Electronic Supplementary Material (ESI) for ChemComm.

Access to Small Molecules Semiconductor *via* C-H Activation for Photovoltaic Applications

Sanchari Shome[a] and Surya Prakash Singh*[a]

Supporting Information

Experimental Section:

General Information: Thin-layer chromatography plates were visualized by exposure to UV light/iodine. ^{1}H was obtained on 400 MHz spectrometers and ^{13}C NMR spectra were obtained on 100 MHz spectrometer with chloroform-d as solvent and tetramethylsilane as the internal standard. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, number of hydrogens). Multiplicity is abbreviated as follows: s (singlet), d (doublet), dd (double doublet), bs (broad singlet), bd (broad doublet), t (triplet), q (quartet), m (multiplet). Mass spectra were recorded on the Shimadzu model LCMS-2010EV system that was equipped with electronspray ionization (ESI) probe.

Materials: The following chemicals were obtained from Sigma-Aldrich, and used as received: ortho-phenylenediamine, 4-Fluoro-1,2-phenylenediamine, piperidine, selenophene Silver Oxide (Ag_2O), all other thiophene and its derivatives. The thionyl chloride ($SOCl_2$) used for cyclization was obtained from Merck and the selenium oxychloride (SeOCl) was obtained from Sigma Aldrich. The solvents used for reaction were AR grade FINAR and solvents used for column chromatography were LR grade. Silica used for column chromatography was either 60-120 or 100-200 as per requirement.

General Procedure for Selective mono-Thienylation with Thiophenes:

To a 25 mL of sealed tube were added $Ru(MesCO_2)_2$(p-cymene) (2.5 mol %), Ag_2O (2.0 equiv) and benzo[c][1,2,5]thiadiazole (50 mg, 1 equiv) under N_2, followed by DMSO (1 mL) with stirring. Piperidine (30 µL 1.5 equiv) and thiophene (0.4 mmol, 2 equiv) was then added subsequently. The reaction mixture was stirred at 80˚C (preheated oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

General Procedure for Selective mono-Arylation with Benzene:

To a 25 mL of sealed tube were added $Ru(MesCO_2)_2$(p-cymene) (2.5 mol %), $AgSbF_6$ (1.5 equiv) and benzo[c][1,2,5]thiadiazole or 5-fluorobenzo[c][1,2,5]thiadiazole (1 equiv) under N_2, followed by DMSO (2 mL) with stirring. Piperidine (1.5 equiv) and benzene (2 equiv) was then added subsequently. The reaction mixture was stirred at 90˚C (preheated oil bath). After stirring for 9 h, the reaction mixture was cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

General Procedure for Selective di-Thienylation with Thiophenes:

To a 25 mL of sealed tube were added $Ru(MesCO_2)_2$(p-cymene) (1.2 mol %), Ag_2O (4.0 equiv) and 4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1 equiv) under N_2, followed by DMSO (1 mL) with stirring. Piperidine (1.5 equiv) and thiophene (6 equiv) was then added subsequently. The reaction mixture was stirred at 110˚C (preheated oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

General Procedure for Selective di-Arylation with Benzene:

To a 25 mL of sealed tube were added $Ru(MesCO_2)_2$(p-cymene) (2.5 mol%), $AgSbF_6$ (1.5 equiv) and 6-fluoro-4-phenylbenzo[c][1,2,5]thiadiazole or 4-phenylbenzo[c][1,2,5]thiadiazole (2 equiv) under N_2, followed by DMSO (2 mL) with stirring. Piperidine (1.5equiv) and benzene (6 equiv) was then added subsequently. The reaction mixture was stirred at 100˚C (preheated oil bath). After stirring for 12h, the reaction mixture was cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

General Procedure for Synthesis of FBT-CAA and BT-CAA Derivatives:

In a 100-ml round-bottomed flask connected to a reflux condenser 67.8 mg (0.60 mmole) of ethyl cyanoacetate, 56.8 mg (0.66 mmole) of 1-(thiophen-2-yl)ethanone, 9.2 mg (0.12 mmole) of ammonium acetate, 30 mg (0.48 mmole) of glacial acetic acid was added. The reaction mixture was stirred for 6-12 hrs, separated using brine water and dicholomethane. The mixture was evaporated and residue was purified using column chromatography in DCM.

Procedure for the Synthesis of Unsymmetrical Thienylated Product 3ac: To a 25 mL of sealed tube were added $Ru(MesCO_2)_2$(p-cymene) (5 mol%), Ag_2O (2 equiv) and 4-phenylbenzo[c][1,2,5]thiadiazole (0.5 mmol) under N_2, followed by DMSO (2 mL) with stirring. Piperidine (1.5 equiv) and 2-bromothiophene (1 mmol) was then added subsequently. The reaction mixture was stirred at 100˚C (preheated oil bath). After stirring for 6h, on the maximum consumption of the first coupling partner 2-bromothiophene, thiophene-2-carbaldehyde (1.2 mmol) was added to the reaction mixture and further refluxed for 6 hrs. The reaction mixture was then cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The

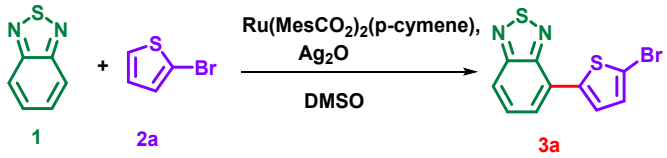
residue was purified with 60-120 silica gel chromatography using hexane-EtOAc mixture to obtain pure product. The unreacted phenylbenzo[c][1,2,5]thiadiazole, 2-bromothiophene and thiophene-2-carbaldehyde were recovered.

Optimization Table:

Table 1: Illustrative optimisation results for the selective C-C bond formation between 1 and 2a

Sl. No	Catalyst	Mol %	Oxidant (mol%)	Solvent	Yield [a](%)
1	$[RuCl_2(p\text{-cymene})]_2$	2.5	AgOAc (5)	Toluene	N.R
2	$[RuCl_2(p\text{-cymene})]_2$	2.5	AgOAc (5)	DMF	32
3	$[RuCl_2(p\text{-cymene})]_2$	5	Ag_2O (10)	DMSO	56
4	$Ru(p\text{-cymene})(MesCO_2)_2$	2.5	AgOAc (5)	Toluene	62
5	$Ru(p\text{-cymene})(MesCO_2)_2$	10	Ag_2O (10)	DMF	65
6	$Ru(p\text{-cymene})(MesCO_2)_2$	20	Ag_2O (10)	DMSO	68
7	$Ru(p\text{-cymene})(MesCO_2)_2$	2.5	Ag_2O (15)	DMSO	74
8	$Ru(p\text{-cymene})(MesCO_2)_2$	25	Ag_2O (15)	DMSO	67
9	$Ru(p\text{-cymene})(diBrbpy)(MesCO_2)$	10	Ag_2O (15)	DMSO	2-3
10	$Ru(p\text{-cymene})(bpy)(MesCO_2)$	10	$AgSbF_6$ (15)	DMSO	N.R
11	$Pd(TFA)_2$	2.5	AgOAc (10)	Toluene	32
12	$Pd(TFA)_2$	5	Ag_2O (15)	DMF	38
13	$Pd(OAc)_2$	5	AgOAc (10)	DMSO	30
14	$Ru(p\text{-cymene})(TFA)_2$	10	Ag_2O (5)	DMSO	60

The scale up reaction was performed for the 3a derivative as shown below.



The synthetic procedure was found to work even when considered for scale up reaction. The selective synthesis of mono-thienylated FBT 3a was possible by reaction of 1 with thiophenes in high concentrations by tuning the ratio between 1 and 2a. The reaction was performed in 2 mmol, 5 mmol, 8 mmol and 10 mmol scale for the better understanding of the scale up reaction. When the reaction was performed in 2 mmol scale, 272 mg of 1 was used with 2.1 mmol of 2a, 2.5 mol % of $Ru(MesCO_2)_2(p\text{-cymene})$ and 15 mol% of Ag_2O under N_2 atmosphere along with 1-1.2 ml of DMSO and 30 µl of piperidine to yield the product 3a as

high as 75%. Increasing the number of milimoles of 1 (2 mmol to 5 mmol) the yield of mono-thienylated product 3a remains as high as 70%. However, when the reaction was performed with 8 mmol and 10 mmol of 1 the yield of the product 3a decreased to 64% and 66%. To achieve an increase in yield we also enhanced the catalyst loading percentage from 2.5 mol% to 5 mol% and increased the oxidant from 15 mol% to 25 mol%. About 70% yield was observed with 4 mol% of $Ru(MesCO_2)_2$(p-cymene) and 20 mol% of Ag_2O. Under this condition we were able to achieve both mono and bi-thienylated product (mono is major). Therefore, we can very clearly say that the methodology works well even in large scale system, and can be used for commercial scale synthesis. The entire large scale screening is tabulated below in Table 2.

Table 2: Illustrative scale up optimisation results for the selective C-C bond formation between 1 and 2a

Sl.No	Catalyst (mol%)	Ag_2O (eqv)	Mmol of 1	Mmol of 2a	Yield(%)[a] of mono
1	2.5	15	1	1.2	75
2	2.5	15	2	2.1	75
3	2.5	15	5	5.0	72
4	2.5	15	8	8.1	64
5	2.5	15	10	10.2	66
6	3	15	10	10.2	66
7	4	20	10	10.2	70
8	5	20	10	10.2	64

[a]GC yield

Mechanistic Study:

To carry out the preliminary mechanistic studies we performed the reaction using $Ru(MesCO_2)_2$(p-cymene) (2.5 mol %), Ag_2O (2.0 equiv) and benzo[c][1,2,5]thiadiazole (50 mg, 1 equiv) under N_2, followed by DMSO (1 mL). Keeping the reaction mixture under stirring conditions in a preheated bath (80˚C) piperidine (1.5 eqv) and thiophene (0.4 mmol, 2 equiv) was then added subsequently. The reaction mixture was stirred for 6 hrs and after every 1 hr an aliquot was taken and diluted with DCM and given for mass analysis. However, after the end of 3.5 hrs the intermediate C was detected via HRMS analysis (Fig. 2). Although the intermediate could not be isolated using column chromatography but a significant peak of the intermediate was observed in the HRMS spectra of the reaction mixture.

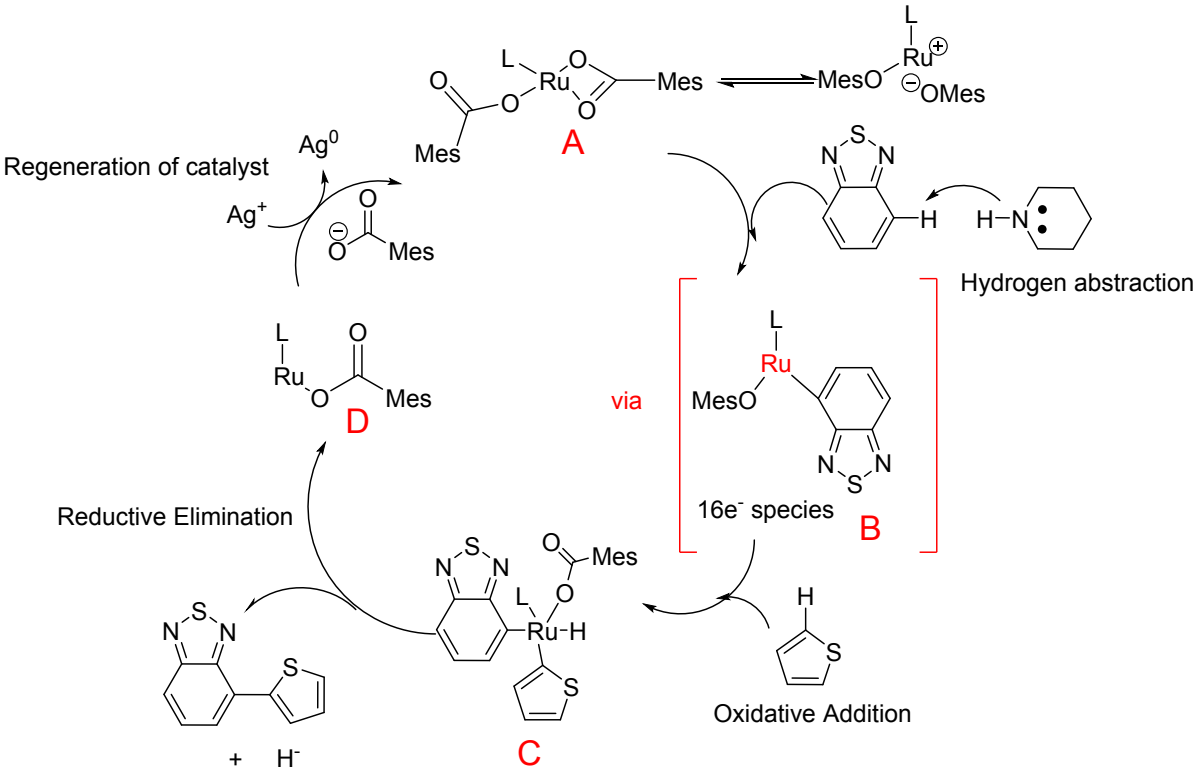


Fig-1: The Illustration of the plausible mechanism

The plausible mechanism of the reaction is illustrated in fig 1, where it is expected that the initial hydrogen abstraction from the benzothiadiazole takes place with the help of the catalytic amount of piperidine that is added in the reaction mixture and the electron rich benzothiadiazole species is attacked by the ruthenium complex that is electron deficient thereby forming a 16e- species which undergoes oxidative addition. Earlier reports on the mechanistic studies of ruthenium(p-cymene) catalyst by Fabre et.al have clearly mentioned that the oxidative addition takes place on the 16e- ruthenium species.[1] The addition of thiophene leads to the formation of the complex C that is indicated in the HRMS spectra (Fig. 2). In the later stage the complex undergoes reductive elimination to give the desired product and a ruthenium complex that undergoes one electron reduction in presence of silver to regenerate the catalyst.

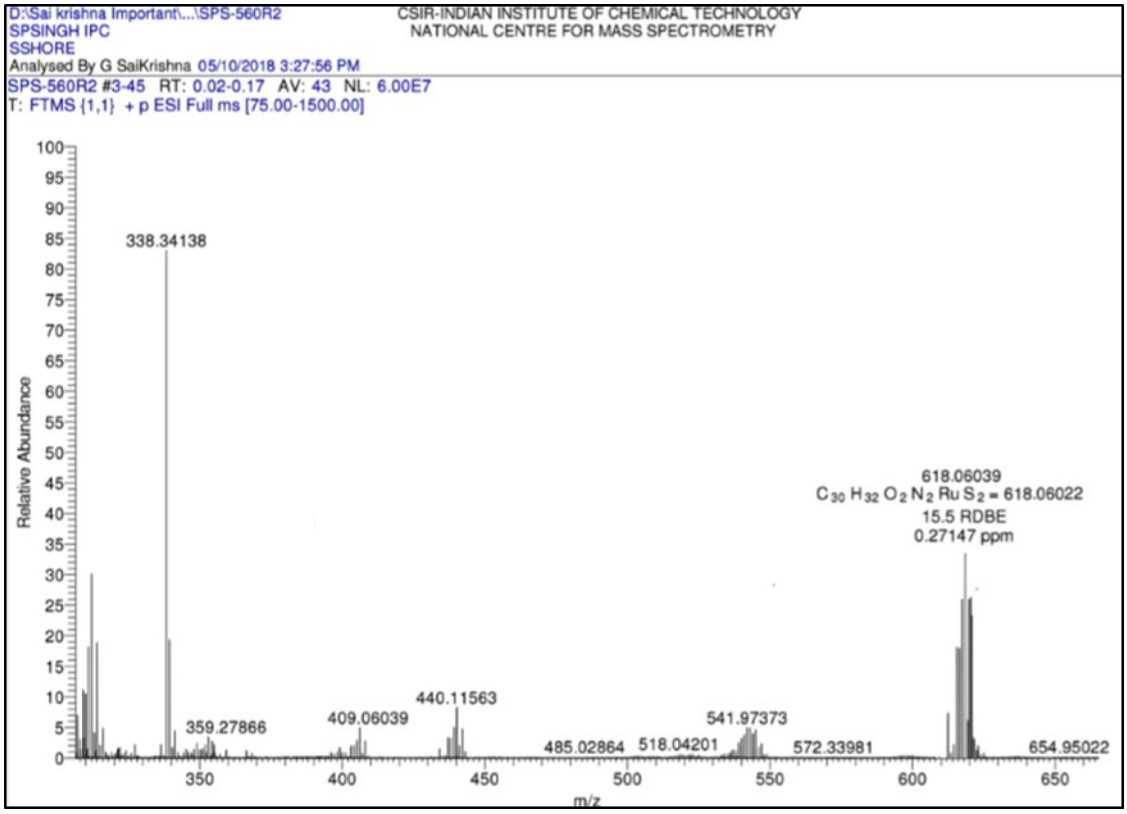


Fig-2: HRMS of ruthenium intermediate.

Optical and electrochemical properties:

The UV-visible absorption spectra of the co-sensitizer (FBT-CAA and BT-CAA) was measured in DMF solution and compared with N749 dye, as presented in Fig-3. The corresponding data are summarised in Table 3.

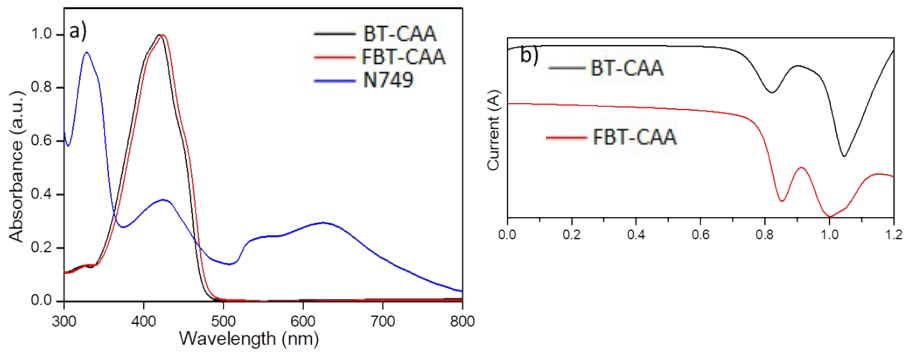


Fig-3: a) UV-visible spectra of FBT-CAA, BT-CAA and N749 in DMF solution, b) Differential pulse voltammetry (DPV) of BT-CAA, FBT-CAA

The co-sensitizers (BT and FBT) have showed a strong absorption band in the wavelength range of 390-430 nm, assigned to intramolecular charge transfer between donor and the

acceptor.[2] The λ_{max} of the both the dyes are 418 and 424 and their corresponding molar extinction co-efficiencies are 3×10^4 M^{-1} cm^{-1}. The high molar extinction co-efficient exhibited by these co-sensitizers are beneficial for achieving optimum efficiency by, minimizing the amount of dye required thereby providing enough space on the semiconductor (TiO_2) for binding the sensitizer molecule. The FBT-CAA dye showed a 5 nm red shifted absorption than BT-CAA that definitely signifies the role of fluorine atom.

Table 3: Illustrative optimisation results for optical and electrochemical properties

Dye	**λ_{max} ($\varepsilon\times10^4$ M^{-1} cm^{-1}) [nm][a]**	**E_{OX} [V][b]**	**E_{0-0} [V][c]**	**LUMO [V][d]**
BT-CAA	418(3.0148)	0.82	2.61	-1.79
FBT-CAA	424(3.0230)	0.85	2.61	-1.76
N749	620	0.64	1.53	-0.89
[a]UV-visible spectra were recorded in DMF, [b]Oxidation potentials were measured by differential pulse voltammetry, [c] the band gap (E_{0-0}) was derived from the onsite potentials of absorption spectra, [d] Exited state oxidation potentials were calculated (E^*_{OX}) were calculated by $E^b_{OX} - E^c_{0-0}$.				

Differential pulse voltammetry (DPV) of co-sensitizers have been measured to calculate the ground and exited state oxidation potentials to understand the effective electron injection from exited state dye to conduction band of TiO_2 and regeneration capacity of dye from redox electrolyte. Oxidative differential pulse voltammetry (DPV) was measured with 0.1M tetrabutylammonium hexaflurophosphate as supporting electrolyte in DMF solution (Fig. 3b). All potentials were internally referenced to the ferrocene/ferrocenium (Fe/Fe^+) couple which has the redox potentials of ($E_{Fe/Fe+}$) 0.510 V versus Ag/AgCl. The first oxidation potentials of the dyes have been determined from their corresponding peak potentials and incorporated in the Table 3. The oxidation potentials are 0.82 and 0.853 V for BT-CAA and FBT-CAA, respectively. The exited state oxidation potentials (E^*_{OX}) of BT-CAA and FBT-CAA have been calculated from E_{OX}-E_{0-0} equation, (ref) where E_{0-0} was calculated using absorption spectra. The E^*_{OX} potentials of BT-CAA and FBT-CAA dyes are -1.79 and -1.76. The potential values of co-sensitizers are sufficient enough to inject electron into TiO_2 band and regeneration from redox electrolytes.

Photovoltaic Properties:

The DSSC photovoltaic performance of FBT-CAA, BT-CAA and N749 were tested using the 0.25 cm^2 active area TiO_2 electrode by thermally stable electrolyte containing 0.5 M 1,2-dimethyl-3-propylimidazole iodide (DMPII), 0.05 M I_2 and 0.1 M LiI in acetonitrile. Fig 4a and 4b shows the comparative IPCE spectra and current-voltage curves of the DSSC using FBT-CAA, BT-CAA, N749 (BD) and their combined performances when they were evaluated for co-sensitization technic using N749 as base dye with systematic replacements of FBT-CAA and BT-CAA. The corresponding data are summarised in Table 4. Fig. 4a shows the IPCE spectra of individual dyes and combined dyes as a function of wavelength from 300 to 900 nm. N749 has shown broad absorption covering from entire visible range to near IR range, while the FBT-CAA and BT-CAA are shown intense IPCE in the range of 300 to 620 nm i.e. 83% and 68% respectively; this is attributed to the high molar extinction co-efficient nature of FBT-CAA and BT-CAA. The improved IPCE is observed for co-sensitized devices of N749 with FBT-CAA and BT-CAA than N749 dye as alone, it is because of increased light harvesting nature at 300 to 600 nm by adding high molar extinction co-efficient dyes FBT-CAA and BT-CAA.

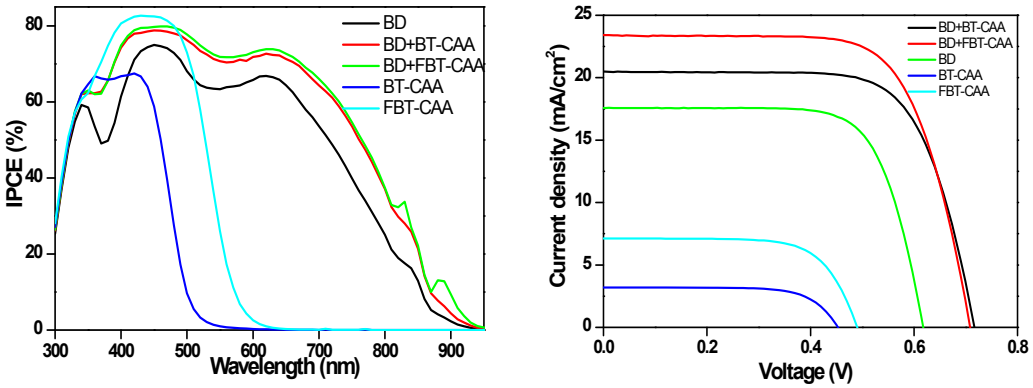


Fig-4: a) Photocurrent action (IPCE) curves of the TiO_2 electrodes sensitized by FBT-CAA (4a) and BT-CAA (4b), b) Current–voltage (J–V) characteristics of FBT-CAA and BT-CAA under illumination.

These dyes decrease the absorption losses arose because of electrolyte competitive absorption with their high molar extinction co-efficient nature resulted to an improved IPCE. The current voltage (J-V) curves (Fig. 4b) gives information about the efficiency of sensitizers when evaluated for DSSC in illumination condition. The efficiency of N749 as alone and co-sensitized with BT-CAA and FBT-CAA are 8.98%, 10.39% and 11.55% respectively, whereas the efficiency of BT-CAA and FBT-CAA individually are 1.02 %and 2.48%. In this context, high efficiency is obtained for cocktail dyes as compared to individual

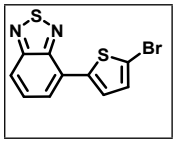
dyes and is attributed to the enhanced values of J_{sc}. The J_{sc} values of N749 as alone and in co-sensitization with BT-CAA and FBT-CAA are 17.56, 20.70 and 23.41 $mAcm^{-2}$ respectively.

Table 4: Illustrative optimised results for co-sensitization

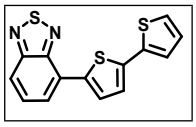
Dye	**J_{sc}[mA cm^{-2}]**	**V_{oc}[V]**	**F.F.**	**Eff[%]**
BT-CAA	3.188	0.453	0.710	1.02
FBT-CAA	7.109	0.500	0.698	2.48
BD	17.567	0.714	0.715	8.98
BD+BT-CAA	20.70	0.717	0.700	10.39
BD+FBT-CAA	23.41	0.708	0.696	11.55

The Jsc values are consistent with the IPCE. Generally, it is well known concept that the IPCE = (1240 × Jsc)100/(λ × P_{in}) (in %) that means the IPCE values are closely related to the J_{sc} at a specific wavelength and a fixed input power (P_{in}). Slight decrease in open circuit voltage are observed (V_{oc}) for N749 when evaluated for Co-sensitization with FBT-CAA and BT-CAA, compared to the N749 as alone. The decreased V_{oc} values indicate the amplified recombination rate. However, this reduction in the V_{oc} values is less compared to the increment in Jsc values. Therefore, the overall efficiency is enhanced. Moreover, the small size of organic co-sensitizers can cover the TiO_2 nano surface more tightly by filling up the space in between the gaps, where three-dimensional ruthenium dyes cannot reach; hence it provides a better surface coverage.[3] Further, this technique also influences the decreasing dye aggregation and increasing π- π stacking resulting in the enhanced efficiency with high IPCE and J_{sc}[2]. When compared, the efficiencies of N749 with FBT-CAA and BT-CAA, FBT-CAA showed better efficiency than BT-CAA, it is probably due to the presence of fluorine atom that shows a significant influence on effective dye regeneration by interacting with electrolyte.

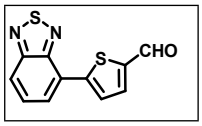
NMR Data:



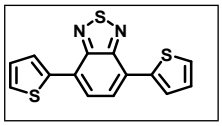
4-(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (3a) : Purified using 5:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (2H, dt); 7.86 (1H, dd); 7.53 (1H, d); 7.31 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.20, 153.73, 136.01, 131.14, 131.01, 129.76, 129.22, 119.73, 113.01. EI-MS [M+H]: 295. HRMS [M+H]: calcd for $C_{10}H_5BrN_2S_2$ 295.9078 found 295.9088.



