



## Supporting Information

for

### Wittig reaction of cyclobisbiphenylenecarbonyl

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### Experimental details and spectral data for all new compounds

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## 1. Instrumentation and materials

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**Materials:** All used reagents, solvents, and materials were purchased from Tokyo Chemical Industry (TCI), FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich, Kanto Chemical, Nakalai Tesque, BLDpharm, or Alfa Aesar. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. CBBC **1**<sup>1</sup> and [MePPh<sub>3</sub>]**I**<sup>2</sup> were synthesized according to the literature.<sup>1</sup> Dry THF was supplied from the Glass Countor solvent purification system. TiCl<sub>4</sub> was distilled before use. If not mentioned otherwise, all reactions were performed under standard conditions (at room temperature, at ambient pressure, and under air).

**Chromatography:** Analytical thin layer chromatography was performed using fluorescent-labeled silica-coated plates (TLC silica gel 60 F<sub>254</sub>, Merck). Detection was conducted using UV light ( $\lambda_{\text{ex}} = 254$  nm). Flash column chromatography was performed using silica gel (Wakogel 60N (particle size: 63–212  $\mu\text{m}$ ), C-300 (particle size: 45–75  $\mu\text{m}$ ), or C-400HG (particle size: 20–40  $\mu\text{m}$ )). The preparative resolution was conducted using a JAI LabACE LC-7080 plus preparative HPLC with a chiral column (DAICEL CHIRALPAK IA,  $\phi$  20 mm  $\times$  250 mm). Analytical HPLC separation was performed on a Shimadzu CBM-20A system with a UV detector (SPD-20A), and Daicel Chiralpak IA-3 placed in a column oven (CTO-20AC).

**Nuclear magnetic resonance (NMR) spectroscopy:** <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to tetramethylsilane ( $\delta = 0.00$  ppm) and residual solvent signals ( $\delta = 1.94$  ppm for CD<sub>3</sub>CN and 2.05 ppm for acetone-*d*<sub>6</sub>) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta = 77.16$  ppm) and CD<sub>3</sub>CN ( $\delta = 1.32$  ppm) for <sup>13</sup>C NMR. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

**Mass spectrometry (MS):** High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) and electrospray ionization time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionization mode.

**X-ray diffraction analysis:** X-ray data were obtained using a Rigaku XtaLAB Synergy-R/NLN diffractometer with a MicroMax007HFMR X-ray generator and a HyPix-6000HE detector. The structures were solved using a direct method (SHELXT) and refined by a full-matrix least-squares method on  $F^2$  for all reflections using the programs of SHELXL-2014. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and refined as riding models with the relative isotropic displacement parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data

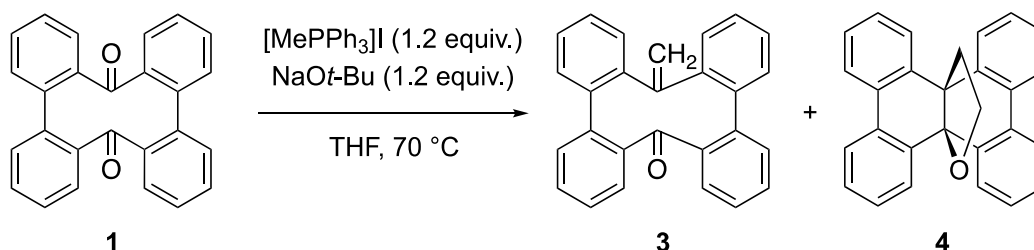
Centre as a supplementary publication.

**Spectroscopic measurements:** UV–vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V 670 spectrometer. Emission spectra were recorded on a JASCO FP-8550 spectrometer. Fluorescence lifetimes were recorded on a HAMAMATSU Quantaaurus-Tau spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-1500 CD spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu IRSpirit-X spectrometer.

**DFT calculations:** All calculations were carried out using the *Gaussian 16* software package.<sup>3</sup> The structural optimization and frequency calculations were performed with the density functional theory (DFT) method with the restricted B3LYP<sup>4</sup> level, employing the 6-31G(d) basis sets. The TD-DFT calculations were conducted at the B3LYP/6-31G(d) level. Calculations for transition states were conducted using the *GRRM17*.<sup>5</sup> Geometry optimizations and vibration frequency calculations were performed at the B3LYP/6-31G level to confirm whether the stationary point structures are transition states.

## 2. Experimental procedures and compound data

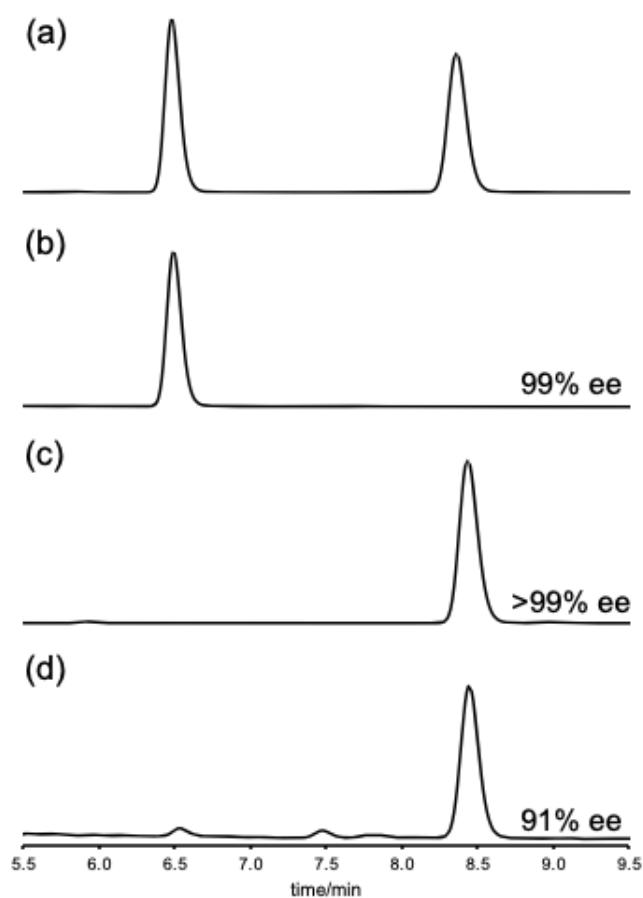
### Wittig reaction of CBBC 1 with 1.2 equiv of methylenetriphenylphosphorane



To a 50-mL Schlenk tube were added sodium *tert*-butoxide (0.16 g, 1.7 mmol) and methyltriphenylphosphonium iodide (0.67 g, 1.7 mmol) in an argon-filled glovebox. To the mixture, degassed dry THF (15 mL) was added. The mixture was stirred at 0 °C for 1 h. To the Schlenk tube was added CBBC 1 (0.50 g, 1.4 mmol). The mixture was stirred at 70 °C for 24 h. The reaction was quenched with HCl aq. (1 M). The organic materials were extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane 3:2), affording compound 3 (249 mg, 0.69 mmol, 49%) as a white solid and compound 4 (28 mg, 0.07 mmol, 5%) as a white solid.

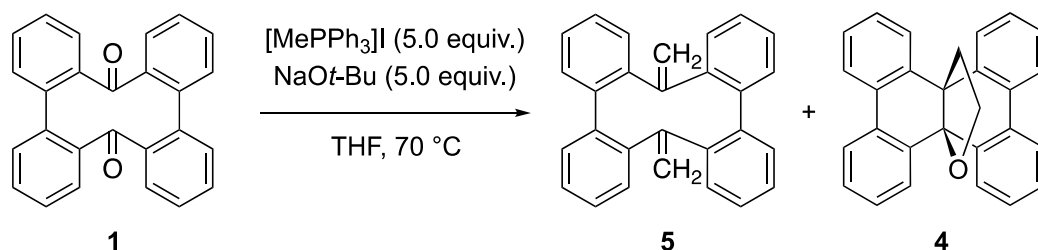
Compound 3: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.34 (dd, *J*<sub>1</sub> = 7.7 Hz, *J*<sub>2</sub> = 1.1 Hz, 2H), 7.23 (ddd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 7.6 Hz, *J*<sub>3</sub> = 1.4 Hz, 2H), 7.13–7.02 (m, 10H), 6.96 (dd, *J*<sub>1</sub> = 7.1 Hz, *J*<sub>2</sub> = 1.4 Hz, 2H), 5.33 (s, 2H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K): δ = 199.4, 148.6, 141.2, 139.8, 139.3, 138.7, 130.8, 130.4, 130.2, 129.4, 128.5, 127.7, 127.6, 127.1, 122.7 ppm; HRMS (APCI): [*M*]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>18</sub>O 358.1352; Found 358.1336; IR *ν*<sub>max</sub> (neat)/cm<sup>-1</sup> 3057(m), 1660(m), 1591(m), 1436(m), 1293(m), 925(m) 770(s), 747(s), 695(m), 638(s), 552(s), 517(m); The preparative resolution was conducted by recycling HPLC using a chiral column (Daicel Chiralpak IE: 20×250 mm, 254 nm UV detector, rt, eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane = 3/2, flow rate: 6 mL/min, injected substrate: 12 mg, obtained enantiomers: 4.7 mg as the 1st fraction and 3.7 mg as the 2nd fraction). Purities of the obtained enantiomers were determined by HPLC analysis using a chiral column (Daicel Chiralpak IE-3: 4.6×250 mm, 254 nm UV detector, 293 K, eluent: 60% CH<sub>2</sub>Cl<sub>2</sub> in hexane, flow rate: 1 mL/min, retention time: 6.4 min for (*Sa,Sa*)-3 and 8.3 min for (*Ra,Ra*)-3.

Compound **4**:  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ , 298 K):  $\delta$  = 8.07 (dd,  $J_1$  = 7.9 Hz,  $J_2$  = 1.4 Hz, 2H), 8.00–7.92 (m, 3H), 7.89 (dd,  $J_1$  = 7.9 Hz,  $J_2$  = 1.2 Hz, 1H), 7.83 (dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.3 Hz, 1H), 7.61–7.51 (m, 4H), 7.29 (ddd,  $J_1$  = 7.4 Hz,  $J_2$  = 7.4 Hz,  $J_3$  = 1.4 Hz, 1H), 7.19 (ddd,  $J_1$  = 7.3 Hz,  $J_2$  = 7.3 Hz,  $J_3$  = 1.4 Hz, 1H), 7.09–7.03 (m, 2H), 6.97 (dd,  $J_1$  = 7.6 Hz,  $J_2$  = 1.1 Hz, 1H), 6.87 (dd,  $J_1$  = 7.9 Hz,  $J_2$  = 1.0 Hz, 1H) 3.76 (ddd,  $J_1$  = 9.9 Hz,  $J_2$  = 8.2 Hz,  $J_3$  = 1.9 Hz, 1H), 3.52 (ddd,  $J_1$  = 9.8 Hz,  $J_2$  = 8.1 Hz,  $J_3$  = 7.2 Hz, 1H), 2.99 (ddd,  $J_1$  = 12.4 Hz,  $J_2$  = 6.7 Hz,  $J_3$  = 1.7 Hz, 1H), 2.34 (ddd,  $J_1$  = 12.9 Hz,  $J_2$  = 9.9 Hz,  $J_3$  = 9.9 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 137.5, 136.8, 135.6, 134.0, 133.4, 133.2, 132.7, 132.6, 130.2, 129.5, 129.1, 123.0, 128.6, 128.4, 128.1, 128.0, 127.8, 127.8, 127.5, 127.5, 125.1, 124.3, 124.1, 123.9, 84.1, 77.4, 65.8, 37.7 ppm; HRMS (APCI):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{21}\text{O}$  373.1587; Found 373.1573; IR  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2878(m), 1477(m), 1436(m), 1264(m), 1224(m), 1028(m), 988(m), 948(m), 758(s), 730(s), 552(m).



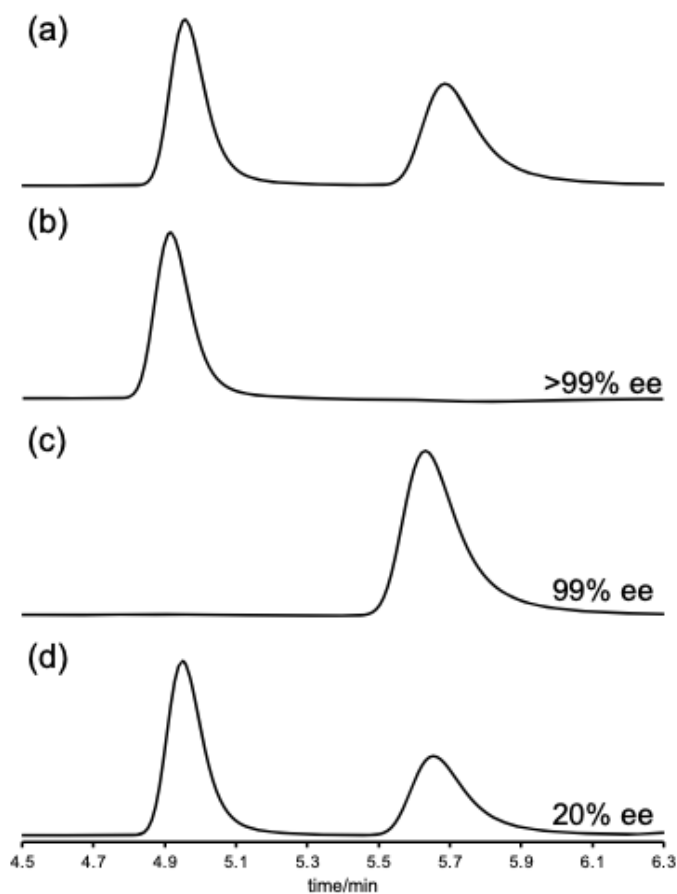
**Figure S1.** (a–c) HPLC charts of isolated (a) rac-**3**, (b) ( $S_a,S_a$ )-**3**, and (c) ( $R_a,R_a$ )-**3**. (d) HPLC chart of compound **3** synthesized from ( $P,P$ )-**1**.

**Wittig reaction of CBBC 1 with 5.0 equiv of methylenetriphenylphosphorane**



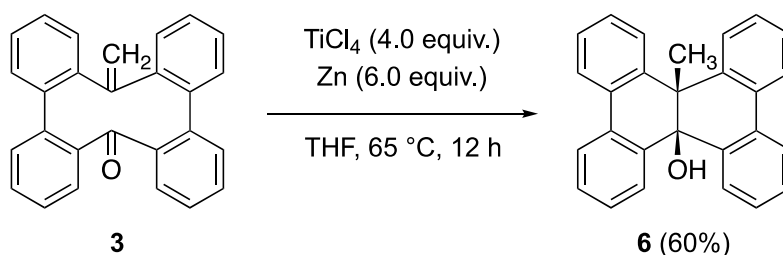
To a 50-mL Schlenk tube were added sodium *tert*-butoxide (0.67 g, 7.0 mmol) and methyltriphenylphosphonium iodide (2.8 g, 7.0 mmol) in an argon-filled glovebox. To the mixture, degassed dry THF (15 mL) was added. The mixture was stirred at 0 °C for 1 h. To the Schlenk tube was added CBBC **1** (0.50 g, 1.4 mmol). The mixture was stirred at 70 °C for 24 h. The reaction was quenched with HCl aq. (1 M). The organic materials were extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:9 to 6:4), affording compound **5** (11 mg, 0.031 mmol, 2%) as a white solid and compound **4** (263 mg, 0.70 mmol, 50%) as a white solid.

