

## Supporting Information for:

### Switchable regioselectivity in PIFA-BF<sub>3</sub>·Et<sub>2</sub>O mediated oxidative coupling of *meso*-brominated Ni(II) porphyrin

Chuan-Mi Feng, Yi-Zhou Zhu,\* Yun Zang, Yu-Zhang Tong and Jian-Yu Zheng\*

State Key Laboratory and Institute of Elemento-organic Chemistry, Collaborative Innovation  
Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

zhuyizhou@nankai.edu.cn; jy Zheng@nankai.edu.cn

1. Instrumentations and Materials.....	S2
2. Optimization of the oxidative coupling.....	S2
3. The absorption spectra of various linked porphyrin dimers.....	S3
4. The Procedure for the Synthesis of Singly Linked Porphyrin Dimers.....	S3
5. The Procedure for the Synthesis of <i>meso</i> - $\beta$ , <i>meso</i> - $\beta$ Doubly Fused Dimer.....	S4
6. The Procedure for the Synthesis of <i>meso</i> - <i>meso</i> , $\beta$ - $\beta$ Doubly Fused Dimer.....	S5
7. The Procedure for the Synthesis of $\beta$ - $\beta$ , <i>meso</i> - <i>meso</i> , $\beta$ - $\beta$ Triply Fused Dimer.....	S5
8. S <sub>N</sub> Ar reaction of <b>2</b> .....	S6
9. Demetalation of <b>2</b> , <b>3</b> and <b>6</b> .....	S6
10. NMR Spectra of Directly Linked Porphyrin Dimers.....	S8
11. Crystal Data for <b>2</b> .....	S18

## 1. Instrumentations and Materials

All NMR solvents were used as received. Chemical shifts of NMR spectra were reported in ppm down field from internal Me<sub>4</sub>Si. Crystal data were collected with a Agilent Technologies SuperNov a single-crystal diffractometer using a confocal monochromator with Mo K $\alpha$  radiation (0.71073 Å) at 273 K. All UV-vis absorption spectra were recorded using a UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu, Japan). High-resolution mass spectra (HRMS) were recorded on a VG ZAB-HS mass spectrometer under electron spray ionization (ESI) and a Bruker ultra fleXtreme MALDI-TOF/TOF spectrometer. All of the solvents were purified and distilled according to the standard procedure. The commercially obtained materials were used directly without further purification unless otherwise noted. PIFA (98%) and BF<sub>3</sub>·Et<sub>2</sub>O (98%) were purchased from Aldrich.

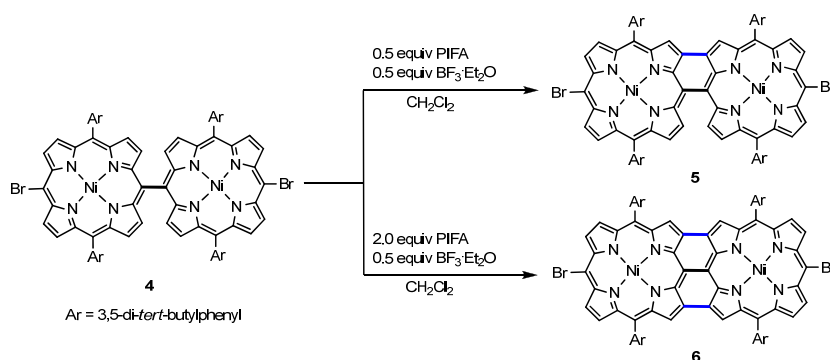
## 2. Optimization of the oxidative coupling

**Table 1** Condition Screening of Oxidative Coupling of **1** with PIFA-BF<sub>3</sub>·Et<sub>2</sub>O<sup>a</sup>

entry	1/BF <sub>3</sub> ·Et <sub>2</sub> O/PIFA (equiv)	yield <sup>b</sup> (%)			time
		2	3	4	
1	1:0:0.5	0	0	90	1 h
2 <sup>c</sup>	1:1:0	0	0	0	2 h
3	1:1:0.5	80	trace	0	30 min
4	1:1:0.75	54	25	0	30 min
5	1:1:1	0	75	0	30 min
6	1:1:1.5	0	68	0	30 min
7	1:0.5:0.5	80	trace	0	30 min
8	1:0.2:0.5	80	trace	0	1.5 h
9	1:0.5:1.0	0	75	0	30 min

<sup>a</sup>To the stirred mixture of **1** and BF<sub>3</sub>·Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> was added dropwise a solution of PIFA in dry CH<sub>2</sub>Cl<sub>2</sub> over 20 min under a nitrogen atmosphere. <sup>b</sup>Isolated yield. <sup>c</sup>Compound **1** was recovered.

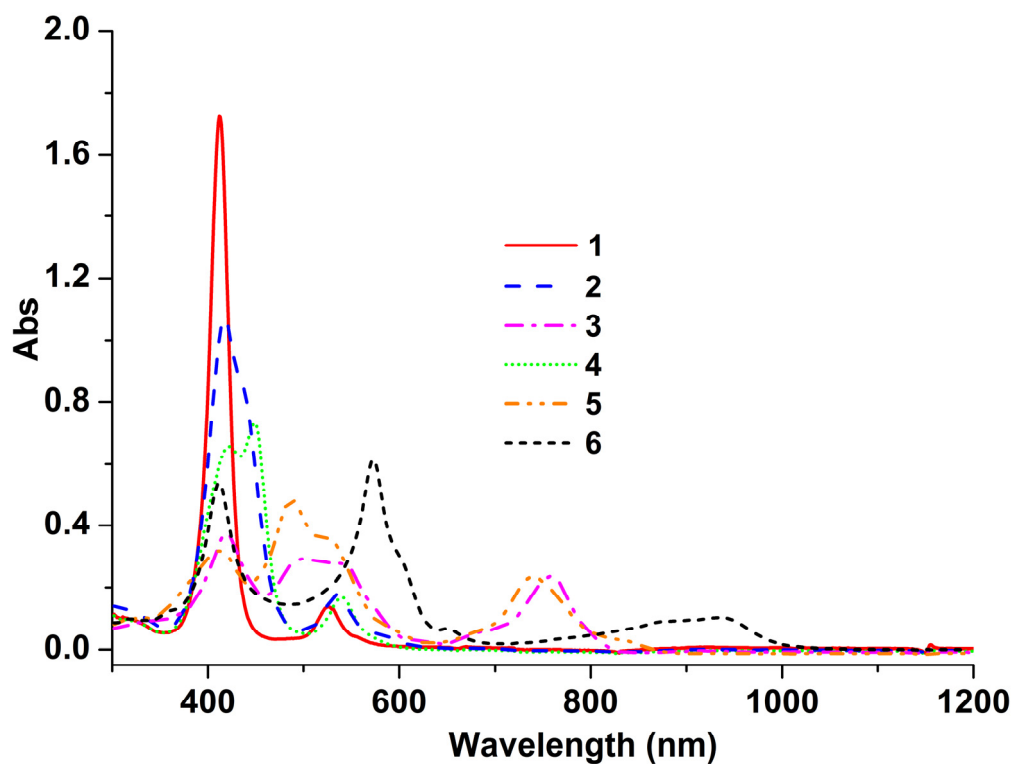
**Table S2.** Reaction Conditions for Synthesizing Doubly and Triply Linked Porphyrin Dimers **5** and **6**



entry	4/PIFA/BF <sub>3</sub> Et <sub>2</sub> O (equiv)	yield <sup>a</sup> (%)	
		5	6
1	1:0.5:0.5	93	0
2	1:1:0.5	65	30
3	1:2:0.5	0	90
4	1:2.5:0.5	0	85

To a stirred solution of **4** in dry CH<sub>2</sub>Cl<sub>2</sub> was added PIFA and BF<sub>3</sub>Et<sub>2</sub>O under a nitrogen atmosphere. <sup>a</sup>Isolated yield.

### 3. The absorption spectra of various linked Ni(II) porphyrin dimer



**Fig. S1.** Ultraviolet-visible-infrared absorption spectra of fused porphyrin dimer **1** (red), **2** (blue), **3** (pink), **4** (green), **5** (yellow) and **6** (black) in CHCl<sub>3</sub>.

