Cover Page for Supporting Information

Selective reduction of 1,5-diazacyclooctatetraenes: synthesis and structures of aromatic diazacyclooctatetraenyl dianions and 2,6-bipyrrolinyl dianionic Co(II) complex

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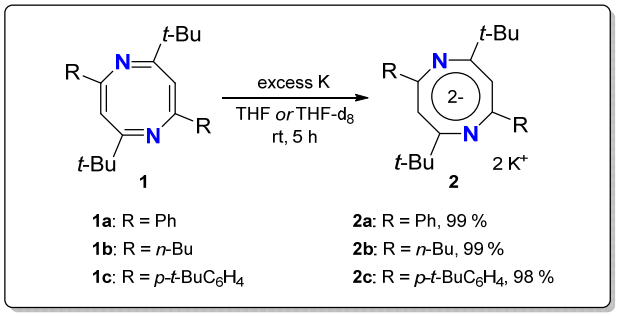
Contents

1) General Information

Compounds **1a-1c**[1] and LCo(Tol)[2] were synthesized according to the reported procedures. All other starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in slight positive pressure by using Schlenk techniques or in a glove box, unless otherwise noted.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) at room temperature, unless otherwise noted. UV-Vis absorption spectra were recorded with an Agilent 8453 UV-Vis spectrometer. XPS was carried out on an Axis Ultra imaging photoelectron spectrometer.

2) Procedures for the Preparation of 2-3



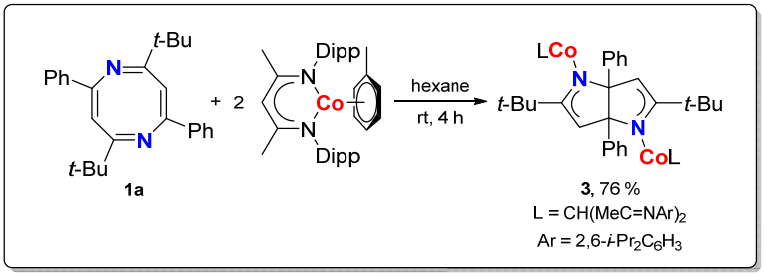
General Procedure for the Preparation of 2a-c: NCOT **1a** (0.074 g, 0.2 mmol) was dissolved in 10 mL THF (or 1 mL THF-d_8) and metallic potassium (0.020 mg, 0.5 mmol) was added to the solution. The solution turned dark brown and the mixture was stirred at room temperature for 5 h. The excess potassium was removed by tweezers and the solvent was removed under vacuum, giving the product **2a** in a quantitative yield. Similarly, **2b** and **2c** were obtained. After the reaction, **2a** was dissolved in a mixed solvent of 0.5 mL diglyme and 1 mL THF, and single crystals of **2a**•2diglyme were obtained by vapor diffusion of hexane into this solution at -10 ^{o}C.

2a: Yellow solid, isolated yield 99% (88.4 mg). ^{1}H NMR (400 MHz, THF-d_8, 25 ^{o}C): δ = 1.68 (s, 18H, CH_3), 6.62 (t, *J* = 7.1 Hz, 2H, CH), 7.00 (s, 2H, CH), 7.03-7.08 (m, 4H, CH), 8.37 (d, *J* = 7.5 Hz, 4H, CH); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 35.33 (6 CH_3), 43.53 (2 quat. C), 86.33 (2 CH), 114.75 (2 quat. C), 119.71 (2 CH), 126.24 (2 quat. C), 126.65 (4 CH), 127.57 (4 CH), 156.05 (2 quat. C).

2a•2diglyme: Yellow crystals, isolated yield 90% (129.5 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.69 (s, 18H, CH_3), 3.17 (s, 12H, CH_3), 3.32-3.44 (m, 16H, CH_2), 6.61 (t, *J* = 7.0 Hz, 2H, CH), 6.99 (s, 2H, CH), 7.04 (t, *J* = 7.6 Hz, 4H, CH), 8.37 (d, *J* = 7.8 Hz, 4H, CH); ^{13}C NMR (100MHz, THF-d_8, 25 ^{o}C): δ = 35.39 (6 CH_3), 43.55 (2 quat. C), 59.14 (4 CH_3), 71.22 (4 CH_2), 72.73 (4 CH_2), 86.33 (2 CH), 114.77 (2 quat. C), 119.62 (2 CH), 126.29 (2 quat. C), 126.70 (4 CH), 127.56 (4 CH), 156.14 (2 quat. C).

2b: Yellow solid, isolated yield 99% (81.0 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 0.97 (t, *J* = 7.4 Hz, 6H, CH_3), 1.39-1.45 (m, 4H, CH_2), 1.50 (s, 18H, CH_3), 1.83-1.91 (m, 4H, CH_2), 2.95-3.10 (t, *J* = 7.6 Hz, 4H, CH_2), 6.18 (s, 2H, CH); ^{13}C NMR (100MHz, THF-d_8, 25 ^{o}C): δ = 15.36 (2 CH_3), 24.57 (2 CH_2), 35.08 (6 CH_3), 38.35 (2 CH_2), 41.43 (2 quat. C), 50.68 (2 CH_2), 87.48 (2 CH), 111.05 (2 quat. C), 119.08 (2 quat. C).

2c: Yellow solid, isolated yield 98% (110.4 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.33 (s, 18H, CH_3), 1.68 (s, 18H, CH_3), 6.99 (s, 2H, CH), 7.13 (d, *J* = 8.3Hz, 4H, CH), 8.28 (d, *J* = 8.3 Hz, 4H, CH); ^{13}C NMR (100MHz, THF-d_8, 25 ^{o}C): δ = 32.37 (6 CH_3), 34.60 (2 quat. C), 35.36 (6 CH_3), 43.48 (2 quat. C), 86.20 (2 CH), 114.35 (2 quat. C), 124.32 (4 CH), 125.86 (2 quat. C), 126.27 (4 CH), 141.62 (2 quat. C), 153.38 (2 quat. C).



Procedure for the Preparation of Complex 3: Hexane (20 mL) was added to the mixture of **1a** (37.0 mg, 0.1 mmol) and LCo(tol) (113.6 mg, 0.2 mmol) in a 50 mL Schlenk flask at room temperature, the solution was stirred for 4 h and filtered. The filtrate was concentrated to ca. 5 mL and left at 5 ^{o}C for two days affording deep-brown block crystals of **3**. Yield: 100 mg, 76%. Elemental analysis for $C_{84}H_{112}Co_2N_6$: Calcd: C 76.22, N 6.35, H 8.53; Found: C 76.31, N 5.96, H 8.90.