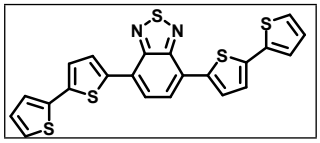
4-(5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3b): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27(2H, dd); 7.91 (1H, dd); 7.80 (1H, d); 7.53 (1H, d); 7.47 (1H, d); 7.43 (1H, s); 7.07-7.01 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.19, 153.83, 137.58, 136.24, 136.01, 131.11, 130.92, 129.23, 126.79, 124.25, 123.89, 122.55, 121.79, 119.70. EI-MS [M+H]: 300. HRMS [M+H]: calcd for $C_{14}H_8N_2S_3$ 300.9922 found 300.9936.



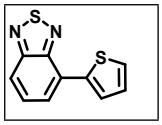
5-(benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carbaldehyde (3c): Purified using 5:2 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (1H, s); 8.34 (1H, dd); 8.20 (1H, dd); 7.94-7.87 (2H, m); 7.85 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.83, 155.17, 153.73, 145.91, 136.14, 136.00, 131.11, 130.95, 129.24, 121.79, 119.81. EI-MS [M+H]: 246; HRMS [M+H]: calcd for $C_{11}H_6N_2OS_2$ 246.99943 found 246.99979.



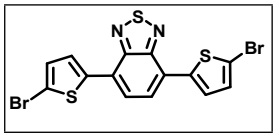
4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3d): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (2H, s); 7.60 (2H, d); 7.56 (2H, d); 7.08 (2H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.92, 135.97, 131.14, 129.97, 129.76, 129.32, 127.62. EI-MS [M+H]: 299; HRMS: [M^+] calcd for $C_{14}H_8N_2S_3$ 299.9846 found 299.9850.



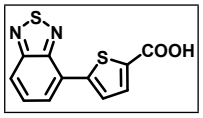
4,7-bis(5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3e): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (2H, s); 7.85 (2H, d); 7.61 (2H, dd); 7.37 (2H, d); 7.22 (2H, dd); 7.03 (2H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.86, 137.58, 136.24, 131.21, 129.24, 126.81, 124.26, 123.89, 122.55, 121.82. EI-MS [M+H]: 464; HRMS: [M^+] calcd for $C_{22}H_{12}N_2S_5$ 463.9604 found 463.9603.



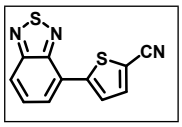
4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3f): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (2H, dd); 7.88 (1H, t); 7.61 (1H, d); 7.57 (1H, d); 7.07 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.19, 153.81, 135.89, 131.13, 130.96, 130.01, 129.84, 129.24, 127.67, 119.82. EI-MS [M+H]: 219; HRMS [M+H]: calcd for $C_{10}H_6N_2S_2$ 219.0045, found 219.0051.



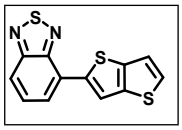
4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (3g): Purified using 10:3 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (2H, s); 7.50 (2H, d); 7.31 (2H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.86, 136.05, 131.14, 129.65,129.22, 113.01. EI-MS [M+H]: 457. HRMS [M+H]: calcd for $C_{14}H_6Br_2N_2S_3$ 457.8033 found 457.8020.



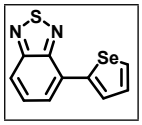
5-(benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carboxylic acid (3h): Purified using 5:2.5 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (1H, dd), 8.19 (1H, dd); 7.95-7.88 (2H, m); 7.85 (1H,d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.79, 155.22, 153.84, 136.03, 134.81, 131.11, 130.96, 129.89, 129.39, 122.01, 119.74. EI-MS [M+H]: 262. HRMS [M+H]: calcd for $C_{11}H_6O_2N_2S_2$ 262.9951 found 262.9938.



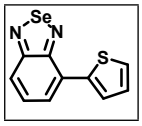
5-(benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carbonitrile (3i): Purified using 5:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (1H, dd); 8.34 (1H, dd); 7.92 (1H, dd); 7.89 (1H, d); 7.83 (1H,d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.21, 153.78, 136.03, 132.61, 131.12, 130.91, 129.24, 119.69, 114.58, 101.33. EI-MS [M+H]: 244. HRMS [M+H]: calcd for $C_{11}H_5N_3S_2$ 243.3075 found 243.3061.



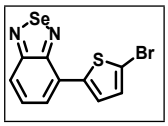
4-(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3j): Purified using 10:3 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (2H, dd); 8.18 (1H, s); 7.90 (1H,dd); 7.69 (1H, d); 7.29 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.12, 153.85, 136.00, 133.02, 131.12, 130.91, 129.23, 128.61, 126.45, 125.37, 119.70. EI-MS [M+H]: 275. HRMS [M^+]: calcd for $C_{12}H_6N_2S_3$ 273.9693 found 273.9691.



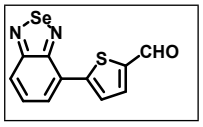
4-(selenophen-2-yl)benzo[c][1,2,5]thiadiazole (3k): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, d); 8.27 (1H, d); 7.82 (1H, t); 7.70 (1H, dd); 7.39 (1H, dd); 7.20 (1H, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.23, 153.79, 144.85, 134.15, 133.25, 131.11, 131.01, 130.71, 129.32, 119.84. EI-MS [M+H]: 266. HRMS [M$^+$]: calcd for $C_{12}H_6N_2S_3$ 265.9421 found 265.9417.



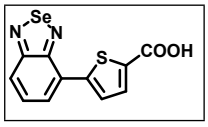
4-(thiophen-2-yl)benzo[c][1,2,5]selenadiazole (3l): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (1H, dd); 8.06 (1H, dd); 7.88 (1H, t); 7.62 (1H, dd); 7.59 (1H, d); 7.09 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.12, 153.81, 136.03, 131.13, 130.93, 129.98, 129.24, 127.63, 119.74. EI-MS [M+H]: 266. HRMS [M$^+$]: calcd for $C_{12}H_6N_2S_3$ 265.9421 found 265.9417.



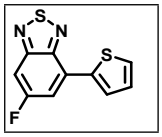
4-(5-bromothiophen-2-yl)benzo[c][1,2,5]selenadiazole (3m): Purified using 5:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dd); 8.19 (1H, dd); 7.83 (1H, t); 7.55 (1H, d); 7.07 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14, 153.81, 135.89, 131.09, 130.88, 129.86, 129.34, 113.01. EI-MS [M+H]: 345. HRMS [M$^+$]: calcd for $C_{12}H_6N_2S_3$ 343.8522 found 343.8515.



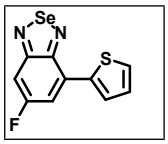
5-(benzo[c][1,2,5]selenadiazol-7-yl)thiophene-2-carbaldehyde (3n): Purified using 5:2 Hexane-EtOAc mixture via column chromatography.^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (1H, s); 8.92 (1H, dd); 8.11 (1H, dd); 7.95 (1H, dd); 7.91 (1H, d); 7.83 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.83, 159.13, 153.84, 145.19, 136.14, 136.01, 131.21, 130.95, 129.32, 121.77, 119.82. EI-MS [M+H]: 294. HRMS [M$^+$]: calcd for $C_{11}H_6N_2OSSe$ 293.9366 found 293.9371.



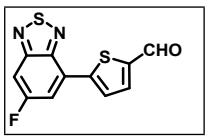
5-(benzo[c][1,2,5]selenadiazol-7-yl)thiophene-2-carboxylic acid (3o): Purified using 2:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (1H, dd); 8.12 (1H, dd); 7.93 (1H, dd); 7.90 (1H, d); 7.82 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.79, 159.12, 153.85, 135.89, 134.81, 131.12, 130.95, 129.86, 129.22, 121.86, 119.68. EI-MS [M+H]: 310. HRMS [M$^+$]: calcd for $C_{11}H_6N_2O_2SSe$ 309.9320 found 309.9316.



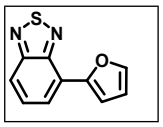
6-fluoro-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3p): Purified using 5:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (1H, d); 7.89 (1H, d); 7.58 (2H, m); 7.05 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.61, 155.21, 153.84, 135.93, 130.00, 129.76, 129.21, 127.64, 119.16, 102.51. EI-MS [M+H]: 237. HRMS [M$^+$]: calcd for $C_{10}H_5FN_2S_2$ 235.9876 found 235.9871.



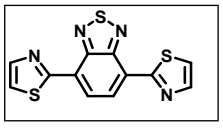
6-fluoro-4-(thiophen-2-yl)benzo[c][1,2,5]selenadiazole (3q): Purified using 5:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (1H, d); 811 (1H, d); 7.60 (1H, dd); 7.55 (1H, dd); 7.08 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.67, 159.12, 153.84, 135.89, 129.97, 129.76, 129.23, 127.63, 119.13, 102.49. EI-MS [M+H]: 284. HRMS [M$^+$]: calcd for $C_{10}H_5FN_2SSe$ 283.9317 found 283.9321.



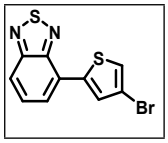
5-(5-fluorobenzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carbaldehyde (3r): Purified using 5:2 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (1H, s); 8.31 (1H, d); 7.82 (1H, d); 7.68 (1H, d); 7.38 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.83, 170.61, 155.20, 153.87, 145.19, 136.14, 129.21, 121.79, 119.15, 102.51. EI-MS [M+H]: 265. HRMS [M$^+$]: calcd for $C_{11}H_5FN_2OS_2$ 263.9827 found 263.9821.



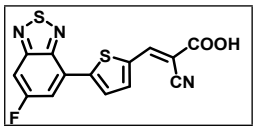
4-(furan-2-yl)benzo[c][1,2,5]thiadiazole (3s): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, dd); 8.25 (1H, dd); 7.97 (1H, d); 7.83 (1H, t); 7.08 (1H, d); 6.53 (1H, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.31, 153.89, 150.18, 143.62, 131.14, 130.92, 129.18, 119.81, 111.84, 111.36. EI-MS [M+]: 202. HRMS [M$^+$]: calcd for $C_{10}H_6N_2OS$ 202.0201 found 202.0199.



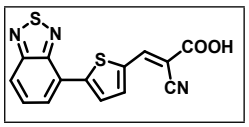
4,7-di(thiazol-2-yl)benzo[c][1,2,5]thiadiazole (3t): Purified using 5:1 Hexane-DCM mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (2H, s); 7.71 (2H, d); 7.34 (2H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.51, 153.92, 141.31, 131.11, 129.24, 115.49. EI-MS [M+H]: 303. HRMS [M+H]: calcd for $C_{10}H_6N_2OS$ 302.9827 found 302.9833.



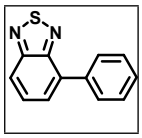
4-(4-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (3u): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.24 (2H, m); 7.88 (1H, t); 7.56 (1H, d); 7.16 (1H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.21, 153.83, 136.01, 131.09, 130.92, 129.24, 129.01, 123.84, 119.81, 109.15. EI-MS [M+H]: 295. HRMS [M+H]: calcd for $C_{10}H_5BrN_2S_2$ 295.9078, found 295.9088.



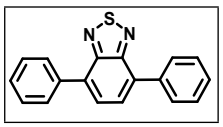
(E)-2-cyano-3-(5-(5-fluorobenzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylic acid (4a): Purified using dichloromethane via column chromatography and further recrystallized from hexane ethanol mixture and 0˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (1H, s); 8.62 (1H, d); 8.12 (1H, d); 7.86 (2H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.60, 163.01, 155.21, 153.91, 146.78, 140.05, 136.00, 134.30, 129.22, 121.81, 119.13, 102.85, 102.50. EI-MS [M+H]: 331 HRMS [M+H]: calcd for $C_{14}H_6FN_3O_2S_2$ 330.9885, found 330.9879.



(E)-3-(5-(benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (4b): Purified using dichloromethane via column chromatography and further recrystallized from hexane ethanol mixture and 0˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (1H, s); 8.78 (1H, d); 8.35 (1H, d); 8.01-8.06 (2H, m); 7.81-7.95 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.00, 155.21, 153.84, 146.80, 140.10, 136.01, 134.31, 131.09, 130.90, 129.24, 121.79, 119.69, 114.91, 102.86. EI-MS [M+H]: 313 HRMS [M+H]: calcd for $C_{14}H_7N_3O_2S_2$ 312.9980, found 312.9977.

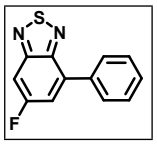


4-phenylbenzo[c][1,2,5]thiadiazole (3v): Purified using 10:0.1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (1H, dd); 8.15 (1H, dd); 8.01-7.95 (1H, m); 7.66 (2H, dd); 7.55-7.43 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.20, 153.95, 132.71, 131.15, 130.95, 129.31, 128.93, 128.58, 127.51, 119.69. EI-MS [M+H]: 213. HRMS: $[M + H]^+$ calcd for $C_{12}H_8N_2S$: 213.0481, found: 213.0485.

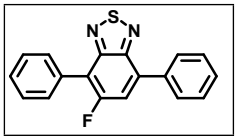


4,7-diphenylbenzo[c][1,2,5]thiadiazole (3w): Purified using Hexane solvent via column chromatography.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (2H, s); 7.85 (4H, dd); 7.52 (6H, ddd).

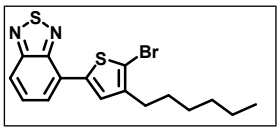
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.94, 132.86, 131.09, 129.19, 128.94, 128.61, 127.48. EI-MS [M+H]: 289. HRMS: $[M]^+$ calcd for $C_{18}H_{12}N_2S$ 288.0722, found 288.0723



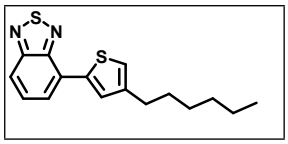
6-fluoro-4-phenylbenzo[c][1,2,5]thiadiazole (3x): Purified using 10:0.2 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (1H, s); 8.03 (1H, s); 7.92 (2H, d); 7.58-7.47 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.58, 155.08, 153.86, 132.73, 129.18, 128.93, 128.61, 127.49, 119.09, 102.51. EI-MS [M+H]: 231. HRMS: $[M+H]^+$ calcd for $C_{12}H_7FN_2S$ 231.0348 found 231.0342.



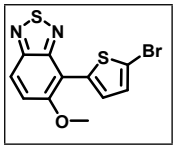
5-fluoro-4,7-diphenylbenzo[c][1,2,5]thiadiazole (3y): Purified using Hexane solvent via column chromatography.^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.82 (1H, s); 7.71 (2H, d); 7.52 (2H, dd); 7.49-7.47 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.86, 149.91, 132.73, 129.17, 128.94, 128.60, 127.53, 119.15. EI-MS [M+H]: 307. HRMS: $[M]^+$ calcd for $C_{18}H_{11}FN_2S$ 306.0627 found 306.0633.



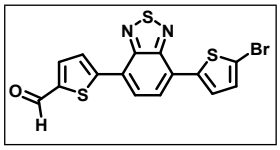
4-(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3z): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.17-8.26 (2H, m); 7.88 (1H, dd); 7.59 (1H, s); 2.83 (2H, t); 1.65 (2H,tt); 1.15-1.37 (6H, m); 0.87 (3H, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ155.23, 153.84, 136.02, 131.12, 130.93, 129.24, 25.05, 19.70, 108.48, 32.41, 30.09, 28.89, 28.64, 22.62, 13.99. EI-MS [M+H]: 383. HRMS: $[M]^+$ calcd for $C_{16}H_{17}BrN_2S_2$ 381.9900 found 382.0022.



4-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3aa): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.22-8.30 (2H, m); 7.87 (1H, dd); 7.81 (1H, d); 7.53 (1H, d); 2.55 (2H, t); 1.61 (2H,tt); 1.15-1.37 (6H, m); 0.88 (3H, t). ^{13}C NMR (100 MHz, $CDCl_3$): 155.18, 153.86, 137.43, 135.98, 131.15, 130.95, 129.27, 123.93, 119.68, 32.40, 30.63, 30.31, 28.85, 22.59, 13.97. EI-MS [M+H]: 303. HRMS: $[M]^+$ calcd for $C_{16}H_{18}N_2S_2$ 303.0984 found 303.0958.

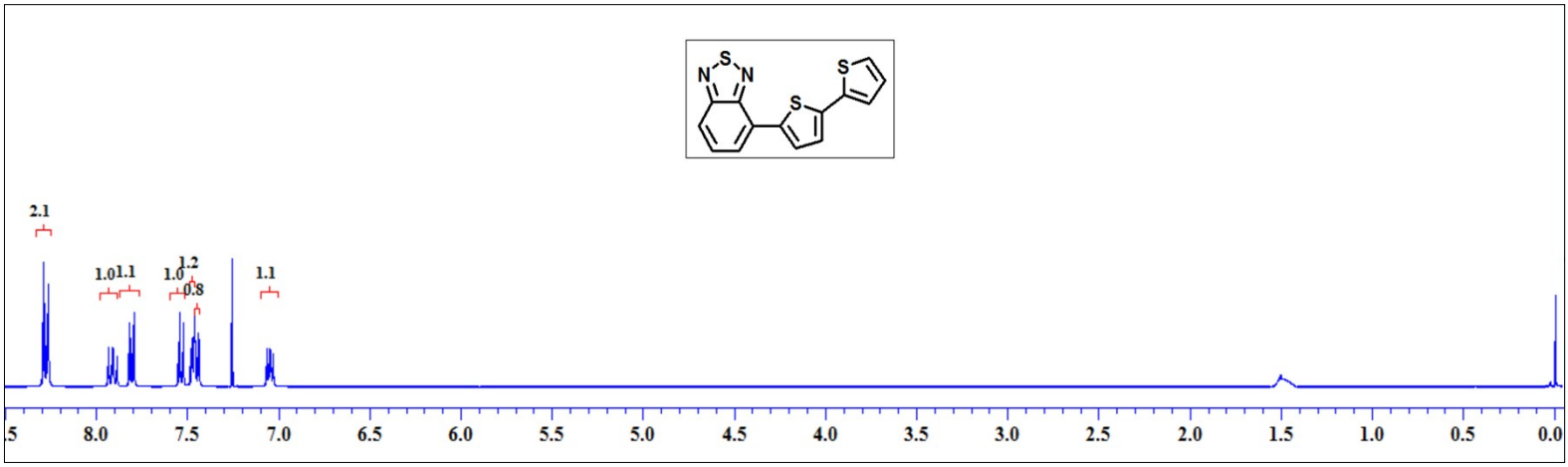


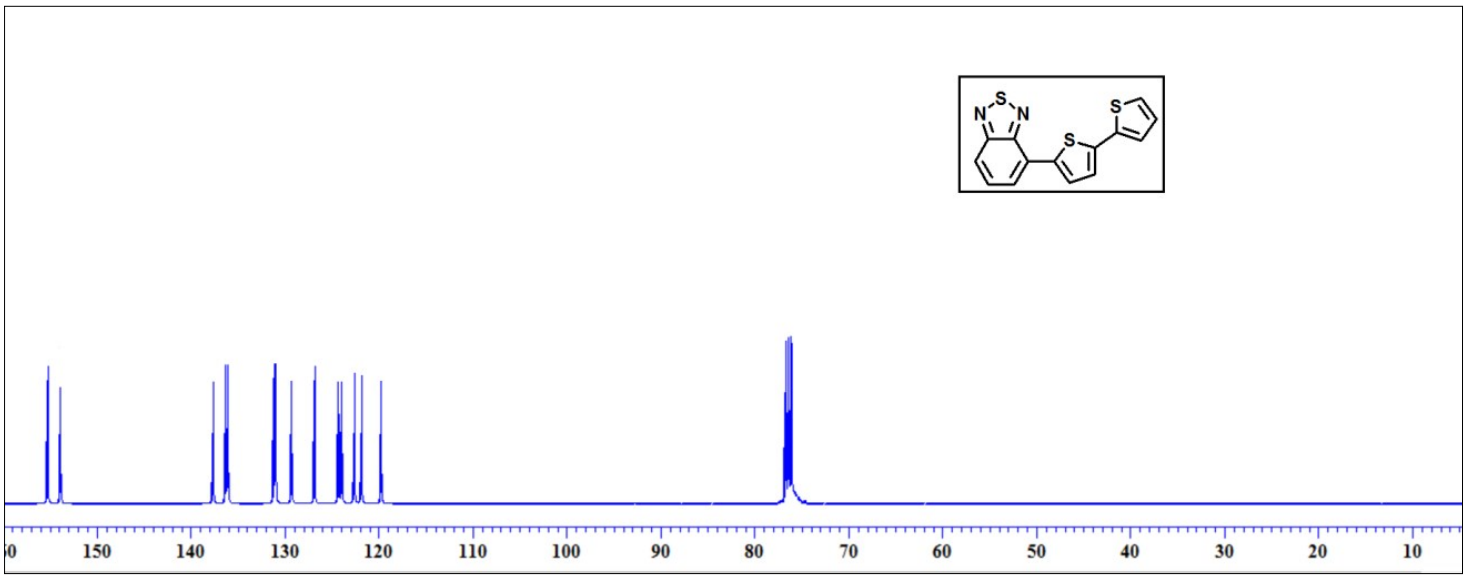
4-(5-bromothiophen-2-yl)-5-methoxybenzo[c][1,2,5]thiadiazole (3ab): Purified using 10:0.5 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.84 (1H, d); 7.74 (1H, d); 7.24 (2H, dd); 3.77 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.19, 155.19, 153.84, 136.01, 129.77, 129.23, 123.60, 119.70, 113.01, 56.83. EI-MS [M+H]: 327. HRMS: $[M+H]^+$ calcd for $C_{11}H_7BrN_2OS_2$ 326.9256 found 326.9248.

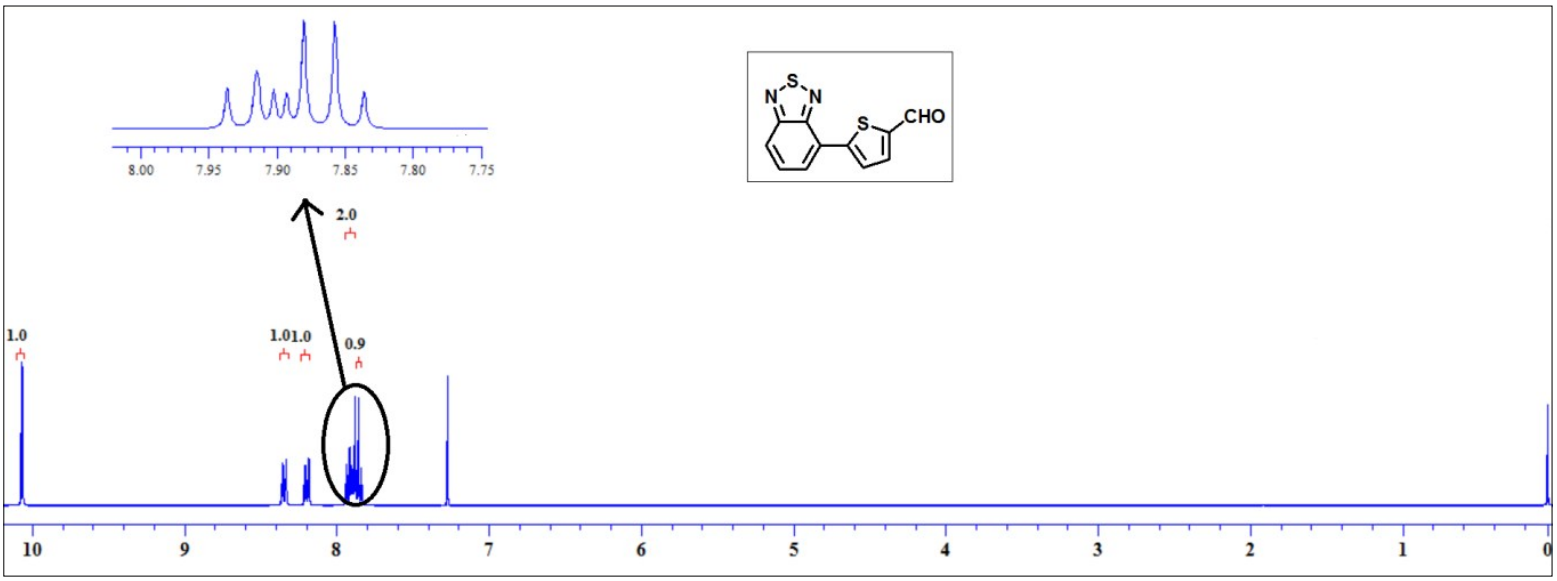


5-(4-(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carbaldehyde (3ac): Purified using 10:1 Hexane-EtOAc mixture via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 10.07 (1H, s); 8.46 (1H, d); 8.25 (1H, d); 7.98 (1H, d); 7.80 (1H, d); 7.58 (1H, d); 7.34 (1H, d) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.84, 153.85, 145.19, 136.13, 136.02, 131.1, 129.78, 129.26, 121.80, 113.01. EI-MS [M+H]: 407. HRMS: $[M+H]^+$ calcd for $C_{15}H_7BrN_2OS_3$ 406.8979 found 406.8990.

