Supporting Information for

Construction of Methylene-Bridged Electron-Deficient Corona[n]arenes and Selective Fluoride Recognition through Anion-π Interactions

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Table of Contents

1. General Information 2
2. Synthesis 2
   2.1 Optimization of the one-pot reaction 2
   2.2 Experimental procedures and characterization of products 4
3. X-ray Crystallographic Data and Molecular Structures 6
   3.1 Molecular structures of corona[3]arene[3]tetrazine **2** 6
   3.2 Crystallographic data 6
4. The Photophysical and Electrochemical Data 11
5. UV-vis Titrations of **1** with Anions 11
   5.1 UV-vis titrations of **1** with tetrabutylammonium salts of different anions 11
   5.2 UV-vis titrations of **1** with (Kcryp)F 12
   5.3 Addition of water to a solution of **1** and (Kcryp)F 14
   5.4 UV-vis titrations of **1** with (Kcryp)OH 14
6. HRMS of a Mixture of **1** and (Kcryp)F 15
7. NMR of **1** and (Kcryp)F 15
8. DFT Calculations 16
9. References 20
10. Copies of ^{1}H and ^{13}C NMR Spectra 21

1. General Information

Reagents and solvents for synthesis were used as received. Anhydrous solvents for titrations were pre-dried by shaking with 4A molecular sieves. Acetonitrile was subsequently stirred with calcium hydride overnight, and then fractionally distilled at high reflux. Tetrahydrofuran (THF) was treated with sodium and refluxed under nitrogen for 2 - 4 hours in the presence of benzophenone as indicator. The dry solvents were kept in a glove box and used within 48 hours.

TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. The silica gel (200-300 mesh) flash column chromatography was used. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer at 298 K. Chemical shifts were reported in ppm with either tetramethylsilane or the residual solvent resonance used as an internal standard. Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet), coupling constant (*J*, Hz). Infrared spectra were recorded using an FT-IR spectrometer with KBr pellets in the 4000-400 cm^{-1} region. UV-vis spectra were recorded using a UV-vis spectrophotometer. Fluorescence spectra were recorded using a fluorescence spectrophotometer. Mass spectrometry was performed at the Institute of Chemistry, CAS and Molecular Scale Laboratory, Shenzhen University. Melting points were uncorrected.

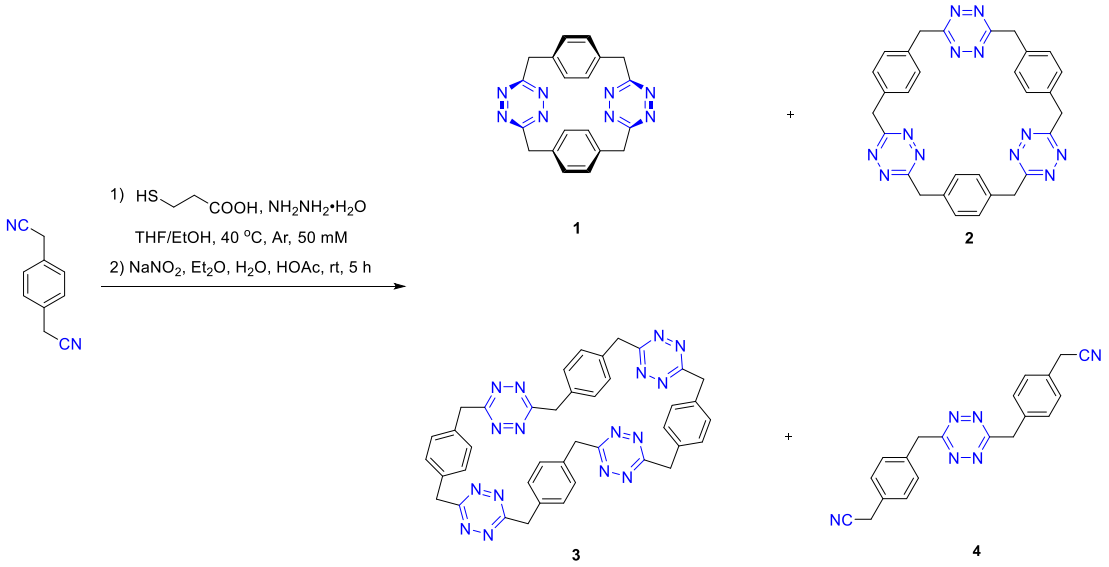
2. Synthesis

2.1 Optimization of the one-pot reaction

Table S1. Optimization of the one-pot reaction

Entry	Microwave	Solv.	Temp.	Equiv. of Catalyst	Equiv. of NH_2NH_2	Time	Conv. [%]	Yield [%]			
								1	**2**	**3**	**4**
1	-	THF : EtOH = 9 : 1	40 °C	4	32	7 d	60	2	1	0	1
2	Standard	THF : EtOH = 9 : 1	40 °C	2	16	1 d	42	2	2	0	4
3	150 W	THF : EtOH = 9 : 1	40 °C	2	16	1 d	76	4	1	1	2
4	300 W	THF : EtOH = 9 : 1	40 °C	2	16	1 d	59	2	2	0	1
5	Standard	THF : EtOH = 9 : 1	40 °C	2	16	2 d	55	3	2	1	2
6	**Standard**	**THF : EtOH = 9 : 1**	**40 °C**	**2**	**16**	**4 d**	**95**	**5**	**2**	**2**	**1**
7	Standard	EtOH	40 °C	2	16	1 d	~0	0	0	0	1
8	Standard	2-Methoxyethanol	40 °C	2	16	1 d	14	0	0	0	2
9	Standard	THF : MTBE : EtOH = 9 : 9 : 2	40 °C	2	16	1 d	91	1	trace	1	Trace
10	Standard	THF : toluene : EtOH = 9 : 9 : 2	40 °C	2	16	1 d	69	1	2	1	Trace
11	Standard	Dioxane : EtOH = 9 : 1	40 °C	2	16	1 d	49	1	2	1	0
12	Standard	DME : EtOH = 9 : 1	40 °C	2	16	1 d	41	2	Trace	0	1
13	Standard	THF : EtOH = 9 : 1	20 °C	2	16	1 d	17	1	2	<1	2
14	Standard	THF : EtOH = 9 : 1	30 °C	2	16	1 d	32	1	3	1	4
15	Standard	THF : EtOH = 9 : 1	50 °C	2	16	1 d	75	1	2	1	3
16	Standard	THF : EtOH = 9 : 1	60 °C	2	16	1 d	80	1	1	0	2
17	Standard	THF : EtOH = 9 : 1	40 °C	1	16	1 d	44	1	2	1	2
18	Standard	THF : EtOH = 9 : 1	40 °C	4	16	1 d	73	1	1	1	3
19	Standard	THF : EtOH = 9 : 1	40 °C	2	8	1 d	23	0	1	0	3
20	Standard	THF : EtOH = 9 : 1	40 °C	2	32	1 d	72	0	1	0	2

2.2 Experimental procedures and characterization of products



Scheme S1. Synthesis of **1-4**

To a 35 mL microwave reaction tube equipped with a stir bar, *p*-phenylenediacetonitrile (156.2 mg, 1.0 mmol), THF (18 mL), anhydrous ethanol (2 mL), and 3-mercaptopropionic acid (0.18 mL, 2.0 mmol) were added. This mixture was cooled to 0 °C, charged with nitrogen, and was added dropwise hydrazine hydrate (0.78 mL, 16.0 mmol). The reaction was carried out at 40 °C using a CEM Discover SP (standard mode) microwave for 4 days. After removal of solvent, ethyl ether (5 mL) was added to form a suspension. Sodium nitrite (248.4 mg, 3.6 mmol) in water (3 mL) were slowly added and followed by slow addition of acetic acid during which the solution turned violet in color and nitrogen oxide gasses evolved. (**Caution!** This step must be performed in a well ventilated fume hood). The suspension was stirred at room temperature for 5 hours. The resulting mixture was diluted with DCM and filtrated over celite®. The red filter cake was washed with DCM (5 × 50 mL) and the filtrate was extracted by brine (3 × 100 mL) to remove acid. The organic phases were then combined and dried over anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was chromatographed on a silica gel column with a mixture of DCM and ethyl acetate (v : v = DCM to 10 : 1) as the mobile phase to give pure product **1** (8.6 mg, 5%), **2** (3.3 mg, 2%), **3** (3.0 mg, 2%), **4** (1.4 mg, 1%), and unreacted *p*-phenylenediacetonitrile (8.5 mg, 5%).

1: red solid; m.p. 290-292 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 8H), 4.47 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 134.9, 129.5, 40.7; IR (KBr) ν 2919, 2849, 1421, 1373, 878 cm^{-1}. HRMS (APCI) Calculated for **1** $[M+H]^+$: 369.1571. Found: 369.1582.

2: red solid; m.p. 281 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 12H), 4.51 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 134.6, 129.8, 40.8; IR (KBr) ν 2920, 2849, 1645, 1426, 1380 cm^{-1}. HRMS (APCI) Calculated for **2** $[M+H]^+$: 553.2320. Found: 553.2329.

3: red solid; m.p. 263 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 16H), 4.56 (s, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 134.8, 129.8, 40.7; IR (KBr) ν 2919, 2849, 1424, 1379, 750 cm^{-1}. HRMS (ESI) Calculated for **3** $[M]^-$: 736.3001. Found: 736.2990.

4: red solid; m.p. 203 - 205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 4H), 7.29 (d, J = 8.4 Hz, 4H), 4.61 (s, 4H), 3.71 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.8, 130.2, 129.3, 128.7, 117.8, 40.9, 23.4; IR (KBr) ν 2917, 2848, 2249, 1417, 1382 cm^{-1}. HRMS (APCI) Calculated for **4** $[M-H]^-$: 339.1364. Found: 339.1361.

Preparation of (Kcryp)F

To a Polytetrafluoroethylene (PTFE) vial which was dried in an oven at 120 °C, KF (8.7 mg, 0.15 mmol), cryptand[2.2.2] (75.3 mg, 0.30 mmol), and anhydrous CH_3CN or CD_3CN (1.5 mL) were added. The mixture was ultrasounded for 2 hours to dissolve the solid and form a pale yellow solution (c = 0.05 M). ^{19}F NMR (376 MHz, CH_3CN) δ -95.6 (s, F^-), -147.2(d, J = 127.8 Hz, HF_2^-).

Preparation of (Kcryp)OH

To a vial which was dried in an oven at 120 ^{o}C, KOH (8.4 mg, 0.15 mmol), cryptand[2.2.2] (75.3 mg, 0.30 mmol), and anhydrous CH_3CN (1.5 mL). The mixture was ultrasounded for 2 hours to dissolve the solid and form a pale yellow solution (*c* = 0.05 M).

3. X-ray Crystallographic Data and Molecular Structures

High-quality single crystals of methylene-connected coronarenes **1**-**3** were obtained by diffusing *n*-hexane or *n*-heptane vapor slowly into their $CHCl_3$, DCM or CH_3CN solution. The complex crystal of **2** @ *p*-phenylenediacetonitrile could be obtained by mixing the two compounds casually and evaporating *n*-hexane slowly into their $CHCl_3$ solution.

