Supporting Information

Electronic Alteration on Oligothiophenes by o-Carborane: Electron Acceptor Character of o-Carborane in Oligothiophene Frameworks with Dicyano-Vinyl End-On Group

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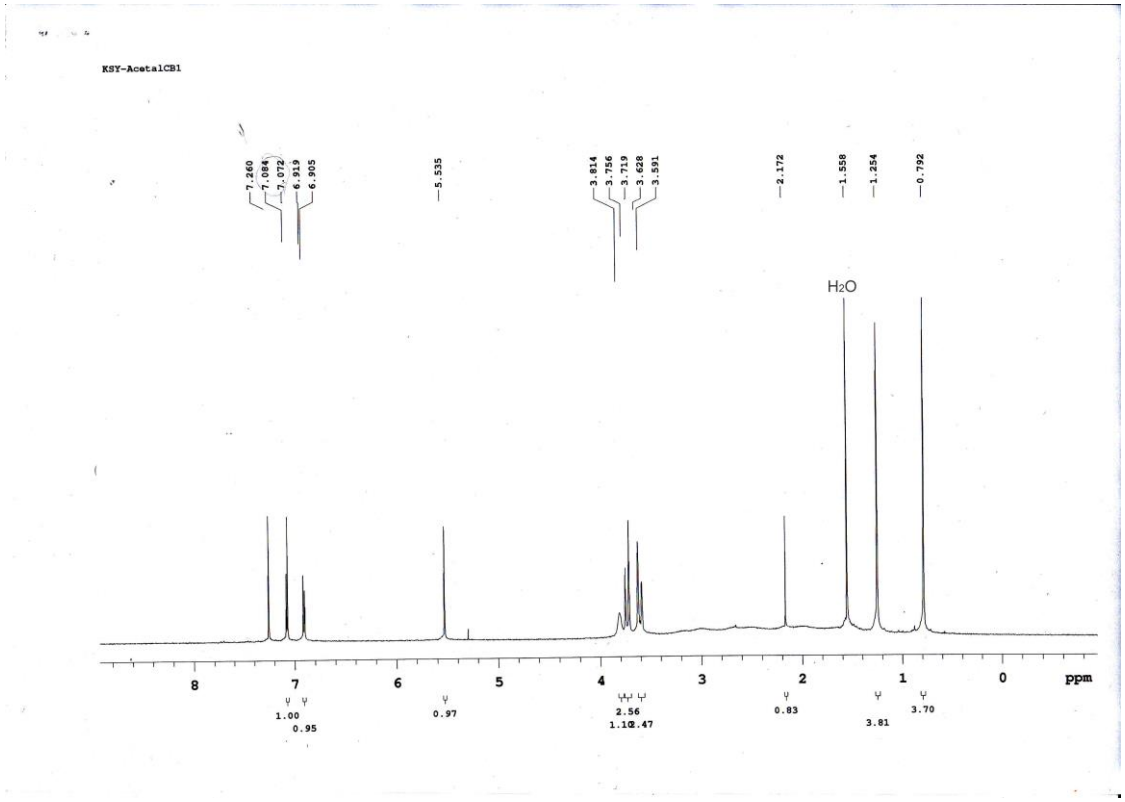
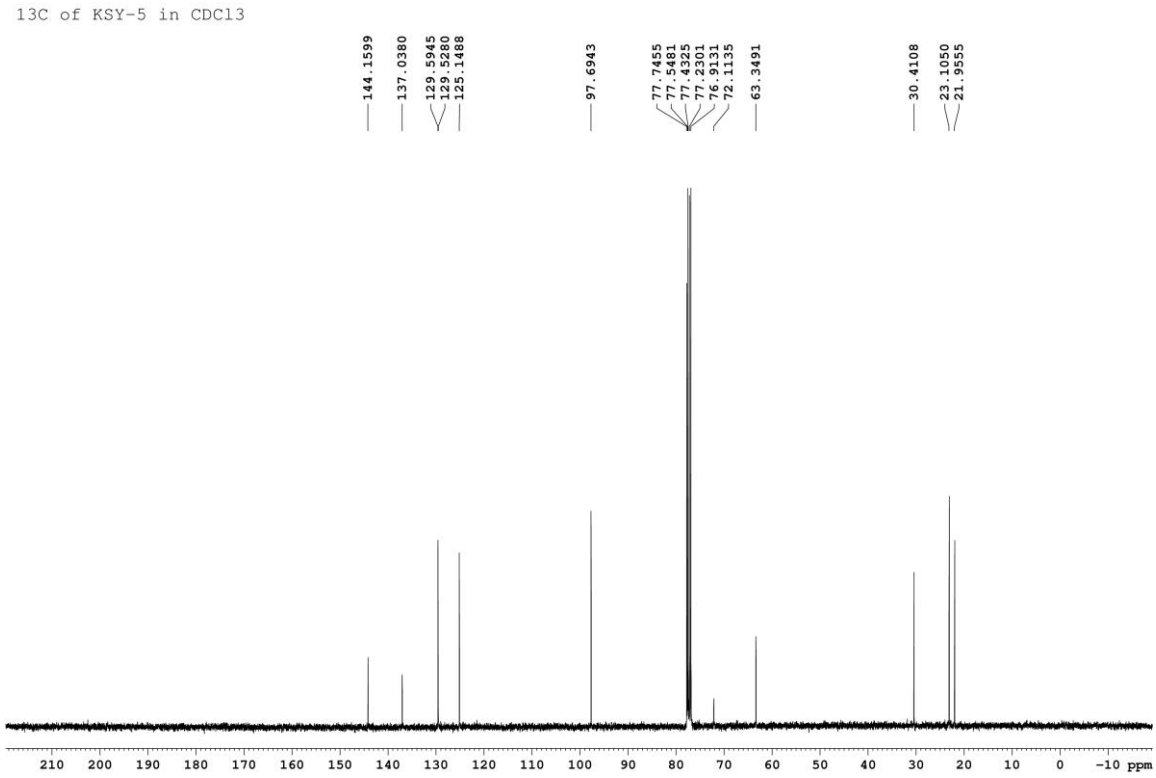
NMR Spectra

