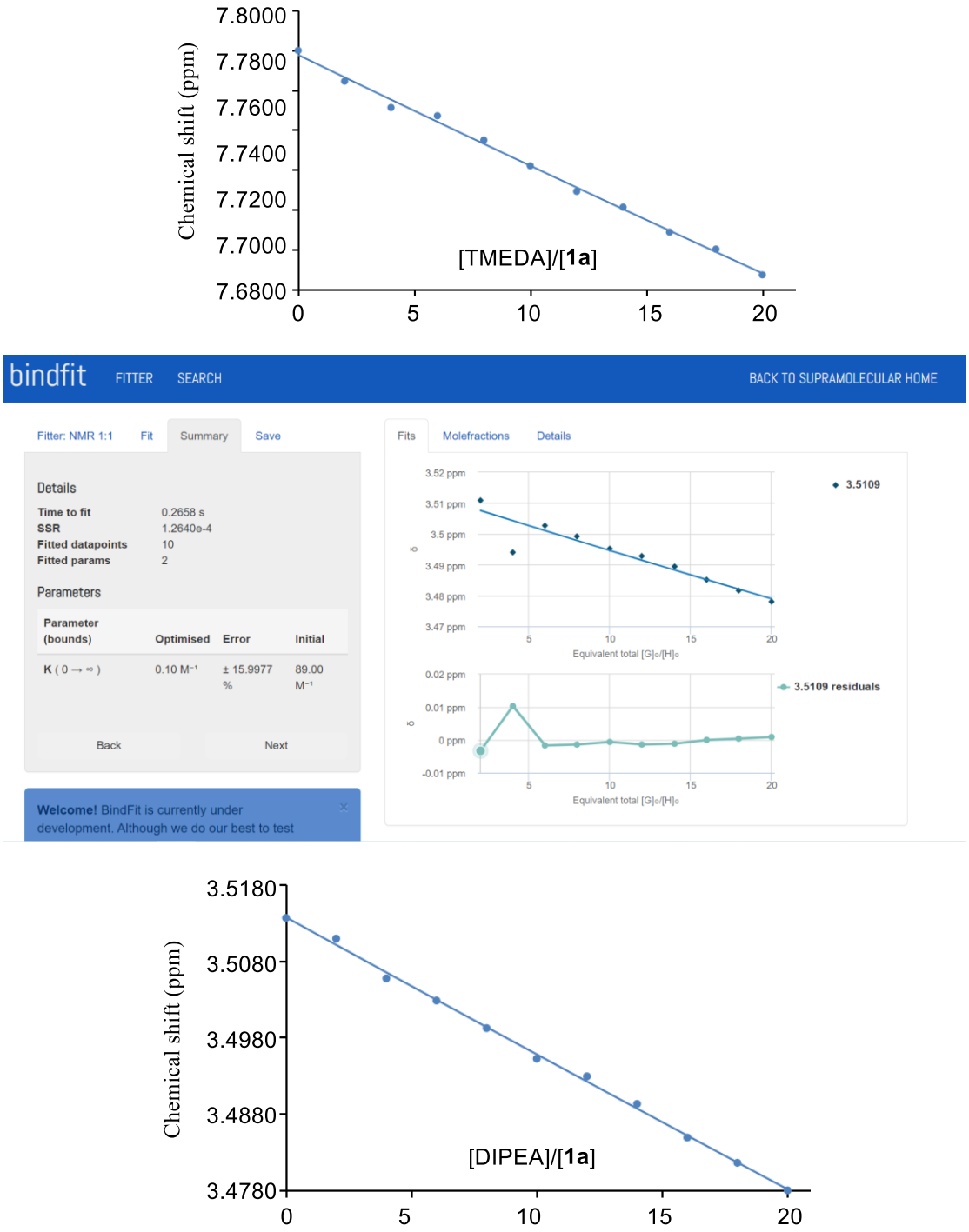
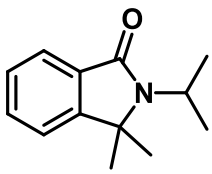


Figure S5. The curve fitting of the ^{1}H NMR titration data by Bindfit program, available online (http://supramolecular.org/); fitting output from Bindfit.

Base	Ka (M^{-1})	Yield/%
TMEDA	3.78 x e^{-5}	trace
DIPEA	0.10	21
DBU	1.08	88

Scheme S6. KA values and yields for TMEDA, DIPEA and DBU.

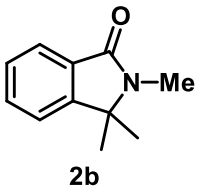
5. Compound Characterization Data



2a

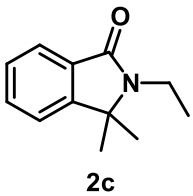
2-isopropyl-3,3-dimethylisoindolin-1-one (2a): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1-30:1) as a white solid (36 mg, 0.177 mmol, 88%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.42 – 7.38 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 3.67 – 3.60 (m, 1H), 1.56 (d, *J* = 6.8 Hz, 6H), 1.47 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.3, 151.3, 132.1, 131.3, 127.9, 123.3, 120.7, 63.4, 44.6, 25.5, 20.6. These data are in agreement with those reported previously in the literature.[6]

For the large-scale reaction, 2-isopropyl-3,3-dimethylisoindolin-1-one (1.1g, 3.3 mmol) was added to a dry schlenk which was then evacuated and filled with argon (three times). After the addition of DMF (10.0 mL) to the mixture via gastight syringe, DBU (0.495g, 9.9 mmol, 3 equiv.) was added. After the reaction completion (overnight) the product was obtained after purification by column chromatography (PE/EA = 10:1 - 30:1) as a white solid (649 mg, 3.2 mmol, 97% yield) and characterized as described above.



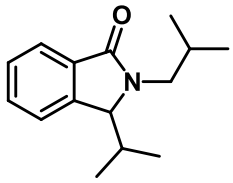
2b

2,3,3–trimethylisoindolin–1–one (2b): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (29 mg, 0.166 mmol, 83%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 3.03 (s, 3H), 1.45 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.4, 151.6, 131.6, 131.0, 128.1, 123.7, 120.8, 62.2, 27.0, 25.1, 24.0. These data are in agreement with those reported previously in the literature.[6]



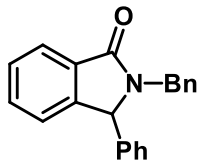
2c

2–ethyl–3,3–dimethylisoindolin–1–one (2c): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (31 mg, 0.166 mmol, 83%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.43 – 7.39 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 3.55 – 3.50 (m, 2H), 1.49 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 177.5, 143.8, 140.6, 140.1, 130.7, 128.4, 99.8, 36.2, 31.9, 20.6, 20.1, 19.7. These data are in agreement with those reported previously in the literature.[7]



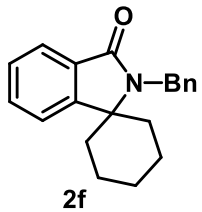
2d

2–isobutyl–3–isopropylisoindolin–1–one (2d): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (33 mg, 0.142 mmol, 71%). **^{1}H NMR** (400 MHz, Chloroform–*d*) δ 7.89 – 7.84 (m, 1H), 7.53 – 7.43(m, 3H), 4.47 (d, *J* = 3.3 Hz, 1H), 3.89 (dd, *J* = 14.0, 10.1 Hz, 1H), 2.92 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.08 – 1.95 (m, 1H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.47 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 168.8, 143.4, 133.5, 130.8, 128.1, 123.8, 123.2, 64.2, 47.1, 28.8, 27.4, 20.7, 19.9, 19.2, 14.9. These data are in agreement with those reported previously in the literature.[6]



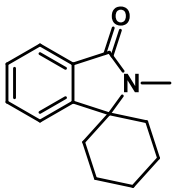
2e

2-benzyl-3-phenylisoindolin-1-one (2e): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (36 mg, 0.120 mmol, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 2H), 7.51 – 7.42 (m, 2H), 7.37 – 7.34(m, 3H), 7.31 – 7.25 (m, 3H), 7.19 – 7.17(m, 2H), 7.13 – 7.05 (m, 3H), 5.41 (d, *J* = 14.8 Hz, 1H), 5.24 (s, 1H), 3.73 (d, *J* = 14.9 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform–*d*) δ 43.9, 63.7, 123.3, 123.9, 127.7, 127.9, 128.5, 128.6, 128.8, 129.3, 131.5, 132.0, 136.9, 137.2, 146.5, 168.7. These data are in agreement with those reported previously in the literature.[8]



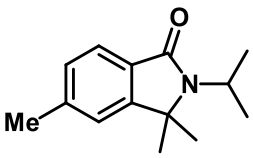
2f

2'–benzylspiro[cyclohexane–1,1'–isoindolin]–3'–one (2e): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (42 mg, 0.144 mmol, 72%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.95 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.31 (d, *J* = 6.7 Hz, 2H), 7.26 (d, *J* = 9.3 Hz, 2H), 7.22 – 7.18 (m, 1H), 4.78 (s, 2H), 1.93 – 1.82 (m, 5H), 1.78 (d, *J* = 15.0 Hz, 2H), 1.40 (d, *J* = 11.3 Hz, 2H), 1.30 – 1.23 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 168.2, 150.9, 138.9, 131.4, 131.0, 128.6, 128.0, 127.2, 127.1, 124.2, 123.8, 65.9, 42.6, 34.4, 24.8, 22.6. These data are in agreement with those reported previously in the literature.[6]



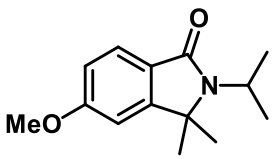
2g

2'–methylspiro[cyclohexane–1,1'–isoindolin]–3'–one (2f): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (27 mg, 0.126 mmol, 63%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.89 (d, *J* = 6.7 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.44 (m, 1H), 3.05 (s, 3H), 1.95 (d, *J* = 9.7 Hz, 5H), 1.92 – 1.86 (m, 2H), 1.44 (d, *J* = 9.8 Hz, 2H), 1.41 – 1.34 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.6, 150.7, 131.8, 130.7, 128.0, 123.9, 123.5, 64.5, 33.0, 24.9, 24.4, 22.5. These data are in agreement with those reported previously in the literature.[6]



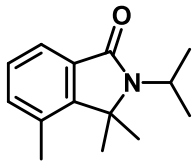
2h

2–isopropyl–3,3,5–trimethylisoindolin–1–one (2g): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a colorless oil (36 mg, 0.166 mmol, 83%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 6.9 Hz, 1H), 7.12 (s, 1H), 2.43 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H), 1.45 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.5, 151.7, 141.8, 129.6, 128.9, 123.1, 121.2, 63.2, 44.6, 25.58, 22.0, 20.6. These data are in agreement with those reported previously in the literature.[6]



2i

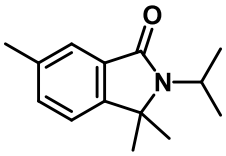
2–isopropyl–5–methoxy–3,3–dimethylisoindolin–1–one (2h): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (29 mg, 0.124 mmol, 62%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.67 (d, *J* = 8.3 Hz, 1H), 6.92 – 6.90(m, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 3.86 (s, 3H), 3.61 (p, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 6.8 Hz, 6H), 1.45 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.2, 162.7, 153.6, 124.8, 124.7, 114.0, 106.0, 63.0, 55.7, 44.6, 25.7, 20.7. These data are in agreement with those reported previously in the literature.[6]



2j

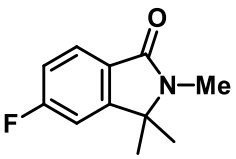
2-isopropyl-3,3,4-trimethylisoindolin-1-one (2j): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (17 mg, 0.078 mmol, 39%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.9 Hz, 1H), 7.33 – 7.29(m, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 3.67 – 3.60 (m, 1H), 2.49 (s, 3H), 1.57 (d, *J*

= 6.9 Hz, 6H), 1.55 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.3, 148.2, 133.8, 132.8, 131.6, 128.0, 121.0, 64.3, 44.4, 23.0, 20.6, 18.8. These data are in agreement with those reported previously in the literature.[9]



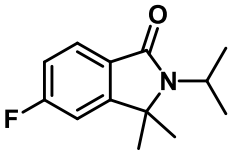
2j'

2-isopropyl-3,3,6-trimethylisoindolin-1-one (2j'): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (8 mg, 0.037 mmol, 18%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 3.65 – 3.61(m, 1H), 2.42 (s, 3H), 1.55 (d, *J* = 6.9 Hz, 6H), 1.46 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform–*d*) δ 167.4, 148.7, 137.9, 132.3, 123.5, 120.5, 63.2, 44.6, 25.6, 21.4, 20.6. These data are in agreement with those reported previously in the literature.[9]



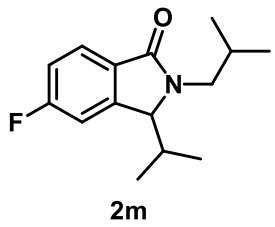
2k

5–fluoro–2,3,3–trimethylisoindolin–1–one (2i) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a yellow solid (22 mg, 0.114 mmol, 57%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.82 – 7.80(m, 1H), 7.09 – 7.05(m, 2H), 3.02 (s, 3H), 1.45 (s, 6H). **^{13}C NMR** (126 MHz,) δ 166.4, 165.4 (d, *J* = 250.8 Hz), 154.2 (d, *J* = 8.9 Hz), 127.2, 125.8 (d, *J* = 9.7 Hz), 115.9 (d, *J* = 23.3 Hz), 108.4 (d, *J* = 23.9 Hz), 62.0, 25.1, 24.2. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -107. 50 – -107.64 (m, 1F). **IR (ATR)** v 3050, 2972, 1677, 1392, 1186, 692, cm^{-1}. **HRMS (ESI)**: *m/z* $[M+H]^+$ calcd for $C_{11}H_{13}FON^+$: 194.0976; found: 194.0975. **Melting Point** (Experimental): 125 °C – 126 °C.



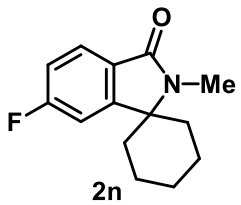
2l

5–fluoro–2–isopropyl–3,3–dimethylisoindolin–1–one (2j): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (35 mg, 0.150 mmol, 75%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.48 – 7.41 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.03 – 6.98 (m, 1H), 3.60 (p, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.8 Hz, 6H), 1.46 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 166.3, 165.2 (d, *J* = 250.5 Hz), 153.8 (d, *J* = 9.0 Hz), 128.1, 125.4 (d, *J* = 9.6 Hz), 115.6 (d, *J* = 23.4 Hz), 108.1 (d, *J* = 23.7 Hz), 63.1, 44.8, 25.5, 20.6. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -107.91 – -107.99 (m, 1F). These data are in agreement with those reported previously in the literature.[6]



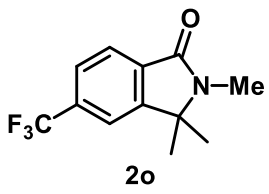
2m

5–fluoro–2–isobutyl–3–isopropylisoindolin–1–one (2k): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (33 mg, 0.142 mmol, 71%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.82 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.44 – 4.41 (m, 1H), 3.88 – 3.82 (m, 1H), 2.94 – 2.87 (m, 1H), 2.40 (dd, *J* = 6.8, 3.5 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.01 – 0.97 (m, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.49 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 167.9, 164.7 (d, *J* = 250.1 Hz), 145.7 (d, *J* = 9.7 Hz), 125.7 (d, *J* = 9.7 Hz), 115.8 (d, *J* = 23.4 Hz), 110.7 (d, *J* = 24.3 Hz), 64.0, 47.2, 28.7, 27.4, 20.7, 19.9, 19.1, 14.9. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -108.34 – -107.42 (m, 1F). **IR (ATR)** v 2961, 2931, 2874, 1685, 1625, 1416, 1244, 1094, 770, cm^{-1}. **HRMS** (ESI): *m/z* [M+Na]$^{+}$ calcd for $C_{15}H_{19}FONNa^{+}$: 271.1343; found: 271.1342. **Melting Point** (Experimental): 55 °C – 56 °C.



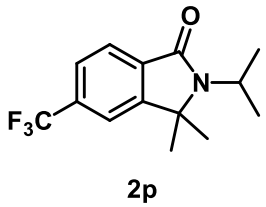
2n

6'–fluoro–2'–methylspiro[cyclopentane–1,1'–isoindolin]–3'–one (2l): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (25 mg, 0.116 mmol, 58%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.86 – 7.82(m, 1H), 7.49 – 7.45 (m, 1H), 7.18 – 7.13 (m, 1H), 3.03 (s, 3H), 1.97 – 1.87 (m, 7H), 1.46 – 1.34 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 166.8, 164.5 (d, *J* = 249.5 Hz), 153.0(d, *J* = 9.7 Hz), 128.0, 125.9 (d, *J* = 9.7 Hz), 115.6 (d, *J* = 23.3 Hz), 111.5 (d, *J* = 24.8 Hz), 64.4, 33.0, 24.9, 24.6, 22.7. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -108.03 – -107.12 (m, 1F). **IR (ATR)** v 2933, 2855, 1683, 1404, 1231, 1052, 693, cm^{-1}. **HRMS** (ESI): *m/z* [M+H]$^{+}$ calcd for $C_{14}H_{17}FON^{+}$: 235.1322; found: 235.1320. **Melting Point** (Experimental): 92 °C – 93 °C.



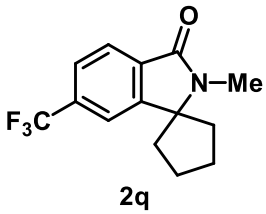
2o

2,3,3–trimethyl–5–(trifluoromethyl)isoindolin–1–one (2m): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a yellow solid (30 mg, 0.124 mmol, 62%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 9.3 Hz, 1H), 7.67 (s, 1H), 3.06 (s, 3H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–d) δ 165.9, 151.9, 134.3, 133.5 (q, *J* = 64.4, 32.4 Hz), 125.5 (q, *J* = 3.4 Hz), 124.3, 122.9(q, *J* = 273.3 Hz), 118.2 (q, *J* = 3.8 Hz) 62.5, 24.9, 24.2. **^{19}F NMR** (471 MHz, Chloroform–d) δ –62.11(s, 3F). **IR (ATR)** v 1683, 1434, 1326, 1167, 1116, 1060, 1030, 795, 697, cm^{-1}. **HRMS** (ESI): *m/z* [M+H]$^{+}$ calcd for $C_{12}H_{13}FON^{+}$: 244.0944; found: 244.0942. **Melting Point** (Experimental): 95 °C – 96 ˚C.



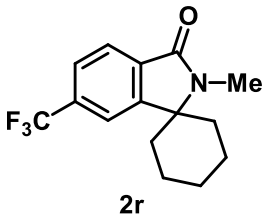
2p

2–isopropyl–3,3–dimethyl–5–(trifluoromethyl)isoindolin–1–one (2n): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a colorless oil (45 mg, 0.167 mmol, 84%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.59 (s, 1H), 3.70 – 3.60 (m, 1H), 1.55 (d, *J* = 6.8 Hz, 6H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 165.9, 151.7, 135.4, 133.3 (q, *J* = 32.1 Hz), 125.4 (q, *J* = 3.8 Hz), 123.9, 122.9 (q, *J* = 273.3 Hz), 118.1 (q, *J* = 3.8 Hz), 63.6, 45.0, 25.4, 20.5. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -62.10(s, 3F). These data are in agreement with those reported previously in the literature.[6]



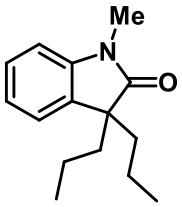
2q

2'–methyl–6'–(trifluoromethyl)spiro[cyclopentane–1,1'–isoindolin]–3'–one (20): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (32 mg, 0.119 mmol, 59%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 1H), 3.06 (s, 3H), 2.12 – 2.07 (m, 2H), 2.06 – 2.01 (m, 4H), 1.97 (dd, *J* = 12.9, 5.3 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 166.1, 153.4, 133.9, 133.8 (q, *J* = 34.4Hz), 125.1 (q, *J* = 3.8 Hz), 123.9, 124.0 (q, *J* = 3.8 Hz), 118.0 (q, *J* = 3.9 Hz), 72.2, 36.0, 26.7, 24.9. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -62.07(s, 3F). **IR (ATR)** ν 2959, 2877, 1699, 1435, 1331, 1159, 1108, 842, cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{15}FON^+$: 270.1100; found: 270.1095. **Melting Point** (Experimental): 115 °C – 116 ˚C.



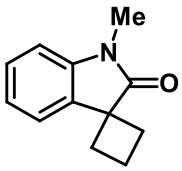
2r

2'–methyl–6'–(trifluoromethyl)spiro[cyclohexane–1,1'–isoindolin]–3'–one (2p): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (32 mg, 0.112 mmol, 57%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 8.03 – 7.96 (m, 2H), 7.74 (d, *J* = 9.5 Hz, 1H), 3.07 (s, 3H), 1.99 (dd, *J* = 12.3, 4.8 Hz, 2H), 1.93 (m, *J* = 10.0, 3.9 Hz, 5H), 1.50 – 1.36 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 166.1, 150.9, 135.0, 132.5 (q, *J* = 32.0 Hz), ,125.4 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 273.7 Hz), 120.4 (q, *J* = 4.2 Hz), 120.4, 64.8, 32.8, 24.7, 24.6, 22.6. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ –67.27(s, 3F). **IR (ATR)** ν 2938, 2873, 1685, 1326, 1166, 1123, 1064,697, cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{17}F_3ON^+$: 284.1257; found: 284.1254. **Melting Point** (Experimental): 115 °C – 116 ˚C.



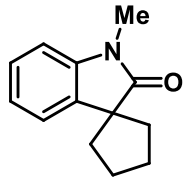
3a

1–methyl–3,3–dipropylindolin–2–one (3a): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (33 mg, 0.142 mmol, 71%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.28 – 7.24 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.20 (s, 3H), 1.89 – 1.83 (m, 2H), 1.71 (dd, *J* = 12.9, 8.6 Hz, 2H), 1.01 – 0.95 (m, 2H), 0.84 – 0.80 (m, 2H), 0.77 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 180.5, 144.2, 132.9, 127.6, 122.8, 122.5, 107.8, 53.5, 40.4, 26.1, 17.6, 14.3. These data are in agreement with those reported previously in the literature.[10]



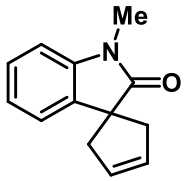
3b

1'–methylspiro[cyclobutane–1,3'–indolin]–2'–one (3b): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) a colorless oil (29 mg, 0.155 mmol, 78%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.51 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.83 – 6.74 (m, 1H), 3.19 (s, 3H), 2.68 – 2.62 (m, 2H), 2.39 – 2.23 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 180.3, 143.1, 134.5, 127.9, 122.7, 122.4, 107.7, 48.2, 31.4, 26.3, 16.9. These data are in agreement with those reported previously in the literature.[6]



3c

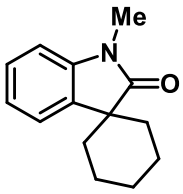
1'–methylspiro[cyclopentane–1,3'–indolin]–2'–one (3c): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a colorless oil (19 mg, 0.095 mmol, 48%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.24 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H), 2.14 (dd, *J* = 11.9, 6.6 Hz, 2H), 2.11 – 2.04 (m, 2H), 1.98 (d, *J* = 6.8 Hz, 2H), 1.84 (dd, *J* = 11.8, 7.1 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 182.1, 143.0, 137.0, 127.5, 122.6, 122.4, 107.8, 54.0, 38.5, 26.8, 26.4. These data are in agreement with those reported previously in the literature.[6]



3d

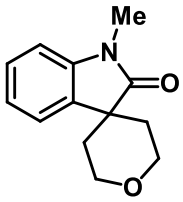
1'–methylspiro[cyclopentane–1,3'–indolin]–3–en–2'–one (3d): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (18 mg, 0.090 mmol, 45%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.26 (d, *J* = 1.5 Hz, 1H),

7.25 (d, *J* = 1.8 Hz, 1H), 7.04 – 7.00(m, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 5.84 (s, 2H), 3.23 (s, 3H), 3.04 – 2.97 (m, 2H), 2.59 (d, *J* = 14.9 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 181.6, 142.7, 137.5, 129.1, 127.8, 123.0, 121.7, 107.9, 52.2, 45.1, 26.5. These data are in agreement with those reported previously in the literature.[6]



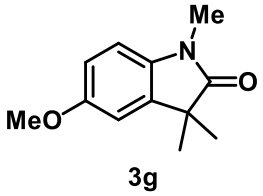
3e

1'–methylspiro[cyclohexane–1,3'–indolin]–2'–one (3e): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (23 mg, 0.106 mmol, 53%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.07 – 7.02 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.20 (s, 3H), 1.97 – 1.91 (m, 2H), 1.87 – 1.81 (m, 2H), 1.79 – 1.71 (m, 3H), 1.69 – 1.59 (m, 2H), 1.59 – 1.53 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 180.9, 142.9, 135.5, 127.6, 124.0, 122.0, 108.0, 47.6, 33.1, 26.3, 25.3, 21.3. These data are in agreement with those reported previously in the literature.[6]



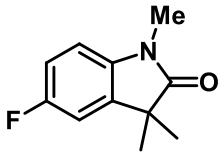
3f

1–methyl–2',3',5',6'–tetrahydrospiro[indoline–3,4'–pyran]–2–one (3f): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (34 mg, 0.156 mmol, 78%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.24 (m, 1H), 7.11 – 7.06 (m, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 4.30 – 4.23 (m, 2H), 3.95 – 3.90 (m, 2H), 3.21 (s, 3H), 1.89 – 1.84 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 179.8, 142.9, 134.2, 128.1, 123.2, 122.6, 108.2, 63.1, 44.4, 33.0, 26.2 These data are in agreement with those reported previously in the literature.[6]



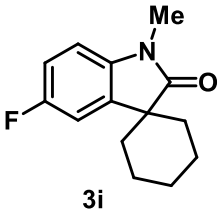
3g

5–methoxy–1,3,3–trimethylindolin–2–one (3g): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (19 mg, 0.092 mmol, 46%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 6.83 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 10.9 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 1.36 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 181.2, 156.2, 137.4, 136.3, 111.7, 110.2, 108.4, 56.0, 44.8, 26.4, 24.5. These data are in agreement with those reported previously in the literature.[6]



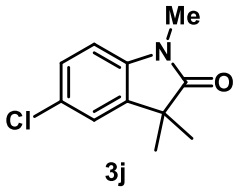
3h

5–fluoro–1,3,3–trimethylindolin–2–one (3h): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a colorless oil (26 mg, 0.135 mmol, 68%). **^{1}H NMR** (400 MHz, Chloroform–*d*) δ 6.99 – 6.93 (m, 2H), 6.79 – 6.74 (m, 1H), 3.21 (s, 3H), 1.37 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform–*d*) δ 181.1, 159,5 (d, *J* = 240.4 Hz), 138.6, 137.5 (d, *J* = 7.7 Hz), 113.8 (d, *J* = 23.5 Hz), 110.6 (d, *J* = 24.6 Hz), 108.5 (d, *J* = 8.2 Hz), 44.8, 26.4, 24.4. **^{19}F NMR** (376 MHz, Chloroform–*d*) δ -120.77. These data are in agreement with those reported previously in the literature.[6]



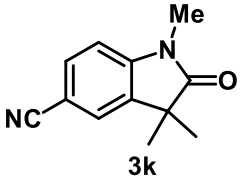
3i

5'–fluoro–1'–methylspiro[cyclohexane–1,3'–indolin]–2'–one (3i): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a light yellow oil (27 mg, 0.116 mmol, 58%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.22 – 7.18 (m, 1H), 7.00 – 6.94 (m, 1H), 6.76 – 6.73 (m, 1H), 3.19 (s, 3H), 1.98 – 1.90 (m, 2H), 1.88 – 1.81 (m, 2H), 1.76 – 1.70 (m, 2H), 1.70 – 1.62 (m, 2H), 1.57 – 1.51 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 180.5, 159.0 (d, *J* = 239.2 Hz), 138.9, 137.0 (d, *J* = 7.7 Hz), 113.5 (d, *J* = 23.2 Hz), 112.4 (d, *J* = 24.9 Hz), 108.2 (d, *J* = 8.3 Hz), 48.1, 33.0, 26.4, 25.2, 21.2. **^{19}F NMR** (471 MHz, Chloroform–*d*) δ -121.08 – -121.17 (m, 1F). These data are in agreement with those reported previously in the literature.[10]



3j

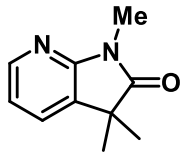
1,3,3,5–tetramethylindolin–2–one (3j): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (24 mg, 0.115 mmol, 57%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.20 (s, 3H), 1.36 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 181.0, 141.4, 137.7, 128.0, 127.7, 123.1, 109.1, 44.6, 26.5, 24.4. These data are in agreement with those reported previously in the literature.[6]



3k

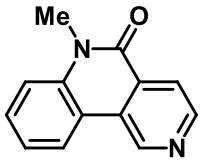
1,3,3–trimethyl–2–oxoindoline–5–carbonitrile (3k): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (34 mg, 0.179 mmol, 85%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.46 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.26 (s, 3H), 1.40 (s, 6H). **^{13}C NMR** (126 MHz,

Chloroform–*d*) δ 181.0, 146.6, 136.8, 133.2, 125.8 119.3, 108.6, 105.6, 44.0, 26.5, 24.2. These data are in agreement with those reported previously in the literature.[6]



3l

1,3,3–trimethyl–1,3–dihydro–2*H*–pyrrolo[2,3–b]pyridin–2–one (3l): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (17 mg, 0.096 mmol, 48%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 8.18 – 8.15 (m, 1H), 7.43 – 7.40 (m, 1H), 6.97 – 9.93 (m, 1H), 3.29 (s, 3H), 1.38 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 181.0, 156.4, 146.7, 130.2, 129.7, 118.2, 44.0, 25.5, 24.0. These data are in agreement with those reported previously in the literature.[6]

