Charge-transfer inclusion complexes formation of tropylium cation with prism[6]arenes

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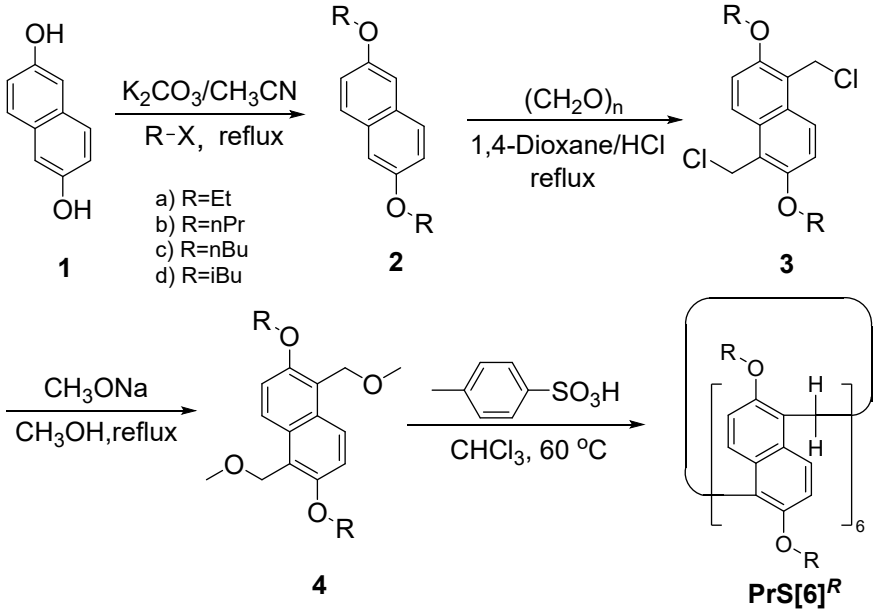
(28 pages)

Supporting Information

1. Materials and methods

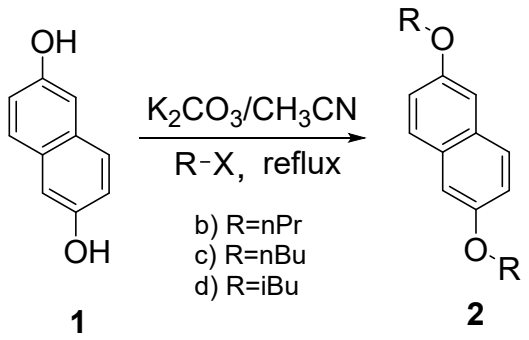
Ethyl-prism[6]arene (**PrS[6]^{Et}**) was synthesized according to literature procedure.[S1] All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. All the NMR spectra were collected on a Bruker Ascend^{TM} 400 MHz spectrometer. The melting points were collected on a SGW$_{®}$X-4A micro melting point apparatus. High Resolution Mass Spectrometry (HRMS) measurements were performed on a waters G2-XS QTof. Ultraviolet-visible (UV-vis) spectra were collected on a Shimadzu UV2550. The fluorescence experiments were conducted on a F-7000 spectrofluorophotometer (Japan Hitachi Nake high-tech enterprise).

2. Synthetic route for prism[6]arenes



Scheme S1. Synthesis of prism[6]arenes (**PrS[6]^{R}**).

3. Synthesis of ***2***[S2]



2b: In a 250 mL three-neck flask, 2,6-naphthalenediol (1.60 g, 0.01 mol), K_2CO_3 (6.90 g, 0.05mol), 1-iodopropane (10.2 g, 0.06 mol) and CH_3CN (60 mL) were added. The reaction mixture was stirred at reflux for 4 h. After the solid was filtered off, the solvent was removed. The residue was partitioned between water (50 mL) and dichloromethane (50 mL). The water layer was extracted with dichloromethane (50 mL × 3). The combined organic phase was washed with water (50 mL) and saturated NaCl solution (50 mL), and dried over anhydrous Na_2SO_4. After filtration, evaporation, and recrystallization in methanol, **2b** was obtained as a white solid (1.30 g, 53%), M.p. 133.7–134.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ(ppm): 7.61 (d, J = 8.8 Hz, 2H), 7.12 (dd, J = 8.8, 2.4 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 4.01 (t, J = 6.6 Hz, 4H), 1.85 (m, 4H), 1.08 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ(ppm): 155.66, 129.84, 128.16, 119.32, 107.09, 69.72, 22.78, 10.76.

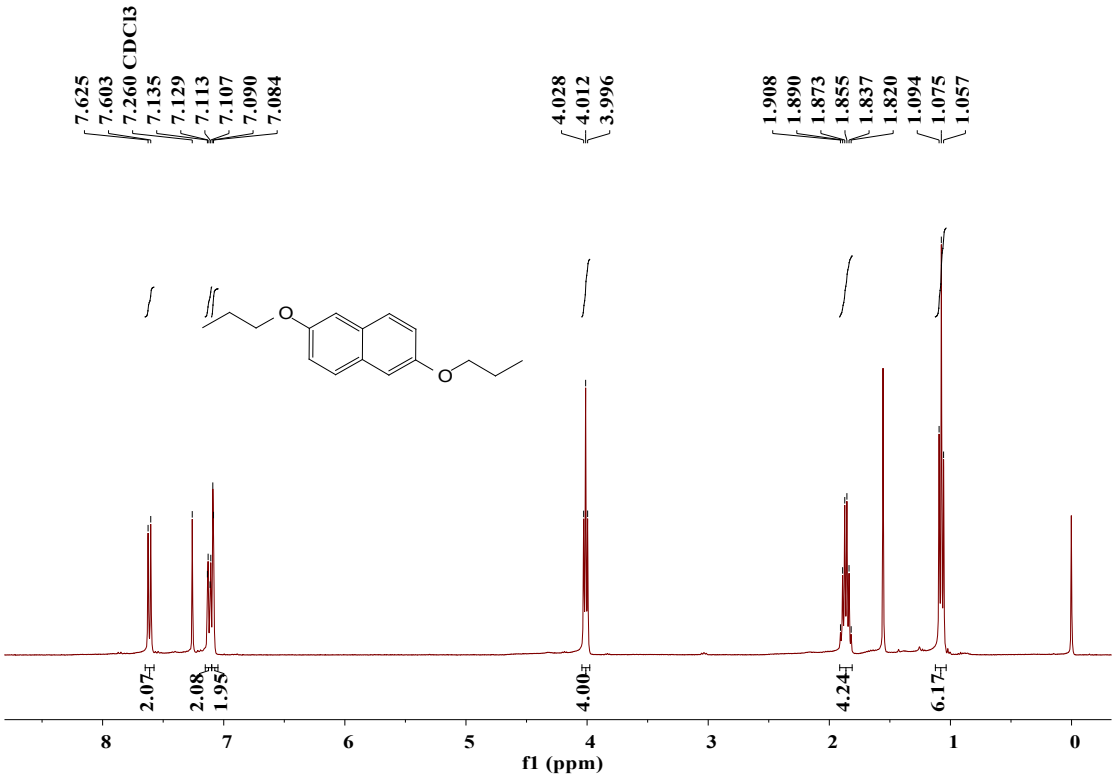


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **2b.**

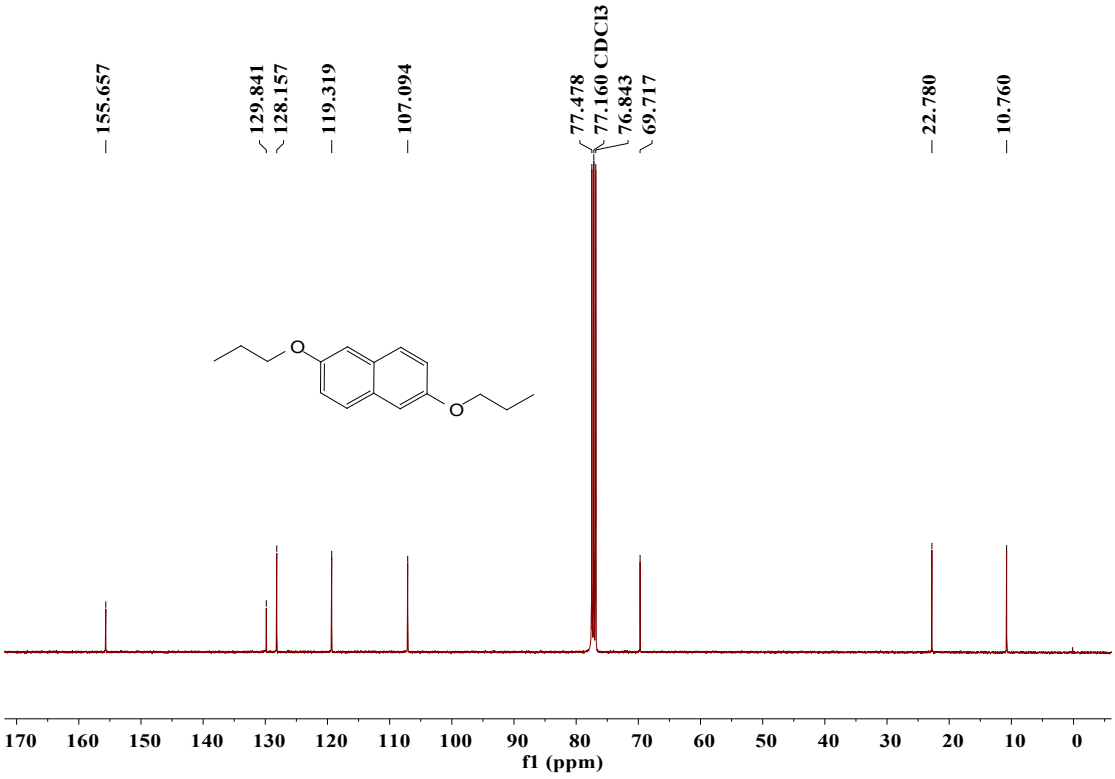


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **2b**.

2c: In a 250 mL three-neck flask, 2,6-naphthalenediol (5.00 g, 0.031 mol), K_2CO_3 (21.5 g, 0.15mol), *n*-butyl bromide (34.0 g, 0.31 mol) and CH_3CN (100 mL) were

added. The reaction mixture was stirred at reflux for 12 h. After the solid was filtered off, the solvent was removed. The residue was partitioned between water (100 mL) and dichloromethane (100 mL). The water layer was extracted with dichloromethane (100 mL × 3). The combined organic phase was washed with water (100 mL) and saturated NaCl solution (100 mL), and dried over anhydrous Na_2SO_4. After filtration, evaporation, and recrystallization in methanol, **2c** was obtained as a white solid (7.25 g, 85%), M.p. 94.6-96.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.61 (d, J = 8.8 Hz, 2H), 7.11 (dd, J = 8.8, 2.4 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 4.05 (t, J = 6.6 Hz, 4H), 1.82 (m, 4H), 1.54 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 155.68, 129.84, 128.15, 119.33, 107.09, 67.90, 31.53, 19.48, 14.05.

