

The Electronic Supplementary Information for

## **Laser Photolysis Studies of $\omega$ -Bond Dissociation in Aromatic Carbonyls Having C-C Triple Bond Stimulated by Triplet Sensitization**

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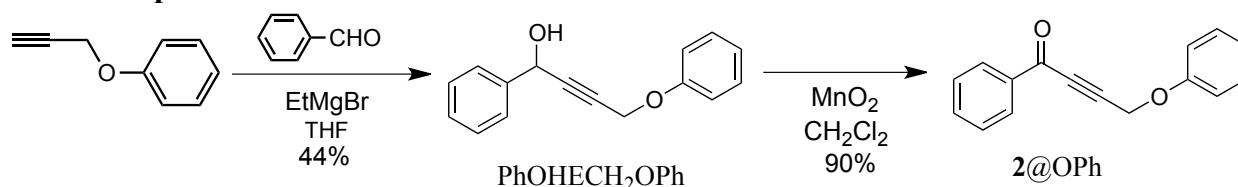
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## 1. Preparation and NMR data for compounds 2-4@X.

### 1-1. Synthesis of 2@X (X = OPh and SPh).

#### 1-1-1. Preparation of 2@OPh



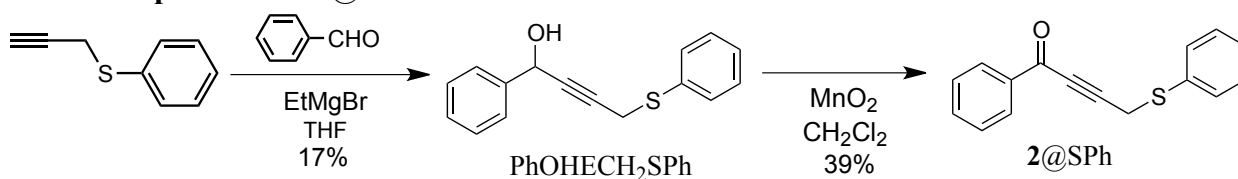
#### Step 1. Synthesis of PhOHECH<sub>2</sub>OPh

To a THF solution (1 M, 2.3 ml) of ethylmagnesium bromide (2.3 mmol), phenylpropargyl ether (0.3 ml, 2 mmol) in THF (13 ml) was dropwise added under N<sub>2</sub> atmosphere at room temperature, and the solution was stirred for 30 min at 40 °C. After cooling to room temperature, benzaldehyde (0.23 ml, 2 mmol) in THF (12 ml) was dropwise added at room temperature, and the solution was stirred under N<sub>2</sub> atmosphere at room temperature for 3 h. The crude product was extracted with benzene, washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>, which was purified by chromatography on silica gel using a mixture of hexane/chloroform (5:1 v/v) as the eluent to provide 210 mg PhOHECH<sub>2</sub>OPh (44 %). Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.28-7.38 (m, 7H), 6.96-7.02 (m, 3H), 5.48 (s, 1H) 4.77 (d, 2H, *J* = 1.8 Hz), 1.44 (s, 1H).

#### Step 2. Synthesis of 2@OPh

PhOHCH<sub>2</sub>OPh (210 mg, 0.88 mmol) in dichloromethane (10 ml) was stirred in the presence of MnO<sub>2</sub> (539 mg, 6.2 mmol) for 2 h at room temperature. The solution was filtrated and the solvent was evaporated. The residue was chromatographed on silica gel using a mixture of hexane/ethyl acetate (5:1 v/v) as the eluent to provide 187 mg BECH<sub>2</sub>OPh (yield 90 %). Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.01 (d, 2H, *J* = 8.4 Hz), 7.56-7.60 (m, 1H), 7.40-7.44 (m, 2H), 7.32-7.37 (m, 2H), 7.03-7.07 (m, 3H), 4.98 (s, 2H).

#### 1-1-2. Preparation of 2@SPh



#### Step 1. Synthesis of PhOHECH<sub>2</sub>SPh

To a THF solution (1 M, 2.2 ml) of ethylmagnesium bromide (2.2 mmol), phenylpropargyl sulfide (0.29 ml, 2 mmol) in THF (10 ml) was dropwise added under N<sub>2</sub> atmosphere at room temperature, and the solution was stirred for 30 h at room temperature. After cooling to room temperature, benzaldehyde (0.23 ml, 2 mmol) in THF (10 ml) was dropwise added at 0 °C, and the solution was stirred under N<sub>2</sub> atmosphere at room temperature for 5 h. The crude product was extracted with benzene, washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>, which was purified by chromatography on silica gel using a mixture of hexane/chloroform (5:1 v/v) as the eluent

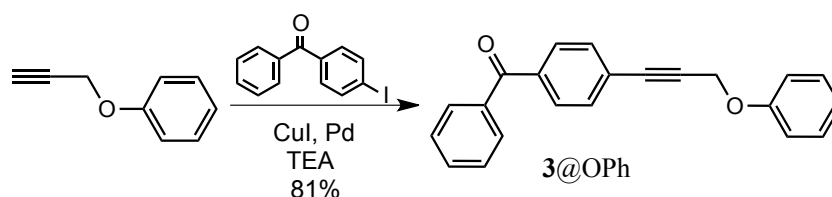
to provide 84 mg PhOHECH<sub>2</sub>SPh. Yield 17 %. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.24-7.38 (m, 10H), 5.41 (s, 1H) 3.68 (d, 2H, *J* = 1.8 Hz), 2.03 (s, 1H).

## Step 2. Synthesis of 2@SPh

PhOHCH<sub>2</sub>SPh (84 mg, 0.3 mmol) in dichloromethane (3 ml) was stirred in the presence of MnO<sub>2</sub> (262 mg, 2.1 mmol) for 2 h at room temperature. The solution was filtrated and the solvent was evaporated. The residue was chromatographed on silica gel using a mixture of hexane/ ethyl acetate (5:1 v/v) as the eluent to provide 30 mg 2@SPh. yield 39 %. Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.93 (dd, 2H, *J* = 9.7 Hz), 7.51-7.58 (m, 3H), 7.28-7.41 (m, 5H), 3.96 (s, 2H).