3.1 Molecular structures of corona[3]arene[3]tetrazine 2

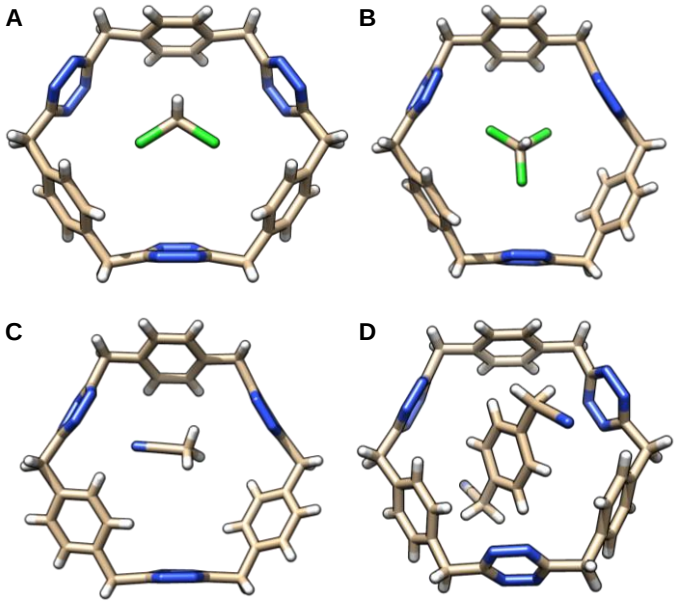


Figure S1. Single crystal X-ray molecular structures of **2** with A) DCM, B) $CHCl_3$, C) CH_3CN, and D) *p*-phenylenediacetonitrile. Disordered structures were omitted for clarity.

3.2 Crystallographic data

Table S2. Crystallographic Data

compound	**1**	**2** @ DCM	**2** @ 0.25 $CHCl_3$	**2** @ CH_3CN	**2** @ *p*-phenylenediacetonitrile	**3**
empirical formula	$C_{20}H_{16}N_8$	$C_{31}H_{26}Cl_2N_{12}$	$C_{30.25}H_{24.25}Cl_{0.75}N_{12}$	$C_{32}H_{27}N_{13}$	$C_{40}H_{32}N_{14}$	$C_{40}H_{32}N_{16}$
M_r	368.41	637.54	582.45	593.66	708.79	736.81
crystal size[mm^3]	0.4 × 0.004 × 0.004	0.2 × 0.15 × 0.1	0.3 × 0.2 × 0.04	0.25 × 0.2 × 0.1	0.312 × 0.156 × 0.135	0.2 × 0.1 × 0.05
crystal system	triclinic	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic
space group	P-1	$Cmc2_1$	$P2_1$	P-1	$Pna2_1$	$P2_1/c$
a [Å]	6.3024(8)	24.4461(4)	13.5363(2)	8.8117(2)	10.96920(10)	9.1552(3)
b [Å]	8.4285(10)	37.2074(6)	10.3837(2)	13.6872(4)	22.0100(2)	33.0314(8)
c [Å]	9.2846(12)	10.1093(2)	22.0547(3)	13.7913(5)	14.5393(2)	11.9403(3)
α [deg]	67.272(12)	90	90	118.189(3)	90	90
β [deg]	89.999(10)	90	96.2010(10)	95.231(2)	90	93.094(2)
γ [deg]	77.645(10)	90	90	93.932(2)	90	90
V [$Å^3$]	442.49(10)	9195.2(3)	3081.80(9)	1448.09(8)	3510.25(7)	3605.59(17)
d [g/cm^3]	1.383	1.382	1.255	1.362	1.341	1.357
Z	1	12	4	2	4	4
T [K]	172.97(10)	169.99(10)	169.98(11)	169.99(12)	170.00(10)	293(2)
R1,wR2 [I>2σ(I)]	0.0558, 0.1455	0.0997, 0.2787	0.1239, 0.3253	0.0912, 0.2763	0.0431, 0.1138	0.0499, 0.1073
R1,wR2 (all data)	0.0709, 0.1581	0.1132, 0.3014	0.1422, 0.3496	0.0971, 0.2800	0.0472, 0.1259	0.0798, 0.1243
quality of fit	1.02	1.035	1.027	1.108	1.045	1.044
CCDC No.	2233693	2233697	2233698	2233699	2233700	2233701

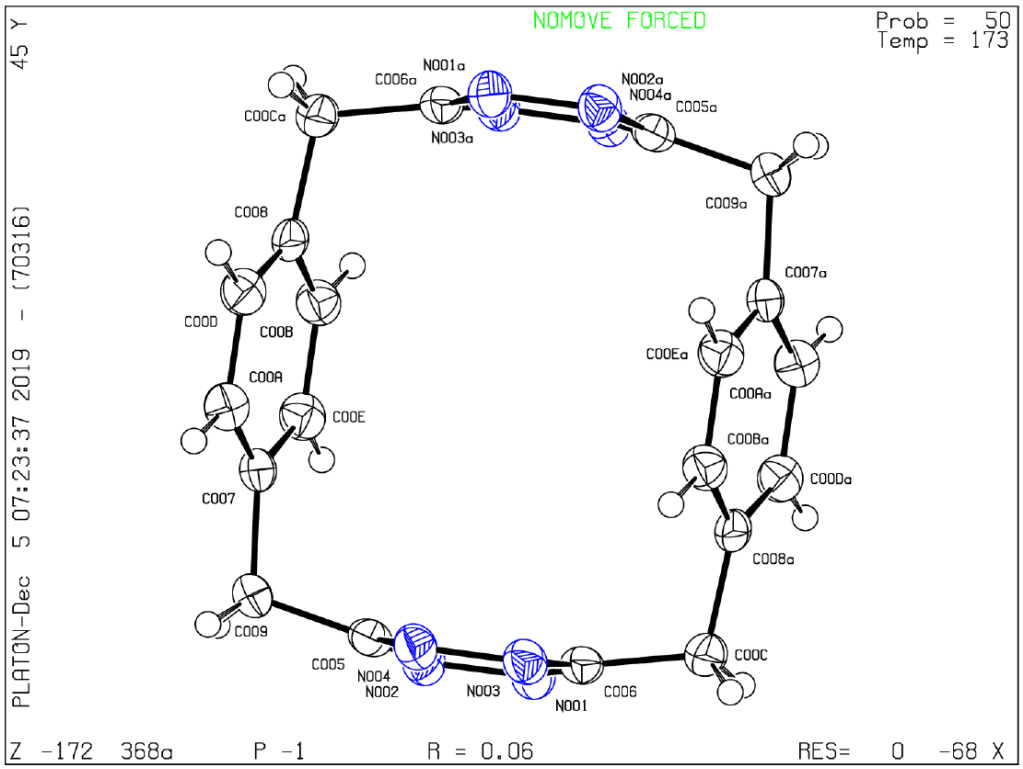


Figure S2. X-ray molecular structure of **1** (CCDC 2233693). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

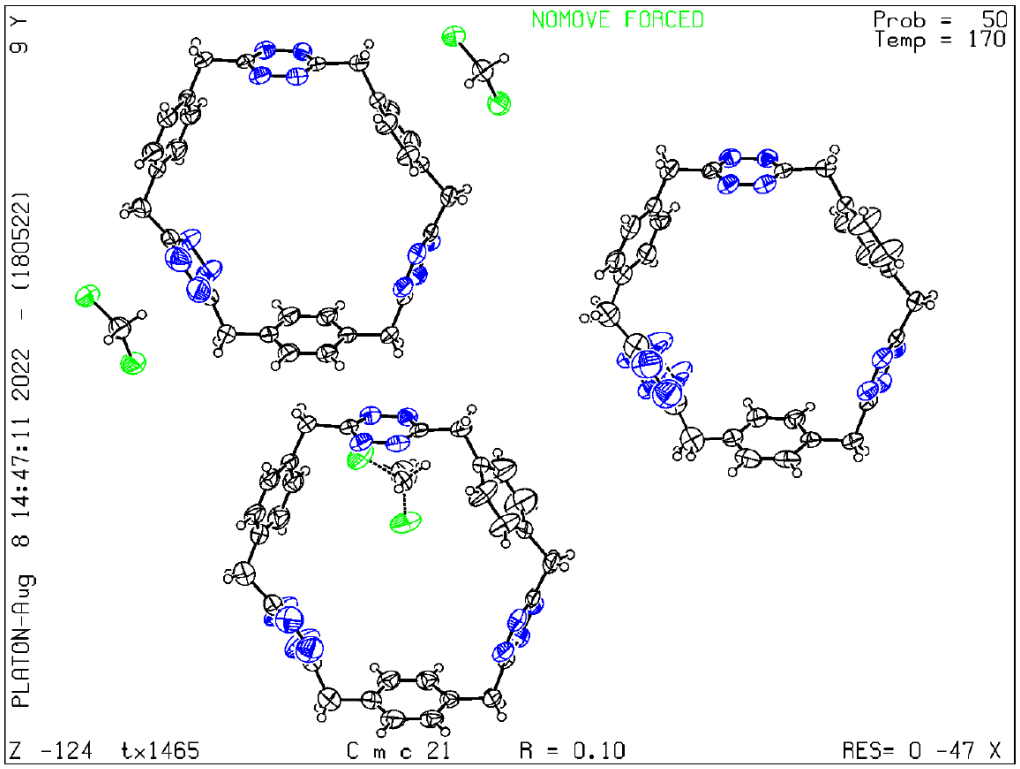


Figure S3. X-ray molecular structure of **2** @ DCM (CCDC 2233697). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

