# **Electronic Supplementary Information**

# Organoselenium-Catalyzed N<sup>1</sup>- and N<sup>2</sup>-selective aza-Wacker reaction

## of alkenes with benzotriazoles

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#### I. General remarks.

All reagents were purchased from commercial sources and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Ascend<sup>TM</sup> 400 spectrometer in deuterated solvents containing TMS as an internal reference standard. High-resolution mass spectrometry (HRMS) analyses were conducted on a Waters LCT Premier/XE. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All the reactions were conducted in oil bath and monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Purification by flash column chromatography was performed over SiO<sub>2</sub> (silica gel 200–300 mesh).

#### **II. GC-MS study**

To a reaction tube equipped with a stir bar, styrene **1a** (0.5 mmol, 52.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg) were addes. The reaction mixture was stirred in DME (2.0 mL) at 120 °C for 1.5 h. And then take 2  $\mu$ L reaction liquid for GC-MS analysis. After scanned for 8.202 min, the signal 260.1, which is more like a mass fragment from intermediate **6**.



#### **III. General procedure:**

#### General procedure for compounds 3:

To a reaction tube equipped with a stir bar, alkenes 1 (0.5 mmol), benzotriazoles 2 (0.5 mmol), (PhSe)<sub>2</sub> (5% mol), and selectfluor (0.6 mmol) were added sequentially. Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3**.

#### General procedure for compounds 4:

To a reaction tube equipped with a stir bar, alkenes 1 (0.5 mmol), benzotriazoles 2 (0.5 mmol), (PhSe)<sub>2</sub> (5% mol), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol) were added sequentially. Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4**.

#### General procedure for compounds 5, 6, 7 and 8, please see references 1-4.

#### IV. Analytical data of products obtained in this study

#### 1-(1-phenylvinyl)-1*H*-benzo[*d*][1,2,3]triazole (3a).

styrene **1a** (0.5 mmol, 52.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were

dried over anhydrous  $Na_2SO_4$  and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3a** as pale yellow liquid (79%, 87.4 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.79 (d, *J* = 0.8, 1H), 5.81 (s, 1H), 7.07 (d, *J* = 6.0, 1H), 7.30 (d, *J* = 7.2, 2H), 7.37-7.44 (m, 5H), 8.12 (t, *J* = 2.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.1, 111.2, 120.1, 124.2, 126.9, 127.8, 128.8, 129.8, 132.9, 134.6, 142.6, 146.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 222.1031; Found 222.1038.

#### 1-(1-(2-fluorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3b).

1-fluoro-2-vinylbenzene **1b** (0.5 mmol, 61.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3b** as as pale yellow liquid (73%, 87.3 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 5.82$  (s, 1H), 6.01 (s, 1H), 7.12-7.20 (m, 3H), 7.25 (d, J = 7.2, 1H), 7.37-7.43 (m, 3H), 8.10 (s, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 110.6$ , 113.6 (d, J = 4.3 Hz), 116.5 (d, J = 21.6 Hz), 120.2, 124.2, 124.5, 127.9, 130.1 (d, J = 2.2 Hz), 131.4, 132.5, 137.4, 146.1, 158.9, 161.4 (d, J = 252.3 Hz). HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub>, [M+H]<sup>+</sup> 240.0937; Found 240.0940.

#### 1-(1-(4-fluorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3c).

1-fluoro-4-vinylbenzene 1c (0.5 mmol, 61.0 mg), benzotriazole 2a (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and

quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3c** as pale yellow liquid (75%, 89.7 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.76 (s, 2H), 7.07-7.13 (m, 3H), 7.30 (q, *J* = 5.2, 2H), 7.39-7.42 (m, 2H), 8.12 (d, *J* = 6.8, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.8, 111.0, 115.8, 116.0, 120.4, 124.3, 127.9, 128.9 (d, *J* = 8.3 Hz), 130.8 (d, *J* = 3.3 Hz), 132.8, 141.7, 146.1, 162.3 (d, *J* = 250.3 Hz), 164.8. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub>, [M+H]<sup>+</sup> 240.0937; Found 240.0933.

#### 1-(1-(2-chlorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3d).

1-chloro-2-vinylbenzene 1d (0.5 mmol, 69.3 mg), benzotriazole 2a (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product 3d as white solid (76%, 97.1 mg), melting point: 68-69 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.59 (s, 1H), 6.08 (s, 1H), 7.08 (d, *J* = 6.8, 1H), 7.37-7.41 (m, 5H), 7.55 (dd, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 6.0, 1H), 8.09 (d, *J* = 2.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.7, 111.7, 120.2, 124.2, 127.2, 128.0, 130.3, 130.9, 131.6, 132.2, 133.4, 134.1, 140.7, 146.2. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0638.

