Supporting Information

Squaraine Rotaxanes with Boat Conformation Macrocycles

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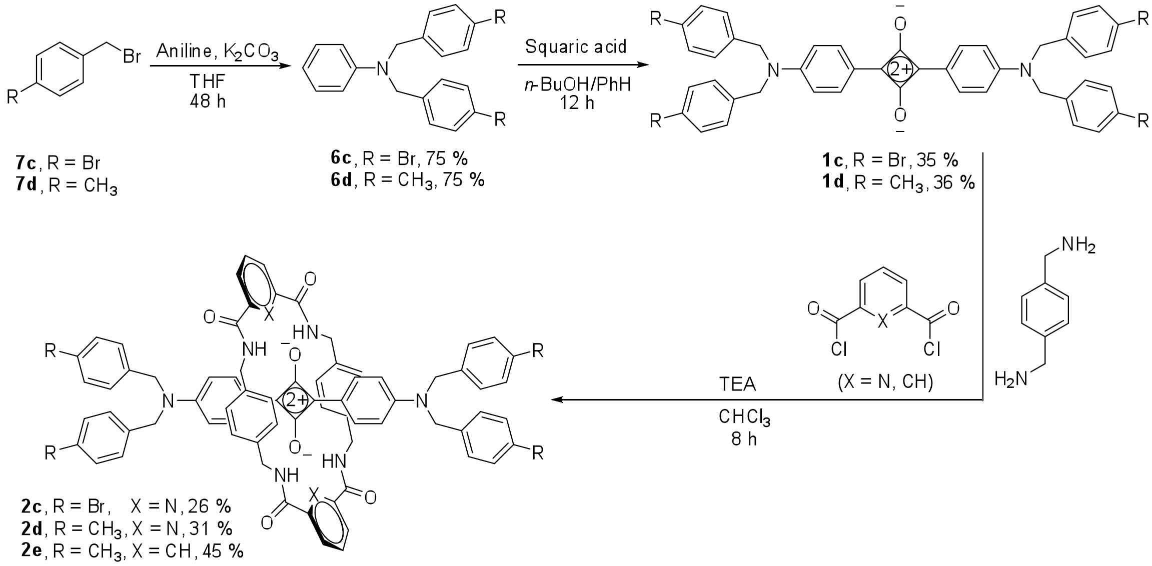
1. Materials

Reagents and starting materials were purchased from commercial suppliers and used without further purification. Compounds **1a**,[1] **2a**,[1] **1b**,[2] **2b**,[2] and **3**,[3] have been previously reported.

2. Synthesis of dyes and rotaxanes



Scheme S1. Synthesis of squaraine rotaxanes

General procedure to synthesize *N,N*-dibenzyl aniline analogues (6c-d): The corresponding benzyl bromide (**7c-d**) was added to a solution of aniline (150 mg, 1.6 mmol) in anhydrous tetrahydrofuran (50 mL). Excess potassium carbonate (1.3 g, 9.4 mmol) was also added and the reaction mixture was refluxed for 48 h. After cooling, cold water (75 mL) was added to dissolve the inorganic salts. After extraction with chloroform, the organic layer was separated and condensed under reduced pressure to remove the solvent. The crude product was further purified using column chromatography over silica gel with MeOH/$CHCl_3$ (1:19) as the eluent for **6c-d**.

6c (75 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.55 (s, 4H), 6.69-6.74 (m, 3H), 7.08 (d, J = 8.2 Hz, 4H), 7.18 (t, J = 8.0 Hz, 2H), 7.44 (d, J = 8.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.0, 112.9, 117.6, 121.0, 128.7, 129.6, 132.0, 137.6, 144.4; HRMS (FAB): calcd for $C_{20}H_{17}Br_2N$ $[M]^+$ 428.9728, found 428.9709.

6d (75 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 6H), 4.59 (s, 4H), 6.71-6.74 (m, 3H), 7.14-7.19 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 54.0, 112.6, 116.7, 126.8, 129.4, 129.5, 135.7, 136.6, 149.5; HRMS (FAB): calcd for $C_{22}H_{23}N$ $[M]^+$ 301.1830, found 301.1819.

General procedure to synthesize squaraine dyes (1a-d): Described in the article.

Squaraine 1c (35 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.70 (s, 8H), 6.83 (d, *J* = 9.0 Hz, 4H), 7.05 (d, *J* = 8.7 Hz, 8H), 7.48 (d, *J* = 9.0 Hz, 8H), 8.38 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 53.8, 113.3, 121.4, 122.0, 128.4, 132.5, 134.0, 134.9, 155.0, 182.9, 192.0; MS (FAB): $[M]^+$ 939.9.

Squaraine 1d (36 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 12H), 4.73 (s, 8H), 6.86 (d, *J* = 8.7 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 8H), 7.16 (d, *J* = 7.8 Hz, 8H), 8.36 (d, *J* = 9.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 54.0, 113.3, 120.9, 126.7, 130.0, 133.0, 133.7, 137.7, 155.3, 183.3, 190.4; HRMS (FAB): calcd for $C_{48}H_{45}N_2O_2$ $[M + H]^+$ 681.3481, found 681.3490.

General procedure to synthesize squaraine rotaxanes (2a-e and 5): Described in the article.

Rotaxane 2c (26 %): ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50 (d, *J* = 6.0 Hz, 8H), 4.58 (s, 8H), 6.21 (d, *J* = 9.0 Hz, 4H), 6.54 (s, 8H), 6.97 (d, *J* = 7.8 Hz, 8H), 7.53 (d, *J* = 7.8 Hz, 8H), 7.98 (t, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 4H), 8.39 (d, *J* =10.5 Hz, 4H), 9.83 (t, *J* = 5.1 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.4, 54.0, 112.6, 120.4, 122.4, 125.4, 128.3, 129.1, 132.6, 134.1, 134.5, 137.0, 138.8, 149.5, 155.0, 163.6, 184.8, 188.0; MS (FAB): $[M]^+$ 1472.2.

Rotaxane 2d (31 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 12H), 4.49 (d, *J* = 6.0 Hz, 8H), 4.60 (s, 8H), 6.25 (d, *J* = 9.6 Hz, 4H), 6.54 (s, 8H), 6.97 (d, *J* = 8.1 Hz, 8H), 7.18 (d, *J* = 7.8 Hz, 8H), 8.00 (t, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 9.3 Hz, 4H), 8.38 (d, *J* = 10.8 Hz, 4H), 9.86 (t, *J* = 5.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 43.5, 54.2, 112.8, 119.9, 125.4, 126.7, 129.1, 130.0, 132.8, 133.8, 136.9, 138.0, 138.8, 149.6, 155.2, 163.7, 185.2, 185.9; MS (FAB): $[M + H]^+$ 1215.6.

Rotaxane 2e (45 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 12H), 4.38 (d, *J* = 4.8 Hz, 8H), 4.70 (s, 8H), 6.47 (d, *J* = 9.3 Hz, 4H), 6.63 (s, 8H), 7.03 (d, *J* = 8.1 Hz, 8H), 7.22 (d, *J* = 7.8 Hz, 8H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 4H), 8.08 (t, *J* = 5.1 Hz, 4H), 8.20 (d, *J* = 6.0 Hz, 4H), 9.24 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 44.4, 54.5, 113.5, 118.8, 124.8, 126.6, 129.3, 130.1, 131.8, 132.5, 133.3, 134.1, 136.6, 138.1, 155.5, 166.3, 182.7, 185.3; MS (FAB): $[M + H]^+$ 1214.7.

Rotaxane 5 (25%): ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.90 (dd, *J* = 1.5 Hz, 14.4 Hz, 4H), 4.59 (s, 4H), 4.78 (s, 4H), 4.97 (dd, *J* = 8.2 Hz, 14.4 Hz, 4H), 5.88 (d, *J* = 9.0 Hz, 2H), 6.66 (s, 8H), 7.08 (d, *J* = 7.0 Hz, 4H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.34-7.58 (m, 20H), 7.85 (d, *J* = 9.0 Hz, 4H), 8.15 (dd, *J* = 1.6 Hz, 6.8 Hz ,4H), 9.05 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.4, 52.4, 54.6, 112.0, 117.0, 124.3, 126.7, 128.1, 129.3, 129.5, 129.6, 129.7, 129.9, 130.5, 132.1, 132.9, 133.9, 136.2, 136.9, 152.9, 166.2, 175.4, 178.3, 182.3; MS (FAB): $[M + H]^+$ 1083.4.

3. Crystallography

Single-crystal experiments were carried out on a CCD system with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data were collected at 100 K. The structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXL-97. Subsequent difference Fourier syntheses led to the location of all the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically otherwise noted. Hydrogen atoms were included and idealized with the standard SHELXL-97.

Crystallographic summary of **2a**: Reported previously in reference 1.

Crystallographic summary of **2b**:
Single crystals were grown by slow diffusion of hexane into a chloroform solution. The crystals grew as green/blue thin plates. Triclinic, $C_{81}H_{73}Cl_3I_4N_8O_6$, FW = 1868.42, P -1, Z = 2 in a cell of dimensions a = 13.2502(7) Å, b = 16.0849(8) Å, c = 17.9953(10) Å, α = 86.541(3)°, β = 82.282(3)°, γ = 82.283(3)°, V = 3762.6(3) Å^3, D_{calc} = 1.649 g/cm^3, F(000) = 1852. The structure was refined on F^2 to wR_2 = 0.2017, conventional R_1 = 0.0789 [13265 reflections with $I > 2\sigma$ (I)], and a goodness of fit = 1.100 for 902 refined parameters. Four chemical moieties were found in the asymmetric unit, thread molecule $C_{44}H_{32}I_4N_2O_2$, macrocycle $C_{30}H_{26}N_6O_4$, one molecule of chloroform, and one highly disordered molecule of hexane. The volume was analyzed with SQUEEZE (Spek, 2006) and modeled as containing a disordered hexane molecule. The chemical formula and dependent values reflect this addition. The void space calculation revealed a void of 370 e. A-3 with a count of 92 electrons. This is a reasonable value for a molecule of hexane.

Crystallographic summary of **2c**:
Single crystals were grown by slow diffusion of diisopropyl ether into a chloroform solution. The crystals grew as green needles. Triclinic, $C_{84}H_{76}Br_4Cl_{12}N_8O_7$, FW = 2054.57, P -1, Z = 2 in a cell of dimensions a = 13.5229(5) Å, b = 16.5761(6) Å, c = 20.5214(8) Å, α = 86.498(2)°, β = 89.086(2)°, γ = 74.047(2)°, V = 4414.6(3) Å^3, D_{calc} = 1.546 g/cm^3, F(000) = 2072. The structure was refined on F^2 to wR_2 = 0.1329, conventional R_1 = 0.0561 [15550 reflections with $I > 2\sigma$ (I)], and a goodness of fit = 1.0024 for 1056 refined parameters. Seven chemical moieties were found in the asymmetric unit, one thread molecule $C_{44}H_{32}Br_4N_2O_2$, one macrocycle $C_{30}H_{26}N_6O_4$, four molecules of chloroform and one molecule of diisopropyl ether.

