

Supporting Information

**Building Trisubstituted Ethylenes from Terminal Alkenes via  
Debrominative Ring-opening Trifluoromethylations of Geminal  
Dibromocyclopropanes**

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# Contents

|                                                                                            |           |
|--------------------------------------------------------------------------------------------|-----------|
| <b>1 General information .....</b>                                                         | <b>1</b>  |
| <b>2 Preparation of alkenes .....</b>                                                      | <b>3</b>  |
| 2.1 Preparation of alkenes .....                                                           | 3         |
| 2.2 Physical data .....                                                                    | 4         |
| <b>3 Preparation of <i>gem</i>-dihalocyclopropanes .....</b>                               | <b>8</b>  |
| 3.1 Preparation of <i>gem</i> -dihalocyclopropanes .....                                   | 8         |
| 3.2 Physical data .....                                                                    | 10        |
| <b>4 Reactions of <i>gem</i>-dihalocyclopropanes with Chen's reagent .....</b>             | <b>25</b> |
| 4.1 Optimization of the conditions for the reaction of <b>1a</b> with Chen's reagent ..... | 25        |
| 4.2 Typical procedure .....                                                                | 27        |
| 4.3 Side product .....                                                                     | 28        |
| 4.4 Physical data .....                                                                    | 28        |
| 4.5 2D Nuclear Overhauser Effect (NOE) analysis .....                                      | 40        |
| <b>5 Photocatalytic preparations of monobromocyclopropanes .....</b>                       | <b>41</b> |
| 5.1 Preparation of photocatalyst PTH .....                                                 | 41        |
| 5.2 Optimization of the conditions for reductive monodebromination of <b>1a</b> .....      | 41        |
| 5.3 Typical procedure for reductive monodebrominations .....                               | 42        |
| 5.4 Physical data .....                                                                    | 43        |
| <b>6 Reactions of monobromocyclopropanes with Chen's reagent .....</b>                     | <b>49</b> |
| 6.1 Optimization of the conditions for the reaction of <b>3a</b> with Chen's reagent ..... | 49        |
| 6.2 Typical procedure .....                                                                | 50        |
| 6.3 Physical data .....                                                                    | 51        |
| <b>7 Conversions of <b>2a</b> .....</b>                                                    | <b>56</b> |
| 7.1 Experimental procedures .....                                                          | 56        |
| 7.2 Physical data .....                                                                    | 61        |
| <b>8 Gram-scale reactions .....</b>                                                        | <b>66</b> |
| <b>9 Mechanistic experiments .....</b>                                                     | <b>67</b> |
| 9.1 Radical-trapping experiments .....                                                     | 67        |

|                                        |           |
|----------------------------------------|-----------|
| 9.2 Physical data .....                | 68        |
| <b>10 Unsuccessful reactants .....</b> | <b>69</b> |
| <b>11 References .....</b>             | <b>70</b> |
| <b>12 Crystal data .....</b>           | <b>72</b> |
| <b>13 NMR spectra.....</b>             | <b>76</b> |

# 1 General information

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## Reagents

All the solvents and reagents were obtained from commercial sources and used without purification unless mentioned otherwise. THF, Et<sub>2</sub>O and 1,4-dioxane were distilled over CaH<sub>2</sub> and LiAlH<sub>4</sub> under N<sub>2</sub> atmosphere. Toluene, DCM and CH<sub>3</sub>CN were distilled over CaH<sub>2</sub> under N<sub>2</sub>. Acetone, EA, DMSO, DMA, DMF, DME, CHCl<sub>3</sub>, HMPA, CH<sub>3</sub>NO<sub>2</sub> were dried over activated 4A molecular sieves.

## Instruments

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECZ 400 MHz or 600 MHz spectrometer. The chemical shift (δ) values are given in ppm and are referenced to TMS or residual solvent peaks. Chemical shifts of <sup>19</sup>F NMR are referred to CFCl<sub>3</sub> (δ = 0). Infrared spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrometer. Gas chromatography coupled with mass spectrometry (GC-MS) was performed on a Orbitrap Exploris GC mass spectrometer under electrospray ionization (EI) mode. Melting points were measured on a WRX-4 (Shanghai Yice) micro melting point apparatus. X-ray diffraction experiment was performed on a Rigaku XtalLAB Synergy diffractometer using Cu or Mo Kα radiation.

## Experimental techniques

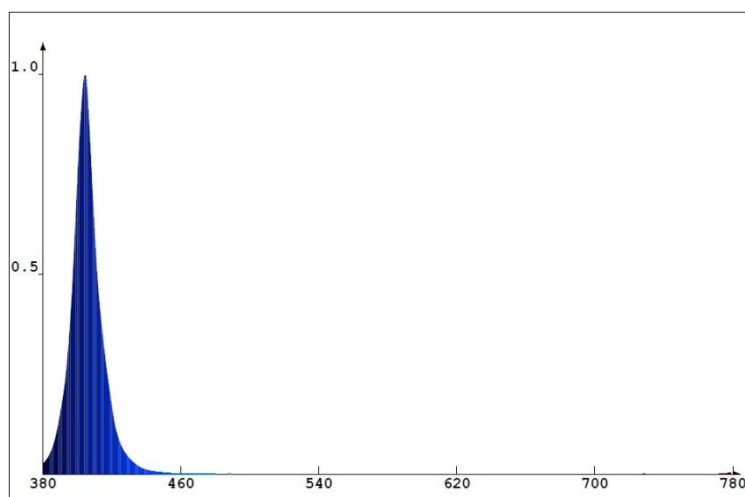
All glassware was dried overnight at 100 °C prior to use. For reactions that require heating, a silicone oil bath was used. Purple light induced photocatalytic reactions were performed in a Schlenk tube under N<sub>2</sub> atmosphere. Thin-layer chromatography (TLC) was performed on silica gel plates (0.2–0.25 mm thickness). Visualization of TLC was achieved by the use of UV light (254 nm), KMnO<sub>4</sub> or PMA stain. Flash column chromatography was performed on a silica gel (Qingdao Haiyang, 200–300 mesh) column.

## Photochemical set-up in our lab

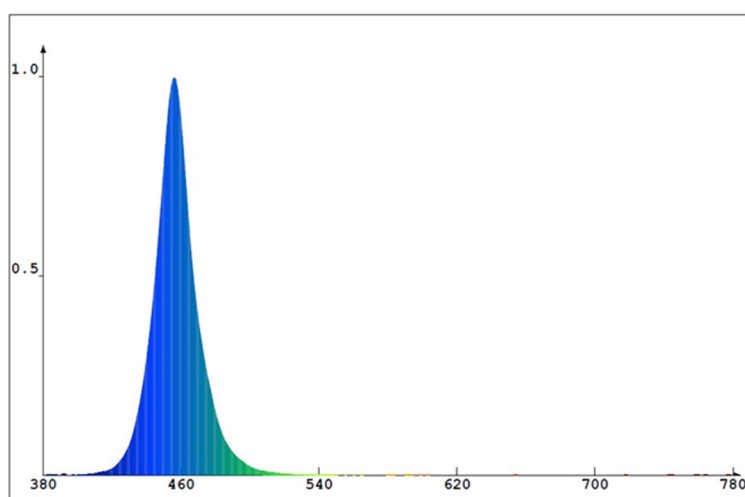
Synthware® glassware made from borosilicate glass 3.3 and strips of 2835 light-emitting diode (120 LEDs/m, DC 12 V, 10 watt/m) surface-mounted on bare printed circuit board from Shenzhen Jinhongyan Lighting Co., Ltd. were used for photochemical reactions. A LED tube (inner diameter and height of 10 cm) was used as the lighting device for all photochemical reactions. The length of purple LED strip is 1.5 meters and the power is 15 W. The reaction temperature is controlled at about 25 °C by a small desk fan.



**Fig. S1** | Photochemical set-up in our lab



**Fig. S2** | Luminous spectrum of purple LED ( $\lambda_p = 405$  nm)



**Fig. S3** | Luminous spectrum of blue LED ( $\lambda_p = 456$  nm)

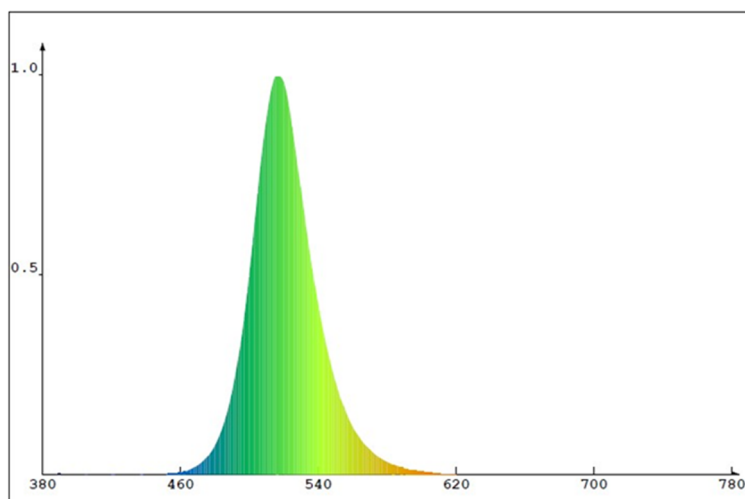
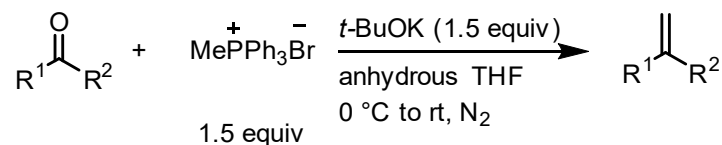


Fig. S4 | Luminous spectrum of green LED ( $\lambda_p = 516$  nm)

## 2 Preparation of alkenes

### 2.1 Preparation of alkenes

#### General procedure<sup>[1]</sup>

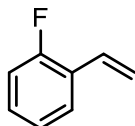


Olefins were synthesized by Wittig reaction of the corresponding aldehydes or ketones according to the known procedures in the literature.

To a 100 mL flame-dried Schlenk flask were added *t*-BuOK (3.37g, 30 mmol, 1.5 equiv), methyltriphenylphosphonium bromide (10.7g, 30 mmol, 1.5 equiv) and anhydrous THF (50 mL) under N<sub>2</sub> atmosphere. Forming sediment, the solution turns orange or yellow. The mixture was stirred at 0 °C for 0.5 h, and the corresponding aldehyde or ketone (20 mmol, 1.0 equiv) was added slowly under N<sub>2</sub> atmosphere. The resulting mixture was stirred at 0 °C for 10 min, and then stirring was continued for 8–12 hours at rt. Afterwards, THF was removed in vacuo to give the crude product. The residue was extracted with chloroform, and washed three times with H<sub>2</sub>O. The solvents were removed by rotary evaporation, and the crude product was purified by column chromatography (hexanes/EA = 100:1 as eluent) to obtain the corresponding product as a colorless oil/solid.

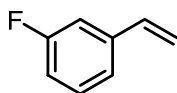
## 2.2 Physical data

### 1-Fluoro-2-vinylbenzene<sup>[2]</sup>



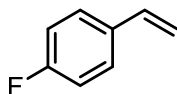
Yellow oil (2.0 g, 82% yield); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.17 – 7.03 (m, 2H), 6.94 (m, 1H), 5.87 (dd, *J* = 17.8 Hz, 1H), 5.42 (d, *J* = 11.2 Hz, 1H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 160.3 (d, *J* = 249.4 Hz), 129.3 (d, *J* = 4.0 Hz), 129.1 (d, *J* = 8.4 Hz), 127.1 (d, *J* = 3.7 Hz), 125.3 (d, *J* = 12.1 Hz), 124.0 (d, *J* = 3.8 Hz), 116.4 (d, *J* = 4.8 Hz), 115.7 (d, *J* = 22.1 Hz) ppm.

### 2-Fluoro-2-vinylbenzene



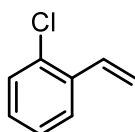
Yellow oil (2.0 g, 82% yield); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 1H), 7.22 – 7.09 (m, 2H), 7.00 – 6.93 (m, 1H), 6.69 (m, 1H), 5.77 (d, *J* = 17.5 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 244.5 Hz), 139.9 (d, *J* = 7.7 Hz), 135.8 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.2 Hz), 122.1 (d, *J* = 3.0 Hz), 115.2, 114.6 (d, *J* = 21.4 Hz), 112.6 (d, *J* = 21.7 Hz) ppm.

### 3-Fluoro-2-vinylbenzene<sup>[3]</sup>



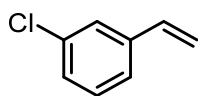
Yellow oil (2.2 g, 92% yield); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.09 – 6.97 (m, 2H), 6.70 (m, 1H), 5.69 (d, *J* = 18.1 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 246.6 Hz), 135.7, 133.7 (d, *J* = 3.4 Hz), 127.7 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.5 Hz), 113.5 (d, *J* = 2.2 Hz) ppm.

### 1-Chloro-2-vinylbenzene



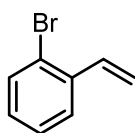
Yellow oil (1.9 g, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.58 (dt,  $J = 7.6, 1.4$  Hz, 1H), 7.37 (dt,  $J = 7.9, 1.3$  Hz, 1H), 7.29 – 7.19 (m, 2H), 7.14 (m, 1H), 5.76 (d,  $J = 17.5$  Hz, 1H), 5.40 (d,  $J = 11.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  135.7, 133.2, 129.6, 128.8, 126.8, 126.5, 116.5 ppm.

#### 2-Chloro-2-vinylbenzene



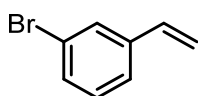
Yellow oil (2.0 g, 72% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 (s, 1H), 7.31 – 7.22 (m, 3H), 6.67 (m, 1H), 5.77 (d,  $J = 17.6$  Hz, 1H), 5.32 (d,  $J = 10.9$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  139.4, 135.6, 134.5, 129.7, 127.7, 126.2, 124.4, 115.3 ppm.

#### 1-Bromo-2-vinylbenzene



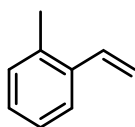
Yellow oil (2.9 g, 80% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 (dd,  $J = 8.0, 1.4$  Hz, 2H), 7.34 – 7.23 (m, 1H), 7.16 – 7.10 (m, 1H), 7.10 – 7.05 (m, 1H), 5.72 (d,  $J = 17.5$  Hz, 1H), 5.38 (d,  $J = 10.9$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.4, 135.8, 132.8, 129.1, 127.5, 126.8, 116.7 ppm.

#### 2-Bromo-2-vinylbenzene



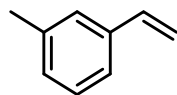
Yellow oil (3.1 g, 85% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.58 (t,  $J = 1.8$  Hz, 1H), 7.40 (ddd,  $J = 7.9, 2.0, 1.1$  Hz, 1H), 7.36 – 7.31 (m, 1H), 7.20 (t,  $J = 7.8$  Hz, 1H), 6.66 (m, 1H), 5.77 (d,  $J = 17.5$  Hz, 1H), 5.32 (d,  $J = 10.9$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  139.6, 135.4, 130.6, 130.0, 129.1, 124.8, 122.7, 115.3 ppm.

#### 1-Methyl-2-vinylbenzene



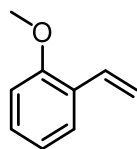
Yellow oil (1.7 g, 72% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.56 – 7.51 (m, 1H), 7.24 – 7.18 (m, 3H), 7.00 (m, 1H), 5.70 (d,  $J$  = 17.4 Hz, 1H), 5.35 (d,  $J$  = 11.0 Hz, 1H), 2.41 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  136.8, 135.4, 134.8, 130.2, 127.6, 126.1, 125.3, 115.1, 19.7 ppm.

### 2-Methyl-2-vinylbenzene



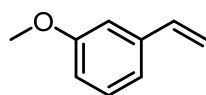
Yellow oil (2.0 g, 85% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.20 (m, 3H), 7.11 (s, 1H), 6.73 (m, 1H), 5.77 (d,  $J$  = 17.6 Hz, 1H), 5.26 (d,  $J$  = 10.9 Hz, 1H), 2.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.0, 137.5, 136.9, 128.6, 128.4, 126.9, 123.3, 113.6, 21.4 ppm.

### 1-Methoxy-2-vinylbenzene



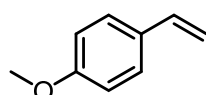
Yellow oil (1.9 g, 71% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.55 (d,  $J$  = 7.6 Hz, 1H), 7.30 (ddd,  $J$  = 8.3, 7.3, 1.7 Hz, 1H), 7.15 (ddd,  $J$  = 17.6, 11.1, 1.5 Hz, 1H), 7.01 (td,  $J$  = 7.4, 0.9 Hz, 1H), 6.93 (m, 1H), 5.82 (d,  $J$  = 17.7 Hz, 1H), 5.35 (d,  $J$  = 11.2 Hz, 1H), 3.89 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  156.7, 131.7, 128.8, 126.5, 120.6, 114.3, 110.8, 55.3 ppm.

### 2-Methoxy-2-vinylbenzene



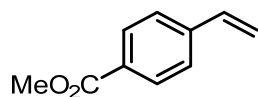
Yellow oil (2.3 g, 86% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.62 – 7.54 (m, 1H), 7.41 – 7.27 (m, 2H), 7.22 – 7.12 (m, 1H), 7.05 (m, 1H), 6.11 (d,  $J$  = 17.5 Hz, 1H), 5.61 (d,  $J$  = 11.1 Hz, 1H), 4.17 (d,  $J$  = 1.7 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.8, 139.0, 136.7, 129.5, 118.9, 114.1, 113.4, 111.5, 55.2 ppm.

### 3-Methoxy-2-vinylbenzene



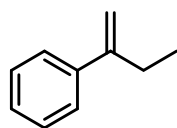
Yellow oil (2.4 g, 90% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 – 7.40 (m, 2H), 6.98 – 6.92 (m, 2H), 6.77 (m, 1H), 5.75 – 5.68 (m, 1H), 5.29 – 5.18 (m, 1H), 3.86 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.3, 136.1, 130.3, 127.3, 113.8, 111.4, 55.0 ppm.

### Methyl 4-vinylbenzoate



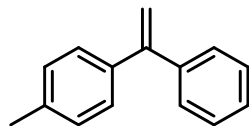
White solid (2.4 g, 73% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.99 (d,  $J$  = 8.4 Hz, 2H), 7.45 (d,  $J$  = 8.3 Hz, 2H), 6.74 (m, 1H), 5.85 (d,  $J$  = 17.5 Hz, 1H), 5.37 (d,  $J$  = 10.9 Hz, 1H), 3.90 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  166.8, 141.8, 136.0, 129.8, 129.2, 126.0, 116.4, 52.0 ppm.

### But-1-en-2-ylbenzene



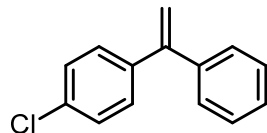
Yellow oil (1.6 g, 61% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.57 – 7.53 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 (m, 1H), 5.43 (d,  $J$  = 3.3 Hz, 1H), 5.21 (d,  $J$  = 1.6 Hz, 1H), 2.69 – 2.63 (m, 2H), 1.25 (m, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  150.1, 141.5, 128.2, 127.2, 126.0, 110.9, 28.1, 12.9 ppm.

### 1-Methyl-4-(1-phenylvinyl)benzene



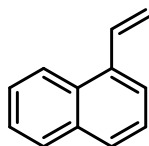
Yellow oil (2.5 g, 64% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.29 (m, 7H), 7.23 (dd,  $J$  = 8.1, 2.3 Hz, 2H), 5.56 – 5.50 (m, 2H), 2.46 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  149.9, 141.7, 138.6, 137.4, 128.8, 128.3, 128.1, 127.6, 113.6, 21.1 ppm.

### 1-Chloro-4-(1-phenylvinyl)benzene



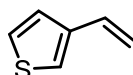
Yellow oil (2.7 g, 64% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.29 (m, 9H), 5.49 (dd,  $J$  = 12.1, 1.1 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  149.0, 141.0, 139.9, 133.6, 129.5, 128.3, 128.2, 128.2, 127.9, 114.7 ppm.

### 1-Vinylnaphthalene



Yellow oil (2.1 g, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.20 (dd,  $J$  = 8.7, 2.7 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.86 (dd,  $J$  = 8.3, 2.5 Hz, 1H), 7.71 (dd,  $J$  = 7.2, 2.9 Hz, 1H), 7.61 – 7.49 (m, 4H), 5.88 (dd,  $J$  = 17.3, 2.0 Hz, 1H), 5.56 (dd,  $J$  = 10.9, 1.8 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  135.6, 134.4, 133.6, 131.1, 128.5, 128.1, 126.0, 125.7, 125.6, 123.7, 123.6, 117.1 ppm.

### 3-Vinylthiophene

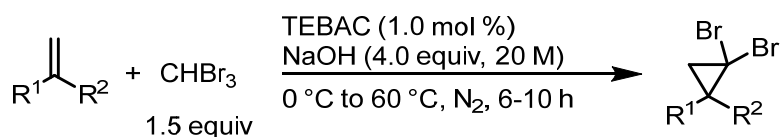


Yellow oil (1.7 g, 77% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.30 (dd,  $J$  = 5.1, 2.9 Hz, 1H), 7.28 (dd,  $J$  = 5.1, 1.4 Hz, 1H), 7.20 (dd,  $J$  = 2.9, 1.4 Hz, 1H), 6.75 (m 1H), 5.62 (d,  $J$  = 17.5 Hz, 1H), 5.23 (d,  $J$  = 10.8 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  140.5, 130.9, 125.9, 124.7, 122.3, 113.5 ppm.

## 3 Preparation of *gem*-dihalocyclopropanes

### 3.1 Preparation of *gem*-dihalocyclopropanes

#### General procedure A<sup>[4]</sup>

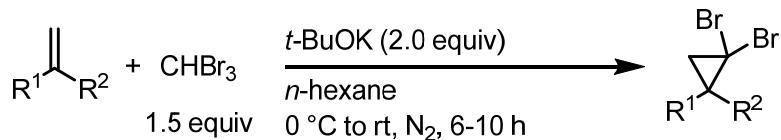


Most *gem*-dibromocyclopropanes were prepared from the alkenes, bromoform and NaOH under phase-transfer catalysis (PTC) according to the known procedures in the literature.

To a solution of the corresponding alkene (20 mmol, 1.0 equiv), bromoform (7.6 g, 30 mmol, 1.5 equiv) and phase transfer catalyst BnNEt<sub>3</sub>Cl (TEBAC, 46 mg, 0.02 mmol, 1.0 mol %) was added dropwise a solution of NaOH (3.2 g, 80 mmol, 4.0 equiv, 20 M) at 0 °C, and the mixture was stirred at room temperature for 0.5 h, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water and EA were added and the aqueous phase was extracted with EA (20 mL × 3). The combined organic phases were washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure. Purification by column

chromatography on silica gel (hexanes as eluent) gave pure *gem*-dibromocyclopropane derivative as a colorless liquid/solid.

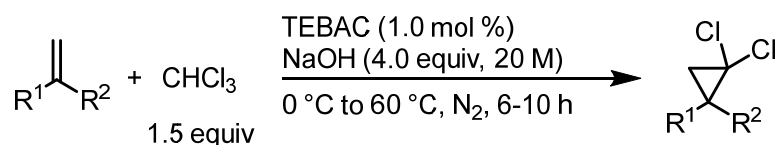
#### General procedure B<sup>[5]</sup>



In a 250 mL two-necked flask equipped with a large stirring bar, the corresponding alkene (20 mmol, 1.0 equiv.) and *t*-BuOK (4.5 g, 40 mmol, 2.0 equiv) were suspended in *n*-hexane at 0 °C. Bromoform (7.6 g, 30 mmol, 1.5 equiv) was added dropwise under N<sub>2</sub> atmosphere. The resulting solution was stirred at 0 °C for 0.5 h and then the stirring was continued for 8–12 hours at rt and further stirred until conversion was complete as observed by TLC analysis. Then, the organic solvent was removed under reduced pressure and the residue was extracted with DCM (20 mL × 3). The organic phases were collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. Purification by column chromatography on silica gel (hexanes as eluent) gave pure *gem*-dibromocyclopropane derivative as a colorless liquid/solid.

Note: It is necessary to use *n*-hexane instead of petroleum ether as the solvent. Usually, petroleum ether contains olefin impurities, which will bring side products after reaction with CHBr<sub>3</sub>.

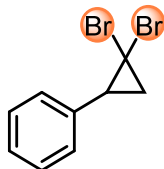
#### General procedure C<sup>[6]</sup>



To a solution of the corresponding alkene (20 mmol, 1.0 equiv), chloroform (7.6 g, 30 mmol, 1.5 equiv) and TEBAC (46 mg, 0.02 mmol, 1.0 mol %) was added dropwise a solution of NaOH (3.2 g, 80 mmol, 4.0 equiv, 20 M) at 0 °C, and the mixture was stirred at room temperature for 0.5 h, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water and EA were added and the aqueous phase was extracted with EA (20 mL × 3). The combined organic phases were washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (hexanes as eluent) gave pure *gem*-dichlorocyclopropane derivative as a colorless oil.

## 3.2 Physical data

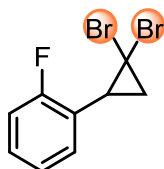
### (2,2-Dibromocyclopropyl)benzene (1a)



General procedure A was applied.

Yellow oil (4.1 g, 75% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 2.97 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.14 (dd,  $J$  = 10.5, 7.7 Hz, 1H), 2.02 (t,  $J$  = 8.0 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  135.9, 128.8, 128.2, 127.6, 35.9, 28.4, 27.2 ppm.

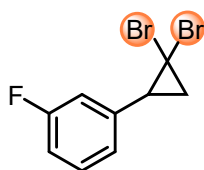
### 1-(2,2-Dibromocyclopropyl)-2-fluorobenzene (1b)



General procedure A was applied.

Yellow oil (3.8 g, 65% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.33 (tdd,  $J$  = 7.6, 5.2, 1.8 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.09 – 7.05 (m, 1H), 3.02 (dd,  $J$  = 10.3, 8.5 Hz, 1H), 2.19 (dd,  $J$  = 10.4, 7.6 Hz, 1H), 2.05 (t,  $J$  = 8.0 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.4 (d,  $J$  = 248.3 Hz), 129.4, 123.8, 115.3 (d,  $J$  = 21.6 Hz), 30.6 (d,  $J$  = 2.7 Hz), 27.1, 26.8 ppm.

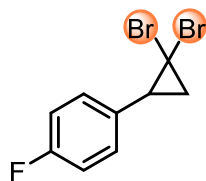
### 1-(2,2-Dibromocyclopropyl)-3-fluorobenzene (1c)



General procedure A was applied.

