Supporting Information

Electrochemical Selective Divergent C-H Chalcogenocyanation of *N*-Heterocyclic Scaffolds

Kusum Ucheniya,‡ Pooja Kumari Jat,‡ Amreen Chouhan, Lalit Yadav and Satpal Singh Badsara*

MFOS Laboratory, Department of Chemistry, University of Rajasthan, JLN Marg, Jaipur, Rajasthan, 302004, India. E-mail: badsarass4@uniraj.ac.in; badsarass4@gmail.com

‡These authors contributed equally and both are first author.

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General information:

All the chemicals and reagents were purchased from commercially suppliers and used without any prior purification. Column chromatography was performed over silica-gel (particle size: 100-200 Mesh) using hexanes and ethyl acetate as eluent, unless otherwise noted. The aluminium supported silica plate Si 60 F_{254} was used for the thin layer chromatography. ^{1}H NMR, ^{13}C NMR, and HRMS techniques were used for the analysis of synthesized compounds. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL ECS-400 instrument in $CDCl_3$ or DMSO-d_6 solvent. Chemical shifts reported in parts per million (ppm) with referencing the TMS at 0.00 ppm for ^{1}H NMR and coupling constants (J) were given in Hz. ^{1}H NMR peak signals were reported as s (singlet), br (broad), d (doublet), dd (double doublet), td (triplet of doublet), ddd (doublet of double doublet), qd (quartet of doublet), quint (pentet), sept (septet), and m (multiplet). In the ^{13}C NMR, chemical shifts were reported in ppm with referencing the center line of a triplet of chloroform-*d* at 77.10 ppm and septet of DMSO-d_6 at 39.50 ppm. High-resolution mass spectra (HRMS) were recorded on a Xevo G2-S Q TOF (Waters, USA) mass spectrometer, and Maxis-TOF analyser. All electrocatalytic reactions were carried out in IKA ElectraSyn 2.0 instrument. Starting precursors **1a-1b**[1], **6p-6q**[1], **1c-1g**[2], **6a-6o**[3], and **1h-1m**[4], **1n-1p**[5] were synthesized using reported literature. CFI refers to chromone-fused-indolizines. CV experiments were recored in a CHI 7087E electrochemical workstation.

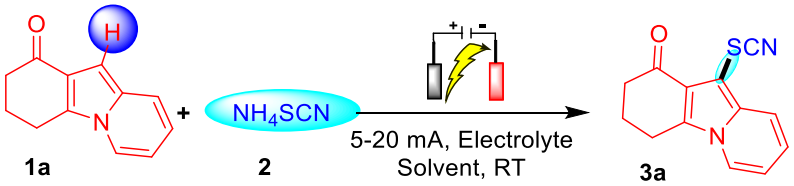
Optimization of Reaction conditions:

We commenced this electro-organic thiocyanation strategy with the reaction of model substrate 3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one (**1a**) and NH_4SCN (**2**) in an undivided cell of IKA electrasyn 2.0 instrument that equipped with a graphite anode and a platinum cathode (Table S1). Gratifyingly, the reaction of indolizine substrate **1a** and NH_4SCN (**2**) under 10 mA electric current with electrolyte $LiClO_4$ and additive NH_4I (50 mol%), in acetonitrile solvent afforded the desired product **3a** in a 60% yield in 3 h (Table S1, entry 1). Distinct parameters were further screened to optimize the reaction conditions and the results are summarized in Table S1.

During the control experiments, we have observed that the reaction was also feasible in the absence of additive NH_4I and supporting electrolyte $LiClO_4$ (entries 2-3). In the absence of electricity, product **3a** was not observed which evidences that electricity is mandatory for this thiocyanation protocol (entry 4). To get optimal reaction conditions solvent system(s) such as DMF, DMSO, EtOH, DCE, EtOAc:CH_3CN (7:1), CH_3CN:DMF (7:1), and CH_3CN:methanol (7:1) were screened (entries 5-11) and acetonitrile was found superior among them that yielded 75% of **3a** (entry 3). To further increase

the yield of **3a**, different types of electrode pairs such as C/C, C/Ni, C/RVC, and RVC/Ni were also tried (entries 12-15), among them C/C provided the 85% yield (entry 12). Decreased current density provided the **3a** in 62% yield with unreactive starting precursor **1a** whereas the increment in current density afforded the **3a** in 76% yield along with the unidentified side products (entry 16). It was found that reduced equimolar concentration of NH_4SCN (**2**, 1.5 equiv) gave only a 68% yield of **3a** whereas on increased equimolar concentration (3.0 equiv.) of **2** provided the **3a** in 84% yield (entry 17).

Table S1- Optimization of Reaction Conditions[a]



1a 2 3a

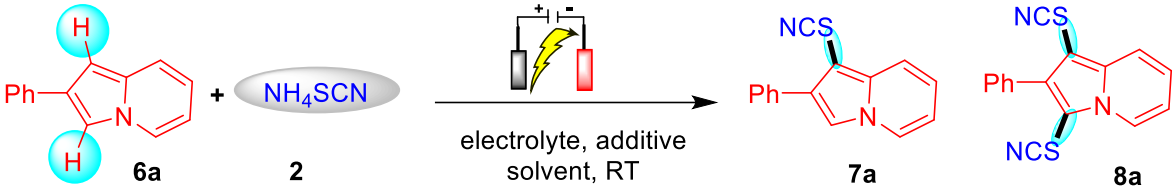
Entry	Electrolyte	Electrode (+)/(-)	Additive	Solvent(s)	Yield of **3a**[b] (%)
1.	$LiClO_4$	C/Pt	NH_4I	CH_3CN	60
2.	$LiClO_4$	C/Pt	-----	CH_3CN	62
3.	------	C/Pt	-----	CH_3CN	75
4.	------	------	-----	CH_3CN	0
5.	-------	C/Pt	-----	DMF	70
6.	------	C/Pt	-----	DMSO	10
7.	------	C/Pt	-----	EtOH	30
8.	------	C/Pt	-----	DCE	65
9.	------	C/Pt	-----	EtOAc:CH_3CN (7:1)	73
10.	------	C/Pt	-----	CH_3CN:DMF(7:1)	70
11.	------	C/Pt	-----	CH_3CN:MeOH (7:1)	15
12.	------	C/C	-----	CH_3CN	85
13.	------	C/Ni	-----	CH_3CN	80
14.	------	C/RVC	-----	CH_3CN	67
15.	------	RVC/Ni	-----	CH_3CN	77
16.	------	C/C	-----	CH_3CN	62[c], 76[d]
17.	------	C/C	-----	CH_3CN	68[e], 84[f]

[a]**Reaction conditions:** 4-Dihydropyrido[1,2-*a*]indol-1(2*H*)-one (**1a**, 0.25 mmol), NH_4SCN (**2**, 0.5 mmol), additive (50 mol%), and electrolyte (50 mol%) in a solvent(s) (4.0 mL) were electrolyzed with continuous current 10 mA at RT in the Electrasyn 2.0 instruments for 3 h. [b]Isolated yields of **3a** are

based on **1a**. [c]5 mA current was used instead of 10 mA. [d]20 mA current was used instead of 10 mA. [e]0.38 mmol of **2** was used instead of 0.5 mmol. [f]0.75 mmol of **2** was used instead of 0.5 mmol.

To gain the leverage of above-appended optimal reaction conditions of model substrate 3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one (**1a**) and NH_4SCN (**2**), for the C-H chalcogenocyanation of indolizine frameworks, **6a** with NH_4SCN (**2**) was chosen as a model substrate for optimization of electrolysis conditions (Table S2). The electrolysis was conducted in an undivided cell of IKA electrasyn 2.0 instrument that equipped with a graphite anode and graphite cathode. Under the optimal reaction conditions of Table S1, mixture of C-H mono and bis-thiocyanated indolizines **7a** and **8a** was obtained in 30% and 10% yields respectively (entry 1). RVC/RVC electrode system also provided the similar results providing **7a** and **8a** in 35% and 12% yields respectively (entry 2). In order to develop the optimized reaction conditions, various parameters were studied but none of them provided significant results (entries 3-15). The use of DBU as additive almost put an end to formation of thiocyanate products **7a** and **8a** (entry 3). Supporting electrolytes $LiClO_4$, $^nBu_4NPF_6$ and altering the electrode pairs such as C/C, C/Pt, C/Ni were all detrimental for the reaction conditions (entries 4-8). In the solvent screening DMSO, acetone, CH_3CN: DMF, and CH_3CN: methanol practically ceased the formation of thiocyanate products (entries 9-12). The use of equimolar concentration of additives NH_4I, KI, and TBAI, and I_2 were profound influence on the C-3 mono-thiocyanate product **7a** (entries 13-16), among them I_2 drastically increased the formation of **7a**. An optimal 91% yield of absolute C-3 thiocyanate **7a** was obtained when **6a** (1.0 equiv.), NH_4SCN (**2**, 2.0 equiv.), and iodine (1.0 equiv.) were charged using EtOAc: CH_3CN (1:1) solvent system in an undivided cell equipped with RVC/RVC electrodes (entry 16). Further, decreased current density from 10 mA to 5 mA provided the **7a** in 60% yield with unreactive starting precursor **6a** and abolished the formation of **8a**, whereas increased current density from 10 mA to 20 mA provided the sole bis- thiocyanate product **8a** in 68% yield (entry 17). The alleviated equimolar concentration of NH_4SCN (**2**, 1.5 equiv.) provided only a 70% yield of **7a** whereas elevated equimolar concentration (3.0 equiv.) of **2** provided the **7a** in 60% and **8a** in 35% yields (entry 18). On account of out-puts observed in controlled experiments the slight modulation in optimal reaction conditions of C-3 mono-thiocyanate product **7a** (entry 16) such as advancement in current density up to 20 mA, concentration of iodine (1.5 equiv.), and reaction time for 3 h, produced exclusively **8a** bis-thiocyanate product in 92% yield (entry 19). Therefore, the mediator I_2 and electric current serves crucial roles in controlling reaction selectivity, and enhancing reaction efficiency.

Table S2. Optimization of Reaction Conditions[a]



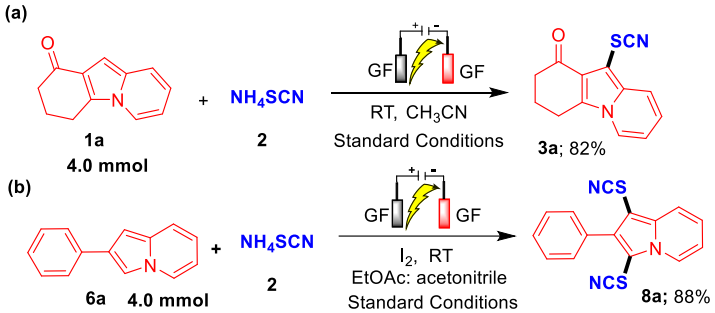
Entry	Electrolyte	Electrode (+)/(-)	Additive	Solvent(s)	Yield of **7a**[b] (%)	Yield of **8a**[b] (%)
1.	----	C/C	----	EtOAc: CH_3CN (1:1)	30	10
2.	----	RVC/RVC	----	EtOAc: CH_3CN (1:1)	35	12
3.		C/C	DBU	CH_3CN	trace	----
4.	$LiClO_4$	C/C	----	CH_3CN	13	----
5.	$LiClO_4$	C/Pt	----	CH_3CN	12	----
6.	$LiClO_4$	C/Ni	----	CH_3CN	10	----
7.	$LiClO_4$	RVC/RVC	----	CH_3CN	15	----
8.	$^nBu_4NPF_6$	RVC/RVC	----	CH_3CN	18	----
9.	----	RVC/RVC	----	DMSO	trace	----
10.	----	RVC/RVC	----	Acetone	trace	----
11.	----	RVC/RVC	----	CH_3CN:DMF (1:1)	trace	----
12.	----	RVC/RVC	----	CH_3CN:Methanol (1:1)	trace	----
13.	----	RVC/RVC	NH_4I	EtOAc:CH_3CN (1:1)	40	18
14.	----	RVC/RVC	KI	EtOAc:CH_3CN (1:1)	48	20
15.	----	RVC/RVC	TBAI	EtOAc:CH_3CN (1:1)	25	trace
16.	----	RVC/RVC	I_2	EtOAc:CH_3CN (1:1)	91	< 5
17.	----	RVC/RVC	I_2	EtOAc:CH_3CN(1:1)	60[c], trace[d]	trace[c], 68[d]
18.	----	RVC/RVC	I_2	EtOAc:CH_3CN (1:1)	70[e], 60[f]	trace[e], 35[f]
19.	----	RVC/RVC	I_2	EtOAc:CH_3CN (1:1)	----	92[g]

[a]**Reaction conditions:** 2-Phenylindolizine (**6a**, 0.25 mmol), NH_4SCN (**2**, 0.5 mmol), and additive (100 mol%), and electrolyte (50 mol%) in EtOAc: acetonitrile (1:1) (4.0 mL) were electrolyzed with continuous current 10 mA at RT in the Electrasyn 2.0 instruments for 1 h. [b]Isolated yields of **7a** and **8a** are based on **1a**. [c]5 mA current was used instead of 10 mA. [d]20 mA current was used instead of 10 mA. [e] 0.38 mmol of **2** was used instead of 0.5 mmol. [f] 0.75 mmol of **2** was used instead of 0.5 mmol. [g] 0.75 mmol of **2** was used instead of 0.5 mmol with I_2 (1.5 equiv.) at 20 mA constant current for 3 h.

Large-scale experiments

To explore the synthetic utility of this interesting electrochemical selective C-H chalcogenocyanation protocol, large-scale experiments were also performed (Scheme S1). As shown in Scheme S1a, indolizine **1a** (4.0 mmol, 0.740 g) was charged with **2** (8.0 mmol, 0.608 g) in CH_3CN under optimized reaction conditions for 6 h afforded the corresponding thiocyanate product **3a** in 82% yields. Similarly, the reaction of **6a** (4.0 mmol, 0.733 g) with **2** (12.0 mmol, 0.913 g) in the presence of I_2 (6.0 mmol, 1.52 g) in EtOAc: acetonitrile solvent under optimized reaction conditions after 7 h provided **8a** in 88% yield (Scheme S1b).

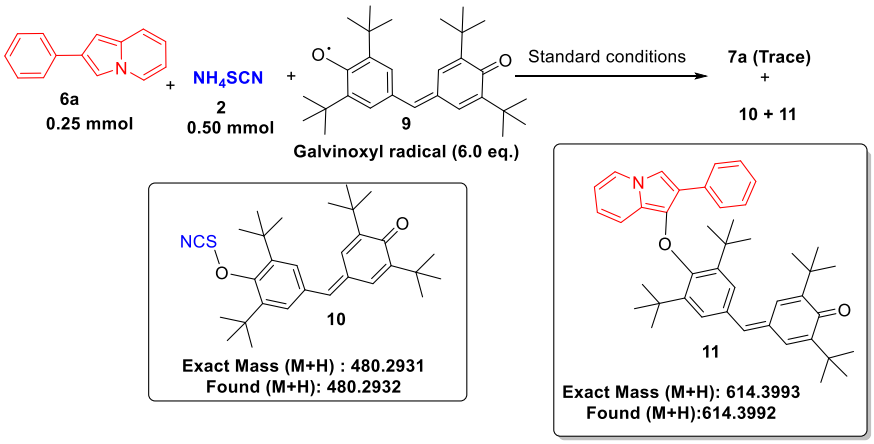
Scheme S1:



Radical trapping experiment

To find out a possible reaction pathway of this selective electrochemical chalcogeno-cyanation protocol, a radical trapping experiment was also carried out (Scheme S2). When, we charged 2-phenylindolizine (**6a**, 0.25 mmol, 0.048 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) in the presence of galvinoxyl free radical **9** (6.0 equiv., 1.5 mmol, 0.633 g) under standard conditions only trace amount of **7a** was obtained instead a galvinoxyl-**2** coupled product **10** and galvinoxyl-**6a** coupled product **11** were formed (confirmed by HRMS data analysis) which supports that a radical-based pathway was involved in this transformation.

Scheme S2



Cyclic Voltammetry (CV) Studies:

To find out a plausible mechanistic pathway for this interesting C-H chalcogenocyanation protocol, cyclic voltammetry (CV) experiments were also performed (Fig. S1-S13). To record CV experiments a CHI 7087E electrochemical workstation was used. All CV studies were measured at room temperature in a three-electrode cell, a glassy carbon electrode (GCE; 5 mm diameter) as working electrode and platinum foil (1 x 2 cm) as counter electrode. The reference was an aqueous Ag/AgCl electrode submerged in saturated 3 M KCl solution, and separated from the reaction mixture by a salt bridge. 0.1 M $LiClO_4$ was used as supporting electrolyte in acetonitrile. The scan rate was 0.05 V/s.

Cyclic voltammetry (CV) studies for the formation of 3a:

The CV of $LiClO_4$ (0.1 M) showed no oxidation peak (graph **a**-blank, Fig. S1). The CV of NH_4SCN (**2**) (5 mM) with supporting electrolyte $LiClO_4$ (0.1 M) showed an oxidation peak at +1.01 V (graph **b**, Fig. S1) which indicates that SCN^- ion gets oxidized into $SCN^\bullet$ radical. The CV of CFI (chromone-fused-indolizine) **1a** (5 mM), and $LiClO_4$ (0.1 M) revealed that it has three prone sites (*N*-atom at indolizine core moiety, a ketonic and an ether functional group at chromone core moiety) for readily oxidation in potential window 0 to 2 V. The irreversible CV of CFI **1a** demonstrates the oxidation peaks at +0.95 V, +1.15 V, and weak oxidation peak at +1.43 V without any quantifiable current (graph **c**- CFI, Fig. S2). The CV of the mixture of **1a**, and **2** (graph **d**- RM, Fig. S2) demonstrated an apparent oxidation peak at +1.22 V along with the peak at +0.98 V with peak current spike of 0.09 mA which is might be due to synergistic peak potential effect of **1a** (+0.95 V) and **2** (+1.01 V). This indicates that the one of the functional sites of **1a** is preferably oxidize at anode and also, the new oxidation peak at +1.22 V supports the formation of intermediate due to radical-radical oxidative coupling of compounds **1a** and **2**. For better representation a comparative CV of **1a**, **2** and **RM** is also depicted in Fig. S3.

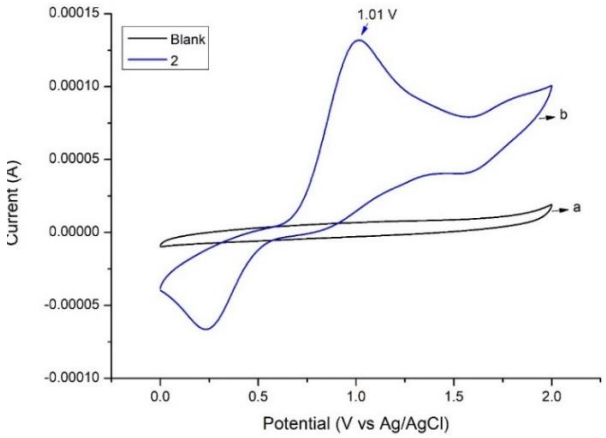


Figure S1. Cyclic voltammetry of NH_4SCN (**2**): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **a**-blank $LiClO_4$ (0.1 M); **b**-NH_4SCN (**2**) (5 mM)

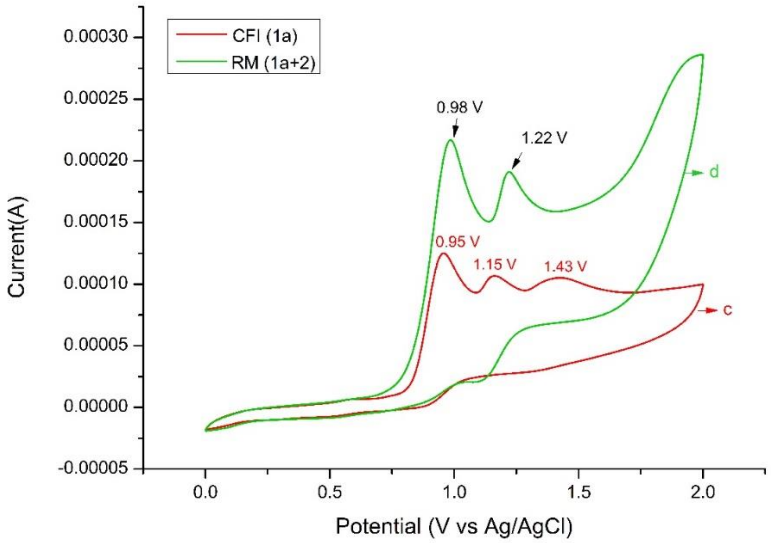


Figure S2. Cyclic voltammetry of **1a** and reaction mixture (RM): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **c**-CFI **1a** (5 mM); **d**-RM **1a** (5 mM) + **2** (5 mM)

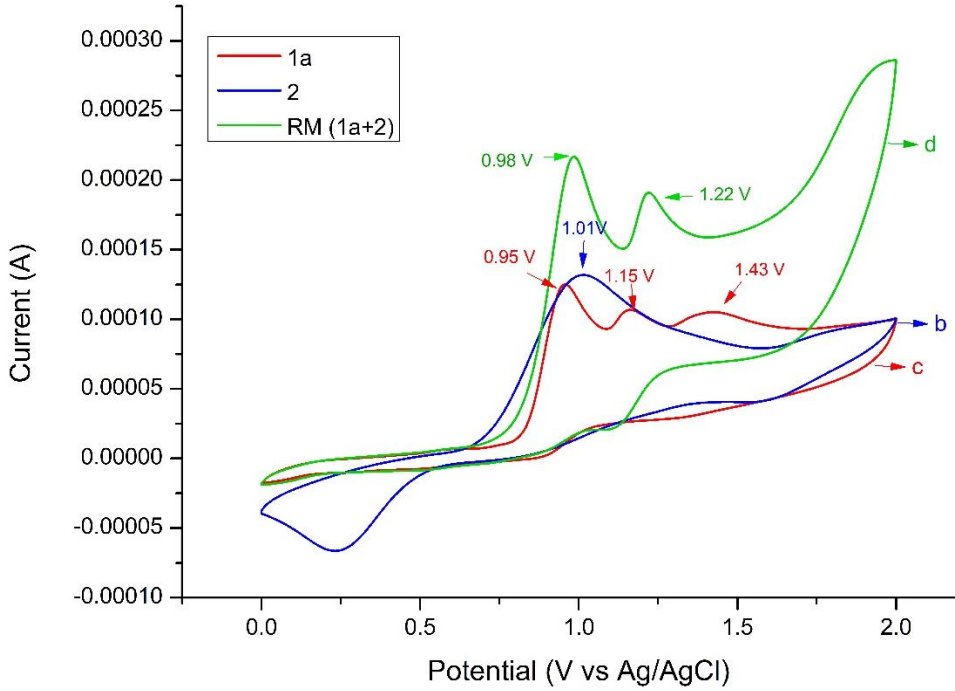


Figure S3. Comparative cyclic voltammetry of **1a**, **2** and RM: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **b**-**1a** (CFI) (5 mM); **c**-**2** (5 mM); **d**-RM **1a** (5 mM) + **2** (5 mM)

Cyclic voltammetry (CV) studies for the formation 7a and 8a:

We have also performed cyclic voltammetry studies for the reaction between **6a** and NH_4SCN (**2**) to further understand the plausible mechanism for the formation of **7a** and **8a**. As shown in graph **b**, Fig. S1, NH_4SCN (**2**) (5 mM) showed an oxidation peak at +1.01 V. The CV of **6a** and $LiClO_4$ (0.1 M) showed an oxidation peak at +1.27 V (graph **f**-6a, Fig. S4). To understand the role of iodine (I_2), we have also carried out CV experiments of **2** and **6a** individually in the presence of iodine as shown in Figs. S5 & S6. The CV of **2** in the presence of iodine showed an enhancement in the peak potential of **2** from +1.01 V to +1.13 V (graph-**e**, Fig. S5) suggesting an interaction between **2** and iodine. The CV of **6a** and $LiClO_4$ (0.1 M) in the presence of iodine showed two oxidation peaks at +0.90 V and +1.43 V (graph **g**-**6a**+I_2, Fig S6) suggesting a favorable chemical interaction between **6a** and iodine. The iodine lowers the onset peak current and oxidation potential of **6a** from +1.27 V to +0.90 V (graph **g**-6a+I_2, Fig. S6) and increased the peak potential of **2** which support the preferential oxidation of **6a** over **2** at anode. The CV of the mixture of **6a** and **2** in presence of iodine (graph **h**- RM, Fig. S7) demonstrated two apparent oxidation peaks at +1.15 V and +1.57 V supporting the paired electrolysis and formation of a possible intermediate(s) to proceed the reaction. Further, it is noteworthy that the CV of product **7a** (C-3 thiocyanate product) exhibited two apparent oxidation potential peaks at +1.22 V and +1.65 V (graph i-**7a**, Fig. S8) whereas, the CV of **7a** in the presence of iodine decreased these potential to +1.16 V and +1.50 V respectively, closest to the peak potential of reaction mixture of **6a**, **2** and iodine confirming that **7a** was initially formed and then converted into **8a** (graph **j-7a** + I_2, Fig. S8).

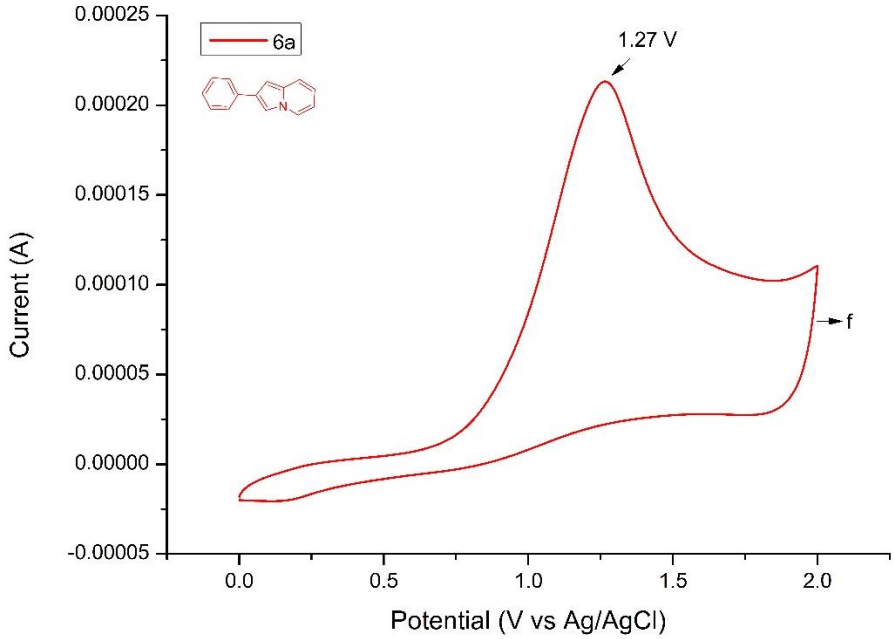


Figure S4. Cyclic voltammetry of **6a**: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammogram: **f**-indolizine **6a** (5 mM)

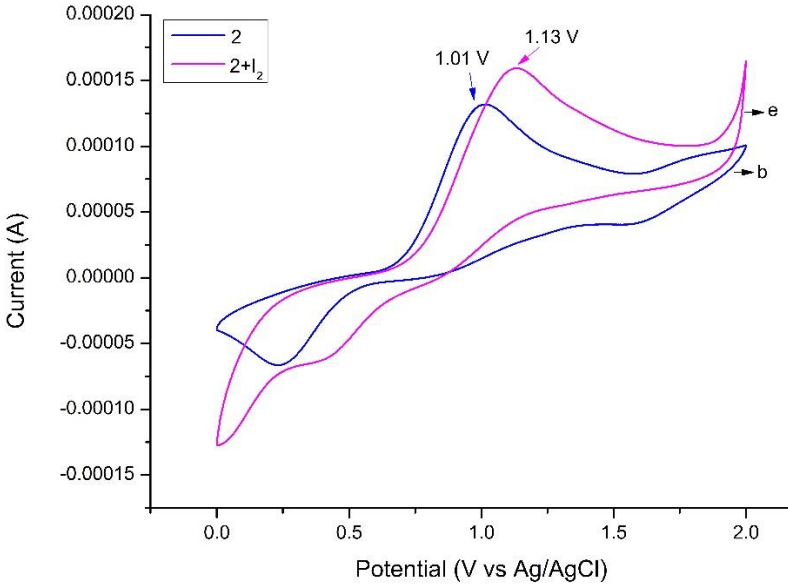


Figure S5. Cyclic voltammetry of **2** and **2**+I_2: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **b**-NH_4SCN (**2**) (5 mM); **e**-NH_4SCN (5 mM) + I_2 (5 mM)

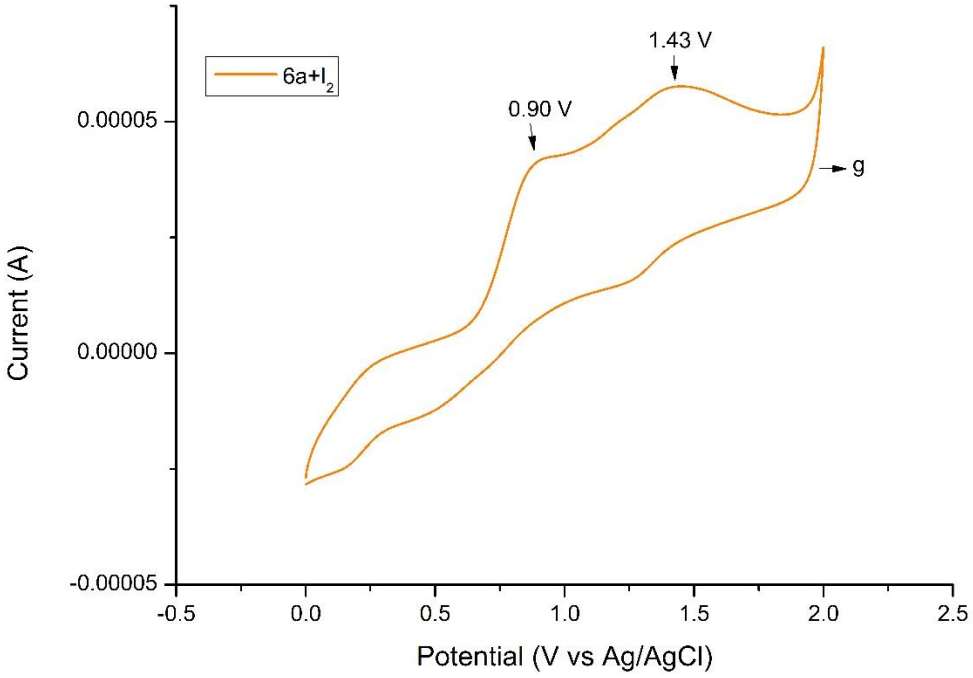


Figure S6. Cyclic voltammetry of **6a**: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammogram: **f**-indolizine **6a** (5mM) +I_2 (5 mM)

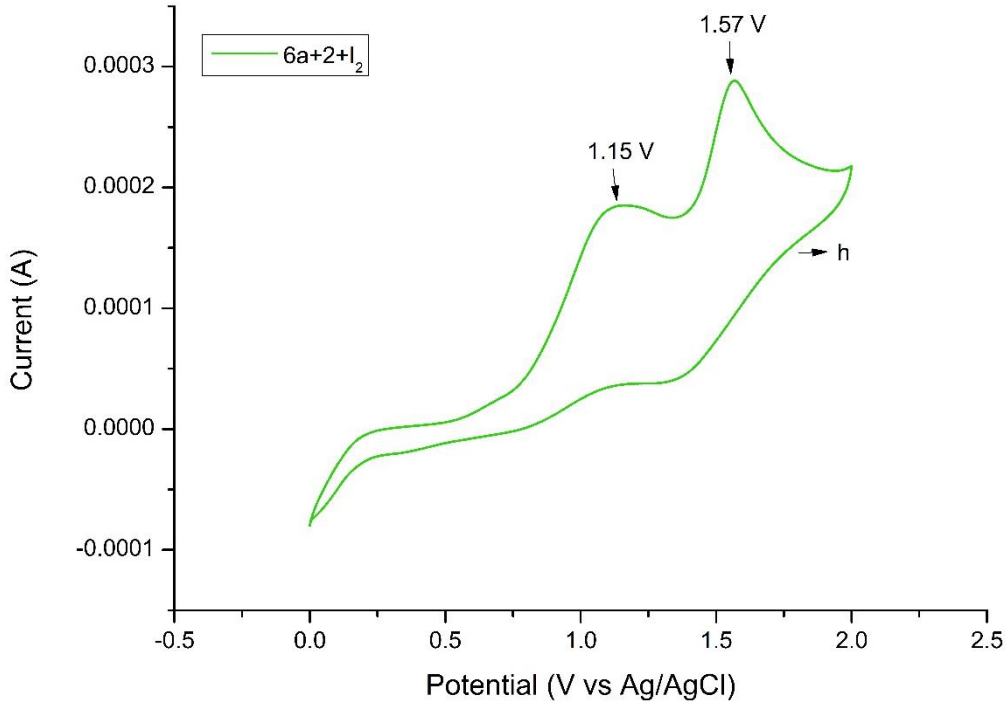


Figure S7. Cyclic voltammetry of reaction mixture (**6a** + **2** + I_2): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammogram: **g**-RM **1a** (5 mM) + **2** (5 mM)

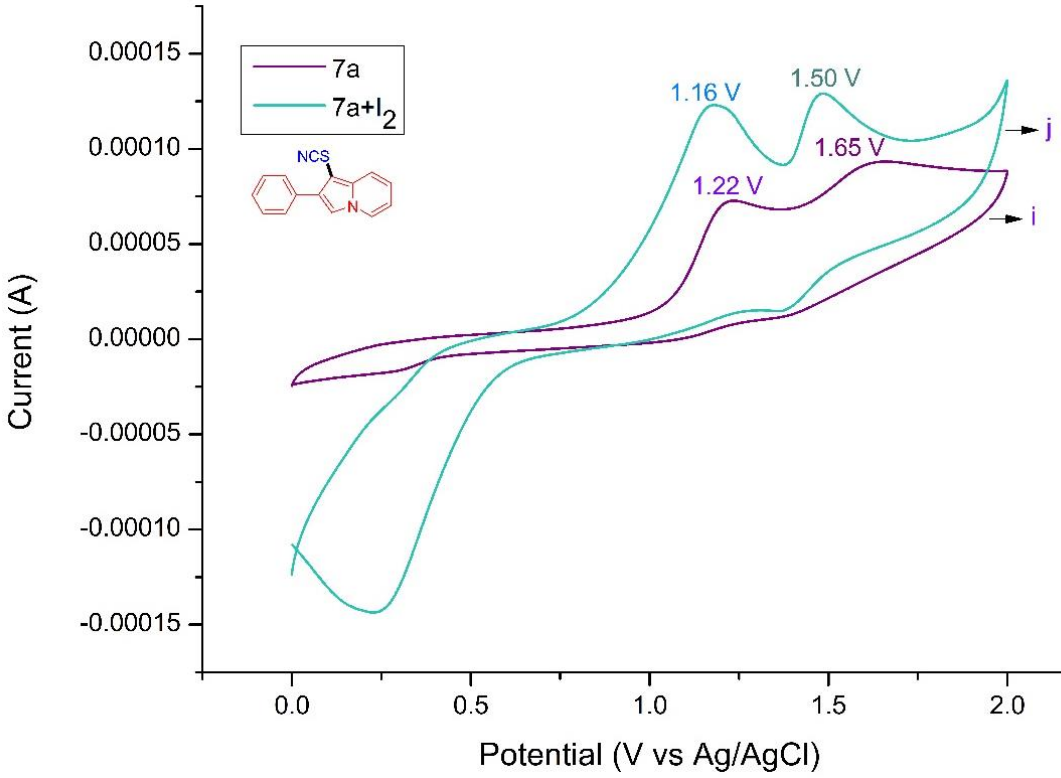


Figure S8. Cyclic voltammetry of **7a**: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **i**-**7a** (5mM); **j**-**7a** (5mM) + I_2 (5 mM)

Cyclic voltammetry (CV) studies for the radical trapping experiments:

To established a radical pathway for this interesting C-H chalcogenocyanation protocol, we have also carried out cyclic voltammetry (CV) studies for the radical trapping experiments. The CV of $LiClO_4$ (0.1 M) and galvinoxyl free radical (**9**) (5 mM) showed a potent oxidation peak at +1.26 V (graph **9**, Fig. S9). The behavior of cyclic voltammetry wave of **9** (5mM) with NH_4SCN (**2**) (5mM) showed an enhancement in the oxidation potential of **2** from +1.01 V to +1.28 V (graph **9**+**b**, Fig-S10). The CV experiment of **6a** with galvinoxyl free radical showed two oxidation peaks +0.95 and +1.58 which support that the addition of galvinoxyl free radical to **6a** declined the peak current of **6a** (graph **9**+**6a**, Fig S11)

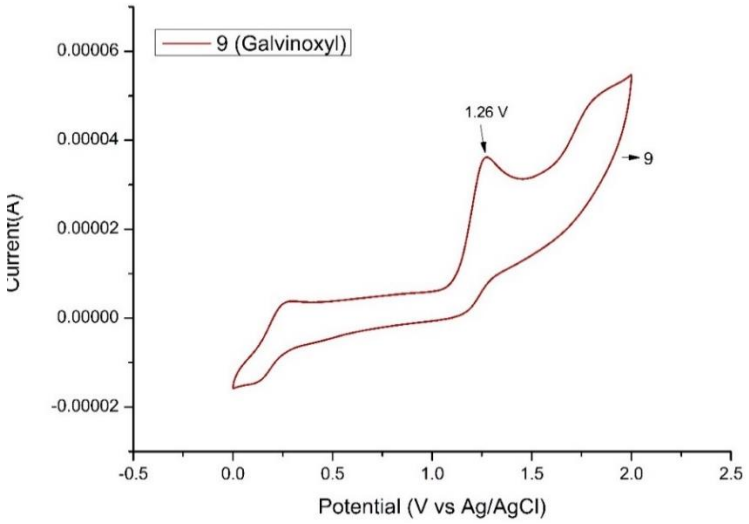


Figure S9. Cyclic voltammetry of galvinoxyl free radical (**9**): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammogram: galvinoxyl **9** (5 mM)

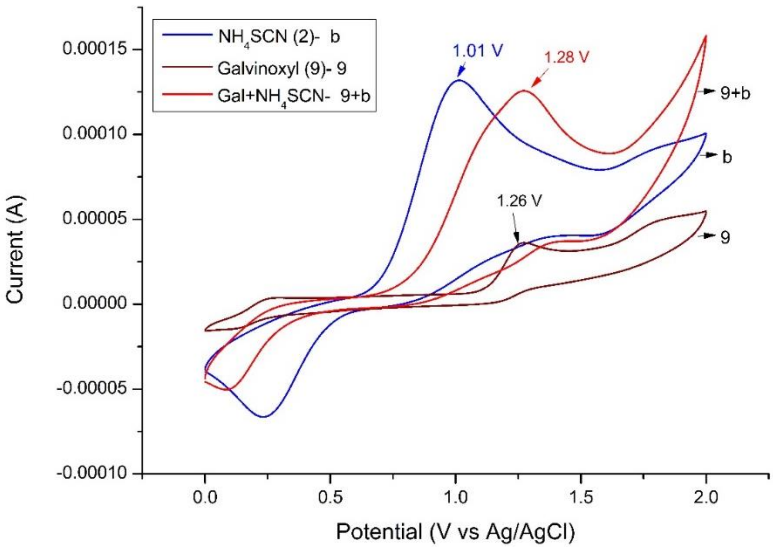


Figure S10. Cyclic voltammetry of galvinoxyl free radical (**9**) with NH_4SCN (**2**): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **b**-NH_4SCN (**2**) (5 mM); **9**-galvinoxyl (5 mM; **9+b**-galvinoxyl free radical (5 mM) NH_4SCN (**2**) (5 mM).

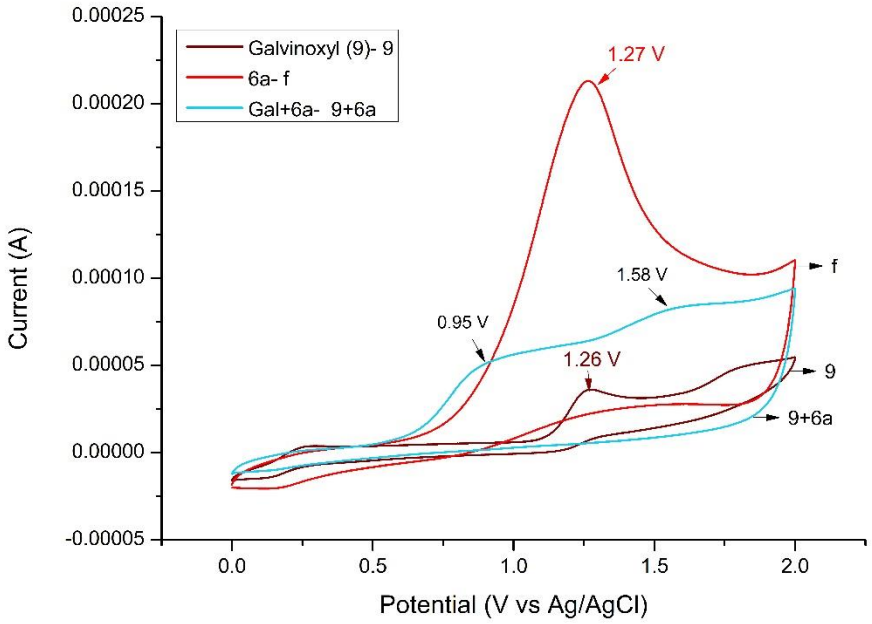


Figure S11. Cyclic voltammetry of galvinoxyl free radical (**9**) with indolizine **6a**: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **9**-galvinoxyl (5 mM); **f**-indolizine **6a** (5 mM); **9+6a**-galvinoxyl (5 mM) + **6a** (5 mM)

The CV of iodine was also recorded which showed the quasi-reversible cyclic voltammetry oxidation peak at +0.71 V and reduction peak at + 0.61 V (graph-I_2, Fig. S12).

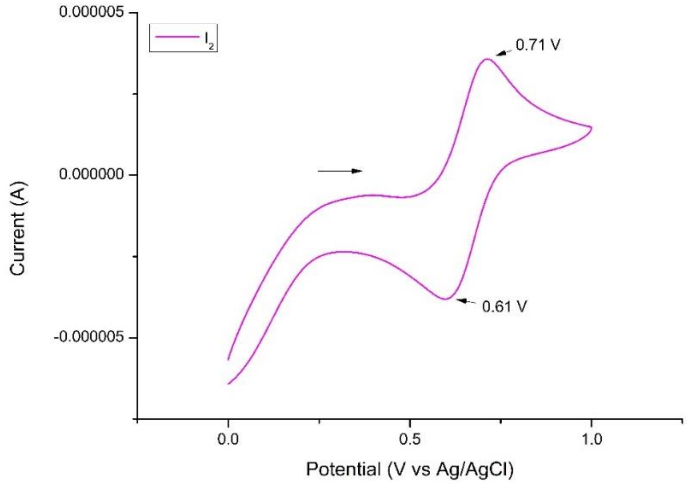


Figure S12. Cyclic voltammetry of Iodine (I_2) as per IUPAC convention: Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: iodine (5mM).

The CV of reaction mixture (**6a**, **2** and iodine) in the presence of galvinoxyl free radical (**9**) demonstrated only two apparent oxidation peak at +0.88 V and +1.55 V (graph-**9**+RM, Fig. S13)

supporting the radical coupling of **6a** and **2** with galvinoxyl free radical (**9**) as it was confirmed by HRMS data analysis (Scheme S2).

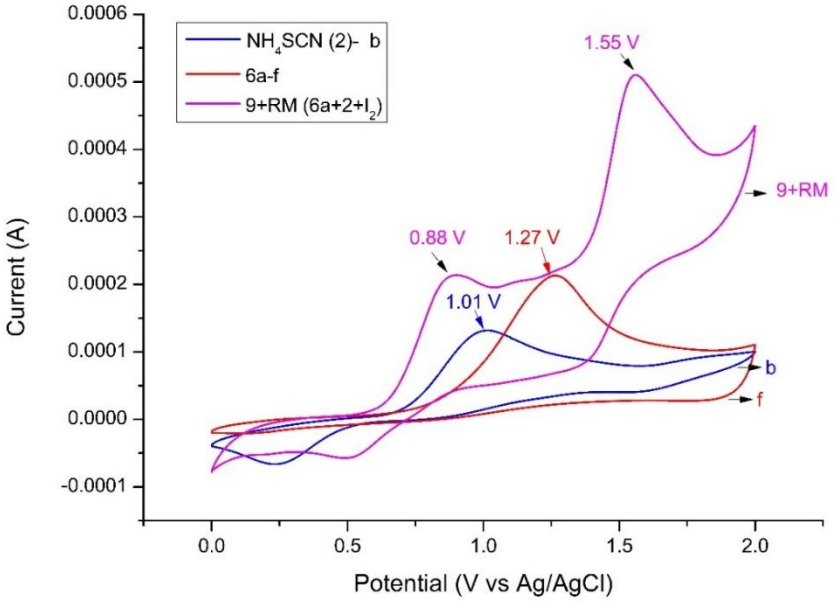
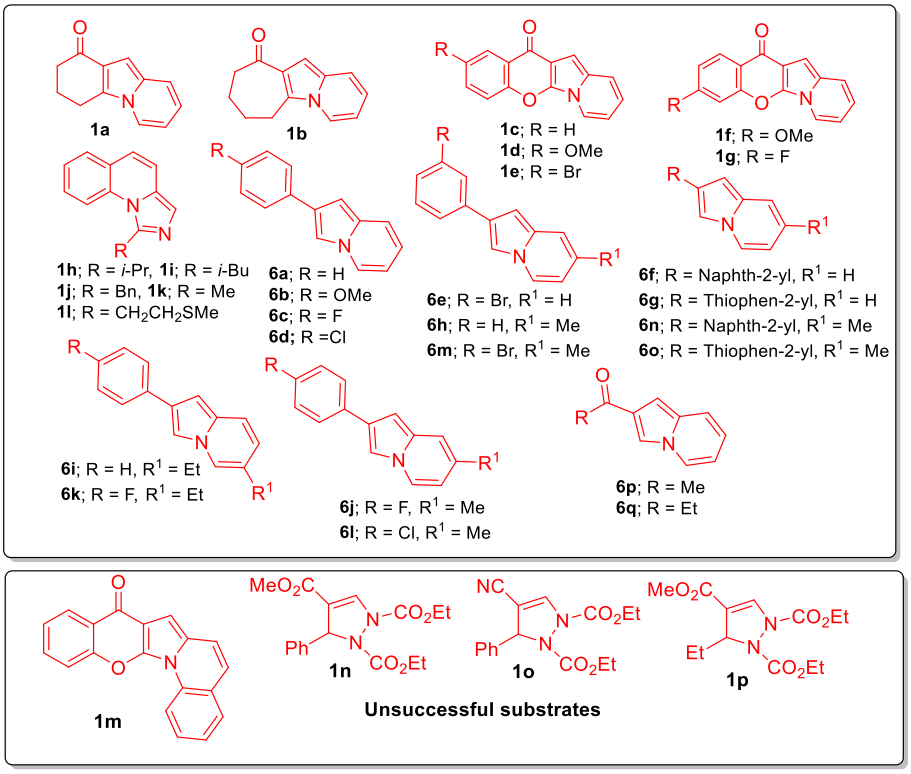


Figure S13. Cyclic voltammetry of reaction mixture with galvinoxyl free radical (**9**): Supporting electrolyte 0.1 M $LiClO_4$ in CH_3CN at 50 mVs^{-1}, Cyclic voltammograms: **b**-NH_4SCN (**2**) (5 mM); **f**-indolizine **6a** (5 mM); **9+RM** (**6b**+**2**+I_2)-galvinoxyl (5 mM) + **6a** (5 mM) + NH_4SCN (**2**) (5 mM) + I_2 (5 mM)

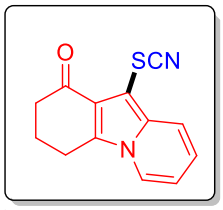
Starting Material Notation:



General procedure for Table 1

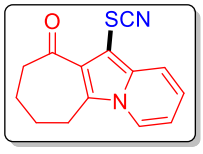
In an undivided Electrasyn 2.0 cell equipped with a graphite anode and a graphite cathode was charged with *N*-heterocycles **1** (0.25 mmol), and ammonium thiocyanate (**2,** 0.5 mmol), or potassium selenocyanate (**4,** 0.5 mmol), in acetonitrile (4 mL) solvent. The reaction mixture was stirred at 400 rpm and electrolyzed at a constant current of 10 mA at room temperature for 4-5 h *via* the manual programming of IKA ElectraSyn 2.0 instrument. After the completion of the reaction, the acetonitrile solvent was evaporated and the crude was diluted with water (20 mL) followed by extracted with ethyl acetate (3 x 20 mL). The combined organic layers were concentrated under reduced pressure to get crude product which were further purified through column chromatography using ethyl acetate/hexanes as an eluent to afford the corresponding products **3** and **5**.

10-Thiocyanato-3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one *(3a)*:



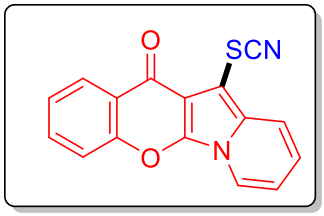
The title compound was prepared following the general procedure for Table 1, using 3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one (**1a**, 0.25 mmol, 0.046 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (25-30% EtOAc/Hexanes) obtained **3a** as a yellow solid; Yield: 0.052 g, 85%; M.P.: 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dt, J = 7.2 and 1.2 Hz, 1H), 7.68 (dt, J = 9.2 and 1.2 Hz, 1H), 7.05 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.81 (td, J = 6.8 and 1.2 Hz, 1H), 3.00 (t, J = 6.4 Hz, 2H), 2.67-2.64 (m, 2H), 2.31 (quint, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 136.3, 134.3, 123.4, 122.5, 122.1, 118.2, 113.8, 111.7, 83.5, 38.9, 23.0, 21.1; HRMS (ESI) exact mass calcd for $C_{13}H_{10}N_2OS$ + H $(M + H)^+$, 243.0587; Found: 243.0585.

11-Thiocyanato-6,7,8,9-tetrahydro-10*H*-cyclohepta[*b*]indolizin-10-one *(3b)*:



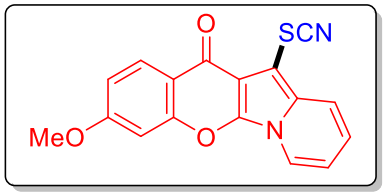
The title compound was prepared following the general procedure for Table 1, using 6,7,8,9-tetrahydro-10*H*-cyclohepta[*b*]indolizin-10-one (**1b**, 0.25 mmol, 0.050 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (25-30% EtOAc/Hexanes) obtained **3b** as a greenish yellow solid; Yield: 0.054 g, 84%; M.P.: 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 9.2 Hz, 1H), 6.98-6.93 (m, 1H), 6.73 (td, J = 6.8 and 1.2 Hz, 1H), 3.00 (t, J = 6.4 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.06-2.00 (m, 2H), 1.95-1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 134.9, 129.6, 126.7, 123.1, 121.5, 118.2, 113.7, 112.2, 86.6, 44.4, 26.0, 25.1, 22.4; HRMS (ESI) exact mass calcd for $C_{14}H_{12}N_2OS$ + H $(M + H)^+$, 257.0743; Found: 257.0743.

11-Thiocyanato-12H-chromeno[3,2-b]indolizin-12-one *(3c)*:



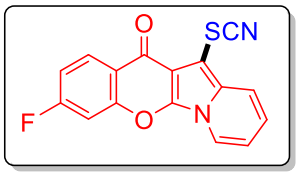
The title compound was prepared following the general procedure for Table 1, using 12*H*-chromeno[3,2-*b*]indolizin-12-one (**1c**, 0.25 mmol, 0.059 g), and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (35-40% EtOAc/Hexanes) obtained **3c** as a yellow solid; Yield: 0.064 g, 87%; M.P.: 182 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.93-7.88 (m, 1H), 7.83-7.80 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.29 (dd, J = 9.6 and 6.8 Hz, 1H), 7.05 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.5, 152.8, 141.7, 134.7, 132.3, 126.4, 125.2, 124.6, 122.8, 122.5, 118.1, 116.9, 113.5, 112.0, 79.5; HRMS (ESI) exact mass calcd for $C_{16}H_8N_2O_2S$ + Na $(M + Na)^+$, 315.0198; Found; 315.0196.

3-Methoxy-11-thiocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(3d)*:



The title compound was prepared following the general procedure for Table 1, using 3-methoxy-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1f**, 0.25 mmol, 0.066 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (40-45% EtOAc/Hexanes) obtained **3d** as a yellow solid; Yield: 0.073 g, 90%; M.P.: 186 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (d, J = 7.2 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 7.30-7.25 (m, 2H), 7.16 (dd, J = 8.8 and 2.0 Hz, 1H), 7.05 (t, J = 6.8 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.8, 166.0, 155.3, 140.5, 133.5, 127.2, 124.3, 122.2, 116.9, 115.5, 113.9, 113.6, 107.4, 101.0, 77.9, 56.2; HRMS (ESI) exact mass calcd for $C_{17}H_{10}N_2O_3S$ + H $(M + H)^+$, 323.0485; Found: 323.0488.

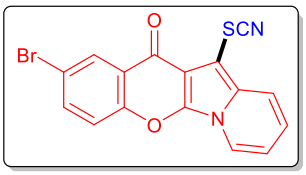
3-Fluoro-11-thiocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(3e)*:



The title compound was prepared following the general procedure for Table 1, using 3-fluoro-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1g**, 0.25 mmol, 0.063 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (35-40% EtOAc/Hexanes) obtained **3e** as a yellow solid; Yield: 0.066 g, 84%; M.P.: 194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 8.8 and 6.4 Hz, 1H), 8.12 (dt, J = 7.2 and 1.2 Hz, 1H), 7.69 (dt, J = 9.6 and 1.2 Hz, 1H), 7.25 (dd, J = 8.8 and 2.4 Hz, 1H), 7.18-7.14 (m, 1H), 7.07 (ddd, J = 9.6, 6.8 and 1.2 Hz, 1H), 6.83 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 165.6 ($J_{C\text{-}F}$ = 254.0 Hz), 154.8 ($J_{C\text{-}F}$ = 13.0 Hz), 141.8, 132.2, 129.5 ($J_{C\text{-}F}$ = 10.0 Hz), 123.6, 121.2, 120.5, 117.9, 113.9, 113.7, 111.2, 108.5, 104.6 ($J_{C\text{-}F}$ = 26.0 Hz), 80.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.5; HRMS (ESI) exact mass calcd for $C_{16}H_7FN_2O_2S$+ H $(M + H)^+$, 311.0285;

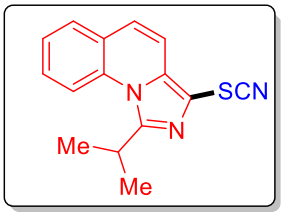
Found: 311.0285.

2-Bromo-11-thiocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(3f)*:



The title compound was prepared following the general procedure for Table 1, using 2-bromo-11-thiocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1e**, 0.25 mmol, 0.079 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (40-45% EtOAc/Hexanes) obtained **3f** as a yellow solid; Yield: 0.072 g, 77%; M.P.: 268 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 2.4 Hz, 1H), 8.18 (d, J = 6.4 Hz, 1H), 7.81 (dd, J = 8.8 and 2.4 Hz, 1H), 7.74 (d, J = 9.2 Hz, 1H), 7.51 (d, J = 8.8 Hz, 1H), 7.14 (dd, J = 6.4, 9.2 Hz, 1H), 6.90 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 152.6, 141.7, 136.6, 132.1, 130.3, 126.2, 123.8, 121.7, 119.9, 118.5, 117.9, 114.5, 111.8, 109.0, 80.6; HRMS (ESI) exact mass calcd for $C_{16}H_7BrN_2O_2S$ + H $(M + H)^+$, 370.9485; Found: 370.9486.

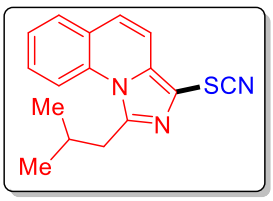
1-Isopropyl-3-thiocyanatoimidazo[1,5-*a*]quinoline *(3g)*:



The title compound was prepared following the general procedure for Table 1, using 1-isopropylimidazo[1,5-*a*]quinoline (**1h**, 0.25 mmol, 0.067 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **3g** as a white solid; Yield: 0.054 g, 80%; M.P.: 148 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 7.77 (dd, J = 8.0 and 1.6 Hz, 1H), 7.64 (ddd, J = 8.8, 7.2 and 1.6 Hz, 1H), 7.53-7.49 (m, 2H)*, 7.29 (d, J = 9.6 Hz, 1H), 3.85 (sept, J = 6.8 Hz, 1H), 1.59 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 134.5, 132.9, 129.5, 129.1, 125.9, 125.5, 125.1, 117.1, 115.3, 110.7, 109.2, 30.3, 21.5; HRMS (ESI) exact mass calcd for $C_{15}H_{13}N_3S$ + H $(M + H)^+$, 268.0903; Found: 268.0908.

* This multiplet contains δ 7.52 (d, J = 9.6 Hz, 1H) and δ 7.51 (td, J = 7.2 and 1.2 Hz, 1H).

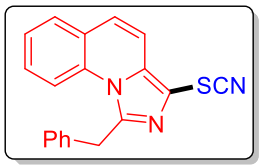
1-Isobutyl-3-thiocyanatoimidazo[1,5-*a*]quinoline *(3h)*:



The title compound was prepared following the general procedure for Table 1, using 1-isobutylimidazo[1,5-*a*]quinoline (**1i**, 0.25 mmol, 0.056 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **3h** as a white solid; Yield: 0.060 g, 85%; M.P.: 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 1H), 7.76 (dd, J = 8.0 and 1.6 Hz, 1H), 7.63 (ddd, J = 8.4, 7.2 and 1.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.28 (d, J = 9.6 Hz, 1H), 3.27 (d, J = 6.8 Hz, 2H), 2.47-2.37 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 134.6, 132.9, 129.5, 129.0, 126.0, 125.5, 125.1, 116.7, 115.2, 110.5, 109.3, 41.1, 26.5, 22.6; HRMS (ESI) exact

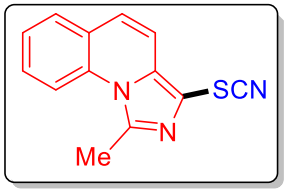
mass calcd for $C_{16}H_{15}N_3S$ + H $(M + H)^+$, 282.1060; Found: 282.1062.

1-Benzyl-3-thiocyanatoimidazo[1,5-*a*]quinoline *(3i)*:



The title compound was prepared following the general procedure for Table 1, using 1-benzylimidazo[1,5-*a*]quinoline (**1j**, 0.25 mmol, 0.065 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **3i** as a pale yellow solid; Yield: 0.064 g, 81%; M.P.: 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.95 (m, 1H), 7.67-7.62 (m, 1H), 7.49 (d, J = 9.6 Hz, 1H), 7.39-7.34 (m, 2H), 7.26-7.21 (m, 3H), 7.19-7.14 (m, 1H), 7.09 (dt, J = 8.0 and 1.2 Hz, 2H), 4.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 135.7, 134.9, 132.3, 129.2, 129.19, 129.15, 128.1, 127.2, 126.1, 125.5, 125.2, 117.1, 115.1, 110.4, 110.0, 37.8; HRMS (ESI) exact mass calcd for $C_{19}H_{13}N_3S$ + H $(M + H)^+$, 316.0903; Found: 316.0901.

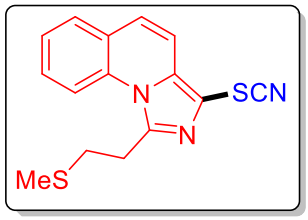
1-Methyl-3-thiocyanatoimidazo[1,5-*a*]quinoline *(3j)*:



The title compound was prepared following the general procedure for Table 1, using 1-methylimidazo[1,5-*a*]quinoline (**1k**, 0.25 mmol, 0.046 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (22-25% EtOAc/Hexanes) obtained **3j** as a white solid; Yield: 0.048 g, 79%; M.P.: 148 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.26 (d, J = 8.4 Hz, 1H), 7.76 (dd, J = 8.0 and 1.6 Hz, 1H), 7.63 (ddd, J = 8.4, 7.2 and 1.6 Hz, 1H), 7.53-7.48 (m, 2H)*, 7.28 (d, J = 9.6 Hz, 1H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 134.5, 133.0, 129.4, 129.1, 126.1, 125.2, 125.1, 116.3, 115.0, 110.5, 109.0, 19.7; HRMS (ESI) exact mass calcd for $C_{13}H_9N_3S$ + H $(M + H)^+$, 240.0590; Found: 240.0594.