Crystallographic summary of **2d**:
Single crystals were grown by slow diffusion of hexane into a chloroform solution. The crystals grew as dark green plates. Triclinic, $C_{79.75}H_{71.75}Cl_{5.25}N_8O_6$, FW = 1424.31, P -1, Z = 2 in a cell of dimensions a = 13.3345(3) Å, b = 16.0184(4) Å, c = 18.1152(4) Å, α = 89.207(2)°, β = 82.158(2)°, γ = 77.832(2)°, V = 3746.61(3) Å^3, D_{calc} = 1.183 g/cm^3, F(000) = 1487. The structure was refined on F^2 to wR_2 = 0.1705, conventional R_1 = 0.0625 [17151 reflections with $I > 2\sigma$ (I)], and a goodness of fit = 1.103 for 886 refined parameters. Three and three fourth chemical moieties were found in the asymmetric unit, one thread molecule $C_{48}H_{44}N_2O_2$, one macrocycle $C_{30}H_{26}N_6O_4$ and one and three fourth molecules of chloroform. A volume of badly disordered solvent was observed during the structure refinement. SQUEEZE (Spek, 2007) was used to model this region. The result was modeled as 0.75 $CHCl_3$ per asymmetric unit, which was included in the chemical formula and dependent results.

Crystallographic summary of **2e**:
Single crystals were grown by slow diffusion of hexane into a chloroform solution. The crystals grew as green blocks. Triclinic, $C_{81}H_{73}Cl_3N_6O_6$, FW = 1332.80, P -1, Z = 2 in a cell of dimensions *a* = 13.5542(7) Å, *b* = 15.7453(8) Å, *c* = 16.3164(8) Å, α = 95.972(2)°, β = 105.166(2)°, γ = 93.929(2)°, V = 3326.0(3) Å^3, D_{calc} = 1.331 g/cm^3, F(000) = 1400. The structure was refined on F^2 to wR_2 = 0.1081, conventional R_1 = 0.0453 [10646 reflections with I > 2σ (I)], and a goodness of fit = 1.0023 for 865 refined parameters. Three chemical moieties were found in the asymmetric unit, one thread molecule $C_{48}H_{44}N_2O_2$, one macrocycle $C_{32}H_{28}N_4O_4$ and one molecule of chloroform.

Crystallographic summary of **5**:
Single crystals were grown by slow diffusion of hexane into an ethyl acetate solution. The crystals grew as yellow plates. Triclinic, $C_{70}H_{60}N_6O_6$, FW = 1081.24, P -1, Z = 2 in a cell of dimensions *a* = 10.5354(4) Å, *b* = 15.9438(6) Å, *c* = 18.2433(7) Å, α = 104.095(2)°, β =100.631(2)°, γ = 103.265(2)°, V = 2797.50(18) Å^3, D_{calc} = 1.284 g/cm^3, F(000) = 1140. The structure was refined on F^2 to wR_2 = 0.1123, conventional R_1 = 0.0464 [11867 reflections with I > 2σ (I)], and a goodness of fit = 1.0059 for 740 refined parameters. Two chemical moieties were found in the asymmetric unit, one thread molecule $C_{38}H_{32}N_2O_2$, one macrocycle $C_{32}H_{28}N_4O_4$. The crystals of compound **5** were found to be twinned by a 180^o rotation about the real -1 1 0 axis (twin law [-0.067 -0.939 -0.003 -1.060 0.067 0.001 0.087 -0.083 -1.001], TWINABS) and data were integrated against this twin law, and subsequently corrected for absorption then, solved and refined successfully. The twin component ratio was found to be 0.6647:0.3353. The data were handled as otherwise described above.

TABLE S1. Crystallographic Details for Rotaxane 2a-e and 5

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**5**
formula	$C_{74}H_{62}N_8O_6$	$C_{74}H_{58}N_8O_6I_4$	$C_{74}H_{58}Br_4N_8O_6$	$C_{78}H_{70}N_8O_6$	$C_{81}H_{73}Cl_3N_6O_6$	C_{70} H_{60} N_6 O_6
crystal description	blue, needle	blue/green thin plate	green, needle	dk green, plate	green block	Yellow plates
	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
a (Å)	9.7987(1)	13.2502(7)	13.5229(5)	13.3345(3)	13.5542(7)	10.5354(4)
b (Å)	10.9613(2)	16.0849(8)	16.5761(6)	16.0184(4)	15.7453(8)	15.9438(6)
c (Å)	14.4900(2)	17.9953(10)	20.5214(8)	18.1152(4)	16.3164(8)	18.2433(7)
α^{o}	86.839(1)	86.541(3)	86.498(2)	89.207(2)	95.972(2)	104.095(2)
β^{o}	78.258(1)	82.282(3)	89.086(2)	82.158(2)	105.166(2)	100.631(2)
γ^{o}	77.305(1)	82.283(3)	74.047(2)	77.832(2)	93.929(2)	103.265(2)
R factor (%)	4.38	7.89	5.61	6.25	4.53	4.64
space group	P -1	P -1	P -1	P -1	P -1	P -1
Z	2	2	2	2	2	2

4. Variable temperature ^{1}H NMR spectra of the rotaxane 5

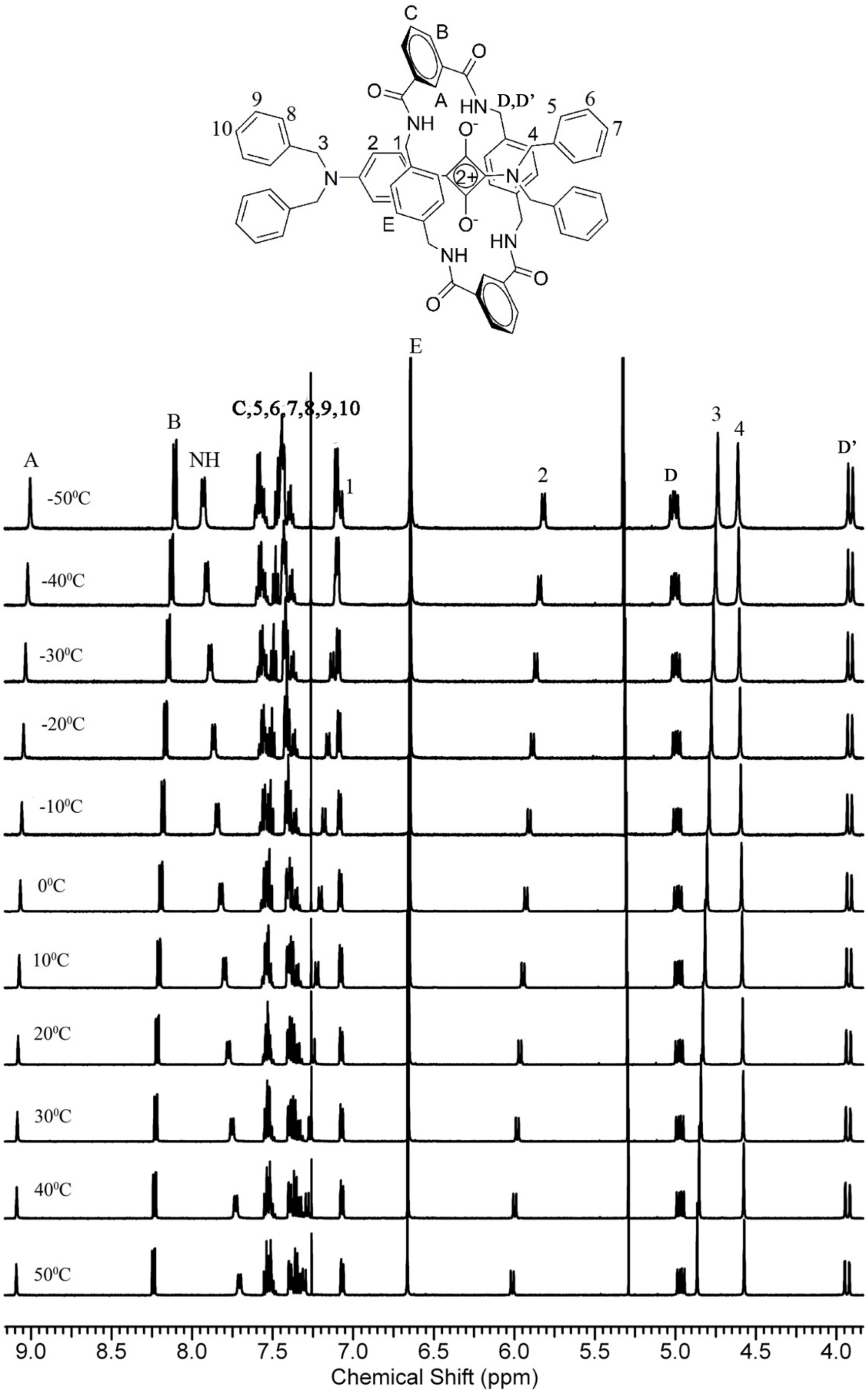


Figure S2. Variable temperature ^{1}H NMR (500 MHz, $CDCl_3$) spectra of rotaxane **5**.

