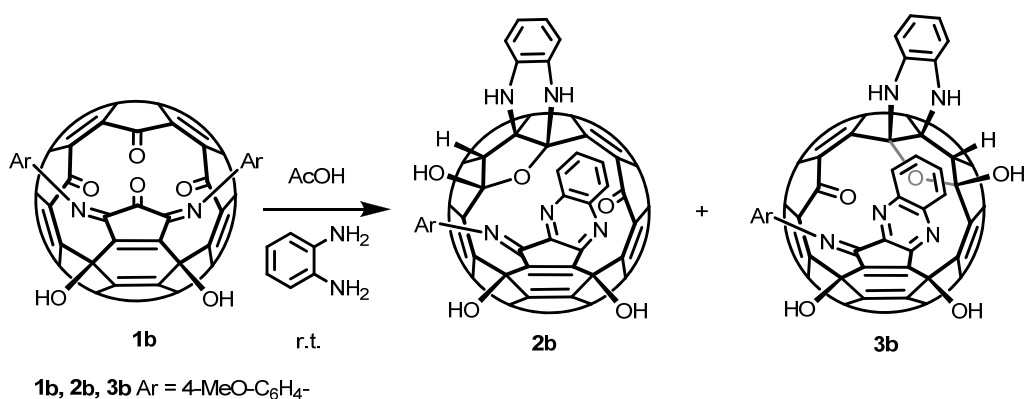


## Supporting Information

### Open-cage fullerene with a stopper acts as a molecular vial for a single water molecule

Liang Xu, Sisi Liang, Jiahao Sun, and Liangbing Gan

Experimental procedures and characterization data for compounds <b>2b</b> , <b>3b</b> , <b>4b</b>	S2
Experimental procedure for reaction between <b>4</b> and <i>o</i> -diaminobenzene	S5
<sup>1</sup> H NMR and HRMS spectra for <b>2a</b>	S7
<sup>1</sup> H, <sup>13</sup> C and HRMS spectra for <b>3a</b>	S8
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Water escape and D <sub>2</sub> O exchange <sup>1</sup> H NMR spectra	S18



### Preparation of Compounds **2b** and **3b**.

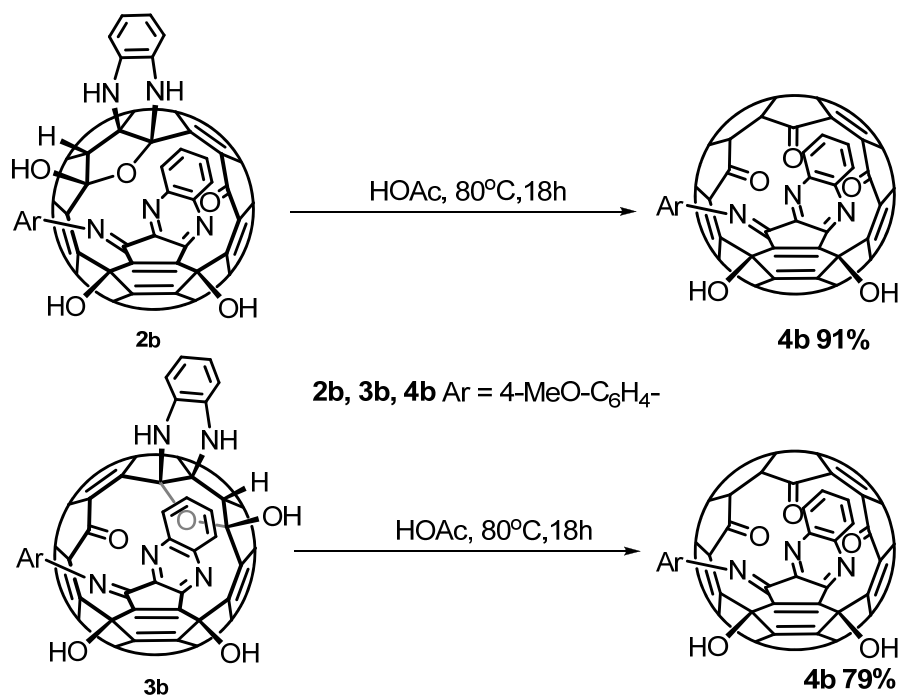
Acetic acid (20 drops, 384 mg) and diaminobenzene (132 mg, 1.22 mmol) were added to a solution of **1b** (128 mg, 0.121 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (20:1). The solution was concentrated, and chromatographed again on a silica gel column eluting with dichloromethane/ethyl acetate (100:1). The first band was collected and evaporated to give **2b** (58 mg, 0.051 mmol, 43%). The second band was collected and evaporated to give **3b** (51 mg, 0.045 mmol, 37%).

*Characterization Data for 2b.* <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>) δ: 8.34-8.32 (d, 1H, *J* = 8.0 Hz), 8.21-8.19 (d, 1H, *J* = 8.2 Hz), 7.89-7.84 (m, 4H), 7.74-7.70 (t, *J* = 7.5 Hz, 2H), 7.61 (s, 1H), 7.08 (s, 1H), 7.03-6.95 (m, 2H), 6.81-6.79 (m, 1H), 6.15-6.09 (m, 2H), 5.47-5.39 (m, 1H), 4.47-4.42 (m, 2H), 4.00 (s, 3H), -10.90 (s). <sup>13</sup>C NMR spectrum could not be obtained due to low solubility. ESI-FT-ICR-HRMS: C<sub>79</sub>H<sub>222</sub>N<sub>5</sub>O<sub>6</sub> (M + H<sup>+</sup>) calcd 1136.1565, found 1136.1563.

*Characterization Data for 3b.* <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>) δ: 8.39 (s, 1H), 8.01-7.99 (d, 1H, *J* = 8.0 Hz), 7.90-7.88 (d, 2H, *J* = 8.0 Hz),

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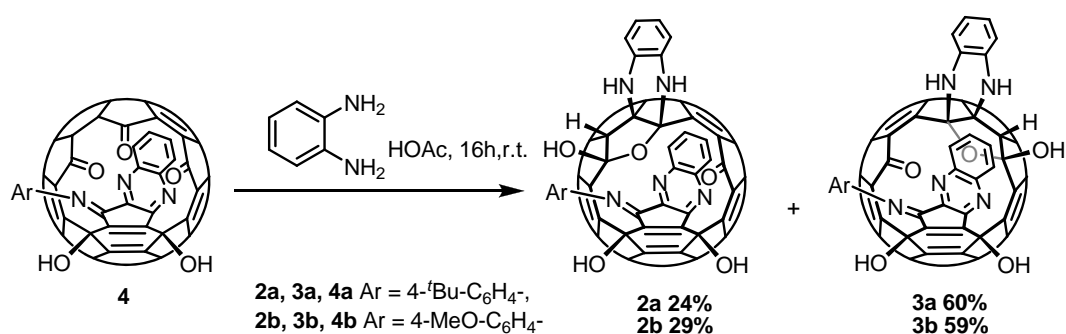
7.58-7.55 (t,  $J = 7.1$  Hz, 2H), 7.46-7.42 (t,  $J = 7.3$  Hz, 1H), 7.31 (s, 1H), 6.91-6.87 (m, 2H), 6.85-6.83 (m, 1H), 6.42-6.41 (m, 1H), 6.37-6.34 (m, 1H), 6.02-5.99 (t,  $J = 7.2$  Hz, 1H), 4.79-4.75 (m, 1H), 4.54-4.44 (m, 1H), 4.07-4.03 (m, 1H), 3.86 (s, 1H), 3.60 (s, 3H), -11.50 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{OD}$ )  $\delta$ : 8.49-8.47 (m, 1H), 8.31-8.29 (m, 1H), 8.04-8.03 (m, 1H), 8.03-8.02 (m, 1H), 7.99-7.92 (m, 2H), 7.88-7.85 (m, 1H), 7.55-7.47 (m, 1H), 7.18-7.15 (m, 2H), 6.78-6.77 (d, 1H,  $J = 7.4$  Hz), 6.67-6.63 (m, 1H), 6.26-6.21 (m, 1H), 5.15-5.09 (m, 1H), 5.05-5.01 (m, 1H), 4.79-4.68 (m, 1H), 4.16-4.15 (m, 1H), 4.00 (s, 3H), -11.14 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_4\text{Cl}_2$ ): all signals represent 1C except noted,  $\delta$ : 190.13, 159.48, 158.75, 154.10, 150.24, 150.09, 150.06, 149.39, 148.79, 148.71, 148.54, 148.38, 148.13, 147.98, 147.93, 147.90, 147.79, 147.77, 147.75, 147.59, 147.46, 147.17, 147.03, 146.80, 146.67, 146.48, 146.12, 146.00, 145.88, 145.33, 145.19, 144.42, 144.28, 144.08, 143.17, 142.68, 142.66, 142.64, 142.45, 142.24, 142.22, 141.71, 141.61, 141.59, 141.22, 140.62, 139.91, 138.83, 138.58, 138.39, 138.11, 138.06, 137.85, 136.82, 135.19, 133.93, 121.15, , 119.29, 116.40, 113.41, 113.11, 112.84, 106.51, 77.74, 76.95, 76.59, 75.99, 63.72, 54.34 (3C). ESI-FT-ICR-HRMS:  $\text{C}_{79}\text{H}_{22}\text{N}_5\text{O}_6$  ( $\text{M} + \text{H}^+$ ) calcd 1136.1565, found 1136.1556.



Acetic acid (1 ml) was added to a solution of **2b** (17 mg, 0.015 mmol) in PhCl (10 mL) at 80°C. After 18 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate. The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane. The first red band was collected and evaporated to give **4b** (14 mg, 0.014 mmol, 91%).

