Supporting Information

Contents

Table S1. Summary of ^{1}H NMR chemical shift for compounds

Compounds	Solvent	^{1}H NMR chemical shift [ppm]				
		Benzocinnoline ring				Other
2	CD_3CN	8.22–8.25	8.30–8.32	8.78–8.80	8.98–9.00	
3	DMSO-d_6	8.00-8.05 (4H)		8.49-8.52	8.93–8.95	
4	DMSO-d_6	8.07–8.16 (4H)		8.55–8.57	9.03–9.06	
5	CD_3CN	8.10–8.13	8.14–8.18	8.57–8.59	8.85–8.87	6.57 (NH_2)
6	CD_3CN	8.09–8.17 (4H)		8.58–8.60	8.85–8.87	1.00, 1.49, 1.75, 3.59 (^{n}Bu), 6.82 (NH)

Referenced by solvent residual signal (DMSO-d_6: 2.05 ppm, CD_3CN: 1.94 ppm)

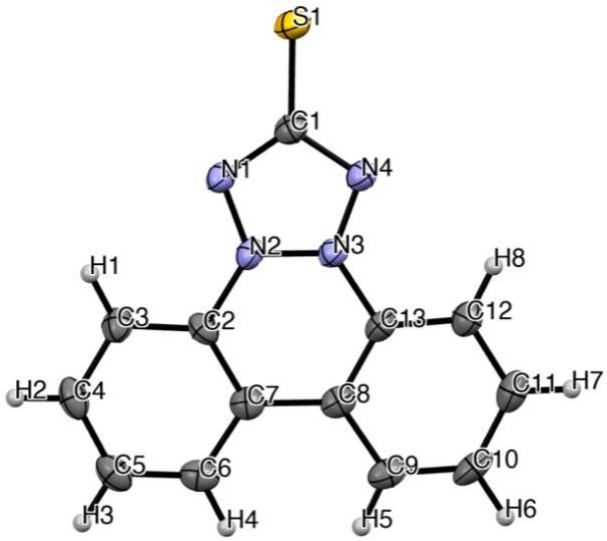
Table S2. Summary of ^{13}C NMR chemical shift for compounds

Compounds	Solvent	^{13}C NMR chemical shift [ppm]		
		Benzocinnoline ring (6C)	Tetrazolo C*	Others
2	CD_3CN	119.45, 123.66, 126.01, 129.49, 134.59, 136.07	158.38	
3	DMSO-d_6	117.76, 121.20, 124.26, 128.05, 131.34, 131.74	181.28	
4	DMSO-d_6	117.92, 119.78, 121.55, 124.49, 128.36, 132.33	168.41	23.78 (methylidene)
5	CD_3CN	118.88, 122.75, 125.58, 129.33, 133.75, 134.16	165.94	
6	CD_3CN	118.89, 122.74, 125.58, 129.42, 133.73, 134.07	166.24	13.98, 20.53, 31.60, 43.93 (^{n}Bu)
Type B Cl 1	CD_3CN	126.88, 131.84, 133.60, 135.90	158.69	
Type B S[a]	DMSO-d_6	126.3, 129.6, 132.5, 133.4	181.4	
Type B dicyanomethylide[b]	DMSO-d_6	126.2 (meta), 129.9 (ortho), 133.1 (para), 133.2 (ipso)	169.2	22.4, 119.6 (CN)

Referenced by solvent signal (DMSO-d_6: 39.52 ppm, CD_3CN: 1.32 ppm). a) W. Koźmiński, J. Jaźwiński, L. Stefaniak, *J. Mol. Struct.* **1993**, *295*, 15. b) S. Araki, J. Mizuya, Y. Butsugan, *J. Chem. Soc. Perkin T. 1*, **1985**, 2439.

Figure S1. Single crystal X-ray structure analysis of BTC thiolate **3**

CCDC deposit number: 2131771



Empirical Formula	$C_{13}H_8N_4S$
Formula Weight	252.29
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 9.3963(7) Å
	b = 9.7124(9) Å
	c = 12.071(1) Å
	V = 1101.6(2) $Å^3$
Space Group	$Pna2_1$ (#33)
Z value	4
D_{calc}	1.521 g/cm^3
Temperature	-100.0°C
No. of Reflections Measured	Total: 9761
	Unique: 2475 (R_{int} = 0.0945)
	Friedel pairs: 1152
Residuals: R1 (I>2.00s(I))	0.0374
Residuals: R (All reflections)	0.0645
Residuals: wR2 (All reflections)	0.0653

atom	Atomic coordinate			B_{eq}
	x	y	z	
S1	-0.1916(1)	0.07721(9)	0.68974(9)	2.50(2)
N1	0.0149(4)	0.1605(3)	0.8322(2)	2.04(6)
N2	0.0563(3)	0.2807(3)	0.8719(3)	1.96(6)
N3	-0.0189(3)	0.3828(3)	0.8253(2)	1.93(6)
N4	-0.1129(3)	0.3323(3)	0.7545(3)	2.15(6)
C1	-0.0921(4)	0.1929(4)	0.7603(3)	2.10(7)

C2	0.1627(4)	0.3066(4)	0.9518(3)	2.05(7)
C3	0.2344(4)	0.1951(4)	0.9979(3)	2.31(7)
C4	0.3386(4)	0.2227(4)	1.0739(3)	2.57(8)
C5	0.3731(4)	0.3567(4)	1.1020(3)	2.65(8)
C6	0.2988(4)	0.4658(4)	1.0569(3)	2.41(7)
C7	0.1891(4)	0.4433(4)	0.9815(3)	2.03(6)
C8	0.1023(4)	0.5535(4)	0.9338(3)	2.08(7)
C9	0.1147(4)	0.6914(4)	0.9640(3)	2.39(7)
C10	0.0292(5)	0.7899(4)	0.9154(3)	2.70(8)
C11	-0.0722(4)	0.7547(4)	0.8383(3)	2.63(7)
C12	-0.0903(4)	0.6193(4)	0.8069(3)	2.40(7)
C13	-0.0025(4)	0.5218(4)	0.8561(3)	1.97(6)

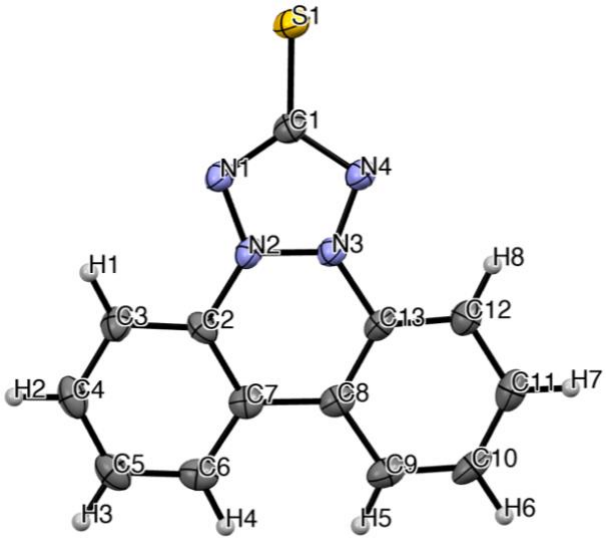
atom	Atomic coordinate			B_{iso}
	x	y	z	
H1	0.2118	0.1032	0.9774	2.77
H2	0.3880	0.1486	1.1079	3.08
H3	0.4485	0.3737	1.1527	3.17
H4	0.3227	0.5572	1.0777	2.89
H5	0.1824	0.7178	1.0185	2.86
H6	0.0406	0.8838	0.9356	3.24
H7	-0.1303	0.8243	0.8064	3.16
H8	-0.1601	0.5937	0.7538	2.88

Table S3. Deviation of the atoms from the plane

Standard plane equation was calculated from X-ray diffraction geometry [angstrom] without hydrogen atoms by singular value decomposition using Numpy (v.1.20.2)[a] at Python (v.3.9.2).

plane equation:

$$-0.666x - 0.096y + 0.740z - 7.20 = 0$$



atom	Deviation of the atoms from the plane [Å]
S1	0.086
N1	-0.011
N2	-0.027
N3	-0.068
N4	-0.065
C1	-0.014
C2	-0.003
C3	0.064
C4	0.065
C5	-0.025
C6	-0.064
C7	-0.031
C8	-0.016
C9	0.048
C10	0.057
C11	0.035
C12	-0.006
C13	-0.025

a) C. R. Harris, K. J. Millman, S. J. van der Walt, R. Gommers, P. Virtanen, D. Cournapeau, E. Wieser, J. Taylor, S. Berg, N. J. Smith, R. Kern, M. Picus, S. Hoyer, M. H. van Kerkwijk, M. Brett, A. Haldane, J. F. del Tio, M. Wiebe, P. Peterson, P. G-Marchant, K. Sheppard, T. Reddy, W. Weckesser, H. Abbasi, C. Gohlke, T. E. Oliphant, *Nature*, **2020**, *585*, 357.

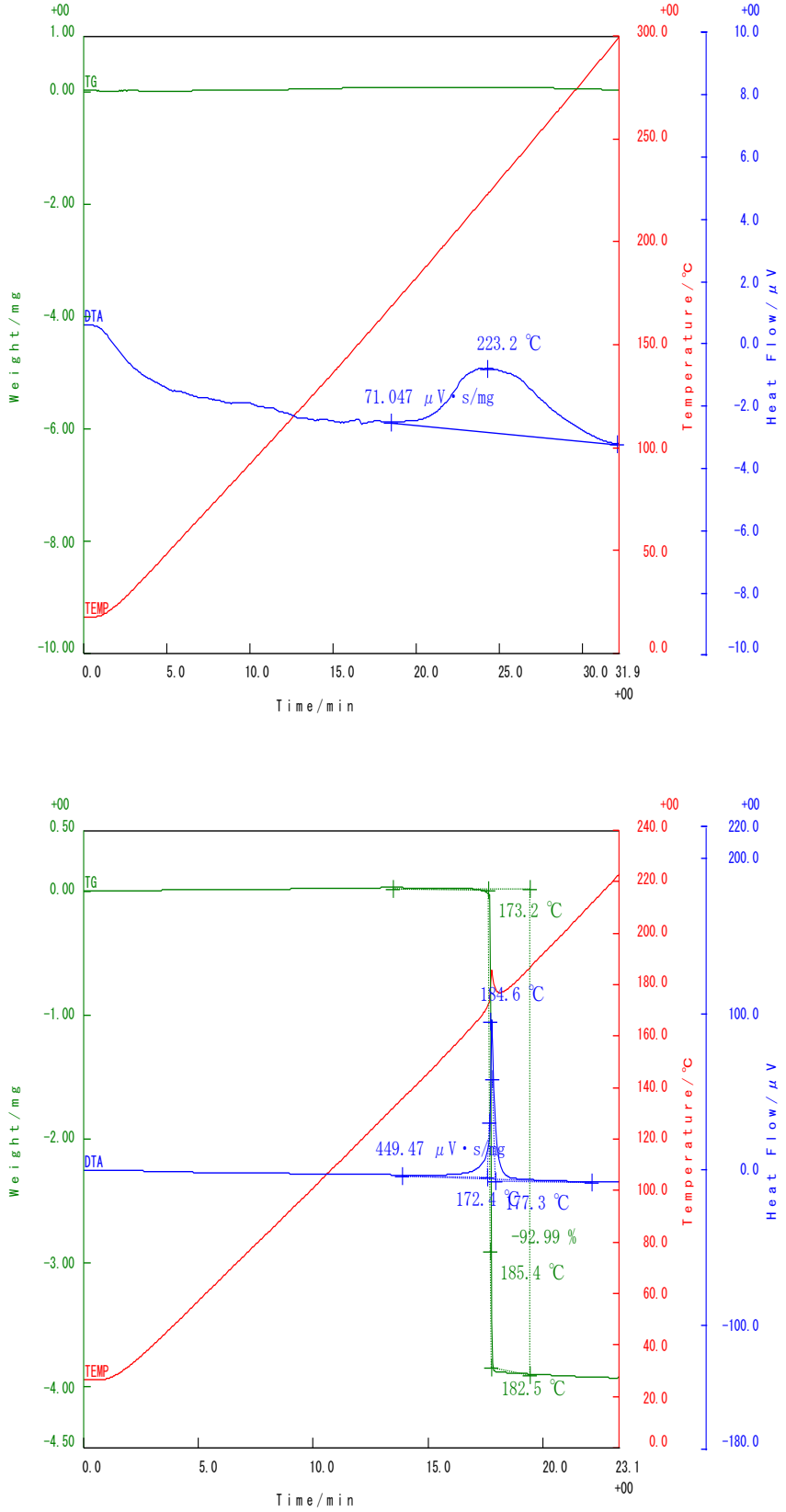


Figure S2. The thermogravimetry analysis and differential thermal analysis of BTC thiolate **3** (upper) and dehydrodithizone (**DD**).

Table S4. Selected optimized geometry and vibration frequency of BTC-S **3**

Functionals	Phase	Bond length [Å]						Vibration frequency [cm^{-1}]	
		C1-S	C1-N1 (C1-N4)	N1-N2 (N3-N4)	N2-N3	N2-C_{Ph} (N3-C_{Ph})	C_{Ph}-C_{Ph}	C-S stretching	Ph-H bending
B3LYP	Vacuum	1.6679	1.3937 (1.3936)	1.3081(1.3082)	1.3526	1.4016 (1.4015)	1.4589	1293	769
	chloroform	1.6950	1.3767 (1.3767)	1.3137 (1.3137)	1.3447	1.4032 (1.4032)	1.4586	1270, 1287	770
M06-2X	Vacuum	1.6662	1.3853 (1.3854)	1.2997 (1.2996)	1.3312	1.4044 (1.4045)	1.4612	1312, 1356	780
	chloroform	1.6946	1.3690 (1.3690)	1.3036 (1.3036)	1.3254	1.4069 (1.4069)	1.4609	1317, 1360	778
CAM-B3LYP	Vacuum	1.6650	1.3828 (1.3826)	1.3006 (1.3007)	1.3327	1.4029 (1.4028)	1.4604	1316, 1354	785
	chloroform	1.6932	1.3662 (1.3662)	1.3048 (1.3048)	1.3270	1.4049 (1.4049)	1.4595	1314, 1356	784
wB97X-D	Vacuum	1.6655	1.3845 (1.3843)	1.3009 (1.3010)	1.3321	1.4027 (1.4027)	1.4618	1323, 1358	774
	chloroform	1.6930	1.3680 (1.3680)	1.3048 (1.3048)	1.3266	1.4046 (1.4046)	1.4609	1318, 1359	773
Experiment	-	1.692(4)	1.365 (5) (1.370 (5))	1.321 (4) (1.323 (4))	1.342 (4)	1.411 (5) (1.408 (4))	1.464 (5)	1273, 1290	767

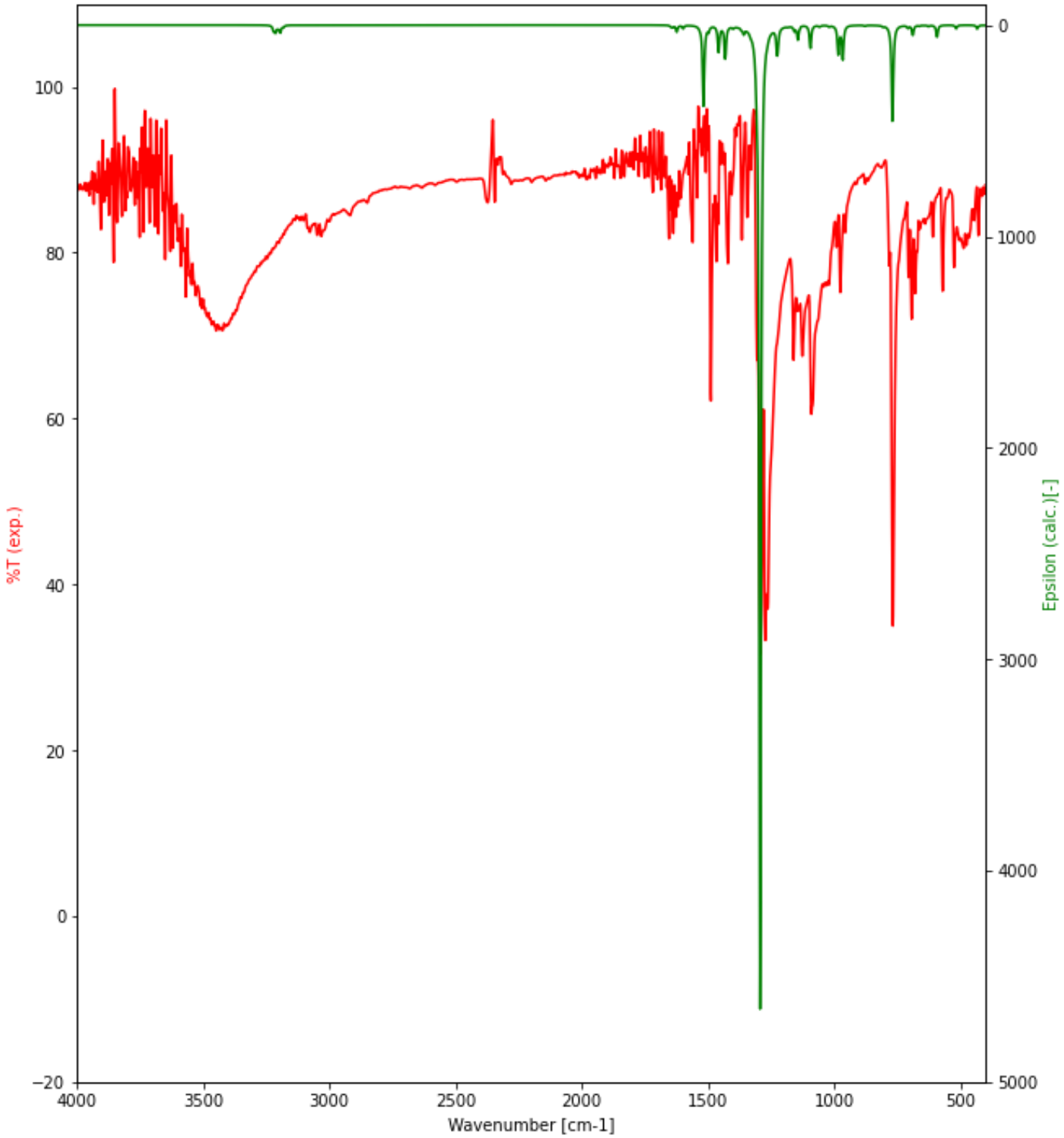


Figure S3. Experimental (red, using KBr) and calculated (green, at the B3LYP/6-311++G(d,p) level) IR spectra of BTC-S **3**.

