Electronic Supplementary Information†

A Semiconducting Supramolecular Co(II)-metallohydrogel: An Efficient Catalyst for Single-pot Aryl-S Bond Formation at Room Temperature

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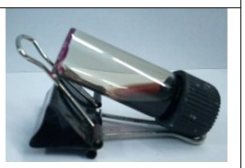
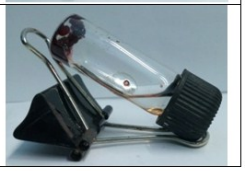
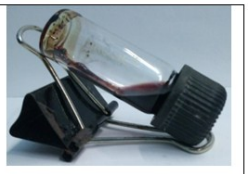
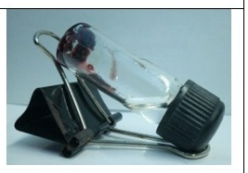
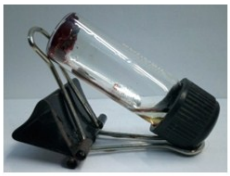
Table S1. Representative influence of the metal counter anion on the gelation ability[a]

Entry	Metal Salt	[Metal Salt][b]	[Ligand]	Vol. Water	Phase[c]	Picture
1	 $Co(OAc)_2.4H_2O$	1 mM	500 µl	500 µl	S	
2	 $Co(NO_3)_2.6H_2O$	1 mM	500 µl	500 µl	G	
3	 $CoCl_2.6H_2O$	1 mM	500 µl	500 µl	P	

[a]Gelation tests were performed as described in the Experimental Section. [b]Concentration of metal salt as per minimum gelation concentration. [c]Abbreviations: S = solution; G = stable gel; P = precipitates.

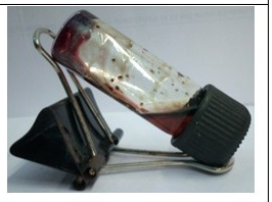
Table S2. Gelation process of CoMEA metallohydrogel[a] with $Co(NO_3)_2.6H_2O$ salt in various solvents[b]

Entry	Solvent[b]	Phase[c]	Conc.[d]	Vol.[e]	Gelation Time	Gel-Phase Colour	Picture
1.	 DMF	Lq	291	1	30s	Wine red	
2.	 MeOH	Lq	291	1	>30s	Wine red	
3.	 EtOH	Lq	291	1	1min	Wine red	
4.	 EtOAc	I	291	1	-	-	
5.	 DMSO	Lq	291	1	1min	Wine red	
6.	 CH_3CN	I	291	1	-	-	
7.	 DCM	I	291	1	-	-	
8.	 THF	Lq	291	1	-	Wine red	
9.	 *n*-Hexane	I	291	1	-	-	

10.	 Acetone	Lq	291	1	-	Wine red	
11.	 Toluene	I	291	1	-	-	
12.	 $CHCl_3$	I	291	1	-	-	
13.	 Benzene	I	291	1	-	-	
14.	 PET	I	291	1	-	-	

[a]Gelation tests were performed as discussed in the Experimental Section: $Co(NO_3)_2.6H_2O$ (0.291g, 1mM) and 500µl monoethanolamine ligand at room temperature instantaneously. [b]Solvent abbreviations: DMF = *N,N*-dimethylformamide; MeOH = Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate, DMSO = Dimethyl sulfoxide, CH_3CN = Acetonitrile, DCM = Dichloromethane, THF = Tetrahydrofuran, $CHCl_3$ = Chloroform, PET = Petroleum ether. [c]Salt Solution Phases: Lq = liquid; I = insoluble. [d]Minimum Gelation Concentration (MGC) of CoMEA metallohydrogel is 291 mg mL^{-1}. [e]Total volume of the solvents.

Table S3. Gelation process of CoMEA metallohydrogel[a] with $Co(OAc)_2.4H_2O$ salt in various solvents[b]

Entry	Solvent[b]	Phase[c]	Conc.[d]	Vol.[e]	Gelation Time	Gel-Phase Colour	Picture
1.	 H_2O	Lq	249	1	30s	Wine red	
1.	 DMF	Lq	249	1	30s	Wine red	
2.	 MeOH	Lq	249	1	>30s	Wine red	
3.	 EtOH	Lq	249	1	1min	Wine red	
4.	 EtOAc	I	249	1	-	-	
5.	 DMSO	Lq	249	1	1min	Wine red	
6.	 CH_3CN	I	249	1	-	-	
7.	 DCM	I	249	1	-	-	

8.	 THF	Lq	249	1	-	Wine red	
9.	 *n*-Hexane	I	249	1	-	-	
10.	 Acetone	Lq	249	1	-	Wine red	
11.	 Toluene	I	249	1	-	-	
12.	 $CHCl_3$	I	249	1	-	-	
13.	 Benzene	I	249	1	-	-	
14.	 PET	I	249	1	-	-	

[a]Gelation tests were performed as discussed in the Experimental Section: $Co(OAc)_2.4H_2O$ (0.249g, 1mM) and 500µl monoethanolamine ligand at room temperature instantaneously. [b]Solvent abbreviations: DMF = *N*,*N*-dimethylformamide; MeOH = Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate, DMSO = Dimethyl sulfoxide, CH_3CN = Acetonitrile, DCM = Dichloromethane, THF = Tetrahydrofuran, $CHCl_3$ = Chloroform, PET = Petroleum ether. [c]Salt Solution Phases: Lq = liquid; I = insoluble. [d]Minimum Gelation Concentration (MGC) of CoMEA metallohydrogel is 291 mg mL^{-1} (i.e. 1 mM of $Co(NO_3)_2.6H_2O$ salt). [e]Total volume of the solvents.

Table S4. Gelation process of CoMEA metallohydrogel[a] with $CoCl_2.6H_2O$ salt in various solvents[b]

Entry	Solvent[b]	Phase[c]	Conc.[d]	Vol.[e]	Gelation Time	Gel-Phase Colour	Picture
1.	 H_2O	Lq	238	1	30s	Wine red	
1.	 DMF	Lq	238	1	30s	Wine red	
2.	 MeOH	Lq	238	1	>30s	Wine red	
3.	 EtOH	Lq	238	1	1min	Wine red	
4.	 EtOAc	I	238	1	-	-	
5.	 DMSO	Lq	238	1	1min	Wine red	
6.	 CH_3CN	I	238	1	-	-	
7.	 DCM	I	238	1	-	-	

8.	 THF	Lq	238	1	-	Wine red	
9.	 *n*-Hexane	I	238	1	-	-	
10.	 Acetone	Lq	238	1	-	Wine red	
11.	 Toluene	I	291	1	-	-	
12.	 $CHCl_3$	I	238	1	-	-	
13.	 Benzene	I	238	1	-	-	
14.	 PET	I	238	1	-	-	

[a]Gelation tests were performed as discussed in the Experimental Section: $CoCl_2.6H_2O$ (0.238g, 1mM) and 500µl monoethanolamine ligand at room temperature instantaneously. [b]Solvent abbreviations: DMF = *N,N*-dimethylformamide; MeOH = Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate, DMSO = Dimethyl sulfoxide, CH_3CN = Acetonitrile, DCM = Dichloromethane, THF = Tetrahydrofuran, $CHCl_3$ = Chloroform, PET = Petroleum ether. [c]Salt Solution Phases: Lq = liquid; I = insoluble. [d]Minimum Gelation Concentration (MGC) of CoMEA metallohydrogel is 291 mg mL^{-1} (i.e. 1 mM of $Co(NO_3)_2.6H_2O$ salt). [e]Total volume of the solvents.

Table S5. Investigation of minimum critical gelation concentration (MGC) of CoMEA metallohydrogel

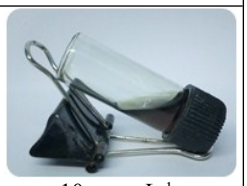
Entry	Weight of $Co(NO_3)_2.6H_2O$	Vol. of Monoethanolamine	Vol. of Water	Picture
1	10 mg	500 µl	500 µl	 10 mg mL^{-1}
2	20 mg	500 µl	500 µl	 20 mg mL^{-1}
3	50 mg	500 µl	500 µl	 50 mg mL^{-1}
4	100 mg	500 µl	500 µl	 100 mg mL^{-1}
5	150 mg	500 µl	500 µl	 150 mg mL^{-1}
6	200 mg	500 µl	500 µl	 200 mg mL^{-1}
7	250 mg	500 µl	500 µl	 250 mg mL^{-1}
8	291 mg	500 µl	500 µl	 291 mg mL^{-1}

Table S6. Investigation of minimum critical gelation concentration (MGC) of CoMEA metallohydrogel with varying monoethanolamine.

Entry	Weight of $Co(NO_3)_2.6H_2O$	Vol. of Monoethanolamine	Vol. of Water	Picture
1	291 mg	10 µl	500 µl	 10 mg mL^{-1}
2	291 mg	50 µl	500 µl	 20 mg mL^{-1}
3	291 mg	100 µl	500 µl	 50 mg mL^{-1}
4	291 mg	200 µl	500 µl	 100 mg mL^{-1}
5	291 mg	250 µl	500 µl	 150 mg mL^{-1}
6	291 mg	300 µl	500 µl	 200 mg mL^{-1}
7	291 mg	400 µl	500 µl	 250 mg mL^{-1}
8	291 mg	500 µl	500 µl	 291 mg mL^{-1}

pH dependent CoMEA metallohydrogel formation strategy

pH dependent CoMEA metallohydrogel formation strategy with water solution of $Co(NO_3)_2.6H_2O$ salt and monoethanolamine clearly shows that the CoMEA metallohydrogel is formed at pH = 9.704. The variation of pH is maintained by monoethanolamine and it also supports minimum critical gelation concentration (MGC) where it is clearly show that the CoMEA metallohydrogel only formed with 500 µl of monoethanolamine and 0.291 gm of $Co(NO_3)_2.6H_2O$ salt.

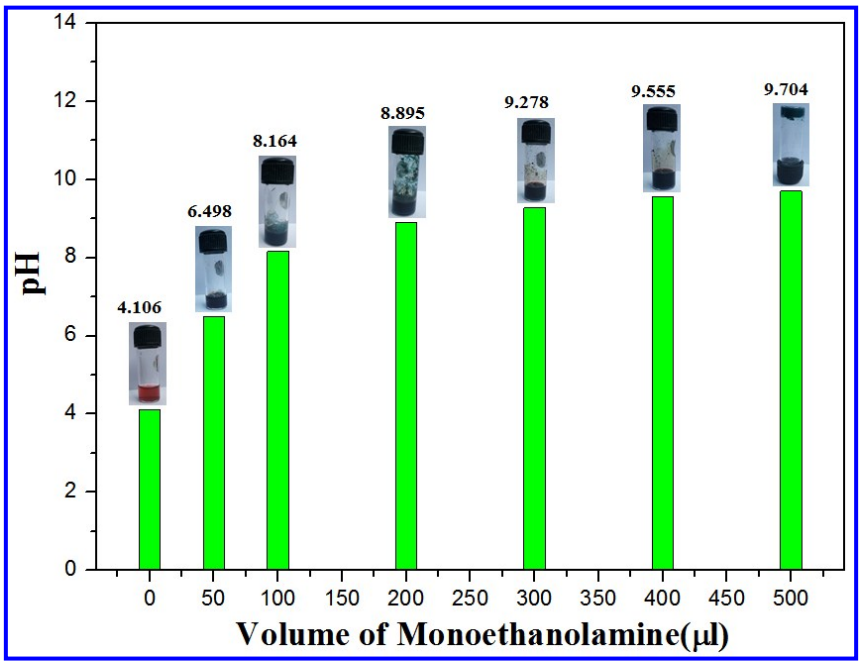


Fig. S1. pH dependent CoMEA metallohydrogel formation strategy with water solution of $Co(NO_3)_2.6H_2O$ salt and monoethanolamine.

pH dependent CoMEA metallohydrogel formation strategy with $Co(OAc)_2.4H_2O$ and $CoCl_2.6H_2O$ salt

pH dependent CoMEA Metallohydrogel formation strategy with water solution of $Co(OAc)_2.4H_2O$ and $CoCl_2.6H_2O$ salt and monoethanolamine clearly shows that the CoMEA metallohydrogel is not formed by varying pH, maintained by monoethanolamine (Fig. S2, S3). This results also supports that CoMEA metallohydrogel is only formed with 500 µl of monoethanolamine and 0.291 gm of $Co(NO_3)_2.6H_2O$ salt.

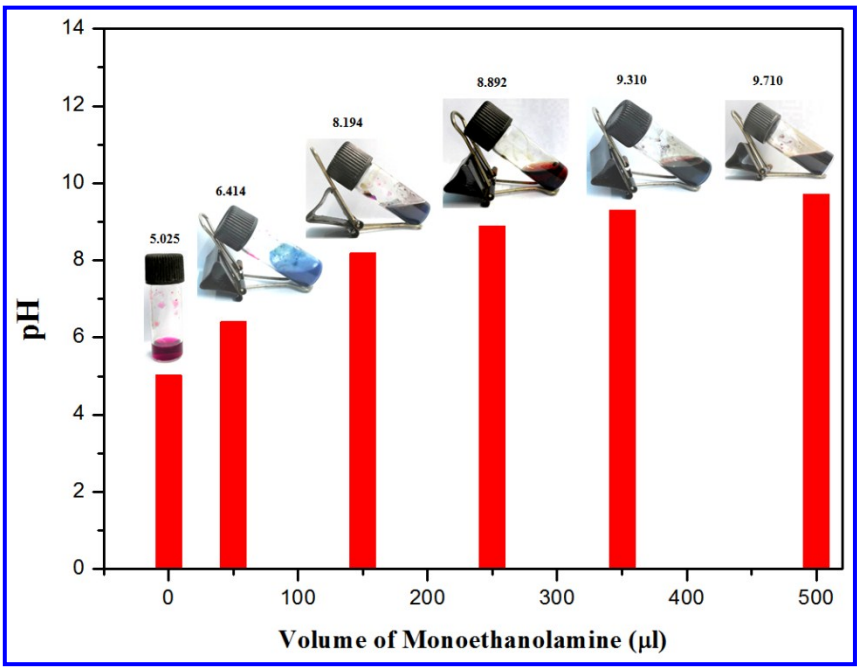


Fig. S2. pH dependent CoMEA metallohydrogel formation strategy with water solution of $Co(OAc)_2.4H_2O$ salt and monoethanolamine.

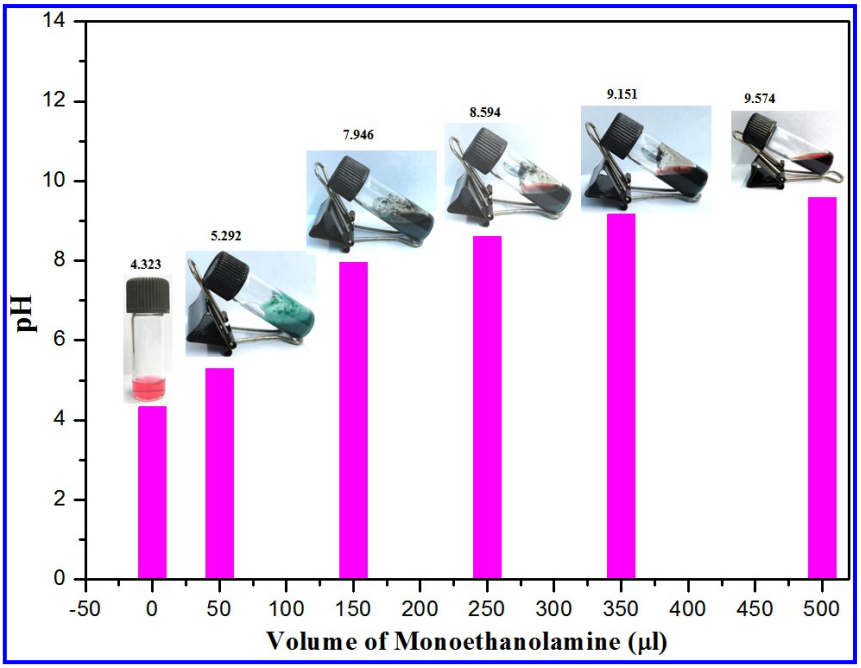


Fig. S3. pH dependent CoMEA metallohydrogel formation strategy with water solution of $CoCl_2.6H_2O$ salt and monoethanolamine.

Thermogravimetric analysis of CoMEA metallohydrogel:

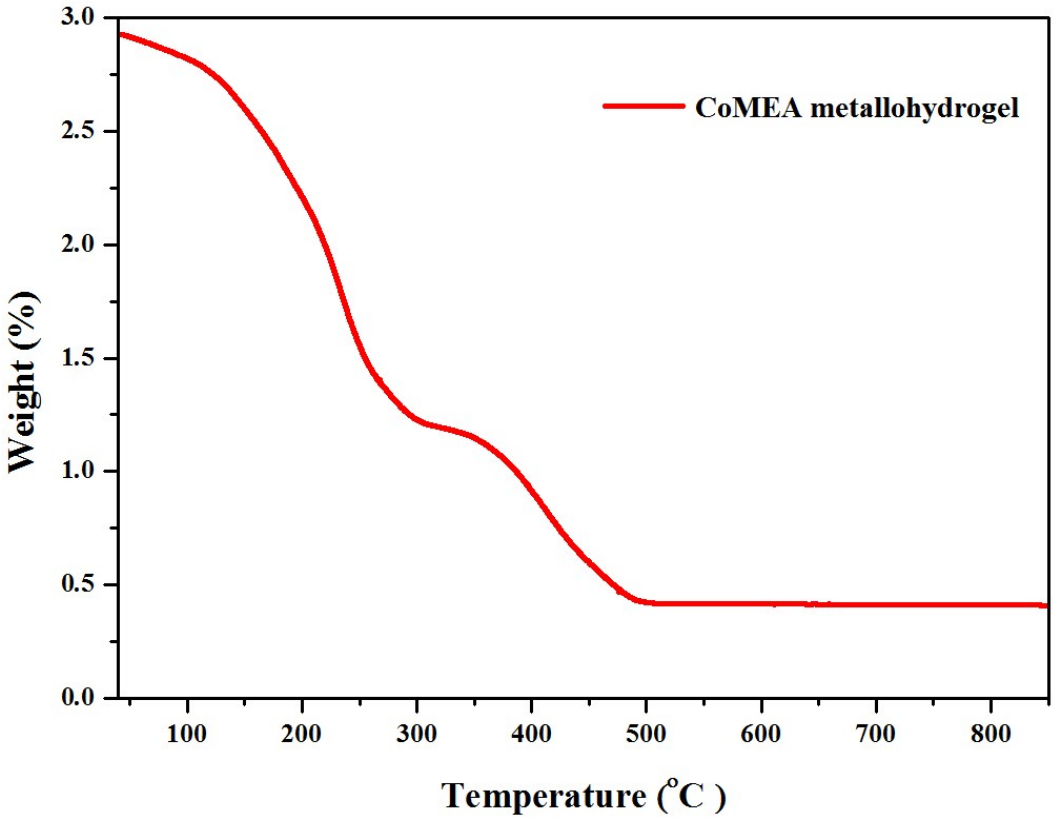


Fig. S4. Thermogravimetric analysis curve of the xerogel from of CoMEA metallohydrogel.

