

SUPPLEMENTARY INFORMATION

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**Bistable [2]Rotaxane Encoding An Orthogonally Tunable  
Fluorescent Molecular System Including White-Light Emission**

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**Experimental Section**

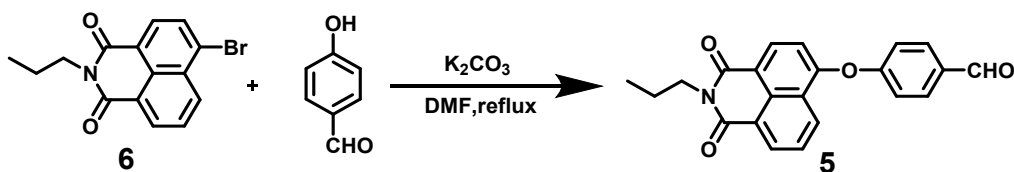
**General Methods**

NMR experiments ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR) were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The UV/Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell used), respectively.

**Materials**

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures of the unknown compounds were confirmed via  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and High Resolution ESI mass spectroscopy. Compound **2**, **3**, **4**, **6** were synthesized and purified according to the references 1-4, respectively.

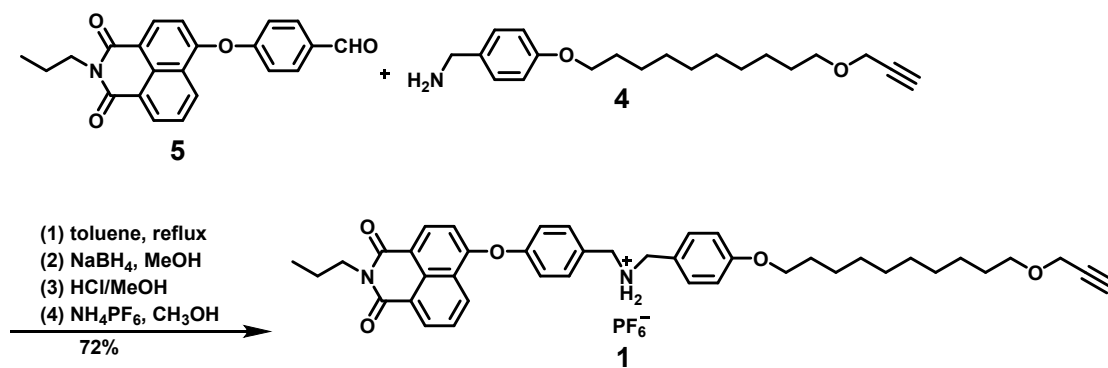
## Synthesis



**Scheme 1.** Synthesis of compound **5**

### Synthesis of compound **5**

A mixture of compound **6** (1.00 g, 3.15 mmol) and 4-hydroxybenzaldehyde (0.58 g, 4.75 mmol) in dry N, N-dimethylformamide (30 mL) was refluxed overnight under argon atmosphere. After removal of the solvent, water (30 mL) was added, the mixture was extracted by  $CH_2Cl_2$  ( $3 \times 50$  mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The crude product was purified via column chromatography ( $SiO_2$ , PE/EA = 3/1) to give compound **5** (0.84 g, 74%) as a yellow solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  10.01 (s, 1H), 8.67 (dd,  $J=1.2$  Hz, 7.6Hz, 1H), 8.57-8.51 (m, 2H), 8.01-7.92 (m, 2H), 7.79 (dd,  $J=7.6, 8.4$  Hz, 1H), 7.31-7.23 (m, 3H), 7.13 (d,  $J=8.0$  Hz, 1H), 4.18-4.12 (m, 2H), 1.86-1.69 (m, 2H), 1.02 (t,  $J=7.2$  Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz, 298 K):  $\delta$  190.51, 164.02, 163.42, 160.80, 157.51, 133.09, 132.31, 132.21, 131.97, 129.68, 128.09, 126.98, 124.36, 122.82, 119.80, 118.31, 113.38, 41.90, 21.38, 11.52. HRMS (ESI) (m/z):  $[M+H]^+$  calcd for  $C_{22}H_{18}NO_4$ , 360.1236; found, 360.1237.



