

Supporting information for

**Completely Solvent-free Synthesis of Double Heterohelicenes
and Their Further Ring Fusion Using Mechanochemical
Reaction**

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†Supporting information for this article is available on the WWW under <http://xxxx>
CCDC 2314579 and 2314580 contain the supplementary crystallographic data for this
paper. These data can be obtained free of charge from The Cambridge Crystallographic
Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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General Information

All the purchased reagents were of standard quality and used without further purification. Benzo[*b*]phenoxazine (**BPO**) and dibenzo[*b,i*]phenoxazines (**DBPO**) were synthesized by solid-state condensation of 2,3-dihydroxynaphthalene and *o*-aminophenol (for **BPO**) or 3-amino-2-naphthol (for **DBPO**) at 230 °C in a similar manner to the literature.^{S1} All the mechanochemical reactions were carried out under air. Mechanochemical reactions were performed using a Retsch MM400 mixer mill or a Fritsch Pulverisette 7 Premium Line planetary mill. Flash chromatography was performed with a Biotage Isorela medium pressure liquid chromatography (MPLC) system and a SNAP Sfär flash silica gel cartridge (Biotage). ¹H and ¹³C NMR spectra were recorded by a Varian 400-MR FT-NMR spectrometer. Matrix-assisted laser desorption ionization TOF mass spectra were obtained on a Shimadzu MALDI-8020 mass spectrometer. UV-vis-NIR absorption spectra were obtained with a JASCO V-670 spectrometer. Emission spectra were measured with a Shimadzu RF-6000 spectrofluorometer with an integrating sphere. The FL lifetime measurement was performed on a Horiba DeltaFlex spectrofluorometer system; excitation was carried out by using visible diode lasers (DeltaDiode 375 nm). Cyclic voltammetry and differential pulse voltammetry were measured in BAS Electrochemical Analyzer ALS Model 612B. Circular dichroism (CD) spectra were recorded on a JASCO J-820 spectropolarimeter with CH₂Cl₂ as a solvent at room temperature. Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-200S with CH₂Cl₂ as a solvent at room temperature.

[S1] Q. Miao, T.-Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 10284–10287.

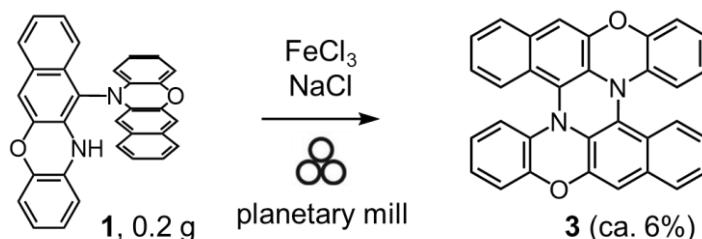
Synthetic Details

Synthesis of **3** from **1**

General Procedure

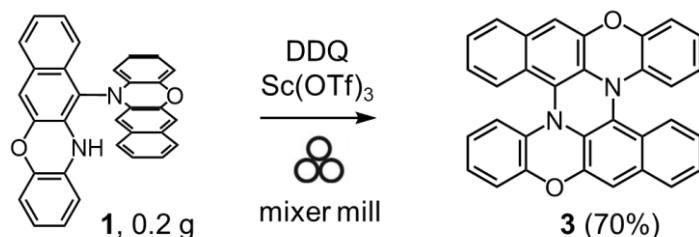
Reactant, oxidizing reagent, and milling balls were placed in a jar in air, and the jar was closed. The jar was set on a ball mill and ground for a set time period. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate. The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel.

Example (Table 1, entry 1)



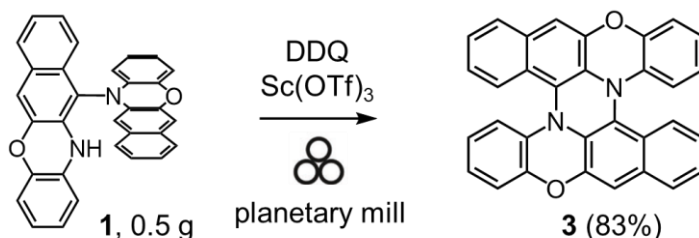
3 (from **1**) : In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **1** (200 mg, 0.431 mmol), FeCl₃ (840 mg, 5.18 mmol, 12 eq.), and NaCl (8.96 g) as a bulking material were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (2 mL). The extracted solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (11.6 mg, ca. 6%, containing small amount of monochlorinated **3**) as an orange powder.

Example (Table 1, entry 2)



3 (from **1**) : In a 50 mL stainless-steel jar for a mixer mill, twelve stainless-steel balls (10 mm ϕ), **1** (200 mg, 0.431 mmol), DDQ (108 mg, 0.475 mmol, 1.1 eq.), and Sc(OTf)₃ (233 mg, 0.473 mmol, 1.1 eq.) were placed under an ambient condition, and the mixture was milled using a mixer mill at a vibration frequency of 30 Hz for 1 h. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (1 mL). The extracted solution was filtered through of celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (139 mg, 70%) as an orange powder.

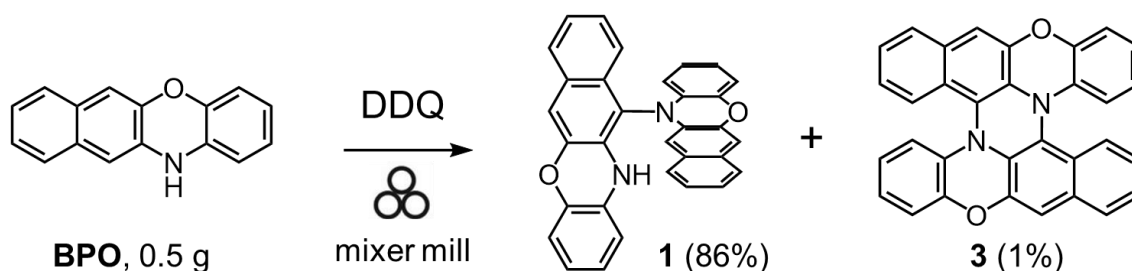
Example (Table 1, entry 5)



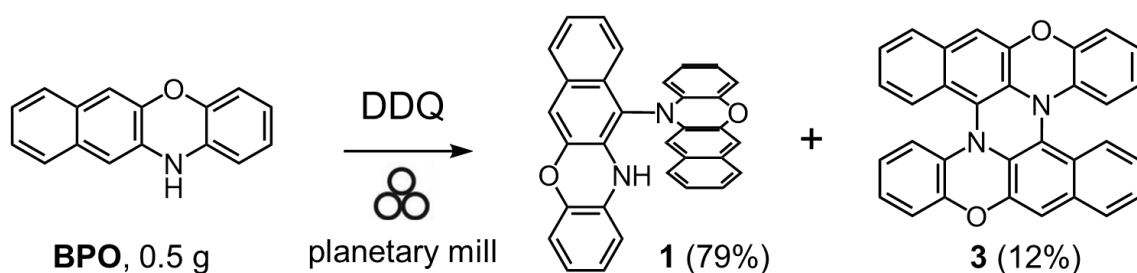
3 (from **1**) : In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **1** (500 mg, 1.08 mmol), DDQ (269 mg, 1.19 mmol, 1.1 eq.), and Sc(OTf)₃ (583 mg, 1.18 mmol, 1.1 eq.) were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the jar was opened, and the

hardened solid sticking to the vessel wall was crushed by a spatula. DDQ (48.9 mg, 0.215 mmol, 0.2 eq.) and Sc(OTf)₃ (106 mg, 0.215 mmol, 0.2 eq.) were added to the jar, and the mixture was milled at 600 rpm for another 30 min. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (2 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (417 mg, 83%) as an orange powder.

Synthesis of **1** from BPO



In a 50 mL stainless-steel jar, twelve stainless-steel balls (10 mm ϕ), **BPO** (500 mg, 2.14 mmol), and DDQ (0.6 eq., 292 mg, 1.29 mmol) were placed under an ambient condition, and the mixture was milled at a vibration frequency of 30 Hz for 30 min using a mixer mill. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (1 mL). The reaction solution was filtered through of celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) and washed with MeOH to afford **1** (428 mg, 86%) as a pale-yellow powder. Additionally, **3** (5.64 mg, 1%) was also obtained as an orange powder.



In a 45 mL ZrO₂ jar, twenty-two ZrO₂ balls (10 mm ϕ), **BPO** (500 mg, 2.14 mmol), and DDQ (0.6 eq., 292 mg, 1.29 mmol) were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (1 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane / CH₂Cl₂ as eluent) and washed with MeOH to afford **1** (391 mg, 79%) as a pale-yellow powder. Additionally, **3** (60.9 mg, 12%) was also obtained as an orange powder.

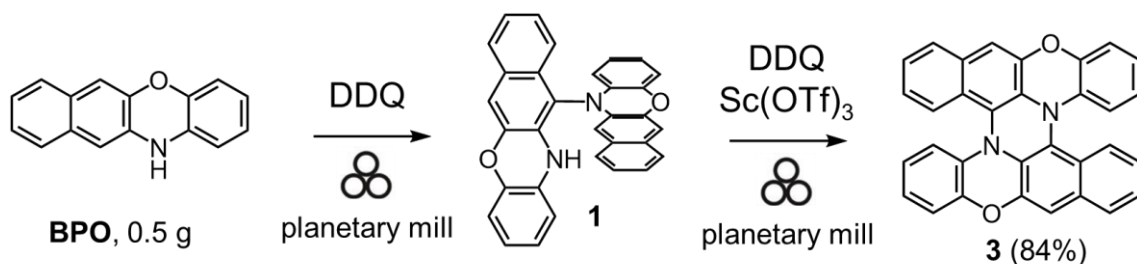
Synthesis of **3** (or **4**) from **BPO** (or **DBPO**)

General Procedure

BPO (or **DBPO**), DDQ (0.6 eq.), and milling balls were placed in a jar in air, and the jar was closed. The jar was set on a ball mill and ground for 30 min. After milling, the jar was opened, and DDQ and Sc(OTf)₃ were added in the jar. The jar was closed and milled for 30 min. After milling, the progress of the reaction was monitored by TLC and MALDI-TOF MS. If the cruciform dimer (**1** or **2**) remained, DDQ and Sc(OTf)₃ were added and milled again. After the reaction was completed, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate. The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was

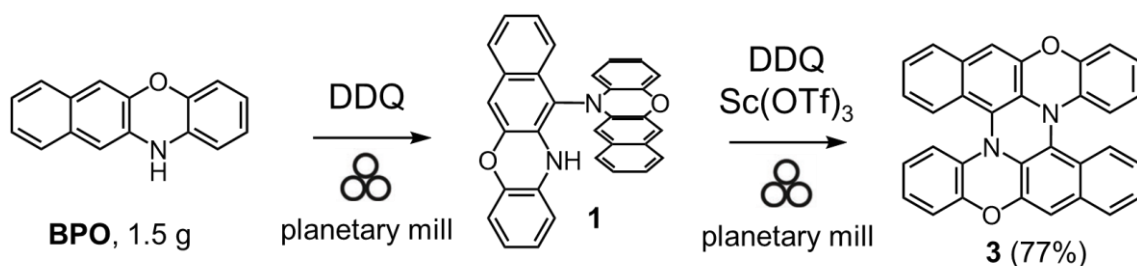
dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel.