Table S5. The Gibbs free energies of restrict or unstrict calculation geometry of BTC-S **3**.

Symmetry	Gibbs free energy
C_1 [Hartree]	-1117.371884
C_{2v} [Hartree]	-1117.371237
Delta [Hartree]	-0.000674
Delta [kcal/mol]	-0.405

Calculated at the B3LYP/6-311++G(d,p) level. T = 298.150.

Functional theory	Energy level [Hartree]				
	LUMO(+1)	LUMO	HOMO	HOMO(-1)	HOMO(-2)
B3LYP	-0.09514	-0.11323	-0.18597	-0.18742	-0.27698
M06-2X	-0.06528	-0.07871	-0.22657	-0.23417	-0.32428
CAM-C3LYP	-0.05331	-0.07074	-0.23273	-0.23807	-0.32738
ωB97X-D	-0.03057	-0.04777	-0.25333	-0.25824	-0.34715

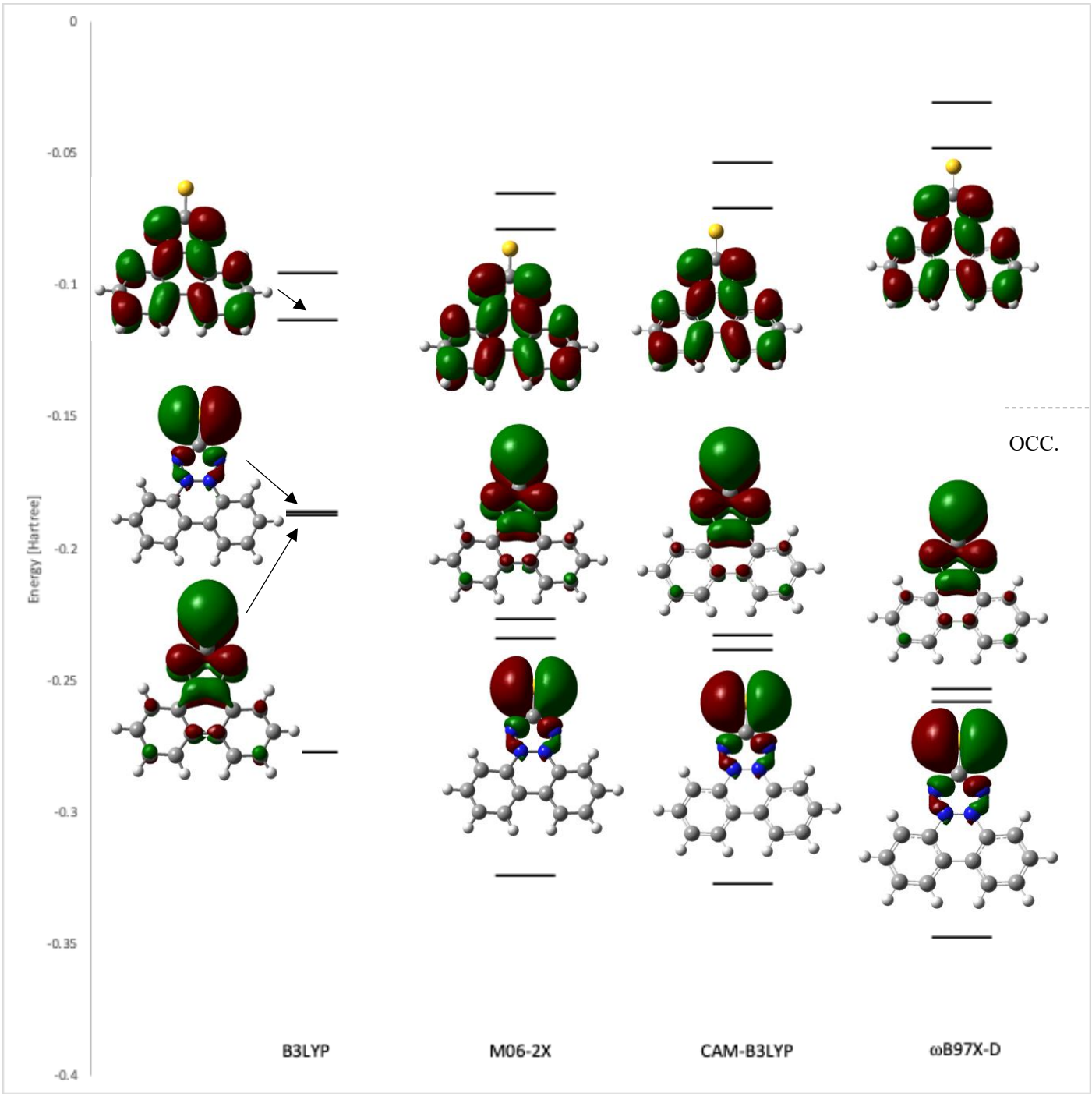


Figure S4. DFT calculated energy plot of BTC-S **3** with 6-311++(d,p) basis set and molecular orbital at LUMO, HOMO and HOMO (-1) (isovalue = 0.002).

Entry	Functionals	Wavelength [nm^{-1}] (Oscillator strength [-])				
		S_1	S_2	S_3	S_4	S_5
1	B3LYP	640.45 (0.0001)	613.93 (0.0219)	436.78 (0.0226)	343.35 (0.0154)	333.77 (0.3049)
2	M06-2X	454.72 (0.0406)	418.77 (0.0003)	321.28 (0.0230)	287.30 (0.3951)	269.44 (0.3581)
3	CAM-B3LYP	459.43 (0.0374)	427.44 (0.0002)	312.10 (0.0034)	261.53 (0.4243)	288.85 (0.4847)
4	ωB97X-D	444.17 (0.0393)	413.73 (0.0003)	303.95 (0.0481)	277.88 (0.6124)	253.76 (0.4276)
5	Experiment	488, 377, 361, 334, 320				

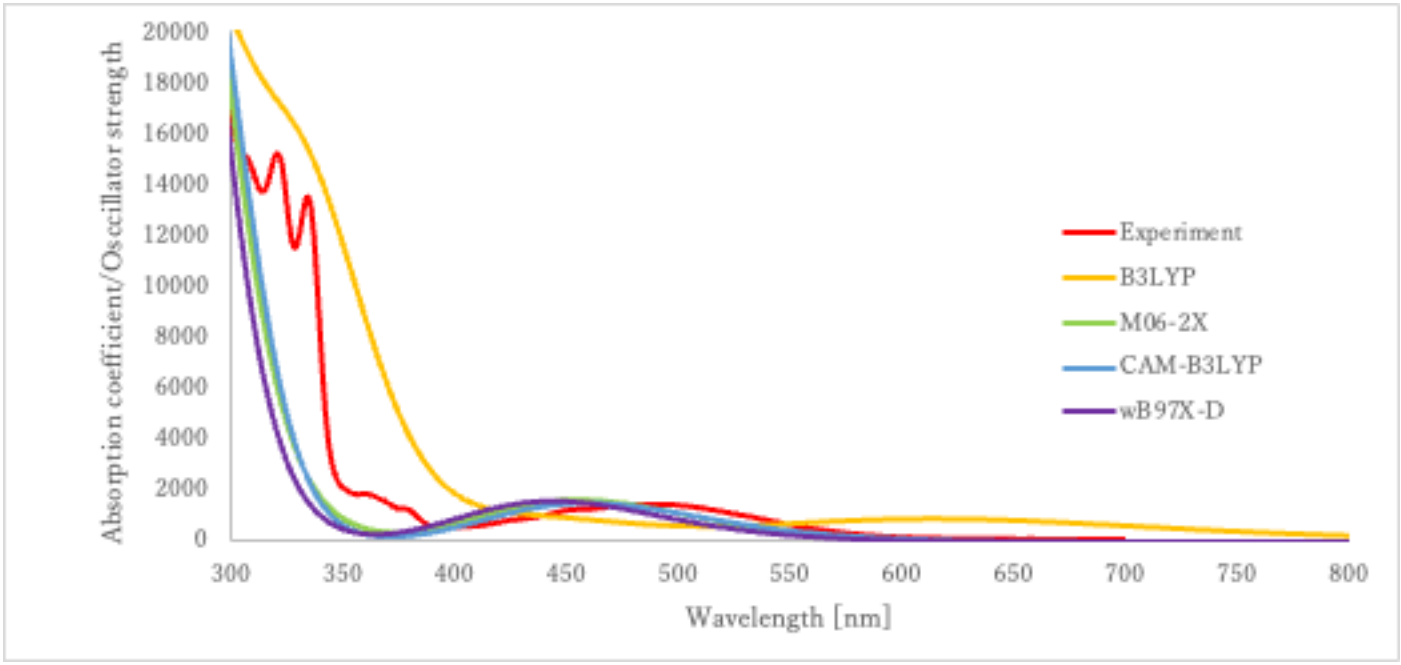
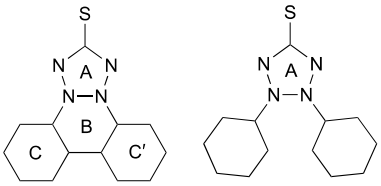


Figure S5. TD-DFT calculated spectra at B3LYP (yellow), M06-2X (green), CAM-B3LYP (blue) and ωB97-D (purple) functionals with 6-311++G(d,p) basis set and experimental spectra (red) of BTC-S **3** in chloroform.

Table S6. Aromaticity indexes of class 5 mesoionic BTC **3** and dehydrodithizone.



BTC-S 3 dehydrodithizone

Molecule	Ring	NICS(1)$_{zz}$ [a]	Bird I (calculated geometry)[a]	Bird I (single crystal X-ray diffraction)
BTC-S **3**	A	-10.1569	71	88
	B	-5.3428	62	60
	C	-24.9640	91	92
	C′	-24.9654	91	94
dehydrodithizone	A	-11.4249	73	88[b]

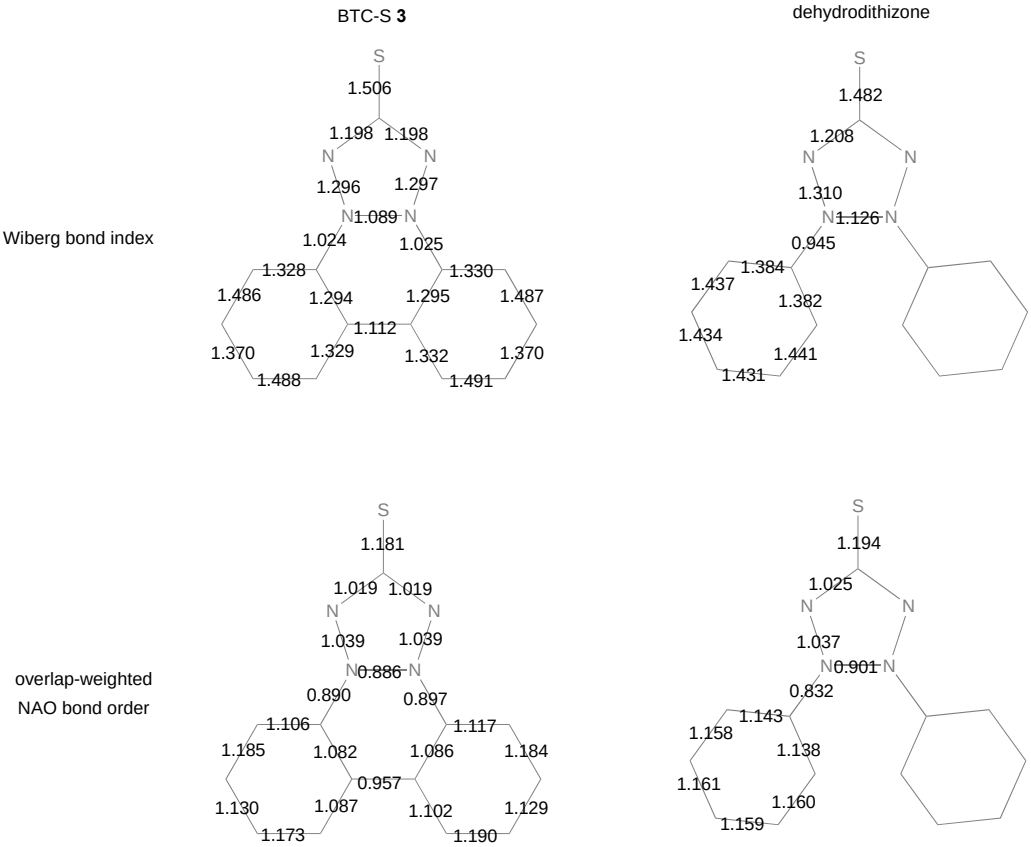
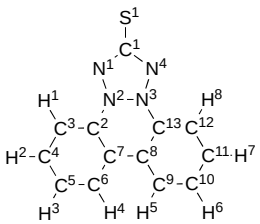
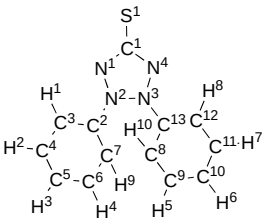


Figure S6. Calculation of bond index by NBO analysis at the B3LYP/6-311++G(d,p) level.

Table S7. The calculation Mulliken atomic charge and NBO natural charge at the B3LYP/6-311++G(d,p) level.





Atom	BTC-S 3		dehydrodithizone	
	Mulliken atomic charge	NBO natural atomic charge	Mulliken atomic charge	NBO natural atomic charge
S1	-0.54	-0.22	-0.64	-0.25
N1	0.10	-0.27	0.06	-0.25
N2	0.30	0.04	0.52	0.03
N3	0.30	0.04	0.52	0.03
N4	0.10	-0.27	0.06	-0.25
C1	-0.15	0.11	0.00	0.11
C2	-0.37	0.15	-1.30	0.11
C3	-0.44	-0.19	0.48	-0.19
C4	-0.06	-0.17	-0.10	-0.19
C5	-0.87	-0.18	-0.44	-0.18
C6	-0.74	-0.16	-0.06	-0.19
C7	1.69	-0.05	0.18	-0.18
C8	1.69	-0.06	0.18	-0.18
C9	-0.74	-0.16	-0.06	-0.19
C10	-0.87	-0.18	-0.44	-0.18
C11	-0.06	-0.17	-0.10	-0.19
C12	-0.44	-0.18	0.48	-0.19
C13	-0.37	0.14	-1.30	0.11
H1	0.24	0.25	0.20	0.23
H2	0.19	0.21	0.21	0.22
H3	0.18	0.21	0.16	0.21
H4	0.12	0.21	0.21	0.22
H5	0.12	0.21	0.21	0.22
H6	0.18	0.21	0.16	0.21
H7	0.19	0.21	0.21	0.22
H8	0.24	0.25	0.20	0.23
H9	-	-	0.21	0.24
H10	-	-	0.21	0.24

◆Experiments of deprotonation and protonation of BTC amine salts **5•H**$^+$ (Procedure **A**) and **6•H**$^+$ (Procedure **B**).

