Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information (ESI)

A Benzimidazole-Based Cu(II) complex catalyzed Site-selective C-H Sulfenylation of Imidazo-[1,2-*a*] pyridines using CS_2 as a Sulfur Source

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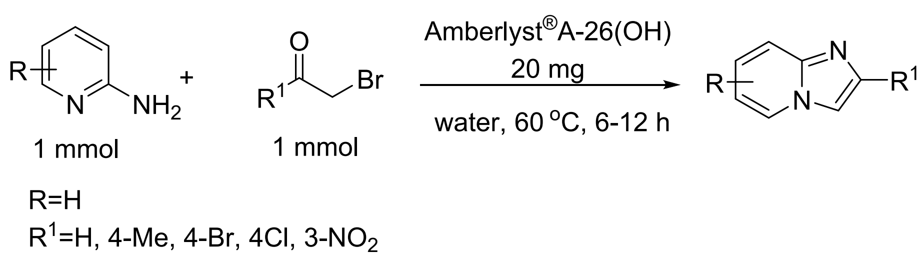
Contents

1. General Information

All reagents and solvents were obtained from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (100~200 mesh). ^{1}H and ^{13}C NMR data were recorded in BRUKER AVANCENEO 400 MHz NMR spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (*J*) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) were recorded using tetramethylsilane (TMS) as the internal standard in $CDCl_3$ and d_6-DMSO. The FT-IR spectra of the prepared compounds were recorded using a Bruker Alpha III IR-spectrophotometer operating in the wavenumber region from 4000 to 400 cm^{-1} in dry KBr. High resolution mass spectra were measured on an ESI source Xevo G-2s Q Tof (Waters, USA) at MNIT, Jaipur, India. Single crystal XRD was done in Bruker Kappa Apex II at STIC Cochin, India. Electron spin resonance (ESR) spectra was measured on JEOL, Model: JES-FA200 at IIT Guwahati, India.

2. General procedure for the preparation of imidazo[1,2-a]pyridines/thiazoles

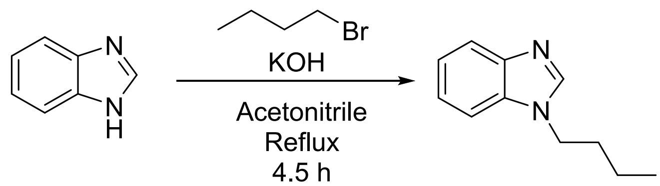
The various imidazo[1,2-a]pyridines/thiazole derivatives were synthesized according to our reported procedures.[1] 2-aminopyridine derivative (1.0 mmol), Amberlyst®A-26(OH) (20 mg) and substituted phenacyl bromide (1.0mmol) were taken in a 25 mL round bottom flask. 5 mL of deionized water was added to it. Then the resulting mixture was stirred for 6-8 hours at 60 °C, till the reaction was completed. The progress of the reaction was monitored using thin layer chromatography (TLC). After completion of the reaction, the organic part of the reaction mixture was extracted in ethyl acetate (3 x 5 mL). The combined organic layer was then dried over anhydrous $Na_2SO_4$and the volume was reduced under vacuum. The white/yellow/light brown coloured products were washed with a mixture of petroleum ether and diethyl ether (7:3) and then finally crystallized in dehydrated ethanol. Few imidazo[1,2-a]pyridines were purified in column chromatography with petroleum ether and ethyl acetate (9:1) as eluent.



3. General methods for Catalyst preparation

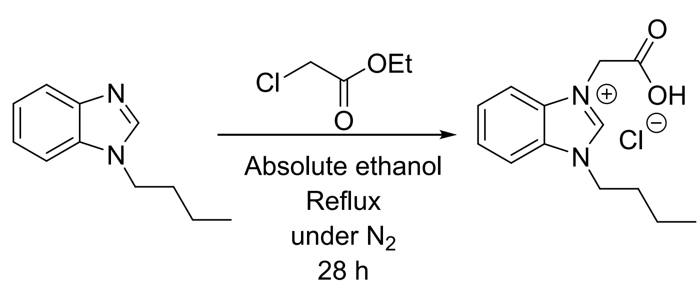
3.1. General methods for 1-butyl benzimidazole preparation

In a round bottomed flask, benzimidazole (5.9 g, 50.0 mmol), 1-bromobutane (7.0 g, 51.0 mmol) and potassium hydroxide (5.6 g, 100.0 mmol) were mixed in 30 mL of acetonitrile (HPLC grade). This mixture was then refluxed for about four and half hours and cooled at room temperature. 50 mL of water was added to the reaction mixture and extracted with ethyl acetate (3 x 30 mL). The combined organic layer was passed through the sodium sulfate and finally charged over column chromatography. The pure 1-butyl benzimidazole (4.9 g, 84% yield) was purified by a mixture of petroleum ether and ethyl acetate (7:3) as an eluting solvent.



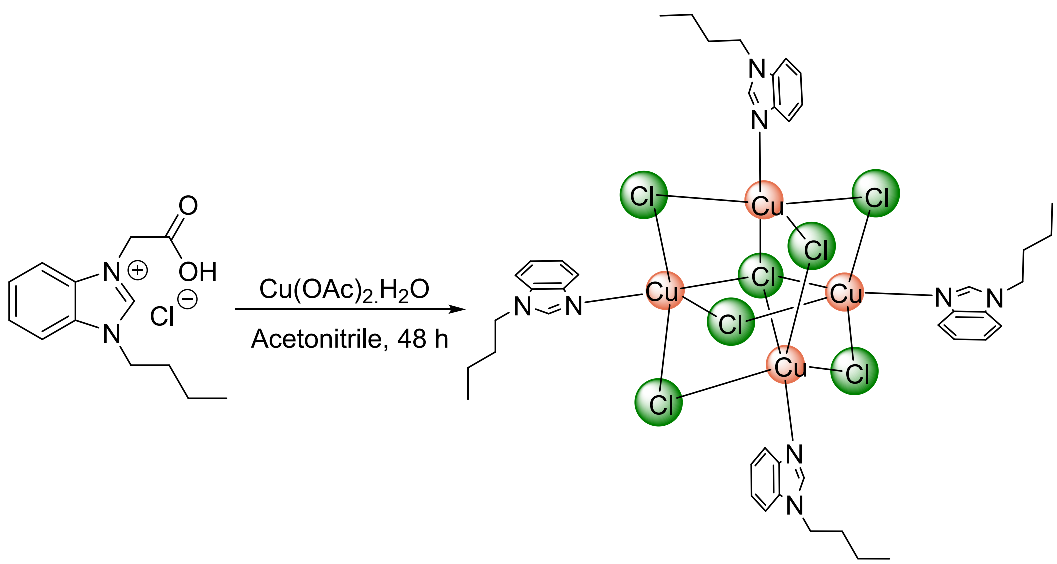
3.2. General methods for ionic liquid (IL) preparation

In the second step, the pure 1-butyl benzimidazole (4.33 g, 25.0 mmol), ethylchloroacetate (3.7 g, 25.0 mmol) and absolute ethanol (21.0 mL) was taken in a 100 mL round bottomed flask. The mixture was refluxed for 28 hours under N_2 atmosphere. After the reaction was completed, the mixture was cooled to room temperature, and the solvent was then removed under vacuum. The resulting gummy solid was then washed several times with ethyl acetate (10 x 10 mL) to obtain a pure white solid of desired ionic liquid (3.42 g, 75% yield). In this procedure, the ester group of the ionic liquid was hydrolyzed to corresponding carboxylic acid group.



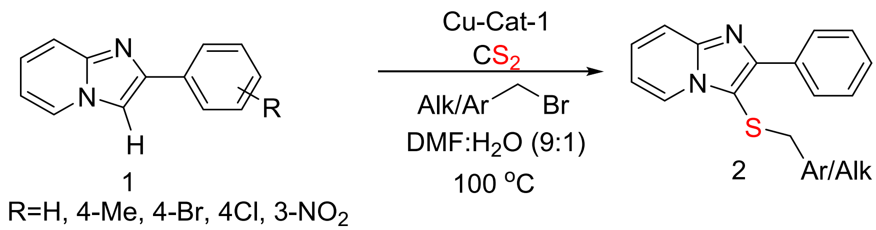
3.3. General methods for copper catalyst (Cu-Cat-1) synthesis

To a solution of ionic liquid (268.75 mg, 1.0 mmol) and acetonitrile (5.0 mL, HPLC grade), $Cu(OAc)_2.H_2O$ (199.5 mg, 1.0 mmol) was added. The resulting reaction mixture was refluxed for 48 h. After cooling the reaction mixture, it was filtrated through a Whatman 42 filter paper and the resulting brownish yellow coloured Cu complex was washed several times with diethyl ether. Finally, the copper complex was crystallized in a binary solvent mixture (acetonitrile and petroleum ether by diffusion method). The isolated yield was 68%.



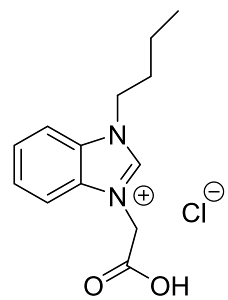
4. General procedure of Cu(II)-catalyzed C-H sulfenylation of imidazo[1,2-*a*]pyridines using CS_2 (2a-2r)

2-Arylimidazo[1,2-*a*]pyridine/thiazole 1a (0.5 mmol, 1.0 equiv.), CS_2 (1.0 mmol, 2 equiv.), and benzyl/alkyl/allyl halide (0.7 mmol, 1.4 equiv.) were added in a high pressure reaction vessel with DMF:H_2O (9:1, 1 mL), followed by the addition of Cu-Cat-1 complex (1 mol%). The mixture was stirred at 100 ^oC in a preheated oil bath. After 14 h, the reaction was cooled down to room temperature, water was added and diluted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by normal column chromatography using a mixture of petroleum ether and ethyl acetate (17:3) as an eluting solvent on silica gel (100-200 mesh) to afford the desired product as a yellow oil in most of the cases (65-74% yield).



5. Characterization of Ionic liquid (IL)

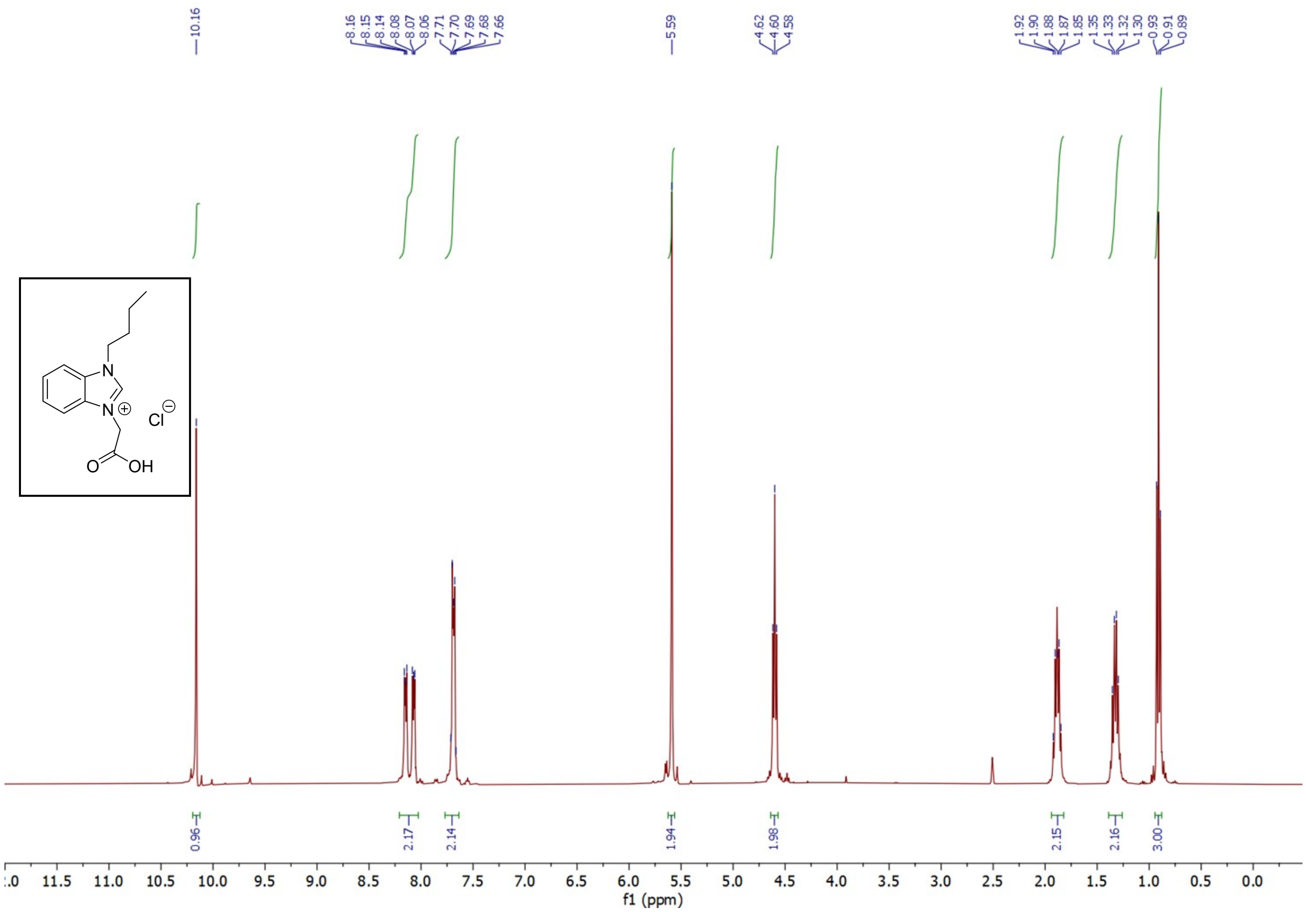
5.1. NMR data of ionic liquid (IL)



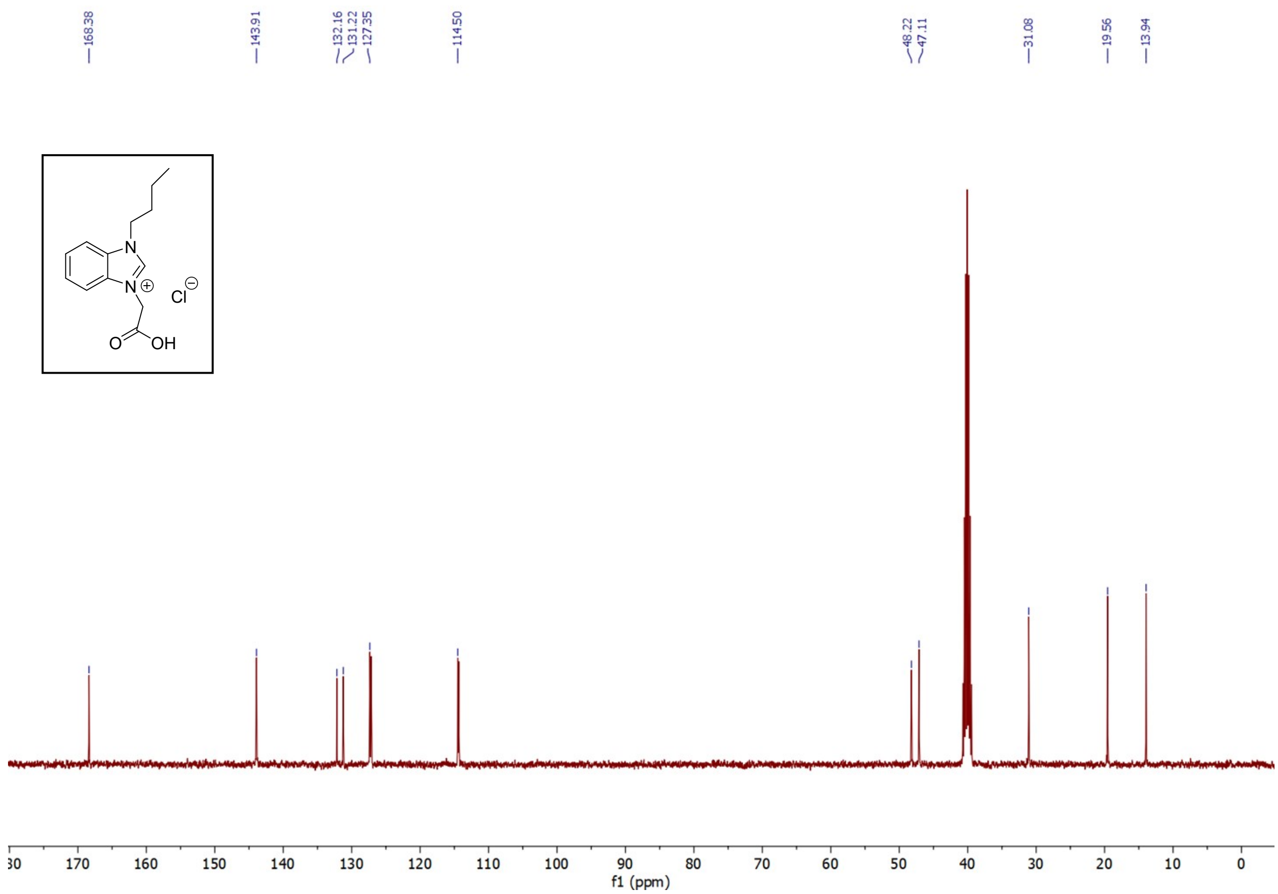
White Solid; ^{1}HNMR (400 MHz, d_6-DMSO): δ (in ppm)0.91(t, *J*=8Hz, 3H), 1.30-1.35 (m, 1H), 1.85-1.92 (m, 2H), 4.60 (t, *J*=8Hz, 2H), 5.59 (s, 2H), 7.66-7.71 (m, 2H), 8.06-8.16 (m,2H), 10.16 (s,1H);

^{13}C NMR (100 MHz, d_6-DMSO): δ (in ppm) 13.94, 19.56, 31.08, 47.11, 48.22, 114.50, 127.35, 131.72, 132.16, 143.91, 168.38

5.2. NMR images of ionic liquid (IL)



[1]H NMR spectra of Ionic liquid



^{13}C NMR spectra of Ionic liquid

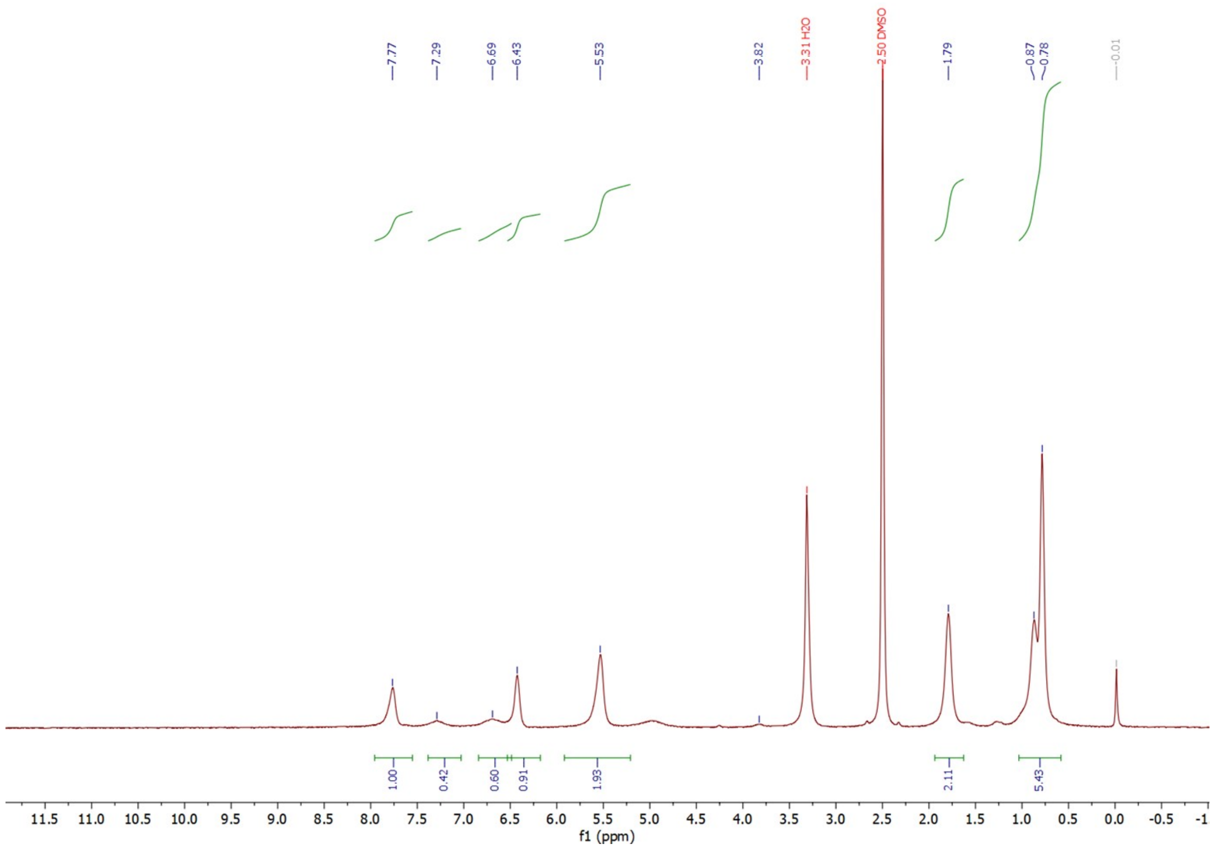
6. Characterization of Cu-Cat-1

6.1. NMR data of Cu-Cat-1

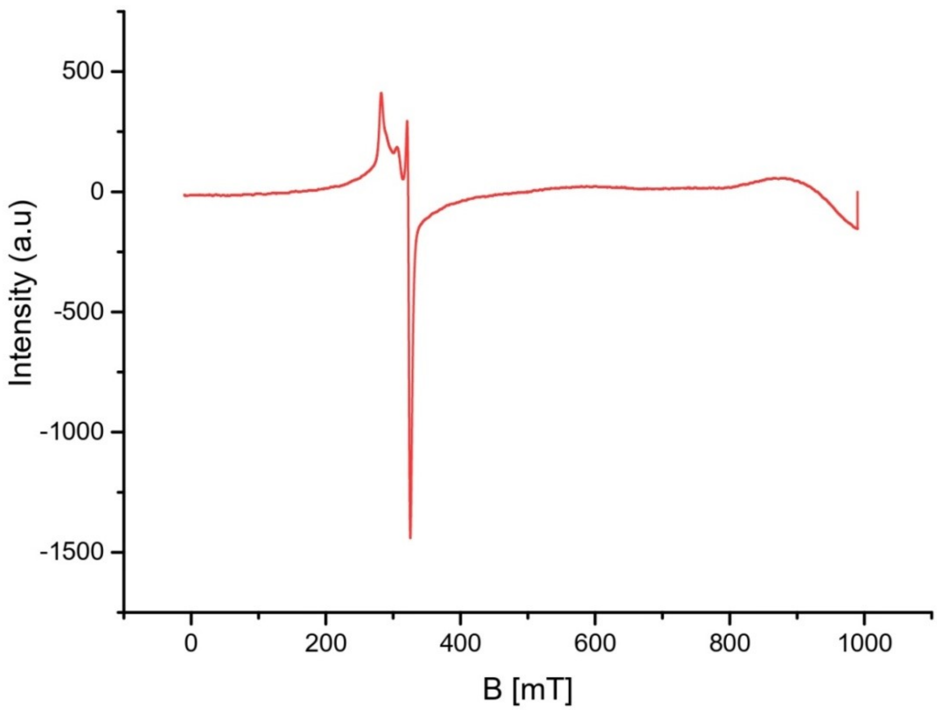
Brownish yellow crystalline solid.

^{1}H NMR (400 MHz, d_6-DMSO): δ (in ppm) 0.78-0.87 (bs, 5H), 1.79 (s, 2H), 5.53 (s, 2H), 6.43 (s, 1H), 6.69 (s, 1H), 7.77 (s, 1H).

6.2. NMR image of Cu-Cat-1



6.3. EPR image of Cu-Cat-1

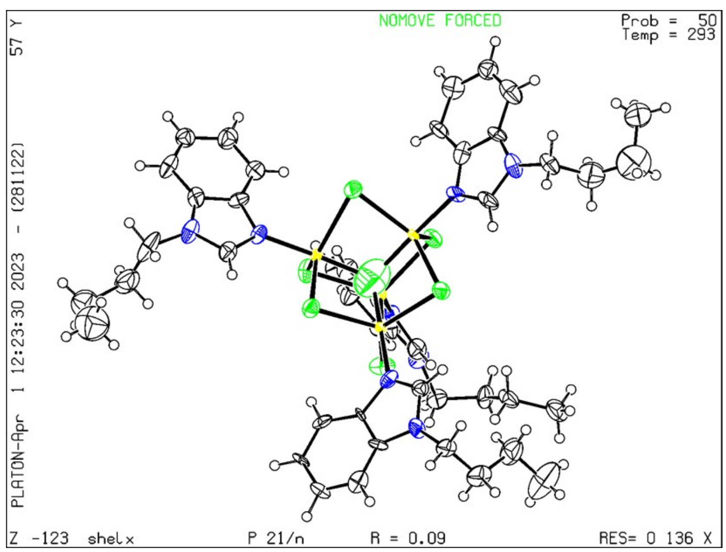


6.4. Single crystal XRD data of the Cu-Cat-1

Identification code	shelx
Empirical formula	$C_{44}H_{56}C_{17}Cu_4N_8$
Formula weight	1199.27
Temperature	293(2) K
Wavelength	1.54016 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 12.1373(11) Å, alpha = 90deg. b = 21.089(3) Å, beta = 90 deg. c = 20.202(2) Å, gamma = 90 deg.
Volume	5171.0(10) $Å^3$
Z, Calculated density	4, 1.540 Mg/m^3
Absorption coefficient	5.379 mm^{-1}
F(000)	2444
Crystal size	0.14 x 0.10 x 0.08 mm^3
Theta range for data collection	3.026 to 52.273^o

Limiting indices	-12<=h<=11, -14<=k<=21, -20<=l<=18
Reflections collected / unique	5769 / 3514 [R(int) = 0.0544]
Completeness to theta =52.273°	60%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.564
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3514 / 49 / 564
Goodness-of-fit on F^2	1.209
Final R indices [I >2sigma (I)]	R1 = 0.0851, wR2 = 0.2250
R indices (all data)	R1 = 0.1052, wR2 = 0.2453
Extinction coefficient	n/a
Largest diff. peak and hole	1.073 and -1.584 e. $Å^{-3}$

6.5. ORTEP image of the Cu-Cat-1



(CCDC 2348375)

7. Optimization of sulfenylation of imidazo[1,2-a]pyridines/thiazoles at various conditions

Table S1. Use of different Solvents

Sl. No	Solvent	% of Yield
1	DMF	66
2	MeCN	NR
3	EtOH	30
4	MeOH	26
5	H_2O	Trace
6	DMSO	35
7	DMF:H_2O(9:1)	70

N.B: NR=Not reacted

Table S2. Effect of Time and temperature in reaction progress

Sl. No	Temp(^{o}C)	Reaction Time(h)	Yields (%)
1	140	20	67
2	120	20	72
3	110	20	71
4	100	20	71
5	90	20	50
6	80	20	Trace
7	60	20	NR
8	RT	20	NR
9	100	18	71
10	100	16	70
11	100	14	70
12	100	12	65
13	100	10	58

N.B: NR=Not reacted

Table S3. Catalyst Loading

Sl. No	Catalyst Loading (mol %)	% of Yield
1	10	62
2	5	60
3	3	59
4	1	59
5	0.5	47

[a]Reaction conditions: Imidazo[1,2-*a*]pyridine=0.5 mmol, Benzyl bromide=0.7 mmol; CS_2=0.7 mmol, solvent=1 mL

Table S4. Use of different Cu based catalyst

Sl. No	Catalyst	% of Yield
1	CuCl	35
2	CuBr	43
3	CuI	53
4	$Cu(OAc)_2$	37
5	**Cu-Cat-1**	70

N.B: NR=Not reacted

Table S5. Use of different sulfur sources

Sl. No	Sulfur source	% of Yield
1	Sulfur powder	58
2	$Na_2S_2O_3$	51
3	DMSO	trace
4	CS_2	70

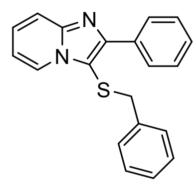
Table S6. Use of different bases

Sl. No	Base	% of Yield
1	K_2CO_3	NR
2	Na_2CO_3	NR
3	DABCO	NR

N.B: NR=Not reacted

S8. Characterization data of synthesized 3-(Alkylthio)-2-arylimidazo [1,2-a]pyridine/thiazole derivatives

3-(Benzylthio)-2-phenylimidazo [1,2-a]pyridine(2a)[2]

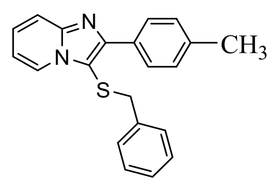


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 68% yield (107.0 mg).