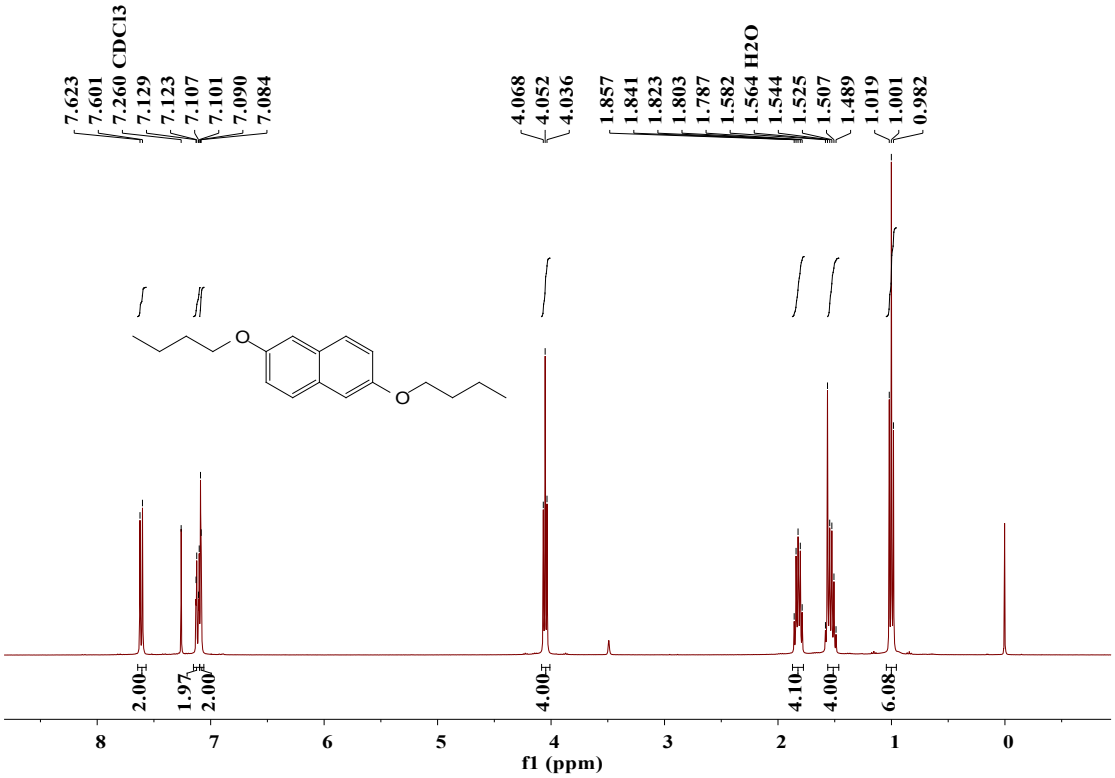


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **2c.**

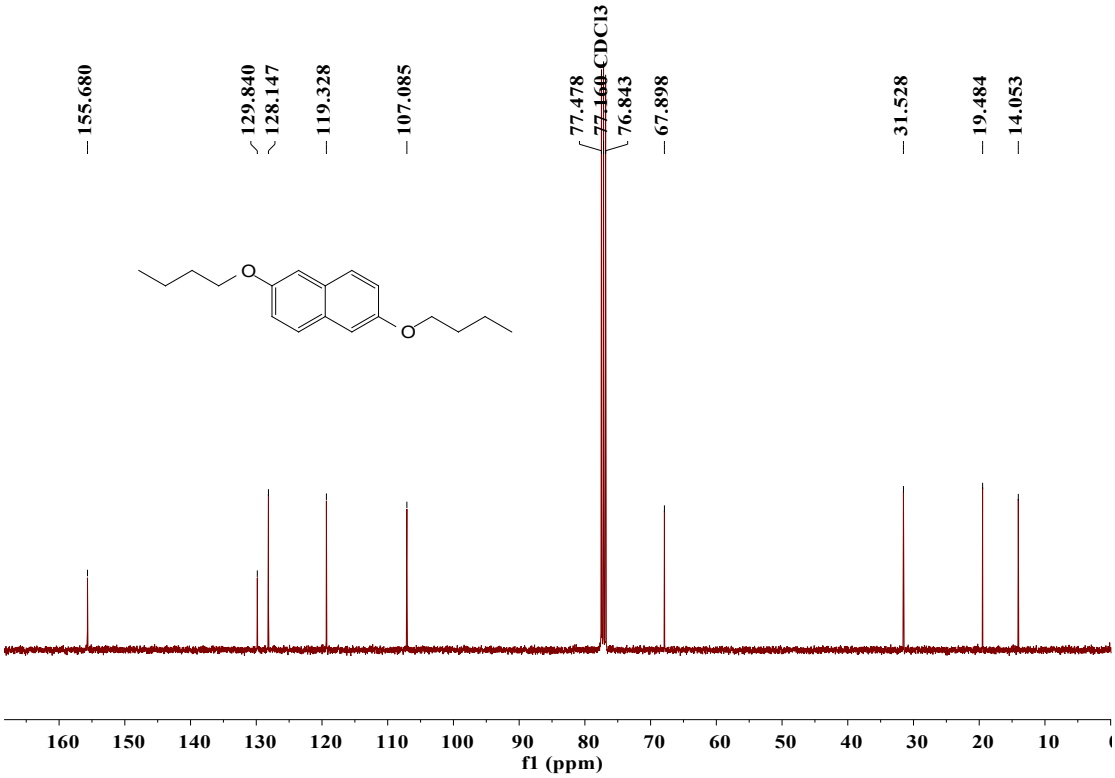


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **2c**.

2d: In a 250 mL three-neck flask, 2,6-naphthalenediol (2.60 g, 0.016 mol), K_2CO_3 (11.2 g, 0.080mol), isobutyl iodide (18.4 g, 0.10 mol) and CH_3CN (60 mL) were added. The reaction mixture was stirred at reflux for 24 h. After the solid was filtered off, the solvent was removed. The residue was partitioned between water (50 mL) and dichloromethane (50 mL). The water layer was extracted with dichloromethane (50 mL × 3). The combined organic phase was washed with water (50 mL) and saturated NaCl solution (50 mL), and dried over anhydrous Na_2SO_4. After filtration, evaporation, and recrystallization in methanol, **2d** was obtained as a white solid (0.22 g, 5%), M.p. 100.5-101.6 °C. ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ(ppm): 7.61 (d, J = 8.8 Hz, 2H), 7.12 (dd, J = 8.8, 2.4 Hz, 2H), 7.08 (d, J = 2.4 Hz, 2H), 3.81 (d, J = 6.6 Hz, 4H), 2.14 (m, 2H), 1.06 (d, J = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ(ppm): 155.78, 129.84, 128.11, 119.34, 107.11, 74.66, 28.47, 19.52.

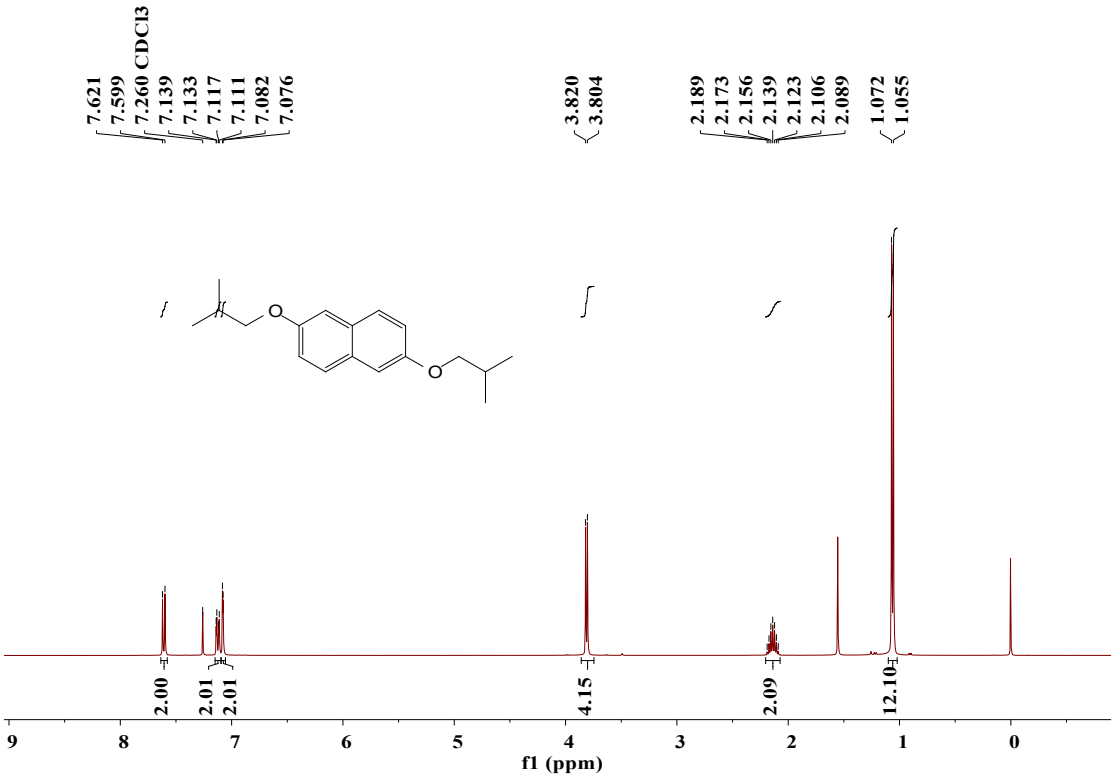


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **2d.**

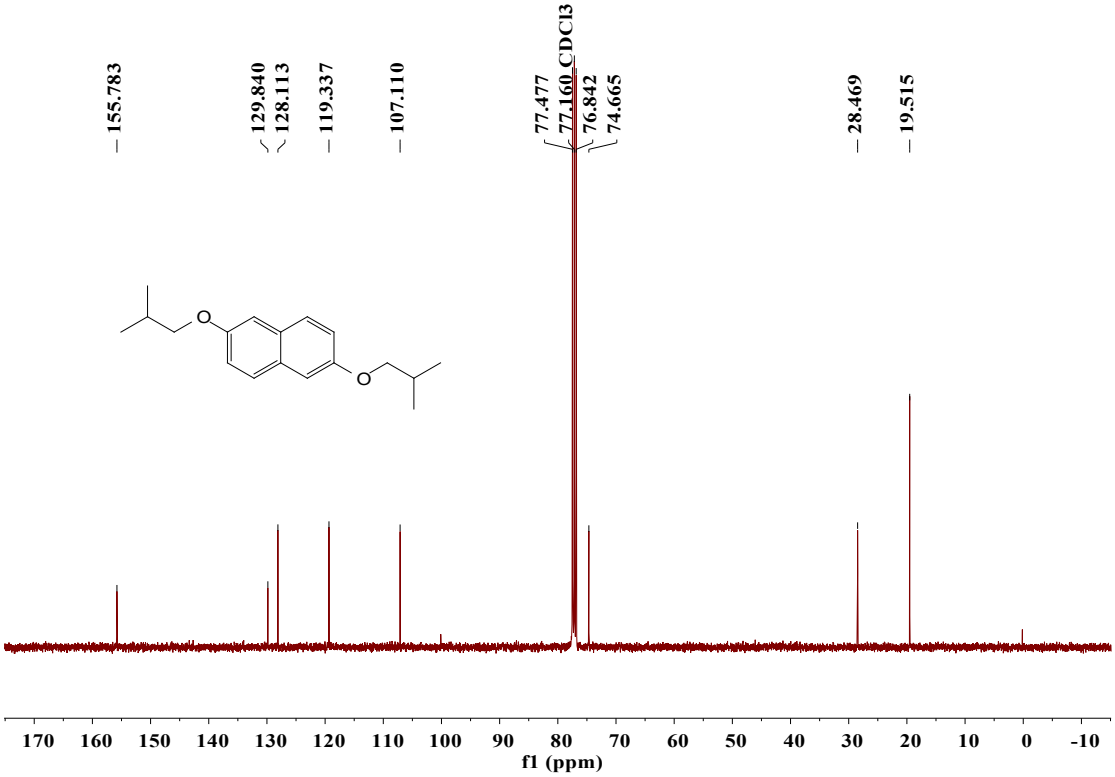
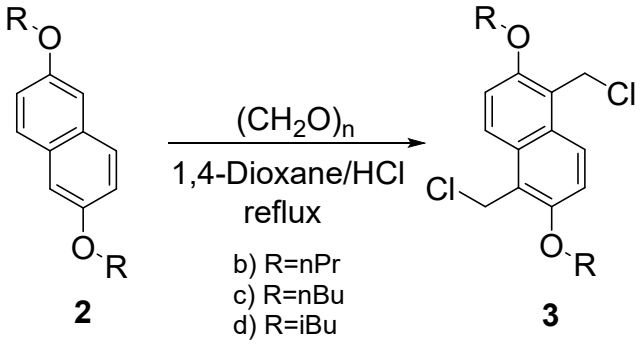


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **2d**.

*4. Synthesis of **3***



3b: Compound **2b** (0.80 g, 3.3 mmol), $(CH_2O)_n$ (0.30 g, 10.0 mmol), 1,4-dioxane 50 ml, and 10 ml 36%-38% HCl solution were added to an 150 ml three-necked flask, and the mixture was stirred at reflux temperature for 12 h. After the reaction solution cooled, the occurring precipitation were filtered and washed several times with distilled water to obtain a white solid which was pure enough for the next step. (1.0 g, 90%), M.p. 112.0-112.6°C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ(ppm): 8.04 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 9.3 Hz, 2H), 5.17 (s, 4H), 4.13 (t, J =6.4 Hz, 4H), 1.85 (m, 4H), 1.10 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ(ppm): 153.43, 128.20, 125.78, 119.19, 116.01, 71.41, 37.36, 23.05, 10.77. HRESI-MS: m/z calcd for $C_{18}H_{22}Cl_2O_2$ $[M + H]^+$ (100%), 341.1075, found 341.1070, error -1.5 ppm.