Example (Table 2, entry 1)



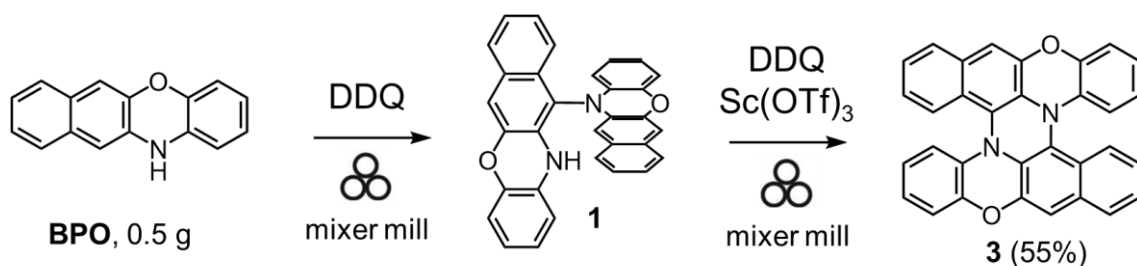
In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **BPO** (500 mg, 2.14 mmol), DDQ (292 mg, 1.29 mmol, 0.6 equiv. for **BPO**) were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the reaction crude was monitored by MALDI-TOF MS and TLC, and the formation of **1** was confirmed. DDQ (292 mg, 1.29 mmol) and Sc(OTf)₃ (633 mg, 1.29 mmol) were added to the jar. The mixture was milled at 600 rpm for 30 min. After milling, the jar was opened, and the hardened solid sticking to the vessel wall was crushed by a spatula. DDQ (49.3 mg, 0.217 mmol) and Sc(OTf)₃ (106 mg, 0.215 mmol) were added to the jar, and the mixture was milled at 600 rpm for another 30 min. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (2 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (416 mg, 84%) as an orange powder.

Example (Table 2, entry 3)



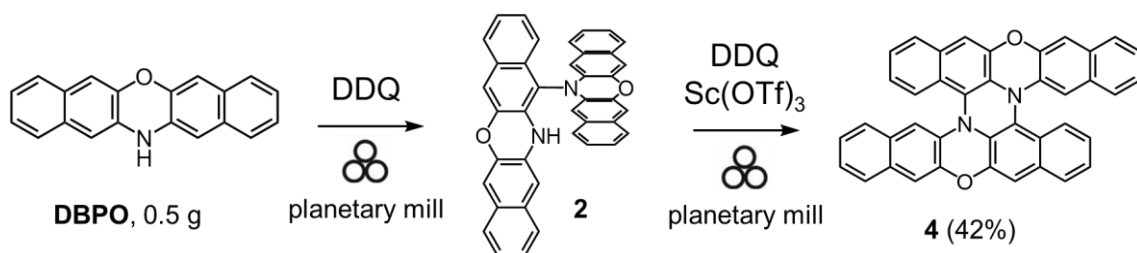
In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **BPO** (1.5 g, 6.43 mmol), DDQ (876 mg, 3.86 mmol, 0.6 equiv. for **BPO**) were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the reaction crude was monitored by MALDI-TOF MS and TLC, and the formation of **1** was confirmed. DDQ (876 mg, 3.86 mmol) and Sc(OTf)₃ (1.90 g, 3.86 mmol) were added to the jar. The mixture was milled at 600 rpm for 30 min. After milling, the jar was opened, and the hardened solid sticking to the vessel wall was crushed by a spatula. DDQ (146 mg, 0.643 mmol) and Sc(OTf)₃ (317 mg, 0.644 mmol) were added to the jar, and the mixture was milled at 600 rpm for another 30 min. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (4 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (1.14 g, 77%) as an orange powder.

Example (Table 2, entry 4)



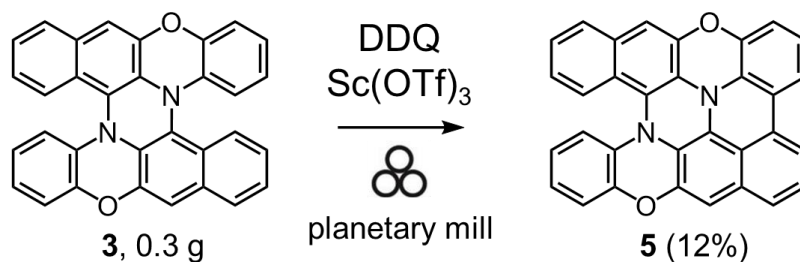
In a 50 mL stainless-steel jar, ten stainless-steel balls (10 mm ϕ), **BPO** (500 mg, 2.14 mmol), DDQ (292 mg, 1.29 mmol, 0.6 equiv. for **BPO**) were placed under an ambient condition, and the mixture was milled at a vibration frequency of 30 Hz for 30 min using a mixer mill. After milling, the reaction crude was monitored by MALDI-TOF MS and TLC, and the formation of **1** was confirmed. DDQ (292 mg, 1.29 mmol) and Sc(OTf)₃ (633 mg, 1.29 mmol) were added to the jar. The mixture was milled at a vibration frequency of 30 Hz for 60 min. After milling, DDQ (97.0 mg, 0.427 mmol) and Sc(OTf)₃ (211 mg, 0.429 mmol) were added to the jar, and the mixture was milled at a vibration frequency of 30 Hz for another 60 min. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (4 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **3** (274 mg, 55%) as an orange powder.

Example (Table 2, entry 5)



In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **DBPO** (500 mg, 1.76 mmol), DDQ (241 mg, 1.06 mmol, 0.6 equiv. for **BPO**) were placed under an ambient condition, and the mixture was milled at 600 rpm for 30 min using a planetary mill. After milling, the jar was opened and DDQ (240 mg, 1.06 mmol) and Sc(OTf)₃ (521 mg, 1.06 mmol) were added to the jar. The mixture was milled at 600 rpm for 30 min. After milling, the reaction mixture was extracted with CH₂Cl₂ and quenched by adding hydrazine hydrate (2 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/CH₂Cl₂ as eluent) to afford **4** (208 mg, 42%) as an orange powder.

Synthesis of **5**

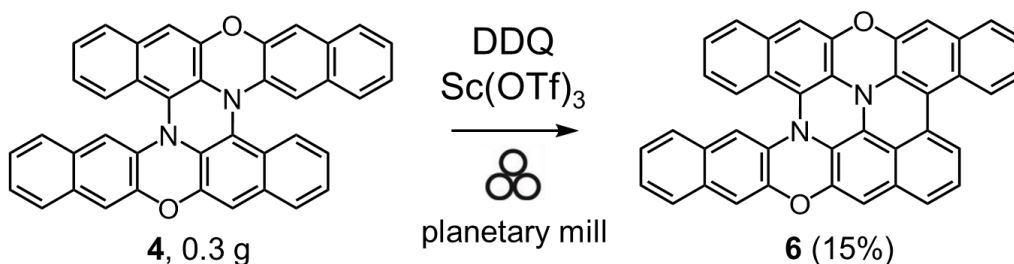


In a 45 mL ZrO₂ jar for a planetary mill, twenty-two ZrO₂ balls (10 mm ϕ), **3** (300 mg, 0.649 mmol), DDQ (162 mg, 0.714 mmol, 1.1 eq.), and Sc(OTf)₃ (351 mg, 0.713 mmol, 1.1 eq.) were placed under an ambient condition, and the mixture was milled at 850 rpm

for 30 min using a planetary mill. After milling, the reaction mixture was extracted with CH_2Cl_2 and quenched by adding hydrazine hydrate (2 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 , and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/toluene as eluent) to remove unreacted **3**. The target compound **5** was strongly adsorbed to silica gel. The silica gel containing **5** was extracted with toluene containing small amount of hydrazine hydrate. The extracted solution was filtered through celite and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/toluene containing 0.5% triethylamine as eluent) and washed with MeOH to afford **5** (34.5 mg, 0.078 mmol, 12%) as a red-brown powder.

^1H NMR (400 MHz, DMSO-d_6): δ 7.61 (d, $J = 7.4$ Hz, 1H), 7.26 (t, $J = 6.9$ Hz, 3H), 7.18 (d, $J = 8.8$ Hz, 1H), 7.15–7.10 (m, 2H), 7.04–6.99 (m, 3H), 6.91–6.83 (m, 2H), 6.77–6.69 (m, 3H), 6.22 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR spectrum was not recorded owing to the low solubility of **5**.

Synthesis of **6**



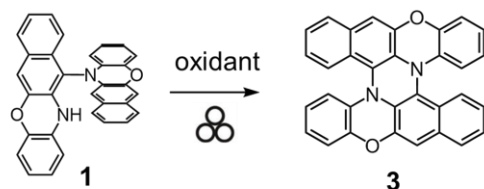
In a 45 mL ZrO_2 jar for a planetary mill, twenty-two ZrO_2 balls (10 mm ϕ), **4** (300 mg, 0.533 mmol), DDQ (133 mg, 0.586 mmol, 1.1 eq.), and $\text{Sc}(\text{OTf})_3$ (289 mg, 0.587 mmol, 1.1 eq.) were placed under an ambient condition, and the mixture was milled at 850 rpm

for 30 min using a planetary mill. After milling, the reaction mixture was extracted with CH_2Cl_2 and quenched by adding hydrazine hydrate (2 mL). The reaction solution was filtered through celite and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 , and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/toluene as eluent) to remove unreacted **4**. The target compound **6** was strongly adsorbed to silica gel. The silica gel containing **6** was extracted with toluene containing small amount of hydrazine hydrate. The extracted solution was filtered through celite and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (hexane/toluene containing 0.5% triethylamine \rightarrow hexane/dichloromethane containing 0.5% triethylamine as eluent) and washed with MeOH to afford **6** (46.0 mg, 0.082 mmol, 15%) as a purple-black powder.

^1H NMR (400 MHz, DMSO-d_6): δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.48 (s, 2H), 7.37 (d, $J = 7.4$ Hz, 2H), 7.33–7.29 (m, 1H), 7.27–7.16 (m, 4H), 7.03 (d, $J = 7.8$ Hz, 1H), 6.98–6.90 (m, 4H), 6.71–6.68 (m, 2H), 6.45 (s, 1H) ;

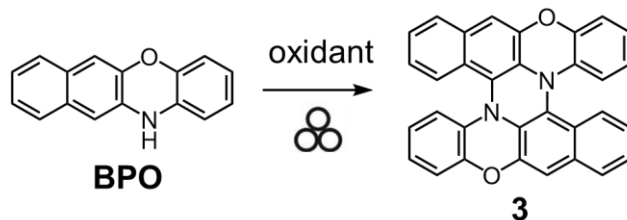
^{13}C NMR spectrum was not recorded owing to the low solubility of **6**.