^{1}HNMR (400 MHz, $CDCl_3$): δ (in ppm) 3.83(s,2H), 6.71-6.72(m,1H), 6.91-6.94(m,2H), 7.05-7.12(m,3H), 7.23-7.26(m,1H), 7.38-7.43(m,1H), 7.46-7.49(m,2H), 7.65-7.68(m,1H), 8.08-8.10 (m,1H) 8.25-8.28(m,2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 40.6, 109.8, 112.8, 116.8, 124.3, 126.9, 127.4, 128.3, 128.4, 128.5, 128.6, 132.7, 136.9, 145.6, 148.9

3-(Benzylthio)-2-(p-tolyl)imidazo[1,2-a]pyridine (2b)

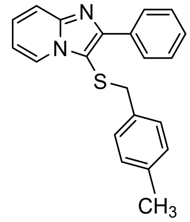


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 67% yield (111.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 2.44 (s,3H), 3.83 (s,2H), 6.67-6.71 (m,1H), 6.93-6.95(m,2H), 7.05-7.11(m,3H), 7.21-7.25(m,1H), 7.28-7.32(m,3H), 7.65-7.68(m,1H), 8.03-8.07(m,1H), 8.19 (d, *J*=8Hz,2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 21.36, 40.45, 109.22, 112.45, 112.94,116.81, 117.50, 124.16, 126.43, 127.34, 127.74, 128.09, 128.46, 128.63, 129.11, 137.08, 138.42, 145.81

3-((4-Methylbenzyl)thio)-2-phenylimidazo[1,2-a]pyridine (2c)[2]

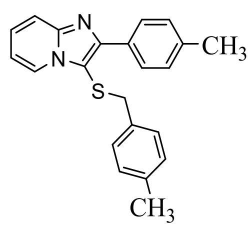


Eluent: petroleum ether/ethyl acetate (17:3), Brown oil, 67% yield (111.0 mg).

^{1}HNMR (400 MHz, $CDCl_3$): δ (in ppm)3.8(s,2H), 6.73-6.81(m,3H), 6.87(d,*J*=7.6Hz,2H), 7.25-7.30(m,1H), 7.41(d, *J*=7.6Hz,1H), 7.45-7.48(m,2H), 7.67-7.72(m,1H), 8.13-8.15 (m, 1H), 8.22-8.25 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm)20.9, 40.2, 109.8, 112.6, 116.9, 124.3, 126.5, 127.5, 128.3, 128.4, 128.5, 129, 132.9, 133.7, 137.1, 145.8, 149.3

3-((4-Methylbenzyl)thio)-2-(p-tolyl)imidazo[1,2-a]pyridine (2d)



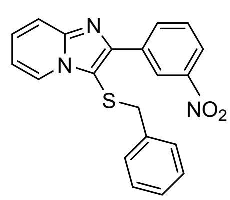
Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 65% yield (111.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 2.23(s,3H), 2.44(s,3H), 3.80(s,2H), 6.72-6.75(m,1H), 6.81-6.89(m,4H), 7.25-7.30 (m, 4H), 7.71(d, *J*=8.8Hz,1H), 8.10-8.17 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm)20.95, 21.45, 40.28, 110.13, 113.43, 116.17, 124.44, 127.38, 127.89, 128.26, 128.53, 129.19, 129.27, 133.57, 137.37, 139.19, 144.54, 147.48

HRMS calculated for $C_{22}H_{20}N_2S^+$ $[M+H]^+$: 345.1427; found 345.1423

3-(Benzylthio)-2-(3-nitrophenyl)imidazo[1,2-a]pyridine (2e)

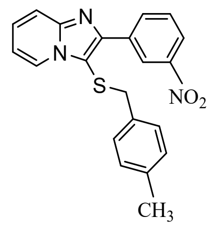


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 74% yield (133.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 3.83 (s,2H), 6.81-6.91(m,3H), 6.97-7.02(m,3H), 7.34-7.38(m,2H), 7.56(t,*J*=8Hz,1H), 7.75(d,*J*=8.8Hz,1H), 8.16-8.26(m,2H), 8.46(d,*J*=7.6Hz,1H), 9.08(s,1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 40.2, 113.6, 117.2, 117.5, 122.9, 123, 124.4, 127.5, 127.7, 128.8, 128.5, 128.7, 129.2, 134, 136.3, 145.9, 148.2

3-((4-Methylbenzyl) thio)-2-(3-nitrophenyl) imidazo [1,2-a] pyridine (2f)



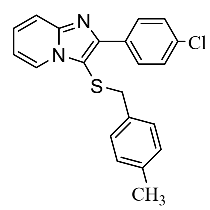
Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 72% yield (135.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 2.14 (s, 3H), 3.79 (s, 2H), 6.67 (d, *J*=8Hz,2H), 6.78 (d, *J*=8Hz, 2H), 6.92 (t, *J*=6Hz, 1H), 7.26 (s, 1H), 7.39(t, *J*=7.6Hz, 1H), 7.54(t, *J*=8Hz, 1H), 7.78(d, *J*=9.2Hz, 1H), 8.15-8.18 (m, 1H), 8.32 (d, *J*=6.8Hz, 1H), 8.43(d, *J*=7.6Hz, 1H), 9.05(s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 20.8, 39.9, 109.9, 111, 113.9, 116.9, 122.9, 123, 124.5, 128.2, 128.6, 128.9, 129.1, 129.2, 134.1, 137.4, 145.4, 146.1, 148.1

HRMS calculated for $C_{21}H_{17}N_3O_2S^+$ $[M+H]^+$: 376.1120; found 376.1112

2-(4-Chlorophenyl)-3-((4-methylbenzyl)thio)imidazo[1,2-a]pyridine (2g)



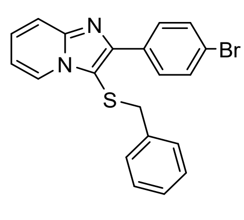
Eluent: petroleum ether/ethyl acetate (17:3), Yellow solid, 74% yield (135.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 2.22(s,3H), 3.79(s,2H), 6.74-6.87(m,5H), 7.28-7.33(m,1H), 7.56(d,*J*=8Hz,2H), 7.70(s,1H), 8.08(d,*J*=8.4Hz,2H), 8.19(d,*J* =6.8Hz,1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 20.9, 40, 112.5, 117.2, 124.4, 126.2, 126.9, 128.3, 129, 129.1, 129.3, 132.2, 133.6, 134, 137.2, 137.9

HRMS calculated for $C_{21}H_{17}ClN_2S^+$$[M+H]^+$: 365.0879; found 365.0872

3-(Benzylthio)-2-(4-bromophenyl) imidazo [1,2-a]pyridine (2h)



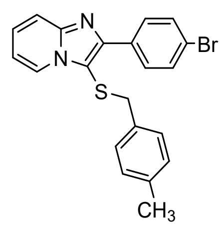
Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 73% yield (143.0 mg).

^{1}HNMR (400 MHz, $CDCl_3$): δ (in ppm) 3.79(s,2H), 6.72(t,*J*=6.8 Hz,1H), 6.85-6.87(m,2H), 7.02-7.09(m,3H), 7.24-7.36(m,2H), 7.54-7.55(m,2H), 8.09-8.11(m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 40.3, 112.5, 117.2, 122.5, 124.3, 126.3, 126.9, 127.3, 128.4, 128.6, 129.6, 130.7, 131.3, 131.3, 131.9, 132.5, 136.8

HRMS calculated for $C_{20}H_{15}BrN_2S^+[M+H]^+$: 395.0218; found 395.0220

2-(4-Bromophenyl)-3-((4-methylbenzyl)thio)imidazo[1,2-a]pyridine(2i)

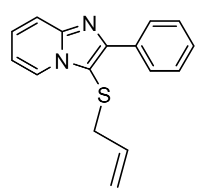


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 69 % yield (140.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 2.23 (s,3H),3.78 (s,2H), 6.75-6.86 (m,5H), 7.29-7.33 (m,1H), 7.56 (d, *J*=8Hz,2H), 7.70 (s,1H) 8.04 (d, *J*=8.4Hz,2H), 8.19(d, *J*=6.8Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm)20.97, 40.12, 109.82, 113.19, 116.80, 122.98, 124.42, 127.35, 128.54, 129.14, 129.83, 131.45, 133.44, 137.40, 145.46, 152.10

3-(Allylthio)-2-phenylimidazo[1,2-a]pyridine (2j)

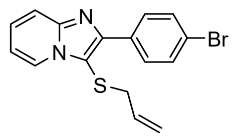


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 69% yield (89.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 3.31(d, *J*=8.4Hz,2H), 4.76-4.82 (m, 2H), 5.67-5.78 (m,1H), 7.02 (t, *J*=8Hz,1H), 7.41-7.44 (m,1H), 7.46-7.50 (m,2H), 7.58-7.63 (m,1H), 7.91(d, *J*=8.4Hz, 1H), 8.11-8.13 (m,2H), 8.27-8.29 (m,1H), 8.57 (d, *J*=6.8Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 39.13, 113.45, 117.30, 118.87, 124.74, 127.37, 128.54, 128.58, 128.65, 128.76, 128.81, 130.25, 132.75, 133.57

3-(Allylthio)-2-(4-bromophenyl)imidazo[1,2-a]pyridine (2k)

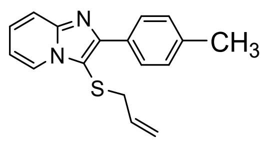


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 65% yield (111.0 mg).

[1]H NMR (400 MHz, $CDCl_3$): δ (in ppm) 3.29 (d, *J*=7.2Hz,2H), 4.71-4.72 (m, 2H), 5.67-5.73 (m,1H), 6.96-6.98 (m,1H), 7.26-7.37(m,2H), 7.60-7.75(m,3H), 8.27(s, 2H);

[13]C NMR (100 MHz, $CDCl_3$): δ (in ppm)38.8, 111, 113.1, 113.41, 117.2, 118.7, 122.8, 124.8, 126.7, 128.8, 129.7, 131.6, 132, 132.5

3-(Allylthio)-2-(p-tolyl)imidazo[1,2-a]pyridine (2l)

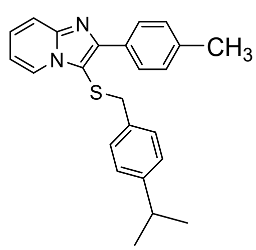


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 61% yield (85.0 mg).

[1]HNMR (400 MHz, $CDCl_3$): δ (in ppm)2.43 (s,3H), 3.32 (d, *J*=7.6Hz, 2H), 4.76-4.82 (m, 2H), 5.69-5.79(m,1H), 6.98-7.02(m,1H), 7.28-7.21(m,5H), 7.82(d, *J*=8.8Hz,1H), 8.04(d, *J*=8.4Hz,1H), 8.24(d, *J*=8.4Hz,2H), 8.56(d, *J*=6.8Hz,2H);

[13]C NMR (100 MHz,$CDCl_3$): δ (in ppm)21.38, 38.94, 113.01, 113.23, 116.86, 117.49, 118.71, 123.92, 124.61, 125.07, 127.23, 127.76, 128.27, 129.23, 132.63, 138.76

3-((4-Isopropylbenzyl)thio)-2-(p-tolyl)imidazo[1,2-a]pyridine(2m)

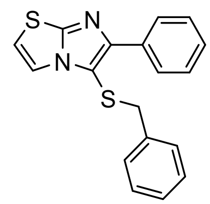


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 74% yield (138.0 mg).

[1]HNMR (400 MHz, $CDCl_3$): δ (in ppm)1.12 (s,3H), 1.44 (s,3H), 2.44 (s,3H), 2.27-2.79 (m,1H), 3.83(s,2H), 6.77-6.83(m,3H), 6.91-6.93(m,2H), 7.31-7.36(m,4H), 8.07(d, *J*=8Hz,1H), 8.44(d, *J*=8Hz,2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.43, 22.90, 33.73, 40.35, 113.83, 117.64, 122.64, 124.47, 126.64, 128.26, 128.57, 129.47, 133.90, 140.07, 145.71, 148.56, 154.45

5-(Benzylthio)-6-phenylimidazo [2,1-b]thiazole (2n)

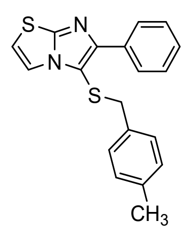


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 66%yield (106.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 3.86(s,2H), 6.69(d, *J*=4.4Hz,1H), 6.92-6.99 (m,3H), 7.14-7.16(m,3H), 7.37-7.42(m,1H), 7.46-7.50(m,2H), 8.17-8.20(m,2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 41.08, 113.17, 116.85, 118.70, 118.70, 127.69, 128.20, 128.63, 129, 129.27, 130.31, 133.38, 136.36, 147.55

5-((4-Methylbenzyl)thio)-6-phenylimidazo[2,1-b]thiazole(2o)



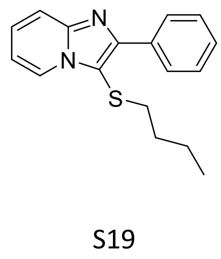
Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil,62 % yield (104.0 mg).

^{1}HNMR (400 MHz, $CDCl_3$): δ (in ppm) 2.26 (s,3H), 3.82(s,2H), 6.71(d, *J*=4.4Hz,1H), 6.86(d, *J*=7.6Hz,2H), 6.94(d, *J*=7.6Hz,2H), 7.99(d, *J*=4.4Hz,1H), 7.39(d, *J*=7.2Hz,1H), 7.59(t, *J*=7.6Hz,2H), 8.15-8.17(m,2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm) 21, 41.03, 113.03, 118.28, 127.44, 128.52, 128.63, 129.29, 134.05, 137.40, 149.52

HRMS calculated for $C_{19}H_{16}N_2S_2^+$ $[M+H]^+$: 337.0835; found 337.0759

3-(Butylthio)-2-phenylimidazo[1,2-a]pyridine(2p)[3]

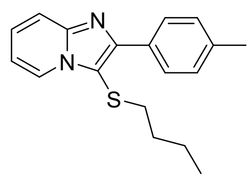


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 71%yield (100.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 0.78(t, *J*=8Hz, 3H), 1.27-1.31 (m,2H), 1.35-1.45 (m,2H), 2.66 (t, *J*=8Hz, 2H), 6.94 (t, *J*=8Hz, 1H), 7.30-7.32 (m,1H), 7.37-7.41 (m,1H), 7.47-7.50 (m,2H), 7.68 (d, *J*=8Hz, 1H), 8.32 (d, *J*=8Hz, 2H), 8.53 (d, *J*=8Hz, 1H);

^{13}CNMR (100 MHz,$CDCl_3$): δ (in ppm)13.6, 21.8, 31.6, 35.6,110.6, 112.7, 117.6, 124.5, 125.9, 128.3, 128.4, 134, 146.5, 149.6

3-(Butylthio)-2-(p-tolyl)imidazo[1,2-a]pyridine (2q)

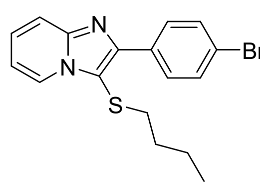


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 67 % yield (98.0 mg).

^{1}HNMR (400MHz, $CDCl_3$): δ (in ppm) 0.79 (t, *J*=8Hz, 3H), 1.31-1.36 (m,2H), 1.41-1.46 (m,2H), 2.42 (s,3H), 2.66(t, *J*=8Hz, 2H), 6.91-6.94 (m,1H), 7.29-7.30 (m,3H), 7.67 (d, *J*=8Hz, 1H), 8.23 (d, *J*=8Hz,2H),8.51-8.52 (m,1H);

^{13}C NMR (100 MHz,$CDCl_3$): δ (in ppm)13.6, 21.4,21.9, 31.6, 35.6,110.2, 112.6, 117.5, 124.4, 125.8, 128.3, 129.1, 131.2,138.1, 146.5, 149.7

2-(4-Bromophenyl)-3-(butylthio)imidazo[1,2-a]pyridine(2r)

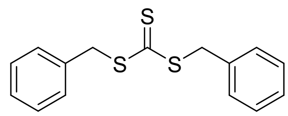


Eluent: petroleum ether/ethyl acetate (17:3), Yellow oil, 73%yield(115.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) 0.79 (t, *J*=8Hz, 3H), 1.27-1.34 (m,2H), 1.39-1.46 (m,2H), 2.65 (t, *J*=8Hz, 2H), 6.93-6.97 (m,1H), 7.30-7.33 (m,1H), 7.37-7.41(m,1H), 7.59-7.67 (m,3H), 8.24 (d, *J*=8Hz, 2H), 8.51(d, *J*=8Hz, 1H);

^{13}C NMR(100 MHz, $CDCl_3$): δ (in ppm)13.6, 21.8, 31.6, 35.6,110.7, 112.9, 117.7, 122.5, 124.5, 126.2, 129.9, 131.5,133, 146.5, 148.3

S9. Characterization data of S,S-Dibenzyltrithiocarbonate[4]



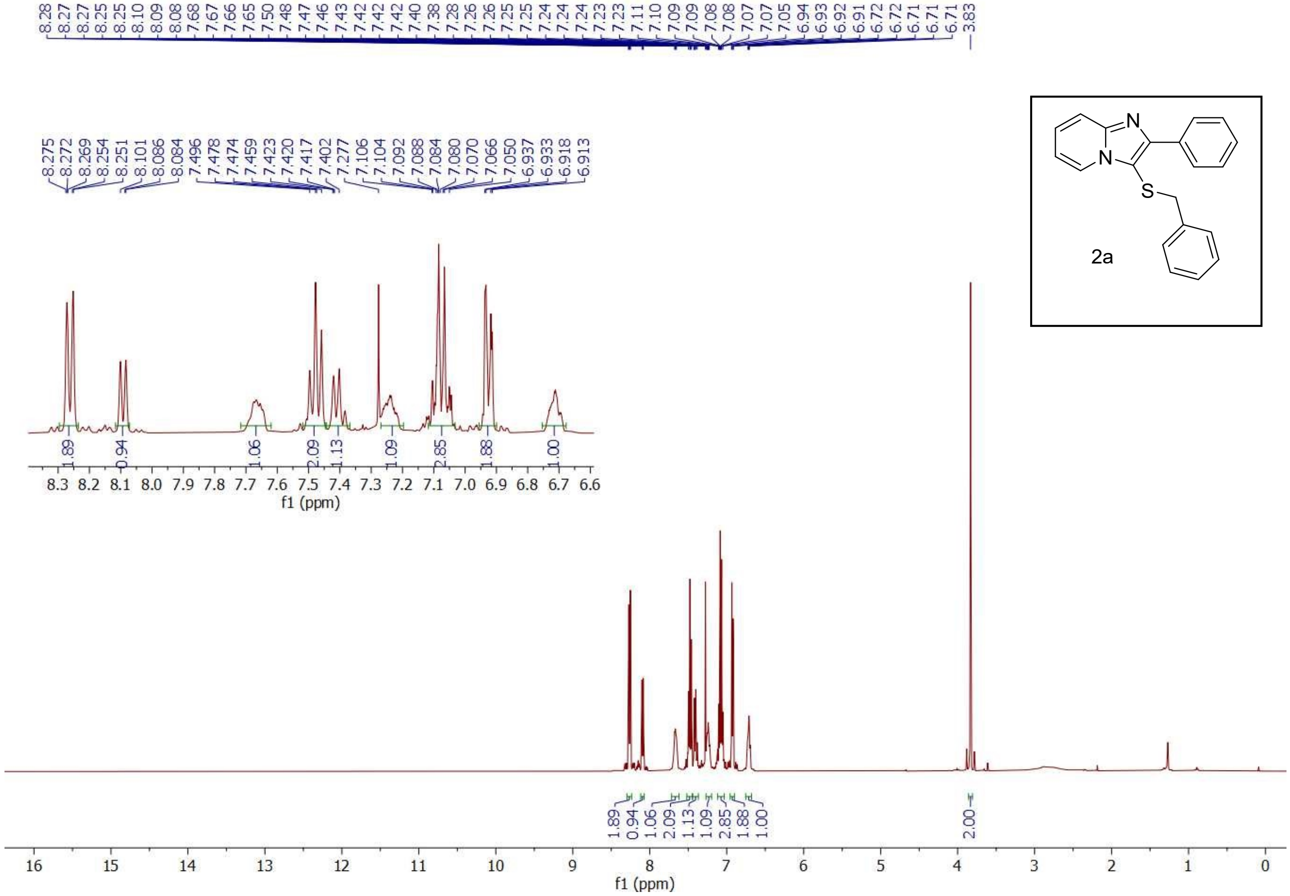
Eluent: petroleum ether, Yellow oil, 86 % yield.

FTIR (KBr): ν_{max} (cm^{-1}) 1048 (C=S *str.*), 791 (C-S *str.*).

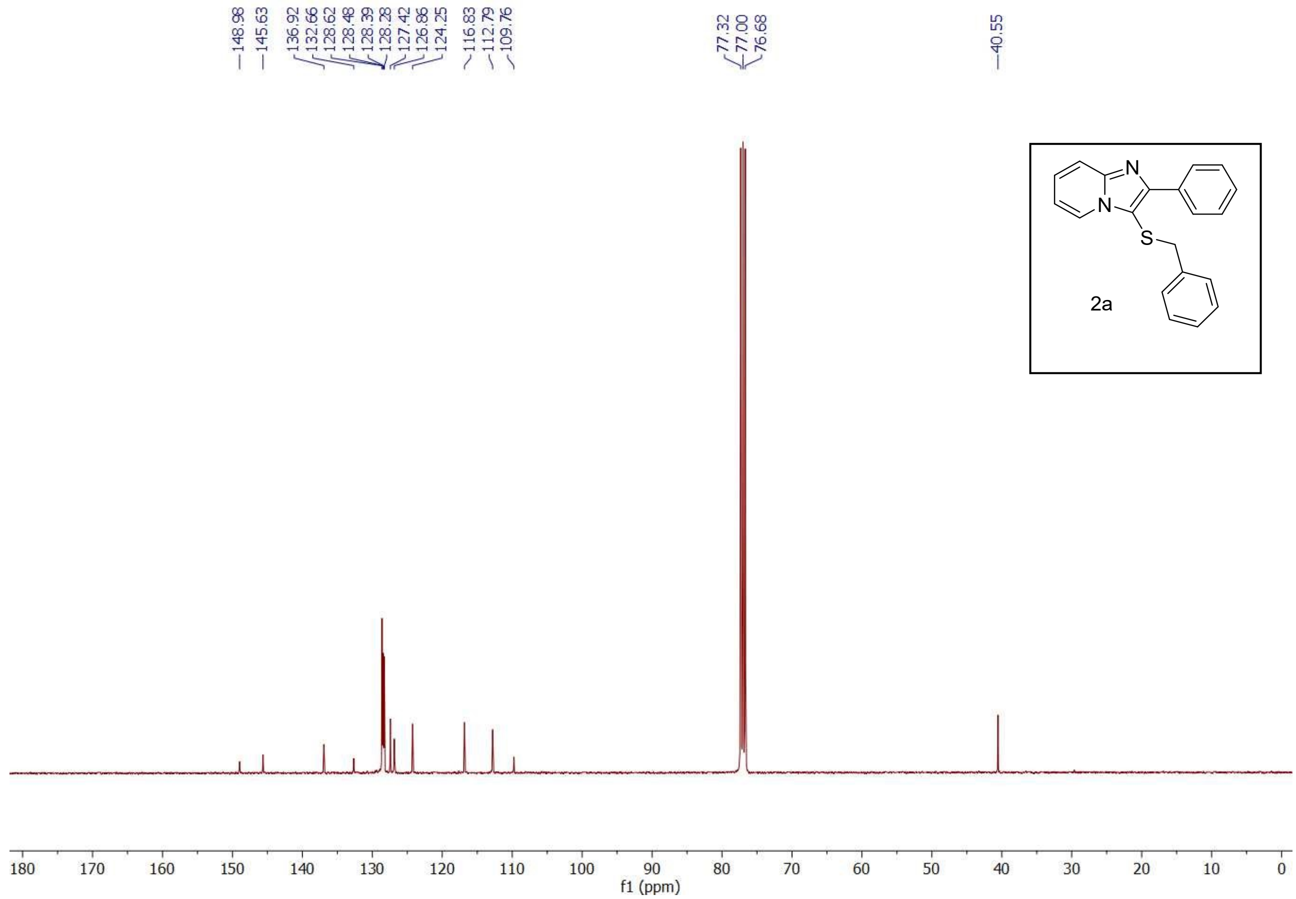
^{1}H NMR (400MHz, $CDCl_3$): δ (in ppm)4.64 (s, 4H), 7.27-7.38 (m, 10H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (in ppm)41.6, 127.9, 128.8, 129.4, 135, 222.9

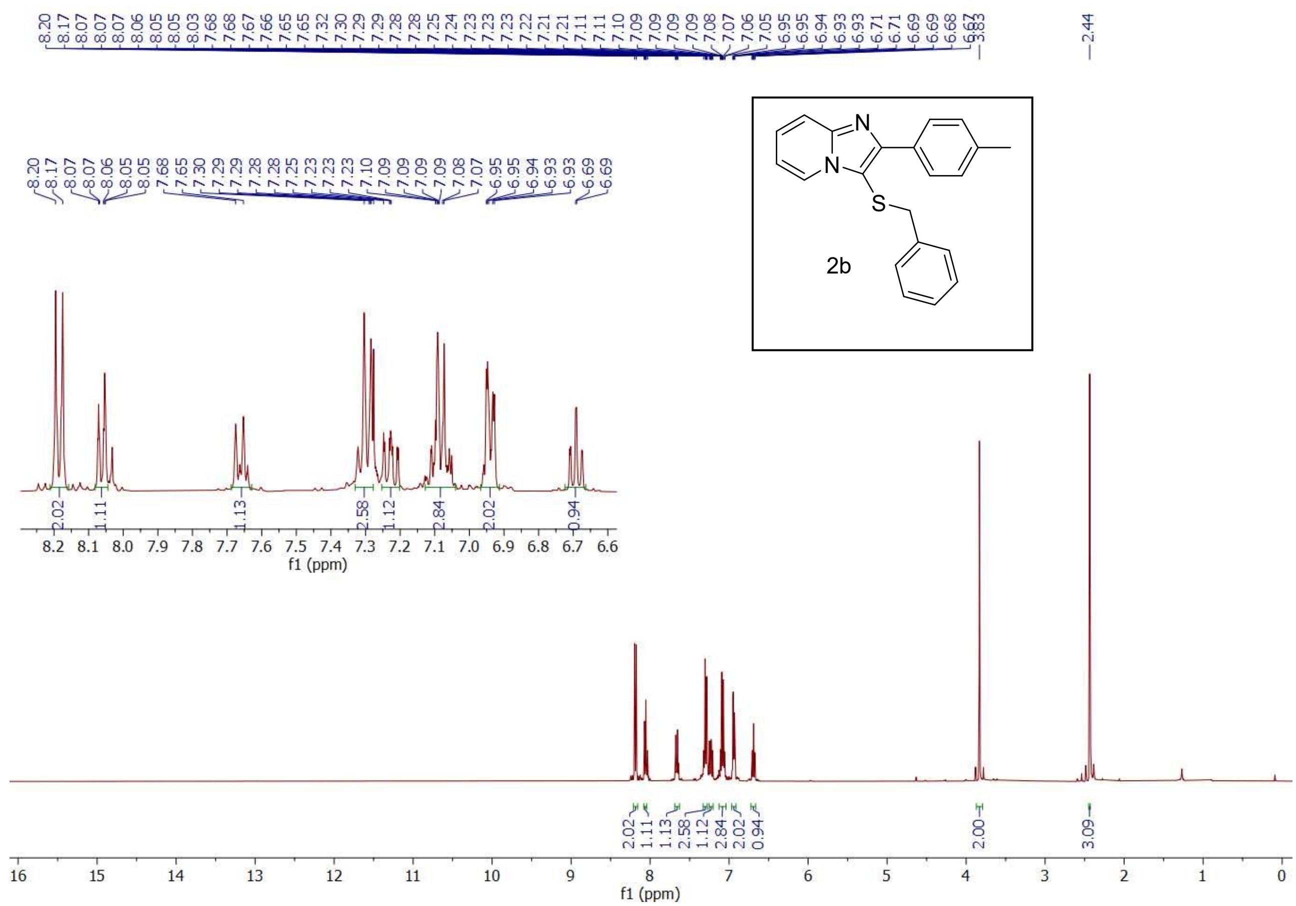
S10. NMR and HRMS spectra of all 3-(Alkylthio)-2-arylimidazo [1,2-a]pyridine/thiazole derivatives