A mixture of BTC amine salts (**A**: 3.5 mg [0.011 mmol], **B**: 4.2 [0.011 mmol]), NaOH (**A**: 0.97 g [24 mmol], **B**: 0.57 g [14 mmol]), CH_2Cl_2 (10 mL), and H_2O (10 mL) was shaken vigorously in the flask. The organic layer was extracted with 1.0 mL and diluted to 10 mL with acetonitrile. The UV-Vis spectra of the acetonitrile solutions were measured on 3 mL in a 1.0 × 1.0 cm crystal cell at 20 ºC. Aq. HBF_4 (42%, 10 µL, 0.066 mmol) was then added to the sample cell, and the measurements were repeated. The concentrations of BTC amine species were calculated from a calibration curve of BTC amine salts in acetonitrile (Figure S14, S15).

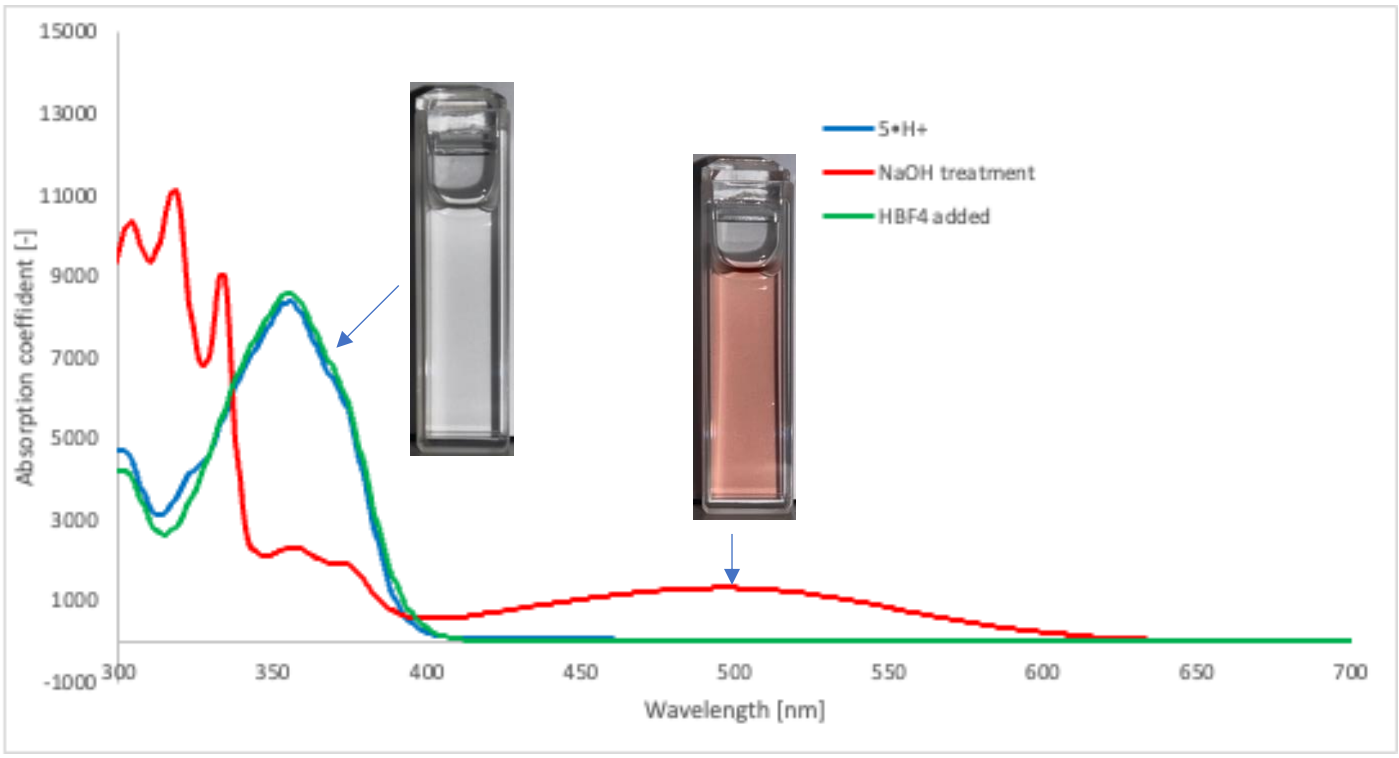


Figure S7. 5•H$^+$/acetonitrile solution (blue, **[5/5•H**$^+$**]** =|0.10 mM), NaOH treatment (red, **[5/5•H**$^+$**]** = 0.15 mM), following added aq. HBF_4 (green, **[5/5•H**$^+$**]** = 0.15 mM)

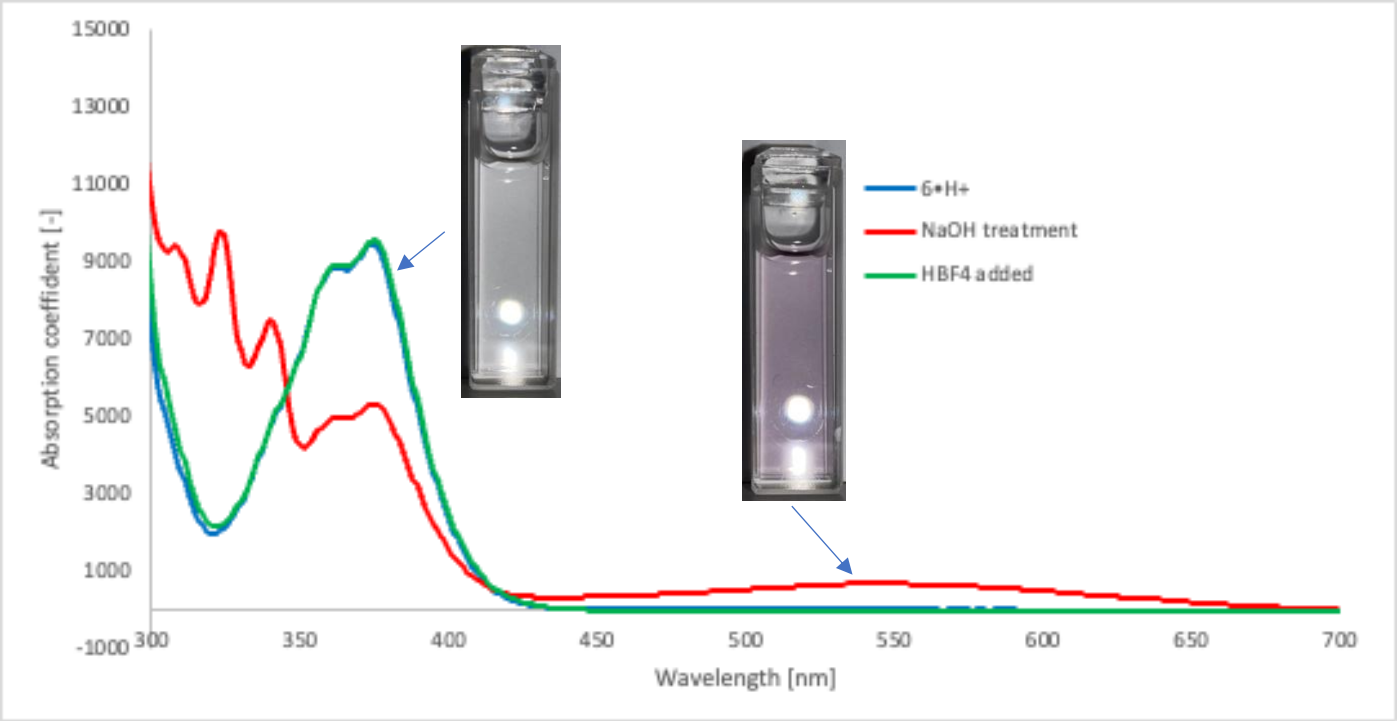


Figure S8. $6•H^+$/acetonitrile solution (blue, [**6**/$6•H^+$] = 0.14 mM), NaOH treatment (red, [**6**/$6•H^+$] = 0.10 mM), following added aq. HBF_4 (green, [**6**/$6•H^+$] = 0.10 mM)

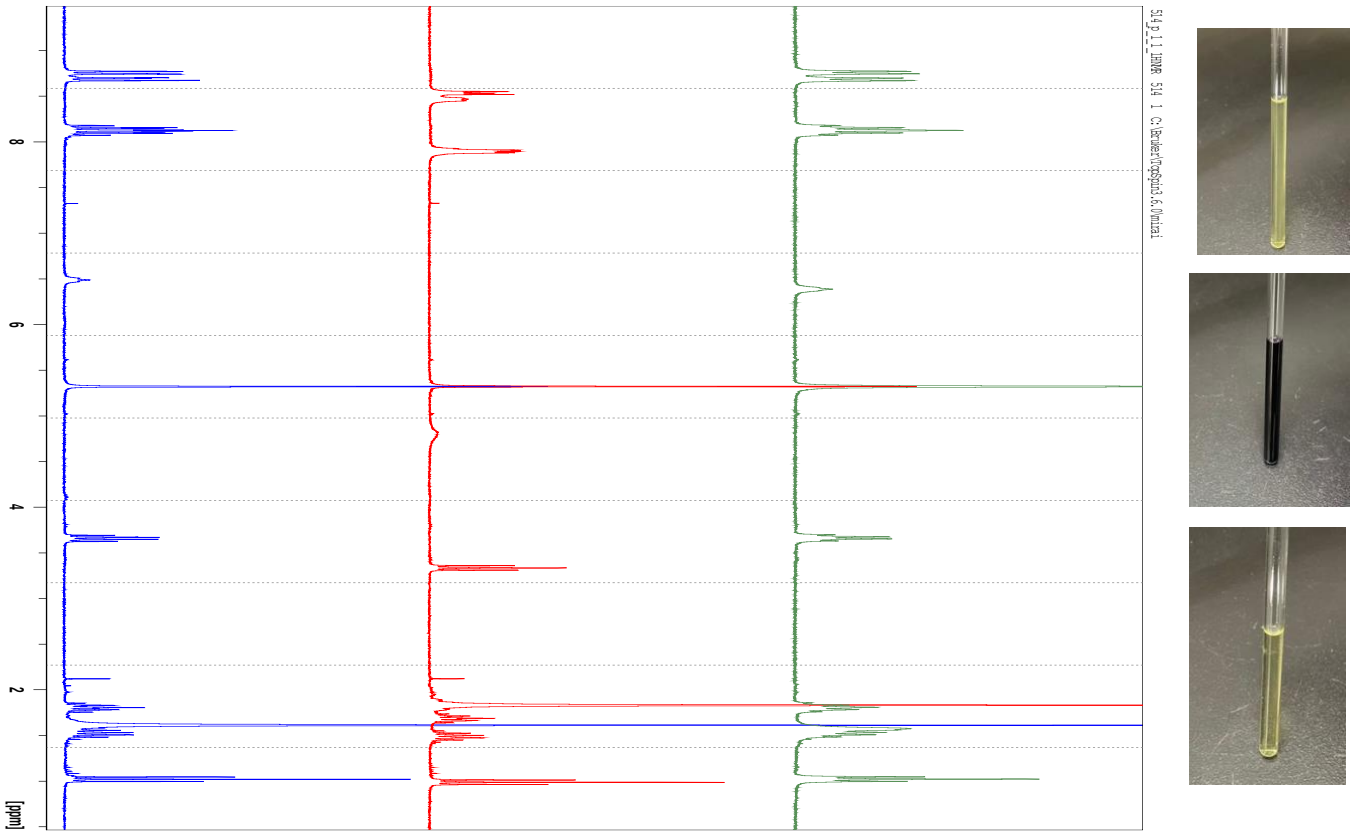
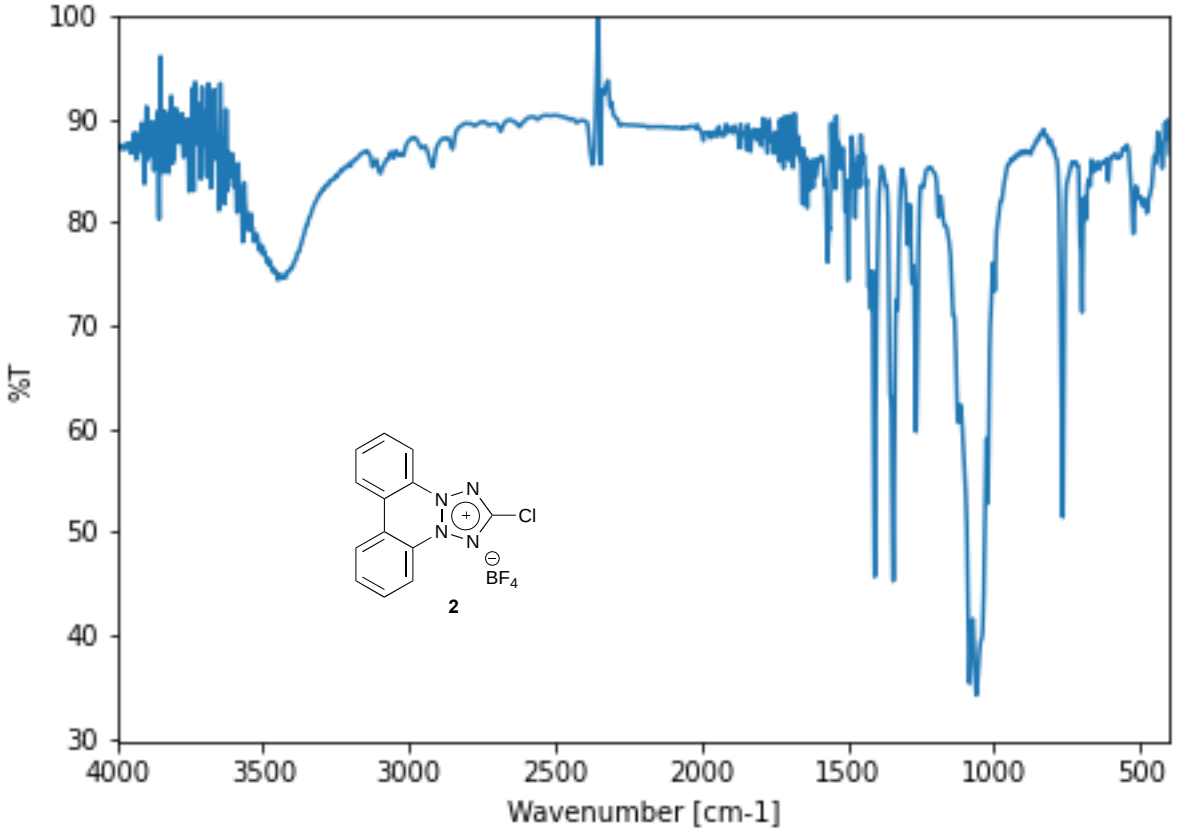


