Electronic Supplementary Information for

Tetrahomo Corona[4]arene-based Spirophanes: Synthesis, Structure, and Properties

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1. General Information

Materials and Methods: Reagents and solvents were used as received. Glassware was dried in an oven (T = 120 °C). Anhydrous solvents were dried by shaking with 4A molecular sieves. 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.

Characterization: ^{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. The high-resolution mass spectra (HRMS) were recorded using a GCT-MS spectrometer, a microTOF-Q spectrometer or a MALDI-FT-ICR mass spectrometer. All yields reported were isolated yields. Crystallographic data were collected on a Rigaku XtaLAB Synergy (Cu) X-ray single crystal diffractometer. Melting points were uncorrected.

Chiral Chemistry: Resolution of racemic compounds and determination of enantiomeric excesses were carried out by HPLC using Daicel chiral stationary phase columns by comparing the samples with the appropriate racemic samples at 25 °C, column and elution details specified in each entry. The optical rotation was determined by Rudolph Autopol VI Automatic polarimeter. UV-vis absorption spectra were recorded using an Agilent® Cary-5000 UV-vis spectrophotometer at room temperature. Electronic circular dichroism (ECD) spectra were recorded on a JASCO J-815 spectropolarimeter at room temperature in a 1 cm-cuvette. Fluorescence spectra were recorded using an Agilent® Eclipse fluorescence spectrophotometer. Fluorescence quantum yields ϕ were measured in diluted solution with an optical density lower than 0.05 using the following equation:

$$\frac{\phi_x}{\phi_r} = \frac{A_r(\lambda)}{A_x(\lambda)} \times \frac{n_x^2}{n_r^2} \times \frac{F_x}{F_r}$$

Where *A* is the absorbance at the excitation wavelength (λ), *n* the refractive index, and

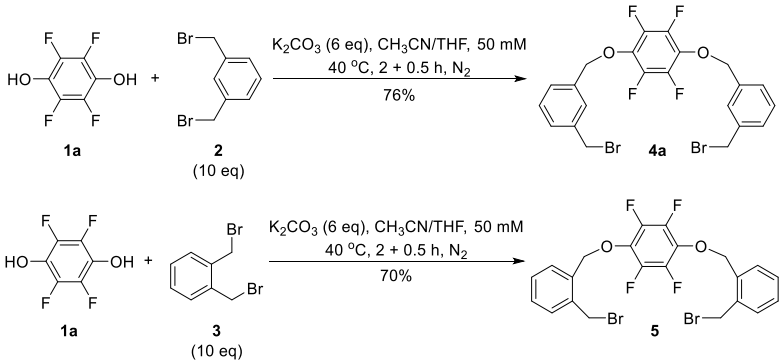
F the integrated intensity. r and x stand for reference and sample respectively. The fluorescence quantum yields were measured in solution relative quinine sulfate (ϕ = 57.7% in 0.1 M H_2SO_4)[1] and Rhodamine B (ϕ = 65.0% in ethanol)[2]. Excitation of reference and sample compounds was performed at 350 nm or 520 nm.

2. Experimental Procedures and Characterization of Products

Preparation of **6a**[3], **6b**[3], **11**[4], and **SI-2**[5] were carried out following the procedure reported in literature.

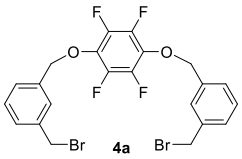
2.1 Synthesis of dibromide intermediates 4 and 5

Procedure A: Synthesis of **4a** and **5**:



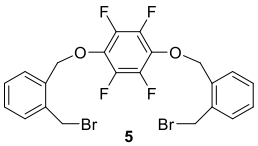
2 or **3** (13.20 g, 50 mmol, 10 equiv.), K_2CO_3 (4.15 g, 30 mmol, 6 equiv.), and anhydrous acetonitrile (75 mL) were put into a 250 mL dry two-necked round bottom flask under N_2 atmosphere. To this mixture at 40 °C was added dropwise a solution of **1a** (0.91 mg, 5 mmol, 1 equiv.) in anhydrous acetonitrile (25 mL) and tetrahydrofuran (25 mL) over 2 hours. The resulting mixture was stirred vigorously for 30 minutes and then cooled to room temperature. Brine (100 mL) and 2N HCl (30 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (200 mL × 1, 50 mL × 3). 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 petroleum ether and dichloromethane (v : v = 9 : 1 – 7 : 3) as the mobile phase to give first the recovered bis(bromomethyl)benzene **2** or **3** and then target product **4a** or **5**. (**Caution! 2** and **3** cause serious eye irritation. Reactions and columns must be performed in a well ventilated fume hood.)

4a (2.08 g, 76%; 10.01 g, 7.6 equiv. of **2** was recovered): white solid, m.p. 143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.44 (s, 2H), 7.40 - 7.32 (m, 6H), 5.14 (s, 4H), 4.49 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 142.0 (dddd, J = 250, 16, 7, 3 Hz), 138.4, 136.5, 132.5 (tt, J = 11, 4 Hz), 129.6, 129.3, 129.0, 128.5, 76.4, 33.2; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.8. **IR** (KBr): ν 2962, 2920, 2846, 1500, 1382 cm^{-1}. **HRMS** (ESI) Calculated for $[M+Na]^+$: 568.9345, Found: 568.9346.



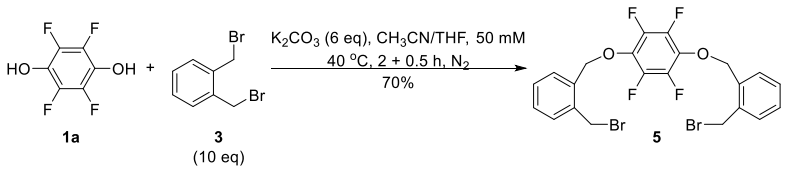
4a

5 (1.91 g, 70%; 10.50 g, 8.0 equiv. of **3** was recovered): white solid, m.p. 150-151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.44 - 7.28 (m, 8H), 5.31 (s, 4H), 4.72 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 142.2 (dddd, J = 230, 19, 4, 3 Hz), 137.1, 134.2, 132.4 (tt, J = 9, 6 Hz), 131.0, 130.8, 129.9, 129.2, 74.1, 30.5; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.6. **IR** (KBr): ν 2920, 2893, 2850, 1504, 1377 cm^{-1}. **HRMS** (ESI) Calculated for $[M+Na]^+$: 568.9345, Found: 568.9350.



5

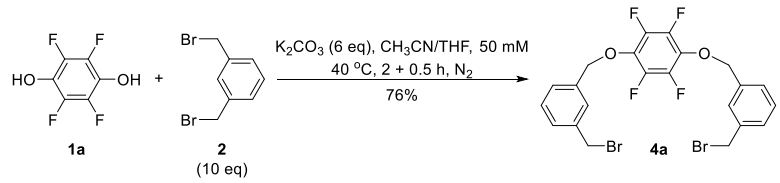
Table S1. Optimization of the synthesis of **4a** and **5**



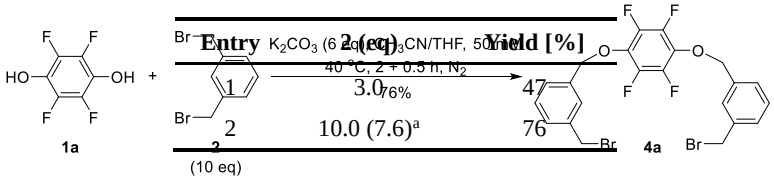
Entry	3 (eq)	Temp.	PTC (eq)	Base (eq)	Time	Yield [%]
1	3.0	rt	--	K_2CO_3 (6.0)	12 + 12 h[a]	29
2	3.0	40 °C	--	K_2CO_3 (6.0)	2 + 0.5 h	33
3	3.0	60 °C	--	K_2CO_3 (6.0)	2 + 0.5 h	30
4	3.0	reflux	--	K_2CO_3 (6.0)	2 + 0.5 h	30
5	3.0	40 °C	TEABr (1.0)	K_2CO_3 (6.0)	2 + 0.5 h	29
6	3.0	rt	--	K_2CO_3 (4.0)	12 + 12 h	23
7	3.0	40 °C	--	K_2CO_3 (8.0)	2 + 0.5 h	32
8	3.0	40 °C	--	K_2CO_3 (6.0)	2 + 2 h	31
9	5.0 (3.1)[a]	40 °C	--	K_2CO_3 (6.0)	2 + 0.5 h	51
10	**10.0 (8.0)**	**40 °C**	**--**	**K_2CO_3 (6.0)**	**2 + 0.5 h**	**70**
11[b]	10.0 (8.1)	40 °C	--	K_2CO_3 (6.0)	2 + 0.5 h	67

[a] 5.0 equiv. of **3** were used and 3.1 equiv. were recovered. [b] Bubble nitrogen through the solvent for 30 minutes.

Table S2. Optimization of the synthesis of **1a** and **2**

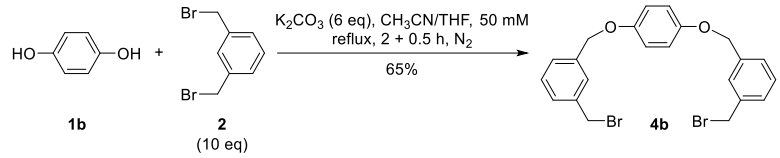


Entry	2 (eq)	Yield [%]
1	3.0	47
2	10.0 (7.6)[a]	76

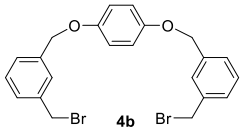


[a] 10.0 equiv. of **2** were used and 7.6 equiv. were recovered.

Procedure B: Synthesis of **4b**



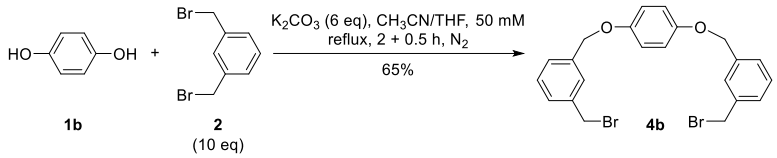
2 (26.40 g, 100 mmol, 10 equiv.), K_2CO_3 (8.30 g, 60 mmol, 6 equiv.), and anhydrous acetonitrile (150 mL) were put into a 500 mL dry two-necked round bottom flask under N_2 atmosphere. To this mixture under reflux was added dropwise a solution of **1b** (1.10 g, 10 mmol, 1 equiv.) in anhydrous acetonitrile (50 mL) and tetrahydrofuran (50 mL) over 2 hours. The resulting mixture was stirred vigorously for 30 minutes and then cooled to room temperature. Brine (200 mL) and 2N HCl (60 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (400 mL × 1, 50 mL × 3). 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 petroleum ether and dichloromethane (v : v = 9 : 1 – 1 : 1) as the mobile phase to give first the recovered **2** (20.32 g, 7.7 equiv.) and then **4b** (3.11 g, 65%). (**Caution! 2** causes serious eye irritation. Reactions and columns must be performed in a well ventilated fume hood.)



4b: white solid, m.p. 137-138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.46 (s, 2H), 7.36 (s, 6H), 6.91 (s, 4H), 5.01 (s, 4H), 4.51 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 153.2, 138.2, 138.1, 129.2, 128.7, 128.1, 127.6, 115.9, 70.4, 33.5. **IR** (KBr): ν 2920, 2869, 1507, 1471, 1384, 1232, 1208 cm^{-1}. **HRMS** (ESI) Calculated for $[M+Na]^+$: 496.9722, Found:

496.9726.

Table S3. Optimization of the condensation reaction between **1b** and **2**

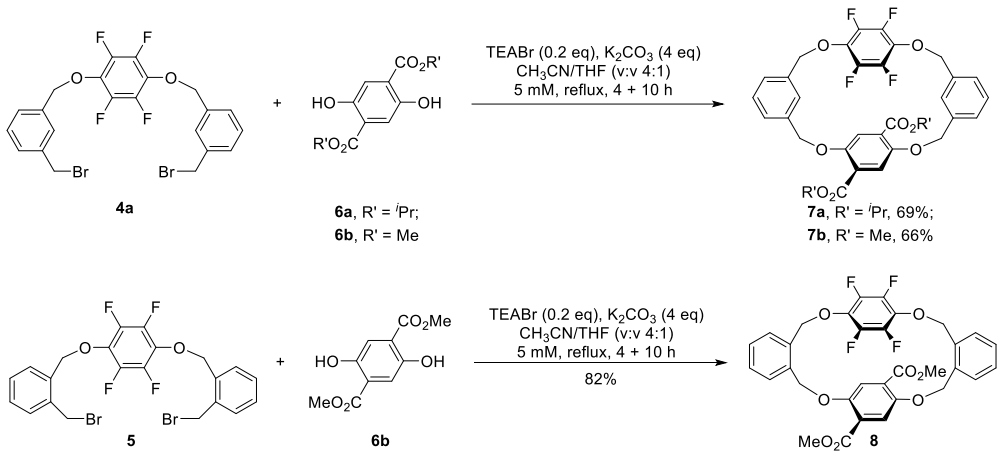


Entry	3 (eq)	Temp.	Yield [%]
1	10.0 (8.5)[a]	40 °C	39
2	10.0 (7.7)	reflux	65

[a] 10.0 equiv. of **3** were used and 8.5 equiv. were recovered.

2.2 Synthesis of homo *i*-corona[4]arenes 7a-f and 8

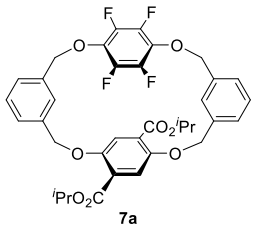
Procedure A: Synthesis of **7a**, **7b**, and **8**



Synthesis of **7a**. TEABr (10.5 mg, 0.05 mmol, 0.2 equiv.), K_2CO_3 (138.2 mg, 1.0 mmol, 4 eq), and anhydrous acetonitrile (25 mL) were put into a 100 mL dry two-necked round bottom flask under ambient atmosphere. To this mixture under reflux was added dropwise a solution of **4a** (137.0 mg, 0.25 mmol, 1 equiv.) and **6a** (70.6 mg, 0.25 mmol, 1 equiv.) in anhydrous acetonitrile (15 mL) and tetrahydrofuran (10 mL) over 4 hours. The resulting mixture was stirred vigorously for 10 hours and then cooled to room temperature. Brine (50 mL) and 2N HCl (1 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (100 mL × 1, 20 mL × 3). 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 petroleum ether and ethyl acetate (v : v = 17 : 3) as the mobile phase to give

pure product **7a** (109.5mg, 66%).

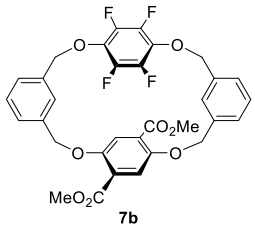
7a: white solid, m.p. 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.36-7.27 (m, 8H), 7.19 (s, 2H), 5.34 (d, *J* = 14.2 Hz, 2H), 5.20 (d, *J* = 12.8 Hz, 2H), 5.17 (hept, *J* = 6.0 Hz, 2H), 5.16 (d, *J* = 14.2 Hz, 2H), 5.06 (d, *J* = 12.8 Hz, 2H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.31 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 164.5, 150.6, 141.4 (dddd, *J* = 240, 15, 9, 3 Hz), 137.3, 136.9, 131.6 (tt, *J* = 9, 4 Hz), 128.8, 127.6, 127.6, 126.6, 124.9, 118.1, 75.8, 70.5, 68.7, 22.0, 21.9; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.7. **IR** (KBr): ν 2922, 2966, 2854, 1723, 1501, 1232 cm^{-1}. **HRMS** (ESI) Calculated for $[M]^-$: 668.2039, Found: 668.2039. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21, t_1 = 16.9 min, $[\alpha]_D^{25}$ = -26.9 (*c* 0.6, DCM), t_2 = 20.0 min, $[\alpha]_D^{25}$ = +26.9 (*c* 0.6, DCM).



7a

Synthesis of **7b**. Follow the general procedure. **4a** (274.1 mg, 0.5 mmol) and **6b** (113.1 mg, 0.5 mmol) were used. The resulting residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (v : v = 4 : 1) as the mobile phase to give pure product **7b** (211.0 mg, 69%).

7b: white solid, m.p. 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.36-7.27 (m, 8H), 7.19 (s, 2H), 5.34 (d, *J* = 14.2 Hz, 2H), 5.20 (d, *J* = 12.8 Hz, 2H), 5.17 (hept, *J* = 6.0 Hz, 2H), 5.16 (d, *J* = 14.2 Hz, 2H), 5.06 (d, *J* = 12.8 Hz, 2H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.31 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 164.5, 150.6, 141.4 (dddd, *J* = 240, 15, 9, 3 Hz), 137.3, 136.9, 131.6 (tt, *J* = 9, 4 Hz), 128.8, 127.6, 127.6, 126.6, 124.9, 118.1, 75.8, 70.5, 68.7, 22.0, 21.9; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.7. **IR** (KBr): ν 2953, 2921, 2850, 1730, 1500 cm^{-1}. **HRMS** (ESI) Calculated for $[M]^-$: 668.2039, Found: 668.2039.

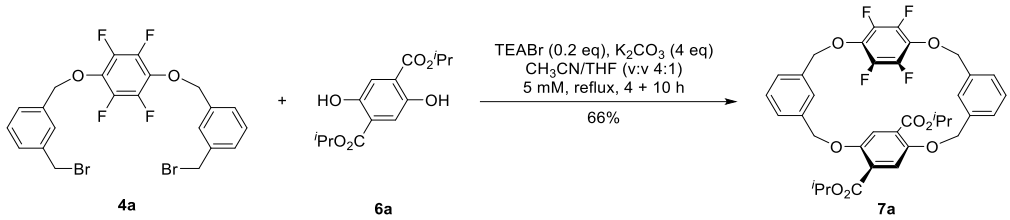


7b

Synthesis of **8**. Follow the general procedure. The resulting residue was chromatographed on a silica gel column with a mixture of petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 3 : 3 : 14) as the mobile phase to give pure product **8**. **5** (1.0964 g, 2 mmol) and **6b** (452.4 g, 2 mmol) were used to give **8** (901.2 g ,74%) while a gram-scale synthesis using **5** (2.7408 g, 5 mmol) and **6b** (1.1305

g, 5 mmol) gave **8** (2.5008 g ,82%).

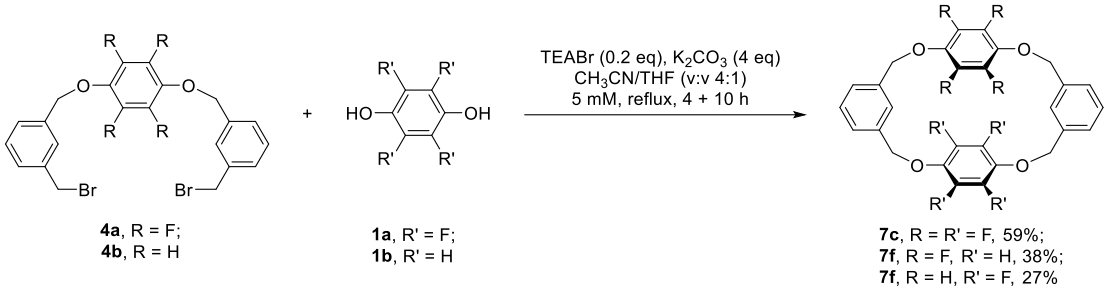
Table S4. Optimization of the macrocyclization reaction between **4a** and **6a**



Entry	Temp.	PTC (eq)	Solv.	Base (eq)	Time	Conc.	Yield [%]
1	reflux	--	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	39
2	reflux	CTAB (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	55
3	60 ºC	CTAB (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	8 + 16 h	5 mM	57
4	40 ºC	CTAB (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	8 + 40 h	5 mM	50
5	rt	CTAB (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	8 + 16 h	5 mM	NR
6	reflux	TBABr (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	54
7	reflux	TEABr (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	57
8	reflux	TMABr (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	56
9	reflux	TEACl (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	42
10	reflux	TEAI (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	51
11	reflux	$TEANO_3$ (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	42
12	reflux	$TEABF_4$ (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	27
13	reflux	$TEAPF_6$ (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	23
14	reflux	AOT (1.0)	CH_3CN/THF (1:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	NR
15	reflux	TEABr (1.0)	THF	K_2CO_3 (6.0)	4 + 10 h	5 mM	NR
16	reflux	TEABr (1.0)	$CHCl_3$	K_2CO_3 (6.0)	4 + 10 h	5 mM	NR
17	reflux	TEABr (1.0)	CH_3CN/THF (4:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	66
18	reflux	TEABr (1.0)	CH_3CN/THF (4:1)	Na_2CO_3 (6.0)	4 + 10 h	5 mM	NR
19	reflux	TEABr (1.0)	CH_3CN/THF (4:1)	Cs_2CO_3 (6.0)	4 + 1 h	5 mM	52
20	reflux	TEABr (1.0)	CH_3CN/THF (4:1)	K_3PO_4 (6.0)	4 + 1 h	5 mM	53
21	reflux	TEABr (0.2)	CH_3CN/THF (4:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	63
22	reflux	TEABr (0.1)	CH_3CN/THF (4:1)	K_2CO_3 (6.0)	4 + 10 h	5 mM	52
23	**reflux**	**TEABr (0.2)**	**CH_3CN/THF (4:1)**	**K_2CO_3 (4.0)**	**4 + 10 h**	**5 mM**	**66**
24	reflux	TEABr (0.2)	CH_3CN/THF (4:1)	K_2CO_3 (2.5)	4 + 10 h	5 mM	40
25	reflux	TEABr (0.2)	CH_3CN/THF (4:1)	K_2CO_3 (4.0)	4 + 10 h	2.5 mM	55
26	reflux	TEABr (0.2)	CH_3CN/THF (4:1)	K_2CO_3 (4.0)	4 + 10 h	10 mM	57
27	reflux	TEABr (0.2)	CH_3CN/THF (4:1)	K_2CO_3 (4.0)	8 + 10 h	5 mM	63

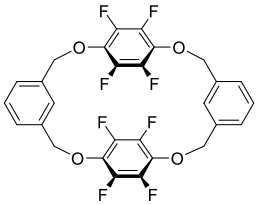
8: white solid, m.p. 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.36-7.27 (m, 8H), 7.19 (s, 2H), 5.34 (d, *J* = 14.2 Hz, 2H), 5.20 (d, *J* = 12.8 Hz, 2H), 5.17 (hept, *J* = 6.0 Hz, 2H), 5.16 (d, *J* = 14.2 Hz, 2H), 5.06 (d, *J* = 12.8 Hz, 2H), 1.33 (d, *J* = 6.0 Hz, 6H), 1.31 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 164.5, 150.6, 141.4 (dddd, *J* = 240, 15, 9, 3 Hz), 137.3, 136.9, 131.6 (tt, *J* = 9, 4 Hz), 128.8, 127.6, 127.6, 126.6, 124.9, 118.1, 75.8, 70.5, 68.7, 22.0, 21.9; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.7. **IR** (KBr): ν 2957, 2919, 2849, 1740, 1506, 1200 cm^{-1}. **HRMS** (ESI) Calculated for $[M]^-$: 668.2039, Found: 668.2039. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21, t_1 = 16.5 min, $[\alpha]_D^{25}$ = +32.4 (*c* 0.6, DCM), t_2 = 40.0 min, $[\alpha]_D^{25}$ = -32.4 (*c* 0.6, DCM).

Procedure B: Synthesis of **7c** and **7f**



Synthesis of **7c**. Acetonitrile and tetrahydrofuran were bubbled with nitrogen for 30 minutes. TEABr (10.5 mg, 0.05 mmol, 0.2 equiv.), K_2CO_3 (138.2 mg, 1.0 mmol, 4 eq), and anhydrous acetonitrile (25 mL) were put into a 100 mL dry two-necked round bottom flask under N_2 atmosphere. To this mixture under reflux was added dropwise a solution of **4a** (137.0 mg, 0.25 mmol, 1 equiv.) and **1a** (45.5 mg, 0.25 mmol, 1 equiv.) in anhydrous acetonitrile (15 mL) and tetrahydrofuran (10 mL) over 4 hours. The resulting mixture was stirred vigorously for 10 hours and then cooled to room temperature. Brine (50 mL) and 2N HCl (1 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (100 mL × 1, 20 mL × 3). 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 petroleum ether and dichloromethane (v : v = 3 : 2) as the mobile phase to give pure product **7c** (84.0 mg, 59%).

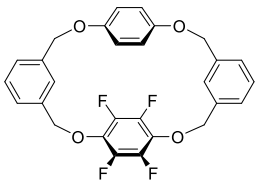
7c: white solid, m.p. 169-170 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.35 (s, 2H), 7.18 (m, 6H), 5.20 (s, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 141.5 (m), 135.8, 130.6 (m), 128.9, 128.8, 128.4, 74.7; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.9. **IR** (KBr): ν 2958, 2920, 2846, 1500, 1465 cm^{-1}. **HRMS** (APCI) Calculated for $[M]^-$: 568.0915, Found: 568.0903.



7c

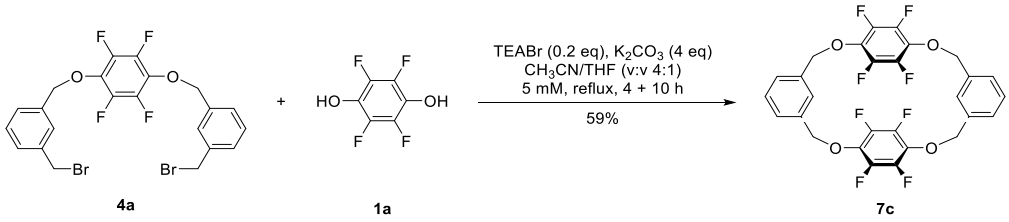
Synthesis of **7f**. Follow the general procedure. **I. 4a** (137.0 mg, 0.25 mmol) and **1b** (27.5 mg, 0.25 mmol) were used to produce **7f** (47.7 mg, 38%). **II. 4b** (119.1 mg, 0.25 mmol) and **1a** (45.5 mg, 0.25 mmol) were used to produce **7f** (33.0 mg, 27%). The resulting residue was chromatographed on a silica gel column with a mixture of petroleum ether and dichloromethane (v : v = 3 : 2 – 1 : 1) as the mobile phase to give pure product **7f**.

7f: white solid, m.p. 198-200 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.48 (s, 2H), 7.20 – 7.14 (m, 4H), 7.10 – 7.06 (m, 2H), 6.58 (s, 4H), 5.24 (s, 4H), 5.12 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 151.6 141.4 (dddd, J = 248, 16, 9, 4 Hz), 138.5 136.1, 130.9 (tt, J = 9, 6 Hz), 128.5, 127.3, 127.0, 126.3, 116.2, 74.9, 69.7; **^{19}F NMR** (367 MHz, $CDCl_3$): δ -156.8. **IR** (KBr): ν 2958, 2921, 2896, 2851, 1499, 1470 cm^{-1}. **HRMS** (APCI) Calculated for $[M]^-$: 497.1370, Found: 497.1365.



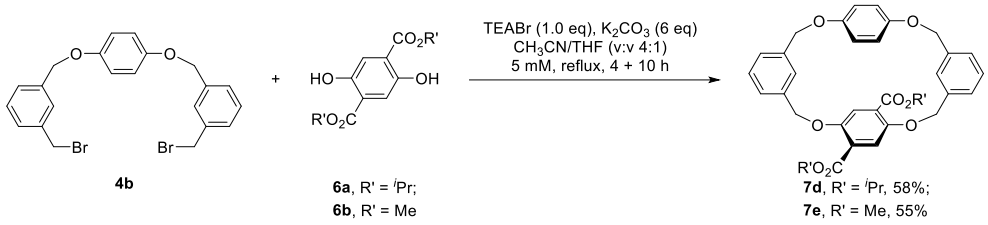
7f

Table S5. Optimization of the macrocyclization reaction between **4a** and **1a**



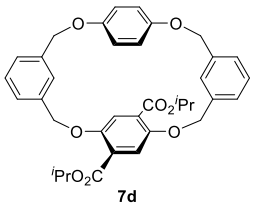
Entry	Solv.	Treatment of Solvents	Yield [%]
1	CH_3CN/THF (4:1)	-	8
2	CH_3CN/THF (4:1)	Bubbled with nitrogen	59

Procedure C: Synthesis of **7d** and **7e**



Synthesis of **7d**. TEABr (52.5 mg, 0.25 mmol, 1.0 equiv.), K_2CO_3 (207.3 mg, 1.5 mmol, 6 eq), and anhydrous acetonitrile (25 mL) were put into a 100 mL dry two-necked round bottom flask under ambient atmosphere. To this mixture under reflux was added dropwise a solution of **4b** (119.1 mg, 0.25 mmol, 1 equiv.) and **6a** (70.6 mg, 0.25 mmol, 1 equiv.) in anhydrous acetonitrile (15 mL) and tetrahydrofuran (10 mL) over 4 hours. The resulting mixture was stirred vigorously for 10 hours and then cooled to room temperature. Brine (50 mL) and 2N HCl (1 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (100 mL × 1, 20 mL × 3). 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 petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 8 : 1 : 1) as the mobile phase to give pure product **7d** (86.4 mg, 58%).

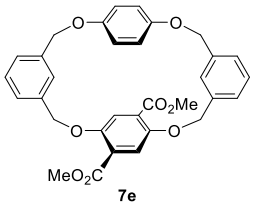
7d: white solid, m.p. 160-162 °C. **^{1}H NMR** (400 MHz, DMSO-d_6, TMS): δ 7.47 (s, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.27 (s, 2H), 7.27 – 7.22 (dd, J = 7.4, 7.4 Hz, 2H), 7.16 (d, J = 7.4 Hz, 2H), 5.34 (d, J = 14.0 Hz, 2H), 5.18 (d, J = 14.0 Hz, 2H), 5.12 (hept, J = 6.2 Hz, 2H), 5.04 (d, J = 14.2 Hz, 2H), 4.98 (d, J = 14.0 Hz, 2H), 1.34 (d, J = 6.2 Hz, 6H), 1.33 (d, J = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 164.9, 152.6, 150.1, 139.1, 137.2, 129.1, 126.9, 126.5, 126.1, 125.0, 117.4, 116.4, 70.9, 70.0, 68.9, 22.1. **IR** (KBr): ν 2958, 2921, 2850, 1721, 1500, 1468 cm^{-1}. **HRMS** (APCI) Calculated for [M]$^-$: 596.2416, Found: 596.2418. **HPLC**: IA column, 25 °C, 0.5 mL/ flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21, t_1 = 21.3 min, $[\alpha]_D^{25}$ = -17.2 (c 0.6, DCM), t_2 = 24.2 min, $[\alpha]_D^{25}$ = +17.2 (c 0.6, DCM).



Synthesis of **7e**. Follow the general procedure. **4b** (1.0953 g, 2.30 mmol) and **6b** (520.2 mg, 2.30 mmol) were used. The resulting residue was chromatographed on a silica gel

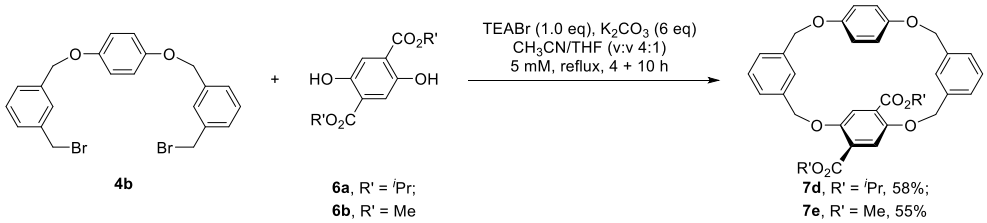
column with a mixture of dichloromethane and ethyl acetate (v : v = 25 : 1) as the mobile phase to give pure product **7e** (678.7 mg, 55%).

7e: white solid, m.p. 169-170 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.46 (s, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.19 (m, 6H), 6.40 (s, 4H), 5.34 (d, *J* = 13.8 Hz, 2H), 5.18 (d, *J* = 13.8 Hz, 2H), 5.06 (d, *J* = 14.6 Hz, 2H), 4.99 (d, *J* = 14.6 Hz, 2H), 3.90 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 165.8, 152.3, 150.0, 138.9, 136.8, 129.0, 126.8, 126.3, 125.9, 124.4, 117.3, 116.0, 70.4, 69.8, 52.4. **IR** (KBr): ν 2950, 2921, 2850, 1733, 1504, 1376 cm^{-1}. **HRMS** (APCI) Calculated for $[M]^-$: 540.1779, Found: 540.1776.



7e

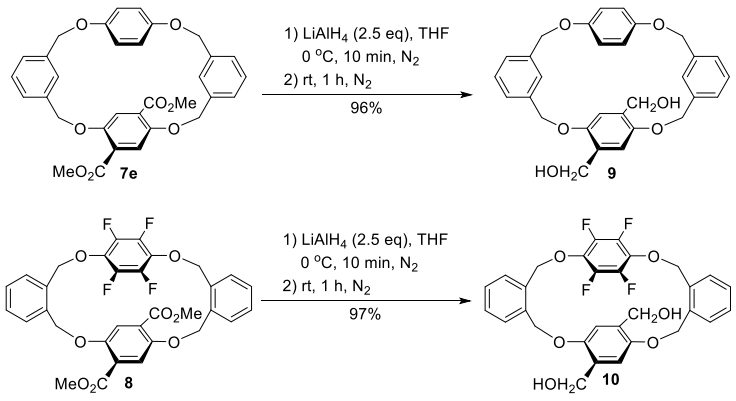
Table S6. Optimization of the macrocyclization reaction between **4b** and **6a, b**



Entry	R'	PTC (eq)	Base (eq)	Yield [%]
1	^{i}Pr	TEABr (0.2)	K_2CO_3 (4.0)	40
2	^{i}Pr	TEABr (1.0)	K_2CO_3 (6.0)	58
3	Me	TEABr (0.2)	K_2CO_3 (4.0)	37
4	Me	TEABr (1.0)	K_2CO_3 (6.0)	55

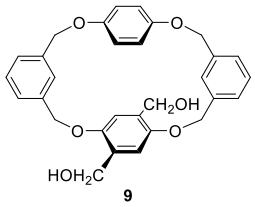
2.3 Synthesis of ditopic spirophanes 15 and 16

Procedure A: Synthesis of diols **9** and **10**



Synthesis of **9**. **7e** (359.0 mg, 0.66 mmol) and anhydrous tetrahydrofuran (33 mL) were put into a 100 mL dry two-necked round bottom flask under nitrogen atmosphere. To this solution under ice bath was added $LiAlH_4$ (63.0 mg, 1.66 mmol, 2.5 equiv.) in portions over 10 minutes. The resulting mixture was warmed to room temperature and stirred for 1 hour. The mixture was again cooled in an ice bath and ammonia (1 mL) was added dropwise to quench the reaction. 2N HCl (20 mL) and brine (50 mL) was added and the mixture was extracted with ethyl acetate (150 mL × 1, 20 mL × 3). The organic phases were then combined and dried over anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was recrystallized with dichloromethane and petroleum ether to give pure product **9** (307.1 mg, 96%). (The residue should be cooled to room temperature because **9** does not precipitate in hot solvents.)

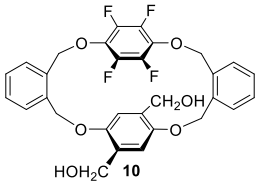
9: white solid, m.p. 161-164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): 7.37 (s, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 6.66 (s, 2H), 6.44 (s, 4H), 5.16 (s, 4H), 5.05 (s, 4H), 4.43 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 152.5, 148.7, 138.9, 137.9, 129.4, 129.1, 126.9, 125.9, 125.4, 116.1, 112.9, 70.4, 69.2, 61.8. **IR** (KBr): ν 3362, 2920, 2850, 1504, 1023 cm^{-1}. **HRMS** (APCI) Calculated for $[M]^-$: 484.1891, Found: 484.1884.



9

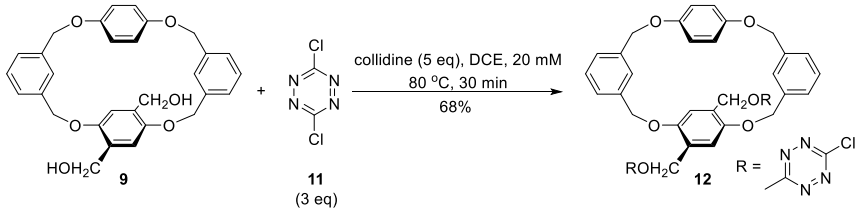
Synthesis of **10**. Follow the general procedure. **8** (813.0 mg, 1.33 mmol) was used to produce **10** (712.9 mg, 97%).

10: white solid, m.p. 238-240 °C. **^{1}H NMR** (400 MHz, DMSO-d_6, TMS): δ 7.59 - 7.43 (m, 8H), 6.95 (s, 2H), 5.44 (d, J = 11.0 Hz, 2H), 5.31 (d, J = 11.0 Hz, 2H), 5.12 (d, J = 11.0 Hz, 2H), 5.07 (d, J = 11.0 Hz, 2H), 5.01 (dd, J = 5.3, 4.7 Hz, 2H), 4.43 (dd, J = 13.5, 4.7 Hz, 2H), 4.26 (dd, J = 13.5, 5.3 Hz, 2H); **^{13}C NMR** (101 MHz, acetone-d_6, TMS): δ 151.8, 141.0 (m), 137.3, 136.6, 133.6 (tt, J = 9, 3 Hz), 131.8, 131.6, 130.8, 130.2, 129.7, 113.5, 76.5, 71.8, 59.2; **^{19}F NMR** (367 MHz, DMSO-d_6, 120 °C): δ -157.5. **IR** (KBr): ν 3423, 2955, 2920, 1636, 1500, 1039 cm^{-1}. **HRMS** (APCI) Calculated for $[M-H]^-$: 555.1436, Found: 555.1428. **HPLC** ID column, 25 °C, 0.5 mL/min flow rate, ^{i}PrOH : Hexane = 2 : 3, t_1 = 19.1 min, t_2 = 25.4 min.



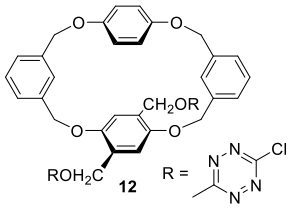
10

Procedure B: Synthesis of **12**



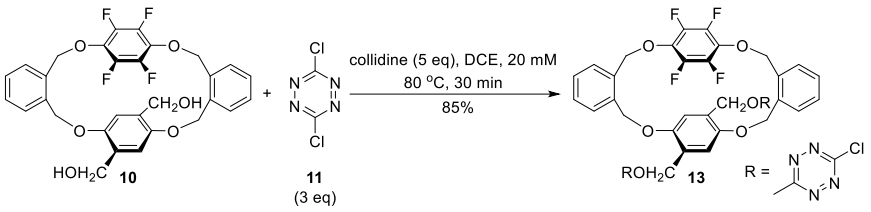
11 (135.9 mg, 0.90 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane (1 mL) were put into a 50 mL dry two-necked round bottom flask under ambient atmosphere. To this solution at 80 °C was added first collidine (198 μL, 1.50 mmol, 5 equiv.) and subsequently dropwise a solution of **9** (145.4 mg, 0.30 mmol, 1 equiv.) in anhydrous 1,2-dichloroethane (14 mL) over 30 minutes. The resulting dark red mixture was cooled to room temperature. Brine (50 mL) and 2N HCl (0.75 mL) were added to quench the reaction, and the mixture was extracted with dichloromethane (50 mL × 3). 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 petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 6 : 3 : 1) as the mobile phase to give the pure product **12** (144.8 mg, 68%).

12: red solid, m.p. 148-149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.41 (s, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 2H), 6.25 (s, 4H), 5.61 (d, *J* = 12.0 Hz, 2H), 5.52 (d, *J* = 12.0 Hz, 2H), 5.30 (d, *J* = 14.0 Hz, 2H), 5.10 (d, *J* = 14.0 Hz, 2H), 5.02 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 166.4, 164.3, 152.5, 149.0, 139.3, 137.1, 129.2, 126.4, 126.1, 125.0, 123.9, 116.0, 114.2, 70.6, 69.2, 67.3. **IR** (KBr): ν 2921, 2850, 1504, 1477 cm^{-1}. **HRMS** (ESI) Calculated for $[M+Na]^+$: 735.1246, Found: 735.1245. **HPLC** IB column, 25 °C, 0.5 mL/min flow rate, DCM : Hexane = 2 : 3, t_1 = 17.0 min, t_2 = 18.3 min.



Procedure C: Synthesis of **13**

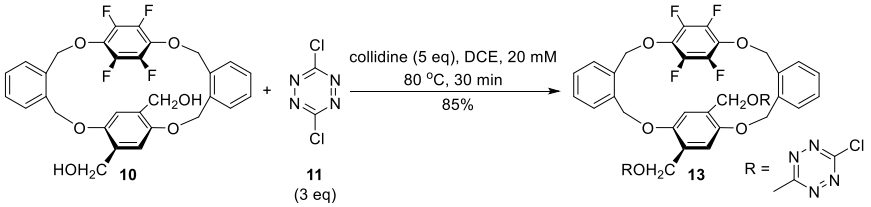
In this procedure, diol **10** was added in one portion instead of dropwise, because **10** has poor solubility in 1,2-dichloroethane and it dissolved along with the consummation in the reaction so that polymerization reactions were restrained.



11 (181.1 mg, 1.20 mmol, 3 equiv.), **10** (222.6 mg, 0.40 mmol, 1 equiv.), and anhydrous 1,2-dichloroethane (20 mL) were put into a 50 mL dry two-necked round bottom flask under ambient atmosphere. To this mixture at 80 °C was added collidine (264 μL, 2.00 mmol, 5 equiv.). The resulting dark red mixture was stirred for 30 minutes and cooled to room temperature. Brine (50 mL) and 2N HCl (1 mL) were added to quench the reaction, and the mixture was extracted with dichloromethane (50 mL × 3). 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 dichloromethane as the mobile phase to give the pure product **13** (267.8 mg, 85%).

13: red solid, m.p. 207-209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.55-7.50 (m, 2H), 7.46-7.40 (m, 6H), 7.06 (s, 2H), 5.71 (d, J = 12.6 Hz, 2H), 5.49 (d, J = 12.6 Hz, 2H), 5.45 (d, J = 11.4 Hz, 2H), 5.32 (d, J = 11.4 Hz, 2H), 5.25 (d, J = 11.4 Hz, 2H), 5.09 (d, J = 11.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 166.7, 164.6, 151.7, 140.4 (dddd, J = 245, 14, 5, 3 Hz), 135.2, 134.9, 132.5 (tt, J = 9, 3 Hz), 131.1, 130.7, 129.7, 129.4, 124.7, 115.3, 75.2, 71.7, 66.9; **^{19}F NMR** (367 MHz, DMSO-d_6, 120 °C): δ -156.9. **IR** (KBr): ν 2854, 2921, 2850, 1501, 1475 cm^{-1}. **HRMS** (MALDI) Calculated for $[M+Na]^+$: 807.0868, Found: 807.0875. **HPLC** IB column, 25 °C, 0.5 mL/min flow rate, DCM : Hexane = 2 : 3, t_1 = 15.7 min, t_2 = 22.5 min.

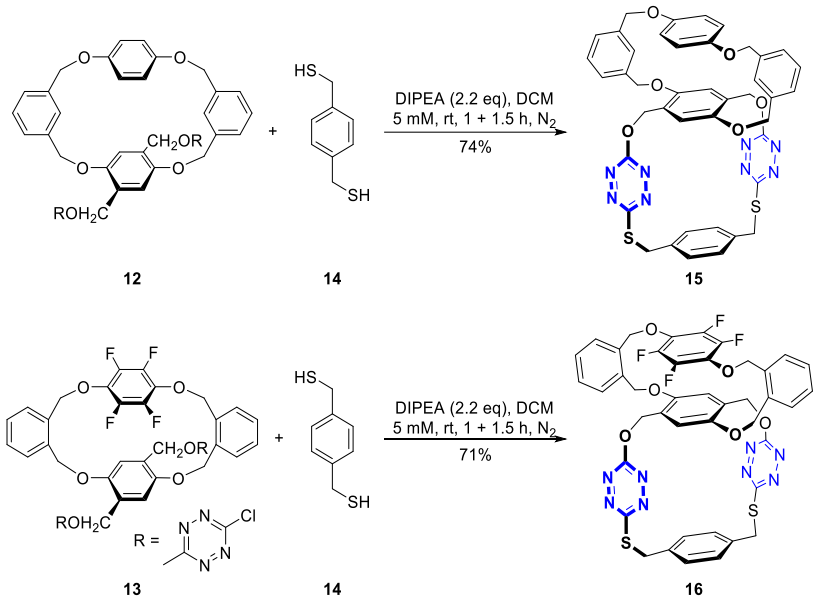
Table S7. Optimization of the condensation reaction between **10** and **11**



Entry	11 (eq)	Temp.	Solv.	Base (eq)	Time	Conc.	Yields
1	5	60 °C	$CHCl_3$	DIPEA (2.5)	4 h	10 mM	N.R.[a]
2	5	60 °C	$CHCl_3$	DMAP (2.5)	4 h	10 mM	N.R.
3	5	60 °C	$CHCl_3$	DABCO (2.5)	4 h	10 mM	N.D.[b]
4	5	60 °C	$CHCl_3$	collidine (2.5)	4 h	10 mM	<10%
5	5	60 °C	$CHCl_3$	Cs_2CO_3 (2.5)	4 h	10 mM	N.R.
6	5	60 °C	$CHCl_3$/CH_3CN	collidine (2.5)	20 h	10 mM	<10%
7	5	80 °C	DCE	collidine (5)	1.5 h	10 mM	81%
8	3	80 °C	DCE	collidine (5)	1.5 h	10 mM	37%
9	3	80 °C	DCE	collidine (5)	1.5 h	20 mM	70%
10	3	80 °C	DCE	collidine (5)	1.5 h	40 mM	63%
11	**3**	**80 °C**	**DCE**	**collidine (5)**	**0.5 h**	**20 mM**	**85%**

[a] Diol **10** did not converse. [b] **13** was not detected.

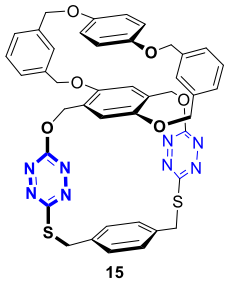
Procedure D: Synthesis of ditopic spirophanes **15** and **16**



Synthesis of **15**. DIPEA (38 μL, 0.22 mmol, 2.2 equiv.) and anhydrous dichloromethane (10 mL) were put into a 50 mL dry two-necked round bottom flask under nitrogen atmosphere. To this mixture was added a solution of **12** (71.4 mg, 0.10 mmol, 1 equiv.) and **14** (17.0 mg, 0.10 mmol, 1 equiv.) in anhydrous dichloromethane (10 mL) over 1 hour. The resulting red mixture was stirred at room temperature for 1.5 hours. Brine (50 mL) and 2N HCl (1 drop) were added to quench the reaction, and the mixture was extracted with dichloromethane (10 mL × 3). 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 petroleum ether,

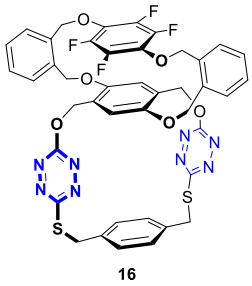
dichloromethane, and ethyl acetate (v : v : v = 6 : 3 : 1) as the mobile phase to give the pure product **15** (60.2 mg, 74%).

15: red solid, m.p. 168 ºC (decomposition). **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.43 (s, 2H), 7.37-7.33 (m, 6H), 7.25-7.19 (m, 4H), 6.77 (s, 2H), 6.50 (s, 4H), 5.80 (d, *J* = 16.4 Hz, 2H), 5.32 (d, *J* = 13.8 Hz, 2H), 5.12 (d, *J* = 14.7 Hz, 2H), 5.09 (d, *J* = 14.7 Hz, 2H), 4.99 (d, *J* = 13.8 Hz, 2H), 4.90 (d, *J* = 16.4 Hz, 2H), 4.49 (d, *J* = 15.1 Hz, 2H), 4.24 (d, *J* = 15.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 170.0, 165.6, 152.2, 149.8, 138.8, 137.9, 136.1, 129.1, 128.9, 126.8, 125.7, 125.0, 124.5, 115.9, 115.7, 70.0, 69.8, 65.6, 33.9. **IR** (KBr): ν 2922, 2852, 1504, 1481 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 811.2116, Found: 811.2121. **HPLC**: ID column, 25 ºC, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 6, t_1 = 28.3 min, $[\alpha]_D^{25}$ = -11.0 (*c* 0.3, DCM), t_2 = 33.9 min, $[\alpha]_D^{25}$ = +11.0 (*c* 0.3, DCM).


15

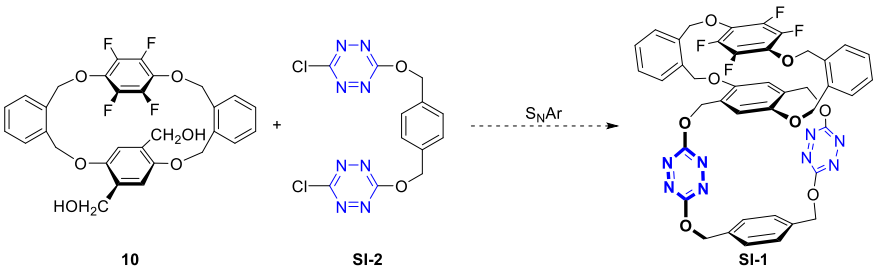
Synthesis of **16**. Follow the general procedure. **13** (157.1 mg, 0.20 mmol) and **14** (34.1 mg, 0.20 mmol) were used. The resulting residue was chromatographed on a silica gel column with a mixture of petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 7 : 2 : 1) as the mobile phase to give pure product **16** (125.4 mg, 71%).

16: red solid, m.p. 262 ºC (decomposition). **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.59-7.52 (m, 4H), 7.51-7.45 (m, 4H), 7.32 (s, 4H), 6.95 (s, 2H), 5.79 (d, *J* = 12.4 Hz, 2H), 5.43 (d, *J* = 11.0 Hz, 2H), 5.20 (d, *J* = 11.0 Hz, 2H), 5.19 (d, *J* = 12.4 Hz, 2H), 5.16 (s, 4H), 4.42 (d, *J* = 15.1 Hz, 2H), 4.26 (d, *J* = 15.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 170.3, 165.4, 152.1, 140.4 (m), 135.9, 135.4, 135.1, 132.3 (m), 131.0, 130.8, 129.6, 129.2, 129.1, 125.1, 116.2, 74.9, 72.0, 64.7, 33.9.; **^{19}F NMR** (367 MHz, DMSO-d_6, 120 ºC): δ -157.4. **IR** (KBr): ν 2923, 2852, 1502, 1482 cm^{-1}. **HRMS** (MALDI) Calculated for $[M+H]^+$: 883.1739, Found: 883.1742. **HPLC**: ID column, 25 ºC, 0.5 mL/min flow rate, DCM : Hexane = 2 : 1, t_1 = 11.9 min, $[\alpha]_D^{25}$ = +4.7 (*c* 0.4, DCM), t_2 = 15.7 min, $[\alpha]_D^{25}$ = -4.7 (*c* 0.4, DCM).


16

Attempted construction of tetraoxa-linked homo corona[2]arene[2]tetrazine **SI-1**:

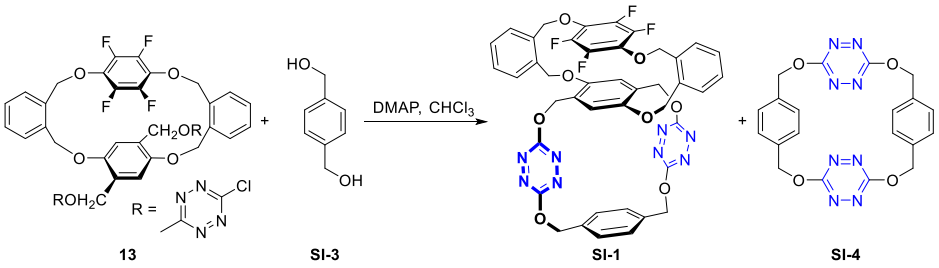
Table S8. The macrocyclization reaction between **10** and **SI-2**



Entry	Temp.	Solv.	Base (eq)	Time	Conc.	Results
1	40 °C	THF	DMAP (2.2)	0.5 + 3.5 h	5 mM	N.R.[a]
2	60 °C	THF	DMAP (2.2)	4 + 8 h	5 mM	N.R.
3	60 °C	CH_3CN	DMAP (2.2)	12 h	5 mM	N.D.[b]
4	60 °C	$CHCl_3$	DMAP (2.2)	12 h	5 mM	N.D.
5	140 °C	DMF	DMAP (2.2)	12 h	5 mM	N.D.
6	140 °C	TCE	DMAP (2.2)	12 h	5 mM	N.D.

[a] Diol **10** did not converse. [b] **SI-1** was not detected.

Table S9. The macrocyclization reaction between **13** and **SI-3**

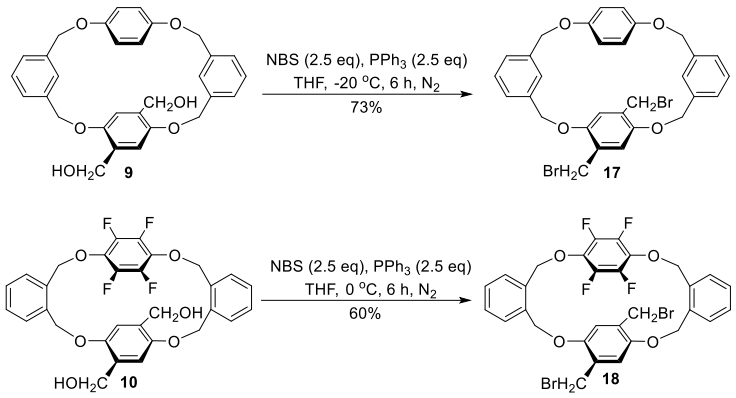


Entry	Temp.	Solv.	Base (eq)	Time	Conc.	Yield [%]	
						SI-1	SI-4
1	60 °C	$CHCl_3$	DMAP (2.5)	0.5 + 4.5 h	2.5 mM	trace	20
2	40 °C	$CHCl_3$	DMAP (2.5)	2 + 22 h	2.5 mM	trace	30
3	rt	$CHCl_3$	DMAP (2.5)	12 + 24 h	2.5 mM	3	15
4	rt	$CHCl_3$	DMAP (5.0)	12 + 12 h	2.5 mM	trace	11

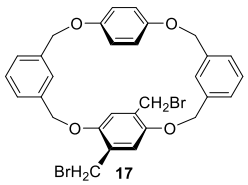
The macrocyclization reaction between **13** and **SI-3** underwent a macrocycle-to-macrocycle transformation to give **SI-4**. Target compound **SI-1** was generated in poor yields. Characterization of **SI-4** has been reported earlier[5].

2.4 Synthesis of intermediates 19-22

Procedure A: Synthesis of dibromide **17**-**18**



Synthesis of **17**. **9** (95.6 mg, 0.20 mmol), PPh_3 (131.1 mg, 0.50 mmol, 2.5 equiv.), NBS (89.0 mg, 0.50 mmol, 2.5 equiv.), and anhydrous tetrahydrofuran (10 mL) were put into a dry Schlenk tube under nitrogen atmosphere. The mixture was stirred at -20 °C for 6 hours. Brine (20 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (20 mL × 3). 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 petroleum ether and dichloromethane (v : v = 1 : 4) as the mobile phase to give the pure product **17** (88.7mg, 73%).

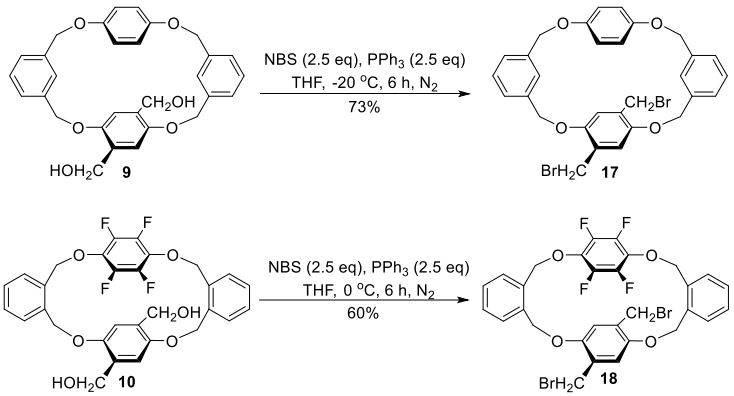


17: white solid, m.p. 205-207 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.42 (s, 2H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.61 (s, 2H), 6.40 (s, 4H), 5.34 (d, *J* = 14.0 Hz, 2H), 5.10 (d, *J* = 14.0 Hz, 2H), 5.06 (d, *J* = 14.6 Hz, 2H), 5.00 (d, *J* = 14.6 Hz, 2H), 4.39 (d, *J* = 9.8 Hz, 2H), 4.22 (d, *J* = 9.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 152.3, 148.6, 139.0, 137.3, 129.0, 127.5, 126.6, 126.1, 125.2, 116.0, 115.2, 70.4, 69.2, 28.9. **IR** (KBr): ν 2920, 2850, 1659, 1633, 1504, 1469 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 609.0271, Found: 609.0271.

Synthesis of **18**. Follow the general procedure. The reaction was conducted at 0 °C. **11** (679.2 mg, 1.26 mmol) was used. The residue was chromatographed on a silica gel column with a mixture of petroleum ether and dichloromethane (v : v = 7 : 3) as the mobile phase to give the pure product **18** (514.2mg, 60%).

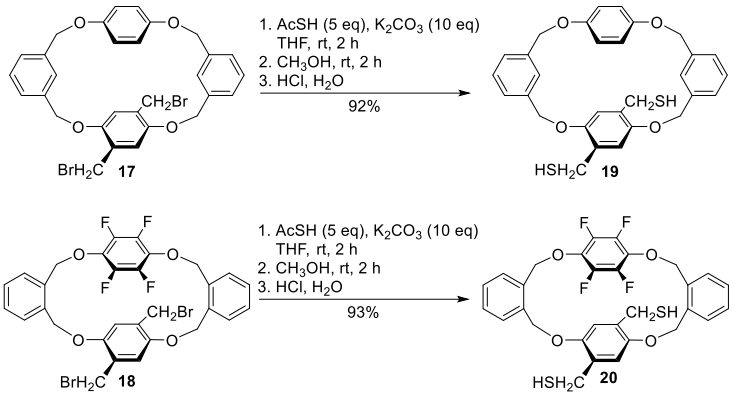
18: white solid, m.p. 218-219 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.58-7.54 (m, 2H), 7.50-7.43 (m, 6H), 6.82 (s, 2H), 5.45 (d, *J* = 11.0 Hz, 2H), 5.29 (d, *J* = 11.0 Hz, 2H), 5.16 (d, *J* = 11.0 Hz, 2H), 5.05 (d, *J* = 11.0 Hz, 2H), 4.40 (d, *J* = 10.0 Hz, 2H), 4.30 (d, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 151.0, 140.5 (dddd, *J* = 241, 17, 6, 4 Hz), 135.4, 135.0, 132.9 (tt, *J* = 11, 3 Hz), 130.9, 130.7, 129.5, 129.4, 128.4, 116.5, 75.6, 71.4, 27.4; **^{19}F NMR** (367 MHz, DMSO-d_6, 120 ºC): δ -157.5. **IR** (KBr): ν 2920, 2850, 1500, 1384 cm^{-1}. **HRMS** (APCI) Calculated for $[M-H]^-$: 678.9748, Found: 678.9770. **HPLC** IB column, 25 ºC, 0.5 mL/min flow rate, ^{i}PrOH : Hexane = 1 : 4, t_1 = 15.2 min, t_2 = 16.3 min.

Table S10. Optimization of the synthesis of **17** and **18**



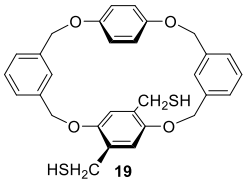
Entry	Substrate	[Br] (eq)	Temp.	Solv.	Time	Yields [%]
1	**9**	NBS (2.5), PPh_3 (2.5)	0 ºC	THF	6 h	65
2	**9**	**NBS (2.5), PPh_3 (2.5)**	**-20 ºC**	**THF**	**6 h**	**73**
3	**9**	NBS (2.5), PPh_3 (2.5)	-40 ºC	THF	6 h	70
4	**10**	NBS (2.5), PPh_3 (2.5)	rt	THF	4 h	54
5	**10**	**NBS (2.5), PPh_3 (2.5)**	**0 ºC**	**THF**	**6 h**	**60**
6	**10**	NBS (2.5), PPh_3 (2.5)	-20 ºC	THF	6 h	42

Procedure B: Synthesis of dithiols **19** and **20**



Synthesis of **19**. Tetrahydrofuran, methanol, and diluted hydrochloric acid were bubbled with nitrogen for 30 minutes. **17** (396.7 mg, 0.65 mmol), K_2CO_3 (898.4 mg, 6.50 mmol, 10 equiv.), anhydrous tetrahydrofuran (13 mL), and thioacetic acid (0.23 mL, 3.25 mmol, 5 eq) were put into a dry 100 mL dry two-necked round bottom flask under nitrogen atmosphere. After stirring vigorously at room temperature for 2 hours, the mixture was added with anhydrous methanol (13 mL) and stirred for another 2 hours. 2N HCl (6.5 mL) and brine (50 mL) were added to quench the reaction, and the mixture was extracted with ethyl acetate (50 mL × 3). The organic phases were then combined and evaporated to remove methanol. Then the residue was extracted again with brine (50 mL) and ethyl acetate (50 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was recrystallized with petroleum ether and dichloromethane to give the pure product **19** (309.4 mg, 92%).

19: white solid, m.p. 146-148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.42 (s, 2H),

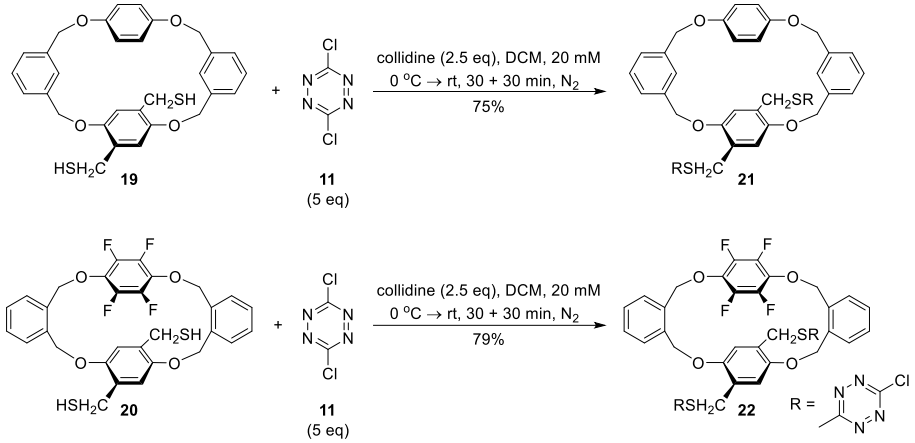


7.32 (dd, J = 7.6, 7.6 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 6.53 (s, 2H), 6.40 (s, 4H), 5.28 (d, J = 13.8 Hz, 2H), 5.08 (d, J = 13.8 Hz, 2H), 5.03 (s, 4H), 3.61 (dd, J = 13.0, 7.0 Hz, 2H , C$\underline{H}_a$H$_b$SH), 3.35 (d, J = 13.0, 8.2 Hz, 2H, CH$_a\underline{H}_b$SH), 1.62 (dd, J = 8.2, 7.0 Hz, 2H, CH$_2$S$\underline{H}$); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 152.4, 148.0, 138.9, 137.9, 129.2, 128.9, 126.5, 125.8, 125.1, 116.0, 113.8, 70.4, 69.1, 24.0. **IR** (KBr): ν 2920, 2850, 1504, 1469, 1202 cm^{-1}. **HRMS** (APCI) Calculated for [M-H]$^-$: 515.1356, Found: 515.1356.

Synthesis of **20**. Follow the general procedure. **18** (409.4 mg, 0.6 mmol) was used to give **20** (330.0 mg, 93%).

20: white solid, m.p. 207-210 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.56-7.52 (m, 2H), 7.49-7.42 (m, 6H), 6.75 (s, 2H), 5.45 (d, *J* = 11.4 Hz, 2H), 5.24 (d, *J* = 11.0 Hz, 2H), 5.19 (d, *J* = 11.4 Hz, 2H), 5.04 (d, *J* = 11.0 Hz, 2H), 3.72 (dd, *J* = 13.4, 7.2 Hz, 2H, $C\underline{H_a}H_bSH$), 3.42 (dd, *J* = 13.4, 8.6 Hz, 2H, $CH_a\underline{H_b}SH$), 1.68 (dd, *J* = 8.6, 7.2 Hz, 2H, $CH_2S\underline{H}$); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 150.5, 140.2 (m), 135.3, 135.3, 132.6 (tt, *J* = 9, 2 Hz), 130.7, 130.6, 129.8, 129.4, 129.1, 115.0, 75.4, 71.3, 23.0; **^{19}F NMR** (367 MHz, DMSO-d_6, 120 °C): δ -156.9. **IR** (KBr): ν 2954, 2920, 2850, 1499 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 589.1125, Found: 589.1131. **HPLC** IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 27 : 9 : 164, t_1 = 11.3 min, t_2 = 16.1 min.

Procedure C: Synthesis of **21** and **22**



Synthesis of **21**. **11** (226.4 mg, 1.50 mmol, 5 equiv.) and anhydrous dichloromethane (10 mL) were put into a 50 mL dry two-necked round bottom flask under nitrogen atmosphere. To this solution in an ice bath was added first collidine (99 μL, 0.75 mmol, 2.5 equiv.) and subsequently dropwise a solution of **19** (155.0 mg, 0.30 mmol, 1 equiv.) in anhydrous dichloromethane (5 mL) over 30 minutes. The resulting dark red mixture was warmed to room temperature and stirred for 30 minutes. Brine (50 mL) and 2N HCl (0.4 mL) were added to quench the reaction, and the mixture was extracted with dichloromethane (50 mL × 3). The organic phases were then combined and dried over

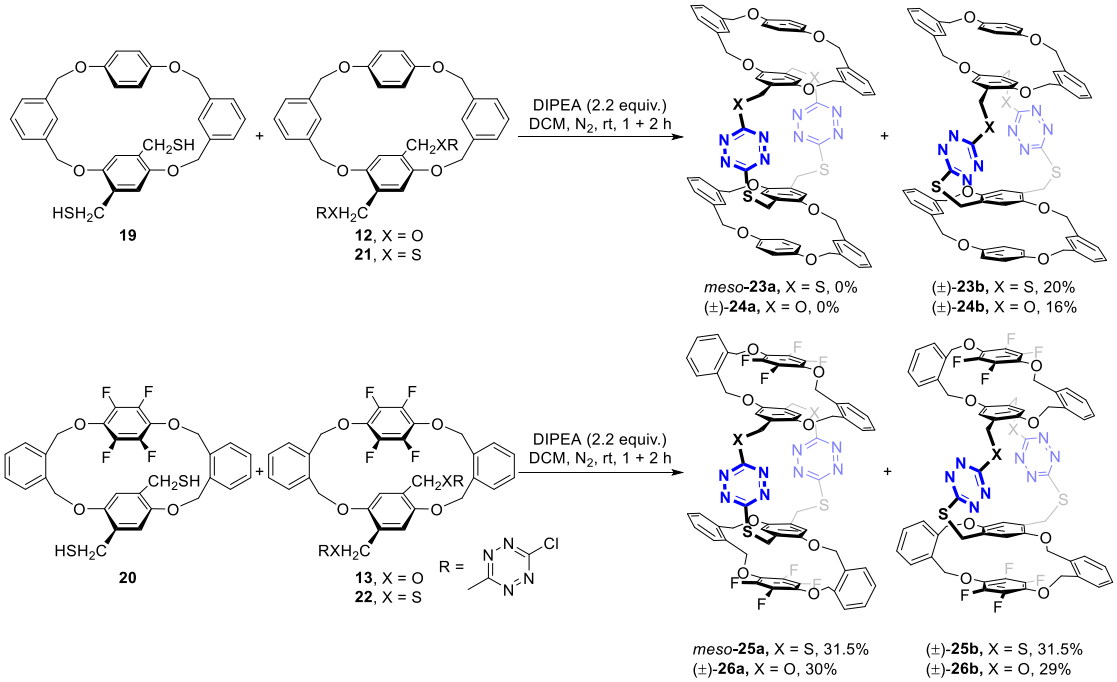
anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 6 : 3 : 1) as the mobile phase to give the pure product **21** (167.2 mg, 75%).

21: red solid, m.p. 87-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.42 (s, 2H), 7.33 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.75 (s, 2H), 6.23 (s, 4H), 5.35 (d, *J* = 14.4 Hz, 2H), 5.08 (d, *J* = 14.4 Hz, 2H), 5.01 (d, *J* = 14.6 Hz, 2H), 4.97 (d, *J* = 14.6 Hz, 2H), 4.35 (d, *J* = 13.6 Hz, 2H), 4.30 (d, *J* = 13.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ175.8, 165.4, 152.5, 148.7, 139.1, 137.4, 129.0, 125.9, 125.8, 124.6, 124.4, 116.0, 114.8, 70.6, 69.3, 30.0. **IR** (KBr): ν 2922, 2852, 1504, 1230 cm^{-1}. **HRMS** (ESI) Calculated for $[M+Na]^+$: 767.0788, Found: 767.0782. **HPLC** IB column, 25 °C, 0.5 mL/min flow rate, DCM : Hexane = 2 : 3, t_1 = 11.2 min, t_2 = 12.2 min.

Synthesis of **22**. Follow the general procedure. **20** (235.5 mg, 0.40 mmol) was used. The residue was chromatographed on a silica gel column with dichloromethane as the mobile phase to give the pure product **22** (235.5 mg, 79%).

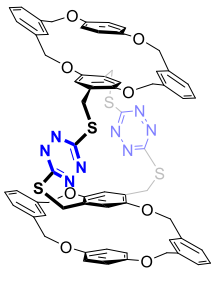
22: red solid, m.p. 109-111 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.57-7.54 (m, 2H), 7.49-7.40 (m, 6H), 6.98 (s, 2H), 5.44 (d, *J* = 11.4 Hz, 2H), 5.26 (d, *J* = 11.4 Hz, 2H), 5.17 (d, *J* = 11.4 Hz, 2H), 5.06 (d, *J* = 11.4 Hz, 2H), 4.39 (d, *J* = 13.2 Hz, 2H), 4.31 (d, *J* = 13.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 175.6, 165.7, 151.2, 140.2 (m), 135.1, 134.9, 132.4 (m), 130.8, 130.7, 129.5, 129.3, 125.2, 116.1, 75.1, 71.3, 29.7; **^{19}F NMR** (376 MHz, DMSO-d_6, 120 °C) δ -156.7. **IR** (KBr): ν 2923, 2852, 1502, 1232 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 817.0591, Found: 817.0588. **HPLC** IB column, 25 °C, 0.5 mL/min flow rate, DCM : Hexane = 2 : 3, t_1 = 11.8 min, t_2 = 12.8 min.

2.5 Synthesis of bispirophanes 23-26



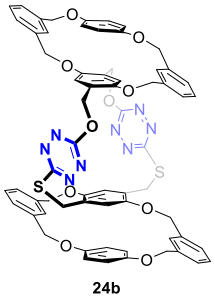
General Procedure: DIPEA (38 μL, 0.22 mmol, 2.2 equiv.) and anhydrous dichloromethane (10 mL) were put into a 50 mL dry two-necked round bottom flask under nitrogen atmosphere. To this solution was added dropwise a solution of dithiols (0.10 mmol, 1 equiv.) and 6-chloro-*s*-tetrazine-appended macrocycles (0.10 mmol, 1 equiv.) in anhydrous dichloromethane (10 mL) over 1 hour. The resulting red mixture was stirred at room temperature for 2 hours. Brine (50 mL) and 2N HCl (1 drop) were added to quench the reaction, and the mixture was extracted with dichloromethane (10 mL × 3). 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 or thin layer chromatography to give pure bispirophanes.

23b: 23.7 mg, 20%. Separated by column with a mixture of petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 6 : 3 : 1) as the mobile phase. Red solid, m.p. 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.40 (s, 4H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.19 (d, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 7.6 Hz, 4H), 6.75 (s, 4H), 6.46 (s, 8H), 5.07 (d, *J* = 15.3 Hz, 4H), 5.07 (d, *J* = 15.3 Hz, 4H), 4.80 (d, *J* = 13.5 Hz, 2H), 4.65 (d, *J* = 13.5 Hz, 2H), 4.65 (d, *J* = 15.1 Hz, 2H), 3.52 (d, *J* = 15.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 172.0, 152.3, 148.8, 138.7,

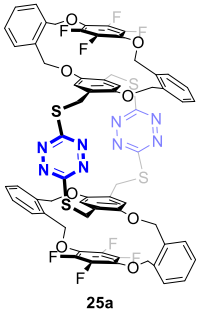

23b

137.7, 128.9, 127.3, 125.7, 125.5, 115.9, 114.6, 70.1, 69.6, 29.3. **IR** (KBr): ν 2921, 2851, 1504, 1461, 1229, 1202 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 1189.2864, Found: 1189.2867. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21, t_1 = 18.6 min, $[\alpha]_D^{25}$ = -10.5 (*c* 0.5, DCM), t_2 = 24.1 min, $[\alpha]_D^{25}$ = +10.5 (*c* 0.5, DCM).

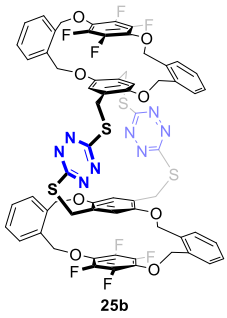
24b: 18.3 mg, 16%. Separated by thin layer chromatography with a mixture of petroleum ether, dichloromethane, and ethyl acetate (v : v : v = 6 : 3 : 1) as the mobile phase (R_f = 0.36). Red solid, m.p. 166-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.41 (s, 2H), 7.38 (s, 2H), 7.33-7.29 (m, 6H), 7.22-7.17 (m, 6H), 6.79 (s, 2H), 6.67 (s, 2H), 6.52 (s, 4H), 6.40 (s, 4H), 6.13 (d, *J* = 12.6 Hz, 2H), 5.11 – 5.04 (m, 10H), 4.84 (d, *J* = 14.3 Hz, 2H), 4.80 (d, *J* = 13.8 Hz, 2H), 4.71 (d, *J* = 12.6 Hz, 2H), 4.61 (d, *J* = 13.8 Hz, 2H), 4.40 (d, *J* = 14.3 Hz, 2H), 3.67 (d, *J* = 14.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 171.0, 165.2, 152.4, 152.2, 149.2, 148.4, 138.8, 138.7, 137.8, 137.6, 129.0, 128.9, 127.2, 127.1, 126.1, 125.8, 125.7, 125.4, 125.2, 125.2, 115.9, 115.8, 115.6, 114.2, 70.3, 69.8, 69.6, 69.4, 64.6, 30.4. **IR** (KBr): ν 2923, 2852, 1504, 1478 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 1157.3321, Found: 1157.3320. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 9 : 3 : 28, t_1 = 14.4 min, $[\alpha]_D^{25}$ = -11.0 (*c* 0.5, DCM), t_2 = 22.5 min, $[\alpha]_D^{25}$ = +11.0 (*c* 0.5, DCM).


