Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Electro-organic Green Synthesis of Dicyano-2-(2-oxoindolin-3-ylidene) malononitriles using Molecular Iodine as Catalyst

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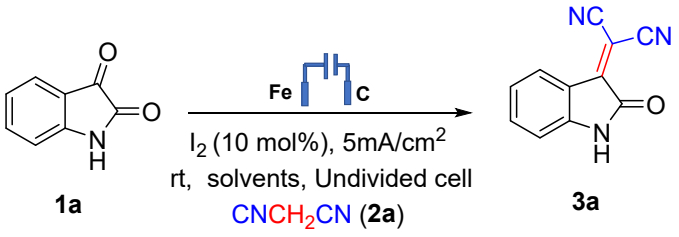
General experimental material and methods

All reactions were performed in an Electrochemical cell at room temperature (~25-26 ºC). 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 ($CDCl_3$) signal. 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.

The electro-organic synthesis was optimized by using different solvents (**Table S1**) and applied current density (**Table S2**).

Table S1. Reaction optimization in different solvents



Entry	Variation in Solvents[a]	Yields (%)
1	MeOH	75
2	CH_3CN	60
3	EtOH	94
4	DCM	47
5	DMF	50
6	H_2O	62

[a] Laboratory Reagents (LR) grade solvents were used which were containing little moister. Reaction in CH_3CN, DCM and DMF may be proceeding due to presence of this little moister and resulting poor yields.

Table S2. Variation of Applied current density under the standard condition

Entry	Applied Current density (mA/cm^2)	Yields (%)
1	No electricity	Not detected
2	2	Negligible
3	4	20
4	5	94
5	10	90
6	15	85

Screening the equivalent ratio of I_2/1a/2a: As shown in Table **S3,** the standard reaction entry 1, the proportion of I_2, **1a,** and **2a** was 0.1:1:1. As the concentration of I_2 is increased to its double, the yield slightly increases but on increasing the concentration of Isatin (**1a**) and malononitrile (**2a**) the yields was slightly decreases. This reaction was carried out in gram-scale adopting optimized reaction protocols which furnished product in very good isolated yields.

Table S3. Gram-scale synthesis of **3a** under various ratio of substrate and Iodine

Entry	Variation	Yields (%)
1	I_2(0.1eq.)/**1a**/(1eq.)/**2a**(1eq.)	94
2	I_2(0.2eq.)/**1a**/(1eq.)/**2a**(1eq.)	96
3	I_2(0.1eq.)/**1a**/(2eq.)/**2a**(1eq.)	93

4	I_2(0.1eq.)/**1a**/((1eq.)/**2a**(2eq.)	89

General Procedure for the Cyclic Voltammetry Experiments in Three electrode Setup: Cyclic voltammetry experiments were carried out in a three-electrode cell setup under an Argon atmosphere at room temperature. Working, counter, and reference electrodes were glassy carbon disc (0.07cm^2), platinum plate (1cm^2), and non-aqueous Ag/$AgNO_3$ submerged in acetonitrile solution, and connected with a salt bridge, respectively. Standard electrolyte for cyclic voltammetric studies was 0.1M $NaClO_4$ (supporting electrolyte) in acetonitrile solution (20ml). The potential range for experiment was +0.9V to -0.9V at different scan rates from 10 mVs^{-1} to 120 mVs^{-1}.

Table S4. Cyclic Voltametric parameters for the reactants

Reactants	Epa/V	Ipa/µA	Epc	Ipc
I_2 (0.182-0.7005)	0.368	35.5 µA	0.005	-104µA
I_2/Isatin **1a** (0.1890.7005)	0.377	76µA	0.018	-82µA
I_2/ Malononitrile **2a** (0.217-0.715)	0.377	41.2µA	0.018	-52µA

Table S4 indicated that during the entire reaction, the anode potential was similar for all and iodine oxidizes readily with **1a** and **2a** both but we observed I_2 charge transfer reaction is more facile with isatin and thus higher current was observed. Therefore, in this reaction process, most probable interaction of I_2 and isatin occurs.

Figure S1 shows chronopotentiometry curves for electro organic synthesis of 1- and 5- substituted isatylidene malononitrile derivatives.

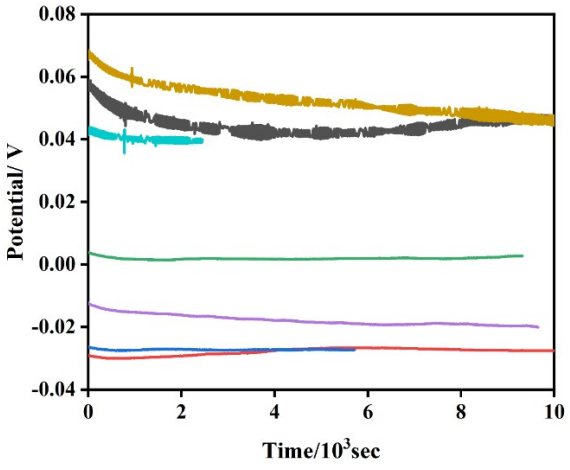


Figure S1. Chronopotentiometric curves.

General Procedure for the electrochemical synthesis of 2-(2-oxoindolin-3-ylidene) malononitrile 3a and its derivatives: In an oven-dried undivided electrochemical cell equipped with a stir bar, isatin **1a** (1.0 mmol, 1.0 equiv.), I_2 (0.1 mmol, 1.0 equiv.) and malononitrile **2a** (1.0 mmol, 1.0 equiv.) in ethanol (10 ml) were combined and added. The anode and cathode were carbon cloth (20.0 mm×10.0 mm×0.2 mm) and platinum plate (10.0 mm×10.0 mm×0.2 mm), respectively. For TLC purpose, solution was taken intermittently into the vial via syringes. The reaction mixture was continuously stirred and electrolyzed with a constant current density of 5 mA cm^{-2} at room temperature. When the reaction was finished, the pure product was washed and dried and further worked up by column chromatography on silica gel (100-200 mesh size) using hexane and ethyl acetate (2:1) as the eluent to furnished **3a** in 94% isolated yield. The product **3a** was confirmed by melting point and sample for NMR was prepared in DMSO-d6 solvent. Similar reaction procedure was adopted for other substrates. All reactions proceed with high yields, and no side products could be detected under the reaction conditions.

Electro-organic synthesis of 3b-3k derivatives:

3b: After setting up the electrodes, an OCP measurement was taken which is found to be ranging from -0.008 to - 0.01V. After OCP, CP started at -0.1V and fall down steeply to 0.008V after the 950s followed by a plateau till the 2400s and then rising up to 0.0091V till the 3600s and staying at 0.009 V for the next 4000s. It again rises continuously to 0.01V up to product formation in 6310s (~2hr and 15 min) which yields 91%.

3c: After setting up the electrodes, an OCP measurement was taken which is found to be 0.07V. After OCP, CP started at 0.056V which steeply fall to 0.047V in 2000 s then fall to 0.042V in 3200s and remain there for up to 7250s (2 h) and raise slightly to 0.047V to form the product after 10600s which yields 84%. The conversion was very slow at 0.042V.

3d: After setting up the electrodes, an OCP was found to be -0.01V. Unlike synthesis of **3a**, here no raise in potential was observed which indicates that the electrochemical synthesis is very facile and reduction of electrophilic species has started at once and during the synthesis, it shows the variation of potential from -0.012 to -0.021V for 10600s. Such a reaction corresponds to high

electron density at the reactant which facilitates a reduction reaction swiftly and it yields 87% of the product.

3e: After setting up the electrodes, an OCP was observed at -0.026V. CP was initiated from OCP value and fall down to -0.0274 V in 500s and then a plateau was observed for the next 500s there after rise in potential was observed to -0.0271V for 6000s synthesis was followed by an almost constant potential of -0.0273V. These steps in synthesis correspond to initial reduction and then diffusion of a reactive moiety at the electrode surface. Further, oxidation of reactive species followed by diffusion and then continuous synthesis of the product reaching towards the product formation in the electro-chemical solution which yields 90%.

3f: Here, OCP was observed at -0.0288V and CP was instigated from OCP value and came down to -0.030V in 400s and observed a plateau for 500s and then raised slowly to -0.0267V till 5110s and formed a plateau for about 6675s and then synthesized slowly at a constant potential of -0.027V until single spot corresponding to 5-BIM was obtained in 10600s. The chronopotentiometry graph indicates an initial reduction followed by oxidation of the reactive species and its diffusion towards the electrode surface and then the formation of the product in the electrochemical solution. It yields 88% of the product.