* This multiplet contains δ7.51 (td, J = 7.6 and 1.2 Hz, 1H), δ 7.49 (d, J = 9.6 Hz, 1H).

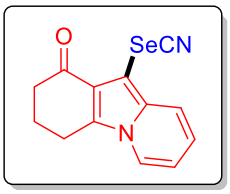
1-(2-(Methylthio)ethyl)-3-thiocyanatoimidazo[1,5-*a*]quinoline *(3k)*:



The title compound was prepared following the general procedure for Table 1, using 1-(2-(methylthio)ethyl)imidazo[1,5-*a*]quinoline (**1l**, 0.25 mmol, 0.061 g) and ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **3k** as a white solid; Yield: 0.059 g, 78%; M.P.: 138 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.19 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 7.6 and 1.6 Hz, 1H), 7.66 (ddd, J = 8.8, 7.2 and 1.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.31 (d, J = 9.6 Hz, 1H), 3.70-3.66 (m, 2H), 3.22-3.18 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 134.7, 132.7, 129.5, 129.3, 126.2, 125.4, 125.0, 116.5, 115.1, 110.4, 109.4, 33.0, 31.2, 16.0; HRMS (ESI) exact mass

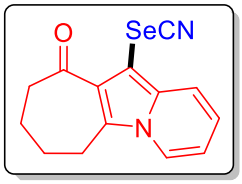
calcd for $C_{15}H_{13}N_3S_2$ + H $(M + H)^+$, 300.0624; Found: 300.0626.

10-Selenocyanato-3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one *(5a)*:



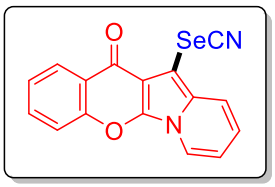
The title compound was prepared following the general procedure for Table 1, using 3,4-dihydropyrido[1,2-*a*]indol-1(2*H*)-one (**1a**, 0.25 mmol, 0.046 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (25-30% EtOAc/Hexanes) obtained **5a** as an orange solid; Yield: 0.061 g, 84%; M.P.: 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dt, J = 7.2 and 1.2 Hz, 1H), 7.71 (dt, J = 9.2 and 1.2 Hz, 1H), 7.00 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.78 (td, J = 6.8 and 1.2 Hz, 1H), 3.00 (t, J = 6.4 Hz, 2H), 2.67-2.63 (m, 2H), 2.32 (quint, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 135.6, 134.0, 123.3, 122.5, 121.8, 119.2, 113.7, 101.9, 80.9, 38.6, 23.1, 21.1; HRMS (ESI) exact mass calcd for $C_{13}H_{10}N_2OSe$ + H $(M + H)^+$, 291.0031; Found: 291.0036.

11-Selenocyanato-6,7,8,9-tetrahydro-10*H*-cyclohepta[*b*]indolizin-10-one *(5b)*:



The title compound was prepared following the general procedure for Table 1, using 6,7,8,9-tetrahydro-10*H*-cyclohepta[*b*]indolizin-10-one (**1b**, 0.25 mmol, 0.050 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (25-30% EtOAc/Hexanes) obtained **5b** as a greenish yellow solid; Yield: 0.063 g, 82%; M.P.: 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 1H), 6.82 (dd, J = 9.2 and 6.4 Hz, 1H), 6.66 (t, J = 7.2 Hz, 1H), 3.00 (t, J = 6.4 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.11-2.05 (m, 2H), 1.97-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 131.5, 128.4, 125.8, 123.0, 119.7, 119.2, 113.7, 104.5, 88.5, 44.0, 27.1, 25.4, 22.6; HRMS (ESI) exact mass calcd for $C_{14}H_{12}N_2OSe$ + H $(M + H)^+$, 305.0188; Found: 305.0189.

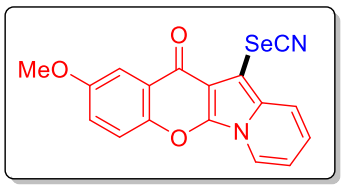
11-Selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(5c)*:



The title compound was prepared following the general procedure for Table 1, using 12*H*-chromeno[3,2-*b*]indolizin-12-one (**1c**, 0.25 mmol, 0.059 g), and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (35-40% EtOAc/Hexanes) obtained **5c** as a yellow solid; Yield: 0.072 g, 84%; M.P.: 205 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.46 (d, J = 7.2 Hz, 1H), 8.26 (dd, J = 8.0 and 1.6 Hz, 1H), 7.88 (ddd, J = 8.4, 6.8 and 1.6 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H), 7.58-7.54 (m, 1H), 7.20 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.99 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.1, 153.4, 141.7, 134.1, 131.6, 125.9, 125.1, 123.6, 122.8, 122.1, 118.3, 118.0, 113.2, 108.0, 104.5, 78.3; HRMS (ESI) exact mass calcd for $C_{16}H_8N_2O_2Se$ + H $(M + H)^+$, 340.9824;

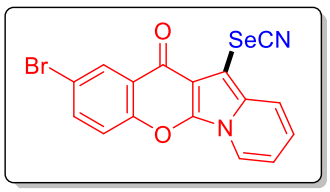
Found: 340.9825.

2-Methoxy-11-selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(5d)*:



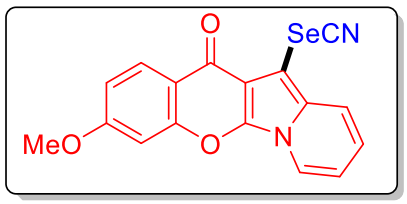
The title compound was prepared following the general procedure for Table 1, using 2-methoxy-11-selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1d**, 0.25 mmol, 0.066 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (40-45% EtOAc/Hexanes) obtained **5d** as a yellow solid; Yield: 0.081 g, 87%; M.P.: 160 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 3.2 Hz, 1H), 7.49 (dd, J = 9.2 and 3.2 Hz, 1H), 7.21 (dd, J = 9.6 and 6.4 Hz, 1H), 6.99 (t, J = 6.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.2, 158.3, 144.0, 123.7, 122.6, 122.1, 119.5, 119.1, 117.6, 113.1, 109.0, 93.1, 65.5; HRMS (ESI) exact mass calcd for $C_{17}H_{10}N_2O_3Se$ + Na $(M + Na)^+$, 392.9749; Found; 392.9750.

2-Bromo-11-selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(5e)*:



The title compound was prepared following the general procedure for Table 1, using 2-bromo-11-thiocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1e**, 0.25 mmol, 0.079 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (40-45% EtOAc/Hexanes) obtained **5e** as a yellow solid; Yield: 0.083 g, 79%; M.P.: 208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 6.8 Hz, 1H), 7.82 (dd, J = 8.8 and 2.4 Hz, 1H), 7.73 (d, J = 9.2 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.13-7.09 (m, 1H), 6.90-6.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 151.7, 141.0, 135.7, 131.8, 128.1, 123.9, 123.0, 120.6, 119.0, 117.8, 117.3, 112.8, 107.7, 101.0; HRMS (ESI) exact mass calcd for $C_{16}H_7BrN_2O_2Se$ + H $(M + H)^+$, 418.8929; Found: 418.8929.

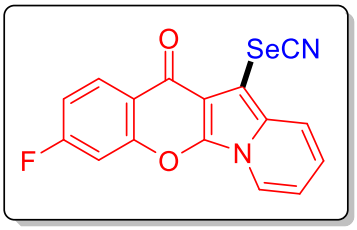
3-Methoxy-11-selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(5f)*:



The title compound was prepared following the general procedure for Table 1, using 3-methoxy-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1f**, 0.25 mmol, 0.066 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (40-45% EtOAc/Hexanes) obtained **5f** as an orange solid; Yield: 0.074 g, 80%; M.P.: 191 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.51 (dt, J = 7.2 and 1.2 Hz, 1H), 8.26 (d, J = 8.8 Hz, 1H), 7.79 (dt, J = 9.2 and 1.2 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.31-7.26 (m, 1H), 7.24 (dd, J = 8.8 and 2.4 Hz, 1H), 7.10 (td, J = 6.8 and 1.2 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.7, 163.7, 155.2, 141.6, 131.3, 127.3, 123.3, 121.8, 118.3,

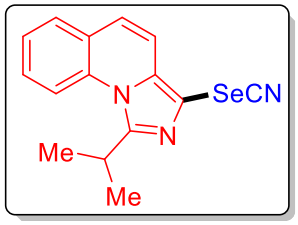
116.6, 113.8, 113.3, 107.6, 104.1, 101.0, 78.42, 56.21; HRMS (ESI) exact mass calcd for $C_{17}H_{10}N_2O_3Se$ + H $(M + H)^+$, 370.9930; Found: 370.9932.

3-Fluoro-11-selenocyanato-12*H*-chromeno[3,2-*b*]indolizin-12-one *(5g)*:



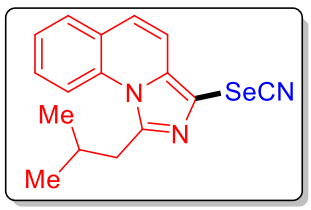
The title compound was prepared following the general procedure for Table 1, using 3-fluoro-12*H*-chromeno[3,2-*b*]indolizin-12-one (**1g**, 0.25 mmol, 0.063 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (35-40% EtOAc/Hexanes) obtained **5g** as an orange solid; Yield: 0.069 g, 77%; M.P.: 199 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.41 (dt, J = 7.2 and 1.2 Hz, 1H), 8.33 (dd, J = 8.8 and 6.4 Hz, 1H), 7.74 (dd, J = 9.2 and 2.4 Hz, 1H), 7.71 (dt, J = 9.6 and 1.2 Hz, 1H), 7.46 (td, J = 8.8 and 2.4 Hz, 1H), 7.21 (ddd, J = 9.6, 6.8 and 1.2 Hz, 1H), 7.01 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 165.5 ($J_{C\text{-}F}$ = 254.0 Hz), 154.8 ($J_{C\text{-}F}$ = 13.0 Hz), 141.8, 132.2, 129.4 ($J_{C\text{-}F}$ = 11.0 Hz), 123.2, 121.1, 120.4, 118.9, 113.8, 113.6, 113.5, 108.8, 104.6 ($J_{C\text{-}F}$ = 26.0 Hz), 101.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.4; HRMS (ESI) exact mass calcd for $C_{16}H_7FN_2O_2Se$ + H $(M + H)^+$, 358.9730; Found: 358.9725.

1-Isopropyl-3-selenocyanatoimidazo[1,5-*a*]quinoline *(5h)*:



The title compound was prepared following the general procedure for Table 1, using 1-isopropylimidazo[1,5-*a*]quinoline (**1h**, 0.25 mmol, 0.053 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **5h** as a white solid; Yield: 0.062 g, 78%; M.P.: 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.8 Hz, 1H), 7.65 (dd, J = 7.6 and 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.16 (d, J = 9.2 Hz, 1H), 3.76 (sept, J = 6.4 Hz, 1H), 1.50 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 135.2, 132.8, 129.4, 128.9, 125.8, 125.6, 124.8, 117.1, 116.1, 107.7, 101.1, 30.2, 21.5; HRMS (ESI) exact mass calcd for $C_{15}H_{13}N_3Se$ + H $(M + H)^+$, 316.0348; Found: 316.0347.

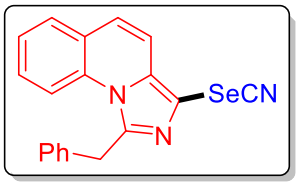
1-Isobutyl-3-selenocyanatoimidazo[1,5-*a*]quinoline *(5i)*:



The title compound was prepared following the general procedure for Table 1, using 1-isobutylimidazo[1,5-*a*]quinoline (**1i**, 0.25 mmol, 0.056 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **5i** as a white solid; Yield: 0.066 g, 80%; M.P.: 320 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 1H), 7.76 (dd, J = 7.6 and 1.6 Hz, 1H), 7.64 (ddd, J = 8.4, 7.2 and 1.6 Hz, 1H), 7.53-7.48 (m, 2H), 7.27 (d, J = 9.2 Hz, 1H), 3.29 (d, J = 7.2

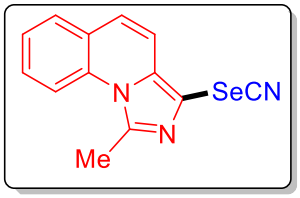
Hz, 2H), 2.47-2.36 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 135.3, 132.9, 129.4, 128.9, 125.9, 125.5, 124.8, 116.74, 116.70, 116.1, 101.0, 41.1, 26.5, 22.6; HRMS (ESI) exact mass calcd for $C_{16}H_{15}N_3Se$ + H $(M + H)^+$, 330.0504; Found: 330.0505.

1-Benzyl-3-selenocyanatoimidazo[1,5-*a*]quinoline *(5j)*:



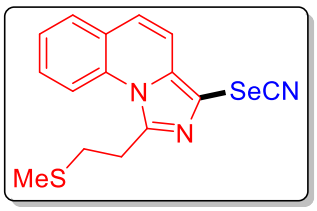
The title compound was prepared following the general procedure for Table 1, using 1-benzylimidazo[1,5-*a*]quinoline (**1j**, 0.25 mmol, 0.065 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **5j** as a pale yellow solid; Yield: 0.072 g, 79%; M.P.: 146 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.05-8.02 (m, 1H), 7.72-7.69 (m, 1H), 7.53 (d, J = 9.2 Hz, 1H), 7.44-7.39 (m, 2H), 7.32-7.28 (m, 3H), 7.25-7.21 (m, 1H), 7.17-7.14 (m, 2H), 4.85 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 135.8, 135.7, 132.2, 129.2, 129.1, 129.0, 128.0, 127.1, 126.0, 125.3, 125.2, 117.0, 115.9, 108.1, 100.9, 37.7; HRMS (ESI) exact mass calcd for $C_{19}H_{13}N_3Se$ + H $(M + H)^+$, 364.0348; Found: 364.0347.

1-Methyl-3-selenocyanatoimidazo[1,5-*a*]quinoline *(5k)*:



The title compound was prepared following the general procedure for Table 1, using 1-methylimidazo[1,5-*a*]quinoline (**1k**, 0.25 mmol, 0.046 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (22-25% EtOAc/Hexanes) obtained **5k** as a pale yellow solid; Yield: 0.054 g, 75%; M.P.: 192 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.27 (d, J = 8.8 Hz, 1H), 7.76 (dd, J = 7.6 and 1.6 Hz, 1H), 7.63 (ddd, J = 8.8, 7.2 and 1.6 Hz, 1H), 7.51 (dd, J = 7.6 and 0.8 Hz, 1H), 7.47 (d, J = 9.2 Hz, 1H), 7.26 (d, J = 9.2 Hz, 1H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 135.3, 133.0, 129.3, 129.0, 126.0, 125.3, 124.9, 116.3, 115.9, 107.4, 100.8, 19.7; HRMS (ESI) exact mass calcd for $C_{13}H_9N_3Se$ + H $(M + H)^+$, 288.0035; Found: 288.0036.

1-(2-(Methylthio)ethyl)-3-selenocyanatoimidazo[1,5-*a*]quinoline *(5l)*:



The title compound was prepared following the general procedure for Table 1, using 1-(2-(methylthio)ethyl)imidazo[1,5-*a*]quinoline (**1l**, 0.25 mmol, 0.065 g) and potassium selenocyanate (**4**, 0.5 mmol, 0.072 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **5l** as a pale yellow solid; Yield: 0.066 g, 76%; M.P.: 146 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.20 (d, J = 8.8 Hz, 1H), 7.78 (dd, J = 8.0 and 1.6 Hz, 1H), 7.66 (ddd, J = 8.8, 7.2 and 1.6 Hz, 1H), 7.55-7.49 (m, 2H)*, 7.29 (d, J = 9.6 Hz, 1H), 3.72-3.68 (m, 2H), 3.22-3.18 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 135.5,

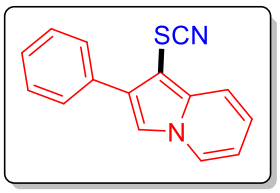
132.7, 129.6, 129.2, 126.1, 125.6, 125.2, 116.5, 115.9, 107.8, 100.9, 33.0, 31.2, 16.0; HRMS (ESI) exact mass calcd for $C_{15}H_{13}N_3SSe$ + H $(M + H)^+$, 348.0068; Found: 348.0065.

* This multiplet contains δ 7.53 (td, J = 7.2 and 1.2 Hz, 1H) and δ 7.50 (d, J = 6.8 Hz, 1H).

General procedure for Table 2

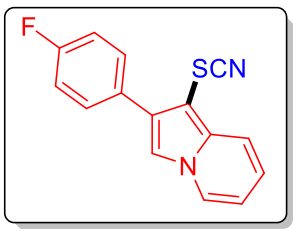
In an undivided Electrasyn 2.0 cell equipped with a graphite anode and a graphite cathode was charged with *N*-heterocycles **6** (0.25 mmol), ammonium thiocyanate (**2,** 0.5 mmol), and iodine (100 mol%) in EtOAc: acetonitrile (1:1) (4 mL) solvent. The reaction mixture was stirred at 400 rpm and electrolyzed at a constant current of 10 mA at room temperature for an hour *via* the manual programming of IKA ElectraSyn 2.0 instrument. After the completion of the reaction, the solvent was evaporated and the crude was diluted with water (20 mL) and ethyl acetate (20 mL), and sat. $Na_2S_2O_3$ solution, followed by extraction with ethyl acetate (3 x 10 mL). The combined organic layers were concentrated under reduced pressure to get crude product which were further purified through column chromatography using basic silica gel as stationary phase and chloroform/hexanes as an eluent to afford the corresponding products **7**.

2-Phenyl-1-thiocyanatoindolizine *(7a)*:



The title compound was prepared following the general procedure for Table 2, using 2-phenylindolizine (**6a**, 0.25 mmol, 0.048 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7a** as a yellow liquid; Yield: 0.057 g, 91%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.46 (dt, J = 7.2 and 1.2 Hz, 1H), 7.99 (d, J = 0.4 Hz, 1H), 7.73-7.69 (m, 3H), 7.55-7.50 (m, 2H), 7.44-7.39 (m, 1H), 7.18 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.89 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.6, 132.7, 131.4, 128.7, 128.6, 127.6, 127.2, 122.4, 116.2, 113.7, 112.7, 82.5; HRMS (ESI) exact mass calcd for $C_{15}H_{10}N_2S$ + H $(M + H)^+$, 251.0638; Found: 251.0642.

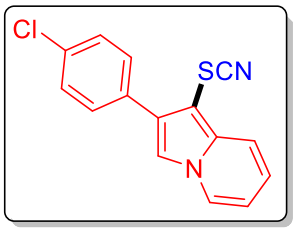
2-(4-Fluorophenyl)-1-thiocyanatoindolizine *(7b)*:



The title compound was prepared following the general procedure for Table 2, using 2-(4-fluorophenyl)indolizine (**6c**, 0.25 mmol, 0.053 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7b** as a yellow viscous liquid; Yield: 0.063 g, 94%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47

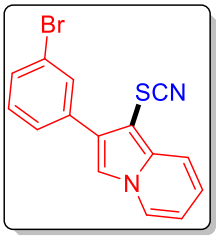
(dt, J = 6.8 and 1.2 Hz, 1H), 8.00 (d, J = 0.4 Hz, 1H), 7.76-7.71 (m, 3H), 7.42-7.36 (m, 2H), 7.20 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.91 (td, J = 6.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8 ($J_{C\text{-}F}$ = 244.0 Hz), 136.6, 130.6 ($J_{C\text{-}F}$ = 8.0 Hz), 130.4, 129.1 ($J_{C\text{-}F}$ = 3.0 Hz), 127.2, 122.5, 116.2, 115.7 ($J_{C\text{-}F}$ = 21.0 Hz), 113.7, 112.7, 112.6, 82.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.1; HRMS (ESI) exact mass calcd for $C_{15}H_9FN_2S$ + H $(M + H)^+$, 269.0543; Found: 269.0545.

2-(4-Chlorophenyl)-1-thiocyanatoindolizine *(7c)*:



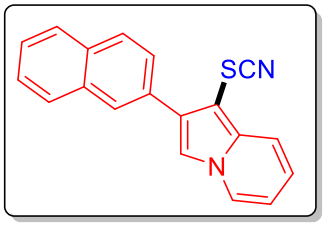
The title compound was prepared following the general procedure for Table 2, using 2-(4-chlorophenyl)indolizine (**6d**, 0.25 mmol, 0.057 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7c** as a yellow solid; Yield: 0.066 g, 92%; M.P.: 115 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.48 (dt, J = 6.8 and 1.2 Hz, 1H), 8.04 (d, J = 0.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 3H), 7.62-7.59 (m, 2H), 7.20 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.91 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.7, 132.5, 131.6, 130.3, 130.0, 128.8, 127.2, 122.6, 116.2, 113.9, 112.8, 112.6, 82.6; HRMS (ESI) exact mass calcd for $C_{15}H_9ClN_2S$ + H $(M + H)^+$, 285.0248; Found: 285.0241.

2-(3-Bromophenyl)-1-thiocyanatoindolizine *(7d)*:



The title compound was prepared following the general procedure for Table 2, using 2-(3-bromophenyl)indolizine (**6e**, 0.25 mmol, 0.068 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7d** as a yellow viscous liquid; Yield: 0.072 g, 87%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (dt, J = 7.2 and 1.2 Hz, 1H), 8.08 (d, J = 0.8 Hz, 1H), 7.91 (t, J = 1.6 Hz, 1H), 7.75-7.71 (m, 2H), 7.63 (ddd, J = 8.0, 2.0 and 1.2 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.21 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.92 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.7, 135.2, 131.0, 130.9, 130.4, 129.6, 127.6, 127.3, 122.8, 122.0, 116.3, 114.2, 112.9, 112.6, 82.8; HRMS (ESI) exact mass calcd for $C_{15}H_9BrN_2S$ + H $(M + H)^+$, 328.9743; Found: 328.9742.

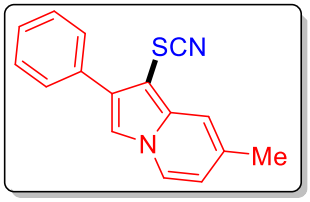
2-(Naphthalen-2-yl)-1-thiocyanatoindolizine *(7e)*:



The title compound was prepared following the general procedure for Table 2, using 2-(naphthalen-2-yl)indolizine (**6f**, 0.25 mmol, 0.061 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7e** as a red

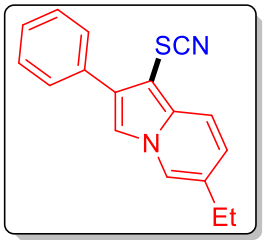
viscous liquid; Yield: 0.066 g, 88%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.51 (dt, J = 6.8 and 1.2 Hz, 1H), 8.27 (d, J = 1.6 Hz, 1H), 8.14 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.01-7.98 (m, 2H), 7.86 (dd, J = 8.4 and 1.6 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.62-7.55 (m, 2H), 7.22 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.93 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.8, 133.0, 132.2, 131.3, 130.3, 128.2, 128.0, 127.6, 127.3, 127.2, 126.8, 126.6, 126.3, 122.6, 116.2, 114.1, 112.8, 112.7, 82.8; HRMS (ESI) exact mass calcd for $C_{19}H_{12}N_2S$ + H $(M + H)^+$, 301.0794; Found: 301.0798.

7-Methyl-2-phenyl-1-thiocyanatoindolizine *(7f)*:



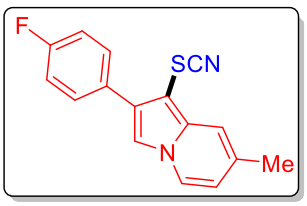
The title compound was prepared following the general procedure for Table 2, using 7-methyl-2-phenylindolizine (**6h**, 0.25 mmol, 0.052 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7f** as a yellow viscous liquid; Yield: 0.062 g, 93%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.38 (d, J = 6.8 Hz, 1H), 7.90 (d, J = 0.8 Hz, 1H), 7.70-7.67 (m, 2H), 7.54-7.50 (m, 3H), 7.44-7.39 (m, 1H), 6.76 (dd, J = 6.8 and 1.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.2, 133.0, 132.9, 131.2, 128.7, 128.5, 127.5, 126.7, 115.2, 114.2, 113.0, 112.8, 80.6, 20.8; HRMS (ESI) exact mass calcd for $C_{16}H_{12}N_2S$ + H $(M + H)^+$, 265.0794; Found: 265.0798.

6-Ethyl-2-phenyl-1-thiocyanatoindolizine *(7g)*:



The title compound was prepared following the general procedure for Table 2, using 6-ethyl-2-phenylindolizine (**6i**, 0.25 mmol, 0.055 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7g** as a yellow viscous liquid; Yield: 0.064 g, 91%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.30 (t, J = 1.2 Hz, 1H), 7.92 (d, J = 0.8 Hz, 1H), 7.70-7.66 (m, 3H), 7.55-7.50 (m, 2H), 7.44-7.40 (m, 1H), 7.13 (dd, J = 9.2 and 1.6 Hz, 1H), 2.61 (qd, J = 7.6 and 1.2 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.7, 132.9, 131.2, 128.7, 128.6, 128.1, 127.5, 124.5, 123.9, 115.9, 113.4, 112.7, 81.9, 24.9, 14.8; HRMS (ESI) exact mass calcd for $C_{17}H_{14}N_2S$ + H $(M + H)^+$, 279.0951; Found: 279.0953.

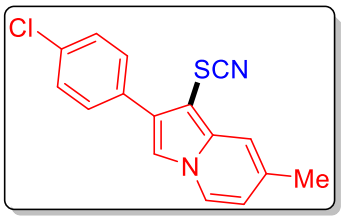
2-(4-Fluorophenyl)-7-methyl-1-thiocyanatoindolizine *(7h)*:



The title compound was prepared following the general procedure for Table 2, using 2-(4-fluorophenyl)-7-methylindolizine (**6j**, 0.25 mmol, 0.056 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7h** as a

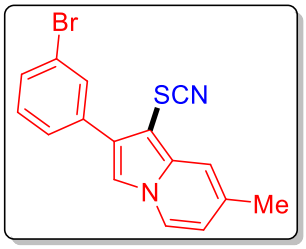
yellow semi solid; Yield: 0.062 g, 88%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, J = 7.2 Hz, 1H), 7.89 (d, J = 0.8 Hz, 1H), 7.74-7.69 (m, 2H), 7.50 (br, 1H), 7.40-7.34 (m, 2H), 6.76 (dd, J = 7.2 and 1.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7 ($J_{C\text{-}F}$ = 244.0 Hz), 137.1, 133.1, 130.5 ($J_{C\text{-}F}$ = 8.0 Hz), 130.2, 129.3 ($J_{C\text{-}F}$ = 3.0 Hz), 126.7, 115.7 ($J_{C\text{-}F}$ = 22.0 Hz), 115.32, 114.2, 113.0, 112.8, 80.7, 20.7; ^{19}F NMR (376 MHz, DMSO-d_6): δ -114.6; HRMS (ESI) exact mass calcd for $C_{16}H_{11}FN_2S$ + H $(M + H)^+$, 283.0700; Found: 283.0700.

2-(4-Chlorophenyl)-7-methyl-1-thiocyanatoindolizine *(7i)*:



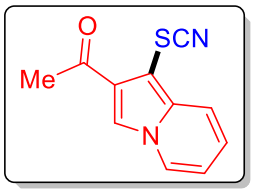
The title compound was prepared following the general procedure for Table 2, using 2-(4-chlorophenyl)-7-methylindolizine (**6l**, 0.25 mmol, 0.060 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g) and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7i** as a brown solid; Yield: 0.065 g, 87%; M.P.: 102 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, J = 7.2 Hz, 1H), 7.93 (br, 1H), 7.73-7.70 (m, 2H), 7.61-7.58 (m, 2H), 7.50 (br, 1H), 6.77 (dd, J = 6.8 and 1.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.2, 133.3, 132.4, 131.8, 130.2, 129.8, 128.8, 126.7, 115.4, 114.2, 113.2, 112.7, 80.7, 20.8; HRMS (ESI) exact mass calcd for $C_{16}H_{11}ClN_2S$ + H $(M + H)^+$, 299.0404; Found: 299.0408.

2-(3-Bromophenyl)-7-methyl-1-thiocyanatoindolizine *(7j)*:



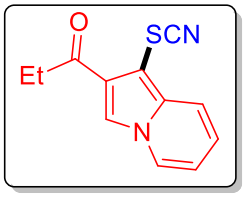
The title compound was prepared following the general procedure for Table 2, using 2-(3-bromophenyl)-7-methylindolizine (**6m**, 0.25 mmol, 0.072 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (15% chloroform/hexanes) obtained **7j** as a green viscous liquid; Yield: 0.079 g, 92%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.36 (d, J = 6.8 Hz, 1H), 7.98 (br, 1H), 7.89 (t, J = 1.6 Hz, 1H), 7.71 (dt, J = 8.0 and 1.6 Hz, 1H), 7.62 (ddd, J = 8.0, 2.0 and 1.2 Hz, 1H), 7.51-7.47 (m, 2H), 6.77 (dd, J = 6.8 and 2.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.3, 135.3, 133.3, 130.9, 130.8, 130.2, 129.4, 127.5, 126.8, 121.9, 115.5, 114.3, 113.5, 112.7, 80.8, 20.8; HRMS (ESI) exact mass calcd for $C_{16}H_{11}BrN_2S$ + H $(M + H)^+$, 342.9899; Found: 342.9899.

Methyl 1-thiocyanatoindolizine-2-carboxylate *(7k)*:



The title compound was prepared following the general procedure for Table 2, using methyl indolizine-2-carboxylate (**6p**, 0.25 mmol, 0.038 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (50% chloroform/hexanes) obtained **7k** as a red solid; Yield: 0.049 g, 90%; M.P.: 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, J = 6.8 and 0.8 Hz, 1H), 7.81 (d, J = 0.8 Hz, 1H), 7.67 (dq, J = 9.2 and 0.8 Hz, 1H), 7.01 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.73 (td, J = 6.8 and 1.2 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 136.8, 128.4, 126.6, 122.8, 118.4, 118.3, 114.2, 111.6, 86.2, 29.0; HRMS (ESI) exact mass calcd for $C_{11}H_8N_2O_2S$ + H $(M + H)^+$, 217.0430; Found: 217.0427.

1-(1-Thiocyanatoindolizin-2-yl)propan-1-one *(7l)*:

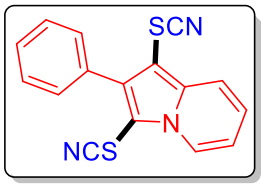


The title compound was prepared following the general procedure for Table 2, using 1-(indolizin-2-yl)propan-1-one (**6q**, 0.25 mmol, 0.043 g), ammonium thiocyanate (**2**, 0.5 mmol, 0.038 g), and iodine (0.25 mmol, 0.063 g) after column chromatography (50% chloroform/hexanes) obtained **7l** as a red solid; Yield: 0.045 g, 78%; M.P.: 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, J = 7.2 and 0.8 Hz, 1H), 7.80 (d, J = 0.8 Hz, 1H), 7.66 (dq, J = 9.2 and 0.8 Hz, 1H), 7.00 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 6.71 (td, J = 6.8 and 1.2 Hz, 1H), 2.96 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 136.7, 128.1, 126.6, 122.7, 118.2, 117.8, 114.1, 111.7, 86.0, 34.4, 8.0; HRMS (ESI) exact mass calcd for $C_{12}H_{10}N_2OS$ + Na $(M + Na)^+$, 253.0406; Found: 253.0408.

General procedure for Table 3

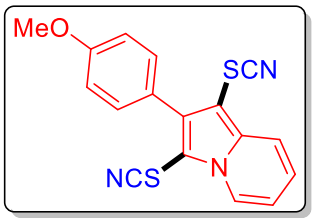
In an undivided Electrasyn 2.0 cell equipped with a graphite anode and a graphite cathode was charged with *N*-heterocycles **6** (0.25 mmol), ammonium thiocyanate (**2,** 0.75 mmol), and iodine (150 mol%) in EtOAc: acetonitrile (1:1) (4 mL) solvent. The reaction mixture was stirred at 400 rpm and electrolyzed at a constant current of 20 mA at room temperature for the 3-5 h *via* the manual programming of IKA ElectraSyn 2.0 instrument. After the completion of the reaction, the acetonitrile solvent was evaporated and the crude was further diluted with water (20 mL) followed by extracted with ethyl acetate (3 x 20 mL). The combined organic layers were concentrated under reduced pressure to get crude products which were further purified through column chromatography using basic silica gel as stationary phase and ethyl acetate/hexanes as an eluent to afford the corresponding products **8**.

2-Phenyl-1,3-dithiocyanatoindolizine *(8a)*:



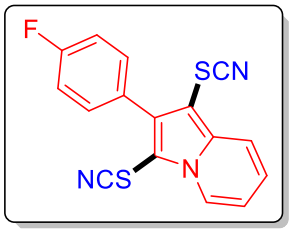
The title compound was prepared following the general procedure for Table 3, using 2-phenylindolizine (**6a**, 0.25 mmol, 0.048 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8a** as a white solid; Yield: 0.071 g, 92%; M.P.: 110 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.84 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.66-7.60 (m, 4H), 7.56 (dd, J = 9.2 and 6.8 Hz, 2H), 7.32 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.4, 138.7, 130.8, 130.3, 128.7, 128.6, 125.8, 125.7, 116.9, 115.0, 112.2, 110.4, 100.2, 88.3; HRMS (ESI) exact mass calcd for $C_{16}H_9N_3S_2$ + H $(M + H)^+$, 308.0311; Found: 308.0311.

2-(4-Methoxyphenyl)-1,3-dithiocyanatoindolizine *(8b)*:



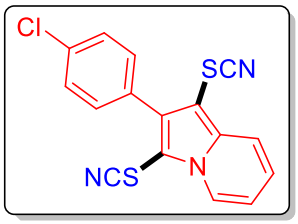
The title compound was prepared following the general procedure for Table 3, using 2-(4-methoxyphenyl)indolizine (**6b**, 0.25 mmol, 0.056 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (8-10% EtOAc/Hexanes) obtained **8b** as a white solid; Yield: 0.072 g, 85%; M.P.: 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dt, J = 6.8 and 1.2 Hz, 1H), 7.82 (dt, J = 9.2 and 1.2 Hz, 1H), 7.45-7.41 (m, 2H), 7.34 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 7.08-7.03 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 142.6, 140.2, 131.9, 125.4, 124.9, 122.7, 117.6, 114.8, 114.3, 111.5, 108.5, 97.4, 88.9, 55.4; HRMS (ESI) exact mass calcd for $C_{17}H_{11}N_3OS_2$ + H $(M + H)^+$, 338.0417; Found: 338.0420.

2-(4-Fluorophenyl)-1,3-dithiocyanatoindolizine *(8c)*:



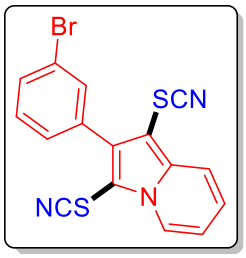
The title compound was prepared following the general procedure for Table 3, using 2-(4-fluorophenyl)indolizine (**6c**, 0.25 mmol, 0.053 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8c** as a pale yellow solid; Yield: 0.065 g, 80%; M.P.: 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dt, J = 6.8 and 1.2 Hz, 1H), 7.83 (dt, J = 8.8 and 1.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.36 (ddd, J = 8.8, 6.8 and 1.2 Hz, 1H), 7.25-7.19 (m, 2H), 7.09 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 ($J_{C\text{-}F}$ = 249.0 Hz), 141.8, 140.2, 132.5 ($J_{C\text{-}F}$ = 8.0 Hz), 126.5 ($J_{C\text{-}F}$ = 3.0 Hz), 125.6, 124.9, 117.7, 116.0 ($J_{C\text{-}F}$ = 22.0 Hz), 115.1, 111.2, 108.2, 97.8, 89.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.5; HRMS (ESI) exact mass calcd for $C_{16}H_8FN_3S_2$ + H $(M + H)^+$, 326.0217; Found: 326.0220.

2-(4-Chlorophenyl)-1,3-dithiocyanatoindolizine *(8d)*:



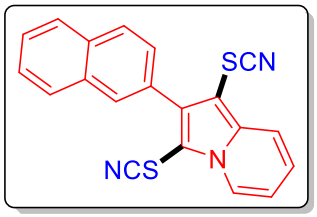
The title compound was prepared following the general procedure for Table 3, using 2-(4-chlorophenyl)indolizine (**6d**, 0.25 mmol, 0.057 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8d** as a yellow solid; Yield: 0.081 g, 94%; M.P.: 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dt, J = 6.8 and 1.2 Hz, 1H), 7.83 (dt, J = 9.2 and 1.2 Hz, 1H), 7.50 (dt, J = 8.8 and 2.4 Hz, 2H), 7.42 (dt, J = 8.8 and 2.4 Hz, 2H), 7.36 (ddd, J = 8.8, 6.8 and 1.2 Hz, 1H), 7.09 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.2, 135.5, 131.9, 129.1, 129.0, 125.7, 124.9, 117.7, 115.1, 111.1, 108.1, 97.8, 89.0; HRMS (ESI) exact mass calcd for $C_{16}H_8ClN_3S_2$ + H $(M + H)^+$, 341.9921; Found: 341.9915.

2-(3-Bromophenyl)-1,3-dithiocyanatoindolizine *(8e)*:



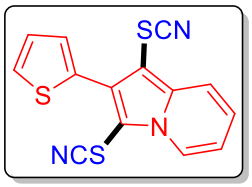
The title compound was prepared following the general procedure for Table 3, using 2-(3-bromophenyl)indolizine (**6e**, 0.25 mmol, 0.068 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8e** as an orange solid; Yield: 0.090 g, 93%; M.P.: 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dt, J = 6.8 and 1.2 Hz, 1H), 7.83 (dt, J = 8.8 and 1.2 Hz, 1H), 7.61-7.58 (m, 2H), 7.43-7.38 (m, 2H), 7.36 (ddd, J = 9.2, 6.8 and 1.2 Hz, 1H), 7.09 (td, J = 6.8 and 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 140.1, 133.3, 132.5, 132.2, 130.3, 129.3, 125.7, 124.9, 122.7, 117.7, 115.2, 110.9, 108.0, 98.0, 89.1; HRMS (ESI) exact mass calcd for $C_{16}H_8BrN_3S_2$ + H $(M + H)^+$, 385.9416; Found: 385.9413.

2-(Naphthalen-2-yl)-1,3-dithiocyanatoindolizine *(8f)*:



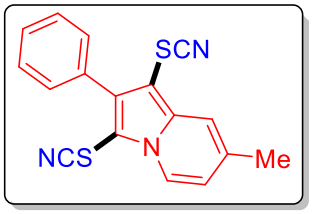
The title compound was prepared following the general procedure for Table 3, using 2-(naphthalen-2-yl)indolizine (**6f**, 0.25 mmol, 0.061 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (8-10% EtOAc/Hexanes) obtained **8f** as a pale yellow solid; Yield: 0.083 g, 92%; M.P.: 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 6.8 Hz, 1H), 7.95 (dd, J = 9.6 and 8.4 Hz, 2H), 7.91-7.87 (m, 2H), 7.84 (d, J = 9.2 Hz, 1H), 7.57 (dd, J = 8.4 and 1.6 Hz, 1H), 7.54-7.49 (m, 2H), 7.35 (dd, J = 9.2 and 6.8 Hz, 1H), 7.08 (td, J = 6.8 and 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 140.2, 133.2, 133.1, 130.5, 128.5, 128.0, 127.9, 127.6, 127.2, 126.8, 125.5, 124.9, 117.7, 115.0, 111.3, 108.4, 97.9, 89.2; HRMS (ESI) exact mass calcd for $C_{20}H_{11}N_3S_2$ + Na $(M + Na)^+$, 380.0286; Found: 380.0285

1,3-Dithiocyanato-2-(thiophen-2-yl)indolizine *(8g)*:



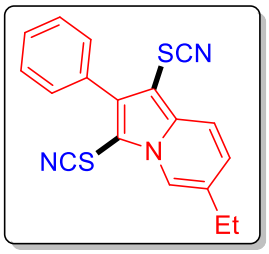
The title compound was prepared following the general procedure for Table 3, using 2-(thiophen-2-yl)indolizine (**6g**, 0.25 mmol, 0.050 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (10-12% EtOAc/Hexanes) obtained **8g** as a yellow solid; Yield: 0.069 g, 88%; M.P.: 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48-8.45 (m, 1H), 7.84-7.81 (m, 1H), 7.38-7.33 (m, 1H), 7.26 (dd, J = 4.0 and 0.8 Hz, 1H), 7.18 (td, J = 4.0 and 0.8 Hz, 2H), 7.11-7.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 134.5, 132.0, 130.8, 130.5, 125.9, 124.9, 117.8, 116.0, 115.4, 110.8, 107.7, 97.7, 88.8; HRMS (ESI) exact mass calcd for $C_{14}H_7N_3S_3$ + Na $(M + Na)^+$, 335.9693; Found: 335.9693.

7-Methyl-2-phenyl-1,3-dithiocyanatoindolizine *(8h)*:



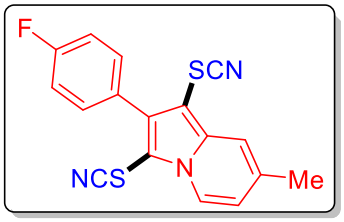
The title compound was prepared following the general procedure for Table 3, using 7-methyl-2-phenylindolizine (**6h**, 0.25 mmol, 0.052 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8h** as a brown solid; Yield: 0.074 g, 91%; M.P.: 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dd, J = 7.2 and 1.2 Hz, 1H), 7.58 (quint, J = 1.2 Hz, 1H), 7.53-7.43 (m, 5H), 6.90 (dd, J = 7.2 and 1.6 Hz, 1H), 2.46 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 140.6, 137.0, 130.7, 130.6, 129.0, 128.7, 124.3, 117.5, 116.1, 111.6, 108.6, 96.6, 87.2, 21.4; HRMS (ESI) exact mass calcd for $C_{17}H_{11}N_3S_2$ + H $(M + H)^+$, 322.0467; Found: 322.0467.

6-Ethyl-2-phenyl-1,3-dithiocyanatoindolizine *(8i)*:



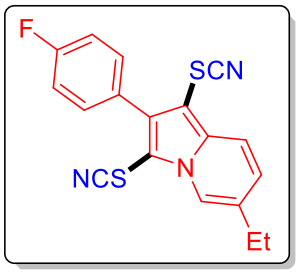
The title compound was prepared following the general procedure for Table 3, using 6-ethyl-2-phenylindolizine (**6i**, 0.25 mmol, 0.055 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g) after column chromatography (5-8% EtOAc/Hexanes) obtained **8i** as a white solid; Yield: 0.074 g, 88%; M.P.: 110 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ8.33-8.32 (m, 1H), 7.83 (dd, J = 9.2 and 0.8 Hz, 1H), 7.60 (dt, J = 7.2 and 1.6 Hz, 1H), 7.58-7.55 (m, 3H), 7.54-7.50 (m, 1H), 7.31 (dd, J = 9.2 and 1.6 Hz, 1H), 2.80 (qd, J = 7.6 and 0.8 Hz, 2H), 1.37 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 139.1, 131.3, 130.8, 130.6, 129.0, 128.7, 127.6, 122.0, 117.2, 111.5, 108.6, 97.1, 88.3, 26.2, 15.0; HRMS (ESI) exact mass calcd for $C_{18}H_{13}N_3S_2$ + H $(M + H)^+$, 336.0624; Found: 336.0623.

2-(4-Fluorophenyl)-7-methyl-1,3-dithiocyanatoindolizine *(8j)*:



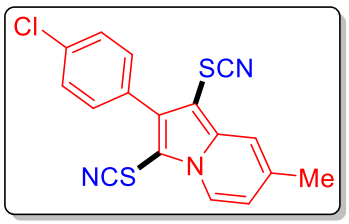
The title compound was prepared following the general procedure for Table 3, using 2-(4-fluorophenyl)-7-methylindolizine (**6j**, 0.25 mmol, 0.056 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (5-8% EtOAc/Hexanes) obtained **8j** as a pale yellow solid; Yield: 0.077 g, 90%; M.P.: 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 7.2 Hz, 1H), 7.58 (br, 1H), 7.48-7.43 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.91 (dd, J = 7.2 and 1.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 ($J_{C\text{-}F}$ = 248.0 Hz), 141.9, 140.6, 137.2, 132.4 ($J_{C\text{-}F}$ = 9.0 Hz), 126.7 ($J_{C\text{-}F}$ = 3.0 Hz), 124.3, 117.7, 116.1, 116.0 ($J_{C\text{-}F}$ = 22.0 Hz), 111.5, 108.5, 96.7, 87.3, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.4; HRMS (ESI) exact mass calcd for $C_{17}H_{10}FN_3S_2$ + H $(M + H)^+$, 340.0373; Found: 340.0370.

7-Ethyl-2-(4-fluorophenyl)-1,3-dithiocyanatoindolizine *(8k)*:



The title compound was prepared following the general procedure for Table 3, using 7-ethyl-2-(4-fluorophenyl)indolizine (**6k**, 0.25 mmol, 0.060 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (5-8% EtOAc/Hexanes) obtained **8k** as a green solid; Yield: 0.077 g, 87%; M.P.: 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33-8.32 (m, 1H), 7.83 (dd, J = 9.2 and 0.8 Hz, 1H), 7.55-7.50 (m, 2H), 7.33 (dd, J = 9.2 and 1.6 Hz, 1H), 7.31-7.27 (m, 2H), 2.80 (qd, J = 7.6 and 0.8 Hz, 2H), 1.37 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2 ($J_{C\text{-}F}$ = 249.0 Hz), 141.4, 139.1, 132.4 ($J_{C\text{-}F}$ = 8.0 Hz), 131.5, 127.7, 126.7 ($J_{C\text{-}F}$ = 4.0 Hz), 122.0, 117.2, 116.0 ($J_{C\text{-}F}$ = 22.0 Hz), 111.4, 108.5, 97.2, 88.4, 26.2, 15.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.8; HRMS (ESI) exact mass calcd for $C_{18}H_{12}FN_3S_2$ + H $(M + H)^+$, 354.0530; Found: 354.0532.

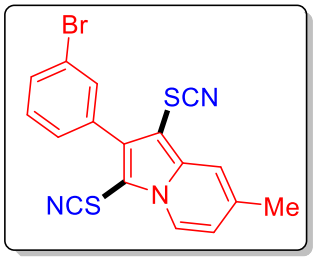
2-(4-Chlorophenyl)-7-methyl-1,3-dithiocyanatoindolizine *(8l)*:



The title compound was prepared following the general procedure for Table 3, using 2-(4-chlorophenyl)-7-methylindolizine (**6l**, 0.25 mmol, 0.060 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (5-8% EtOAc/Hexanes) obtained **8l** as a pale yellow solid; Yield: 0.082 g, 92%; M.P.: 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 7.2 Hz, 1H), 7.58 (quint, J = 1.2 Hz, 1H), 7.51-7.47 (m, 2H), 7.42-7.39 (m, 2H), 6.91 (dd, J = 7.2 and 1.6 Hz, 1H), 2.46 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6,

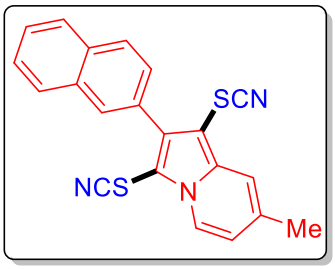
140.6, 137.3, 135.4, 131.9, 129.2, 129.1, 124.3, 117.7, 116.2, 111.4, 108.4, 96.7, 87.3, 21.5; HRMS (ESI) exact mass calcd for $C_{17}H_{10}ClN_3S_2$ + H $(M + H)^+$, 356.0078; Found: 356.0078.

2-(3-Bromophenyl)-7-methyl-1,3-dithiocyanatoindolizine *(8m)*:



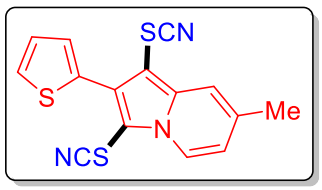
The title compound was prepared following the general procedure for Table 3, using 2-(3-bromophenyl)-7-methylindolizine (**6m**, 0.25 mmol, 0.072 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (5-8% EtOAc/Hexanes) obtained **8m** as a dark brown solid; Yield: 0.089 g, 88%; M.P.: 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 7.2 Hz, 1H), 7.61-7.59 (m, 3H), 7.42-7.37 (m, 2H), 6.92 (dd, J = 7.2 and 1.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.6, 137.3, 133.3, 132.7, 132.2, 130.3, 129.3, 124.3, 122.7, 117.8, 116.2, 111.2, 108.2, 96.9, 87.4, 21.5; HRMS (ESI) exact mass calcd for $C_{17}H_{10}BrN_3S_2$ + H $(M + H)^+$, 399.9573; Found: 399.9568.

7-Methyl-2-(naphthalen-2-yl)-1,3-dithiocyanatoindolizine *(8n)*:



The title compound was prepared following the general procedure for Table 3, using 7-methyl-2-(naphthalen-2-yl)indolizine (**6n**, 0.25 mmol, 0.100 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (8-10% EtOAc/Hexanes) obtained **8n** as a brown solid; Yield: 0.076 g, 81%; M.P.: 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 6.8 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 1.6 Hz, 1H), 7.94-7.88 (m, 2H), 7.62 (quint, J = 1.2 Hz, 1H), 7.58 (dd, J = 8.4 and 1.6 Hz, 1H), 7.54-7.51 (m, 2H), 6.92 (dd, J = 7.2 and 1.6 Hz, 1H), 2.48 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 140.7, 137.1, 133.2, 133.1, 130.5, 128.57, 128.50, 128.2, 127.9, 127.7, 127.1, 126.8, 124.3, 117.6, 116.2, 111.6, 108.6, 96.9, 87.5, 21.5; HRMS (ESI) exact mass calcd for $C_{21}H_{13}N_3S_2$ + H $(M + H)^+$, 372.0624; Found: 372.0629.

7-Methyl-1,3-dithiocyanato-2-(thiophen-2-yl)indolizine *(8o)*:



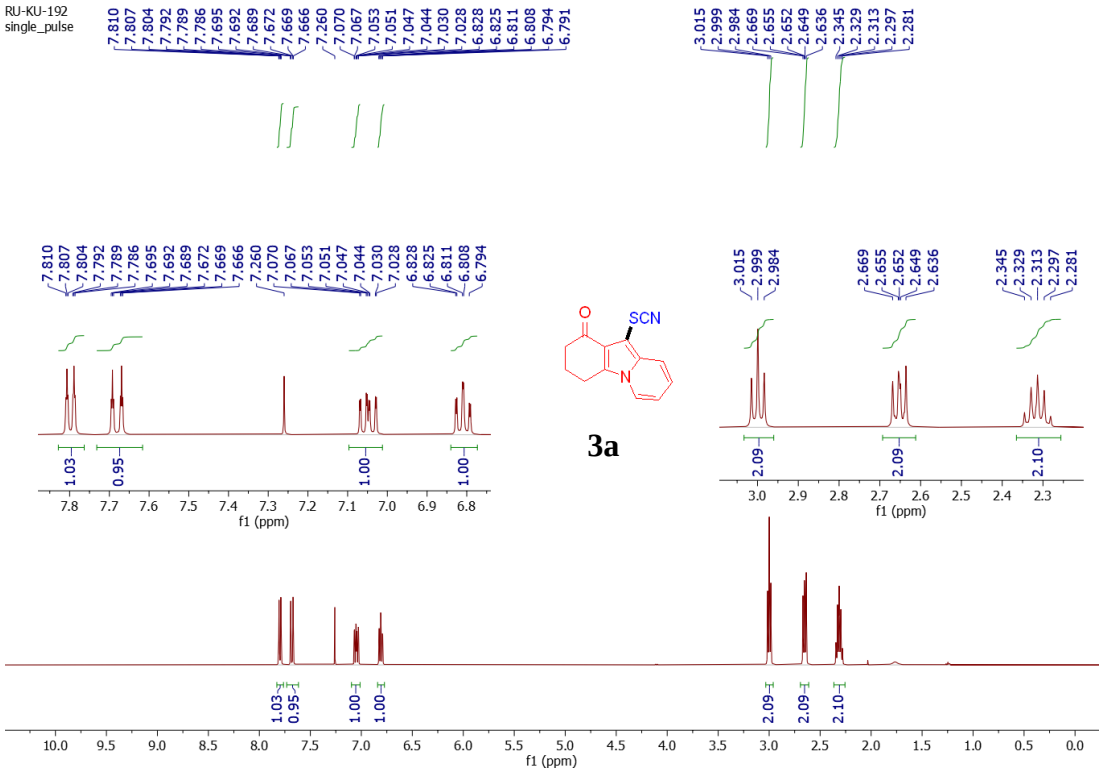
The title compound was prepared following the general procedure for Table 3, using 7-methyl-2-(thiophen-2-yl)indolizine (**6o**, 0.25 mmol, 0.082 g), ammonium thiocyanate (**2**, 0.75 mmol, 0.057 g) and iodine (0.375 mmol, 0.095 g), after column chromatography (10-12% EtOAc/Hexanes) obtained **8o** as a yellow solid; Yield: 0.076 g, 93%; M.P.: 274 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, J = 6.8 and 1.2 Hz, 1H), 7.57 (quint, J = 1.2 Hz, 1H), 7.24 (dd, J = 3.6 and 1.6 Hz, 1H), 7.19 (s, 1H), 7.16 (dd, J = 3.6 and 1.6 Hz, 1H), 6.91 (dd, J = 7.2 and 2.0 Hz, 1H), 2.46 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$): δ 140.9, 137.6, 134.5, 132.3, 130.7, 130.4, 124.3, 118.0, 116.2, 115.8, 111.0, 108.0, 96.6, 87.1, 21.5; HRMS (ESI) exact mass calcd for $C_{21}H_{13}NO_2S$ + H $(M + H)^+$, 328.0032; Found: 328.0032.

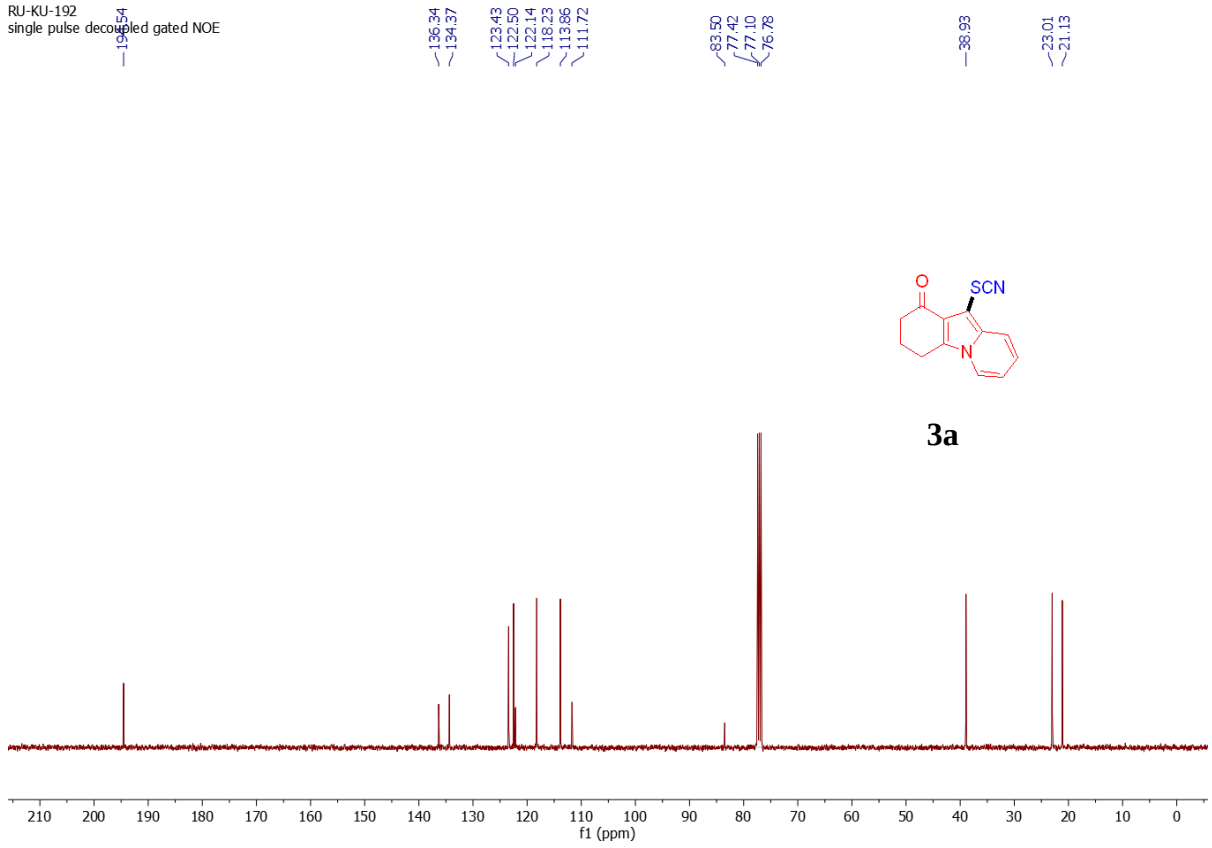
References:

1. Basavaiah, D.; Rao, A. J. First example of electrophile induced Baylis–Hillman reaction: a novel facile one-pot synthesis of indolizine derivatives. *Chem. Commun.* **2003**, *2003*, 604-605.
2. Basavaiah, D.; Rao, A. J. 1-Benzopyran-4 (4H)-ones as novel activated alkenes in the Baylis–Hillman reaction: A simple and facile synthesis of indolizine-fused-chromones. *Tetrahedron Lett.* **2003**, *44*, 4365-4368.
3. Penteado, F.; Gomes, C. S.; Monzon, L. I.; Perin, G.; Silveira, C. C.; Lenardão, E. J. Photocatalytic synthesis of 3-sulfanyl and 1, 3-bis (sulfanyl) indolizines mediated by visible light. *Eur. J. Org. Chem.* **2020**, *2020*, 2110-2115.
4. Wang, Q.; Zhang, S.; Guo, F.; Zhang, B.; Hu, P.; Wang, Z.; Natural α-amino acids applied in the synthesis of imidazo[1,5-*a*]*N*-heterocycles under mild conditions. *J. Org. Chem.* **2012**, *77*, 11161-11166.
5. Basavaiah, D.; Roy, S. Dimethyl sulfide induced [3 + 2] annulation strategy: an efficient synthesis of functionalized dihydropyrazole derivatives using the Baylis-Hillman bromides. *Org. Lett.* **2008**, *10*, 1819-1822.