#### 1-(1-(3-chlorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3e).

1-chloro-3-vinylbenzene **1e** (0.5 mmol, 69.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the

reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3e** as pale yellow liquid (74%, 94.6 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.81 (s, 1H), 5.84 (s, 1H), 7.15 (d, *J* = 8.0, 2H), 7.32-7.43 (m, 5H), 8.13 (t, *J* = 1.2, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.9, 112.1, 120.2, 124.3, 125.1, 127.0, 128.1, 129.8, 130.1, 132.8, 134.9, 136.5, 141.4, 146.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0647.

#### 1-(1-(4-chlorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3f).

1-chloro-4-vinylbenzene **1f** (0.5 mmol, 69.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3f** as white solid (78%, 99.7 mg), melting point: 57-58 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.80 (s, 1H), 5.81 (s, 1H), 7.13 (d, *J* = 6.8, 1H), 7.24 (d, *J* = 8.4, 2H), 7.33-7.42 (m, 4H), 8.13 (d, *J* = 2.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.0, 111.4, 120.2, 124.3, 128.0, 128.2, 129.1, 132.7, 133.1, 135.8, 141.6, 146.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0639.

#### 1-(1-(2-bromophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3g).

1-bromo-2-vinylbenzene 1g (0.5 mmol, 91.5 mg), benzotriazole 2a (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the

reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3g** as white solid (75%, 112.6 mg), melting point: 67-68 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 5.55$  (d, J = 0.8, 1H), 6.08 (d, J = 0.8, 1H), 7.05 (d, J = 6.8, 1H), 7.34-7.38 (m, 3H), 7.46 (q, J = 6.4, 1H), 7.57-7.62 (m, 2H), 8.09 (dd,  $J_I = 2.8$ ,  $J_2 = 6.8$ , 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 110.8$ , 111.2, 120.2, 122.9, 124.2, 127.8, 128.0, 131.1, 131.9, 132.2, 133.5, 136.0, 142.0, 146.3. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub>, [M+H]<sup>+</sup> 300.0137; Found 300.0142.

#### 1-(1-(3-bromophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3h).

1-bromo-3-vinylbenzene **1h** (0.5 mmol, 91.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3h** as pale yellow liquid (72%, 108.1 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.82 (s, 1H), 5.84 (s, 1H), 7.14 (d, *J* = 8.0, 2H), 7.19 (d, *J* = 8.4, 1H), 7.24-7.28 (m, 2H), 7.39-7.46 (m, 2H), 7.56 (d, *J* = 8.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.9, 112.1, 120.3, 124.4, 125.5, 128.1, 129.9, 130.3, 132.8, 136.7, 141.3, 146.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub>, [M+H]<sup>+</sup> 300.0137; Found 300.0148.

#### 1-(1-(4-bromophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3i).

1-bromo-4-vinylbenzene 1i (0.5 mmol, 91.5 mg), benzotriazole 2a (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the

reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3i** as white solid (80%, 120.1 mg), melting point: 57-58 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 5.80$  (d, J = 1.2, 1H), 5.82 (d, J = 0.8, 1H), 7.11-7.13 (m, 1H), 7.17 (dd,  $J_1 = 1.6, J_2 = 6.8, 2$ H), 7.40 (dd,  $J_1 = 1.6, J_2 = 4.8, 2$ H), 7.43 (d, J = 1.6, 2H), 7.53 (t, J = 6.4, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 110.9, 111.4, 120.2, 124.1, 124.3, 128.0, 128.4, 132.0, 132.8, 133.6, 141.7, 146.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub>, [M+H]<sup>+</sup> 300.0137; Found 300.0141.$ 

### 1-(1-(4-(trifluoromethyl)phenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3j).

1-(trifluoromethyl)-4-vinylbenzene **1j** (0.5 mmol, 86.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3j** as white solid (77%, 111.4 mg), melting point: 83-84 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.89 (s, 1H), 5.92 (s, 1H), 7.13 (d, *J* = 7.6, 1H), 7.42-7.44 (m, 4H), 7.64 (d, *J* = 8.4, 2H), 8.13 (d, *J* = 7.2, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.8, 112.9 (J<sub>C-F</sub> = 209 Hz), 120.3, 123.8 (d, *J* = 272.9 Hz), 124.4, 125.8 (q, *J* = 3.7 Hz), 126.7, 128.2, 131.6 (q, *J* = 32.7 Hz), 132.7, 138.1, 141.4, 146.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 290.0905; Found 290.0909.