Yellow oil (4.0 g, 68% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 (td,  $J$  = 8.0, 5.9 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.98 (dt,  $J$  = 9.9, 2.2 Hz, 1H), 2.96 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.17 (dd,  $J$  = 10.5, 7.8 Hz, 1H), 2.01 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.8 (d,  $J$  = 246.2 Hz), 138.6 (d,  $J$  = 7.8 Hz), 130.0 (d,  $J$  = 8.3 Hz), 125.0 (d,  $J$  = 3.3 Hz), 116.1 (d,  $J$  = 22.1 Hz), 114.8 (d,  $J$  = 21.0 Hz), 35.7 (d,  $J$  = 2.2 Hz), 27.8, 27.6 ppm.

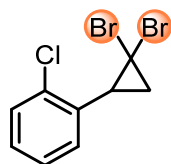
**1-(2,2-Dibromocyclopropyl)-4-fluorobenzene (1d)**



General procedure A was applied.

Yellow oil (4.2 g, 72% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.44 – 7.35 (m, 2H), 7.26 – 7.17 (m, 2H), 3.08 (dd,  $J$  = 10.6, 8.3 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.16 – 2.09 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.2 (d,  $J$  = 246.4 Hz), 131.8 (d,  $J$  = 3.4 Hz), 130.5 (d,  $J$  = 8.3 Hz), 115.4 (d,  $J$  = 2.8 Hz), 115.2 (d,  $J$  = 2.6 Hz), 35.2, 28.1, 27.4 ppm.

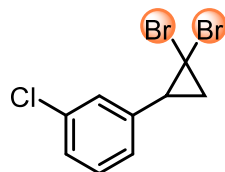
**1-Chloro-2-(2,2-dibromocyclopropyl)benzene (1e)**



General procedure A was applied.

Yellow oil (4.3 g, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.48 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.27 (m, 2H), 7.10 – 7.02 (m, 1H), 3.01 (dd,  $J$  = 10.3, 8.4 Hz, 1H), 2.19 (dd,  $J$  = 10.3, 7.7 Hz, 1H), 2.05 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  136.6, 134.9, 129.3, 128.9, 126.6, 34.9, 27.3, 27.0 ppm.

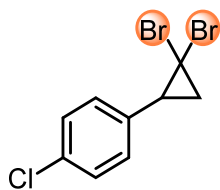
**1-Chloro-3-(2,2-dibromocyclopropyl)benzene (1f)**



General procedure A was applied.

Yellow oil (4.2 g, 68% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.27 (m, 2H), 7.24 (d,  $J$  = 2.2 Hz, 1H), 7.14 (dt,  $J$  = 5.8, 2.1 Hz, 1H), 2.92 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.14 (dd,  $J$  = 10.5, 7.8 Hz, 1H), 1.98 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.9, 134.1, 129.5, 129.0, 127.7, 127.1, 35.3, 27.5, 27.3 ppm.

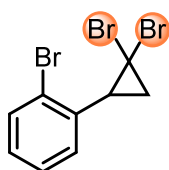
**1-Chloro-4-(2,2-dibromocyclopropyl)benzene (1g)**



General procedure A was applied.

Yellow oil (4.7 g, 76% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.31 (m, 2H), 7.23 – 7.17 (m, 2H), 2.93 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.16 (dd,  $J$  = 10.5, 7.8 Hz, 1H), 1.98 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  134.7, 133.6, 130.4, 128.7, 35.4, 28.1, 27.6 ppm.

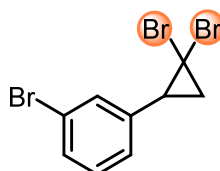
**1-Bromo-2-(2,2-dibromocyclopropyl)benzene (1h)**



General procedure A was applied.

Yellow oil (5.1 g, 72% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.69 (dt,  $J$  = 7.9, 1.6 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.23 (m, 1H), 7.08 (dd,  $J$  = 7.7, 2.0 Hz, 1H), 3.00 (ddd,  $J$  = 10.5, 8.2, 2.2 Hz, 1H), 2.22 (ddd,  $J$  = 10.3, 7.7, 2.3 Hz, 1H), 2.08 (td,  $J$  = 8.1, 2.3 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  136.7, 132.5, 129.5, 129.1, 127.2, 127.0, 36.9, 27.6, 27.2 ppm.

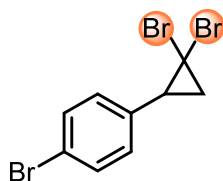
**1-Bromo-3-(2,2-dibromocyclopropyl)benzene (1i)**



General procedure A was applied.

Yellow oil (5.6 g, 79% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 (dt,  $J$  = 7.6, 1.7 Hz, 1H), 7.42 (d,  $J$  = 1.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 2.93 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.15 (dd,  $J$  = 10.5, 7.9 Hz, 1H), 2.00 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.1, 131.8, 130.6, 129.7, 127.5, 122.2, 35.2, 27.5, 27.2 ppm.

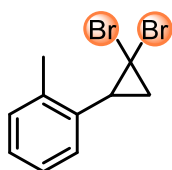
**1-Bromo-4-(2,2-dibromocyclopropyl)benzene (1j)**



General procedure A was applied.

Yellow solid (5.9 g, 83% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.49 (d,  $J$  = 8.4 Hz, 2H), 7.13 (d,  $J$  = 8.5 Hz, 2H), 2.90 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.15 (ddd,  $J$  = 10.4, 7.8, 0.7 Hz, 1H), 2.01 – 1.94 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  135.0, 131.4, 130.6, 121.6, 35.3, 27.6, 27.4 ppm.

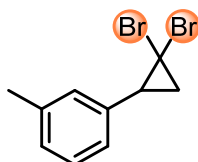
**1-(2,2-Dibromocyclopropyl)-2-methylbenzene (1k)**



General procedure A was applied.

Yellow oil (4.0 g, 69% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 (m, 2H), 7.30 (td,  $J$  = 7.2, 2.3 Hz, 1H), 7.11 (d,  $J$  = 7.6 Hz, 1H), 2.94 (dd,  $J$  = 10.4, 8.4 Hz, 1H), 2.64 (s, 3H), 2.25 (dd,  $J$  = 10.4, 7.6 Hz, 1H), 2.19 – 2.09 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.9, 135.3, 129.8, 127.7, 127.5, 125.7, 35.2, 28.4, 26.7, 20.2 ppm.

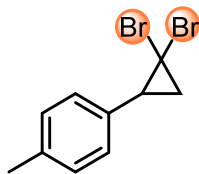
**1-(2,2-Dibromocyclopropyl)-3-methylbenzene (1l)**



General procedure A was applied.

Yellow oil (4.4 g, 76% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (t,  $J$  = 7.6 Hz, 1H), 7.19 (d,  $J$  = 7.7 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.10 (dd,  $J$  = 7.8, 1.7 Hz, 1H), 2.98 (dd,  $J$  = 10.5, 8.4 Hz, 1H), 2.43 (s, 3H), 2.16 (dd,  $J$  = 10.5, 7.8 Hz, 1H), 2.05 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.8, 135.8, 129.7, 128.3, 128.1, 125.8, 35.8, 28.6, 27.1, 21.4 ppm.

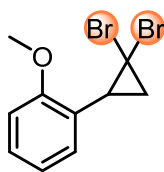
**1-(2,2-Dibromocyclopropyl)-4-methylbenzene (1m)**



General procedure A was applied.

Yellow oil (5.1 g, 88% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.26 – 7.16 (m, 4H), 2.95 (dd,  $J$  = 10.8, 7.7 Hz, 1H), 2.44 (s, 3H), 2.18 (dd,  $J$  = 10.7, 7.7 Hz, 1H), 2.07 (t,  $J$  = 8.0 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.3, 133.1, 129.1, 128.8, 35.7, 28.9, 27.3, 21.4 ppm.

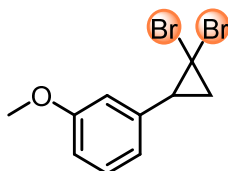
#### 1-(2,2-Dibromocyclopropyl)-2-methoxybenzene (1n)



General procedure A was applied.

Yellow oil (4.8 g, 78% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.29 (m, 1H), 6.99 – 6.82 (m, 3H), 3.95 (s, 3H), 3.04 – 2.92 (m, 1H), 2.10 (dd,  $J$  = 10.4, 7.6 Hz, 1H), 1.98 (dd,  $J$  = 8.6, 7.6 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  159.3, 128.9, 128.4, 125.5, 120.1, 110.4, 55.8, 32.1, 29.0, 26.7 ppm.

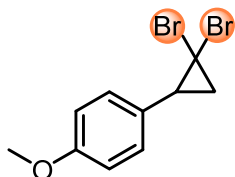
#### 1-(2,2-Dibromocyclopropyl)-3-methoxybenzene (1o)



General procedure A was applied.

Yellow oil (4.6 g, 75% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 (t,  $J$  = 7.9 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.81 (t,  $J$  = 2.3 Hz, 1H), 3.84 (s, 3H), 2.95 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.14 (dd,  $J$  = 10.5, 7.7 Hz, 1H), 2.01 (t,  $J$  = 8.0 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.4, 137.4, 129.2, 121.2, 114.7, 112.9, 55.2, 35.8, 28.3, 27.2 ppm.

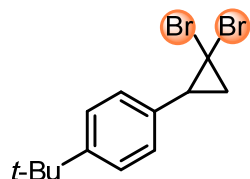
#### 1-(2,2-Dibromocyclopropyl)-4-methoxybenzene (1p)



General procedure A was applied.

Yellow oil (920 mg, 69% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.02 (m, 2H), 7.00 – 6.80 (m, 2H), 3.82 (s, 3H), 2.91 (ddd,  $J$  = 10.6, 8.1, 2.2 Hz, 1H), 2.11 (ddd,  $J$  = 10.1, 7.7, 2.0 Hz, 1H), 1.96 (td,  $J$  = 8.0, 2.2 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.0, 130.0, 128.1, 113.7, 55.2, 35.3, 29.3, 27.3 ppm.

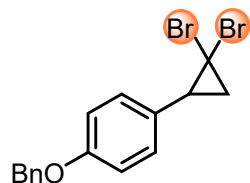
**1-(*tert*-Butyl)-4-(2,2-dibromocyclopropyl)benzene (1q)**



General procedure A was applied.

White solid (5.1 g, 77% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.34 (m, 2H), 7.21 – 7.16 (m, 2H), 2.92 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.12 (dd,  $J$  = 10.6, 7.7 Hz, 1H), 1.99 (t,  $J$  = 8.0 Hz, 1H), 1.33 (s, 9H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  150.6, 133.0, 128.5, 125.2, 35.6, 34.6, 31.3, 28.8, 27.4 ppm.

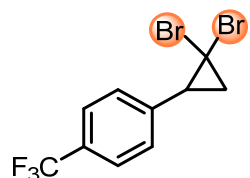
**1-(Benzyloxy)-4-(2,2-dibromocyclopropyl)benzene (1r)**



General procedure A was applied.

White solid (6.7 g, 88% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.53 – 7.49 (m, 2H), 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 1H), 7.25 – 7.22 (m, 2H), 7.06 – 7.02 (m, 2H), 5.11 (s, 2H), 2.96 (dd,  $J$  = 10.6, 8.2 Hz, 1H), 2.15 (dd,  $J$  = 10.6, 7.7 Hz, 1H), 2.01 (t,  $J$  = 8.0 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.2, 136.8, 129.9, 128.5, 128.3, 127.9, 127.4, 114.5, 69.9, 35.2, 29.2, 27.2 ppm.

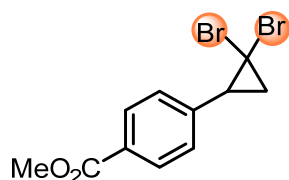
**1-(2,2-Dibromocyclopropyl)-4-(trifluoromethyl)benzene (1s)**



General procedure A was applied.

Yellow oil (4.9 g, 71% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.62 (d,  $J$  = 8.1 Hz, 2H), 7.41 – 7.36 (m, 2H), 3.06 – 2.95 (m, 3H), 2.21 (dd,  $J$  = 10.5, 7.9 Hz, 1H), 2.06 (t,  $J$  = 8.1 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  139.9, 129.7 (q,  $J$  = 33.1 Hz), 129.3, 125.3 (q,  $J$  = 3.8 Hz), 124.1 (q,  $J$  = 272.1 Hz), 35.5, 27.5, 27.0 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.36 ppm.

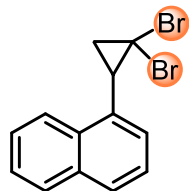
**Methyl 4-(2,2-dibromocyclopropyl)benzoate (1t)**



General procedure B was applied.

White solid (5.0 g, 76% yield);  $R_f$  = 0.5 (50:1 hexanes/EA); m.p. 54.2–54.6 °C; IR (film)  $\nu_{\text{max}}$  2965, 1969, 1752, 1365, 806, 676, 605  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.01 (dd,  $J$  = 8.4, 2.7 Hz, 2H), 7.30 (dd,  $J$  = 8.3, 3.1 Hz, 2H), 3.89 (s, 3H), 2.97 (dd,  $J$  = 10.5, 8.3 Hz, 1H), 2.16 (m, 1H), 2.09 – 1.98 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  166.5, 140.9, 129.4, 129.3, 128.8, 52.0, 35.6, 27.4, 27.3 ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{Br}_2\text{O}_2$  331.90475; Found 331.90479.

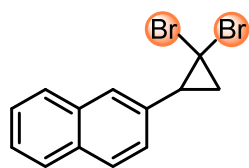
**1-(2,2-Dibromocyclopropyl)naphthalene (1u)**



General procedure B was applied.

White solid (5.8 g, 89% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.28 (m, 1H), 7.93 (m, 1H), 7.85 (m, 1H), 7.72 – 7.64 (m, 1H), 7.62 – 7.55 (m, 1H), 7.44 (m, 1H), 7.22 (m, 1H), 3.30 (t,  $J$  = 9.5 Hz, 1H), 2.34 – 2.30 (m, 1H), 2.22 (td,  $J$  = 8.1, 2.6 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  133.7, 133.5, 133.2, 128.6, 128.4, 126.8, 126.2, 125.7, 125.2, 124.7, 34.8, 28.3, 27.0 ppm.

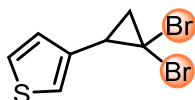
**2-(2,2-Dibromocyclopropyl)naphthalene (1v)**



General procedure B was applied.

White solid (5.1 g, 78% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.90 (m, 3H), 7.71 (m, 1H), 7.62 – 7.46 (m, 3H), 3.18 (t,  $J$  = 9.3 Hz, 1H), 2.23 (t,  $J$  = 8.6 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  133.8, 133.3, 132.9, 128.1, 128.0, 128.0, 127.8, 127.3, 126.5, 126.3, 36.3, 28.7, 27.5 ppm.

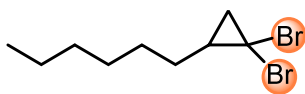
### 3-(2,2-Dibromocyclopropyl)thiophene (1w)



General procedure B was applied.

Yellow oil (5.0 g, 89% yield); IR (film)  $\nu_{\text{max}}$  3246, 2769, 1530, 848  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (dd,  $J$  = 5.0, 3.0 Hz, 1H), 7.10 (dt,  $J$  = 3.0, 1.1 Hz, 1H), 7.04 (dd,  $J$  = 5.0, 1.3 Hz, 1H), 2.89 (ddd,  $J$  = 10.5, 8.1, 0.9 Hz, 1H), 2.16 (dd,  $J$  = 10.5, 7.6 Hz, 1H), 1.95 – 1.90 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.5, 128.1, 125.6, 123.3, 31.5, 28.8, 28.4 ppm; HRMS (EI) Calcd for  $\text{C}_7\text{H}_6\text{Br}_2\text{S}$  279.85570; Found 279.85578.

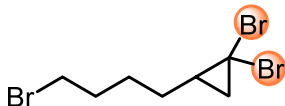
### 1,1-Dibromo-2-hexylcyclopropane (1x)



General procedure B was applied.

Colorless oil (2.3 g, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  1.74 (dd,  $J$  = 10.2, 7.1 Hz, 1H), 1.65 – 1.51 (m, 3H), 1.50 – 1.40 (m, 2H), 1.39 – 1.25 (m, 6H), 1.19 (t,  $J$  = 7.4 Hz, 1H), 0.90 (t,  $J$  = 7.0 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  32.6, 31.7, 31.5, 29.7, 28.9, 28.5, 28.3, 22.6, 14.1 ppm.

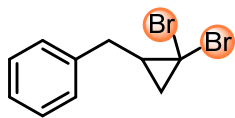
### 1,1-Dibromo-2-(4-bromobutyl)cyclopropane (1y)



General procedure A was applied.

Yellow oil (5.3 g, 79% yield); IR (film)  $\nu_{\text{max}}$  3346, 3105, 2933, 651  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.50 – 3.34 (m, 2H), 1.92 (m, 2H), 1.74 (m, 1H), 1.70 – 1.39 (m, 5H), 1.25 – 1.16 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  33.7, 32.4, 31.9, 31.2, 29.3, 28.6, 27.1 ppm; HRMS (EI) Calcd for  $\text{C}_7\text{H}_{11}\text{Br}_3$  331.84109; Found 331.84116.

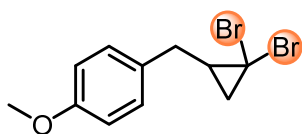
### ((2,2-Dibromocyclopropyl)methyl)benzene (1z)



General procedure B was applied.

Colorless oil (4.4 g, 77% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.30 (m, 4H), 7.29 (d,  $J$  = 7.1 Hz, 1H), 3.06 (dd,  $J$  = 15.3, 6.7 Hz, 1H), 2.79 (dd,  $J$  = 15.4, 6.2 Hz, 2H), 1.89 (qd,  $J$  = 10.4, 4.9 Hz, 1H), 1.42 (t,  $J$  = 6.6 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  139.2, 128.6, 128.3, 126.5, 38.1, 31.9, 29.0, 28.4 ppm.

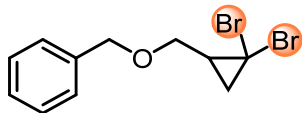
**1-((2,2-Dibromocyclopropyl)methyl)-4-methoxybenzene (1a')**



General procedure B was applied.

Colorless oil (5.3 g, 83% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.26 – 7.20 (m, 2H), 6.90 (dd,  $J$  = 9.2, 2.4 Hz, 2H), 3.82 (s, 3H), 3.01 – 2.92 (m, 1H), 2.76 – 2.69 (m, 1H), 1.92 – 1.80 (m, 2H), 1.39 (td,  $J$  = 6.2, 5.7, 1.8 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  158.2, 131.2, 129.3, 114.0, 55.2, 37.3, 32.1, 29.1, 28.4 ppm.

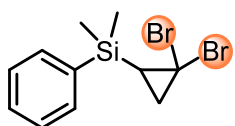
**((2,2-Dibromocyclopropyl)methoxy)methylbenzene (1b')**



General procedure B was applied.

Colorless oil (5.0 g, 79% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 4.65 – 4.56 (m, 2H), 3.67 – 3.55 (m, 2H), 1.96 (m, 1H), 1.82 (dd,  $J$  = 10.5, 7.4 Hz, 1H), 1.38 (t,  $J$  = 7.6 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.9, 128.4, 127.8 (d,  $J$  = 2.6 Hz), 72.9, 71.5, 30.2, 26.6, 26.1 ppm.

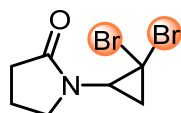
**(2,2-Dibromocyclopropyl)dimethyl(phenyl)silane (1c')**



General procedure B was applied.

Colorless oil (4.1 g, 61% yield); IR (film)  $\nu_{\max}$  2984, 1846, 1220, 887  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.69 – 7.62 (m, 2H), 7.48 – 7.42 (m, 3H), 1.95 (dd,  $J$  = 12.5, 6.0 Hz, 1H), 1.62 (dd,  $J$  = 10.0, 6.0 Hz, 1H), 0.55 (s, 3H), 0.44 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.2, 133.9, 129.4, 127.9, 26.2, 25.4, 22.5, -2.8, -2.9 ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{Si}$  331.92315; Found 331.92307.

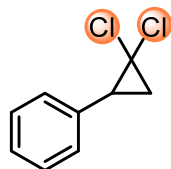
**1-(2,2-Dibromocyclopropyl)pyrrolidin-2-one (1d')**



General procedure B was applied.

Yellow oil (4.0 g, 72% yield); IR (film)  $\nu_{\max}$  3320, 1762, 1254, 884  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  3.48 (dt,  $J$  = 9.0, 6.7 Hz, 1H), 3.42 – 3.34 (m, 1H), 3.15 (dd,  $J$  = 9.7, 6.4 Hz, 1H), 2.38 (td,  $J$  = 7.9, 2.6 Hz, 2H), 2.19 (dd,  $J$  = 9.0, 6.3 Hz, 1H), 2.11 – 1.92 (m, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  176.2, 47.6, 40.9, 31.3, 28.0, 25.4, 18.2 ppm; HRMS (EI) Calcd for  $\text{C}_7\text{H}_9\text{Br}_2\text{NO}$  280.90509; Found 280.90492.

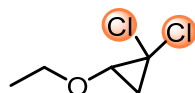
**(2,2-Dichlorocyclopropyl)benzene (1e')**



General procedure C was applied.

Colorless oil (3.1 g, 82% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.38 (td,  $J$  = 7.9, 7.5, 2.1 Hz, 2H), 7.33 (td,  $J$  = 7.1, 1.9 Hz, 1H), 7.30 – 7.26 (m, 2H), 2.94 (m, 1H), 2.00 (m, 1H), 1.89 (m, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  134.6, 128.8, 128.3, 127.6, 60.7, 35.4, 25.7 ppm.

**1,1-Dibromo-2-hexylcyclopropane (1f')**

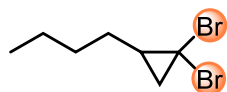


General procedure C was applied.

Colorless oil (2.1 g, 67% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  3.85 – 3.78 (m, 1H), 3.77 – 3.67 (m, 1H), 3.53 (ddd,  $J$  = 8.1, 5.0, 1.1 Hz, 1H), 1.65 (td,  $J$  = 8.4, 1.2 Hz, 1H), 1.51 (ddd,  $J$  = 8.5, 5.1, 1.4

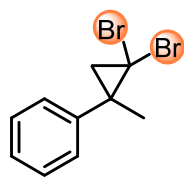
Hz, 1H), 1.28 (td,  $J = 7.1, 1.2$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  67.2, 63.1, 29.7, 27.9, 14.9 ppm.

**1,1-Dibromo-2-butylcyclopropane (1g')**



Yellow oil (2.2 g, 86% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  1.74 (dd,  $J = 10.2, 7.0$  Hz, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.50 (m, 2H), 1.49 – 1.42 (m, 2H), 1.41 – 1.36 (m, 2H), 1.19 (dd,  $J = 7.8, 7.1$  Hz, 1H), 0.93 (t,  $J = 7.3$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  32.3, 31.4, 30.5, 29.7, 28.5, 22.4, 14.0 ppm.

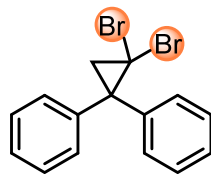
**(2,2-Dibromo-1-methylcyclopropyl)benzene (1h')**



General procedure B was applied.

Yellow oil (3.9 g, 68% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.39 (td,  $J = 7.5, 0.8$  Hz, 2H), 7.36 – 7.30 (m, 3H), 2.20 (d,  $J = 7.5$  Hz, 1H), 1.81 (d,  $J = 7.6$  Hz, 1H), 1.75 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  142.3, 128.4, 128.3, 127.2, 36.7, 35.7, 33.7, 27.7 ppm.

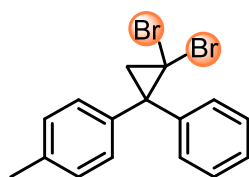
**(2,2-Dibromocyclopropane-1,1-diyl)dibenzene (1j')**



General procedure B was applied.

White solid (5.3 g, 75% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.50 (m, 4H), 7.32 (m, 4H), 7.25 – 7.20 (m, 2H), 2.48 (s, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  141.9, 129.2, 128.4, 127.3, 45.1, 34.5, 33.9 ppm.

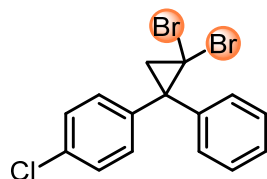
**1-(2,2-Dibromo-1-phenylcyclopropyl)-4-methylbenzene (1k')<sup>[7]</sup>**



General procedure B was applied.

White solid (5.6 g, 77% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.51 (m, 2H), 7.44 – 7.41 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.15 (dd,  $J$  = 7.6, 1.2 Hz, 2H), 2.47 (d,  $J$  = 1.0 Hz, 2H), 2.31 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  142.1, 139.0, 137.1, 129.2, 129.1, 129.0, 128.4, 127.2, 44.8, 34.5, 34.2, 21.1 ppm.

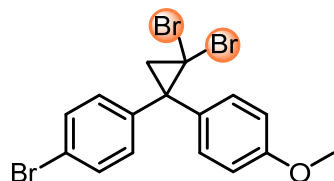
**1-Chloro-4-(2,2-dibromo-1-phenylcyclopropyl)benzene (1l')**



General procedure B was applied.

White solid (5.9 g, 77% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.51 – 7.38 (m, 4H), 7.36 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 2.49 (dd,  $J$  = 7.6, 1.5 Hz, 1H), 2.44 (dd,  $J$  = 7.5, 1.4 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  141.4, 140.4, 133.3, 130.6, 129.1, 128.7, 128.6, 127.5, 44.4, 34.6, 33.3 ppm.

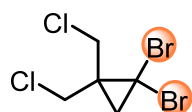
**1-Bromo-4-(2,2-dibromo-1-(4-methoxyphenyl)cyclopropyl)benzene (1m')**



General procedure B was applied.

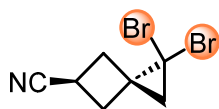
White solid (5.8 g, 63% yield);  $R_f$  = 0.5 (50:1 hexanes/EA); m.p. 121.9–122.4 °C; IR (film)  $\nu_{max}$  3108, 2653, 1657, 859, 643  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.85 – 7.34 (m, 6H), 7.00 – 6.69 (m, 2H), 3.77 (s, 3H), 2.42 (d,  $J$  = 10.4 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  158.9, 141.2, 133.6, 131.6, 130.8, 130.2, 121.3, 113.9, 55.2, 43.9, 34.6, 33.8 ppm; HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{13}\text{Br}_3\text{O}$  457.85165; Found 457.85157.

**1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (1n')**



From commercial source.

**(3*r*,5*r*)-1,1-Dibromospiro[2.3]hexane-5-carbonitrile (1o'-*trans*)**

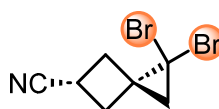


General procedure B was applied.

*trans* means the cyano group and the dibrominated carbon are on the opposite sides of the cyclobutane ring.