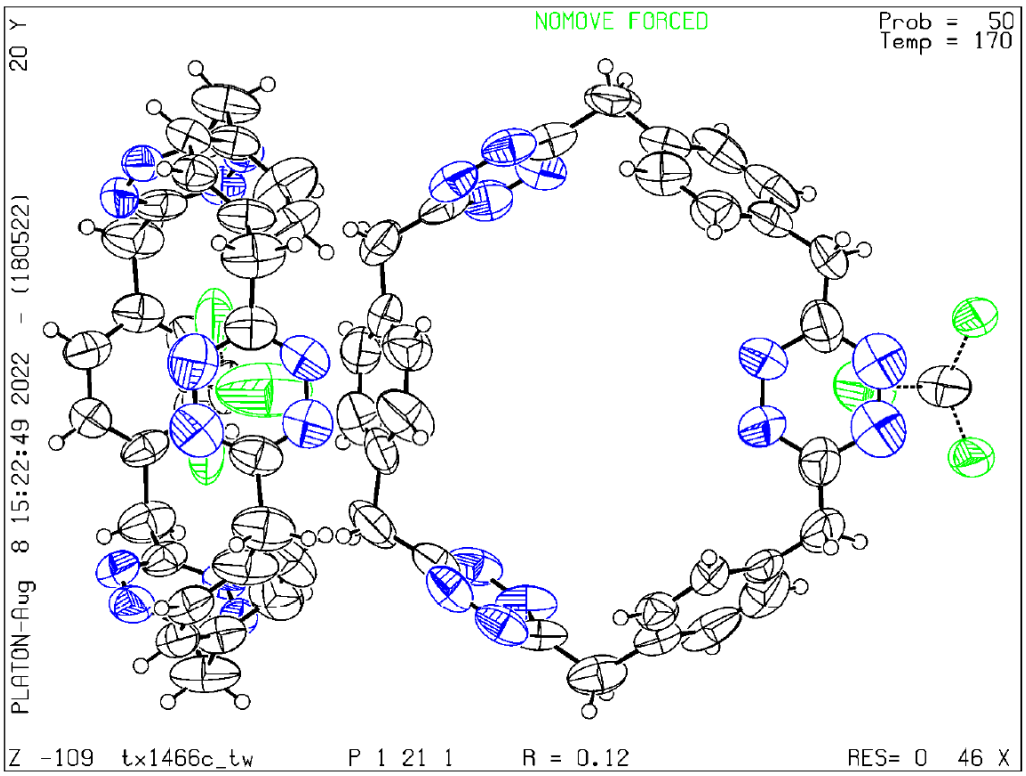


Figure S4. X-ray molecular structure of **2** @ 0.25 $CHCl_3$ (CCDC 2233698). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

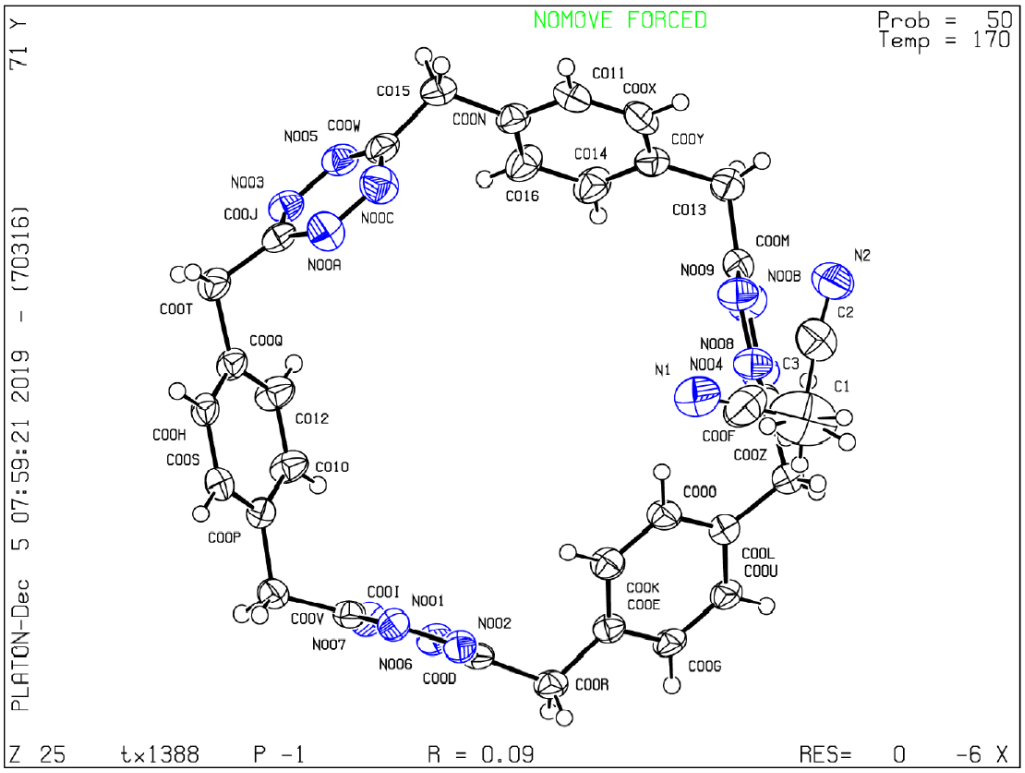


Figure S5. X-ray molecular structure of **2** @ CH_3CN (CCDC 2233699). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

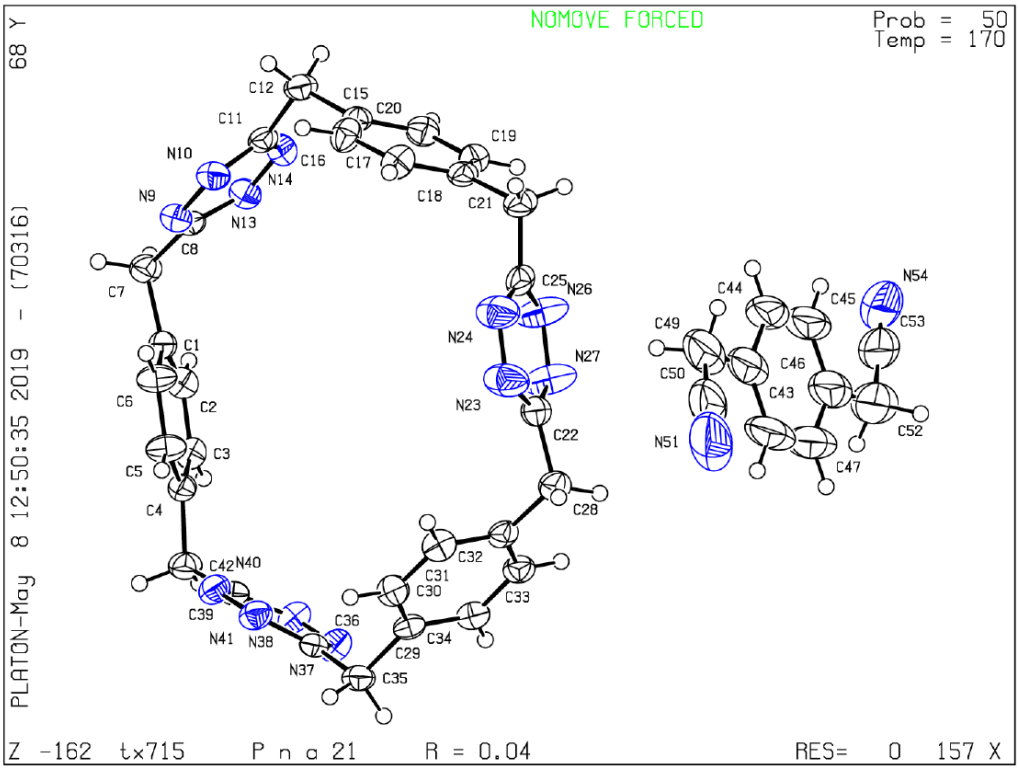


Figure S6. X-ray molecular structure of **2** @ *p*-phenylenediacetonitrile (CCDC 2233700). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

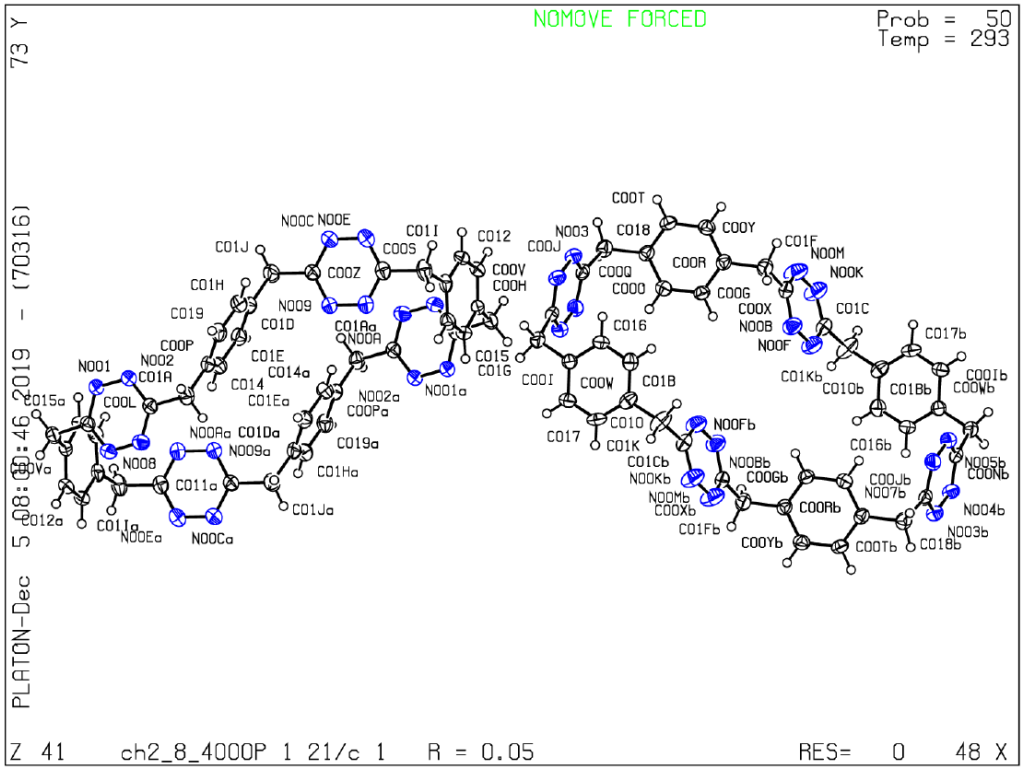


Figure S7. X-ray molecular structure of **3** (CCDC 2233701). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

4. The Photophysical and Electrochemical Data

Table S3. Summary of the photophysical and electrochemical data

Compound	1	2	3	4
λ_{max} (nm)	246 (1.42)	238 (1.67)	237 (2.31)	230 (0.85)
		268 (0.96)	268 (1.17)	268 (0.32)
(ε, $\times 10^4$ L·mol^{-1}·cm^{-1})	308 (0.16)	308 (0.26)	314 (0.30)	304 (0.10)
	524 (0.10)	546 (0.17)	544 (0.20)	546 (0.06)
λ_{ex} (nm)	583	595	596	590
λ_{em} (nm)	524	546	544	546
$E_{1/2}$ (mV)	-1398, -1508	-1401	-1366	-1356