FESEM Microstructural study and EDX spectral analysis.

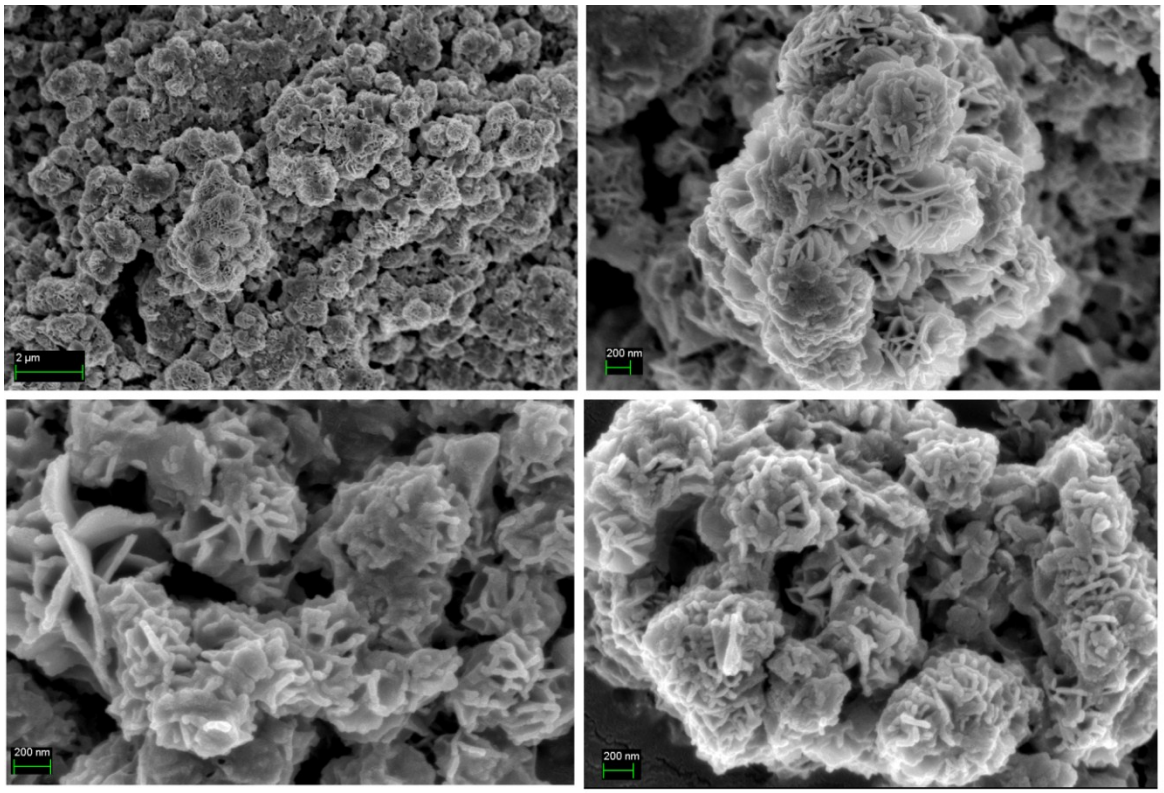


Fig. S5. The FESEM microstructural feature of CoMEA metallohydrogel.

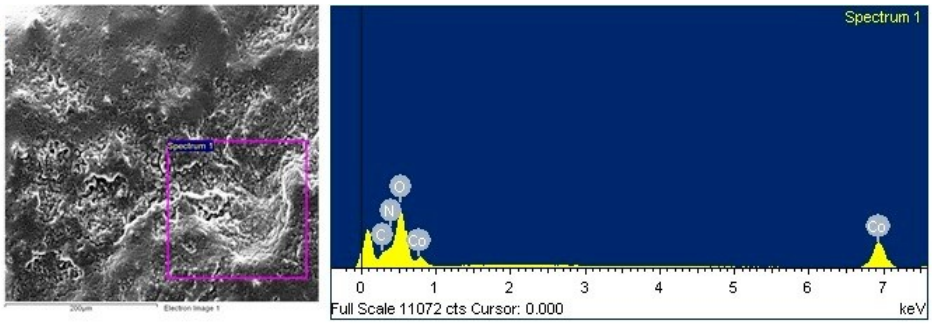


Fig. S6. EDX pattern of CoMEA metallohydrogel showing the presence of C, N, O, and Co elements.

Infrared Spectral Study.

Fig. S7 provides the FT-IR spectra of CoMEA metallohydrogel. The FT-IR spectra of CoMEA metallohydrogel shows broad absorption band at 3406 cm^{-1} for OH stretching vibration, due to strong hydrogen bonding.[1] Another two sharp bands at 3227 and 3141 cm^{-1} are for NH stretching vibration. CH stretching absorption band between 2800-3000 cm^{-1} indicates the presence of ethanolate functional group.[2]

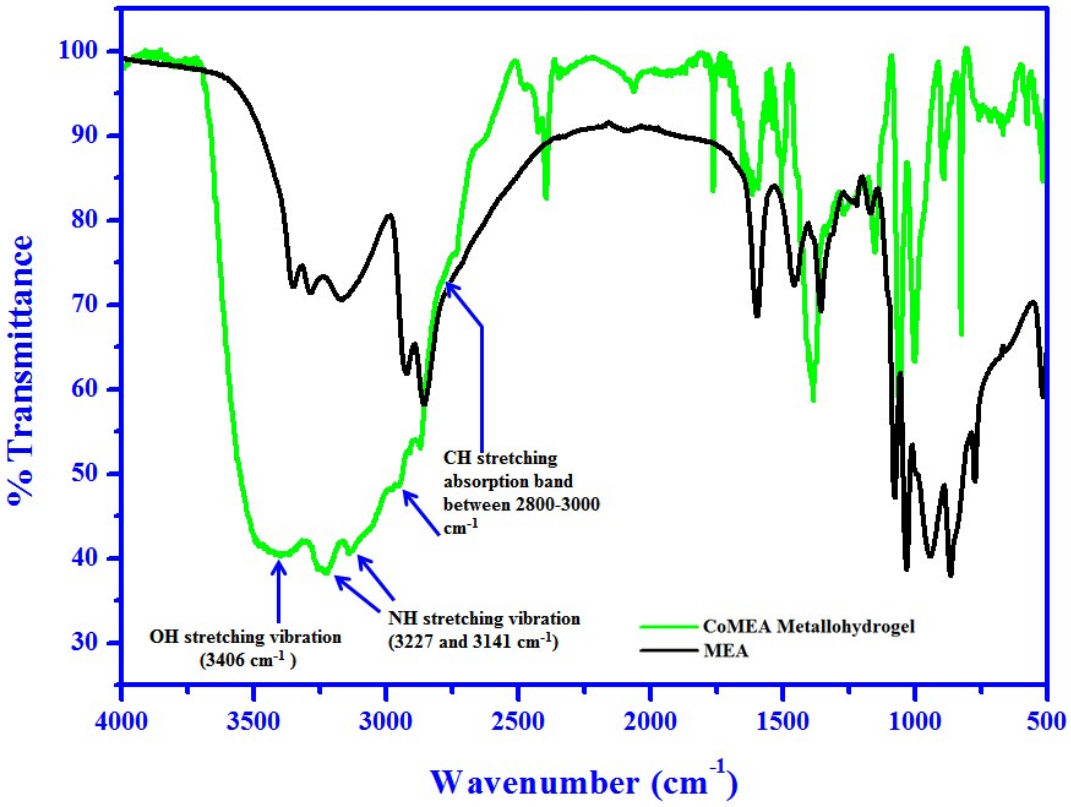


Fig. S7. FT-IR spectra of CoMEA metallohydrogel.

PXRD of CoMEA metallohydrogel.

Powder X-Ray Diffraction pattern of CoMEA metallohydrogel exhibits the amorphous nature of the CoMEA (Fig. S6).

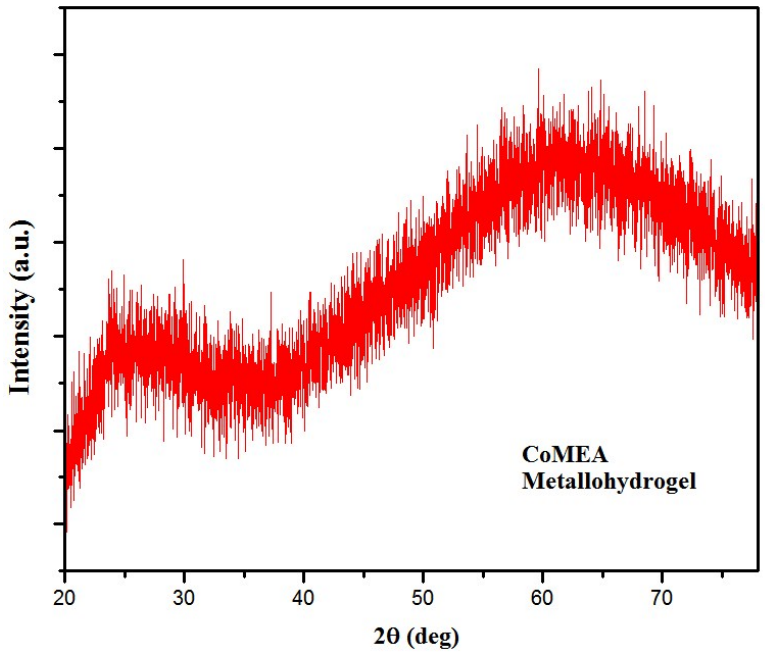
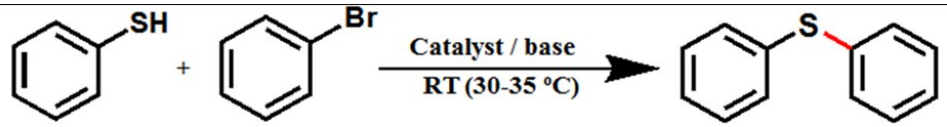


Fig. S8. PXRD pattern of xerogel form of CoMEA metallohydrogel.

Table S7. Optimization Studies for the Co-Catalyzed Coupling of Aryl Iodides and Thiophenols[a]

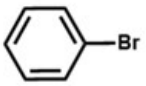
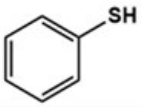
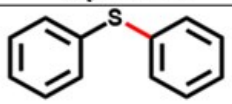
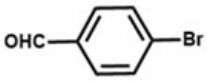
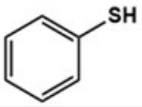
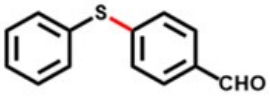
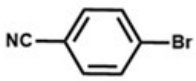
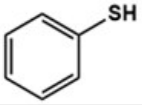
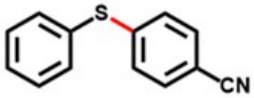
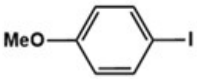
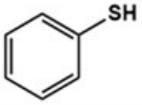
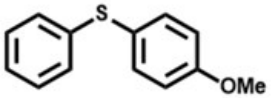
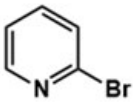
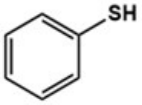
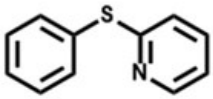
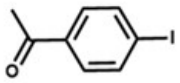
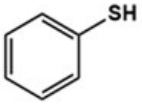
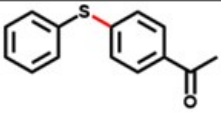
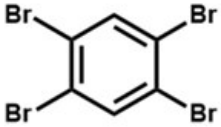
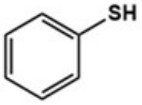
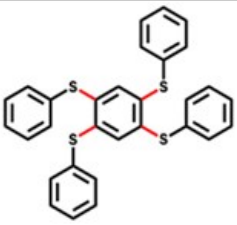
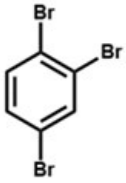
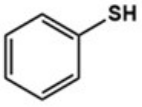
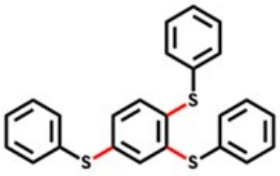
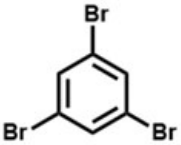
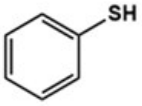
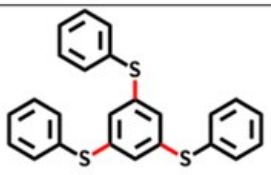
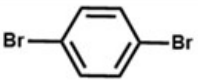
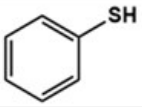
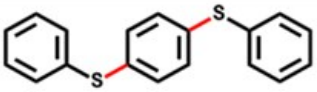
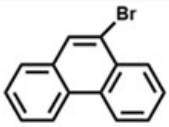
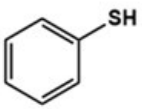
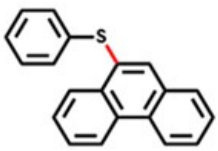


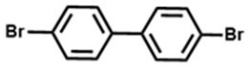
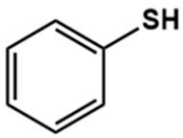
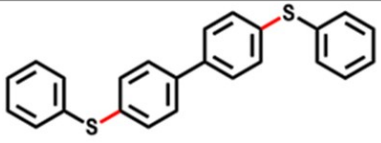
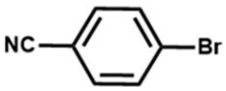
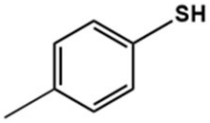
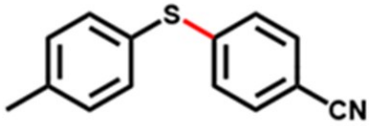
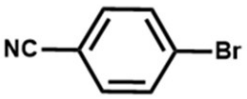
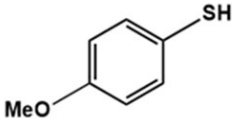
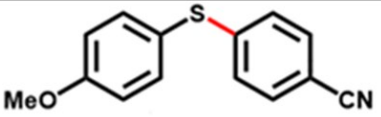
entry	catalyst (mol %)	base	solvent	time (h)	yields (%)
1	CoI_2 (10)	pyridine	DMF	24	trace
2	CoI_2 (10)	pyridine	CH_3CN	24	trace
3	$CoCl_2$ (10)	Et_3N	ethyl acetate	24	trace
4	CoI_2 (10)	pyridine	DMF	24	trace
5	CoI_2 (10)	K_2CO_3	ethyl acetate	24	trace
6	$Co(NO_3)_2$ (10)	MEA	ethyl acetate	48	50
7	$CoCl_2$ (10)	MEA	ethyl acetate	48	52
8	$Co(OAc)_2$ (10)	MEA	ethyl acetate	48	51
9	CoMEA (5)	pyridine	ethyl acetate	12	61
10	CoMEA (5)	K_2CO_3	ethyl acetate	12	45
11	CoMEA (5)	Et_3N	ethyl acetate	12	39
12	**CoMEA (5)**	**Zn**	**ethyl acetate**	**6**	**89**
13	CoMEA (5)	Zn	toluene	24	trace
14	CoMEA (5)	Zn	chloroform	12	44
15	CoMEA (5)	Zn	acetone	12	40
16	CoMEA (5)	Zn	DMF	24	trace
17	CoMEA (5)	Zn	CH_3CN	12	42
18	-	Zn	ethyl acetate	48	nr[b]

[a]Reaction conditions: 0.50 mmol of bromobenzene, 0.50 mmol of thiophenol, 1.5 equiv of Zn, or 0.50 mmol of base in 2 mL of ethylacetate at room temperature for 6 h. Yields were determined by the ^{1}H NMR. [b]No reaction.

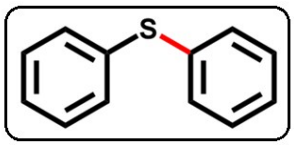
General experimental procedure for the synthesis of diphenylsulfide (entry 1, table 2): The mixture of thiol (0.50 mmol), bromobenzene (0.50 mmol), zinc (0.750 mmol), CoMEA metallohydrogel (10 mol %) and ethyl acetate (2 mL) were taken in a reaction vessel (tube) equipped with a magnetic stir bar, and the mixture was allowed to stir for 6 h at room temperature (~30-35 °C). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with chloroform (25 mL) and then CoMEA metallohydrogel washed with deionized water due to its compatibility with the aqueous solvent and separated from the reaction mixture by simple filtration process followed by drying to reuse. The organic phase was dried over anhydrous Na_2SO_4 and the concentrated pure coupling product of diphenylsulfane (Table 2, entry 1) was obtained with 89% yield without any column chromatographic purification protocol.