Compound **5**

^{1}H NMR

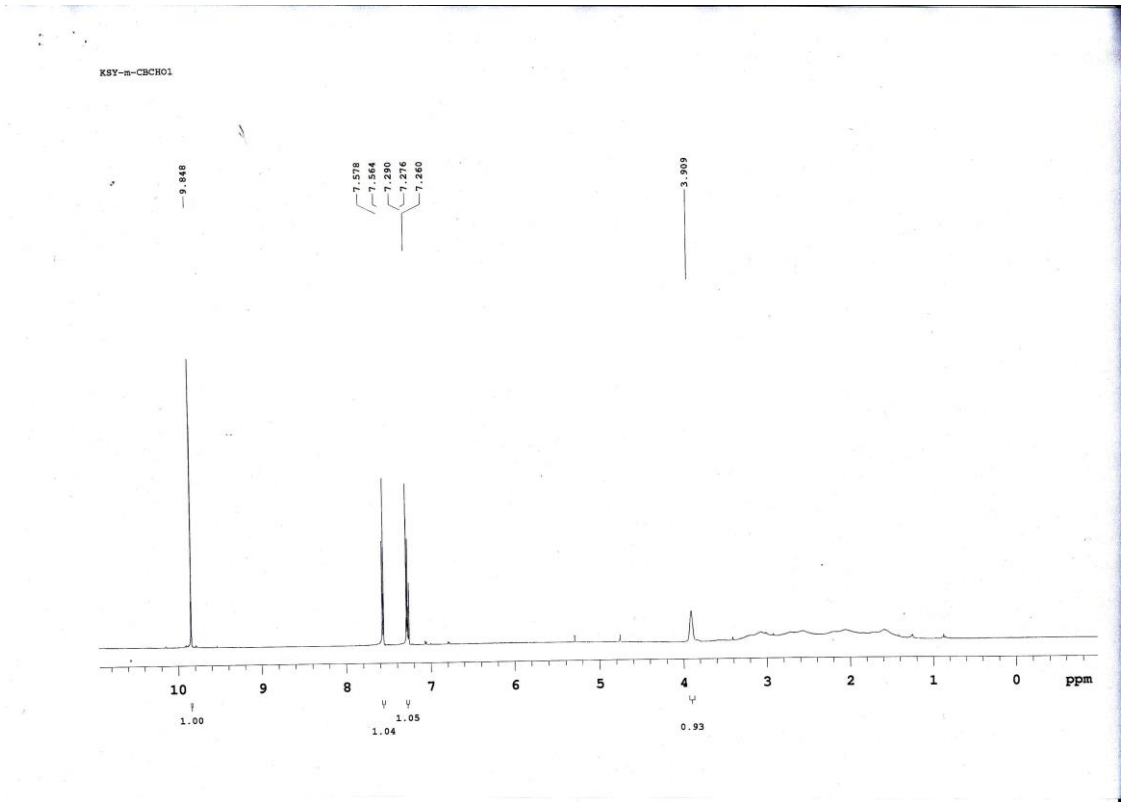


^{13}C NMR

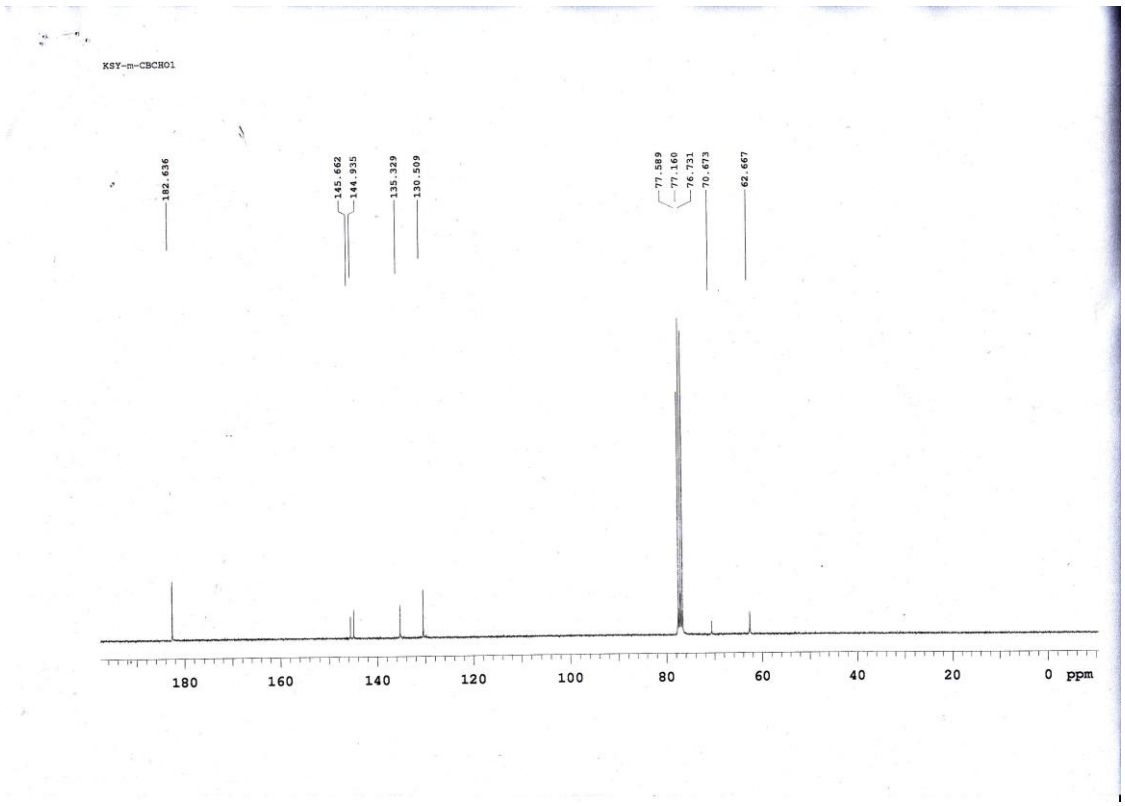


Compound **6**

^{1}H NMR

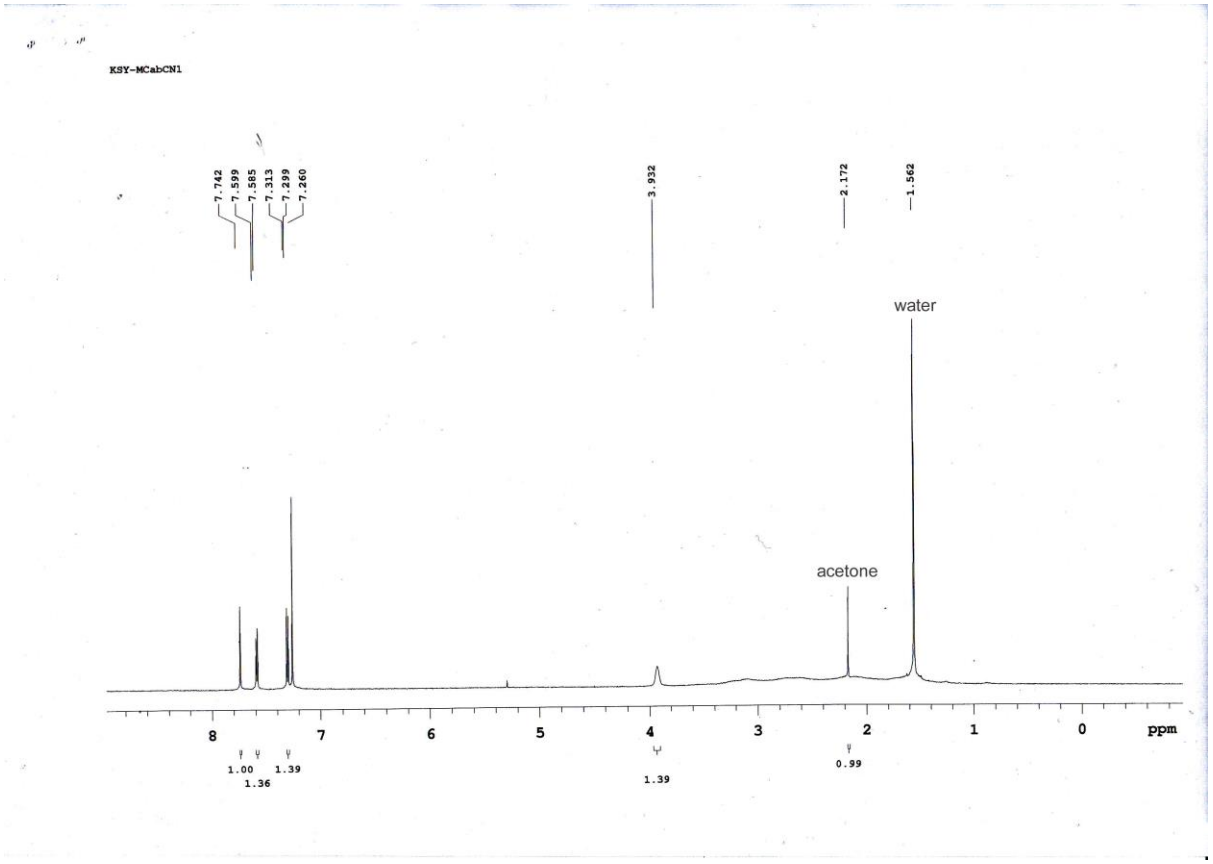


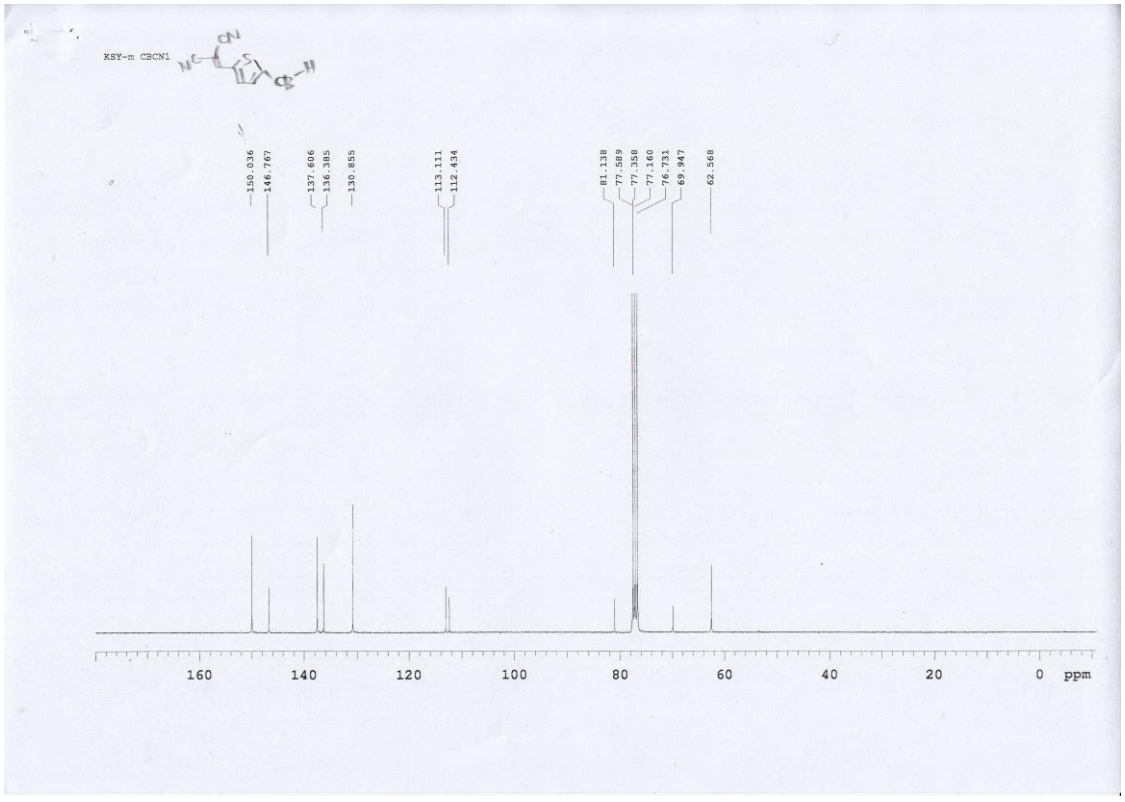
^{13}C NMR



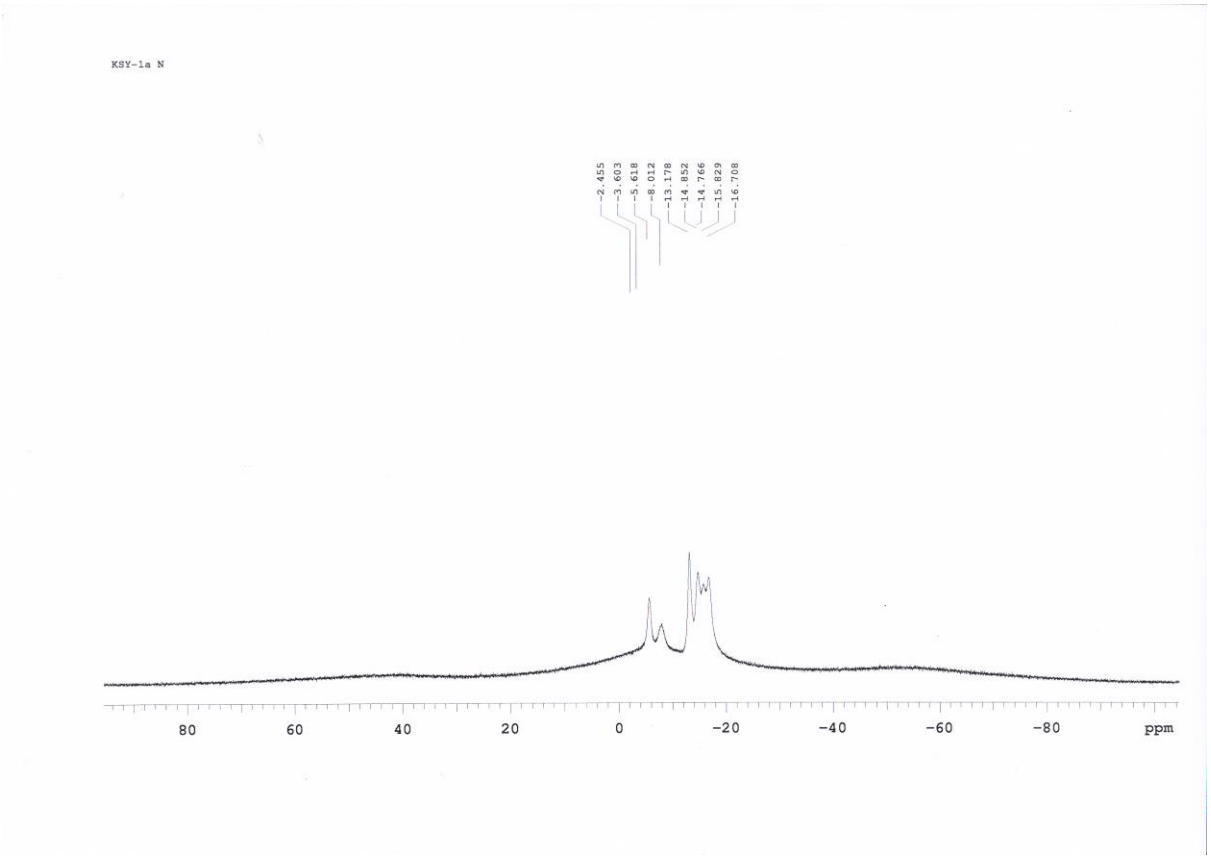
Compound **1a**

^{1}H NMR





^{11}B NMR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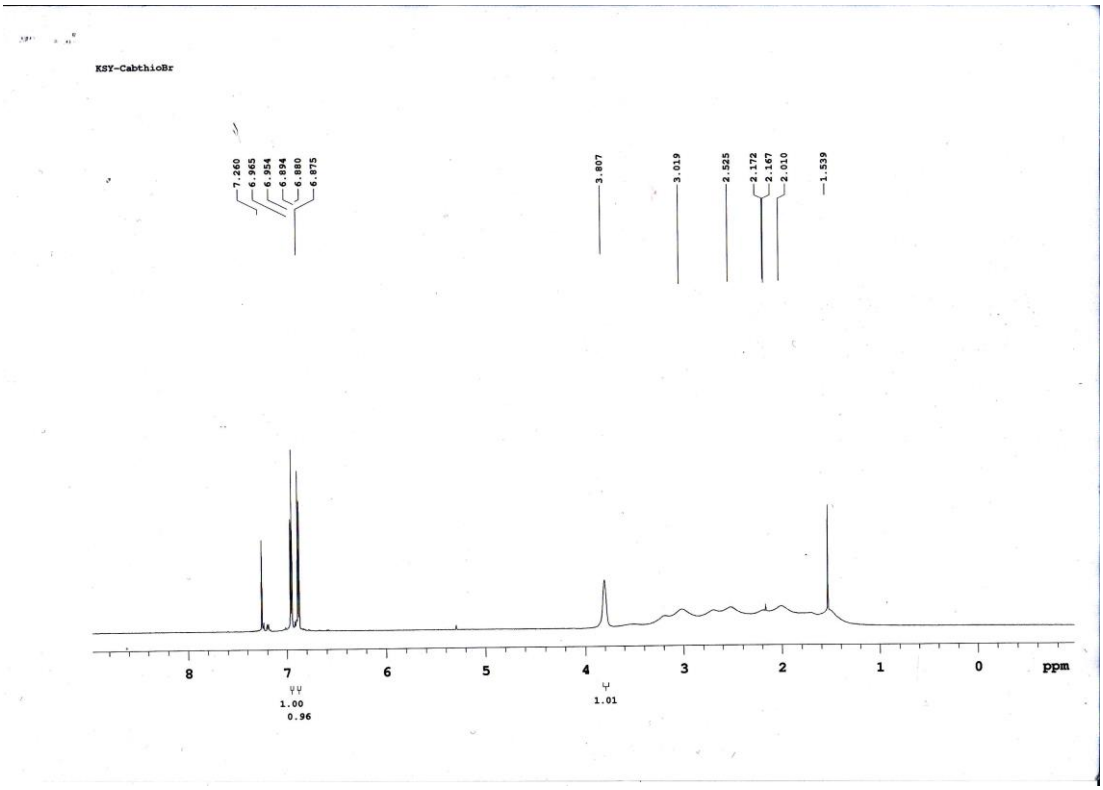
-3.603
-5.618
-8.012
-13.178
-14.852
-14.766
-15.829
-16.708
80
60
40
20
0
-20
-40
-60
-80
ppm

Compound **7**

^{1}H NMR



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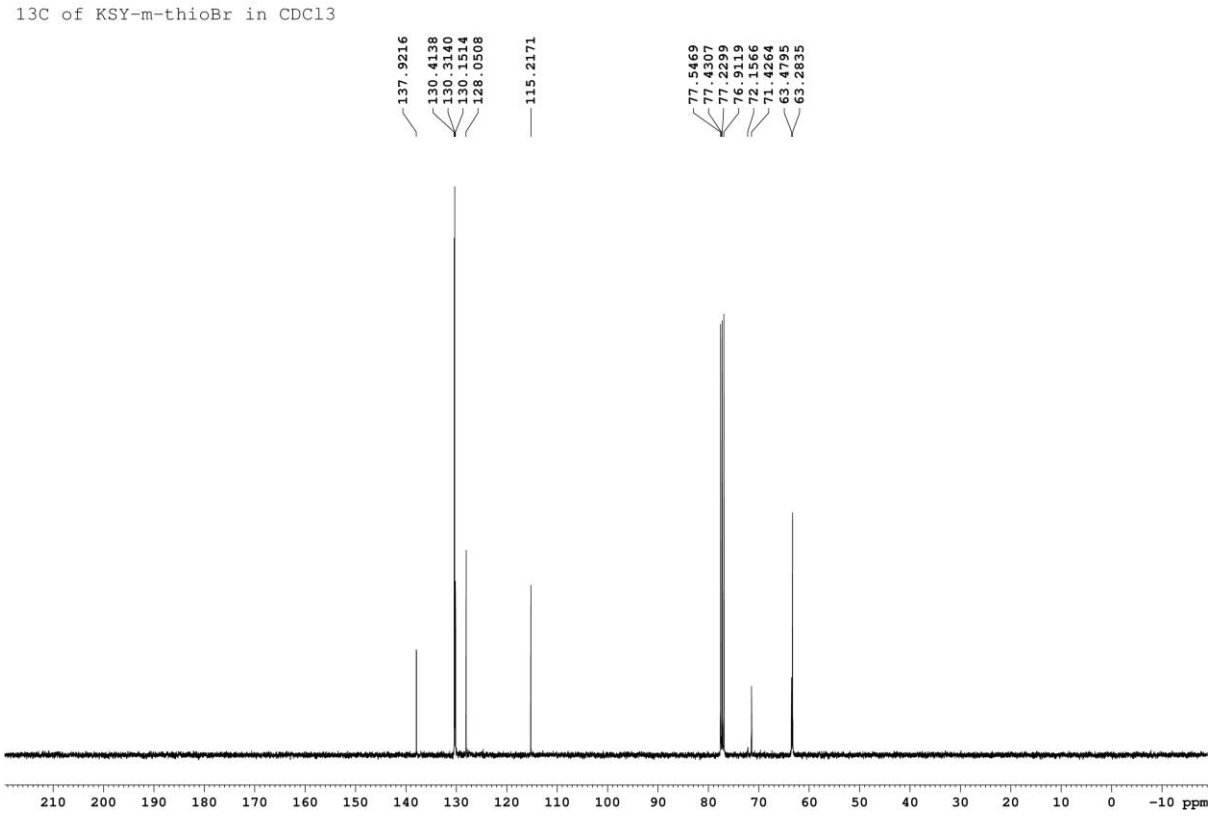
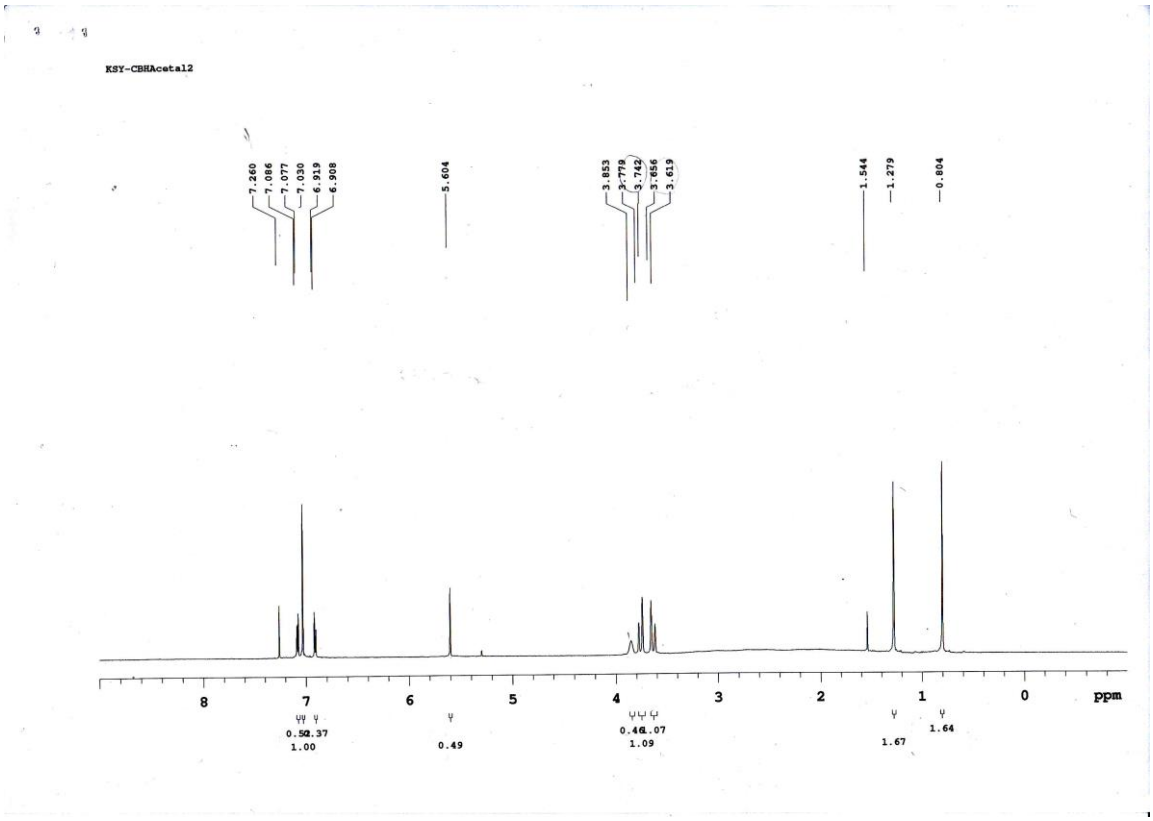
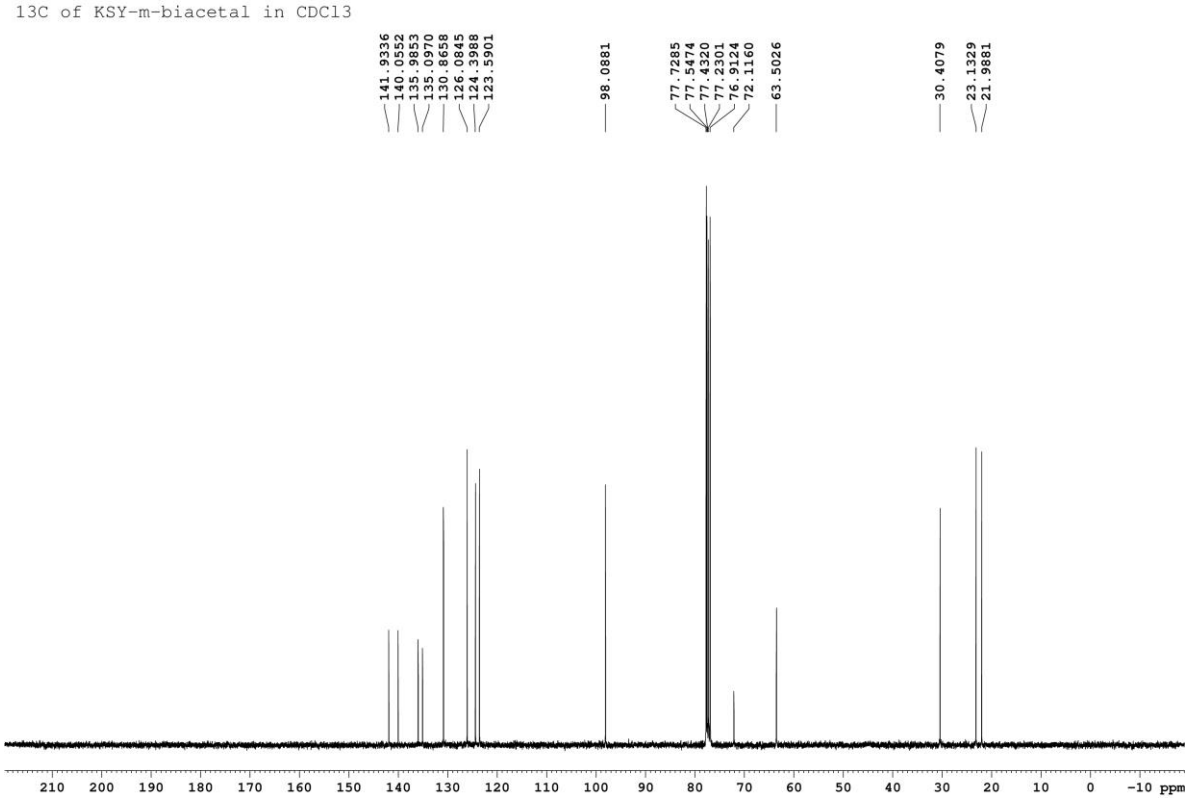


