Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Electro-Organic Synthesis of Isatines and Hydrazones through C-N Cross-coupling and C(sp2)-H/C(sp3)-H Functionalization

Neetu Verma,[a] Rajdeep Tyagi,[b] Ashish Khanna,[c] Manisha Malviya,*[a] Ram Sagar*[b,c]

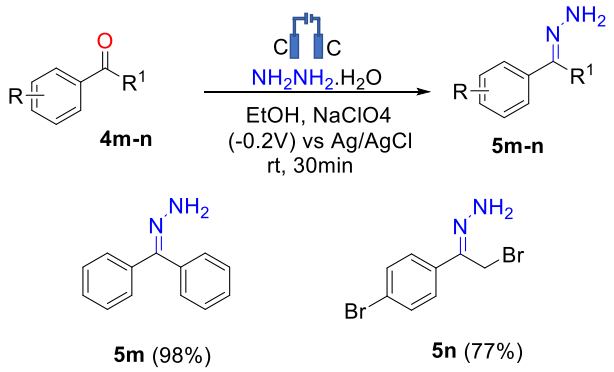
[a] Department of Chemistry, IIT (Banaras Hindu University) Varanasi-221005, India
[b] Glycochemistry Laboratory, School of Physical Sciences, Jawaharlal Nehru University, New Delhi-110067, India.
[c]Department of Chemistry, Institute of Science, Banaras Hindu University Varanasi-221005, India

*E-mail: manisha.apc@itbhu.ac.in, ram.sagar@jnu.ac.in

Experimental Section

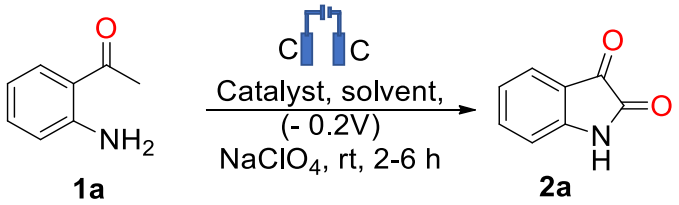
General experimental material and methods

All reactions were performed in an Electrochemical cell at room temperature (~25-26 ^{o}C). Solvents and chemicals were purchased from Merck. Prior to usage, all glassware underwent an extended 110 °C oven drying period. All commercial materials and solvents were used without purification unless otherwise indicated. Anhydrous acetonitrile, Methanol, and Ethanol were purchased from Sigma-Aldrich. A CHI-608C Potentiostat/Galvanostat has been used for all electrochemical studies. All electrochemical experiments were performed in an undivided electrochemical cell using redried glassware. Each electro organic synthesis was performed using two electrodes system viz., carbon cloth (2cm^2) as anode and iron electrode (2cm^2) as cathode. All electrodes were purchased from Sinsil International India (CH Instruments). Thin-layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as eluent. Melting points were recorded on a digital melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded in Bruker Avance 500 MHz NMR spectrophotometer with operating frequencies of 500 MHz (^{1}H) and 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$ and DMSO-d_6) signal. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet. The information for the 1H NMR spectra is given in the order, chemical shifts (multiplicity, coupling constants, and the number of hydrogen. All chemical shifts are reported relative to TMS. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz.



Scheme S1. The electro-organic synthesis of hydrazones **5m** and **5n**

Table S1. Optimization conditions for the solvent and promoter



Entry	Promoter	Solvents	Time (h)	Yield%
1	-	-	6	NR
2	-	DMSO	6	NR
3	I_2	Dioxane	6	NR
4	I_2	DMF	6	NR
5	I_2	DMSO	2	94

NR = No Reaction

Table S2. Optimization of the Potential

Potential	Yield%
(-0.2) V	94
(-0.3) V	60

Table S3. Compound (3-hydrazonoindolin-2-one) **3a** at pH=4

Entry	Potential (V vs Ag/AgCl)	R_{ct} (Ω/cm^2)
1	-0.9	3.48
2	-0.7	4.52
3	0	5.42

Table S3 shows the lowest charge transfer resistance for (3-hydrazonoindolin-2-one**)** compared **3a** at pH = 4 with -0.9V, -0.7 V and 0V (vs Ag/AgCl). At -0.9 V, the lowest charge transfer resistance (R_{ct}) value was calculated to be 3.48 Ω/cm^2, which was lower compared to -0.7 V (4.52 Ω/cm^2) and 0 V (5.42 Ω/cm^2). It has been observed that the charge transfer resistance value was decreased when potential was decreased from 0 V to -0.9 V.

Table S4. Compound (3-hydrazonoindolin-2-one) **3a** at pH= 7

Entry	Potential (V vs Ag/AgCl)	R_{ct} (Ω/ cm^2)
1	-0.9	3.25
2	-0.7	4.12
3	-0.4	4.67
4	0	5.36

Table S4 shows the lowest charge transfer resistance for (3-hydrazonoindolin-2-one**)** compared **3a** at pH =7 with -0.9 V, -0.7 V and 0 V (vs Ag/AgCl). Similar to the previous calculation, the lowest charge transfer resistance (R_{ct}) value was observed at -0.9 V (3.25 Ω/cm^2) in contrast to -0.7 V (4.12 Ω/cm^2), -0.4 V (4.67 Ω/cm^2) and 0 V (5.42 Ω/cm^2). The result has established that the increment in the potential leads to the increasing of the charge transfer resistance.

Table S5. Compound (1-phenylethylidene)hydrazine **5a** at pH=4

Entry	Potential (V vs Ag/AgCl)	R_{ct} (Ω/cm^2)
1	-0.9	3.89
2	-0.7	3.95
3	-0.4	4.67
4	0	5.52

Table S5 shows the lowest charge transfer resistance (R_{ct}) value was determined for -0.9 V (3.89 Ω/cm^2) compared to -0.7 V (3.95 Ω/cm^2), -0.4 V (4.67 Ω/cm^2), and 0 V (5.52 Ω/cm^2). It can be concluded here that the charge transfer resistance (R_{ct}) value was decreased after decreases in voltage from 0 to -0.9 V (vs Ag/AgCl) when compared with the different potentials.

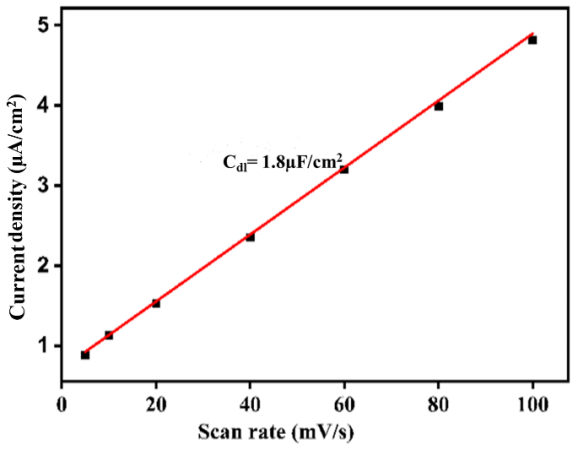


Figure S1. C_{dl} curve of **3a** different scan rate at pH =7

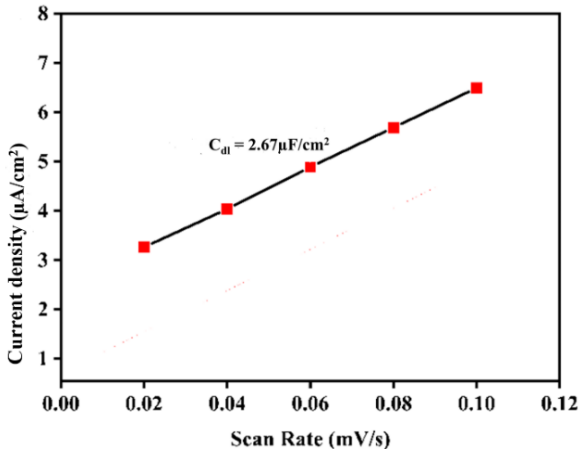


Figure S2. C_{dl} curve of **3a** different scan rate at pH =4

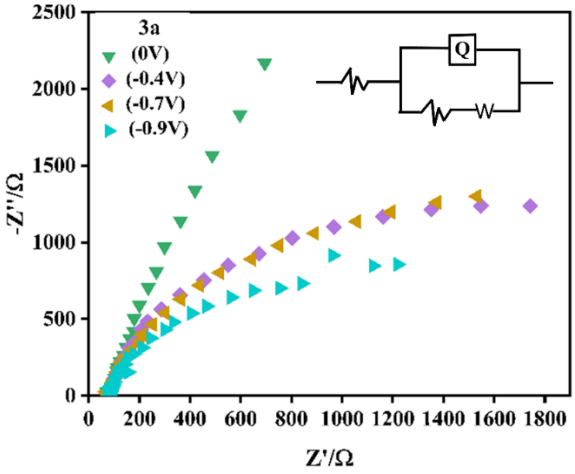


Figure S3. Show that Electrochemical impedance Spectroscopy (EIS) graph of **3a** at different potentials (pH = 7), the fitted circuit plot corresponds to R(QR)W parameter.

The chrono-amperometry graph of 3-hydrazonoindolin-2-one **3a** at (-0.2 V) exhibits a strong current of 80 microamperes at 1800 seconds, as shown in (Figure S4). Moreover, the current density of 30 microamperes was attained at -0.3 V in chrono-amperometry.

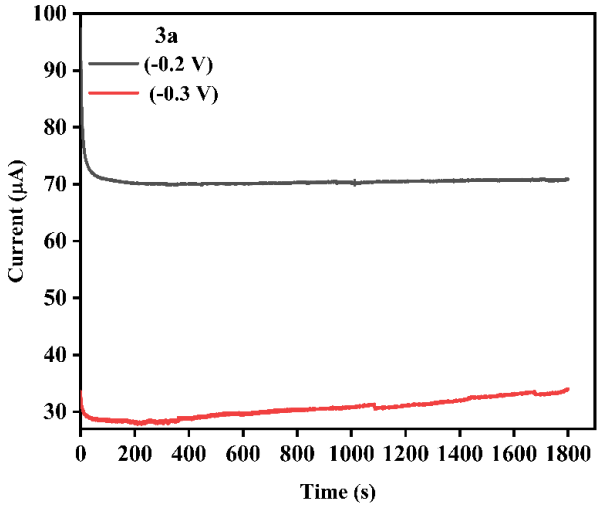


Figure S4. Chrono-amperometry graph for the synthesis of 3-hydrazonoindolin-2-one **3a.**

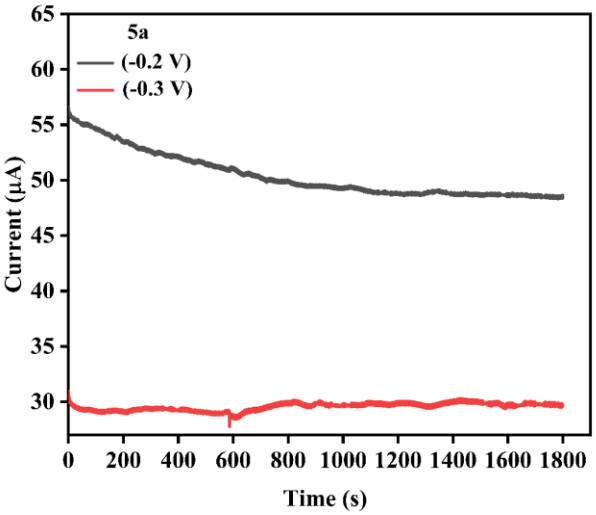


Figure S5. Chrono-amperometry graph for the synthesis (1-Phenylethylidene) hydrazine **5a.**

Table S6. OCP data for electro-organic synthesis of hydrazonoindolin derivatives **3a-p**

Entry	Electrochemical reaction mixture reaction (substrate +$NH_2NH_2.H_2O$ + 0.1M $NaClO_4$)	Open circuit Potential OCP (in Volts)
1.	**2a**	-0.036
2.	**2b**	-0.023
3.	**2c**	-0.058
4.	**2d**	-0.136
5.	**2e**	-0.122
6.	**2f**	-0.280
7.	**2g**	-0.216
8.	**2h**	-0.180
9.	**2i**	-0.079
10	**2j**	-0.084
11	**2k**	-0.066
12	**2l**	-0.069
13	**2m**	-0.126
14	**2n**	-0.109
15	**2o**	-0.118
16.	**2p**	-0.111

Table S7. OCP data for electro-organic synthesis of hydrazone derivatives **5a-n**

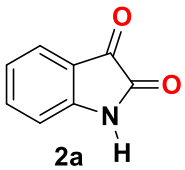
Entry	Electrochemical reaction mixture reaction (substrate +$NH_2NH_2.H_2O$ + (0.1M $NaClO_4$)	Open circuit Potential OCP (in Volts)
1	**4a**	-0.224
2	**4b**	-0.278
3	**4c**	-0.470
4	**4d**	0.022
5	**4e**	0.046
6	**4f**	-0.402
7	**4g**	-0.467
8	**4h**	0.024
9	**4i**	-0.485
10	**4j**	-0.432
11	**4k**	-0.412
12	**4l**	0.042
13	**4m**	-0.275
14	**4n**	-0.193

The Table S7 contains the OCP data for hydrazone formation from acetophenone. Compound **4i** (-0.485) and **4c** (-0.470) have a high reduction potential of the OCP, which indicates that the electrode has a strong tendency to accept electrons and undergo reduction. A high reduction potential facilitates electron transfer from the electrode to the organic substrate, promoting the reduction reaction. This enhanced reactivity can lead to faster reaction rates and short reaction times. Here**, 4g, 4j, 4k, 4b and 4m** have reduction potential of the OCP (-0.467, -0.432, -0.412, -0.278 and -0.275) can influence the selectivity of the reaction. Different functional groups within an organic molecule may have varying affinities for electrons, and a high reduction potential can favour the reduction of specific functional groups, while leaving others unaffected. This selectivity control is valuable in organic synthesis, as it allows for the targeted formation of desired products. In electro-organic synthesis, the OCP reduction potential of an electrode material can influence the selectivity of the desired electrochemical transformation. Different organic compounds have varying tendencies to be reduced at different potential, it is possible to promote the selective reduction of specific functional groups or bonds within a complex organic molecule.

Experimental Procedure and Spectral data of all compounds

Typical Experimental Procedure for synthesis of Indolin-2,3-diones (2a-2p).

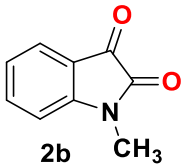
To a solution of 2-aminoacetophenone **1a** (1.0 mmol), in DMSO solvent (5 ml), I_2 (1.3 mmol) and drops of $NaClO_4$ (0.1 M), with two graphite electrode (anode and cathode) and reference electrode Ag/AgCl, at room temperature (25 °C), electric current passes for 2 h (7.2×10^3 sec). The progress of the reaction was monitored by TLC. After completion of the reaction (TLC), mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished isatin product **2a** in 94% isolated yield. The similar reaction protocol was adopted for other 2- amino acetophenone derivatives (**1b-1p**) and the corresponding isatin products (**2b-2p**) were obtained in 60-94% yields.



2a

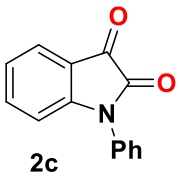
Indolin-2,3-dione (2a). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (202-203 ℃); Yield (94%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ =

11.03 (s, 1H), 7.57 (d, *J* = 7.7, 1.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.2, 159.2, 150.5, 138.2, 124.5, 122.6, 117.6, 112.0 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_5NO_2$ $[M+H]^+$ 148.0399, found 148.0389.



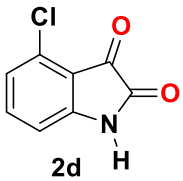
2b

1-methylindoline-2,3-dione (2b). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (129-130 ℃); yield (91%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.67 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.12 (brt, *J* = 7.7 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.4, 158.1, 151.3, 138.1, 124.2, 123.1, 117.3, 110.5, 26.0 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_7NO_2$ $[M+H]^+$ 162.0555, found 162.0572.



2c

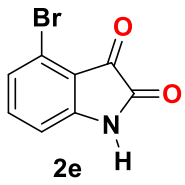
1-phenylindoline-2,3-dione (2c). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (137-138 ℃); Yield (82%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.66-7.61 (m, 1H), 7.60 – 7.58 (m, 3H), 7.50 – 7.48 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.9, 157.5, 151.3, 138.1, 133.4, 129.8, 128.5, 126.6, 124.8, 123.7, 117.7, 110.8 ppm; HRMS (ESI) *m/z*: calcd for $C_{14}H_9NO_2$ $[M+H]^+$ 224.0712, found 224.0731.



2d

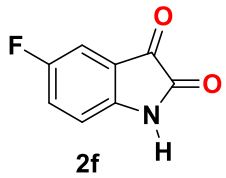
4-chloro-indolin-2,3-dione (2d). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (254-255 ℃); Yield (90%),**^{1}H NMR** (500 MHz, DMSO-

d_6) δ = 11.20 (s, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 181.3, 158.8, 152.3, 139.1, 131.1, 123.7, 114.9, 111.0 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0023.



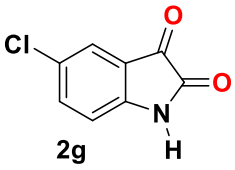
2e

4-bromo-indolin-2,3-dione (2e). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (257-258 °C), Yield (93%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.18 (s, 1H), 7.43 (brt, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 181.3, 158.2, 152.1, 138.4, 126.2, 119.0, 116.0, 110.9 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9525.



2f

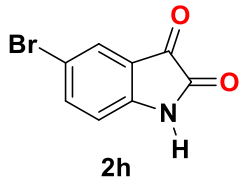
5-fluoro-indoline-2,3-dione (2f). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (221-222 °C); Yield (60%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.04 (s, 1H), 7.45-7.39 (m, 2H), 6.91 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.2, 159.3, 157.4, 147.3, 124.7, 118.8, 113.8, 111.6 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4FNO_2$ $[M+H]^+$ 166.0304, found 166.0345.



2g

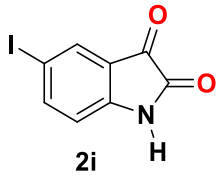
5-Chloro-indolin-2,3-dione (2g). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (245-246 °C); Yield (89%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.12 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.51 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H); **^{13}C**

NMR (125 MHz, DMSO-d_6) δ = 183.3, 159.1, 149.2, 137.2, 126.8, 124.1, 119.0, 113.8 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0031.



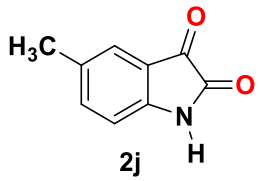
2h

5-Bromo-indolin-2,3-dione (2h). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Yellow solid: m.p. (254-256 ℃); yield (87%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.13 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H**); ^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.8, 158.6, 149.2, 139.6, 126.5, 124.3, 119.1, 113.9 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9541.



2i

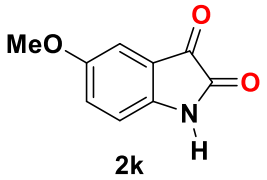
5-iodo-indolin-2,3-dione (2i). The Product was purified by silica column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (263-264 ℃); Yield (80%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.11 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.75 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 182.7, 158.4, 149.6, 145.4, 132.1, 119.6, 114.3, 85.1 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4INO_2$ $[M+H]^+$ 273.9365, found 273.9381.



2j

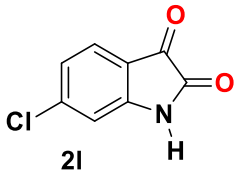
5-methyl-indolin-2,3-dione (2j). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (196-197 ℃); Yield (74%),**^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.92 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.30 (s, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 2.25 (s, 3H);

^{13}C NMR (125 MHz, DMSO-d_6) δ = 184.3, 159.1, 148.2, 138.5, 131.7, 124.5, 117.4, 111.7, 19.8 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_7NO_2$ $[M+H]^+$ 162.0555, found 162.0572.



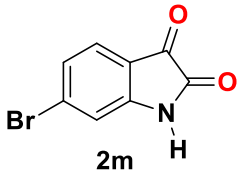
2k

5-methoxy-indolin-2,3-dione (2k). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Mustered yellow solid: m.p. (200-201 ℃); Yield (90%), **^{1}H NMR** (500MHz, DMSO-d_6) δ= 10.83 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 184.3, 159.2, 155.0, 144.3, 124.5, 117.8, 112.9, 108.5, 55.4 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_7NO_3$ $[M+H]^+$ 178.0504, found 178.0532.



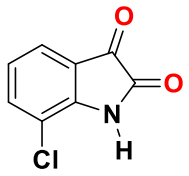
2l

6-chloro-indolin-2,3-dione (2l). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Red Solid: m.p. (254-255 ℃); Yield (75%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.14 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.1, 159.5, 151.9, 142.5, 126.4, 122.8, 116.9, 112.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0042.



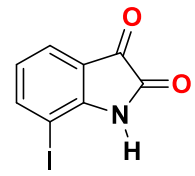
2m

6-bromo-indolin-2,3-dione (2m). The Product was Purified by column chromatography (Ethyl acetate: Hexane 1:2) Red solid, m.p. (255-256 ℃); yield (89%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.15 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.08 (s, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.5, 159.6, 152.0, 131.9, 126.5, 126.0, 117.4, 115.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9534.



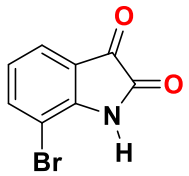
2n

7- chloro-indolin-2,3-dione (2n). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), Orange Solid: m.p. (181-182 ℃); Yield (74%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.16 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.7, 159.9, 148.0, 137.6, 124.0, 123.4, 120.2, 116.4 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4ClNO_2$ $[M+H]^+$ 182.0009, found 182.0015.



2o

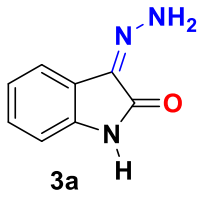
7-iodo-indolin-2,3-dione (2o). The Product was purified by column chromatography (Ethyl acetate: Hexane 1:2), yellow solid: m.p. (202-203 ℃); Yield (75%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.31 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.5, 159.5, 149.2, 140.2, 124.0, 123.4, 119.9, 104.5 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4INO_2$ $[M+H]^+$ 273.9365, found 273.9375.



2p

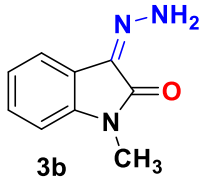
7-bromo-indolin-2,3-dione (2p). The Product was purified by column chromatography (Ethyl acetate:Hexane 1:2), Orange Solid: m.p. (208-209 ℃); Yield (78%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.62 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 183.9, 159.9, 149.6, 140.6, 124.4, 123.8, 120.4, 104.9 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_4BrNO_2$ $[M+H]^+$ 225.9504, found 225.9541.

Typical Experimental Procedure for the synthesis of 3-hydrazonoindolin-2-ones (3a-3p). To a solution of isatin **2a** (0.68 mmol), hydrazine hydrates (0.81 mmol) in C_2H_5OH solvent (5 ml) and drops of $NaClO_4$ (0.1 M), with two graphite electrode (anode and cathode) and reference electrode Ag/AgCl, at room temperature (25 °C), electric current passes for 1800 sec (30 min). The progress of the reaction was monitored by TLC. After complete consumption of isatin **2a**, the reaction mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished hydrazone product **3a** in 92% isolated yield. The similar reaction protocol was adopted for other isatin derivatives (**2b-2p**) and the corresponding products (**3b-3p**) were obtained in 75-94% yields.



3a

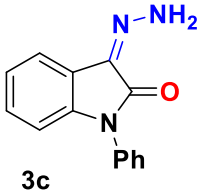
3-hydrazonoindolin-2-one (3a). The Product was purified by silica gel column chromatography Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (238-239 °C); Yield (92%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.36 (s, 1H, NH), 8.77 (s, 2H, NH_2), 7.91 (d, *J* = 7.5 Hz, 1H, ArH), 7.20 (t, 1H, *J* = 7.6 Hz, ArH), 6.96 (d, *J* = 7.6 Hz, 1H, ArH), 6.85 (t, *J* = 7.8 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO - d_6) δ = 162.5, 138.3, 126.7, 125.9, 121.9, 121.0, 117.1, 109.6 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_7N_3O$ $[M+H]^+$ 162.0667, found 162.0671.



3b

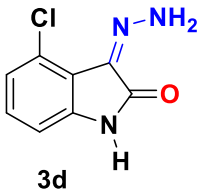
1-Methyl-1H-indole-2,3-dione 3-hydrazone (3b). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (105-106°C); Yield (90%);**^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.52 (d, *J* = 14.6 Hz, 1H, NH), 9.65 (d, *J* = 14.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H, ArH), 7.22 (t, *J* = 7.7 Hz, 1H, ArH), 7.04-6.99 (m, 2H, ArH), 3.18 (s, 3H, CH_3);

^{13}C NMR (125 MHz, DMSO-d_6) δ = 160.6, 139.8, 126.8, 125.2, 121.7, 121.2, 117.0, 108.4, 24.9 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_9N_3O$ $[M+H]^+$ 176.0824, found 176.0851.



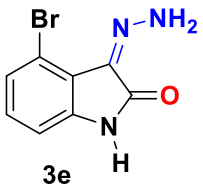
3c

1-Phenyl-1H-indole-2,3-dione 3-hydrazone (3c). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Brown red Solid; m. p. (116-117℃); Yield (88%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 9.12 (brs, 2H, NH_2), 8.06 (d, *J* = 7.5 Hz, 1H, ArH), 7.56 (t, *J* = 7.6 Hz, 2H, ArH), 7.46 (t, *J* = 7.9 Hz, 1H, ArH), 7.43 (d, *J* = 7.5 Hz, 2H, ArH), 7.24 (t, *J* = 7.8 Hz, 1H, ArH), 7.09 (t, *J* = 7.6 Hz, 1H, ArH), 6.79 (d, *J* = 7.9 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 164.1, 141.4, 134.8, 129.8, 128.8, 128.0, 127.3, 127.0, 122.9, 122.5, 116.7, 109.0 ppm; HRMS (ESI) *m/z*: calcd for $C_{14}H_{11}N_3O$ $[M+H]^+$ 238.0980, found 238.0989.



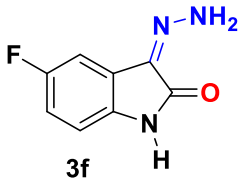
3d

4 – (Chloro-1H- indole-2,3- dione 3-hydrazone) (3d). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), mustard yellow solid: m.p. (236-236 ℃);Yield (90%), **^{1}H NMR** (500 MHz, DMSO - d_6) δ = 10.98 (d, *J* = 13.5 Hz, 1H, NH), 10.92 (s, 1H, NH), 9.95 (d, *J* = 13.5 Hz, 1H, NH), 7.14 (d, *J* = 7.9 Hz, 1H, ArH), 7.05 (t, *J* = 7.9 Hz, 1H, ArH), 6.87 (d, *J* = 8.1 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.6, 140.1, 128.0, 125.8, 125.3, 120.4, 112.2, 109.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0291.



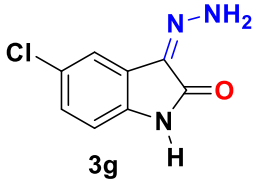
3e

4-(Bromo-1H-indole-2,3-dione 3-hydrazone) (3e). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (220-221 °C); Yield (90%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.99 (d, *J* = 15.3 Hz, 1H, NH), 10.93 (s, 1H, NH), 9.98 (d, *J* = 15.4 Hz, 1H, NH), 7.16 (d, *J* = 8.0 Hz, 1H, ArH), 7.06 (t, *J* = 7.9 Hz, 1H, ArH), 6.89 (d, *J* = 7.8 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.6, 140.1, 128.0, 125.8, 125.3, 120.4, 112.2, 109.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9782.



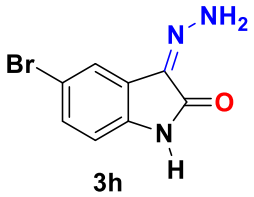
3f

5- Fluoro-1H-indole-2,3-dione 3-hydrazone (3f). The Product was purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (184-186 °C); Yield (80%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.71 (s, 1H, NH), 10.66 (d, *J* = 14.9 Hz, 1H, NH), 9.80 (d, *J* = 14.9 Hz, 1H, NH), 7.15 (d, *J* = 1.8 Hz, 1H, ArH), 6.98 (d, *J* = 8.0 Hz, 1H, ArH), 6.84 (d, *J* = 8.1 Hz, 1H, ArH); **^{13}CNMR** (125 MHz, DMSO-d_6) δ = 163.4, 159.4, 157.6, 135.1, 126.1, 113.4, 111.2, 104.9 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6FN_3O$ $[M+H]^+$ 180.0573, found 180.0591.