Table S8. Optimization Studies for the CoMEA metallohydrogel Catalyzed Coupling of Aryl Iodides and Thiophenols[a]

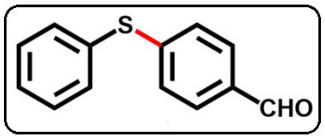
entry	aryl halide	Thiophenol	aryl sulfide	yield (%)
1				89
2				84
3				83
4				87
5				85
6				82
7				79
8				80
9				78
10				82
11				90

12				**84**
13				**82**
14				**85**
[a]Reaction conditions: 0.50 mmol of aryl halide, 0.5 mmol of thiophenol, 1.5 equiv of Zn, and in 2 mL of ethyl acetate at room temperature for 6h. [b]Isolated yield.				

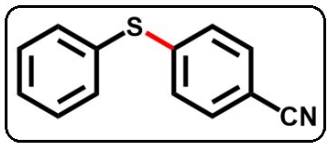
Characterization data of the isolated compounds



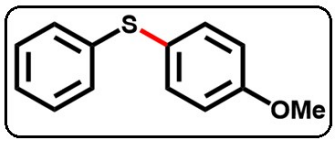
Diphenylsulfane (entry 1, Table 2): colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.56 (d, 4H, J = 7.6Hz), 7.32-7.36 (t, 4H, J = 14.8Hz), 7.25-7.28 (dd, 2H, J = 14.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.2, 127.6, 129.1, 137.1.



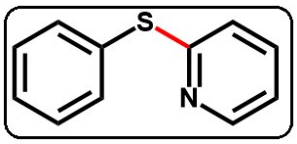
4-(phenylthio)benzaldehyde (entry 2, Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.873 (s, 1H), 7.633-7.654 (d, 2H, J = 8.4Hz), 7.565-7.585 (d, 2H, J = 8Hz), 7.407-7.426 (d, 2H, J = 7.6Hz), 7.19-7.22 (t, 2H, J = 12Hz), 7.114-7.149 (dd, 1H, J = 14Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.11, 127.34, 129.03, 130.90, 132.33, 134.96, 136.50, 136.85, 191.04.



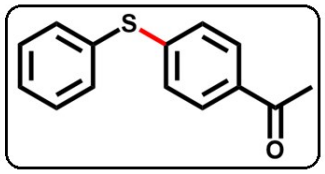
4-(phenylthio)benzonitrile (entry 3, Table 2): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.53 (m, 4H, J = 13.6Hz), 7.48-7.49 (dd, 1H, J = 3.2Hz), 7.46-7.15 (d, 1H, J = 2Hz), 7.41-7.44 (m, 2H, J = 14Hz), 7.14-7.17 (dd, 2H, J = 12.4Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 108.8, 118.9, 127.4, 129.5, 130.0, 130.9, 132.5, 134.6, 145.8.



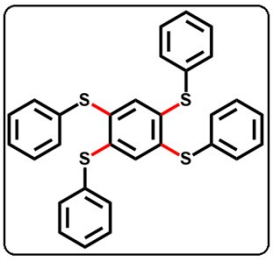
(4-methoxyphenyl)(phenyl)sulfane (entry 4, Table 2): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.34 (dd, 2H, J = 8.8Hz), 7.13-7.17 (m, 2H, J = 15.2Hz), 7.03-7.09 (m, 3H, J = 24Hz), 6.79-6.83 (dd, 2H, J = 14.8 Hz), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 115.1, 122.9, 124.4, 125.8, 128.3, 129.0, 135.5, 138.7, 159.9.



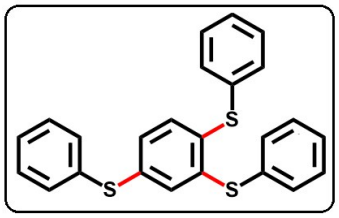
2-(phenylthio)pyridine (entry 5, Table 2): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42-8.43 (m, 1H, J = 5.2 Hz), 7.57-7.61 (m, 2H, J = 13.6 Hz), 7.40-7.47 (m, 4H, J = 26.8 Hz), 6.97-7.01 (m, 1H, J = 13.2 Hz), 6.84-6.89 (d, 1H, J = 17.2 Hz); 13C NMR (100 MHz, $CDCl_3$): δ 120.0, 121.4, 129.2, 129.7, 131.1, 135.1, 136.8, 149.7, 161.7.



1-(4-(phenylthio)phenyl)ethanone (entry 6, Table 2): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.654-7.676 (dd, 2H, J = 8.8Hz), 7.434-7.456 (dd, 2H, J = 8.8Hz), 7.350-7.373 (m, 2H, J = 9.2Hz), 7.136-7.208 (m, 2H, J = 28.8Hz), 7.061-7.096 (m, 1H, J = 14Hz), 2.432 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.45, 127.10, 127.36, 129.01, 129.76, 131.76, 135.68, 136.86, 196.84.

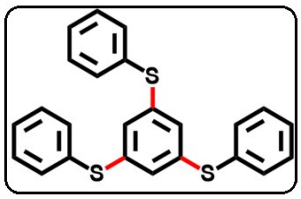


1,2,4,5-tetrakis(phenylthio)benzene (entry 7, Table 2): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.390-7.411 (d, 10H, J = 8.4Hz), 7.173-7.210 (t, 8H, J = 14.8Hz), 7.114-7.132 (dd, 4H, J = 7.2Hz),^{13}C NMR (100 MHz, $CDCl_3$): δ 124.40, 127.25, 127.59, 129.16, 136.69, 137.10, 137.24.

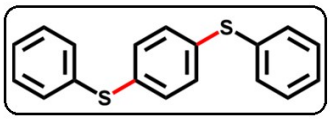


benzene-1,2,4-triyltris(phenylsulfane) (entry 8, Table 2): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.748-7.754 (d, 1H, J = 2.4 Hz), 7.472-7.502 (dd, 6H, J = 12 Hz), 7.435-7.457 (d, 1H, J = 8.8 Hz), 7.300-7.305 (d, 1H, J = 2 Hz), 7.254-7.287 (m, 6H, J = 13.2 Hz),

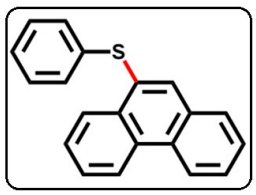
7.190-7.234 (m, 3H, *J* = 17.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.46, 123.81, 125.89, 127.25, 127.59, 129.17, 131.78, 134.71, 136.12, 137.11.



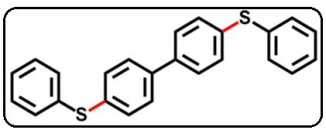
1,3,5-tris(phenylthio)benzene (entry 9, Table 2): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.456 (s, 3H), 7.370-7.391 (dd, 6H, *J* = 8.4Hz), 7.141-7.179 (t, 6H, *J* =15.2Hz), 7.065-7.102 (dd, 3H, *J* = 14.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.45, 127.20, 127.57, 129.12, 129.51, 133.04, 136.68, 137.09.



1,4-bis(phenylthio)benzene (entry 10, Table 2): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.428-7.436 (dd, 2H, *J* = 3.2 Hz), 7.413-7.414 (d, 3H, *J* = 0.4 Hz), 7.214-7.242 (m, 4H, *J* = 11.2 Hz), 7.195-7.199 (d, 2H, *J* = 1.6 Hz), 7.155-7.157 (m, 3H, *J* = 0.8 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.11, 127.20, 127.54, 129.13, 133.18, 136.64, 137.07.

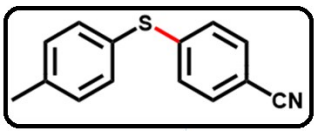


Phenanthren-9-yl(phenyl)sulfane (entry 11, Table 2): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.75 (m, 2H, *J* = 23.6 Hz), 8.498-8.522 (m, 1H, *J* = 9.6 Hz), 8.20 (s, 1H), 7.86-7.88 (d, 1H, *J* = 8.4 Hz), 7.79-7.81 (m, 2H, *J* = 9.2 Hz), 7.66-7.76 (m, 4H, *J* = 40.4 Hz), 7.42-7.46 (dd, 2H, *J* = 15.2 Hz), 7.34-7.38 (m, 1H, *J* = 14.4 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.7, 122.7, 122.8, 127.0, 127.2, 127.4, 127.5, 127.5, 127.8, 128.0, 128.2, 129.1, 129.7, 130.3, 130.5, 131.3, 132.2, 137.1.

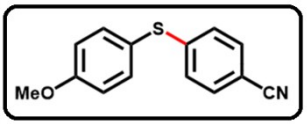


4,4'-bis(phenylthio)-biphenyl (entry 12, Table 2): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.381-7.442 (dd, 4H, *J* =24.4 Hz), 7.260-7.281 (d, 2H, *J* =8.4 Hz), 7.158-7.196 (t, 2H, *J* =15.2 Hz), 7.082-7.118 (dd, 1H, *J* = 14.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.05,

127.23, 127.57, 128.57, 129.15, 132.10, 137.10, 138.92.



4-(p-tolylthio)benzonitrile (entry 13, Table 2): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.48 (m, 4H, J =23.6 Hz), 7.25-7.28 (d, 2H, J =9.2 Hz), 7.12-7.14 (d, 2H, J =8.4 Hz), 2.427 (s, 3H,); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 108.4, 119.0, 126.8, 130.8, 132.4, 135.0, 140.1, 146.7.



4-(4-methoxyphenylthio)benzonitrile (entry 14, Table 2): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.48 (t, 1H, J =5.2 Hz), 7.44-7.46 (m, 2H, J =5.2 Hz), 7.42-7.43 (t, 1H, J =4 Hz), 7.05-7.07 (dd, 2H, J =8.4 Hz), 6.95-6.99 (dd, 2H, J =15.2 Hz), 3.856 (s, 3H,); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 108.1, 115.7, 119.0, 120.5, 126.1, 132.3, 137.2, 147.5, 161.0.

Fig. S9 ^{1}H NMR spectra of (entry 1, Table 2)

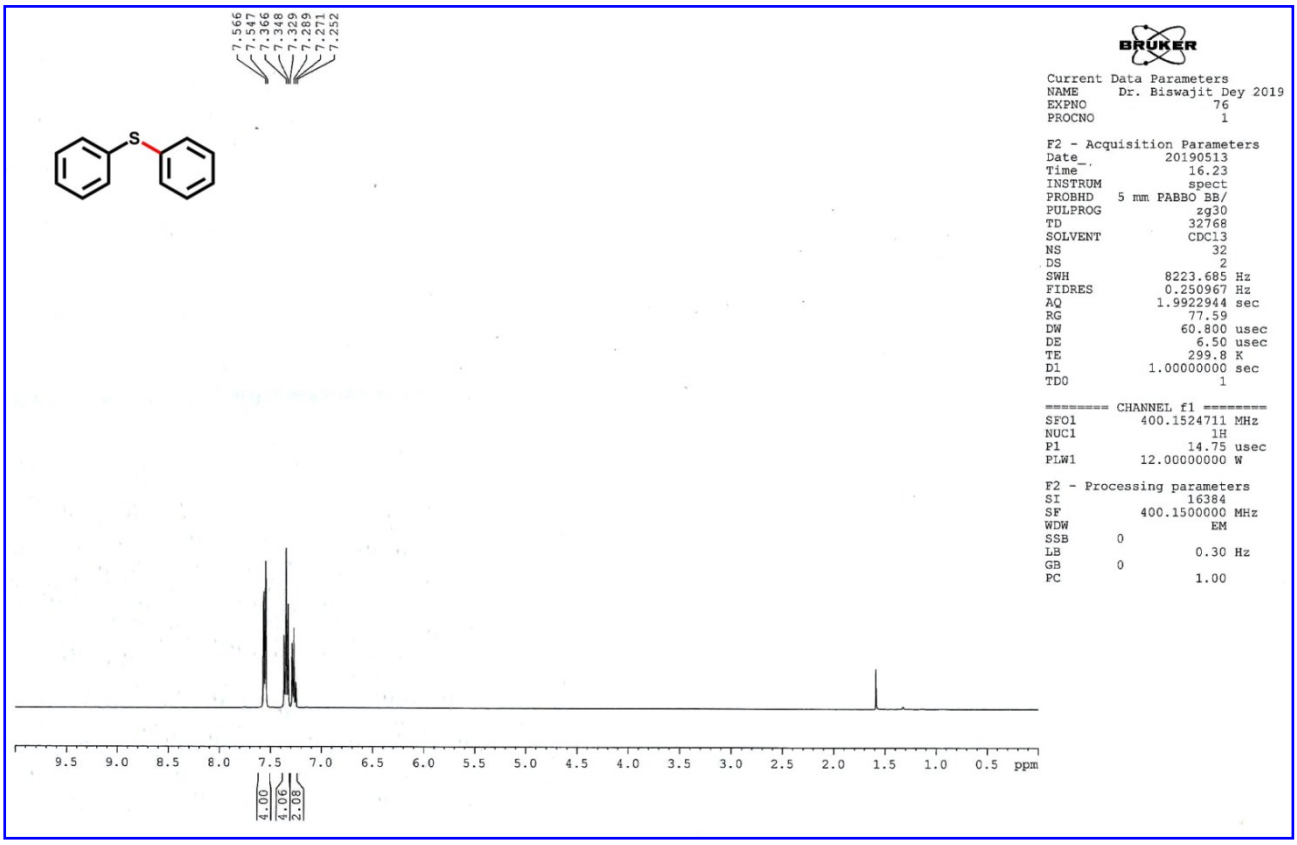


Fig. S10 ^{13}C NMR spectra of (entry 1, Table 2)

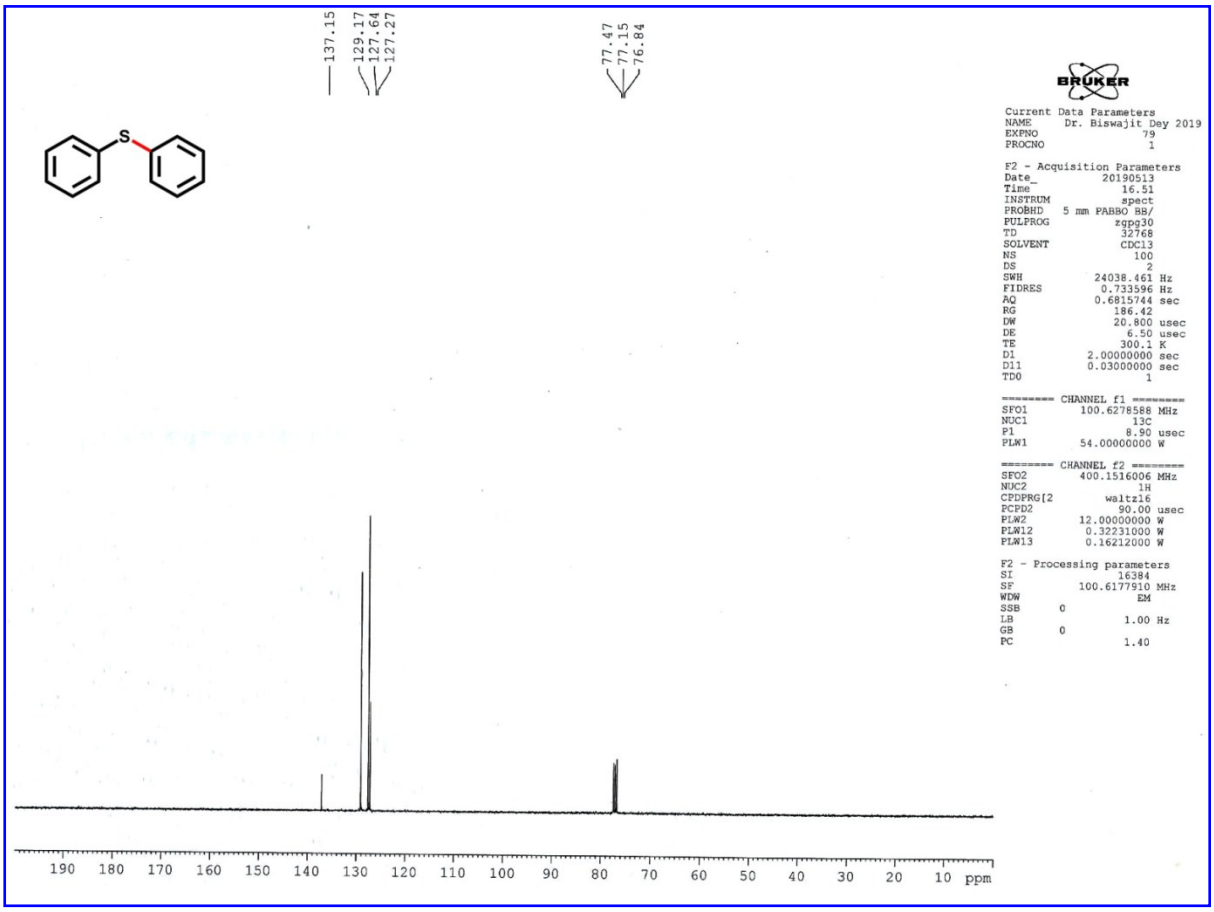


Fig. S11 ^{1}H NMR spectra of (entry 2, Table 2)

