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# **Electronic Supplementary Information**

# Brønsted and Lewis acid adducts of triazenes

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#### 1. Materials and methods

Unless otherwise noted, all reactions were carried out under inert atmosphere of dry N<sub>2</sub> using Schlenk or glovebox techniques. All reagents were purchased from commercial suppliers (Sigma Aldrich, Acros, TCI, VWR, Fluorochem, ABCR) and used without additional purification. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was purified by sublimation under vacuum prior to use. Dry solvents were obtained from a solvent purification system with aluminum oxide column (Innovative Technologies). The triazenes 1–7 were prepared according to published procedures. *NMR spectra* were recorded on Bruker spectrometers: AvanceIII 400 MHz Prodigy probe 5 mm ICONNMR ATMA, Avance 400 MHz BBIz 5mm ATMA, Avance 500 MHz CPTCIxyz 5 mm, or Avance III HD 600 MHz CPTCIz 5 mm. Chemical shifts in ppm were aligned with respect to the residual peak of deuterated solvent. *Electrosprayionization HRMS* data were acquired on a Q-Tof Ultima mass spectrometer (Waters) or a Q-Tof 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. *IR spectra* were recorded on a Perkin Elmer (UATR Two) spectrometer, using PerkinElmer Spectrum software (V 10.5.4).

### 2. NMR study of 1(HOTf)



In a Schlenk tube, a solution of triazene 1 (19 mg, 0.1 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1.8 mL) was cooled down to -78 °C and HOTf (27 µL, 45 mg, 0.3 mmol) was added slowly under vigorous stirring. After 20 min, an aliquot (0.5 mL) of the reaction mixture was rapidly transferred into a J-Young NMR tube under N<sub>2</sub> flow maintaining the temperature at -78 °C. NMR measurements were performed in a precooled Bruker AV NEO-400 instrument (-75 °C). NMR data for **1(HOTf)**: <sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  11.98 (s, 1H), 7.43–7.41 (m, 2H), 7.22–7.20 (m, 2H), 4.22–4.19 (br m, 2H), 3.88–3.84 (br m, 2H), 2.31 (s, 3H), 2.30–2.27 (br m, 2H), 2.16–2.14 (br m, 2H). <sup>13</sup>C **NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  138.70, 135.11, 130.24, 117.01, 57.26, 51.53, 23.58, 23.25, 20.92.



**Figure S2-1.** <sup>1</sup>H NMR spectra of triazene **1** in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C before (top) and after (bottom) addition of HOTf.



Figure S2-2. <sup>1</sup>H NMR spectrum of 1(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S2-3. <sup>13</sup>C NMR spectrum of 1(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S2-4. <sup>1</sup>H-<sup>15</sup>N HSQC correlation spectrum of 1(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S2-5. <sup>1</sup>H-<sup>15</sup>N HMBC correlation spectrum of 1(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S2-6. <sup>1</sup>H-<sup>13</sup>C HMBC correlation spectrum of 1(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



**Figure S2-7.** <sup>1</sup>H NMR spectra of **1(HOTf)** in CD<sub>2</sub>Cl<sub>2</sub> at various temperatures. The sample was gradually heated from -75 to 25 °C (0.5 °C/min).