Acetic acid (1 ml) was added to a solution of **3b** (14 mg, 0.012 mmol) in PhCl (10 mL) at 80°C. After 18 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate. The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane. The first red band was collected and evaporated to give **4b** (10 mg, 0.010 mmol, 79%).

*Characterization Data for 4b.*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.21-8.13 (m, 3H), 8.09-8.07 (m, 2H), 7.82-7.74 (m, 2H), 7.17-7.15 (d,  $J = 8.6$  Hz, 2H), 6.81-6.69 (d,  $J = 7.4$  Hz, 1H), 4.00 (s, 3H), -12.87 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): all signals represent 1C except noted,  $\delta$ : 184.63, 184.49, 184.42, 184.37, 184.25, 184.20, 184.17, 183.97, 160.40, 160.37, 158.81, 158.77, 155.55, 155.50, 150.03, 149.76, 149.73, 149.68, 149.66, 149.62, 149.60, 149.59, 149.57, 149.55, 149.46, 149.43, 149.40, 149.36, 149.31, 149.27, 148.30, 148.29, 148.27, 148.23, 148.20, 148.18, 148.15, 147.91, 147.90, 147.39, 147.29, 147.27, 147.11, 147.01, 146.88, 146.69, 146.53, 146.35, 146.23, 146.21, 146.06, 146.01, 145.83, 145.76, 145.70, 145.63, 145.53, 145.45, 145.43, 145.34, 145.25, 145.20, 145.16, 144.89, 144.81, 144.71, 144.67, 144.64, 144.55, 144.49, 144.47, 144.42, 144.34, 144.30, 144.26, 143.72, 143.69, 143.65, 143.50, 143.43, 143.42, 143.39, 143.34, 143.31, 143.27, 142.85, 142.69, 142.60, 142.49, 142.47, 141.75, 141.73, 141.59, 141.55, 141.05, 140.90, 140.68, 140.66, 140.44, 139.78, 139.76, 136.82, 136.66, 136.57, 136.49, 136.47, 136.32, 135.96, 135.81, 131.82, 131.17, 129.60, 129.58, 129.24, 127.74, 127.70, 127.64, 127.33, 126.95, 126.66, 113.69, 78.31, 78.26, 77.60, 77.55, 55.69. ESI-FT-ICR-HRMS:  $\text{C}_{73}\text{H}_{14}\text{N}_3\text{O}_6$  ( $\text{M} + \text{H}^+$ ) calcd 1028.0877, found 1028.0867.  $\text{C}_{146}\text{H}_{27}\text{N}_6\text{O}_{12}$  ( $2\text{M} + \text{H}^+$ ) calcd 2055.1682, found 2055.1590.

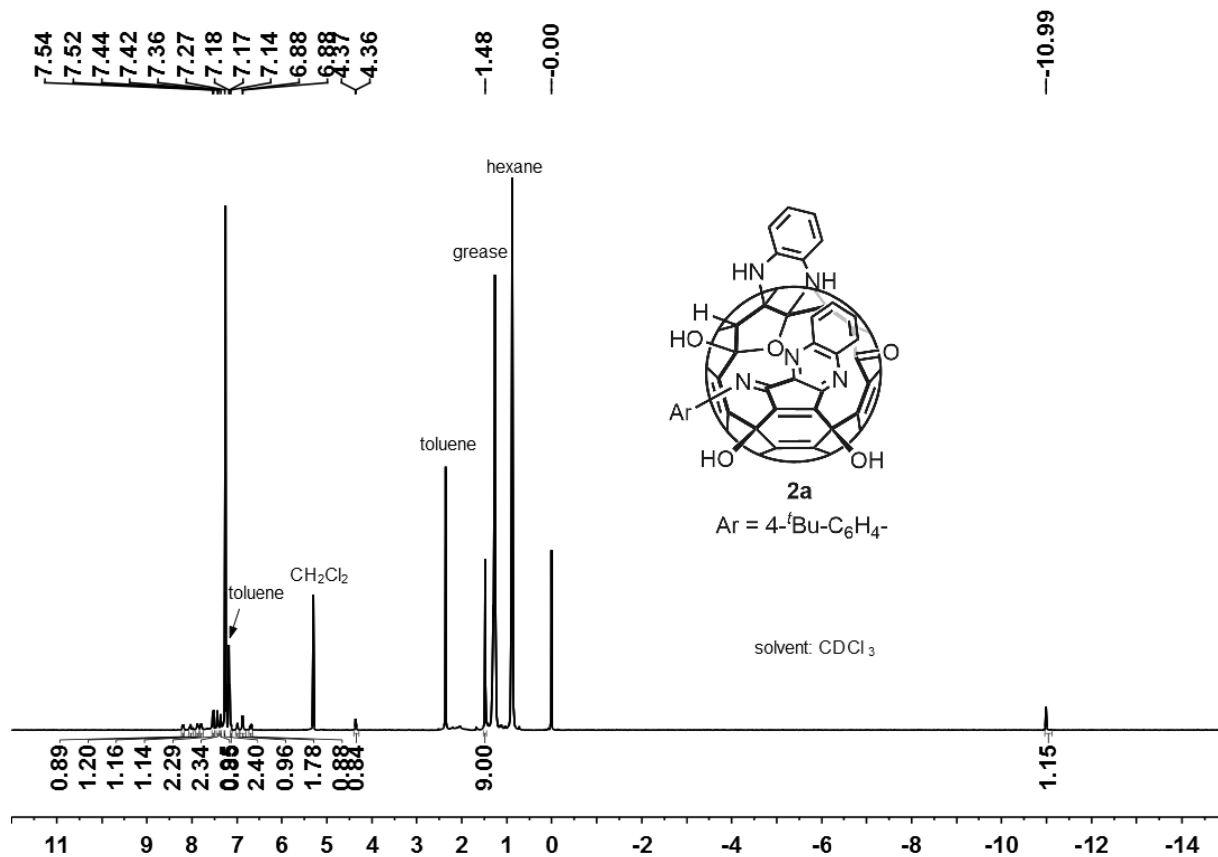


Acetic acid (15 drops, 288mg) and diaminobenzene (58 mg, 0.52 mmol) were added to a solution of **4a** (103 mg, 0.0978 mmol) in  $\text{CH}_2\text{Cl}_2$

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(60 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (40:1). The solution was concentrated, and chromatographed again on a silica gel column eluting with dichloromethane. The first band was collected and evaporated to give **2a** (27 mg, 0.023 mmol, 24%). The second band was eluted with dichloromethane/ethyl acetate (100:1) and evaporated to give **3a** (68 mg, 0.059 mmol, 60%).

Acetic acid (6 drops, 115 mg) and diaminobenzene (17 mg, 0.16 mmol) were added to a solution of **4b** (15 mg, 0.013 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (20:1). The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate = 100:1. The first band was collected and evaporated to give **2b** (4 mg, 0.004 mmol, 29%). The second band was collected and evaporated to give **3b** (8 mg, 0.008 mmol, 59%).