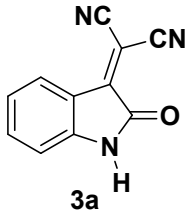
3g: Here, OCP was observed at 0.050V and found to be very stable among all 5 substituted isatin derivatives. CP was started at 0.04V and fall down to 0.002V in 700s and react (oxidize) slowly up to 1800s to 0.001V then starts to reduce till 2600s and then a limited mass transfer plateau (at 0.002V) was observed (~7500 s) which shows product formation. Electro-organic synthesis curve shows that initial oxidation for 2s is followed by a reductive step. This oxidation process may be due to the bonding interaction of isatin and I_2, where I_2 gets reduced. The plateau represents the transition time of the 30s which corresponds to the greater extent of reaction and diffusion at the electrode surface and completes in 2 h which yields 91%.

3h: Here, OCP was found at -0.03V and electro-organic synthesis took place at constant -0.3 V. Reaction completed in 10500s which yields 87%.

3i-3k: a constant OCP of 0.073V ± 0.01V was observed here. A similar pattern was observed for 7-substituted derivatives, for example in **3i**, CP started at 0.06 ± 0.01V and slowly fall down to 0.059V in 900s and then slowly downfall in the potential to 0.054V took the next 3000s while

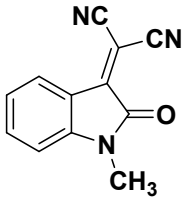
falling in the potential to 0.051V took next 5800s and finally reached to product formation at 0.046V in (10000-10100s) and yields final products in range of 88-89%. The conversion was very slow at 0.051V.

Spectroscopic data of all compounds (3a-3k)



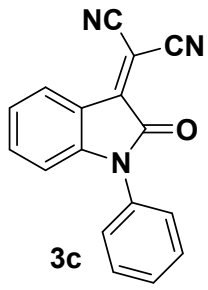
3a

2-(2-oxoindolin-3-ylidene) malononitrile (3a). The Product was purified by silica gel column chromatography (Ethyl acetate: Hexane, 1:4), Red Solid, Yield (94%); m.p.197-199°C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.21 (s, 1H, NH), 7.87 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, DMSO-d_6): δ 163.8, 150.7, 146.5, 137.9, 125.9, 123.0, 118.7, 113.1, 111.7, 111.6, 80.7 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_5N_3O$ $[M+H]^+$ 196.0511, found 196.0521.



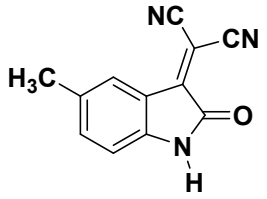
3b

2-(1-methyl-2-oxoindolin-3-ylidene) malononitrile (3b). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, yield (91%); m.p.235-236°C**; ^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 3.16 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 162.4, 149.8, 147.2, 137.7, 125.4, 123.4, 118.0, 112.9, 111.4, 110.5, 81.2, 26.2 ppm; HRMS (ESI) *m/z*: calcd for $C_{12}H_7N_3O$ $[M+H]^+$ 210.0667, found 210.0621.



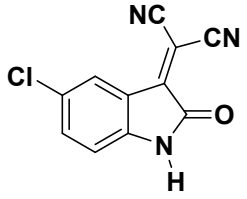
3c

2-(2-oxo-1-phenylindolin-3-ylidene) malononitrile (3c). The Product was Purified by silica gel column chromatography (Ethyl acetate :Hexane, 1:4) Red Solid, Yield (84%); m.p.197-199 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.55 – 7.51 (m, 1H), 7.50 – 7.49 (m, 1H), 7.49 – 7.47 (m, 1H), 7.30 – 7.25 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, DMSO- d_6) δ 161.9, 149.9, 147.0, 137.7, 132.6, 129.8, 128.9, 126.7, 125.7, 123.9, 118.2, 113.0, 111.4, 110.7, 81.2 ppm; HRMS (ESI) *m/z*: calcd for $C_{17}H_9N_3O$ $[M+H]^+$ 272.0824, found 272.0812.



3d

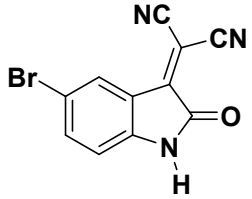
2-(5-methyl-2-oxoindolin-3- ylidene) malononitrile (3d). The Product was Purified by silica gel column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, Yield (87%); m.p. 263-266 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) *δ* 11.10 (s, 1H, NH), 7.65 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) *δ* 163.9, 150.7, 144.6, 138.7, 132.1, 125.8, 118.8, 113.2, 111.7, 111.6, 79.5, 19.9 ppm; HRMS (ESI) *m/z*: calcd for $C_{12}H_7N_3O$ $[M+H]^+$ 210.0667, found 210.0632.



3e

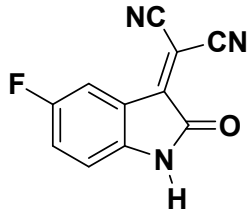
2-(5-chloro-2-oxoindolin-3-ylidene) malononitrile (3e). The Product was purified by silica gel column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, Yield (90%); m.p. 221-223 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6: *δ* 10.15 (s, 1H, NH), 6.56 (s, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 5.77 (d, *J* = 8.0 Hz, 1H), ppm; **^{13}C NMR** (125 MHz, DMSO-d_6) *δ* 163.8, 149.9, 145.4, 137.3, 126.9,

125.2, 120.2, 113.6, 112.3, 111.5, 82.2 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4ClN_3O$ $[M+H]^+$ 230.0121, found 230.0152.



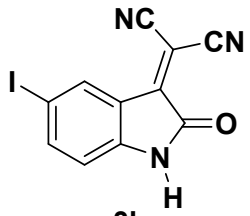
3f

2-(5-bromo-2-oxoindolin-3-ylidene) malononitrile (3f). The Product was purified by silica gel column chromatography (Ethyl acetate: Hexane,1:4) Brown Red Solid, Yield (88%); m.p.222-224℃; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 11.16 (s, 1H, NH), 7.51 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.92 (s, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 163.7, 149.7, 145.78, 140.0, 128.0, 120.6, 114.4, 114.0, 112.9, 111.4, 82.6 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4BrN_3O$ $[M+H]^+$ 273.9616, found 273.9651.



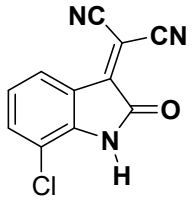
3g

2-(5-fluoro-2-oxoindolin-3-ylidene) malononitrile (3g). The Product was purified by silica gel column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, Yield (91%)**;** m.p**.**232-233℃**; ^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.80 (s, 1H, NH), 7.60 (s, 1H), 7.44 (dd, J = 8.0 Hz, J = 2.1 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6) δ 164.2, 151.1, 146.9, 138.2, 126.3, 123.3, 119.1, 112.6 112.1, 81.0 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4FN_3O$ $[M+H]^+$ 214.0417, found 214.0432.



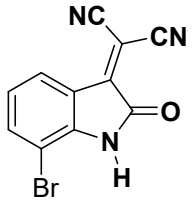
3h

2-(5-iodo-2-oxoindolin-3-ylidene) malononitrile (3h). The Product was purified by silica gel column chromatography (Ethyl acetate: Hexane, 1:4) Red Solid, Yield (87%); m.p. 230-233 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.03 (s, 1H, NH), 7.44 (d, *J* = 8.9 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 6.92 (s, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6) δ 164.1, 157.0, 150.6, 143.4, 125.0, 124.8, 113.4, 113.3,112.5,112.3, 82.7 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4IN_3O$ $[M+H]^+$ 321.9477, found 321.9432.



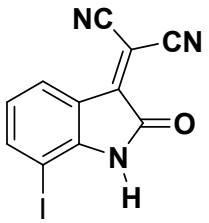
3i

2-(7-chloro-2-oxoindolin-3-ylidene) malononitrile (3i). The Product was Purified by column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, Yield (89%); m. p. 189-194 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.31 (s, 1H, NH), 7.78 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.02 (t, *J* = 8.2 Hz, 1H) ppm; **^{13}NMR** (125 MHz, DMSO-d_6) δ 163.8, 150.2, 143.7, 136.7, 124.3, 124.0, 120.4, 115.7, 112.8, 111.3, 82.1 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4ClN_3O$ $[M+H]^+$ 230.0121, found 230.0128.