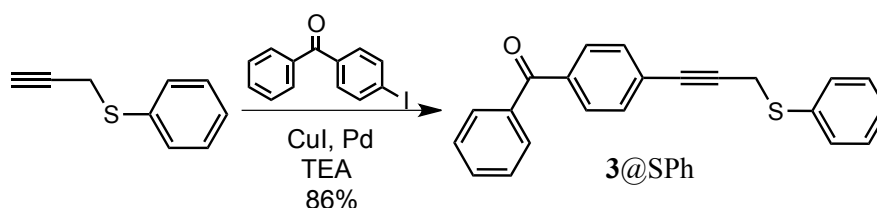
## 1-2. Synthesis of 3@X (X = OPh and SPh)

### 1-2-1. Preparation of 3@OPh



Triethylanime (TEA, 14 ml) solution of phenylpropargyl ether (0.12 ml, 0.97 mmol), CuI (20 mg, 0.097 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (35 mg, 0.049 mmol) and 4-iodobenzophenone 300 mg (0.97 mmol) was stirred under N<sub>2</sub> atmosphere for 3 h at room temperature. Benzene (100 ml) was added, and filtrated. The solution was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, saturated aqueous NaHCO<sub>3</sub> and brine, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (5:1, v/v) as the developing solvent to provide 244 mg 3@OPh. Yield 81 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.74-7.78 (m, 4H), 7.46-7.61 (m, 5H), 7.33 (t, 2H, *J* = 8.7 Hz), 6.99-7.06 (m, 3H), 4.94 (s, 2H).

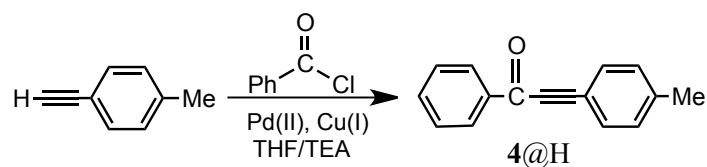
### 1-2-2. Preparation of 3@SPh



Triethylanime (TEA, 11 ml) solution of phenylpropargyl sulfide (0.13 ml, 0.97 mmol), CuI (20 mg, 0.097 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (35 mg, 0.049 mmol) and 4-iodobenzophenone 300 mg (0.97 mmol) was stirred under N<sub>2</sub> atmosphere for 3 h at room temperature. Benzene (100 ml) was added, and filtrated. The solution was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, saturated aqueous NaHCO<sub>3</sub> and brine, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (9:1, v/v) as the developing solvent to provide 273 mg 3@SPh. Yield 86 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.70-7.78 (m, 4H), 7.42-7.60 (m, 7H), 7.24-7.36 (m, 3H), 3.85 (s, 2H).

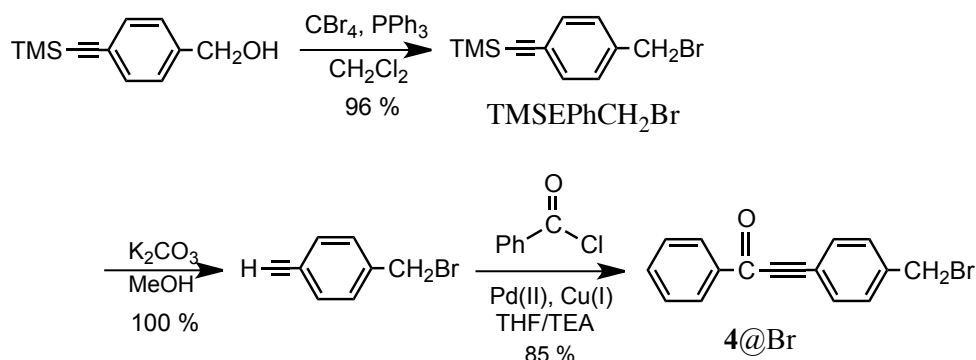
### 1-3. Synthesis of 4@X (X = H, Br, SPh, OPh)

#### 1-3-1. Preparation of 4@H



To a THF (20 ml) solution of *trans*-dichlorobis(triphenylphosphine)palladium(II) ( $\text{PdCl}_2(\text{PPh}_3)_2$ ) (79.4 mg, 0.112 mmol) and copper(I)iodide (CuI, 44.3 mg, 0.224 mmol) stirred for 10 min under  $\text{N}_2$  atmosphere, trimethylamine (TEA, 0.8 ml, 5.68 mmol), benzoyl chloride (0.96 ml, 6.8 mmol) and *p*-ethynyltoluene (0.86 ml, 6.8 mmol) were added, and the solution was refluxed for 3 h. The crude product was extracted with benzene (50 ml  $\times$  3). The benzene solution was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, and dried with  $\text{Na}_2\text{SO}_4$ . The product was purified by passing through a silica-gel column with a mixture of hexane/ethyl acetate (9:1, v/v) as the eluent. Pale yellow solid. Yield 55% (0.68 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.22 (dd, 2H,  $J = 8.4$  Hz), 7.57-7.64 (m, 3H), 7.49-7.53 (m, 2H), 7.21-7.25 (m, 2H), 2.40 (s, 3H).