Table S1: Examples of mechanochemical ring-fusion reactions of **1**. (Mill type: p = planetary, m = mixer).



entry	weight of 1	mill type	milling material	oxidant	milling speed	total reaction time	yield of 3
1	0.20 g	p	ZrO ₂ (45 mL)	FeCl ₃ (12 eq.) + NaCl (9 g)	600 rpm	30 min	ca. 6%
2	0.05 g	m	Steel (5 mL)	FeCl ₃ (12 eq.)	30 Hz	60 min	3 , mono, di, tri-chlorinated products by MS (not isolated)
3	0.05 g	m	Steel (5 mL)	FeBr ₃ (13 eq.)	30 Hz	60 min	3 and monobrominated products by MS significant amount of 1 (not isolated)
4	0.20 g	m	Steel (50 mL)	DDQ (1.1 eq.)	30 Hz	60 min	23%
5	0.20 g	m	Steel (50 mL)	DDQ/Sc(OTf) ₃ (1.1 eq.)	30 Hz	60 min	70%
6	0.05 g	m	Steel (5 mL)	DDQ/Sc(OTf) ₃ (1.1 eq.)	30 Hz	60 min	65%
7	0.20 g	p	ZrO ₂ (45 mL)	DDQ/Sc(OTf) ₃ (1.1 eq.)	400 rpm	30 min	68%
8	0.20 g	p	ZrO ₂ (45 mL)	DDQ/Sc(OTf) ₃ (1.1 eq.)	600 rpm	30 min	72%
9	0.20 g	p	ZrO ₂ (45 mL)	DDQ/Sc(OTf) ₃ (1.1 eq.)	800 rpm	30 min	63%
10	0.20 g	p	ZrO ₂ (45 mL)	DDQ/Sc(OTf) ₃ (1.1 + 0.2 eq.)	600 rpm	60 min	71%
11	0.50 g	p	ZrO ₂ (45 mL)	DDQ/Sc(OTf) ₃ (1.1 + 0.2 eq.)	600 rpm	60 min	83%

Table S2: Examples of mechanochemical synthesis of **3** from **BPO**. (Mill type: p = planetary, m = mixer).



entry	weight of BPO	mill type	milling material	oxidant	milling speed	total reaction time	yield of 3
1	0.50 g	m	Steel (50 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.5 eq)	30 Hz	30 + 60 min	49%
2	0.50 g	m	Steel (50 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.2 eq)	30 Hz	30 + 60 + 60 min	55%
3	1.50 g	m	Steel (50 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.1 eq)	30 Hz	30 + 60 + 30 min	56%
4	0.50 g	p	ZrO ₂ (45 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.1 eq)	600 rpm	30 + 30 + 30 min	84%
5	1.50 g	p	ZrO ₂ (45 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.1 eq)	600 rpm	30 + 30 + 30 min	77%
6	1.50 g	p	ZrO ₂ (45 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq)	400 rpm	30 + 30 min	44%
7	1.50 g	p	ZrO ₂ (45 mL)	DDQ (0.6 eq) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.1 eq)	800 rpm	30 + 30 + 30 min	79%
8	1.50 g	p	ZrO ₂ (45 mL)	DDQ (0.6 eq) + silica gel (4.5 g) → DDQ/Sc(OTf) ₃ (0.6 eq + 0.1 eq)	600 rpm	30 + 30 + 60 min	52%

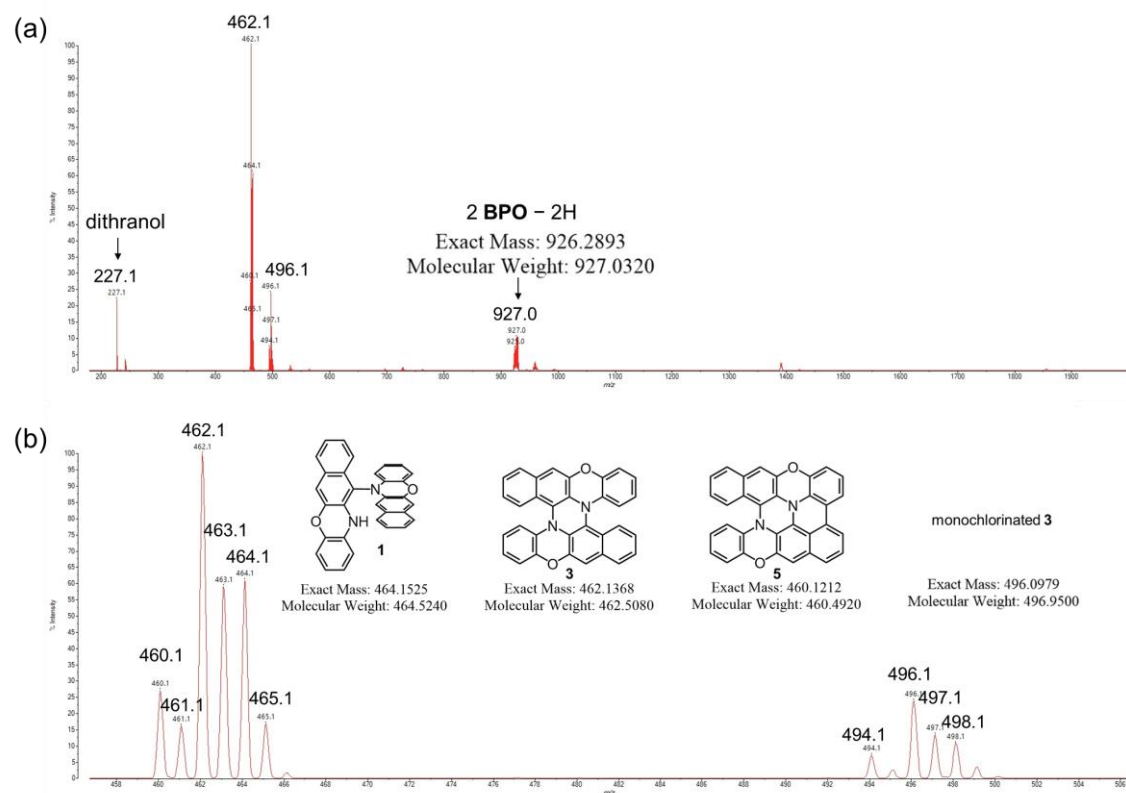


Figure S1. MALDI-TOF MS of the reaction crude (before chromatography) of **1** using FeCl_3 as an oxidant and a planetary mill (Table 1, entry 1). Mass range: (a)200–2000, (b) 458–506.

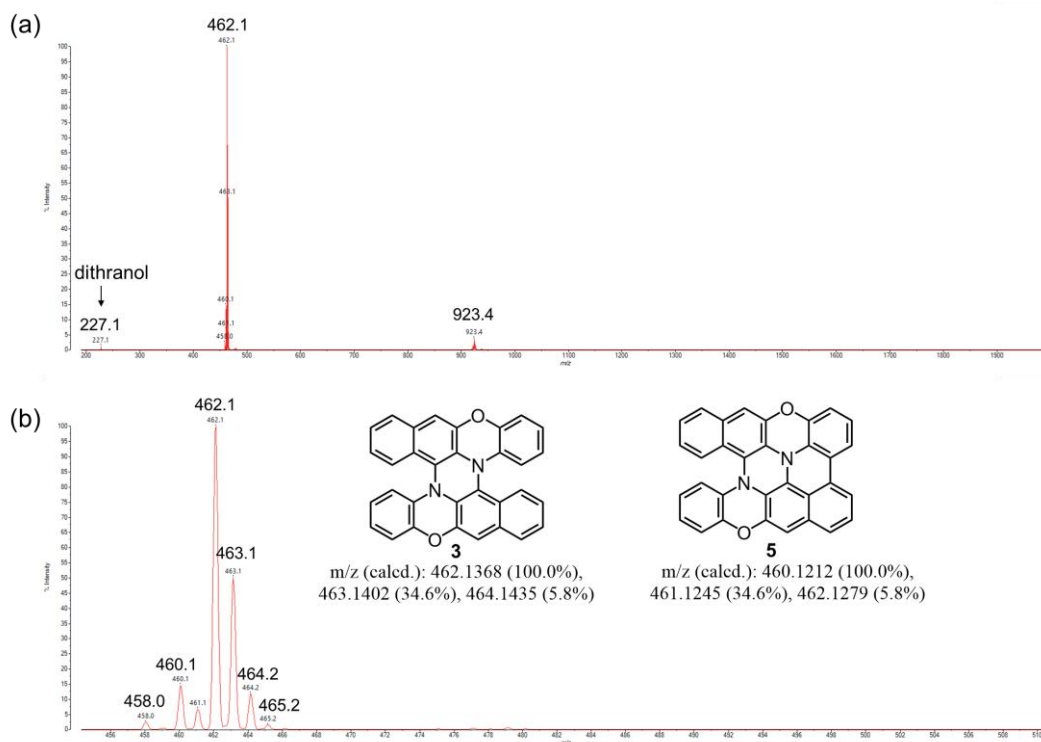


Figure S2. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **1** using DDQ/Sc(OTf)₃ as oxidants and a planetary mill (Table 1, entry 5). Mass range: (a)200–2000, (b) 456–510.

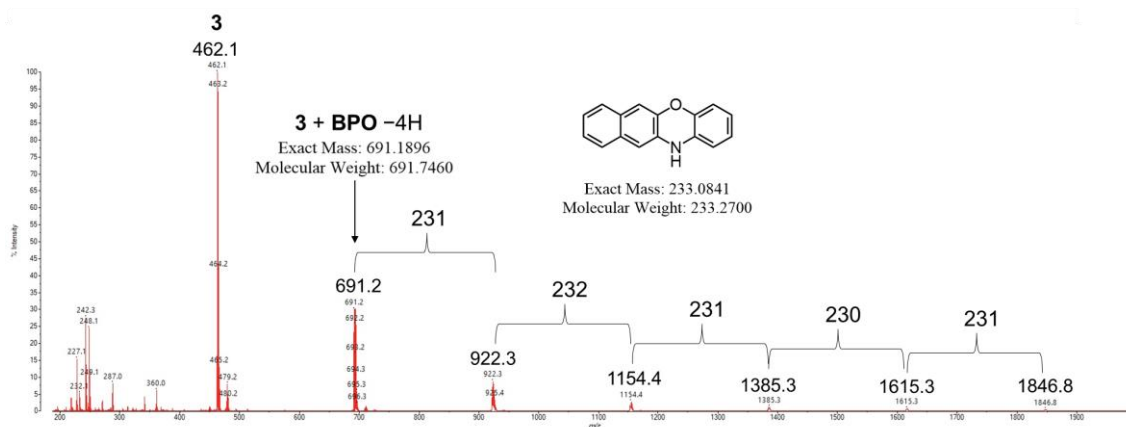


Figure S3. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **BPO** using DDQ/Sc(OTf)₃ (by adding simultaneously at the first stage) as oxidants and a planetary mill.