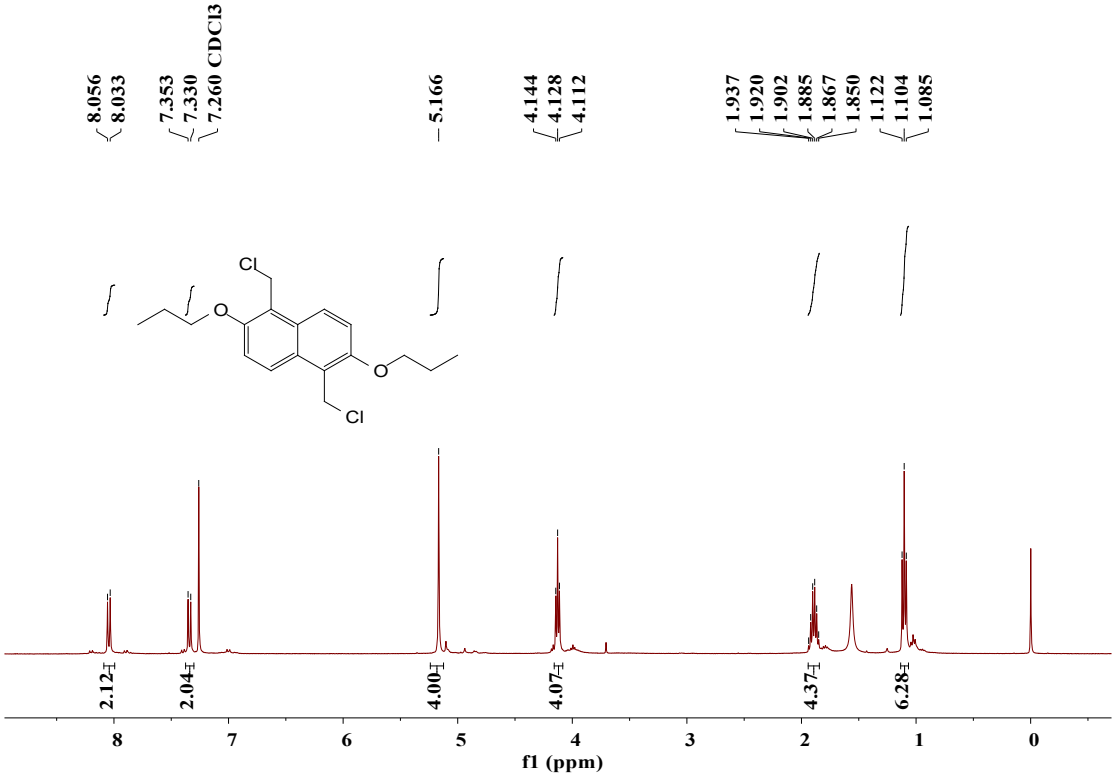


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **3b.**

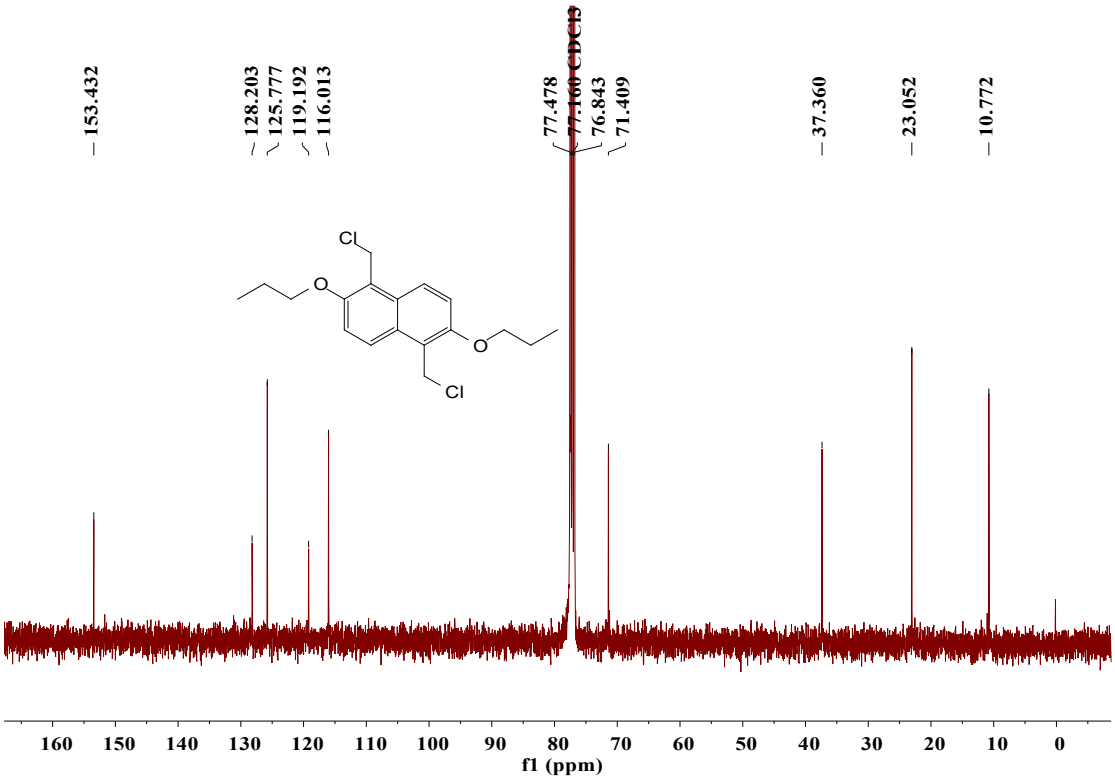


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **3b**.

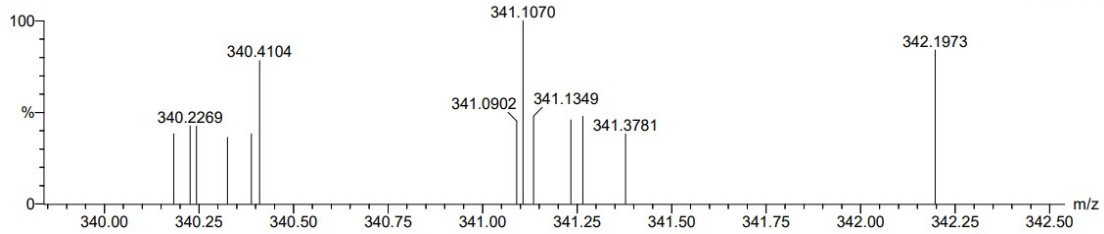


Figure S9. High-resolution mass spectrometry of **3b**. Assignment of main peaks: m/z 341.1070 $[M + H]^+$ (100%).

3c: Compound **2c** (2.20 g, 8.10 mmol), $(CH_2O)_n$ (0.73 g, 24.2 mmol), 1,4-dioxane 60 ml, and 10 ml 36%-38% HCl solution were added to an 150 ml three-necked flask, and the mixture was stirred at reflux temperature for 12 h. After the reaction solution cooled, the occurring precipitation were filtered and washed several times with distilled water to obtain a white solid which was pure enough for the next step (2.80 g, 94%), M.p. 123.7-124.1°C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ(ppm): 8.04 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 9.3 Hz, 2H), 5.17 (s, 4H), 4.13 (t, J = 6.4 Hz, 4H), 1.89 (m, 4H), 1.10 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm):153.43, 128.20, 125.78, 119.19, 116.01, 71.41, 37.36, 23.05, 10.77. HRESI-MS:

m/z calcd for $C_{20}H_{26}Cl_2O_2$ $[M + Na]^+$ (100%), 391.1202, found 391.1202, error 0 ppm.

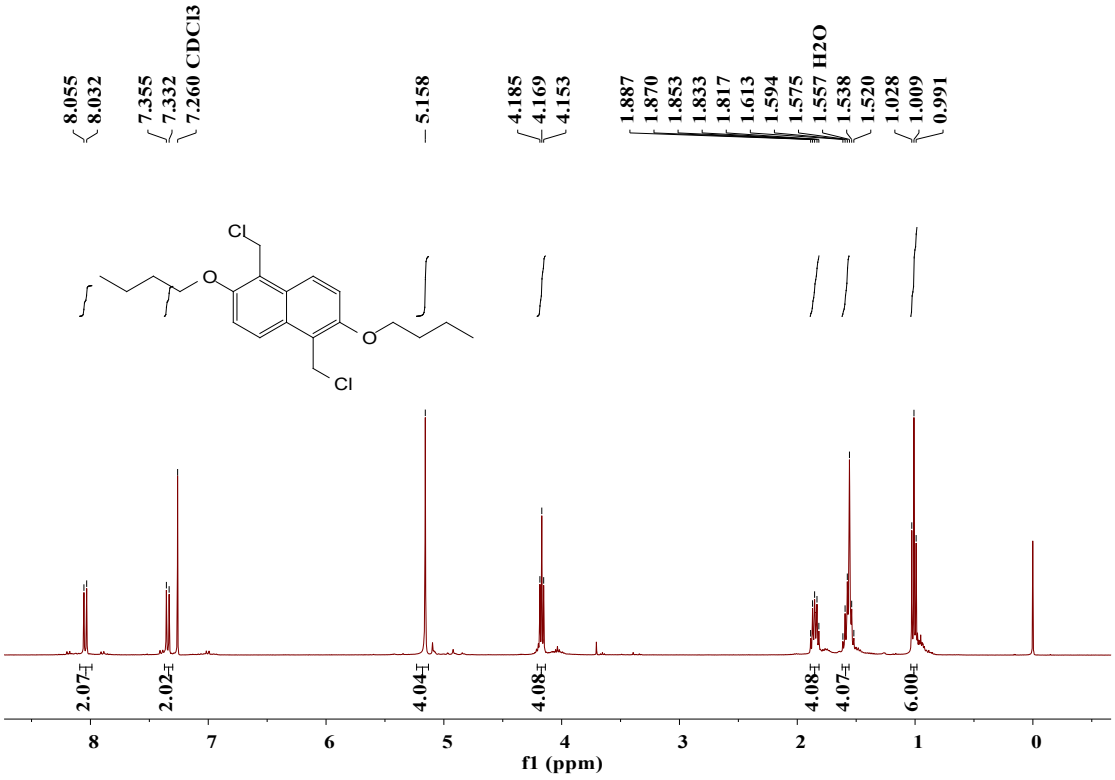


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **3c.**

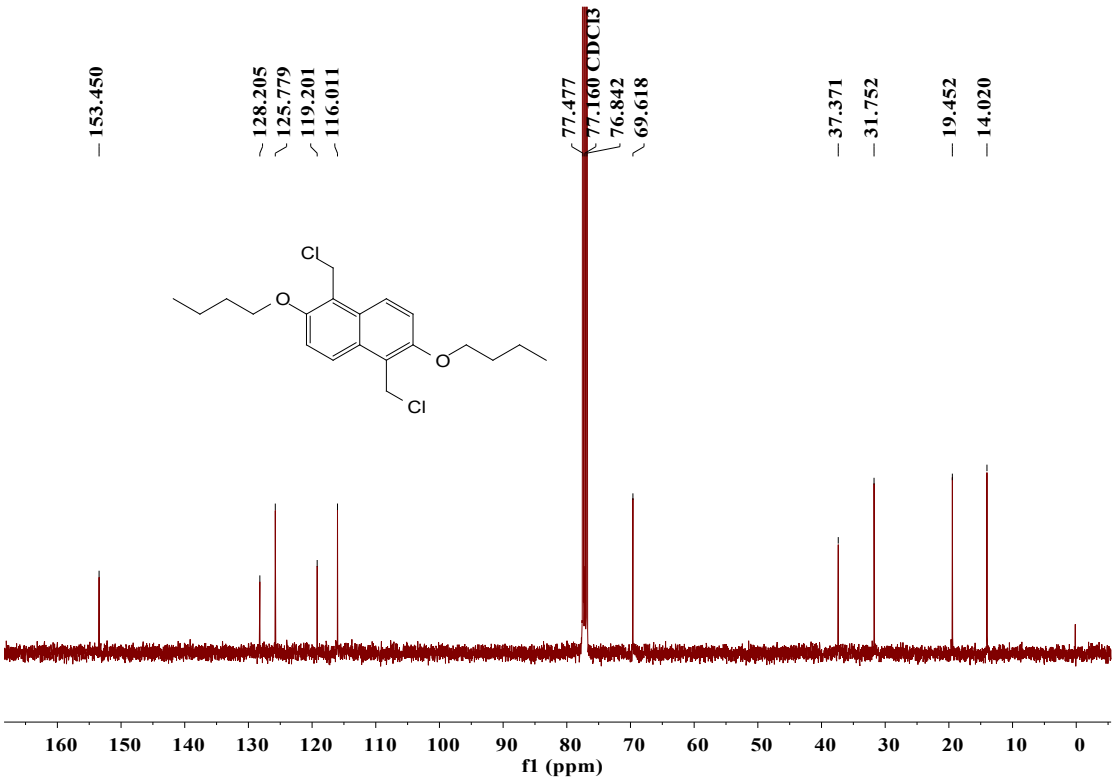


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **3c**.

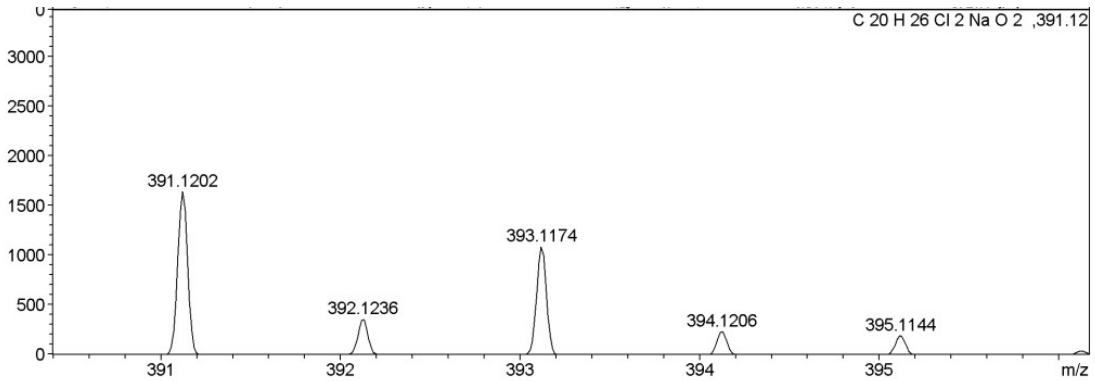


Figure S12. High-resolution mass spectrometry of **3c**. Assignment of main peaks: m/z 391.1202 $[M + Na]^+$ (100%).

3d: Compound **2d** (1.10 g, 4 mmol), $(CH_2O)_n$ (0.36 g, 12 mmol), 1,4-dioxane 50 ml, and 10 ml 36%-38% HCl solution were added to an 150 ml three-necked flask, and the mixture was stirred at reflux temperature for 12 h. After the reaction solution cooled, the occurring precipitation were filtered and washed several times with distilled water to obtain a white solid which was pure enough for the next step (1.35 g, 92%), M.p. 98.7- 99.5°C. ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.04 (d, J = 9.3 Hz, 2H), 7.33 (d, J = 9.3 Hz, 2H), 5.17 (s, 4H), 3.93 (d, J = 6.4 Hz, 4H), 2.2 (m, 2H), 1.10 (d, J = 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 153.47, 128.13, 125.71, 118.98, 115.85, 76.09, 37.33, 28.77, 19.45. HREI-MS: m/z calcd for $C_{20}H_{26}Cl_2O_2$ $[M + H]^+$ (100%), 369.1388, found 369.1395, error 1.9 ppm.