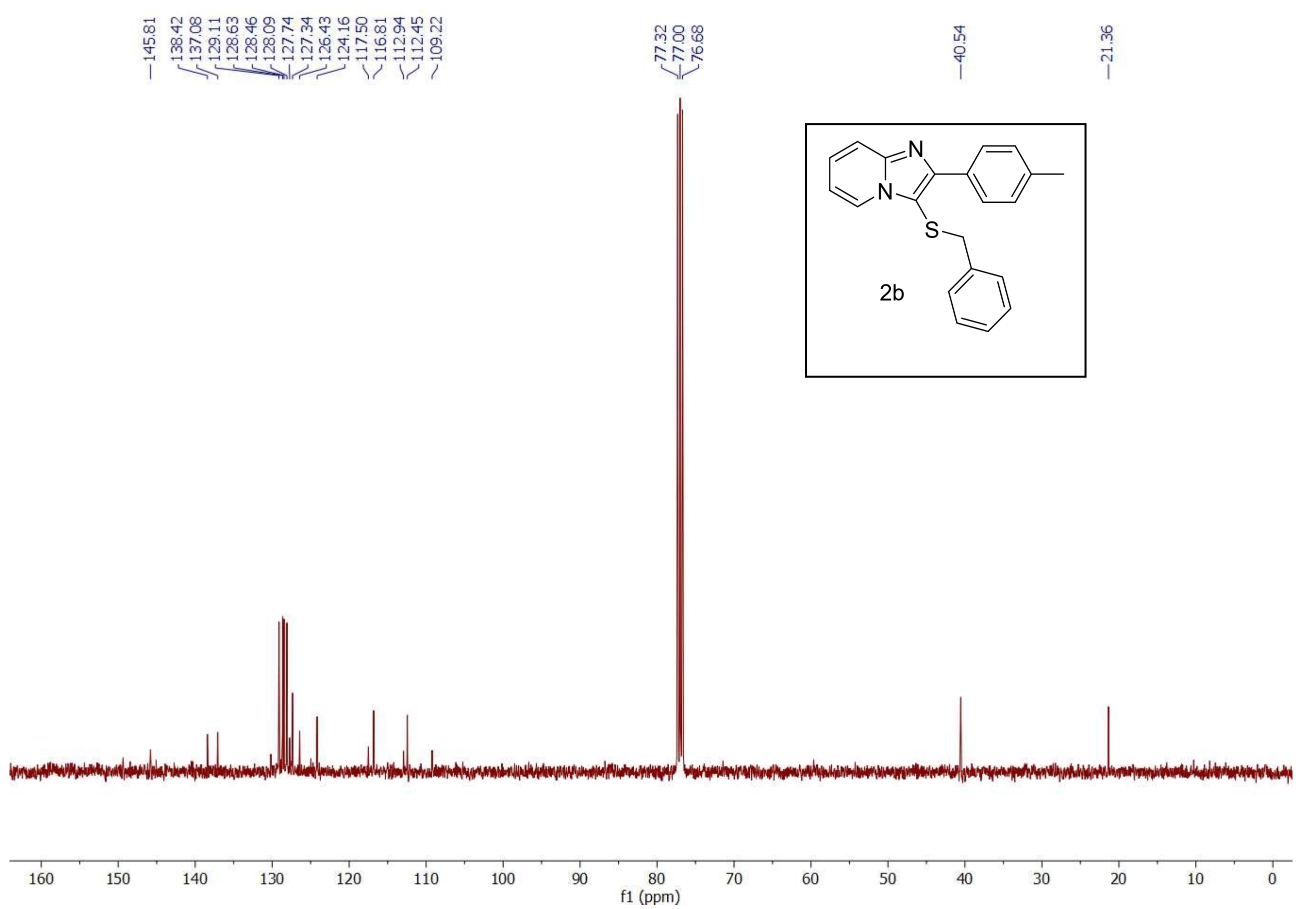
[1]H NMR spectra of (2a)



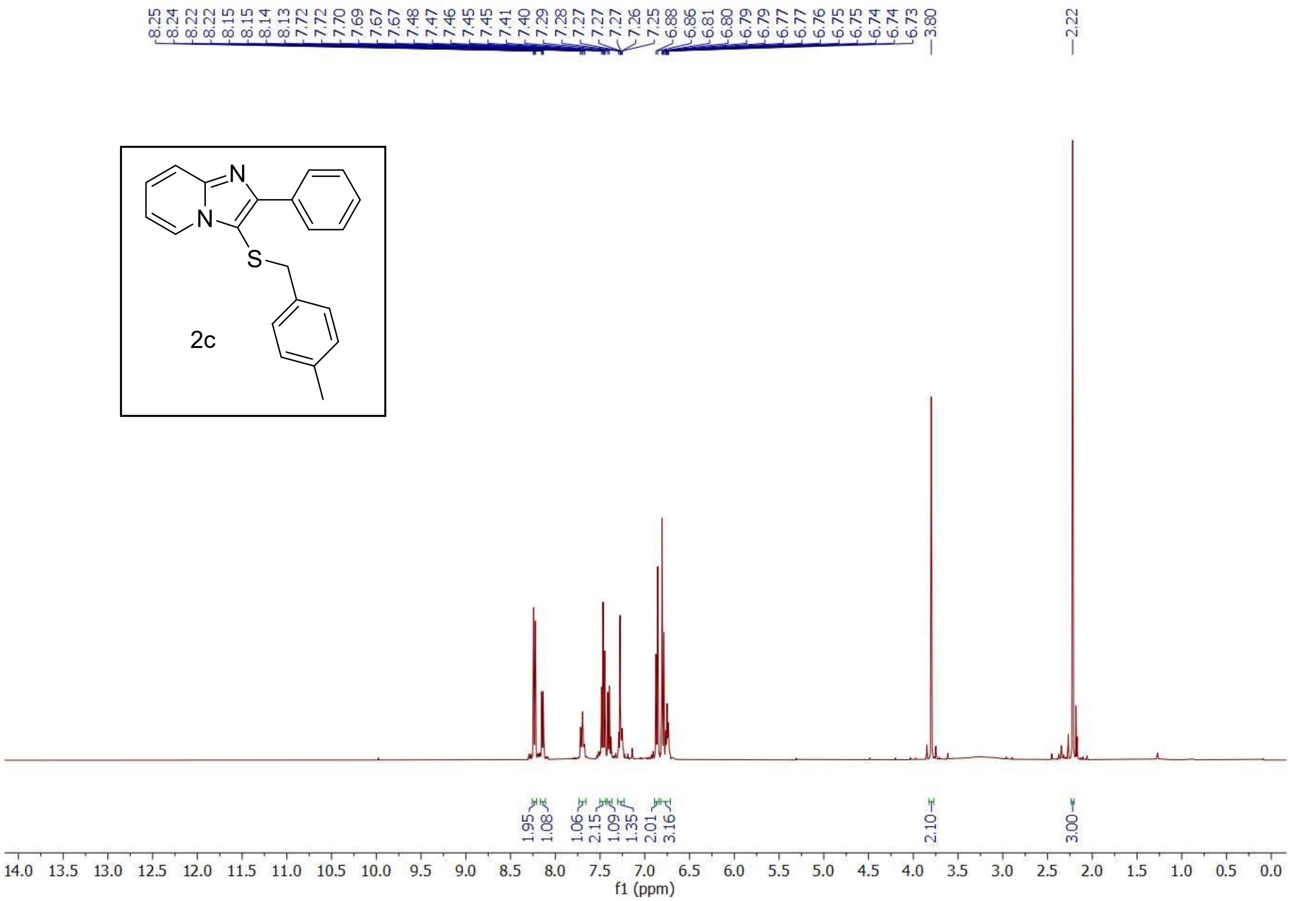
^{13}C NMR spectra of (2a)



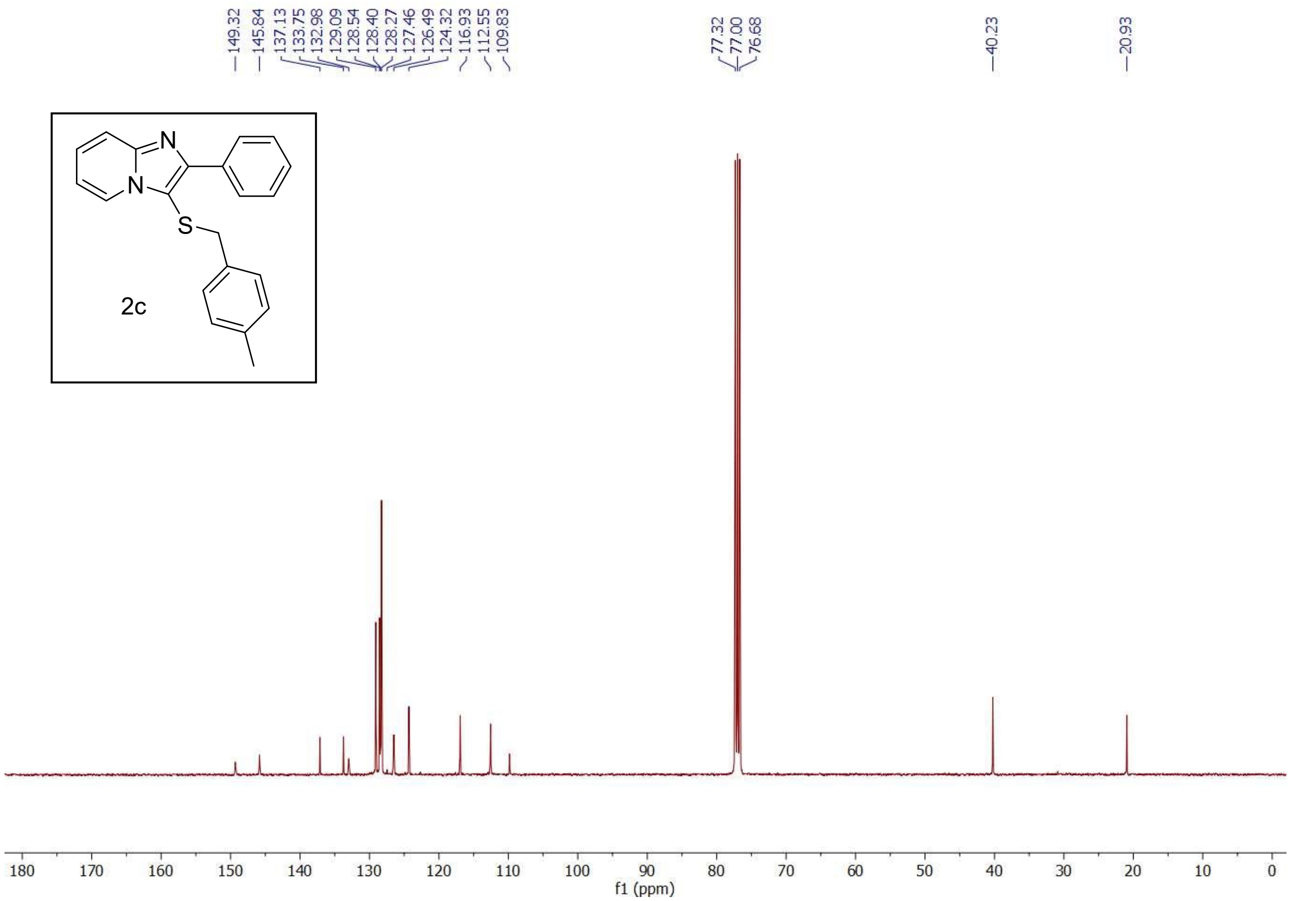
[1]H NMR spectra of (2b)



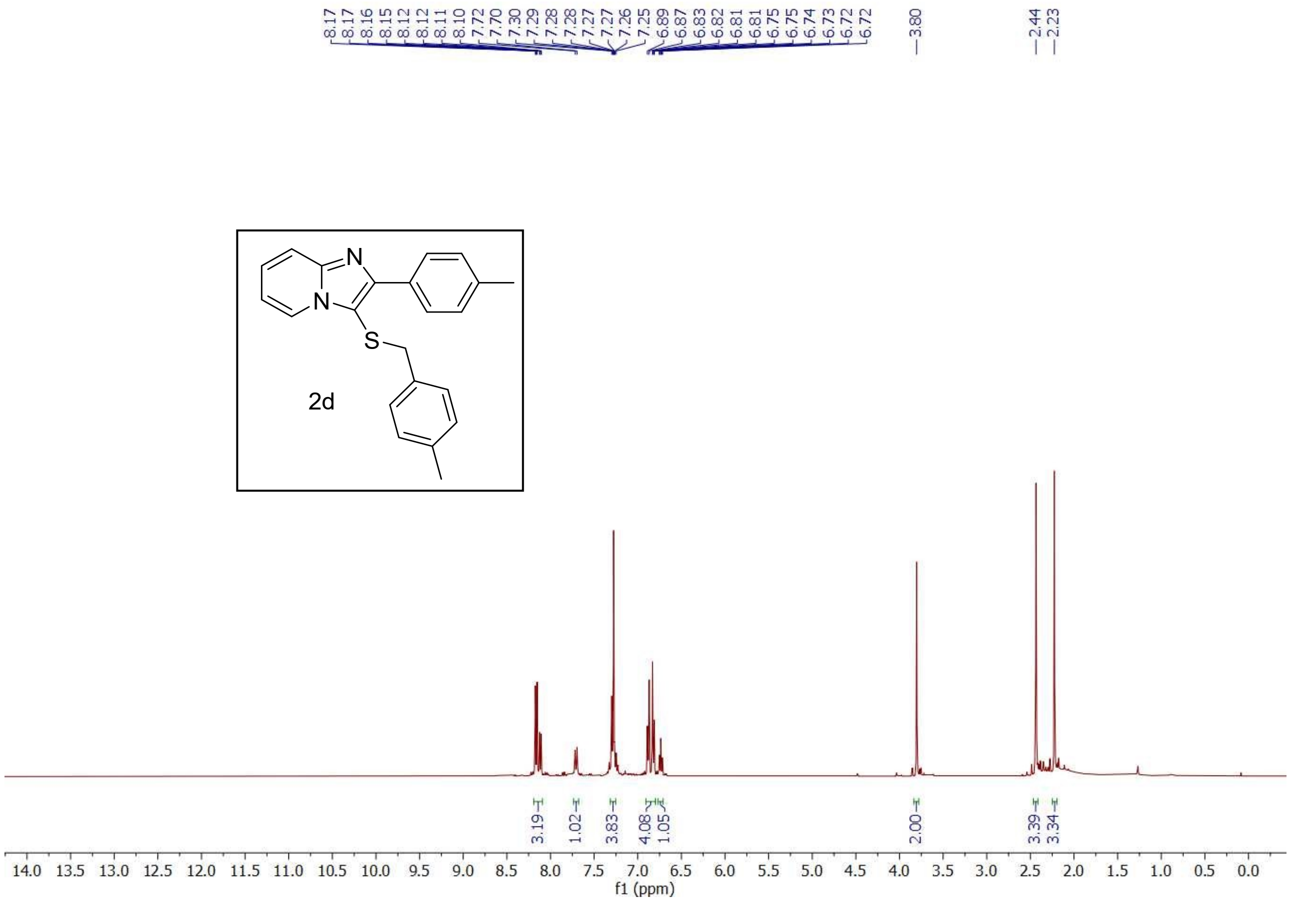
^{13}C NMR spectra of (2b)



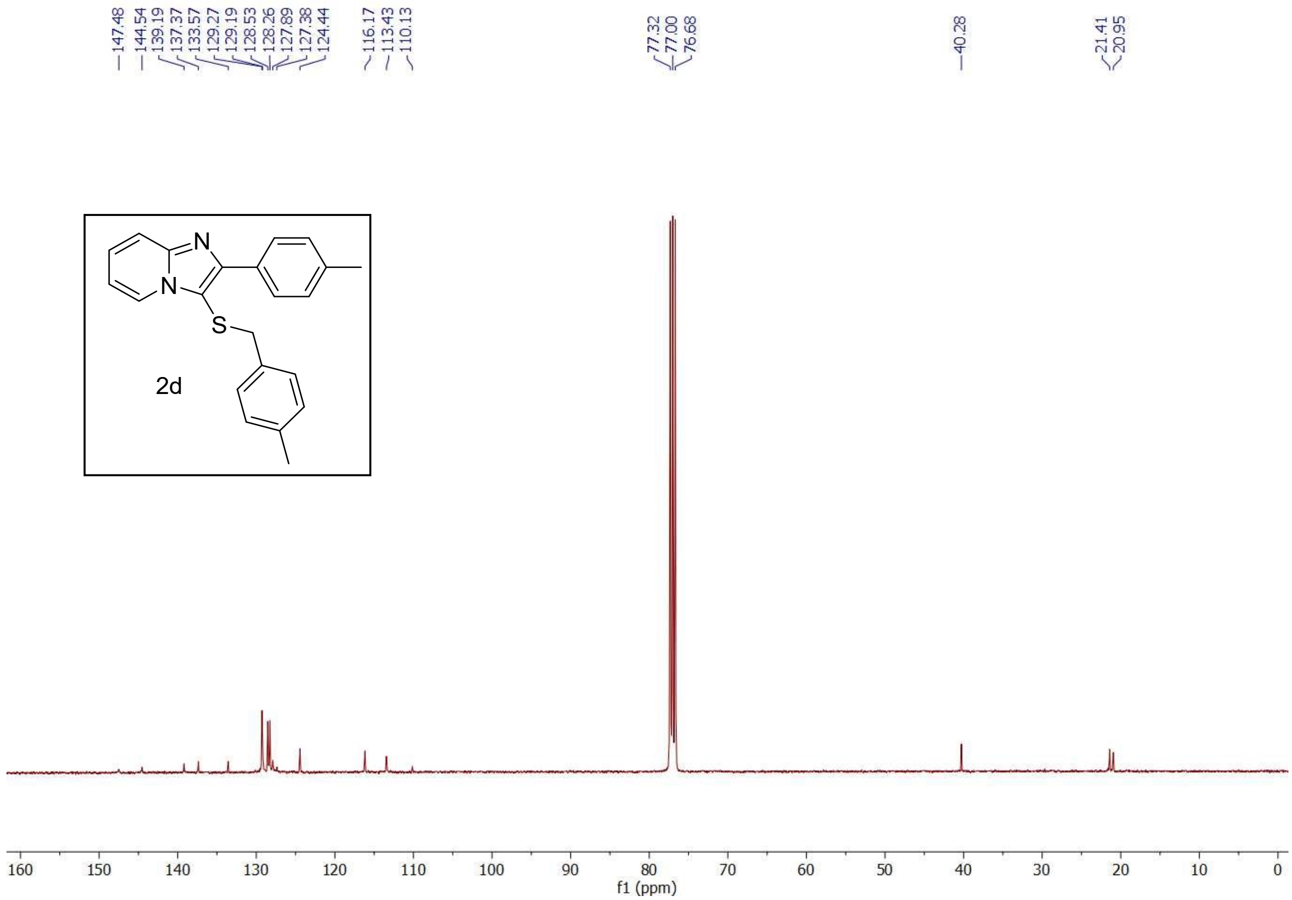
^{1}H NMR spectra of (2c)



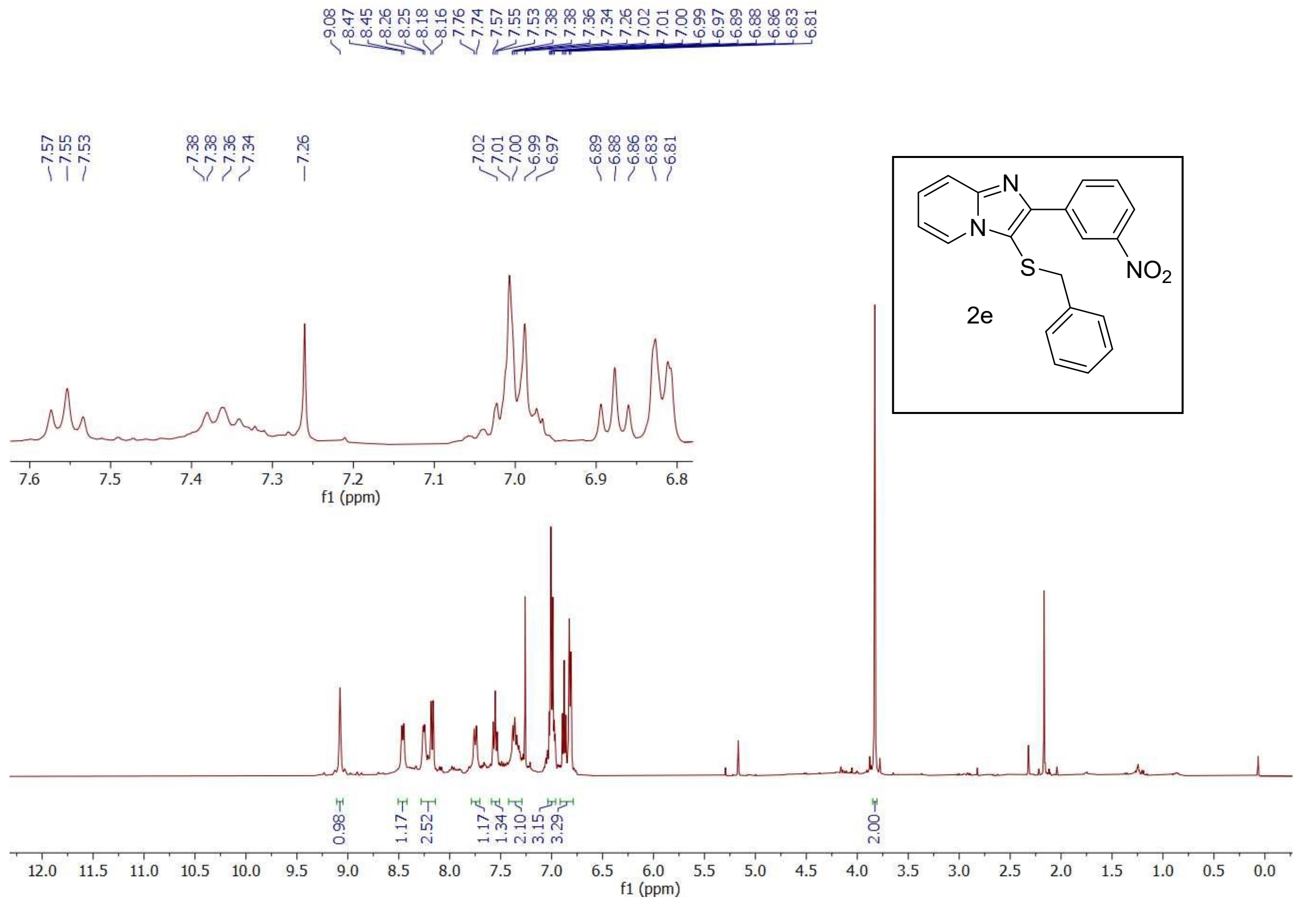
^{13}C NMR spectra of (2c)



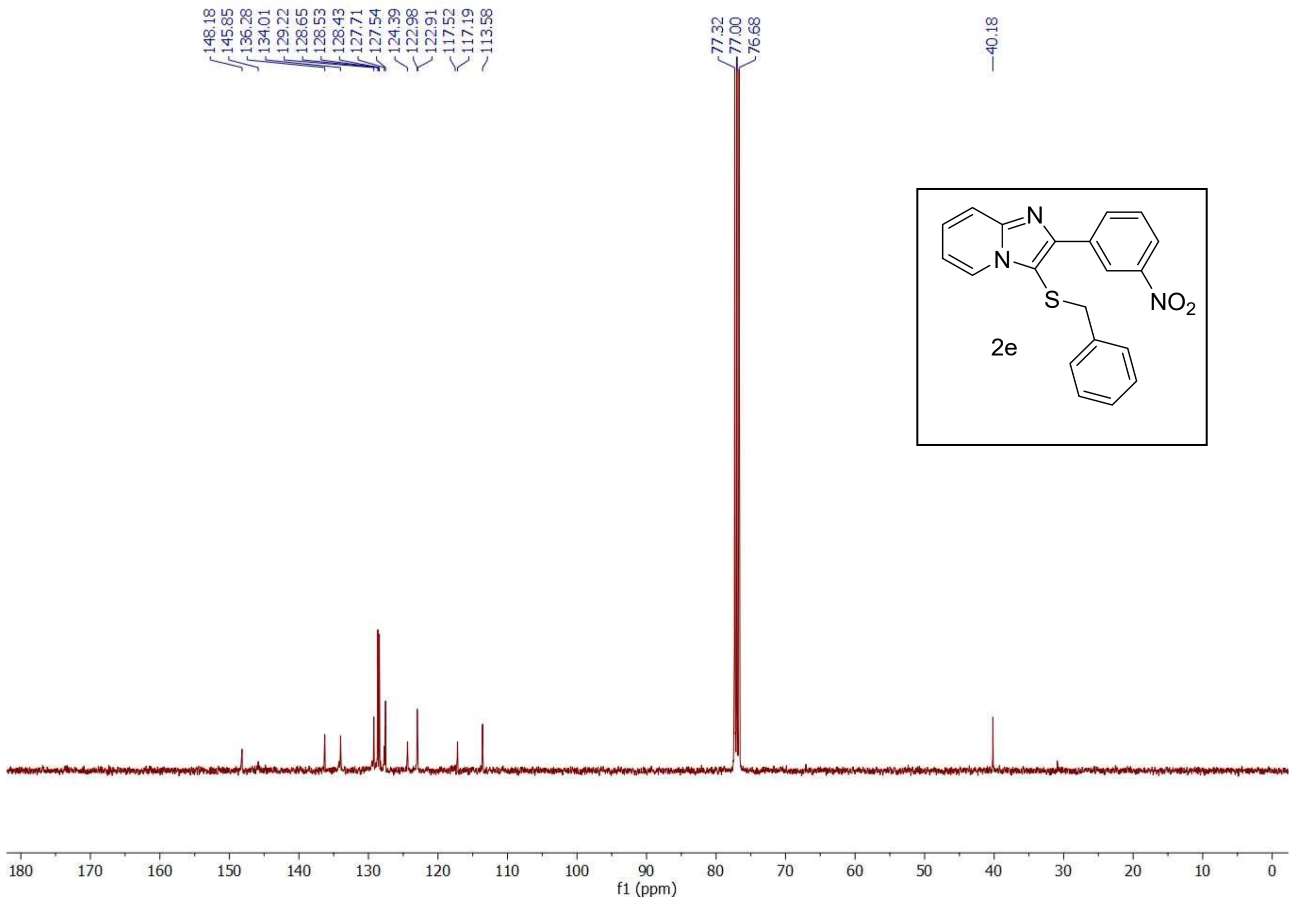
[1]H NMR spectra of (2d)



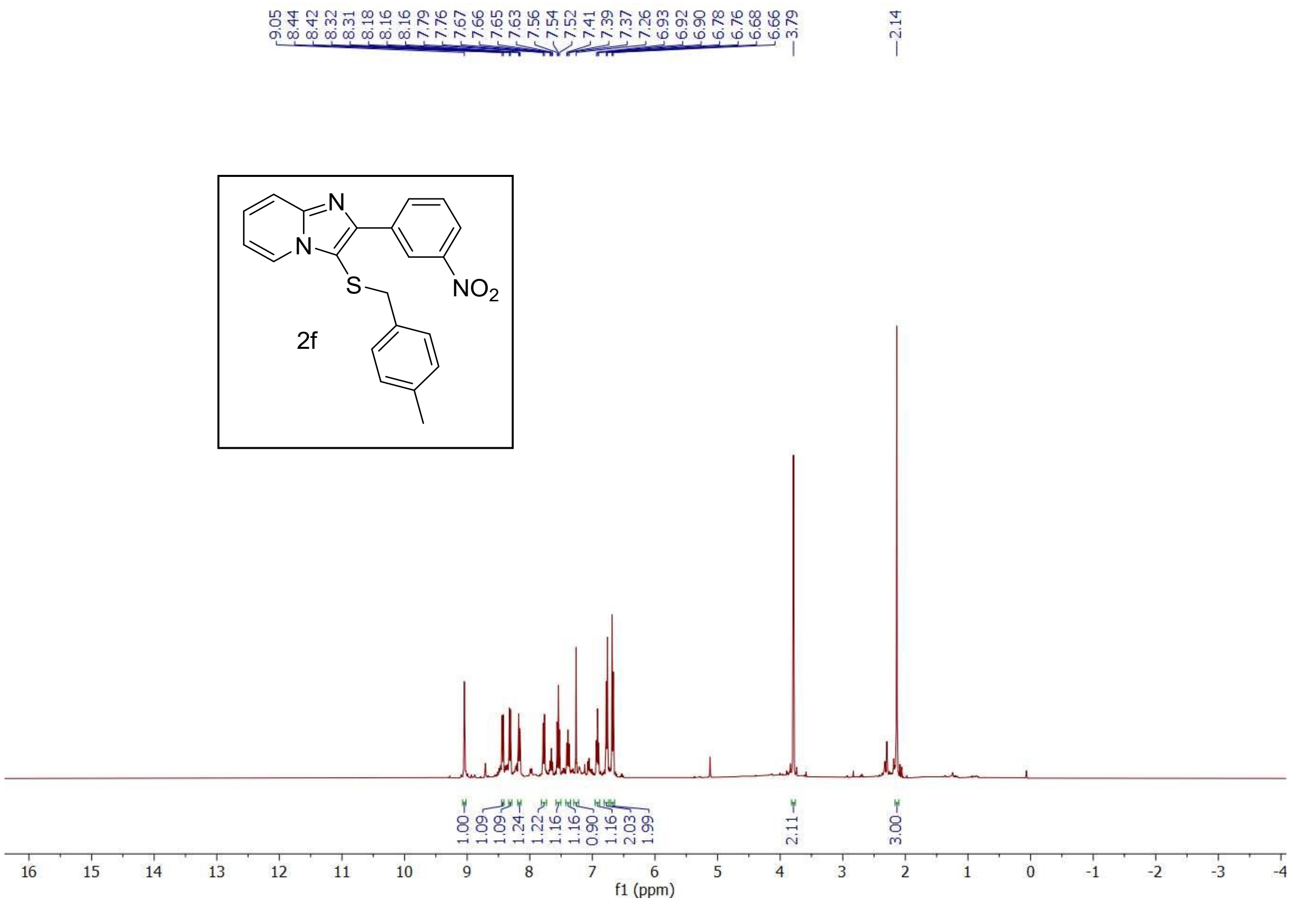
^{13}C NMR spectra of (2d)