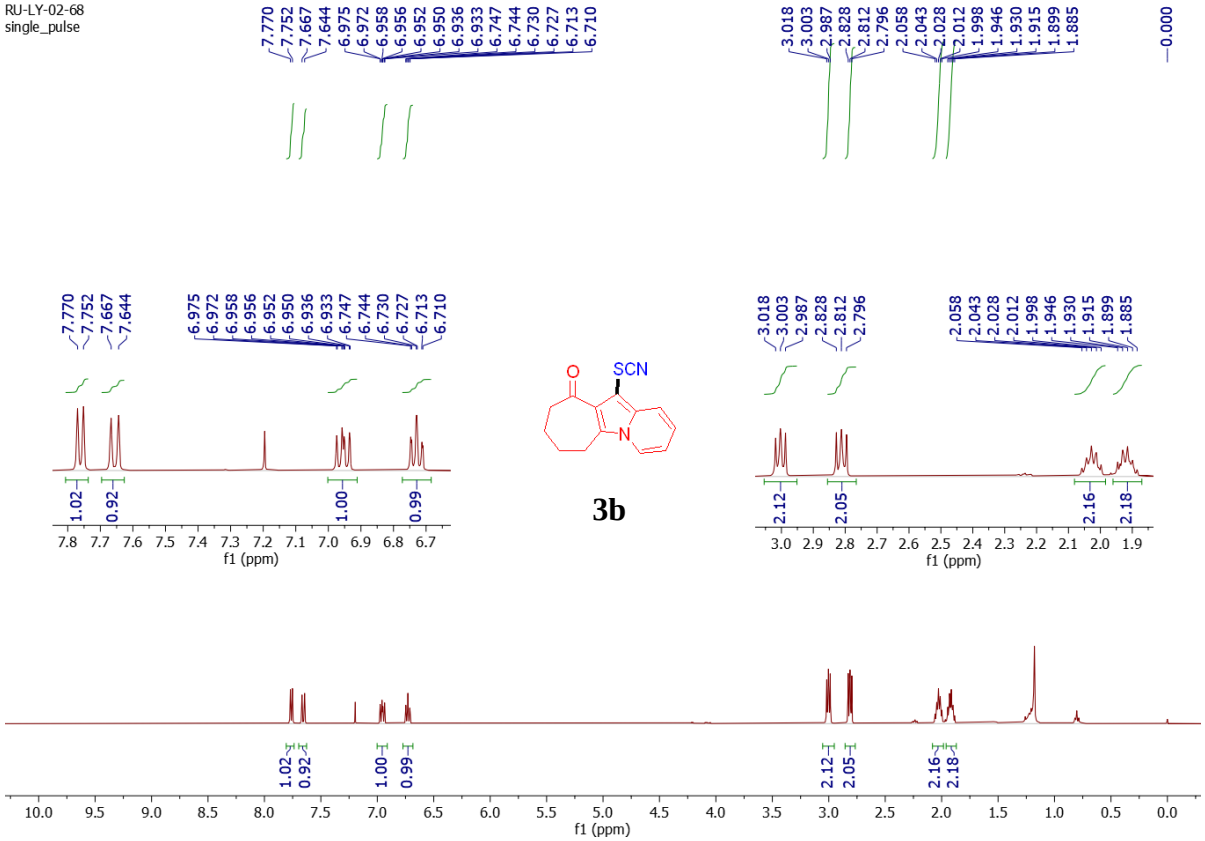
^{1}H NMR spectrum of 3a (400 MHz, $CDCl_3$)



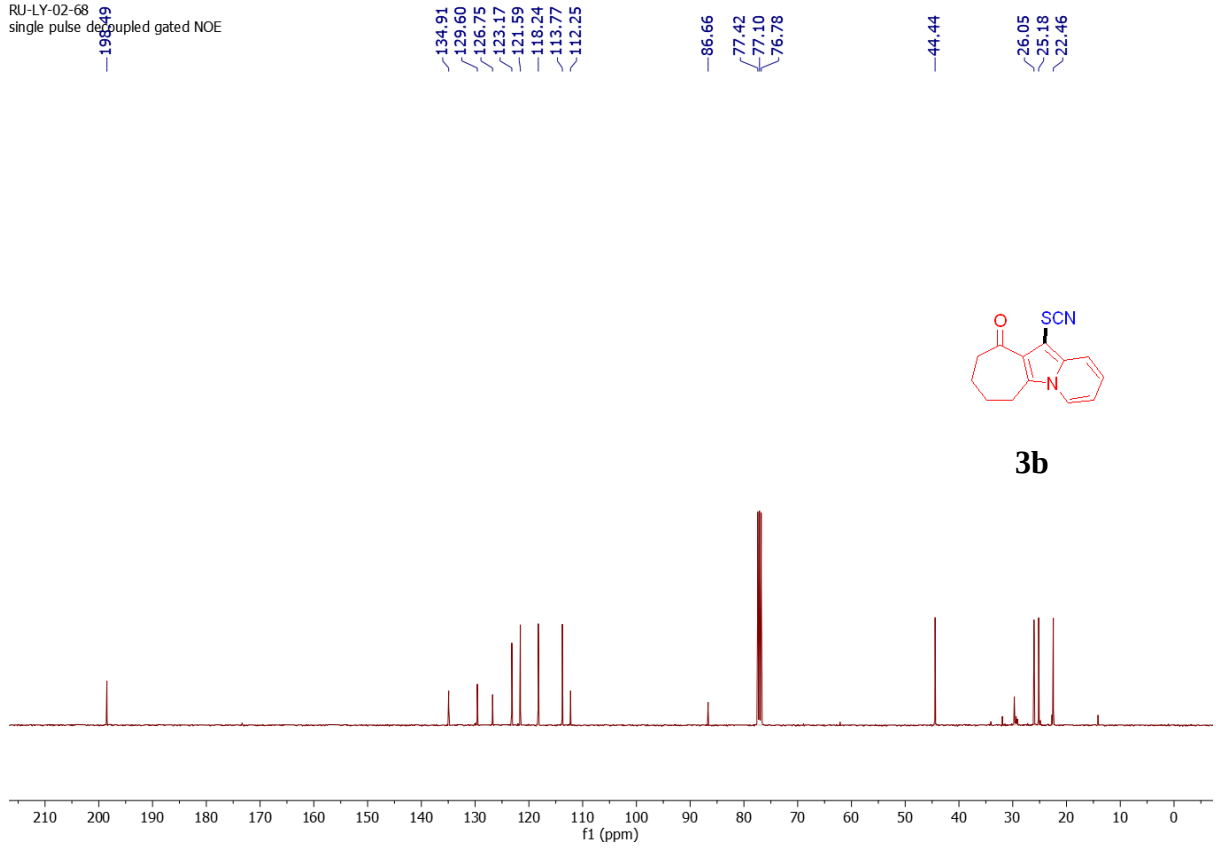
^{13}C NMR spectrum of 3a (100 MHz, $CDCl_3$)



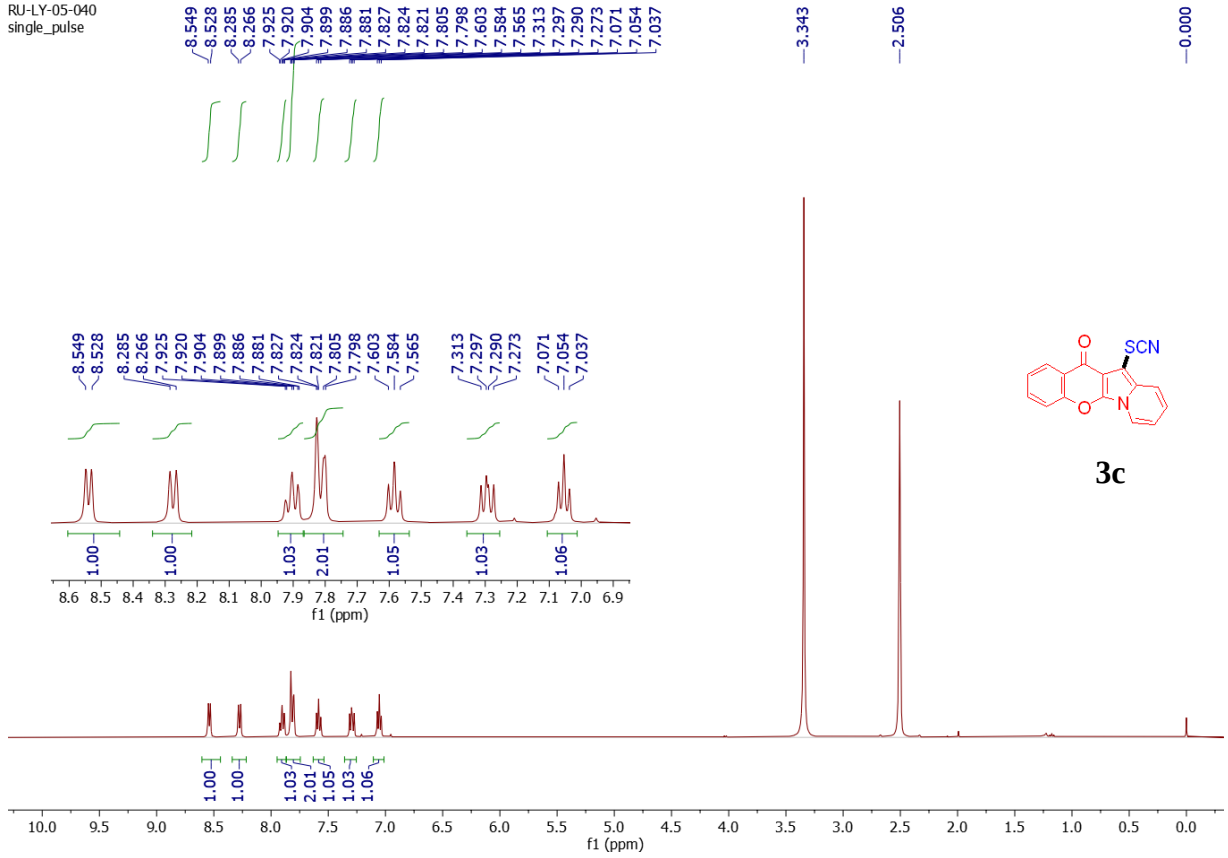
^{1}H NMR spectrum of 3b (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3b (100 MHz, $CDCl_3$)

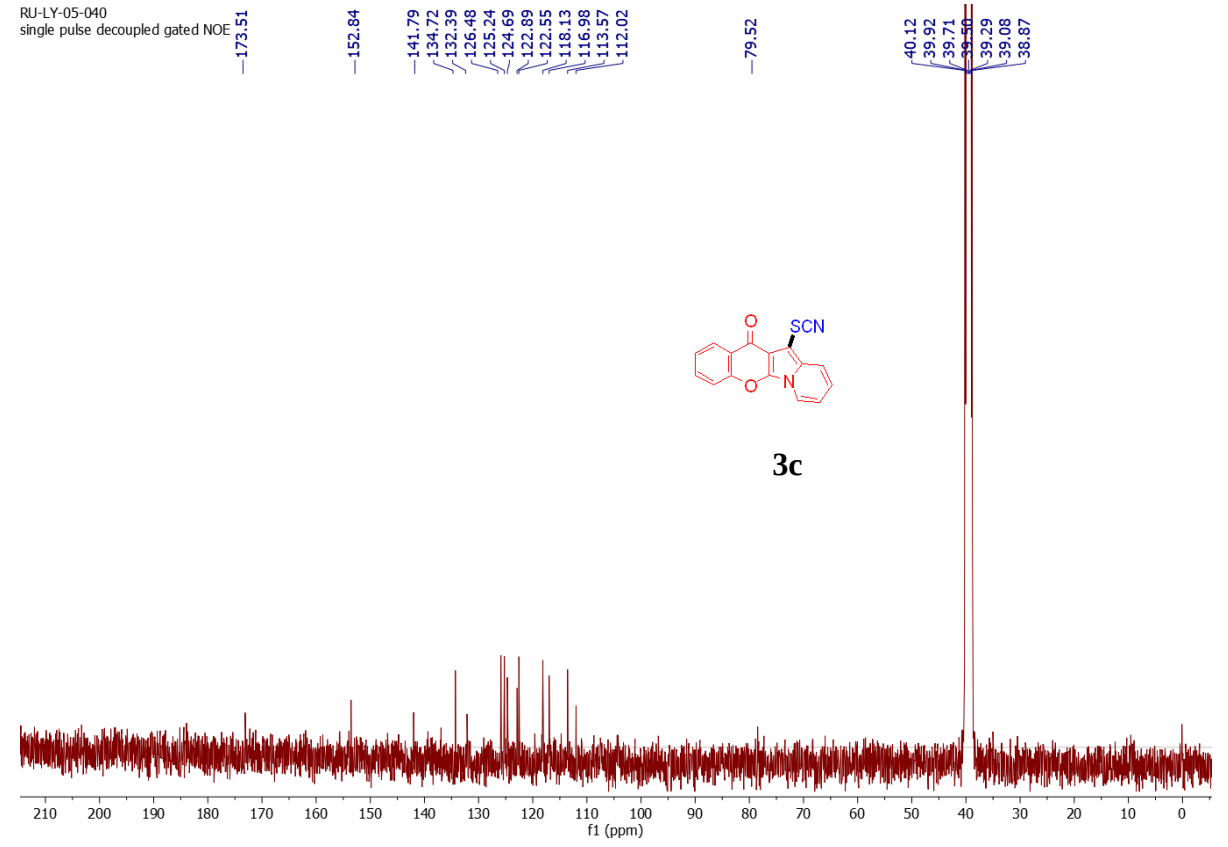


^{1}H NMR spectrum of 3c (400 MHz, DMSO-d_6)



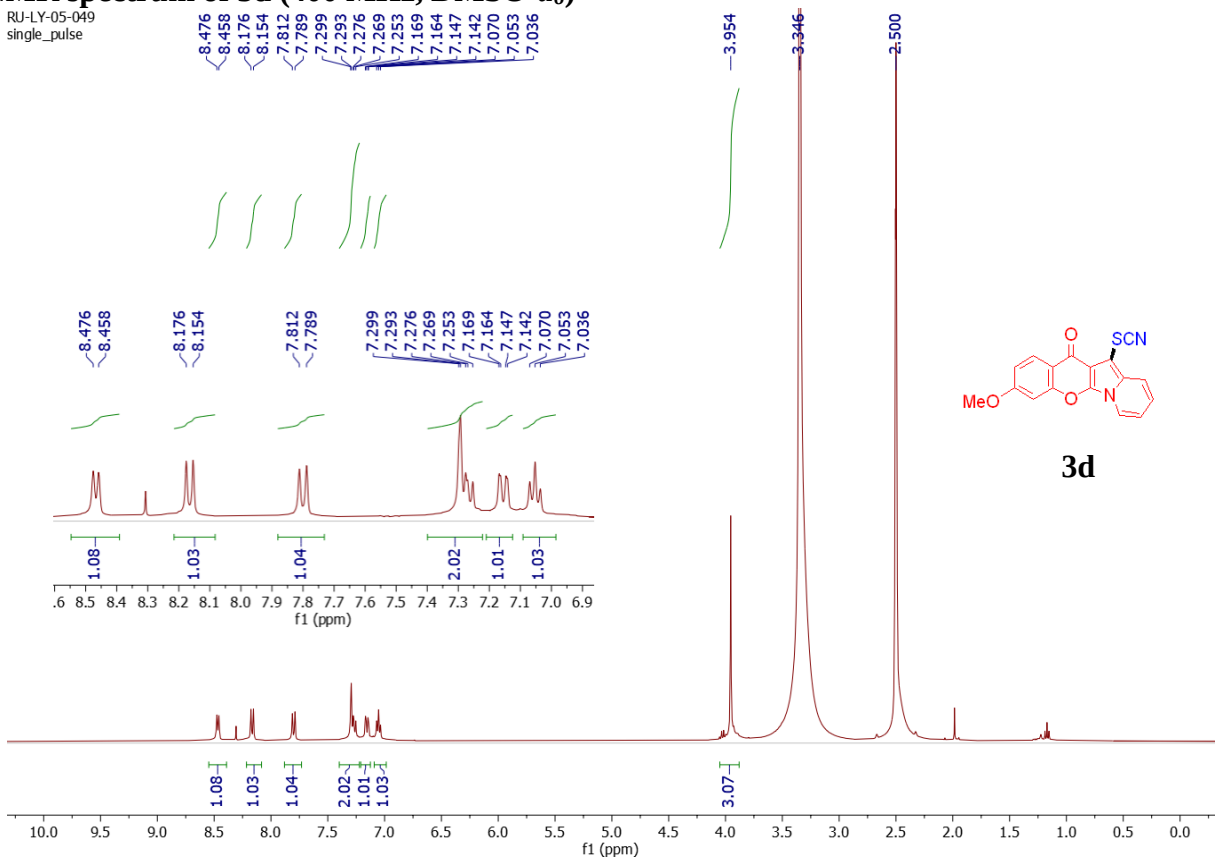
3c

^{13}C NMR spectrum of 3c (100 MHz, DMSO-d_6)-(Less soluble)



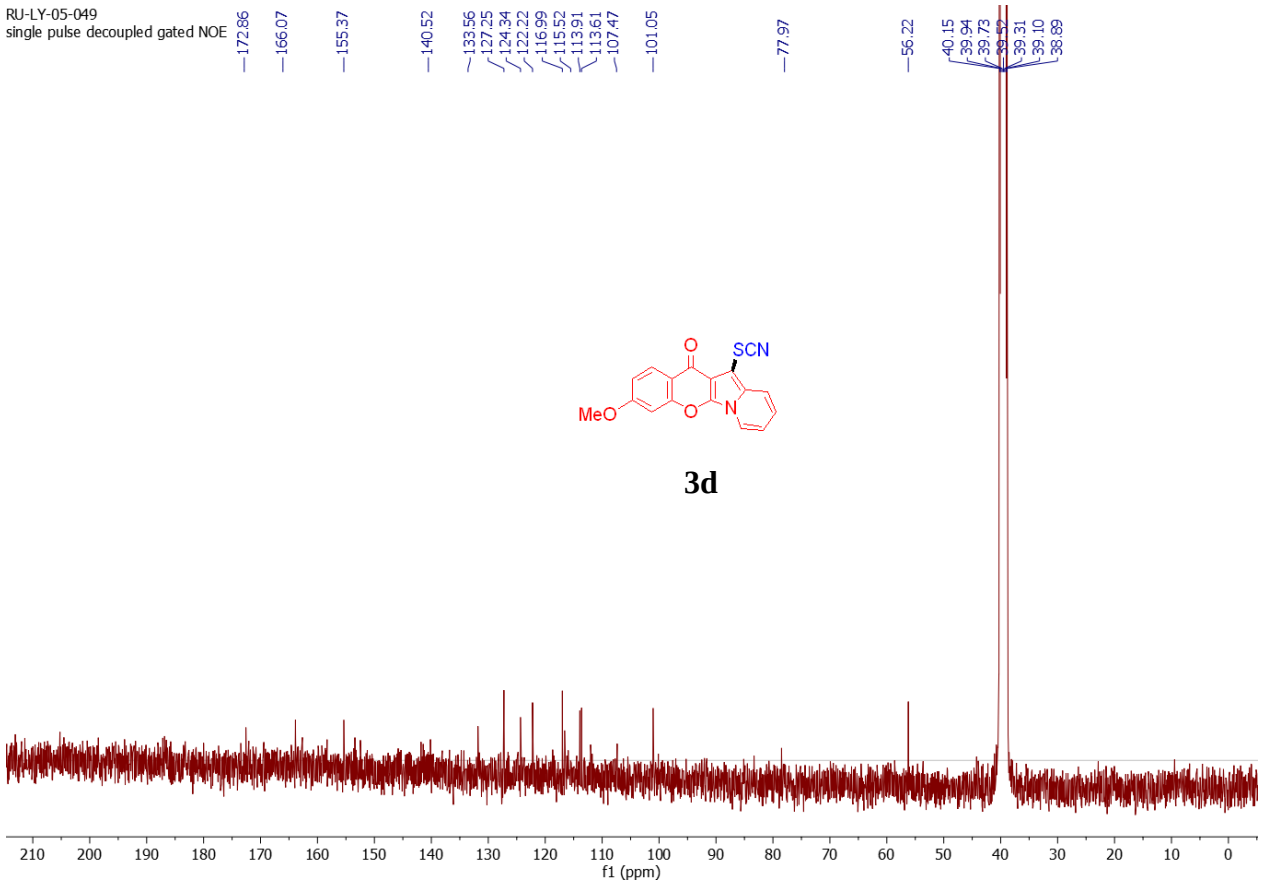
3c

^{1}H NMR spectrum of 3d (400 MHz, DMSO-d_6)



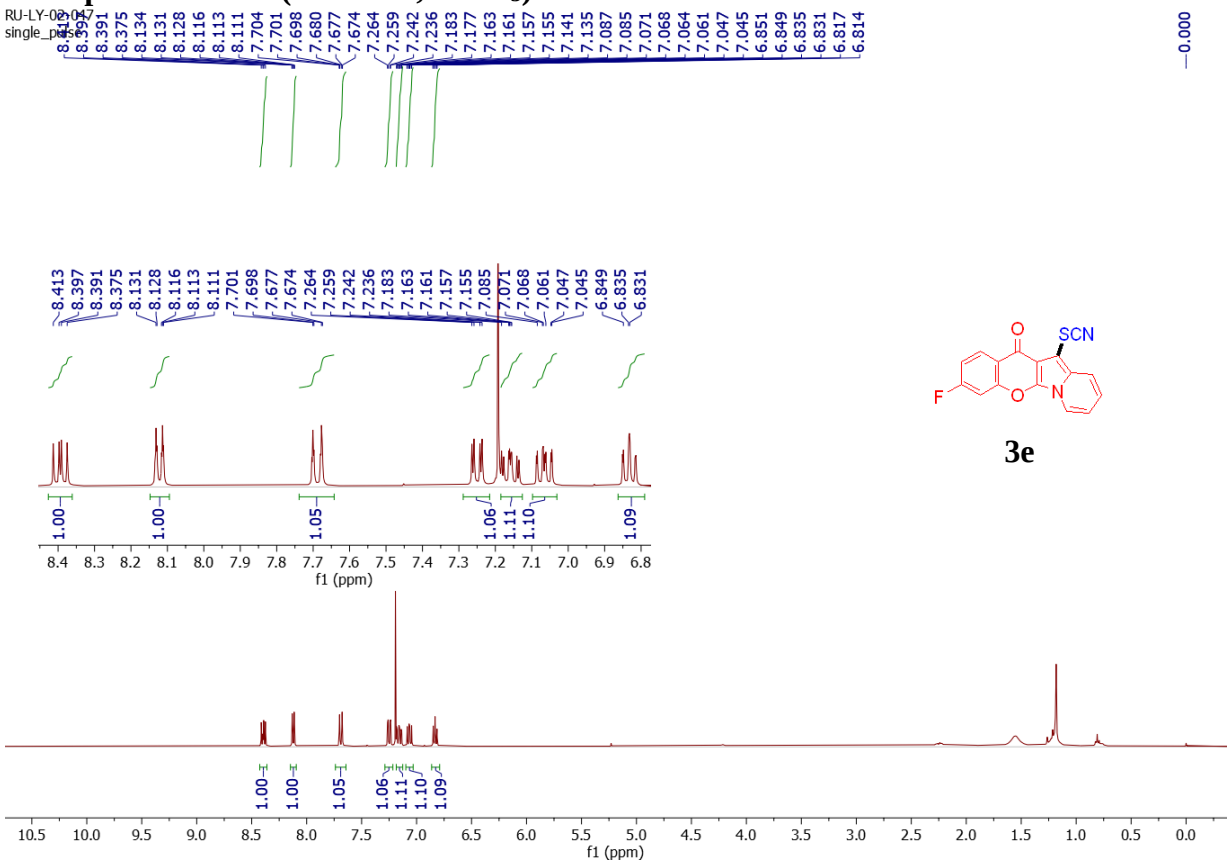
3d

^{13}C NMR spectrum of 3d (100 MHz, DMSO-d_6)- (Less soluble)

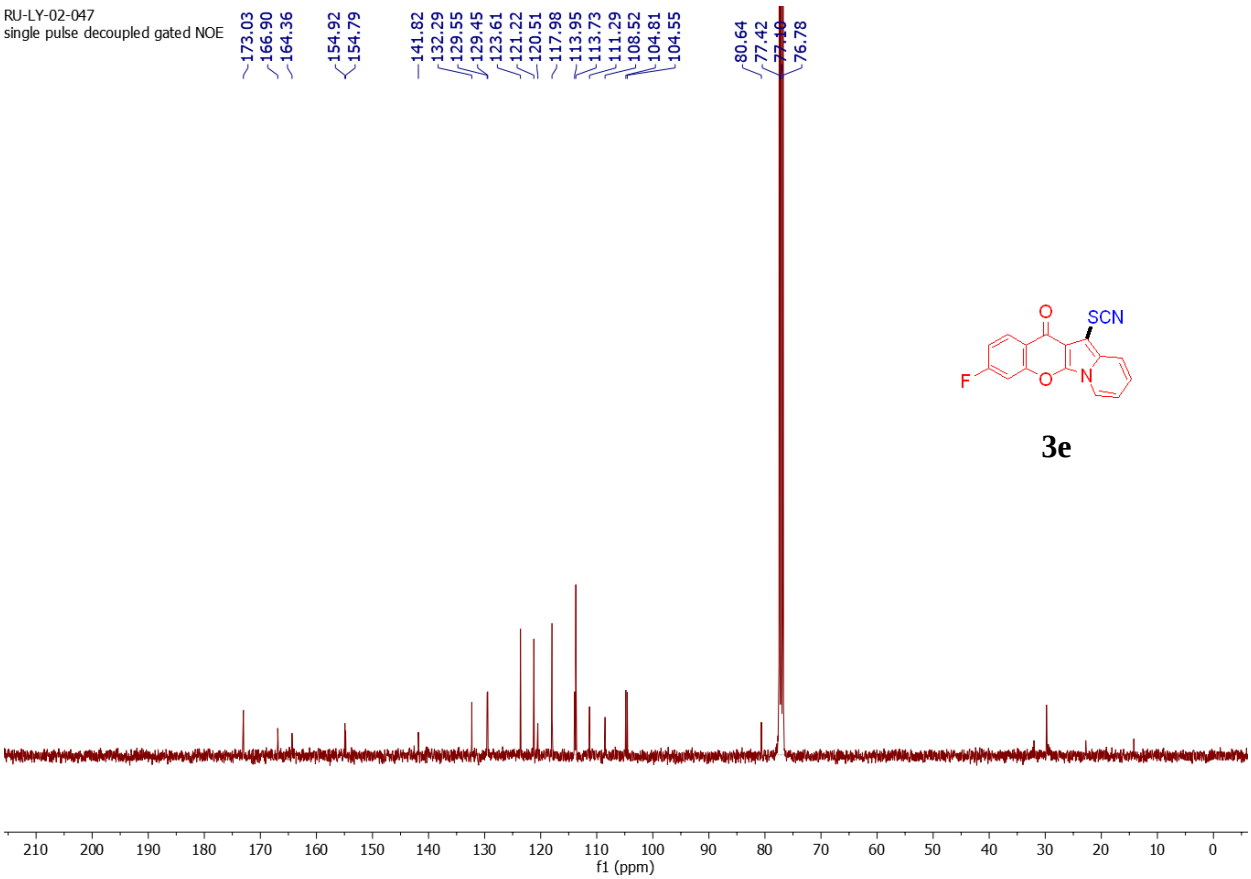


3d

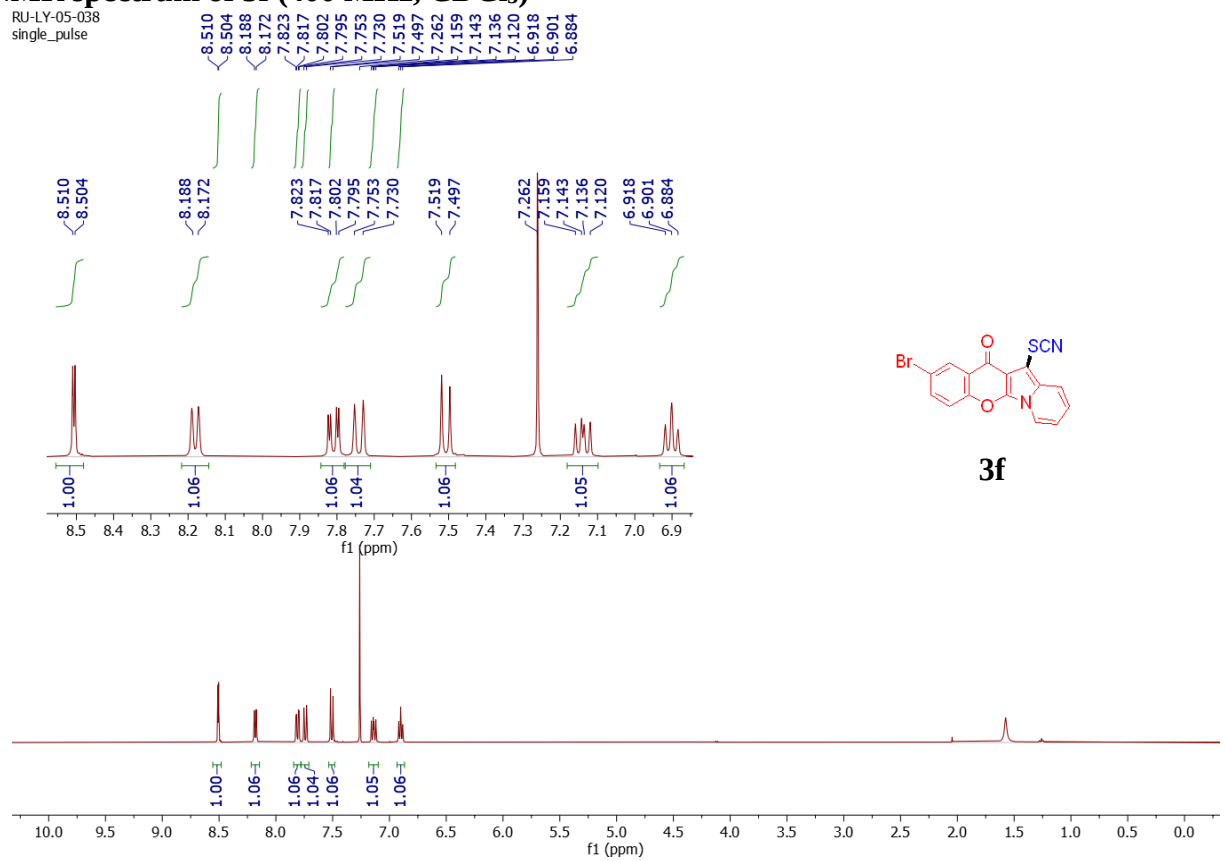
^{1}H NMR spectrum of 3e (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3e (100 MHz, $CDCl_3$)

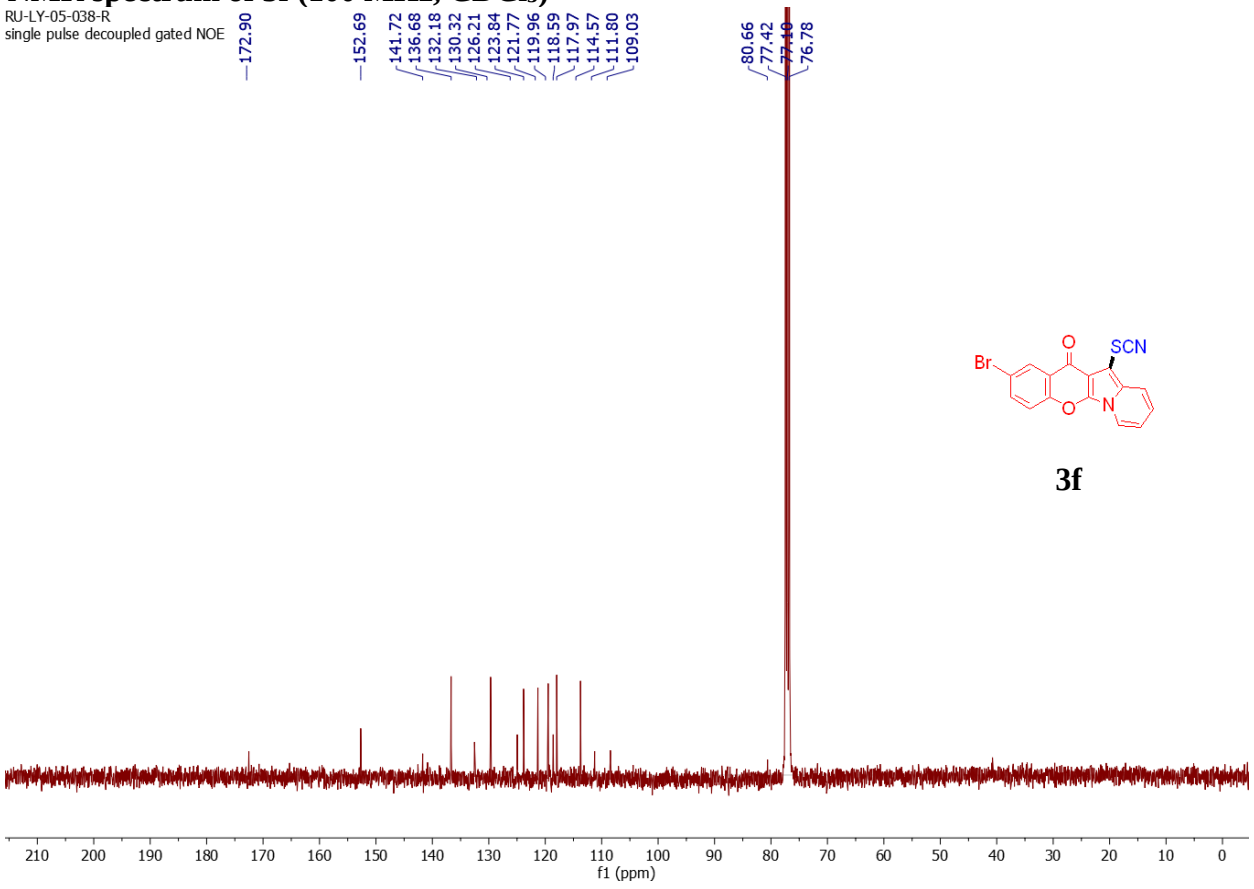


^{1}H NMR spectrum of 3f (400 MHz, $CDCl_3$)



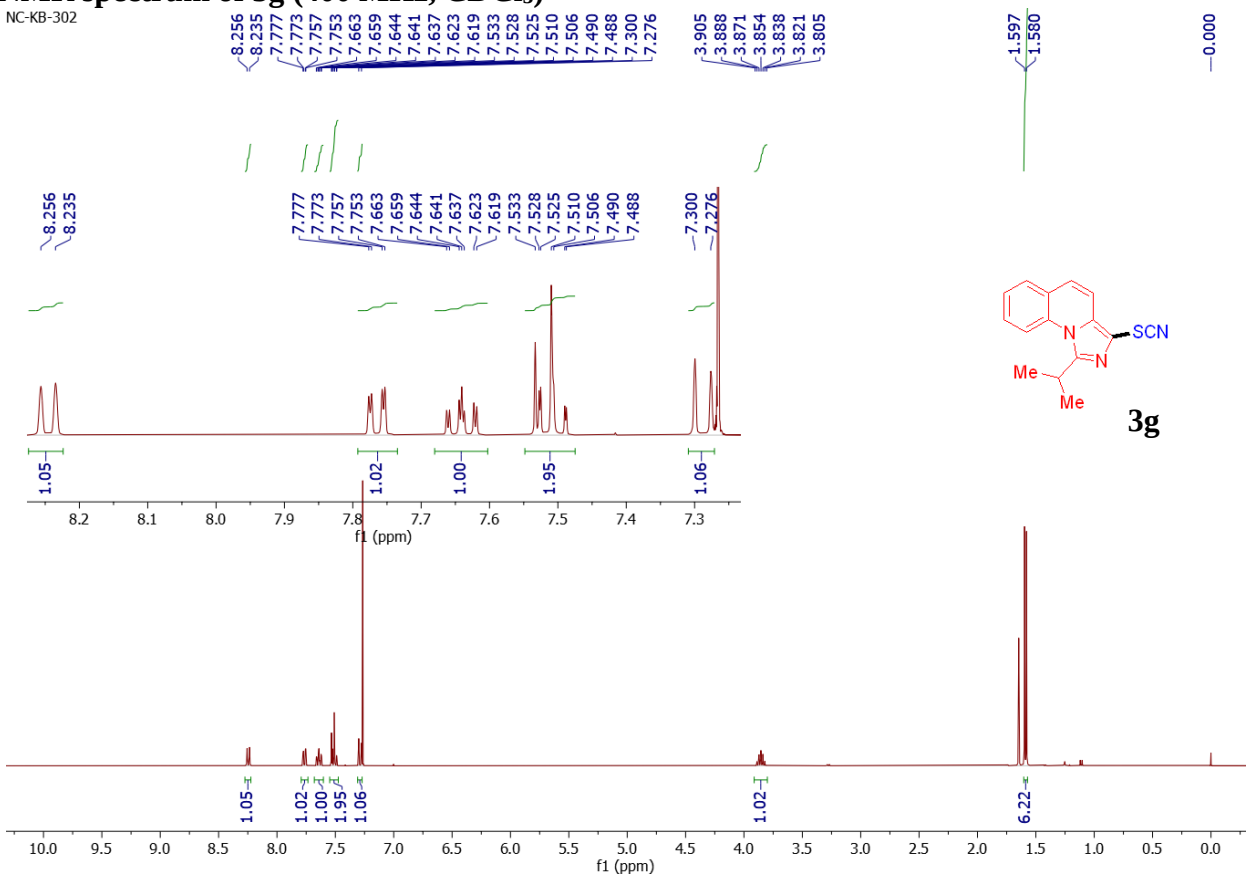
3f

^{13}C NMR spectrum of 3f (100 MHz, $CDCl_3$)

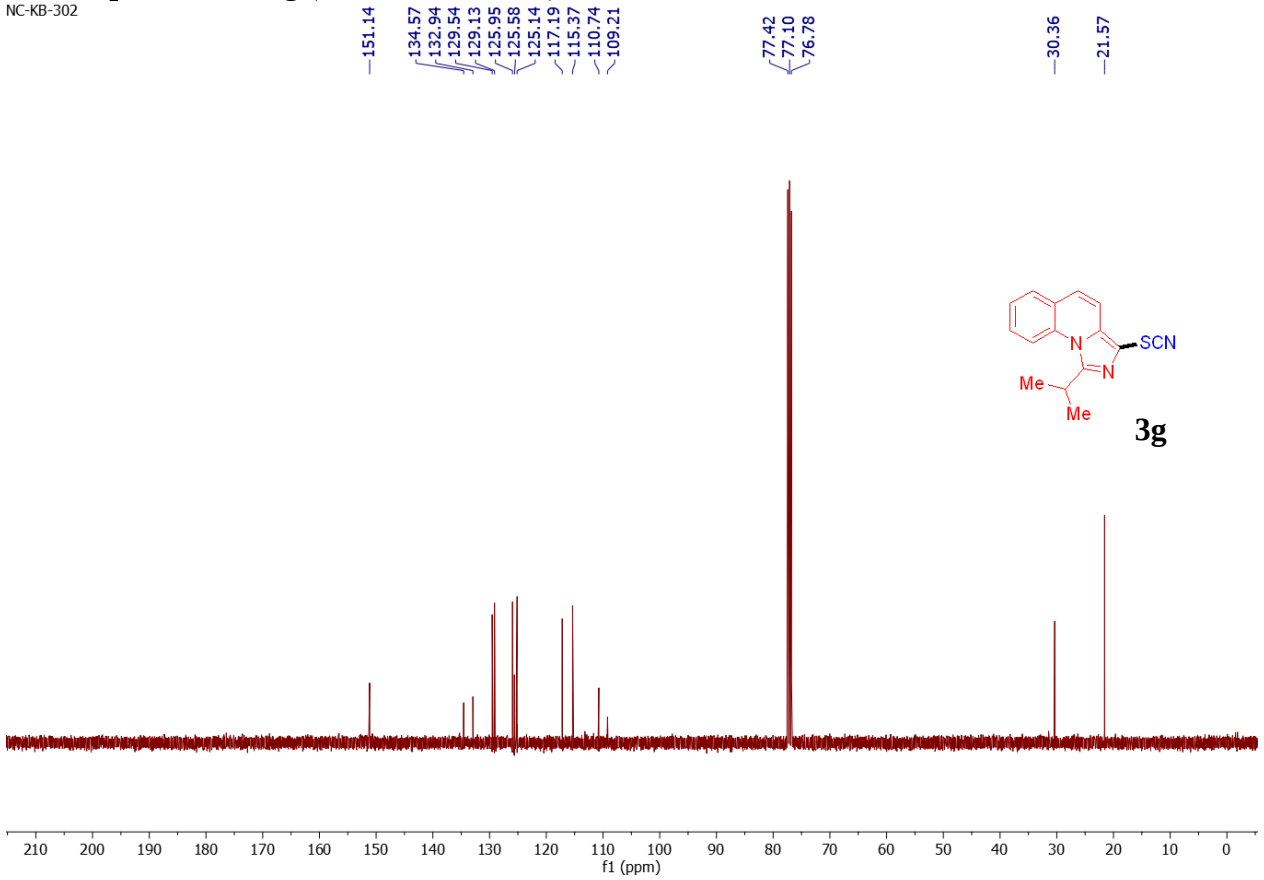


3f

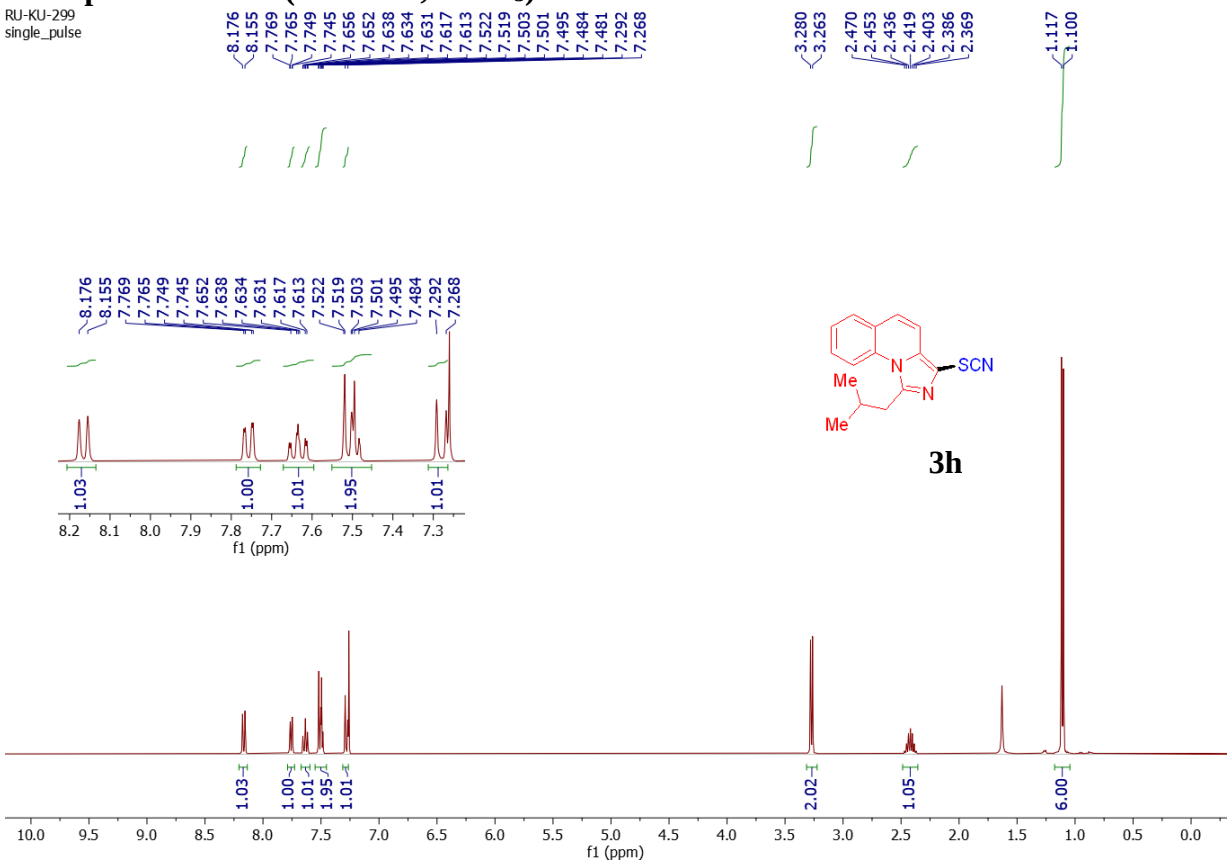
^{1}H NMR spectrum of 3g (400 MHz, $CDCl_3$)



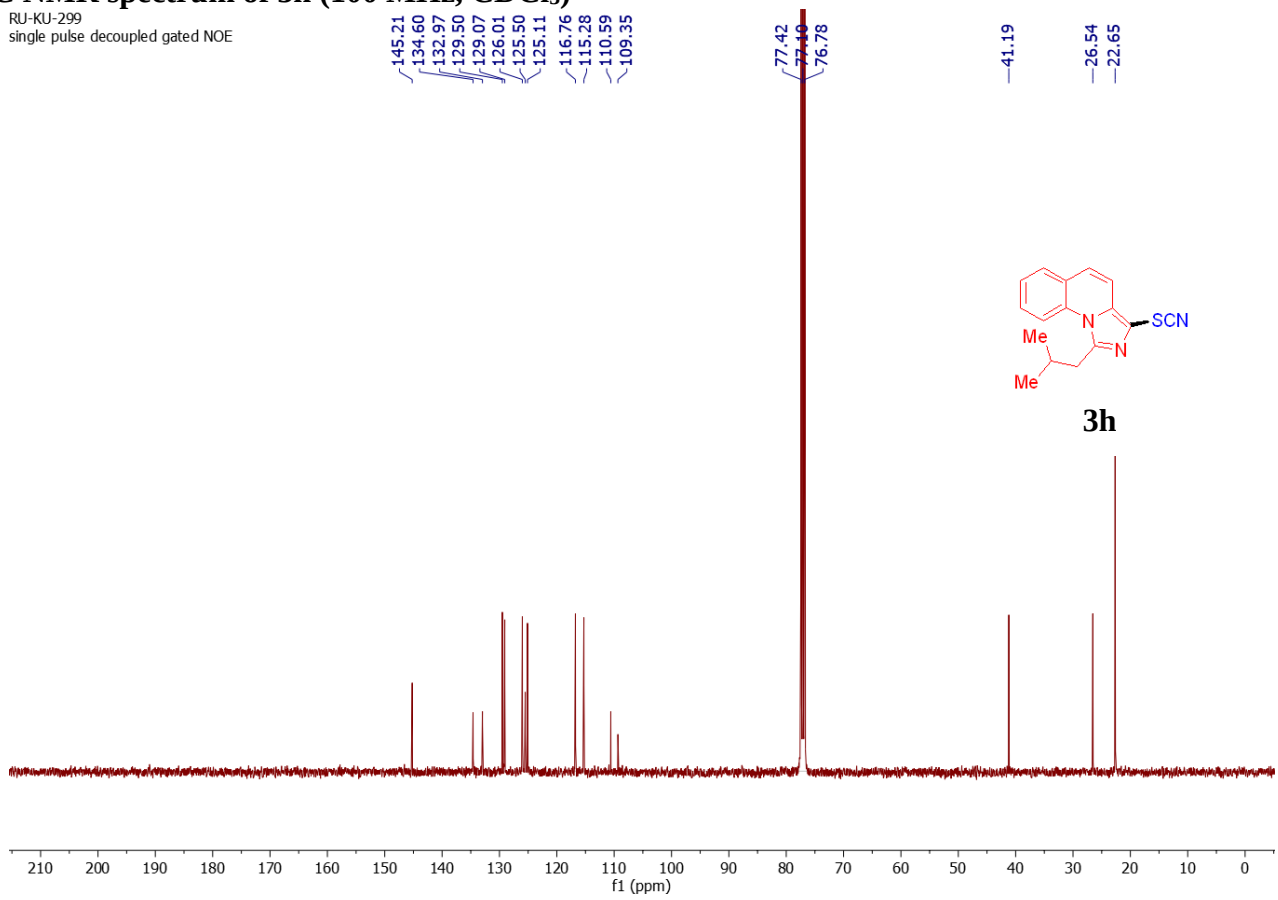
^{13}C NMR spectrum of 3g (100 MHz, $CDCl_3$)



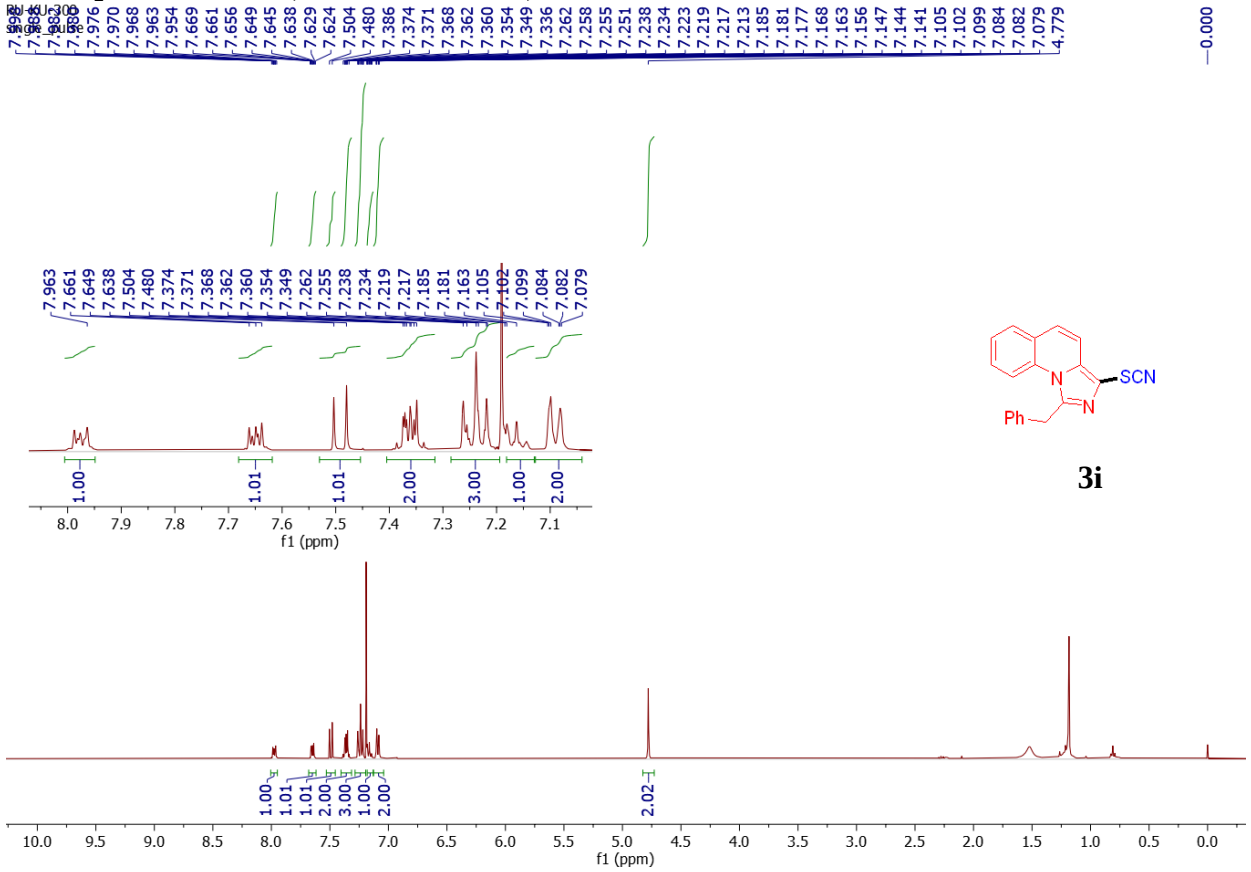
^{1}H NMR spectrum of 3h (400 MHz, $CDCl_3$)



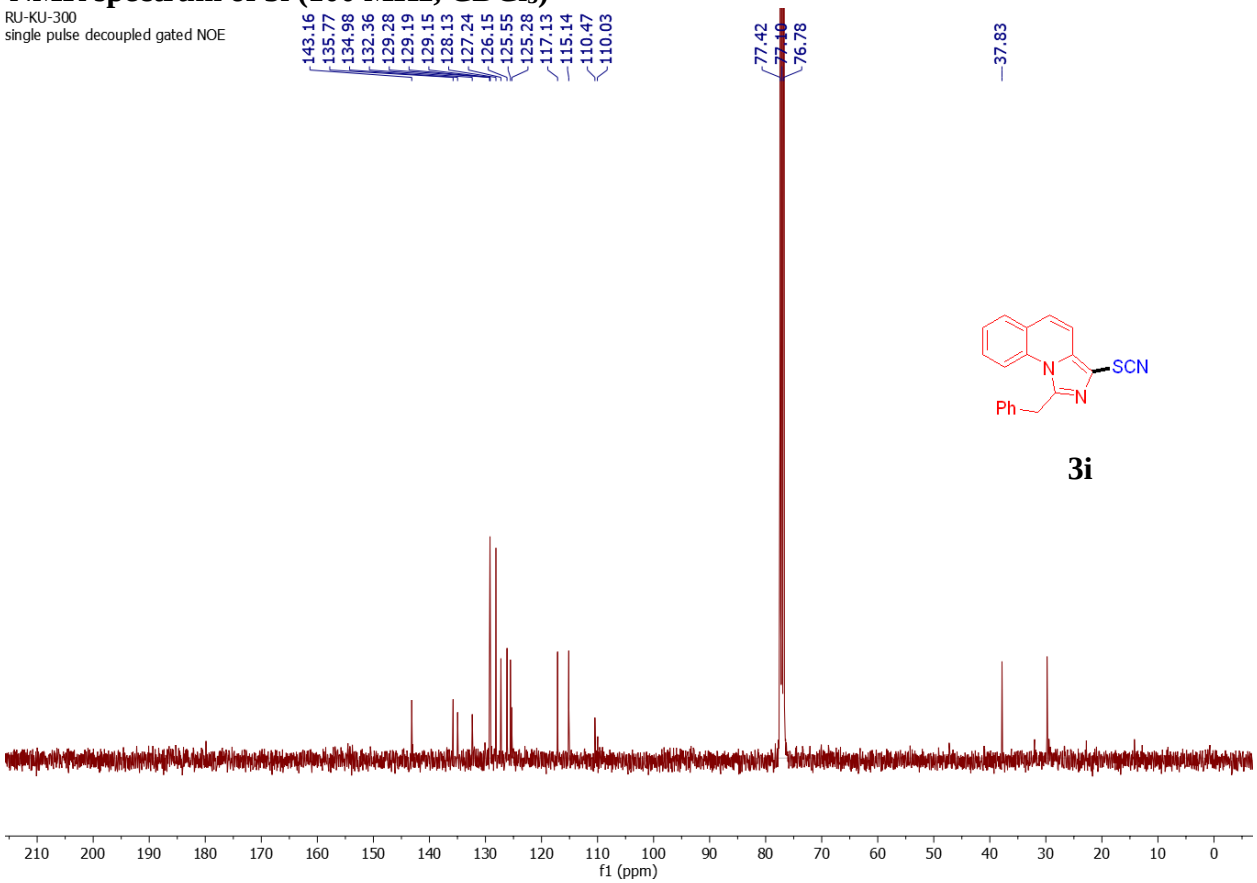
^{13}C NMR spectrum of 3h (100 MHz, $CDCl_3$)



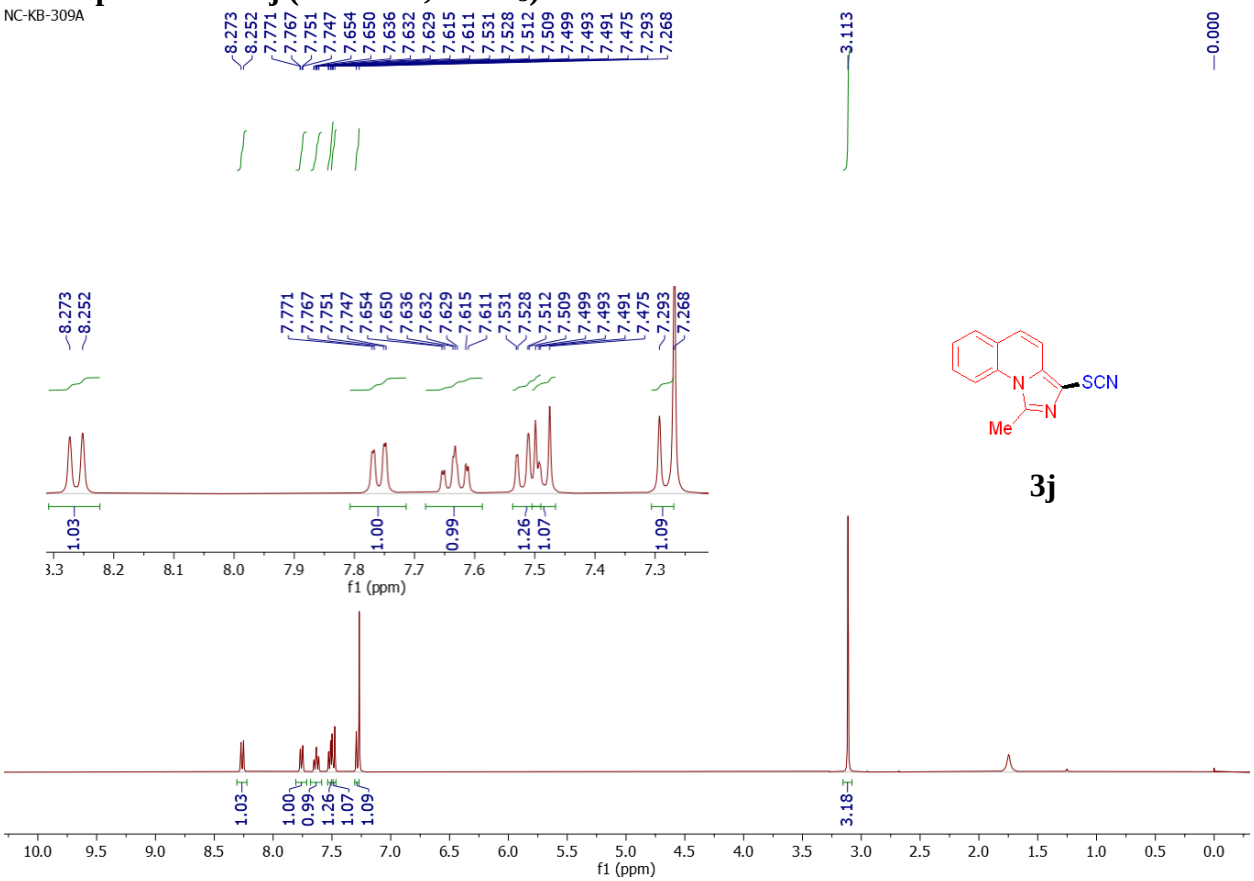
^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3i (100 MHz, $CDCl_3$)

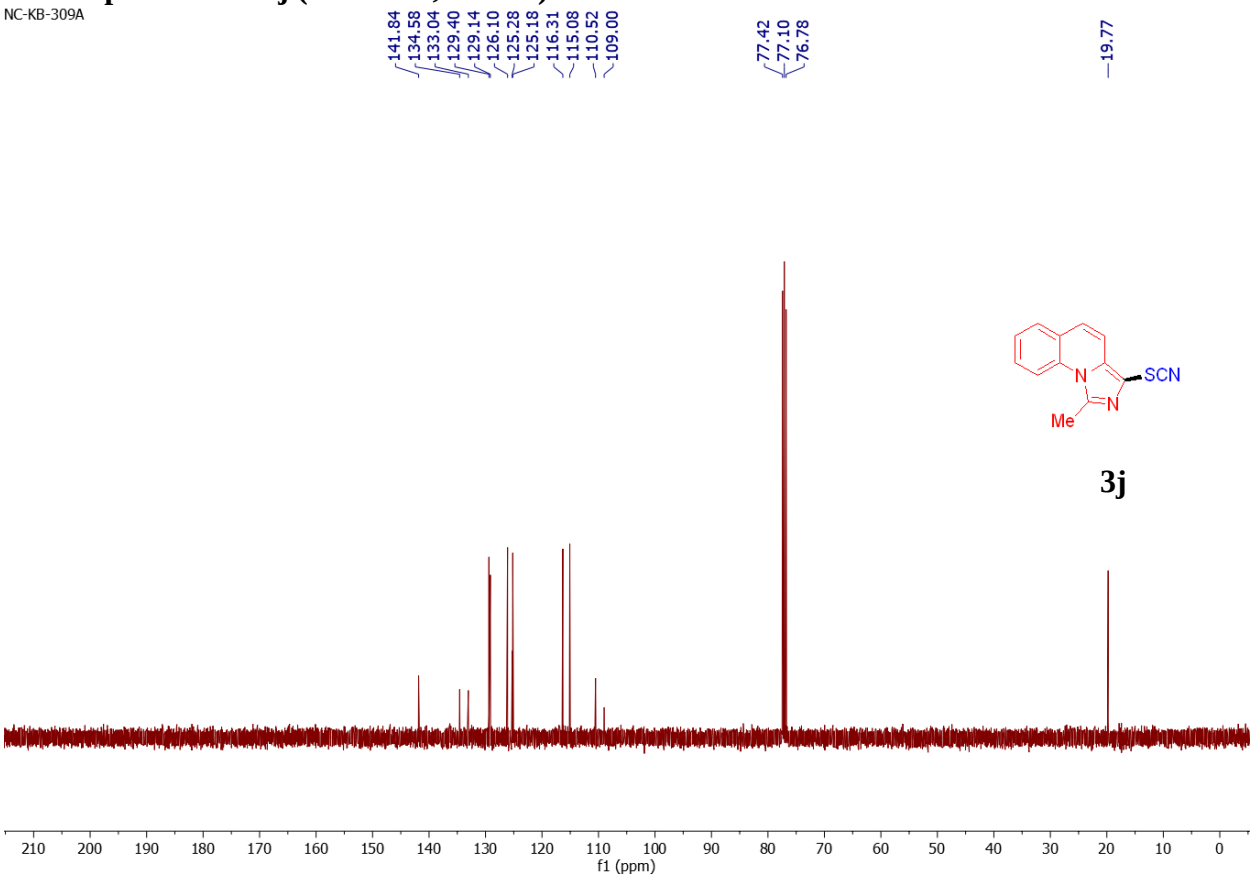


^{1}H NMR spectrum of 3j (400 MHz, $CDCl_3$)