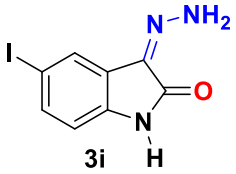
3g

5-Chloro-1H-indole-2,3-dione 3-hydrazone (3g). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane,1:1), Orange Solid; m. p. (176-177 °C); Yield (89%); **^{1}H NMR** (500 MHz, DMSO – d_6) δ = 10.82 (s, 1H, NH), 10.65 (d, *J* = 15.0 Hz, 1H, NH), 9.86 (d, *J* = 15.0 Hz, 1H, NH), 7.32 (d, *J* = 2.1 Hz, 1H, ArH), 7.16 (dd, *J* = 8.3, 2.2 Hz, 1H, ArH), 6.86 (d, *J* = 8.3 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO -d_6) δ = 162.4, 137.0, 126.1, 125.4, 124.8, 123.9, 116.8, 111.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0285.



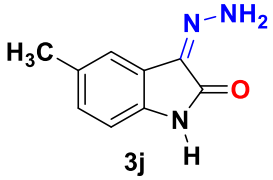
3h

5-Bromo-1*H*-indole-2,3-dione 3-hydrazone (3h). The Product was purified by silica gel column chromatography Ethyl Acetate: Hexane ,1:1), Yellow Solid; m. p. (167-168 °C); Yield (93%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.80 (s, 1H, NH), 10.63 (d, *J* = 14.9 Hz, 1H, NH), 9.83 (d, *J* = 14.9 Hz, 1H, NH), 7.60 (d, *J* = 1.8 Hz, 1H, ArH), 7.44 (dd, *J* = 8.3, 1.8 Hz, 1H, ArH), 6.71 (d, *J* = 8.1 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.5, 138.3, 135.3, 125.7, 125.2, 125.0, 112.7, 84.7 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9791.



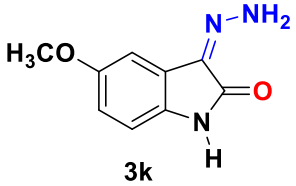
3i

5-Iodo-1H-indole-2,3-dione 3-hydrazone (3i). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane,1:1), Yellow Solid; m. p. (159-160 °C); Yield (92%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.82 (s, 1H, NH), 10.65 (d, *J* = 14.9 Hz, 1H, NH), 9.85 (d, *J* = 14.9 Hz, 1H, NH), 7.32 (d, *J* = 1.7 Hz, 1H, ArH), 7.16 (dd, *J* = 8.1, 1.7 Hz, 1H, ArH), 6.86 (d, *J* = 8.2 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.4, 137.0, 126.1, 125.4, 124.8, 123.9, 116.8, 111.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6IN_3O$ $[M+H]^+$ 287.9634, found 287.9651.



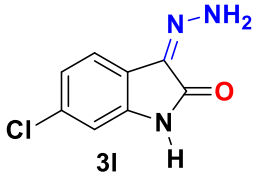
3j

5-Methyl-1H-indole-2,3-dione 3-hydrazone (3j). The Product was purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), light yellow Solid; m. p. (208-210 °C); Yield (93%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.58 (s, 1H, NH), 10.52 (d, *J* = 14.6 Hz, 1H, NH), 9.50 (d, *J* = 14.7 Hz, 1H, NH), 7.18 (d, *J* = 1.7 Hz, 1H, ArH), 6.96 (dd, *J* = 8.1, 1.7 Hz, 1H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 2.27 (s, 3H, CH_3); **^{13}NMR** (125 MHz, DMSO-d_6) δ = 163.2, 136.8, 130.4, 127.9, 126.7, 122.6, 118.3, 110.0, 21.1 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_9N_3O$ $[M+H]^+$ 176.0824, found 176.0852.



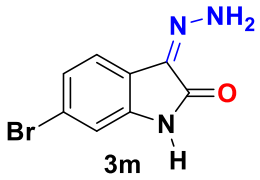
3k

5-(Methoxy-1H-indole-2,3-dione 3-hydrazone) (3k). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (187-189 ℃); yield (94%). **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.56 (d, *J* = 14.8 Hz, 1H, NH), 10.49 (s, 1H, NH), 9.53 (d, *J* = 14.8 Hz, 1H, NH), 6.93 (d, *J* = 1.8 Hz, 1H, ArH), 6.77 (d, *J* = 8.6 Hz, 1H, ArH), 6.73 (d, *J* = 8.6 Hz, 1H, ArH), 3.71 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.9, 154.6, 132.3, 126.4, 123.0, 112.8, 110.4, 102.9, 55.2 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_9N_3O_2$ $[M+H]^+$ 192.0773, found 192.0791.



3l

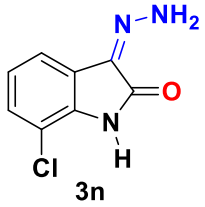
6-(Chloro-1H-indole-2,3-dione 3-hydrazone) (3l). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), light yellow solid: m.p. (181-182 ℃); Yield (87%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.82 (s, 1H, NH), 10.58 (d, *J* = 14.8 Hz, 1H, NH), 9.75 (d, *J* = 14.8 Hz, 1H, NH), 7.28 (d, *J* = 8.1 Hz, 1H, ArH), 7.14 (dd, *J* = 8.0, 1.8 Hz, 1H, ArH), 7.02 (d, *J* = 1.7 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.9, 140.2, 125.6, 124.4, 121.9, 119.6, 119.4, 113.1 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0262.



3m

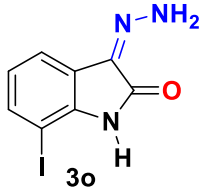
6-(Bromo-1H-indole-2,3-dione 3-hydrazone) (3m). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Brown red solid: m. p. (161-162 ℃); Yield (88%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.81 (s, 1H, NH), 10.59 (d, *J* = 14.8 Hz, 1H, NH), 9.77 (d, *J* = 14.8 Hz, 1H, NH), 7.28 (d, *J* = 7.8 Hz, 1H, ArH), 7.12 (d, *J* = 8.6 Hz, 1H, ArH), 7.00 (s, 1H,

ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.3, 139.6, 124.9, 123.7, 121.4, 118.9, 118.8, 112.5 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9761.



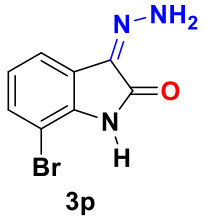
3n

7- Chloro-1H-indole-2,3-dione 3-hydrazone (3n). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane, 1:1), Orange Solid; m. p. (242-243 °C); Yield (86%); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 11.12 (s, 1H, NH), 10.67 (d, *J* = 14.8 Hz, 1H, NH), 9.88 (d, *J* = 14.8 Hz, 1H, NH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.20 (dd, *J* = 8.1, 1.0 Hz, 1H, ArH), 6.99 (t, *J* = 7.9 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 162.8, 135.8, 126.6, 125.5, 124.4, 122.7, 116.0, 114.4 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6ClN_3O$ $[M+H]^+$ 196.0278, found 196.0291.



3o

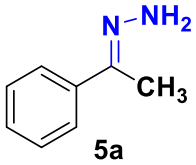
7-(Iodo-1H-indole-2,3-dione 3-hydrazone) (3o). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), brown red solid: m.p. (219-220 °C); yield (75%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.80 (s, 1H, NH), 10.62 (d, *J* = 14.8 Hz, 1H, NH), 9.83 (d, *J* = 14.8 Hz, 1H, NH), 7.60 (d, *J* = 7.9 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 1H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 176.0, 142.7, 130.2, 127.5, 123.4, 122.8, 116.3, 101.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6IN_3O$ $[M+H]^+$ 287.9634, found 287.9674.



3p

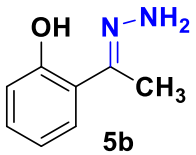
7- (Bromo-1H-indole-2,3-dione 3-hydrazone) (3p). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Yellow Solid: m. p. (227-228 °C); Yield (83%), **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.97 (s, 1H, NH), 10.63 (brs, 2H, NH_2), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.18 (d, *J* = 7.9 Hz, 1H, ArH), 6.88 (t, *J* = 8.0 Hz, 1H, ArH); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 175.6, 142.6, 129.9, 127.3, 123.1, 122.4, 115.9, 101.0 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_6BrN_3O$ $[M+H]^+$ 239.9772, found 239.9779.

Typical Experimental Procedure for the synthesis of (1-Phenylethylidene) hydrazines (5a-5n). To a solution of acetophenone **4a** (0.83 mmol), hydrazine hydrates (0.99 mmol), in C_2H_5OH solvent (5 ml) and drops of $NaClO_4$ (0.1 M), with two graphite electrode (anode and cathode) and reference electrode Ag/AgCl, at room temperature (25 °C), electric current passes for 1800 sec (30 min). The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was extracted with EtOAc (3 × 5 ml) and combined organic layer, dried over Na_2SO_4, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane/ethyl acetate as solvent which furnished hydrazone product **5a** in 89% isolated yield. The similar reaction protocol was adopted for other acetophenone derivatives (**4b-4m**) and the corresponding hydrazone products (**5b-5m**) were obtained in 80-94% yields.



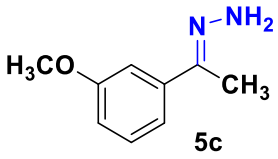
5a

(1-Phenylethylidene) hydrazone (5a). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:1), Colourless liquid, yield (89%), **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.92 (d, *J* = 7.8 Hz, 2H), 7.43-7.46 (m, 3H), 2.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.1, 138.8, 130.0, 128.7, 127.0, 15.4 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_{10}N_2$ $[M+H]^+$ 135.0922, found 135.0942.



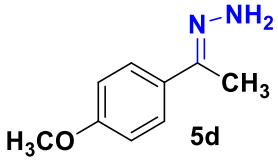
5b

1-(2-hydroxy phenyl) ethanone hydrazone (5b). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless liquid, Yield (89%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 12.93 (brs, 1H, OH), 7.37 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.22 (dt, *J* = 8.5, 1.6 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.87 (dt, *J* = 7.7, 1.3 Hz, 1H), 5.30 (s, 2H, NH_2), 2.14 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.2, 152.2, 129.5, 126.3, 119.7, 118.1, 116.8, 10.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_{10}N_2O$ $[M+H]^+$ 151.0871, found 151.0879.



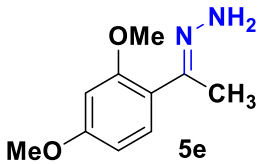
5c

1-(3-methoxy phenyl) ethanone hydrazone (5c). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless liquid, Yield (92%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.28-7.25 (m, 3H, ArH), 6.87-6.86 (m, 1H, ArH), 5.42 (s, 2H, NH_2), 3.81 (s, 3H, OCH_3), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.7, 147.0, 140.9, 129.3, 118.2, 114.1, 110.7, 55.3, 11.7 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_{12}N_2O$ $[M+H]^+$ 165.1028, found 165.1035.



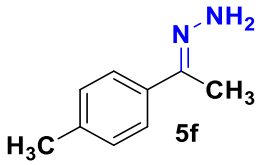
5d

1-(4-methoxy phenyl) ethanone hydrazone (5d). The Product was Purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Colourless liquid, Yield (94%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.9 Hz, 2H, ArH), 6.90 (d, *J* = 8.9 Hz, 2H, ArH), 5.27 (s, 2H, NH_2), 3.84 (s, 3H, OCH_3), 2.14 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.5, 147.3, 132.0, 126.6, 113.5, 55.1, 1 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_{12}N_2O$ $[M+H]^+$ 165.1028, found 165.1042.



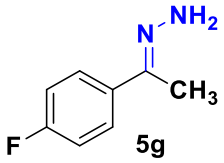
5e

1-(2,4-dimethoxy phenyl) ethanone hydrazone (5e). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane 1:9), Colourless Solid; m. p. (122-123 ℃); Yield (95%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 2.2 Hz, 1H, ArH), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H, ArH), 6.71 (d, *J* = 8.4 Hz, 1H, ArH), 5.25 (s, 2H, NH_2), 3.80 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 1.98 (s, 3H,CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.1, 148.7, 146.7, 132.3, 118.1, 110.4, 108.2, 55.8, 55.7, 11.3 ppm; HRMS (ESI) *m/z*: calcd for $C_{10}H_{14}N_2O_2$ $[M+H]^+$ 195.1134, found 195.1171.



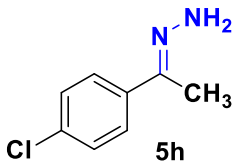
5f

1-(4-methyl phenyl) ethenone hydrazone (5f). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), colourless liquid; Yield (90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.3 Hz, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 2H, NH_2), 2.31 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.5, 139.5, 135.7, 128.9, 126.4, 21.2, 14.8 ppm; HRMS (ESI) *m/z*: calcd for $C_9H_{12}N_2$ $[M+H]^+$ 149.1079, found 149.1091.



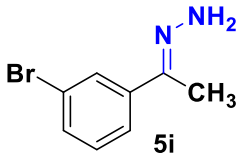
5g

1-(4-Fluoro Phenyl) ethanone hydrazone (5g). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Yellow Solid; Yield (86%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H, ArH), 7.00 (d, *J* = 8.4 Hz, 2H, ArH), 5.34 (s, 2H, NH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.5, 164.5, 133.4, 130.7, 115.3, 26.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9FN_2$ $[M+H]^+$ 153.0828, found 153.0852.



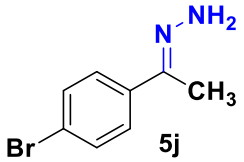
5h

1-(4-Chloro phenyl) ethanone hydrazone (5h). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Colourless liquid; yield (88%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.7 Hz, 2H, ArH), 7.46 (d, *J* = 8.6 Hz, 2H, ArH), 5.38 (s, 2H, NH_2), 2.10 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.7, 138.1, 131.2, 128.0, 126.9, 121.9, 11.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9ClN_2$ $[M+H]^+$ 169.0533, found 169.0563.



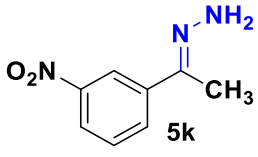
5i

1-(3-Bromo phenyl) ethanone hydrazone (5i). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Brown sticky solid; Yield (80%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (s, 1H, ArH), 7.54 (d, *J* = 7.9 Hz, 1H, ArH), 7.40 (d, *J* = 8.9 Hz, 1H, ArH), 7.19 (t, *J* = 7.9 Hz, 1H, ArH), 5.42 (s, 2H, NH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.4, 141.4, 130.9, 129.8, 128.6, 124.0, 122.6, 11.5 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9BrN_2$ $[M+H]^+$ 213.0027, found 213.0065.



5j

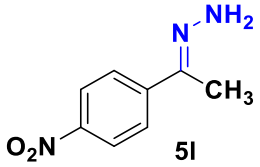
1-(4-Bromo phenyl) ethanone hydrazone (5j). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), Brown solid; m. p. (164-165 ℃); yield (89%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.7 Hz, 2H, ArH), 7.46 (d, *J* = 8.8 Hz, 2H, ArH), 5.38 (s, 2H, NH_2), 2.10 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 146.3, 138.6, 131.7, 127.4, 122.5, 11.7 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9BrN_2$ $[M+H]^+$ 213.0027, found 213.0052.



5k

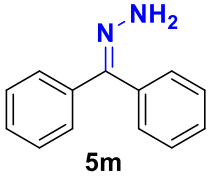
1-(3-Nitro phenyl) ethanone hydrazone (5k). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), yellow Solid; m. p. (78-79 ℃); Yield (86%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.47 (d, *J* = 2.0 Hz, 1H, ArH), 8.12 (dd, *J* = 8.1, 2.3 Hz, 1H, ArH),

7.99 (dd, *J* = 7.9, 1.8 Hz, 1H, ArH), 7.48 (t, *J* = 8.0 Hz, 1H, ArH), 5.56 (s, 2H, NH_2), 2.16 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.8, 144.1, 141.3, 131.4, 129.5, 122.8, 120.6, 11.6 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9N_3O_2$ $[M+H]^+$ 180.0773, found 180.0791.



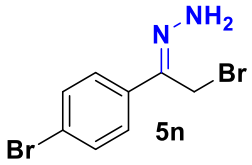
5l

1-(4-Nitro Phenyl) ethenone hydrazone (5l). The Product was purified by silica column chromatography (Ethyl Acetate: Hexane 1:9), yellow Solid: m. p. (148-149 ℃); Yield (82%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 5.70 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.1, 145.4, 143.6, 125.9, 123.6, 11.2 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_9N_3O_2$ $[M+H]^+$ 180.0773, found 180.0752.



5m

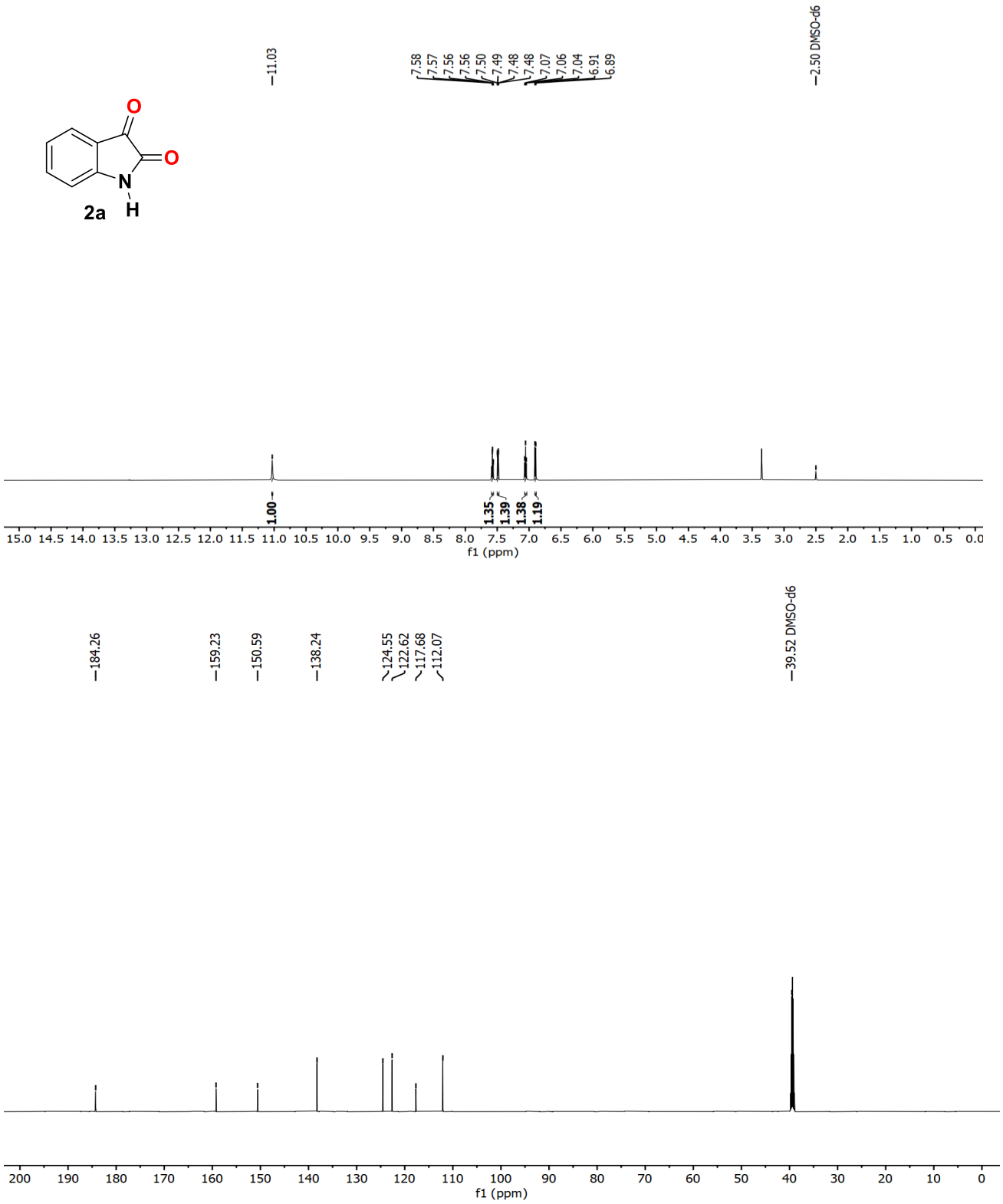
(diphenyl methylene) hydrazone (5m). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), White solid; m. p. (98-99 ℃); Yield (98%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 – 7.54 (m, 2H, ArH), 7.52 – 7.47 (m, 3H, ArH), 7.32-7.30 (m, 5H, ArH), 5.46 (s, 2H, NH_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.5, 138.8, 133.3, 129.7, 129.1, 128.4, 126.8 ppm; HRMS (ESI) *m/z*: calcd for $C_{13}H_{12}N_2$ $[M+H]^+$ 197.1079, found 197.1032.



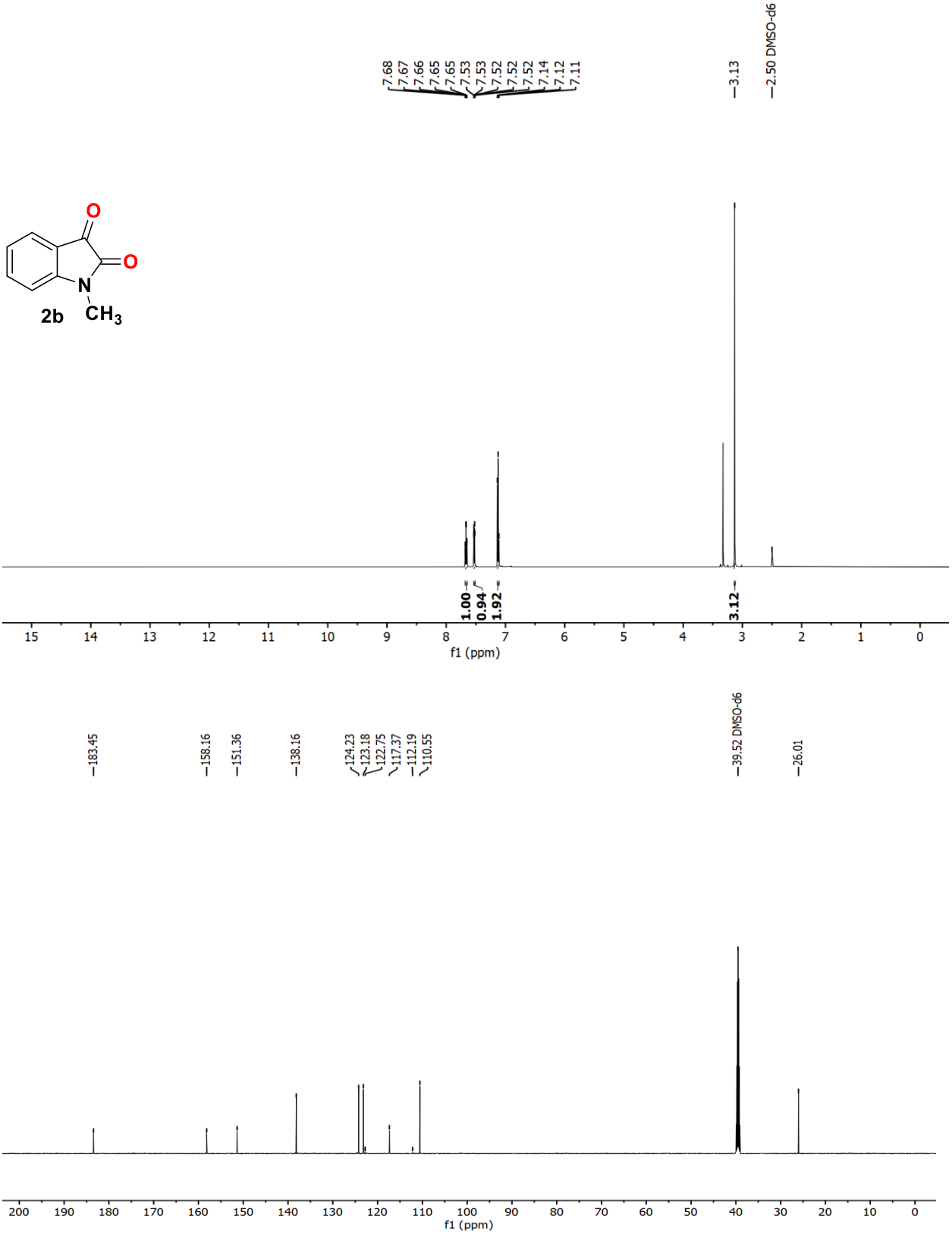
5n

2- bromo-1-(4-bromophenyl) ethylidene) hydrazine (5n). The product was purified by silica gel column chromatography (Ethyl Acetate: Hexane 1:9), brown solid; m. p. (107-108 ℃); Yield (77%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.9 Hz, 2H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH), 5.41 (s, 2H, NH_2), 2.12 (s, 2H, CH_2Br); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 146.6, 138.2, 134.1, 132.8, 130.8, 129.4, 127.0, 15.3 ppm; HRMS (ESI) *m/z*: calcd for $C_8H_8Br_2N_2$ $[M+H]^+$ 290.9132, found 290.9172.