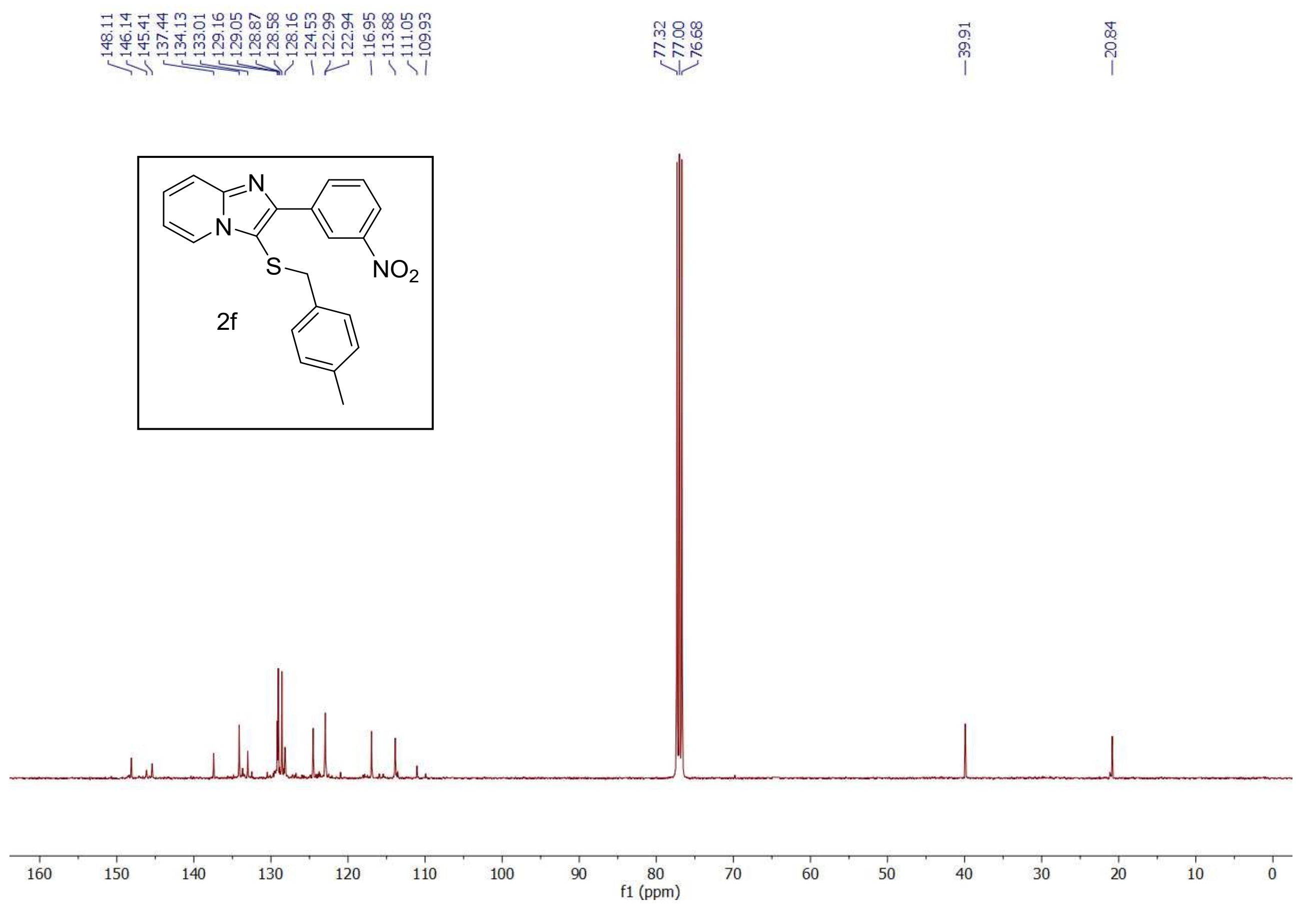
^{1}H NMR spectra of (2e)



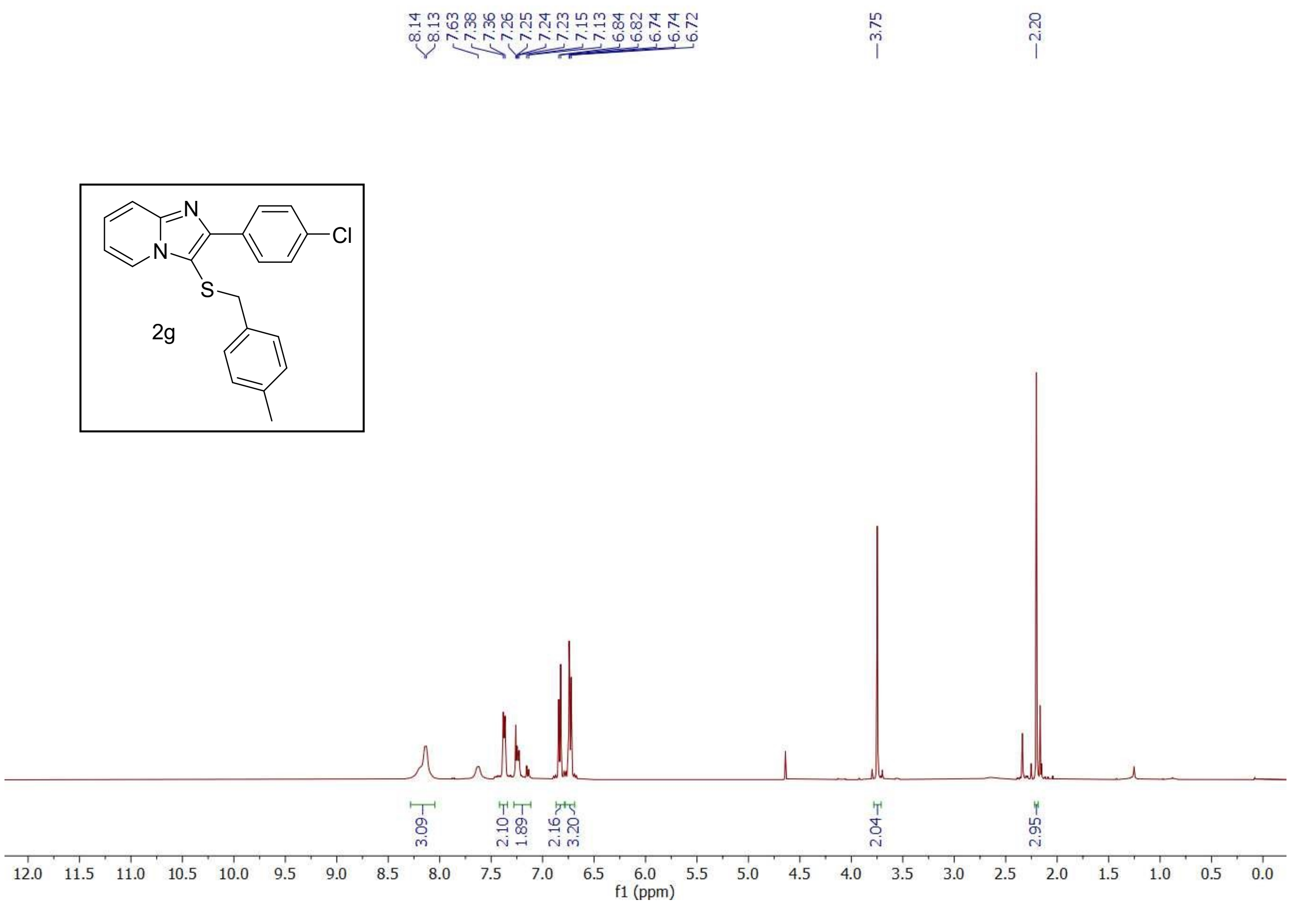
^{13}C NMR spectra of (2e)



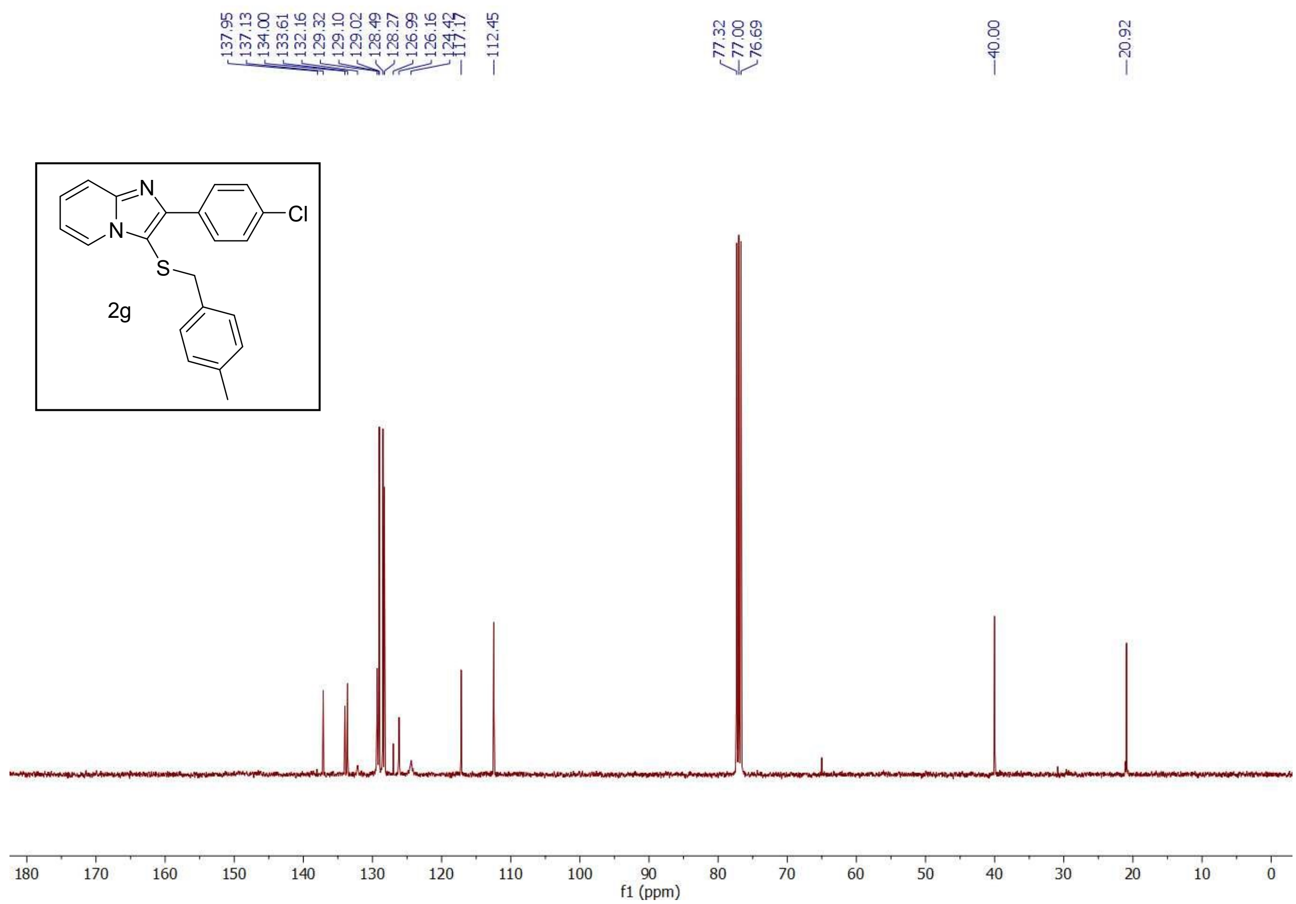
^{1}H NMR spectra of (2f)



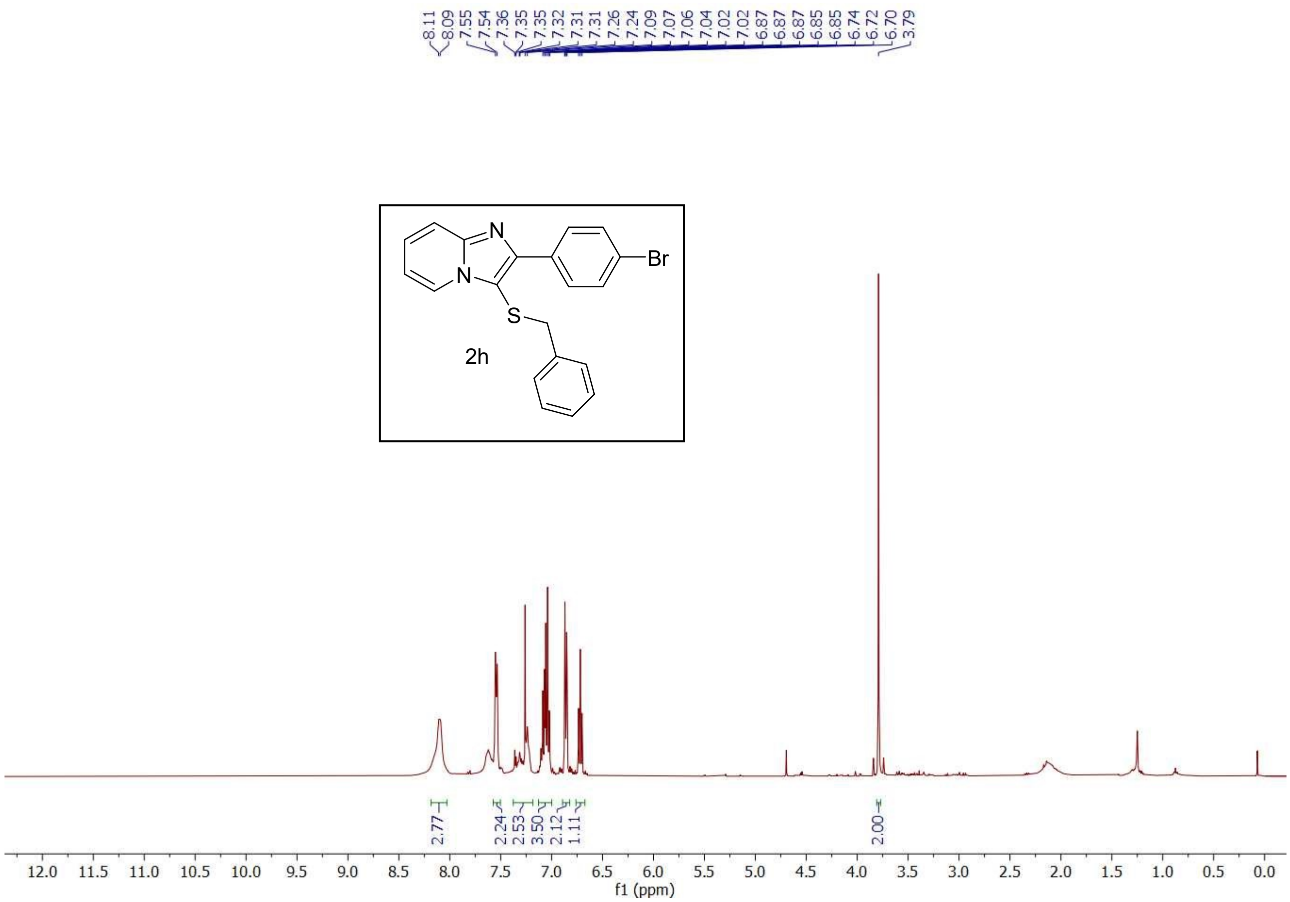
^{13}C NMR spectra of (2f)



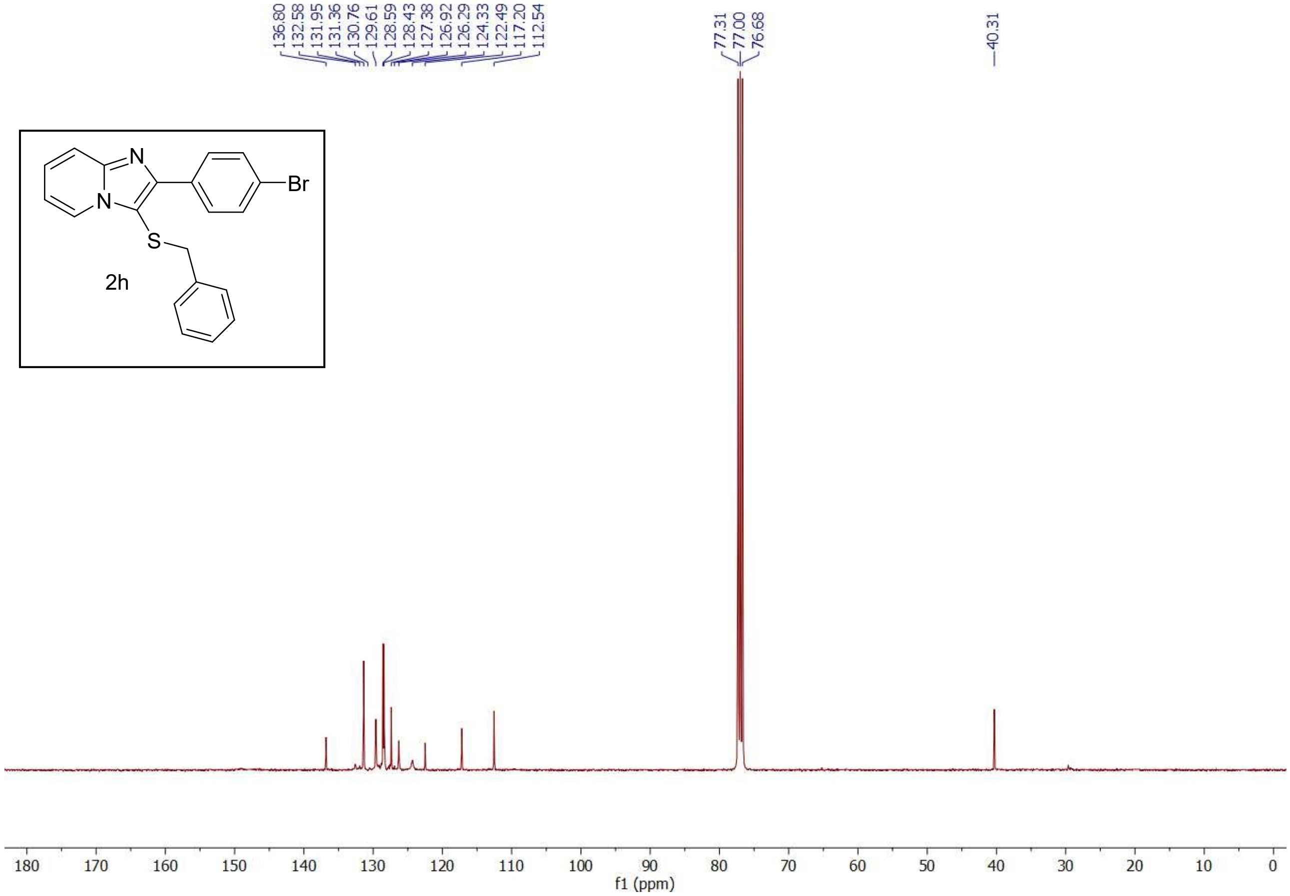
^{1}H NMR spectra of (2g)



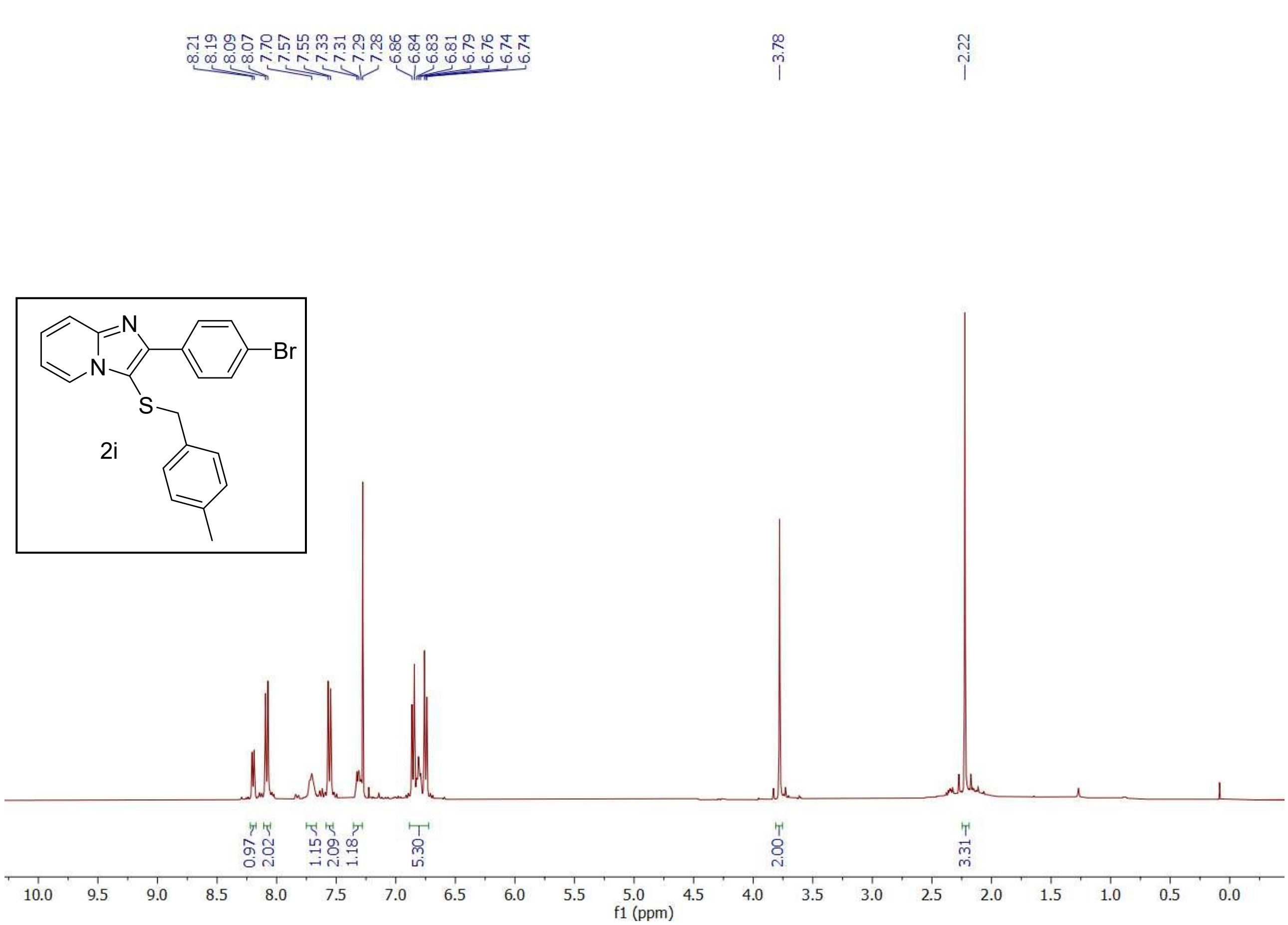
^{13}C NMR spectra of (2g)



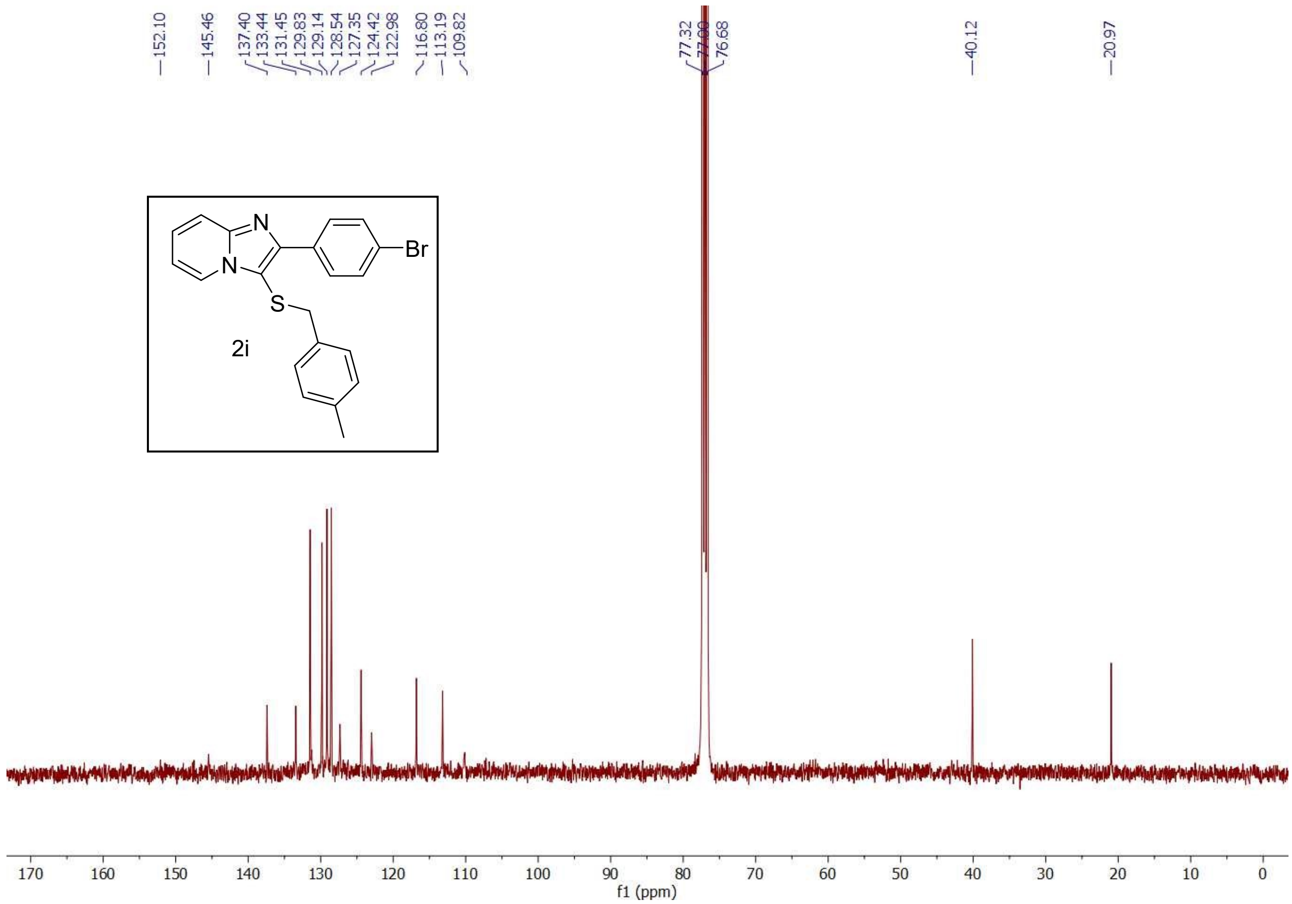
^{1}H NMR spectra of (2h)