Compound **9b**

^{1}H NMR

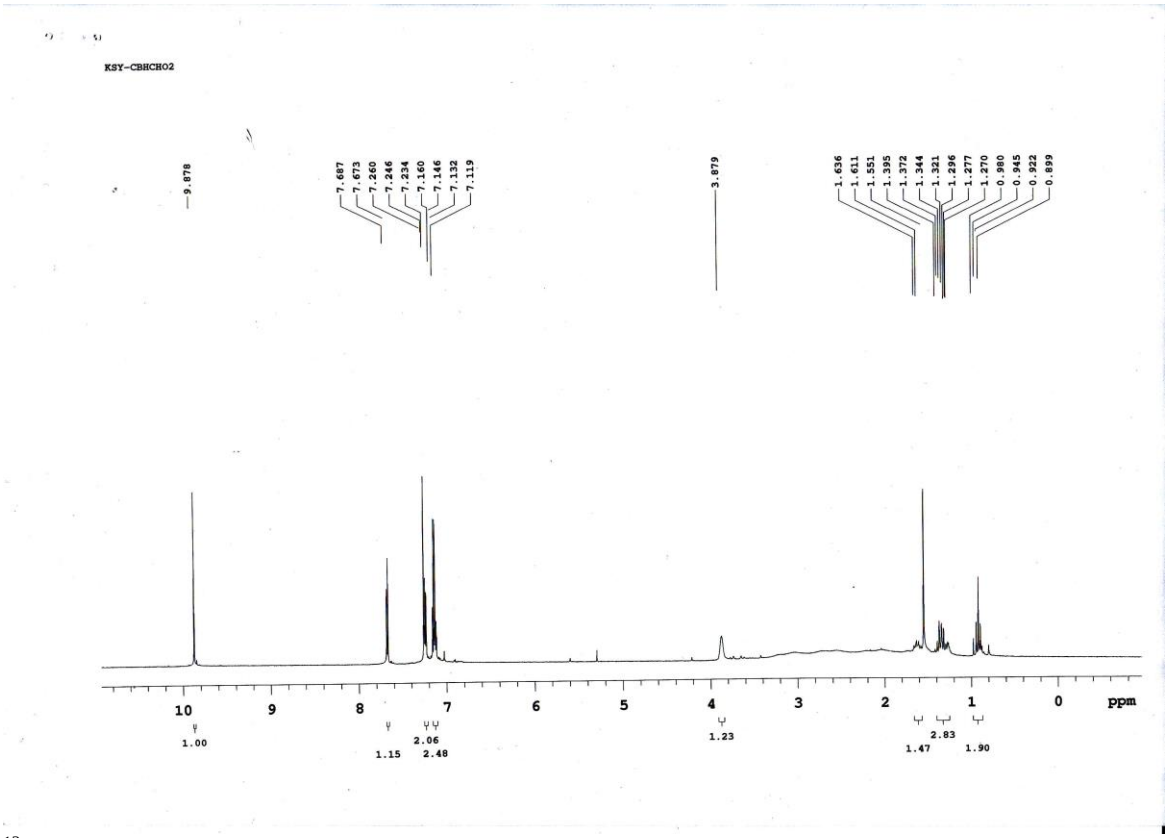


^{13}C NMR

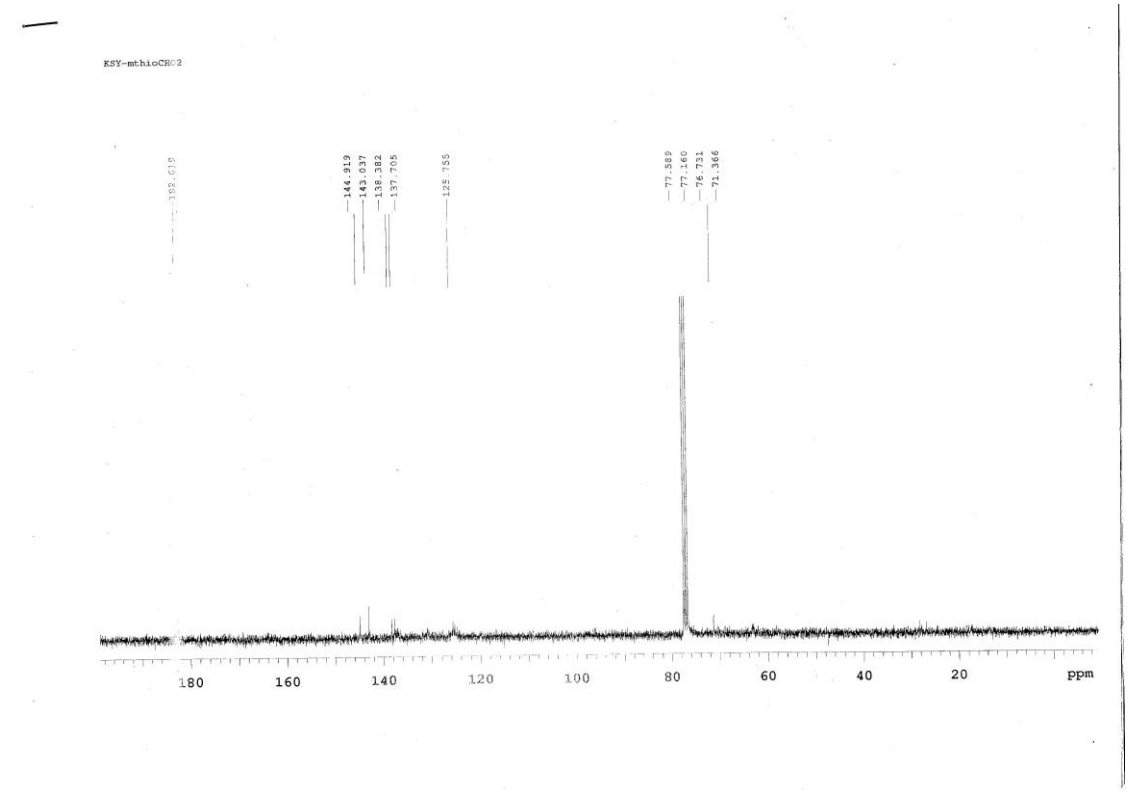


Compound **10b**

^{1}H NMR

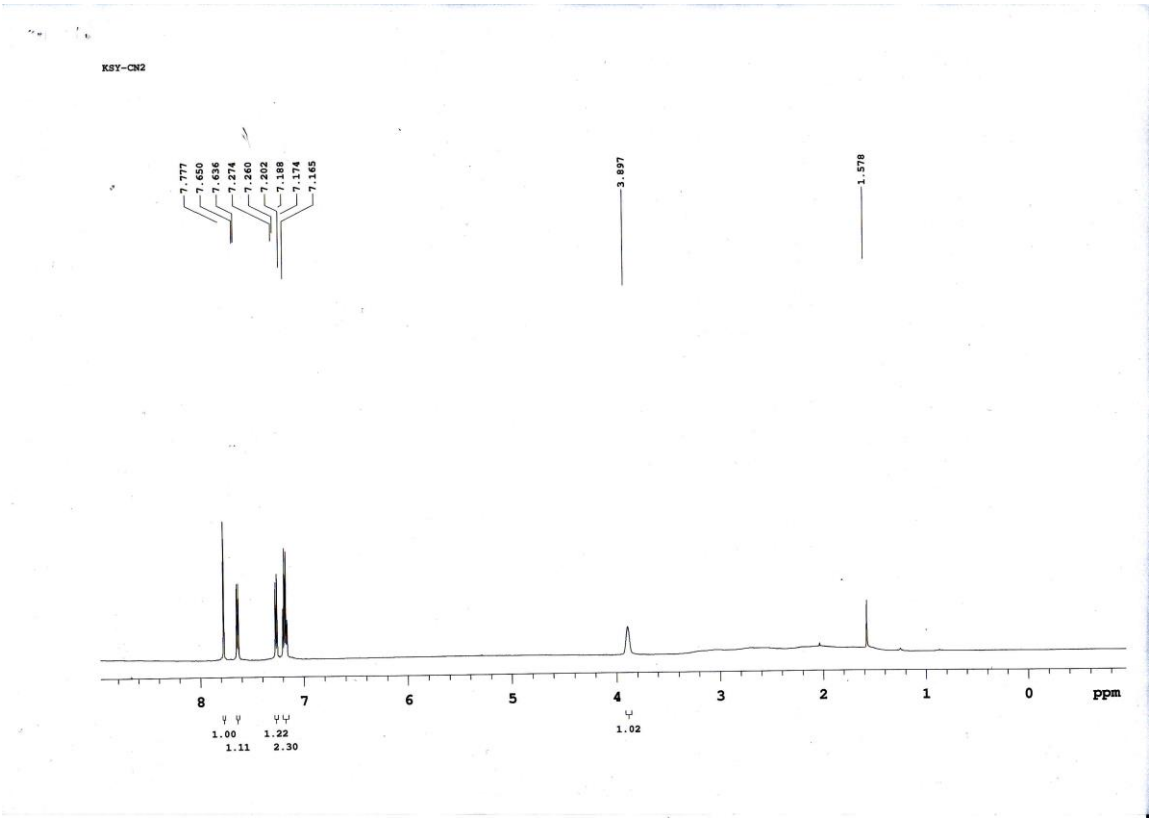


^{13}C NMR

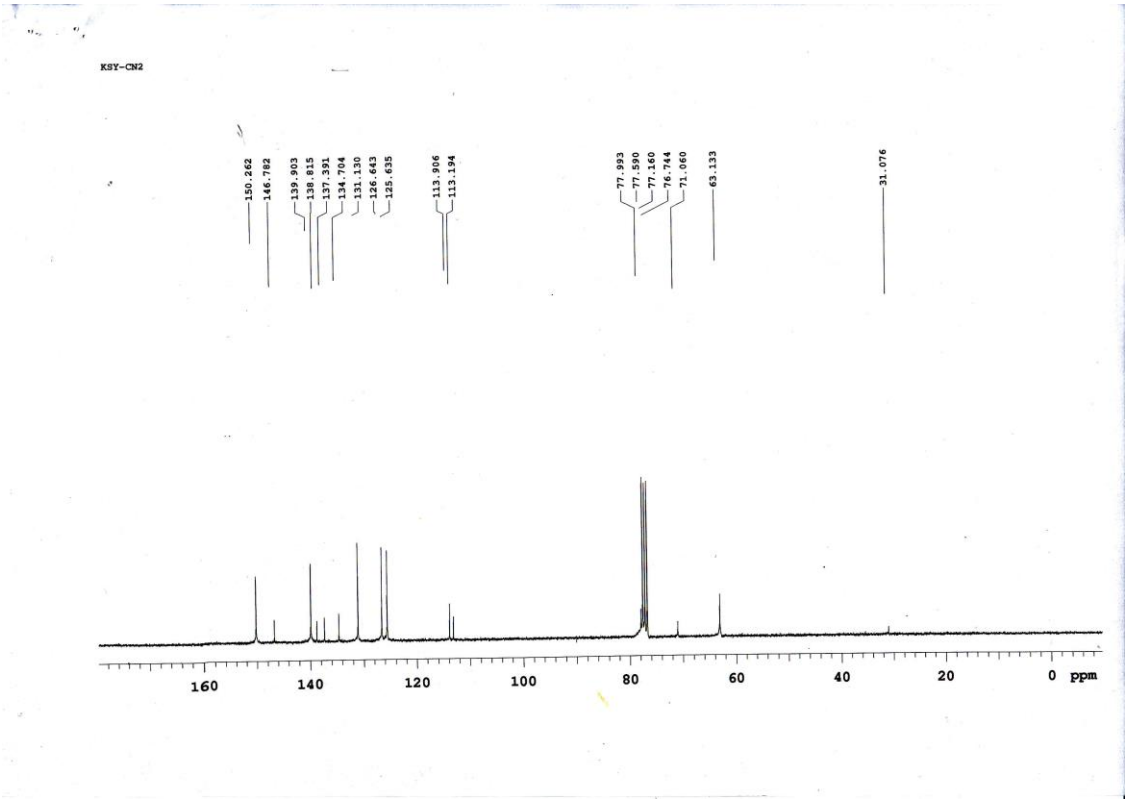


Compound **1b**

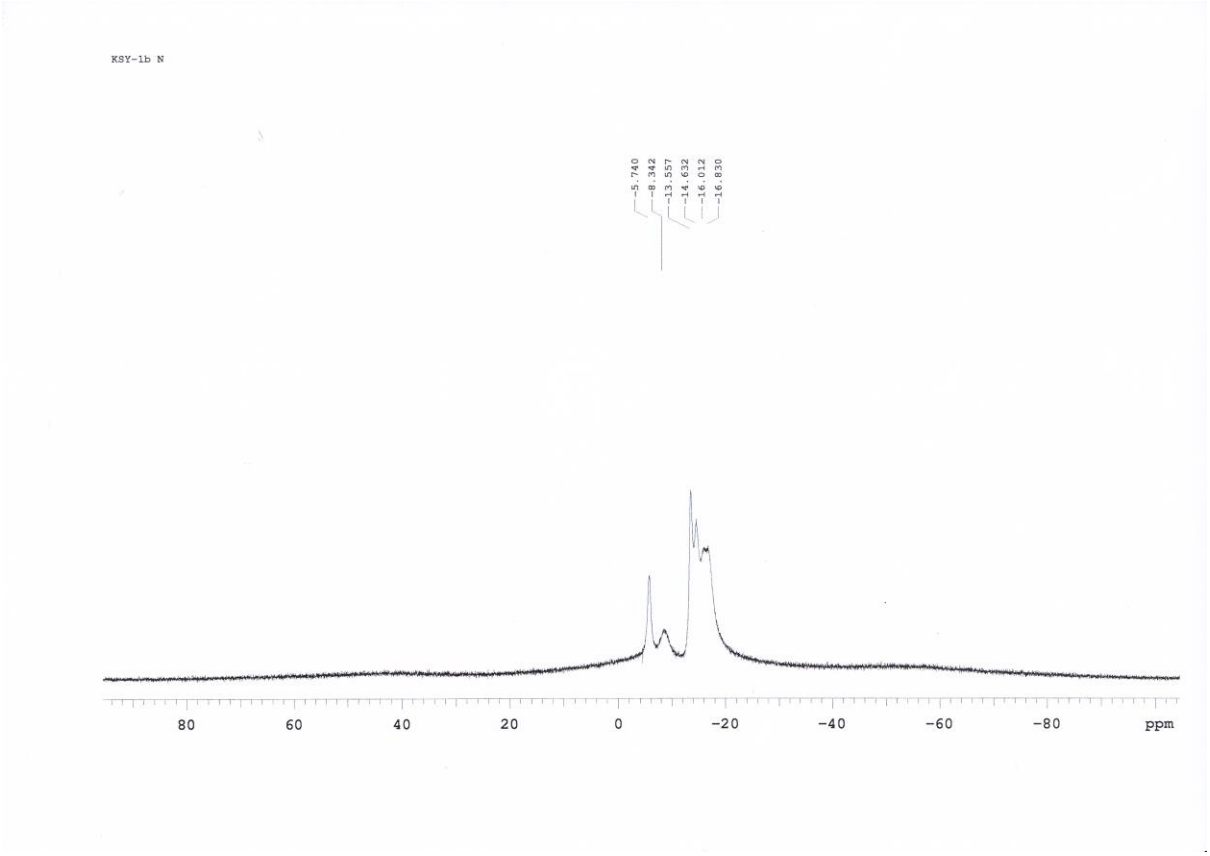
^{1}H NMR



^{13}C NMR

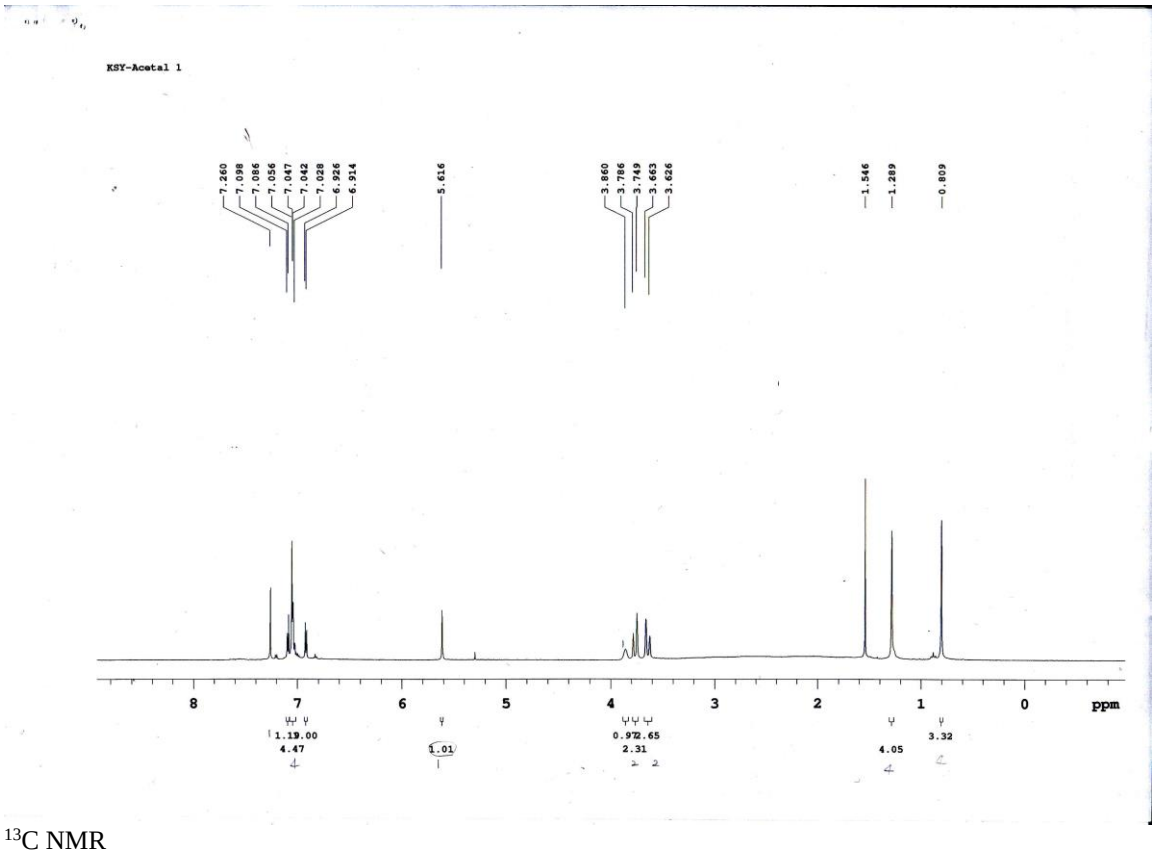


^{11}B NMR

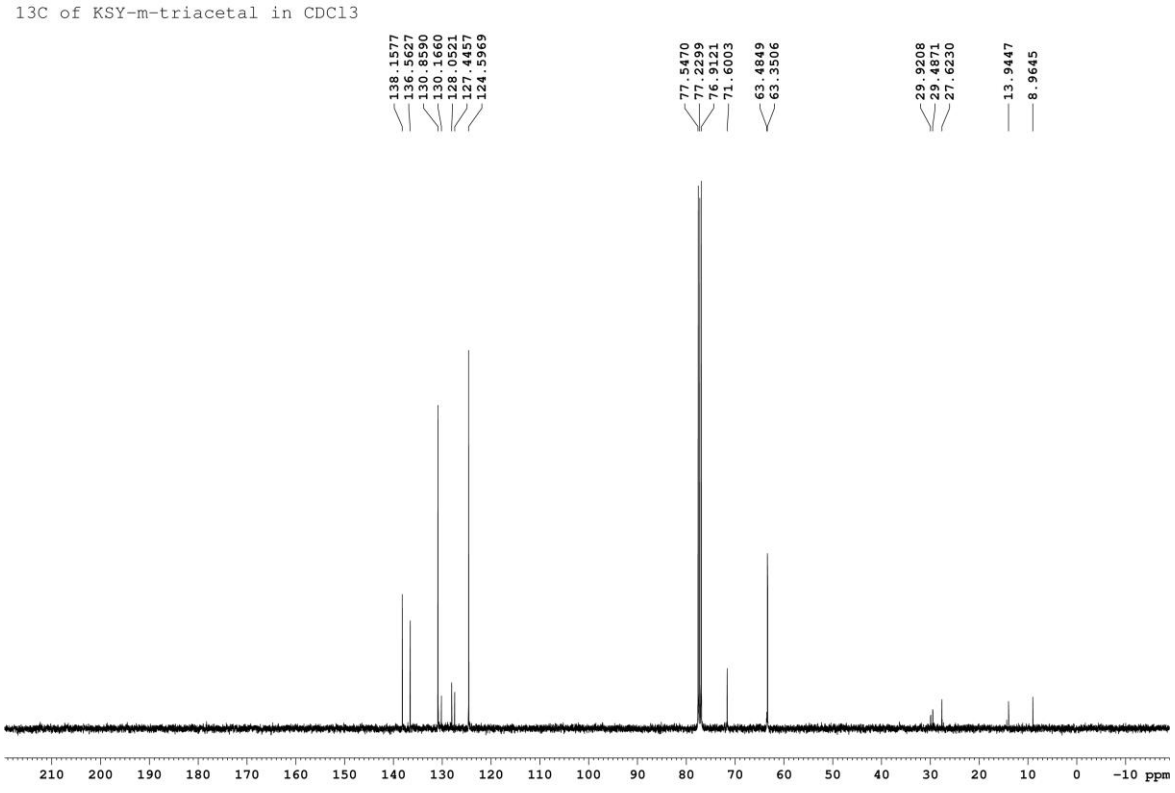

KSY-1b N
-5.740
-8.342
-13.557
-14.632
-16.012
-16.830
80
60
40
20
0
-20
-40
-60
-80
ppm