3) X-ray Crystallographic Studies for 2a•2diglyme and 3

The single crystals of **2a**•2diglyme and **3** suitable for X-ray analysis were grown as shown in the experimental section. Data collection for **2a**•2diglyme was performed at 180 K on SuperNova diffractometer, while data of **3** was collected at 123 K on Bruker D8 Venture diffractometer, using monochromated Mo Kα radiation (λ = 0.71073 Å). Using Olex2,[3] the structures were solved with Superflip[4] structure solution program using Charge Flipping or ShelXS-97[5] structure solution program using Direct Methods and refined with the ShelXL[6] refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2a**•2diglyme and **3** are summarized in **Table S1**. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1570796 (**2a**•2diglyme), CCDC 1882722 (**3**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The thermal ellipsoid plot in the Figures were drawn by Ortep-3 v1.08.[7]

Table S1 Crystal Data and Structure Refinements for **2a**•2diglyme and **3**

Identification code	**2a**•2diglyme	**3**
Empirical formula	$C_{19}H_{29}KNO_3$	$C_{84}H_{112}Co_2N_6$
Formula weight	358.53	1323.65
Temperature/K	100.00(10)	123(2)
Crystal system	triclinic	Monoclinic
Space group	*P*-1	$P2_1/n$
a/Å	9.3241(3)	23.3208(18)
b/Å	10.8056(3)	14.4351(12)
c/Å	11.7204(4)	25.484(2)
α/°	116.878(3)	90
β/°	104.713(3)	97.497(2)
γ/°	98.473(3)	90
Volume/Å^3	970.57(6)	8505.4(12)
Z	2	4
ρ_{calc}g/cm^3	1.227	1.034
μ/mm^{-1}	0.289	0.431
F(000)	386.0	2848
Crystal size/mm^3	0.1 × 0.05 × 0.05	0.22 × 0.19 × 0.15
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.378 to 52.044	2.142 to 24.999
Index ranges	-11 ≤ h ≤ 11 -13 ≤ k ≤ 13 -14 ≤ l ≤ 14	-26 ≤ h ≤ 27 -17 ≤ k ≤ 17 -30 ≤l ≤ 27
Reflections collected	24305	56408
Independent reflections	3803 [R_{int} = 0.0351, R_{sigma} = 0.0220]	14951 [R_{int} = 0.0606, R_{sigma} = 0.0562]
Data/restraints/parameters	3803/0/231	14951/0/ 855
Goodness-of-fit on F^2	1.061	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0979	R_1 = 0.0421, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0995	R_1 = 0.0555, wR_2 = 0.1182
Largest diff. peak/hole / e Å^{-3}	0.58/-0.63	0.516/-0.579
CCDC number	1570796	1882722

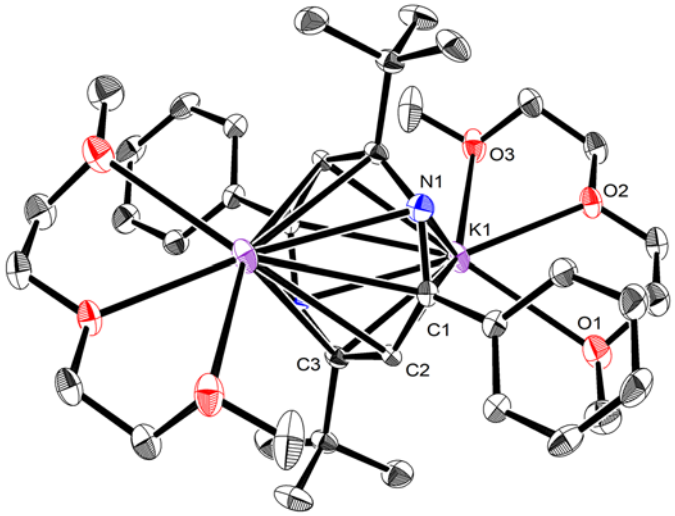


Fig. S1 ORTEP drawing of one K_2NCOT unit in **2a**•2diglyme with 30% probability thermal ellipsoids.

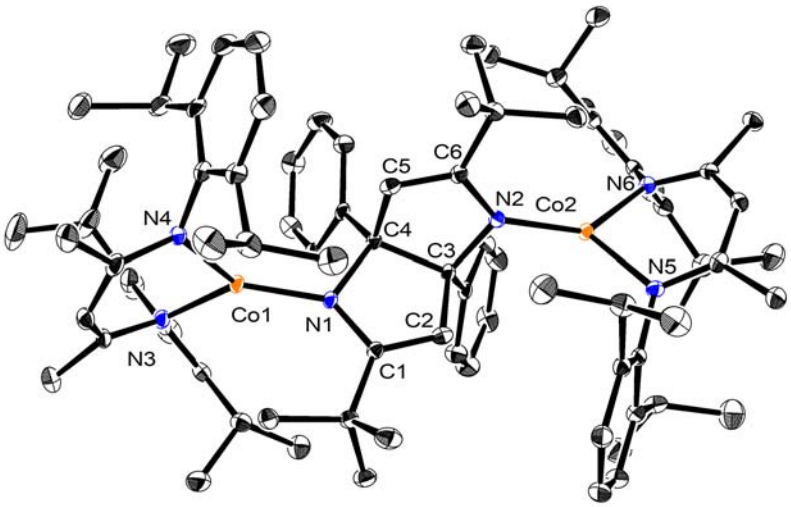


Fig. S2 ORTEP drawing of **3** with 30% probability thermal ellipsoids.