5. Thermal ellipsoid plots for 2b-e and 5

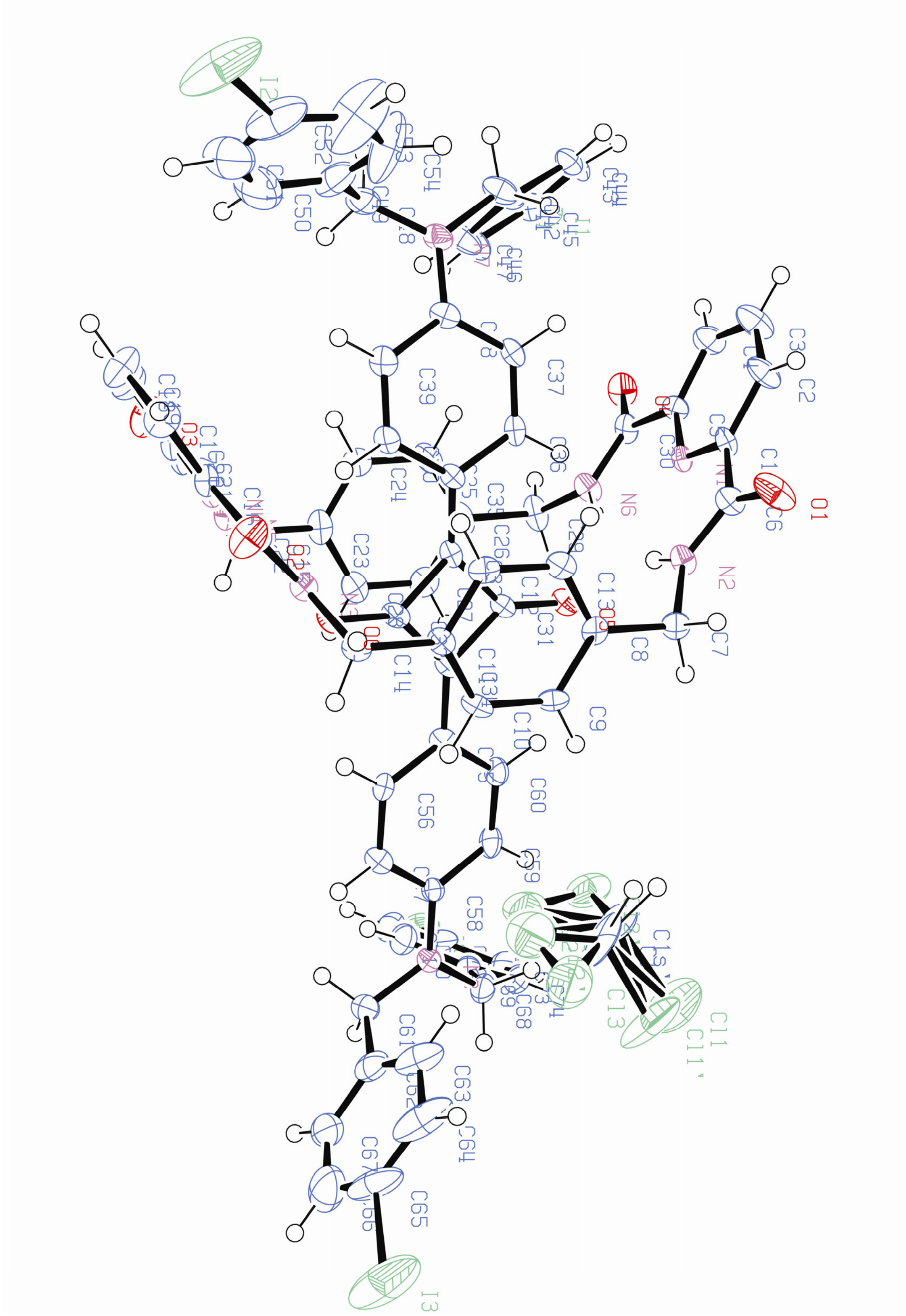


Figure S3. ORTEP of **2b** displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50 % probability level.

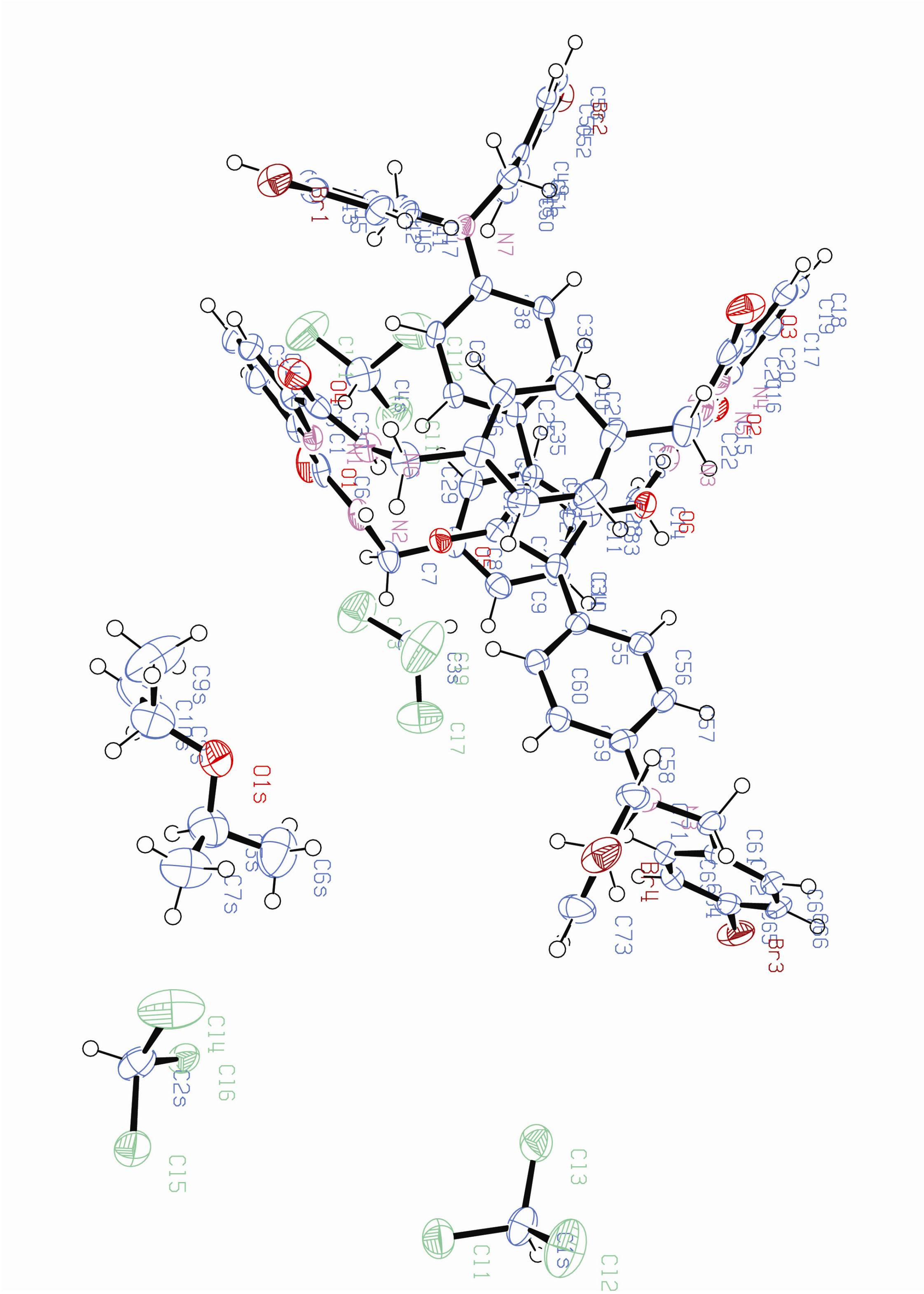


Figure S4. ORTEP of **2c** displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50 % probability level.

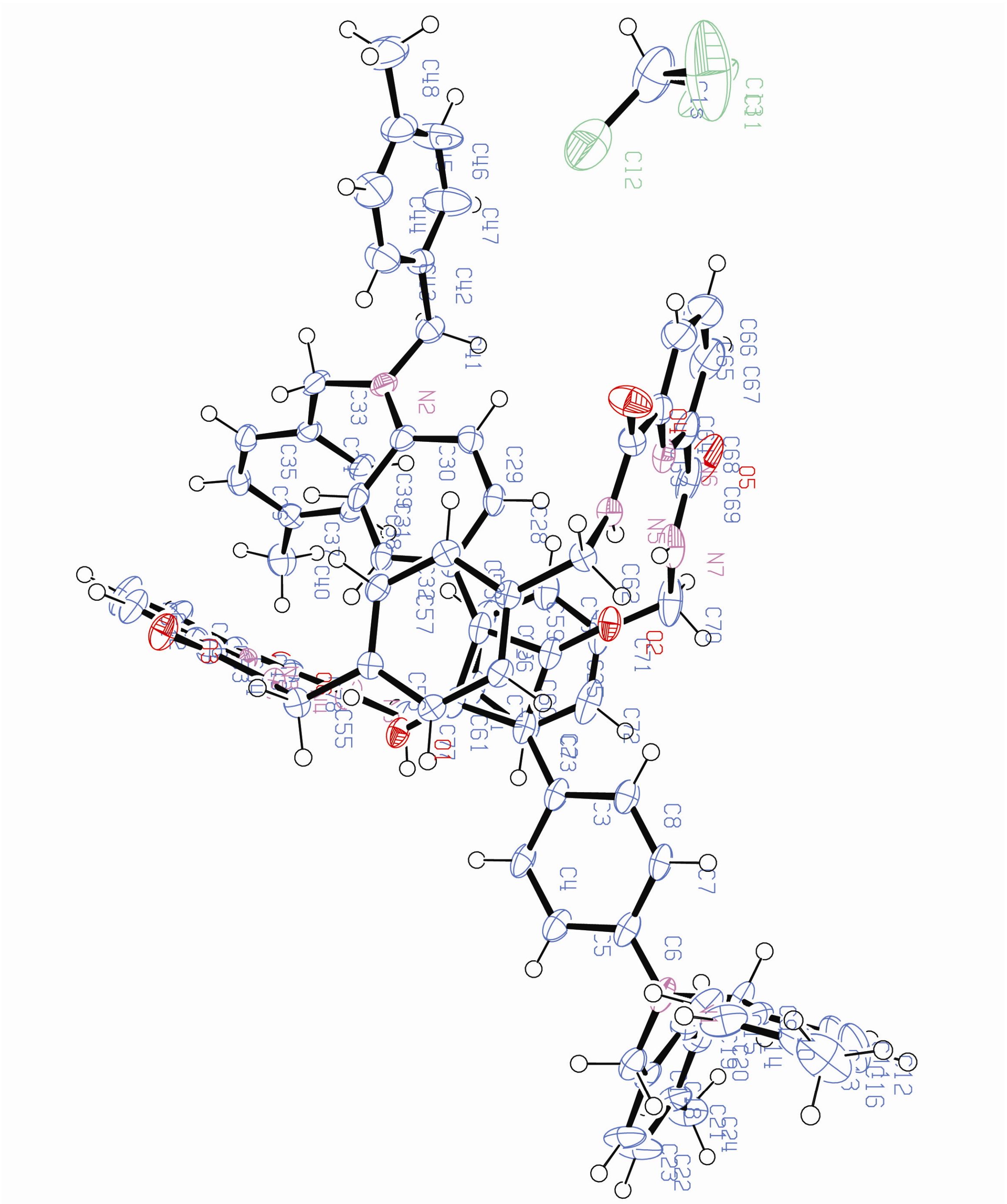


Figure S5. ORTEP of **2d** displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50 % probability level.