24b

Column chromatography with dichloromethane as the mobile phase gave a mixture of **25a** and **25b** (82.2 mg, 63%). The later compound was obtained as high-quality single crystals from recrystallization of a mixed sample in toluene and *n*-hexane.


25a

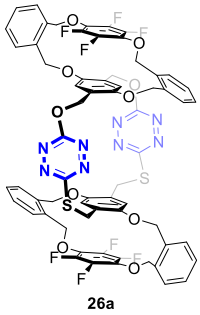
25a: red solid. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.60-7.57 (m, 4H), 7.50-7.43 (m, 12H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.89 (s, 4H), 5.36 (d, *J* = 11.5 Hz, 4H), 5.13 (d, *J* = 11.5 Hz, 4H), 5.01 (s, 8H), 4.38 (d, *J* = 14.7 Hz, 4H), 3.92 (d, *J* = 14.7 Hz, 2H). **HRMS** (ESI) Calculated for $[M+Na]^+$: 1355.1929, Found: 1355.1951.



25b

25b: red solid. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.62-7.57 (m, 4H), 7.49-7.42 (m, 4H), 7.41-7.36 (m, 4H), 7.19 (d, *J* = 7.8 Hz, 4H), 6.82 (s, 4H), 5.38 (d, *J* = 11.4 Hz, 4H), 5.12 (d, *J* = 11.4 Hz, 4H), 4.95 (d, *J* = 12.0 Hz, 4H), 4.92 (d, *J* = 12.0 Hz, 4H), 4.50 (d, *J* = 15.6 Hz, 4H), 3.86 (d, *J* = 15.6 Hz, 4H). **HRMS** (ESI) Calculated for $[M+Na]^+$: 1355.1929, Found: 1355.1951.

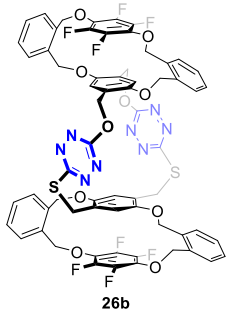
26a: 39.2 mg, 30%. Separated by thin layer chromatography with dichloromethane as the mobile phase (R_f = 0.32). Red solid, m.p. 255 °C (decomposition).



26a

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.54-7.34 (m, 12H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.86 (s, 2H), 6.74 (s, 2H), 5.84 (d, *J* = 12.8 Hz, 2H), 5.37 (d, *J* = 11.2 Hz, 2H), 5.37 (d, *J* = 12.0 Hz, 2H), 5.14 – 5.00 (m, 8H), 5.17 (d, *J* = 11.2 Hz, 2H), 4.83 (d, *J* = 12.0 Hz, 2H), 4.77 (d, *J* = 11.2 Hz, 2H), 4.42 (d, *J* = 15.6 Hz, 2H), 3.74 (d, *J* = 15.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 170.9, 165.4, 152.0, 151.9, 141.1 (m), 140.4 (m), 136.0, 135.4, 135.1, 135.0, 132.4, 132.1, 130.8, 130.8, 130.5, 129.6, 129.4, 129.2, 129.2, 126.8, 125.4, 116.7, 114.9, 75.1, 74.1, 72.6, 71.9, 64.7, 28.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -156.7, -157.0, -157.5. **IR** (KBr): ν 2922, 2852, 1501, 1485 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 1301.2567, Found: 1301.2587. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 1 : 1 : 8, t_1 = 18.3 min, $[\alpha]_D^{25}$ = +4.1 (*c* 0.5, DCM), t_2 = 24.0 min, $[\alpha]_D^{25}$ = -4.1 (*c* 0.5, DCM).

26b: 38.1 mg, 29%. Separated by thin layer chromatography with dichloromethane as the mobile phase (R_f = 0.30). red solid, m.p. 253 °C (decomposition).

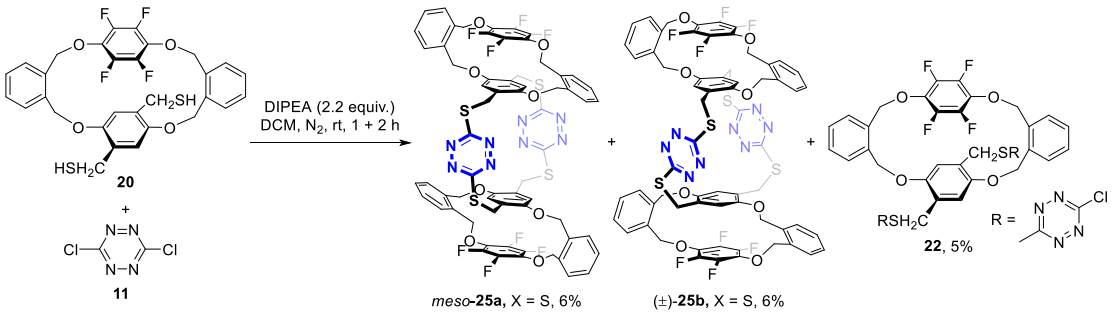


26b

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.58 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.53 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.48 – 7.37 (m, 8H), 7.20 (dd, *J* = 7.2, 1.4 Hz, 2H), 6.82 (s, 2H), 6.74 (s, 2H), 5.92 (d, *J* = 12.6 Hz, 2H), 5.42 (d, *J* = 11.4 Hz, 2H), 5.37 (d, *J* = 11.8 Hz, 2H), 5.19 (d, *J* = 11.4 Hz, 2H), 5.14 (d, *J* = 12.6 Hz, 2H), 5.14 (d, *J* = 11.8 Hz, 2H), 5.09 (d, *J* = 11.4 Hz, 2H), 5.04 (d, *J* = 12.0 Hz, 2H), 4.88 (d, *J* = 12.0 Hz, 2H), 4.82 (d, *J* = 11.4 Hz, 2H), 4.41 (d, *J* = 14.6 Hz, 2H), 3.79 (d, *J* = 14.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, TMS): δ 171.0, 165.3, 152.1, 151.1, 140.4 (m),

140.4 (m), 135.6, 135.2, 135.1, 134.9, 132.3 (m), 132.1 (m), 130.9, 130.8, 130.7, 129.6, 129.5, 129.2, 129.0, 126.7, 125.3, 117.1, 115.6, 75.0, 74.3, 71.9, 71.8, 64.6, 29.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -156.0, -157.3, -157.8. **IR** (KBr): ν 2922, 2852, 1501, 1485 cm^{-1}. **HRMS** (APCI) Calculated for $[M+H]^+$: 1301.2567, Found: 1301.2587. **HPLC**: IA column, 25 °C, 0.5 mL/min flow rate, $CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21, t_1 = 22.4 min, $[\alpha]_D^{25}$ = +15.9 (*c* 0.5, DCM), t_2 = 27.8 min, $[\alpha]_D^{25}$ = -15.9 (*c* 0.5, DCM).

25a and **25b** were also prepared from the direct reaction of **20** and **11**.



DIPEA (19 μL, 0.11 mmol, 2.2 equiv.) and anhydrous dichloromethane (5 mL) were put into a 50 mL dry two-necked round bottom flask under nitrogen atmosphere. To this solution was added dropwise a solution of **20** (29.4 mg, 0.05 mmol, 1 equiv.) and **11** (7.5 mg, 0.05 mmol, 1 equiv.) in anhydrous dichloromethane (5 mL) over 1 hour. The resulting red mixture was stirred at room temperature for 2 hours. Brine (20 mL) and 2N HCl (1 drop) were added to quench the reaction, and the mixture was extracted with dichloromethane (10 mL × 3). 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 petroleum ether and dichloromethane (v : v = 2 : 1 – 4 : 1) to give first 22 (1.8 mg, 5%) and then a mixture of **25a** and **25b** (4.0 mg, 12%).

3. Molecular Structures and Crystallographic Data

Table S11. Conditions of crystal cultivation

Compound	(±)-**7a**	**7b**	**7c**	*P*-**7d**
Solv.	DCE/*n*-Heptane	EA/*n*-Heptane	THF/*n*-Hexane	DCM/*n*-Hexane
Compound	**7e**	**7f**	(±)-**8**	(±)-**15**
Solv.	DCE/*n*-Heptane	THF/*n*-Hexane	EA/*n*-Hexane	DCE/*n*-Hexane
Compound	*M*-**15**	(±)-**16**	(±)-**25b**	(±)-**26a**
Solv.	$CHCl_3$/*n*-Hexane	Acetone/*n*-Hexane	Toluene/*n*-Hexane	THF/*n*-Hexane
Compound	*P*,*M*-**26a**	(±)-**26b**	*P*,*P*-**26b**	(±)-**25b**·H_3OCl
Solv.	THF/*n*-Hexane	CH_3CN/CH_3OH	THF/*n*-Hexane	DCE/CH_3OH
Compound	(±)-**15**·3TTF		(±)-**16**·2TTF	
Solv.	Acetone&DCE/*n*-Hexane		$CHCl_3$/*n*-Hexane -25 °C	
Compound	(±)-**16**·TTF		*M*-**16**·TTF	*P*-**16**·TTF
Solv.	THF&1,4-dioxane/*n*-Hexane		DCE/*n*-Hexane	DCE/*n*-Heptane

3.1 Molecular structures of homo *i*-corona[4]arenes

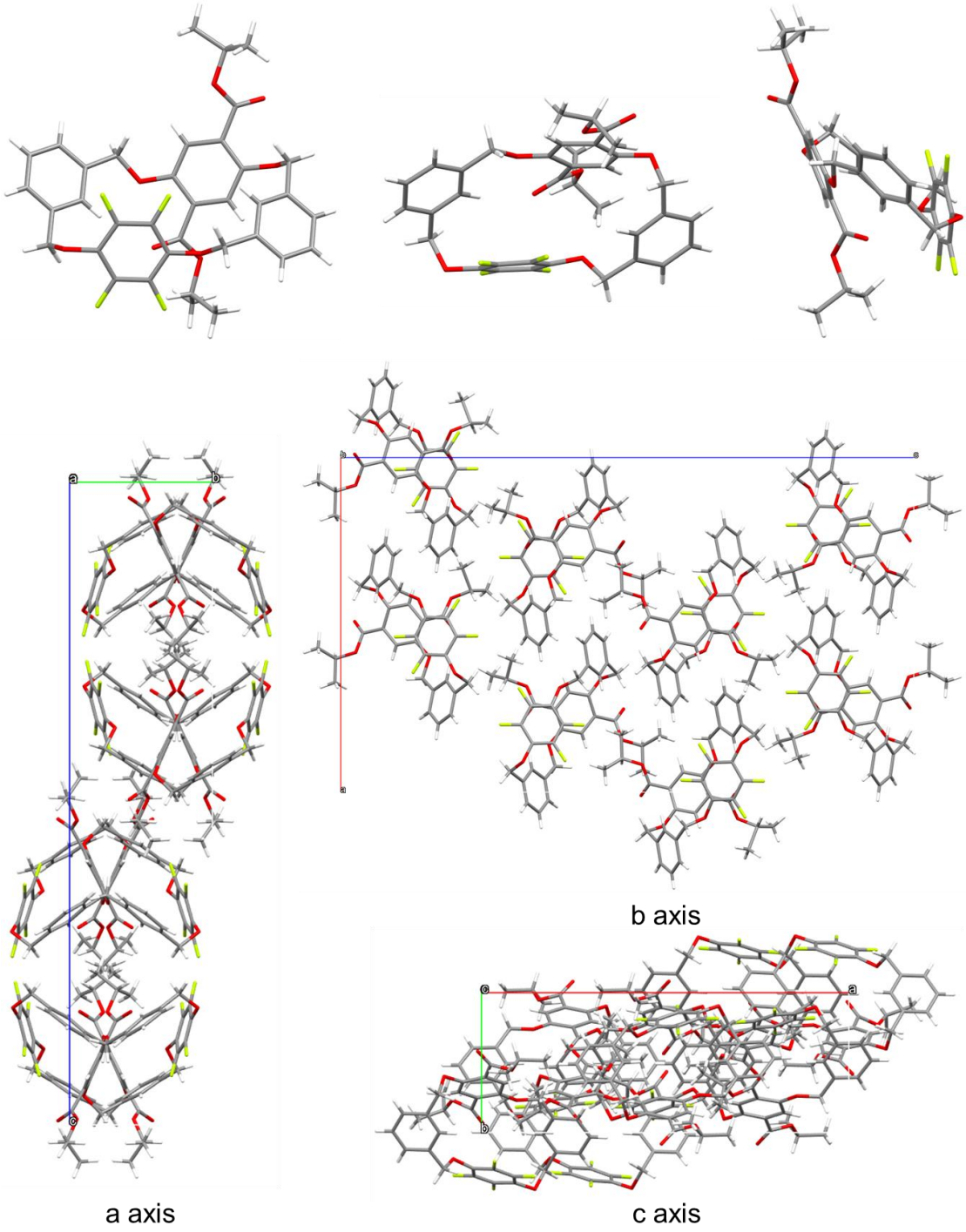


Figure S1A. X-Ray molecular structures of *race*-**7a** with three different views (top) and packing models of *race*-**7a** viewed from three different axes (bottom). Disordered structures are omitted for clarity.

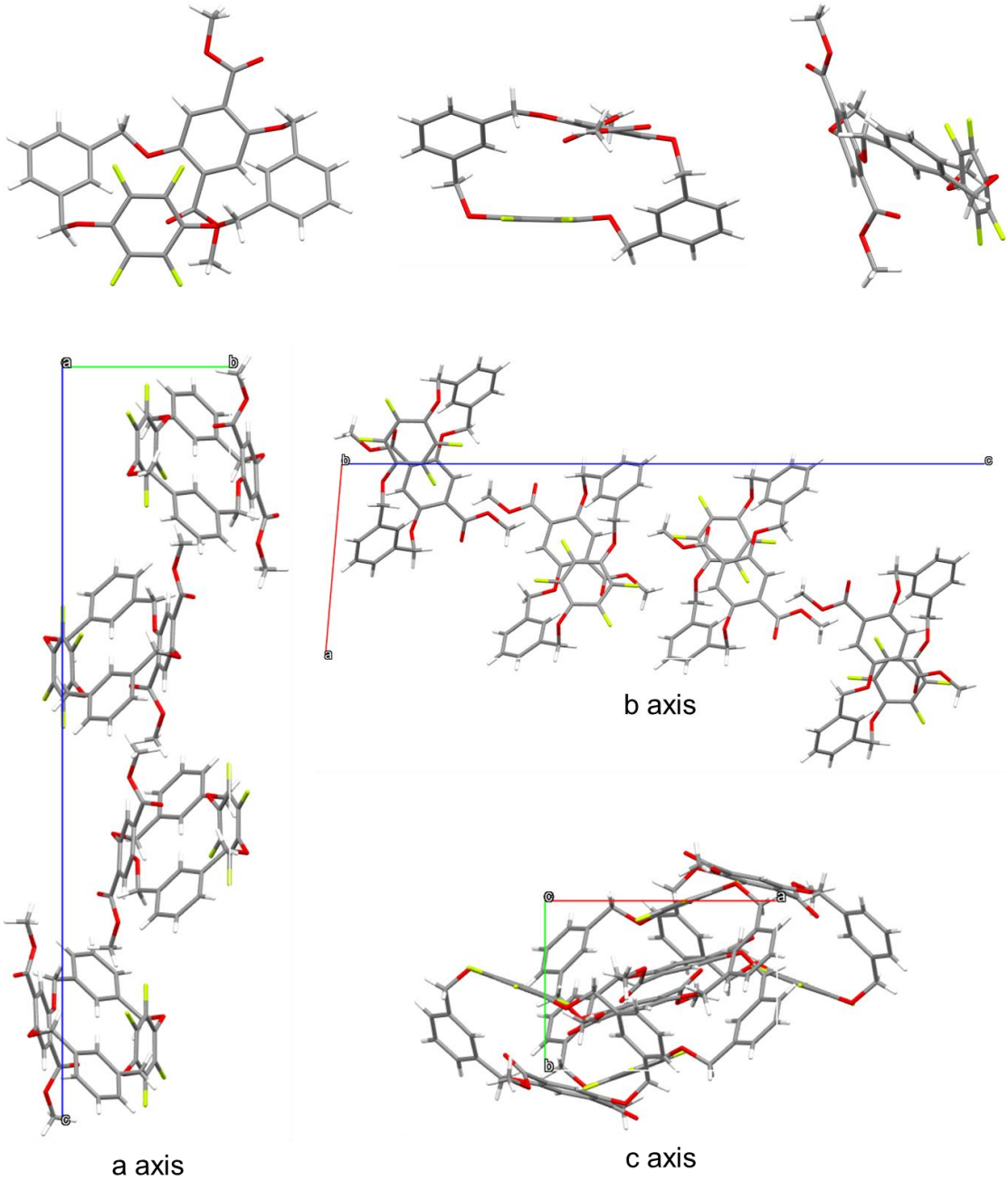


Figure S1B. X-Ray molecular structures of **7b** with three different views (top) and packing models of **7b** viewed from three different axes (bottom).

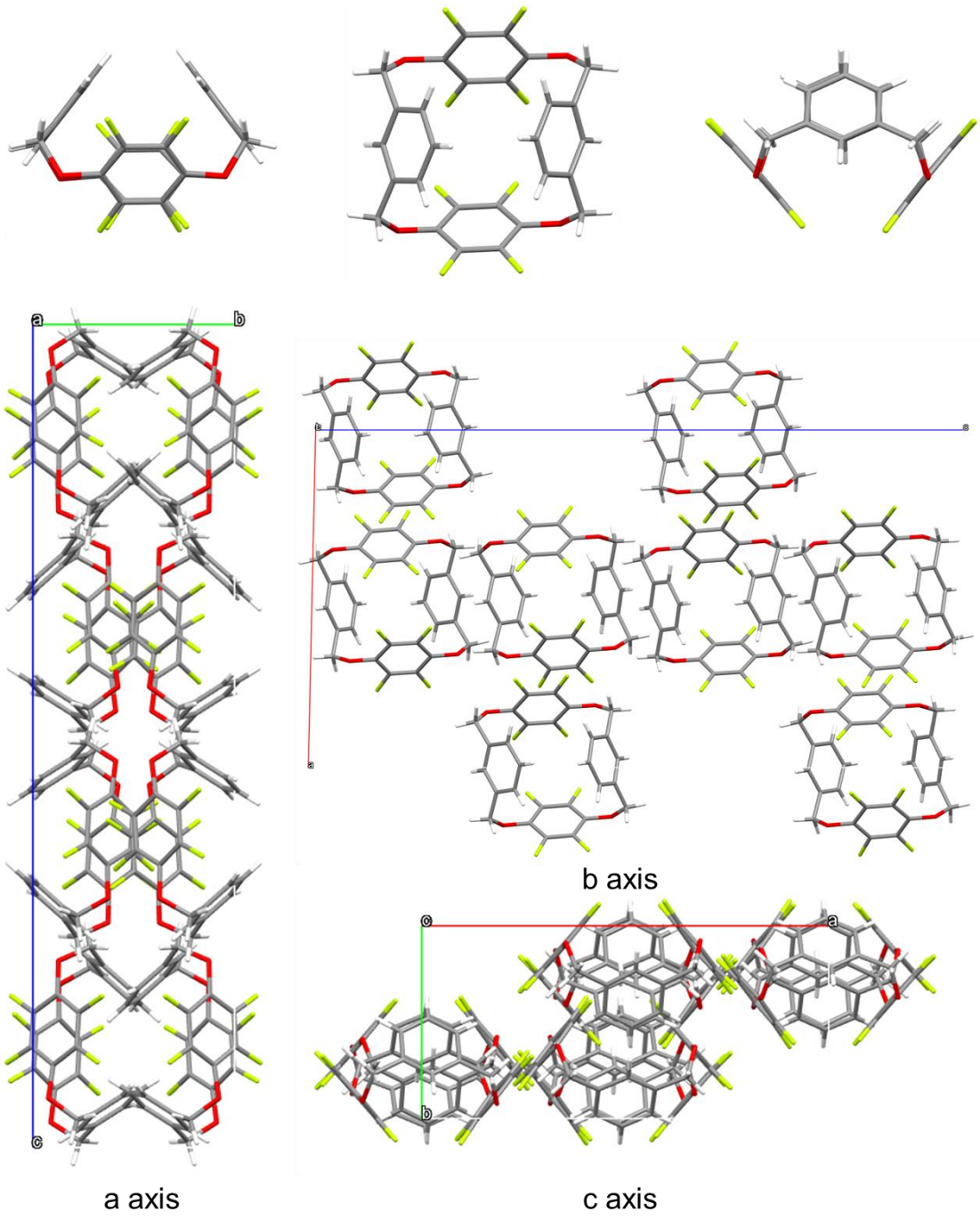


Figure S1C. X-Ray molecular structures of **7c** with three different views (top) and packing models of **7c** viewed from three different axes (bottom).

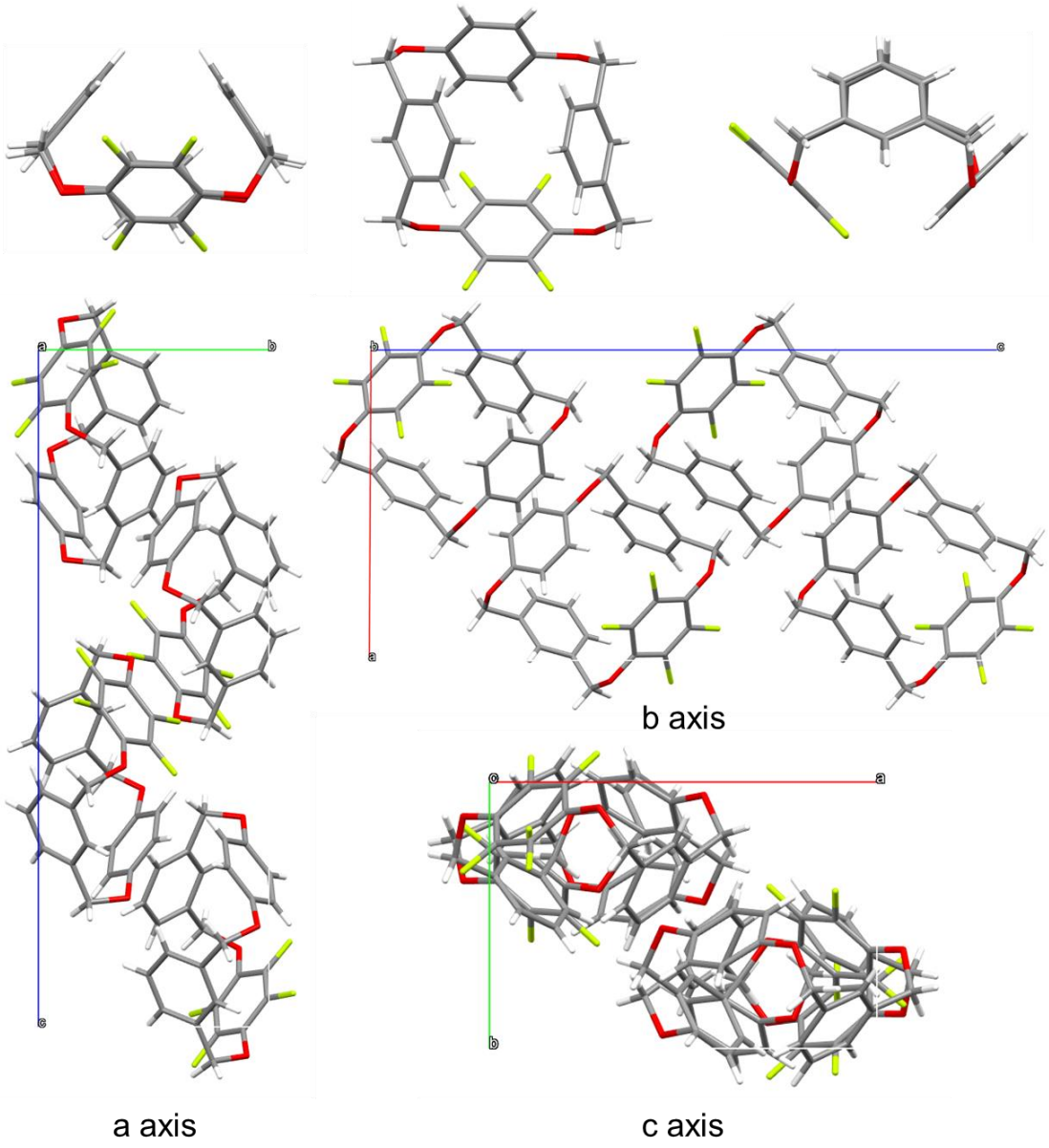


Figure S1D. X-Ray molecular structures of **7f** with three different views (top) and packing models of **7f** viewed from three different axes (bottom).

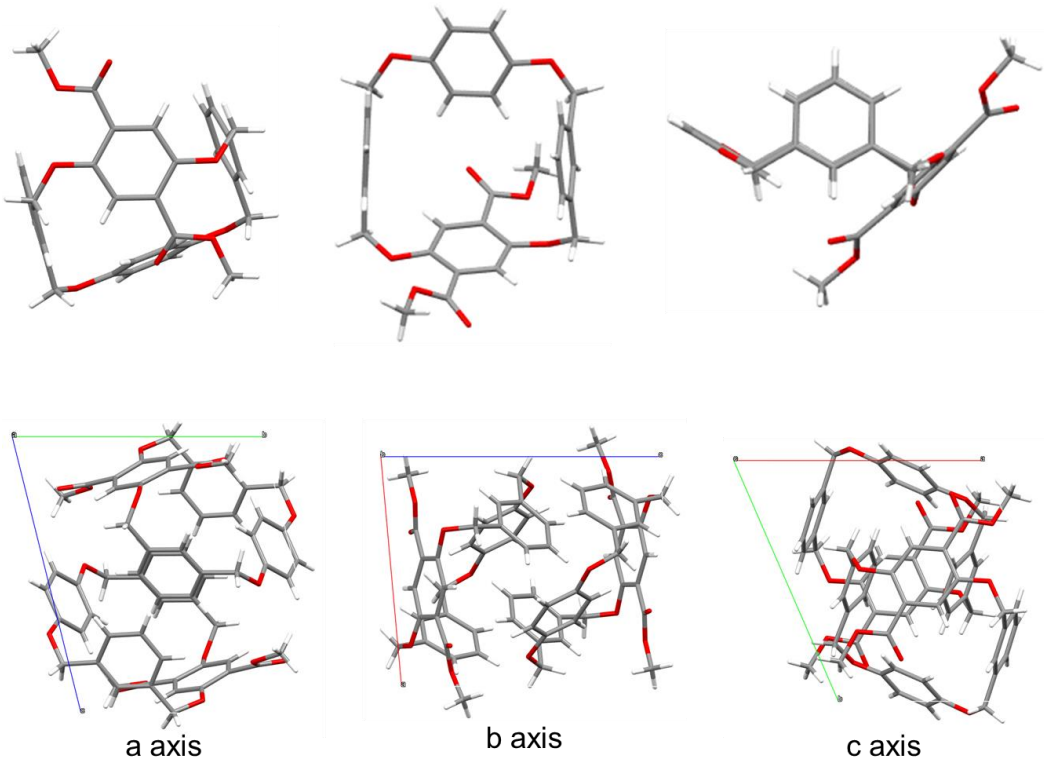


Figure S1E. X-Ray molecular structures of **7e** with three different views (top) and packing models of **7e** viewed from three different axes (bottom).

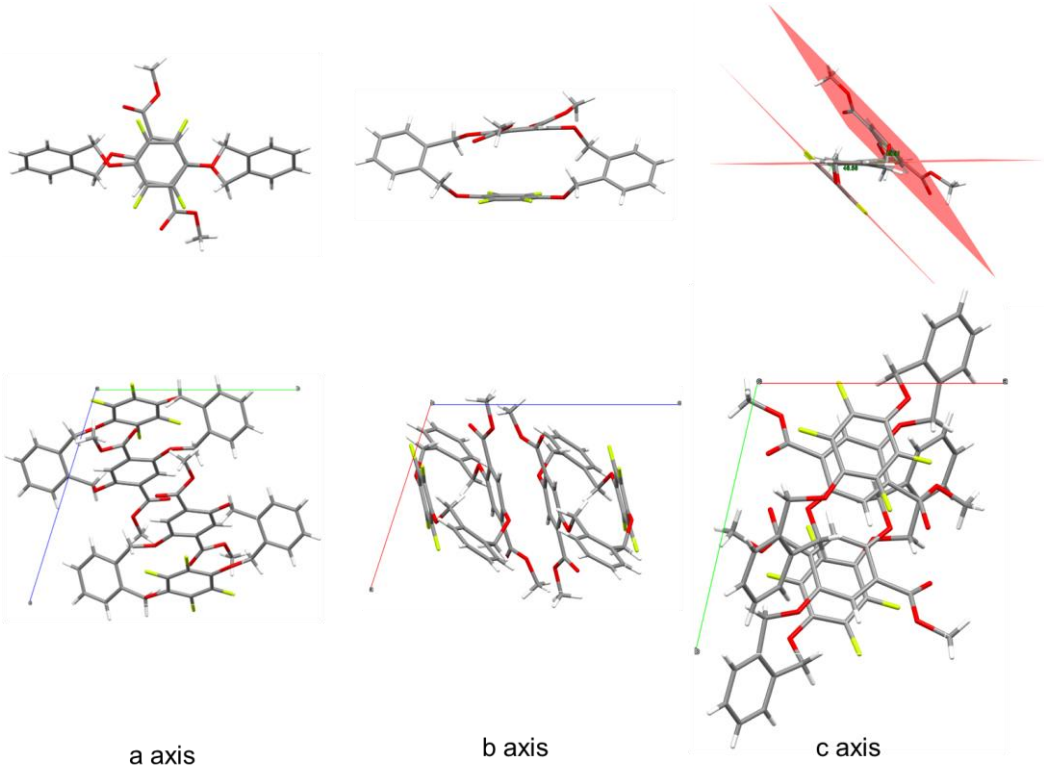


Figure S2. X-Ray molecular structures of *race*-**8** with three different views (top) and packing models of *race*-**8** viewed from three different axes (bottom).

3.2 Molecular structures of spirophanes and bispirophanes

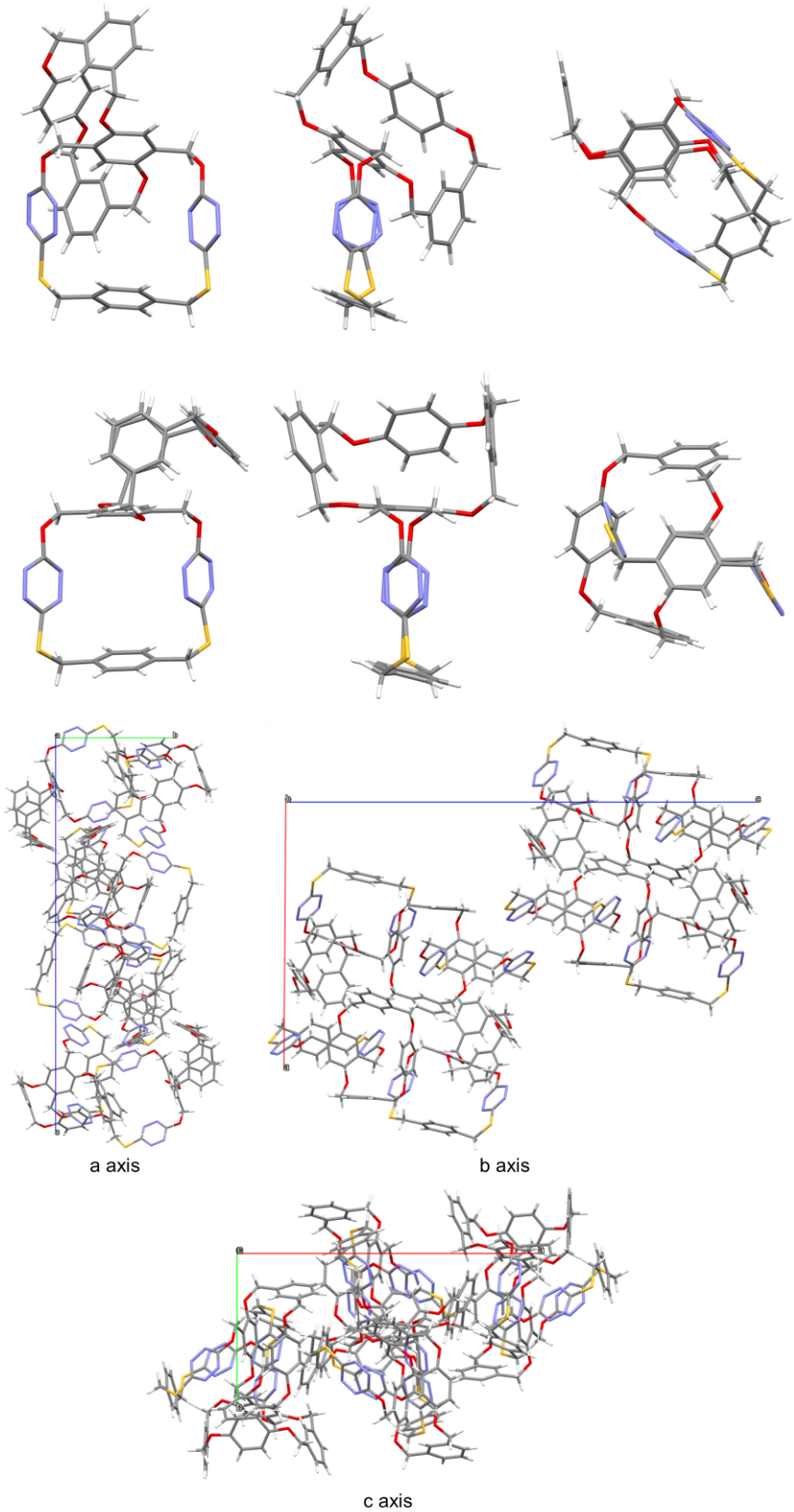


Figure S3A. X-Ray molecular structures of *race*-**15** with two different conformations and three different views (top) and packing models of *race*-**15** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

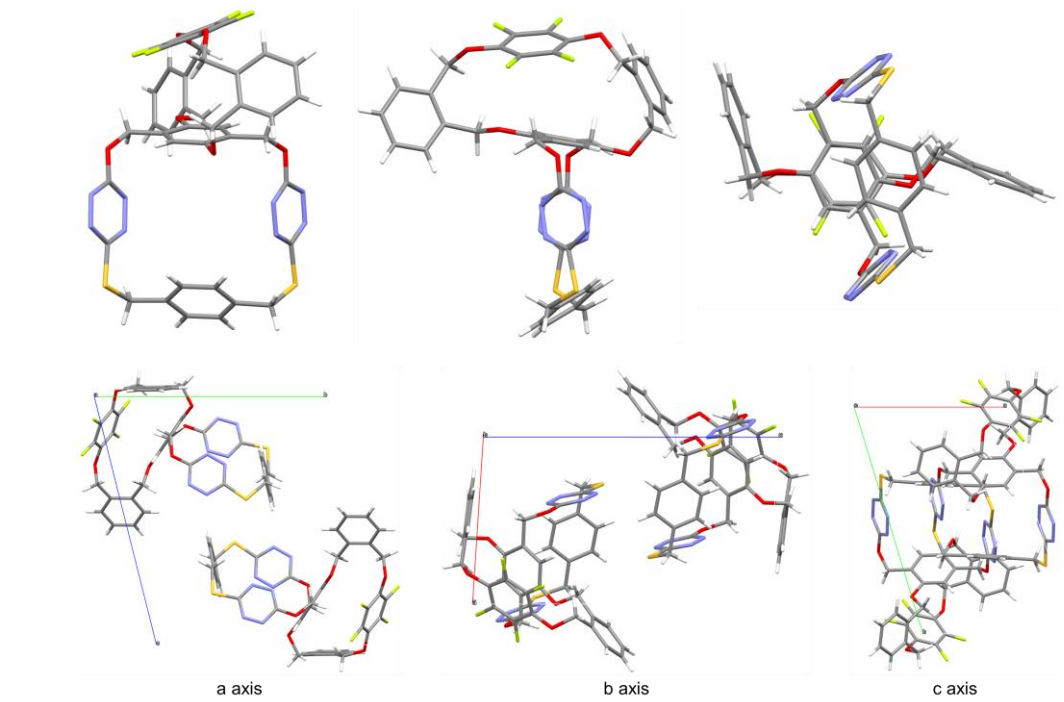


Figure S3B. X-Ray molecular structures of *race*-**16** with three different views (top) and packing models of *race*-**16** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

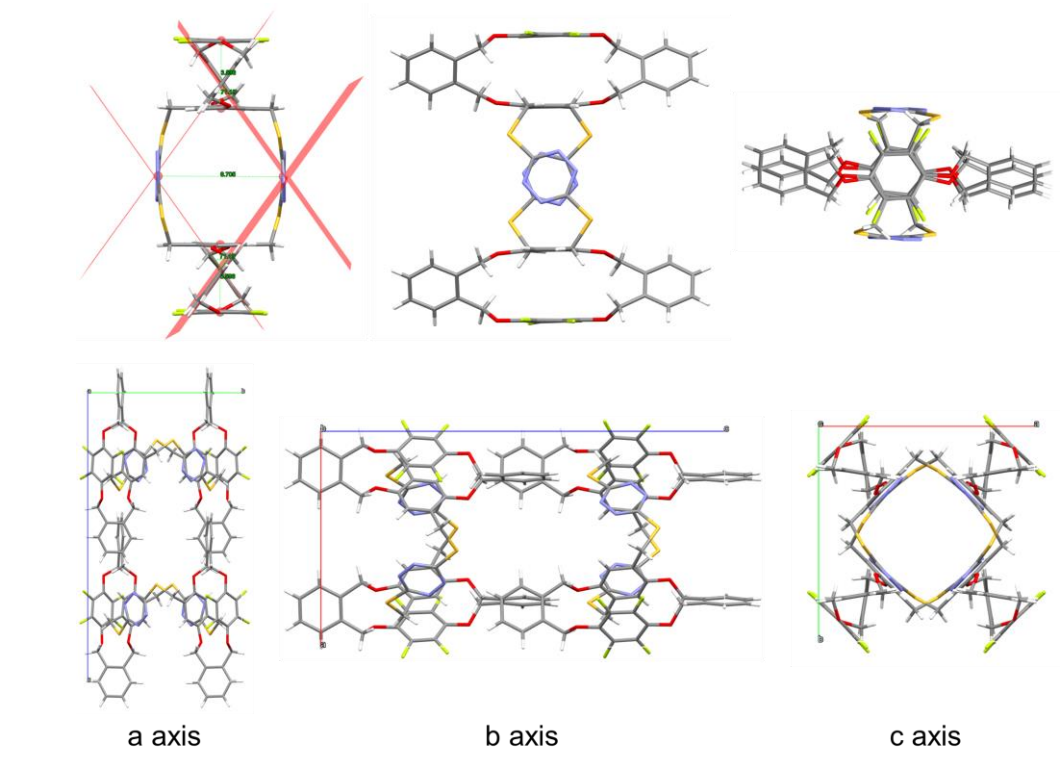


Figure S4A. X-Ray molecular structures of *race*-**25b** with three different views (top) and packing models of *race*-**25b** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

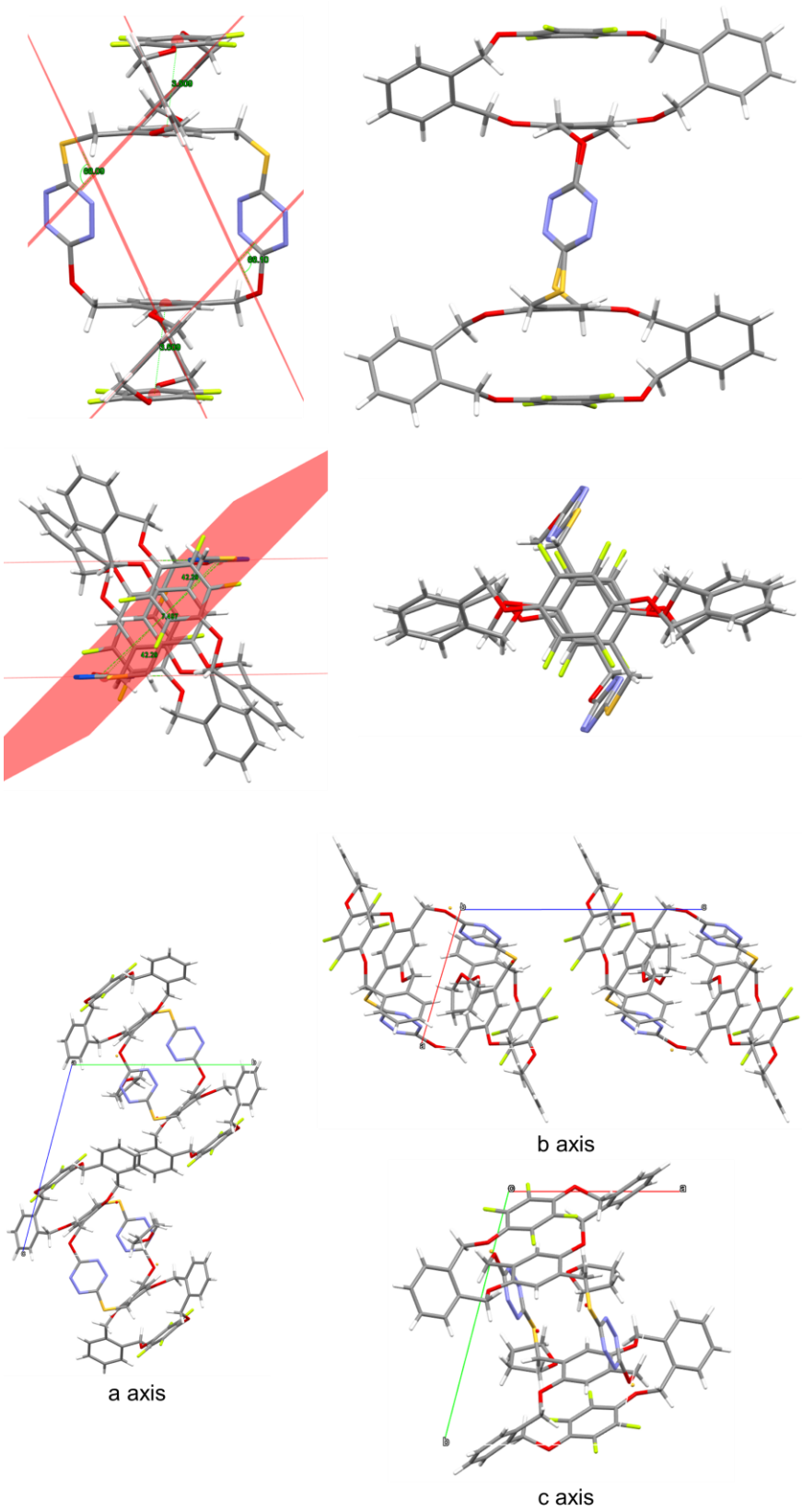


Figure S4B. X-Ray molecular structures of *race*-**26a** with four different views (top) and packing models of *race*-**26a** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

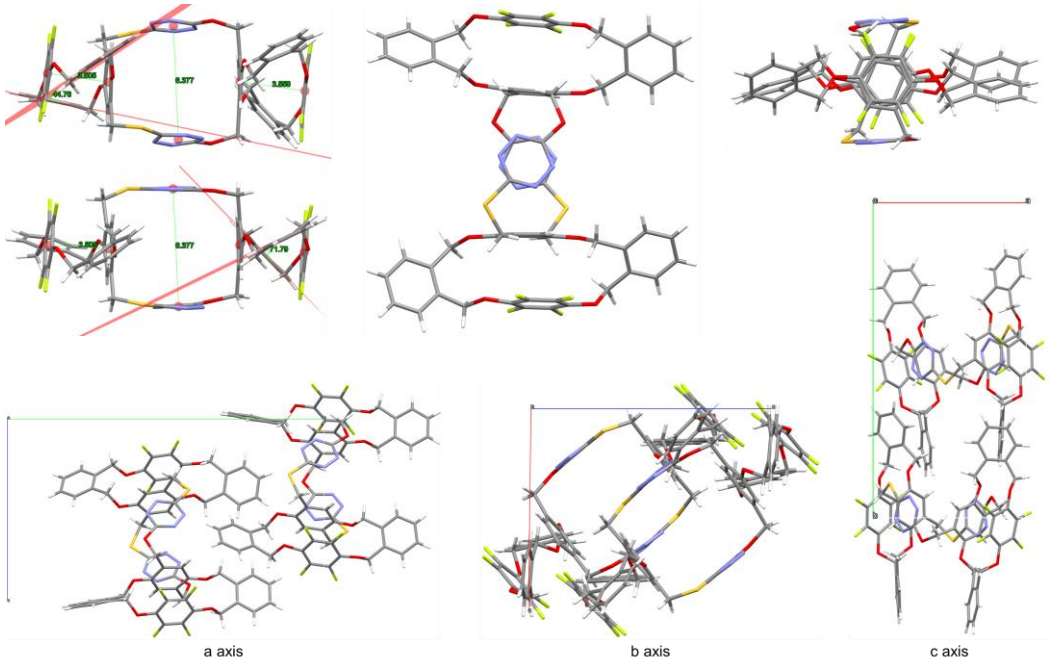


Figure S4C. X-Ray molecular structures of *race*-**26b** with four different views (top) and packing models of *race*-**26b** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

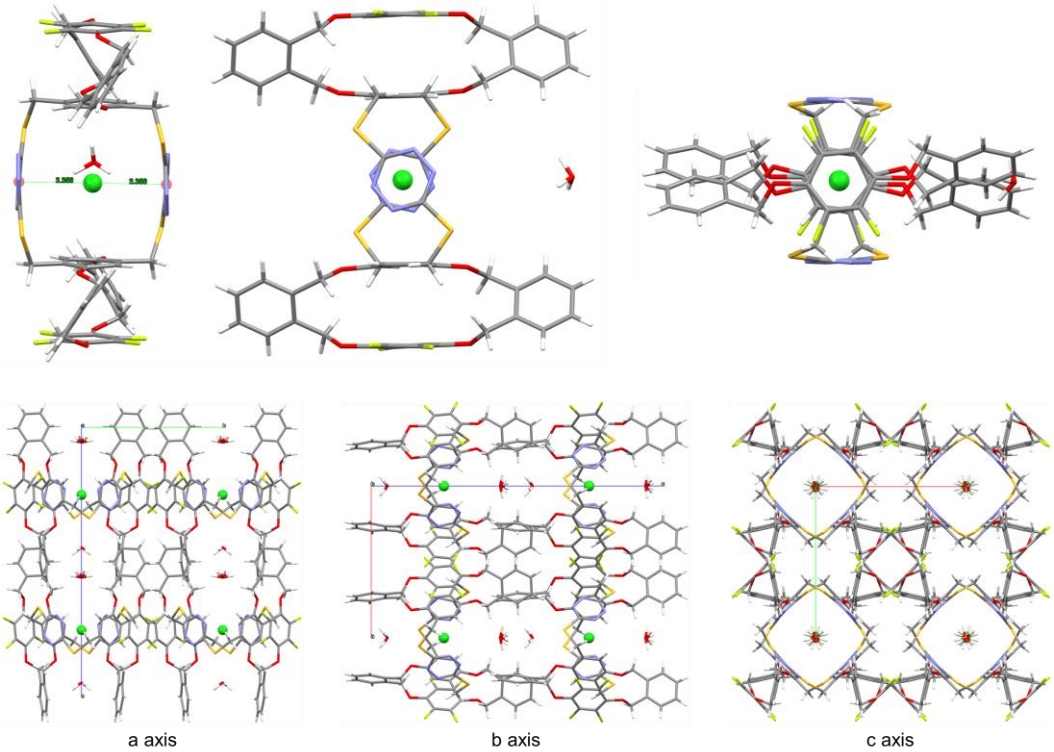


Figure S5. X-ray molecular structures of [*race*-**25b**·H_3OCl] with three different views (top) and packing models of [*race*-**25b**·H_3OCl] viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

3.3 Molecular structures of complexation of spirophanes and tetrathiafulvalene

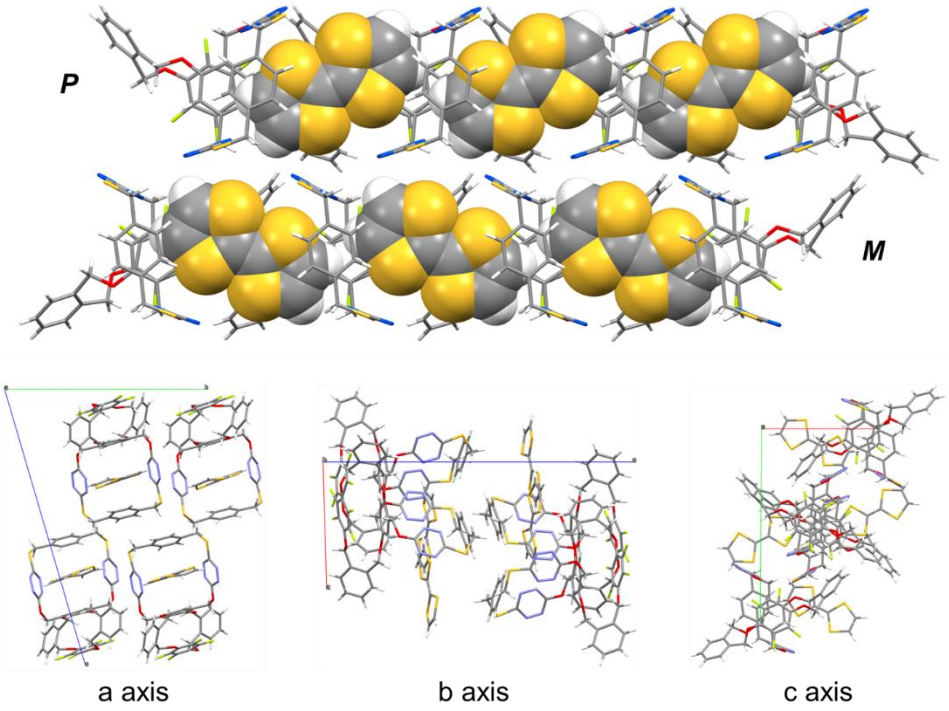


Figure S6. X-ray molecular structures of [*race*-**16**·TTF] (top) and packing models of [*race*-**16**·TTF] viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

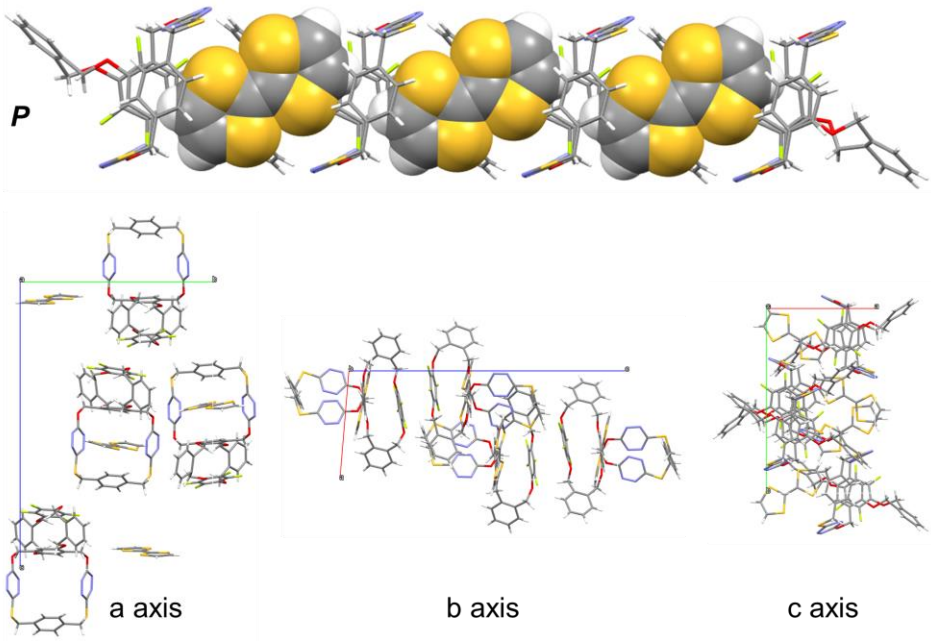


Figure S7A. X-ray molecular structures of [*P*-**16**·TTF] (top) and packing models of [*P*-**16**·TTF] viewed from three different axes (bottom). Solvent molecules and disordered structures are omitted for clarity.

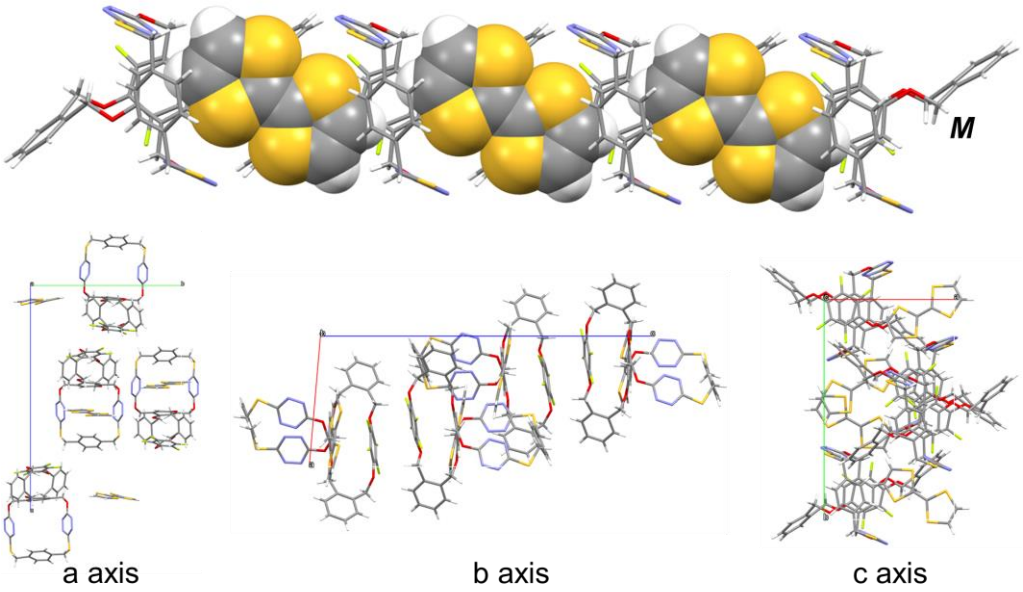
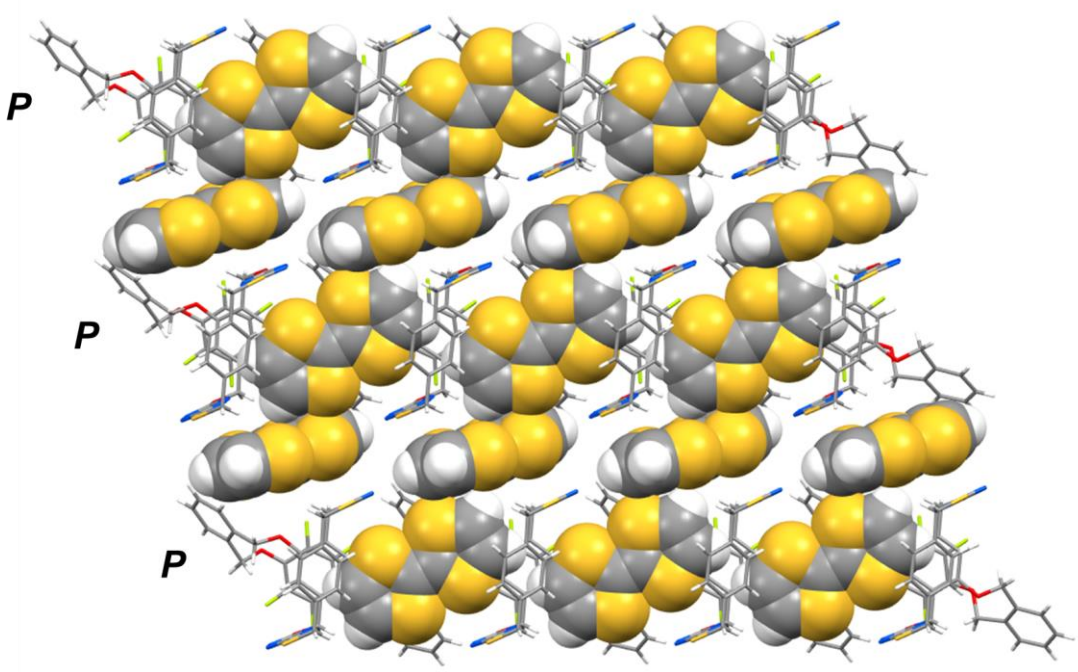


Figure S7B. X-ray molecular structures of [*M*-**16**·TTF] (top) and packing models of [*P*-**16**·TTF] viewed from three different axes (bottom). Solvent molecules are omitted for clarity.



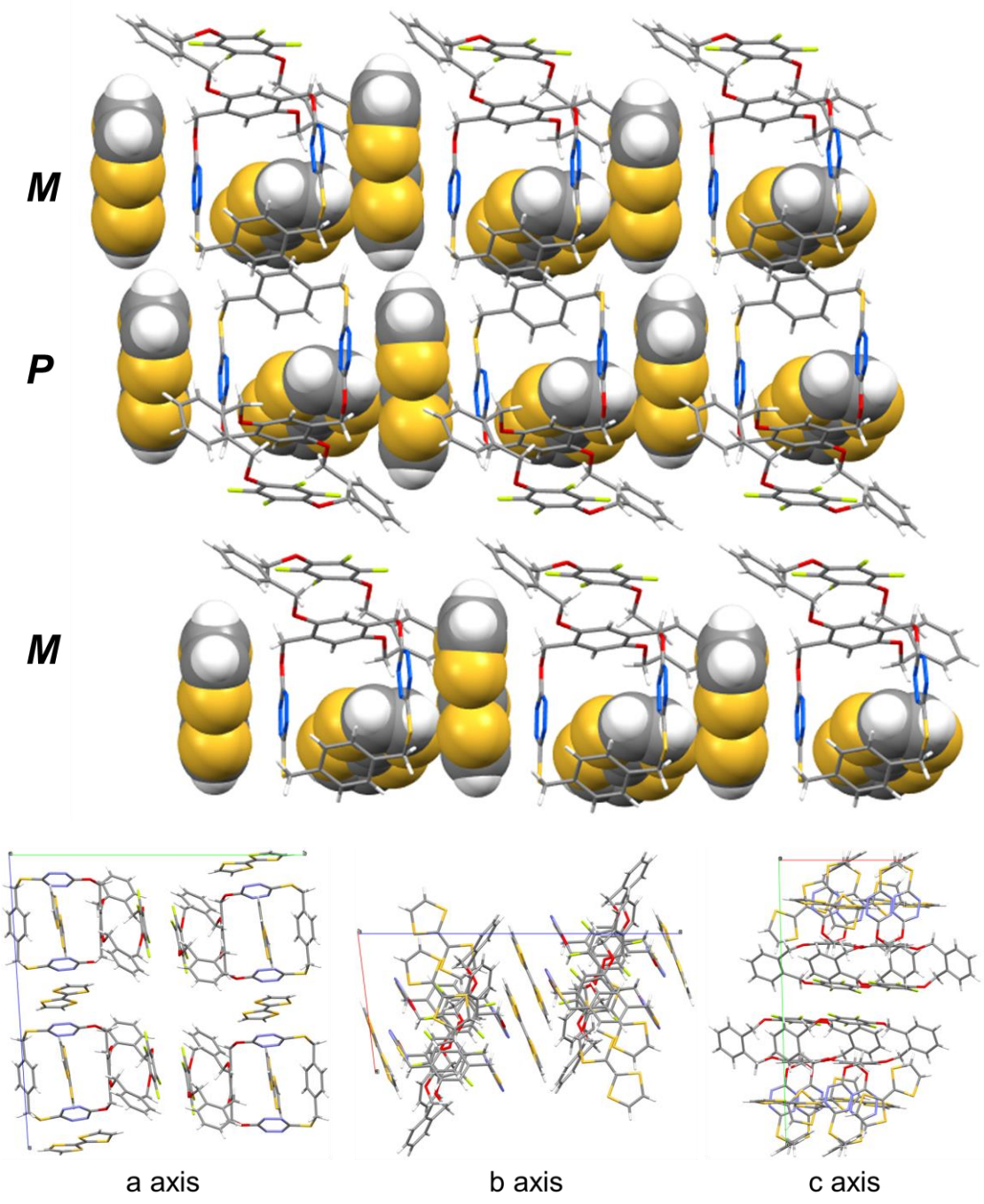


Figure S8. X-ray molecular structures of [*race*-**16**·2TTF] with two different views and packing models of [*race*-**16**·2TTF] viewed from three different axes. Solvent molecules are omitted for clarity.

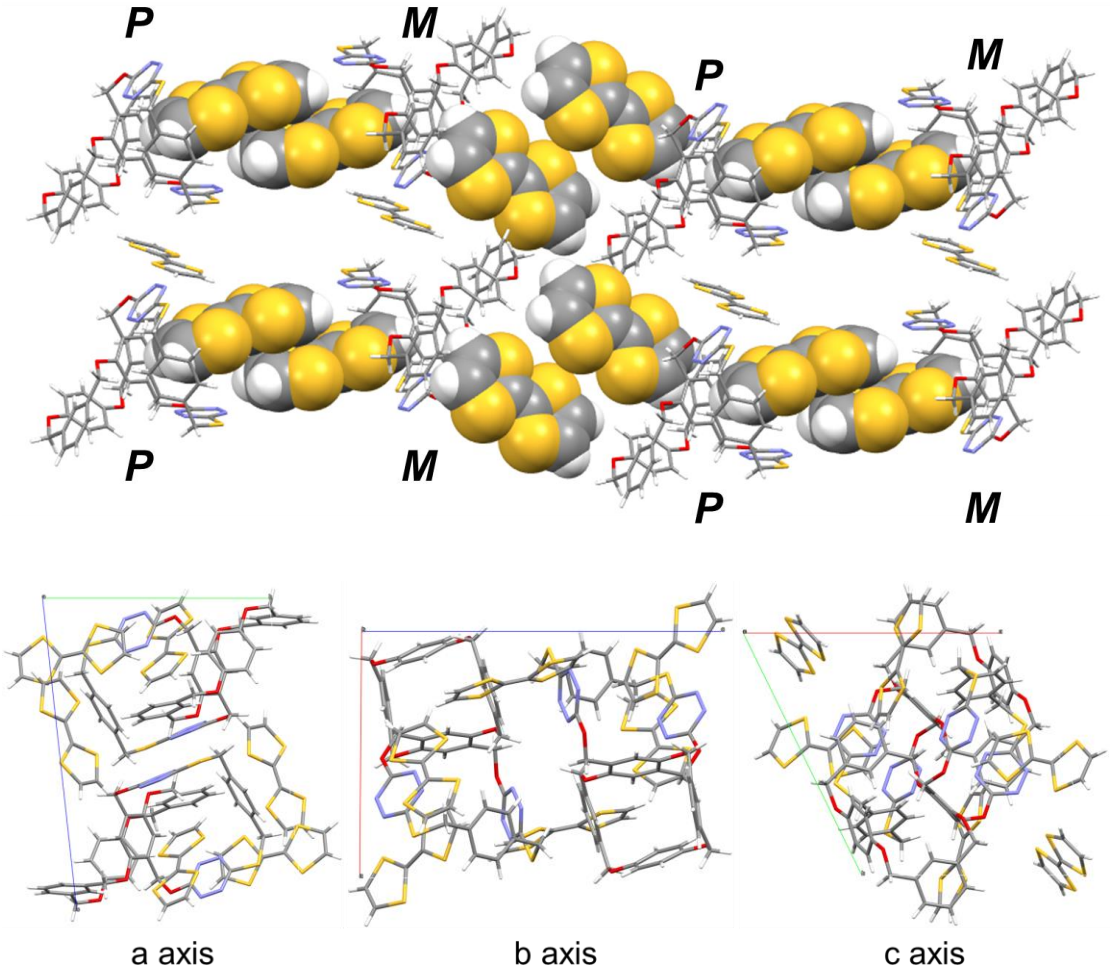


Figure S9. X-ray molecular structures of [*race*-**15**·3TTF] (top) and packing models of [*race*-**15**·3TTF] viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

3.4 Molecular structures of enantiopure macrocycles

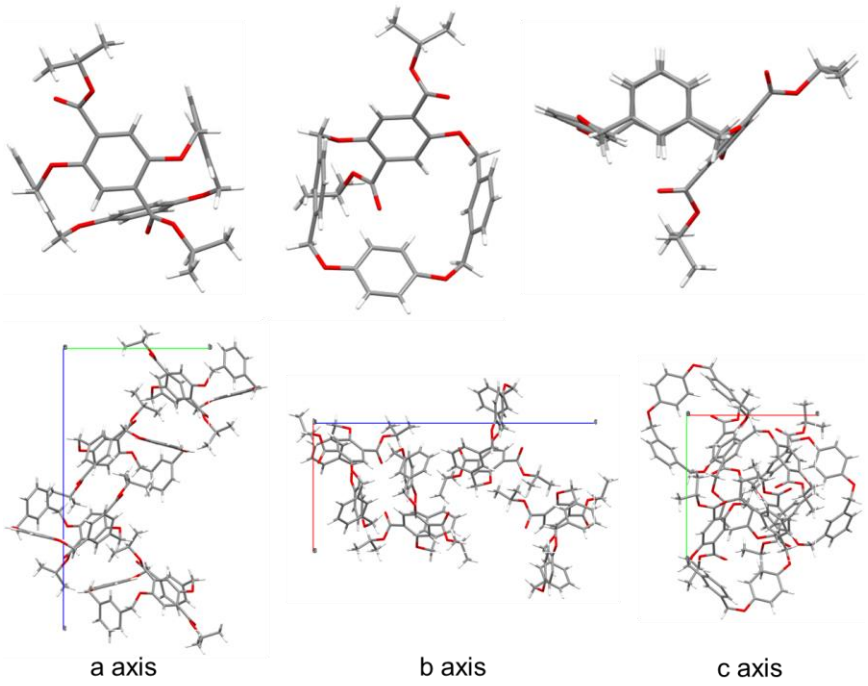


Figure S10. X-ray molecular structures of *P*-**7d** with three different views (top) and packing models of *P*-**7d** viewed from three different axes (bottom).

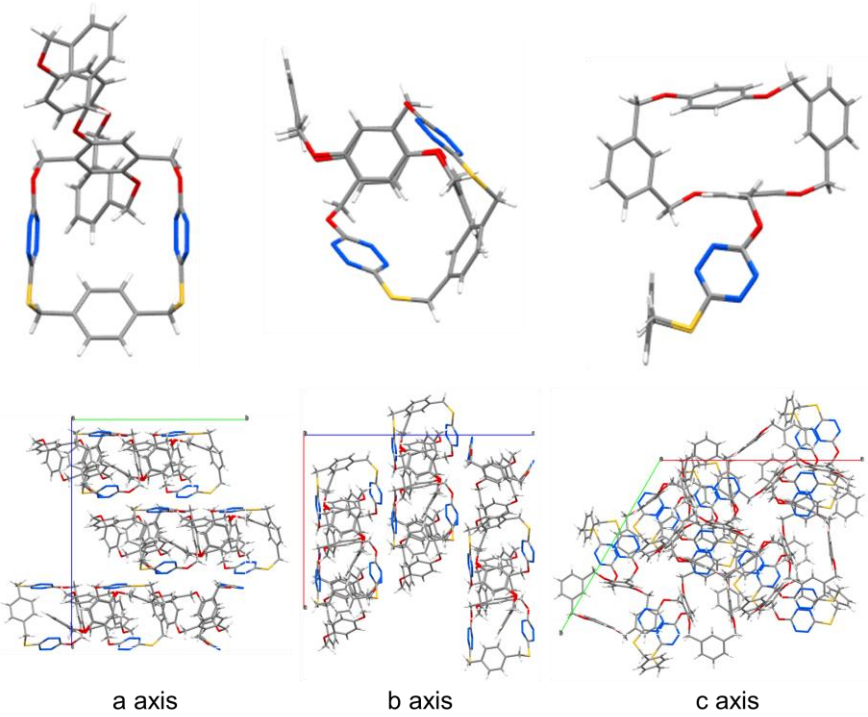


Figure S11. X-ray molecular structures of *M*-**15** with three different views (top) and packing models of *M*-**15** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

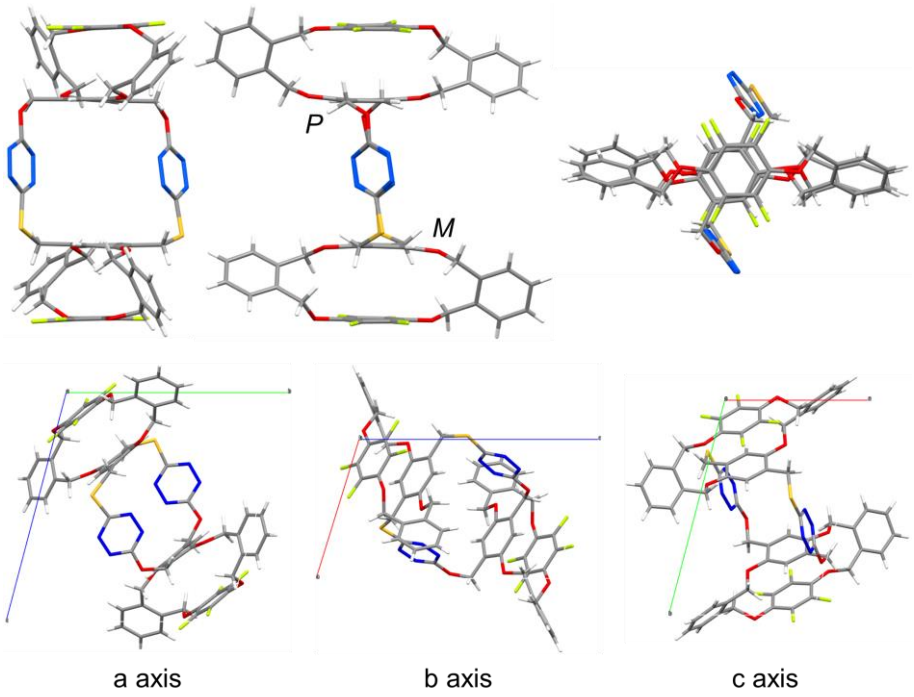


Figure S12. X-ray molecular structures of *P,M*-**26a** with three different views (top) and packing models of *P,M*-**26a** viewed from three different axes (bottom). Solvent molecules are omitted for clarity.

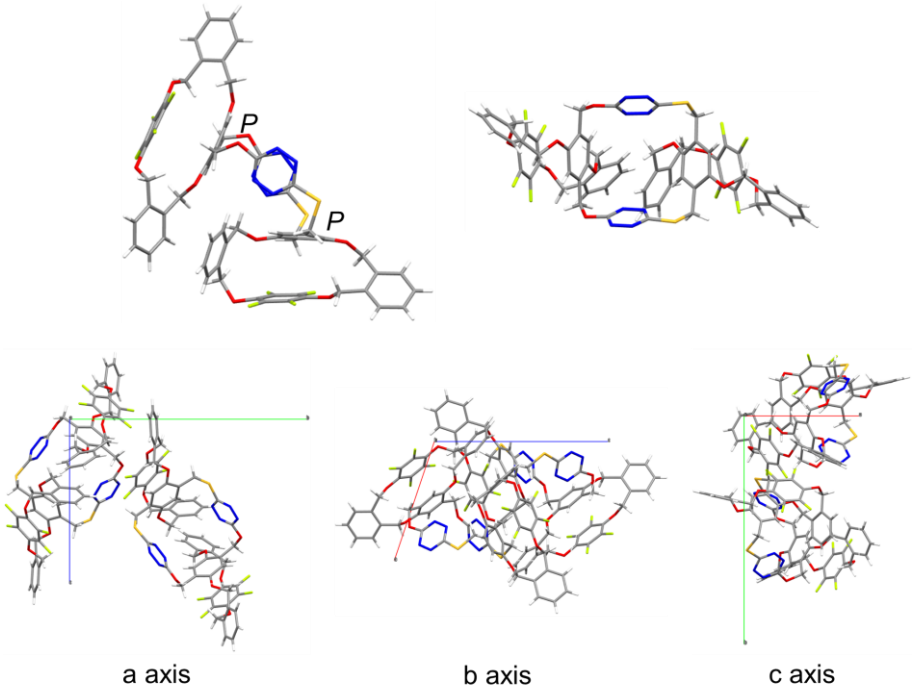


Figure S13. X-ray molecular structure of *P,P*-**26b** with two different views (top) and packing models of *P,P*-**26b** viewed from three different axes (bottom).