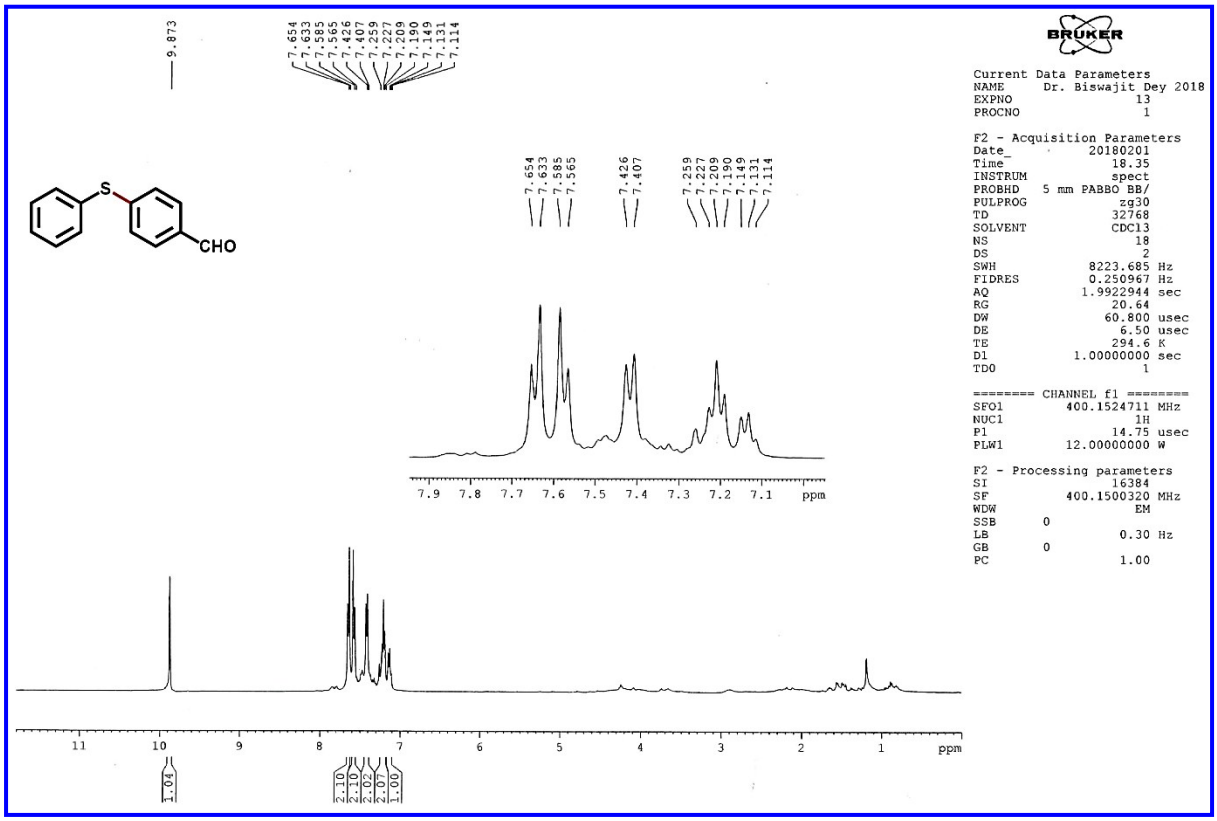


Fig. S12 ^{13}C NMR spectra of (entry 2, Table 2)

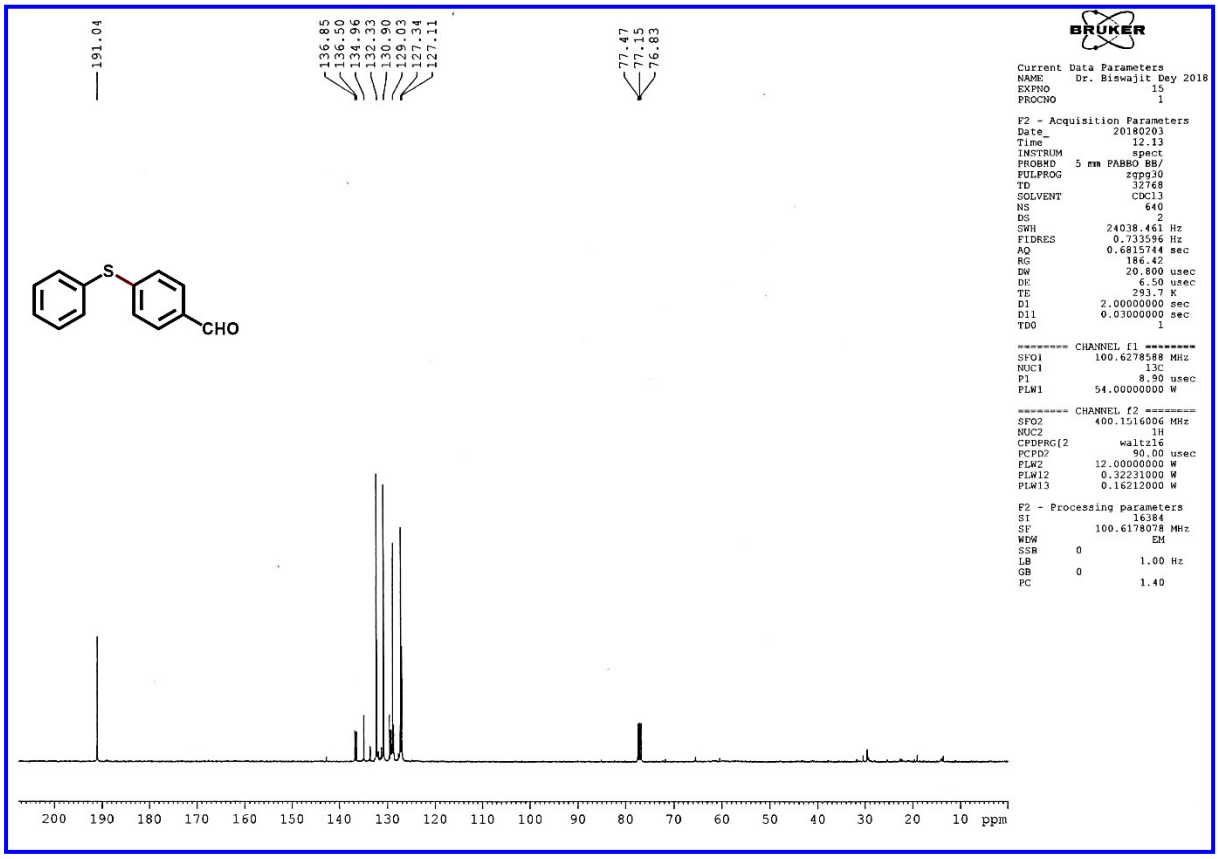


Fig. S13[1]H NMR spectra of (entry 4, Table 2)

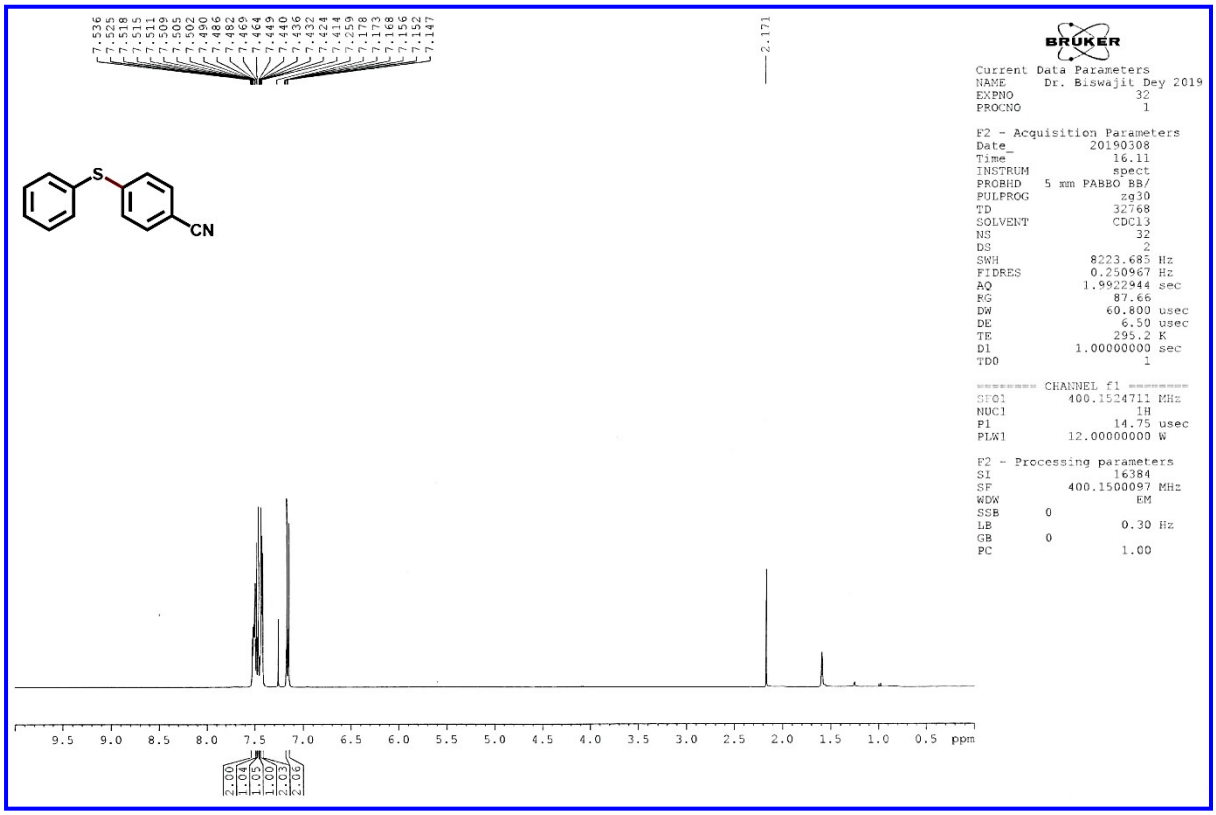


Fig. S14 ^{13}C NMR spectra of (entry 3, Table 2)

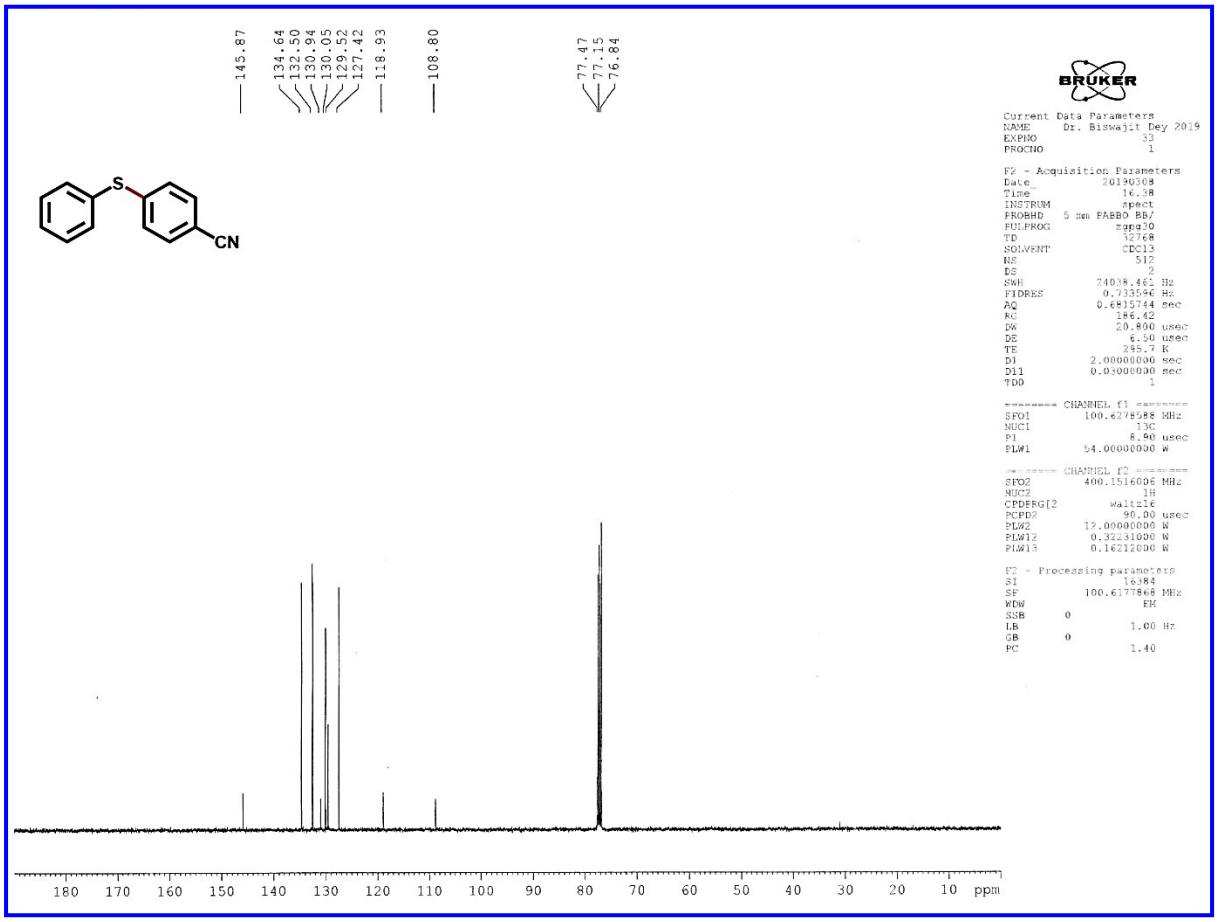


Fig. S15 ^{1}H NMR spectra of (entry 3, Table 2)

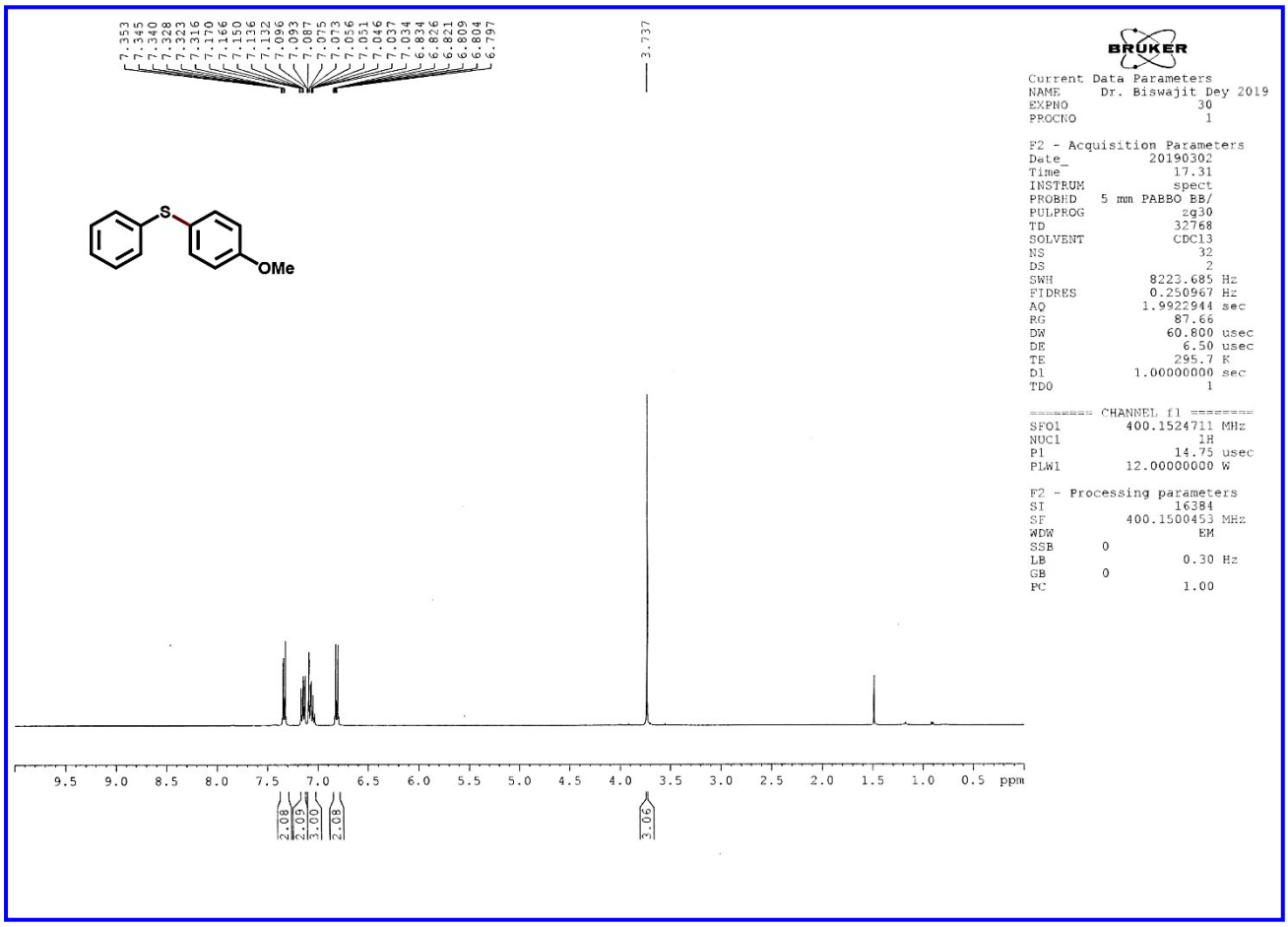


Fig. S16 ^{13}C NMR spectra of (entry 3, Table 2)