Copies of ^{1}H NMR and ^{13}C NMR:



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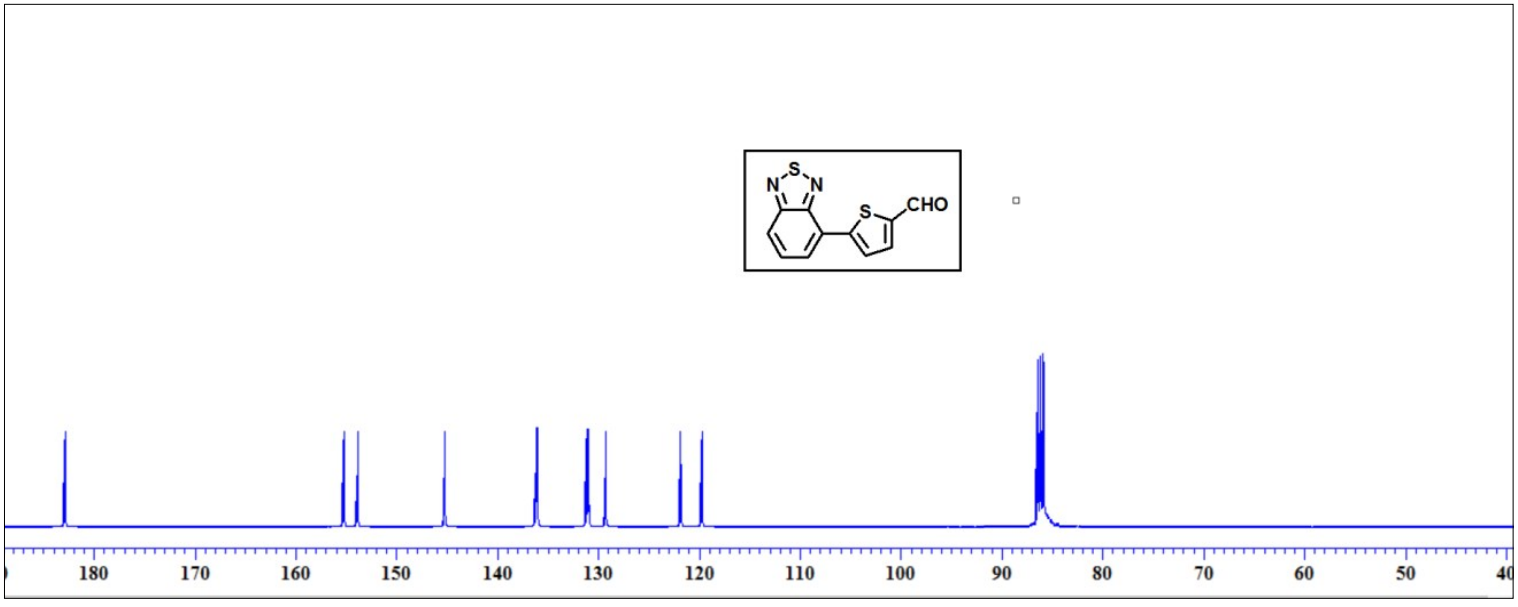
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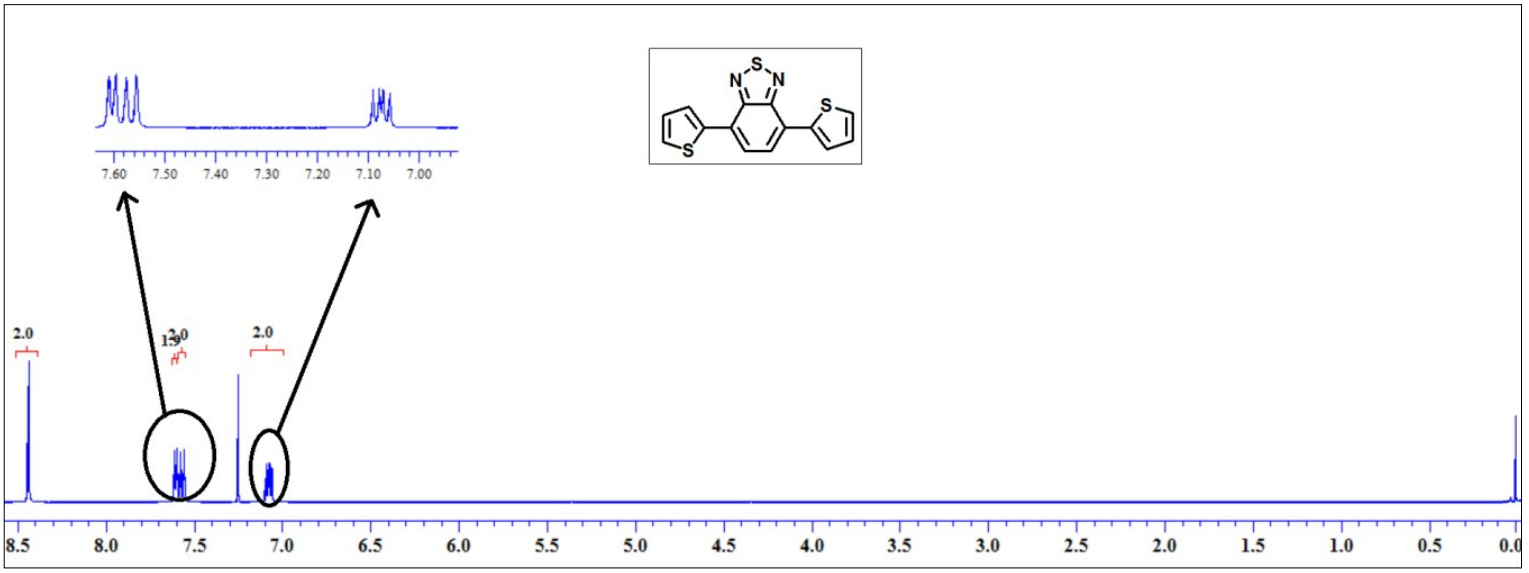
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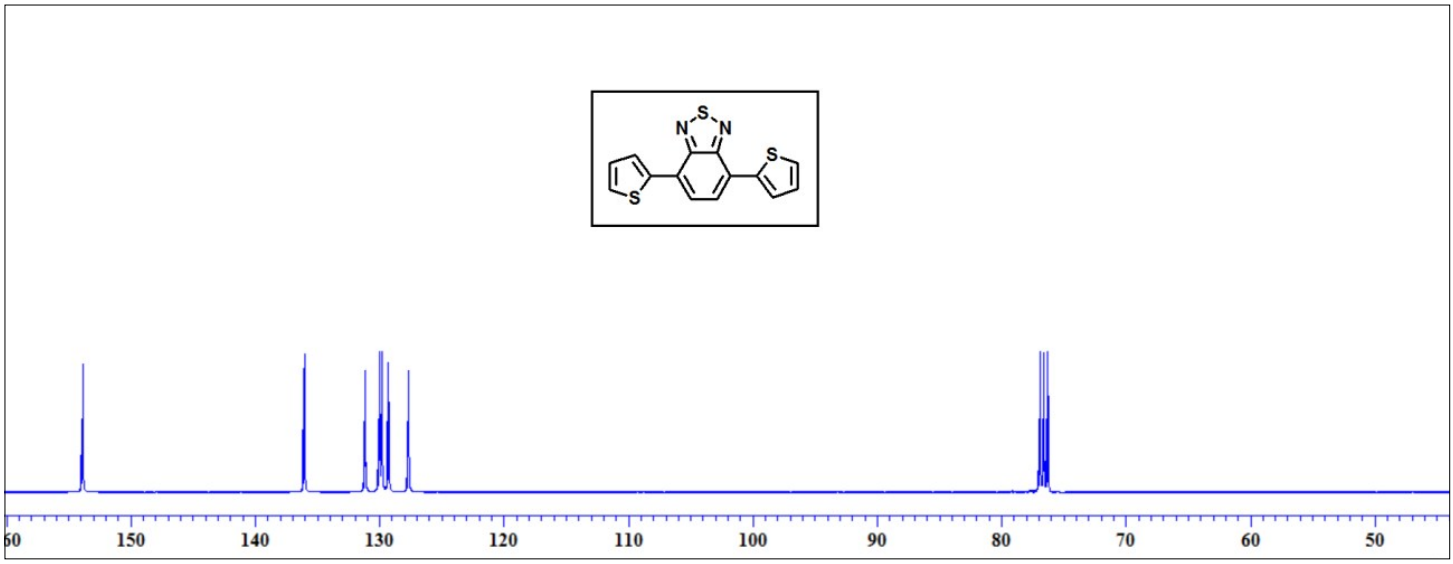
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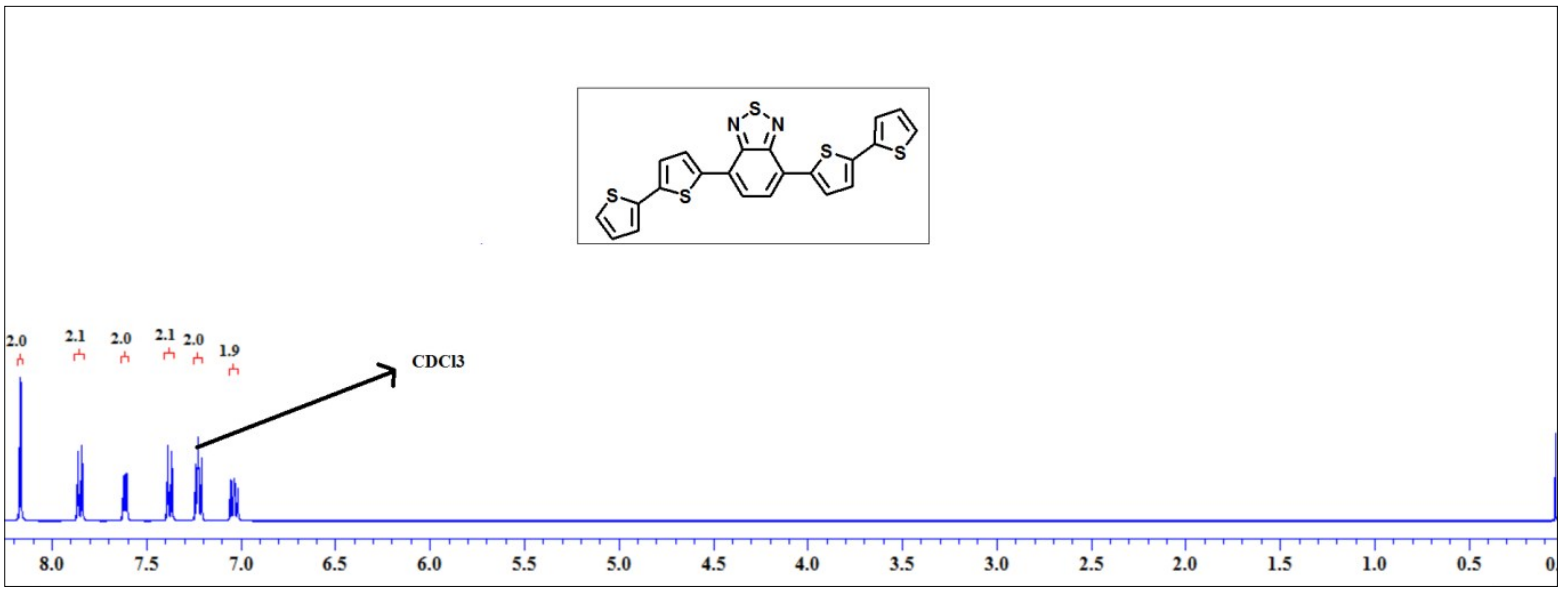
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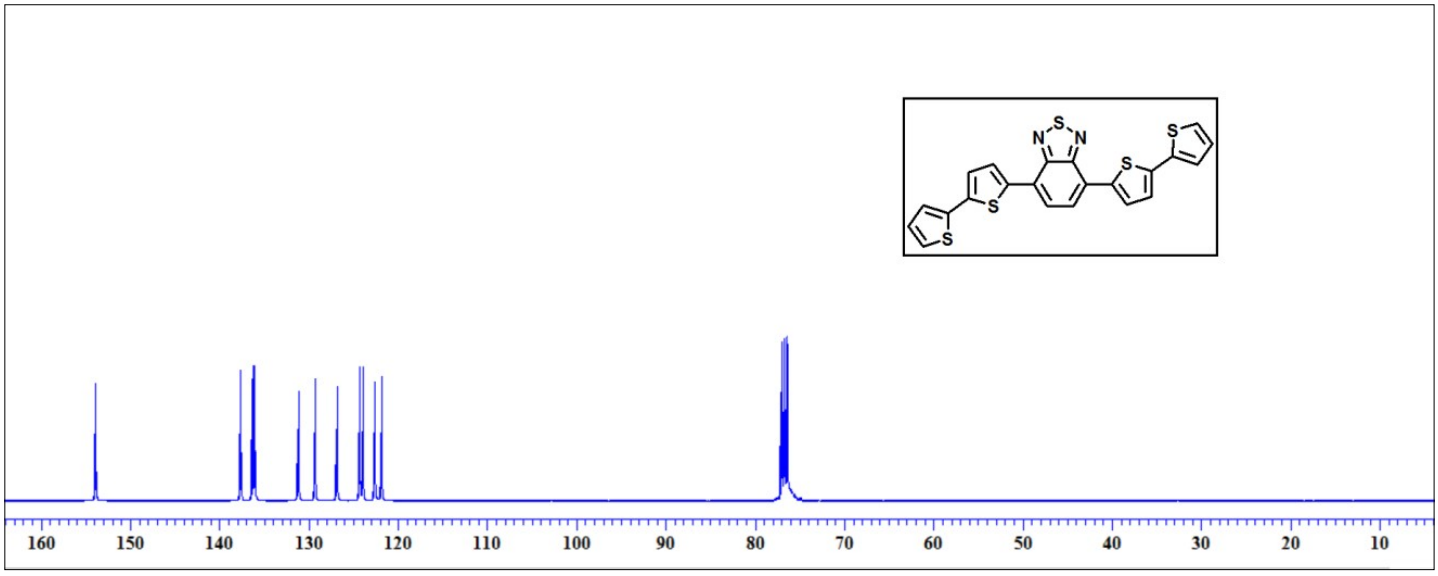
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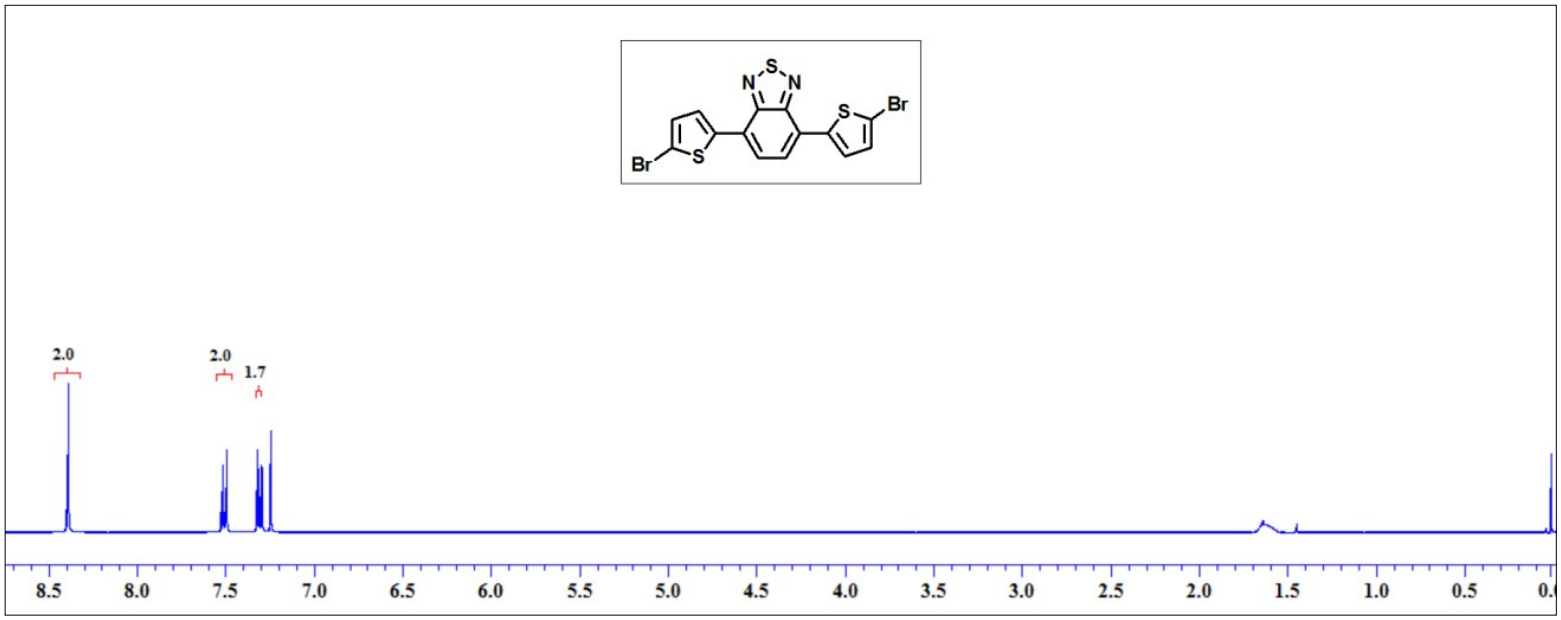
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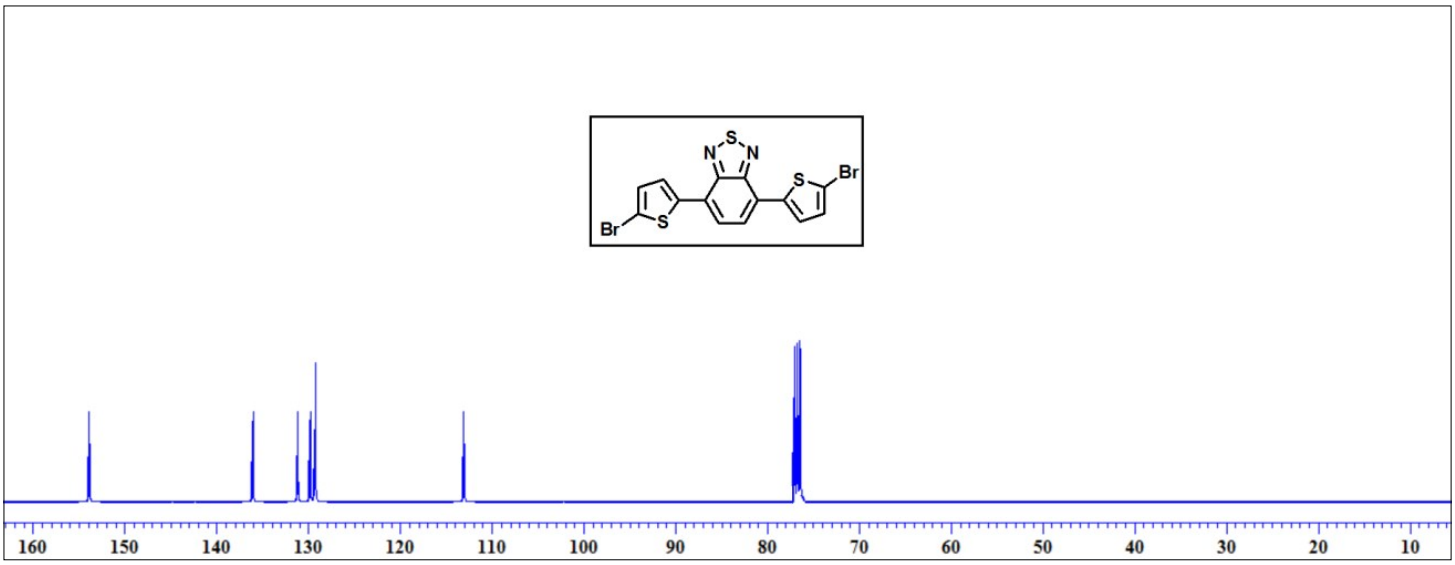
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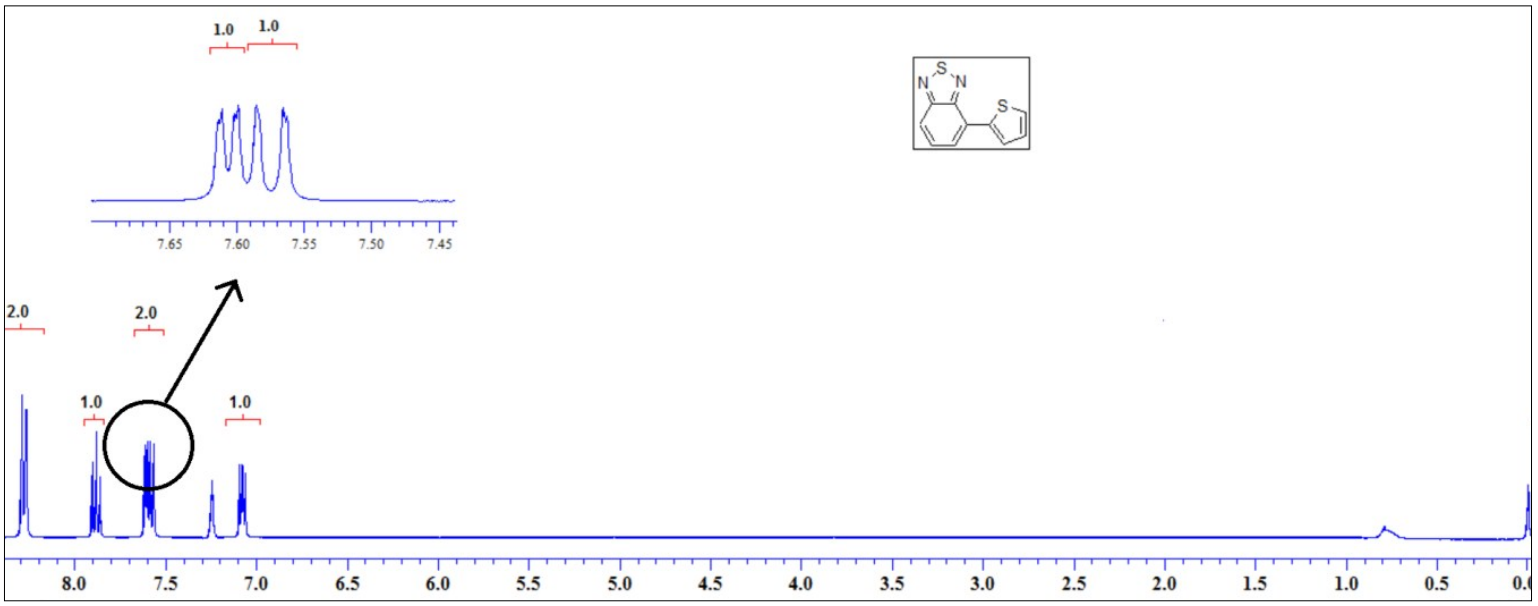
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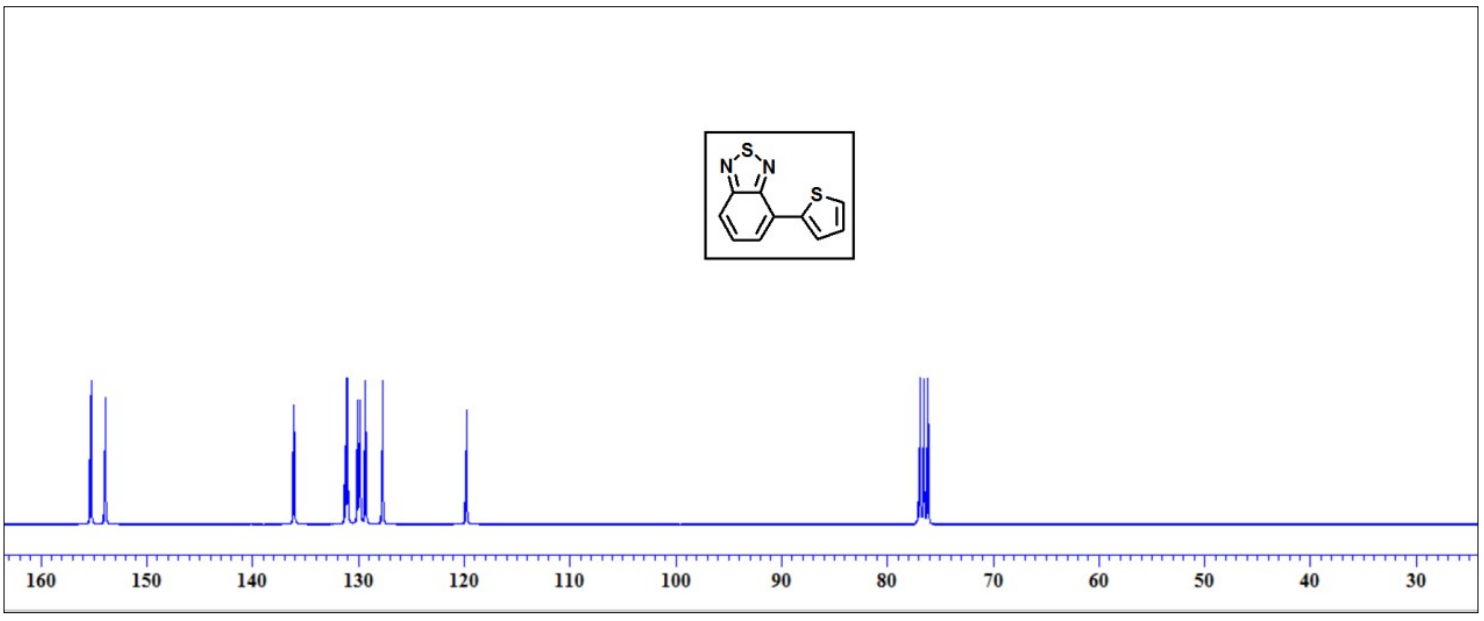
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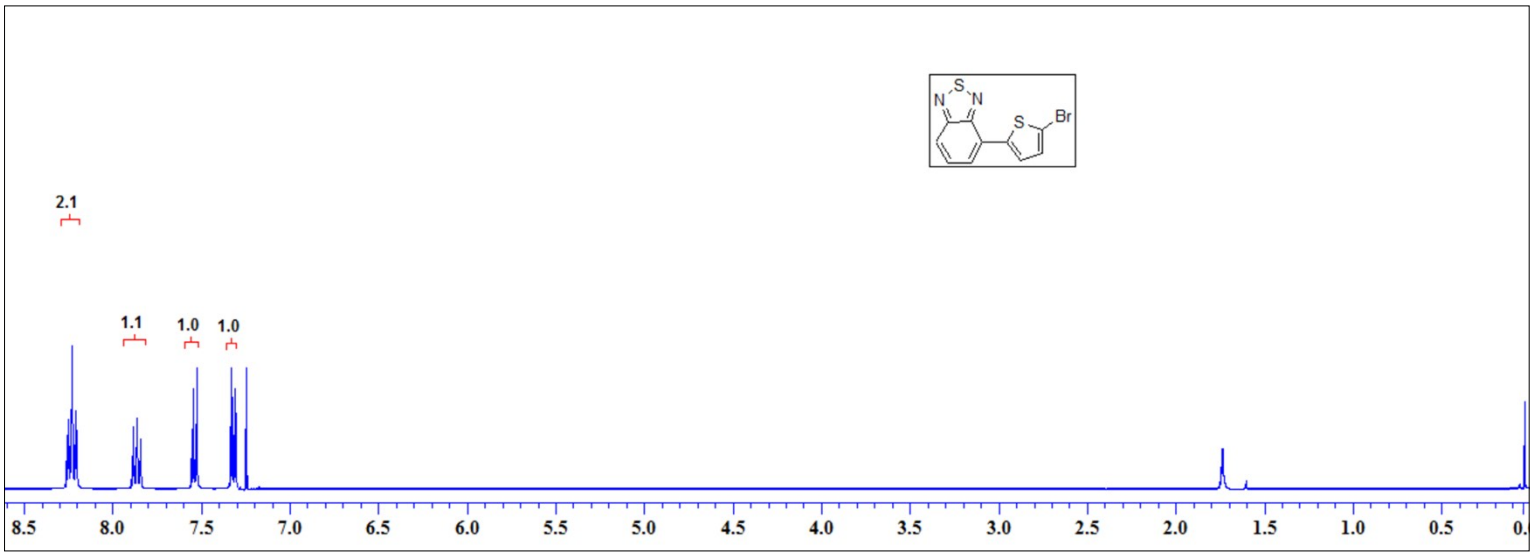
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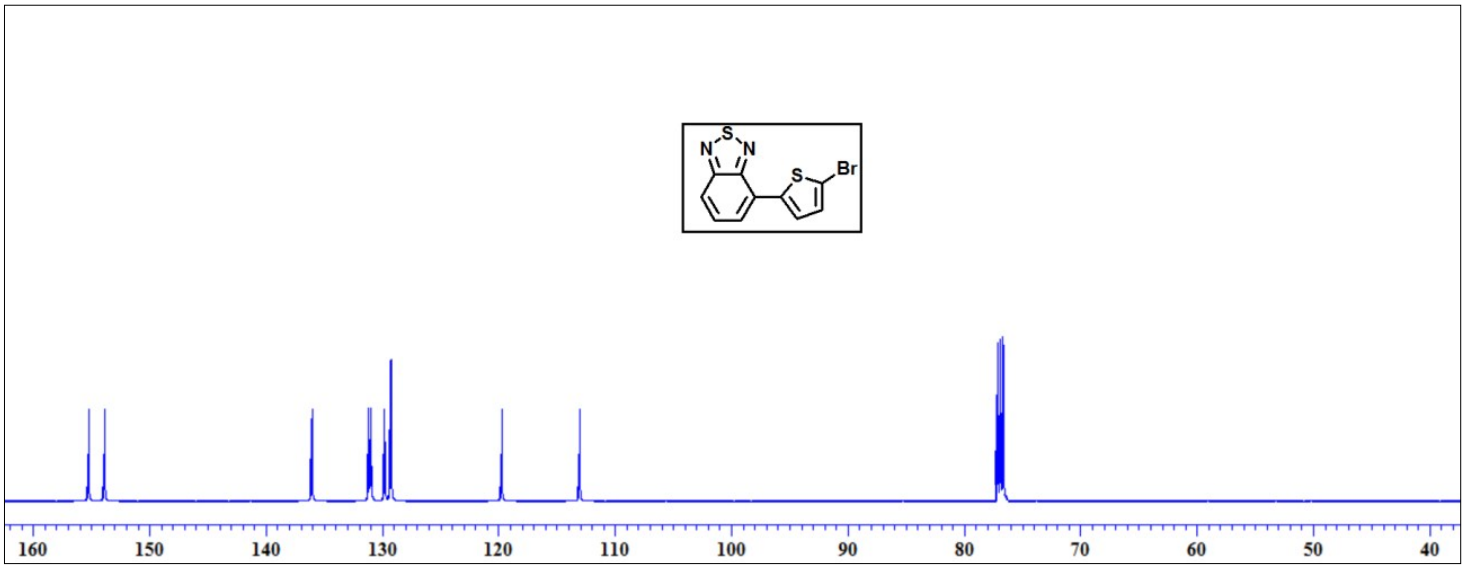
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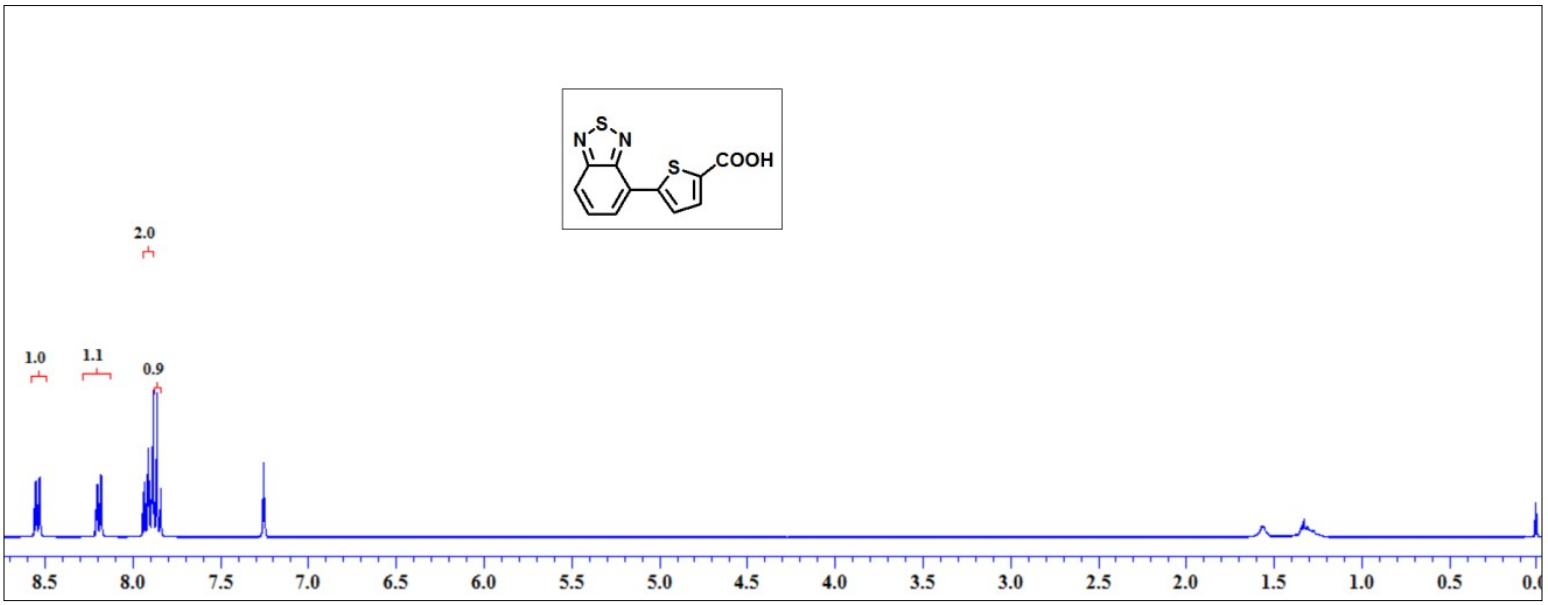
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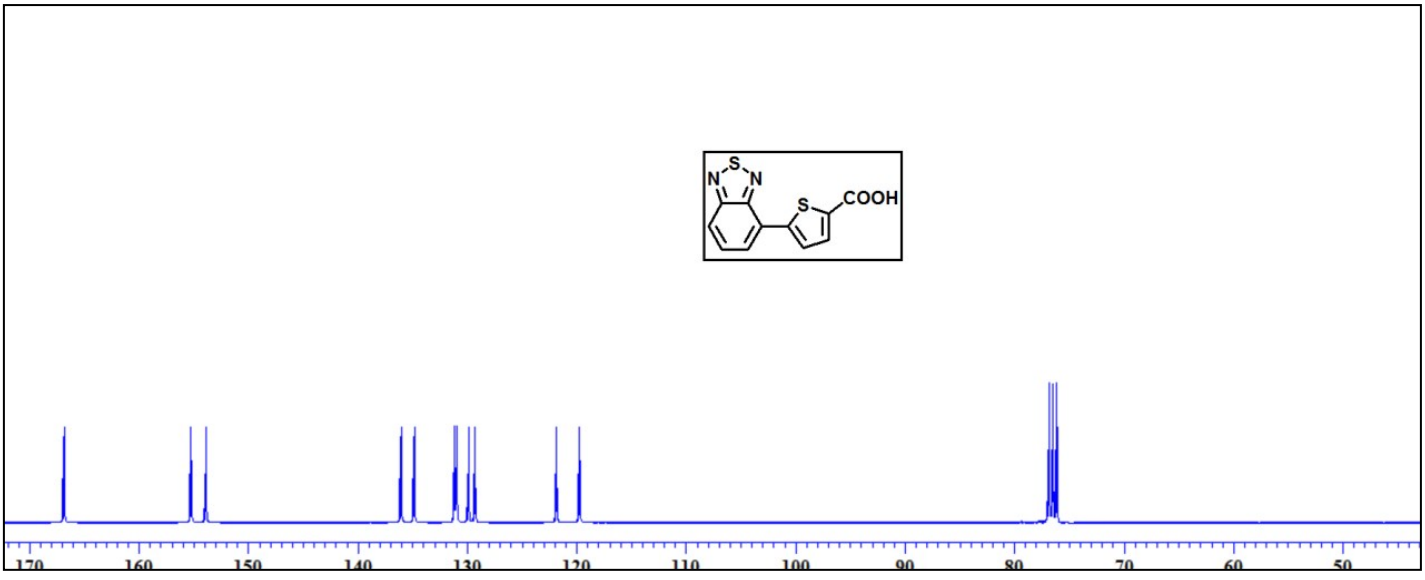