3j

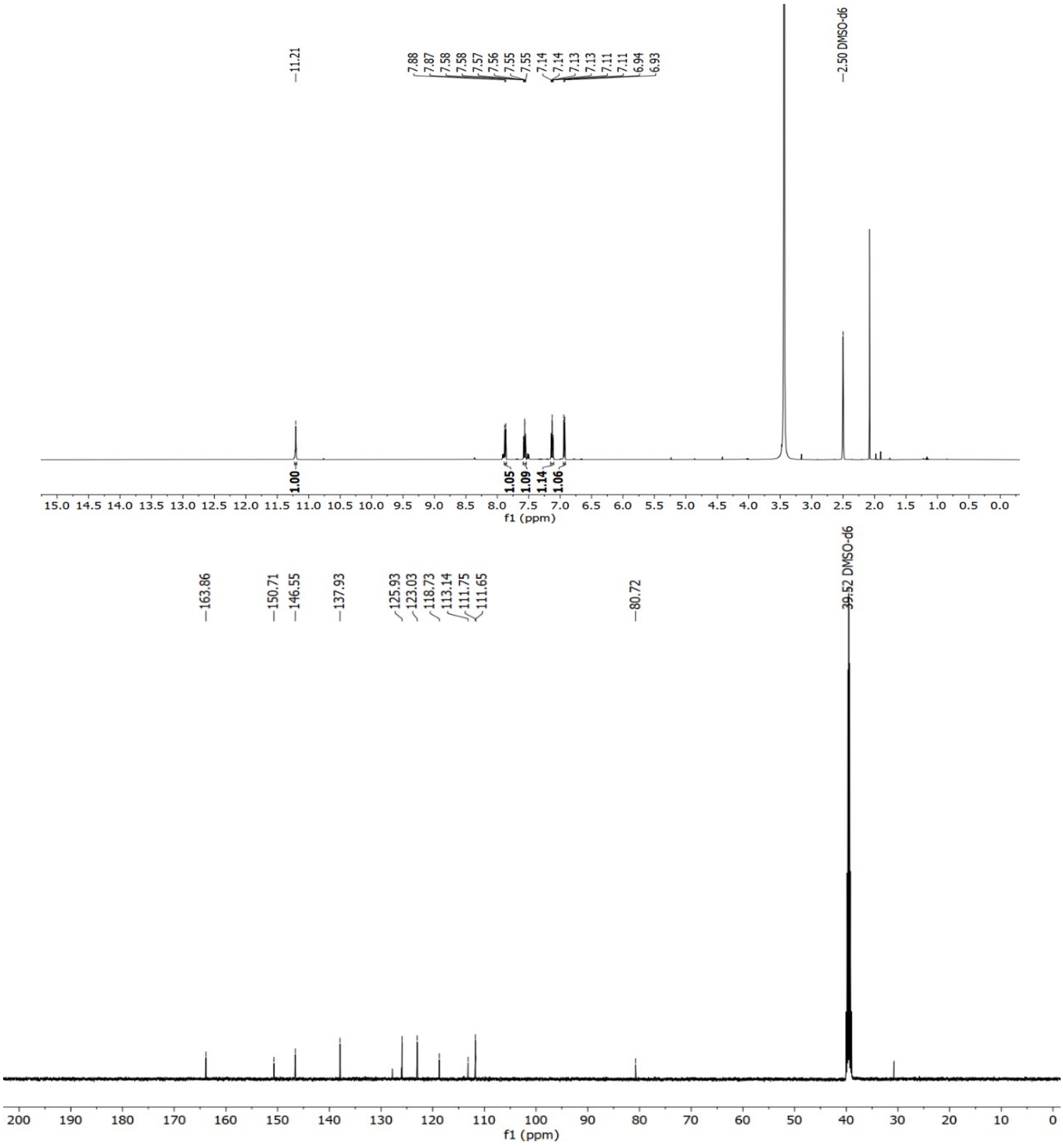
2-(7-bromo-2-oxoindolin-3-ylidene) malononitrile (3j). The Product was Purified by column chromatography (Ethyl acetate: Hexane,1:4) Brown Red Solid, Yield (88%); m.p. 190-195 ℃; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.63 (s, 1H, NH), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 8.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6) δ 164.2, 150.7, 144.2, 137.1, 124.8, 128.5, 120.9, 116.2, 113.2, 111.8, 82.6 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4BrN_3O$ $[M+H]^+$ 273.9616, found 273.9625.



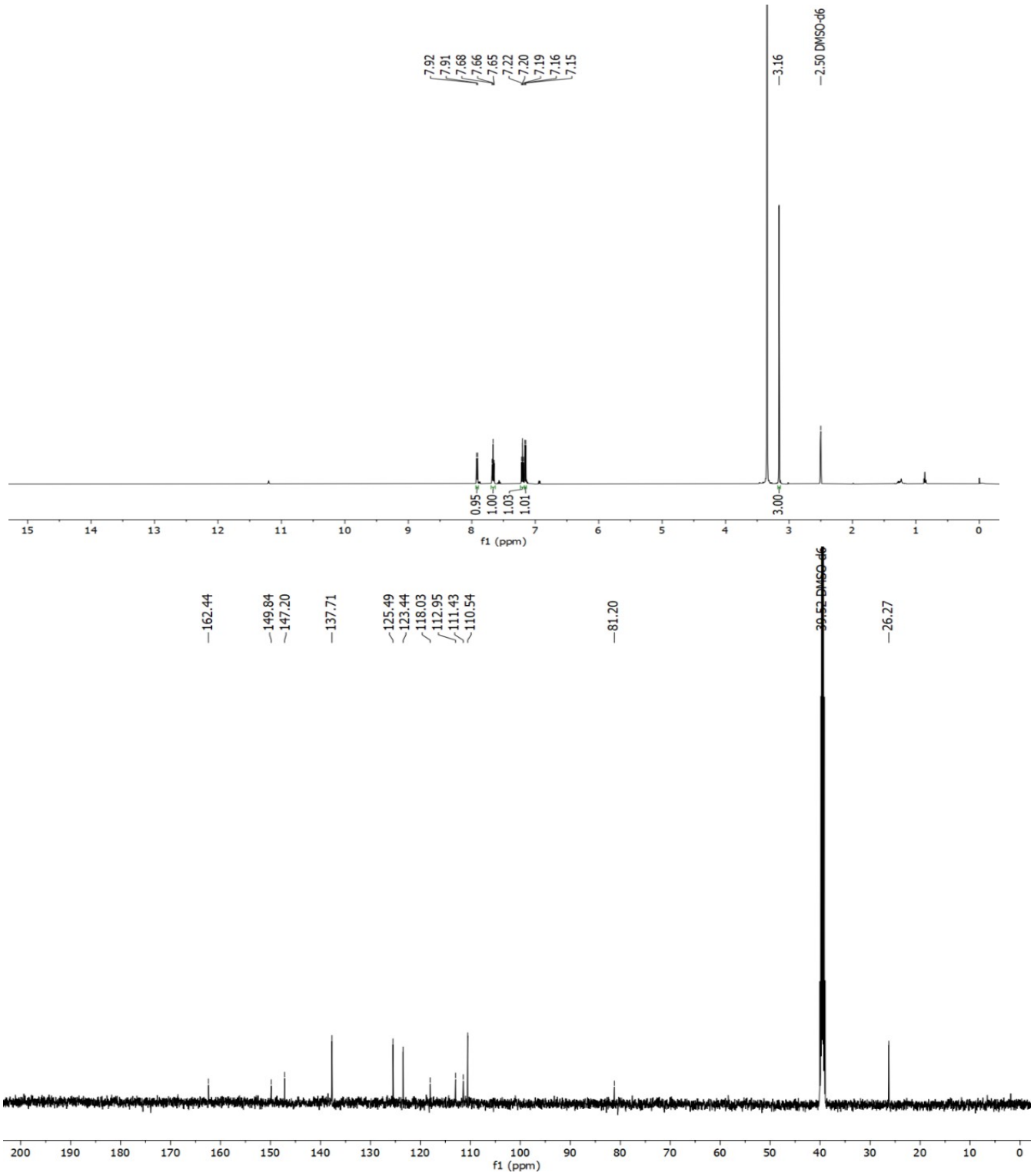
3k

2-(7-chloro-2-oxoindolin-3-ylidene) malononitrile (3k). The Product was Purified by column chromatography (Ethyl acetate: Hexane,1:4) Red Solid, Yield (89%); m.p.192-197 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.45 (s, 1H, NH), 7.66 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6) δ 163.7, 150.2, 143.7, 136.6, 124.3, 124.0, 120.4, 115.7, 112.7, 111.3, 82.1 ppm; HRMS (ESI) *m/z*: calcd for $C_{11}H_4IN_3O$ $[M+H]^+$ 321.9477, found 321.9482.