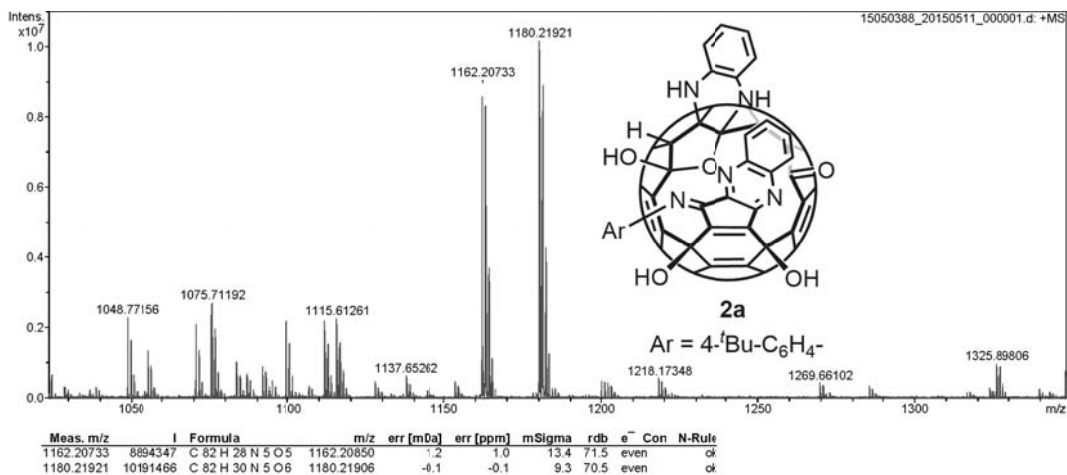


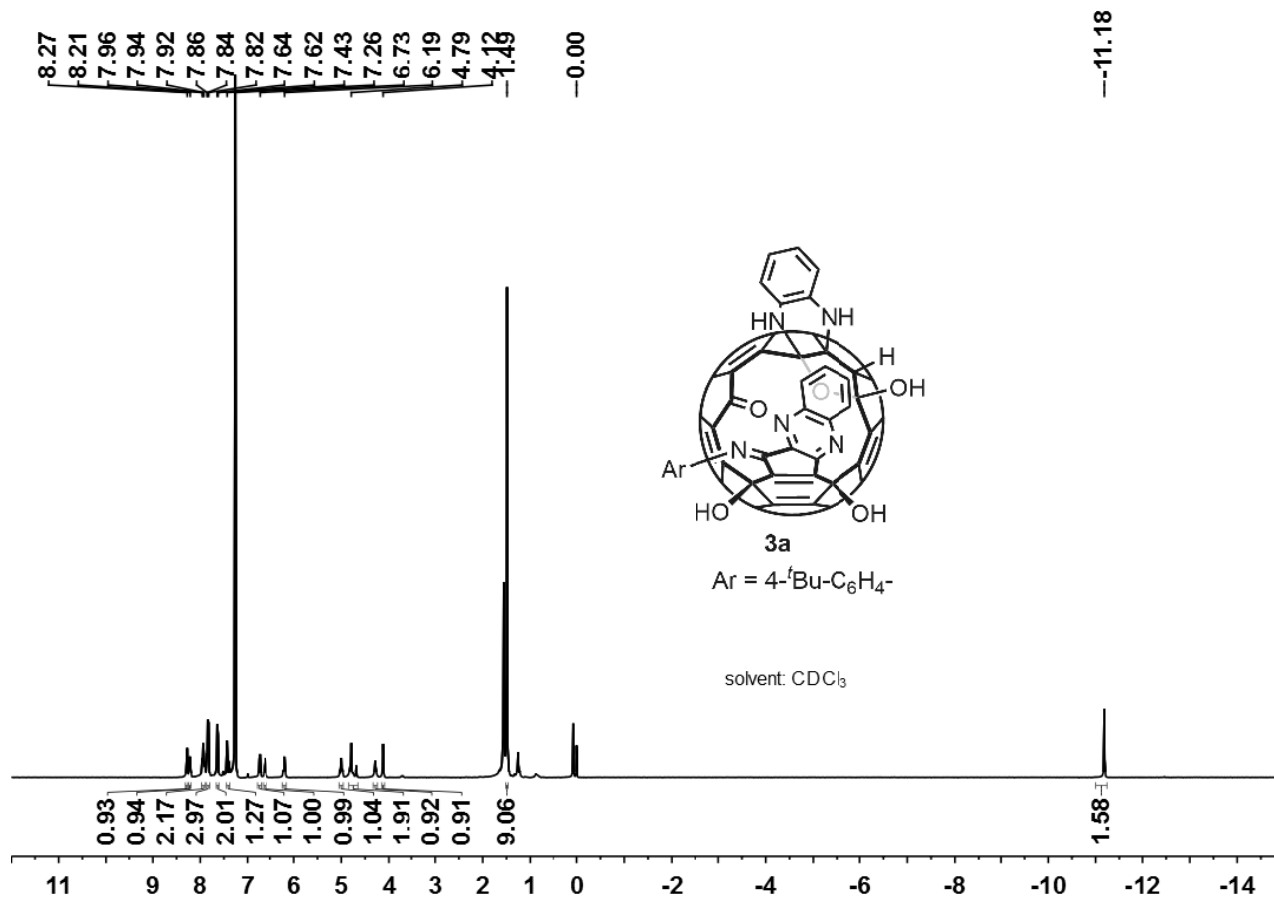
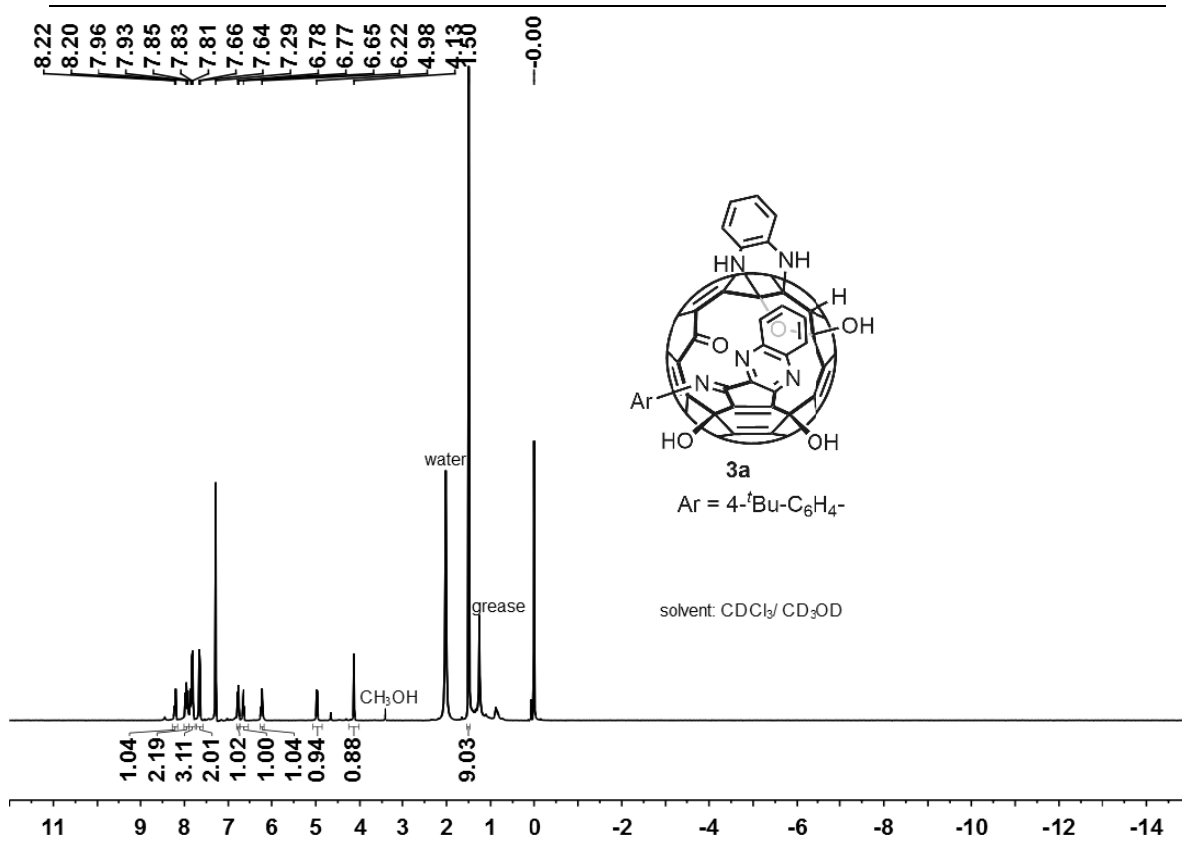
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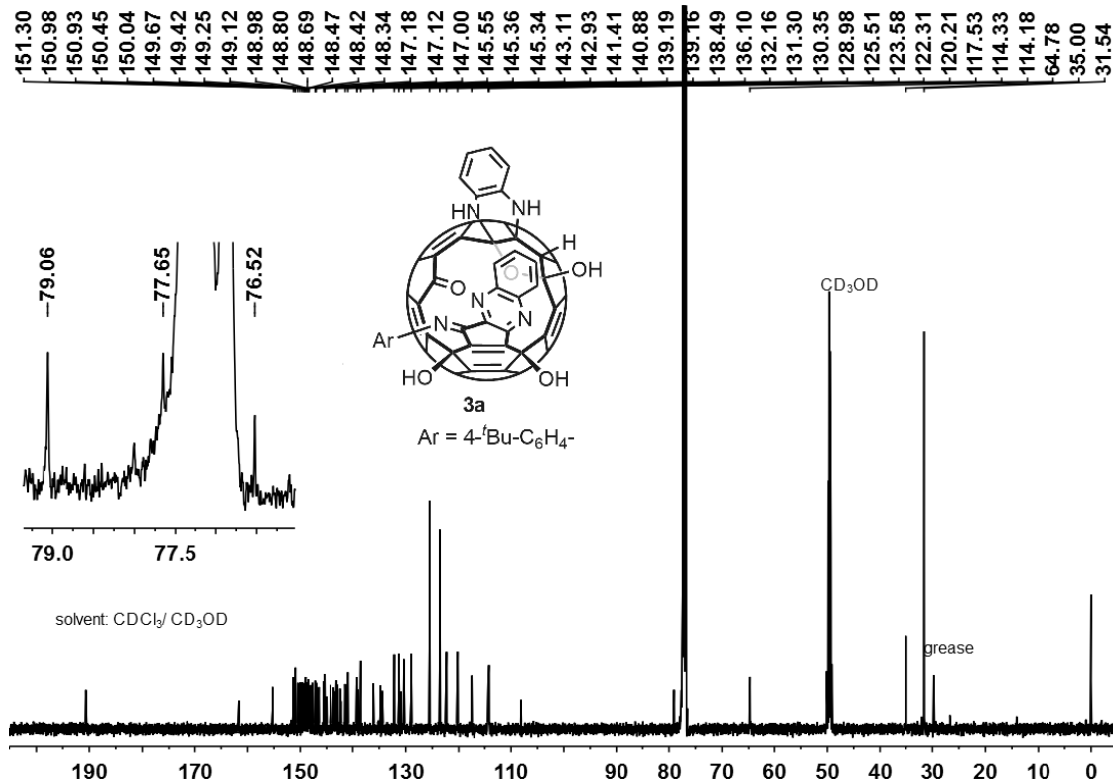
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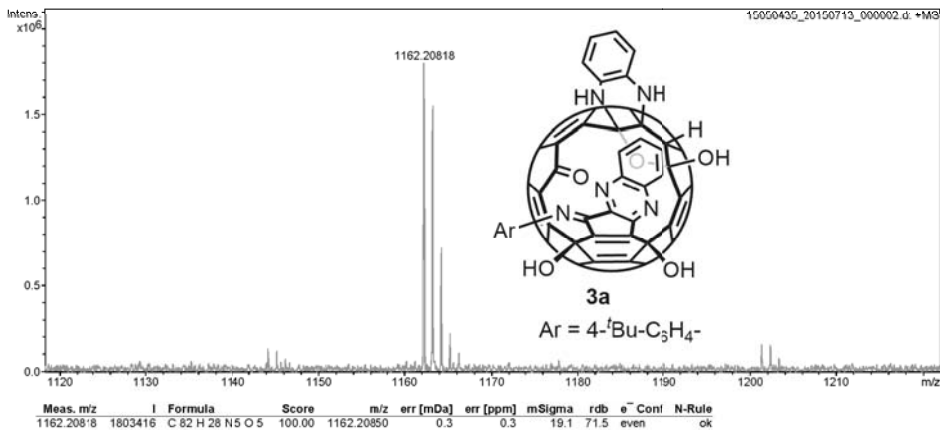