5. UV-vis Titrations of 1 with Anions

5.1 UV-vis titrations of 1 with tetrabutylammonium salts of different anions

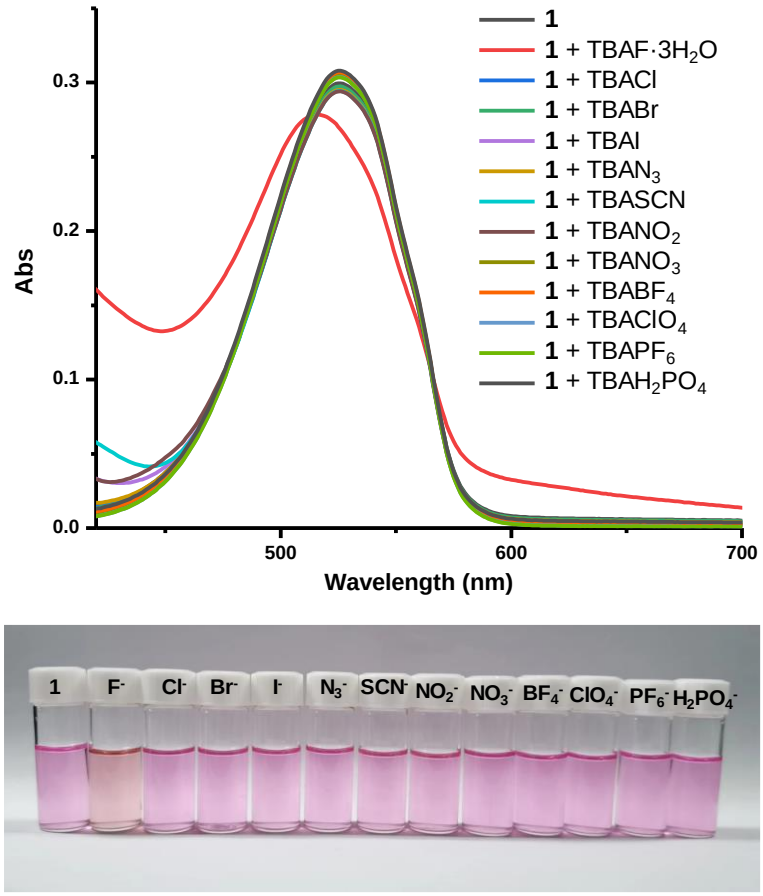


Figure S8. UV-vis titration spectra at 298 K of **1** (0.25 mM) with addition of tetrabutylammonium salts of different anions in CH_3CN/THF (v:v=1:1). 1 equiv of TBAF·3H_2O and 100 equiv of other guests were added, respectively.

5.2 UV-vis titrations of 1 with (Kcryp)F

Titration 1

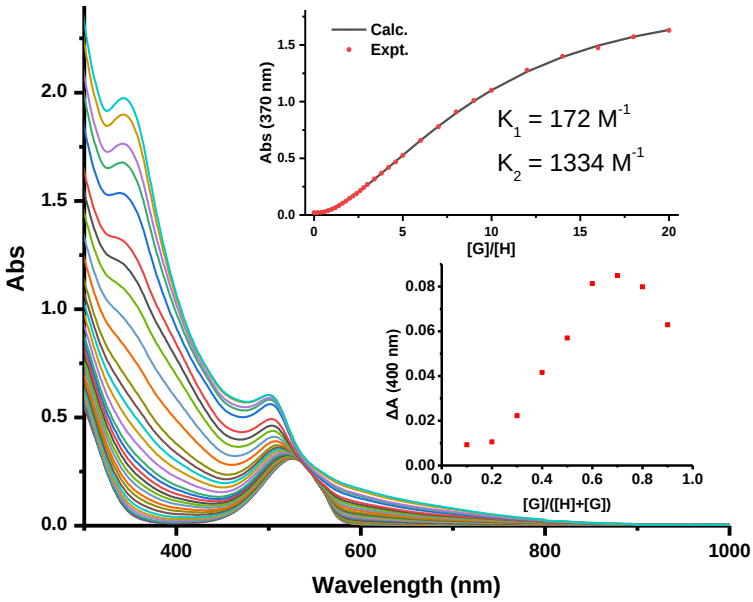


Figure S9. UV-vis titration spectra at 298 K of **1** (0.25 mM) with addition of 0 - 20 equiv of (Kcryp)F in CH_3CN/THF. The insets show the observed data (black points) and calculated data (red line) based on the absorbance values recorded at 370 nm (up) and the Job's plot (bottom).

Titration 2

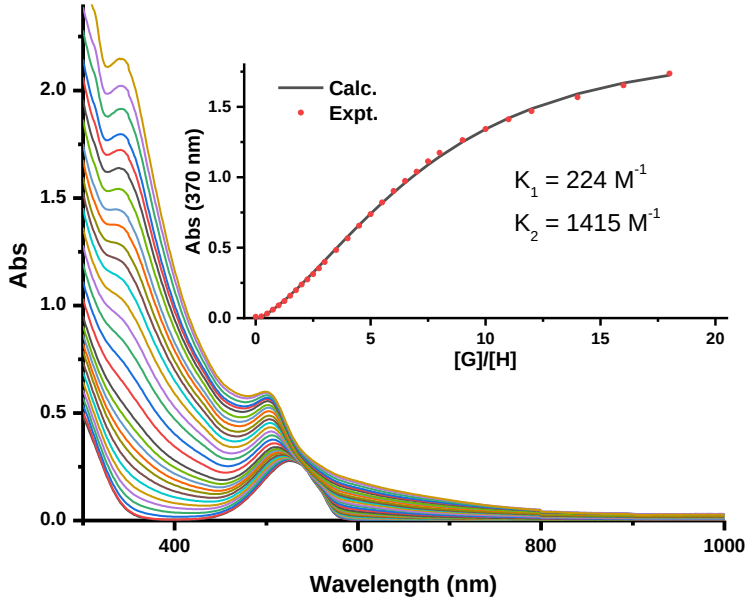


Figure S10. UV-vis titration spectra at 298 K of **1** (0.26 mM) with addition of 0 - 18 equiv of (Kcryp)F in CH_3CN/THF. The inset shows the observed data (black points) and calculated data (red line) based on the absorbance values recorded at 370 nm.

Titration 3

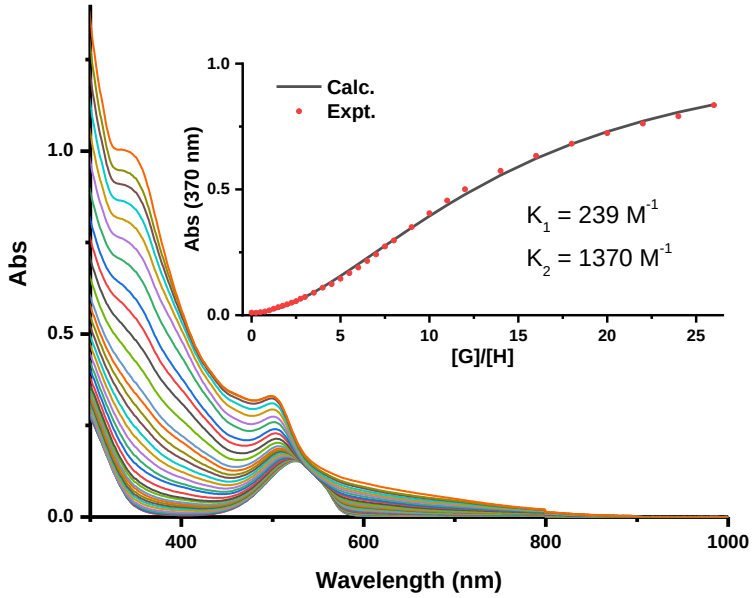


Figure S11. UV-vis titration spectra at 298 K of **1** (0.14 mM) with addition of 0 - 26 equiv of (Kcryp)F in CH_3CN/THF. The inset shows the observed data (black points) and calculated data (red line) based on the absorbance values recorded at 370 nm.

Table S4. Summary of UV-vis titrations of **1** with (Kcryp)F

	K_1 (M^{-1})	K_2 (M^{-1})
Titration 1	172	1334
Titration 2	224	1415
Titration 3	239	1370
Average	212 ± 29	1373 ± 33

5.3 Addition of water to a solution of 1 and (Kcryp)F

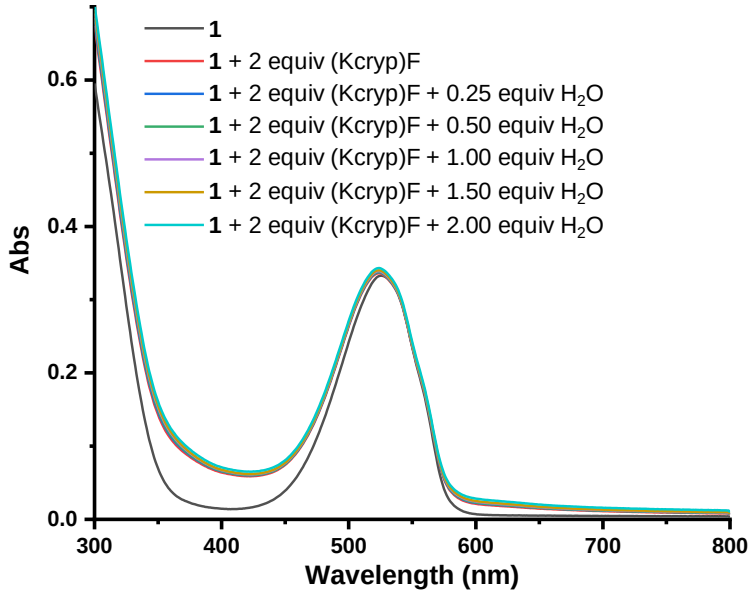


Figure S12. UV-vis titration spectra at 298 K of **1** (0.28 mM) and (Kcryp)F (0.56 mM) with addition of 0 - 2.00 equiv of water in CH_3CN/THF.

5.4 UV-vis titrations of 1 with (Kcryp)OH

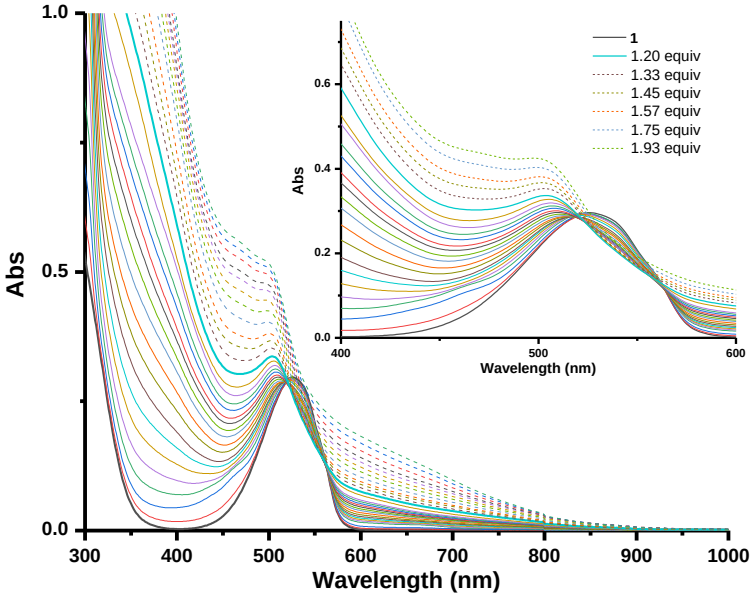


Figure S13. UV-vis titration spectra at 298 K of **1** (0.28 M) with addition of 0 - 3.37 equiv of (Kcryp)OH in CH_3CN/THF. The inset shows an enlarged view of spectra from 400 to 600 nm. Isosbestic points were observed at 563 nm and 518 nm. When more than 1.20 equiv of (Kcryp)OH were added, isosbestic points drifted. The refinement of binding constants could not converge with Hypspec program.