4) UV-Vis Absorption Spectra of 1a and 2a

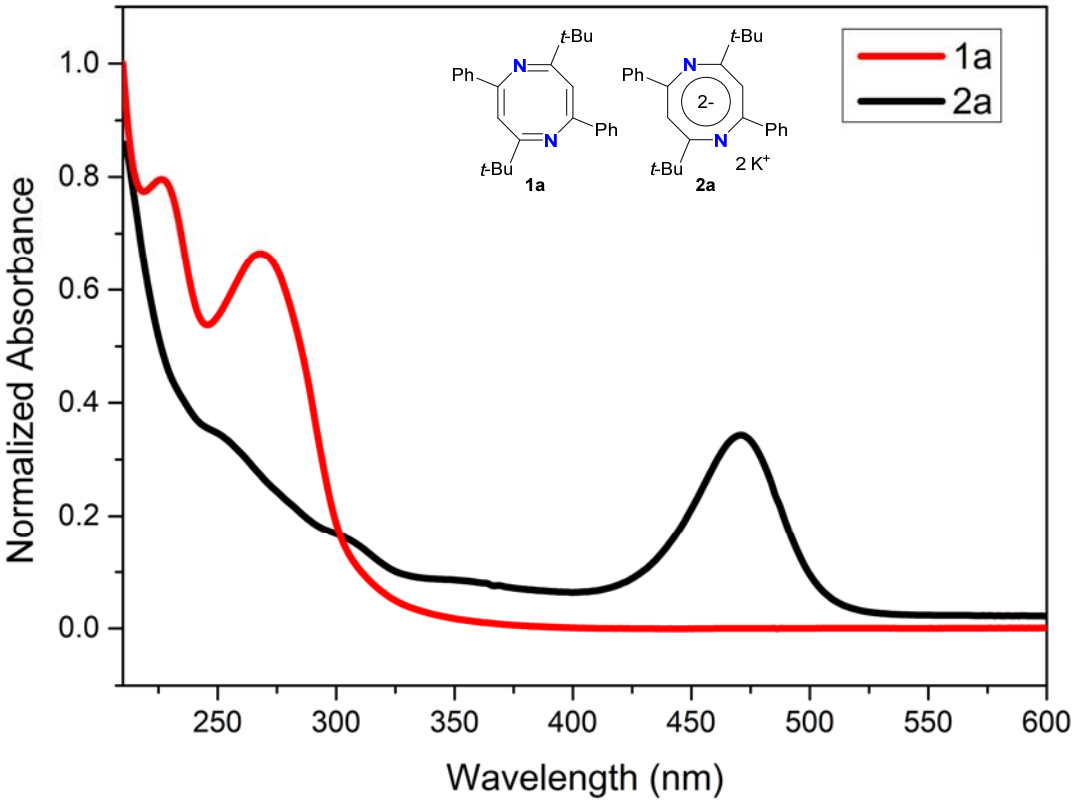


Fig. S3 UV-Vis absorption spectra of **1a** and **2a** in THF.

5) Cyclic Voltammetry Study

Cyclic voltammetry was performed using a CHI760E electrochemical workstation with a sweep rate of 100mV/s in THF/0.1 M [NBu_4][PF_6] in a dry and oxygen-free glove box. Potentials were measured relative to a SCE reference electrode. Under these conditions, $E_{1/2}$ = 0.56 V was observed for the $[Cp_2Fe]^{0/+1}$ couple.

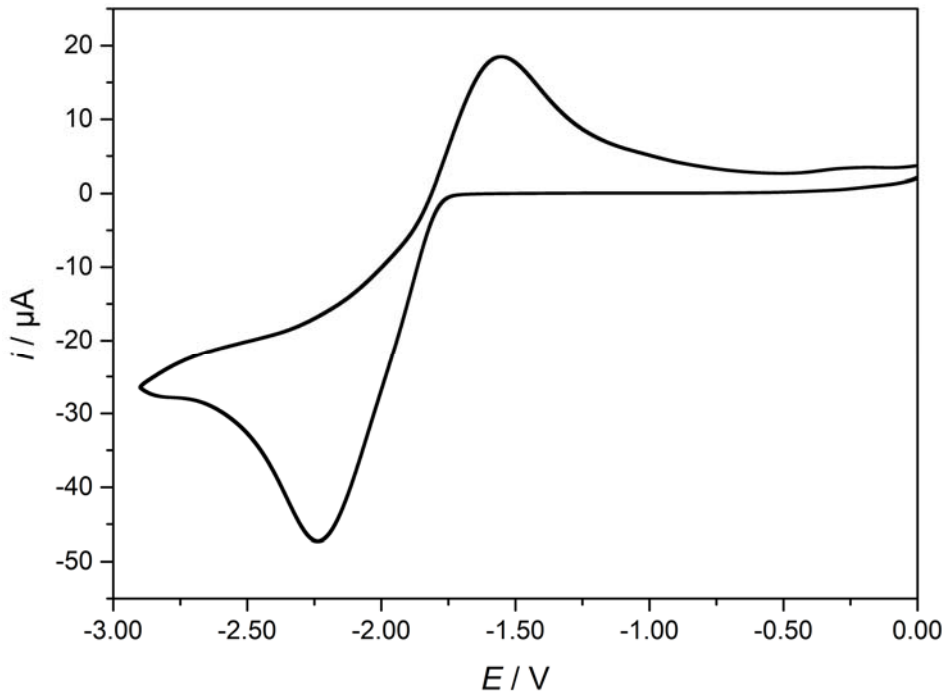


Fig. S4 Cyclic voltammetry (0.1 V s^{-1}) of NCOT **1a** in THF/0.1 M [NBu_4][PF_6].

6) XPS Spectra

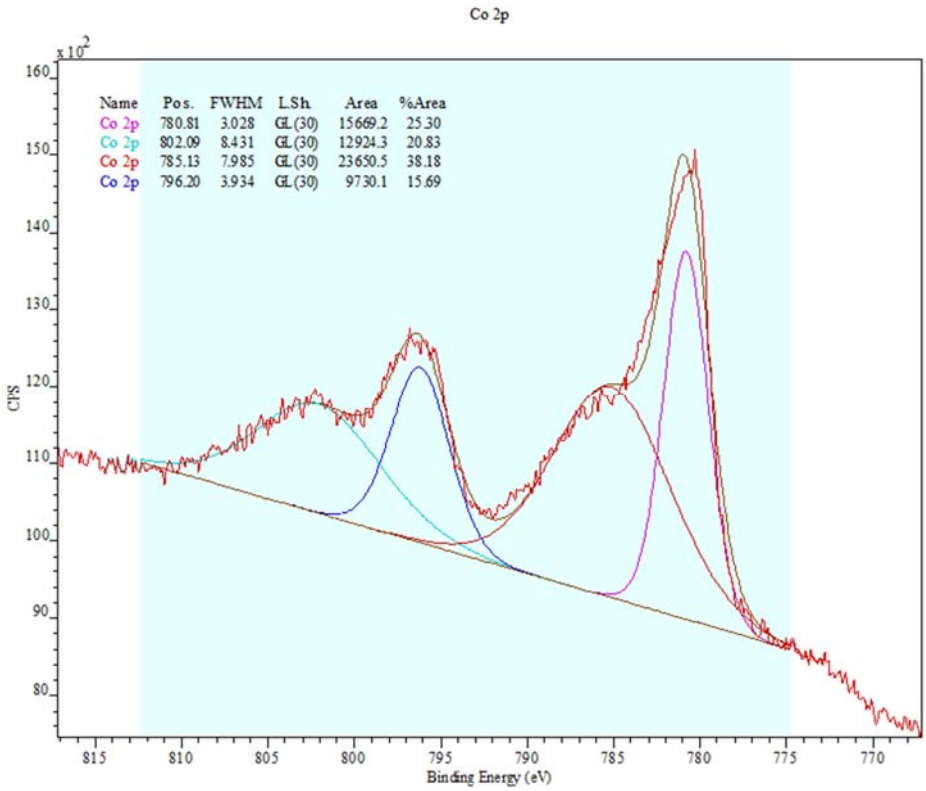
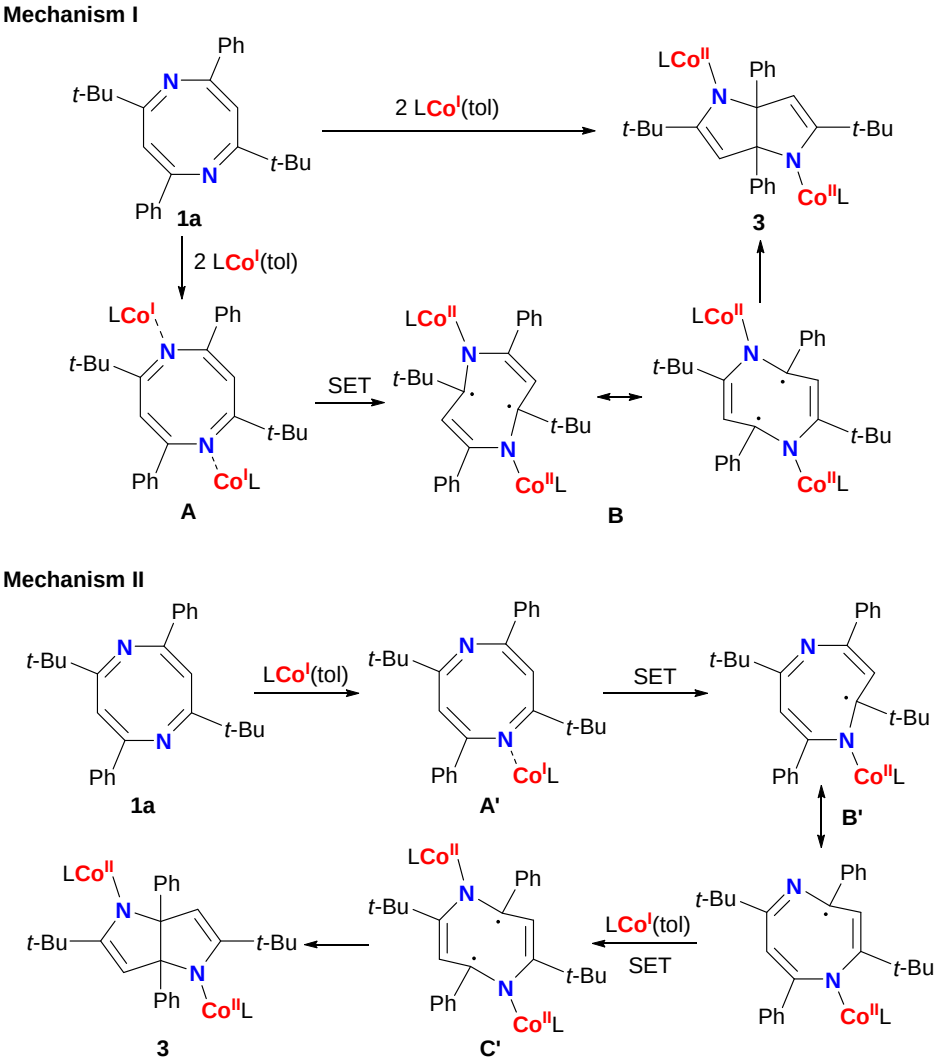