Compound **5**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.11–6.99 (m, 16H), 5.16 (s, 4H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298K): δ = 149.6, 140.3, 140.2, 130.6, 128.9, 127.2, 127.0, 120.9 ppm; HRMS (APCI): [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>21</sub> 357.1638; Found 357.1647; IR ν<sub>max</sub> (neat)/cm<sup>-1</sup> 3051(m), 1614(m), 1471(m), 1436(m), 1321(m), 902(m), 764(s), 741(s), 609(m), 546(m), 523(m); The preparative resolution was conducted by recycling HPLC using a chiral column (Daicel Chiralpak IE: 20×250 mm, 254 nm UV detector, rt, eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/9, flow rate: 6 mL/min, injected substrate: 4.4 mg, obtained enantiomers: 1.9 mg as the 1st fraction and 2.3 mg as the 2nd fraction). Purities of the obtained enantiomers were determined by HPLC analysis using a chiral column (Daicel Chiralpak IC-3: 4.6×250 mm, 254 nm UV detector, 293 K, eluent: 10% CH<sub>2</sub>Cl<sub>2</sub> in hexane, flow rate: 1 mL/min, retention time: 4.8 min for (*Ra,Ra*)-**5** and 5.5 min for (*Sa,Sa*)-**5**).



**Figure S2.** (a–c) HPLC charts of isolated (a) rac-**5**, (b) (*R<sub>a</sub>*,*R<sub>a</sub>*)-**5**, and (c) (*S<sub>a</sub>*,*S<sub>a</sub>*)-**5**. (d) HPLC chart of compound **5** synthesized from (*P,P*)-**1**.

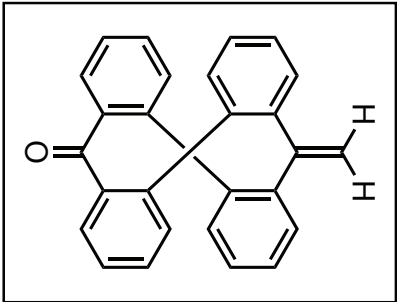
### Synthesis of compound **6**



A Schlenk tube containing zinc powder (20 mg, 0.30 mmol) and compound **3** (18 mg, 0.050 mmol) was purged with N<sub>2</sub>. To the mixture, degassed dry THF (1 mL) was added. After stirring at 0 °C, TiCl<sub>4</sub> (0.02 mL, 0.2 mmol) was added. The reaction mixture was stirred at 65 °C for 12 h. The reaction was quenched with NaHCO<sub>3</sub>. The organic materials were extracted with

CH<sub>2</sub>Cl<sub>2</sub>. The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:1), affording compound **6** (11 mg, 0.030 mmol, 60%) as a white solid.

Compound **6**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.99 (dd,  $J_1$  = 6.8 Hz,  $J_2$  = 1.8 Hz, 1H), 7.83 (ddd,  $J_1$  = 7.3 Hz,  $J_2$  = 4.6 Hz,  $J_3$  = 2.1 Hz, 1H), 7.79–7.75 (m, 2H), 7.63 (dd,  $J_1$  = 7.9 Hz,  $J_2$  = 1.1 Hz, 1H), 7.56 (dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.2 Hz, 1H), 7.54–7.47 (m, 4H), 7.16 (ddd,  $J_1$  = 7.7 Hz,  $J_2$  = 7.7 Hz,  $J_3$  = 1.4, 1H), 7.05 (ddd,  $J_1$  = 7.5 Hz,  $J_2$  = 7.5 Hz,  $J_3$  = 1.3, 1H), 6.91 (ddd,  $J_1$  = 7.4 Hz,  $J_2$  = 7.4 Hz,  $J_3$  = 1.3, 1H), 6.87 (ddd,  $J_1$  = 7.7 Hz,  $J_2$  = 7.7 Hz,  $J_3$  = 1.3, 1H), 6.61 (dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.2 Hz, 1H), 6.52 (dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.1 Hz, 1H), 2.22 (s, 1H), 1.58 (s, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 143.8, 140.4, 140.0, 140.0, 134.8, 134.0, 133.7, 133.5, 129.7, 129.3, 128.7, 128.6, 128.5, 128.5, 128.2, 128.0, 127.8, 126.3, 125.3, 124.5, 124.0, 123.8, 77.3, 48.8, 19.8 ppm (Two peaks are missing due to the overlapping.); HRMS (APCI): [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>20</sub>O 360.1509; Found 360.1513; IR  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3459(m), 3062(m), 1482(m), 1442(m), 1362(m), 1195(m), 1017(m), 758(s), 735(s), 643(m), 580(m), 506(m), 442(m).





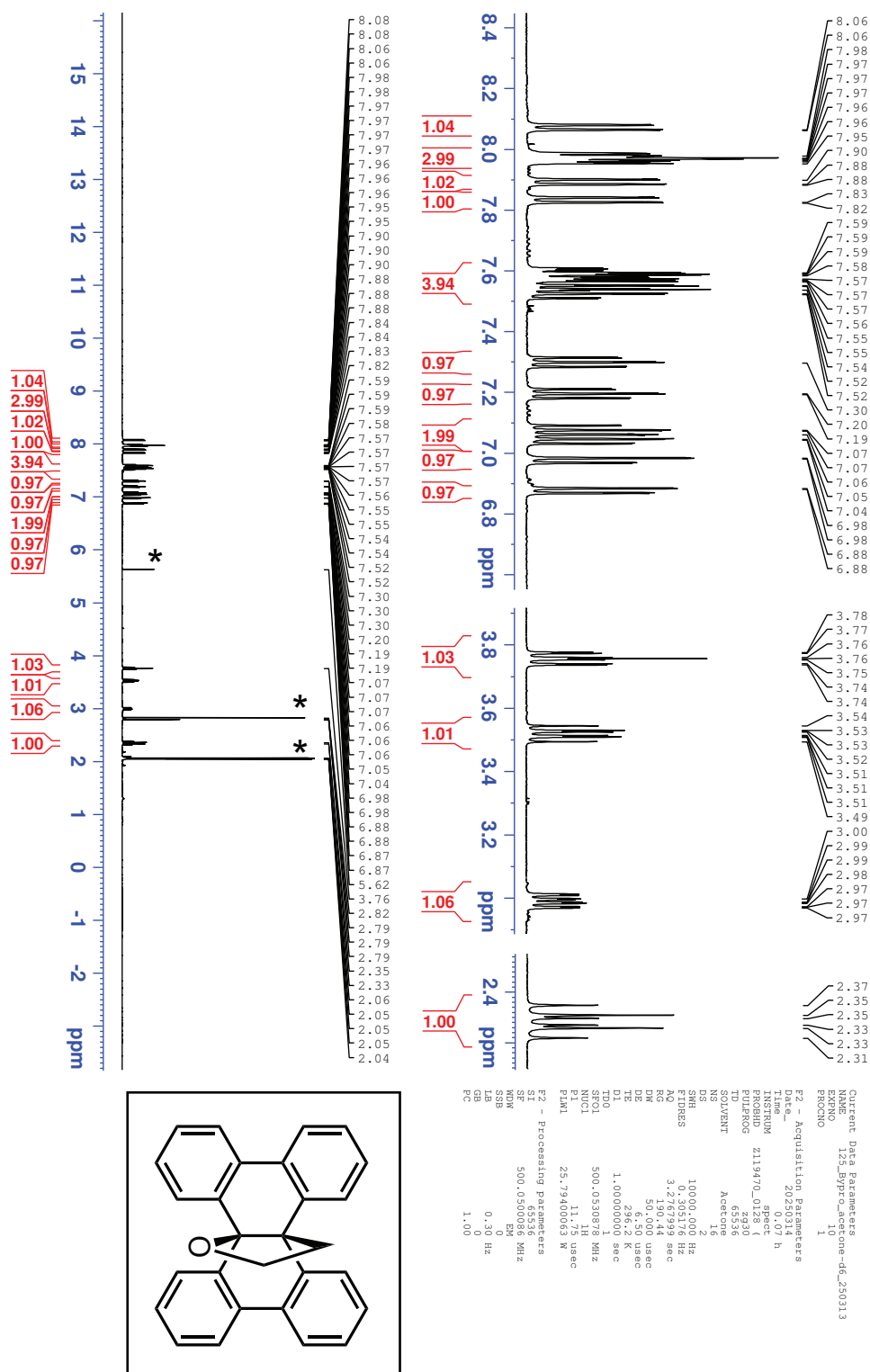


Figure S3.  $^1\text{H}$  NMR spectrum of **4** in acetone- $d_6$  at 25  $^\circ\text{C}$ .





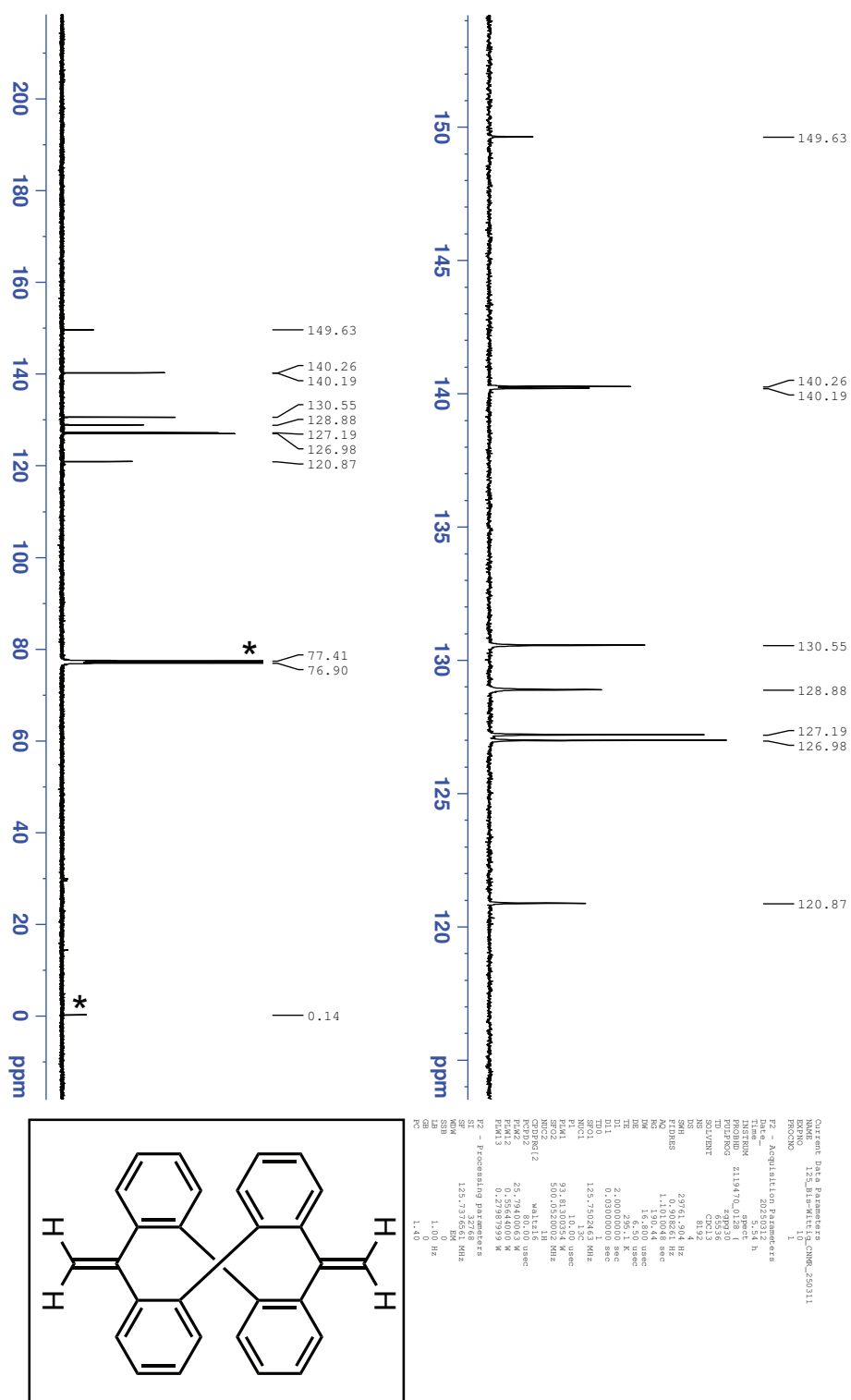


Figure S6.  $^{13}\text{C}$  NMR spectrum of **5** in  $\text{CDCl}_3$  at 25  $^{\circ}\text{C}$ .