### 4. The Procedure for the Synthesis of Singly Linked Porphyrin Dimers

For the *meso*- $\beta$  linked **2**

Under the nitrogen atmosphere, to a stirred solution of **1** (49 mg, 0.06 mmol) and BF<sub>3</sub>Et<sub>2</sub>O (4 mg, 0.03 mmol, 0.5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 10 min at the same temperature. Et<sub>3</sub>N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl<sub>3</sub>, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous

Na<sub>2</sub>SO<sub>4</sub> and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **2** (39 mg, 80%) was obtained after recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT): δ = 9.66 (d, *J* = 5.0 Hz, 1H), 9.63 (s, 1H), 9.60 – 9.56 (m, 3H), 9.07 – 9.04 (m, 2H), 8.91 – 8.86 (m, 3H), 8.76 (d, *J* = 5.0 Hz, 2H), 8.66 (bs, 3H), 8.46 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 1.7 Hz, 2H), 7.80 (d, *J* = 1.7 Hz, 2H), 7.71 – 7.68 (m, 4H), 1.48 – 1.40 (m, 72H).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, -40°C): δ = 9.66 (s, 1H), 9.68 (d, *J* = 5.0 Hz, 1H), 9.62 – 9.58 (m, 3H), 9.14 (d, *J* = 5.0 Hz, 1H), 9.01 (s, 1H), 8.96 (d, *J* = 5.0 Hz, 2H), 8.92 (d, *J* = 5.0 Hz, 1H), 8.80 (d, *J* = 5.0 Hz, 2H), 8.73 – 8.67 (m, 3H), 8.47 (d, *J* = 4.8 Hz, 1H), 8.17 – 8.12 (m, 4H), 7.80 (d, *J* = 1.8 Hz, 2H), 7.71 (bs, 1H), 7.69 (s, 3H), 7.59 (s, 2H), 1.51 – 1.46 (m, 32H), 1.44 (s, 18H), 1.40 (s, 18H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT): δ = 149.24, 149.09, 149.04, 145.90, 144.42, 143.90, 143.85, 143.78, 143.62, 143.56, 143.34, 143.05, 142.43, 142.38, 142.24, 141.38, 139.55, 139.35, 137.88, 133.72, 133.68, 133.64, 133.20, 133.16, 133.12, 133.07, 132.52, 129.27, 128.90, 128.74, 121.46, 121.32, 121.21, 121.12, 120.54, 112.16, 106.74, 102.76, 102.66, 35.00, 34.96, 31.67, 31.62.

HRMS (ESI) *m/z* [M]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>8</sub>Ni<sub>2</sub>: 1642.5080, found 1642.5073; Ultraviolet-visible absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>): 417 (2.14 × 10<sup>5</sup>), 431 (1.80 × 10<sup>5</sup>), 534 (3.57 × 10<sup>4</sup>).

#### For the *meso-meso* linked **4**

Under the nitrogen atmosphere, to a stirred solution of **1** (49 mg, 0.06 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 50 min at the same temperature. Et<sub>3</sub>N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl<sub>3</sub>, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **4** (44 mg, 90%) was obtained after recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT): δ = 9.58 (d, *J* = 5.0 Hz, 4 H), 8.85 (d, *J* = 5.0 Hz, 4 H), 8.53 (d, *J* = 5.0 Hz, 4 H), 8.02 (d, *J* = 5.0 Hz, 4 H), 7.83 (d, *J* = 1.6 Hz, 8 H), 7.66 (s, 4 H), 1.41 (s, 72 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT): δ = 149.00, 146.84, 143.95, 142.72, 142.26, 139.41, 134.08, 133.54, 133.10, 133.00, 128.71, 121.62, 121.30, 115.83, 102.97, 34.94, 31.60.

HRMS (MALDI) *m/z* [M+H]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>8</sub>Ni<sub>2</sub>: 1643.5158, found 1643.5175; Ultraviolet-visible absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>): 421 (1.64 × 10<sup>5</sup>), 449 (1.84 × 10<sup>5</sup>), 539 (4.20 × 10<sup>4</sup>).

## 5. The Procedure for the Synthesis of *meso-β*, *meso-β* Doubly Fused Dimer

Under the nitrogen atmosphere, to a stirred solution of **1** (49 mg, 0.06 mmol) and BF<sub>3</sub>·Et<sub>2</sub>O (4 mg, 0.03 mmol, 0.5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added dropwise a solution of PIFA (26 mg, 0.06 mmol, 1 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 10 min at the same temperature. Et<sub>3</sub>N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl<sub>3</sub>, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **3** (37 mg, 75%) was obtained after recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT): δ = 9.41 (s, 2H), 9.12 – 9.11 (m, 4H), 8.96 (s, 2H), 8.74 (d, *J* = 3.8 Hz, 2H), 8.44 (d, *J* = 5.0 Hz, 2H), 8.39 (d, *J* = 4.8 Hz, 2H), 7.91 (s, 4H), 7.84 – 7.65 (m, 8H), 1.54 (s, 36H), 1.51 (s, 36H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , RT):  $\delta = 149.44, 149.41, 144.68, 144.61, 143.45, 143.37, 143.31, 142.84, 142.39, 142.11, 140.22, 138.83, 138.61, 134.96, 134.00, 133.70, 133.21, 132.91, 132.41, 132.27, 128.90, 128.55, 123.15, 122.55, 121.66, 121.43, 110.10, 104.24, 35.09, 35.04, 31.73, 31.68$ .

HRMS (ESI)  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{96}\text{H}_{98}\text{Br}_2\text{N}_8\text{Ni}_2$ : 1640.4924, found 1640.4943; Ultraviolet-visible-infrared absorption: (in  $\text{CHCl}_3$ ,  $\lambda_{\text{max}}/\text{nm}$ ,  $\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ): 419 ( $0.76 \times 10^5$ ), 498 ( $0.59 \times 10^5$ ), 533 ( $0.56 \times 10^5$ ), 684 ( $1.16 \times 10^4$ ), 758 ( $4.66 \times 10^4$ ).

## 6. The Procedure for the Synthesis of *meso-meso*, $\beta\text{-}\beta$ Doubly Fused Dimer

Under the nitrogen atmosphere, a solution of **1** (49 mg, 0.06 mmol) and PIFA (26 mg, 0.06 mmol, 1 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (50 mL) was stirred at RT for 1 h. When the porphyrin monomer was completely consumed,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (4 mg, 0.03 mmol, 0.5 equiv) was added to the mixture. The mixture was stirred for additional 10 min at the same temperature.  $\text{Et}_3\text{N}$  (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with  $\text{CHCl}_3$ , then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **5** (41 mg, 84%) was obtained after recrystallization from  $\text{CHCl}_3/\text{CH}_3\text{OH}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , RT):  $\delta = 9.21$  (d,  $J = 5.0$  Hz, 2H), 9.16 (d,  $J = 4.9$  Hz, 2H), 8.78 (s, 2H), 8.55 – 8.51 (m, 2H), 8.48 (d,  $J = 5.0$  Hz, 4H), 7.76 (bs, 2H), 7.64 (bs, 2H), 7.46 (d,  $J = 5.1$  Hz, 2H), 1.70 – 1.20 (m, 72 H).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $-40^\circ\text{C}$ ):  $\delta = 9.23$  (d,  $J = 5.0$  Hz, 2H), 9.18 (d,  $J = 4.9$  Hz, 2H), 8.84 (s, 2H), 8.61 (d,  $J = 4.9$  Hz, 2H), 8.59 (d,  $J = 5.0$  Hz, 2H), 8.57 (d,  $J = 5.0$  Hz, 2H), 8.54 – 8.50 (m, 4H), 7.74 (bs, 2H), 7.63 (bs, 2H), 7.48 (d,  $J = 5.1$  Hz, 2H), 7.15 (s, 2H), 6.98 (s, 2H), 1.67 (s, 18H), 1.64 (s, 18H), 1.35 (s, 18H), 1.22 (s, 18H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , RT):  $\delta = 149.39, 145.98, 144.82, 143.85, 142.98, 142.51, 142.13, 141.88, 139.67, 139.64, 138.68, 137.77, 137.69, 137.49, 133.53, 133.44, 133.40, 133.26, 132.36, 128.68, 128.46, 126.49, 124.04, 121.55, 121.42, 120.40, 113.23, 103.98, 35.03, 34.98, 31.70, 31.60$ .

HRMS (ESI)  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{96}\text{H}_{98}\text{Br}_2\text{N}_8\text{Ni}_2$ : 1640.4924, found 1640.4950; Ultraviolet-visible-infrared absorption: (in  $\text{CHCl}_3$ ,  $\lambda_{\text{max}}/\text{nm}$ ,  $\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ): 412 ( $0.63 \times 10^5$ ), 487 ( $0.96 \times 10^5$ ), 526 ( $0.72 \times 10^5$ ), 738 ( $4.07 \times 10^4$ ).

## 7. The Procedure for the Synthesis of $\beta\text{-}\beta$ , *meso-meso*, $\beta\text{-}\beta$ Triply Fused Dimer

Under the nitrogen atmosphere, a solution of **1** (49 mg, 0.06 mmol) and PIFA (65 mg, 0.15 mmol, 2.5 equiv) in dry  $\text{CH}_2\text{Cl}_2$  (50 mL) was stirred at RT for 1 h. When porphyrin monomer was completely consumed,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (4mg, 0.03mmol, 0.5 equiv) was added to mixture. The mixture was stirred for additional 10 min at the same temperature.  $\text{Et}_3\text{N}$  (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with  $\text{CHCl}_3$ , then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **6** (39 mg, 80%) was obtained after recrystallization from  $\text{CHCl}_3/\text{petroleum ether}$ .

$^1\text{H}$  NMR (400 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$ , RT):  $\delta = 8.52$  (d,  $J = 4.9$  Hz, 4H), 7.77 (d,  $J = 4.9$  Hz, 4H), 7.60 (s, 4H), 7.54 (s, 8H), 7.47 (s, 4H), 1.43 (s, 72H).

$^{13}\text{C}$  NMR (100 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$ , RT):  $\delta = 149.15, 147.45, 146.53, 145.52, 145.47, 138.37, 134.76, 132.04, 131.70, 127.65, 127.49, 125.01, 121.40, 113.31, 107.89, 34.81, 31.59$ .