Fig. S5 XPS spectrum of Co($2p_{1/2}$ and $2p_{3/2}$) in **3**.

7) Proposed Mechanisms for the Formation of 3

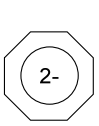
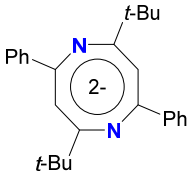
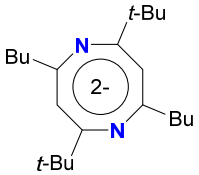


Scheme. S1 Proposed mechanisms for the formation of **3**.

8) Computational Details

All calculations were carried out with the GAUSSIAN09 program package.[8] Structures were optimized at B3LYP/6-311+G(d,p) level.[9] NICSs were calculated based on the optimized structures at the PBE1PBE/ 6-311+G(d,p) level.[10]

Table S2 Calculated NICS values (ppm) of COT^{2-} and $NCOT^{2-}$

		 **2a'**	 **2b'**
NICS(0)	-13.2	-6.7	-10.1
NICS(1)	-11.3	-6.8	-9.1

Cartesian coordinates (Å) of optimized structures

COT^{2-}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.850467	0.000003	0.000000
2	1	0	-2.947528	-0.000002	0.000000
3	6	0	-1.308574	1.308551	0.000000
4	1	0	-2.084258	2.084275	0.000000
5	6	0	-1.308544	-1.308519	0.000000
6	1	0	-2.084233	-2.084252	0.000000
7	6	0	0.000000	1.850408	0.000000
8	1	0	0.000005	2.947475	0.000000
9	6	0	1.308524	1.308519	0.000000
10	1	0	2.084233	2.084244	0.000000
11	6	0	1.850497	-0.000008	0.000000
12	1	0	2.947545	0.000009	0.000000
13	6	0	1.308549	-1.308539	0.000000
14	1	0	2.084256	-2.084264	0.000000
15	6	0	0.000012	-1.850417	0.000000
16	1	0	-0.000008	-2.947481	0.000000

2a’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.188505	1.790542	-0.022580
2	6	0	1.815656	-0.042586	0.009719
3	6	0	1.129230	-1.289069	0.026304
4	1	0	1.839272	-2.100580	0.103082
5	6	0	-0.188475	-1.790556	0.022377
6	6	0	-1.815675	0.042570	-0.010059
7	6	0	-1.129226	1.289039	-0.027132
8	1	0	-1.839225	2.100516	-0.104561
9	7	0	1.400923	1.242517	0.016017
10	7	0	-1.400960	-1.242547	-0.015722
11	6	0	-0.248705	-3.368453	0.115976
12	6	0	0.528578	-4.040334	-1.043120
13	6	0	0.342079	-3.851586	1.464242
14	6	0	-1.693827	-3.892744	0.042326
15	1	0	0.129504	-3.706495	-2.006181
16	1	0	1.592098	-3.793451	-1.025613
17	1	0	0.436108	-5.136318	-0.994233
18	1	0	-0.213623	-3.405312	2.295157
19	1	0	0.277876	-4.947387	1.556925
20	1	0	1.388957	-3.560079	1.575483
21	1	0	-1.695091	-4.987696	0.150976
22	1	0	-2.313978	-3.451029	0.822850
23	1	0	-2.154410	-3.638128	-0.914937
24	6	0	0.248760	3.368476	-0.115415
25	6	0	-0.342381	3.852711	-1.463117
26	6	0	-0.528133	4.039529	1.044474
27	6	0	1.693933	3.892647	-0.041937
28	1	0	0.213072	3.407140	-2.294585
29	1	0	-1.389315	3.561448	-1.574449
30	1	0	-0.278105	4.948575	-1.554824
31	1	0	-0.128676	3.704927	2.007104
32	1	0	-0.435726	5.135563	0.996422
33	1	0	-1.591607	3.792482	1.027080
34	1	0	1.695256	4.987644	-0.150187
35	1	0	2.154789	3.637674	0.915090
36	1	0	2.313871	3.451185	-0.822789
37	6	0	-3.299153	0.135938	0.001345
38	6	0	-4.095699	-0.969842	-0.405998
39	6	0	-4.038033	1.275521	0.426225
40	6	0	-5.482959	-0.929660	-0.422433
41	1	0	-3.566660	-1.861292	-0.711738
42	6	0	-5.429767	1.313952	0.412020
43	1	0	-3.510032	2.139849	0.808900