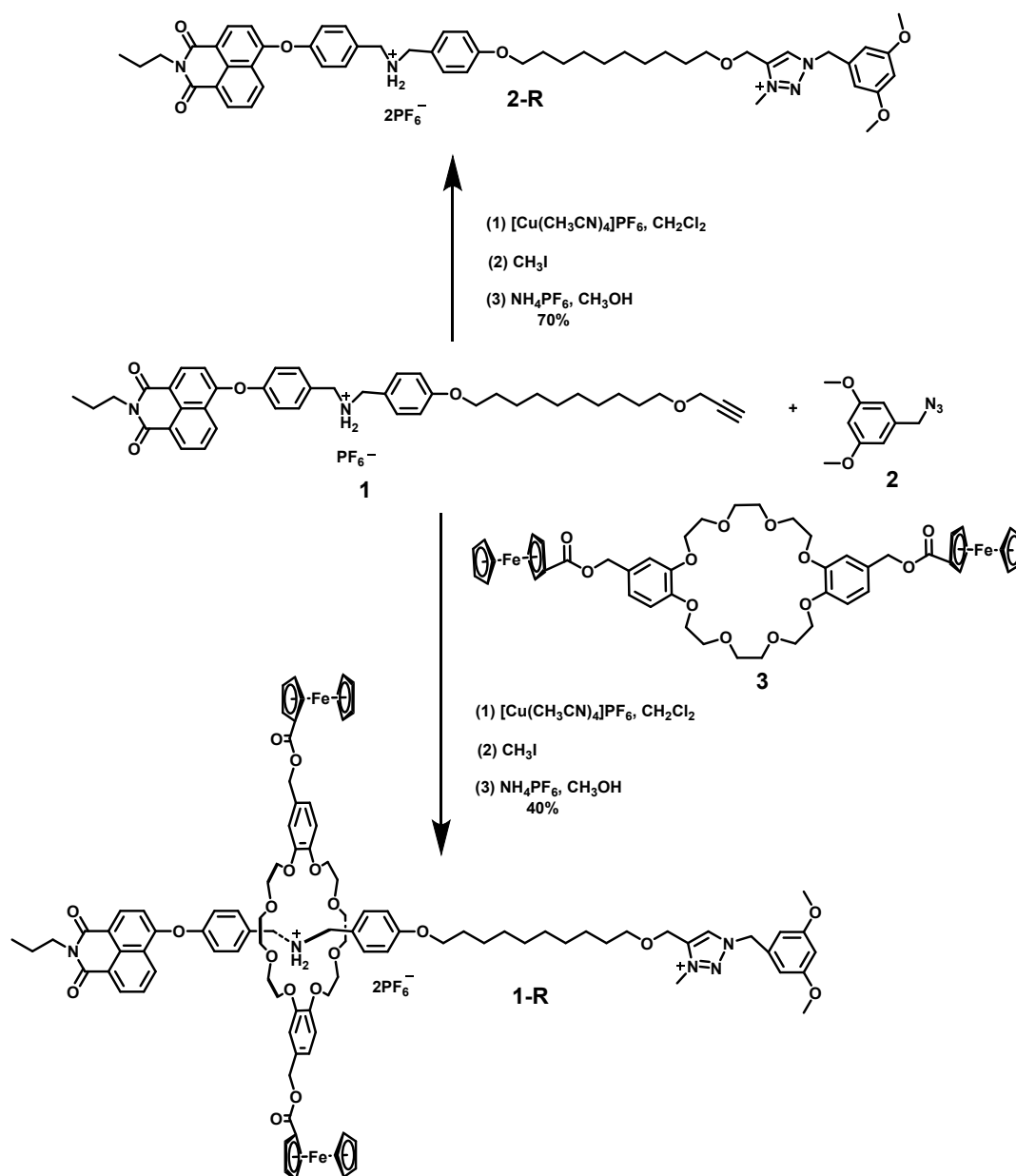
Scheme 2. Synthesis of compound 1

### Synthesis of compound 1

A mixture of compound **5** (0.50 g, 1.4 mmol) and **4** (0.53 g, 1.67 mmol) in dry toluene (20 mL) was refluxed overnight under argon atmosphere. The solvent was removed under vacuum, and the residue was dissolved in MeOH (25 mL). To the solution was added NaBH<sub>4</sub> (0.21 g, 5.5 mmol) in portion under ice bath. After the mixture was stirred for 4 h, the solution was poured into water, and the mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated to give the free amine compound. The residue was dissolved in MeOH (25 mL), and then added saturated NH<sub>4</sub>PF<sub>6</sub> (10 mL). After the mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum, and then water (30 mL) was added, the mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The crude product was purified via column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 30/1) to give compound **1** (0.88 g, 72%) as a pale solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 6.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.34-7.22 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.89 (t, *J* = 8.4 Hz, 3H), 4.20-4.10 (m, 4H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 2H), 3.80 (s, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.42 (t, *J* = 2.4 Hz, 1H), 1.83-1.74 (m, 5H), 1.63-1.55 (m, 2H), 1.52-1.42 (m, 2H), 1.38-1.26 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298 K): δ 164.41, 163.78, 159.97, 158.32, 153.69, 137.84, 132.77, 131.93, 131.83, 130.12, 129.68, 129.32, 128.52, 126.44, 123.89, 122.66, 120.69, 116.67, 116.55, 114.47, 110.48, 80.08, 74.07, 70.30, 68.05, 58.01, 53.44, 52.73, 52.39, 41.85, 29.51, 29.49, 29.41, 29.38, 29.31, 26.08, 21.43, 11.54.

## SUPPLEMENTARY INFORMATION

HRMS (ESI) (m/z):  $[M-PF_6]^+$  calcd for  $C_{42}H_{49}N_2O_5$ , 661.3636; found, 661.3649.



**Scheme 3.** Synthesis of compound **1-R** and **2-R**

### Synthesis of 2-R

A mixture of **1** (102 mg, 0.126 mmol), **2** (49 mg, 0.25 mmol) and  $[Cu(CH_3CN)_4]PF_6$  (71 mg, 0.19 mmol) were stirred in dry  $CH_2Cl_2$  (4 ml) at room temperature for three days. After removal of the solvent, the residue was dissolved in iodomethane (6 mL), and the mixture was stirred for 1 d at 40 °C. The excess iodomethane was evaporated, and the solid was washed with  $CH_2Cl_2$  to give a yellow solid. To a suspension of the solid was then added saturated  $NH_4PF_6$  (10 mL) and  $CH_3OH$  (6 mL), respectively. The resulted mixture was vigorously stirred at room temperature for 2 h. The aqueous