## 1-(1-(2,6-dichlorophenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3k).

1,3-dichloro-2-vinylbenzene **1k** (0.5 mmol, 86.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3k** as white solid (73%, 105.9 mg), melting point: 91-92 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.50 (s, 1H), 6.26 (s, 1H), 7.24 (d, *J* = 8.4, 1H), 7.30-7.42 (m, 5H), 8.06 (dd, *J*<sub>1</sub> = 0.8, *J*<sub>2</sub> = 8.4, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.7, 111.9, 120.3, 124.3, 128.4, 131.0, 131.7, 133.2, 135.8, 136.9, 146.2. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 290.0252; Found 290.0258.

#### 1-(1-(*m*-tolyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3l).

1-methyl-3-vinylbenzene **11** (0.5 mmol, 59.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **31** as pale yellow liquid (85%, 100.0 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.33 (s, 3H), 5.75 (s, 1H), 5.78 (s, 1H), 7.07-7.11 (m, 3H), 7.25 (d, *J* = 3.6, 2H), 7.37 (dd, *J*<sub>*I*</sub> = 3.2, *J*<sub>2</sub> = 6.4, 2H), 8.11 (dd, *J*<sub>*I*</sub> = 1.2, *J*<sub>2</sub> = 4.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 21.4, 110.9, 111.3, 120.0, 124.1, 127.5, 127.7, 128.7, 130.6, 132.9, 134.6, 138.6, 142.7, 146.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 236.1188; Found 236.1184.

## 1-(1-(*p*-tolyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3m).

1-methyl-4-vinylbenzene **1m** (0.5 mmol, 59.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3m** as pale yellow liquid (83%, 97.6 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 2.40$  (s, 3H), 5.73 (s, 1H), 5.76 (s, 1H), 7.08 (d, *J* = 6.4, 1H), 7.20 (s, 4H), 7.37 (dd, *J*<sub>1</sub> = 3.2, *J*<sub>2</sub> = 6.4, 2H), 8.11-8.14 (m, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 21.3$ , 110.2, 111.3, 120.1, 124.1, 126.8, 127.6, 129.5, 131.8, 132.9, 139.9, 142.6, 146.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 236.1188; Found 236.1191.

#### 1-(1-(4-(*tert*-butyl)phenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3n).

1-(*tert*-butyl)-4-vinylbenzene **1n** (0.5 mmol, 80.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3n** as pale yellow liquid (79%, 109.6 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 1.34$  (s, 9H), 5.71 (s, 1H), 5.80 (s, 1H), 7.14 (d, J = 6.4, 1H), 7.22 (d, J = 8.4, 2H), 7.37-7.41 (m, 4H), 8.12 (d, J = 2.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 31.2$ , 34.8, 110.4, 111.2, 120.0, 124.1, 125.7, 126.5, 127.7, 131.7, 133.0, 142.5, 146.0, 153.1. HRMS (ESI-TOF) Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 278.1657; Found 278.1652.

### 1-(1-(4-(chloromethyl)phenyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (30).

1-(chloromethyl)-4-vinylbenzene **10** (0.5 mmol, 76.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **30** as pale yellow liquid (76%, 102.5 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 4.60 (s, 2H), 5.78 (s, 1H), 5.83 (d, *J* = 0.8, 1H), 7.11-7.13 (m, 1H), 7.28 (d, *J* = 8.0, 2H), 7.38-7.41 (m, 4H), 8.11 (t, *J* = 2.0, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 31.2, 34.8, 110.4, 111.2, 120.0, 124.1, 125.7, 126.5, 127.7, 131.7, 133.0, 142.5, 146.0, 153.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>13</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 270.0798; Found 270.0792.

#### 4-(1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)vinyl)phenyl acetate (3p).

4-vinylphenyl acetate **1p** (0.5 mmol, 81.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3p** as white solid (69%, 96.4 mg), melting point: 95-96 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 2.30$  (s, 3H), 5.75 (s, 1H), 5.79 (s, 1H), 7.11 (d, J = 6.8, 3H), 7.30 (d, J = 8.4, 2H), 7.37-7.39 (m, 2H), 8.09 (t, J = 2.4, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 21.1, 111.1, 111.3, 120.1, 122.1, 124.3, 128.0, 132.2, 132.8, 141.7, 146.0, 151.7, 169.1$ . HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>, [M+H]<sup>+</sup> 280.1086; Found 280.1082.