44	6	0	-6.183232	0.216835	-0.017728
45	1	0	-6.033463	-1.806633	-0.759220
46	1	0	-5.934569	2.214013	0.758857
47	1	0	-7.269213	0.248407	-0.027361
48	6	0	3.299110	-0.135882	-0.001820
49	6	0	4.095708	0.969523	0.406385
50	6	0	4.037889	-1.275147	-0.427708
51	6	0	5.482957	0.929227	0.422811
52	1	0	3.566734	1.860784	0.712836
53	6	0	5.429635	-1.313697	-0.413510
54	1	0	3.509835	-2.139107	-0.811143
55	6	0	6.183156	-0.216996	0.017181
56	1	0	6.033513	1.805917	0.760243
57	1	0	5.934361	-2.213518	-0.761082
58	1	0	7.269135	-0.248648	0.026874

2b’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.491414	1.755443	0.032550
2	6	0	1.668235	-0.331092	0.551527
3	6	0	0.832566	-1.461951	0.372864
4	1	0	1.384272	-2.367209	0.618028
5	6	0	-0.491364	-1.755339	-0.032296
6	6	0	-1.668116	0.331181	-0.551494
7	6	0	-0.832500	1.462051	-0.372666
8	1	0	-1.384223	2.367314	-0.617772
9	7	0	1.524805	0.996437	0.415244
10	7	0	-1.524709	-0.996343	-0.415138
11	6	0	3.101552	-0.668642	0.980406
12	6	0	4.150088	-0.559145	-0.149060
13	1	0	3.156001	-1.683290	1.401231
14	1	0	3.404355	0.028511	1.777549
15	6	0	5.589542	-0.814909	0.311369
16	1	0	3.888357	-1.268634	-0.945513
17	1	0	4.069688	0.443688	-0.583317
18	6	0	6.636798	-0.689959	-0.801925
19	1	0	5.837240	-0.112363	1.118911
20	1	0	5.656963	-1.817737	0.757221
21	1	0	7.656211	-0.878179	-0.434743
22	1	0	6.439981	-1.402467	-1.610932
23	1	0	6.622808	0.312856	-1.242947
24	6	0	-3.101361	0.668706	-0.980651
25	6	0	-4.150148	0.558995	0.148554
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27	1	0	-3.155764	1.683403	-1.401360

28	6	0	-5.589524	0.814653	-0.312180
29	1	0	-4.069738	-0.443869	0.582733
30	1	0	-3.888685	1.268439	0.945138
31	6	0	-6.637013	0.689523	0.800875
32	1	0	-5.656947	1.817506	-0.757976
33	1	0	-5.836975	0.112139	-1.119824
34	1	0	-7.656363	0.877678	0.433484
35	1	0	-6.623027	-0.313323	1.241825
36	1	0	-6.440436	1.401990	1.609977
37	6	0	-0.836212	-3.290266	-0.035679
38	6	0	0.093840	-4.074691	-0.997462
39	6	0	-0.704002	-3.895857	1.386095
40	6	0	-2.281471	-3.550416	-0.501861
41	1	0	-0.000973	-3.675653	-2.012395
42	1	0	1.143504	-3.986602	-0.707757
43	1	0	-0.166665	-5.145904	-1.022633
44	1	0	-1.372134	-3.371756	2.076926
45	1	0	-0.969533	-4.966235	1.394263
46	1	0	0.312543	-3.793321	1.772593
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50	6	0	0.836192	3.290385	0.036155
51	6	0	0.704035	3.896187	-1.385534
52	6	0	-0.093957	4.074620	0.998001
53	6	0	2.281414	3.550535	0.502453
54	1	0	1.372215	3.372211	-2.076413
55	1	0	-0.312488	3.793693	-1.772102
56	1	0	0.969539	4.966572	-1.393520
57	1	0	0.000830	3.675446	2.012883
58	1	0	0.166477	5.145847	1.023334
59	1	0	-1.143598	3.986497	0.708228
60	1	0	2.483282	4.633318	0.498709
61	1	0	2.444781	3.157129	1.507578
62	1	0	2.999562	3.048901	-0.148503