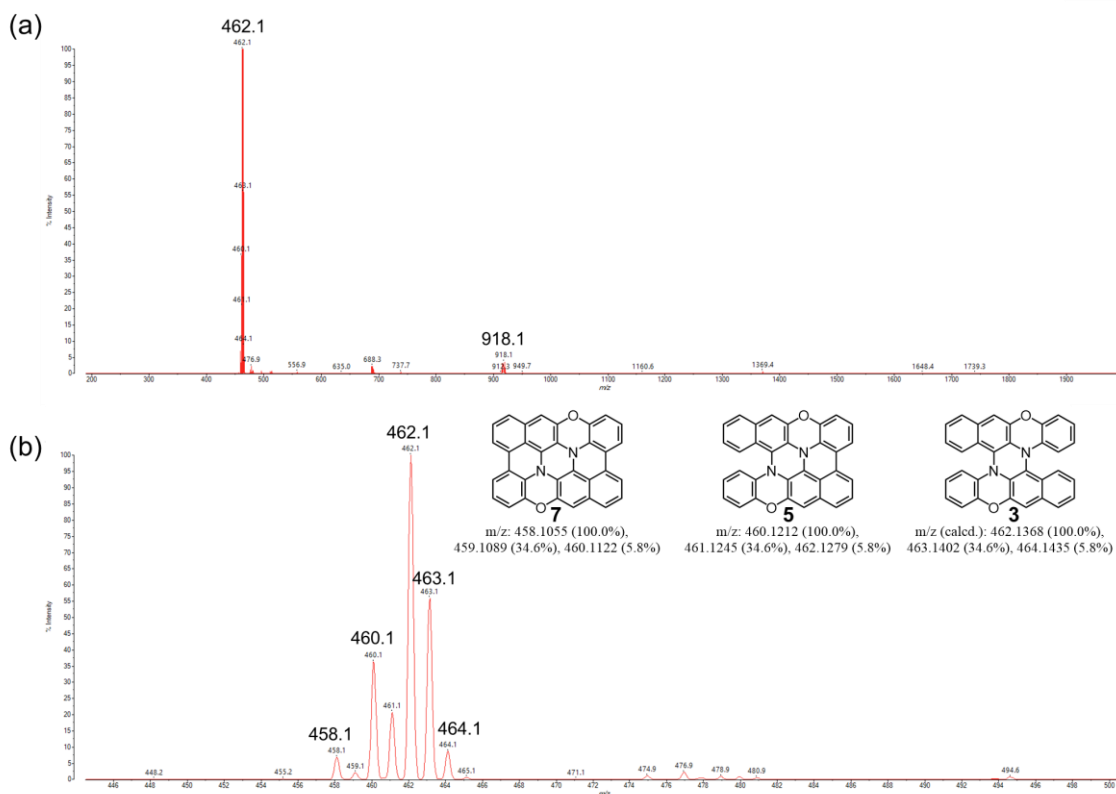


Figure S4. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **BPO** using DDQ \rightarrow DDQ/Sc(OTf)₃ as oxidants and a planetary mill (Table 2, entry 2). Mass range: (a) 200–2000, (b) 446–500.

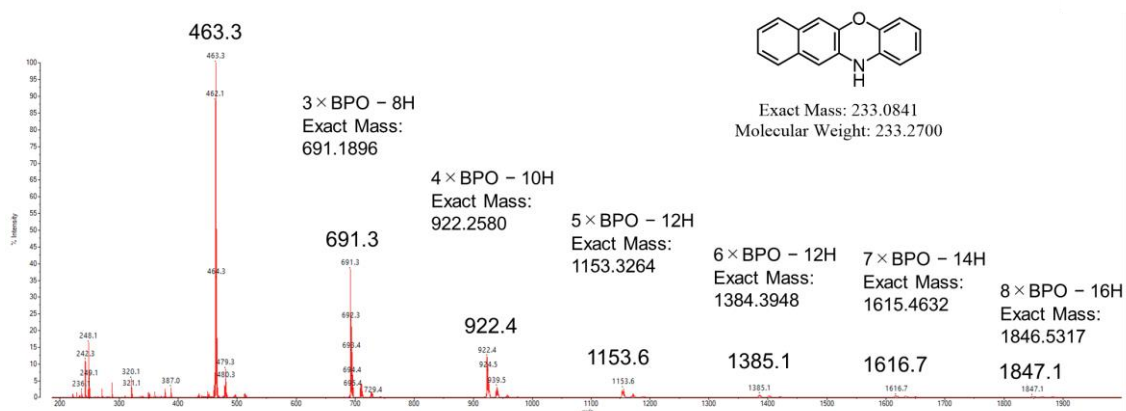


Figure S5. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **BPO** using DDQ \rightarrow DDQ/Sc(OTf)₃ as oxidants and a mixer mill (Table 2, entry 4).

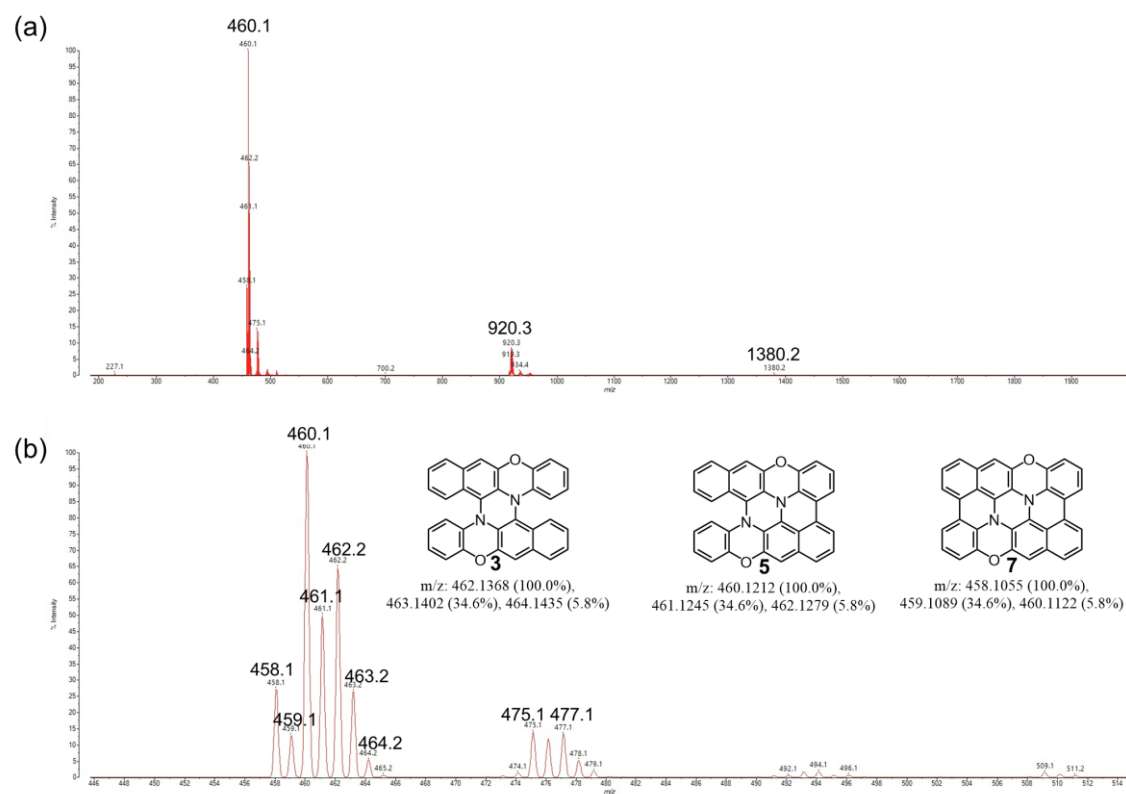


Figure S6. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **3** using DDQ/Sc(OTf)₃ as oxidants and a planetary mill. Mass range: (a)200–2000, (b) 446–514.

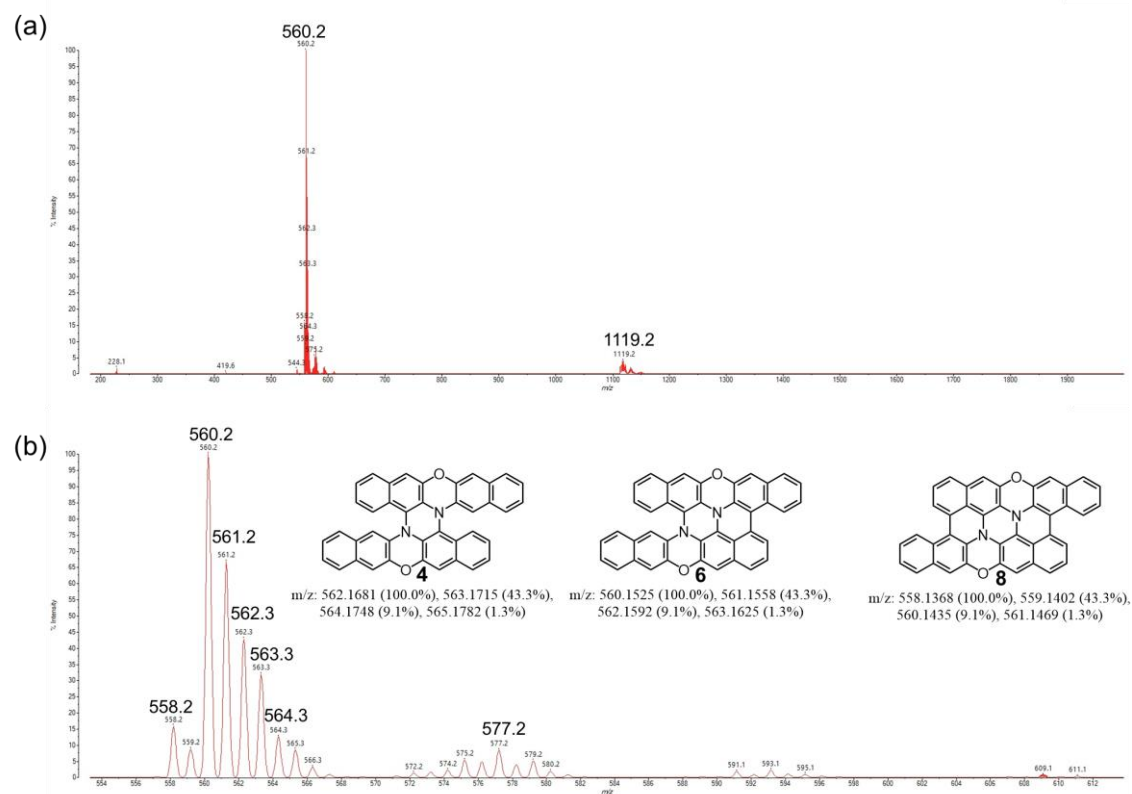
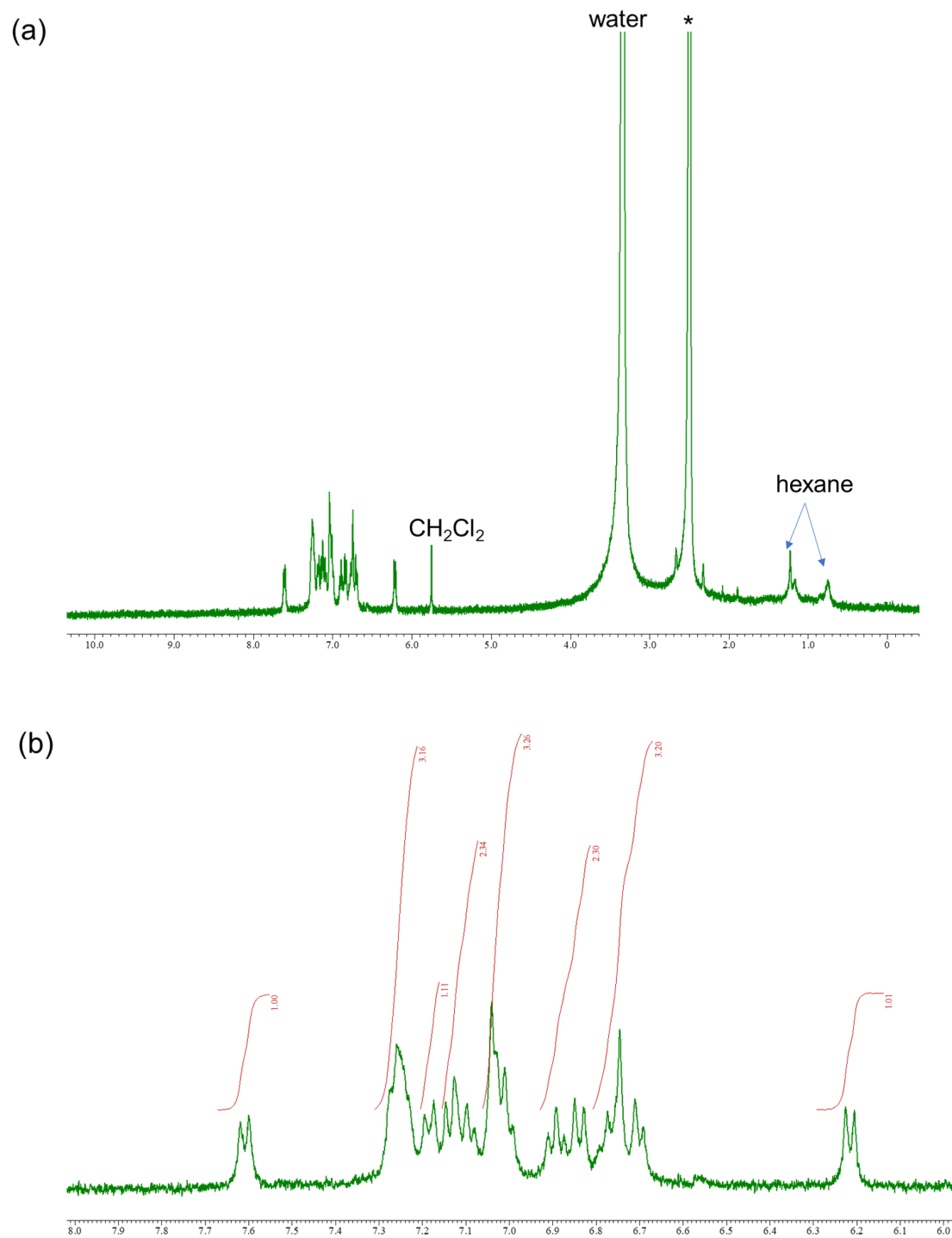