6. HRMS of a Mixture of 1 and (Kcryp)F

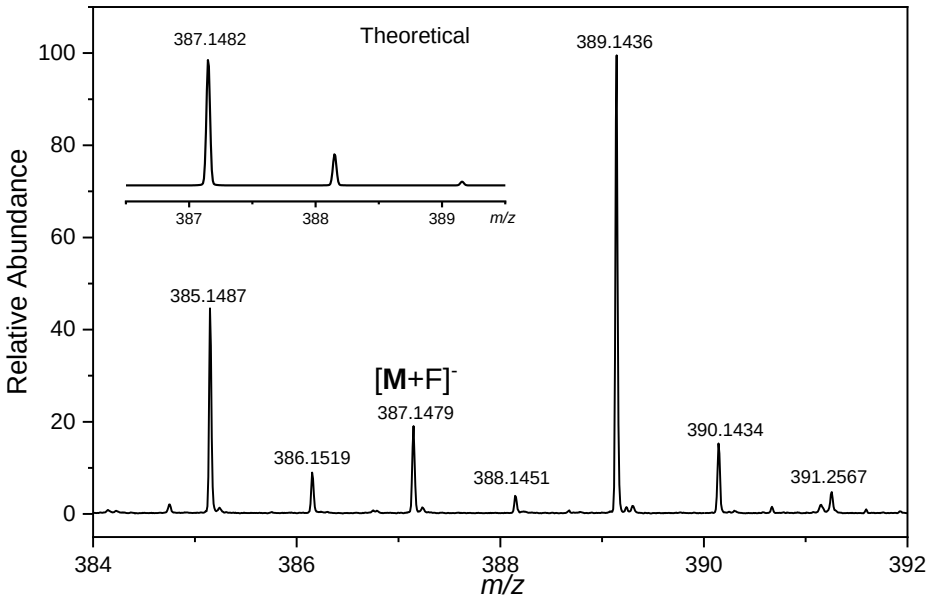


Figure S14. HRMS of **1** and (Kcryp)F.

7. NMR of 1 and (Kcryp)F

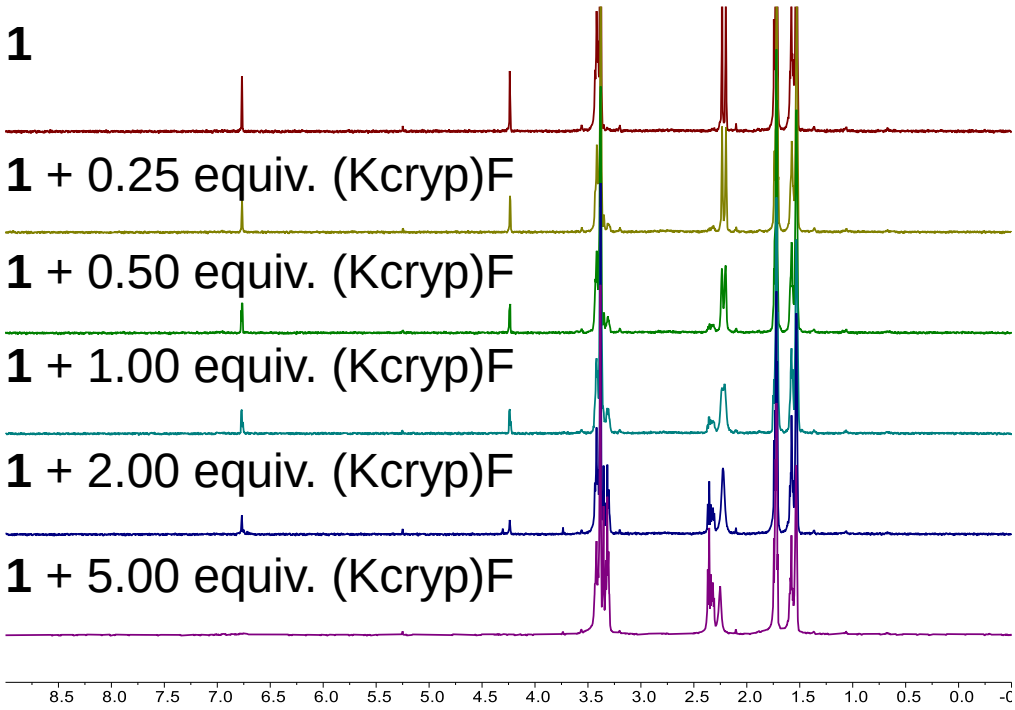


Figure S15. ^{1}H NMR spectra of **1** (0.20 mM) in CD_3CN/THF-d_8 at 298 K in the absence and presence of (Kcryp)F.

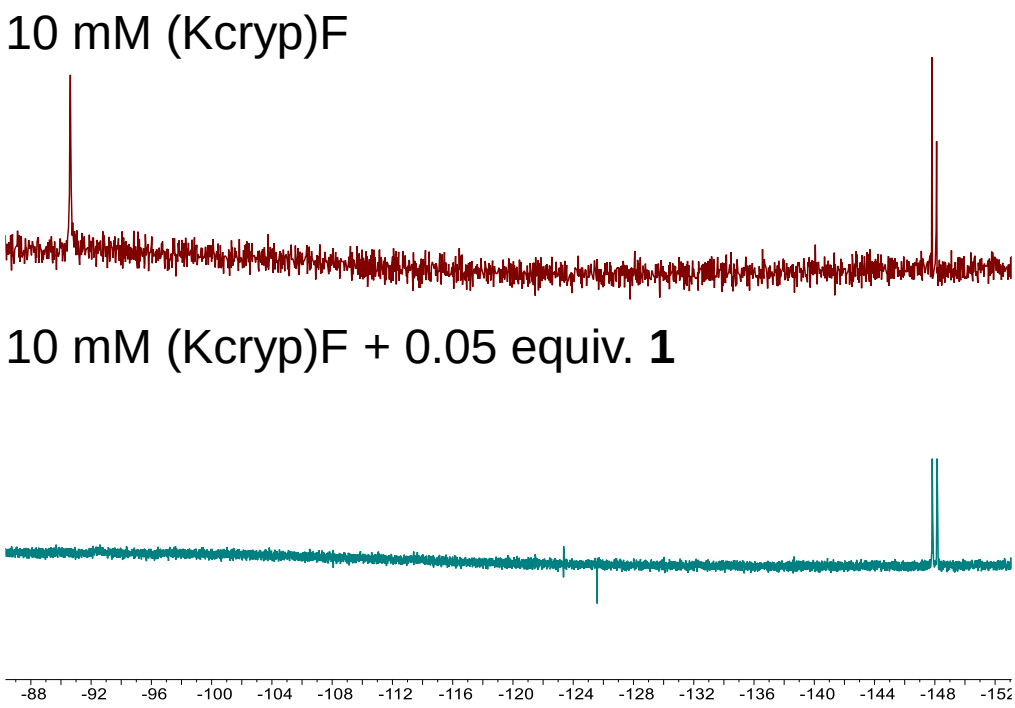


Figure S16. ^{19}F NMR spectra of (Kcryp)F (10 mM) in CH_3CN/THF at 298 K in the absence and presence of **1** (0.25 mM).

8. DFT Calculations

DFT studies were performed using Gaussian 16[1] package. Geometry optimization and frequency calculations were carried out in gas-phase using M06-2X[2]-D3(0)[3] functional with 6-31+G(d)[4] basis set. Single point energies were calculated at M06-2X-D3(0)/ma-TZVP[5] level, using Solvation Model Based on Density (SMD) implicit solvent model[6]. The mixture solvent was defined by using an average permittivity, namely eps = 21.556, epsinf = 1.976. Other parameters took the value of CH_3CN.

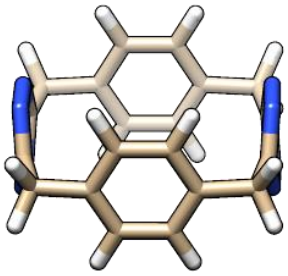
F^-

Gibbs free energy: -100.007377 a.u.

$F^{\cdot}$

Gibbs free energy: -99.748527 a.u.

1



Gibbs free energy: -1209.341481 a.u.

Table S5. Coordinates of **1**

N	-3.29584000	-0.65477100	-1.18201700
N	-3.29588800	0.65422800	-1.18230100
N	-3.29725000	-0.65432000	1.18191200
N	-3.29724700	0.65483500	1.18162900
C	-3.20298400	1.27684800	-0.00034900
C	-3.20292700	-1.27685700	0.00020900
C	-1.40520100	2.91215200	-0.00086300
C	1.40517600	2.91216700	-0.00077700
C	-2.91483200	2.75105800	-0.00065900
C	-0.69640600	2.92503600	1.20258200
C	0.69636500	2.91936200	-1.20429000
C	-2.91478700	-2.75106700	0.00055800
C	0.69630600	2.92503600	1.20262700
C	-0.69631900	2.91934900	-1.20433300
H	-3.35524000	3.20242200	0.89201500
H	-3.35550000	-3.20210600	0.89325600
H	-3.35550300	3.20214400	-0.89335200
H	-3.35522100	-3.20249600	-0.89207900
H	-1.23834900	2.90653300	2.14517400
H	1.23831600	2.89633300	-2.14679000
H	-1.23822500	2.89626700	-2.14685800
H	1.23821600	2.90650200	2.14523400

N	3.29584000	0.65477200	1.18203000
N	3.29586200	-0.65422500	1.18230100
N	3.29727400	0.65434300	-1.18190100
N	3.29725000	-0.65481400	-1.18162800
C	3.20293700	-1.27683000	0.00034200
C	3.20297100	1.27687300	-0.00019400
C	1.40520000	-2.91216900	0.00084800
C	-1.40517500	-2.91218400	0.00078200
C	2.91482600	-2.75104800	0.00063800
C	0.69639600	-2.92490800	-1.20259500
C	-0.69635600	-2.91953100	1.20428700
C	2.91479300	2.75107500	-0.00053200
C	-0.69631300	-2.92490700	-1.20263100
C	0.69632900	-2.91951700	1.20432100
H	3.35523600	-3.20239200	-0.89204500
H	3.35551600	3.20213300	-0.89321600
H	3.35551100	-3.20213900	0.89332200
H	3.35520400	3.20250100	0.89211800
H	1.23833400	-2.90627800	-2.14518800
H	-1.23829900	-2.89661200	2.14679500
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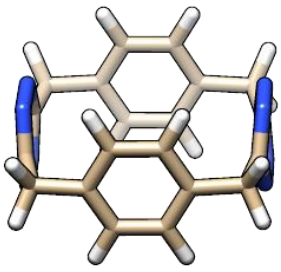
H	-1.23823200	-2.90624300	-2.14523000

1$^{-\cdot}$



Gibbs free energy: -1209.470871 a.u.