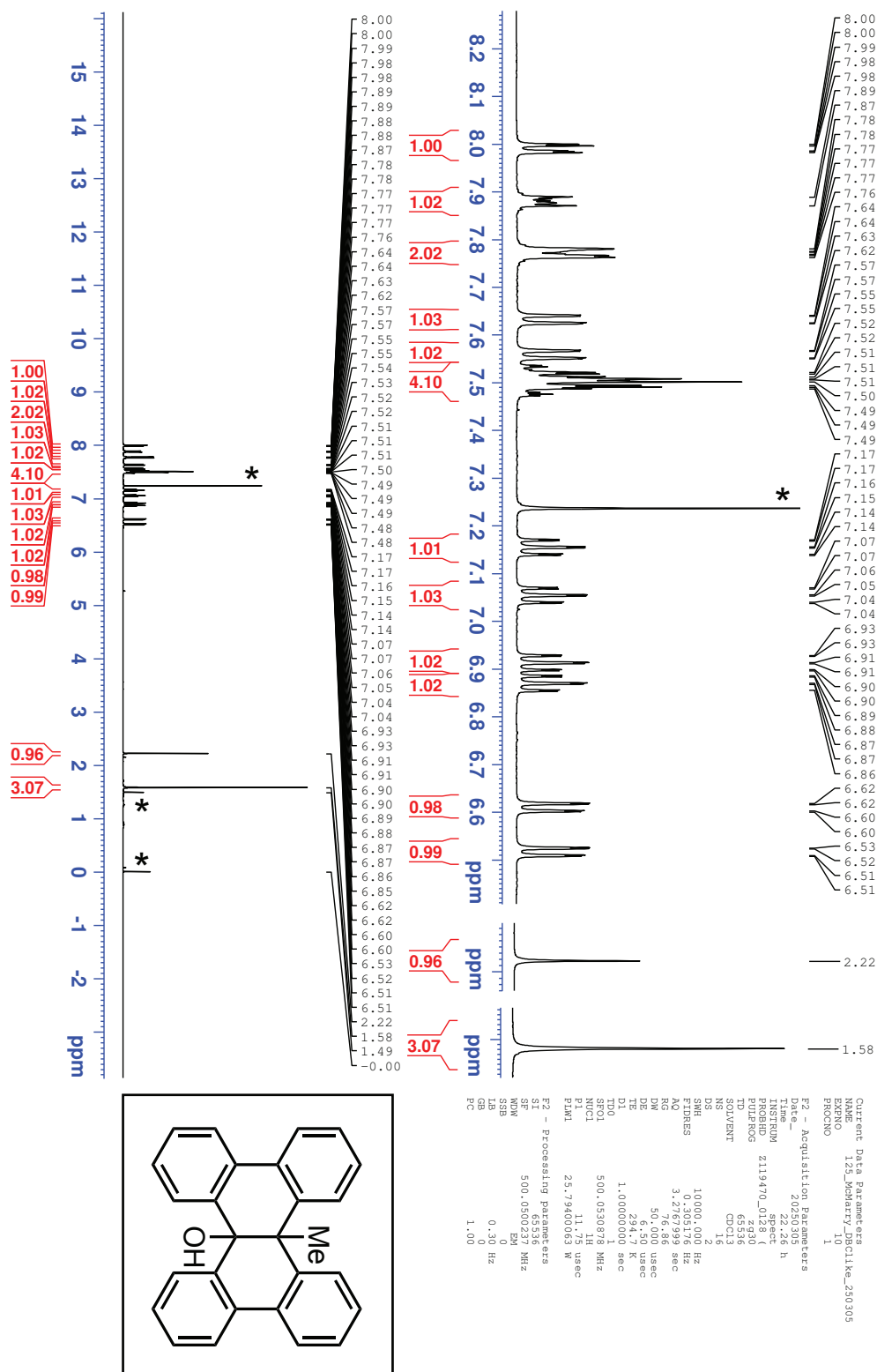
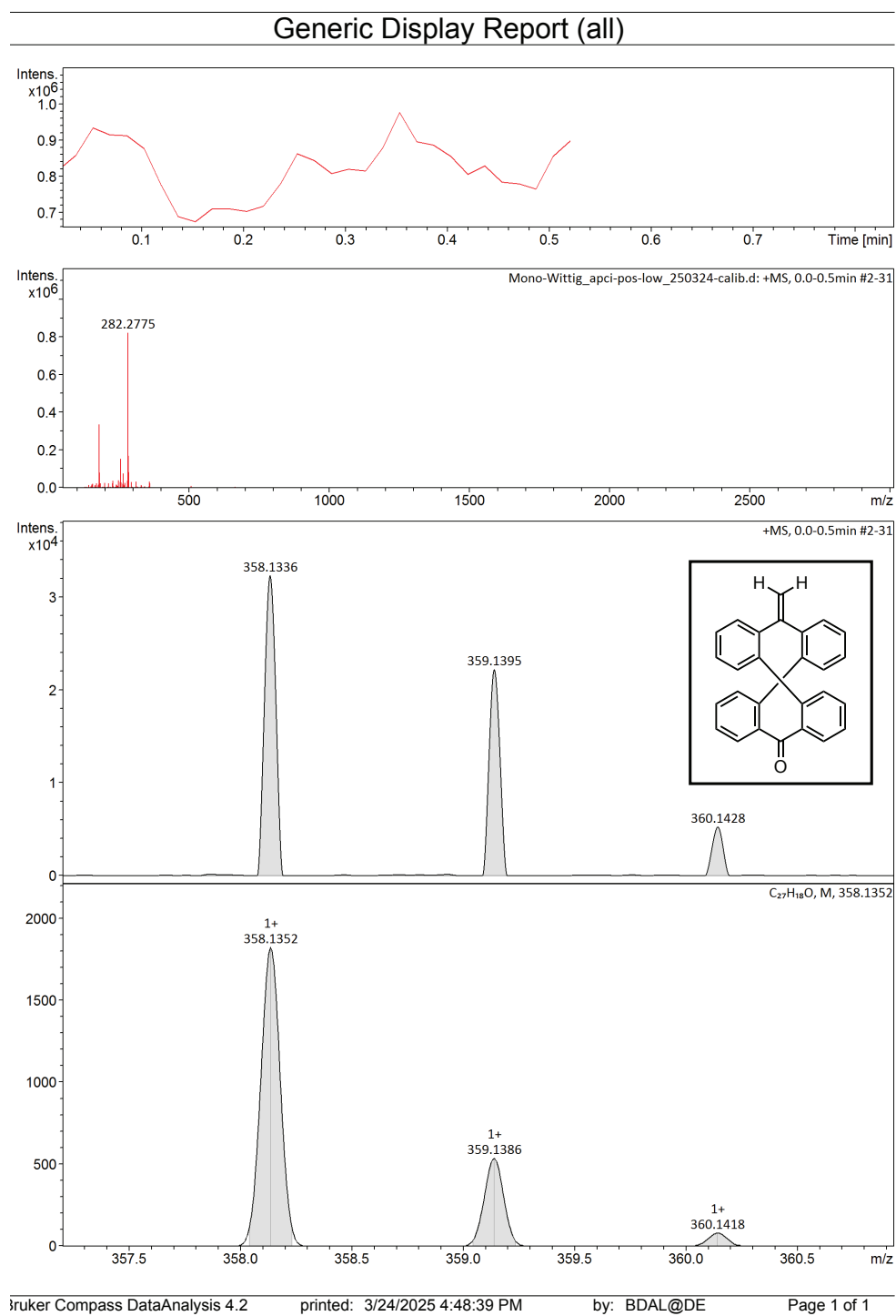


Figure S7.  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ .

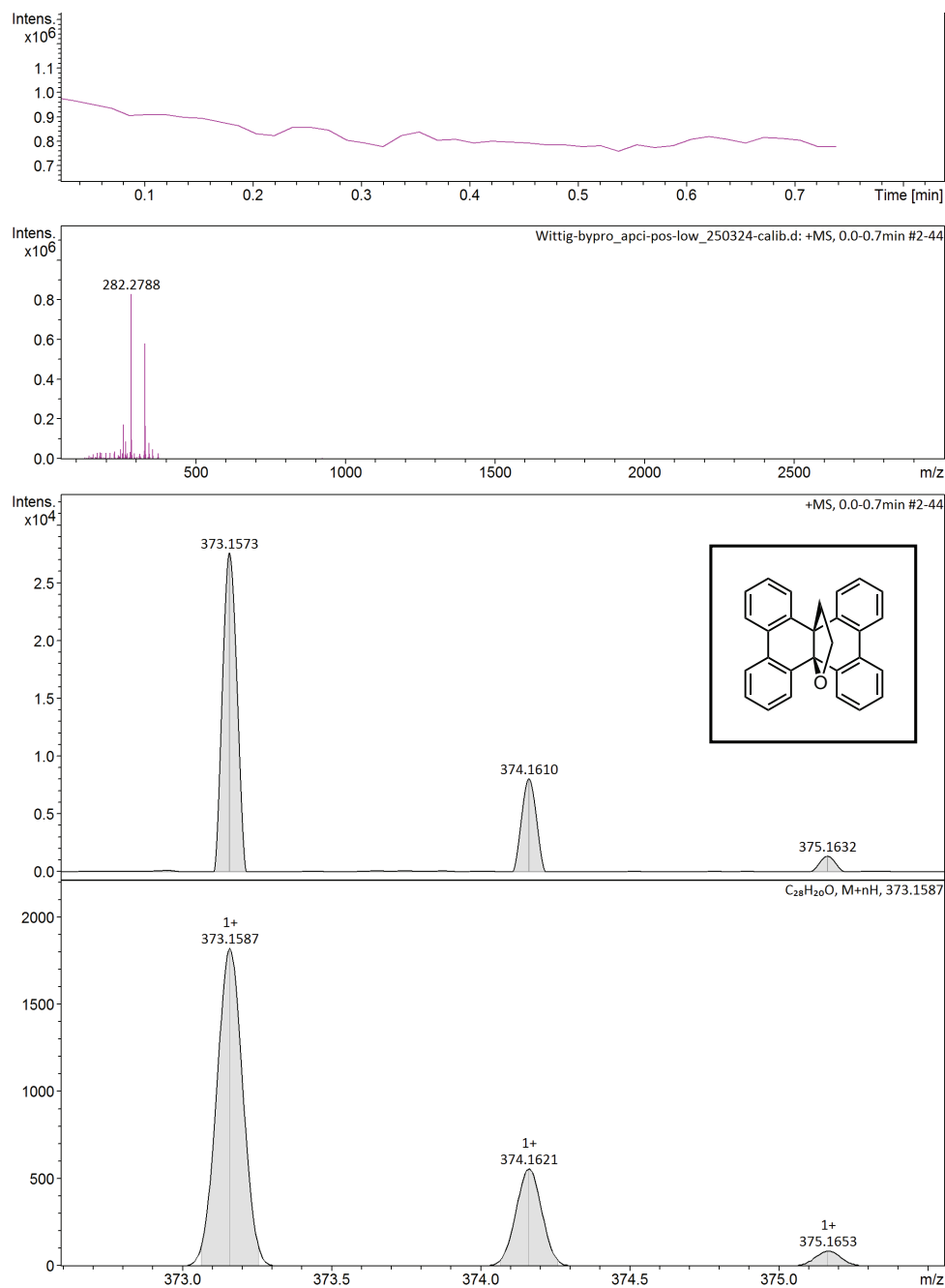


## 4. Mass spectra



**Figure S9.** APCI-TOF mass spectrum of **3**.

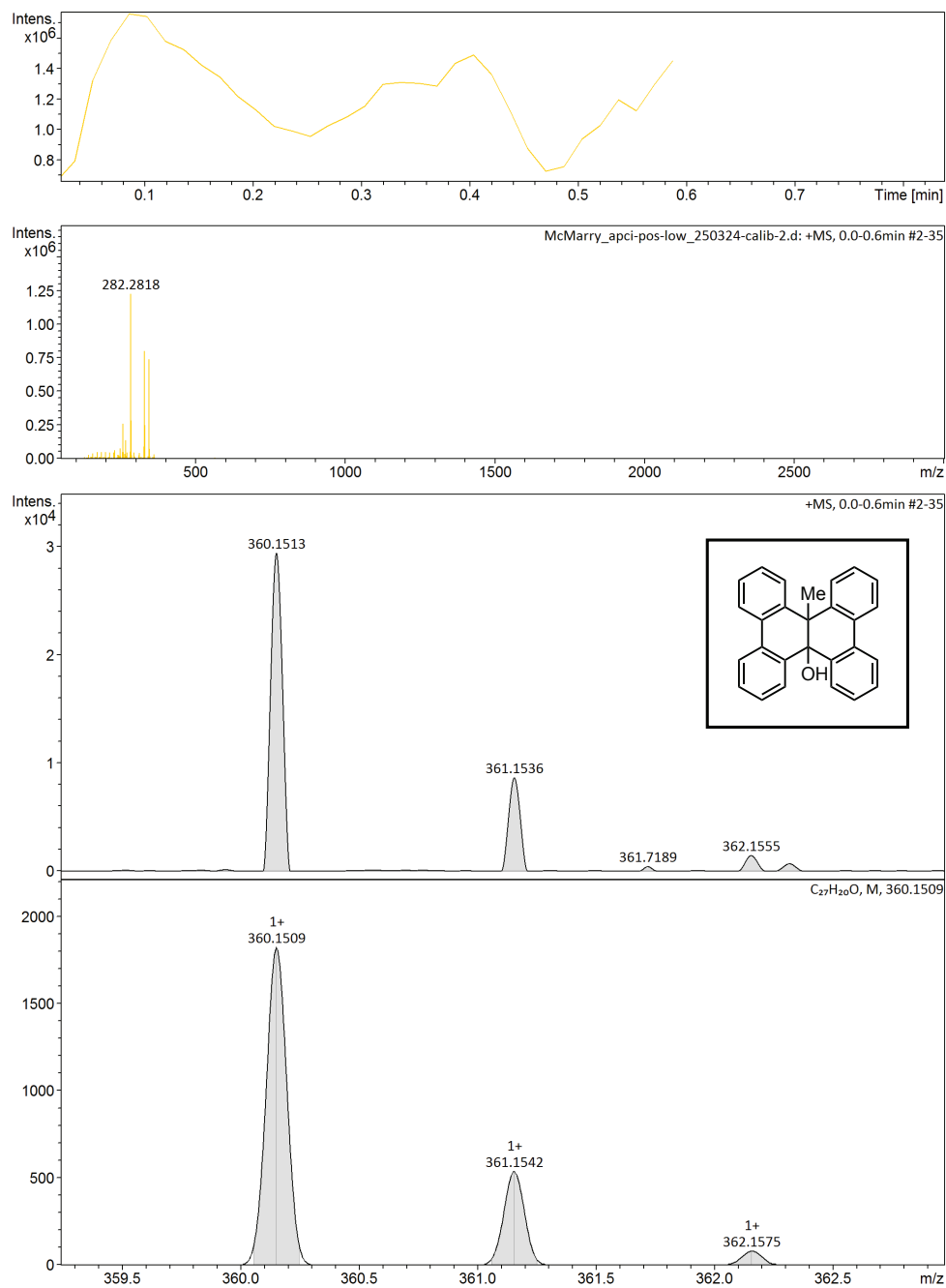
## Generic Display Report (all)



**Figure S10.** APCI-TOF mass spectrum of **4**.

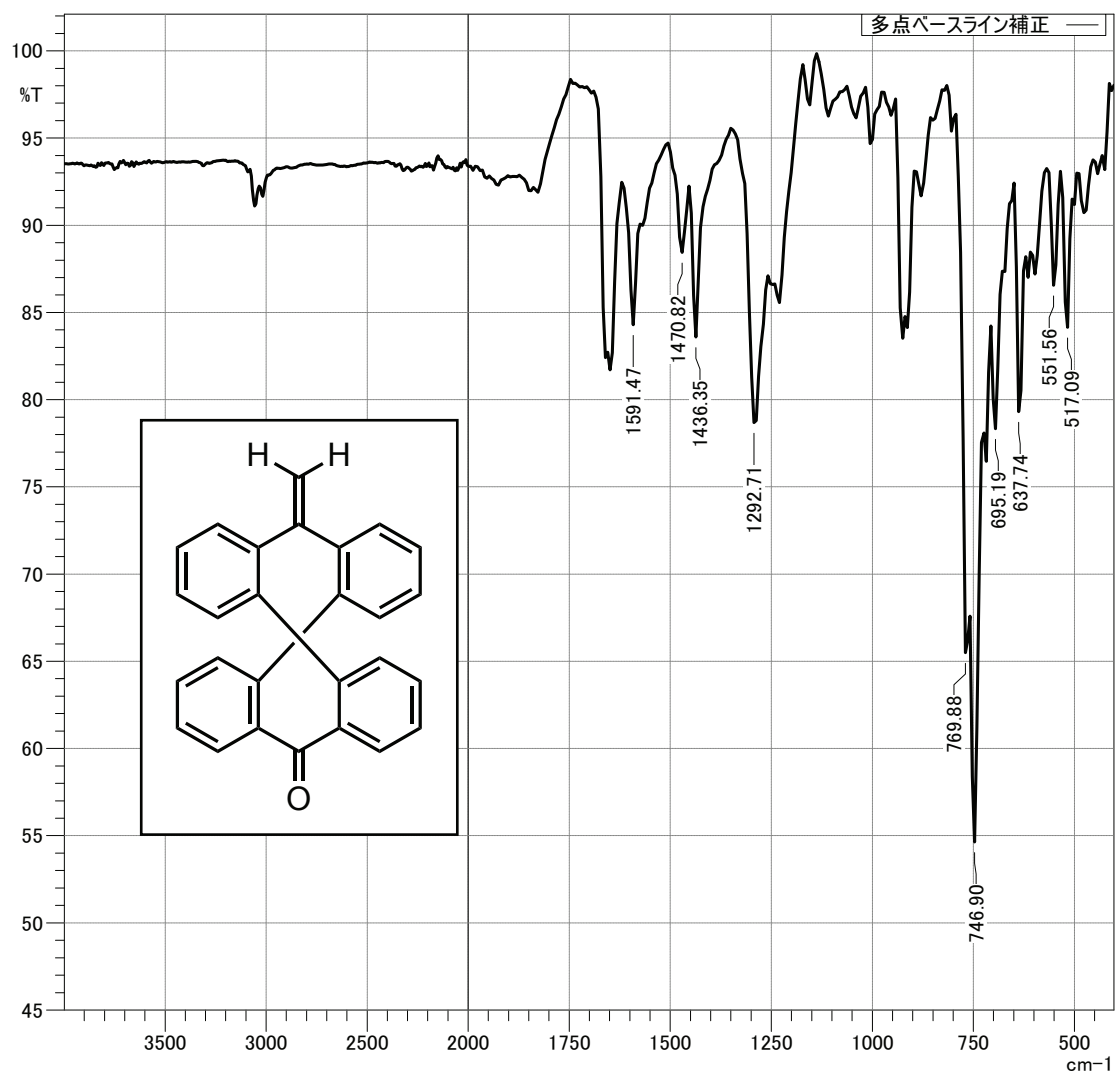


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**Figure S12.** APCI-TOF mass spectrum of **6**.