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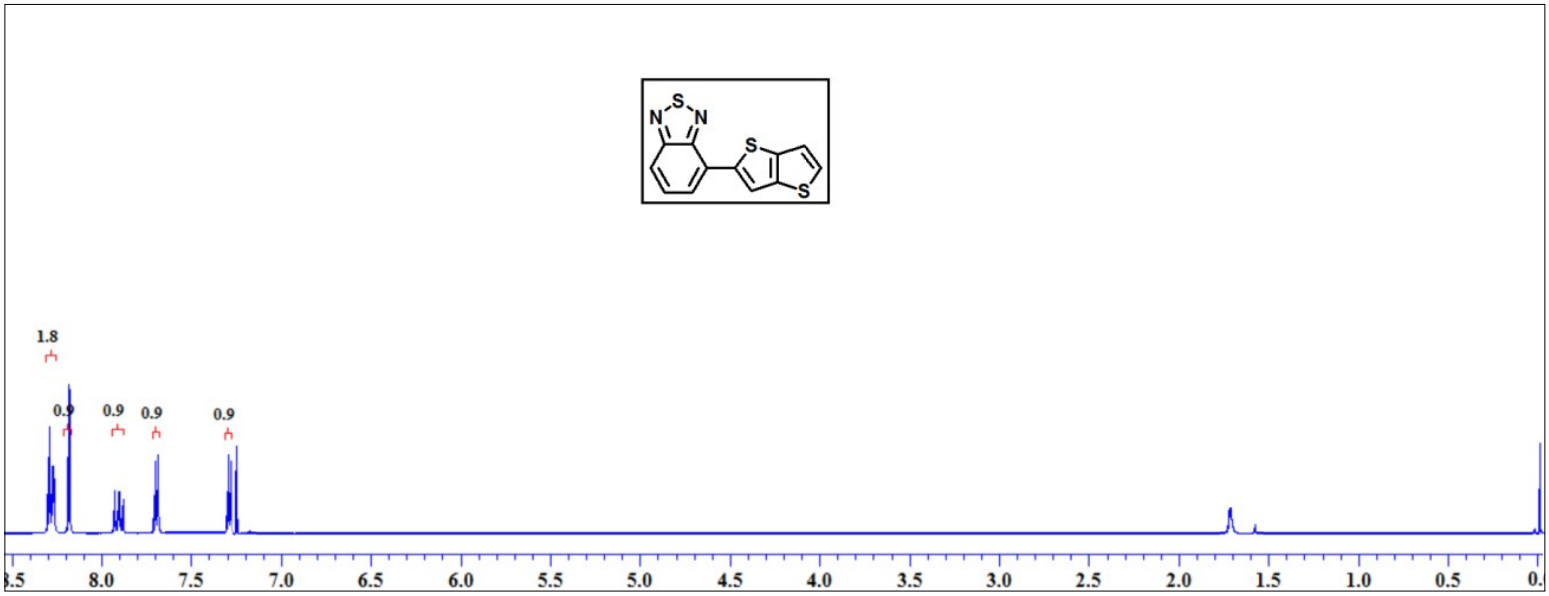
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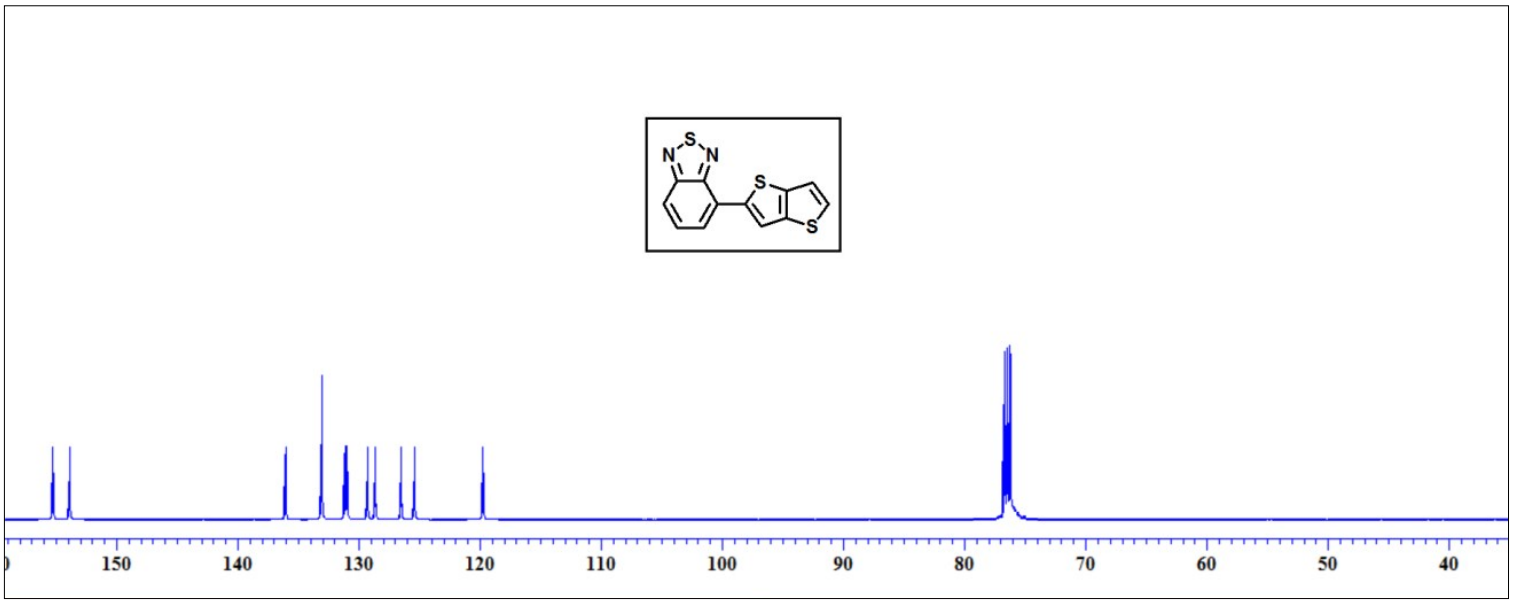
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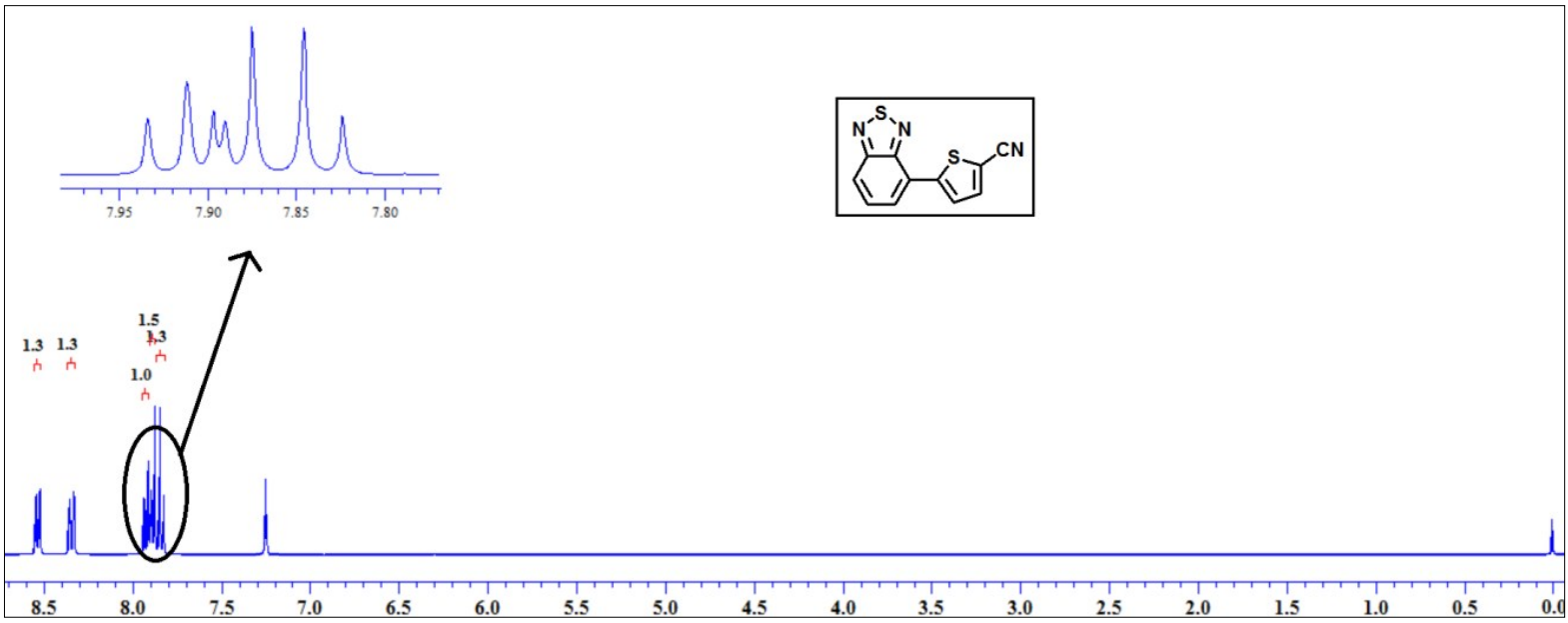
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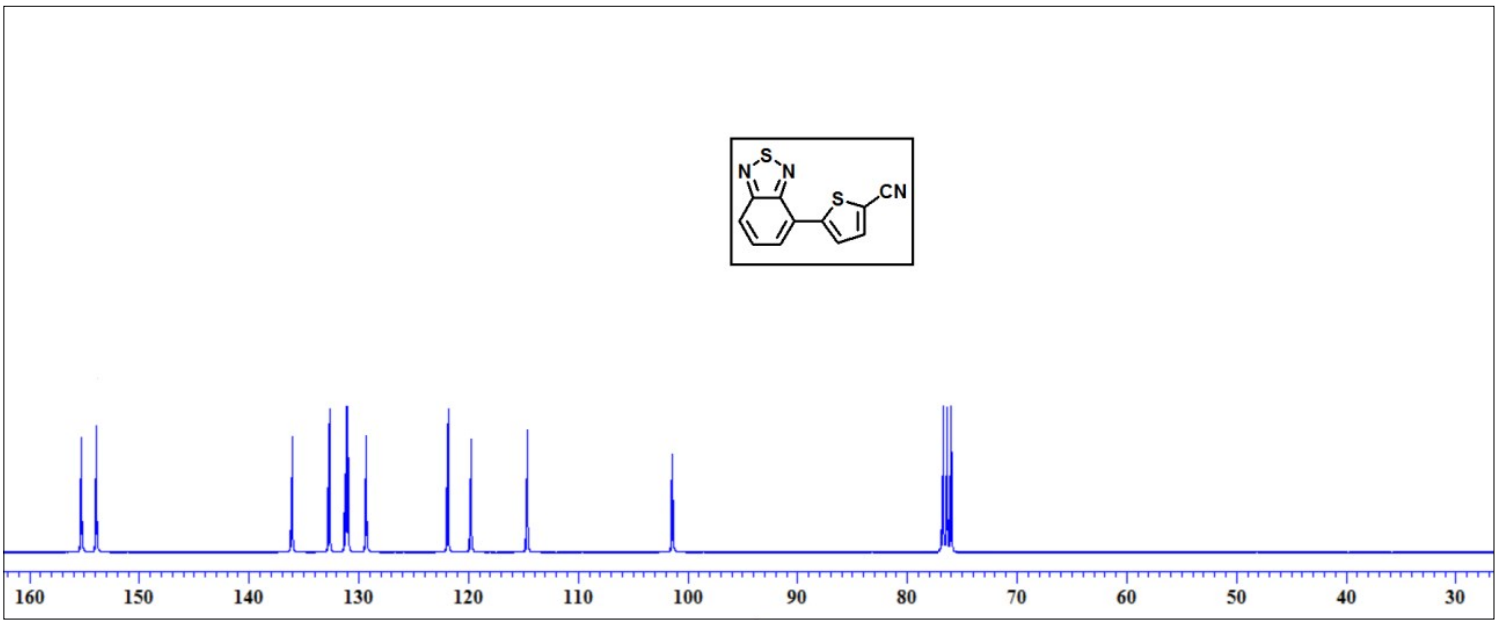
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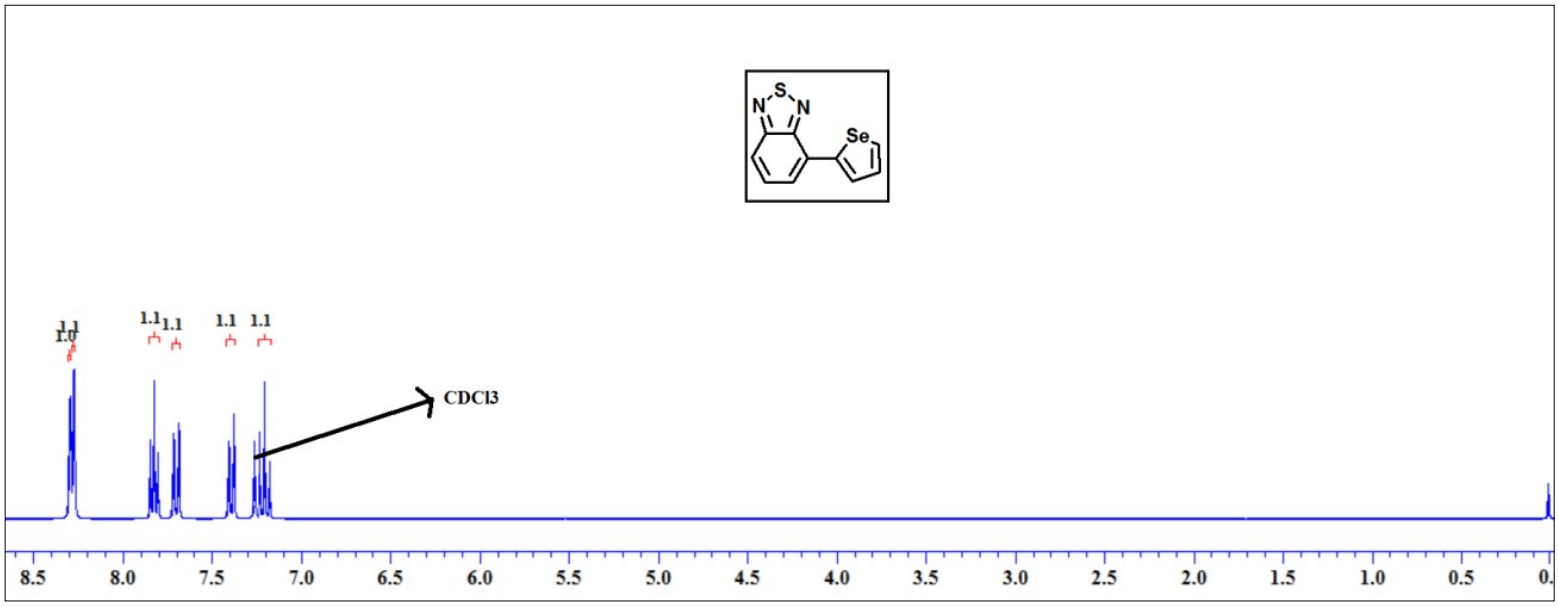
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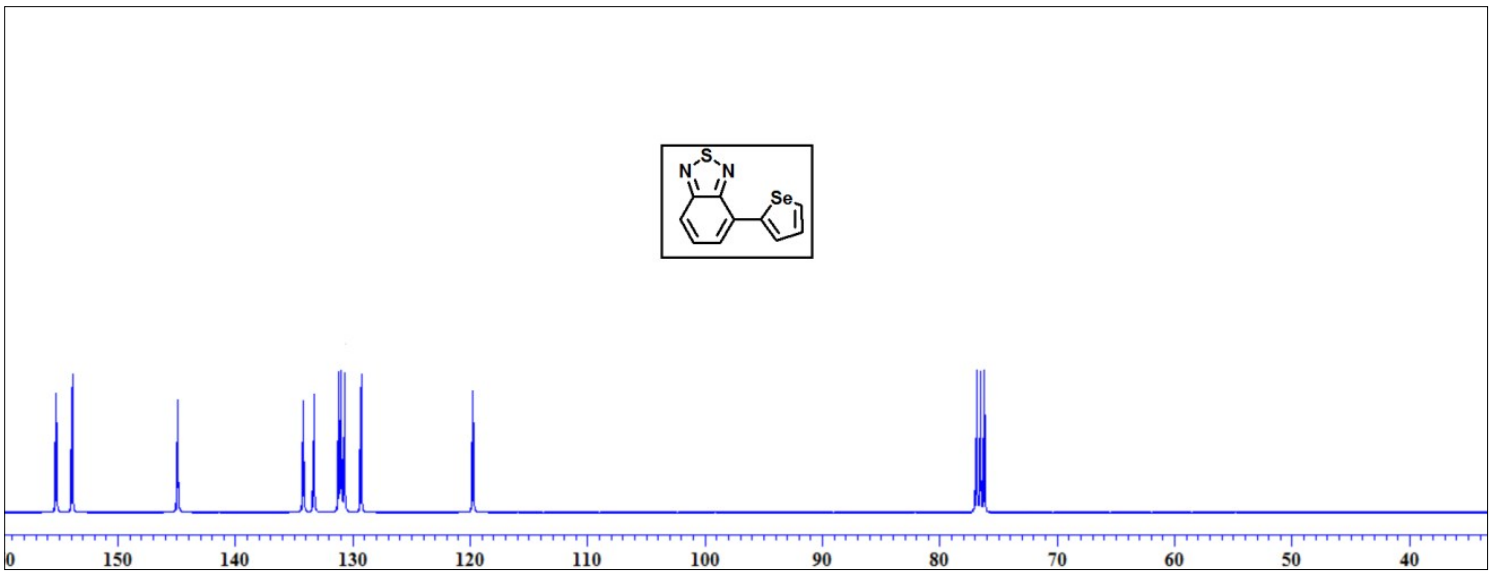
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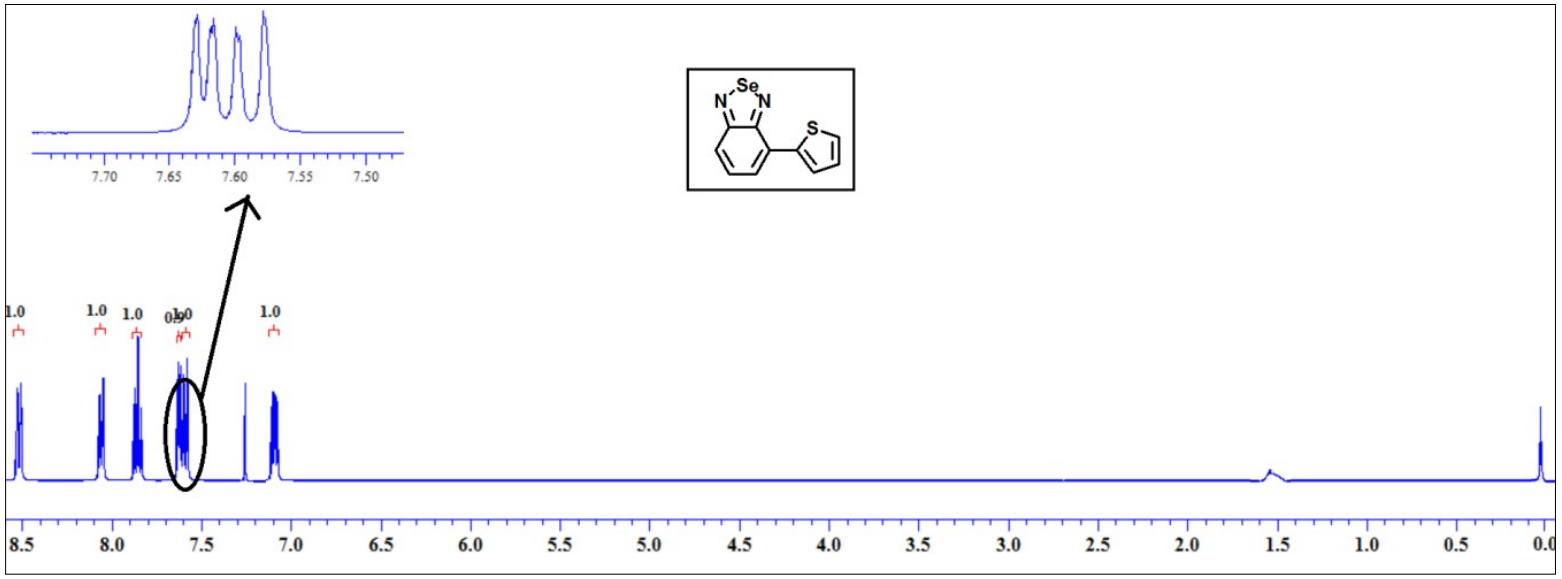
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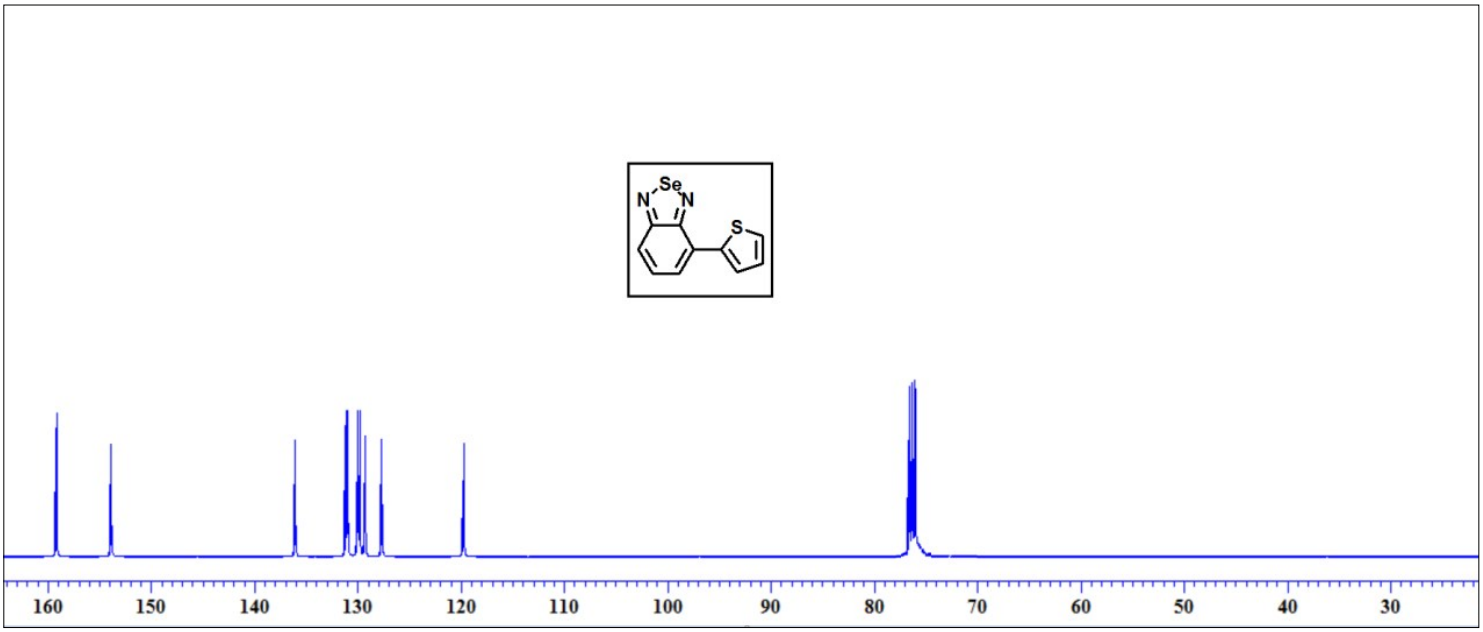
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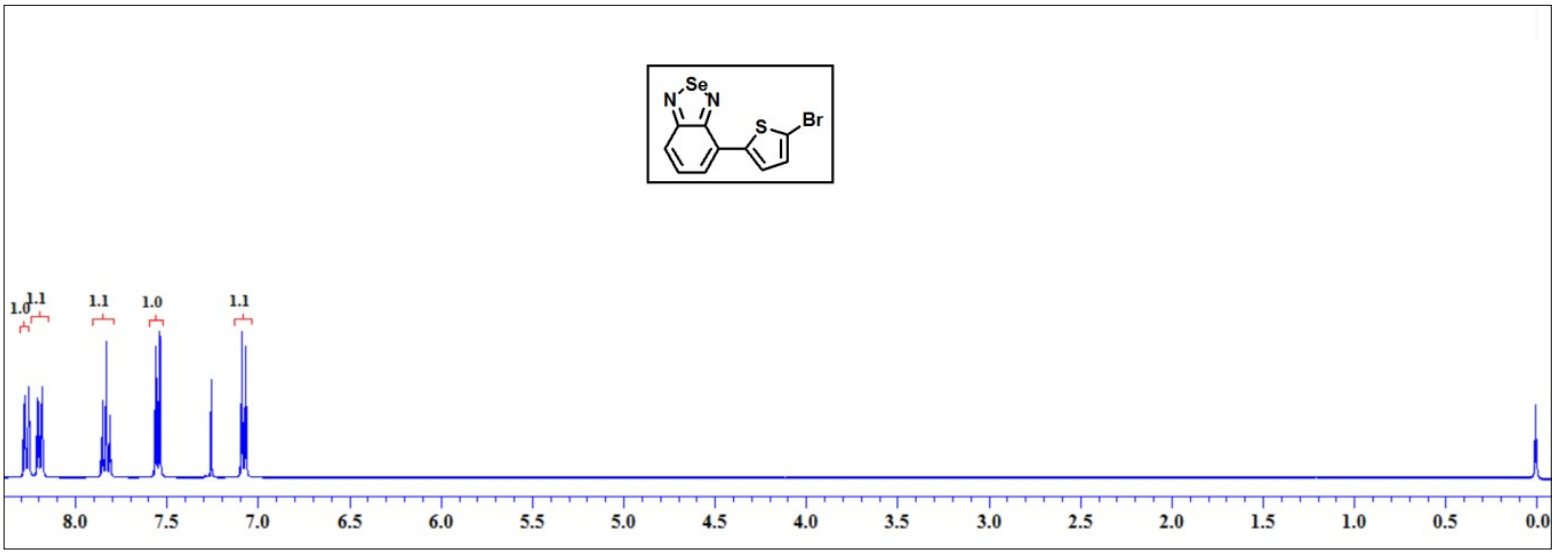
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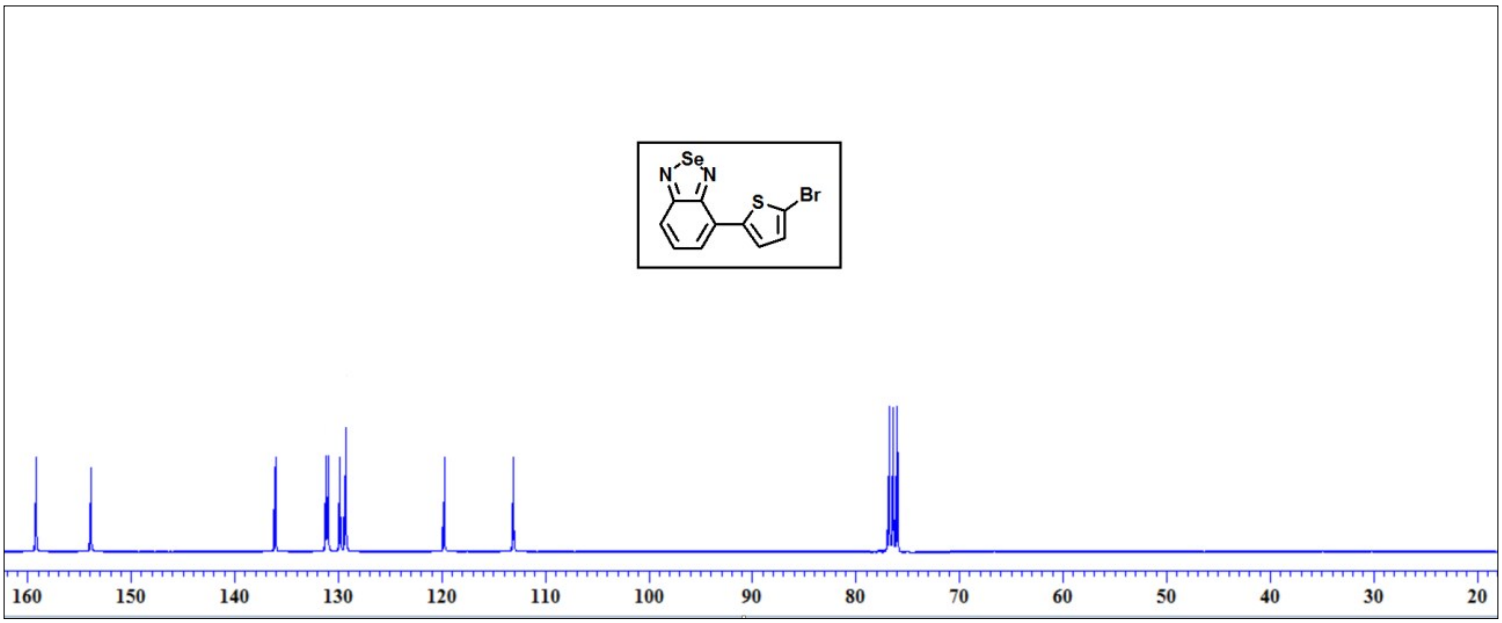
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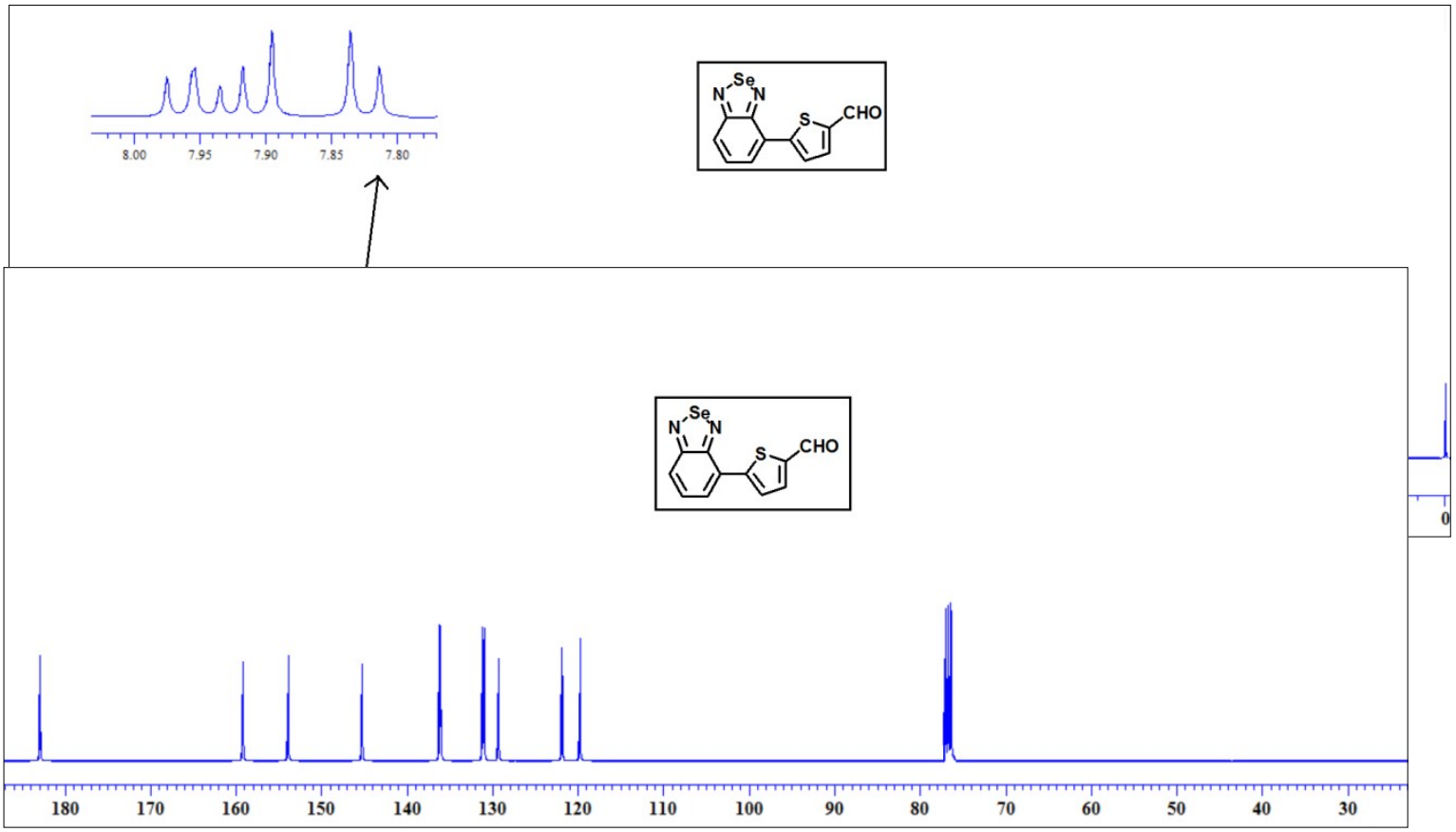
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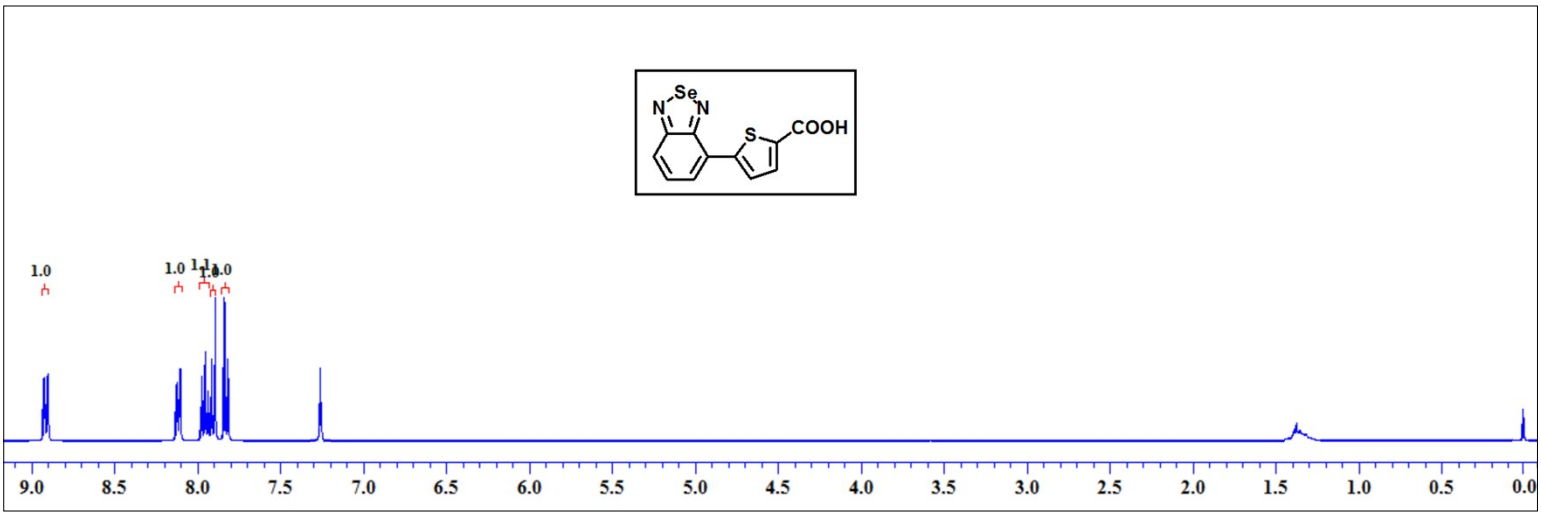
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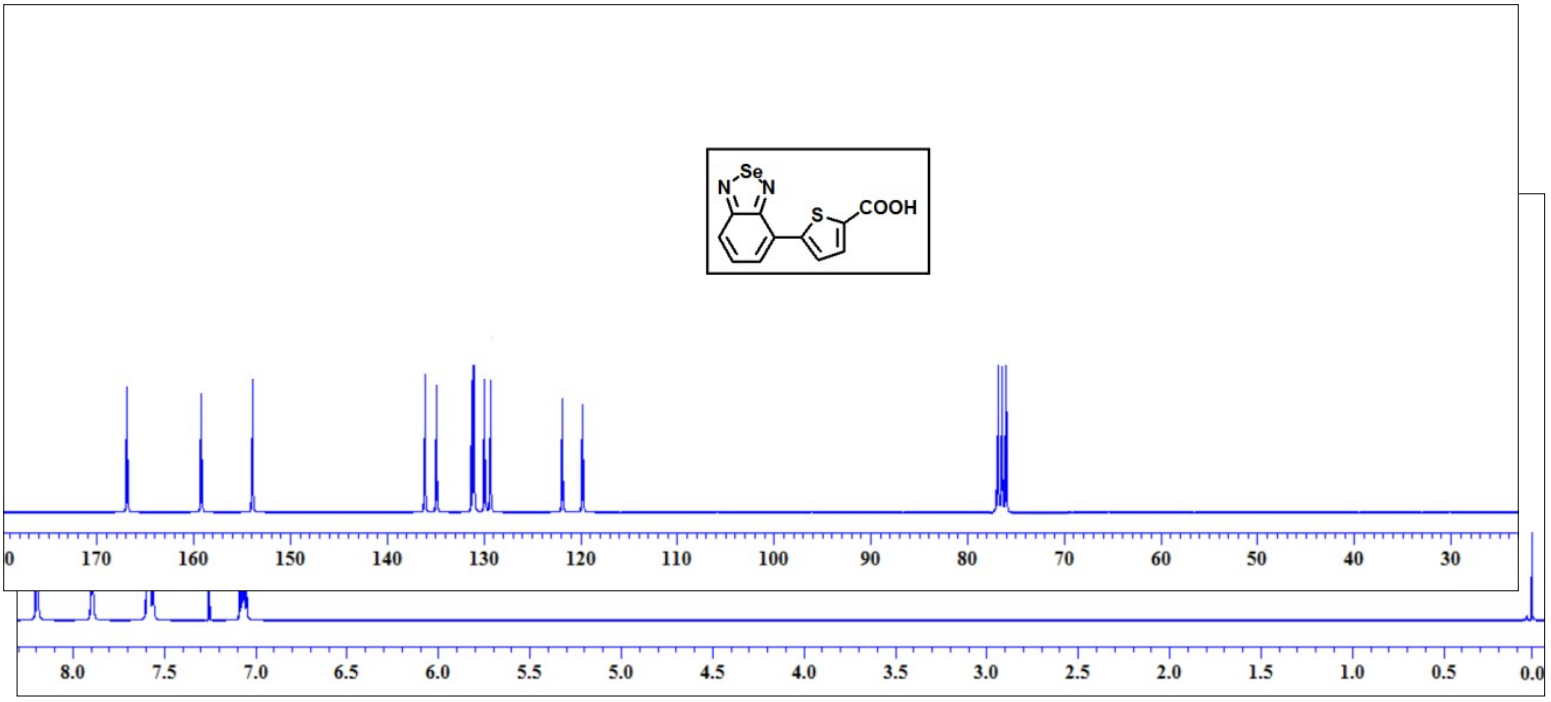
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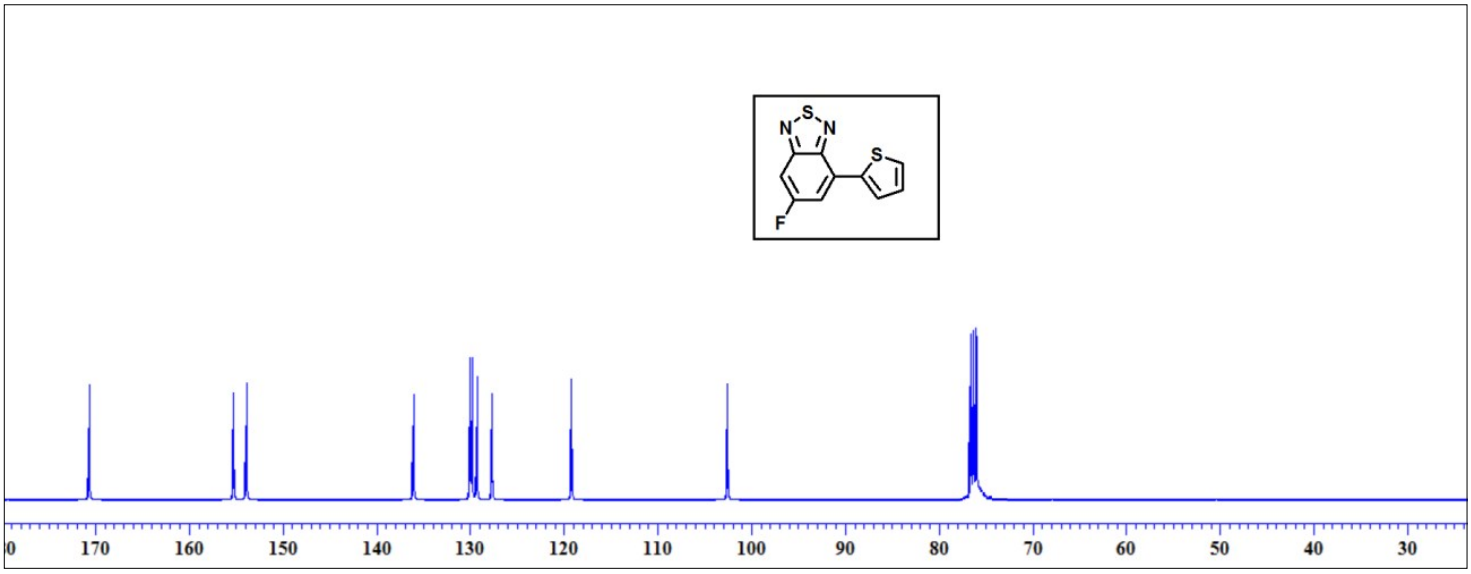