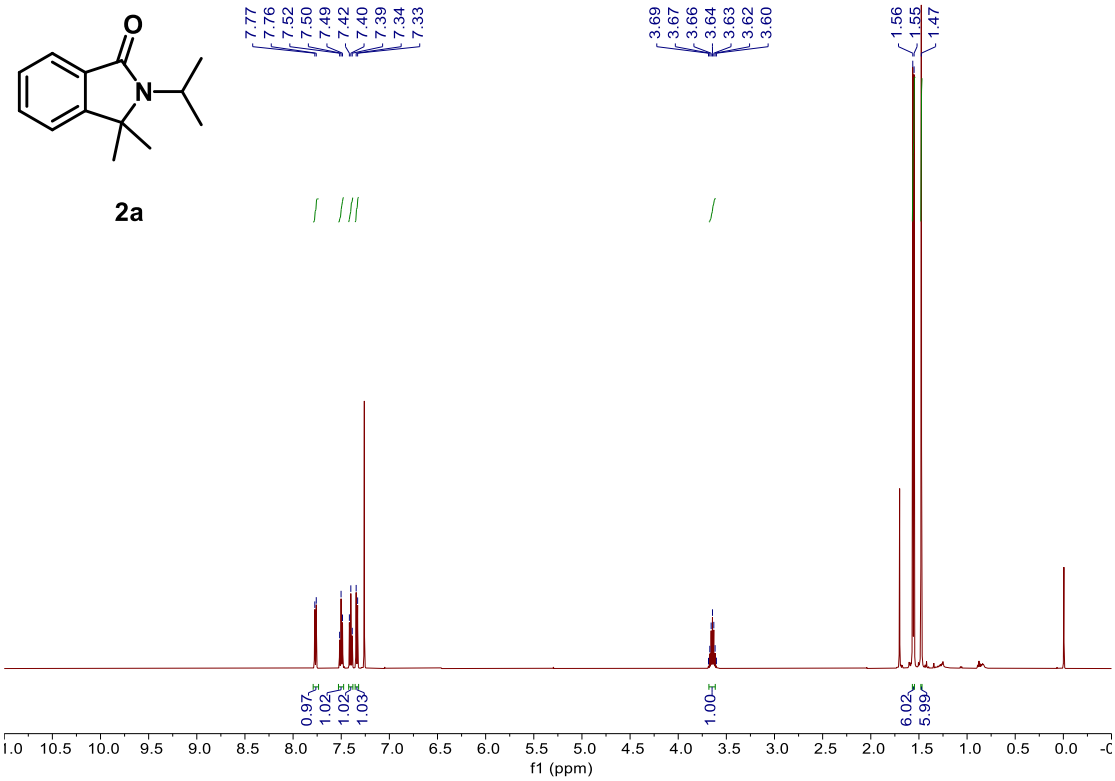


4a

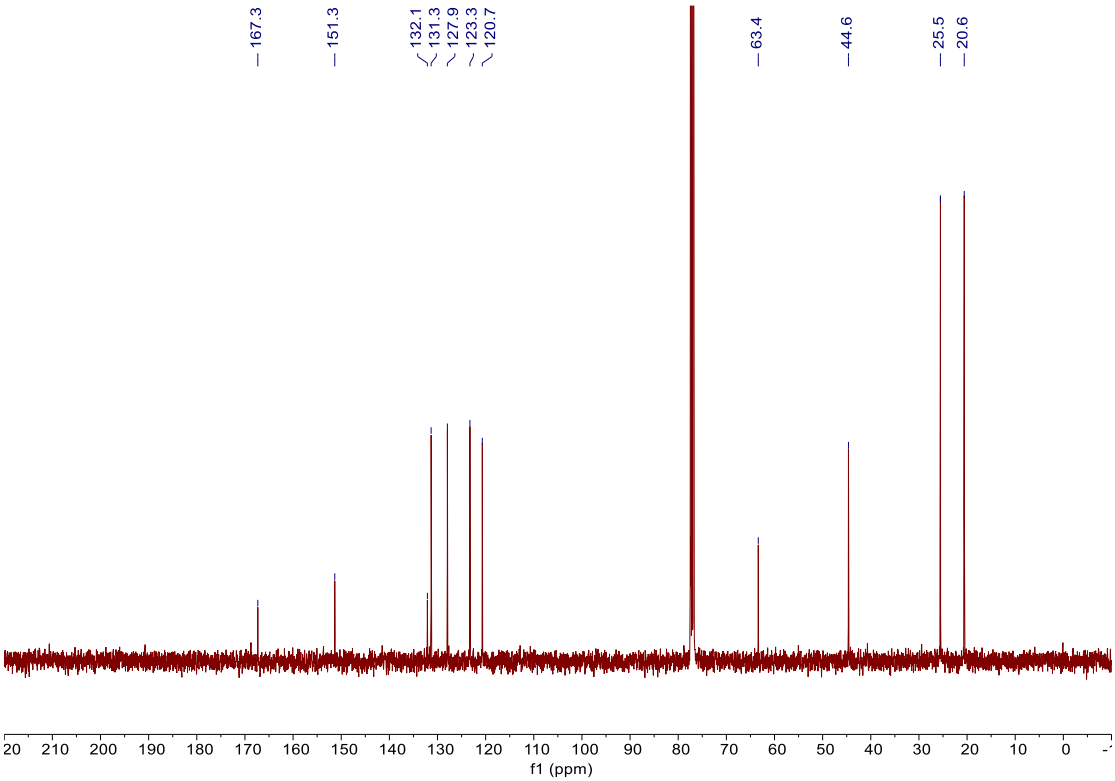
6–methylbenzo[c][2,6]naphthyridin–5(6*H*)–one (4a): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1–30:1) as a white solid (20 mg, 0.095 mmol, 48%). **^{1}H NMR** (500 MHz, Chloroform–*d*) δ 9.70 (s, 1H), 8.82 (d, *J* = 5.2 Hz, 1H), 8.41 (d, *J* = 9.5 Hz, 1H), 8.30 (d, *J* = 5.2 Hz, 1H), 7.65 – 7.60 (m, *J* = 7.1 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.38 (m, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform–*d*) δ 160.5, 148.2, 145.8, 138.4, 130.8, 130.7, 128.0, 123.4, 123.0, 121.0, 117.4, 115.5, 30.4. These data are in agreement with those reported previously in the literature[6].

6. NMR Spectra

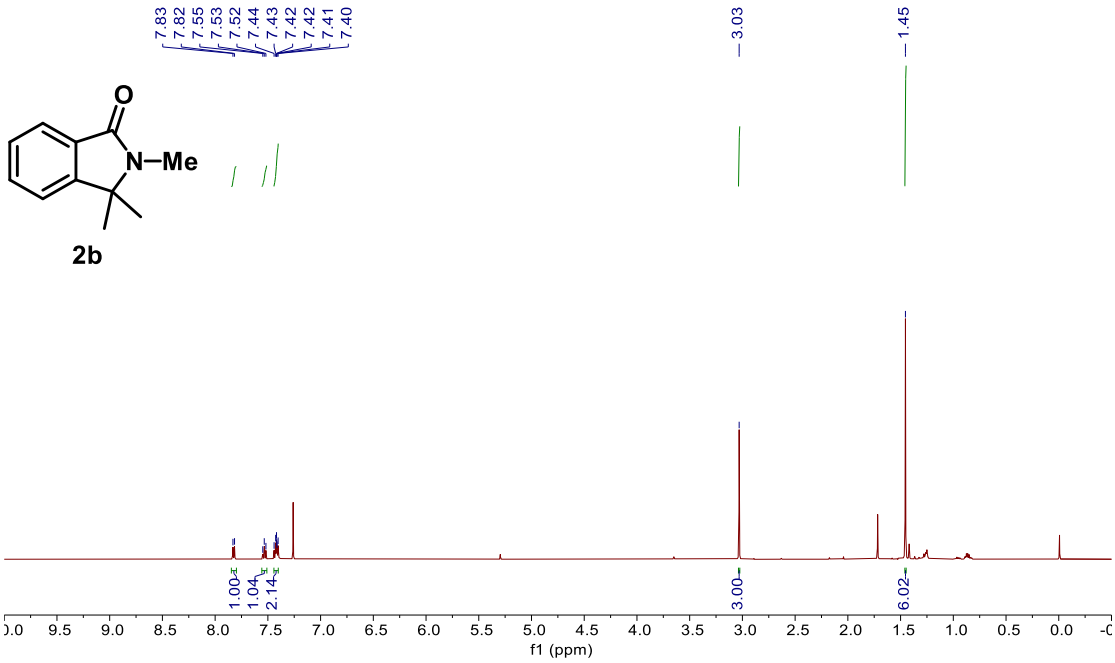
^{1}H NMR of compound **2a** (500 MHz in $CDCl_3$)



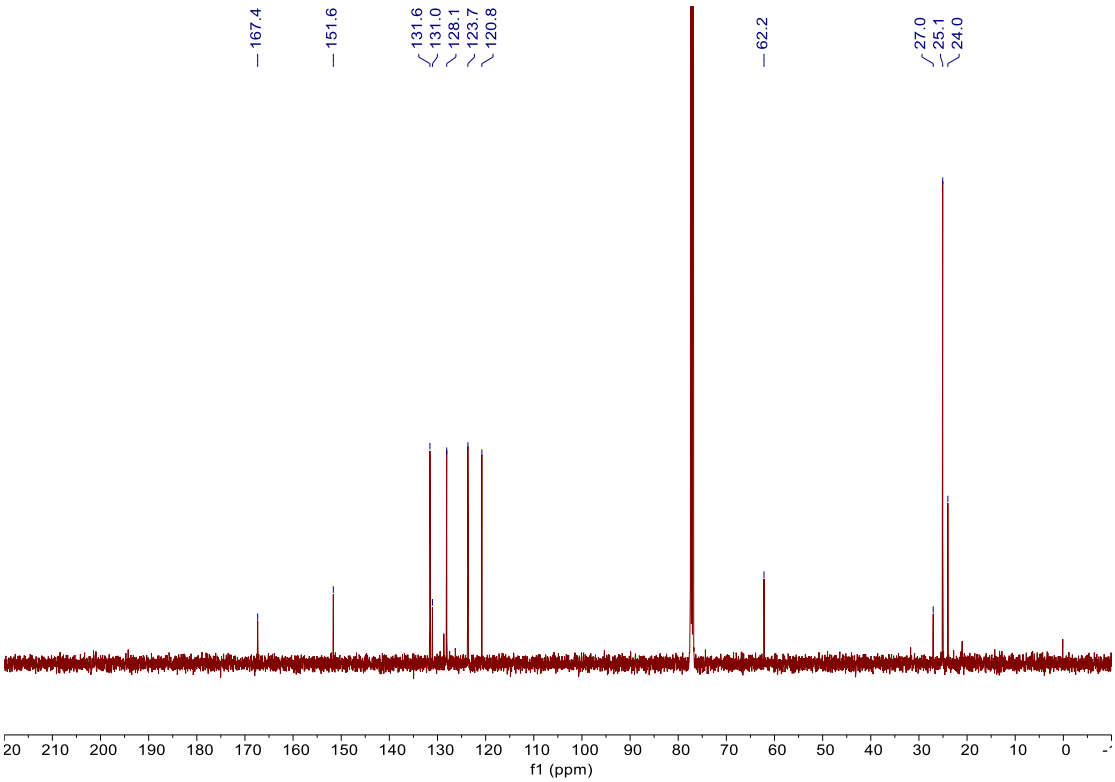
^{13}C NMR of compound **2a** (126 MHz in $CDCl_3$)



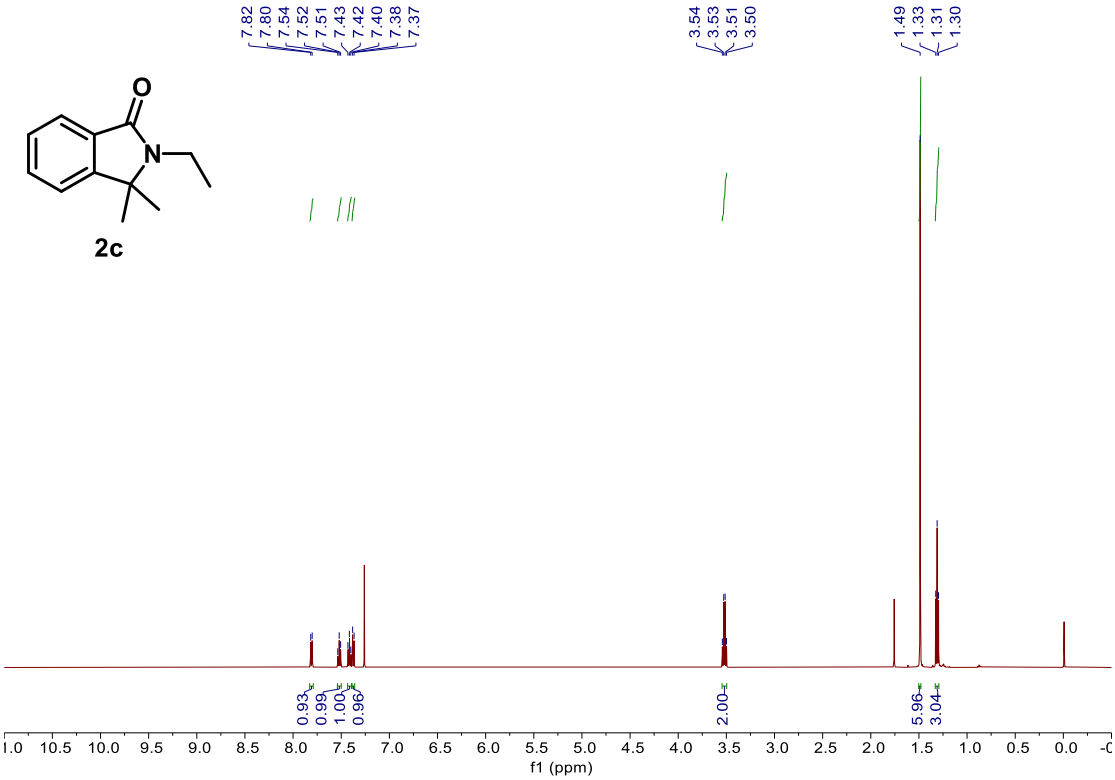
^{1}H NMR of compound **2b** (500 MHz in $CDCl_3$)



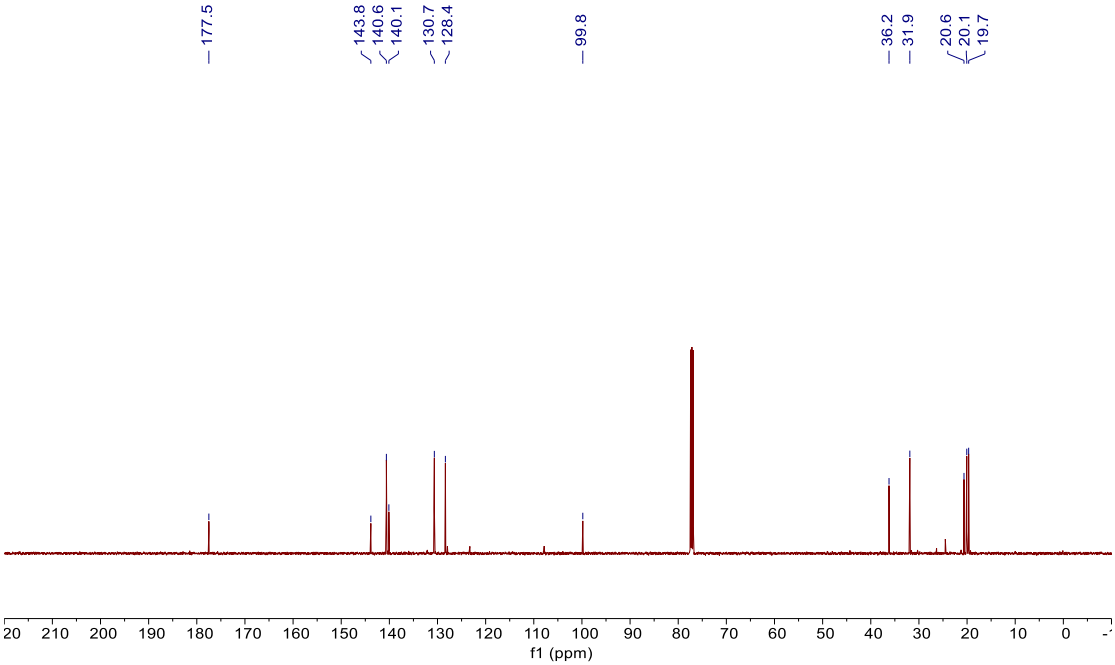
^{13}C NMR of compound **2b** (126 MHz in $CDCl_3$)



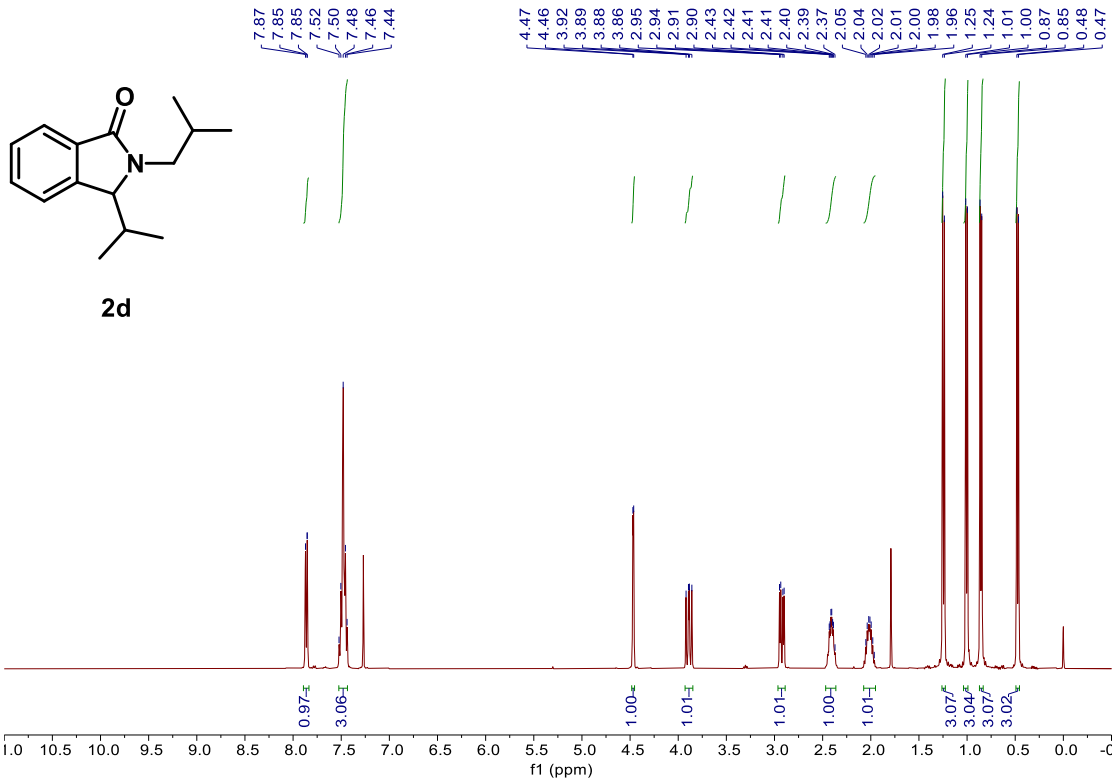
^{1}H NMR of compound **2c** (500 MHz in $CDCl_3$)



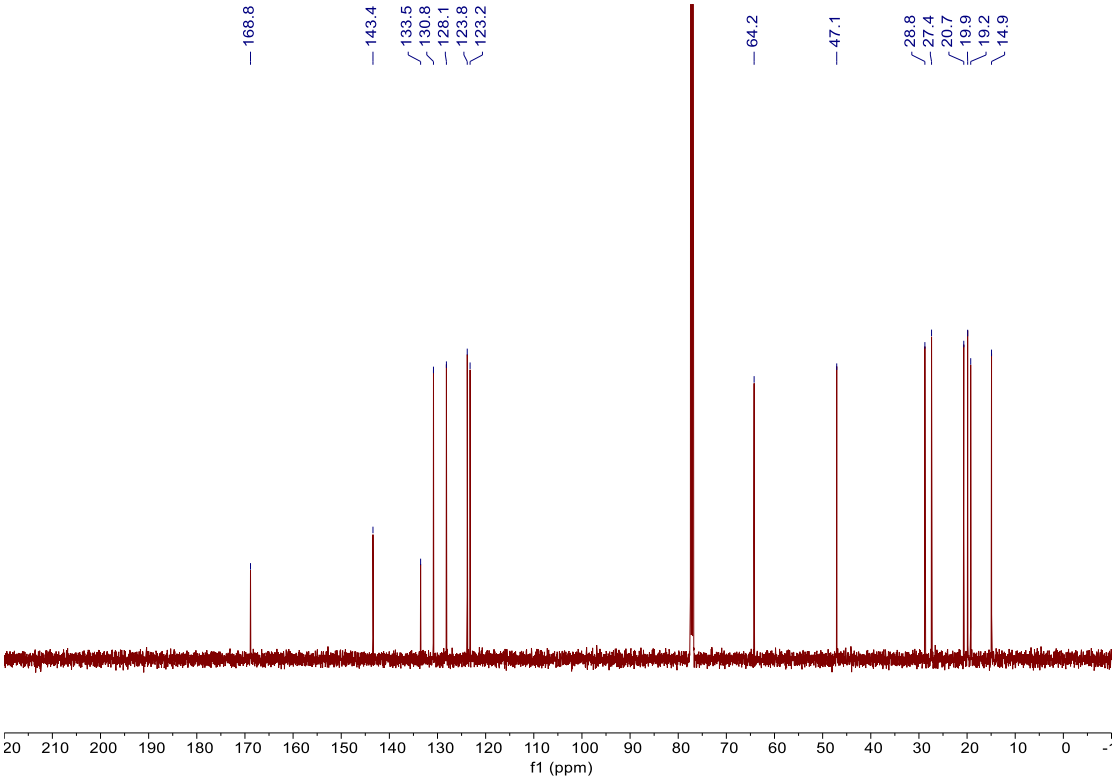
^{13}C NMR of compound **2c** (126 MHz in $CDCl_3$)



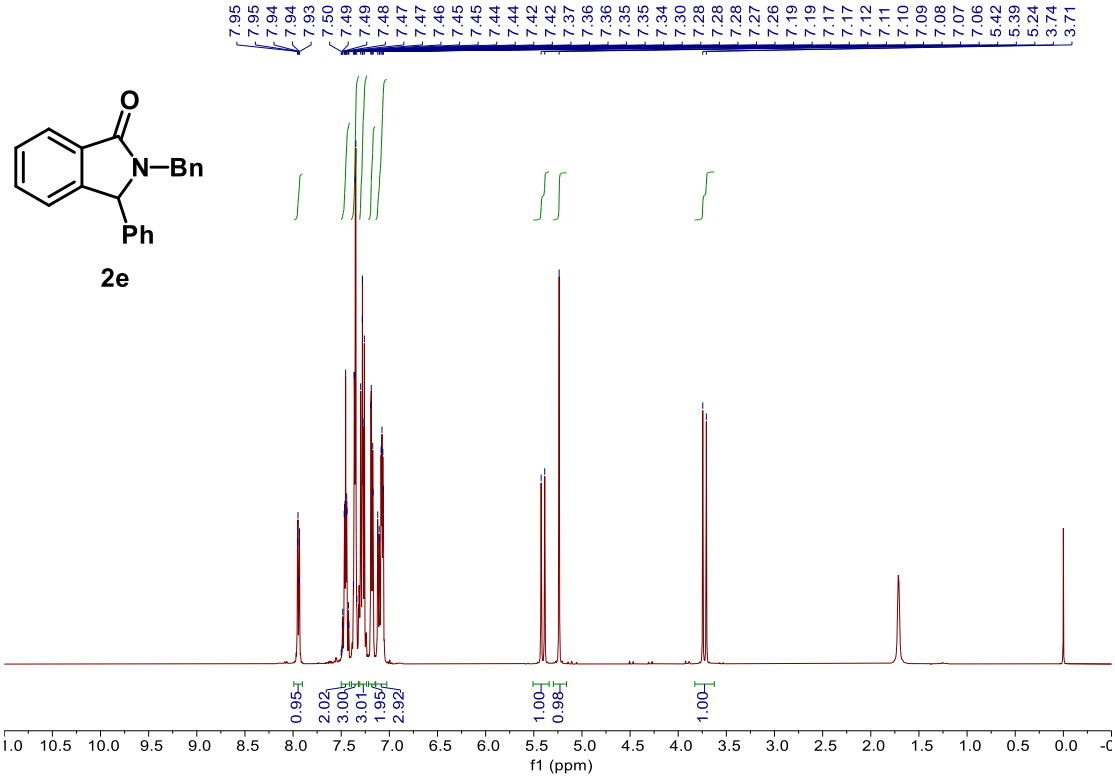
^{1}H NMR of compound **2d** (500 MHz in $CDCl_3$)



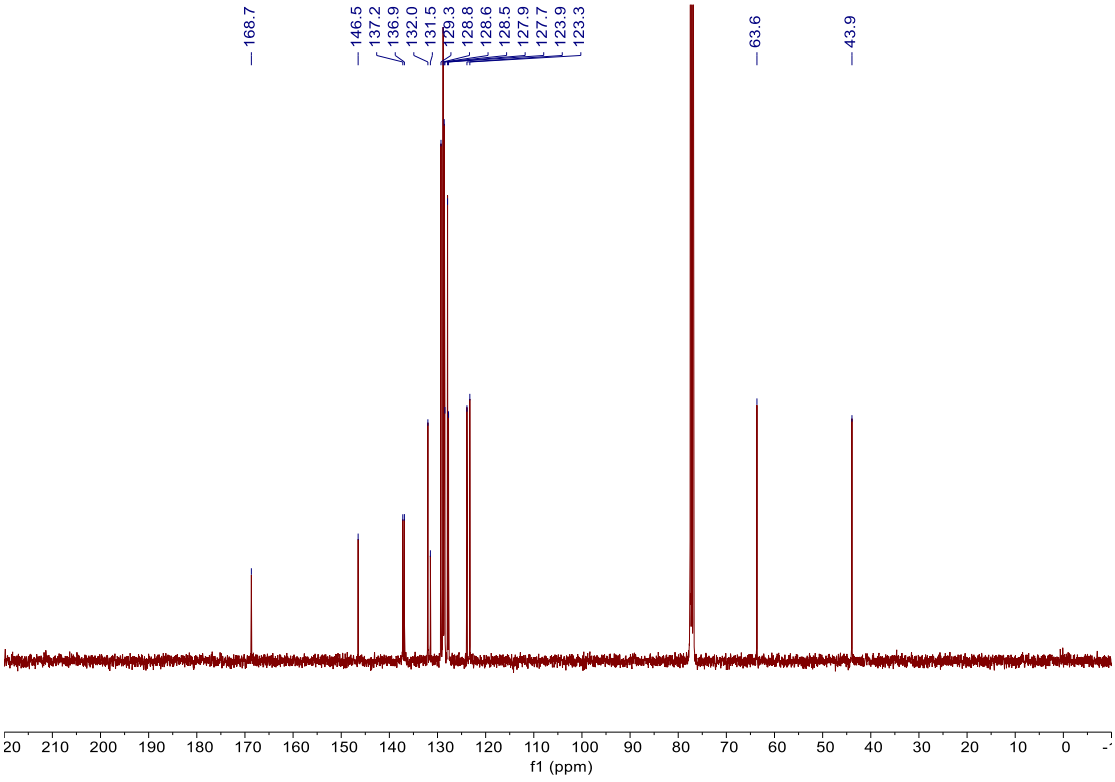
^{13}C NMR of compound **2d** (126 MHz in $CDCl_3$)



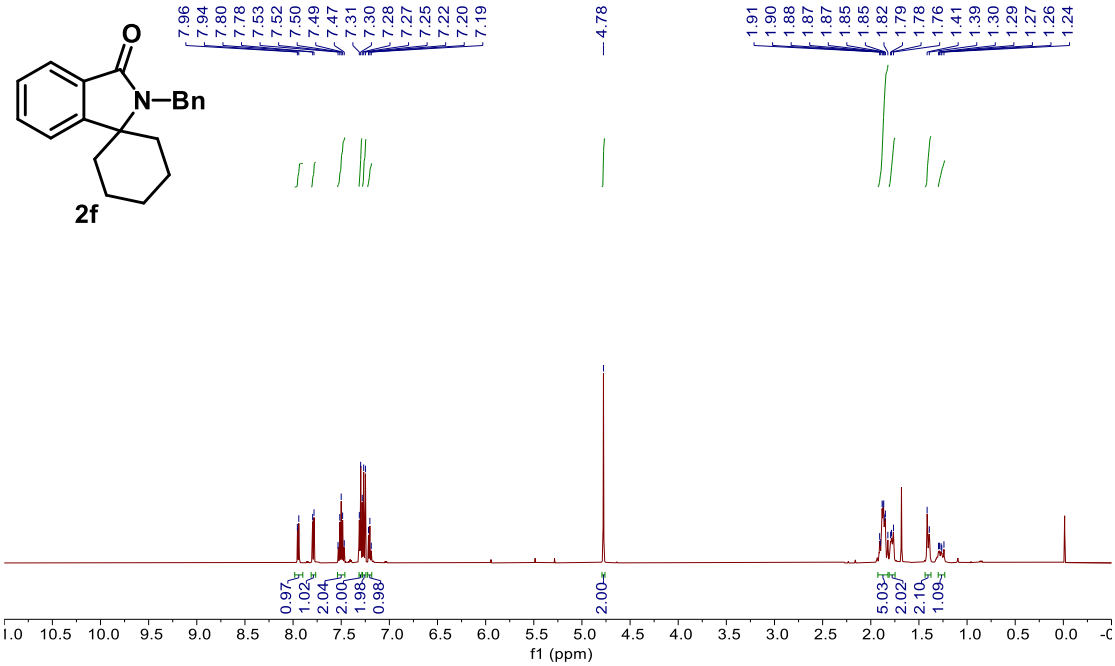
^{1}H NMR of compound **2e** (400 MHz in $CDCl_3$)