### 3. NMR study of 3(HOTf)



In a Schlenk tube, a solution of triazene **3** (37 mg, 0.1 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1.8 mL) was cooled down to  $-78 \,^{\circ}$ C and HOTf (27 µL, 45 mg, 0.3 mmol) was added slowly under vigorous stirring. A color change from yellow to red-orange was observed. After 20 min, an aliquot (0.5 mL) of the reaction mixture was rapidly transferred into a J-Young NMR tube under N<sub>2</sub> flow maintaining the temperature at  $-78 \,^{\circ}$ C. NMR measurements were performed in a precooled Bruker AV NEO-400 instrument ( $-75 \,^{\circ}$ C). *Warning:* **3(HOTf)** *in solution rapidly decomposes with active gas evolution at temperatures higher than*  $-75 \,^{\circ}$ C. *This point should be taken into consideration when carrying such experiments. The J-Young NMR tube should be equipped for overpressure.* NMR data for **3(HOTf)**: <sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  11.82 (s, 1H), 11.64 (s, 1H), 7.54–7.51 (m, 3H), 7.45–7.32 (m, 10H), 7.21–7.05 (m, 5H), 6.95–6.92 (m, 2H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  138.71, 138.24, 136.20, 135.90, 133.95, 130.98, 130.87, 130.84, 130.51, 130.47, 130.17, 129.70, 129.60, 129.45, 128.83, 128.46, 127.92, 122.76, 119.61, 116.84, 116.46, 113.31.



**Figure S3-1.** <sup>1</sup>H NMR spectra of triazene **3** in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C before (top) and after (bottom) addition of HOTf.



Figure S3-2. <sup>1</sup>H NMR spectrum of 3(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S3-4. <sup>1</sup>H-<sup>15</sup>N HSQC correlation spectrum of 3(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S3-5. <sup>1</sup>H-<sup>15</sup>N HMBC correlation spectrum of 3(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.



Figure S3-6. <sup>1</sup>H-<sup>13</sup>C HMBC correlation spectrum of 3(HOTf) in CD<sub>2</sub>Cl<sub>2</sub> at -75 °C.

#### 4. Protonation of 1-acyl triazenes



**4(HOTf):** In the glovebox, triazene **4** (68.4 mg, 0.30 mmol) was dissolved in diethyl ether (0.6 mL) and cooled to -40 °C. HOTf (26.7 µL, 1 equiv) was added and the reaction mixture was cooled to -40 °C. The precipitate was isolated by vacuum filtration, rinsed with a small amount of diethyl ether, and dried under vacuum. Yield (white solid): 79.0 mg (70%). The product was stored in the glovebox at -40 °C.

<sup>1</sup>**H NMR** (600 MHz, CD<sub>3</sub>CN)  $\delta$  11.82 (s, 1H, N*H*), 4.76 (hept, *J* = 6.5 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 4.64 (hept, *J* = 6.5 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 2.80 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 1.77–1.63 (m, 2H, CH<sub>2</sub>), 1.46 (dd, *J* = 7.4, 6.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.37 (ddd, *J* = 7.3, 4.4, 3.1 Hz, 4H, CH<sub>2</sub>), 0.99–0.84 (m, 3H, CH<sub>3</sub>). <sup>13</sup>**C NMR** (151 MHz, CD<sub>3</sub>CN)  $\delta$  173.96, 59.93, 59.70, 34.42, 31.69, 24.03, 23.25, 23.03, 18.44, 14.17. **IR** (v<sub>max</sub>, cm<sup>-1</sup>): 1765 (m, C=O stretch), 1545 (m, N-H bend). **HRMS** (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>26</sub>N<sub>3</sub>O<sup>+</sup> 228.2070; Found 228.2066. [M + K]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>25</sub>KN<sub>3</sub>O<sup>+</sup> 266.1629; Found 266.1624.

**5(HOTf):** In the glovebox, triazene **5** (36.7 mg, 0.16 mmol) was dissolved in diethyl ether (1.6 ml). HOTf (14.0  $\mu$ l, 1 equiv) was added and a white precipitate formed immediately. The precipitate was isolated by vacuum filtration, rinsed with a small amount of diethyl ether, and dried under vacuum. Yield (white solid): 49.5 mg (81%). The product was stored in the glovebox at -40 °C.