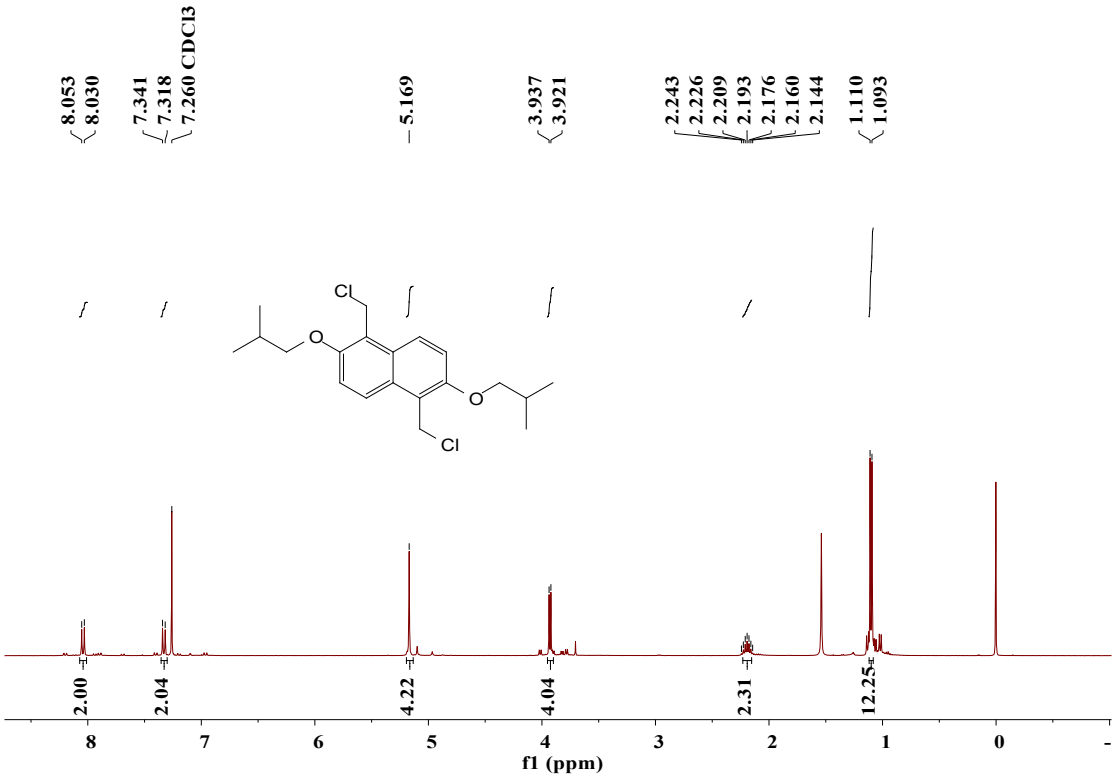


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **3d.**

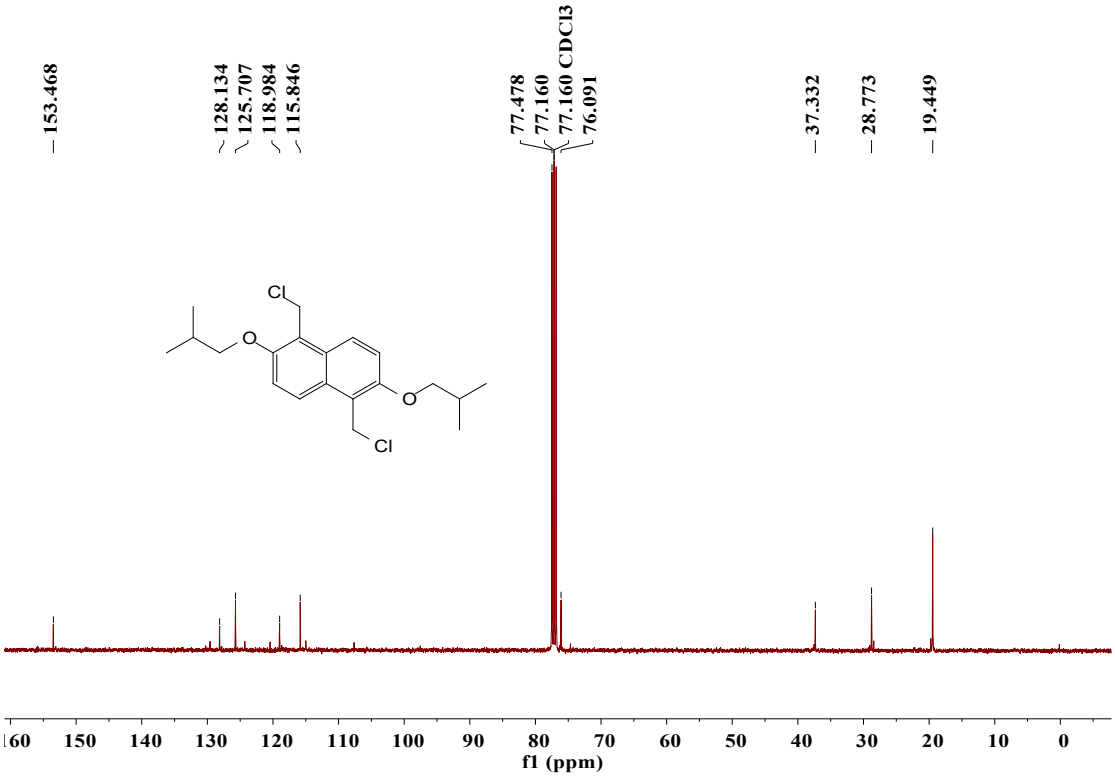


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **3d**.

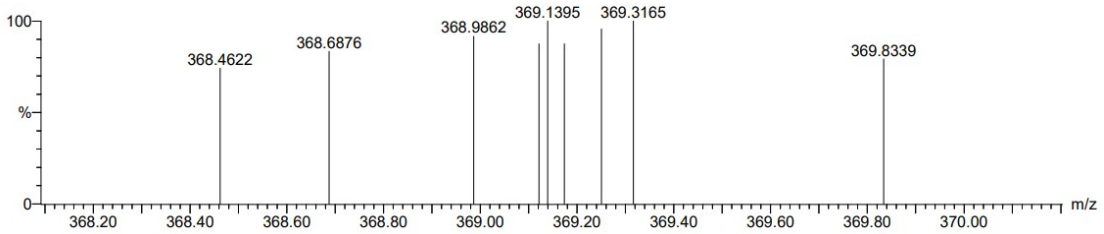
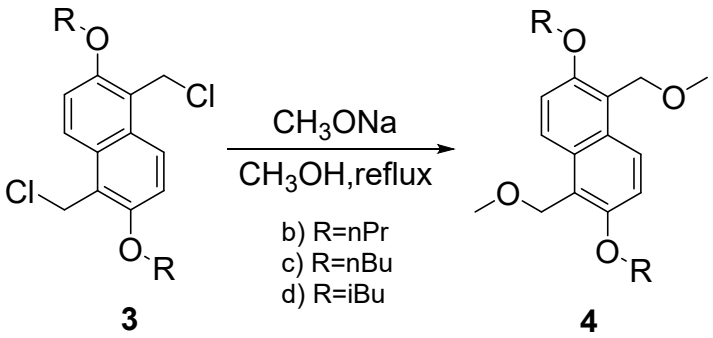


Figure S15. High-resolution mass spectrometry of **3d**. Assignment of main peaks: m/z 369.1395 $[M + H]^+$ (100%).

*5. Synthesis of **4***



4b: In a 150 ml round-bottom flask, compound **3b** (1.50 g, 4.4 mmol), methanol (50 ml), CH_3ONa (2.38 g, 44.0 mmol) were added and the mixture was under reflux for 8 h. After the reaction solution was concentrated, it was poured into ice water, and the precipitate was collected and filtered to obtain a white solid. After it was purified by chromatography on silica gel (PE/DCM = 1/2, *v*/*v*), 1.15 g of **4b** was obtained as a white solid (yield: 78%), M.p. 128.9-129.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.08 (d, J = 9.3 Hz, 2H), 7.29 (d, J = 9.3 Hz, 2H), 4.98 (s, 4H), 4.06 (t, J = 6.4 Hz, 4H), 3.39 (s, 6H), 1.85 (m, 4H), 1.08 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ(ppm): 153.73, 129.65, 126.21, 119.28, 115.95, 71.58, 64.65, 57.81, 23.12, 10.84. HREI-MS: m/z calcd for $C_{20}H_{28}O_4$ $[M + Na]^+$ (100%), 355.1885, found 355.1875, error -2.8 ppm.

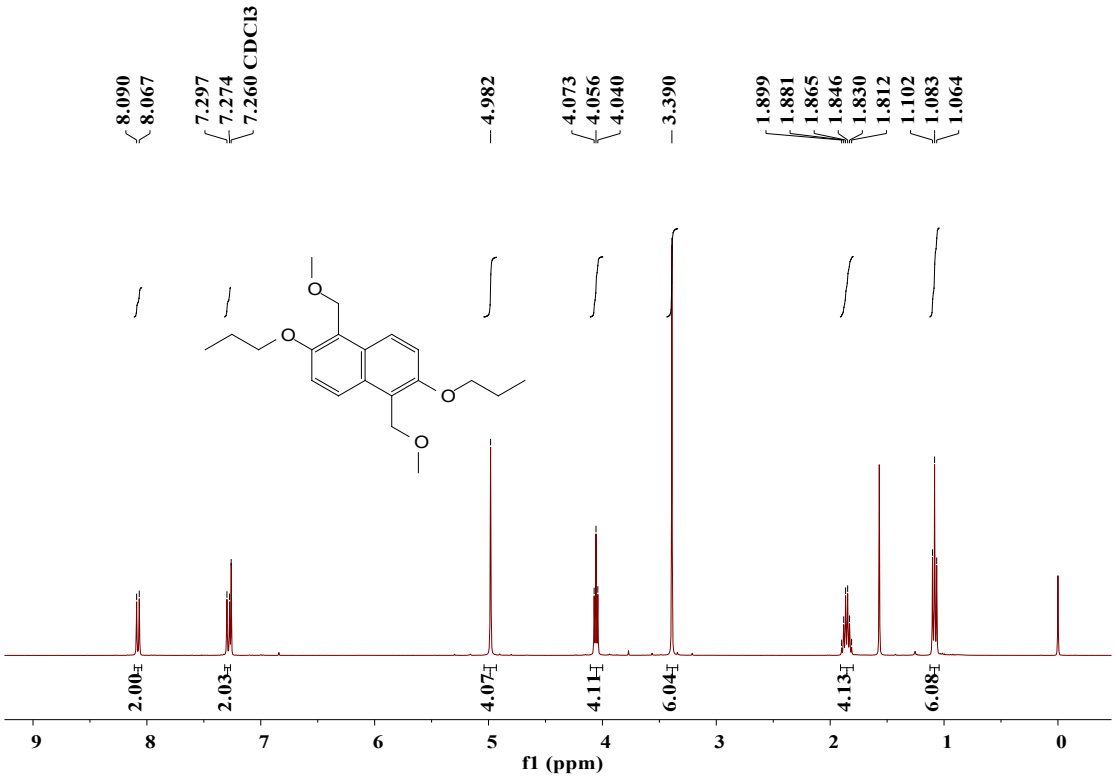


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **4b.**

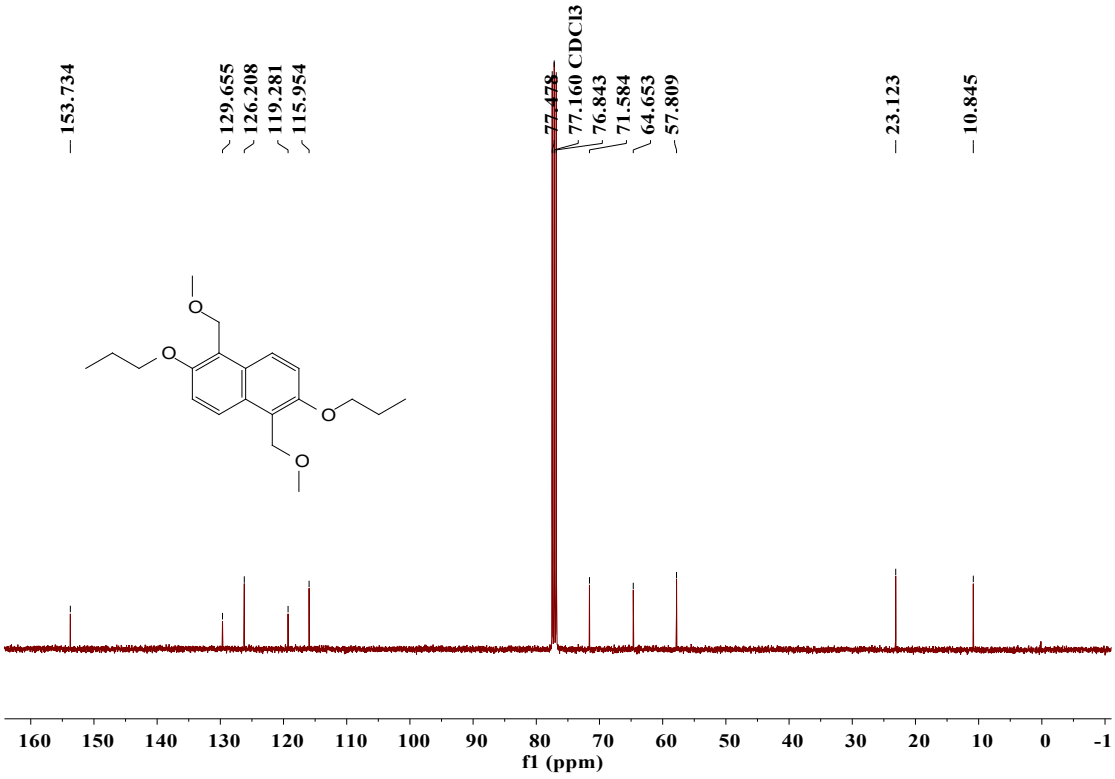


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **4b**.

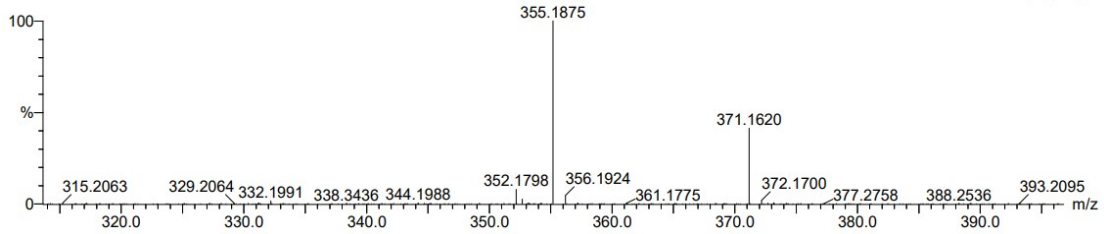


Figure S18. High-resolution mass spectrometry of **4b**. Assignment of main peaks: m/z 355.1875 $[M + Na]^+$ (100%).