#### 1-3-2. Preparation of 4@Br



##### Step 1. Synthesis of *p*-trimethylsilylethynylbenzyl bromide (TMSEPhCH<sub>2</sub>Br)

To  $\text{CH}_2\text{Cl}_2$  solution (20 ml) of trimethylsilylethynylbenzyl alcohol (1.6 g) tetrabromomethane (4.5 g) and 2,6-lutidine (4.4 ml), a  $\text{CH}_2\text{Cl}_2$  solution (5 ml) of triphenylphosphine (3.9 g) was added dropwise at 0 °C. The solution was stirred at room temperature for 16 h. The crude product was extracted with benzene (50 ml  $\times$  3). The benzene solution was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, and dried with  $\text{Na}_2\text{SO}_4$ . The product was purified by passing through a silica-gel column with a mixture of hexane/ethyl acetate (9:1, v/v) as the eluent. Yellow liquid. Yield 96% (1.92 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.45 (d, 2H,  $J = 8.2$  Hz), 7.30 (d, 2H,  $J = 8.2$  Hz), 4.45 (s, 2H), 0.24 (s, 9H).

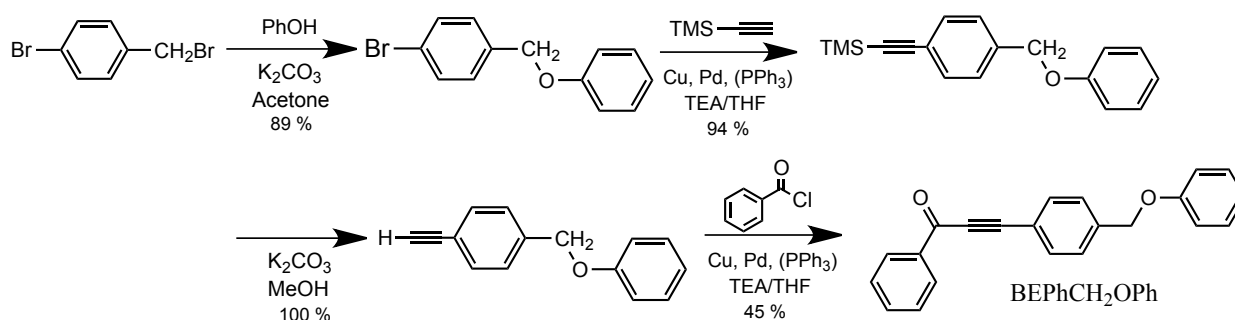
##### Step 2. Synthesis of *p*-ethynylbenzyl bromide (EPhCH<sub>2</sub>Br)

The methanol solution (25 ml) of TMSEPhCH<sub>2</sub>Br (1.0 g) in the presence of  $\text{K}_2\text{CO}_3$  (5.2 g) was stirred at room temperature. The solution was filtrated, and evaporated. The product solved in benzene was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, dried with  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated. The product was used for the next process without further purification.

### Step 3. Synthesis of 4@Br

In THF (5 ml), added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (17 mg, 0.024 mmol) and CuI (9 mg, 0.048 mmol), triethylamine (TEA, 0.17 ml, 1.26 mmol), benzoyl chloride (0.17 ml, 1.5 mmol) and EPhCH<sub>2</sub>Br (0.29 ml, 1.5 mmol) were stirred under N<sub>2</sub> atmosphere for 3 h at room temperature. Benzene (100ml) was added. The filtrated solution was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was chromatographed on a silica gel column using a mixture of hexane and ethyl acetate (9:1, v/v) as the developing solvent to obtain 4@Br (0.38 g). Yield 85 %. Yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.20 (dd, 2H, *J* = 8.36 Hz), 7.60-7.65 (m, 3H), 7.51 (dd, 2H, *J* = 7.7 Hz), 7.42-7.44 (m, 2H).

### 1-3-3. Preparation of 4@OPh



### Step 1. Synthesis of *p*-bromobenzylphenyl ether (BrPhCH<sub>2</sub>OPh)

To acetone 50 ml, *p*-bromobenzylbromide (1.28 g, 5 mmol), phenol (1.0 g, 10 mmol), K<sub>2</sub>CO<sub>3</sub> (3.6 g, 25 mmol) were added, and the solution was stirred for 4 h under N<sub>2</sub> atmosphere at 60 °C. The filtrated solution was evaporated. The residual was dissolved with benzene, and the solution was washed with brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by column chromatography on silica gel with hexane/chloroform (5:1, v/v) as the eluent. White solid. Yield 89 % (1.18 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.50 (d, 2H, *J* = 8.5 Hz), 7.26-7.32 (m, 4H), 6.93-6.98 (m, 3H), 5.01 (s, 2H).

### Step 2. Synthesis of *p*-trimethylsilylethynylbenzylphenyl ether (TMSEPhCH<sub>2</sub>OPh)

In THF (17 ml), added BrPhCH<sub>2</sub>OPh (755 mg, 2.9 mmol), CuI (55 mg, 0.29 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (105 mg, 0.15 mmol), trimethylsilylethyne (0.41 ml, 2.9 mmol) and TEA (17.1 ml) were stirred under N<sub>2</sub> atmosphere for 1 h at room temperature. Benzene (100ml) was added. The filtrated solution was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was chromatographed on a silica gel column using a mixture of hexane and chloroform (3:1, v/v) as the developing solvent to obtain TMSEPhCH<sub>2</sub>OPh (761 mg). Yield 94 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.50 (d, 2H, *J* = 8.5 Hz), 7.26-7.37 (m, 4H), 6.94-6.96 (m, 3H), 5.05 (s, 2H), 0.24 (s, 9H).