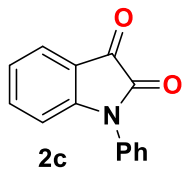
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



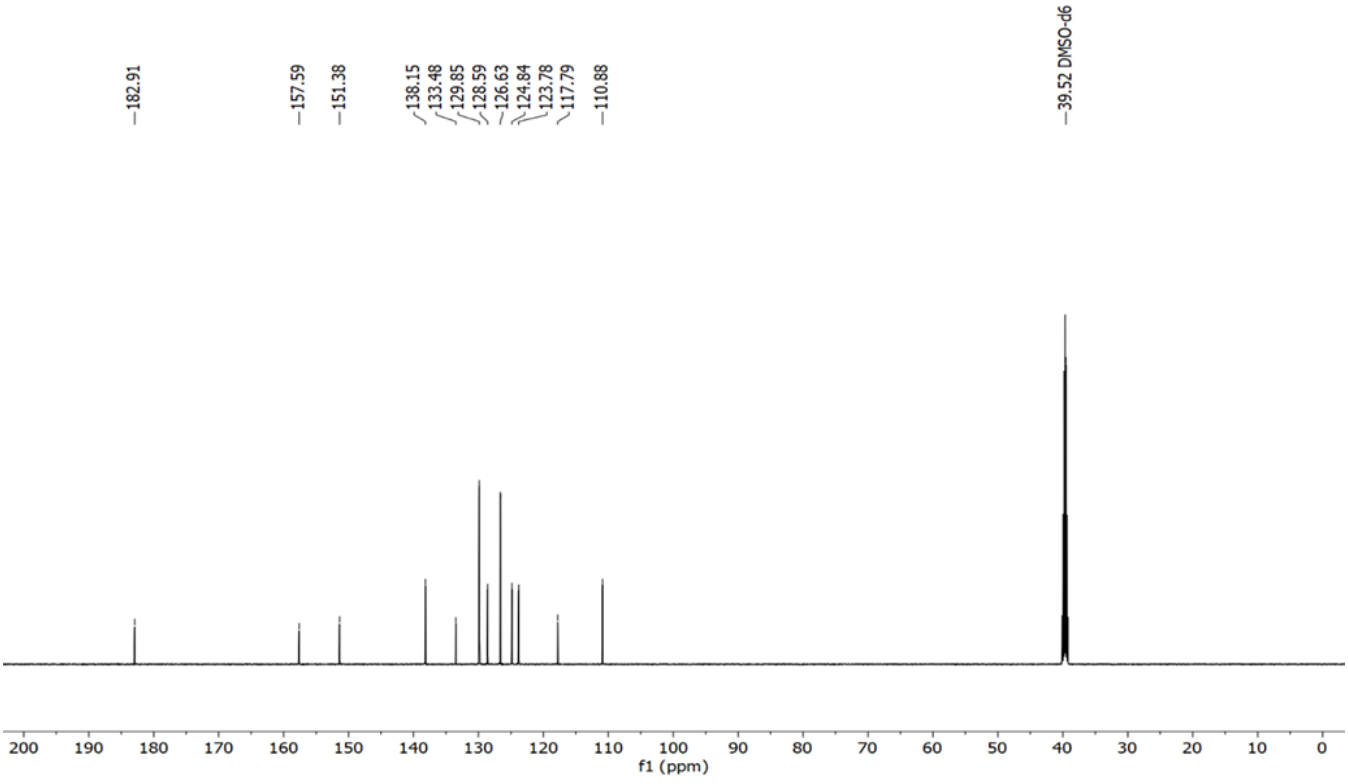
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



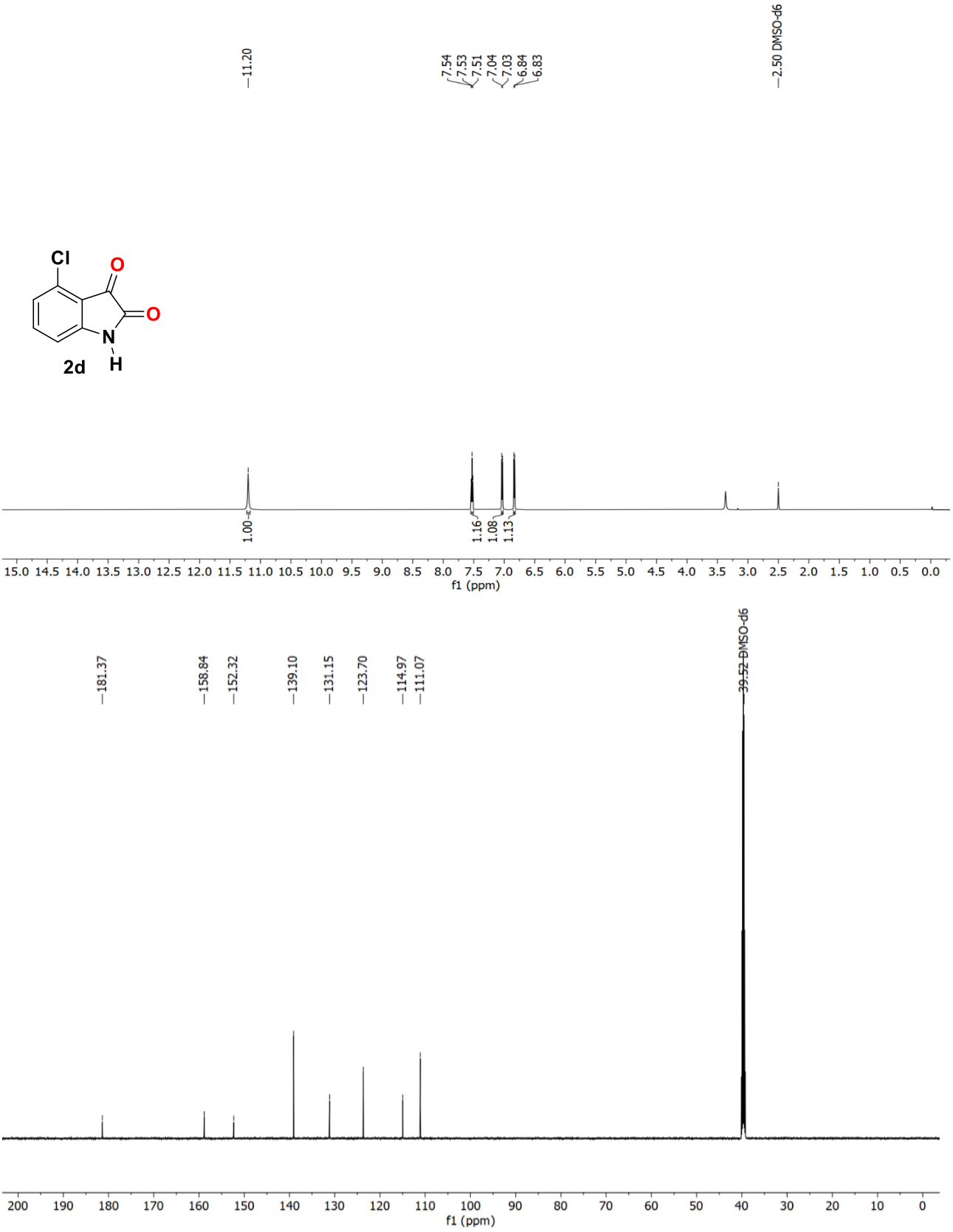
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



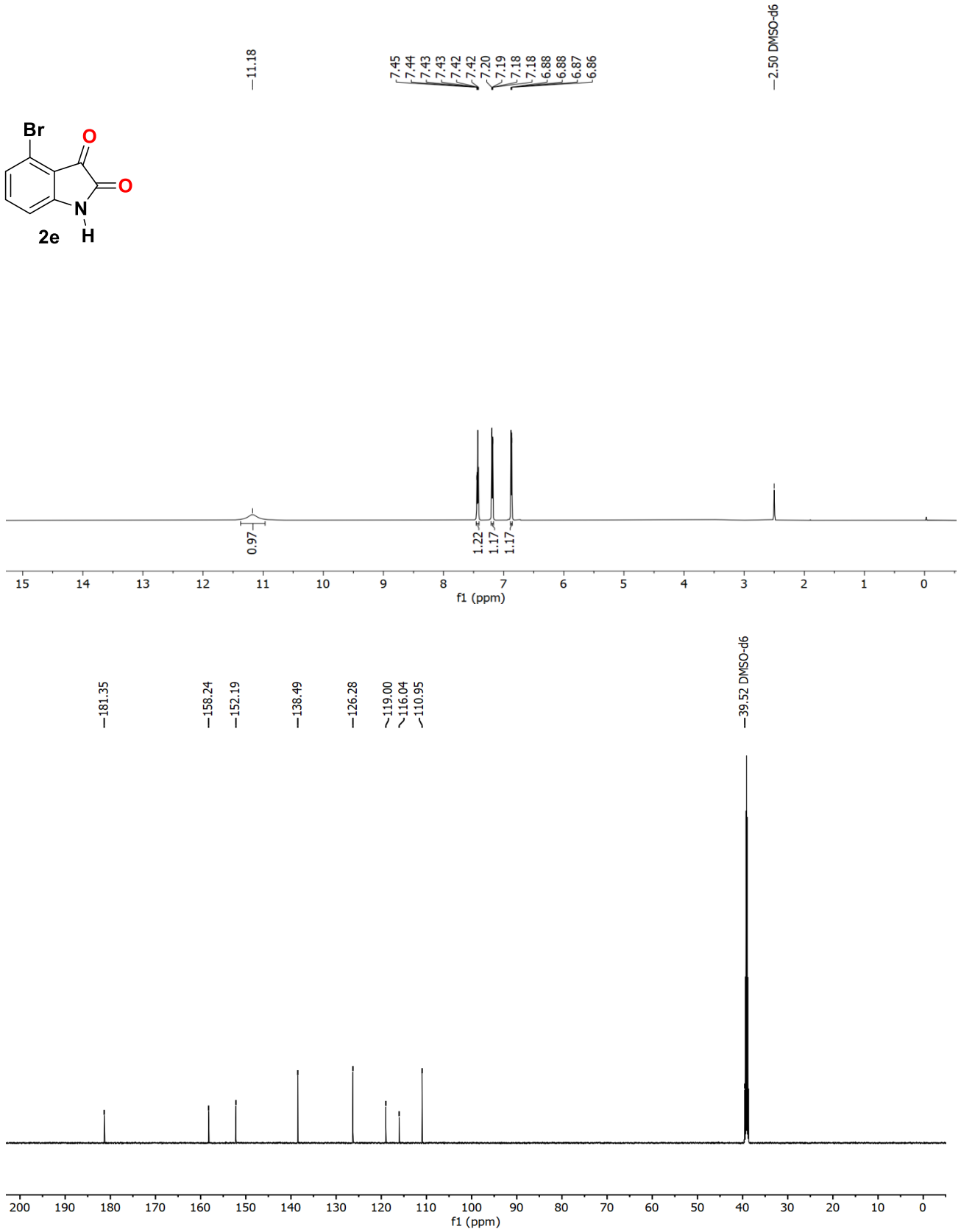
2c



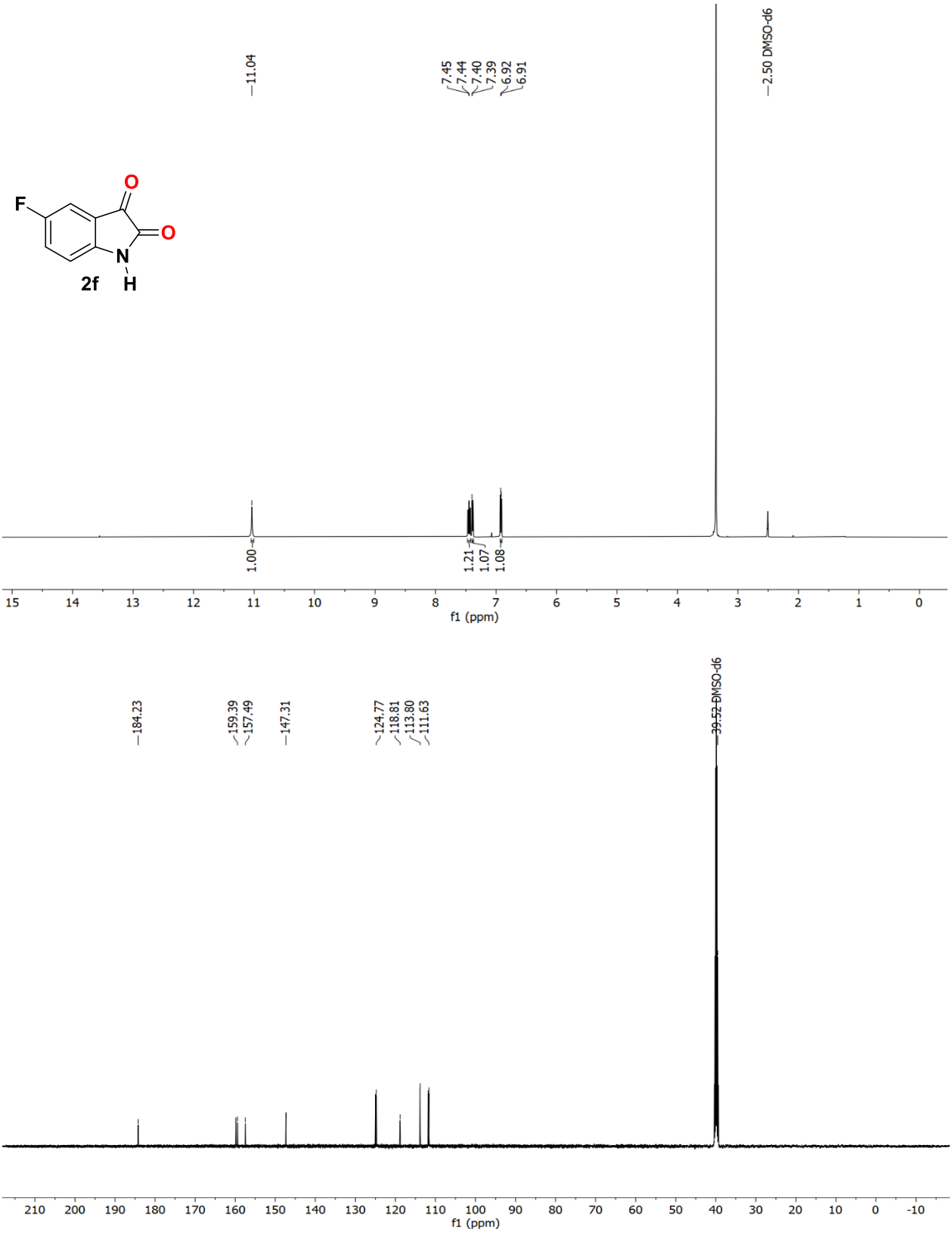
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



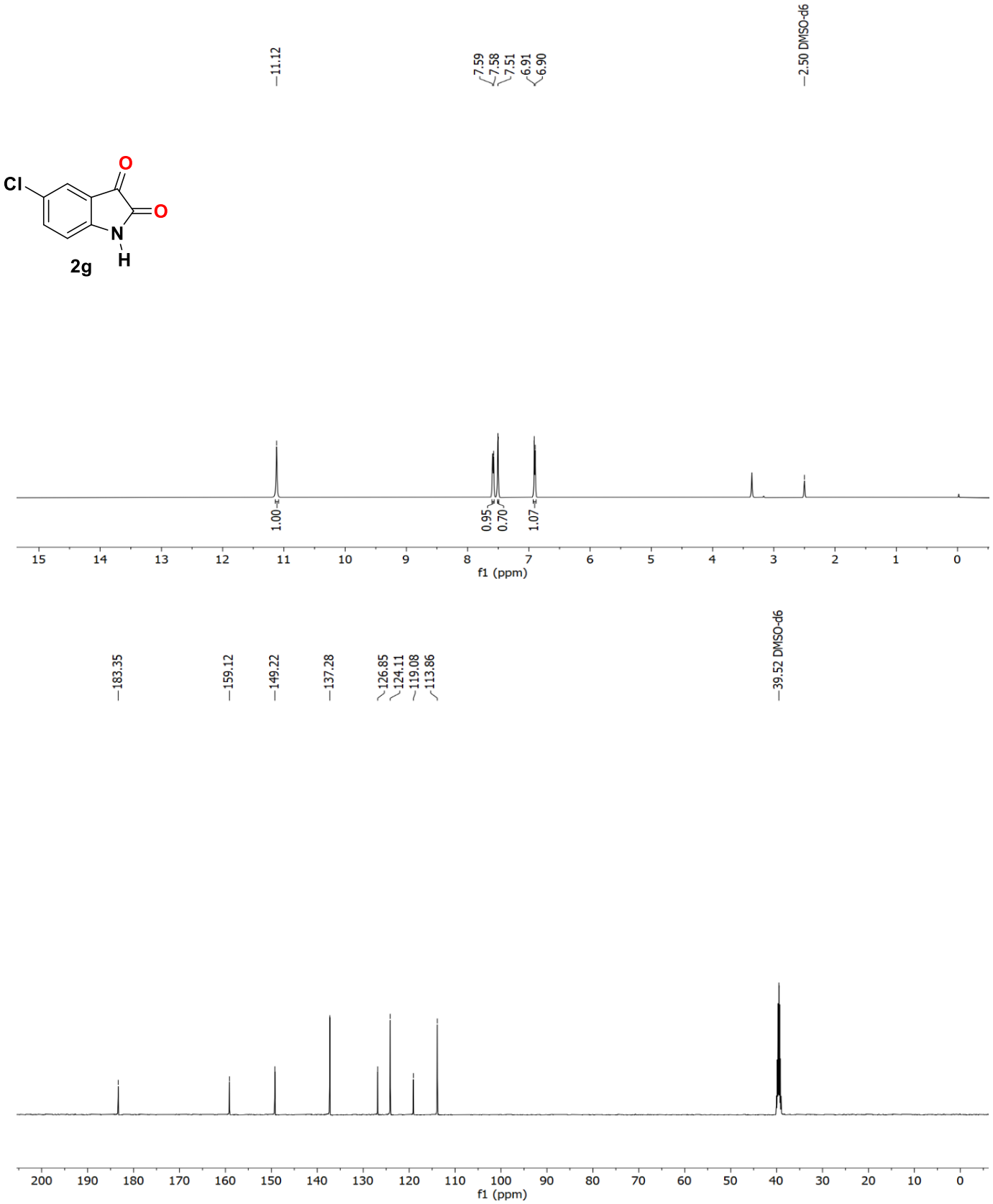
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



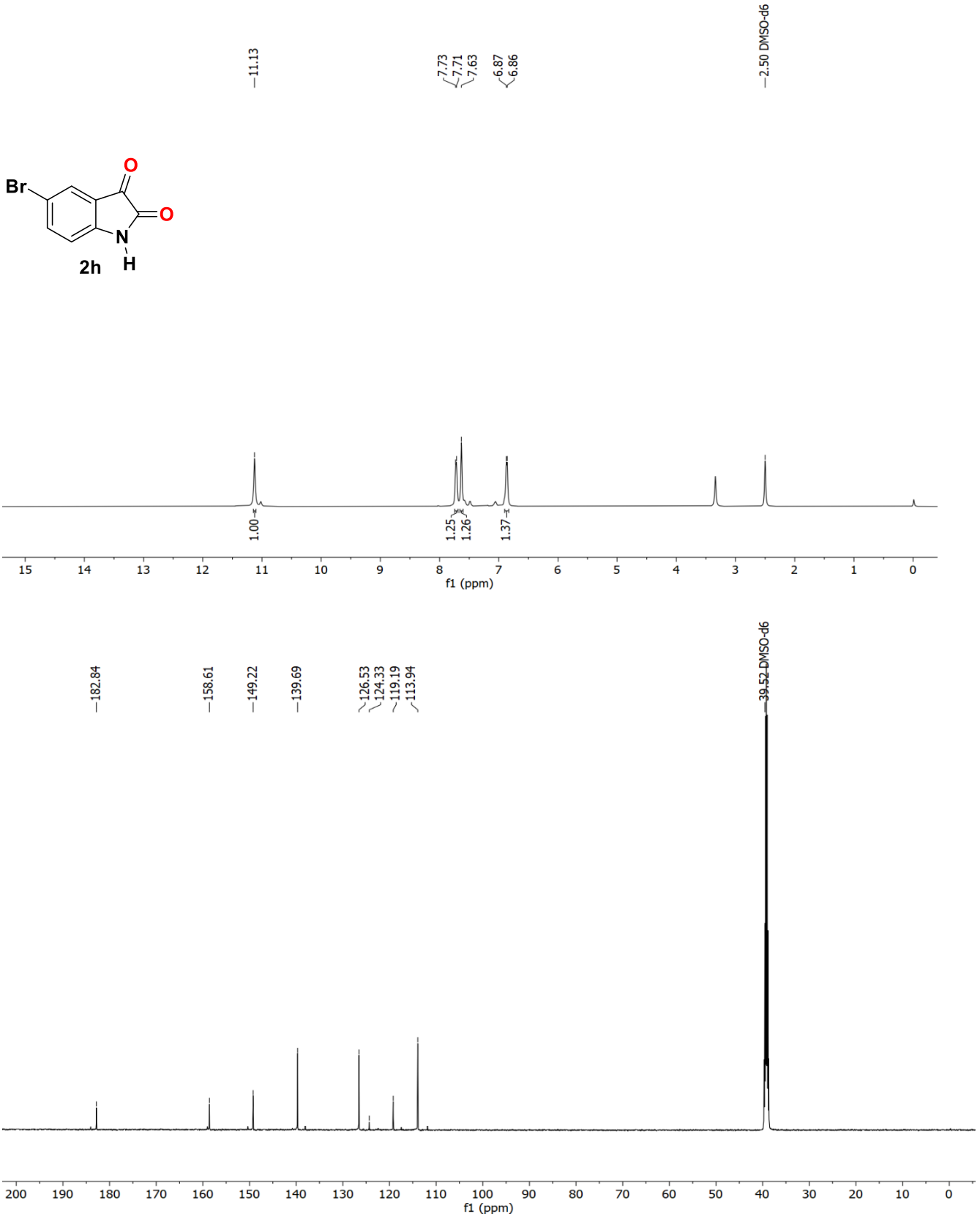
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



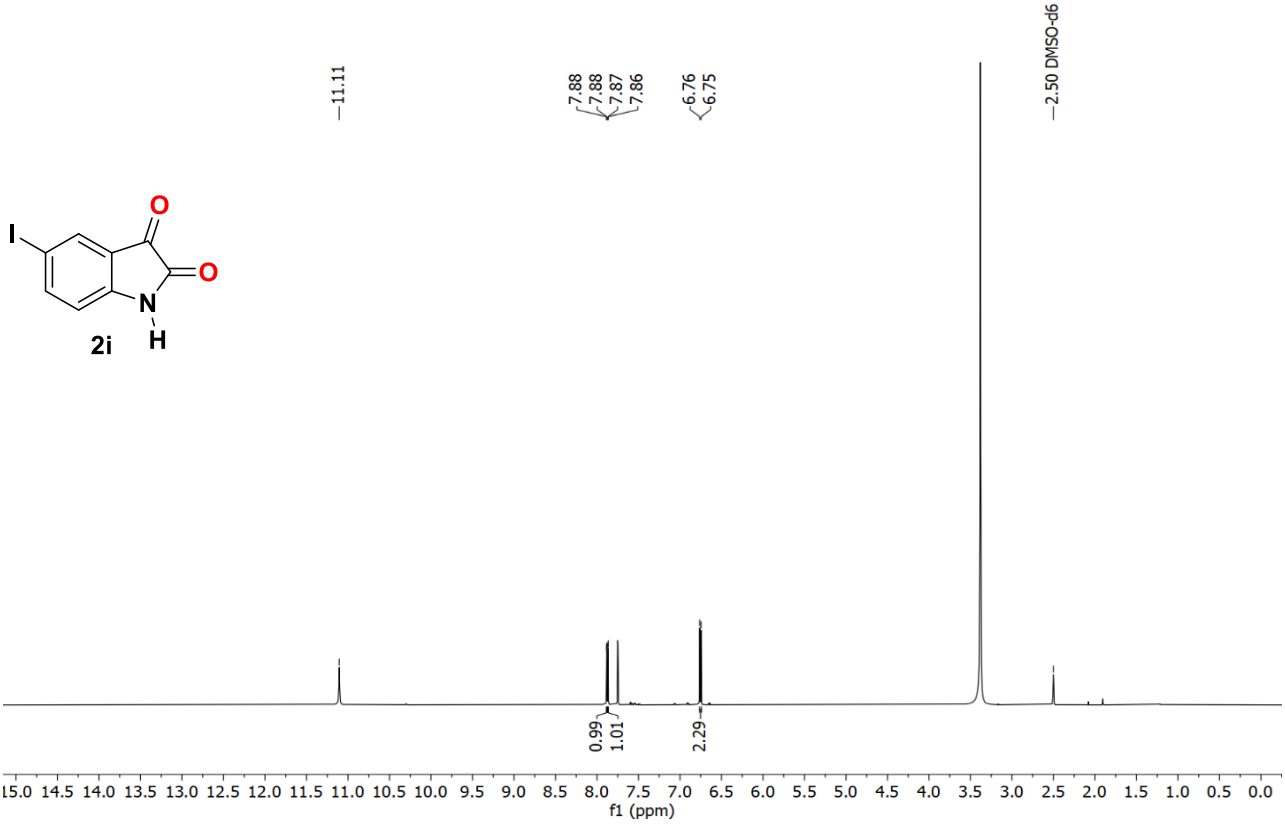
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

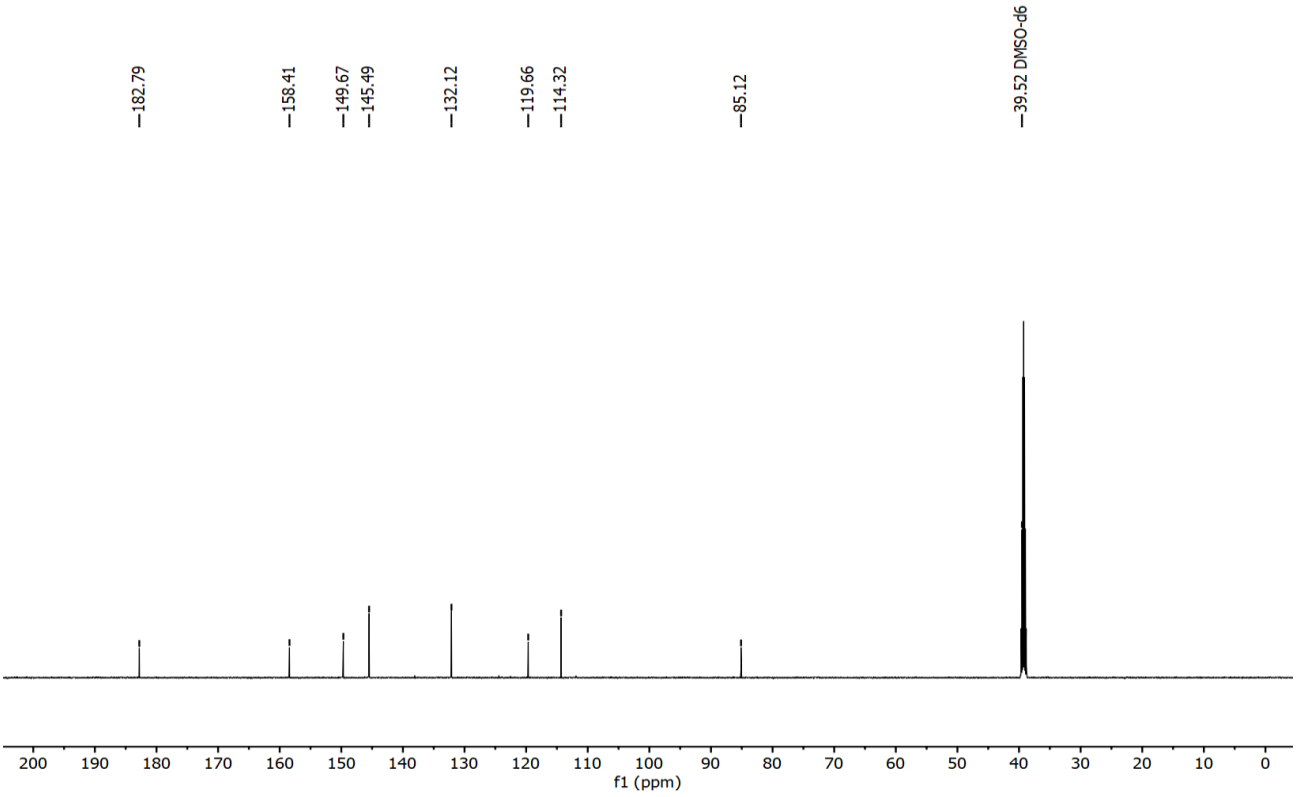


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

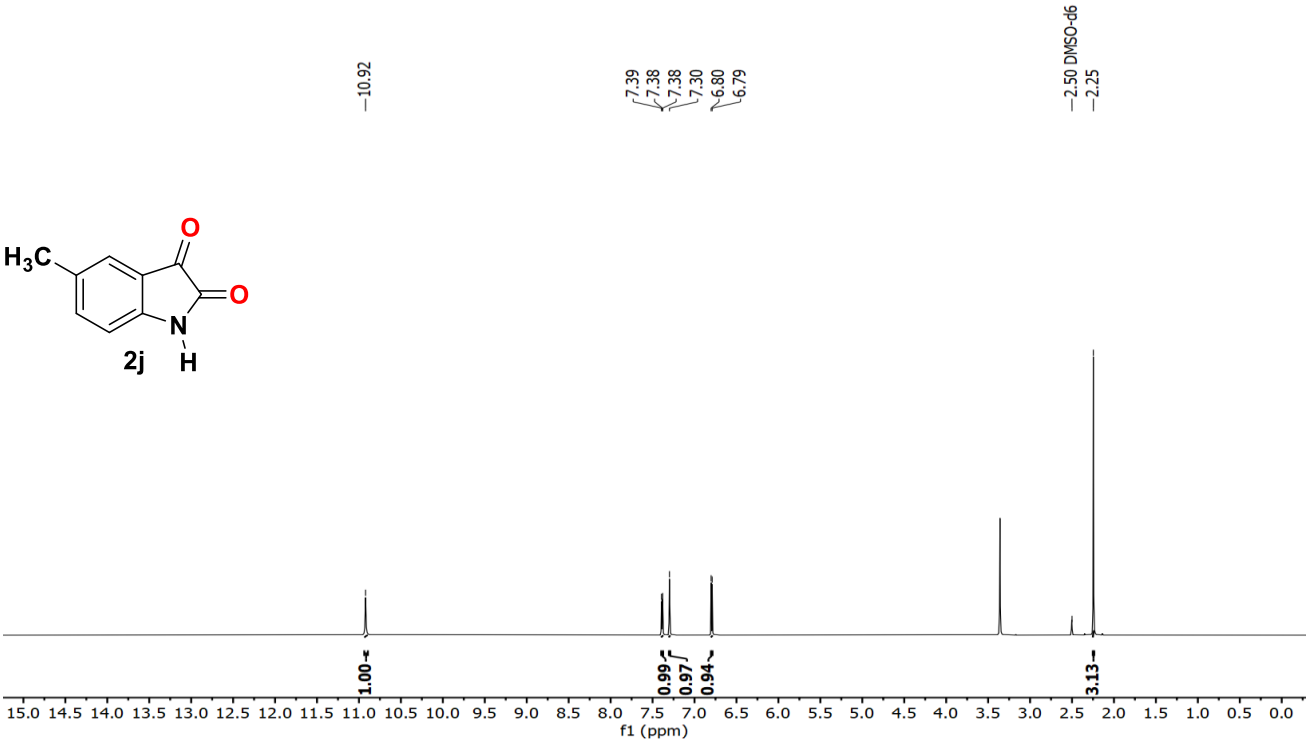


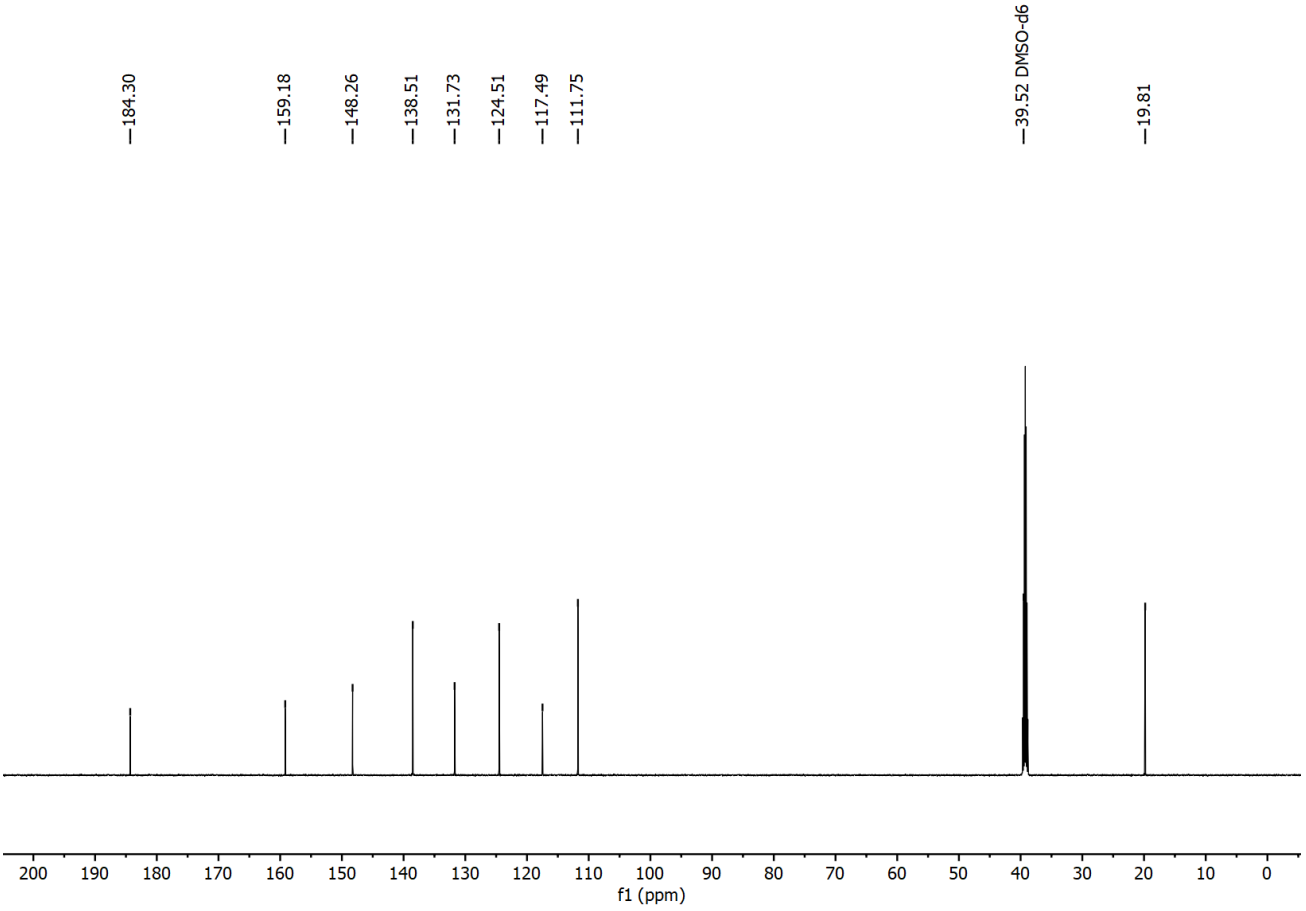
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