4c: In a 250 ml round-bottom flask, compound **3c** (5.0 g, 13.5 mmol), methanol (100 ml), CH_3ONa (7.33 g, 135 mmol), were added and the mixture was under reflux for 8 h. After the reaction solution was concentrated, it was poured into ice water, and the precipitate was collected and filtered to obtain a white solid. After it was purified by chromatography on silica gel (PE/DCM = 1/1, *v*/*v*), 3.0 g of **4c** was obtained as a white solid (yield: 61%), M.p. 121.5-121.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.08 (d, J = 9.3 Hz, 2H), 7.29 (d, J = 9.3 Hz, 2H), 4.97 (s, 4H), 4.10 (t, J = 6.4 Hz, 4H), 3.39 (s, 6H), 1.82 (m, 4H), 1.55 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 153.75, 129.65, 126.20, 119.29, 115.95, 69.76, 64.67, 57.79, 31.86, 19.51, 14.03.

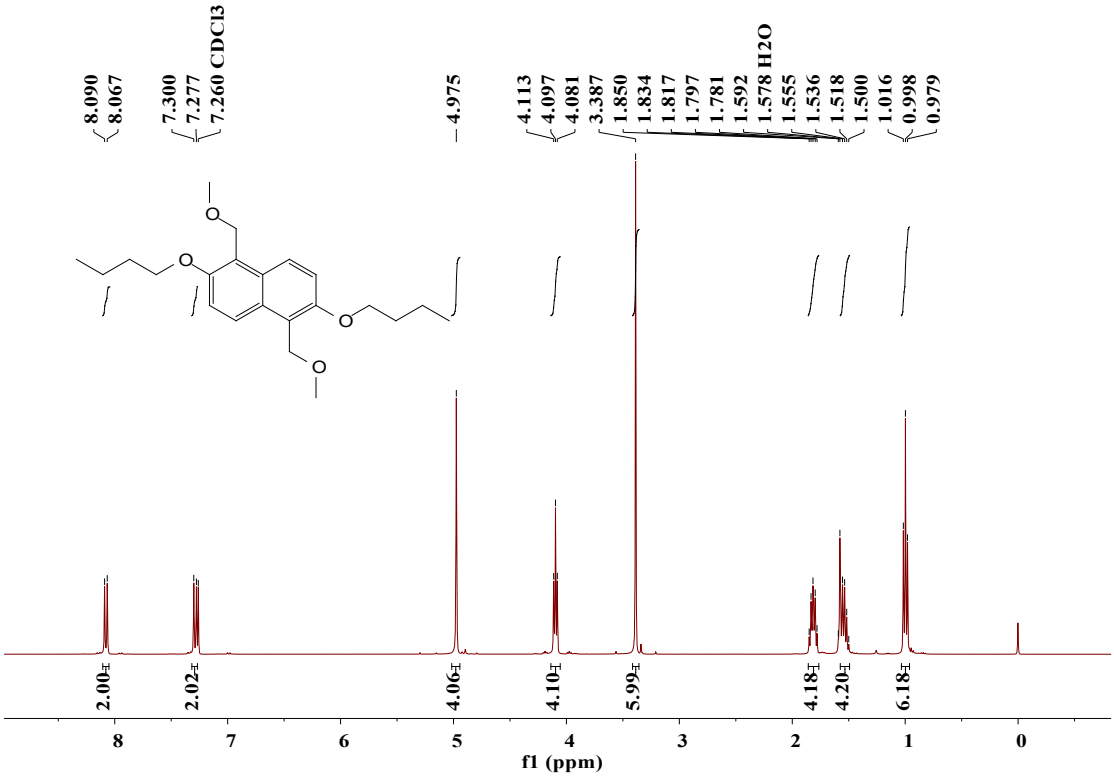


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **4c.**

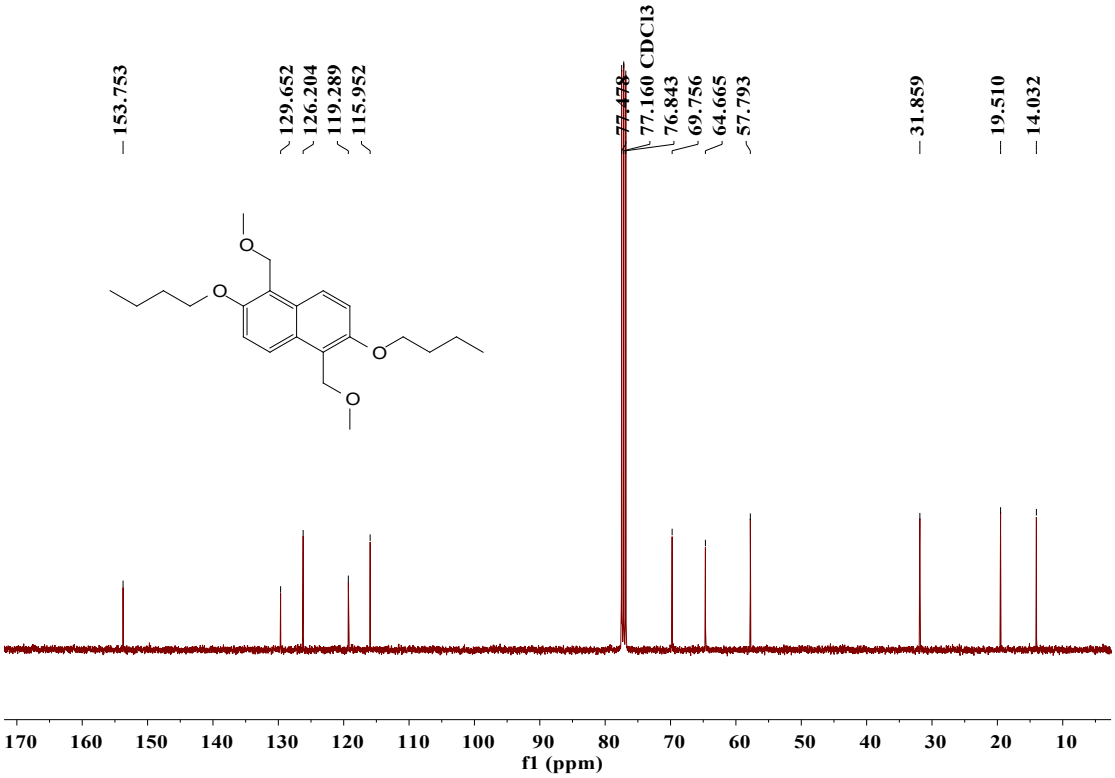


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **4c**.

4d: In a 150 ml round-bottom flask, compound **3d** (1.35 g, 3.67 mmol), methanol (50 ml), CH_3ONa (1.98 g, 36.7 mmol), were added and the mixture was under reflux for 8 h. After the reaction solution was concentrated, it was poured into ice water, and the precipitate was collected and filtered to obtain a white solid. After it was purified by chromatography on silica gel (PE/DCM = 1/1, *v*/*v*), 1.0 g of **4d** was obtained as a white solid (yield: 76%), M.p. 75.4-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.10 (d, J = 9.3 Hz, 2H), 7.29 (d, J = 9.3 Hz, 2H), 5.01 (s, 4H), 3.87 (d, J = 6.4 Hz, 4H), 3.40 (s, 6H), 2.17 (m, 2H), 1.10 (d, J = 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 153.77, 129.58, 126.17, 119.04, 115.72, 64.59, 57.72, 28.82, 19.50. HREI-MS: m/z calcd for $C_{22}H_{32}O_4$ $[M + H]^+$ (100%), 361.2373, found 361.2373, error 0 ppm.

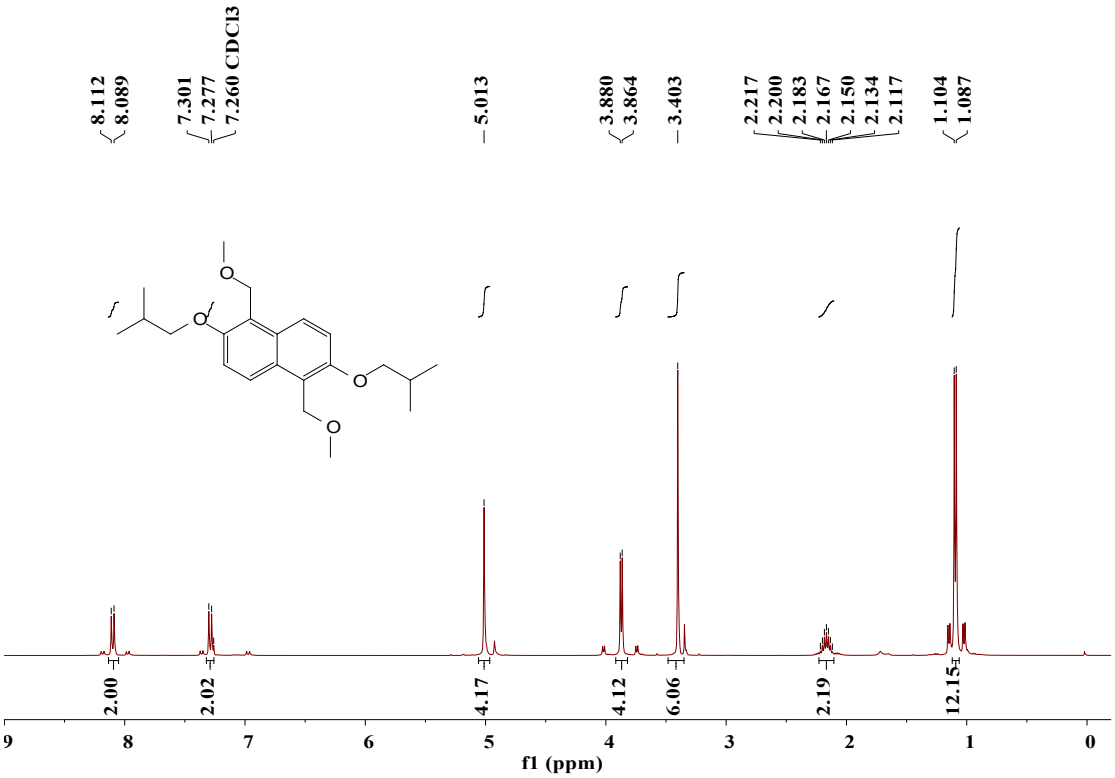


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **4d.**

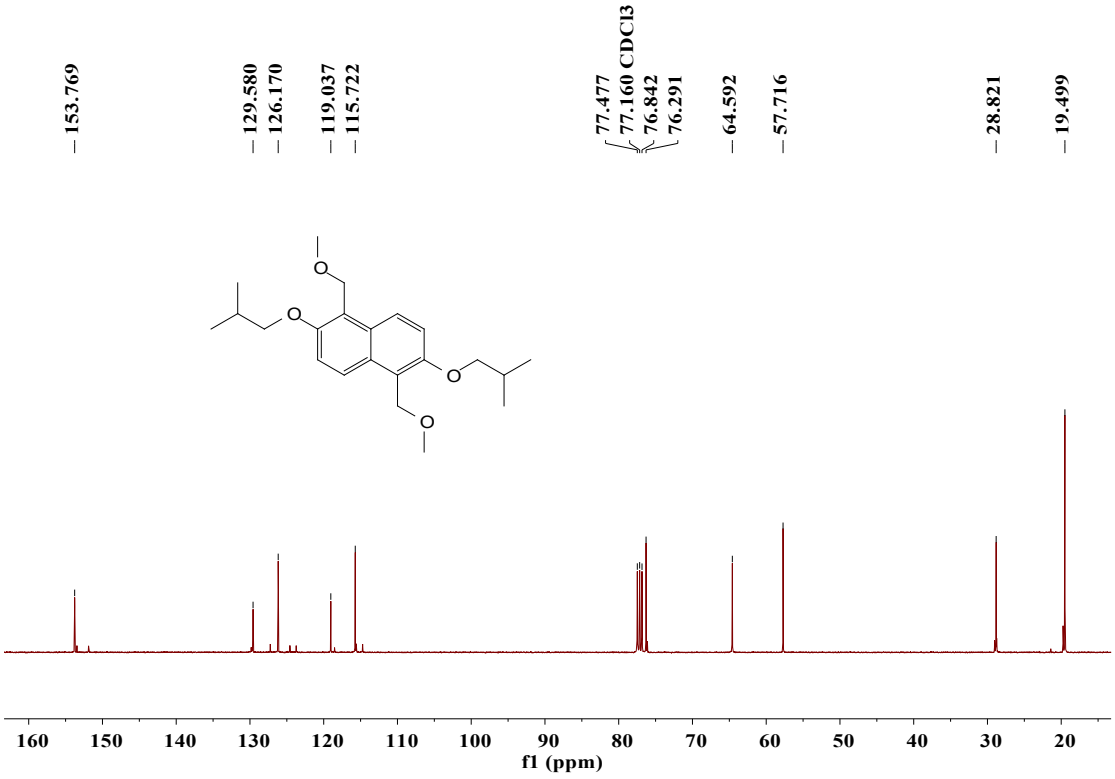


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **4d**.