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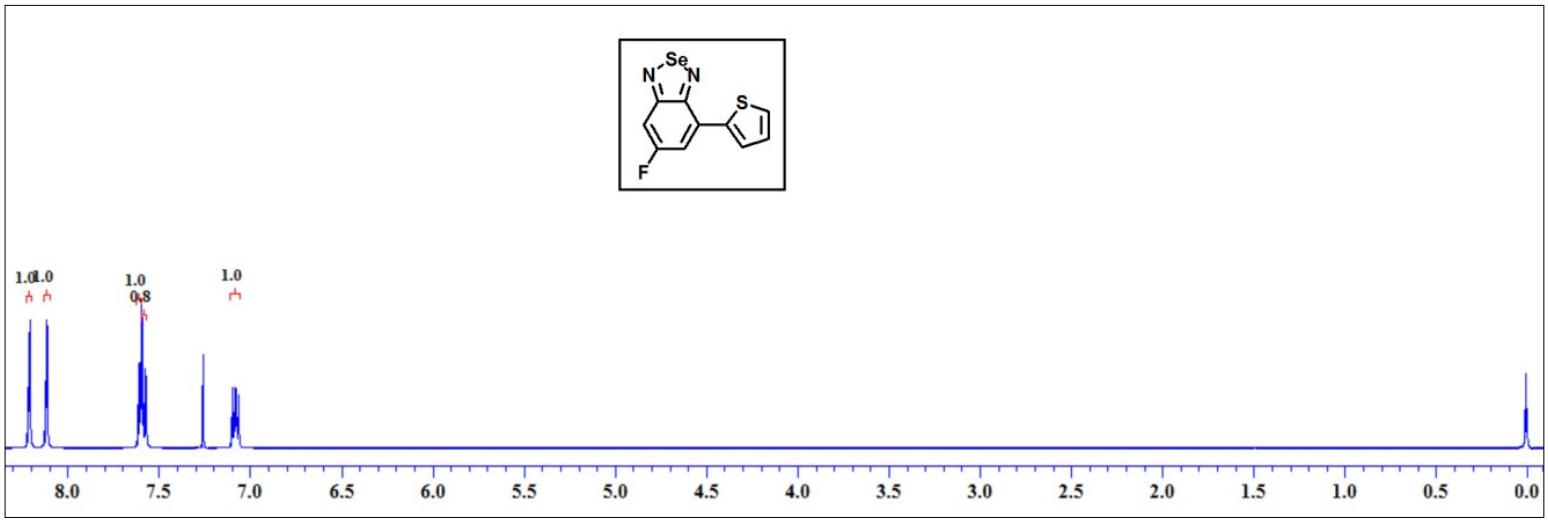
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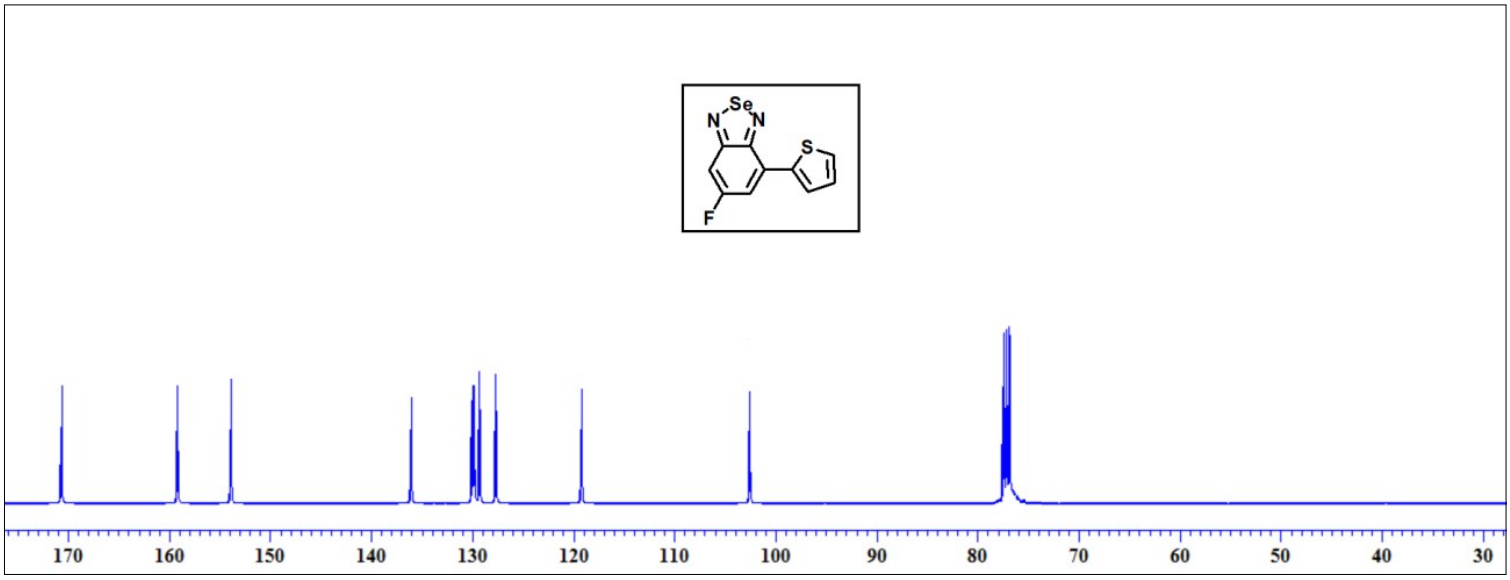
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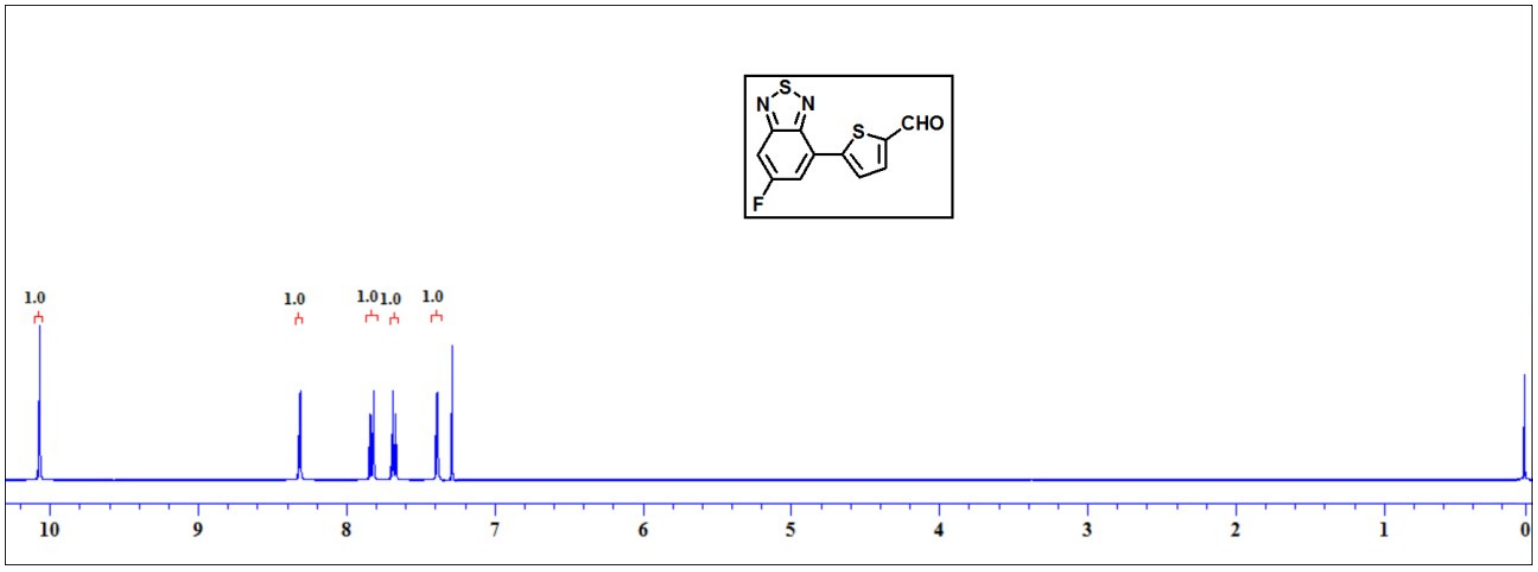
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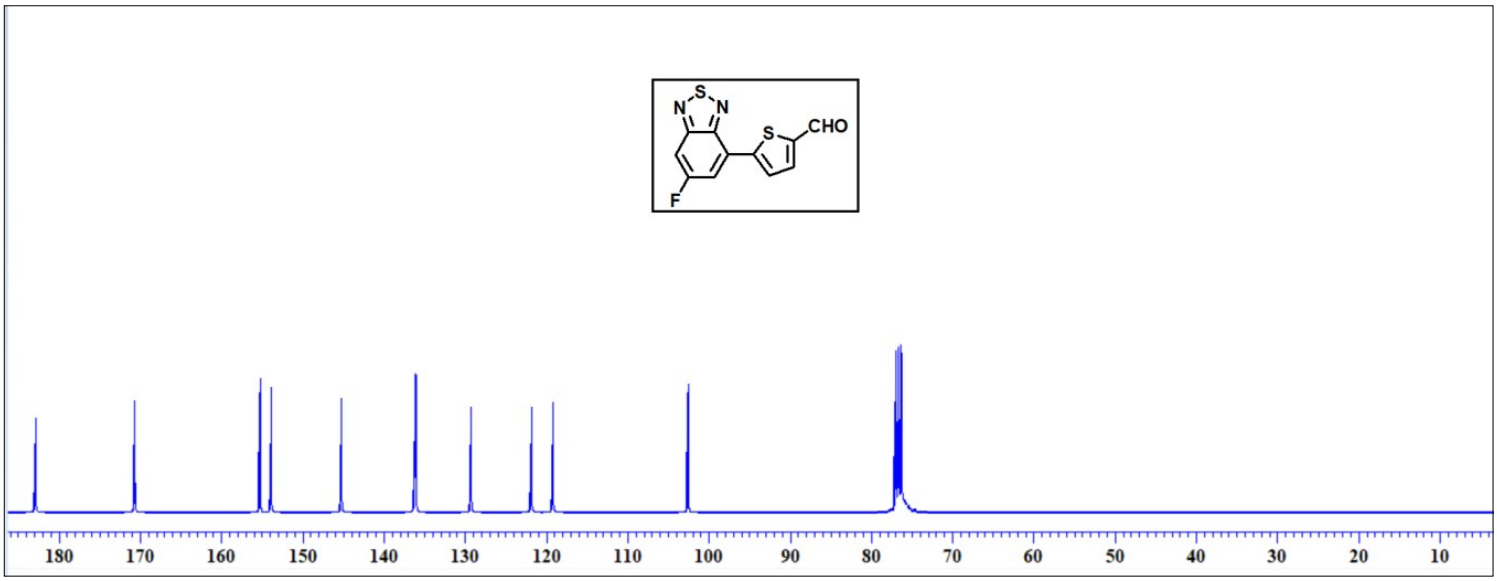
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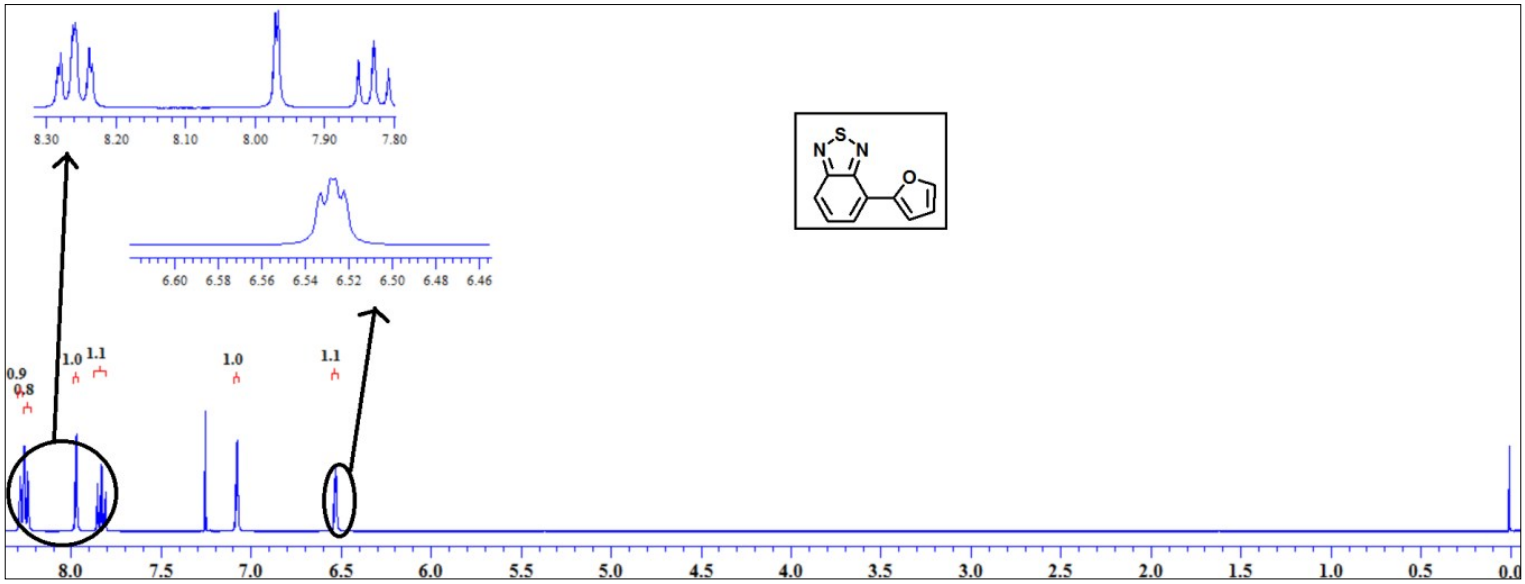
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6.48
6.46
N
S
N
O
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0.8
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1.1
1.0
1.1
8.0
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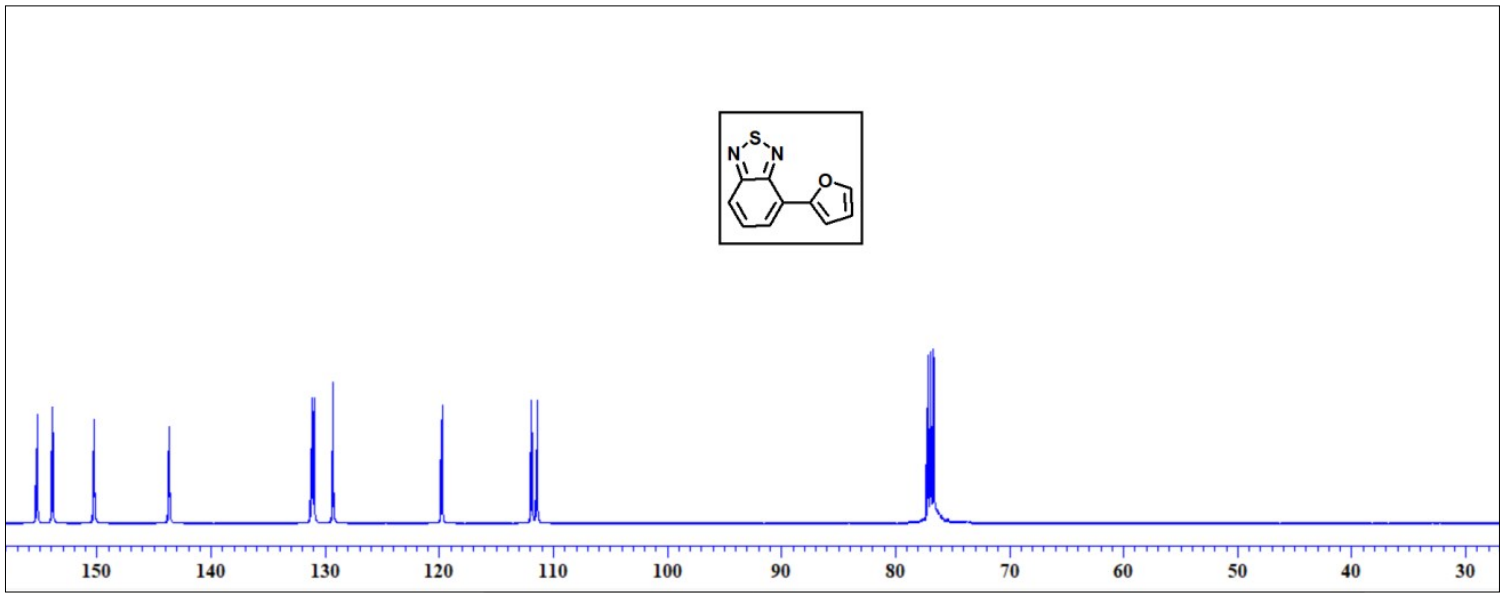
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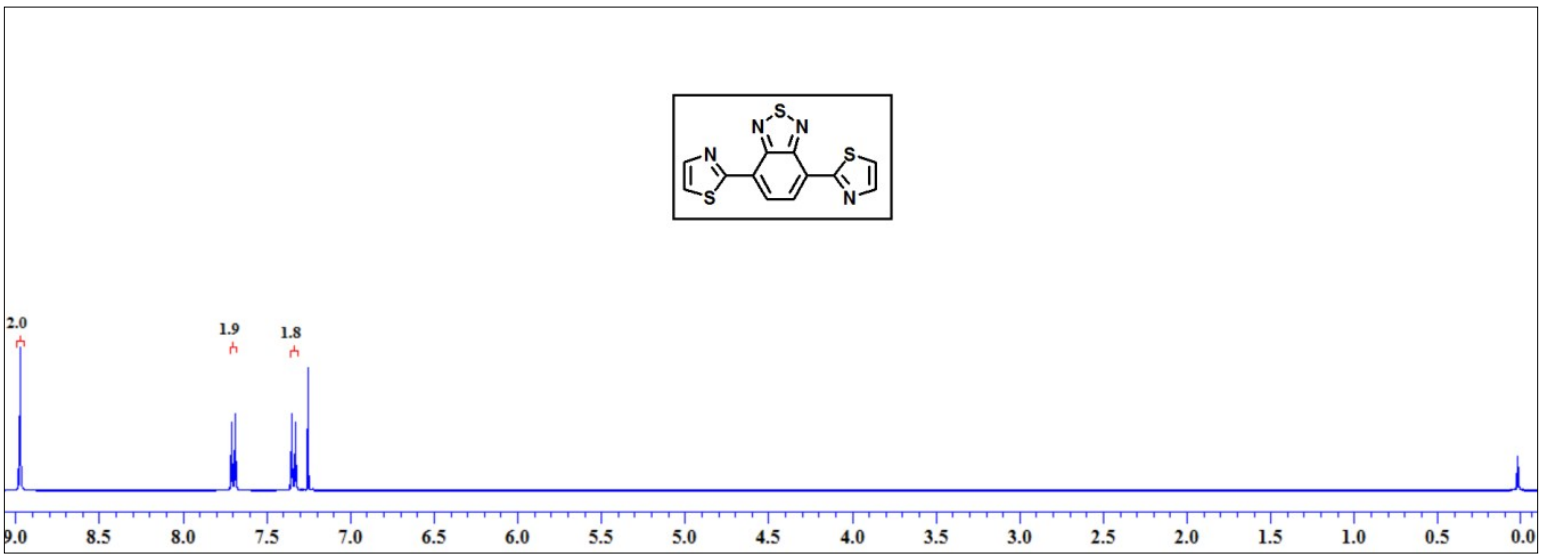
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6.0
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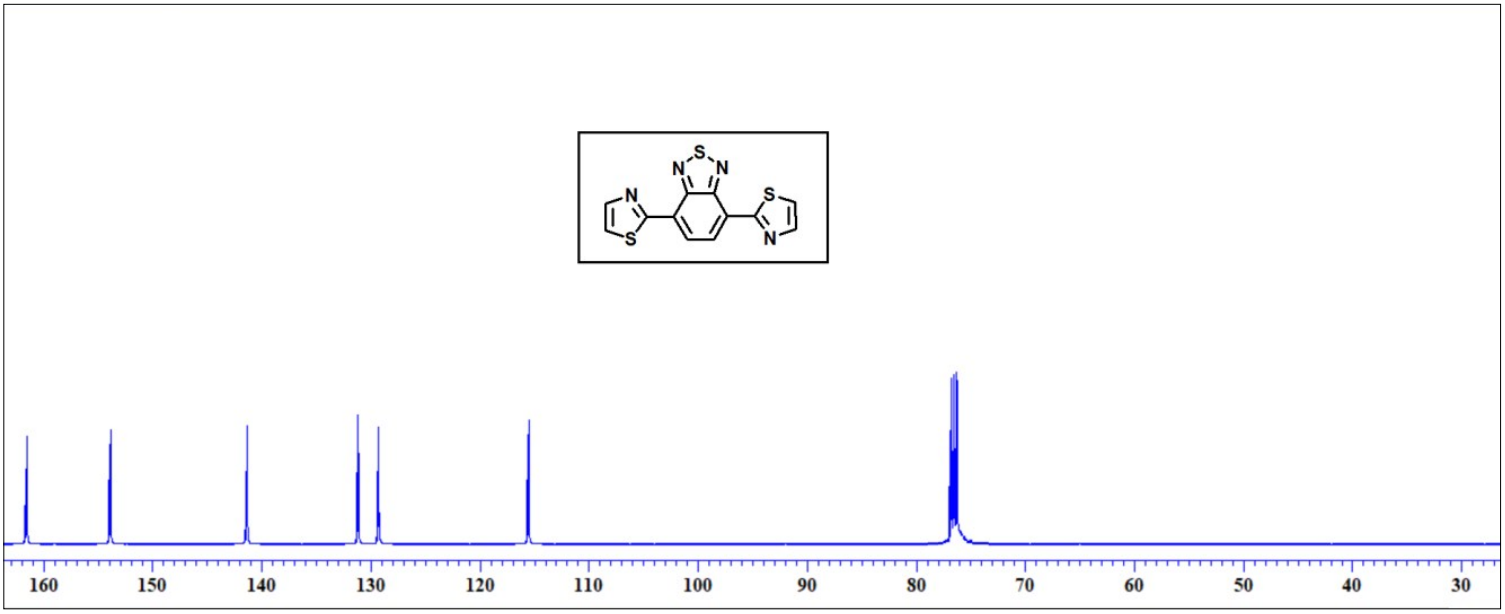
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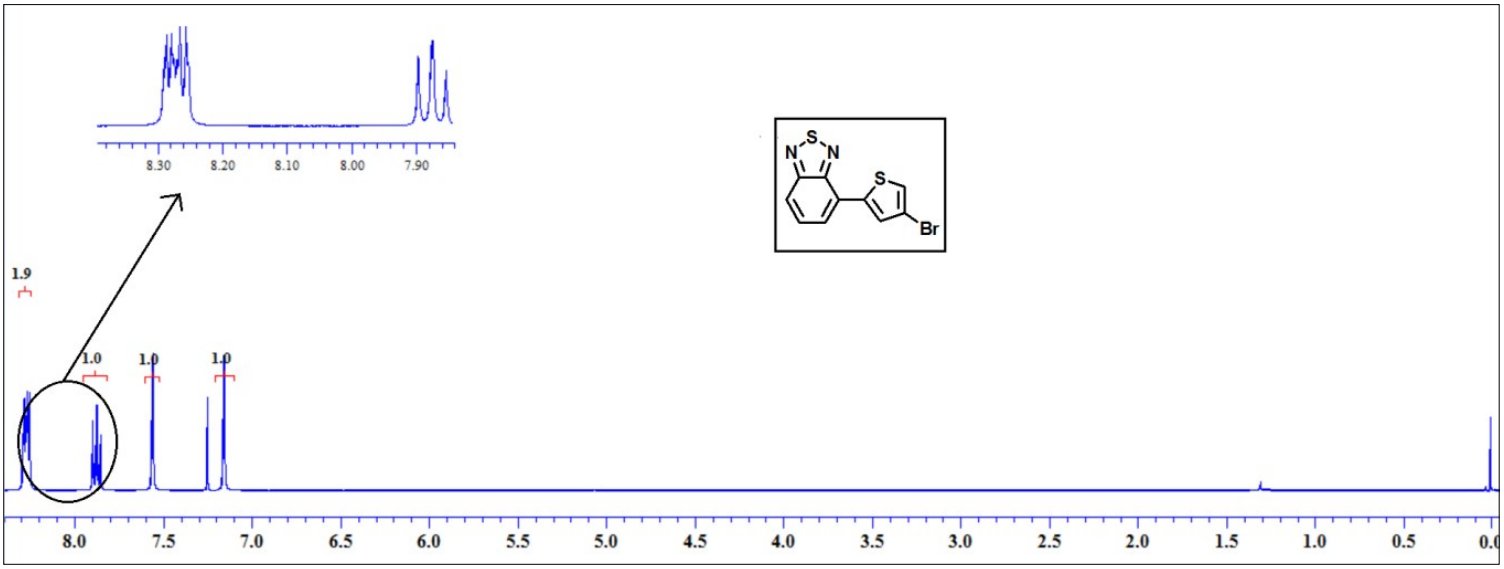
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7.90
1.9
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1.0
1.0
Br
8.0
7.5
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6.5