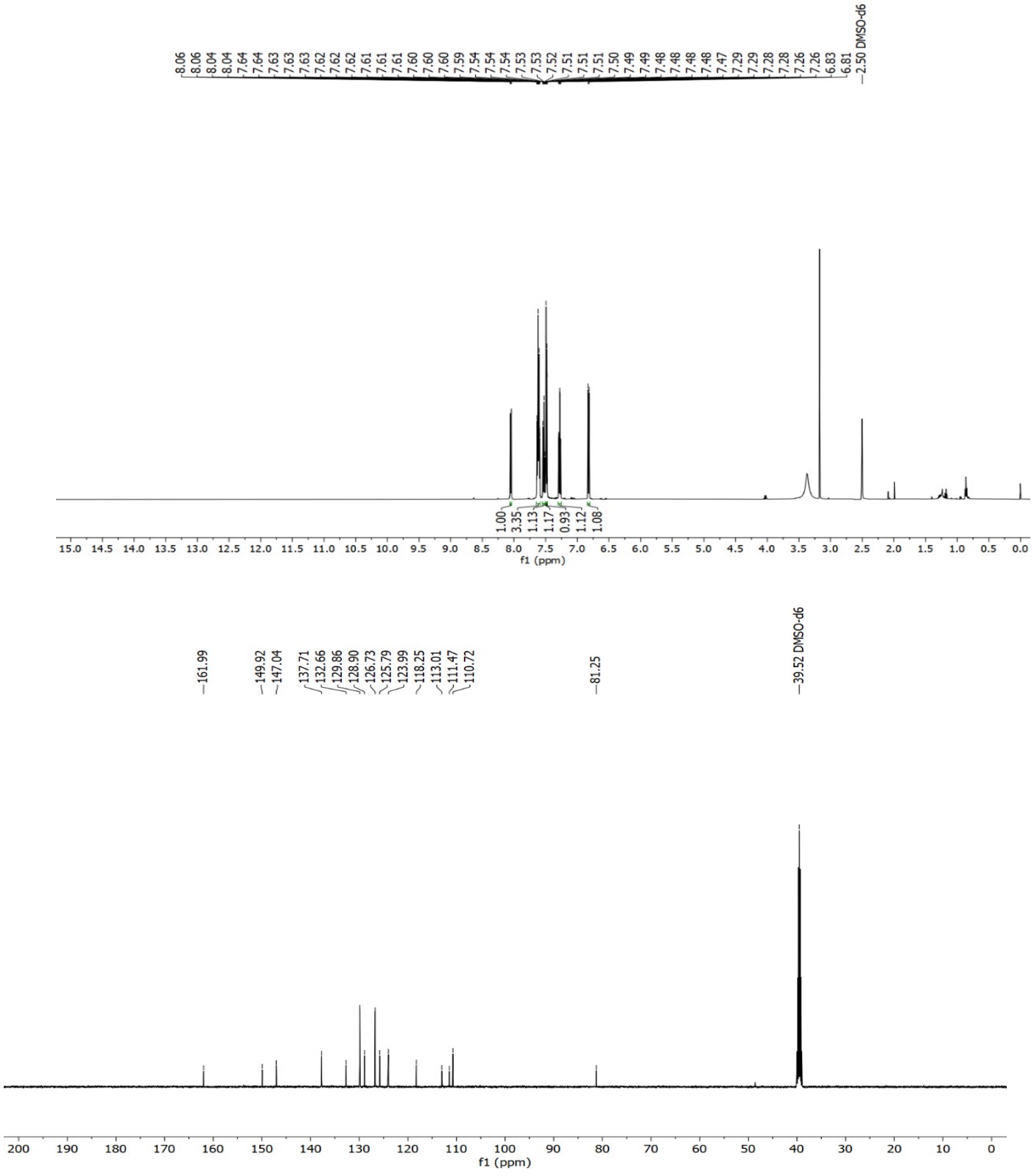
^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



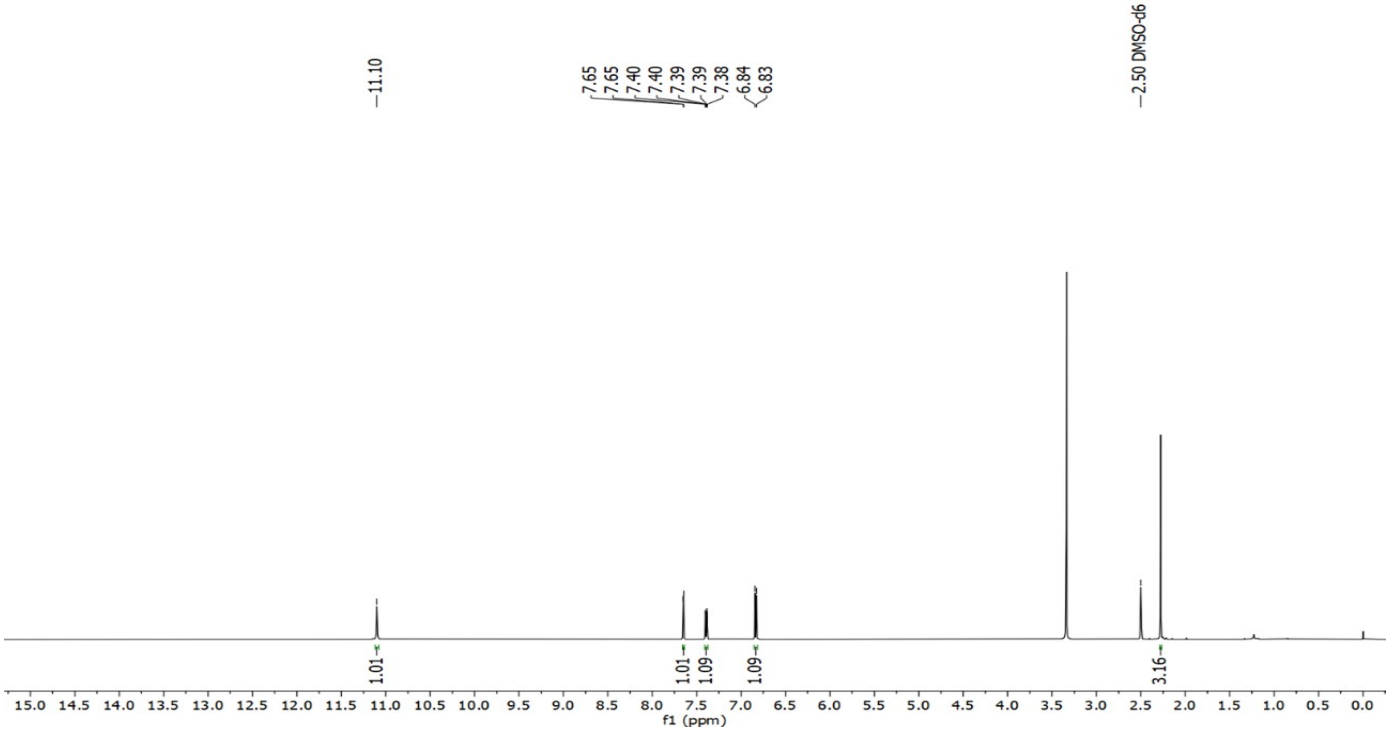
^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