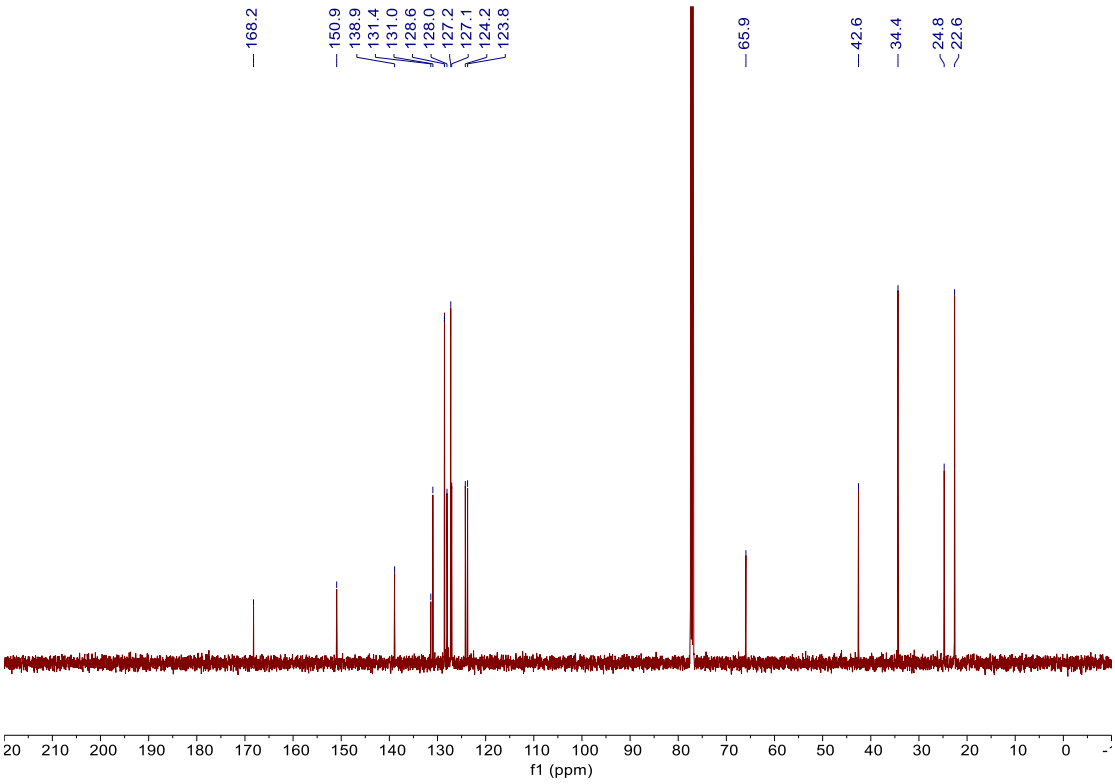
^{13}C NMR of compound **2e** (400 MHz in $CDCl_3$)



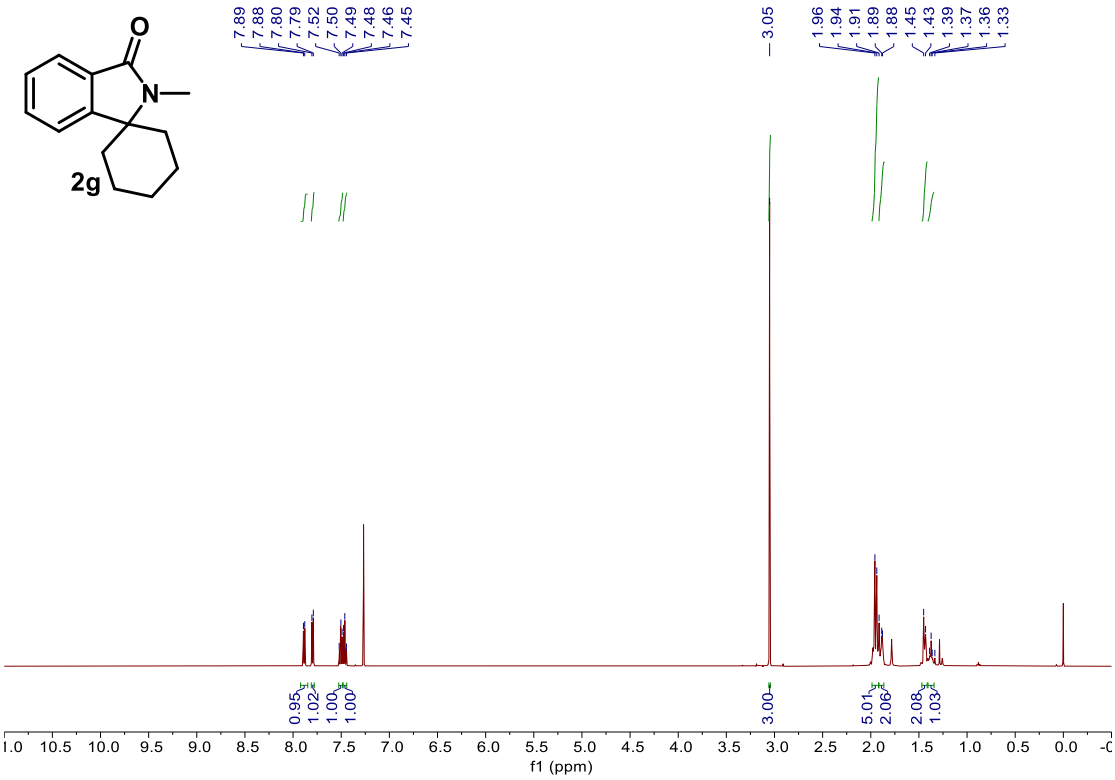
^{1}H NMR of compound **2e** (500 MHz in $CDCl_3$)



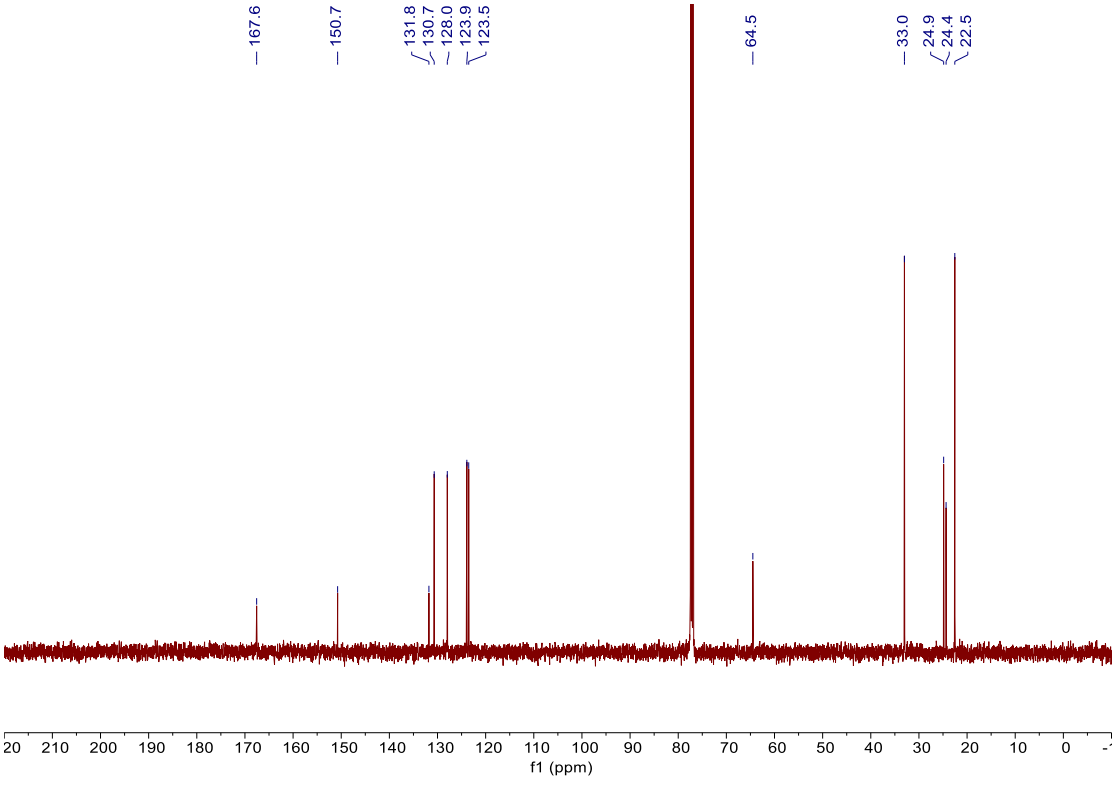
^{13}C NMR of compound **2e** (126 MHz in $CDCl_3$)



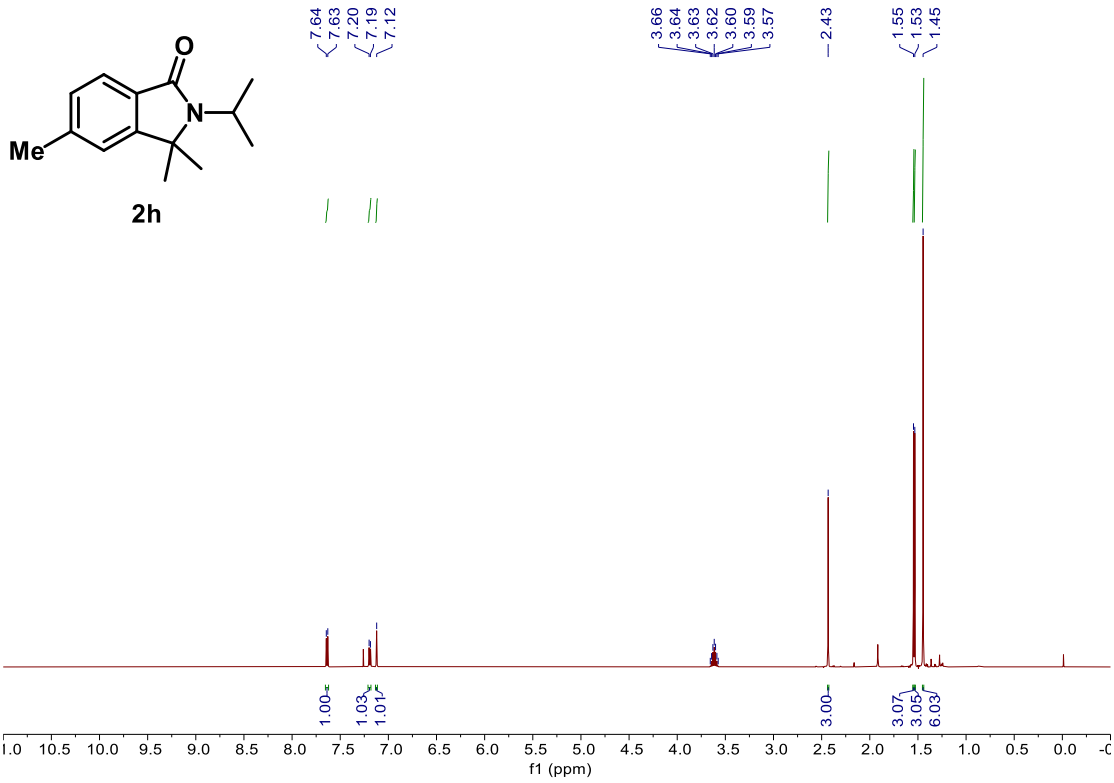
^{1}H NMR of compound **2g** (500 MHz in $CDCl_3$)



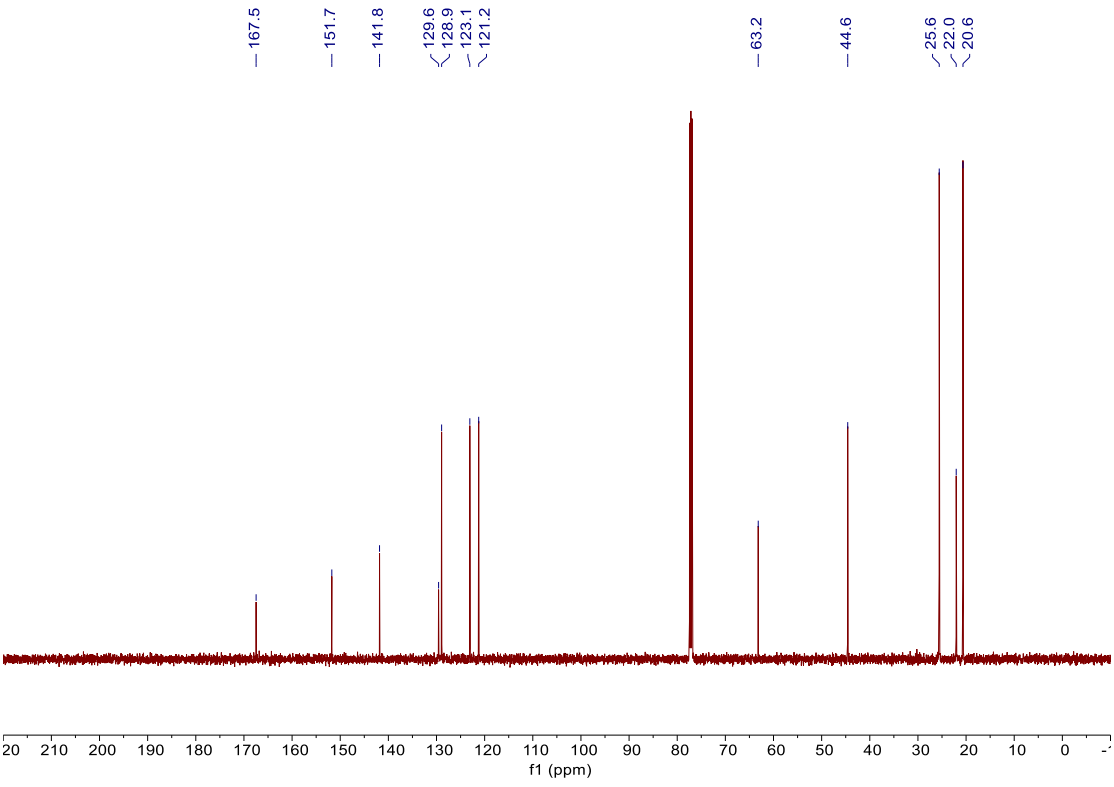
^{13}C NMR of compound **2g** (126 MHz in $CDCl_3$)



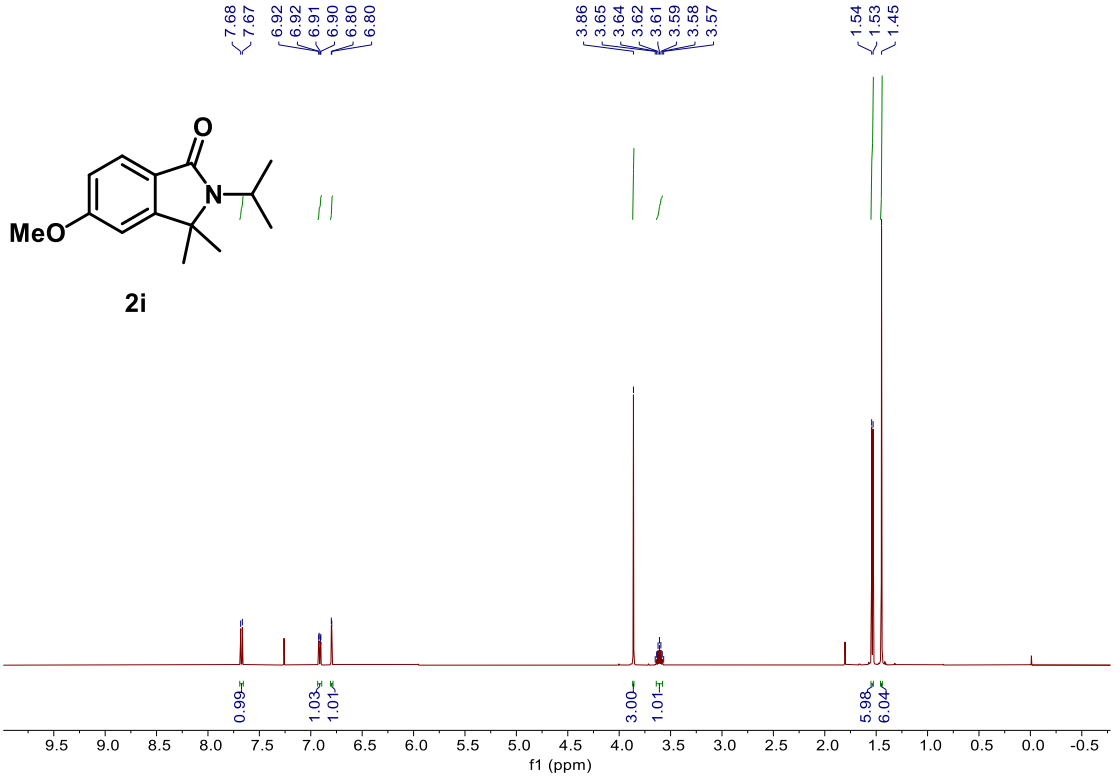
^{1}H NMR of compound **2h** (500 MHz in $CDCl_3$)



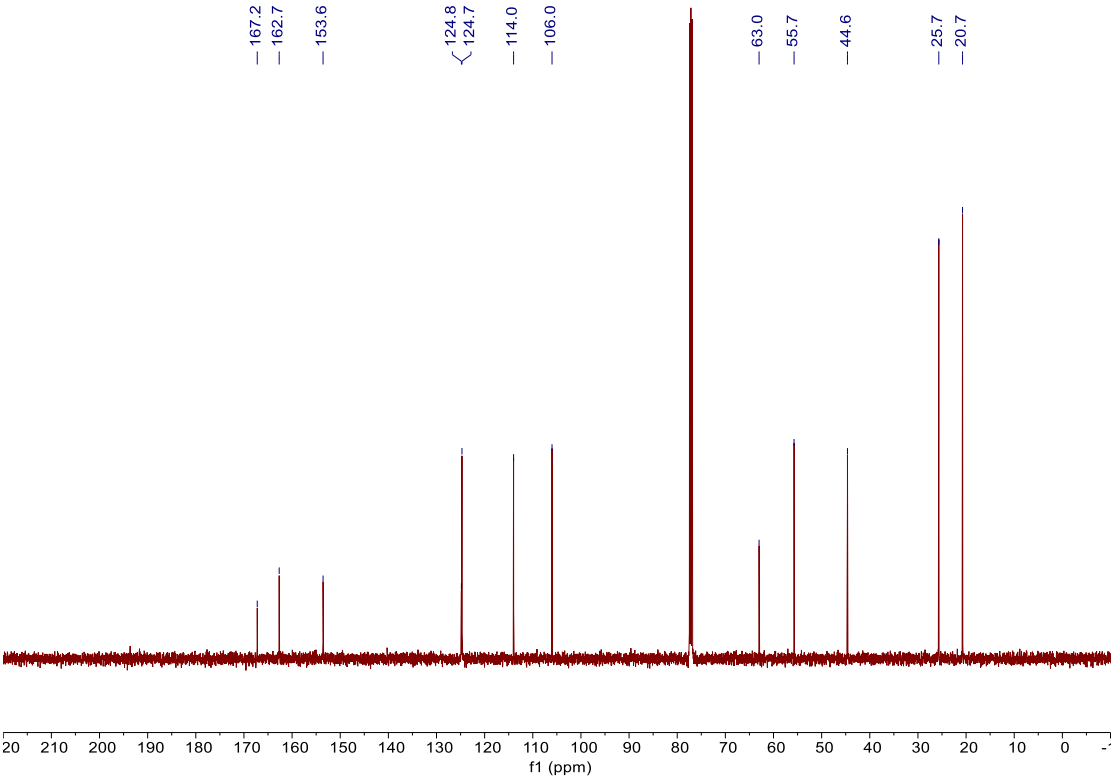
^{13}C NMR of compound **2h** (126 MHz in $CDCl_3$)



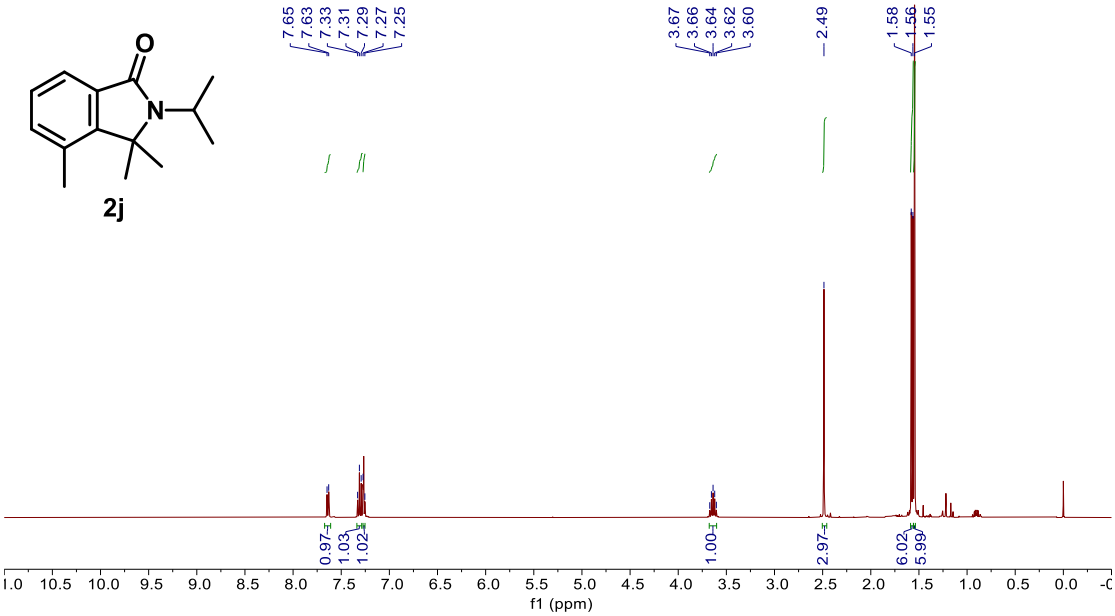
^{1}H NMR of compound **2i** (500 MHz in $CDCl_3$)



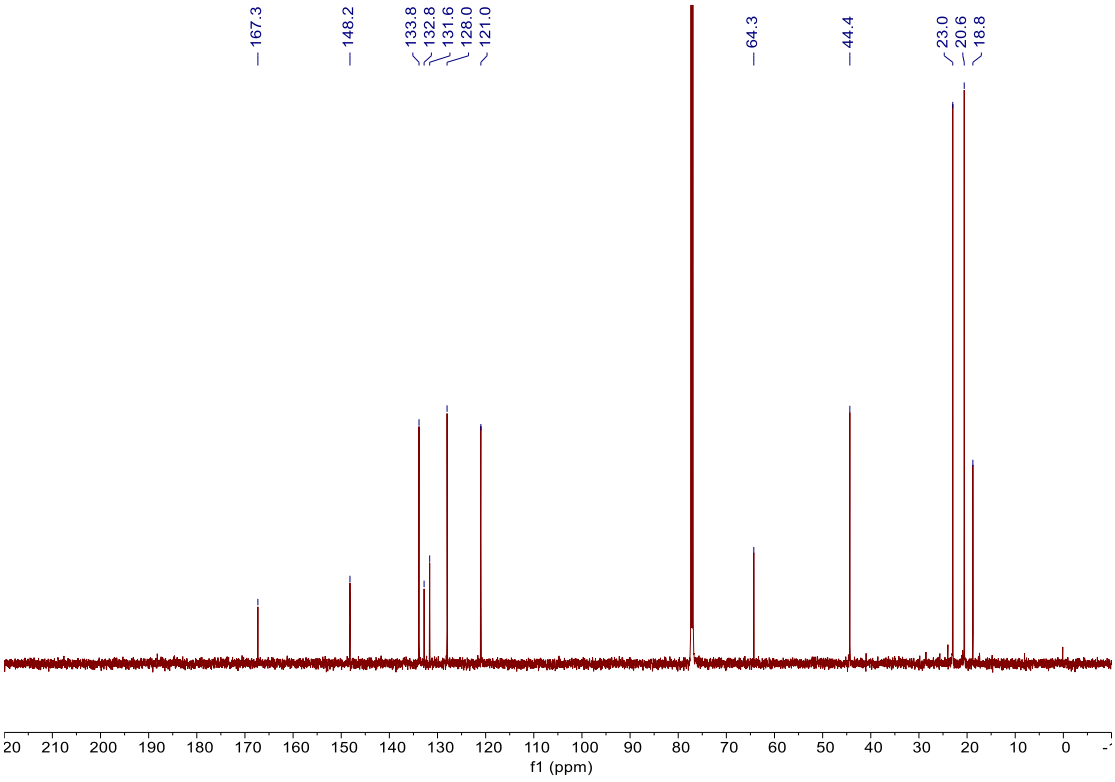
^{13}C NMR of compound **2i** (126 MHz in $CDCl_3$)



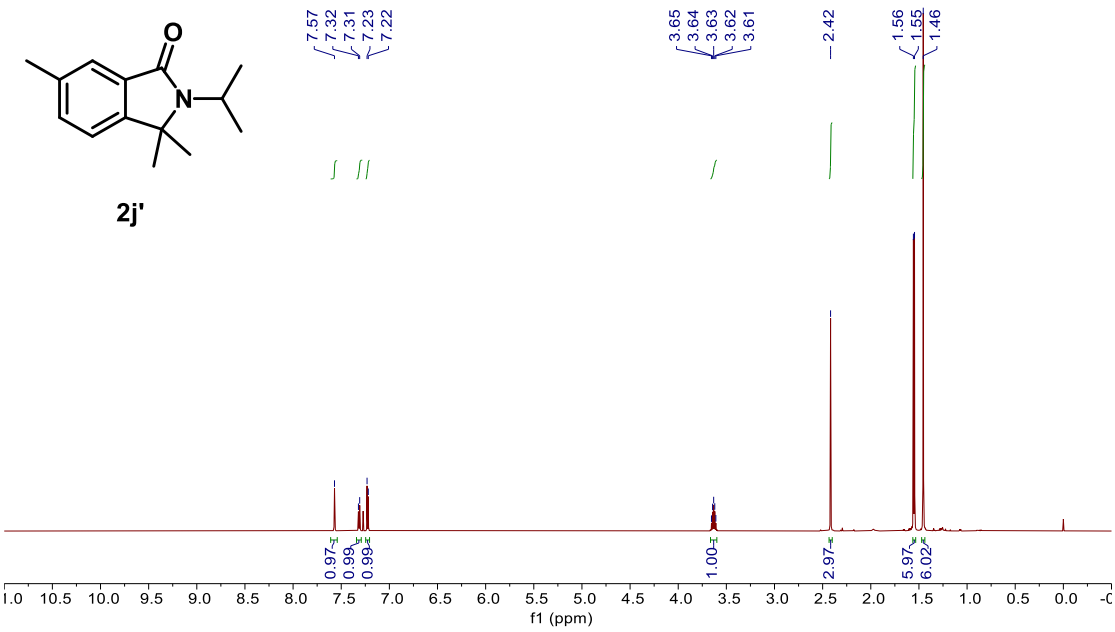
^{1}H NMR of compound **2j** (500 MHz in $CDCl_3$)



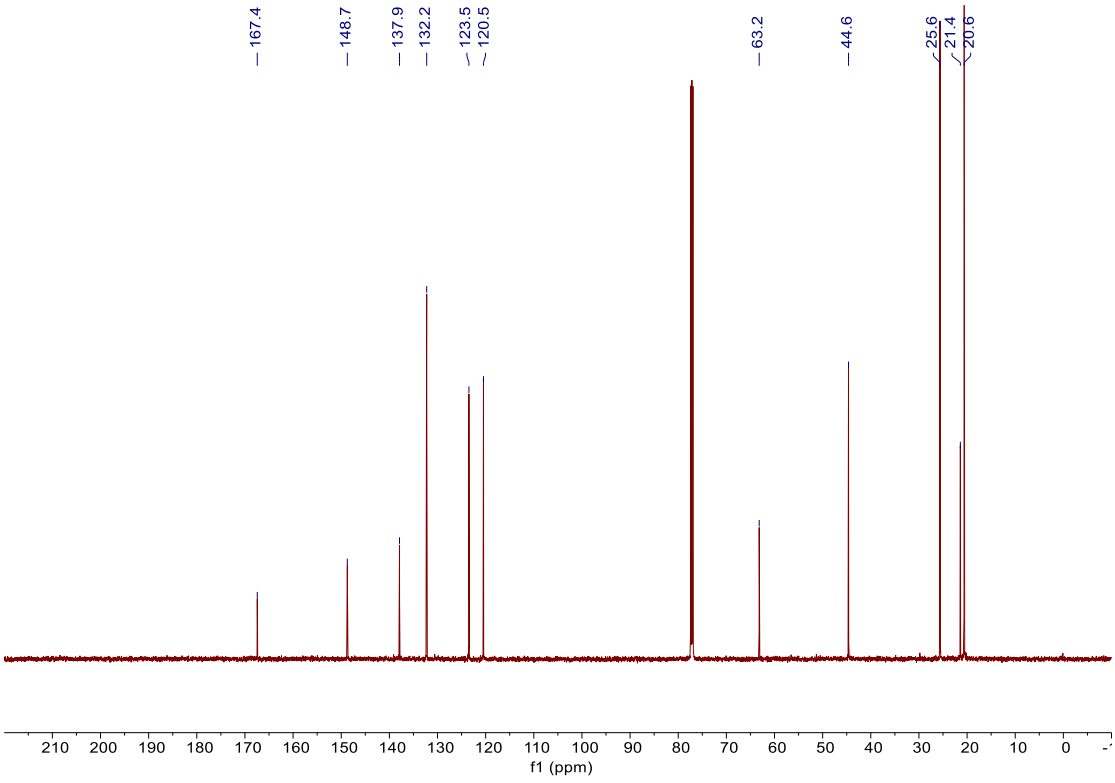
^{13}C NMR of compound **2j** (151 MHz in $CDCl_3$)



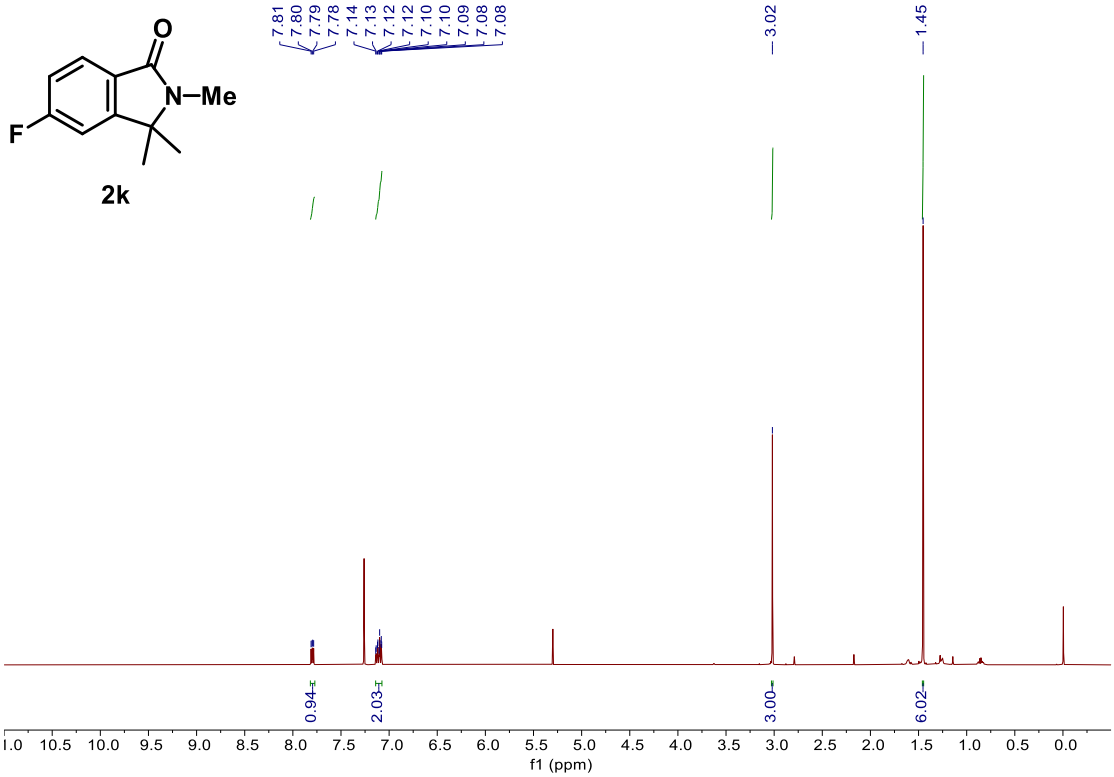
^{1}H NMR of compound **2j'** (600 MHz in $CDCl_3$)