**Figure S14.** FT-IR spectrum of **3**.

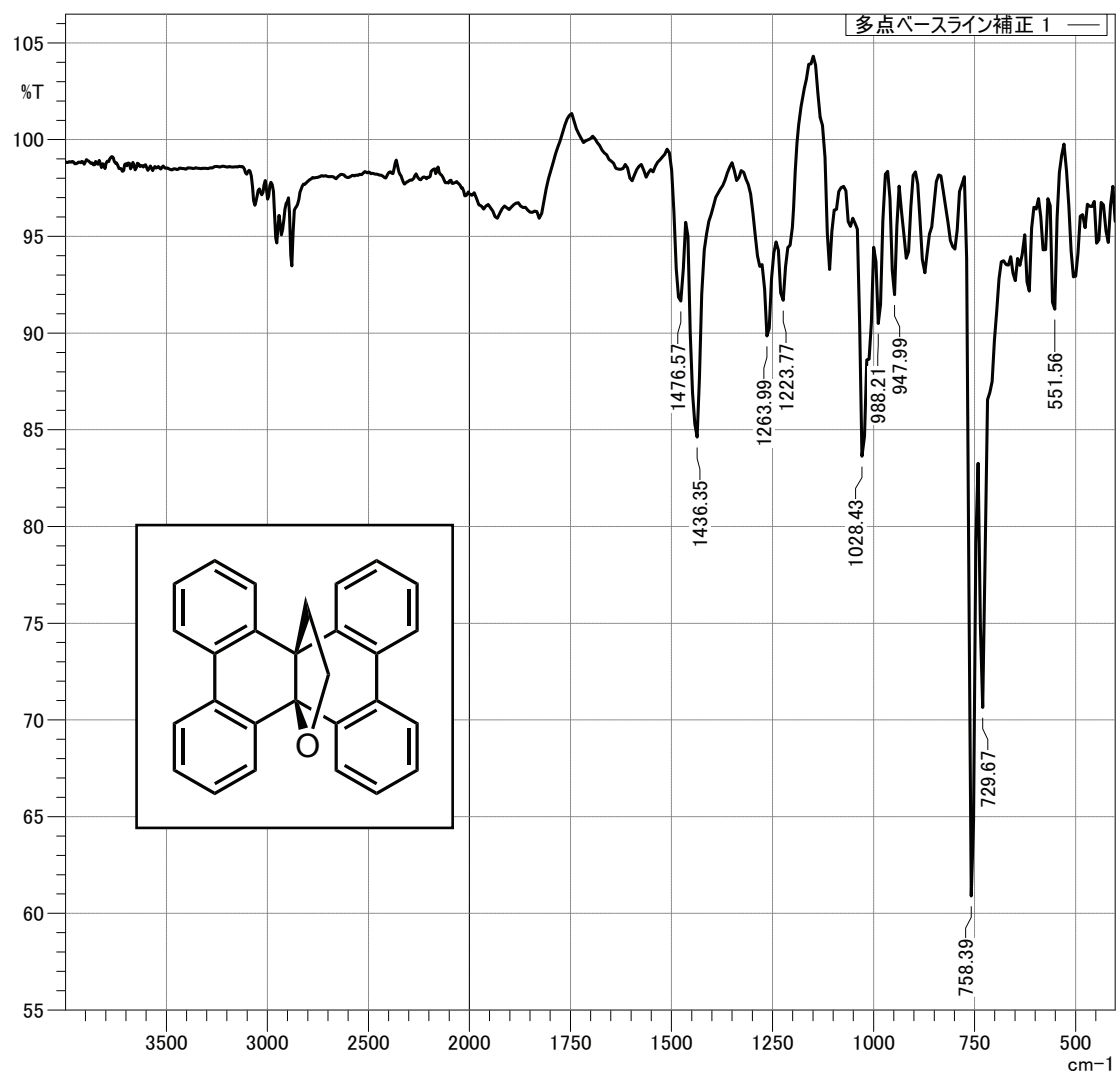


Figure S15. FT-IR spectrum of 4.

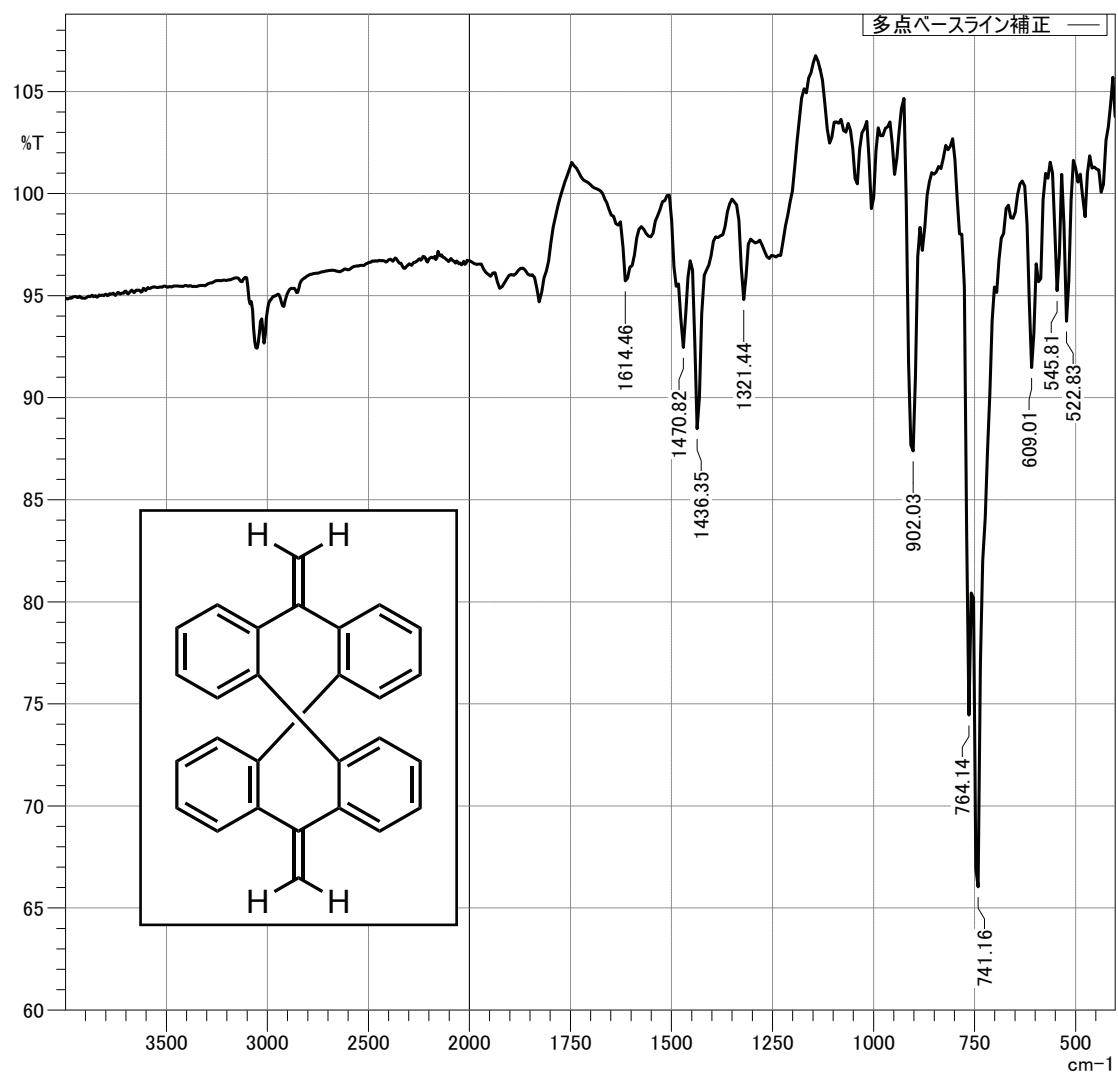
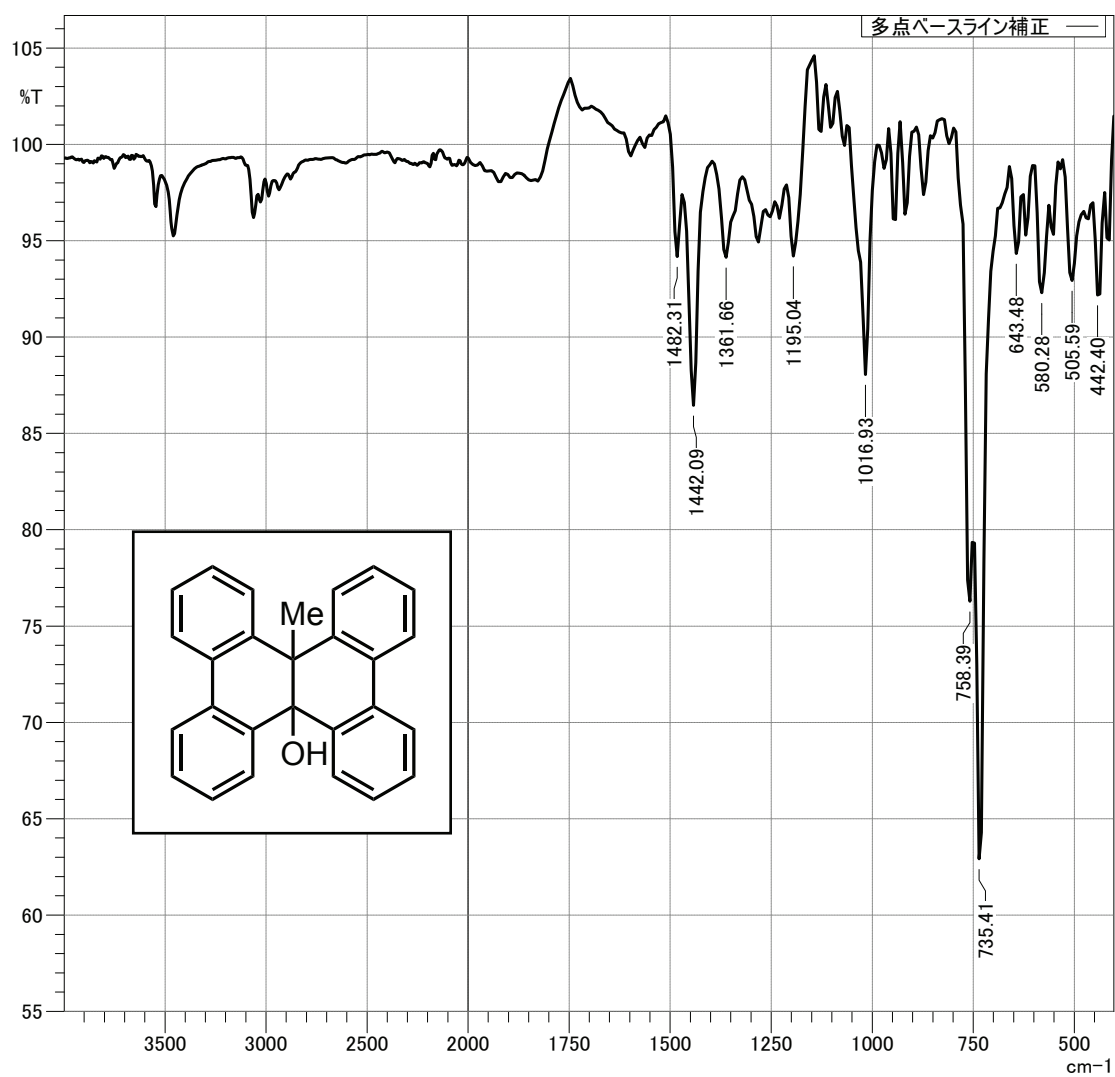


Figure S16. FT-IR spectrum of 5.



**Figure S17.** FT-IR spectrum of **6**.

## 5. Crystal data

**Table S1.** Crystallographic data of **3**, **4**, and **5**.

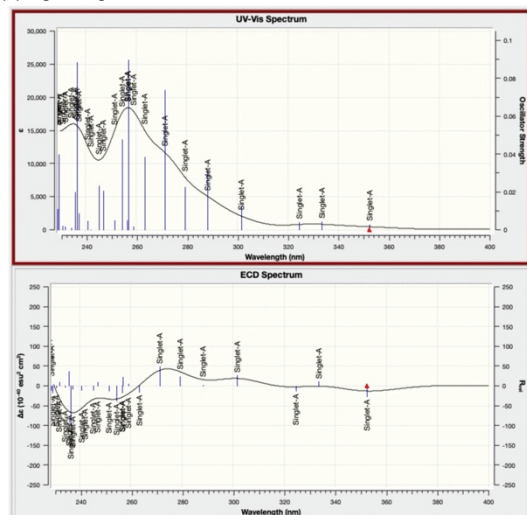
| compound                                           | <b>3</b>                                    | <b>4</b>                          | <b>5</b>                        |
|----------------------------------------------------|---------------------------------------------|-----------------------------------|---------------------------------|
| Formula                                            | C <sub>27</sub> H <sub>18</sub> O           | C <sub>28</sub> H <sub>20</sub> O | C <sub>28</sub> H <sub>20</sub> |
| Formula weight                                     | 356.40                                      | 374.45                            | 356.44                          |
| Crystal system                                     | monoclinic                                  | orthorhombic                      | monoclinic                      |
| Space group                                        | <i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14) | <i>Pbcn</i> (No. 60)              | <i>Cc</i> (No. 9)               |
| Crystal color                                      | colorless                                   | colorless                         | colorless                       |
| Crystal description                                | block                                       | block                             | plate                           |
| <i>a</i> [Å]                                       | 8.1475(3)                                   | 16.2309(3)                        | 8.02857(14)                     |
| <i>b</i> [Å]                                       | 28.7163(10)                                 | 7.0737(1)                         | 17.8783(3)                      |
| <i>c</i> [Å]                                       | 8.0068(3)                                   | 16.0738(3)                        | 13.5369(9)                      |
| $\alpha$ [°]                                       | —                                           | —                                 | —                               |
| $\beta$ [°]                                        | 98.642(3)                                   | —                                 | 98.7140(16)                     |
| $\gamma$ [°]                                       | —                                           | —                                 | —                               |
| <i>V</i> [Å <sup>3</sup> ]                         | 1852.06(11)                                 | 1845.47(6)                        | 1920.61(6)                      |
| <i>Z</i>                                           | 4                                           | 4                                 | 4                               |
| <i>d</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]    | 1.278                                       | 1.348                             | 1.233                           |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) | 0.0410                                      | 0.0496                            | 0.0290                          |
| <i>wR</i> <sub>2</sub> (all data)                  | 0.1129                                      | 0.1307                            | 0.0745                          |
| Goodness-of-fit                                    | 1.050                                       | 1.084                             | 1.082                           |
| Temperature [K]                                    | 93(2)                                       | 93(2)                             | 93(2)                           |
| CCDC No.                                           | 2432952                                     | 2432953                           | 2432954                         |