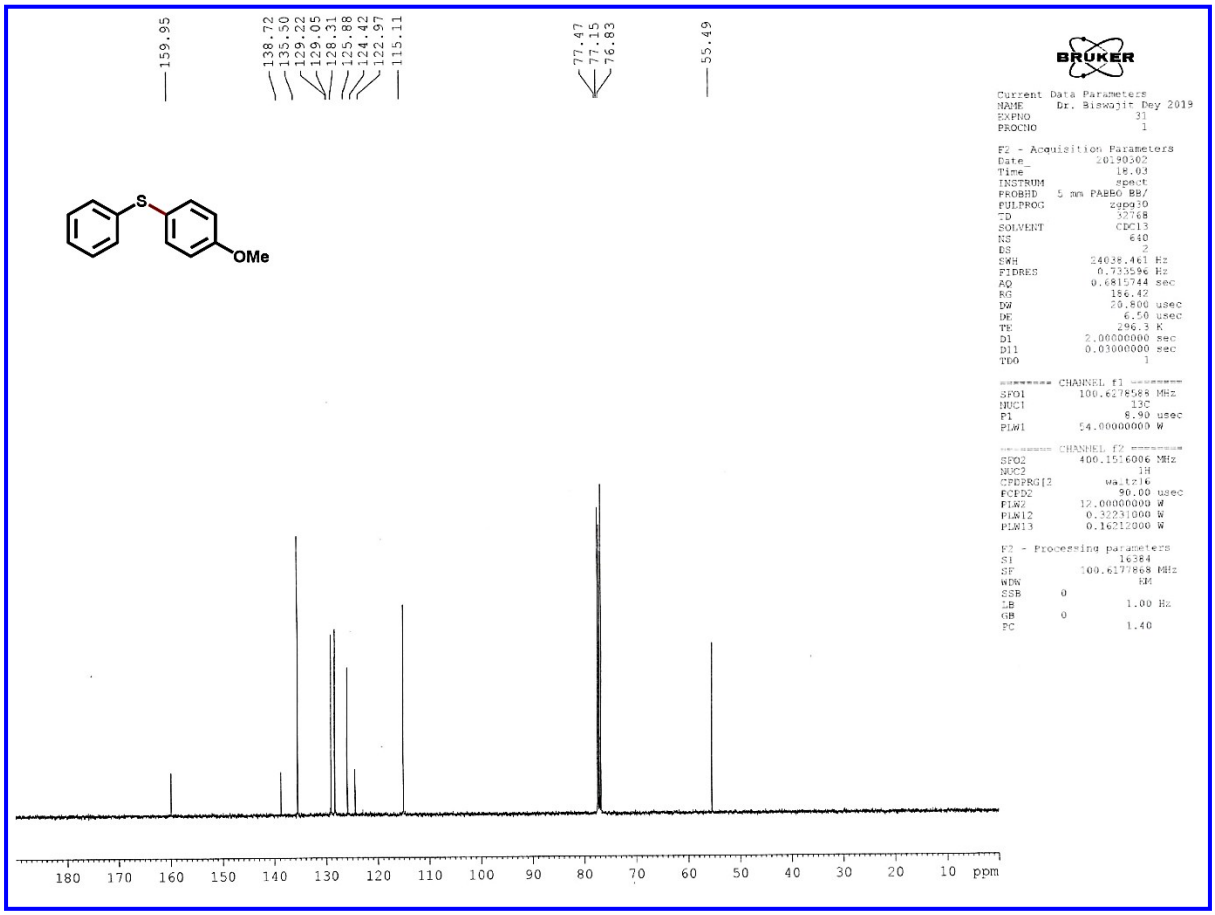


Fig. S17 ^{1}H NMR spectra of (entry 5, Table 2)

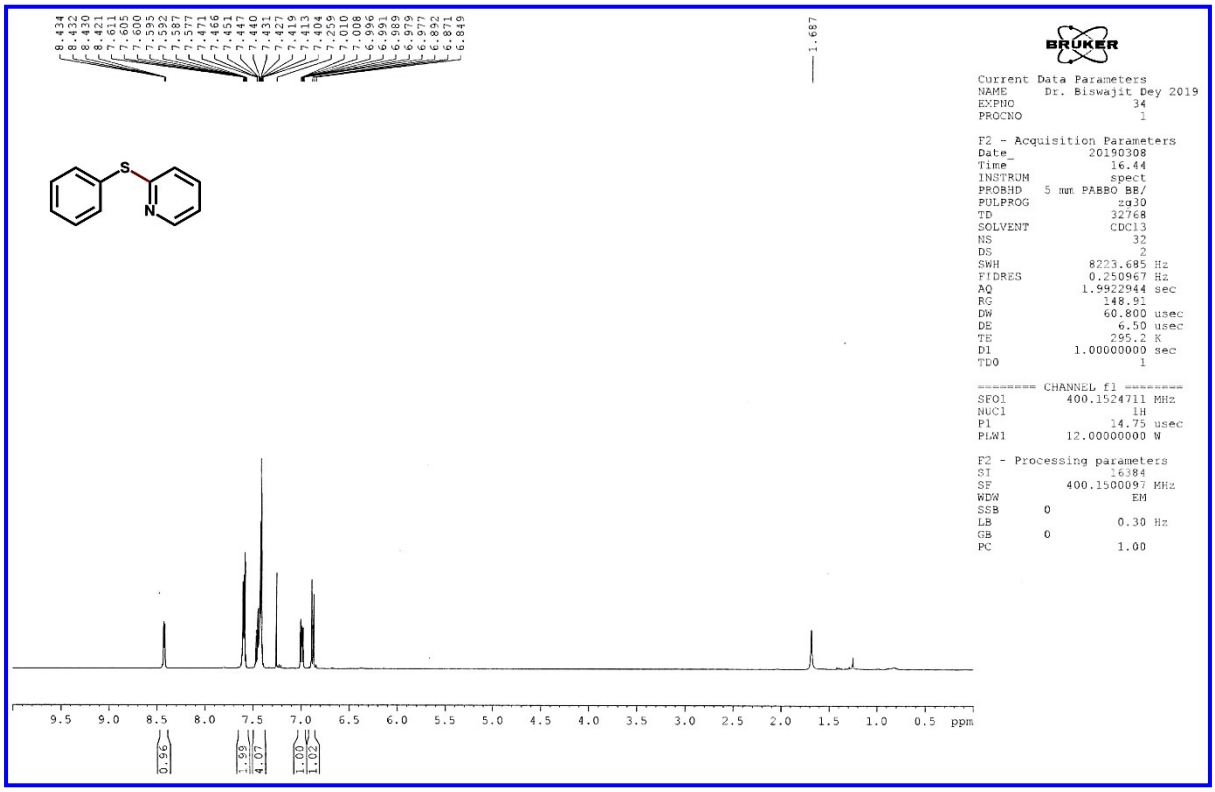


Fig. S18 ^{13}C NMR spectra of (entry 5, Table 2)

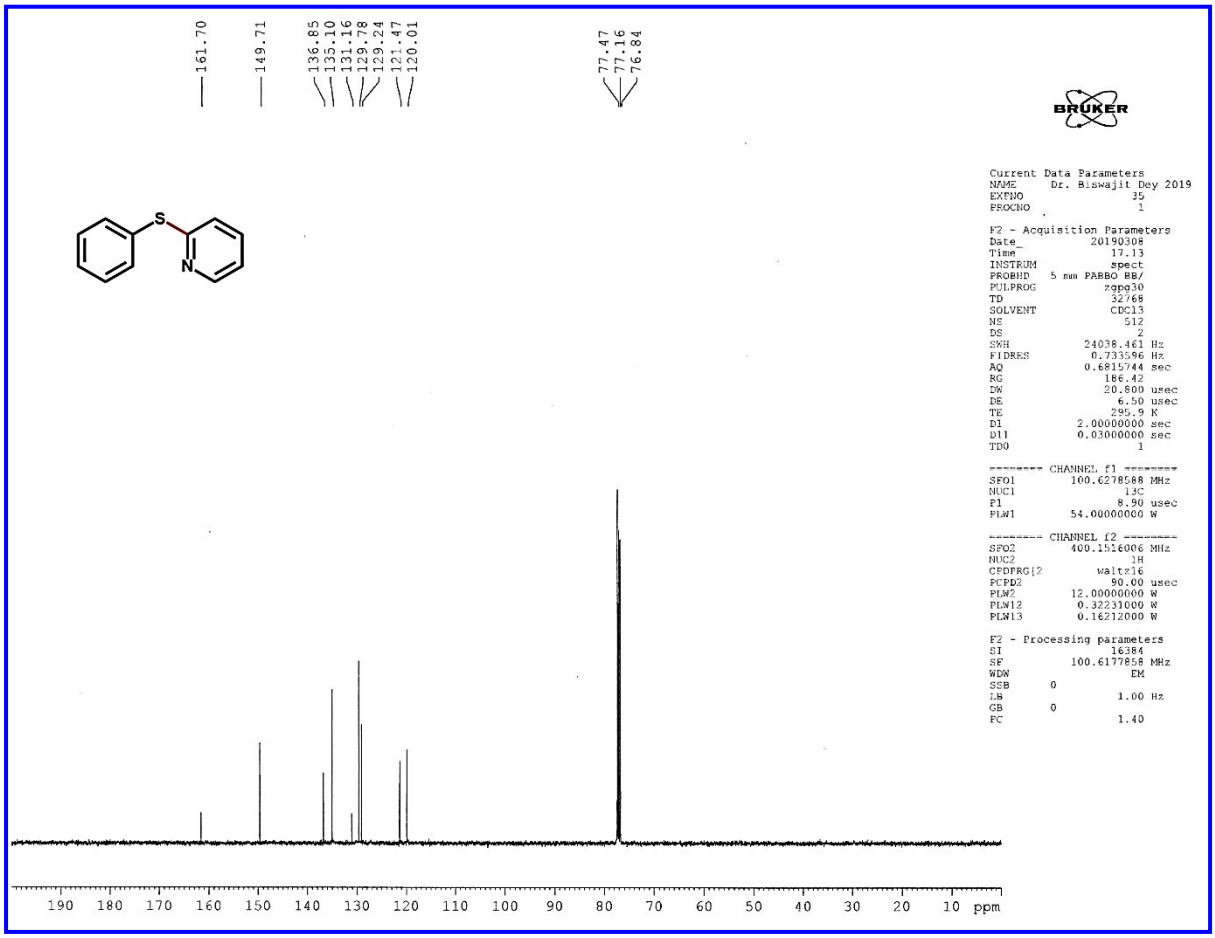


Fig. S19 ^{1}H NMR spectra of (entry 6, Table 2)

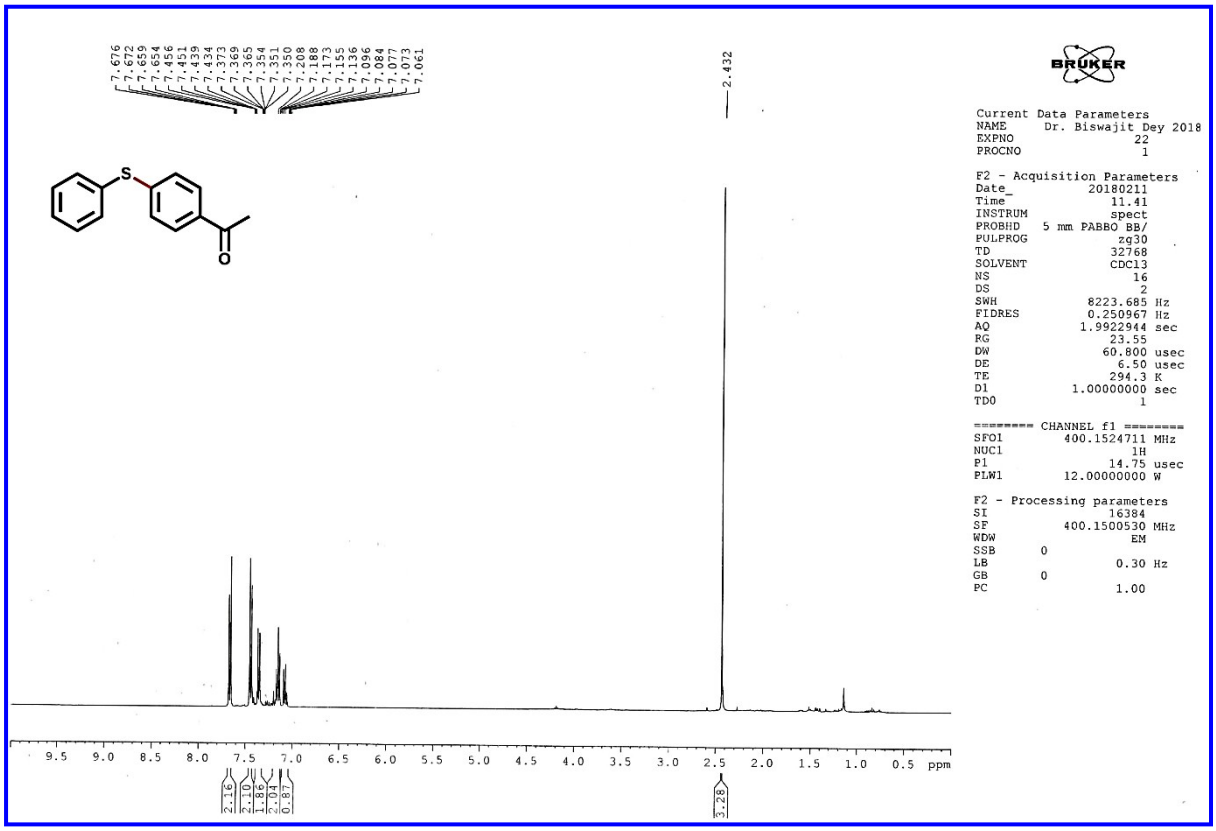


Fig. S20 ^{13}C NMR spectra of (entry 7, Table 2)

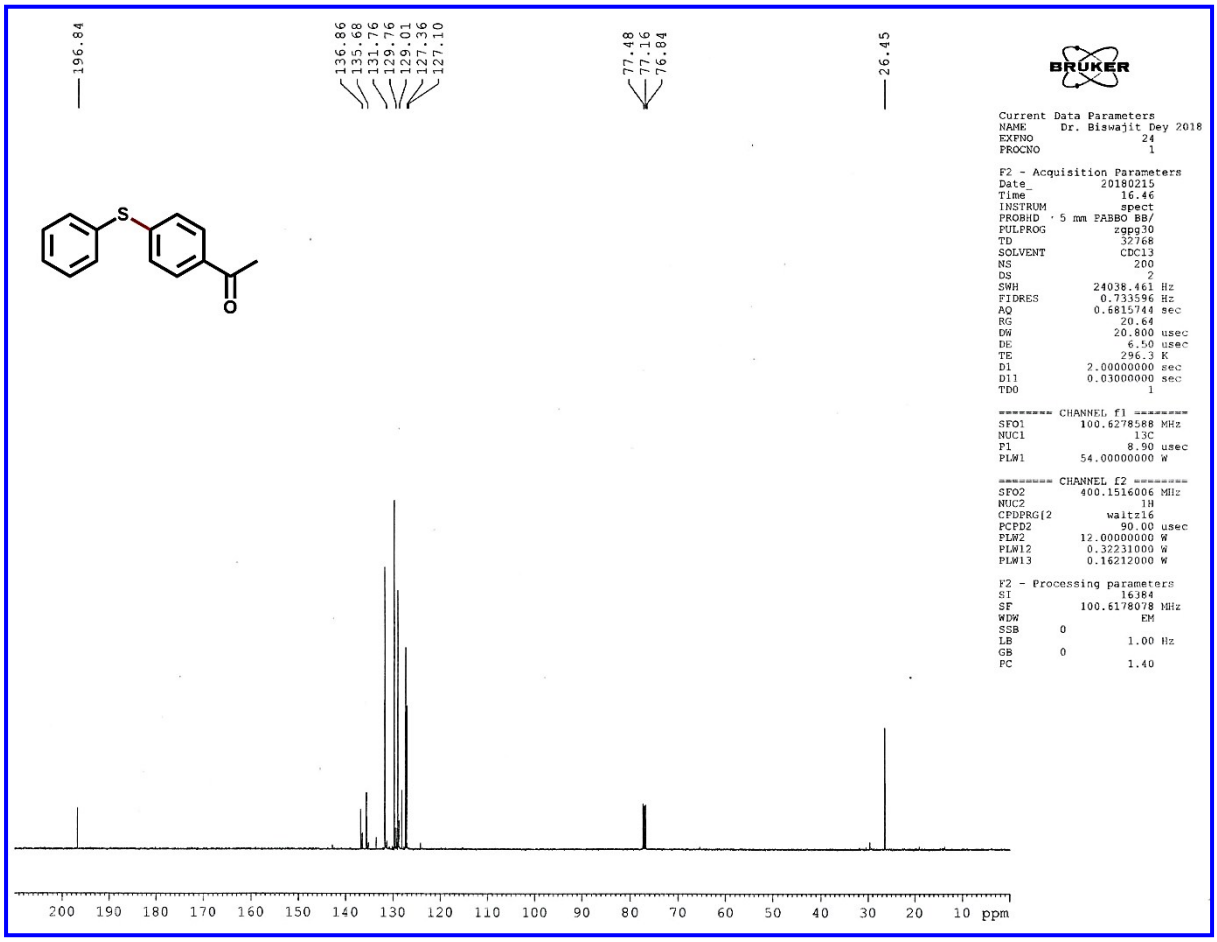


Fig. S21 ^{1}H NMR spectra of (entry 11, Table 2)

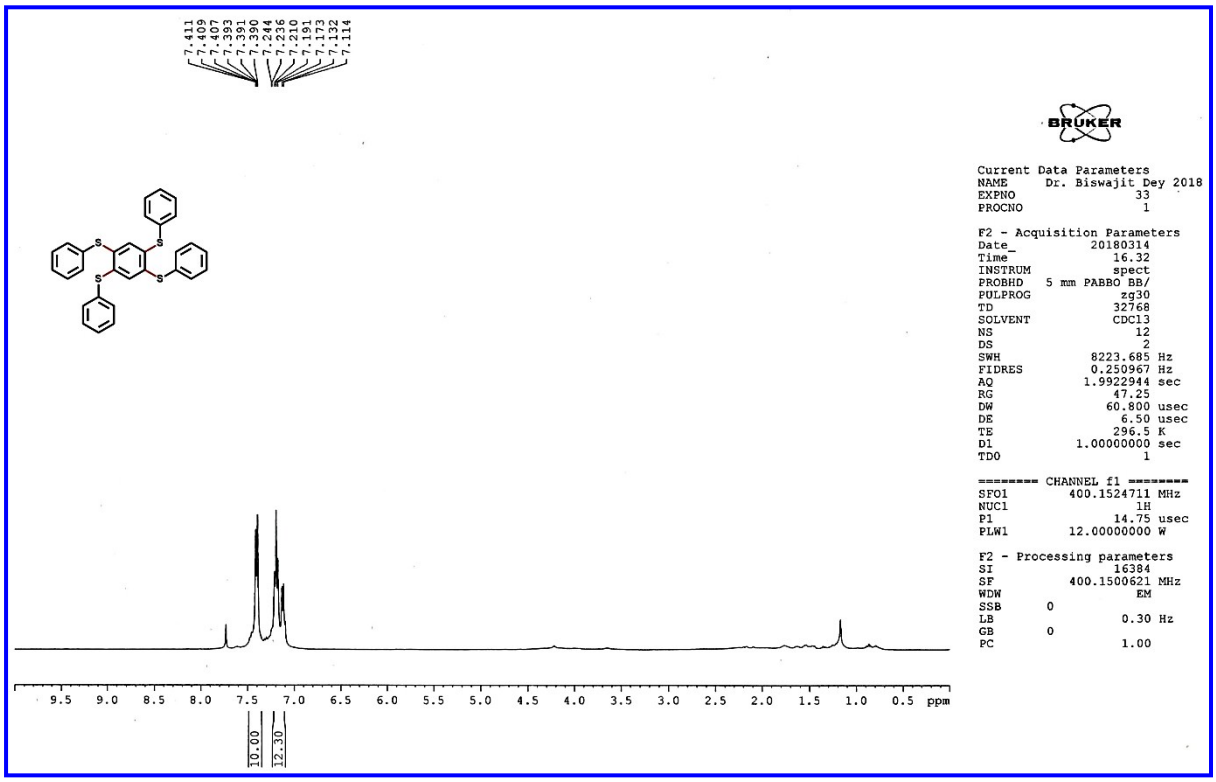


Fig. S22 ^{13}C NMR spectra of (entry 11, Table 2)