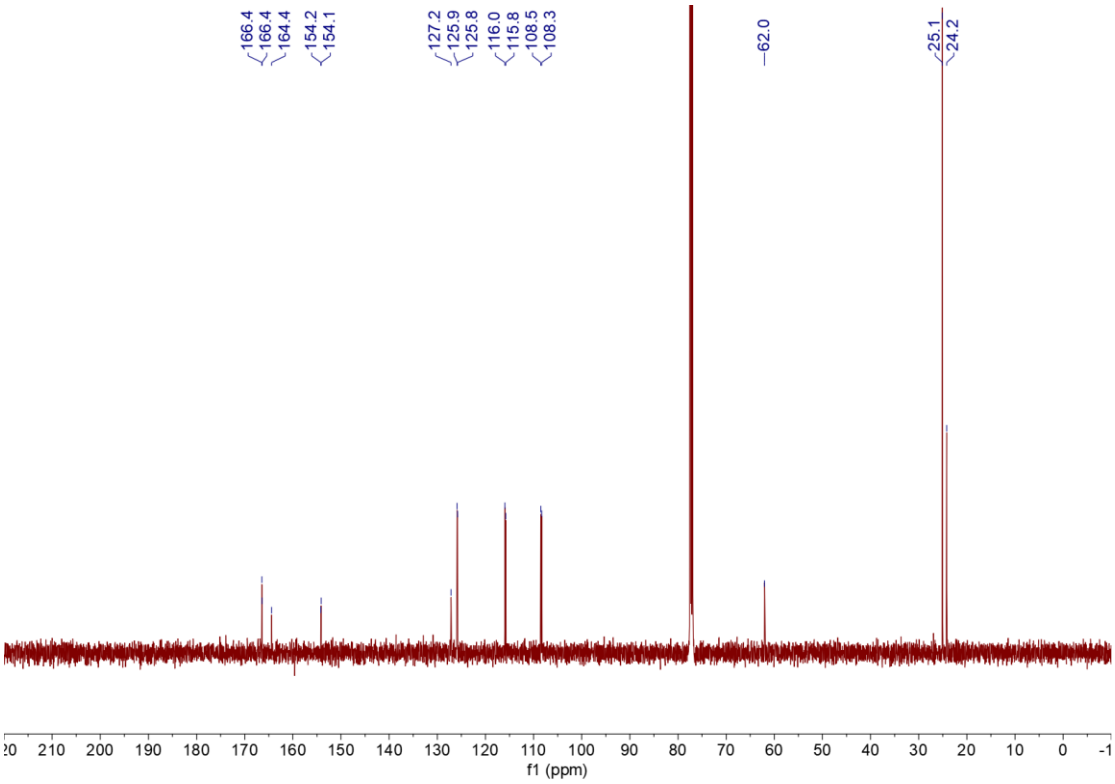
^{13}C NMR of compound **2j'** (600 MHz in $CDCl_3$)



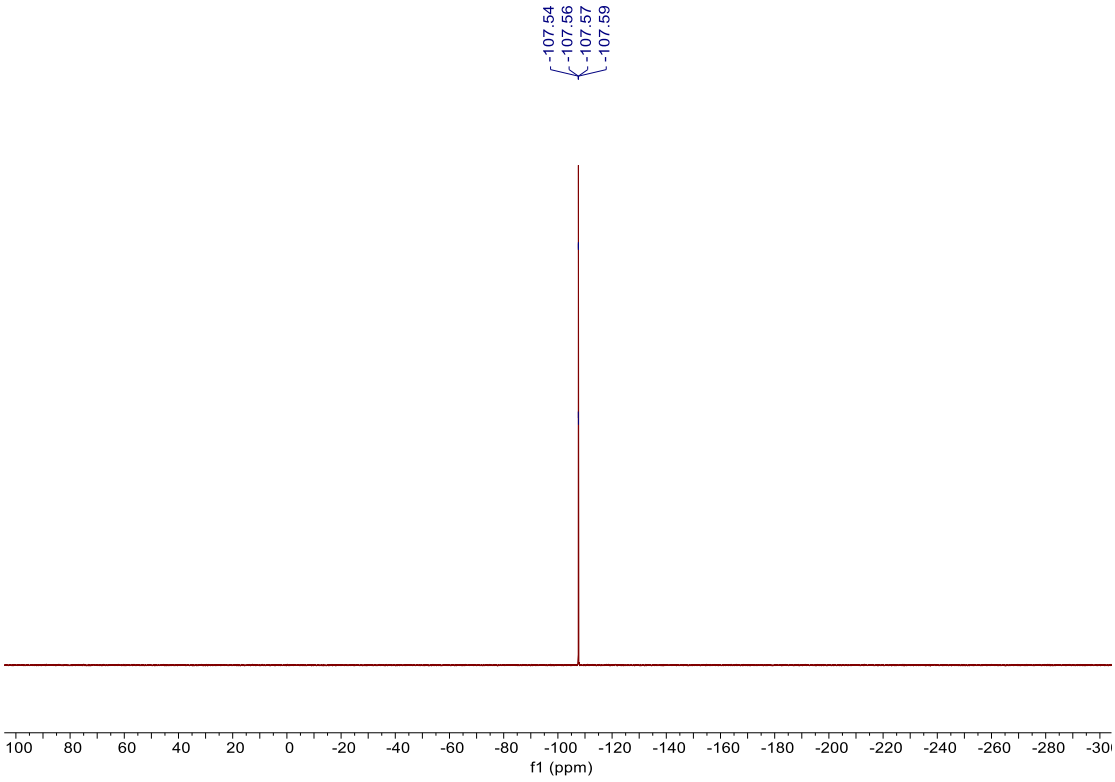
^{1}H NMR of compound **2k** (500 MHz in $CDCl_3$)



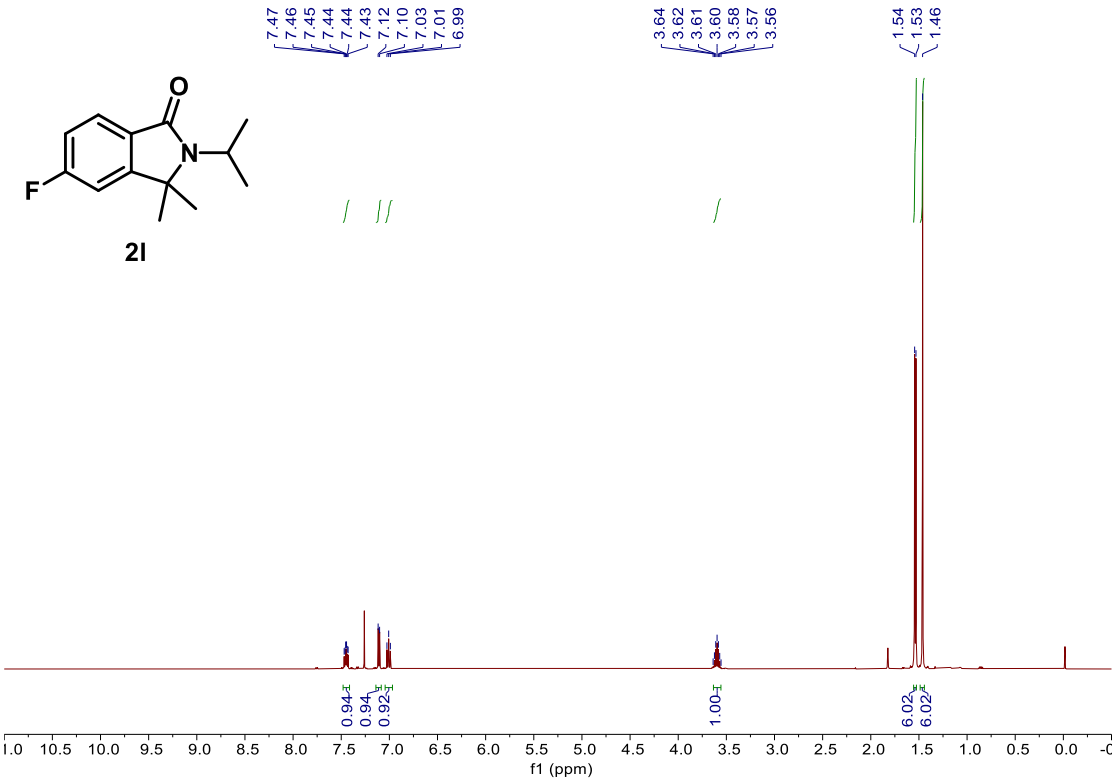
^{13}C NMR of compound **2k** (126 MHz in $CDCl_3$)



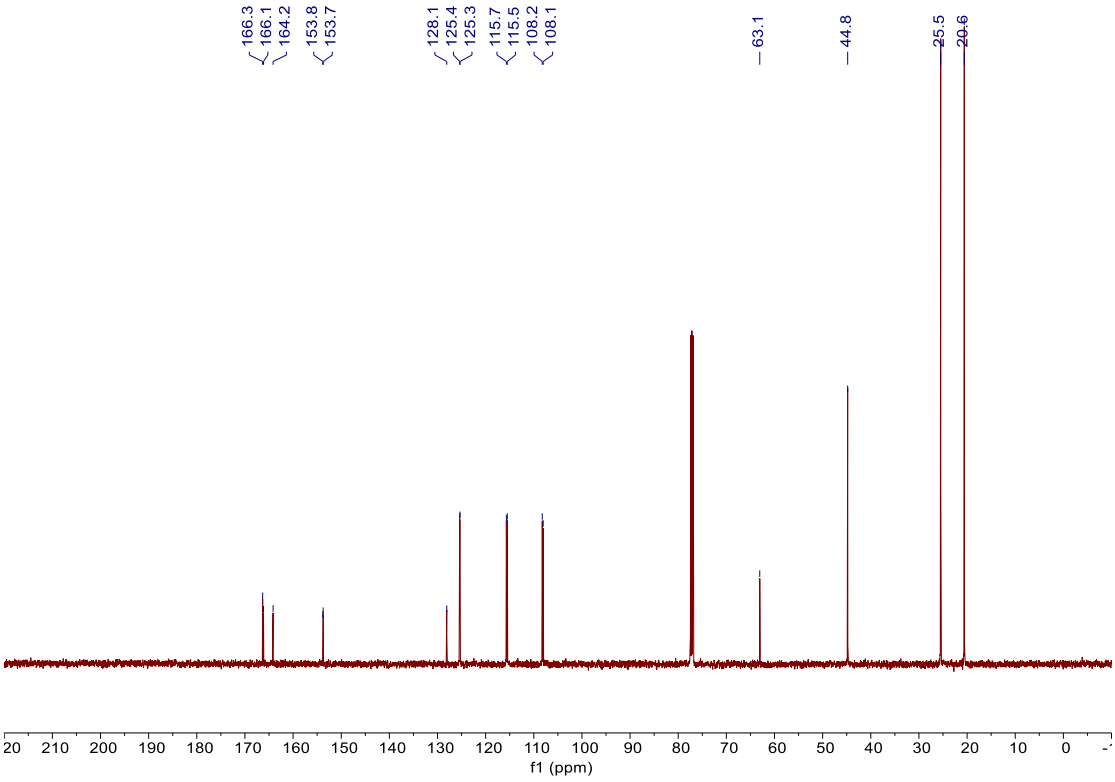
^{19}F NMR of compound **2k** (471 MHz in $CDCl_3$)



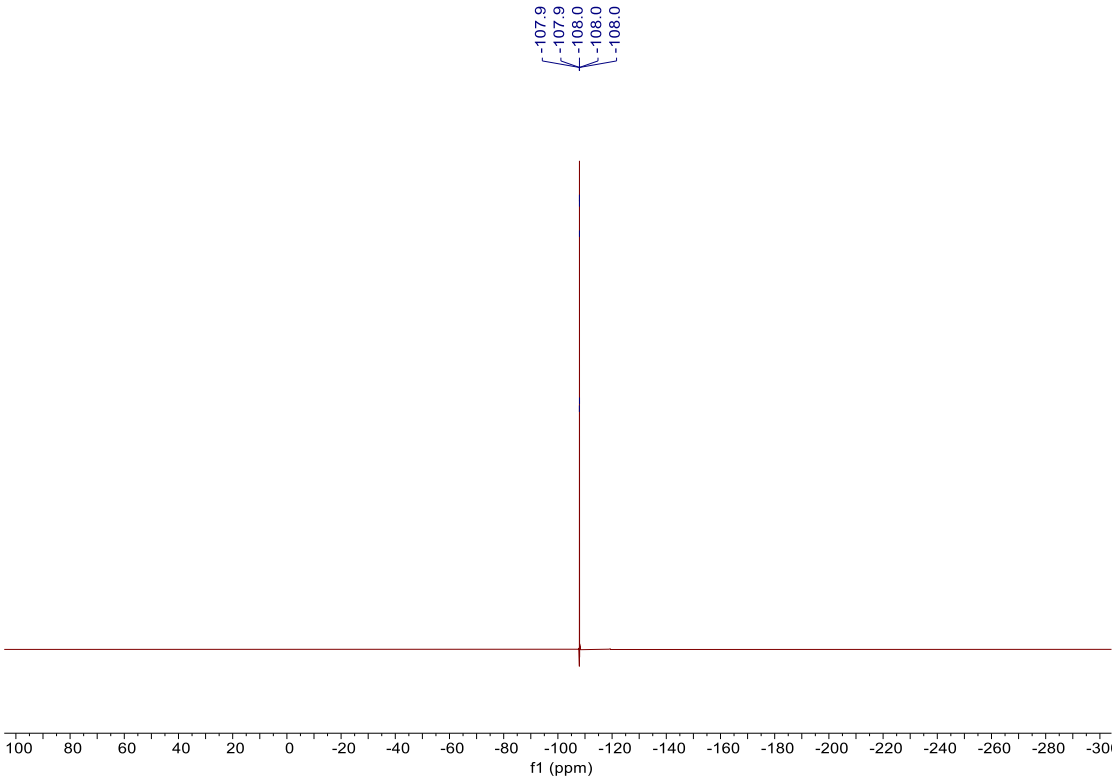
^{1}H NMR of compound **2l** (500 MHz in $CDCl_3$)



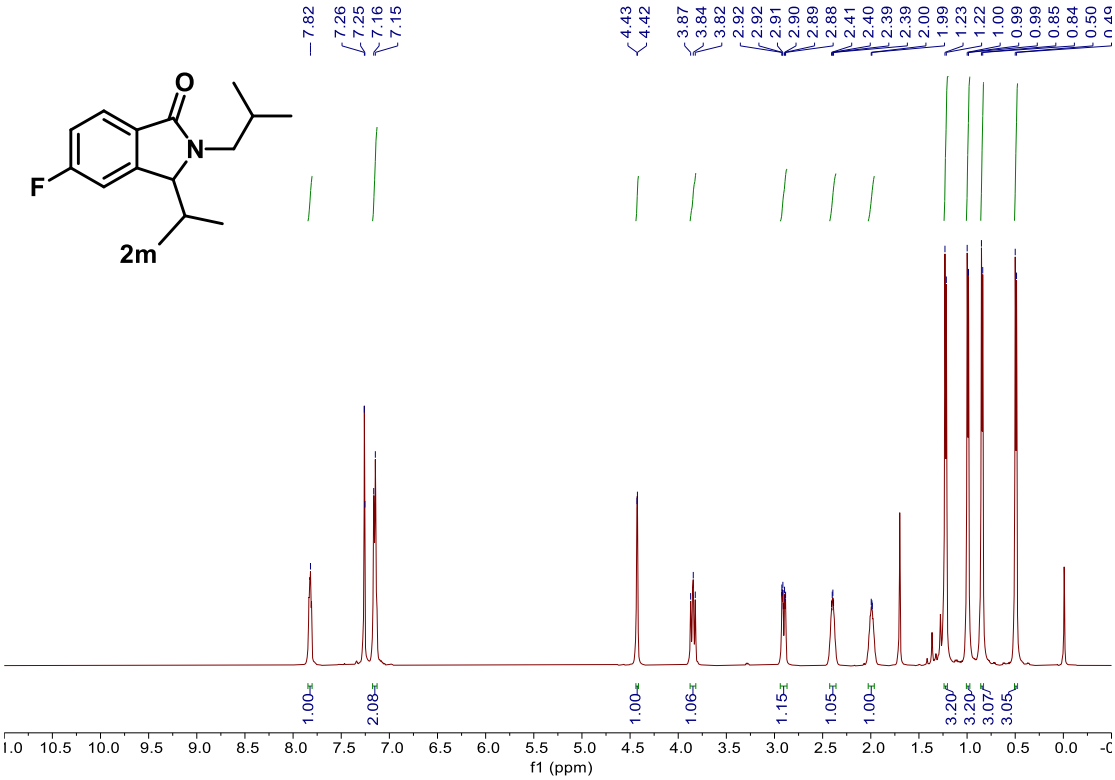
^{13}C NMR of compound **2l** (126 MHz in $CDCl_3$)



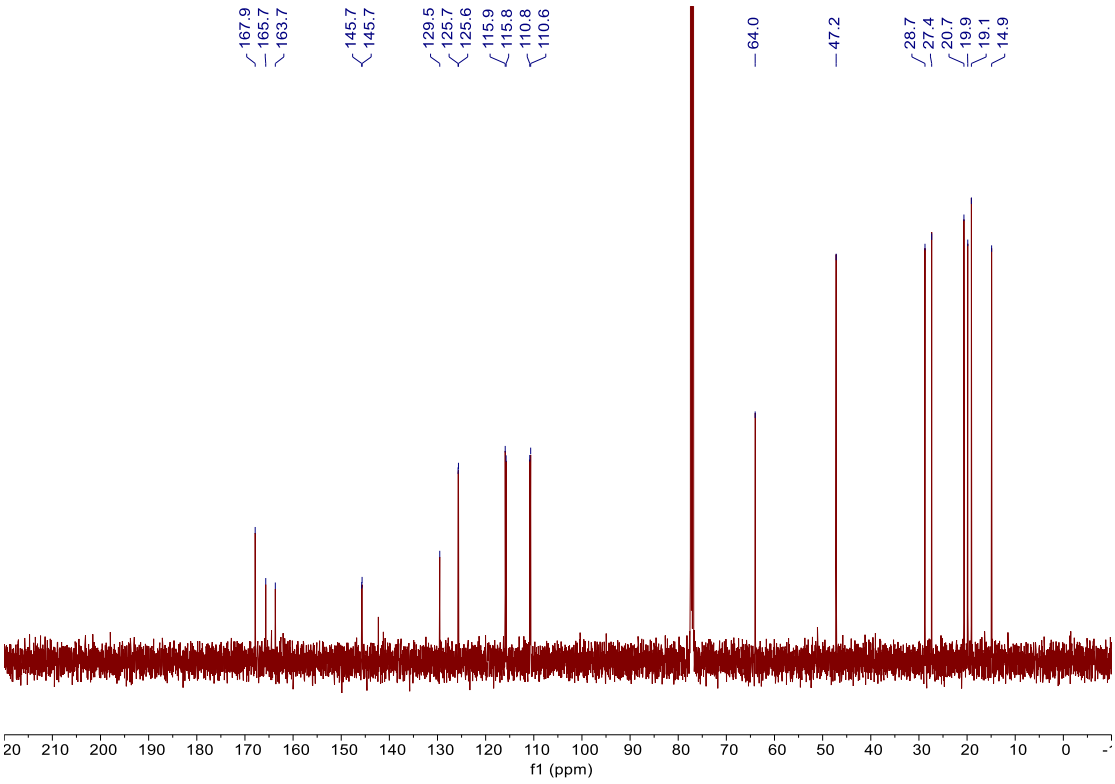
^{19}F NMR of compound **2l** (471 MHz in $CDCl_3$)



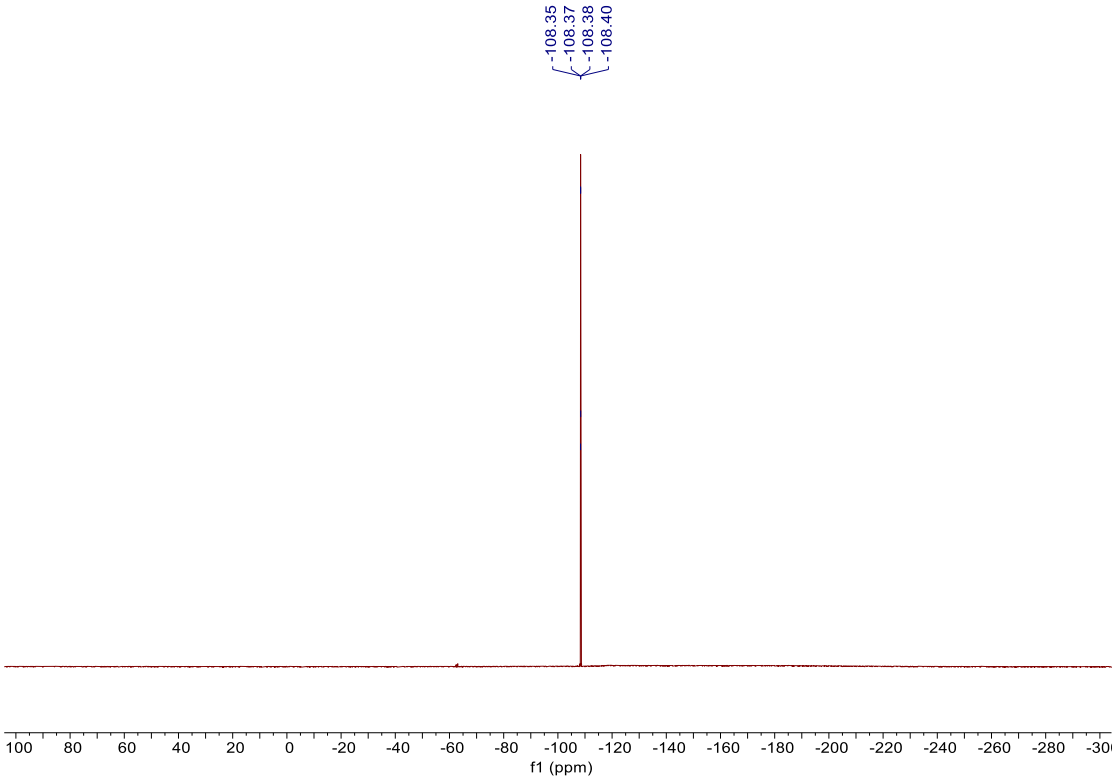
^{1}H NMR of compound **2m** (500 MHz in $CDCl_3$)



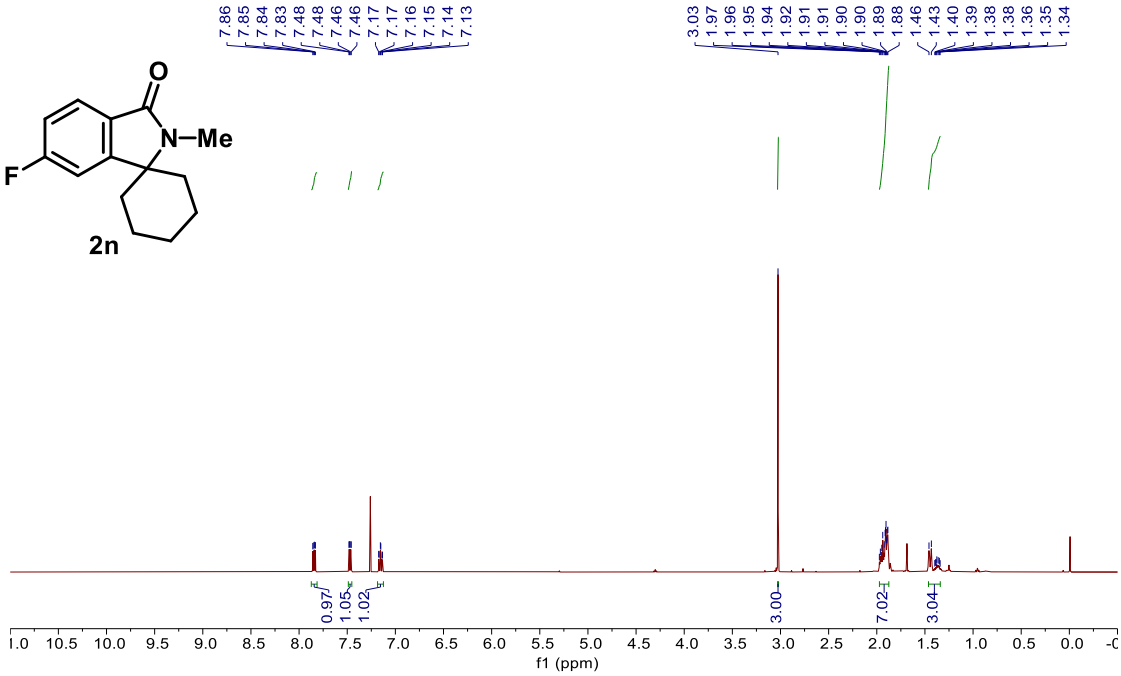
^{13}C NMR of compound **2m** (126 MHz in $CDCl_3$)



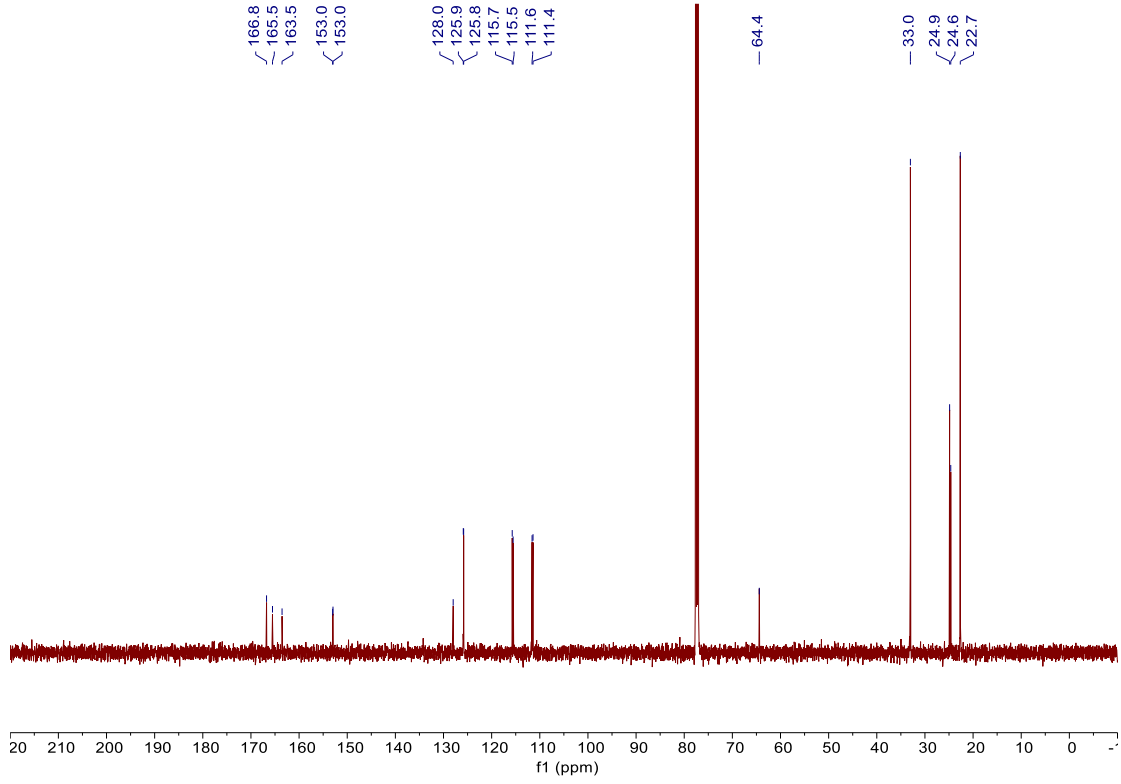
^{19}F NMR of compound **2m** (471 MHz in $CDCl_3$)



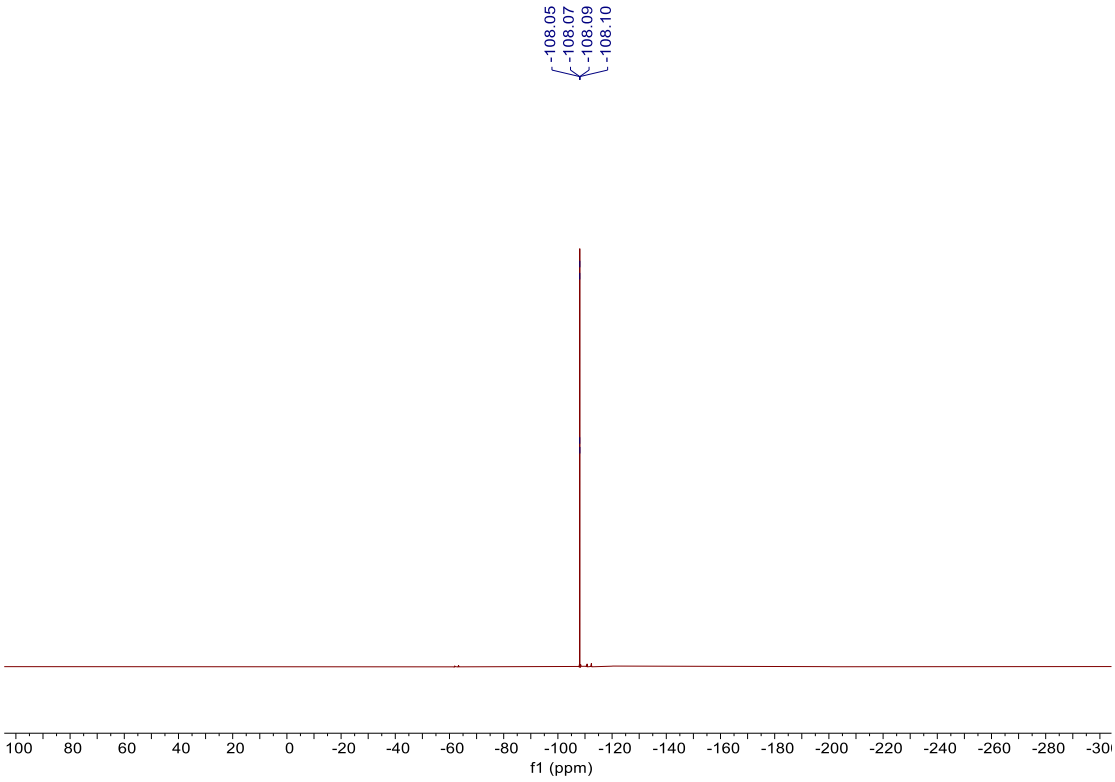
^{1}H NMR of compound **2n** (500 MHz in $CDCl_3$)