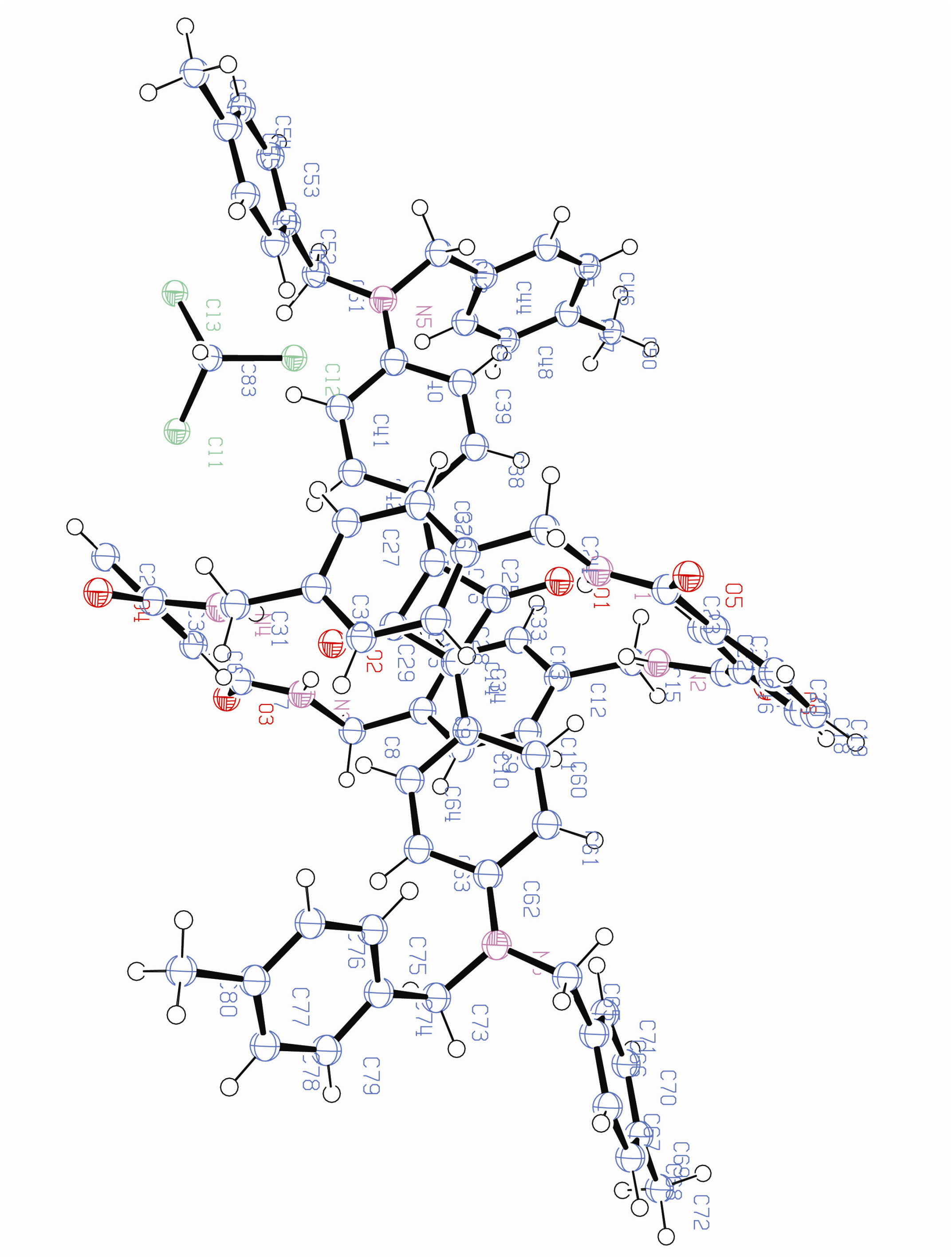


Figure S6. ORTEP of **2e** displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50 % probability level.

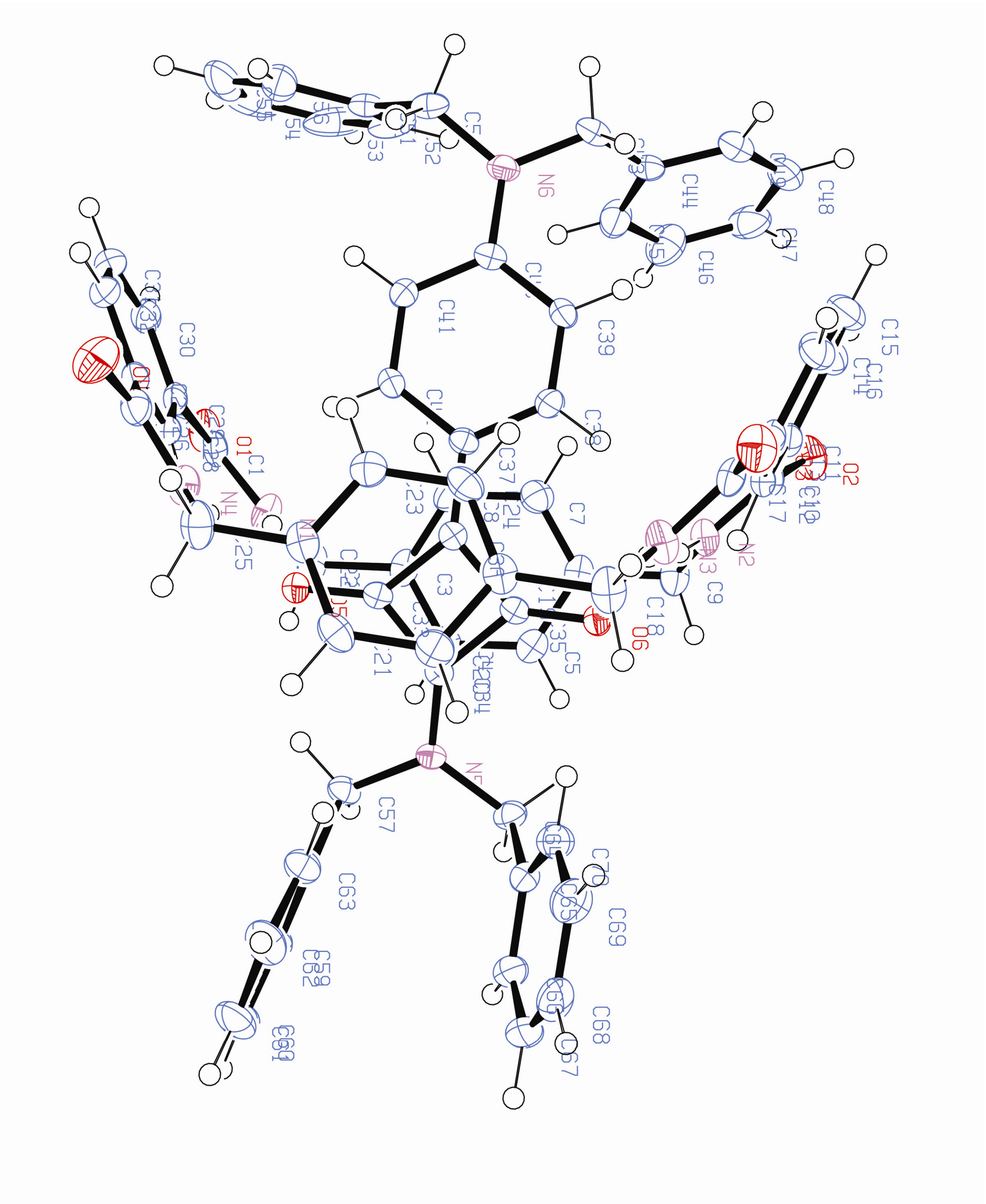
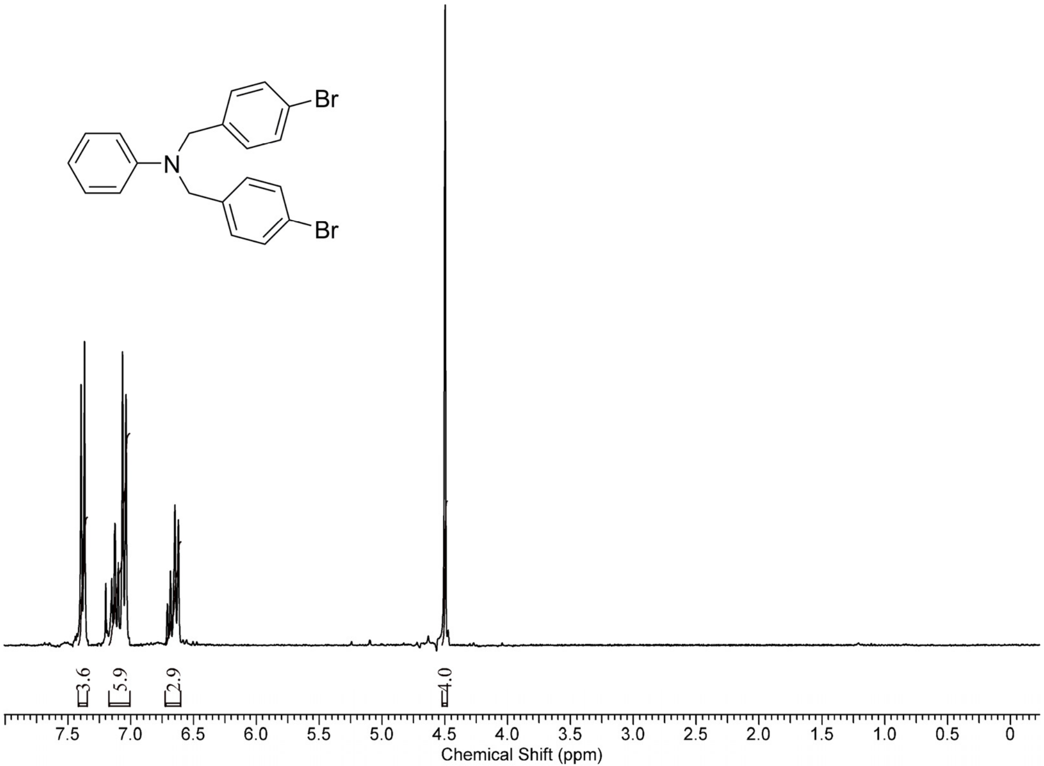


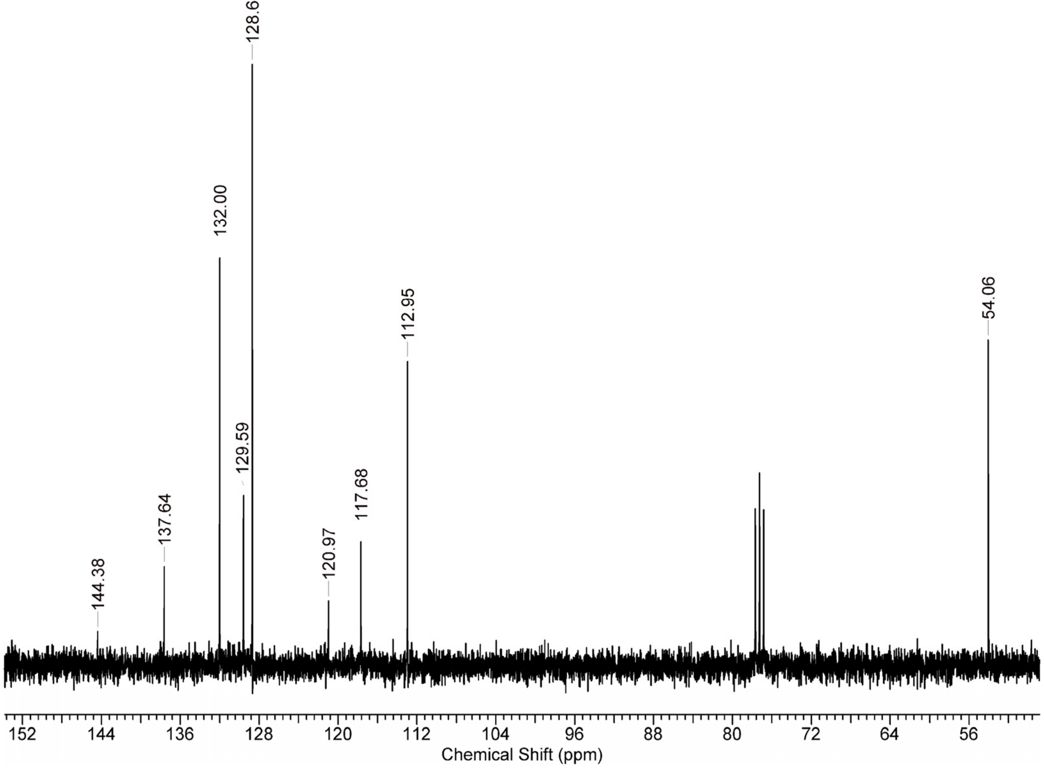
Figure S7. ORTEP of **5** displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50 % probability level.