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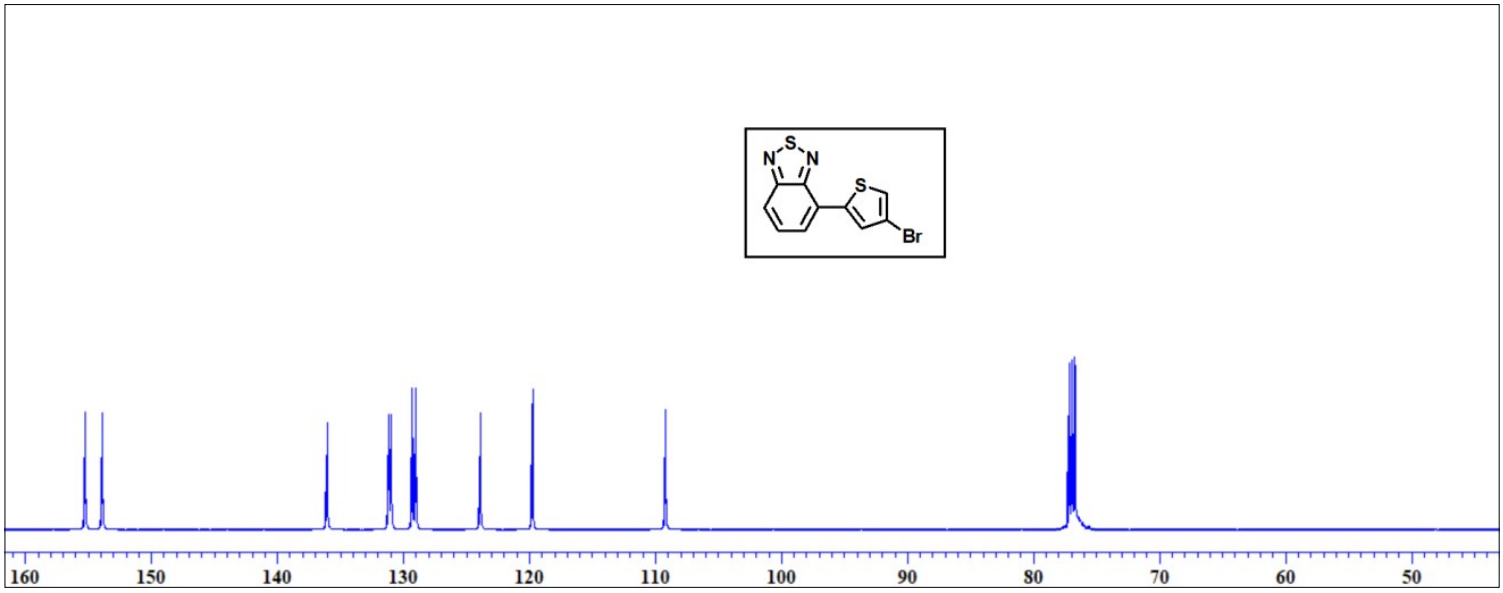
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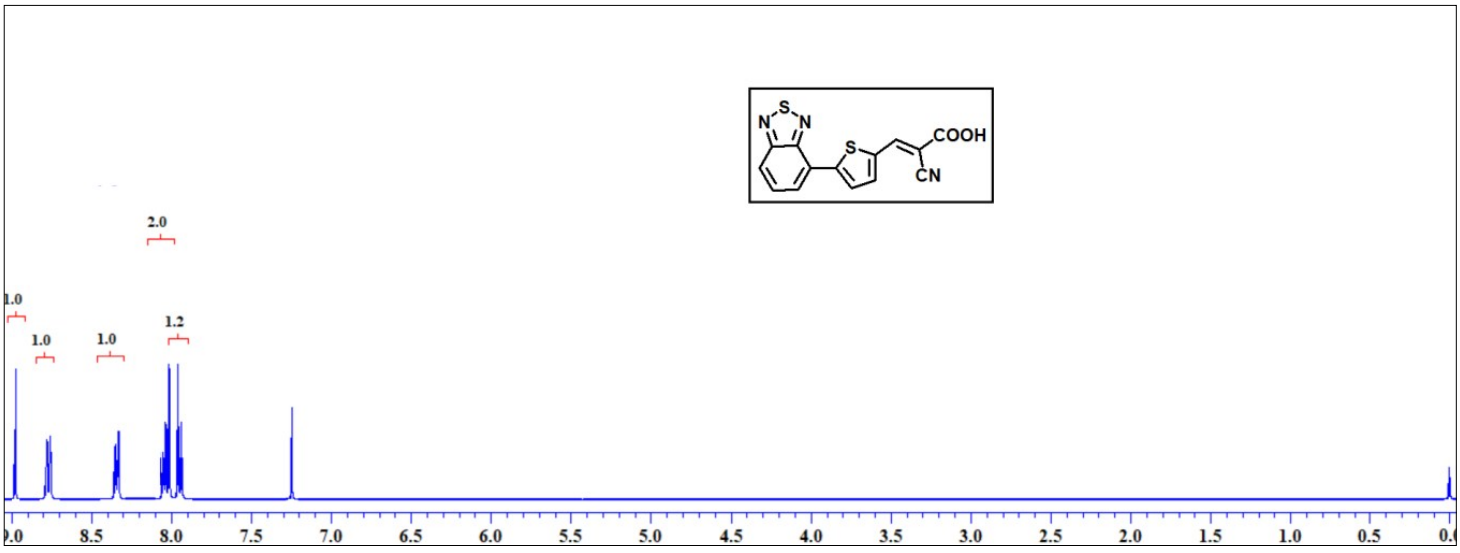
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1.0
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6.5
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4.5
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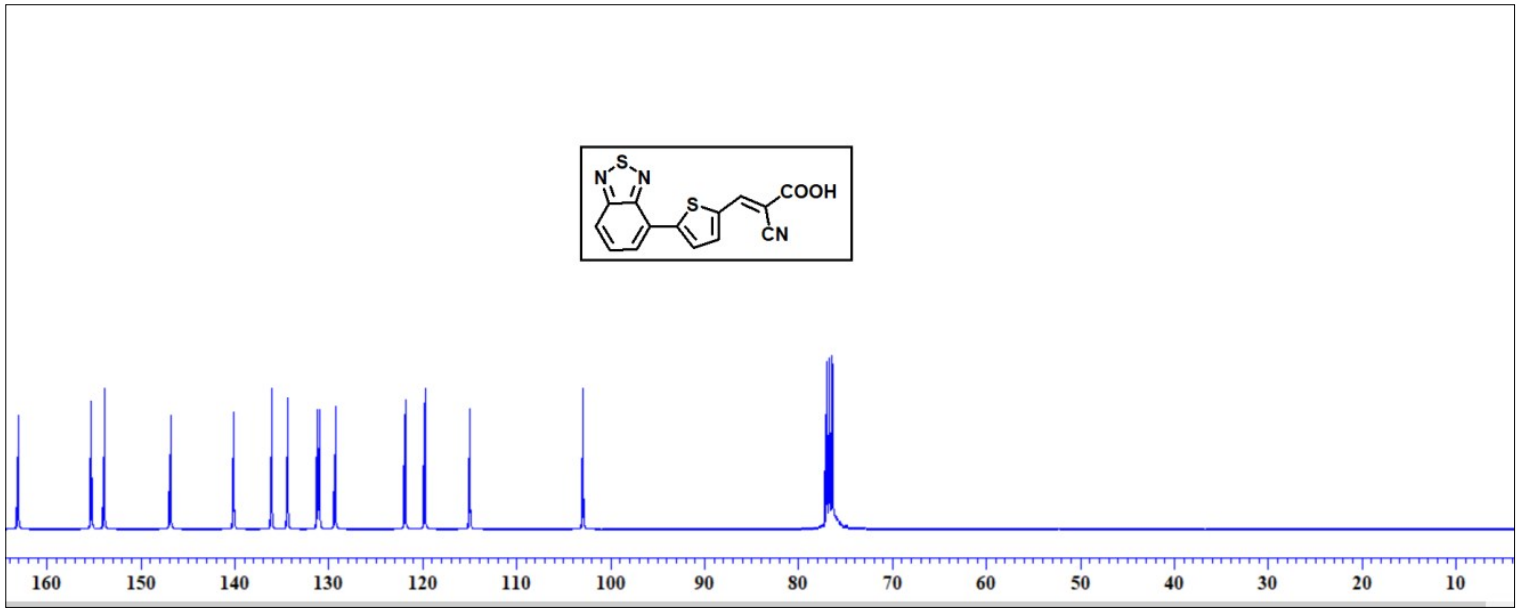
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COOH
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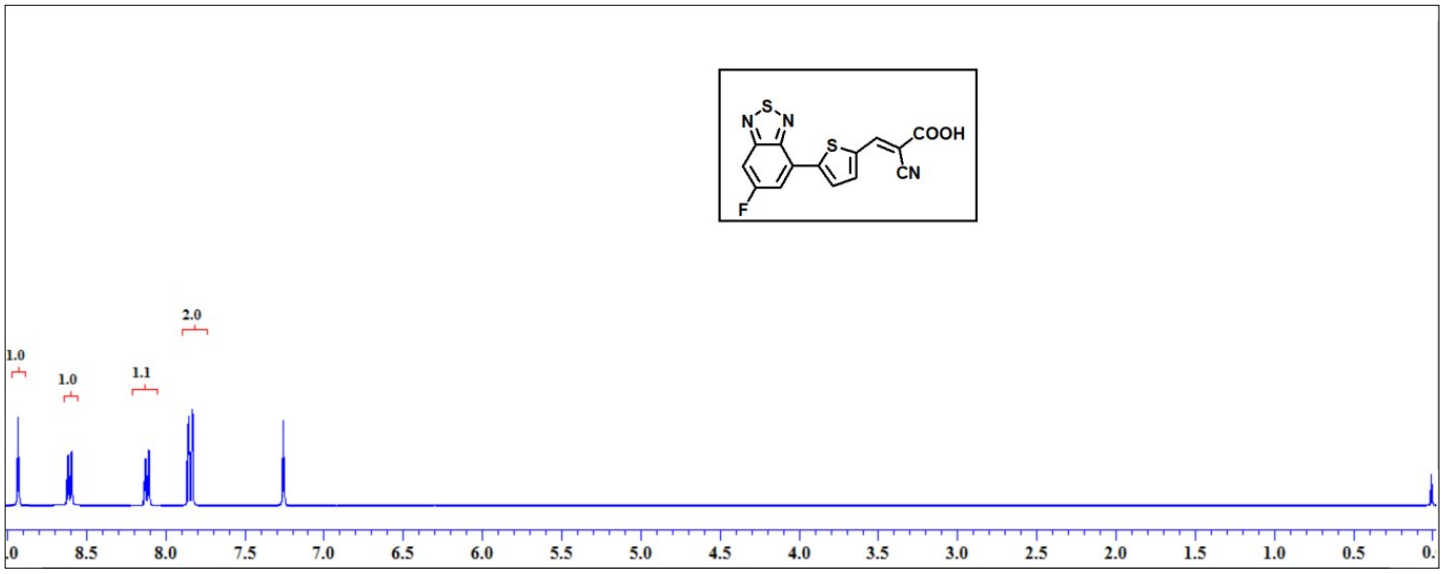
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6.5
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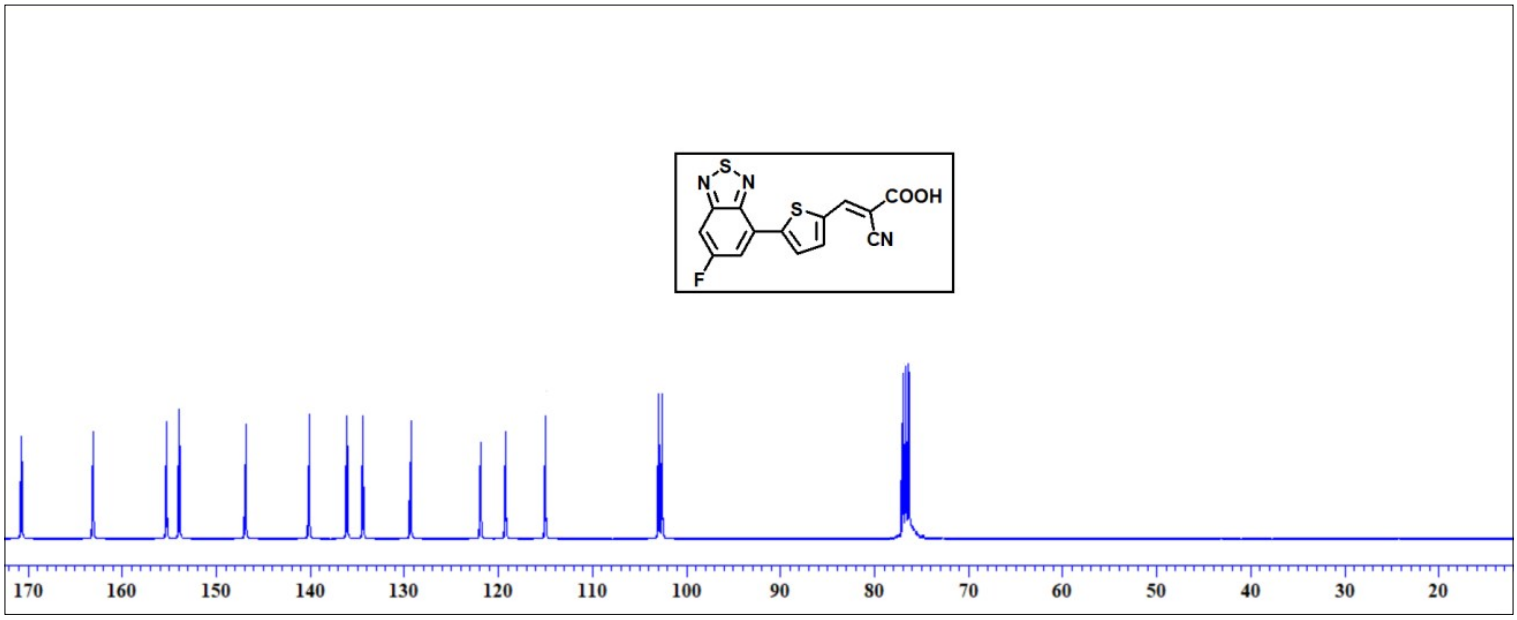
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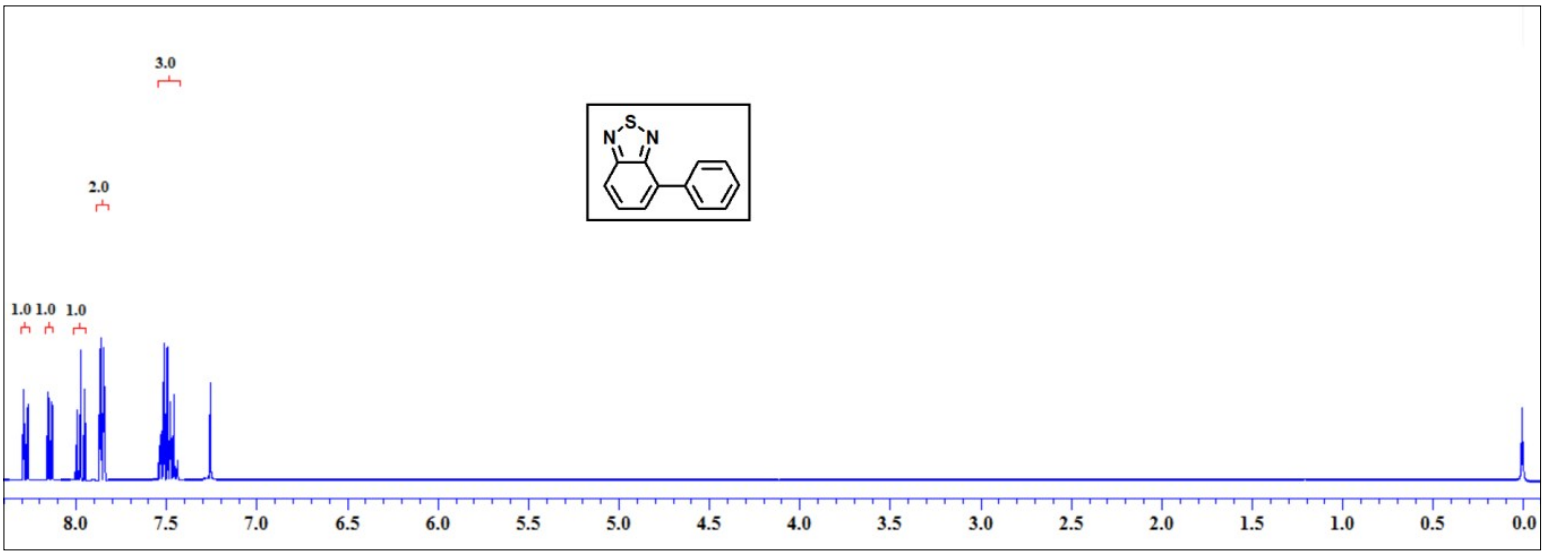
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1.0
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7.0
6.5
6.0
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4.5
4.0
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2.0
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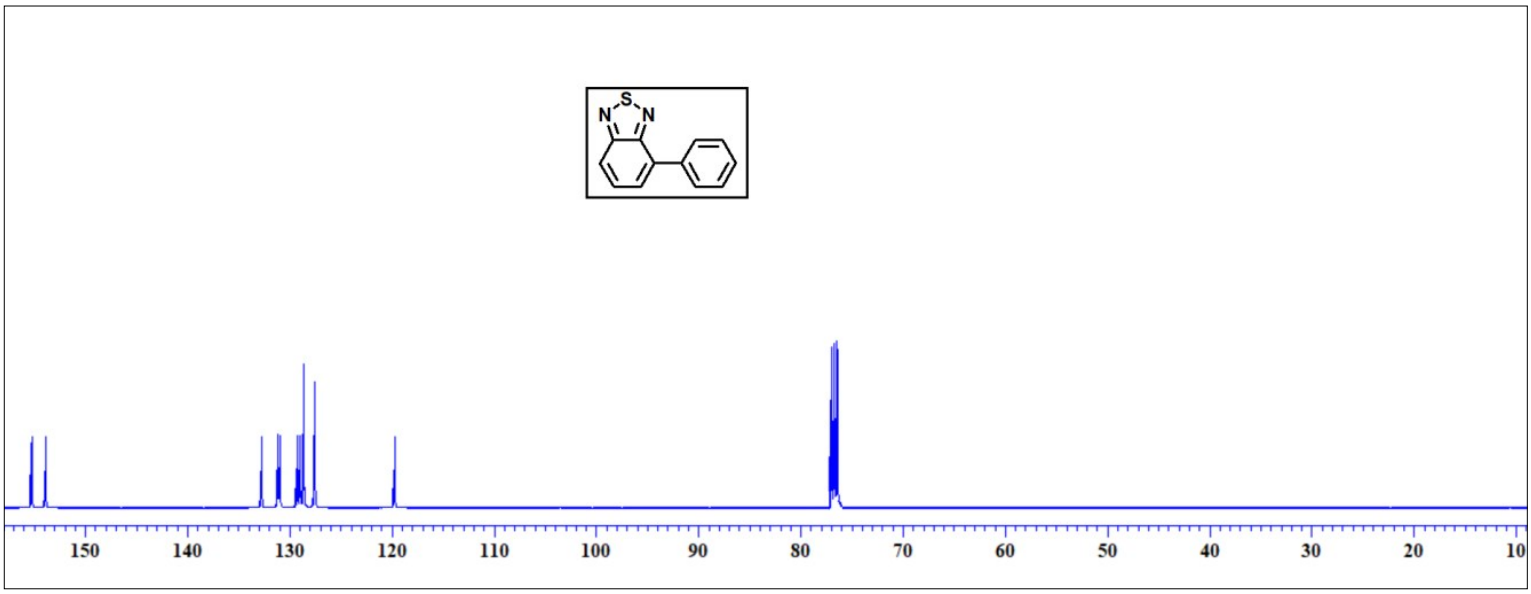
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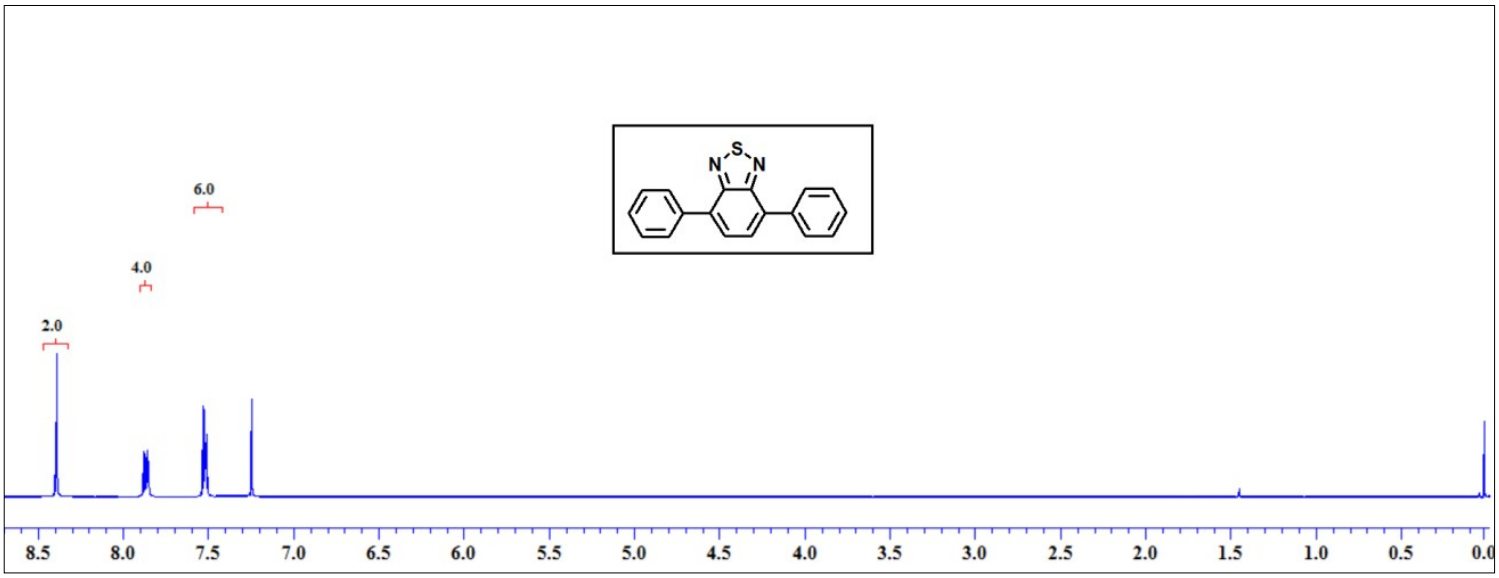