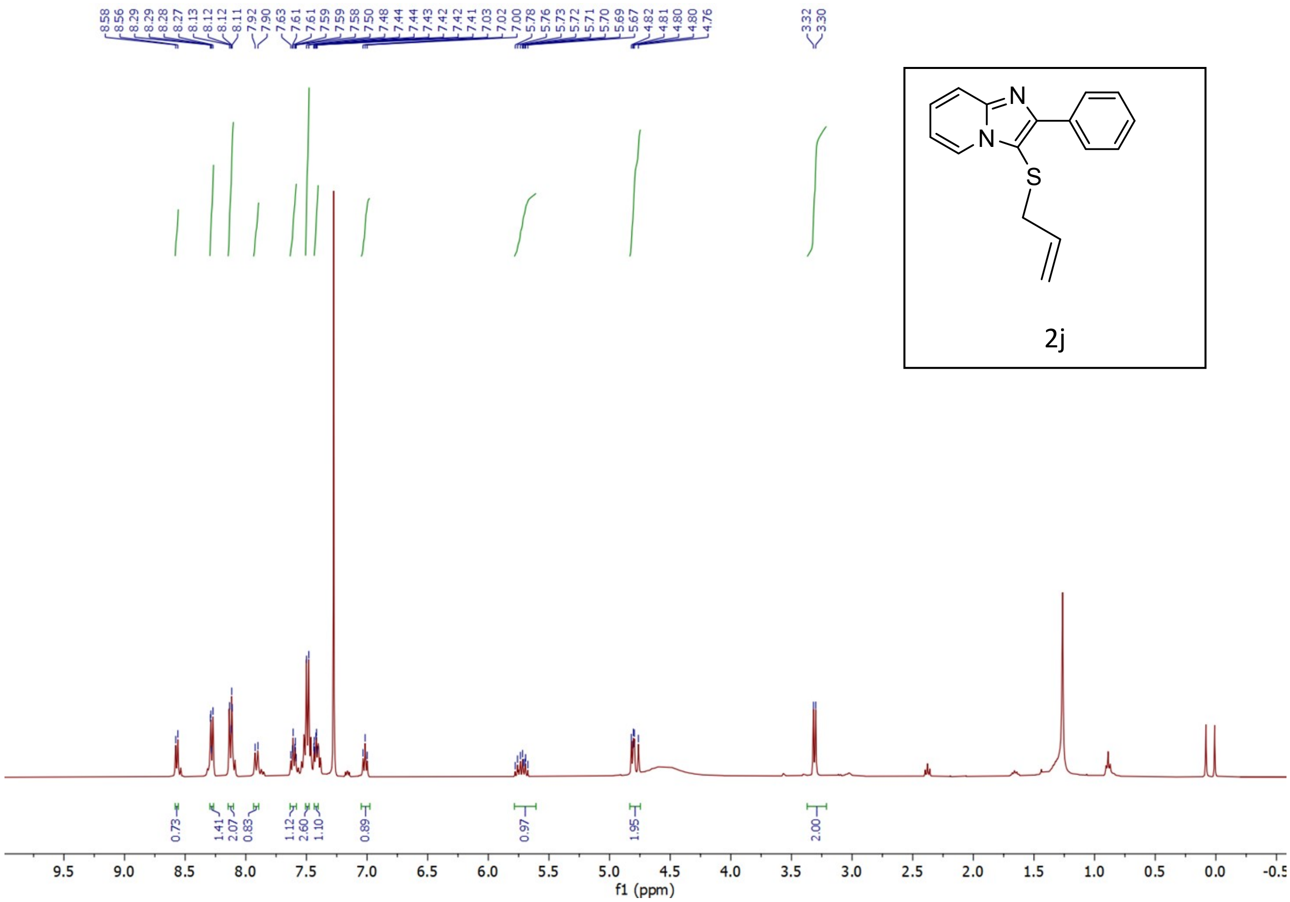
^{13}C NMR spectra of (2h)



^{1}H NMR spectra of (2i)

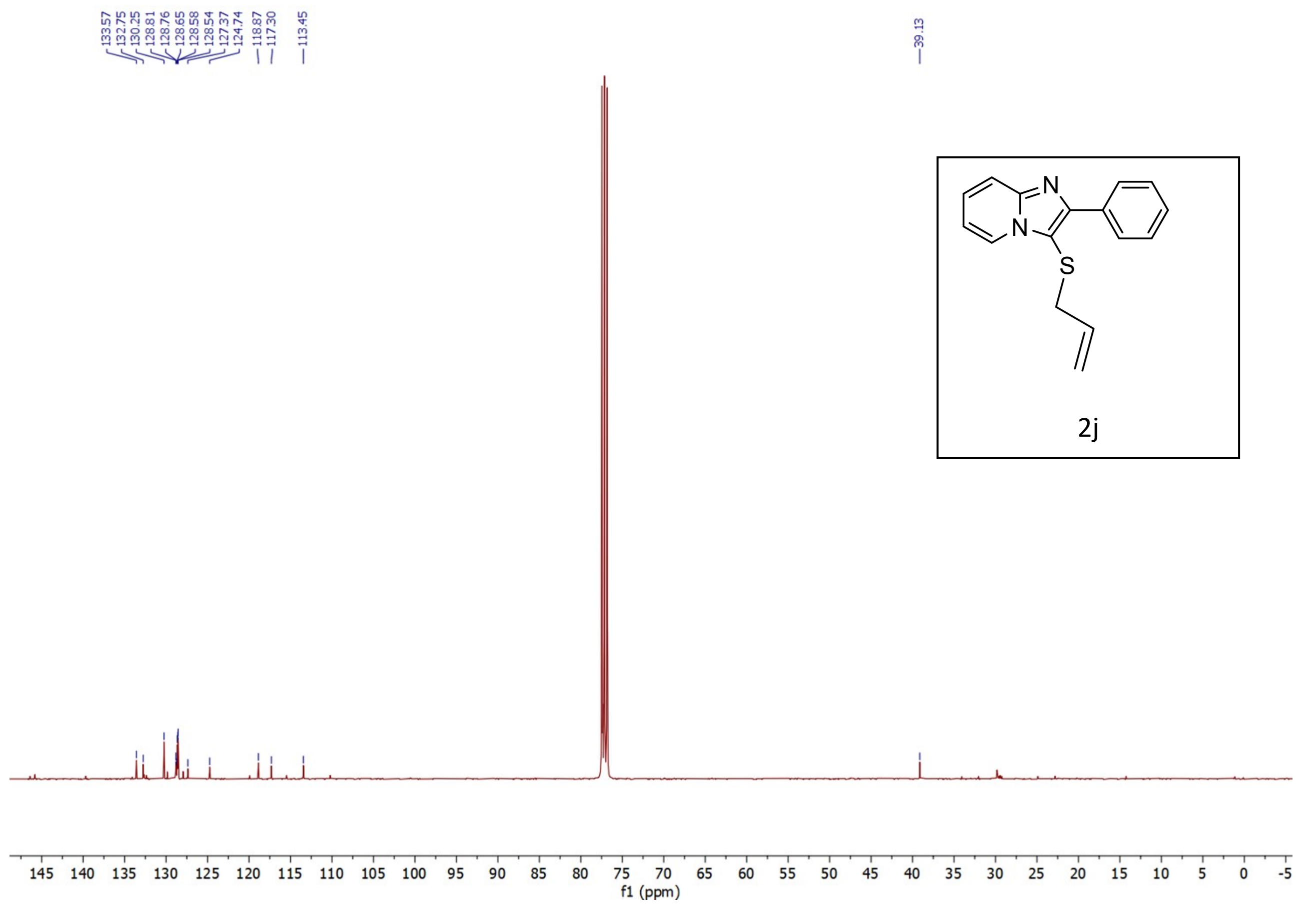


^{13}C NMR spectra of (2i)

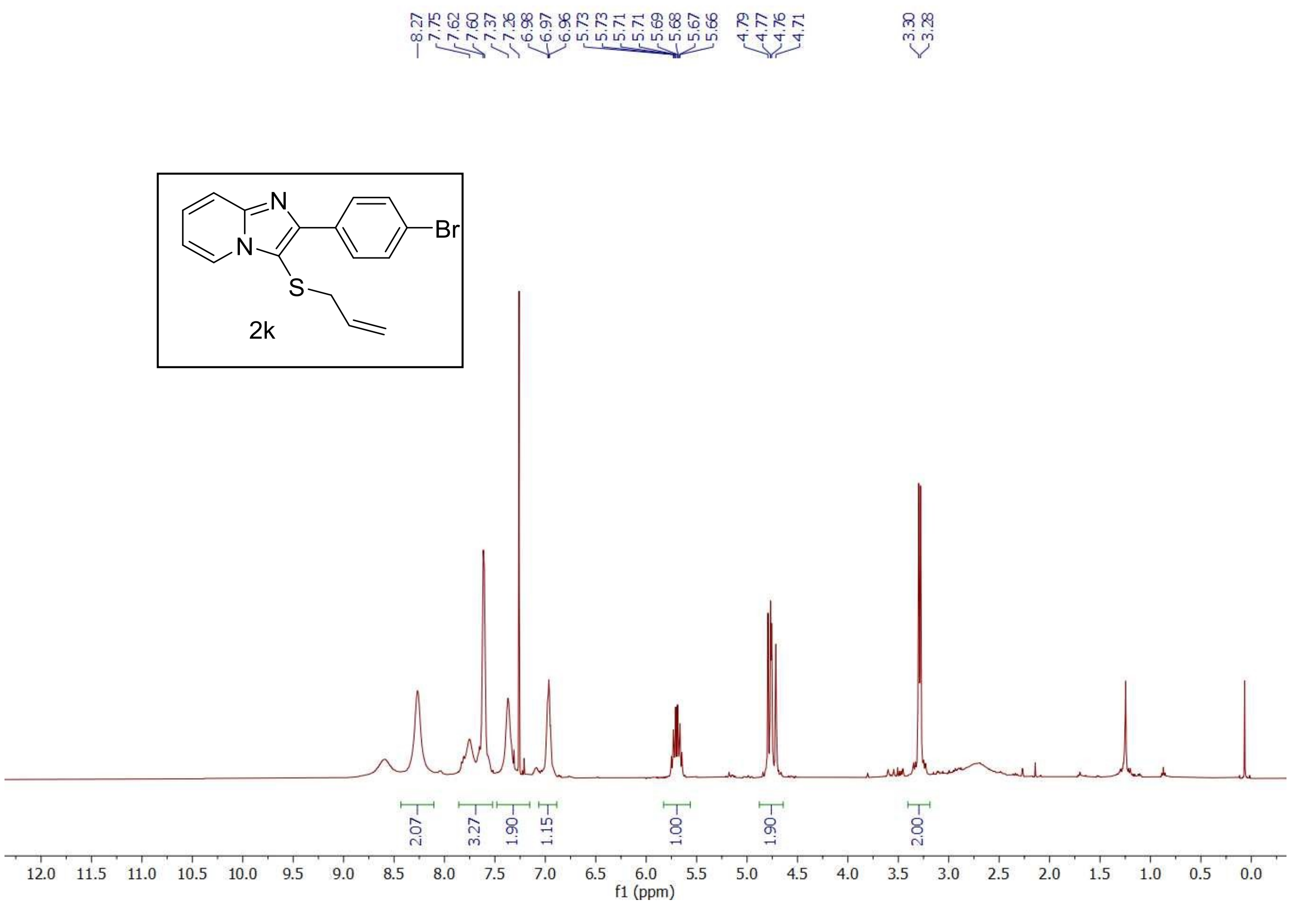


2j

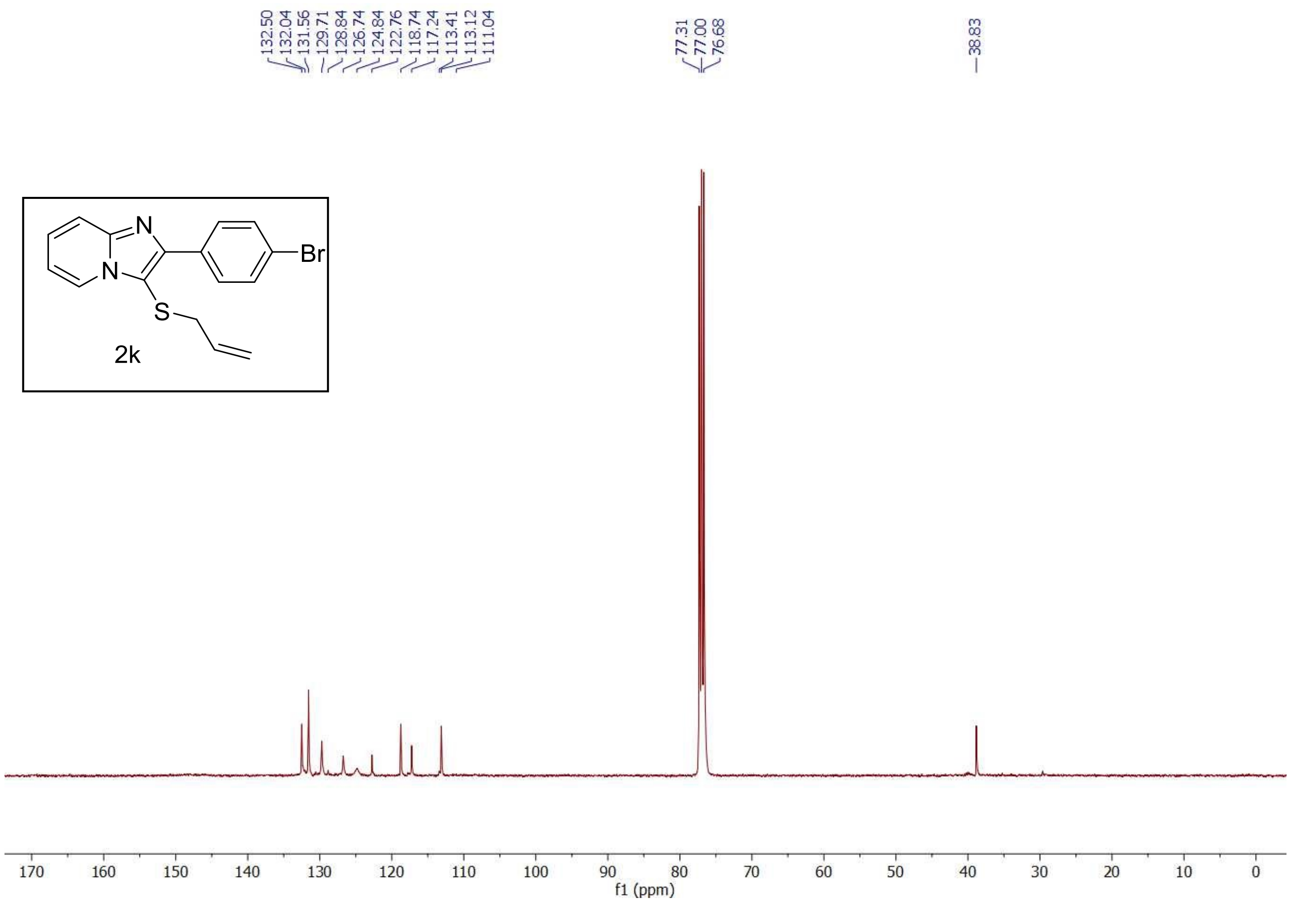
[1]H NMR spectra of (2j)



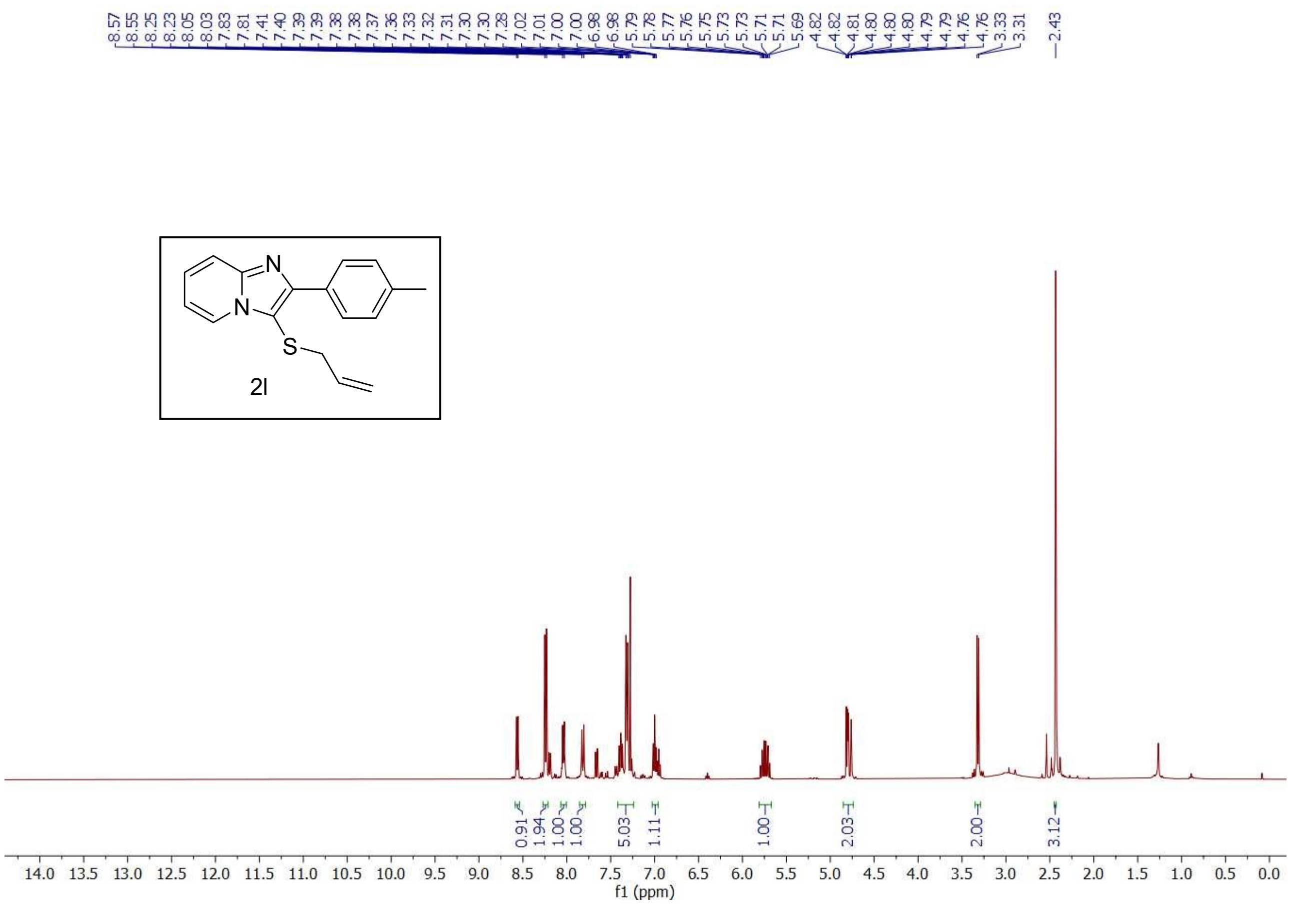
^{13}C NMR spectra of (2j)



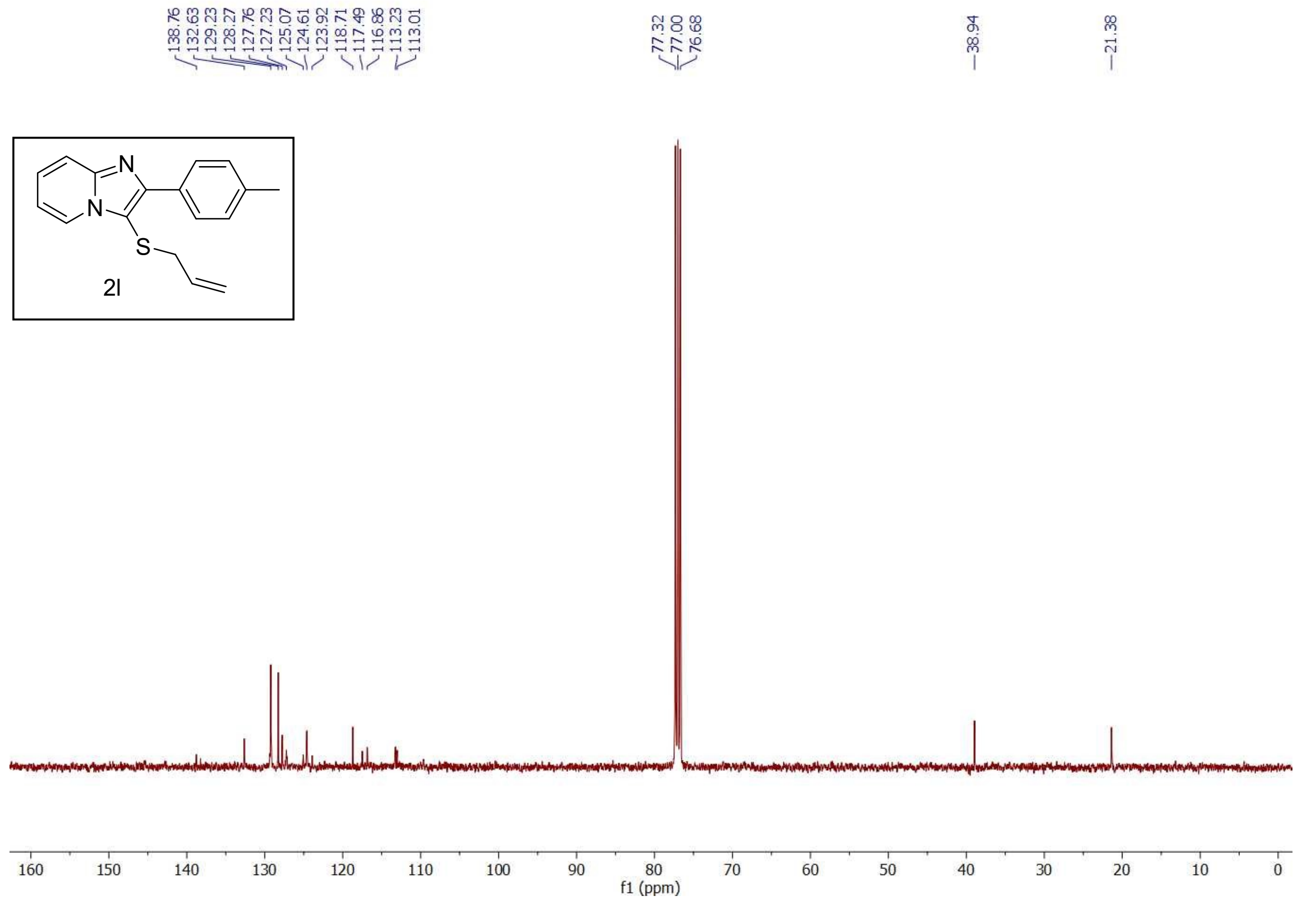
^{1}H NMR spectra of (2k)



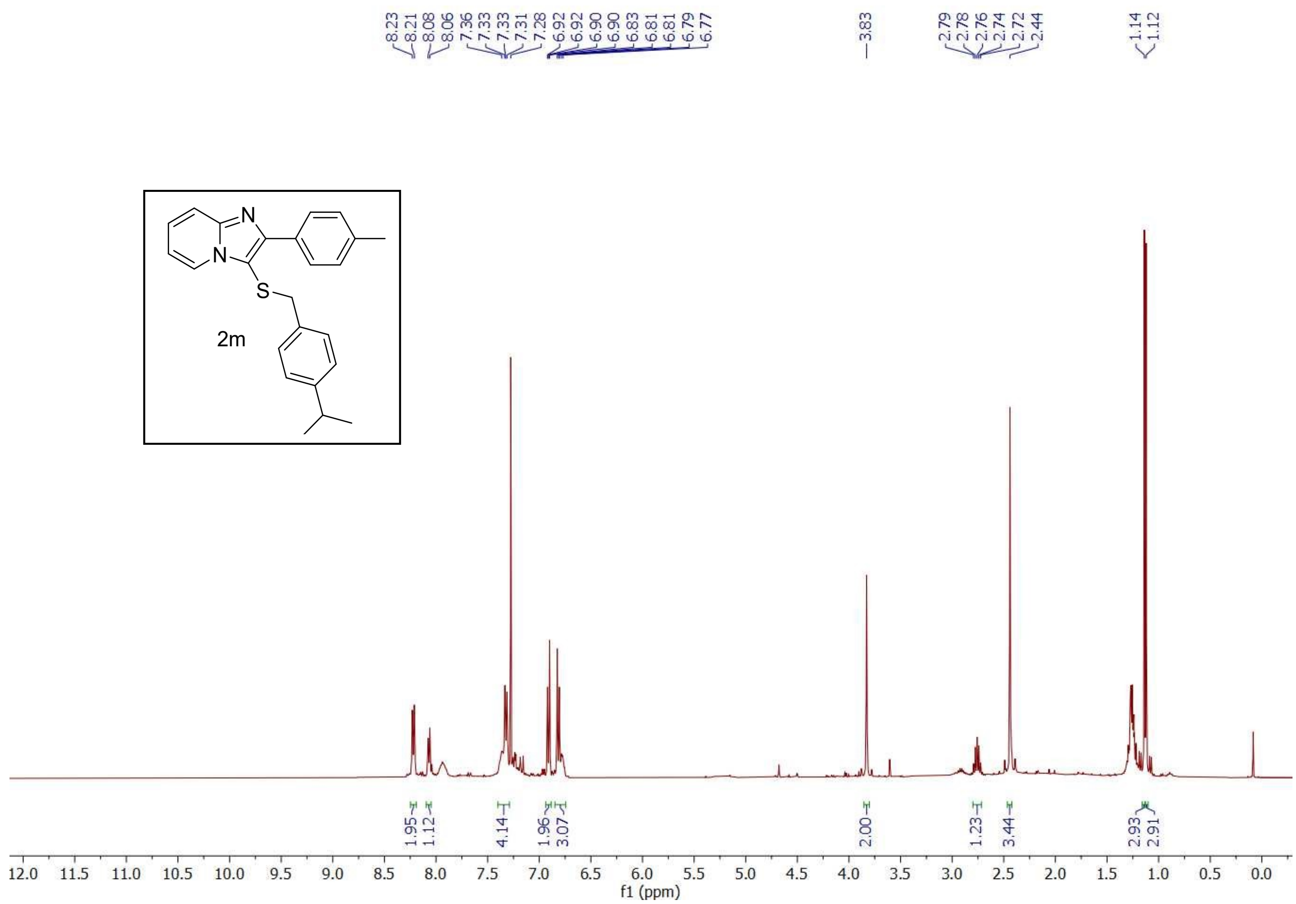
^{13}C NMR spectra of (2k)



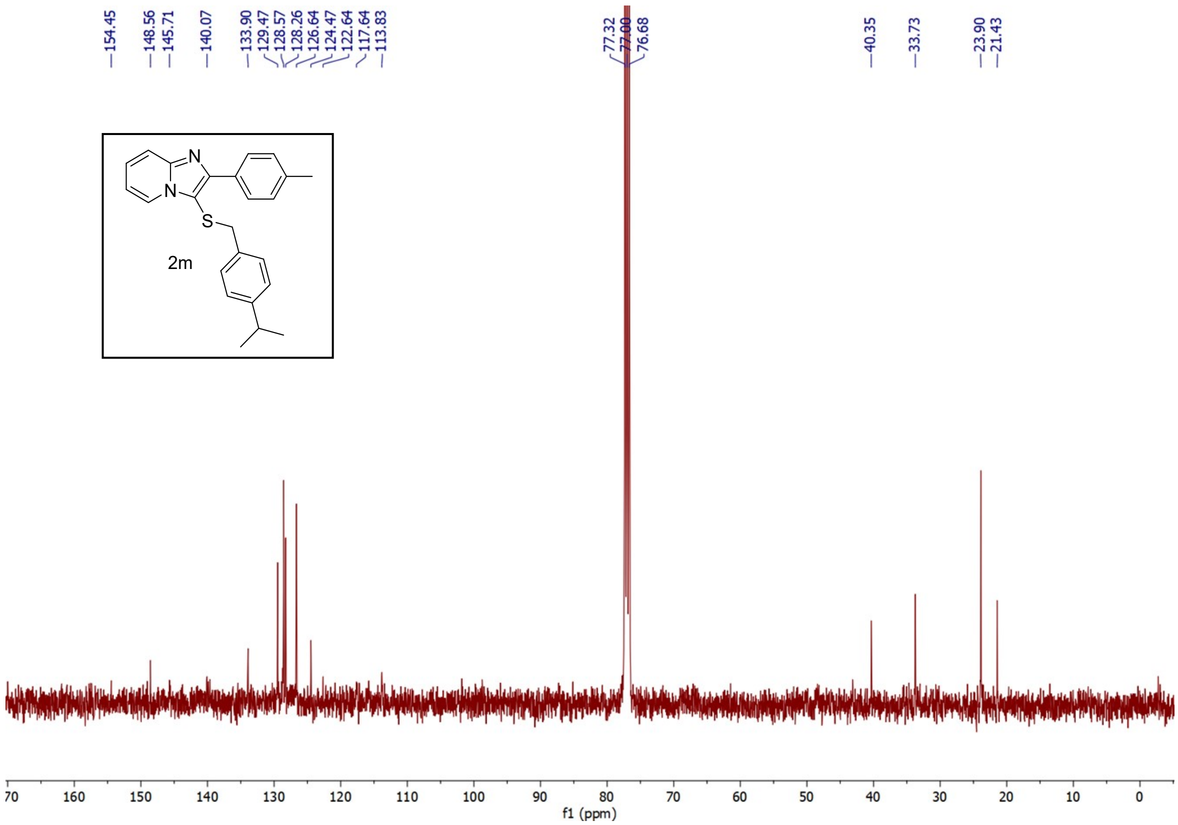
^{1}H NMR spectra of (2l)