3.5 Crystallographic data

Table S12. Crystallographic Data

Identification code	(±)-**7a**	**7b**	**7c**	**7e**
CCDC No.	2261277	2261278	2261279	2261280
Empirical formula	$C_{36}H_{32}F_4O_8$	$C_{32}H_{24}F_4O_8$	$C_{28}H_{16}F_8O_4$	$C_{32}H_{28}O_8$
Formula weight	668.61	612.51	568.41	540.54
Temperature/K	173.00(10)	99.99(10)	169.99(11)	169.98(11)
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$Pna2_1$	$P2_1/n$	I2/a	P-1
a/Å	21.2891(4)	10.4892(2)	17.2008(2)	10.6793(3)
b/Å	8.10320(10)	7.62230(10)	8.13200(10)	11.6277(2)
c/Å	36.4586(7)	34.5522(6)	33.0797(3)	12.1410(3)
α/°	90	90	90	72.256(2)
β/°	90	94.927(2)	91.2430(10)	77.897(2)
γ/°	90	90	90	64.159(2)
Volume/$Å^3$	6289.47(19)	2752.30(8)	4626.00(9)	1287.12(6)
Z	8	4	8	2
$\rho_{calc}g/cm^3$	1.412	1.478	1.632	1.395
μ/mm^{-1}	0.977	1.063	1.336	0.828
F(000)	2784	1264	2304	568
Crystal size/mm^3	0.8 × 0.1 × 0.05	0.6 × 0.3 × 0.05	0.2 × 0.1 × 0.05	0.6 × 0.5 × 0.2
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.306 to 130.21	5.134 to 150.84	5.344 to 150.754	7.676 to 150.664
Index ranges	-24 ≤ h ≤ 25, -9 ≤ k ≤ 8, -42 ≤ l ≤ 42	-13 ≤ h ≤ 12, -9 ≤ k ≤ 3, -42 ≤ l ≤ 42	-18 ≤ h ≤ 21, -9 ≤ k ≤ 9, -40 ≤ l ≤ 41	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	57052	18855	16169	16920
Independent reflections	10364 [R_{int} = 0.0664, R_{sigma} = 0.0412]	5468 [R_{int} = 0.0333, R_{sigma} = 0.0315]	4549 [R_{int} = 0.0204, R_{sigma} = 0.0191]	5085 [R_{int} = 0.0202, R_{sigma} = 0.0180]
Data/restraints/parameters	10364/73/894	5468/0/399	4549/0/361	5085/0/363
Goodness-of-fit on F^2	1.06	1.023	1.049	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1888	R_1 = 0.0381, wR_2 = 0.0965	R_1 = 0.0367, wR_2 = 0.1005	R_1 = 0.0488, wR_2 = 0.1345
Final R indexes [all data]	R_1 = 0.0780, wR_2 = 0.1945	R_1 = 0.0448, wR_2 = 0.1005	R_1 = 0.0396, wR_2 = 0.1025	R_1 = 0.0524, wR_2 = 0.1373
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.33	0.18/-0.26	0.22/-0.23	0.76/-0.25

Identification code	**7f**	(±)-**8**	(±)-**15**·2DCE	(±)-**16**·2acetone
CCDC No.	2261281	2261282	2261283	2261284
Empirical formula	$C_{28}H_{20}F_4O_4$	$C_{32}H_{24}F_4O_8$	$C_{44}H_{38}Cl_2N_8O_6S_2$	$C_{48}H_{42}F_4N_8O_8S_2$
Formula weight	496.44	612.51	909.84	999.01
Temperature/K	169.99(11)	172.99(10)	105(4)	137(50)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	P-1	$P2_1/n$	P-1
a/Å	11.69180(10)	10.04050(10)	21.3087(3)	9.5906(2)
b/Å	8.03030(10)	11.2749(2)	11.0893(2)	15.6459(3)
c/Å	23.5644(2)	12.9240(2)	37.4232(5)	16.7187(2)
α/°	90	104.2800(10)	90	76.4380(10)
β/°	90.3250(10)	105.1950(10)	90.3860(10)	89.655(2)
γ/°	90	98.3680(10)	90	73.552(2)
Volume/Å^3	2212.39(4)	1333.29(4)	8842.8(2)	2334.04(8)
Z	4	2	8	2
ρ_{calc}g/cm^3	1.49	1.526	1.367	1.421
μ/mm^{-1}	1.037	1.098	2.679	1.722
F(000)	1024	632	3776	1036
Crystal size/mm^3	0.5 × 0.4 × 0.1	0.8 × 0.2 × 0.2	0.6 × 0.2 × 0.02	0.6 × 0.2 × 0.02
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.504 to 150.622	7.426 to 155.582	8.19 to 134.98	7.108 to 133.372
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 7, -29 ≤ l ≤ 28	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -12 ≤ l ≤ 16	-25 ≤ h ≤ 25, -12 ≤ k ≤ 13, -44 ≤ l ≤ 44	-11 ≤ h ≤ 10, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	14843	25157	101790	37781
Independent reflections	4415 [R_{int} = 0.0242, R_{sigma} = 0.0224]	5461 [R_{int} = 0.0227, R_{sigma} = 0.0128]	15613 [R_{int} = 0.1147, R_{sigma} = 0.0611]	8027 [R_{int} = 0.1085, R_{sigma} = 0.0698]
Data/restraints/parameters	4415/0/325	5461/0/399	15613/0/1117	8027/0/635
Goodness-of-fit on F^2	1.055	1.053	1.04	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.0956	R_1 = 0.0384, wR_2 = 0.1025	R_1 = 0.0769, wR_2 = 0.2023	R_1 = 0.0628, wR_2 = 0.1594
Final R indexes [all data]	R_1 = 0.0397, wR_2 = 0.0982	R_1 = 0.0396, wR_2 = 0.1035	R_1 = 0.0874, wR_2 = 0.2115	R_1 = 0.0709, wR_2 = 0.1658
Largest diff. peak/hole / e Å^{-3}	0.20/-0.23	0.31/-0.21	1.24/-0.51	0.59/-0.72

Identification code	(±)-**25b**·Toluene	(±)-**26a**·THF	(±)-**26b**·3CH_3CN·CH_3OH	*P*-**7d**
CCDC No.	2261285	2261286	2261287	2261291
Empirical formula	$C_{78}H_{60}F_8N_8O_8S_4$	$C_{72}H_{60}F_8N_8O_{12}S_2$	$C_{70}H_{55.5}F_8N_{10.5}O_{11}S_2$	$C_{36}H_{36}O_8$
Formula weight	1517.58	1445.4	1435.87	596.65
Temperature/K	225(40)	172.98(17)	173(2)	112(8)
Crystal system	tetragonal	triclinic	monoclinic	orthorhombic
Space group	P-4c2	P-1	$P2_1$	$P2_12_12_1$
a/Å	12.7227(4)	8.8879(2)	11.22933(19)	10.6803(7)
b/Å	12.7227(4)	13.4255(5)	23.1073(6)	12.0458(8)
c/Å	23.8456(5)	14.8388(4)	13.31714(19)	23.3062(19)
α/°	90	101.412(3)	90	90
β/°	90	103.513(2)	90.7038(14)	90
γ/°	90	101.034(3)	90	90
Volume/$Å^3$	3859.8(3)	1634.29(9)	3455.26(11)	2998.4(4)
Z	2	1	2	4
$\rho_{calc}g/cm^3$	1.306	1.469	1.38	1.322
μ/mm^{-1}	1.8	1.558	1.471	0.759
F(000)	1568	748	1482	1264
Crystal size/mm^3	0.8 × 0.02 × 0.02	0.1 × 0.05 × 0.05	0.6 × 0.5 × 0.1	0.2 × 0.2 × 0.2
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.948 to 154.624	6.334 to 156.648	6.638 to 154.986	8.262 to 156
Index ranges	-12 ≤ h ≤ 14, -15 ≤ k ≤ 16, -12 ≤ l ≤ 29	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -18 ≤ l ≤ 14	-14 ≤ h ≤ 14, -28 ≤ k ≤ 27, -15 ≤ l ≤ 16	-11 ≤ h ≤ 13, -15 ≤ k ≤ 13, -29 ≤ l ≤ 29
Reflections collected	11709	29356	34533	25654
Independent reflections	3719 [R_{int} = 0.0391, R_{sigma} = 0.0440]	6698 [R_{int} = 0.0892, R_{sigma} = 0.0660]	11655 [R_{int} = 0.0449, R_{sigma} = 0.0338]	6203 [R_{int} = 0.0302, R_{sigma} = 0.0203]
Data/restraints/parameters	3719/3/241	6698/90/460	11655/174/861	6203/0/402
Goodness-of-fit on F^2	1.023	1.103	1.082	1.09
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1020	R_1 = 0.1171, wR_2 = 0.2816	R_1 = 0.0962, wR_2 = 0.2736	R_1 = 0.0316, wR_2 = 0.0829
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1151	R_1 = 0.1457, wR_2 = 0.2904	R_1 = 0.1012, wR_2 = 0.2803	R_1 = 0.0320, wR_2 = 0.0832
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.14	0.53/-0.41	1.37/-0.62	0.18/-0.20
Flack parameter				0.02(5)

Identification code	*M*-**15**·5/3$CHCl_3$	*P*,*M*-**26a**·2THF	*P*,*P*-**26b**	(±)-**25b**·H_3OCl·2DCE·H_2O
CCDC No.	2261299	2261294	2261295	2261288
Empirical formula	$C_{43.67}H_{35.67}Cl_5N_8O_6S_2$	$C_{70}H_{56}F_8N_8O_{11.5}S_2$	$C_{64}H_{44}F_8N_8O_{10}S_2$	$C_{68}H_{57}Cl_5F_8N_8O_{10}S_4$
Formula weight	1009.84	1409.34	1301.19	1603.7
Temperature/K	172.99(10)	173.00(10)	172.99(10)	174(3)
Crystal system	trigonal	triclinic	monoclinic	tetragonal
Space group	R3	P1	$P2_1$	P-4c2
a/Å	21.6918(2)	8.9270(2)	10.48012(13)	12.4912(3)
b/Å	21.6918(2)	13.6209(3)	19.7332(2)	12.4912(3)
c/Å	24.6601(2)	14.7225(3)	14.4640(2)	23.9051(7)
α/°	90	101.208(2)	90	90
β/°	90	104.314(2)	108.5819(15)	90
γ/°	120	101.040(2)	90	90
Volume/$Å^3$	10048.9(2)	1646.58(7)	2835.32(7)	3729.9(2)
Z	9	1	2	2
$\rho_{calc}g/cm^3$	1.502	1.421	1.524	1.428
μ/mm^{-1}	4.326	1.526	1.702	3.52
F(000)	4668	728	1336	1644
Crystal size/mm^3	0.6 × 0.5 × 0.3	0.5 × 0.3 × 0.3	0.2 × 0.2 × 0.02	0.2 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.914 to 157.244	6.406 to 154.804	6.446 to 156.27	7.396 to 154.822
Index ranges	-21 ≤ h ≤ 27, -27 ≤ k ≤ 24, -31 ≤ l ≤ 31	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-12 ≤ h ≤ 13, -24 ≤ k ≤ 24, -18 ≤ l ≤ 18	-15 ≤ h ≤ 15, -13 ≤ k ≤ 15, -29 ≤ l ≤ 30
Reflections collected	64749	58642	53870	17203
Independent reflections	9218 [R_{int} = 0.0527, R_{sigma} = 0.0207]	12534 [R_{int} = 0.0777, R_{sigma} = 0.0398]	11743 [R_{int} = 0.0402, R_{sigma} = 0.0257]	3794 [R_{int} = 0.1085, R_{sigma} = 0.0591]
Data/restraints/parameters	9218/1/583	12534/3/919	11743/43/829	3794/39/237
Goodness-of-fit on F^2	1.041	0.909	1.03	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0554, wR_2 = 0.1649	R_1 = 0.0570, wR_2 = 0.1691	R_1 = 0.0413, wR_2 = 0.1091	R_1 = 0.0922, wR_2 = 0.2541
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1658	R_1 = 0.0592, wR_2 = 0.1726	R_1 = 0.0453, wR_2 = 0.1121	R_1 = 0.1088, wR_2 = 0.2765
Largest diff. peak/hole / e $Å^{-3}$	0.92/-1.00	0.86/-0.43	0.62/-0.30	1.09/-0.38
Flack parameter	0.015(4)	0.043(8)	0.011(10)	-

Identification code	(±)-**15**·3TTF·0.5DCE	(±)-**16**·TTF·0.5dioxane	(±)-**16**·2TTF·$CHCl_3$
CCDC No.	2261289	2261298	2261290
Empirical formula	$C_{61}H_{48}Cl_{0.5}N_8O_6S_{14}$	$C_{50}H_{38}F_4N_8O_7S_6$	$C_{55}H_{39}Cl_3F_4N_8O_6S_{10}$
Formula weight	1455.64	1131.24	1410.89
Temperature/K	99.98(10)	100.00(10)	100.00(10)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.7566(3)	10.4191(2)	10.46661(10)
b/Å	14.5509(3)	18.3885(3)	23.8858(3)
c/Å	18.1357(4)	26.4258(6)	24.0457(2)
α/°	83.2409(18)	73.686(2)	86.0189(9)
β/°	87.432(2)	88.364(2)	82.6961(8)
γ/°	63.772(2)	89.8450(10)	88.0689(9)
Volume/$Å^3$	3233.74(14)	4857.05(17)	5946.46(11)
Z	2	4	4
$\rho_{calc}g/cm^3$	1.495	1.547	1.576
μ/mm^{-1}	5.036	3.281	5.287
F(000)	1501	2328	2880
Crystal size/mm^3	1 × 0.8 × 0.03	0.2 × 0.1 × 0.02	0.4 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.906 to 156.35	5.008 to 155.986	3.71 to 157.104
Index ranges	-17 ≤ h ≤ 17, -14 ≤ k ≤ 18, -21 ≤ l ≤ 22	-11 ≤ h ≤ 13, -23 ≤ k ≤ 22, -33 ≤ l ≤ 32	-13 ≤ h ≤ 11, -29 ≤ k ≤ 30, -30 ≤ l ≤ 30
Reflections collected	44015	55744	112360
Independent reflections	13170 [R_{int} = 0.0818, R_{sigma} = 0.0562]	19059 [R_{int} = 0.0507, R_{sigma} = 0.0380]	24377 [R_{int} = 0.0705, R_{sigma} = 0.0379]
Data/restraints/parameters	13170/93/912	19059/2/1351	24377/0/1586
Goodness-of-fit on F^2	1.086	1.068	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.2201	R_1 = 0.1140, wR_2 = 0.3014	R_1 = 0.0869, wR_2 = 0.2143
Final R indexes [all data]	R_1 = 0.0835, wR_2 = 0.2322	R_1 = 0.1215, wR_2 = 0.3080	R_1 = 0.0940, wR_2 = 0.2175
Largest diff. peak/hole / e $Å^{-3}$	1.16/-0.74	2.73/-1.25	1.44/-1.07

Identification code	*M*-**16**·TTF·0.5 DCE	*P*-**16**·TTF·0.5 DCE
CCDC No.	2261292	2261293
Empirical formula	$C_{49}H_{36}ClF_4N_8O_6S_6$	$C_{49}H_{36}ClF_4N_8O_6S_6$
Formula weight	1136.67	1136.67
Temperature/K	172.99(10)	100.01(10)
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a/Å	10.6988(4)	10.6362(5)
b/Å	17.9646(7)	18.0095(11)
c/Å	27.0532(16)	26.978(2)
α/°	90	90
β/°	94.936(5)	94.741(6)
γ/°	90	90
Volume/Å^3	5180.3(4)	5150.1(6)
Z	4	4
ρ_{calc}g/cm^3	1.457	1.466
μ/mm^{-1}	3.528	3.549
F(000)	2332	2332
Crystal size/mm^3	0.3 × 0.05 × 0.005	0.6 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.92 to 155.812	8.208 to 179.436
Index ranges	$-13 \le h \le 13$, $-22 \le k \le 22$, $-32 \le l \le 34$	$-13 \le h \le 13$, $-22 \le k \le 22$, $0 \le l \le 34$
Reflections collected	97629	20346
Independent reflections	19867 [R_{int} = 0.1474, R_{sigma} = 0.0648]	20346 [R_{int} = ?, R_{sigma} = 0.0768]
Data/restraints/parameters	19867/721/1286	20346/893/1364
Goodness-of-fit on F^2	1.063	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.1347, wR_2 = 0.3117	R_1 = 0.1335, wR_2 = 0.2780
Final R indexes [all data]	R_1 = 0.1556, wR_2 = 0.3245	R_1 = 0.1602, wR_2 = 0.2956
Largest diff. peak/hole / e Å^{-3}	1.06/-0.68	1.27/-0.97
Flack parameter	0.105(13)	0.069(13)

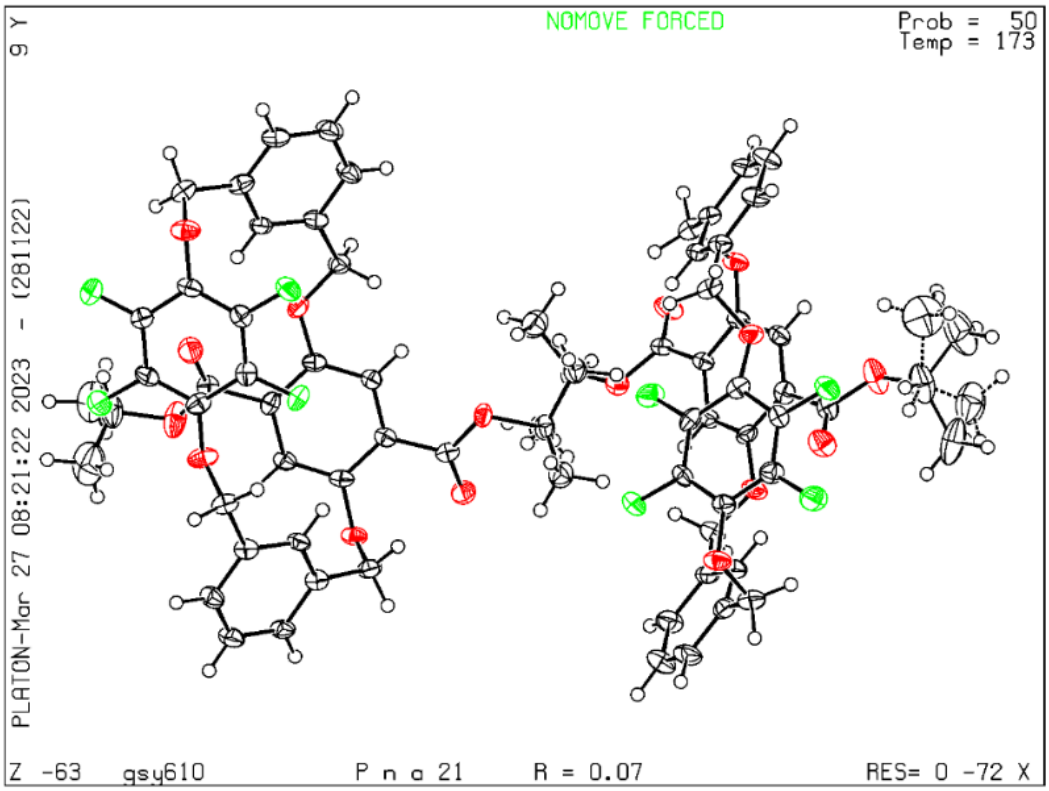


Figure S14A. X-ray molecular structure of *race*-**7a** (CCDC 2261277). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

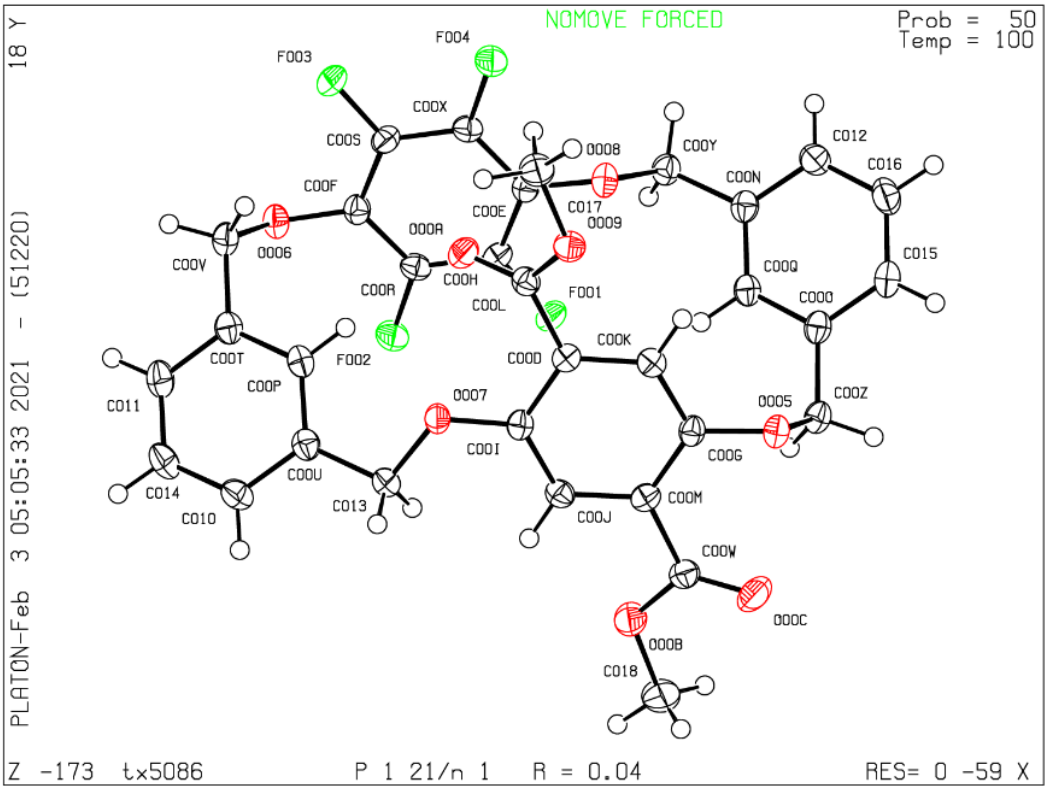


Figure S14B. X-ray molecular structure of **7b** (CCDC 2261278). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

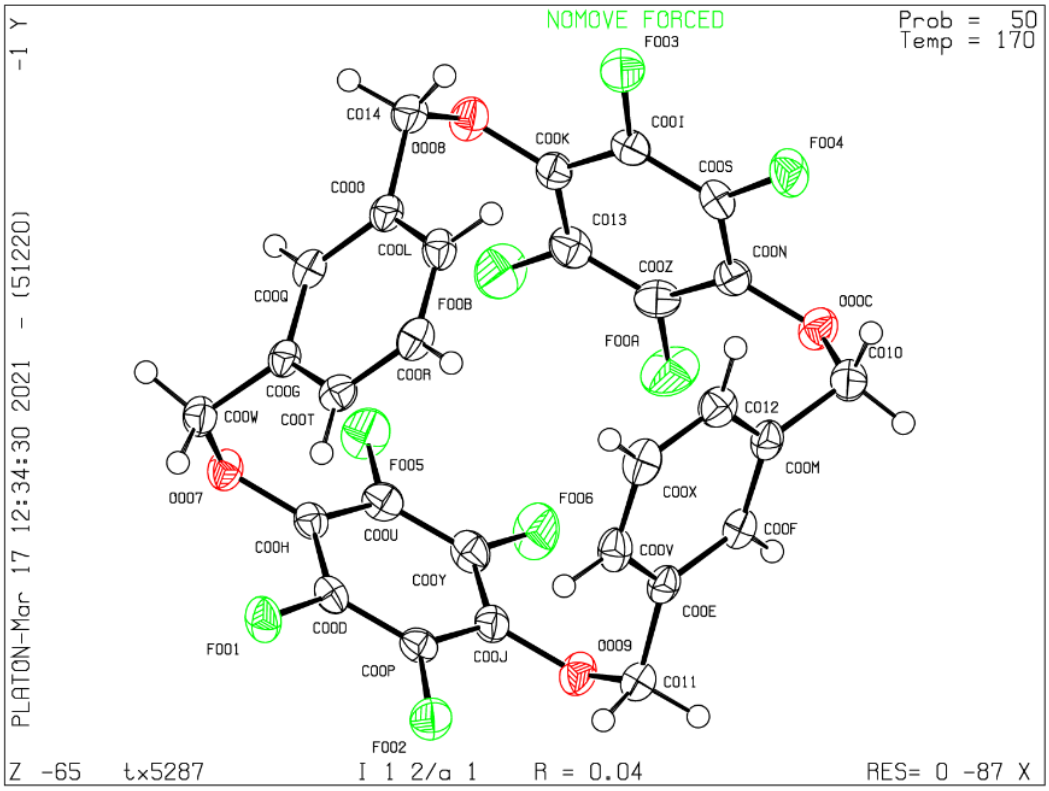


Figure S14C. X-ray molecular structure of **7c** (CCDC 2261279). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

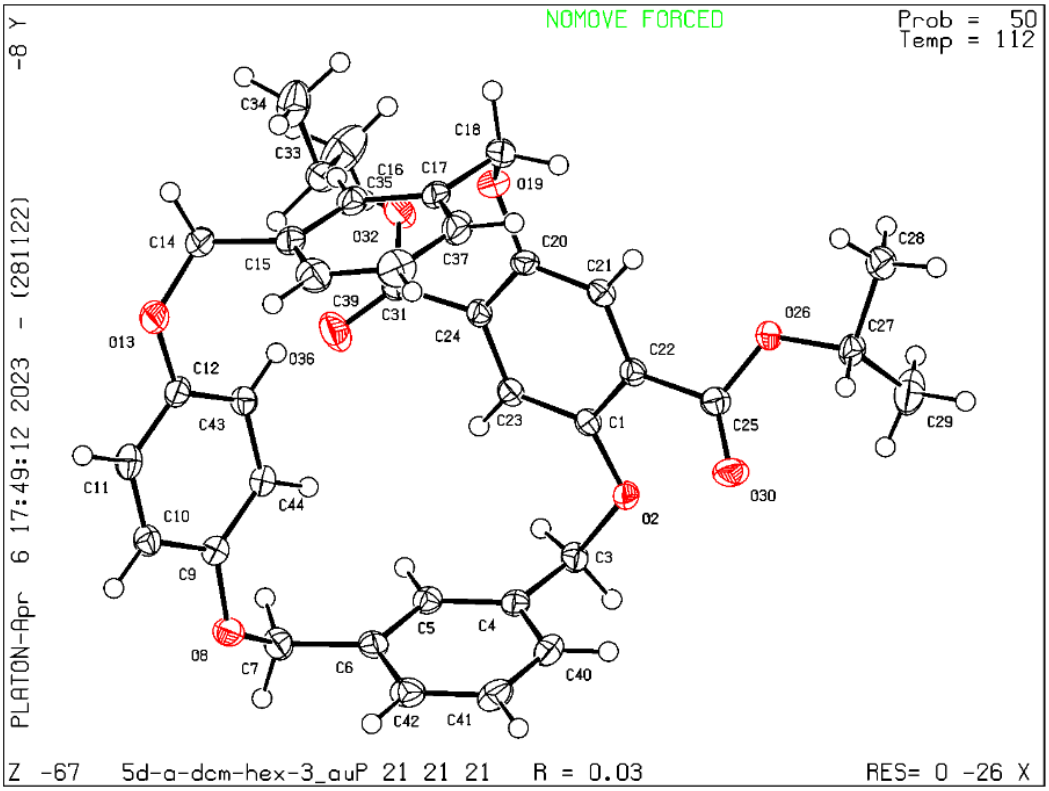


Figure S14D. X-ray molecular structure of *P*-**7d** (CCDC 2261291). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

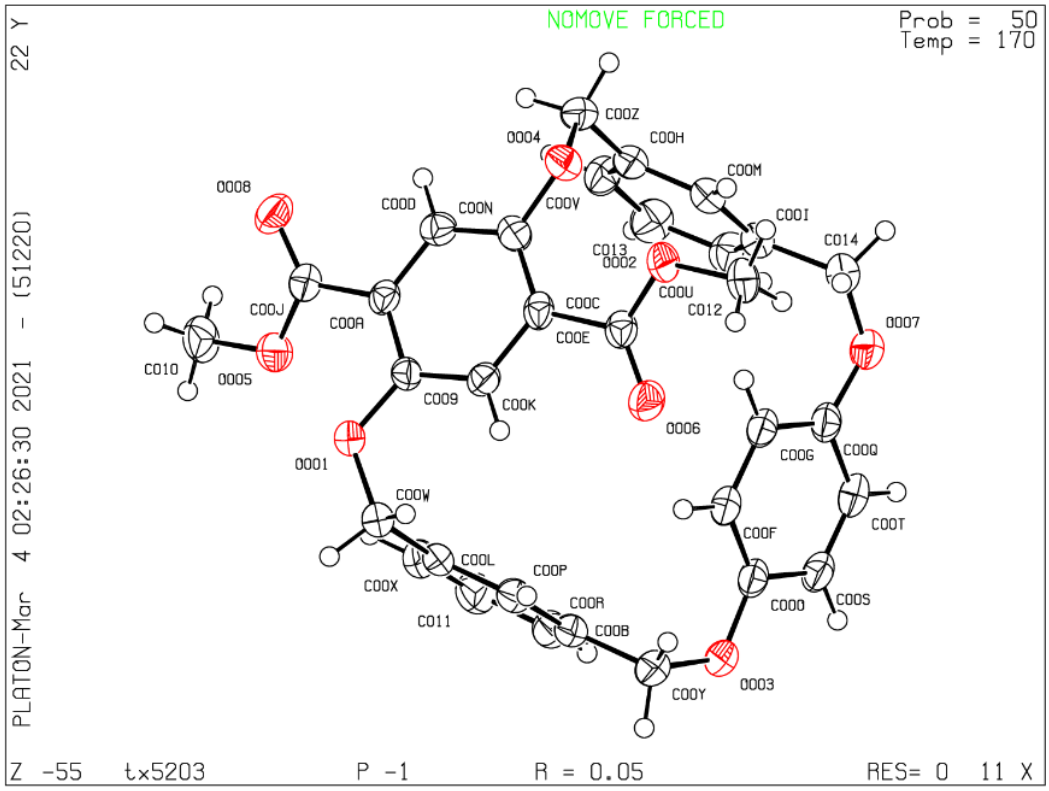


Figure S14E. X-ray molecular structure of **7e** (CCDC 2261280). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

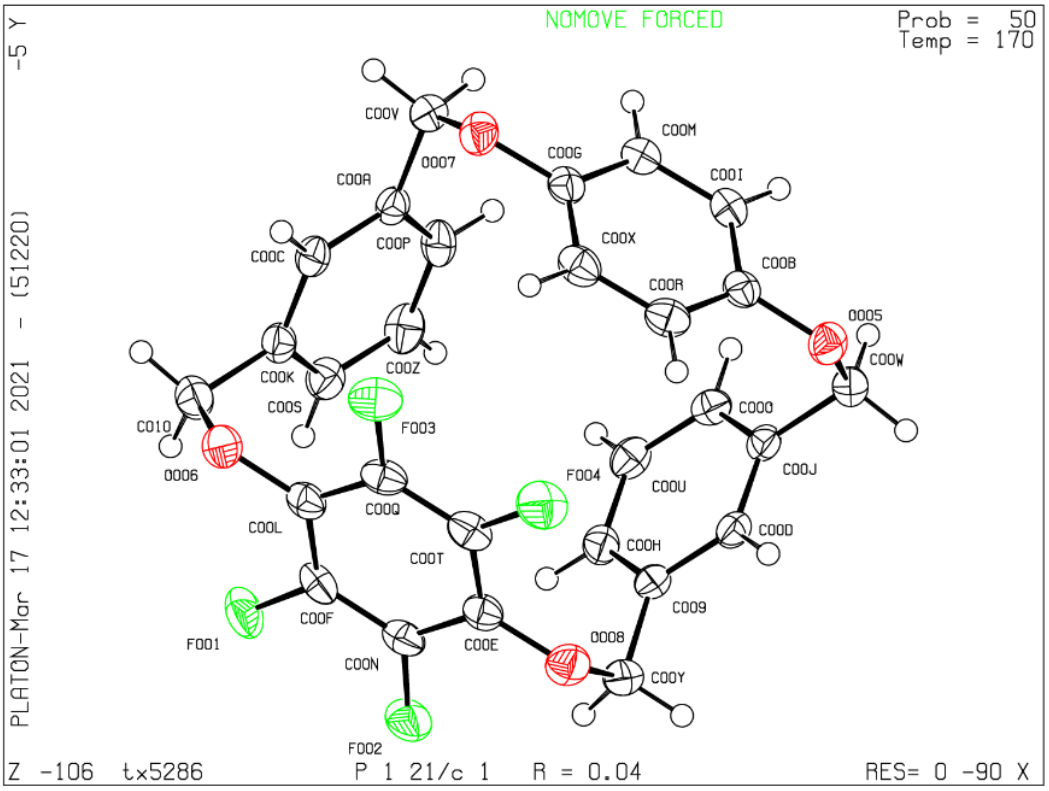


Figure S14F. X-ray molecular structure of **7f** (CCDC 2261281). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

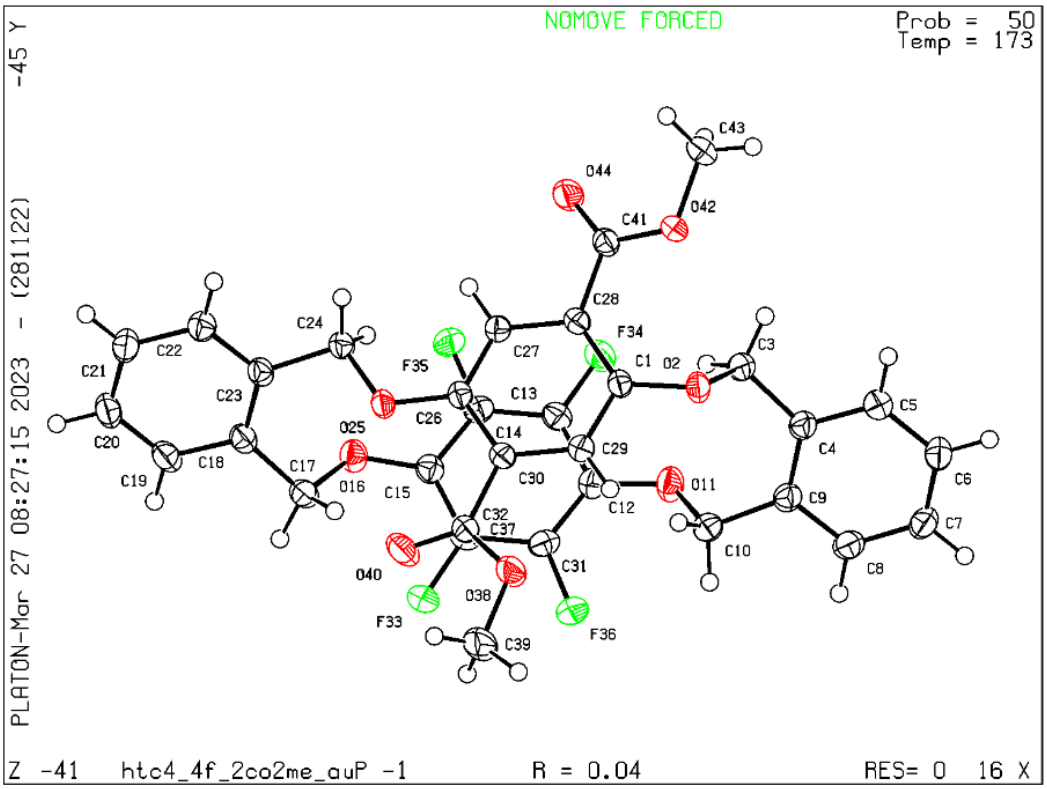


Figure S14G. X-ray molecular structure of *race*-**8** (CCDC 2261282). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

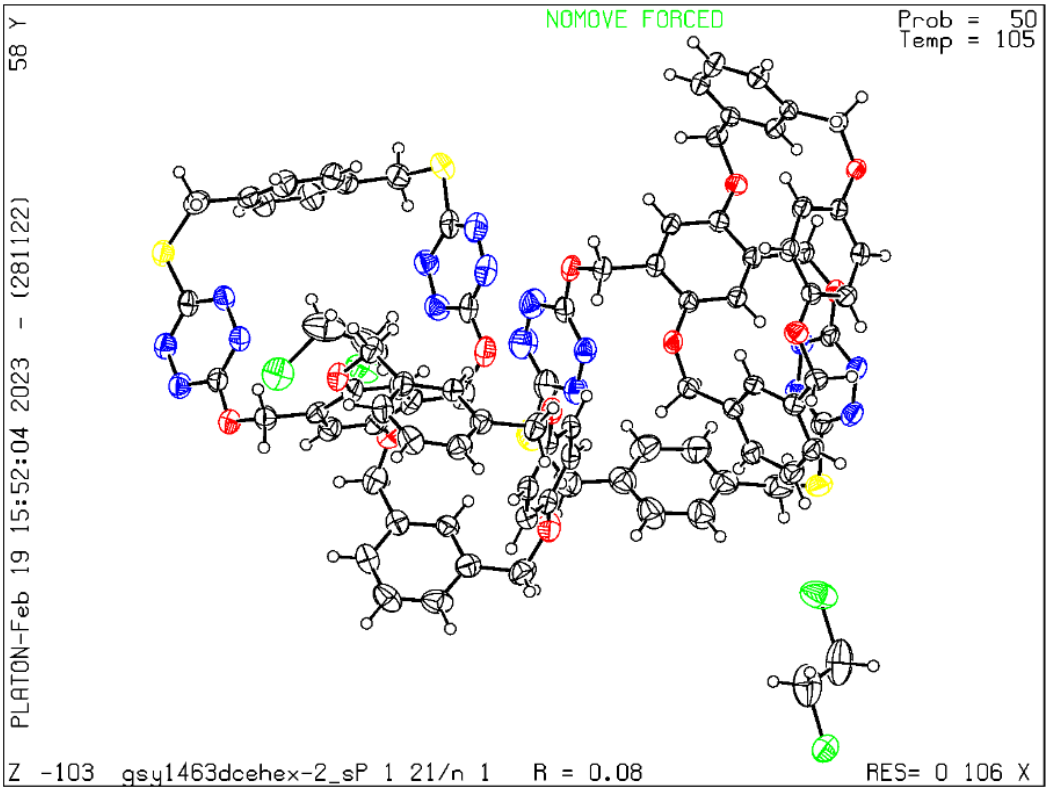


Figure S14H. X-ray molecular structure of *race*-**15** (CCDC 2261283). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

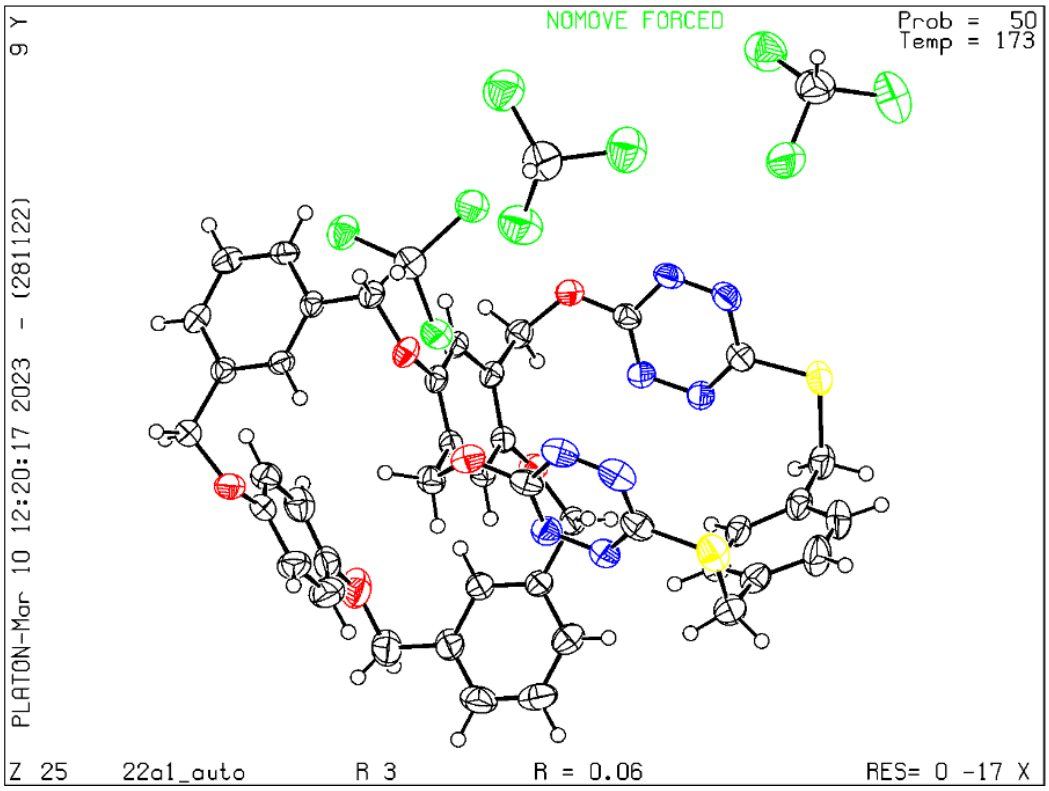


Figure S14I. X-ray molecular structure of *M*-**15** (CCDC 2261299). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

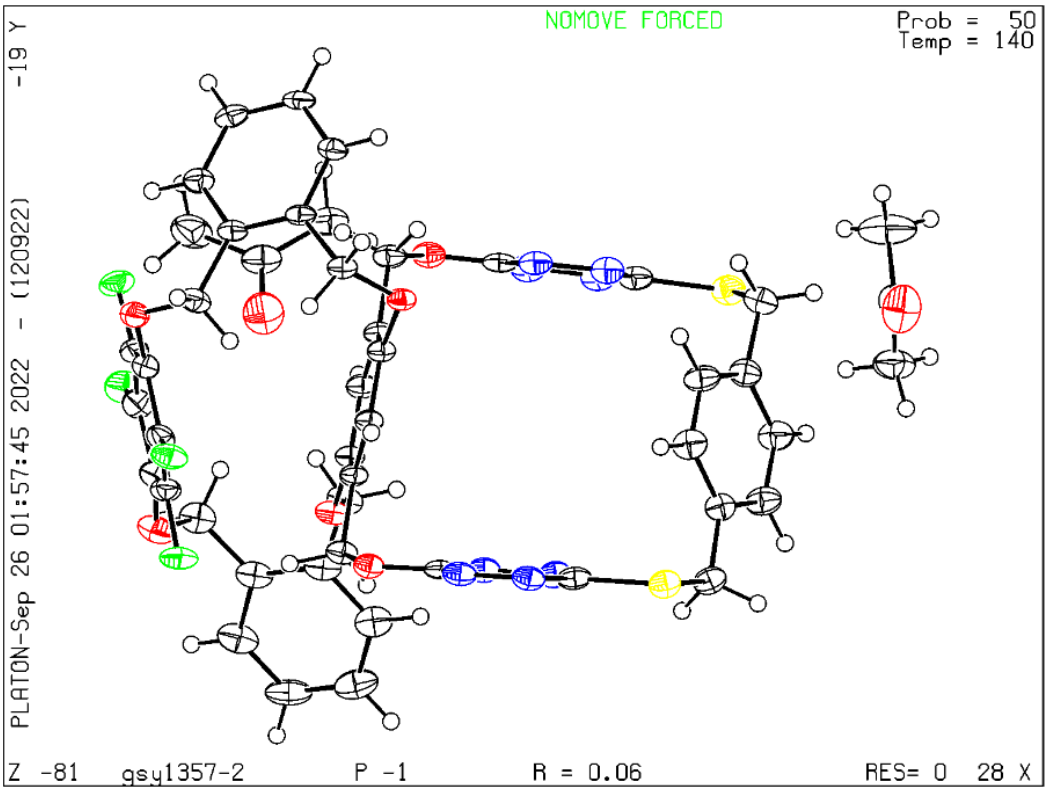


Figure S14J. X-ray molecular structure of *race*-**16** (CCDC 2261284). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

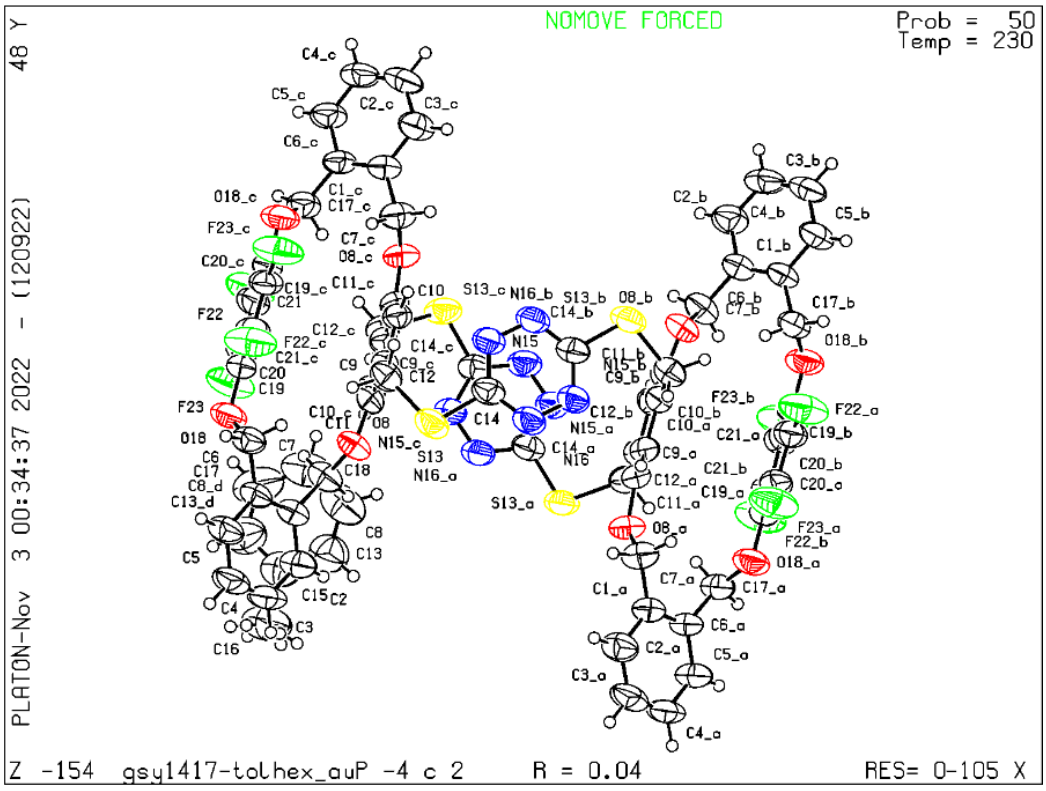


Figure S14K. X-ray molecular structure of *race*-**25b** (CCDC 2261285). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

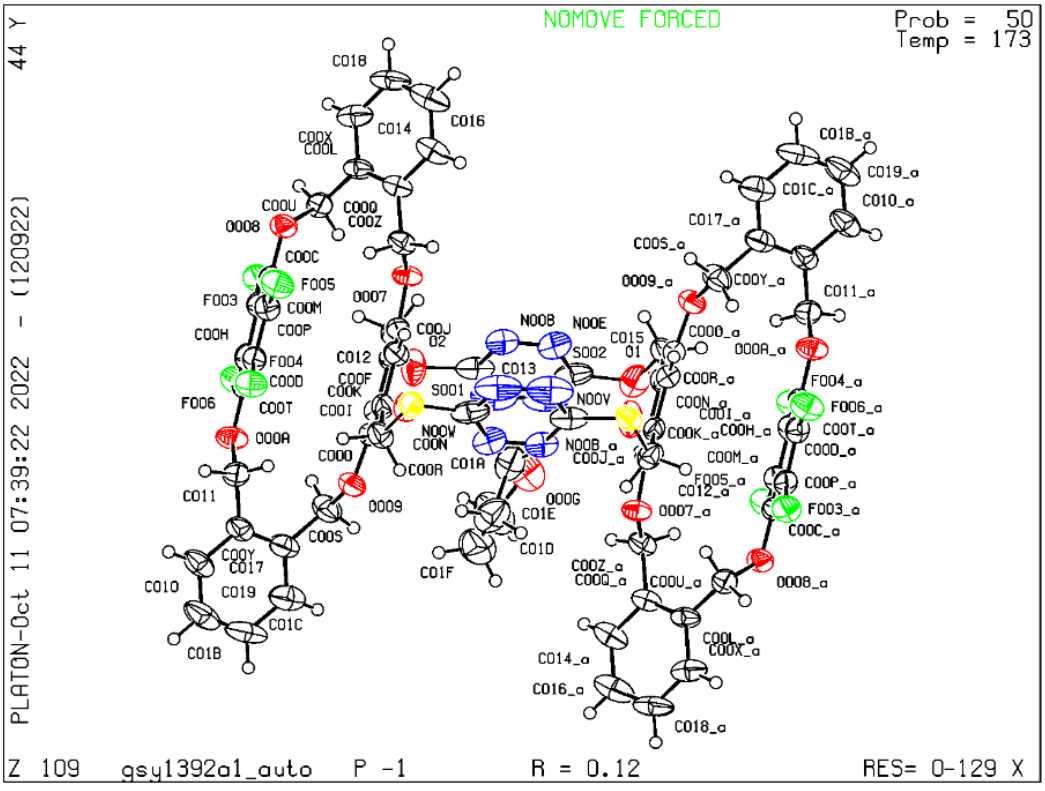


Figure S14L. X-ray molecular structure of *race*-**26a** (CCDC 2261286). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

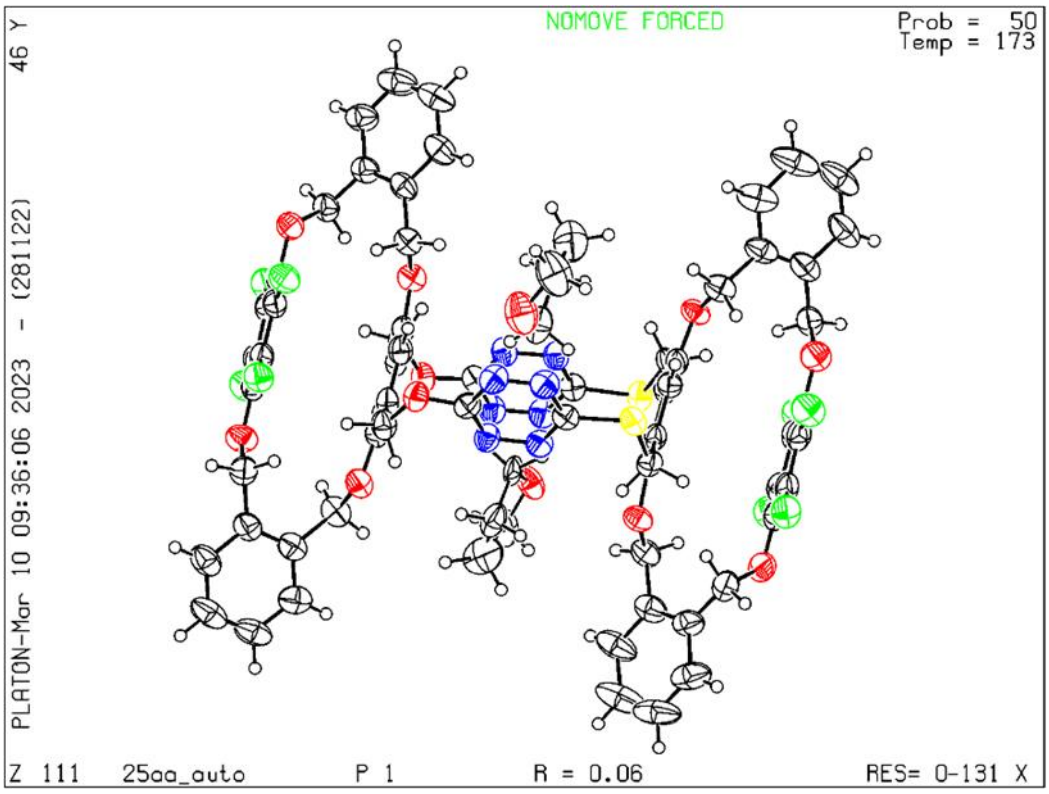


Figure S14M. X-ray molecular structure of *P,M*-**26a** (CCDC 2261294). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

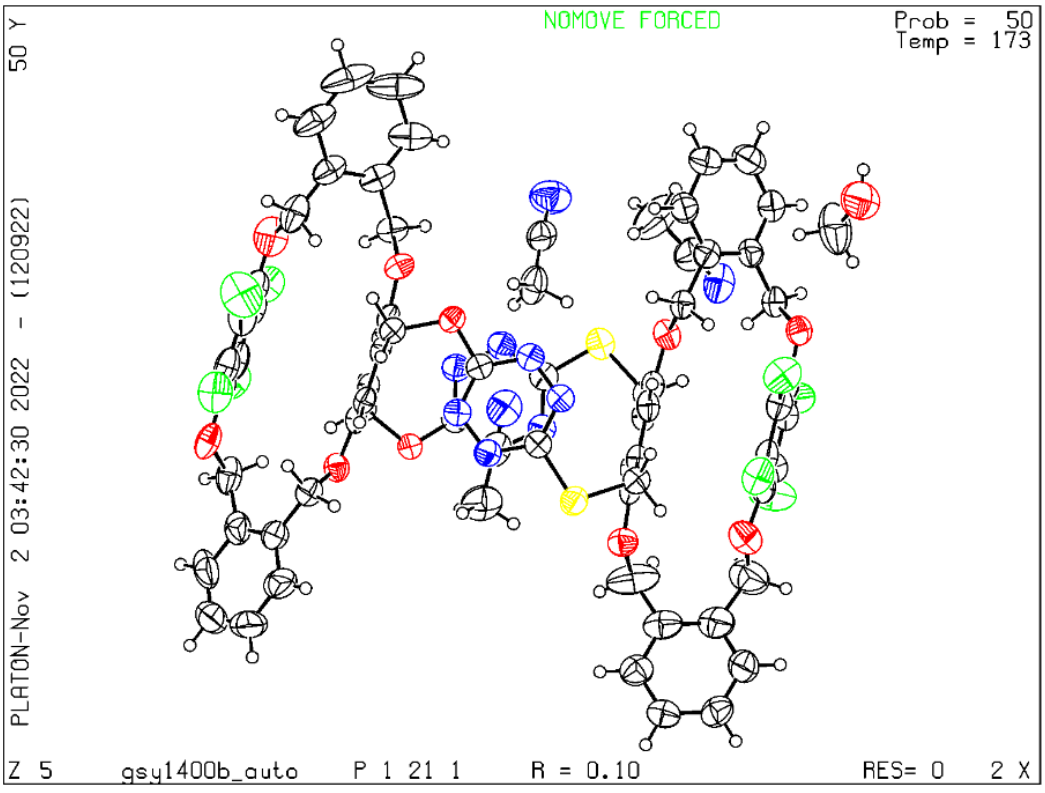


Figure S14N. X-ray molecular structure of *race*-**26b** (CCDC 2261287). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

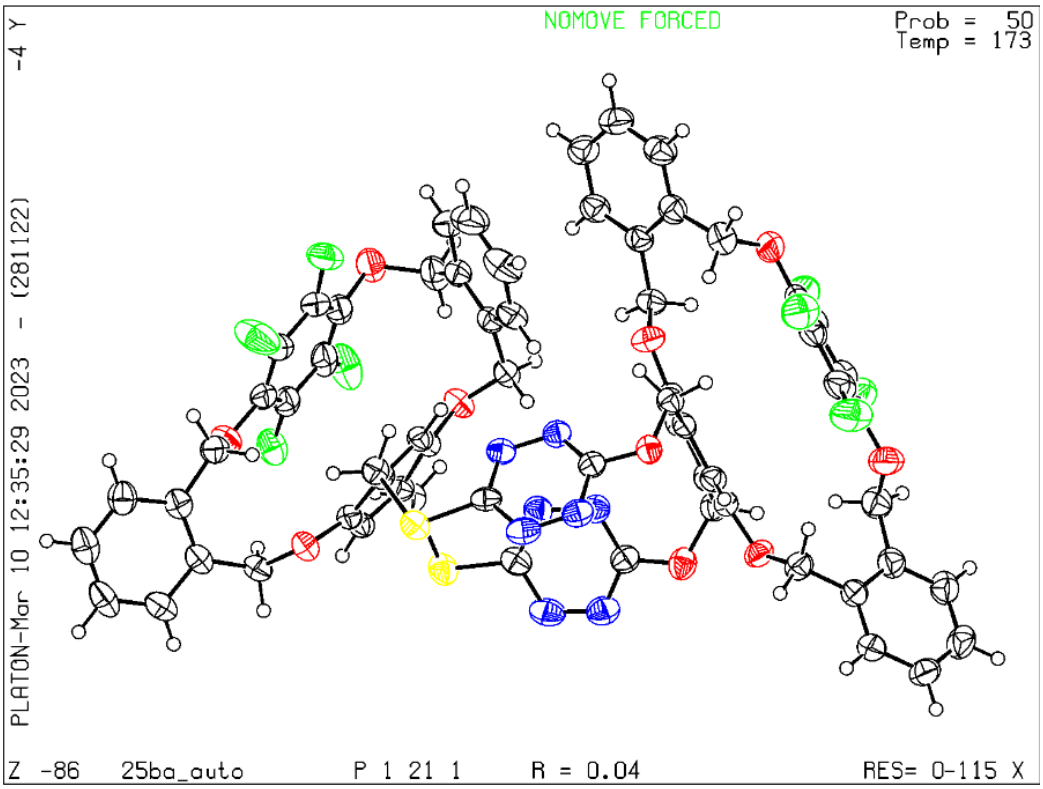


Figure S14O. X-ray molecular structure of *P,P*-**26b** (CCDC 2261295). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

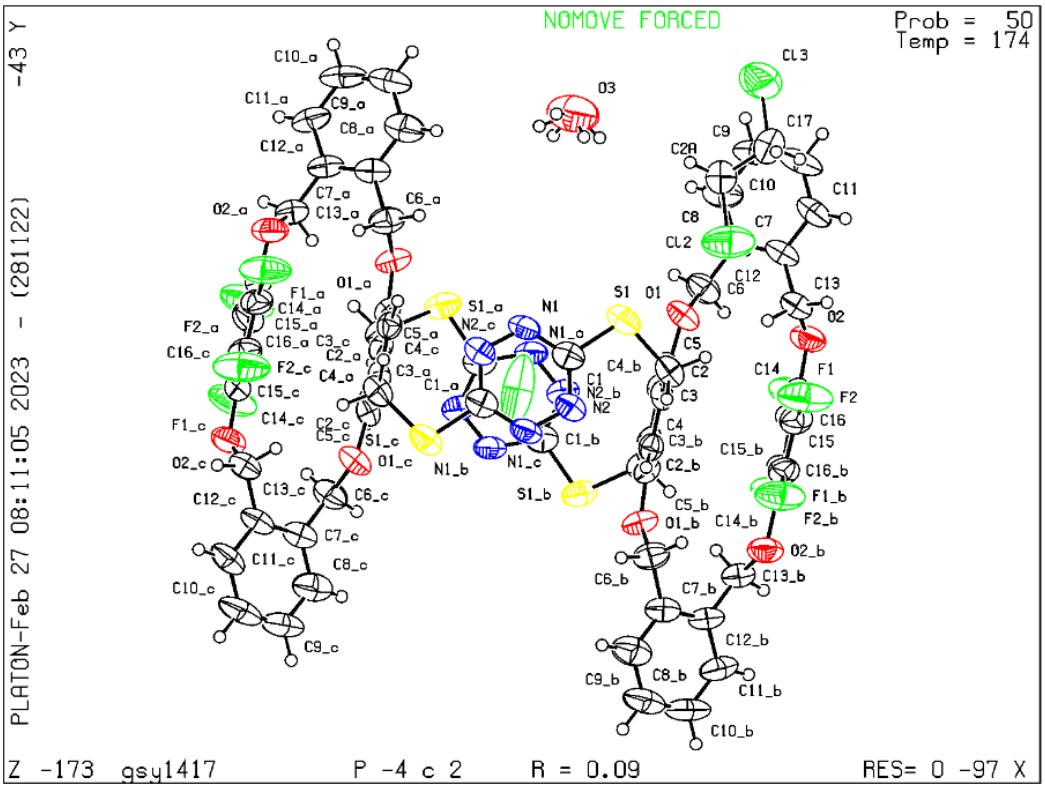


Figure S14P. X-ray molecular structure of [*race*-**25b**·$H_3O^+Cl^-$] (CCDC 2261288). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

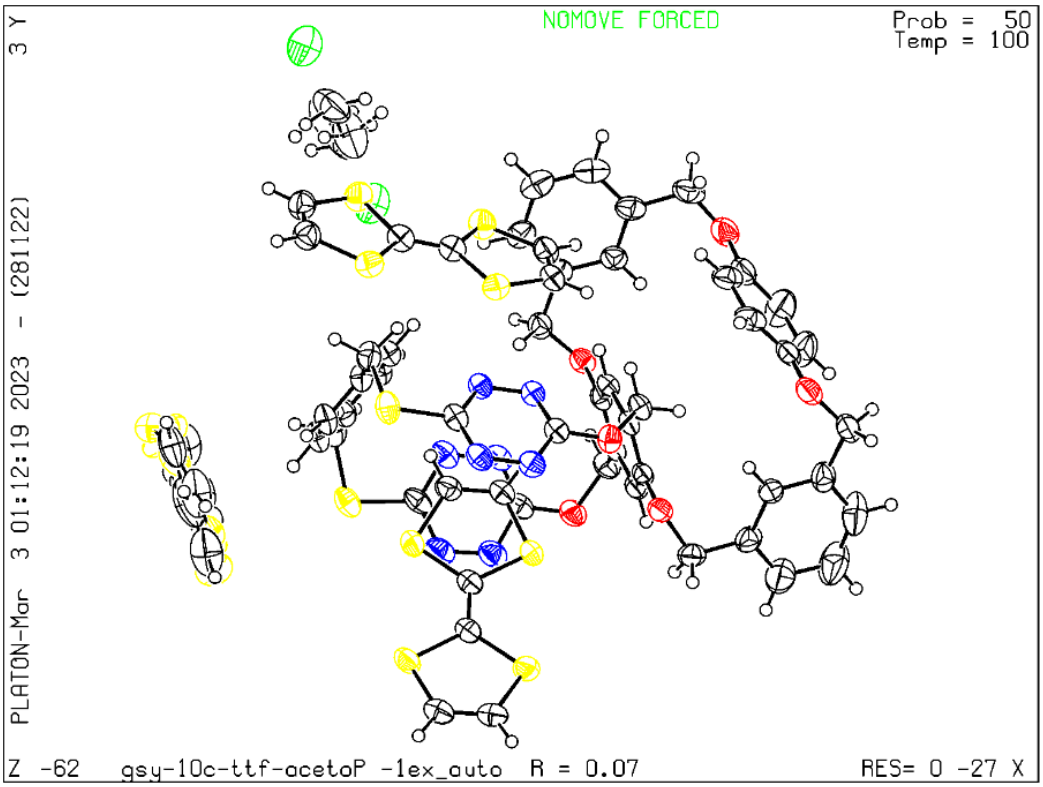


Figure S14Q. X-ray molecular structure of [*race*-**15**·3TTF] (CCDC 2261289). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

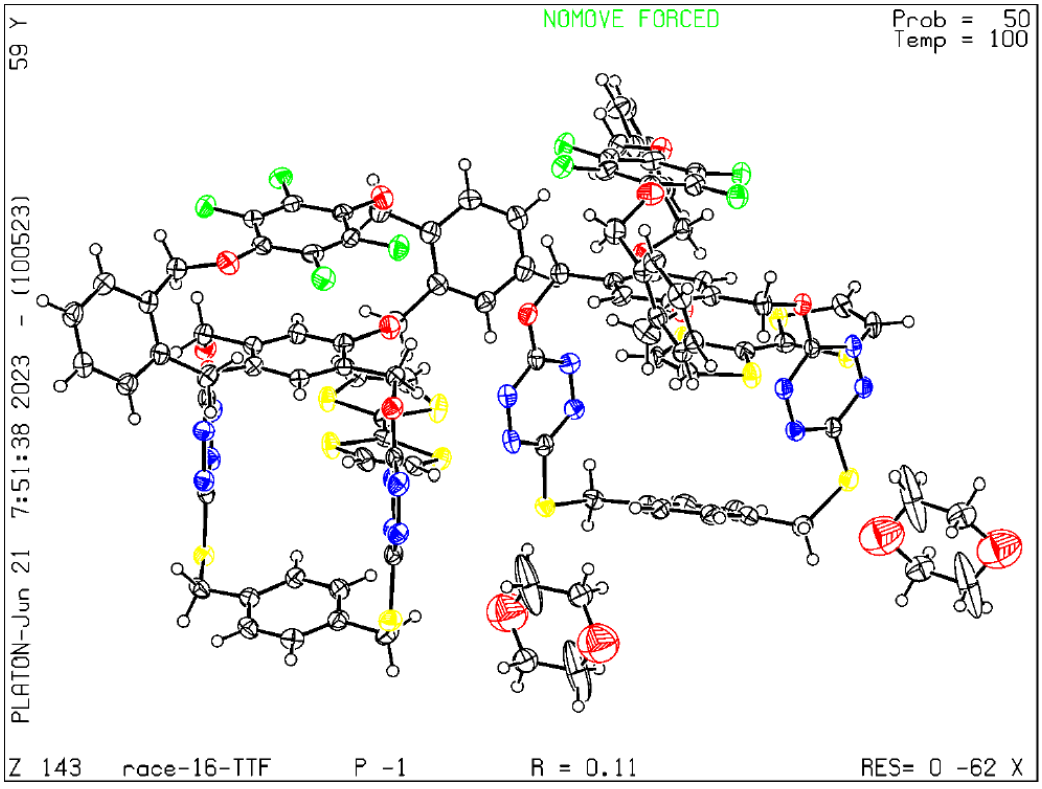


Figure S14R. X-ray molecular structure of **[***race*-**16**·TTF] (CCDC 2261298). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

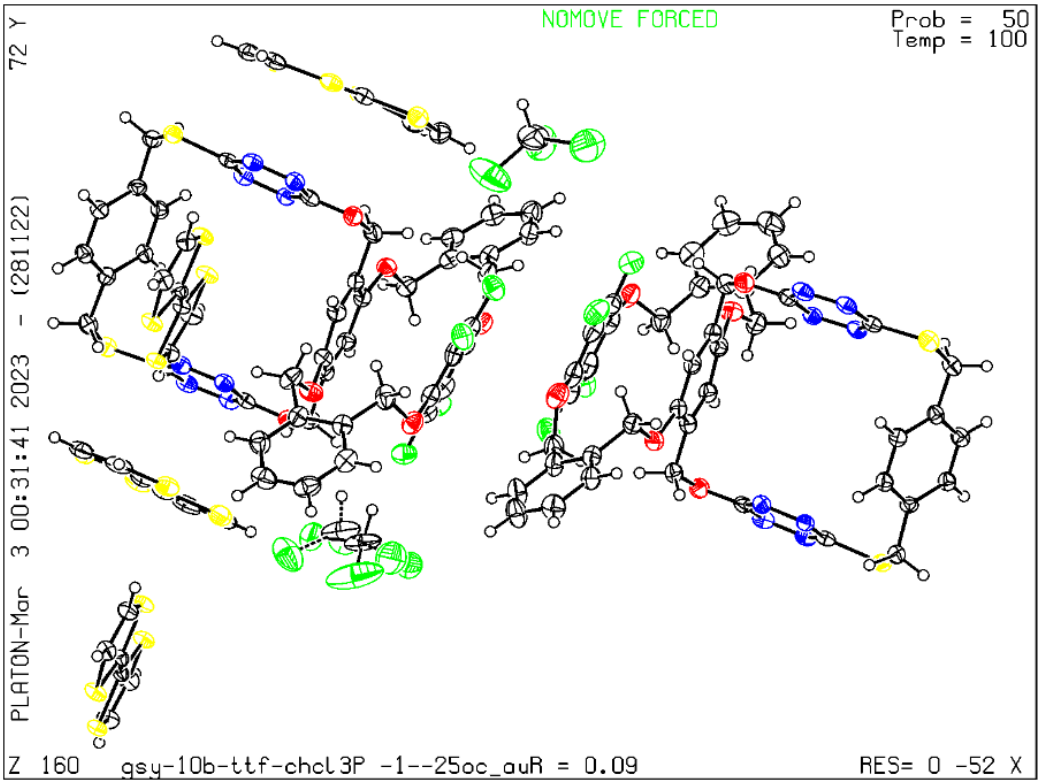


Figure S14S. X-ray molecular structure of **[***race*-**16**·2TTF] (CCDC 2261290). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

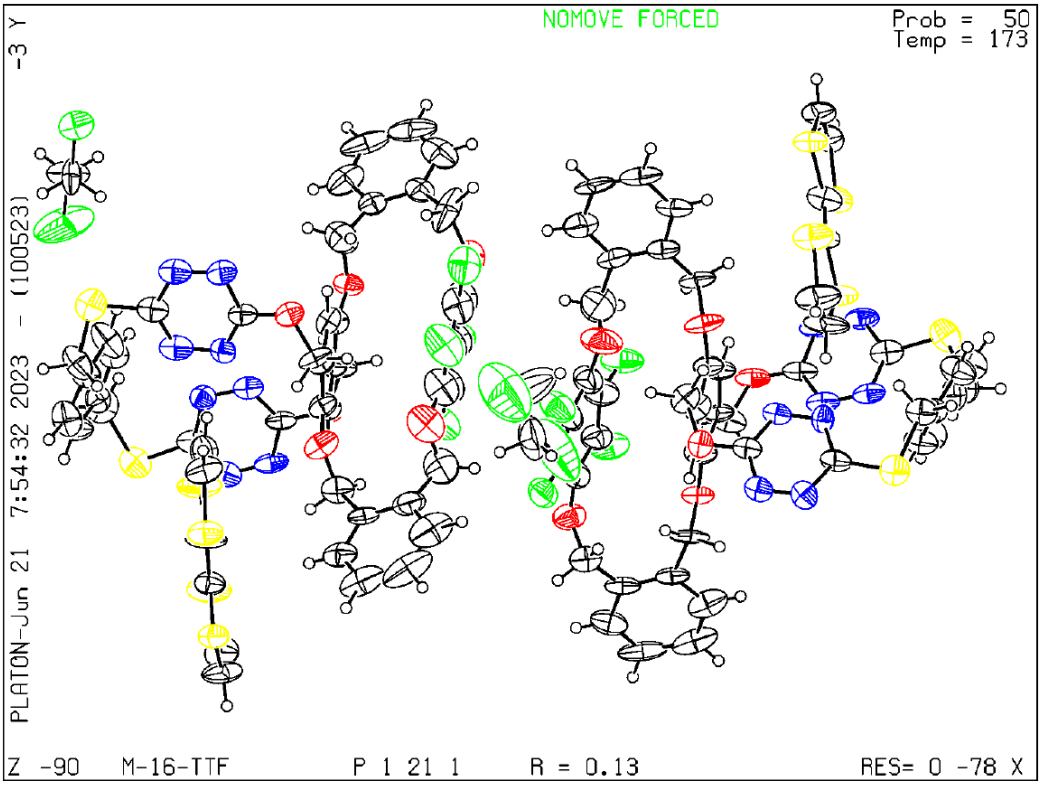


Figure S14T. X-ray molecular structure of **[***M*-**16**·TTF] (CCDC 2261292). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

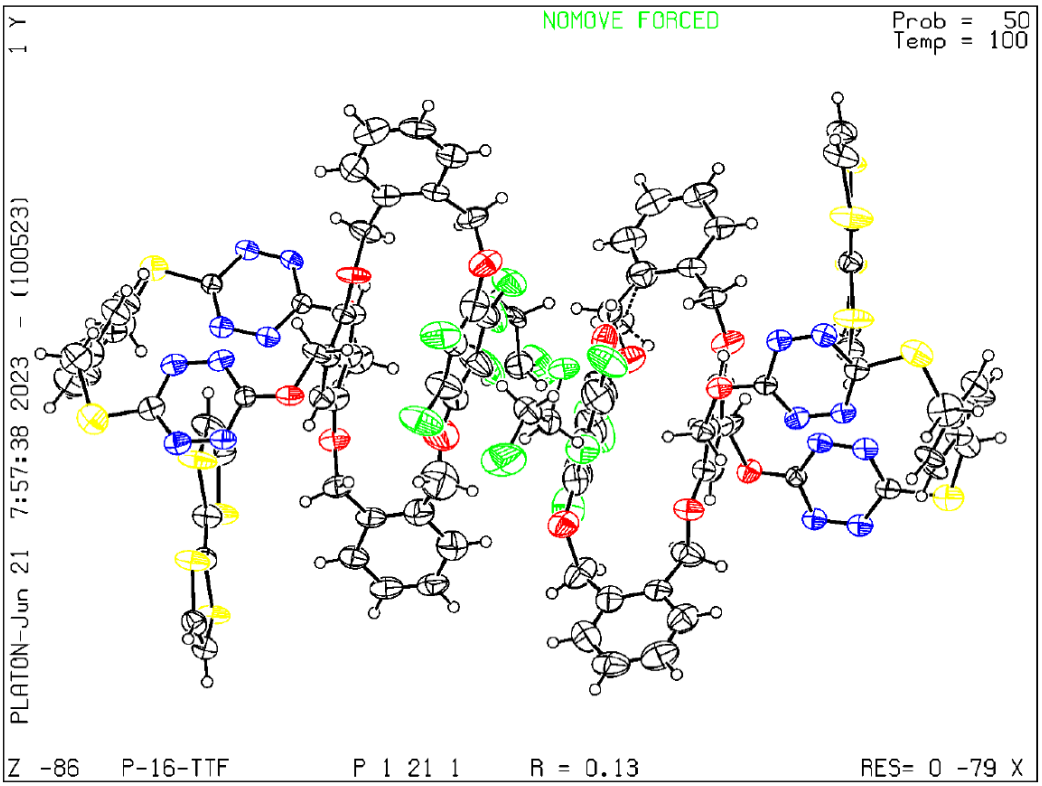
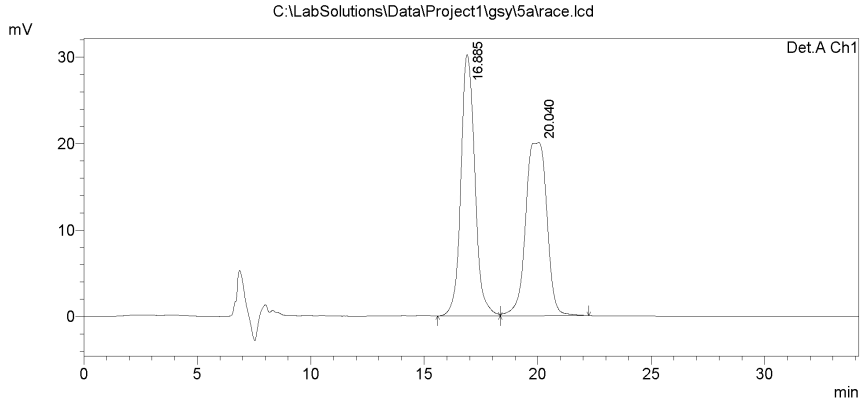


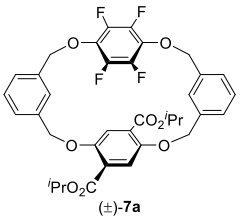
Figure S14U. X-ray molecular structure of [*P*-**16**·TTF] (CCDC 2261293). The molecular is depicted in stick-ellipsoid style at 50% probability level for all atoms.