White solid (2.2 g, total 83% yield);  $R_f = 0.5$  (20:1 hexanes/AcOEt);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.26 (tt,  $J = 9.5, 6.4$  Hz, 1H), 2.90 – 2.75 (m, 2H), 2.61 – 2.47 (m, 2H), 1.74 (s, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  121.9, 33.8, 33.1, 33.0, 31.8, 16.3 ppm.

**(3s,5s)-1,1-Dibromospiro[2.3]hexane-5-carbonitrile (10'-cis)**

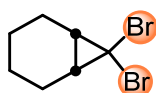


General procedure B was applied.

*cis* means the cyano group and the dibrominated carbon are on the same side of the cyclobutane ring.

White solid (2.2 g, total 83% yield);  $R_f = 0.3$  (20:1 hexanes/AcOEt);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.25 (ttd,  $J = 9.3, 8.0, 1.6$  Hz, 1H), 2.87 (ddt,  $J = 11.7, 8.0, 1.4$  Hz, 2H), 2.55 – 2.34 (m, 2H), 1.72 (d,  $J = 1.5$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  121.2, 34.1, 33.5, 31.8, 31.3, 14.9 ppm.

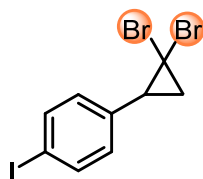
**1-(2,2,7,7-Dibromobicyclo[4.1.0]heptane (1p')**



General procedure B was applied.

Yellow oil (3.6 g, 92% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  2.00 (dq,  $J = 13.9, 6.5$  Hz, 2H), 1.83 (dd,  $J = 5.9, 2.7$  Hz, 2H), 1.57 (dt,  $J = 14.1, 6.0$  Hz, 2H), 1.42 – 1.32 (m, 2H), 1.27 – 1.12 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  40.8, 27.0, 20.7, 20.1 ppm.

**Dibromocyclopropyl)-4-iodobenzene**

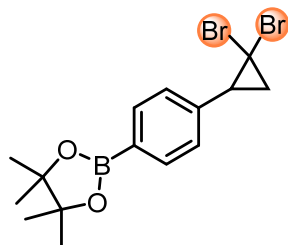


General procedure B was applied.

Yellow solid (6.8 g, 85% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.7 – 7.6 (m, 2H), 7.0 (dd,  $J =$

8.4, 2.5 Hz, 2H), 2.9 (dd,  $J = 10.5, 8.2$  Hz, 1H), 2.1 (dd,  $J = 10.5, 7.7$  Hz, 1H), 2.0 (t,  $J = 8.1$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  137.4, 135.7, 130.8, 93.2, 35.4, 27.6, 27.3 ppm.

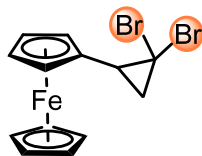
**2-(4-(2,2-Dibromocyclopropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



General procedure B was applied.

Yellow oil (6.6 g, 83% yield);  $R_f = 0.5$  (50:1 hexanes/AcOEt); IR (film)  $\nu_{\max}$  3162, 2153, 1766, 962  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.80 (d,  $J = 7.7$  Hz, 2H), 7.28 – 7.24 (m, 2H), 2.97 (dd,  $J = 10.4, 8.4$  Hz, 1H), 2.19 – 2.10 (m, 1H), 2.05 (t,  $J = 8.1$  Hz, 1H), 1.35 (s, 12H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  139.0, 134.7, 128.2, 83.8, 36.0, 28.2, 27.2, 24.9 ppm; HRMS (EI) Calcd for  $\text{C}_{15}\text{H}_{19}\text{BBr}_2\text{O}_2$  399.98449; Found 399.98456.

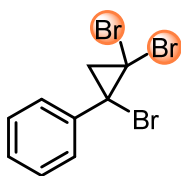
**(2,2-Dibromocyclopropyl)ferrocene**



General procedure B was applied.

Red solid (6.4 g, 84% yield);  $R_f = 0.4$  (50:1 hexanes/AcOEt); m.p. 63.4–64.2  $^{\circ}\text{C}$ ; IR (film)  $\nu_{\max}$  3965, 2106, 1763, 626  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  4.41 (dt,  $J = 2.6, 1.4$  Hz, 1H), 4.22 (td,  $J = 2.5, 1.2$  Hz, 1H), 4.18 (s, 5H), 4.14 (td,  $J = 2.5, 1.2$  Hz, 1H), 4.00 (dt,  $J = 2.6, 1.4$  Hz, 1H), 2.64 (dd,  $J = 10.6, 8.1$  Hz, 1H), 2.07 (dd,  $J = 10.6, 7.5$  Hz, 1H), 1.65 (t,  $J = 7.8$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  83.4, 69.6, 68.7, 68.6, 67.7, 67.4, 32.4, 30.3, 28.4 ppm; HRMS (EI) Calcd for  $\text{C}_{13}\text{H}_{12}\text{Br}_2\text{Fe}$  381.86552; Found 381.86549.

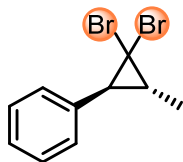
**(1,2,2-Tribromocyclopropyl)benzene**



General procedure B was applied.

Yellow oil (5.0 g, 71% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.50 – 7.45 (m, 1H), 7.42 – 7.30 (m, 2H), 2.52 (dt,  $J$  = 9.3, 1.2 Hz, 1H), 2.26 (dt,  $J$  = 9.3, 1.3 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  140.0, 129.1, 128.9, 128.6, 42.9, 37.1, 31.8 ppm.

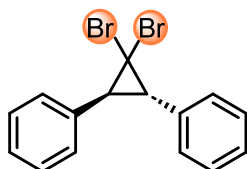
**2,2-Dibromo-3-methylcyclopropyl)benzene**



General procedure B was applied.

White solid (4.3 g, 73% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.44 – 7.36 (m, 3H), 7.32 – 7.28 (m, 2H), 2.52 (d,  $J$  = 8.4 Hz, 1H), 2.02 (dq,  $J$  = 8.5, 6.2 Hz, 1H), 1.52 (dd,  $J$  = 6.3, 1.1 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  136.3, 128.6, 128.2, 127.4, 42.2, 38.9, 30.2, 17.4 ppm.

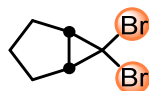
**(3,3-Dibromocyclopropane-1,2-diyl)dibenzene**



General procedure B was applied.

White solid (3.6 g, 93% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.43 (m, 10H), 3.36 (s, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  136.0, 128.9, 128.5, 127.9, 40.1, 36.8 ppm.

**6,6-Dibromobicyclo[3.1.0]hexane<sup>[8]</sup>**



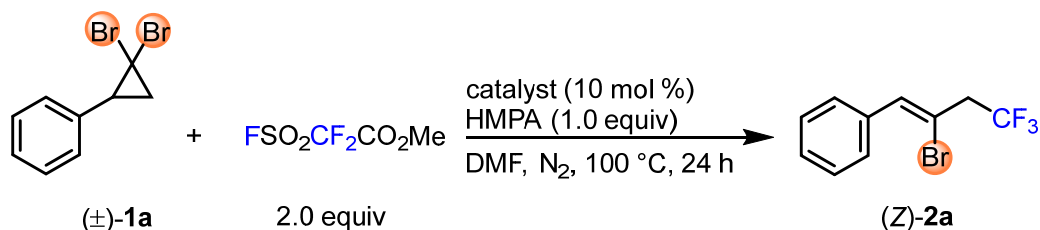
General procedure B was applied.

Yellow oil (3.7 g, 78% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  2.24 (dd,  $J$  = 4.2, 1.7 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.88 (ddd,  $J$  = 13.9, 8.7, 4.4 Hz, 1H), 1.78 – 1.67 (m, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz, Chloroform-*d*)  $\delta$  40.8, 39.9, 29.5, 25.9 ppm.

## 4 Reactions of *gem*-dihalocyclopropanes with Chen's reagent

### 4.1 Optimization of the conditions for the reaction of **1a** with Chen's reagent

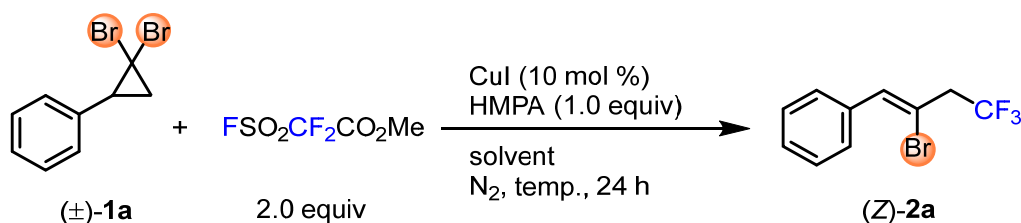
**Table S1** Effect of catalyst.



| Entry | Catalyst | Yield (%) <sup>a</sup> | Entry | Catalyst          | Yield (%) <sup>a</sup> |
|-------|----------|------------------------|-------|-------------------|------------------------|
| 1     | CuCl     | 57                     | 6     | CuOAc             | 12                     |
| 2     | CuBr     | 69                     | 7     | CuOTf             | trace                  |
| 3     | CuI      | 88                     | 8     | CuCl <sub>2</sub> | 0                      |
| 4     | CuCN     | 36                     | 9     | CuBr <sub>2</sub> | 0                      |
| 5     | CuTc     | 22                     | 10    | —                 | 0                      |

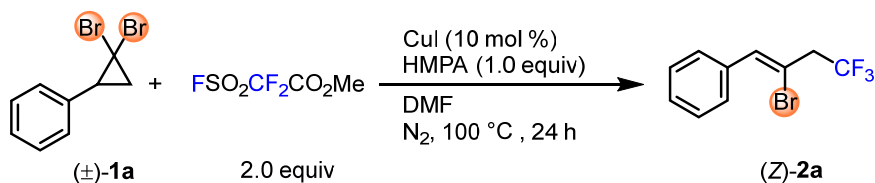
<sup>a</sup> Yield was based on **1a**.

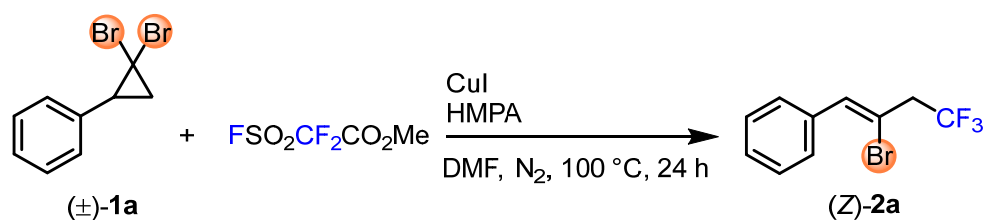
**Table S2** Effect of solvent.



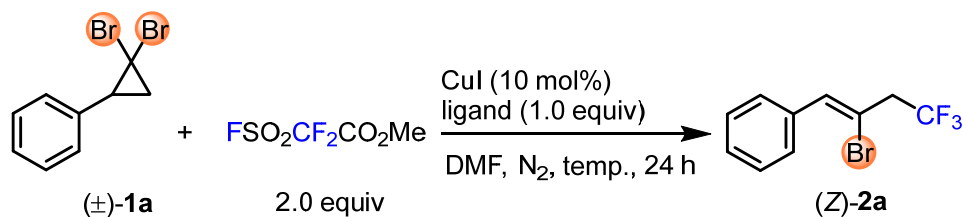
| Entry | Solvent            | Temp. (°C) | Yield (%) <sup>a</sup> | Entry | Solvent            | Temp. (°C) | Yield (%) <sup>a</sup> |
|-------|--------------------|------------|------------------------|-------|--------------------|------------|------------------------|
| 1     | benzene            | 80         | 0                      | 9     | EA                 | 80         | 0                      |
| 2     | toluene            | 110        |                        | 10    | acetone            | 60         | 0                      |
| 3     | DCM                | 40         |                        | 11    | HMPA               | 120        | 16                     |
| 4     | DCE                | 80         |                        | 12    | DMSO               | 100        | 31                     |
| 5     | THF                | 60         |                        | 13    | DMI                | 100        | 25                     |
| 6     | DME                | 80         |                        | 14    | DMF                | 80         | 88                     |
| 7     | 1,4-dioxane        | 100        |                        | 15    | CH <sub>3</sub> OH | 65         | 0                      |
| 8     | CH <sub>3</sub> CN | 80         |                        |       |                    |            |                        |

<sup>a</sup> Yield was based on **1a**.

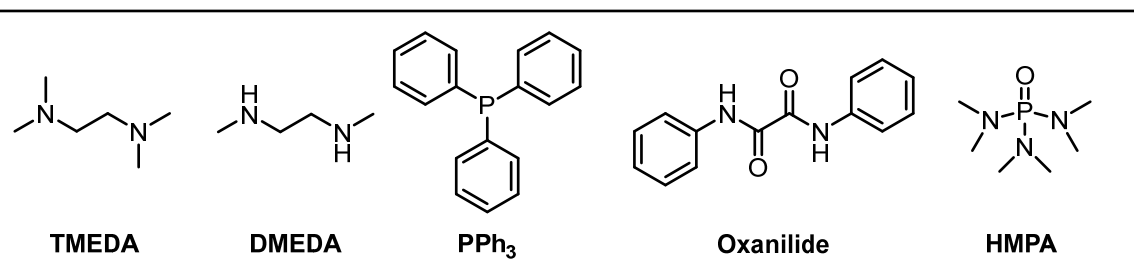


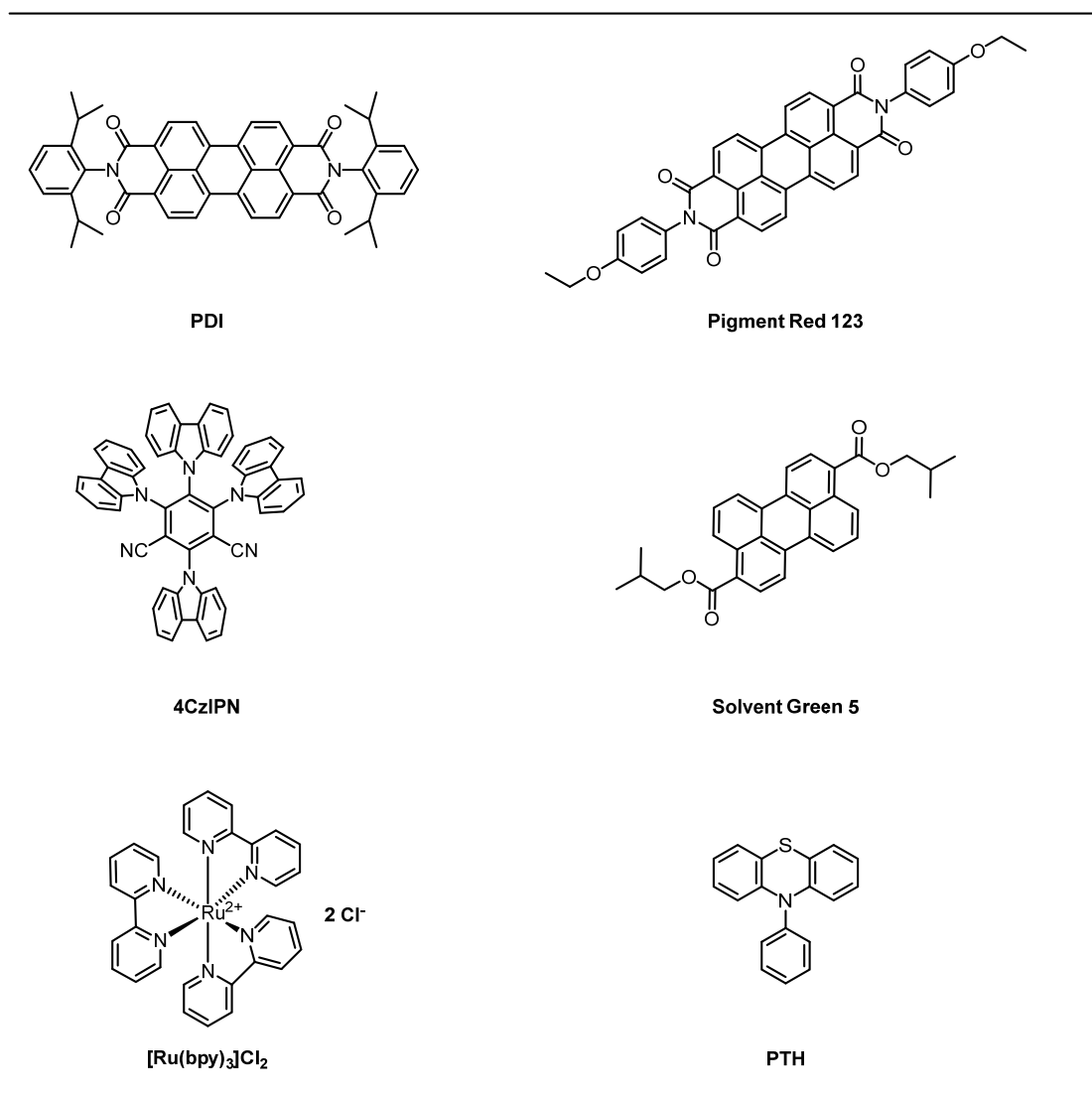
**Table S3** Effect of the molar ratio of reactants.

| Entry | Chen's reagent :<br>HMPA : CuI | Yield (%) <sup>a</sup> | Entry | Chen's reagent :<br>HMPA : CuI | Yield (%) <sup>a</sup> |
|-------|--------------------------------|------------------------|-------|--------------------------------|------------------------|
| 1     | 2.0 : 1.0 : 0.0                | 0                      | 9     | 2.0 : 1.0 : 0.1                | 88                     |
| 2     | 2.0 : 1.0 : 0.05               | 60                     | 10    | 2.0 : 2.0 : 0.1                | 79                     |
| 3     | 2.0 : 1.0 : 0.1                | 88                     | 11    | 2.0 : 3.0 : 0.1                | 77                     |
| 4     | 2.0 : 1.0 : 0.5                | 74                     | 11    | 1.0 : 1.0 : 0.1                | 70                     |
| 5     | 2.0 : 1.0 : 1.0                | 58                     | 12    | 1.5 : 1.0 : 0.1                | 81                     |
| 6     | 2.0 : 0.0 : 0.1                | 10                     | 13    | 2.0 : 1.0 : 0.1                | 88                     |
| 7     | 2.0 : 0.1 : 0.1                | 30                     | 14    | 3.0 : 1.0 : 0.1                | 80                     |
| 8     | 2.0 : 0.5 : 0.1                | 62                     |       |                                |                        |

<sup>a</sup> Yield was based on limited reactant.**Table S4** Effect of the ligand and temperature.

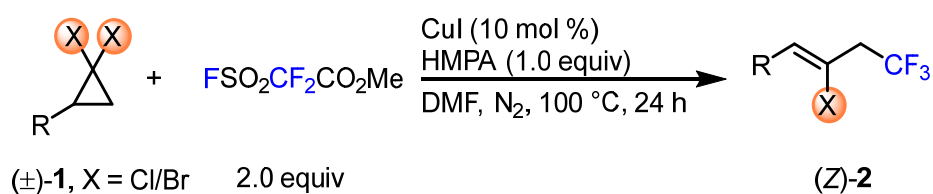
| Entry | Temp. (°C) | Ligand           | Yield (%) <sup>a</sup> |
|-------|------------|------------------|------------------------|
| 1     |            | —                | 10                     |
| 2     |            | TMEDA            | 28                     |
| 3     |            | DMEDA            | 19                     |
| 4     | 100        | Oxanilide        | 22                     |
| 5     |            | HMPA             | 88                     |
| 6     |            | PPh <sub>3</sub> | 62                     |
| 7     | 60         |                  | 0                      |
| 8     | 80         |                  | 0                      |
| 9     | 100        | HMPA             | 88                     |
| 10    | 120        |                  | 67                     |

<sup>a</sup> Yield was based on **1a**.**Fig. S5** | Structures of ligands used in screening.



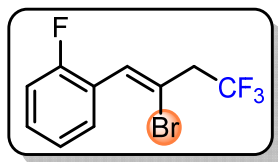
**Fig. S6** | Structures of photocatalysts used in screening.

## 4.2 Typical procedure



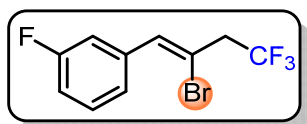
A dry 50 mL Schlenk tube charged with a stirring bar was evacuated and backfilled with N<sub>2</sub> (three times). Copper(I) iodide (20 mg, 0.1 mmol, 10 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv) and anhydrous DMF (4.0 mL) were added under N<sub>2</sub> atmosphere. After the mixture had been stirred for 15 min at room temperature, *gem*-dihalocyclopropane (1.0 mmol, 1.0 equiv), FSO<sub>2</sub>CF<sub>2</sub>COOMe (384 mg,





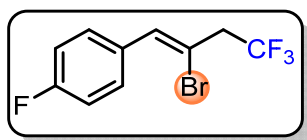
Colorless oil (200 mg, 71% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3022, 1687, 1430, 1358, 1032, 877, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.83 (td,  $J = 7.3, 1.4$  Hz, 1H), 7.33 (m, 1H), 7.17 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.10 – 7.05 (m, 2H), 3.46 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  160.0 (d,  $J = 249.3$  Hz), 130.3 (d,  $J = 8.5$  Hz), 129.9 (d,  $J = 2.6$  Hz), 128.2 (d,  $J = 4.9$  Hz), 124.8 (q,  $J = 278.2$  Hz), 123.7 (d,  $J = 3.7$  Hz), 123.1 (d,  $J = 13.4$  Hz), 115.4 (d,  $J = 21.6$  Hz), 114.6, 46.9 (q,  $J = 30.4$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.93, -114.48 ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{BrF}_4$  281.96673; Found 281.96635.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-3-fluorobenzene (2c)**



Colorless oil (192 mg, 68% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3028, 1652, 1522, 1263, 1135, 1029, 825  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.42 – 7.30 (m, 3H), 7.04 (td,  $J = 7.5, 2.3$  Hz, 1H), 6.96 (s, 1H), 3.43 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  162.5 (d,  $J = 245.8$  Hz), 136.9 (d,  $J = 8.0$  Hz), 133.9, 129.8 (d,  $J = 8.3$  Hz), 124.9 (d,  $J = 3.0$  Hz), 124.8 (q,  $J = 278.2$  Hz), 115.6 (d,  $J = 17.1$  Hz), 115.5 (d,  $J = 15.2$  Hz), 113.1 (q,  $J = 3.1$  Hz), 47.0 (q,  $J = 30.5$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.93 (t,  $J = 9.7$  Hz), -112.63 ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{BrF}_4$  281.96673; Found 281.96625.

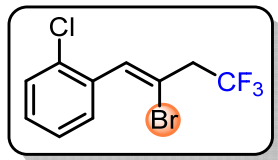
**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-fluorobenzene (2d)**



Colorless oil (197 mg, 70% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3019, 1666, 1347, 1251, 1140, 1031, 815, 757  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.68 – 7.53 (m, 2H), 7.13 – 7.02 (m, 2H), 6.95 (s, 1H), 3.42 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  162.5 (d,  $J = 249.3$  Hz), 141.9, 133.9, 130.9 (d,  $J = 8.2$  Hz), 124.9 (q,  $J = 278.3$  Hz), 115.3 (d,  $J = 21.6$  Hz), 111.7, 47.0 (q,

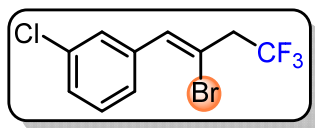
$J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, )  $\delta$  -65.03 (t,  $J = 9.9$  Hz), -111.82 ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{BrF}_4$  281.96673; Found 281.96643.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-2-chlorobenzene (2e)**



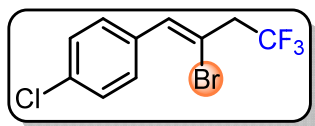
Colorless oil (197 mg, 66% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  2922, 1712, 1467, 1381, 1026, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.71 – 7.63 (m, 1H), 7.43 – 7.38 (m, 1H), 7.32 – 7.27 (m, 2H), 7.10 (s, 1H), 3.48 (q,  $J = 9.6$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  133.9, 133.5, 132.8, 130.6, 129.7, 129.3, 126.4, 124.8 (q,  $J = 278.3$  Hz), 115.0 (q,  $J = 3.7$  Hz), 46.4 (q,  $J = 30.5$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.88 (t,  $J = 9.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{BrClF}_3$  297.93718; Found 297.93635.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-3-chlorobenzene (2f)**



Colorless oil (209 mg, 70% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{\text{max}}$  3037, 1672, 1452, 1044, 764, 694  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.60 (m, 1H), 7.46 (ddd,  $J = 5.4, 3.9, 1.7$  Hz, 1H), 7.32 (td,  $J = 4.3, 1.9$  Hz, 2H), 6.94 (s, 1H), 3.43 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  136.7, 134.2, 133.7, 129.5, 128.8, 128.6, 127.1, 124.8 (q,  $J = 278.3$  Hz), 113.4 (q,  $J = 3.7$  Hz), 46.9 (q,  $J = 30.4$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.92 (t,  $J = 10.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{BrClF}_3$  297.93718; Found 297.93633.

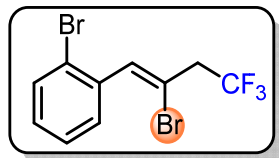
**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-chlorobenzene (2g)**



Colorless oil (218 mg, 73% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  2974, 1704, 1544, 1410, 1031, 686  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.55 (d,  $J = 8.5$  Hz, 2H), 7.36 (d,  $J = 8.5$  Hz, 2H), 6.94 (s, 1H), 3.43 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  134.4, 133.9, 133.3, 130.3, 128.5, 124.8 (q,  $J = 280.5$  Hz), 112.5 (q,  $J = 3.4$  Hz), 47.0 (q,  $J = 30.4$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz,

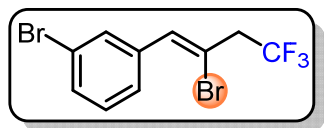
Chloroform-*d*)  $\delta$  -64.95 (t,  $J$  = 10.0 Hz) ppm; HRMS (EI) Calcd for C<sub>10</sub>H<sub>7</sub>BrClF<sub>3</sub> 297.93718; Found 297.93617.

**(Z)-1-Bromo-2-(2-bromo-4,4,4-trifluorobut-1-en-1-yl)benzene (2h)**



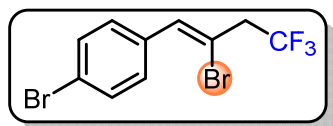
Colorless oil (270 mg, 79% yield);  $R_f$  = 0.7 (hexanes); IR (film)  $\nu_{max}$  3014, 1677, 1541, 1024, 688 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.61 (t,  $J$  = 8.5 Hz, 2H), 7.34 (t,  $J$  = 7.6 Hz, 1H), 7.21 (dd,  $J$  = 8.7, 6.8 Hz, 1H), 7.05 (s, 1H), 3.47 (q,  $J$  = 9.7 Hz, 2H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  135.9, 135.0, 132.5, 130.8, 129.8, 127.0, 124.8 (q,  $J$  = 278.5 Hz), 123.5, 114.9 (q,  $J$  = 4.5 Hz), 46.3 (q,  $J$  = 30.5 Hz) ppm; <sup>19</sup>F NMR (565 MHz, Chloroform-*d*)  $\delta$  -64.81 (t,  $J$  = 9.8 Hz) ppm; HRMS (EI) Calcd for C<sub>10</sub>H<sub>7</sub>Br<sub>2</sub>F<sub>3</sub> 341.88666; Found 341.88618.