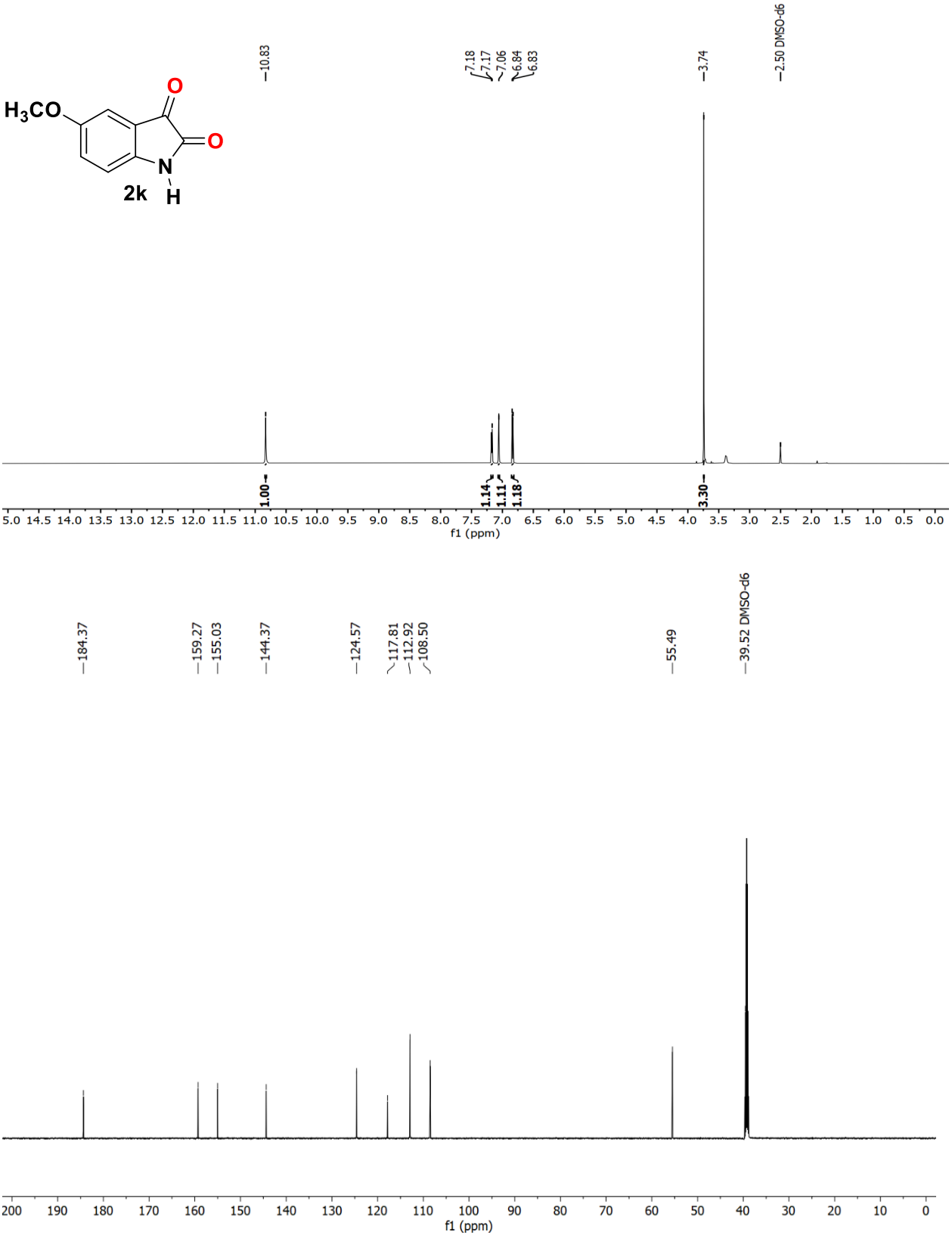


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

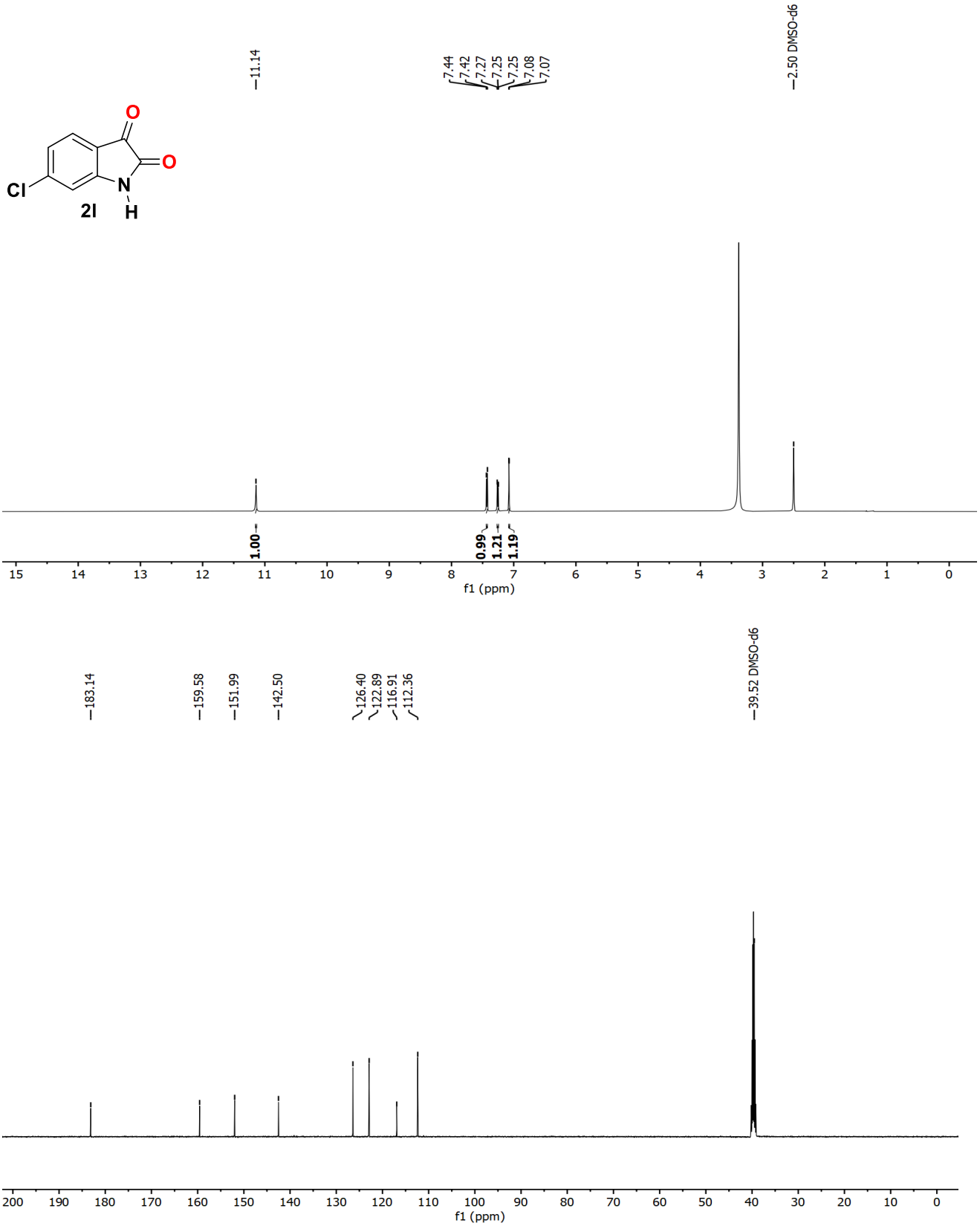




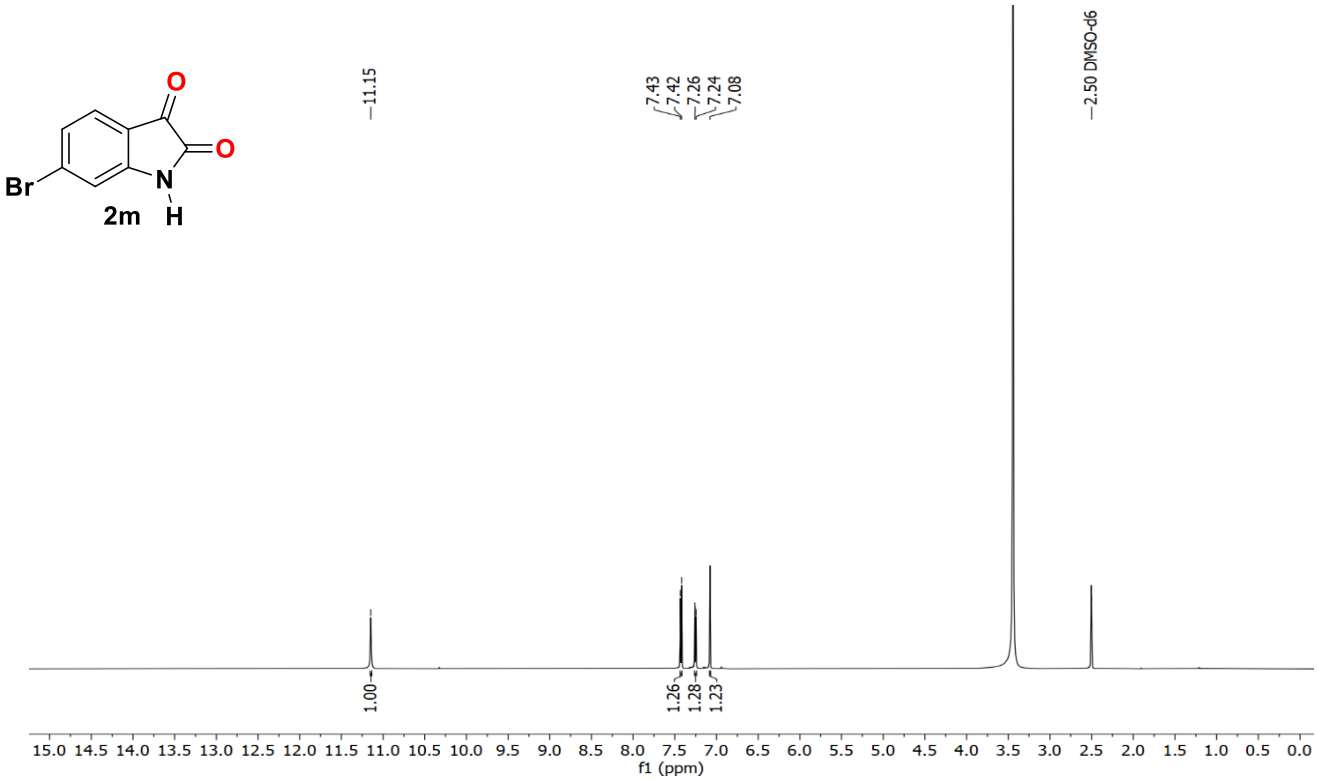
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

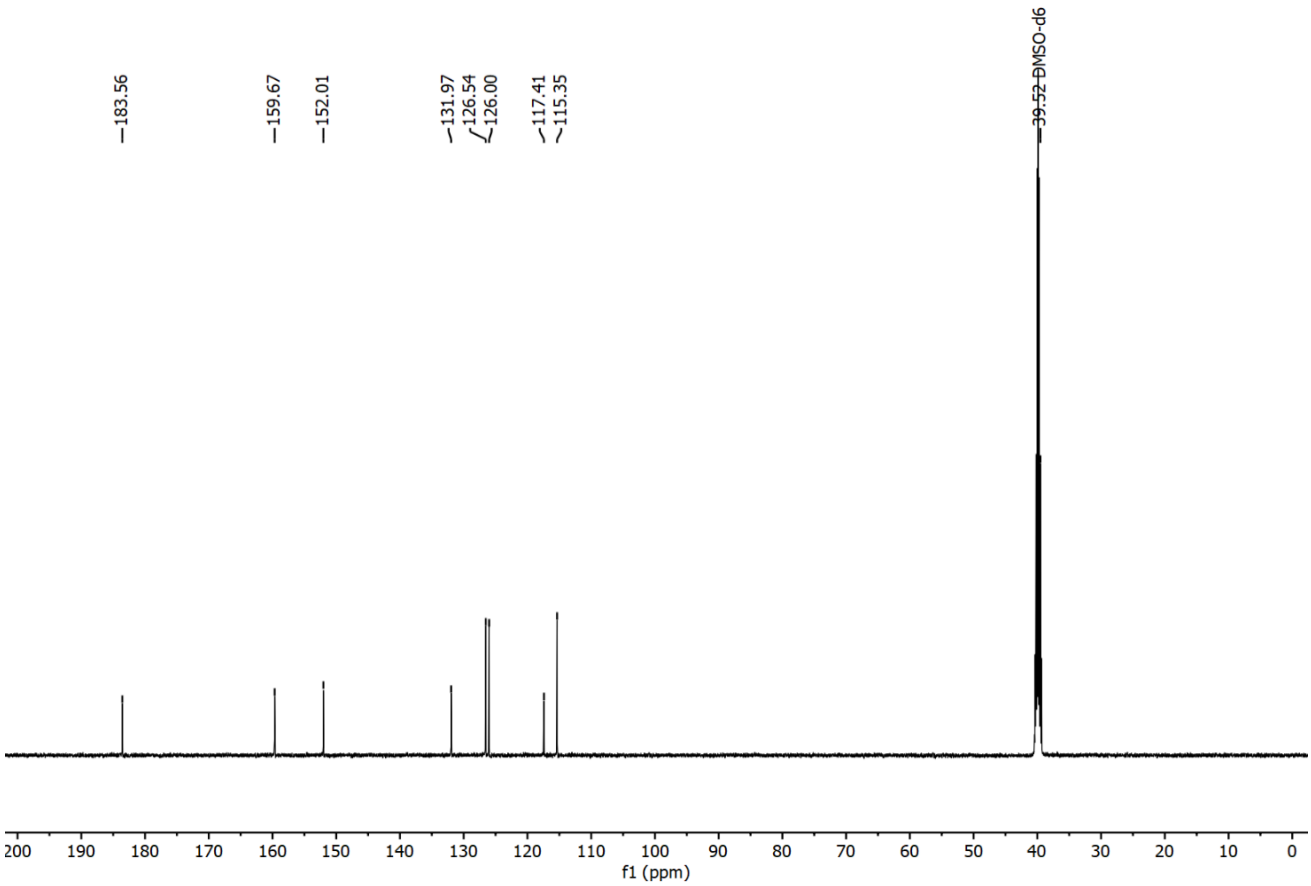


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

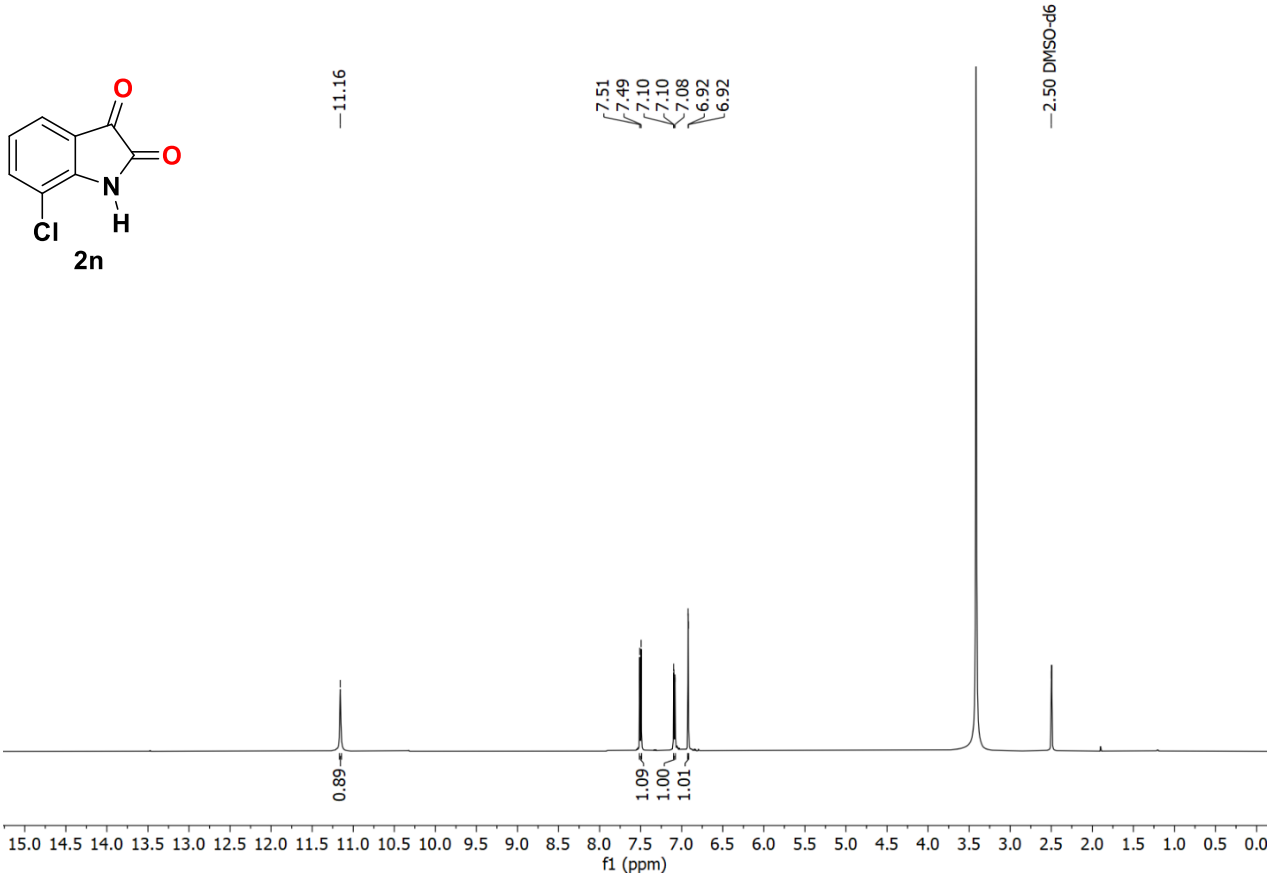


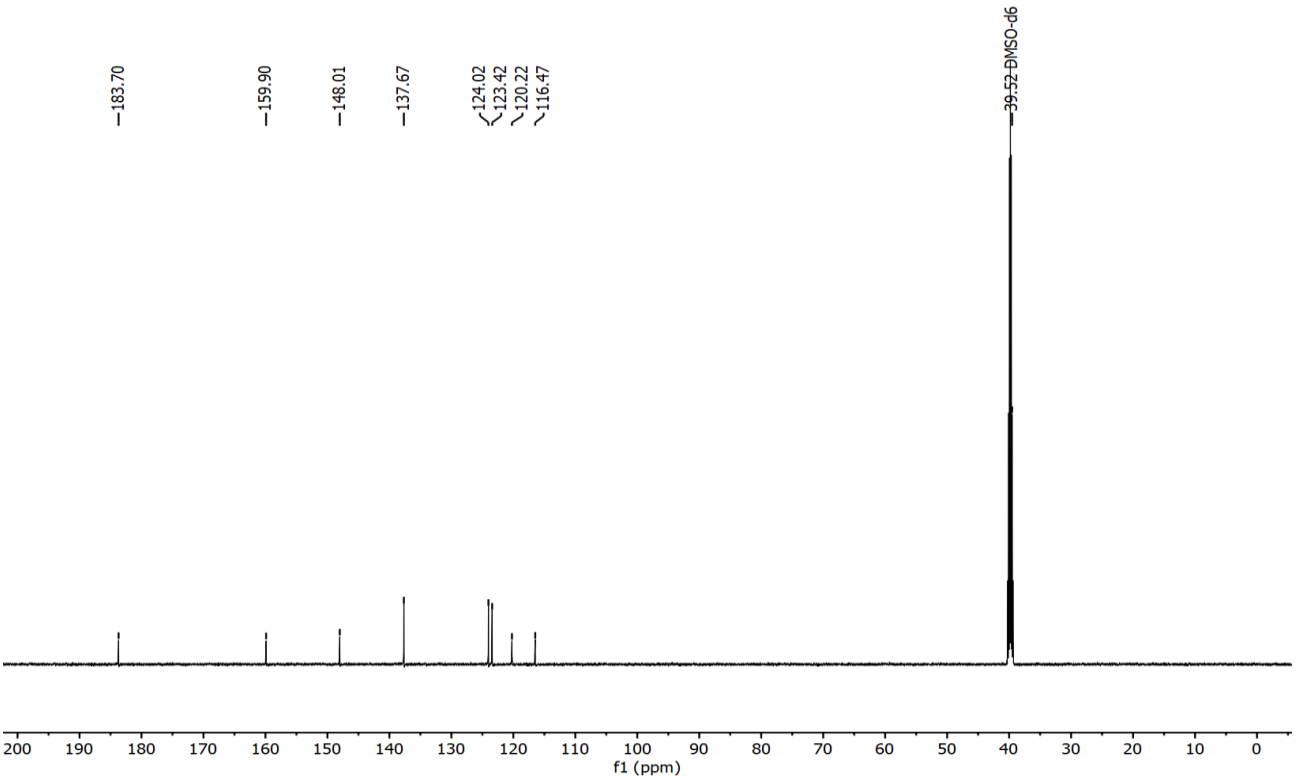
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