### 1-(1-(cyclohex-1-en-1-yl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole (3q).

cyclohexene **1q** (0.5 mmol, 41.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3q** as pale yellow liquid (72%, 81.1 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 1.79-1.82 (m, 2H), 1.94-1.97 (m, 2H), 2.36-2.38 (m, 2H), 2.78-2.80 (m, 2H), 6.19-6.21 (m, 1H), 7.40 (m, 1H), 7.47 (t, *J* = 7.6, 1H), 7.66 (d, *J* = 8.4, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 21.6, 22.4, 24.4, 27.6, 111.0, 120.0, 121.3, 124.0, 127.5, 131.9, 135.2, 146.0. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 226.1344; Found 226.1347.

#### (E)-1-(1-(cyclooct-1-en-1-yl)vinyl)-1H-benzo[d][1,2,3]triazole (3r).

(Z)-cyclooctene **1r** (0.5 mmol, 55.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3r** as pale yellow liquid (70%, 88.7 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 1.68-1.75 (m, 8H), 2.41-2.46 (m, 2H), 2.93-2.93 (m, 2H), 6.11 (t, *J* = 8.4, 1H), 7.38 (t, *J* = 7.2, 1H), 7.47-7.51 (m, 1H), 7.65 (d, *J* = 8.4, 1H), 8.07 (d, *J* = 8.4, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 26.0, 26.1, 26.5, 28.5, 29.1, 29.9, 111.0, 120.0, 123.9, 124.2, 127.5, 132.4, 137.4, 145.9. HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>20</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 254.1657; Found 254.1656.

#### 5,6-dimethyl-1-(1-phenylvinyl)-1*H*-benzo[*d*][1,2,3]triazole (3s).

styrene **1a** (0.5 mmol, 54.0 mg), 5,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazole (0.5 mmol, 73.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg) and selectfluor (0.6 mmol, 212.4 mg). Then the reaction mixture was stirred in DME (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3s** as white solid (79%, 98.5 mg), melting point: 81-82 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.30 (s, 3H), 2.40 (s, 3H), 5.73 (s, 1H), 5.78 (s, 1H), 6.86 (s, 1H), 7.29 (d, *J* = 7.6, 2H), 7.36-7.42 (m, 3H), 7.85 (s, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 20.3, 20.9, 110.5, 110.7, 119.1, 126.8, 128.7, 129.6, 132.0, 134.0, 138.2, 142.7, 145.3. HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 250.1344; Found 250.1340.

#### 2-(1-phenylvinyl)-2*H*-benzo[*d*][1,2,3]triazole (4a).

styrene **1a** (0.5 mmol, 52.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4a** as pale yellow liquid (79%, 87.3 mg). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.67 (s, 1H), 6.21 (s, 1H), 7.42-7.45 (m, 7H), 7.92 (dd,  $J_1$  = 2.8,  $J_2$  = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.0, 118.5, 127.2,

128.4, 129.6, 134.6, 144.7, 147.1. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 222.1031; Found 222.1037.

#### 2-(1-(2-fluorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4b).

1-fluoro-2-vinylbenzene **1b** (0.5 mmol, 61.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4b** as white solid (74%, 88.5 mg), melting point:67-68 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 5.63$  (s, 1H), 6.50 (s, 1H), 7.14 (t, J = 8.4, 1H), 7.27 (d, J = 7.2, 1H), 7.40 (dd,  $J_1 = 3.2$ ,  $J_2 = 6.8$ , 2H), 7.47 (t, J = 7.2, 2H), 7.88 (d, J = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 112.6$ , 115.8, 116.1, 118.5, 124.2, 127.2, 131.1, 131.2 (d, J = 2.5 Hz), 131.4 (d, J = 8.3 Hz), 131.5, 141.9, 144.7, 159.0, 160.2 (d, J = 251.4 Hz), 161.5 . HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub>, [M+H]<sup>+</sup> 240.0937; Found 240.0942.

#### 2-(1-(4-fluorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4c).

1-fluoro-4-vinylbenzene **1c** (0.5 mmol, 61.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4c** as pale yellow liquid (70%, 83.7 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.61 (s, 1H), 6.22 (s, 1H), 7.15 (t, *J* = 8.4, 2H), 7.41-7.45 (m, 4H), 7.91 (dd, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 110.8, 115.4 (d, *J* = 21.9 Hz), 115.6, 118.4, 127.4, 130.3 (d, *J* = 8.5 Hz), 130.7 (d, *J* = 3.4 Hz), 144.7, 146.1, 162.2, 163.4 (d, *J* = 249.8 Hz), 164.7. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub>, [M+H]<sup>+</sup> 240.0937; Found 240.0941.