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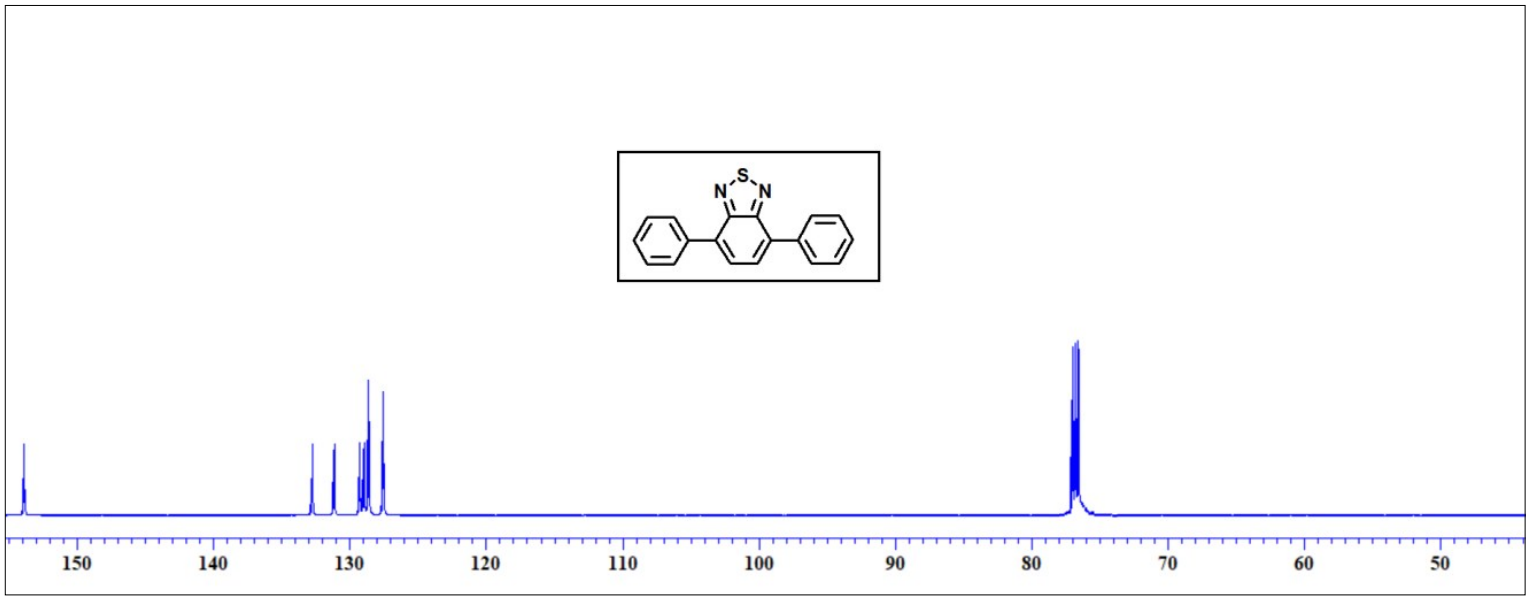
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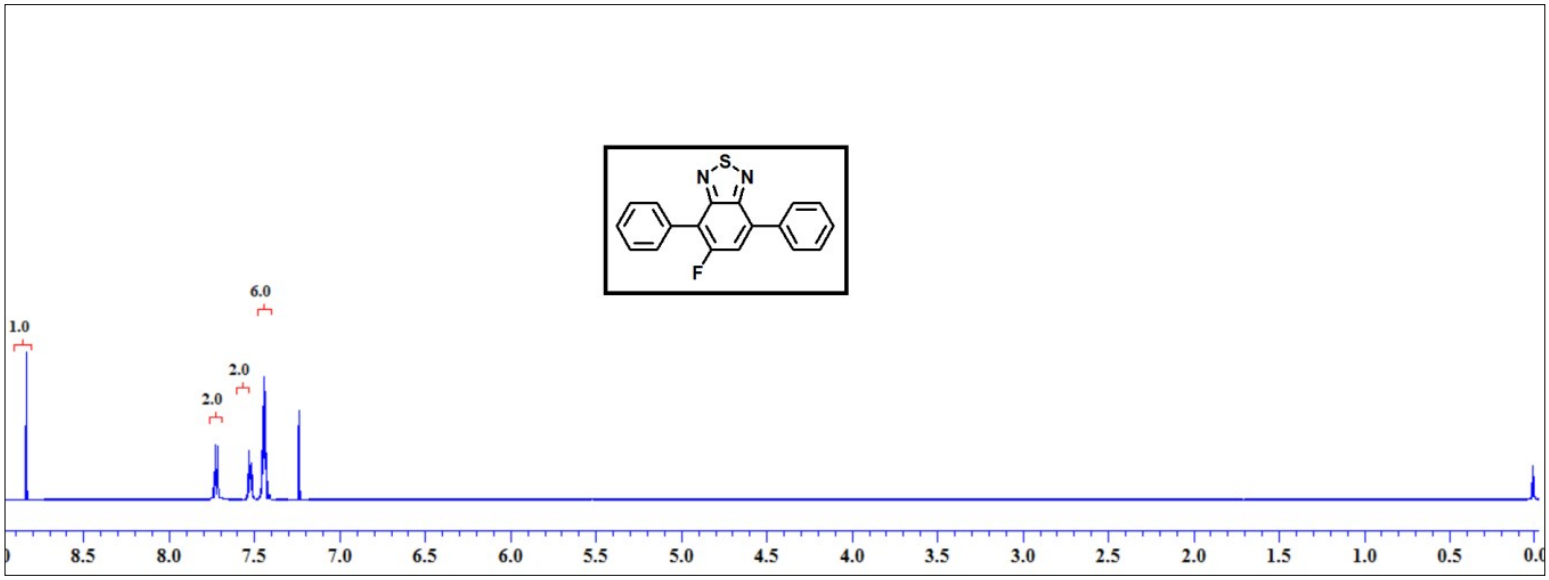
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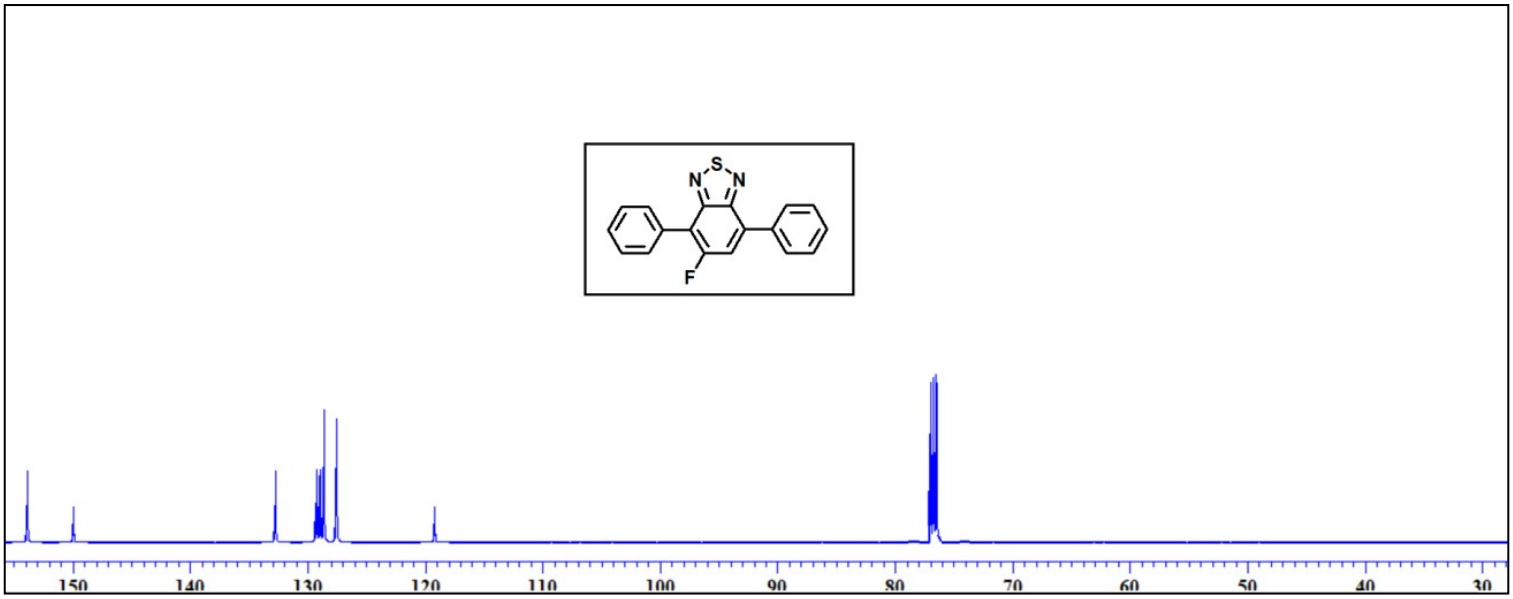
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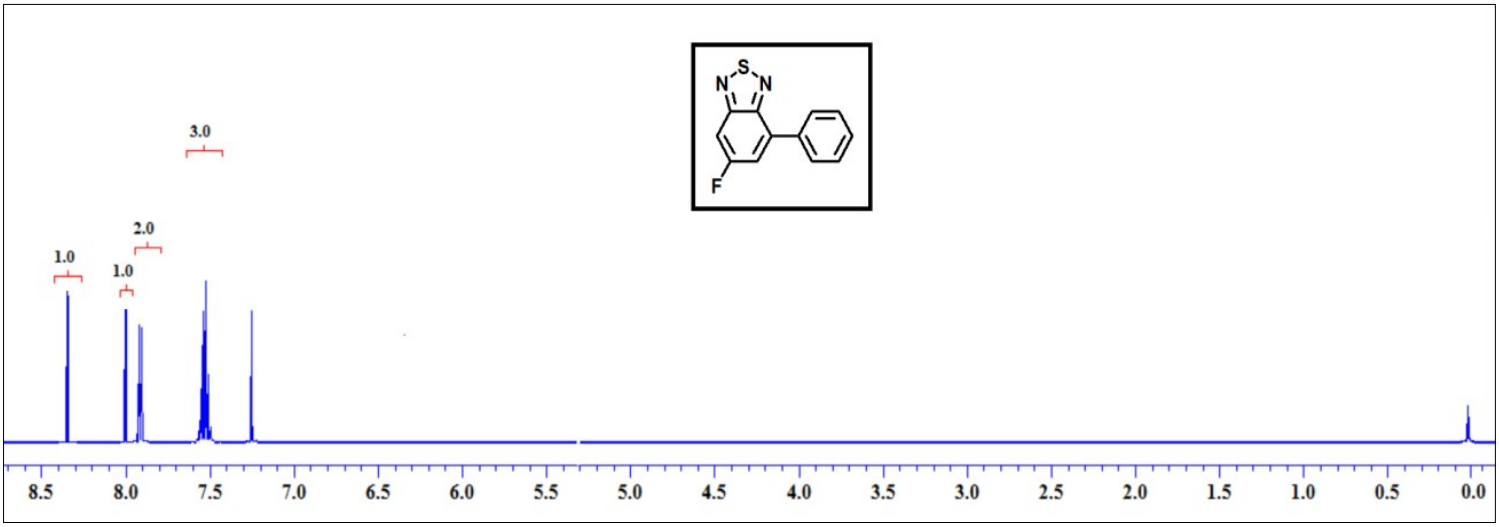
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7.5
7.0
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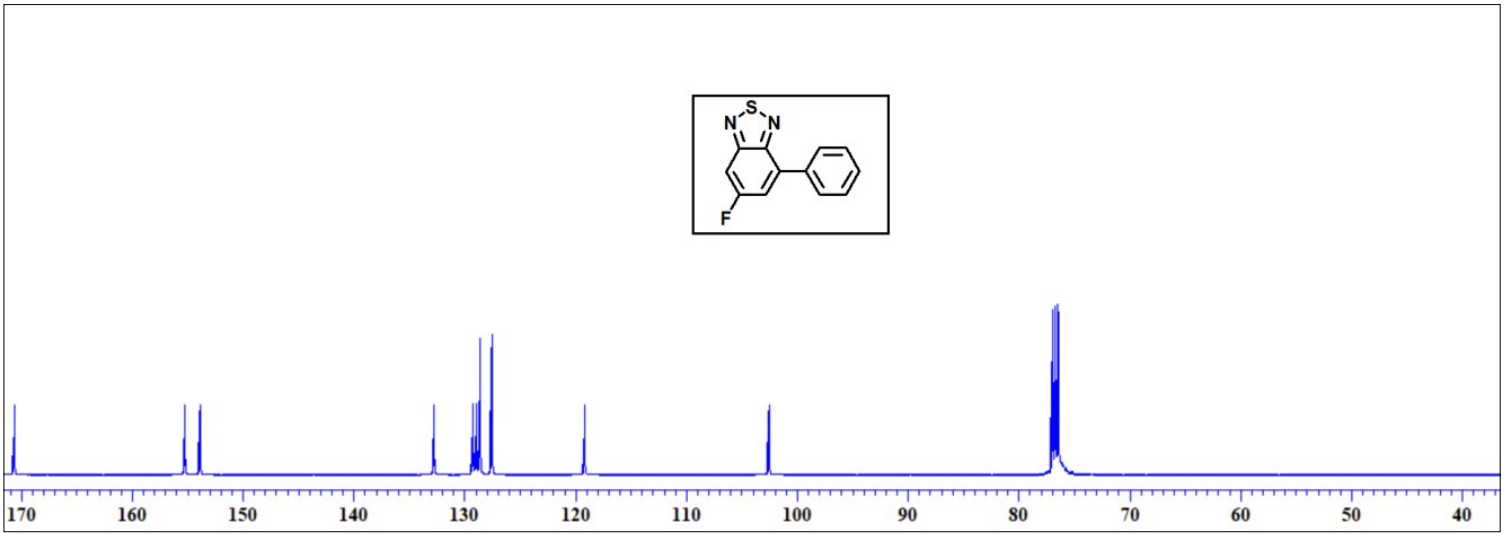
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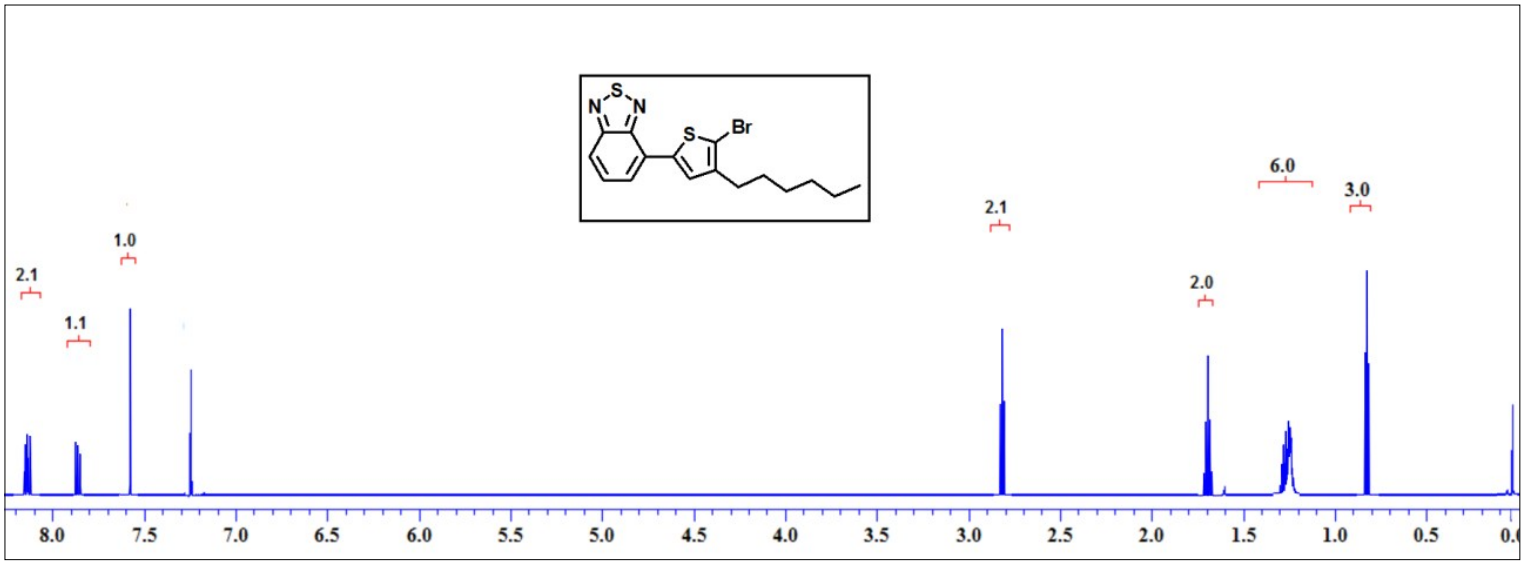
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Br
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7.0
6.5
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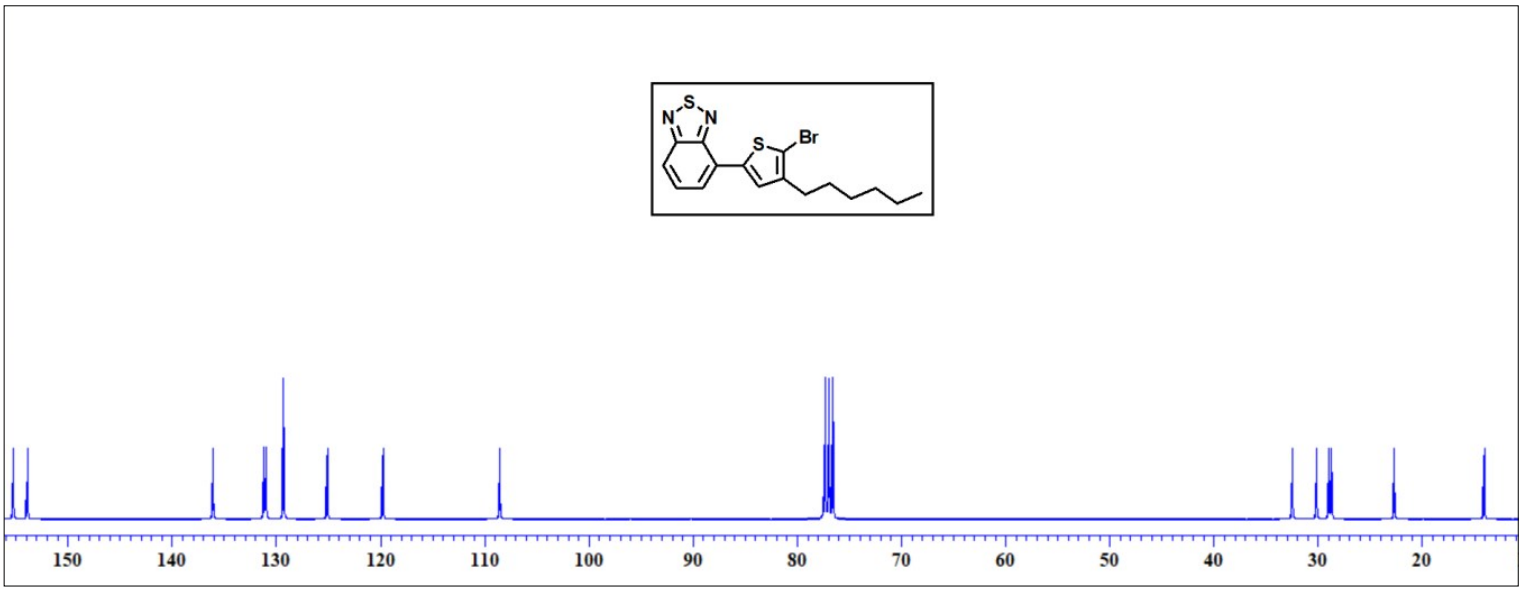
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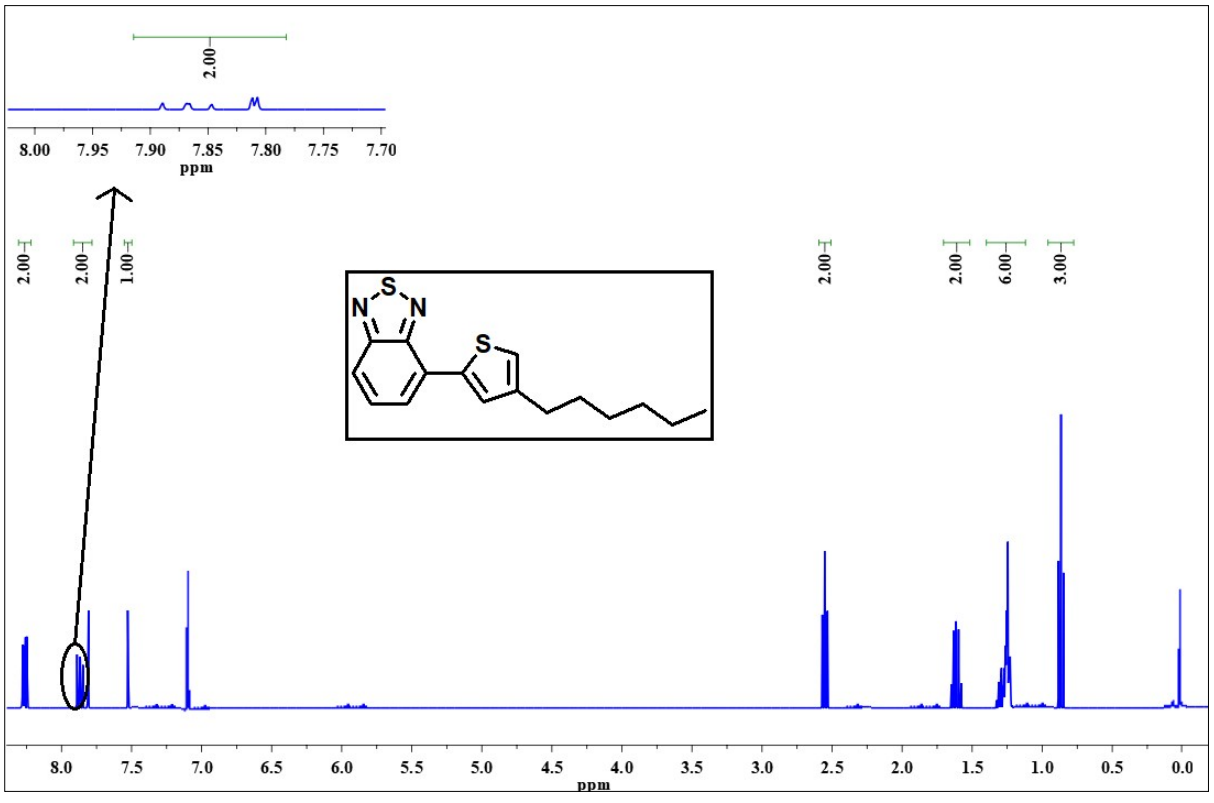
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2.00
2.00
6.00
3.00
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S
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S
8.0
7.5
7.0
6.5
6.0
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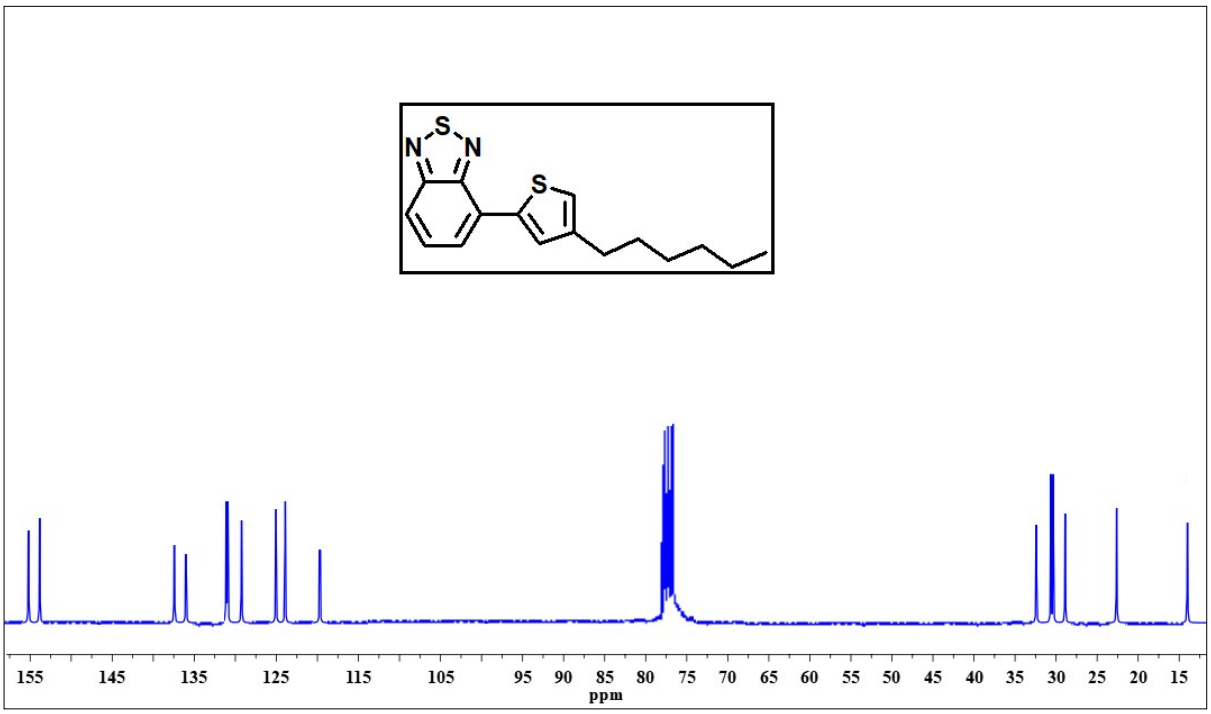
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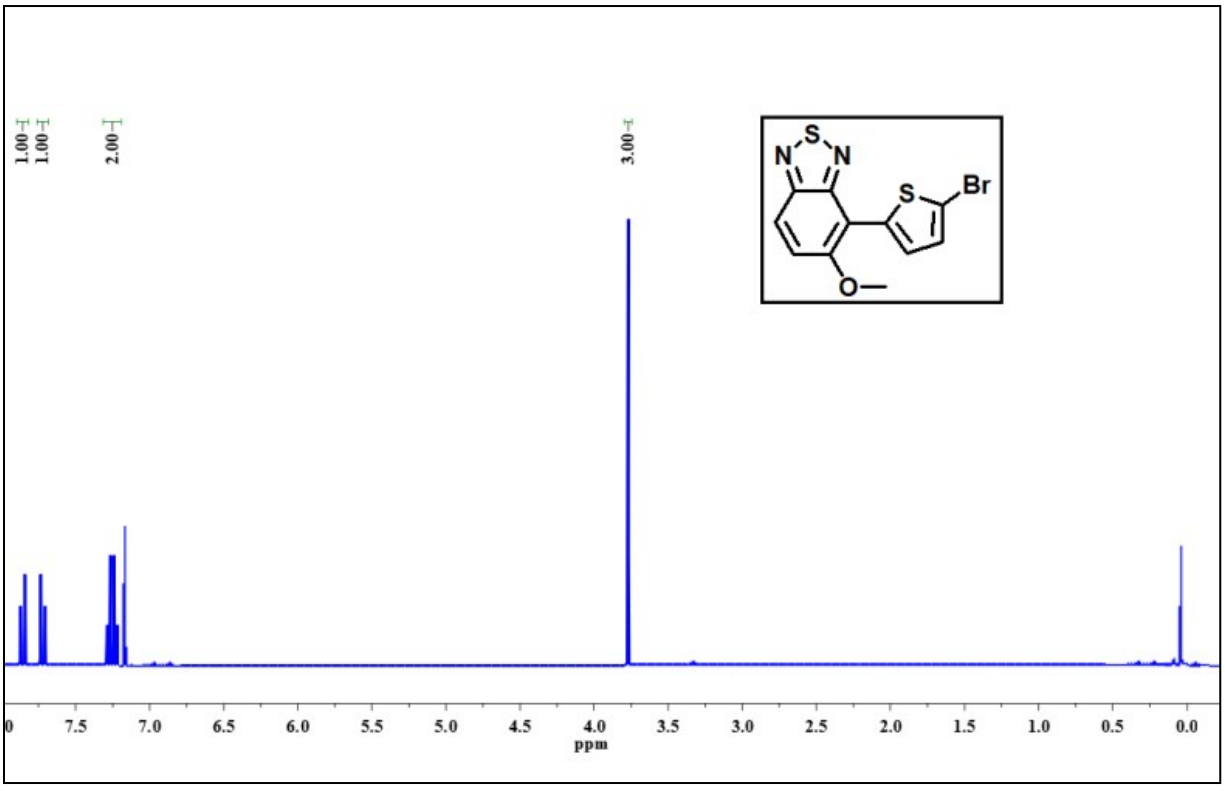
15
ppm