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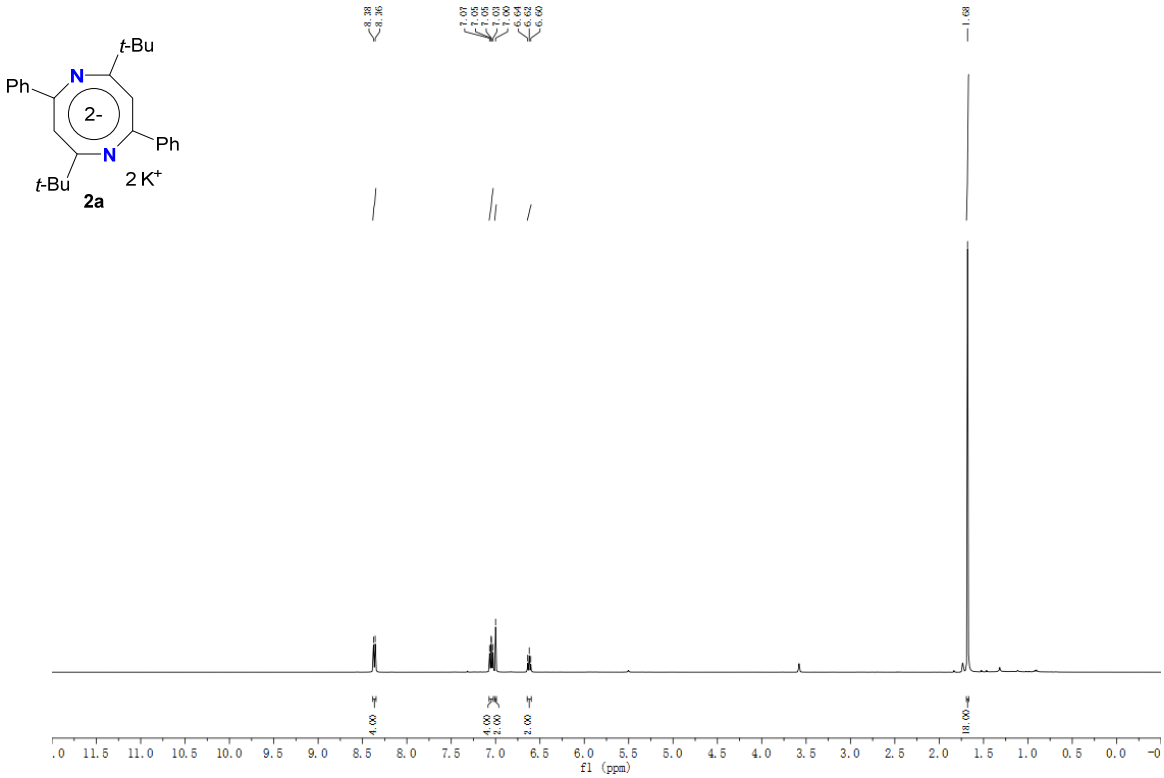
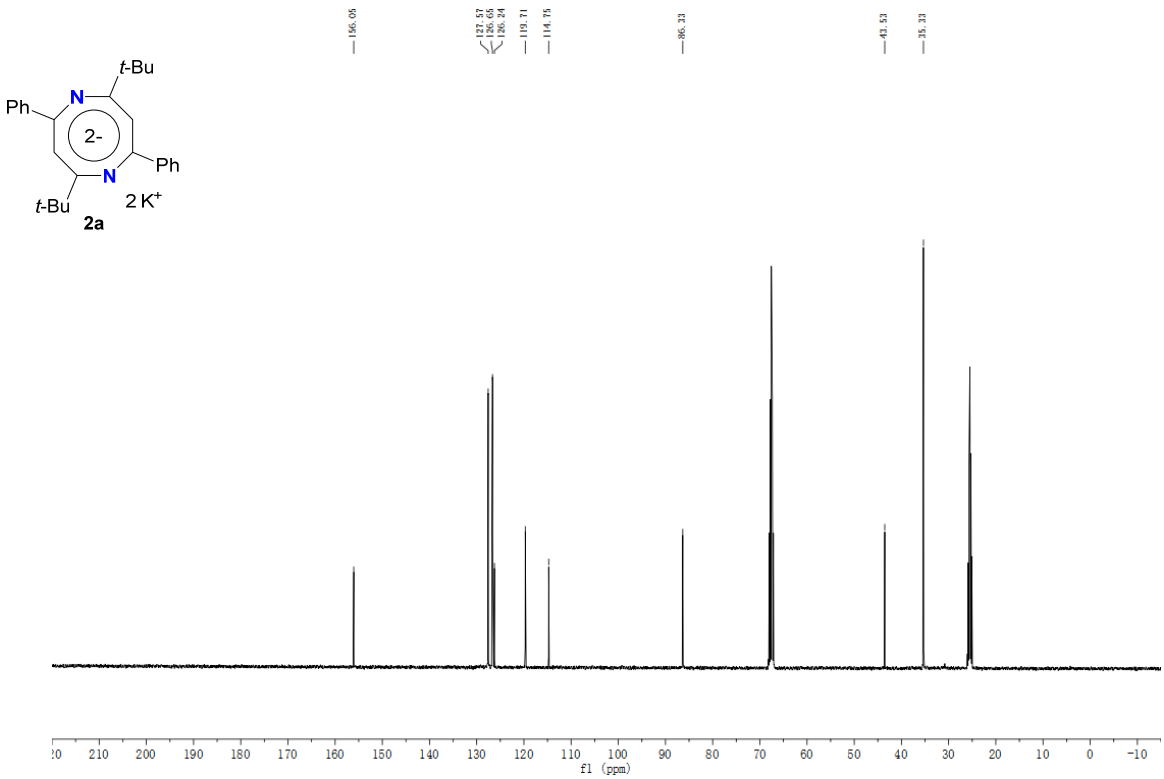
9) Copies of ^{1}H NMR and ^{13}C NMR Spectra