Figure S9. ^1H NMR (left) and the color of samples (right) for tracking of BTC-NH^{n}Bu **6** with acid and base in CD_2Cl_2. Initial (top), after NaOH aq. separating (middle), after HBF_4 aq. separating (bottom).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Cl
BF4
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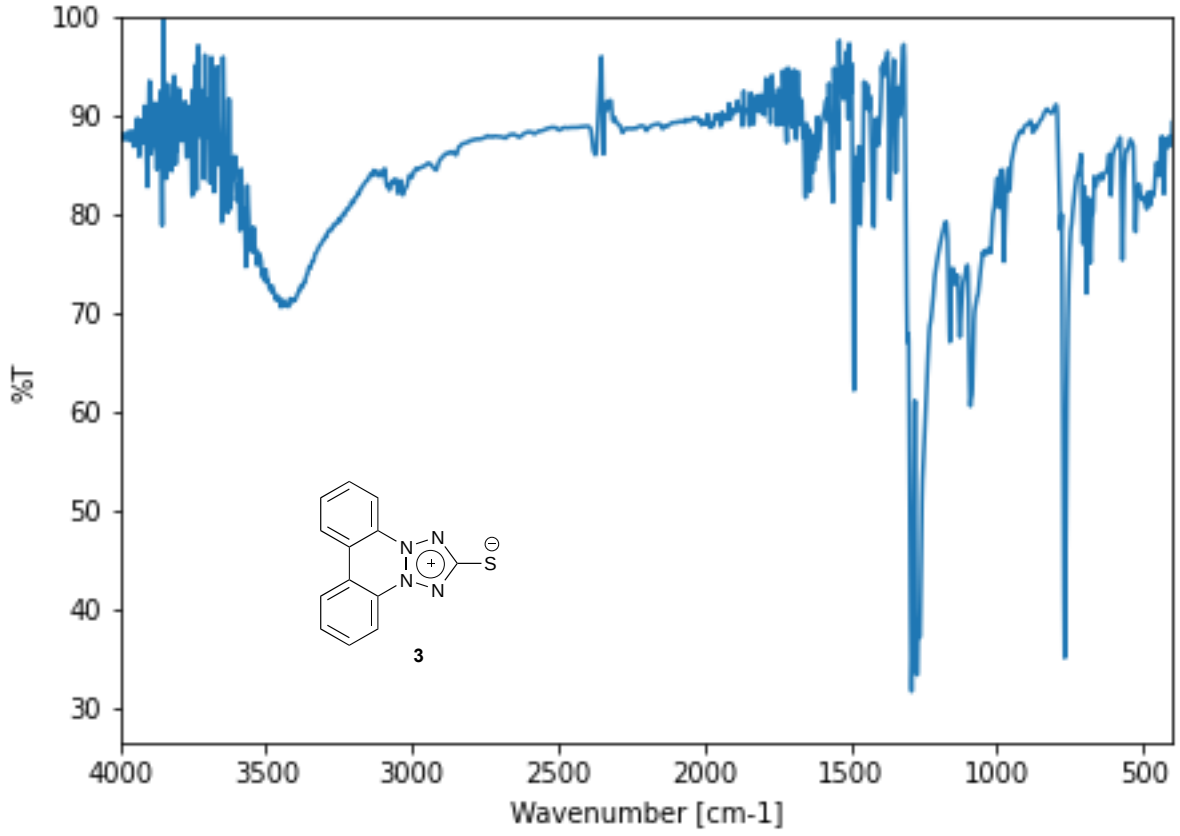
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S
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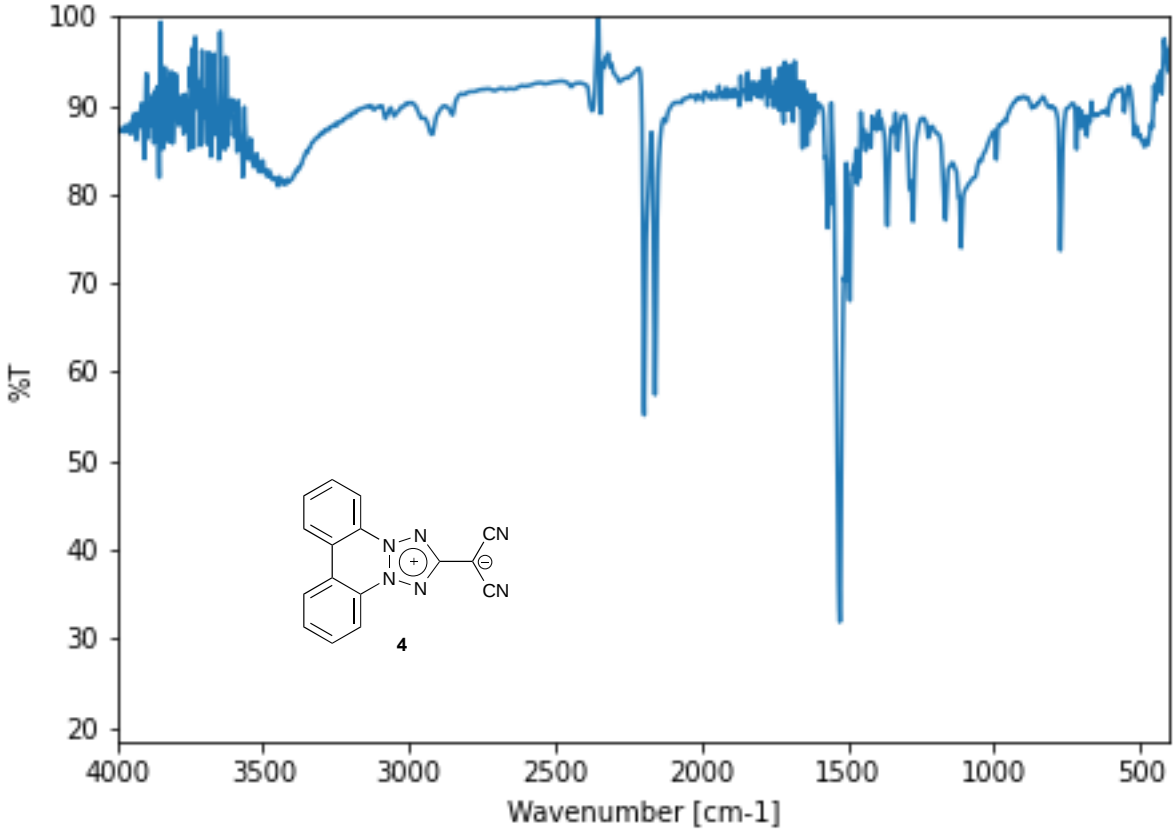
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N
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CN
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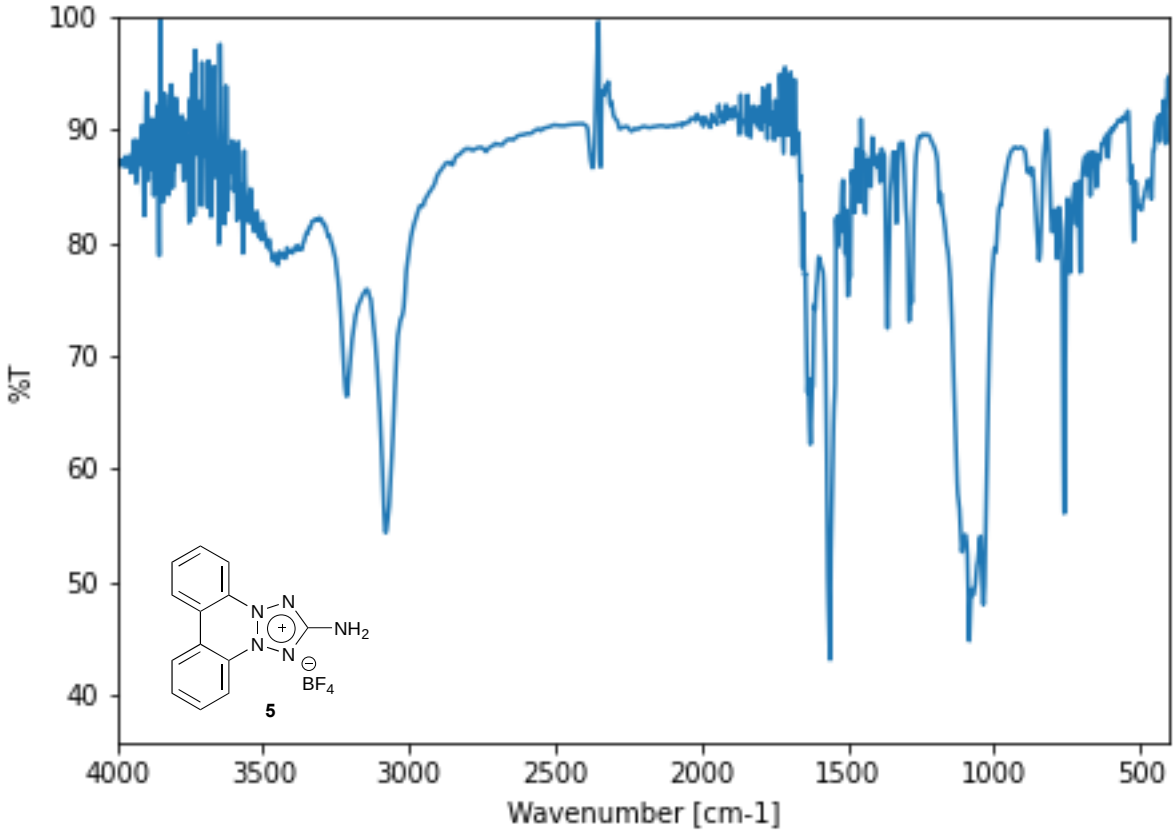
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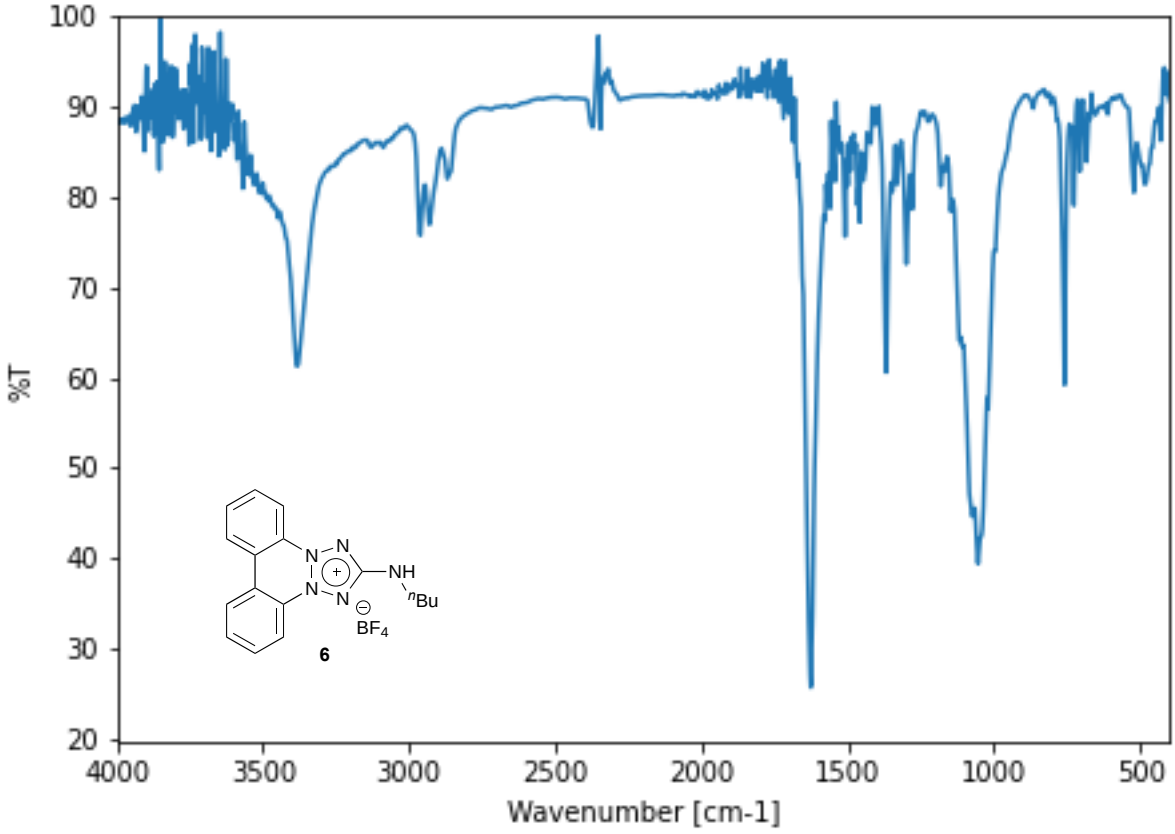
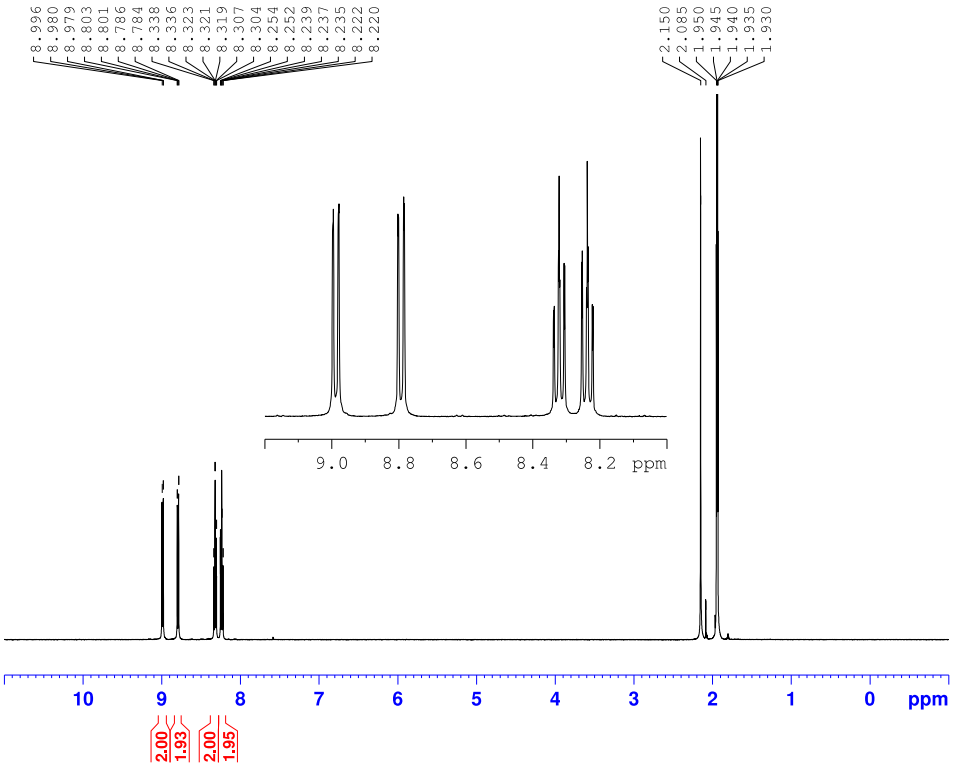


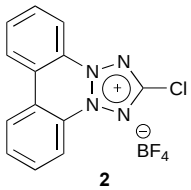
Figure S10. IR spectra of BTC **2-6** using KBr.



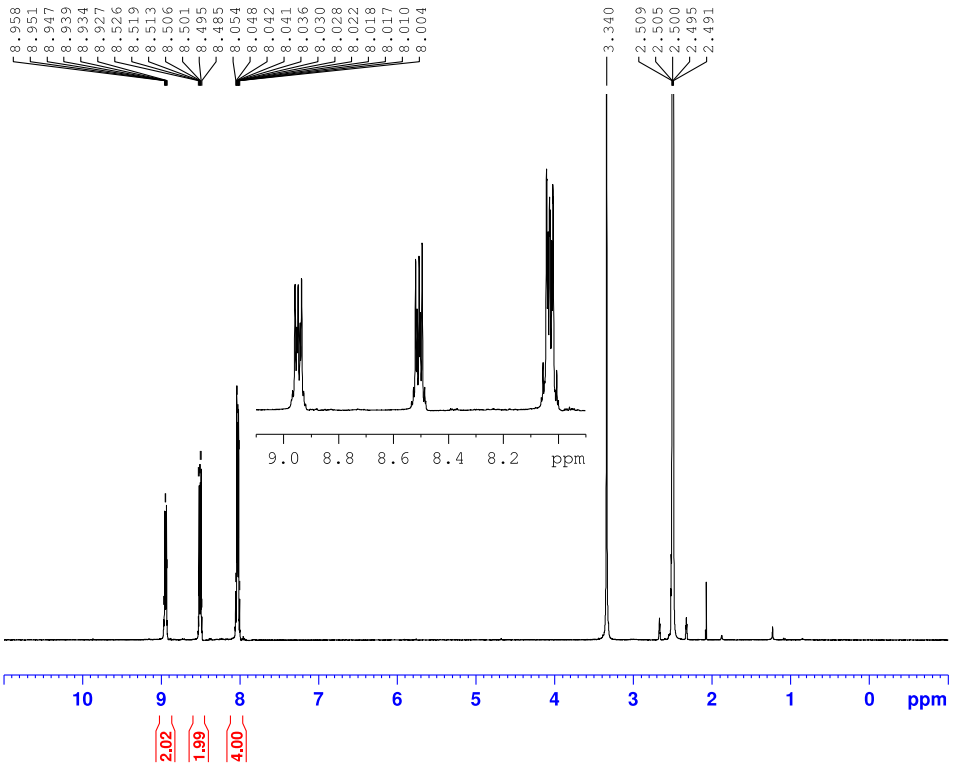
```
Current Data Parameters
NAME      NMexp.164-1-H-500-CD3CN
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181026
Time              12.39 h
INSTRUM             spect
PROBHD   Z107909_0012 (
PULPROG             zg30
TD                 65536
SOLVENT            CD3CN
NS                     8
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                    18
DW                50.000 usec
DE                10.00 usec
TE                297.0 K
D1             5.00000000 sec
TD0                    1
SFO1          500.0330002 MHz
NUC1                  1H
P1                15.00 usec
PLW1           6.21000004 W

F2 - Processing parameters
SI                 32768
SF            500.0300141 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



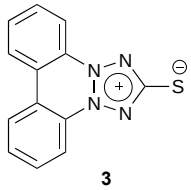
2



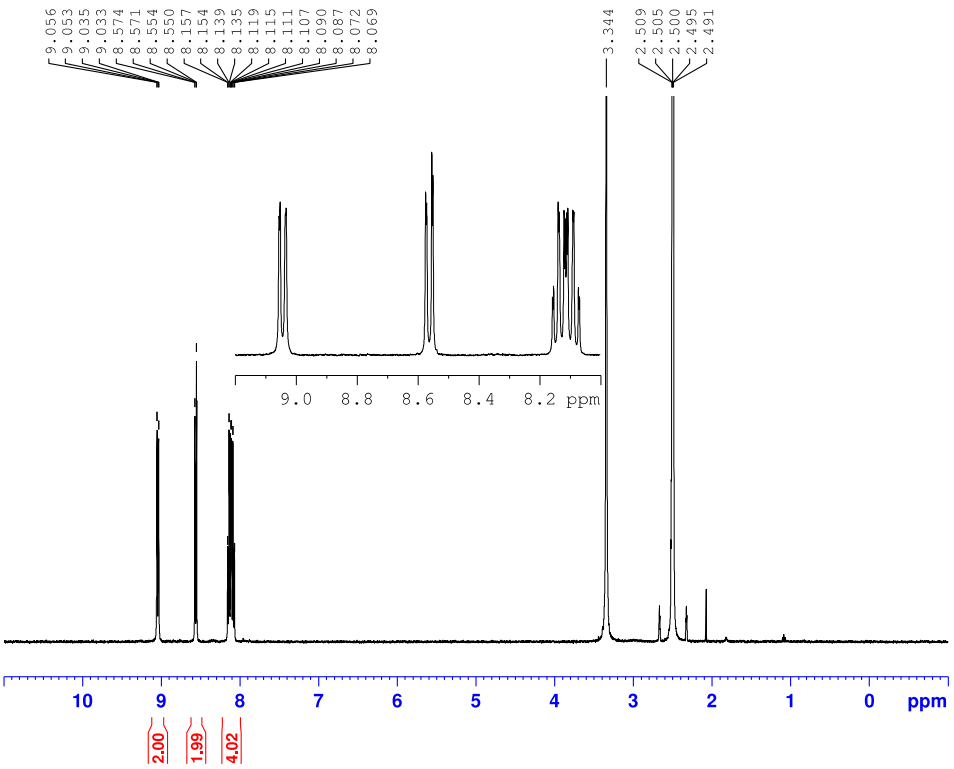
```
Current Data Parameters
NAME          531_p_1_NMR
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211201
Time              2.56 h
INSTRUM             spect
PROBHD   Z108618_0210 (
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    64
DS                     1
SWH            8012.820 Hz
FIDRES            0.244532 Hz
AQ                4.0894465 sec
RG                   203
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
D1             2.00000000 sec
TD0                    1
SFO1          400.1324710 MHz
NUC1                  1H
P1                16.00 usec
PLW1          13.73499966 W