**Table S2.** Crystallographic data of **6**.

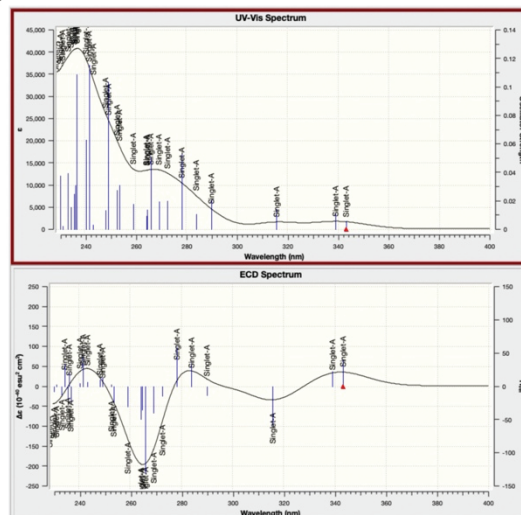
|                                                    |                                      |
|----------------------------------------------------|--------------------------------------|
| compound                                           | <b>6</b>                             |
| Formula                                            | C <sub>27</sub> H <sub>20</sub> O    |
| Formula weight                                     | 360.43                               |
| Crystal system                                     | trigonal                             |
| Space group                                        | <i>P</i> 3 <sub>1</sub> 21 (No. 152) |
| Crystal color                                      | colorless                            |
| Crystal description                                | block                                |
| <i>a</i> [Å]                                       | 9.6005(2)                            |
| <i>b</i> [Å]                                       | 9.6005(2)                            |
| <i>c</i> [Å]                                       | 34.7275(6)                           |
| $\alpha$ [°]                                       | —                                    |
| $\beta$ [°]                                        | —                                    |
| $\gamma$ [°]                                       | —                                    |
| <i>V</i> [Å <sup>3</sup> ]                         | 2771.99(13)                          |
| <i>Z</i>                                           | 6                                    |
| <i>d</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]    | 1.295                                |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) | 0.0324                               |
| <i>wR</i> <sub>2</sub> (all data)                  | 0.0793                               |
| Goodness-of-fit                                    | 1.051                                |
| Temperature [K]                                    | 93(2)                                |
| CCDC No.                                           | 2432955                              |

## 6. DFT calculations

(a) Figure-eight

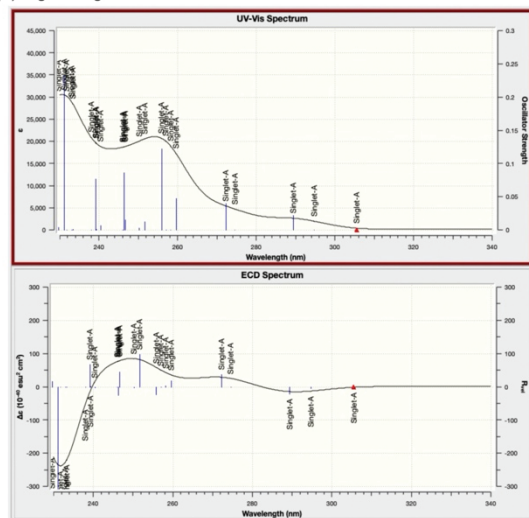


(b) Bathtub

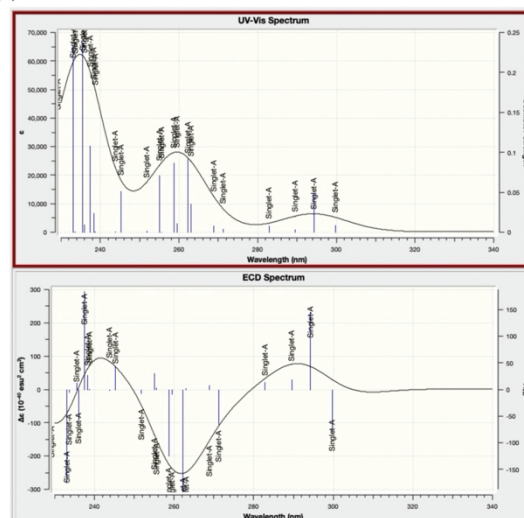


**Figure S18.** Simulated absorption (top) and CD (bottom) spectra of (a) (*M,M*)-figure-eight and (b) (*Sa,Sa*)-bathtub conformers of **3**. Half-width at half height = 0.13 eV.

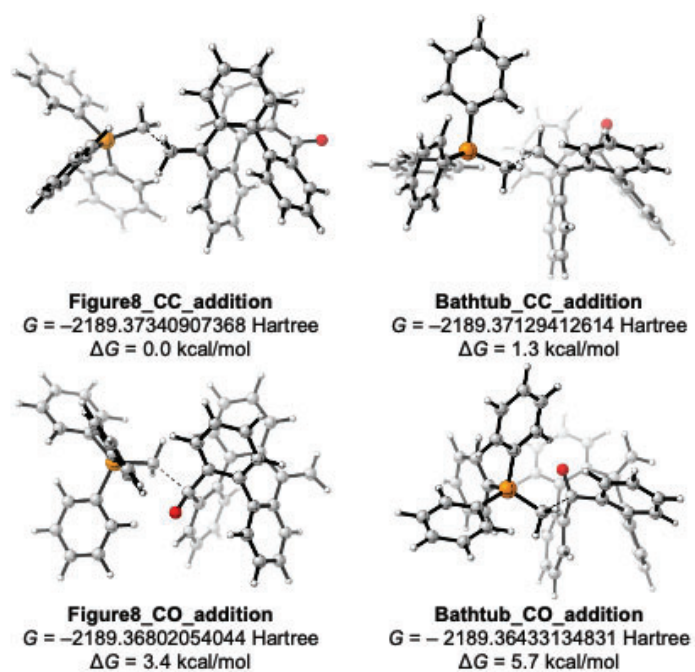
(a) Figure-eight



(b) Bathtub



**Figure S19.** Simulated absorption (top) and CD (bottom) spectra of (a) (*M,M*)-figure-eight and (b) (*Sa,Sa*)-bathtub conformers of **5**. Half-width at half height = 0.13 eV



**Figure S20.** Transition state (TS) structures for the addition of methylenetriphenylphosphorane to the C=C or C=O bonds of **3**.

**Table S3.** Cartesian coordinate and geometry of (M,M)-3 (figure-eight).

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.004165 | 0.85962   | 1.488496  |
| C | -0.74375  | 1.552963  | 0.286503  |
| C | -1.764609 | 2.329837  | -0.278119 |
| H | -1.558237 | 2.876028  | -1.194431 |
| C | -3.018765 | 2.42477   | 0.322587  |
| H | -3.794198 | 3.031047  | -0.138335 |
| C | -3.267217 | 1.755437  | 1.522149  |
| H | -4.237873 | 1.83273   | 2.004238  |
| C | -2.260547 | 0.990077  | 2.101111  |
| H | -2.428614 | 0.47091   | 3.039077  |
| C | 1.00389   | -0.855588 | 1.490848  |
| C | 0.743661  | -1.552133 | 0.290664  |
| C | 1.764638  | -2.330436 | -0.271776 |
| H | 1.558405  | -2.879079 | -1.186653 |
| C | 3.018735  | -2.423682 | 0.329318  |
| H | 3.794261  | -3.031129 | -0.129905 |
| C | 3.267009  | -1.751141 | 1.527121  |
| H | 4.237619  | -1.827081 | 2.009519  |
| C | 2.260219  | -0.984323 | 2.103938  |
| H | 2.428144  | -0.462655 | 3.040541  |
| C | -0.000207 | 0.002932  | 2.215646  |
| O | -0.000208 | 0.004612  | 3.442025  |
| C | 0.954315  | 0.890159  | -1.51665  |
| C | 0.616283  | 1.595838  | -0.339318 |
| C | 1.57034   | 2.429844  | 0.261568  |
| H | 1.291563  | 2.974649  | 1.15958   |
| C | 2.848466  | 2.579212  | -0.271946 |
| H | 3.568463  | 3.23169   | 0.214376  |
| C | 3.192197  | 1.876329  | -1.425706 |
| H | 4.189482  | 1.964155  | -1.848394 |
| C | 2.256299  | 1.040543  | -2.027882 |
| H | 2.541324  | 0.460695  | -2.900225 |
| C | -0.954199 | -0.894263 | -1.514476 |
| C | -0.61629  | -1.596775 | -0.335213 |
| C | -1.570366 | -2.429239 | 0.26778   |
| H | -1.291663 | -2.971636 | 1.167272  |
| C | -2.848423 | -2.580091 | -0.265475 |
| H | -3.568447 | -3.231301 | 0.222504  |
| C | -3.192074 | -1.88025  | -1.421106 |
| H | -4.189329 | -1.969197 | -1.84363  |
| C | -2.256154 | -1.04602  | -2.025398 |
| H | -2.541172 | -0.468429 | -2.899234 |
| C | 0.000105  | -0.002972 | -2.244124 |
| C | 0.000622  | -0.005037 | -3.592059 |
| H | -0.622708 | -0.687614 | -4.160891 |
| H | 0.624571  | 0.675656  | -4.162474 |

**Table S4.** Cartesian coordinate and geometry of (Sa,Sa)-**3** (bathtub).

|   |           |           |           |
|---|-----------|-----------|-----------|
| O | -0.046238 | -1.871463 | -1.890856 |
| C | -1.484403 | 0.69167   | -1.078557 |
| C | 0.497563  | -0.886768 | -1.414203 |
| C | 1.881114  | -0.985569 | -0.831395 |
| C | -0.159936 | 0.463883  | -1.507489 |
| C | 0.552371  | 1.477809  | -2.160318 |
| H | 1.574456  | 1.284304  | -2.474915 |
| C | 0.158925  | 0.382851  | 1.54907   |
| C | 2.317741  | -0.264373 | 0.307025  |
| C | -2.311186 | -0.310009 | -0.342227 |
| C | -0.487896 | -0.953807 | 1.360041  |
| C | 1.464573  | 0.684403  | 1.088754  |
| C | 2.74957   | -1.886122 | -1.464033 |
| H | 2.371716  | -2.443012 | -2.315767 |
| C | 2.004569  | 1.947335  | 1.388543  |
| H | 2.995799  | 2.19129   | 1.016805  |
| C | -3.62639  | -0.507372 | -0.796699 |
| H | -3.94966  | 0.022248  | -1.688113 |
| C | -2.049823 | 1.950756  | -1.339997 |
| H | -3.055026 | 2.155297  | -0.982881 |
| C | -1.870276 | -1.036228 | 0.795856  |
| C | 1.290785  | 2.899222  | 2.111584  |
| H | 1.736179  | 3.868568  | 2.318425  |
| C | -0.552751 | 1.359606  | 2.261754  |
| H | -1.556319 | 1.122585  | 2.604226  |
| C | 3.63819   | -0.46795  | 0.743001  |
| H | 3.978856  | 0.053342  | 1.633147  |
| C | -0.035817 | 2.711419  | -2.429998 |
| H | 0.525709  | 3.481006  | -2.952283 |
| C | -1.345748 | 2.946412  | -2.014974 |
| H | -1.81676  | 3.907963  | -2.200882 |
| C | 0.142383  | -2.070564 | 1.76269   |
| C | 4.058359  | -2.059523 | -1.023936 |
| H | 4.721001  | -2.750904 | -1.536973 |
| C | 0.000495  | 2.603996  | 2.550499  |
| H | -0.57218  | 3.335955  | 3.113623  |
| C | -2.782632 | -1.896906 | 1.432841  |
| H | -2.45857  | -2.41635  | 2.329433  |
| C | -4.505939 | -1.379913 | -0.162559 |
| H | -5.513077 | -1.510962 | -0.548804 |
| C | 4.503497  | -1.341587 | 0.086116  |
| H | 5.51861   | -1.470065 | 0.452617  |
| C | -4.081689 | -2.076607 | 0.967297  |
| H | -4.756529 | -2.750014 | 1.488771  |
| H | 1.124581  | -2.031826 | 2.22281   |
| H | -0.292773 | -3.054117 | 1.615497  |

**Table S5.** Cartesian coordinate and geometry of (*M,M*)-**5** (figure-eight).

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.993983 | -0.85924  | -1.463715 |
| C | -0.682674 | -1.608529 | -0.305536 |
| C | -1.664182 | -2.423871 | 0.273537  |
| H | -1.403822 | -3.000468 | 1.157114  |
| C | -2.947826 | -2.510692 | -0.261041 |
| H | -3.691223 | -3.150622 | 0.206824  |
| C | -3.267252 | -1.761268 | -1.392425 |
| H | -4.268168 | -1.799418 | -1.814246 |
| C | -2.301639 | -0.945254 | -1.975191 |
| H | -2.565474 | -0.33384  | -2.832568 |
| C | 0.993808  | 0.858865  | -1.464056 |
| C | 0.682689  | 1.608383  | -0.305969 |
| C | 1.664319  | 2.423746  | 0.27287   |
| H | 1.404089  | 3.000522  | 1.156369  |
| C | 2.947922  | 2.510359  | -0.261834 |
| H | 3.69142   | 3.150298  | 0.205858  |
| C | 3.267188  | 1.760675  | -1.393089 |
| H | 4.268085  | 1.798617  | -1.814971 |
| C | 2.301455  | 0.944636  | -1.97562  |
| H | 2.565213  | 0.332968  | -2.832833 |
| C | -0.000167 | -0.000255 | -2.184322 |
| C | 0.99397   | -0.858874 | 1.463947  |
| C | 0.682665  | -1.608395 | 0.305932  |
| C | 1.664214  | -2.423812 | -0.273015 |
| H | 1.403822  | -3.000606 | -1.156451 |
| C | 2.947879  | -2.510434 | 0.261518  |
| H | 3.691321  | -3.150393 | -0.206236 |
| C | 3.267307  | -1.760768 | 1.39274   |
| H | 4.268252  | -1.798752 | 1.814507  |
| C | 2.30166   | -0.944712 | 1.975388  |
| H | 2.565494  | -0.333108 | 2.83262   |
| C | -0.993827 | 0.859232  | 1.463844  |
| C | -0.682588 | 1.608482  | 0.305638  |
| C | -1.664131 | 2.423862  | -0.27337  |
| H | -1.403786 | 3.000457  | -1.15695  |
| C | -2.947734 | 2.510694  | 0.26128   |
| H | -3.691174 | 3.150616  | -0.206527 |
| C | -3.267101 | 1.761285  | 1.392689  |
| H | -4.267997 | 1.799438  | 1.814557  |
| C | -2.301455 | 0.945278  | 1.975407  |
| H | -2.565239 | 0.333885  | 2.832805  |
| C | 0.000087  | 0.00024   | 2.18436   |
| C | 0.000138  | 0.000386  | 3.532373  |
| H | -0.651577 | 0.655651  | 4.101696  |
| H | 0.651896  | -0.654756 | 4.10179   |
| C | -0.000631 | -0.000106 | -3.532336 |
| H | -0.652624 | -0.65522  | -4.101524 |
| H | 0.650828  | 0.655249  | -4.101853 |