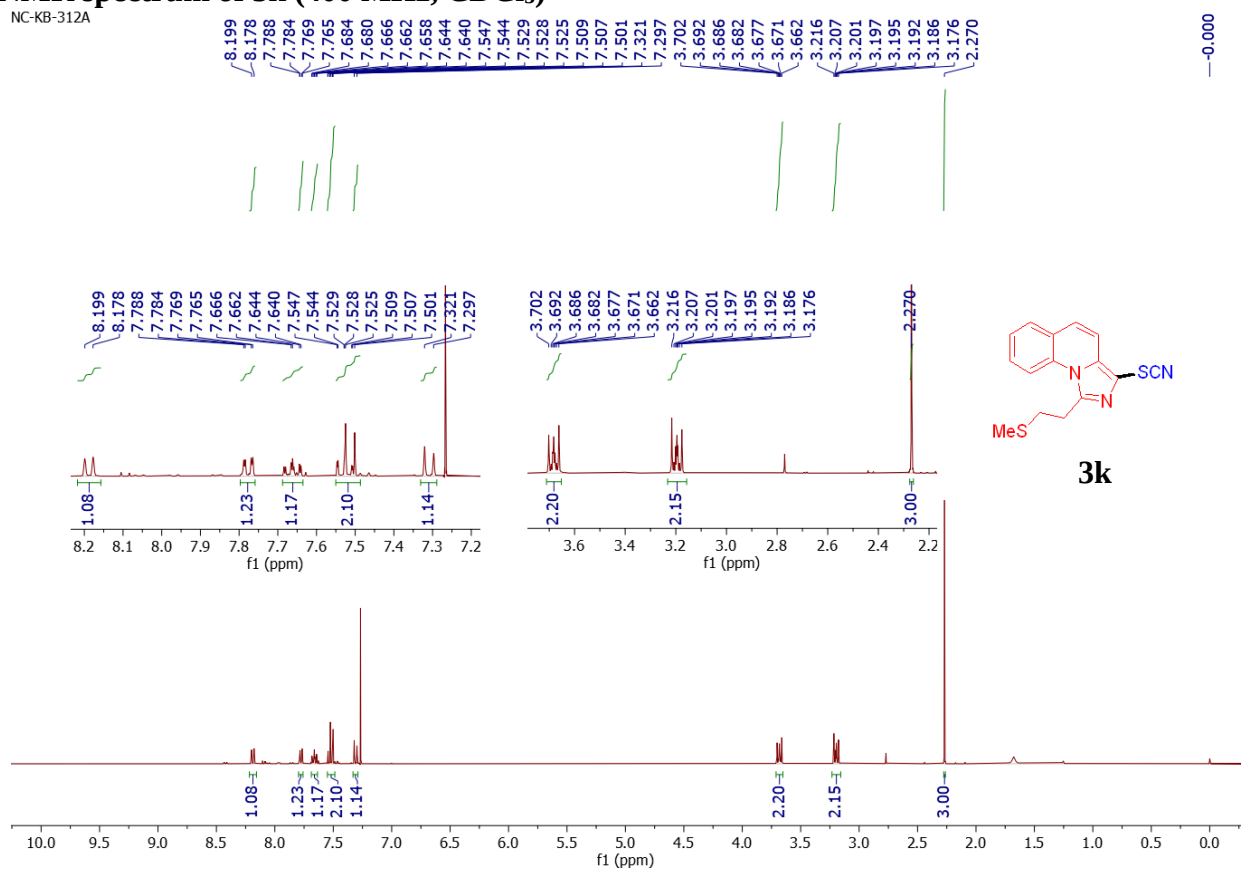
3j

^{13}C NMR spectrum of 3j (100 MHz, $CDCl_3$)

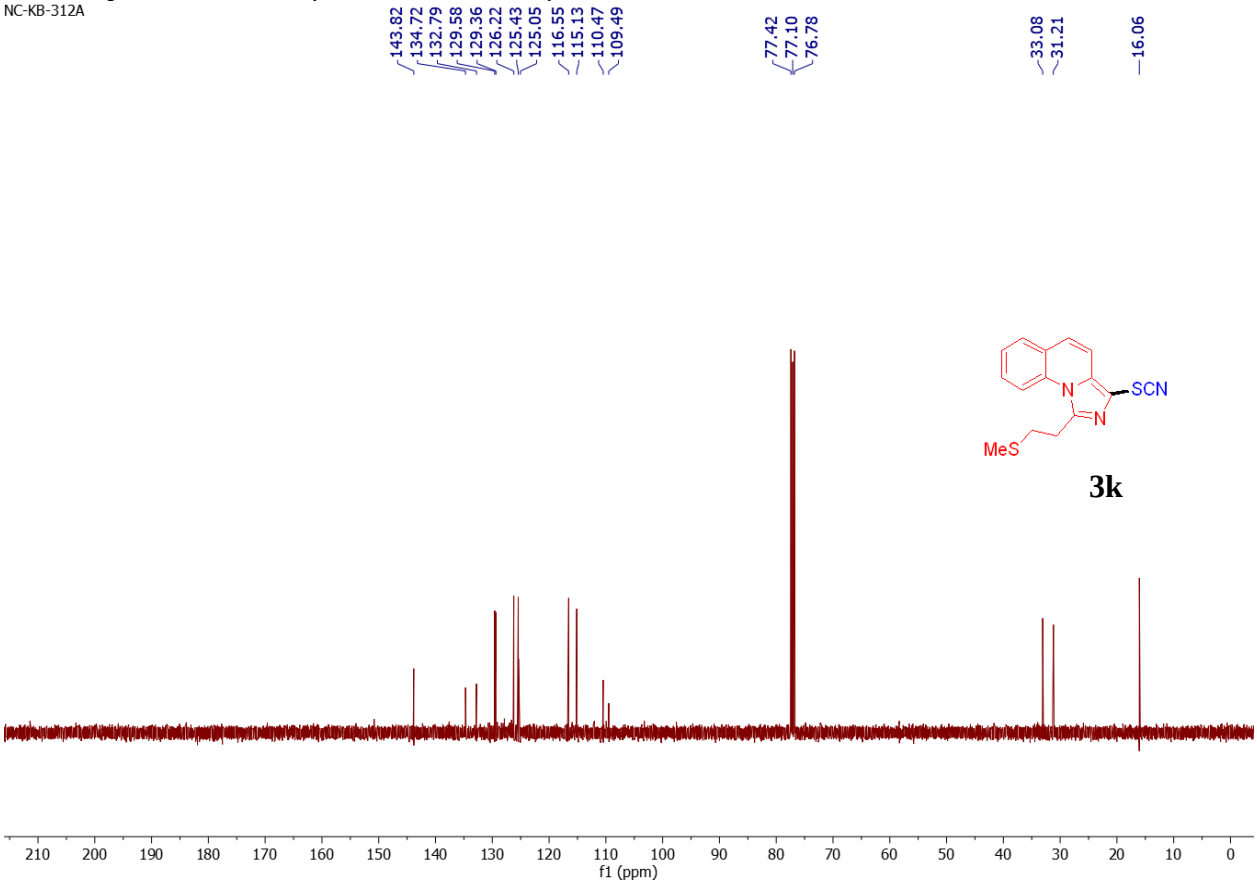


3j

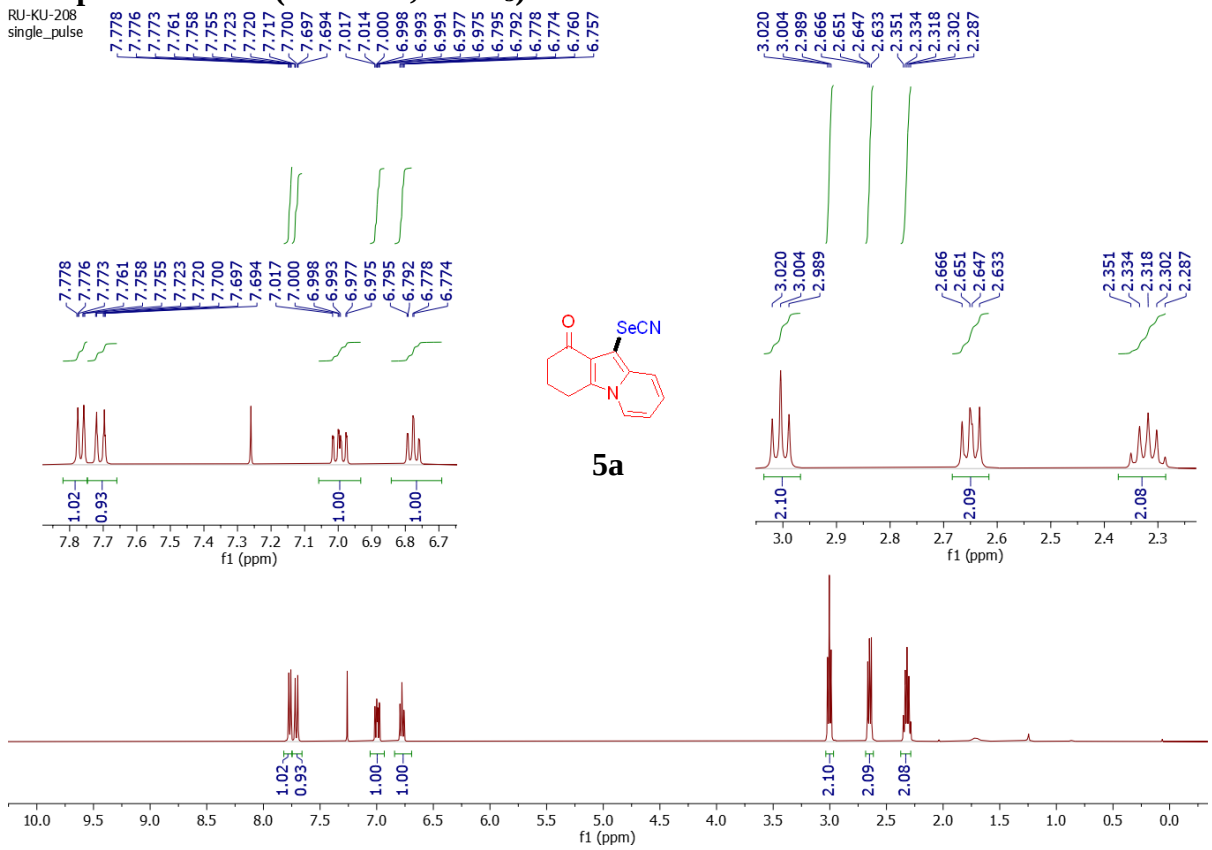
^{1}H NMR spectrum of 3k (400 MHz, $CDCl_3$)



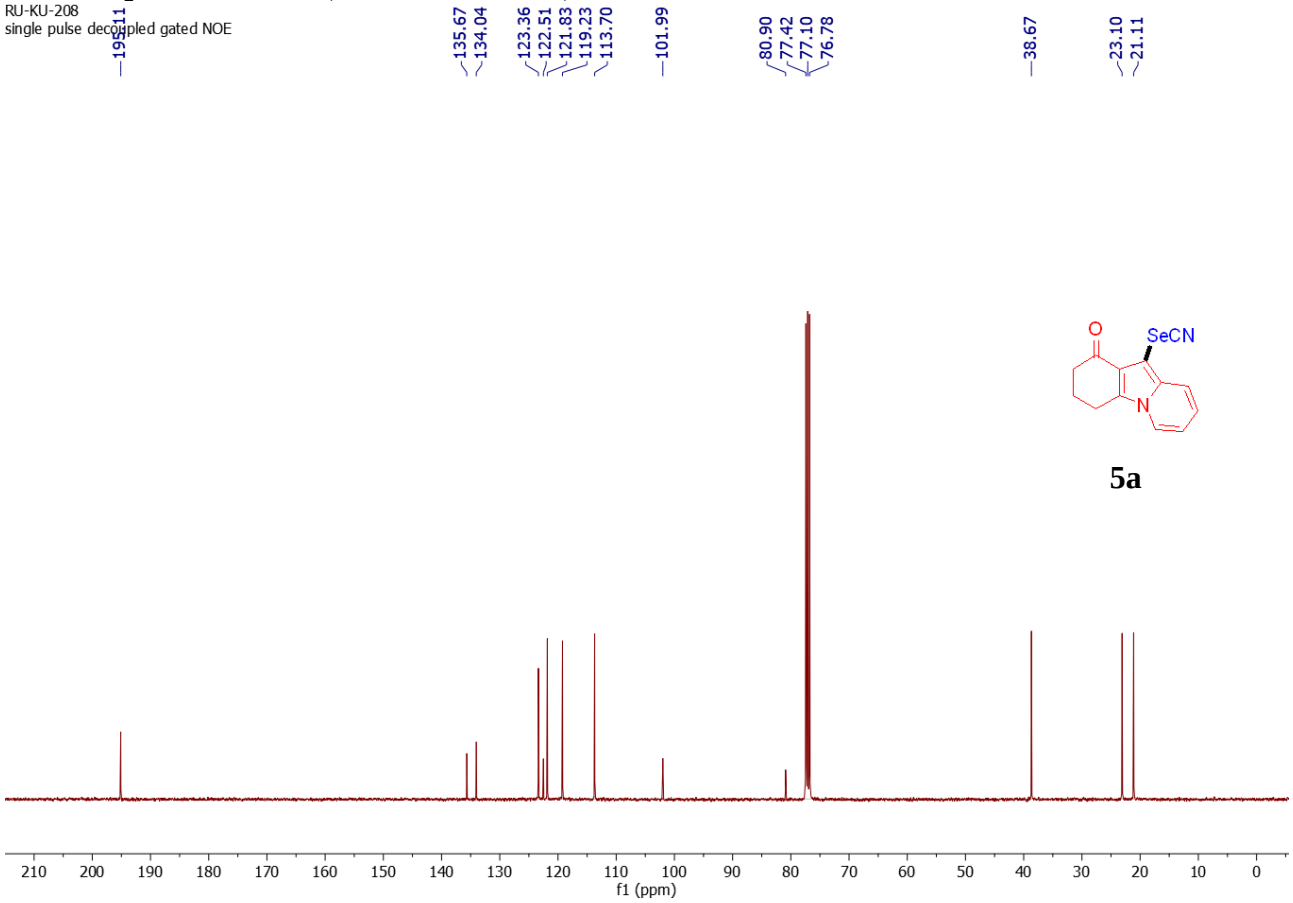
^{13}C NMR spectrum of 3k (100 MHz, $CDCl_3$)



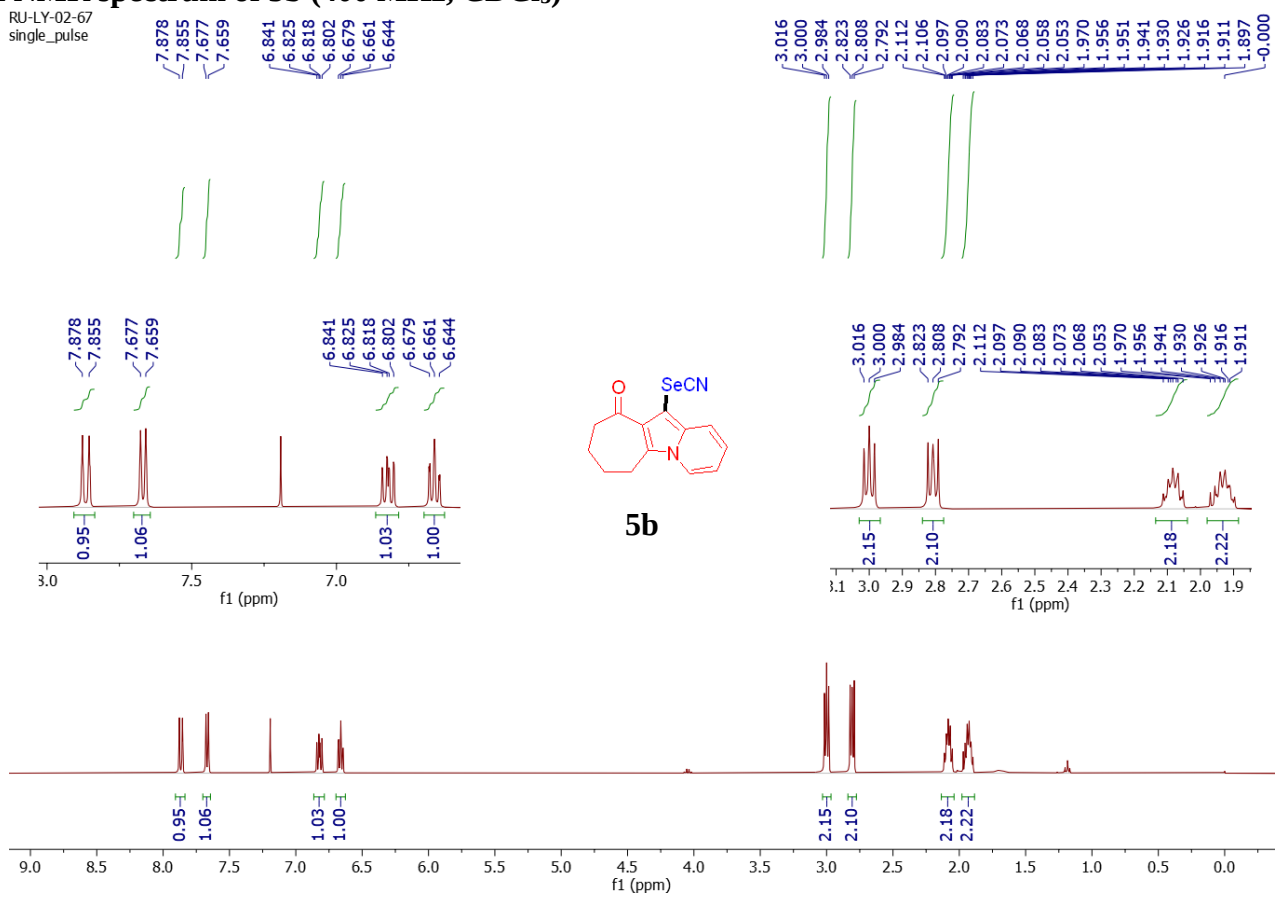
^{1}H NMR spectrum of 5a (400 MHz, $CDCl_3$)



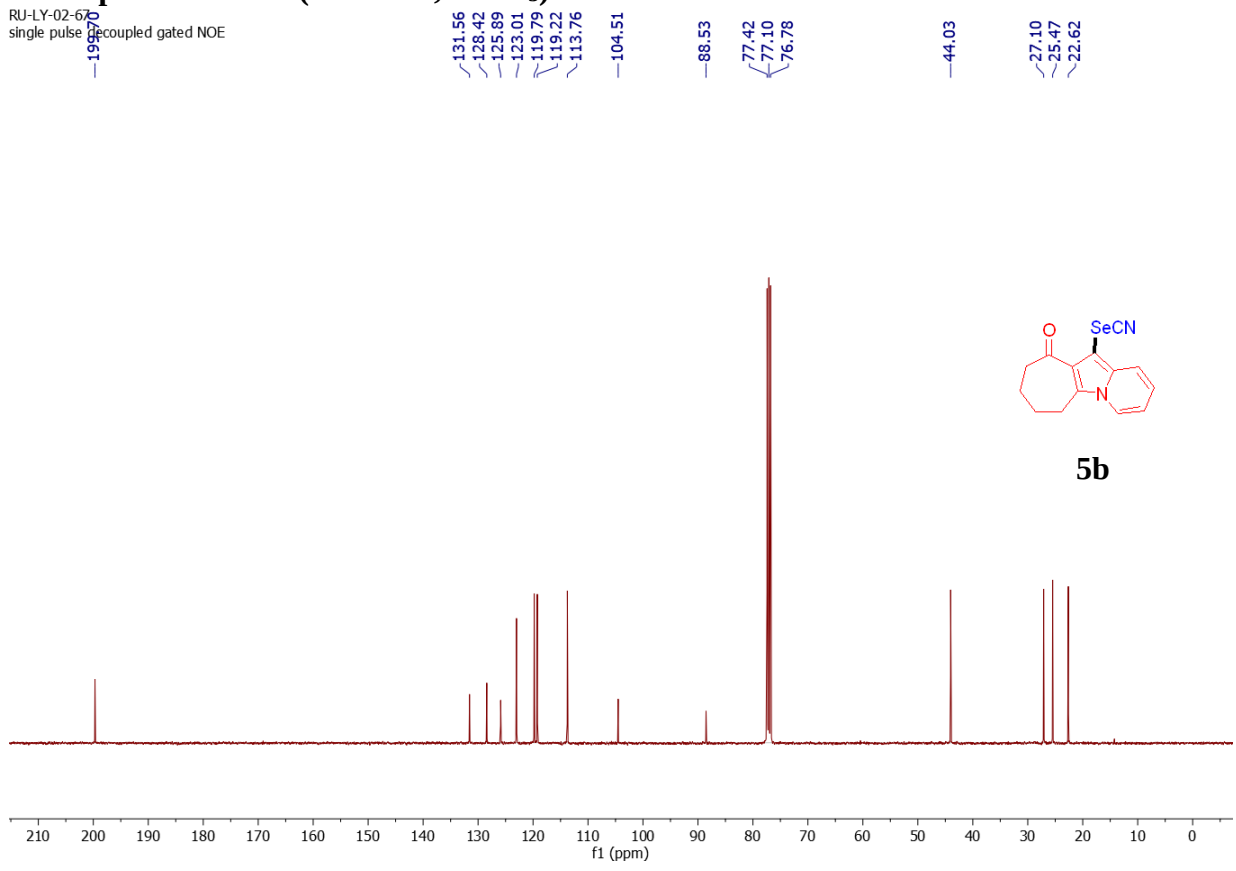
^{13}C NMR spectrum of 5a (100 MHz, $CDCl_3$)



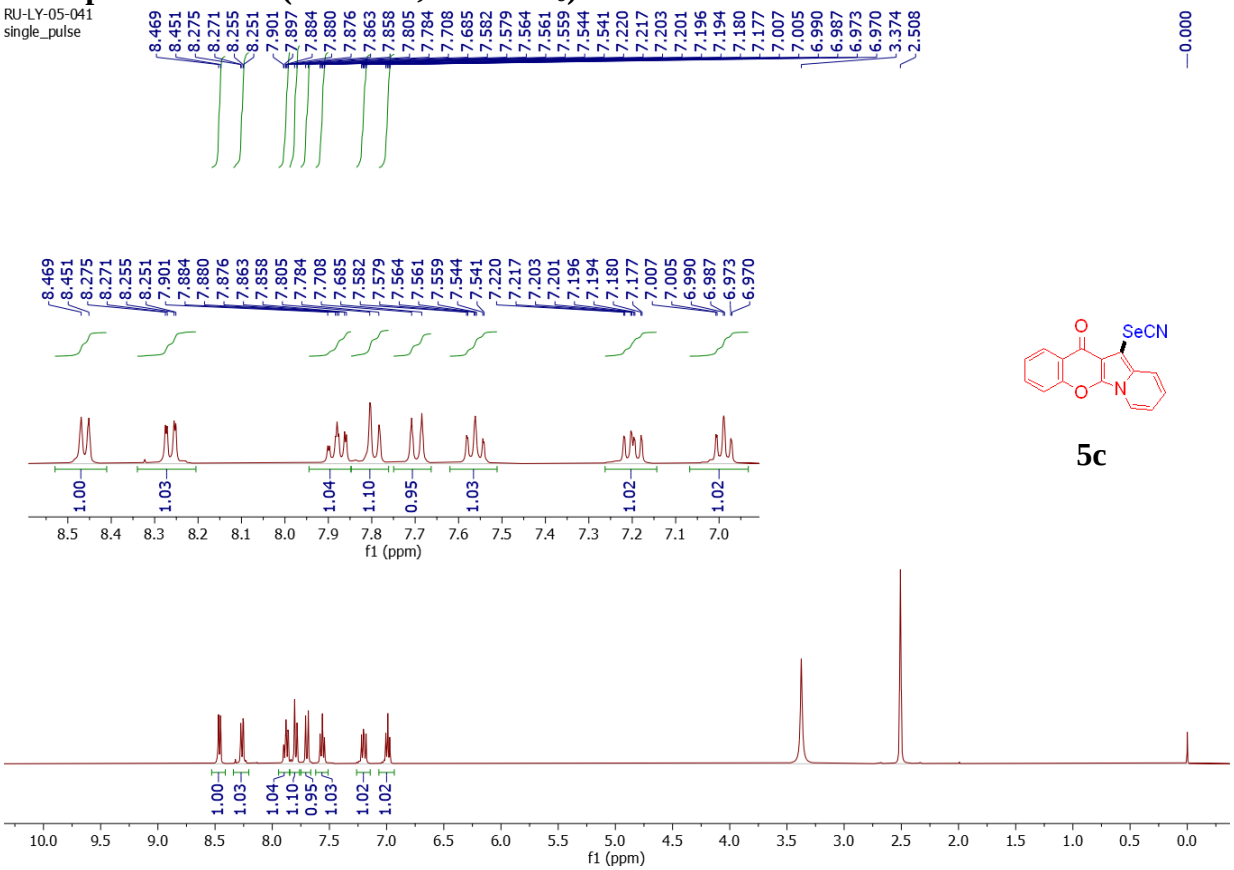
^{1}H NMR spectrum of 5b (400 MHz, $CDCl_3$)



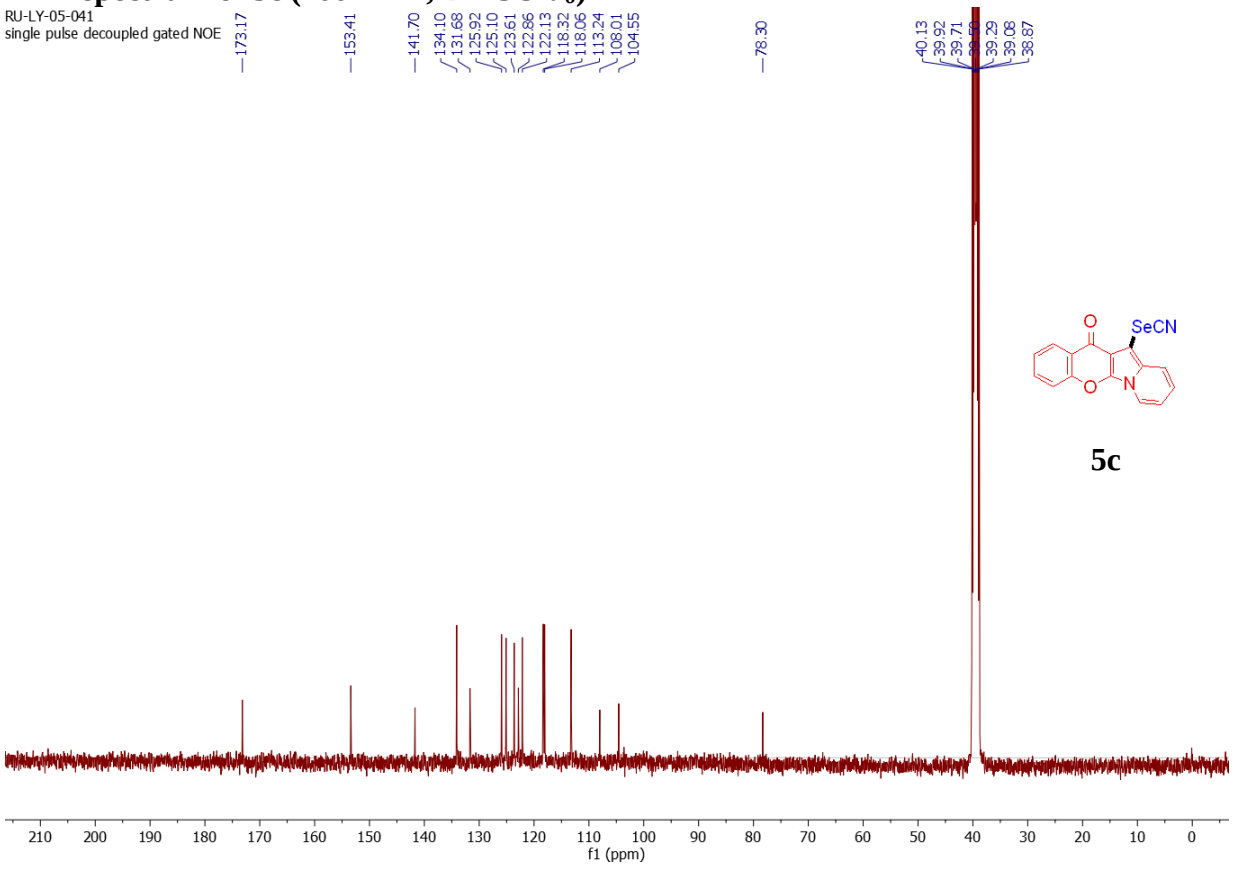
^{13}C NMR spectrum of 5b (100 MHz, $CDCl_3$)



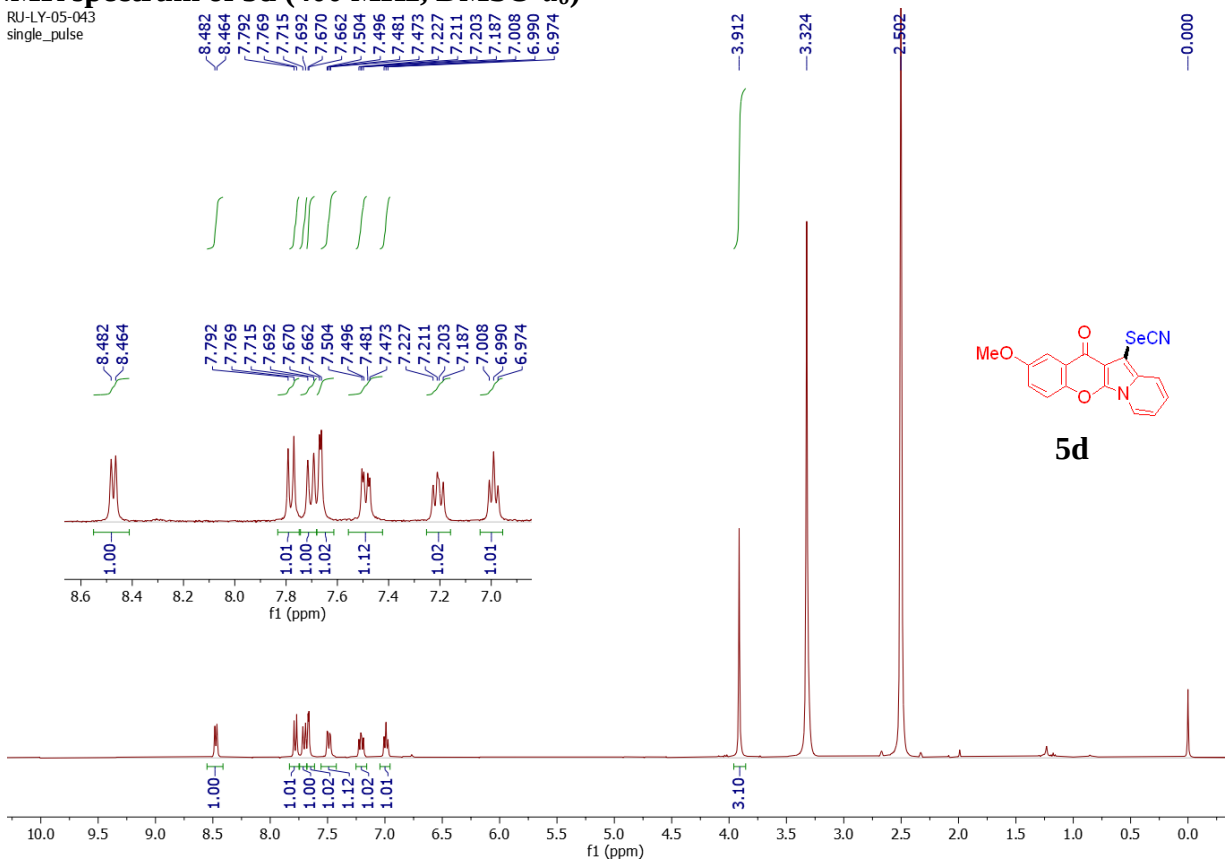
^{1}H NMR spectrum of 5c (400 MHz, DMSO-d_6)



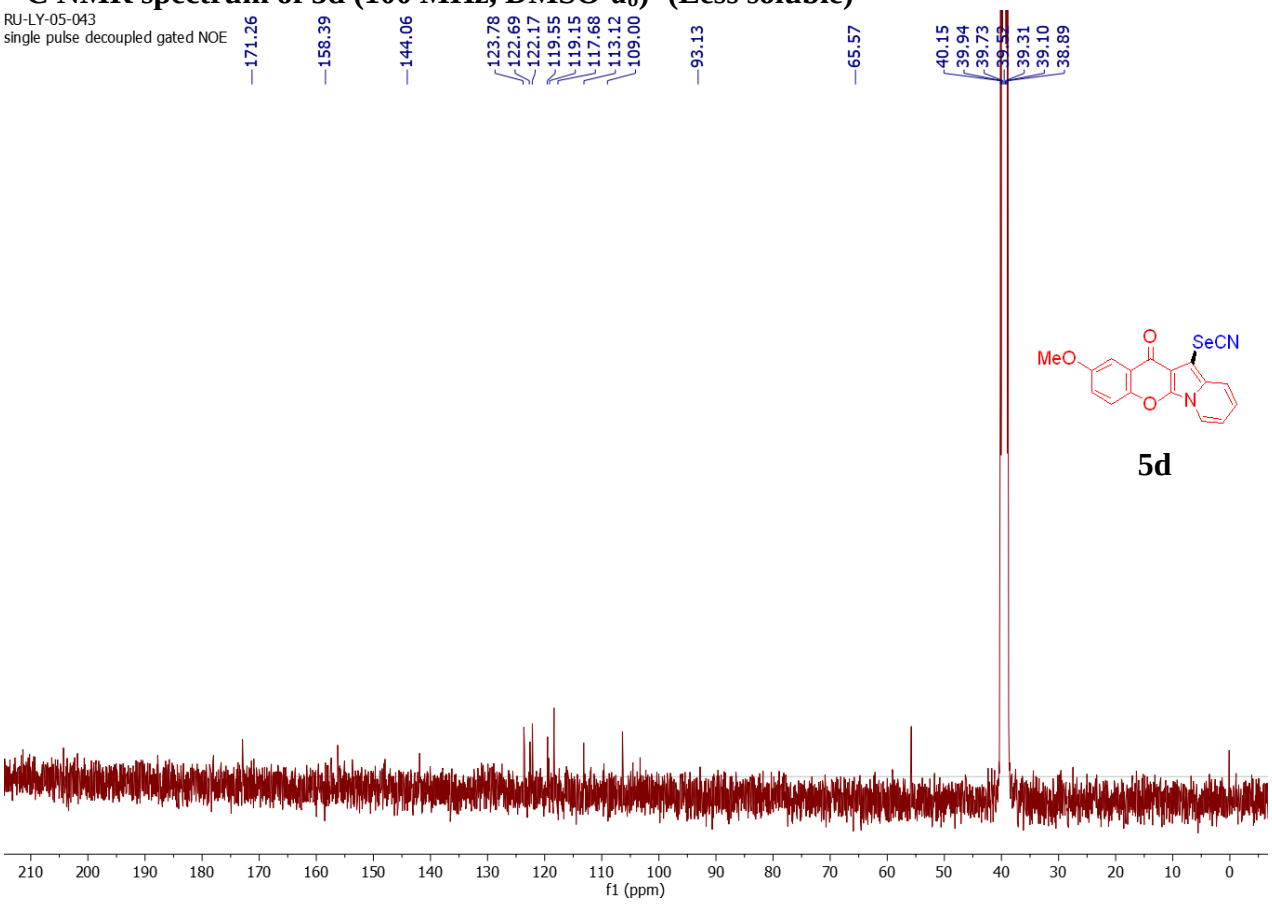
^{13}C NMR spectrum of 5c (100 MHz, DMSO-d_6)



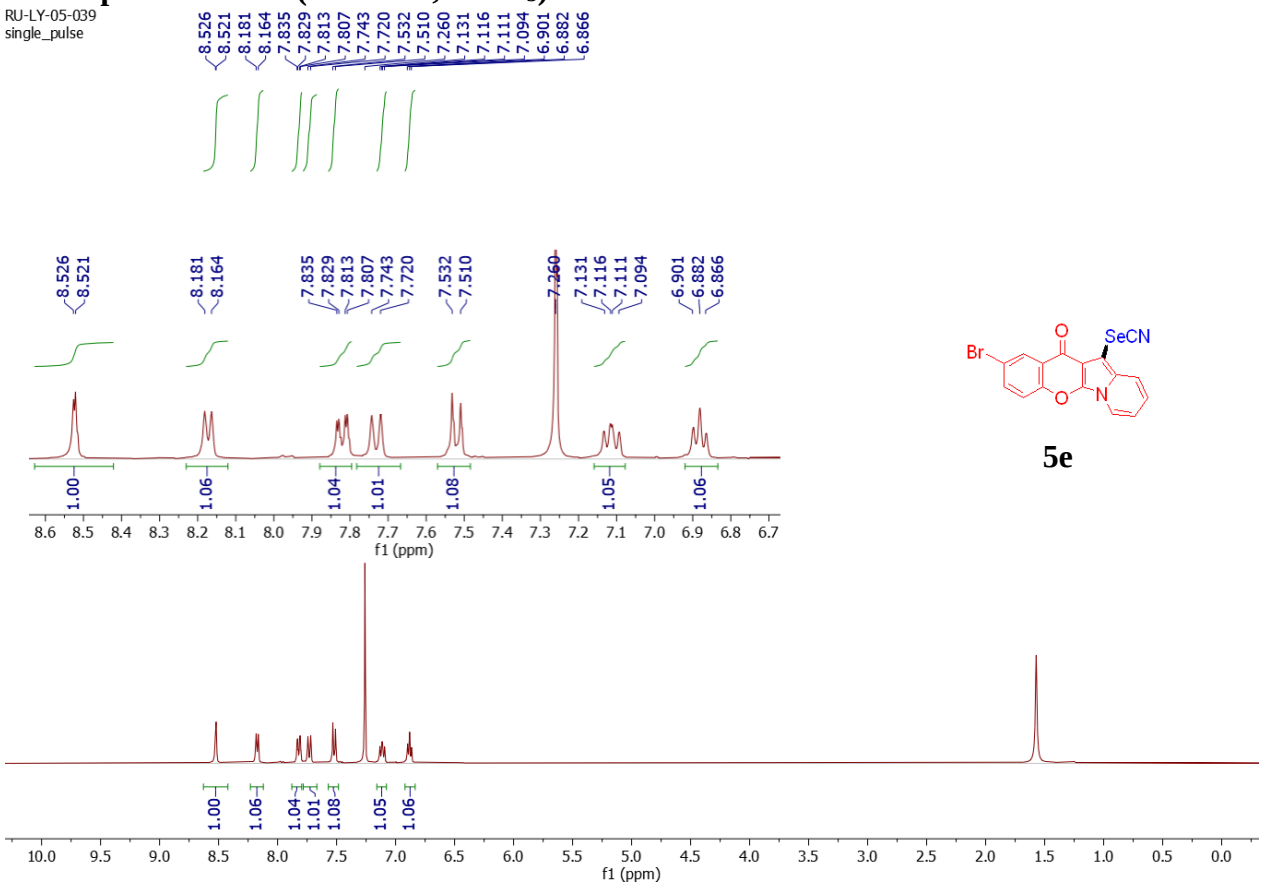
^{1}H NMR spectrum of 5d (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 5d (100 MHz, DMSO-d_6)- (Less soluble)

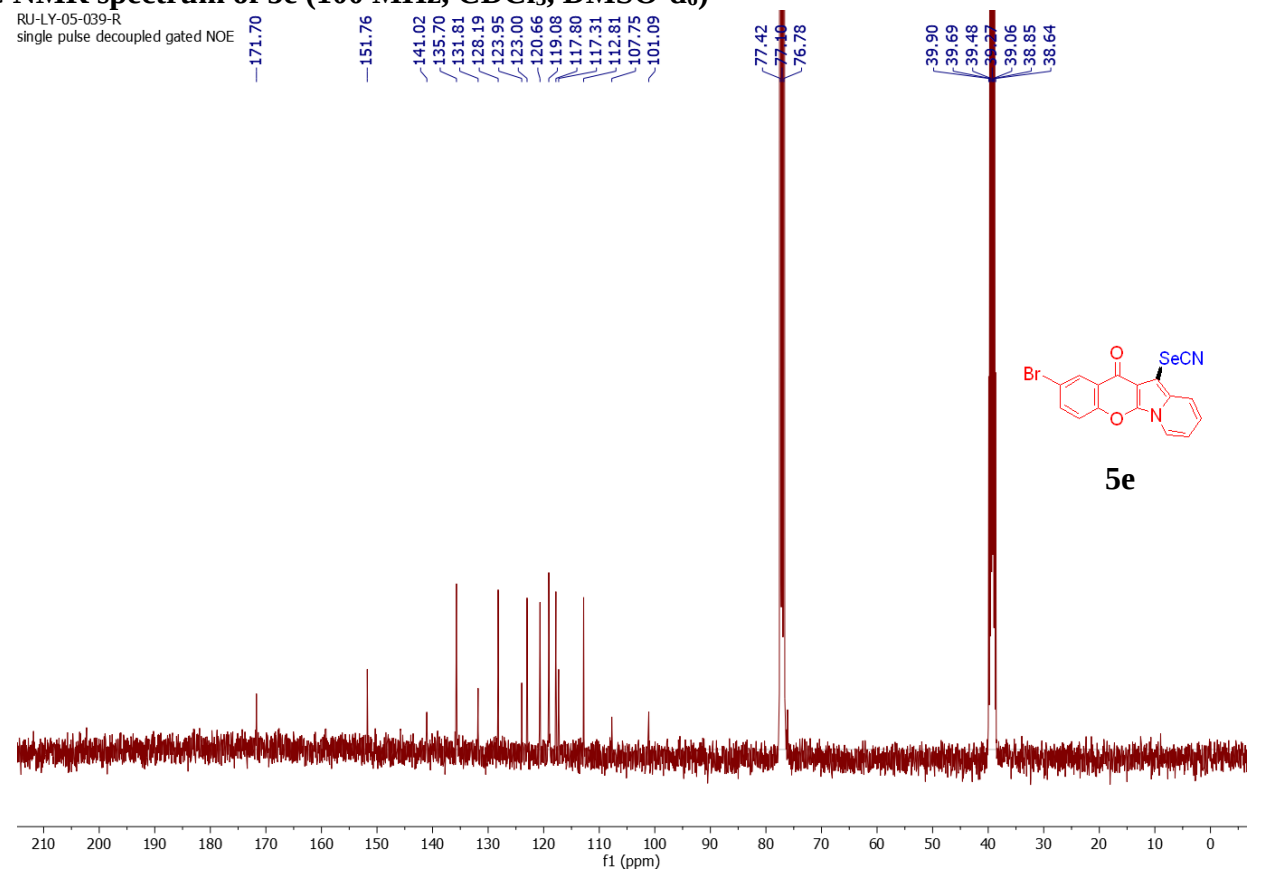


^{1}H NMR spectrum of 5e (400 MHz, $CDCl_3$)



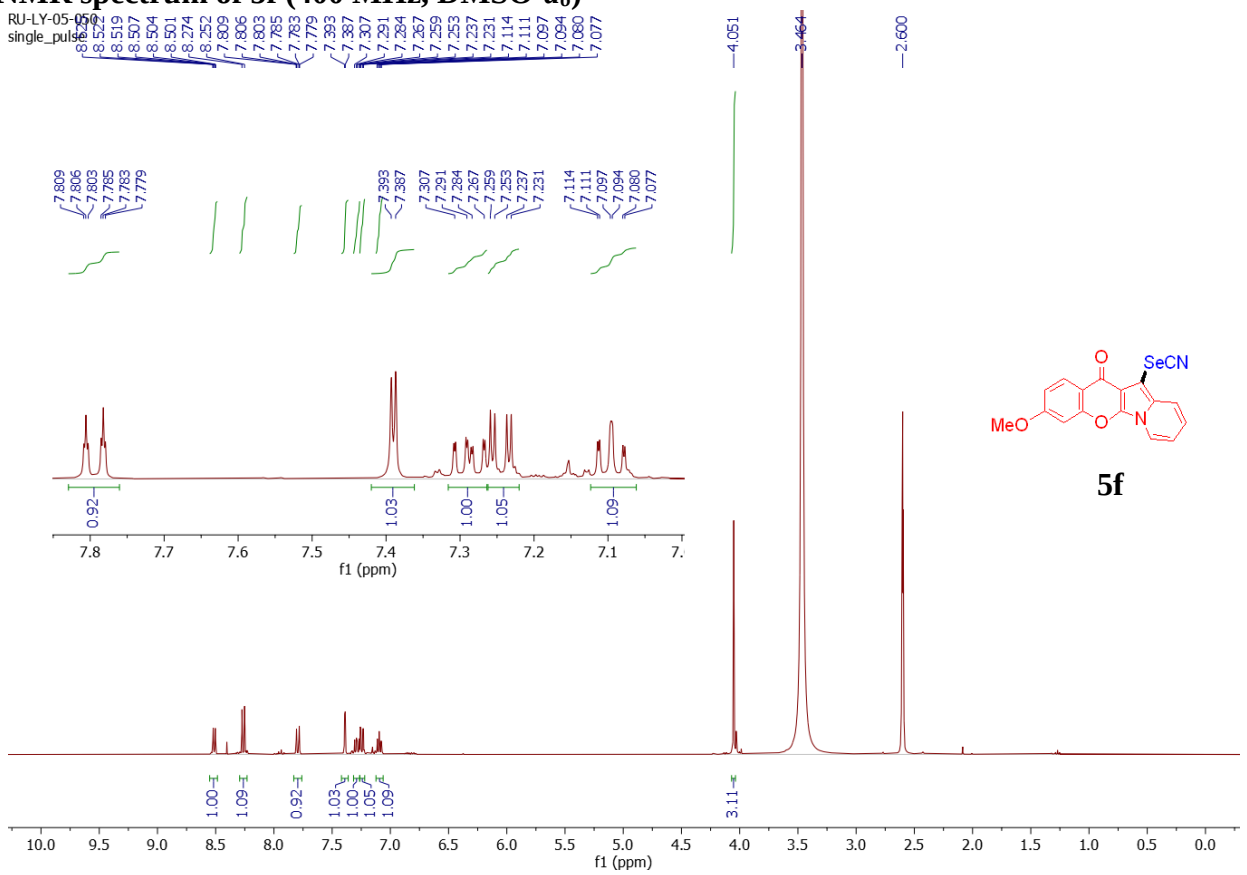
5e

^{13}C NMR spectrum of 5e (100 MHz, $CDCl_3$, DMSO-d_6)



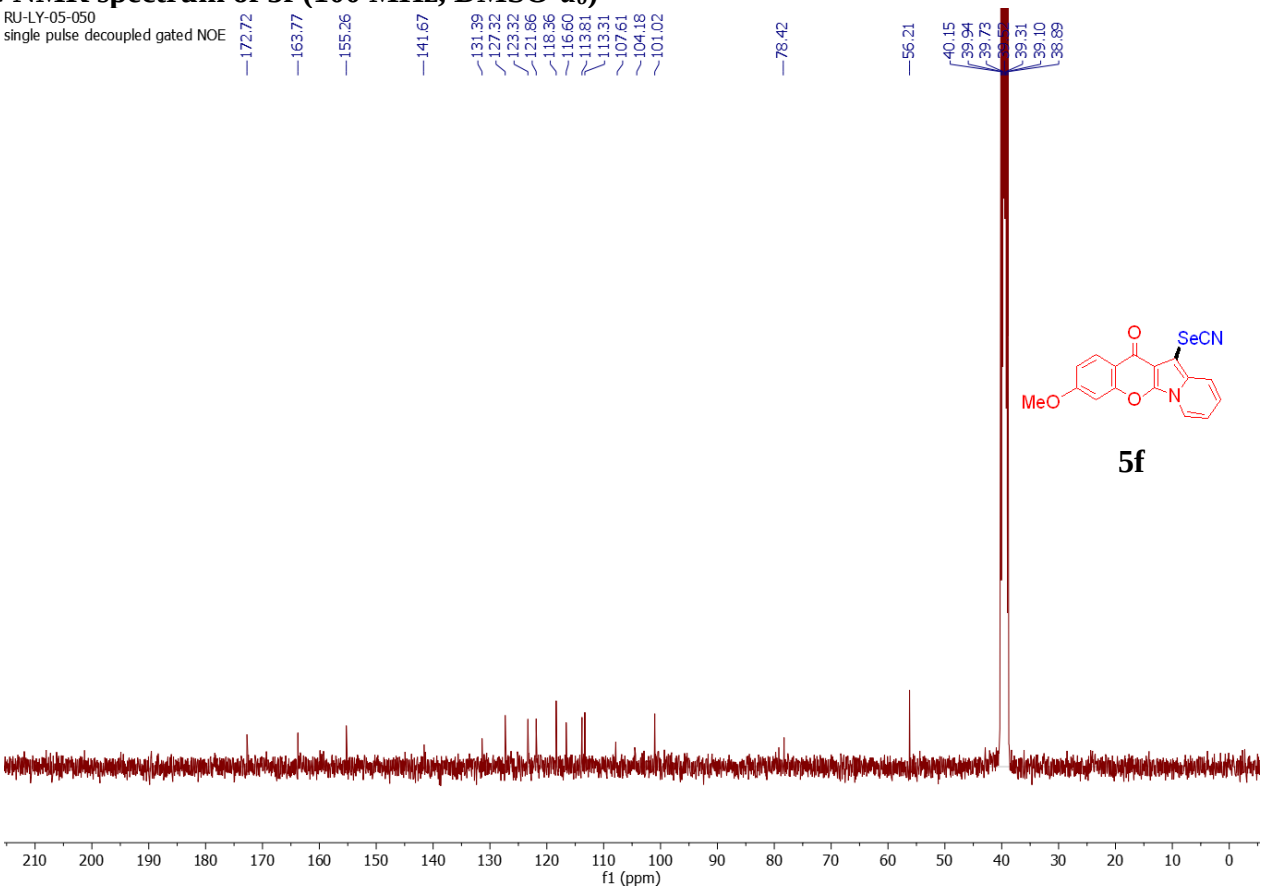
5e

^{1}H NMR spectrum of 5f (400 MHz, DMSO-d_6)



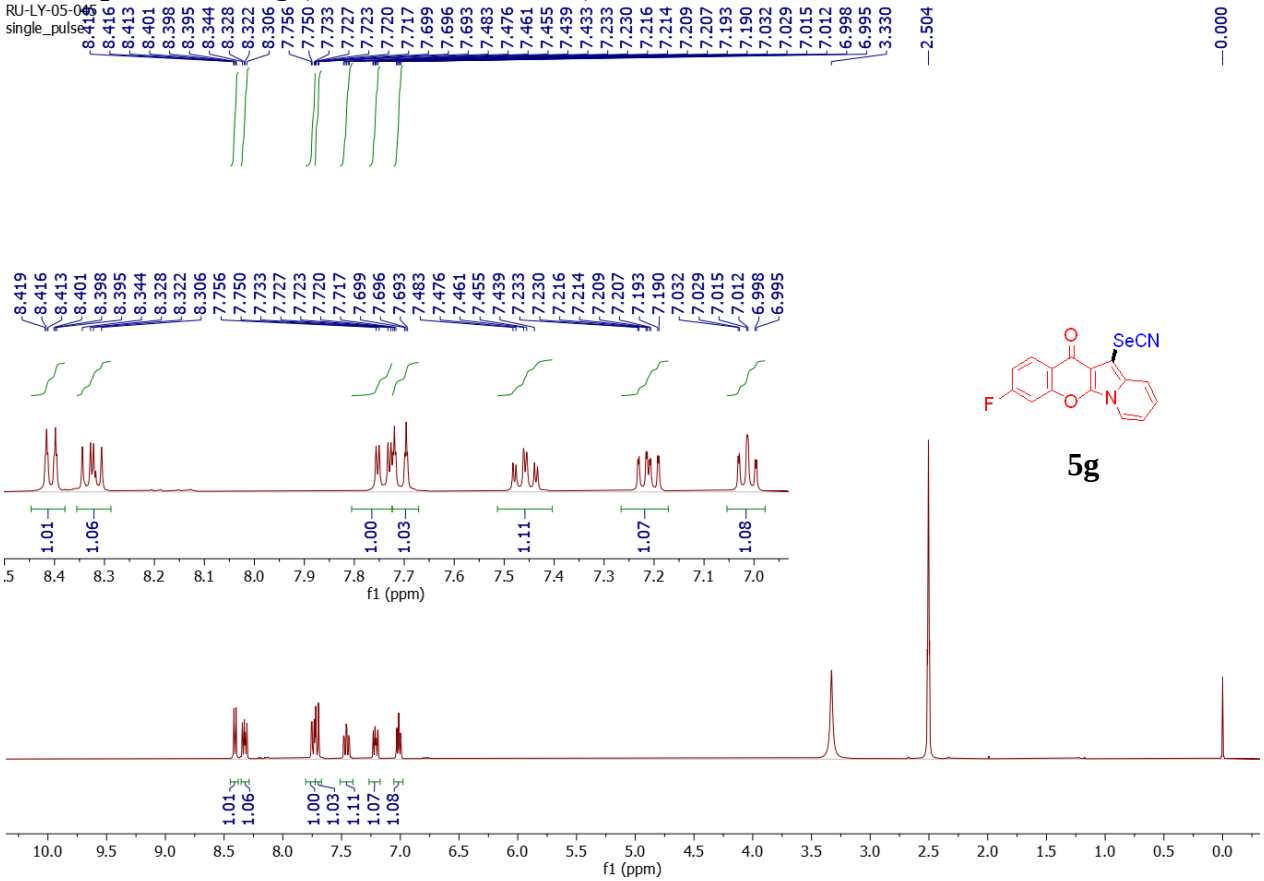
5f

^{13}C NMR spectrum of 5f (100 MHz, DMSO-d_6)

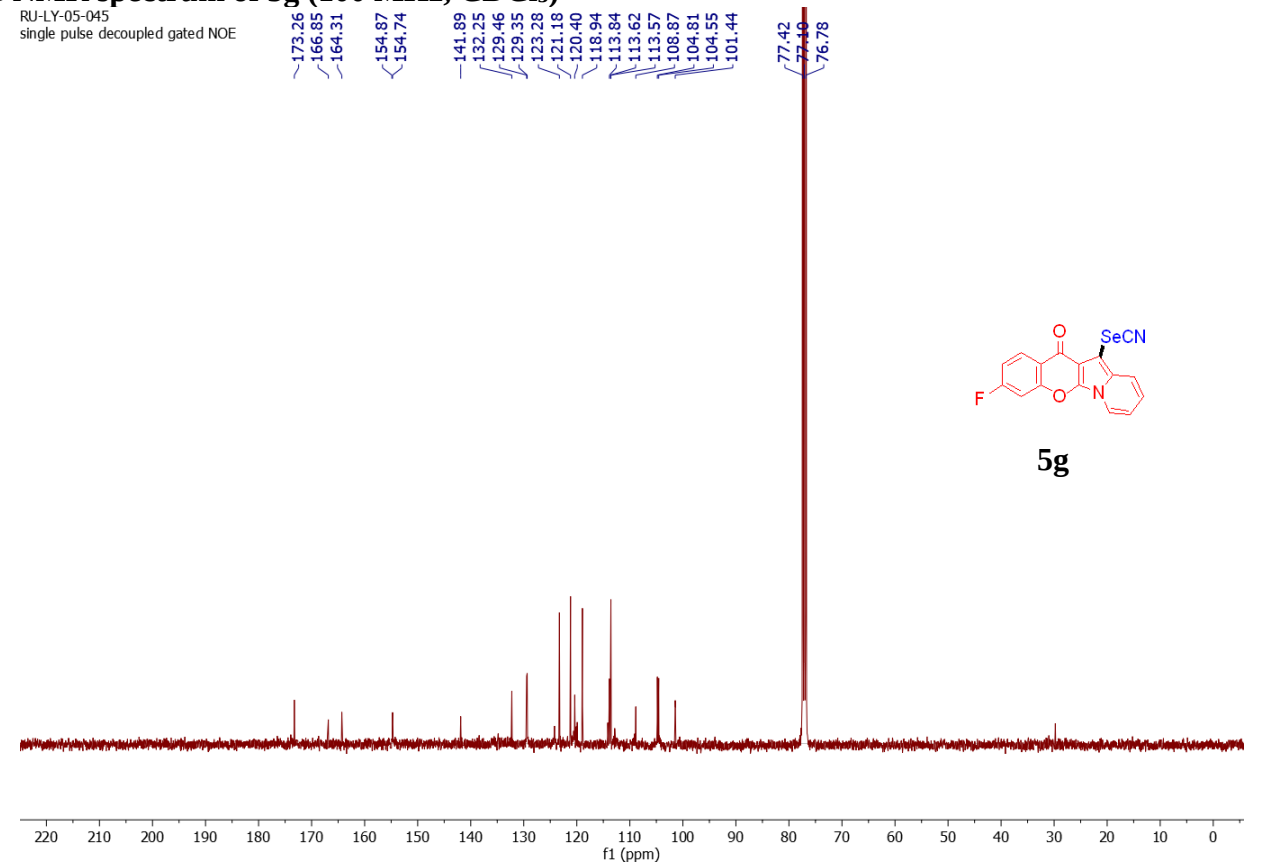


5f

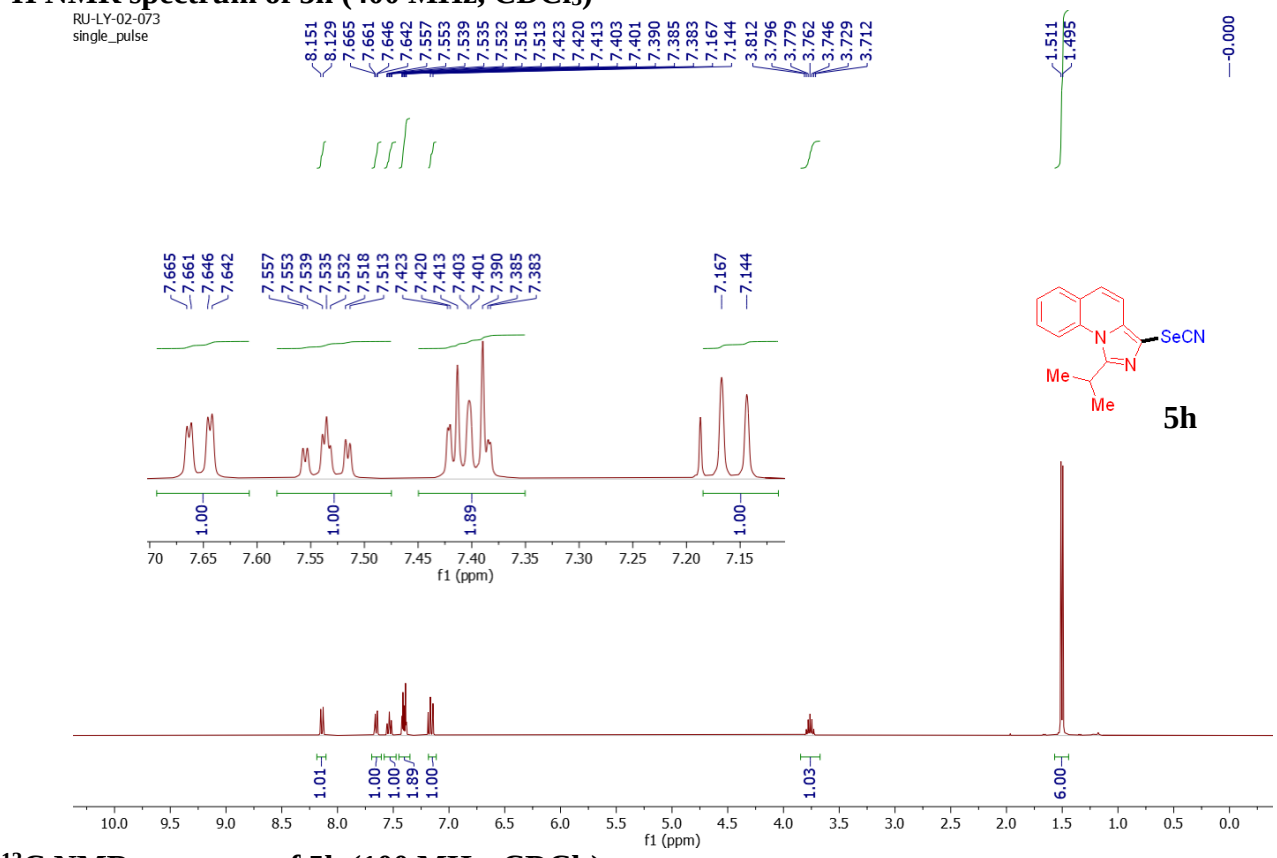
^{1}H NMR spectrum of 5g (400 MHz, DMSO-d_6)