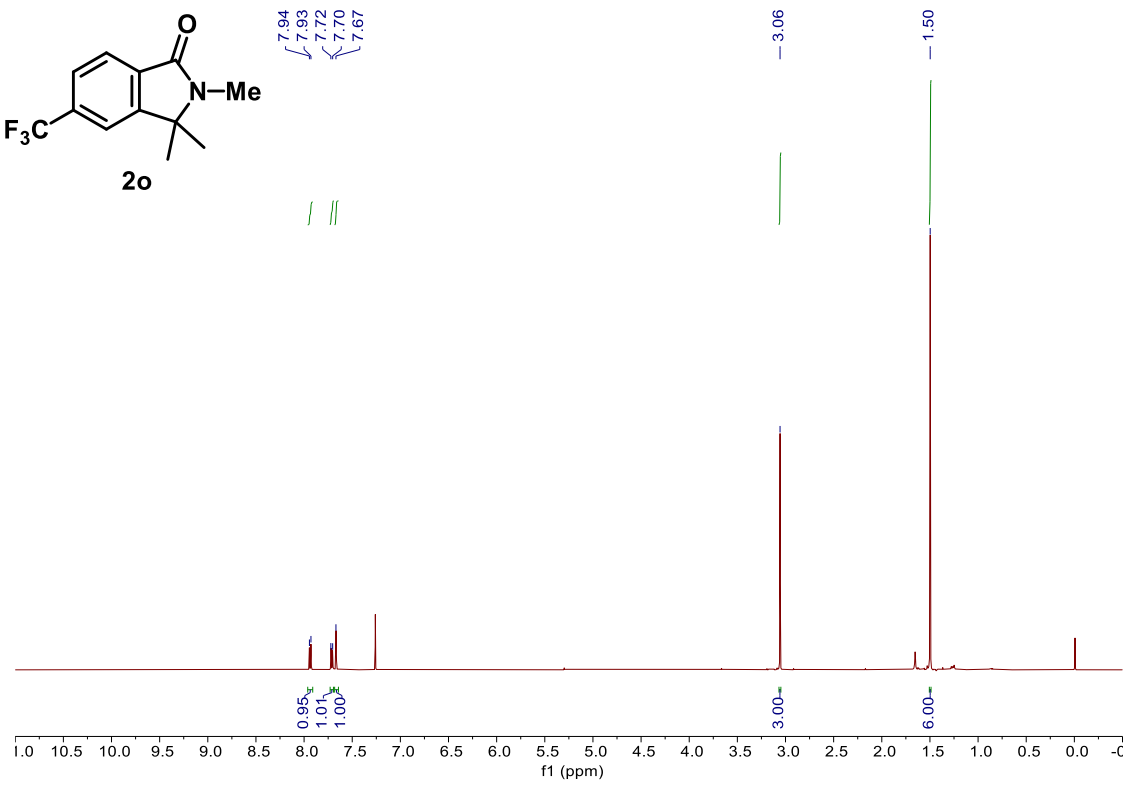
^{13}C NMR of compound **2n** (126 MHz in $CDCl_3$)



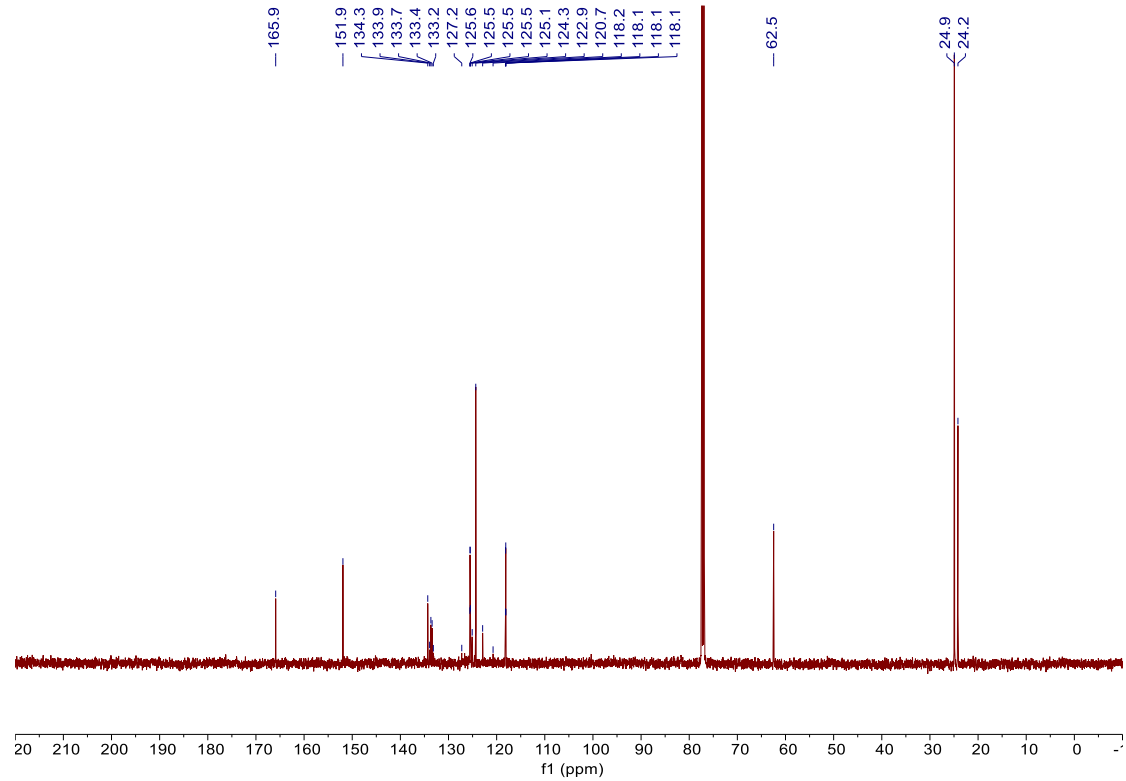
^{19}F NMR of compound **2n** (471 MHz in $CDCl_3$)



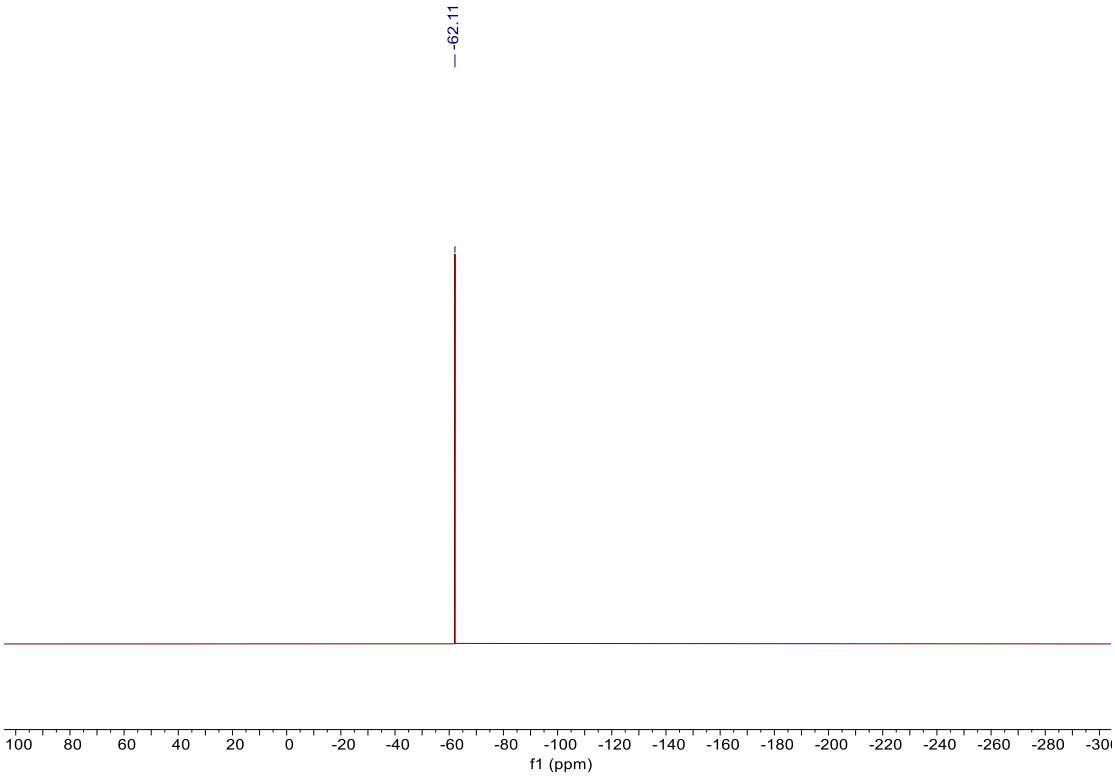
^{1}H NMR of compound **2o** (500 MHz in $CDCl_3$)



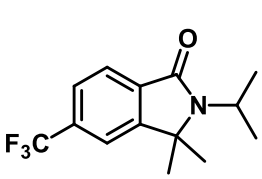
^{13}C NMR of compound **2o** (126 MHz in $CDCl_3$)



^{19}F NMR of compound **2o** (471 MHz in $CDCl_3$)

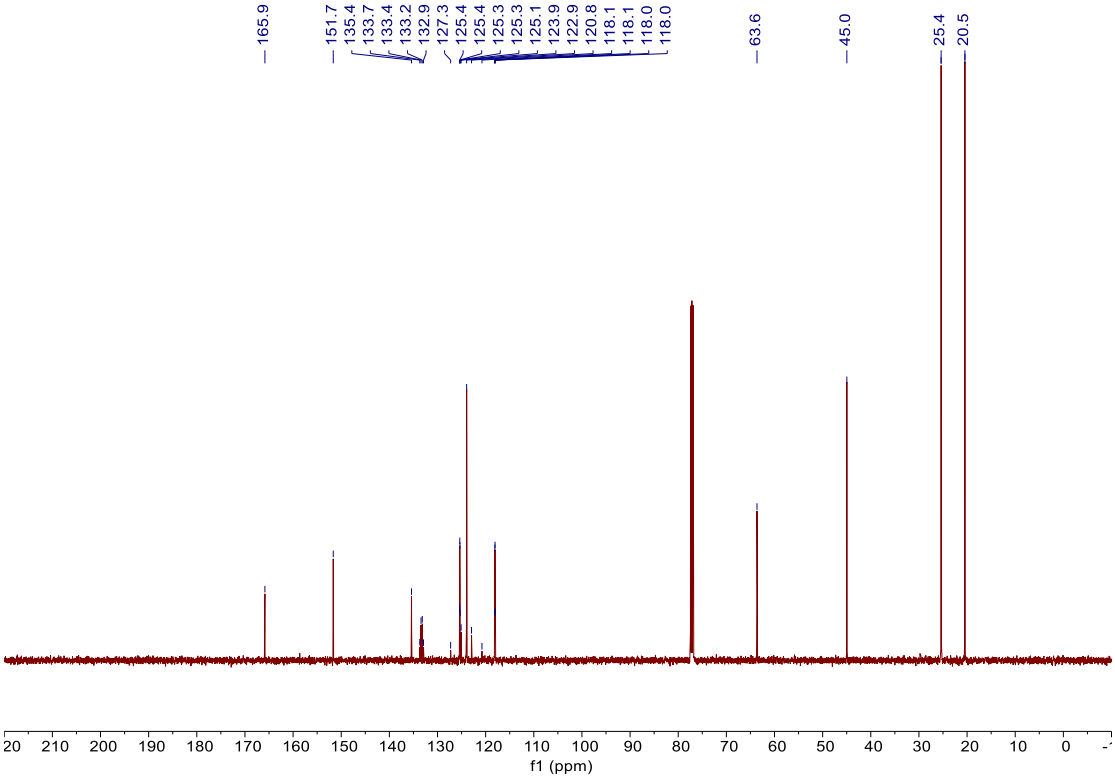


^{1}H NMR of compound **2p** (500 MHz in $CDCl_3$)

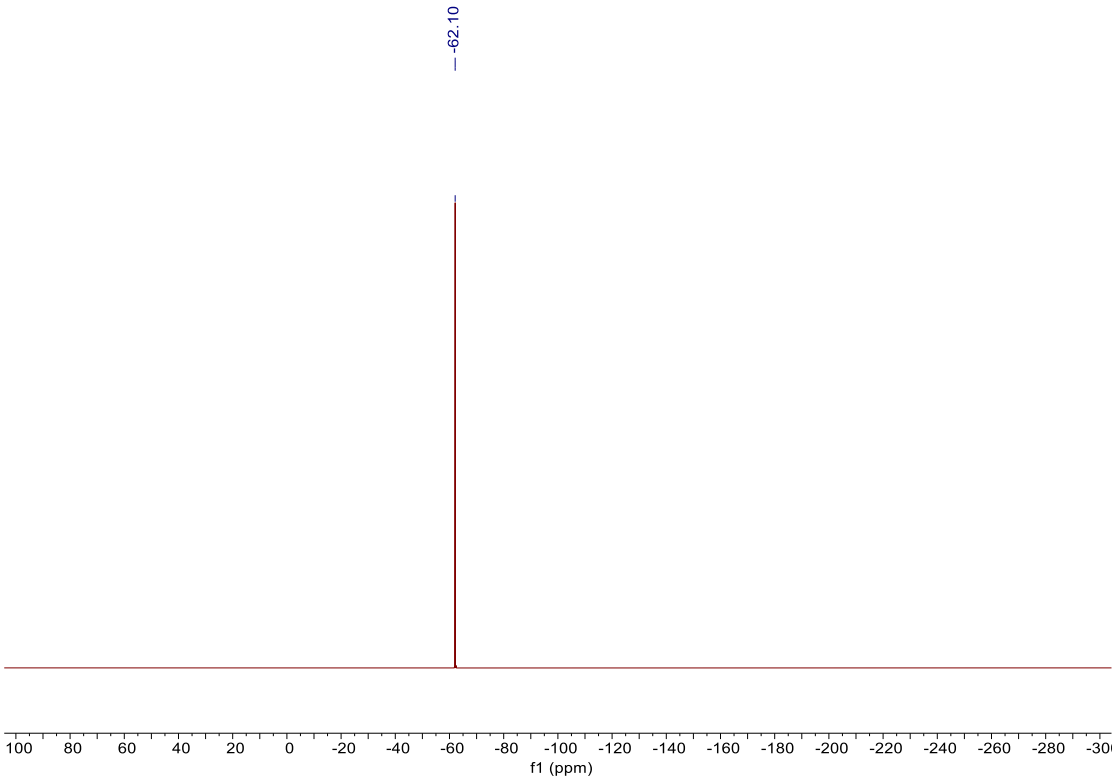


2p

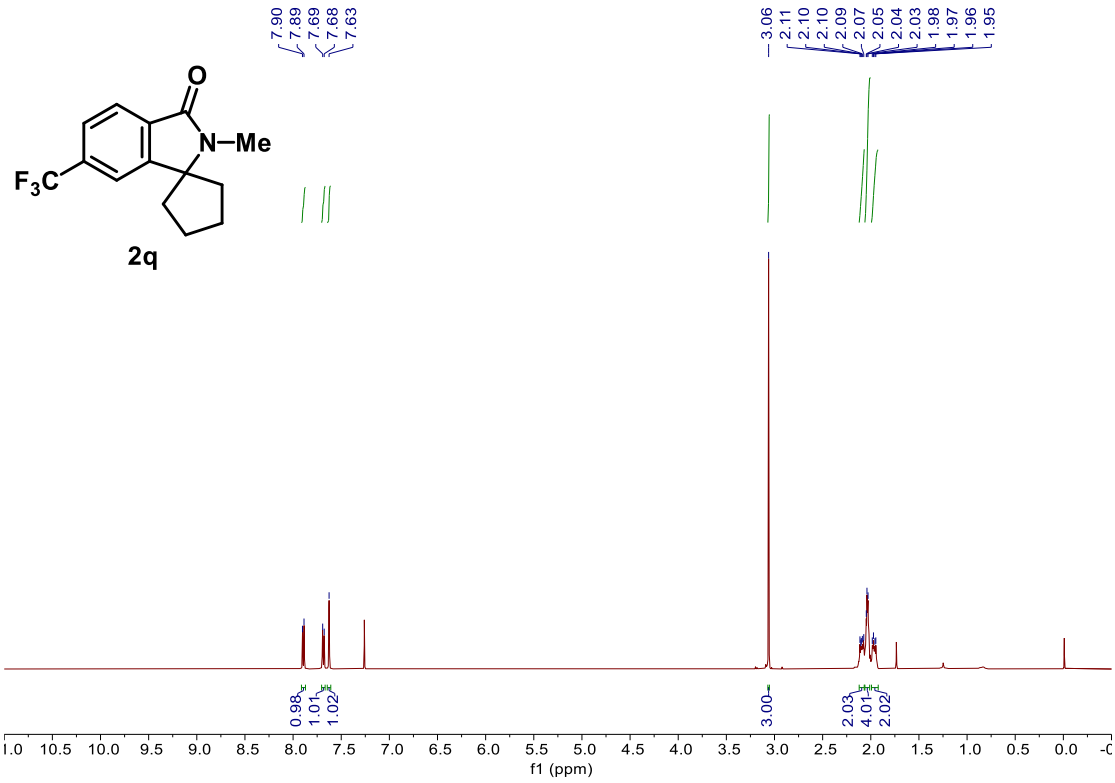
^{13}C NMR of compound **2p** (126 MHz in $CDCl_3$)



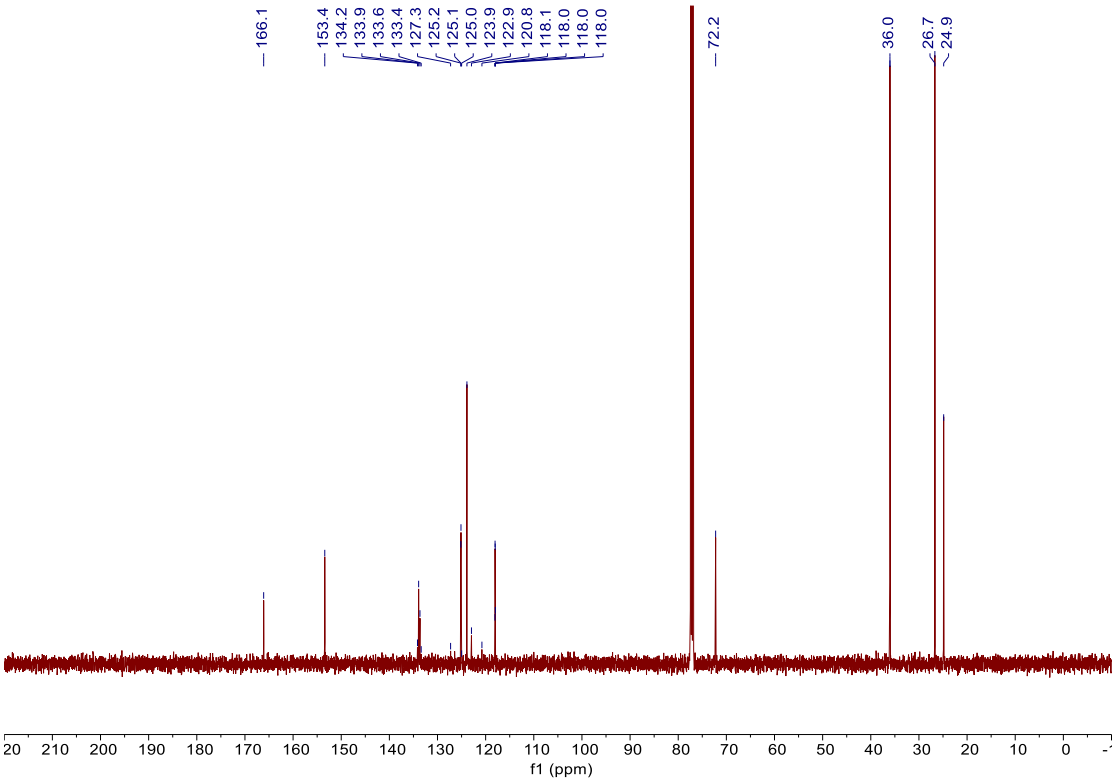
^{19}F NMR of compound **2p** (471 MHz in $CDCl_3$)



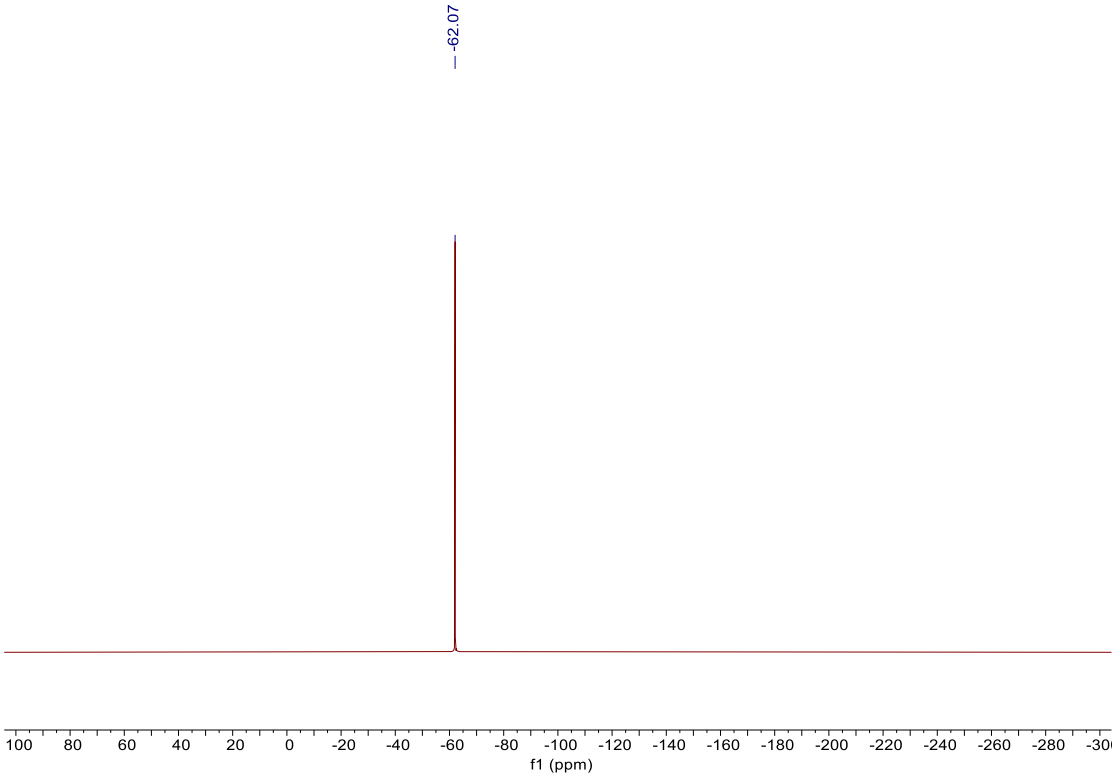
^{1}H NMR of compound **2q** (500 MHz in $CDCl_3$)



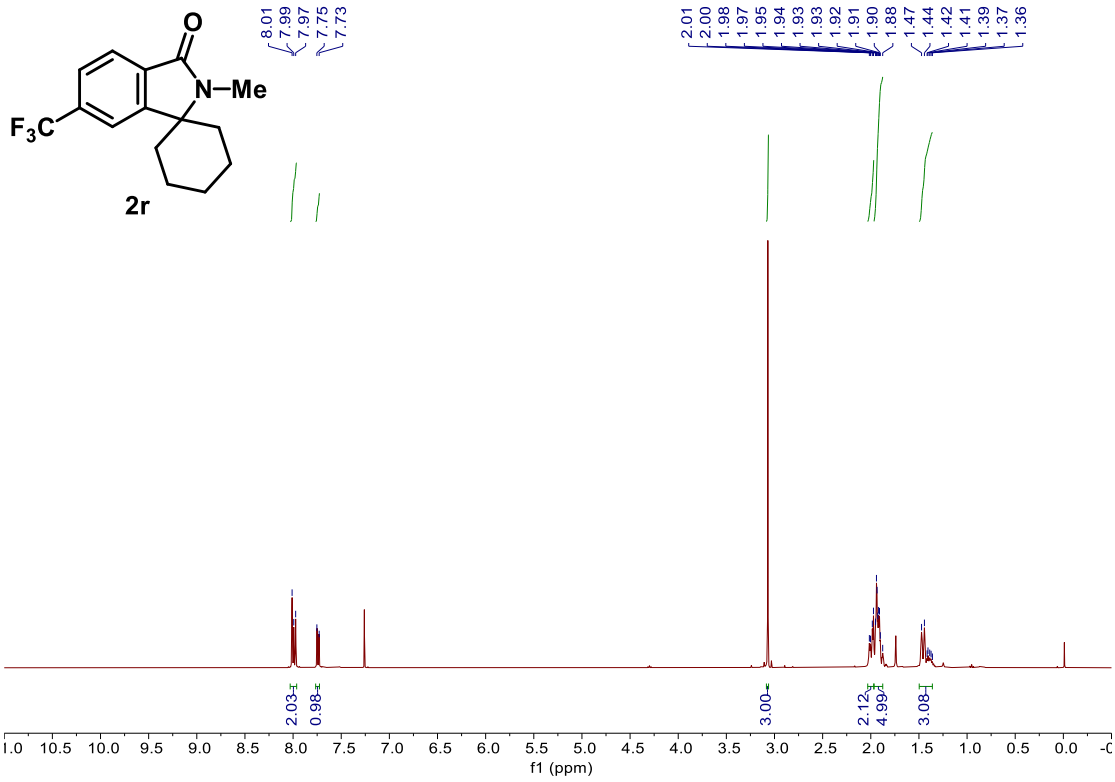
^{13}C NMR of compound **2q** (126 MHz in $CDCl_3$)



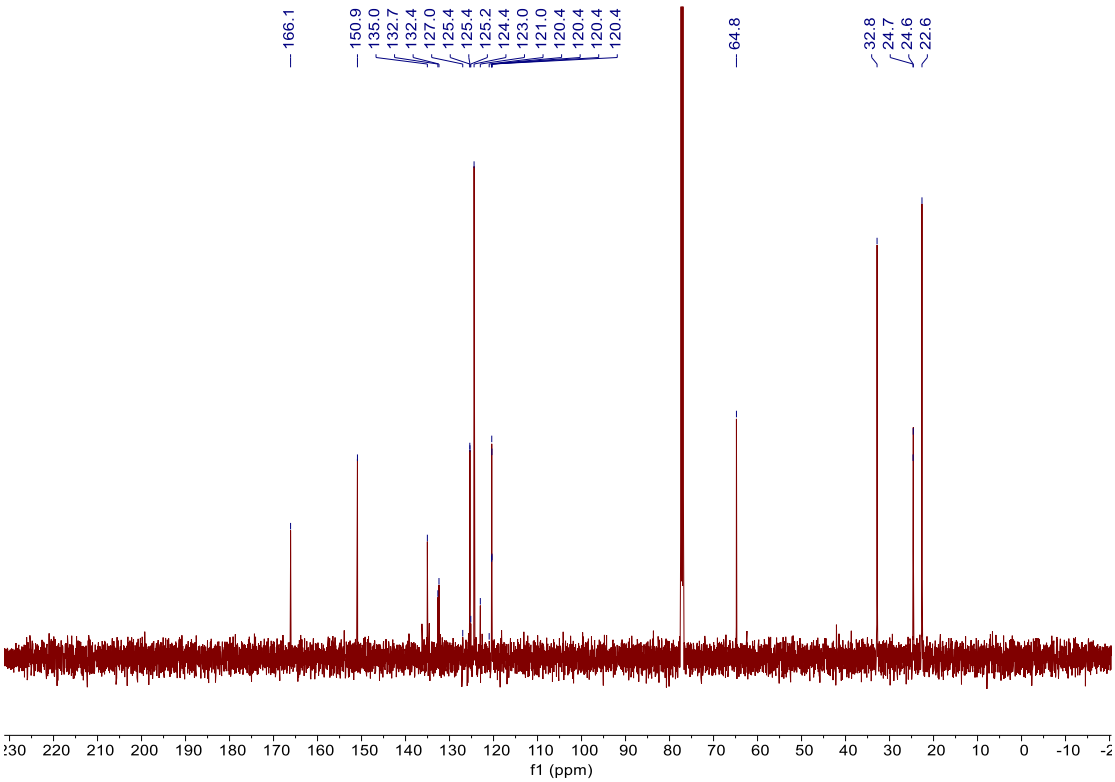
^{19}F NMR of compound **2q** (471 MHz in $CDCl_3$)



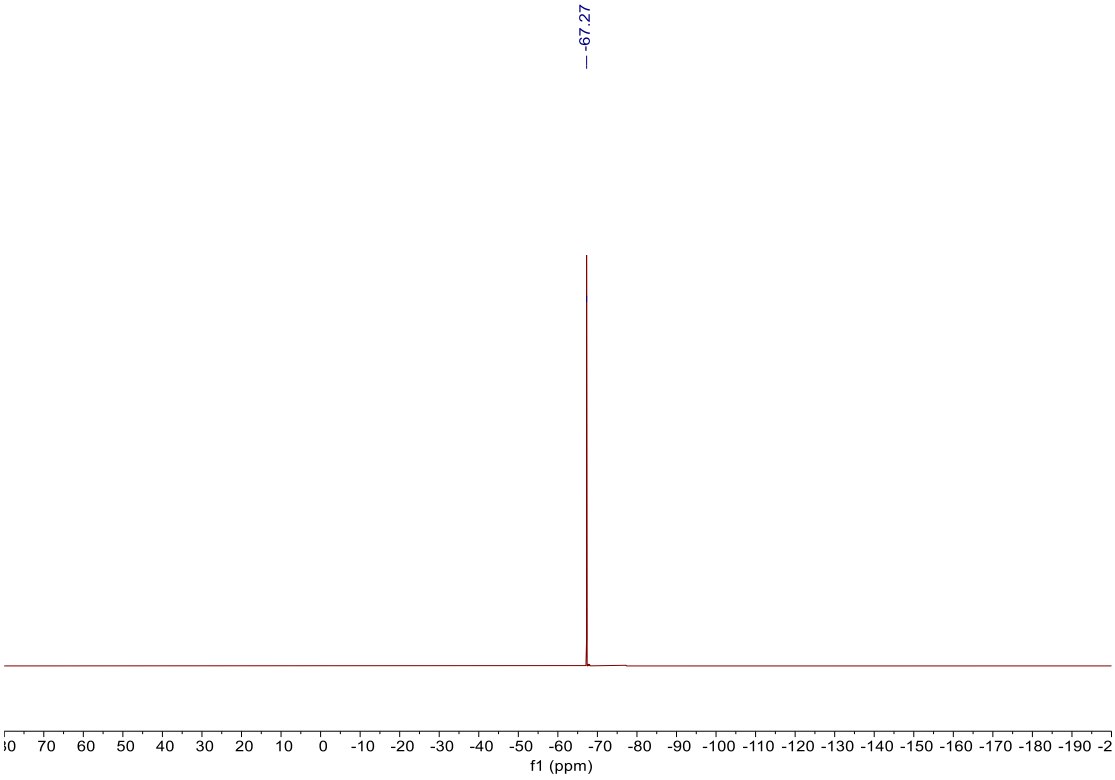
^{1}H NMR of compound **2r** (400 MHz in $CDCl_3$)