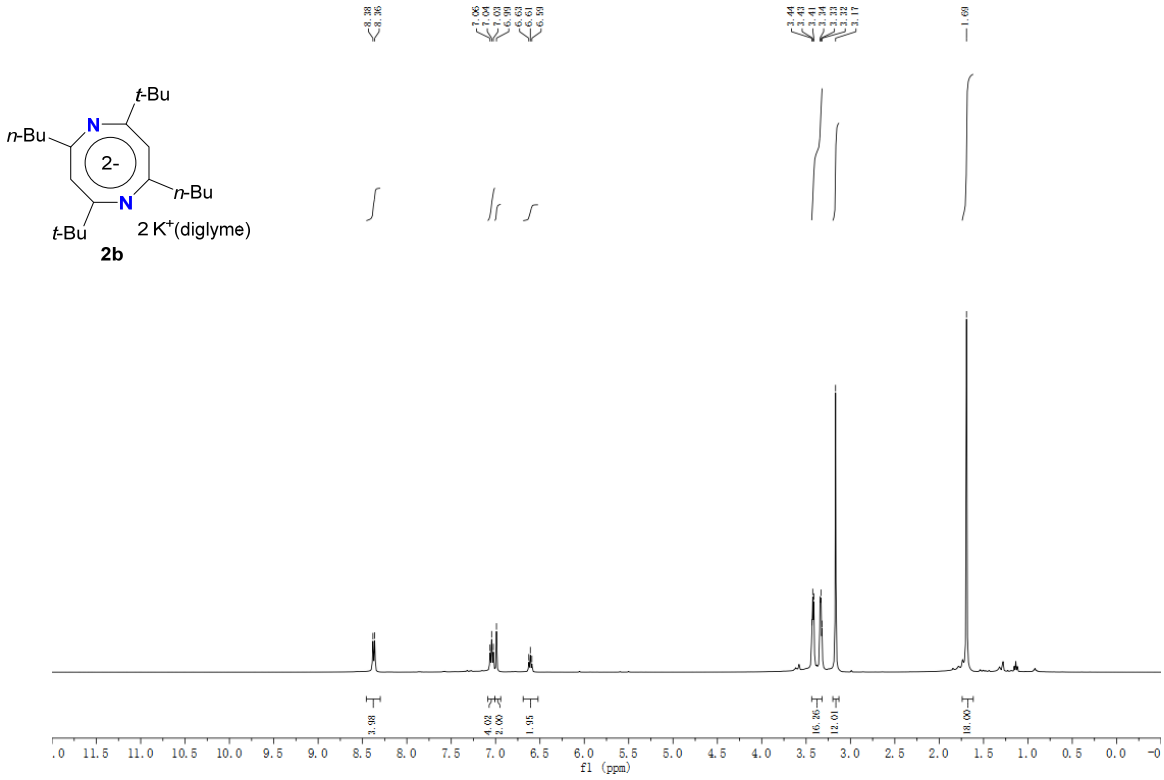
2a-^{1}H NMR



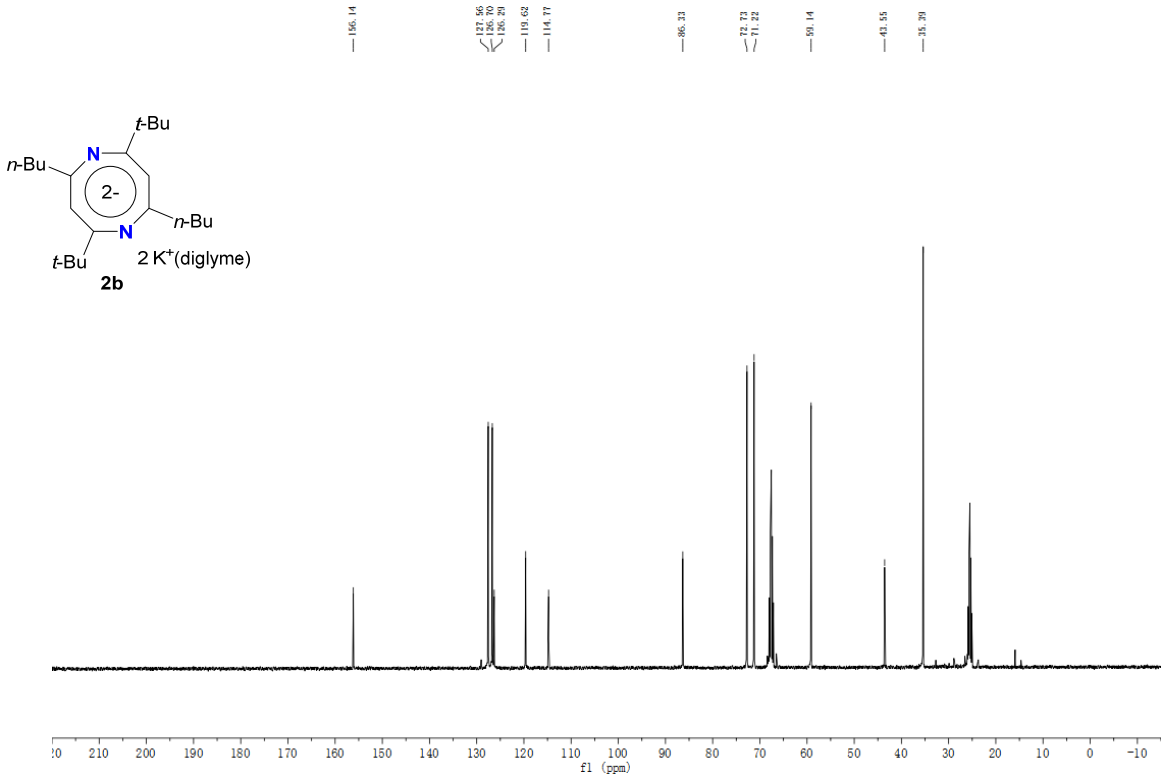
2a-^{13}C NMR



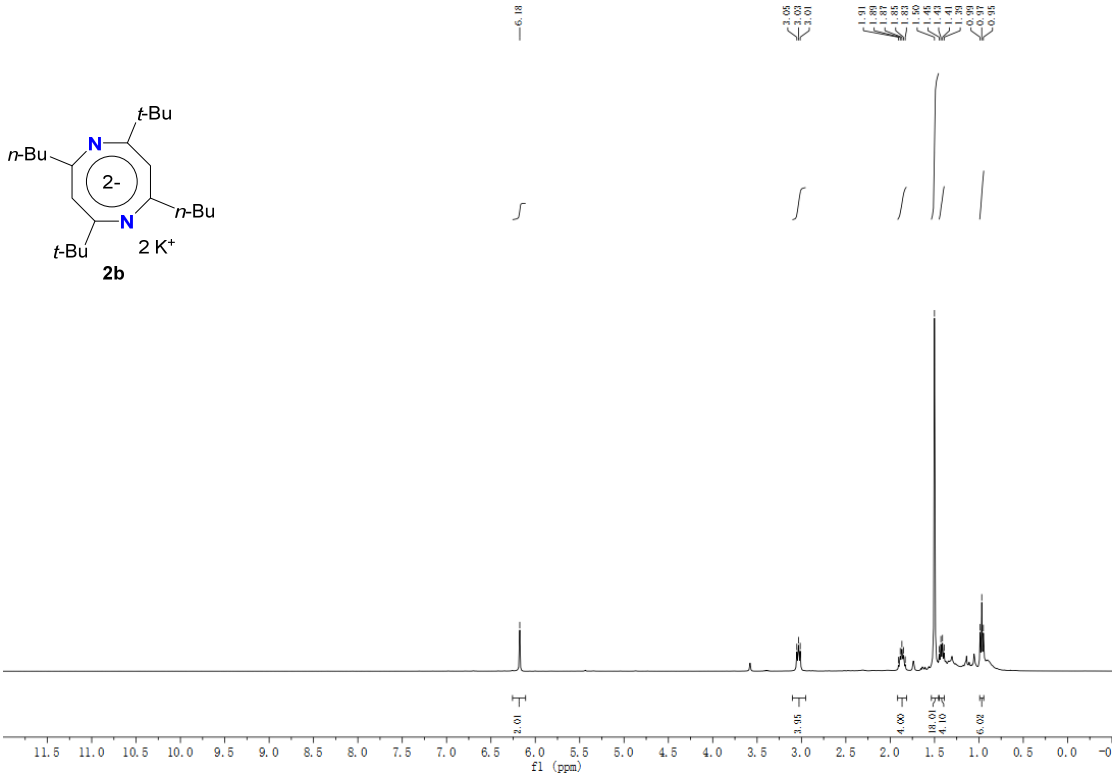
2a•2diglyme-^{1}H NMR



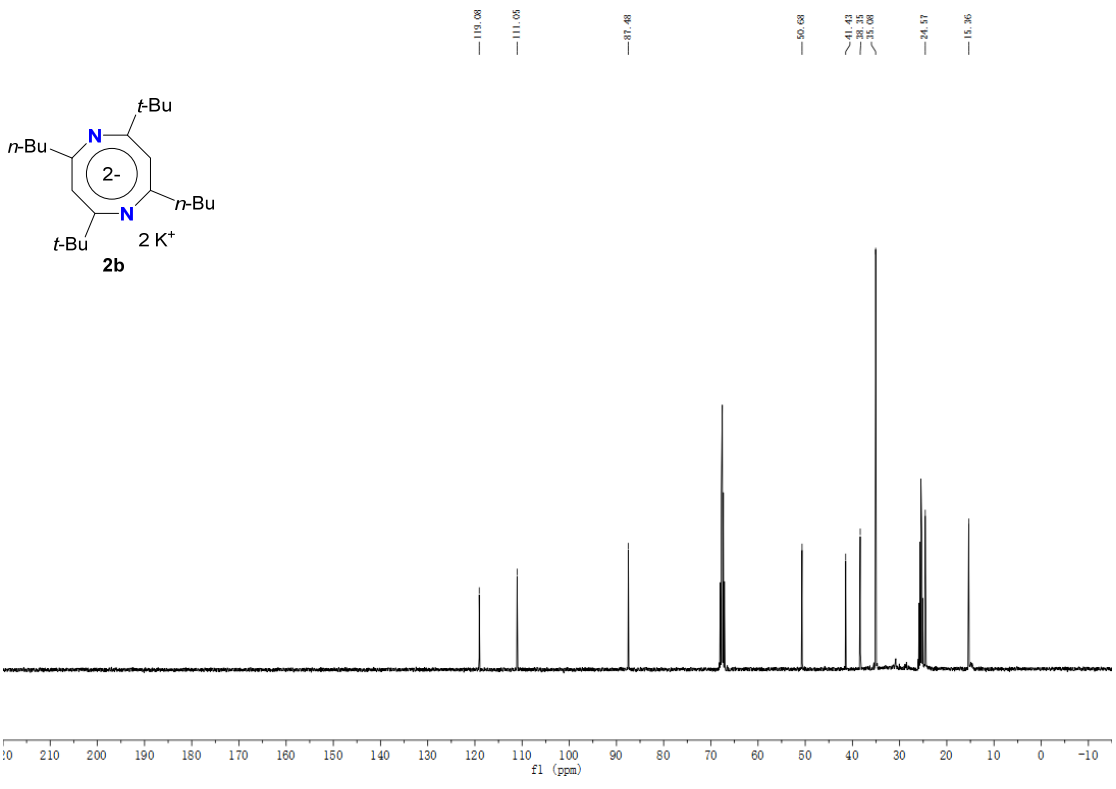