F2 - Processing parameters
SI                 65536
SF            400.1300033 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



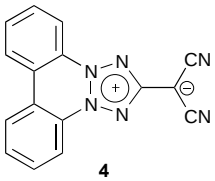
3



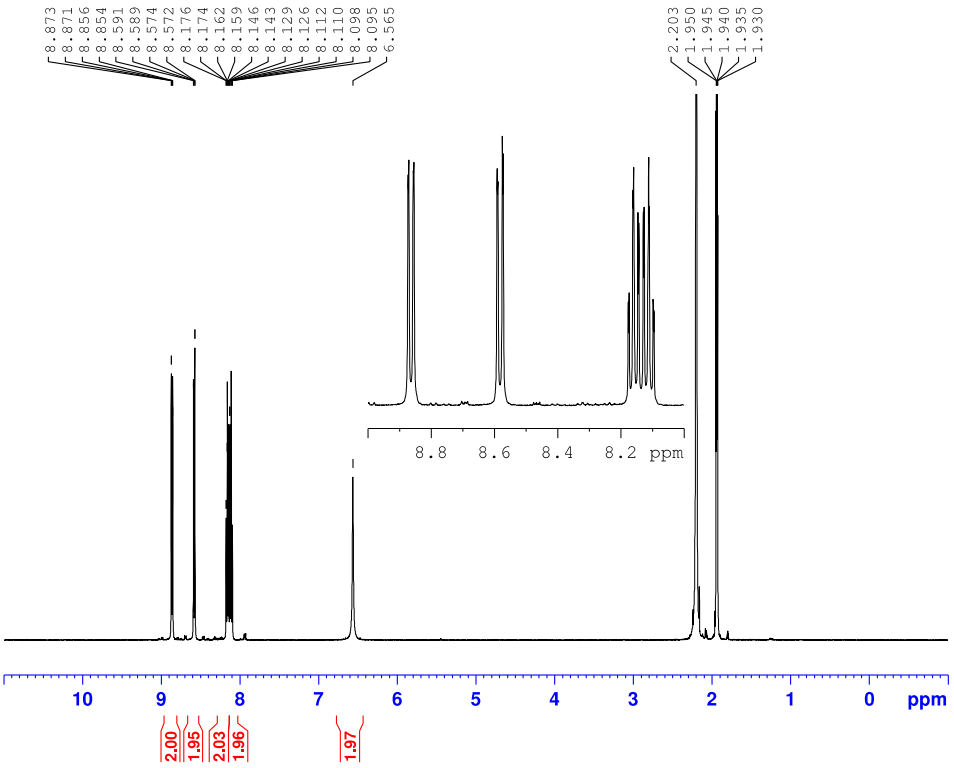
Current Data Parameters
NAME 478_p_1_1_NMR
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210615
Time 19.06 h
INSTRUM spect
PROBHD Z108618_0210 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 203
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 16.00 usec
PLW1 13.73499966 W

F2 - Processing parameters
SI 65536
SF 400.1300034 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



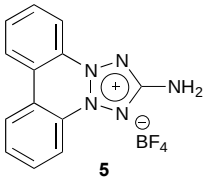
4



Current Data Parameters
NAME NMexp.146-Crude-2-H-500
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180918
Time 18.57 h
INSTRUM spect
PROBHD Z107909_0012 (
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 18
DW 50.000 usec
DE 10.00 usec
TE 297.0 K
D1 5.00000000 sec
TD0 1
SFO1 500.0330002 MHz
NUC1 1H
P1 15.00 usec
PLW1 6.21000004 W

F2 - Processing parameters
SI 32768
SF 500.0300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



5

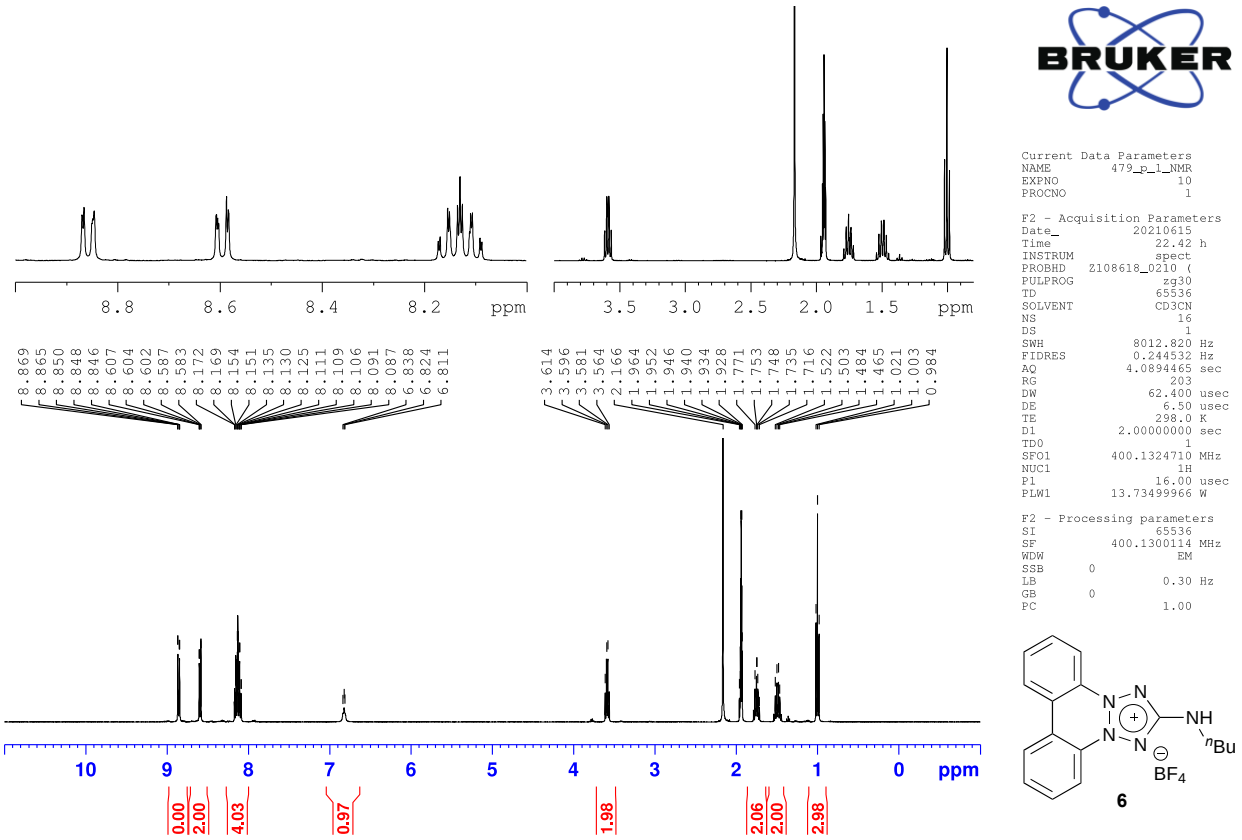
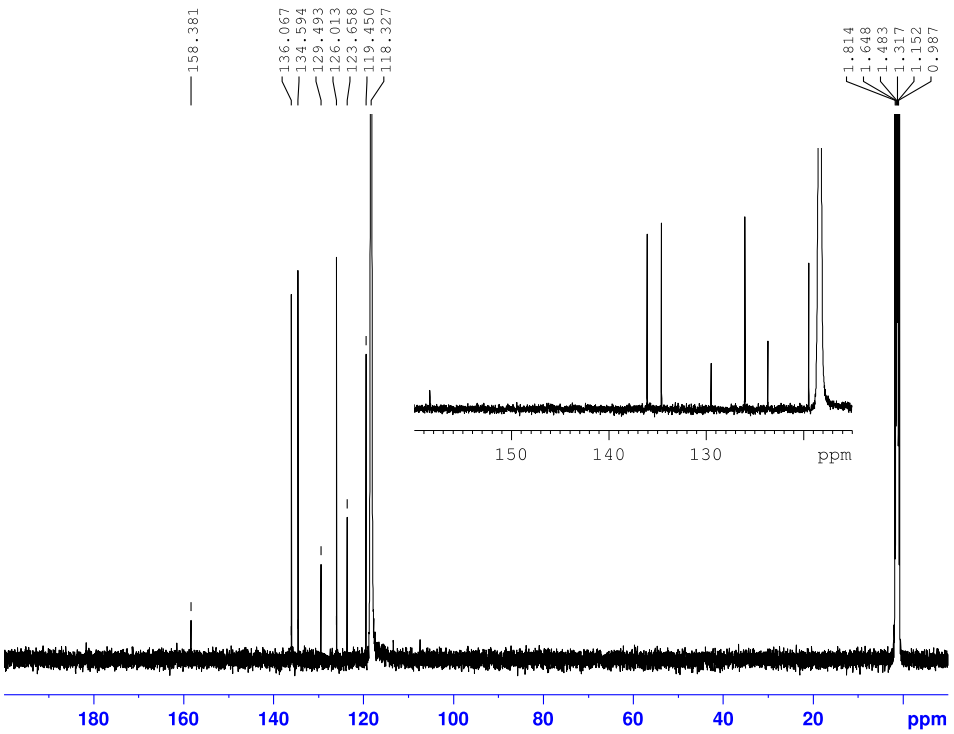


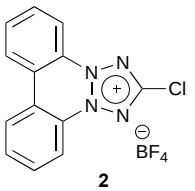
Figure S11. ^{1}H NMR spectra of BTC **2-6**.



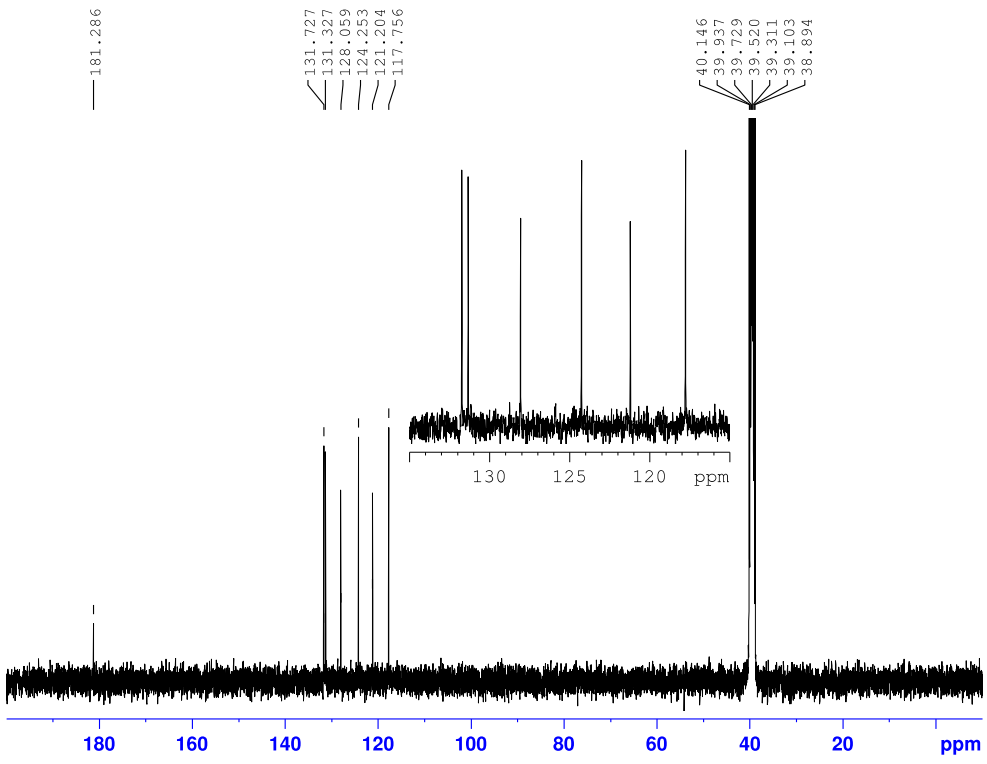
```
Current Data Parameters
NAME      NMexp.164-1-C-500-CD3CN
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181026
Time              12.59 h
INSTRUM             spect
PROBHD   Z107909_0012 (
PULPROG           zgpg30
TD                65536
SOLVENT           CD3CN
NS                  256
DS                    4
SWH           29761.904 Hz
FIDRES         0.910763 Hz
AQ             1.0979809 sec
RG                 45.2
DW               16.800 usec
DE               18.00 usec
TE                297.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         125.7452168 MHz
NUC1                13C
P1                10.00 usec
PLW1         25.45199966 W
SFO2         500.0320001 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          6.21000004 W
PLW12         0.21832000 W
PLW13         0.10981000 W

F2 - Processing parameters
SI                 32768
SF           125.7325241 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



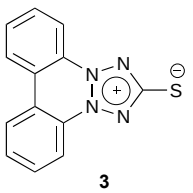
2



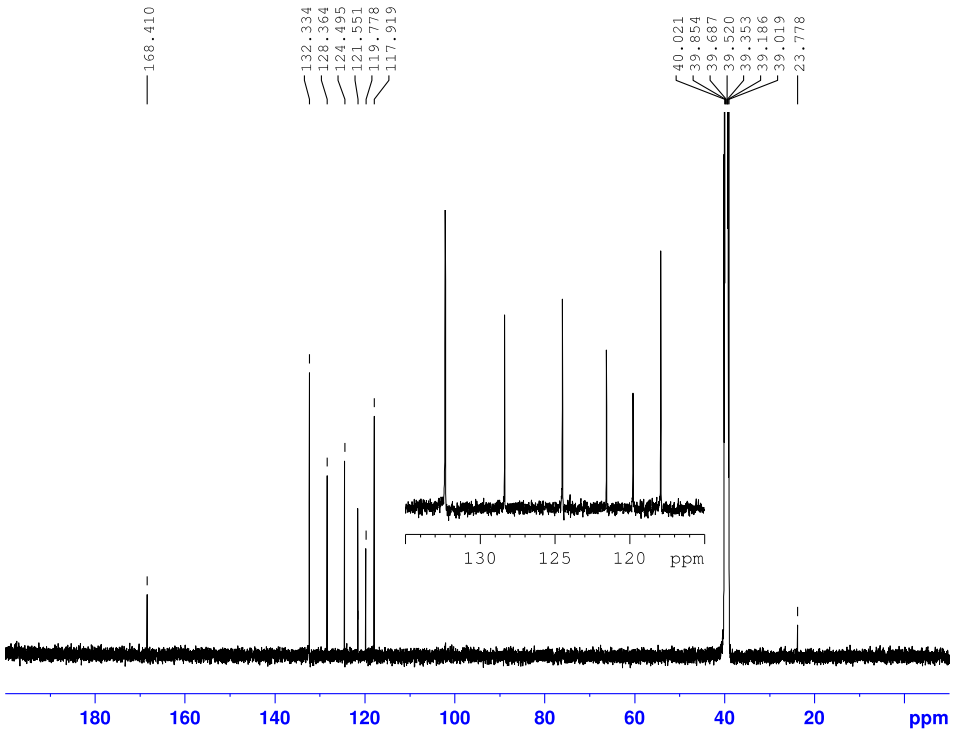
```
Current Data Parameters
NAME      531_p_1_13CNMR
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211201
Time              4.55 h
INSTRUM             spect
PROBHD   Z108618_0210 (
PULPROG           zgpg30
TD                65536
SOLVENT            DMSO
NS                 2048
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P1                9.50 usec
PLW1         59.31800079 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         13.73499966 W
PLW12         0.43408999 W
PLW13         0.21834999 W