<sup>1</sup>**H** NMR (600 MHz, CD<sub>3</sub>CN)  $\delta$  11.68 (s, 1H, N*H*), 4.75 (hept, *J* = 6.5 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 4.68 (hept, *J* = 6.6 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 1.88 (s, 3H, CH<sub>3</sub>), 1.85–1.81 (s, 3H, CH<sub>3</sub>), 1.78 (s, 3H, CH<sub>3</sub>), 1.48 (d, *J* = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, *J* = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN)  $\delta$  171.13, 142.27, 122.89, 59.92, 59.82, 23.18, 22.64, 19.05, 18.47, 15.93. **IR** (v<sub>max</sub>, cm<sup>-1</sup>): 1743 (m, C=O stretch), 1553 (m, N-H bend). **HRMS** (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>24</sub>N<sub>3</sub>O<sup>+</sup> 226.1914; Found 226.1911. [M + K]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>23</sub>KN<sub>3</sub>O<sup>+</sup> 264.1473; Found 264.1470. *Single crystals were obtained by layering a solution of* **5** *in THF with THF and then a solution of HOTf in THF (~1 equiv). The mixture was kept at –40 °C in the glovebox.* 

**6(HOTf):** In the glovebox, triazene **6** (19.1 mg, 0.073 mmol) was dispersed in 1.5 mL diethyl ether, it did not dissolve completely. HOTf (6.4  $\mu$ L, 1 equiv) was added and a white precipitate formed immediately. The precipitate was isolated by vacuum filtration, rinsed with small amount of diethyl ether and dried under vacuum. Yield (white solid): 27.3 mg (91%). The product was stored in the glovebox at -40 °C.

<sup>1</sup>**H** NMR (600 MHz, CD<sub>3</sub>CN)  $\delta$  8.17–7.88 (m, 2H, Ph), 7.88–7.72 (m, 1H, Ph), 7.63 (t, *J* = 7.9 Hz, 2H, Ph), 6.98 (s, 1H, NH), 4.86 (hept, *J* = 6.6 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 4.65 (hept, *J* = 6.5 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, *J* = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, *J* = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN)  $\delta$  136.81, 132.98, 130.58, 130.44, 59.66, 23.03, 18.56 (C=O signals were not detected). IR (v<sub>max</sub>, cm<sup>-1</sup>) 1763 (m, C=O stretch), 1679 (m, C=O stretch), 1579 (m, N-H bend). HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> 262.1550; Found 262.1546. [M + K]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>19</sub>KN<sub>3</sub>O<sub>2</sub><sup>+</sup> 300.1109; Found 300.1104. *Single crystals were obtained by layering a solution of 6 in diethyl ether with diethyl ether and then a solution of HOTf in diethyl ether (~1 equiv). The mixture was kept at -40 °C in the glovebox.* 

#### 5. Synthesis of the adducts 8 and 9



**8:** In the glovebox, triazene 7 (98.4 mg, 0.47 mmol) was dissolved in hexane (5 mL) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (241.0 mg, 0.47 mmol) was dissolved in DCM (1 mL) and hexane (1 mL). The solutions were combined and the mixture was immediately placed in a freezer (-40 °C). After 12 h, the resulting precipitate was collected by decanting the liquid, washed with hexane (3 x 3 mL), and dried under vacuum. Yield (pale yellow solid): 295.0 mg (87 %). The product was stored in the glovebox at -40 °C.

<sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  6.62 (hept, J = 6.6 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.16 (hept, J = 6.6 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.42 (d, J = 6.6 Hz, 7H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, J = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.05 (s, 9H, CH<sub>3</sub>). <sup>13</sup>**C NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  148.55 (dm, *o*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 242 Hz), 139.96 (dm, *p*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 248 Hz), 137.28 (dm, *m*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 257 Hz), 118.99 (*ipso*, C), 95.47 (alkyne), 74.95 (alkyne), 56.04 (CH(CH<sub>3</sub>)<sub>2</sub>), 54.86 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.78 (*t*Bu), 28.33 (*t*Bu), 23.23 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.12 (CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>**B NMR** (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -3.46. <sup>19</sup>**F NMR** (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -132.61, -159.46, -165.85. **HRMS** (APPI/QTOF) m/z: [M]<sup>-</sup> Calcd for C<sub>30</sub>H<sub>23</sub>BF<sub>15</sub>N<sub>3</sub><sup>-</sup> 721.1751; Found 721.1725. *Single crystals were from DCM/hexane*.