4. HPLC Resolution of Chiral Macrocycles

Table S13. HPLC resolution of chiral macrocycles

Compound	Column	Speed	Mobile phase	Retention time (min)
7a	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21	t_1 = 16.9, t_2 = 20.0
7d	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21	t_1 = 21.3, t_2 = 24.2
8	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21	t_1 = 16.5, t_2 = 40.0
10	Daciel® ID	0.5 mL/min	^{i}PrOH : Hexane = 2 : 3	t_1 = 19.1, t_2 = 25.4
12	Daciel® IB	0.5 mL/min	DCM : Hexane = 2 : 3	t_1 = 17.0, t_2 = 18.3
13	Daciel® IB	0.5 mL/min	DCM : Hexane = 2 : 3	t_1 = 15.7, t_2 = 22.5
15	Daciel® ID	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 6	t_1 = 28.3, t_2 = 33.9
16	Daciel® ID	0.5 mL/min	DCM : Hexane = 2 : 1	t_1 = 11.9, t_2 = 15.7
18	Daciel® IB	0.5 mL/min	^{i}PrOH : Hexane = 1 : 4	t_1 = 15.2, t_2 = 16.3
20	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 27 : 9 : 164	t_1 = 11.3, t_2 = 16.1
21	Daciel® IB	0.5 mL/min	DCM : Hexane = 2 : 3	t_1 = 11.2, t_2 = 12.2
22	Daciel® IB	0.5 mL/min	DCM : Hexane = 2 : 3	t_1 = 11.8, t_2 = 12.8
23b	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 12	t_1 = 18.6, t_2 = 24.1
24b	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 9 : 3 : 28	t_1 = 14.4, t_2 = 22.5
26a	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 1 : 1 : 8	t_1 = 18.3, t_2 = 24.0
26b	Daciel® IA	0.5 mL/min	$CHCl_3$: ^{i}PrOH : Hexane = 3 : 1 : 21	t_1 = 22.4, t_2 = 27.8



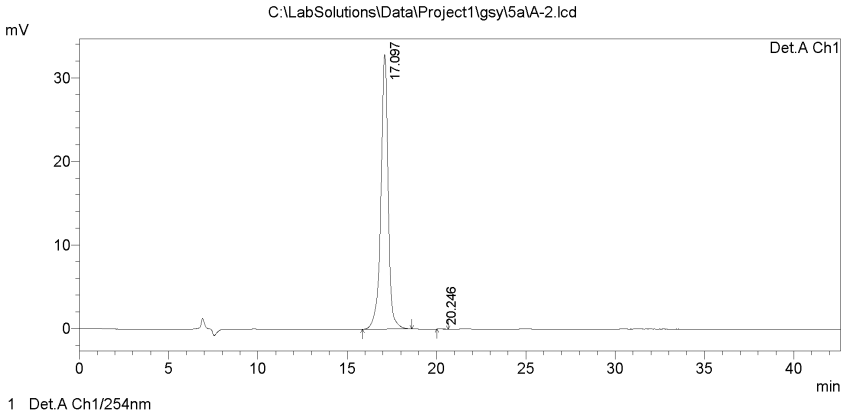


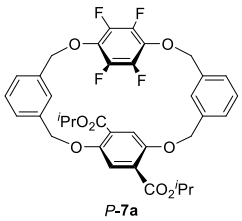
(±)-**7a**

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.885	1296314	30227	49.843	60.140
2	20.040	1304499	20034	50.157	39.860
Total		2600812	50261	100.000	100.000



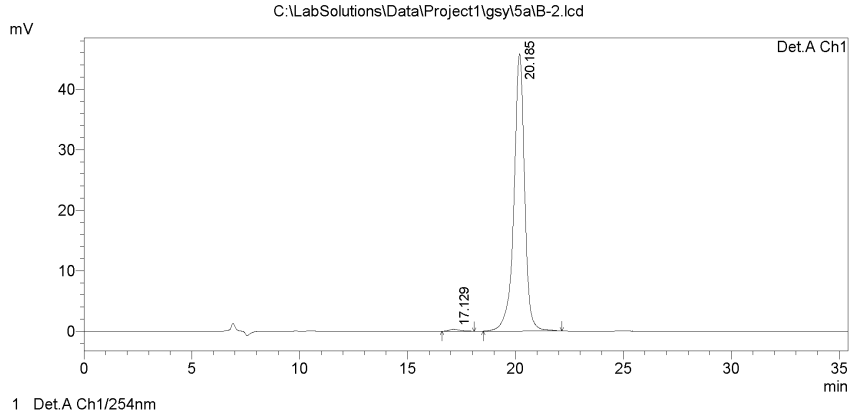


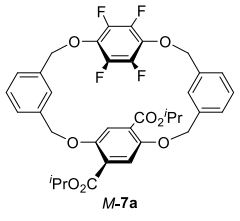
P-**7a**

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.097	931331	32816	99.883	99.847
2	20.246	1086	50	0.117	0.153
Total		932417	32866	100.000	100.000





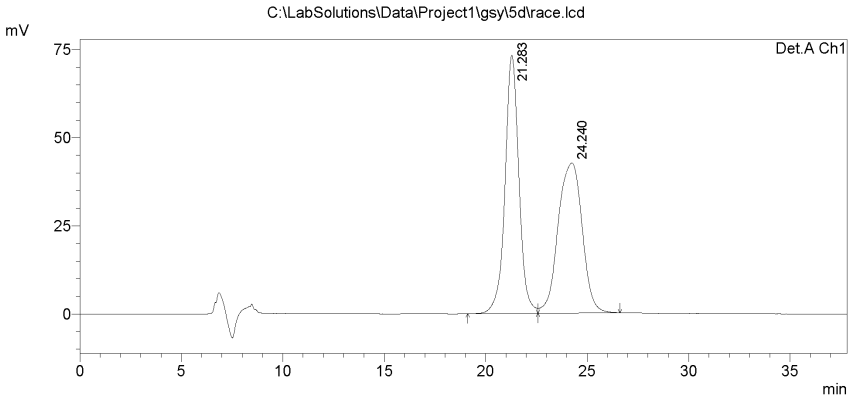
M-**7a**

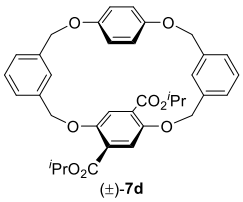
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.129	10847	312	0.683	0.676
2	20.185	1577863	45813	99.317	99.324
Total		1588711	46125	100.000	100.000

Figure S15. HPLC spectra of racemic, *P*-, and *M*-**7a**





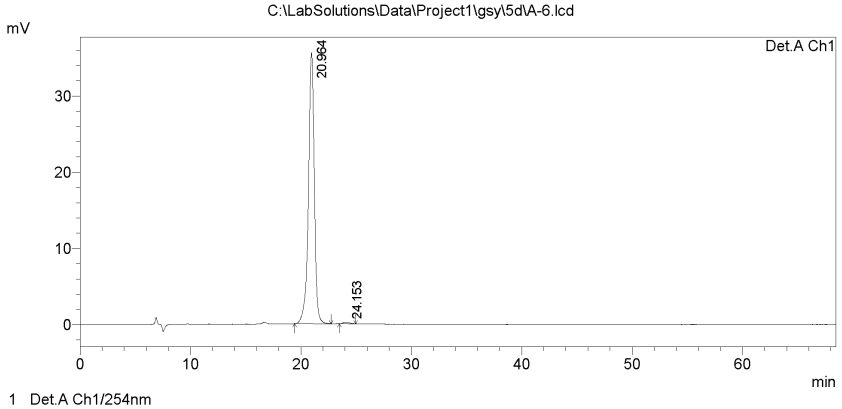
(±)-**7d**

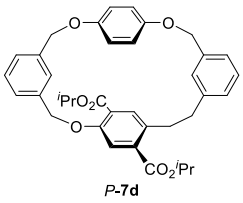
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.283	3479477	73205	49.778	63.221
2	24.240	3510502	42587	50.222	36.779
Total		6989979	115792	100.000	100.000





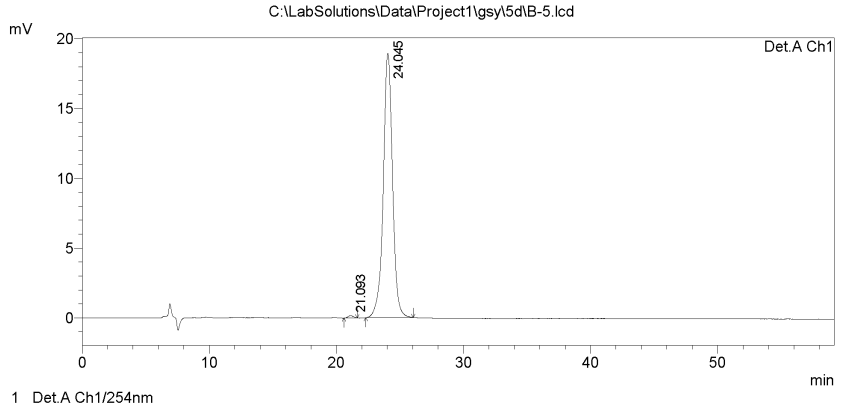
P-**7d**

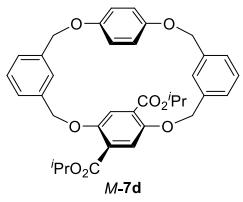
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.964	1317140	35536	99.473	99.548
2	24.153	6978	161	0.527	0.452
Total		1324118	35698	100.000	100.000





M-**7d**

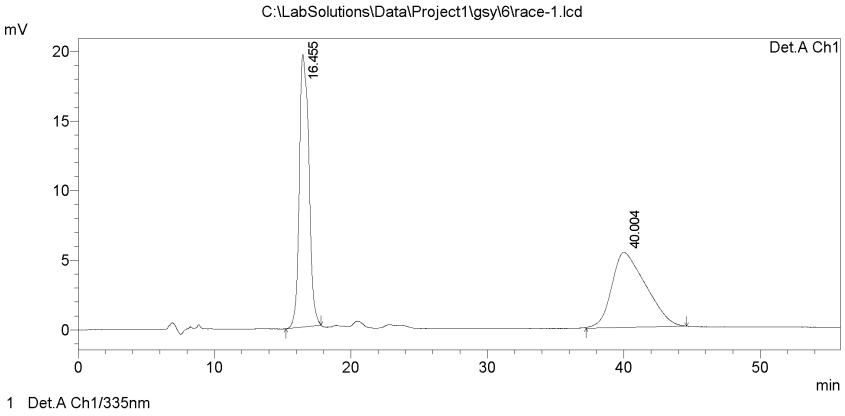
1 Det.A Ch1/254nm

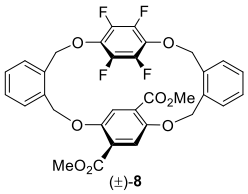
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.093	5050	164	0.522	0.856
2	24.045	961606	18935	99.478	99.144
Total		966657	19098	100.000	100.000

Figure S16. HPLC spectra of racemic, *P*-, and *M*-**7d**





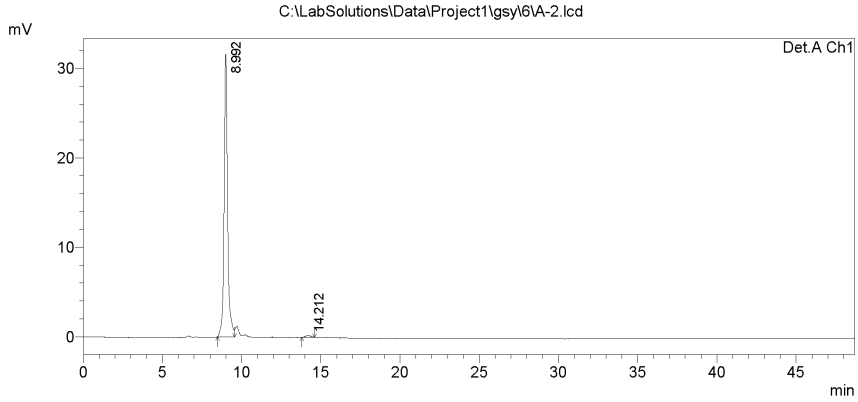
(±)-**8**

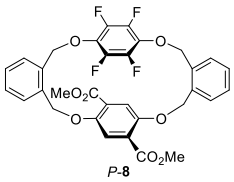
1 Det.A Ch1/335nm

PeakTable

检测器 A Ch1 335nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.455	954986	19595	50.651	78.439
2	40.004	930446	5386	49.349	21.561
Total		1885433	24981	100.000	100.000





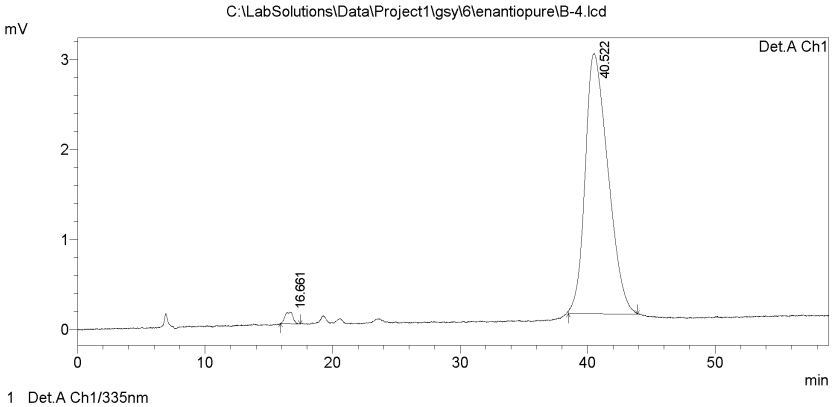
P-**8**

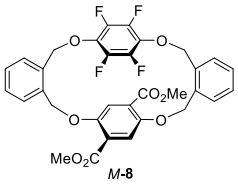
1 Det.A Ch1/335nm

PeakTable

检测器 A Ch1 335nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.992	480802	31597	98.947	99.319
2	14.212	5118	217	1.053	0.681
Total		485919	31814	100.000	100.000





M-**8**

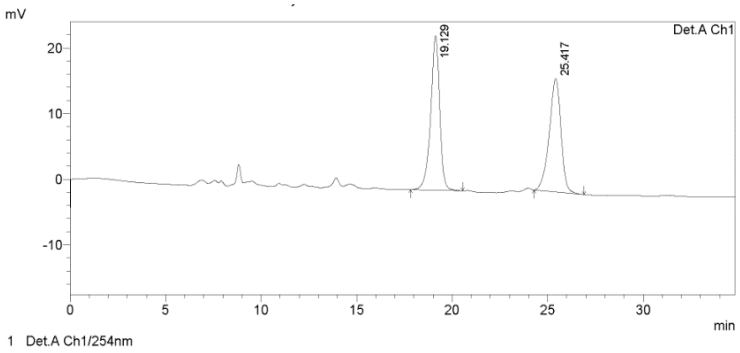
1 Det.A Ch1/335nm

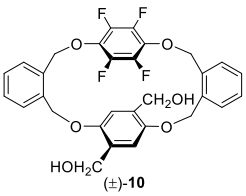
PeakTable

检测器 A Ch1 335nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.661	5335	126	1.456	4.182
2	40.522	361049	2896	98.544	95.818
Total		366384	3022	100.000	100.000

Figure S17. HPLC spectra of racemic, *P*-, and *M*-**8**



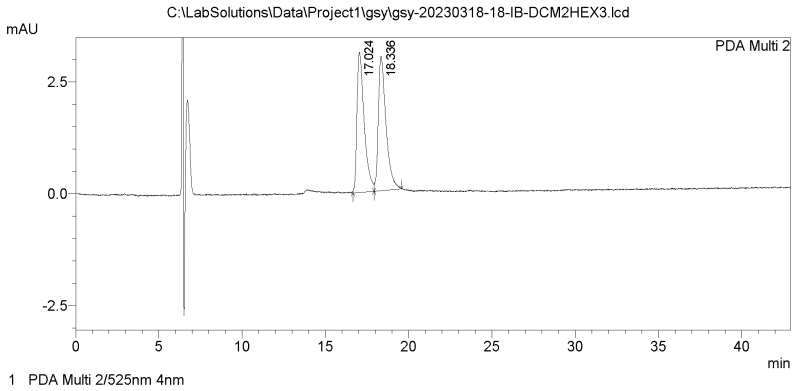


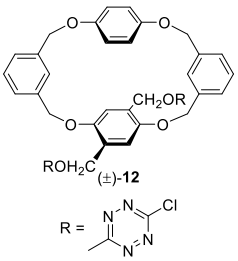
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.129	772861	23532	51.104	57.670
2	25.417	739463	17272	48.896	42.330
Total		1512324	40804	100.000	100.000

Figure S18. HPLC spectra of racemic **10**



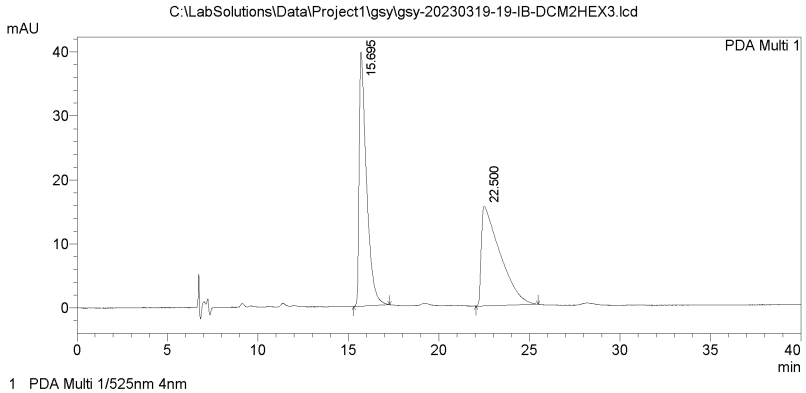


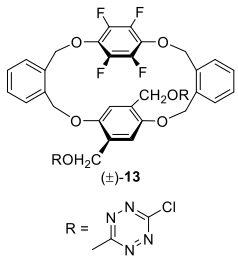
PeakTable

PDA Ch2 525nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.024	94503	3132	49.548	51.050
2	18.336	96227	3003	50.452	48.950
Total		190730	6134	100.000	100.000

Figure S19. HPLC spectra of racemic **12**



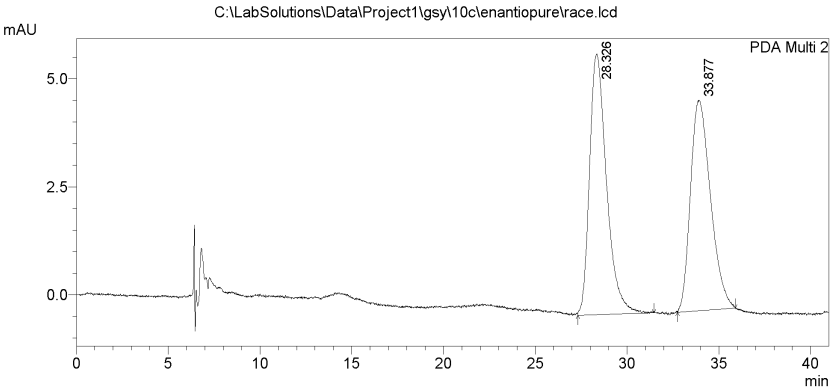


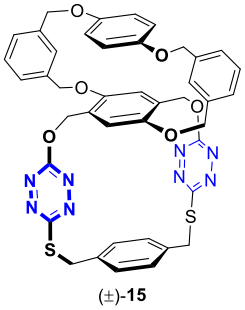
PeakTable

PDA Ch1 525nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.695	1117848	39709	50.011	71.831
2	22.500	1117352	15572	49.989	28.169
Total		2235200	55281	100.000	100.000

Figure S20. HPLC spectra of racemic **13**





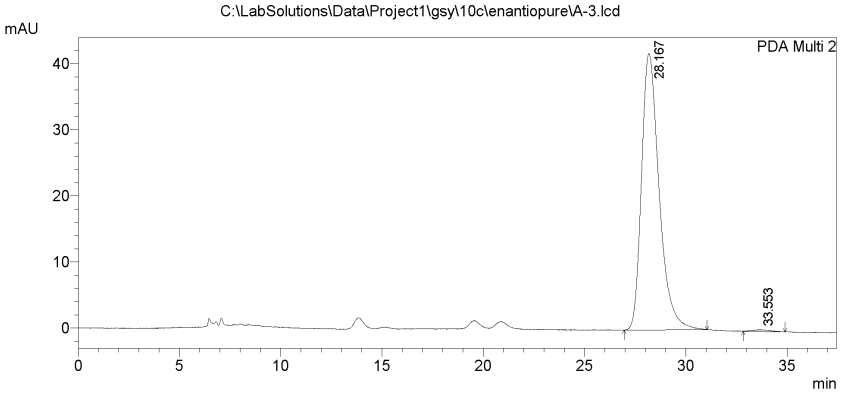
(±)-**15**

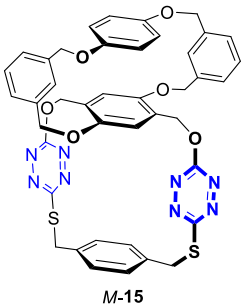
1 PDA Multi 2/385nm 4nm

PeakTable

PDA Ch2 385nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.326	388294	6037	51.219	55.307
2	33.877	369816	4878	48.781	44.693
Total		758110	10915	100.000	100.000





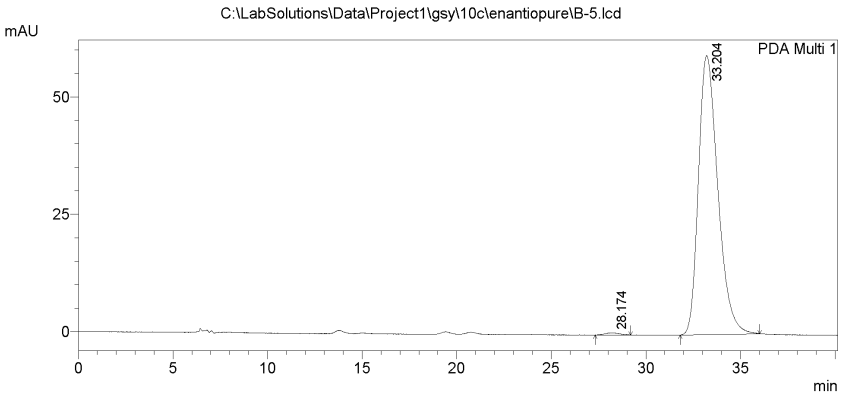
M-**15**

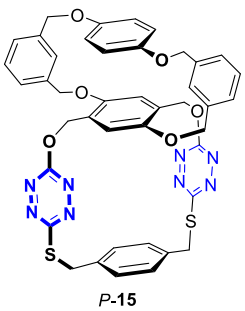
1 PDA Multi 2/254nm 4nm

PeakTable

PDA Ch2 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.167	2536390	41854	99.384	99.374
2	33.553	15710	264	0.616	0.626
Total		2552100	42118	100.000	100.000





P-**15**

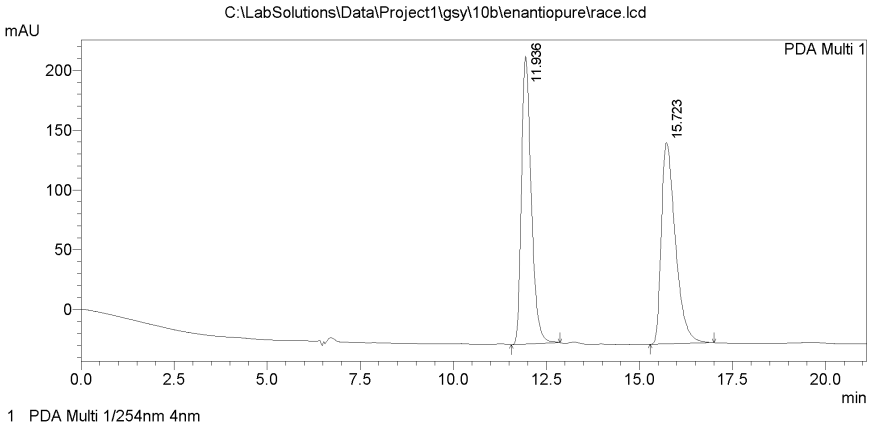
1 PDA Multi 1/254nm 4nm

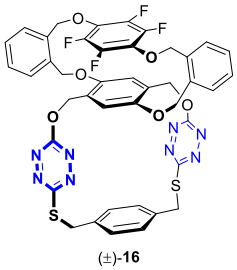
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.174	24543	473	0.576	0.791
2	33.204	4234723	59390	99.424	99.209
Total		4259266	59864	100.000	100.000

Figure S21. HPLC spectra of racemic, *M*-, and *P*-**15**



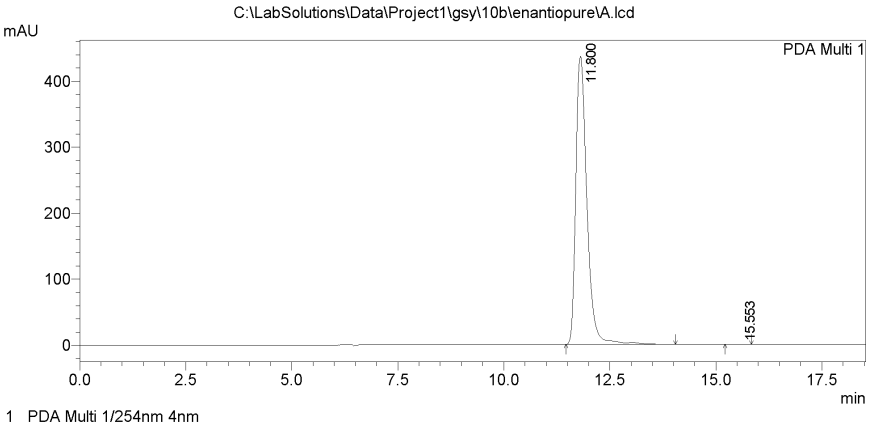


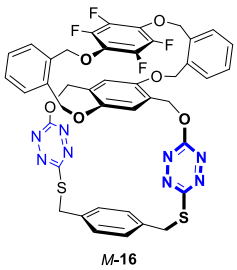
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.936	4408380	240579	49.879	58.854
2	15.723	4429851	168193	50.121	41.146
Total		8838231	408772	100.000	100.000



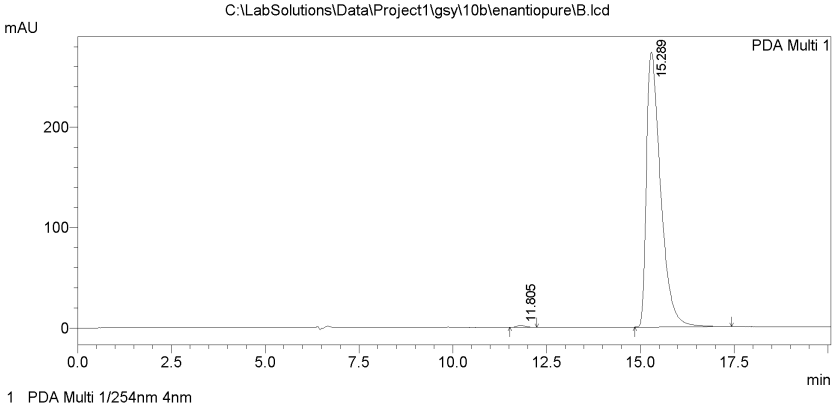


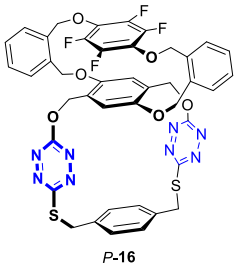
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.800	7770324	436182	99.939	99.943
2	15.553	4718	251	0.061	0.057
Total		7775042	436433	100.000	100.000





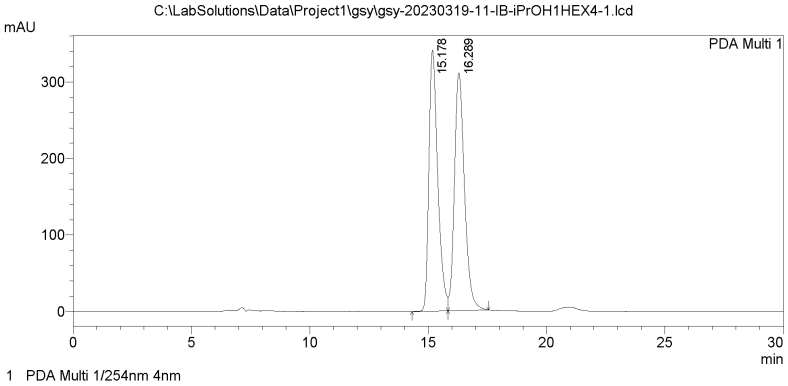
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.805	33869	2012	0.470	0.730
2	15.289	7178965	273598	99.530	99.270
Total		7212834	275610	100.000	100.000

Figure S22. HPLC spectra of racemic, *M*-, and *P*-**16**



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.178	8858471	340976	49.148	52.283
2	16.289	9165489	311201	50.852	47.717
Total		18023960	652176	100.000	100.000

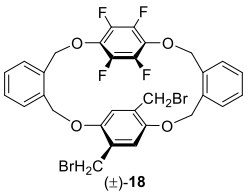
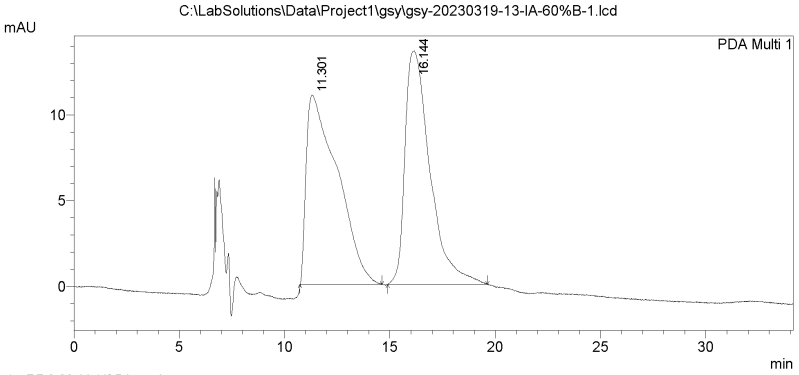


Figure S23. HPLC spectra of racemic **18**



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.301	1141642	11061	50.282	44.800
2	16.144	1128833	13629	49.718	55.200
Total		2270475	24690	100.000	100.000

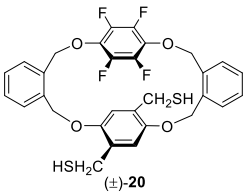
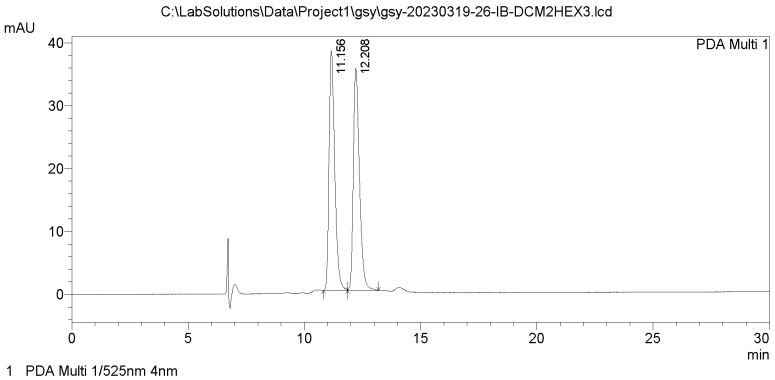


Figure S24. HPLC spectra of racemic **20**



1 PDA Multi 1/525nm 4nm

PeakTable

PDA Ch1 525nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.156	650981	38123	50.014	51.916
2	12.208	650604	35309	49.986	48.084
Total		1301585	73432	100.000	100.000

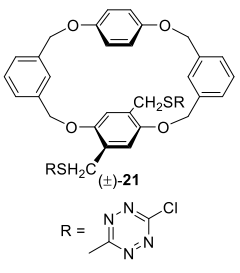
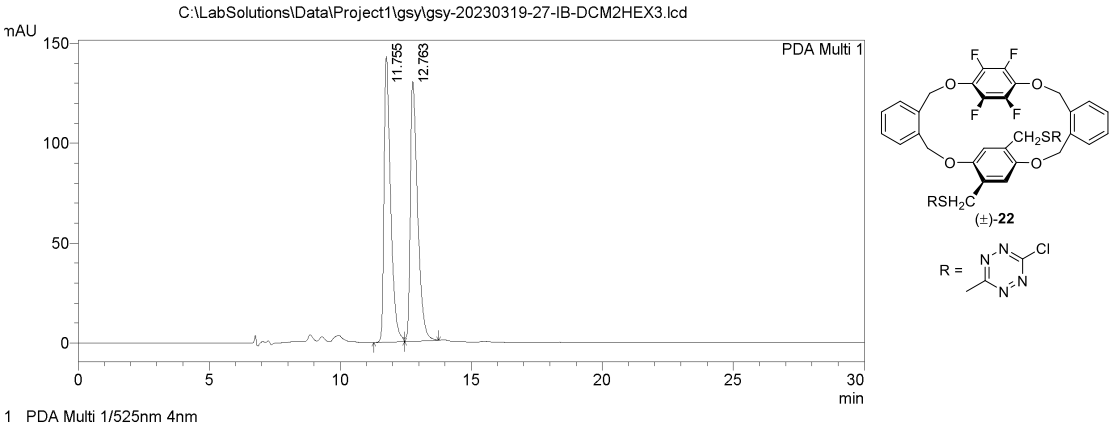


Figure S25. HPLC spectra of racemic **21**



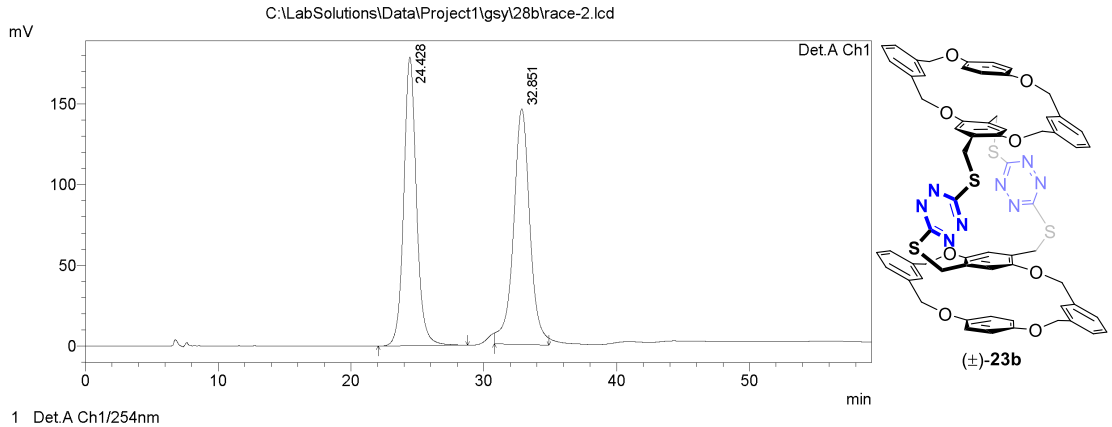
1 PDA Multi 1/525nm 4nm

PeakTable

PDA Ch1 525nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.755	2500298	143008	49.994	52.356
2	12.763	2500860	130139	50.006	47.644
Total		5001157	273147	100.000	100.000

Figure S26. HPLC spectra of racemic **22**

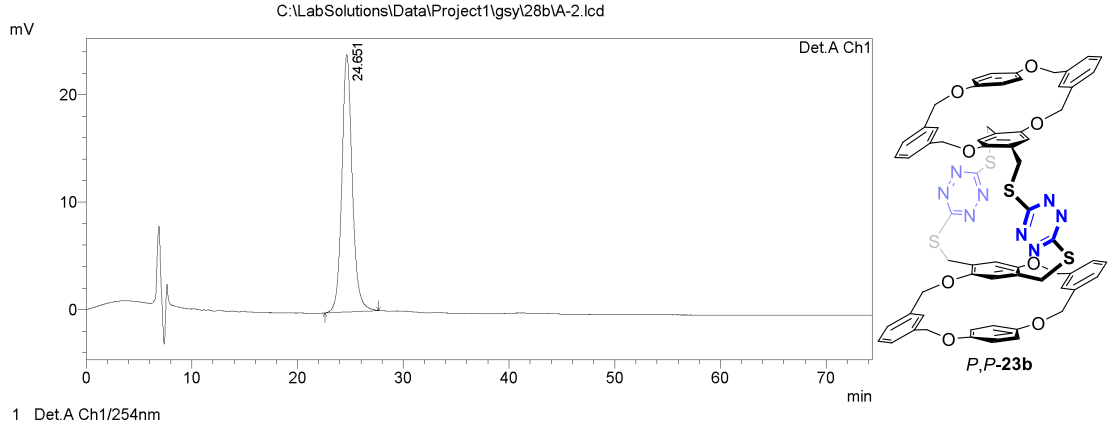


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.428	11908107	178747	48.809	55.052
2	32.851	12489161	145940	51.191	44.948
Total		24397268	324687	100.000	100.000

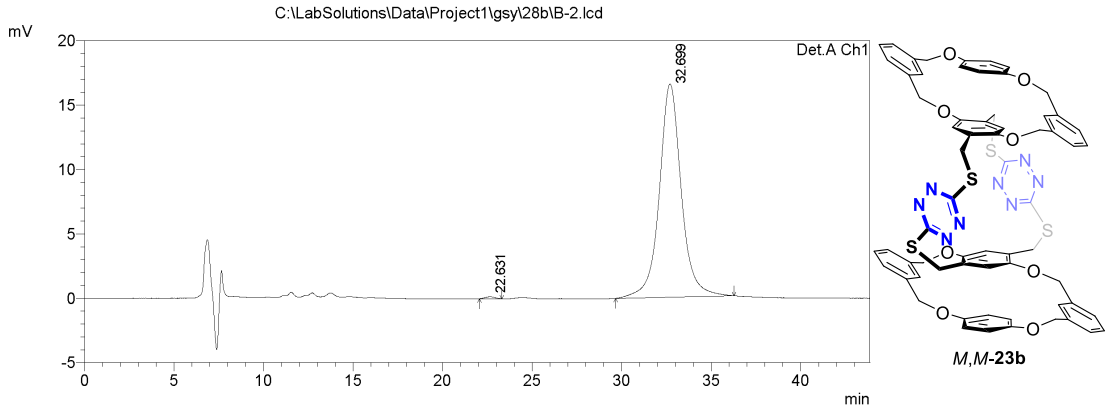


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.651	1641249	23948	100.000	100.000
Total		1641249	23948	100.000	100.000



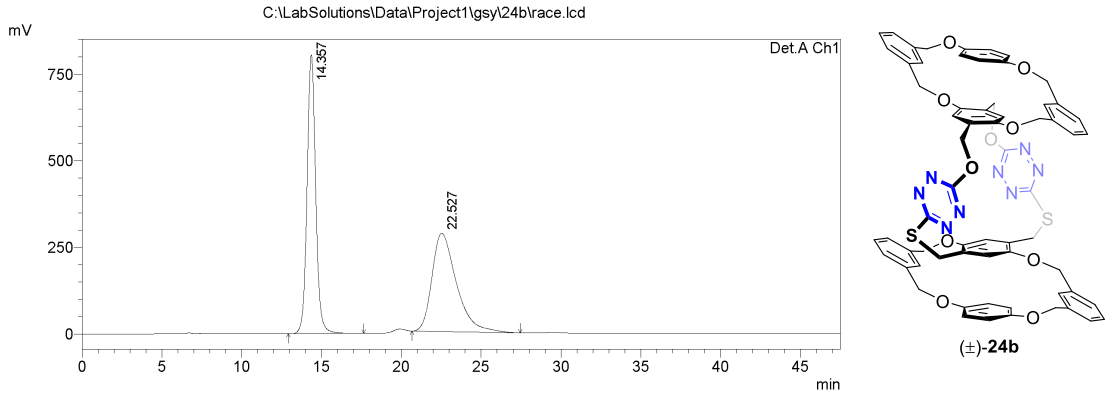
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.631	5697	153	0.401	0.914
2	32.699	1414767	16558	99.599	99.086
Total		1420464	16711	100.000	100.000

Figure S27. HPLC spectra of racemic, *P*,*P*-, and *M*,*M*-**23b**

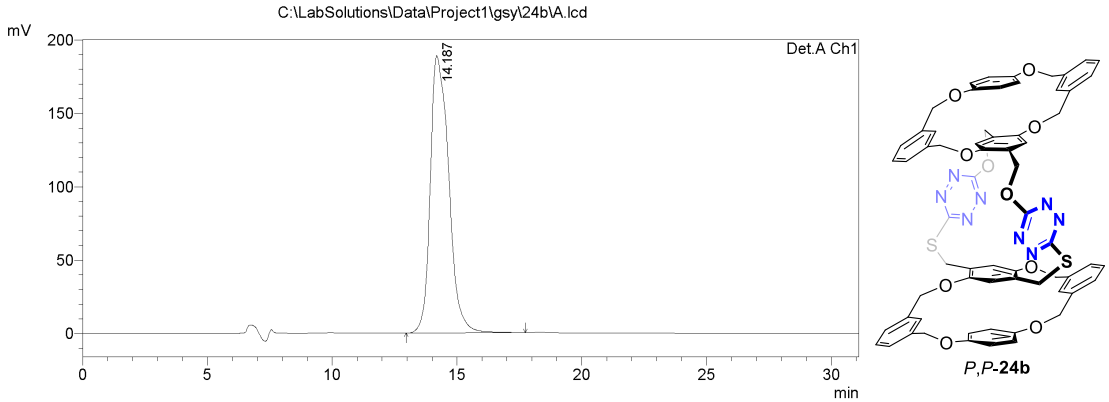


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.357	30374526	805566	50.137	73.917
2	22.527	30208728	284254	49.863	26.083
Total		60583254	1089820	100.000	100.000

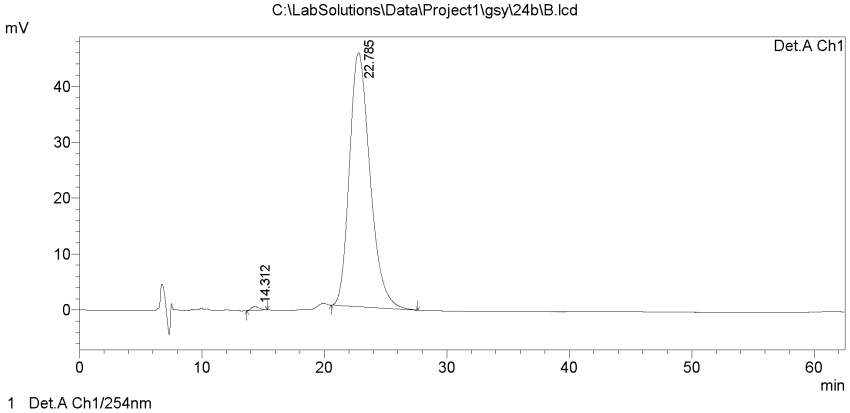


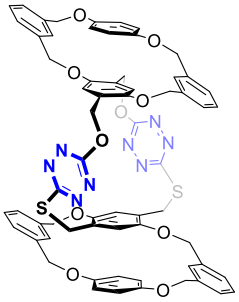
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.187	9718357	188870	100.000	100.000
Total		9718357	188870	100.000	100.000





M,*M*-**24b**

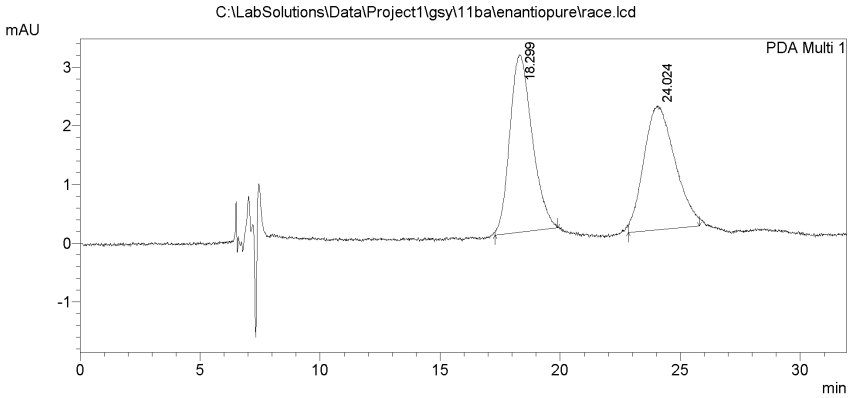
1 Det.A Ch1/254nm

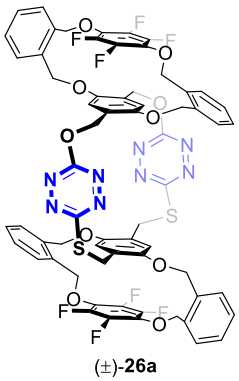
PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.312	30275	665	0.566	1.442
2	22.785	5318104	45428	99.434	98.558
Total		5348379	46092	100.000	100.000

Figure S28. HPLC spectra of racemic, *P*,*P*-, and *M*,*M*-**24b**





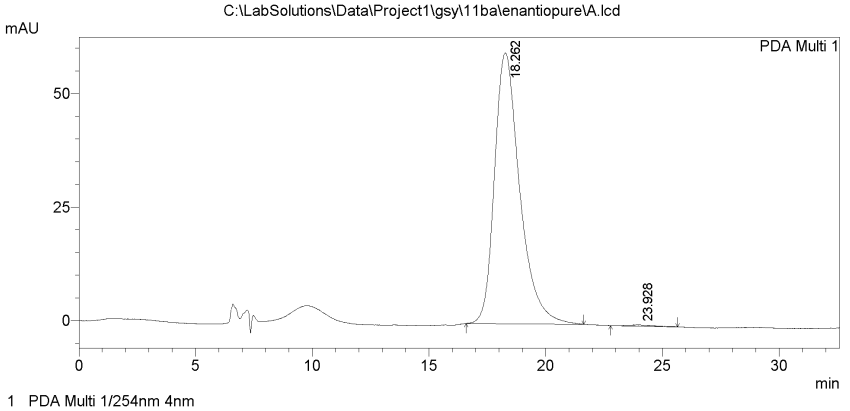
(±)-**26a**

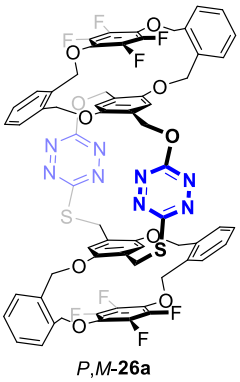
1 PDA Multi 1/385nm 4nm

PeakTable

PDA Ch1 385nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.299	195971	3021	50.723	58.787
2	24.024	190383	2118	49.277	41.213
Total		386354	5139	100.000	100.000





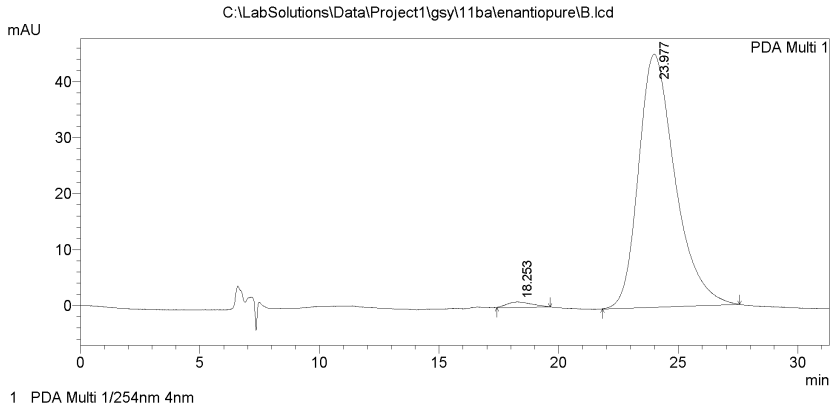
P,*M*-**26a**

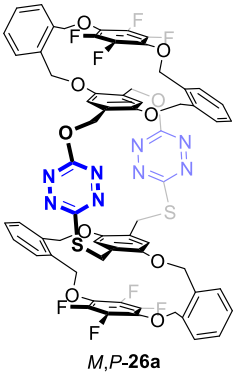
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.262	4495748	59631	99.552	99.554
2	23.928	20231	267	0.448	0.446
Total		4515979	59898	100.000	100.000



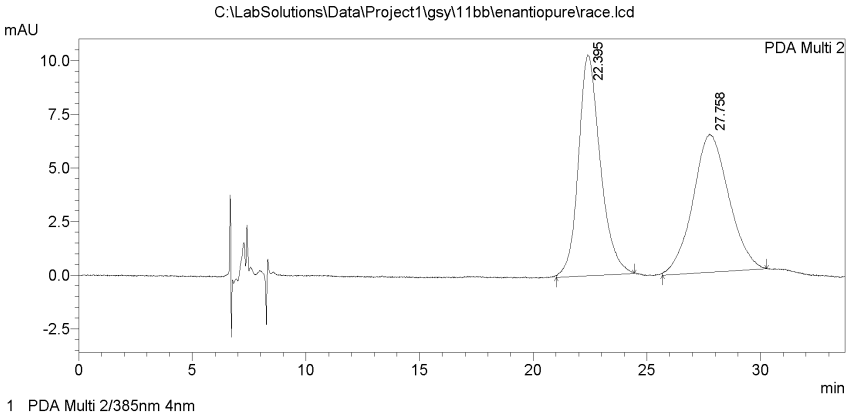


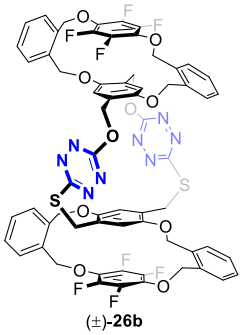
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.253	69614	979	1.425	2.119
2	23.977	4814771	45210	98.575	97.881
Total		4884384	46189	100.000	100.000

Figure S29. HPLC spectra of racemic, *P*,*M*-, and *M*,*P*-**26a**

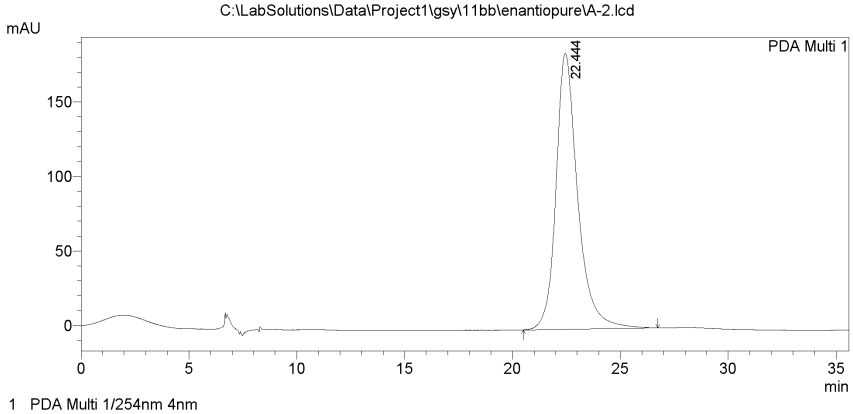


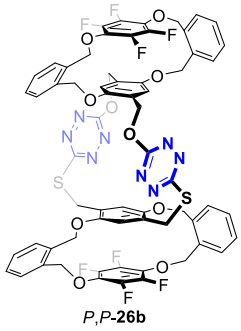


PeakTable

PDA Ch2 385nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.395	689502	10294	49.422	61.523
2	27.758	705638	6438	50.578	38.477
Total		1395140	16732	100.000	100.000

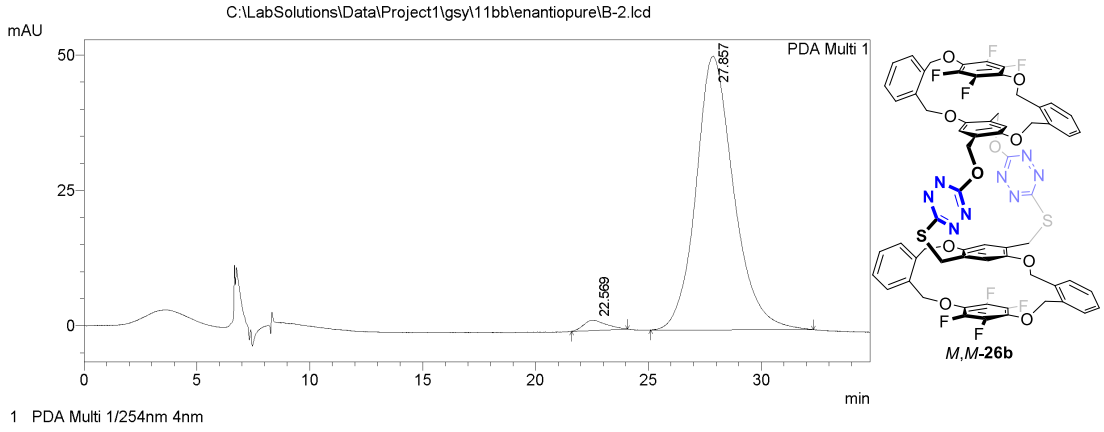




PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.444	13010119	185338	100.000	100.000
Total		13010119	185338	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.569	136331	1940	2.265	3.697
2	27.857	5883003	50552	97.735	96.303
Total		6019335	52492	100.000	100.000

Figure S30. HPLC spectra of racemic, *P*,*P*-, and *M*,*M*-**26b**

5. Photophysical Data

5.1 UV-vis and fluorescence spectra

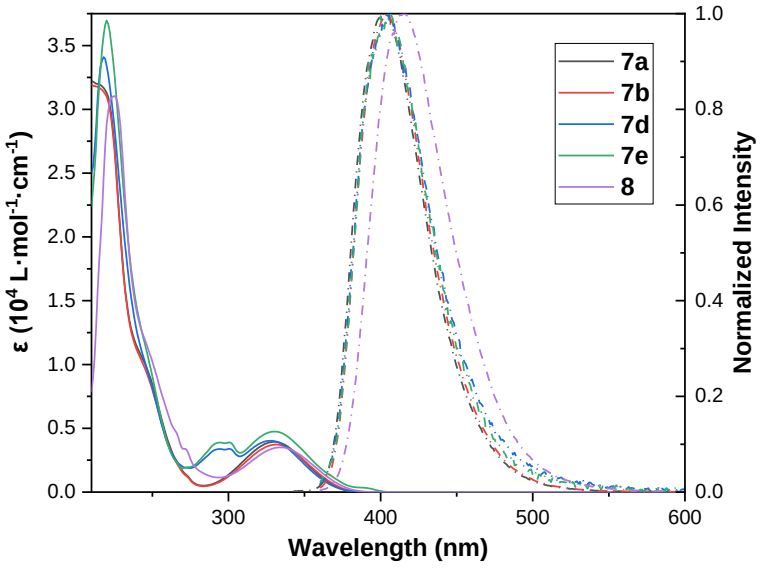


Figure S31. UV-vis spectra (1×10^{-4} M) and normalized fluorescence spectra (1.0×10^{-5} M) of **7a**, **7b**, **7d**, **7e**, and **8** in acetonitrile at 22 °C.

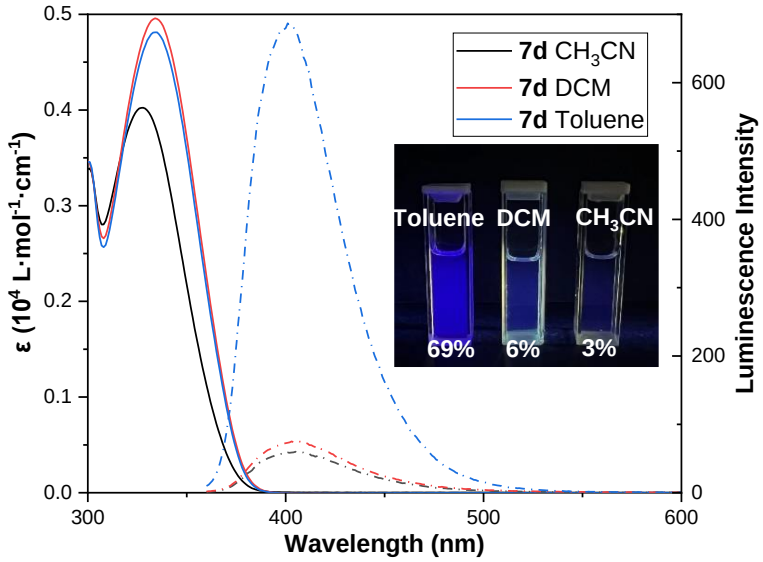


Figure S32. UV-vis (1×10^{-4} M) and fluorescence spectra (1.0×10^{-5} M) of **7d** in acetonitrile, dichloromethane, and toluene at 22 °C. The inset shows the fluorescence of **7d** (1.0×10^{-8} M) under the irradiation of UV light (365 nm).

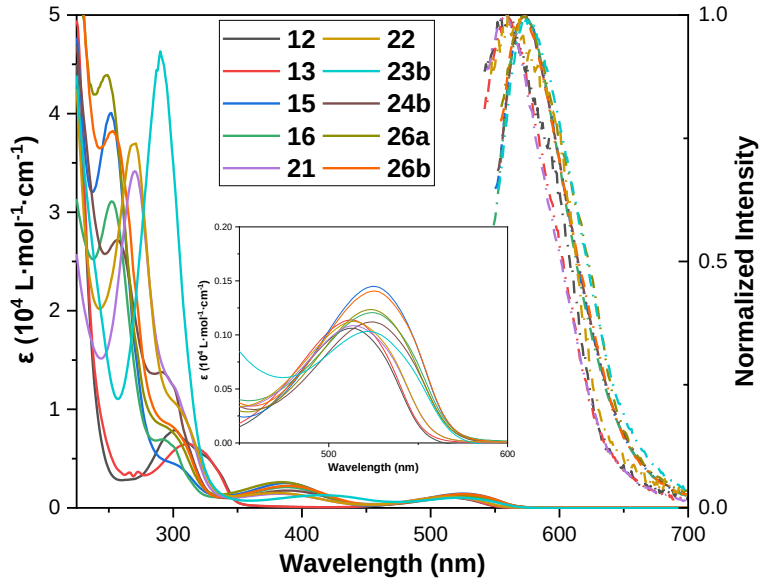


Figure S33. UV-vis spectra (1×10^{-4} M) and normalized fluorescence spectra (1.0×10^{-4} M) of **12**, **13**, **15**, **16**, **21**-**24**, and **26** in acetonitrile at 22 °C.

Table S14. Data of UV-vis and fluorescence spectra

Compound	Solv.	λ_{max} (nm) (ε, × 10^4 L·mol^{-1}·cm^{-1})	λ_{ex} (nm)	λ_{em} (nm)	ϕ
7a	Toluene	333 (0.42)	335	402	67.3%
7a	DCM	335 (0.42), 249 (1.02)	335	402	64.1%
7a	CH_3CN	330 (0.39), 243 (1.06), 216 (3.19)	335	403	64.5%
7b	Toluene	337 (0.41)	340	402	65.8%
7b	DCM	337 (0.42), 248 (1.04)	338	403	61.3%
7b	CH_3CN	331 (0.37), 244 (1.00), 215 (3.17)	335	405	69.9%
7d	Toluene	334 (0.48), 300 (0.35), 293 (0.36)	337	402	69.4%
7d	DCM	334 (0.50), 300 (0.35), 292 (0.36)	332	406	5.7%
7d	CH_3CN	328 (0.40), 301 (0.34), 294 (0.34), 218 (3.41)	330	405	3.1%
7e	Toluene	337 (0.57), 300 (0.39), 294 (0.41)	340	403	61.6%
7e	DCM	337 (0.57), 300 (0.38), 293 (0.40)	337	410	2.2%
7e	CH_3CN	330 (0.47), 301 (0.39), 294 (0.39), 220 (3.70)	333	407	1.5%
8	Toluene	335 (0.38)	336	414	61.5%
8	DCM	337 (0.40), 273 (0.40), 232 (2.39)	337	413	55.0%
8	CH_3CN	334 (0.35), 272 (0.34), 266 (0.46), 225 (3.10)	335	415	57.8%
12	Toluene	522 (0.15), 330 (0.47), 299 (0.96)	530	568	-[a]
12	DCM	522 (0.13), 338 (0.70), 325 (0.98)	524	563	-[a]
12	CH_3CN	513 (0.11), 327 (0.51), 301 (0.79), 221 (4.90)	514	560	-[a]
13	Toluene	522 (0.15), 307 (0.69)	527	567	-[a]
13	DCM	521 (0.14), 313 (0.73), 273 (0.43), 267 (0.44)	528	566	-[a]
13	CH_3CN	513 (0.11), 311 (0.65), 273 (0.37), 266 (0.36), 224 (5.09)	515	558	-[a]
15	Toluene	532 (0.14), 389 (0.22), 293 (0.86)	535	576	1.7%
15	DCM	530 (0.13), 392 (0.22), 292 (0.73), 255 (3.11)	531	575	-[a]

Table S14. Data of UV-vis and fluorescence spectra

15	CH_3CN	524 (0.12), 387 (0.21), 291 (0.69), 252 (3.11)	528	573	-[a]
16	Toluene	532 (0.17), 389 (0.25), 300 (0.56)	537	574	1.8%
16	DCM	530 (0.16), 392 (0.26), 305 (0.46), 254 (4.03)	531	575	-[a]
16	CH_3CN	525 (0.15), 388 (0.25), 304 (0.43), 252 (4.00), 220 (5.22)	525	571	-[a]
21	Toluene	524 (0.15), 385 (0.14), 300 (1.47)	533	570	-[a]
21	DCM	524 (0.12), 391 (0.14), 307 (1.11), 274 (3.32)	519	571	-[a]
21	CH_3CN	514 (0.11), 382 (0.14), 302 (1.20), 270 (3.42)	513	558	-[a]
22	Toluene	523 (0.14), 387 (0.14), 308 (1.03)	529	570	-[a]
22	DCM	523 (0.13), 386 (0.16), 309 (1.04), 272 (3.88)	519	575	-[a]
22	CH_3CN	514 (0.11), 380 (0.15), 304 (1.02), 271 (3.70), 224 (5.03)	518	563	-[a]
23b	Toluene	532 (0.12), 411 (0.15)	533	582	-[a]
23b	DCM	529 (0.11), 415 (0.14), 292 (4.45)	529	580	-[a]
23b	CH_3CN	523 (0.10), 416 (0.13), 290 (4.63)	524	573	-[a]
24b	Toluene	533 (0.14), 389 (0.20), 301 (1.52), 290 (1.73)	524	578	-[a]
24b	DCM	530 (0.11), 392 (0.18), 301 (1.23), 290 (1.44), 257 (2.06)	513	565	-[a]
24b	CH_3CN	525 (0.11), 389 (0.18), 301 (1.20), 391 (1.38), 257 (2.72), 219 (5.10)	525	572	-[a]
26a	Toluene	532 (0.15), 389 (0.26), 296 (0.99)	535	576	-[a]
26a	DCM	528 (0.15), 389 (0.28), 307 (0.76), 252 (4.25)	525	576	-[a]
26a	CH_3CN	524 (0.12), 384 (0.26), 304 (0.70), 249 (4.39), 221 (5.21)	527	573	-[a]
26b	Toluene	532 (0.18), 389 (0.26), 303 (1.02)	535	574	-[a]
26b	DCM	530 (0.15), 392 (0.24), 307 (0.74), 254 (3.81)	526	574	-[a]
26b	CH_3CN	526 (0.14), 390 (0.22), 302 (0.79), 253 (3.82), 221 (5.32)	526	572	-[a]

[a] Fluorescence was too weak to calculate the quantum yield.

5.2 CD and CPL spectra

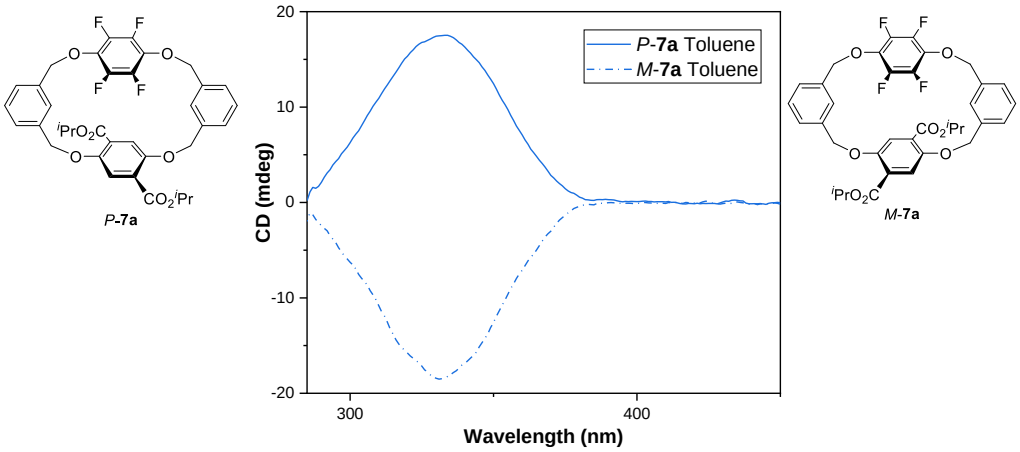


Figure S34A. CD spectra of *P*-**7a** and *M*-**7a** in toluene at 25 °C (ca. 5 × 10^{-5} M)

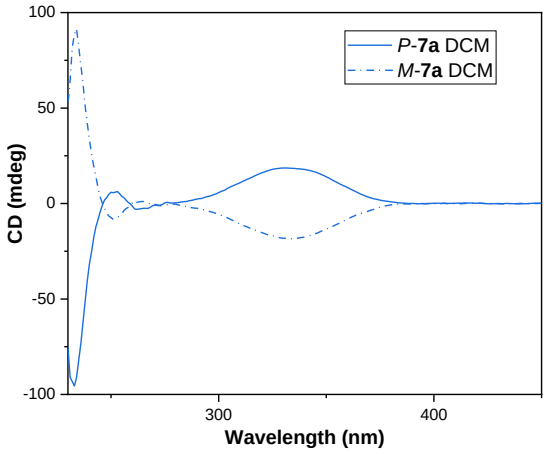


Figure S34B. CD spectra of *P*-**7a** and *M*-**7a** in dichloromethane at 25 °C (ca. 6 × 10^{-5} M)

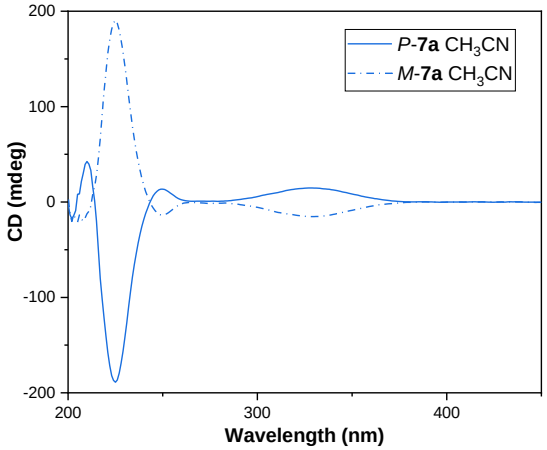


Figure S34C. CD spectra of *P*-**7a** and *M*-**7a** in acetonitrile at 25 °C (ca. 5 × 10^{-5} M)

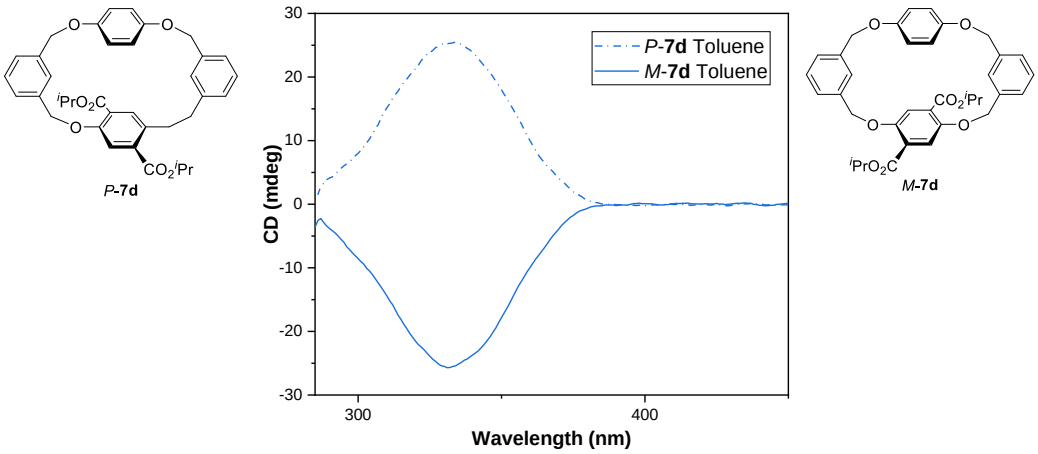


Figure S34D. CD spectra of *P*-**7d** and *M*-**7d** in toluene at 25 °C (ca. 7 × 10^{-5} M)

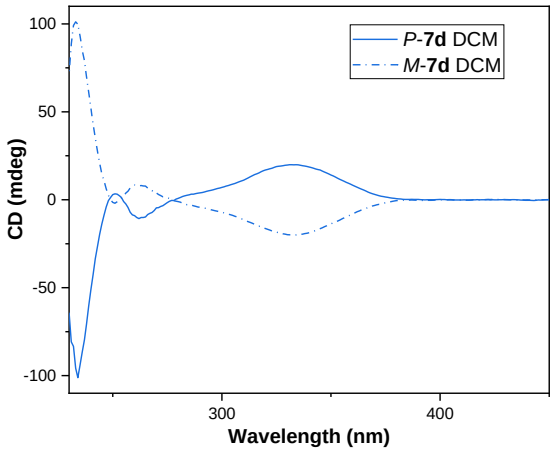


Figure S34E. CD spectra of *P*-**7d** and *M*-**7d** in dichloromethane at 25 °C (ca. 5 × 10^{-5} M)

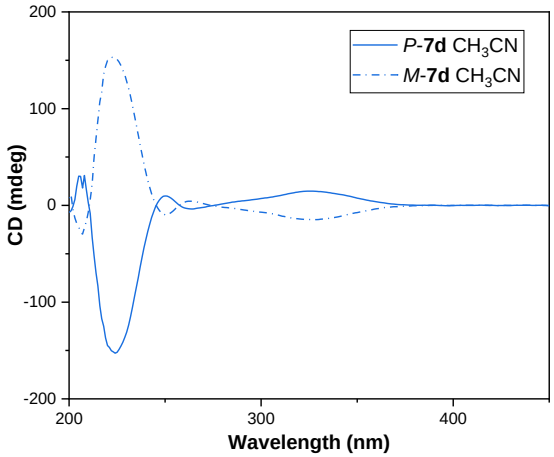


Figure S34F. CD spectra of *P*-**7d** and *M*-**7d** in acetonitrile at 25 °C (ca. 5 × 10^{-5} M)

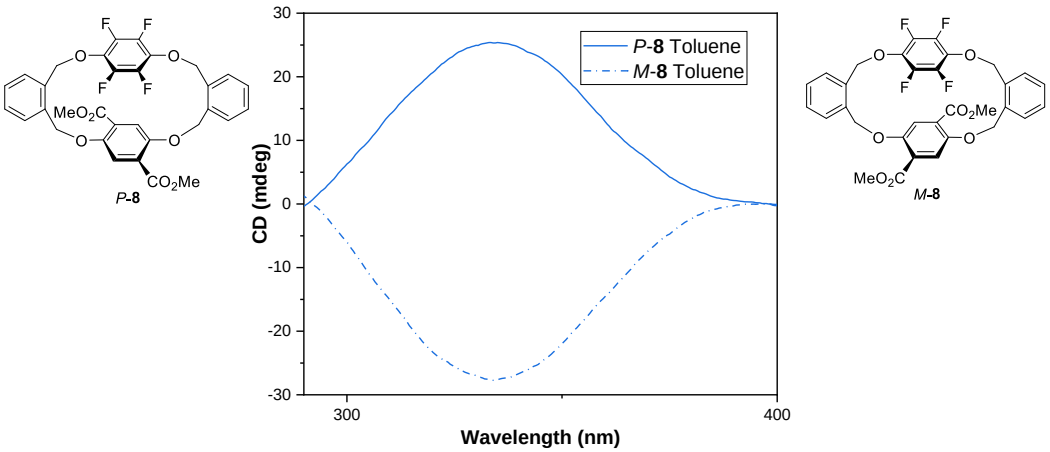


Figure S34G. CD spectra of *P*-**8** and *M*-**8** in toluene at 25 °C (ca. 1.0×10^{-4} M)

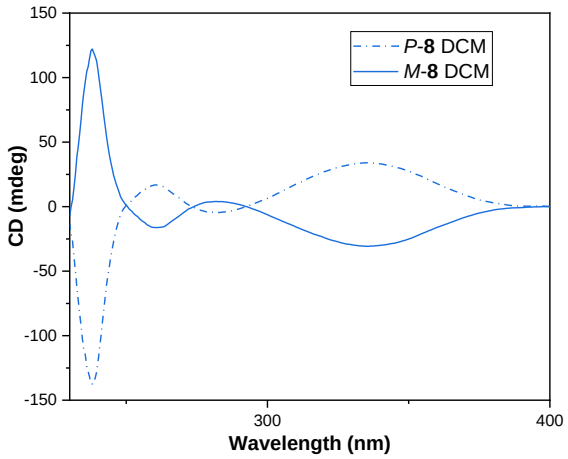


Figure S34H. CD spectra of *P*-**8** and *M*-**8** in dichloromethane at 25 °C (ca. 1.2×10^{-4} M)

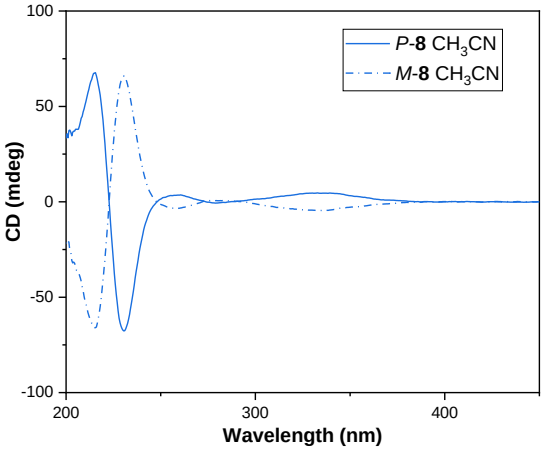


Figure S34I. CD spectra of *P*-**8** and *M*-**8** in acetonitrile at 25 °C (ca. 3×10^{-5} M)

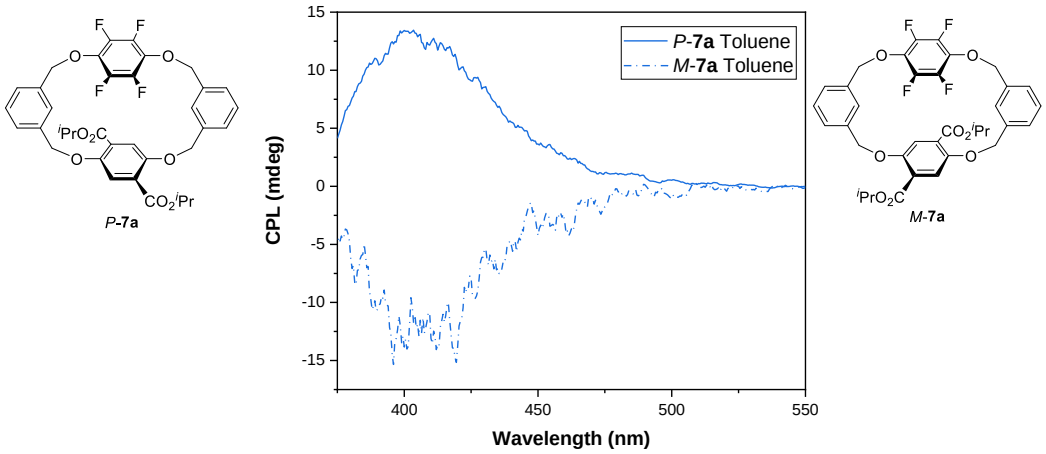


Figure S35A. CPL spectra of *P*-**7a** and *M*-**7a** in toluene at 25 °C (ca. 1 × 10^{-4} M)

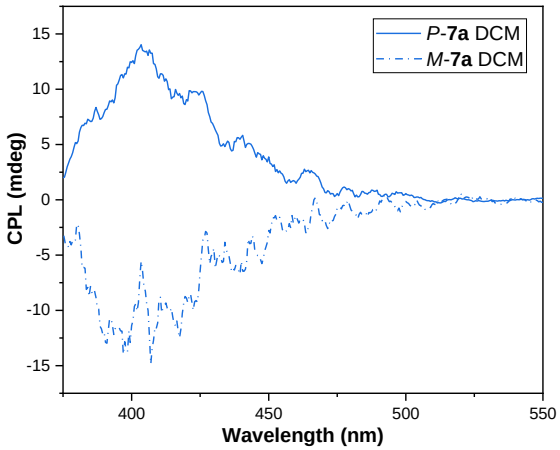


Figure S35B. CPL spectra of *P*-**7a** and *M*-**7a** in dichloromethane at 25 °C (ca. 1 × 10^{-4} M)