Figure S7. MALDI-TOF MS of the crude product (before chromatography) on the reaction of **4** using DDQ/Sc(OTf)₃ as oxidants and a planetary mill. Mass range: (a)200–2000, (b) 554–612.



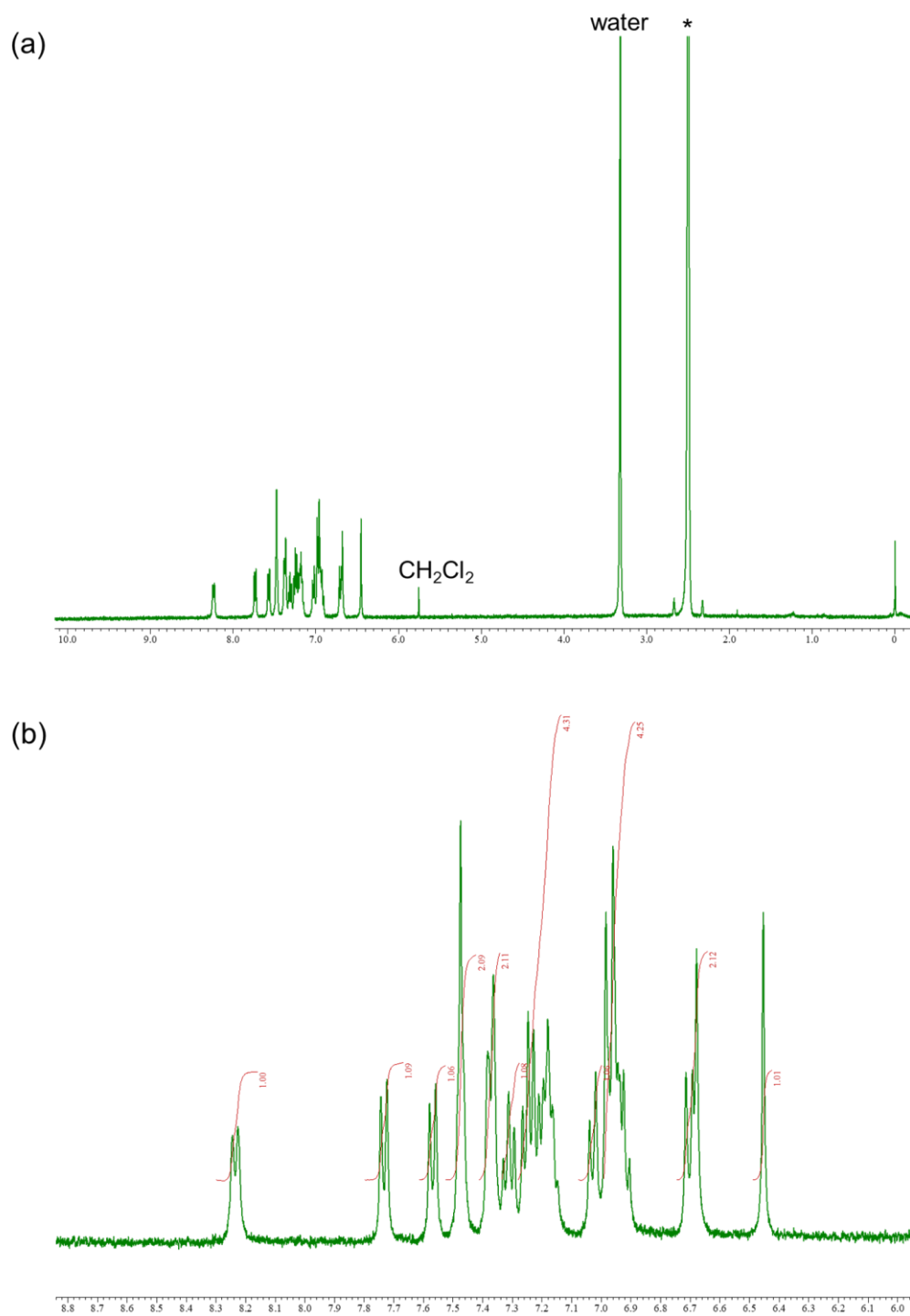


Figure S9. ^1H NMR spectra of **6** in $\text{DMSO-}d_6$. a) 0–10 ppm and b) aromatic region. Asterisk denotes the solvent residual peak.

X-ray Crystallography

The single crystals of **5** and **6** were obtained by the slow evaporation of mixed solutions of CH₂Cl₂/hexane and CH₂Cl₂/ethanol, respectively. Data collections were performed on a Rigaku Synergy-S diffractometer with Cu-K α radiation at 100 K. The hydrogen atoms were refined using the riding model. All the calculations were performed by using CrystalStructure crystallographic software package,^{S3} except for refinement, which was performed by using SHELXL Version 2017/1.^{S3} The CIF files have been deposited on the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2314579 (**5**) and CCDC 2314580 (**6**).

[S2] CrystalStructure 4.3: Crystal Structure Analysis Package, Rigaku Corporation (2000-2018). Tokyo 196-8666, Japan.

[S3] G. M. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112.

Table S3: X-ray crystallographic data for **5** (CCDC 2314579).

empirical formula	2(C ₃₂ H ₁₆ N ₂ O ₂ ·CH ₂ Cl ₂)
formula weight	1090.84
<i>T</i> [°C]	−173
λ [Å]	1.54187
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>Z</i>	4
<i>a</i> [Å]	7.4675(4)
<i>b</i> [Å]	23.5001(15)
<i>c</i> [Å]	26.7405(17)
<i>V</i> [Å ³]	4692.6(5)
ρ_{calcd} [g cm ^{−3}]	1.544
collected data	18824
unique data / <i>R</i> _{int}	8733/0.0535
no. of parameters	703
goodness-of-fit ^[a]	1.555
<i>R</i> 1 (<i>I</i> > 2σ), <i>wR</i> 2 (all reflections) ^[b]	0.1275, 0.3537
residual density [e Å ^{−3}]	3.20/−1.28

[a] GOF = $\left\{ \sum [w(F_0^2 - F_c^2)^2] / (n - p) \right\}^{1/2}$, where *n* and *p* denote the number of data and parameters.

[b] $R1 = \sum (\|F_0\| - \|F_c\|) / \sum \|F_0\|$ and $wR2 = \left\{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \right\}^{1/2}$ where

$w = 1 / [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]$ and $P = [(\text{Max}; 0, F_0^2) + 2 \cdot F_c^2] / 3$.

Table S4: X-ray crystallographic data for **6** (CCDC 2314580).

empirical formula	C ₄₀ H ₂₀ N ₂ O ₂
formula weight	560.61
<i>T</i> [°C]	−173
<i>λ</i> [Å]	1.54187
crystal system	orthorhombic
space group	<i>P c a</i> 2 ₁
<i>Z</i>	4
<i>a</i> [Å]	12.2040(13)
<i>b</i> [Å]	27.327(3)
<i>c</i> [Å]	7.5073(8)
<i>V</i> [Å ³]	2503.7(5)
ρ_{calcd} [g cm ^{−3}]	1.487
collected data	8908
unique data / <i>R</i> _{int}	3804/ 0.0514
no. of parameters	397
goodness-of-fit ^[a]	1.063
<i>R</i> 1 (<i>I</i> > 2σ), <i>wR</i> 2 (all reflections) ^[b]	0.0744, 0.2225
residual density [e Å ^{−3}]	0.74/−0.44

[a] GOF = $\left\{ \sum [w(F_0^2 - F_c^2)^2] / (n - p) \right\}^{1/2}$, where *n* and *p* denote the number of data and parameters.

[b] $R1 = \sum (\|F_0\| - \|F_c\|) / \sum \|F_0\|$ and $wR2 = \left\{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \right\}^{1/2}$ where

$w = 1 / [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]$ and $P = [(\text{Max}; 0, F_0^2) + 2 \cdot F_c^2] / 3$.