Compound **9c**

^{1}H NMR

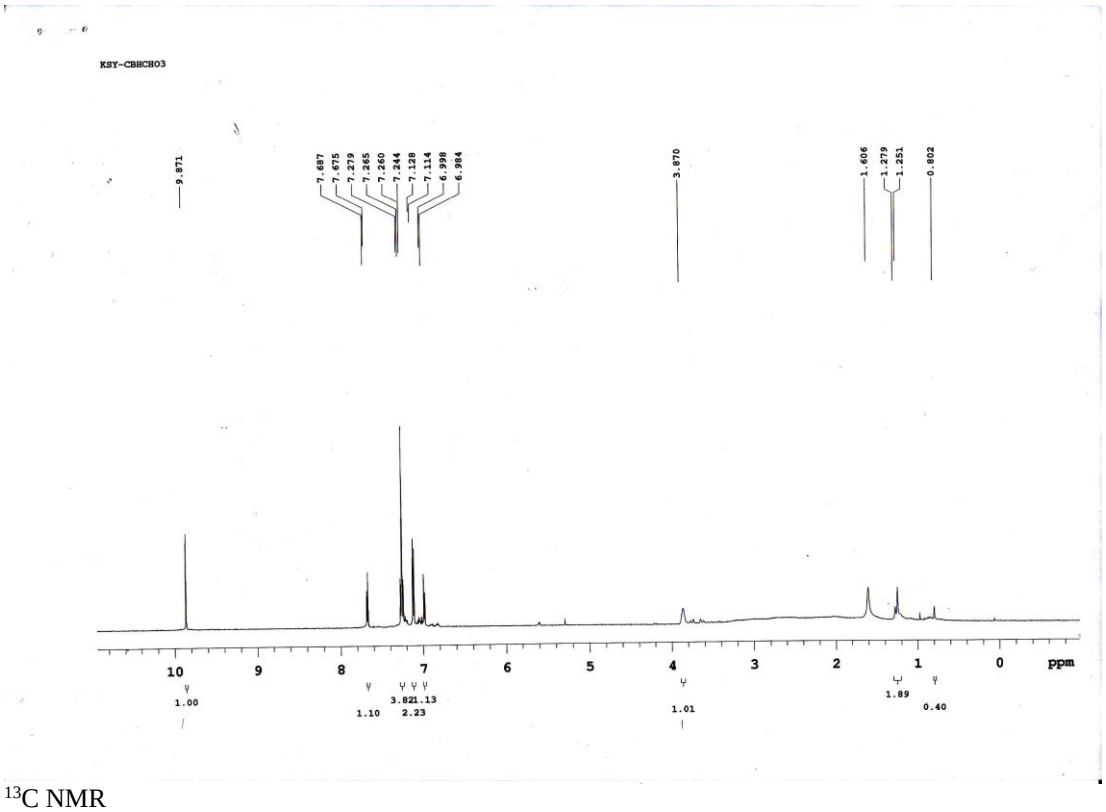


^{13}C NMR

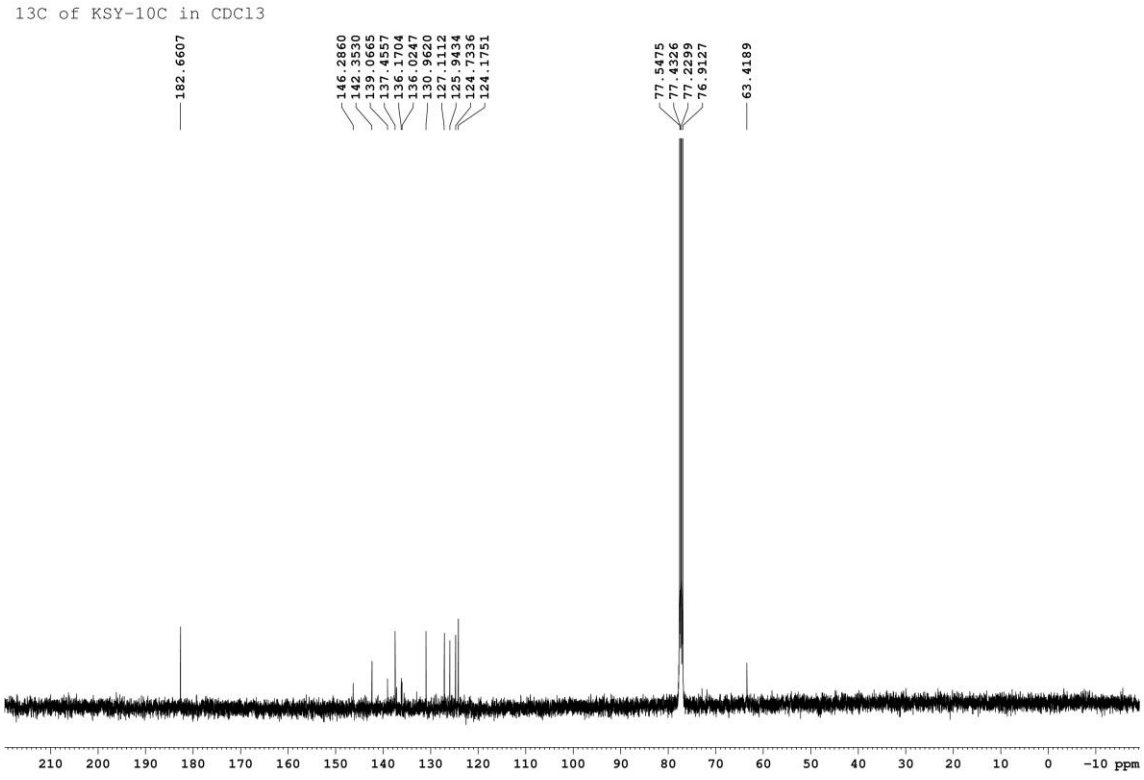


Compound **10c**

^{1}H NMR

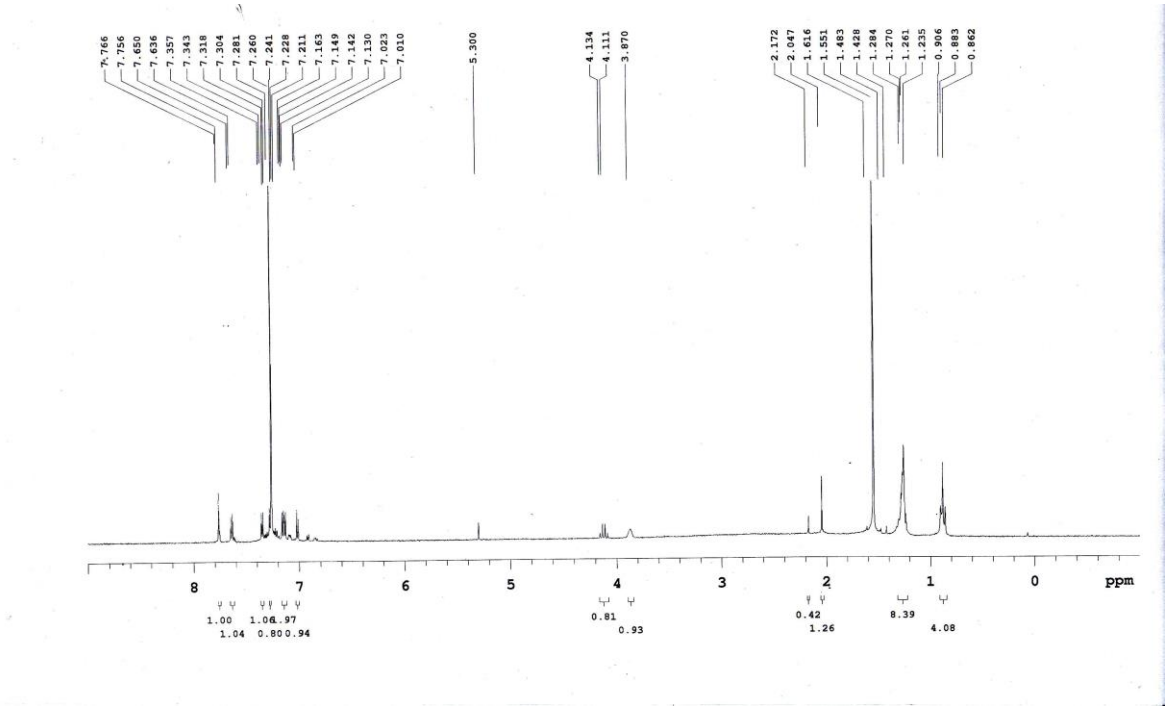


^{13}C NMR



Compound **1c**

^{1}H NMR



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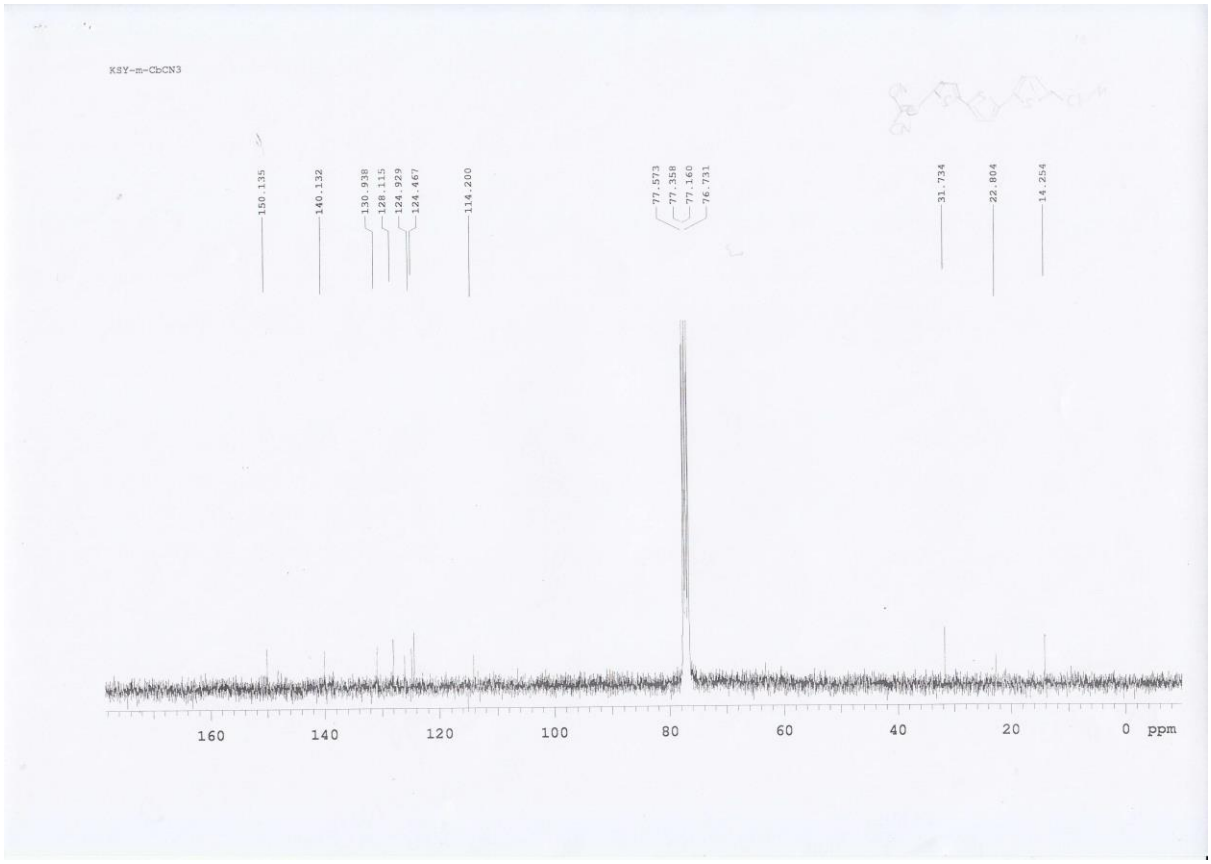
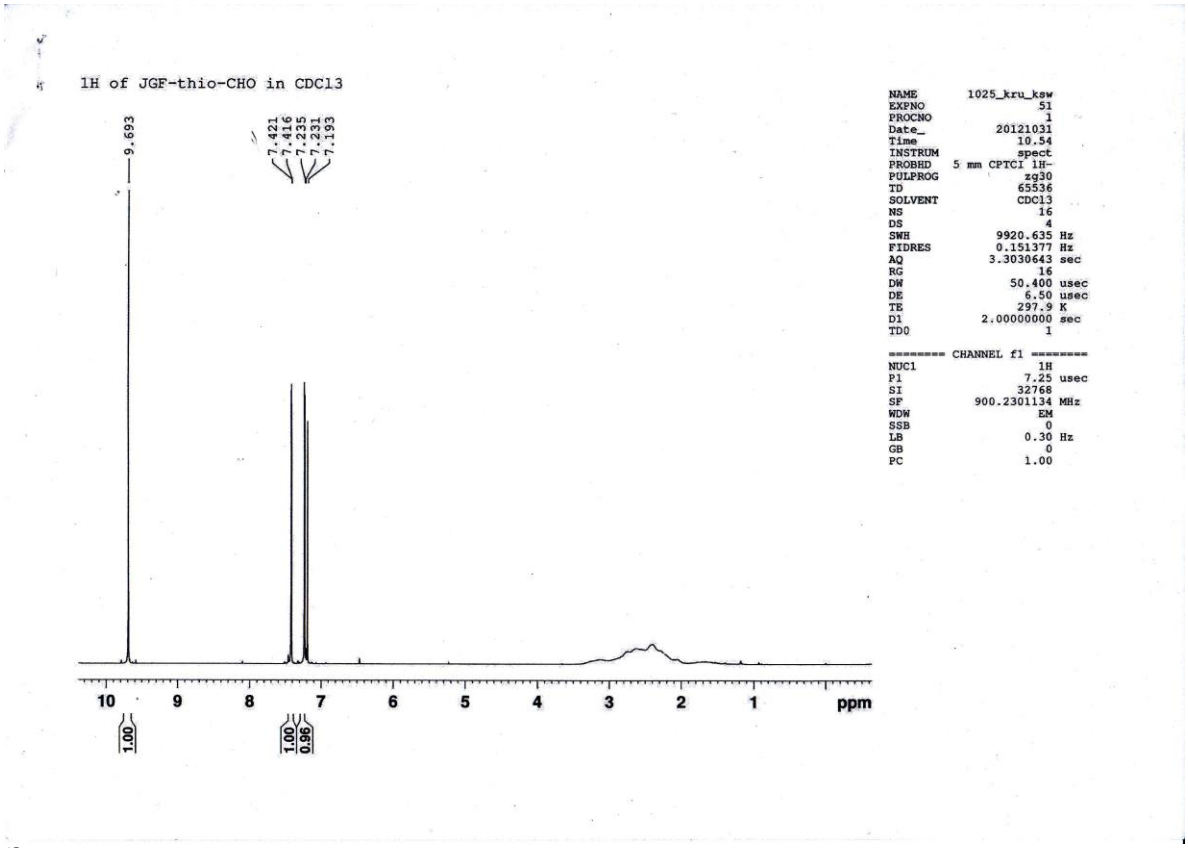


Compound **11**

^{1}H NMR



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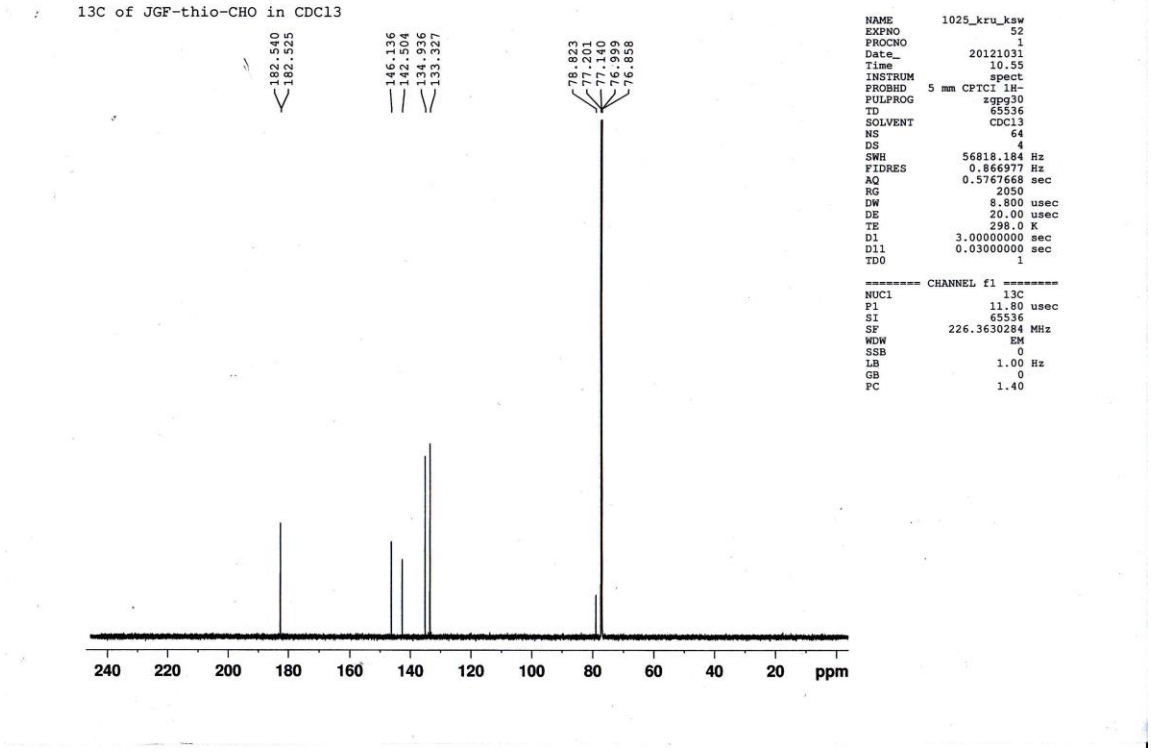
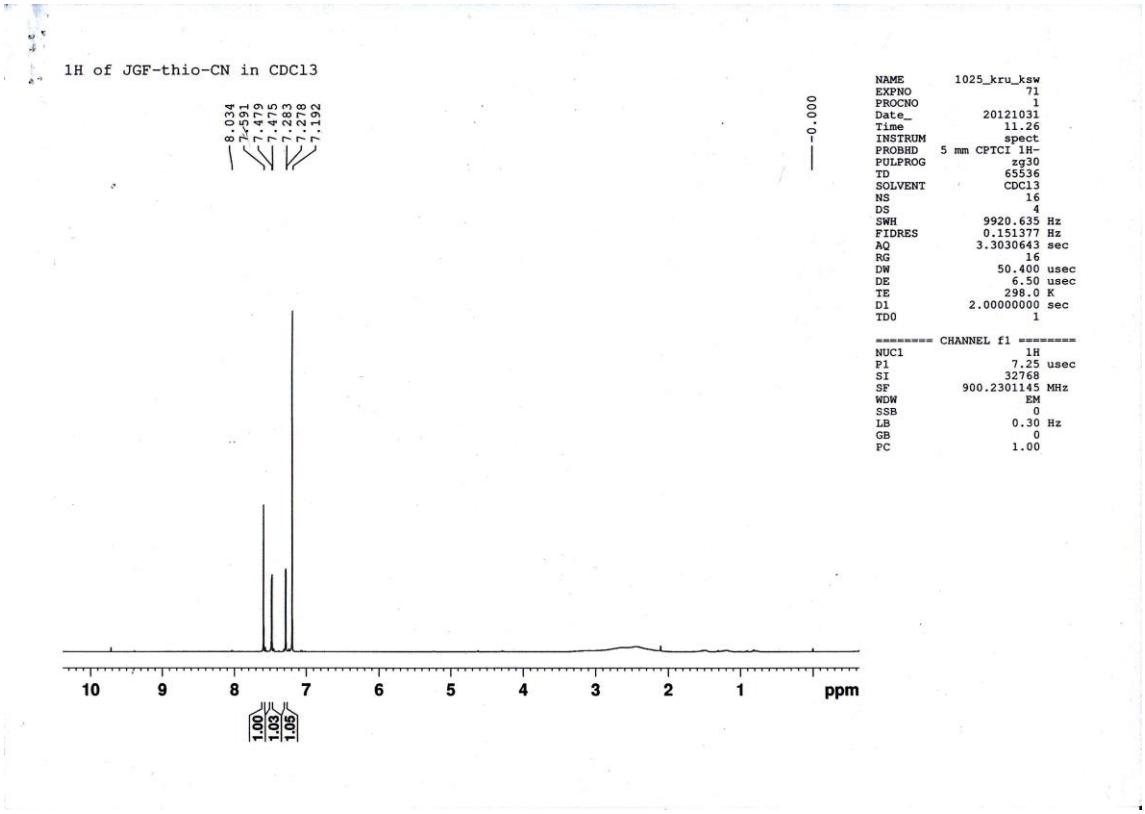


Compound **2a**

^{1}H NMR



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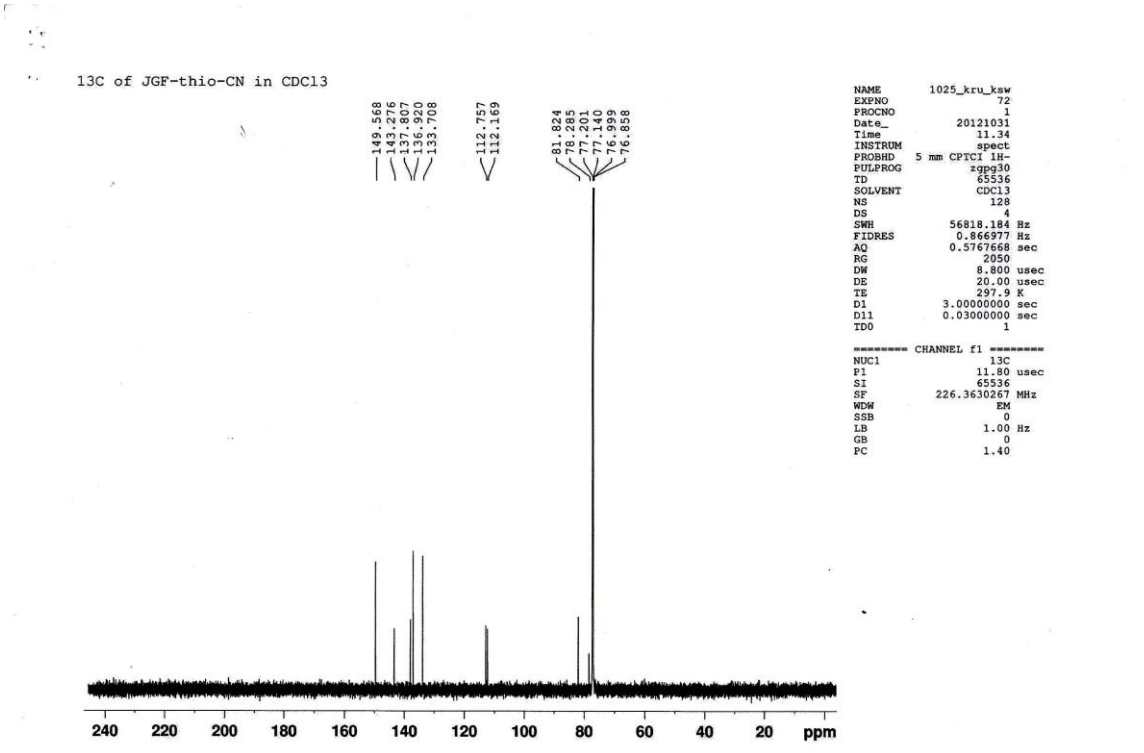
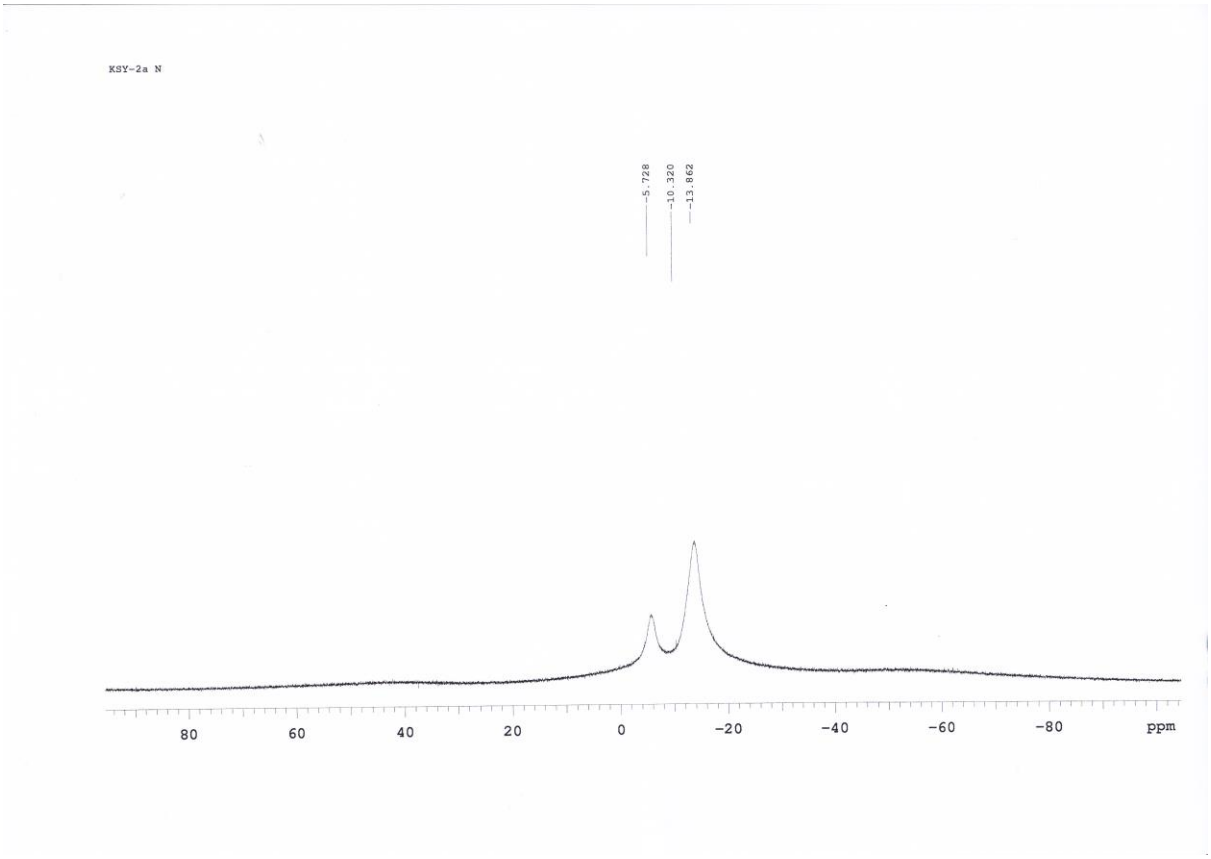