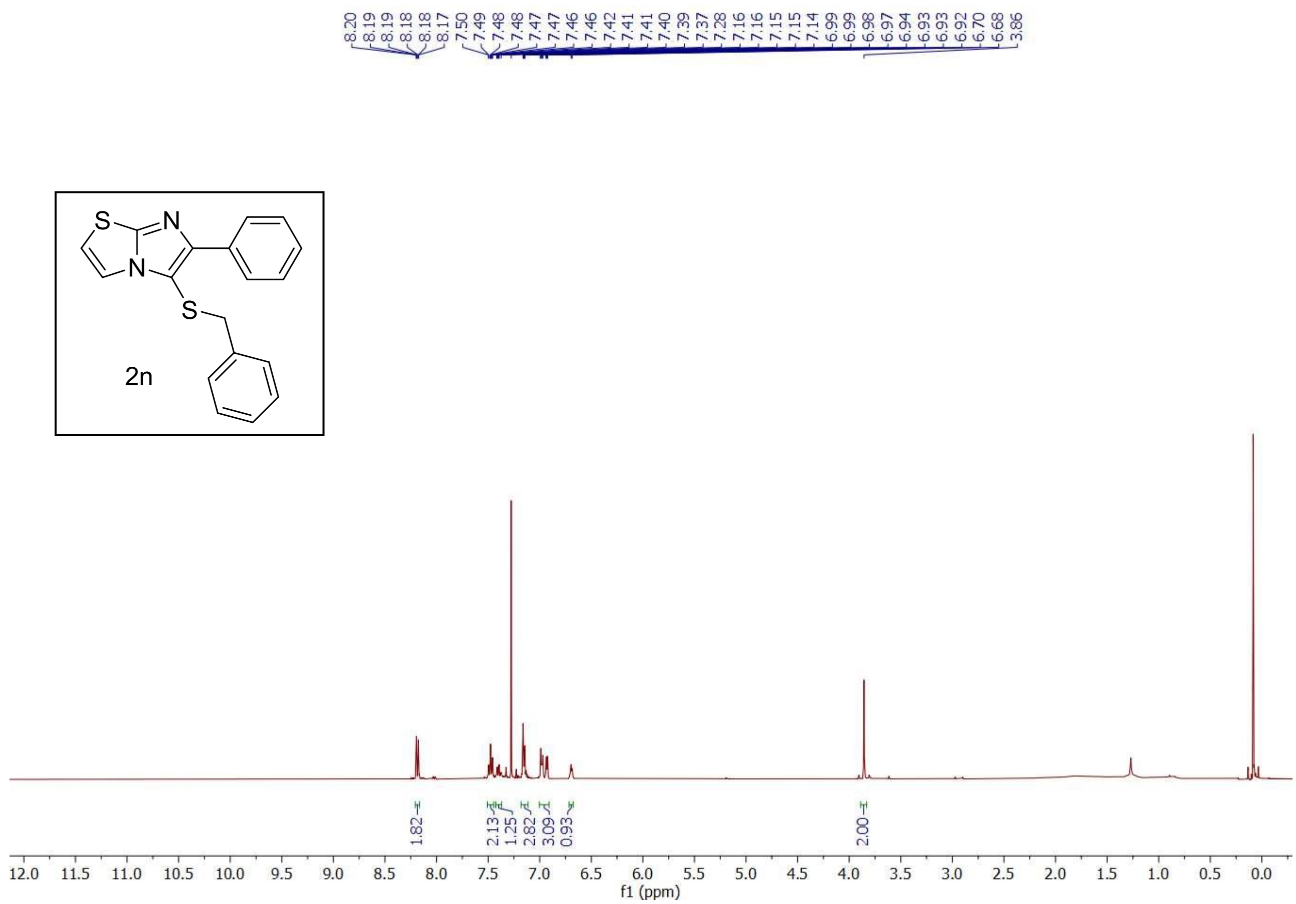
^{13}C NMR spectra of (2l)



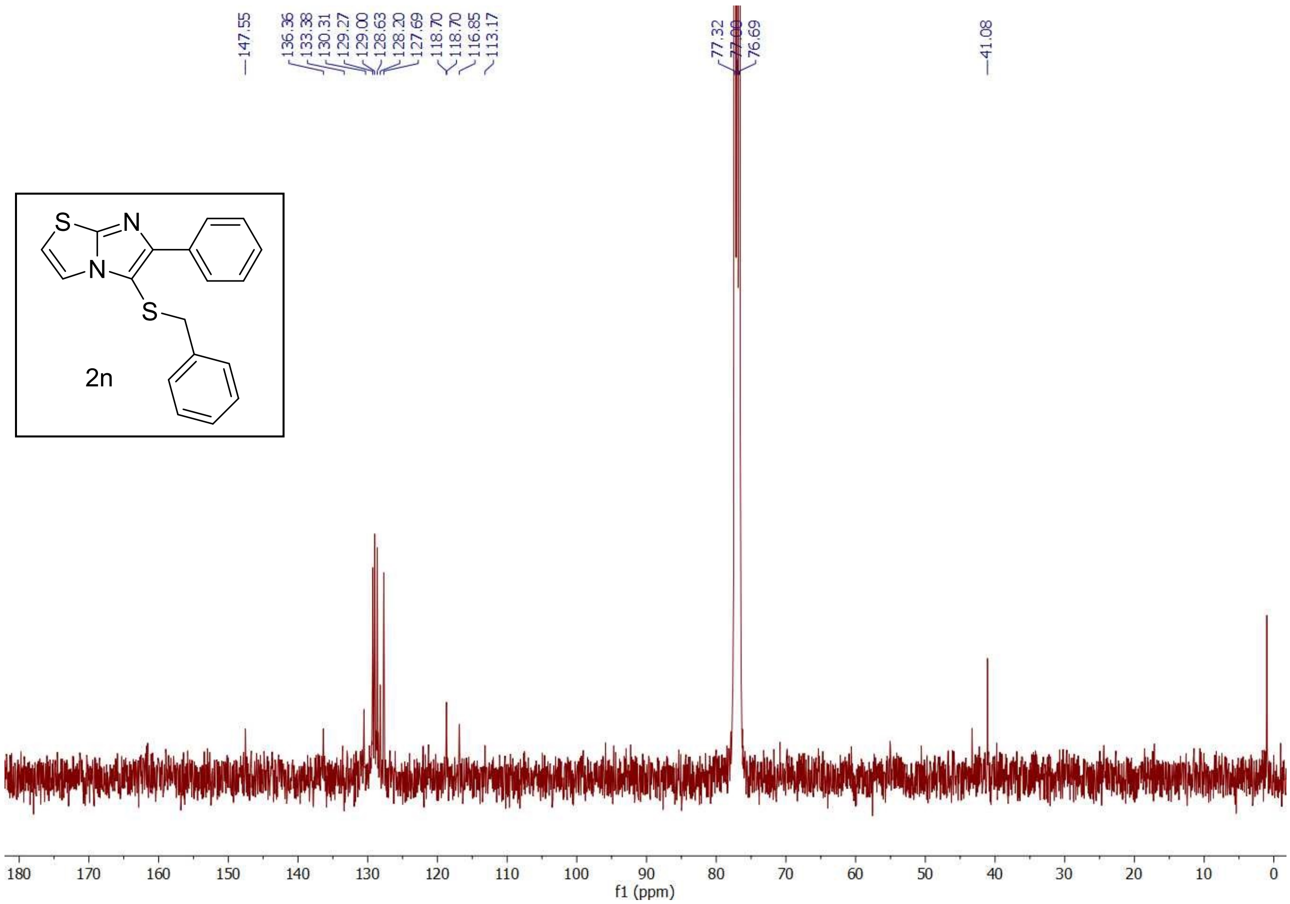
^{1}H NMR spectra of (2m)



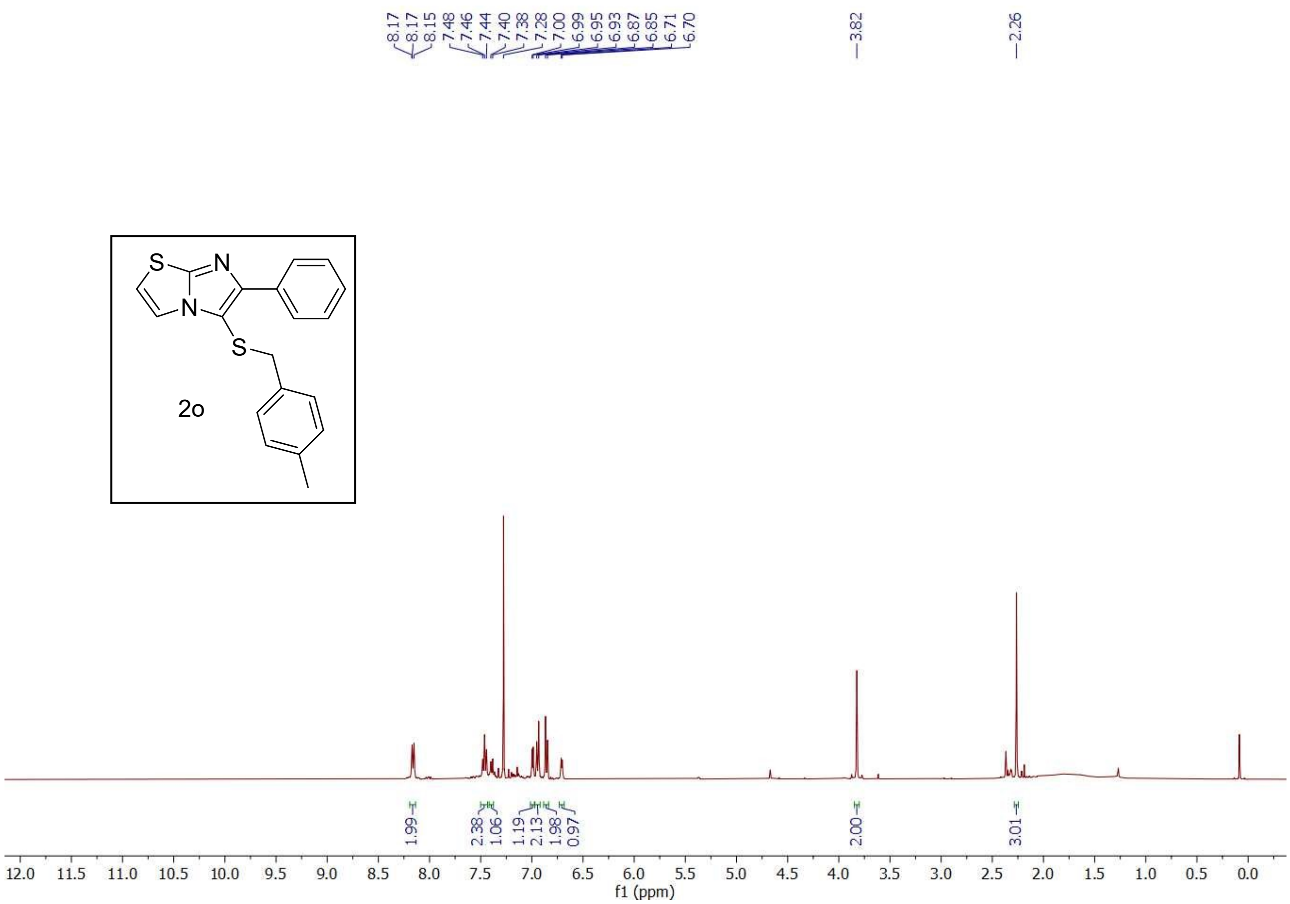
^{13}C NMR spectra of (2m)



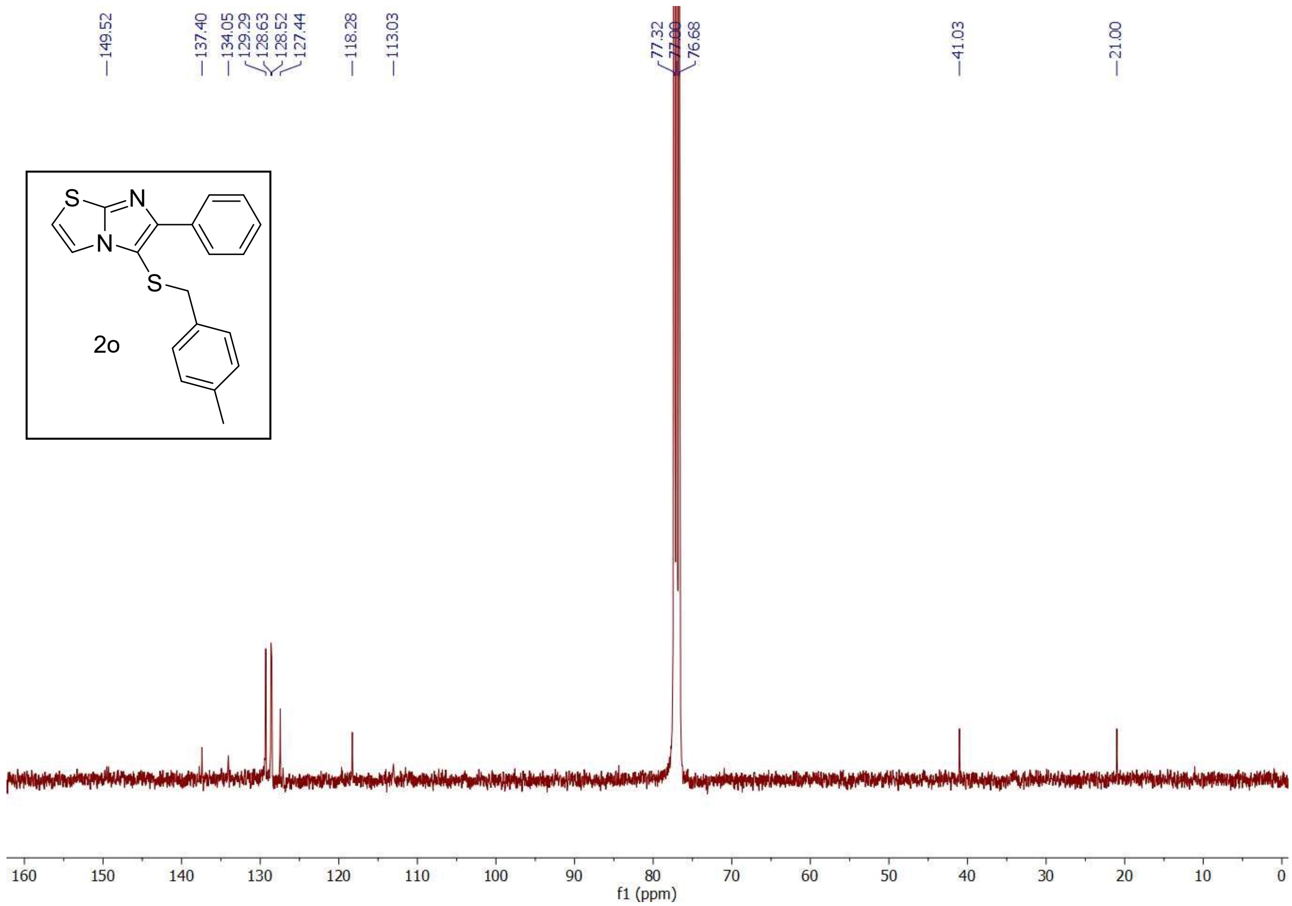
^1H NMR spectra of (2n)



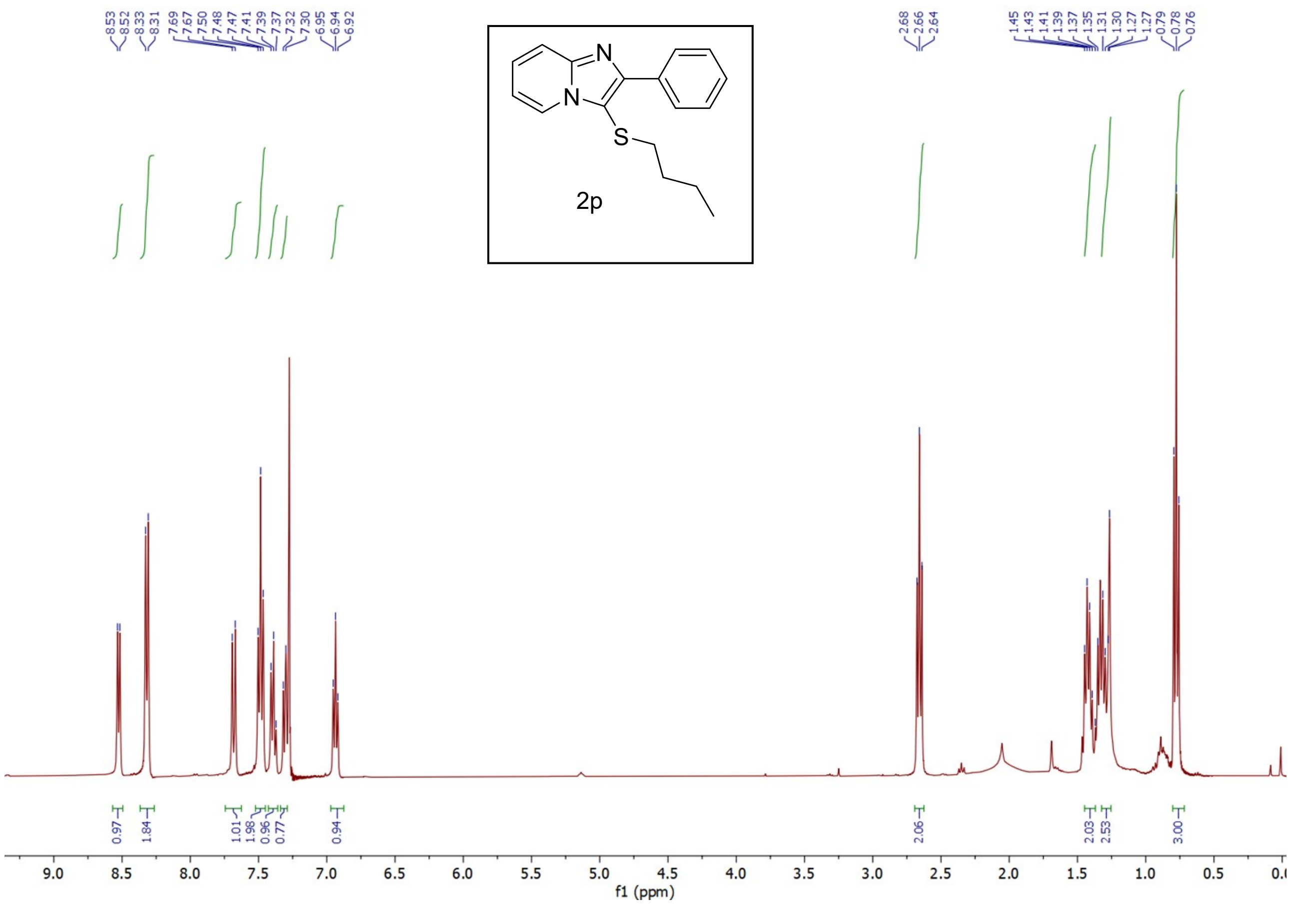
^{13}C NMR spectra of (2n)



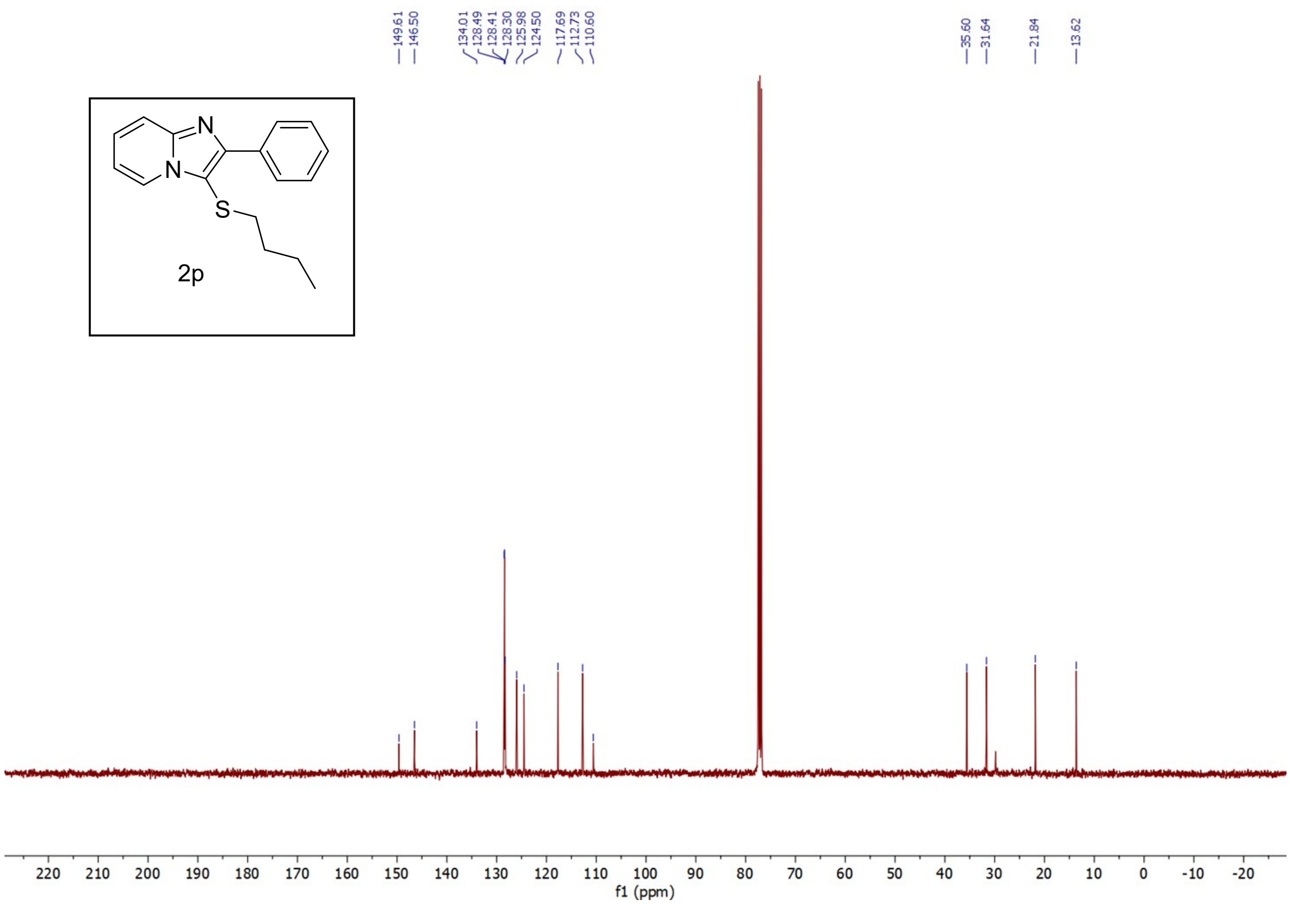
^{1}H NMR spectra of (2o)



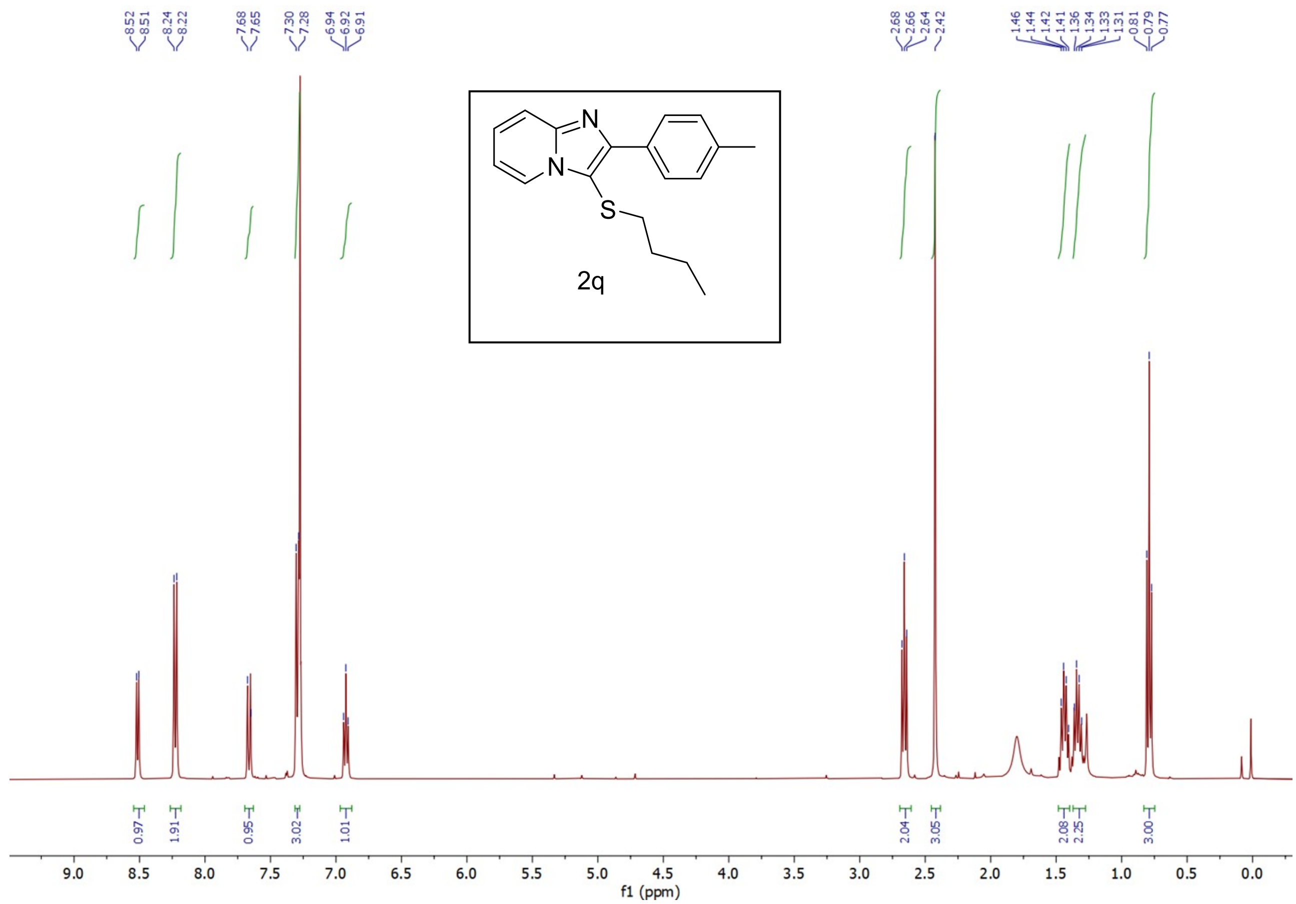
^{13}C NMR spectra of (2o)