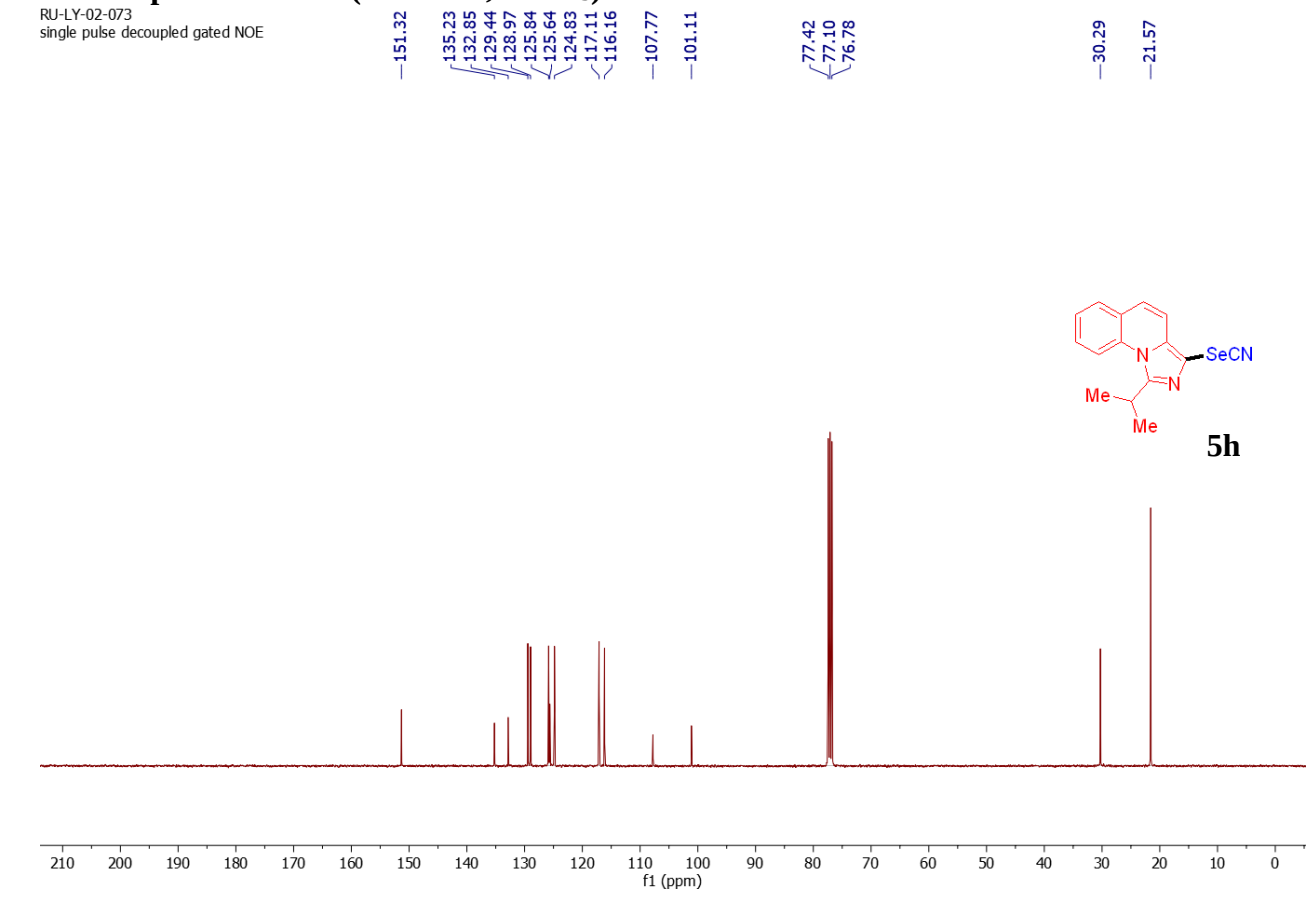
^{13}C NMR spectrum of 5g (100 MHz, $CDCl_3$)



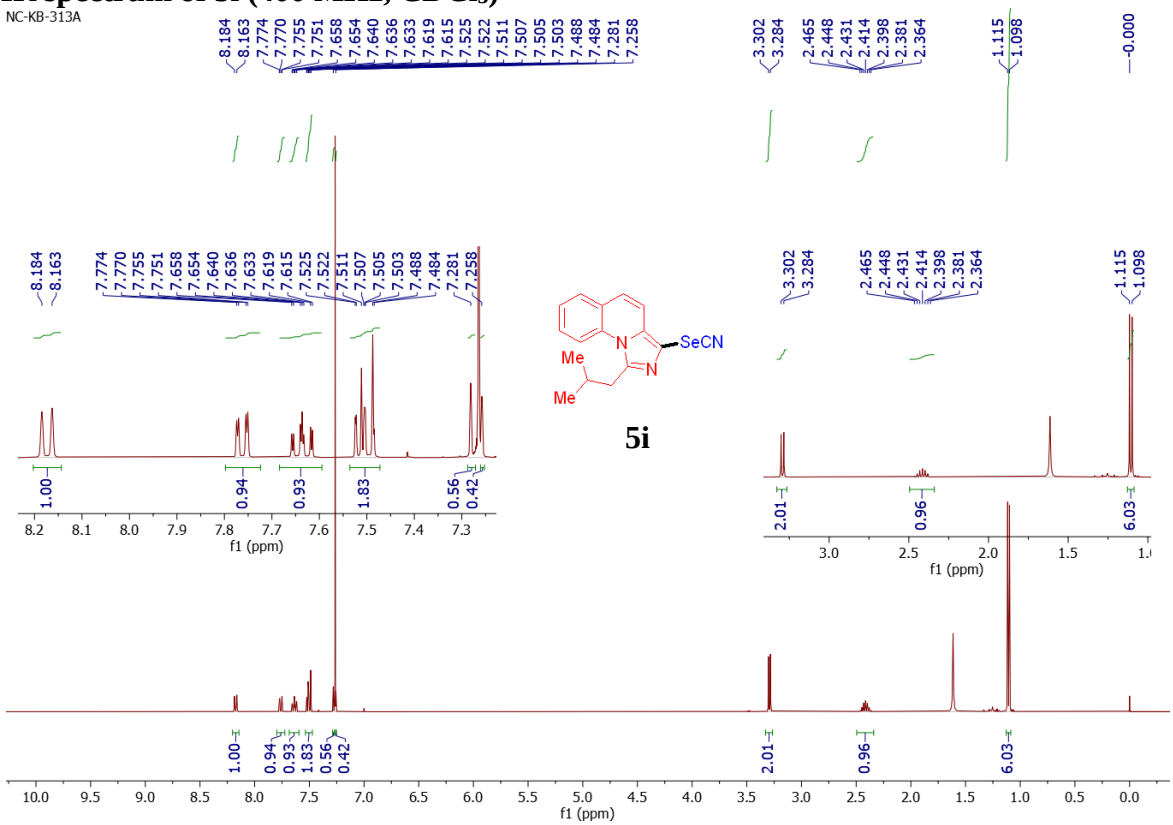
^{1}H NMR spectrum of 5h (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 5h (100 MHz, $CDCl_3$)

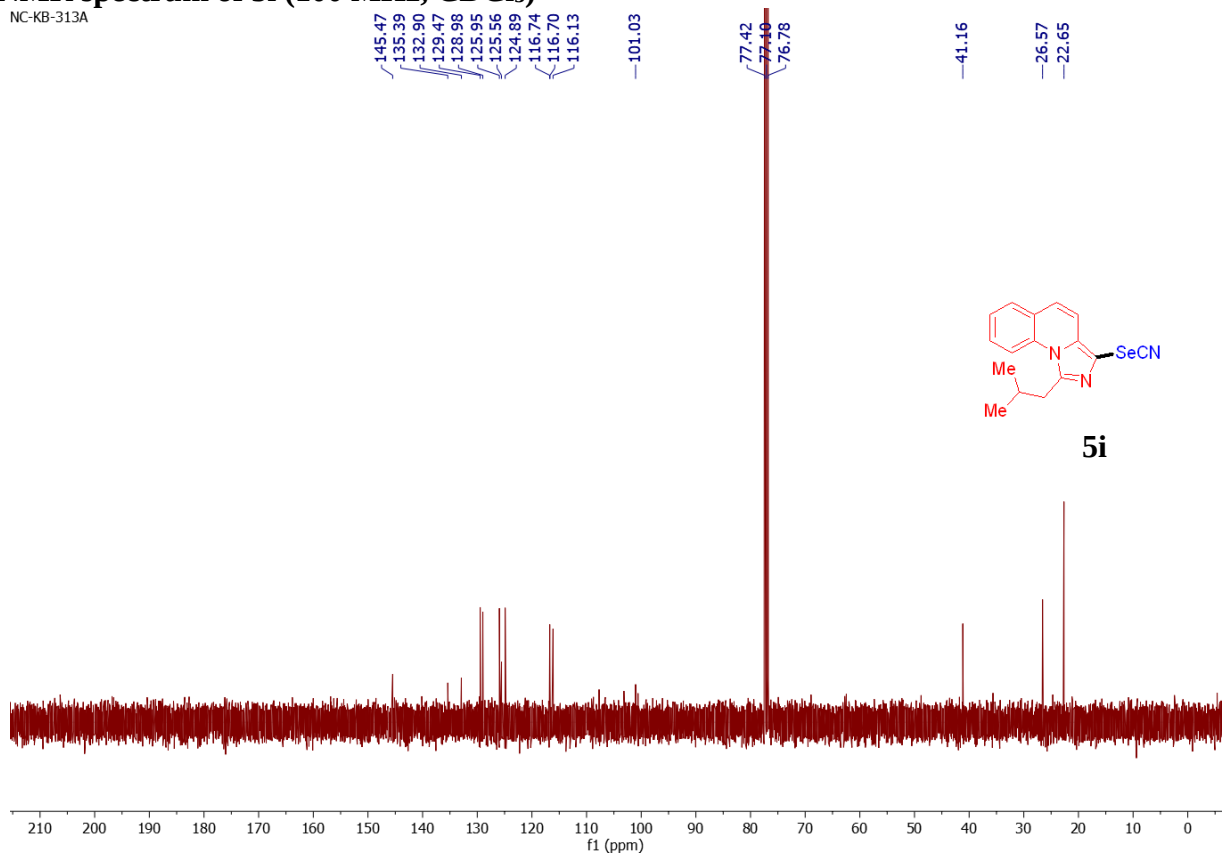


^{1}H NMR spectrum of 5i (400 MHz, $CDCl_3$)



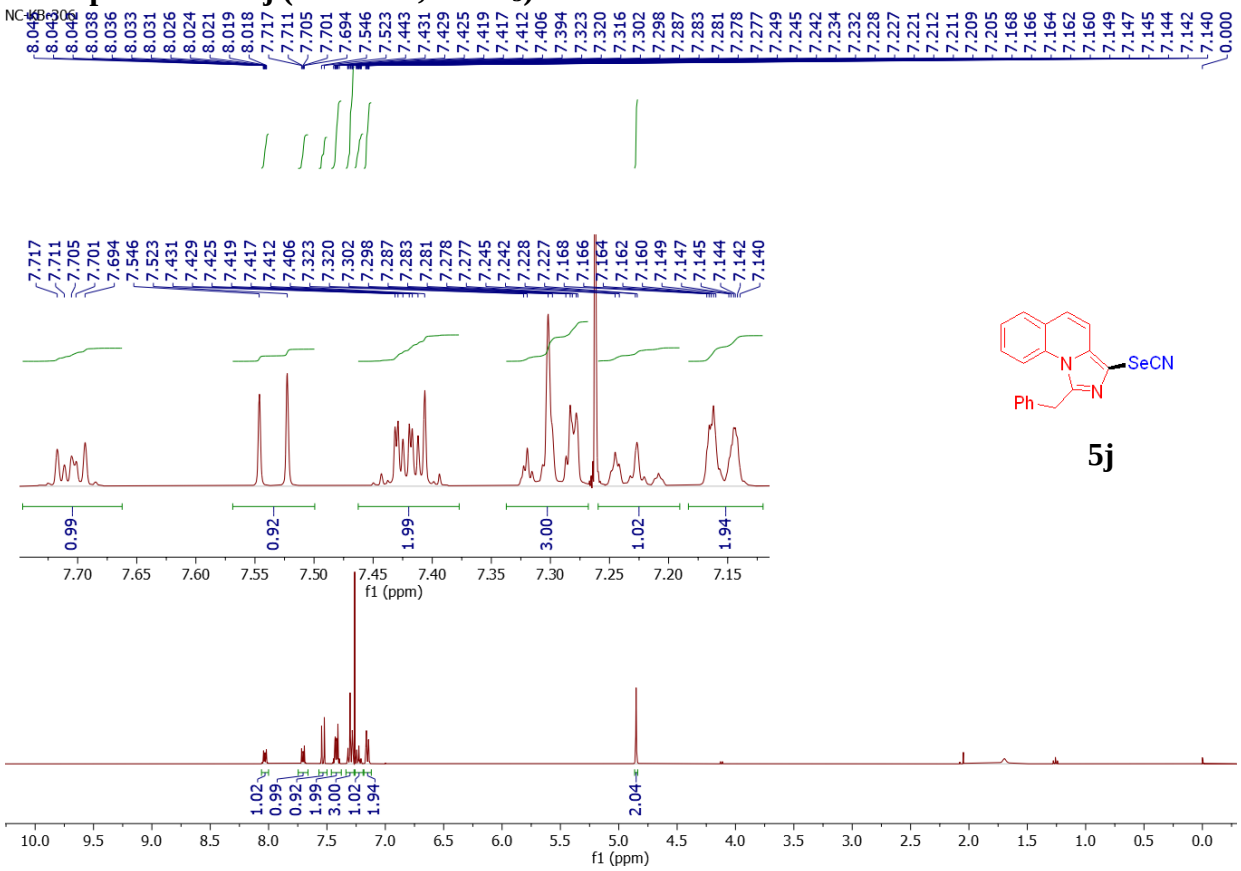
5i

^{13}C NMR spectrum of 5i (100 MHz, $CDCl_3$)



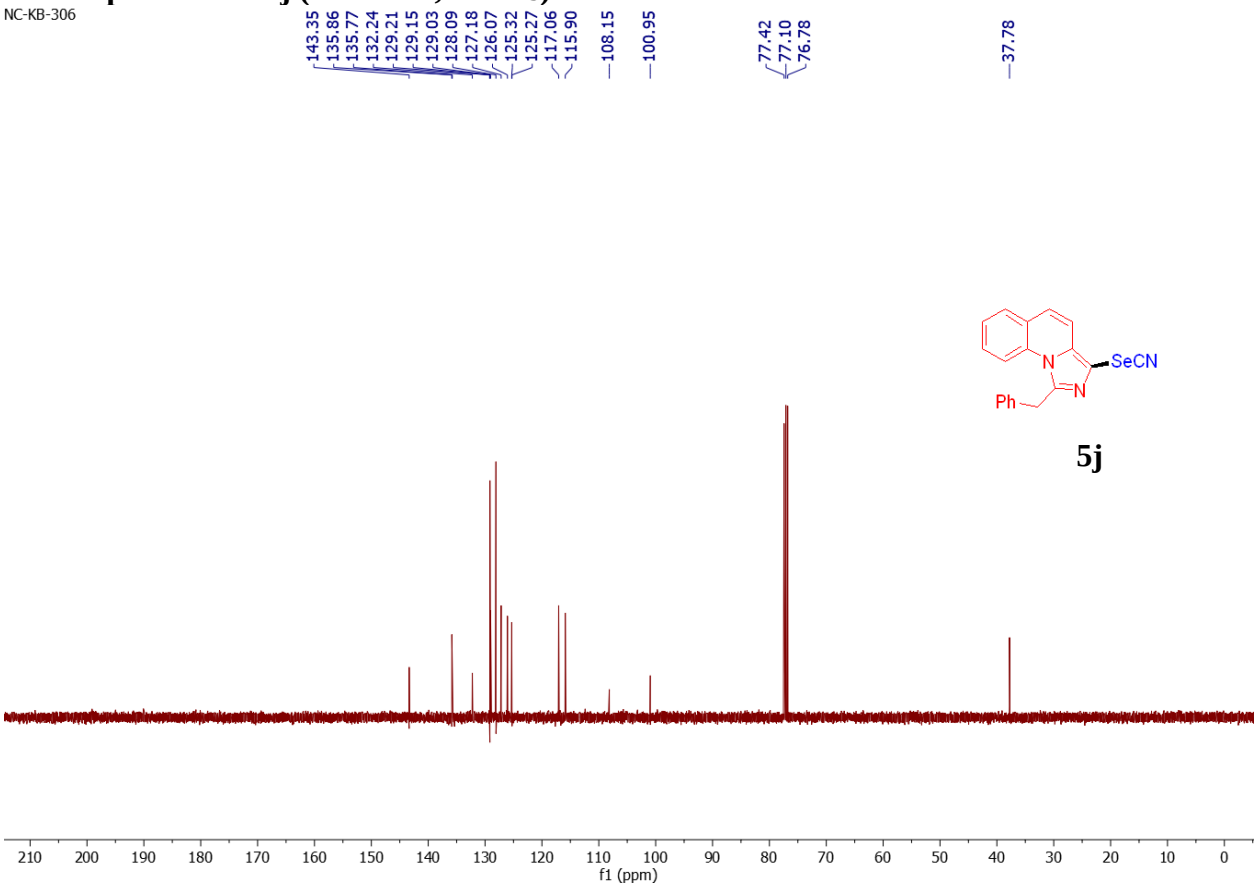
5i

^{1}H NMR spectrum of 5j (400 MHz, $CDCl_3$)



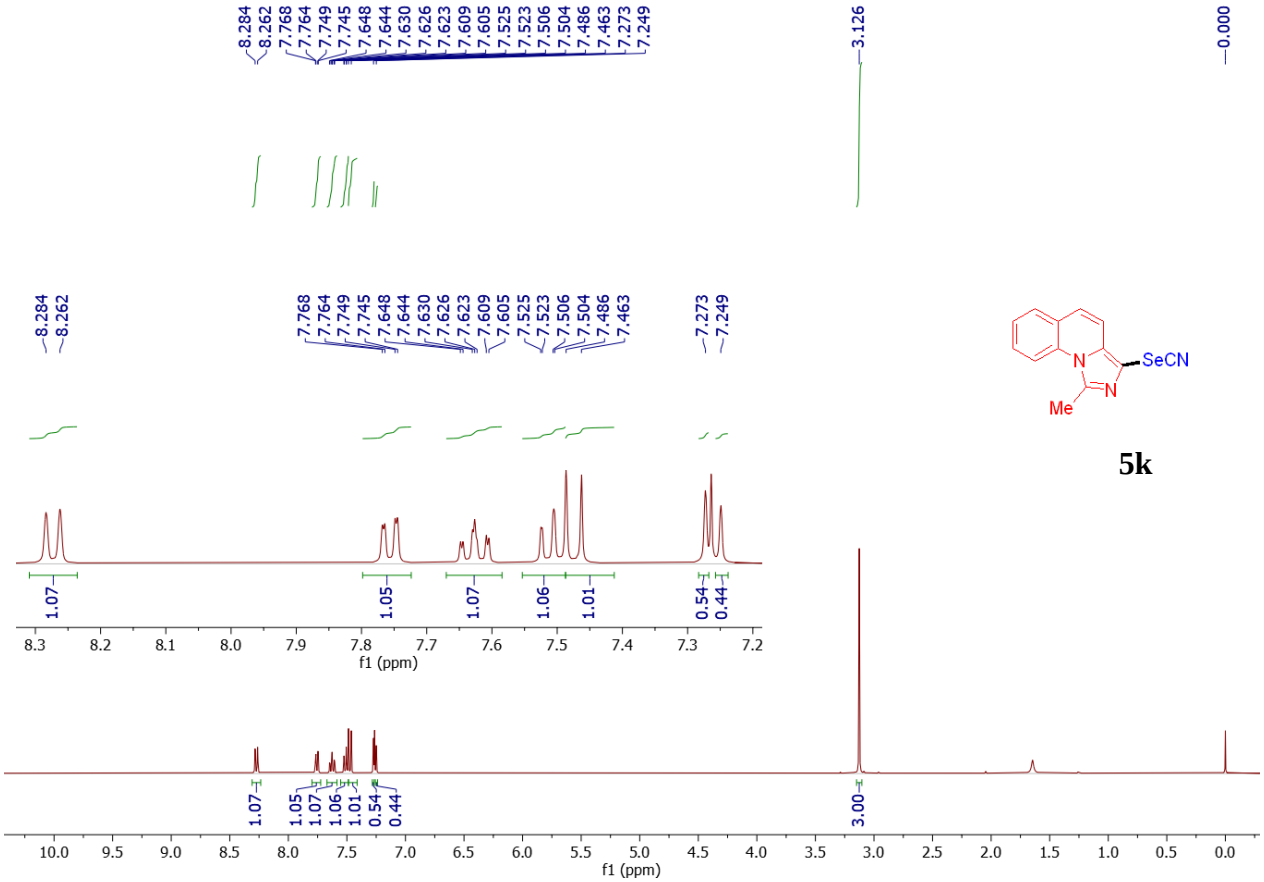
5j

^{13}C NMR spectrum of 5j (100 MHz, $CDCl_3$)



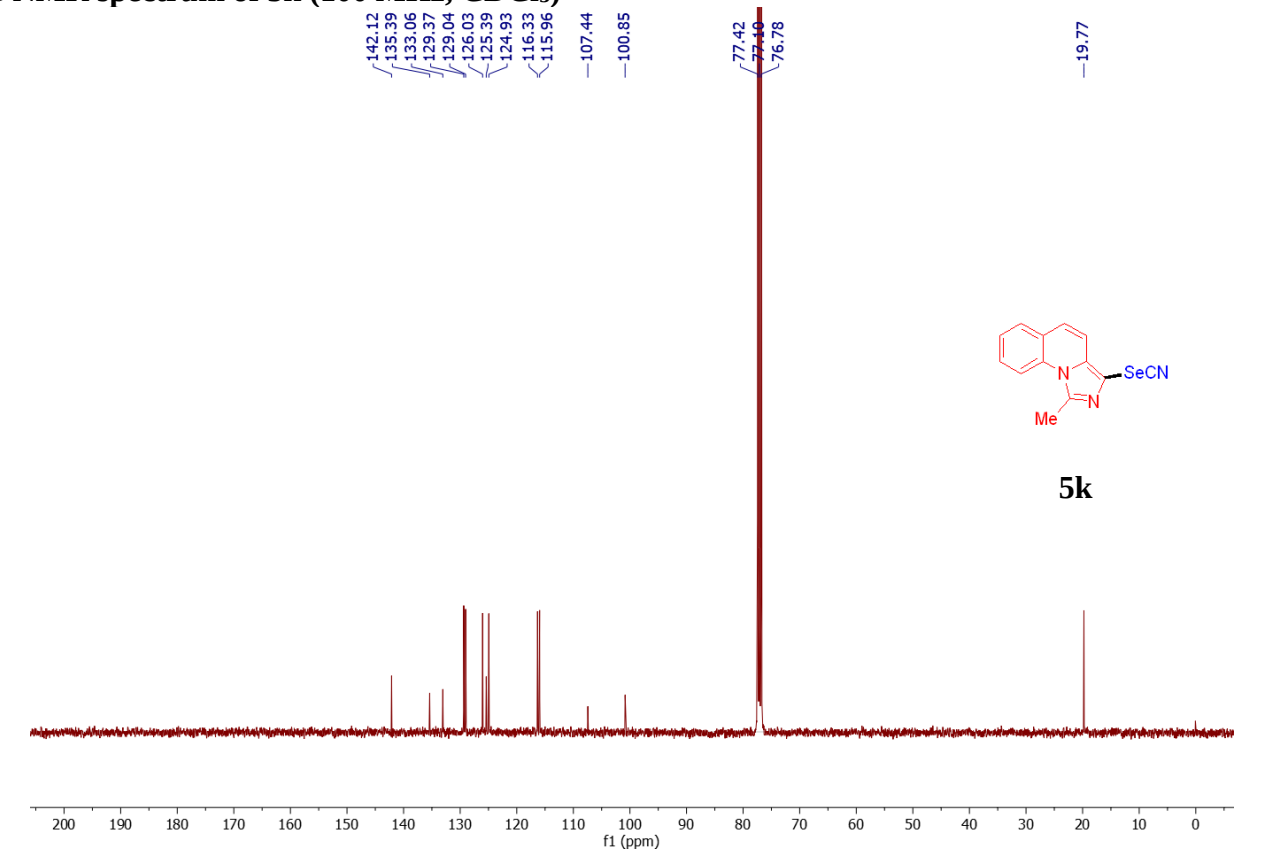
5j

^{1}H NMR spectrum of 5k (400 MHz, $CDCl_3$)



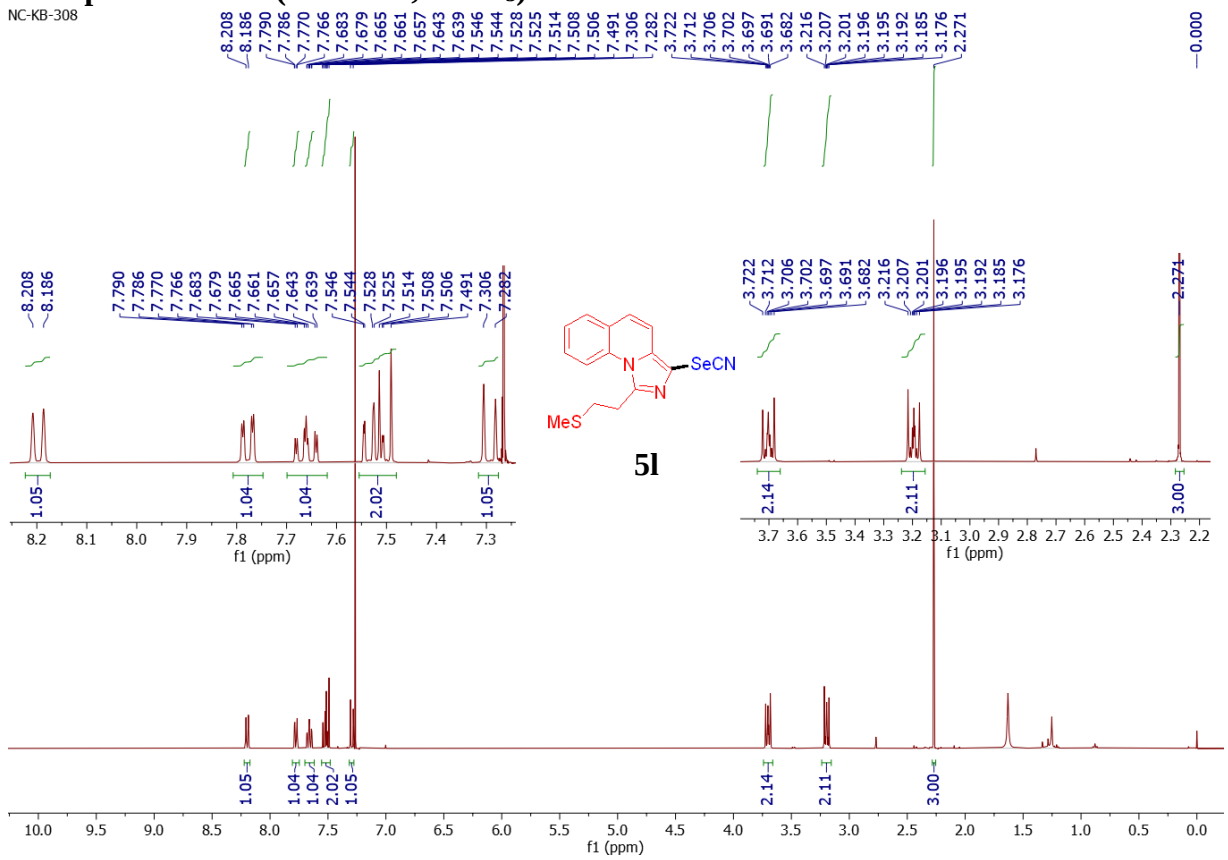
5k

^{13}C NMR spectrum of 5k (100 MHz, $CDCl_3$)

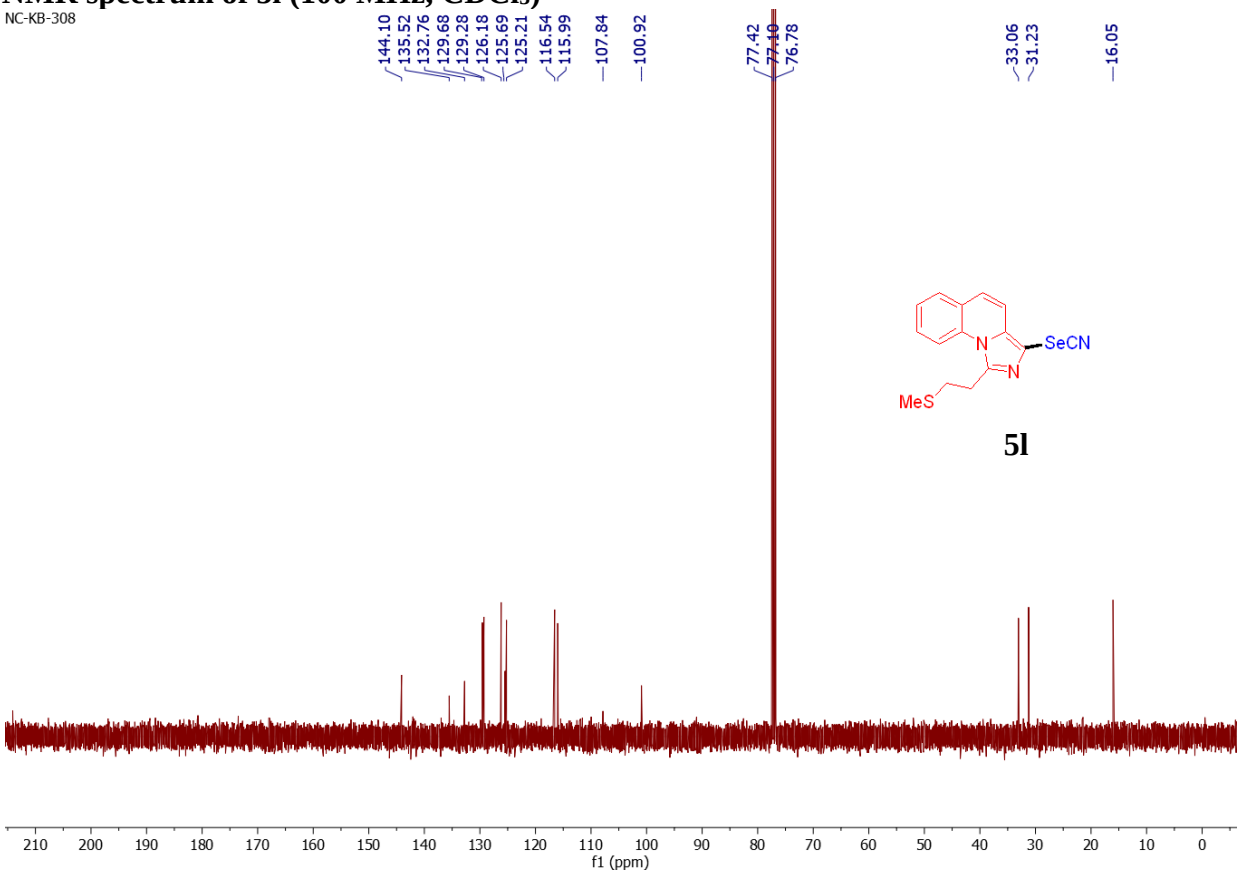


5k

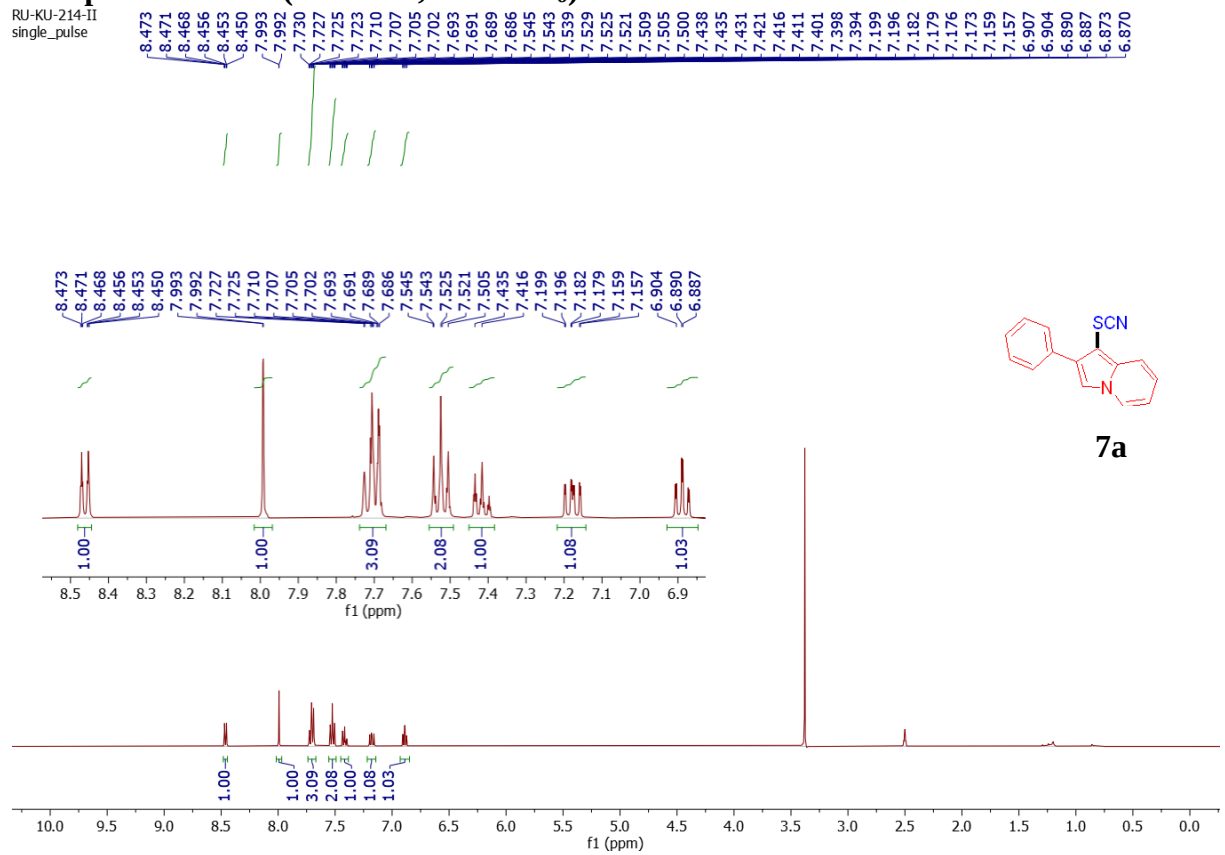
^{1}H NMR spectrum of 5l (400 MHz, $CDCl_3$)



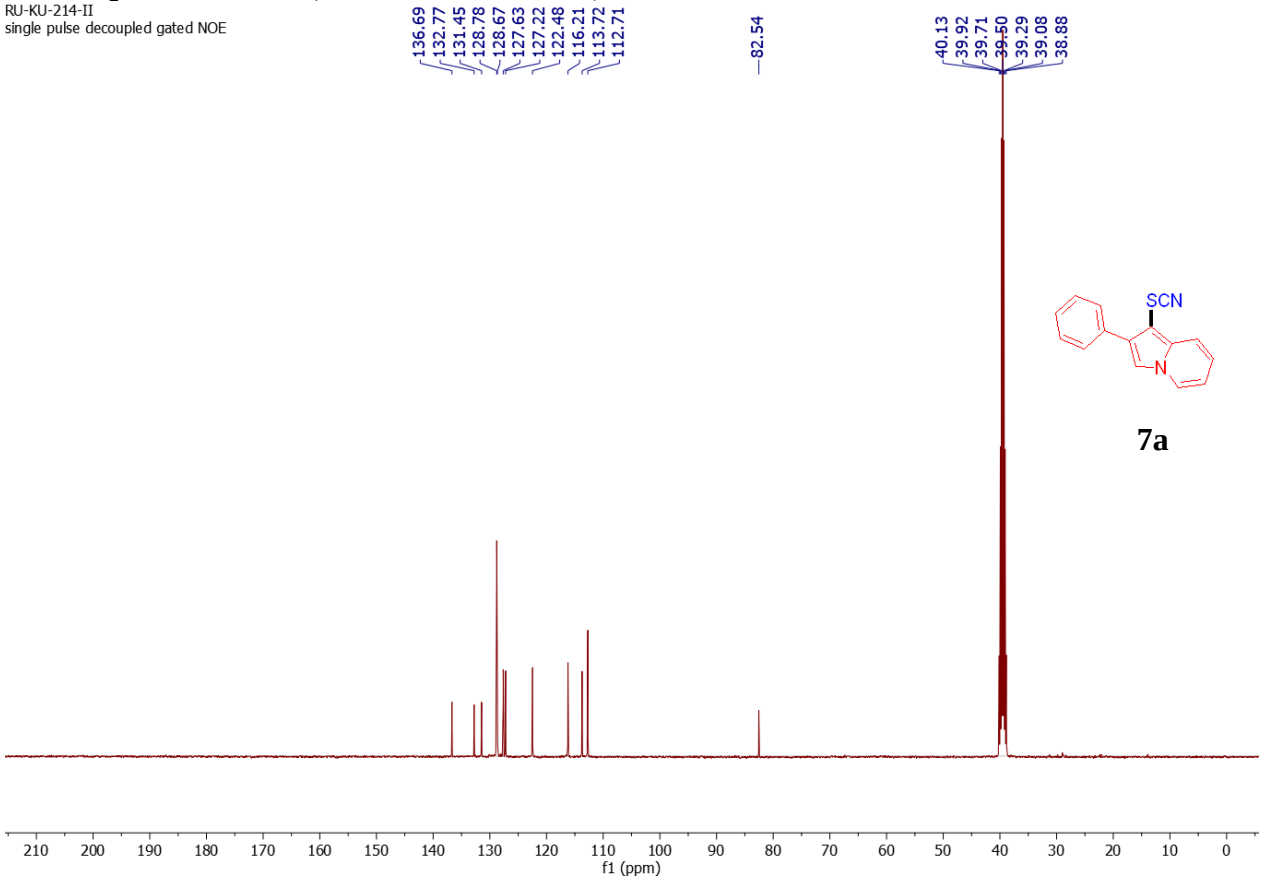
^{13}C NMR spectrum of 5l (100 MHz, $CDCl_3$)



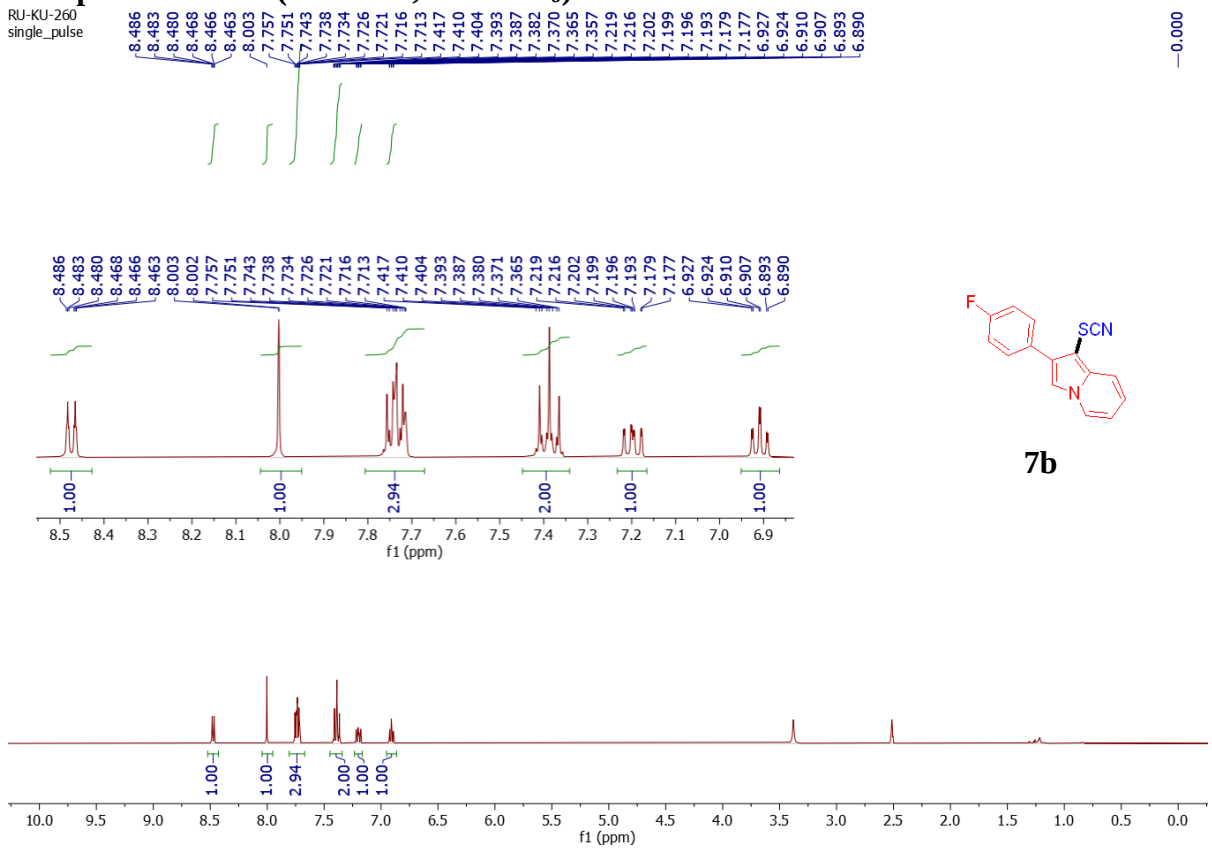
^{1}H NMR spectrum of 7a (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 7a (100 MHz, DMSO-d_6)

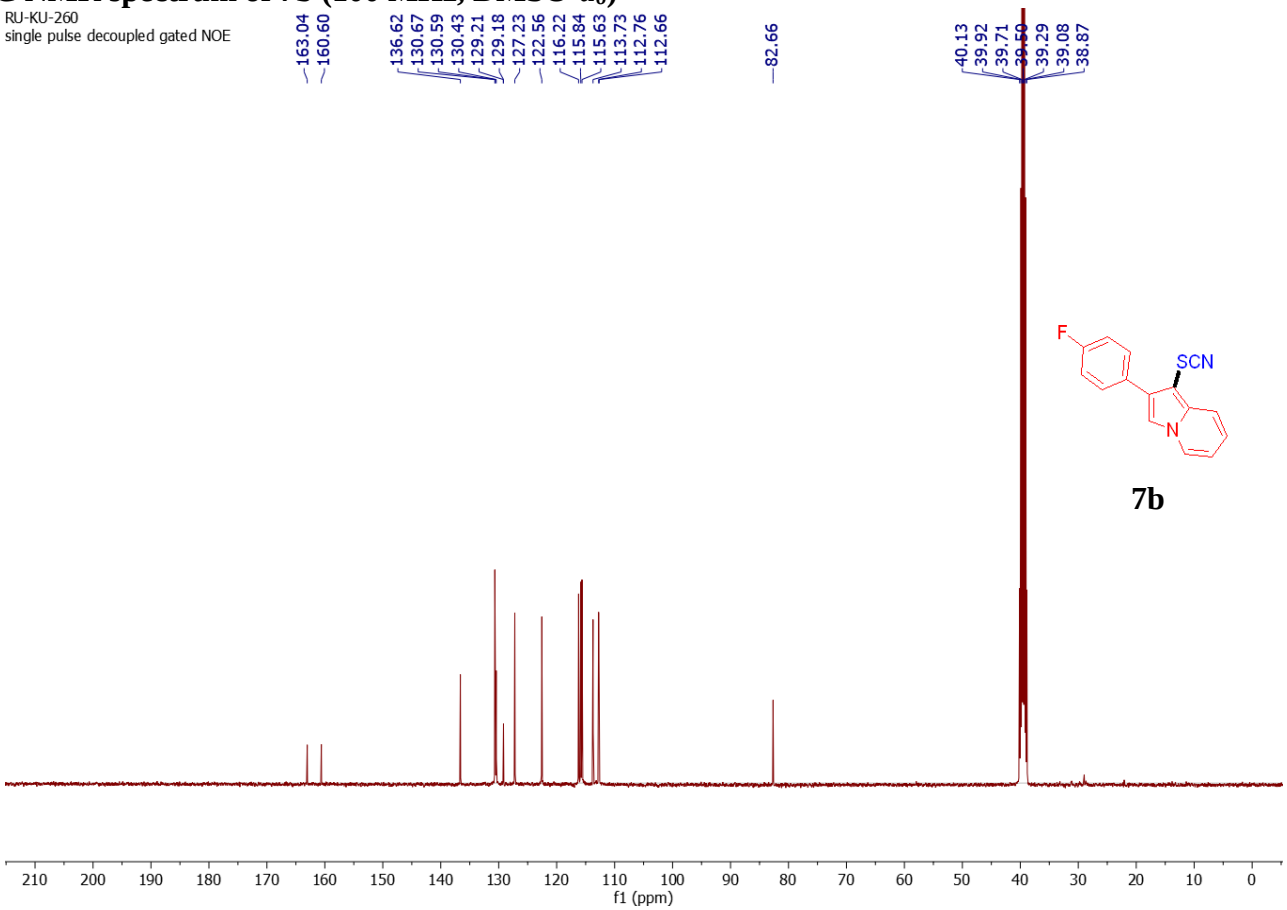


^{1}H NMR spectrum of 7b (400 MHz, DMSO-d_6)



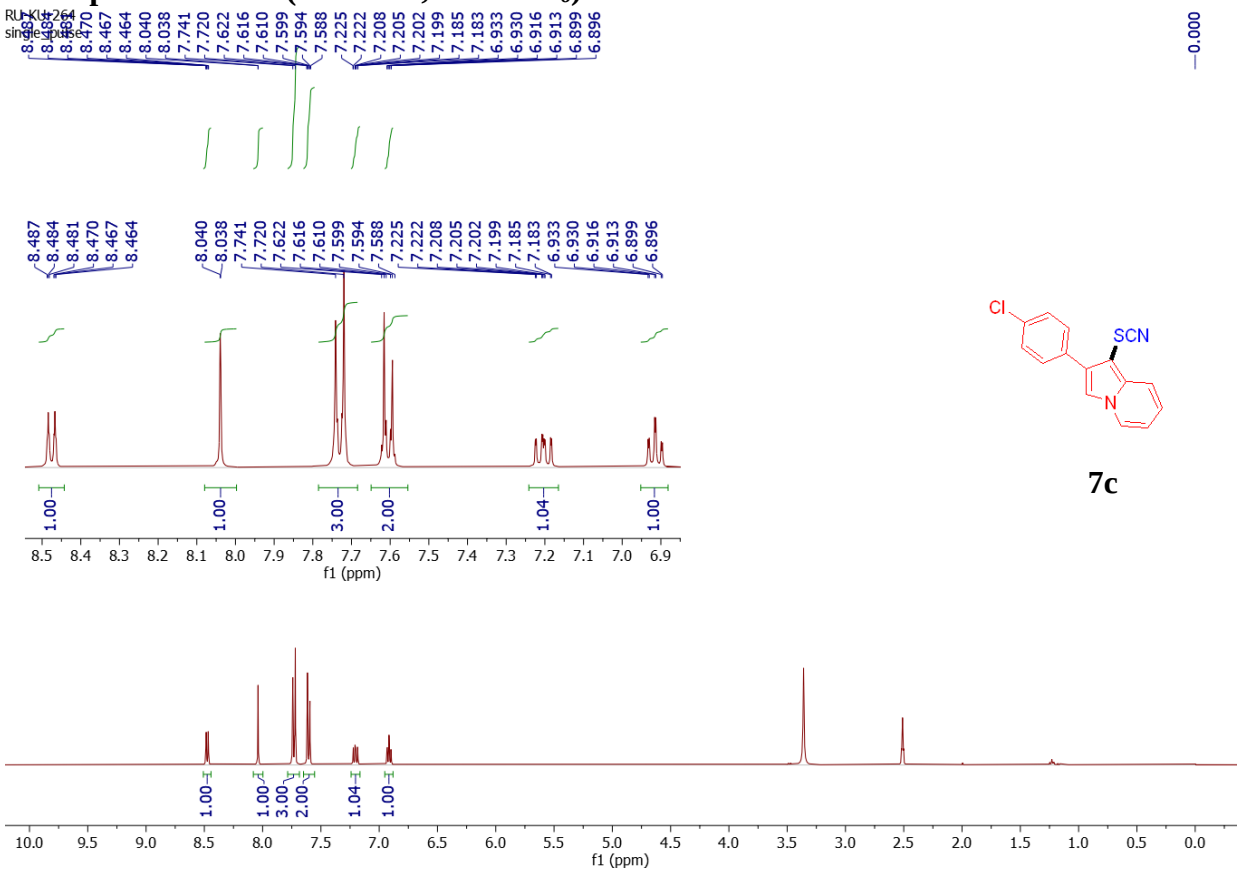
7b

^{13}C NMR spectrum of 7b (100 MHz, DMSO-d_6)

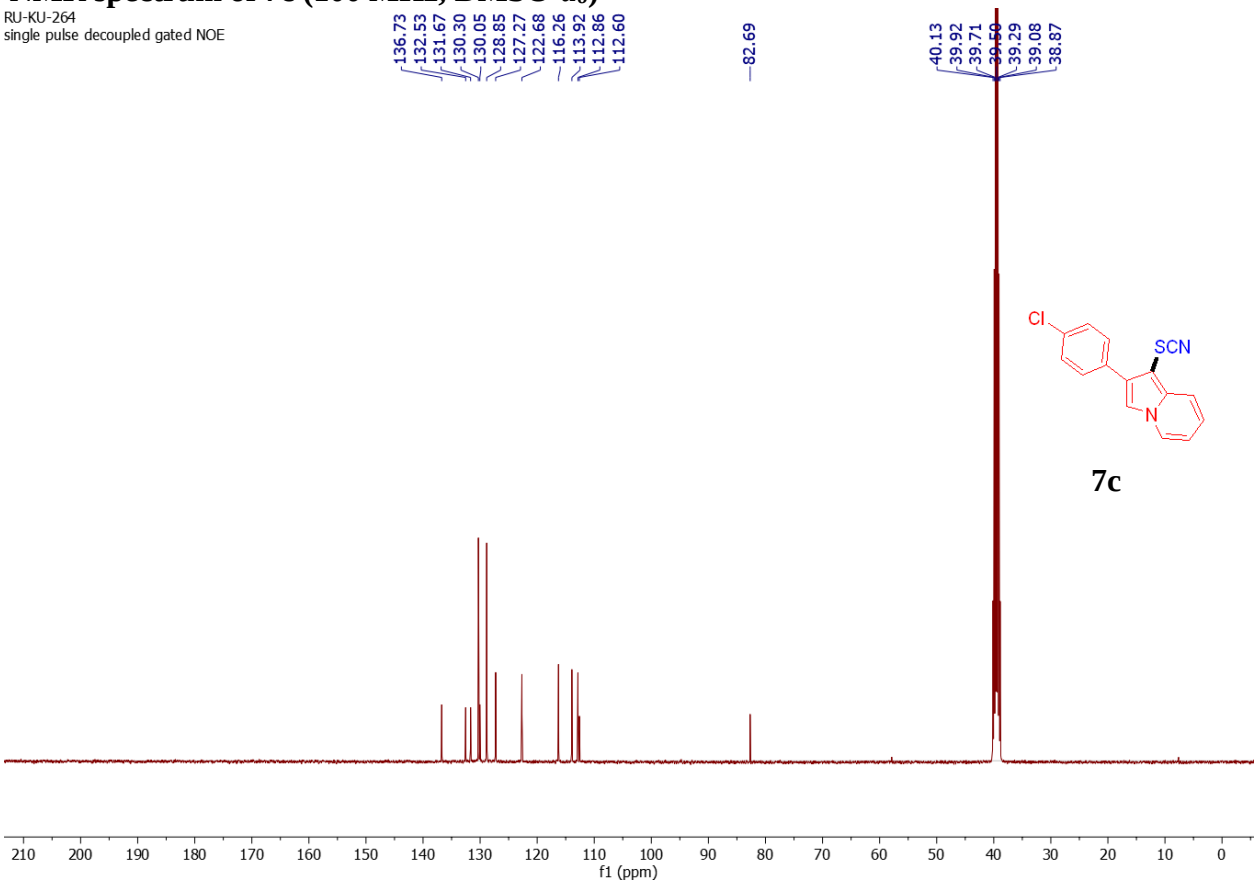


7b

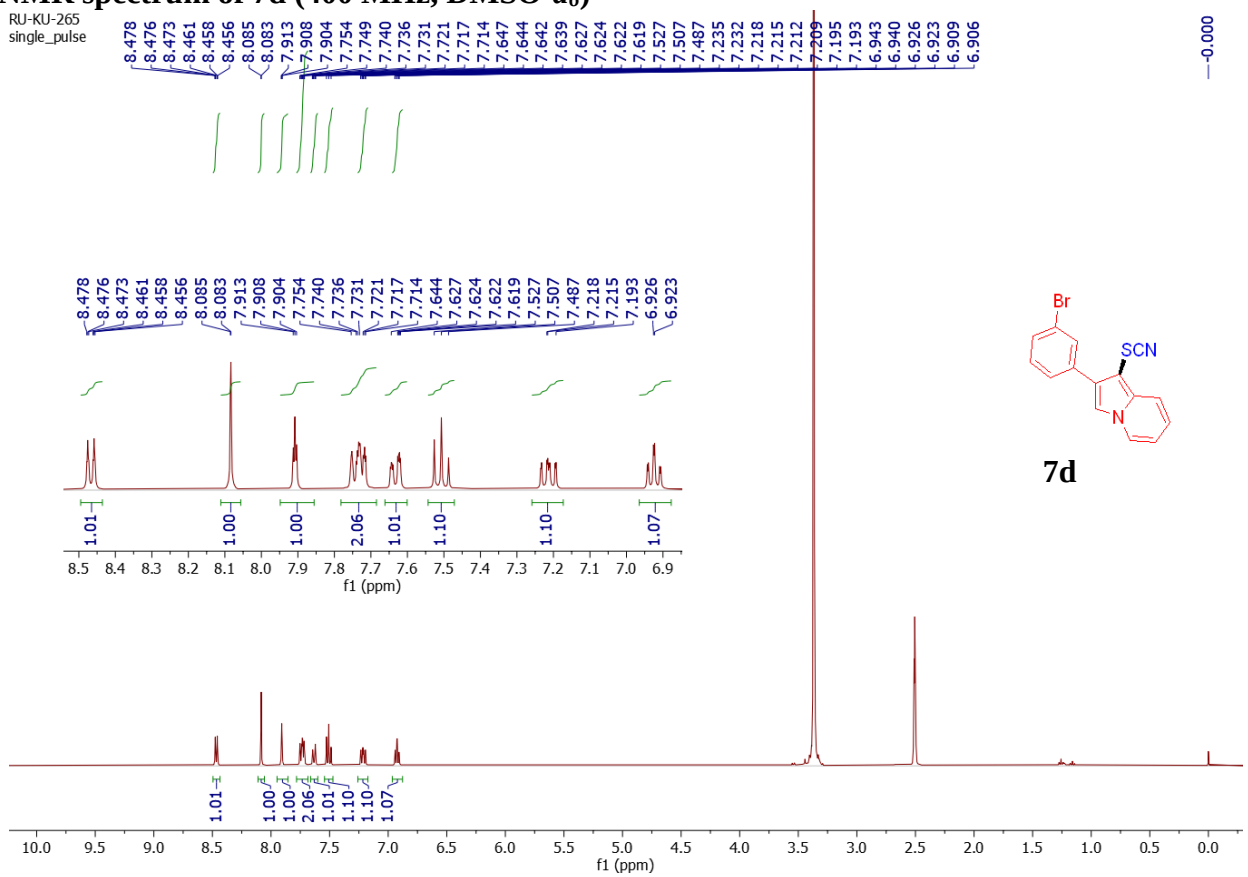
^{1}H NMR spectrum of 7c (400 MHz, DMSO-d_6)



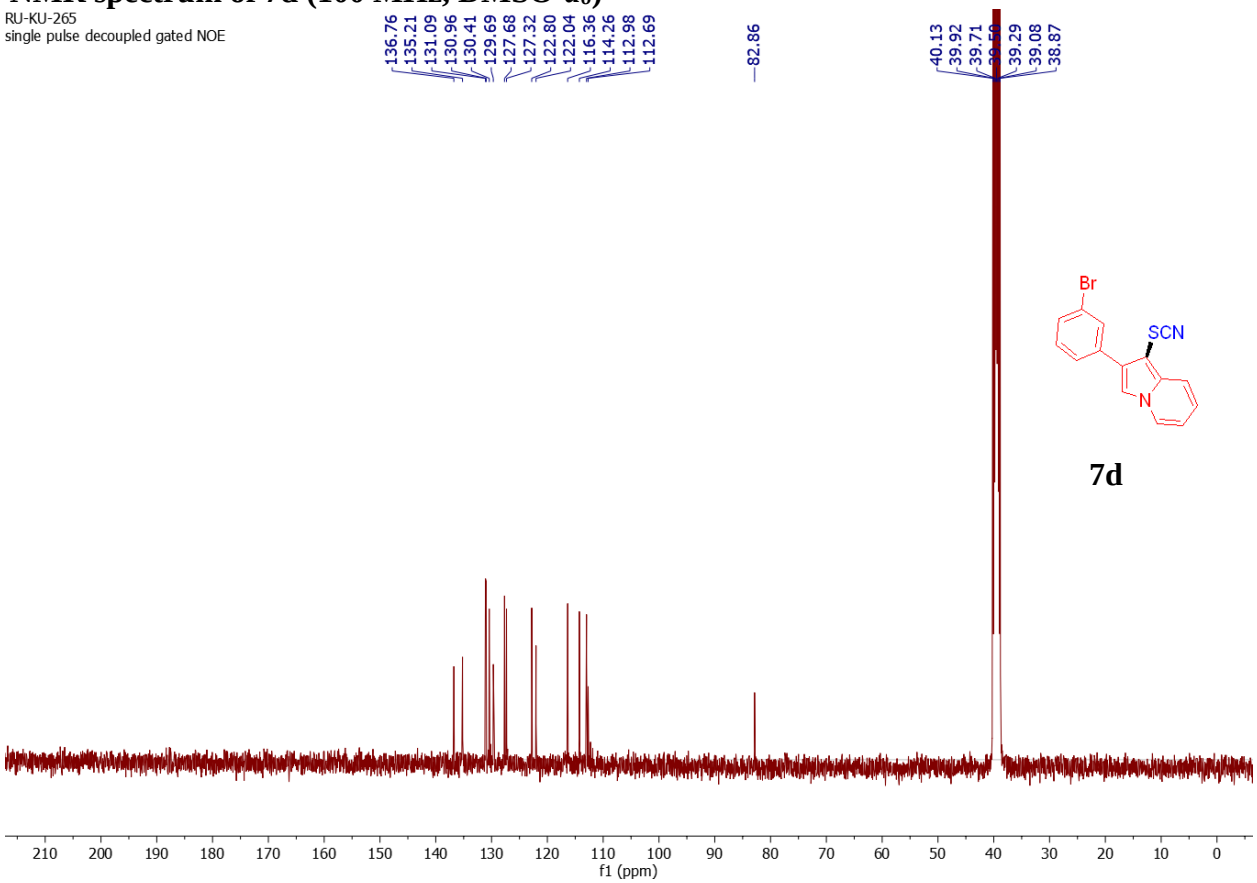
^{13}C NMR spectrum of 7c (100 MHz, DMSO-d_6)