### Step 3. Synthesis of *p*-ethynylbenzylphenyl ether (EPhCH<sub>2</sub>OPh)

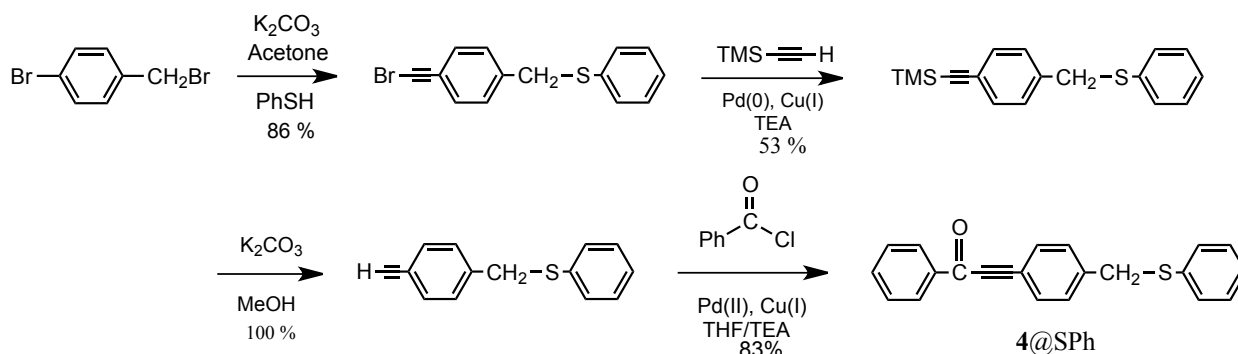
In methanol (31 ml), added TMSEPhCH<sub>2</sub>OPh (761 mg, 2.7 mmol) and K<sub>2</sub>CO<sub>3</sub> (3.7 g) were stirred under N<sub>2</sub> atmosphere for 3.5 h at room temperature. The filtrated solution was evaporated. Benzene solution of the residue was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>,

and the solvent was evaporated. The product was used for the next process without further purification.

#### Step 4. Synthesis of 4@OPh

In THF (15.9 ml), added EPhCH<sub>2</sub>Oph (562 mg, 2.7 mmol), CuI (53 mg, 0.27 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (99 mg, 0.14 mmol), PPh<sub>3</sub> (59 mg, 0.22 mmol), benzoyl chloride (0.37 ml, 3.2 mmol) and TEA (15.4 ml) were refluxed under N<sub>2</sub> atmosphere for 8 h. Benzene (100ml) was added. The filtrated solution was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was chromatographed on a silica gel column using a mixture of hexane and ethyl acetate (5:1, v/v) as the developing solvent to obtain 4@OPh (383 mg). Yield 45 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.22 (dd, 2H, *J* = 8.4 Hz), 8.15 (dd, 2H, *J* = 8.4 Hz), 7.70 (d, 2H, *J* = 8.2 Hz), 7.50-7.54 (m, 5H), 6.95-6.99 (m, 3H).

#### 1-3-4. Preparation of 4@SPh



#### Step 1. Synthesis of *p*-bromobenzylphenyl sulfide (BrPhCH<sub>2</sub>SPh)

To acetone 50 ml, *p*-bromobenzylbromide (1.2 g, 4.4 mmol), thiophenol (0.9 ml, 8.8 mmol), K<sub>2</sub>CO<sub>3</sub> (3.1 g, 22 mmol) were added, and the solution was stirred for 8 h under N<sub>2</sub> atmosphere at 60 °C. The filtrated solution was evaporated. The residue was dissolved with benzene, and the solution was washed with brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by column chromatography on silica gel with hexane/chloroform (3:1, v/v) as the eluent to obtain BrPhCH<sub>2</sub>SPh (1.11 g). Yield 86 %. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.38 (d, 2H, *J* = 8.5 Hz), 7.22-7.29 (m, 5H), 6.90 (d, 2H, *J* = 8.2 Hz), 4.02 (s, 2H).

#### Step 2. Synthesis of *p*-trimethylsilylethynylbenzylphenyl sulfide (TMSEPhCH<sub>2</sub>SPh)

In THF (21 ml), added BrPhCH<sub>2</sub>SPh (1.38 g, 4.9 mmol), CuI (94 mg, 0.49 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (175 mg, 0.25 mmol), triphenylphosphin (103 mg, 0.39 mmol), trimethylsilylethynyl (0.83 ml, 5.9 mmol) and TEA (31 ml) were stirred under N<sub>2</sub> atmosphere for 5 h at 70 °C. Benzene (100 ml) was added. The filtrated solution was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was chromatographed on a silica gel column using a mixture of hexane and chloroform (5:1, v/v) as the developing solvent to obtain TMSEPhCH<sub>2</sub>SPh (774 mg). Yield 53 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.40 (d, 2H, *J* = 8.0 Hz), 7.23-7.31 (m, 4H), 7.18-7.21 (m, 3H), 4.07 (s, 2H), 0.29 (s, 9H).

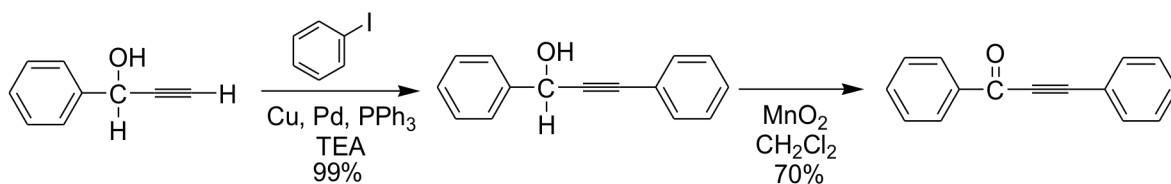
### Step 3. Synthesis of *p*-ethynylbenzylphenyl sulfide (EPhCH<sub>2</sub>SPh)

In methanol (20 ml), added TMSEPhCH<sub>2</sub>SPh (772 mg, 2.6 mmol) and K<sub>2</sub>CO<sub>3</sub> (3.7 g) were stirred under N<sub>2</sub> atmosphere for 3.5 h at room temperature. The filtrated solution was evaporated. Benzene solution of the residue was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The product was used for the next process without further purification.