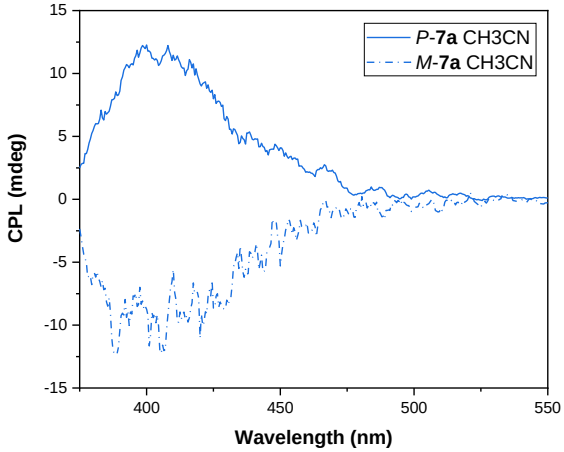


Figure S35C. CPL spectra of *P*-**7a** and *M*-**7a** in acetonitrile at 25 °C (ca. 1 × 10^{-4} M)

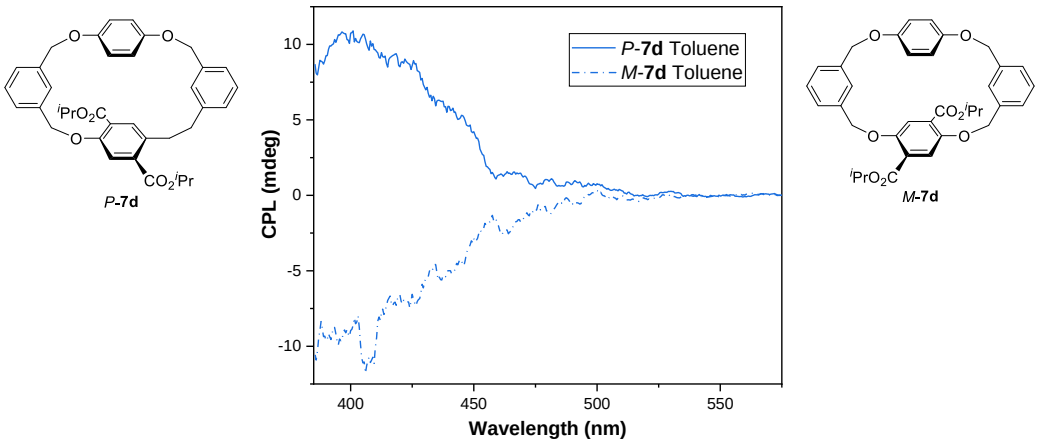


Figure S35D. CPL spectra of *P*-**7d** and *M*-**7d** in toluene at 25 °C (ca. 1 × 10^{-4} M)

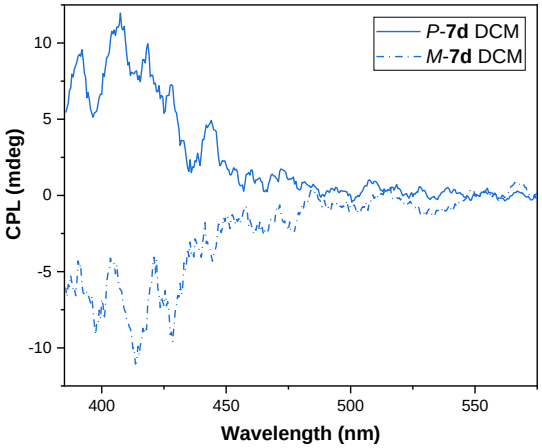


Figure S35E. CPL spectra of *P*-**7d** and *M*-**7d** in dichloromethane at 25 °C (ca. 1 × 10^{-4} M)

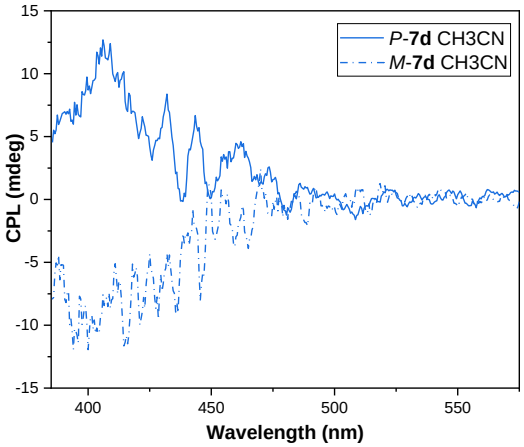


Figure S35F. CPL spectra of *P*-**7d** and *M*-**7d** in acetonitrile at 25 °C (ca. 1 × 10^{-4} M)

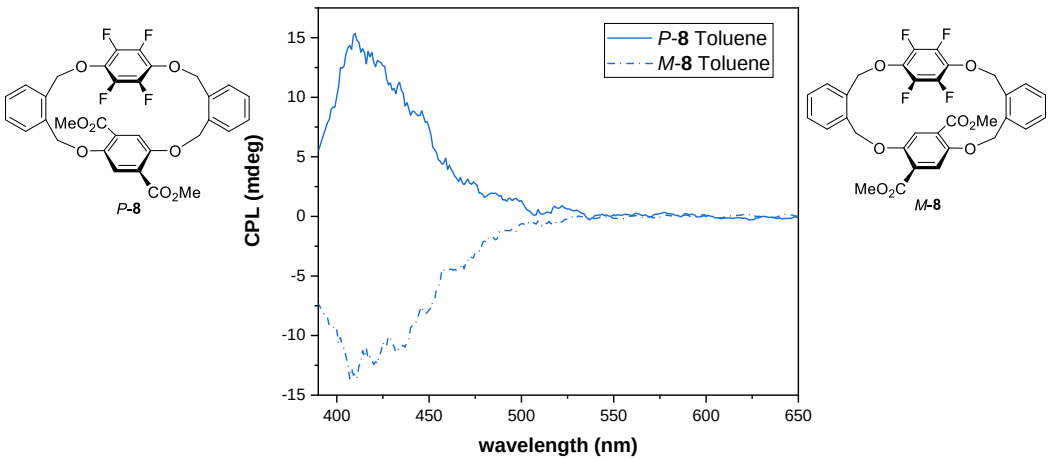


Figure S35G. CPL spectra of *P*-**8** and *M*-**8** in toluene at 25 °C (ca. 1 × 10^{-4} M)

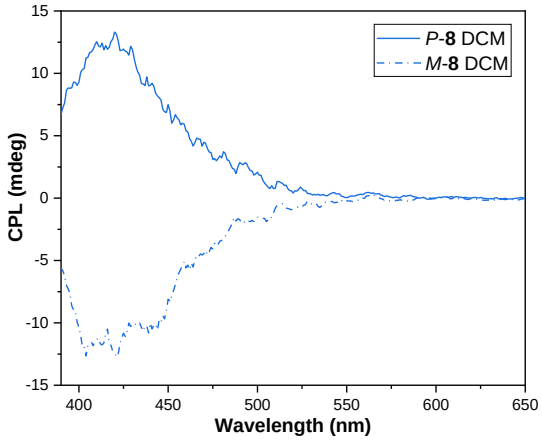


Figure S35H. CPL spectra of *P*-**8** and *M*-**8** in chloromethane at 25 °C (ca. 1 × 10^{-4} M)

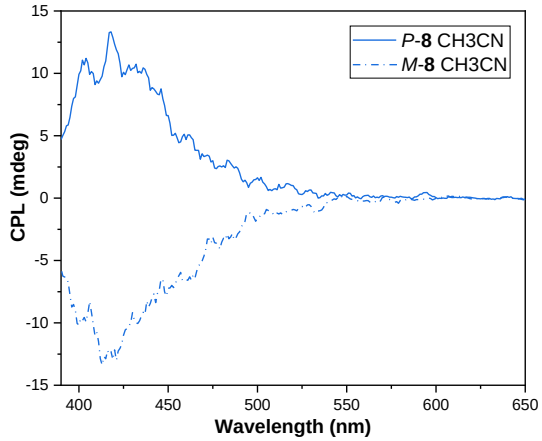


Figure S35I. CPL spectra of *P*-**8** and *M*-**8** in acetonitrile at 25 °C (ca. 1 × 10^{-4} M)

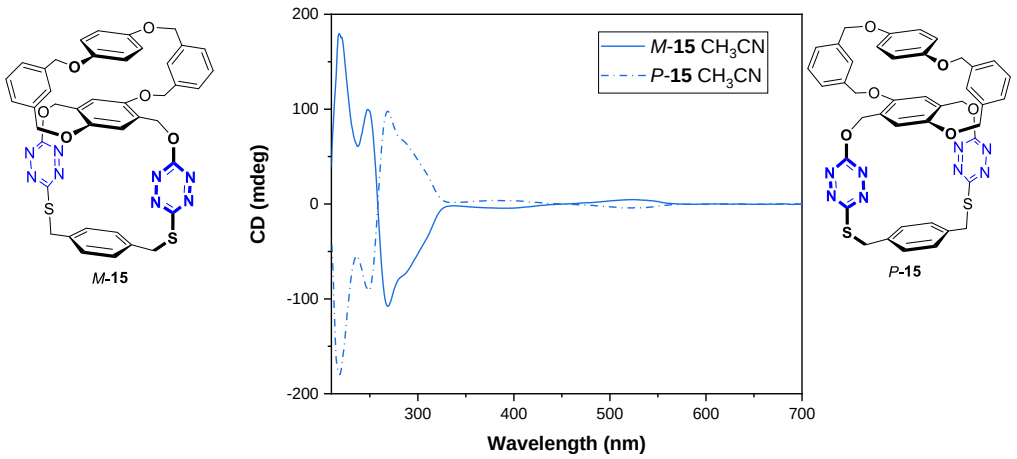


Figure S36A. CD spectra of *M*-**15** and *P*-**15** in acetonitrile at 25 °C (ca. 8 × 10^{-5} M)

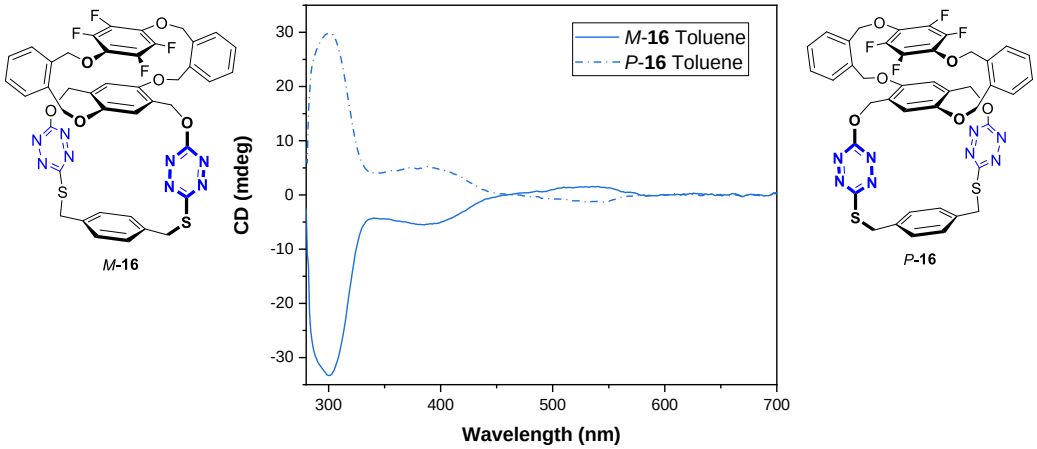


Figure S36B. CD spectra of *M*-**16** and *P*-**16** in toluene at 25 °C (ca. 6 × 10^{-5} M)

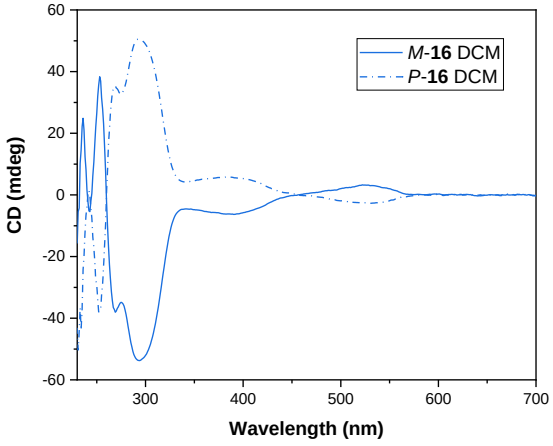


Figure S36C. CD spectra of *M*-**16** and *P*-**16** in chloromethane at 25 °C (ca. 8 × 10^{-5} M)

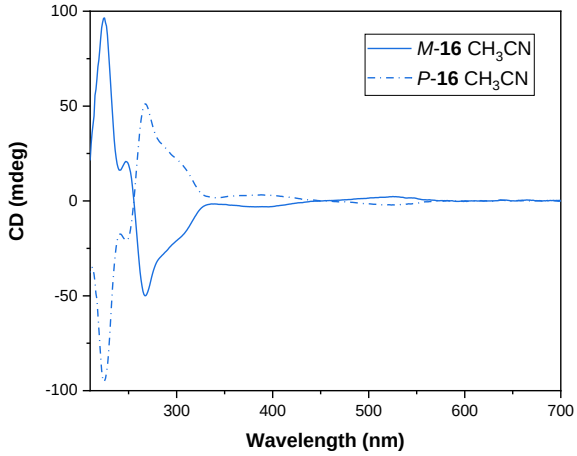


Figure S36D. CD spectra of *M*-**16** and *P*-**16** in acetonitrile at 25 ºC (ca. 4 × 10^{-5} M)

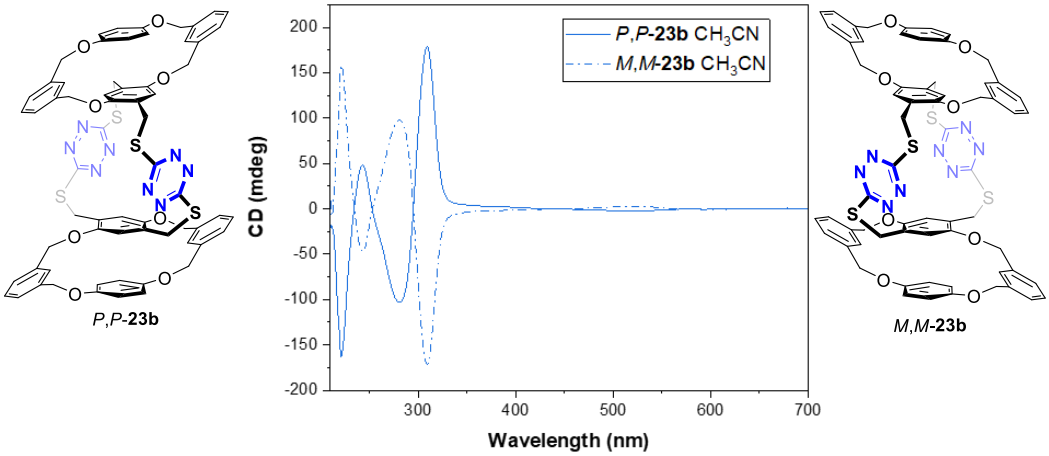


Figure S36E. CD spectra of *P*,*P*-**23b** and *M*,*M*-**23b** in acetonitrile at 25 ºC (ca. 4 × 10^{-5} M)

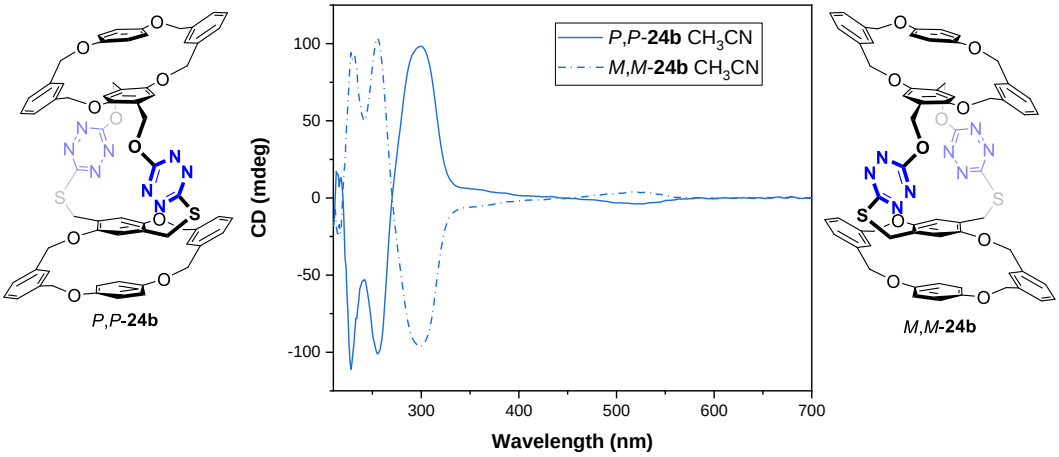


Figure S36F. CD spectra of *P*,*P*-**24b** and *M*,*M*-**24b** in acetonitrile at 25 ºC (ca. 9 × 10^{-5} M)

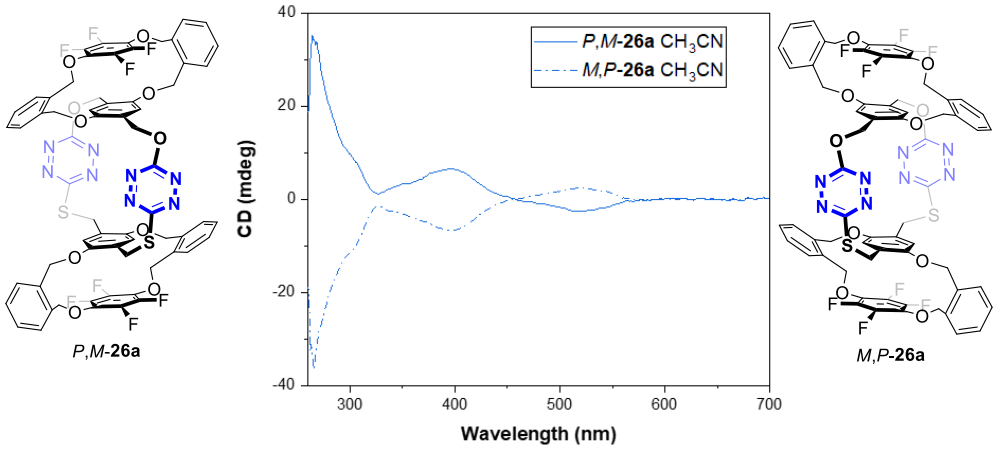


Figure S36G. CD spectra of *P*,*M*-**26a** and *M*,*P*-**26a** in acetonitrile at 25 ºC (ca. 2 × 10^{-5} M)

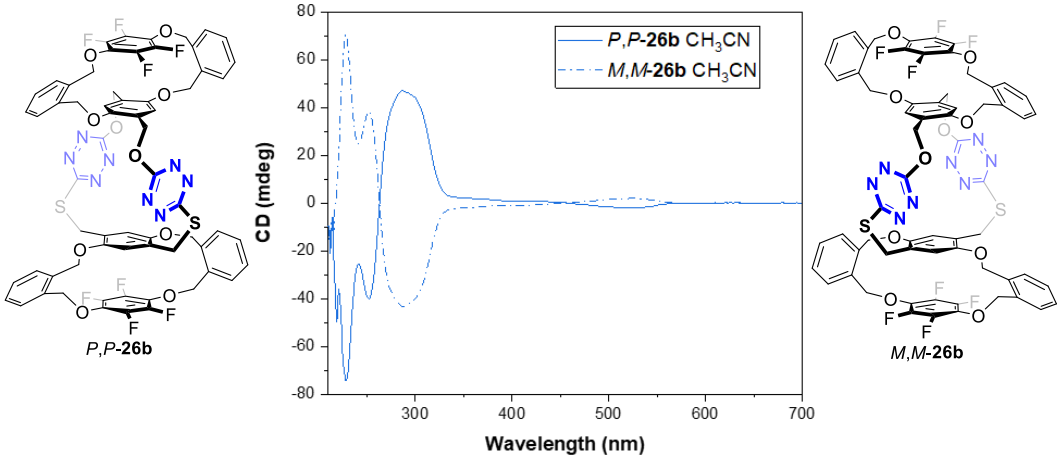


Figure S36H. CD spectra of *P*,*P*-**26b** and *M*,*M*-**26b** in acetonitrile at 25 ºC (ca. 5 × 10^{-5} M)

Table S15. Data of CD and CPL spectra

Compound	Solv.	CD g_{abs}	CPL g_{lum}
P-**7a**	Toluene	2.5 × 10^{-3} (333 nm)	1.9 × 10^{-3} (403 nm)
M-**7a**	Toluene	-2.6 × 10^{-3} (331 nm)	-2.0 × 10^{-3} (401 nm)
P-**7a**	DCM	2.3 × 10^{-3} (331 nm)	2.0 × 10^{-3} (404 nm)
M-**7a**	DCM	-2.4 × 10^{-3} (334 nm)	-2.1 × 10^{-3} (407 nm)
P-**7a**	CH_3CN	2.3 × 10^{-3} (327 nm)	1.7 × 10^{-3} (408 nm)
M-**7a**	CH_3CN	-2.3 × 10^{-3} (329 nm)	-1.7 × 10^{-3} (406 nm)
P-**7d**	Toluene	2.2 × 10^{-3} (334 nm)	1.5 × 10^{-3} (401 nm)
M-**7d**	Toluene	-2.3 × 10^{-3} (331 nm)	-1.6 × 10^{-3} (406 nm)
P-**7d**	DCM	2.2 × 10^{-3} (331 nm)	1.6 × 10^{-3} (408 nm)
M-**7d**	DCM	-2.3 × 10^{-3} (333 nm)	-1.6 × 10^{-3} (413 nm)
P-**7d**	CH_3CN	2.2 × 10^{-3} (325 nm)	1.7 × 10^{-3} (406 nm)
M-**7d**	CH_3CN	-2.2 × 10^{-3} (328 nm)	-1.6 × 10^{-3} (400 nm)
P-**8**	Toluene	1.8 × 10^{-3} (332 nm)	2.1 × 10^{-3} (410 nm)
M-**8**	Toluene	-1.9 × 10^{-3} (335 nm)	-1.9 × 10^{-3} (411 nm)

Table S15. Data of CD and CPL spectra

P-**8**	DCM	1.9×10^{-3} (335 nm)	1.9×10^{-3} (420 nm)
M-**8**	DCM	-1.9×10^{-3} (335 nm)	-1.8×10^{-3} (421 nm)
P-**8**	CH_3CN	2.1×10^{-3} (334 nm)	1.9×10^{-3} (418 nm)
M-**8**	CH_3CN	-2.1×10^{-3} (335 nm)	-1.8×10^{-3} (419 nm)
M-**15**	CH_3CN	1.5×10^{-3} (523 nm)	-
P-**15**	CH_3CN	-1.5×10^{-3} (523 nm)	-
M-**16**	Toluene	4.2×10^{-4} (531 nm)	-
P-**16**	Toluene	-4.2×10^{-4} (531 nm)	-
M-**16**	DCM	6.7×10^{-4} (529 nm)	-
P-**16**	DCM	-6.2×10^{-4} (529 nm)	-
M-**16**	CH_3CN	1.3×10^{-3} (525 nm)	-
P-**16**	CH_3CN	-1.2×10^{-3} (524 nm)	-
M,*P*-**23b**	CH_3CN	-2.0×10^{-3} (518 nm)	-
P,*M*-**23b**	CH_3CN	2.0×10^{-3} (517 nm)	-
P,*P*-**24b**	CH_3CN	-1.0×10^{-3} (520 nm)	-
M,*M*-**24b**	CH_3CN	1.1×10^{-3} (521 nm)	-
M,*P*-**26a**	CH_3CN	-5.5×10^{-4} (521 nm)	-
P,*M*-**26a**	CH_3CN	5.0×10^{-4} (521 nm)	-
P,*P*-**26b**	CH_3CN	-1.2×10^{-3} (523 nm)	-
M,*M*-**26b**	CH_3CN	1.5×10^{-3} (522 nm)	-

6. References

[1] J. R. Lakowicz, *Principle of fluorescence spectroscopy.* Springer. Boston, **1999**.

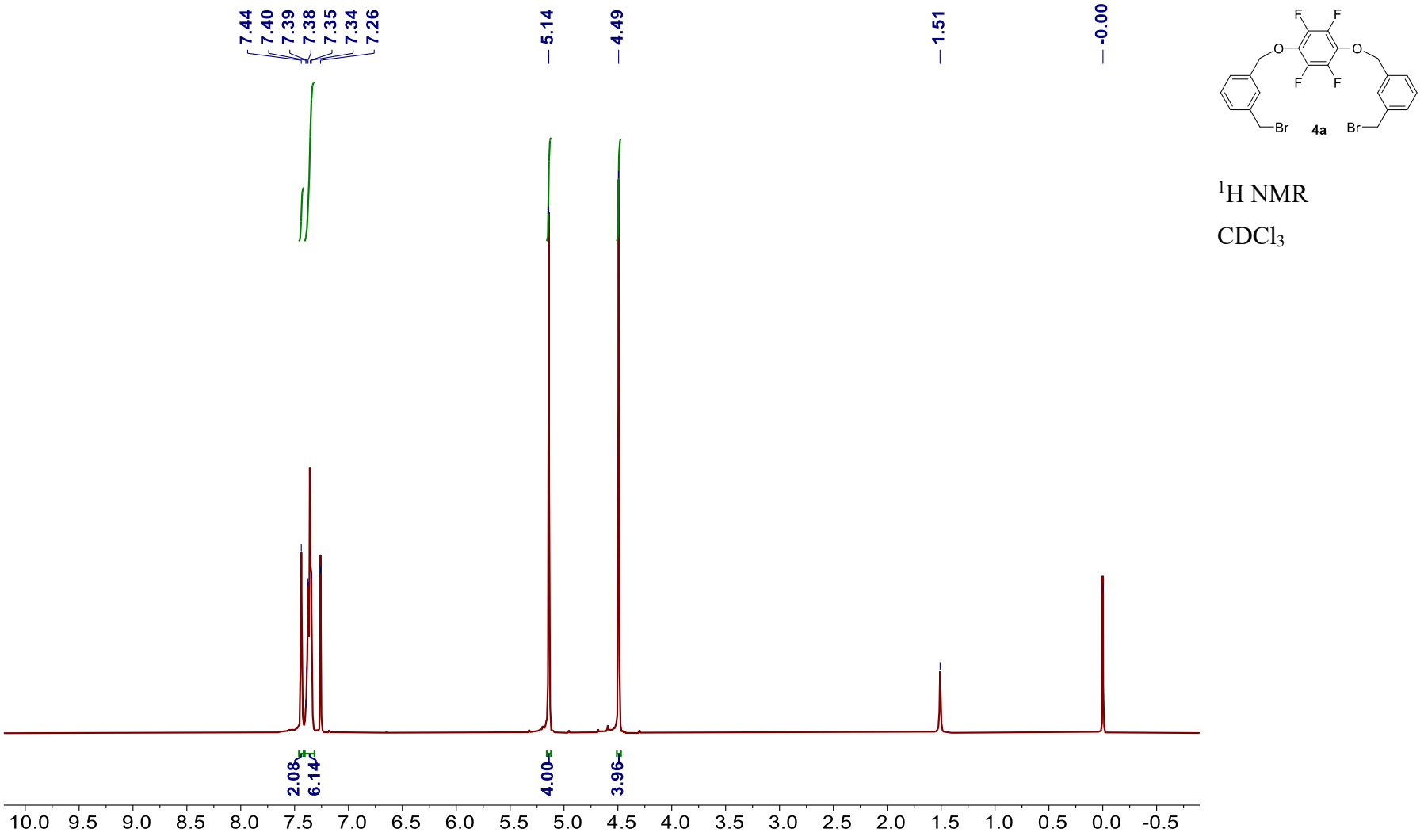
[2] R. F. Kubin, A. N. Fletcher, *J. Lumin.* **1982**, *27*, 255.

[3] H.-L. Liu, Q.-Z. Wang, *Asian J. Chem.* **2014**, *26*, 5165.

[4] G. Clavier, P. Audebert, *Chem. Rev.* **2010**, *110*, 3299.

[5] H.-B. Liu, Q. Zhang, M.-X. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 6536.

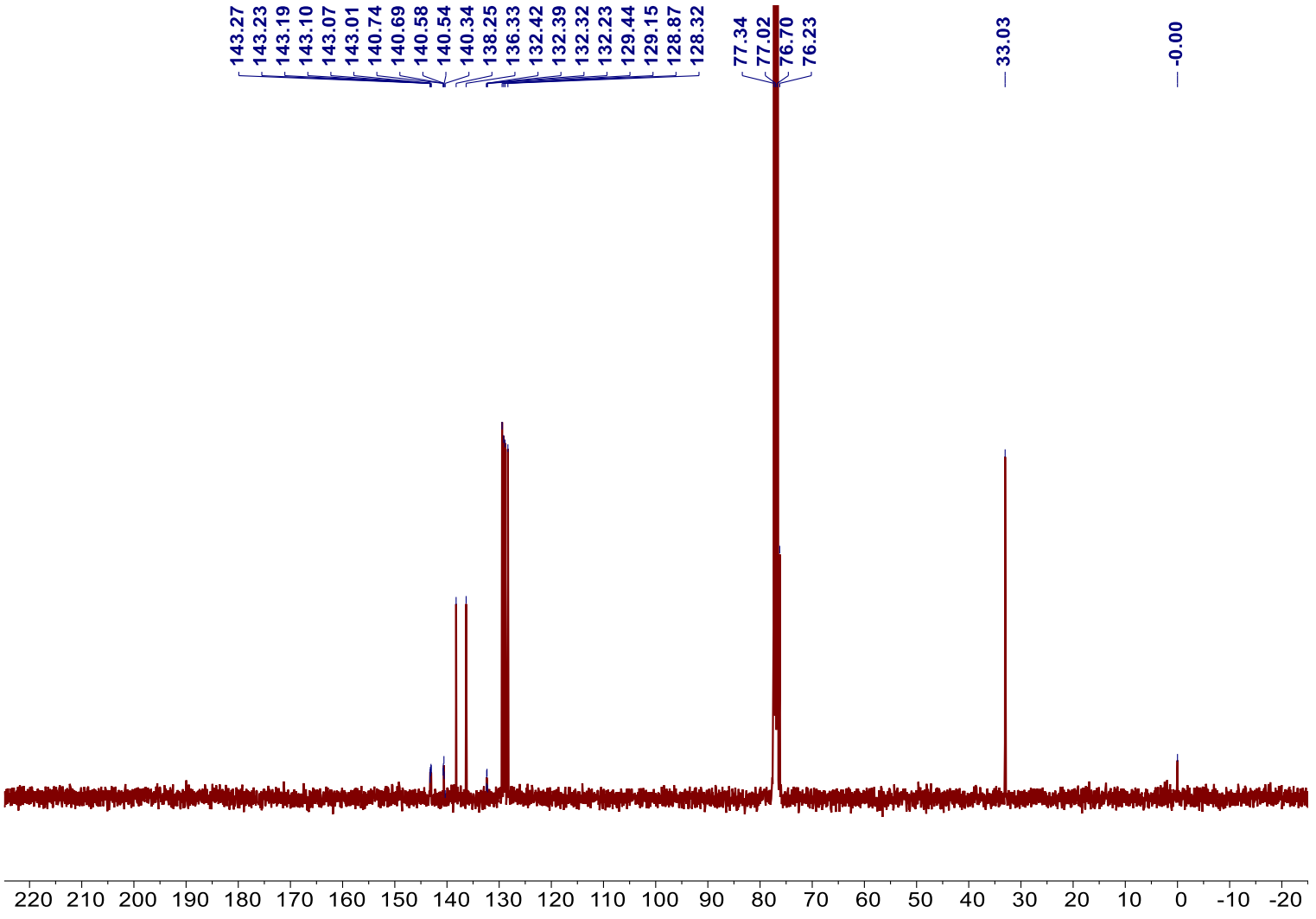
7. Copies of NMR Spectra

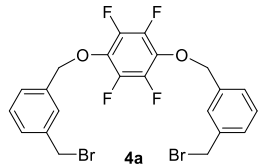


4a

^{1}H NMR

$CDCl_3$

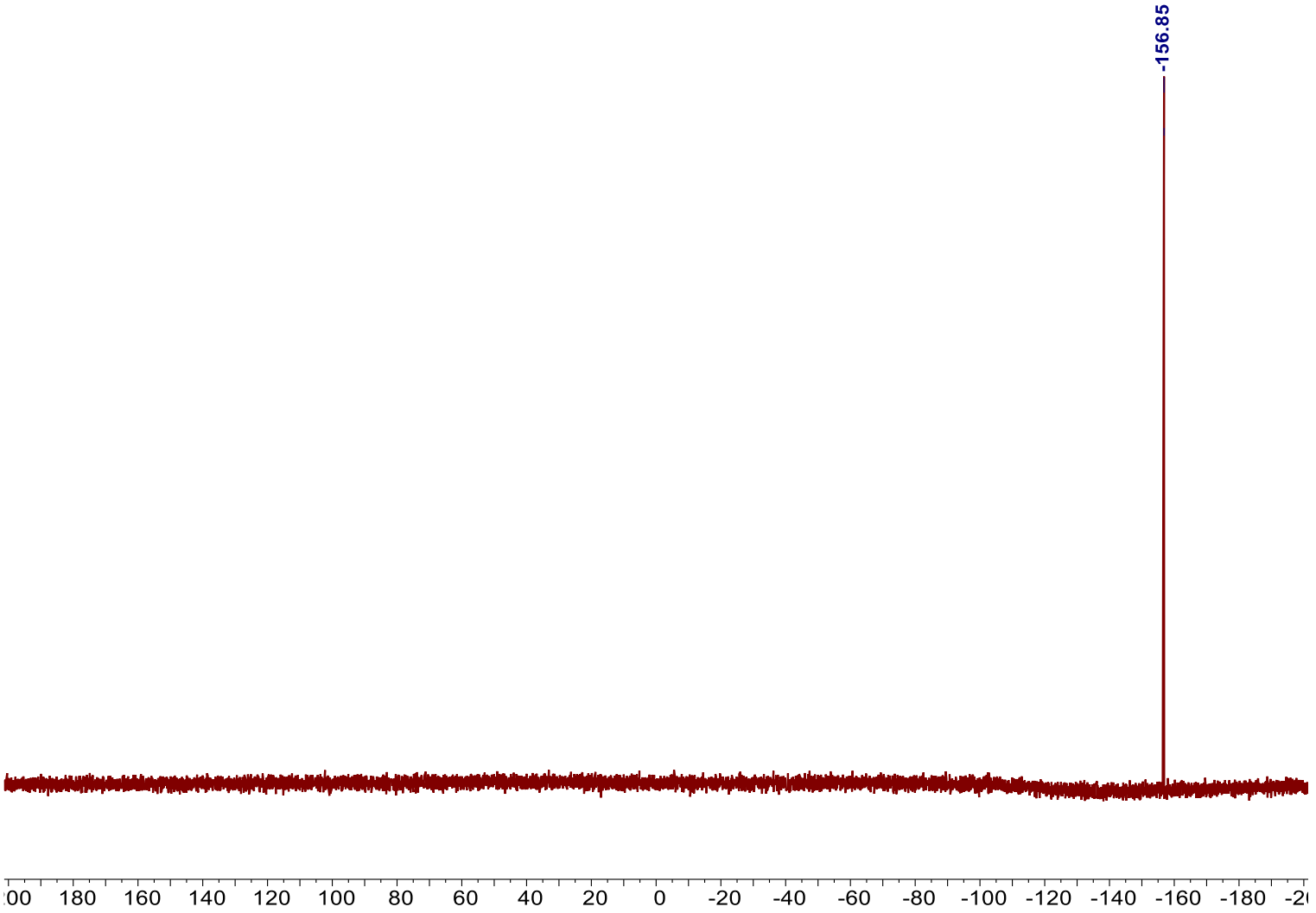


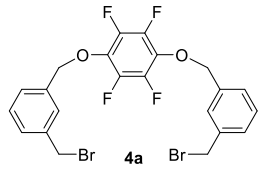


4a

^{13}C NMR

$CDCl_3$

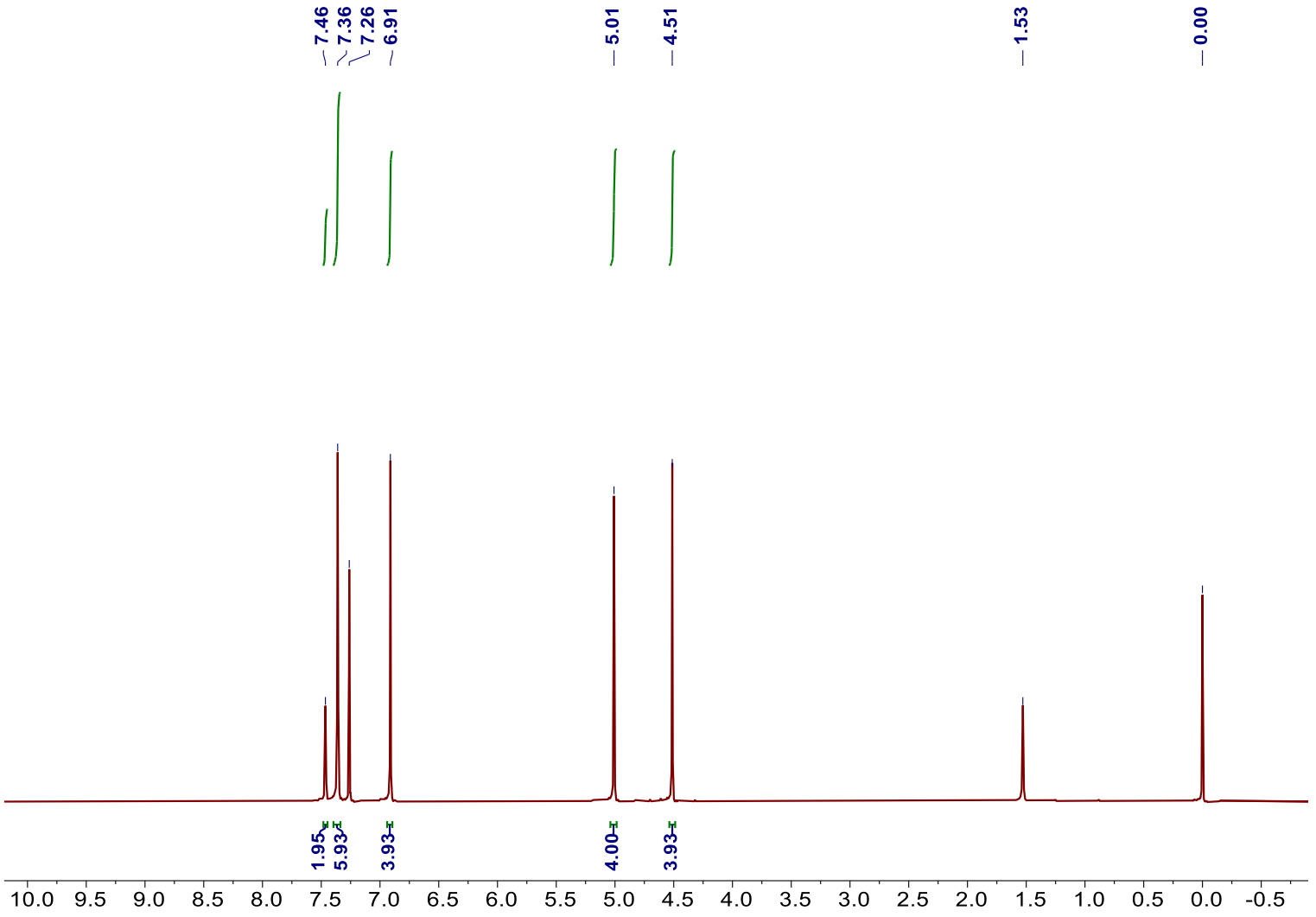


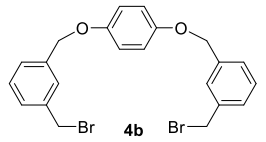


4a

^{19}F NMR

$CDCl_3$

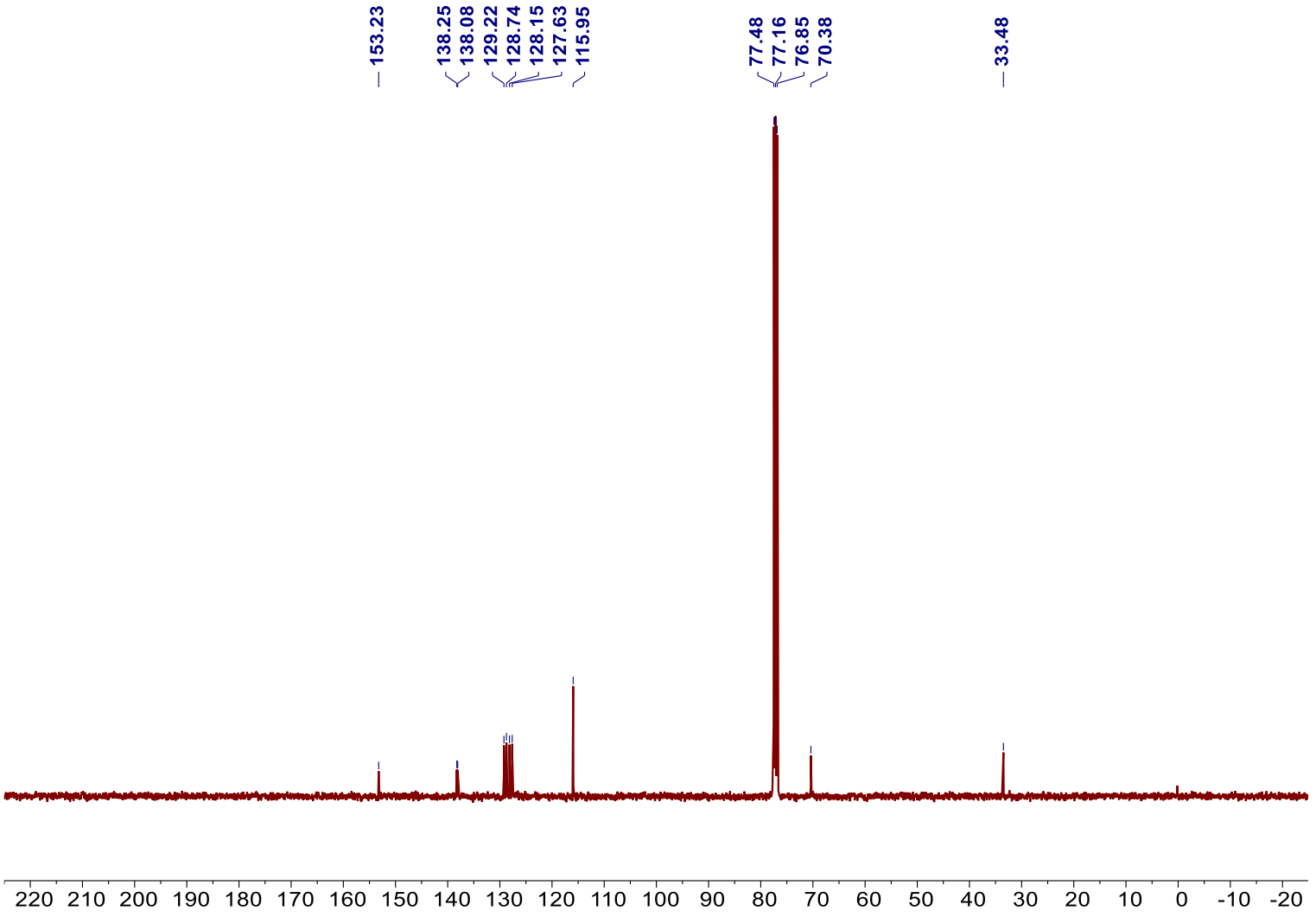


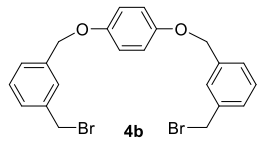


4b

^{1}H NMR

$CDCl_3$

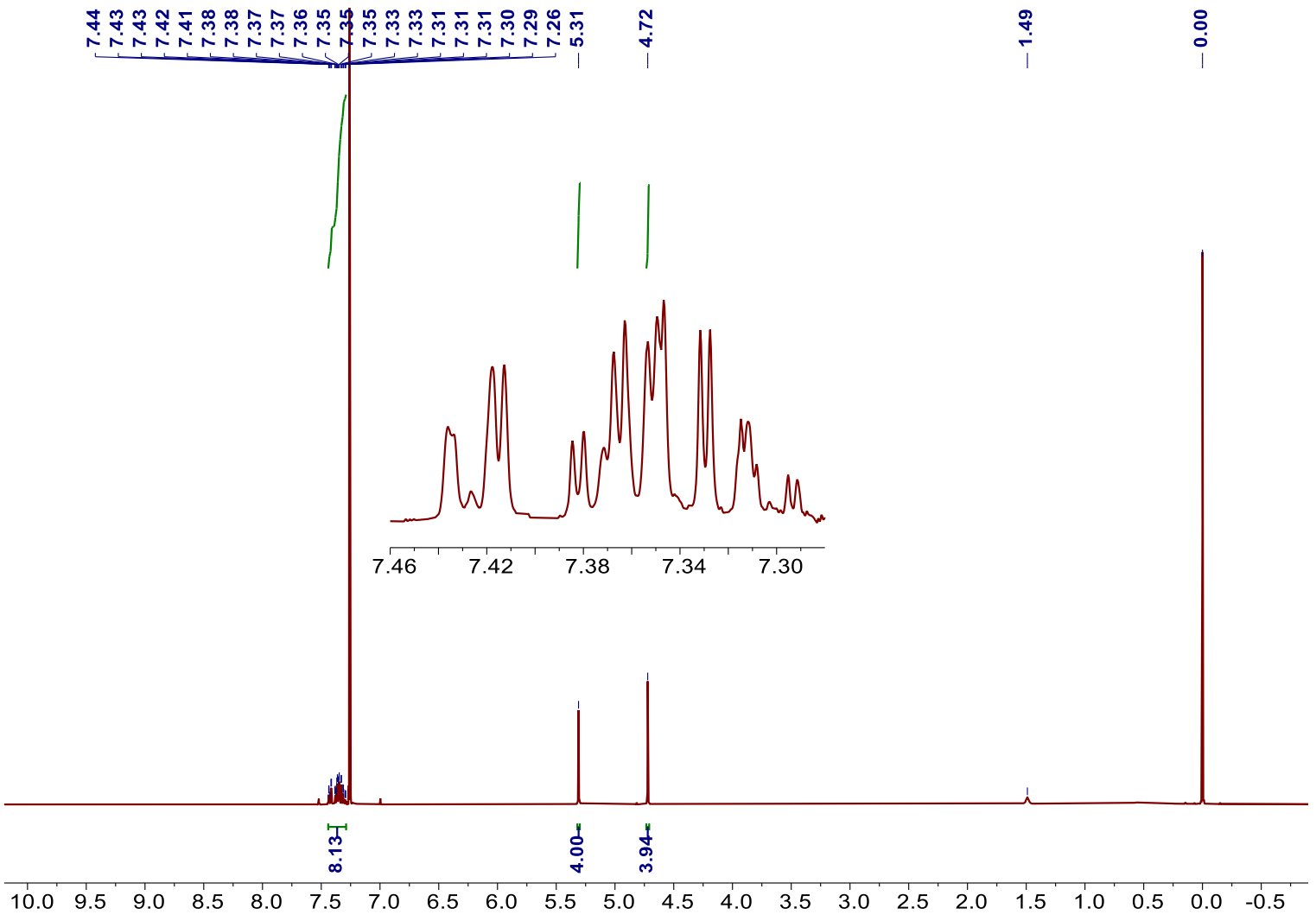




4b

^{13}C NMR

$CDCl_3$


7.44
7.43
7.43
7.42
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7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.33
7.33
7.31
7.31
7.31
7.30
7.29
7.26
5.31
4.72
1.49
0.00
7.46
7.42
7.38
7.34
7.30
8.13
4.00
3.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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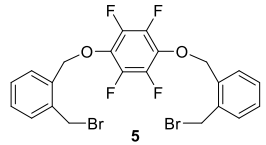
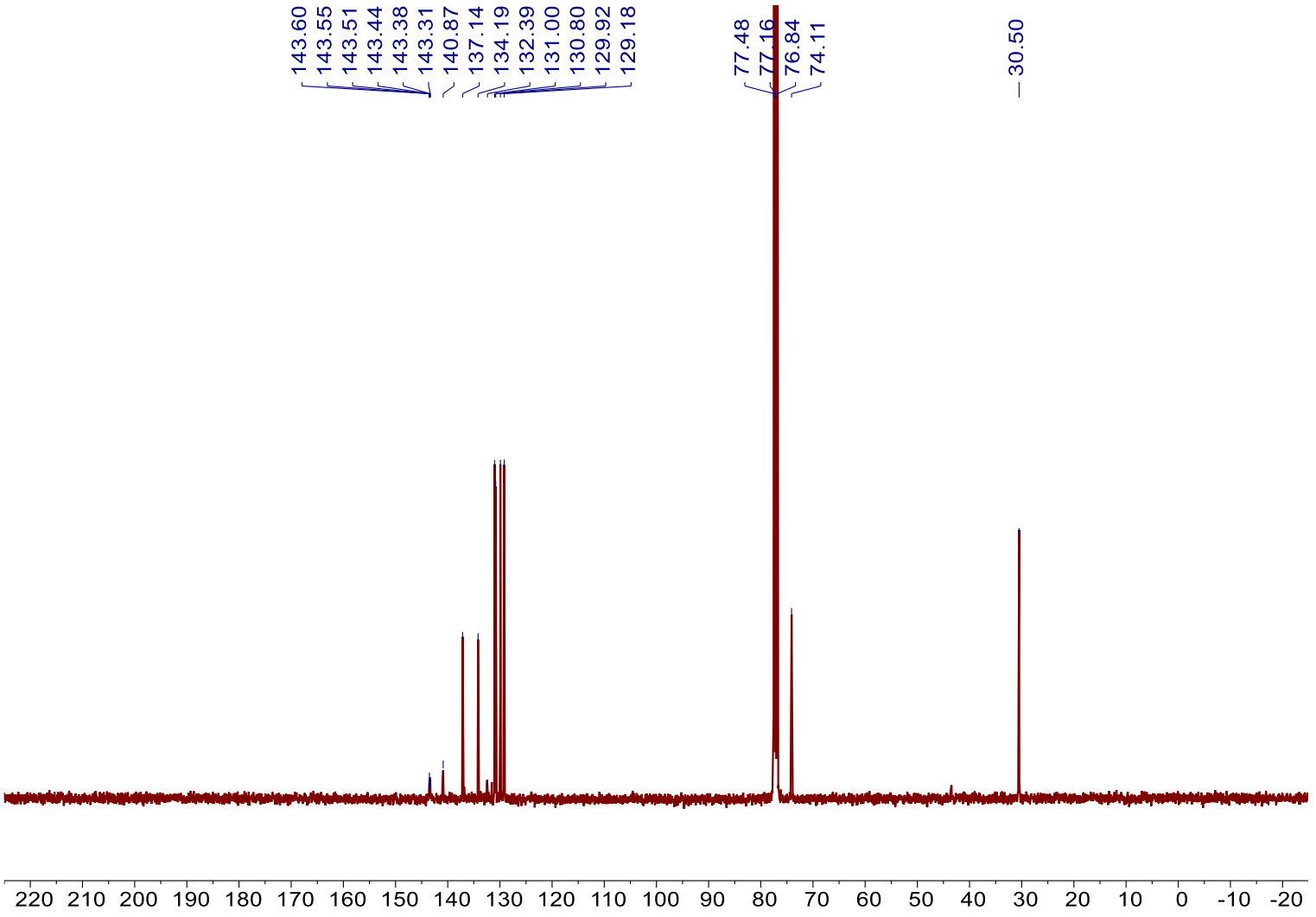
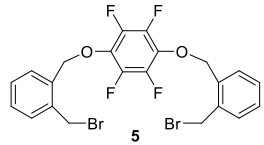
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


F
F
O
O
F
F
Br
Br
5

^{1}H NMR

$CDCl_3$

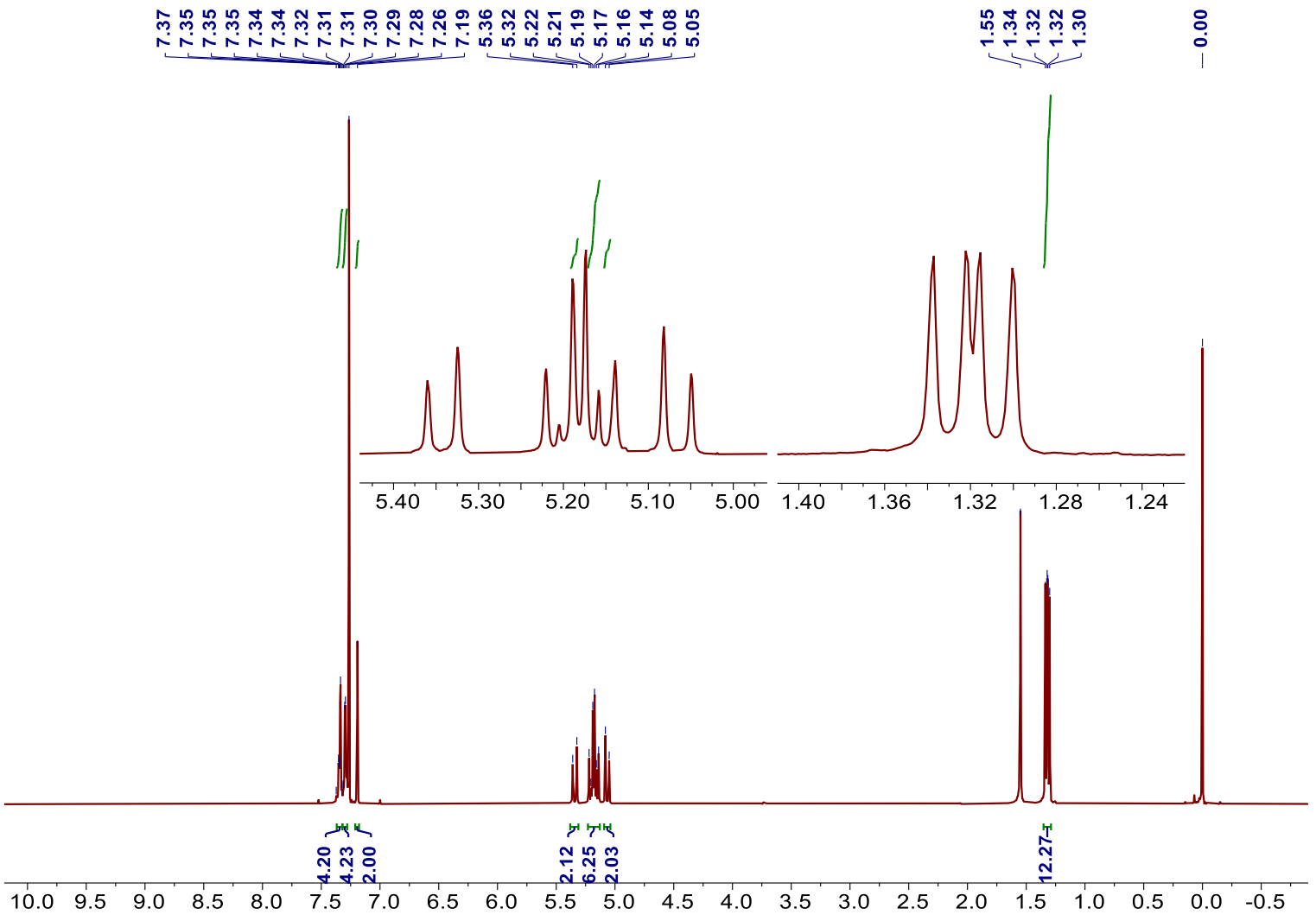


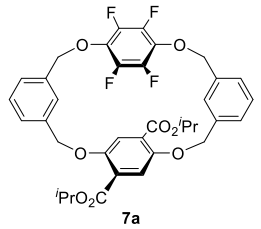


^{13}C NMR

$CDCl_3$


-156.58
F
F
O
O
F
F
Br
Br
5
^{19}F NMR
$CDCl_3$
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

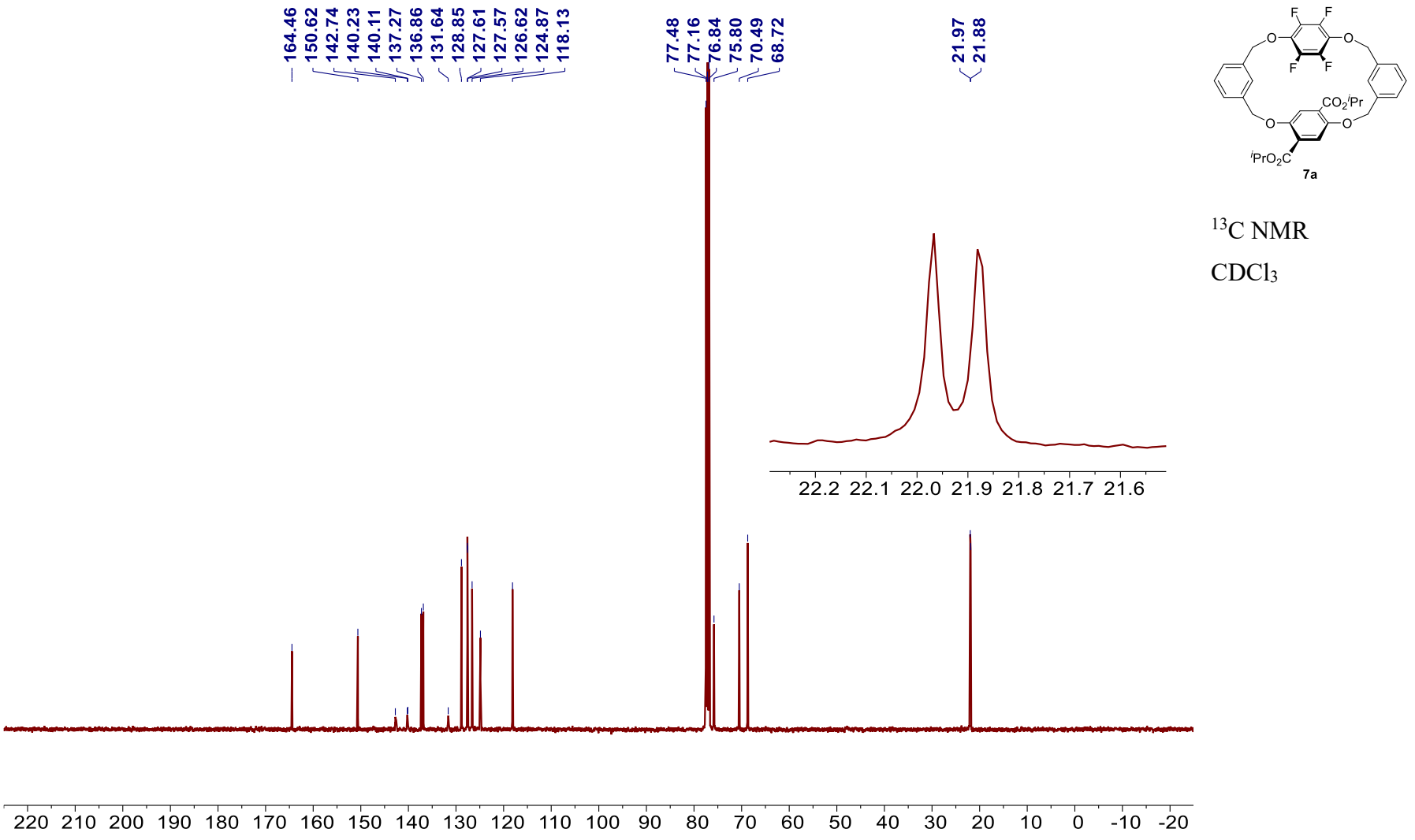




7a

^{1}H NMR

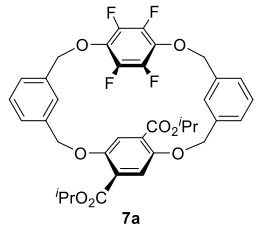
$CDCl_3$



7a

^{13}C NMR

$CDCl_3$



7a

^{19}F NMR

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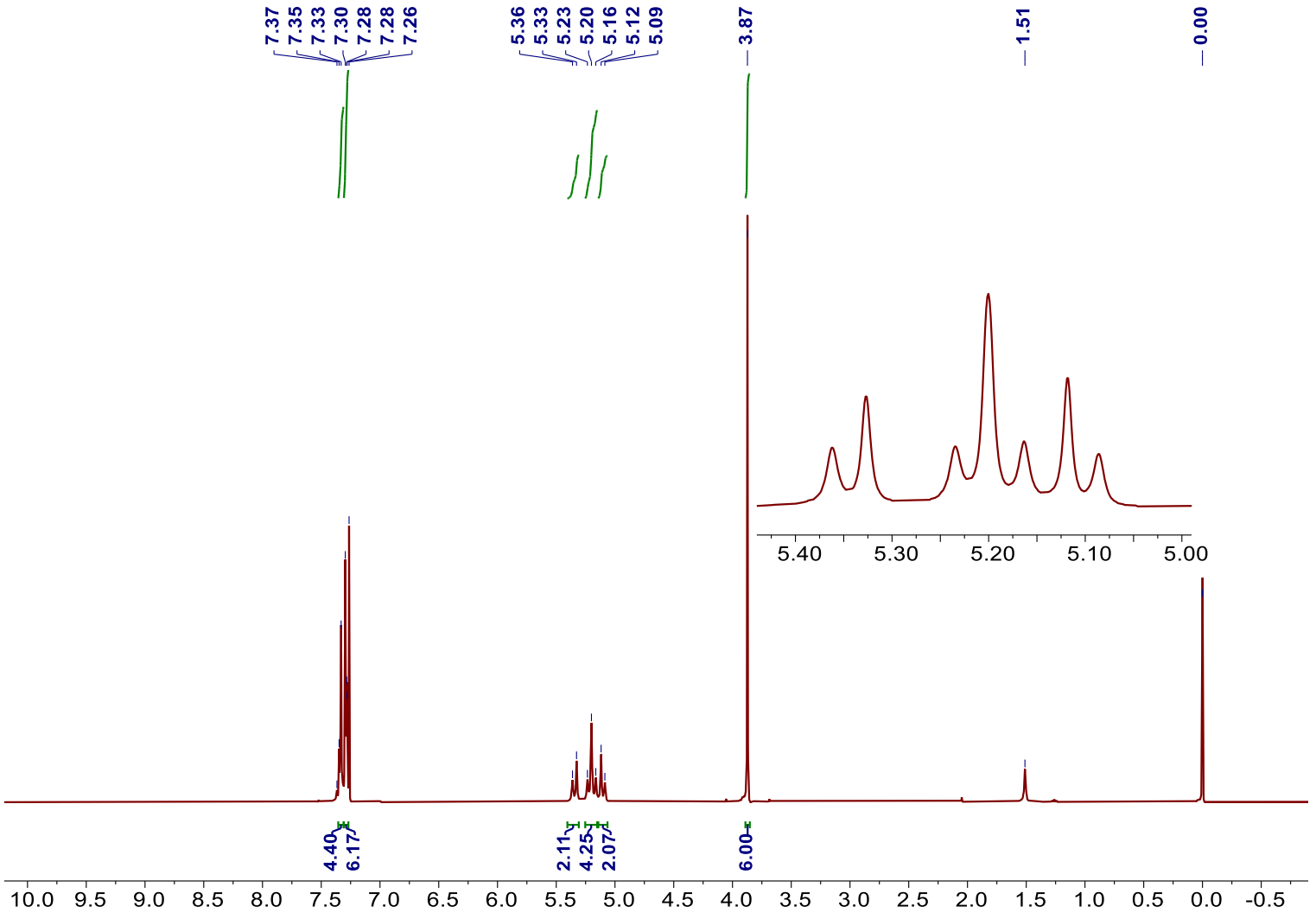
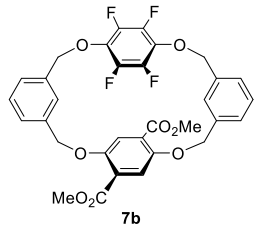
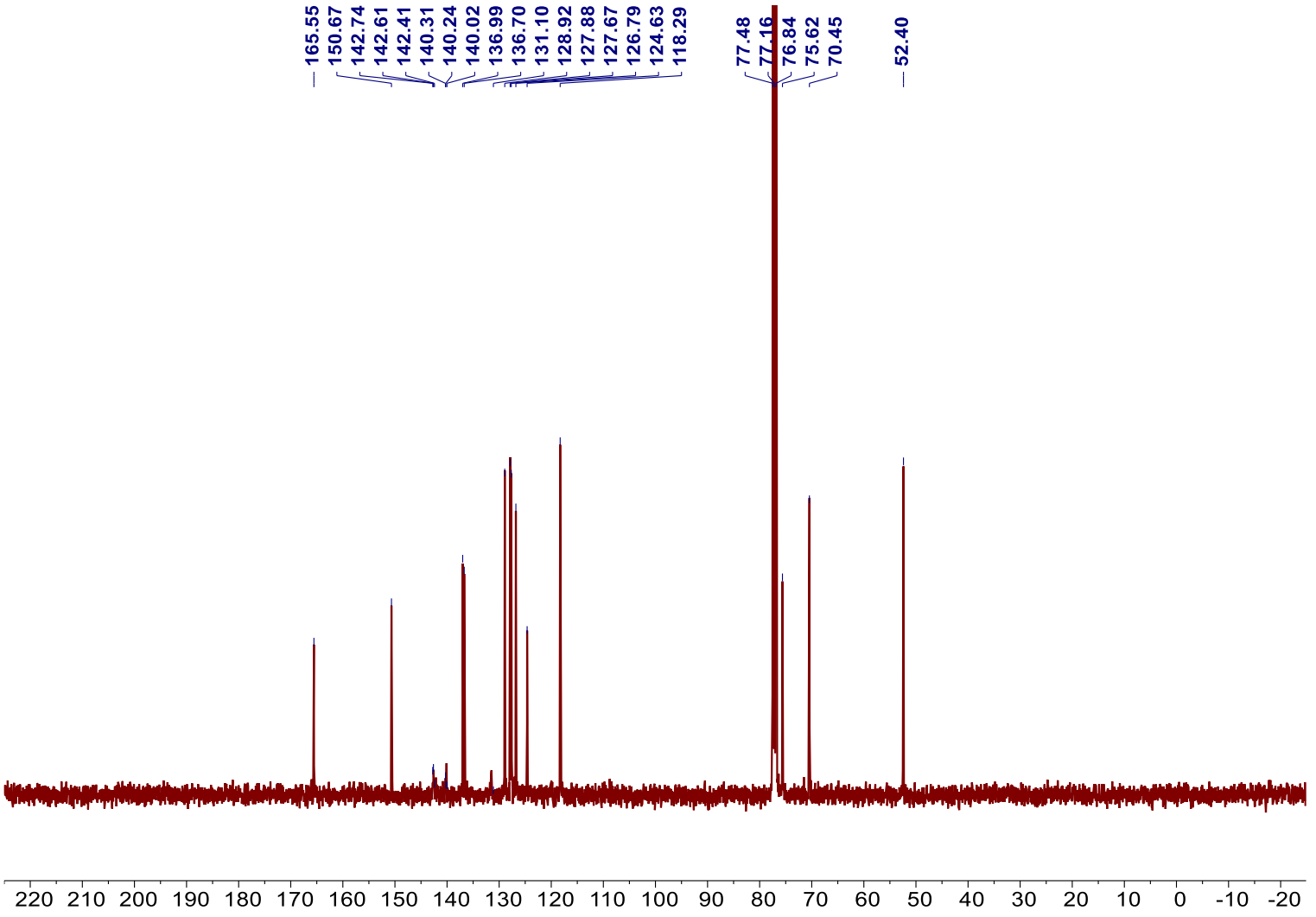


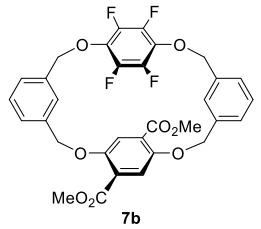


7b

^{1}H NMR

$CDCl_3$

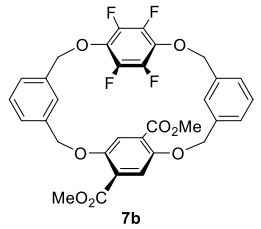




7b

^{13}C NMR

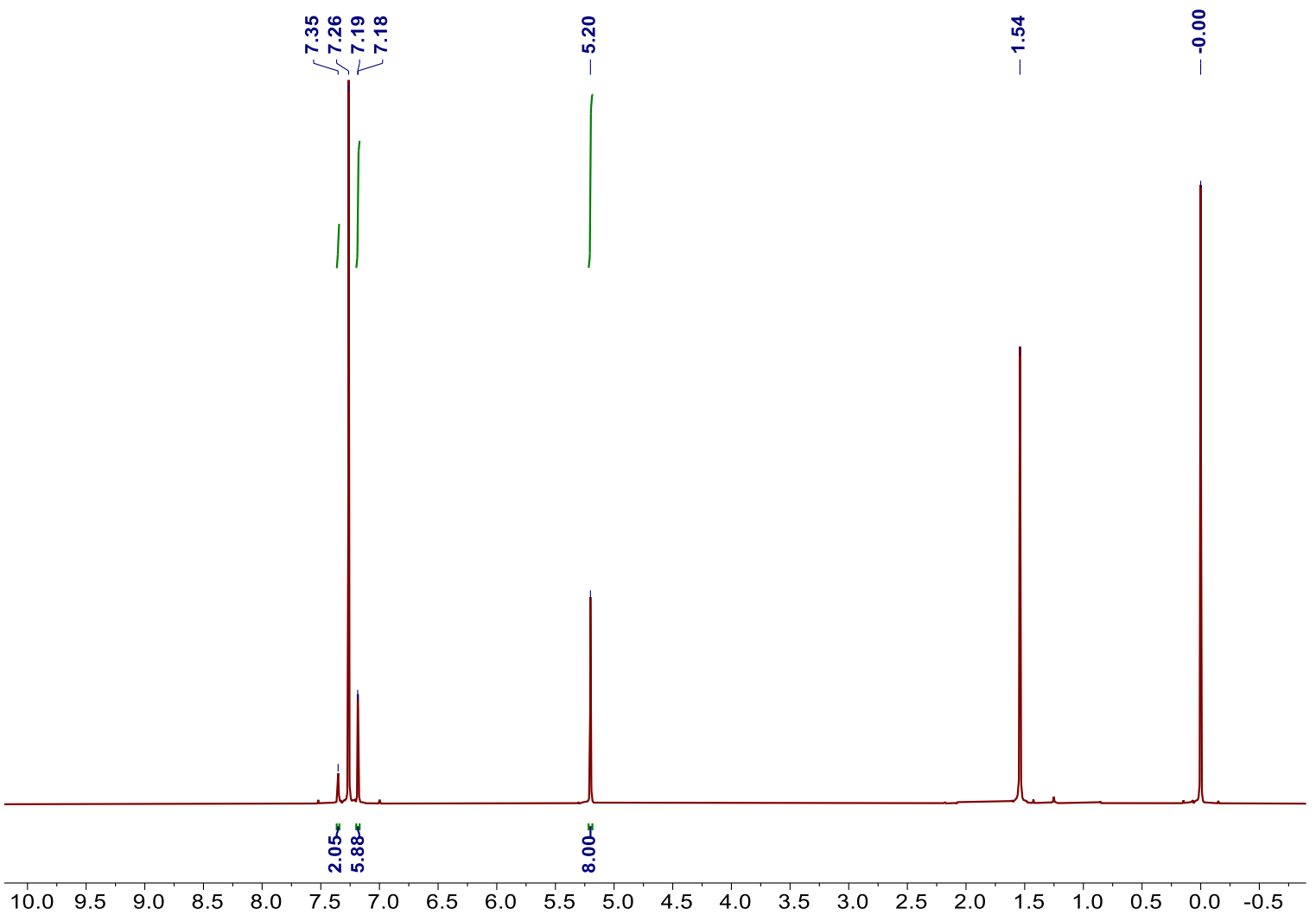
$CDCl_3$

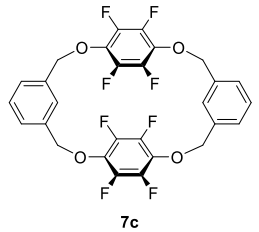


7b

^{19}F NMR

$CDCl_3$

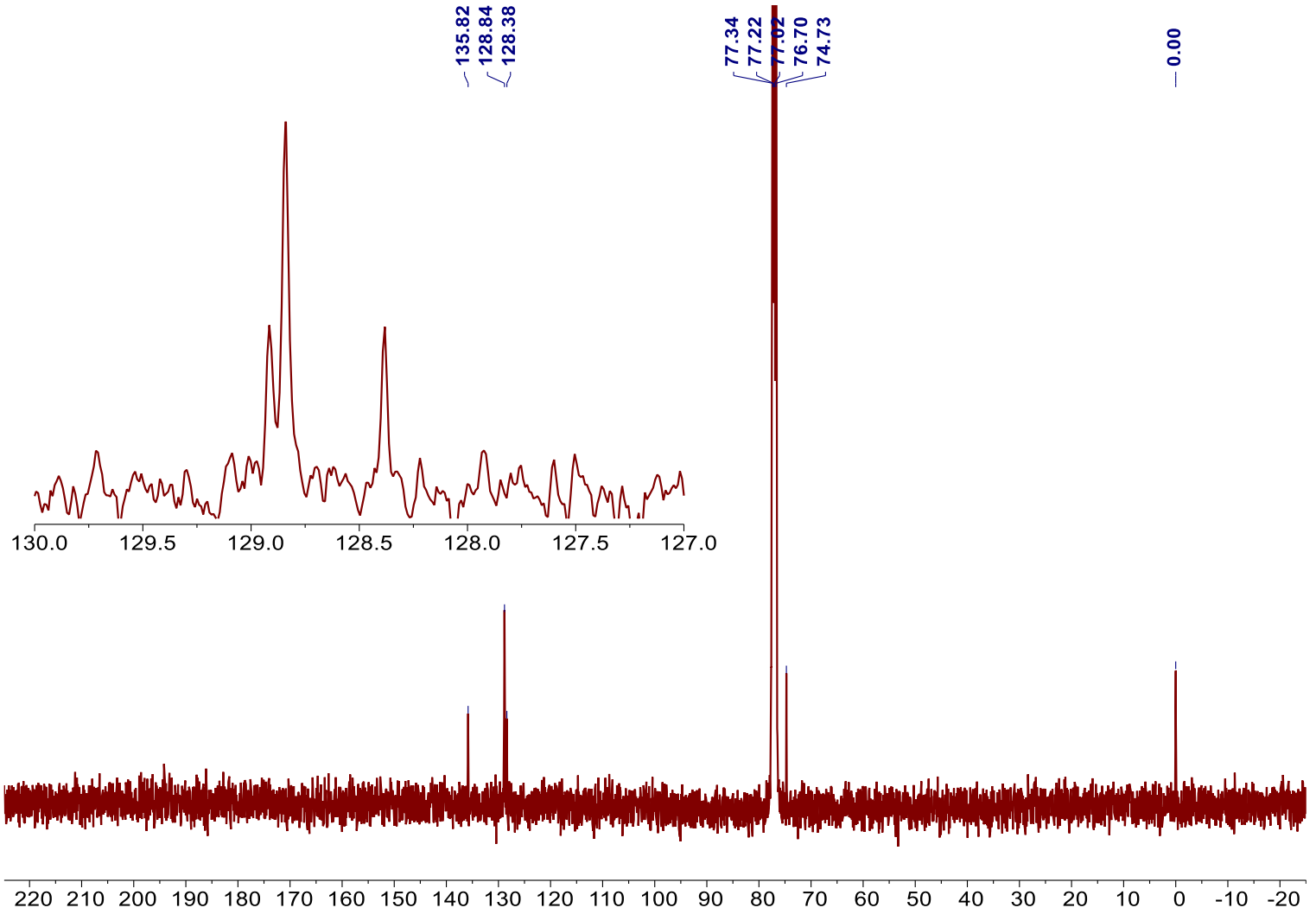


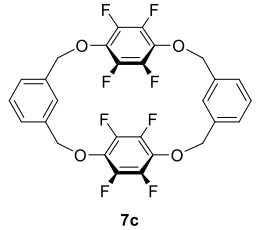


7c

^{1}H NMR

$CDCl_3$





7c

^{13}C NMR

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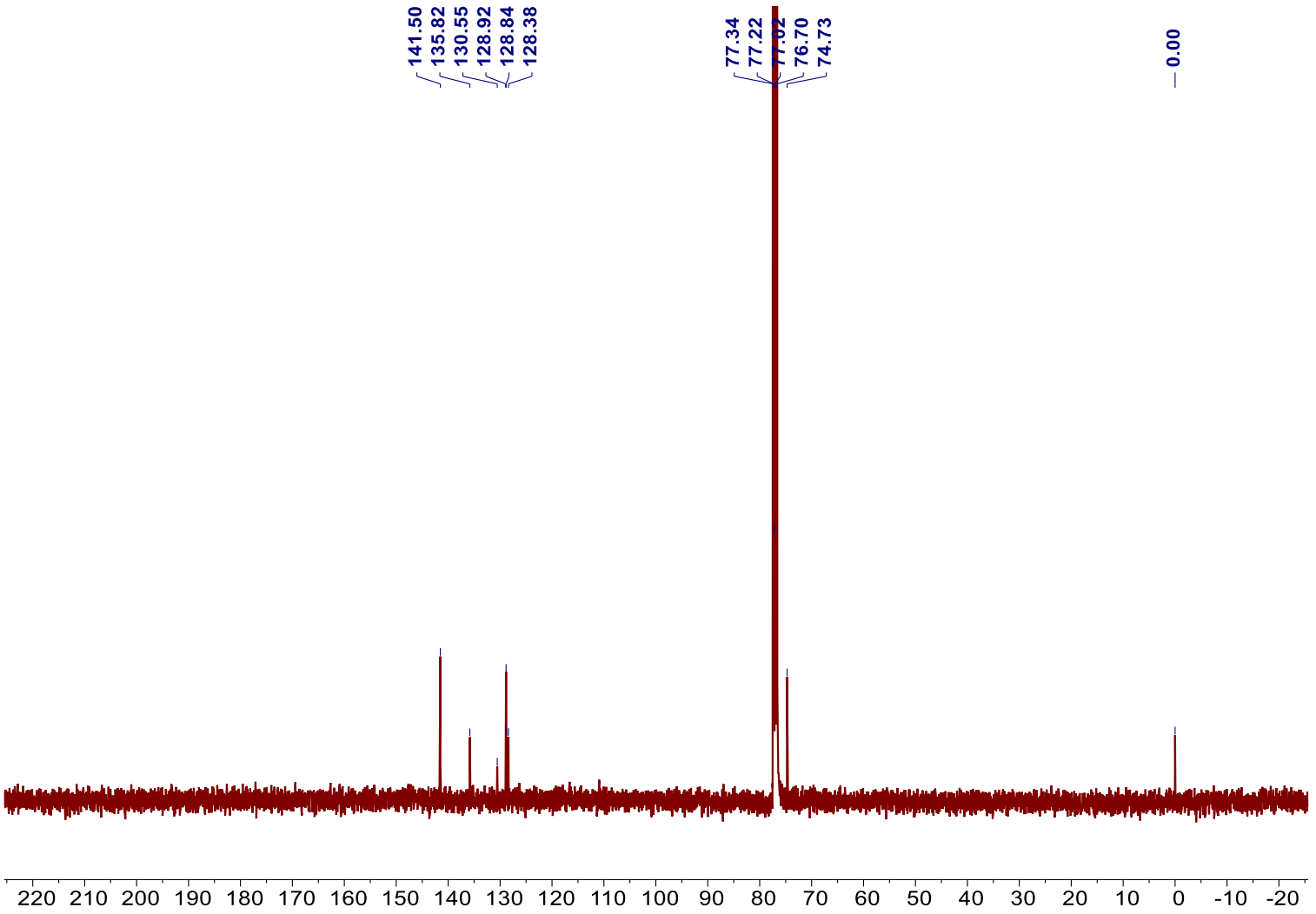
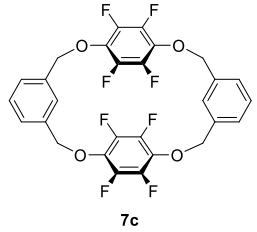