^{11}B NMR



Compound **12b**

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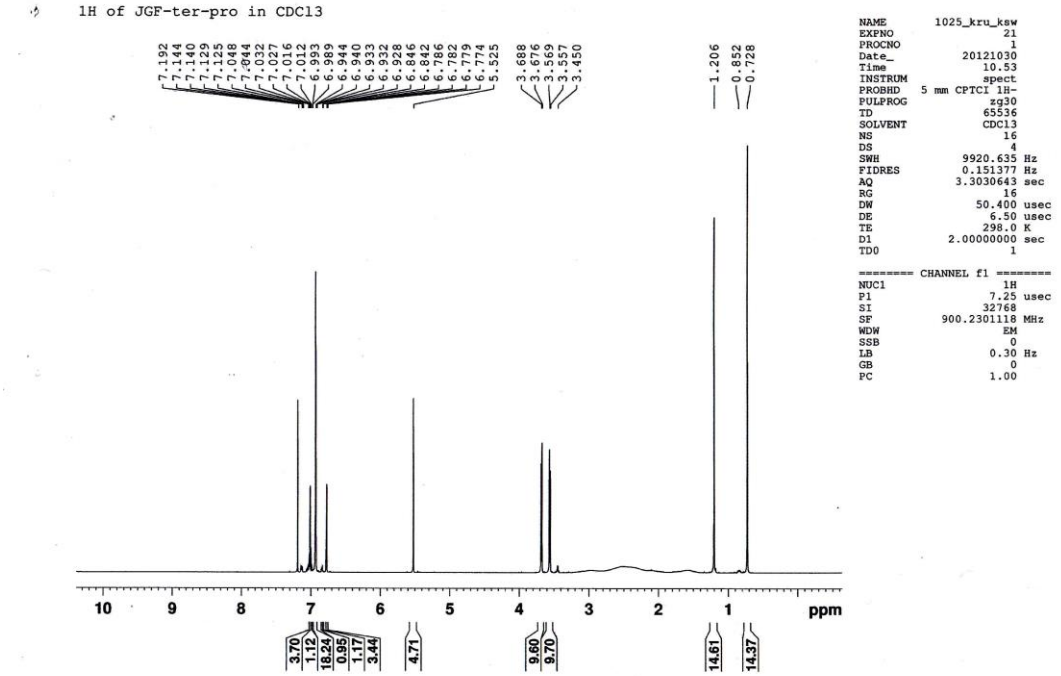

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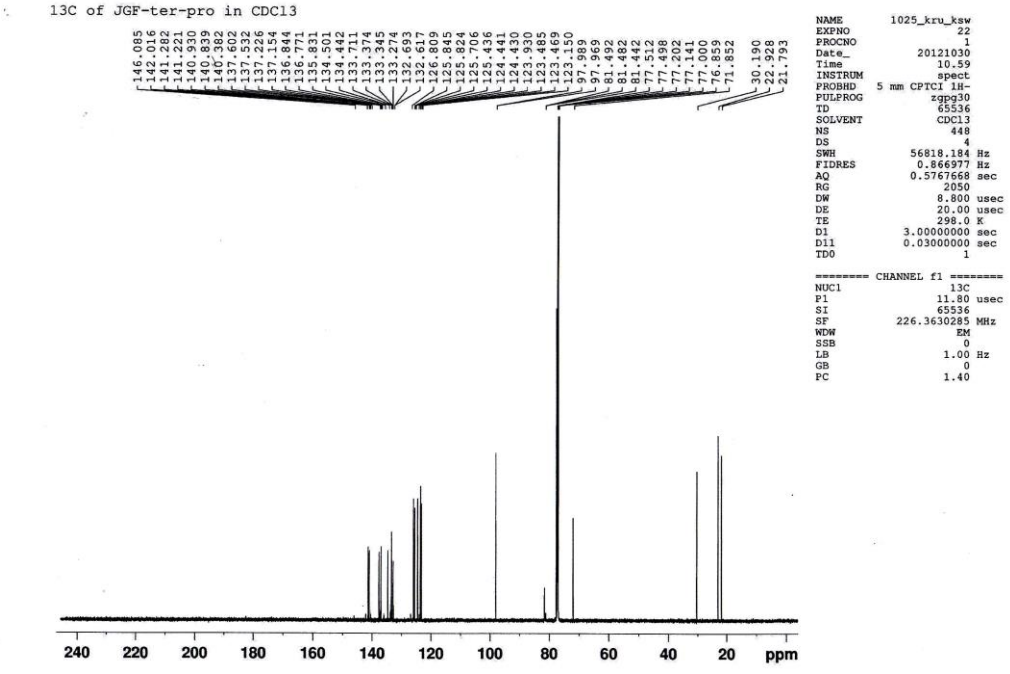
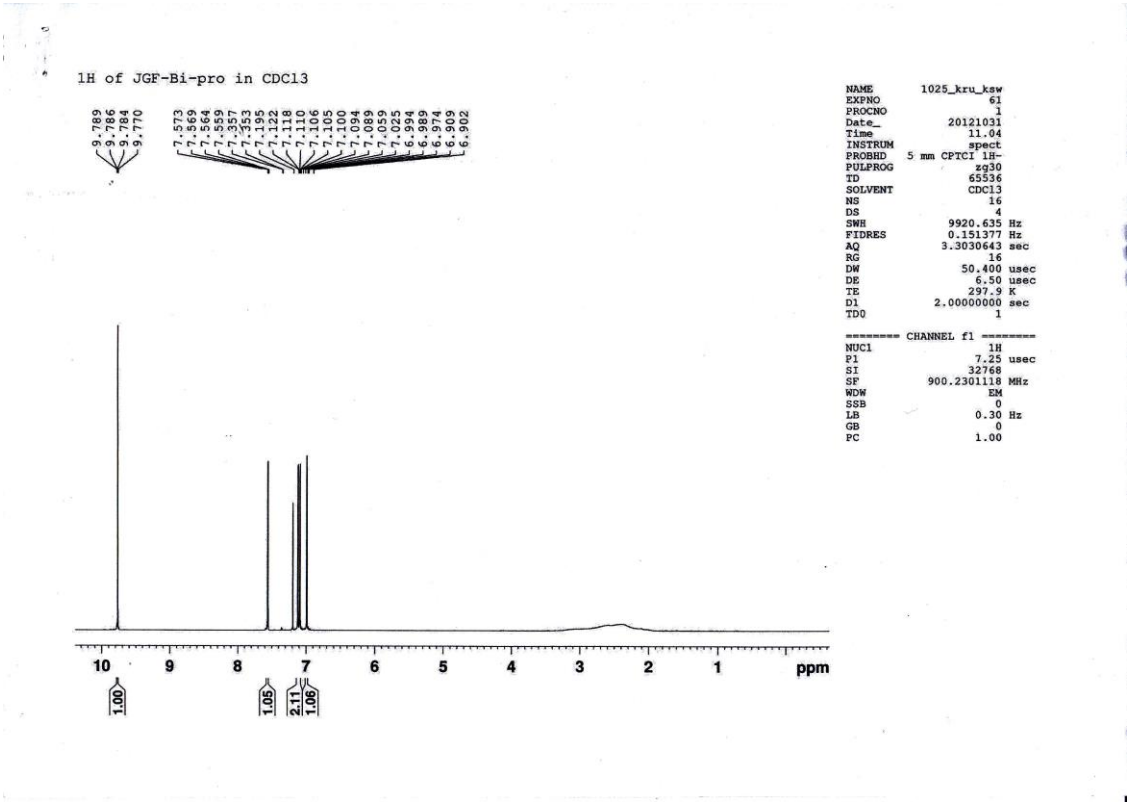
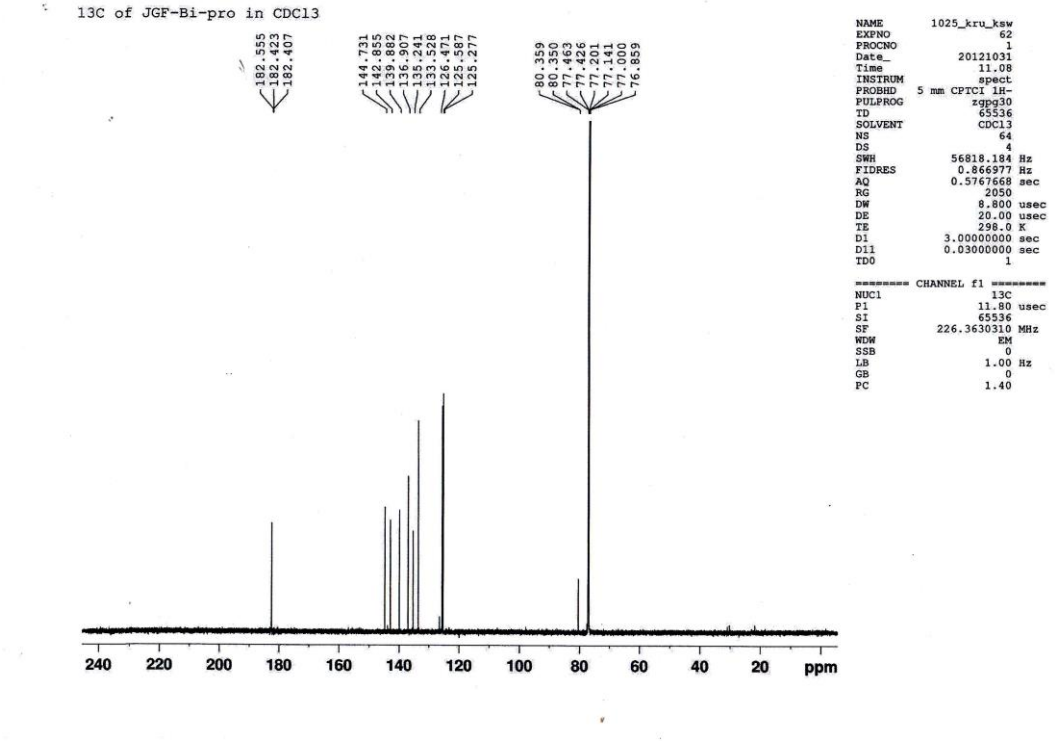


Compound **13b**

^{1}H NMR

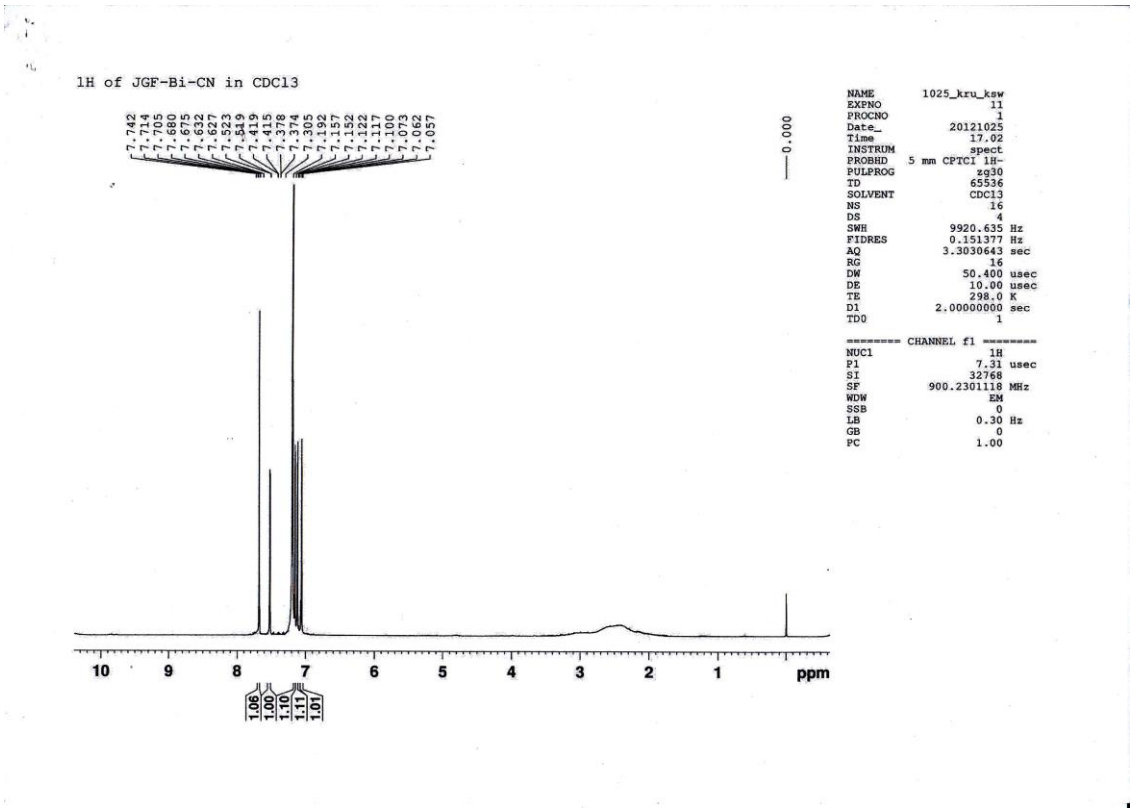


^{13}C NMR



Compound **2b**

^{1}H NMR



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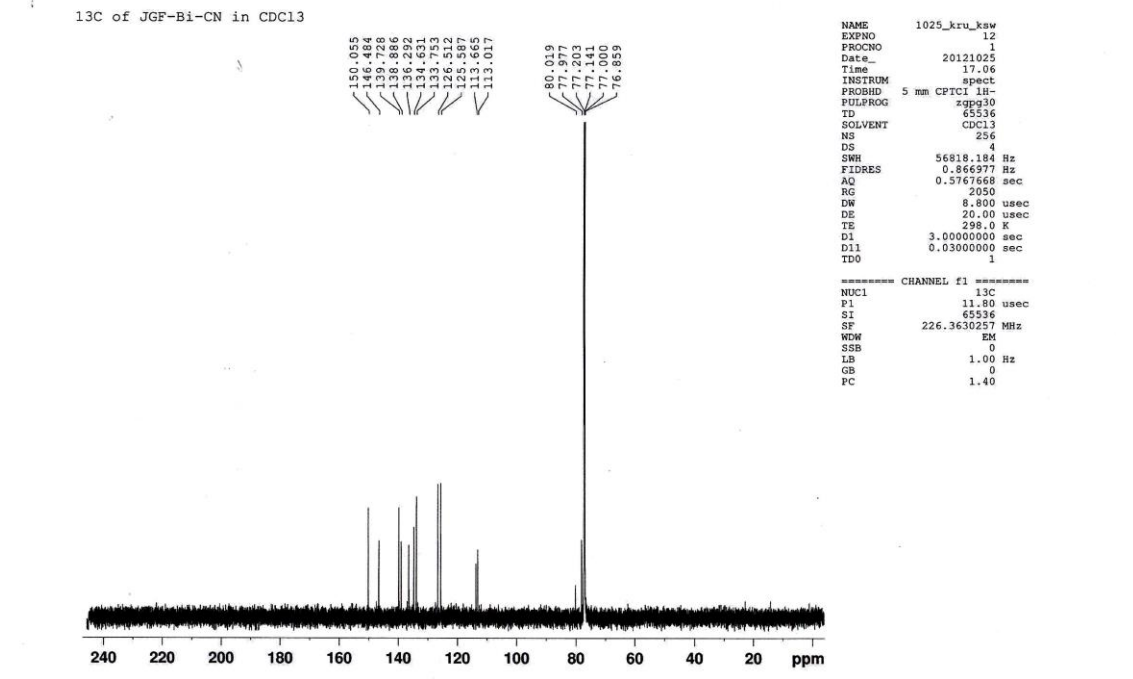
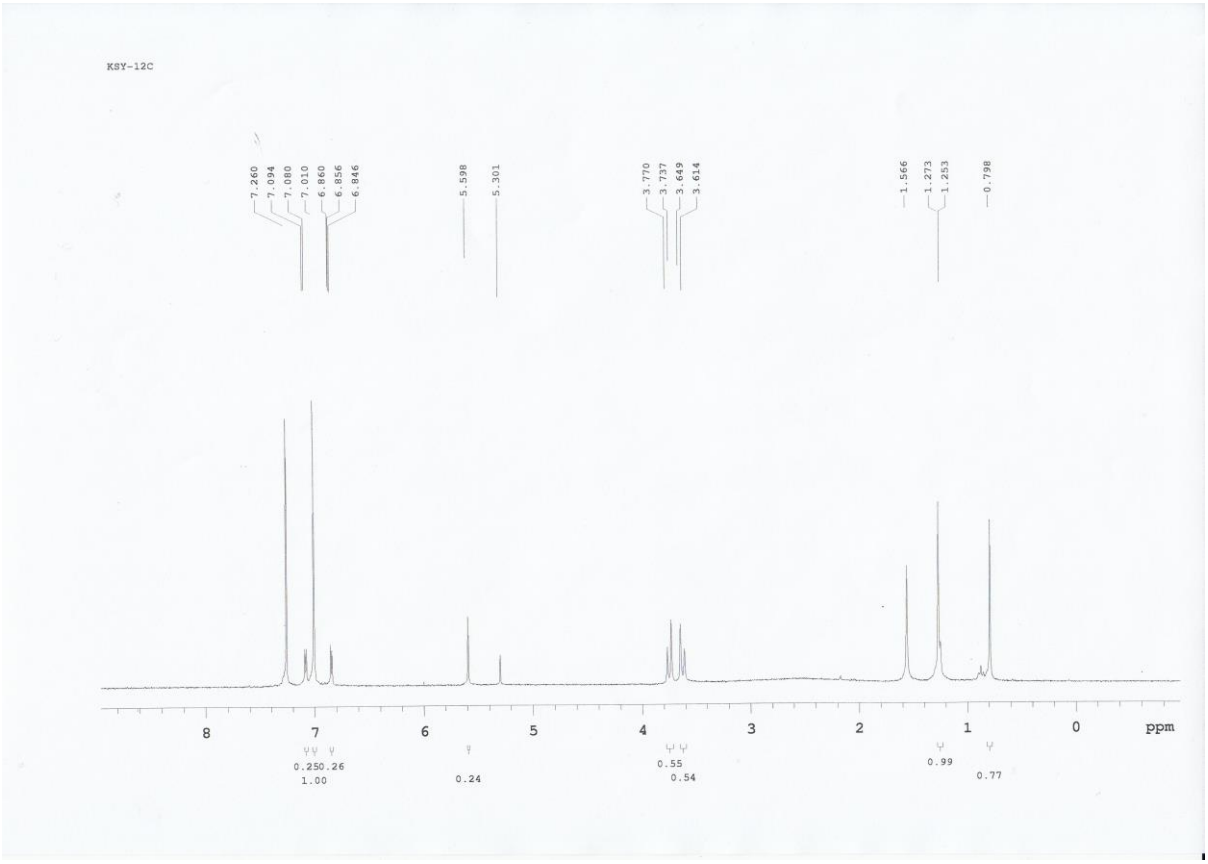