#### 2-(1-(2-chlorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4d).

1-chloro-2-vinylbenzene **1d** (0.5 mmol, 69.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4d** as pale yellow liquid (71%, 90.8 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.52 (s, 1H), 6.56 (s, 1H), 7.38-7.46 (m, 5H), 7.56 (dd,  $J_1$  = 2.0,  $J_2$  = 6.8, 1H), 7.87 (d, J = 3.2, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.9, 118.5, 126.9, 127.2, 129.8, 130.8, 131.8, 134.0, 134.1, 144.6, 144.8. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0640.

#### 2-(1-(3-chlorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4e).

1-chloro-3-vinylbenzene **1e** (0.5 mmol, 69.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4e** as pale yellow liquid (73%, 93.3 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.67 (s, 1H), 6.26 (s, 1H), 7.34 (q, *J* = 7.6, 2H), 7.43-7.47 (m, 4H), 7.91 (dd, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.8, 118.5, 124.6, 126.5, 127.4, 128.4, 129.7, 134.4, 136.3, 144.7, 145.8. HRMS

#### 2-(1-(4-chlorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4f).

1-chloro-4-vinylbenzene **1f** (0.5 mmol, 69.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4f** as white solid (75%, 95.9 mg), melting point: 156-157 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.65 (s, 1H), 6.24 (s, 1H), 7.39-7.44 (m, 6H), 7.90 (dd,  $J_1$  = 3.2,  $J_2$  = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.2, 118.4, 127.4, 128.7, 129.6, 133.0, 135.6, 144.7, 146.0. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0648.

#### 2-(1-(2-bromophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4g).

1-bromo-2-vinylbenzene **1g** (0.5 mmol, 91.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4g** as pale yellow liquid (68%, 102.1 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.50 (s, 1H), 5.67 (s, 1H), 7.36-7.41 (m, 3H), 7.56-7.58 (m, 2H), 7.65 (d, *J* = 8.0, 1H), 7.89 (t, *J* = 3.6, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.7, 118.5, 123.8, 127.3, 127.6, 130.9, 132.1, 133.0, 136.0, 144.8, 145.8.

#### 2-(1-(3-bromophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4h).

1-bromo-3-vinylbenzene **1h** (0.5 mmol, 91.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4h** as white solid (62%, 93.0 mg), melting point: 125-126 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.66 (s, 1H), 6.26 (s, 1H), 7.29-7.44 (m, 4H), 7.60 (d, *J* = 7.6, 2H), 7.90 (s, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.8, 118.5, 122.5, 127.0, 127.4, 129.9, 131.3, 132.5, 136.7, 144.7, 145.7. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub>, [M+H]<sup>+</sup> 300.0136; Found 300.0141.

#### 2-(1-(4-bromophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4i).

1-bromo-4-vinylbenzene **1i** (0.5 mmol, 91.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4i** as pale yellow liquid (70%, 105.1 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.65 (s, 1H), 6.24 (d, *J* = 0.8, 1H), 7.33 (d, *J* = 8.4, 2H), 7.43 (dd, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 6.4, 2H), 7.57 (d, *J* = 8.8, 2H), 7.89 (dd, *J*<sub>1</sub> = 3.2, *J*<sub>2</sub> = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.2, 118.4, 123.9, 127.4, 129.9, 131.6,

133.5, 144.7, 146.1. HRMS (ESI-TOF) Calcd for  $C_{14}H_{11}BrN_3$ ,  $[M+H]^+$  300.0136; Found 300.0139.

#### 2-(1-(4-(trifluoromethyl)phenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4j).

1-(trifluoromethyl)-4-vinylbenzene **1j** (0.5 mmol, 86.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4j** as white solid (72%, 104.1 mg), melting point: 89-90 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.72 (s, 1H), 6.35 (s, 1H), 7.44 (dd,  $J_1$  = 3.2,  $J_2$  = 6.8, 2H), 7.59 (d, J = 4.4, 2H), 7.70 (d, J = 8.0, 2H), 7.91 (dd,  $J_1$  = 3.2,  $J_2$  = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.2, 118.1, 118.4, 123.8 (d, J = 272.9 Hz), 125.4 (q, J = 3.7 Hz), 127.5, 127.6, 128.8, 131.4 (q, J = 32.5 Hz), 138.0, 144.8, 145.8. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 290.0905; Found 290.0911.