**(Z)-1-Bromo-3-(2-bromo-4,4,4-trifluorobut-1-en-1-yl)benzene (2i)**



Colorless oil (280 mg, 82% yield);  $R_f$  = 0.7 (hexanes); IR (film)  $\nu_{max}$  3028, 1644, 1564, 1374, 1041, 678 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.73 (t,  $J$  = 1.9 Hz, 1H), 7.48 (m, 2H), 7.28 – 7.21 (m, 1H), 6.91 (s, 1H), 3.41 (q,  $J$  = 9.7 Hz, 2H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  137.0, 133.6, 131.7, 131.5, 129.8, 127.5, 124.8 (q,  $J$  = 278.9 Hz), 122.3, 113.5 (q,  $J$  = 2.1 Hz), 46.9 (q,  $J$  = 30.4 Hz) ppm; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -64.90 (t,  $J$  = 9.4 Hz) ppm; HRMS (EI) Calcd for C<sub>10</sub>H<sub>7</sub>Br<sub>2</sub>F<sub>3</sub> 341.88666; Found 341.88604.

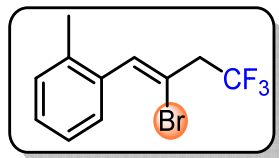
**(Z)-1-Bromo-4-(2-bromo-4,4,4-trifluorobut-1-en-1-yl)benzene (2j)**



Colorless oil (280 mg, 82% yield);  $R_f$  = 0.8 (hexanes); IR (film)  $\nu_{max}$  2975, 1743, 1420, 1403, 1071, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.41 (m, 4H), 6.92 (s, 1H), 3.42 (q,  $J$  = 9.7 Hz, 2H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  137.4, 133.9, 131.5, 130.5, 124.8 (q,  $J$  = 278.5 Hz),

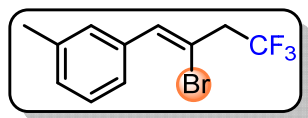
122.6, 112.7 (q,  $J = 3.2$  Hz), 47.0 (q,  $J = 30.4$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.93 (t,  $J = 9.7$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_7\text{Br}_2\text{F}_3$  341.88666; Found 341.88610.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-2-methylbenzene (2k)**



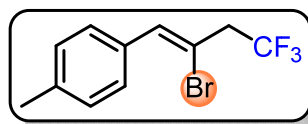
Colorless oil (189 mg, 68% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  3008, 1683, 1367, 1110, 1028, 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.44 – 7.38 (m, 1H), 7.28 – 7.17 (m, 4H), 7.03 (s, 1H), 3.46 (q,  $J = 9.7$  Hz, 2H), 2.26 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  136.1, 135.2, 135.0, 129.9, 128.7, 128.3, 125.6, 124.9 (q,  $J = 278.2$  Hz), 114.3 (q,  $J = 3.3$  Hz), 46.1 (q,  $J = 30.5$  Hz), 19.6 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.07 (t,  $J = 9.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{BrF}_3$  277.99180; Found 277.99194.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-3-methylbenzene (2l)**



Colorless oil (211 mg, 76% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  2988, 1710, 1462, 1363, 1017, 772  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.48 – 7.39 (m, 2H), 7.29 (t,  $J = 7.7$  Hz, 1H), 7.17 (m, 1H), 6.97 (s, 1H), 3.43 (q,  $J = 9.7$  Hz, 2H), 2.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  137.9, 135.2, 134.9, 129.6, 129.3, 128.1, 126.0, 125.0 (q,  $J = 278.4$  Hz), 111.4 (q,  $J = 3.3$  Hz), 47.0 (q,  $J = 30.3$  Hz), 21.4 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.01 (t,  $J = 9.5$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{BrF}_3$  277.99180; Found 277.99190.

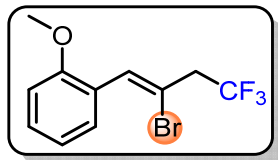
**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-methylbenzene (2m)**



Colorless oil (234 mg, 84% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{\text{max}}$  3015, 1688, 1355, 1263, 1024, 812, 756  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.55 – 7.50 (m, 2H), 7.23 – 7.17 (m, 2H), 6.96 (s, 1H), 3.42 (q,  $J = 9.5$  Hz, 2H), 2.37 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  138.6, 135.0, 132.1, 128.9, 128.9 125.0 (q,  $J = 278.2$  Hz), 110.7 (q,  $J = 3.4$  Hz), 47.1 (q,  $J = 30.3$  Hz), 21.3 ppm;  $^{19}\text{F}$

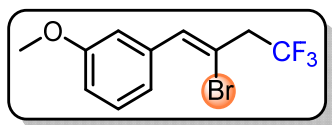
NMR (376 MHz, Chloroform-*d*)  $\delta$  -65.05 (t,  $J$  = 10.0 Hz) ppm; HRMS (EI) Calcd for C<sub>11</sub>H<sub>10</sub>BrF<sub>3</sub> 277.99180; Found 277.99179.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-2-methoxybenzene (2n)**



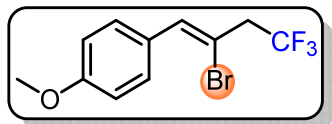
Colorless oil (168 mg, 57% yield);  $R_f$  = 0.7 (hexanes); IR (film)  $\nu_{max}$  3128, 1658, 1582, 1262, 1112, 1038, 778 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (ddd,  $J$  = 7.7, 1.8, 0.7 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.14 (s, 1H), 6.99 (td,  $J$  = 7.6, 1.1 Hz, 1H), 6.89 (dd,  $J$  = 8.3, 1.1 Hz, 1H), 3.84 (s, 3H), 3.45 (q,  $J$  = 9.8 Hz, 2H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  157.0, 131.0, 129.9, 129.8, 125.0 (q,  $J$  = 278.3 Hz), 124.1, 120.0, 112.1 (q,  $J$  = 3.3 Hz), 110.4, 55.5, 46.9 (q,  $J$  = 30.2 Hz) ppm; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -64.99 (t,  $J$  = 9.7 Hz) ppm; HRMS (EI) Calcd for C<sub>11</sub>H<sub>10</sub>BrF<sub>3</sub>O 293.98671; Found 293.98630.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-3-methoxybenzene (2o)**



Colorless oil (182 mg, 62% yield);  $R_f$  = 0.7 (hexanes); IR (film)  $\nu_{max}$  3074, 1652, 1577, 1259, 1114, 1041, 770 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 (t,  $J$  = 8.0 Hz, 1H), 7.20 (t,  $J$  = 2.1 Hz, 1H), 7.15 (m, 1H), 6.96 (s, 1H), 6.90 (ddd,  $J$  = 8.2, 2.6, 1.0 Hz, 1H), 3.83 (s, 3H), 3.42 (q,  $J$  = 9.7 Hz, 2H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  159.4, 136.2, 134.9, 125.0 (q,  $J$  = 278.5 Hz), 121.6, 114.4, 114.1, 111.9 (q,  $J$  = 3.5 Hz), 55.3, 47.1 (q,  $J$  = 30.2 Hz) ppm; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -64.98 (t,  $J$  = 9.6 Hz) ppm; HRMS (EI) Calcd for C<sub>11</sub>H<sub>10</sub>BrF<sub>3</sub>O 293.98671; Found 293.98632.

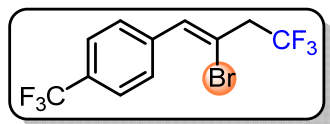
**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-methoxybenzene (2p)**



Colorless oil (185 mg, 63% yield);  $R_f$  = 0.7 (hexanes); IR (film)  $\nu_{max}$  3079, 1662, 1585, 1267, 1115, 1035, 786 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64 – 7.57 (m, 2H), 6.92 (m, 1H), 6.91 – 6.90 (m, 2H), 3.83 (s, 3H), 3.40 (q,  $J$  = 9.7 Hz, 2H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  159.7,

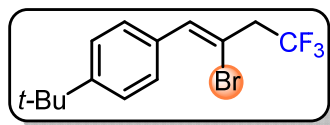
134.4, 130.5, 127.3, 125.1 (q,  $J = 278.4$  Hz), 113.6, 109.4 (q,  $J = 3.2$  Hz), 55.3, 47.1 (q,  $J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.12 (t,  $J = 9.9$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{BrF}_3\text{O}$  293.98671; Found 293.98630.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-(trifluoromethyl)benzene (2q)**



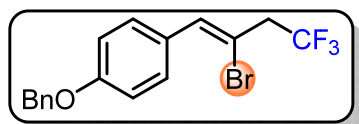
Colorless oil (199 mg, 60% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  3016, 2988, 1652, 1558, 1458, 1038, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.73 (d,  $J = 8.4$  Hz, 2H), 7.66 (d,  $J = 8.4$  Hz, 2H), 7.03 (s, 1H), 3.46 (q,  $J = 9.6$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  138.5, 133.8, 130.3 (q,  $J = 33.0$  Hz), 129.2, 125.2 (q,  $J = 3.9$  Hz), 124.8 (q,  $J = 279.7$  Hz), 124.1 (q,  $J = 273.7$  Hz), 114.3 (q,  $J = 3.4$  Hz), 46.9 (q,  $J = 30.6$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -62.66, -64.87 (t,  $J = 9.5$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_7\text{BrF}_6$  331.96353; Found 331.96340.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)-4-(*tert*-butyl)benzene (2r)**



Colorless oil (275 mg, 86% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{\text{max}}$  3016, 2988, 1652, 1558, 1458, 1038, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.66 – 7.51 (m, 2H), 7.44 – 7.38 (m, 2H), 6.96 (s, 1H), 3.42 (q,  $J = 9.7$  Hz, 2H), 1.35 (s, 9H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  151.8, 134.8, 132.0, 128.8, 125.2, 125.0 (q,  $J = 278.0$  Hz), 110.6 (q,  $J = 4.2$  Hz), 47.2 (q,  $J = 30.0$  Hz), 34.7, 31.2 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.06 (t,  $J = 9.9$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_{16}\text{BrF}_3$  320.03875; Found 320.03841.

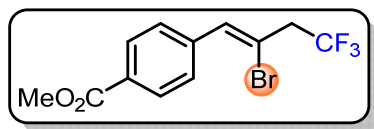
**(Z)-1-(Benzyloxy)-4-(2-bromo-4,4,4-trifluorobut-1-en-1-yl)benzene (2s)**



Colorless oil (311 mg, 84% yield);  $R_f = 0.6$  (hexanes); IR (film)  $\nu_{\text{max}}$  3078, 2826, 1672, 1581, 1442, 1026, 782  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.71 – 7.63 (m, 2H), 7.51 – 7.48 (m, 2H), 7.45 (ddd,  $J = 7.7, 6.4, 1.2$  Hz, 2H), 7.43 – 7.37 (m, 1H), 7.07 – 7.02 (m, 2H), 6.94 (s, 1H), 5.13 (s, 2H), 3.43 (q,  $J = 9.8$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  158.9, 136.7, 134.4, 130.5, 128.6,

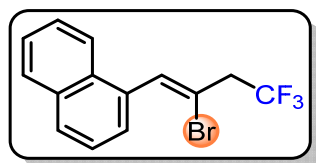
128.0, 127.4, 125.1 (q,  $J = 278.5$  Hz), 114.5, 109.5 (q,  $J = 4.3$  Hz), 70.0, 47.1 (q,  $J = 30.2$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.95 (t,  $J = 9.7$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{17}\text{H}_{14}\text{BrF}_3\text{O}$  370.01801; Found 370.01750.

**Methyl (Z)-4-(2-bromo-4,4,4-trifluorobut-1-en-1-yl)benzoate (2t)**



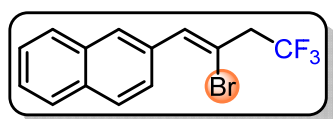
Colorless oil (184 mg, 57% yield);  $R_f = 0.5$  (50:1 hexanes/EA); IR (film)  $\nu_{\text{max}}$  3132, 2930, 1544, 1104, 767  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  8.07 – 7.96 (m, 2H), 7.65 (d,  $J = 8.2$  Hz, 2H), 7.03 (s, 1H), 3.93 (s, 3H), 3.45 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  166.6, 139.4, 134.2, 129.9, 129.5, 128.9, 124.8 (q,  $J = 276.6$  Hz), 114.0 (q,  $J = 2.6$  Hz), 52.2, 47.1 (q,  $J = 31.4$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.86 (t,  $J = 9.3$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{10}\text{BrF}_3\text{O}_2$  321.98163; Found 321.98159.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)naphthalene (2u)**



Colorless oil (207 mg, 66% yield);  $R_f = 0.7$  (hexanes); m.p. 66.5–67.1  $^{\circ}\text{C}$ ; IR (film)  $\nu_{\text{max}}$  3068, 3054, 2867, 1703, 1672, 1209, 867, 676, 481  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.95 – 7.82 (m, 3H), 7.61 (d,  $J = 7.1$  Hz, 1H), 7.59 – 7.48 (m, 3H), 7.45 (s, 1H), 3.58 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  134.2, 133.4, 133.0, 130.9, 128.7, 128.6, 126.8, 126.5, 126.1, 125.2, 125.0 (q,  $J = 278.4$  Hz), 124.1, 115.7 (q,  $J = 3.0$  Hz), 46.2 (q,  $J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.81 (t,  $J = 9.6$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_{10}\text{BrF}_3$  313.99180; Found 313.99155.

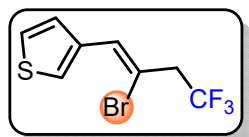
**(Z)-2-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)naphthalene (2v)**



White solid (239 mg, 76% yield);  $R_f = 0.7$  (hexanes); m.p. 67.1–67.6  $^{\circ}\text{C}$ ; IR (film)  $\nu_{\text{max}}$  3073, 3048, 2876, 1712, 1654, 872, 688, 476  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  8.15 – 8.06 (m, 1H), 7.90

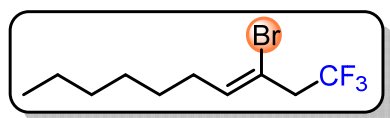
– 7.82 (m, 3H), 7.72 (dd,  $J = 8.5, 1.8$  Hz, 1H), 7.55 – 7.47 (m, 2H), 7.15 (s, 1H), 3.49 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  135.1, 133.1, 133.0, 132.4, 128.7, 128.3, 127.8, 127.7, 126.7, 126.4, 126.3, 125.0 (q,  $J = 278.1$  Hz), 112.0 (q,  $J = 3.6$  Hz), 47.1 (q,  $J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.89 (t,  $J = 9.6$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_{10}\text{BrF}_3$  313.99180; Found 313.99136.

**(Z)-3-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)thiophene (2w)**



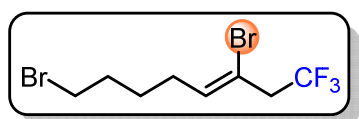
Colorless oil (170 mg, 63% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{\text{max}}$  3922, 3106, 2916, 1772, 1671, 876, 615, 453  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.83 (dt,  $J = 3.0, 0.9$  Hz, 1H), 7.47 (dd,  $J = 5.1, 1.3$  Hz, 1H), 7.33 (dd,  $J = 5.1, 3.0$  Hz, 1H), 7.00 (s, 1H), 3.41 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  135.8, 129.4, 128.3, 126.2, 125.0, 125.0 (q,  $J = 278.5$  Hz), 110.2 (q,  $J = 3.4$  Hz), 46.9 (q,  $J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.10 (t,  $J = 9.1$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_8\text{H}_6\text{BrF}_3\text{S}$  269.93257; Found 269.93263.

**(Z)-3-Bromo-1,1,1-trifluorodec-3-ene (2x)**



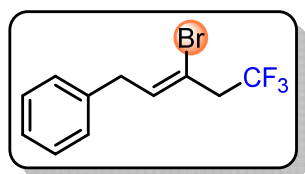
Colorless oil (207 mg, 76% yield);  $R_f = 0.9$  (hexanes); The assignment of the structure was based on NOE experiments. IR (film)  $\nu_{\text{max}}$  3075, 1641, 1443, 1376, 1179, 877  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  5.96 (t,  $J = 6.9$  Hz, 1H), 3.23 (q,  $J = 9.8$  Hz, 2H), 2.20 (q,  $J = 7.2$  Hz, 2H), 1.48 – 1.38 (m, 2H), 1.36 – 1.25 (m, 6H), 0.93 – 0.85 (m, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  137.5, 125.0 (q,  $J = 277.9$  Hz), 112.6 (q,  $J = 3.4$  Hz), 45.4 (q,  $J = 30.3$  Hz), 31.7, 31.6, 28.8, 27.9, 22.6, 14.0 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.39 (t,  $J = 10.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_{16}\text{BrF}_3$  272.03875; Found 272.03881.

**(Z)-3,8-Dibromo-1,1,1-trifluorooct-3-ene (2y)**



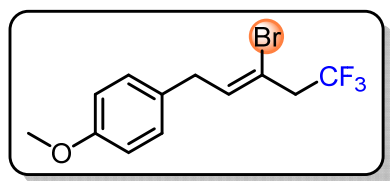
Colorless oil (270 mg, 84% yield);  $R_f = 0.9$  (hexanes); IR (film)  $\nu_{max}$  3122, 2963, 1657, 1488, 1326, 1237, 857  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  5.95 (t,  $J = 7.0$  Hz, 1H), 3.42 (t,  $J = 6.6$  Hz, 2H), 3.30 – 3.15 (m, 2H), 2.25 (q,  $J = 7.3$  Hz, 2H), 1.88 (dt,  $J = 15.1, 6.8$  Hz, 2H), 1.68 – 1.50 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  136.4, 124.9 (q,  $J = 278.3$  Hz), 113.5 (q,  $J = 3.6$  Hz), 45.3 (q,  $J = 30.3$  Hz), 33.3, 31.9, 30.7, 26.4 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.29 (t,  $J = 10.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_8\text{H}_{11}\text{Br}_2\text{F}_3$  321.91796; Found 321.91787.

**(Z)-(3-Bromo-5,5,5-trifluoropent-2-en-1-yl) benzene (2z)**



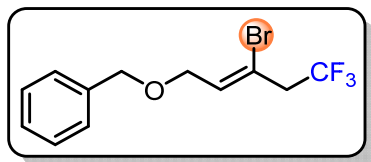
Colorless oil (170 mg, 61% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3044, 2874, 1684, 1251, 1114, 851, 662  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.35 (t,  $J = 7.6$  Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 6.18 (t,  $J = 7.0$  Hz, 1H), 3.61 (d,  $J = 7.0$  Hz, 2H), 3.31 (q,  $J = 9.8$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  138.2, 135.9, 128.7, 128.4, 126.6, 124.9 (q,  $J = 278.3$  Hz), 113.7 (q,  $J = 3.8$  Hz), 45.3 (q,  $J = 30.3$  Hz), 38.0 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.06 (t,  $J = 9.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{BrF}_3$  277.99180; Found 277.99179.

**(Z)-1-(3-Bromo-5,5,5-trifluoropent-2-en-1-yl)-4-methoxybenzene (2a')**



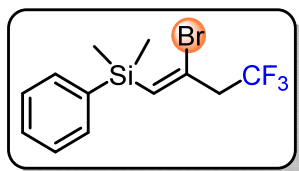
Colorless oil (250 mg, 81% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3057, 2901, 1645, 1209, 1184, 884, 775  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.15 (d,  $J = 8.6$  Hz, 2H), 6.88 (d,  $J = 8.6$  Hz, 2H), 6.15 (t,  $J = 7.0$  Hz, 1H), 3.81 (s, 3H), 3.54 (d,  $J = 7.0$  Hz, 2H), 3.30 (q,  $J = 9.8$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  158.3, 136.3, 130.1, 129.3, 124.9 (q,  $J = 278.1$  Hz), 114.0, 113.3 (q,  $J = 3.2$  Hz), 55.2, 45.3 (q,  $J = 30.4$  Hz), 37.1 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.09 (t,  $J = 9.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{12}\text{BrF}_3\text{O}$  308.00236; Found 308.00200.

**(Z)-(((3-Bromo-5,5,5-trifluoropent-2-en-1-yl)oxy)methyl)benzene (2b')**



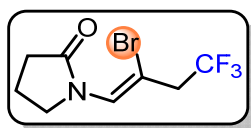
Colorless oil (256 mg, 83% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3098, 2876, 1673, 1255, 1174, 812, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.34 (m, 5H), 7.32 (td,  $J = 6.0, 2.5$  Hz, 1H), 6.25 (t,  $J = 5.4$  Hz, 1H), 4.54 (s, 2H), 4.20 (d,  $J = 5.5$  Hz, 2H), 3.27 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.6, 134.5, 128.5, 127.9, 124.6 (q,  $J = 278.8$  Hz), 114.0 (q,  $J = 4.9$  Hz), 72.8, 69.6, 45.3 (q,  $J = 30.7$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -65.02 (t,  $J = 9.7$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{12}\text{BrF}_3\text{O}$  308.00236; Found 308.00221.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)dimethyl(phenyl)silane (2c')**



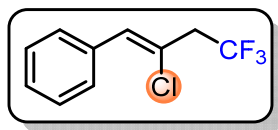
Colorless oil (254 mg, 79% yield);  $R_f = 0.8$  (hexanes); IR (film)  $\nu_{max}$  3085, 2946, 1722, 1244, 1209, 1074, 846, 667  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.59 – 7.52 (m, 2H), 7.39 (d,  $J = 6.3$  Hz, 3H), 6.51 (s, 1H), 3.34 (q,  $J = 9.9$  Hz, 2H), 0.51 (s, 6H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.1, 136.8, 133.8, 129.3, 127.9, 127.7 (q,  $J = 2.8$  Hz), 124.6 (q,  $J = 278.3$  Hz), 49.2 (q,  $J = 29.8$  Hz), -2.4 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -64.96 (t,  $J = 9.7$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{21}\text{H}_{14}\text{BrF}_3\text{Si}$  322.00002; Found 322.00013.

**(Z)-1-(2-Bromo-4,4,4-trifluorobut-1-en-1-yl)pyrrolidin-2-one (2d')**



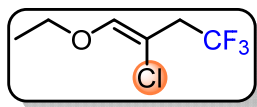
Colorless oil (89.4 mg, 33% yield);  $R_f = 0.4$  (10:1 hexanes/EA); IR (film)  $\nu_{max}$  1669, 1275, 1188, 831  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.21 (s, 1H), 3.84 (ddd,  $J = 9.1, 6.1, 1.9$  Hz, 2H), 3.02 (q,  $J = 10.0$  Hz, 2H), 2.51 (t,  $J = 8.1$  Hz, 2H), 2.15 (m, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  175.7, 133.4 (q,  $J = 3.3$  Hz), 123.1 (q,  $J = 277.5$  Hz), 47.3 (q,  $J = 6.8$  Hz), 31.9, 29.8, 29.7 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -65.10 (t,  $J = 9.9$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_8\text{H}_9\text{BrF}_3\text{NO}$  270.98196; Found 270.98203.

**(Z)-(2-Chloro-4,4,4-trifluorobut-1-en-1-yl) benzene (2e')**



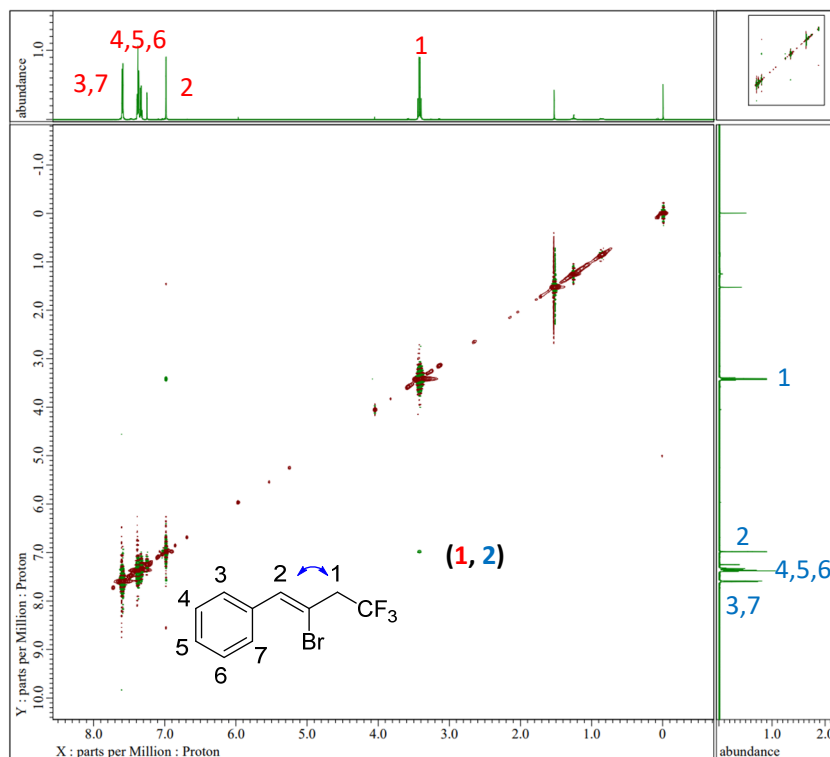
Colorless oil (172 mg, 78% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{max}$  3021, 1684, 1354, 1273, 1146, 1027, 823, 691  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.68 – 7.62 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 6.70 (s, 1H), 3.27 (q,  $J = 9.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  133.9, 131.5, 129.2, 128.5, 128.3, 124.8 (q,  $J = 278.3$  Hz), 121.8 (q,  $J = 3.5$  Hz), 45.2 (q,  $J = 30.6$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -65.09 (t,  $J = 10.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_8\text{ClF}_3$  220.02666; Found 220.02660.