Compound **12c**

^{1}H NMR



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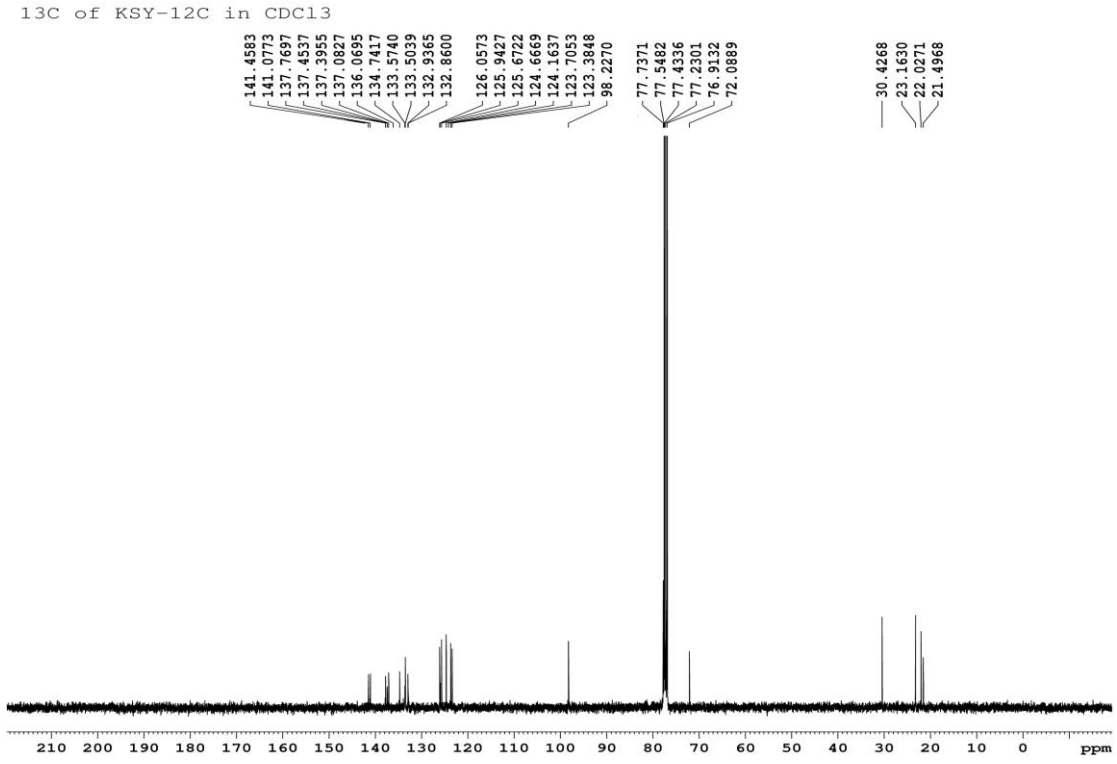
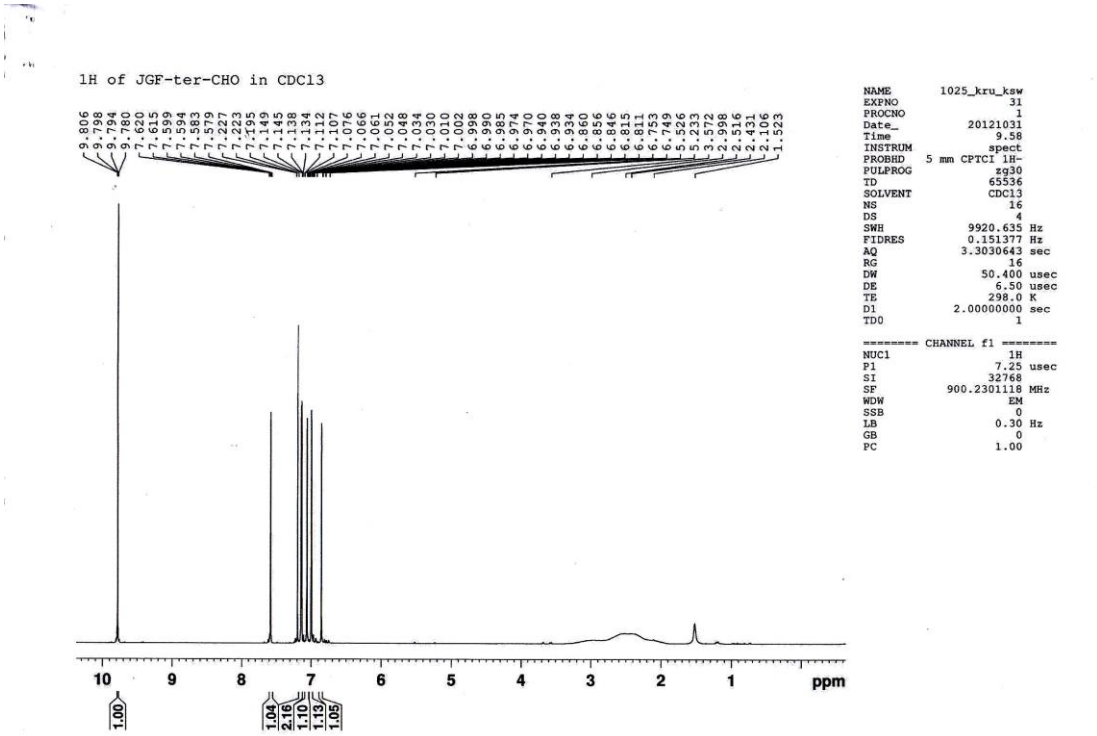


Compound **13c**

^{1}H NMR



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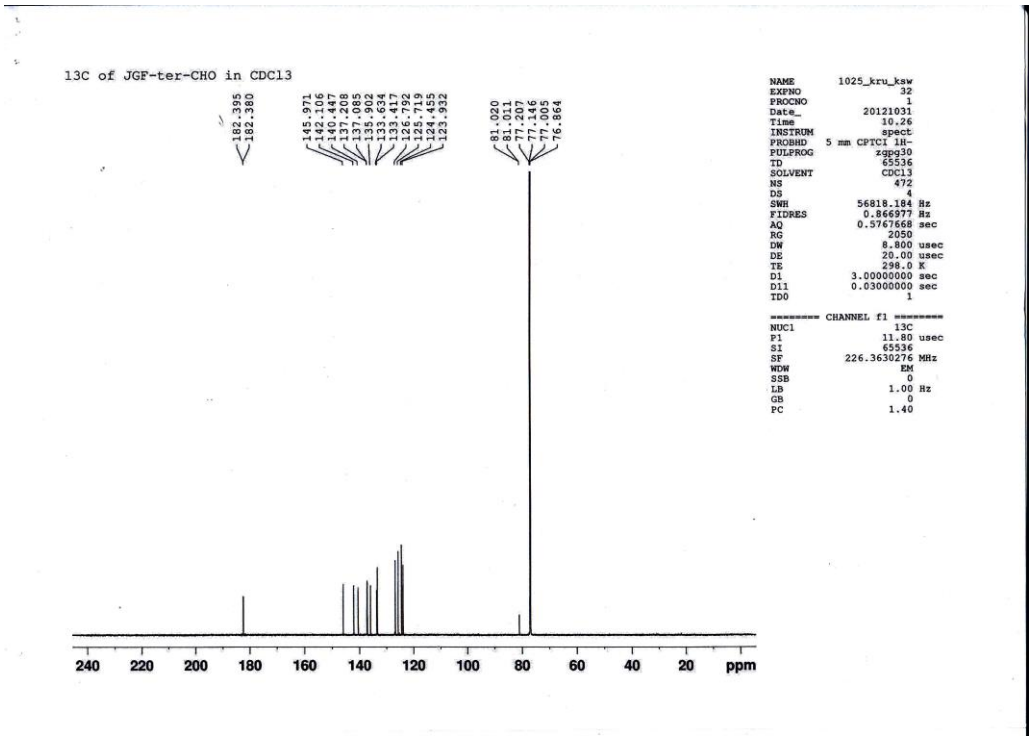
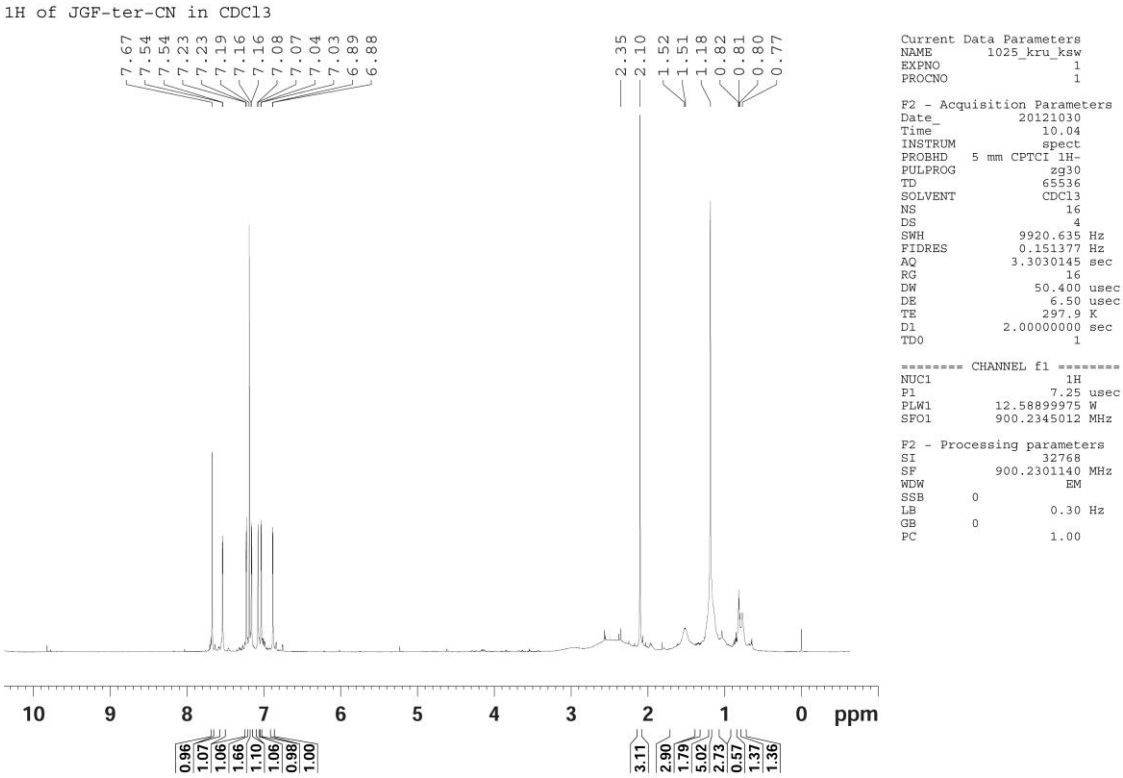


Compound **2c**

^{1}H NMR

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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
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DS                      4
SWH               9920.635 Hz
FIDRES            0.151377 Hz
AQ                3.3030145 sec
RG                     16
DW                  50.400 usec
DE                   6.50 usec
TE                  297.9 K
D1               2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.25 usec
PLW1          12.58899975 W
SFO1          900.2345012 MHz

F2 - Processing parameters
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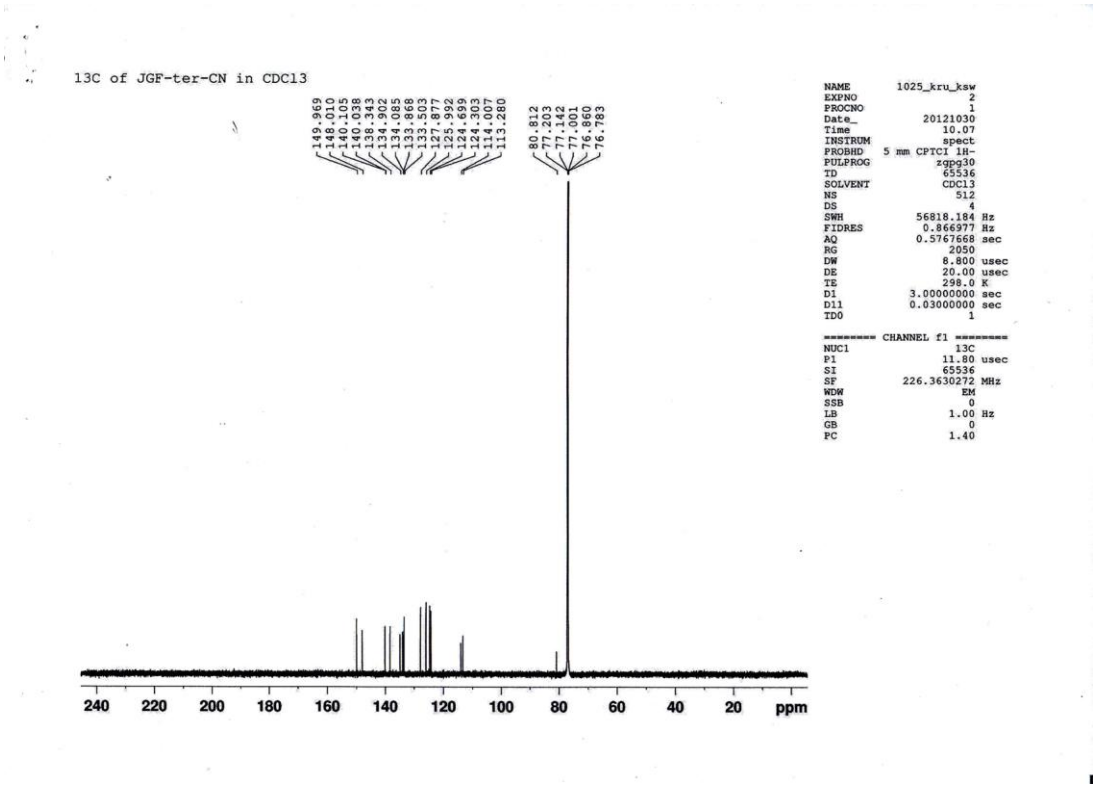
^{13}C NMR

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D1               3.00000000 sec
D11              0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
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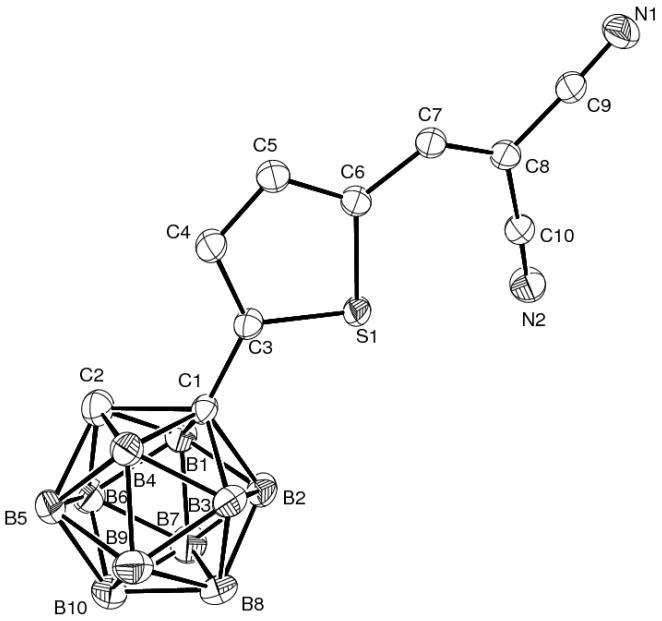


Figure S1. ORTEP drawing of compound **1a** with 30% probability for the thermal ellipsoids. Hydrogens were omitted for clarity.

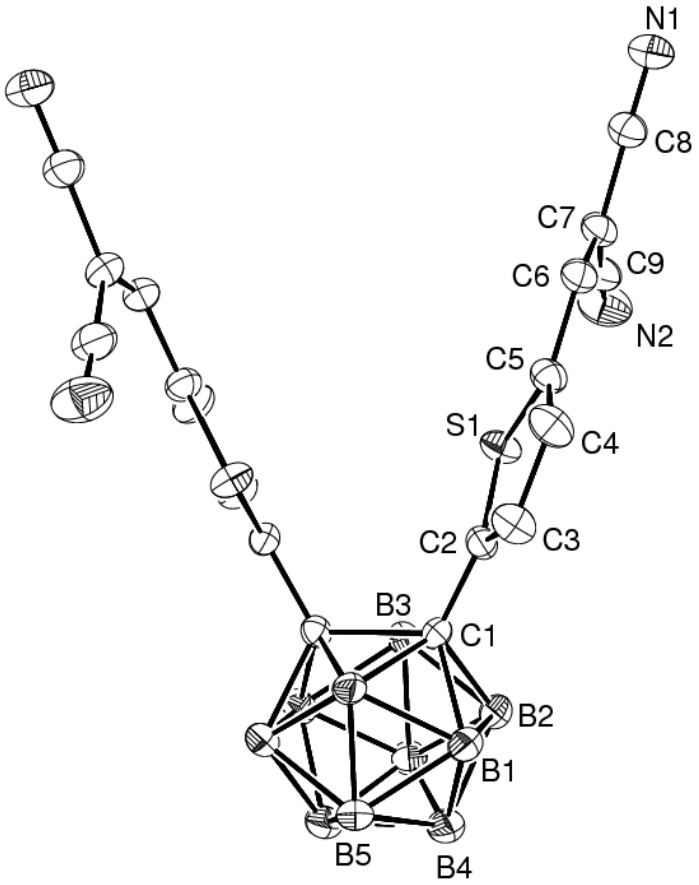


Figure S2. ORTEP drawing of compound **2a** with 30% probability for the thermal ellipsoids. Hydrogens were omitted for clarity.

Table S1. Crystal data and structure refinement for **1a** and **2a**

Identification code	**1a**	**2a**
Empirical formula	$C_{10}H_{14}B_{10}N_2S$	$C_{18}H_{16}B_{10}N_4S_2$
Formula weight	302.39	460.57
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$	Monoclinic, C 2/c
Unit cell dimensions	a = 18.348(6) Å	a = 15.986(8) Å
	b = 7.522(2) Å β = 104.643(6)°	b = 11.333(6) Å β = 114.529(8) °
	c = 12.006(4) Å	c = 14.165(7) Å
Volume	1603.0(9) Å^3	2334(2) Å^3
Z, Calculated density	4, 1.253 Mg/m^3	4, 1.310 Mg/m^3
Absorption coefficient, μ	0.190 mm^{-1}	0.244 mm^{-1}
F(000)	616	936
Crystal size	0.23 × 0.15 × 0.09 mm	0.15 × 0.13 × 0.11 mm
θ range for data collection	1.15 to 28.40°	2.278 to 28.850°
Limiting indices	$-24\leq h\leq 24$, $-10\leq k\leq 9$, $-16\leq l\leq 16$	$-21\leq h\leq 21$, $-14\leq k\leq 15$, $-18\leq l\leq 18$
Reflections collected / unique	20624 / 3984 [R_{int} = 0.0871]	8144 / 2567 [R_{int} = 0.0440]
Completeness to θ = 28.40	99.2 %	85.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3984 / 0 / 208	2567 / 0 / 155
Goodness-of-fit on F^2	1.066	1.184
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0758, wR_2 = 0.2002	R_1 = 0.0932, wR_2 = 0.2462
R indices (all data)	R_1 = 0.1278, wR_2 = 0.2479	R_1 = 0.1313, wR_2 = 0.2616
Largest diff. peak and hole	0.726 and -0.411 e. Å^3	0.504 and -0.578 e. Å^3

[a]$R_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$), [b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$; , $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

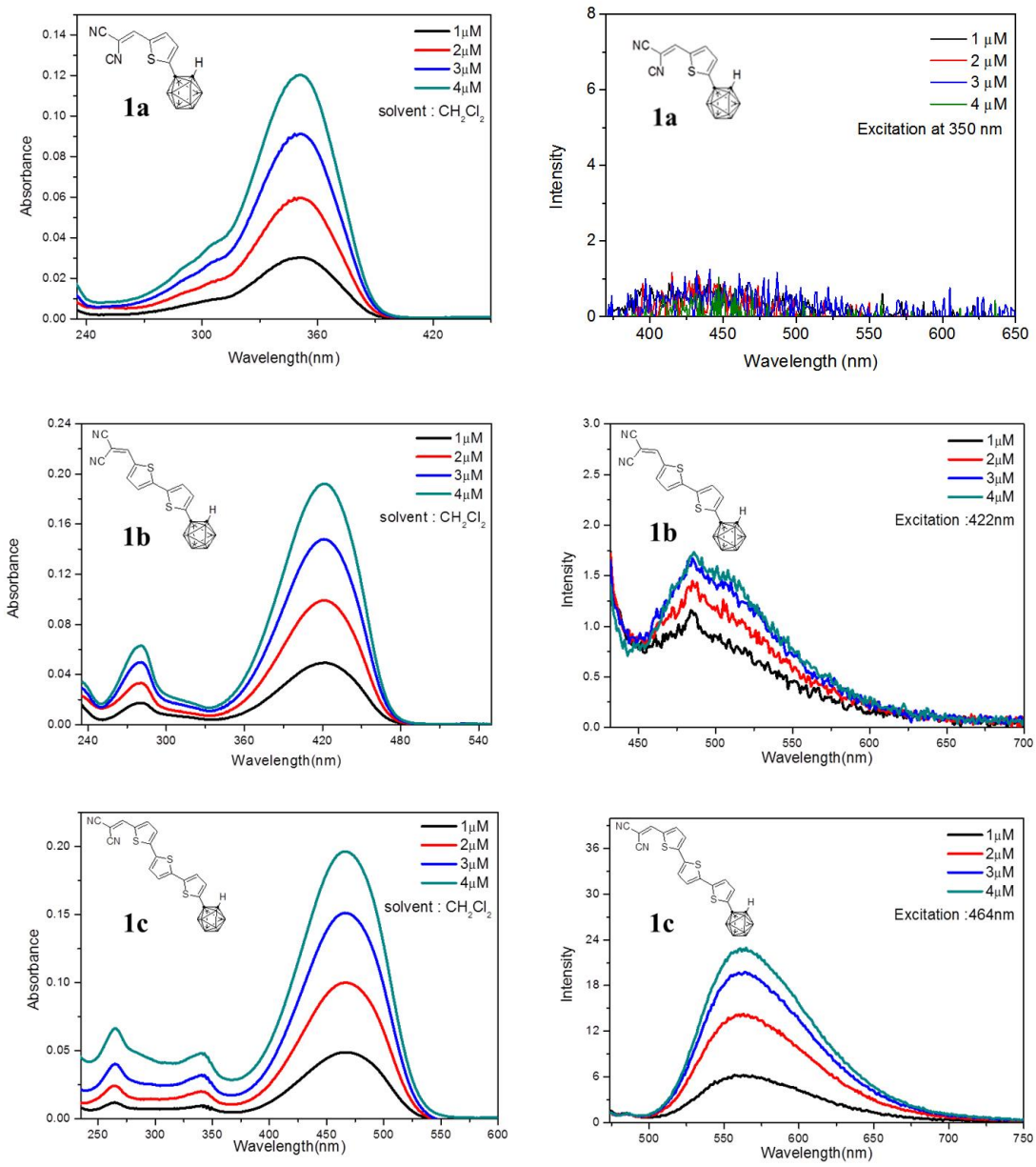


Figure S3. Absorption and emission spectra of **1** in dichloromethane (DCM).