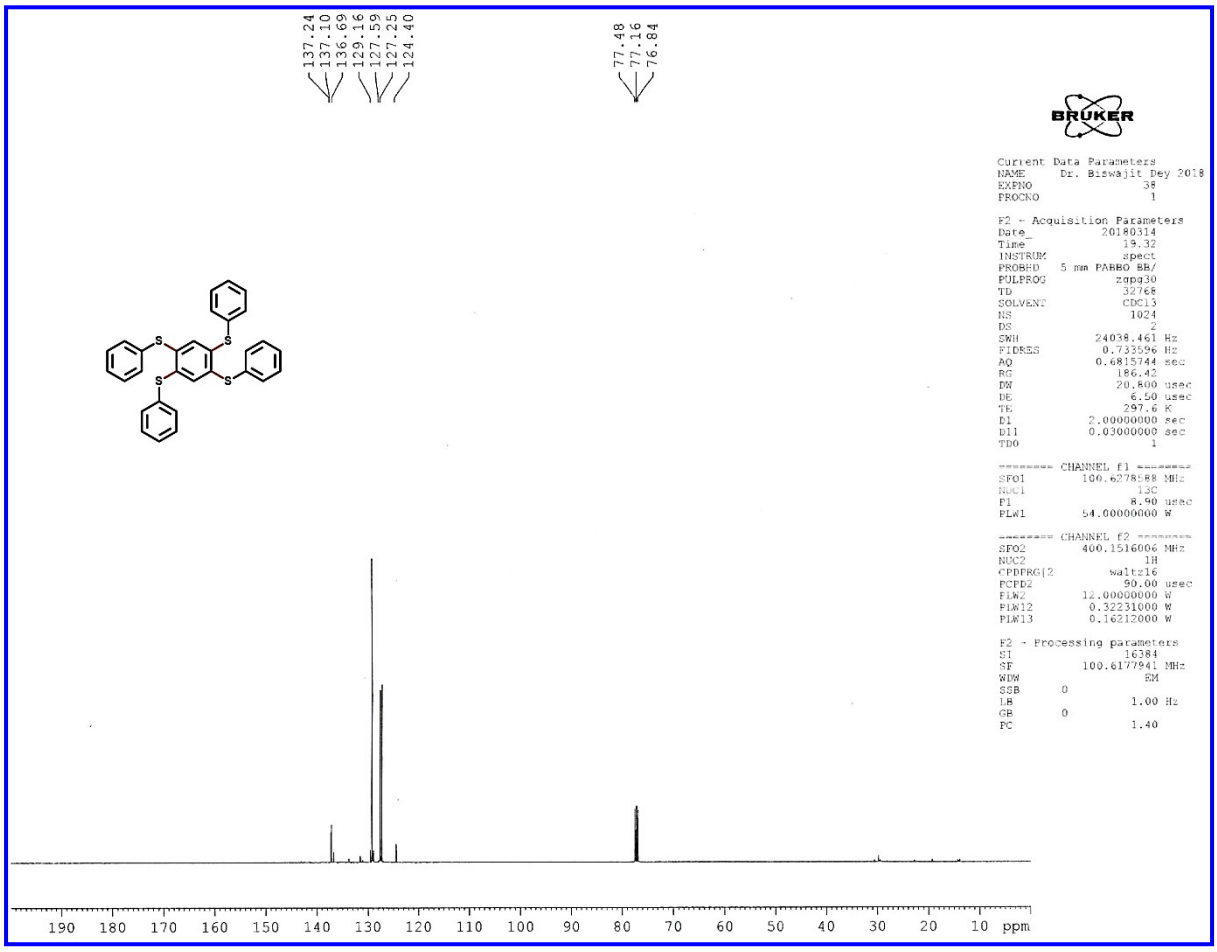


Fig. S23 ^{1}H NMR spectra of (entry 8, Table 2)

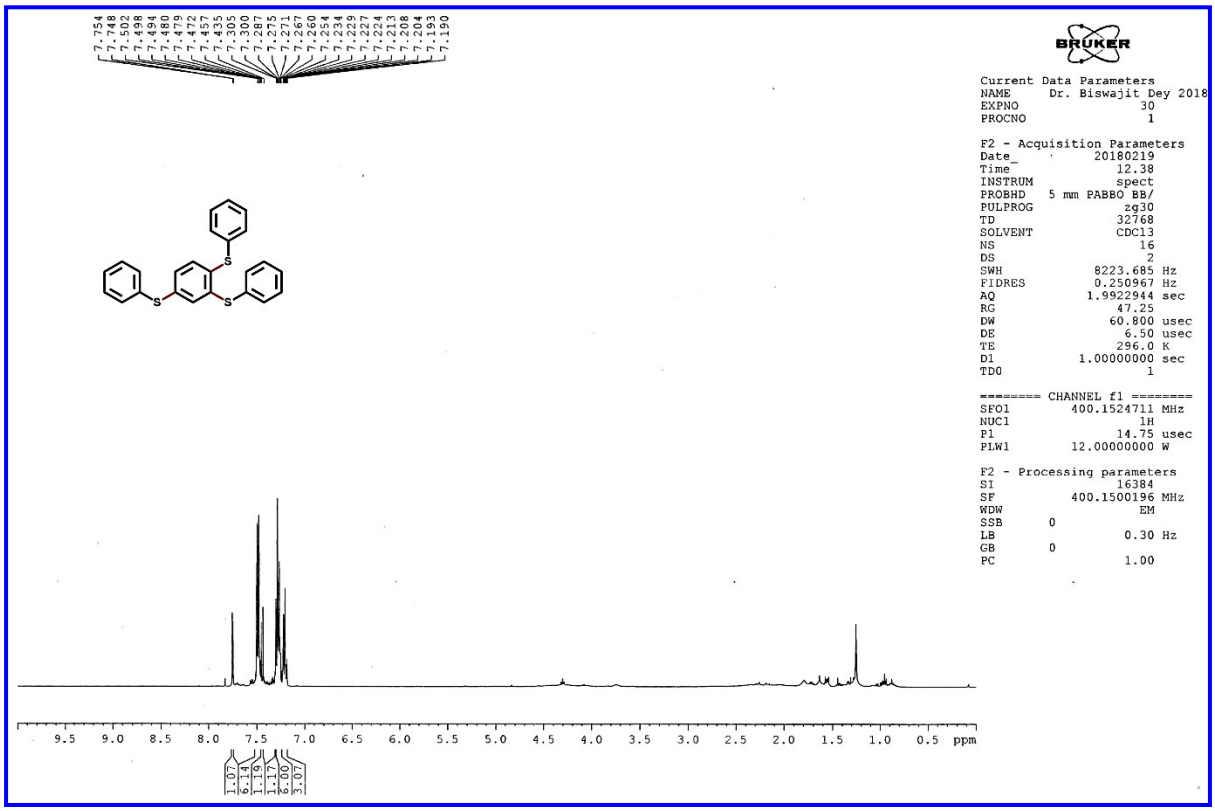


Fig. S24 ^{13}C NMR spectra of (entry 8, Table 2)

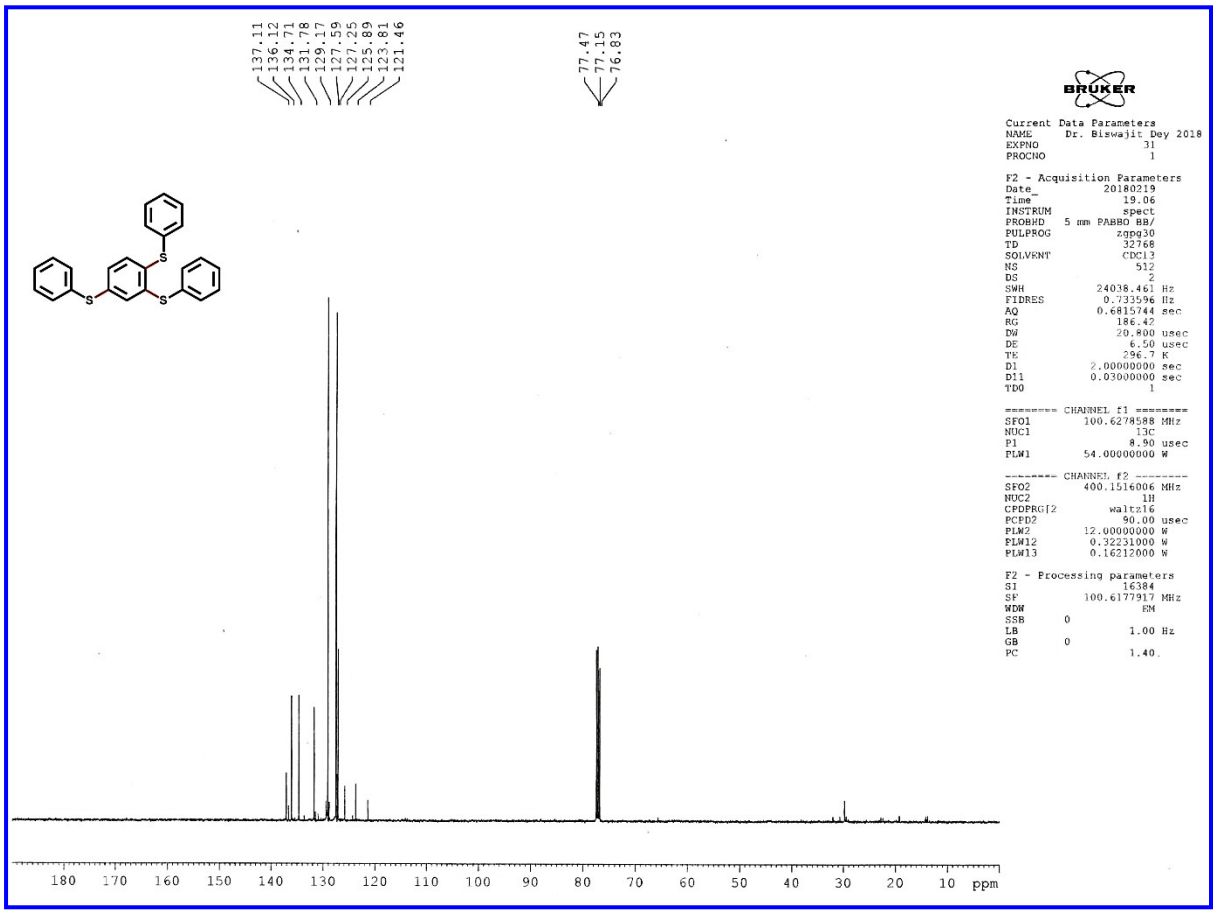


Fig. S25 ^{1}H NMR spectra of (entry 13, Table 2)

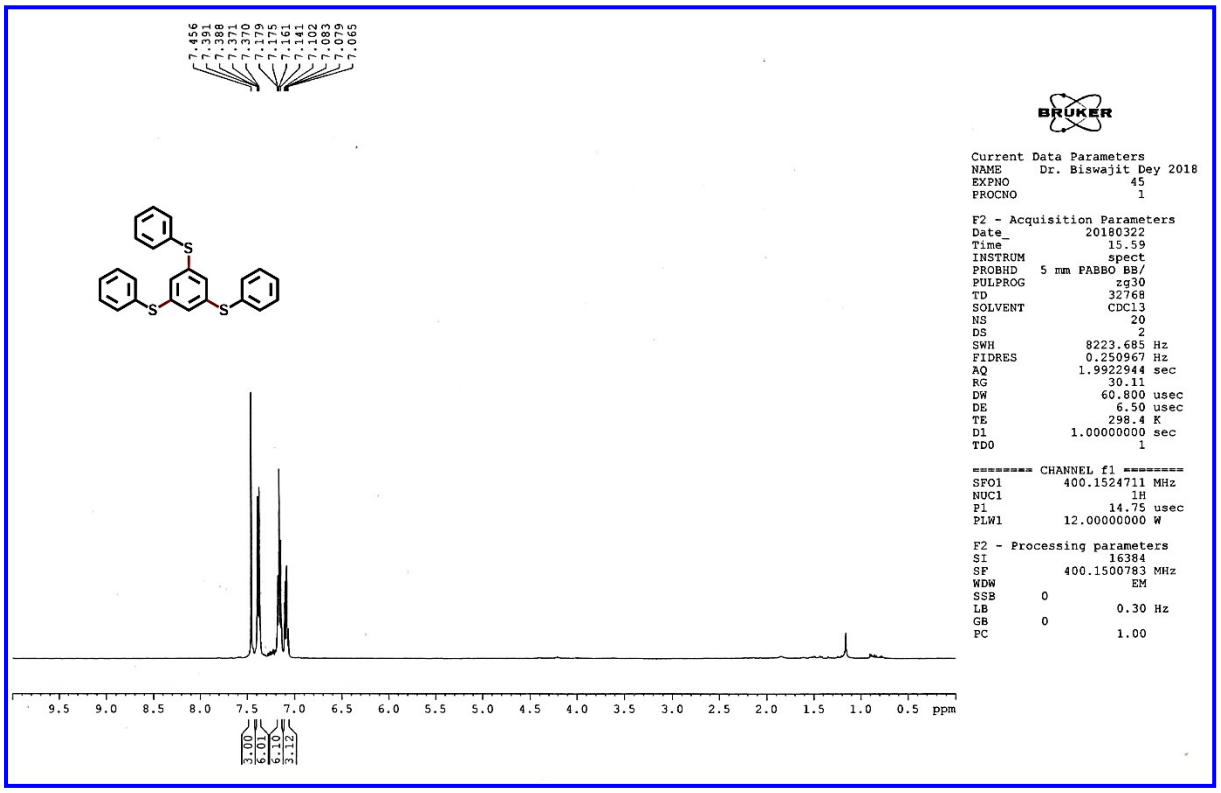


Fig. S26 ^{13}C NMR spectra of (entry 13, Table 2)

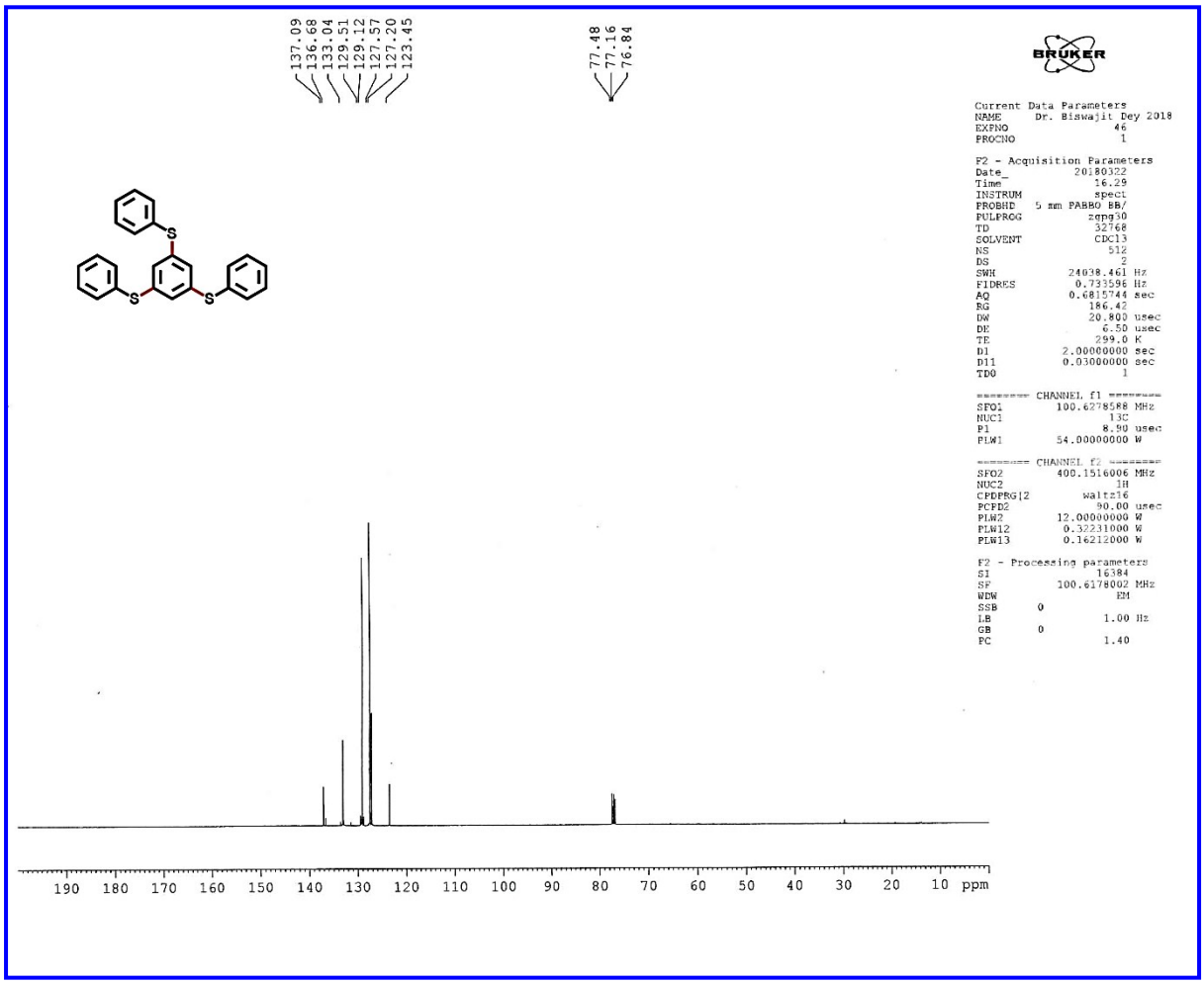


Fig. S27 ^{1}H NMR spectra of (entry 9, Table 2)