**(Z)-2-Chloro-1-ethoxy-4,4,4-trifluorobut-1-ene (2f')**

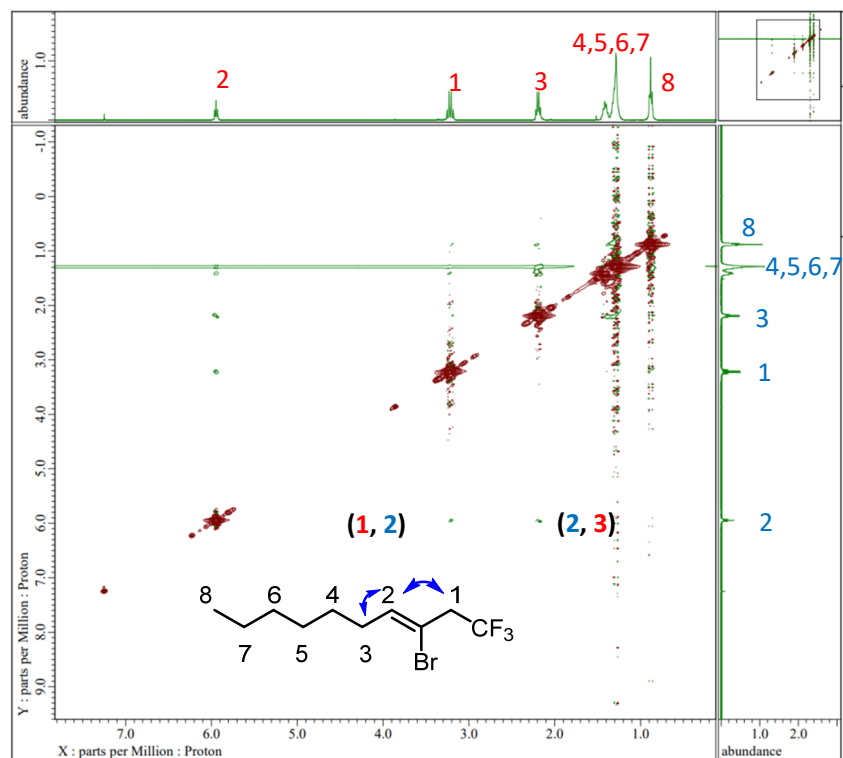


Colorless oil (920 mg, 52% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{max}$  3021, 1684, 1354, 1273, 1146, 1027, 823, 691  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  6.38 (s, 1H), 3.98 (q,  $J = 7.1$  Hz, 2H), 3.00 – 2.92 (m, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  145.7, 125.0 (q,  $J = 278.0$  Hz), 100.2, 69.3, 39.1 (q,  $J = 31.2$  Hz), 15.2 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -66.10 (t,  $J = 10.4$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_6\text{H}_8\text{ClF}_3\text{O}$  188.02158; Found 188.02164.

## 4.5 2D Nuclear Overhauser Effect (NOE) analysis



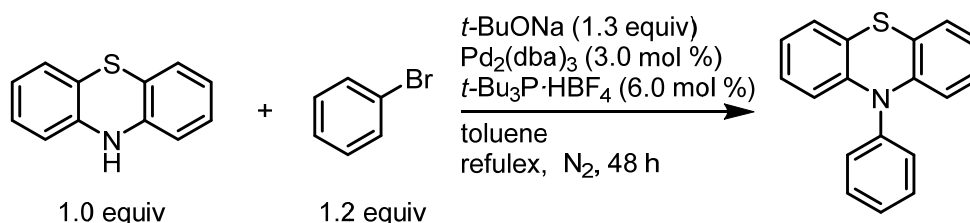
**Fig. S7** | 2D NOESY spectrum ( $\text{CDCl}_3$ , 600 MHz, 25 °C, mixing time = 500 ms) of **2a**.



**Fig. S8** | 2D NOESY spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C, mixing time = 500 ms) of **2x**.

## 5 Photocatalytic preparations of monobromocyclopropanes

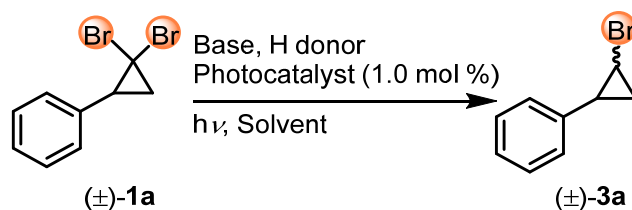
### 5.1 Preparation of photocatalyst PTH



10-Phenyl-10*H*-phenothiazine was similarly synthesized according to the reported procedure<sup>[9]</sup>.

A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with  $\text{N}_2$  (three times). Phenothiazine (2.0 g, 10 mmol, 1.0 equiv) was dissolved in anhydrous toluene (0.50 M). Bromobenzene (1.9 g, 12 mmol, 1.2 equiv),  $t\text{-BuONa}$  (1.3 g, 13 mmol, 1.3 equiv) and  $t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$  (17 mg, 0.60 mmol, 6.0 mol %) were added, followed by  $\text{Pd}_2(\text{dba})_3$  (27 mg, 0.30 mmol, 3.0 mol %). The reaction mixture was degassed in three freeze-pump-thaw cycles and finally stirred under reflux for 48 h. After cooling to room temperature, 100 mL EA and 50 mL water were added to the reaction mixture. After phase separation, the aqueous phase was extracted additionally with EA ( $3 \times 100$  mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , the solvent evaporated and the residue was purified by column chromatography on silica gel using a mixture of hexanes and ethyl acetate (V/V = 30:1) as eluent to give the desired product.

### 5.2 Optimization of the conditions for reductive monodebromination of **1a**



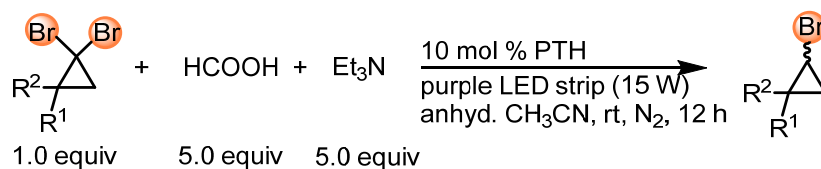
**Table S5** Optimization of the conditions for debrominative reduction of **1a**.

| Entry | Base                  | H donor | Photocatalyst (1.0 mol %)                                       | Ligth source | Solvent | Yield (%) <sup>a</sup> |
|-------|-----------------------|---------|-----------------------------------------------------------------|--------------|---------|------------------------|
| 1     | $\text{Et}_3\text{N}$ | none    | $[\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot 6\text{H}_2\text{O}$ | Blue LED     | DMSO    | 0                      |

|    |                   |                                |                                                           |            |                    |    |
|----|-------------------|--------------------------------|-----------------------------------------------------------|------------|--------------------|----|
| 2  |                   |                                | Pigment Red 123                                           | Green LED  |                    |    |
| 3  |                   |                                | Solvent Green 5                                           | Blue LED   |                    |    |
| 4  |                   |                                | PDI                                                       | Blue LED   |                    |    |
| 5  |                   |                                | PTH                                                       | Purple LED |                    |    |
| 6  | Et <sub>3</sub> N | 2,4,6-triisopropylbenzenethiol | [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O | Blue LED   |                    |    |
| 7  |                   |                                | 4-CzIPN                                                   | Blue LED   |                    |    |
| 8  | Et <sub>3</sub> N | HCOOH                          | PTH (10 mol %)                                            | Purple LED | CH <sub>3</sub> CN | 85 |
| 9  | none              | HCOOH                          |                                                           | Purple LED |                    | 0  |
| 10 | Et <sub>3</sub> N | none                           |                                                           | Purple LED |                    | 0  |
| 11 | Et <sub>3</sub> N | HCOOH                          | PDI                                                       | Blue LED   | DMSO               | 50 |

<sup>a</sup> Yield was based on **1a**.

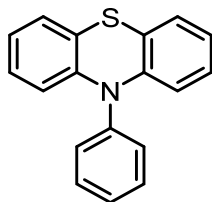
### 5.3 Typical procedure for reductive monodebrominations



A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N<sub>2</sub> (three times). *gem*-Dibromocyclopropane (1.0 mmol, 1.0 equiv), PTH (312 mg, 0.01 mmol, 10 mol %), Et<sub>3</sub>N (605 mg, 5.0 mmol, 5.0 equiv) and anhydrous acetonitrile (10 mL) were added under N<sub>2</sub> atmosphere. The mixture was stirred for 30 min before HCOOH (230 mg, 5.0 mmol, 5.0 equiv) was added dropwise. The reaction mixture was degassed by freeze-pump-thaw method and then stirred under irradiation with purple LEDs (400 nm, approximately 3.0 cm distance from the tube). The mixture was maintained at approximately 25 °C by a desk fan in air-conditioned room. The reaction was monitored by TLC. Upon completion (12 h), the mixture was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100:1 hexanes/EA) to give pure monobromocyclopropane derivative as a colorless oil/solid.

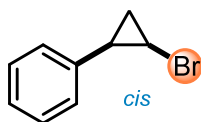
## 5.4 Physical data

### 10-Phenyl-10*H*-phenothiazine<sup>[9]</sup>



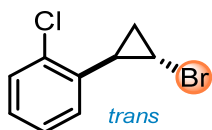
White solid (2.5 g, 92% yield); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.03 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.83 (m, 2H), 6.22 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 144.2, 141.0, 130.8, 130.7, 128.1, 126.8, 126.7, 122.4, 120.2, 116.0 ppm.

### (*cis*-2-Bromocyclopropyl)benzene (3a)



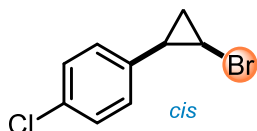
Yellow oil (188 mg, total 96% yield); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 3.31 (td, *J* = 7.6, 4.6 Hz, 1H), 2.31 (dt, *J* = 9.6, 7.6 Hz, 1H), 1.58 (ddd, *J* = 9.6, 7.5, 6.8 Hz, 1H), 1.33 (td, *J* = 7.2, 4.6 Hz, 1H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.1, 129.2, 127.9, 126.8, 24.0, 22.0, 14.1 ppm.

### 1-(*trans*-2-Bromocyclopropyl)-2-chlorobenzene (3e)



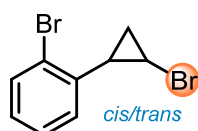
Yellow oil (184 mg, total 80% yield); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 1H), 7.22 – 7.10 (m, 2H), 6.96 – 6.88 (m, 1H), 2.98 (m, 1H), 2.65 (ddd, *J* = 10.1, 6.8, 3.8 Hz, 1H), 1.54 (ddd, *J* = 9.7, 6.7, 4.5 Hz, 1H), 1.48 (q, *J* = 6.9 Hz, 1H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.2, 135.6, 129.4, 127.9, 126.8, 126.7, 25.0, 20.8, 17.6 ppm.

### 1-(*cis*-2-Bromocyclopropyl)-4-chlorobenzene (3g)



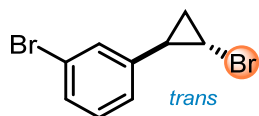
Yellow oil (214 mg, total 93% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.31 (m, 2H), 7.22 – 7.15 (m, 2H), 3.31 (td,  $J$  = 7.6, 4.6 Hz, 1H), 2.28 (dt,  $J$  = 9.5, 7.5 Hz, 1H), 1.60 (ddd,  $J$  = 9.5, 7.6, 6.9 Hz, 1H), 1.30 (ddd,  $J$  = 7.5, 6.9, 4.6 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  135.6, 132.4, 130.5, 128.0, 23.7, 21.4, 14.4 ppm.

**1-Bromo-2-(2-bromocyclopropyl)benzene (3h)**



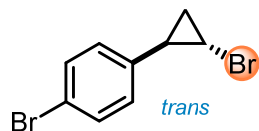
Yellow oil (208 mg, 76% yield); *trans* : *cis* = 3 : 1;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 (dt,  $J$  = 8.1, 1.5 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.33 – 7.25 (m, 1H), 7.22 (tt,  $J$  = 7.6, 1.7 Hz, 3H), 7.20 – 7.12 (m, 2H), 7.09 (tt,  $J$  = 7.6, 1.8 Hz, 3H), 6.95 – 6.89 (m, 3H), 3.42 (m, 1H), 2.95 (m, 3H), 2.61 (m, 3H), 2.46 – 2.33 (m, 1H), 1.64 (m, 1H), 1.57 – 1.43 (m, 6H), 1.38 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.9, 137.1, 132.7, 132.4, 130.2, 128.4, 128.2, 127.4, 127.2, 127.0, 126.9, 126.1, 27.6, 23.7, 23.1, 21.1, 17.7, 14.5 ppm.

**1-Bromo-3-(*trans*-2-bromocyclopropyl)benzene (3i)**



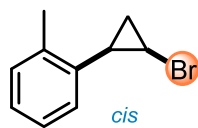
Yellow oil (233 mg, total 85% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 (ddd,  $J$  = 8.0, 2.0, 1.0 Hz, 1H), 7.20 (t,  $J$  = 1.9 Hz, 1H), 7.15 (t,  $J$  = 7.8 Hz, 1H), 6.99 (dt,  $J$  = 7.7, 1.4 Hz, 1H), 3.01 (ddd,  $J$  = 7.8, 4.6, 3.5 Hz, 1H), 2.36 (ddd,  $J$  = 9.9, 6.5, 3.5 Hz, 1H), 1.52 (ddd,  $J$  = 9.8, 6.8, 4.6 Hz, 1H), 1.45 (dt,  $J$  = 7.7, 6.7 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.2, 130.0, 129.6, 129.1, 124.7, 122.7, 26.5, 21.2, 19.0 ppm.

**1-Bromo-4-(*trans*-2-bromocyclopropyl)benzene (3j)**



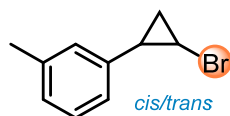
Yellow oil (249 mg, total 91% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.37 (m, 2H), 6.97 – 6.87 (m, 2H), 2.98 (ddd,  $J$  = 7.8, 4.5, 3.5 Hz, 1H), 2.35 (ddd,  $J$  = 9.9, 6.5, 3.5 Hz, 1H), 1.51 (ddd,  $J$  = 9.8, 6.8, 4.5 Hz, 1H), 1.42 (dt,  $J$  = 7.6, 6.7 Hz, 1H).ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.8, 131.6, 127.7, 120.2, 26.4, 21.2, 18.9 ppm.

### 1-(*cis*-2-Bromocyclopropyl)-2-methylbenzene (3k)



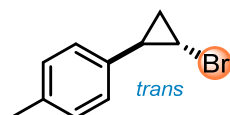
Yellow oil (158 mg, total 75% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.25 – 7.22 (m, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.12 (m, 1H), 3.39 (td,  $J$  = 7.4, 4.2 Hz, 1H), 2.40 (s, 3H), 2.23 (dt,  $J$  = 9.4, 7.6 Hz, 1H), 1.60 (ddd,  $J$  = 9.4, 7.4, 6.7 Hz, 1H), 1.39 (ddd,  $J$  = 7.7, 6.7, 4.2 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  138.8, 135.8, 129.6, 128.7, 127.0, 125.5, 23.0, 21.1, 19.7, 13.6 ppm.

### 1-(2-Bromocyclopropyl)-3-methylbenzene (3l)



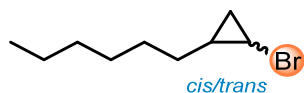
Yellow oil (193 mg, 92% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 (dd,  $J$  = 14.4, 6.8 Hz, 2H), 7.14 – 7.06 (m, 8H), 6.95 – 6.84 (m, 2H), 3.33 (td,  $J$  = 7.6, 4.5 Hz, 2H), 3.05 (dt,  $J$  = 7.8, 4.1 Hz, 1H), 2.40 (s, 8H), 2.36 (s, 3H), 2.33 – 2.28 (m, 2H), 1.59 (dt,  $J$  = 9.6, 7.1 Hz, 2H), 1.50 (ddd,  $J$  = 14.0, 8.0, 4.6 Hz, 2H), 1.35 (td,  $J$  = 7.2, 4.5 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  139.7, 138.2, 137.5, 137.0, 130.0, 128.4, 127.8, 127.5, 127.3, 126.8, 126.1, 122.9, 26.8, 24.0, 22.0, 21.7, 21.4, 21.3, 18.8, 14.1 ppm.

### 1-(*trans*-2-Bromocyclopropyl)-4-methylbenzene (3m)



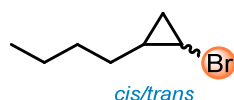
Yellow oil (185 mg, total 88% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.13 (dd,  $J$  = 8.3, 2.8 Hz, 2H), 7.01 – 6.96 (m, 2H), 3.02 (m, 1H), 2.40 (m, 1H), 2.35 (s, 3H), 1.50 (m, 1H), 1.47 – 1.42 (m, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  136.7, 136.1, 129.2, 125.9, 26.5, 21.6, 21.0, 18.7 ppm.

### 1-Bromo-2-hexylcyclopropane (3x)



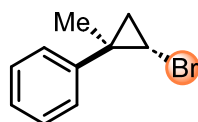
Colorless oil (182 mg, 89% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  3.05 (td,  $J$  = 7.4, 4.3 Hz, 1H), 2.59 (dt,  $J$  = 7.1, 3.4 Hz, 0.55H), 1.73 (dd,  $J$  = 10.2, 7.1 Hz, 0.26H), 1.56 – 1.13 (m, 25.50H), 0.97 (ddd,  $J$  = 9.6, 6.2, 3.8 Hz, 0.76H), 0.93 – 0.81 (m, 7.85H), 0.74 (dt,  $J$  = 7.4, 6.1 Hz, 0.60H), 0.49 (td,  $J$  = 6.7, 4.2 Hz, 1.05H) ppm.

### 1-Bromo-2-butylcyclopropane (3g')



Colorless oil (121 mg, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  3.05 (td,  $J = 7.4, 4.3$  Hz, 1H), 2.59 (dt,  $J = 7.2, 3.3$  Hz, 0.5H), 1.59 – 1.43 (m, 3.5H), 1.41 – 1.28 (m, 6.5H), 1.21 – 1.11 (m, 2H), 0.97 (ddd,  $J = 9.3, 6.2, 3.8$  Hz, 0.5H), 0.85 – 0.79 (m, 5.5H), 0.75 (dt,  $J = 7.4, 6.1$  Hz, 2H), 0.49 (ddd,  $J = 7.0, 6.2, 4.3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  32.5, 31.2, 30.9, 30.8, 24.0, 22.9, 22.5, 22.3, 20.0, 16.8, 15.8, 15.0, 14.1, 14.0 ppm.

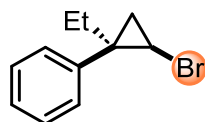
### *trans*-2-Bromo-1-methylcyclopropylbenzene (3h')



*trans* means Br and the phenyl group are on the opposite sides of the cyclopropane ring.

Yellow oil (172 mg, total 82% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 3.11 (dd,  $J = 7.4, 4.4$  Hz, 1H), 1.47 (s, 3H), 1.42 – 1.36 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.2, 129.4, 128.1, 126.8, 28.3, 27.6, 26.9, 22.1 ppm.

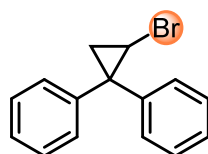
### *cis*-2-Bromo-1-ethylcyclopropylbenzene (3i')



*cis* means Br and the phenyl group are on the same side of the cyclopropane ring.

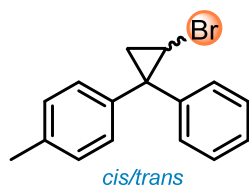
Yellow oil (186 mg, total 83% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.23 (m, 5H), 3.31 (ddd,  $J = 8.0, 4.6, 1.1$  Hz, 1H), 2.08 – 1.84 (m, 2H), 1.59 (m, 1H), 1.33 (d,  $J = 1.7$  Hz, 1H), 1.06 (ddd,  $J = 6.0, 4.5, 1.2$  Hz, 1H), 0.95 (td,  $J = 7.4, 1.5$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.6, 128.8, 128.3, 126.6, 31.9, 30.8, 30.0, 29.7, 21.7, 11.0 ppm.

### (2-Bromocyclopropane-1,1-diyl)dibenzene (3j')



Yellow solid (248 mg, 91% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 – 7.38 (m, 4H), 7.38 – 7.20 (m, 6H), 3.76 (dd,  $J$  = 7.8, 4.8 Hz, 1H), 2.00 – 1.77 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  144.1, 140.6, 130.4, 128.5, 128.2, 127.7, 127.1, 126.6, 36.2, 28.3, 23.8 ppm.

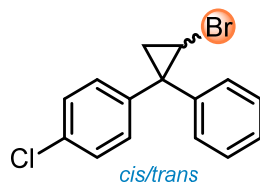
**1-(2-Bromo-1-phenylcyclopropyl)-4-methylbenzene (3k')**



*trans* means Br and the *p*-tolyl group are on the opposite sides of the cyclopropane ring.

Yellow solid (243 mg, 85% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.53 – 7.47 (m, 1H), 7.47 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 7.29 – 7.20 (m, 3H), 7.20 – 7.13 (m, 1H), 3.76 (m, 1H), 2.41 (dd,  $J$  = 31.8, 5.1 Hz, 3H), 1.97 – 1.84 (m, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  144.3, 141.2, 140.8, 137.7, 136.6, 136.2, 130.3, 130.2, 129.2, 128.9, 128.5, 128.1, 127.6, 127.6, 126.9, 126.5, 35.9, 35.8, 28.5, 28.3, 23.8, 23.7, 21.1, 20.9 ppm.

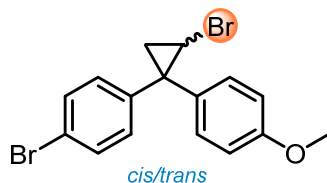
**1-(2-Bromo-1-phenylcyclopropyl)-4-chlorobenzene (3l')**



*trans* means Br and the *p*-chlorophenyl group are on the opposite sides of the cyclopropane ring.

Yellow solid (269 mg, 88% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.27 (m, 6H), 7.21 (ddd,  $J$  = 20.3, 8.0, 2.0 Hz, 4H), 3.69 (m, 1H), 1.96 – 1.76 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.5, 142.6, 140.1, 139.2, 133.0, 132.5, 131.7, 129.1, 128.7, 128.4, 128.3, 127.6, 127.3, 126.8, 35.7, 35.7, 28.0, 28.0, 23.9, 23.9 ppm.

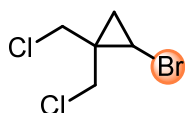
**1-Bromo-4-(2-bromo-1-(4-methoxyphenyl)cyclopropyl)benzene (3m')**



Yellow solid (289 mg, 76% yield);  $R_f$  = 0.5 (50:1 hexanes/EA); m.p. 110.6–111.4 °C; IR (film)  $\nu_{max}$  3104, 2740, 1544, 718  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.43 (m, 2H), 7.38 – 7.34 (m, 4H), 7.29 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.15 – 7.12 (m, 2H), 7.10 – 7.04 (m, 4H), 6.91 – 6.85

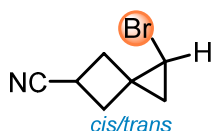
(m, 4H), 6.81 – 6.78 (m, 2H), 3.80 (s, 6H), 3.75 (s, 3H), 3.62 (ddd,  $J = 7.9, 6.2, 4.8$  Hz, 3H), 1.82 (td,  $J = 7.8, 6.5$  Hz, 3H), 1.78 (dd,  $J = 6.6, 4.8$  Hz, 2H), 1.73 (dd,  $J = 6.5, 4.7$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  158.7, 158.4, 143.5, 140.2, 135.6, 132.3, 131.9, 131.6, 131.4, 131.3, 129.3, 128.8, 121.0, 120.4, 114.1, 113.7, 55.3, 55.2, 35.2, 35.0, 28.4, 27.9, 24.2, 23.7 ppm; HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{14}\text{Br}_2\text{O}$  379.94114; Found 379.94122.

### 2-Bromo-1,1-bis(chloromethyl)cyclopropane (3n')



Colorless oil (186 mg, 87% yield);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.00 (d,  $J = 11.8$  Hz, 1H), 3.87 – 3.64 (m, 2H), 3.45 (dt,  $J = 11.7, 1.2$  Hz, 1H), 3.12 (ddd,  $J = 7.9, 4.9, 0.7$  Hz, 1H), 1.46 (ddd,  $J = 7.9, 7.0, 0.8$  Hz, 1H), 1.12 (ddd,  $J = 7.2, 5.0, 1.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  47.6, 47.5, 28.8, 26.4, 22.7 ppm.

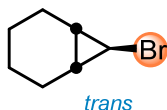
### 1-Bromospiro[2.3]hexane-5-carbonitrile (3o')



The starting *gem*-dibromocyclopropane was used as a mixture of diastereomers.

White solid (186 mg, 91% yield);  $R_f = 0.5$  (50:1 hexanes/EA); m.p. 56.9–57.5 °C; IR (film)  $\nu_{\text{max}}$  2375, 2263, 1553, 1047, 852, 617  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  3.27 (tt,  $J = 9.2, 7.4$  Hz, 1H), 2.92 (dd,  $J = 8.0, 4.5$  Hz, 1H), 2.82 – 2.73 (m, 1H), 2.66 – 2.56 (m, 1H), 2.49 – 2.38 (m, 2H), 1.34 – 1.25 (m, 1H), 0.90 (dd,  $J = 7.1, 4.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  121.8, 34.1, 33.4, 33.2, 33.2, 24.9, 23.1, 21.8, 17.0, 14.8 ppm; HRMS (EI) Calcd for  $\text{C}_7\text{H}_8\text{BrN}$  184.98401; Found 184.98414.

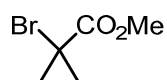
### 7-Bromobicyclo[4.1.0]heptane (3p')<sup>[10]</sup>



Only *trans*-diastereomer was obtained. *trans* means Br and the cyclohexane ring are on the opposite sides of the cyclopropane ring.

Colorless oil (120 mg, 69% yield);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  2.05 – 1.95 (m, 1H), 1.87 – 1.80 (m, 1H), 1.61 – 1.55 (m, 1H), 1.37 (d,  $J = 1.3$  Hz, 2H), 1.29 (s, 1H), 1.26 – 1.24 (m, 3H), 1.23 – 1.16 (m, 1H), 0.87 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  29.7, 21.3, 19.9, 12.0 ppm.

### Methyl 1-bromocyclopropanecarboxylate (3q')

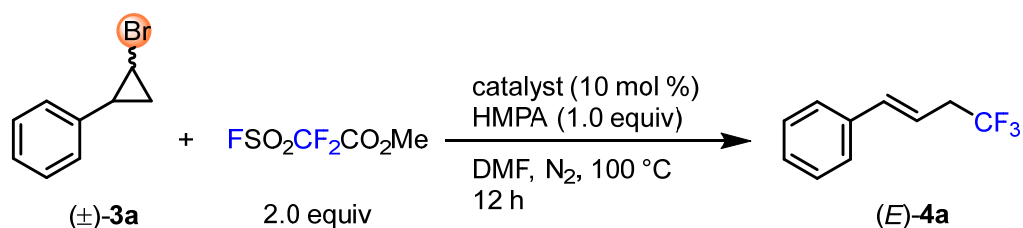


From commercial source.