6. ^{1}H NMR and ^{13}C NMR spectra

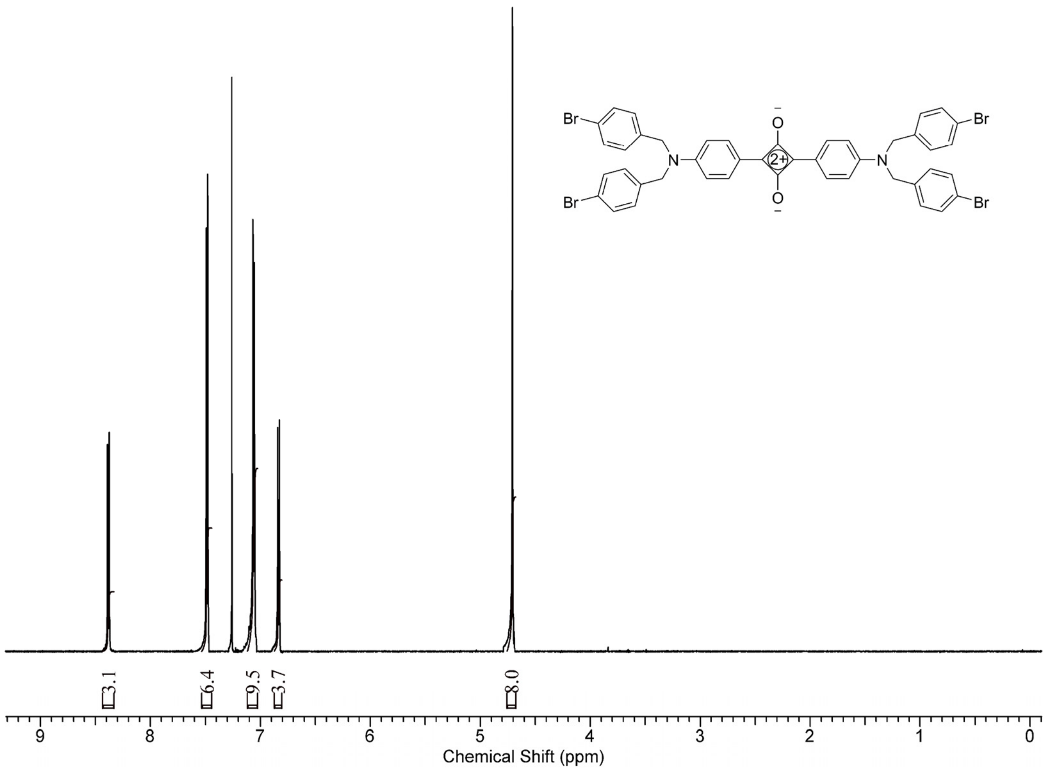
^{1}H NMR (300MHz, $CDCl_3$) of compound **6c**



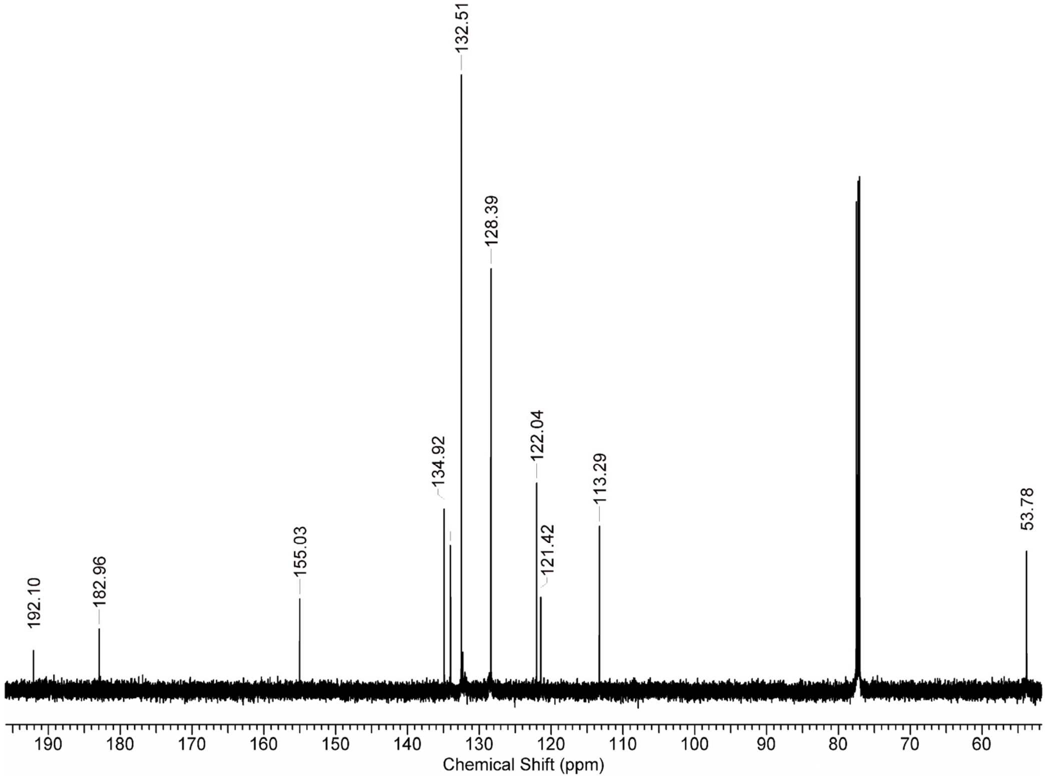
^{13}C NMR (75MHz, $CDCl_3$) of compound **6c**



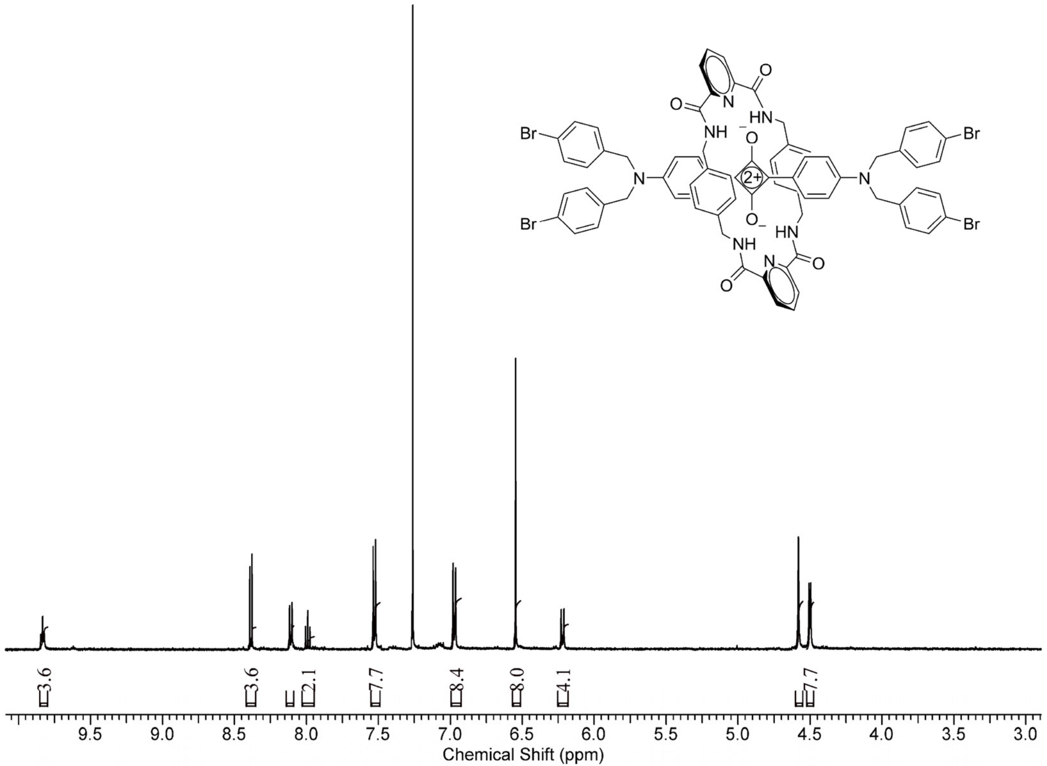
^{1}H NMR (300MHz, $CDCl_3$) of compound **1c**



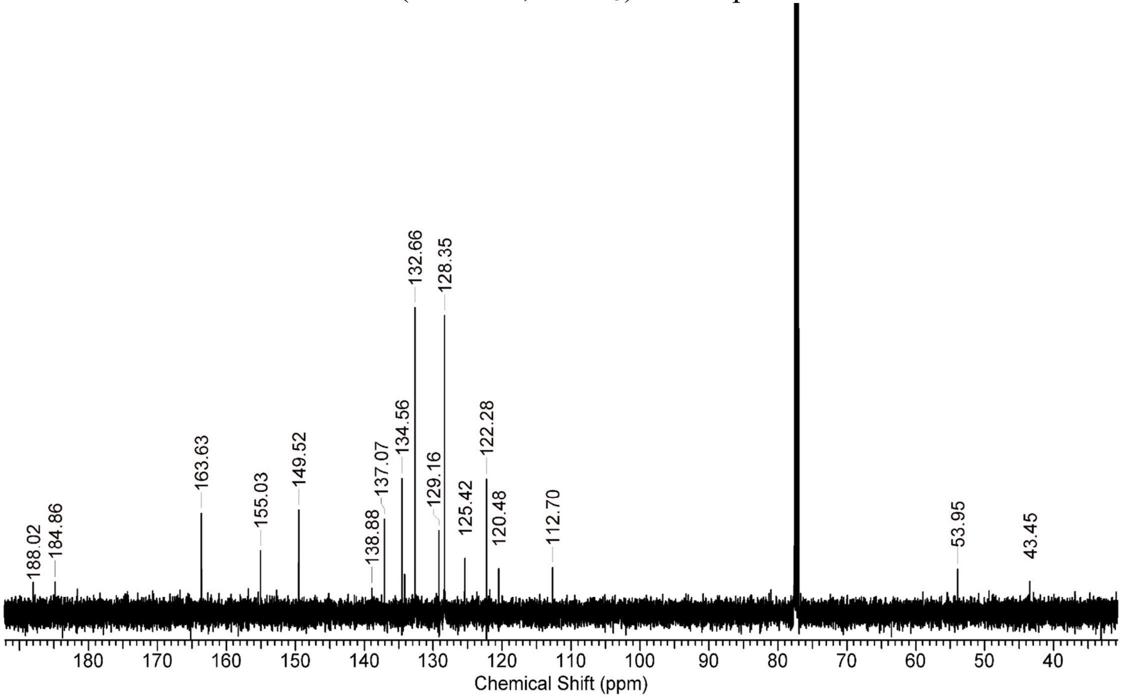
^{13}C NMR(75MHz, $CDCl_3$) of compound **1c**