### Step 4. Synthesis of 4@SPh

In THF (15 ml), added EPhCH<sub>2</sub>SPh (628 mg, 2.8 mmol), CuI (53 mg, 0.27 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (99 mg, 0.14 mmol), PPh<sub>3</sub> (60 mg, 0.22 mmol), benzoyl chloride (0.65 ml, 5.6 mmol) and TEA (20 ml) were refluxed under N<sub>2</sub> atmosphere for 8 h. Benzene (100 ml) was added. The filtrated solution was washed with saturated aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was chromatographed on a silica gel column using a mixture of hexane and ethyl acetate (7:1, v/v) as the developing solvent to obtain 4@SPh (767 mg). Yield 83 %. Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.20 (d, 2H, *J* = 7.8 Hz), 8.15 (d, 2H, *J* = 8.0 Hz), 7.57-7.69 (m, 4H), 7.48-7.54 (m, 3H), 7.27-7.30 (m, 3H), 4.10 (s, 2H).

### 1-4. Synthesis of benzoylphenyl acetylene (BPA)



#### Step 1. Synthesis of PhOHEPh

To triethyl amine (TEA) 25 ml, iodobenzene 0.27 ml (2.4 mmol), 1-phenyl-2-propyn-1-ol 0.3 ml (2.4 mmol), CuI 46 mg (0.24 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> 86 mg (0.12 mmol), PPh<sub>3</sub> 55 mg (0.19 mmol) were added, the solution was stirred at 50 °C for 4 h under N<sub>2</sub> atmosphere. Benzene (100 ml) was added. The solution was filtrated, washed with aqueous NaHCO<sub>3</sub> and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the product was purified on silica gel chromatograph with hexane/ethyl acetate (4:1, v/v) as the eluent to obtain 495 mg PhOHEPh. Yield. 99 %. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.61 (d, 2H, *J* = 7.3 Hz), 7.29-7.48 (m, 7H), 5.68 (s, 1H), 2.59 (s, 1H).

#### Step 2. Synthesis of BPA

To dichloromethane 25 ml, PhOHEPh 495 mg (2.38 mmol) and MnO<sub>2</sub> 1.5 g (17 mmol) were added. The solution was vigorously stirred at room temperature for 1.5 h, and filtrated. After the solvent was evaporated, the product was purified on silica gel chromatograph with hexane/ethyl acetate (5:1, v/v) as the eluent to obtain 341 mg BPA. Yield 70 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.06-8.09 (m, 2H), 7.45-7.54 (m, 3H), 7.23-7.38 (m, 5H).

## 2. Quenching data for triplet energy transfer.

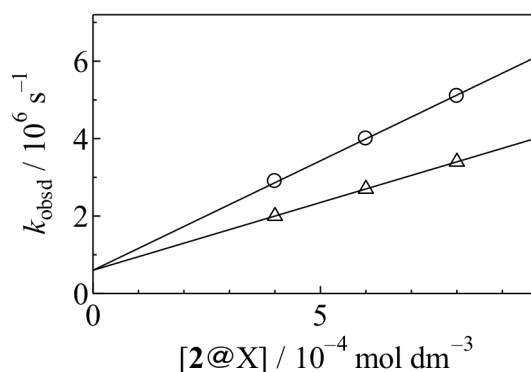
Quenching rate constants,  $k_q$  were obtained from the slope of the plots for the observed rates ( $k_{\text{obsd}}$ ) on triplet sensitization as a function of the concentration of  $n@X$  ( $n = 2 - 4$ ),  $[n@X]$ . When the plots of  $k_{\text{obsd}}$  show a straight line,  $k_{\text{obsd}}$  is expressed by eq S1.

$$k_{\text{obsd}} = k_0 + k_q[n@X] \quad (\text{S1})$$

Here,  $k_0$  is the decay rate of the triplet sensitizer.

### 2-1. Quenching data for 2@X.

Figure S1 shows rates ( $k_{\text{obsd}}$ ) of the triplet formation for the Ac/2@OPh system and the PTR formation for the Ac/2@SPh system plotted as a function of [2@X]. Since the plots show straight lines,  $k_{\text{obsd}}$  is expressed with eq S1. The  $k_0$  value was  $6.0 \times 10^5 \text{ s}^{-1}$  extrapolated for the decay rate of triplet Ac. From the slope of the line the  $k_q$  values were determined to be  $5.7 \times 10^9$  and  $3.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the Ac/2@OPh and Ac/2@SPh, respectively. The  $k_q$  values are rate constants for the triplet energy transfer from triplet Ac to 2@X.



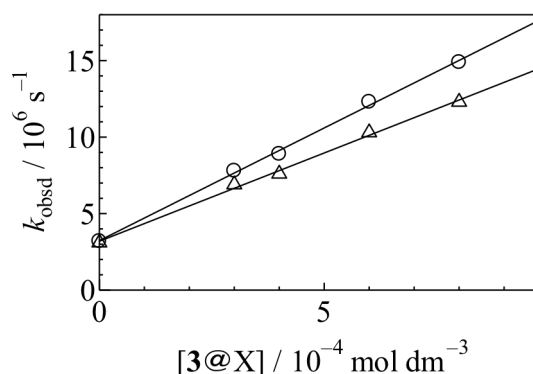
**Figure S1.** Formation rates of the intermediates plotted as a function of [2@X] upon 308 nm laser pulsing in ACN solution of the Ac ( $0.6 \text{ mol dm}^{-3}$ )/2@X systems.

### 2-2. Quenching data for 3@X.

Figure S2 shows decay rates ( $k_{\text{obsd}}$ ) of triplet XT for the XT/3@X system plotted as a function of [3@X]. Since the plots show straight lines,  $k_{\text{obsd}}$  is expressed with eq S1. The  $k_0$  value was  $3.2 \times 10^6 \text{ s}^{-1}$  for the decay rate of triplet XT. From the slope of the line, the  $k_q$  values were determined to be  $1.5 \times 10^{10}$  and  $1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the XT/3@OPh and XT/3@SPh, respectively. The  $k_q$  values



are rate constants for the triplet energy transfer from triplet XT to **3@X**.