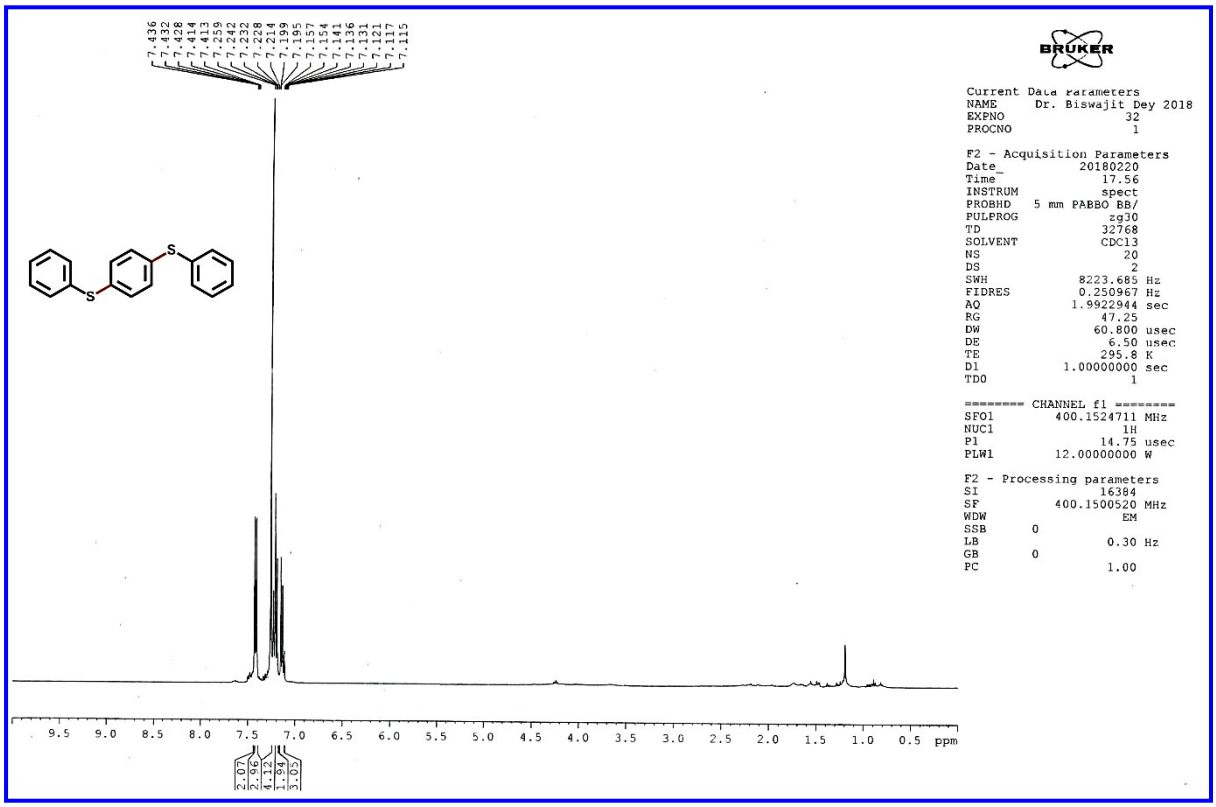


Fig. S28 ^{13}C NMR spectra of (entry 10, Table 2)

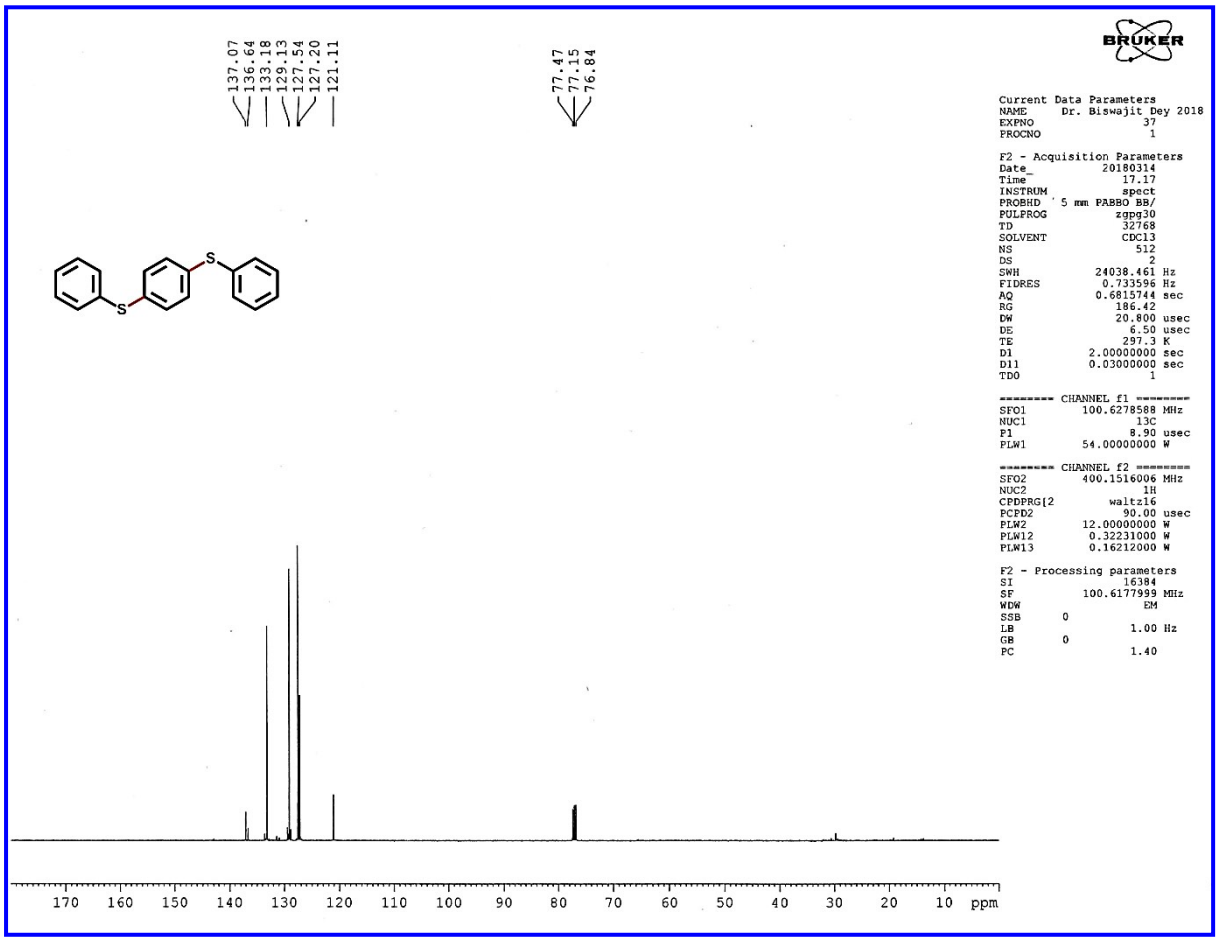


Fig. S29 ^{1}H NMR spectra of (entry 12, Table 2)

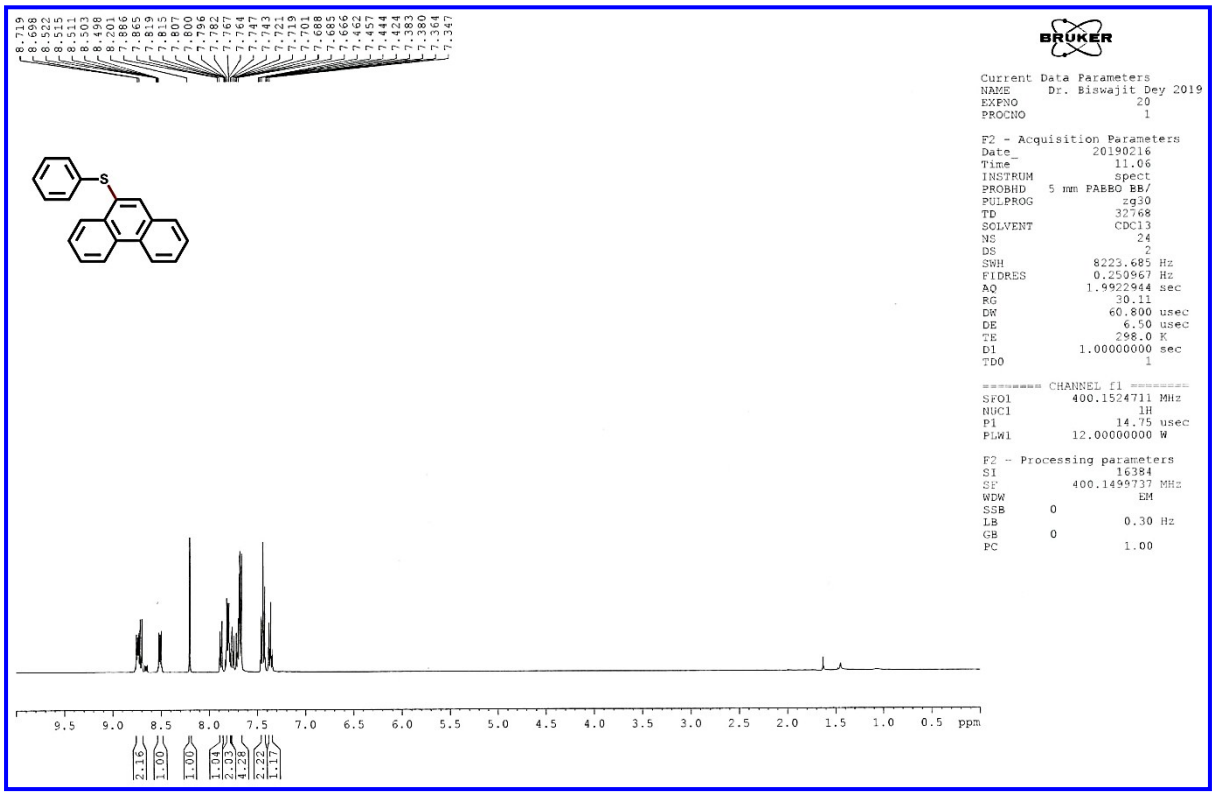


Fig. S30 ^{13}C NMR spectra of (entry 12, Table 2)

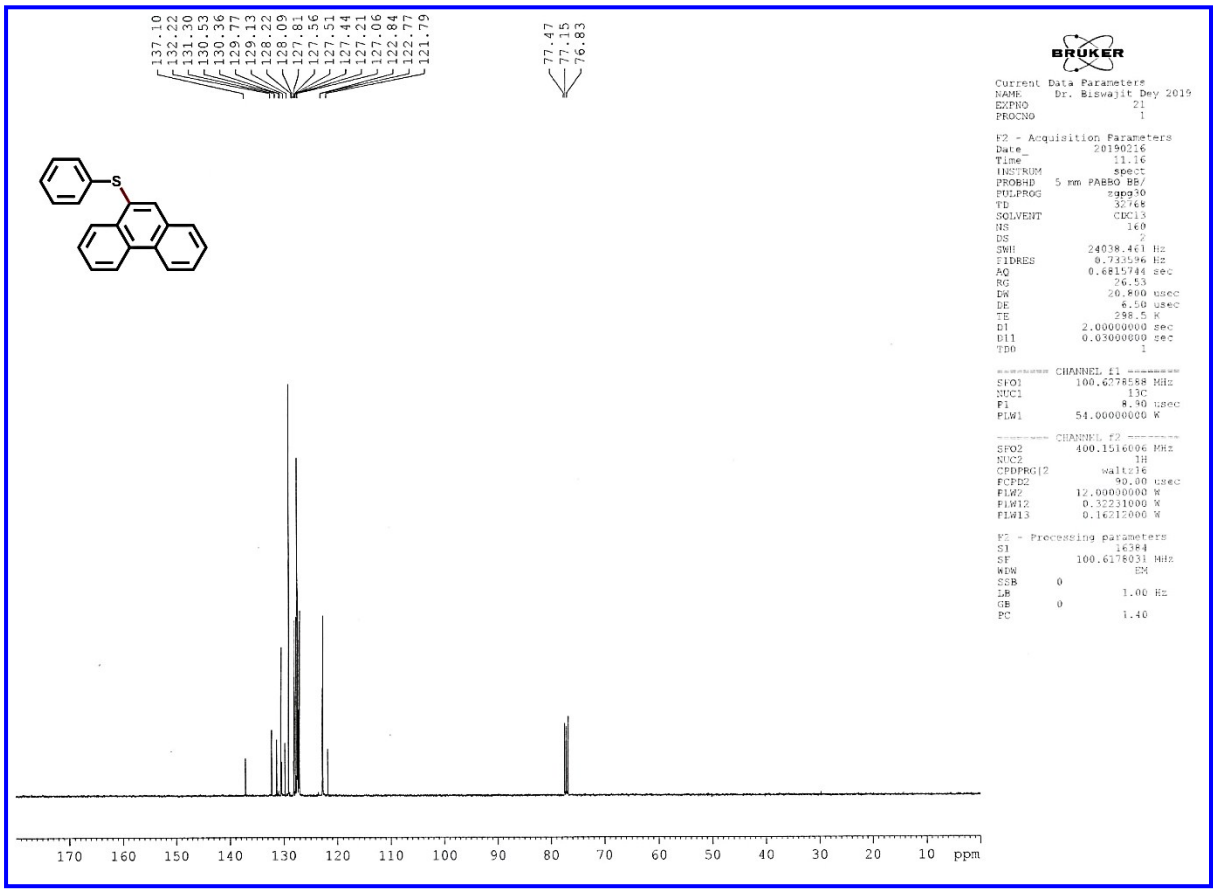


Fig. S31 ^{1}H NMR spectra of (entry 12, Table 2)

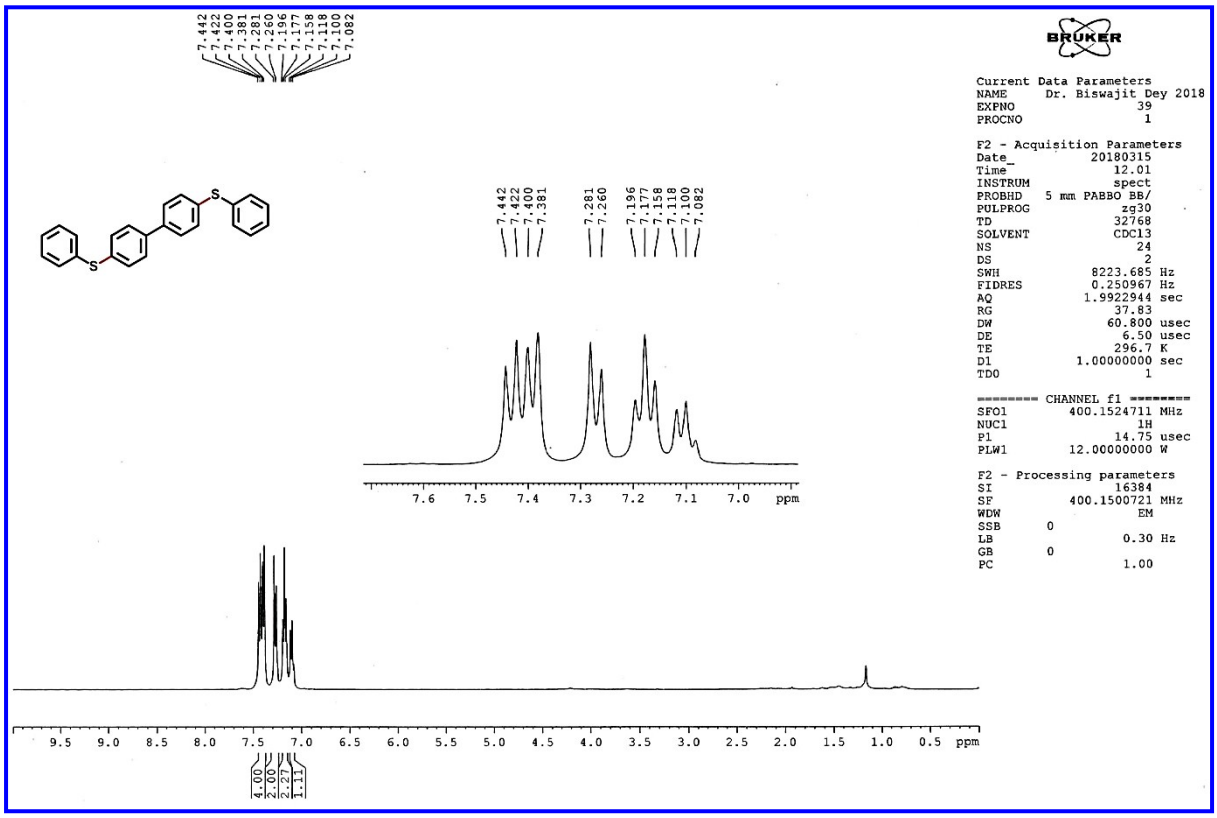


Fig. S32 ^{13}C NMR spectra of (entry 12, Table 2)