## SUPPLEMENTARY INFORMATION

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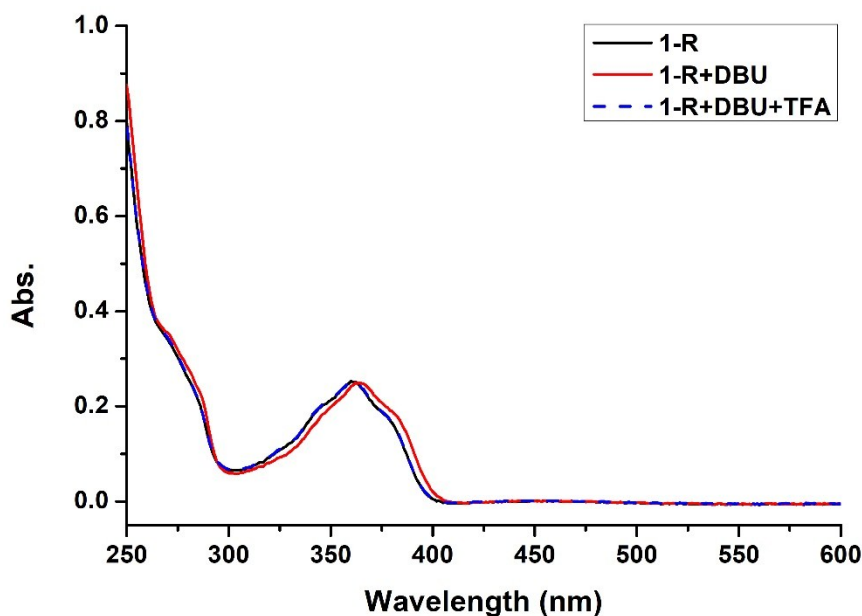
layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The residue was purified via column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH} = 20/1$ ) to give compound **2-R** (103 mg, 70 %) as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  8.69 (d,  $J = 8.4$  Hz, 1H), 8.66 (d,  $J = 6.0$  Hz, 1H), 8.44 (d,  $J = 8.0$  Hz, 1H), 8.23 (s, 1H), 7.77 (dd,  $J = 7.2, 7.6$  Hz, 1H), 7.46 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 6.90 (d,  $J = 8.0$  Hz, 1H), 6.87 (d,  $J = 8.4$  Hz, 2H), 6.58 (d,  $J = 2.0$  Hz, 2H), 6.49 (t,  $J = 2.0$  Hz, 1H), 5.55 (s, 2H), 4.66 (s, 2H), 4.28 (s, 3H), 4.20-4.10 (m, 2H), 3.94 (t,  $J = 6.4$  Hz, 2H), 3.80 (s, 6H), 3.61-3.51 (m, 6H), 3.49 (s, 2H), 1.77-1.74 (m, 2H), 1.69-1.58 (m, 5H), 1.48-1.41 (m, 2H), 1.36-1.27 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 298 K):  $\delta$  164.44, 163.82, 161.70, 140.93, 132.79, 132.18, 131.87, 130.98, 130.26, 129.93, 129.71, 128.87, 128.55, 126.48, 123.94, 122.68, 120.55, 116.60, 114.35, 110.59, 107.30, 102.23, 72.27, 68.00, 61.23, 60.73, 60.08, 57.83, 55.63, 53.42, 41.85, 29.78, 29.70, 29.53, 29.48, 29.42, 29.39, 29.32, 29.27, 27.22, 26.02, 25.91, 25.54, 21.43, 11.52. HRMS (ESI) ( $m/z$ ):  $[\text{M}-2\text{PF}_6]^{2+}$  calcd for  $\text{C}_{100}\text{H}_{115}\text{Fe}_2\text{N}_5\text{O}_{19}$ , 434.7358; found, 434.7346.

### Synthesis of **1-R**

A mixture of **1** (102 mg, 0.126 mmol) and crown ether **3** (234 mg, 0.25 mmol) were stirred in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) at room temperature for 1 h. Then **2** (49 mg, 0.25 mmol) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (70.6 mg, 0.19 mmol) were added to the solution, the mixture was stirred for three days. After removal of the solvent, the residue was dissolved in iodomethane (6 mL), and the mixture was stirred for 1 d at  $40^\circ\text{C}$ . The excess iodomethane was evaporated, and the solid was washed with  $\text{CH}_2\text{Cl}_2$  to give a yellow solid. To a suspension of the solid was then added saturated  $\text{NH}_4\text{PF}_6$  (10 mL) and  $\text{CH}_3\text{OH}$  (6 mL), respectively. The resulted mixture was vigorously stirred at room temperature for 2 h. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The residue was purified via column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH} = 20/1$ ) to give compound **1-R** (47 mg, 40 %) as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  8.63 (d,  $J = 7.2$  Hz, 1H), 8.59 (dd,  $J = 1.2, 8.4$  Hz, 1H), 8.41 (dd,  $J = 1.6, 8.4$  Hz, 1H), 8.23 (s, 1H), 7.776 (t,  $J = 8.4$  Hz, 1H), 7.31 (dd,  $J = 2.8, 8.8$  Hz, 2H), 7.24 (d,  $J =$