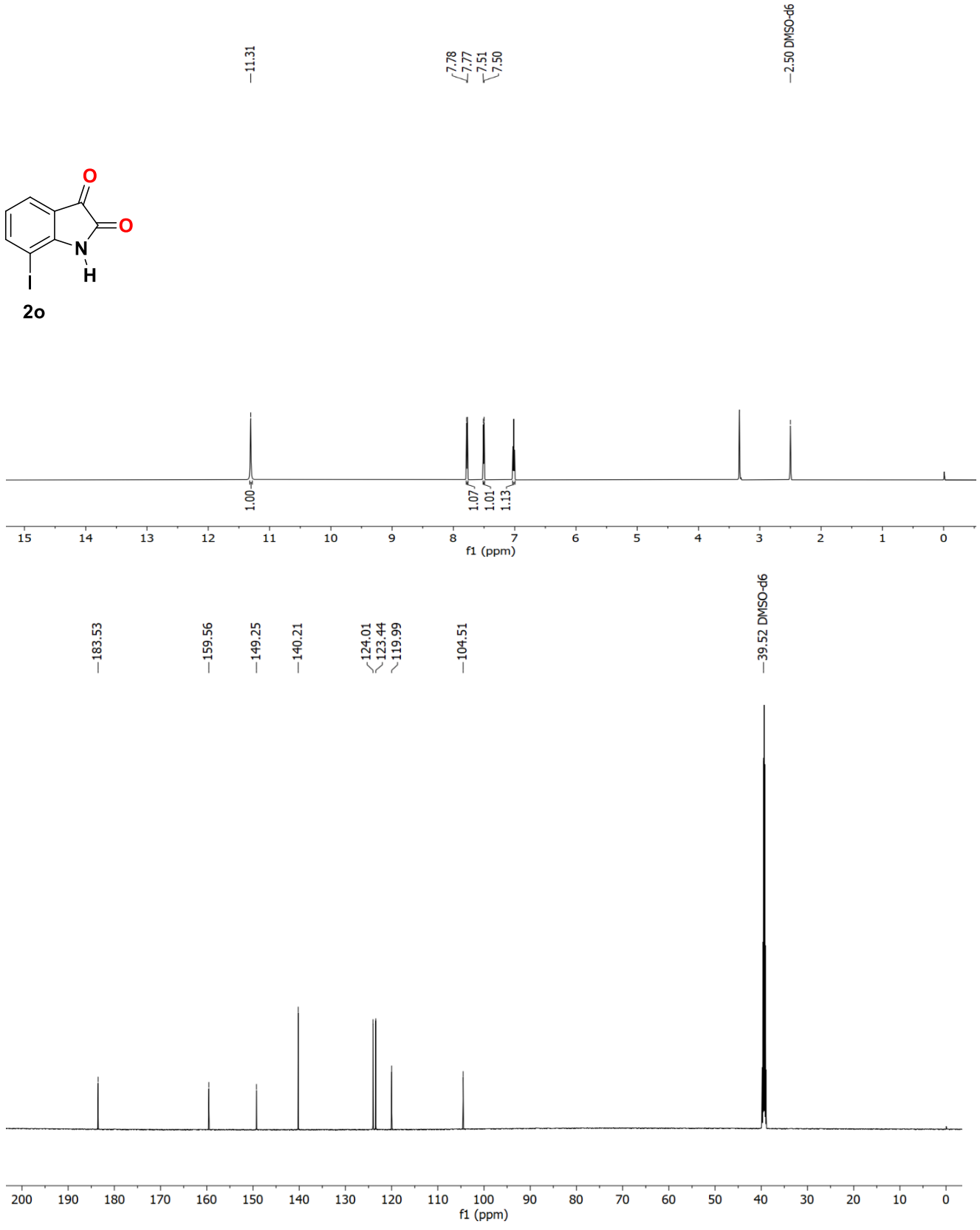


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

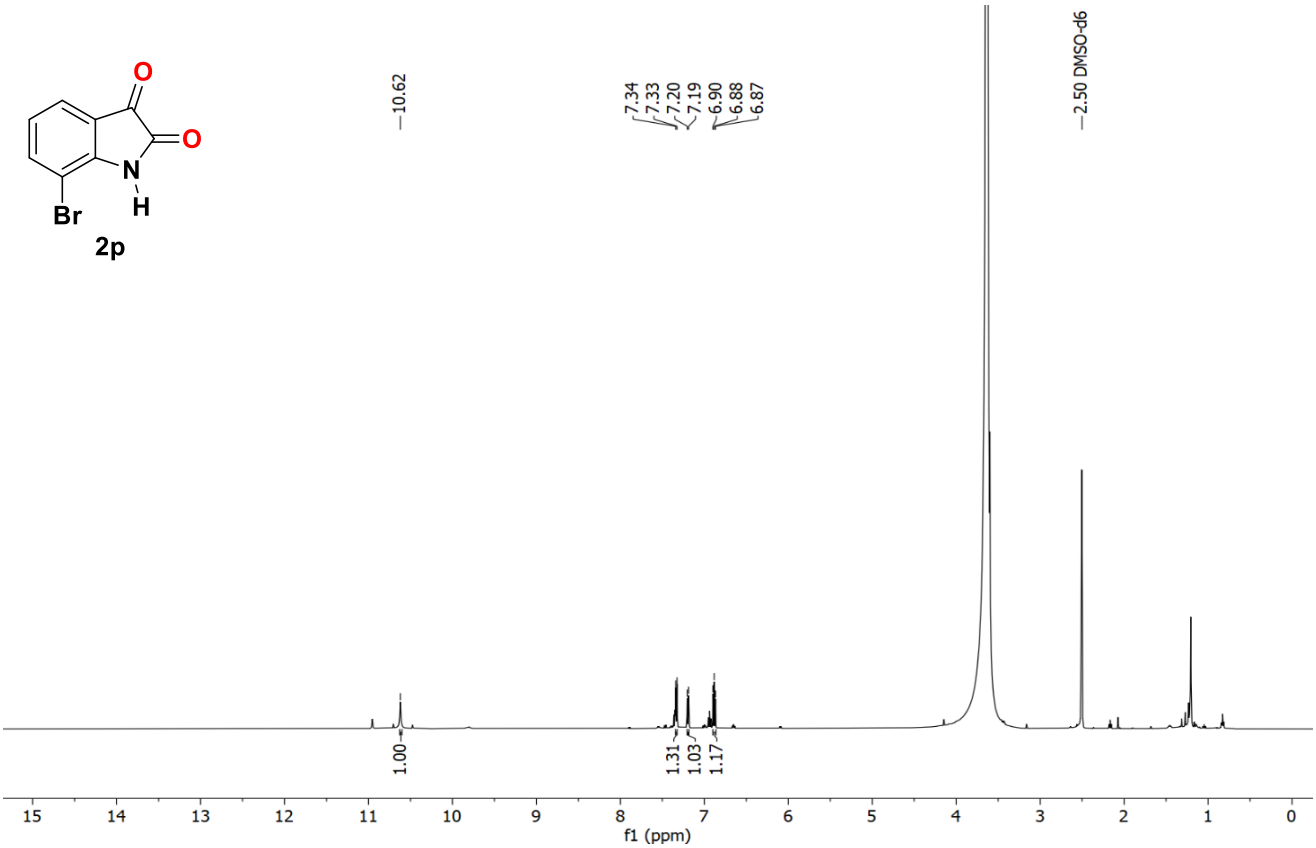


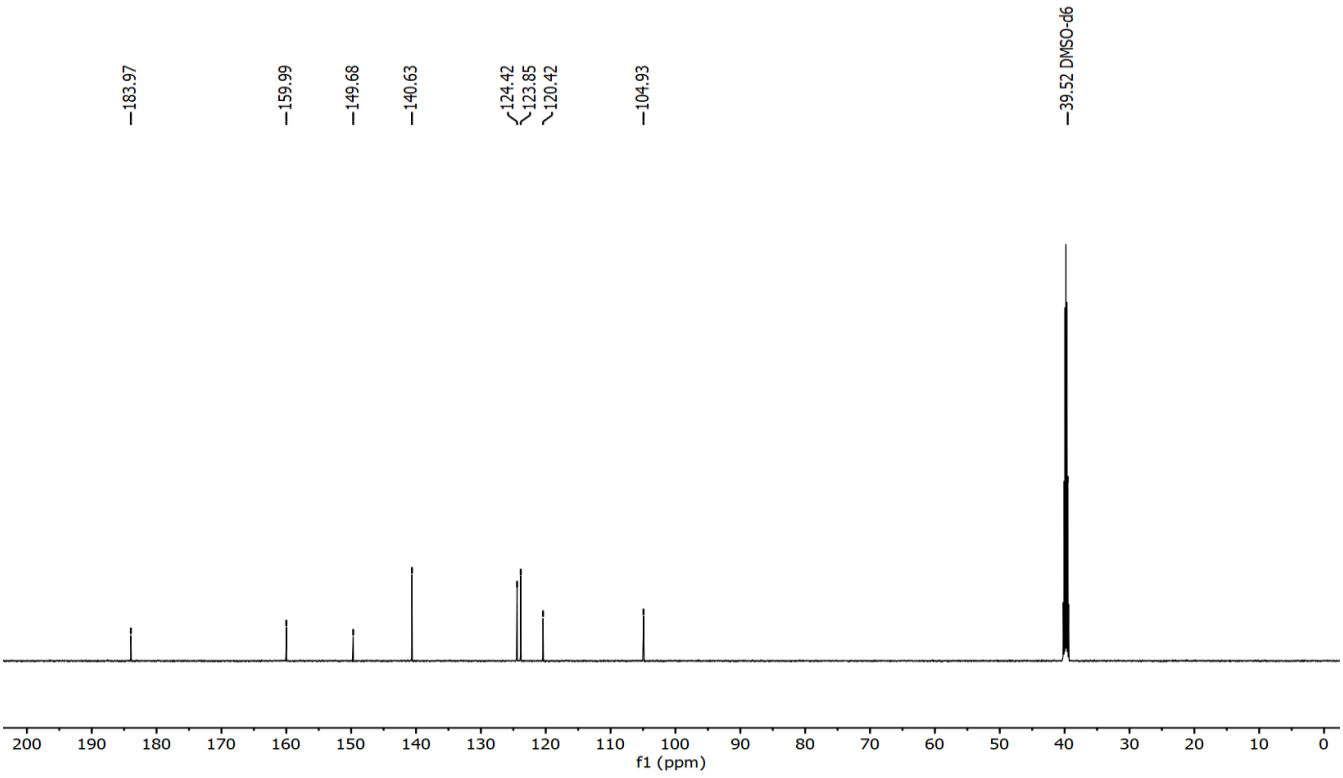


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

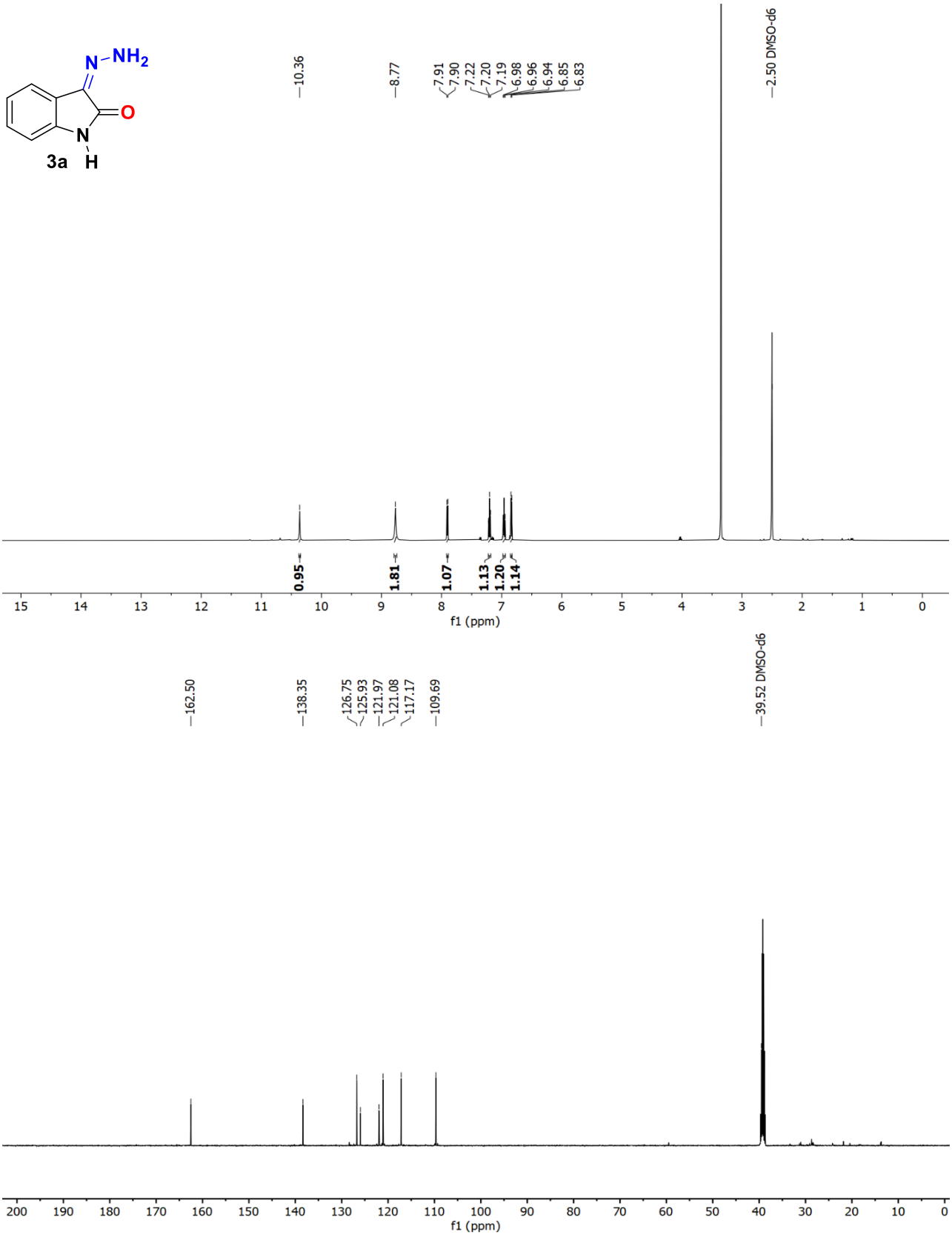


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

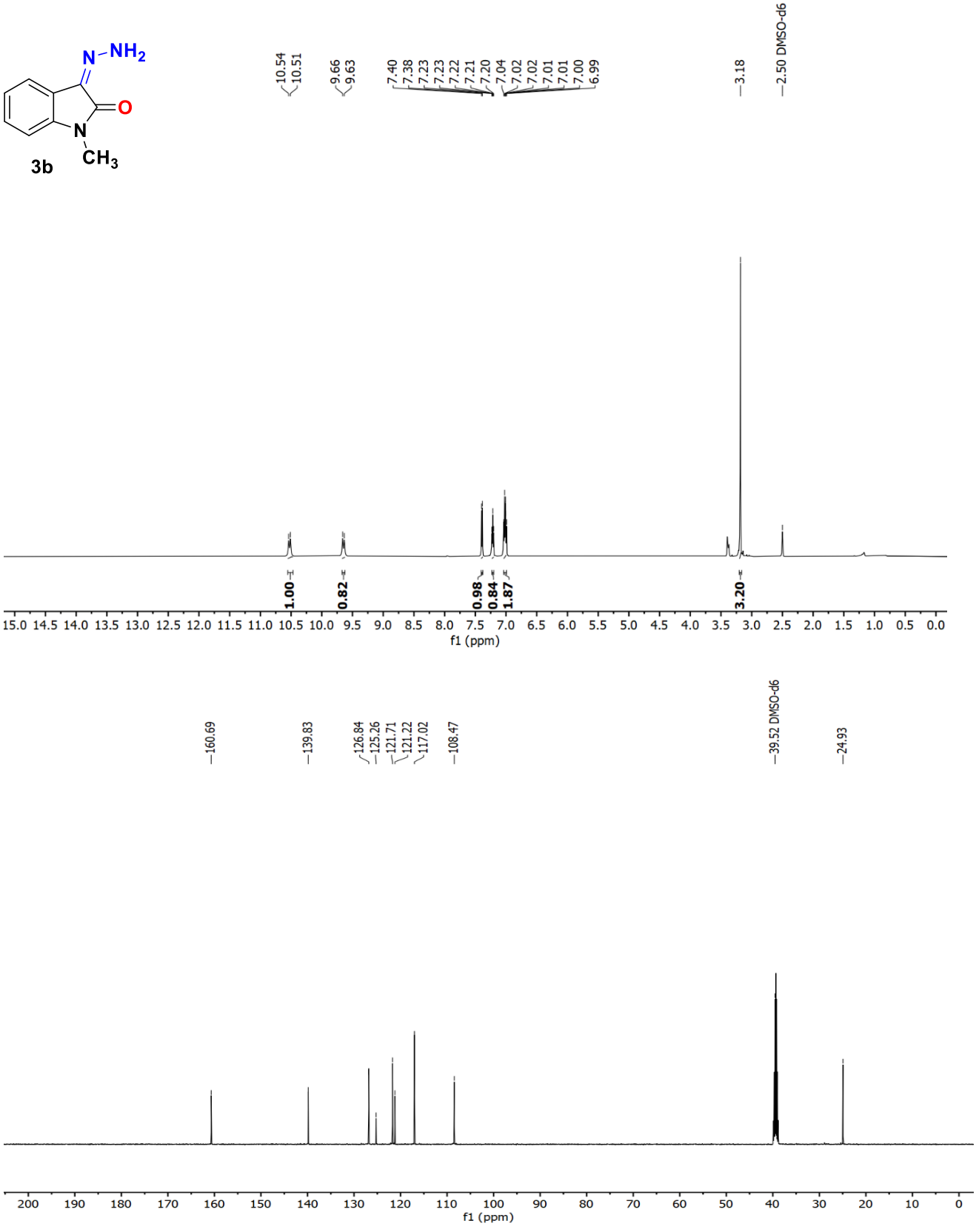




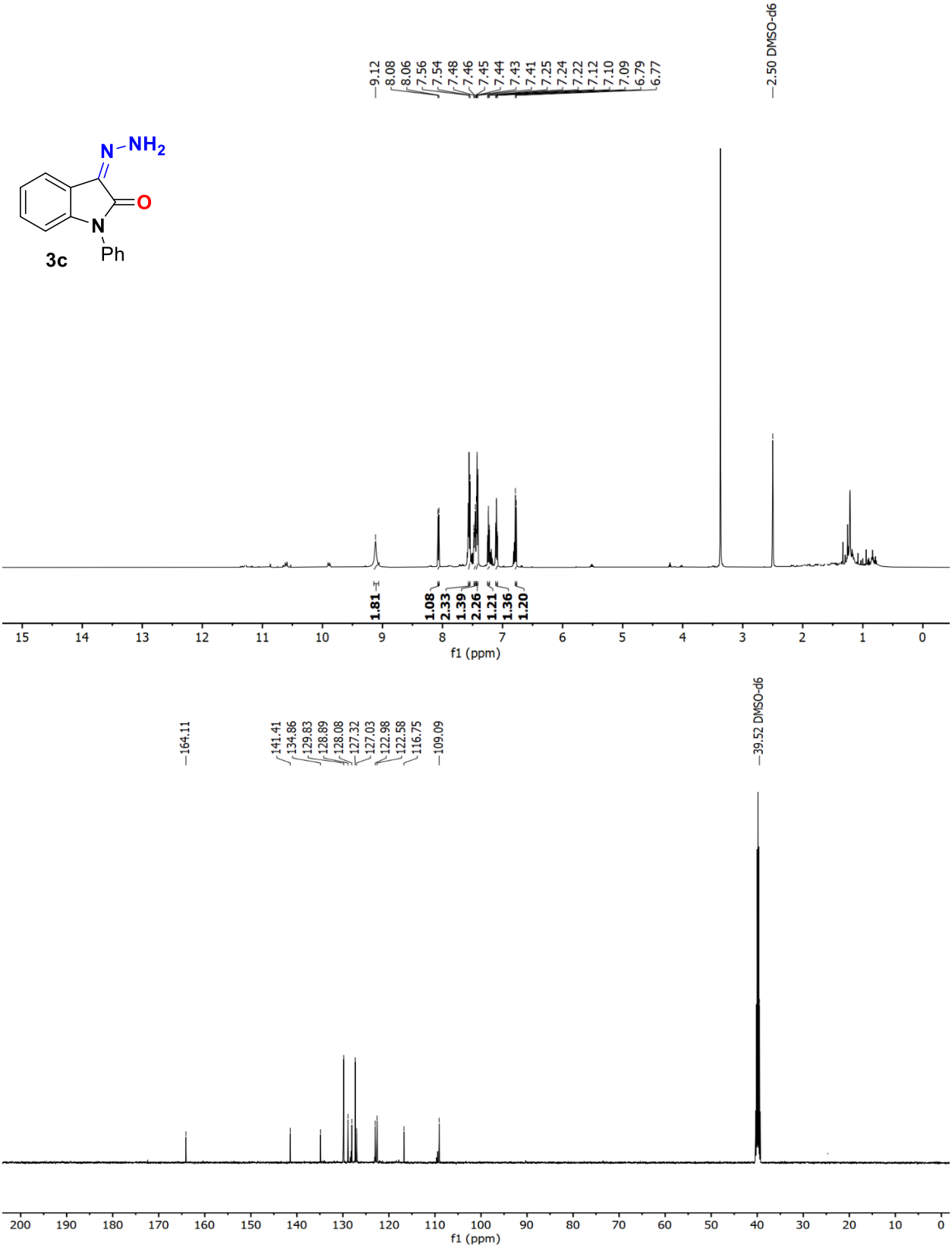
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



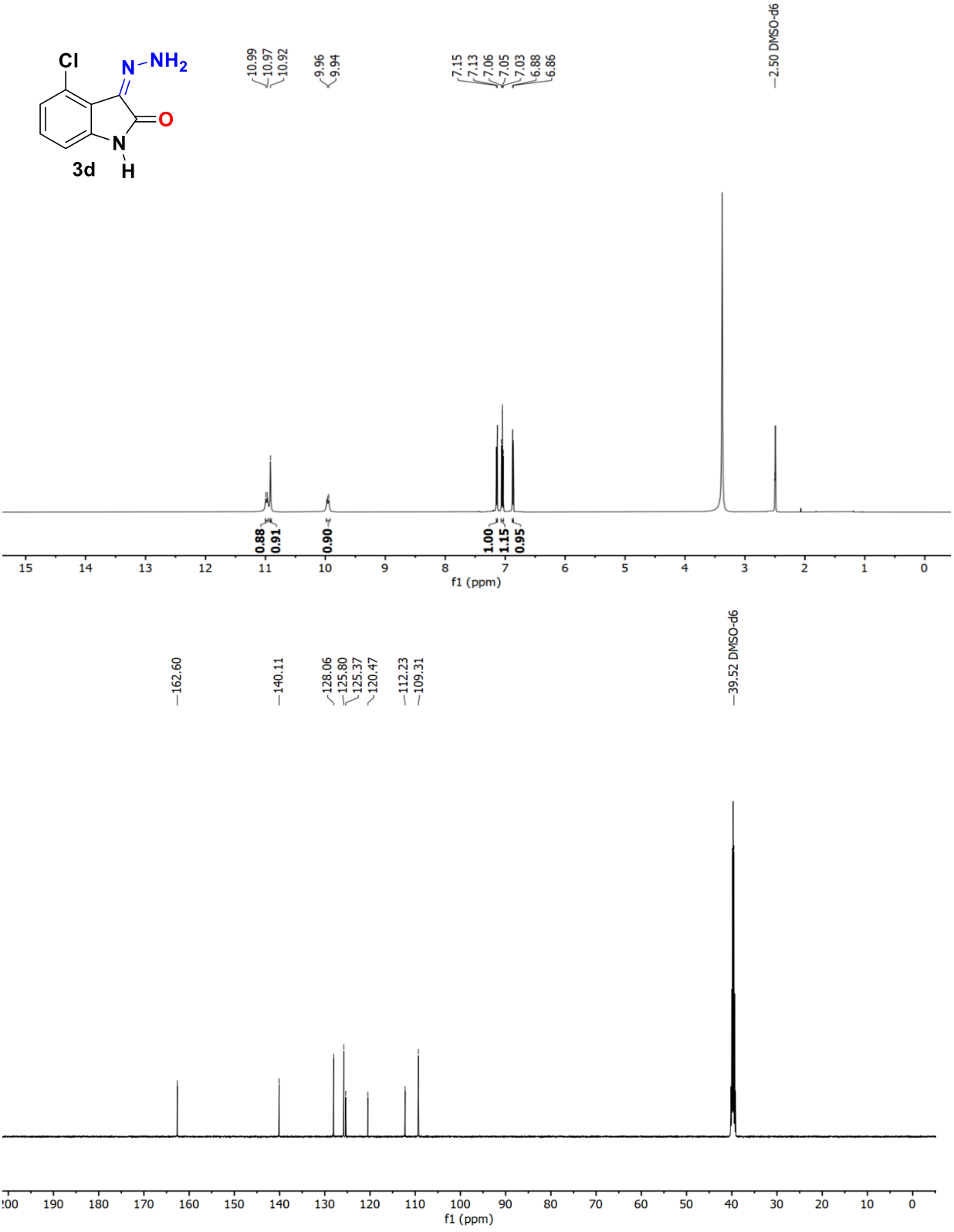
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



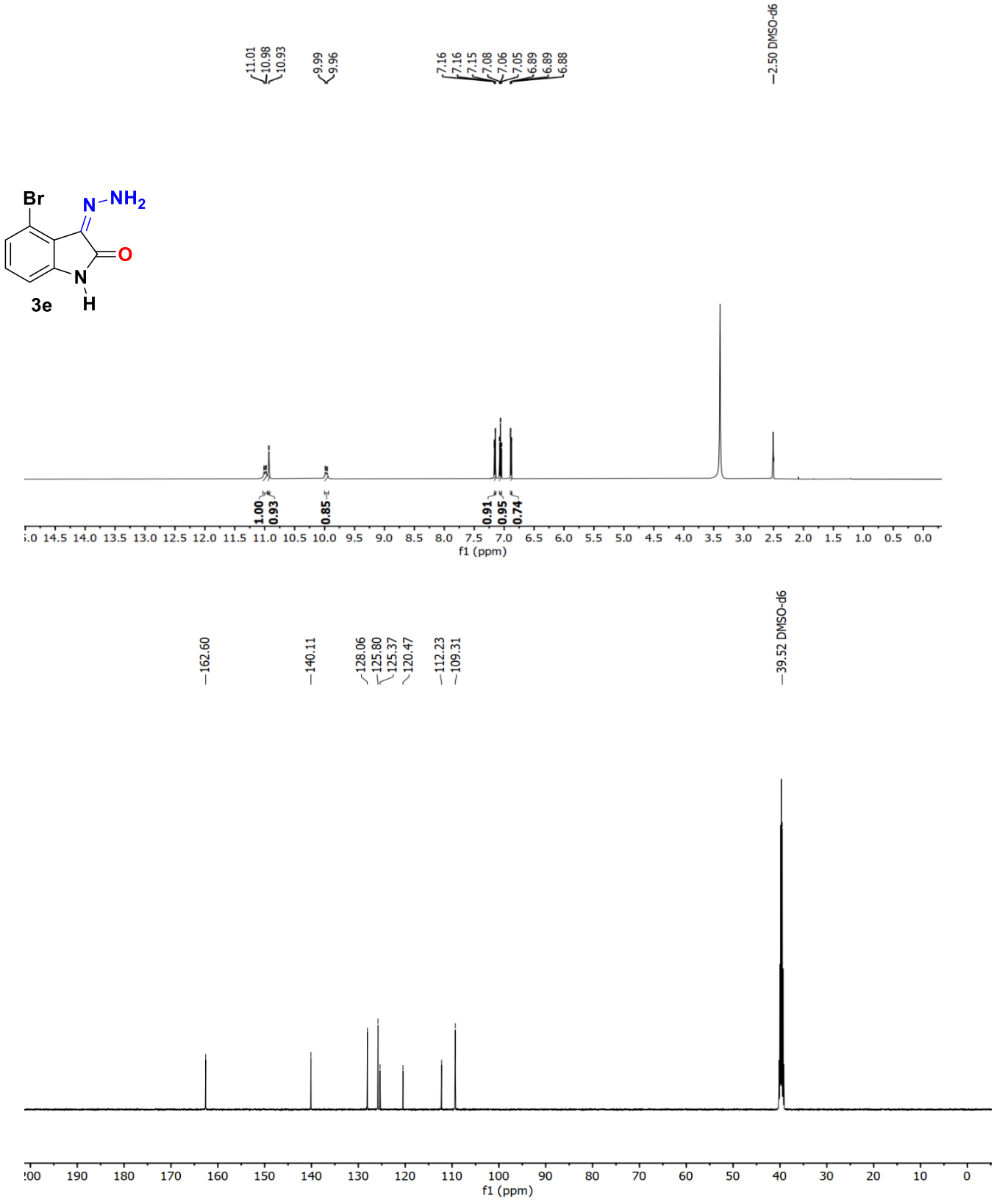
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



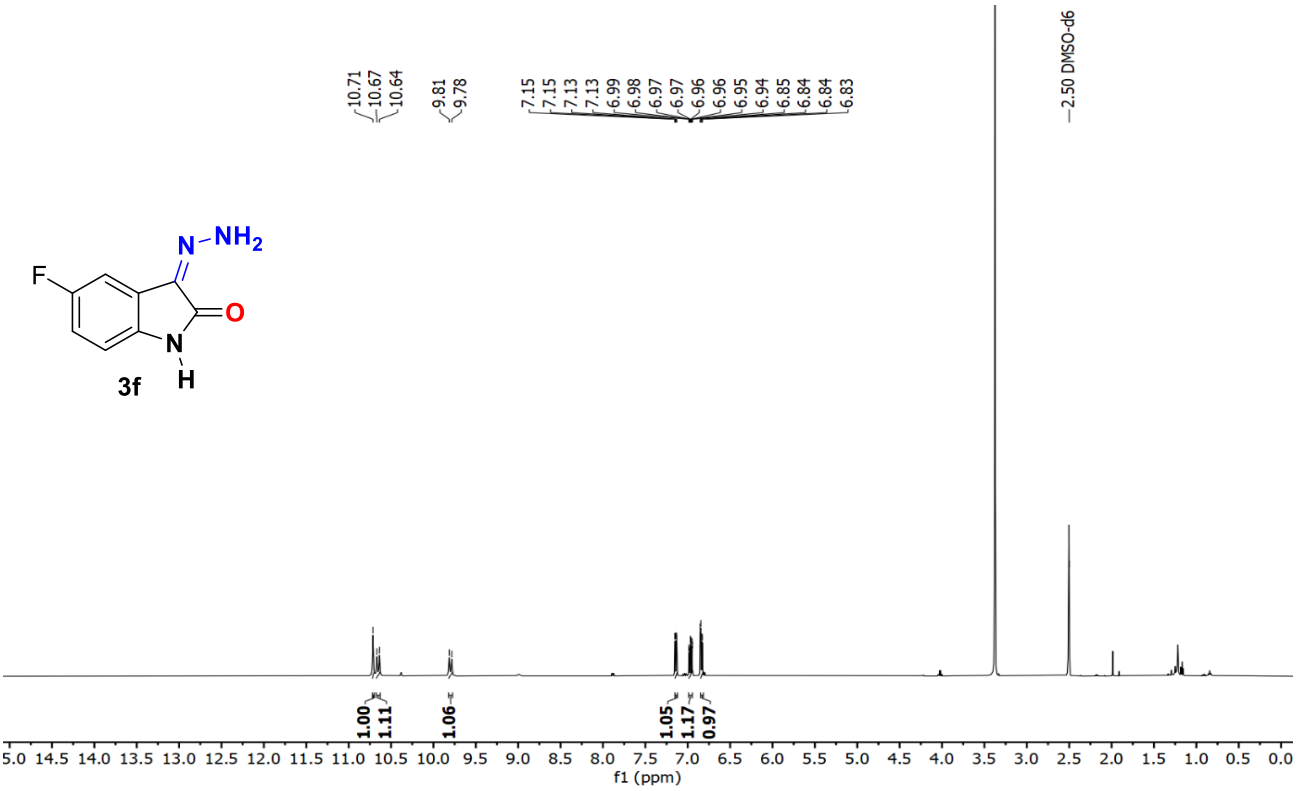
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