1.00
1.00
2.00
3.00
N
S
N
S
Br
O
7.5
7.0
6.5
6.0
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1.5
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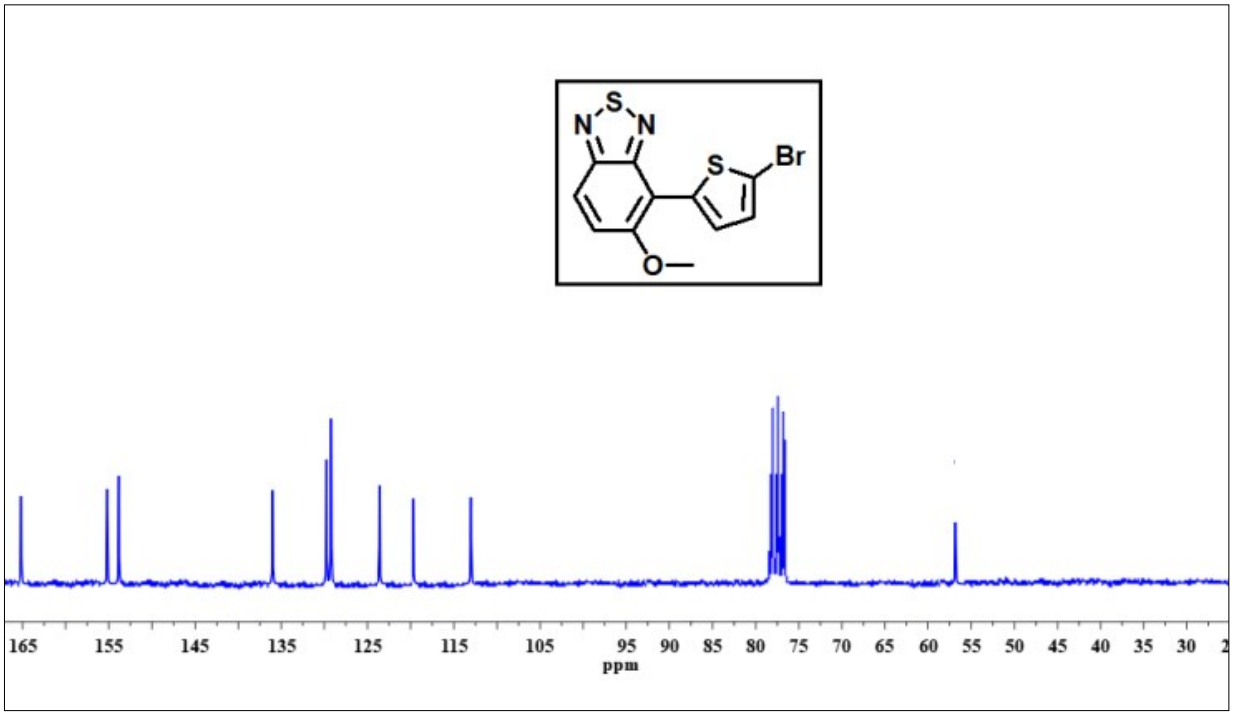
0.5
0.0
ppm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S
Br
O
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80
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60
55
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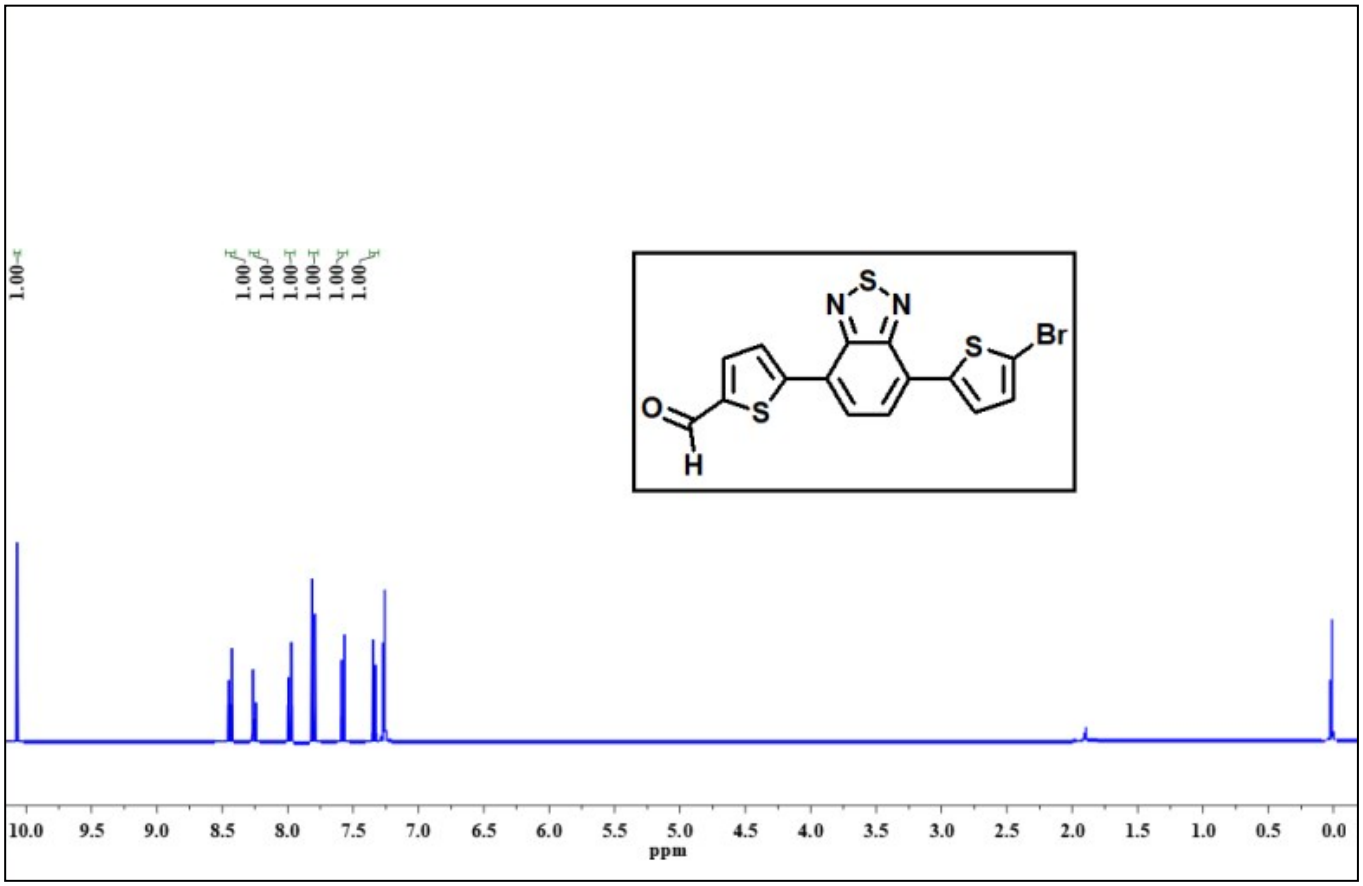
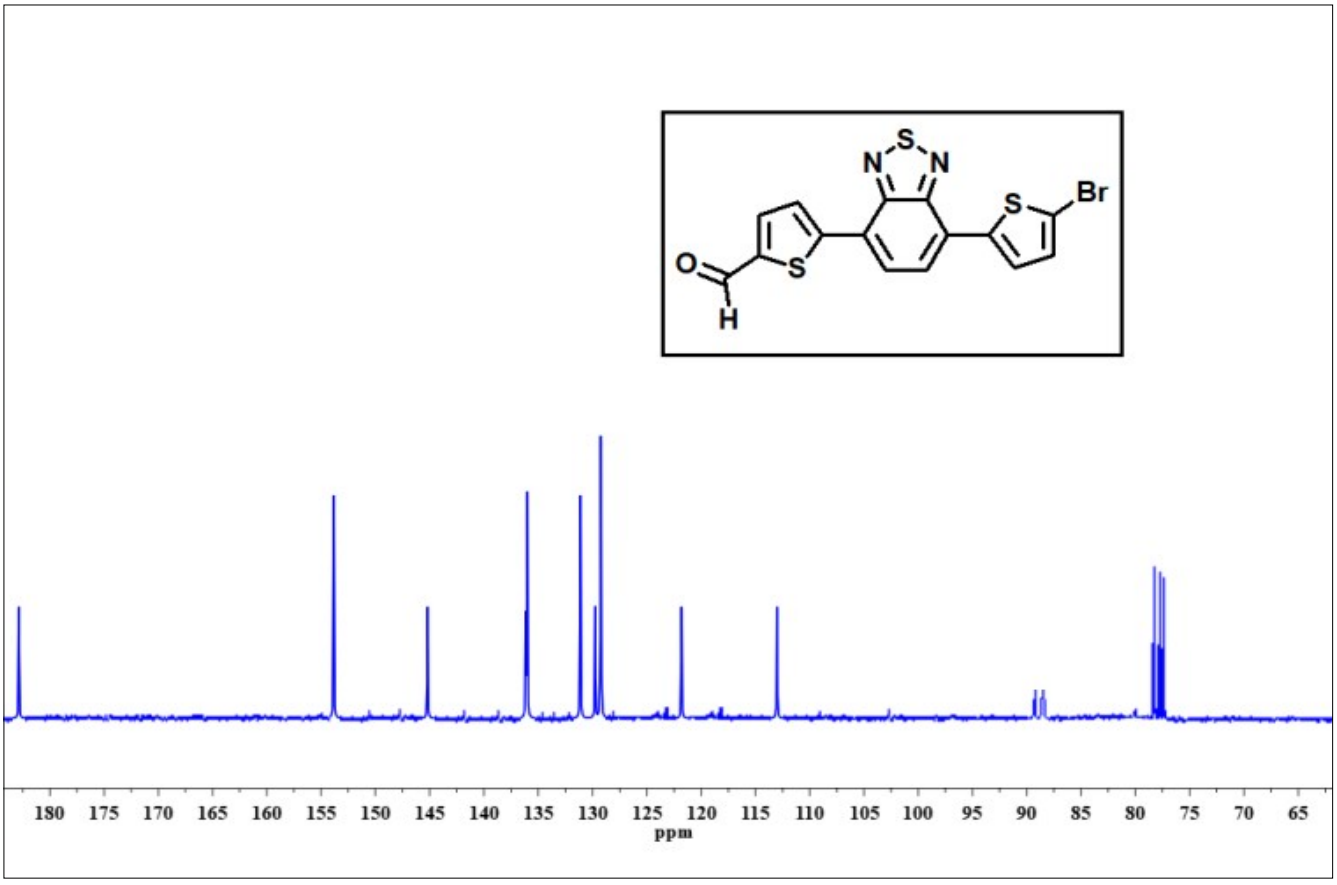
45
40
35
30
ppm


1.00
1.00
1.00
1.00
1.00
1.00
1.00
N
S
N
S
Br
O
S
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


N
S
N
S
Br
O
S
H
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65
ppm

References:

1. I. Fabre, N. von Wolff, G.tan Le Duc, E.F. Flegeau, C. Bruneau, P. H. Dixneuf and A. Jutand, *Chem. Eur. J*. 2013, **19**, 7595.
2. S. K. Panja, N.Dwivedi, S. Saha*, RSC Adv.* **2016**,*6*, 105786-105794.
3. Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li, P. Wang**,** *J. Am. Chem. Soc*. **2015**, *137*, 3799-3802.