HRMS (ESI)  $m/z$   $[M]^+$  calcd. for  $C_{96}H_{96}Br_2N_8Ni_2$ : 1638.4767, found 1638.4787; Ultraviolet-visible-infrared absorption: (in  $CHCl_3$ ,  $\lambda_{max}/nm$ ,  $\epsilon/mol^{-1}dm^3cm^{-1}$ ): 411 ( $1.58 \times 10^5$ ), 572 ( $1.23 \times 10^5$ ), 651 ( $1.13 \times 10^4$ ), 864 ( $1.72 \times 10^4$ ), 937 ( $2.10 \times 10^4$ ).

## 8. $S_NAr$ reaction of **2**

**2** (40 mg, 0.02 mmol),  $Cs_2CO_3$  (33 mg, 0.10 mmol, 5 equiv) and phenol (9 mg, 0.10 mmol, 5 equiv) were added to a 25 mL two-necked round bottom flask, then the flask was evacuated and backfilled with  $N_2$  for 3 times. DMF (5 mL) was added using a syringe, then the reaction was heated to  $100^\circ C$ . The solution was continuously stirred at the temperature for 1.5 h. When compound **2** was completely consumed, the mixture was cooled down to room temperature, and water (5.0 mL) was added to precipitate the product. **8** (33 mg, 81%) was obtained after recrystallization from  $CHCl_3/CH_3OH$ .

$^1H$  NMR (400 MHz,  $CDCl_3$ , RT):  $\delta$  = 9.69 (s, 1H), 9.36 (d,  $J$  = 4.9 Hz, 1H), 9.31 – 9.27 (m, 3H), 9.10 (s, 1H), 9.02 (d,  $J$  = 4.9 Hz, 1H), 8.88 – 8.78 (m, 5H), 8.70 – 8.66 (m, 3H), 8.48 (d,  $J$  = 4.8 Hz, 1H), 8.16 – 8.08 (m, 4H), 7.83 (d,  $J$  = 1.7 Hz, 2H), 7.72 – 7.60 (m, 4H), 7.24 – 7.19 (m, 2H), 7.01 (t,  $J$  = 7.3 Hz, 2H), 6.95 (t,  $J$  = 7.5 Hz, 4H), 1.48 – 1.40 (m, 72H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ , RT):  $\delta$  = 164.39, 164.33, 164.18, 149.21, 149.06, 149.01, 146.27, 144.70, 143.88, 143.62, 143.40, 143.33, 143.31, 143.05, 143.02, 141.44, 139.85, 139.65, 139.63, 139.40, 139.37, 139.13, 137.95, 133.09, 132.97, 132.79, 132.69, 132.10, 132.00, 129.62, 129.30, 128.90, 128.76, 128.30, 128.13, 128.09, 121.80, 121.77, 121.36, 121.22, 120.99, 120.91, 120.35, 116.49, 111.63, 106.23, 35.01, 34.97, 31.69, 31.64.

HRMS (MALDI)  $m/z$   $[M]^+$  calcd. for  $C_{108}H_{110}O_2N_8Ni_2$ : 1667.7486, found 1667.7500; Ultraviolet-visible absorption: (in  $CHCl_3$ ,  $\lambda_{max}/nm$ ,  $\epsilon/mol^{-1}dm^3cm^{-1}$ ): 419 ( $2.19 \times 10^5$ ), 432 ( $2.03 \times 10^5$ ), 530 ( $4.20 \times 10^4$ ).

## 9. Demetalation of **2**, **3** and **6**

For *meso*- $\beta$  singly linked dimer **7**

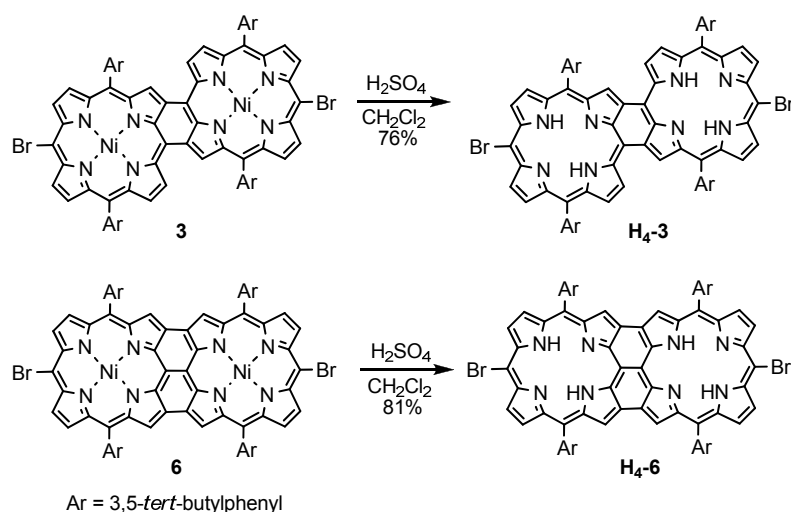
Porphyrin dimer **2** (82 mg, 0.05 mmol) was dissolved in dry  $CH_2Cl_2$  (20 mL) in a 100 mL round-bottomed flask. The solution was cooled to  $-10^\circ C$ , and then treated with 0.5 mL of  $H_2SO_4/TFA$  (1:10) 30 min. After neutralization by aqueous  $NaHCO_3$ , the solution was extracted with  $CH_2Cl_2$ , washed by brine, dried over anhydrous  $Na_2SO_4$ , and the solvent was removed under vacuum. The crude residue was purified by column chromatography (silica-gel). **7** (43 mg, 57%) was obtained after recrystallization from  $CHCl_3/CH_3OH$ .

$^1H$  NMR (400 MHz,  $CDCl_3$ , RT):  $\delta$  = 9.89 (d,  $J$  = 4.9 Hz, 1H), 9.81 – 9.74 (m, 4H), 9.70 (s, 1H), 9.24 (d,  $J$  = 4.9 Hz, 1H), 9.00 (d,  $J$  = 4.6 Hz, 2H), 8.97 (d,  $J$  = 4.8 Hz, 1H), 8.91 (d,  $J$  = 4.6 Hz, 2H), 8.81 (d,  $J$  = 4.7 Hz, 1H), 8.75 (d,  $J$  = 4.7 Hz, 2H), 8.65 (d,  $J$  = 4.7 Hz, 1H), 8.37 (d,  $J$  = 1.8 Hz, 2H), 8.14 (d,  $J$  = 1.4 Hz, 2H), 8.06 – 7.99 (4 H, m), 7.79 – 7.72 (4 m, 4 H), 1.51 – 1.49 (m, 36H), 1.49 – 1.47 (m, 36H), -2.30 (s, 2 H), -2.55 (s, 2 H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ , RT):  $\delta$  = 149.41, 149.39, 149.27, 149.25, 149.20, 149.02, 148.91, 148.87, 146.27, 144.33, 140.72, 140.43, 140.27, 138.73, 138.64, 133.91, 133.81, 132.41, 132.32, 132.09, 131.93, 131.67, 131.30, 131.02, 130.52, 130.47, 130.40, 129.97, 129.95, 129.85, 122.65, 122.43, 121.97, 121.44, 121.26, 113.64, 107.28, 103.66, 103.46, 35.05, 35.03, 31.72, 31.69.

HRMS (MALDI)  $m/z$   $[M+H]^+$  calcd. for  $C_{96}H_{104}Br_2N_8$ : 1529.6807, found 1529.6827; Ultraviolet-visible absorption: (in  $CHCl_3$ ,  $\lambda_{max}/nm$ ,  $\epsilon/mol^{-1}dm^3cm^{-1}$ ): 423 ( $3.12 \times 10^5$ ), 438 ( $2.65 \times 10^5$ ), 539 ( $4.40 \times 10^4$ ), 557 ( $2.50 \times 10^4$ ), 597 ( $1.75 \times 10^4$ ), 653 ( $12.5 \times 10^4$ ).

For fused dimers **H<sub>4</sub>-3** and **H<sub>4</sub>-6**



**Scheme S1.** Demetalation reaction of **3** and **6**

Porphyrin dimer **3** (50 mg, 0.03 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) in a 50 mL round-bottomed flask. The solution was treated with concentrated H<sub>2</sub>SO<sub>4</sub> (0.1 mL) 30 min at RT. After neutralization by aqueous NaHCO<sub>3</sub>, the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. The crude residue was purified by column chromatography (silica-gel). **H<sub>4</sub>-3** (35 mg, 76%) was obtained after recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH.

**H<sub>4</sub>-3:**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT): δ = 9.47 (d, *J* = 4.6 Hz, 2H), 9.26 – 9.20 (m, 4H), 9.10 (s, 2H), 8.62 – 8.56 (m, 4H), 8.49 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 1.4 Hz, 4H), 7.98 (d, *J* = 1.4 Hz, 4H), 7.88 – 7.85 (m, 2H), 7.82 – 7.78 (m, 2H), 1.59 – 1.56 (m, 72H), 0.52 (s, 4H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT): δ = 149.33, 149.25, 147.07, 146.93, 146.10, 145.79, 145.26, 145.12, 144.51, 143.41, 143.23, 142.54, 142.31, 140.24, 140.04, 138.37, 137.65, 135.61, 135.50, 135.19, 129.98, 129.88, 124.96, 124.19, 121.62, 121.41, 105.43, 94.92, 35.17, 35.11, 31.83, 31.74.