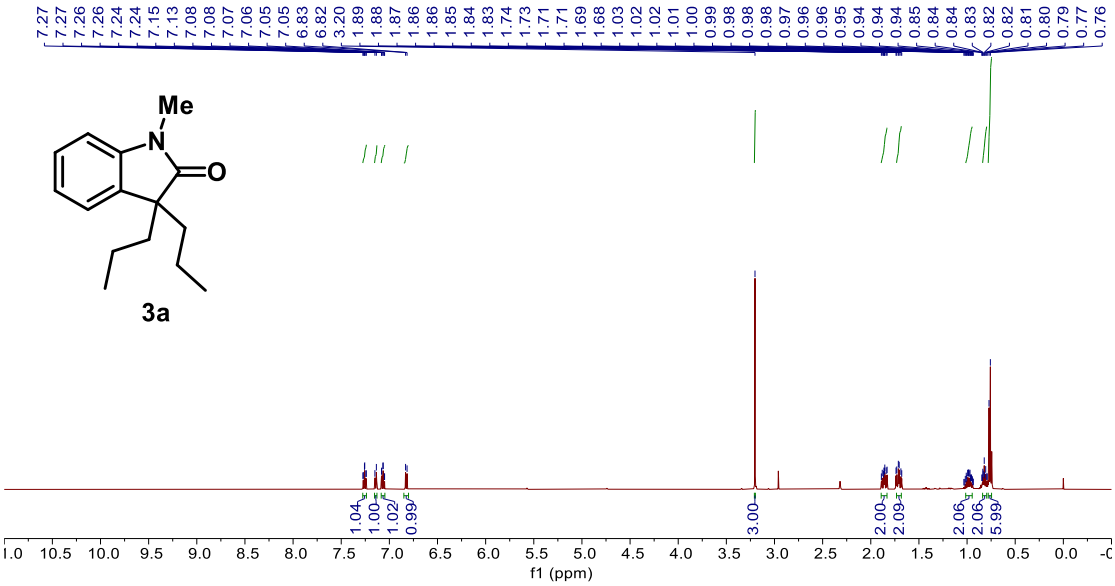
^{13}C NMR of compound **2r** (126 MHz in $CDCl_3$)



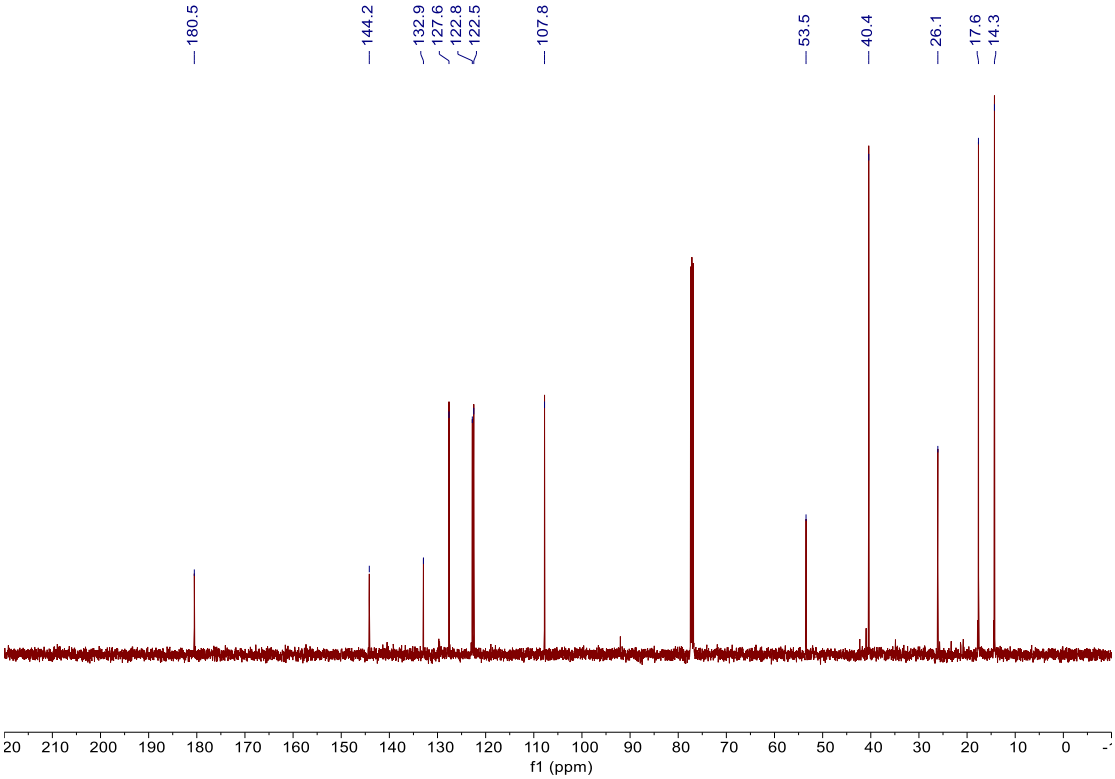
^{19}F NMR of compound **2r** (471 MHz in $CDCl_3$)



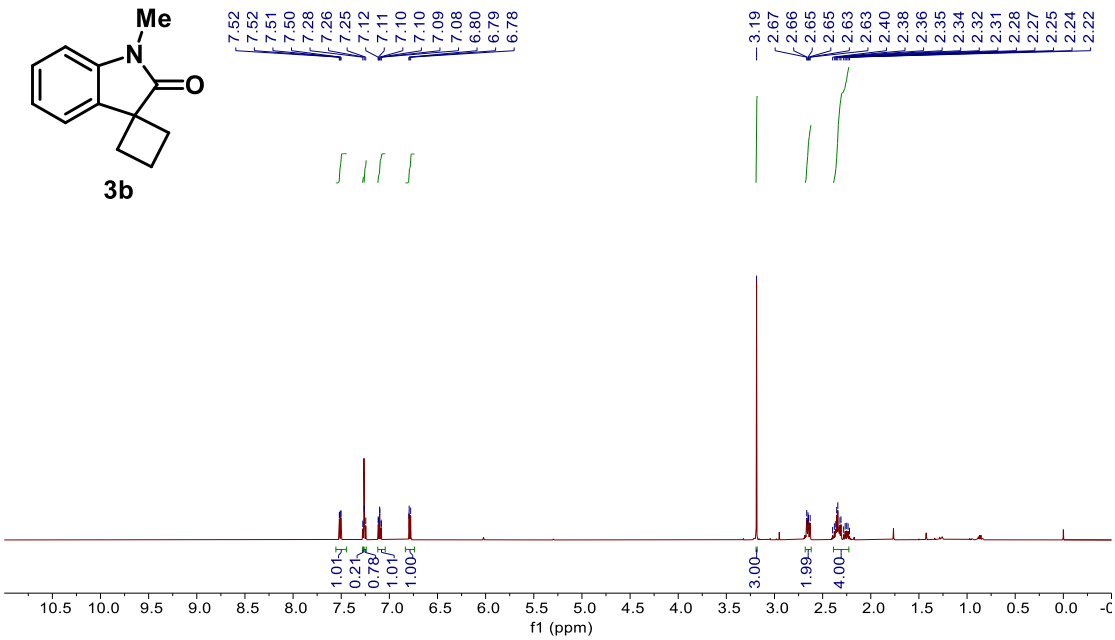
^{1}H NMR of compound **3a** (500 MHz in $CDCl_3$)



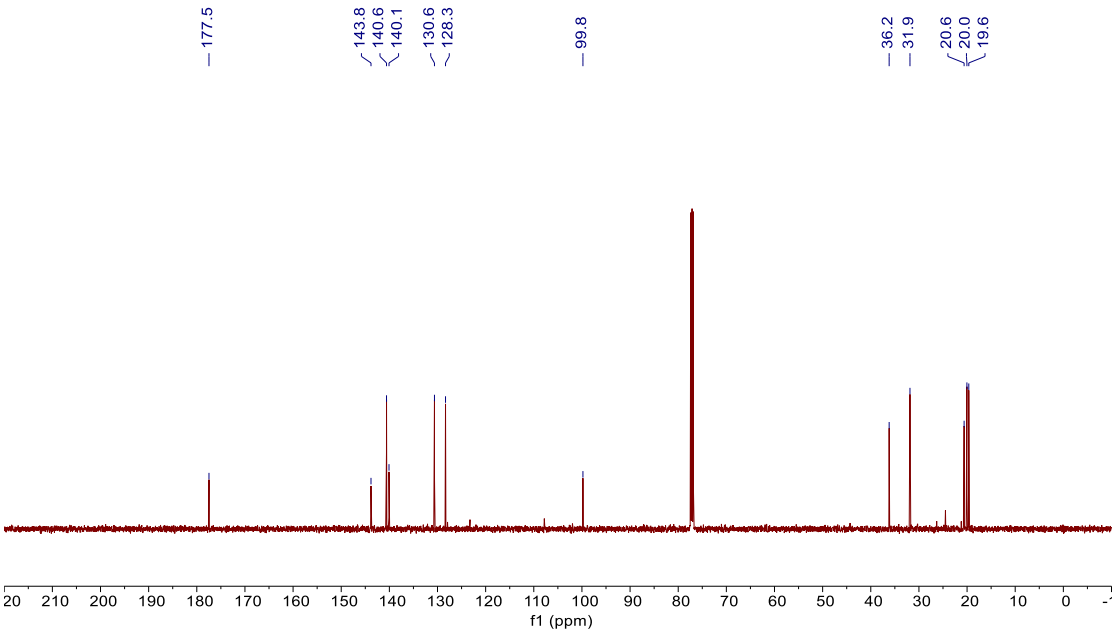
^{13}C NMR of compound **3a** (126 MHz in $CDCl_3$)



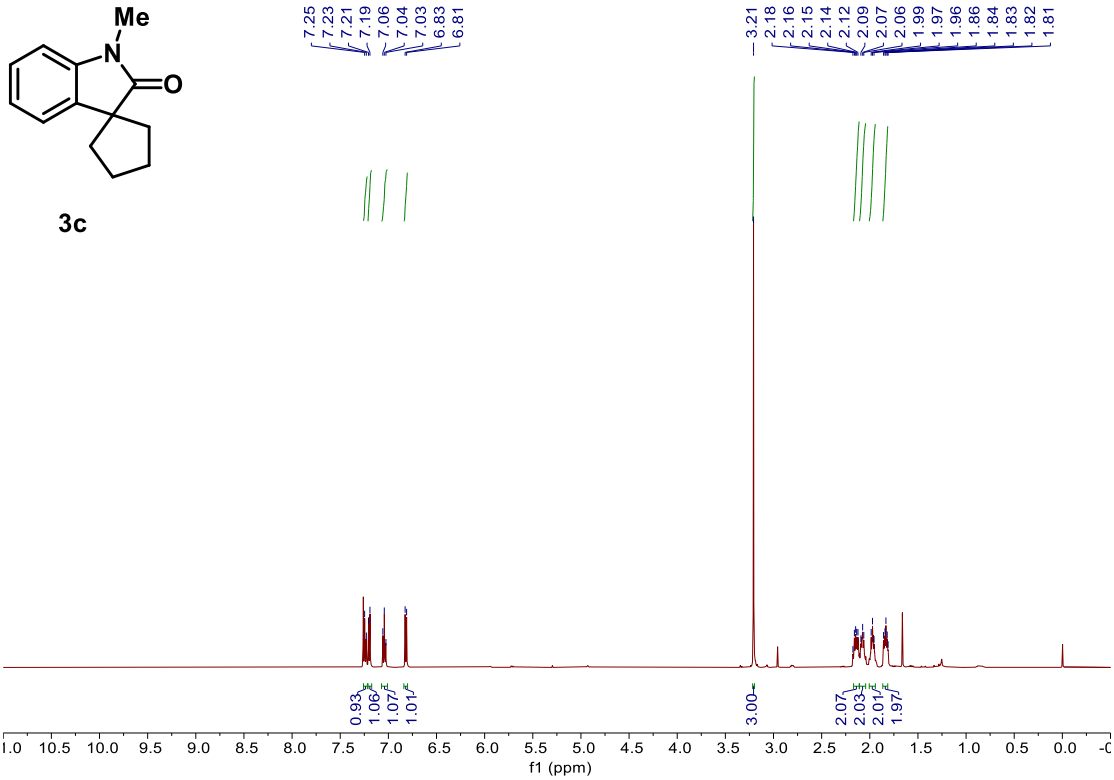
^{1}H NMR of compound **3b** (500 MHz in $CDCl_3$)



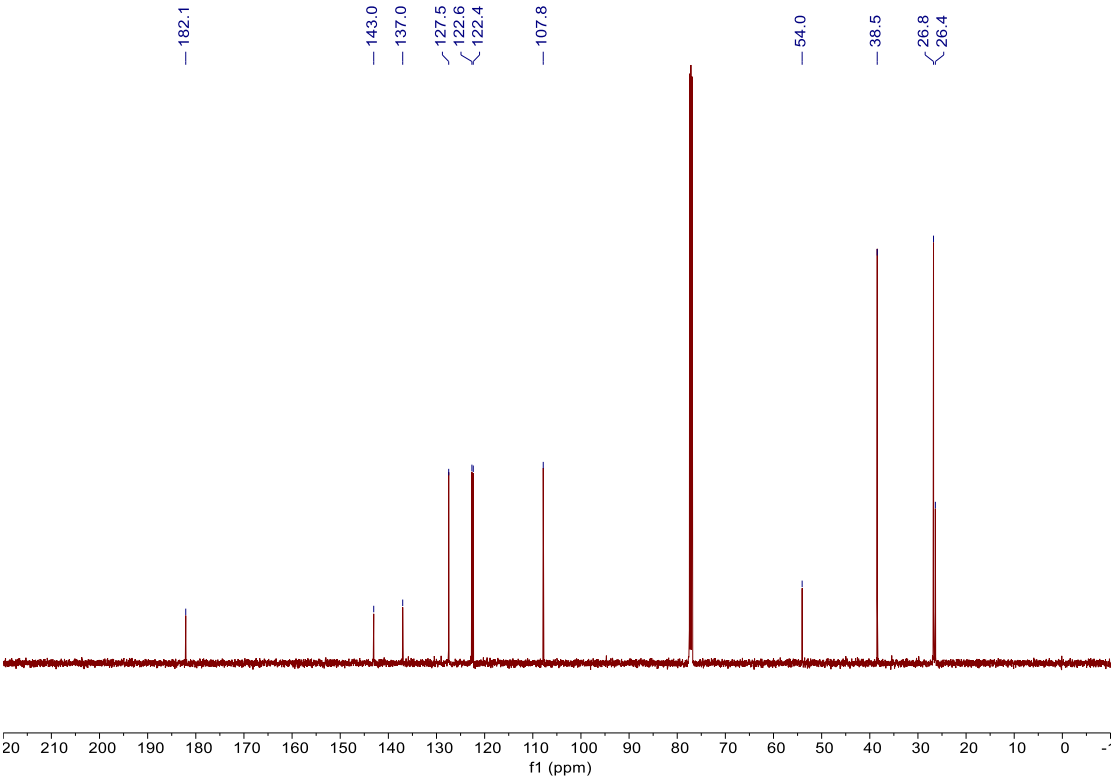
^{13}C NMR of compound **3b** (126 MHz in $CDCl_3$)



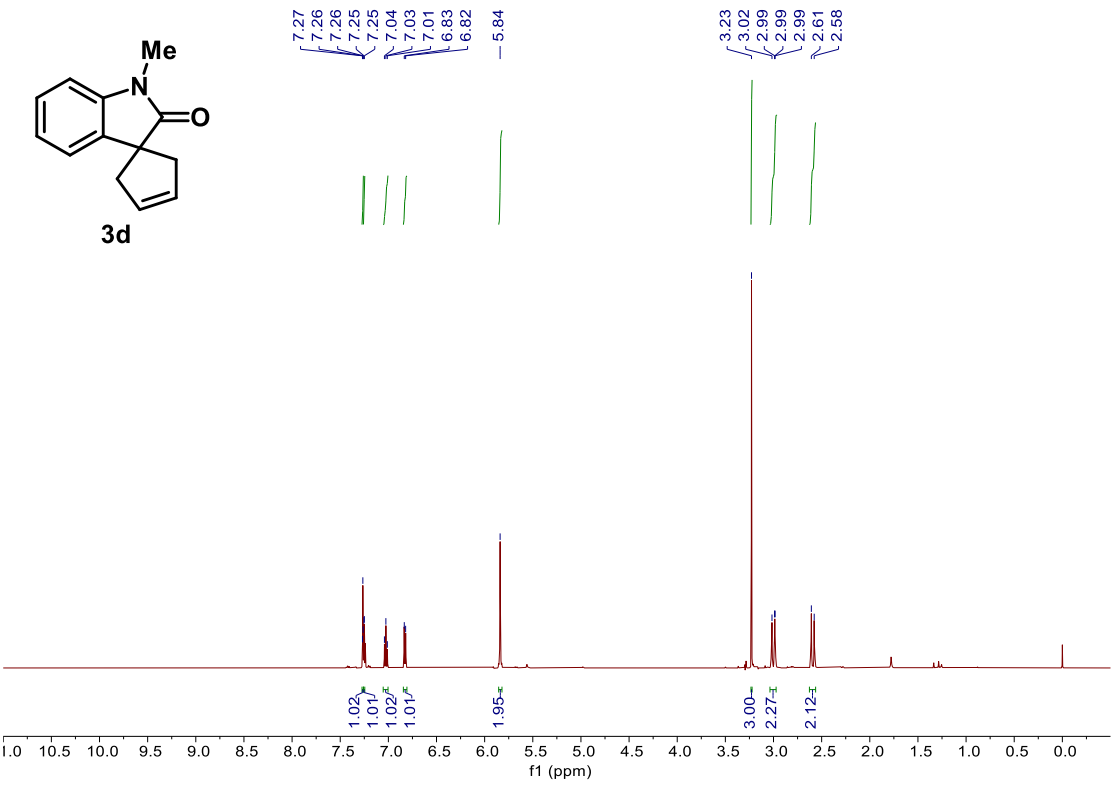
^{1}H NMR of compound **3c** (500 MHz in $CDCl_3$)



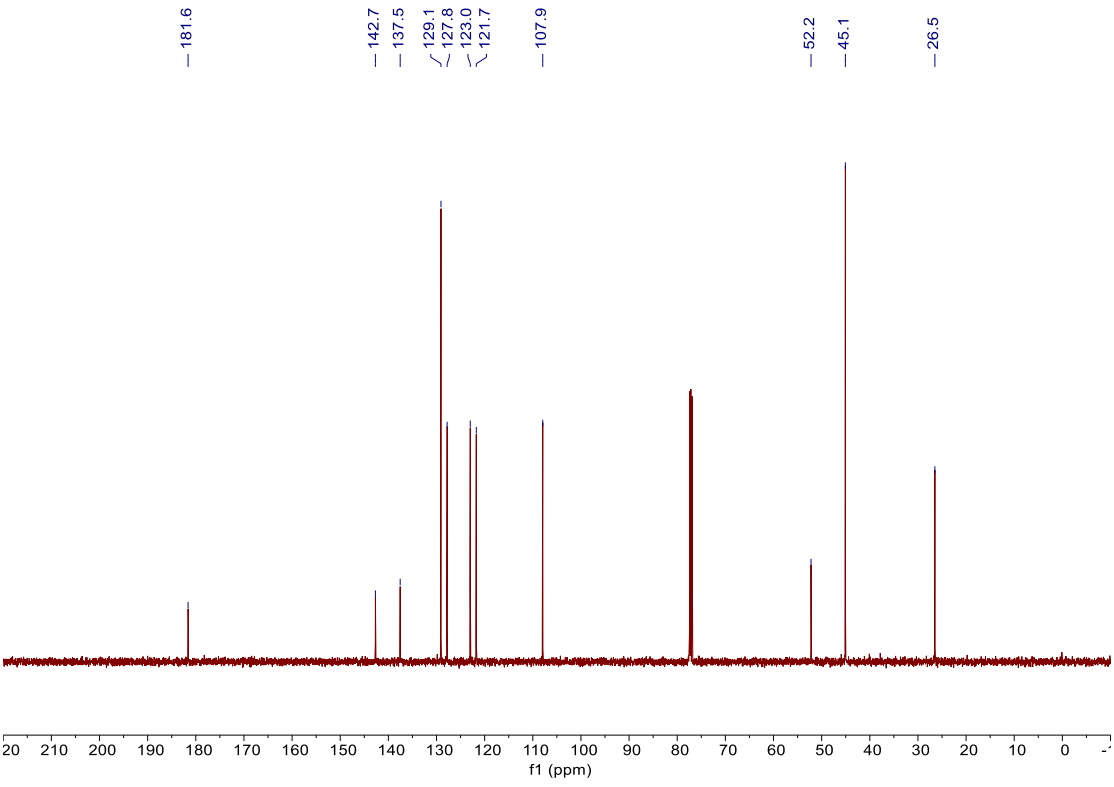
^{13}C NMR of compound **3c** (126 MHz in $CDCl_3$)



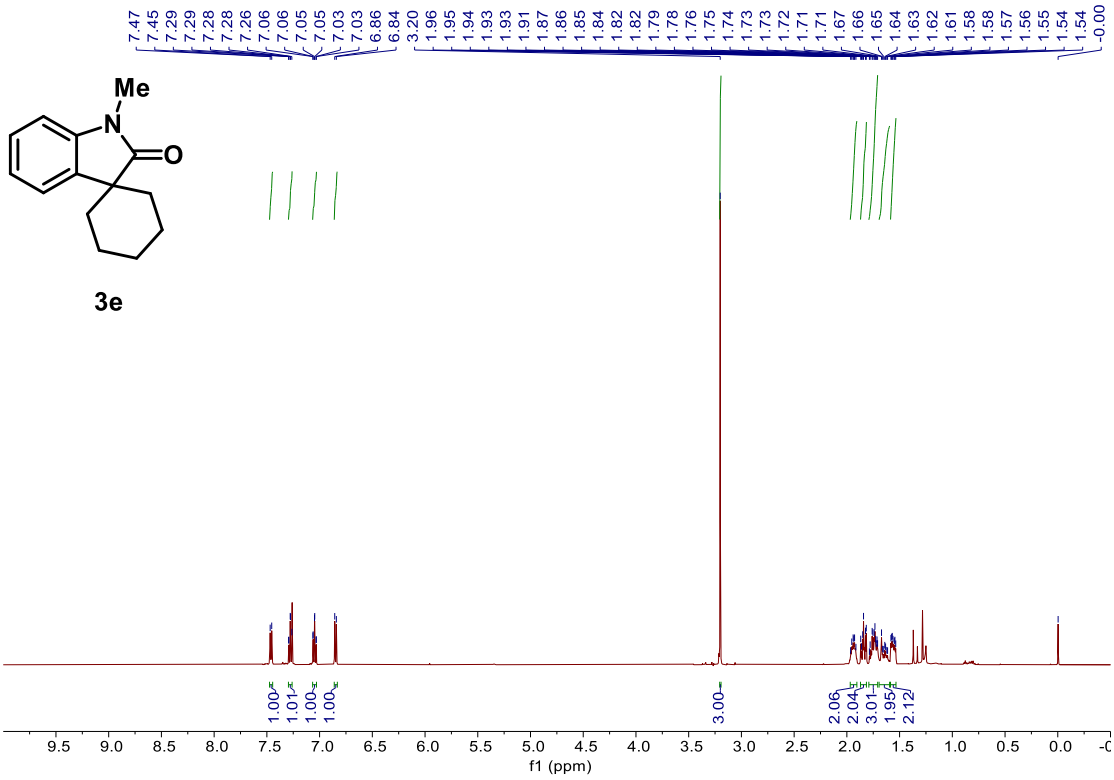
^{1}H NMR of compound **3d** (500 MHz in $CDCl_3$)



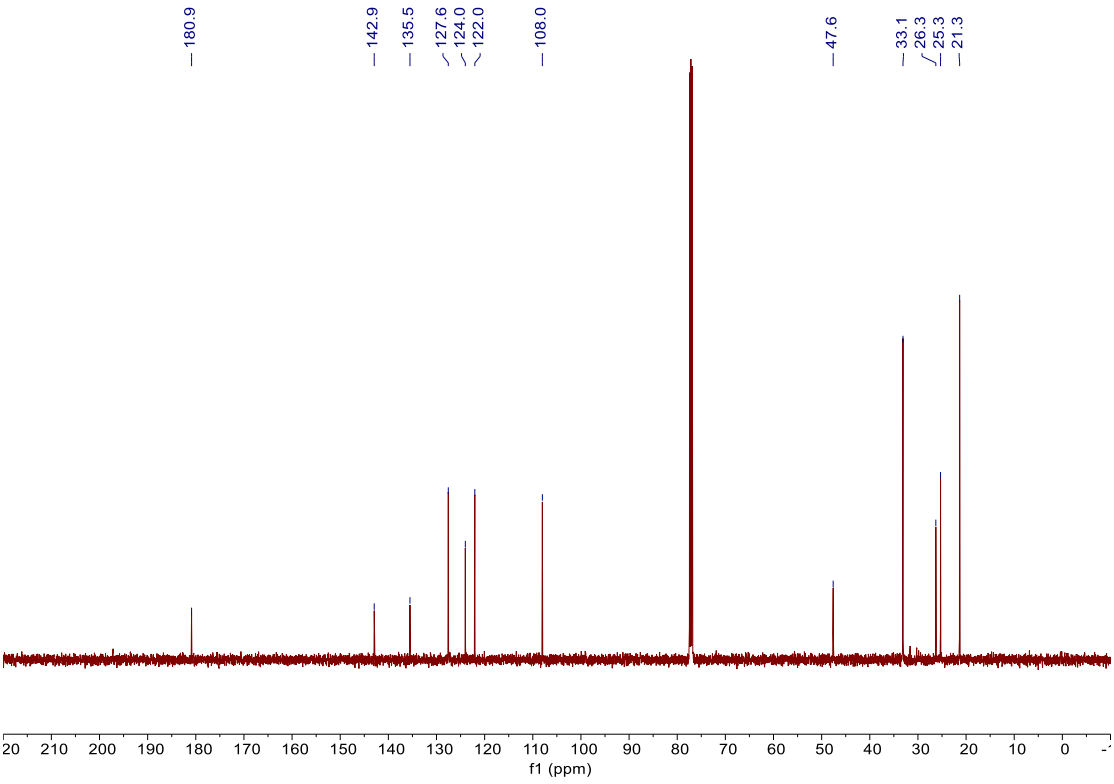
^{13}C NMR of compound **3d** (126 MHz in $CDCl_3$)



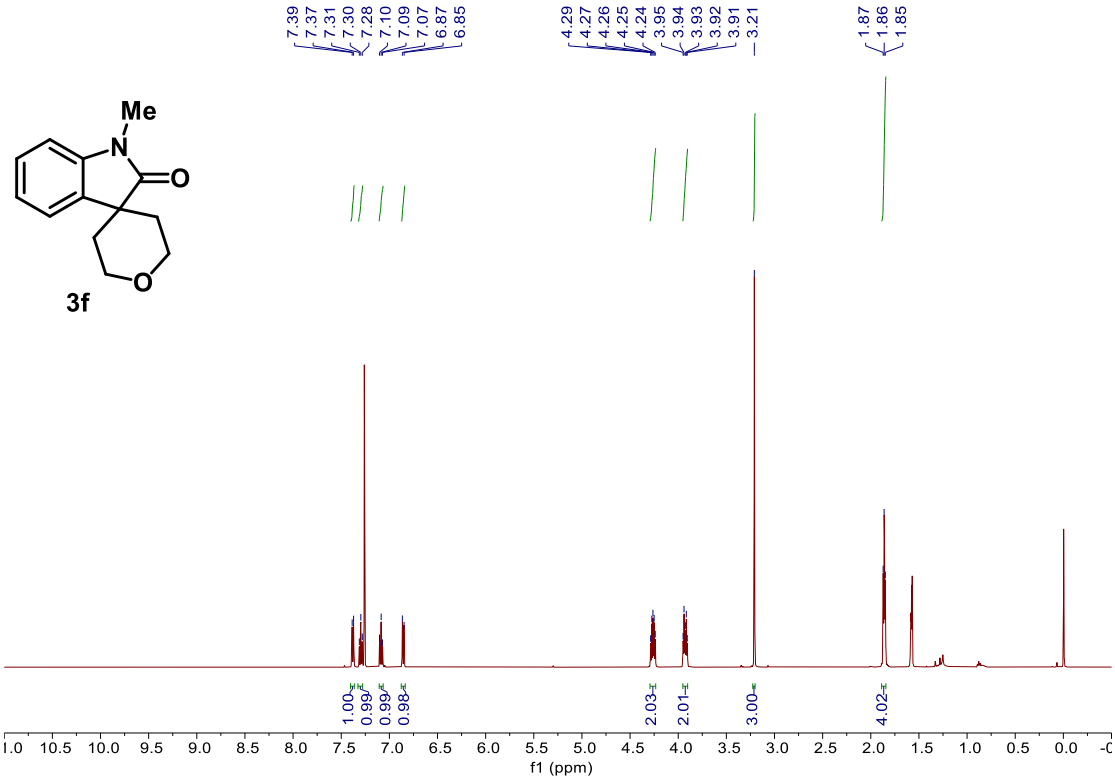
^{1}H NMR of compound **3e** (500 MHz in $CDCl_3$)