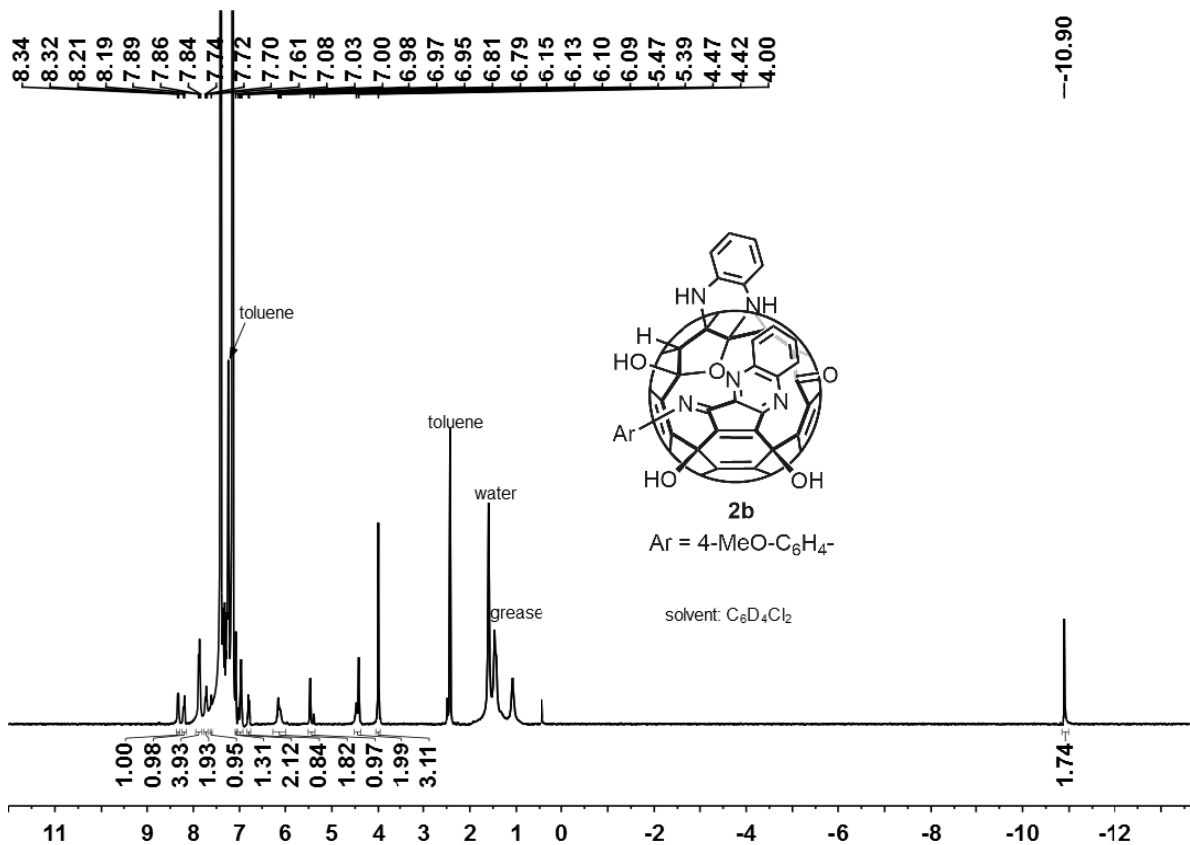
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Operator Peking University