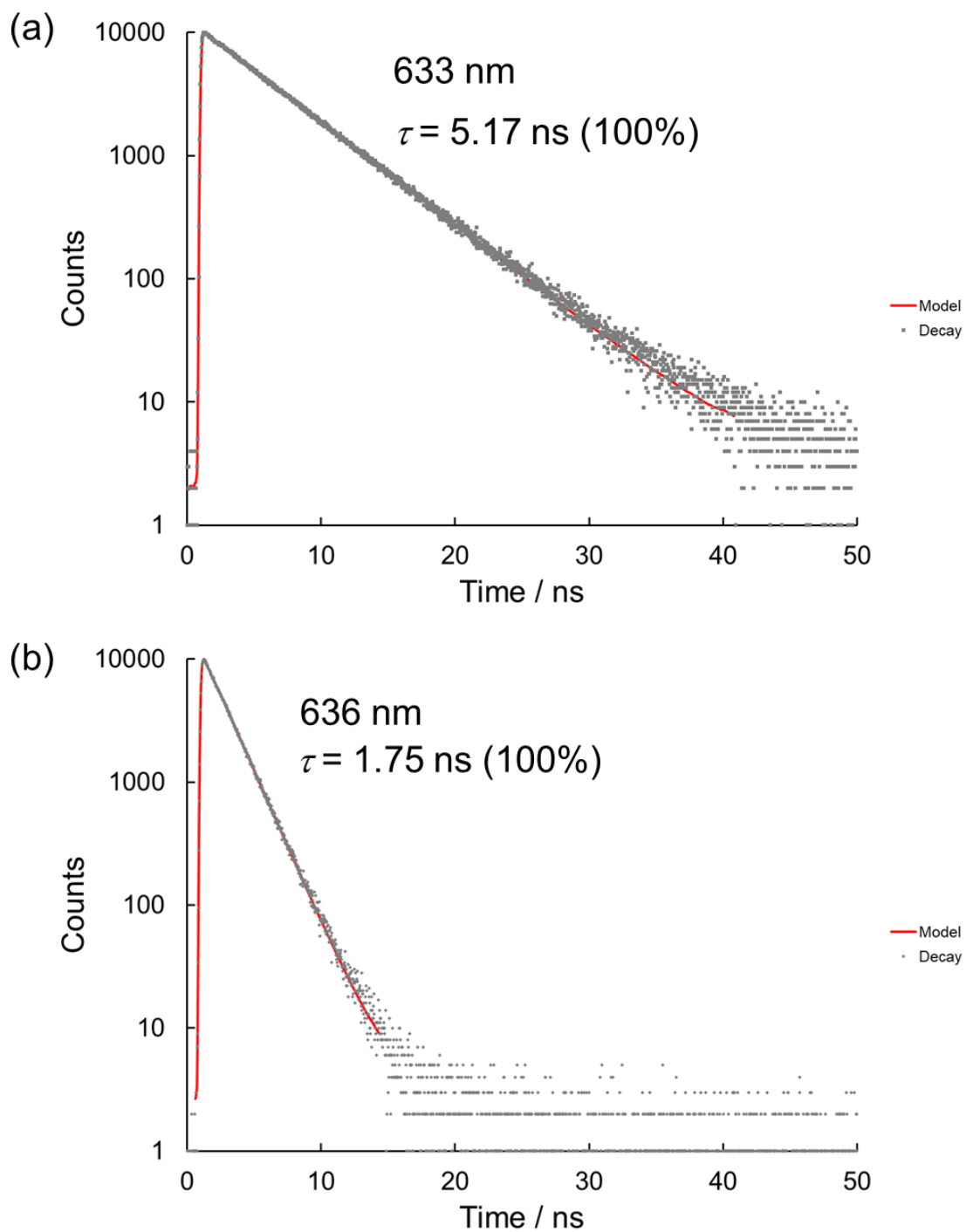


Figure S10. Emission decay curves of (a) **5** and (b) **6** in dichloromethane at room temperature. Red lines are the fitting curves using first order decay curves.

Optical resolution of **6**

Optical resolution of **6** was carried out as follows.

Racemic-**6** was dissolved in CH_2Cl_2 , and the solution was evaporated along with diatomite (ca. 5 g). Racemic-**6** adsorbed on Diatomite was filled in a cartridge for MPLC and the cartridge was connected to a DAICEL CHIRALFLASH-IA column (3 cm (i.d.) \times 10 cm).

MPLC: Biotage Isorela, eluent: *n*-hexane/2-propanol (5/1, v/v), flow rate: 12 mL/min.

Electrochemistry

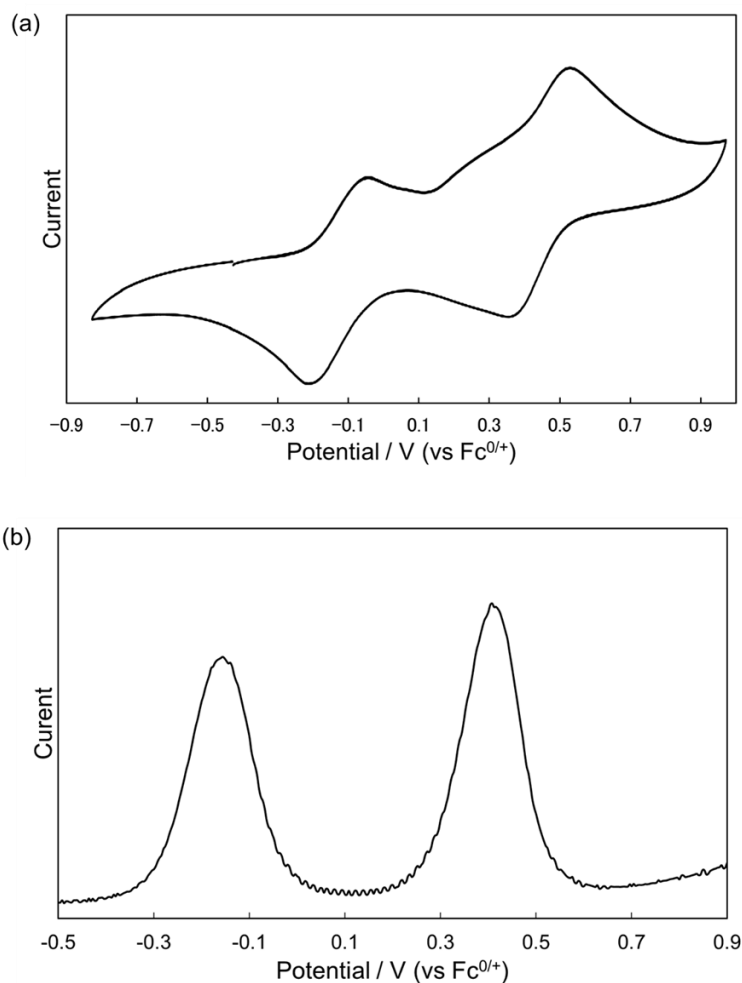


Figure S11. (a) Cyclic voltammogram (scan rate: 0.1 V/s) and (b) differential pulse voltammograms of **5** in CH_2Cl_2 (1×10^{-3} M) containing 0.1 M $n\text{Bu}_4\text{NBF}_4$ at 298 K.

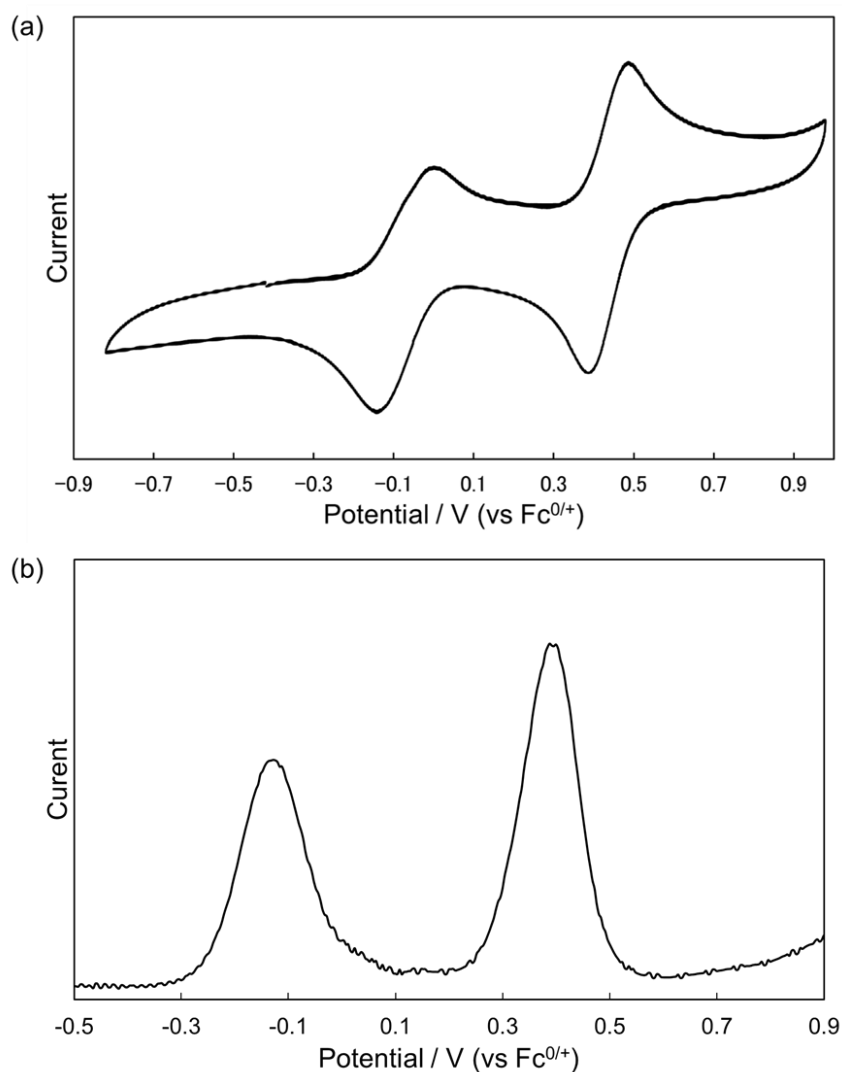


Figure S12. (a) Cyclic voltammogram (scan rate: 0.1 V/s) and (b) differential pulse voltammograms of **6** in CH₂Cl₂ containing 0.1 M *n*Bu₄NBF₄ at 298 K.

Table S5. Oxidation potentials (V vs. Fc⁰/Fc¹⁺) of **3–6** in CH₂Cl₂ (0.1 M *n*Bu₄NBF₄) determined from DPV.

	E_1	E_2	$E_2 - E_1$
3	0.05	0.68	0.63
4	0.15	0.72	0.57
5	-0.13	0.44	0.57
6	-0.07	0.44	0.51

DFT Calculations

All the DFT calculations were carried out by using Gaussian 09 program package (Revision E.01). We adopted two theoretical levels: B3LYP/6-31G(d) and B3LYP-GD3BJ/6-311G(2d,p), and we found no significant differences between the results given by the two. The transition electronic dipole moments (TEDM) and transition magnetic dipole moments (TMDM) were calculated by TD-DFT calculations. From the magnitudes of TEDM and TMDM, the electric dipole strength ($D = |\boldsymbol{\mu}|^2$), magnetic dipole strength ($G = |\mathbf{m}|^2$), and rotatory strength ($R = |\boldsymbol{\mu}| |\mathbf{m}| \cos \theta_{\mu,m}$) were calculated.