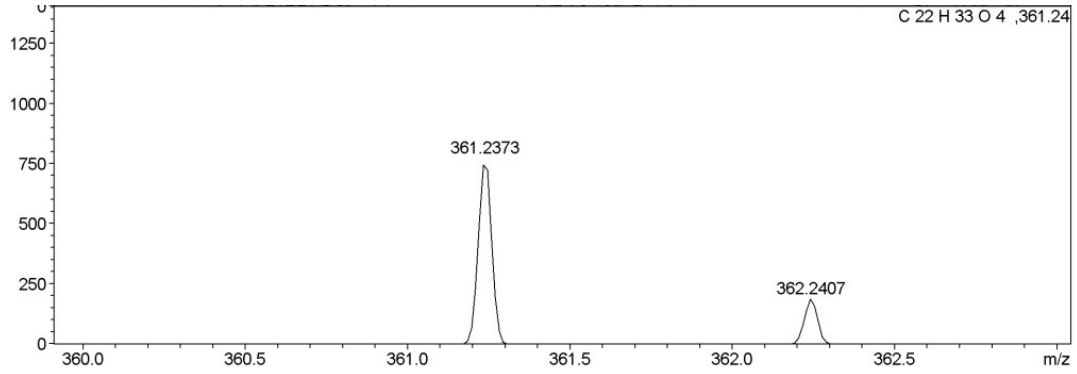
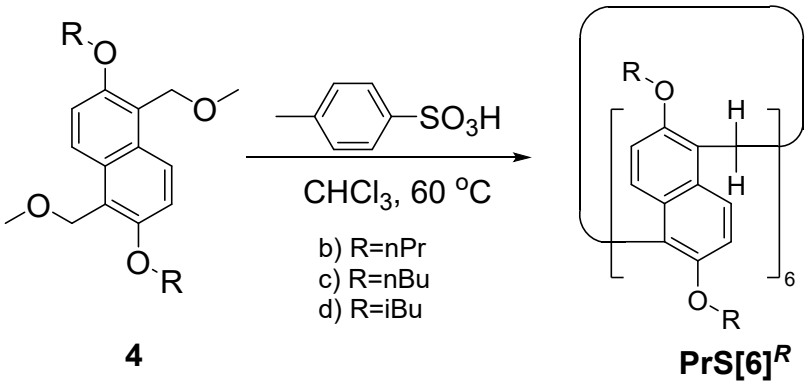


Figure S23. High-resolution mass spectrometry of **4d**. Assignment of main peaks: m/z 361.2373 $[M + H]^+$ (100%).

*6. Synthesis of prism[6]arenes (**PrS[6]^R**)*



4 **PrS[6]^R**

PrS[6]^{nPr}: To a 100 mL round bottom flask **4b** (120 mg, 0.36 mmol), 4-methylbenzenesulfonic acid monohydrate (68.7 mg, 0.36 mmol) and $CHCl_3$ (40 mL) were added. The mixture was heated at 60 ºC for 15 min. Then dichloromethane (20 mL) was added and the solution was washed with water (30 mL × 3). The solvent was removed and the residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 2:1 → 1:2) to obtain **PrS[6]^{nPr}** as a white solid (63.7 mg, 69%), M.p.＞310 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature) δ (ppm): 8.29 (s, 4H), 7.96 (d, 4H), 7.56 (s, 4H), 7.37 (s, 4H), 7.02 (d, J = 8.7 Hz, 4H), 6.36 (s, 4H), 4.87 (s, 8H), 4.46 (s, 4H), 4.22 (d, J = 32.2 Hz, 12H), 4.06 – 3.96 (m, 4H), 3.01 (s, 4H), 2.26 (s, 4H), 1.94 (d, J = 37.3 Hz, 16H), 1.23 – 0.99 (m, 24H), -0.10 (d, J = 27.7 Hz, 8H), -0.58 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 152.91, 151.50, 129.97, 125.20, 124.55, 124.07, 115.55, 114.74, 114.07, 71.60, 71.58, 71.19, 23.42, 21.74, 21.38, 11.16, 10.16. HREI-MS: m/z calcd for $C_{102}H_{120}O_{12}$ $[M + H]^+$ (100%), 1537.8858, found 1537.8877, error 1 ppm.

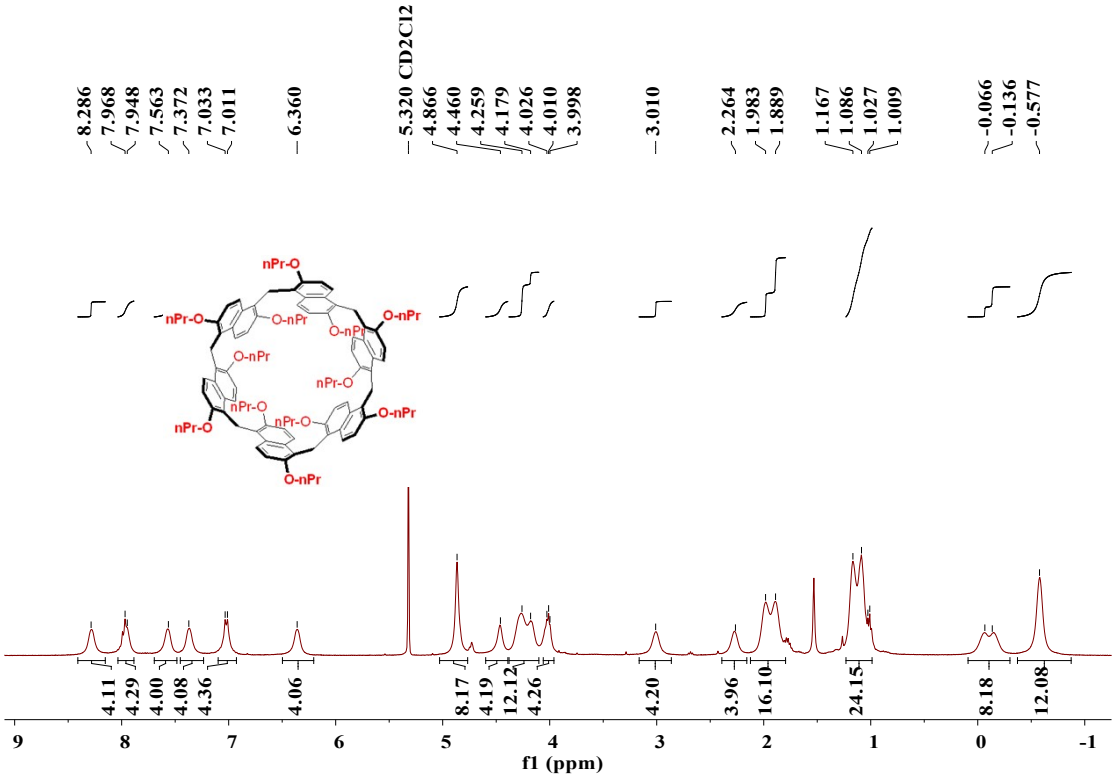


Figure S24. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, room temperature) of **PrS[6]^{nPr}.**

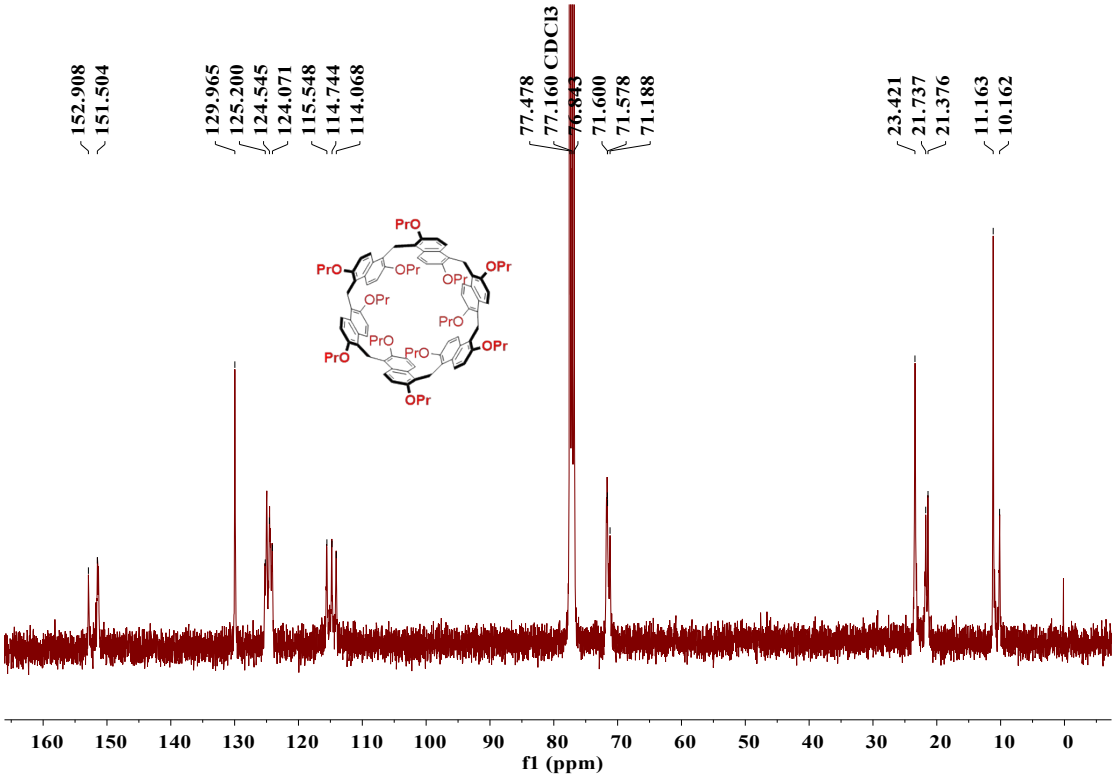


Figure S25. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **PrS[6]^{nPr}**.

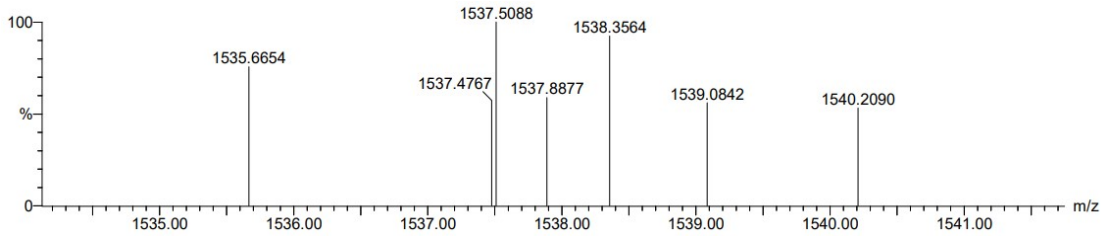


Figure S26. High-resolution mass spectrometry of **PrS[6]^{nPr}**. Assignment of main peaks: m/z 1537.8877 $[M + H]^+$ (100%).

PrS[6]^{nBu}: To a 100 mL round bottom flask **4c** (200 mg, 0.55 mmol), 4-methylbenzenesulfonic acid monohydrate (105 mg, 0.55 mmol) and $CHCl_3$ (50 mL) were added. The mixture was heated at 60 ºC for 15 min. Then dichloromethane (20 mL) was added and the solution was washed with water (30 mL × 3). The solvent was removed and the residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 2:1 → 1:1) to obtain **PrS[6]^{nBu}** as a white solid (64 mg, 40%), M.p.＞310 °C. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, room temperature) δ (ppm): 7.70 (s, 4H), 7.37 (d, J = 26.4 Hz, 4H), 7.05 (s, 4H), 6.74 (s, 4H), 6.41 (d, J = 9.3 Hz, 4H), 5.77 (s, 4H), 4.23 (s, 8H), 3.84 – 3.39 (m, 20H), 2.33 (s, 4H), 1.97 (s, 4H), 1.27 (d, J = 32.9 Hz, 26H), 0.96 – 0.68 (m, 14H), 0.37 (d, J = 22.4 Hz, 24H), -0.78 (d, J = 60.9 Hz, 12H), -1.22 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 151.75, 151.54, 151.48, 130.06, 124.88, 124.62, 124.37, 115.08, 114.58, 114.52, 69.46, 31.94, 19.61, 19.55, 14.01. HREI-MS: m/z calcd for $C_{114}H_{144}O_{12}$ $[M + Na]^+$ (100%), 1728.0555, found 1728.0548, error -0.4 ppm.

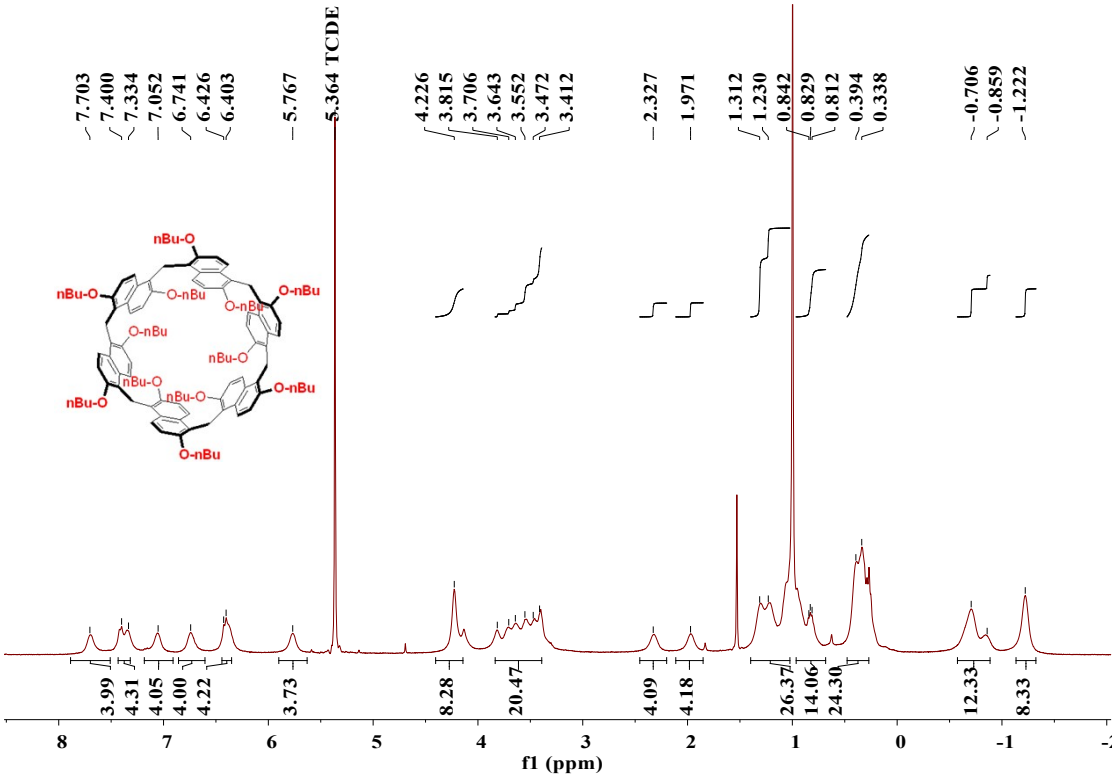


Figure S27. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, room temperature) of **PrS[6]**^{nBu}.