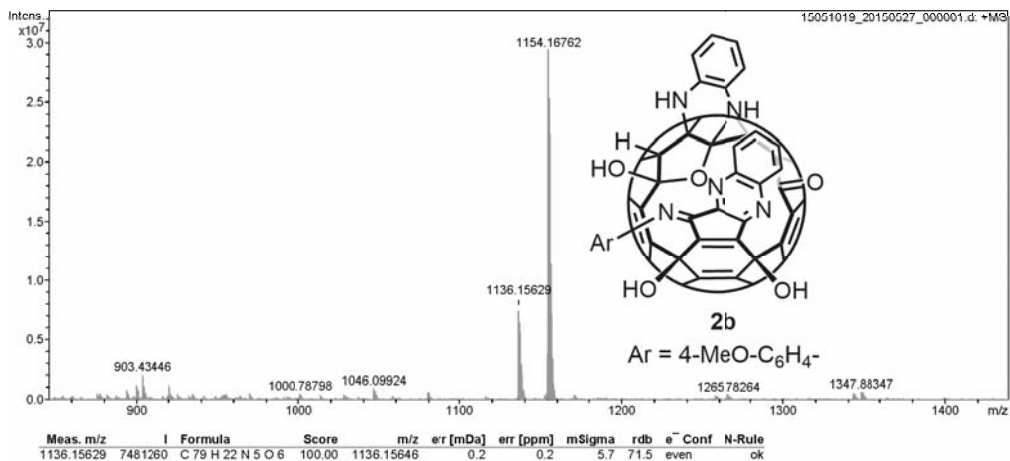


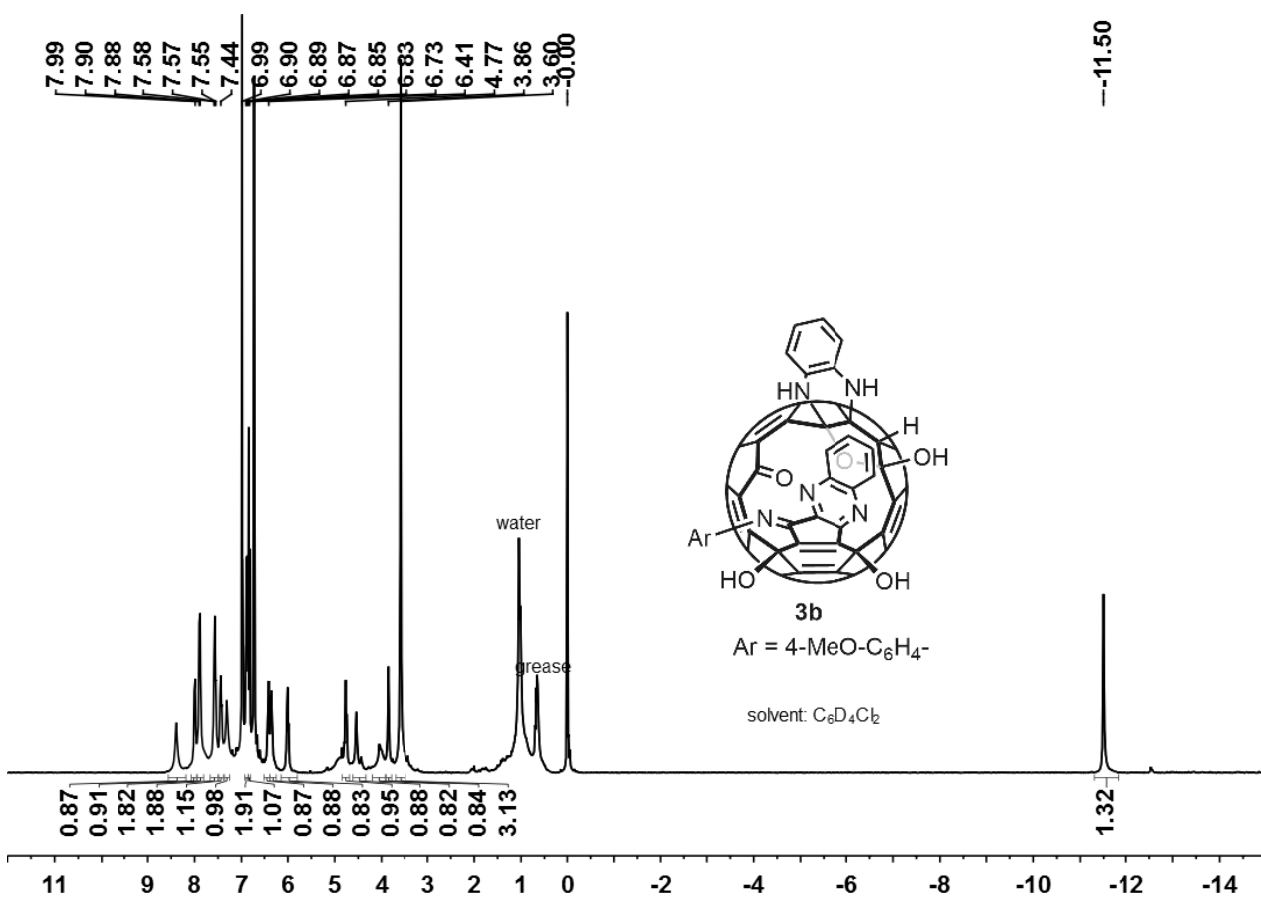
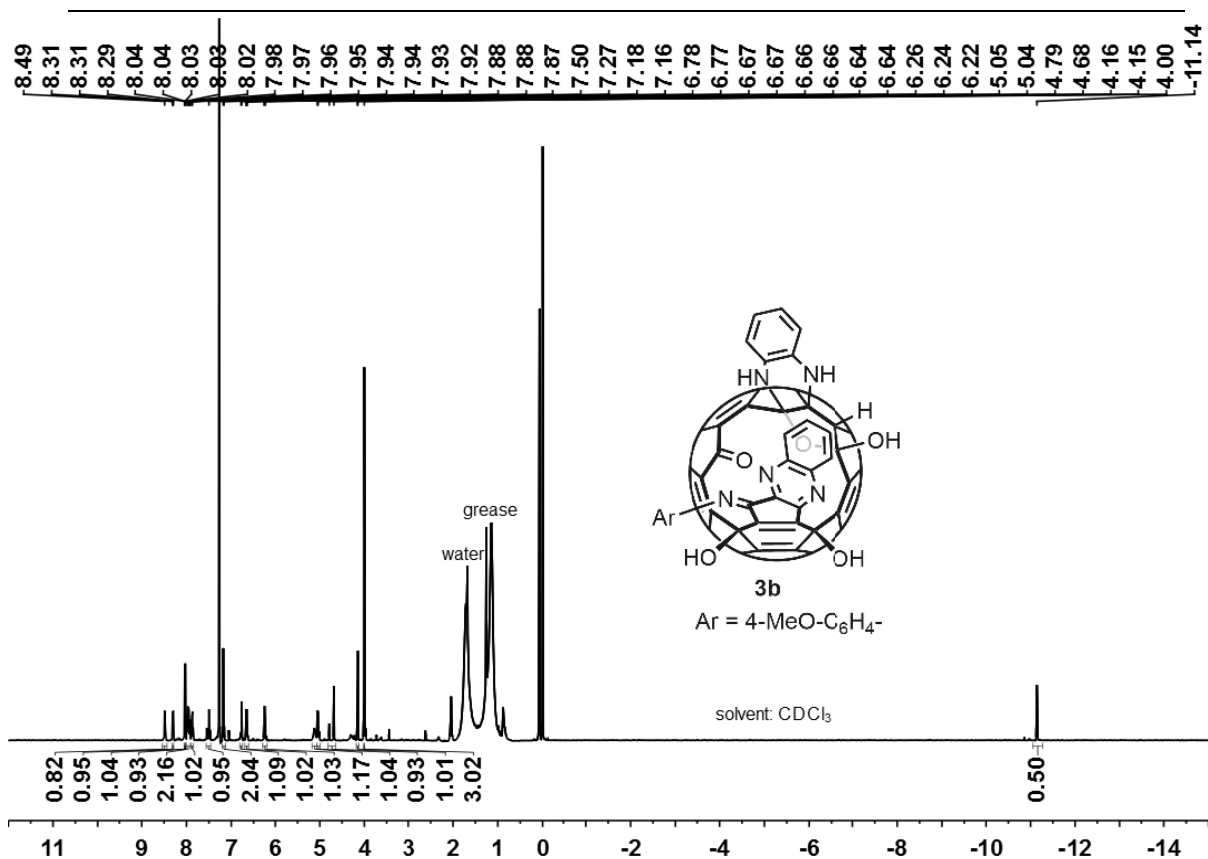
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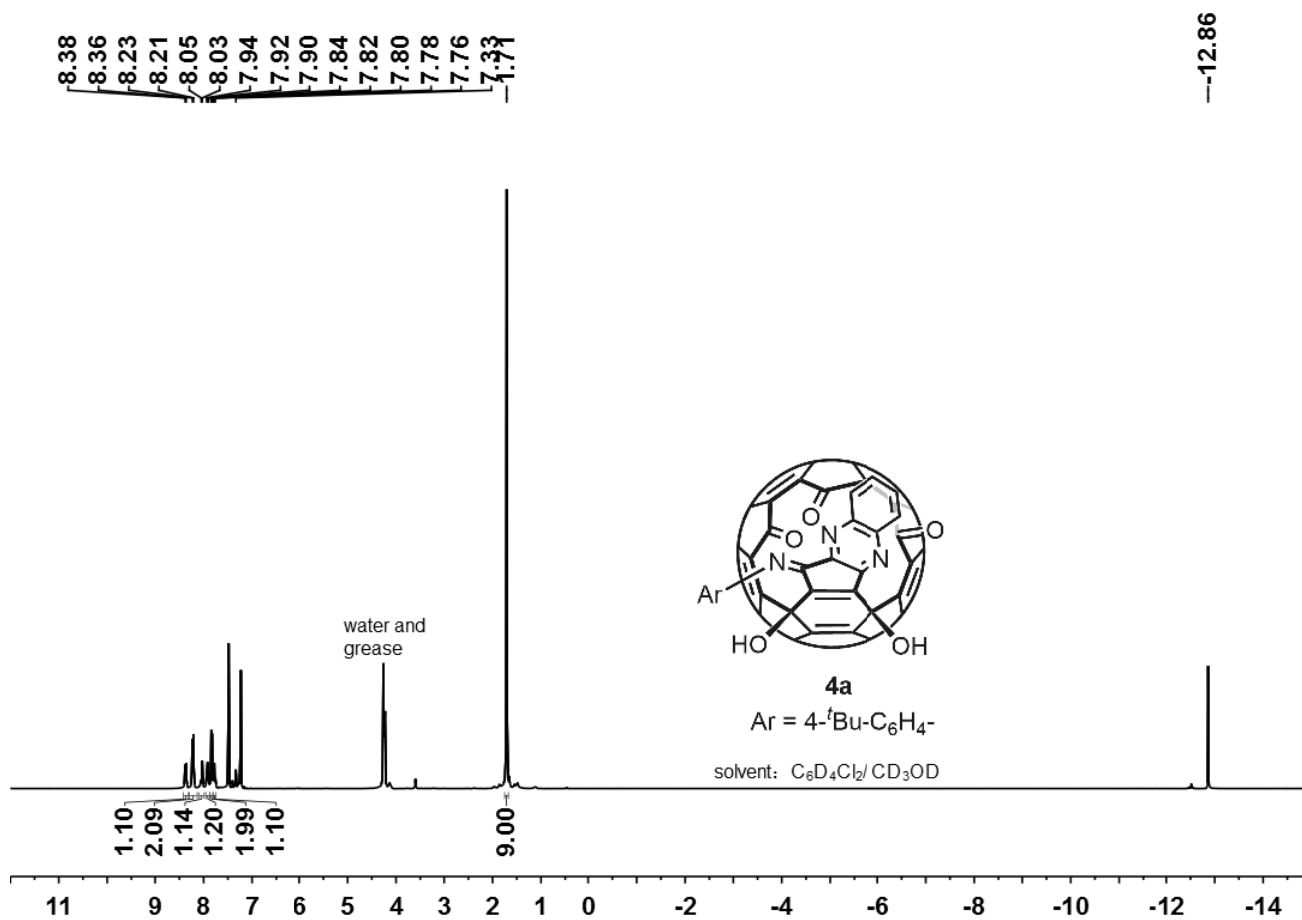
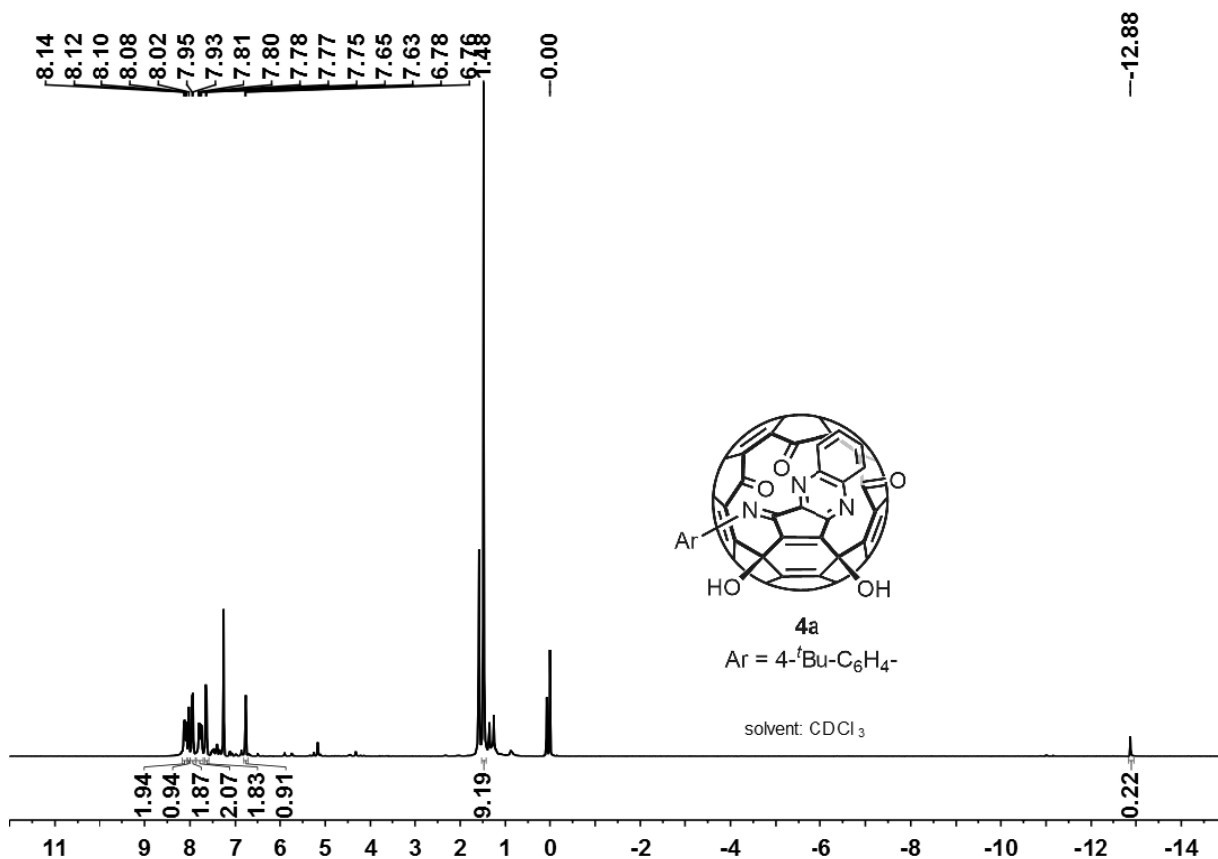
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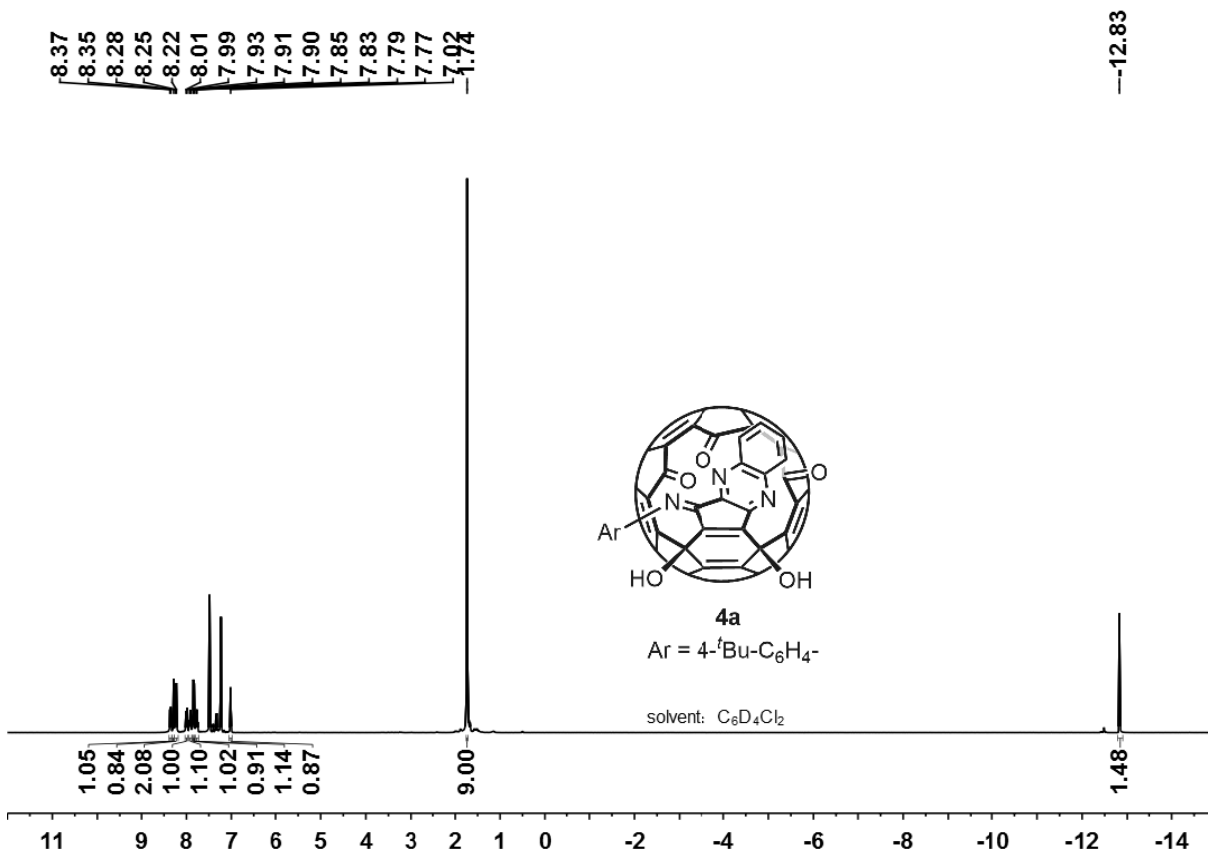
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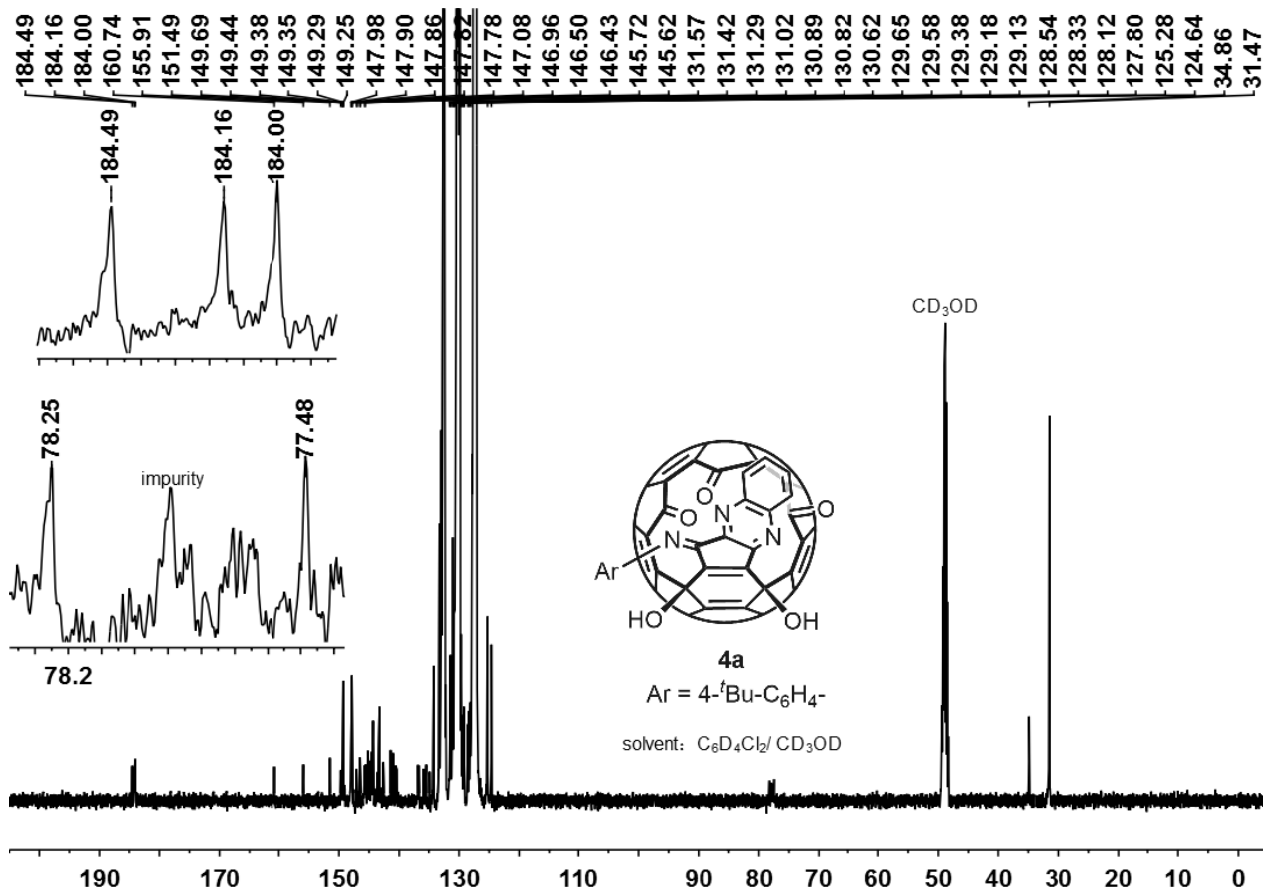