Table S6. Summary of the results of TD-DFT calculations of **5** and **6** at the B3LYP-GD3BJ/6-311G(2d,p) level.

compound ^{a)} (transition)	Energy / nm	$ \boldsymbol{\mu} $ /	$ \mathbf{m} $	$\cos \theta_{\mu,m}$	$D / 10^{-40}$ esu ² ·cm ²	$G /$ 10^{-40} erg ² ·G ⁻²	$R^b) / 10^{-40}$ erg·esu· cm·G ⁻¹	f	g_{CD}
		10^{-20} esu·cm	$/ 10^{-20}$ erg·G ⁻¹						or g_{CPL} (theoretical)
5 (S ₀ →S ₁)	573	187	2.06	0.06	35105	4.25	24.9	2.9×10^{-2}	2.8×10^{-3}
5 (S ₁ →S ₀)	750	148	2.07	0.03	21837	4.28	8.83	1.4×10^{-2}	1.6×10^{-3}
6 (S ₀ →S ₁)	504	255	2.14	0.15	65027	4.59	83.8	5.1×10^{-2}	5.2×10^{-3}
6 (S ₁ →S ₀)	634	214	2.20	0.11	45664	4.86	52.1	2.8×10^{-2}	4.6×10^{-3}

a) (*M*)-isomer, b) $|\boldsymbol{\mu}| |\mathbf{m}| \cos \theta_{\mu,m}$

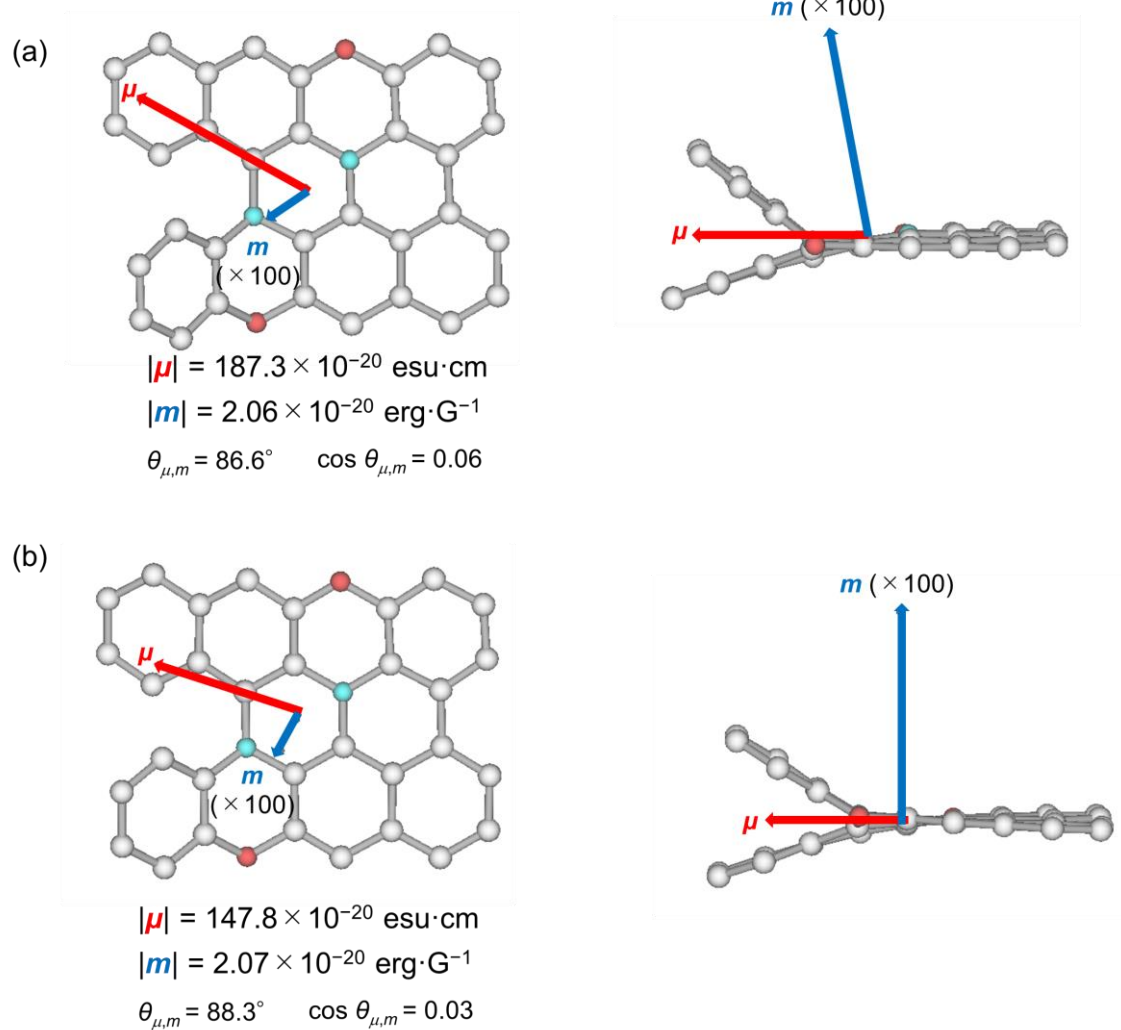


Figure S13. TEDM and TMDM of (*M*)-**5** for the (a) $S_0 \rightarrow S_1$ and (b) $S_1 \rightarrow S_0$ transitions calculated at the B3LYP-GD3BJ/6-311G(2d,p) level of theory.

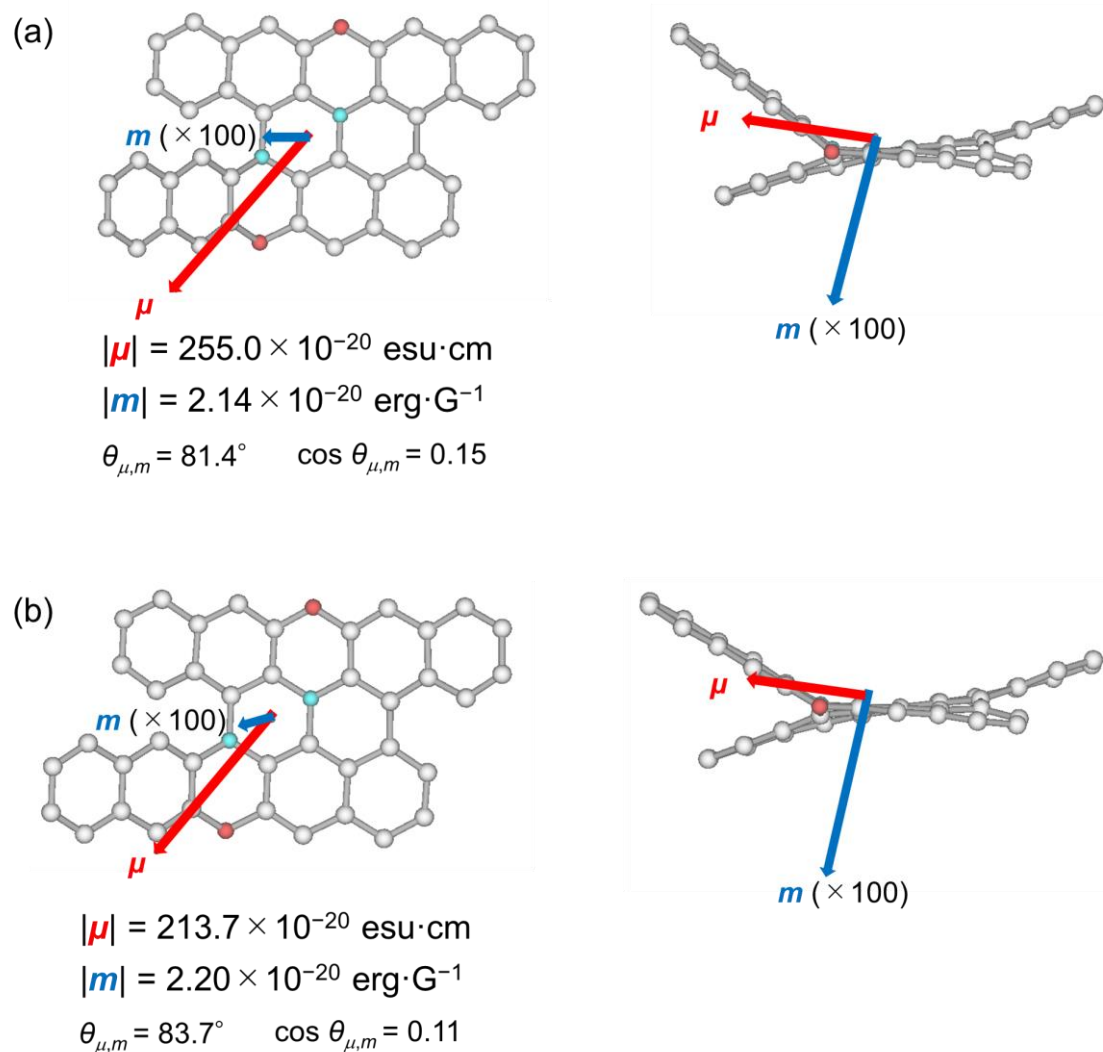


Figure S14. TEDM and TMDM of (*M*)-**6** for the (a) $S_0 \rightarrow S_1$ and (b) $S_1 \rightarrow S_0$ transitions calculated at the B3LYP-GD3BJ/6-311G(2d,p) level of theory.