HRMS (MALDI) *m/z* [M+H]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>102</sub>Br<sub>2</sub>N<sub>8</sub>: 1527.6651, found 1527.6655; Ultraviolet-visible-infrared absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>): 425 (1.31 × 10<sup>5</sup>), 501 (6.70 × 10<sup>4</sup>), 545 (5.45 × 10<sup>4</sup>), 616 (4.35 × 10<sup>4</sup>), 821 (5.50 × 10<sup>4</sup>).

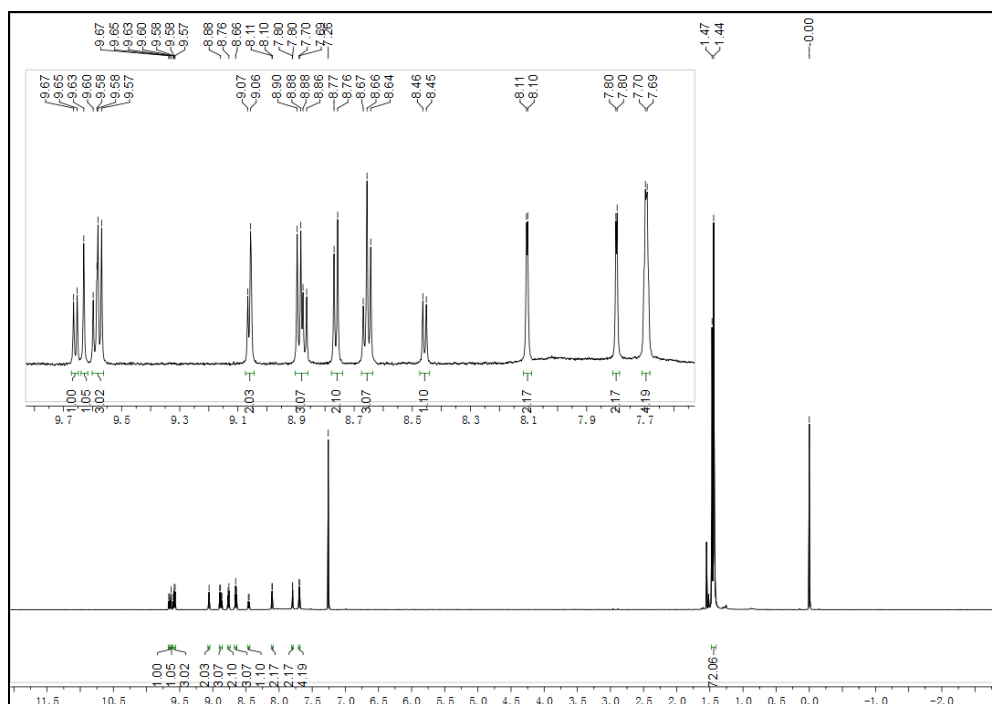
**H<sub>4</sub>-6:** Following the same procedure for demetalation of **3**.

<sup>1</sup>H NMR (400 MHz, V<sub>CDCl<sub>3</sub></sub>/V<sub>CS<sub>2</sub></sub> = 4:1, RT): δ = 8.46 – 8.38 (m, 6H), 7.65 – 7.63 (m, 6H), 7.61 – 7.57 (m, 12H), 1.46 – 1.42 (m, 76H)

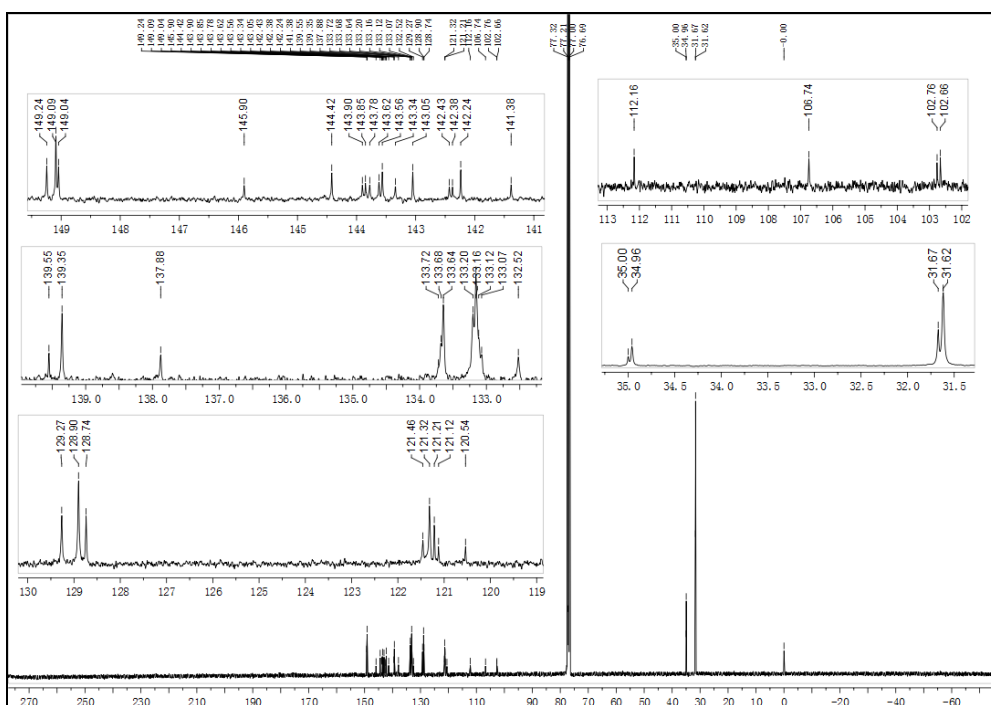
<sup>13</sup>C NMR (100 MHz, V<sub>CDCl<sub>3</sub></sub>/V<sub>CS<sub>2</sub></sub> = 4:1, RT): δ = 148.94, 147.60, 146.65, 145.47, 145.45, 138.83, 133.97, 128.95, 128.18, 125.84, 125.81, 125.53, 121.33, 114.28, 107.83, 34.73, 31.57.

HRMS (MALDI) *m/z* [M+H]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>8</sub>: 1525.6494, found 1525.6508; Ultraviolet-visible-infrared absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>): 415 (1.19 × 10<sup>5</sup>), 482 (5.90 × 10<sup>4</sup>), 565 (1.24 × 10<sup>5</sup>), 1044 (2.73 × 10<sup>4</sup>), 1090 (3.07 × 10<sup>4</sup>).

## 10. NMR Spectra of Directly Linked Porphyrin Dimers







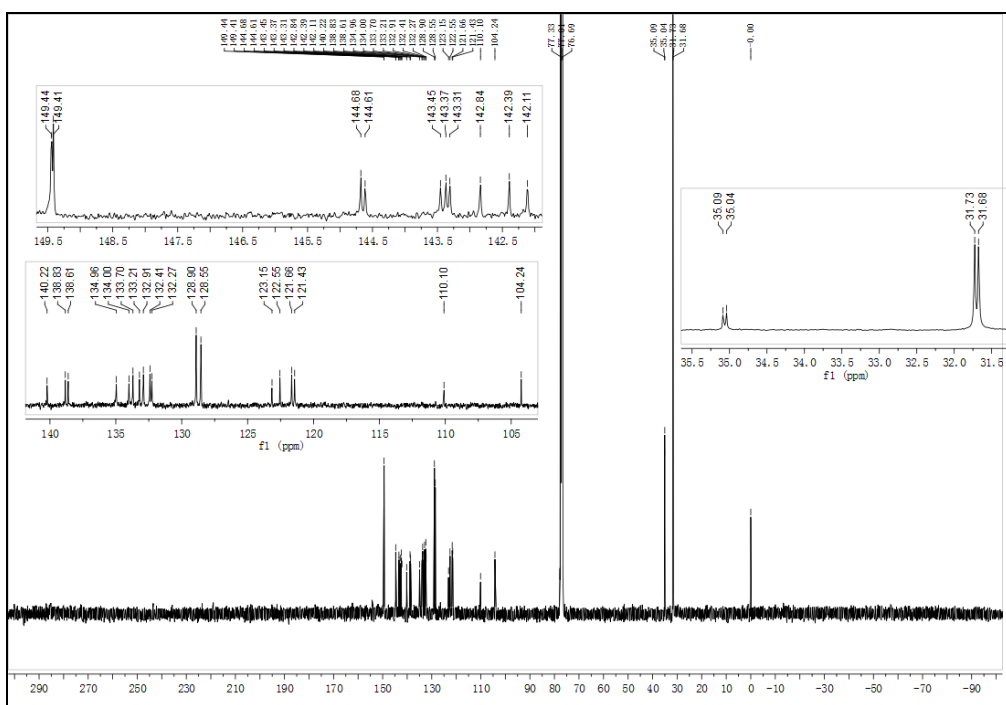


Figure S6.  $^{13}\text{C}$  NMR spectrum of **3** (100 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