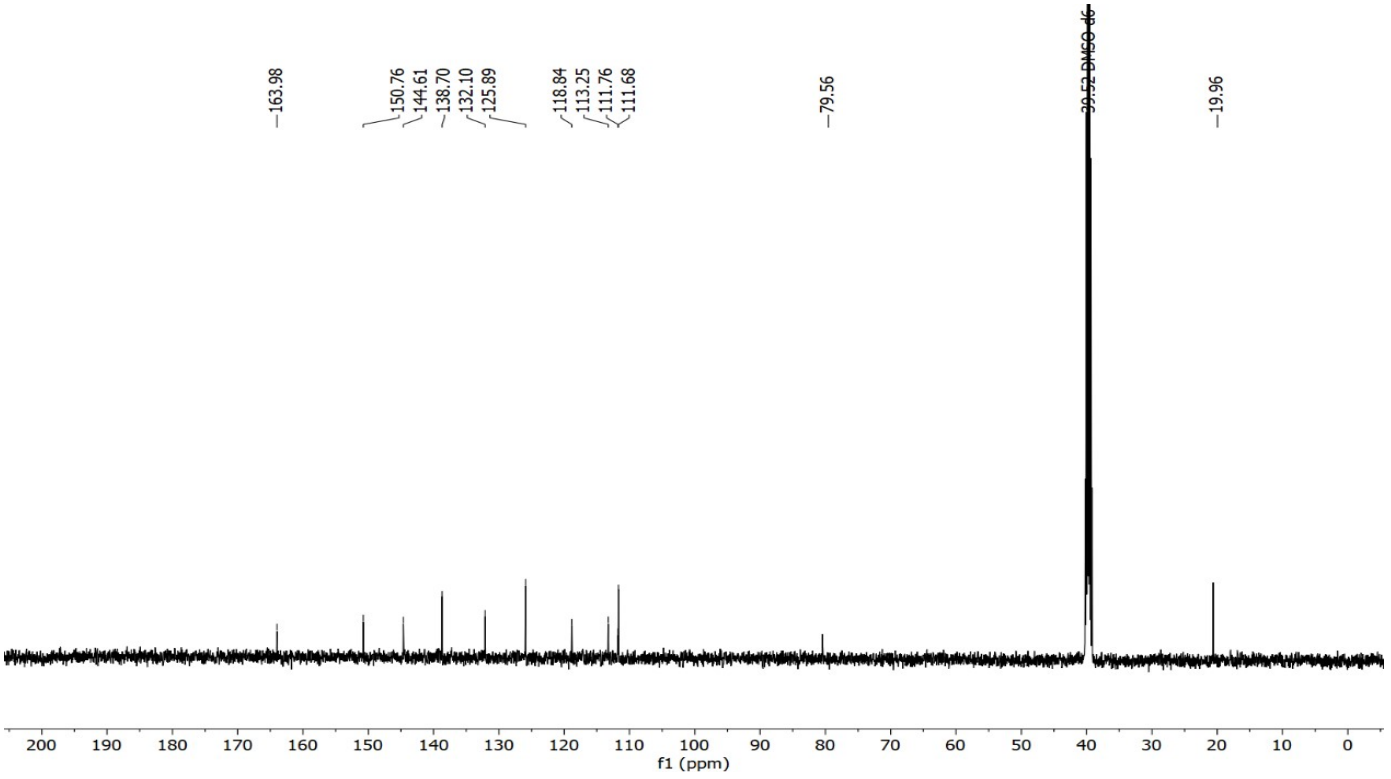


^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

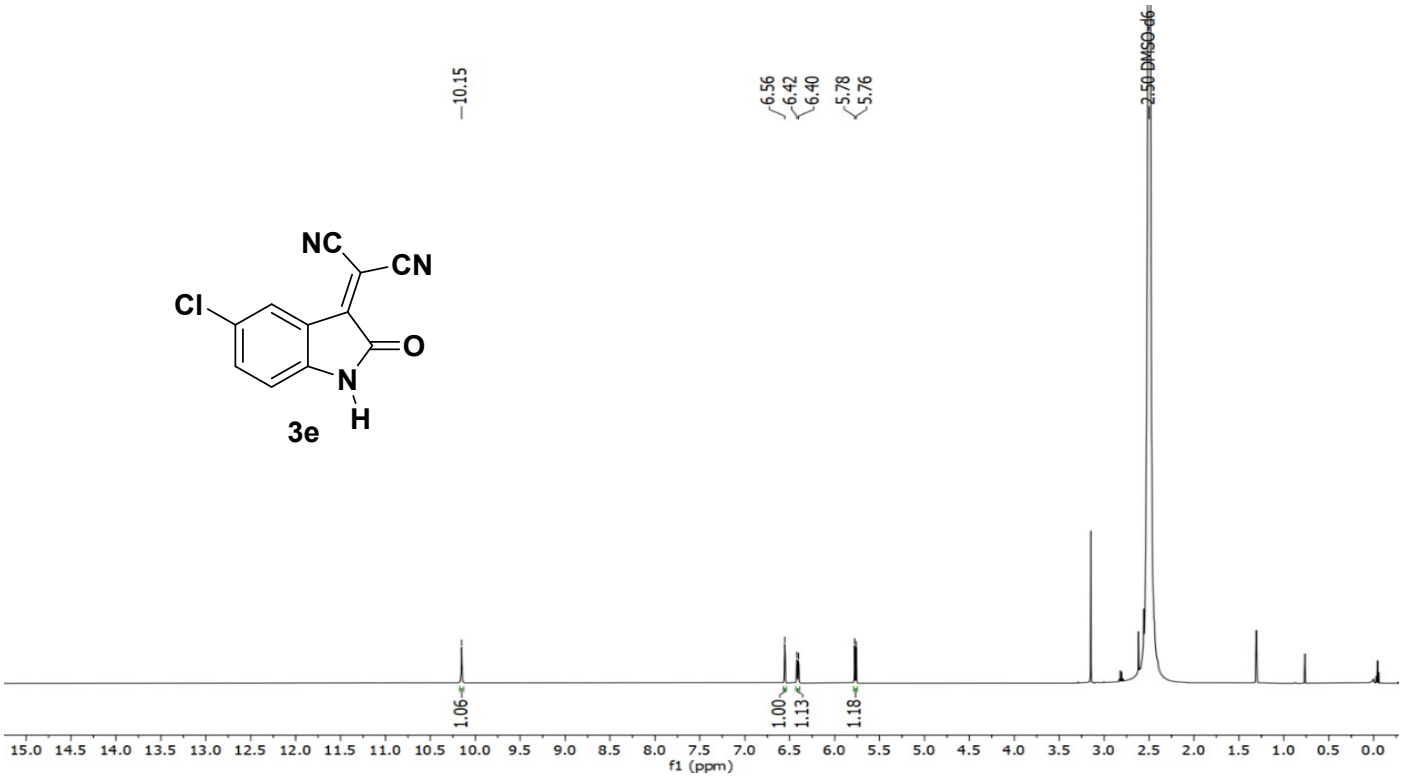


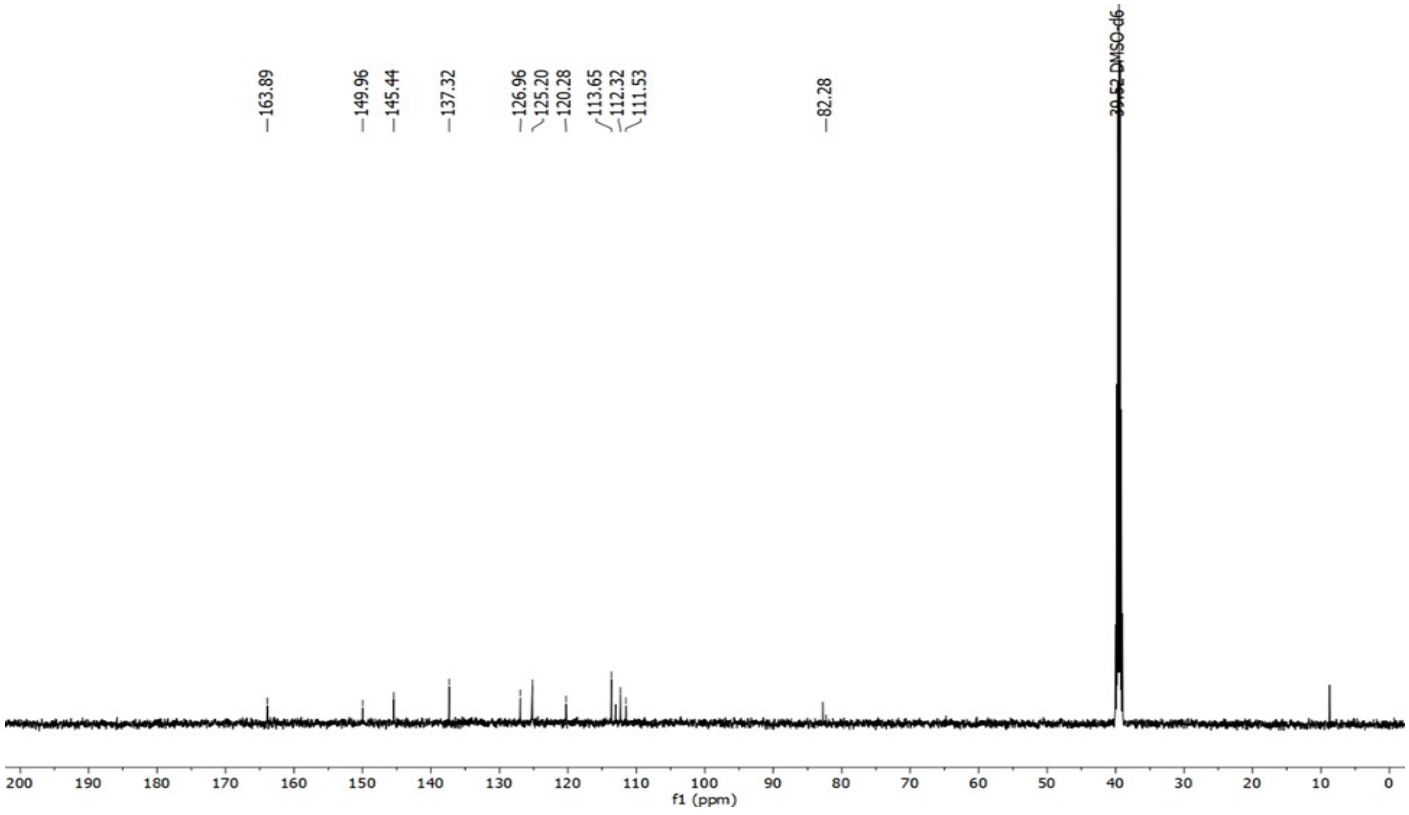
^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