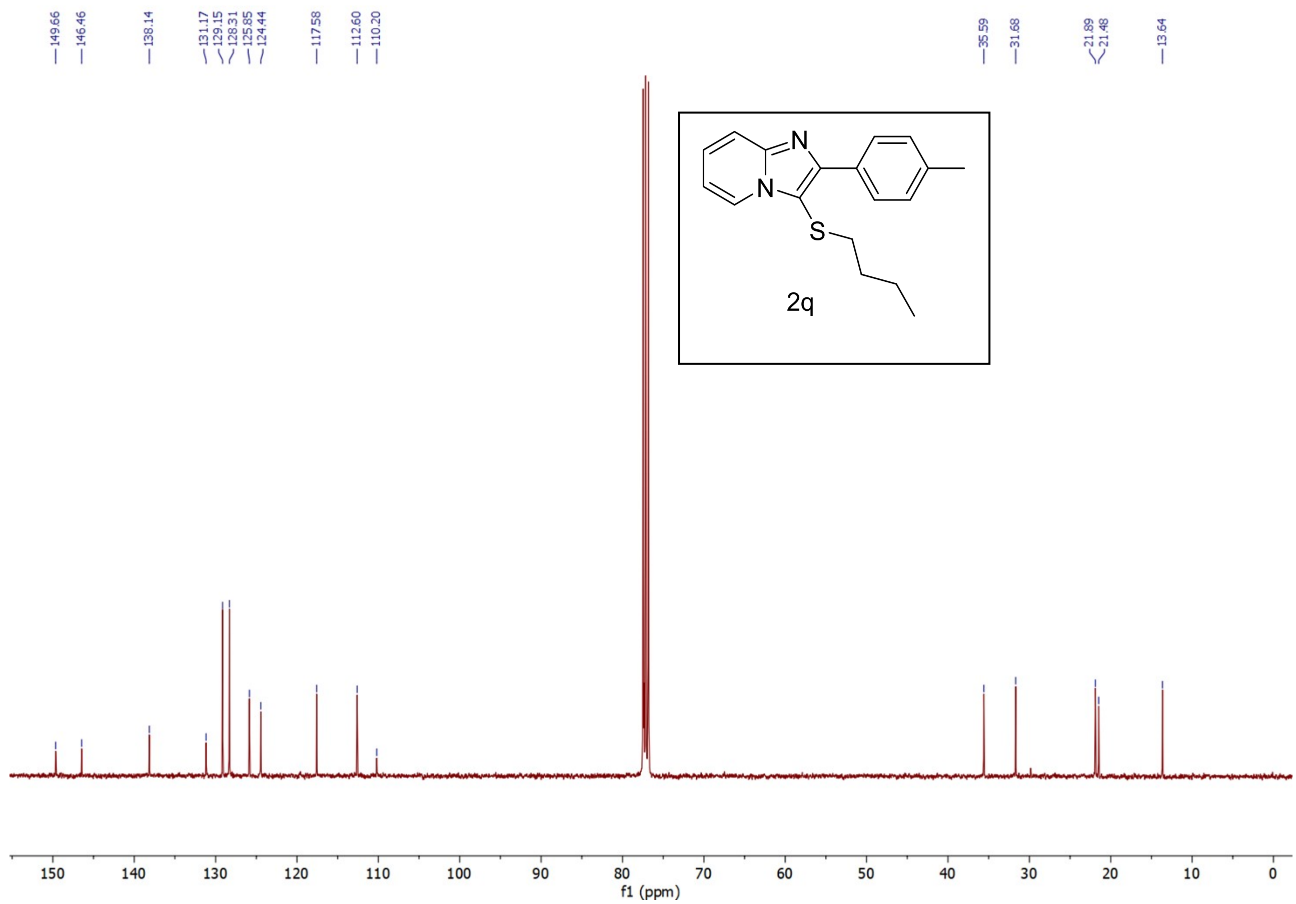
[1]H NMR spectra of (2p)



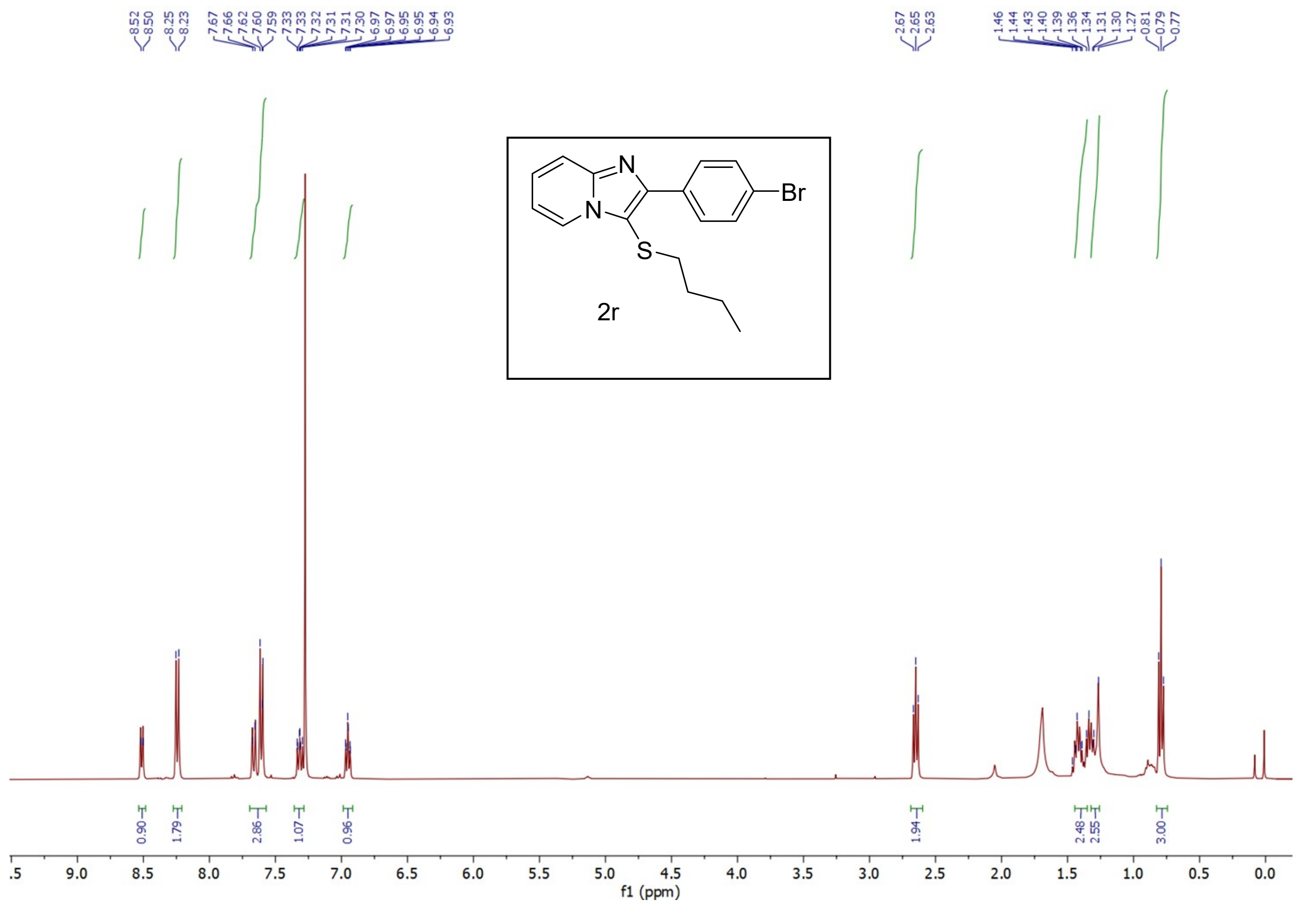
^{13}C NMR spectra of (2p)



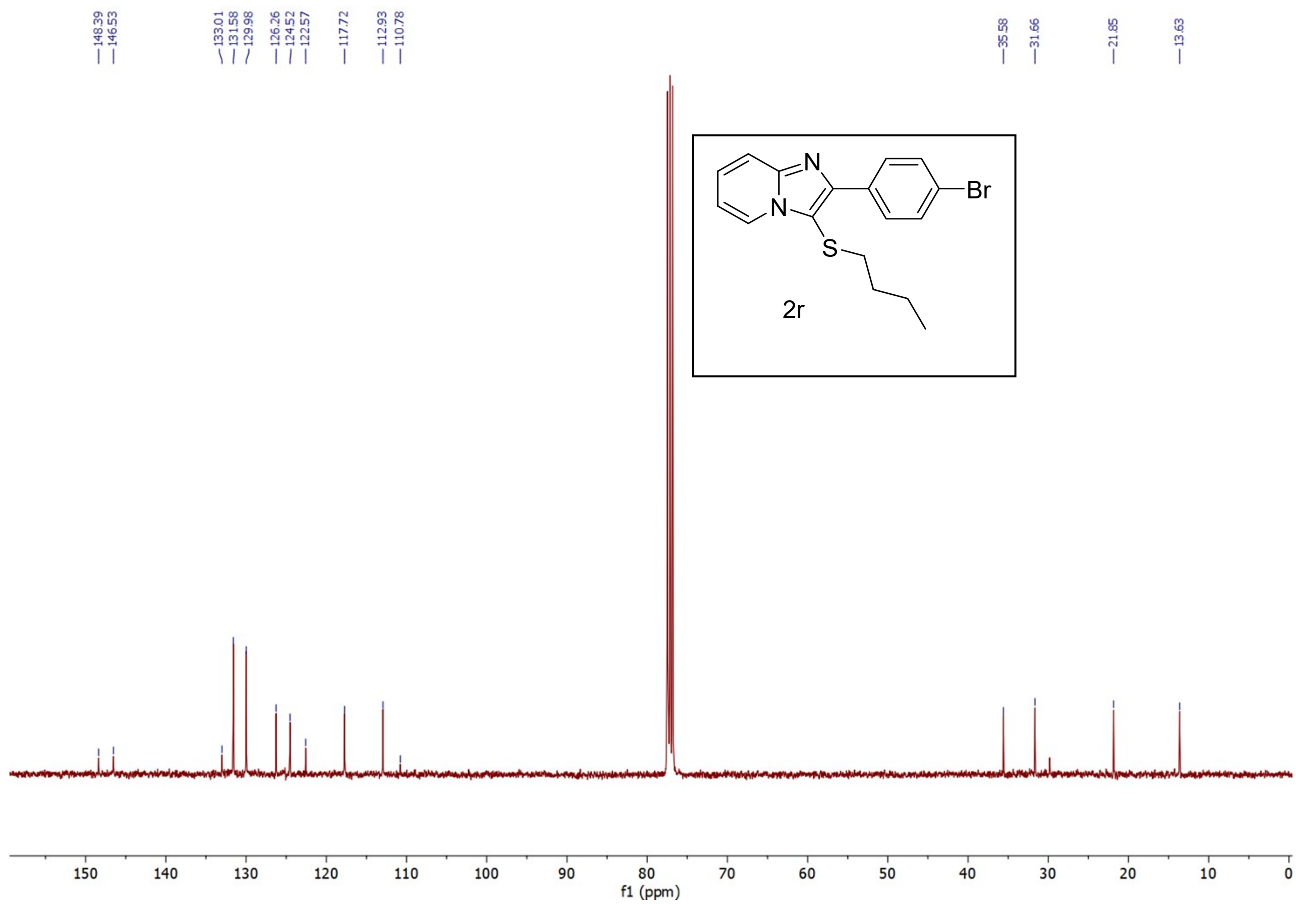
^{1}H NMR spectra of (2q)



^{13}C NMR spectra of (2q)

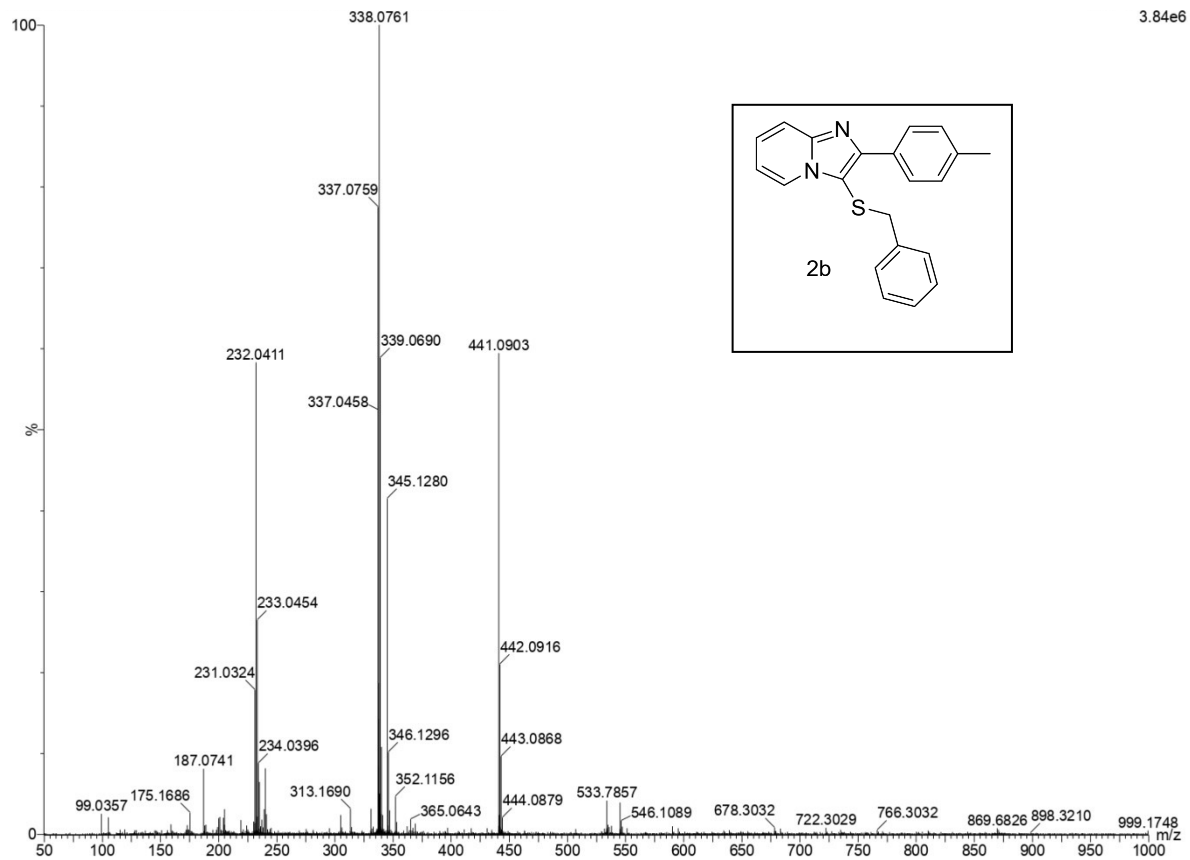


^{1}H NMR spectra of (2r)



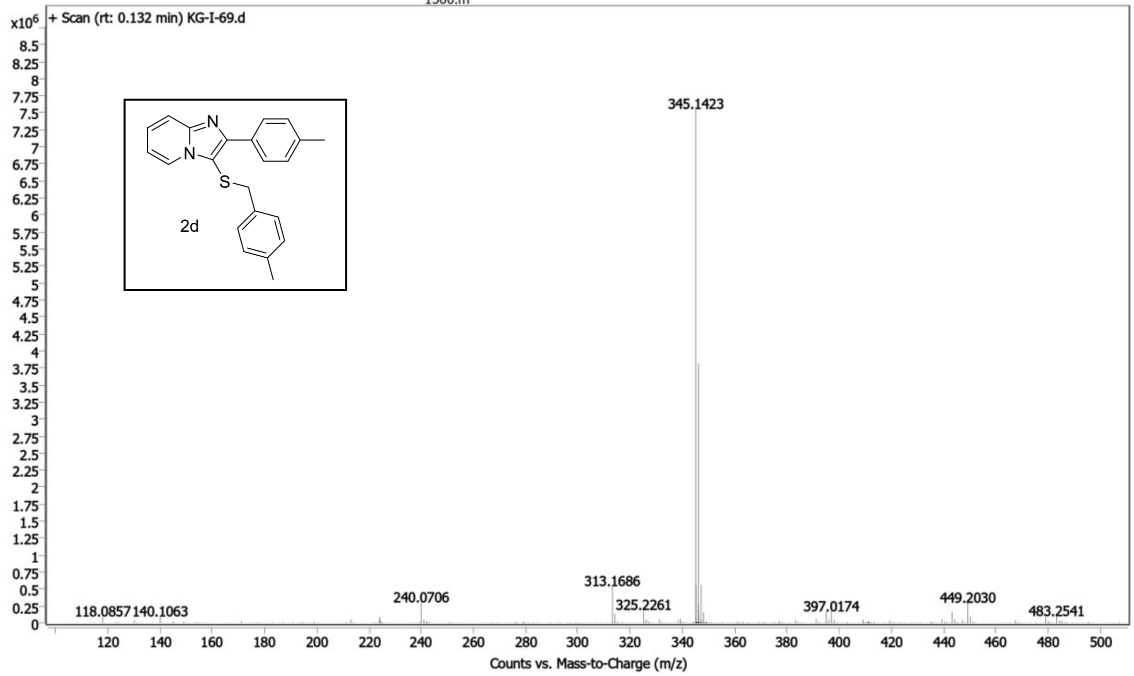
^{13}C NMR spectra of (2r)

HRMS Spectra



User Spectrum Plot Report

Name	Sample5	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
Data File	KG-I-69.d	Method (Acq)	DIRECT MASS_POSITIVE_100_ 1500.m	Comment		Acq. Time (Local)	29-07-2024 12:47:54 (UTC+05:30)



Page 1 of 1

Generated at 15:18 on 29-07-2024

User Spectrum Plot Report

Name	Sample2	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
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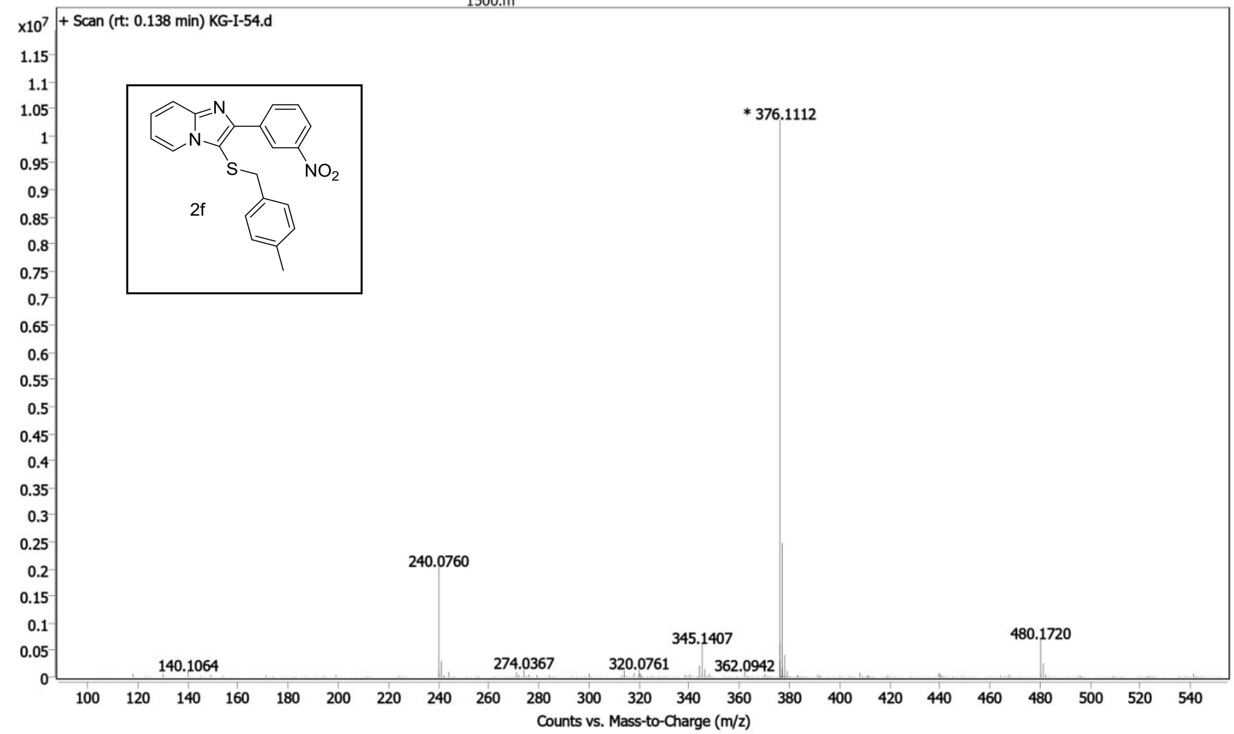
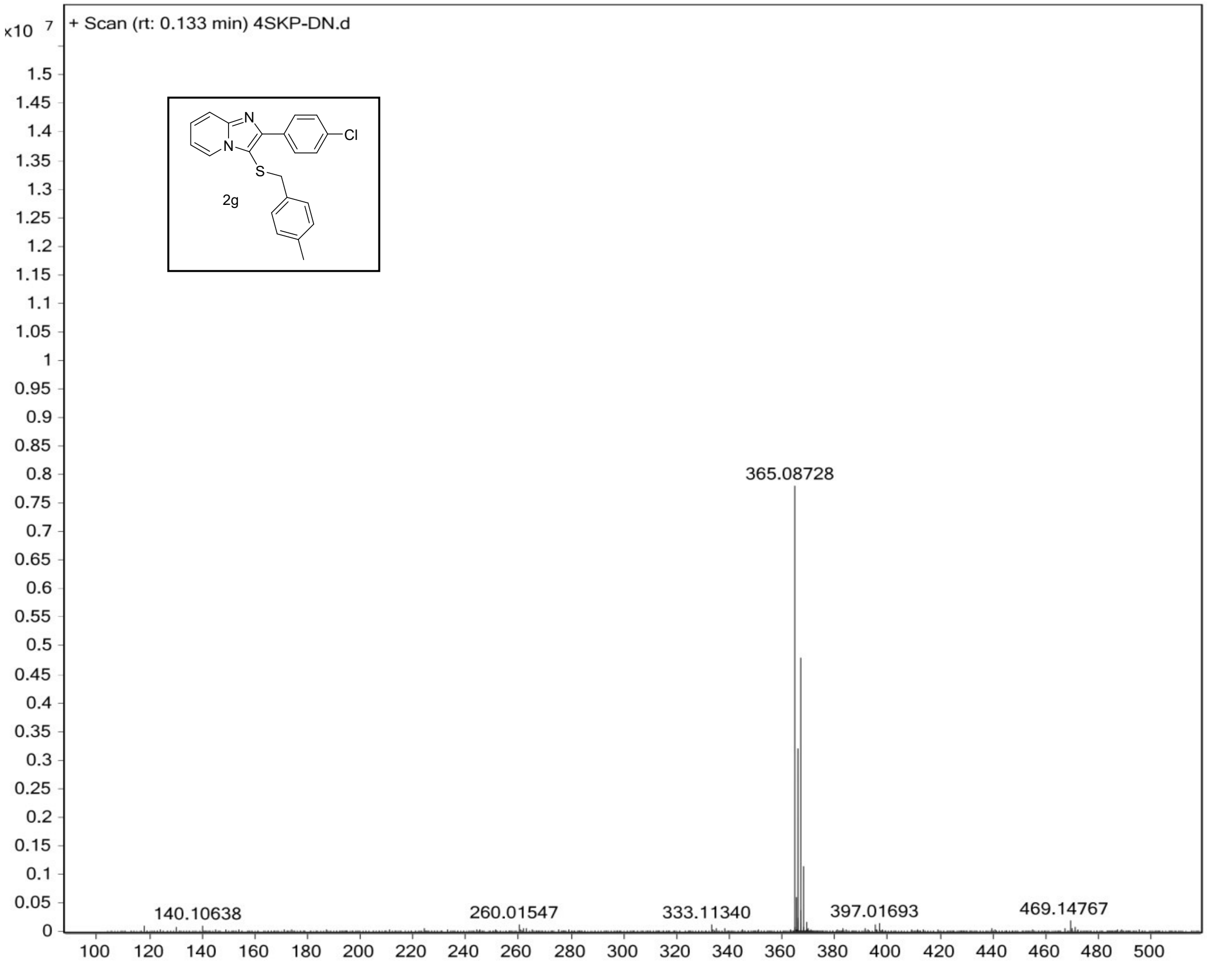


Page 1 of 1 Generated at 15:16 on 29-07-2024



+ Scan (rt: 0.133 min) 4SKP-DN.d
x10 7
2g
Cl
N
S
365.08728
140.10638
260.01547
333.11340
397.01693
469.14767

User Spectrum Plot Report

Agilent Trusted Answers

Name	Sample5	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
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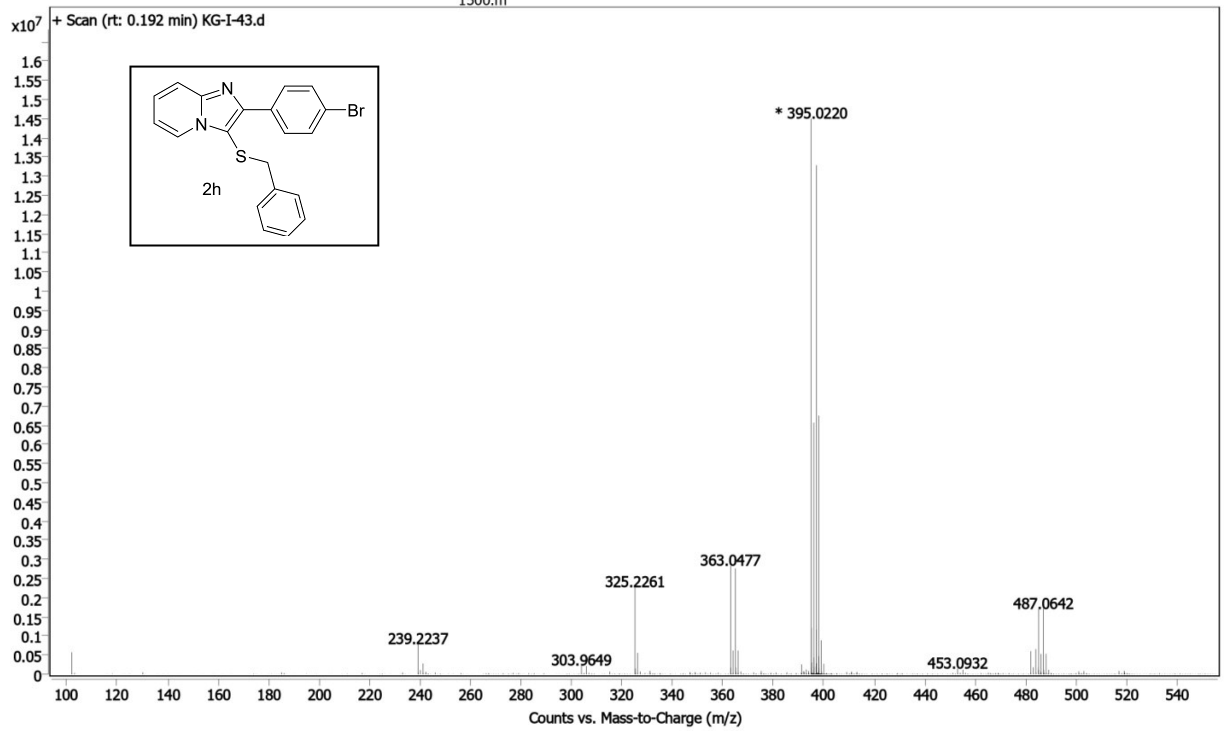