2a•2diglyme-^{13}C NMR



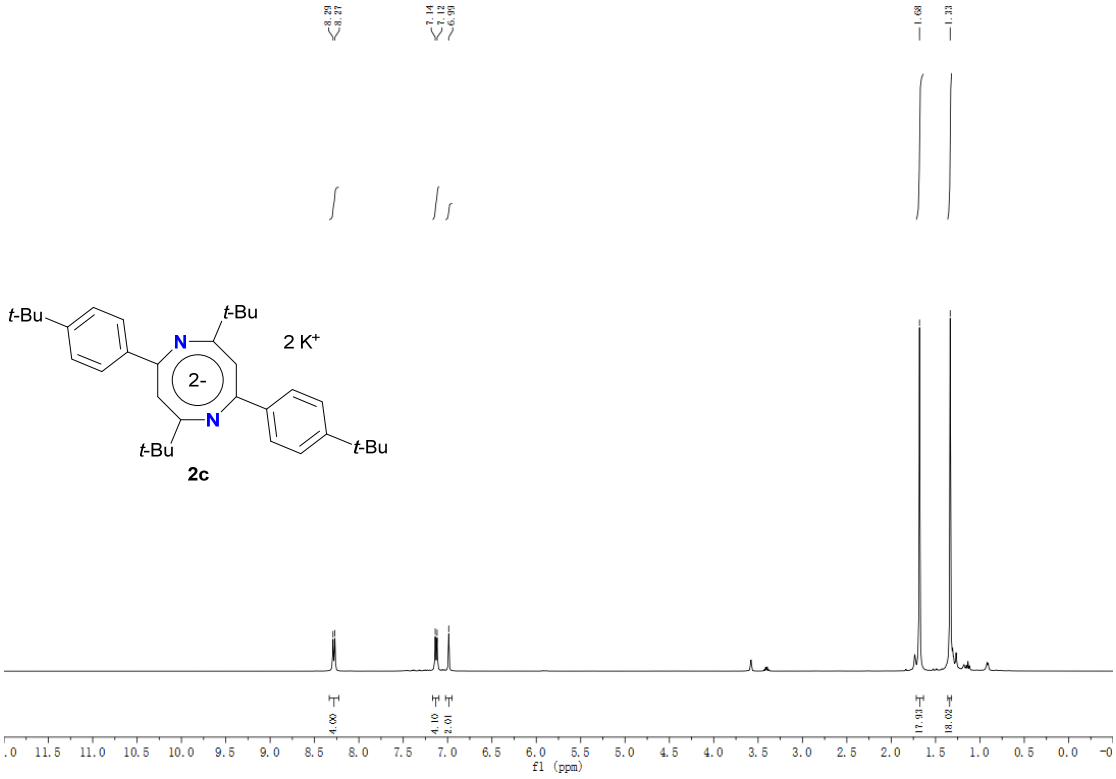
2b-^{1}H NMR



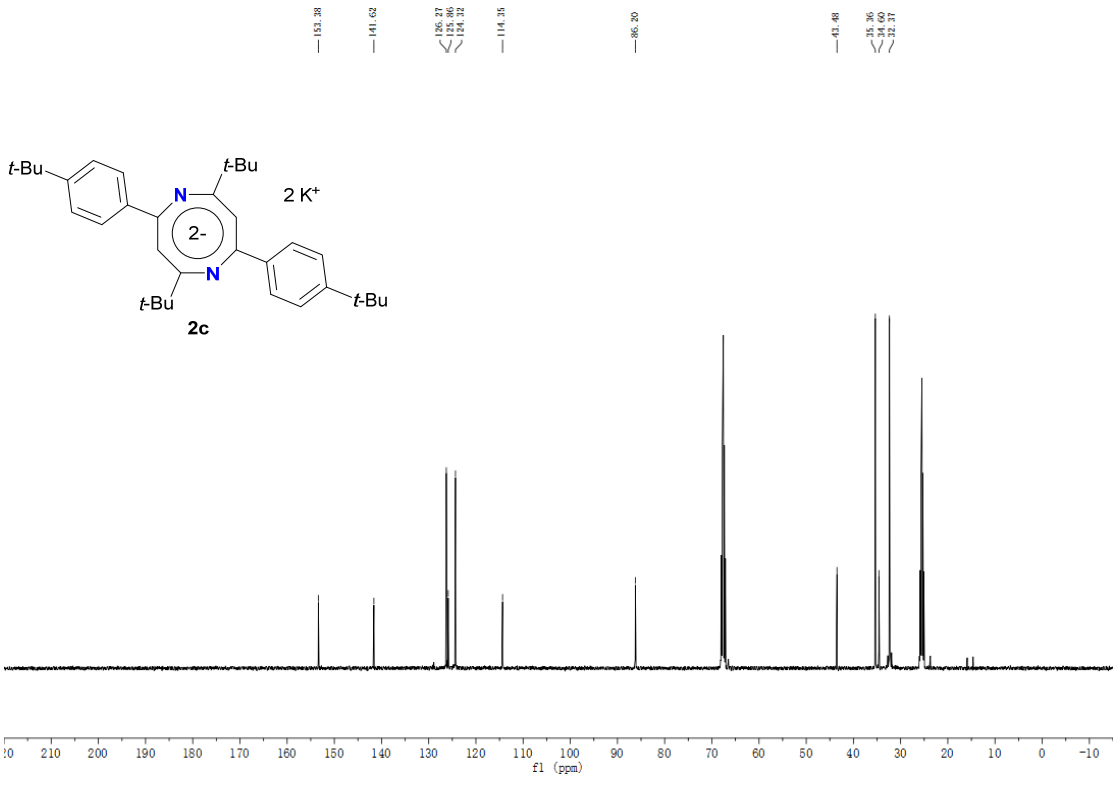
2b-^{13}C NMR



2c-^{1}H NMR



2c-^{13}C NMR



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