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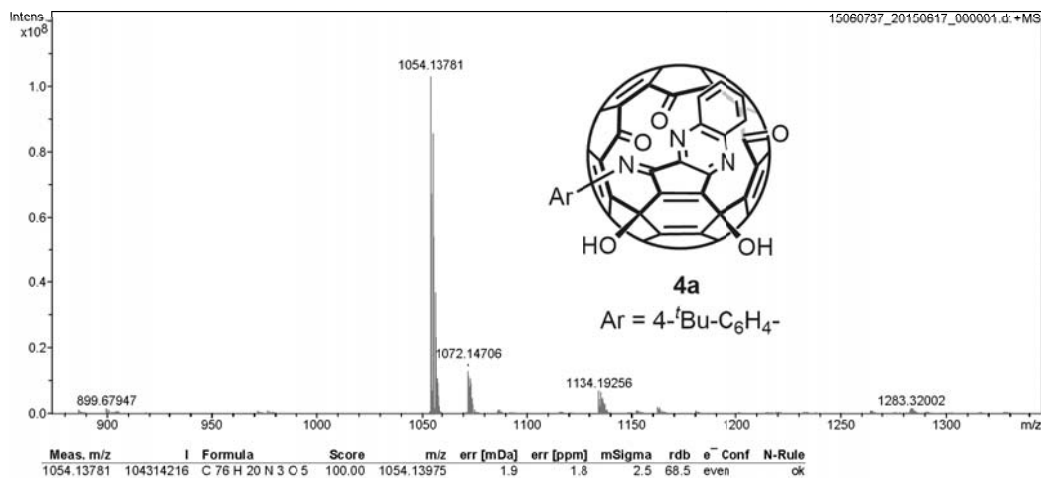