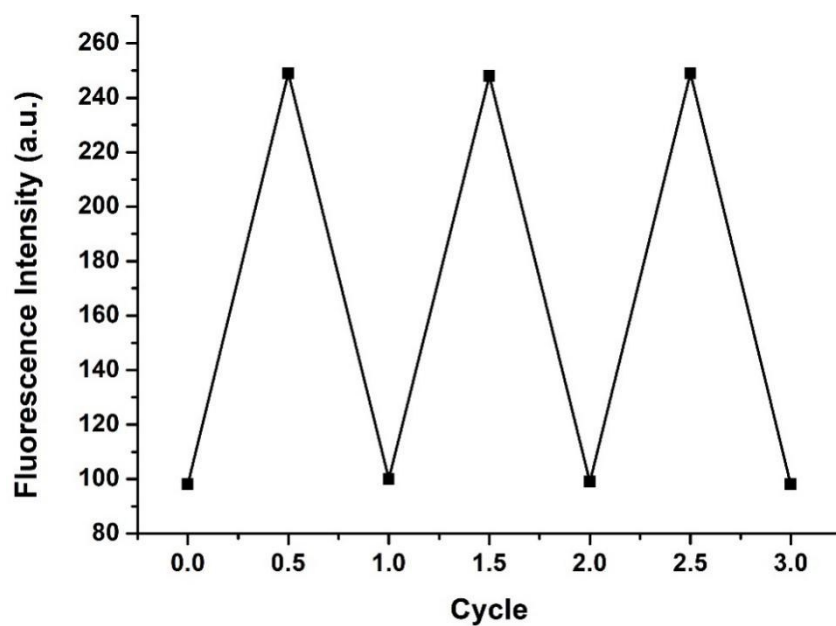
2.0 Hz, 2H), 7.02 (dd,  $J = 2.0, 8.4\text{Hz}$ , 2H), 6.97-6.98 (m, 4H), 6.83-6.77 (m, 4H), 6.73-6.68 (m, 1H), 6.59 (d,  $J = 2.4\text{ Hz}$ , 2H), 6.45 (t,  $J = 2.0\text{ Hz}$ , 1H), 5.54 (s, 2H), 5.14 (s, 4H), 4.75-4.68 (m, 4H), 4.66 (s, 2H), 4.60-4.53 (m, 2H), 4.51-4.43 (m, 2H), 4.33-4.27 (m, 4H), 4.25 (s, 3H), 4.18 (s, 2H), 4.14-4.05 (m, 8H), 4.02 (s, 10H), 3.90 (t,  $J = 6.6\text{ Hz}$ , 2H), 3.84-3.73 (m, 14H), 3.55-3.45 (m, 10H), 1.78-1.73 (m, 2H), 1.69-1.62 (m, 5H), 1.56-1.53 (m, 2H), 1.45-1.41 (m, 2H), 1.35-1.26 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 298 K):  $\delta$  174.76, 170.52, 163.28, 162.62, 160.49, 158.94, 157.83, 154.56, 146.36, 139.96, 131.62, 131.47, 130.93, 130.42, 129.77, 129.20, 128.89, 128.64, 127.79, 127.76, 127.44, 125.73, 123.00, 122.03, 121.63, 121.11, 119.38, 116.16, 113.75, 112.35, 111.54, 110.15, 106.12, 101.38, 70.91, 70.45, 69.75, 69.69, 69.11, 68.67, 67.37, 67.05, 64.48, 59.00, 56.58, 54.60, 54.58, 51.35, 50.63, 40.85, 37.44, 28.76, 28.68, 28.30, 28.24, 28.18, 28.08, 28.00, 26.20, 24.79, 24.74, 21.67, 20.40, 13.10, 10.53. HRMS (ESI) ( $m/z$ ):  $[\text{M}-2\text{PF}_6]^{2+}$  calcd for  $\text{C}_{100}\text{H}_{115}\text{Fe}_2\text{N}_5\text{O}_{19}$ , 901.3454; found, 901,3438.

### The photophysical property of 1-R

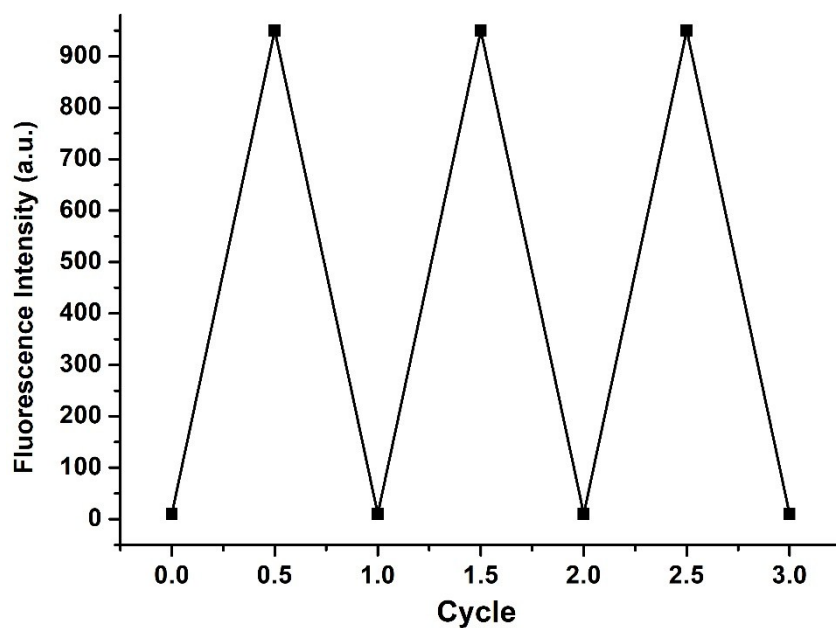


**Fig. S1** The UV/Vis absorption spectrum changes of [2]rotaxane **1-R** ( $1 \times 10^{-5}$  M,  $\text{CHCl}_3$ , r.t.), the mixture obtained after adding 1.2 equiv. **DBU** to the solution of **1-R**, and the mixture obtained after adding 2.0 equiv. **TFA** to the **DBU**-added solution of **1-R**.

## SUPPLEMENTARY INFORMATION



**Fig. S2** Fluorescence intensity of rotaxane **1-R** ( $1 \times 10^{-5}$  M,  $\text{CHCl}_3$ , r.t.) at 421 nm upon addition of alternate compound (**DBU** and **TFA**) for three cycles. The excitation wavelength is 365 nm.



**Fig. S3** Fluorescence intensity of **PBI 1** ( $1 \times 10^{-5}$  M,  $\text{CHCl}_3$ , r.t.) at 543 nm upon addition of alternate compound (**TFA** and **DBU**) for three cycles. The excitation wavelength is 365 nm.

## SUPPLEMENTARY INFORMATION

**Table S1.** Fluorescence quantum yield of white light emission in CHCl<sub>3</sub> at r.t. ( $\lambda_{\text{ex}} = 365 \text{ nm}$ )

Compound	molar ratio	TFA (equiv.)	$\Phi^{\text{a}}$ (%)
<b>1-R -H &amp; PBI 1</b>	1:1	2.2	0.52

<sup>a</sup> Quantum yields were calculated using anthracene (C<sub>2</sub>H<sub>5</sub>OH,  $\Phi_{\text{R}} = 0.31$ ) as reference and using the following formula  $\Phi = \Phi_{\text{R}} \cdot F/F_{\text{R}} \cdot A_{\text{R}}/A \cdot (n/n_{\text{R}})^2$ . Where  $\Phi$  = quantum yield, F = emission intensity, A = absorbance, n = refractive index of solvent, R = reference.