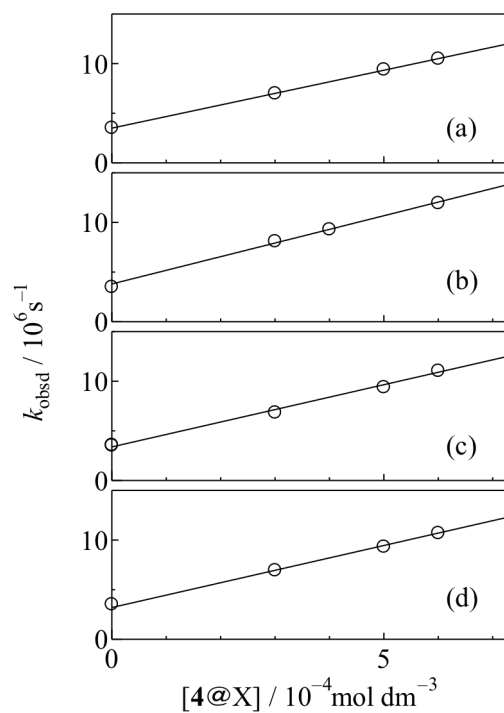
**Figure S2.** Decay rates of triplet XT plotted as a function of [**3@X**] upon 355 nm laser pulsing in ACN solution of the XT ( $9.0 \times 10^{-3}$  mol dm<sup>-3</sup>)/**3@X** systems.

### 2-3. Quenching data for **4@X**.

Figure S3 shows decay rates ( $k_{\text{obsd}}$ ) of triplet XT for the XT/**4@X** system plotted as a function of [**4@X**]. Since the plots show straight lines,  $k_{\text{obsd}}$  is expressed with eq S1. The  $k_0$  value was  $3.2 \times 10^6$  s<sup>-1</sup> for the decay rate of triplet XT. From the slope of the line, the  $k_q$  values were determined as listed in Table S1. The  $k_q$  values are rate constants for the triplet energy transfer from triplet XT to **4@X**.

**Table S1.** Quenching rate constant ( $k_q$ ) of **4@X** by XT in ACN.

X	$k_q / 10^{10}$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
H	1.2
OPh	1.4
Br	1.3
SPh	1.3



**Figure S3.** Decay rates of triplet XT plotted as a function of [4@X] upon 355 nm laser pulsing in ACN solution of XT ( $9.0 \times 10^{-3} \text{ mol dm}^{-3}$ )/4@H (a), /4@OPh (b), /4@Br (c) and /4@SPh (d) systems.

### 3. Results of DFT calculation

The calculation was carried out at the DFT level, using the Gaussian 09 software package.<sup>2</sup> The geometries of  $n@SPh$  and  $n@R$  were fully optimized by using the 6-31G(d) base set at the (U)B3LYP method. The calculated  $\Delta_f H$  values for  $n@SPh$  and  $n@R$  are, respectively, listed in Tables S2 and 3.

**Table S2.** Calculated heats of formation for  $n@SPh$ .

Compound	$\Delta_f H(n@SPh) / \text{hartree}^a$
1@SPh	-1244.872295
2@SPh	-1090.03458
3@SPh	-1321.011247
4@SPh	-1321.013713

a) 1 Hartree = 627.5095 kcal mol<sup>-1</sup>.

**Table S3.** Calculated heats of formation for the radicals ( $\Delta_f H(\text{Rad})$ ).

Radical	$\Delta_f H(\text{Rad}) / \text{hartree}^a$
1@R	-615.089064
2@R	-460.256824
3@R	-691.235753
4@R	-691.232522
PTR	-629.706786

a) 1 Hartree = 627.5095 kcal mol<sup>-1</sup>.

Atom coordinates for the optimized geometries of  $n@SPh$ ,  $n@R$  and PTR in acetonitrile are as follows.

**Table S4.** Atom coordinates for the optimized geometry of 1@SPh

	X	Y	Z
C	-5.70589	1.46745	0.49706
C	-5.75509	1.66819	-0.88684
C	-4.81840	1.04722	-1.71564

C	-3.82176	0.24026	-1.16453
C	-3.76273	0.03591	0.22381
C	-4.72484	0.64686	1.04618
C	-2.76548	-0.87789	0.86749
O	-3.06094	-1.46619	1.90821
C	-1.41377	-1.08311	0.25917
C	-0.75565	-0.09821	-0.49277
C	0.53211	-0.32332	-0.97931
C	1.18875	-1.53741	-0.73936
C	0.52900	-2.52009	0.01841
C	-0.74560	-2.29300	0.51975
C	2.57499	-1.77888	-1.27064
S	3.93050	-1.48940	-0.02434
C	3.87743	0.29487	0.18055
C	4.37942	1.14119	-0.81946
C	4.36383	2.52465	-0.63742
C	3.86618	3.07137	0.54921
C	3.37731	2.23085	1.55125
C	3.37591	0.84571	1.36725
H	-6.43527	1.94761	1.14324
H	-6.52459	2.30337	-1.31675
H	-4.86337	1.18841	-2.79167
H	-3.10753	-0.25073	-1.81721
H	-4.68449	0.47098	2.11635
H	-1.23694	0.85534	-0.68271
H	1.03016	0.45214	-1.55463
H	1.02473	-3.46744	0.21488
H	-1.24858	-3.05142	1.11096
H	2.78373	-1.15844	-2.14543
H	2.71335	-2.82611	-1.55543
H	4.78388	0.71606	-1.73360
H	4.75069	3.17446	-1.41754
H	3.86264	4.14831	0.69209
H	2.98938	2.65091	2.47512
H	2.98750	0.19094	2.14121