## 6 Reactions of monobromocyclopropanes with Chen's reagent

### 6.1 Optimization of the conditions for the reaction of 3a with Chen's reagent

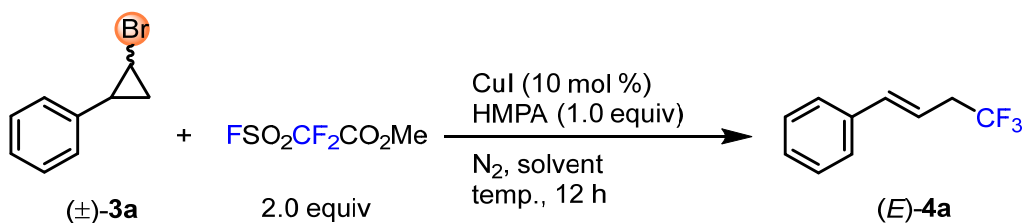
Table S6 Effect of catalyst.



| Entry | Catalyst | Yield (%) <sup>a</sup> | Entry | Catalyst          | Yield (%) <sup>a</sup> |
|-------|----------|------------------------|-------|-------------------|------------------------|
| 1     | CuCl     | 37                     | 6     | CuOAc             | 32                     |
| 2     | CuBr     | 72                     | 7     | CuOTf             | 46                     |
| 3     | CuI      | 81                     | 8     | CuCl <sub>2</sub> | 0                      |
| 4     | CuCN     | 24                     | 9     | CuBr <sub>2</sub> | 0                      |
| 5     | CuTc     | 47                     | 10    | —                 | 0                      |

<sup>a</sup> Yield was based on 3a.

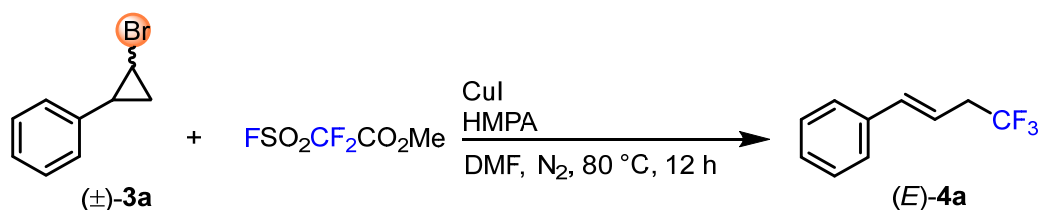
Table S7 Effect of solvent.



| Entry | Solvent            | Temp. (°C) | Yield (%) <sup>a</sup> | Entry | Solvent            | Temp. (°C) | Yield (%) <sup>a</sup> |
|-------|--------------------|------------|------------------------|-------|--------------------|------------|------------------------|
| 1     | benzene            | 80         | 0                      | 9     | EA                 | 80         | 0                      |
| 2     | toluene            | 110        |                        | 10    | acetone            | 60         | 0                      |
| 3     | DCM                | 40         |                        | 11    | HMPA               | 120        | 18                     |
| 4     | DCE                | 80         |                        | 12    | DMSO               | 100        | 21                     |
| 5     | THF                | 60         |                        | 13    | DMI                | 100        | 44                     |
| 6     | DME                | 80         |                        | 14    | DMF                | 80         | 92                     |
| 7     | 1,4-dioxane        | 40         |                        | 15    | CH <sub>3</sub> OH | 65         | 0                      |
| 8     | CH <sub>3</sub> CN | 80         |                        |       |                    |            |                        |

<sup>a</sup> Yield was based on **3a**.

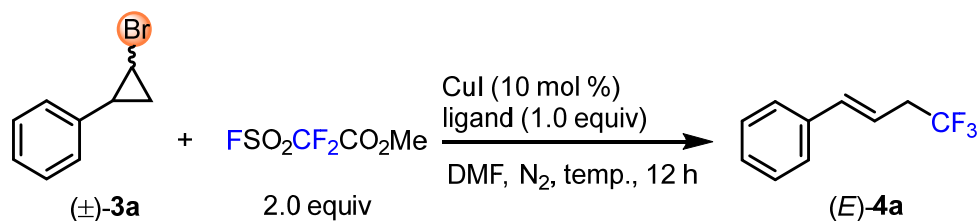
**Table S8** Effect of the molar ratio of reactants.



| Entry | Chen's reagent :<br>HMPA : CuI | Yield (%) <sup>a</sup> | Entry | Chen's reagent :<br>HMPA : CuI | Yield (%) <sup>a</sup> |
|-------|--------------------------------|------------------------|-------|--------------------------------|------------------------|
| 1     | 2.0 : 1.0 : 0.0                | 0                      | 9     | 2.0 : 1.0 : 0.1                | 92                     |
| 2     | 2.0 : 1.0 : 0.05               | 60                     | 10    | 2.0 : 2.0 : 0.1                | 81                     |
| 3     | 2.0 : 1.0 : 0.1                | 92                     | 11    | 2.0 : 3.0 : 0.1                | 78                     |
| 4     | 2.0 : 1.0 : 0.5                | 83                     | 11    | 1.0 : 1.0 : 0.1                | 61                     |
| 5     | 2.0 : 1.0 : 1.0                | 68                     | 12    | 1.5 : 1.0 : 0.1                | 81                     |
| 6     | 2.0 : 0.0 : 0.1                | 43                     | 13    | 2.0 : 1.0 : 0.1                | 92                     |
| 7     | 2.0 : 0.1 : 0.1                | 57                     | 14    | 3.0 : 1.0 : 0.1                | 86                     |
| 8     | 2.0 : 0.5 : 0.1                | 83                     |       |                                |                        |

<sup>a</sup> Yield was based on **3a**.

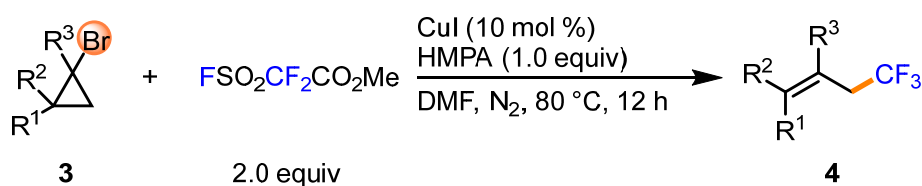
**Table S9** Effect of the temperature and ligand.



| Entry | Temp. (°C) | Ligand           | Yield (%) <sup>a</sup> |
|-------|------------|------------------|------------------------|
| 1     |            | —                | 22                     |
| 2     |            | TMEDA            | 31                     |
| 3     | 100        | DMEDA            | 24                     |
| 4     |            | Oxanilide        | 18                     |
| 5     |            | HMPA             | 92                     |
| 6     |            | PPh <sub>3</sub> | 60                     |
| 7     | 20         |                  | 0                      |
| 8     | 40         |                  | 0                      |
| 9     | 60         | HMPA             | 0                      |
| 10    | 80         |                  | 92                     |
| 11    | 100        |                  | 75                     |

<sup>a</sup> Yield was based on **3a**.

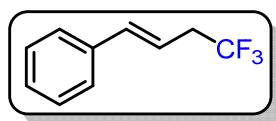
## 6.2 Typical procedure



A dry 50 mL Schlenk tube charged with a stirring bar was evacuated and backfilled with N<sub>2</sub> (three times). Copper(I) iodide (20 mg, 0.1 mmol, 10 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv) and anhydrous DMF (4.0 mL) were added under N<sub>2</sub> atmosphere. After the mixture had been stirred for 15 min at room temperature, monobromocyclopropane (1.0 mmol, 1.0 equiv), FSO<sub>2</sub>CF<sub>2</sub>COOMe (384 mg, 2.0 mmol, 2.0 equiv) and DMF (6.0 mL) were added. The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 80 °C (oil bath). The reaction was monitored by TLC. Upon completion (12 h), the reaction mixture was cooled to room temperature, quenched carefully with H<sub>2</sub>O (50 mL), extracted with DCM (30 mL × 3). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by column chromatography on silica gel using hexanes as eluent to afford the desired trifluoromethylated product.

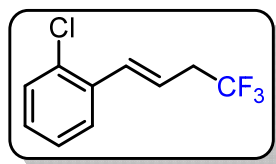
## 6.3 Physical data

### (*E*)-(4,4,4-Trifluorobut-1-en-1-yl)benzene (**4a**)<sup>[11]</sup>



Colorless oil (172 mg, 92% yield); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.35 (dt, *J* = 28.7, 6.3 Hz, 3H), 7.30 – 7.18 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 13.2, 5.7 Hz, 1H), 3.04 – 2.90 (m, 2H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 136.7, 136.2, 128.6, 128.1, 126.4, 125.0 (q, *J* = 277.1 Hz), 117.2 (q, *J* = 3.1 Hz), 37.7 (q, *J* = 29.8 Hz) ppm; <sup>19</sup>F NMR (565 MHz, Chloroform-*d*) δ -66.12 (t, *J* = 10.7 Hz) ppm.

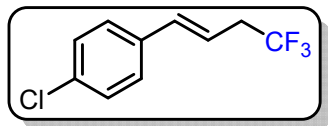
### (*E*)-1-Chloro-2-(4,4,4-trifluorobut-1-en-1-yl)benzene (**4e**)



Colorless oil (161 mg, 73% yield); *R*<sub>f</sub> = 0.7 (hexanes); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.46 (m, 1H), 7.44 – 7.31 (m, 1H), 7.23 (dt, *J* = 9.0, 7.4 Hz, 2H), 7.03 (d, *J* = 15.8 Hz, 1H), 6.18 – 5.97 (m, 1H), 3.17 – 2.92 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 134.4, 129.7, 129.1, 126.9,

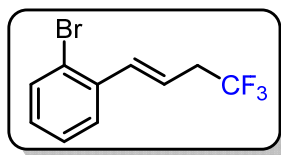
125.8 (q,  $J = 276.6$  Hz), 120.0 (q,  $J = 3.8$  Hz), 37.8 (q,  $J = 29.6$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.88 (t,  $J = 9.8$  Hz) ppm.

**(*E*)-1-Chloro-4-(4,4,4-trifluorobut-1-en-1-yl)benzene (4g)**



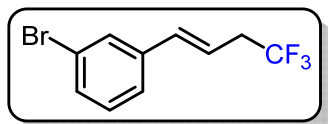
Colorless oil (196 mg, 89% yield);  $R_f = 0.7$  (hexanes);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.30 (s, 4H), 6.56 (dt,  $J = 16.0, 1.5$  Hz, 1H), 6.09 (dt,  $J = 15.8, 7.2$  Hz, 1H), 2.99 (qdd,  $J = 10.6, 7.2, 1.4$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  135.4, 134.7, 133.8, 128.8, 127.6, 125.8 (q,  $J = 276.7$  Hz), 117.9 (q,  $J = 3.4$  Hz), 37.6 (q,  $J = 30.3$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -66.06 (t,  $J = 10.7$  Hz) ppm.

**(*E*)-1-Bromo-2-(4,4,4-trifluorobut-1-en-1-yl)benzene (4h)**



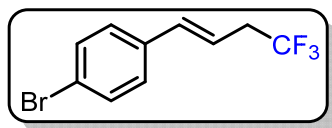
Colorless oil (198 mg, 75% yield);  $R_f = 0.7$  (hexanes);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.54 (ddd,  $J = 18.5, 7.9, 1.5$  Hz, 2H), 7.29 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.14 (td,  $J = 7.7, 1.7$  Hz, 1H), 6.97 (d,  $J = 15.7$  Hz, 1H), 6.07 (dt,  $J = 15.7, 7.2$  Hz, 1H), 3.06 (qdd,  $J = 10.6, 7.2, 1.5$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  136.1, 135.5, 133.0, 129.4, 127.6, 127.2, 125.8 (q,  $J = 277.6$  Hz), 123.5, 120.2 (q,  $J = 3.7$  Hz), 37.7 (q,  $J = 30.1$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.97 (t,  $J = 10.5$  Hz) ppm.

**(*E*)-1-Bromo-3-(4,4,4-trifluorobut-1-en-1-yl)benzene (4i)**



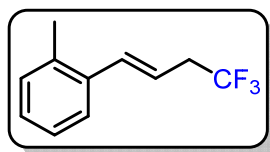
Colorless oil (216 mg, 82% yield);  $R_f = 0.7$  (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.54 (t,  $J = 1.8$  Hz, 1H), 7.41 (ddd,  $J = 7.9, 2.0, 1.1$  Hz, 1H), 7.30 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.20 (td,  $J = 7.8, 1.2$  Hz, 1H), 6.53 (d,  $J = 15.9$  Hz, 1H), 6.22 – 6.01 (m, 1H), 3.01 (qdd,  $J = 10.8, 7.2, 1.6$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  138.2, 135.2, 130.9, 130.1, 129.3, 125.8 (q,  $J = 276.7$  Hz), 125.1, 122.8, 118.8 (q,  $J = 3.7$  Hz), 37.5 (q,  $J = 30.1$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.96 (t,  $J = 10.8$  Hz) ppm.

**(E)-1-Bromo-4-(4,4,4-trifluorobut-1-en-1-yl)benzene (4j)**



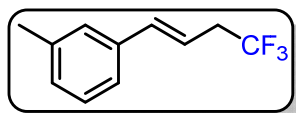
Colorless oil (230 mg, 87% yield);  $R_f$  = 0.7 (hexanes);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.56 – 7.36 (m, 2H), 7.29 – 7.18 (m, 2H), 6.55 (d,  $J$  = 15.8 Hz, 1H), 6.11 (dt,  $J$  = 15.9, 7.2 Hz, 1H), 2.99 (qdd,  $J$  = 10.6, 7.3, 1.4 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  135.5, 135.1, 131.8, 127.9, 125.8 (q,  $J$  = 276.7 Hz), 122.0, 118.0 (q,  $J$  = 3.5 Hz), 37.6 (q,  $J$  = 29.9 Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -66.02 (t,  $J$  = 10.8 Hz) ppm.

**(E)-1-Methyl-2-(4,4,4-trifluorobut-1-en-1-yl)benzene (4k)**



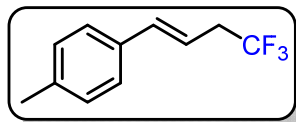
Colorless oil (160 mg, 80% yield);  $R_f$  = 0.7 (hexanes);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.47 – 7.38 (m, 1H), 7.22 – 7.12 (m, 3H), 6.84 (dd,  $J$  = 15.7, 1.9 Hz, 1H), 6.00 (dt,  $J$  = 15.7, 7.2 Hz, 1H), 3.03 (qdd,  $J$  = 10.6, 7.2, 1.4 Hz, 2H), 2.36 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  135.4, 134.7, 130.3, 128.0, 126.2, 125.9 (q,  $J$  = 276.6 Hz), 125.8, 118.6 (q,  $J$  = 3.6 Hz), 37.9 (q,  $J$  = 29.8 Hz), 19.7 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -66.16 (t,  $J$  = 10.5 Hz) ppm.

**(E)-1-Methyl-3-(4,4,4-trifluorobut-1-en-1-yl)benzene (4l)**



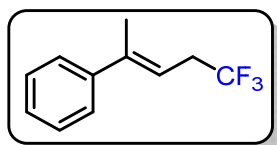
Colorless oil (174 mg, 87% yield);  $R_f$  = 0.7 (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.25 – 7.17 (m, 3H), 7.11 (d,  $J$  = 7.4 Hz, 1H), 6.59 (d,  $J$  = 15.8 Hz, 1H), 6.12 (m, 1H), 3.00 (qdd,  $J$  = 10.6, 7.2, 1.4 Hz, 2H), 2.38 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  138.2, 136.7, 136.1, 128.9, 128.5, 127.1, 125.9 (q,  $J$  = 276.6 Hz), 123.6, 116.9 (q,  $J$  = 3.7 Hz), 37.7 (q,  $J$  = 30.0 Hz), 21.3 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -66.13 (t,  $J$  = 10.8 Hz) ppm.

**(E)-1-Methyl-4-(4,4,4-trifluorobut-1-en-1-yl)benzene (4m)**



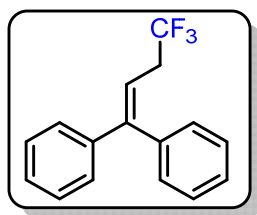
Colorless oil (186 mg, 93% yield);  $R_f = 0.7$  (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.35 – 7.28 (m, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 6.59 (d,  $J = 15.8$  Hz, 1H), 6.08 (dt,  $J = 15.9, 7.3$  Hz, 1H), 2.99 (qdd,  $J = 10.7, 7.2, 1.4$  Hz, 2H), 2.36 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  138.0, 136.5, 133.5, 129.3, 126.3, 126.0 (q,  $J = 276.6$  Hz), 116.1 (q,  $J = 3.7$  Hz), 37.7 (q,  $J = 29.9$  Hz), 21.2 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -66.16 (t,  $J = 10.8$  Hz) ppm.

**(*E*)-(5,5,5-Trifluoropent-2-en-2-yl)benzene (4h')**



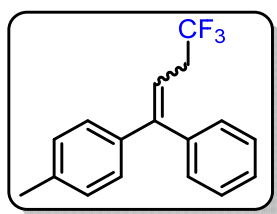
Colorless oil (108 mg, 54% yield);  $R_f = 0.7$  (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.40 (d,  $J = 7.1$  Hz, 2H), 7.35 (t,  $J = 7.5$  Hz, 2H), 7.30 (d,  $J = 7.3$  Hz, 1H), 5.74 (t,  $J = 7.4$  Hz, 1H), 3.02 (qd,  $J = 10.8, 7.2$  Hz, 2H), 2.10 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  142.7, 141.4, 128.3, 127.5, 126.4 (q,  $J = 276.7$  Hz), 125.9, 115.0 (q,  $J = 3.4$  Hz), 33.7 (q,  $J = 29.6$  Hz), 16.3 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -65.82 (t,  $J = 10.8$  Hz) ppm.

**(4,4,4-Trifluorobut-1-ene-1,1-diyl)dibenzene (4j')<sup>[10]</sup>**



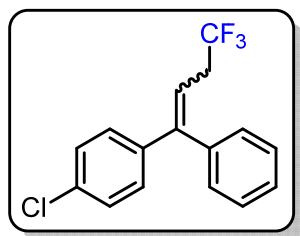
Colorless oil (199 mg, 76% yield);  $R_f = 0.5$  (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.44 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 7.29 (td,  $J = 6.1, 2.9$  Hz, 3H), 7.26 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 6.08 (t,  $J = 7.4$  Hz, 1H), 2.92 (qd,  $J = 10.7, 7.4$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  147.7, 141.4, 138.7, 129.5, 128.5, 128.3, 127.9, 127.7, 127.4, 126.1 (q,  $J = 277.6$  Hz), 116.0 (q,  $J = 3.9$  Hz), 34.8 (q,  $J = 29.6$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -65.5 (t,  $J = 10.9$  Hz) ppm.

**1-Methyl-4-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl)benzene (4k')**



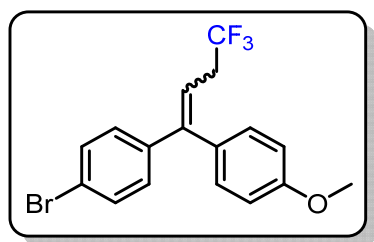
Colorless oil (190 mg, 69% yield); ratio = 1:2;  $R_f$  = 0.6 (hexanes); IR (film)  $\nu_{max}$  2922, 1712, 1467, 1381, 1026, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 (ddd,  $J$  = 13.4, 7.8, 6.0 Hz, 1H), 7.30 – 7.18 (m, 4H), 7.16 – 7.04 (m, 4H), 6.04 (t,  $J$  = 7.4 Hz, 1H), 3.12 – 2.69 (m, 2H), 2.38 (d,  $J$  = 24.4 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  147.6, 147.5, 141.6, 138.9, 138.6, 137.8, 137.4, 135.7, 129.5, 129.5, 129.2, 129.0, 128.5, 128.2, 127.8, 127.6, 127.6, 127.4, 127.3, 124.8, 121.7 (q,  $J$  = 276.0 Hz), 115.8 (q,  $J$  = 3.2 Hz), 115.1 (q,  $J$  = 3.2 Hz), 34.8 (q,  $J$  = 29.6 Hz), 34.7 (q,  $J$  = 29.6 Hz), 21.2, 21.1 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -65.59 (q,  $J$  = 10.9 Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{17}\text{H}_{15}\text{F}_3$  276.11259; Found 276.11206.

**1-Chloro-4-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl)benzene (4l')<sup>[12]</sup>**



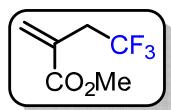
Colorless oil (213 mg, 72% yield); ratio = 4:5;  $R_f$  = 0.7 (hexanes);  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.35 (m, 3H), 7.29 (d,  $J$  = 1.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.09 (m, 3H), 6.06 (dt,  $J$  = 17.8, 7.5 Hz, 1H), 2.90 (m, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  151.5, 151.4, 139.8, 138.6, 136.7, 135.6, 134.7, 134.6, 130.7, 129.2, 129.0, 128.8, 128.6, 128.5, 128.4, 127.5, 119.4 (q,  $J$  = 328.2 Hz), 109.3, 109.2, 51.6 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -65.53 (q,  $J$  = 11.0 Hz) ppm.

**1-Bromo-4-(4,4,4-trifluoro-1-(4-methoxyphenyl)but-1-en-1-yl)benzene (4m')**



Colorless oil (289 mg, 78% yield); ratio = 1:2;  $R_f$  = 0.6 (50:1 hexanes/EA); IR (film)  $\nu_{max}$  3102, 1686, 1465, 1044, 622  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.59 – 7.49 (m, 2H), 7.16 – 7.13 (m, 2H), 7.07 – 7.00 (m, 2H), 6.85 – 6.79 (m, 2H), 5.98 (t,  $J$  = 7.5 Hz, 1H), 3.80 (s, 3H), 2.86 (qd,  $J$  = 10.6, 7.5 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  159.6, 146.1, 137.8, 133.4, 131.8, 131.3, 128.5, 126.0 (q,  $J$  = 278.2 Hz), 121.8, 114.6 (q,  $J$  = 3.5 Hz), 113.7, 55.3, 34.7 (q,  $J$  = 29.7 Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -65.59 (t,  $J$  = 10.8 Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{17}\text{H}_{14}\text{BrF}_3\text{O}$  370.01801; Found 370.01752.

## Methyl 4,4,4-trifluoro-2-methylenebutanoate (4q')



Colorless oil (80.7 mg, 48% yield);  $R_f = 0.7$  (hexanes); IR (film)  $\nu_{max}$  2984, 1742, 1398, 1301, 1072  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  6.49 (s, 1H), 5.91 (s, 1H), 3.79 (s, 3H), 3.18 (q,  $J = 10.6$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  166.1, 131.3, 130.1 (q,  $J = 2.4$  Hz), 126.3 (q,  $J = 277.0$  Hz), 52.4, 35.3 (q,  $J = 31.0$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.69 (t,  $J = 10.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_6\text{H}_7\text{F}_3\text{O}_2$  168.03981; Found 168.03976.

## 7 Conversions of 2a

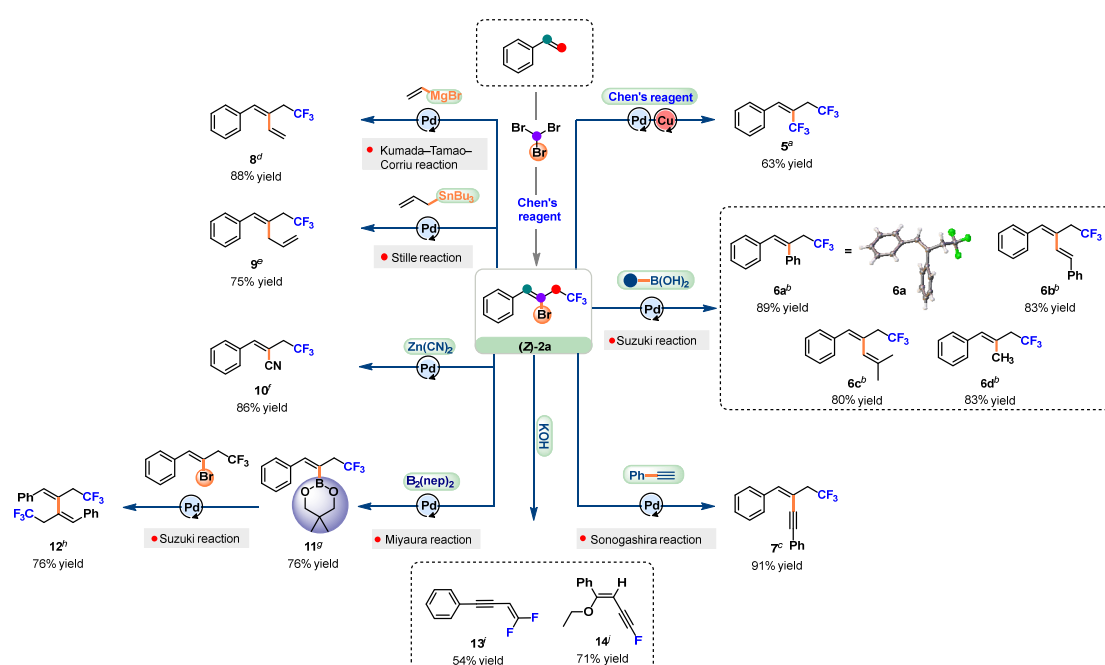
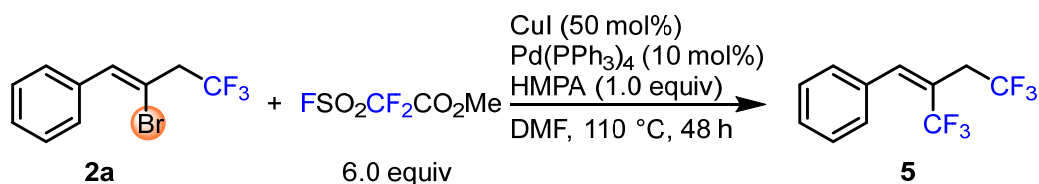


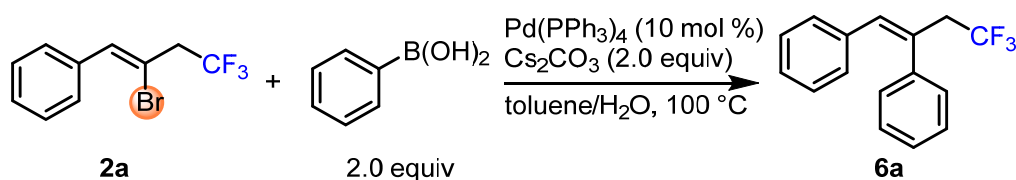
Fig. S9 | The transformations of (Z)-2a.