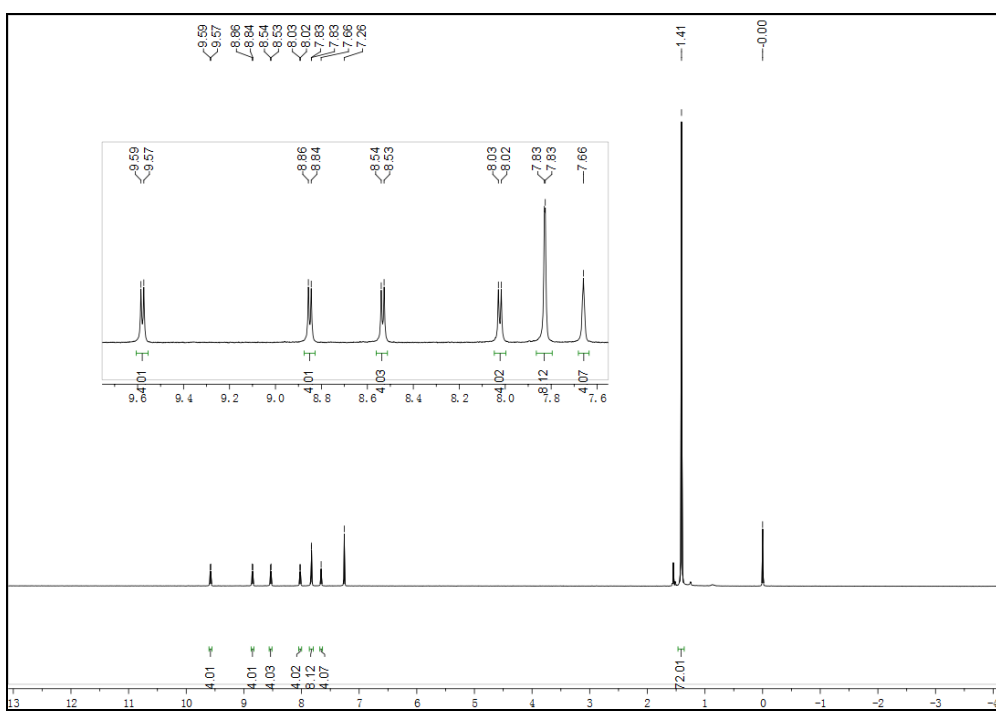


Figure S7.  $^1\text{H}$  NMR spectrum of **4** (400 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

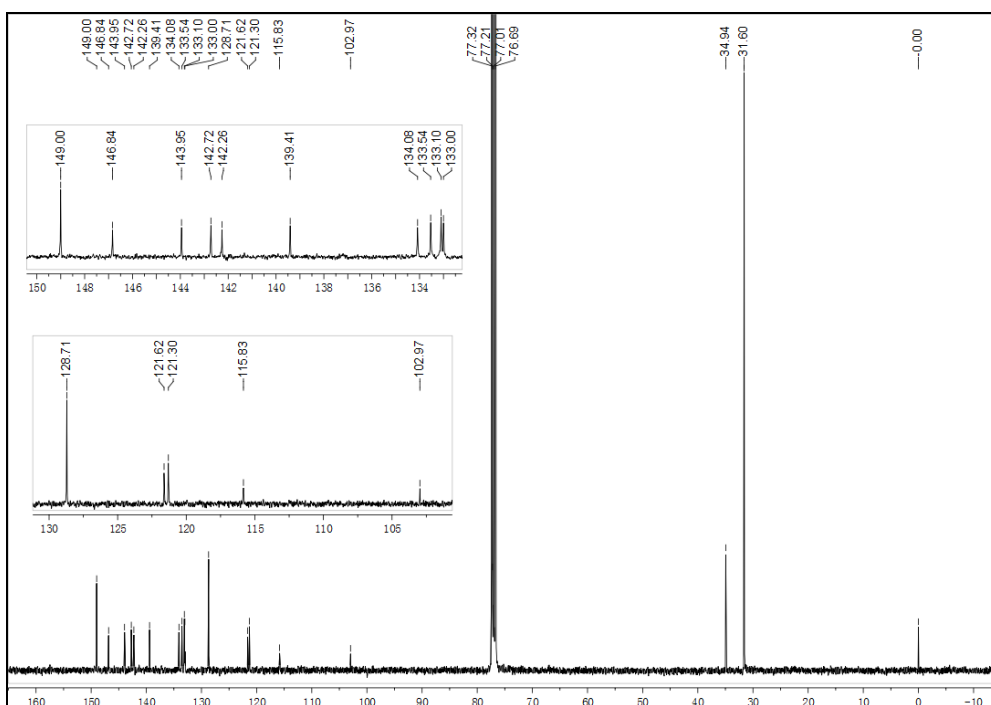


Figure S8.  $^{13}\text{C}$  NMR spectrum of **4** (100 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

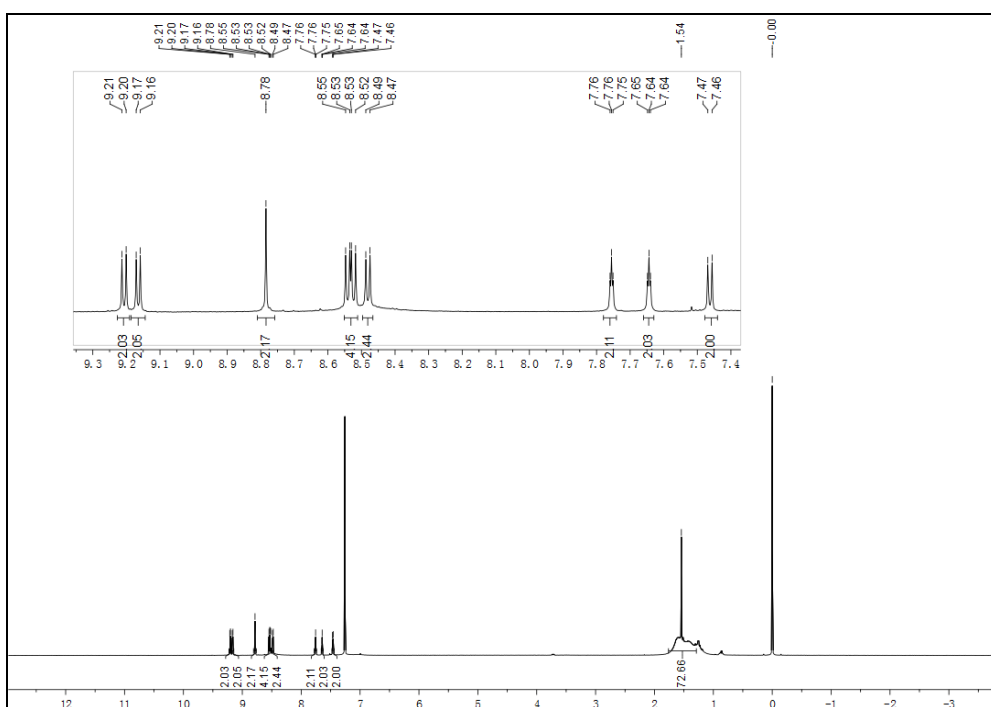


Figure S9.  $^1\text{H}$  NMR spectrum of **5** (400 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

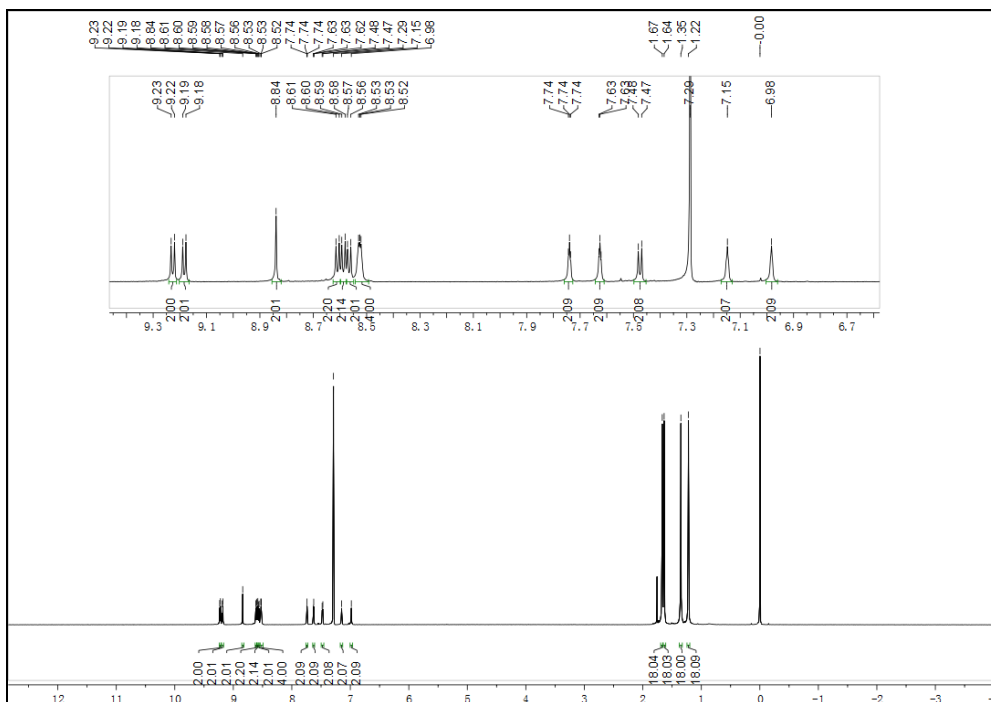


Figure S10. <sup>1</sup>H NMR spectrum of 5 (400 MHz, CDCl<sub>3</sub> at -40°C).