Table S6. Coordinates of $\mathbf{1}^{\cdot-}$

N	-3.26172300	-0.69289600	-1.19957800
N	-3.26677200	0.69173400	-1.20041200
N	-3.26677700	-0.69169600	1.20041600
N	-3.26170300	0.69293400	1.19958200
C	-3.20740900	1.26142800	-0.00022800
C	-3.20743300	-1.26139200	0.00023200
C	-1.42542500	2.92373100	-0.01165100
C	1.39373600	2.91557500	-0.02198700
C	-2.92733600	2.75181300	-0.00205000
C	-0.70535500	2.98770300	1.18446800
C	0.67849500	2.86781500	-1.22126700
C	-2.92737500	-2.75178000	0.00205200
C	0.68834700	2.98222100	1.18119000
C	-0.71420700	2.87294000	-1.21494900
H	-3.36051500	3.20324500	0.89539900
H	-3.37215400	-3.20156200	0.89489700
H	-3.37210900	3.20159900	-0.89489600
H	-3.36055800	-3.20320500	-0.89539800
H	-1.24812600	2.98772200	2.12633600
H	1.21732200	2.78710100	-2.16352400
H	-1.26572900	2.77995600	-2.14706300
H	1.23389200	2.99209500	2.12286500
N	3.31962600	0.66447300	1.17462200
N	3.32005700	-0.64506100	1.18519000
N	3.32002000	0.64502000	-1.18520200
N	3.31956900	-0.66451000	-1.17463300
C	3.20356500	-1.27861100	0.01038900
C	3.20358600	1.27857400	-0.01039200

C	1.39369600	-2.91559000	0.02198800
C	-1.42546600	-2.92371400	0.01165400
C	2.90359400	-2.74919300	0.02274900
C	0.68830500	-2.98226200	-1.18118600
C	-0.71424600	-2.87289800	1.21495100
C	2.90363200	2.74916000	-0.02274900
C	-0.70539600	-2.98772800	-1.18446300
C	0.67845600	-2.86778900	1.22126700
H	3.34568400	-3.20856000	-0.86592800
H	3.34438100	3.19250500	-0.92031900
H	3.34433800	-3.19254200	0.92032000
H	3.34572900	3.20851900	0.86592800
H	1.23384900	-2.99216900	-2.12286200
H	-1.26576700	-2.77988000	2.14706100
H	1.21728400	-2.78705600	2.16352200
H	-1.24816800	-2.98777000	-2.12633100

Scheme S2. Electron transfer from fluoride anion to **1**.

9. References

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Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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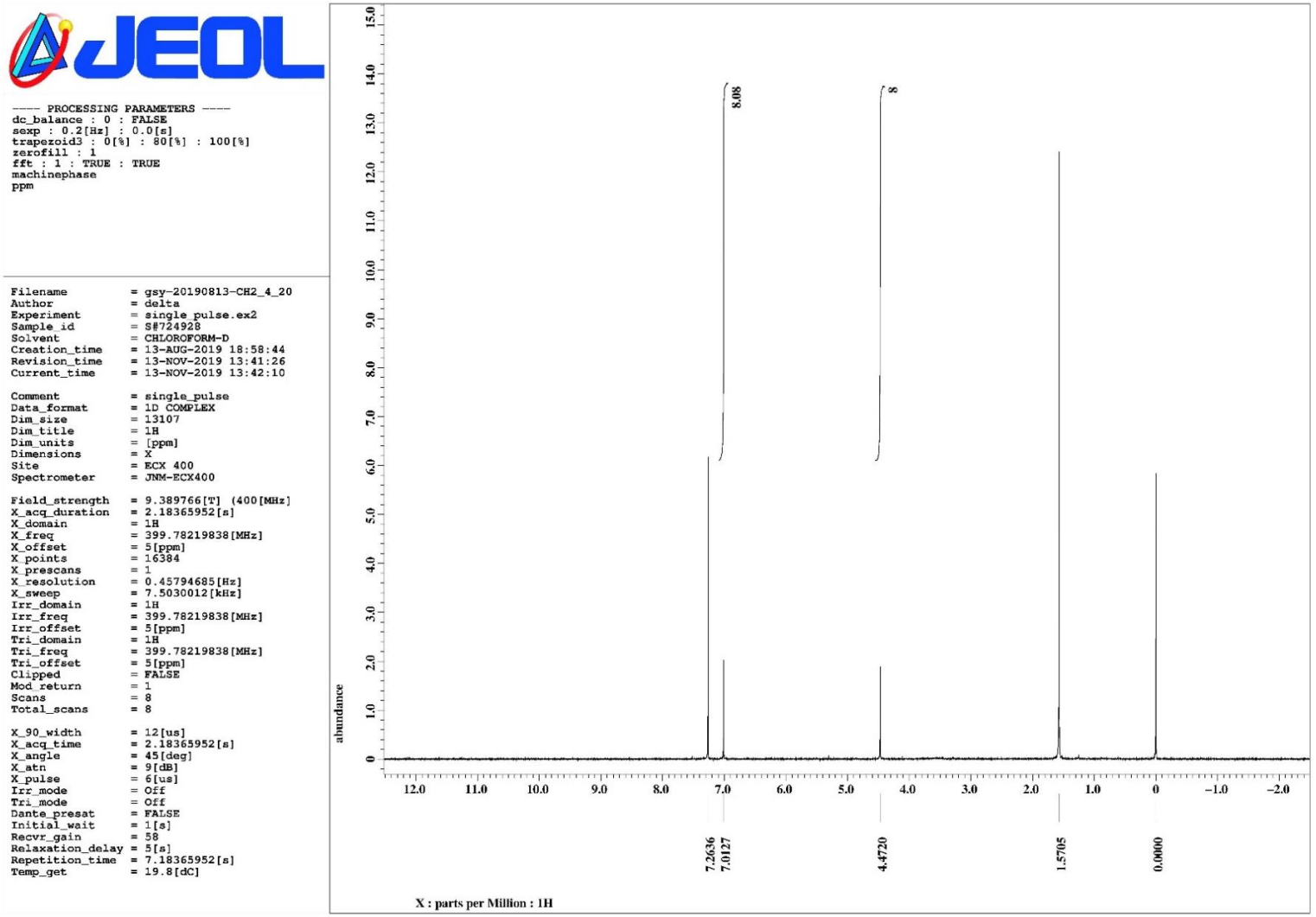
10. Copies of ^{1}H and ^{13}C NMR Spectra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X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 9[dB]
X_pulse = 6[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 58
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 19.8[dC]
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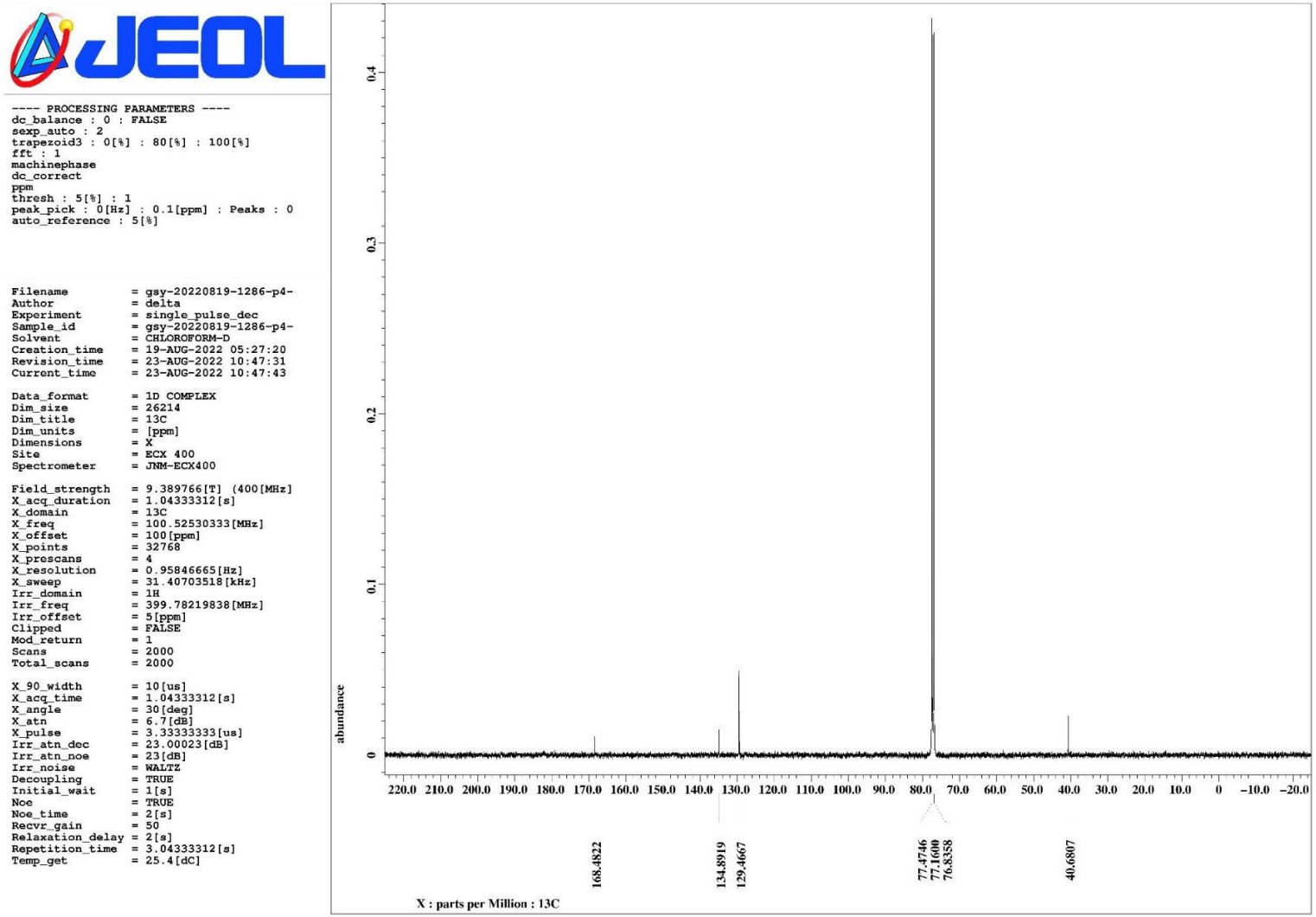
8
7.2636
7.0127
4.4720
1.5705
0.0000
X : parts per Million : 1H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machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
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Author = delta
Experiment = single_pulse_dec
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Solvent = CHLOROFORM-D
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Dimensions = X
Site = ECX 400
Spectrometer = JNM-ECX400
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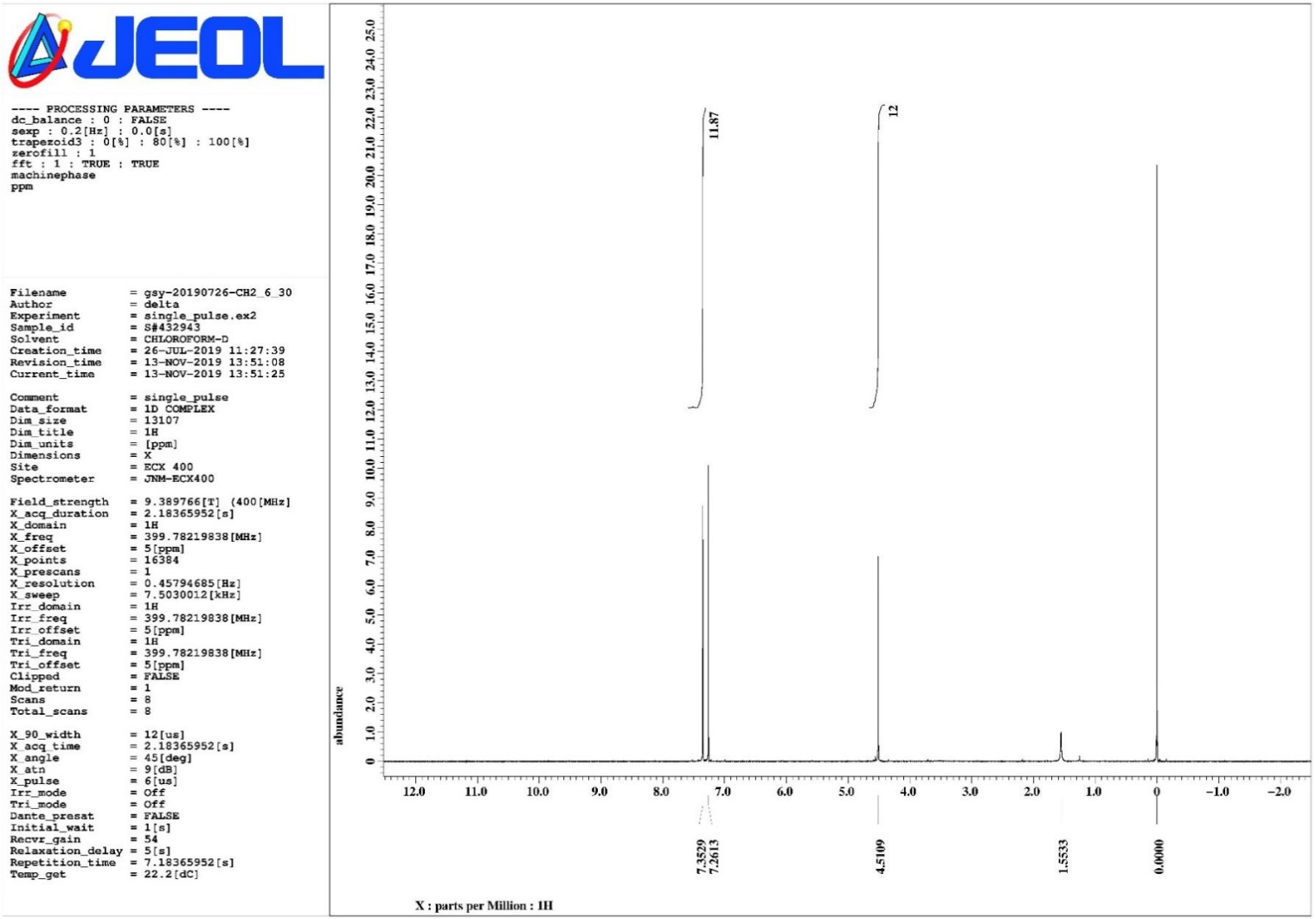
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2000
Total_scans = 2000
X_90_width = 10[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 6.7[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 23.00023[dB]
Irr_atn_noe = 23[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 25.4[dC]
abundance
0
0.1
0.2
0.3
0.4
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
168.4822
134.8919
129.4667
77.4746
77.1600
76.8358
40.6807
X : parts per Million : 13C
N
N
N
N
N
N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Author = delta
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X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 9[dB]
X_pulse = 6[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 54
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 22.2[dC]
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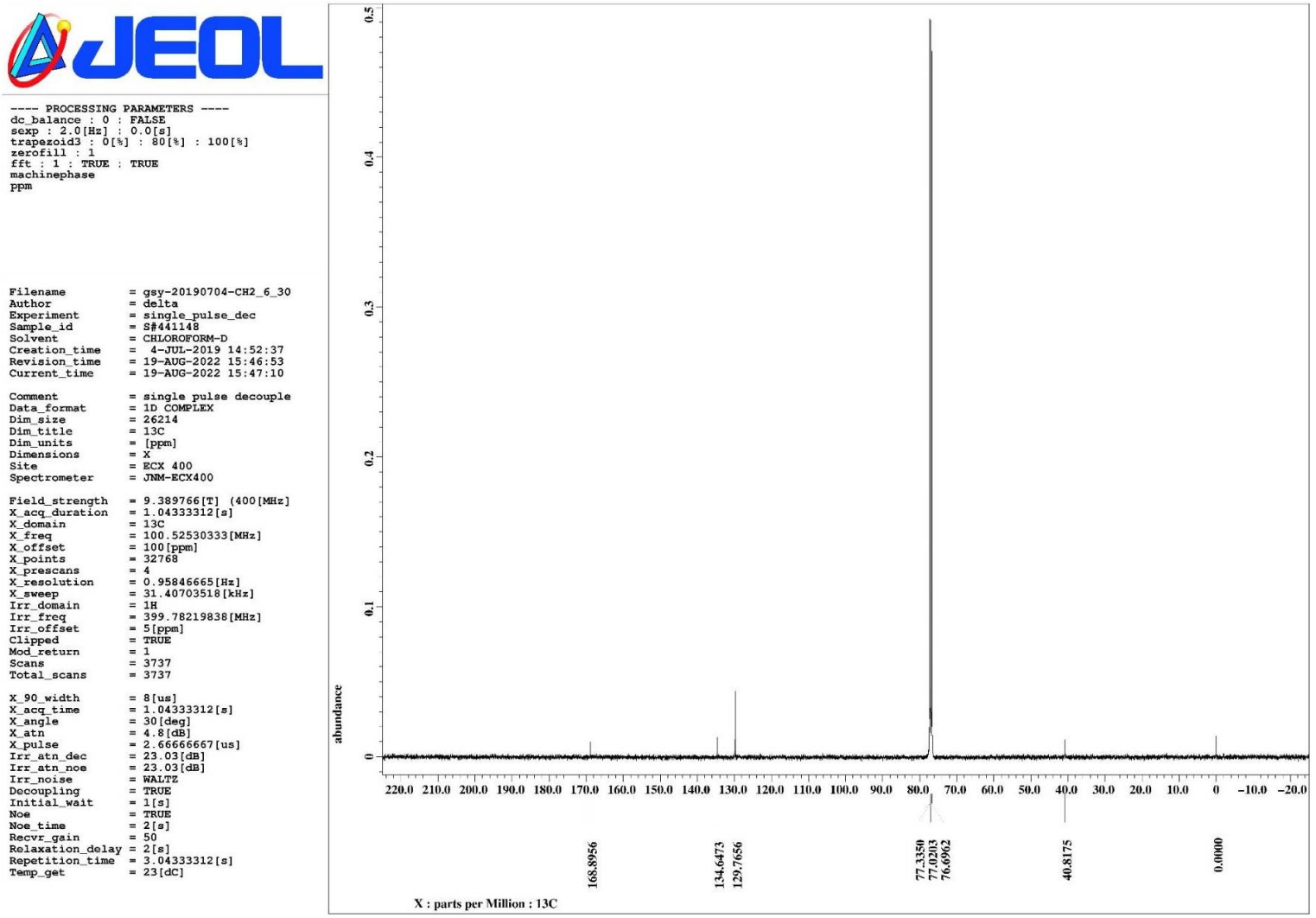
11.87
12
7.3529
7.2613
4.5109
1.5533
0.0000
X : parts per Million : 1H