**Table S6.** Cartesian coordinate and geometry of (Sa,Sa)-**5** (bathtub).

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 3.599402  | -0.480852 | 0.823159  |
| H | 3.894793  | 0.044221  | 1.727256  |
| C | 4.510417  | -1.327393 | 0.195777  |
| H | 5.511381  | -1.44447  | 0.602402  |
| C | 1.893184  | -1.009961 | -0.82063  |
| C | 1.432774  | 0.679628  | 1.086697  |
| C | 0.526703  | -0.928821 | -1.41796  |
| C | 0.127687  | 0.406556  | 1.557961  |
| C | -2.29105  | -0.295931 | -0.342183 |
| C | -1.893174 | -1.01028  | 0.820213  |
| C | 2.291127  | -0.296303 | 0.342172  |
| C | -1.432673 | 0.680356  | -1.086197 |
| C | 0.080541  | -2.030618 | 1.890188  |
| C | -0.127643 | 0.407374  | -1.557717 |
| C | 1.97817   | 1.95191   | 1.33854   |
| H | 2.970427  | 2.176114  | 0.957442  |
| C | -0.526769 | -0.929512 | 1.417653  |
| C | -1.270983 | 2.934949  | -2.02512  |
| H | -1.722164 | 3.909116  | -2.193856 |
| C | 4.125519  | -2.012627 | -0.954497 |
| H | 4.824148  | -2.665171 | -1.471279 |
| C | -2.834908 | -1.845086 | 1.447902  |
| H | -2.542086 | -2.35238  | 2.362129  |
| C | -4.125419 | -2.013193 | 0.953312  |
| H | -4.82401  | -2.666195 | 1.469566  |
| C | 0.579328  | 1.413106  | -2.23518  |
| H | 1.58394   | 1.193471  | -2.586576 |
| C | -0.081109 | -2.029709 | -1.890335 |
| C | -1.97801  | 1.952739  | -1.337538 |
| H | -2.970214 | 2.176904  | -0.956269 |
| C | -0.57938  | 1.412204  | 2.2355    |
| H | -1.584094 | 1.192554  | 2.586578  |
| C | -3.599313 | -0.480223 | -0.82334  |
| H | -3.894677 | 0.045404  | -1.727119 |
| C | -4.510305 | -1.327219 | -0.196536 |
| H | -5.511251 | -1.444102 | -0.603261 |
| C | 2.834967  | -1.844267 | -1.448932 |
| H | 2.542189  | -2.350932 | -2.363519 |
| C | 1.27111   | 2.933939  | 2.026317  |
| H | 1.722298  | 3.908026  | 2.195502  |
| C | 0.020218  | 2.663986  | -2.477585 |
| H | 0.588207  | 3.419567  | -3.013744 |
| C | -0.020228 | 2.662947  | 2.478401  |
| H | -0.588262 | 3.418475  | 3.014591  |
| H | -1.053448 | -1.976621 | -2.369346 |
| H | 0.361421  | -3.015851 | -1.785416 |
| H | -0.362408 | -3.016546 | 1.785116  |
| H | 1.052707  | -1.977767 | 2.369536  |

**Table S7.** Cartesian coordinate and geometry of TS1 of 5.

|   |        |        |        |
|---|--------|--------|--------|
| C | 1.258  | 1.307  | -0.813 |
| C | 2.356  | 0.436  | -0.607 |
| C | 3.348  | 0.346  | -1.588 |
| H | 4.194  | -0.318 | -1.426 |
| C | 3.232  | 1.047  | -2.79  |
| H | 4.007  | 0.956  | -3.548 |
| C | 2.107  | 1.836  | -3.028 |
| H | 1.998  | 2.366  | -3.971 |
| C | 1.131  | 1.97   | -2.039 |
| H | 0.277  | 2.623  | -2.201 |
| C | -1.133 | 1.752  | 0.333  |
| C | -2.1   | 0.7    | 0.299  |
| C | -3.358 | 1.019  | 0.878  |
| H | -4.063 | 0.212  | 1.035  |
| C | -3.747 | 2.296  | 1.264  |
| H | -4.735 | 2.452  | 1.688  |
| C | -2.863 | 3.352  | 1.083  |
| H | -3.142 | 4.375  | 1.321  |
| C | -1.575 | 3.056  | 0.656  |
| H | -0.842 | 3.854  | 0.601  |
| C | 0.367  | 1.658  | 0.332  |
| C | 1.258  | -1.307 | 0.813  |
| C | 2.357  | -0.436 | 0.607  |
| C | 3.348  | -0.346 | 1.588  |
| H | 4.195  | 0.318  | 1.426  |
| C | 3.233  | -1.047 | 2.79   |
| H | 4.007  | -0.955 | 3.548  |
| C | 2.107  | -1.836 | 3.028  |
| H | 1.999  | -2.365 | 3.971  |
| C | 1.131  | -1.97  | 2.039  |
| H | 0.277  | -2.623 | 2.201  |
| C | -1.133 | -1.753 | -0.333 |
| C | -2.1   | -0.7   | -0.299 |
| C | -3.358 | -1.02  | -0.878 |
| H | -4.063 | -0.213 | -1.035 |
| C | -3.747 | -2.296 | -1.264 |
| H | -4.735 | -2.453 | -1.688 |
| C | -2.863 | -3.352 | -1.084 |
| H | -3.142 | -4.375 | -1.321 |
| C | -1.575 | -3.056 | -0.657 |
| H | -0.841 | -3.854 | -0.601 |
| C | 0.367  | -1.658 | -0.332 |
| C | 0.957  | 2.087  | 1.464  |
| H | 2.036  | 2.14   | 1.559  |
| H | 0.376  | 2.376  | 2.334  |
| C | 0.957  | -2.087 | -1.464 |
| H | 0.376  | -2.376 | -2.334 |
| H | 2.037  | -2.14  | -1.559 |

**Table S8.** Cartesian coordinate and geometry of TS2 of **5**.

|   |        |        |        |
|---|--------|--------|--------|
| C | 0.37   | 0.641  | 1.597  |
| C | 1.406  | 0.977  | 0.697  |
| C | 1.861  | 2.301  | 0.645  |
| H | 2.666  | 2.553  | -0.039 |
| C | 1.294  | 3.289  | 1.45   |
| H | 1.659  | 4.311  | 1.392  |
| C | 0.263  | 2.958  | 2.329  |
| H | -0.182 | 3.719  | 2.965  |
| C | -0.19  | 1.641  | 2.399  |
| H | -0.982 | 1.375  | 3.095  |
| C | -1.249 | -1.369 | 1.115  |
| C | -1.89  | -0.797 | -0.014 |
| C | -2.977 | -1.472 | -0.598 |
| H | -3.45  | -1.022 | -1.467 |
| C | -3.459 | -2.677 | -0.1   |
| H | -4.3   | -3.17  | -0.579 |
| C | -2.863 | -3.22  | 1.038  |
| H | -3.24  | -4.142 | 1.474  |
| C | -1.79  | -2.568 | 1.628  |
| H | -1.369 | -2.986 | 2.536  |
| C | -0.044 | -0.794 | 1.785  |
| C | 1.565  | -0.757 | -1.227 |
| C | 2.095  | -0.1   | -0.086 |
| C | 3.33   | -0.523 | 0.435  |
| H | 3.731  | 0.01   | 1.293  |
| C | 4.021  | -1.612 | -0.085 |
| H | 4.969  | -1.918 | 0.349  |
| C | 3.453  | -2.326 | -1.14  |
| H | 3.943  | -3.212 | -1.536 |
| C | 2.252  | -1.9   | -1.691 |
| H | 1.824  | -2.477 | -2.503 |
| C | -0.554 | 0.793  | -1.533 |
| C | -1.593 | 0.548  | -0.613 |
| C | -2.506 | 1.577  | -0.333 |
| H | -3.316 | 1.375  | 0.362  |
| C | -2.398 | 2.835  | -0.923 |
| H | -3.117 | 3.612  | -0.68  |
| C | -1.367 | 3.08   | -1.828 |
| H | -1.268 | 4.052  | -2.304 |
| C | -0.464 | 2.063  | -2.128 |
| H | 0.334  | 2.242  | -2.842 |
| C | 0.399  | -0.261 | -2.025 |
| C | 0.748  | -1.537 | 2.579  |
| H | 1.611  | -1.094 | 3.065  |
| H | 0.598  | -2.598 | 2.748  |
| C | 0.22   | -0.637 | -3.307 |
| H | -0.62  | -0.256 | -3.878 |
| H | 0.892  | -1.305 | -3.834 |

**Table S9.** Cartesian coordinate and geometry of conformer **C** of **5**.

|   |        |        |        |
|---|--------|--------|--------|
| C | 1.298  | 1.6    | -0.282 |
| C | 2.34   | 0.644  | -0.376 |
| C | 3.438  | 0.898  | -1.213 |
| H | 4.222  | 0.148  | -1.279 |
| C | 3.526  | 2.058  | -1.979 |
| H | 4.385  | 2.225  | -2.623 |
| C | 2.489  | 2.985  | -1.918 |
| H | 2.523  | 3.893  | -2.514 |
| C | 1.397  | 2.748  | -1.086 |
| H | 0.604  | 3.485  | -1.064 |
| C | -1.244 | 1.718  | 0.117  |
| C | -2.209 | 0.729  | -0.194 |
| C | -3.397 | 1.155  | -0.829 |
| H | -4.119 | 0.399  | -1.126 |
| C | -3.682 | 2.492  | -1.079 |
| H | -4.61  | 2.766  | -1.574 |
| C | -2.784 | 3.468  | -0.655 |
| H | -3.005 | 4.524  | -0.781 |
| C | -1.586 | 3.07   | -0.07  |
| H | -0.895 | 3.829  | 0.284  |
| C | 0.128  | 1.421  | 0.652  |
| C | 1.299  | -1.6   | 0.282  |
| C | 2.34   | -0.644 | 0.376  |
| C | 3.438  | -0.898 | 1.213  |
| H | 4.222  | -0.147 | 1.279  |
| C | 3.526  | -2.058 | 1.979  |
| H | 4.386  | -2.224 | 2.623  |
| C | 2.49   | -2.984 | 1.918  |
| H | 2.524  | -3.893 | 2.514  |
| C | 1.397  | -2.748 | 1.086  |
| H | 0.605  | -3.485 | 1.064  |
| C | -1.243 | -1.718 | -0.117 |
| C | -2.209 | -0.729 | 0.194  |
| C | -3.397 | -1.155 | 0.829  |
| H | -4.118 | -0.4   | 1.126  |
| C | -3.682 | -2.493 | 1.079  |
| H | -4.61  | -2.767 | 1.574  |
| C | -2.783 | -3.468 | 0.655  |
| H | -3.004 | -4.524 | 0.781  |
| C | -1.585 | -3.07  | 0.07   |
| H | -0.894 | -3.829 | -0.284 |
| C | 0.128  | -1.421 | -0.652 |
| C | 0.29   | 1.083  | 1.938  |
| H | 1.269  | 0.898  | 2.368  |
| H | -0.565 | 0.976  | 2.6    |
| C | 0.29   | -1.083 | -1.938 |
| H | -0.565 | -0.976 | -2.6   |
| H | 1.269  | -0.898 | -2.368 |

**Table S10.** Cartesian coordinate and geometry of TS **Figure8\_CO**.

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 1.315854622  | 0.7410455    | 1.091726103  |
| C | 2.673990064  | 0.748704531  | 1.501293151  |
| C | 3.197515418  | 1.873564293  | 2.160539371  |
| H | 4.240668607  | 1.860180374  | 2.46158928   |
| C | 2.403751001  | 2.989158283  | 2.434947206  |
| H | 2.826363989  | 3.848279751  | 2.946889555  |
| C | 1.062089875  | 2.97938165   | 2.048271916  |
| H | 0.423145414  | 3.831853121  | 2.258518657  |
| C | 0.532579561  | 1.864346303  | 1.391604454  |
| H | -0.511161752 | 1.868182278  | 1.115764635  |
| C | 1.401754768  | -1.210213967 | -0.690703281 |
| C | 2.156985433  | -0.551285748 | -1.696227047 |
| C | 2.698749702  | -1.309821893 | -2.752783516 |
| H | 3.274612222  | -0.792948439 | -3.514589649 |
| C | 2.52070676   | -2.691531011 | -2.835858868 |
| H | 2.949670226  | -3.247749719 | -3.663829287 |
| C | 1.795967436  | -3.344513851 | -1.834576342 |
| H | 1.65997285   | -4.421447445 | -1.867763521 |
| C | 1.25658015   | -2.607618723 | -0.781629318 |
| H | 0.71838389   | -3.09981951  | 0.017881157  |
| C | 0.731762375  | -0.561313769 | 0.527657808  |
| O | 0.280998031  | -1.365992135 | 1.440264806  |
| C | 4.555543324  | -0.432026929 | 0.252741333  |
| C | 3.578301667  | -0.423766717 | 1.278027469  |
| C | 3.467029124  | -1.529662284 | 2.138301676  |
| H | 2.692463454  | -1.517560819 | 2.89634688   |
| C | 4.308474959  | -2.636312548 | 2.008656361  |
| H | 4.203083517  | -3.480436772 | 2.683002392  |
| C | 5.270438034  | -2.654881649 | 0.993944325  |
| H | 5.918009369  | -3.516979143 | 0.866103076  |
| C | 5.381178884  | -1.568675123 | 0.125443923  |
| H | 6.095604015  | -1.605308339 | -0.689793711 |
| C | 3.628761111  | 1.505297617  | -1.269705432 |
| C | 2.423024996  | 0.927046238  | -1.747386131 |
| C | 1.491308311  | 1.747445283  | -2.40853809  |
| H | 0.600347542  | 1.285947365  | -2.820862073 |
| C | 1.691730706  | 3.121617333  | -2.558275136 |
| H | 0.951317151  | 3.728225097  | -3.070876608 |
| C | 2.850421254  | 3.703447093  | -2.038107469 |
| H | 3.015909952  | 4.77313796   | -2.121167135 |
| C | 3.79925979   | 2.899555282  | -1.406350356 |
| H | 4.690307265  | 3.354116165  | -0.987798766 |
| C | 4.764851888  | 0.714715051  | -0.687686752 |
| C | 6.028357186  | 1.049924826  | -1.038272886 |
| H | 6.232042693  | 1.821423185  | -1.772635548 |
| H | 6.889424176  | 0.557118331  | -0.600409069 |
| C | -0.997407193 | 0.14397972   | -0.693670153 |
| H | -0.86647084  | -0.516343476 | -1.551777042 |
| H | -0.760699731 | 1.183737994  | -0.917918676 |
| P | -2.714017988 | -0.03267901  | -0.103638019 |
| C | -3.156836806 | -1.857989846 | -0.081987071 |
| C | -2.952843857 | 0.665763345  | 1.627697593  |
| C | -4.01595867  | 0.811450848  | -1.187734781 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -2.28054233  | -2.740346131 | 0.571328622  |
| C | -4.314862234 | -2.344902187 | -0.707680799 |
| C | -2.155971977 | 0.149993496  | 2.665686366  |
| C | -3.880667176 | 1.685002766  | 1.892937561  |
| C | -3.581956682 | 1.453582798  | -2.354929227 |
| C | -5.386848772 | 0.798521153  | -0.871562777 |
| C | -2.587534345 | -4.105929823 | 0.613009376  |
| H | -1.353970115 | -2.373625702 | 1.0145615    |
| C | -4.607299799 | -3.713116518 | -0.662545626 |
| H | -4.981799172 | -1.678122344 | -1.239159423 |
| C | -2.324984629 | 0.635100417  | 3.967359143  |
| H | -1.367343278 | -0.56952889  | 2.45474327   |
| C | -4.035964075 | 2.165768811  | 3.198936228  |
| H | -4.473734215 | 2.116170239  | 1.096472127  |
| C | -4.505075321 | 2.081271051  | -3.200605037 |
| H | -2.524401592 | 1.456828337  | -2.600193883 |
| C | -6.307375259 | 1.425198969  | -1.719151624 |
| H | -5.739173259 | 0.305374409  | 0.028642912  |
| C | -3.748468642 | -4.59424488  | 0.003102969  |
| H | -1.909386223 | -4.78614863  | 1.118256978  |
| H | -5.501923836 | -4.085691766 | -1.151339885 |
| C | -3.267033677 | 1.6340008    | 4.2391001    |
| H | -1.703575941 | 0.239598127  | 4.763919519  |
| H | -4.753020241 | 2.956219309  | 3.396781019  |
| C | -5.86731743  | 2.067824933  | -2.883692404 |
| H | -4.159425813 | 2.576281461  | -4.102255615 |
| H | -7.363694746 | 1.411546454  | -1.470333761 |
| H | -3.978151484 | -5.654653857 | 0.037578802  |
| H | -3.389891351 | 2.006482604  | 5.251257893  |
| H | -6.583405458 | 2.553439803  | -3.5386826   |