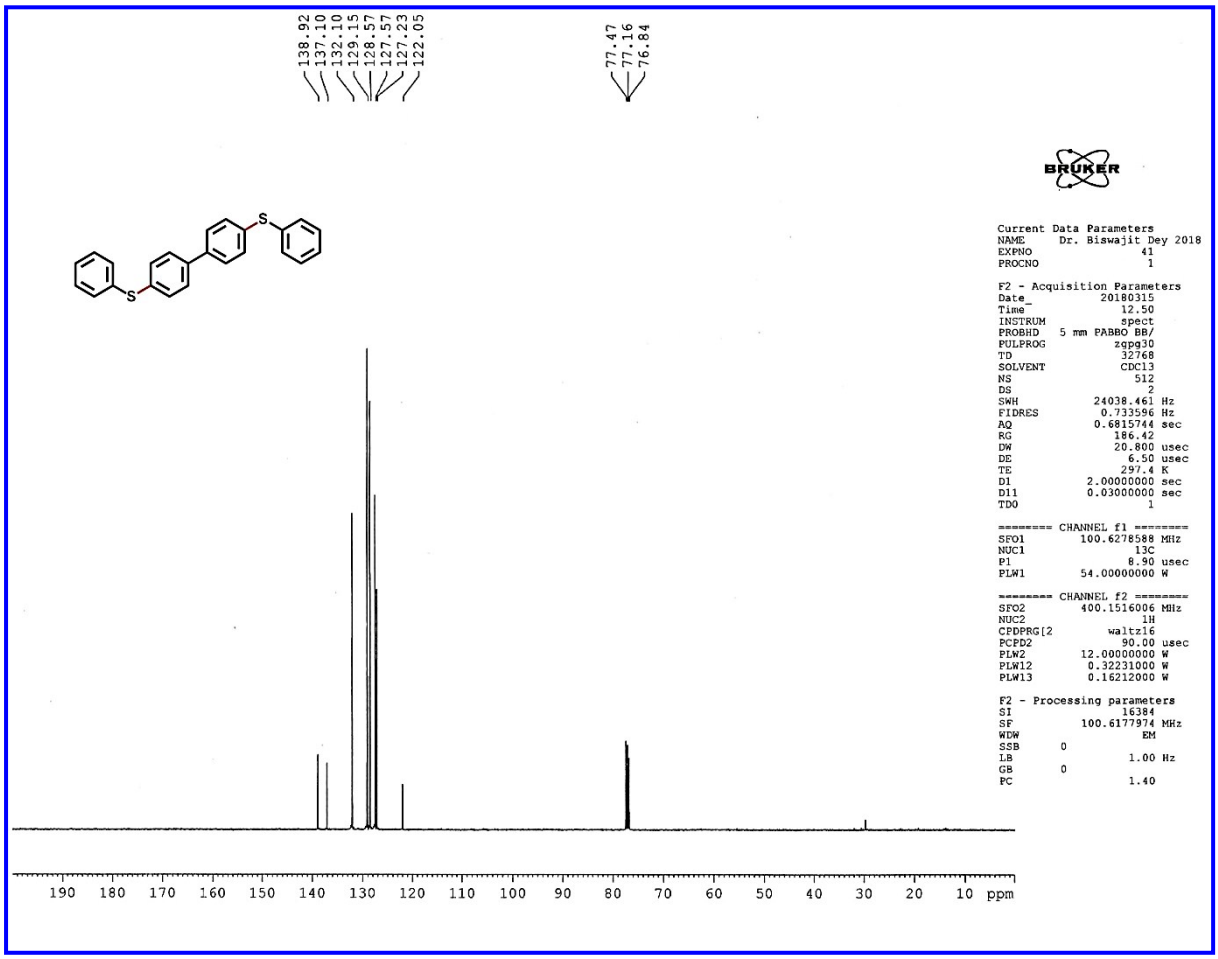


Fig. S33 ^{1}H NMR spectra of (entry 13, Table 2)

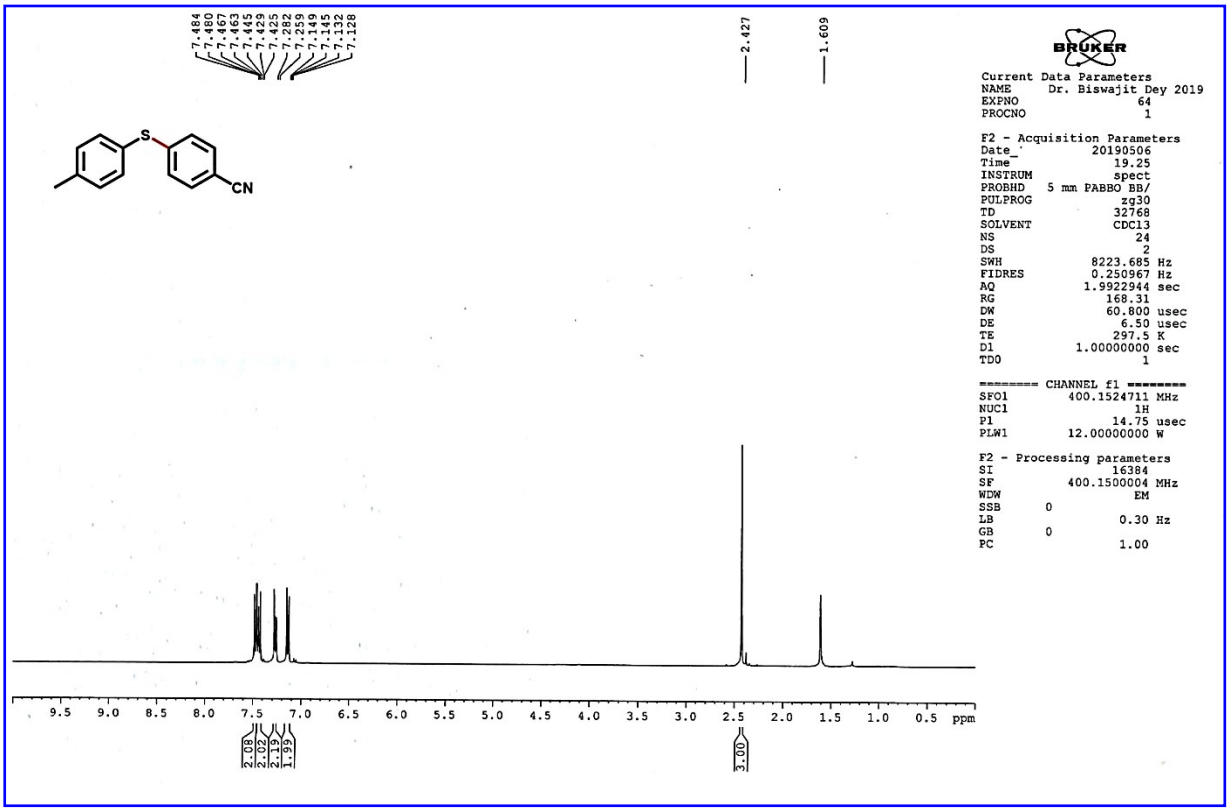


Fig. S34 ^{13}C NMR spectra of (entry 12, Table 2)

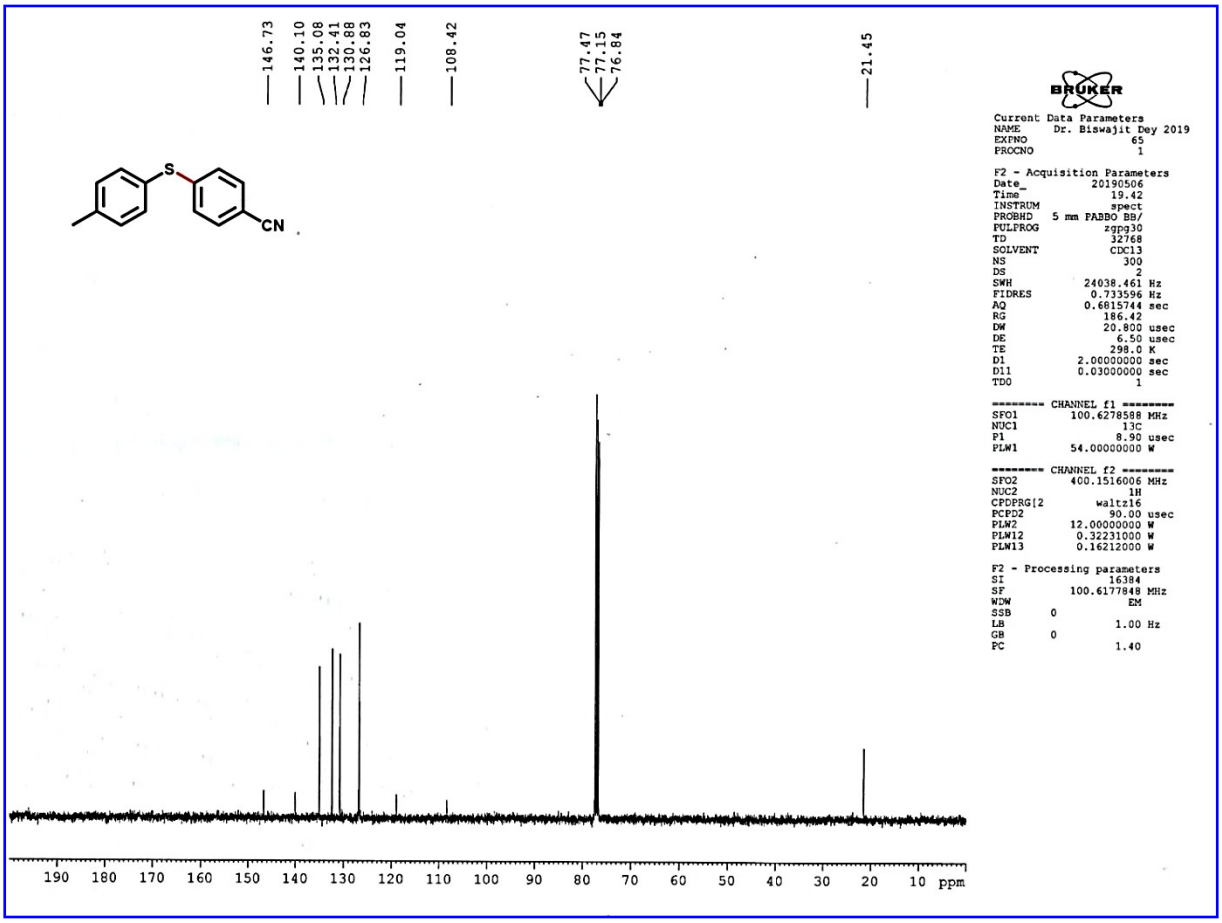


Fig. S35 ^{1}H NMR spectra of (entry 13, Table 2)

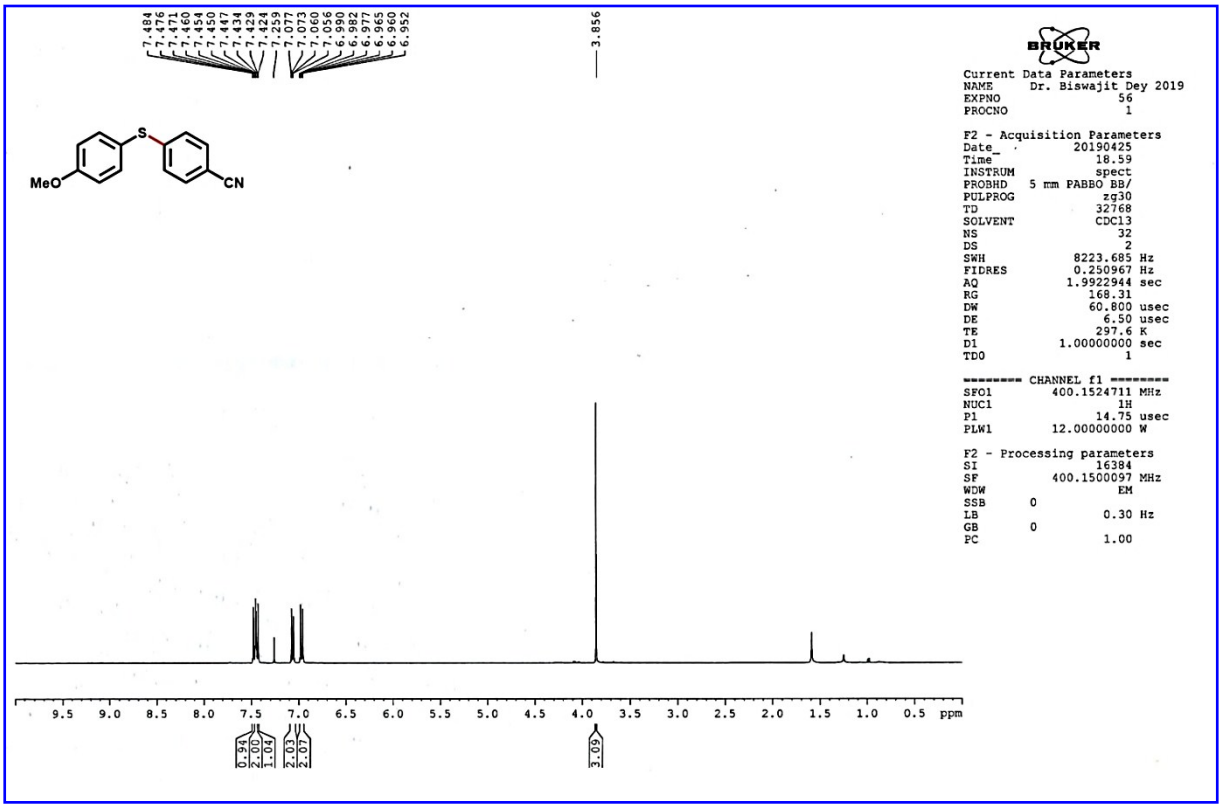
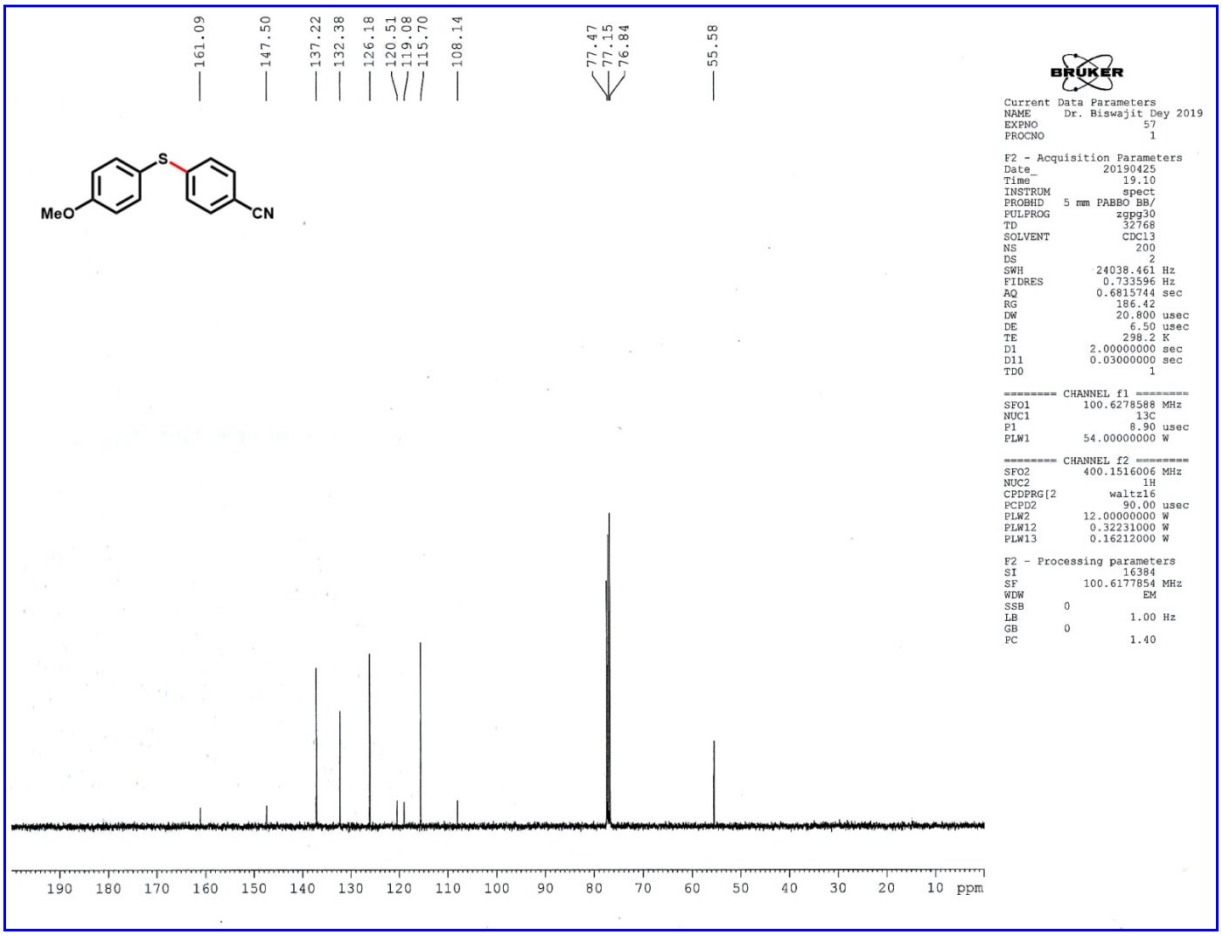


Fig. S36 ^{13}C NMR spectra of (entry 12, Table 2)



Reference:

1. D. G. Brannon, R. H. Morrison, J. L. Hall, G. L. Humphrey, D. N. Zimmerman, *J. Inorg. Nucl. Chem*. **1971**, *33*, 981-990.
2. V. T. Yilmaz, O. Andac, A. Karadag, W. T. A. Harrison, *Journal of Molecular Structure.* **2001**, *641*, 119-124.