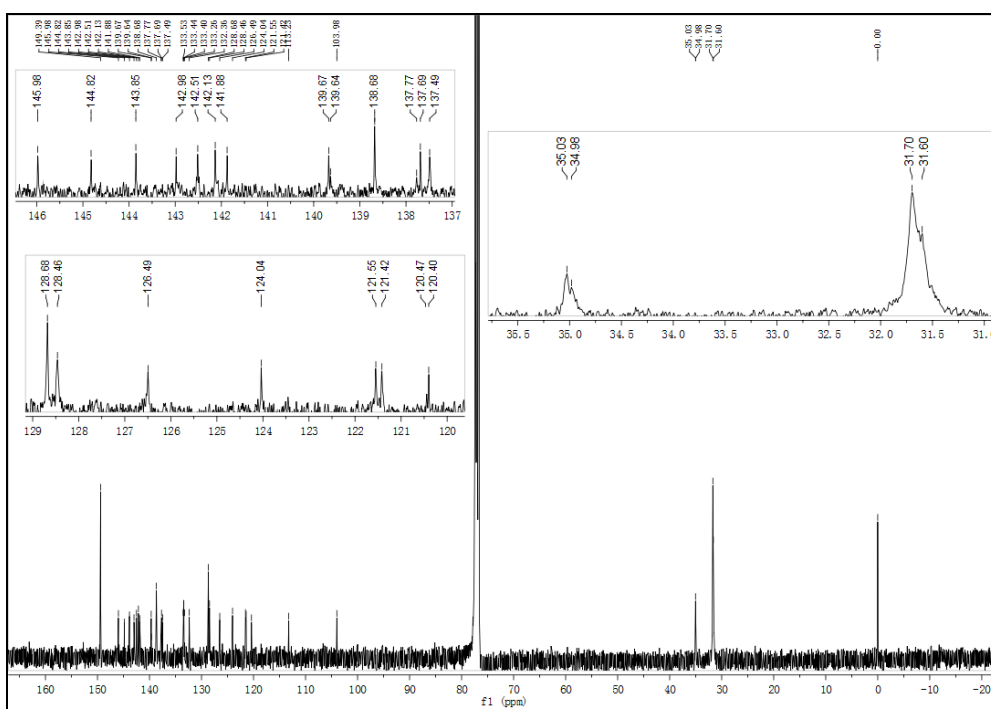


Figure S11. <sup>13</sup>C NMR spectrum of 5 (100 MHz, CDCl<sub>3</sub> at 25°C).

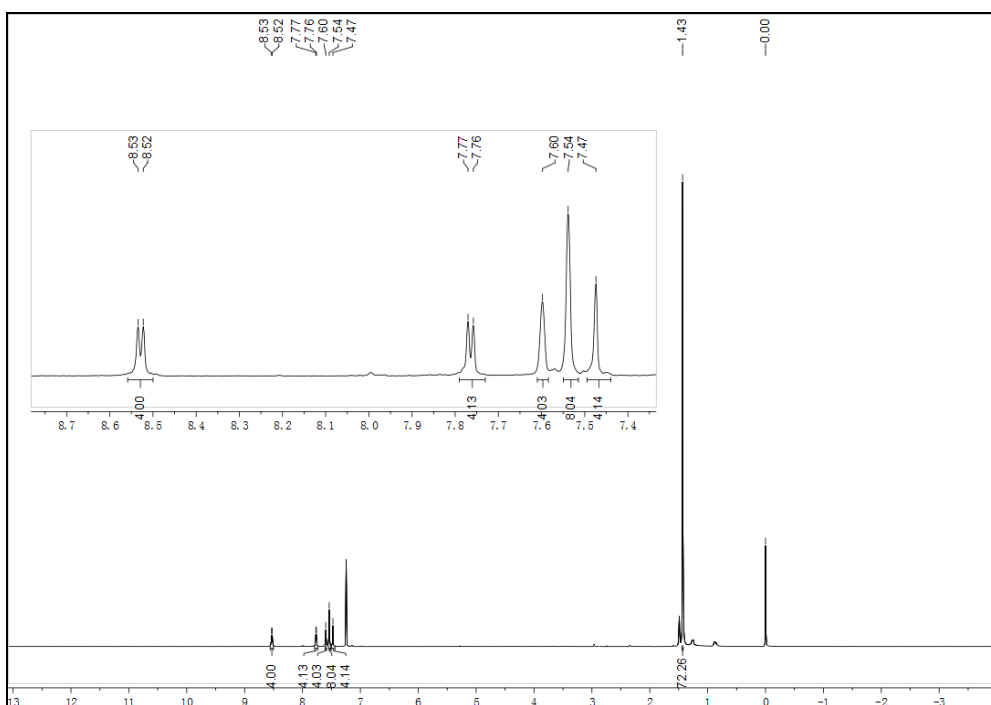


Figure S12.  $^1\text{H}$  NMR spectrum of **6** (400 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$  at  $25^\circ\text{C}$ ).

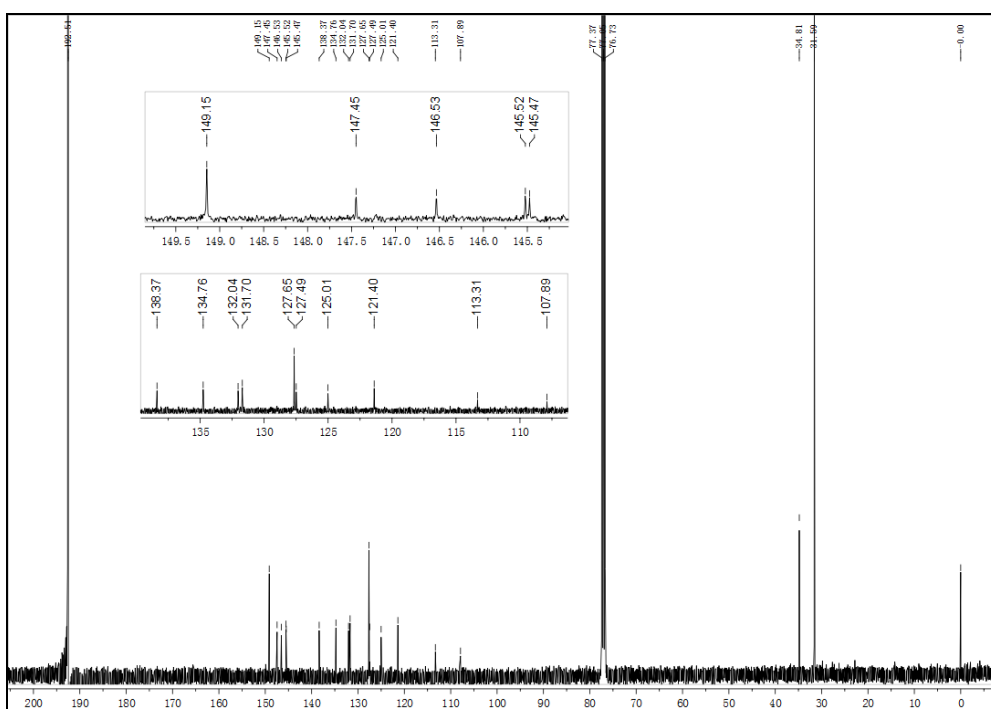


Figure S13.  $^{13}\text{C}$  NMR spectrum of **6** (100 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$  at  $25^\circ\text{C}$ ,  $\delta(^{13}\text{C}_{\text{CS}_2}) = 192.51$ ).

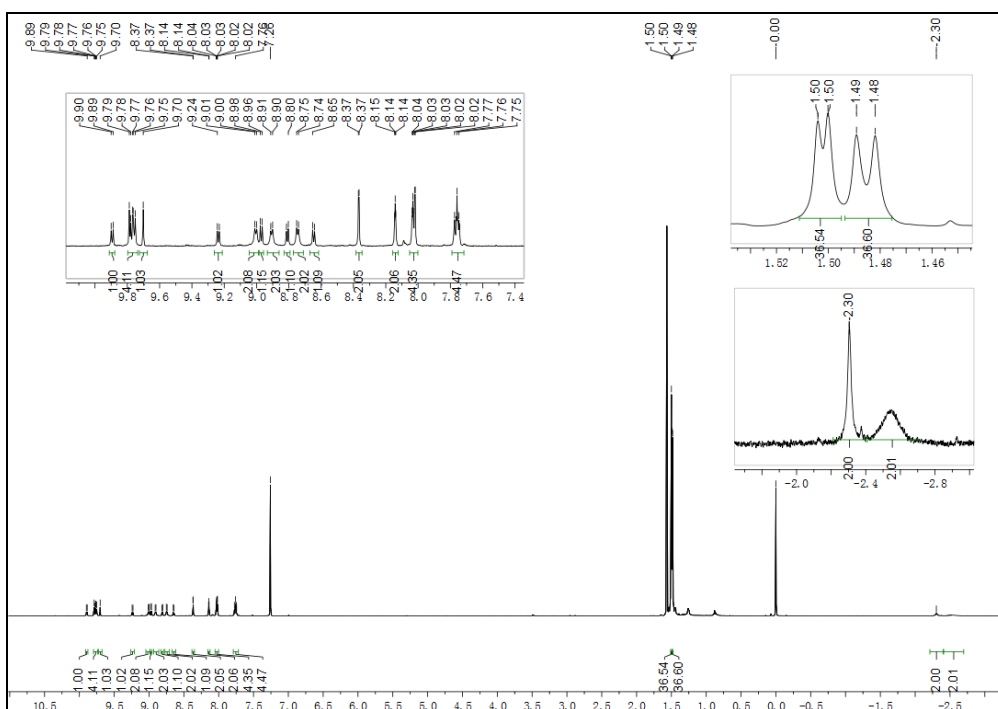


Figure S14.  $^1\text{H}$  NMR spectrum of **7** (400 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