**Table S11.** Cartesian coordinate and geometry of TS **Figure8\_CC**.

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 3.951930058  | 1.586705677  | -1.033330804 |
| C | 2.649007986  | 1.07599907   | -1.2492622   |
| C | 1.620094085  | 1.981330518  | -1.565449917 |
| H | 0.627437398  | 1.588138624  | -1.760576353 |
| C | 1.858859603  | 3.353494459  | -1.666853243 |
| H | 1.043867213  | 4.02863247   | -1.910406165 |
| C | 3.153815686  | 3.850564051  | -1.476063174 |
| H | 3.352946472  | 4.913749944  | -1.565015602 |
| C | 4.188574275  | 2.967914382  | -1.175023353 |
| H | 5.201845567  | 3.327528959  | -1.036481383 |
| C | 5.038571853  | -0.490775809 | 0.132357684  |
| C | 4.146171754  | -0.620576004 | 1.222695323  |
| C | 4.113699205  | -1.842234416 | 1.919762301  |
| H | 3.431072987  | -1.941566964 | 2.757242891  |
| C | 4.951406805  | -2.902419538 | 1.568413298  |
| H | 4.906558685  | -3.833950746 | 2.124804714  |
| C | 5.863369707  | -2.753789489 | 0.514959674  |
| H | 6.529809269  | -3.56745097  | 0.24676238   |
| C | 5.907516644  | -1.552520917 | -0.188318078 |
| H | 6.605359466  | -1.41204679  | -1.006226746 |
| C | 5.14418793   | 0.738486515  | -0.710071594 |
| O | 6.263365036  | 1.069467723  | -1.173272909 |
| C | 1.584776271  | -1.056126582 | -0.282401015 |
| C | 2.341931203  | -0.391578653 | -1.293285318 |
| C | 2.759026481  | -1.094372683 | -2.438694495 |
| H | 3.332755447  | -0.561590373 | -3.19179394  |
| C | 2.43625993   | -2.438068282 | -2.637375387 |
| H | 2.772928958  | -2.957139047 | -3.529206612 |
| C | 1.685138693  | -3.103332376 | -1.658896425 |
| H | 1.442988877  | -4.156166912 | -1.775587207 |
| C | 1.281796225  | -2.425034385 | -0.510327233 |
| H | 0.756107042  | -2.97340338  | 0.2649694    |
| C | 1.92136655   | 0.587446429  | 1.6913734    |
| C | 3.347522466  | 0.527358289  | 1.761886394  |
| C | 4.061640688  | 1.509495462  | 2.47032713   |
| H | 5.144847291  | 1.433878666  | 2.506779941  |
| C | 3.417250274  | 2.543833837  | 3.152029776  |
| H | 3.992621878  | 3.285577008  | 3.696478703  |
| C | 2.019115648  | 2.594027052  | 3.126494208  |
| H | 1.49045162   | 3.386761437  | 3.649054204  |
| C | 1.297767656  | 1.643691     | 2.407324327  |
| H | 0.219374025  | 1.737009467  | 2.363490855  |
| C | 1.108718009  | -0.398033957 | 0.958355142  |
| C | -0.202018383 | -0.685576676 | 1.405069408  |
| H | -0.432591446 | -0.486548198 | 2.448777107  |
| H | -0.680539461 | -1.585955618 | 1.036160675  |
| P | -3.269562468 | 0.126766511  | 0.114731505  |
| C | -1.598963329 | 0.63195406   | 0.673440504  |
| H | -1.06847743  | 1.088581499  | -0.164439936 |
| H | -1.699822215 | 1.346385537  | 1.495089569  |
| C | -3.942139567 | -1.112976258 | 1.34753441   |
| C | -3.510829238 | -1.068890004 | 2.682290544  |
| C | -4.875099887 | -2.080995574 | 0.945489127  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -4.018305699 | -1.984997325 | 3.610813403  |
| H | -2.777683651 | -0.334723917 | 2.995316259  |
| C | -5.376016082 | -2.997654162 | 1.876501665  |
| H | -5.199864918 | -2.131970032 | -0.088327491 |
| C | -4.950204952 | -2.949332616 | 3.209298002  |
| H | -3.681112452 | -1.947824542 | 4.641347419  |
| H | -6.091615456 | -3.749267078 | 1.559702536  |
| H | -5.338031463 | -3.662373047 | 3.929403187  |
| C | -4.653325119 | 1.409813169  | -0.069744982 |
| C | -5.695218757 | 1.502491379  | 0.866231745  |
| C | -4.540849988 | 2.37709923   | -1.084982984 |
| C | -6.626020292 | 2.545388045  | 0.77617605   |
| H | -5.786678941 | 0.765914434  | 1.656829368  |
| C | -5.476337128 | 3.410824581  | -1.174660712 |
| H | -3.728556687 | 2.320943178  | -1.803649592 |
| C | -6.520682281 | 3.497951646  | -0.243030213 |
| H | -7.432214874 | 2.609101425  | 1.500126565  |
| H | -5.389783746 | 4.148162511  | -1.966275932 |
| H | -7.242849908 | 4.304965999  | -0.310631114 |
| C | -3.123968543 | -0.68534081  | -1.55574176  |
| C | -1.893443322 | -1.230926289 | -1.953588008 |
| C | -4.240546305 | -0.776365538 | -2.405253133 |
| C | -1.780093167 | -1.858769887 | -3.199351354 |
| H | -1.02551437  | -1.171114055 | -1.309110107 |
| C | -4.120194482 | -1.409677797 | -3.646883296 |
| H | -5.189882643 | -0.341267524 | -2.111862454 |
| C | -2.891199054 | -1.950419881 | -4.04540462  |
| H | -0.821400844 | -2.270566264 | -3.495281223 |
| H | -4.983042022 | -1.474634415 | -4.301871396 |
| H | -2.800805754 | -2.438023765 | -5.010657326 |

**Table S12.** Cartesian coordinate and geometry of TS **Bathtub\_CO**.

|   |              |              |              |
|---|--------------|--------------|--------------|
| O | 1.306562073  | -0.576297507 | -2.048091715 |
| C | 2.401712697  | -1.648252196 | 0.403113428  |
| C | 0.893547501  | -0.033427485 | -0.929993634 |
| C | 0.910515635  | 1.516661671  | -0.932404133 |
| C | 1.339198976  | -0.715281943 | 0.378916359  |
| C | 0.634895003  | -0.46846648  | 1.569333379  |
| H | -0.140384812 | 0.288282796  | 1.559680072  |
| C | 3.928448697  | 0.983608849  | 0.319185012  |
| C | 1.798673527  | 2.329338115  | -0.17696972  |
| C | 3.336405421  | -1.944597829 | -0.73104634  |
| C | 4.054309601  | 0.497501029  | -1.093455837 |
| C | 2.876472618  | 1.835838353  | 0.744075158  |
| C | 0.081244965  | 2.158314379  | -1.873868575 |
| H | -0.524868949 | 1.544072586  | -2.528158758 |
| C | 2.887316337  | 2.308065107  | 2.071520823  |
| H | 2.077117115  | 2.95231071   | 2.399670028  |
| C | 3.490987527  | -3.294068515 | -1.099912312 |
| H | 2.853129478  | -4.034219485 | -0.626599427 |
| C | 2.654920149  | -2.347397898 | 1.605982752  |
| H | 3.473997189  | -3.059739091 | 1.622649373  |
| C | 4.155102502  | -0.968586284 | -1.364453786 |
| C | 3.890960638  | 1.946717773  | 2.97212007   |
| H | 3.867048674  | 2.321866112  | 3.990845331  |
| C | 4.923300206  | 0.615740506  | 1.243641206  |
| H | 5.717552027  | -0.046313739 | 0.912564923  |
| C | 1.714119307  | 3.735823173  | -0.30913893  |
| H | 2.392585473  | 4.346254275  | 0.279363166  |
| C | 0.910805339  | -1.149057594 | 2.756370264  |
| H | 0.348950289  | -0.92297545  | 3.658347373  |
| C | 1.920101792  | -2.118494273 | 2.768387037  |
| H | 2.150999348  | -2.667166915 | 3.676586733  |
| C | 4.130184437  | 1.385218839  | -2.103634651 |
| C | 0.026693393  | 3.545458317  | -2.01248672  |
| H | -0.631513715 | 3.992915834  | -2.751703328 |
| C | 4.916106098  | 1.091361859  | 2.555771592  |
| H | 5.702800008  | 0.79893105   | 3.244561392  |
| C | 5.096525999  | -1.400000259 | -2.319377727 |
| H | 5.745643307  | -0.658340106 | -2.773000429 |
| C | 4.41240738   | -3.697876471 | -2.068537082 |
| H | 4.495017691  | -4.747222629 | -2.335514117 |
| C | 0.834526628  | 4.348849953  | -1.199485183 |
| H | 0.806720413  | 5.431111436  | -1.28354154  |
| C | 5.227646045  | -2.742620107 | -2.679332953 |
| H | 5.964148994  | -3.036689257 | -3.421000749 |
| H | 4.098553899  | 2.454216593  | -1.923522213 |
| H | 4.176729996  | 1.06416936   | -3.138085832 |
| C | -0.889463309 | -0.59590348  | -1.056031509 |
| H | -1.083377725 | -0.348309168 | -2.101334878 |
| H | -0.716013432 | -1.671532095 | -0.964790778 |
| P | -2.588266375 | -0.335663537 | -0.19426311  |
| C | -3.218707065 | -1.929501729 | 0.561999928  |
| C | -2.62696561  | 0.941062758  | 1.175688199  |
| C | -3.885743822 | 0.231697599  | -1.426269528 |

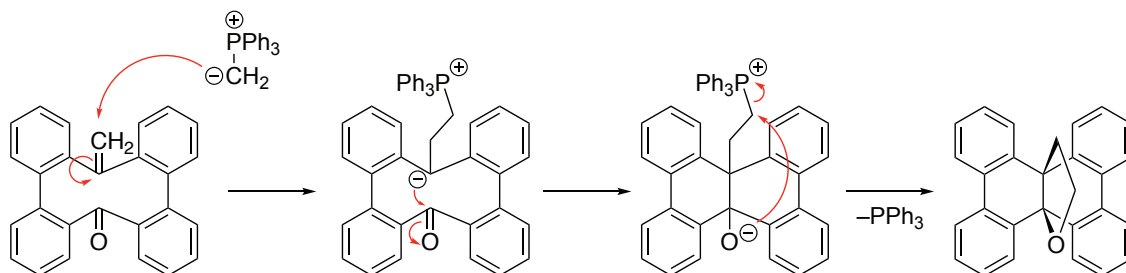
|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -2.320016841 | -2.732143468 | 1.286700866  |
| C | -4.548566869 | -2.343379928 | 0.386146194  |
| C | -3.203241685 | 0.638642278  | 2.418934163  |
| C | -2.094753295 | 2.219853477  | 0.939677637  |
| C | -3.89341475  | -0.353427349 | -2.703758733 |
| C | -4.838319178 | 1.208146419  | -1.097858429 |
| C | -2.759211488 | -3.94228765  | 1.834045572  |
| H | -1.290203335 | -2.419430919 | 1.427431794  |
| C | -4.977443966 | -3.55790624  | 0.934542213  |
| H | -5.243897427 | -1.729995796 | -0.176060277 |
| C | -3.242378991 | 1.612233699  | 3.424556458  |
| H | -3.613126053 | -0.346891758 | 2.607276802  |
| C | -2.138005266 | 3.186780202  | 1.949804936  |
| H | -1.632193868 | 2.458505622  | -0.010629564 |
| C | -4.850954871 | 0.037931641  | -3.645139624 |
| H | -3.154764055 | -1.104246819 | -2.965605899 |
| C | -5.792944691 | 1.597219948  | -2.045471281 |
| H | -4.833068495 | 1.668740168  | -0.11654894  |
| C | -4.085105234 | -4.357444561 | 1.657991289  |
| H | -2.062831978 | -4.559168068 | 2.392172915  |
| H | -6.005183835 | -3.876777224 | 0.794142044  |
| C | -2.70996718  | 2.885198974  | 3.19186932   |
| H | -3.684872847 | 1.372524655  | 4.38592512   |
| H | -1.715180361 | 4.168066331  | 1.763260079  |
| C | -5.800222312 | 1.013918625  | -3.317520424 |
| H | -4.850371892 | -0.414071989 | -4.631348286 |
| H | -6.524941799 | 2.35621568   | -1.78939829  |
| H | -4.419644462 | -5.299746855 | 2.079555356  |
| H | -2.737289241 | 3.636571255  | 3.974430558  |
| H | -6.538758412 | 1.320291019  | -4.051116851 |