JEOL
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sexp : 2.0[Hz] : 0.0[s]
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zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = gsy-20190704-CH2_6_30
Author = delta
Experiment = single_pulse_dec
Sample_id = S#441148
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Spectrometer = JNM-ECX400
Field_strength = 9.389766[T] (400[MHz]
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X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 3737
Total_scans = 3737
X_90_width = 8[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.8[dB]
X_pulse = 2.66666667[us]
Irr_atn_dec = 23.03[dB]
Irr_atn_noe = 23.03[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 23[dC]
abundance
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
168.8956
134.6473
129.7656
77.3350
77.0203
76.6962
40.8175
0.0000
X : parts per Million : 13C
N=N
N-N
N
N
N
N
N
N
N
N

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
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Revision_time     = 29-NOV-2022 18:39:00
Current_time      = 29-NOV-2022 18:39:49

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12.4[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 9[dB]
X_pulse           = 6.2[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 64
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 22.2[dC]
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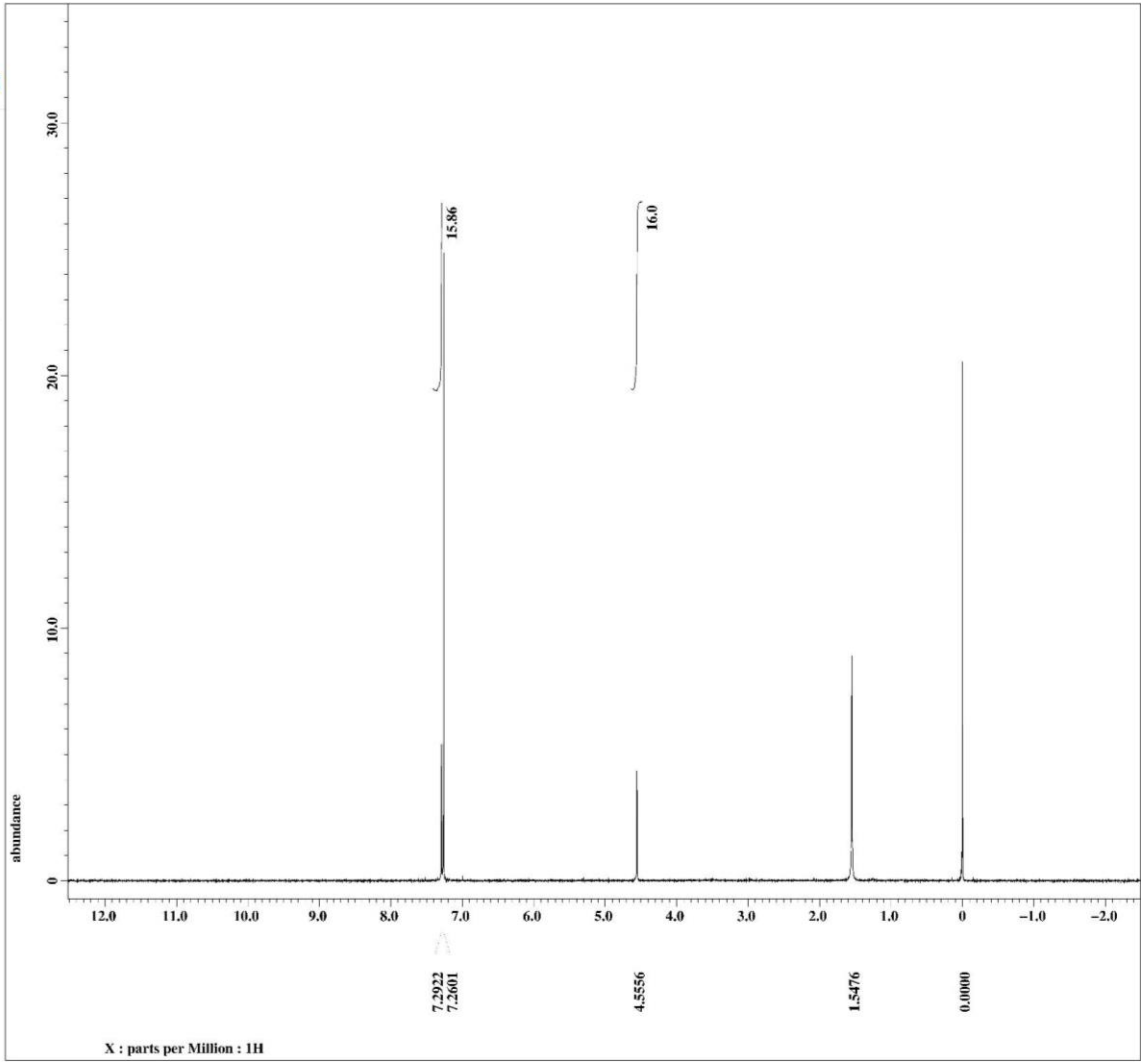