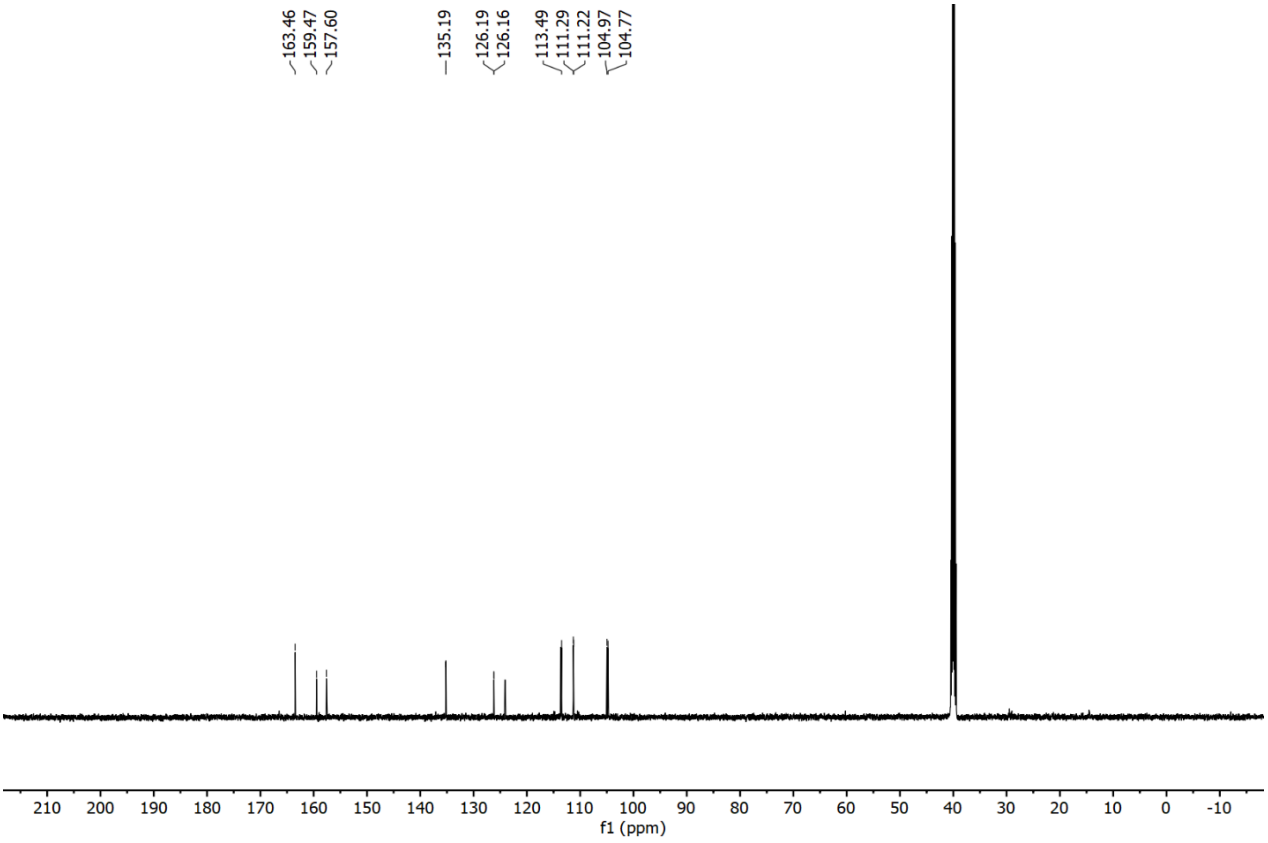


^{1}H NMR (500 MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$)

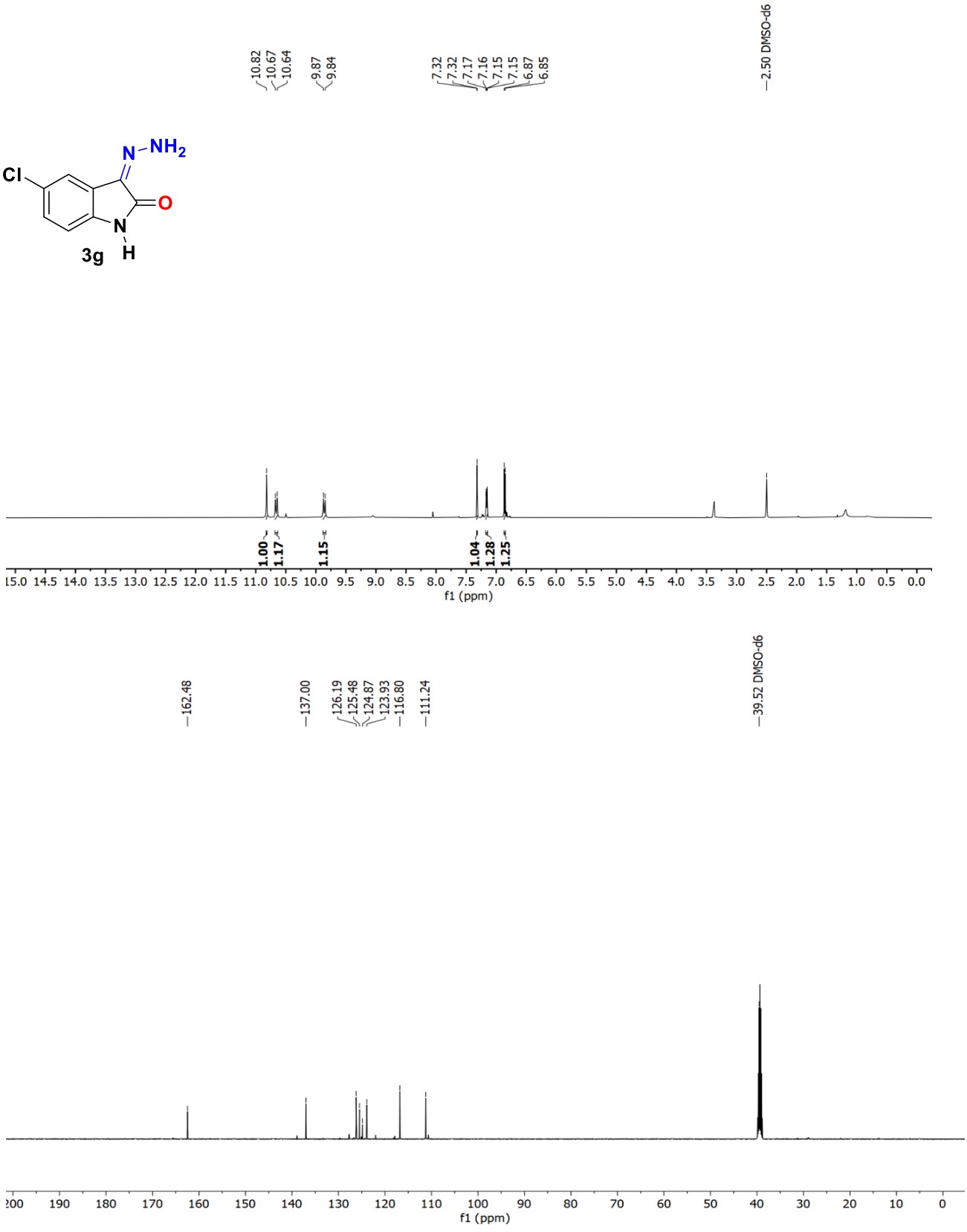


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

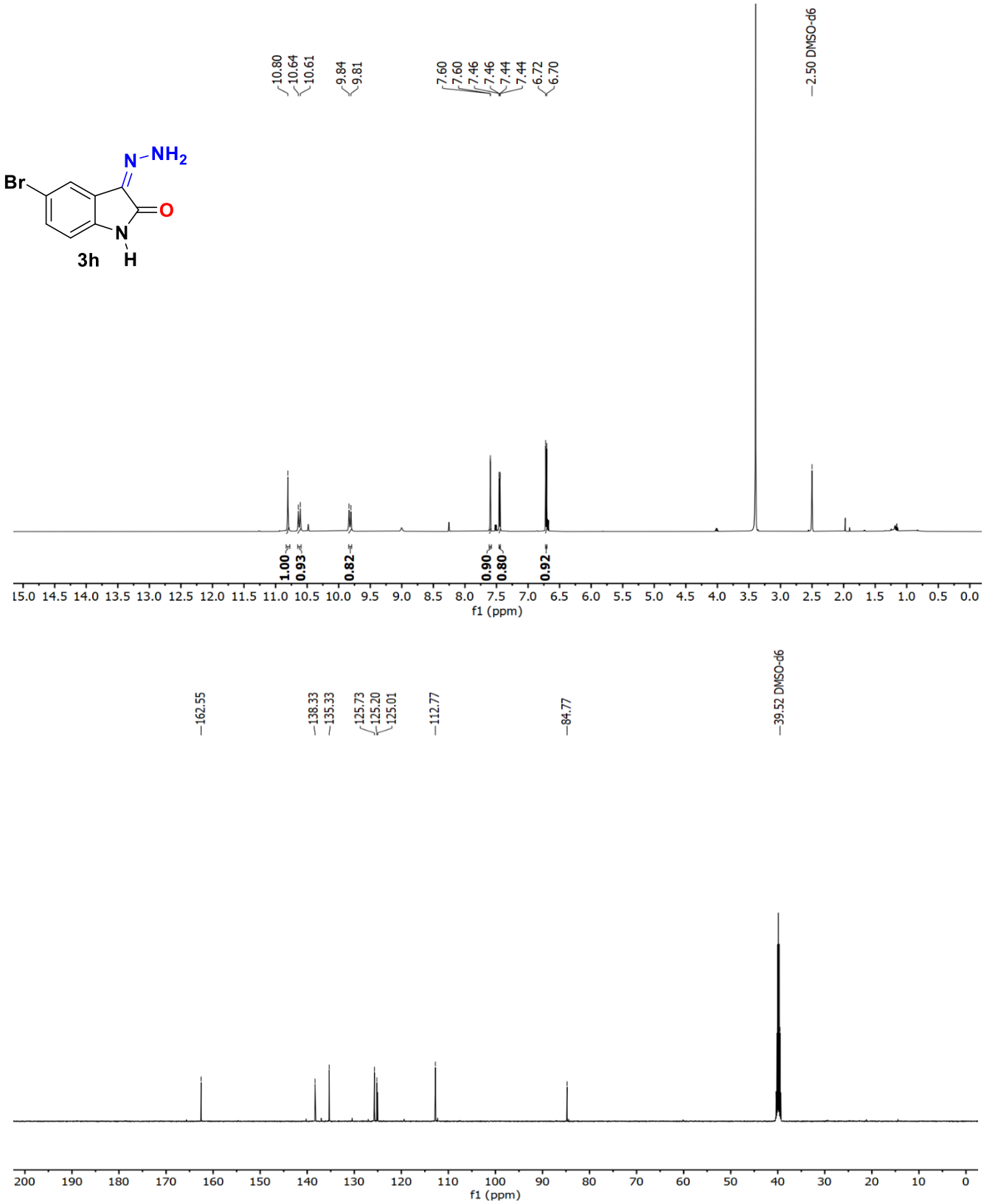




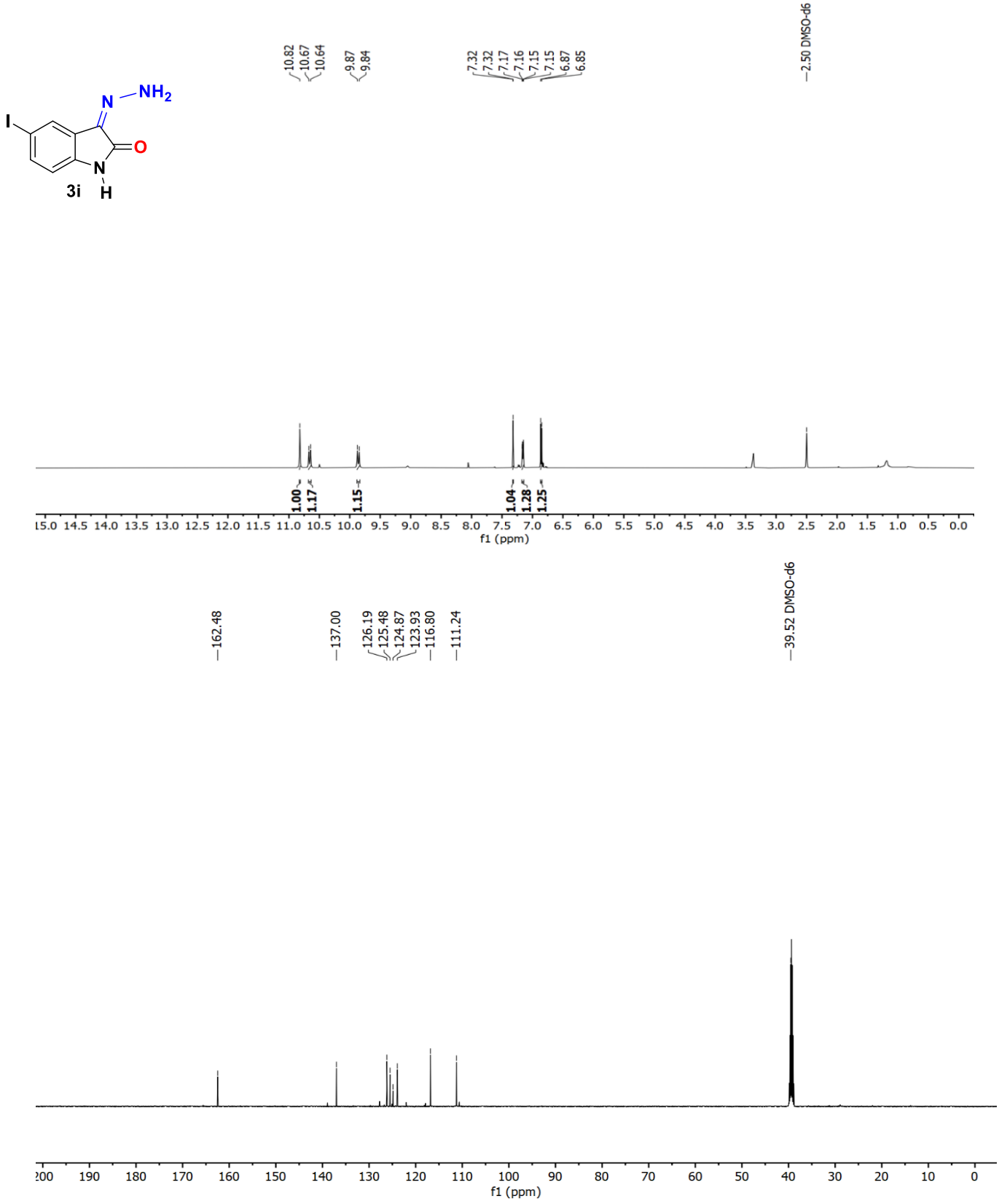
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



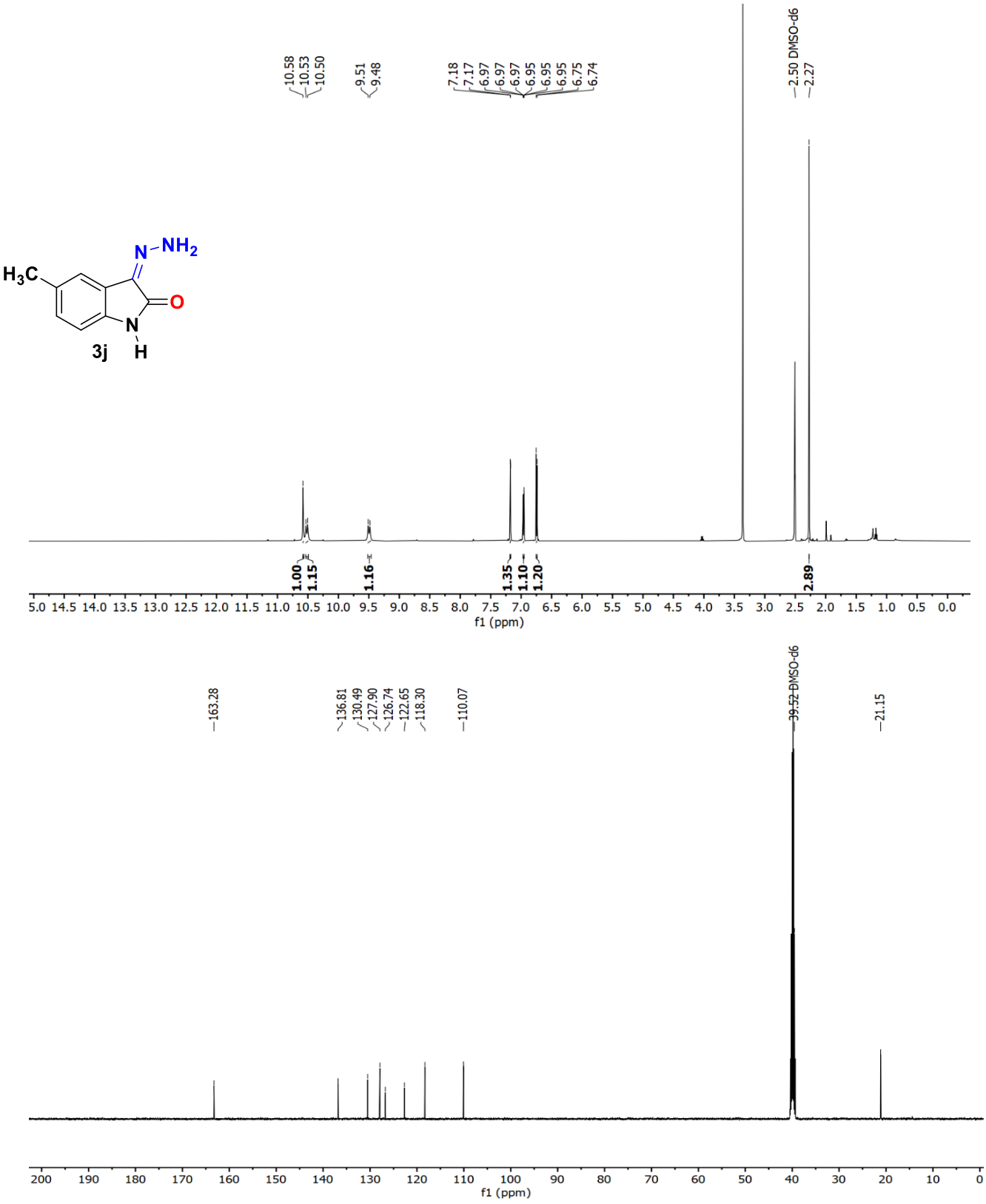
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



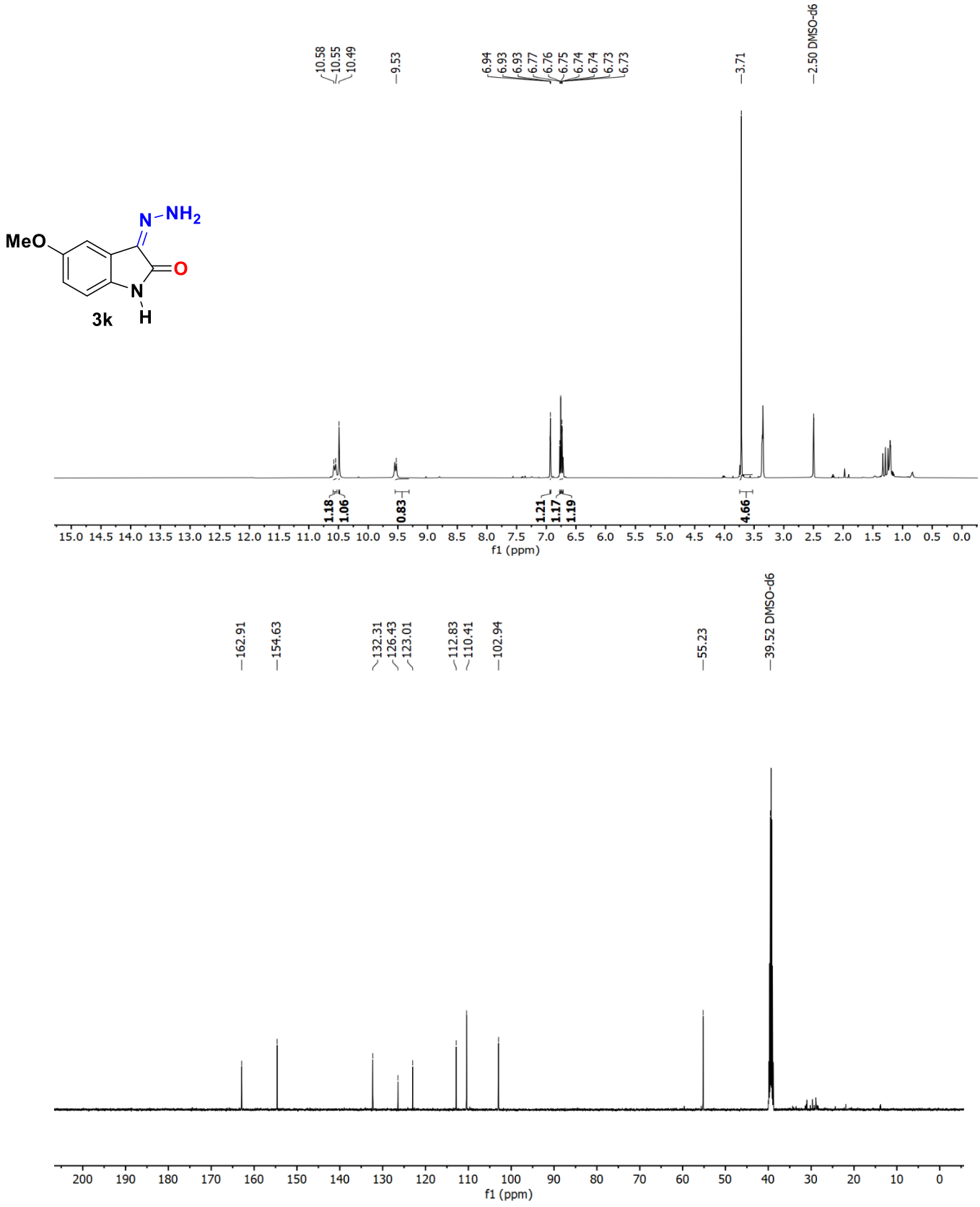
^{1}H NMR (500 MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$)



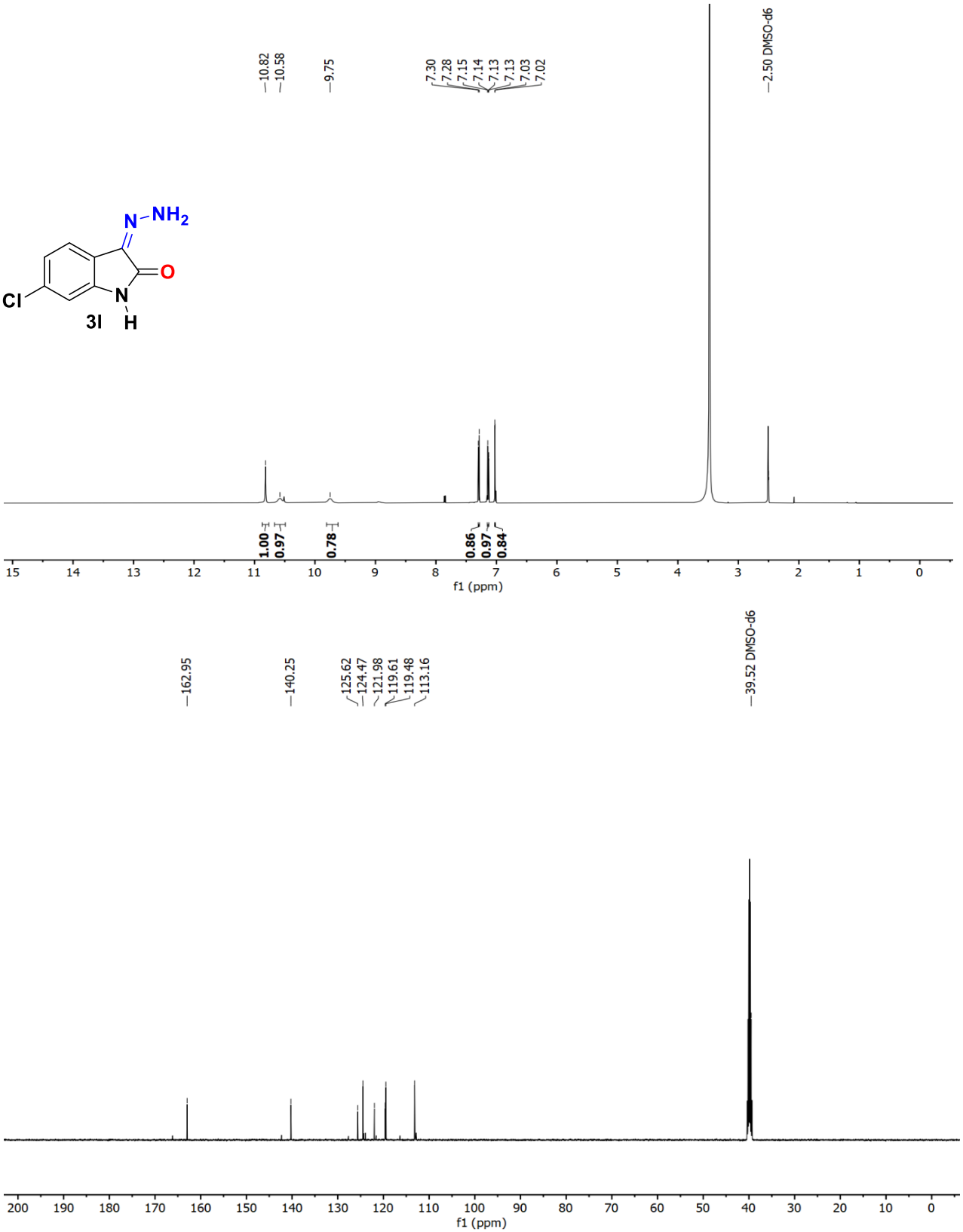
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



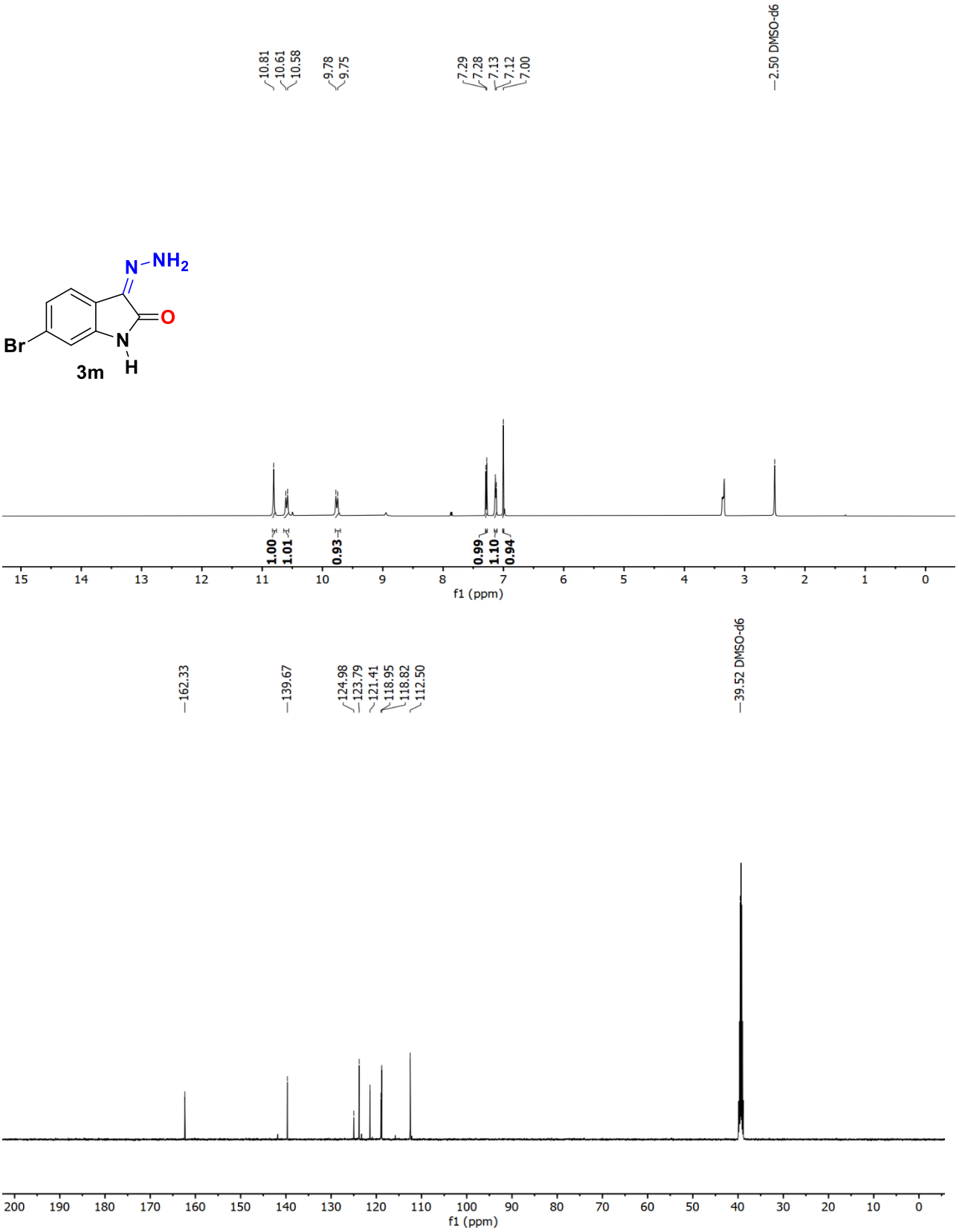
^{1}H NMR (500 MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$)