F2 - Processing parameters
SI                 32768
SF           100.6128172 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



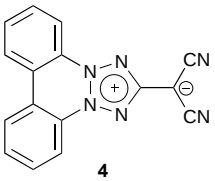
3



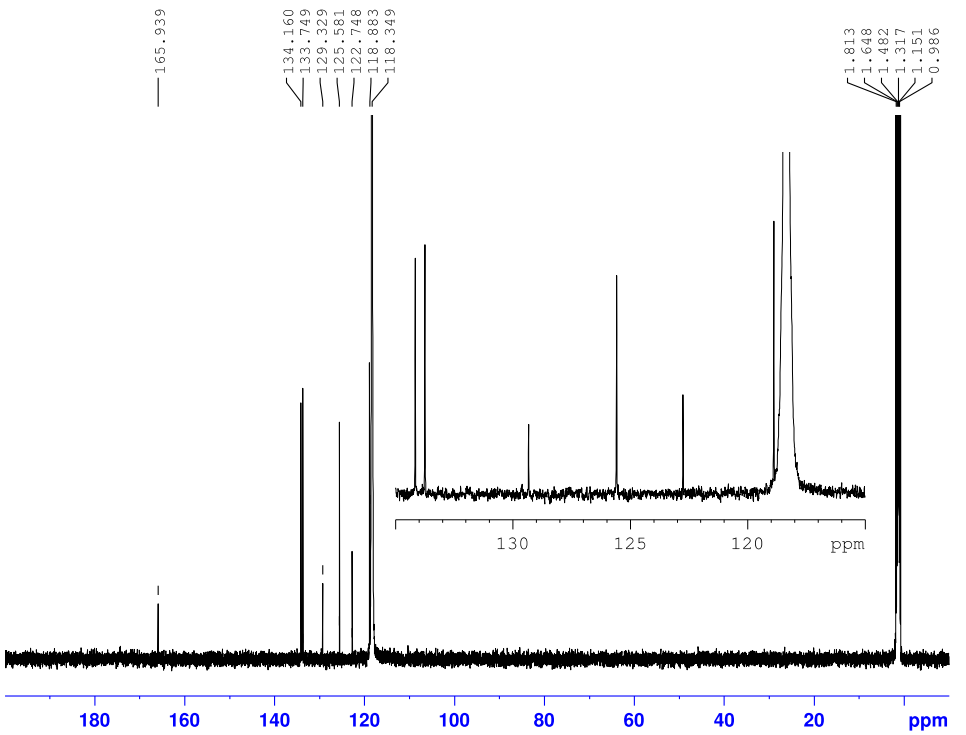
```
Current Data Parameters
NAME      478_p_1_1_13CNMR
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210616
Time              17.22 h
INSTRUM             spect
PROBHD    Z107909_0012 (
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   512
DS                     4
SWH           29761.904 Hz
FIDRES         0.910763 Hz
AQ             1.0979809 sec
RG                    10
DW               16.800 usec
DE               18.00 usec
TE                300.0 K
D1            4.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1        125.7452168 MHz
NUC1                  13C
P1               10.00 usec
PLW1        27.00000000 W
SFO2        500.0320001 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        15.00000000 W
PLW12        0.23438001 W
PLW13        0.11789000 W

F2 - Processing parameters
SI                 32768
SF          125.7327016 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



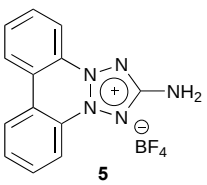
4



```
Current Data Parameters
NAME      NMexp.146-Crude-2-C-500
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180918
Time              19.08 h
INSTRUM             spect
PROBHD    Z107909_0012 (
PULPROG          zgpg30
TD                65536
SOLVENT            CD3CN
NS                   128
DS                     4
SWH           29761.904 Hz
FIDRES         0.910763 Hz
AQ             1.0979809 sec
RG                  50.8
DW               16.800 usec
DE               18.00 usec
TE                297.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1        125.7452168 MHz
NUC1                  13C
P1               10.00 usec
PLW1        25.45199966 W
SFO2        500.0320001 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         6.21000004 W
PLW12        0.21832000 W
PLW13        0.10981000 W

F2 - Processing parameters
SI                 32768
SF          125.7325241 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



5

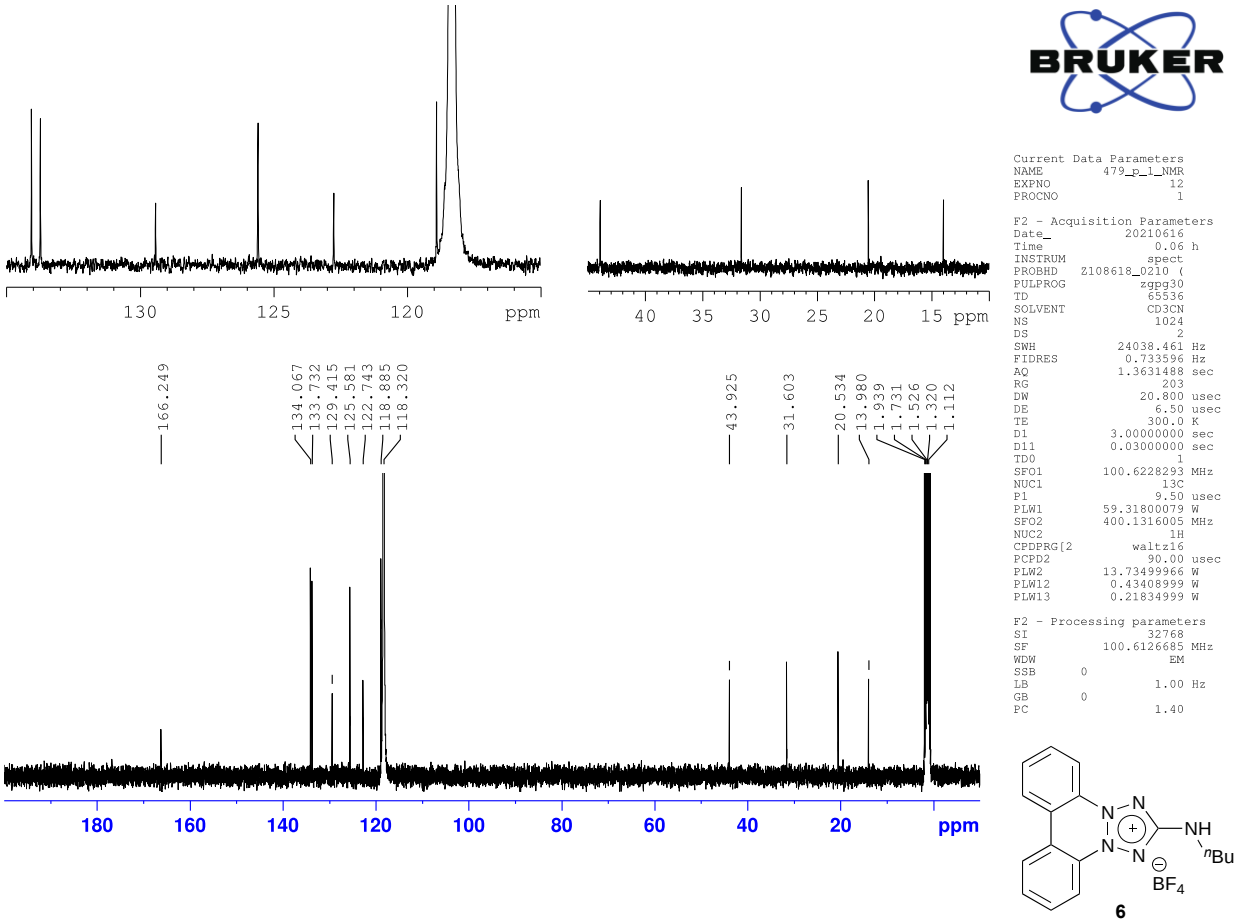
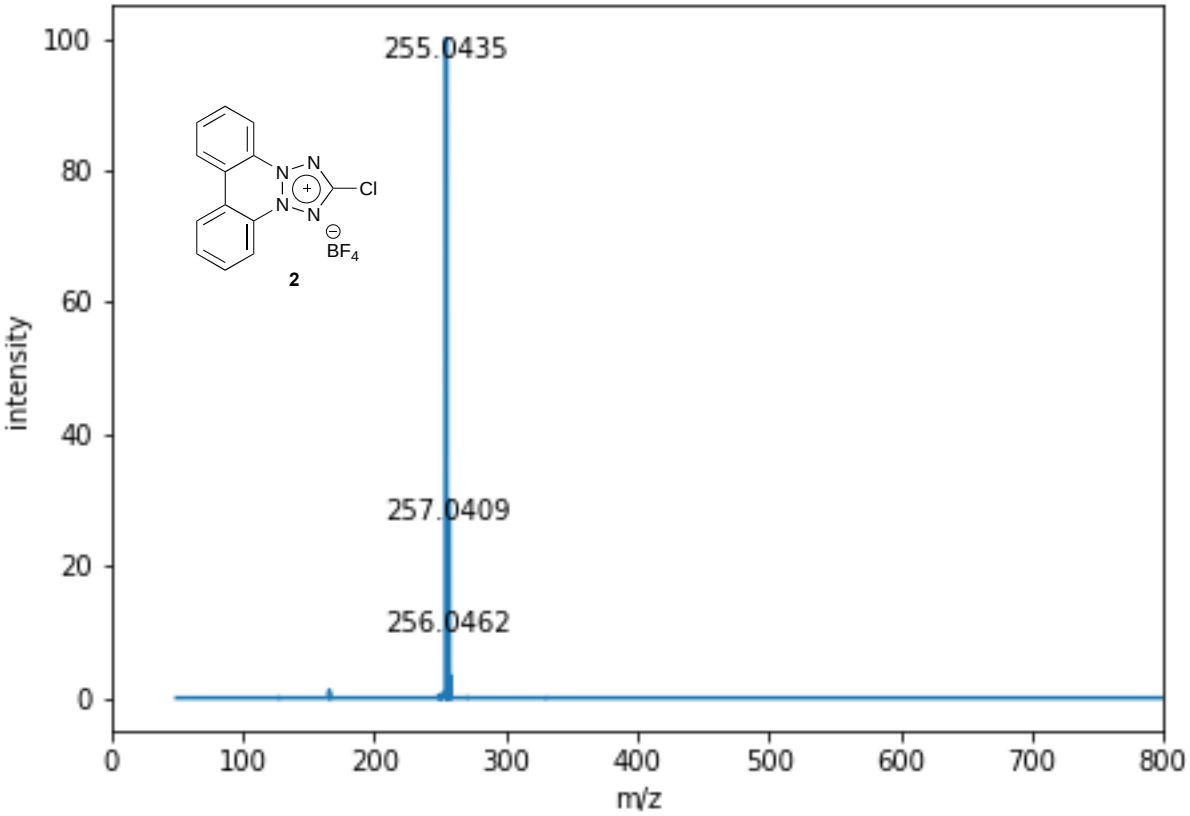
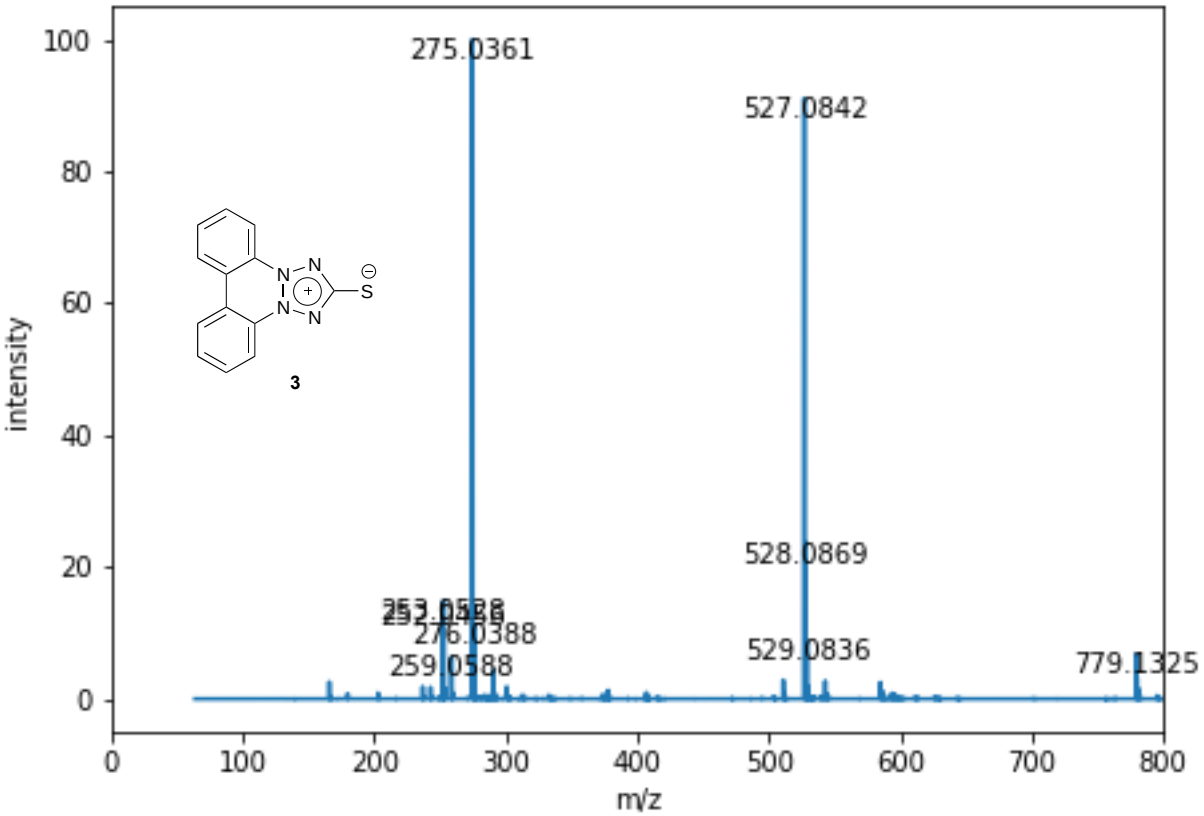
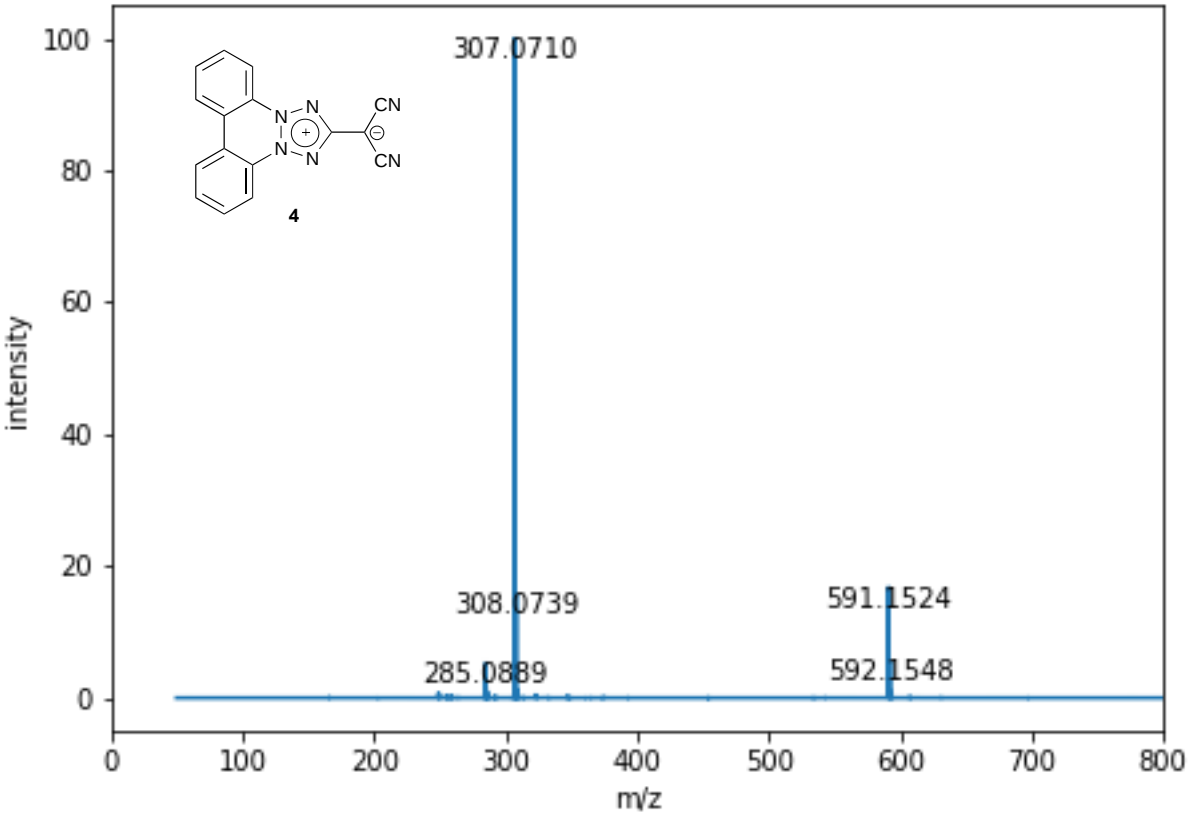
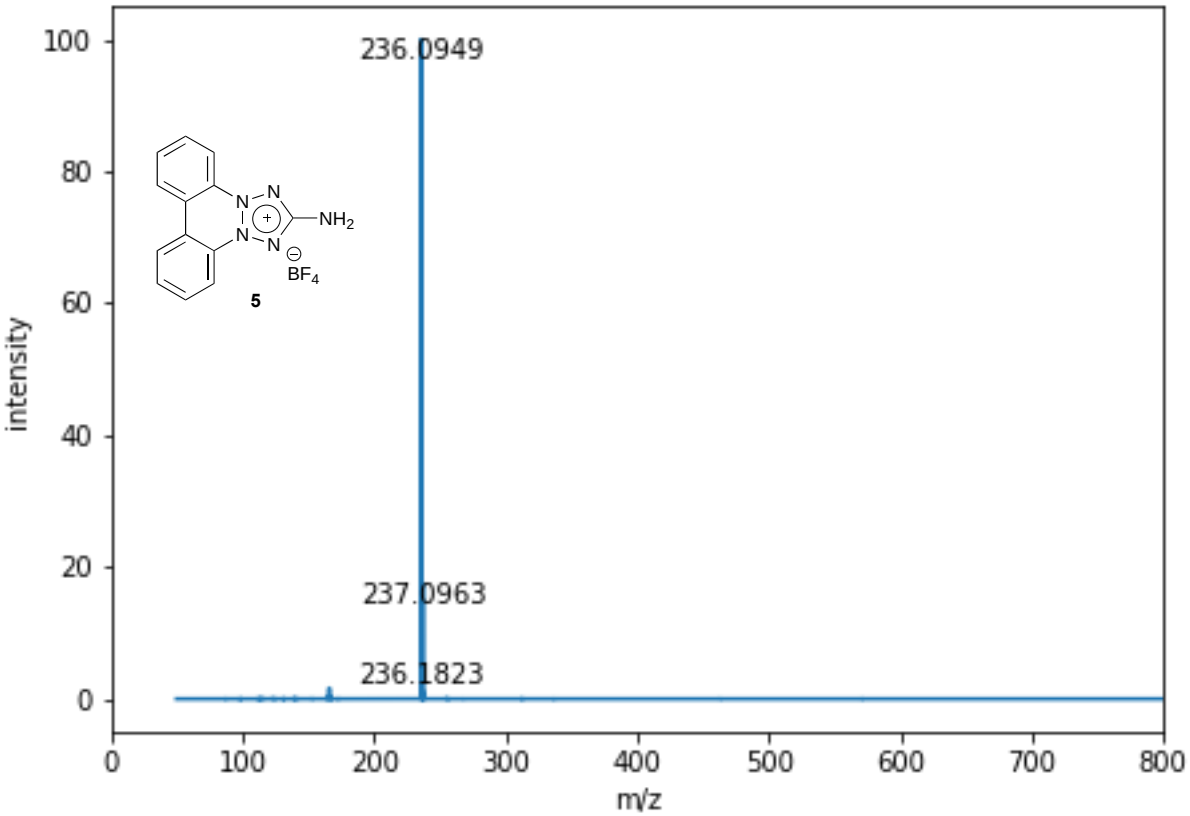