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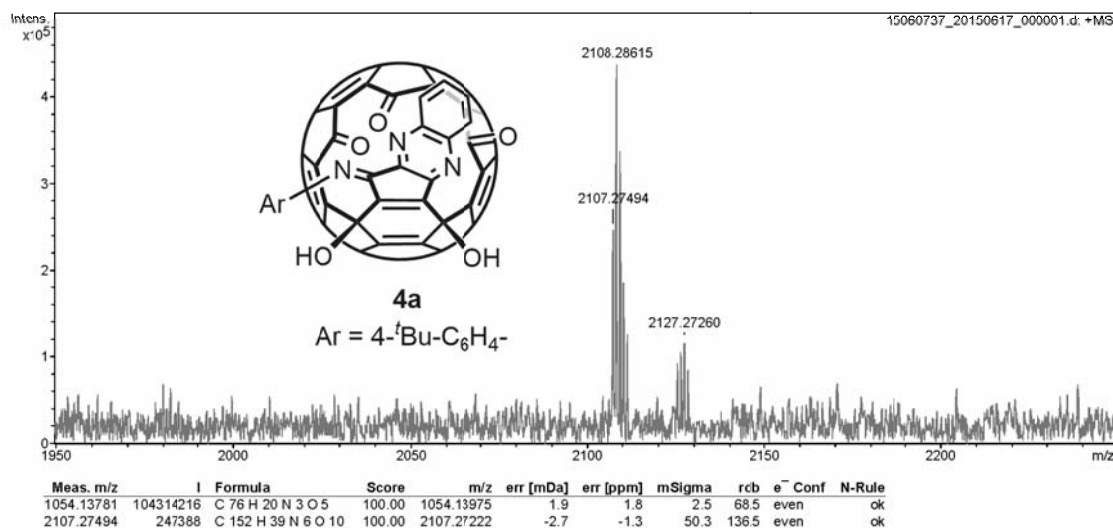


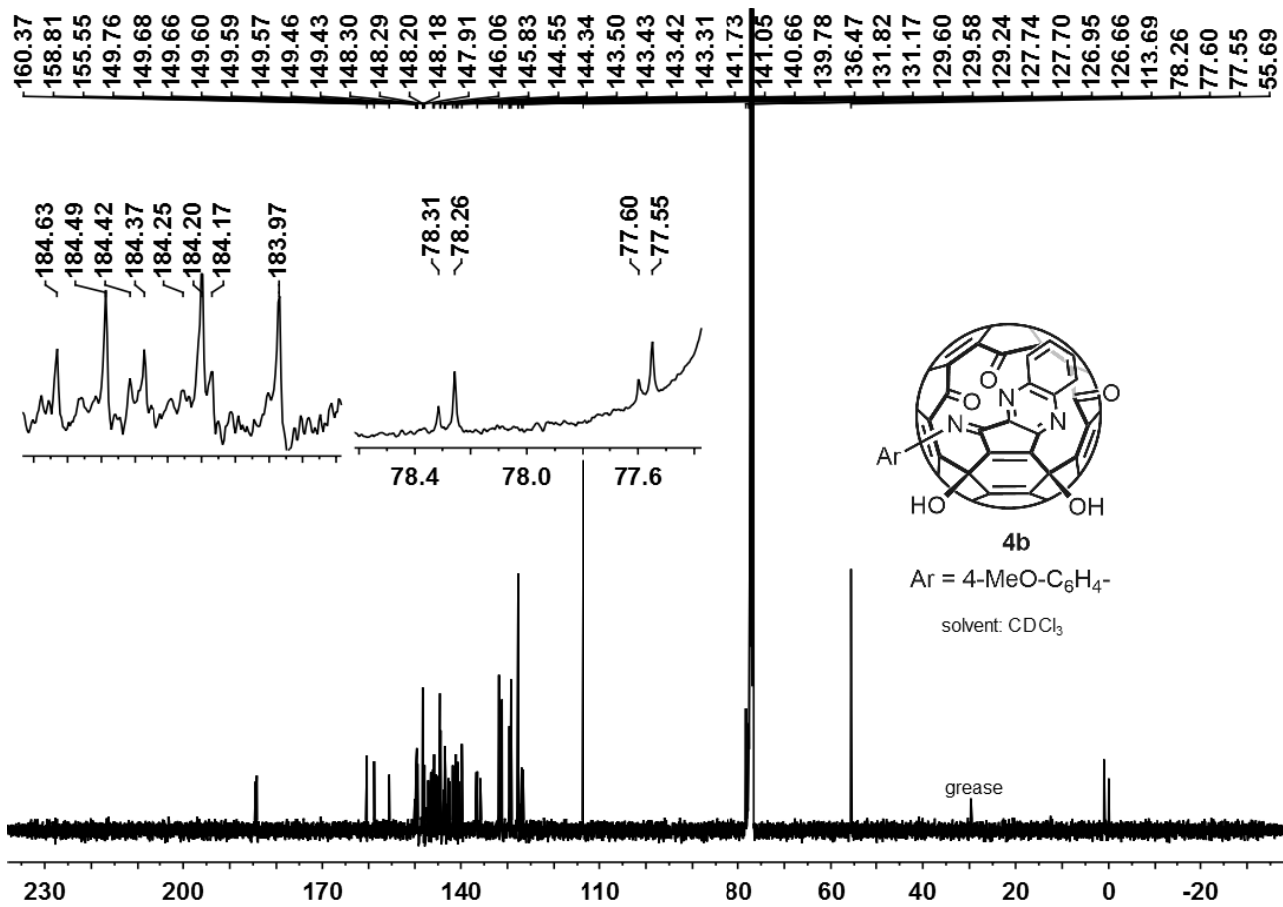
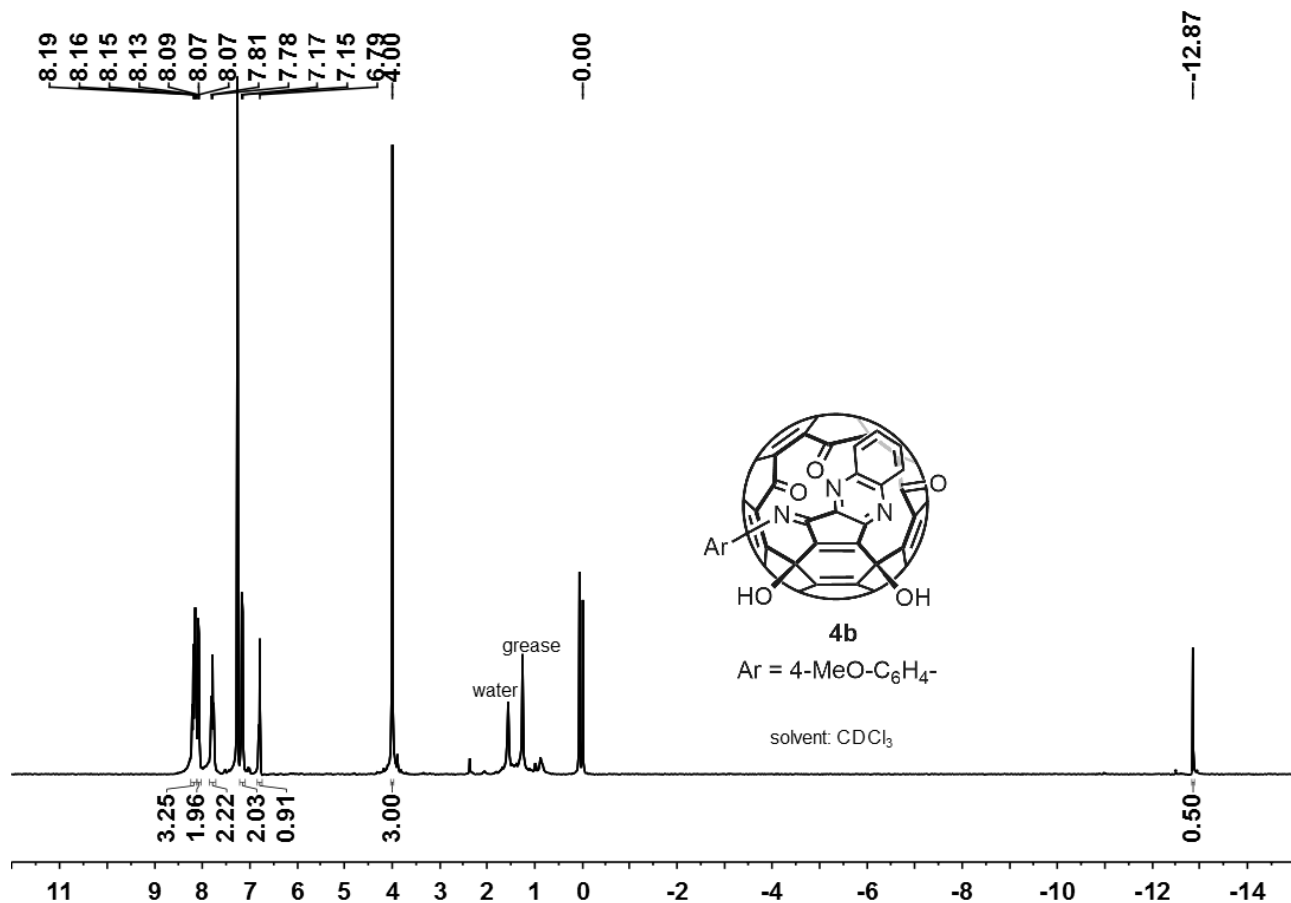
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 Instrument Bruker Apex IV FTMS  
 Operator Peking University