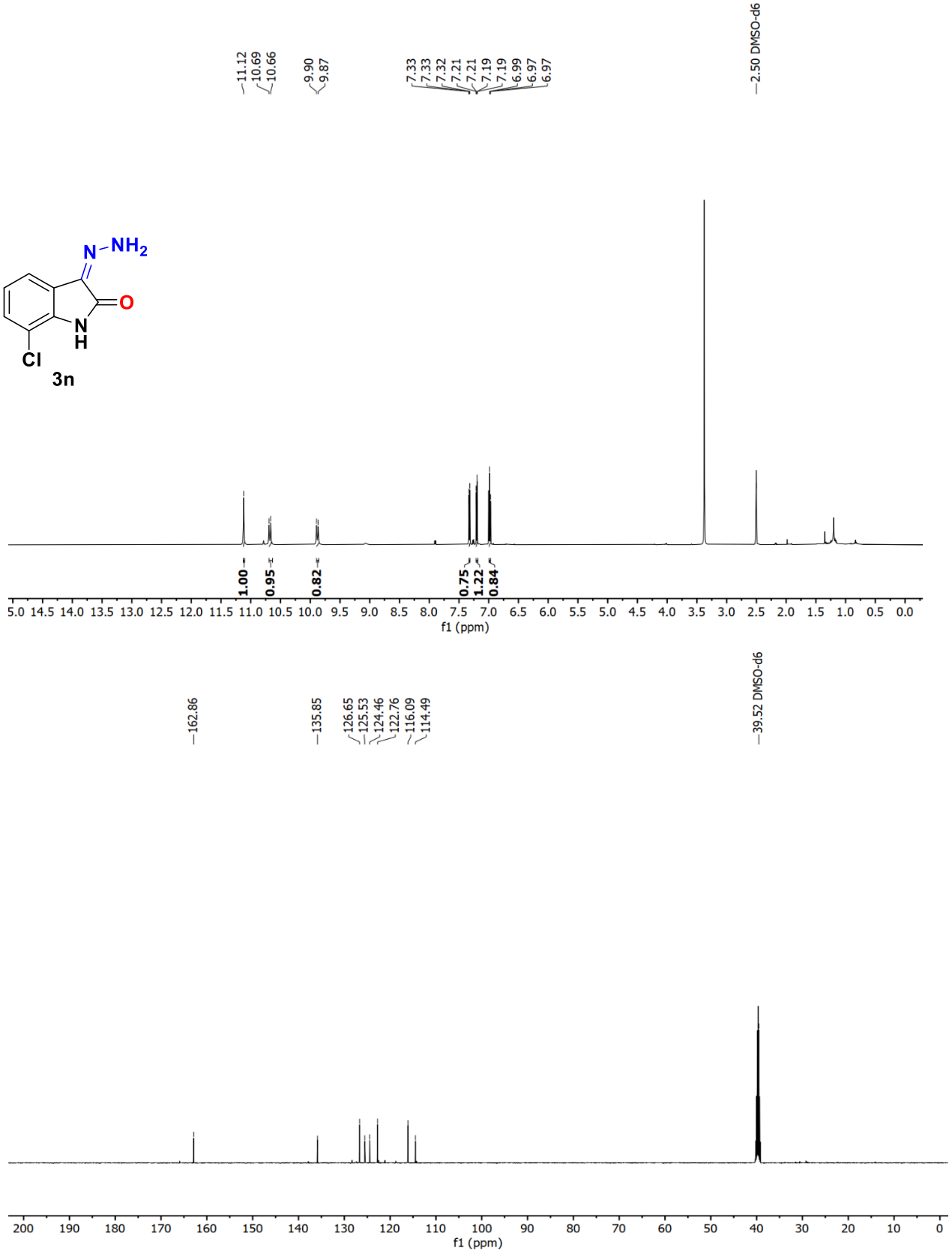
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



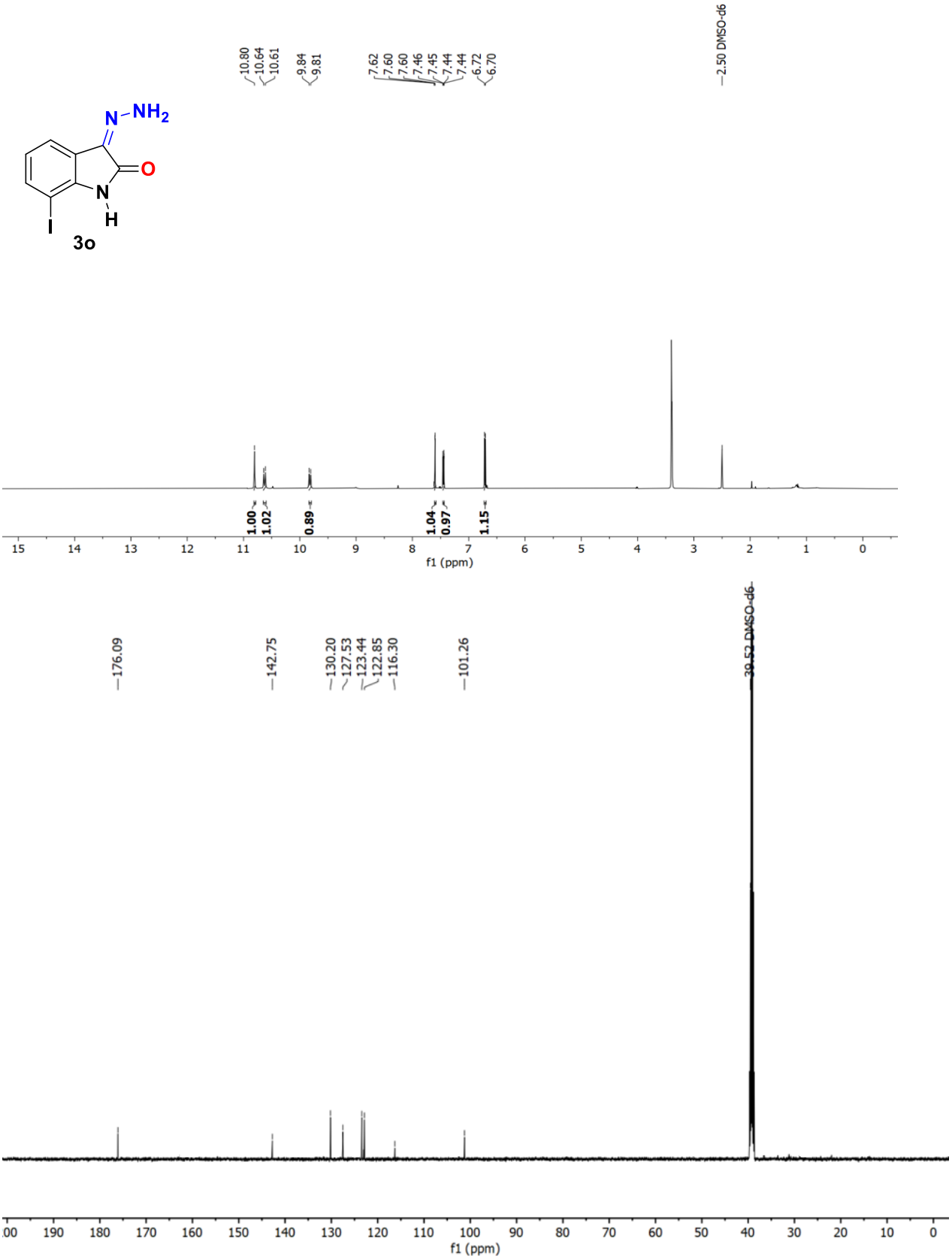
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



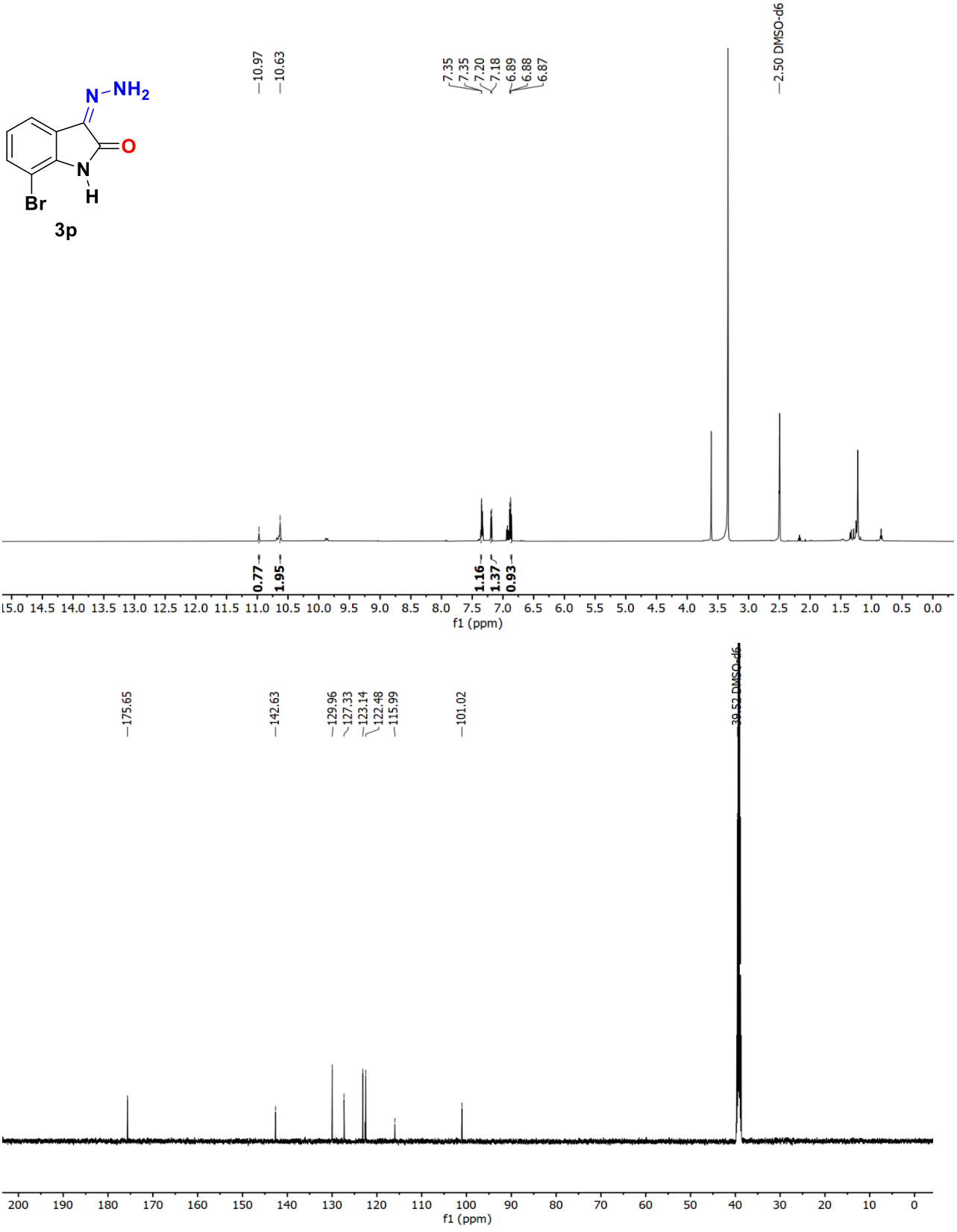
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



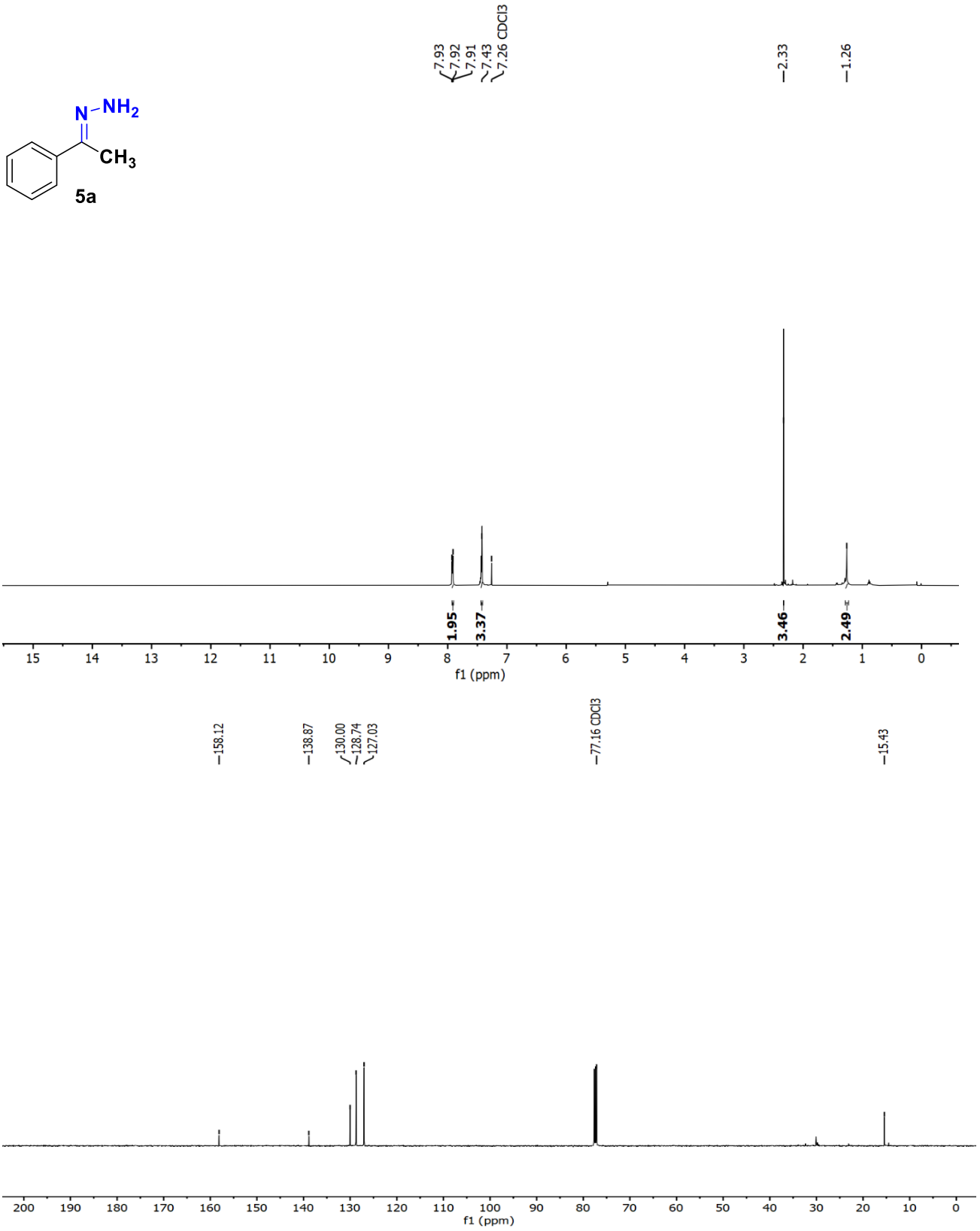
^{1}H NMR (500 MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$)



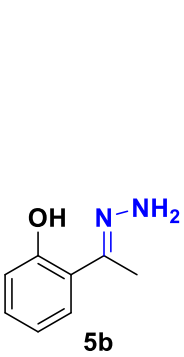
^{1}H NMR (500 MHz, DMSO-d$_6$) and ^{13}C NMR (125 MHz, DMSO-d$_6$)



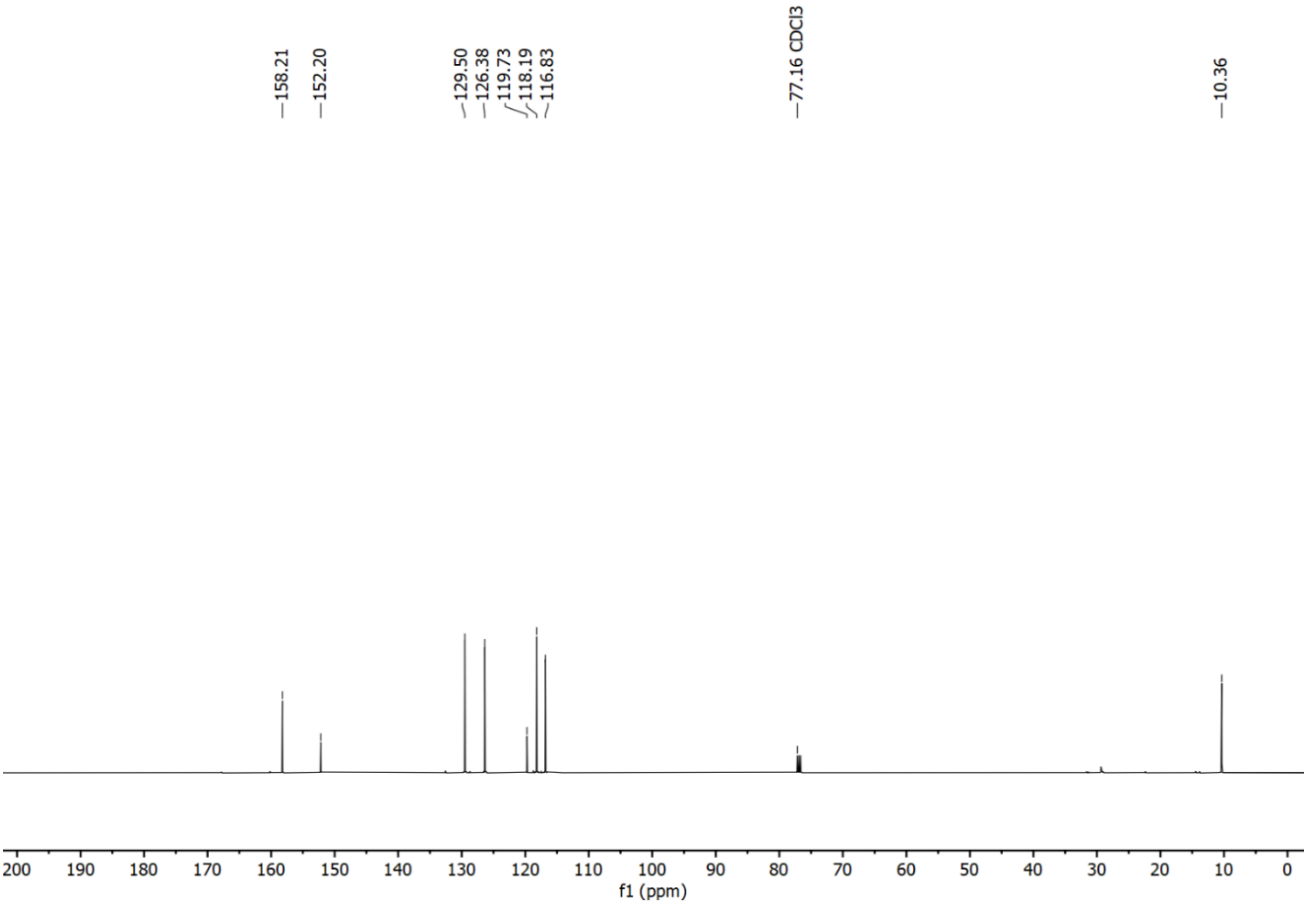
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



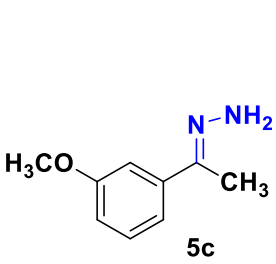
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



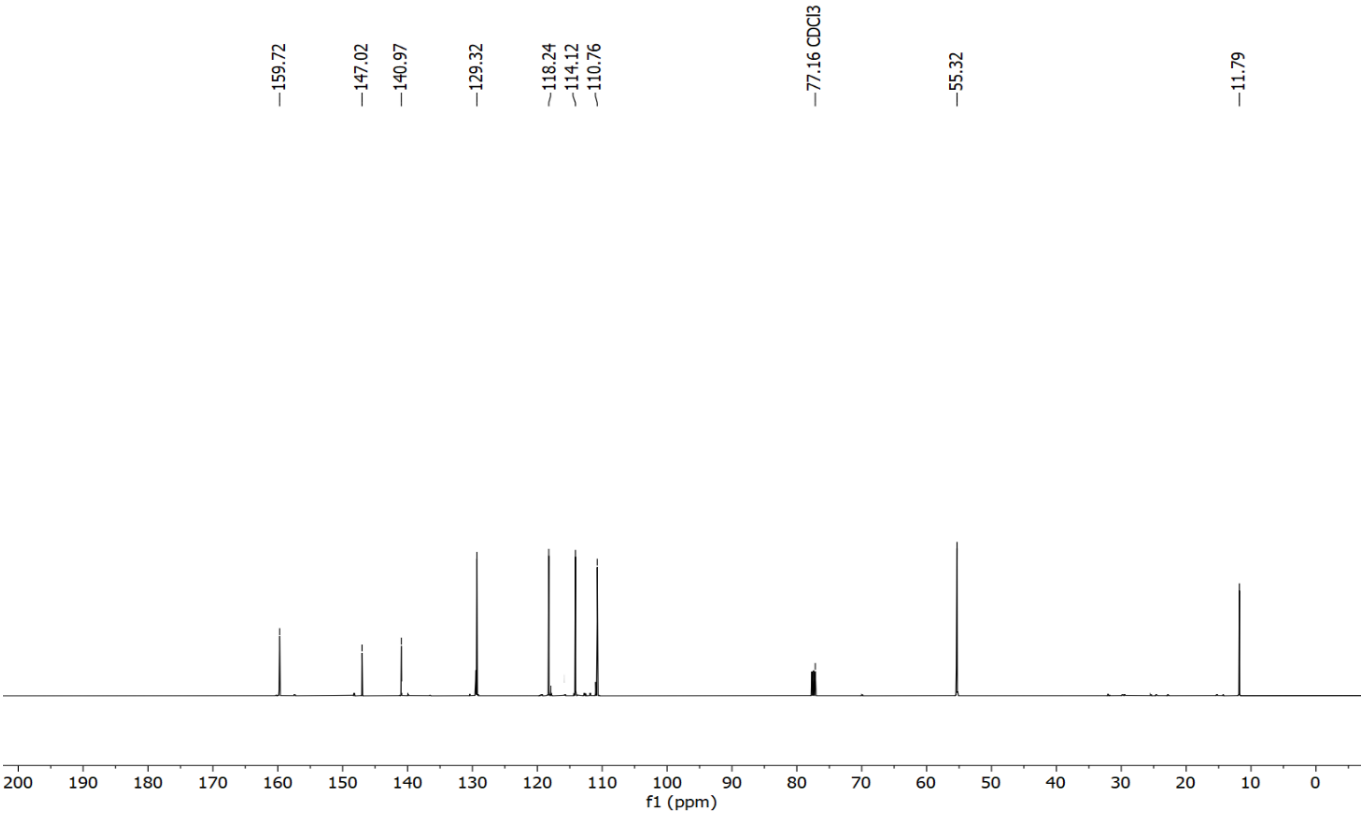
5b



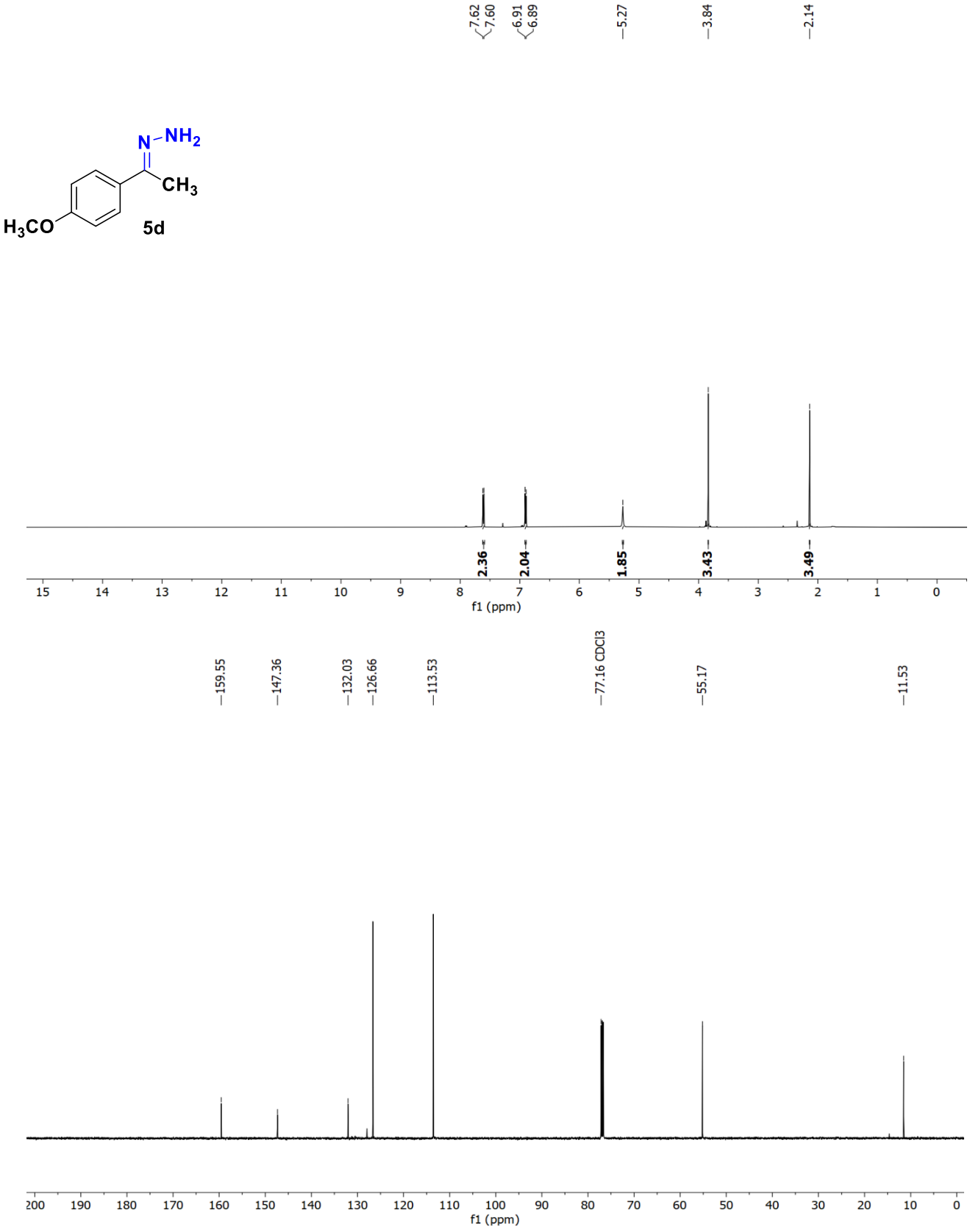
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