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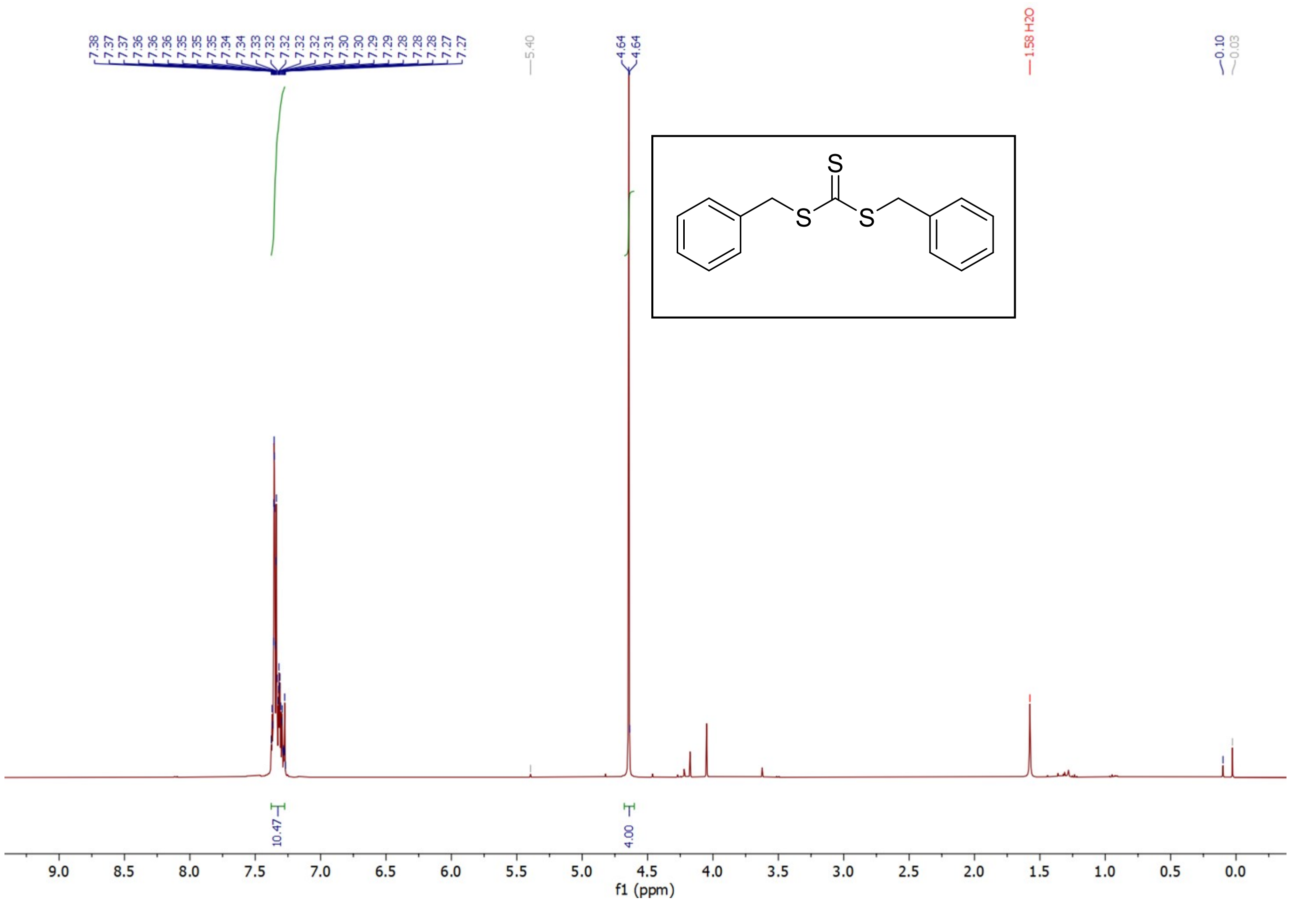
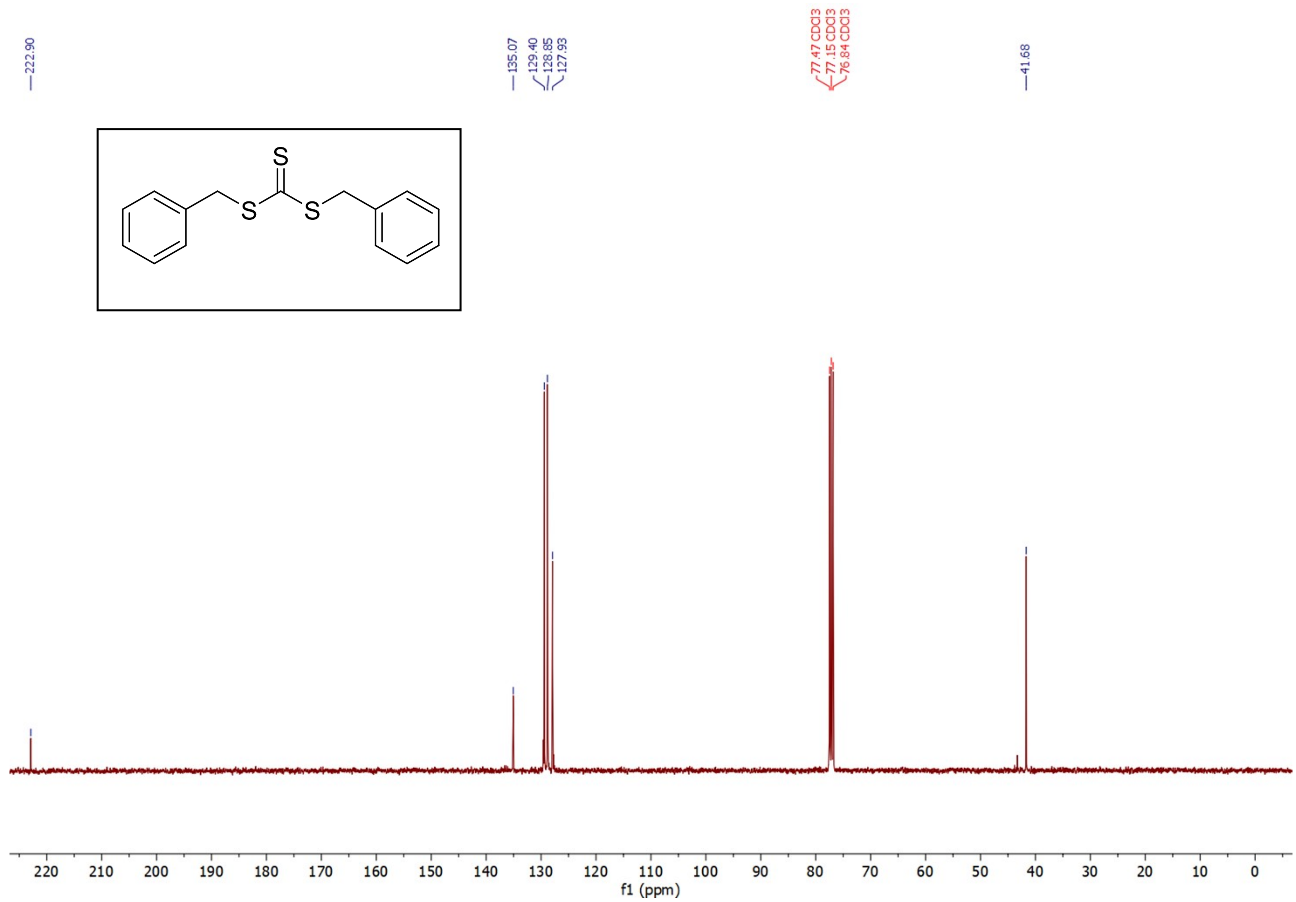
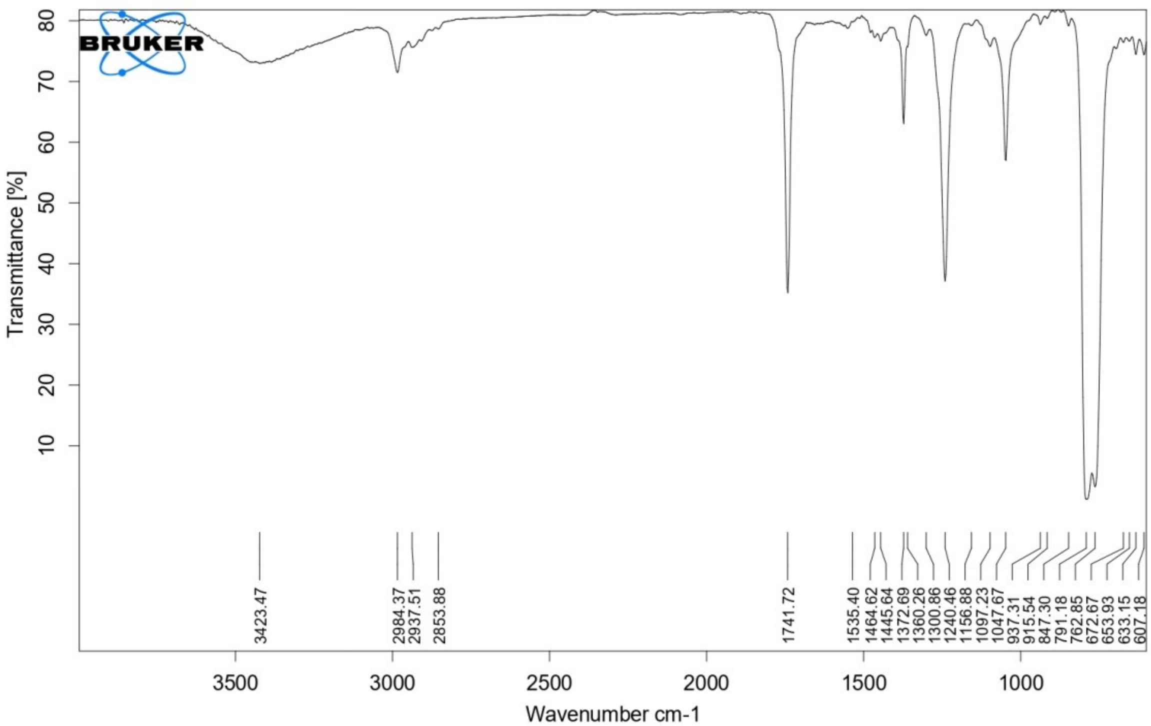
S11. NMR and FTIR spectra of S,S-Dibenzyltrithiocarbonate



^{1}H NMR spectra of *S,S*-Dibenzyltrithiocarbonate



^{13}C NMR spectra of *S,S*-Dibenzyltrithiocarbonate

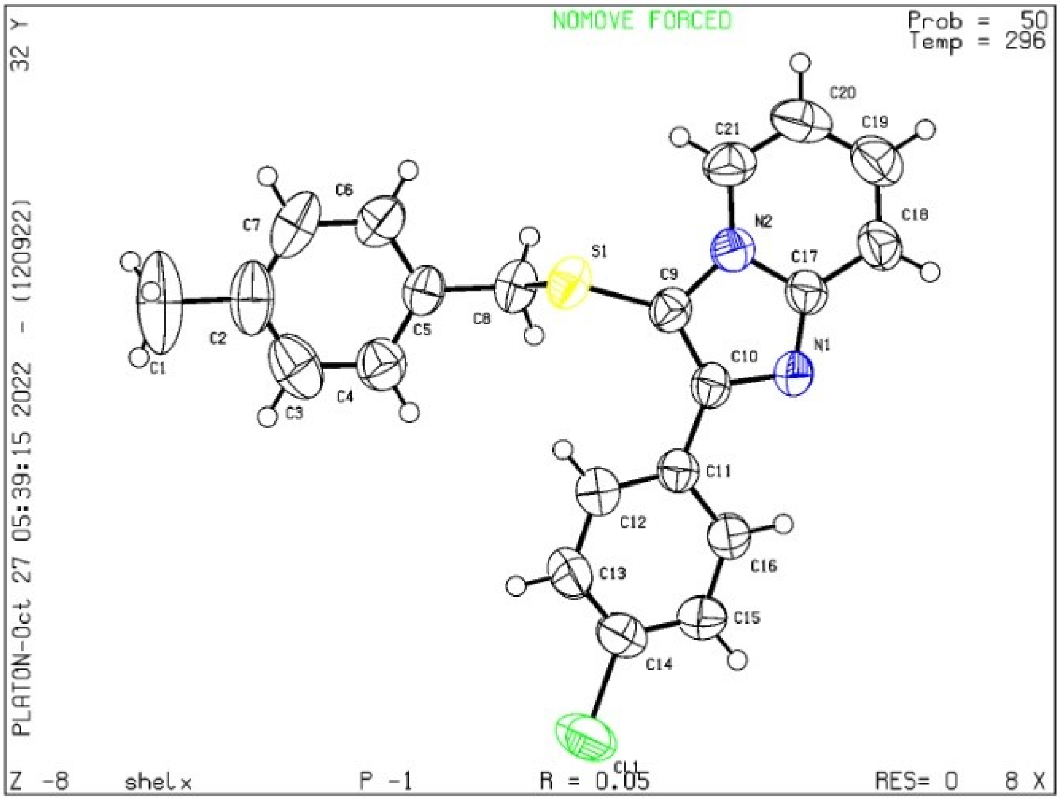


FTIR Spectra of *S,S*-Dibenzyltrithiocarbonate

12. Single crystal XRD data of the 2-(4-chlorophenyl)-3-((4-methylbenzyl)thio)imidazo[1,2-a]pyridine (2g)

Identification code	shelx
Empirical formula	$C_{21}H_{17}ClN_2S$
Formula weight	364.88
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.7958(9) Å, alpha = 101.374(7)° b = 11.0760(19) Å, beta = 107.360(6)° c = 11.1247(14) Å, gamma = 90.842(8)°
Volume	896.0(2) $Å^3$
Z	2
Calculated density	1.352 Mg/m^3
Absorption coefficient	0.335 mm^{-1}
F(000)	380
Crystal size	0.300 x 0.200 x 0.100 mm^3
Theta range for data collection	2.746 to 28.357 °
Limiting indices	-10<=h<=10; -14<=k<=5; -14<=l<=14
Reflections collected / unique	7361 / 4183 [R(int) = 0.0257]
Completeness to theta	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.967 and 0.906
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4183 / 0 / 227
Goodness-of-fit on F^2	Å0.746
Final R indices [I>2sigma (I)]	R1 = 0.0469, wR2 = 0.1489
R indices (all data)	R1 = 0.0795, wR2 = 0.1963
Extinction coefficient	n/a
Largest diff. peak and hole	0.325 and -0.174 e. $Å^{-3}$

13. ORTEP image of the 2-(4-chlorophenyl)-3-((4-methylbenzyl)thio)imidazo[1,2-a]pyridine (2g)



(CCDC 2348383)

14. Computational Details

All density functional theory (DFT) computations in this study were performed employing the Gaussian 16 program package.[5] Ground state energy minimization for all the reactants, products and intermediates were performed with the B3LYP functional. All non-metallic elements like H, C, N, S were described by using localized 6-31+G(d) basis set while for Cu atom an effective core potentials (ECP) basis LANL2DZ was employed. Previous studies report that dispersion corrected B3LYP level of theory offers precise geometry and found to account satisfactory results for this type of Cu-catalyzed mechanism.[6,7] Solvation was introduced implicitly by applying the Polarizable Continuum Model (PCM),[8-9] using the integral equation formalism variant as implemented in Gaussian 16 package with DMF as the solvent. In solution phase all ground state energy minimizations were carried out without symmetry restrictions. Thermodynamic parameters like free energy, enthalpy corrections were evaluated at 298.15 K and 1 atm pressure, incorporating zero-point energy corrections (ZPE). Vibration frequency calculation at the same level of theory confirms that the optimized geometries correspond to minima on the potential energy surfaces. The electronic structures of the reaction intermediates 1a-d and transition sates TS_{c-d} are estimated and stability analysis were performed and all of them were found to be stable.

15. Optimized geometric coordinates (XYZ coordinates)

1a

C	-1.35722500	1.21491100	-0.33101700
C	0.02767100	1.29267000	-0.07536800
C	0.60877900	2.48635200	0.36955000
C	-0.23415200	3.58129800	0.54541800
C	-1.61877200	3.49696600	0.28044800
C	-2.20636200	2.31331600	-0.16335400
H	1.67363100	2.55475900	0.57022500
H	0.18216100	4.52277200	0.89155700
H	-2.24121500	4.37497200	0.42570000
H	-3.27029000	2.25552300	-0.36870600
C	-0.41136400	-0.73434500	-0.75007100
N	0.59224700	0.04961100	-0.36063000
N	-1.59511100	-0.09126000	-0.75923000
C	-2.89365600	-0.67455000	-1.12763700
H	-3.41271900	0.05586900	-1.75631100
H	-2.68596900	-1.55117500	-1.74712300
C	-3.74193800	-1.05721300	0.09174300
H	-3.89483400	-0.17435200	0.72577400
H	-3.19048600	-1.79113000	0.69407600
C	-5.10184300	-1.63668900	-0.32264600

H	-5.64067600	-0.89860200	-0.93315300
H	-4.94336800	-2.51498000	-0.96407400
C	-5.96485800	-2.03187000	0.88173400
H	-6.16724000	-1.16585400	1.52460600
H	-6.92886700	-2.44133900	0.55778800
H	-5.46542000	-2.79365500	1.49360400
Cl	4.48610700	-0.79407000	-0.99957400
Cu	2.44948300	-0.49771300	-0.18852100
H	-0.30809800	-1.77199600	-1.03556900
Cl	2.55158500	-1.17302800	1.98986500

1b

C	-2.98384200	-0.40788200	1.11414500
C	-1.89135200	-1.22524100	0.75268500
C	-1.70260700	-2.47495500	1.35671400
C	-2.62916800	-2.86880800	2.31912400
C	-3.71810400	-2.04267200	2.67695900
C	-3.91626200	-0.79823700	2.08157200
H	-0.86434000	-3.10976500	1.08529800
H	-2.51278900	-3.83188900	2.80776000
H	-4.41817100	-2.38558900	3.43329900
H	-4.75541300	-0.16849000	2.35905000
C	-1.76416200	0.59918600	-0.42390200
N	-1.14781200	-0.56031400	-0.22172400
N	-2.86540800	0.74749200	0.34475800
C	-3.78429800	1.89353300	0.32522000
H	-4.05705400	2.11173800	1.36258400
H	-3.21945400	2.75111700	-0.05106700
C	-5.03151000	1.64517600	-0.53255900
H	-5.55946700	0.75594200	-0.16399500
H	-4.71839000	1.42675400	-1.56224200
C	-5.98070800	2.85158600	-0.52044400
H	-6.27881600	3.06933400	0.51477700
H	-5.44473600	3.74002200	-0.88300000
C	-7.23291200	2.62539700	-1.37622500
H	-7.80719200	1.76213500	-1.01668600
H	-7.89205600	3.50105900	-1.34935600
H	-6.96734700	2.43768400	-2.42432200
Cl	1.61457700	-2.38706000	-2.60008300
Cu	0.48627700	-1.16730700	-1.12775100
S	2.03644600	0.15226500	0.02430500
C	3.72199500	-0.20998600	-0.66378400
H	3.93802800	-1.27152800	-0.52625800
H	3.72196800	0.01072700	-1.73321400
C	4.72566800	0.64734300	0.06780100
C	5.05017400	1.93096900	-0.40308300
C	5.34449000	0.18322700	1.24097400
C	5.97673500	2.72750700	0.27572900

H	4.57841200	2.30281800	-1.31004600
C	6.27109600	0.97779900	1.92194800
H	5.10227600	-0.80849100	1.61666600
C	6.58942500	2.25358300	1.44174200
H	6.22245900	3.71508500	-0.10648500
H	6.74630200	0.60045000	2.82391900
H	7.31134400	2.87146100	1.96942400
H	-1.43396100	1.35972600	-1.11774200

1c

C	2.34124100	-2.65031900	-0.92474200
C	1.53721400	-2.64846800	0.23484900
C	1.79688000	-3.53388700	1.28875400
C	2.87526900	-4.40325600	1.14457000
C	3.67576200	-4.39847200	-0.01972500
C	3.42518900	-3.52260800	-1.07436800
H	1.17944000	-3.53996100	2.18202600
H	3.10668400	-5.10309200	1.94241600
H	4.50754300	-5.09296500	-0.09469700
H	4.04459300	-3.52252100	-1.96540000
C	0.74470400	-1.14052900	-1.11653100
N	0.54398100	-1.68156200	0.08014100
N	1.80264500	-1.67649600	-1.76226300
C	2.29779800	-1.28486200	-3.08893100
H	2.52211600	-2.20423300	-3.63964100
H	1.47043200	-0.78798300	-3.60294600
C	3.52602500	-0.36873000	-3.02626800
H	4.32853500	-0.86691900	-2.46670000
H	3.26602600	0.54181700	-2.47045200
C	4.02687700	-0.00037800	-4.43009900
H	4.26419300	-0.91967300	-4.98389800
H	3.21901900	0.49699100	-4.98504900
C	5.26084300	0.90980300	-4.39772600
H	6.09625700	0.42415600	-3.87772400
H	5.59501500	1.15615400	-5.41245400
H	5.04422200	1.85142900	-3.87775400
Cl	-1.67678400	-0.71841400	3.34729700
Cu	-0.88935400	-1.21551000	1.33653800
S	-2.67404100	-1.26854400	-0.16293900
C	-4.18645500	-0.68213400	0.74457600
H	-4.38112000	-1.36322800	1.57537900
H	-3.99102000	0.31471600	1.14489100
C	-5.34355600	-0.65883500	-0.22372000
C	-5.62267300	0.49300100	-0.97869200
C	-6.15660800	-1.79189200	-0.39603800
C	-6.69307600	0.51525400	-1.87753000
H	-5.00152900	1.37741900	-0.85467600
C	-7.22770600	-1.77205000	-1.29368500
H	-5.95160600	-2.68971300	0.18278300

C	-7.49857600	-0.61802200	-2.03841500
H	-6.90037000	1.41681000	-2.44853900
H	-7.85231000	-2.65430700	-1.40889000
H	-8.33250200	-0.60115100	-2.73537600
H	0.13566100	-0.35901400	-1.54855200
C	-1.77223800	4.69985100	-1.18963200

1d

C	5.26613500	-0.72986200	0.03538400
C	4.40412300	-1.57213300	0.77146600
C	4.92232400	-2.58121800	1.59342400
C	6.30768900	-2.71603800	1.65183900
C	7.16231700	-1.86971600	0.90998600
C	6.65831400	-0.86176400	0.08933500
H	4.26389400	-3.23194000	2.16159700
H	6.74263300	-3.48810600	2.28023600
H	8.23759600	-2.00653300	0.98132400
H	7.31989900	-0.21341000	-0.47648800
C	3.16119100	-0.18818800	-0.34983000
N	3.08623500	-1.20224600	0.50434300
N	4.43641900	0.13700000	-0.66977900
C	4.84984800	1.22849100	-1.55994400
H	5.66743700	0.85393600	-2.18478900
H	4.00442700	1.44080000	-2.22064700
C	5.27326000	2.49247600	-0.80049000
H	6.09402200	2.24983700	-0.11282000
H	4.43160500	2.83614800	-0.18438300
C	5.71281400	3.61202000	-1.75465300
H	6.54947500	3.25593500	-2.37209700
H	4.89129500	3.84277000	-2.44745600
C	6.13057500	4.88857400	-1.01442900
H	6.97212900	4.69553900	-0.33709300
H	6.43975600	5.66981300	-1.71891200
H	5.30248900	5.28665600	-0.41430900
Cl	-0.27280500	-2.93146800	2.13401300
Cu	1.46833000	-1.94829800	1.22611100
S	-3.78636900	-0.08339300	-0.18136400
C	-5.30417400	0.39623900	-1.14490000
H	-5.20531600	1.45003800	-1.42434600
H	-5.36068900	-0.20711200	-2.05412000
C	-6.52679100	0.17489600	-0.29017400
C	-7.22555500	-1.04153800	-0.34806700
C	-6.98285300	1.17541200	0.58408800
C	-8.35590400	-1.25393200	0.44755600
H	-6.88488700	-1.82394000	-1.02274900
C	-8.11273900	0.96598600	1.37933600
H	-6.45142000	2.12302200	0.63857800
C	-8.80248100	-0.25064300	1.31427900

H	-8.88754500	-2.20020500	0.38787300
H	-8.45611500	1.75244000	2.04658300
H	-9.68218800	-0.41344600	1.93153600
H	2.29578700	0.32162900	-0.75401600
C	-0.48753800	-2.17441200	-3.64746300
C	-1.79574600	-1.75604200	-4.03818500
C	-2.45038600	-0.80829300	-3.29672400
N	-1.83350100	-0.26206200	-2.20569400
C	-0.54715600	-0.63010200	-1.79880000
C	0.12882100	-1.62193900	-2.54335900
C	-2.37636200	0.66958500	-1.23032200
C	-1.14406400	0.91829300	-0.39359600
N	-0.13820300	0.07215100	-0.73500300
C	-1.02939600	1.91767800	0.63962900
C	0.13595500	1.99210400	1.44577600
C	0.26629200	2.96913800	2.42862300
C	-0.75519100	3.90659700	2.64349900
C	-1.91235700	3.84914700	1.85536600
C	-2.05238500	2.87223400	0.87082000
H	0.02546700	-2.93495000	-4.22823900
H	-2.27884600	-2.17868600	-4.91152400
H	-3.44418100	-0.44569000	-3.53000100
H	1.12236700	-1.92443200	-2.23126600
H	-2.81572100	1.54887400	-1.71289300
H	0.93025100	1.27018600	1.29016200
H	1.16860200	3.00069300	3.03469400
H	-0.65042900	4.66770800	3.41194900
H	-2.71133100	4.57041900	2.00880700
H	-2.96059700	2.84967200	0.27727800

1e

S	0.74686500	-0.20801300	-0.81814000
C	1.76748500	-0.30481000	0.75748900
H	1.38519400	0.45312900	1.44556100
H	1.61249000	-1.29314200	1.19640500
C	3.21689900	-0.07160200	0.42676100
C	4.05074800	-1.14375900	0.07025300
C	3.75675600	1.22429500	0.45118700
C	5.39416300	-0.92724100	-0.24835100
H	3.64639000	-2.15340200	0.04870800
C	5.09992400	1.44371400	0.13266300
H	3.12336500	2.06419800	0.72782200
C	5.92252400	0.36800400	-0.21845900
H	6.02769000	-1.76892100	-0.51614600
H	5.50367400	2.45246300	0.16231900
H	6.96771700	0.53719700	-0.46391800
C	-2.79952100	-4.17930300	0.25359600
C	-1.42452500	-4.22668900	-0.11255200

C	-0.71790300	-3.06863700	-0.30098900
N	-1.35218500	-1.86293000	-0.13272900
C	-2.70308800	-1.77375900	0.21179900
C	-3.43391000	-2.96763800	0.41366900
C	-0.87664100	-0.55242400	-0.25838500
C	-1.98726400	0.25999300	0.01567100
N	-3.09131500	-0.49779100	0.29662100
C	-2.09371700	1.73283500	0.00031300
C	-3.33035400	2.32446100	-0.32168500
C	-3.47702500	3.71232300	-0.33902800
C	-2.39175200	4.53966700	-0.02920400
C	-1.16101100	3.96388400	0.30127900
C	-1.01254400	2.57478100	0.31720800
H	-3.34597400	-5.10519200	0.40403500
H	-0.91982300	-5.17712800	-0.24645800
H	0.32578700	-3.02721100	-0.58665600
H	-4.48124700	-2.89368700	0.68672200
H	-4.17341600	1.68461000	-0.56225600
H	-4.43915300	4.14806000	-0.59635800
H	-2.50514100	5.62056000	-0.04144000
H	-0.31366100	4.59564100	0.55518100
H	-0.05469700	2.14754000	0.59006100

TS c-d

C	3.31147100	-1.61143400	-1.47981200
C	2.30907300	-2.28327500	-0.74455500
C	2.47310000	-3.62623500	-0.37956600
C	3.64896400	-4.26241600	-0.77093000
C	4.64324600	-3.58281100	-1.51085300
C	4.49424600	-2.24585100	-1.87703700
H	1.70632600	-4.14434500	0.18909300
H	3.80722800	-5.30370200	-0.50441800
H	5.54502000	-4.11444000	-1.80148600
H	5.26041200	-1.72964500	-2.44704000
C	1.61361000	-0.26289100	-1.07977000
N	1.25640700	-1.40189200	-0.50448000
N	2.82693400	-0.32376100	-1.68484800
C	3.49580400	0.77236300	-2.39430000
H	3.91454800	0.36412300	-3.32041100
H	2.72184600	1.49254200	-2.67625600
C	4.58212600	1.45572100	-1.55465500
H	5.35426100	0.72368500	-1.28366600
H	4.13512700	1.81009900	-0.61632500
C	5.22342300	2.63193800	-2.30390400
H	5.64133100	2.27402000	-3.25545100
H	4.44542000	3.36405900	-2.56238000
C	6.32503300	3.32189800	-1.49030700
H	7.15197600	2.63226300	-1.27866400

H	6.73589400	4.18165600	-2.03262700
H	5.93853300	3.68550100	-0.52963700
Cl	-1.57070700	-3.42864000	1.56266000
Cu	-0.45730200	-1.76034800	0.47386300
S	-1.94613800	0.22513700	0.07992400
C	-3.67984700	-0.26798700	0.51683700
H	-3.63557200	-1.04231200	1.28606100
H	-4.15705400	0.61453900	0.95078300
C	-4.44319700	-0.76763800	-0.69135500
C	-4.60305700	0.02526800	-1.84128500
C	-5.03818000	-2.03801400	-0.66297800
C	-5.34929400	-0.43691900	-2.92766600
H	-4.13811600	1.00685400	-1.88573000
C	-5.78582800	-2.50347500	-1.75101100
H	-4.91747600	-2.66692000	0.21565700
C	-5.94308300	-1.70481000	-2.88715100
H	-5.46489000	0.19067500	-3.80779000
H	-6.23989600	-3.49025200	-1.70953300
H	-6.52016400	-2.06545500	-3.73465900
H	1.01495200	0.63803200	-1.08505200
C	-1.93228200	5.29124700	-0.80036100
C	-3.14970500	4.64196000	-0.43597100
C	-3.11093000	3.49539400	0.31108400
N	-1.89703100	2.99231700	0.70635200
C	-0.68202700	3.61074300	0.38719300
C	-0.71308200	4.78656000	-0.38899400
C	-1.60341100	1.75200700	1.36177200
C	-0.14721000	1.90965700	1.62033500
N	0.35673900	2.96892400	0.94388400
C	0.66068500	1.05017600	2.45903400
C	2.05999400	1.24875700	2.54384200
C	2.84448400	0.44646300	3.36740900
C	2.26026600	-0.57609100	4.12992200
C	0.87887700	-0.78691100	4.05365000
C	0.08617100	0.01019500	3.22702400
H	-1.96882600	6.19712900	-1.39724100
H	-4.10918500	5.04942300	-0.73374300
H	-3.99268400	2.96354700	0.64748900
H	0.22466300	5.27052300	-0.63986300
H	-2.26854400	1.51687700	2.19219400
H	2.51445200	2.04067300	1.95720300
H	3.91713300	0.61612600	3.41804400
H	2.87537500	-1.20073900	4.77195800
H	0.41525200	-1.57834400	4.63648600
H	-0.98331800	-0.17206900	3.19076700

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