---

Sum of electronic and zero-point energies = -1244.891787 Hartree

**Table S5.** Atom coordinates for the optimized geometry of **2**@SPh

---

	X	Y	Z
C	5.10626	-1.25027	0.21200
C	4.59443	-1.97517	-0.87083
C	3.34062	-1.65730	-1.39951
C	2.59615	-0.61543	-0.84820
C	3.10423	0.11472	0.23743

C	4.36564	-0.21024	0.76426
C	2.34251	1.23390	0.85484
O	2.77816	1.88599	1.80321
C	1.03648	1.55347	0.30127
C	-0.05901	1.87198	-0.11347
C	-1.36557	2.24961	-0.62929
S	-2.22862	0.93969	-1.61303
C	-3.04865	-0.04821	-0.36063
C	-2.55263	-0.22528	0.93783
C	-3.24516	-1.03493	1.84150
C	-4.41541	-1.69109	1.45582
C	-4.89997	-1.52568	0.15584
C	-4.22891	-0.70115	-0.74743
H	6.08105	-1.49932	0.62116
H	5.17396	-2.78707	-1.30120
H	2.94422	-2.21985	-2.23957
H	1.62202	-0.36535	-1.25712
H	4.74531	0.36287	1.60363
H	-1.25919	3.09057	-1.32347
H	-2.03138	2.57581	0.17604
H	-1.62972	0.25260	1.24929
H	-2.85619	-1.15888	2.84848
H	-4.94550	-2.32442	2.16117
H	-5.81274	-2.02623	-0.15529
H	-4.62529	-0.55735	-1.74880

---

Sum of electronic and zero-point energies = - 1090.051569 Hartree

**Table S6.** Atom coordinates for the optimized geometry of **3@SPh**

	X	Y	Z
C	-7.48196	0.34358	-1.02814
C	-7.62897	-0.95135	-0.51876
C	-6.58274	-1.54588	0.18977
C	-5.38307	-0.85748	0.37621
C	-5.22587	0.44154	-0.13437
C	-6.29377	1.03936	-0.82555
C	-3.99327	1.25882	0.09607
O	-4.07344	2.48579	0.15458
C	-2.65781	0.59919	0.25566
C	-2.32431	-0.61232	-0.37192

C	-1.04545	-1.14605	-0.24775
C	-0.06788	-0.48551	0.52123
C	-0.40189	0.73455	1.14694
C	-1.67363	1.27003	1.00223
C	1.24045	-1.03963	0.66184
C	2.35136	-1.51333	0.78555
C	3.68188	-2.08601	0.92313
S	4.77816	-1.88482	-0.56092
C	5.45799	-0.23754	-0.36523
C	4.80594	0.79907	0.31609
C	5.40367	2.05927	0.39974
C	6.63591	2.30447	-0.20858
C	7.27789	1.27348	-0.89959
C	6.70022	0.00598	-0.97179
H	-8.29559	0.80843	-1.57762
H	-8.55861	-1.49266	-0.67082
H	-6.69964	-2.54500	0.59942
H	-4.58121	-1.32115	0.94129
H	-6.17160	2.04962	-1.20277
H	-3.05681	-1.13017	-0.98164
H	-0.79329	-2.07631	-0.74639
H	0.34610	1.25167	1.73943
H	-1.92664	2.21526	1.47101
H	3.62130	-3.17089	1.06058
H	4.20858	-1.67442	1.78995
H	3.83462	0.63688	0.77129
H	4.89249	2.85381	0.93665
H	7.09225	3.28802	-0.14474
H	8.23996	1.44890	-1.37324
H	7.21704	-0.79661	-1.49097

---

Sum of electronic and zero-point energies = -1321.032847 Hartree

**Table S7.** Atom coordinates for the optimized geometry of **4@SPh**

---

	X	Y	Z
C	8.26619	0.76104	-0.26176
C	7.79119	2.06156	-0.05554
C	6.42335	2.28990	0.11641
C	5.52872	1.22110	0.08247
C	5.99893	-0.08508	-0.12344

C	7.37532	-0.30721	-0.29548
C	5.07852	-1.25636	-0.16605
O	5.48700	-2.40642	-0.34215
C	3.66287	-1.01142	0.00690
C	2.46098	-0.87097	0.14461
C	1.05693	-0.70216	0.30429
C	0.19468	-1.81676	0.26077
C	-1.17581	-1.64641	0.41910
C	-1.72390	-0.37132	0.62834
C	-0.86318	0.73671	0.66757
C	0.50904	0.58039	0.51077
C	-3.20980	-0.19195	0.78178
S	-3.97594	0.08525	-0.89806
C	-5.70912	0.26790	-0.45420
C	-6.51196	-0.86435	-0.25409
C	-7.86234	-0.71579	0.06716
C	-8.42057	0.56047	0.17955
C	-7.62510	1.68999	-0.02693
C	-6.27160	1.54677	-0.34052
H	9.32967	0.58511	-0.39536
H	8.48763	2.89499	-0.02908
H	6.05466	3.29883	0.27648
H	4.46549	1.39585	0.21538
H	7.72460	-1.32206	-0.45400
H	0.60967	-2.80735	0.10509
H	-1.83054	-2.51297	0.38571
H	-1.27420	1.72966	0.82822
H	1.16662	1.44294	0.54847
H	-3.44323	0.67629	1.40271
H	-3.67368	-1.07895	1.21987
H	-6.07936	-1.85560	-0.35337
H	-8.47890	-1.59673	0.22282
H	-9.47295	0.67380	0.42440
H	-8.05585	2.68385	0.05757
H	-5.65069	2.42336	-0.49903

---

Sum of electronic and zero-point energies = - 1321.035550 Hartree

**Table S8.** Atom coordinates for the optimized geometry of **1**@R

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	X	Y	Z
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---