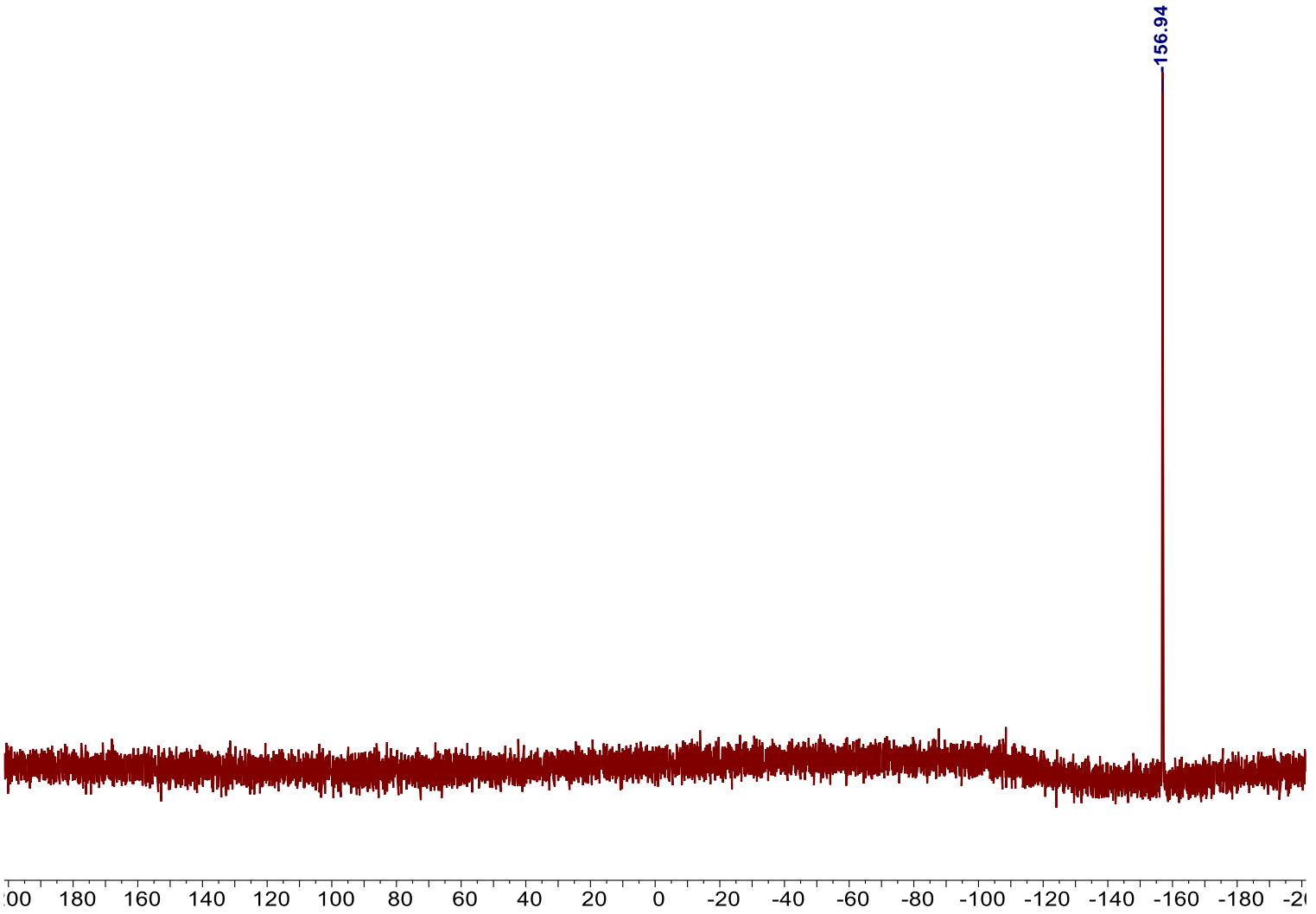


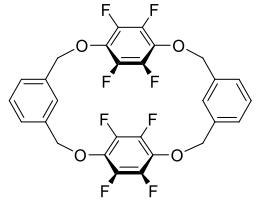
7c

^{13}C-^{19}F decoupled

NMR

$CDCl_3$

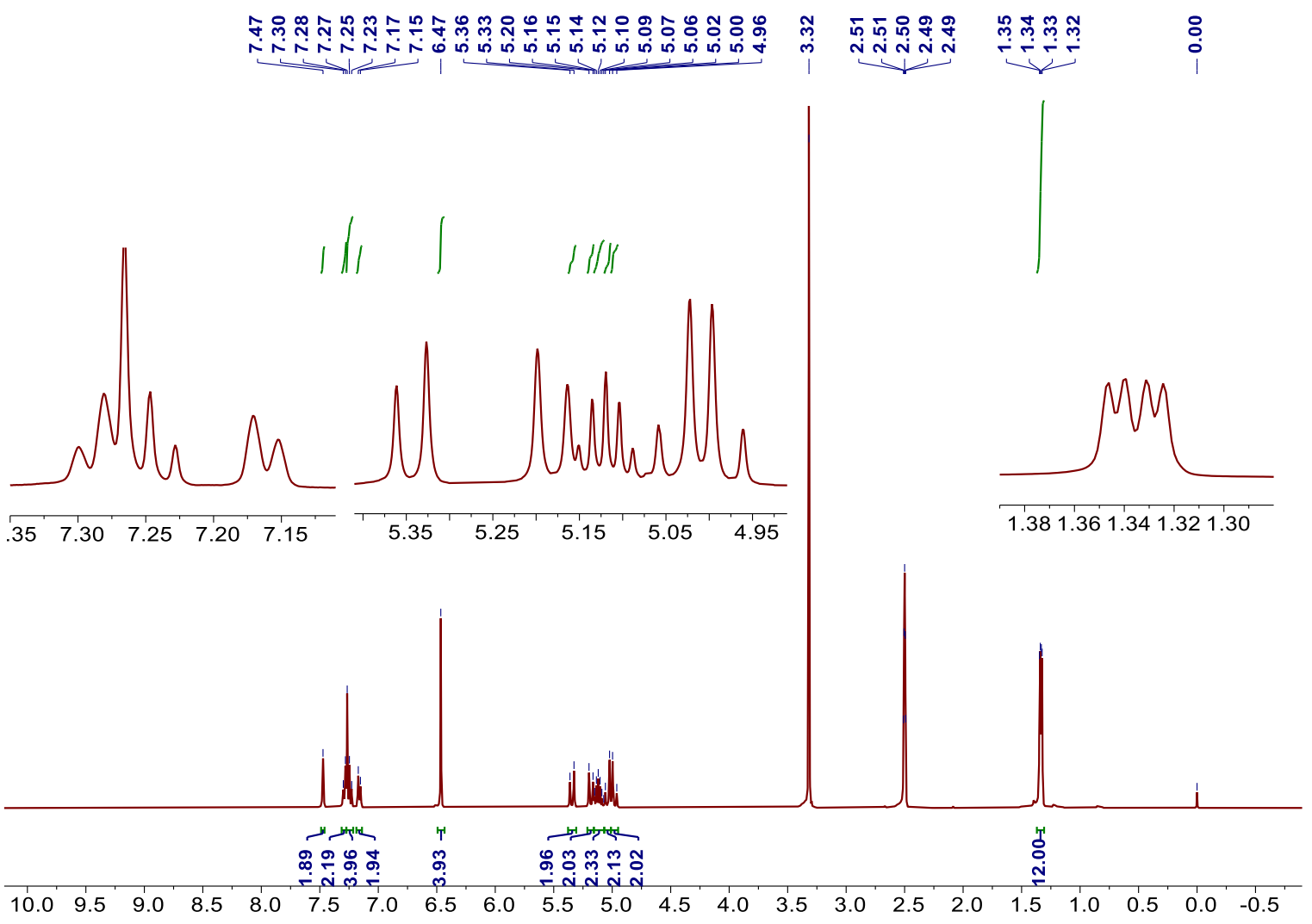


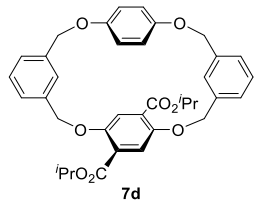


7c

^{19}F NMR

$CDCl_3$

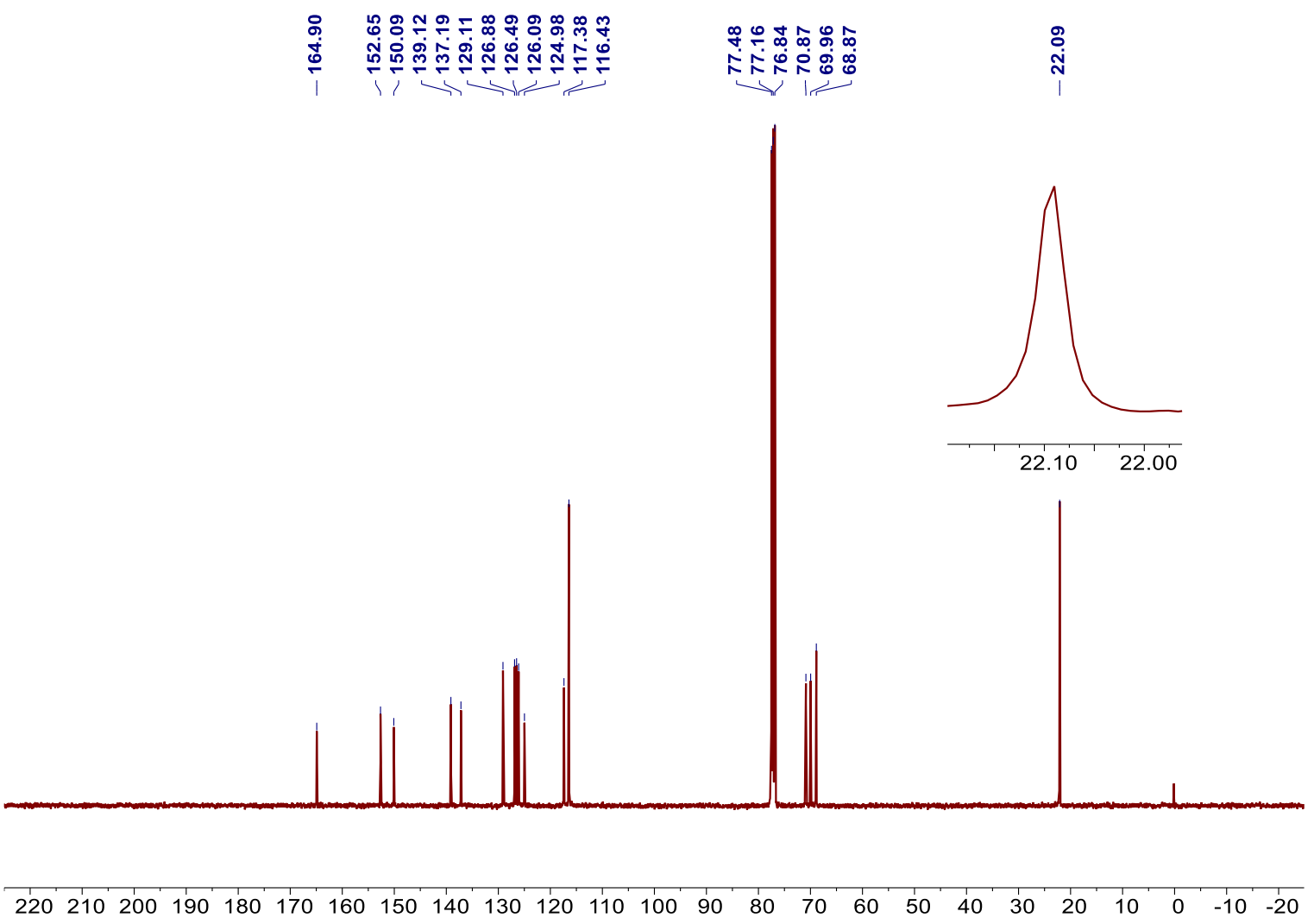


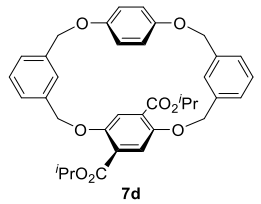


7d

1H NMR

DMSO-d_6

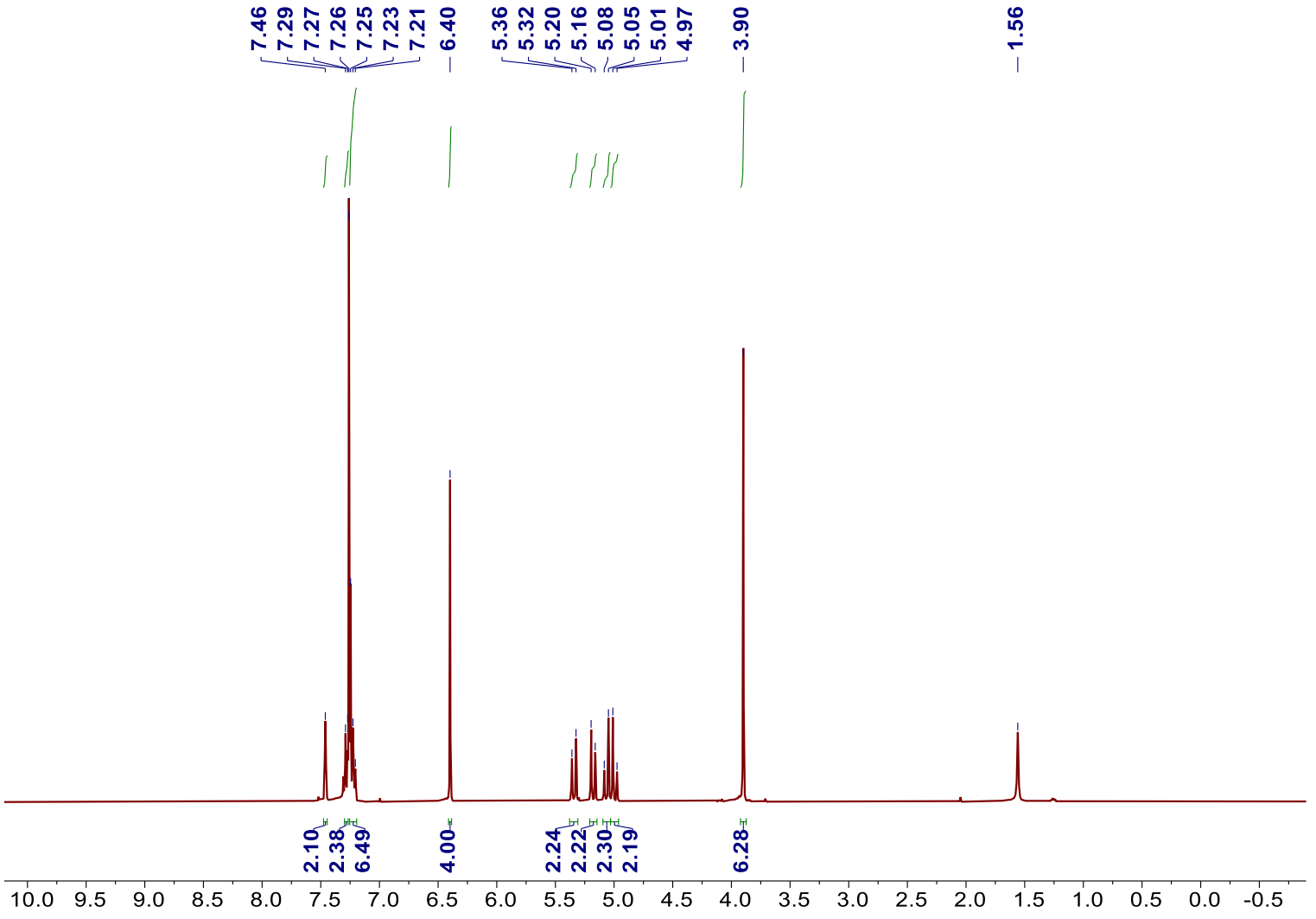


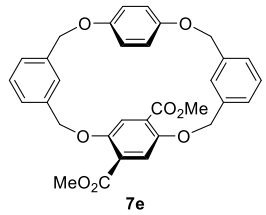


7d

^{13}C NMR

$CDCl_3$

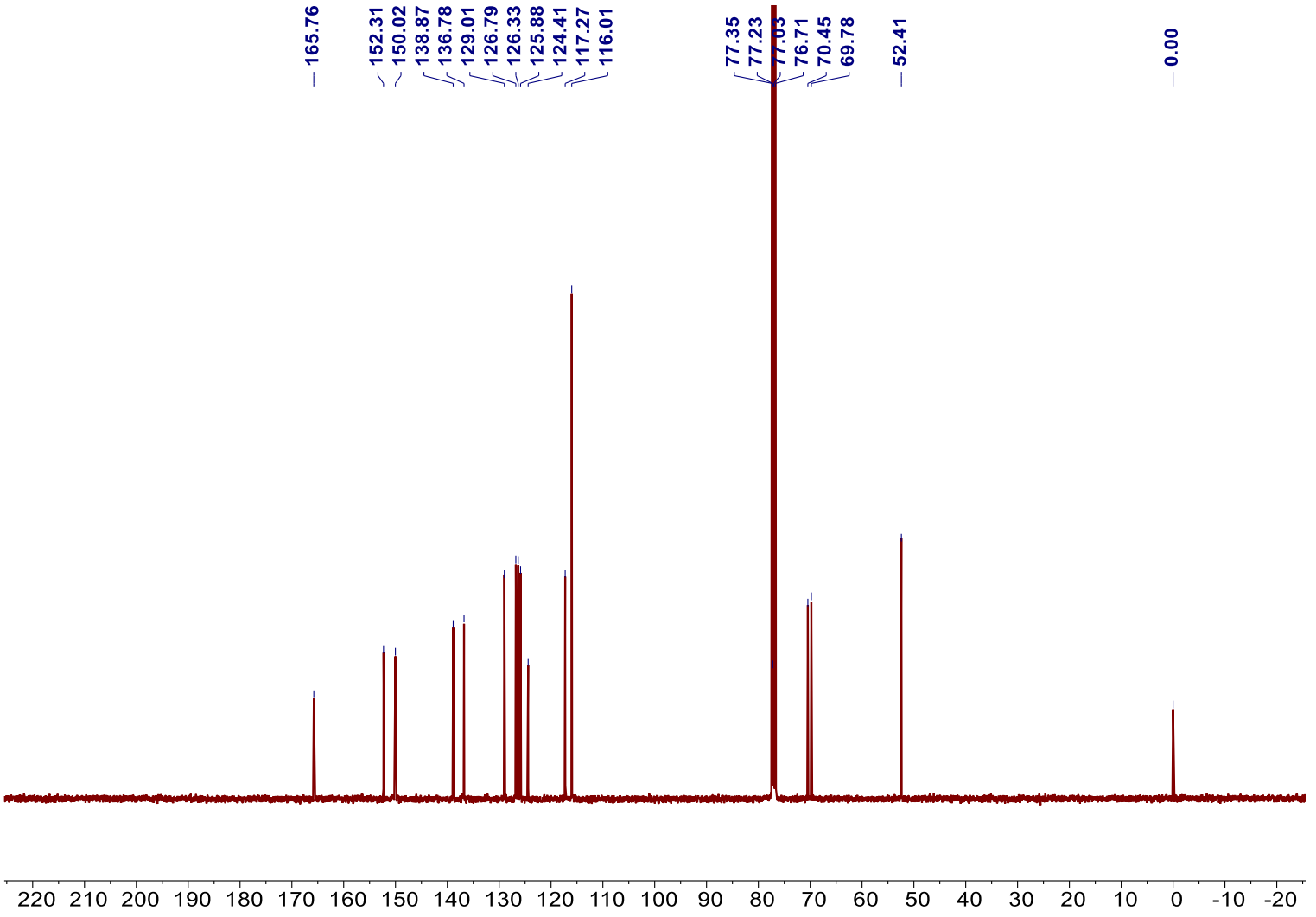


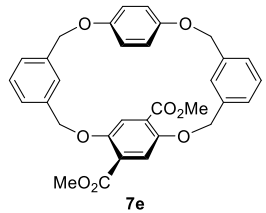


7e

^{1}H NMR

$CDCl_3$

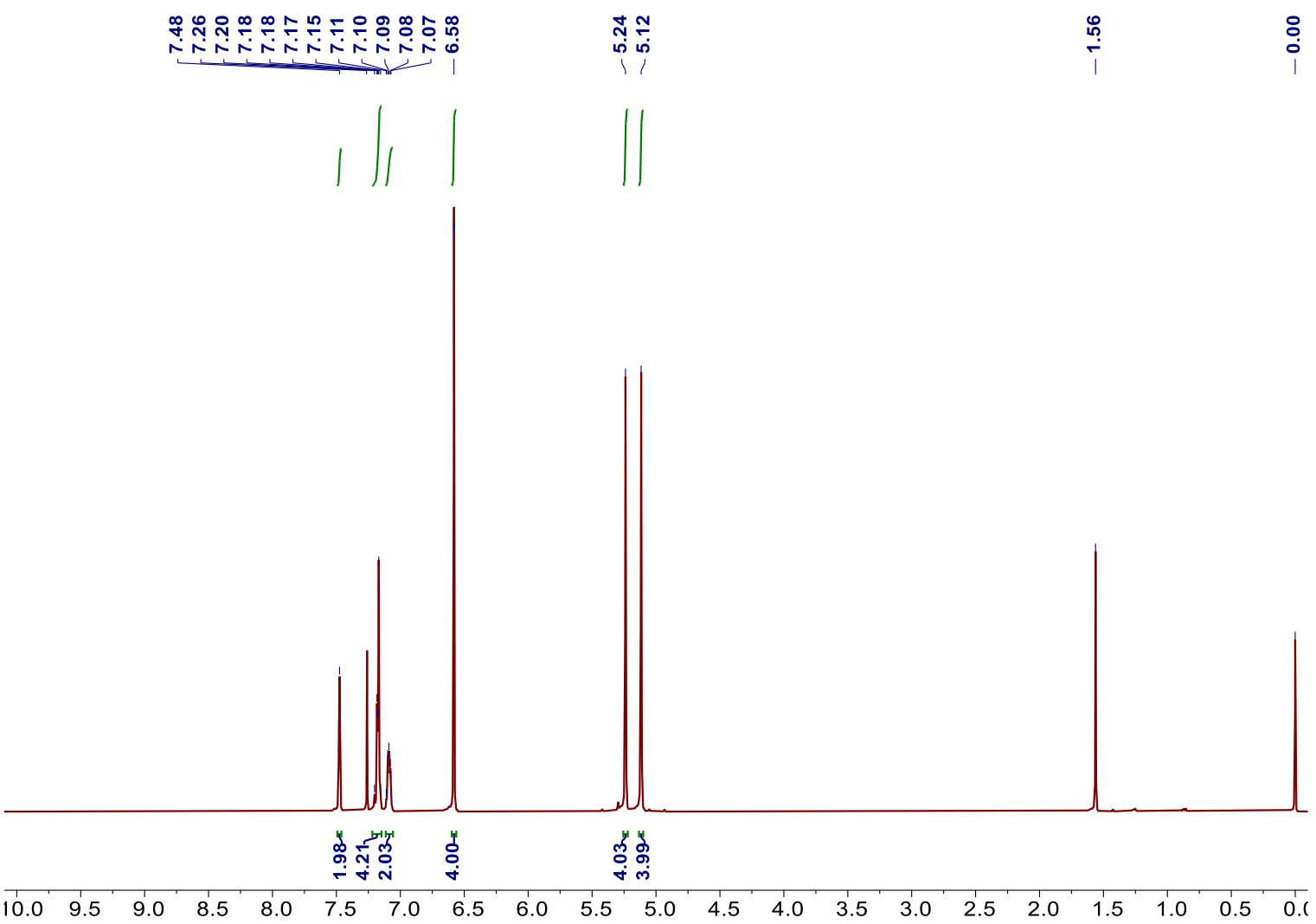


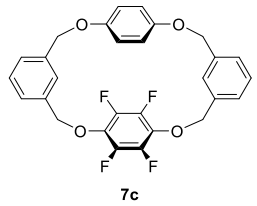


7e

^{13}C NMR

$CDCl_3$

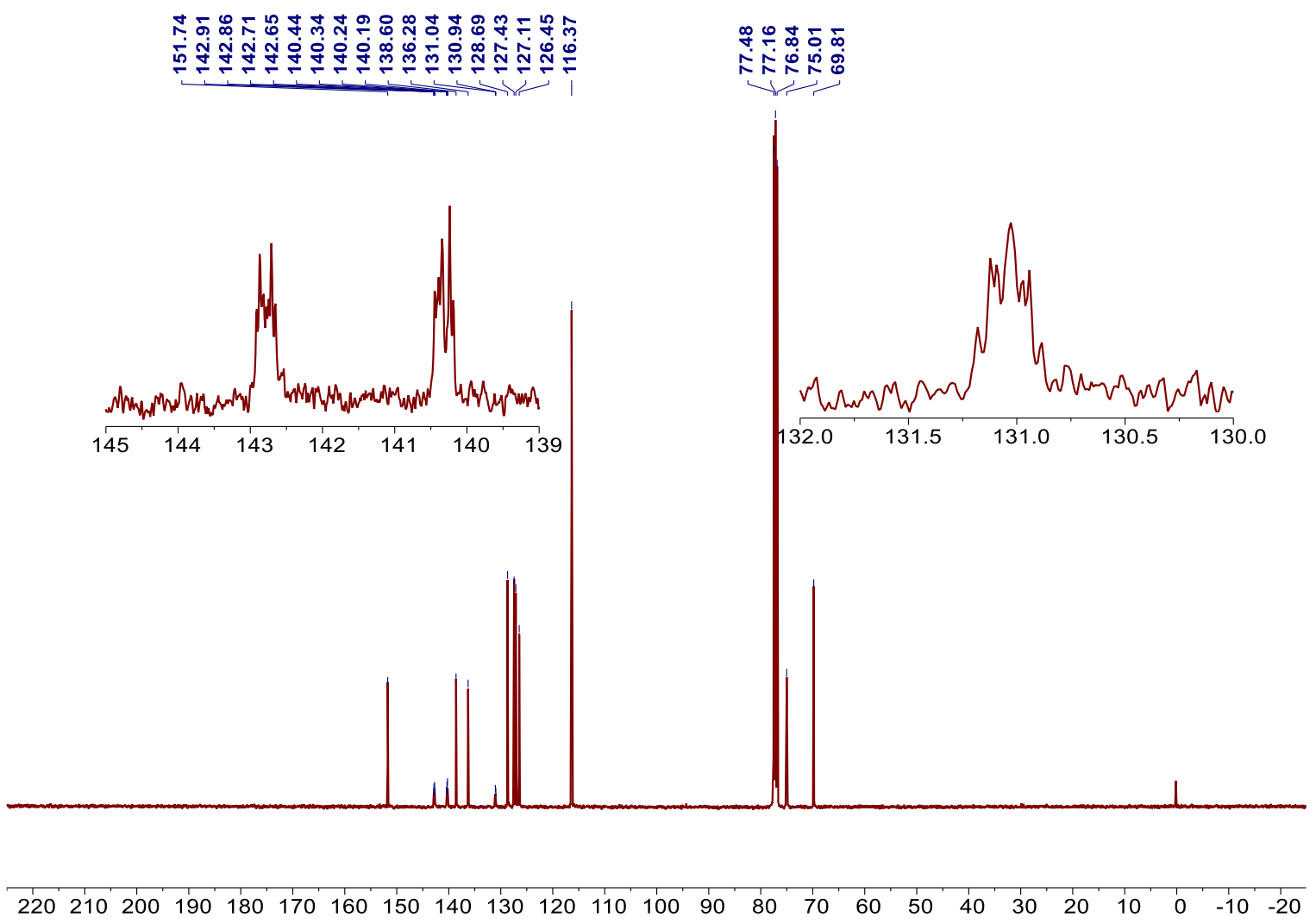


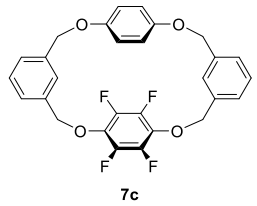


7c

^{1}H NMR

$CDCl_3$

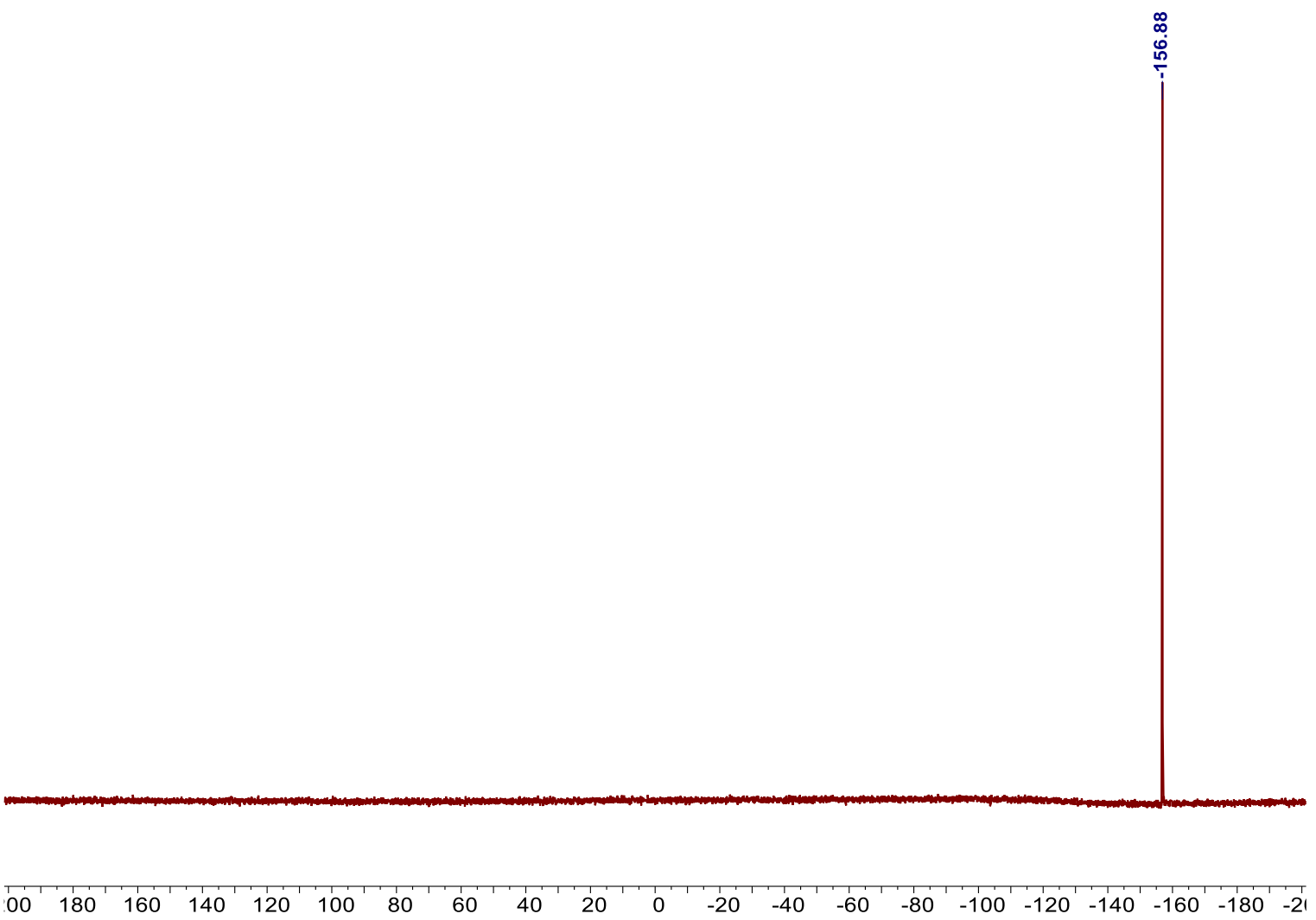


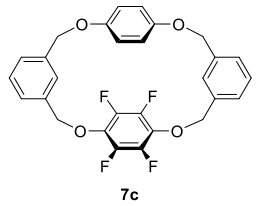


7c

^{13}C NMR

$CDCl_3$

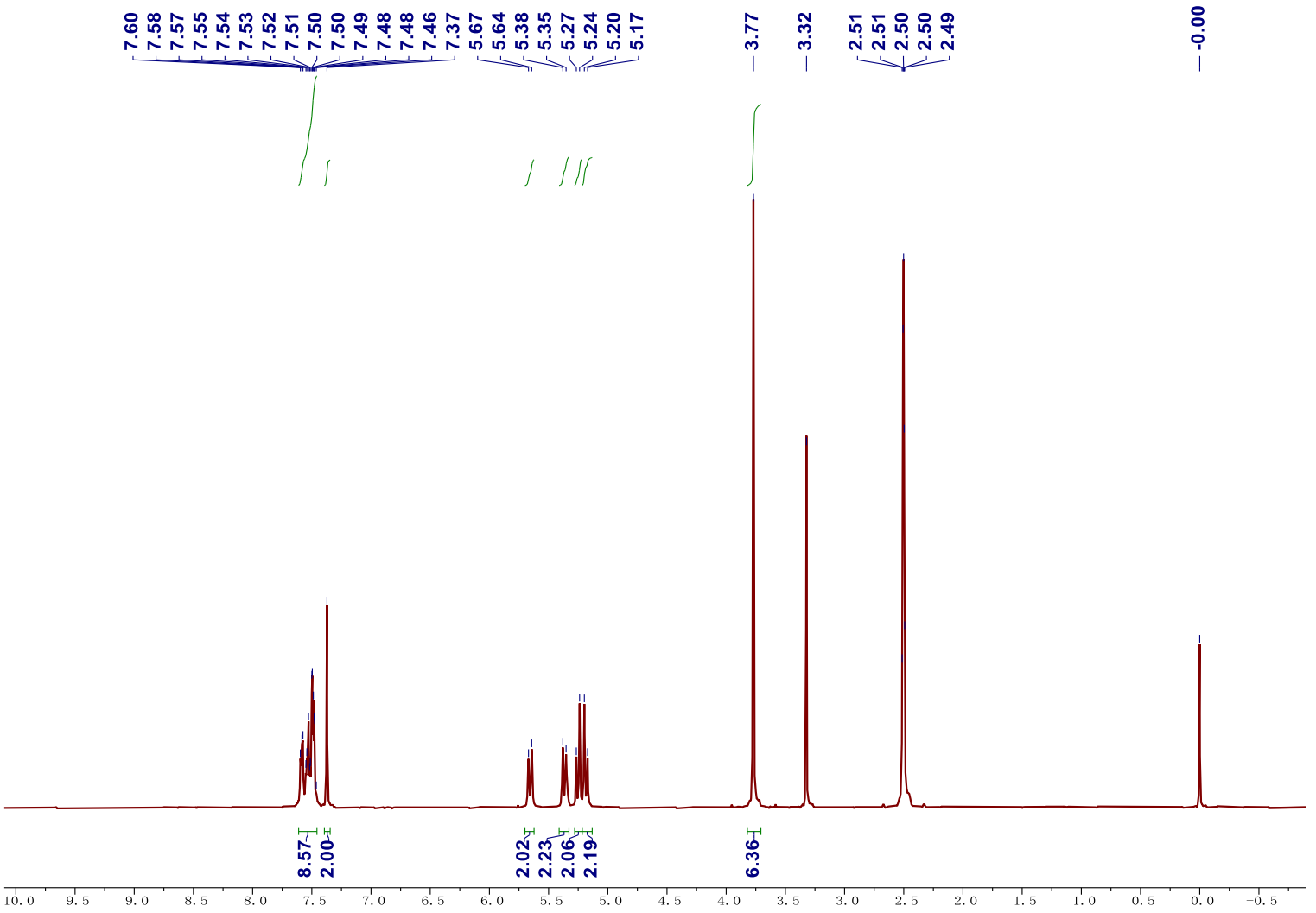


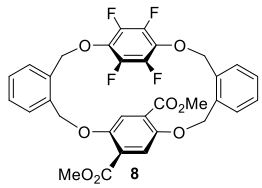


7c

^{19}F NMR

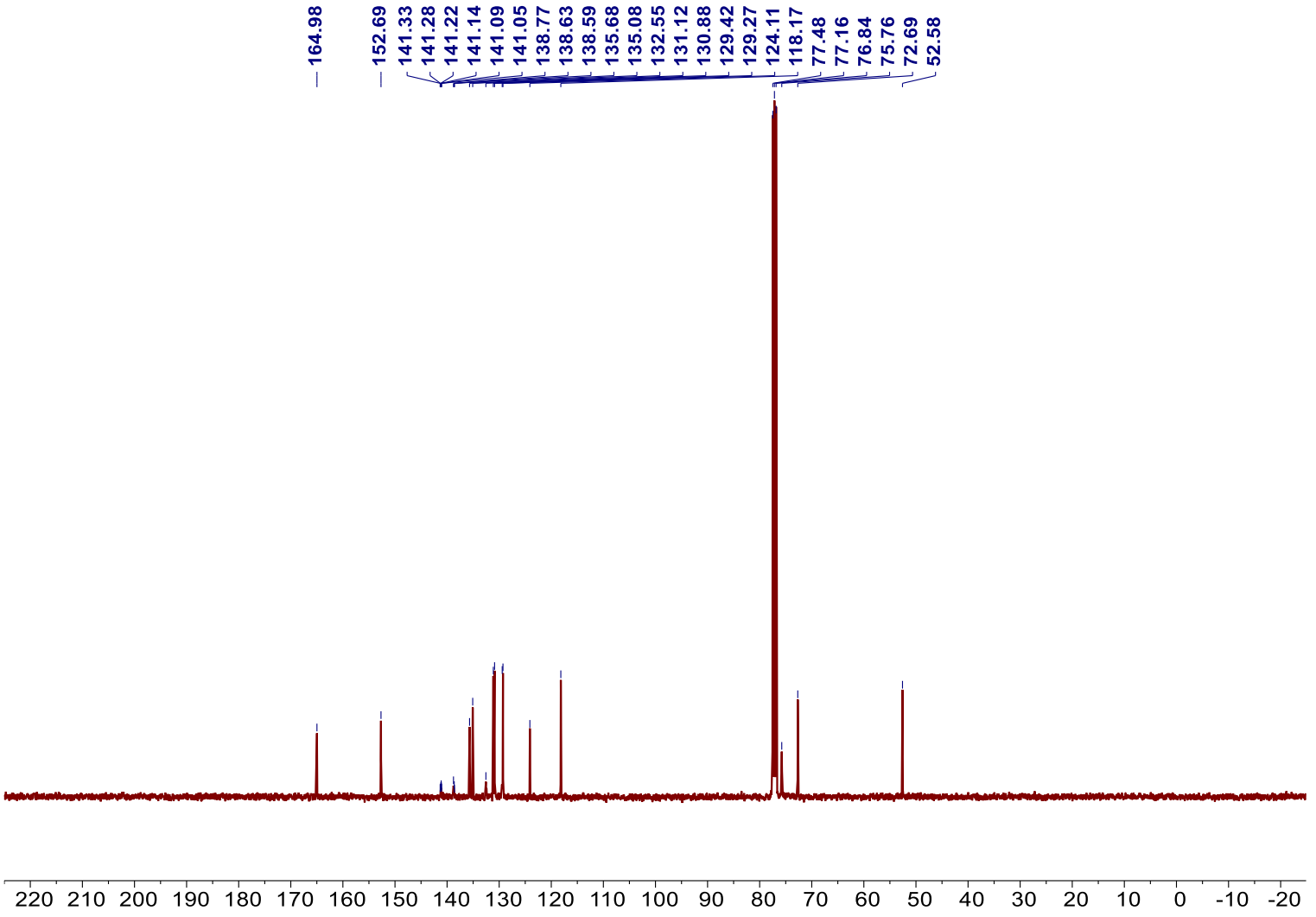
$CDCl_3$

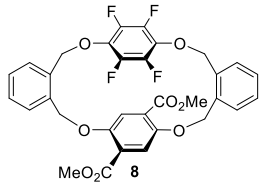




^{1}H NMR

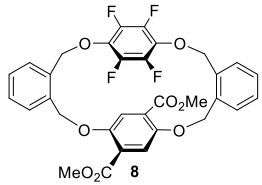
DMSO-d_6





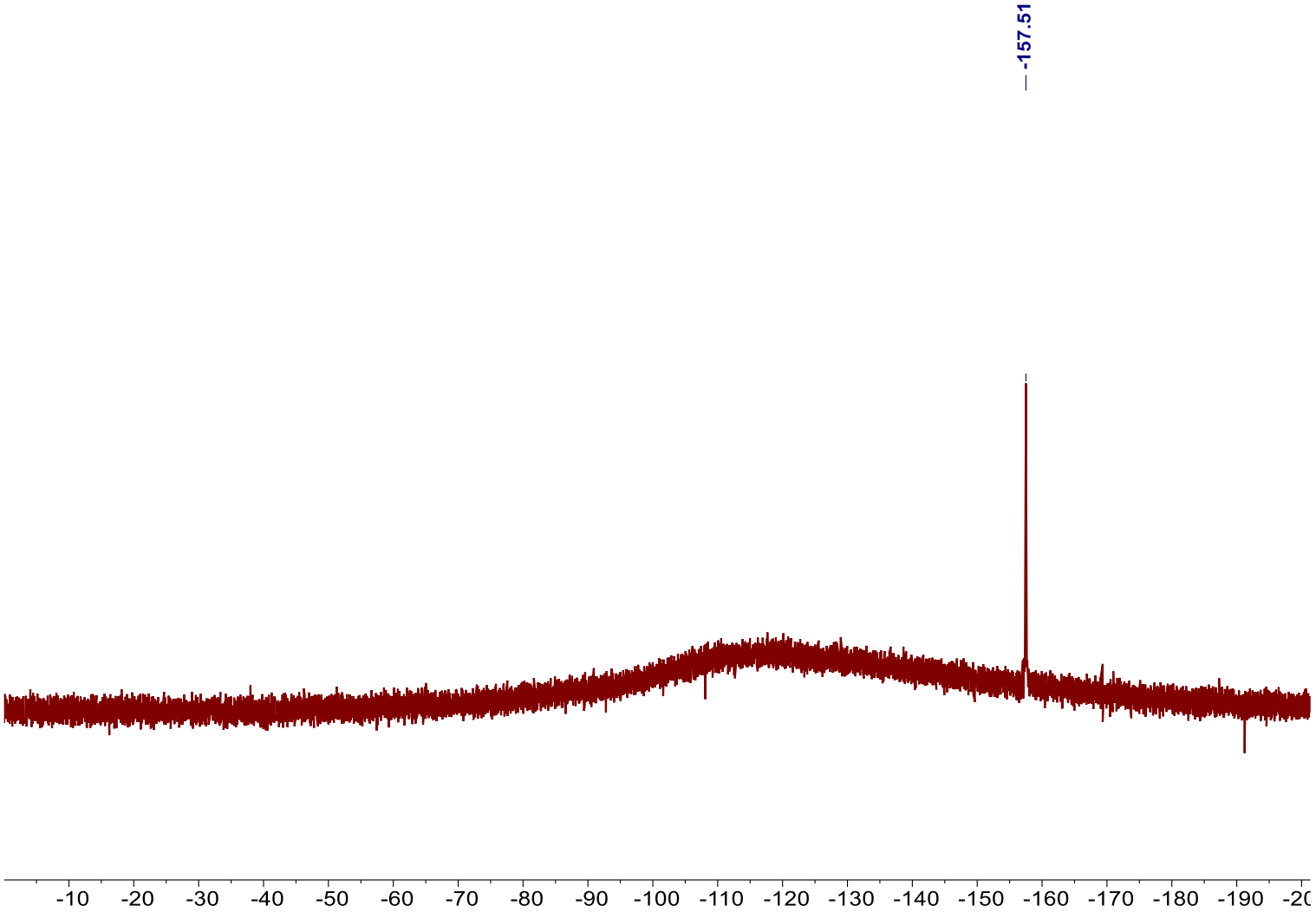
^{13}C NMR

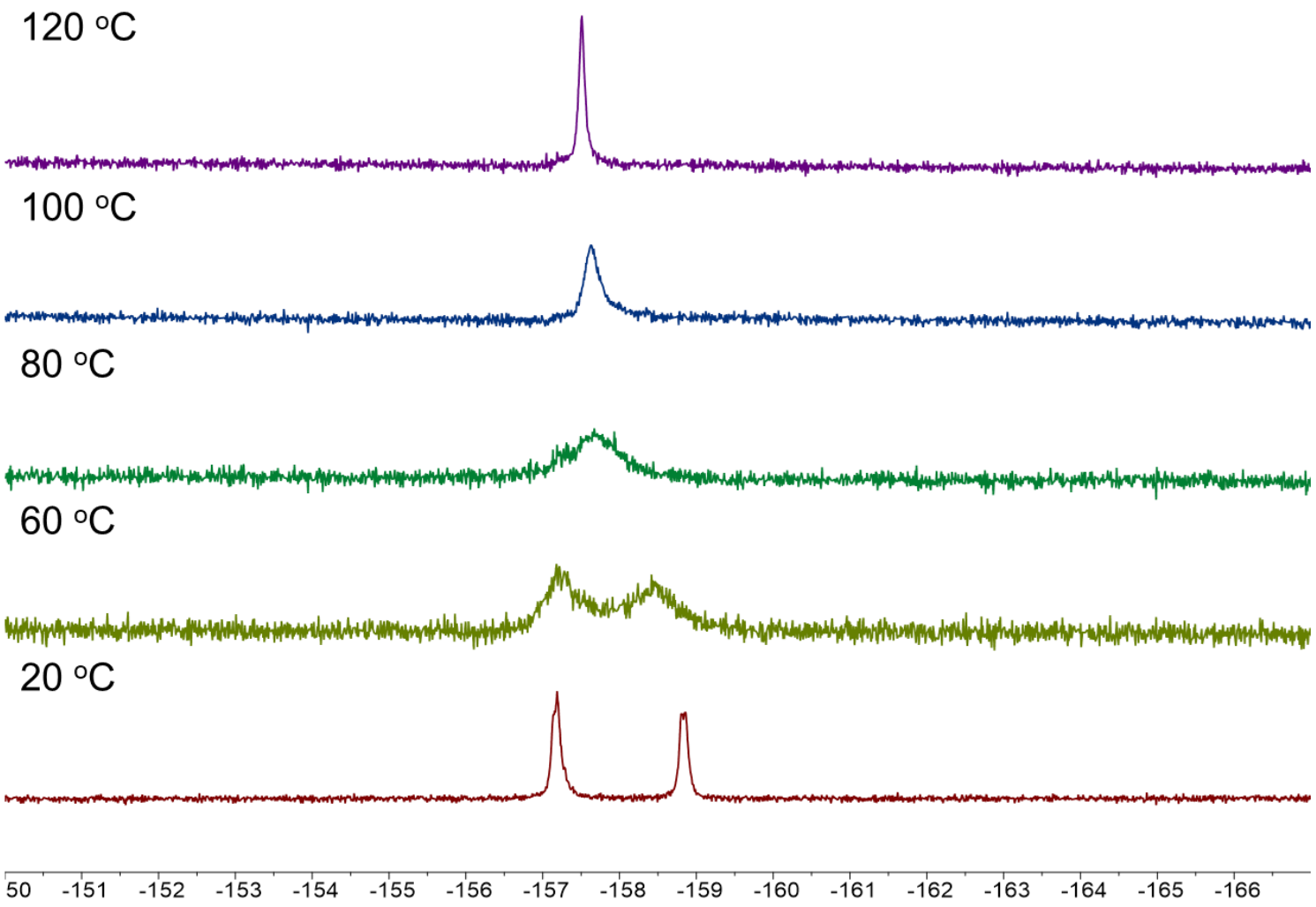
$CDCl_3$

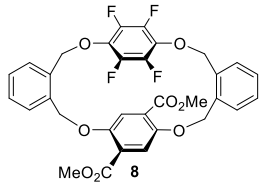


^{19}F NMR

DMSO-d_6 (120 °C)

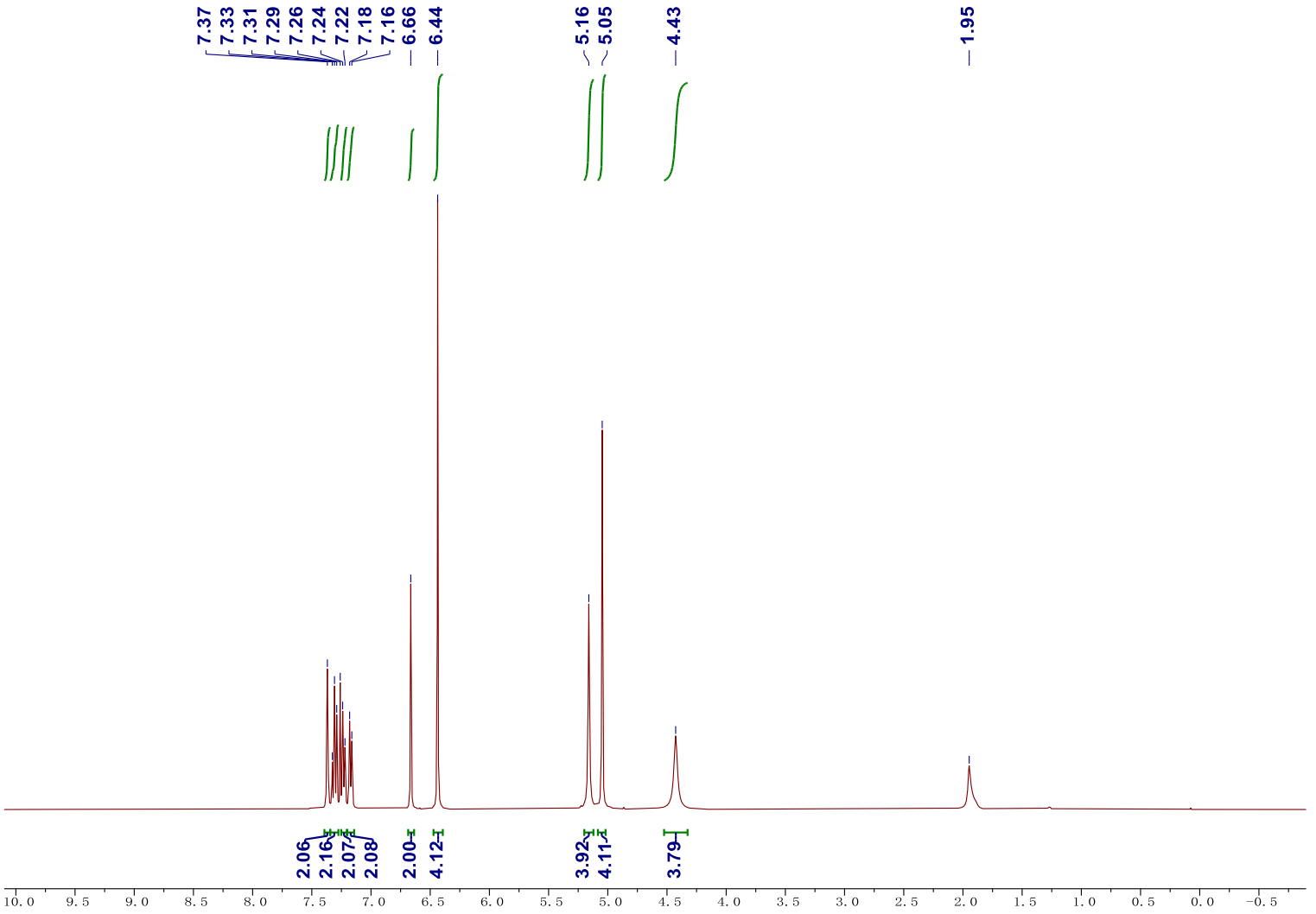


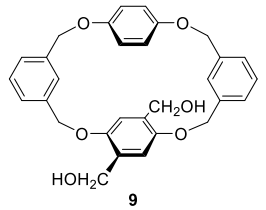




VT ^{19}F NMR

DMSO-d6

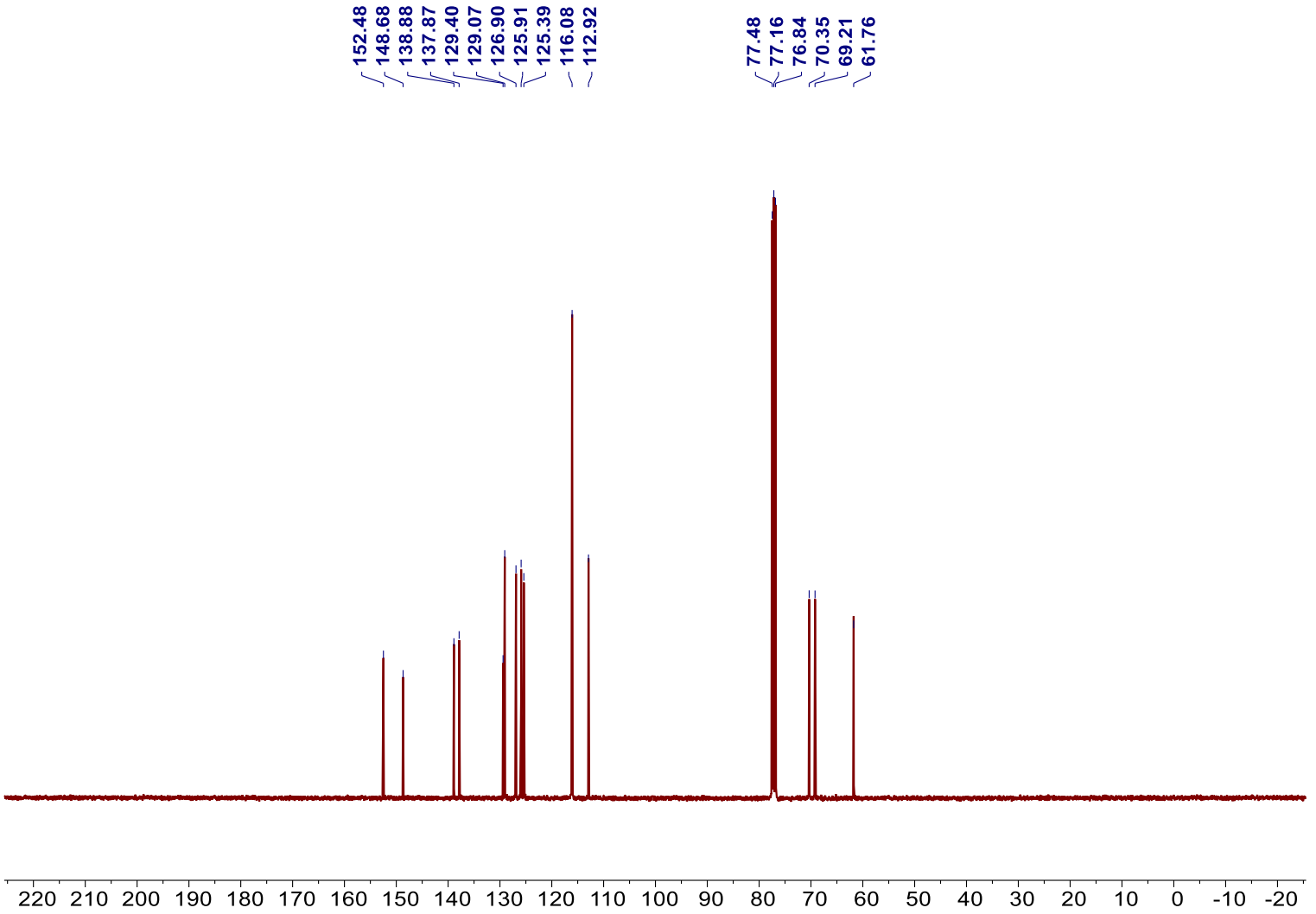


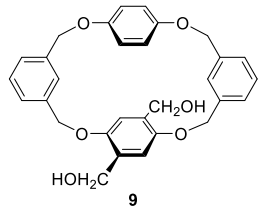


9

^{1}H NMR

$CDCl_3$

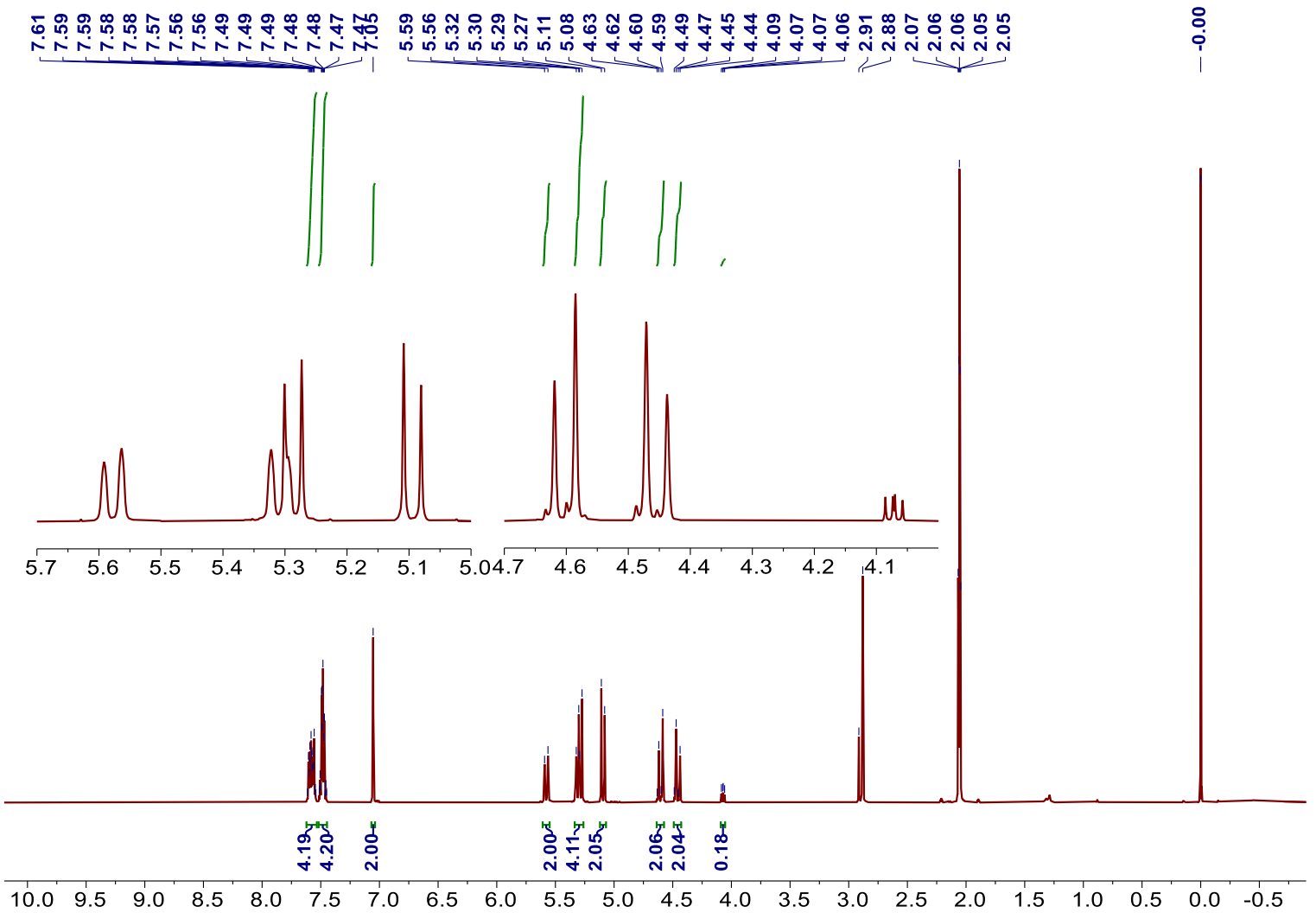


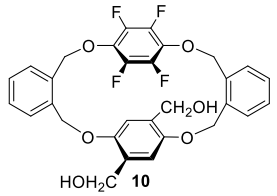


9

^{13}C NMR

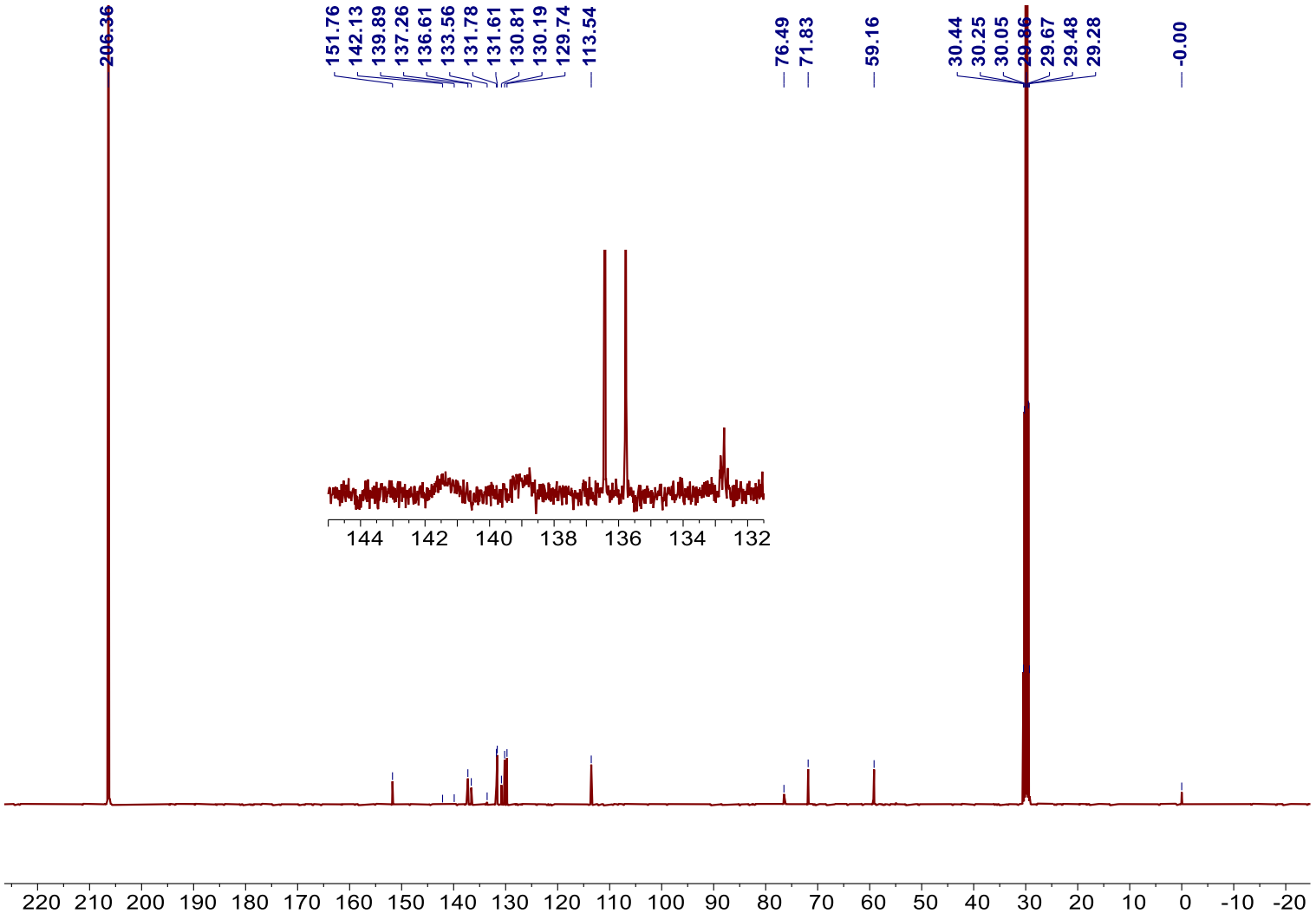
$CDCl_3$

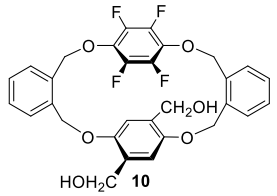




^{1}H NMR

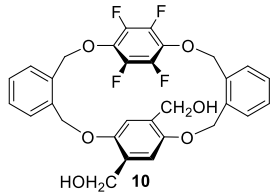
acetone-d_6





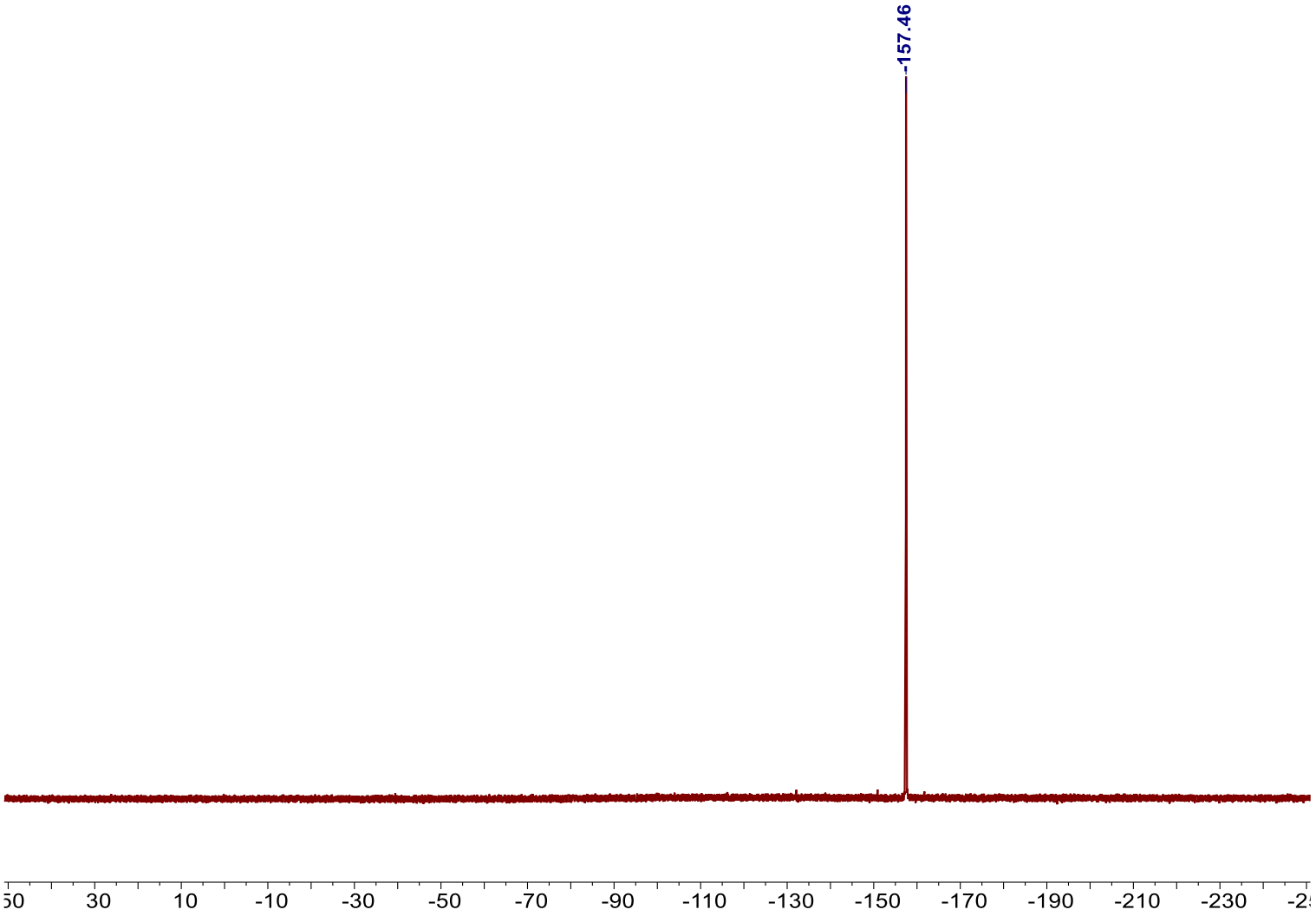
^{13}C NMR

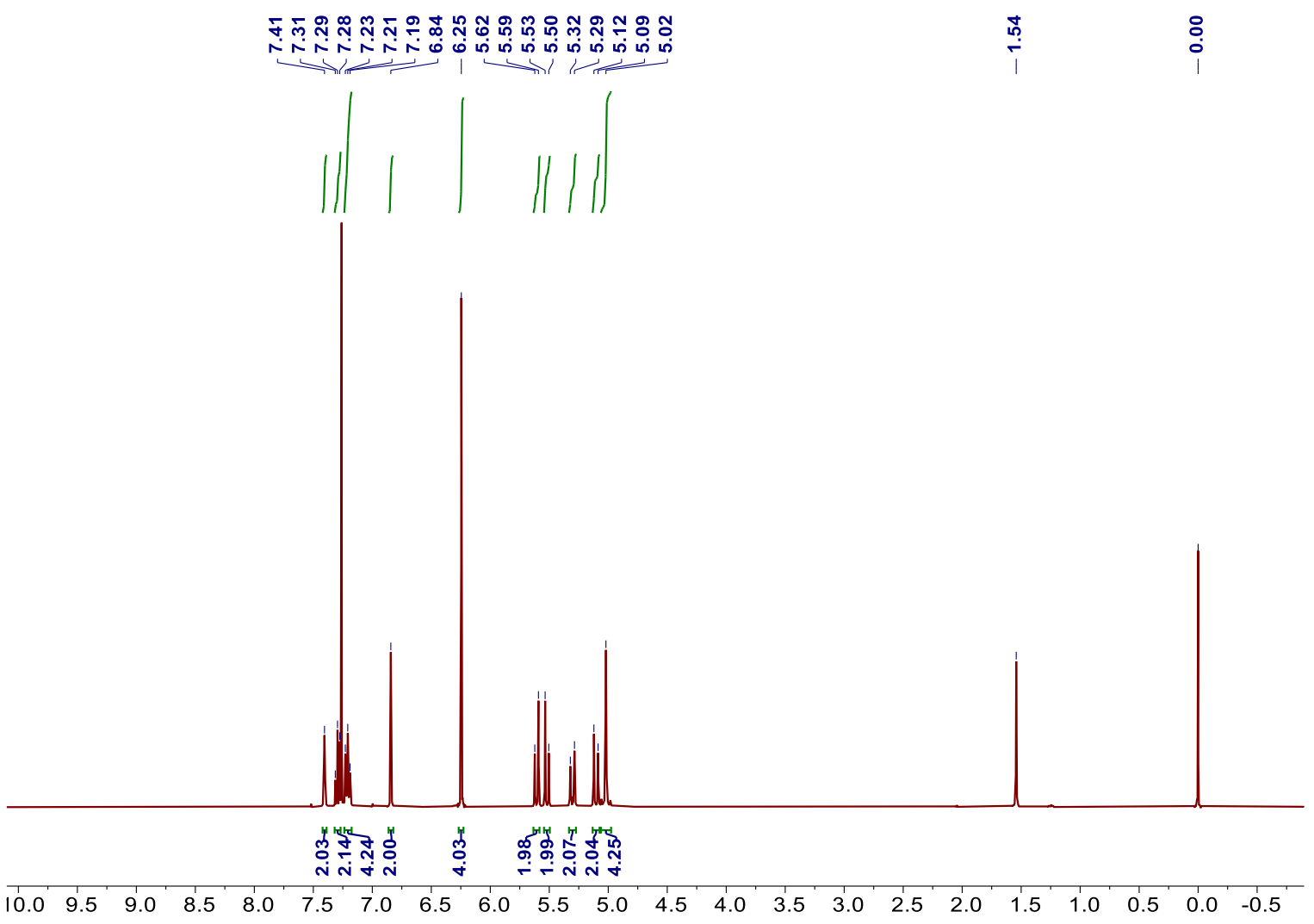
acetone-d_6



^{19}F NMR

DMSO-d_6 (120 oC)