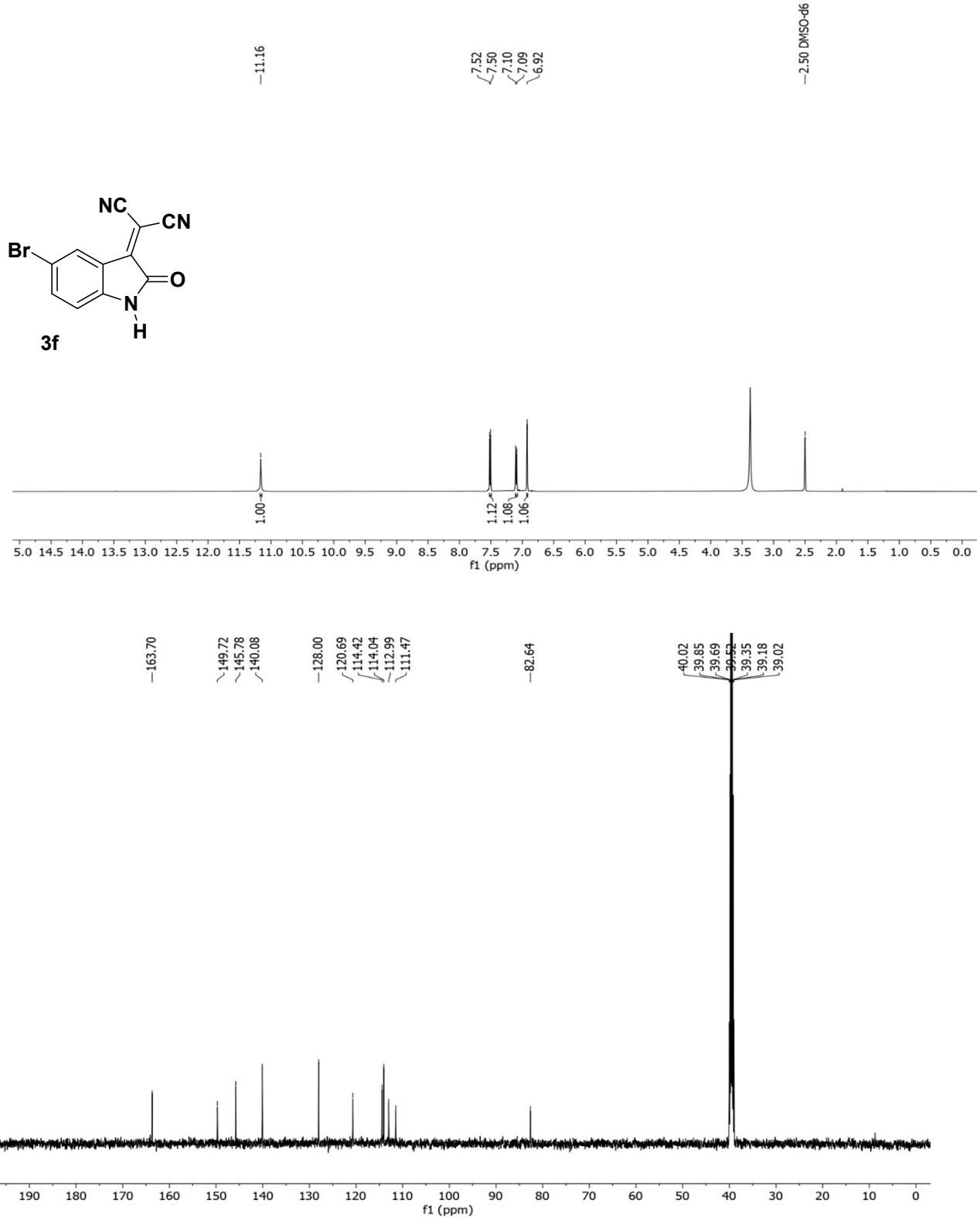


^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

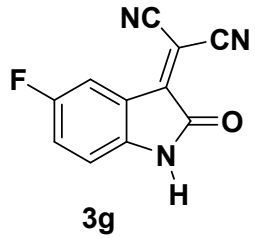




^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

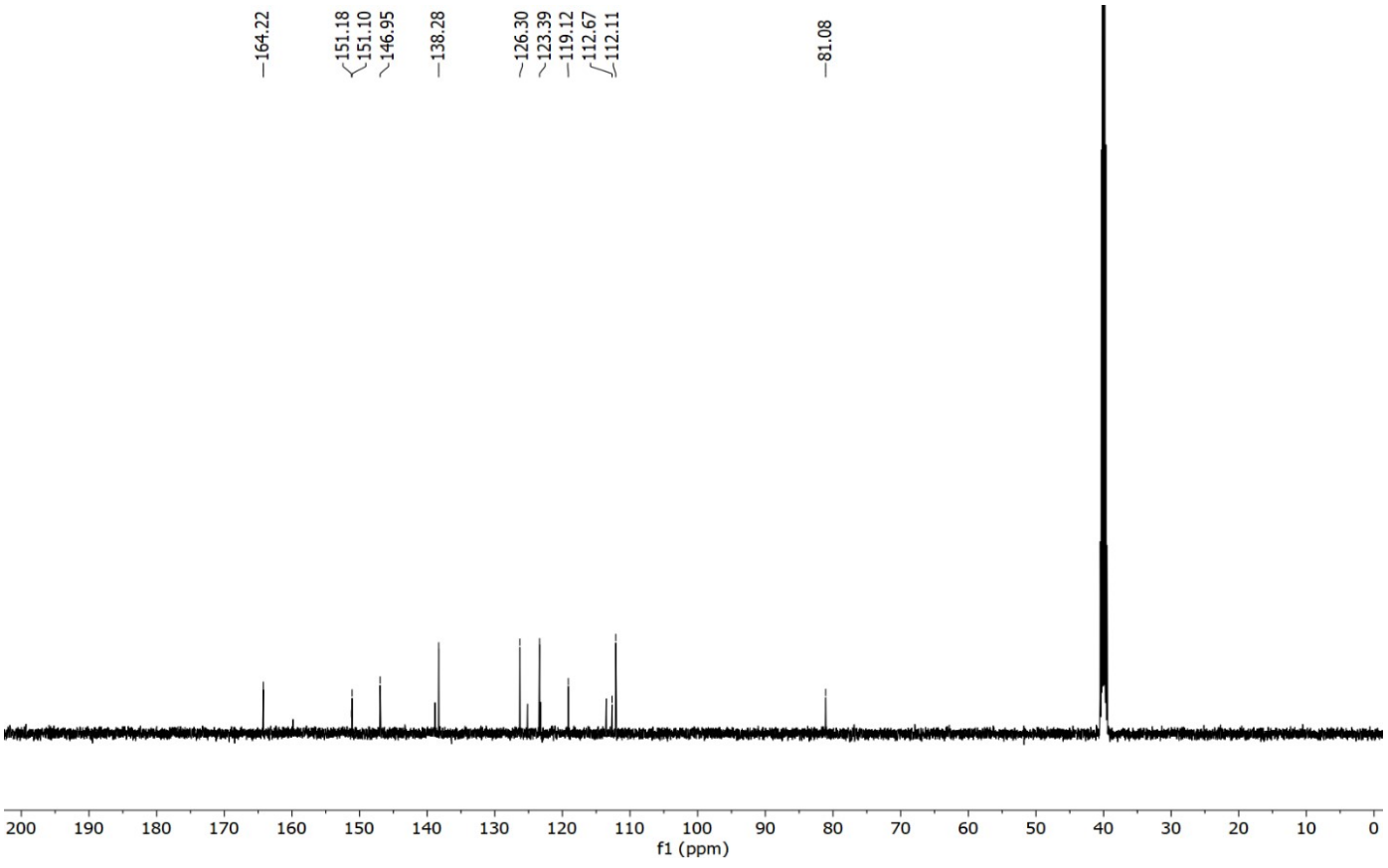


^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

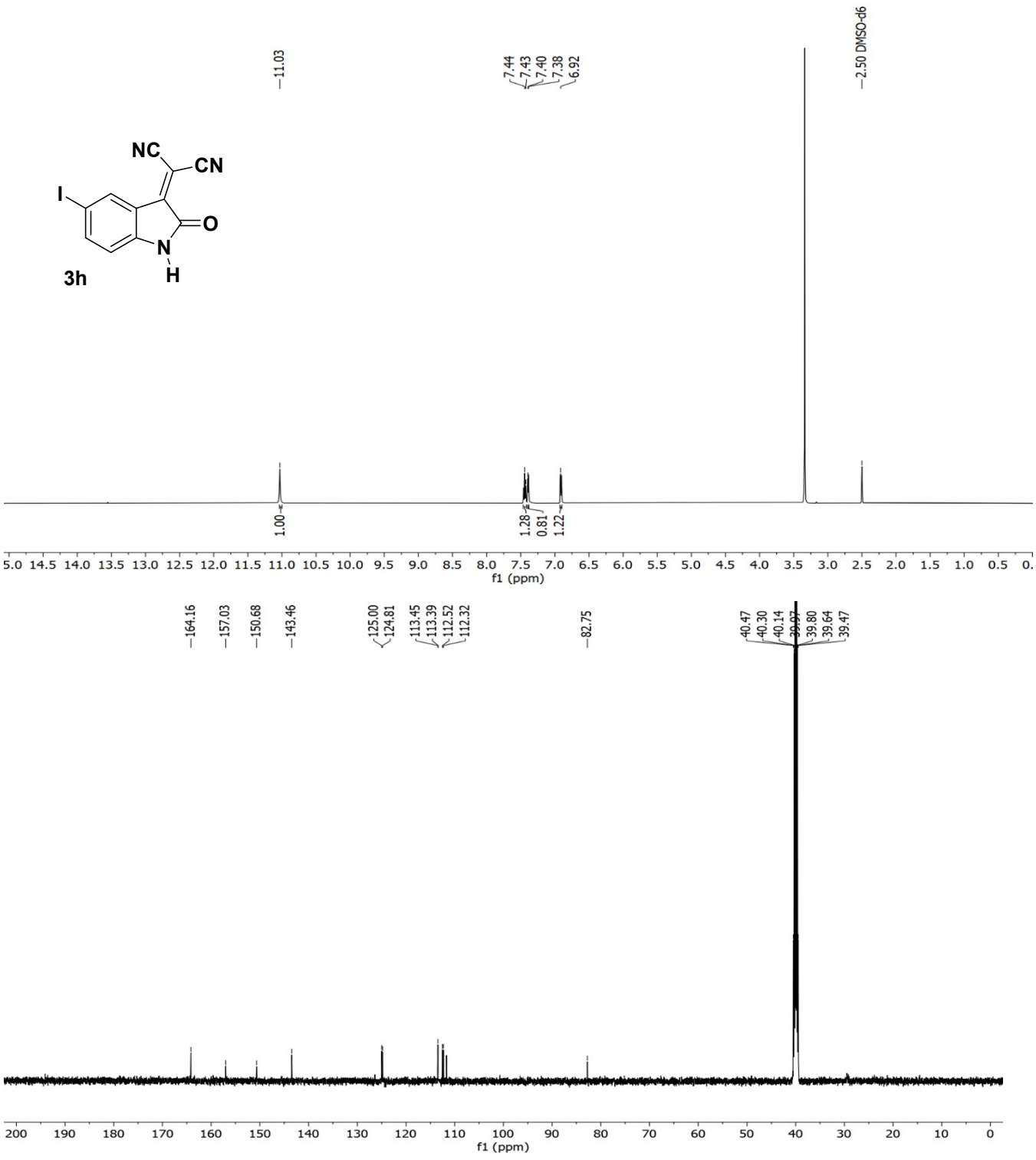