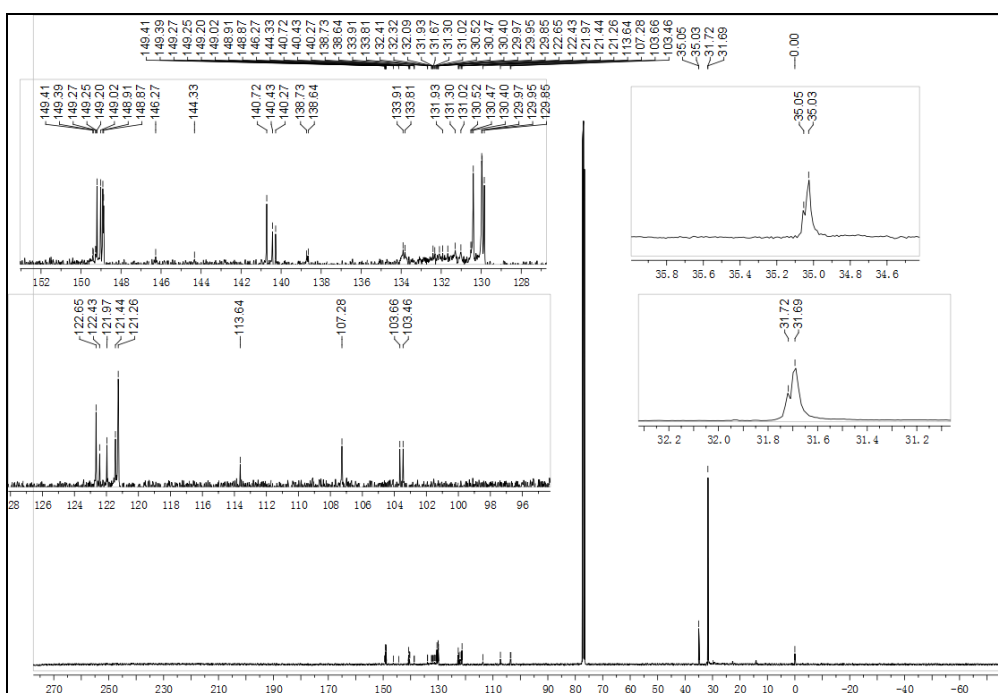


Figure S15.  $^{13}\text{C}$  NMR spectrum of **7** (100 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

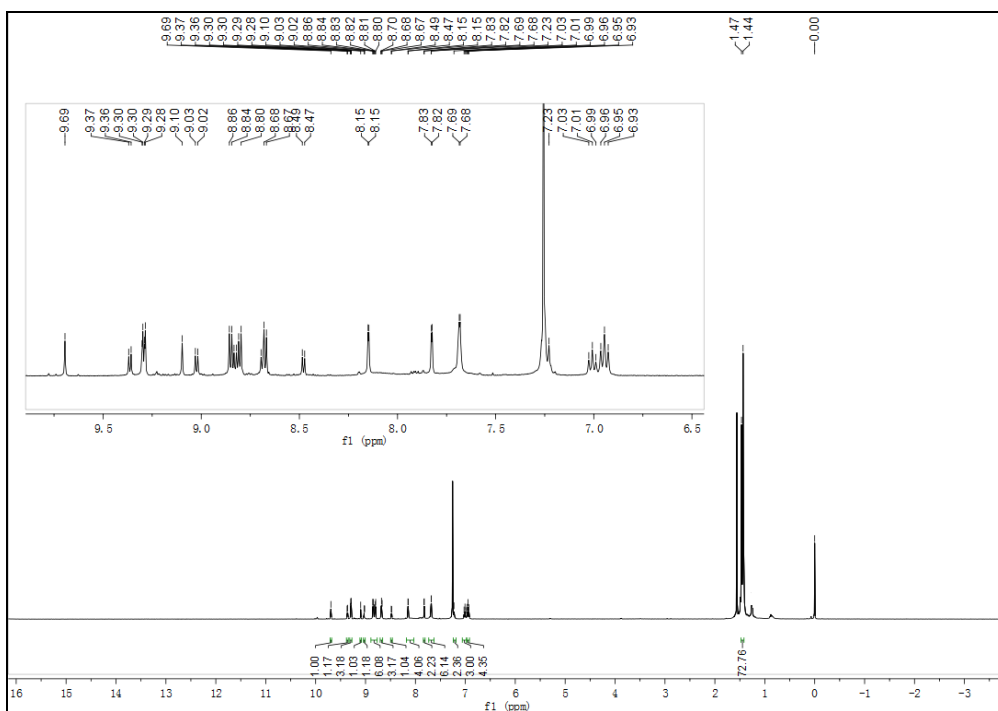


Figure S16.  $^1\text{H}$  NMR spectrum of **8** (400 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

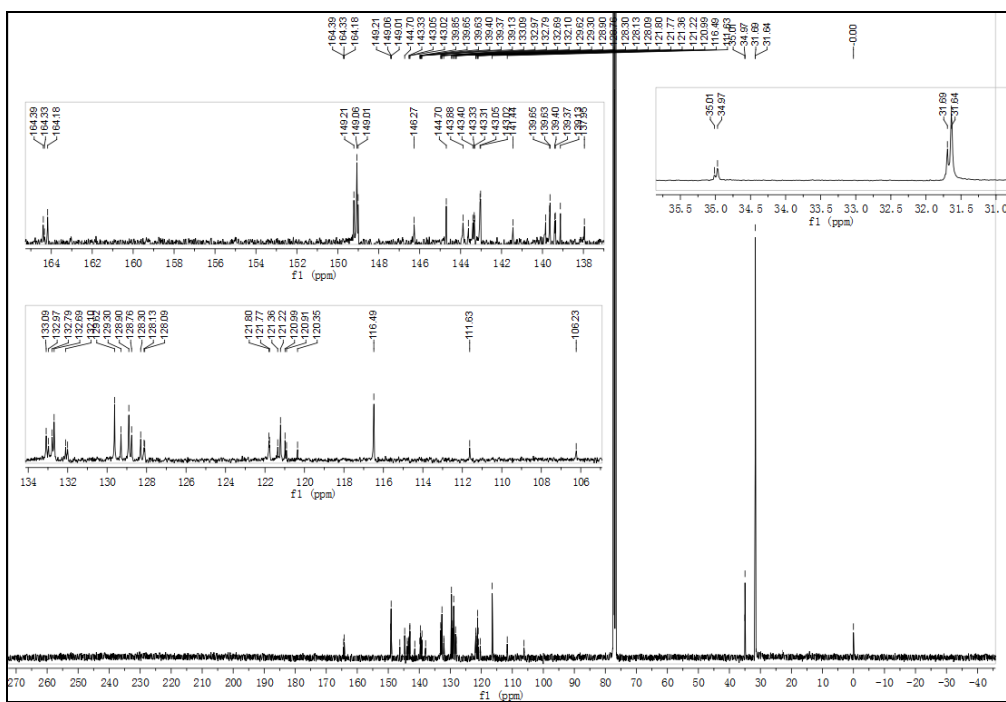


Figure S17.  $^{13}\text{C}$  NMR spectrum of **8** (100 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

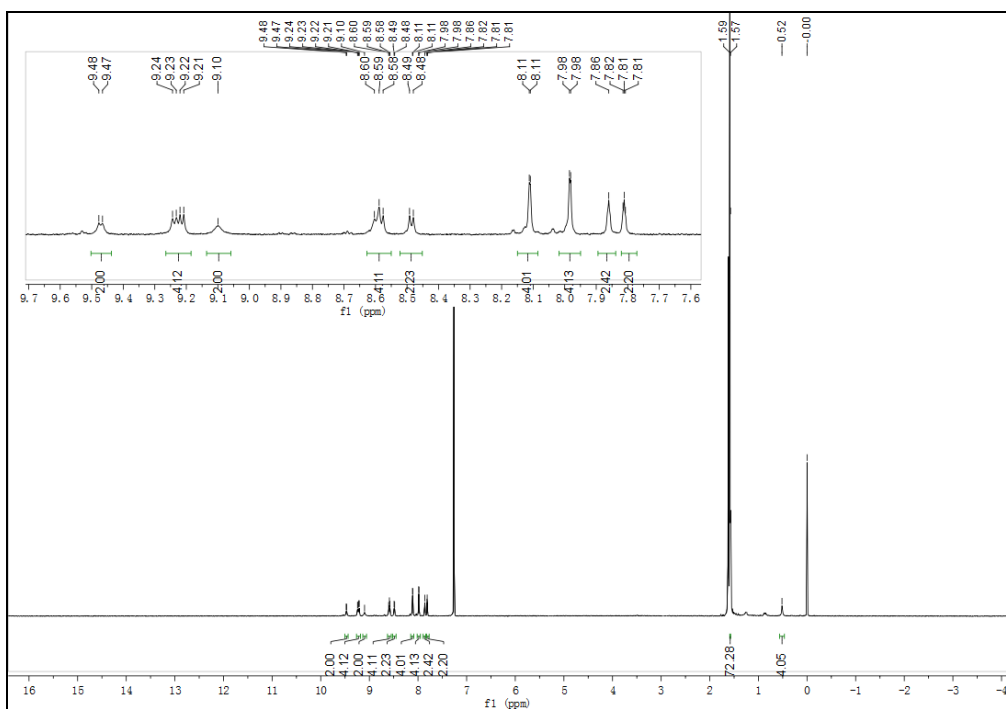


Figure S18.  $^1\text{H}$  NMR spectrum of H4-3 (400 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).