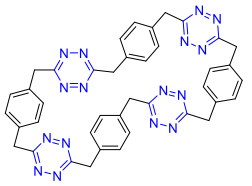

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fft : 1
machinephase
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ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
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Site              = ECX 400
Spectrometer      = JNM-ECX400

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X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 9000
Total_scans       = 9000

X_90_width        = 10[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 6.7[dB]
X_pulse           = 3.33333333[us]
Irr_atn_dec       = 23.00023[dB]
Irr_atn_noe       = 23[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 25.5[dC]
```

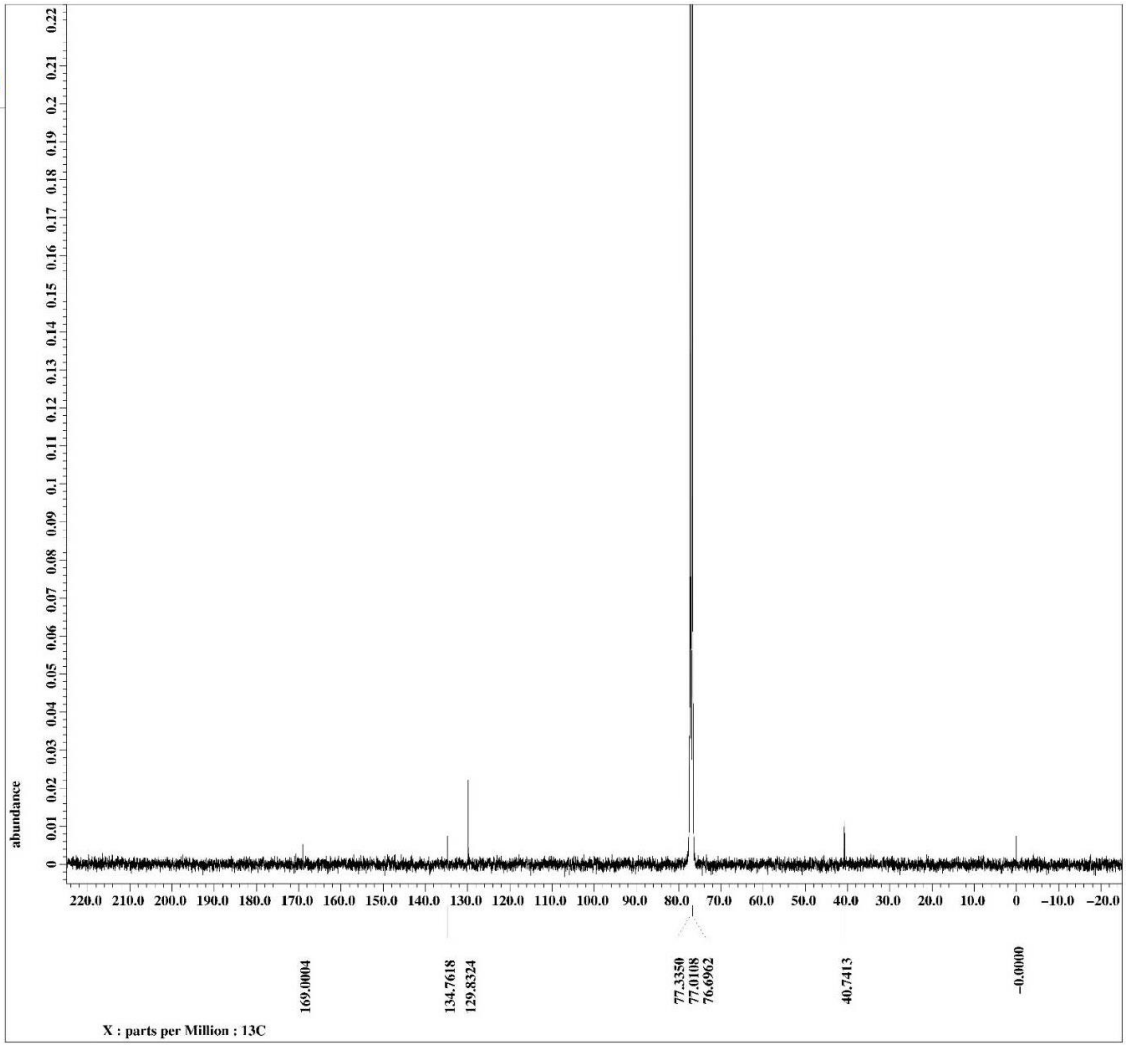

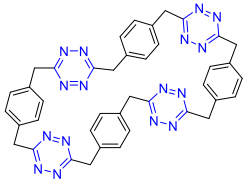

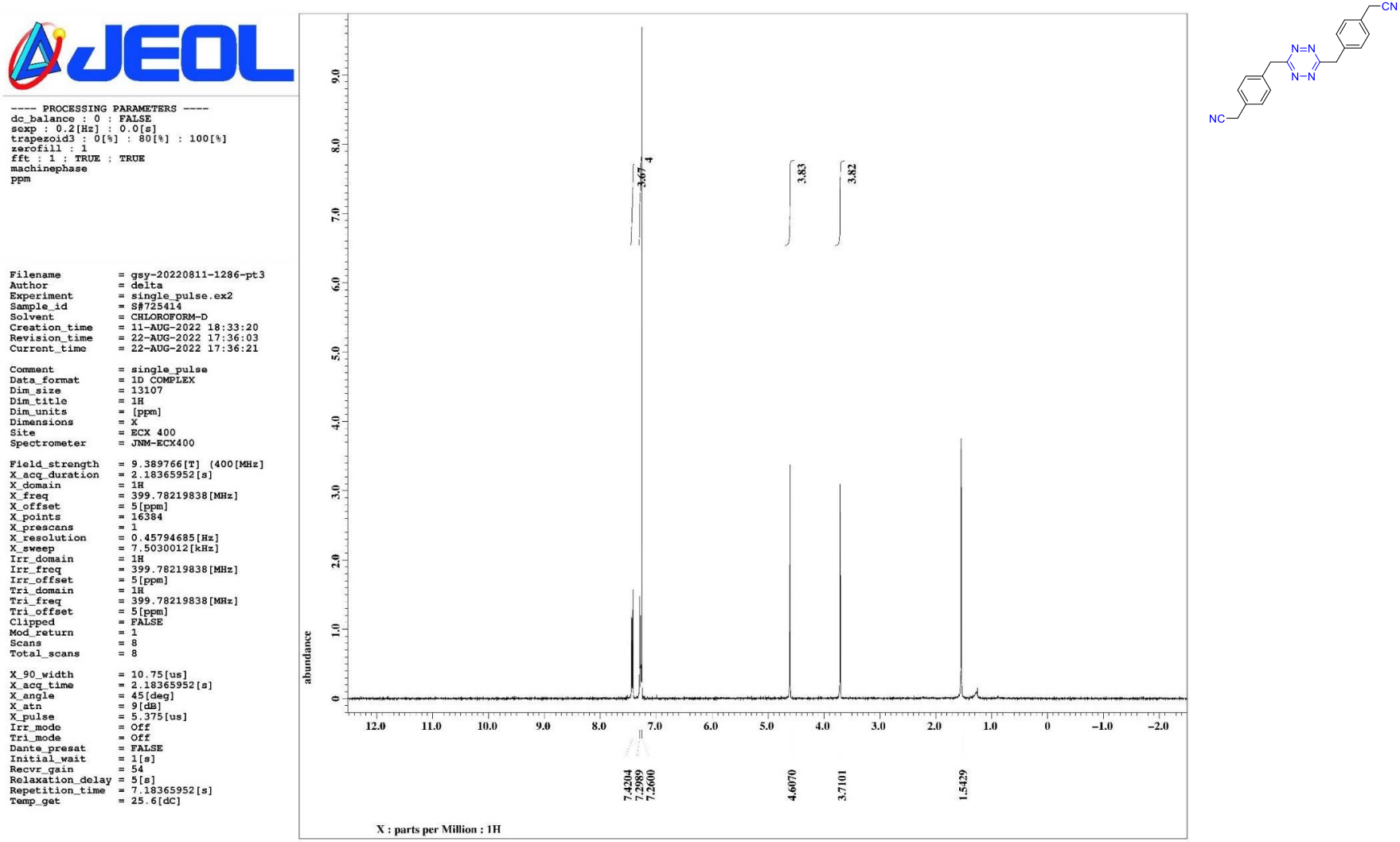
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Filename = gsy-20220811-1286-pt3
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#725414
Solvent = CHLOROFORM-D
Creation_time = 11-AUG-2022 18:33:20
Revision_time = 22-AUG-2022 17:36:03
Current_time = 22-AUG-2022 17:36:21
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = JNM-ECX400
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.75[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 9[dB]
X_pulse = 5.375[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 54
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 25.6[dC]
abundance
3.67
4
3.83
3.82
7.4204
7.2098
7.2600
4.6070
3.7101
1.5429
X : parts per Million : 1H
CN
N=N
N–N
NC

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
Filename          = gsy-20220815-1286-pt3
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#277712
Solvent           = CHLOROFORM-D
Creation_time     = 15-AUG-2022 07:02:43
Revision_time     = 23-AUG-2022 17:09:23
Current_time      = 23-AUG-2022 17:09:37

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1084
Total_scans       = 1084

X_90_width        = 10[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 6.7[dB]
X_pulse           = 3.33333333[us]
Irr_atn_dec       = 23.00023[dB]
Irr_atn_noe       = 23[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 25.7[dC]
```