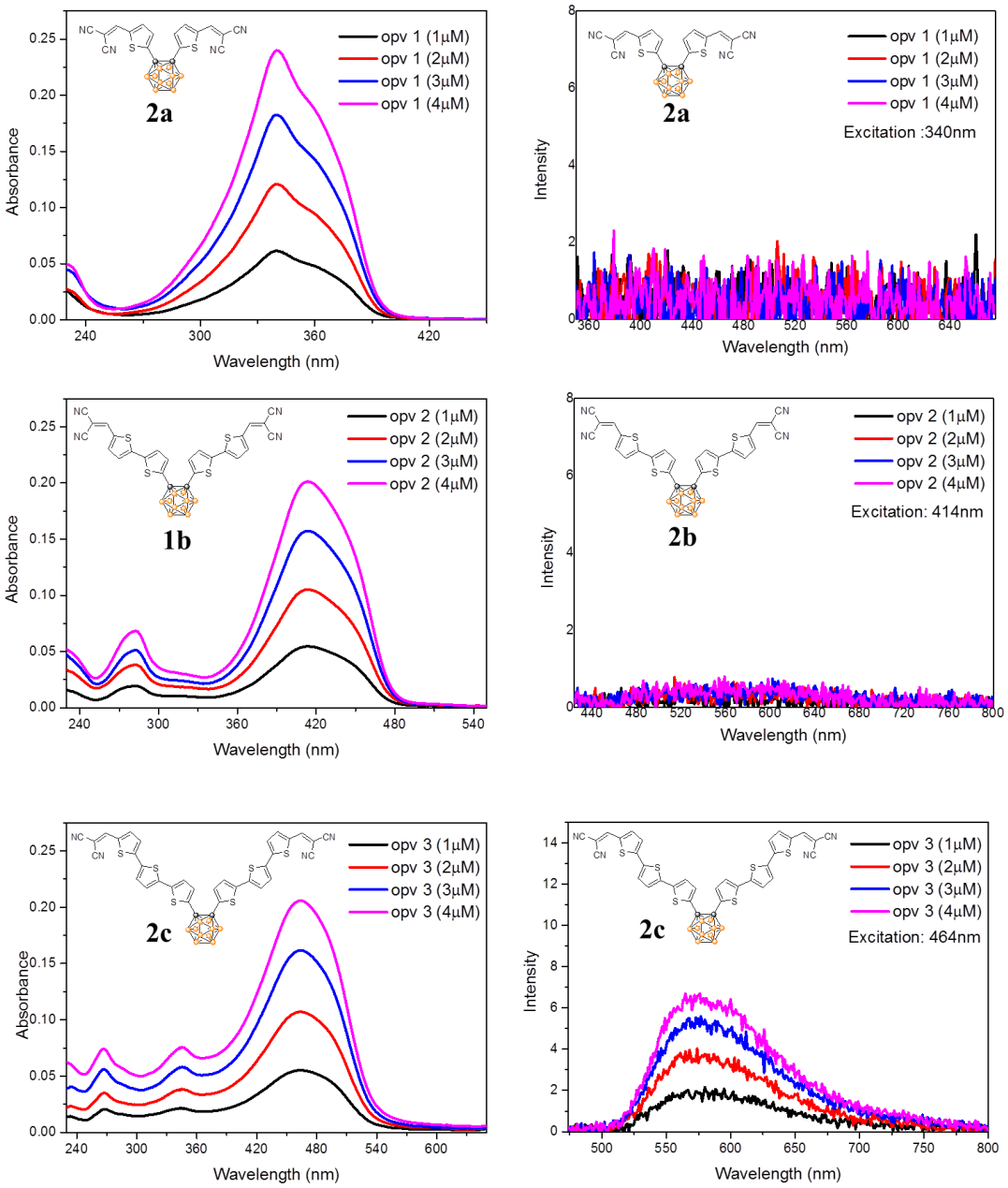


Figure S4. Absorption and emission spectra of **2** in DCM.

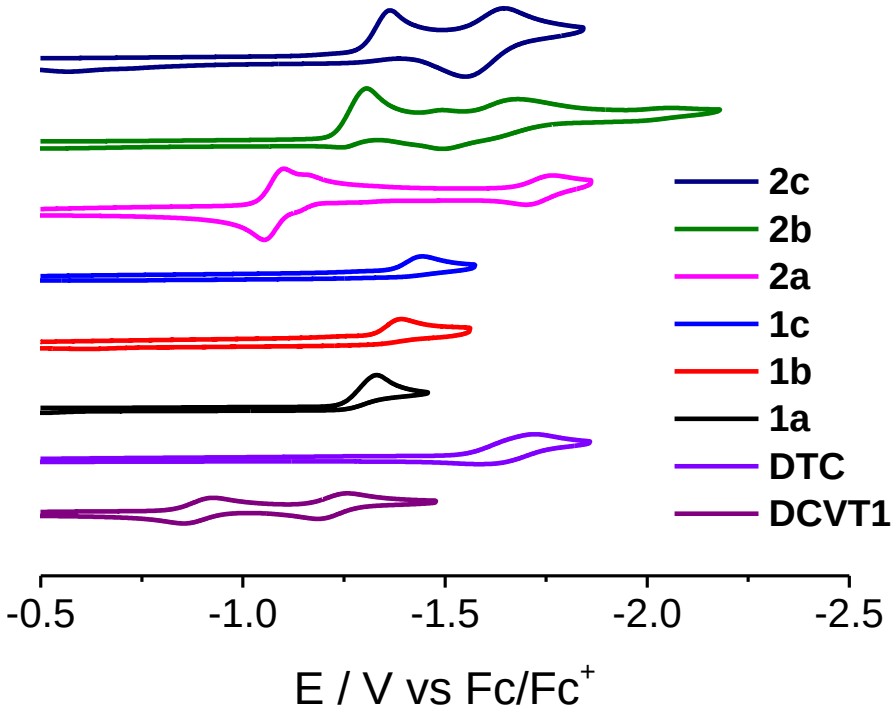


Figure S5. CVs of **DCVT1**, **DTC**, **1** and **2** (10^{-3} M substrate) in 0.10 M Bu_4NPF_6 in DCM with scan rate 100 mV s^{-1}.

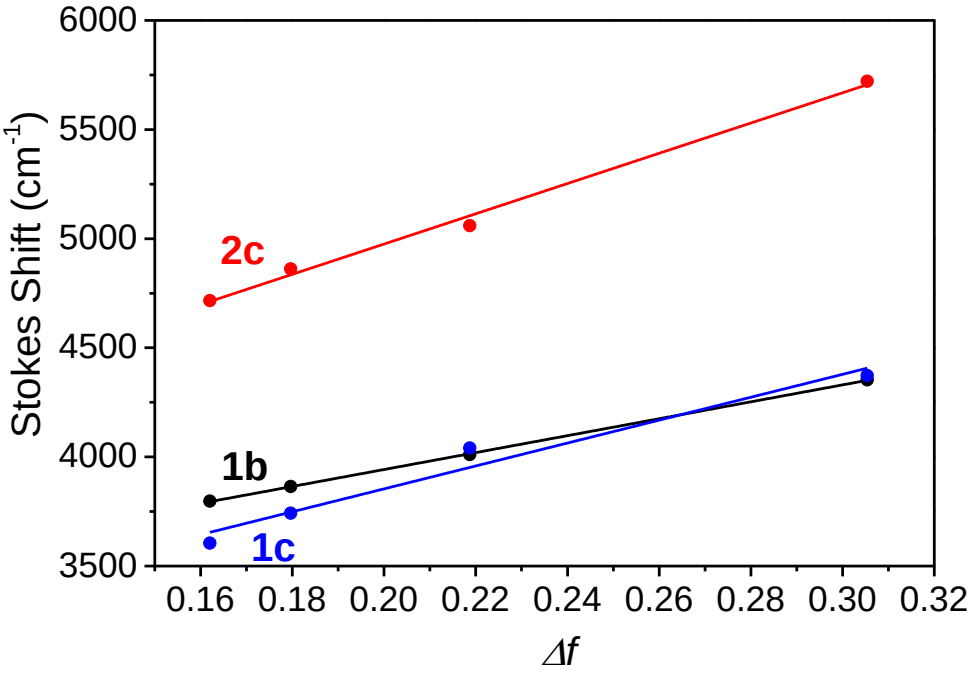
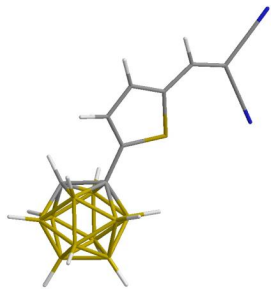
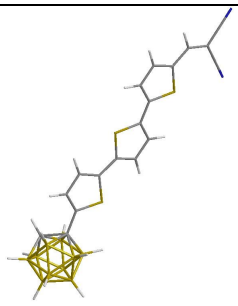
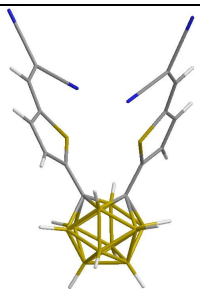
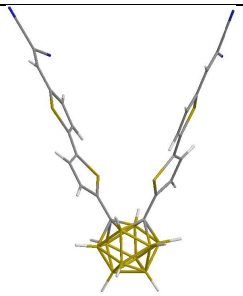
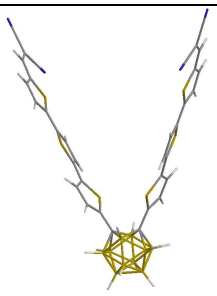


Figure S6. Mataga–Lippert plots for CT emissions of **1b** (black), **1c** (blue) and **2c** (red).

DFT Calculations. The ground-state geometries of **1a**−**1c** and **2a**−**2c** were optimized at the density function theory (DFT) level. The characterization of the low-lying excited singlet states relies on the time-dependent DFT (TD-DFT) calculation that is performed on the basis of the ground-state geometry by B3LYP[S1] density functional theory (DFT), using a 6-31G(d,p)[S2] basis set and no imaginary frequencies were found. All calculations were performed with the Gaussian 09 package.[S3] Molecular orbital plots were made by using Chem3D Pro (version 10.0).

Table S2. Selected energy levels, orbital contributions, and oscillation strengths of **1a** and **2a**

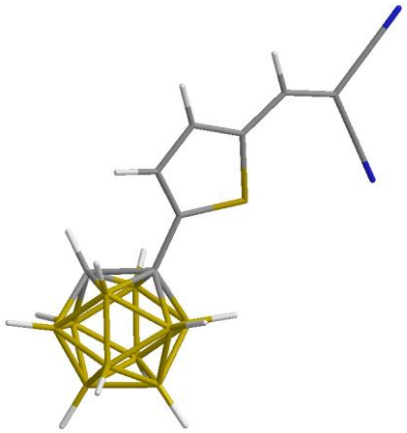
	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Orbital contributions
1a	29540.26	338.5	0.779	HOMO → LUMO (98%) and H-1 → LUMO (2%)
	34270.73	291.8	0.036	H-1 → LUMO (94%), HOMO → LUMO (2%), and HOMO → L+1 (2%)
	46613.52	214.5	0.0429	H-12 → LUMO (15%), H-11 → LUMO (75%), and H-9 → L+2 (2%)
2a	25494.56	392.2	0.1396	H-1 → L+1 (12%) and HOMO → LUMO (88%)
	28776.45	347.5	0.4143	H-1 → L+1 (85%), HOMO → LUMO (11%), and H-2 → LUMO (3%)
	29900.79	334.4	0.8843	H-1 → LUMO (41%), HOMO → L+1 (56%), and H-2 → L+1 (2%)
	33844.87	295.5	0.0221	H-2 → L+1 (96%)

 **1a**	 **1b**	 **1c**
-1145.80102527 a.u.	-1697.62291184 a.u.	-2249.4244680 a.u.
 **2a**	 **2b**	 **2c**
-1959.37135122 a.u.	-3063.03110368 a.u.	-4166.68213352 a.u.

CARTESIAN COORDINATES AND ENERGIES FOR OPTIMIZED STRUCTURES

1a

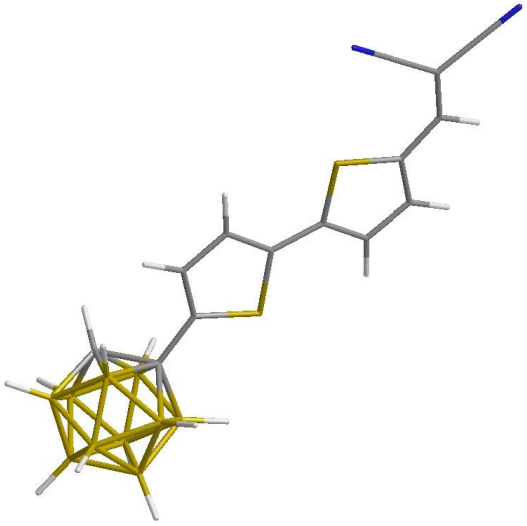
Energy: -1145.80102527 a.u.



S	-1.1207	0.3437	0.0434
N	-7.0722	-0.0944	-0.0520
N	-3.6080	2.6505	0.0340
B	2.1793	0.5909	-1.3566
H	1.4142	0.6613	-2.2512
B	1.9880	1.4357	0.1990
H	1.0798	2.1830	0.3198
B	2.3922	0.3085	1.5224
H	1.7398	0.2977	2.5078
B	2.8342	-1.2529	0.7957
H	2.4833	-2.3015	1.2055
B	4.2810	-1.0154	-0.2051
H	4.9543	-1.9630	-0.4223
B	3.8843	0.1181	-1.5209
H	4.2912	-0.0781	-2.6136
B	3.4420	1.6826	-0.7966
H	3.6262	2.7040	-1.3668
B	3.5811	1.5122	0.9803
H	3.8656	2.4271	1.6768
B	4.1001	-0.1601	1.3469
H	4.7526	-0.4522	2.2912
B	4.7553	0.6950	-0.0829
H	5.8934	1.0157	-0.1532
C	1.6274	-0.2320	0.0795
C	2.7342	-0.9677	-0.8987
H	2.3478	-1.7862	-1.4921
C	0.2308	-0.7527	0.0540
C	-0.1782	-2.0700	0.0273
H	0.5059	-2.9089	0.0418
C	-1.5804	-2.2057	-0.0036
H	-2.0956	-3.1594	-0.0248
C	-2.2566	-0.9933	0.0041
C	-3.6844	-0.8894	-0.0134
H	-4.1958	-1.8486	-0.0351
C	-4.4951	0.2132	-0.0093
C	-5.9175	0.0481	-0.0324
C	-4.0064	1.5568	0.0153

1b

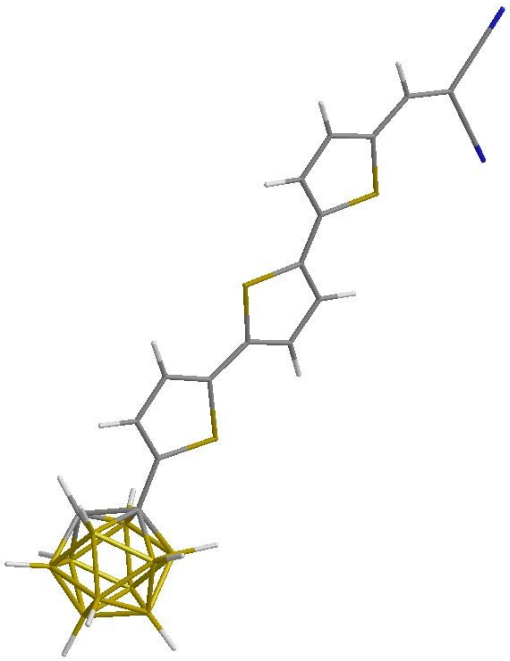
Energy: -1697.62291184 a.u.



S	0.9092	-1.0383	-0.0848
B	4.1934	-0.6792	1.2712
H	3.4697	-1.0203	2.1377
B	4.1857	-1.3663	-0.3710
H	3.4690	-2.2815	-0.5896
B	4.3220	-0.0395	-1.5550
H	3.6810	-0.0654	-2.5477
B	4.4035	1.4875	-0.6508
H	3.8292	2.4727	-0.9502
B	5.8735	1.4702	0.3455
H	6.3194	2.5141	0.6773
B	5.7517	0.1373	1.5201
H	6.1113	0.2949	2.6355
B	5.6640	-1.3948	0.6194
H	6.0745	-2.4074	1.0769
B	5.7521	-1.0004	-1.1252
H	6.2307	-1.7466	-1.9114
B	5.8814	0.7751	-1.2942
H	6.4476	1.3094	-2.1870
B	6.7196	-0.0663	0.0445
H	7.9012	-0.1308	0.1009
C	3.4590	0.1521	-0.0779
C	4.3821	1.0012	1.0005
H	3.8246	1.6419	1.6714
C	1.9825	0.3373	-0.0249
C	1.2727	1.5112	0.0763
H	1.7398	2.4873	0.1156
C	-0.1294	1.3190	0.1129
H	-0.8403	2.1331	0.1957
C	-0.5035	-0.0080	0.0332
C	-1.8329	-0.5738	0.0302
S	-3.2393	0.4631	-0.0092
C	-2.1988	-1.9128	0.0558
C	-4.3226	-0.9219	0.0181
H	-1.4803	-2.7234	0.0870
C	-3.5888	-2.1043	0.0481
C	-5.7469	-0.8758	0.0098
H	-4.0651	-3.0782	0.0681
H	-6.2208	-1.8543	0.0238
C	-6.6042	0.1957	-0.0125
C	-8.0177	-0.0266	-0.0159
C	-6.1688	1.5564	-0.0316
N	-9.1663	-0.2158	-0.0184
N	-5.8111	2.6647	-0.0464

1c

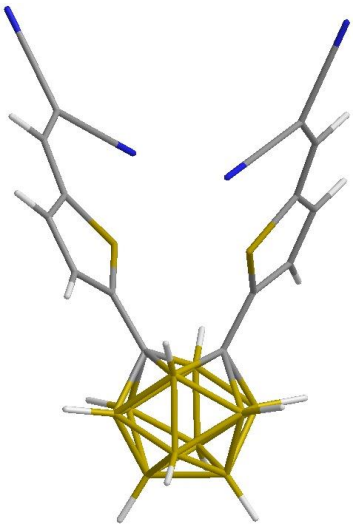
Energy: -2249.4244680 a.u.