#### 2-(1-(4-nitrophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4k).

1-nitro-4-vinylbenzene **1k** (0.5 mmol, 74.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4k** as white solid (65%, 86.5 mg), melting point: 110-111 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.78 (s, 1H), 6.43 (s, 1H), 7.45 (dd,  $J_1$  = 3.2,  $J_2$  = 6.8,

2H), 7.65 (d, J = 8.8, 2H), 7.89 (dd,  $J_1 = 3.2$ ,  $J_2 = 6.8$ , 2H), 8.30 (d, J = 8.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 113.2$ , 118.4, 123.7, 127.7, 129.4, 140.6, 144.8, 145.1, 148.3. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>N<sub>4</sub>, [M+H]<sup>+</sup> 267.0882; Found 267.0887.

#### 2-(1-(2,6-dichlorophenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4l).

1,3-dichloro-2-vinylbenzene **11** (0.5 mmol, 86.5 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), NIS (0.5 mmol, 112.5 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4l** as white solid (80%, 116.1 mg), melting point: 150-151 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.51 (d, *J* = 0.8, 1H), 6.85 (s, 1H), 7.36-7.40 (m, 3H), 7.47 (d, *J* = 7.6, 2H), 7.85-7.88 (m, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 112.5, 118.5, 127.3, 128.1, 130.8, 133.0, 136.0, 140.6, 144.8. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 290.0252; Found 290.0257.

#### 2-(1-(naphthalen-2-yl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4m).

2-vinylnaphthalene **1m** (0.5 mmol, 72.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4m** as pale yellow liquid (76%, 102.7 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.80 (s, 1H), 6.31 (s, 1H), 7.44 (dd,  $J_1$  = 3.2,  $J_2$  = 6.4,

2H), 7.53 (dd,  $J_1$  = 3.6,  $J_2$  = 7.2, 2H), 7.89-7.99 (m, 7H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.4, 118.5, 125.4, 126.5, 127.0, 127.3, 127.7, 128.0, 128.1, 128.5, 132.0, 133.0, 133.7, 144.7, 147.2. HRMS (ESI-TOF) Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 272.1188; Found 272.1182.

#### 2-(1-(*m*-tolyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4n).

1-methyl-3-vinylbenzene **1n** (0.5 mmol, 59.7 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4n** as pale yellow liquid (75%, 88.2 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 2.39$  (s, 3H), 5.65 (s, 1H), 6.18 (s, 1H), 7.24 (t, J = 8.0, 3H), 7.32 (d, J = 7.6, 1H), 7.42 (dd,  $J_1 = 3.2, J_2 = 6.4, 2H$ ), 7.92 (dd,  $J_1 = 3.2, J_2 = 6.8, 2H$ ). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 21.4, 110.9, 118.5, 125.4, 127.2, 128.3, 128.8, 130.4, 134.6, 138.1, 144.7, 147.3. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 236.1188; Found 236.1192.$ 

#### 2-(1-(*p*-tolyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (40).

1-methyl-4-vinylbenzene **10** (0.5 mmol, 59.7 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **40** as pale yellow liquid (79%,

92.9 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta = 2.42$  (s, 3H), 5.63 (s, 1H), 6.16 (s, 1H), 7.24 (d, J = 8.0, 2H), 7.34 (d, J = 8.4, 2H), 7.42 (dd,  $J_1 = 2.8, J_2 = 6.8, 2H$ ), 7.92 (dd,  $J_1 = 3.2, J_2 = 6.8, 2H$ ). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta = 21.3, 110.3, 118.5, 127.1, 128.2, 129.1, 131.8, 139.7, 144.6, 147.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 236.1188; Found 236.1195.$ 

#### 2-(1-(4-(*tert*-butyl)phenyl)vinyl)-2*H*-benzo[*d*][1,2,3]triazole (4p).

1-(*tert*-butyl)-4-vinylbenzene **1p** (0.5 mmol, 80.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4p** as pale yellow liquid (74%, 102.6 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 1.36 (s, 9H), 5.65 (s, 1H), 6.15 (s, 1H), 7.38-7.47 (m, 6H), 7.91 (dd,  $J_1$  = 3.2,  $J_2$  = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 31.2, 34.7, 110.5, 118.5, 125.4, 127.1, 127.9, 131.6, 144.6, 147.1, 152.7. HRMS (ESI-TOF) Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 278.1657; Found 278.1651.