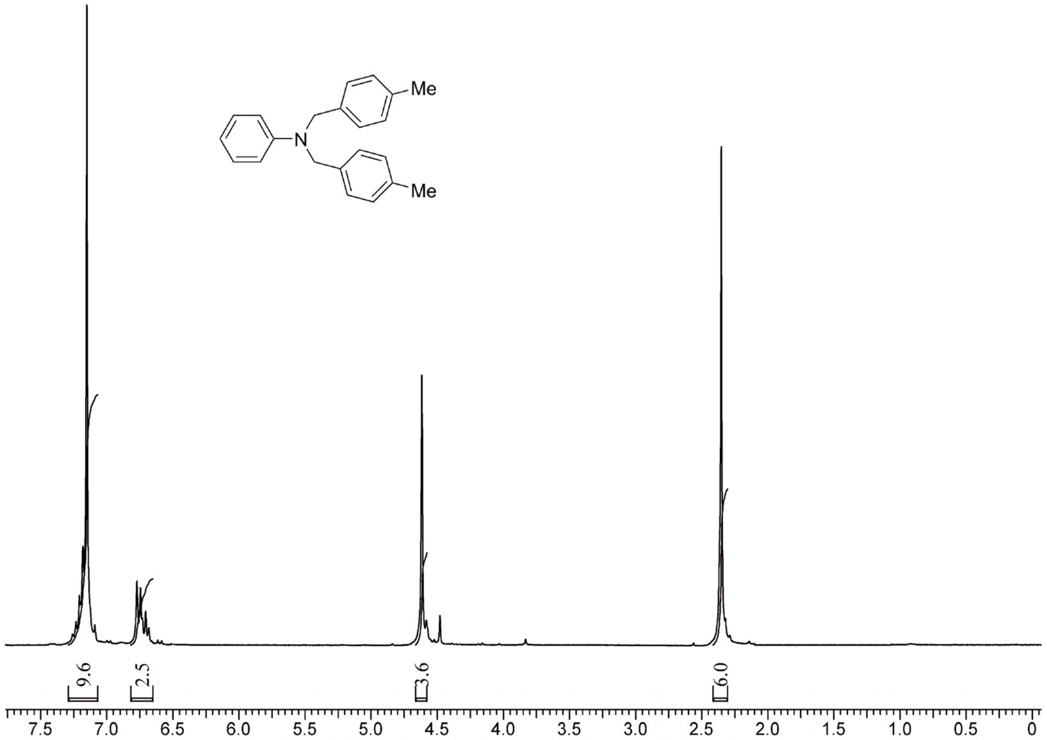
^{1}H NMR (500MHz, $CDCl_3$) of compound **2c**



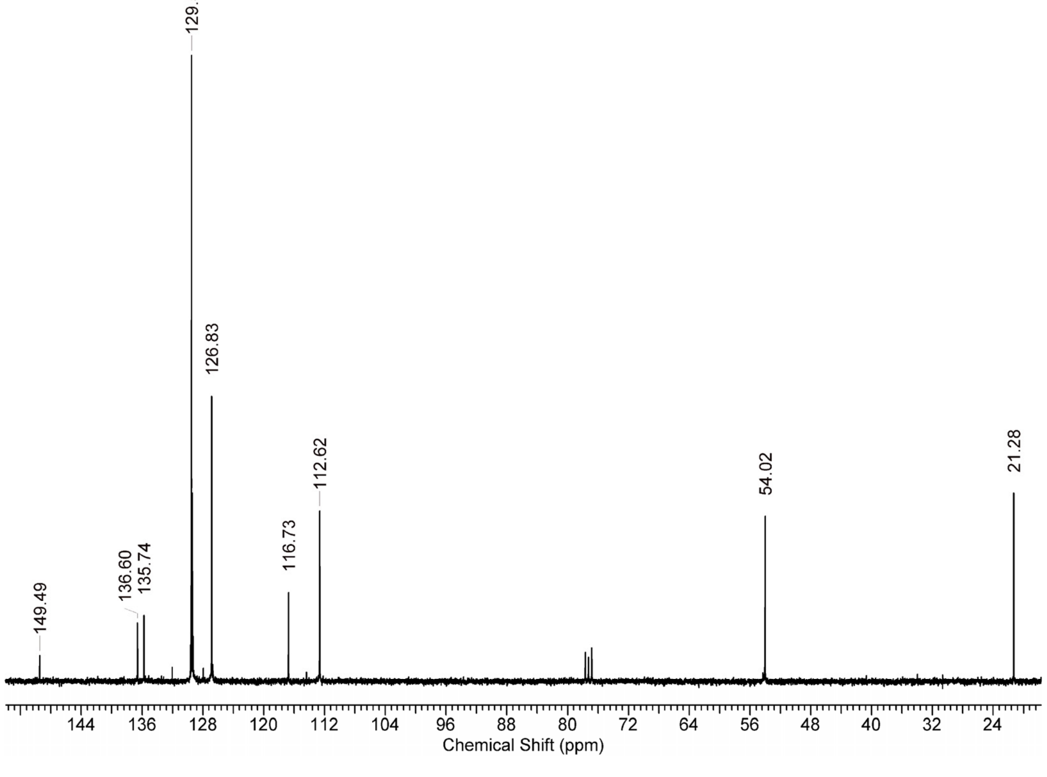
^{13}C NMR (125MHz, $CDCl_3$) of compound **2c**



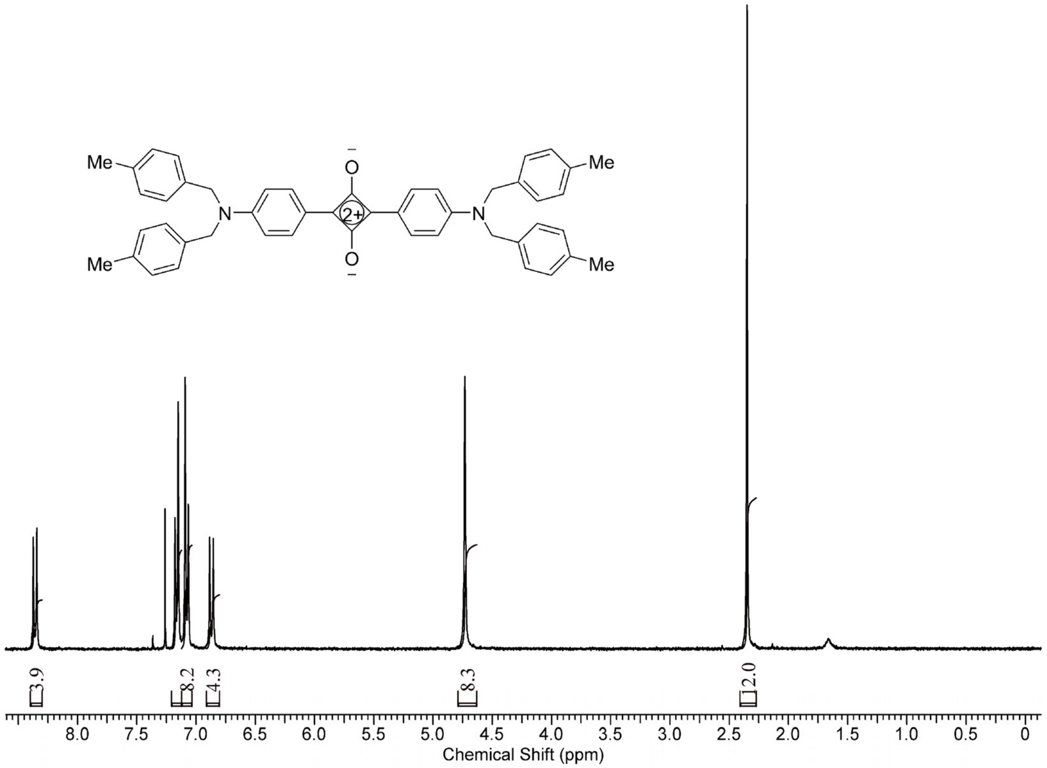
^{1}H NMR (300MHz, CDCl$_3$) of compound **6d**



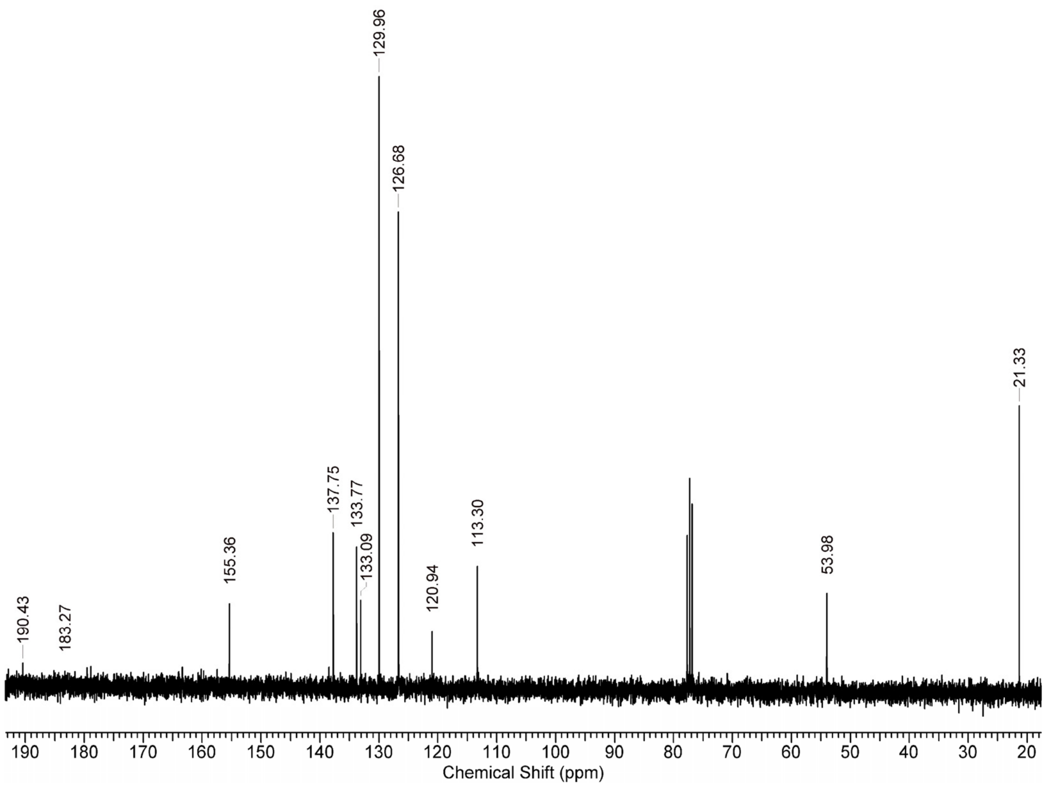
^{13}C NMR (75MHz, CDCl$_3$) of compound **6d**