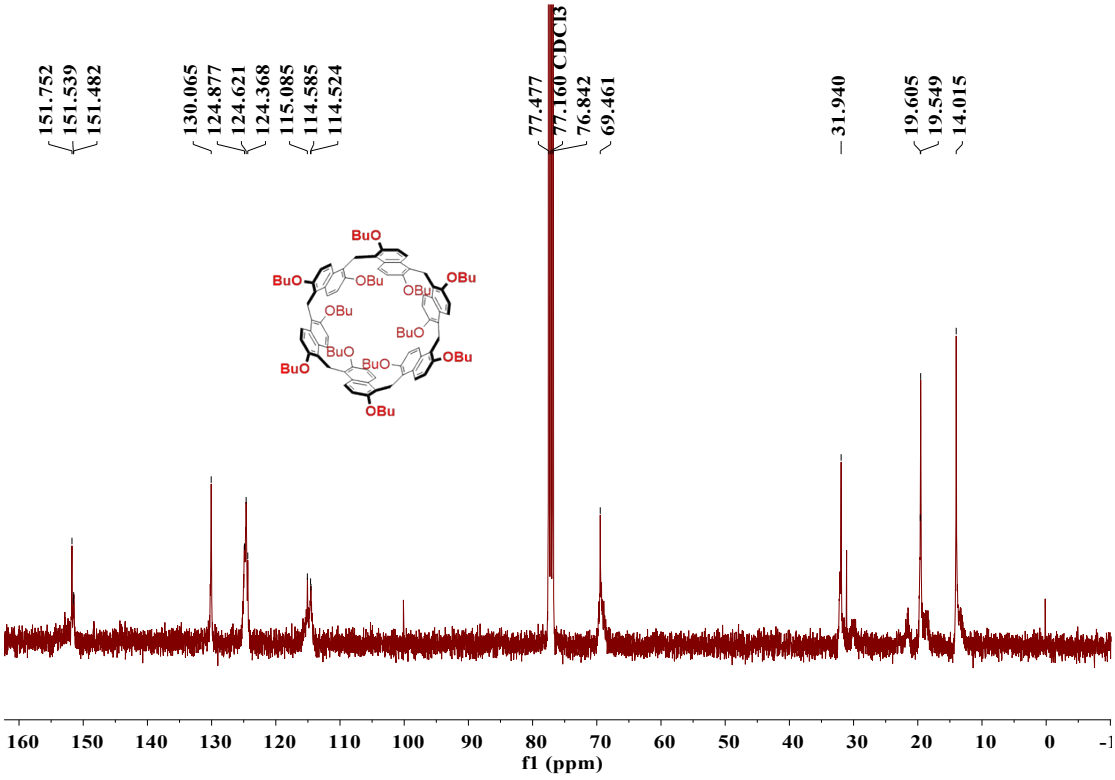


Figure S28. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **PrS[6]**^{nBu}.

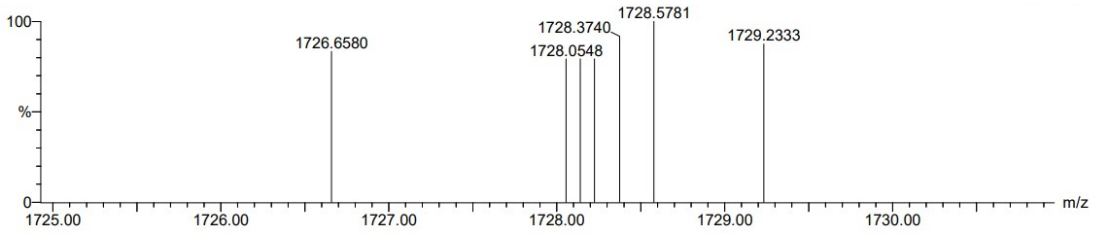


Figure S29. High-resolution mass spectrometry of **PrS[6]^{nBu}**. Assignment of main peaks: m/z 1728.0548 $[M + Na]^+$ (100%).

PrS[6]^{iBu}: To a 100 mL round bottom flask **4d** (100 mg, 0.28 mmol), 4-methylbenzenesulfonic acid monohydrate (52.9 mg, 0.28 mmol) and $CHCl_3$ (30 mL) were added. The mixture was heated at 60 ºC for 15 min. Then dichloromethane (20 mL) was added and the solution was washed with water (30 mL × 3). The solvent was removed and the residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 2:1 → 1:1) to obtain **PrS[6]^{iBu}** as a white solid (33.8 mg, 43%), M.p.＞310 °C. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.31 (d, J = 9.5 Hz, 4H), 8.07 (d, *J* = 9.2 Hz, 4H), 7.72 (d, *J* = 9.3 Hz, 4H), 7.31 (d, *J* = 9.4 Hz, 4H), 7.02 (d, *J* = 9.4 Hz, 4H), 6.38 (d, *J* = 9.3 Hz, 4H), 4.90 (s, 7H), 4.45 (s, 3H), 4.11 (t, *J* = 7.6 Hz, 3H), 4.04 – 3.90 (m, 7H), 3.88 – 3.72 (m, 7H), 2.99 (t, *J* = 8.0 Hz, 3H), 2.56 (t, *J* = 8.4 Hz, 3H), 2.36 – 1.97 (m, 10H), 1.28 – 0.93 (m, 55H), 0.47 – 0.27 (m, 4H), -0.27 (d, *J* = 6.2 Hz, 9H), -1.11 (d, *J* = 5.9 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 152.90, 151.07, 130.07, 129.54, 125.05, 124.80, 124.52, 124.29, 124.12, 123.11, 114.41, 114.01, 113.91, 75.59, 75.37, 29.23, 29.04, 28.94, 26.72, 21.33, 19.89, 19.78, 19.68, 18.07. HREI-MS: m/z calcd for $C_{114}H_{144}O_{12}$ $[M + Na]^+$ (100%), 1728.0555, found 1728.0580, error 1.4 ppm.

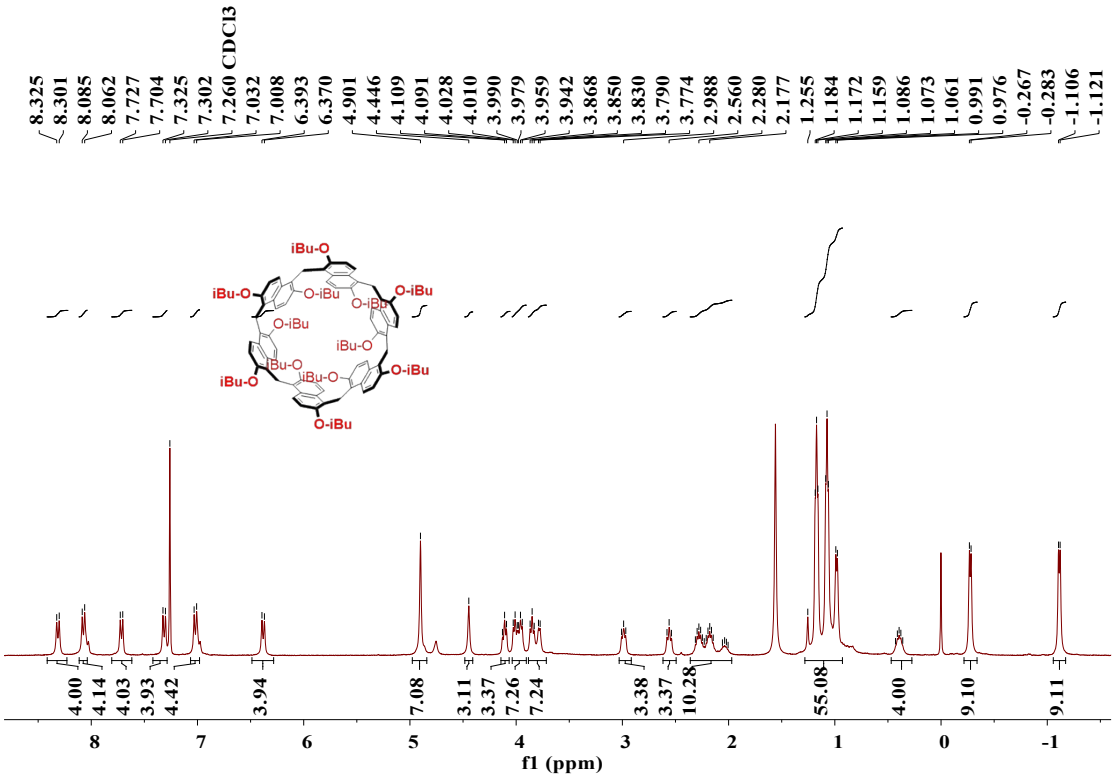


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **PrS[6]^{iBu}.**

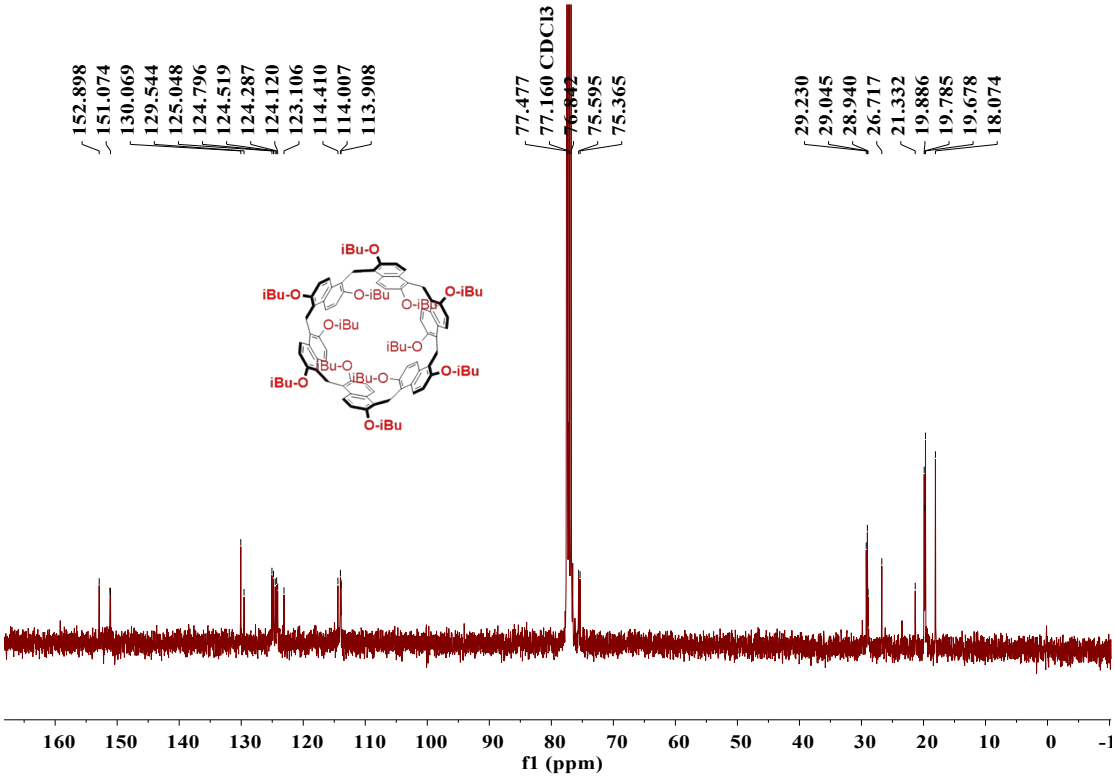


Figure S31. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **PrS[6]^{iBu}**.

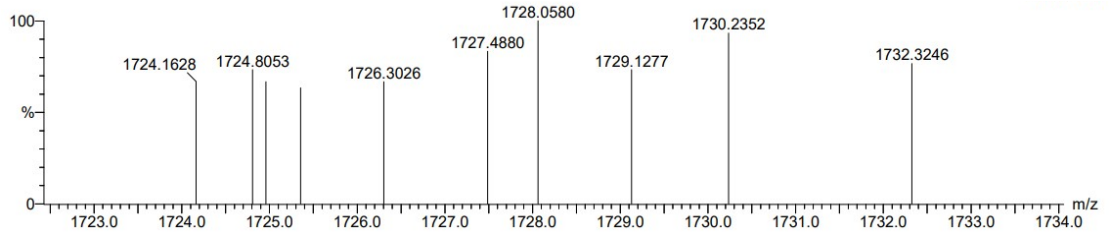
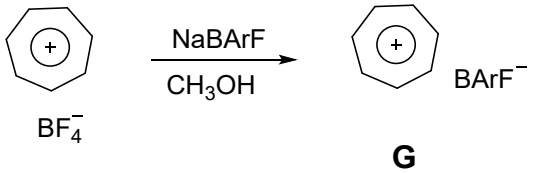


Figure S32. High-resolution mass spectrometry of **PrS[6]^{iBu}**. Assignment of main peaks: m/z 1728.0580 $[M + Na]^+$ (100%).

*7. Synthesis of tropylium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (**G**)*



G

The solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate hydrate (NaBArF) (135 mg, 0.15 mmol) in 30 ml dry methanol was added tropylium tetrafluoroborate (25 mg, 0.14 mmol). The resulting solution was stirred at room temperature for 12 hours. Then the solvent was removed in vacuo. The residue was suspended in H_2O (15 mL), extracted with CH_2Cl_2 (15 mL × 3). The organic layer was collected, dried (Na_2SO_4), and concentrated to give **G** (120 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ(ppm): 8.79 (s, 7H), 7.73 (s, 8H), 7.49 (s, 4H).