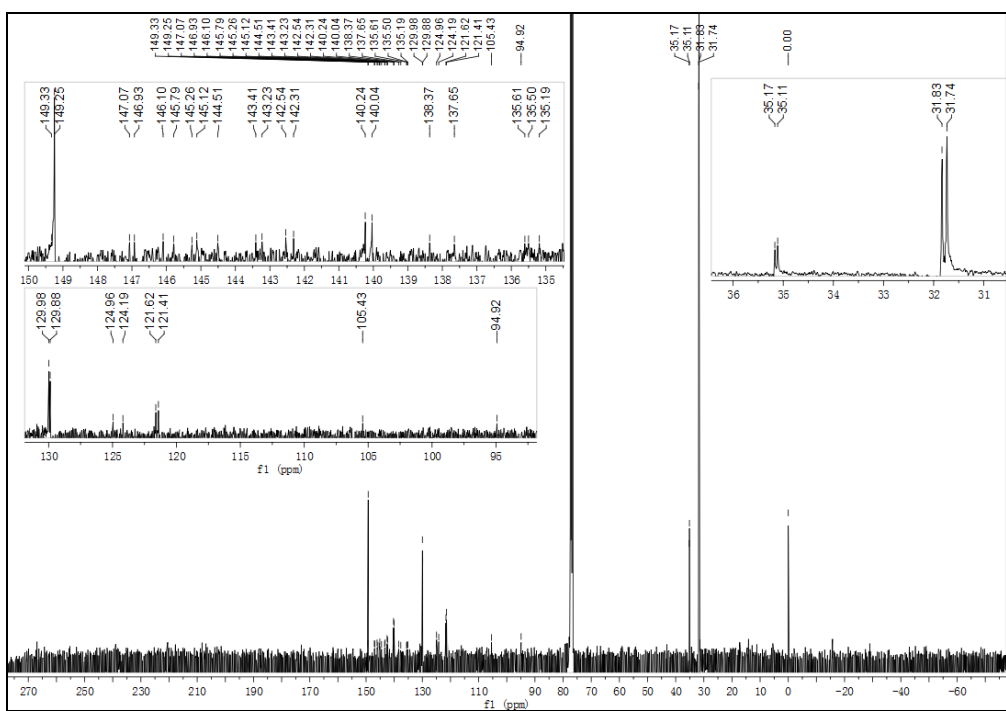


Figure S19.  $^{13}\text{C}$  NMR spectrum of H4-3 (100 MHz,  $\text{CDCl}_3$  at  $25^\circ\text{C}$ ).



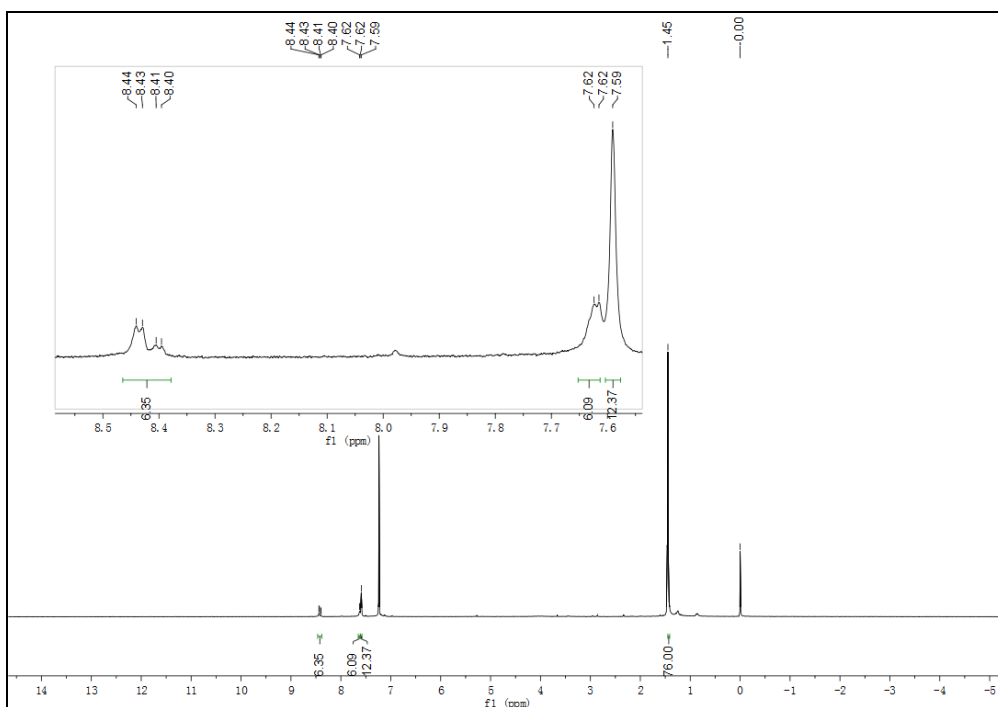


Figure S20.  $^1\text{H}$  NMR spectrum of **H4-6** (400 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$  at  $25^\circ\text{C}$ ).

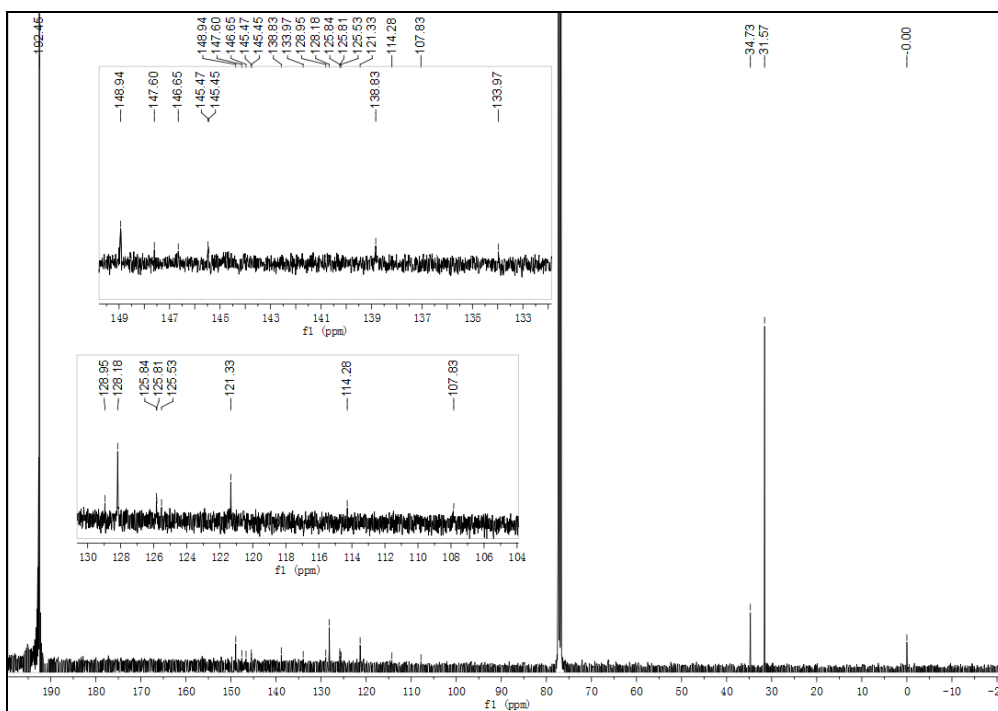


Figure S21.  $^{13}\text{C}$  NMR spectrum of **H4-6** (100 MHz,  $V_{\text{CDCl}_3}/V_{\text{CS}_2} = 4:1$  at  $25^\circ\text{C}$ ,  $\delta(^{13}\text{C}_{\text{CS}_2}) = 192.45$ ).

## 11. Crystal Data for 2

Compound reference	<b>2</b>
Chemical formula	C <sub>96</sub> H <sub>100</sub> Br <sub>2</sub> N <sub>8</sub> Ni <sub>2</sub>
Formula Mass	1643.02
Crystal system	Monoclinic
<i>a</i> /Å	38.7(10)
<i>b</i> /Å	9.0001(13)
<i>c</i> /Å	33.3200(3)
<i>α</i> /°	90.00
<i>β</i> /°	109.69
<i>γ</i> /°	90.00
Unit cell volume/Å <sup>3</sup>	10927
Temperature/K	273(2)
Space group	<i>P</i> 21/ <i>c</i>
No. of formula units per unit cell, <i>Z</i>	4
No. of reflections measured	47293
No. of independent reflections	19023
<i>R</i> <sub>int</sub>	0.0420
Final <i>R</i> <sub>I</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0994
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.2754
Final <i>R</i> <sub>I</sub> values (all data)	0.1410
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.3090