**Table S13.** Cartesian coordinate and geometry of TS **Bathtub\_CC**.

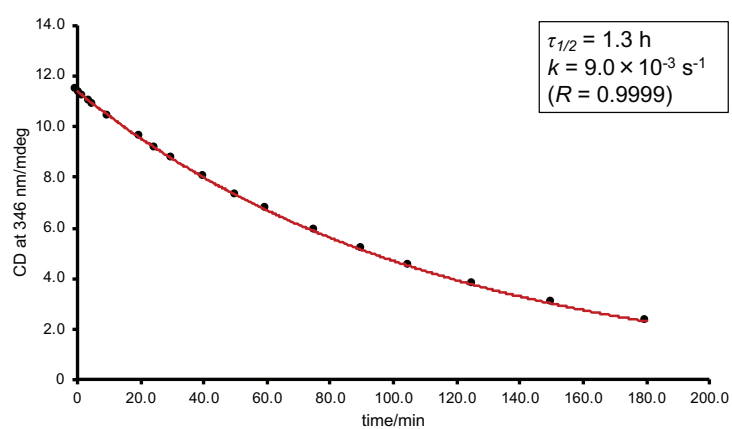
|   |              |              |              |
|---|--------------|--------------|--------------|
| O | -3.49209997  | 0.549498344  | 2.512709421  |
| C | -4.446431024 | 1.39994217   | -0.300054682 |
| C | -3.580800431 | -0.191666223 | 1.509560594  |
| C | -2.914530486 | -1.53788379  | 1.51277166   |
| C | -4.516692214 | 0.165005549  | 0.389508823  |
| C | -5.565490836 | -0.728942537 | 0.121174184  |
| H | -5.600904139 | -1.673432804 | 0.655735624  |
| C | -2.021865826 | -0.196425053 | -1.232575948 |
| C | -2.387463123 | -2.172398787 | 0.355802677  |
| C | -3.366579897 | 2.40355345   | -0.072671653 |
| C | -1.475421646 | 0.687407869  | -0.163611914 |
| C | -2.400808477 | -1.551642807 | -1.002575377 |
| C | -2.813361298 | -2.175081428 | 2.761537095  |
| H | -3.200026642 | -1.650913195 | 3.628634753  |
| C | -2.821910606 | -2.343607841 | -2.088469758 |
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| H | -2.189732706 | -3.922232687 | 3.861454328  |
| C | -2.560621478 | -0.492957548 | -3.611794856 |
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| C | -1.075546108 | 3.120382321  | 0.290751236  |
| H | -0.016209051 | 2.896982194  | 0.34078267   |
| C | -2.848216528 | 4.759233641  | 0.383742955  |
| H | -3.190859791 | 5.778184613  | 0.532711784  |
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| H | -1.302015166 | -5.074734136 | 1.830728629  |
| C | -1.491655768 | 4.436763978  | 0.483436006  |
| H | -0.758143511 | 5.208893558  | 0.699127764  |
| H | -0.160061509 | -0.802088508 | 0.623966923  |
| H | -0.032496048 | 0.818741128  | 1.418067585  |
| P | 3.089745143  | 0.174199565  | -0.226168437 |
| C | 1.359844959  | 0.607621721  | -0.637504855 |
| H | 1.065815306  | 0.076203715  | -1.546236949 |
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| C | 5.362040832  | 1.914559228  | -0.652829475 |
| C | 4.718344338  | 0.529543371  | -2.541379566 |

|   |             |              |              |
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| C | 6.340057784 | 2.530380849  | -1.444539654 |
| H | 5.237065673 | 2.217841399  | 0.380785014  |
| C | 5.700472637 | 1.140952587  | -3.324809492 |
| H | 4.083568068 | -0.237967297 | -2.974637699 |
| C | 6.513265858 | 2.144033395  | -2.777898634 |
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| H | 7.27132969  | 2.622589979  | -3.38933333  |
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| C | 4.423591098 | 0.040893804  | 2.293063328  |
| C | 2.659085662 | 1.702112795  | 2.134420865  |
| C | 4.664593554 | 0.426256605  | 3.616304954  |
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| C | 2.906740072 | 2.087440409  | 3.457154095  |
| H | 1.870466088 | 2.187914773  | 1.57256893   |
| C | 3.908038649 | 1.450236063  | 4.198867586  |
| H | 5.435938578 | -0.076259521 | 4.190832592  |
| H | 2.311747924 | 2.87564352   | 3.906040061  |
| H | 4.093334215 | 1.745090437  | 5.226552612  |
| C | 3.295120721 | -1.673812637 | -0.373696939 |
| C | 2.167797809 | -2.506552638 | -0.290366631 |
| C | 4.571231741 | -2.240800675 | -0.536150506 |
| C | 2.318678348 | -3.895097982 | -0.371700848 |
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| C | 4.714379412 | -3.630248237 | -0.614177118 |
| H | 5.445522882 | -1.604509996 | -0.619711936 |
| C | 3.589281217 | -4.459394687 | -0.531333987 |
| H | 1.44147058  | -4.529902847 | -0.306599368 |
| H | 5.701733042 | -4.061704437 | -0.743145897 |
| H | 3.702679386 | -5.536889076 | -0.592381884 |

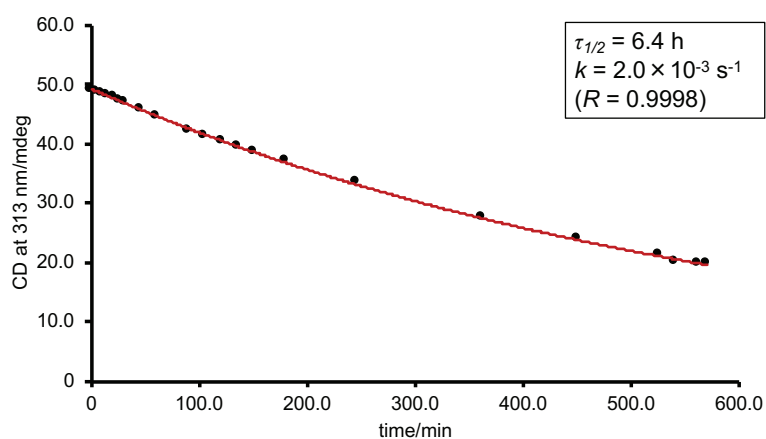
## 7. Others



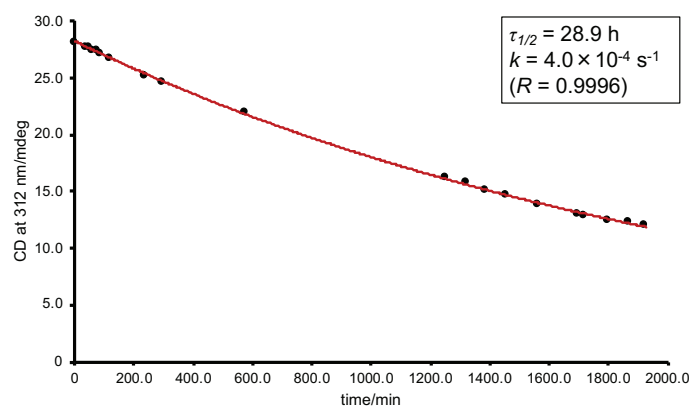
**Figure S21.** Proposed mechanism for the generation of **4** from **3**.



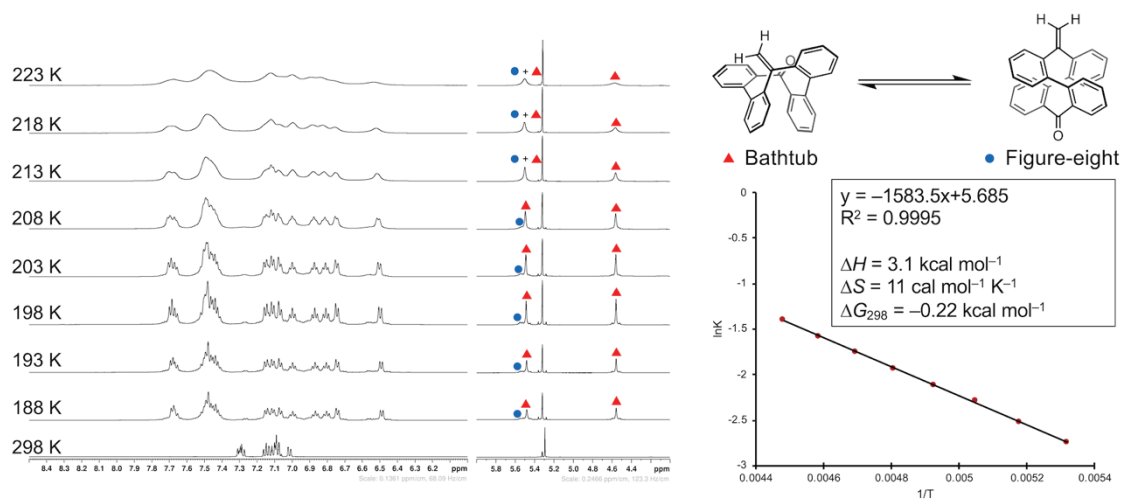
**Figure S22.** Plots of absolute values of CD intensities of **1** at 346 nm versus time in *o*-dichlorobenzene at 170 °C.



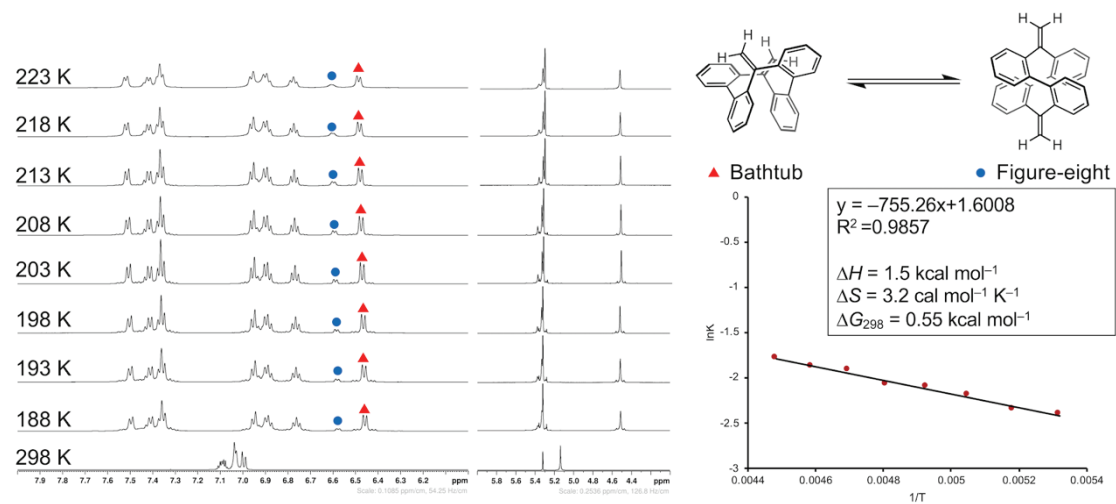
**Figure S23.** Plots of absolute values of CD intensities of **3** at 313 nm versus time in *o*-dichlorobenzene at 170 °C.



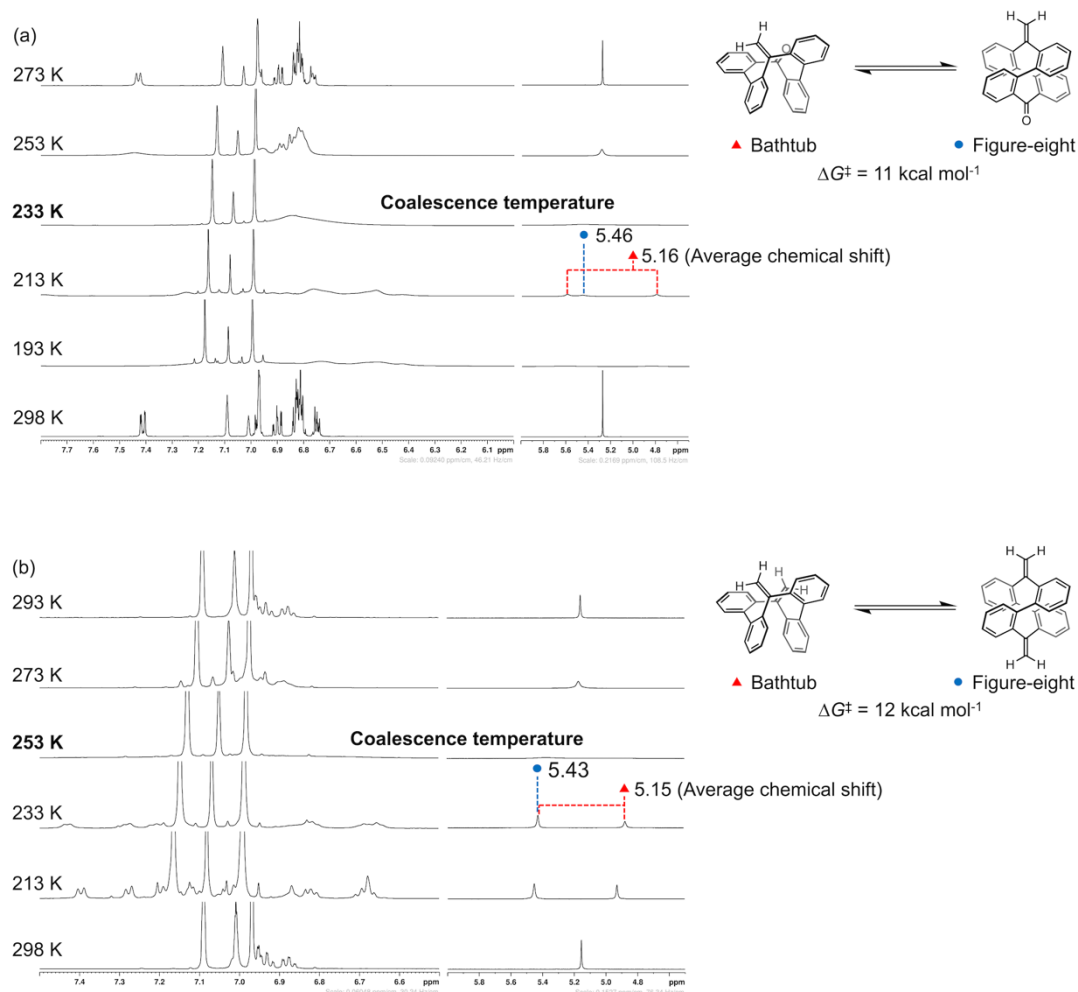
**Figure S24.** Plots of absolute values of CD intensities of **5** at 312 nm versus time in *o*-dichlorobenzene at 170 °C.



**Figure S25.** (a) VT  $^1\text{H}$  NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$ . (b) van't Hoff plot.



**Figure S26.** (a) VT  $^1\text{H}$  NMR spectra of **5** in  $\text{CD}_2\text{Cl}_2$ . (b) van't Hoff plot.



**Figure S27.** VT  $^1\text{H}$  NMR spectra of (a) **3** and (b) **5** in toluene- $d_8$ . Activation barriers were estimated according to the literature.<sup>6</sup>

## 8. References

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1. (a) Suszko, S.; Schillak, R. *Roczniki Chem.* **1934**, *14*, 1216. (b) Yoshina, R.; Hirano, J.; Nishimoto, E.; Sakamoto, Y.; Tajima, K.; Minabe, S.-s.; Uyanik, M.; Ishihara, K.; Ikai, T.; Yashima, E.; Omine, T.; Ishiwari, F.; Saeki, A.; Kim, J.; Oh, J.; Kim, D.; Liu, G.; Yasuda, T.; Shinokubo, H.; Fukui, N. *J. Am. Chem. Soc.* **2024**, *146*, 29383.
2. Hussain, M. I.; Feng, Y.; Hu, L.; Deng, Q.; Zhang, X.; Xiong, Y. *J. Org. Chem.* **2018**, *83*, 7852.
3. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
4. (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
5. a) Maeda, S.; Harabuchi, Y.; Sumiya, Y.; Takagi, M.; Suzuki, K.; Hatanaka, M.; Osada, Y.; Taketsugu, T.; Morokuma, K.; Ohno, K. GRRM17, see [http://iqce.jp/GRRM/index\\_e.shtml](http://iqce.jp/GRRM/index_e.shtml) (accessed date: 21th May, 2025); b) Maeda, S.; Ohno, K.; Morokuma, K. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683-3701.
6. Gasparro, F. P.; Kolodny, N. H. *J. Chem. Educ.* **1977**, *54*, 258.