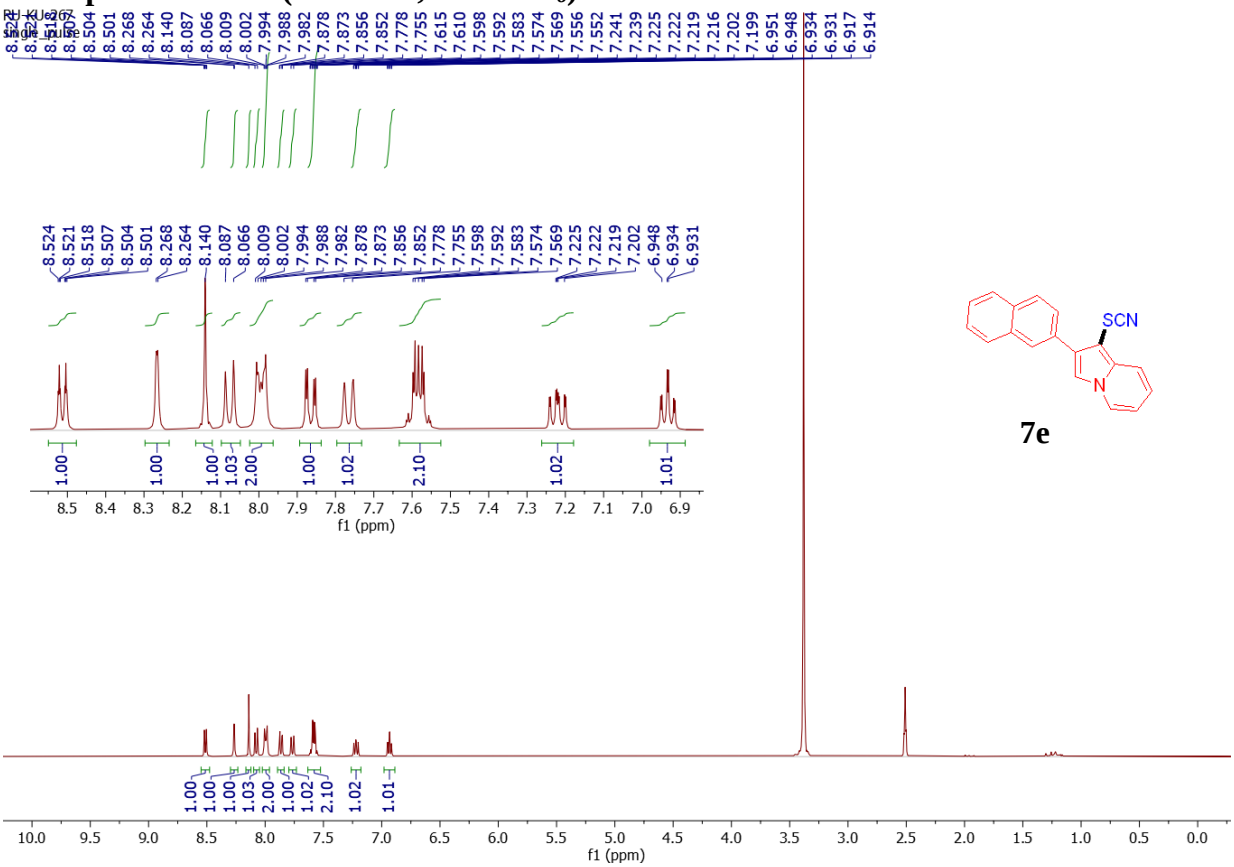
^{1}H NMR spectrum of 7d (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 7d (100 MHz, DMSO-d_6)

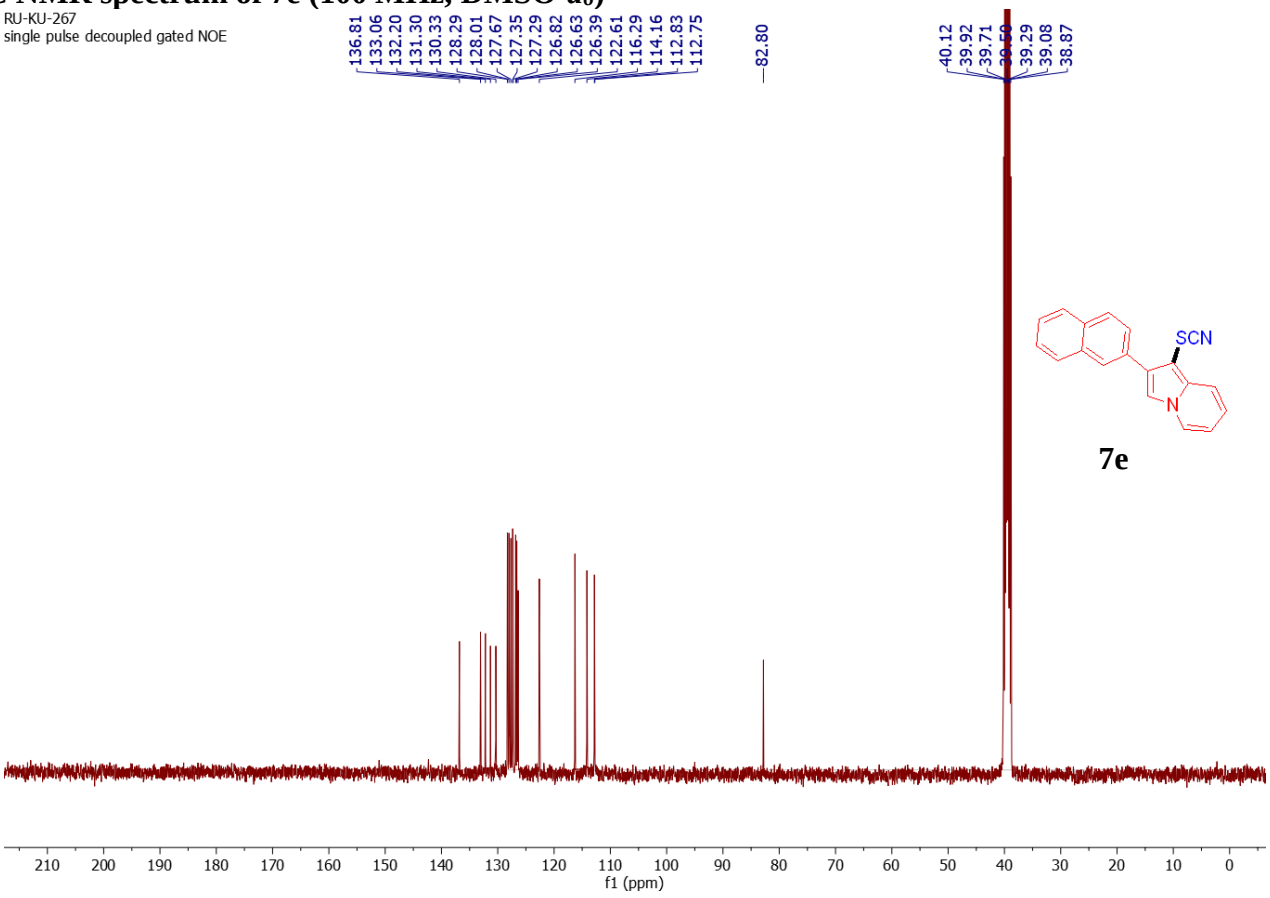


^{1}H NMR spectrum of 7e (400 MHz, DMSO-d_6)



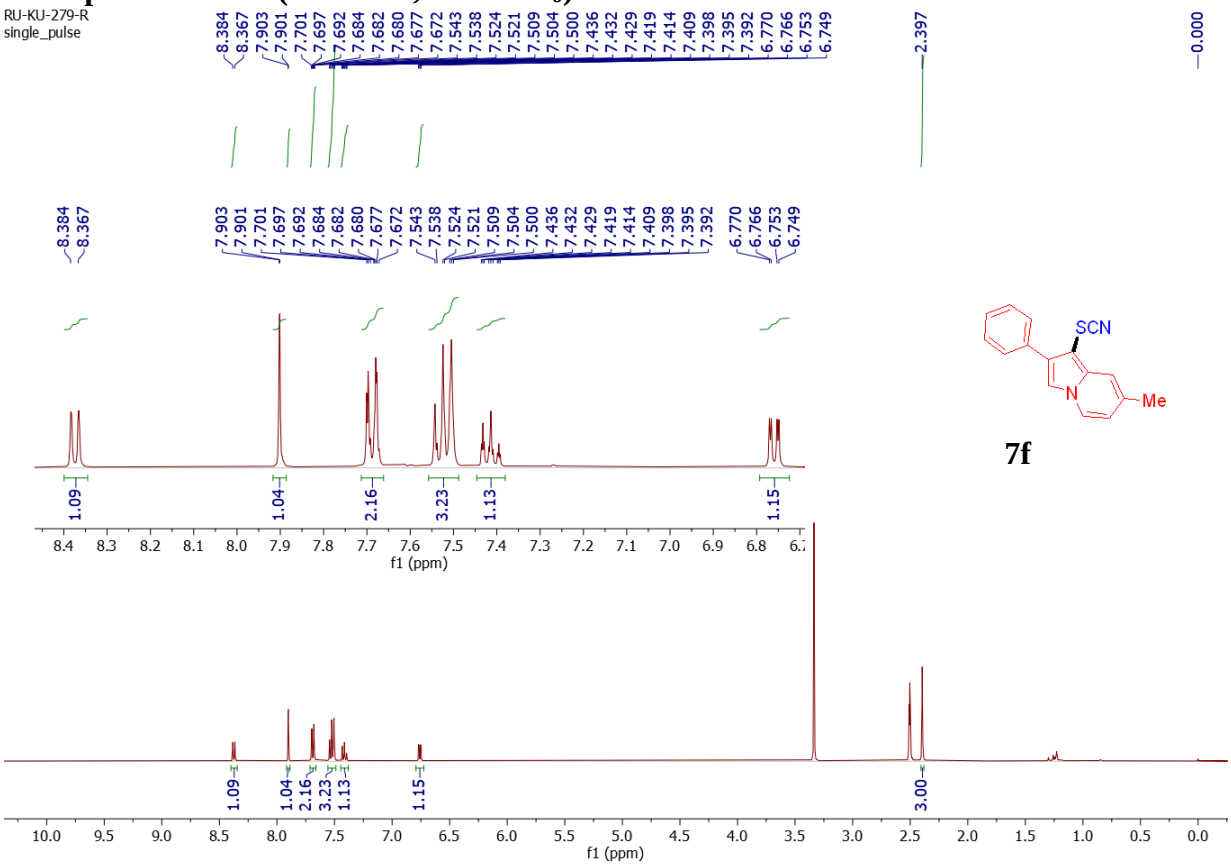
7e

^{13}C NMR spectrum of 7e (100 MHz, DMSO-d_6)



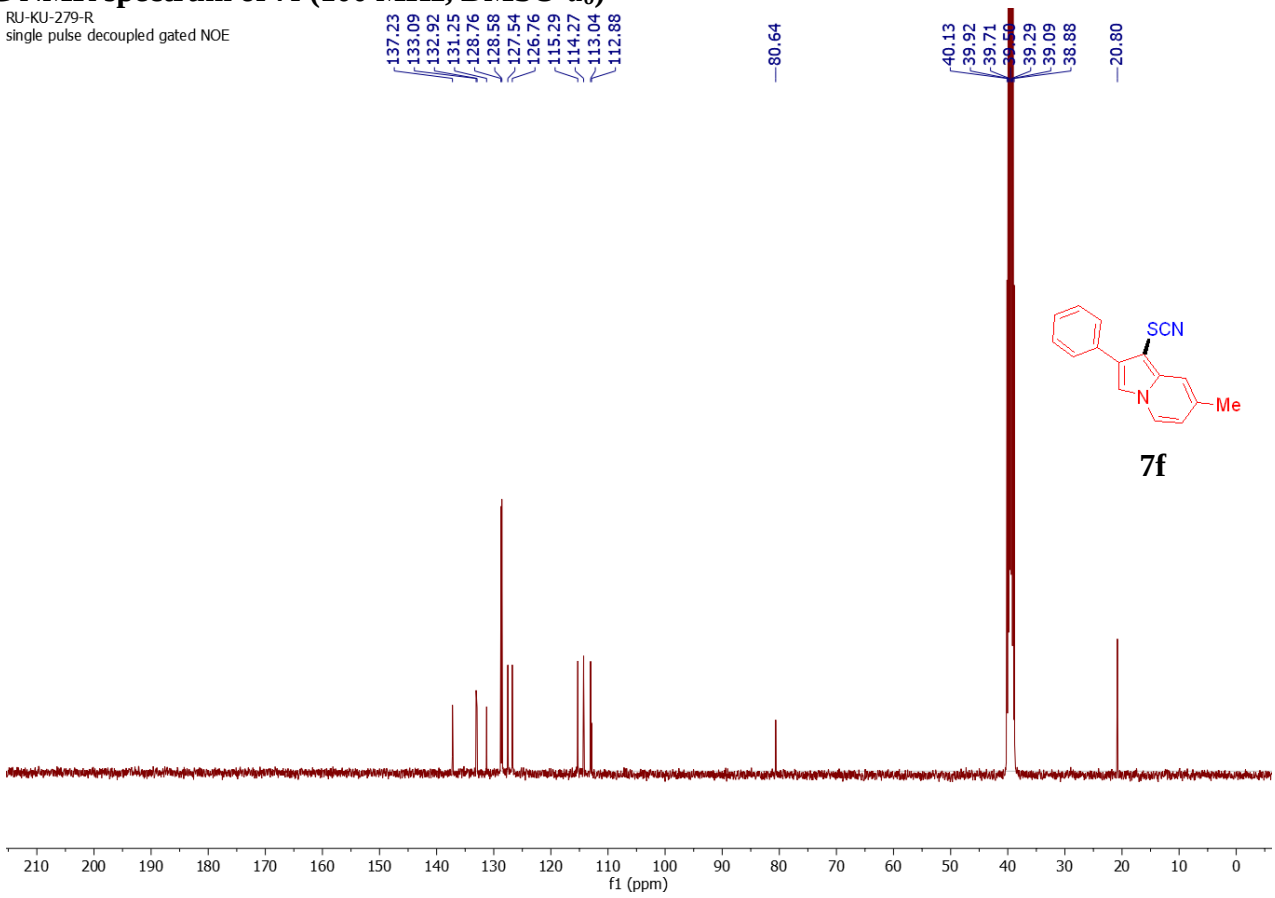
7e

^{1}H NMR spectrum of 7f (400 MHz, DMSO-d_6)



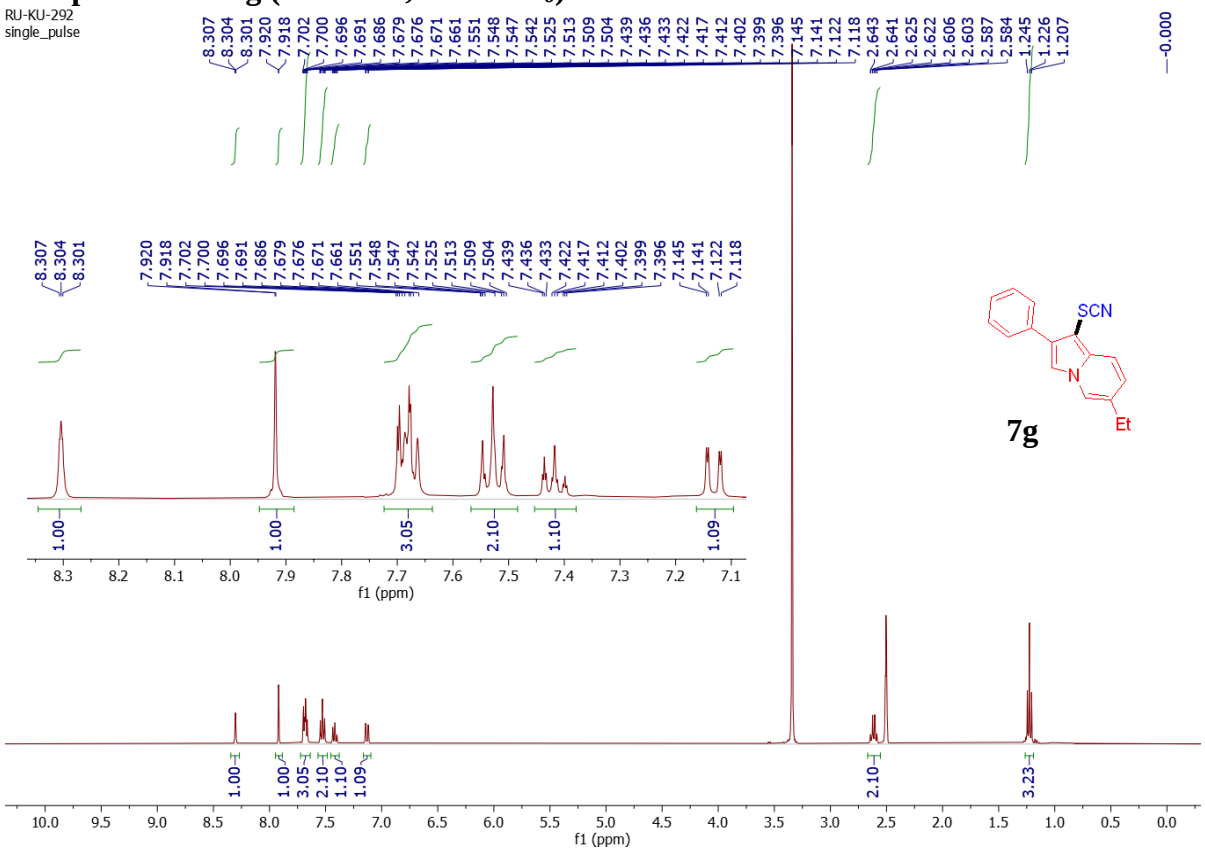
7f

^{13}C NMR spectrum of 7f (100 MHz, DMSO-d_6)

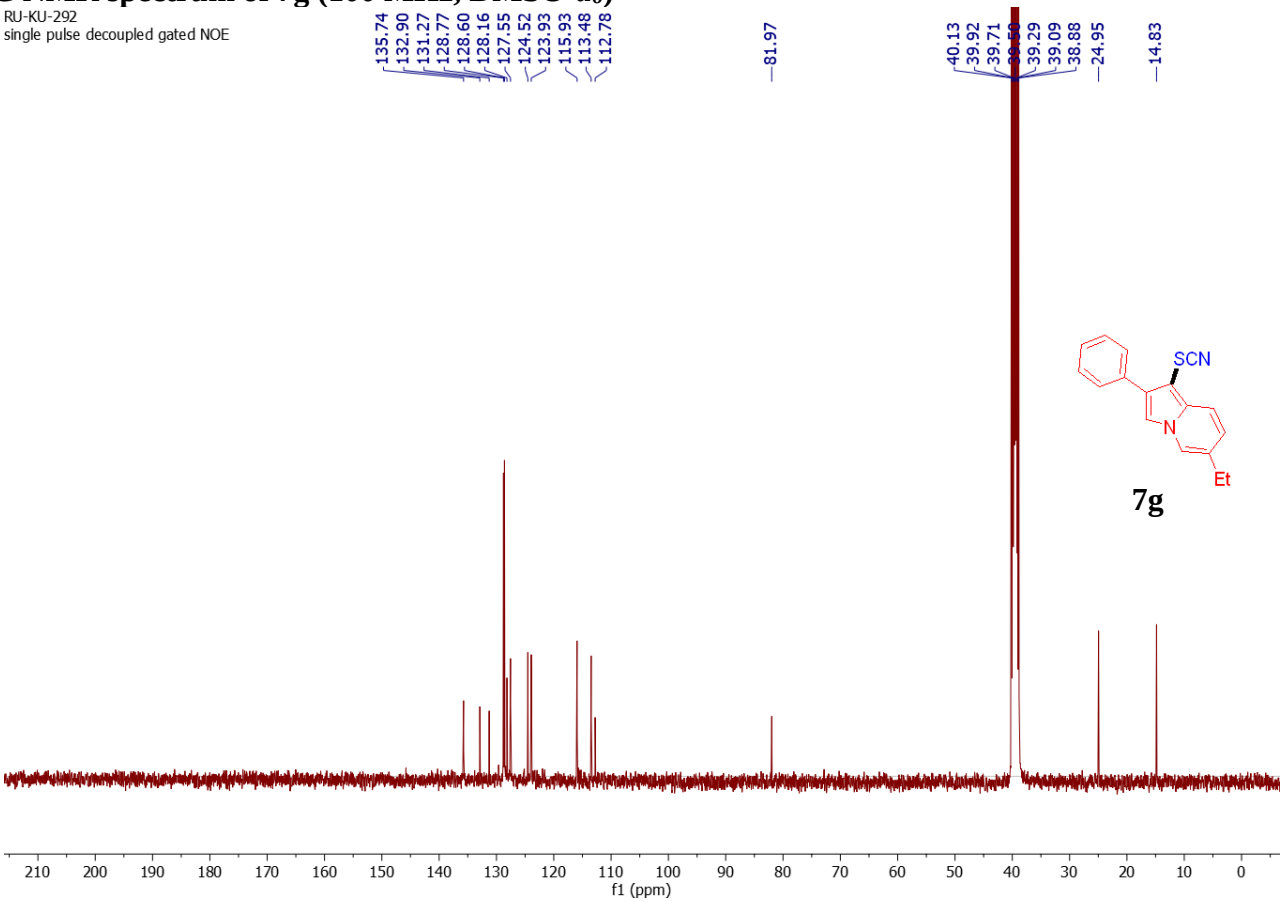


7f

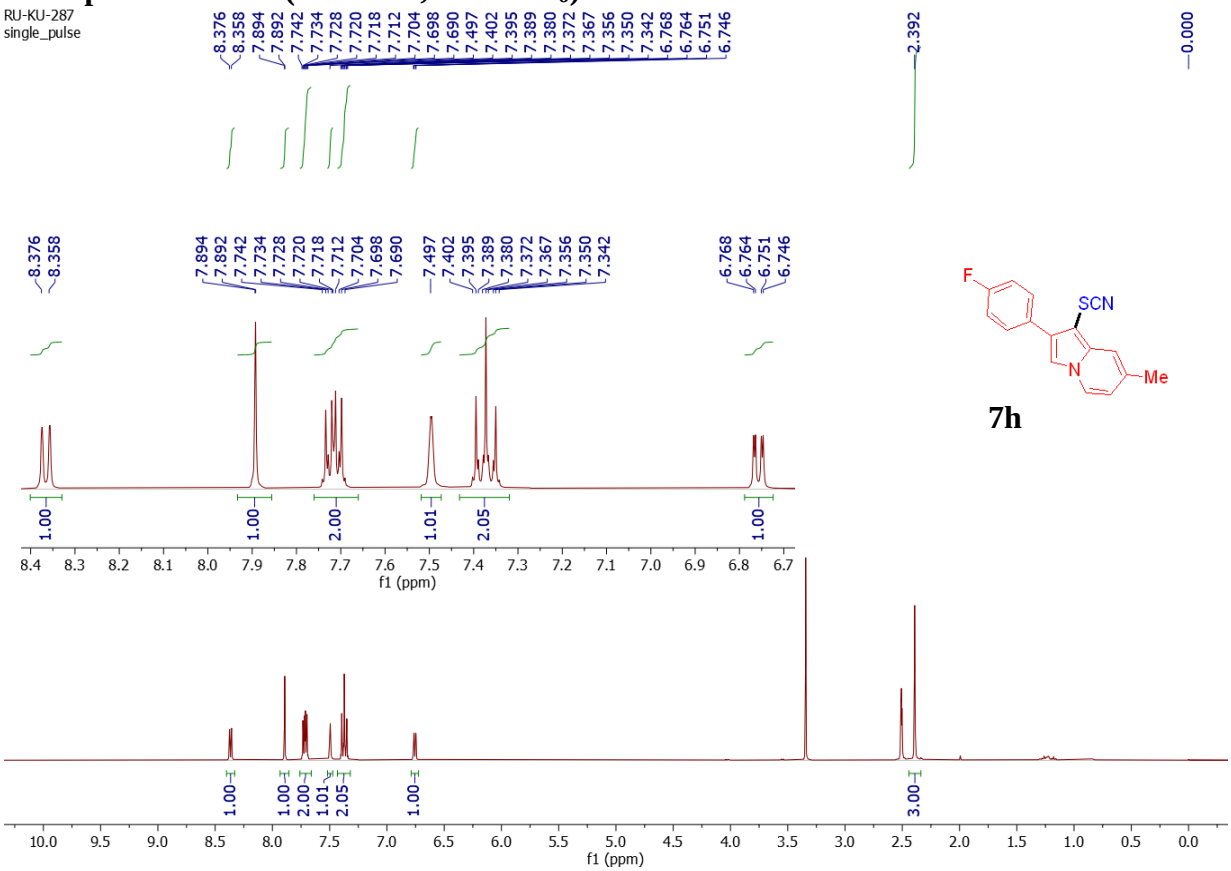
^{1}H NMR spectrum of 7g (400 MHz, DMSO-d_6)



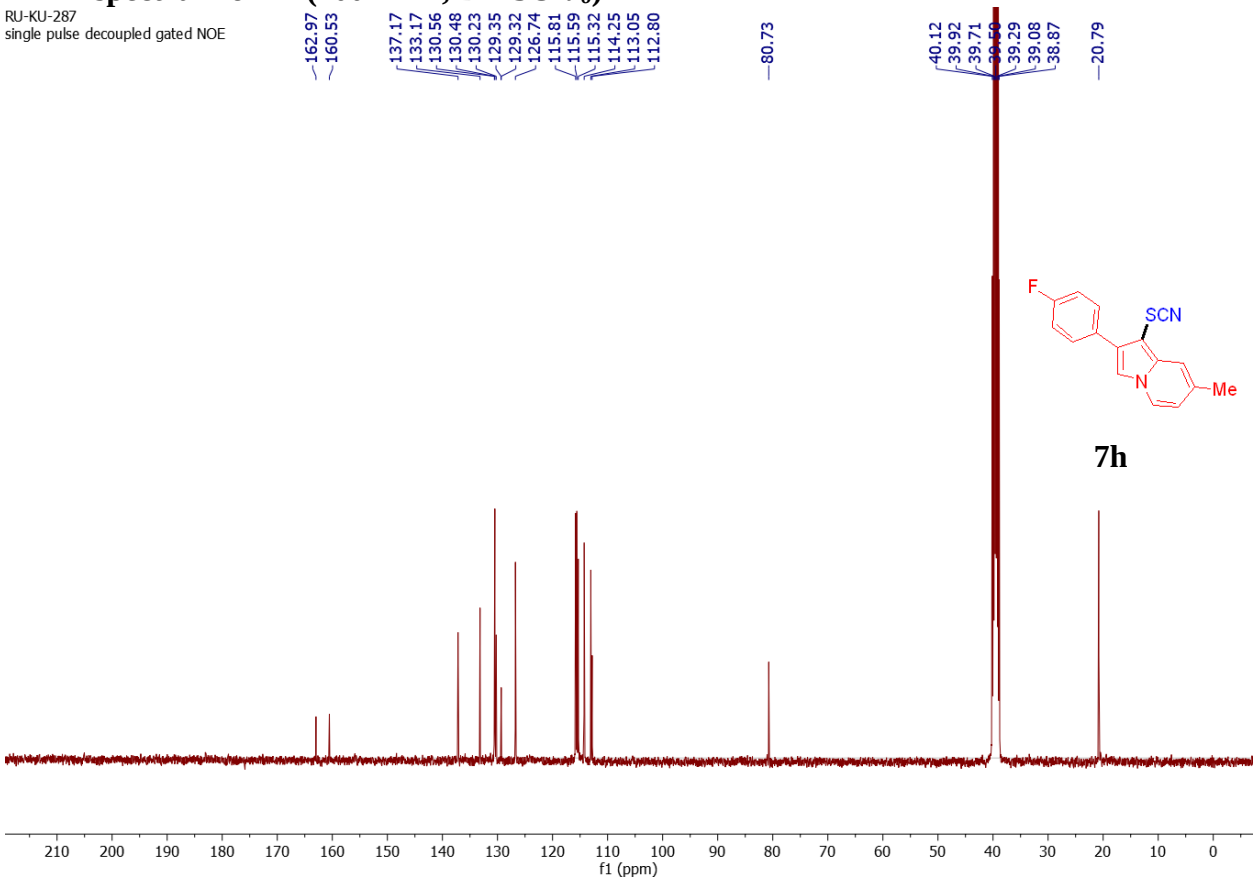
^{13}C NMR spectrum of 7g (100 MHz, DMSO-d_6)



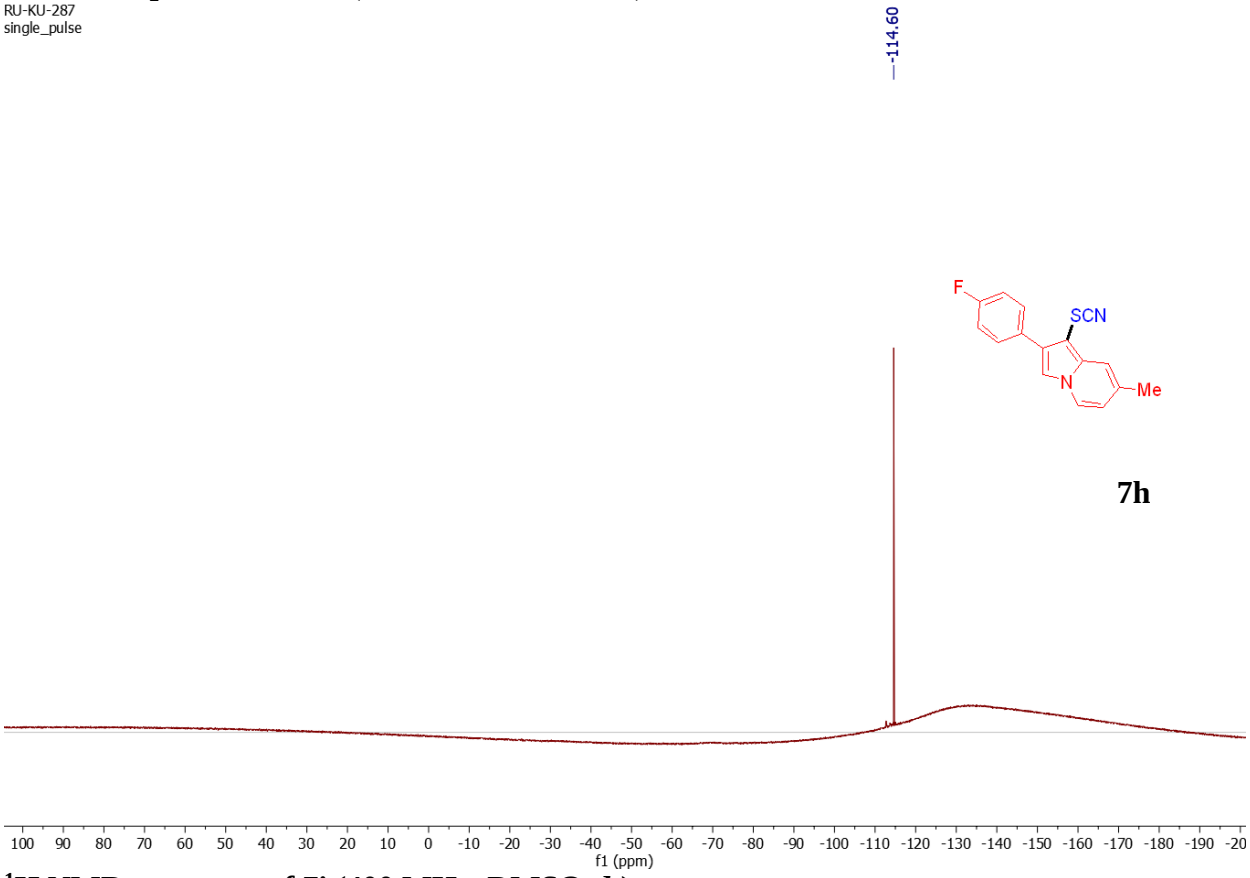
^{1}H NMR spectrum of 7h (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of 7h (100 MHz, DMSO-d_6)

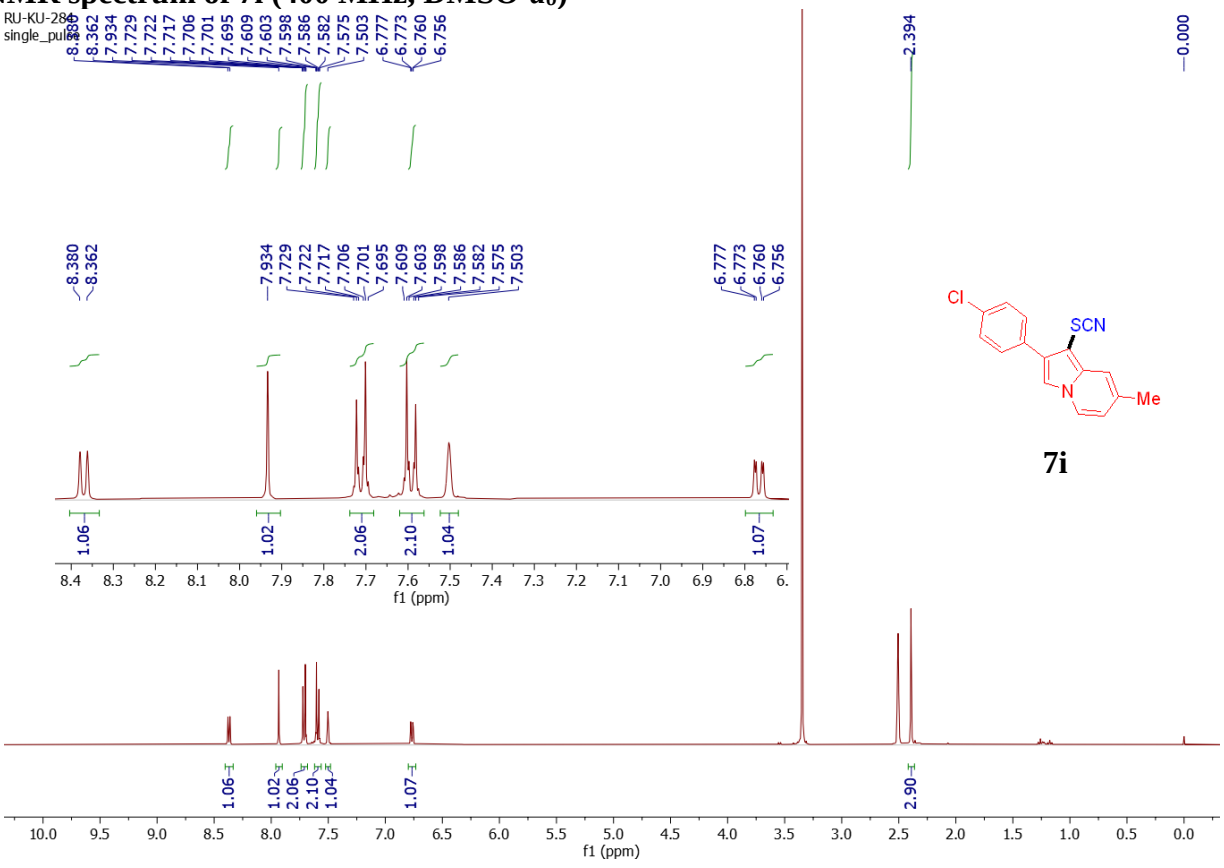


^{19}F NMR spectrum of 7h (376 MHz, DMSO-d_6)



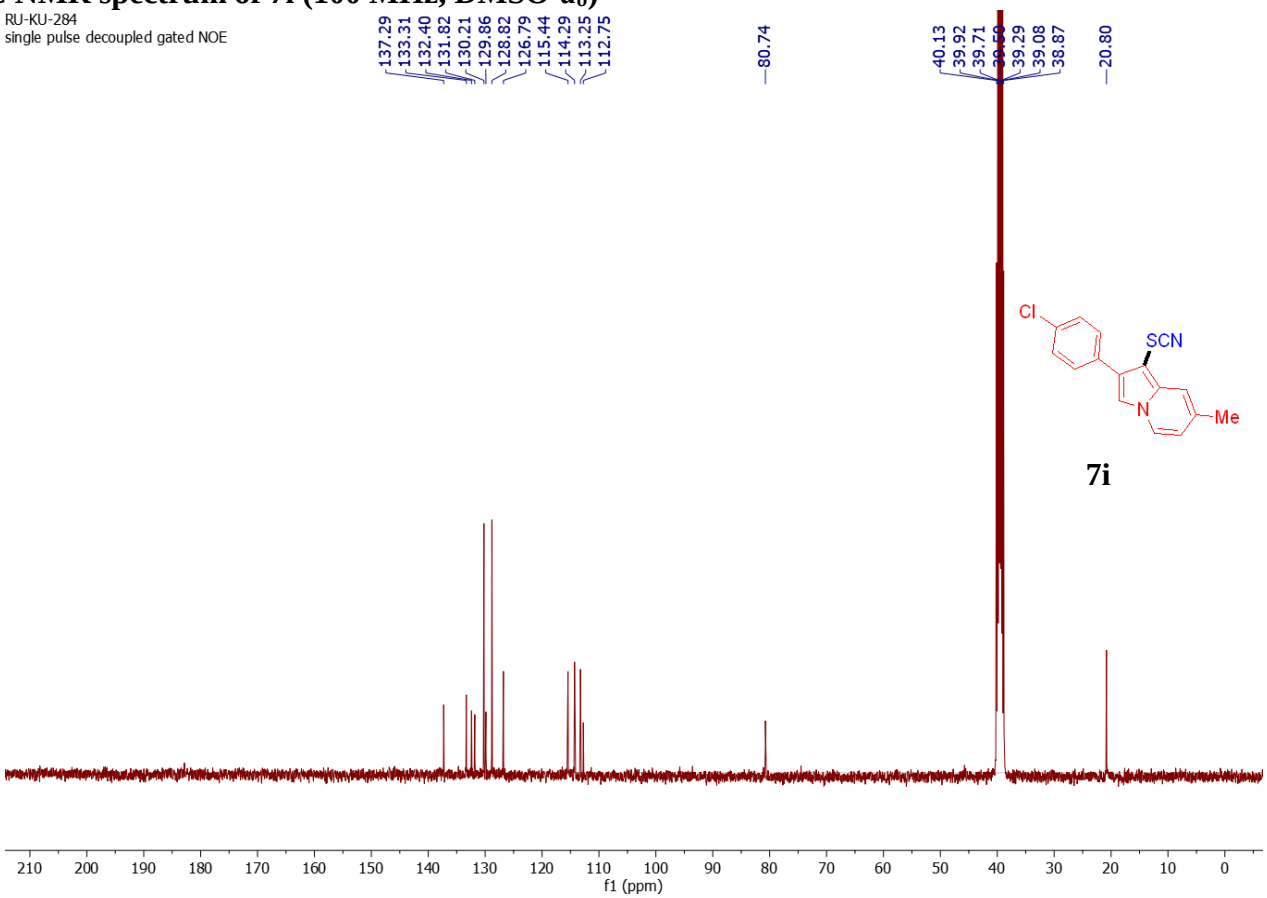
7h

^{1}H NMR spectrum of 7i (400 MHz, DMSO-d_6)



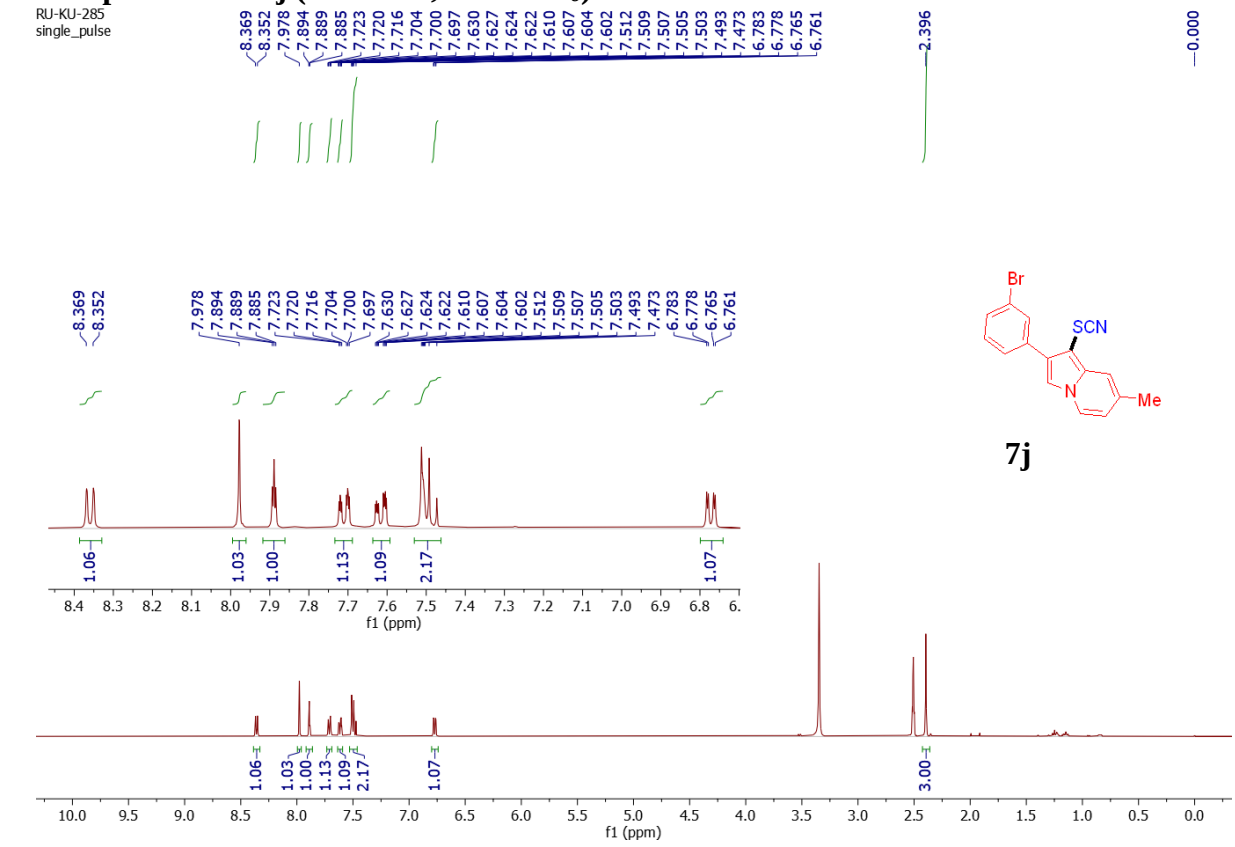
7i

^{13}C NMR spectrum of 7i (100 MHz, DMSO-d_6)



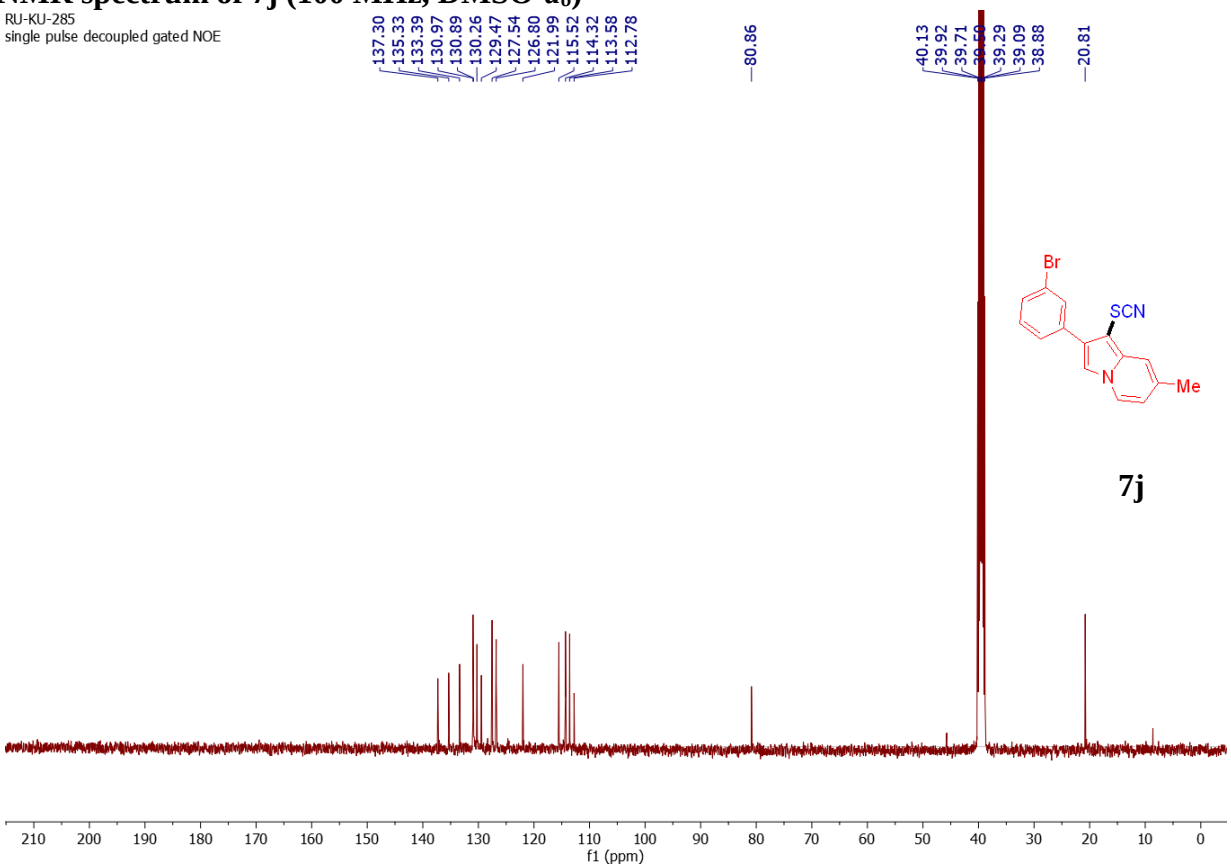
7i

^{1}H NMR spectrum of 7j (400 MHz, DMSO-d_6)



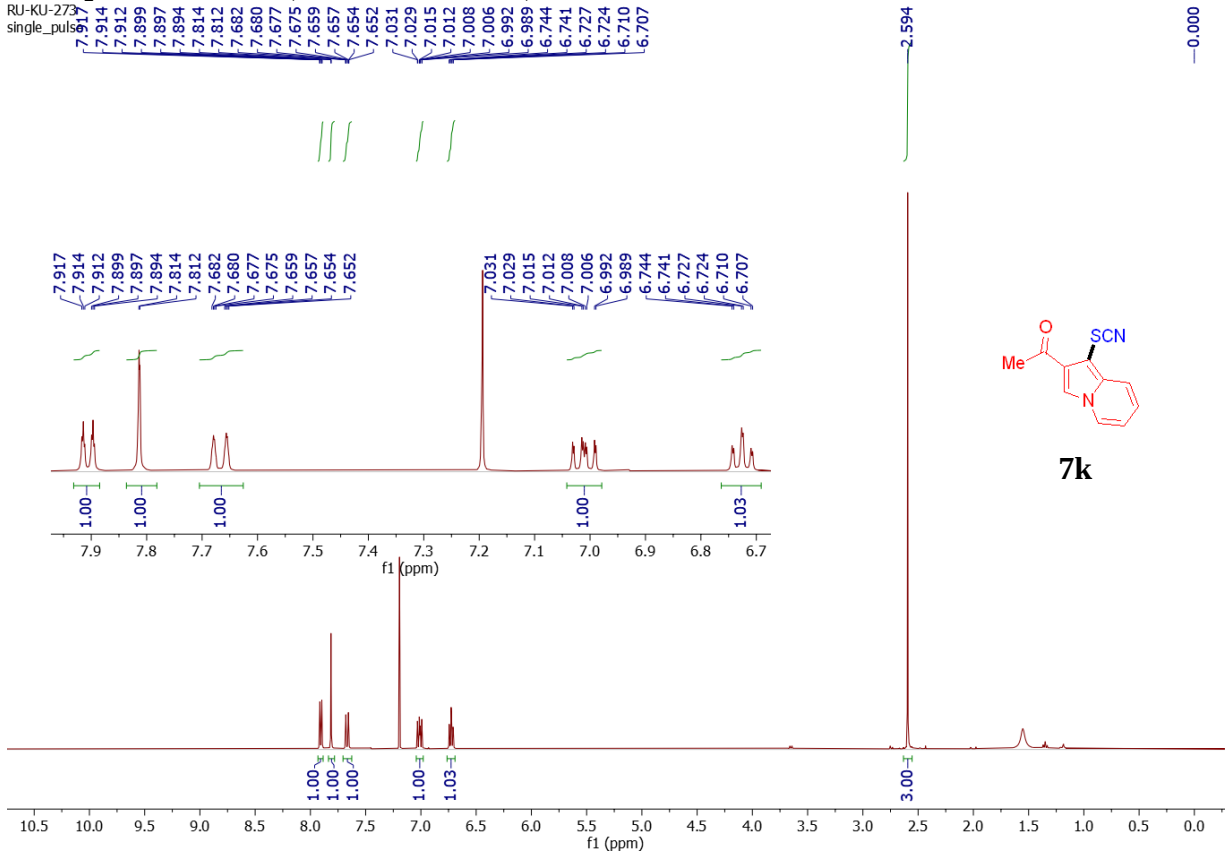
7j

^{13}C NMR spectrum of 7j (100 MHz, DMSO-d_6)



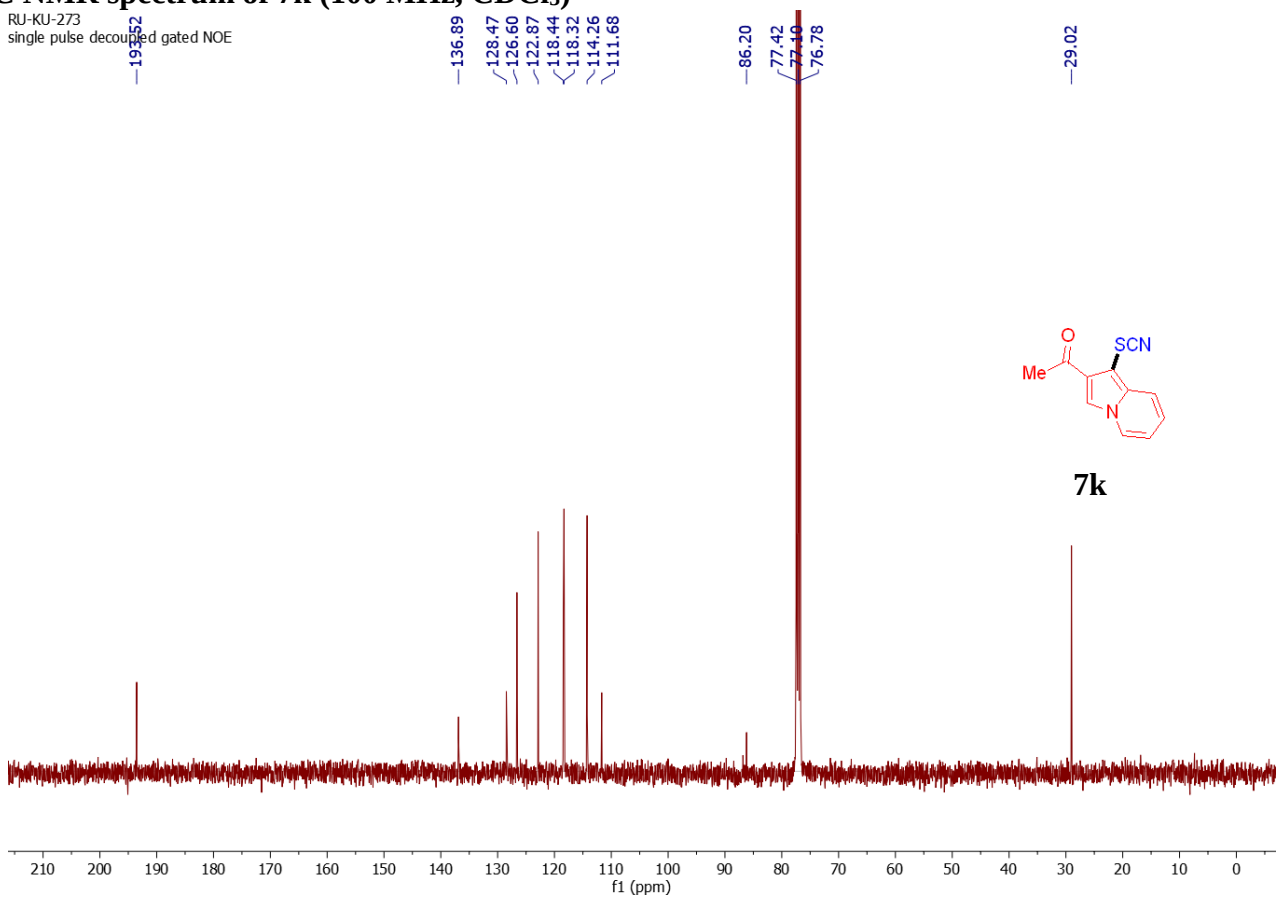
7j

^{1}H NMR spectrum of 7k (400 MHz, $CDCl_3$)



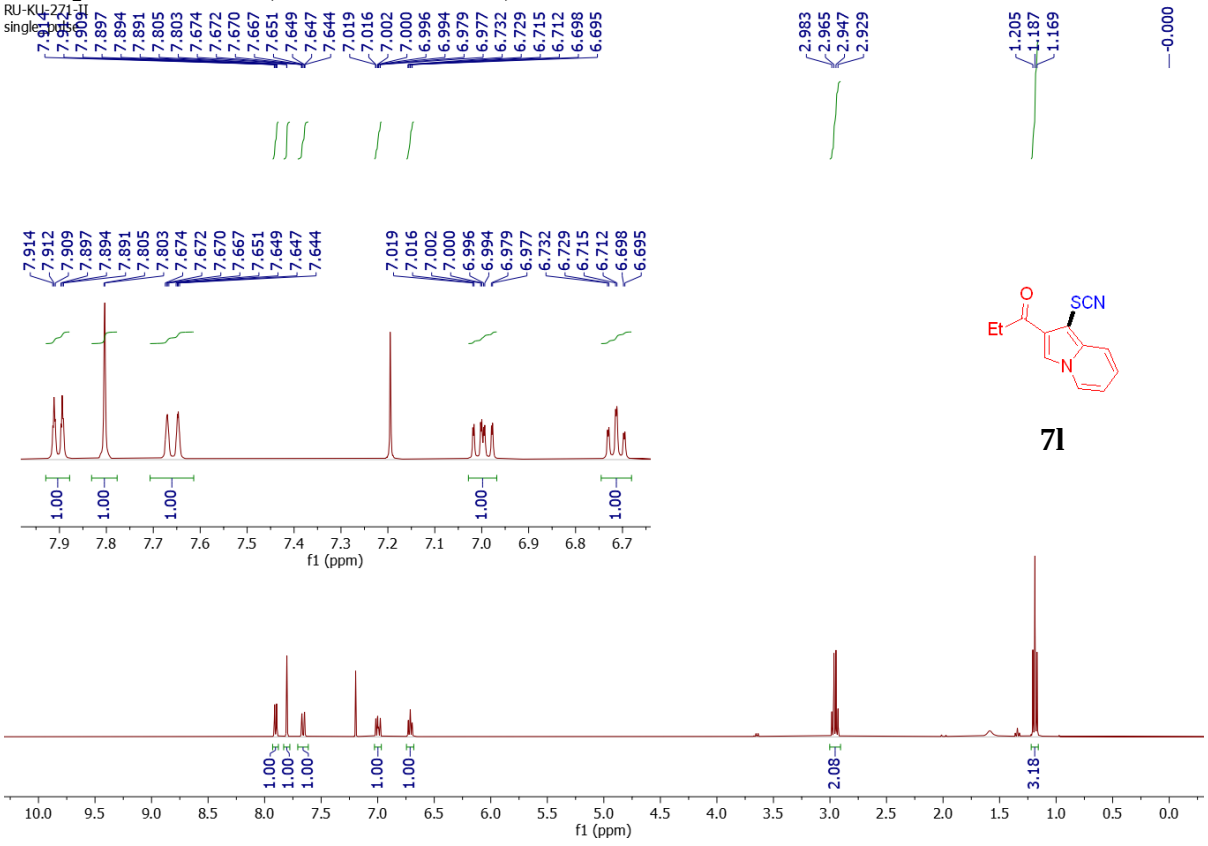
7k

^{13}C NMR spectrum of 7k (100 MHz, $CDCl_3$)



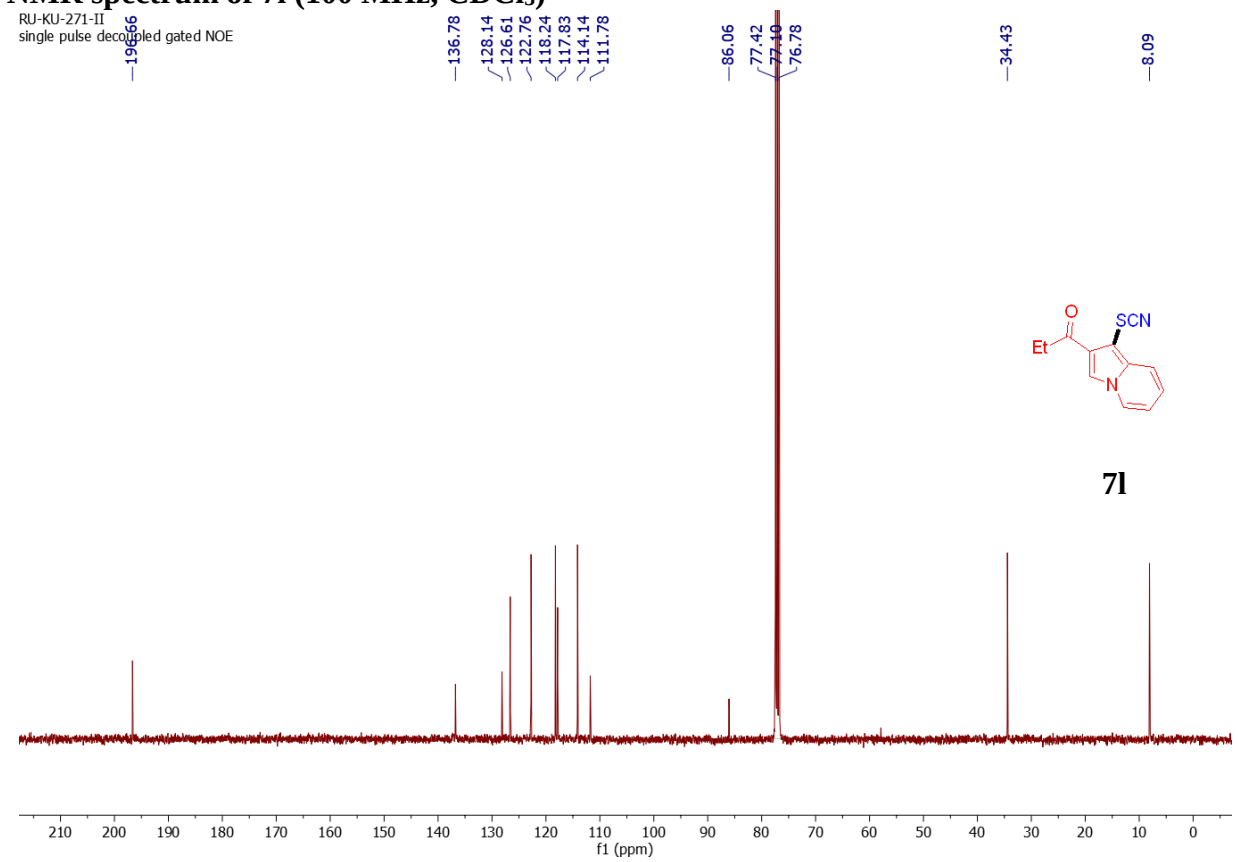
7k

^{1}H NMR spectrum of 7l (400 MHz, $CDCl_3$)