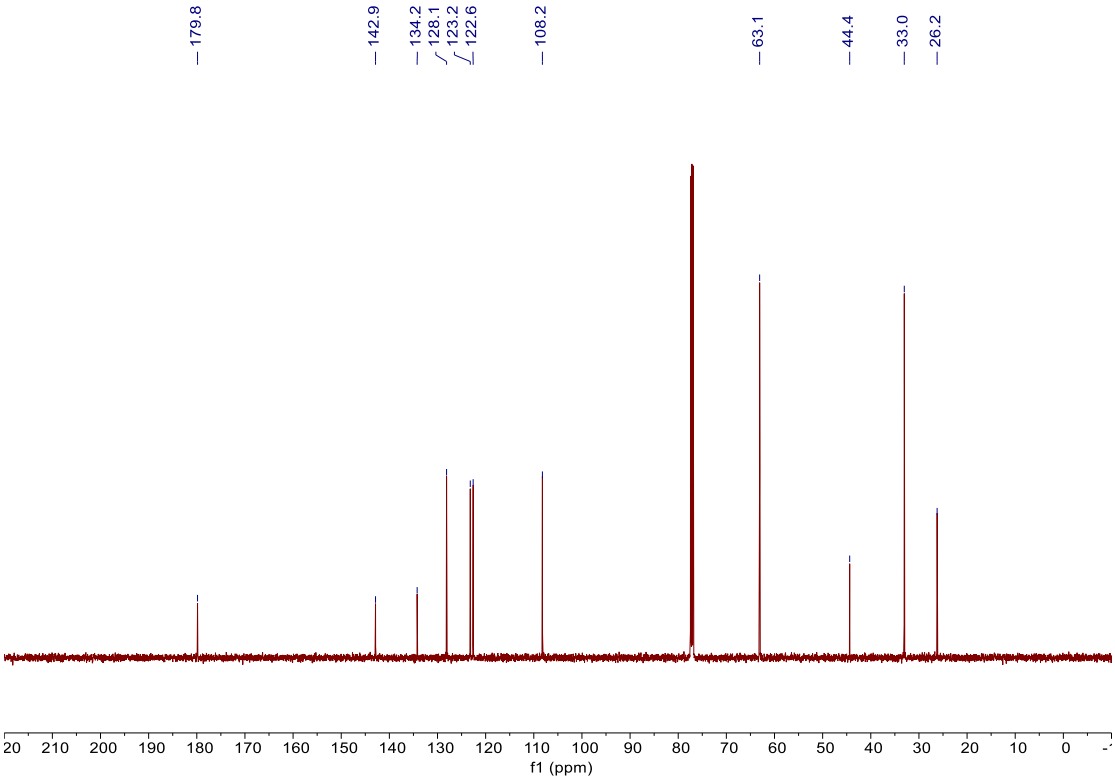
^{13}C NMR of compound **3e** (126 MHz in $CDCl_3$)



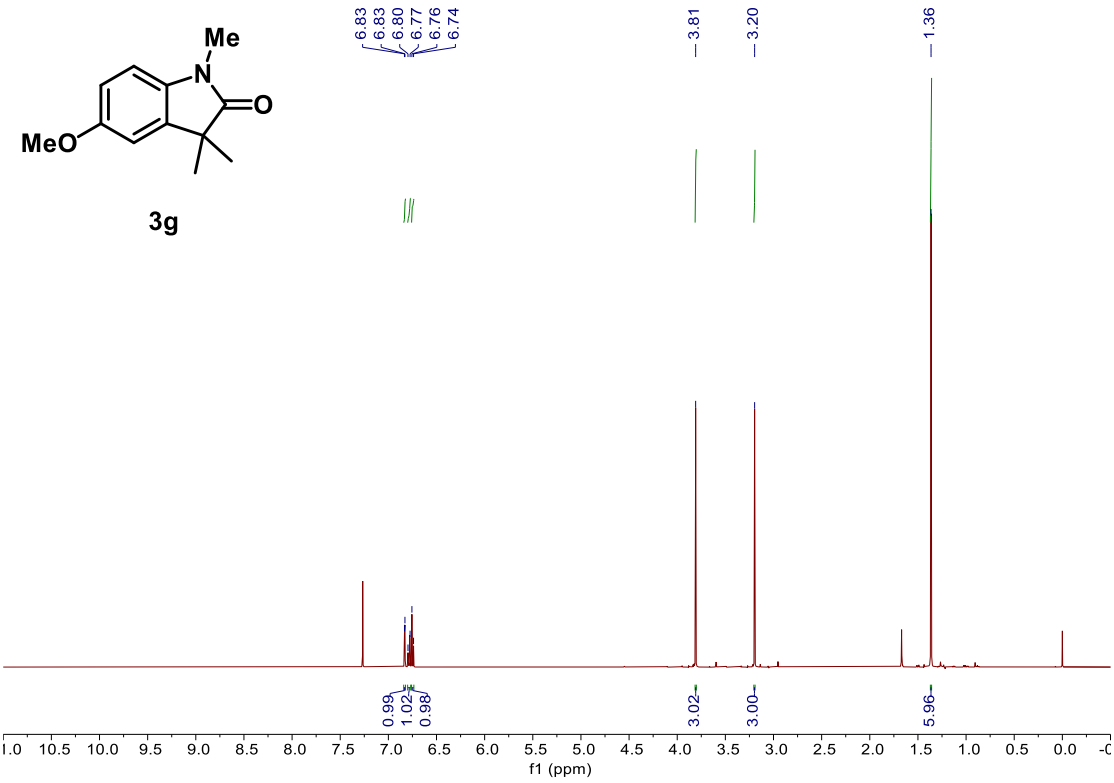
^{1}H NMR of compound **3f** (500 MHz in $CDCl_3$)



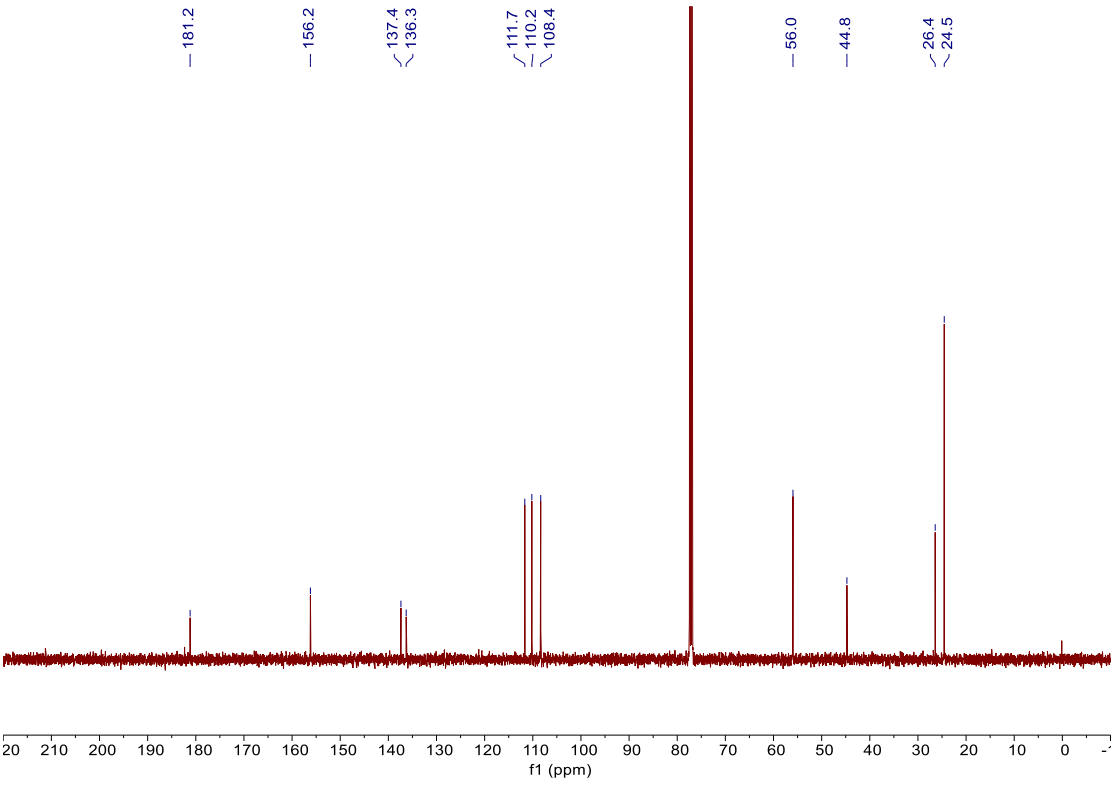
^{13}C NMR of compound **3f** (126 MHz in $CDCl_3$)



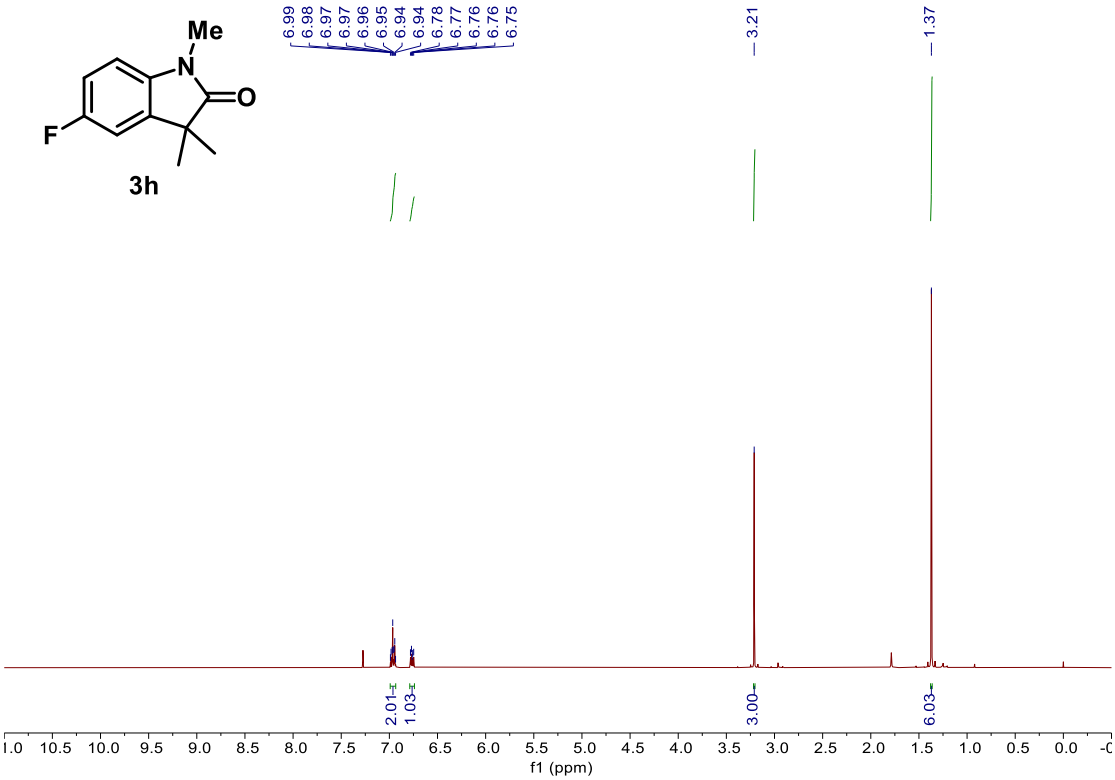
^{1}H NMR of compound **3g** (500 MHz in $CDCl_3$)



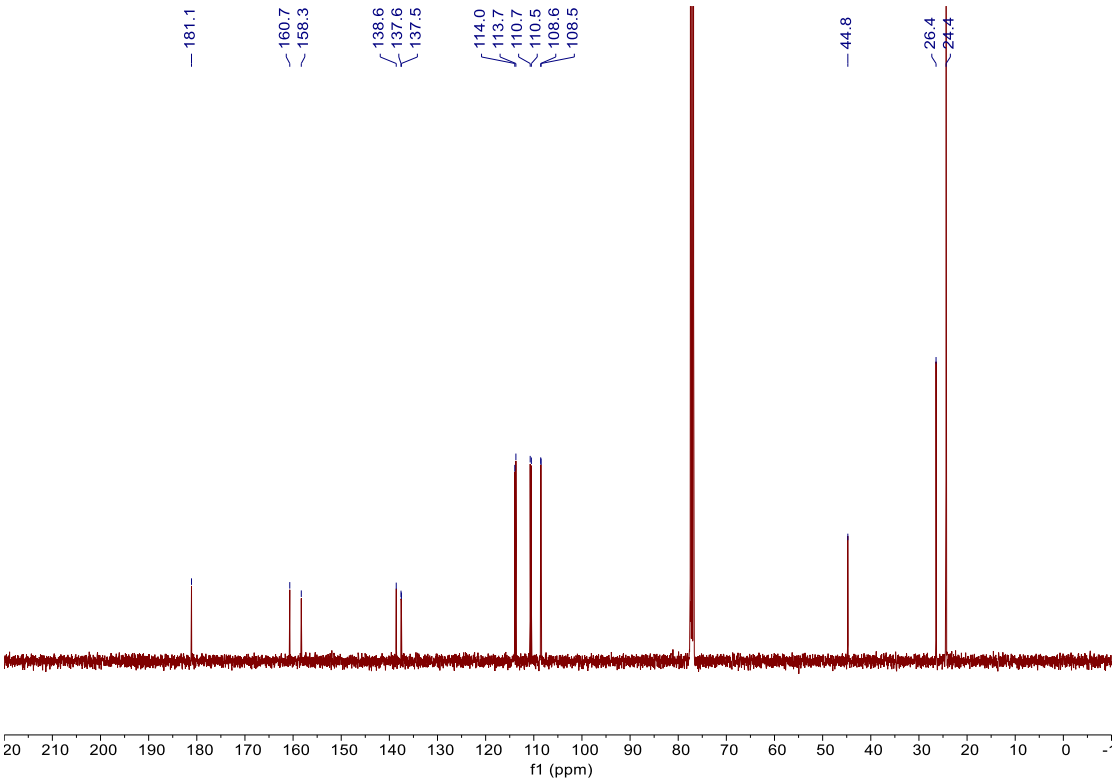
^{13}C NMR of compound **3g** (126 MHz in $CDCl_3$)



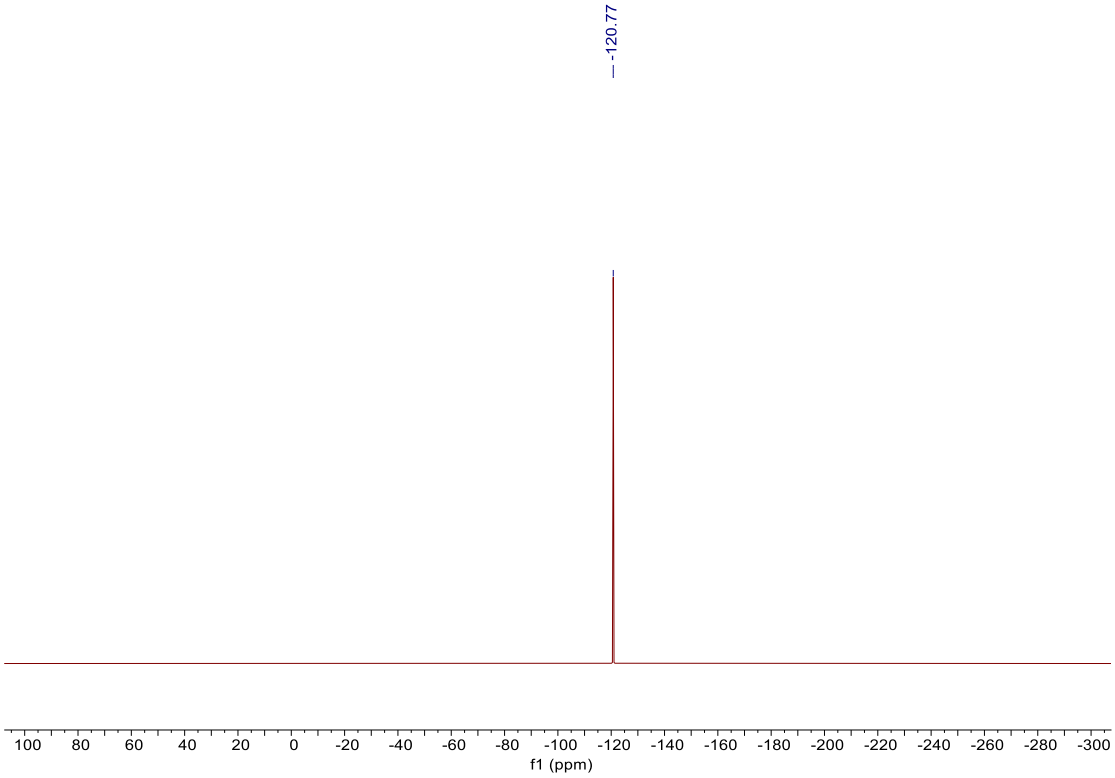
^{1}H NMR of compound **3h** (500 MHz in $CDCl_3$)



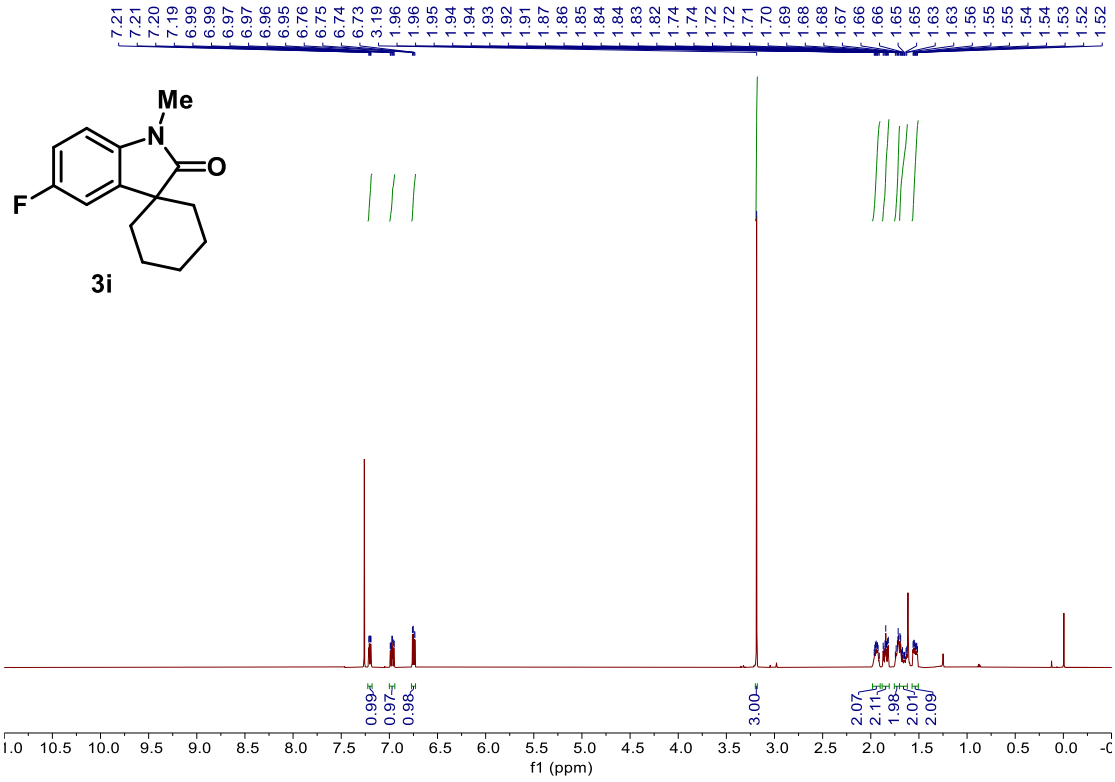
^{13}C NMR of compound **3h** (101 MHz in $CDCl_3$)



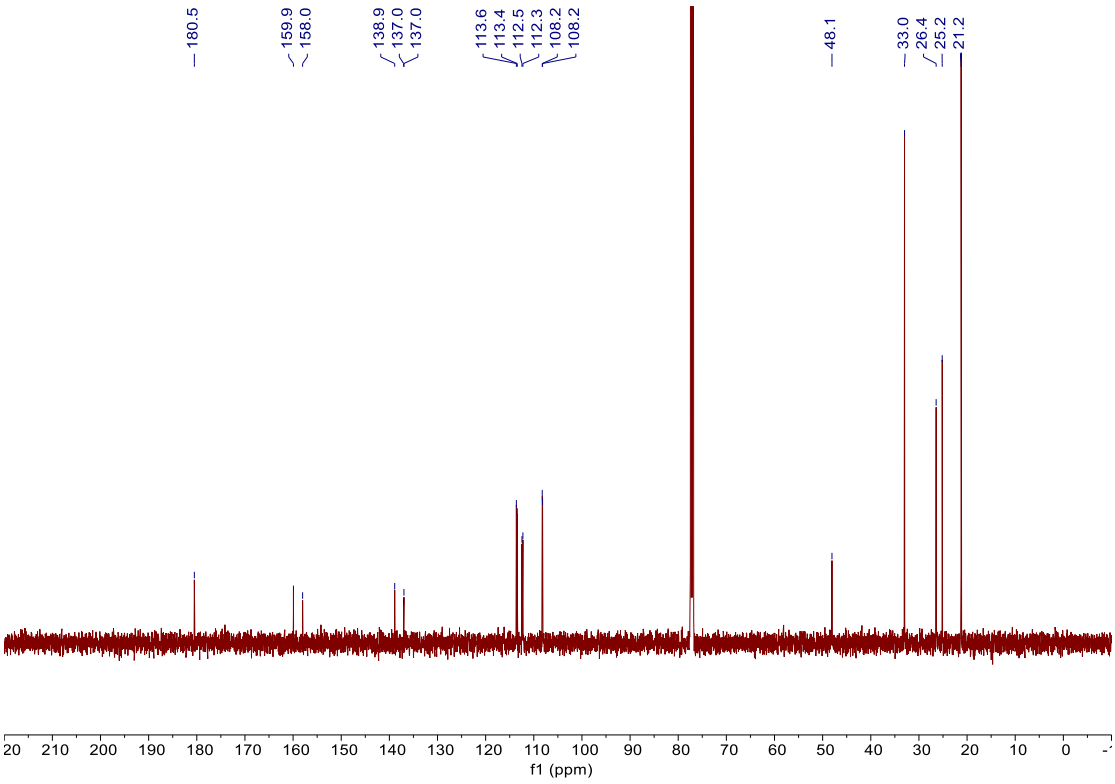
^{19}F NMR of compound **3h** (376 MHz in $CDCl_3$)



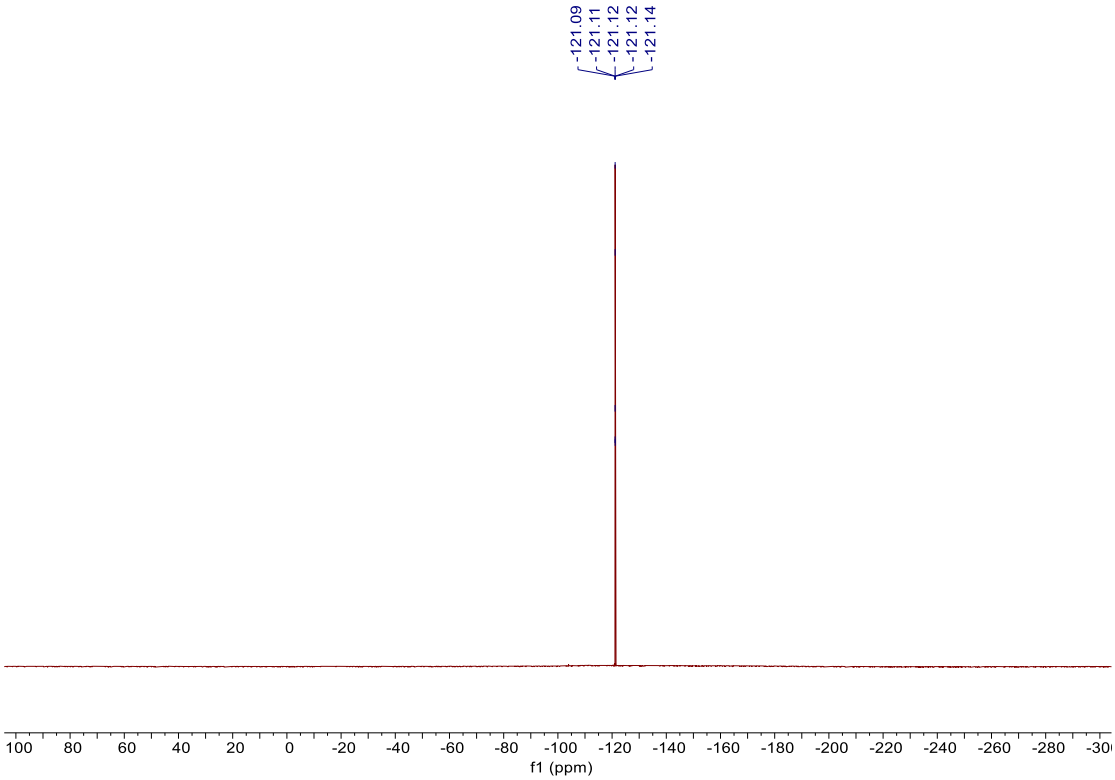
^{1}H NMR of compound **3i** (500 MHz in $CDCl_3$)



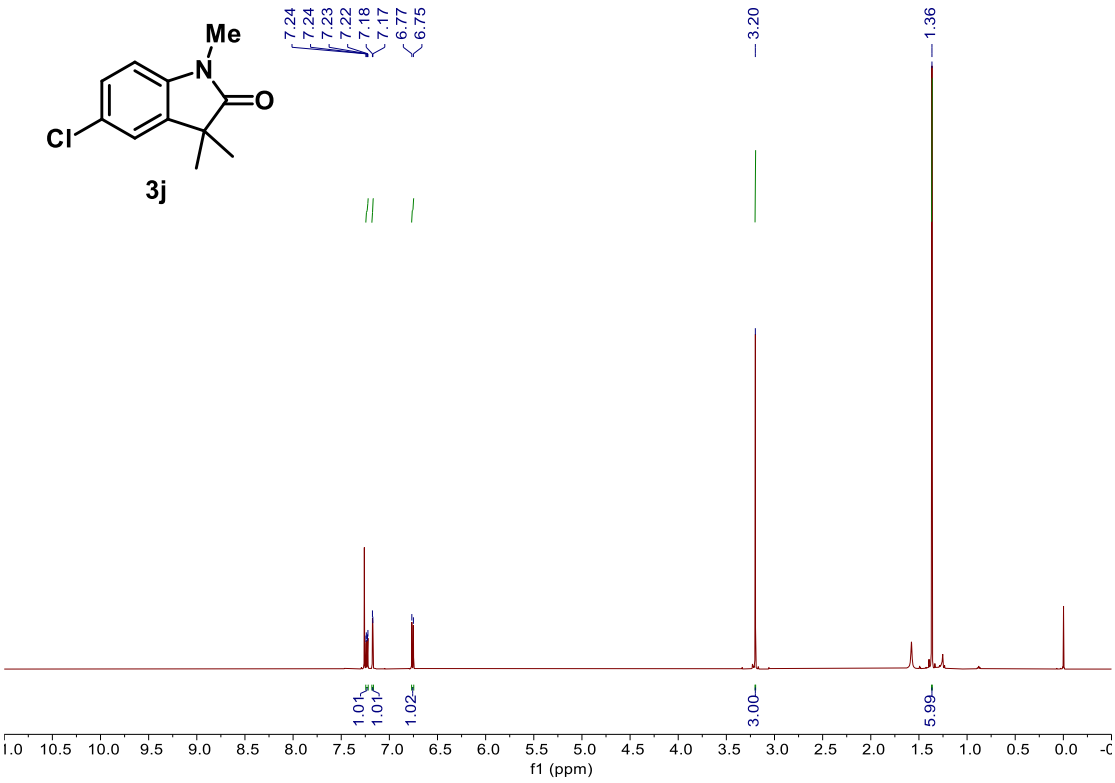
^{13}C NMR of compound **3i** (126 MHz in $CDCl_3$)



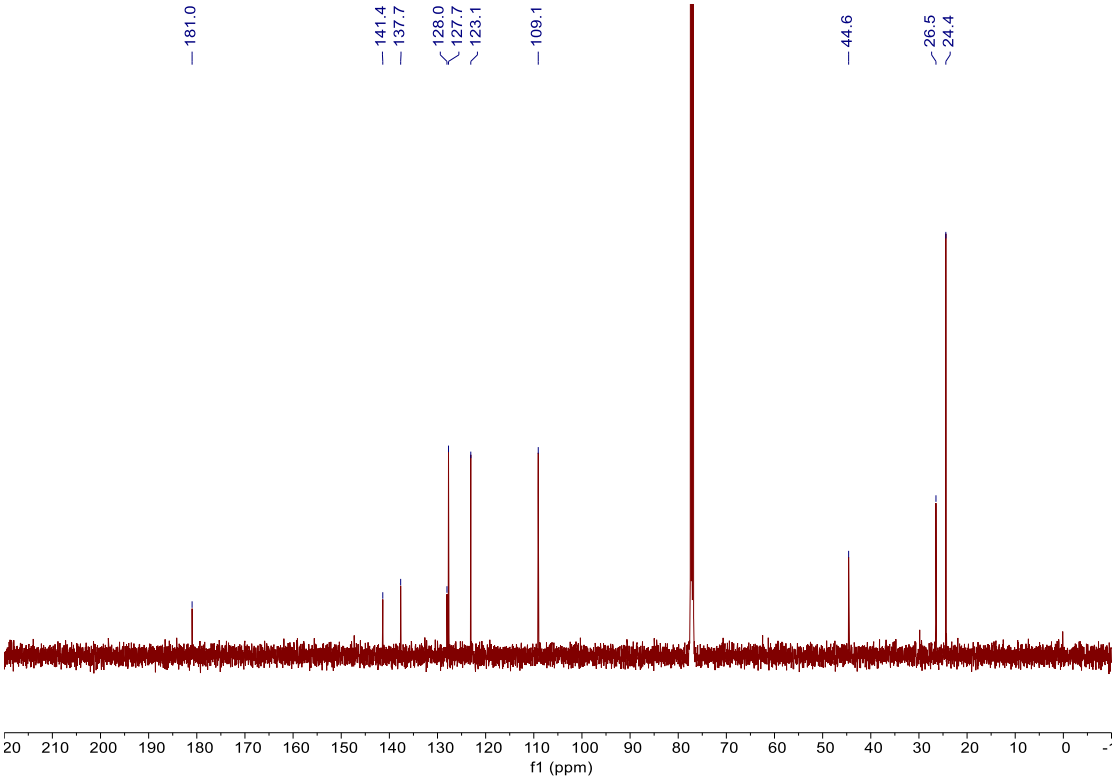
^{19}F NMR of compound **3i** (471 MHz in $CDCl_3$)