## 7.1 Experimental procedures

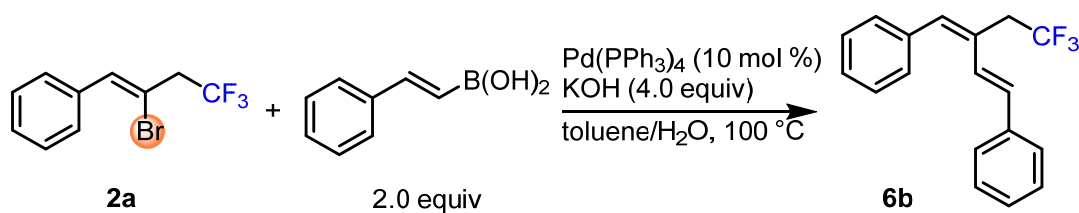


A dry 50 mL Schlenk tube charged with a stirring bar was evacuated and backfilled with  $\text{N}_2$  (three times). Copper(I) iodide (50 mg, 0.5 mmol, 50 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv),  $\text{Pd}(\text{PPh}_3)_4$  (115 mg, 0.1 mmol, 10 mol %) and anhydrous DMF (4.0 mL) were added under  $\text{N}_2$

atmosphere. After the mixture had been stirred for 15 min at room temperature, **2a** (264 mg, 1.0 mmol, 1.0 equiv.), FSO<sub>2</sub>CF<sub>2</sub>COOMe (1.15 g, 6.0 mmol, 6.0 equiv) and DMF (6.0 mL) were added. The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 110 °C (oil bath). Every 16 hours 2.0 equiv of FSO<sub>2</sub>CF<sub>2</sub>COOMe was added for two times. The reaction was monitored by TLC. Upon completion (48 h), the reaction mixture was cooled to room temperature, quenched carefully with H<sub>2</sub>O (50 mL), and extracted with DCM (30 mL × 3). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by column chromatography on silica gel using hexanes as eluent to afford **5** as a colorless oil (160 mg, 63% yield).

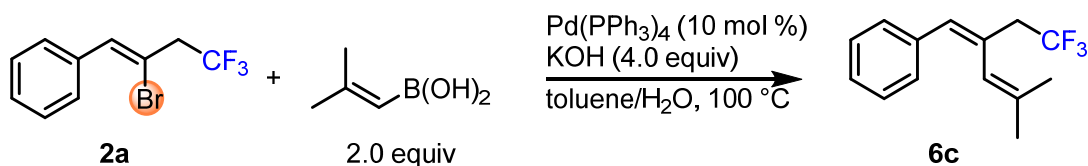


An oven-dried flask was charged with **2a** (264mg, 1.0 mmol), phenyl boronic acid (244 mg, 2.0 mmol, 2.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (115 mg, 0.1 mmol, 10 mol %), toluene/water (10/1 v/v ratio) (10.0 mL), and Cs<sub>2</sub>CO<sub>3</sub> (752 mg, 2.0 mmol, 2.0 equiv). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (100:1 hexanes/EA) to give the Suzuki coupling product **6a** (232 mg, 89% yield).

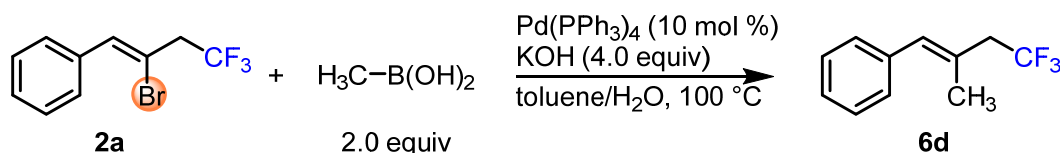


An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), (*E*)-styrylboronic acid (244 mg, 2.0 mmol, 2.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (115mg, 0.1 mmol, 10 mol %), toluene/water (10/1 v/v ratio) (10 mL), and KOH (264 mg, 85%, 4.0 mmol, 4.0 equiv). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel

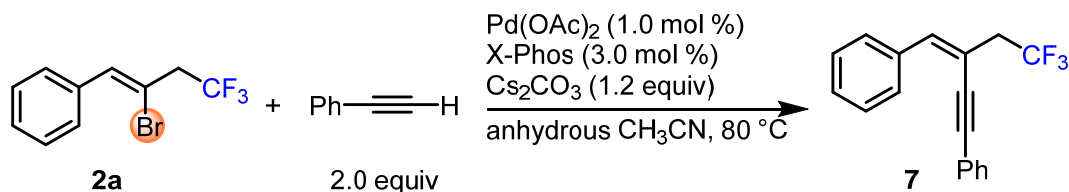
(100:1 hexanes/EA) to give **6b** (239 mg, 83% yield).



An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), (2-methylprop-1-en-1-yl)boronic acid (244 mg, 2.0 mmol, 2.0 equiv),  $\text{Pd(PPh}_3)_4$  (115mg, 0.1 mmol, 10 mol %), toluene/water (10/1 v/v ratio) (10 mL), and KOH (98.8 mg, 85%, 1.5 mmol, 1.5 equiv). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (100:1 hexanes/EA) to give **6c** (192 mg, 80% yield).

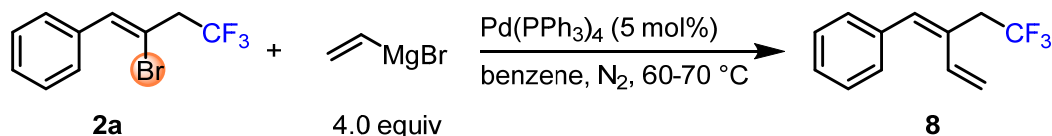


An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), methylboronic acid (120 mg, 2.0 mmol, 2.0 equiv),  $\text{Pd(PPh}_3)_4$  (115mg, 0.1 mmol, 10 mol %), toluene/water (10/1 v/v ratio) (10 mL), and KOH (264 mg, 85%, 4.0 mmol, 4.0 equiv). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (100:1 hexanes/EA) to give **6d** (168 mg, 84% yield).

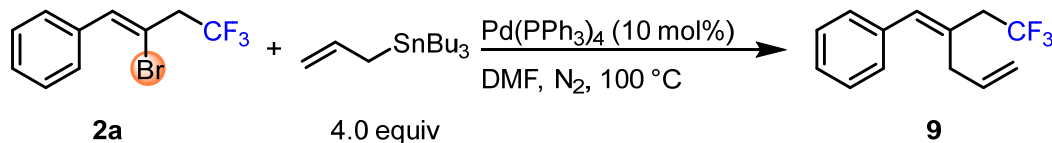


An oven-dried Schlenk tube was evacuated and backfilled with  $\text{N}_2$  (the cycle was performed three times), and then charged under a positive pressure of  $\text{N}_2$  with  $\text{Pd(OAc)}_2$  (2.25 mg, 1.0 mmol, 1 mol %), X-Phos (14.3 mg, 3.0 mmol, 3 mol %), and  $\text{Cs}_2\text{CO}_3$  (391 mg, 1.2 mmol, 1.2 equiv), followed by anhydrous acetonitrile (6.0 mL), **2a** (264 mg, 1.0 mmol, 1.0 equiv) and phenylacetylene (204 mg, 2.0 mmol, 2.0 equiv). The reaction mixture was degassed by freeze-

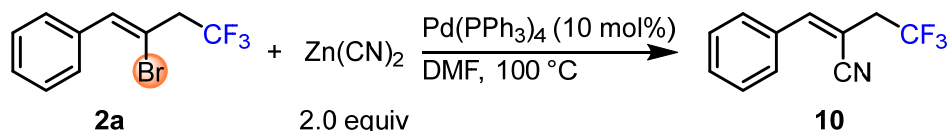
pump-thaw method and then stirred at 80 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (100:1 hexanes/EA) to give the corresponding product **7** (260 mg, 91% yield).



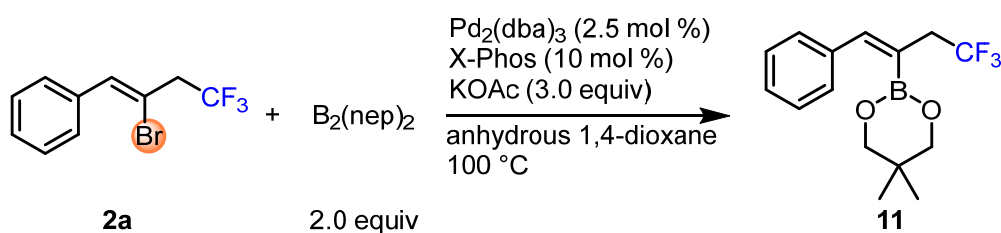
To a Schlenk flask charged with **2a** (264 mg, 1.0 mmol), vinyl magnesium bromide (1.0 M in THF, 8 mL, 8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.1 mmol) was added benzene (6 mL) under N<sub>2</sub> atmosphere. This reaction mixture was heated at 70 °C for 12 hours. The reaction was monitored by TLC. Upon completion, sat. aq. NH<sub>4</sub>Cl (4 mL) was added to quench the reaction. The aqueous mixture was extracted with ethyl acetate (3 × 20 mL). The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the crude product was purified by flash chromatography on silica gel (200:1 hexanes/AcOEt) to give product **8** (187 mg, 88% yield).



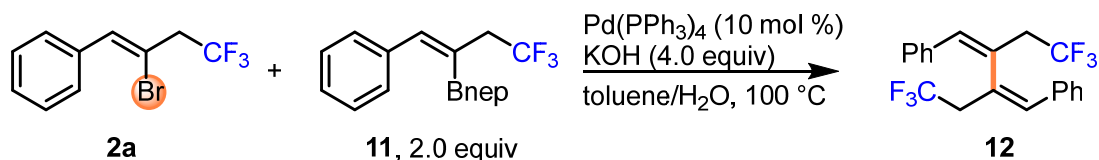
An oven-dried Schlenk tube was evacuated and backfilled with nitrogen (the cycle was performed three times), and then charged under a positive pressure of nitrogen with **2a** (264 mg, 1.0 mmol), allyltributylstannane (336 mg, 2.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.1 mmol), and DMF (10 mL). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere for 24 h. More allyltributylstannane (336 mg, 2.0 mmol) was added and stirring was continued for another 12 h until maximum conversion of **2a** to product occurred. Upon completion of the reaction, the mixture was cooled to room temperature. Saturated brine was added to dilute the reaction mixture, followed by extraction with DCM (30 mL × 3). The organic layers were collected, dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure to afford the crude product. The residue was purified by flash chromatography on silica gel (hexanes) to give product **9** (170 mg, 75% yield).



To a Schlenk flask charged with **2a** (264 mg, 1.0 mmol),  $\text{Zn(CN)}_2$  (50 mg, 2.0 mmol), and  $\text{Pd(PPh}_3)_4$  (115 mg, 0.1 mmol, 10 mol %) was added DMF (10 mL) under nitrogen. Then the mixture was heated to 100 °C for 12 h. After cooling to room temperature, the mixture was filtered under vacuum and the filter cake was washed by DCM, and then the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (100:1 hexanes/EA as eluent) to afford **10** (181 mg, 86%) as a solid.

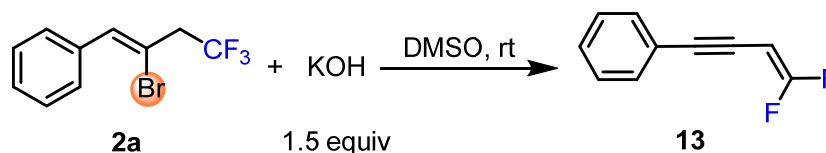


An oven-dried Schlenk tube was evacuated and backfilled with nitrogen (the cycle was performed three times), and then charged under a positive pressure of nitrogen with  $\text{Pd}_2(\text{dba})_3$  (23 mg, 0.025 mmol, 2.5 mol %), X-Phos (48 mg, 0.10 mmol, 10 mol %), KOAc (294 mg, 3.0 mmol, 3.0 equiv),  $\text{B}_2(\text{nep})_2$  (452 mg, 2.0 mmol, 2.0 equiv), **2a** (264 mg, 1.0 mmol, 1.0 equiv), and 10 mL anhydrous 1,4-dioxane. The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. Then the reaction mixture was cooled to rt, filtered through Celite, and the filter cake washed with DCM (20 mL  $\times$  3). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed and the residue was purified by flash chromatography on silica gel (50:1 hexanes/EA) to give **11** (227 mg, 62% yield).

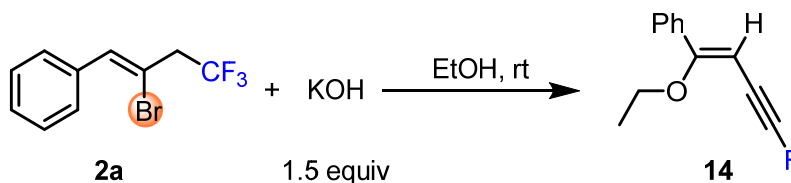


An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), **11** (120 mg, 2.0 mmol, 2.0 equiv),  $\text{Pd(PPh}_3)_4$  (115mg, 0.1 mmol, 10 mol %), toluene/water (10/1 v/v ratio) (10 mL), and KOH (264 mg, 85%, 4.0 mmol, 4.0 equiv). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath) under a nitrogen atmosphere, and was stirred until maximum conversion of

**2a** to product occurred. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (50:1 hexanes/EA) to give **12** (281 mg, 76% yield).



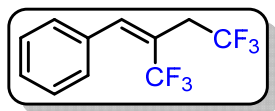
An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), KOH (98.8 mg, 85%, 1.5 mmol, 1.5 equiv), and anhydrous DMSO (6.0 mL). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at rt under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was quenched carefully with H<sub>2</sub>O (50 mL), extracted with DCM (30 mL × 3). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by column chromatography on silica gel using hexanes as eluent to afford the desired product **13** as a colorless oil (88.6 mg, 54% yield).



An oven-dried flask was charged with **2a** (264 mg, 1.0 mmol), KOH (98.8 mg, 85%, 1.5 mmol, 1.5 equiv), and anhydrous EtOH (6.0 mL). The reaction mixture was degassed by freeze-pump-thaw method and then stirred at rt under a nitrogen atmosphere, and was stirred until maximum conversion of **2a** to product occurred. The reaction mixture was quenched carefully with H<sub>2</sub>O (50 mL), extracted with DCM (30 mL × 3). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by column chromatography on silica gel using hexanes as eluent to afford the desired product **14** as a colorless oil (135 mg, 71% yield).

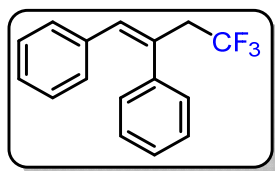
## 7.2 Physical data

(*Z*)-(4,4,4-Trifluoro-2-(trifluoromethyl)but-1-en-1-yl)benzene (**5**)



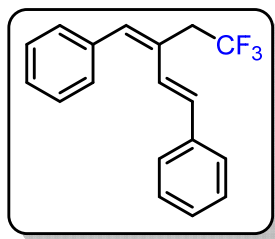
Colorless oil (160 mg, 63% yield);  $R_f = 0.7$  (100:1 hexanes/EA); IR (film)  $\nu_{max}$  3009, 1570, 1324, 1124, 682  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.33 (m, 5H), 7.10 (s, 1H), 3.15 (qd,  $J = 10.2$ , 0.9 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.1 (q,  $J = 3.4$  Hz), 133.6, 129.0, 129.0, 128.6 (q,  $J = 2.4$  Hz), 128.3, 124.9 (q,  $J = 276.0$  Hz), 122.7 (q,  $J = 276.5$  Hz), 37.0 (q,  $J = 31.6$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -58.66 (t,  $J = 4.6$  Hz), -65.69 (t,  $J = 12.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_8\text{F}_6$  254.05302; Found 254.05324.

**(Z)-(4,4-Trifluorobut-1-ene-1,2-diyl)dibenzene (6a)**



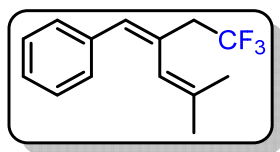
White solid (232 mg, 89% yield);  $R_f = 0.7$  (100:1 hexanes/EA); IR (film)  $\nu_{max}$  3015, 1668, 1417, 1035, 759  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.29 (m, 3H), 7.24 – 7.19 (m, 2H), 7.16 – 7.10 (m, 3H), 7.01 – 6.94 (m, 2H), 6.70 (s, 1H), 3.29 (q,  $J = 10.5$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  139.6, 136.1, 133.3, 131.5, 129.2, 128.7, 128.6, 128.0, 127.6, 127.2, 125.8 (q,  $J = 279.5$  Hz), 44.0 (q,  $J = 28.1$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -64.07 (t,  $J = 9.9$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3$  262.09694; Found 262.09699.

**((1Z,3E)-2-(2,2,2-Trifluoroethyl)buta-1,3-diene-1,4-diyl)dibenzene (6b)**



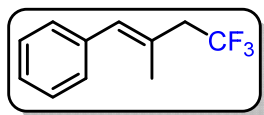
White solid (239 mg, 83% yield);  $R_f = 0.7$  (100:1 hexanes/EA); m.p. 62.5–63.1  $^{\circ}\text{C}$ ; IR (film)  $\nu_{max}$  3036, 1693, 1650, 1304, 1012, 842  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.45 – 7.29 (m, 10H), 7.29 – 7.20 (m, 2H), 6.80 – 6.73 (m, 1H), 3.28 (q,  $J = 10.7$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  137.1, 136.5, 135.5, 132.8, 131.0, 129.6, 129.2, 128.7, 128.4, 127.9, 127.6, 126.7, 125.7 (q,  $J = 279.5$  Hz), 38.3 (q,  $J = 29.5$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform-*d*)  $\delta$  -64.15 (t,  $J = 10.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3$  288.11259; Found 288.11263.

**(Z)-(4-Methyl-2-(2,2,2-trifluoroethyl)penta-1,3-dien-1-yl)benzene (6c)**



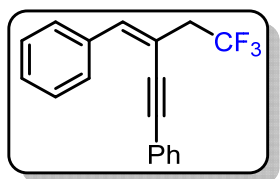
Colorless oil (192 mg, 80% yield);  $R_f = 0.6$  (100:1 hexanes/EA); IR (film)  $\nu_{max}$  3312, 1573, 1043, 687  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.44 – 7.36 (m, 2H), 7.28 (q,  $J = 7.6, 6.5$  Hz, 2H), 7.19 (q,  $J = 7.2, 6.4$  Hz, 1H), 6.44 (s, 1H), 5.77 (s, 1H), 2.96 (qd,  $J = 11.3, 10.7, 5.3$  Hz, 2H), 1.76 (s, 3H), 1.36 (s, 3H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  137.3, 136.5, 132.9, 128.6, 128.5, 128.1, 127.0 (q,  $J = 6.1$  Hz), 124.2 (q,  $J = 277.5$  Hz), 122.5, 43.2 (q,  $J = 28.1$  Hz), 25.5, 19.4 ppm; HRMS (EI) Calcd for  $\text{C}_{15}\text{H}_{14}\text{F}_3$  240.11259; Found 240.11220.

**(E)-(4,4,4-Trifluoro-2-methylbut-1-en-1-yl)benzene (6d)<sup>[13]</sup>**



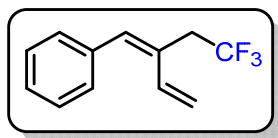
Colorless oil (168 mg, 84% yield);  $R_f = 0.8$  (100:1 hexanes/EA);  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.37 (t,  $J = 7.5$  Hz, 2H), 7.28 (d,  $J = 7.8$  Hz, 2H), 6.50 (s, 1H), 2.95 (q,  $J = 10.9$  Hz, 2H), 1.99 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  137.1, 132.2, 128.9, 128.2, 127.8 (q,  $J = 2.4$  Hz), 126.9, 126.2 (q,  $J = 278.8$  Hz), 44.3 (q,  $J = 28.6$  Hz), 18.3 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.48 (t,  $J = 10.9$  Hz) ppm.

**(Z)-(2-(2,2,2-Trifluoroethyl)but-1-en-3-yne-1,4-diyl)dibenzene (7)**



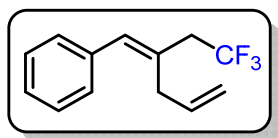
Colorless oil (260 mg, 91% yield);  $R_f = 0.6$  (100:1 hexanes/EA); IR (film)  $\nu_{max}$  3248, 3072, 1588, 664  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.92 (dd,  $J = 7.7, 2.6$  Hz, 2H), 7.50 (dq,  $J = 5.9, 3.4$  Hz, 2H), 7.38 (tqd,  $J = 9.5, 7.0, 3.0$  Hz, 6H), 6.77 (s, 1H), 3.17 (q,  $J = 10.2$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  140.1, 135.6, 131.5, 128.8, 128.7, 128.4, 128.3, 125.6 (q,  $J = 277.9$  Hz), 110.5 (q,  $J = 3.6, 3.1$  Hz), 96.5, 88.2, 43.1 (q,  $J = 29.3$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.11 (t,  $J = 10.8$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_3$  286.09694; Found 286.09687.

**(Z)-(2-(2,2,2-trifluoroethyl)buta-1,3-dien-1-yl)benzene (8)**



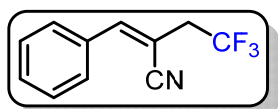
Colorless oil (187 mg, 88% yield);  $R_f = 0.5$  (200:1 hexanes/AcOEt); IR (film)  $\nu_{max}$  2926, 2855, 1492, 1440, 1351, 1255, 1133, 1094, 910, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.41 – 7.28 (m, 5H), 6.94 – 6.83 (m, 1H), 6.70 (s, 1H), 5.44 (d,  $J = 17.6$  Hz, 1H), 5.29 (dd,  $J = 11.2, 1.7$  Hz, 1H), 3.16 (qd,  $J = 10.7, 0.9$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  136.2, 135.3, 133.4, 129.4, 128.2, 128.2, 128.1, 127.5, 116.4, 37.6 (q,  $J = 29.6$  Hz) ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -64.3 ppm; HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{11}\text{F}_3$  212.08128; Found 212.08096.

**(E)-2-(2,2,2-trifluoroethyl)penta-1,4-dien-1-ylbenzene (9)**



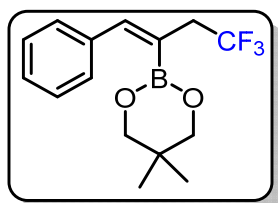
Colorless oil (170 mg, 75% yield);  $R_f = 0.2$  (hexanes); IR (film)  $\nu_{max}$  3027, 1638, 1601, 1495, 1257, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.40 – 7.33 (m, 2H), 7.31 – 7.24 (m, 3H), 6.66 (s, 1H), 5.85 (dd,  $J = 16.5, 10.1$  Hz, 1H), 5.25 – 5.10 (m, 2H), 3.12 (d,  $J = 6.2$  Hz, 2H), 2.95 (q,  $J = 10.9$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  136.7, 134.9, 133.6, 129.3, 128.5, 128.3, 127.1, 126.2 (q,  $J = 277.8$  Hz), 117.1, 40.2 (q,  $J = 28.8$  Hz), 35.3 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -64.26 (t,  $J = 11.0$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{13}\text{H}_{13}\text{F}_3$  226.09694; Found 226.09676.

**(Z)-2-Benzylidene-4,4,4-trifluorobutanenitrile (10)<sup>[14]</sup>**



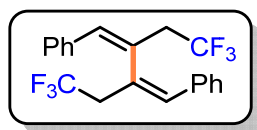
White solid (182 mg, 86% yield);  $R_f = 0.3$  (20:1 hexanes/EA);  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.82 – 7.78 (m, 2H), 7.48 – 7.43 (m, 3H), 7.17 (s, 1H), 3.16 (q,  $J = 9.8$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  150.3, 132.5, 131.3, 129.1, 129.0, 124.6 (q,  $J = 277.9$  Hz), 117.5, 99.2 (q,  $J = 3.4$  Hz), 40.0 (q,  $J = 31.2$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -65.80 (t,  $J = 10.0$  Hz) ppm.

**(E)-5,5-Dimethyl-2-(4,4,4-trifluoro-1-phenylbut-1-en-2-yl)-1,3,2-dioxaborinane (11)**



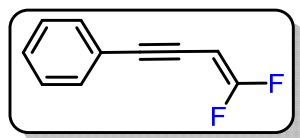
Colorless oil (227 mg, 62% yield);  $R_f = 0.4$  (50:1 hexanes/EA); IR (film)  $\nu_{max}$  3051, 1647, 1318, 746  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.40 – 7.24 (m, 5H), 7.07 (s, 1H), 3.62 (s, 4H), 3.08 (q,  $J = 11.0$  Hz, 2H), 1.00 (s, 6H) ppm;  $^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  146.1, 138.1, 128.2, 127.9, 127.9, 127.5, 126.4 (q,  $J = 277.0$  Hz), 72.1, 41.4 (q,  $J = 28.5$  Hz), 31.5, 22.0 ppm;  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -65.29 (t,  $J = 11.7$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{15}\text{H}_{18}\text{BF}_3\text{O}_2$  298.13519; Found 298.13526.

**((1Z,3Z)-2,3-Bis(2,2,2-trifluoroethyl)buta-1,3-diene-1,4-diyl)dibenzene (12)**



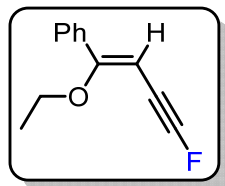
Colorless oil (281 mg, 76% yield);  $R_f = 0.5$  (50:1 hexanes/EA); IR (film)  $\nu_{max}$  3072, 1564, 1372, 1128, 760  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.52 – 7.47 (m, 4H), 7.39 – 7.27 (m, 6H), 6.75 (s, 2H), 2.91 (q,  $J = 10.7$  Hz, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  135.8, 133.5, 129.8, 128.7, 128.3, 128.1, 125.7 (q,  $J = 279.1$  Hz), 40.6 (q,  $J = 29.5$  Hz) ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -63.53 (t,  $J = 10.4$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{20}\text{H}_{16}\text{F}_6$  370.11562; Found 370.11520.

**(4,4-Difluorobut-3-en-1-yn-1-yl)benzene (13)<sup>[15]</sup>**



Colorless oil (88.6 mg, 54% yield);  $R_f = 0.8$  (hexanes);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.44 (dd,  $J = 6.7, 3.0$  Hz, 2H), 7.34 – 7.29 (m, 3H), 4.81 (d,  $J = 23.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz, Chloroform- $d$ )  $\delta$  161.8 (dd,  $J = 300.4, 294.4$  Hz), 131.4, 128.5, 128.3, 122.8, 93.2 (dd,  $J = 9.1, 3.8$  Hz), 77.6 (dd,  $J = 12.1, 4.5$  Hz), 65.7 (dd,  $J = 42.3, 18.1$  Hz);  $^{19}\text{F}$  NMR (282 MHz, Chloroform- $d$ )  $\delta$  -74.50 (dd,  $J = 22.9, 4.2$  Hz), -79.78 (d,  $J = 4.2$  Hz) ppm.