#### 2-(1-(4-(chloromethyl)phenyl)vinyl)-2H-benzo[d][1,2,3]triazole (4q).

1-(chloromethyl)-4-vinylbenzene **1q** (0.5 mmol, 76.3 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was

purified by flash column chromatography to give the desired product **4q** as pale yellow liquid (70%, 94.4 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 4.64 (s, 2H), 5.67 (s, 1H), 6.24 (s, 1H), 7.42-7.46 (m, 6H), 7.90 (dd,  $J_1$  = 3.2,  $J_2$  = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 45.6, 111.3, 118.4, 127.3, 128.6, 128.7, 134.6, 138.7, 144.7, 146.5. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>13</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 270.0798; Found 270.0793.

#### 4-(1-(2*H*-benzo[*d*][1,2,3]triazol-2-yl)vinyl)phenyl acetate (4r).

4-vinylphenyl acetate **1r** (0.5 mmol, 81.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4r** as white solid (67%, 93.6 mg), melting point: 90-91 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.33 (s, 3H), 6.56 (s, 1H), 6.22 (s, 1H), 7.17 (d, *J* = 8.4, 2H), 7.42-7.49 (m, 4H), 7.90 (dd, *J*<sub>1</sub> = 3.2, *J*<sub>2</sub> = 6.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 21.2, 111.2, 18.4, 121.7, 127.3, 129.5, 132.2, 144.7, 146.2, 151.1, 169.2. HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>, [M+H]<sup>+</sup> 280.1086; Found 280.1092.

#### 2-(cyclopent-1-en-1-yl)-2H-benzo[d][1,2,3]triazole (4s).

cyclopentene **1s** (0.5 mmol, 34.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash

column chromatography to give the desired product **4s** as white solid (78%, 72.2 mg), melting point: 91-92 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.16-2.23 (m, 2H), 2.65-2.69 (m, 2H), 3.16-3.20 (m, 2H), 6.63 (s, 1H), 7.37 (dd,  $J_1$  = 3.2,  $J_2$  = 6.8, 2H), 7.86 (dd,  $J_1$  = 2.8,  $J_2$  = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 22.1, 31.2, 31.4, 118.0, 121.2, 126.9, 141.8, 144.5. HRMS (ESI-TOF) Calcd for C<sub>11</sub>H<sub>12</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 186.1031; Found 186.1037.

#### 2-(cyclohex-1-en-1-yl)-2*H*-benzo[*d*][1,2,3]triazole (4t).

cyclohexene **1t** (0.5 mmol, 41.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4t** as white solid (73%, 72.7 mg), melting point: 65-66 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 1.72-1.76 (m, 2H), 1.90-1.93 (m, 2H), 2.35-2.37 (m, 2H), 2.90-2.92 (m, 2H), 6.98 (s, 1H), 7.35 (dd,  $J_1$  = 2.8,  $J_2$  = 6.4, 2H), 7.86 (dd,  $J_1$  = 3.2,  $J_2$  = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 21.6, 22.3, 24.4, 25.6, 118.0, 120.7, 126.5, 138.2, 144.1. HRMS (ESI-TOF) Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 200.1188; Found 200.1195.

#### (E)-2-(cyclooct-1-en-1-yl)-2H-benzo[d][1,2,3]triazole (4u).

(Z)-cyclooctene **1u** (0.5 mmol, 55.1 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product 4u as white solid (82%, 93.2 mg), melting point: 64-65 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 1.59-1.84 (m, 8H), 2.38-2.43 (m, 2H), 3.11-3.14 (m, 2H), 6.96 (s, 1H), 7.35 (dd,  $J_1$  = 2.8,  $J_2$  = 6.4, 2H), 7.86 (dd,  $J_1$  = 3.2,  $J_2$  = 6.4, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 25.9, 26.3, 26.4, 26.7, 28.5, 29.9, 118.0, 123.1, 126.5, 140.5, 144.2. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 228.1501; Found 228.1509.

#### 2-(2,5-dihydrofuran-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (4v).

2,5-dihydrofuran **1v** (0.5 mmol, 35.0 mg), benzotriazole **2a** (0.5 mmol, 59.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5  $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4v** as white solid (69%, 64.6 mg), melting point: 116-117 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 4.99-5.02 (m, 2H), 5.30-5.33 (m, 2H), 6.69 (t, *J* = 2.0, 1H), 7.42 (dd, *J*<sub>1</sub> = 3.2, *J*<sub>2</sub> = 7.2, 2H), 7.86 (d, *J* = 2.8, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 72.2, 75.5, 115.2, 118.1, 127.6, 144.7. HRMS (ESI-TOF) Calcd for C<sub>10</sub>H<sub>10</sub>ON<sub>3</sub>, [M+H]<sup>+</sup> 188.0824; Found 188.0827.