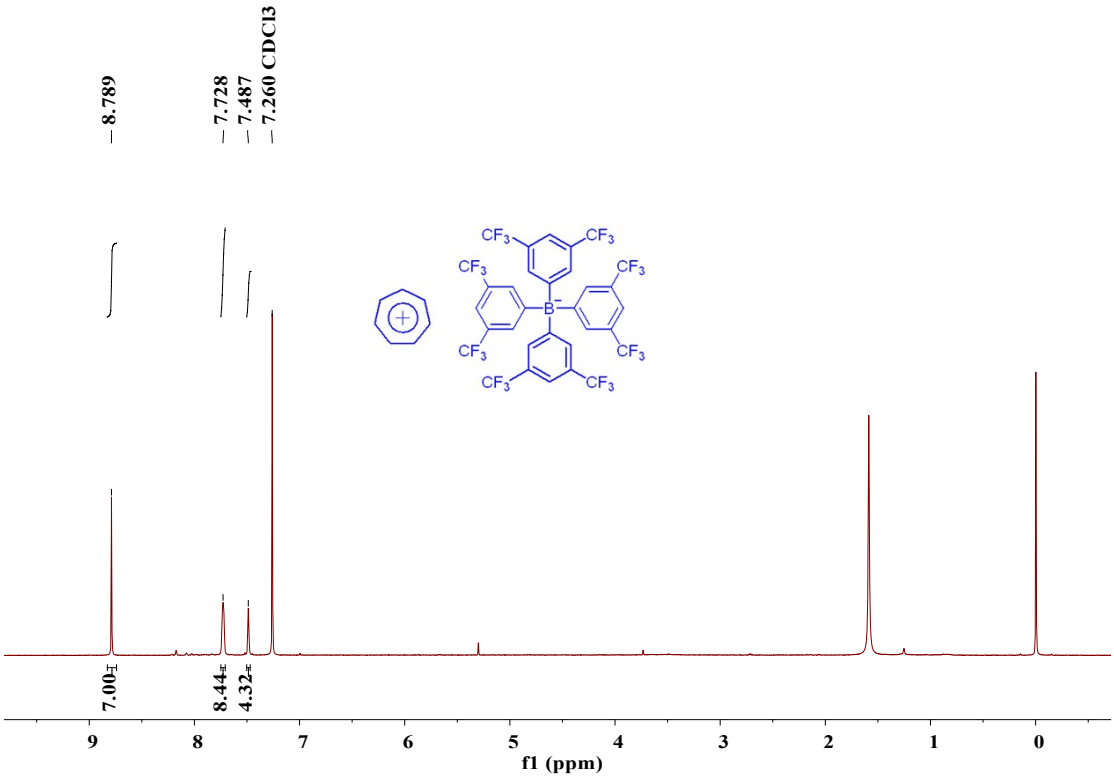


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **G**.

*8. Host-guest complexation of **PrS[6]^{Et}** and **G** in $CDCl_3$ with different ratios*

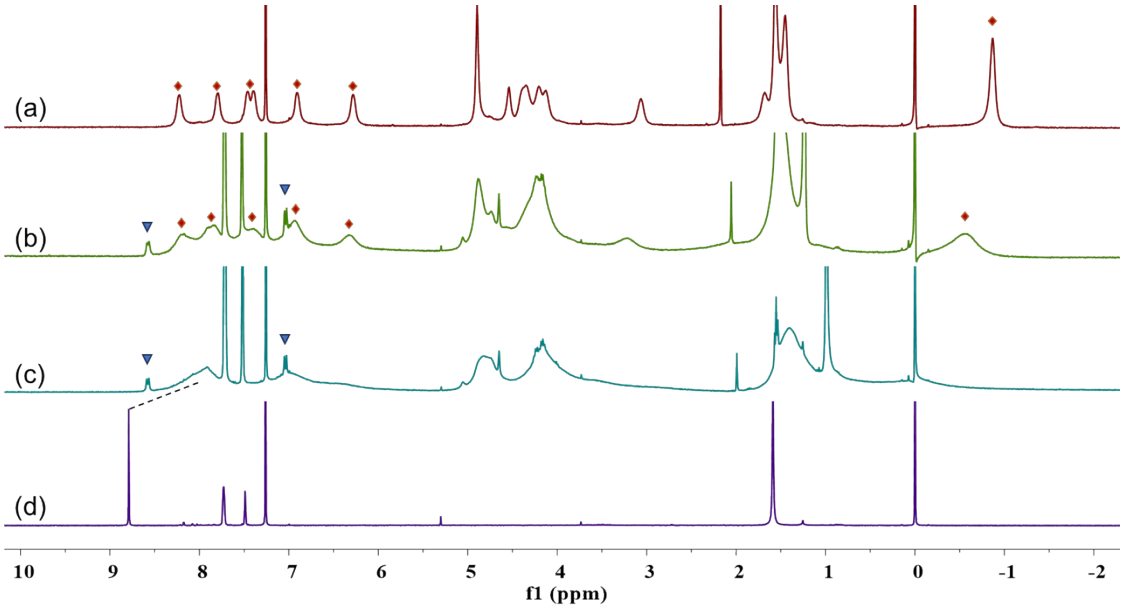


Figure S34. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 22 °C) of: (a) **PrS[6]^{Et}**, (b) an 1: 0.5 mixture of **PrS[6]^{Et}** and **G** (8.3 mM), (c) an 1 : 1 mixture of **PrS[6]^{Et}** and **G** (8.3 mM), (d) **G**

*9. High-resolution mass spectrometry of a solution of **PrS[6]^{Et}** and **G***

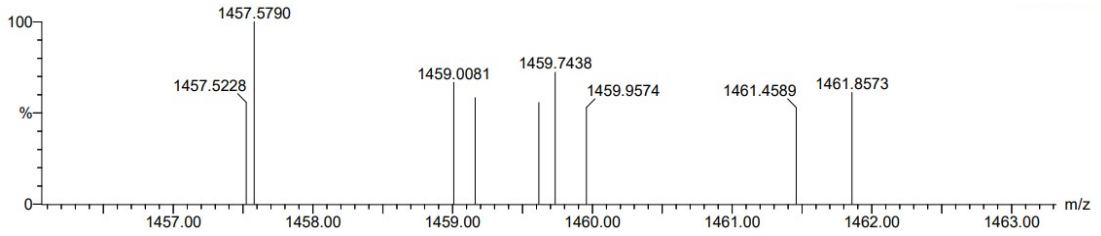


Figure S35. High-resolution mass spectrometry of **PrS[6]**^{Et} and **G**. Assignment of main. peaks: m/z 1459.7438 [**PrS[6]**^{Et}⊃**G** – $BArF^-$].

*10. Fluorescence titration experiments of **PrS[6]**^{R} and **G** in $CHCl_3$*

To determine the stoichiometry and association constant for the complexation between **PrS[6]**^{R} and **G**, the binding constants were determined by fluorescence titration in an 1 cm quartz cuvette in $CHCl_3$ at 298 K. The host concentration remained constant (0.01 mM), while **G** varied between 0.0 and 0.05 mM. The binding constant (K_a) was determined by fitting the experimental data. The association constant (K_a) of **PrS[6]**^{R}⊃**G** was estimated by a non-linear curve-fitting method.

The non-linear curve-fitting was based on the equation:[S3]

$\Delta F = (\Delta F_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\ ([G]_0^2 + (2[G]_0(1/Ka - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$ Where ΔF is the fluorescence intensity change at H_0, ΔF_∞ is the fluorescence intensity change when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **G**.

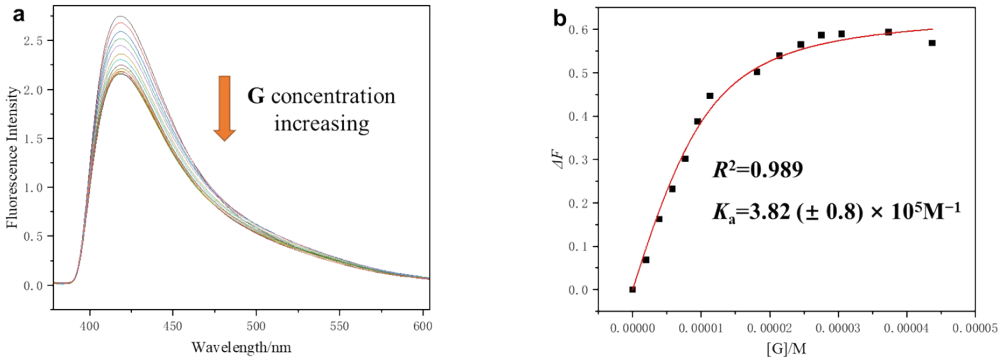


Figure S36. (a) Fluorescence spectra of **PrS[6]**^{Et} at a concentration of 0.01 mM upon gradual addition of **G** (0.044 mM). (b) The fluorescence intensity changes of **PrS[6]**^{Et} upon addition of **G**, and the host-guest association constant K_a was estimated to be 3.82(± 0.8) × 10^5 M^{-1}.

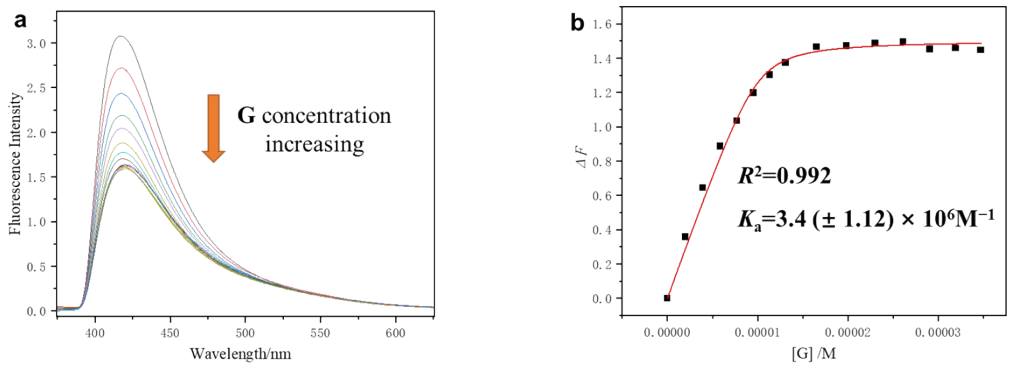


Figure S37. (a) Fluorescence spectra of **PrS[6]**^{nPr} at a concentration of 0.01 mM upon gradual addition of **G** (0.035 mM). (b) The fluorescence intensity changes of **PrS[6]**^{nPr} upon addition of **G**, and the host-guest association constant K_a was estimated to be 3.40 (± 1.12) × 10^6 M^{-1}.

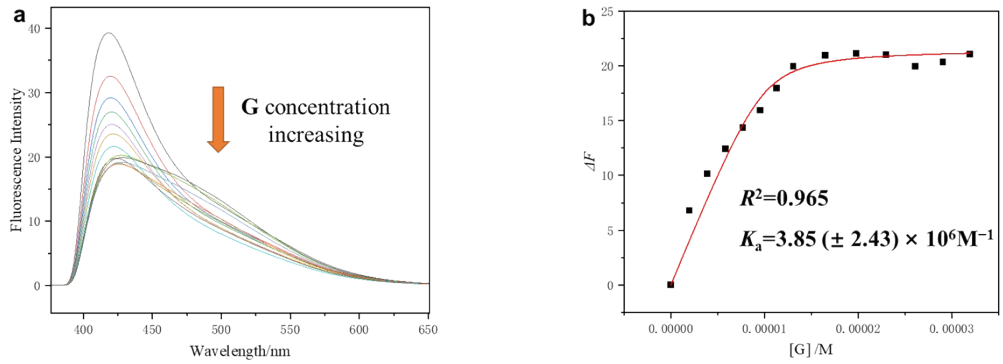


Figure S38. (a) Fluorescence spectra of **PrS[6]**^{nBu} at a concentration of 0.01 mM upon gradual addition of **G** (0.032 mM). (b) The fluorescence intensity changes of **PrS[6]**^{nBu} upon addition of **G**, and the host-guest association constant K_a was estimated to be 3.85 (± 2.43) × 10^6 M^{-1}.

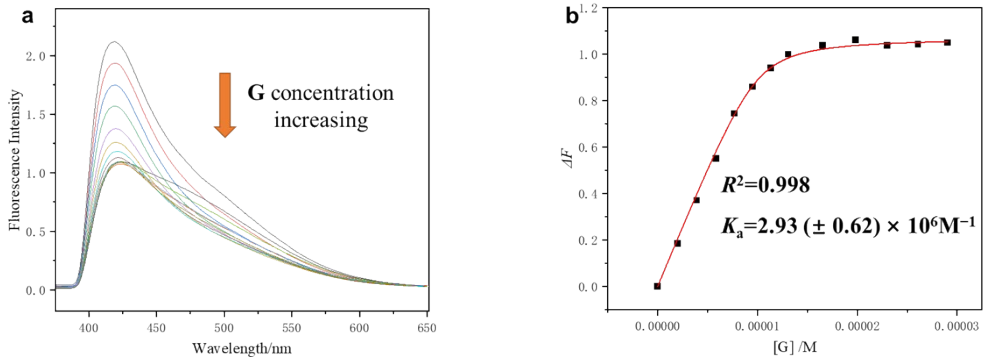


Figure S39. (a) Fluorescence spectra of **PrS[6]**^{iBu} at a concentration of 0.01 mM upon gradual addition of **G** (0.029 mM). (b) The fluorescence intensity changes of **PrS[6]**^{iBu} upon addition of **G**, and the host-guest association constant K_a was estimated to be 2.93 (± 0.62) × 10^6 M^{-1}.

References:

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S2. M. Tobisu, T. Morioka, A. Ohtsuki, N. Chatani, *Chem. Sci.* **2015**, *6*, 3410-3414.

S3. a) T. Ackermann, *Berichte der Bunsengesellschaft für physikalische Chemie* **1987**, *91*, 1398-1398; b) P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1996**, *118*, 4931-4951; c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2.* **1998**, 1807−1816.