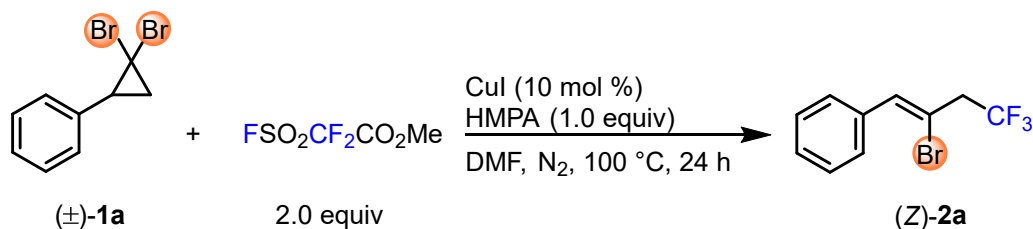
**(Z)-(1-Ethoxy-4-fluorobut-1-en-3-yn-1-yl)benzene (14)**



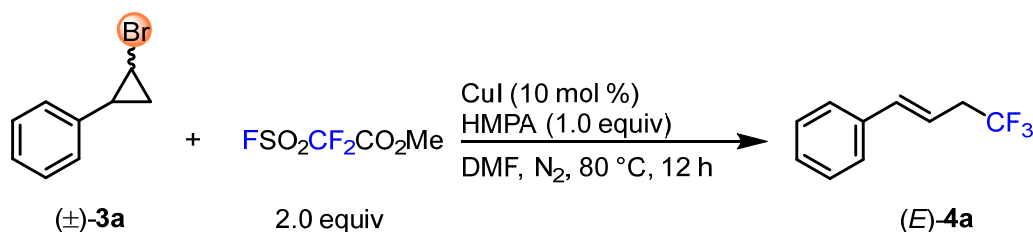
Colorless oil (135 mg, 71% yield);  $R_f = 0.4$  (hexanes); IR (film)  $\nu_{max}$  3210, 1874, 1653, 1554, 951, 772  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.43 – 7.38 (m, 2H), 7.33 – 7.25 (m, 4H), 4.25 (d,  $J = 27.8$

Hz, 1H), 4.00 (q,  $J = 7.0$  Hz, 2H), 1.39 (td,  $J = 7.1, 0.8$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.7 (d,  $J = 268.7$  Hz), 131.1, 128.2, 127.6, 123.9, 90.9, 81.5, 66.1 (d,  $J = 2.8$  Hz), 61.6 (d,  $J = 25.2$  Hz), 14.1 ppm;  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -72.16 (d,  $J = 28.2$  Hz) ppm; HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{11}\text{FO}$  190.07939; Found 190.07946.

## 8 Gram-scale reactions



A dry 100 mL Schlenk tube charged with a stirring bar was evacuated and backfilled with  $\text{N}_2$  (three times). Copper(I) iodide (100 mg, 0.5 mmol, 10 mol %), HMPA (895 mg, 5.0 mmol, 1.0 equiv) and anhydrous DMF (10 mL) were added under  $\text{N}_2$  atmosphere. After the mixture had been stirred for 15 min at room temperature, *gem*-dibromocyclopropane **1a** (1.38 g, 5.0 mmol, 1.0 equiv),  $\text{FSO}_2\text{CF}_2\text{COOMe}$  (1.92 g, 10.0 mmol, 2.0 equiv) and DMF (15 mL) were added. The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath). The reaction was monitored by TLC. Upon completion (24 h), the reaction was cooled to room temperature, quenched carefully with  $\text{H}_2\text{O}$  (50 mL), and extracted with DCM (30 mL  $\times$  3). The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by flash chromatography on silica gel using hexanes as eluent to give **2a** (colorless oil, 1.10 g, 83% yield).

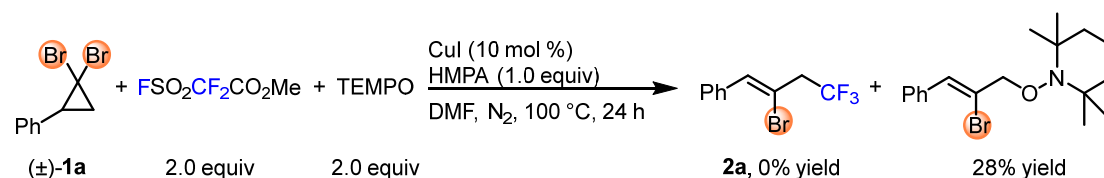


Copper(I) iodide (200 mg, 1.0 mmol, 10 mol %), HMPA (1.79 g, 10 mmol, 1.0 equiv), monobromocyclopropane **3a** (1.97 g, 10 mmol, 1.0 equiv) and  $\text{FSO}_2\text{CF}_2\text{COOMe}$  (3.84 g, 10 mmol, 2.0 equiv) were reacted in anhydrous DMF at 80 °C (oil bath) for 12 h. The crude product was purified by flash chromatography on silica gel using petroleum ether as eluent to give **4a** (colorless oil, 1.60 g, 86%

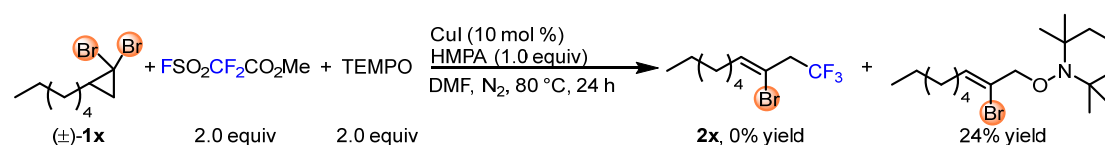
yield).

## 9 Mechanistic experiments

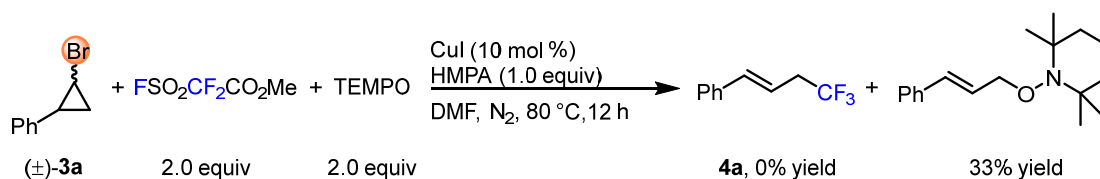
### 9.1 Radical-trapping experiments



A dry 50 mL Schlenk tube charged with a stirring bar was evacuated and backfilled with  $\text{N}_2$  (three times). Copper(I) iodide (20 mg, 0.1 mmol, 10 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv) and anhydrous DMF (4.0 mL) were added under  $\text{N}_2$  atmosphere. After the mixture had been stirred for 15 min at room temperature, *gem*-dibromocyclopropane **1a** (274 mg, 1.0 mmol, 1.0 mmol, 1.0 equiv),  $\text{FSO}_2\text{CF}_2\text{COOMe}$  (384 mg, 2.0 mmol, 2.0 equiv), TEMPO (312 mg, 2.0 mmol, 2.0 equiv) and anhydrous DMF (6.0 mL) were added. The reaction mixture was degassed by freeze-pump-thaw method and then stirred at 100 °C (oil bath). After 24 h, the reaction mixture was cooled to room temperature, quenched carefully with a significant amount of water, and extracted with DCM (20 mL  $\times$  5). Subsequently, the combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under vacuum with a rotary evaporator, the crude product was purified by column chromatography on silica gel (50:1 hexanes/EA as eluent) to give the TEMPO coupling product (70 mg, 28% yield).



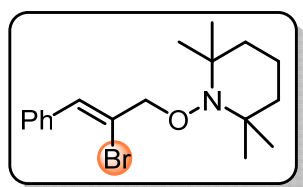
Copper(I) iodide (20 mg, 0.1 mmol, 10 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv), *gem*-dibromocyclohexane **1x** (282 mg, 1.0 mmol, 1.0 equiv),  $\text{FSO}_2\text{CF}_2\text{COOMe}$  (384 mg, 2.0 mmol, 2.0 equiv) and TEMPO (312 mg, 2.0 mmol, 2.0 equiv) were reacted at 80 °C (oil bath) in anhydrous DMF for 24 h. The crude product was purified by flash chromatography on silica gel (50:1 hexanes/EA as eluent) to give the TEMPO coupling product (87 mg, 24% yield).



Copper(I) iodide (20 mg, 0.1 mmol, 10 mol %), HMPA (179 mg, 1.0 mmol, 1.0 equiv), monobromocyclopropane **3a** (196 mg, 1.0 mmol, 1.0 equiv),  $\text{FSO}_2\text{CF}_2\text{COOMe}$  (384 mg, 2.0 mmol, 2.0 equiv) and TEMPO (312 mg, 2.0 mmol, 2.0 equiv) were reacted at  $80^\circ\text{C}$  (oil bath) in anhydrous DMF for 12 h. The crude product was purified by flash chromatography on silica gel (50:1 hexanes/EA as eluent) to give the TEMPO coupling product (91 mg, 33% yield).

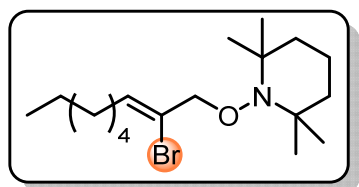
## 9.2 Physical data

### (Z)-1-((2-Bromo-3-phenylallyl)oxy)-2,2,6,6-tetramethylpiperidine



Colorless oil (28% yield);  $R_f = 0.3$  (50:1 hexanes/EA); IR (film)  $\nu_{\text{max}}$  3253, 3020, 1532, 1441, 899, 741  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.68 – 7.59 (m, 2H), 7.41 – 7.27 (m, 3H), 7.10 (s, 1H), 4.58 (d,  $J = 1.5$  Hz, 2H), 1.65 – 1.52 (m, 2H), 1.52 – 1.38 (m, 4H), 1.24 (s, 6H), 1.18 (s, 6H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  135.4, 129.1, 128.7, 128.1, 127.9, 121.2, 82.0, 60.1, 39.7, 32.9, 20.3, 17.1 ppm; HRMS (EI) Calcd for  $\text{C}_{18}\text{H}_{26}\text{BrNO}$  351.11978; Found 351.11983.

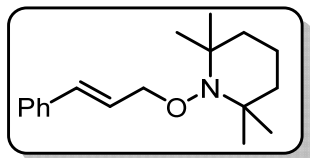
### (Z)-1-((2-Bromopent-2-en-1-yl)oxy)-2,2,6,6-tetramethylpiperidine



Colorless oil (24% yield);  $R_f = 0.5$  (50:1 hexanes/EA); IR (film)  $\nu_{\text{max}}$  3320, 3002, 1842, 1311, 659  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  5.99 (t,  $J = 6.9$  Hz, 1H), 4.39 (s, 2H), 2.19 (q,  $J = 7.2$  Hz, 2H), 1.44 (dd,  $J = 12.2, 5.3$  Hz, 6H), 1.31 (dt,  $J = 14.7, 5.0$  Hz, 8H), 1.20 – 1.10 (m, 12H), 0.89 (t,  $J = 6.2$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  131.0, 122.0, 81.3, 60.0, 39.7, 32.9, 31.6, 30.8,

28.9, 28.3, 22.6, 20.2, 17.1, 14.1 ppm; HRMS (EI) Calcd for C<sub>18</sub>H<sub>34</sub>BrNO 359.18238; Found 359.18249.

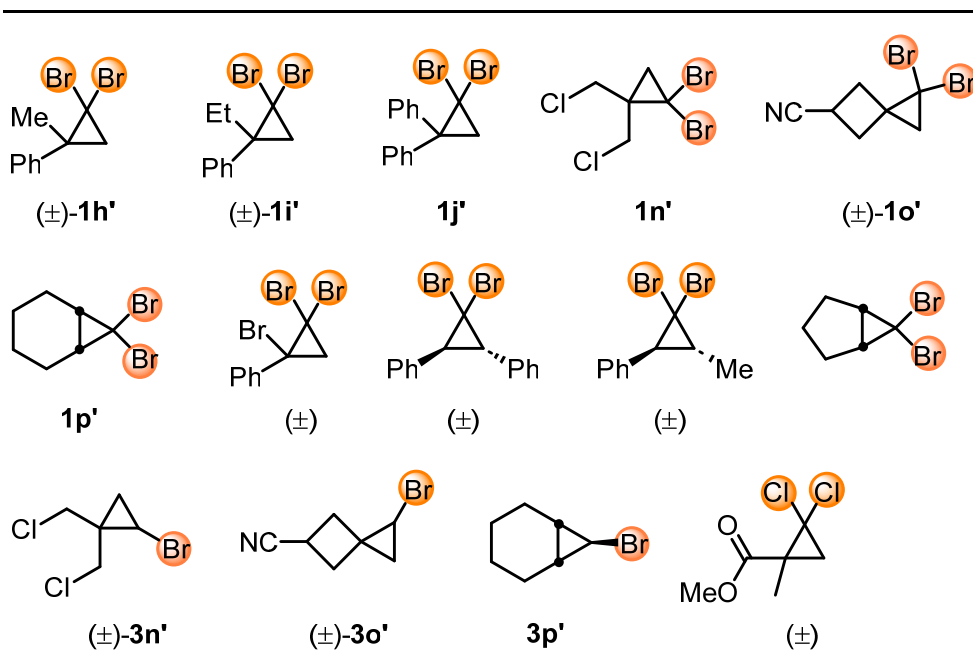
#### 1-(Cinnamyloxy)-2,2,6,6-tetramethylpiperidine<sup>[16]</sup>



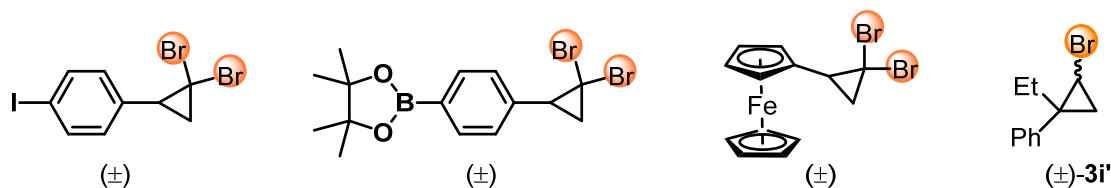
Colorless oil (33% yield); *R*<sub>f</sub> = 0.4 (50:1 hexanes/EA); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.47 (dd, *J* = 5.9, 1.5 Hz, 2H), 1.59 (m, 1H), 1.49 (dd, *J* = 8.9, 4.4 Hz, 4H), 1.35 (dt, *J* = 13.3, 3.4 Hz, 1H), 1.23 (s, 6H), 1.16 (s, 6H) ppm; <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.1, 131.4, 128.5, 127.4, 126.4, 125.6, 78.0, 59.8, 39.7, 33.0, 20.2, 17.2 ppm.

## 10 Unsuccessful reactants

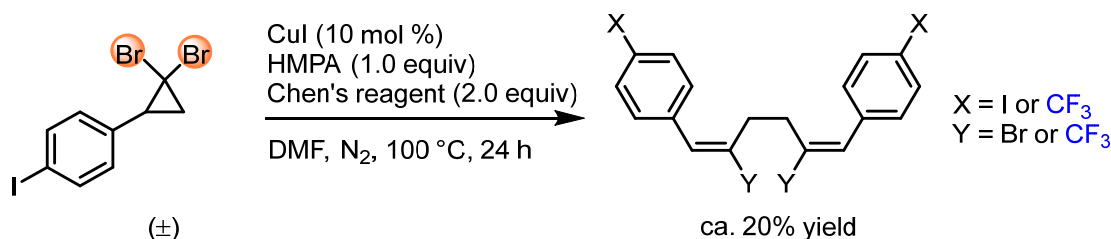
### 10.1 Unconverted reactants for dehalogenative ring-opening trifluoromethylations



### 10.2 Unsuccessful reactants for debrominative ring-opening trifluoromethylations

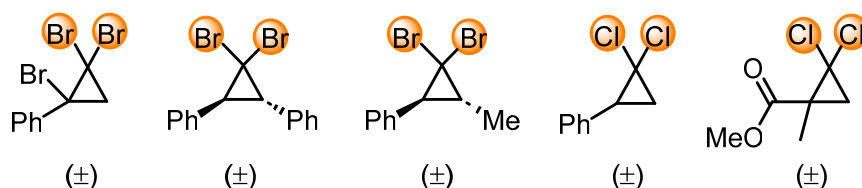


The above bromocyclopropanes were all converted under the reaction conditions but each gave a complicated mixture.



After column chromatography on silica gel, colorless crystals (ca. 20% yield based on dibromocyclopropane) were obtained from the reaction of 1,1-dibromo-2-(4-iodophenyl)cyclopropane and Chen's reagent. Single crystal XRD analysis indicated the crystals consisted of two or more products, in which the two C=C bonds were both in *trans*-configuration and the iodo or bromo group was substituted by CF<sub>3</sub>.

### 10.3 Unconverted reactants for reductive dehalogenations



## 11 References

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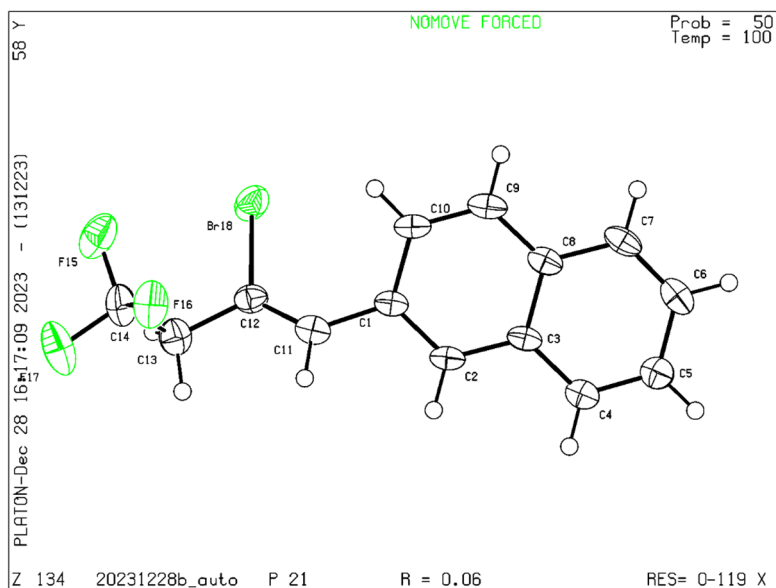
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## 12 Crystal data

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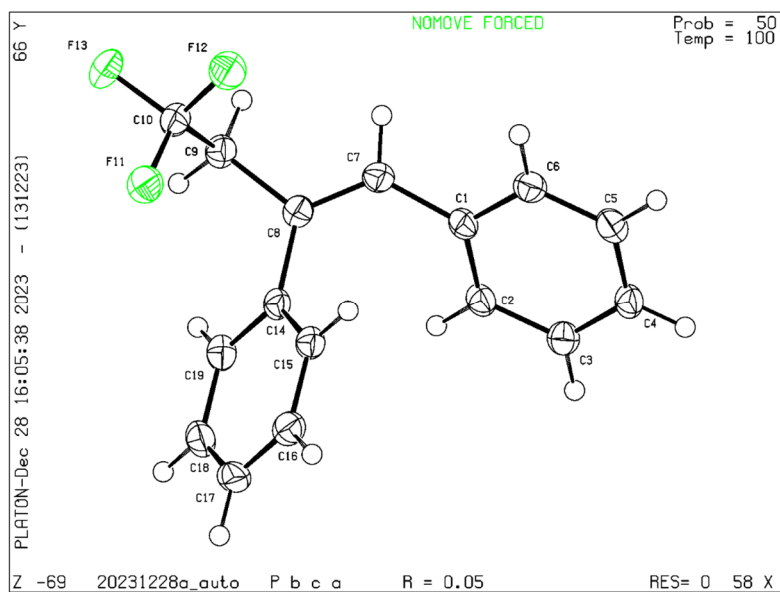
CCDC numbers: 2322379; 2322380; 2348125.

Single crystals of **2v** or **6a** were obtained from a *n*-hexane solution by slow evaporation of the solvent at rt. Single crystals of (*E*)-*N,N*-dimethyl-2-((trifluoromethyl)sulfonyl)ethen-1-amine were obtained by layering an EA solution with *n*-hexane and subsequent slow evaporation of the solvents at rt. The ellipsoid contour probability level is 50%.



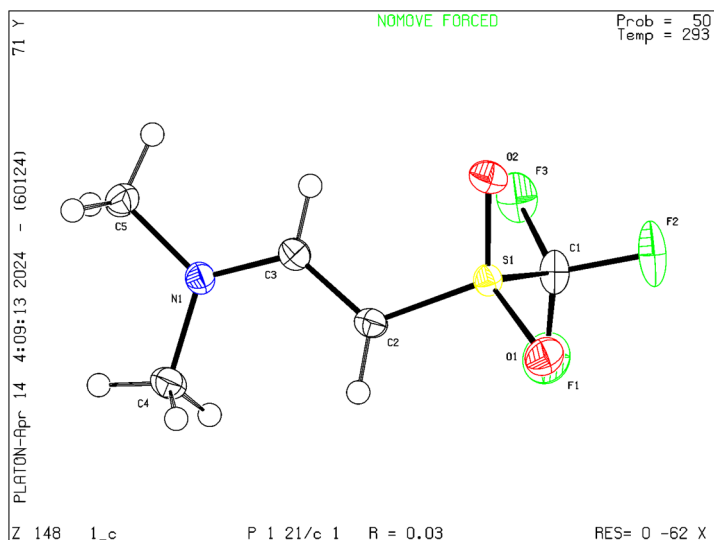
### Crystal data and structure refinement for 2v.

|                                                |                                                                |
|------------------------------------------------|----------------------------------------------------------------|
| Temperature/K                                  | 100(2)                                                         |
| Crystal system                                 | monoclinic                                                     |
| Space group                                    | P2 <sub>1</sub>                                                |
| a/Å                                            | 7.78987(17)                                                    |
| b/Å                                            | 5.88492(15)                                                    |
| c/Å                                            | 13.8221(3)                                                     |
| $\alpha/^\circ$                                | 90                                                             |
| $\beta/^\circ$                                 | 101.509(2)                                                     |
| $\gamma/^\circ$                                | 90                                                             |
| Volume/Å <sup>3</sup>                          | 620.90(2)                                                      |
| Z                                              | 2                                                              |
| $\rho_{\text{calc}}/\text{cm}^3$               | 1.686                                                          |
| $\mu/\text{mm}^{-1}$                           | 4.690                                                          |
| F(000)                                         | 312.0                                                          |
| Crystal size/mm <sup>3</sup>                   | 0.05 × 0.02 × 0.02                                             |
| Radiation                                      | CuK $\alpha$ ( $\lambda$ = 1.54184)                            |
| 2 $\theta$ range for data collection/ $^\circ$ | 6.526 to 152.518                                               |
| Index ranges                                   | -9 ≤ h ≤ 9, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17                           |
| Reflections collected                          | 11084                                                          |
| Independent reflections                        | 2484 [ $R_{\text{int}}$ = 0.0751, $R_{\text{sigma}}$ = 0.0376] |
| Data/restraints/parameters                     | 2484/1/163                                                     |
| Goodness-of-fit on F <sup>2</sup>              | 1.131                                                          |
| Final R indexes [ $I \geq 2\sigma(I)$ ]        | $R_1$ = 0.0618, $wR_2$ = 0.1723                                |
| Final R indexes [all data]                     | $R_1$ = 0.0627, $wR_2$ = 0.1738                                |
| Largest diff. peak/hole / e Å <sup>-3</sup>    | 0.77/-0.73                                                     |



### Crystal data and structure refinement for 6a.

|                                                |                                                                |
|------------------------------------------------|----------------------------------------------------------------|
| Temperature/K                                  | 100(2)                                                         |
| Crystal system                                 | orthorhombic                                                   |
| Space group                                    | Pbca                                                           |
| a/Å                                            | 5.6746(10)                                                     |
| b/Å                                            | 17.7150(18)                                                    |
| c/Å                                            | 25.651(2)                                                      |
| $\alpha/^\circ$                                | 90                                                             |
| $\beta/^\circ$                                 | 90                                                             |
| $\gamma/^\circ$                                | 90                                                             |
| Volume/Å <sup>3</sup>                          | 2578.6(6)                                                      |
| Z                                              | 8                                                              |
| $\rho_{\text{calc}}/\text{cm}^3$               | 1.351                                                          |
| $\mu/\text{mm}^{-1}$                           | 0.912                                                          |
| F(000)                                         | 1088.0                                                         |
| Crystal size/mm <sup>3</sup>                   | 0.300 × 0.300 × 0.100                                          |
| Radiation                                      | CuK $\alpha$ ( $\lambda$ = 1.54184)                            |
| 2 $\theta$ range for data collection/ $^\circ$ | 6.892 to 151.912                                               |
| Index ranges                                   | -6 ≤ h ≤ 7, -21 ≤ k ≤ 20, -31 ≤ l ≤ 32                         |
| Reflections collected                          | 22921                                                          |
| Independent reflections                        | 2646 [ $R_{\text{int}}$ = 0.1343, $R_{\text{sigma}}$ = 0.0747] |
| Data/restraints/parameters                     | 2646/0/173                                                     |
| Goodness-of-fit on $F^2$                       | 1.081                                                          |
| Final R indexes [ $I \geq 2\sigma(I)$ ]        | $R_1$ = 0.0533, $wR_2$ = 0.1338                                |
| Final R indexes [all data]                     | $R_1$ = 0.0615, $wR_2$ = 0.1416                                |




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**Crystal data and structure refinement for *N,N*-dimethyl-2-triflylethenamine.**

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|                                    |                                                               |
|------------------------------------|---------------------------------------------------------------|
| Temperature/K                      | 100.00(10)                                                    |
| Crystal system                     | monoclinic                                                    |
| Space group                        | P2 <sub>1</sub> /c                                            |
| a/Å                                | 9.4692(3)                                                     |
| b/Å                                | 9.0363(2)                                                     |
| c/Å                                | 10.2290(3)                                                    |
| α/°                                | 90                                                            |
| β/°                                | 108.996(3)                                                    |
| γ/°                                | 90                                                            |
| Volume/Å <sup>3</sup>              | 827.59(4)                                                     |
| Z                                  | 4                                                             |
| ρ <sub>calc</sub> /cm <sup>3</sup> | 1.631                                                         |
| μ/mm <sup>-1</sup>                 | 0.403                                                         |
| F(000)                             | 416.0                                                         |
| Crystal size/mm <sup>3</sup>       | 0.200 × 0.200 × 0.100                                         |
| Radiation                          | MoKα (λ = 0.71073)                                            |
| 2θ range for data collection/°     | 6.806 to 59.596                                               |
| Index ranges                       | -13 ≤ h ≤ 13, -12 ≤ k ≤ 12, -13 ≤ l ≤ 14                      |
| Reflections collected              | 17782                                                         |
| Independent reflections            | 2206 [R <sub>int</sub> = 0.0353, R <sub>sigma</sub> = 0.0202] |
| Data/restraints/parameters         | 2206/0/111                                                    |
| Goodness-of-fit on F <sup>2</sup>  | 1.146                                                         |
| Final R indexes [I ≥ 2σ (I)]       | R <sub>1</sub> = 0.0342, wR <sub>2</sub> = 0.0884             |
| Final R indexes [all data]         | R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.0913             |

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# 13 NMR spectra