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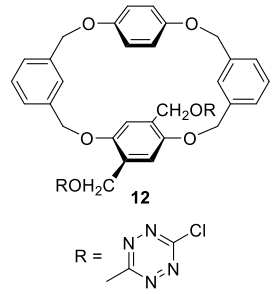
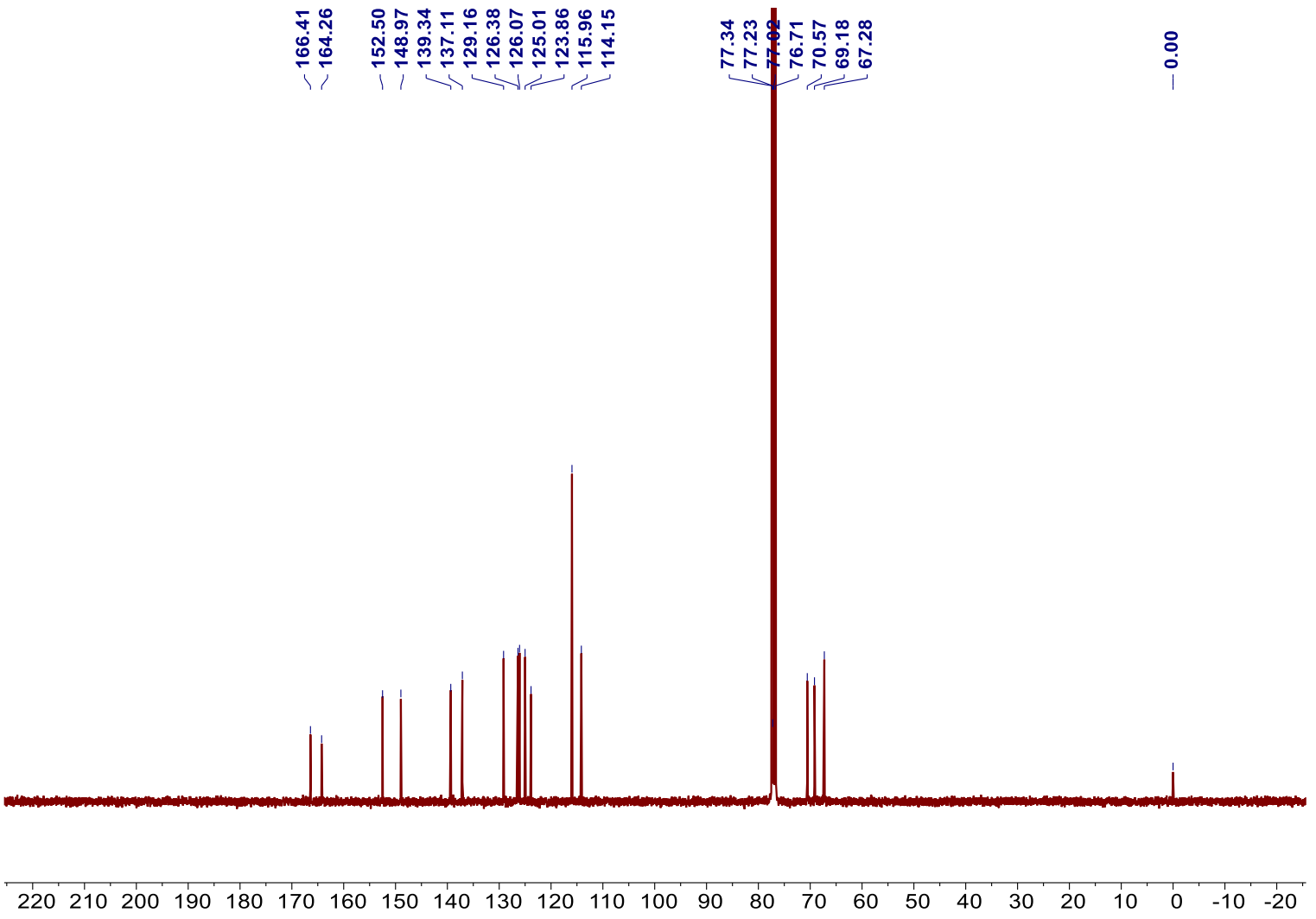
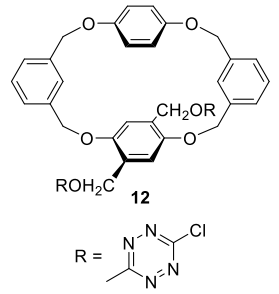
7.21
7.19
6.84
6.25
5.62
5.59
5.53
5.50
5.32
5.29
5.12
5.09
5.02
1.54
0.00
2.03
2.14
4.24
2.00
4.03
1.98
1.99
2.07
2.04
4.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


O
O
O
O
CH2OR
ROH2C
12
R =
N
N
N
N
Cl

^{1}H NMR

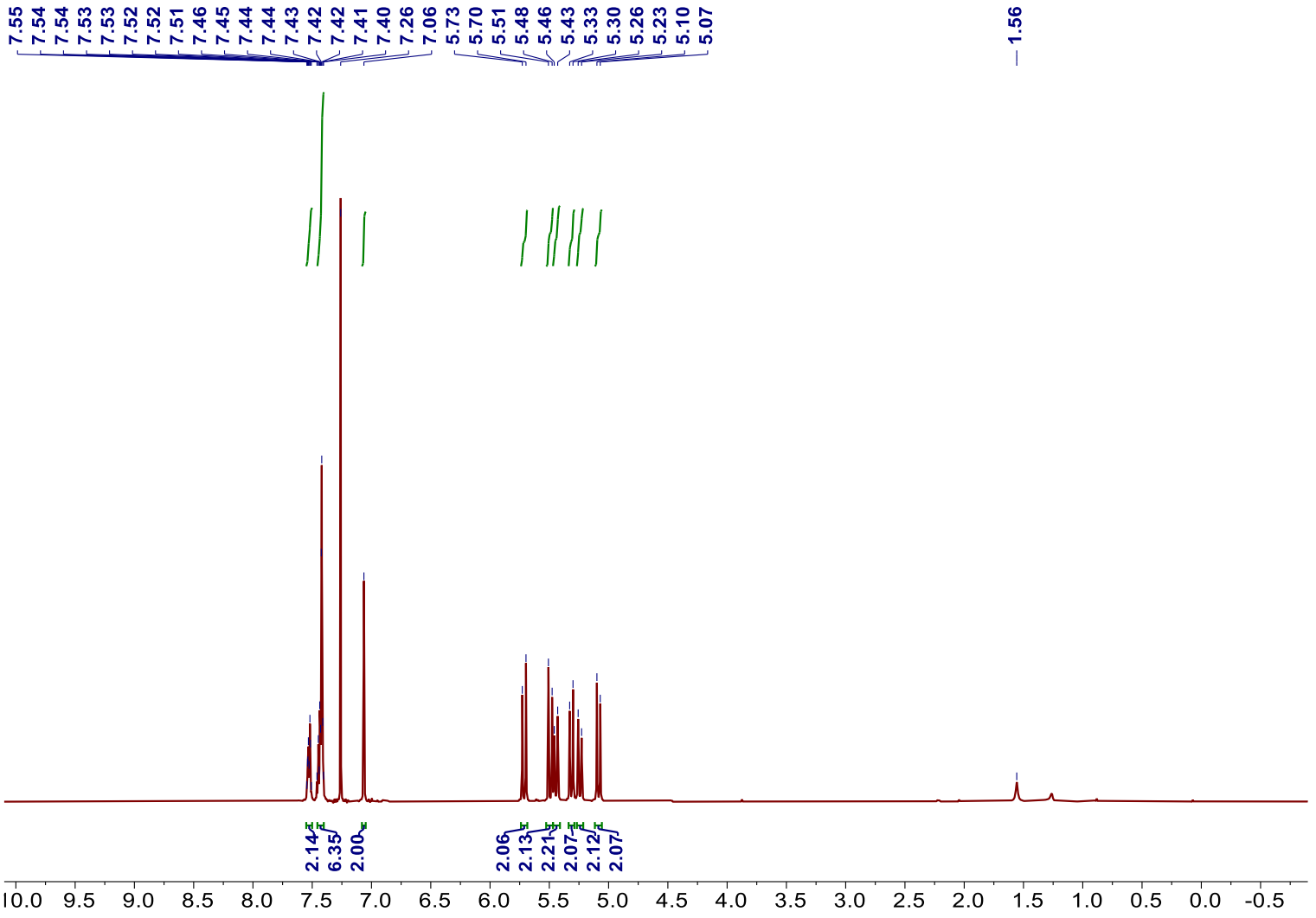
$CDCl_3$





^{13}C NMR

$CDCl_3$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7.44
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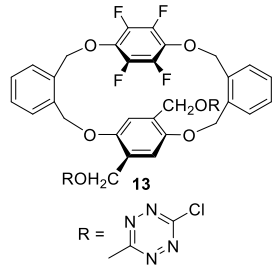
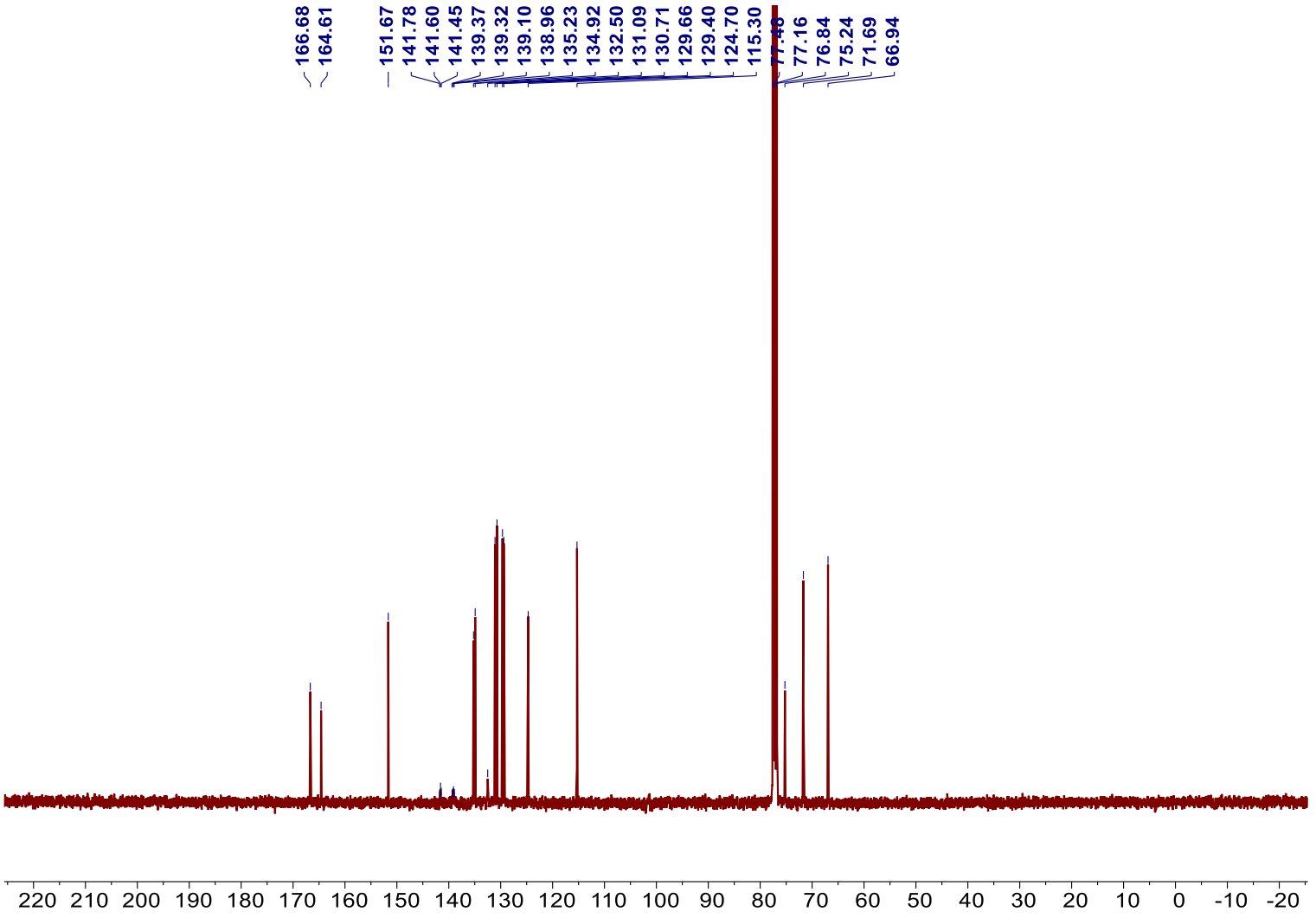
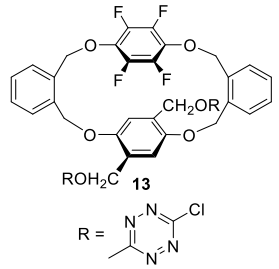
7.42
7.41
7.40
7.26
7.06
5.73
5.70
5.51
5.48
5.46
5.43
5.33
5.30
5.26
5.23
5.10
5.07
1.56
2.14
6.35
2.00
2.06
2.13
2.21
2.07
2.12
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


F
F
O
O
F
F
CH2OR
O
O
ROH2C
13
R =
N
N
Cl
N
N

^{1}H NMR

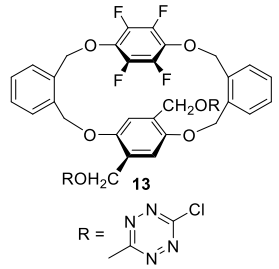
$CDCl_3$





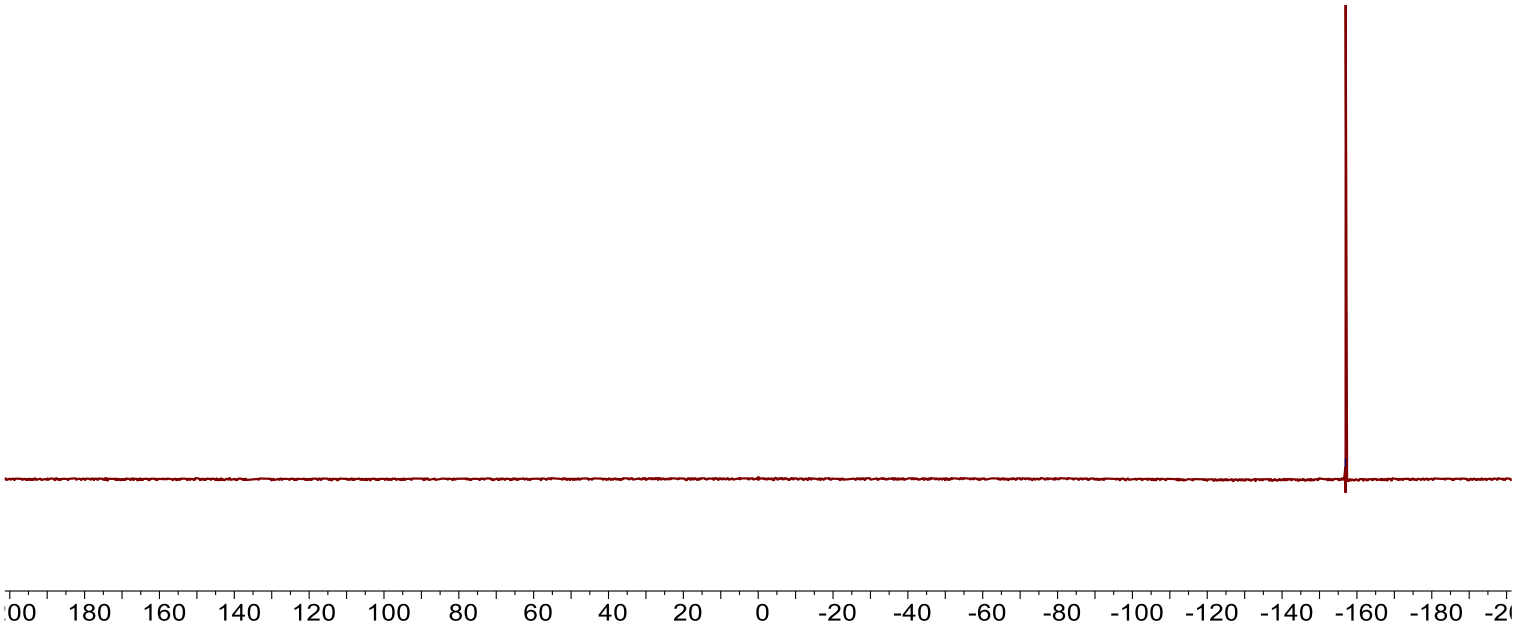
^{13}C NMR

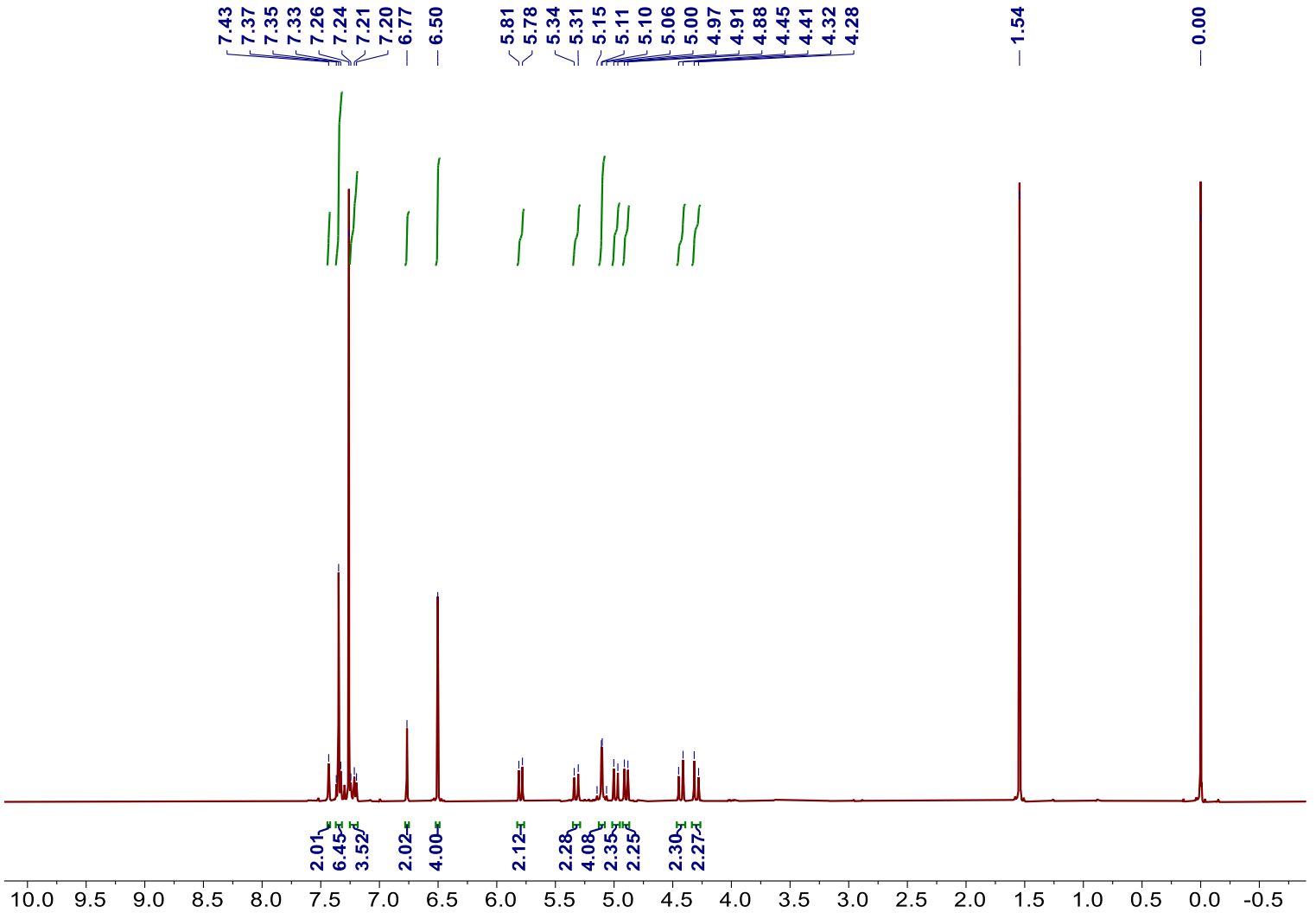
$CDCl_3$

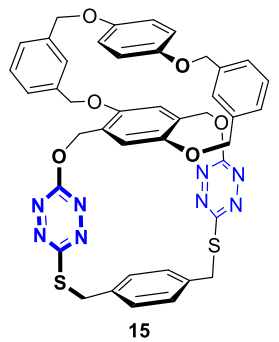


^{19}F NMR

CDCl3



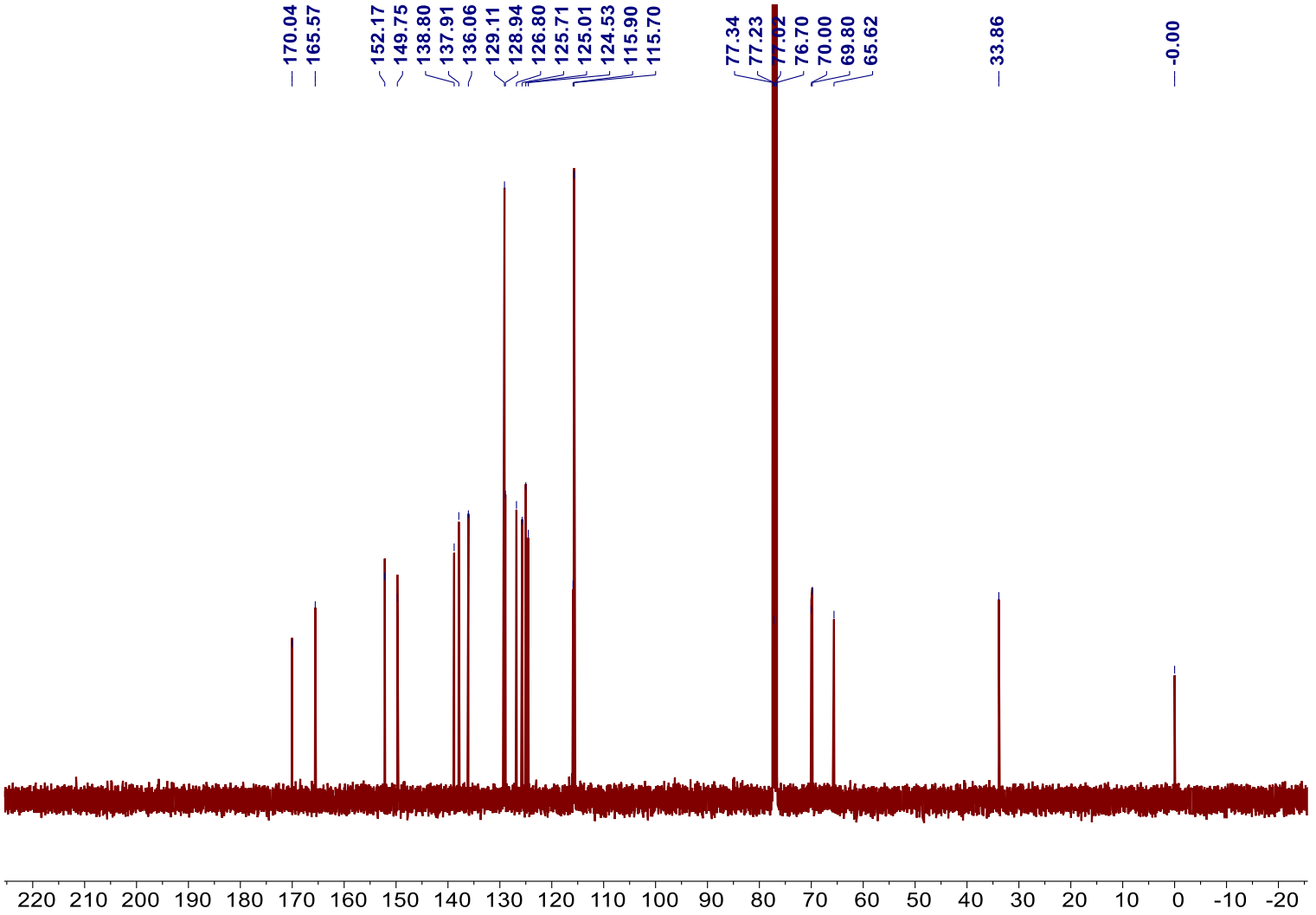


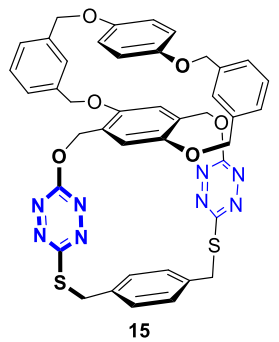


15

^{1}H NMR

$CDCl_3$

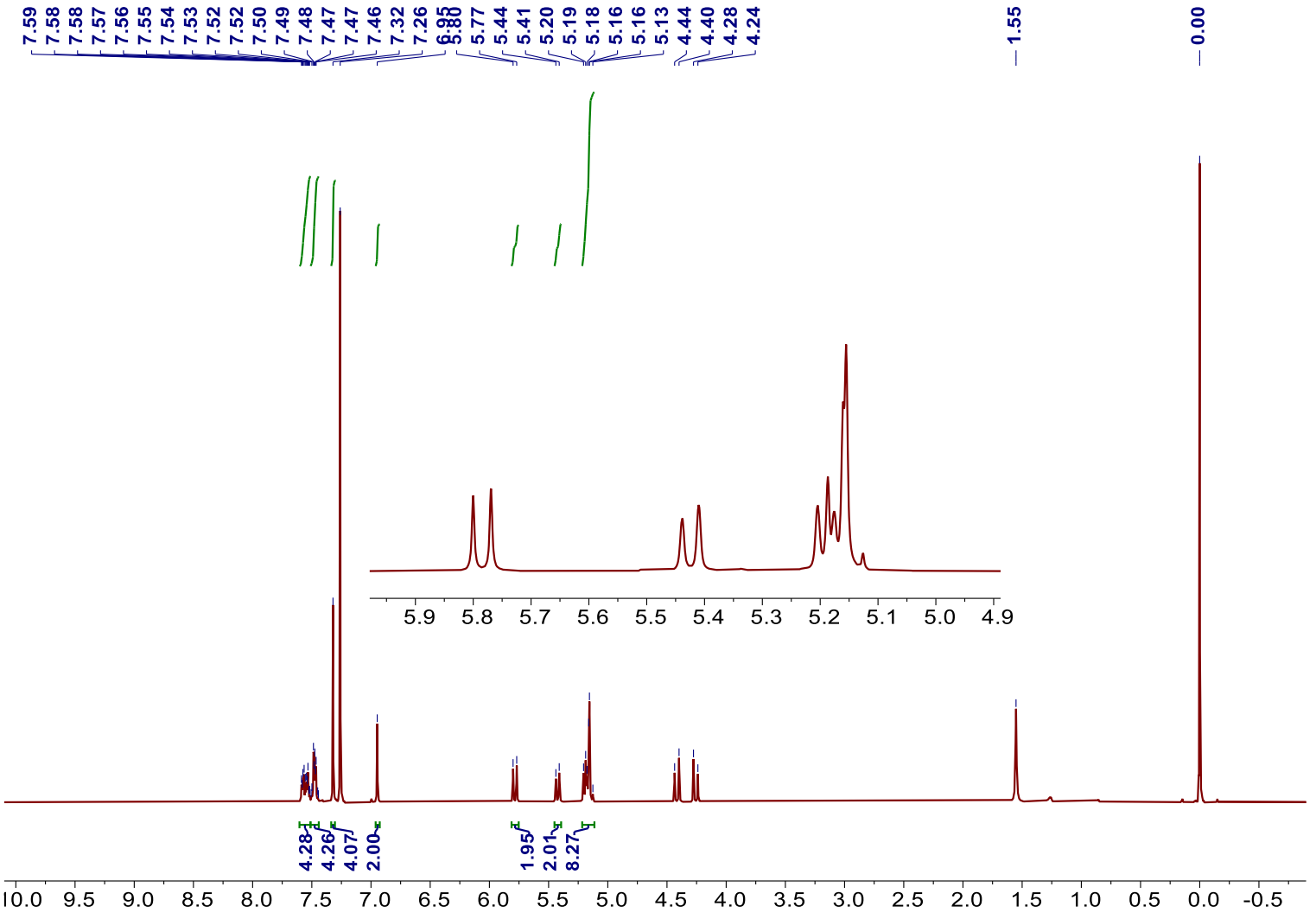


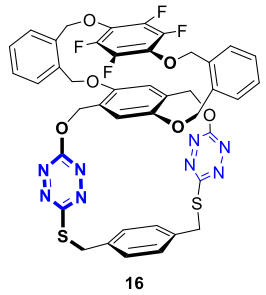


15

^{13}C NMR

$CDCl_3$

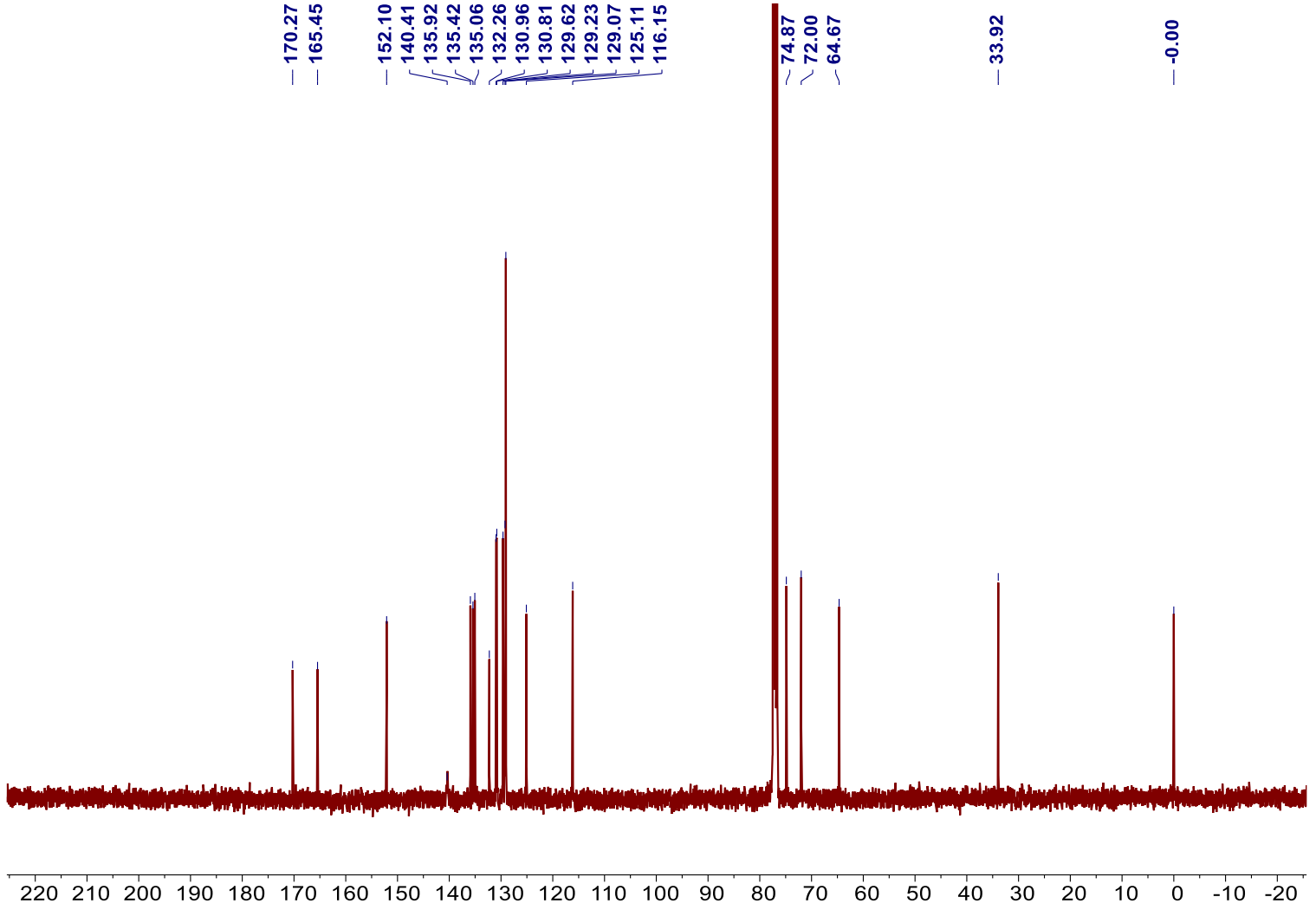


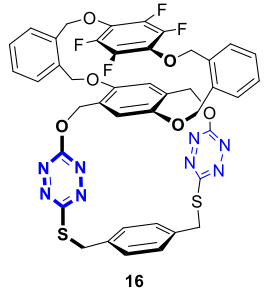


16

^{1}H NMR

$CDCl_3$

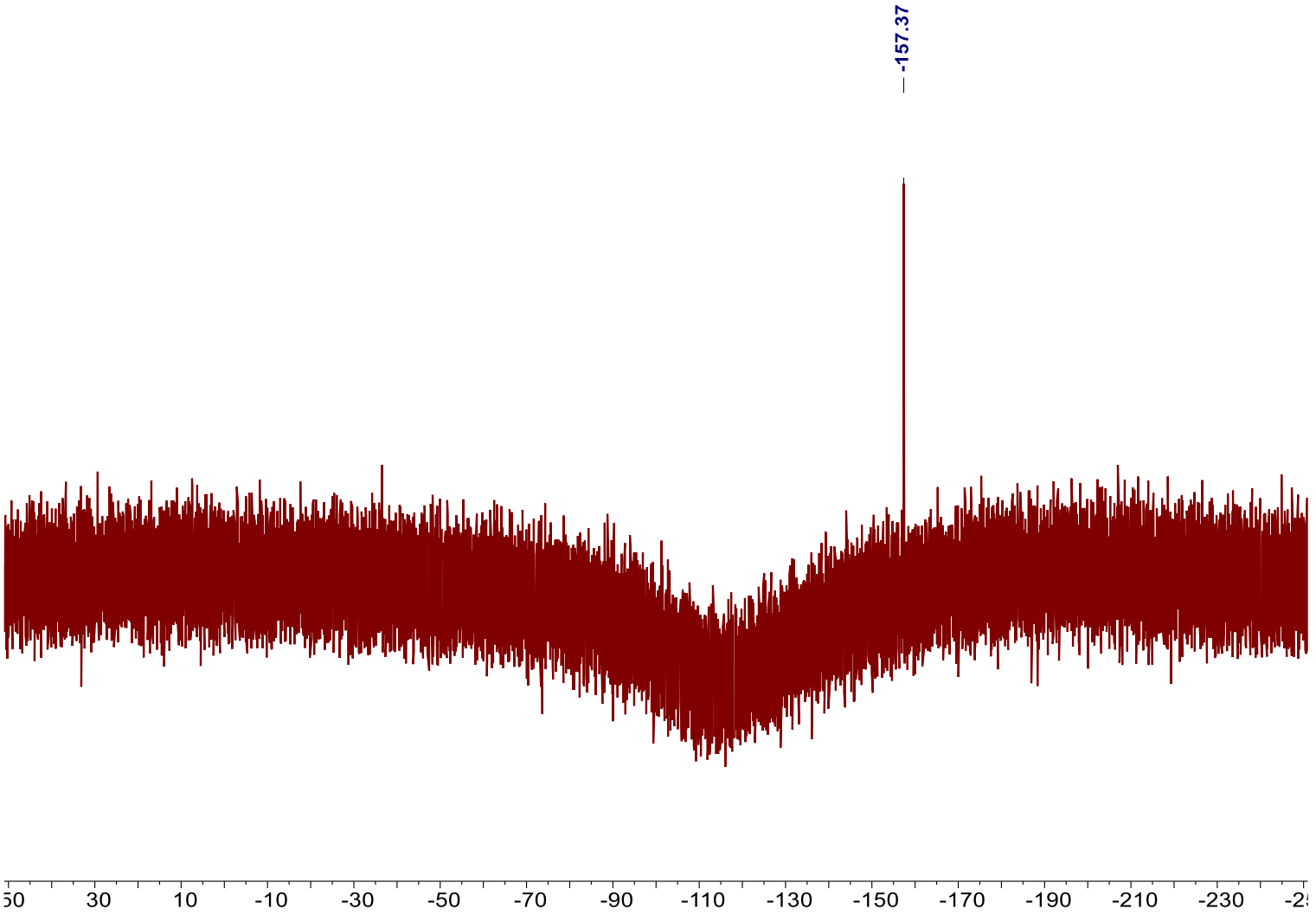


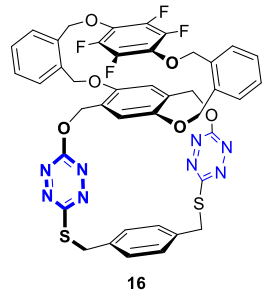


16

^{13}C-^{19}F decoupled NMR

$CDCl_3$

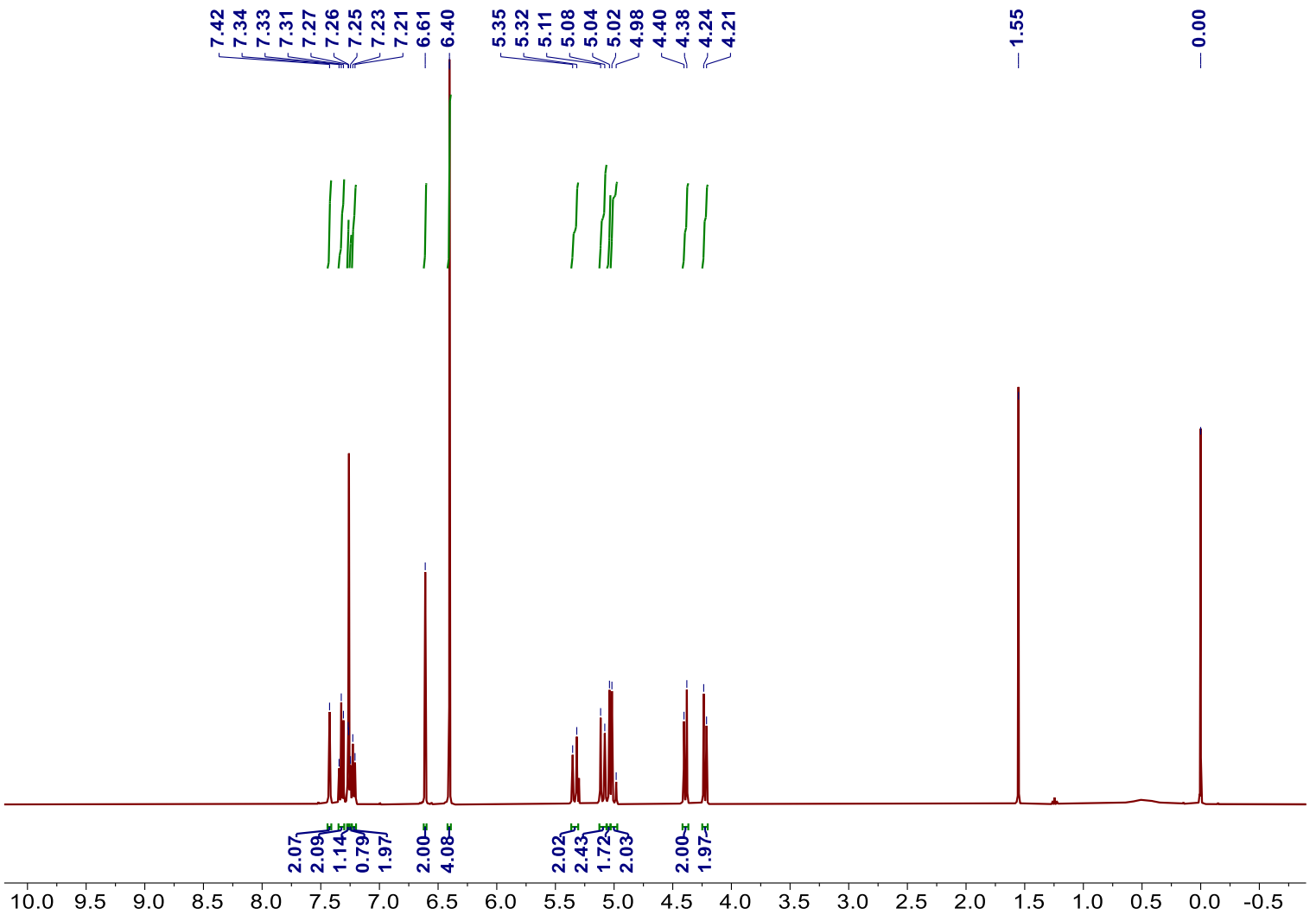




16

^{19}F NMR

DMSO-d_6 (120 ºC)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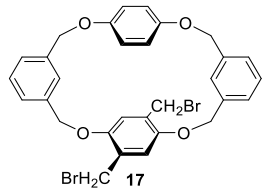
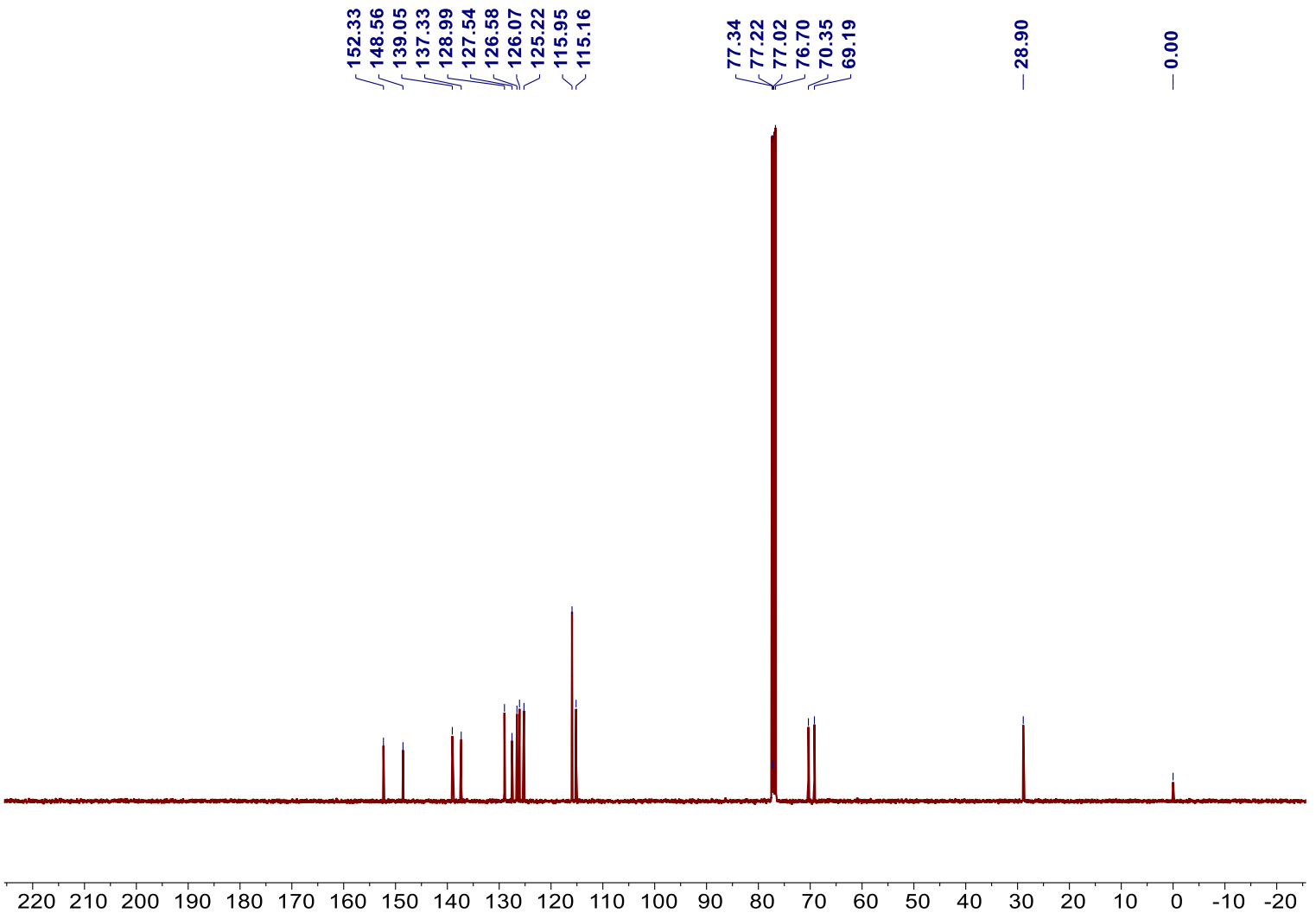
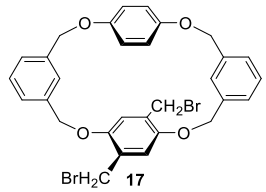
7.27
7.26
7.25
7.23
7.21
6.61
6.40
5.35
5.32
5.11
5.08
5.04
5.02
4.98
4.40
4.38
4.24
4.21
1.55
0.00
2.07
2.09
1.14
0.79
1.97
2.00
4.08
2.02
2.43
1.72
2.03
2.00
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


O
O
O
O
CH2Br
BrH2C
17

^{1}H NMR

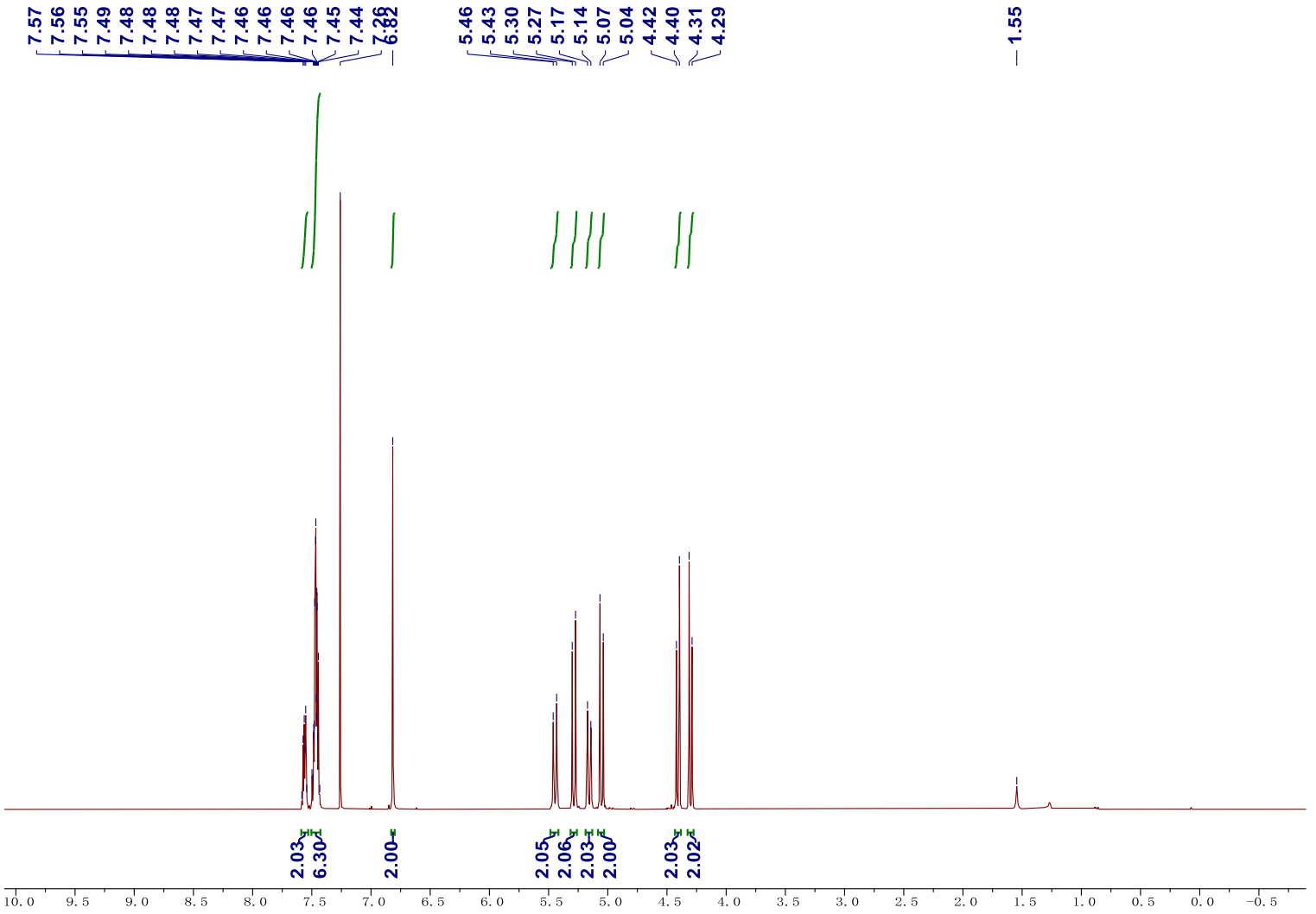
$CDCl_3$





^{13}C NMR

$CDCl_3$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7.56
7.55
7.49
7.48
7.48
7.48
7.47
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7.46
7.46
7.46
7.46
7.45
7.44
7.26
6.82
5.46
5.43
5.30
5.27
5.17
5.14
5.07
5.04
4.42
4.40
4.31
4.29
1.55
2.03
6.30
2.00
2.05
2.06
2.03
2.00
2.03
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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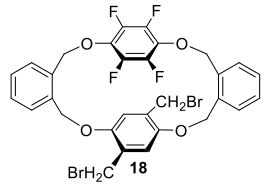
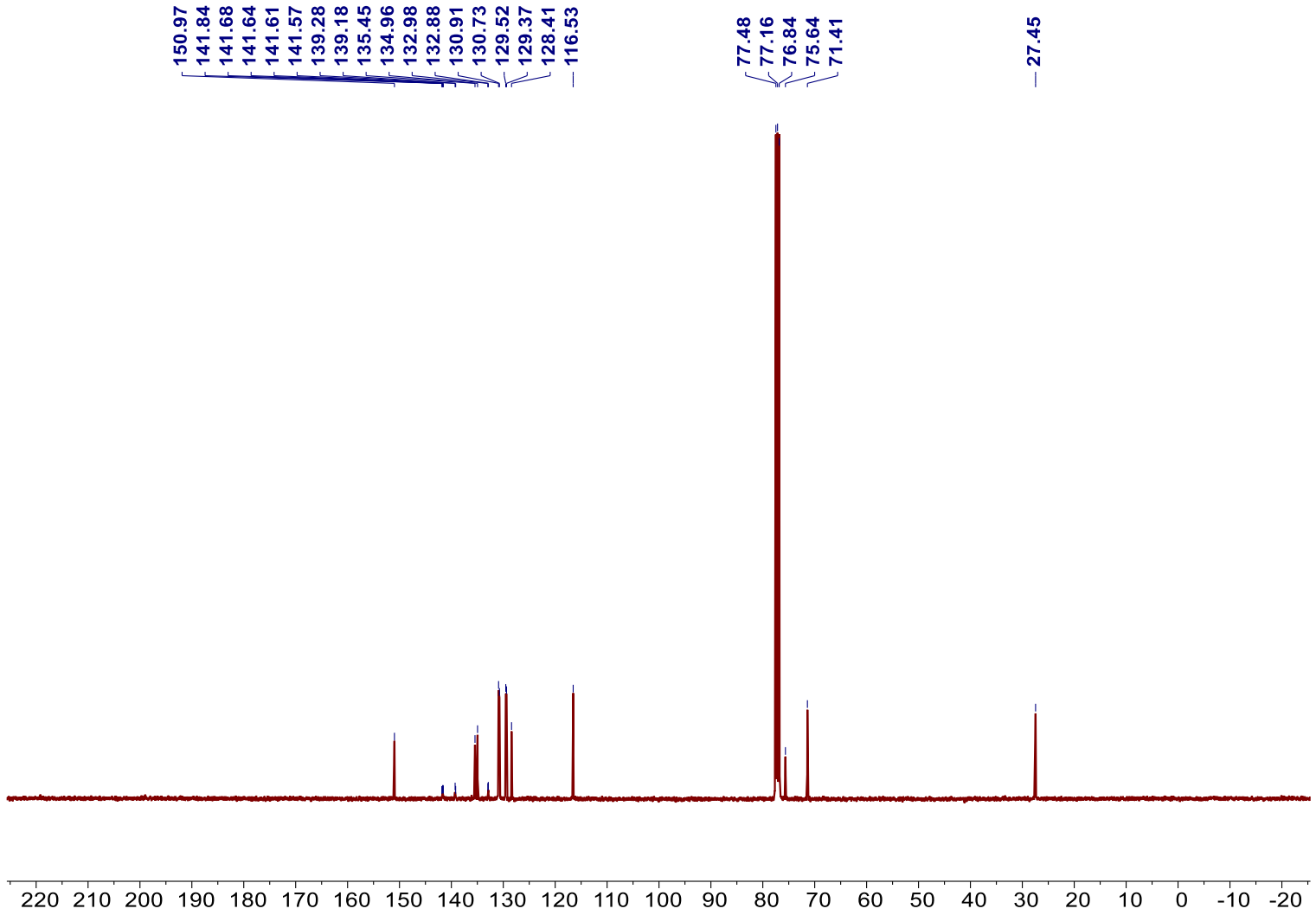
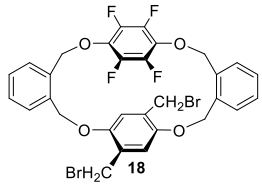
2.5
2.0
1.5
1.0
0.5
0.0
−0.5


F
F
O
O
F
F
CH2Br
O
O
BrH2C
18

^{1}H NMR

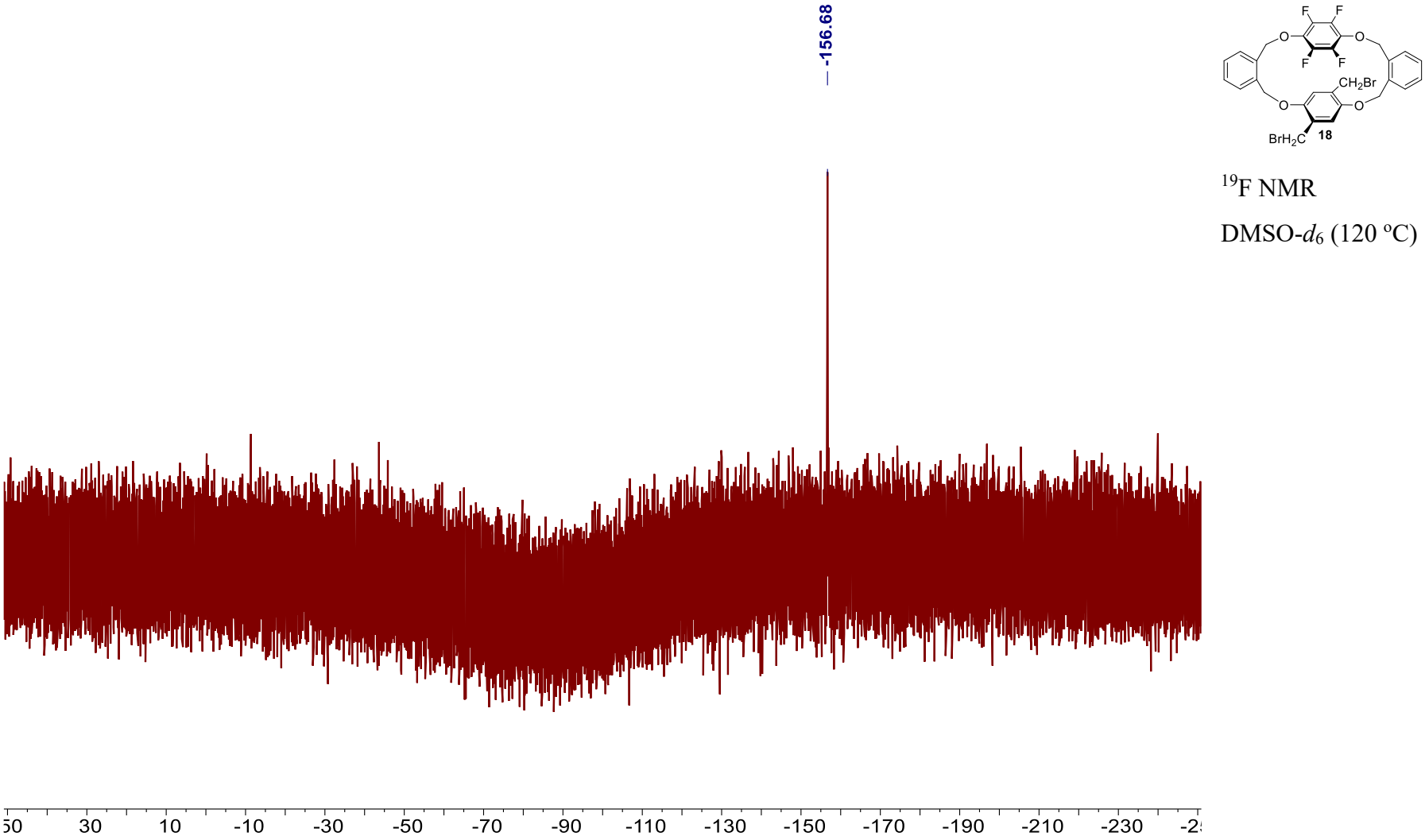
$CDCl_3$





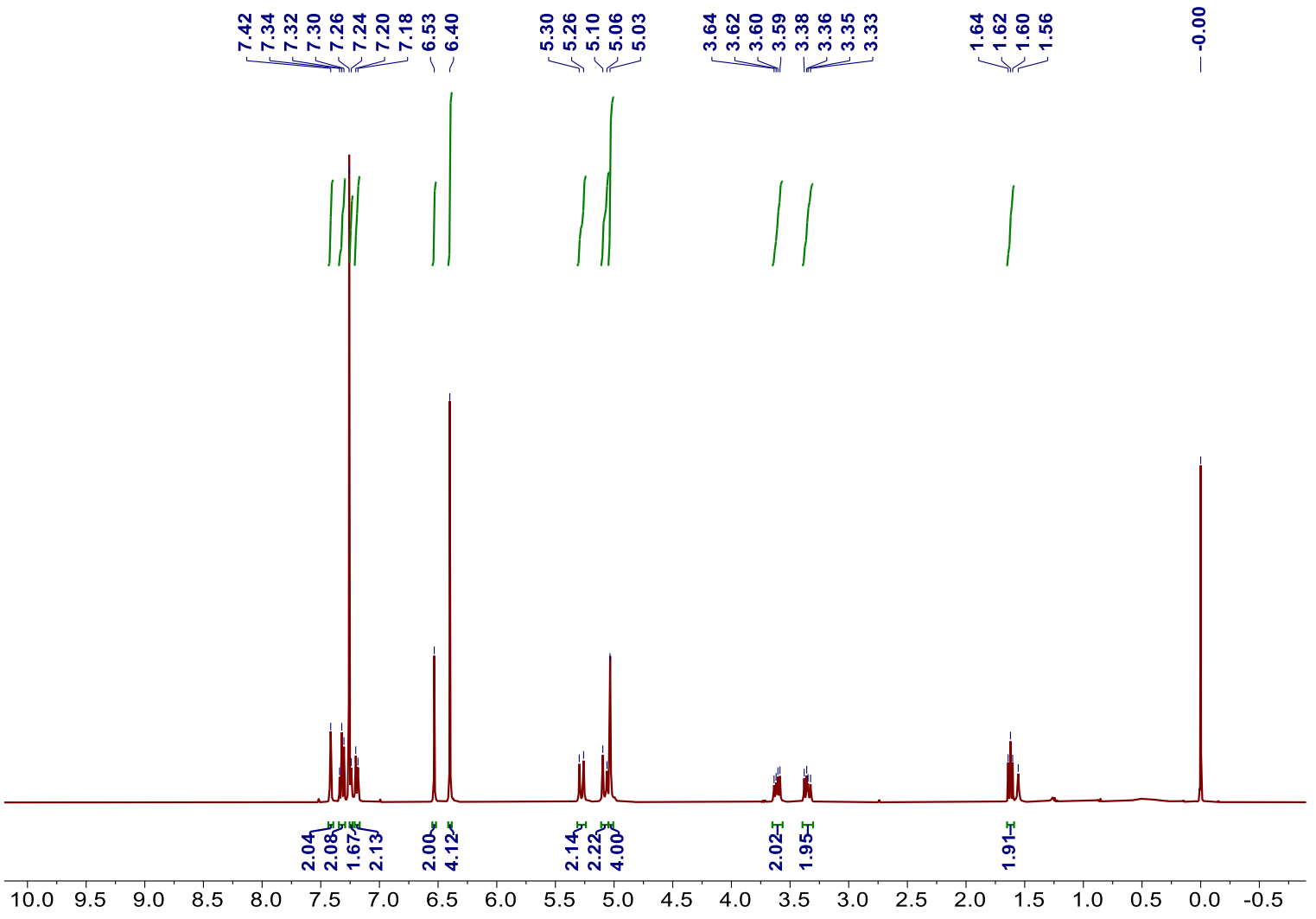
^{13}C NMR

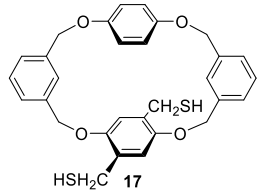
$CDCl_3$



^{19}F NMR

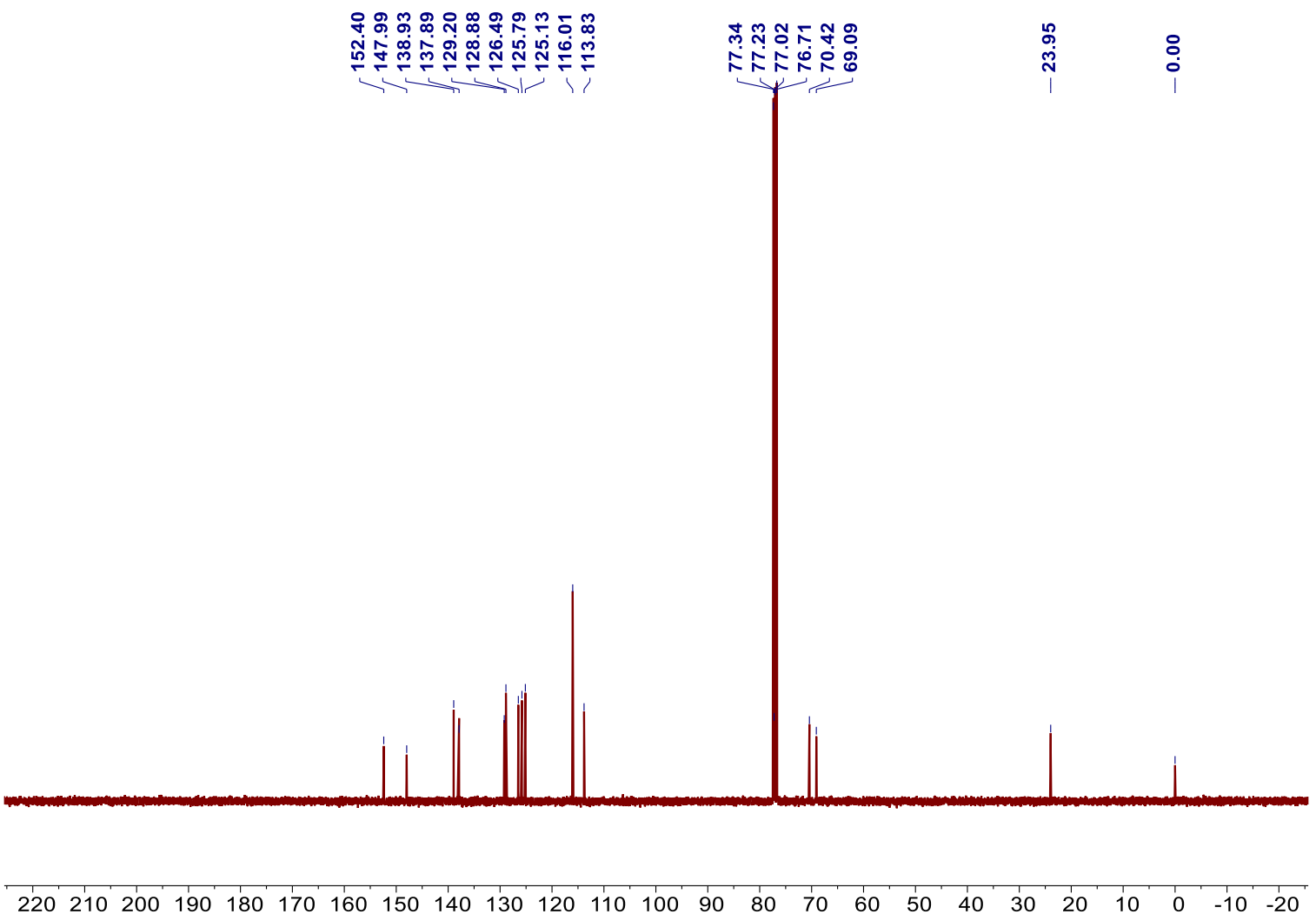
DMSO-d_6 (120 ºC)

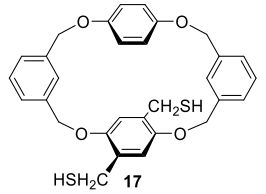

7.42
7.34
7.32
7.30
7.26
7.24
7.20
7.18
6.53
6.40
5.30
5.26
5.10
5.06
5.03
3.64
3.62
3.60
3.59
3.38
3.36
3.35
3.33
1.64
1.62
1.60
1.56
-0.00
2.04
2.08
1.67
2.13
2.00
4.12
2.14
2.22
4.00
2.02
1.95
1.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


O
O
O
O
CH2SH
HSH2C
17

^{1}H NMR

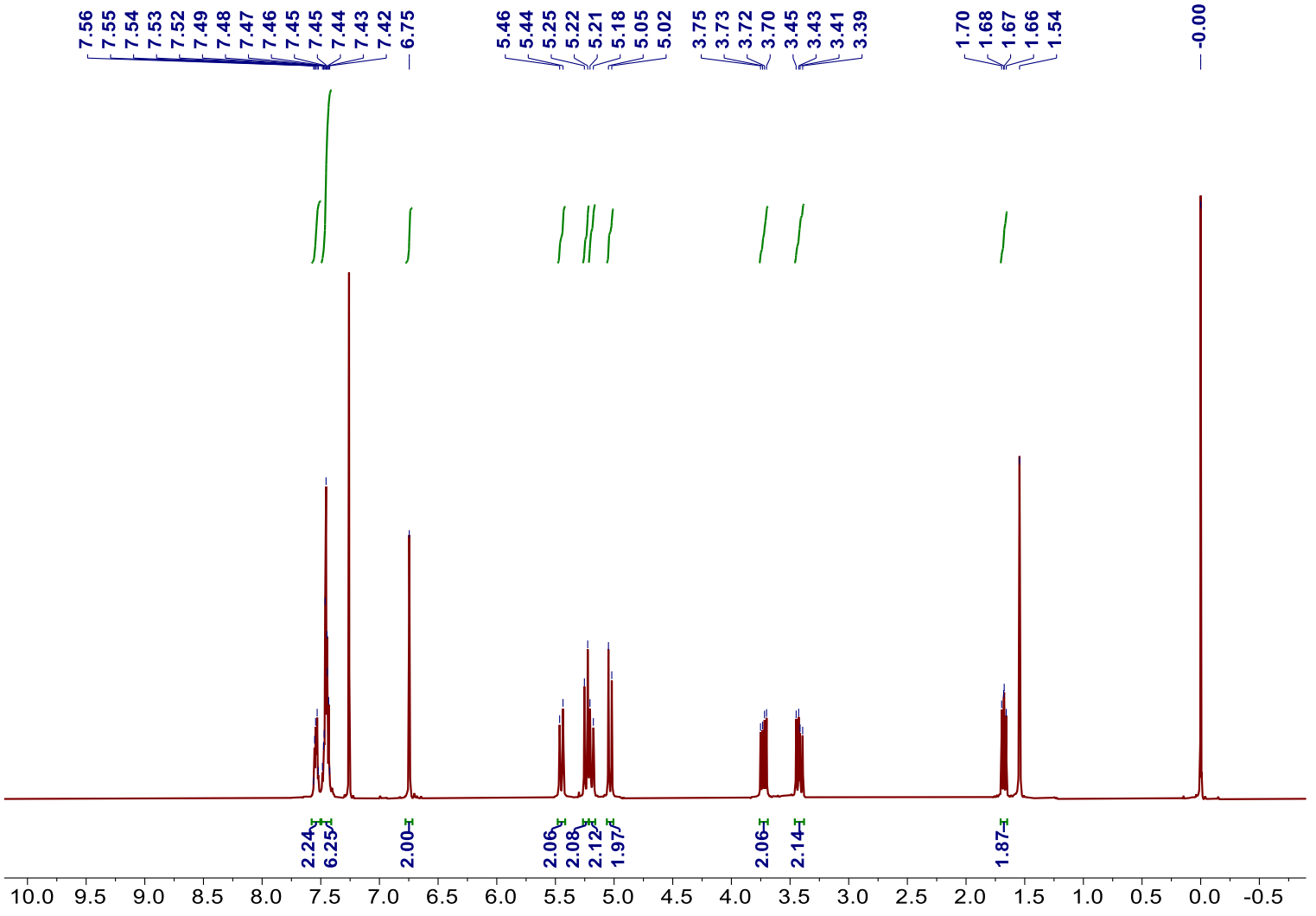
$CDCl_3$





^{13}C NMR

$CDCl_3$


7.56
7.55
7.54
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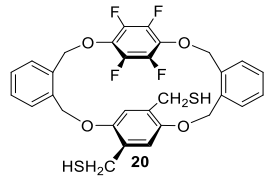
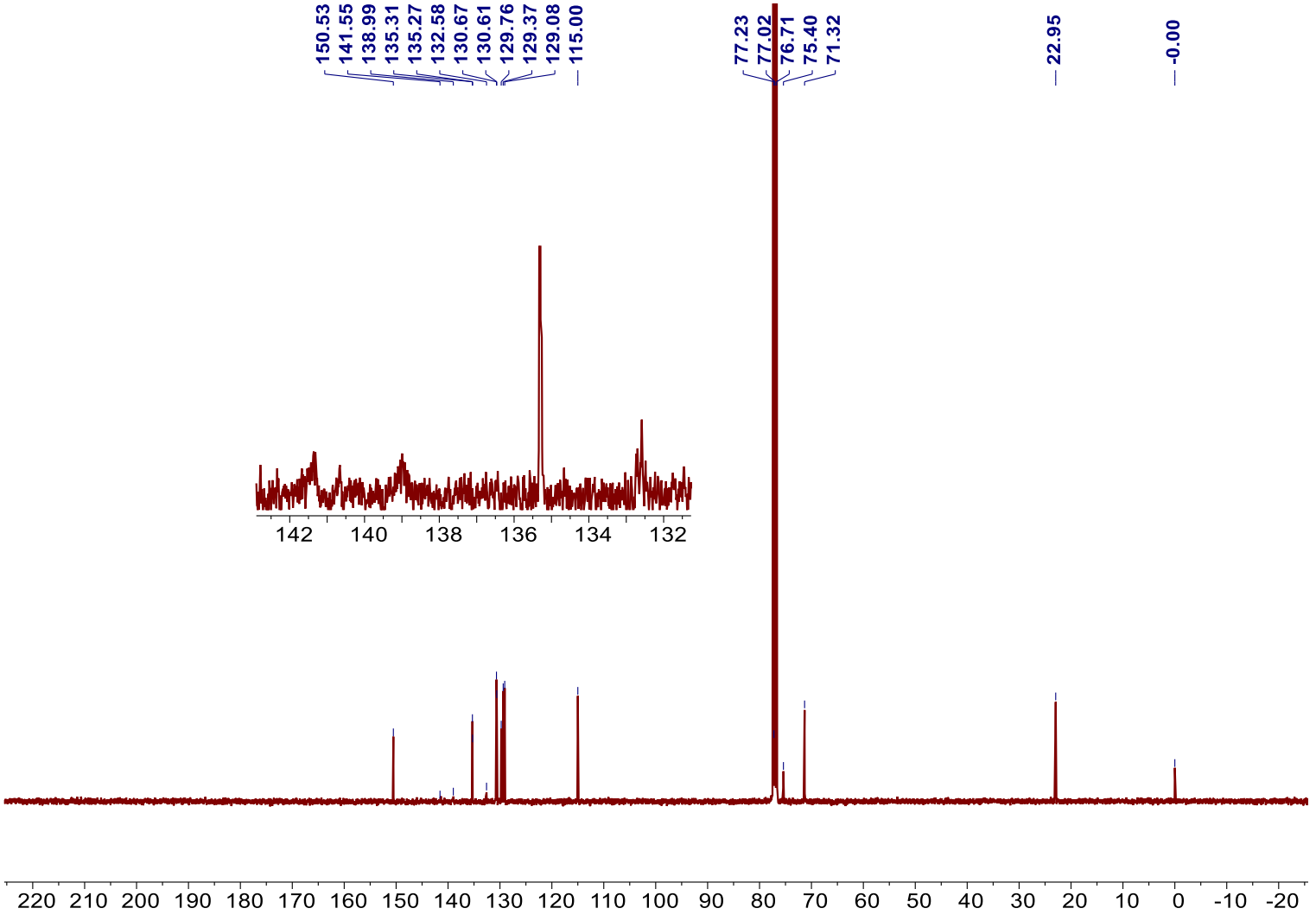
7.52
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.42
6.75
5.46
5.44
5.25
5.22
5.21
5.18
5.05
5.02
3.75
3.73
3.72
3.70
3.45
3.43
3.41
3.39
1.70
1.68
1.67
1.66
1.54
0.00
2.24
6.25
2.00
2.06
2.08
2.12
1.97
2.06
2.14
1.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