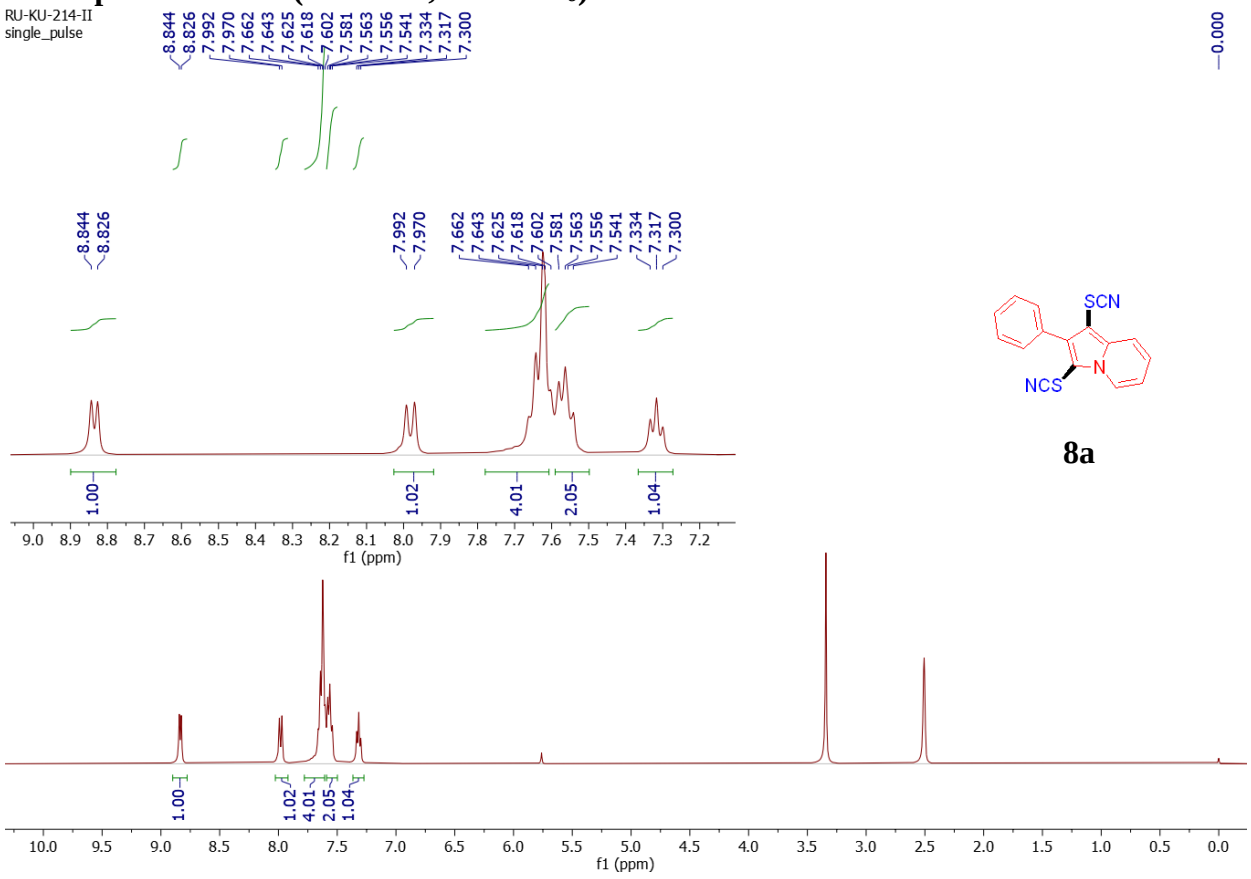
7l

^{13}C NMR spectrum of 7l (100 MHz, $CDCl_3$)



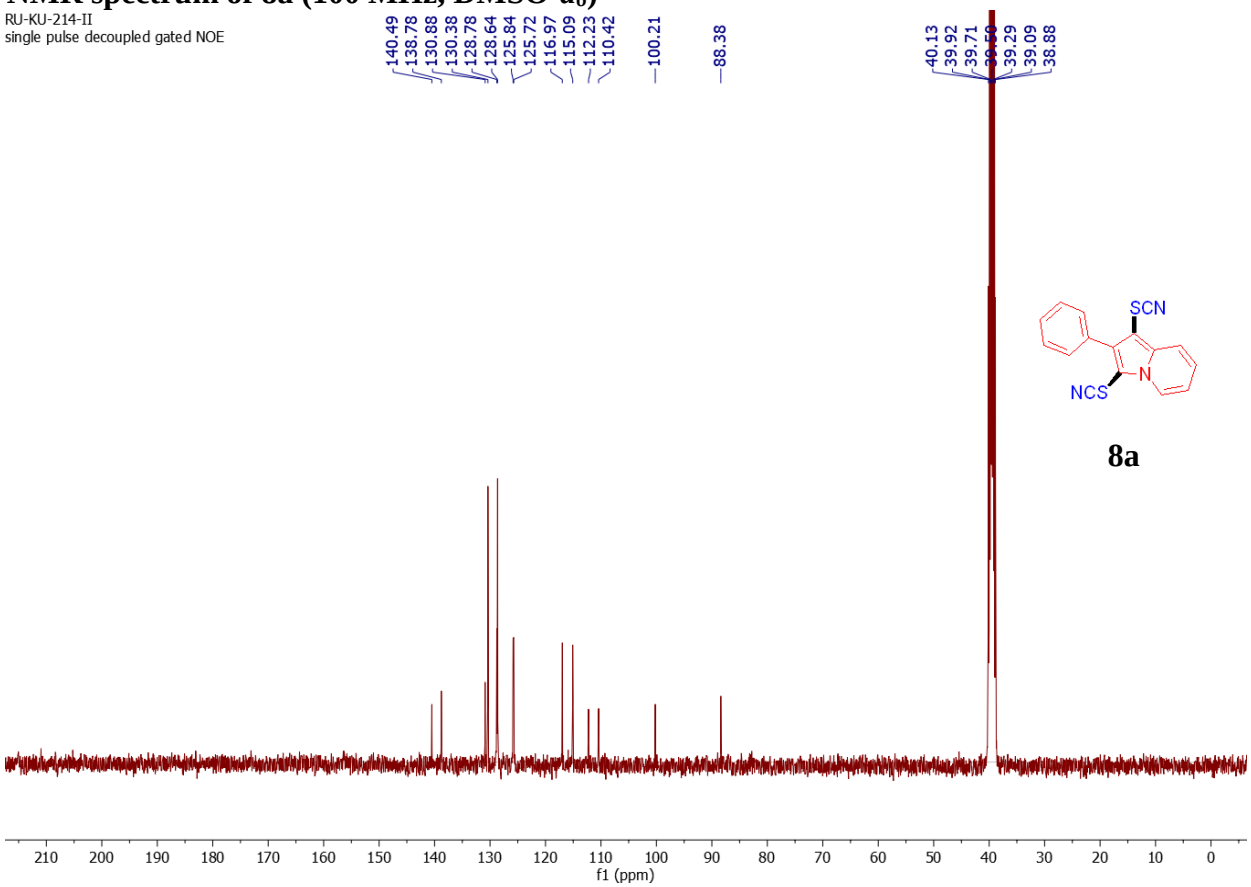
7l

^{1}H NMR spectrum of 8a (400 MHz, DMSO-d_6)



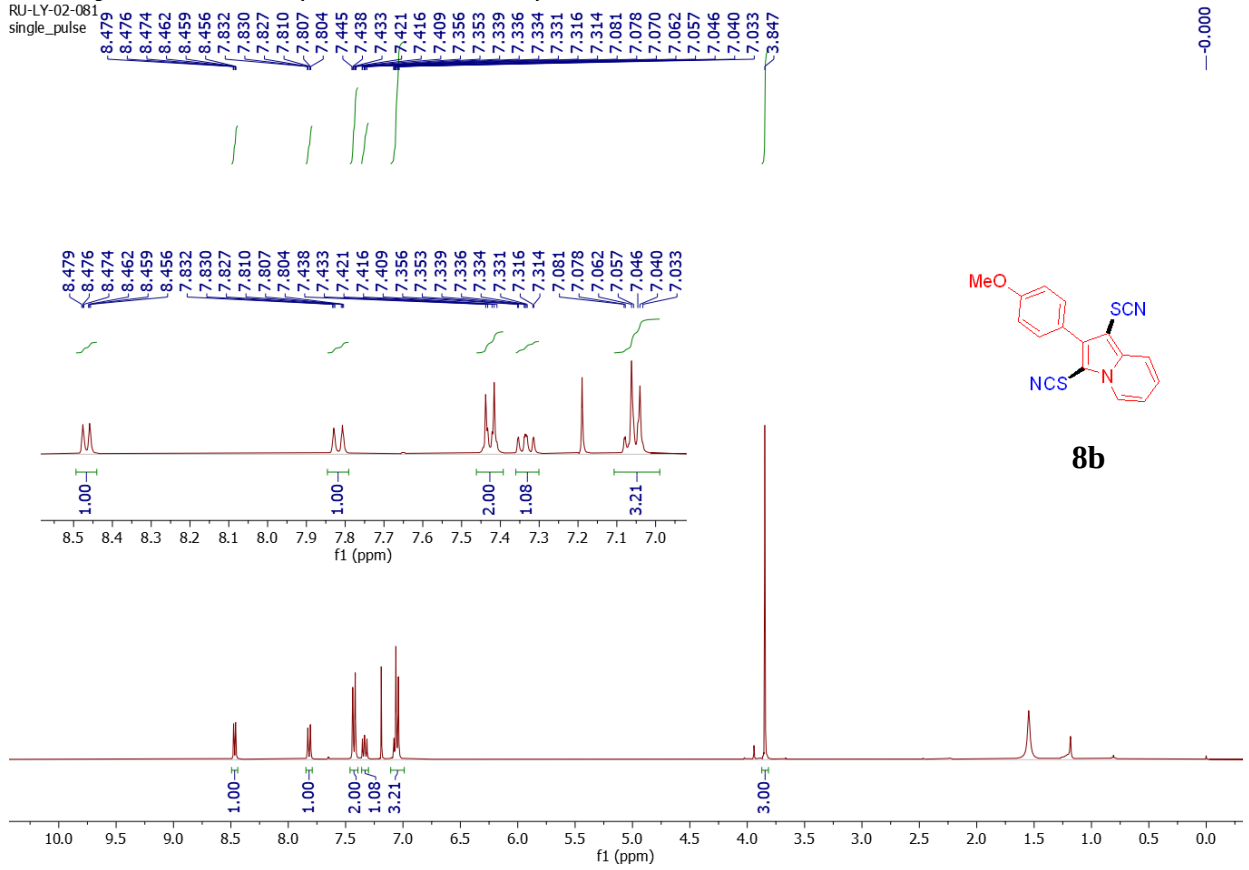
8a

^{13}C NMR spectrum of 8a (100 MHz, DMSO-d_6)



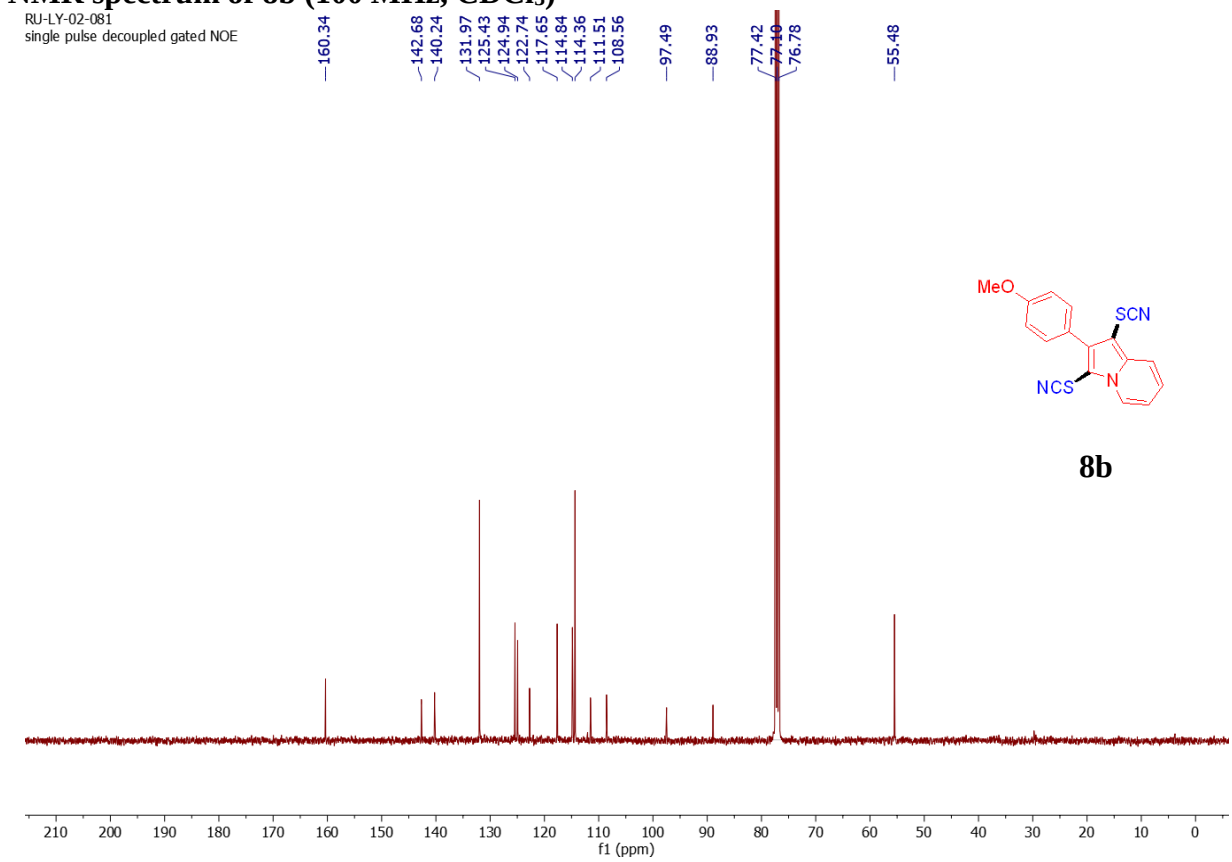
8a

^{1}H NMR spectrum of 8b (400 MHz, $CDCl_3$)



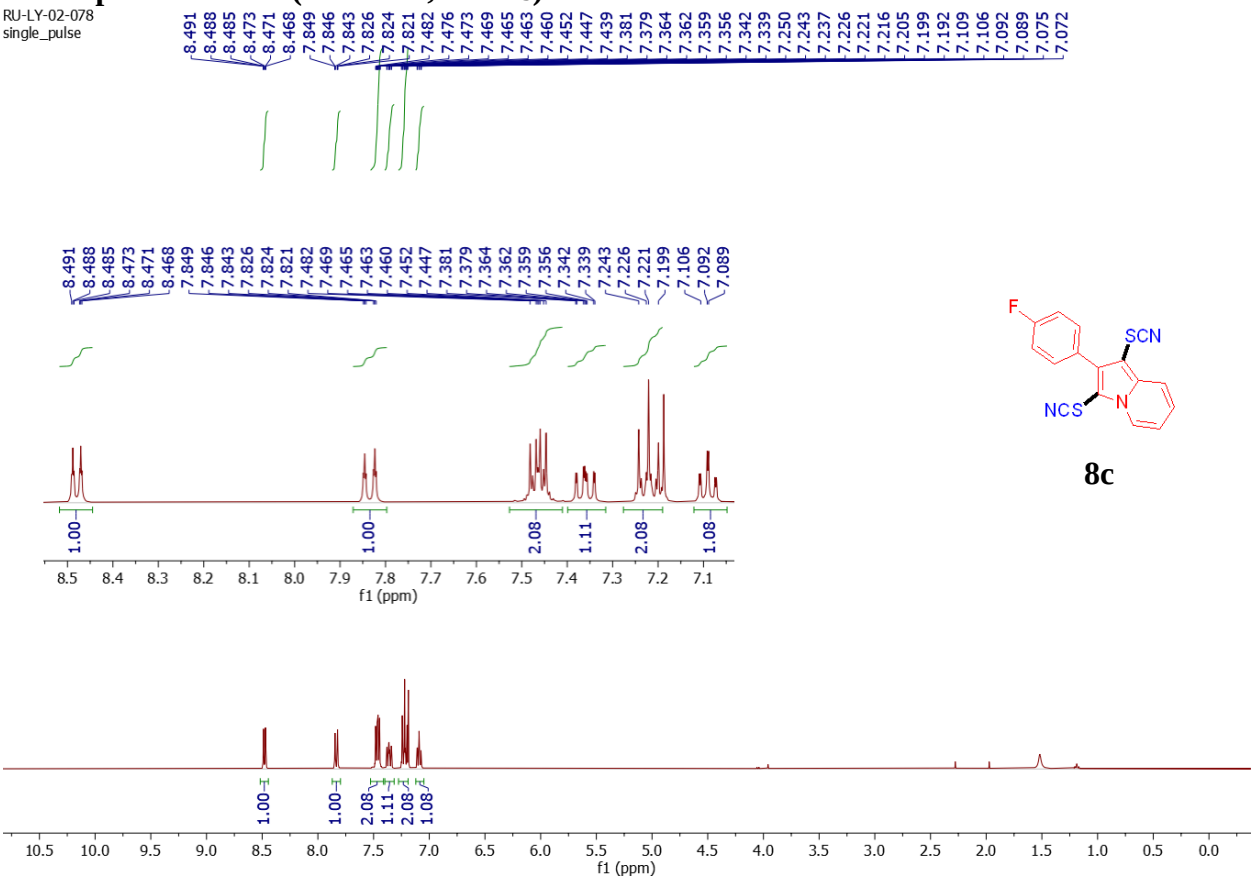
8b

^{13}C NMR spectrum of 8b (100 MHz, $CDCl_3$)



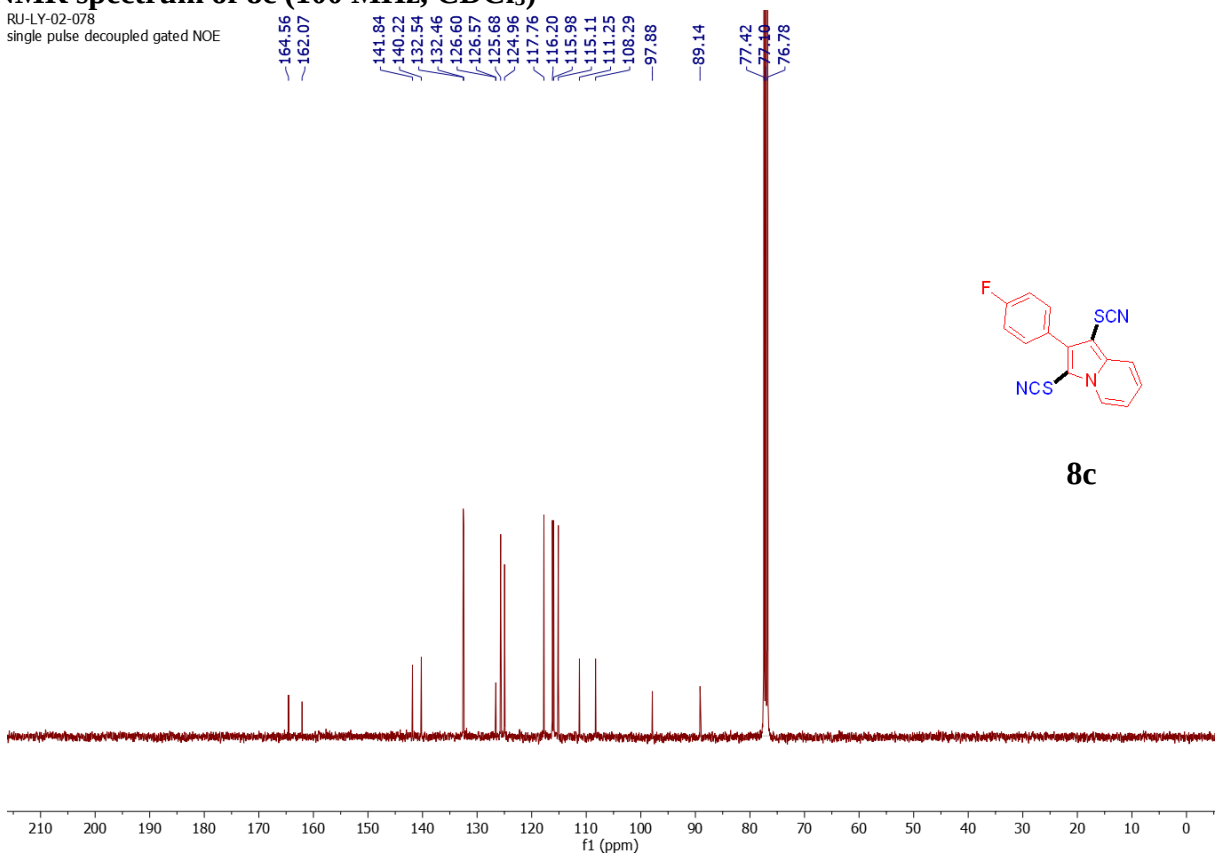
8b

^{1}H NMR spectrum of 8c (400 MHz, $CDCl_3$)



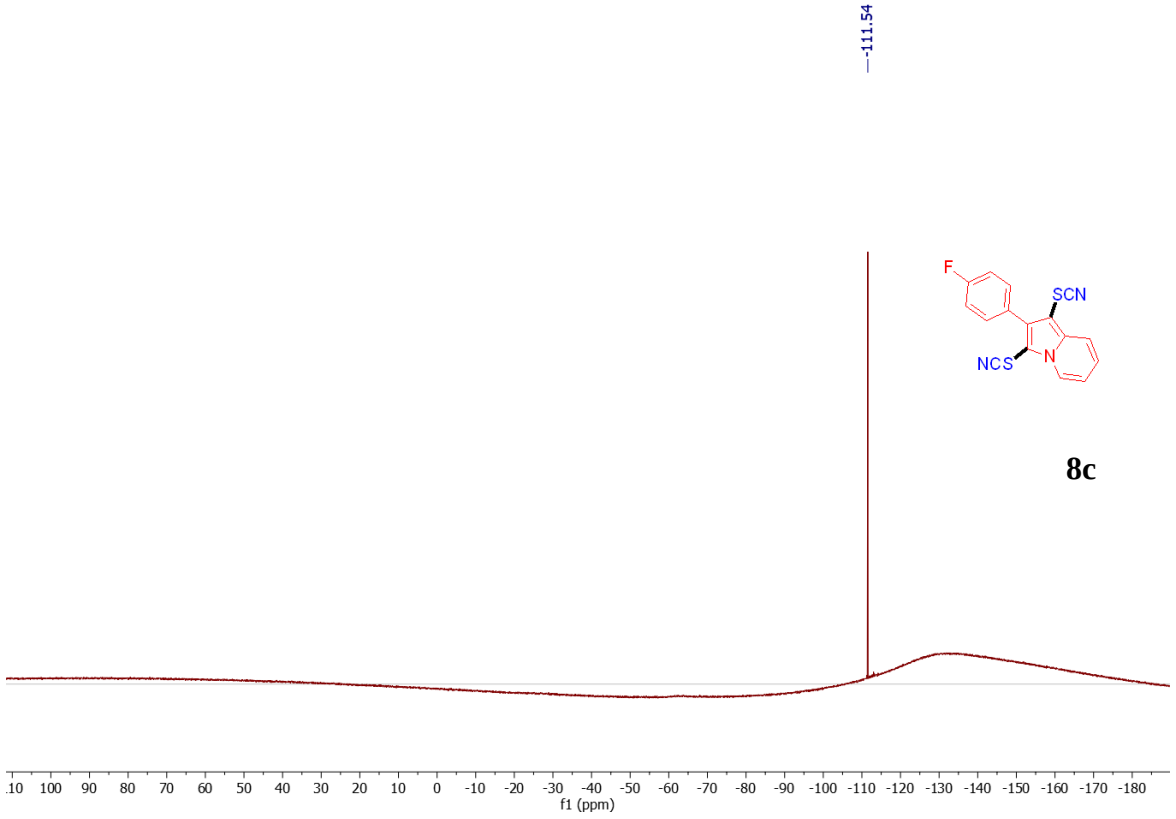
8c

^{13}C NMR spectrum of 8c (100 MHz, $CDCl_3$)



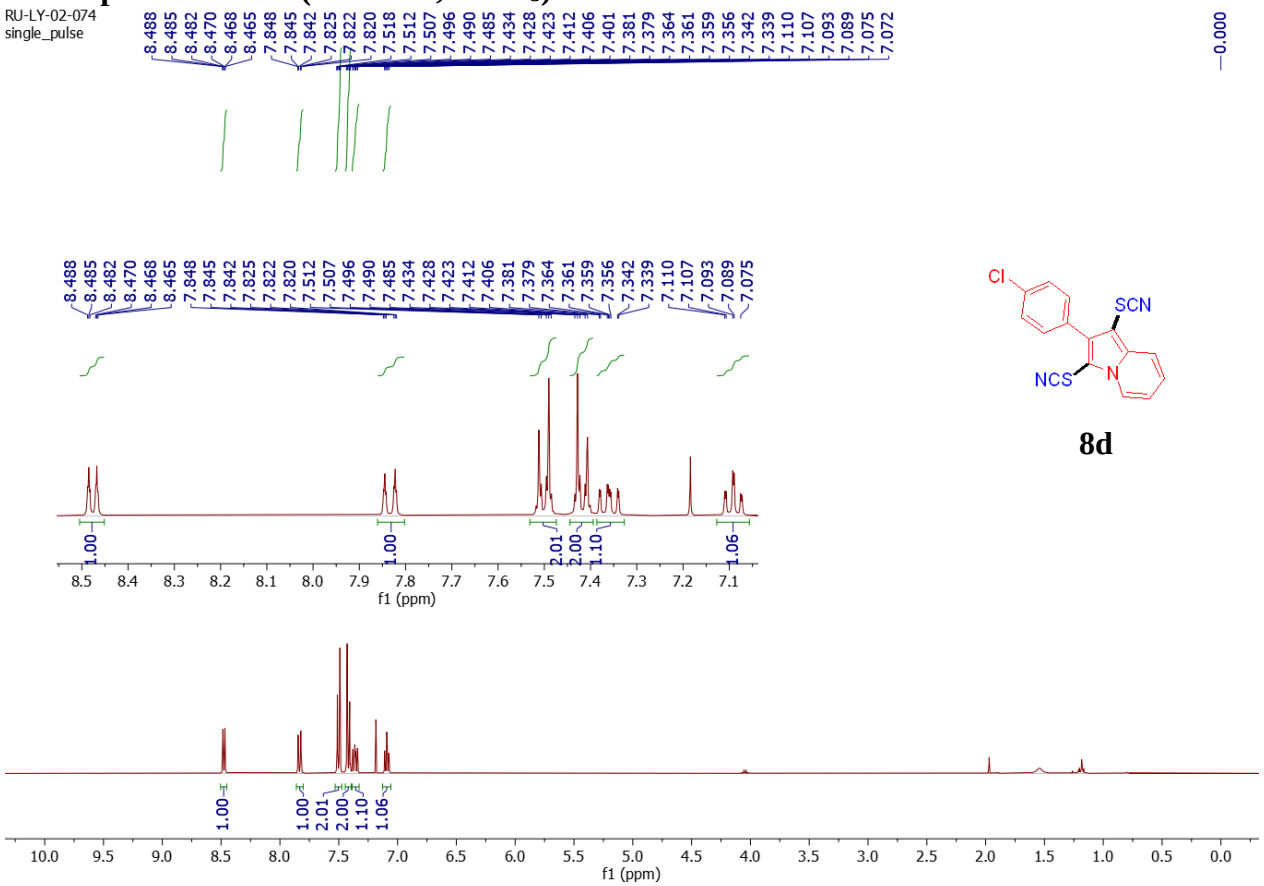
8c

^{19}F NMR spectrum of 8c (376 MHz, $CDCl_3$)



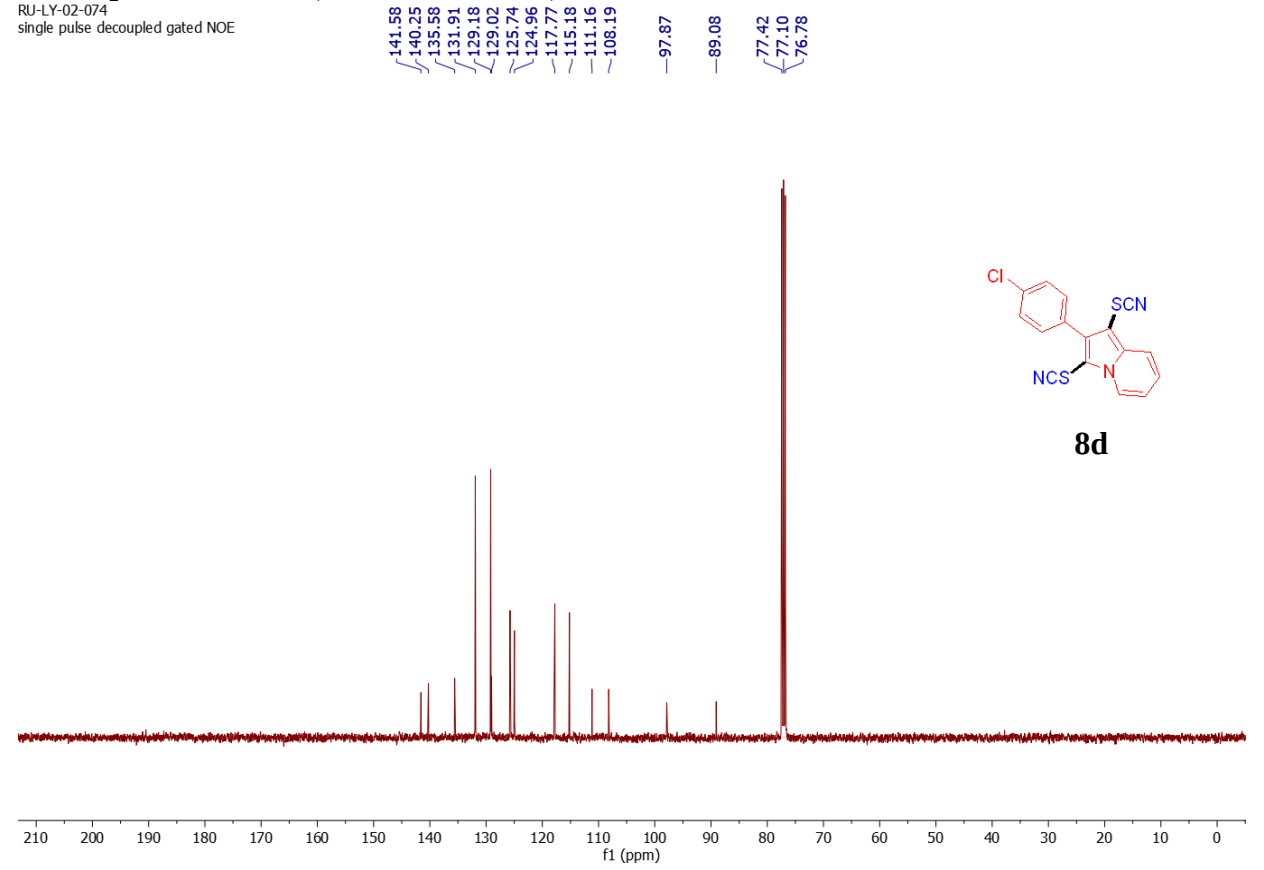
8c

^{1}H NMR spectrum of 8d (400 MHz, $CDCl_3$)



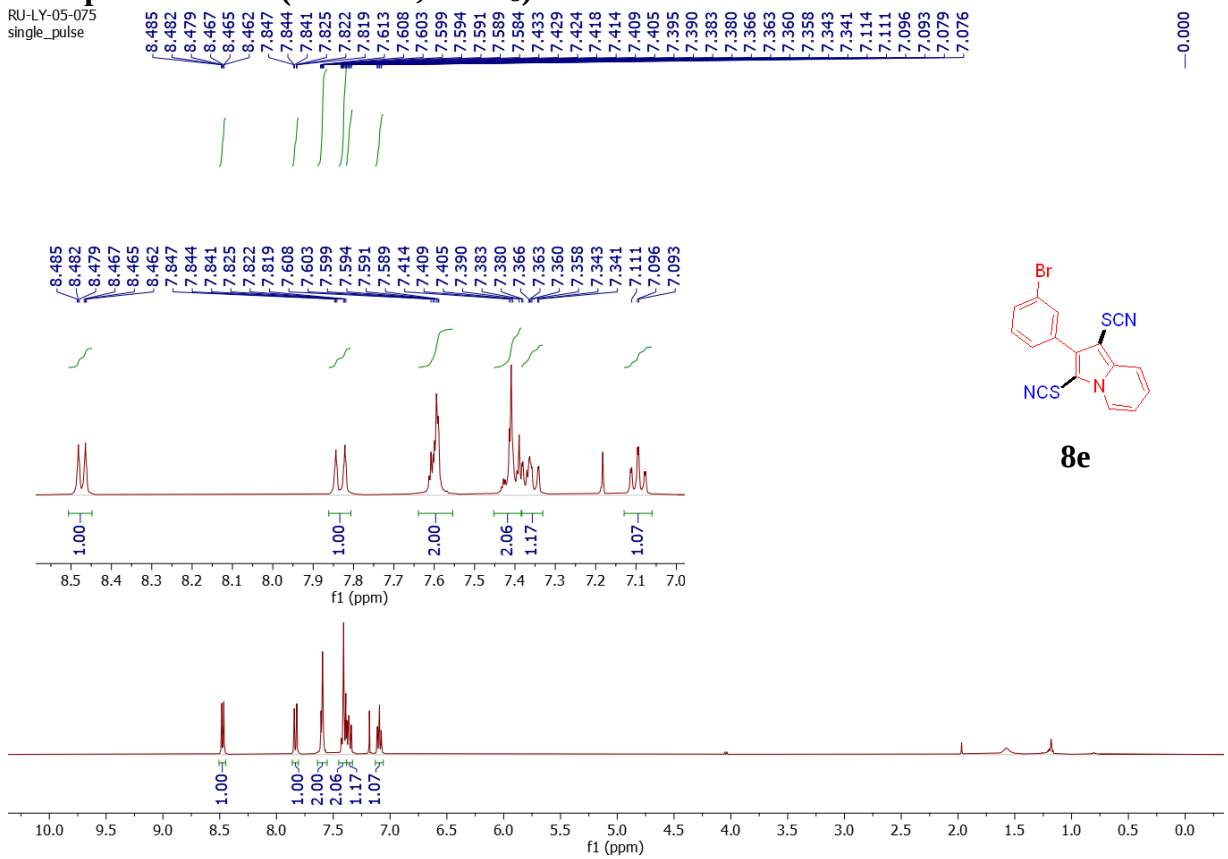
8d

^{13}C NMR spectrum of 8d (100 MHz, $CDCl_3$)



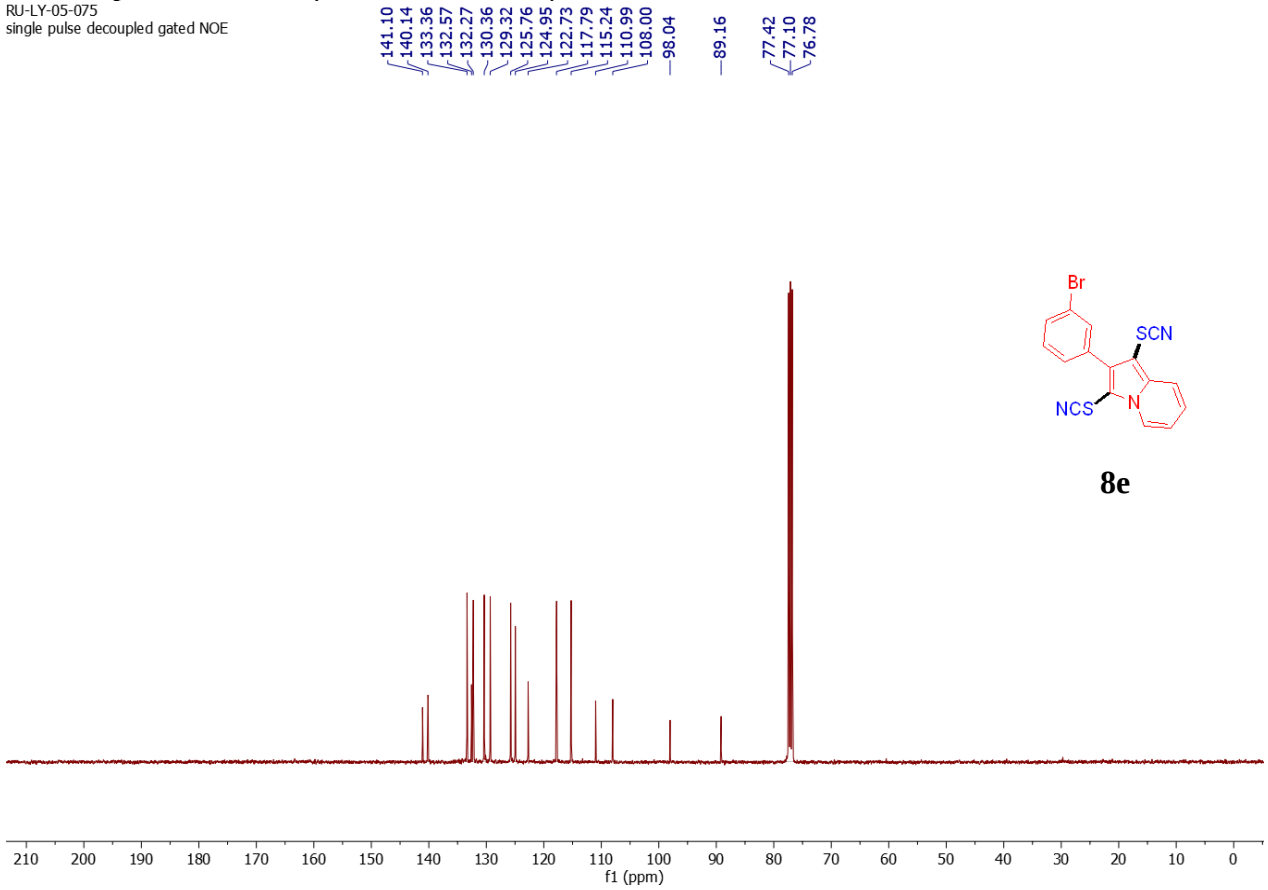
8d

^{1}H NMR spectrum of 8e (400 MHz, $CDCl_3$)



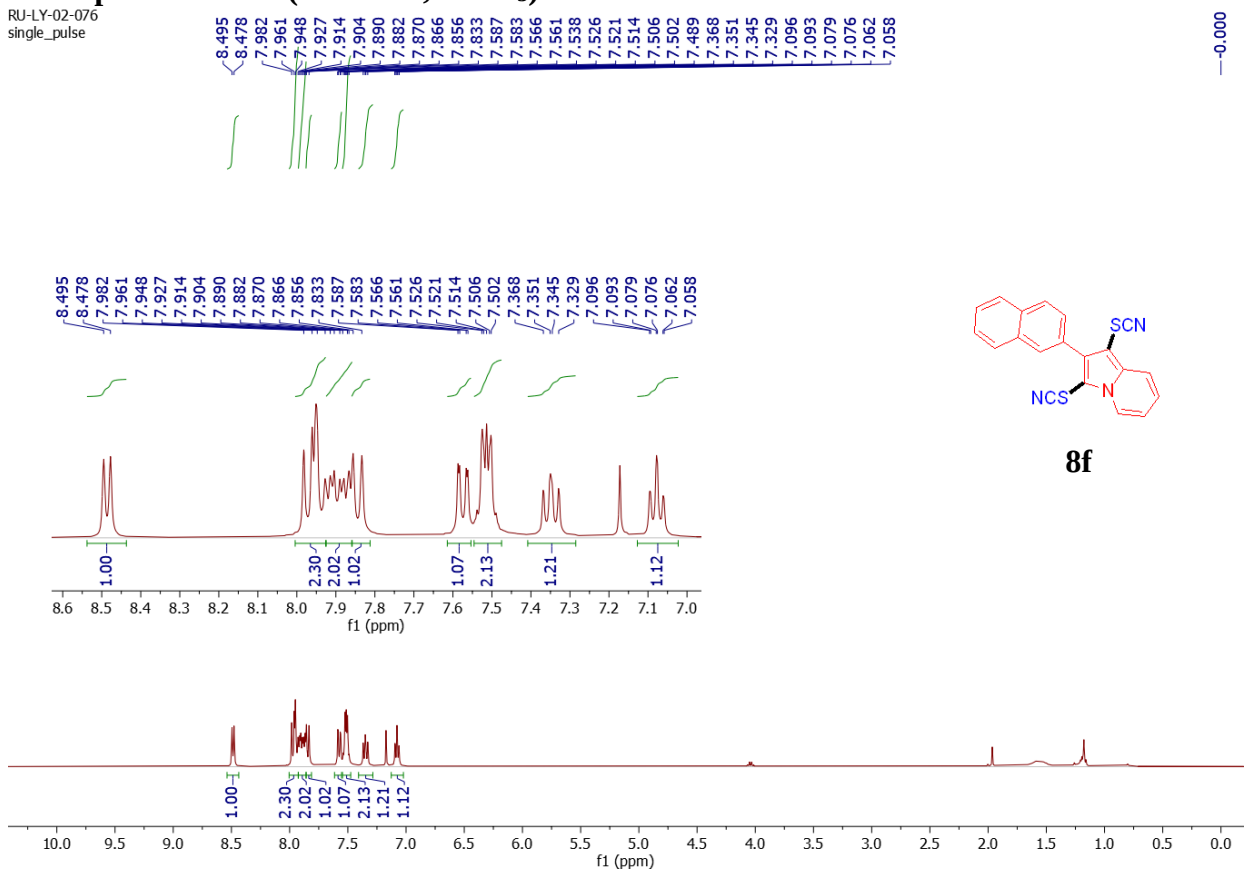
8e

^{13}C NMR spectrum of 8e (100 MHz, $CDCl_3$)



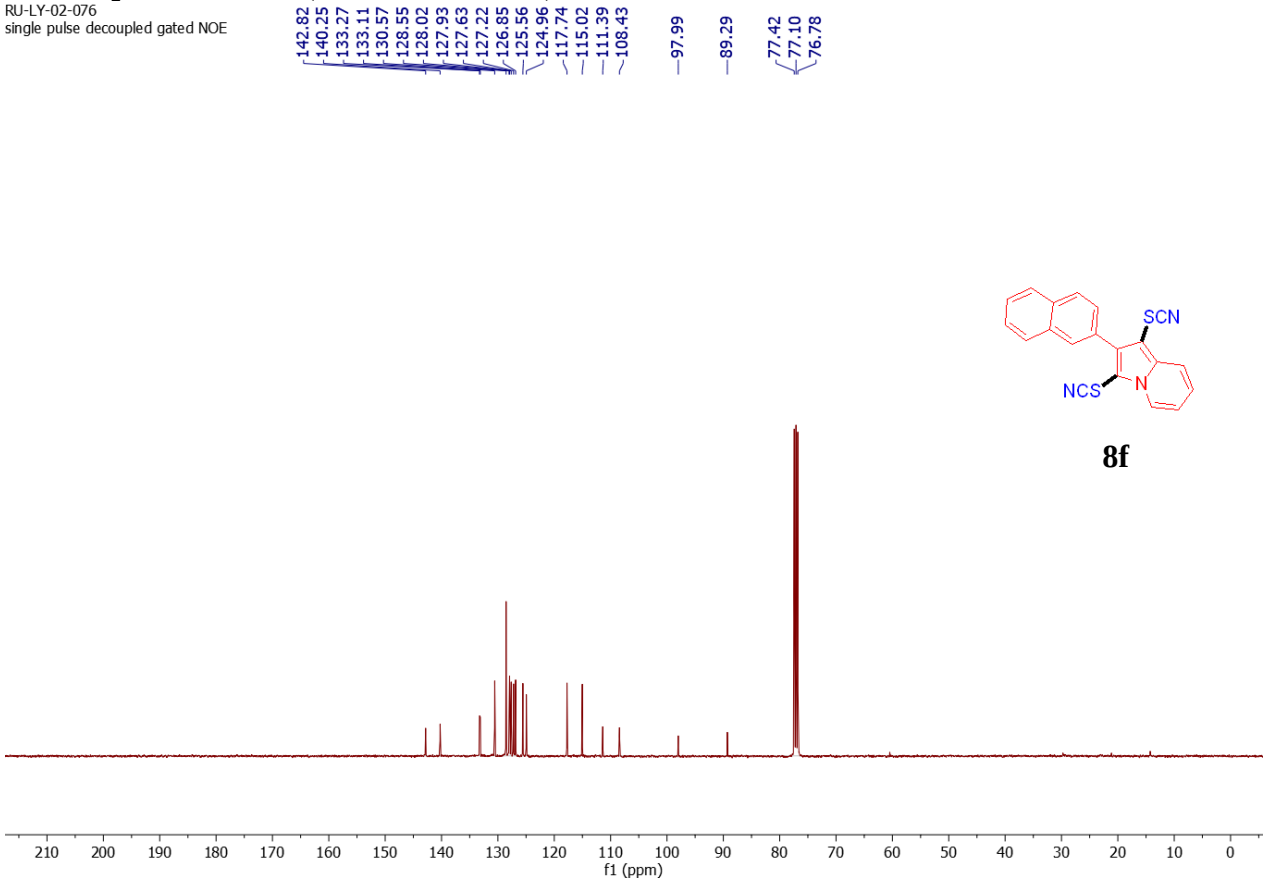
8e

^{1}H NMR spectrum of 8f (400 MHz, $CDCl_3$)



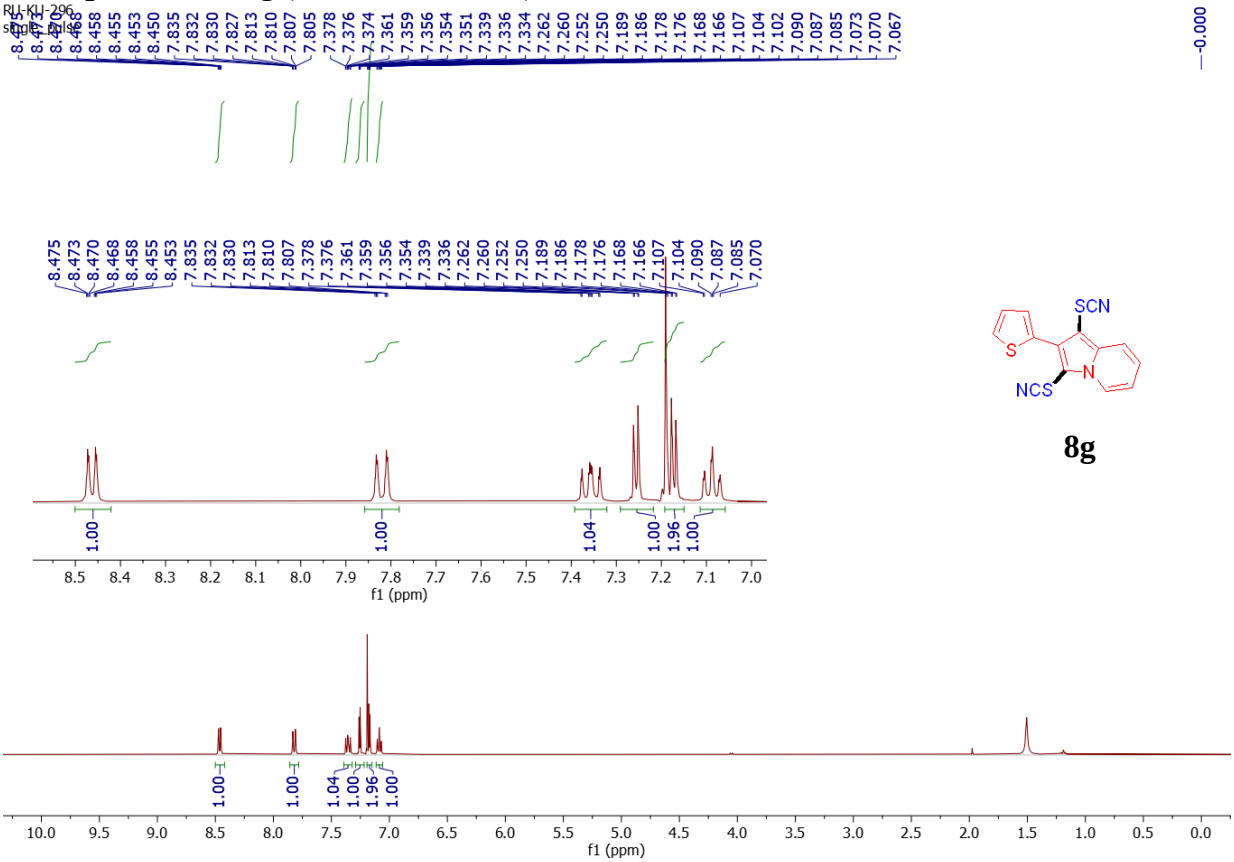
8f

^{13}C NMR spectrum of 8f (100 MHz, $CDCl_3$)



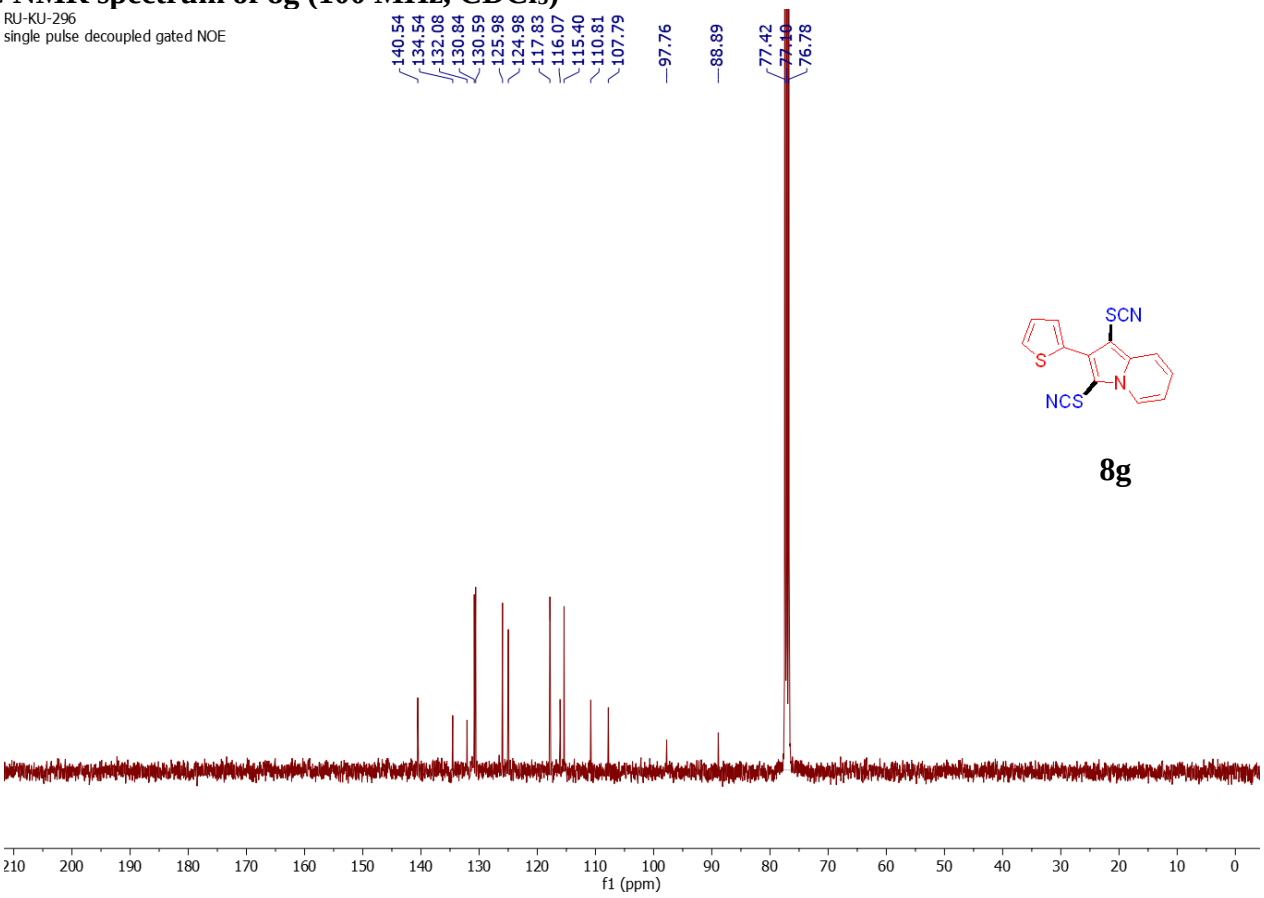
8f

^{1}H NMR spectrum of 8g (400 MHz, $CDCl_3$)



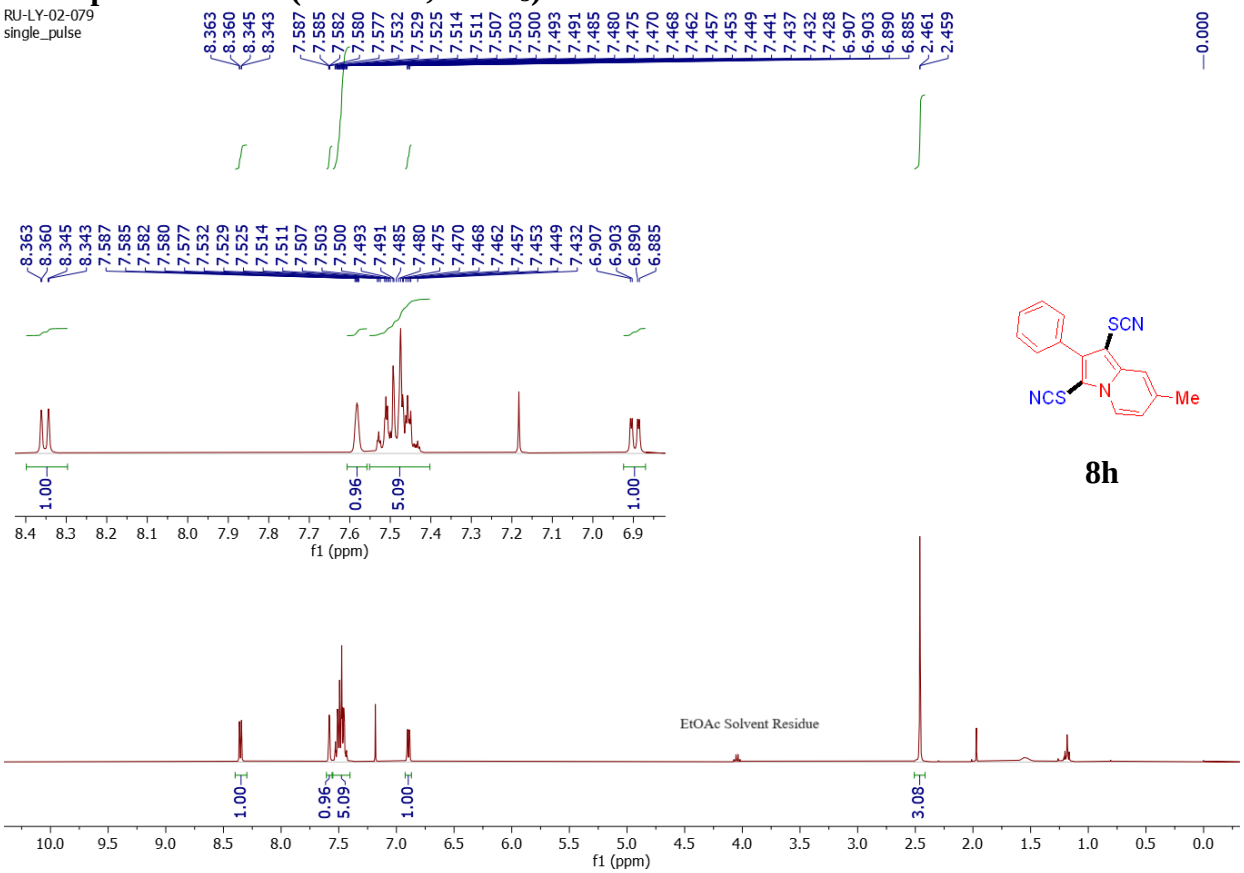
8g

^{13}C NMR spectrum of 8g (100 MHz, $CDCl_3$)

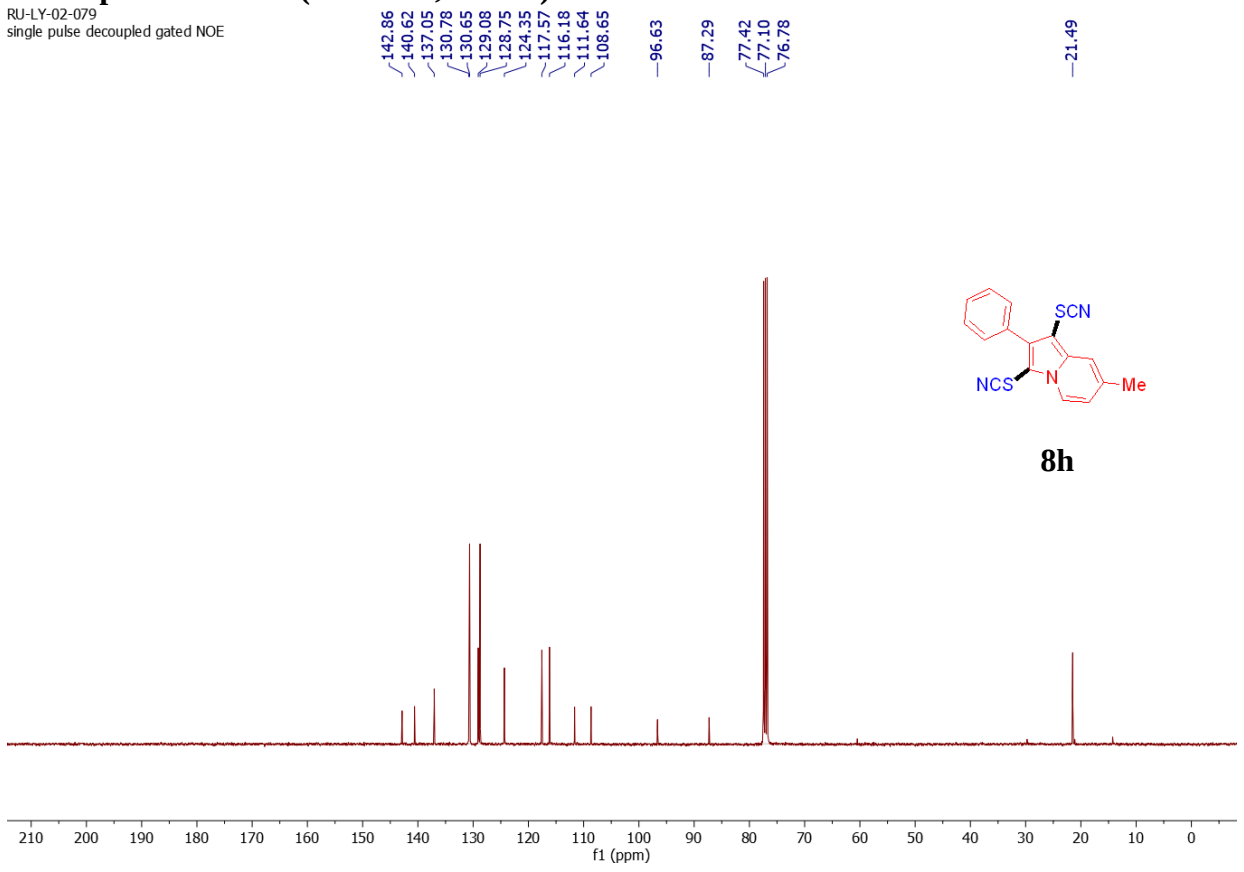


8g

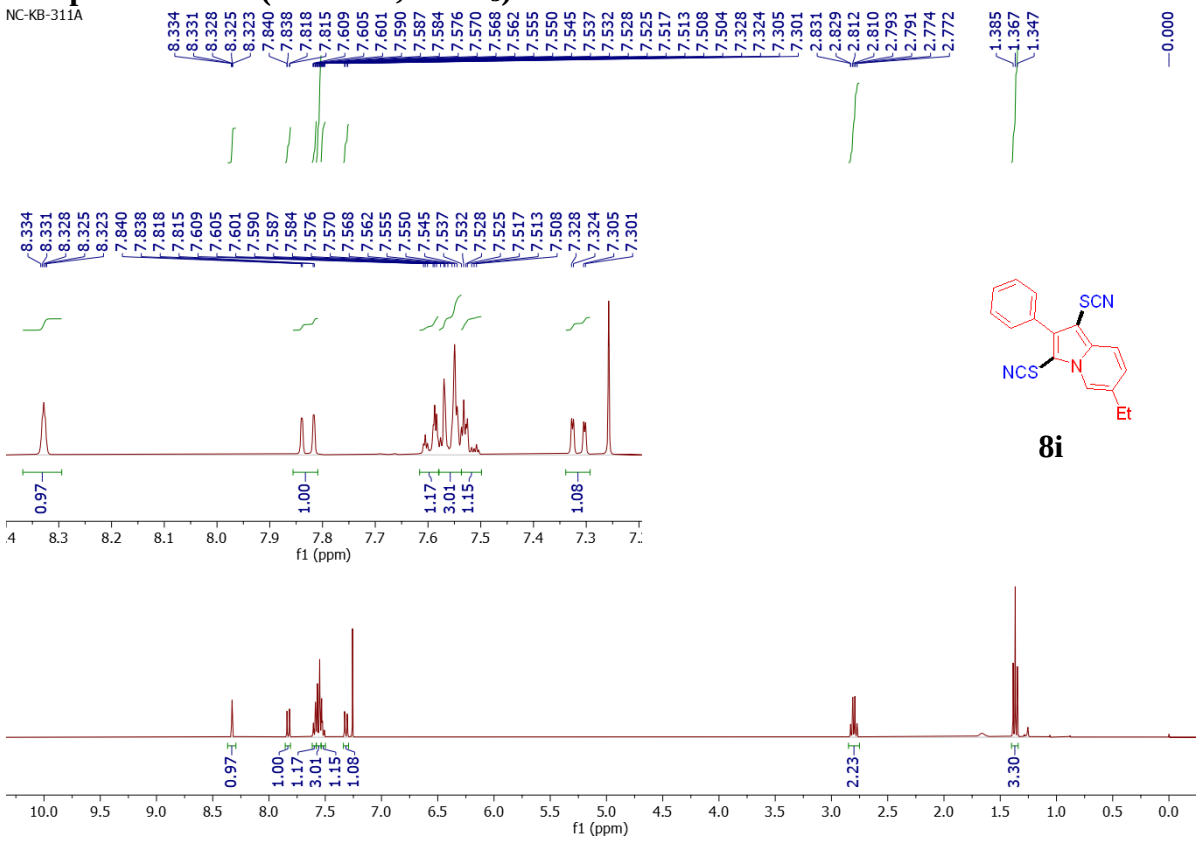
^{1}H NMR spectrum of 8h (400 MHz, $CDCl_3$)