### Reference:

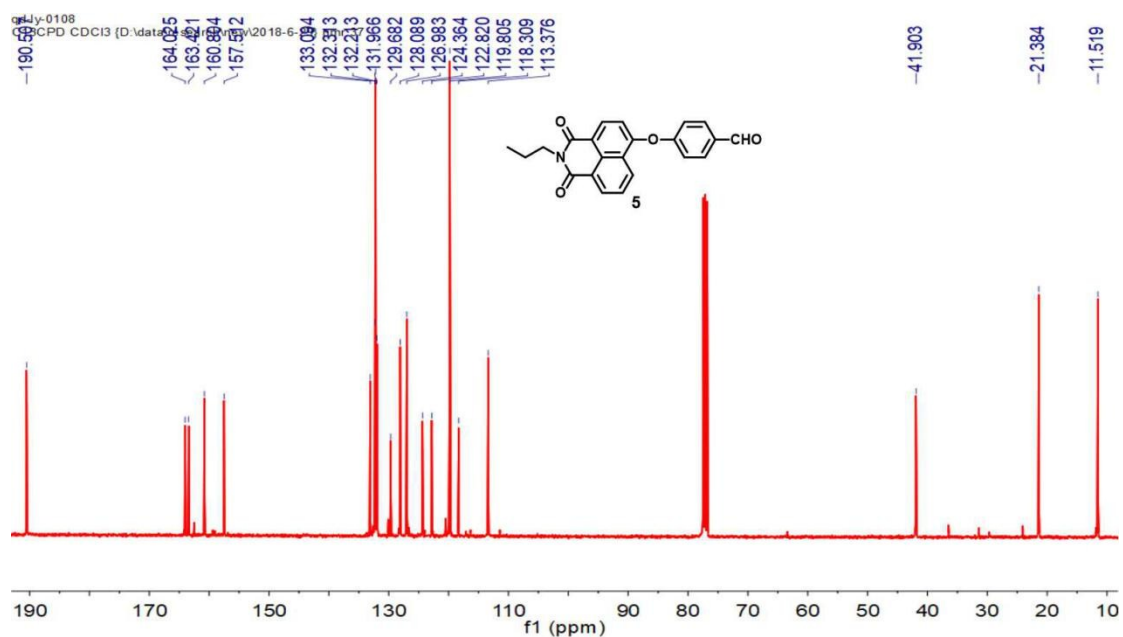
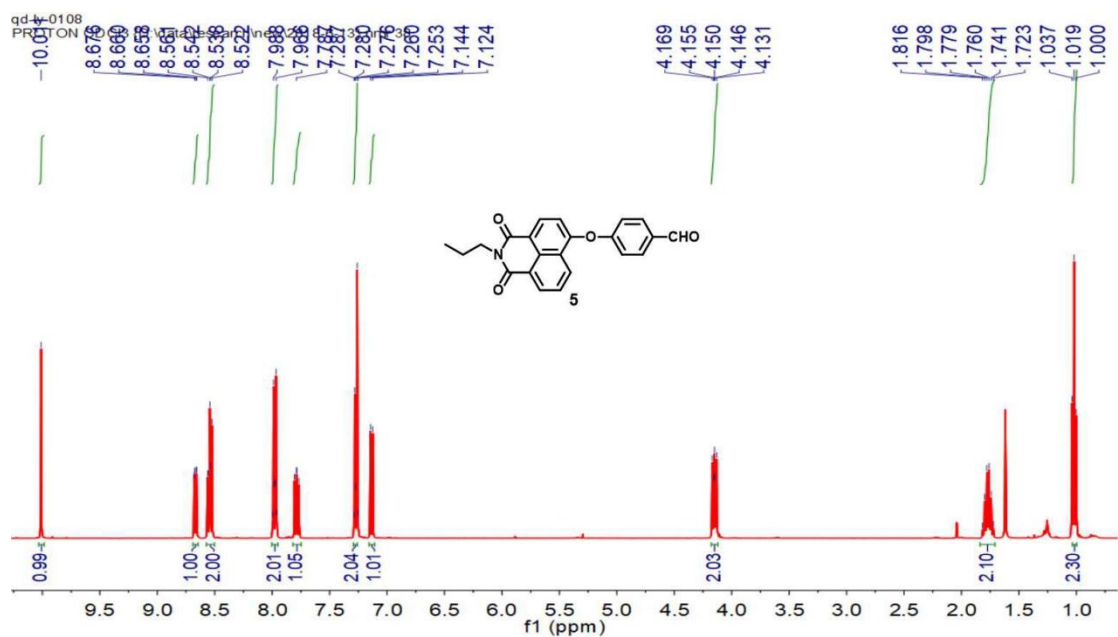
- (1) D. González-Calderón, M. A. Morales-Reza, E. Díaz-Torres, A. Fuentes-Benites and C. González-Romero, *RSC Advances*, 2016, **6**, 83547-83550.
- (2) H. Zhang, J. Hu and D.-H. Qu, *Org. Lett.*, 2012, **14**, 2334-2337.
- (3) Y. Jiang, J.-B. Guo and C.-F. Chen, *Org. Lett.*, 2010, **12**, 4248-4251.
- (4) Y. Tang, X. Kong, A. Xu, B. Dong and W. Lin, *Angew. Chem. Int. Ed.*, 2016, **55**, 3356-3359.