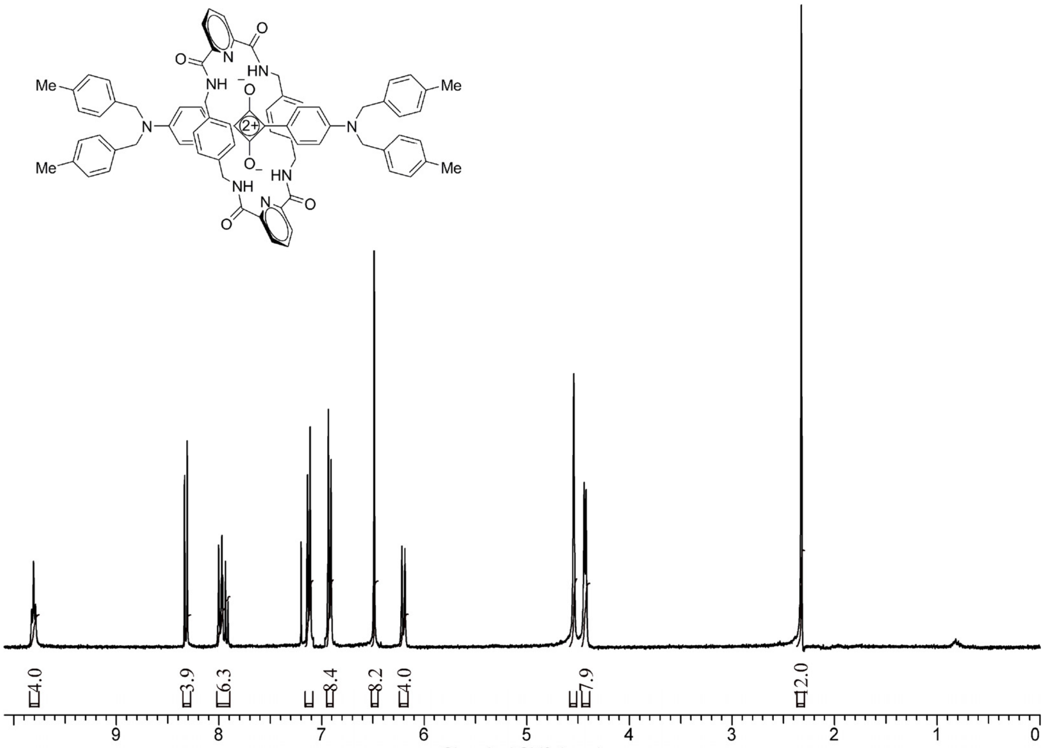
^{1}H NMR (300MHz, $CDCl_3$) of compound **1d**



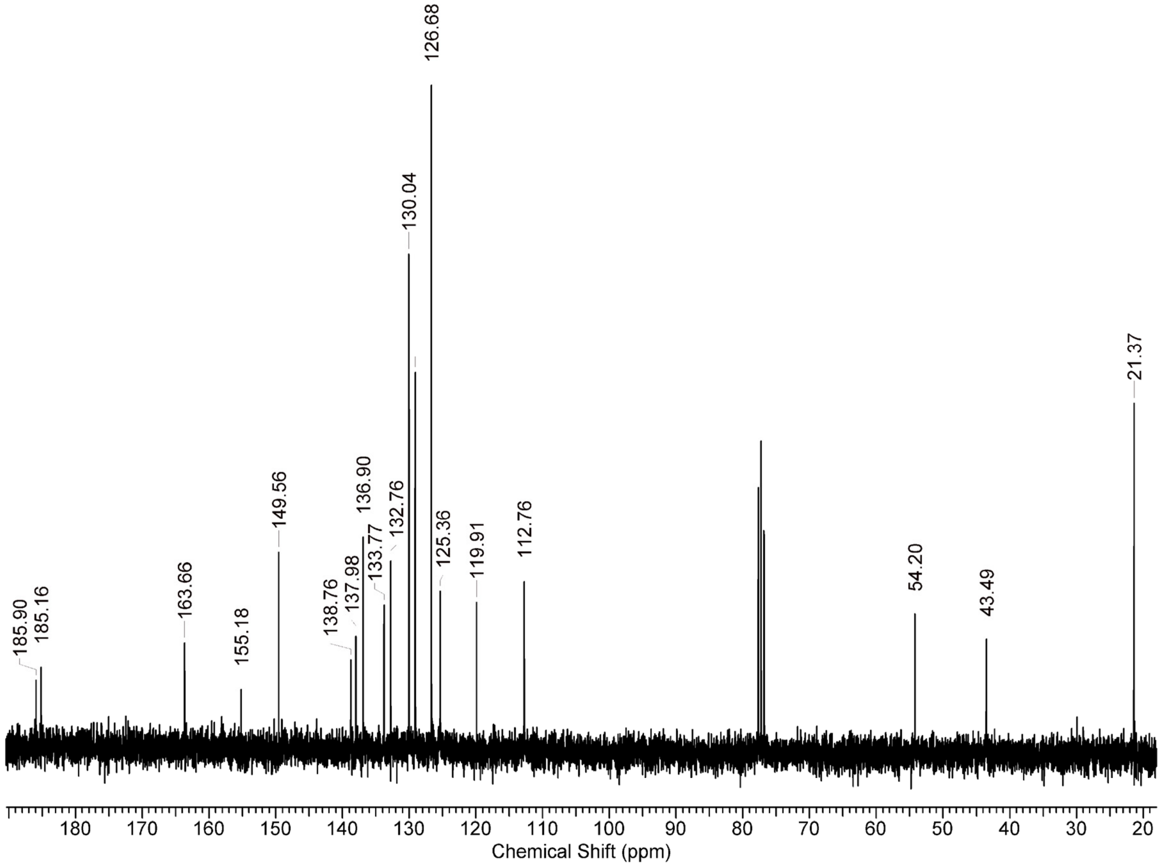
^{13}C NMR (75MHz, $CDCl_3$) of compound **1d**



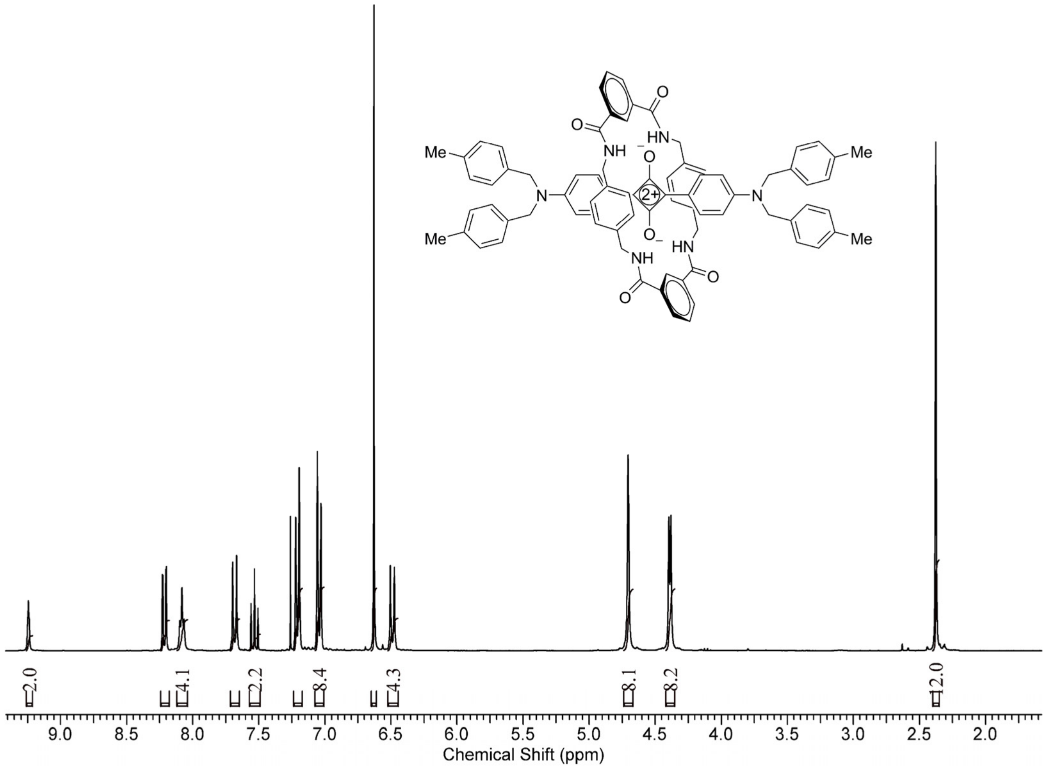
^{1}H NMR (300MHz, CDCl$_3$) of compound **2d**



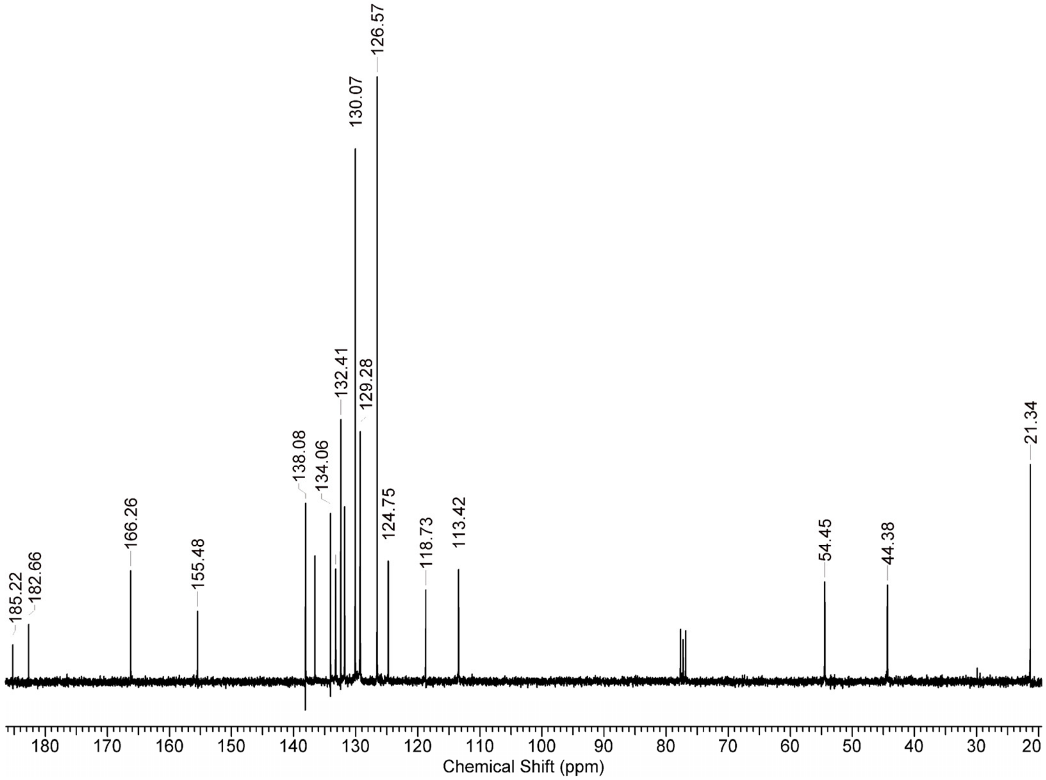
^{13}C NMR (75MHz, CDCl$_3$) of compound **2d**