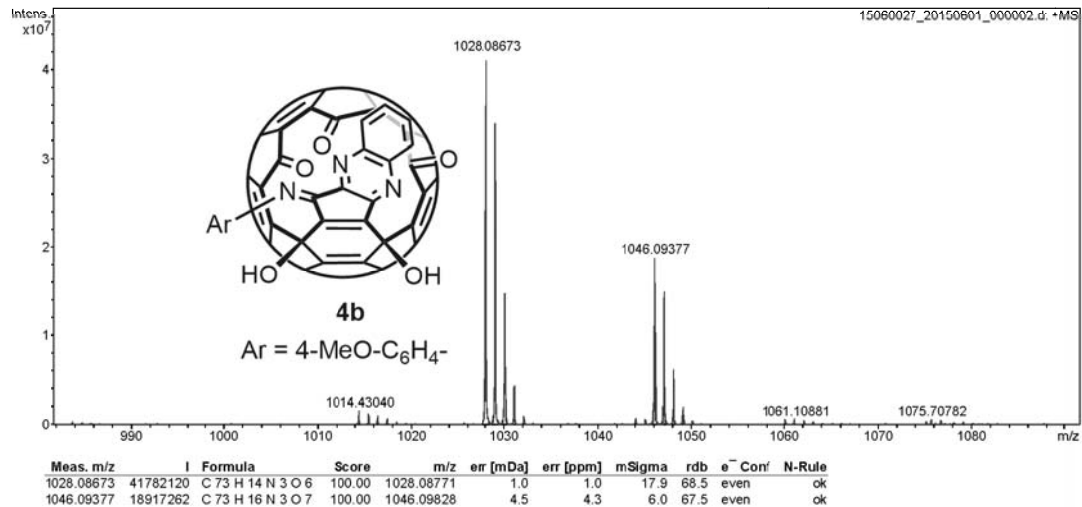


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 Operator Peking University

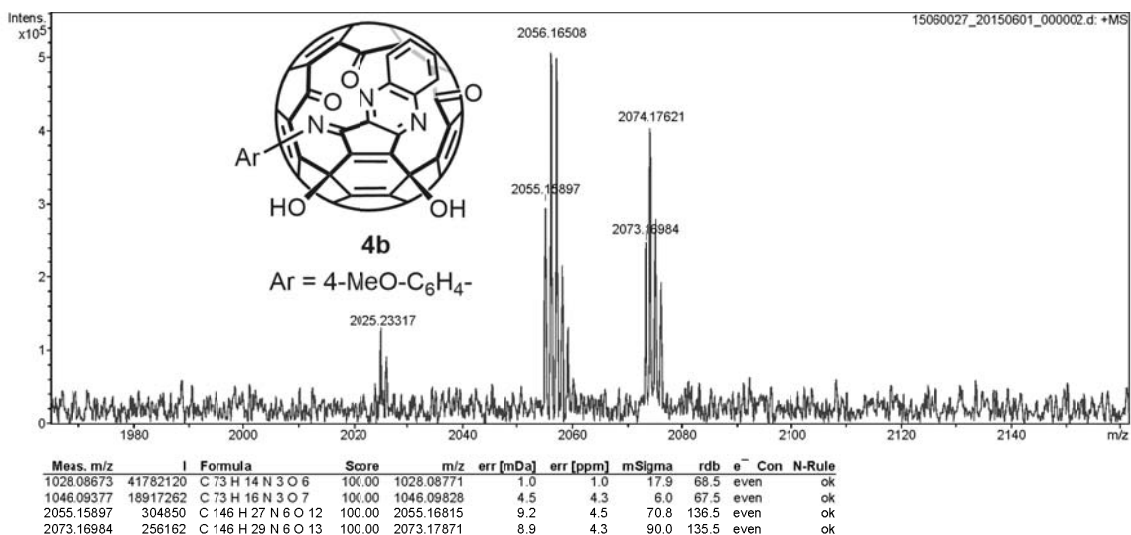


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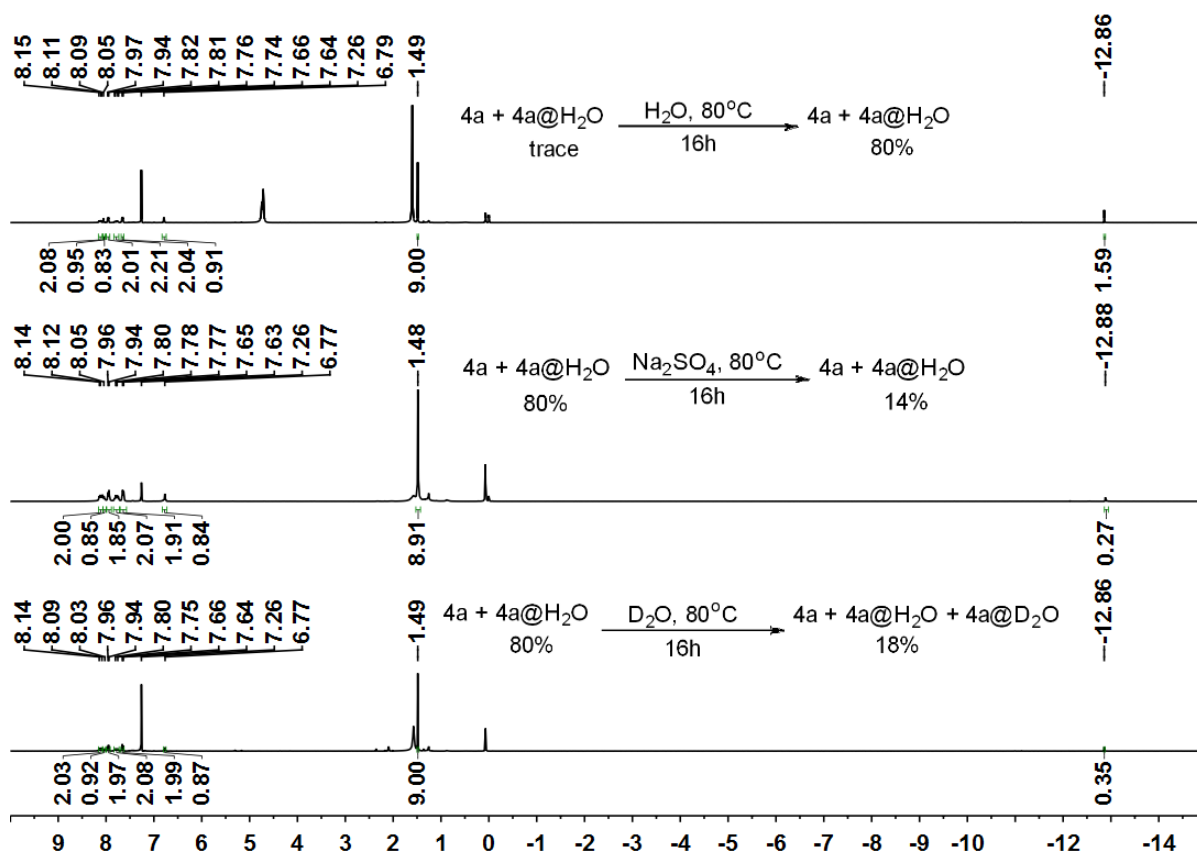
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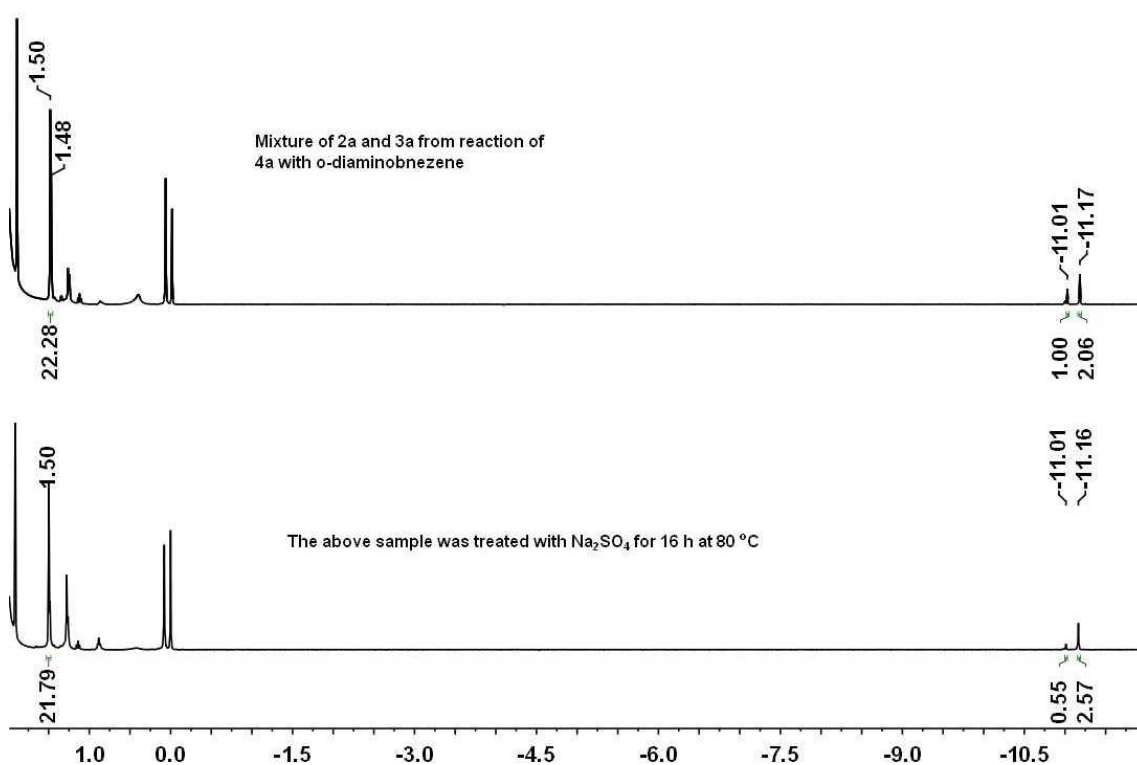
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 Operator Peking University



**<sup>1</sup>H NMR spectra for water encapsulation and release and D<sub>2</sub>O exchange with 4a**  
 (the experiments were carried out in CDCl<sub>3</sub> in a sealed flask)



**<sup>1</sup>H NMR spectra for addition of *o*-diaminobenzene to 4a and dehydration of 2a and 3a with Na<sub>2</sub>SO<sub>4</sub>**  
 (the experiments were carried out in CDCl<sub>3</sub> in a sealed flask)



<sup>1</sup>H NMR spectra for dehydration of 3a with Na<sub>2</sub>SO<sub>4</sub>  
(the experiments were carried out in CDCl<sub>3</sub> in a sealed flask)