SUPPLEMENTARY INFORMATION

<sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectra

Compound 5



# SUPPLEMENTARY INFORMATION

## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

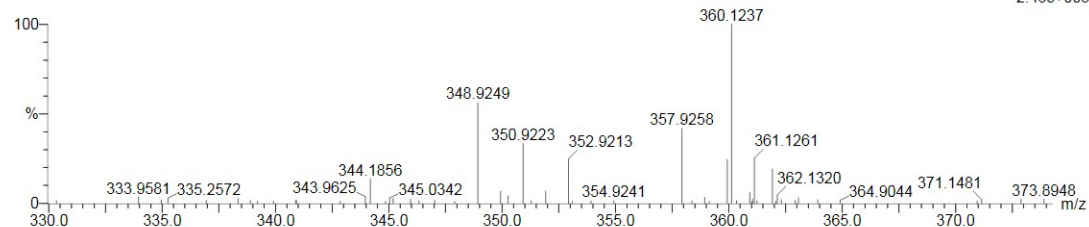
Elements Used:

C: 0-22 H: 0-18 N: 0-1 O: 0-4

DH-QU

QD-LY-80 14 (0.149) Cm (14:17)

1: TOF MS ES+  
2.46e+003

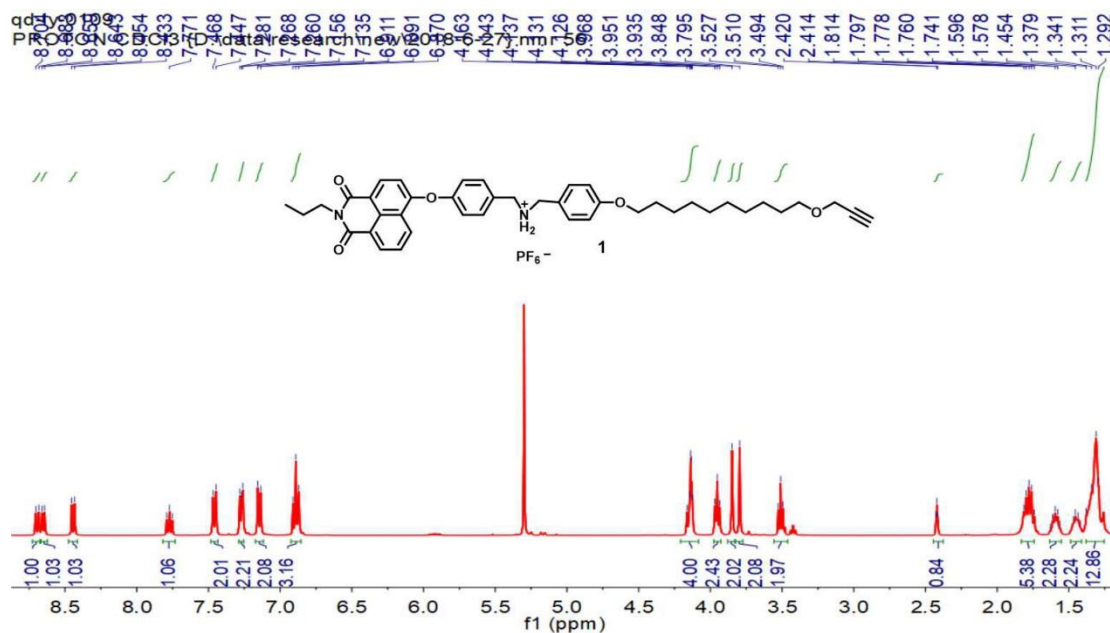


Minimum:  
Maximum:

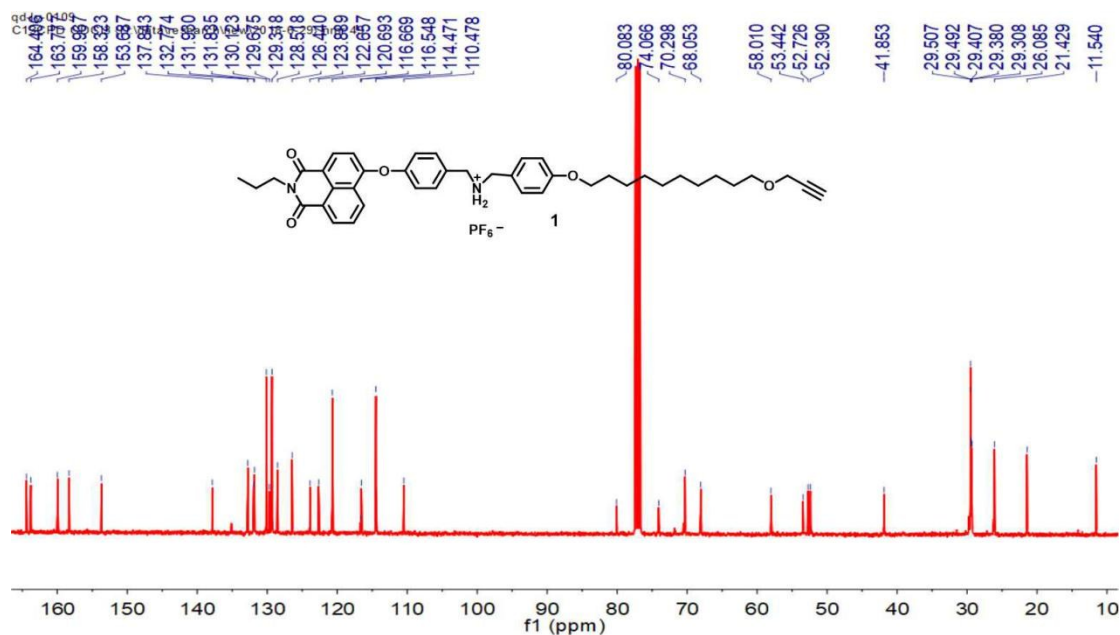
5.0      5.0      -1.5  
50.0      50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
360.1237	360.1236	0.1	0.3	14.5	45.8	0.0	C22 H18 N O4