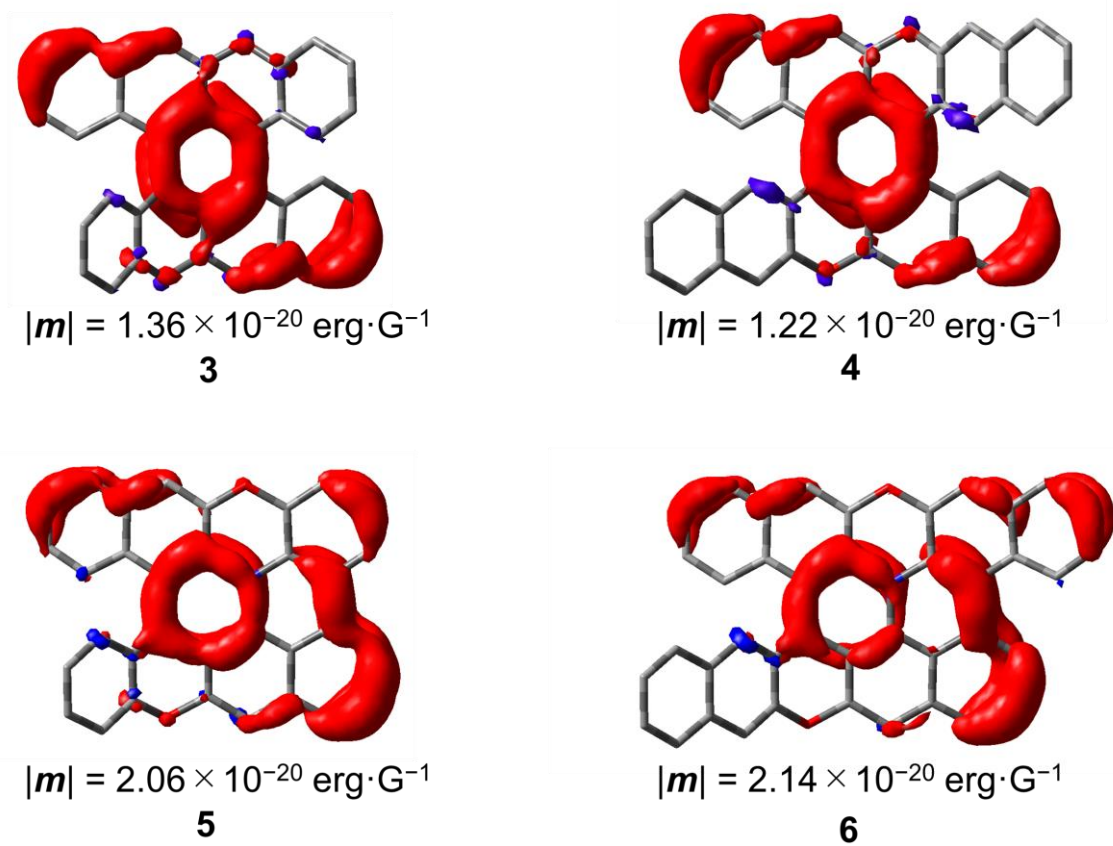


Figure S15. TMDM densities for the $S_0 \rightarrow S_1$ transitions and frontier MOs at the S_0 states of **3–6** calculated at the B3LYP-GD3BJ/6-311G(2d,p) level of theory.

Optimized geometries

(*M*)-5 (S₀ state), C₁ symmetry, B3LYP-GD3BJ/6-311G(2d,p)

O 1.008332 3.451385 0.623914
N 1.116705 0.686914 0.207213
N -1.281863 -0.713403 -0.189487
O -1.213653 -3.378081 -0.690313
C 2.219262 2.800552 0.545723
C 3.356183 3.565826 0.706906
C 4.604452 2.955818 0.635065
H 5.50065 3.548268 0.764307
C 4.699315 1.59946 0.385188
C 3.557442 0.805741 0.215447
C 2.299182 1.422815 0.3213
C -0.112591 1.37094 0.098326
C -1.290584 0.700085 -0.177753
C -2.46397 1.435925 -0.517037
C -3.628259 0.824896 -1.042146
C -4.739047 1.570802 -1.342846
C -4.748114 2.962671 -1.126012
C -3.625238 3.588478 -0.6506
C -2.452019 2.855319 -0.358678
C -1.26394 3.500167 0.048216
C -0.123163 2.776807 0.236899
C -0.021581 -1.344528 -0.337339
C 1.158682 -0.667346 -0.138818
C 2.400414 -1.332153 -0.278638
C 3.624756 -0.631842 -0.086614
C 4.811573 -1.329043 -0.211849
C 4.816104 -2.698103 -0.527237
C 3.645027 -3.383979 -0.718387
C 2.398899 -2.725677 -0.595693
C 1.170367 -3.409717 -0.738559
C -0.00382 -2.720631 -0.603363
C -2.19284 -2.888529 0.164048
C -3.102729 -3.773851 0.70674
C -4.097482 -3.298641 1.557372
H -4.822774 -3.985716 1.973548
C -4.141389 -1.949021 1.879876
C -3.213056 -1.061755 1.344987
C -2.245731 -1.519877 0.455588
H -1.234118 4.573276 0.183093
H -3.611566 4.662889 -0.509267
H -5.637113 3.538035 -1.352992
H -5.614823 1.084983 -1.754713
H -3.632823 -0.239125 -1.222959
H 3.244719 4.627529 0.882235

H 5.75797 -0.827213 -0.070624
H 5.764185 -3.213911 -0.619322
H 3.655912 -4.440094 -0.959129
H 1.148456 -4.474489 -0.927112
H -3.022195 -4.82237 0.451235
H -3.250967 -0.012744 1.599393
H 5.676736 1.145588 0.313034
H -4.900218 -1.575577 2.55572

(*M*)-**5** (*S*₁ state), *C*₁ symmetry, B3LYP-GD3BJ/6-311G(2d,p)

O 1.108641 3.44863 0.552534
N 1.169357 0.689868 0.089072
N -1.247037 -0.699835 -0.05617
O -1.230068 -3.426751 -0.499906
C 2.294167 2.777555 0.497939
C 3.446947 3.512922 0.693777
C 4.682481 2.872289 0.636401
H 5.586473 3.446056 0.795868
C 4.766663 1.520014 0.370944
C 3.61378 0.745686 0.162187
C 2.362129 1.396968 0.250793
C -0.045691 1.37812 0.103122
C -1.274622 0.699141 -0.13336
C -2.437346 1.444338 -0.504883
C -3.589719 0.877289 -1.087225
C -4.705332 1.649867 -1.369498
C -4.704837 3.01655 -1.096088
C -3.565189 3.613718 -0.582403
C -2.409506 2.864534 -0.301757
C -1.208063 3.493343 0.135048
C -0.056121 2.765613 0.264124
C -0.045625 -1.35887 -0.215736
C 1.18669 -0.667968 -0.148447
C 2.411663 -1.359289 -0.269172
C 3.650276 -0.673845 -0.136228
C 4.838668 -1.400389 -0.288072
C 4.80996 -2.76061 -0.550387
C 3.603243 -3.44352 -0.657873
C 2.386278 -2.769028 -0.513861
C 1.131787 -3.443021 -0.578933
C -0.032135 -2.753388 -0.41479
C -2.281312 -2.86366 0.184076
C -3.298421 -3.695529 0.618198
C -4.35072 -3.161102 1.351165
H -5.150285 -3.806931 1.690281
C -4.359433 -1.806724 1.669629

C -3.344481 -0.972412 1.226119
C -2.310764 -1.490512 0.446345
H -1.173012 4.563846 0.283794
H -3.542172 4.682529 -0.40428
H -5.583459 3.614557 -1.30437
H -5.577575 1.183517 -1.810825
H -3.606075 -0.175054 -1.328062
H 3.357906 4.573769 0.883437
H 5.793292 -0.901605 -0.204033
H 5.741737 -3.300006 -0.667505
H 3.593492 -4.509558 -0.848743
H 1.093048 -4.509168 -0.756127
H -3.237207 -4.750734 0.387537
H -3.34947 0.077938 1.470282
H 5.737468 1.049638 0.328183
H -5.161457 -1.392528 2.26631

(M)-6 (S₀ state), C₁ symmetry, B3LYP-GD3BJ/6-311G(2d,p)

C -7.077102 1.585478 -2.235572
C -6.705403 0.275842 -2.601889
C -5.526493 -0.261177 -2.15133
C -4.662692 0.484634 -1.315769
C -5.039594 1.810556 -0.946483
C -6.261042 2.334473 -1.425669
C -3.443354 -0.050121 -0.836825
C -2.638644 0.676051 0.004013
C -3.008707 2.009927 0.336886
C -4.165623 2.561982 -0.122715
N -1.452239 0.211546 0.604267
C -0.447872 1.198293 0.738141
C -0.8435 2.503046 1.058026
O -2.191664 2.764228 1.163905
C 0.878856 0.919933 0.512203
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C 4.174403 2.564234 0.832118
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C 2.455691 4.16483 1.414543
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C -1.906576 -2.192505 0.983926
C -1.456796 -3.541058 0.842197
C -0.135856 -3.792951 0.416145
C 0.722373 -2.754178 0.199272
C 0.30144 -1.413504 0.325275

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C 2.918771 -2.042317 -0.350635
C 2.585237 -0.686122 -0.099489
N 1.258031 -0.386774 0.192031
C 4.176479 -2.400273 -0.719023
C 5.159173 -1.412187 -0.951495
C 4.850533 -0.039479 -0.701913
C 3.570642 0.300723 -0.131941
C -3.194938 -1.964611 1.526386
C -4.015522 -3.012795 1.854164
C -3.595775 -4.342523 1.651704
C -2.340817 -4.597193 1.164471
C 6.424894 -1.769576 -1.465935
C 7.348975 -0.813561 -1.79942
C 7.016257 0.54376 -1.656264
C 5.806603 0.917817 -1.122341
H -8.01098 1.998901 -2.596188
H -7.357323 -0.307167 -3.24095
H -5.24044 -1.269478 -2.427756
H -6.543561 3.342092 -1.142669
H -3.165968 -1.057398 -1.11322
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H -0.256888 4.487116 1.538622
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H 4.542245 4.539874 1.592371
H 2.159113 5.150254 1.752487
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H -3.52687 -0.952692 1.698753
H -4.992739 -2.815529 2.276773
H -4.259839 -5.161136 1.900115
H -1.996405 -5.616557 1.035254
H 6.640827 -2.820877 -1.617396
H 8.313219 -1.098946 -2.201165
H 7.711682 1.306557 -1.984526
H 5.563214 1.966541 -1.077419

(M)-6 (S₁ state), C₁ symmetry, B3LYP-GD3BJ/6-311G(2d,p)

C -7.251978 1.453379 -1.988336
C -6.879235 0.13783 -2.335369
C -5.660792 -0.358623 -1.951546
C -4.759736 0.436356 -1.203561
C -5.138122 1.76824 -0.852366
C -6.401086 2.24949 -1.2638
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C -2.659092 0.716516 -0.032605

C -3.01979 2.056962 0.262554
C -4.223263 2.567485 -0.126828
N -1.407695 0.26051 0.44683
C -0.437594 1.232883 0.590772
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O -2.151756 2.871763 0.953244
C 0.932796 0.924893 0.475488
C 1.915218 1.914453 0.615281
C 1.506373 3.239898 0.975963
C 0.114122 3.53851 1.052026
C 3.299726 1.60129 0.419143
C 4.238292 2.581493 0.800841
C 3.836053 3.840492 1.207818
C 2.488221 4.193121 1.250225
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C 0.716756 -2.72815 0.144554
C 0.329754 -1.386988 0.281981
O 2.011803 -3.051265 -0.170305
C 2.94925 -2.059297 -0.291118
C 2.628214 -0.701217 -0.064418
N 1.297402 -0.386329 0.221694
C 4.219982 -2.438012 -0.607652
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C -4.03502 -2.948213 1.840959
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C 6.496869 -1.837474 -1.29548
C 7.435463 -0.894416 -1.635788
C 7.110042 0.466902 -1.551917
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H 2.189848 5.195023 1.532374

H 0.163658 -4.767752 0.190435
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H -3.512552 -0.888738 1.736171
H -4.999319 -2.7409 2.288091
H -4.310145 -5.085284 1.840066
H -2.057232 -5.545226 0.931314
H 6.71412 -2.893402 -1.406262
H 8.408831 -1.199932 -1.999581
H 7.818441 1.214967 -1.885447
H 5.640783 1.911197 -1.062755