C	-3.99636	0.75852	1.61951
C	-4.00095	-0.44478	2.31667
C	-2.79820	-1.06760	2.63604
C	-1.59248	-0.49617	2.24683
C	-1.58566	0.70824	1.54098
C	-2.79234	1.33918	1.23533
C	-0.29326	1.33813	1.13541
O	-0.10207	2.53176	1.28669
C	0.74344	0.45547	0.52564
C	0.36933	-0.66114	-0.23186
C	1.33684	-1.46070	-0.82953
C	2.69733	-1.15429	-0.67381
C	3.07301	-0.04890	0.10455
C	2.10129	0.75944	0.68511
C	3.69966	-2.01404	-1.24065
H	-4.94198	1.25294	1.37372
H	-4.95006	-0.89955	2.61897
H	-2.80053	-2.01051	3.19265
H	-0.64373	-0.98788	2.49207
H	-2.78881	2.29458	0.69759
H	-0.69381	-0.90426	-0.34999
H	1.03991	-2.32939	-1.42683
H	4.13481	0.18120	0.24369
H	2.39782	1.63980	1.26811
H	4.41574	-2.52483	-0.60869
H	3.76047	-2.16986	-2.31062

---

Sum of electronic and zero-point energies = - 615.102042 Hartree

**Table S9.** Atom coordinates for the optimized geometry of **2**@R

	X	Y	Z
C	-2.96721	0.45330	0.00082
C	-3.04654	-0.94418	0.00020
C	-1.87936	-1.71264	-0.00058
C	-0.63312	-1.08755	-0.00072
C	-0.54718	0.31336	-0.00014
C	-1.72448	1.07952	0.00063
C	0.76383	1.02258	-0.00040
O	0.84410	2.25777	-0.00070
C	1.96338	0.22829	-0.00027



C	3.03610	-0.38840	0.00022
C	4.21083	-1.07289	0.00075
H	-3.87502	1.04972	0.00147
H	-4.01726	-1.43204	0.00031
H	-1.94020	-2.79699	-0.00107
H	0.27478	-1.68293	-0.00127
H	-1.64361	2.16145	0.00108
H	4.22759	-2.15908	0.00144
H	5.16338	-0.55058	0.00052

---

Sum of electronic and zero-point energies = - 460.267725 Hartree

**Table S10.** Atom coordinates for the optimized geometry of **3@R**

---

	X	Y	Z
C	-4.78189	-0.25497	-0.55085
C	-4.68853	-1.49048	0.09932
C	-3.49341	-1.86556	0.71664
C	-2.38522	-1.01825	0.67067
C	-2.46881	0.22195	0.01663
C	-3.68401	0.60013	-0.57973
C	-1.34036	1.20599	-0.00255
O	-1.58357	2.41374	-0.02842
C	0.07979	0.73966	0.00500
C	0.48507	-0.49649	-0.53300
C	1.82597	-0.85179	-0.56425
C	2.81517	0.01922	-0.04207
C	2.40182	1.26858	0.49315
C	1.06350	1.61883	0.50025
C	4.17254	-0.34223	-0.05753
C	5.37168	-0.65986	-0.06916
C	6.68207	-1.00788	-0.08194
H	-5.71146	0.03997	-1.02929
H	-5.54700	-2.15571	0.12789
H	-3.42271	-2.81675	1.23621
H	-1.46626	-1.31097	1.16785
H	-3.74765	1.56732	-1.06797
H	-0.25057	-1.17354	-0.95342
H	2.12918	-1.80147	-0.99278
H	3.14964	1.94581	0.89308
H	0.75084	2.57916	0.89666

H	7.00768	-1.95991	-0.49184
H	7.44446	-0.34486	0.31752

---

Sum of electronic and zero-point energies = - 691.251111 Hartree

**Table S11.** Atom coordinates for the optimized geometry of **4@R**

	X	Y	Z
C	-5.26210	-0.22672	0.00050
C	-4.95023	-1.59126	0.00021
C	-3.61552	-2.00508	-0.00024
C	-2.59199	-1.05833	-0.00039
C	-2.89811	0.31129	-0.00009
C	-4.24201	0.71985	0.00034
C	-1.83617	1.35840	-0.00027
O	-2.10595	2.56383	-0.00067
C	-0.46024	0.92497	0.00008
C	0.72317	0.62272	0.00009
C	2.09027	0.26906	0.00016
C	3.09609	1.27323	0.00029
C	4.42959	0.93017	0.00025
C	4.84599	-0.44114	0.00002
C	3.81860	-1.44044	-0.00014
C	2.48543	-1.09614	-0.00005
C	6.19825	-0.78870	-0.00002
H	-6.29995	0.09398	0.00087
H	-5.74720	-2.32965	0.00037
H	-3.37276	-3.06372	-0.00046
H	-1.55439	-1.37806	-0.00075
H	-4.46397	1.78192	0.00055
H	2.79843	2.31714	0.00049
H	5.18905	1.70704	0.00036
H	4.10752	-2.48779	-0.00030
H	1.72054	-1.86645	-0.00016
H	6.97281	-0.02863	0.00010
H	6.51140	-1.82773	-0.00021

---

Sum of electronic and zero-point energies = - 691.247712 Hartree

**Table S12.** Atom coordinates for the optimized geometry of PTR.

	X	Y	Z
S	2.32862	0.00000	0.00002

C	0.55325	0.00000	-0.00020
C	-0.14999	1.21567	0.00002
C	-1.54576	1.20576	0.00006
C	-2.25029	0.00000	-0.00008
C	-1.54576	-1.20576	0.00006
C	-0.14999	-1.21567	0.00002
H	0.38558	2.16035	0.00013
H	-2.08090	2.15145	0.00011
H	-3.33615	0.00000	-0.00009
H	-2.08090	-2.15145	0.00010
H	0.38558	-2.16035	0.00013

---

Sum of electronic and zero-point energies = - 629.706786 Hartree