NC
CN
F
O
N
H

3g

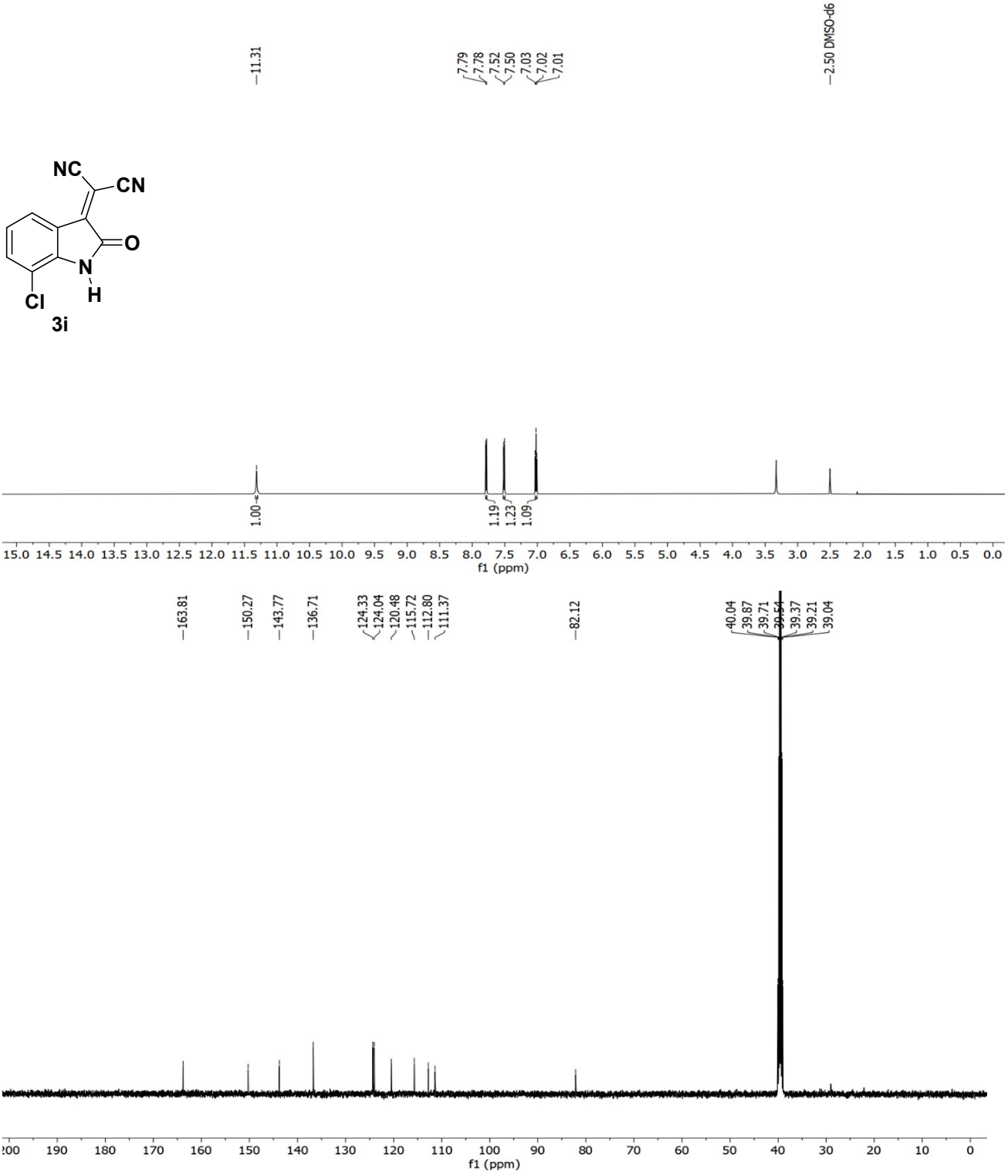
10.80
7.60
7.60
7.46
7.46
7.44
7.44
6.72
6.70
2.50 DMSO-d6
1.00
0.90
0.80
0.92
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.22
151.18
151.10
146.95
138.28
126.30
123.39
119.12
112.67
112.11
81.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