## Compound 1



# SUPPLEMENTARY INFORMATION



## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

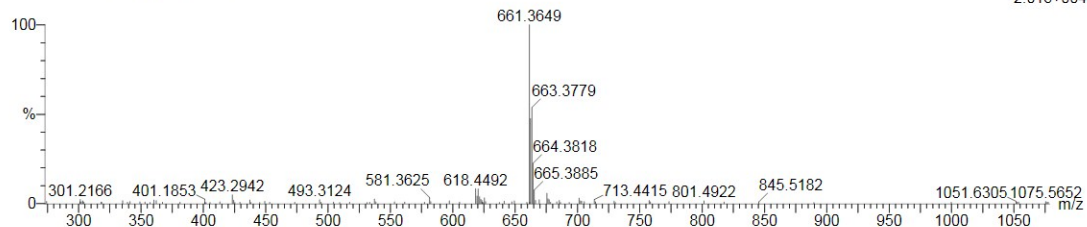
Elements Used:

C: 0-42 H: 0-49 N: 0-2 O: 0-5

DH-QU

QD-LY-81 21 (0.221) Cm (20:24)

1: TOF MS ES+  
2.01e+004



Minimum:

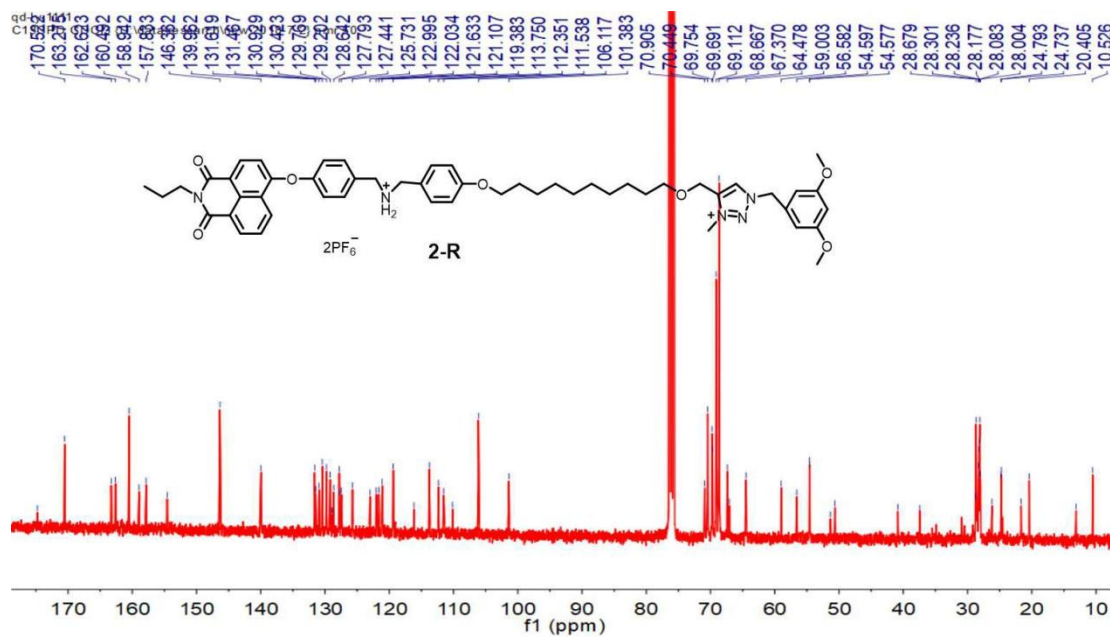
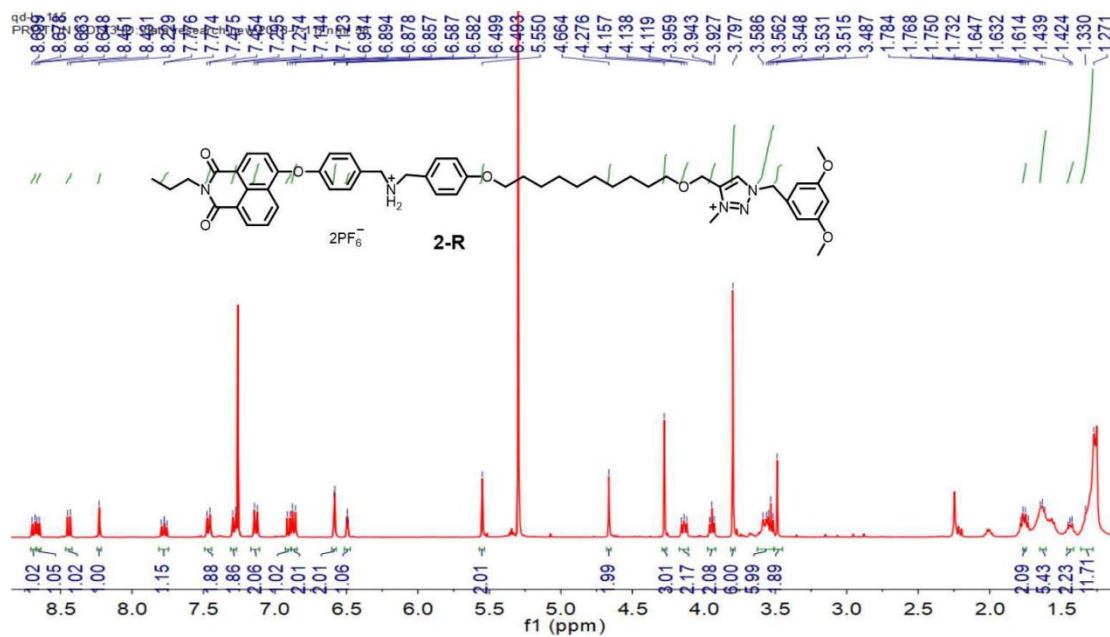
Maximum:

Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula

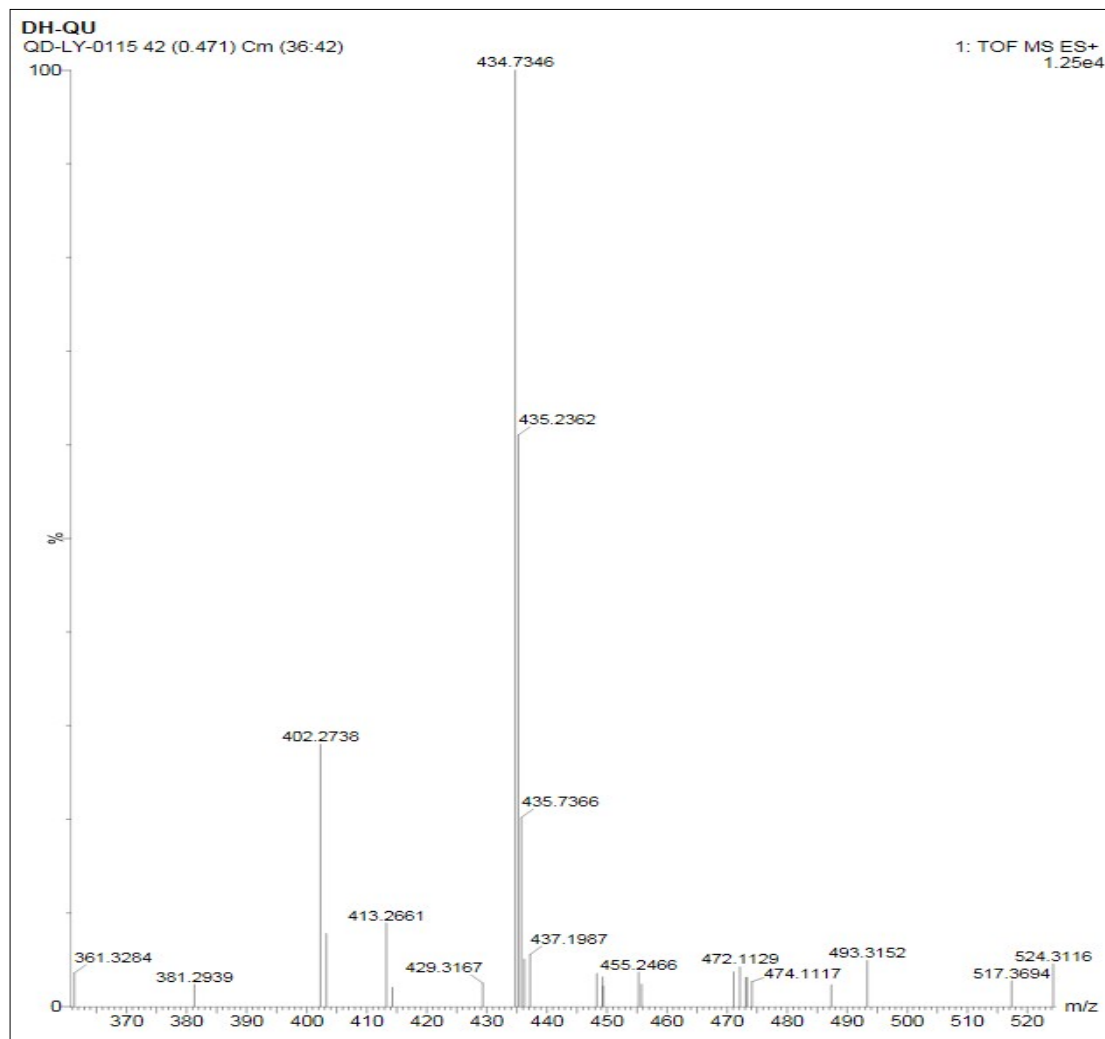
661.3649 661.3641 0.8 1.2 19.5 19.6 0.0 C42 H49 N2 O5

SUPPLEMENTARY INFORMATION

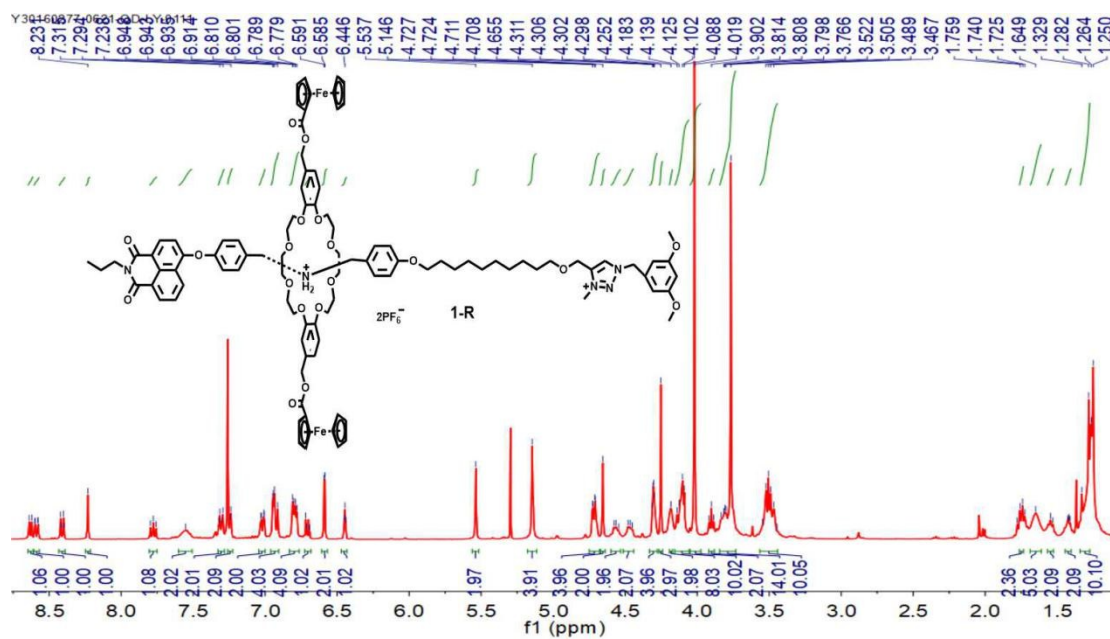
Compound 2-R



# SUPPLEMENTARY INFORMATION



## Compound 1-R



## SUPPLEMENTARY INFORMATION