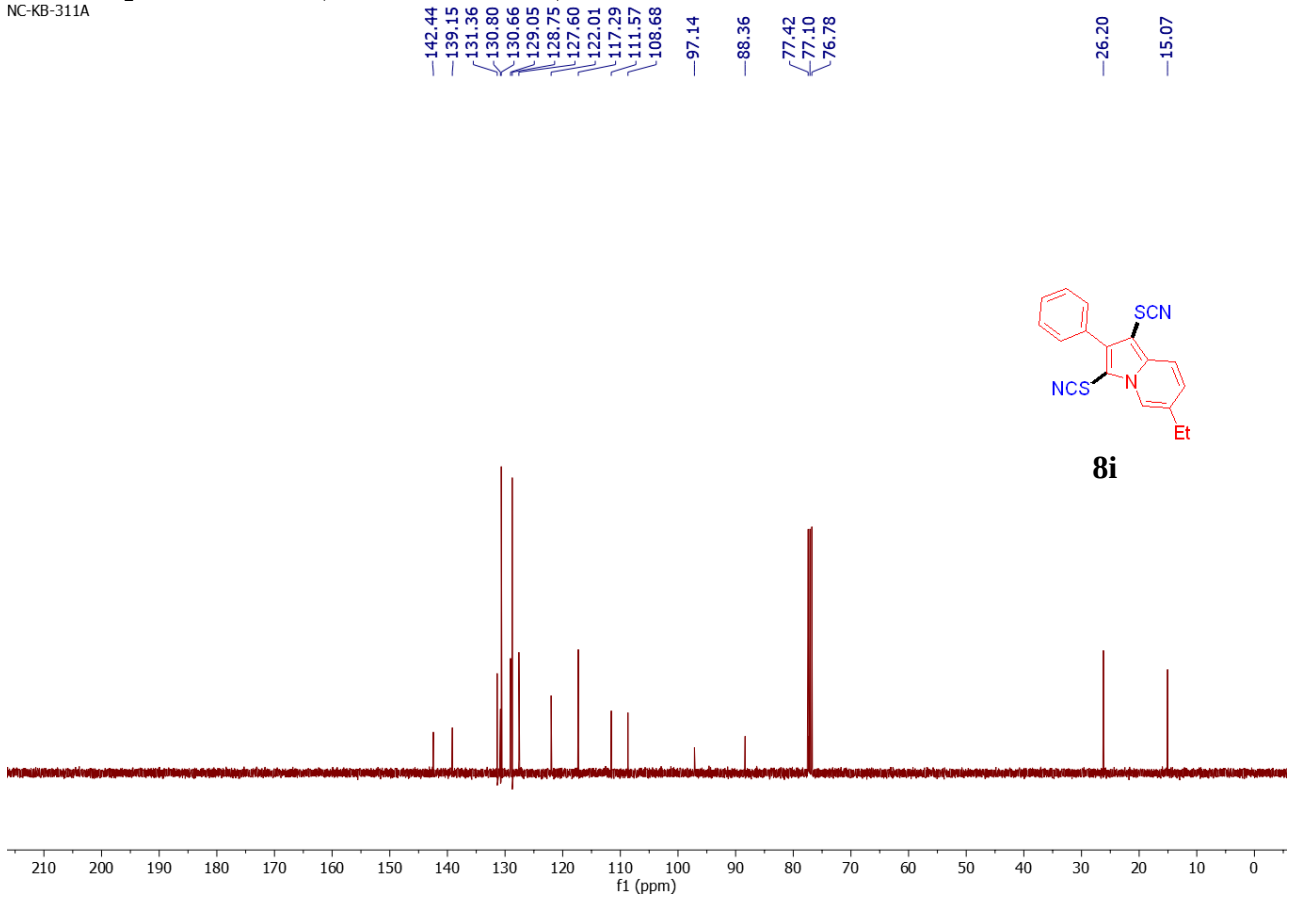
^{13}C NMR spectrum of 8h (100 MHz, $CDCl_3$)



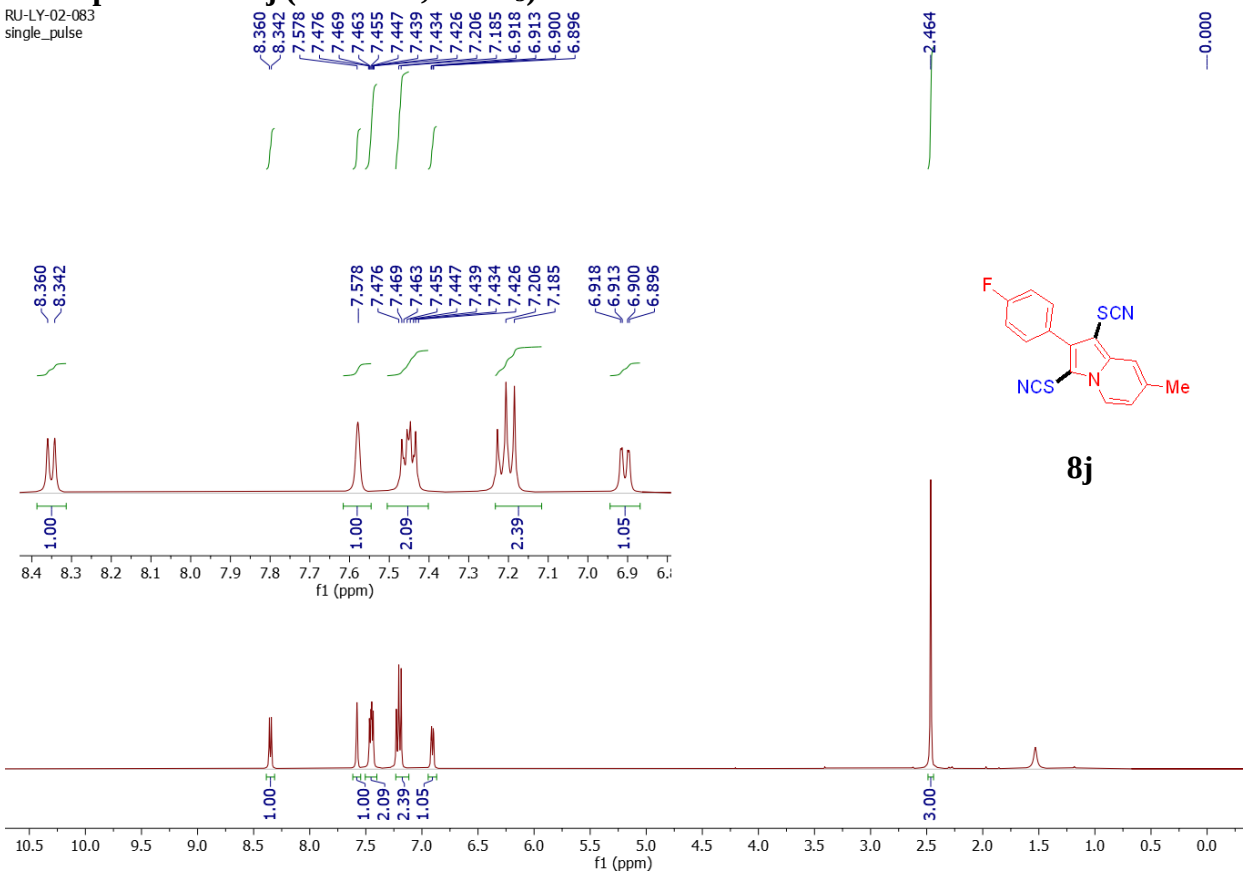
^{1}H NMR spectrum of 8i (400 MHz, $CDCl_3$)



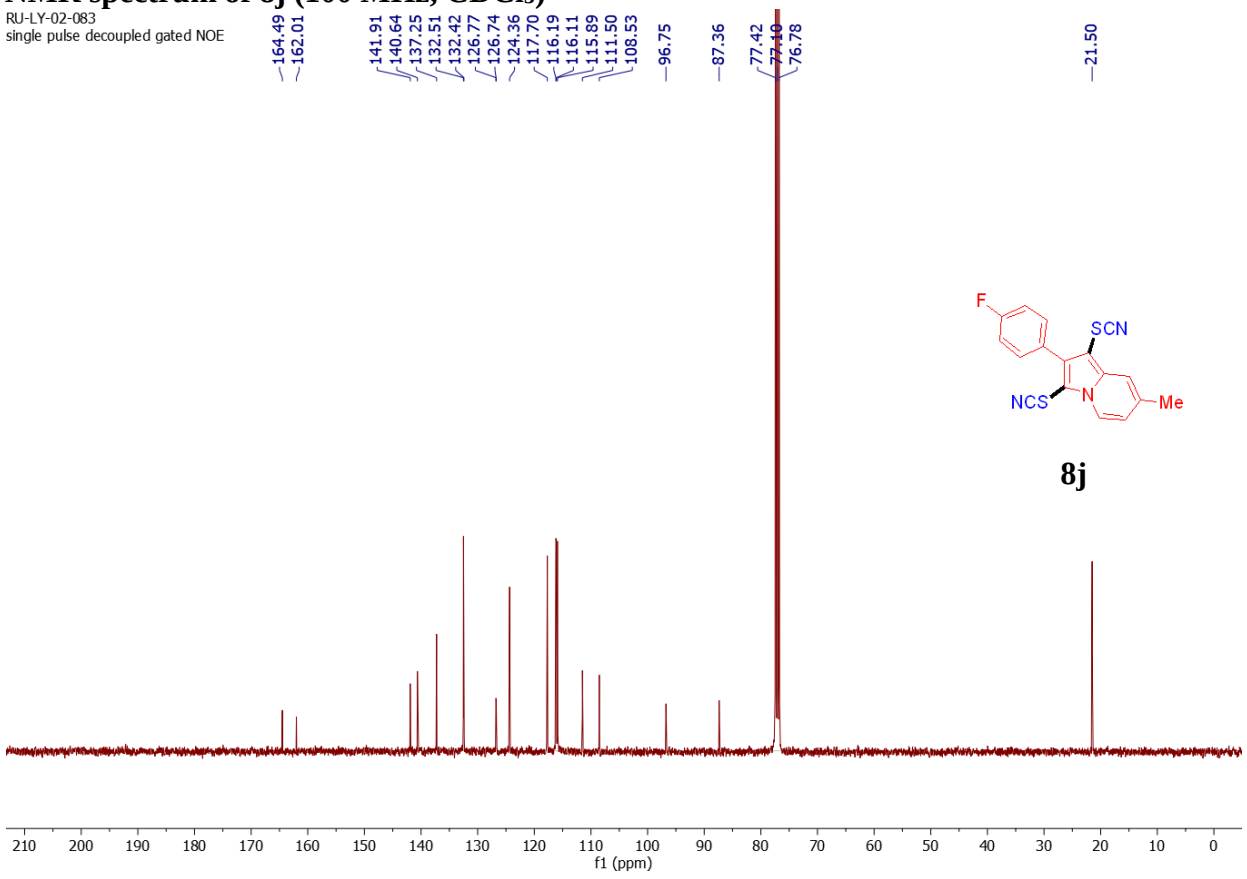
^{13}C NMR spectrum of 8i (100 MHz, $CDCl_3$)



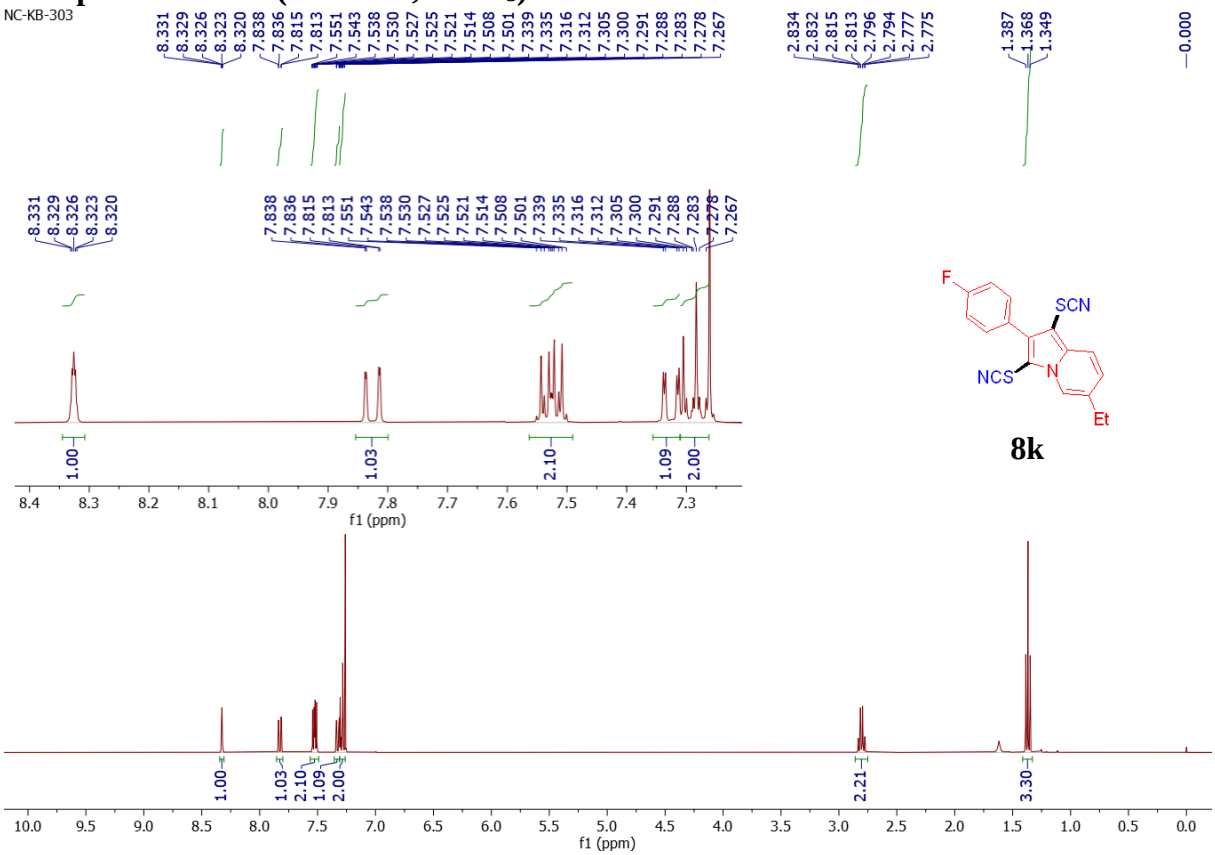
^{1}H NMR spectrum of 8j (400 MHz, $CDCl_3$)



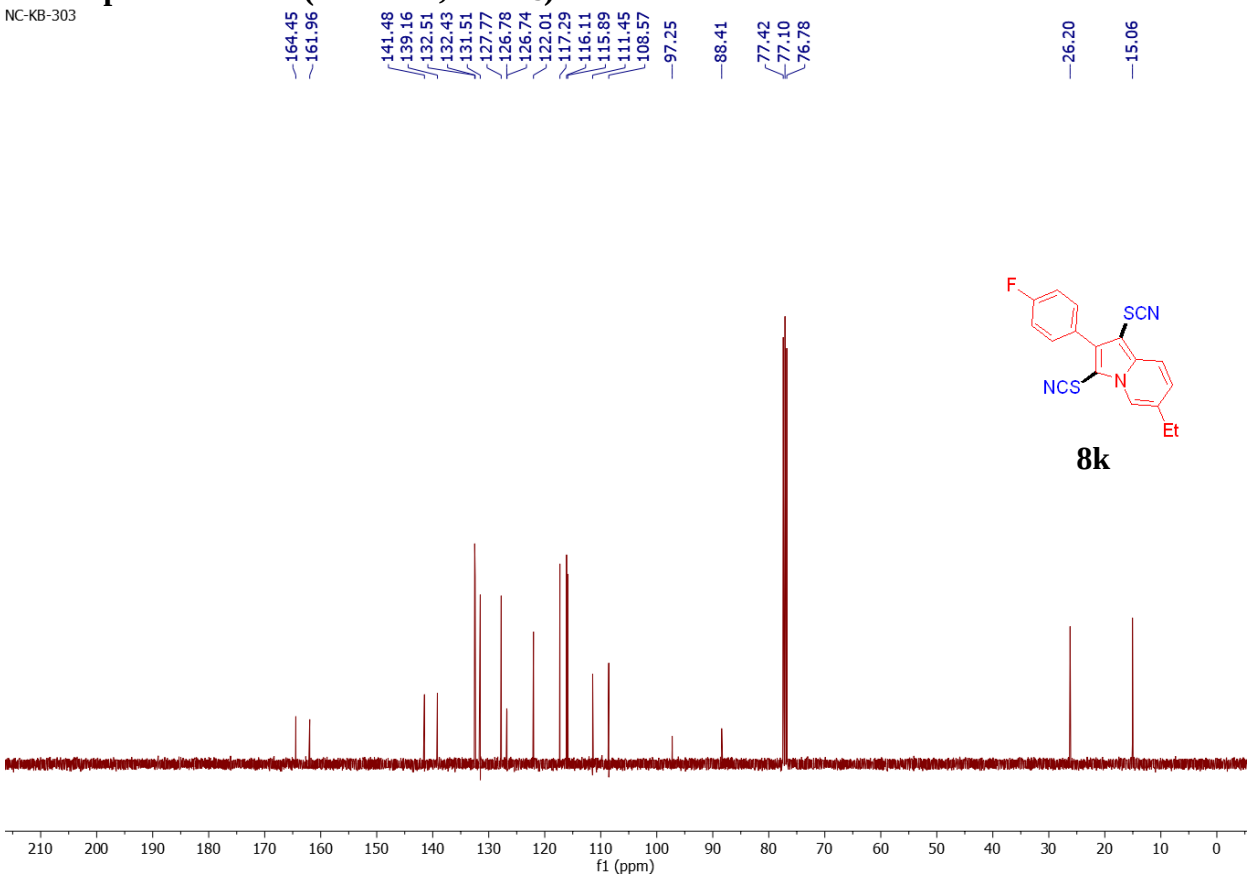
^{13}C NMR spectrum of 8j (100 MHz, $CDCl_3$)



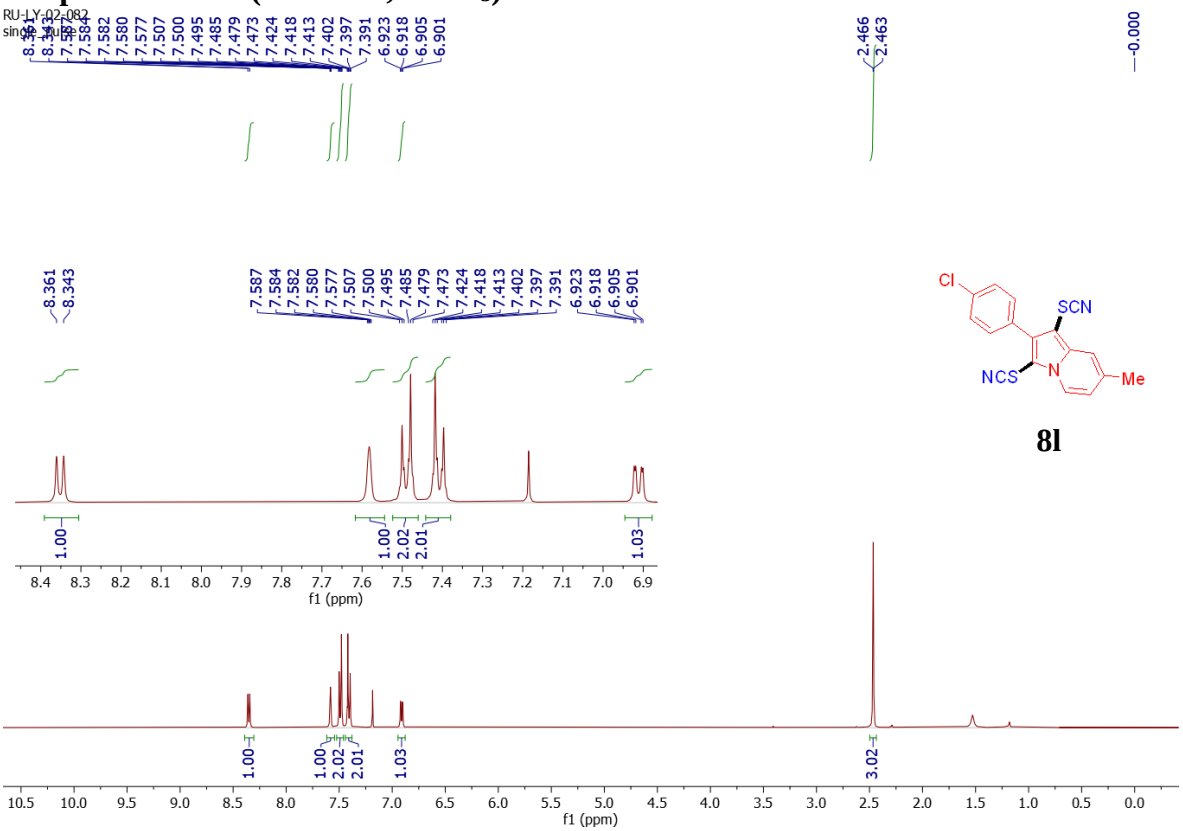
^{1}H NMR spectrum of 8k (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 8k (100 MHz, $CDCl_3$)

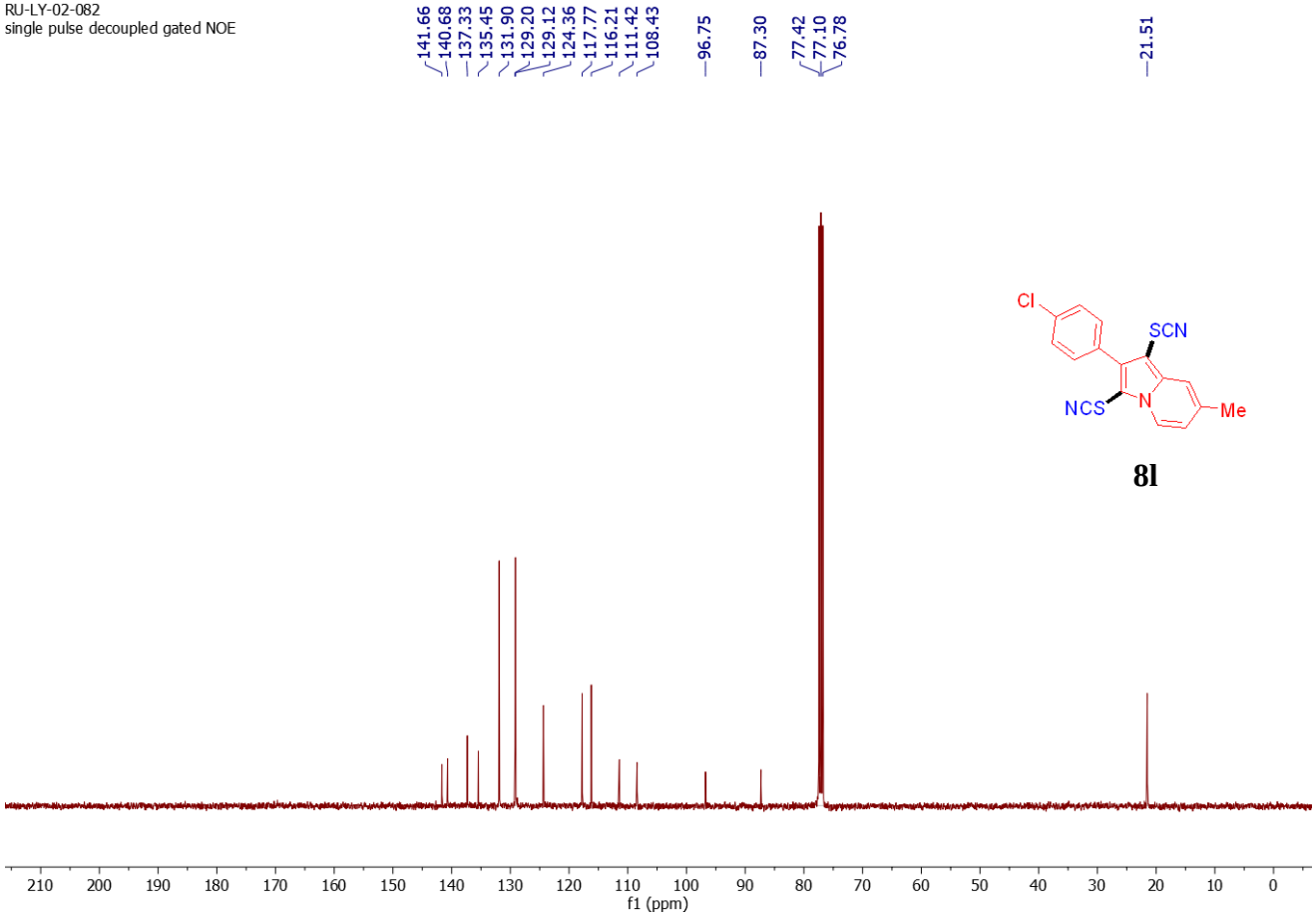


^{1}H NMR spectrum of 8l (400 MHz, $CDCl_3$)



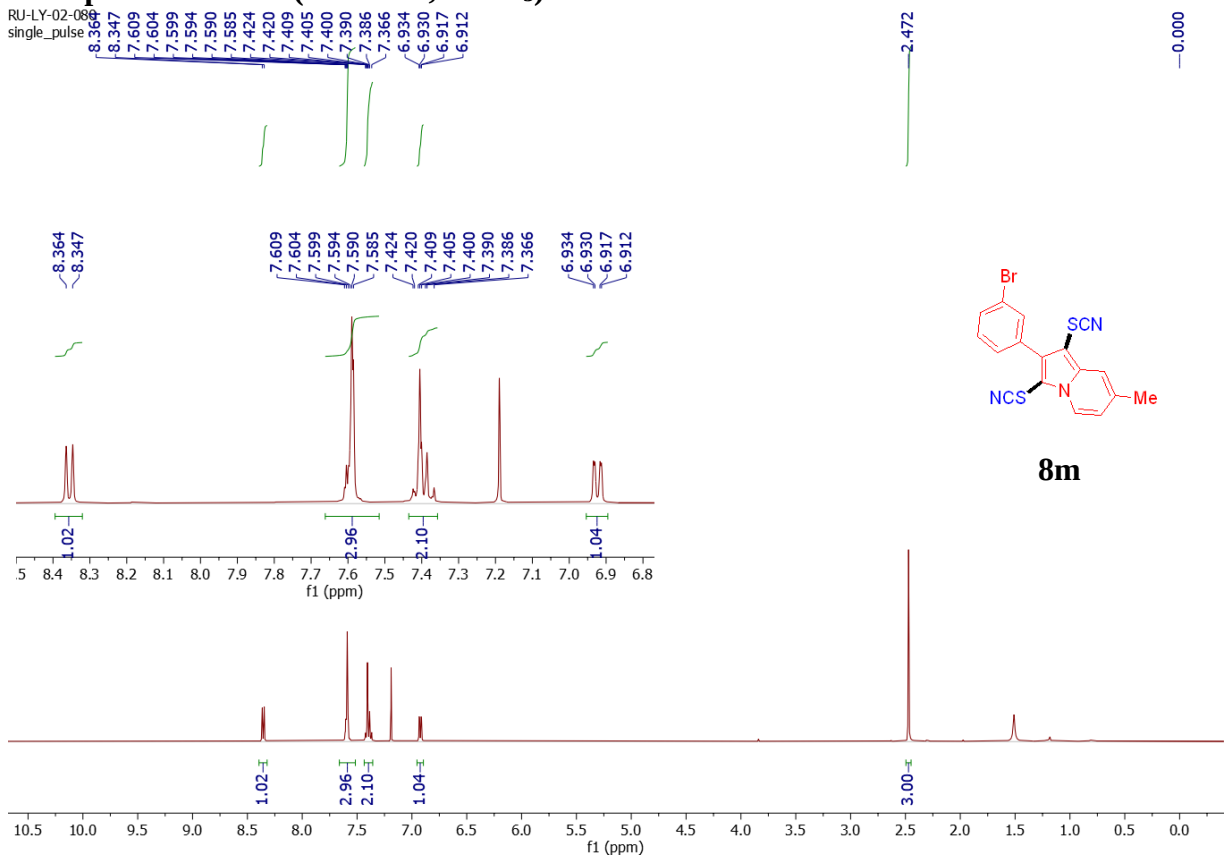
8l

^{13}C NMR spectrum of 8l (100 MHz, $CDCl_3$)



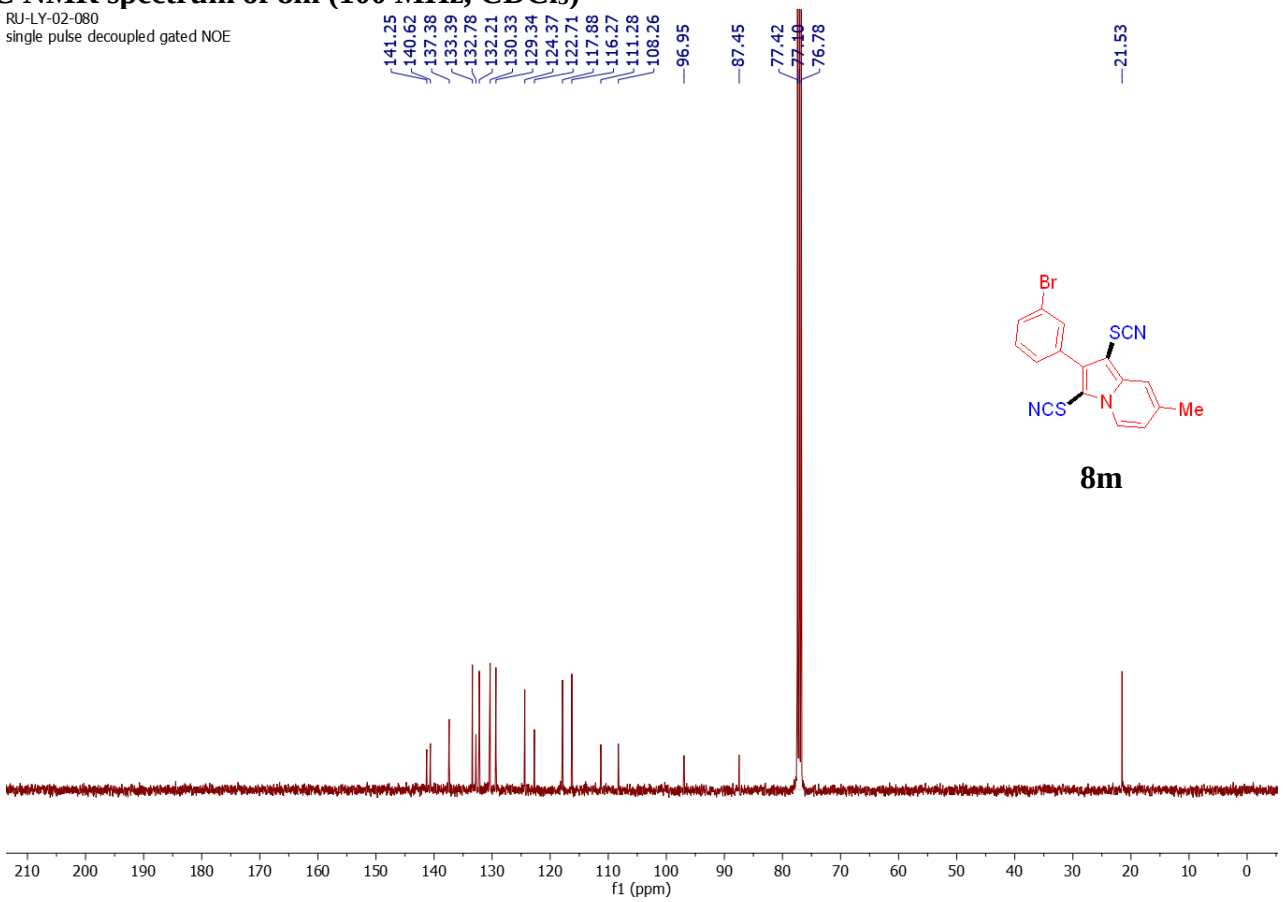
8l

^{1}H NMR spectrum of 8m (400 MHz, $CDCl_3$)



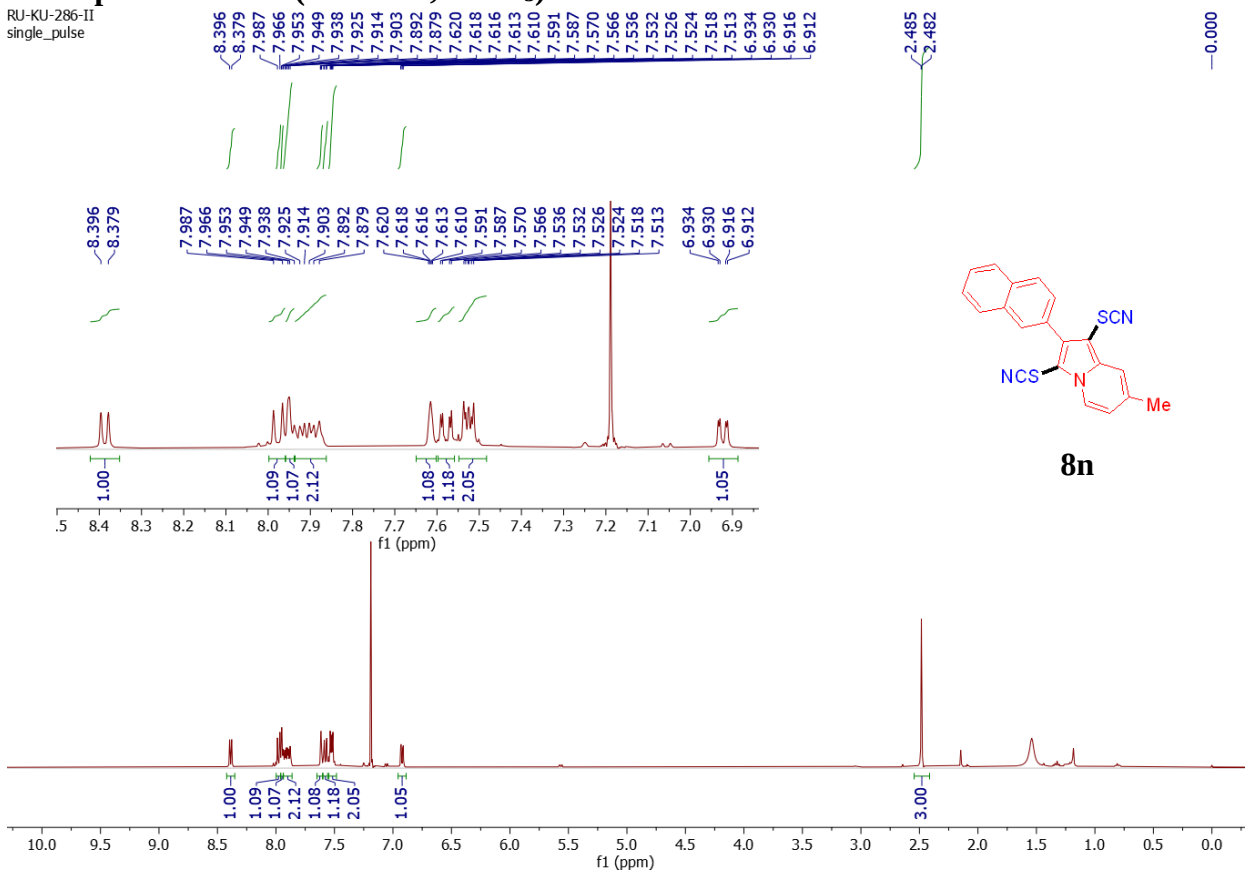
8m

^{13}C NMR spectrum of 8m (100 MHz, $CDCl_3$)



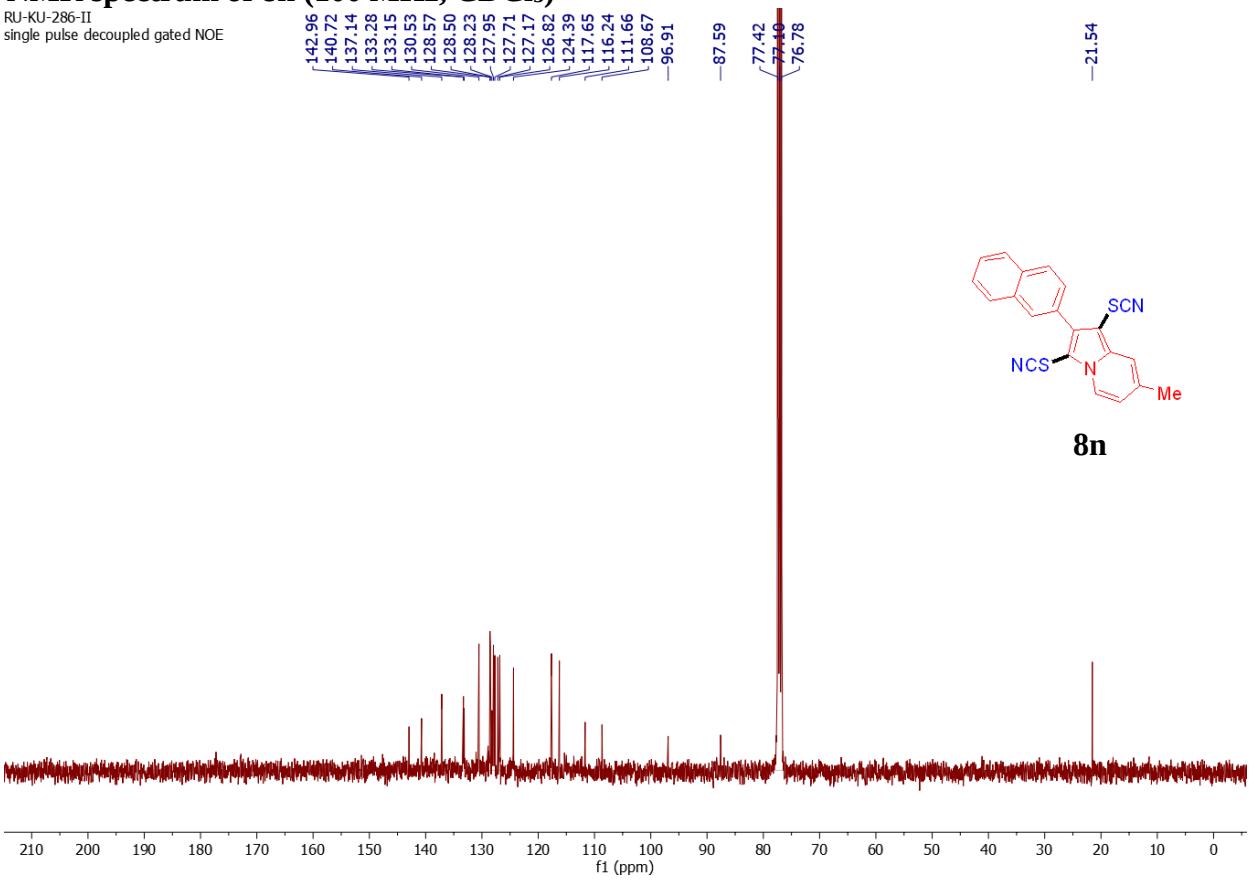
8m

^{1}H NMR spectrum of 8n (400 MHz, $CDCl_3$)



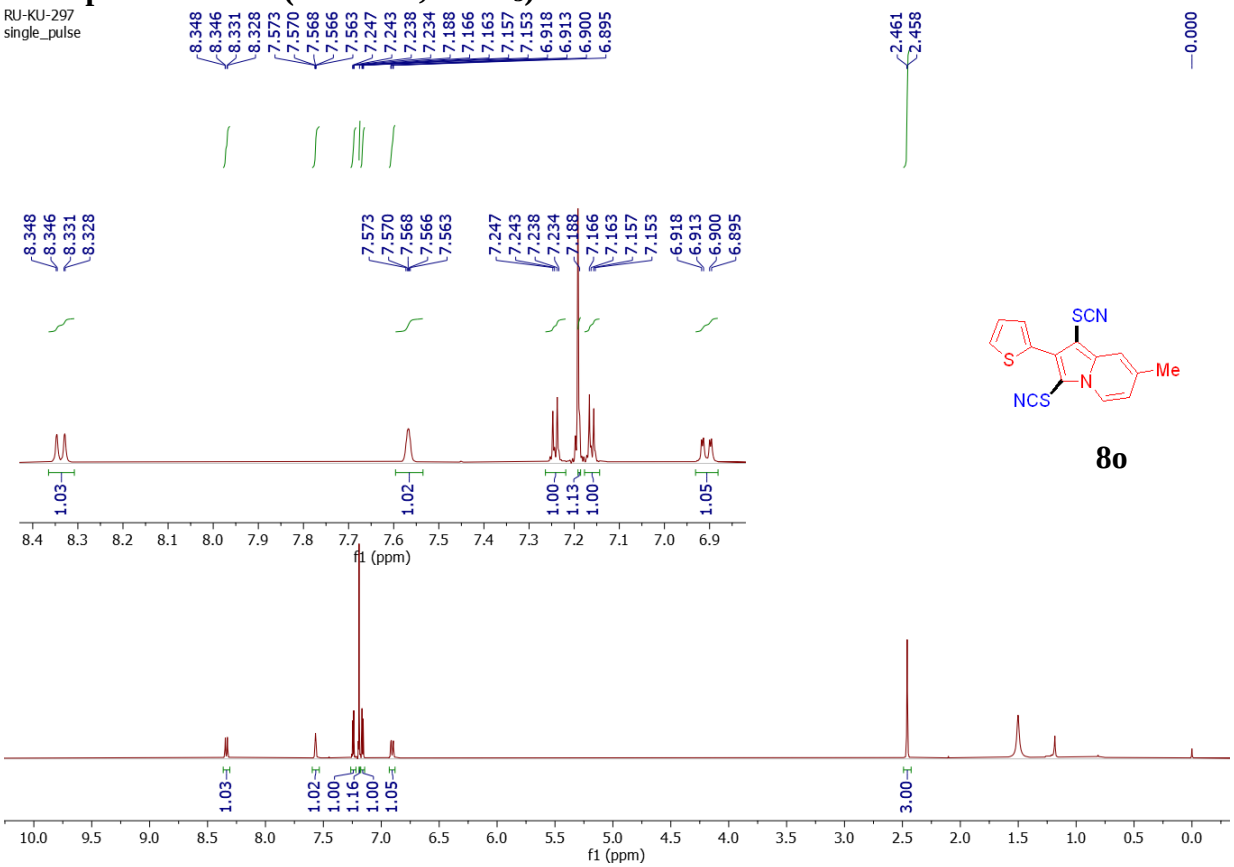
8n

^{13}C NMR spectrum of 8n (100 MHz, $CDCl_3$)



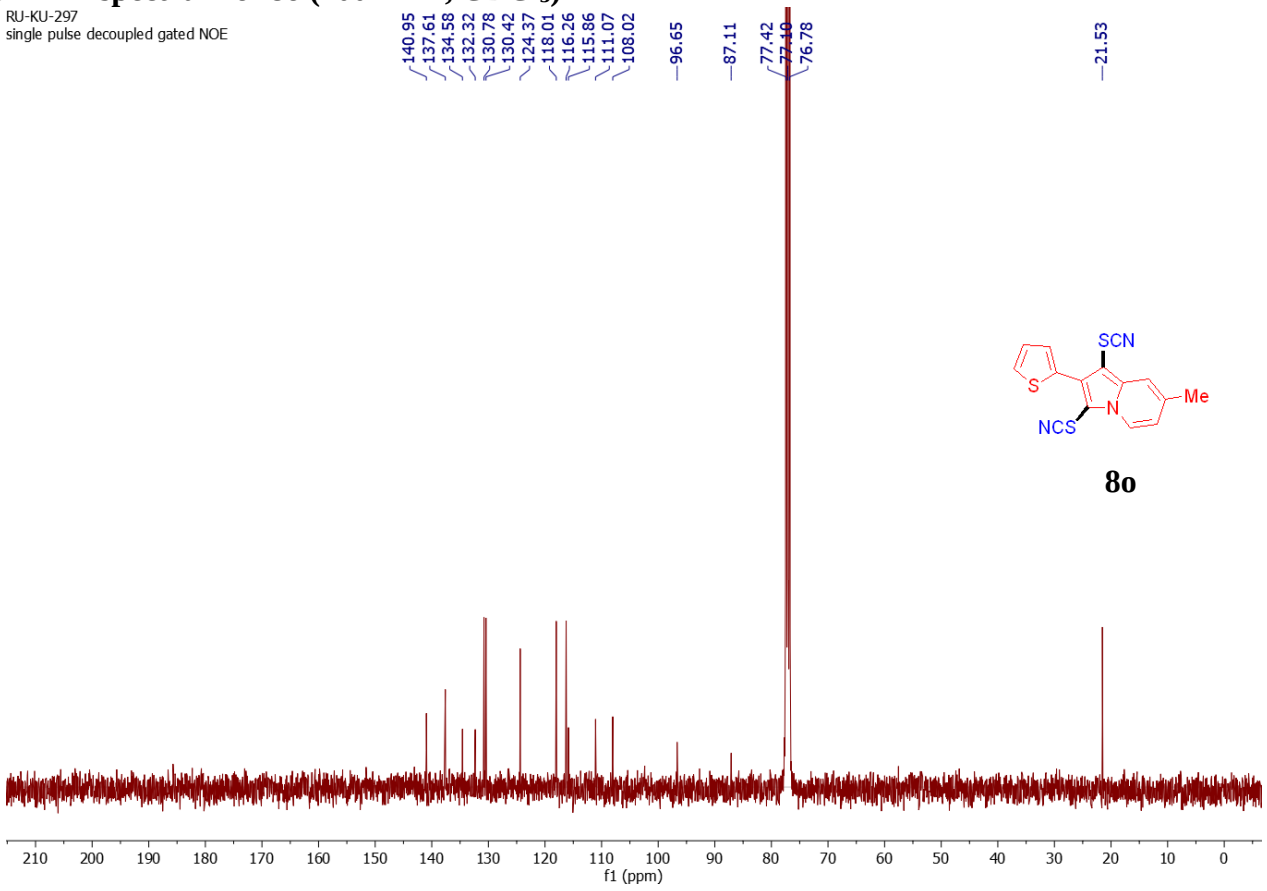
8n

^{1}H NMR spectrum of 8o (400 MHz, $CDCl_3$)



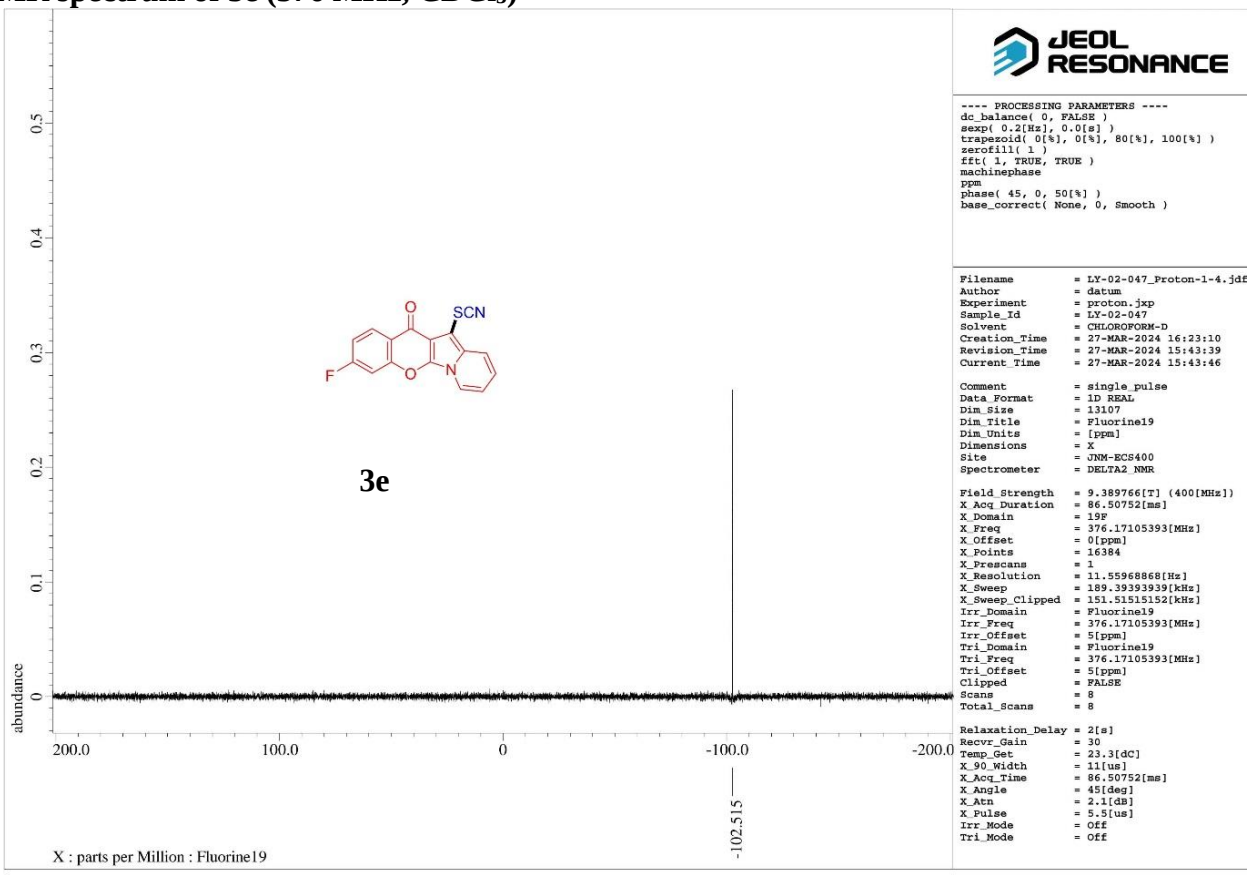
8o

^{13}C NMR spectrum of 8o (100 MHz, $CDCl_3$)

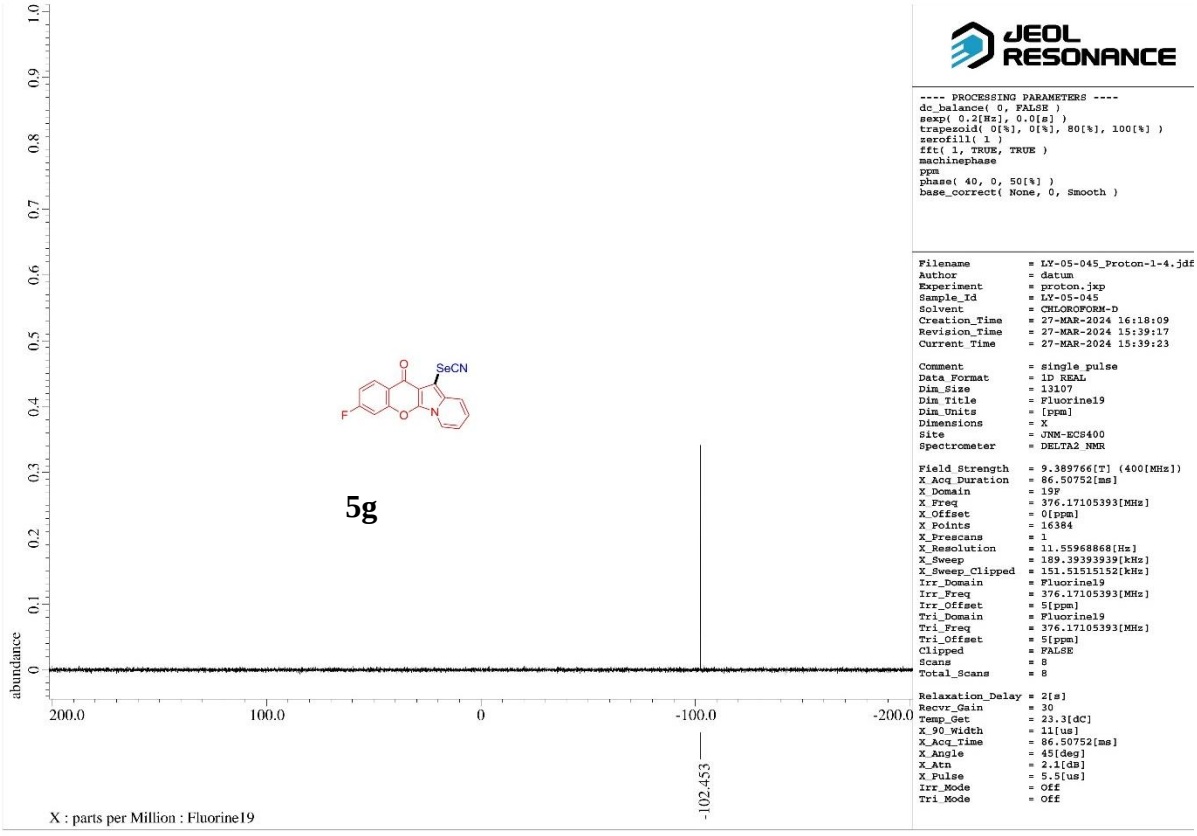


8o

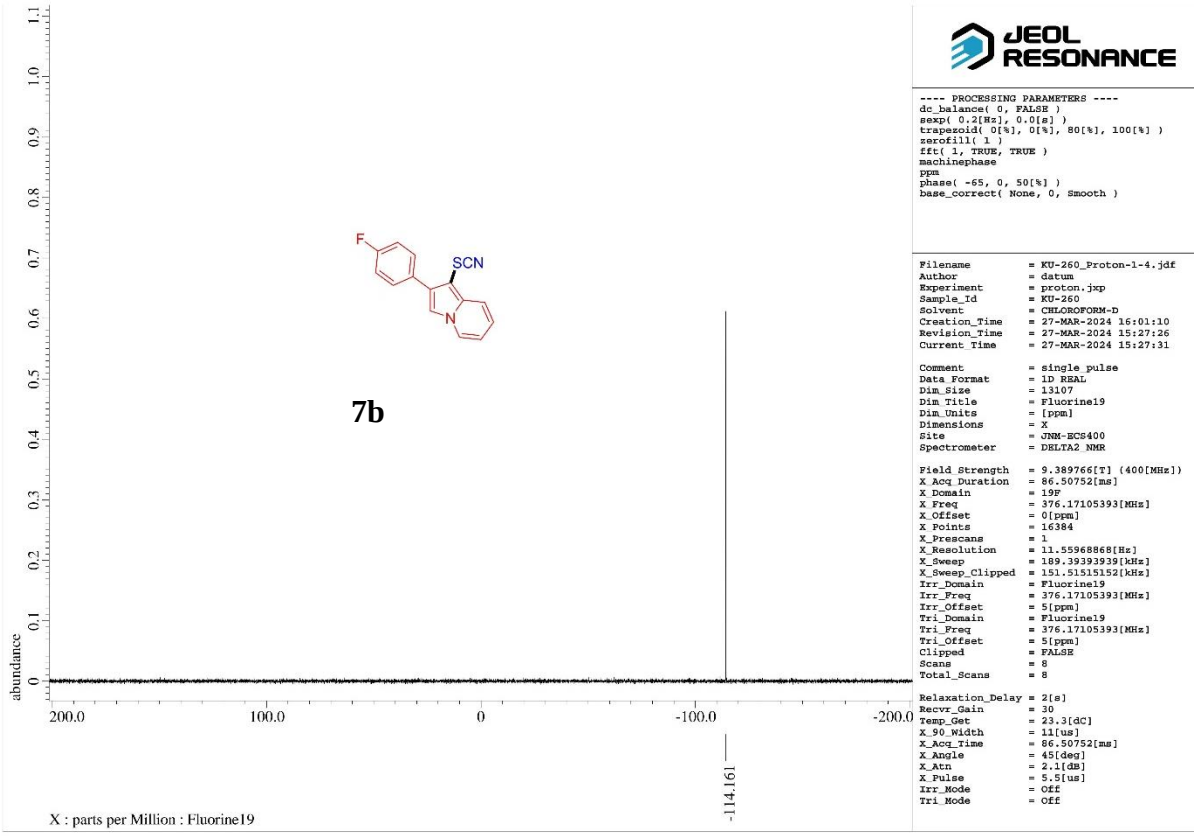
^{19}F NMR spectrum of 3e (376 MHz, $CDCl_3$)



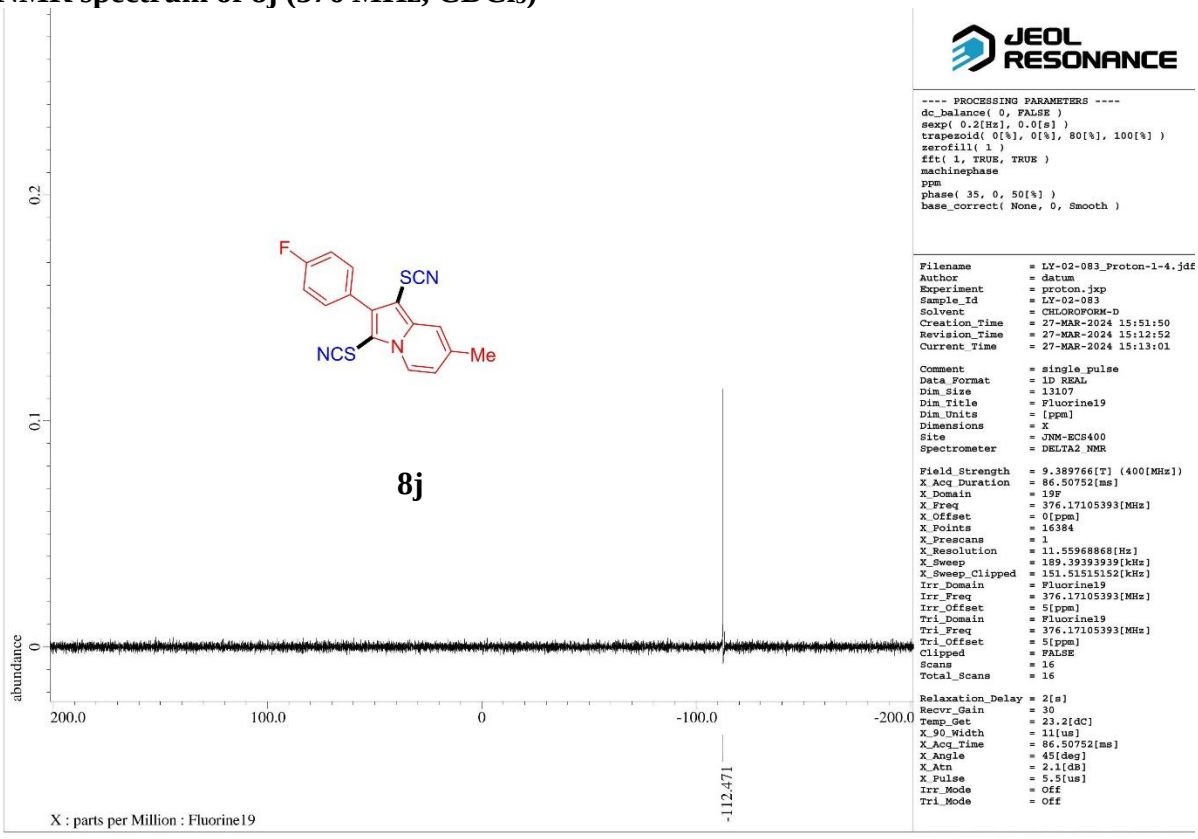
^{19}F NMR spectrum of 5g (376 MHz, $CDCl_3$)



^{19}F NMR spectrum of 7b (376 MHz, $CDCl_3$)



^{19}F NMR spectrum of 8j (376 MHz, $CDCl_3$)



^{19}F NMR spectrum of 8k (376 MHz, $CDCl_3$)