#### 5-methyl-2-(1-phenylvinyl)-2*H*-benzo[*d*][1,2,3]triazole (4w).

styrene **1a** (0.5 mmol, 54.0 mg), 5-methyl-2*H*-benzo[*d*][1,2,3]triazole (0.5 mmol, 66.5 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5

 $\times$  3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4w** as pale yellow liquid (70%, 82.4 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.51 (s, 3H), 5.64 (d, *J* = 0.8, 1H), 6.18 (d, *J* = 0.8, 1H), 7.25 (d, *J* = 1.2, 1H), 7.44-7.46 (m, 5H), 7.66 (d, *J* = 1.2, 1H), 7.79 (d, *J* = 8.8, 1H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 22.2, 110.5, 116.5, 117.9, 128.2, 128.4, 129.5, 130.2, 134.7, 143.4, 145.2, 147.1. HRMS (ESI-TOF) Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 236.1188; Found 236.1194.

#### 5-chloro-2-(1-phenylvinyl)-2*H*-benzo[*d*][1,2,3]triazole (4x).

styrene **1a** (0.5 mmol, 54.0 mg), 5-chloro-2*H*-benzo[*d*][1,2,3]triazole (0.5 mmol, 76.7 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4x** as white solid (74%, 94.6 mg), melting point: 65-66 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 5.68 (s, 1H), 6.24 (s, 1H), 7.35-7.46 (m, 6H), 7.84-7.92 (m, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 111.4, 117.4, 119.7, 128.3, 128.5, 128.8, 129.6, 133.1, 134.3, 143.2, 145.0, 147.0. HRMS (ESI-TOF) Calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub>, [M+H]<sup>+</sup> 256.0642; Found 256.0647.

#### 5,6-dimethyl-2-(1-phenylvinyl)-2*H*-benzo[*d*][1,2,3]triazole (4y).

styrene **1a** (0.5 mmol, 54.0 mg), 5,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazole (0.5 mmol, 73.6 mg), (PhSe)<sub>2</sub> (5% mol, 7.8 mg), Me<sub>3</sub>SiH (0.5 mmol, 37.1 mg) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.6 mmol, 162.0 mg). Then the reaction mixture was stirred in dioxane (2.0 mL) at 120 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled

to room temperature and quenched with water before being extracted with dichloromethane ( $5 \times 3$  mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4y** as pale yellow liquid (75%, 93.5 mg).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  = 2.42 (s, 6H), 5.61 (s, 1H), 6.16 (s, 1H), 7.44-7.45 (m, 5H), 7.65 (s, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  = 20.9, 110.2, 116.7, 128.2, 128.4, 129.4, 134.8, 137.9, 144.2, 147.1. HRMS (ESI-TOF) Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>, [M+H]<sup>+</sup> 250.1344; Found 250.1339.

#### **References:**

1. E. Tang, W.-L. Wang, Y.-J. Zhao, M. Zhang, X. Dai, Org. Lett., 2016, 18, 176.

2. K. Sun, X. Wang, Y.-H. Lv, G. Li, H.-Z. Jiao, C.-W. Dai, Y.-Y. Li, C. Zhang, L. Liu, *Chem. Commun.*, 2016, **52**, 8471.

3. L. Sun, Y. Yuan, M. Yao, H. Wang, D.-X. Wang, M. Gao, Y.-H. Chen, A.-W. Lei, *Org. Lett.*, 2019, **21**, 1297.

4. 1-(Trimethylsilyl)-1H-benzotriazole **8** (CAS: 43183-36-4) is purchased directly from Sigma-Aldrich or TCI.

V. <sup>1</sup>H NMR, and <sup>13</sup>C NMR Spectra of Compounds 3 and 4

# Compound 3a



## Compound 3b



## Compound 3c





180 160 140 120 100 80 60 40 20 0 ppm

200

## Compound 3d



## Compound 3e



# Compound 3f







# Compound 3g



## Compound 3h





## **Compound 3i**



# Compound 3j


### Compound 3k



## Compound 31



### Compound 3m



### Compound 3n



### **Compound 3o**



## Compound 3p



### Compound 3q



### **Compound 3r**



### Compound 3s



# Compound 4a



### **Compound 4b**











### **Compound 4d**







### **Compound 4e**







### **Compound 4f**



### **Compound 4g**



### **Compound 4h**







### **Compound 4i**







### Compound 4j





### **Compound 4k**



### **Compound 41**



### **Compound 4m**



60







Compound 4p



Compound 4q



**Compound 4r** 



**Compound 4s** 















**Compound 4v** 



**Compound 4w** 







Compound 4y