S	-2.6250	0.7234	-0.1407
B	-5.8790	1.0243	1.2104
H	-5.0786	1.2995	2.0317
B	-5.8150	1.5804	-0.4796
H	-4.9632	2.3415	-0.7865
B	-6.2187	0.2163	-1.5536
H	-5.6216	0.0596	-2.5614
B	-6.5210	-1.2042	-0.5305
H	-6.1375	-2.2937	-0.7671
B	-7.9308	-0.8665	0.4969
H	-8.5336	-1.7928	0.9179
B	-7.5423	0.5075	1.5603
H	-7.8811	0.4958	2.6933
B	-7.2297	1.9324	0.5426
H	-7.4462	3.0307	0.9303
B	-7.4503	1.4349	-1.1636
H	-7.8255	2.1934	-1.9931
B	-7.8818	-0.2999	-1.1912
H	-8.5627	-0.7936	-2.0256
B	-8.5167	0.7668	0.0984
H	-9.6676	1.0367	0.1781
C	-5.3438	-0.0146	-0.0886
C	-6.3594	-0.6130	1.0763
H	-5.8908	-1.2904	1.7784
C	-3.9199	-0.4477	-0.0506
C	-3.4189	-1.7220	0.0713
H	-4.0454	-2.6030	0.1342
C	-2.0035	-1.7708	0.1027
H	-1.4419	-2.6924	0.2030
C	-1.4079	-0.5298	-0.0009
C	-0.0015	-0.1970	-0.0074
S	1.2178	-1.4561	-0.0446
C	0.5954	1.0503	0.0178
C	2.5212	-0.2785	-0.0127
H	0.0297	1.9744	0.0483
C	2.0053	1.0050	0.0139
H	2.6291	1.8914	0.0369
C	3.8980	-0.6987	-0.0140
S	5.1912	0.4798	-0.0022
C	4.4041	-1.9939	-0.0218
C	6.4134	-0.7863	-0.0057
H	3.7740	-2.8755	-0.0286
C	5.8048	-2.0391	-0.0172
C	7.8235	-0.5942	0.0032
H	6.3802	-2.9583	-0.0210
H	8.3951	-1.5193	-0.0018
C	8.5685	0.5599	0.0178
C	9.9968	0.4808	0.0255
C	7.9979	1.8694	0.0268
N	11.1586	0.4070	0.0319
N	7.5308	2.9364	0.0344

2a

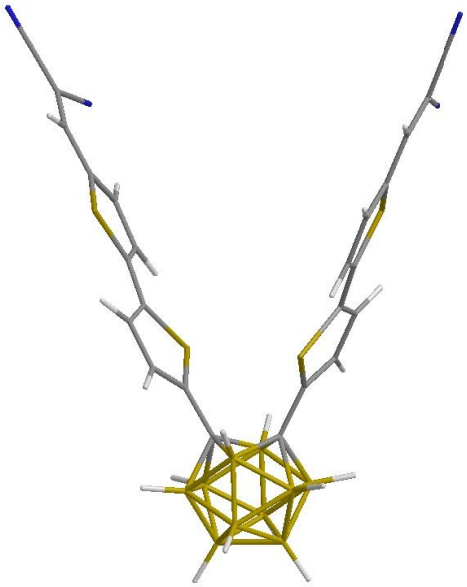
Energy: -1959.37135122 a.u.



C	2.2550	-0.7297	0.4927
C	2.2550	0.7298	-0.4927
B	3.5985	-1.7007	0.0817
B	2.6950	0.8070	1.1682
B	2.6950	-0.8069	-1.1681
B	4.4609	0.8189	1.1943
B	3.5986	1.7008	-0.0816
B	3.5889	-0.6888	1.5476
B	5.0273	-0.7316	0.5031
B	4.4609	-0.8188	-1.1943
B	3.5890	0.6889	-1.5476
B	5.0273	0.7316	-0.5031
H	3.4386	-2.8698	0.1460
H	1.9370	-1.3137	-1.9158
H	3.4389	1.1700	-2.6165
H	5.0364	-1.3999	-2.0506
H	6.0197	1.2635	-0.8707
H	6.0197	-1.2635	0.8707
H	3.4388	-1.1700	2.6165
H	1.9370	1.3138	1.9158
H	3.4387	2.8698	-0.1460
H	5.0364	1.3999	2.0506
C	0.9551	1.2987	-0.9254
C	0.4016	1.2087	-2.1872
S	-0.0391	2.2459	0.1469
C	-0.8194	1.9000	-2.2992
H	0.8684	0.6676	-2.9999
C	-1.2172	2.5209	-1.1216
H	-1.4064	1.9474	-3.2094
C	0.9551	-1.2986	0.9254
C	0.4016	-1.2086	2.1872
S	-0.0391	-2.2459	-0.1469
C	-0.8195	-1.8998	2.2991
H	0.8683	-0.6674	2.9998
C	-1.2172	-2.5209	1.1216
H	-1.4065	-1.9472	3.2093
C	-2.4314	3.2697	-0.9960
C	-2.9792	3.8929	0.0926
H	-3.0021	3.3447	-1.9183
C	-2.4314	-3.2697	0.9959
C	-2.9791	-3.8930	-0.0926
H	-3.0021	-3.3446	1.9183
C	-4.2237	-4.5895	0.0363
N	-5.2355	-5.1535	0.1459
C	-2.3812	-3.8871	-1.3916
N	-1.8953	-3.8740	-2.4496
C	-2.3813	3.8869	1.3917
N	-1.8955	3.8738	2.4496
C	-4.2238	4.5894	-0.0363
N	-5.2356	5.1534	-0.1459

2b

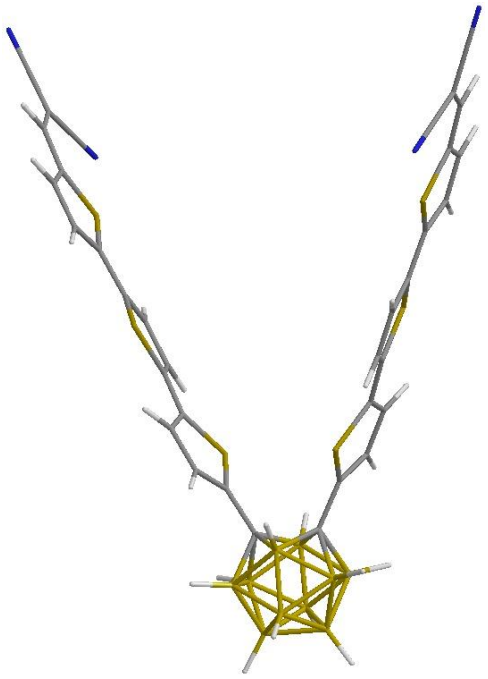
Energy: -3063.03110368 a.u.



C	2.9709	2.9270	-0.1883
C	3.8834	1.4865	0.3832
B	3.5740	4.3126	0.5936
B	4.1443	2.1380	-1.1858
B	3.4232	2.7600	1.4620
B	5.6108	3.1210	-1.0591
B	5.4955	1.6038	-0.1484
B	4.0232	3.9167	-1.0820
B	5.2641	4.4667	0.0683
B	4.8723	3.7544	1.6646
B	5.0338	1.9915	1.5262
B	6.1604	3.0478	0.6437
H	2.7862	5.1596	0.8369
H	2.5715	2.5396	2.2476
H	5.2604	1.2457	2.4146
H	5.0822	4.3000	2.6947
H	7.3054	3.0877	0.9454
H	5.7568	5.5377	-0.0486
H	3.5539	4.4977	-1.9982
H	3.7583	1.5179	-2.1124
H	6.0314	0.5861	-0.4210
H	6.3465	3.2168	-1.9826
C	3.1691	0.1993	0.5156
C	2.6491	-0.3492	1.6675
S	2.9616	-0.8893	-0.8372
C	2.0920	-1.6343	1.4790
H	2.6869	0.1530	2.6257
C	2.1820	-2.0846	0.1750
H	1.6563	-2.2205	2.2798
C	1.5498	2.7633	-0.5600
C	1.0328	2.6139	-1.8282
S	0.2682	2.8223	0.6283
C	-0.3788	2.5510	-1.8574
H	1.6541	2.5698	-2.7135
C	-0.9590	2.6526	-0.6067
H	-0.9534	2.4517	-2.7711
C	-2.3606	2.6269	-0.2559
C	-2.9510	2.9477	0.9599
S	-3.5712	2.1490	-1.4141
C	-4.3501	2.8213	0.9650
H	-2.3816	3.2815	1.8196
C	-4.8715	2.3989	-0.2537
H	-4.9648	3.0384	1.8284
C	1.7274	-3.3400	-0.3777
C	2.0447	-3.9056	-1.6049
S	0.6376	-4.3636	0.5266
C	1.4293	-5.1499	-1.8126
H	2.7170	-3.4398	-2.3157
C	0.6284	-5.5682	-0.7539
H	1.5629	-5.7494	-2.7063
C	-6.2114	2.1495	-0.6849
C	-7.3825	2.2580	0.0234
H	-6.3288	1.8277	-1.7164
C	-0.0849	-6.8029	-0.7436
C	-0.8985	-7.3534	0.2140
H	0.0448	-7.3956	-1.6459
C	-1.5072	-8.6274	-0.0190
N	-1.9984	-9.6640	-0.2166
C	-1.1868	-6.7226	1.4634
N	-1.4195	-6.2047	2.4802
C	-7.4463	2.6653	1.3913
N	-7.4823	2.9997	2.5061
C	-8.6270	1.9549	-0.6145
N	-9.6358	1.7075	-1.1398

2c

Energy: -4166.68213352 a.u.



C	0.8104	5.7030	0.4044
C	-0.8090	5.7030	-0.4045
B	1.6970	7.0462	-0.1419
B	-0.6354	6.1331	1.2512
B	0.6367	6.1331	-1.2513
B	-0.6513	7.9029	1.2905
B	-1.6956	7.0462	0.1418
B	0.8926	7.0400	1.4453
B	0.7915	8.4763	0.4009
B	0.6527	7.9029	-1.2905
B	-0.8912	7.0400	-1.4454
B	-0.7902	8.4763	-0.4009
H	2.8651	6.8960	-0.2439
H	1.0502	5.3835	-2.0629
H	-1.5035	6.8956	-2.4463
H	1.1178	8.4771	-2.2167
H	-1.3649	9.4705	-0.6927
H	1.3663	9.4705	0.6927
H	1.5049	6.8955	2.4462
H	-1.0489	5.3836	2.0629
H	-2.8637	6.8961	0.2438
H	-1.1164	8.4771	2.2166
C	-1.4277	4.4078	-0.7504
C	-1.4214	3.7867	-1.9797
S	-2.3717	3.4866	0.4010
C	-2.1707	2.5886	-2.0121
H	-0.9071	4.1957	-2.8400
C	-2.7617	2.2775	-0.8022
H	-2.2917	1.9829	-2.9027
C	1.4290	4.4077	0.7504
C	1.4228	3.7869	1.9798
S	2.3725	3.4862	-0.4011
C	2.1719	2.5885	2.0122
H	0.9088	4.1960	2.8402
C	2.7626	2.2772	0.8022
H	2.2930	1.9830	2.9028
C	3.5907	1.1409	0.4679
C	4.4166	0.9597	-0.6264
S	3.6405	-0.2664	1.5113
C	5.0917	-0.2792	-0.6277
H	4.5497	1.7127	-1.3946
C	4.7986	-1.0737	0.4667
H	5.7917	-0.5760	-1.4005
C	-3.5902	1.1415	-0.4680
C	-4.4164	0.9607	0.6261
S	-3.6401	-0.2660	-1.5112
C	-5.0918	-0.2781	0.6275
H	-4.5494	1.7138	1.3942
C	-4.7987	-1.0728	-0.4667
H	-5.7920	-0.5746	1.4002
C	-5.3068	-2.3798	-0.7950
C	-5.1206	-3.1093	-1.9638
S	-6.2954	-3.2635	0.3461
C	-5.7663	-4.3535	-1.9460
H	-4.5443	-2.7420	-2.8047
C	-6.4637	-4.6143	-0.7689
H	-5.7412	-5.0599	-2.7684
C	5.3064	-2.3808	0.7951
C	5.1203	-3.1101	1.9640
S	6.2945	-3.2649	-0.3461
C	5.7656	-4.3544	1.9462
H	4.5443	-2.7424	2.8050
C	6.4627	-4.6156	0.7691
H	5.7405	-5.0607	2.7688
C	7.1942	-5.8139	0.5341
C	7.9260	-6.2144	-0.5571
H	7.1614	-6.5208	1.3598
C	-7.1956	-5.8124	-0.5340
C	-7.9277	-6.2125	0.5571
H	-7.1629	-6.5193	-1.3596
C	8.5773	-7.4881	-0.5451
N	9.1039	-8.5262	-0.5273
C	8.0846	-5.4237	-1.7361
N	8.2120	-4.7776	-2.6969
C	-8.0864	-5.4216	1.7360
N	-8.2137	-4.7754	2.6968
C	-8.5794	-7.4860	0.5452
N	-9.1063	-8.5240	0.5274

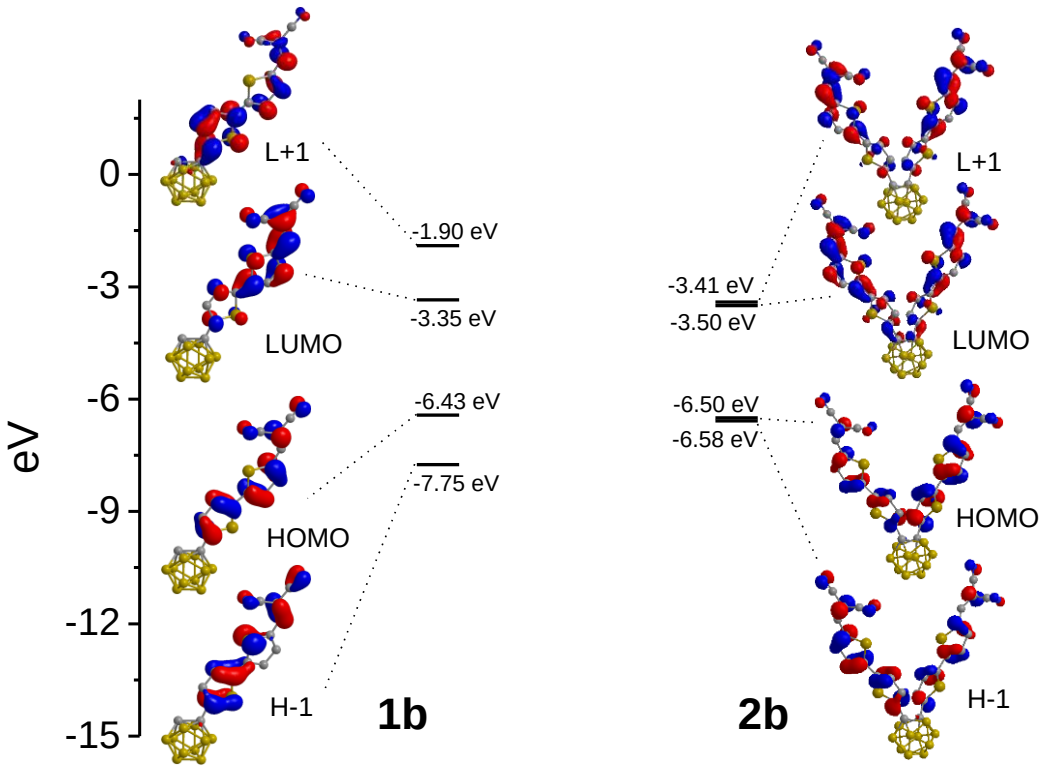


Figure S7. TD-DFT calculation results for **1b** and **2b**. Energy levels and isodensity plots for HOMO-LUMOs are shown.

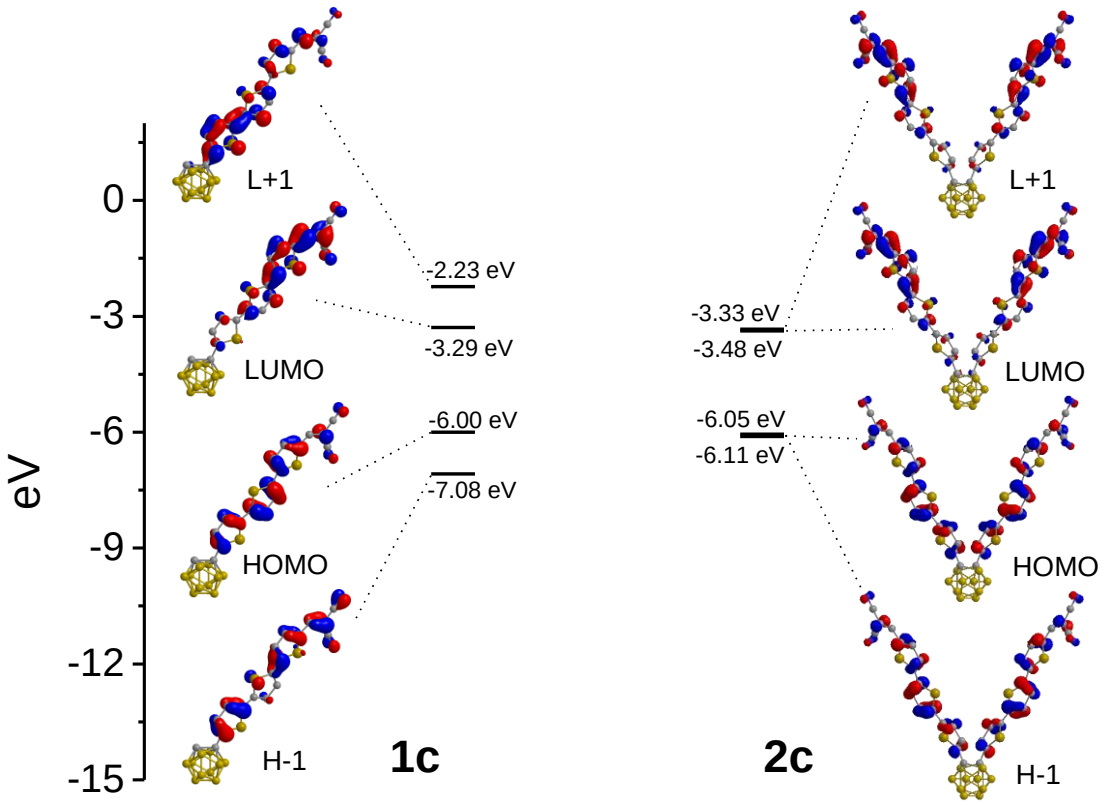


Figure S8. TD-DFT calculation results for **1c** and **2c**. Energy levels and isodensity plots for HOMO-LUMOs are shown.

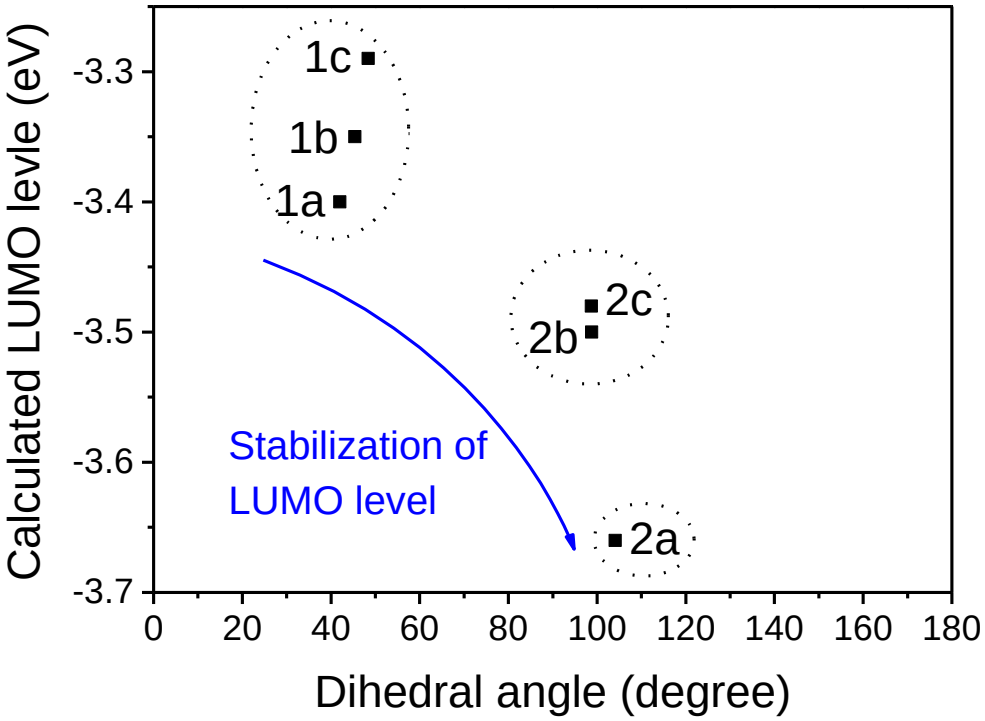


Figure S9. Diagram of calculated LUMO energy levels vs dihedral angles of C–C bonds of the carborane cage with C–C bonds in the thiophene rings.

References

(S1) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem*. **1994**, *98*, 11623-11627.

(S2) (a) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* 1988, 89, 2193-218. (b) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys*. **1991**, *94*, 6081-90.

(S3) Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.