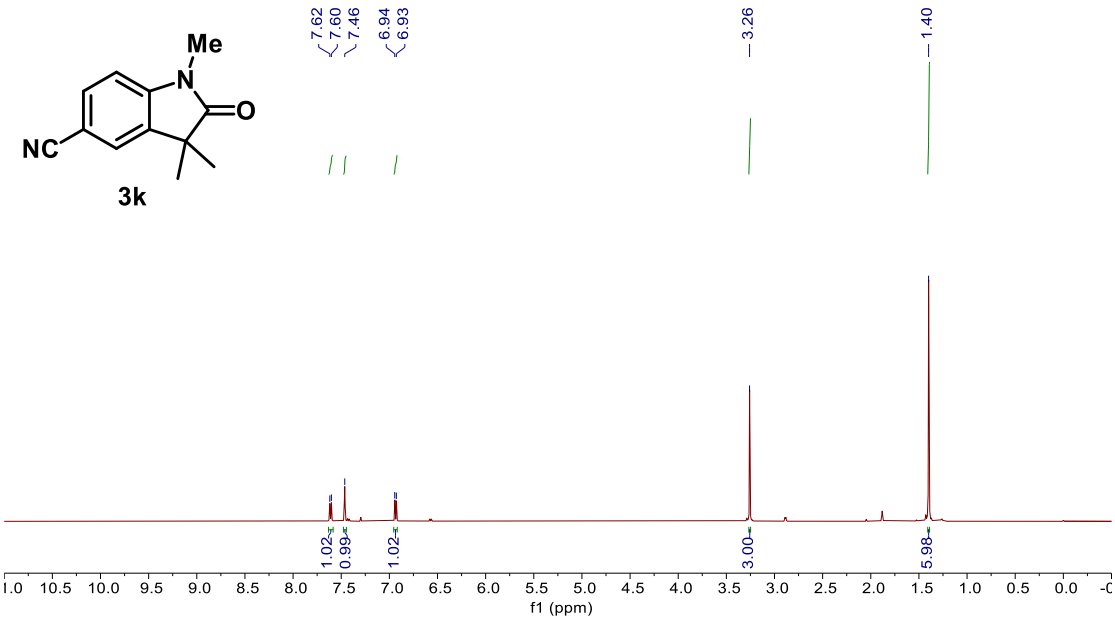
^{1}H NMR of compound **3j** (500 MHz in $CDCl_3$)



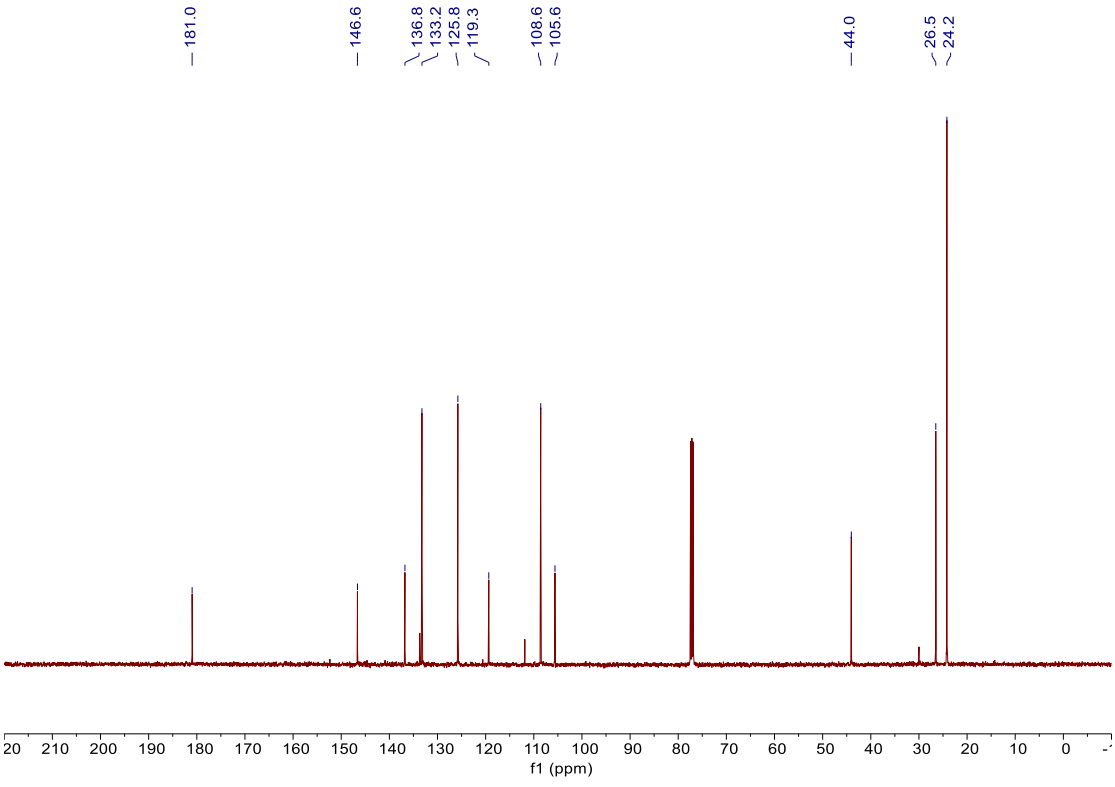
^{13}C NMR of compound **3j** (126 MHz in $CDCl_3$)



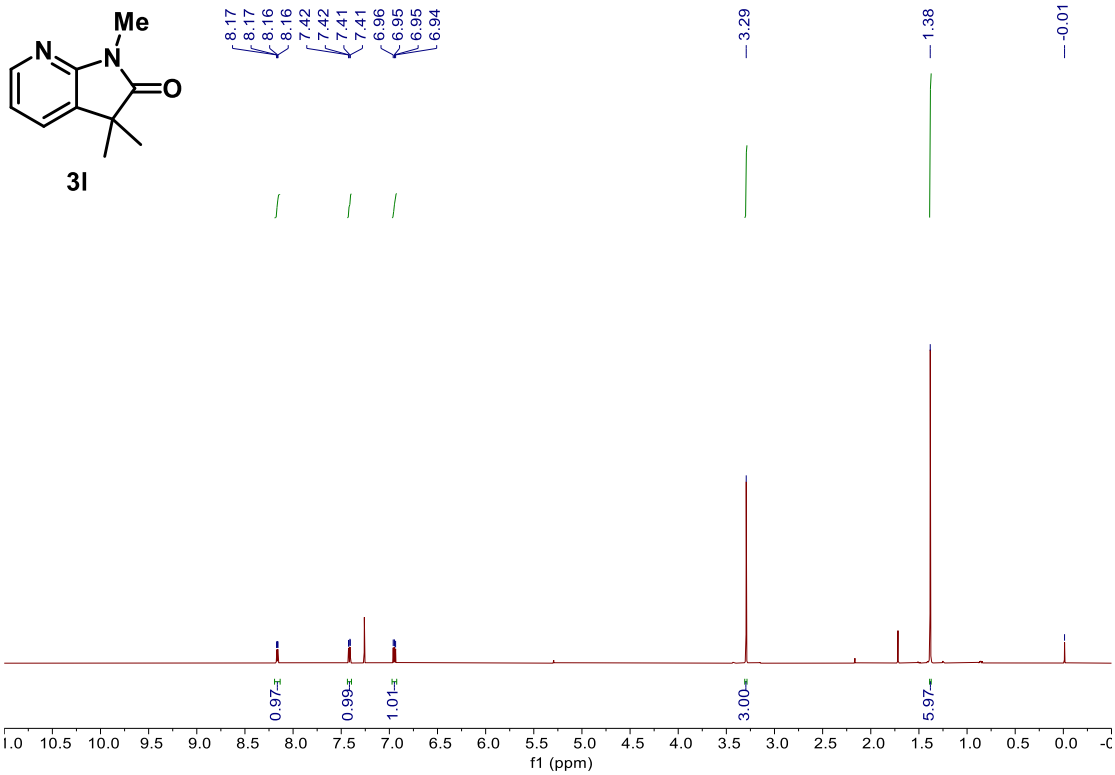
^{1}H NMR of compound **3k** (500 MHz in $CDCl_3$)



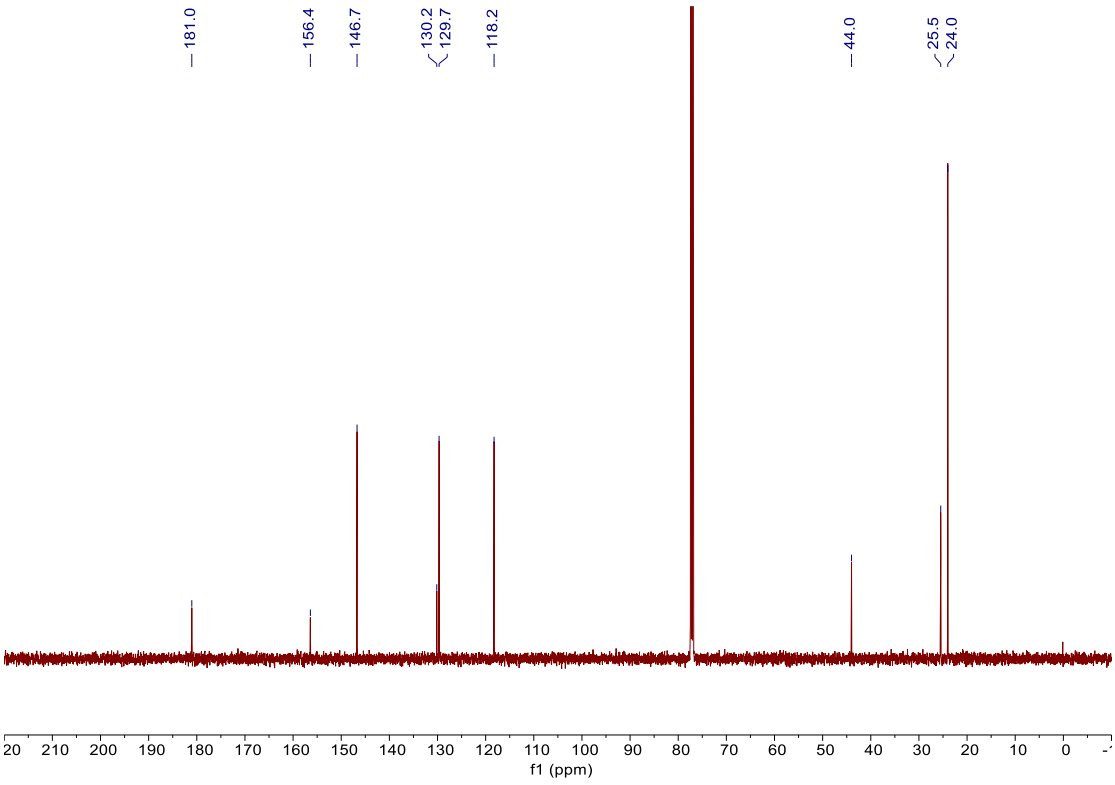
^{13}C NMR of compound **3k** (126 MHz in $CDCl_3$)



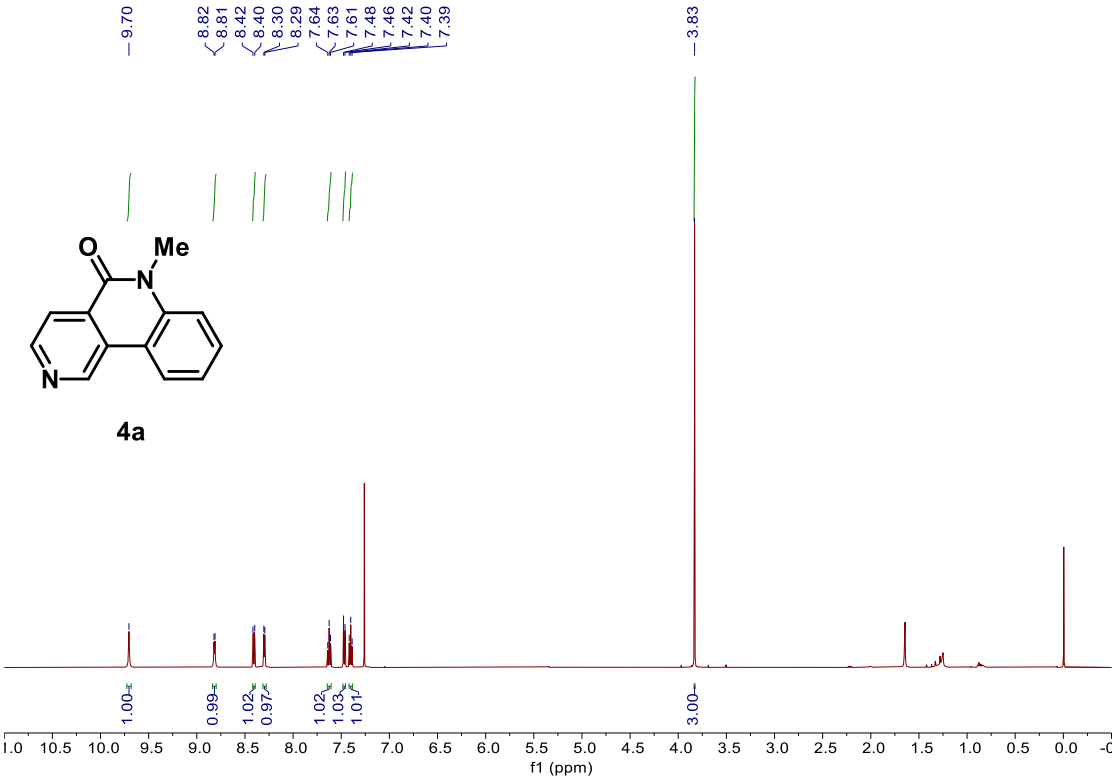
^{1}H NMR of compound **3l** (500 MHz in $CDCl_3$)



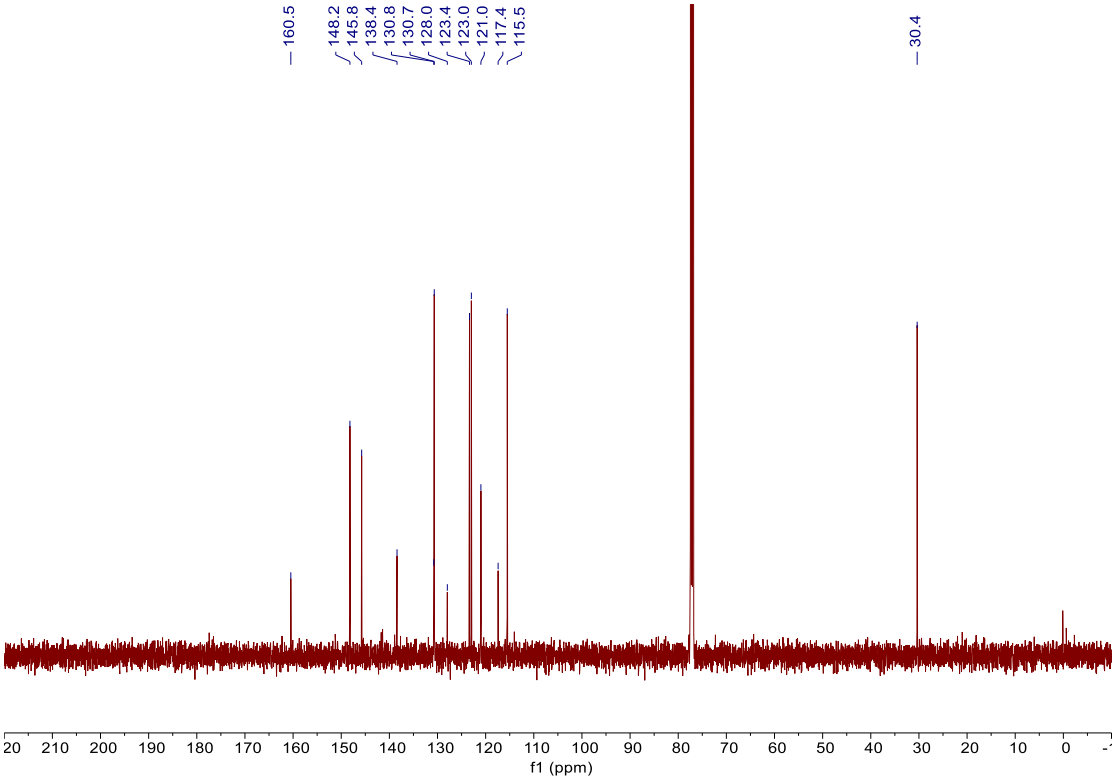
^{13}C NMR of compound **3l** (126 MHz in $CDCl_3$)



^{1}H NMR of compound **4a** (500 MHz in $CDCl_3$)



^{13}C NMR of compound **4a** (126 MHz in $CDCl_3$)



7.Computational details

All calculations were carried out by using Gaussian 16 program.[11] Geometries were optimized at B3LYP[12]-D[13](BJ)3/BSI level in N,N-dimethylformamide (DMF) with SMD[14] solvation model, BSI denoting a basis set with SDD[15] for I atom and 6-31G(d,p) for other atoms. Harmonic vibrational frequencies were calculated at the same level to verify the optimized geometries to be minima (no imaginary frequency) or transition states (having unique one imaginary frequency), and obtain the thermal corrections. The energies were further refined by B3LYP-D3(BJ)/BSII single-point-energy calculations with SMD solvent model in DMF, BSII representing a basis set with SDD for I atom and 6-311++G(d,p) for other atoms. The selected calculated structures were illustrated using the CYLview.[16]

Cartesian Coordinates in Å and Energies (in a.u.) at 298.15 K for the Optimized Structures

1

B3LYP-D3BJ/BSI SCF energy in DMF:

-647.7272379 a.u.

B3LYP-D3BJ/BSII SCF energy in DMF:

-647.88922 a.u.

B3LYP-D3BJ/BSII enthalpy in DMF:

-647.5812471 a.u.

B3LYP-D3BJ/BSII free energy in DMF:

-647.6461051 a.u.

C	2.661160	1.384221	0.156502
C	1.555945	0.586684	-0.135286
C	0.343457	1.137987	-0.559836
C	0.281746	2.527246	-0.742098
C	1.379937	3.338863	-0.464254
C	2.567234	2.767960	-0.005373
H	3.585748	0.934993	0.500316
H	-0.641260	2.966212	-1.106545
H	1.307257	4.412325	-0.607652
H	3.427443	3.390910	0.219672
C	-0.821491	0.286218	-1.003059
O	-0.770936	-0.168446	-2.152884
N	-1.861972	0.067487	-0.153965
C	-2.019813	0.598350	1.226345
H	-2.935004	0.118982	1.575075
C	-2.954016	-0.806253	-0.650230
H	-2.663438	-1.052903	-1.670612
C	-4.293494	-0.067799	-0.700630
H	-4.213207	0.843201	-1.301851
H	-5.048637	-0.713955	-1.160234
H	-4.657016	0.205880	0.295220

C	-3.026225	-2.106809	0.154353
H	-3.322055	-1.935706	1.194709
H	-3.768361	-2.776116	-0.293179
H	-2.058127	-2.617480	0.150302
C	-2.279518	2.108064	1.280656
H	-1.366214	2.687519	1.135400
H	-3.008234	2.409927	0.523184
H	-2.684436	2.365728	2.265096
C	-0.921019	0.165355	2.199730
H	-0.759099	-0.914067	2.152938
H	0.028571	0.667368	2.007566
H	-1.233835	0.420969	3.217694
I	1.780524	-1.548286	0.087977

DBU

B3LYP-D3BJ/BSI SCF energy in DMF:

-462.1714993 a.u.

B3LYP-D3BJ/BSII SCF energy in DMF:

-462.2836715 a.u.

B3LYP-D3BJ/BSII enthalpy in DMF:

-462.0236666 a.u.

B3LYP-D3BJ/BSII free energy in DMF:

-462.0694716 a.u.

C	0.903490	1.321609	-0.773929
C	1.974070	1.310532	0.325131
C	-0.393274	-0.766322	-0.361455
C	2.775592	0.006441	0.383274
C	0.902898	-1.533214	-0.526234
C	1.940905	-1.263552	0.582908
H	1.319805	0.920602	-1.705330
H	1.486596	1.506621	1.289118
H	3.340780	-0.094575	-0.554034
H	1.352919	-1.324411	-1.505388
H	0.605730	2.351119	-0.988399
H	2.666129	2.142350	0.144084
H	3.519155	0.075613	1.186811
H	0.621072	-2.588093	-0.520720
H	2.623737	-2.120242	0.623384
H	1.428239	-1.230608	1.553118
C	-2.479863	0.620393	0.759522
C	-1.468407	1.433488	-0.036619
C	-2.708543	-0.715131	0.051769
H	-1.938978	1.856509	-0.935649
H	-1.098193	2.274502	0.560602
H	-2.089221	0.429843	1.766363
H	-3.410521	1.186817	0.864725
H	-3.187832	-0.531906	-0.923482
H	-3.405760	-1.338352	0.624793
N	-1.465734	-1.460577	-0.135804
N	-0.322103	0.603255	-0.422224

Complex1

B3LYP-D3BJ/BSI SCF energy in DMF:

-1109.913708 a.u.

B3LYP-D3BJ/BSII SCF energy in DMF:

-1110.183638 a.u.

B3LYP-D3BJ/BSII enthalpy in DMF:

-1109.6163800 a.u.

B3LYP-D3BJ/BSII free energy in DMF:

-1109.7090990 a.u.

C	-2.233499	-3.107785	-0.381971
C	-1.879057	-1.799746	-0.049432
C	-2.726676	-1.002712	0.730032
C	-3.913898	-1.565200	1.218884
C	-4.272828	-2.872861	0.895765
C	-3.436112	-3.641772	0.085905
H	-1.573517	-3.709976	-0.997361
H	-4.557987	-0.965971	1.854661
H	-5.200375	-3.288346	1.277242
H	-3.708207	-4.660124	-0.175256
C	-2.303806	0.370393	1.194267
O	-1.618939	0.427244	2.223876
N	-2.658059	1.468469	0.471055
C	-3.602484	1.514078	-0.676090
H	-3.618052	2.570284	-0.946899
C	-2.089624	2.766807	0.907796
H	-1.422532	2.508970	1.729595
C	-3.169853	3.706959	1.447587
H	-3.721298	3.234446	2.266493
H	-2.705324	4.621357	1.831510
H	-3.885736	4.000696	0.672665
C	-1.254320	3.404443	-0.206154
H	-1.868019	3.742564	-1.047743
H	-0.726890	4.279551	0.187398
H	-0.511422	2.696808	-0.583593
C	-5.042751	1.151533	-0.296976
H	-5.180678	0.074641	-0.186957
H	-5.336714	1.637988	0.637588
H	-5.718505	1.494738	-1.087565
C	-3.125835	0.763767	-1.922360
H	-2.103845	1.047336	-2.184250
H	-3.162415	-0.319345	-1.793572
H	-3.779756	1.024566	-2.761403
I	0.027794	-1.043057	-0.736033
C	5.496281	0.550452	0.629093
C	5.192082	-0.197767	1.933011
C	3.558885	0.015012	-0.835377
C	4.876769	-1.682177	1.723956
C	3.904486	-1.448608	-0.663927
C	3.708477	-1.970845	0.774896
H	6.168563	-0.045081	0.001655
H	4.357735	0.306004	2.438246
H	5.775932	-2.175405	1.328576
H	4.936716	-1.637891	-0.984708
H	6.022717	1.482619	0.848946
H	6.063013	-0.110352	2.594163
H	4.670549	-2.146918	2.695832
H	3.251667	-1.992968	-1.348491
H	3.566001	-3.056509	0.723052
H	2.778198	-1.556068	1.182072
C	2.411023	2.473919	-0.417328
C	3.865921	2.318120	0.001228
C	2.195121	1.719075	-1.727847
H	4.513134	2.964955	-0.606875
H	3.999323	2.615262	1.047346
H	1.753386	2.050914	0.351025
H	2.166191	3.535582	-0.517562
H	2.799747	2.184850	-2.521725

H	1.149589	1.786957	-2.046933
N	2.545983	0.305626	-1.600171
N	4.303137	0.922680	-0.134913

Complex2

B3LYP-D3BJ/BSI SCF energy in DMF:

-1109.91074 a.u.

B3LYP-D3BJ/BSII SCF energy in DMF:

-1110.182994 a.u.

B3LYP-D3BJ/BSII enthalpy in DMF:

-1109.6157918 a.u.

B3LYP-D3BJ/BSII free energy in DMF:

-1109.7086908 a.u.

C	-2.001906	3.253906	0.021868
C	-1.782593	1.897757	-0.215474
C	-2.832026	1.037795	-0.557501
C	-4.112979	1.586023	-0.712352
C	-4.345576	2.941551	-0.485839
C	-3.291253	3.774024	-0.109210
H	-1.177218	3.899822	0.301999
H	-4.928683	0.936512	-1.013117
H	-5.346478	3.344382	-0.604948
H	-3.462514	4.830336	0.074497
C	-2.587596	-0.402828	-0.937400
O	-2.218986	-0.616772	-2.099700
N	-2.772538	-1.387750	-0.016927
C	-3.276234	-1.231444	1.373406
H	-3.217734	-2.243198	1.775807
C	-2.435774	-2.768779	-0.441981
H	-2.113491	-2.664293	-1.477171
C	-3.659173	-3.687356	-0.413136
H	-4.466669	-3.278948	-1.028812
H	-3.388089	-4.669633	-0.814023
H	-4.041224	-3.840023	0.601578
C	-1.260977	-3.320166	0.370758
H	-1.522373	-3.486979	1.421115
H	-0.944062	-4.281517	-0.046713
H	-0.412802	-2.631979	0.331499
C	-4.752424	-0.826162	1.448917
H	-4.897765	0.236091	1.245354
H	-5.355019	-1.402304	0.741064
H	-5.127419	-1.026196	2.458273
C	-2.392264	-0.367430	2.276110
H	-1.346753	-0.677868	2.214943
H	-2.453559	0.693511	2.027854
H	-2.725680	-0.488205	3.312298
I	0.228470	1.146213	-0.045645
C	3.525815	0.447382	1.483972
C	5.029370	0.347342	1.771207
C	3.368270	-0.341636	-0.877595
C	5.889803	1.106817	0.756334
C	4.282134	0.804715	-1.254235
C	5.716516	0.668841	-0.702093
H	3.265592	1.474415	1.206684
H	5.313534	-0.712747	1.802690
H	5.645914	2.176081	0.829365
H	3.850292	1.761022	-0.932724
H	2.954640	0.220449	2.387710
H	5.219707	0.756031	2.771233

H	6.946606	1.010779	1.034130	H	3.042859	-2.041808	1.846307
H	4.307975	0.813098	-2.345821	H	3.532944	-3.220273	-0.188471
H	6.379116	1.280040	-1.325878	H	1.861663	-3.653699	0.198421
H	6.047638	-0.370595	-0.825587	H	1.050011	-1.887018	-1.379807
C	2.513468	-2.826708	-0.098557	H	2.127410	-2.991296	-2.229854
C	2.471995	-1.735653	0.962255	N	2.959743	-1.118560	-1.830418
C	2.094620	-2.229644	-1.442058	N	3.043992	-0.478737	0.455392
H	1.438970	-1.553871	1.286147				

8. Reference

(1) M. Ratushnyy, N. Kvasovs, S. Sarkar, V. Gevorgyan, Visible-Light-Induced Palladium-Catalyzed Generation of Aryl Radicals from Aryl Triflates. *Angew. Chem. Int. Ed*. **2020**, *59*, 10316-10320.

(2) Berkeley; Hanna. N.M.R. STUDIES OF HYDROGEN BONDING. I. BINARY MIXTURES OF CHLOROFORM AND NITROGEN BASES1. *J. Physic. Chem.* **1963**, *67*, 846–849.

(3) Hanna; Ashbaugh. Nuclear Magnetic Resonance Study of Molecular Complexes of 7,7,8,8-Tetracyanoquinodimethane and Aromatic Donors[1,2]. *J. Physic. Chem.* **1964**, *68*, 811–816.

(4) Foster, R.; Fyfe, C. A. Interaction of electron acceptors with bases. Part 15.—Determination of association constants of organic charge-transfer complexes by n.m.r. spectroscopy. *Trans. Faraday Soc.* **1965**, *61*, 1626-1631.

(5) Du, L.; Cao, P.; Xing, J.; Lou, Y.; Jiang, L.; Li, L.; Liao, J., Hydrogen-bond-promoted palladium catalysis: allylic alkylation of indoles with unsymmetrical 1,3-disubstituted allyl acetates using chiral bis(sulfoxide) phosphine ligands. *Angew. Chem. Int. Ed*. **2013**, *52*, 4207-4211;

(6) Chen, K.–Q.; Zhang, B.–B.; Wang, Z.–X.; Chen, X.–Y. *N*-Heterocyclic Nitreniums Can Be Employed as Photoredox Catalysts for the Single-Electron Reduction of Aryl Halides. *Org. Lett.* **2022**, *24, 25,* 4598–4602.

(7) Cheng, X.–F.; Wang, T.; Li, Y.; Wu, Y.; Sheng, J.; Wang, R.; Li, C.; Bian, K.–J.; Wang, X.–S. Palladium(II)-Catalyzed C(sp2)–H Carbonylation of Sterically Hindered Amines with Carbon Monoxide. *Org. Lett.* **2018**, *20*, 6530–6533.

(8) Shen, J.-H.; You, Q.-H.; Fu, Q.; Kuai, C.-S.; Huang, H.-B.; Zhao, L.; Zhuang, Z.-X. Base-Promoted Cascade C–C Coupling/N-α-sp3C–H Hydroxylation for the Regiospecific Synthesis of 3-Hydroxyisoindolinones. *Org. Lett.* **2017**, *19*, 5170-5173.

(9) Cybularczyk-Cecotka, M.; Predygier, J.; Crespi, S.; Szczepanik, J.; Giedyk, M. Photocatalysis in Aqueous Micellar Media Enables Divergent C–H Arylation and NDealkylation of Benzamides. *ACS Catal.* **2022**, *12*, 3543–354.

(10) Chen, J.–Q.; Wei, Y.–L.; Xu, G.–Q.; Liang, Y.– M.; Xu, P.–F. Intramolecular 1,5-H transfer reaction of aryl iodides through visible-light photoredox catalysis: a concise method for the synthesis of natural product scaffolds. *Chem. Commun.* **2016**, *52*, 6455–6458.

(11) Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JAJ, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 16, Rev. A.03; Gaussian, Inc.: Wallingford, CT, 2016.

(12) Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. *Phys. Chem*. **1994**, *98*: 11623–11627.

(13) (a) Grimme S, Ehrlich J, Krieg SH. J. *Chem. Phys*. **2010**, *132*: 154104–154119. (b) Grimme S, Ehrlich S, Goerigk L. *J. Comput. Chem*. **2011**, *32*: 1456-1465.

(14) Marenich AV, Cramer CJ, Truhlar DG. *J. Phys. Chem. B*. **2009**, *113*: 6378-6396.

(15) (a) Dolg M, Wedig U, Stoll H, Preuss H. *J.* Chem. Phys. 1987, 86: 866-872. (b) Andrae D, Häußermann U, Dolg M, Stoll H, Preuß H. *Theor. Chim. Acta.* **1990**, *77*: 123-141.

(16) Legault *CY. CYLView, version 1.0 b*; Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009. http://www.cylview.org.