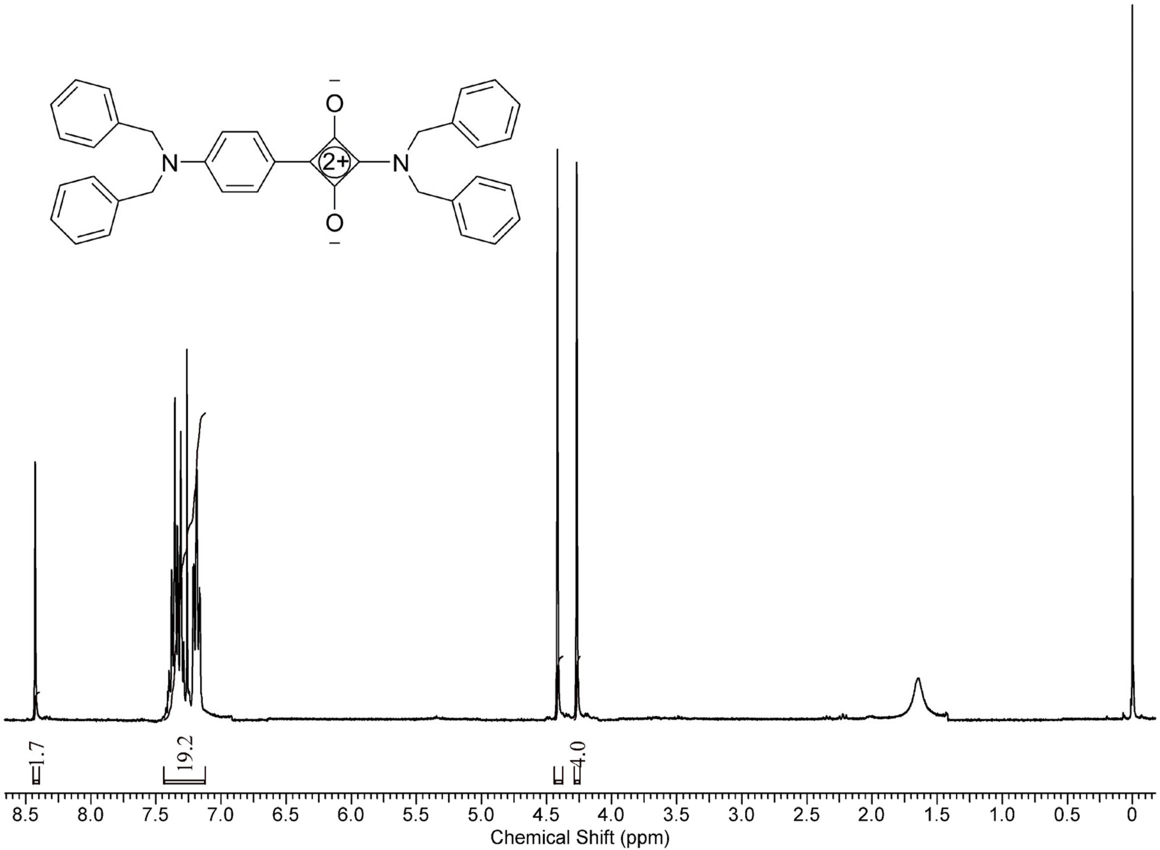
^{1}H NMR (300MHz, $CDCl_3$) of compound **2e**



^{13}C NMR (75MHz, $CDCl_3$) of compound **2e**

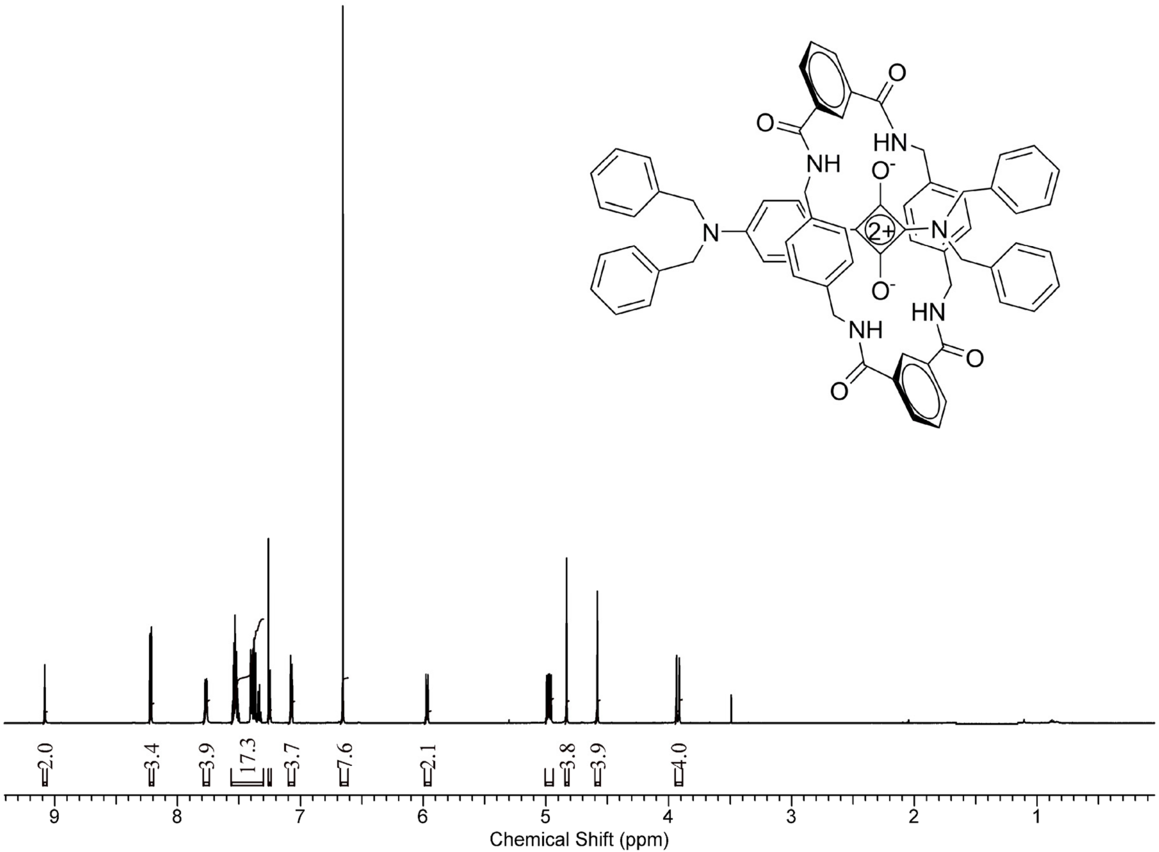


^{1}H NMR (300MHz, CDCl$_3$) of compound **4**

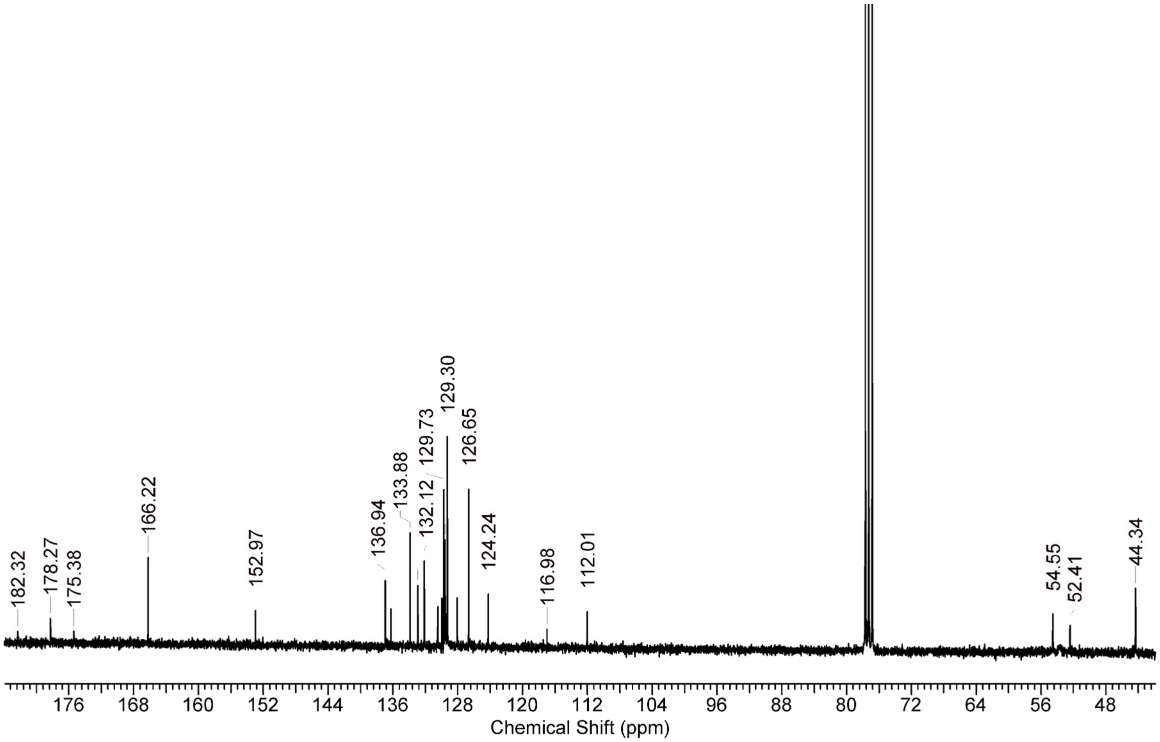


^{13}C NMR data was not acquired because of poor solubility

^{1}H NMR (600MHz, CDCl$_3$) of compound **5**



^{13}C NMR (150MHz, CDCl$_3$) of compound **5**



7. References

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