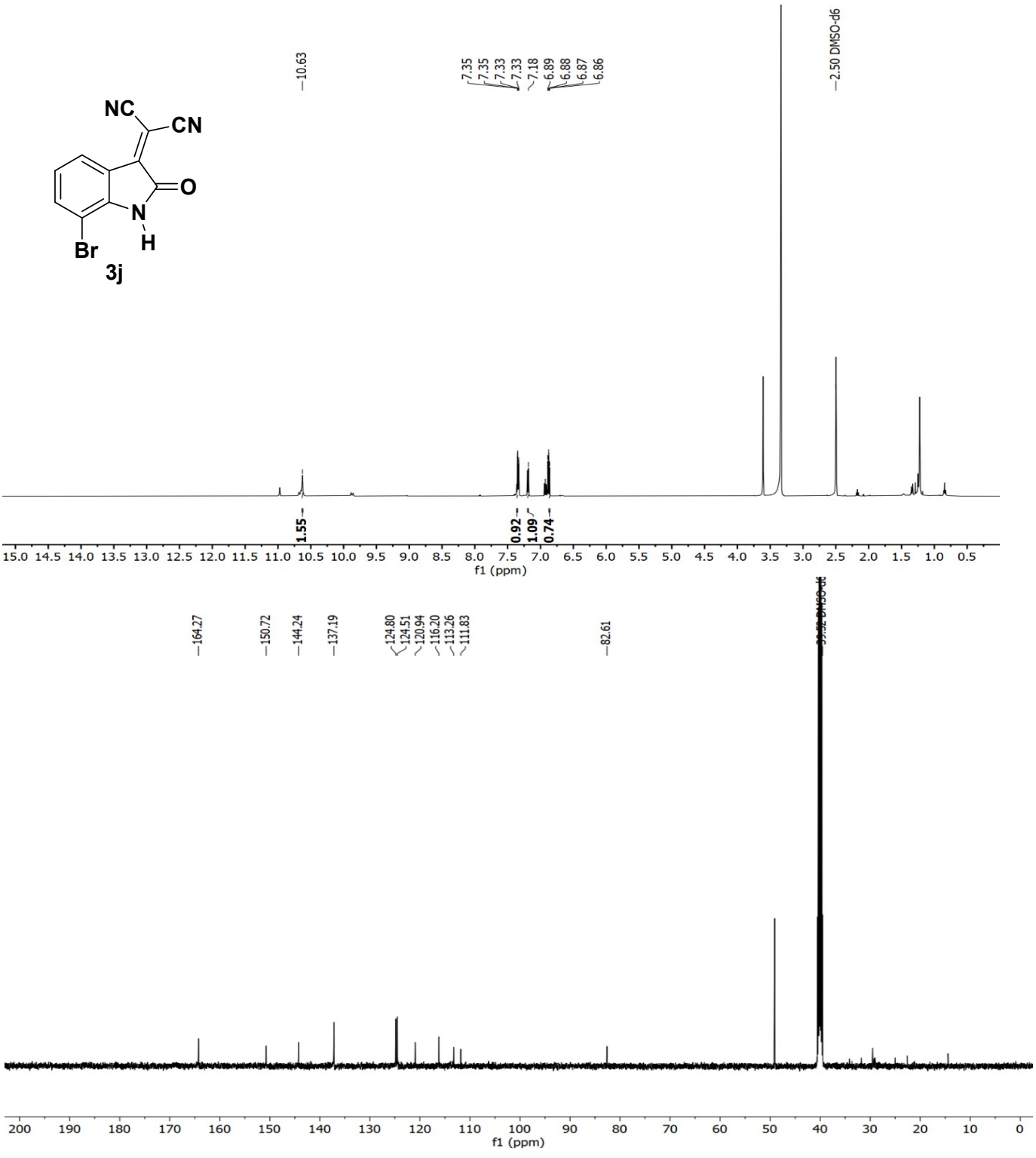
^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



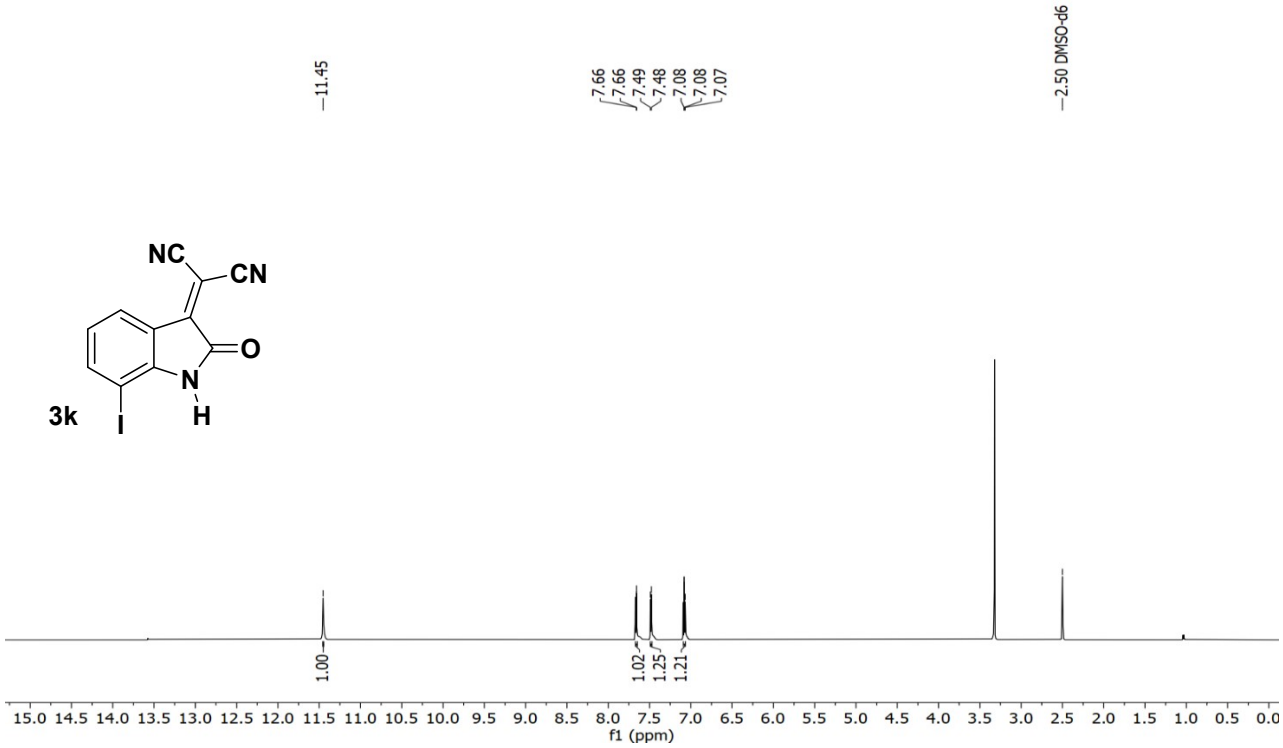
^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)

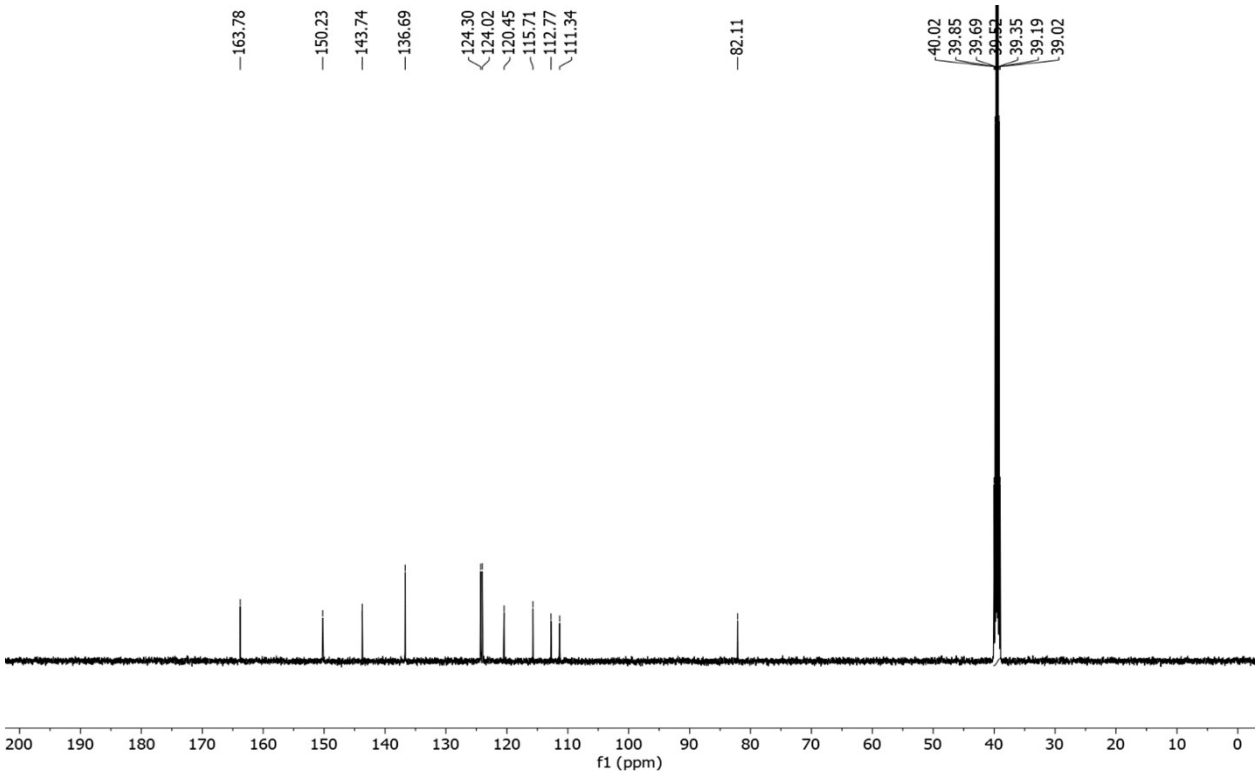


^{1}H NMR (500MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6)



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


11.45
7.66
7.66
7.49
7.48
7.08
7.08
7.07
2.50 DMSO-d6
NC
CN
O
N
H
3k
I
1.00
1.02
1.25
1.21
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.78
150.23
143.74
136.69
124.30
124.02
120.45
115.71
112.77
111.34
82.11
40.02
39.85
39.69
39.52
39.35
39.19
39.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)