Figure S12. ^{13}C NMR spectra of BTC **2-6**.


255.0435
257.0409
256.0462
intensity
m/z
2


275.0361
527.0842
528.0869
276.0388
259.0588
529.0836
779.1325
intensity
m/z
3


307.0710
308.0739
285.0889
591.1524
592.1548
intensity
m/z
4


236.0949
237.0963
236.1823
intensity
m/z
5

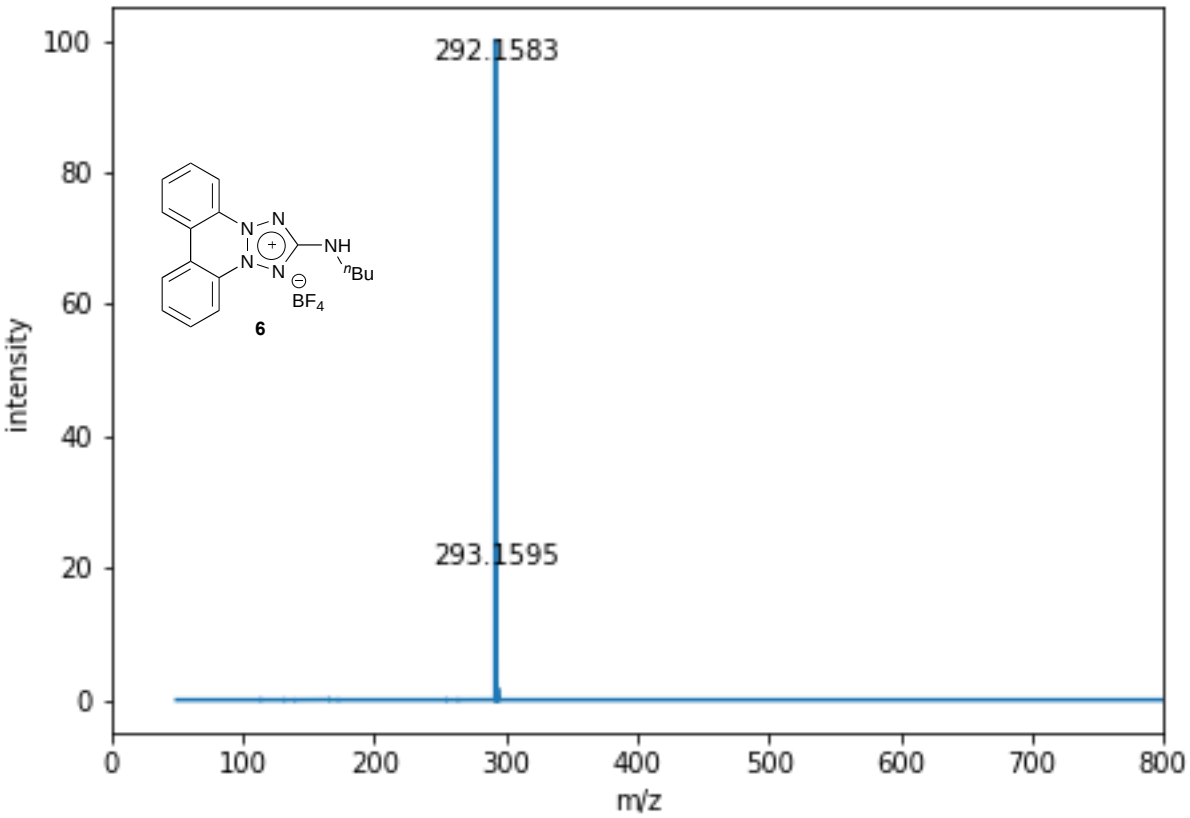


Figure S13. MS of BTC **2-6** using ESI-TOF positive mode.

Table S8. The calculation of optimized geometry of BTC-S **3** in gas phase.

Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	-4.499500	0.000156	0.000237
2	N	-2.017441	-1.130903	0.000099
3	N	-0.790915	-0.676221	0.000045
4	N	-0.790800	0.676350	-0.000540
5	N	-2.017359	1.131113	-0.000491
6	C	-2.831630	0.000192	-0.000066
7	C	0.395096	-1.423056	0.000018
8	C	0.311637	-2.819962	0.000133
9	C	1.483600	-3.552810	0.000096
10	C	2.724231	-2.898365	-0.000072
11	C	2.790382	-1.516220	-0.000154
12	C	1.623046	-0.729534	-0.000052
13	C	1.623147	0.729388	-0.000057
14	C	2.790575	1.515918	0.000214
15	C	2.724627	2.898079	0.000295
16	C	1.484066	3.552666	0.000159
17	C	0.312012	2.819974	-0.000094
18	C	0.395268	1.423051	-0.000165
19	H	-0.663030	-3.288590	0.000252
20	H	1.438732	-4.635018	0.000173
21	H	3.639713	-3.477691	-0.000151
22	H	3.759396	-1.035334	-0.000301
23	H	3.759533	1.034905	0.000353
24	H	3.640182	3.477279	0.000519
25	H	1.439321	4.634888	0.000233
26	H	-0.662581	3.288749	-0.000197

Calculated at the B3LYP/6-311++G(d,p) level. HF = -1117.5189847, Number of imaginary frequencies = 0

Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	0.000000	0.000000	-4.499448
2	N	0.000000	-1.131013	-2.017337
3	N	0.000000	-0.676164	-0.790767
4	N	0.000000	0.676164	-0.790767
5	N	0.000000	1.131013	-2.017337
6	C	0.000000	0.000000	-2.831577
7	C	0.000000	-1.423088	0.395267

8	C	0.000000	-2.819928	0.311733
9	C	0.000000	-3.552894	1.483681
10	C	0.000000	-2.898542	2.724280
11	C	0.000000	-1.516336	2.790486
12	C	0.000000	-0.729591	1.623211
13	C	0.000000	0.729591	1.623211
14	C	0.000000	1.516336	2.790486
15	C	0.000000	2.898542	2.724280
16	C	0.000000	3.552894	1.483681
17	C	0.000000	2.819928	0.311733
18	C	0.000000	1.423088	0.395267
19	H	0.000000	-3.288597	-0.662896
20	H	0.000000	-4.635027	1.438690
21	H	0.000000	-3.477928	3.639722
22	H	0.000000	-1.035611	3.759536
23	H	0.000000	1.035611	3.759536
24	H	0.000000	3.477928	3.639722
25	H	0.000000	4.635027	1.438690
26	H	0.000000	3.288597	-0.662896

Calculated at the B3LYP/6-311++G(d,p) level with C_{2v} symmetry . HF = -1117.5189847, Number of imaginary frequencies = 0

Center number	**Atomic symbol**	**Coordinates (Angstroms)**		
		X	**Y**	**Z**
1	S	-1.733799	0.728422	8.284052
2	N	0.119002	1.571724	10.088487
3	N	0.483902	2.726392	10.560412
4	N	-0.224014	3.705419	10.001467
5	N	-1.086648	3.221760	9.158325
6	C	-0.893252	1.850220	9.184768
7	C	1.504335	2.975483	11.492662
8	C	2.218810	1.890186	11.999899
9	C	3.216692	2.138407	12.920050
10	C	3.491432	3.450002	13.324706
11	C	2.770754	4.510581	12.811278
12	C	1.745833	4.301358	11.875232
13	C	0.943761	5.372882	11.289009
14	C	1.093298	6.730983	11.610895
15	C	0.298897	7.693200	11.018522
16	C	-0.678120	7.334344	10.082505

17	C	-0.858750	6.009812	9.740360
18	C	-0.047236	5.054027	10.351507
19	H	1.973227	0.892938	11.659261
20	H	3.786550	1.313004	13.327352
21	H	4.276663	3.637270	14.046447
22	H	3.001877	5.515579	13.137836
23	H	1.840824	7.031989	12.332478
24	H	0.434291	8.734520	11.282886
25	H	-1.296562	8.094912	9.623170
26	H	-1.601564	5.688044	9.022347

Calculated at the M06-2X/6-311++G(d,p) level. HF = -1117.2023457 Number of imaginary frequencies = 0

Center	**Atomic**	**Coordinates (Angstroms)**		
number	**symbol**	**X**	**Y**	**Z**
1	S	-1.733637	0.728661	8.284735
2	N	0.130855	1.573454	10.071088
3	N	0.495986	2.727284	10.547744
4	N	-0.235938	3.704423	10.013728
5	N	-1.100773	3.216901	9.173197
6	C	-0.893608	1.849925	9.184441
7	C	1.506730	2.974675	11.488631
8	C	2.225125	1.895673	11.996453
9	C	3.215780	2.143745	12.919943
10	C	3.482000	3.452789	13.327979
11	C	2.760039	4.508241	12.813908
12	C	1.743742	4.298721	11.872241
13	C	0.941257	5.369550	11.287288
14	C	1.098144	6.725836	11.602558
15	C	0.307094	7.688943	11.014251
16	C	-0.673972	7.333186	10.085826
17	C	-0.859716	6.011176	9.748927
18	C	-0.051001	5.052811	10.353747
19	H	1.987383	0.898023	11.654265
20	H	3.786891	1.319734	13.327905
21	H	4.261997	3.642419	14.054510
22	H	2.984909	5.512286	13.145652
23	H	1.850704	7.026371	12.318141
24	H	0.449121	8.729967	11.275596
25	H	-1.291599	8.095001	9.627817
26	H	-1.607309	5.693663	9.035340

Calculated at the CAM-B3LYP/6-311++G(d,p) level. HF = -1117.1342889. Number of imaginary frequencies = 0

Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	-1.733857	0.729280	8.286121
2	N	0.132200	1.572342	10.073220
3	N	0.495788	2.727651	10.548109
4	N	-0.235536	3.704492	10.013878
5	N	-1.101687	3.219390	9.172977
6	C	-0.893305	1.850878	9.185799
7	C	1.506780	2.974620	11.488603
8	C	2.224841	1.892859	11.995153
9	C	3.217007	2.140573	12.919838
10	C	3.484286	3.450121	13.329540
11	C	2.762109	4.508162	12.816143
12	C	1.744613	4.299132	11.873492
13	C	0.941432	5.370956	11.287946
14	C	1.097891	6.728809	11.603137
15	C	0.305075	7.691887	11.012821
16	C	-0.676143	7.334327	10.083508
17	C	-0.861577	6.010377	9.746577
18	C	-0.051045	5.052831	10.353705
19	H	1.987749	0.894167	11.653037
20	H	3.787739	1.314776	13.326608
21	H	4.264886	3.639407	14.056590
22	H	2.988362	5.512392	13.149699
23	H	1.850481	7.031539	12.319302
24	H	0.446829	8.733720	11.274074
25	H	-1.294934	8.095252	9.623903
26	H	-1.609780	5.693521	9.032131

Calculated at the ωB97X-D/6-311++G(d,p) level. HF = -1117.2406949. Number of imaginary frequencies = 0

Table S9. The calculation of optimized geometry of BTC-S **3** in chloroform IEF-PCM.

Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	-4.509384	0.000285	-0.000126
2	N	-2.021732	-1.125417	0.000067
3	N	-0.788667	-0.672277	0.000067
4	N	-0.788585	0.672399	-0.000103
5	N	-2.021597	1.125687	-0.000166
6	C	-2.814391	0.000183	-0.000048
7	C	0.395215	-1.425523	0.000042
8	C	0.310514	-2.821482	0.000047
9	C	1.483476	-3.552977	0.000010
10	C	2.722978	-2.896282	-0.000045
11	C	2.790021	-1.514180	-0.000042
12	C	1.621224	-0.729401	0.000028
13	C	1.621312	0.729232	0.000053
14	C	2.790205	1.513869	0.000178
15	C	2.723329	2.895979	0.000173
16	C	1.483906	3.552824	0.000053
17	C	0.310856	2.821471	-0.000041
18	C	0.395388	1.425502	-0.000025
19	H	-0.659992	-3.297416	0.000071
20	H	1.440096	-4.634899	0.000009
21	H	3.638578	-3.474859	-0.000098
22	H	3.759185	-1.034818	-0.000110
23	H	3.759310	1.034390	0.000295
24	H	3.638999	3.474445	0.000269
25	H	1.440658	4.634751	0.000048
26	H	-0.659593	3.297523	-0.000115

Calculated at the B3LYP/6-311++G(d,p) level in chloroform IEF-PCM. HF = -1117.5400429, Number of imaginary frequencies = 0

Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	-4.493664	-0.000084	0.000130
2	N	-2.008302	-1.117577	-0.000571
3	N	-0.786662	-0.662741	-0.000396
4	N	-0.786684	0.662704	0.000470

5	N	-2.008341	1.117498	0.000703
6	C	-2.799105	-0.000053	0.000077
7	C	0.398946	-1.420136	-0.000708
8	C	0.301790	-2.810980	-0.001459
9	C	1.470872	-3.544119	-0.002040
10	C	2.710094	-2.892542	-0.002025
11	C	2.783553	-1.513164	-0.001284
12	C	1.617966	-0.730425	-0.000541
13	C	1.617941	0.730472	0.000504
14	C	2.783500	1.513251	0.001193
15	C	2.709993	2.892627	0.001937
16	C	1.470749	3.544161	0.002011
17	C	0.301692	2.810981	0.001484
18	C	0.398897	1.420141	0.000728
19	H	-0.673285	-3.278893	-0.001549
20	H	1.424539	-4.625463	-0.002574
21	H	3.622923	-3.474770	-0.002600
22	H	3.753632	-1.035359	-0.001442
23	H	3.753597	1.035480	0.001306
24	H	3.622802	3.474887	0.002470
25	H	1.424378	4.625503	0.002547
26	H	-0.673399	3.278861	0.001619

Calculated at the M06-2X/6-311++G(d,p) level in chloroform IEF-PCM. HF = -1117.2249129. Number of imaginary frequencies = 0

Center	**Atomic**	**Coordinates (Angstroms)**		
number	**symbol**	**X**	**Y**	**Z**
1	S	-0.664323	3.281071	-0.000173
2	N	-2.010292	-1.115232	0.000067
3	N	-0.786249	-0.663435	0.000101
4	N	-0.786169	0.663552	-0.000118
5	N	-2.010166	1.115489	-0.000230
6	C	-2.799131	0.000177	0.000130
7	C	0.397562	-1.419884	0.000041
8	C	0.307250	-2.808766	0.000026
9	C	1.474185	-3.539333	-0.000021
10	C	2.709338	-2.886467	-0.000058
11	C	2.778298	-1.510011	-0.000041
12	C	1.614066	-0.729855	0.000034
13	C	1.614152	0.729694	0.000041

14	C	2.778475	1.509713	0.000150
15	C	2.709676	2.886178	0.000124
16	C	1.474599	3.539187	-0.000003
17	C	0.307578	2.808757	-0.000090
18	C	0.397728	1.419864	-0.000046
19	H	-0.664707	-3.280967	0.000044
20	H	1.429813	-4.620546	-0.000041
21	H	3.623586	-3.465983	-0.000114
22	H	3.747228	-1.031555	-0.000098
23	H	3.747349	1.031144	0.000263
24	H	3.623991	3.465587	0.000208
25	H	1.430353	4.620405	-0.000023
26	H	-0.664323	3.281071	-0.000173

Calculated at the CAM-B3LYP/6-311++G(d,p) level in chloroform IEF-PCM. HF = -1117.1572301. Number of imaginary frequencies = 0

Center	**Atomic**	**Coordinates (Angstroms)**		
number	**symbol**	**X**	**Y**	**Z**
1	S	-4.490578	0.000224	-0.001234
2	N	-2.008954	-1.117731	-0.000068
3	N	-0.785872	-0.663250	0.000078
4	N	-0.785806	0.663349	-0.000339
5	N	-2.008848	1.117945	-0.000630
6	C	-2.797536	0.000147	0.000157
7	C	0.397495	-1.419862	0.000009
8	C	0.304020	-2.810088	-0.000076
9	C	1.471957	-3.542483	-0.000111
10	C	2.709060	-2.890680	-0.000079
11	C	2.780423	-1.512441	-0.000001
12	C	1.615551	-0.730528	0.000093
13	C	1.615622	0.730395	0.000118
14	C	2.780571	1.512193	0.000406
15	C	2.709342	2.890439	0.000317
16	C	1.472302	3.542362	-0.000053
17	C	0.304294	2.810082	-0.000289
18	C	0.397633	1.419846	-0.000156
19	H	-0.668613	-3.282760	-0.000124
20	H	1.425347	-4.624266	-0.000188
21	H	3.623480	-3.471174	-0.000147
22	H	3.751263	-1.035692	-0.000041
23	H	3.751364	1.035350	0.000723

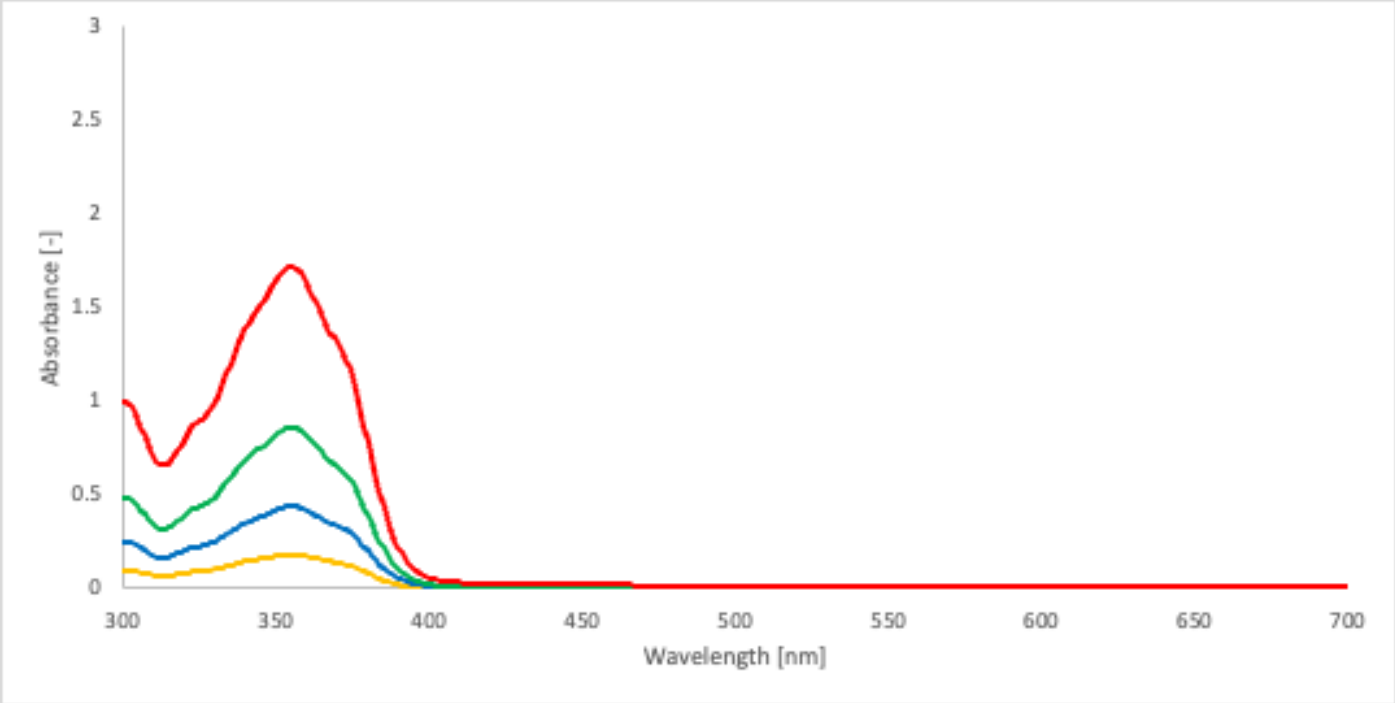
24	H	3.623819	3.470845	0.000538
25	H	1.425798	4.624151	-0.000132
26	H	-0.668292	3.282848	-0.000543

Calculated at the ωB97X-D/6-311++G(d,p) level in chloroform IEF-PCM. HF = -1117.2635142. Number of imaginary frequencies = 0

Table S10. The calculation of optimized geometry of dehydrodithizone **(DD)** in gas phase.

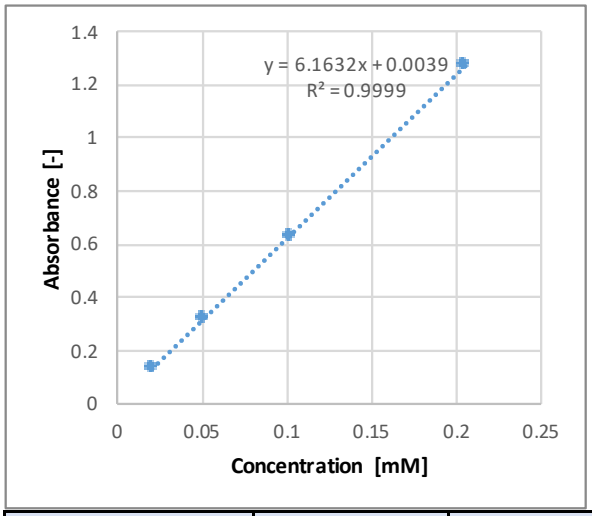
Center number	Atomic symbol	Coordinates (Angstroms)		
		X	Y	Z
1	S	0.000000	0.000000	-4.463581
2	C	0.000000	0.000000	-2.791206
3	N	0.032025	1.124694	-1.973847
4	N	0.022690	0.673629	-0.743303
5	C	0.116020	1.529641	0.404546
6	C	1.087887	1.301201	1.376164
7	C	1.171649	2.174821	2.456690
8	C	0.307493	3.264954	2.548697
9	C	-0.643542	3.490547	1.553652
10	C	-0.745428	2.622740	0.471060
11	H	1.771500	0.466896	1.286434
12	H	1.924157	2.009721	3.218413
13	H	0.382897	3.944917	3.389088
14	H	-1.306441	4.345171	1.616261
15	H	-1.463752	2.787975	-0.321647
16	N	-0.032025	-1.124694	-1.973847
17	N	-0.022690	-0.673629	-0.743303
18	C	-0.116020	-1.529641	0.404546
19	C	-1.087887	-1.301201	1.376164
20	C	-1.171649	-2.174821	2.456690
21	C	-0.307493	-3.264954	2.548697
22	C	0.643542	-3.490547	1.553652
23	C	0.745428	-2.622740	0.471060
24	H	-1.771500	-0.466896	1.286434
25	H	-1.924157	-2.009721	3.218413
26	H	-0.382897	-3.944917	3.389088
27	H	1.306441	-4.345171	1.616261
28	H	1.463752	-2.787975	-0.321647

Calculated at the B3LYP/6-311++G(d,p) level. HF = -1118.6980846, Number of imaginary frequencies = 0



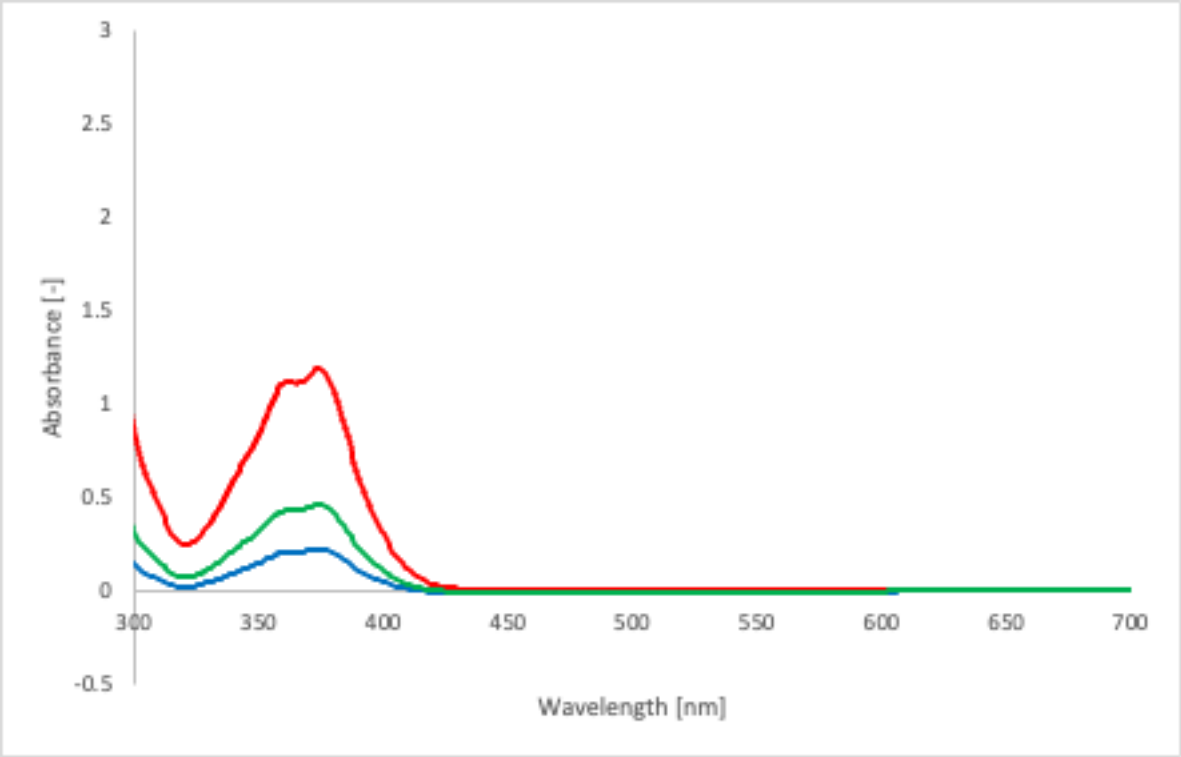
Caribration	exp.211			
Mol No.	15	Sovent	MeCN	
Wavelength [nm]	337	Temperature [°C]	20	
Caribration	p_1	p_5	p_8	p_10
Concentration [mM]	0.020553458	0.051383644	0.102767288	0.205534576
Absorbance [−]	0.132	0.323	0.631	1.273

a	b
6.163181957	0.003879518



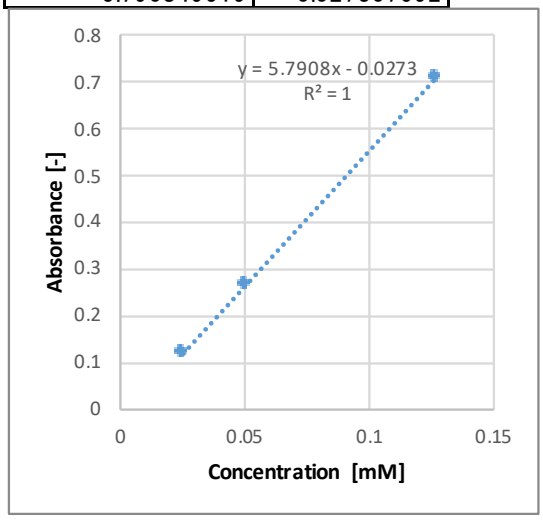
Observed	NaOH treatment	HBF4 treatment
Absorbance [−]	0.925	0.945
Concentration [mM]	0.149455344	0.152700421

Figure S14. UV-Vis spectra (top) and calibration curve (bottom) of **5•H**$^+$ in acetonitrile. Concentration [mM] = 0.21 (red), 0.10 (green), 0.051 (blue) and 0.021 (yellow).



Caribration	exp.585		
Mol No.	**47**	Sovent	MeCN
Wavelength [nm]	345	Temperature [°C]	20
Caribration	p_1	p_4	p_5
Concentration [mM]	0.126592294	0.025318459	0.050636917
Absorbance [−]	0.706	0.12	0.265

a	b
5.790849519	−0.027307692



Observed	NaOH treatment	HBF4 treatment
Absorbance [−]	0.581	0.562
Concentration [mM]	0.105046365	0.101765327

Figure S15. UV-Vis spectra (top) and calibration curve (bottom) of **6•H**$^+$ in acetonitrile. Concentration [mM] = 0.13 (red), 0.051 (green), and 0.025 (blue).