F
F
O
O
F
F
CH2SH
O
O
HSH2C
20

^{1}H NMR

$CDCl_3$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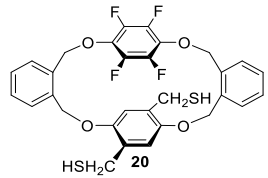
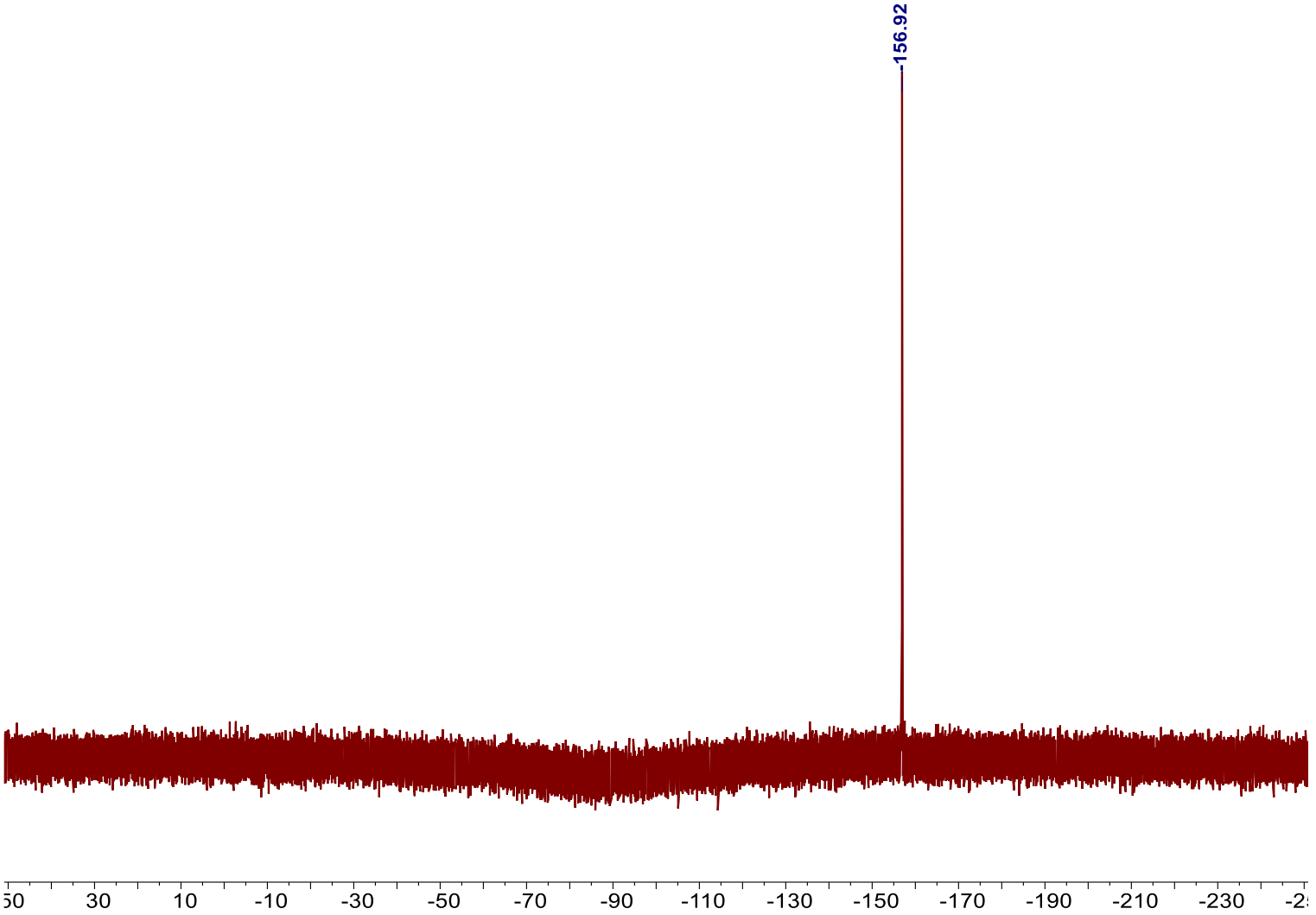
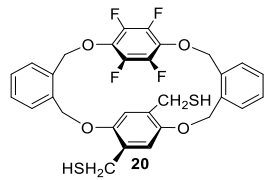
135.27
132.58
130.67
130.61
129.76
129.37
129.08
115.00
77.23
77.02
76.71
75.40
71.32
22.95
-0.00
142
140
138
136
134
132
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


F
F
O
O
F
F
CH2SH
O
O
HSH2C
20

^{1}H NMR

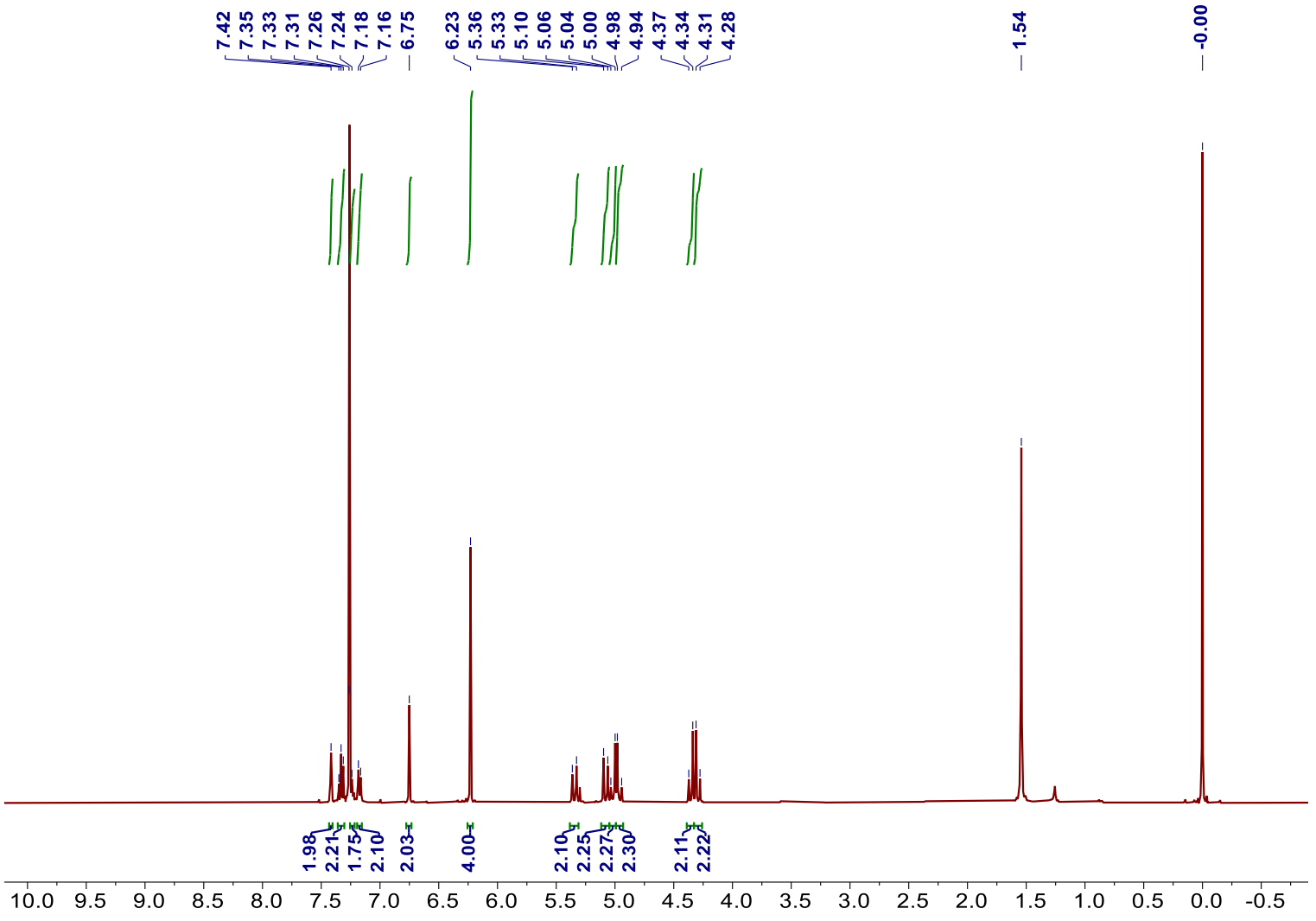
$CDCl_3$

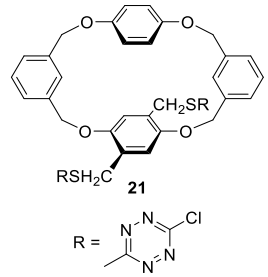




^{19}F NMR

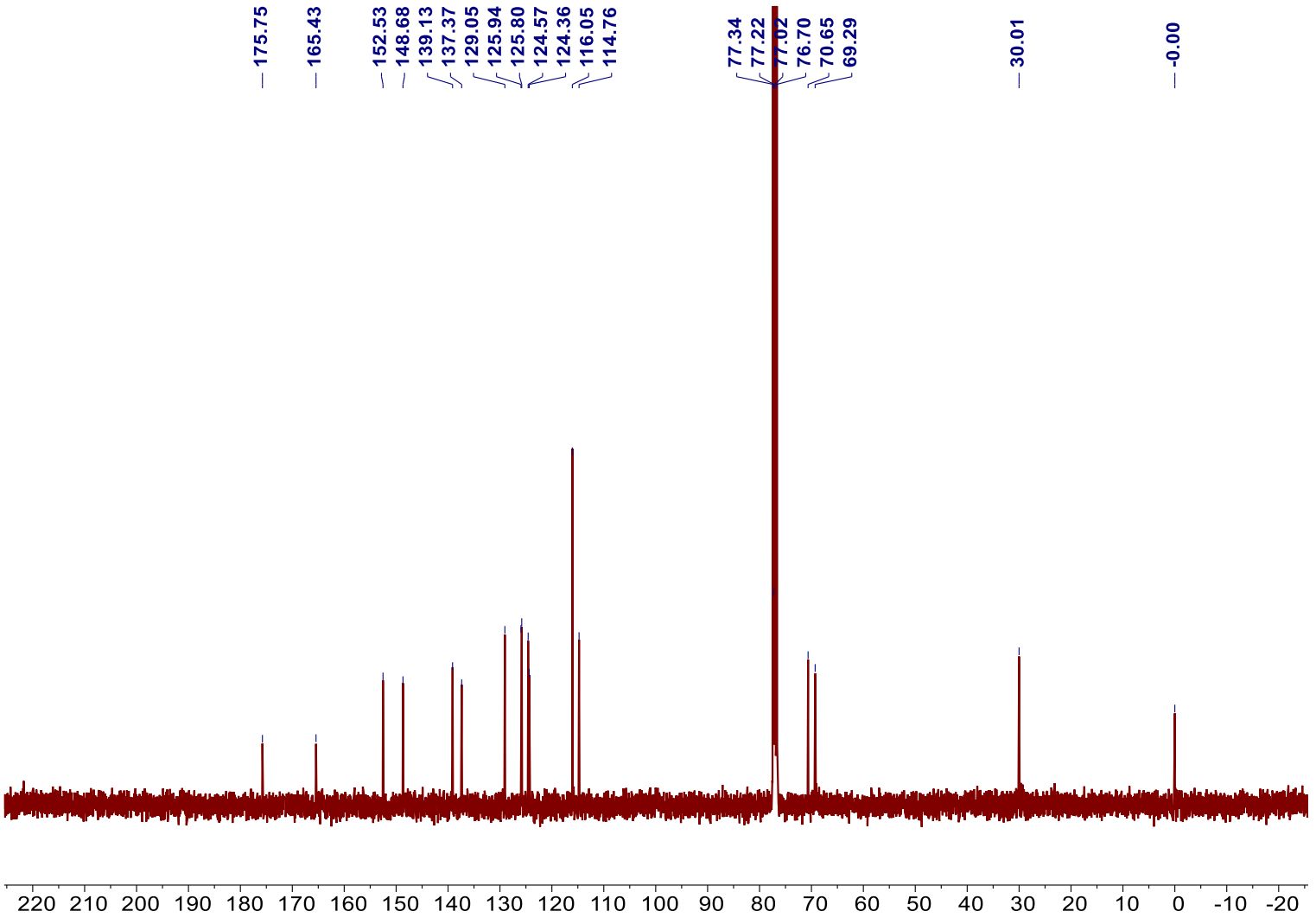
DMSO-d_6 (120 ºC)

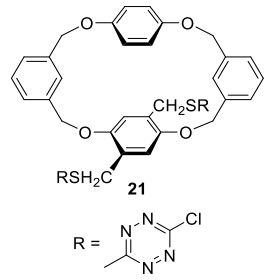

7.42
7.35
7.33
7.31
7.26
7.24
7.18
7.16
6.75
6.23
5.36
5.33
5.10
5.06
5.04
5.00
4.98
4.94
4.37
4.34
4.31
4.28
1.54
-0.00
1.98
2.21
1.75
2.10
2.03
4.00
2.10
2.25
2.27
2.30
2.11
2.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


O
O
O
O
CH2SR
RSH2C
21
R =
N
N
N
N
Cl

^{1}H NMR

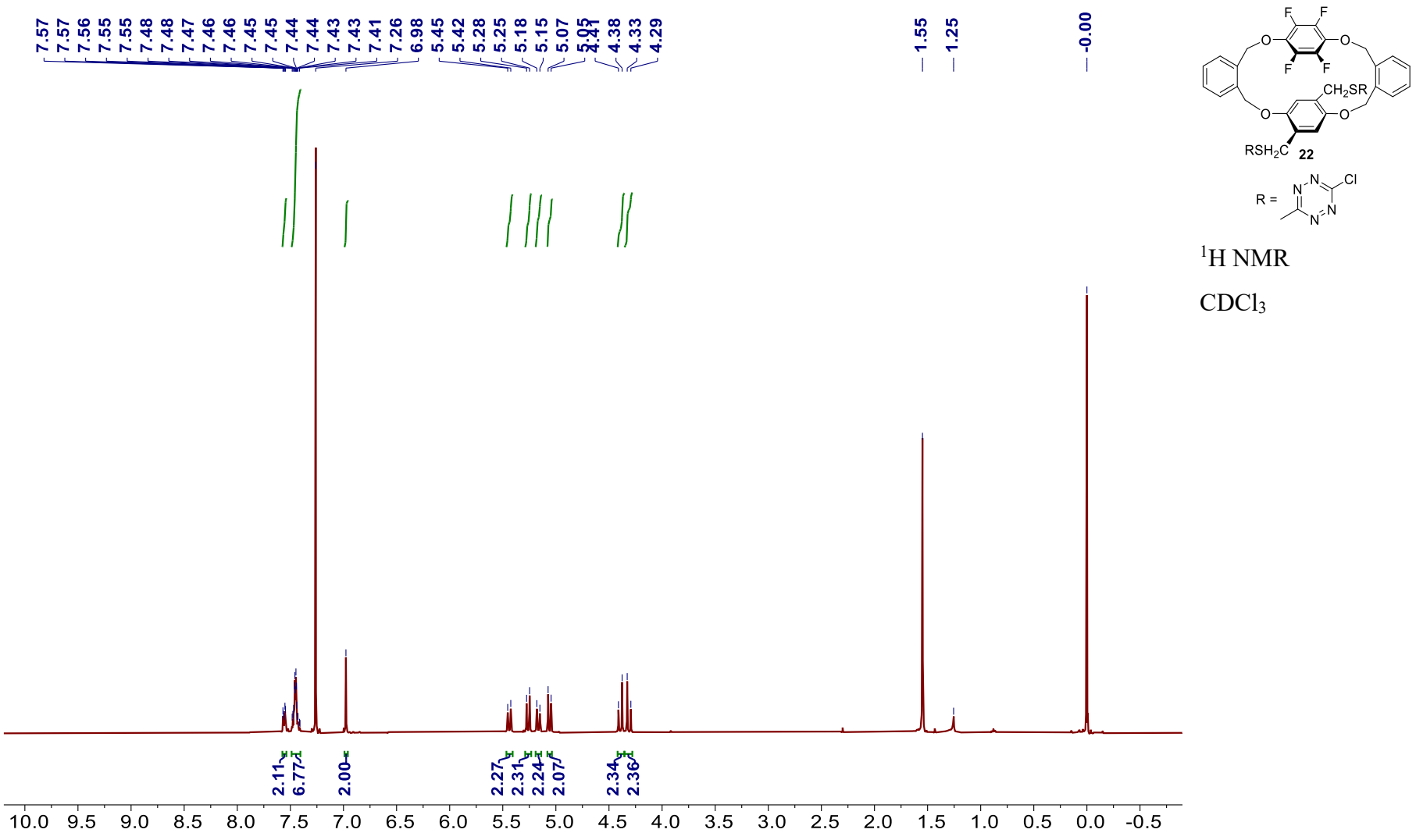
$CDCl_3$





^{13}C NMR

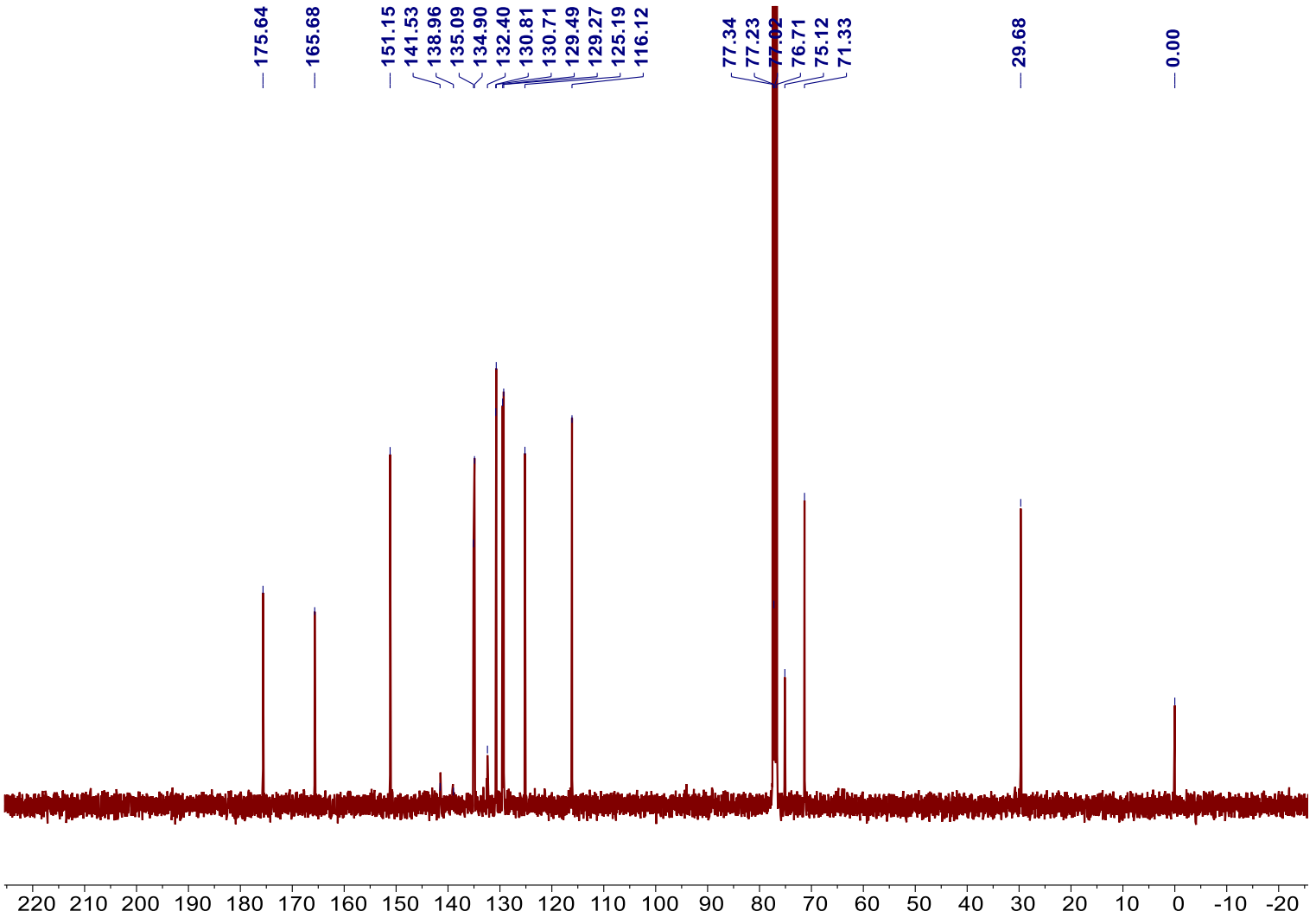
$CDCl_3$

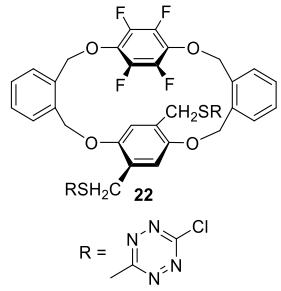

7.57
7.57
7.56
7.55
7.55
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.41
7.26
6.98
5.45
5.42
5.28
5.25
5.18
5.15
5.07
5.05
4.41
4.38
4.33
4.29
1.55
1.25
-0.00
2.11
6.77
2.00
2.27
2.31
2.24
2.07
2.34
2.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

F
F
O
O
F
F
CH2SR
O
O
RSH2C
22
R =
N
N
Cl
N
N

^{1}H NMR

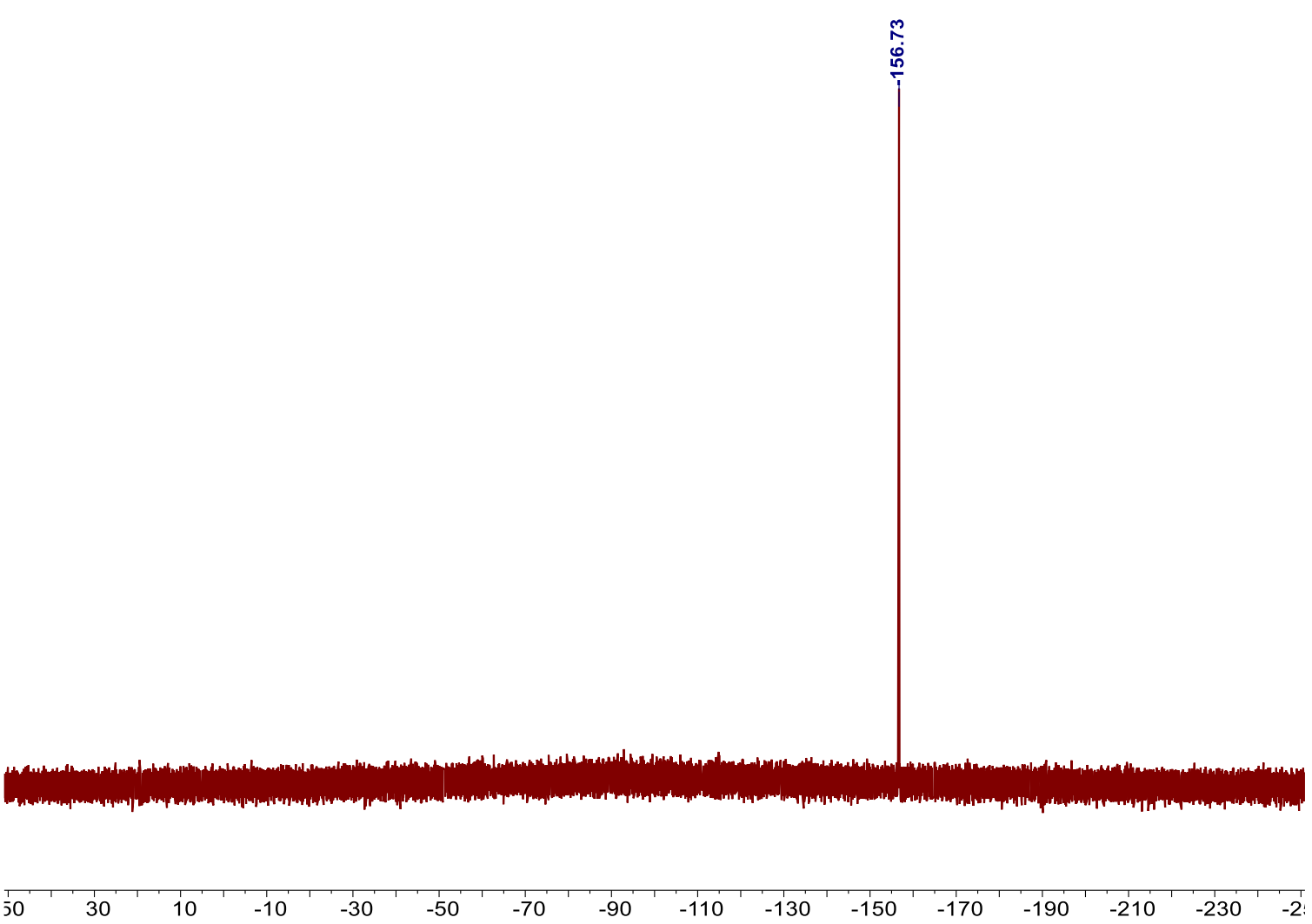
$CDCl_3$

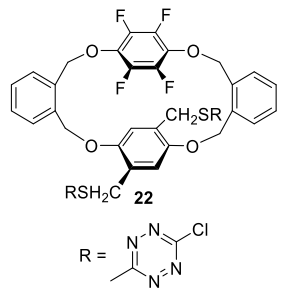




13C NMR

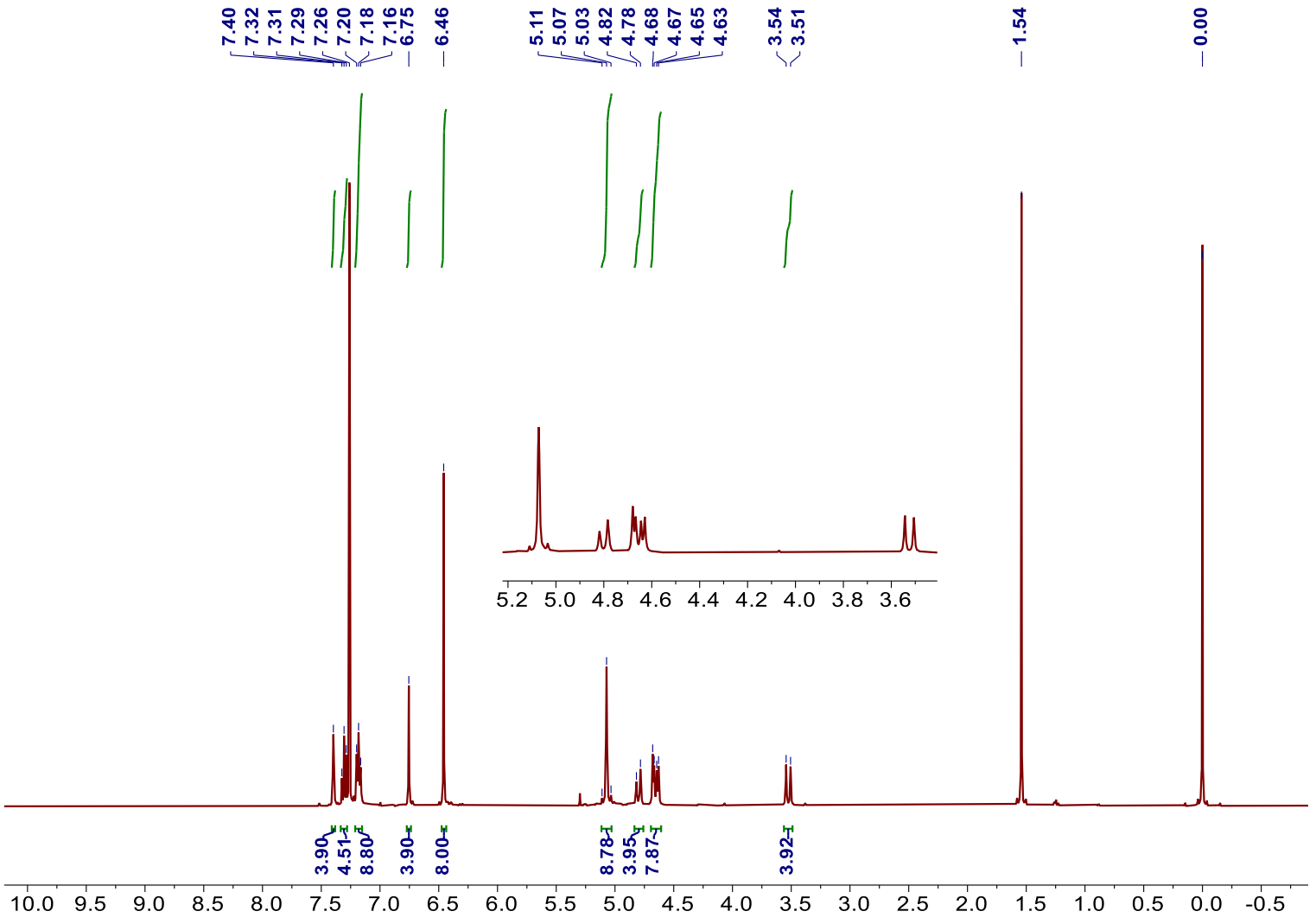
CDCl3

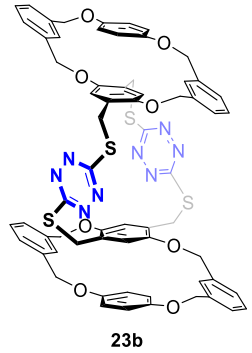




19F NMR

DMSO-d6 (120 oC)

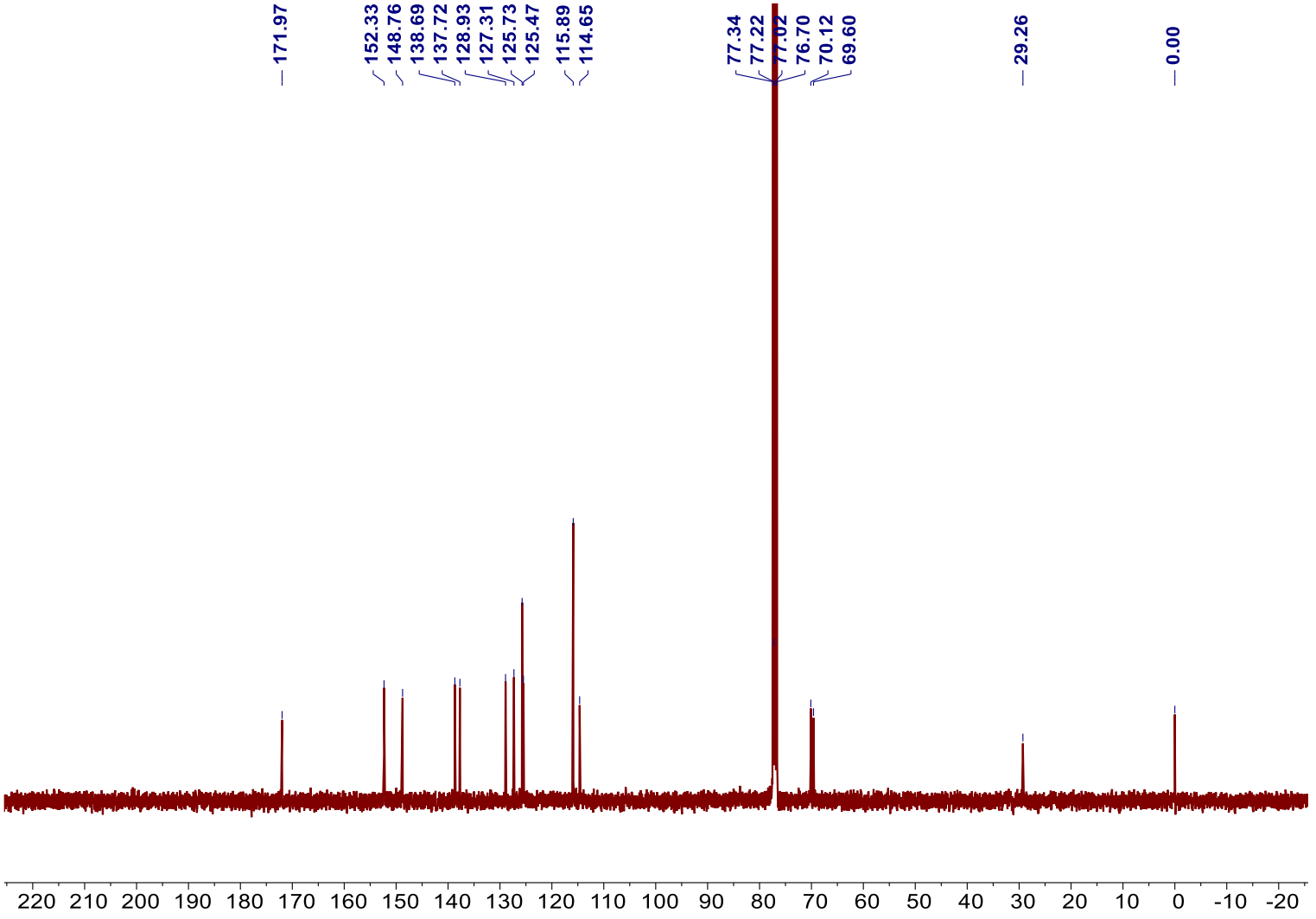


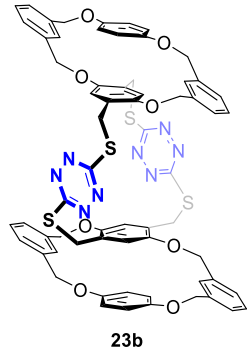


23b

^{1}H NMR

$CDCl_3$

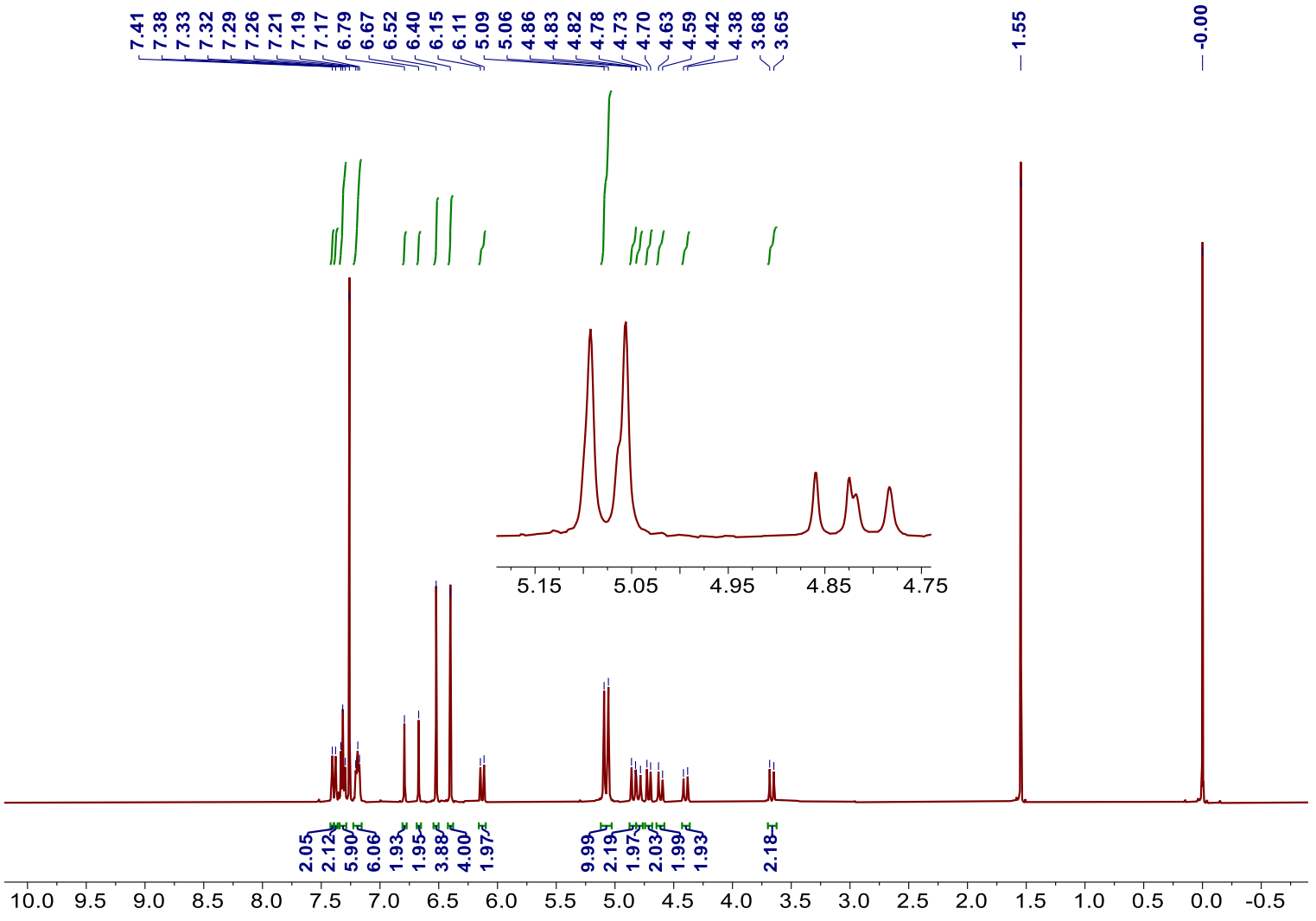


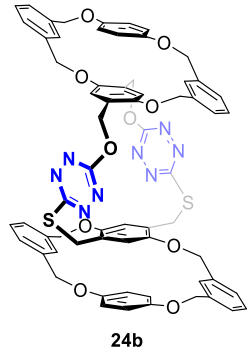


23b

^{13}C NMR

$CDCl_3$

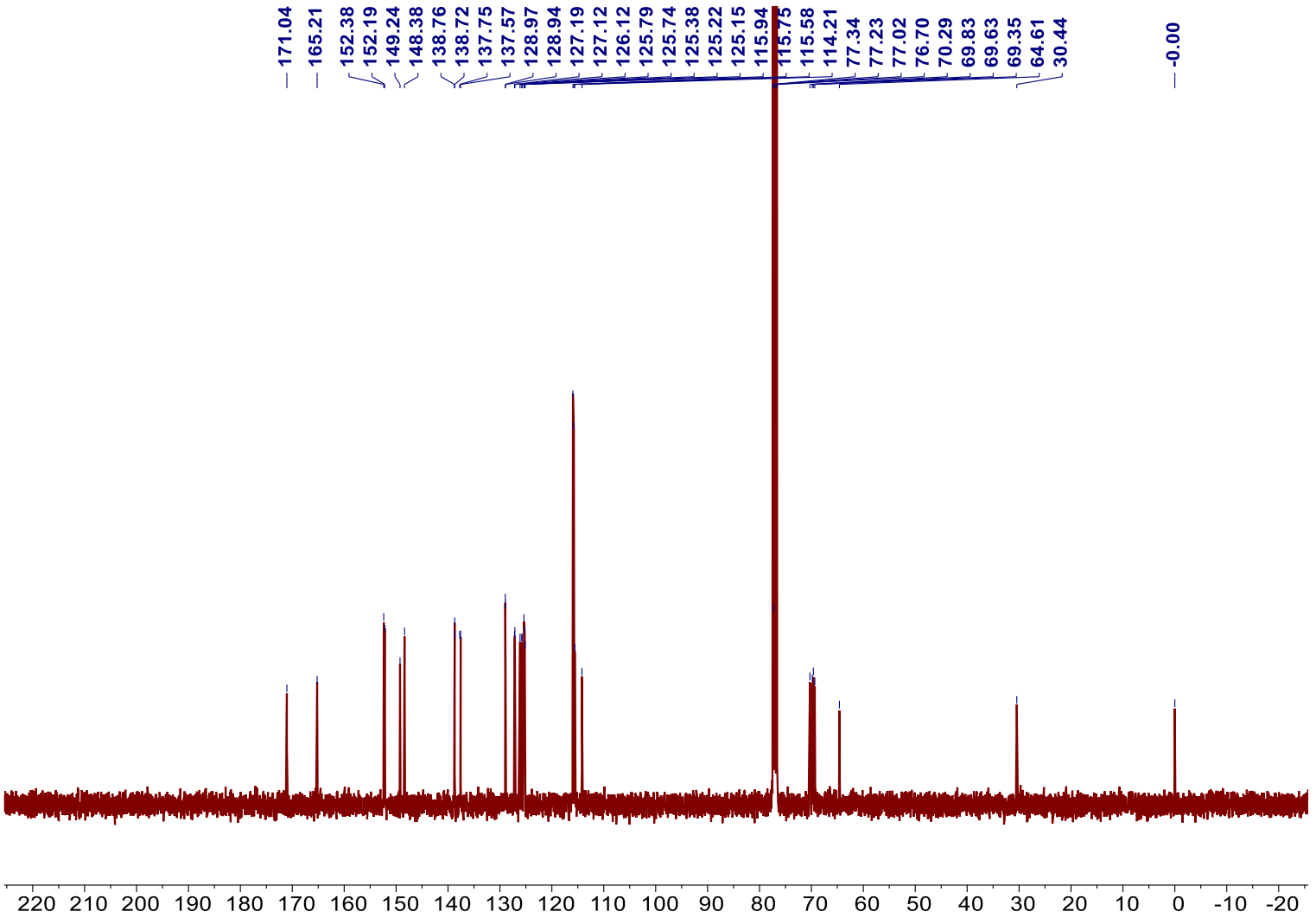


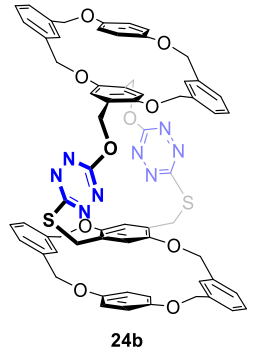


24b

^{1}H NMR

$CDCl_3$

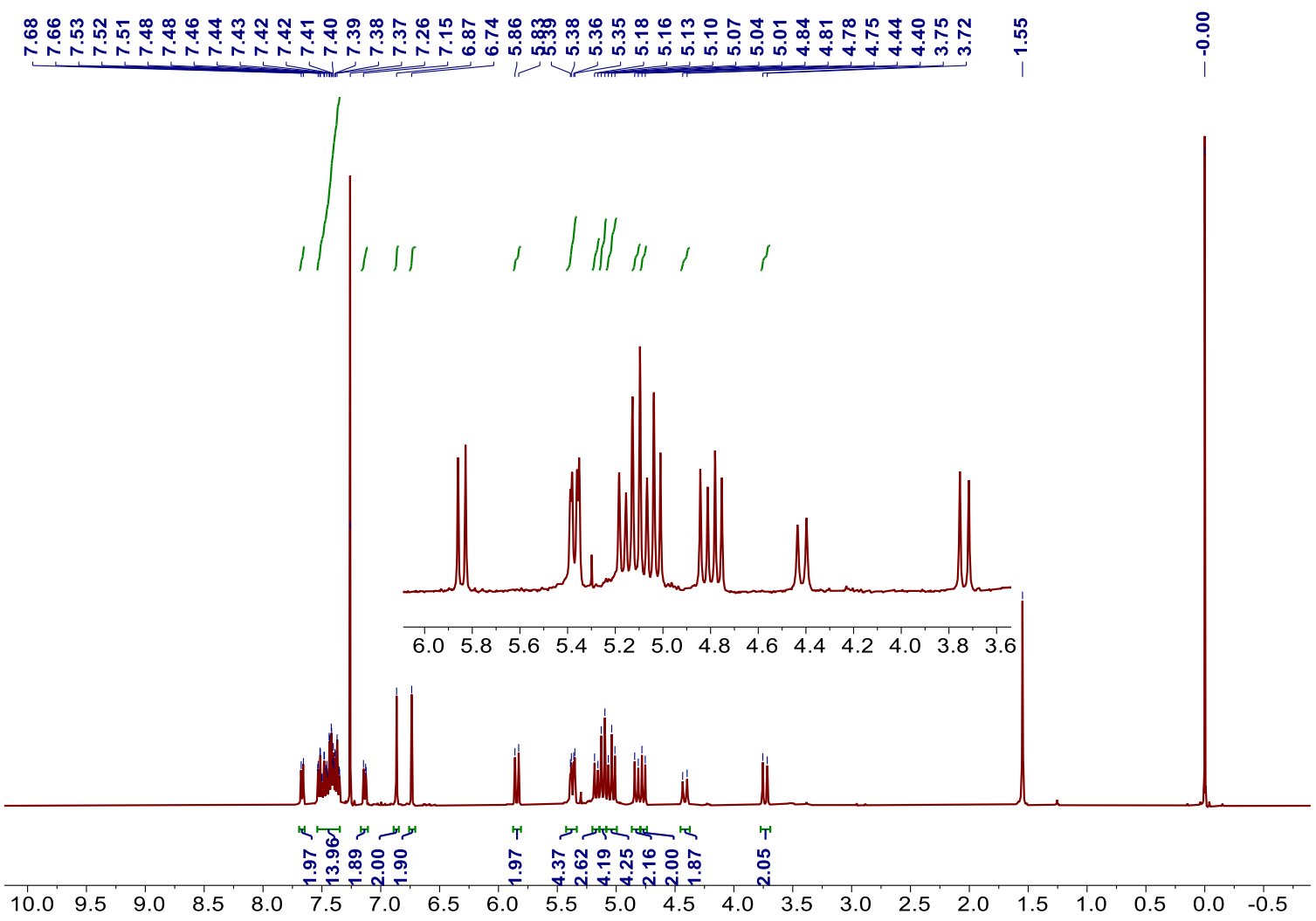


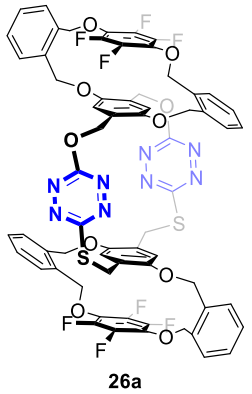


24b

^{13}C NMR

$CDCl_3$

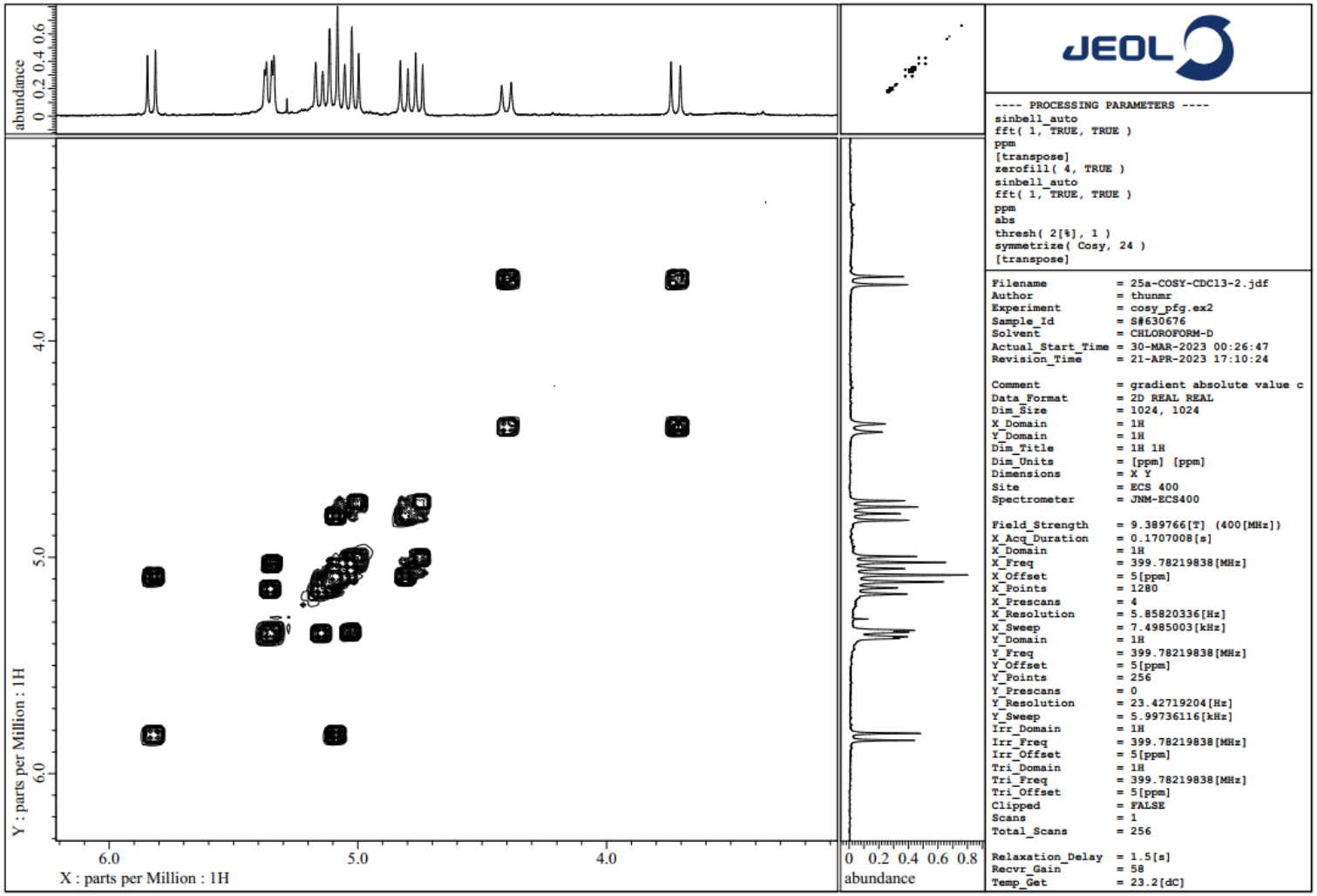




26a

^{1}H NMR

$CDCl_3$




```
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fft( 1, TRUE, TRUE )
ppm
[transpose]
zerofill( 4, TRUE )
sinbell_auto
fft( 1, TRUE, TRUE )
ppm
abs
thresh( 2[%], 1 )
symmetrize( Cosy, 24 )
[transpose]

Filename            = 25a-COSY-CDCl3-2.jdf
Author              = thunmr
Experiment          = cosy_pfg.ex2
Sample_Id           = S#630676
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-MAR-2023 00:26:47
Revision_Time       = 21-APR-2023 17:10:24

Comment             = gradient absolute value c
Data_Format         = 2D REAL REAL
Dim_Size            = 1024, 1024
X_Domain            = 1H
Y_Domain            = 1H
Dim_Title           = 1H 1H
Dim_Units           = [ppm] [ppm]
Dimensions          = X Y
Site                = ECS 400
Spectrometer        = JNM-ECS400

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 0.1707008[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 1280
X_Prescans          = 4
X_Resolution        = 5.85820336[Hz]
X_Sweep             = 7.4985003[kHz]
Y_Domain            = 1H
Y_Freq              = 399.78219838[MHz]
Y_Offset            = 5[ppm]
Y_Points            = 256
Y_Prescans          = 0
Y_Resolution        = 23.42719204[Hz]
Y_Sweep             = 5.99736116[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
Scans               = 1
Total_Scans         = 256

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Recvr_Gain          = 58
Temp_Get            = 23.2[dC]
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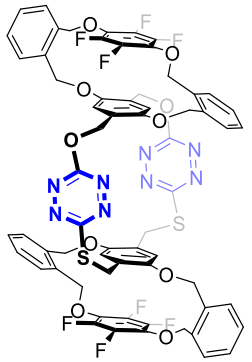
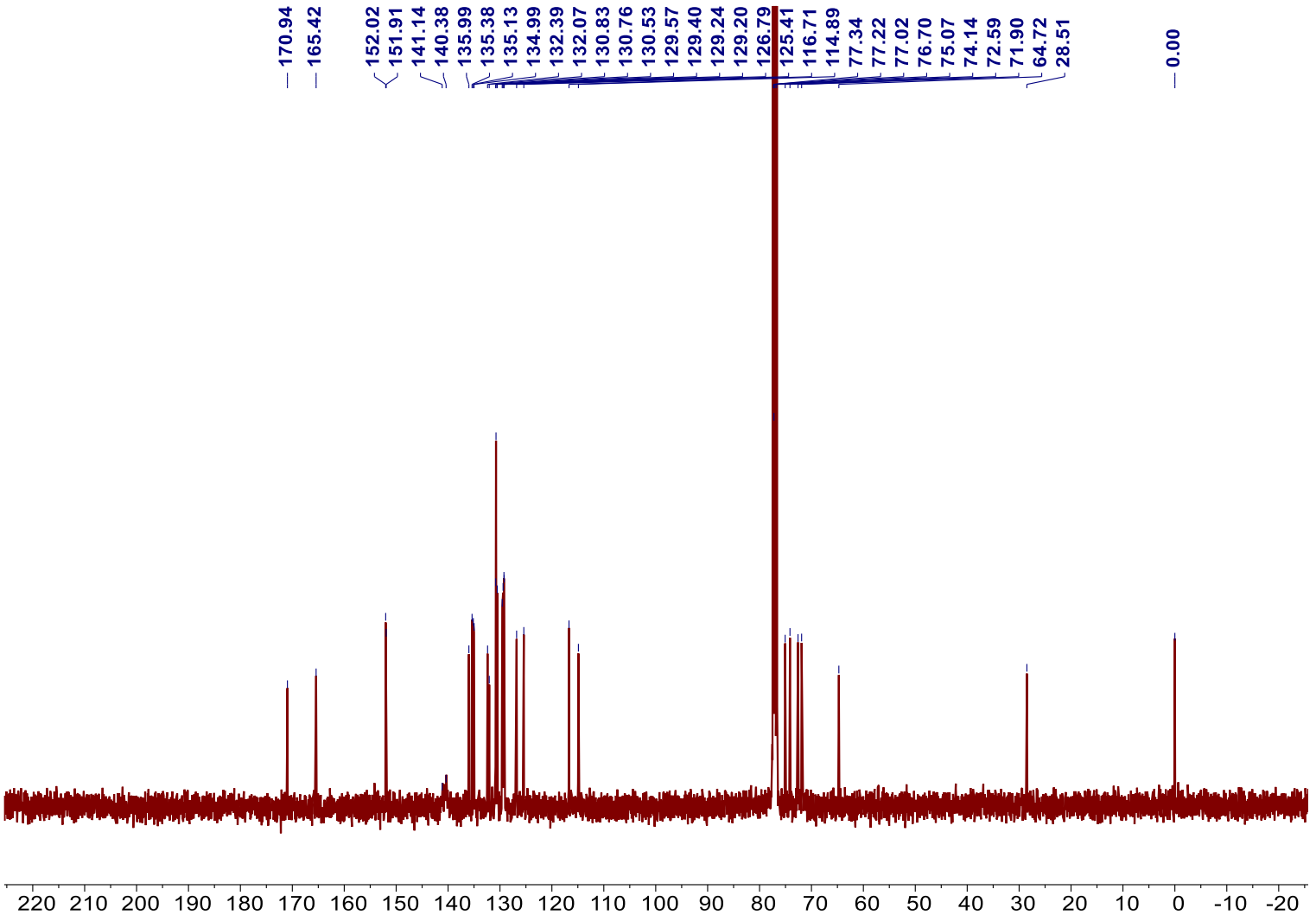
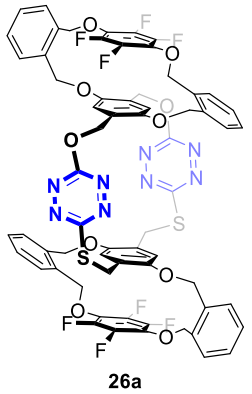


26a

COSY

$CDCl_3$

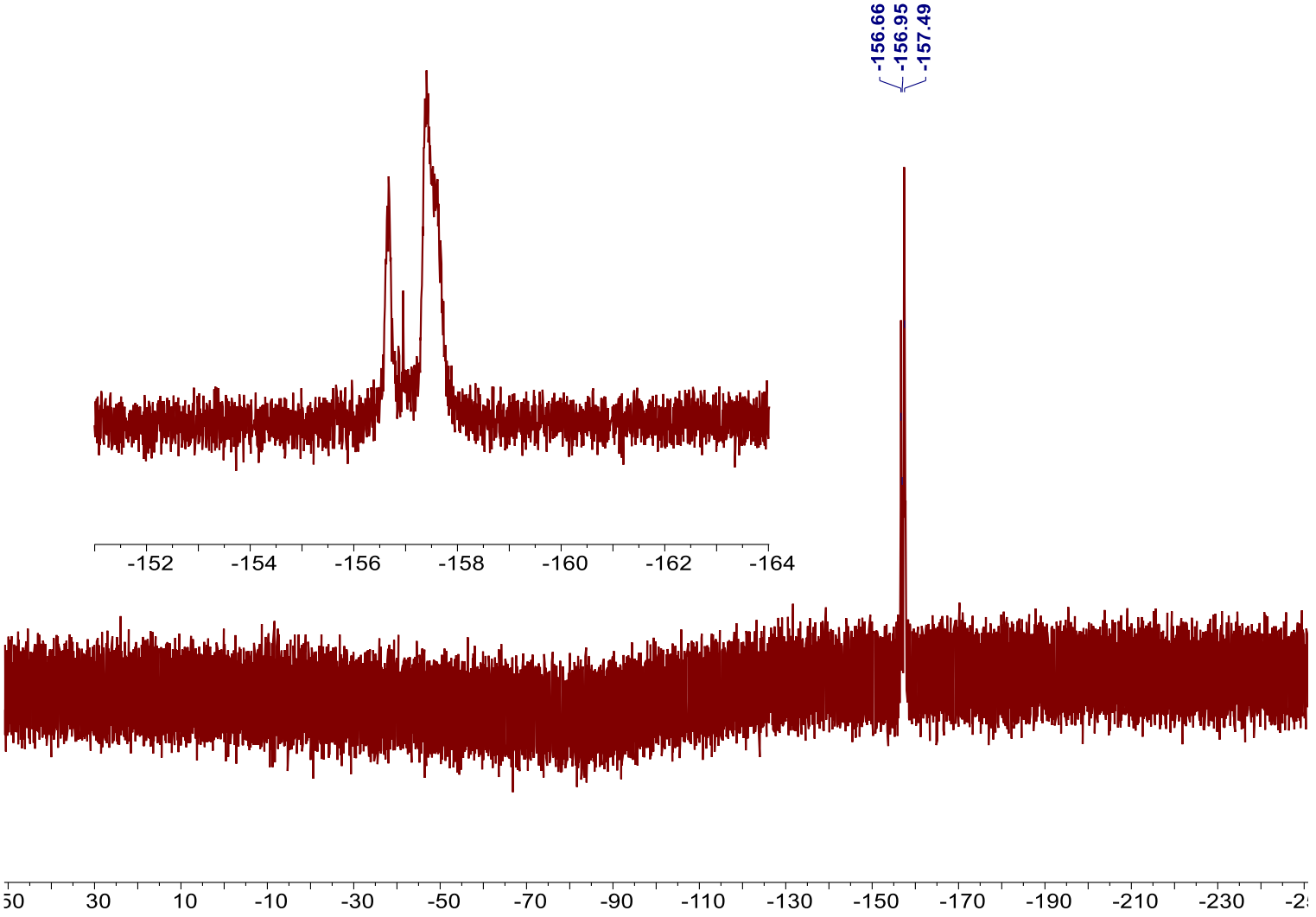


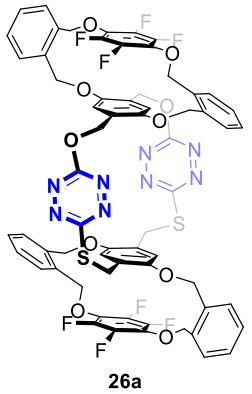


26a

^{13}C-^{19}F Decoupled NMR

$CDCl_3$

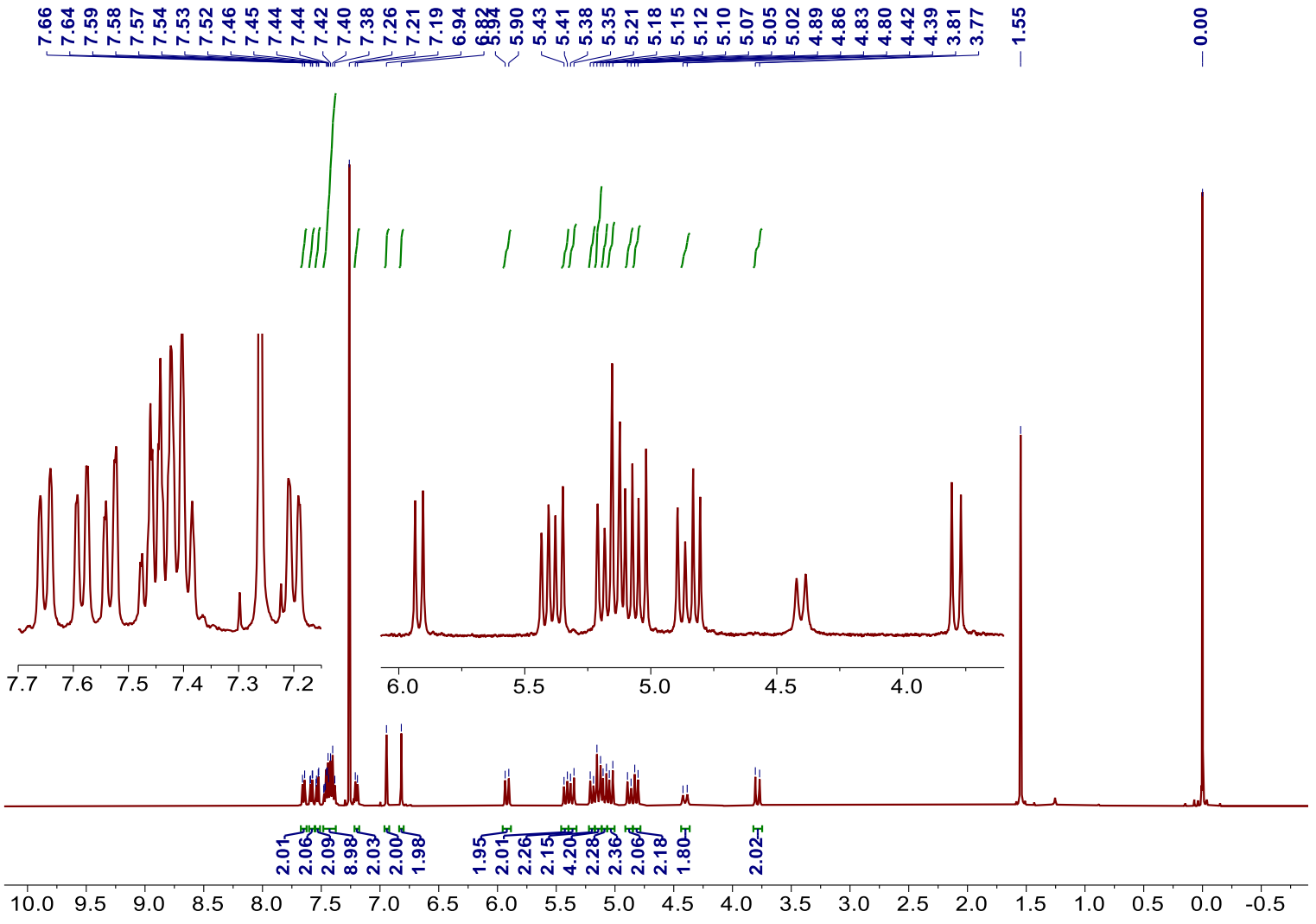


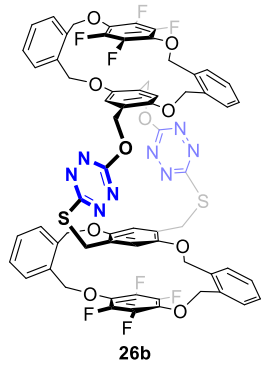


26a

^{19}F NMR

$CDCl_3$

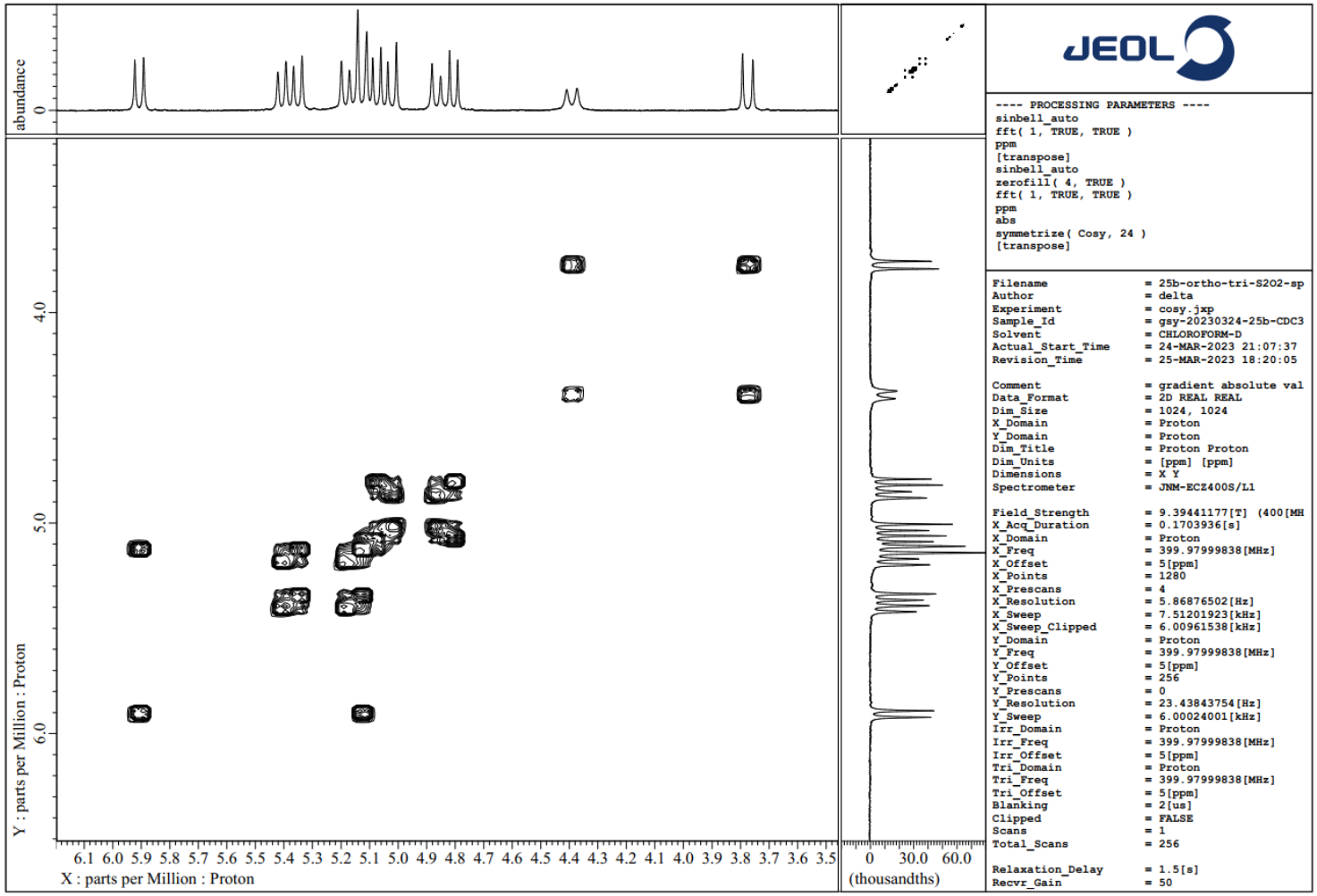


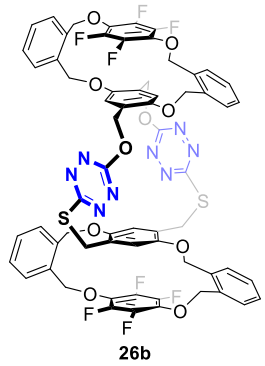


26b

^{1}H NMR

$CDCl_3$

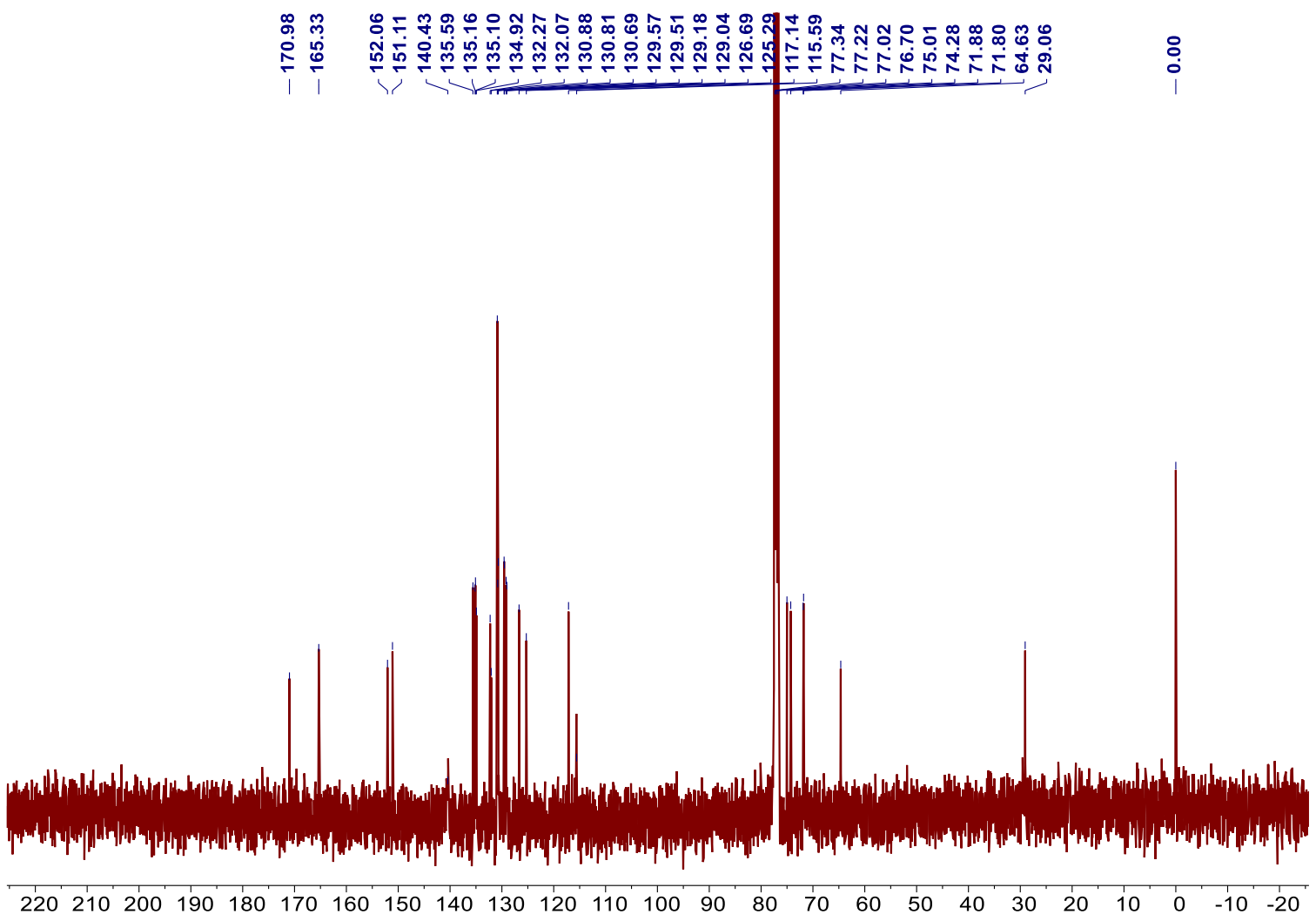


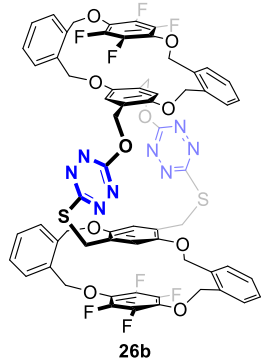


26b

COSY

$CDCl_3$

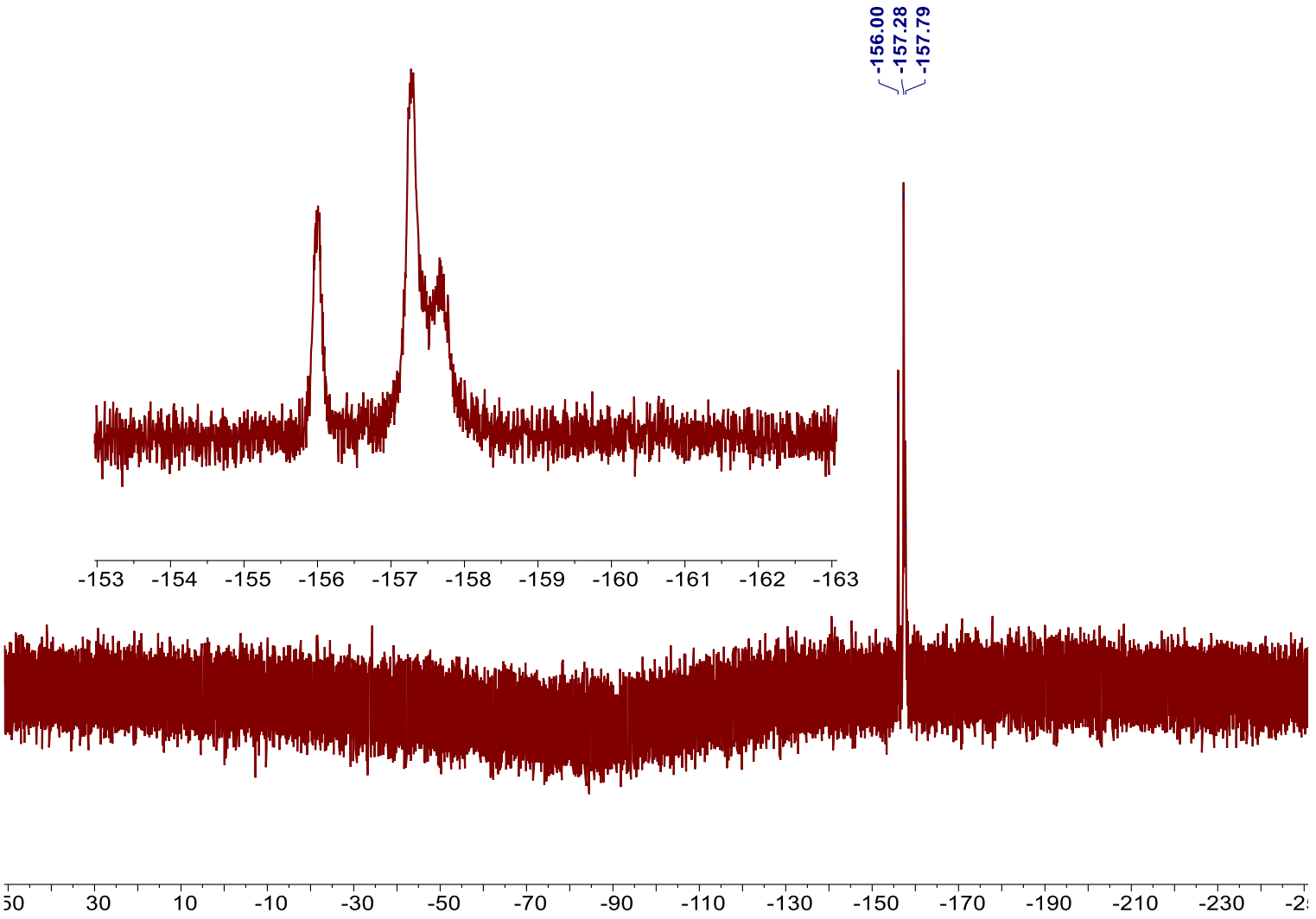


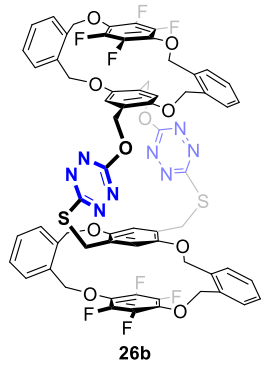


26b

^{13}C-^{19}F decoupled NMR

$CDCl_3$





26b

^{19}F NMR

$CDCl_3$