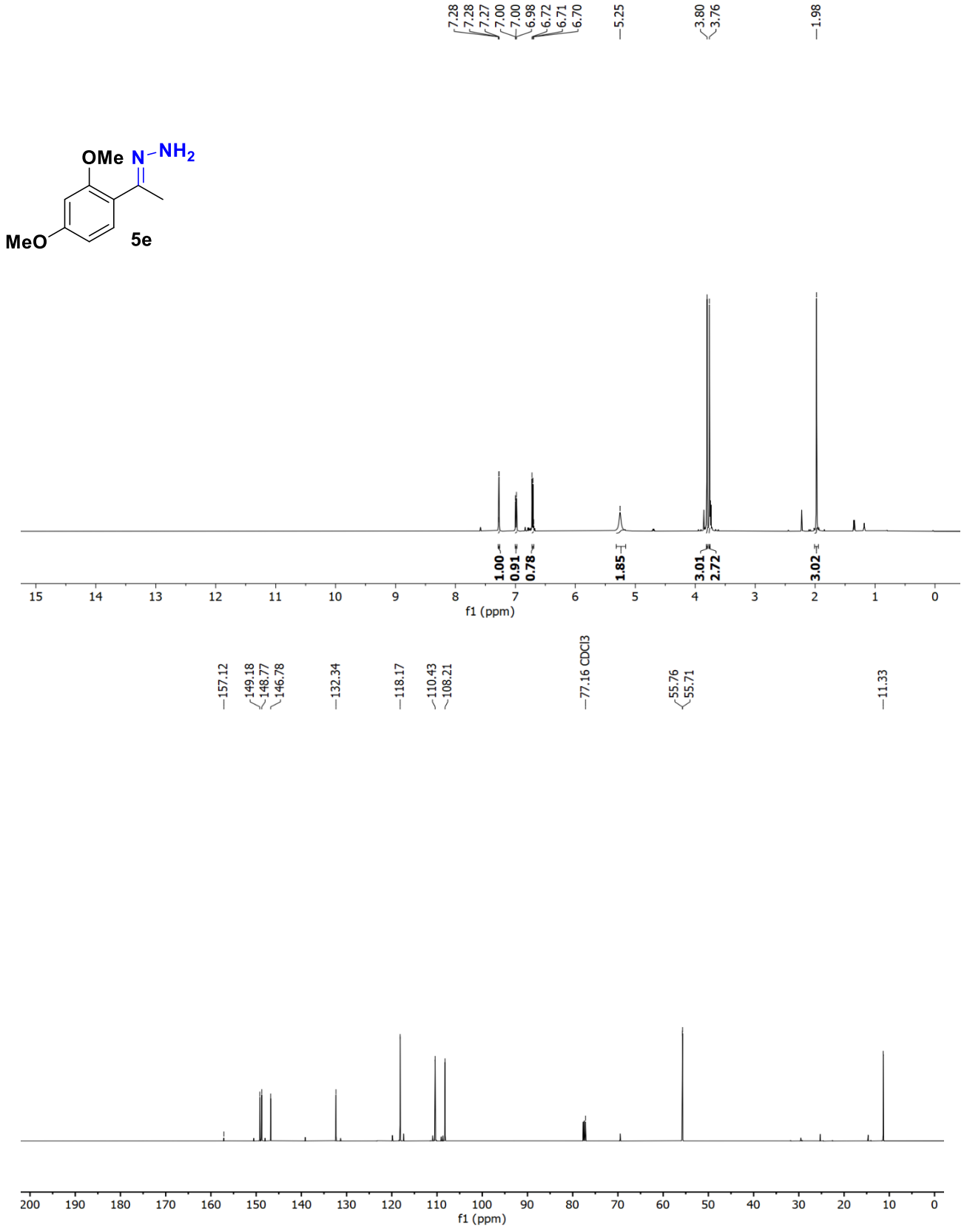
5c



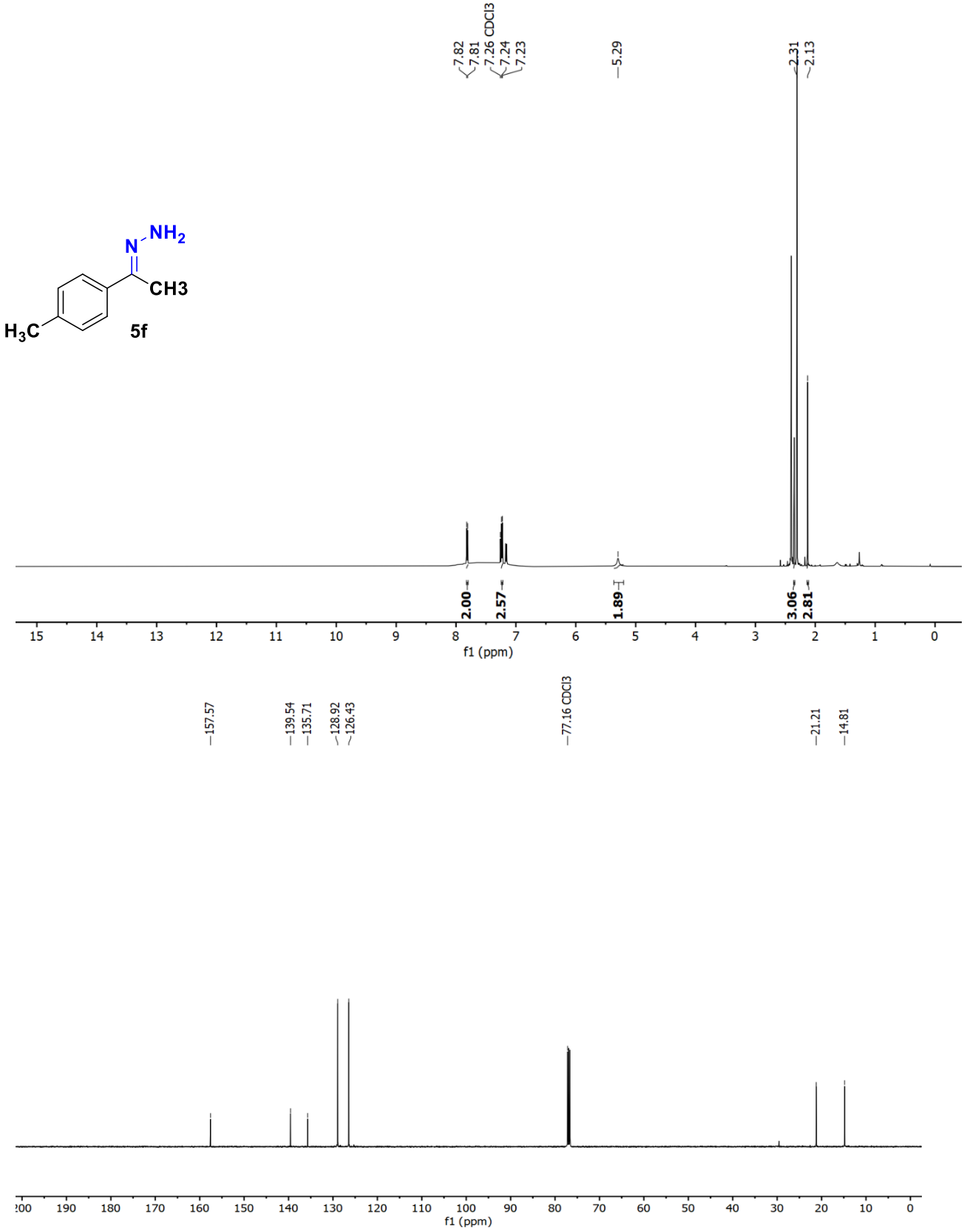
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



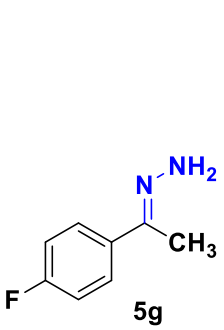
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)

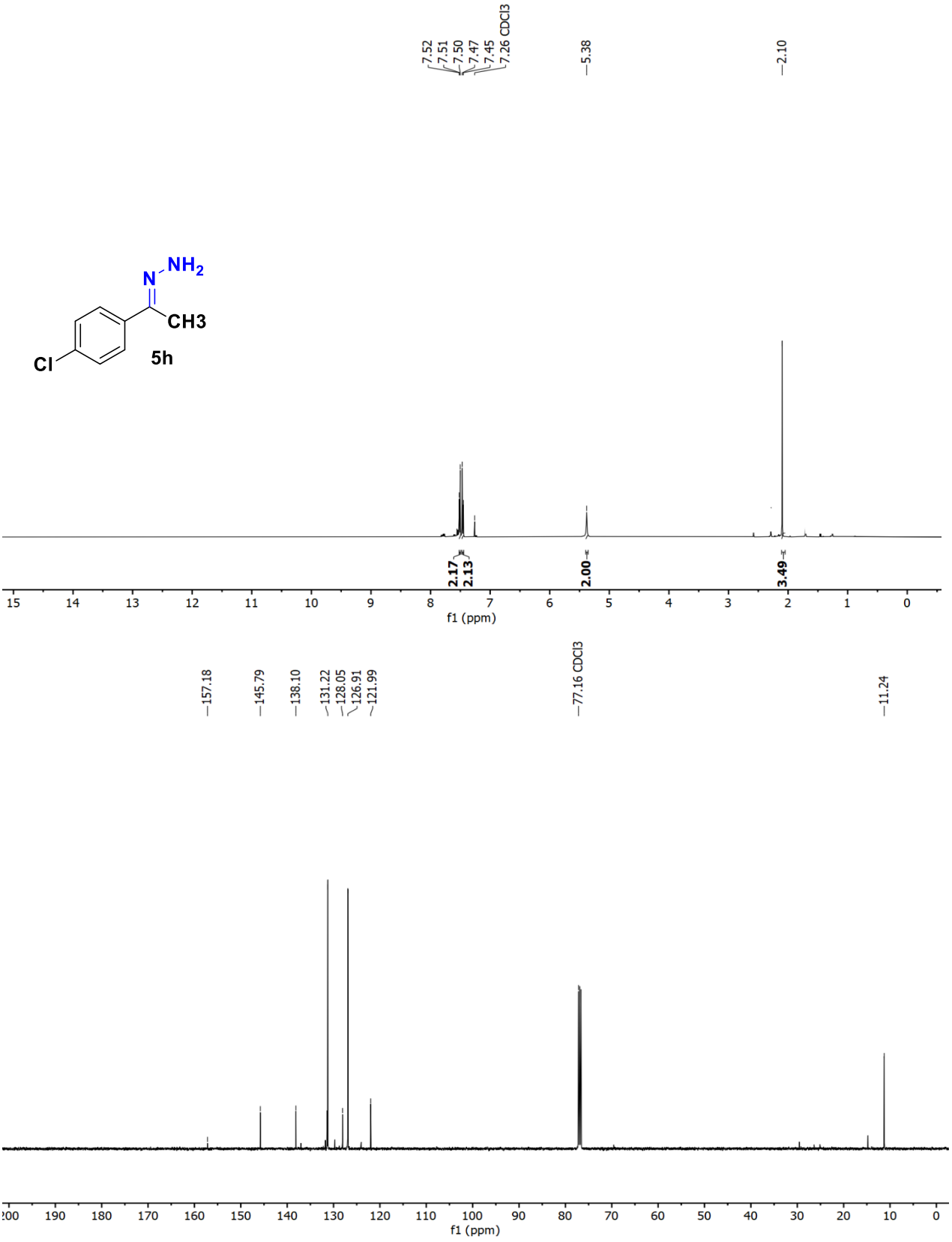


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)

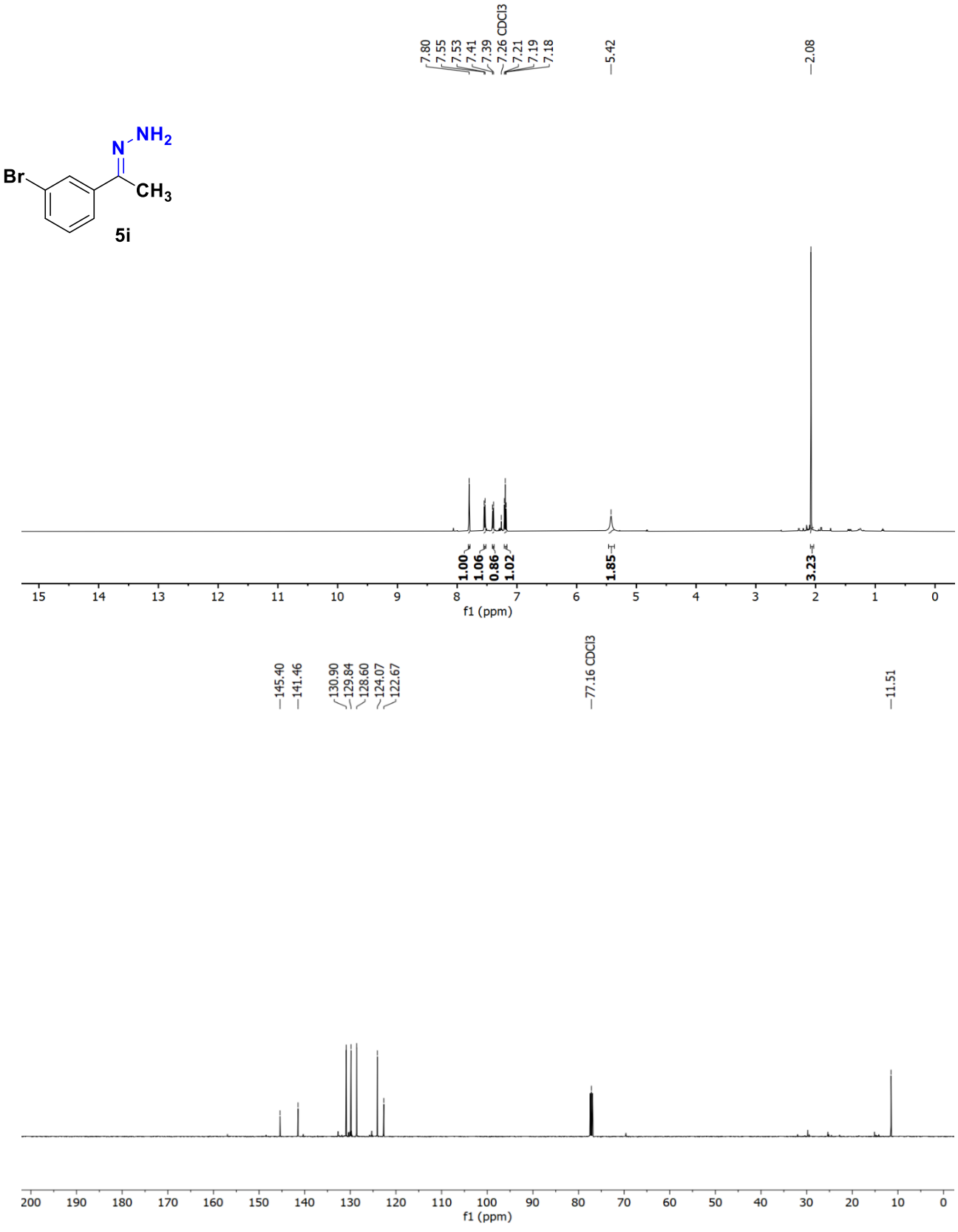


5g

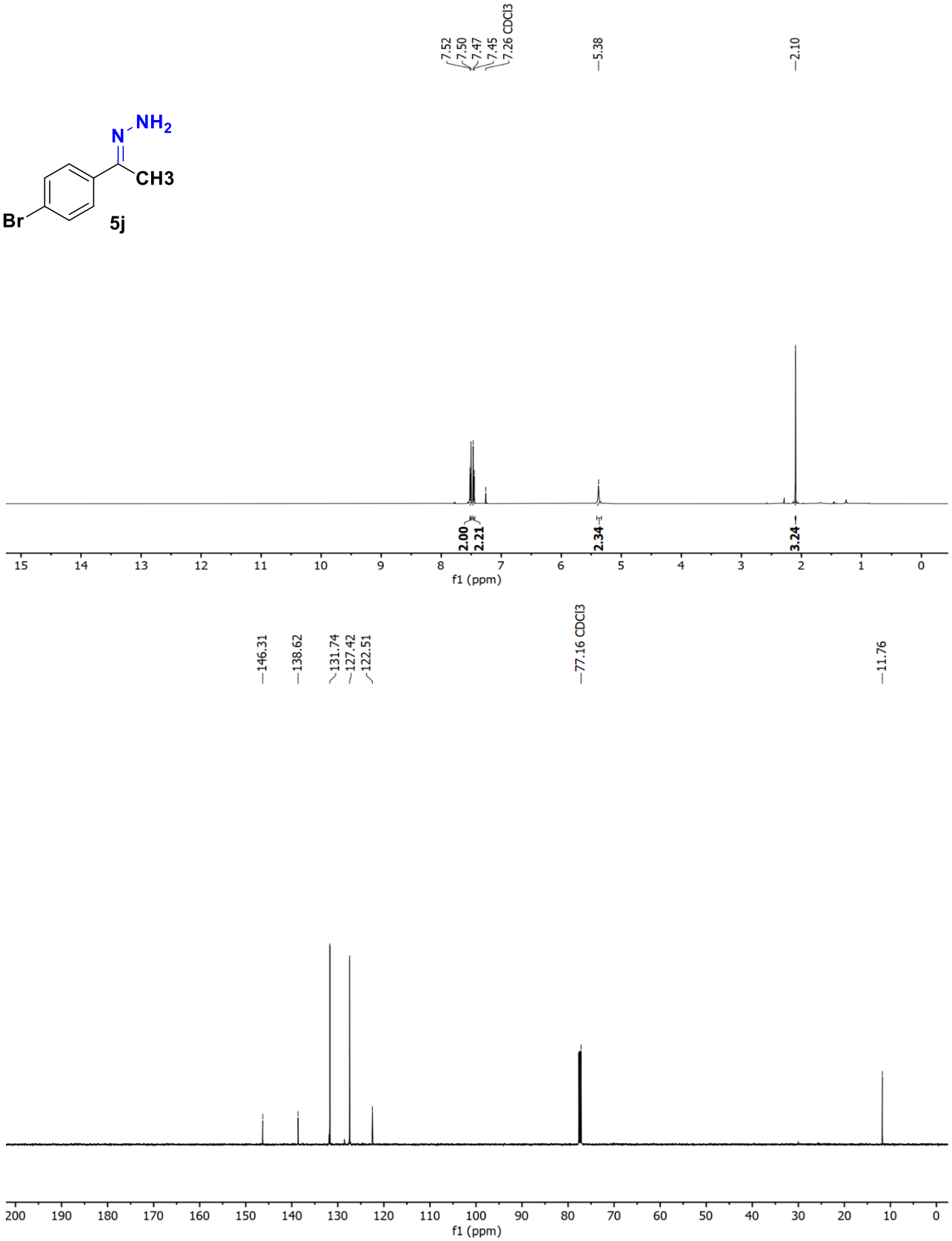
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



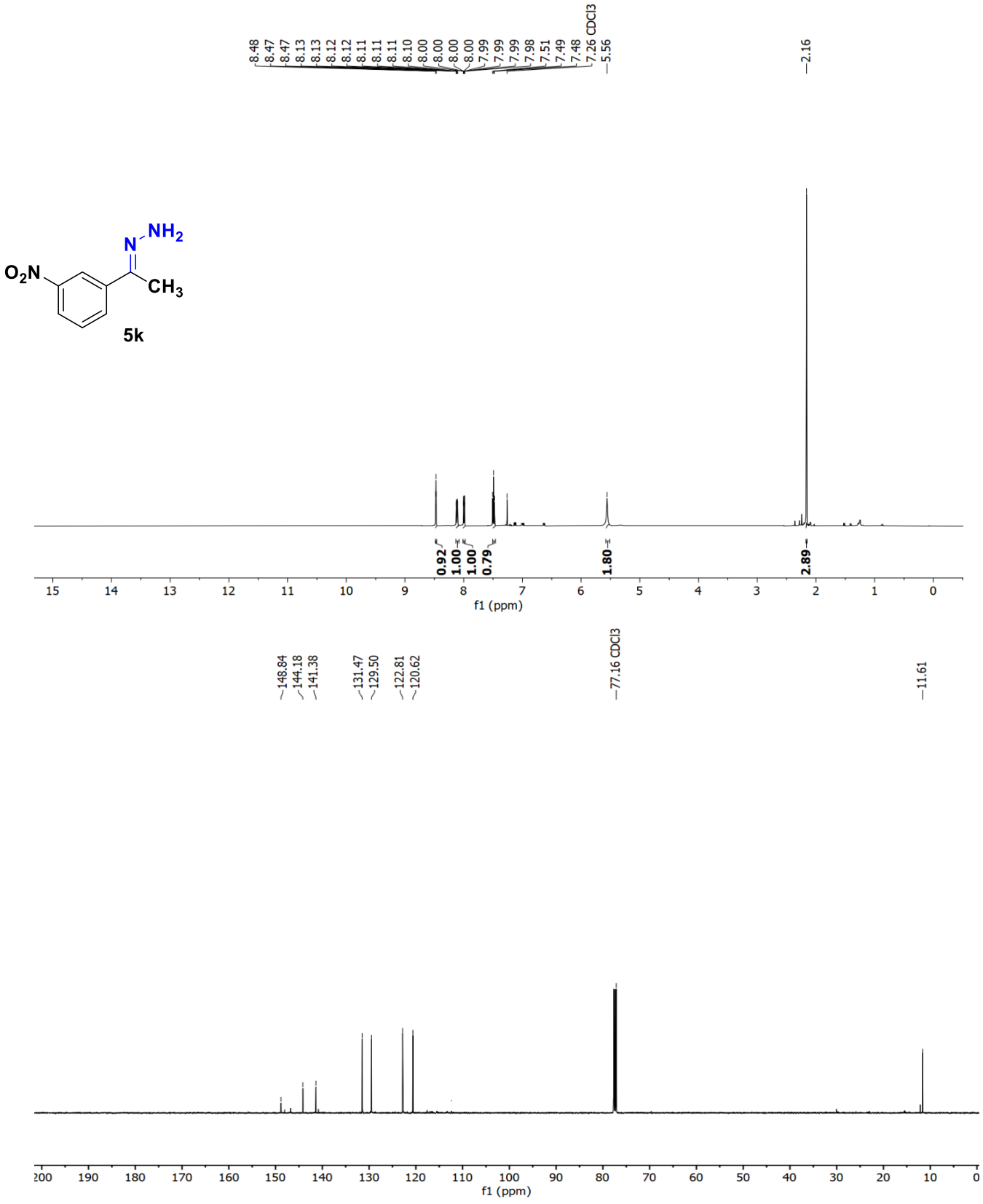
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



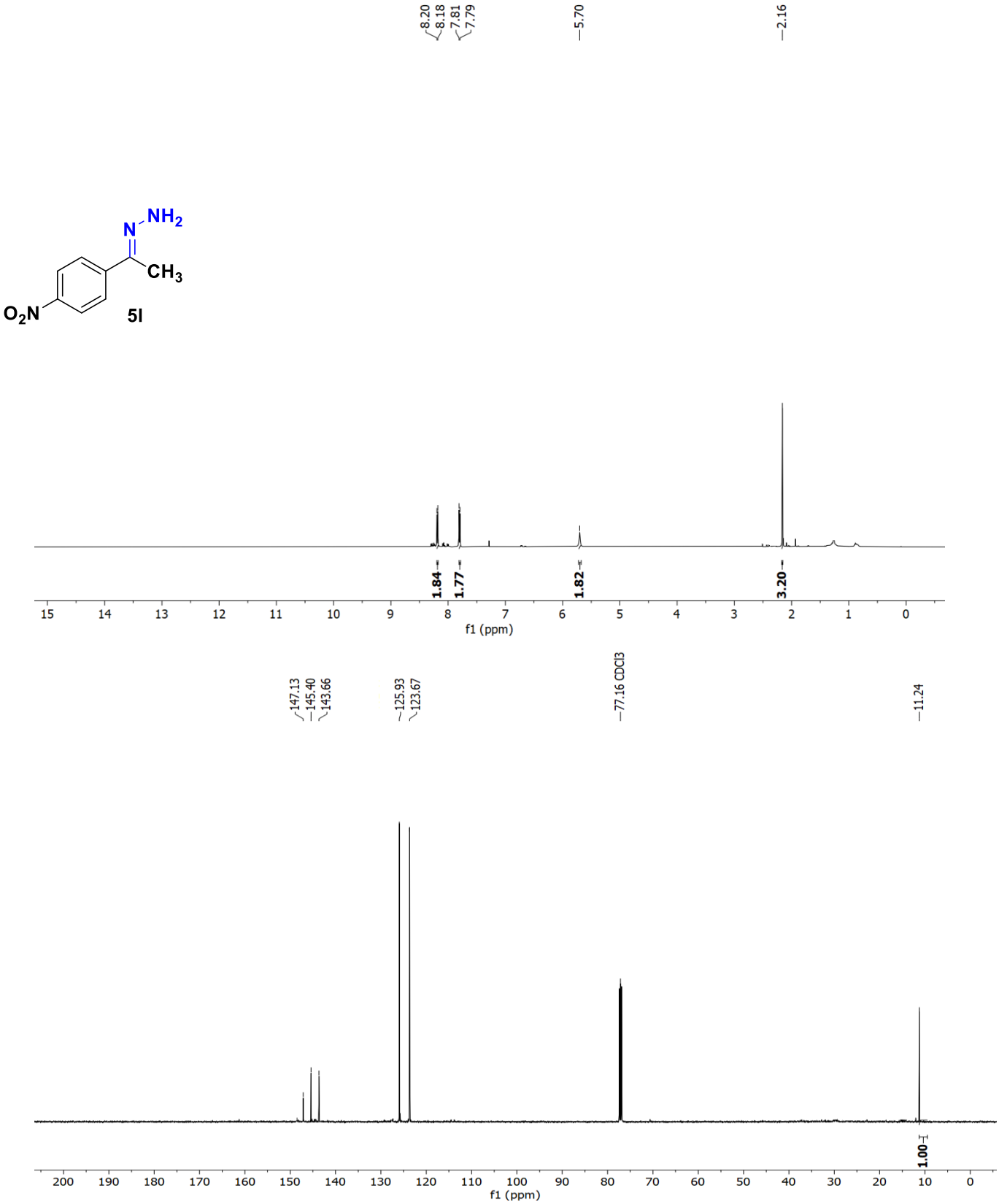
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)



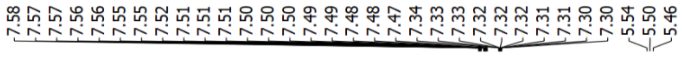
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)

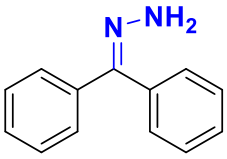


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)

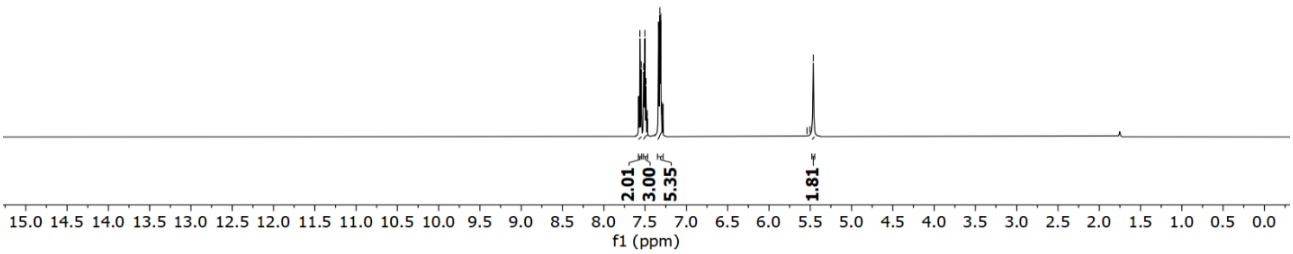


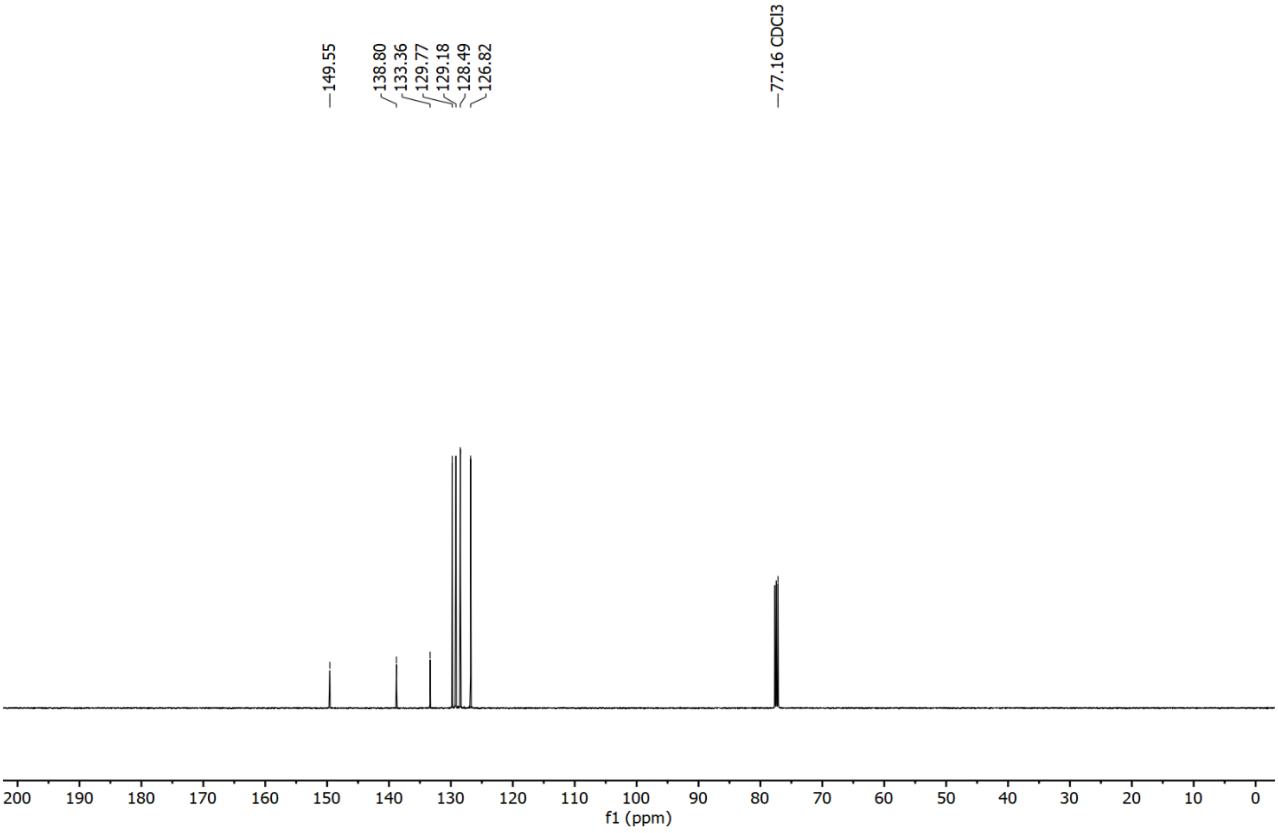
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)





5m





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$)