**9:** In the glovebox, triazene **2** (30.8 mg, 0.15 mmol) was dissolved in pentane (0.5 mL) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (72.0 mg, 0.14 mmol) was dissolved in DCM (0.5 ml) and pentane (1 mL). The solutions were combined and the mixture was immediately placed in a freezer (-40 °C). After 12 h, the resulting precipitate was collected by filtration and washed with pentane. The filtrate was kept at -40 °C for another12 h, resulting in the formation of more precipitate, which was isolated by filtration and combined with the first fraction. Yield (pale pink solid): 47.0 mg (47 %). The product was stored in the glovebox at -40 °C.

<sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.26 (dd, J = 5.4, 2.0 Hz, 3H, Ph), 7.15–7.02 (m, 2H, Ph), 4.36 (p, J = 6.6 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.09 (p, J = 6.5 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, J = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, J = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>**C NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  148.35 (dm, *o*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz), 145.73 (Ph), 139.87 (dm, *p*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 245 Hz), 137.13 (dm, *m*-CF, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 250 Hz), 129.92 (Ph), 129.57 (Ph), 123.70 (Ph), 120.53 (*ipso*, C), 57.44 (CH(CH<sub>3</sub>)<sub>2</sub>), 54.55 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.13 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.10 (CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>**B NMR** (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  –3.95. <sup>19</sup>**F NMR** (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  –131.85, –159.39, –165.78. **HRMS** (APPI/QTOF) m/z: [M]<sup>-</sup> Calcd for C<sub>30</sub>H<sub>19</sub>BF<sub>15</sub>N<sub>3<sup>-</sup></sub> 717.1438; Found 717.1415. *Single crystals were obtained by mixing triazene* **2** *and B*(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> *in pentane and a small amount of DCM to dissolve. The mixture was kept at –40 °C in the glovebox.* 

#### 6. Synthesis of the Pd complexes 10 and 11



**Complex 10:** PdCl<sub>2</sub>(PhCN)<sub>2</sub> (38 mg, 0.1 mmol) was added under stirring to a solution of triazene **1** (38 mg, 0.2 mmol) in DCM (1 mL). The color of the solution changed immediately from pale-yellow to deep-red. The mixture was stirred for 4 h at room temperature. Subsequently, the solvent was removed and the residue was washed with Et<sub>2</sub>O (3 x 2 mL) and hexane (2 mL). The resulting solid was crystallized from DCM/hexane at 4 °C. Yield (orange crystals): 50 mg (90%).

<sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298*K*)  $\delta$  7.67 (d, *J* = 8.3 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 4H), 5.32–4.28 (br m, 8H), 2.38 (s, 6H), 2.13–2.02 (br m, 8H). <sup>13</sup>**C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298*K*)  $\delta$  149.95, 137.48, 129.60, 124.58, 24.34, 21.31 (at 298K, peaks of N<u>C</u>H<sub>2</sub> are not visible due to broadening). <sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 200*K*)  $\delta$  7.63 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 4H), 5.76–5.67 (m, 4H), 3.96–3.84 (m, 4H), 2.33 (s, 6H), 2.20–2.10 (m, 4H), 1.97–1.90 (m, 4H). <sup>13</sup>**C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 200*K*)  $\delta$  148.78, 136.87, 129.10, 123.37, 55.23, 50.92, 24.68, 22.68, 20.82. **HRMS** (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>6</sub>NaPd<sup>+</sup> 577.0836; Found 577.0848. **Anal. Calcd** for C<sub>22</sub>H<sub>30</sub>Cl<sub>4</sub>N<sub>6</sub>Pd: C, 47.54; H, 5.44; N, 15.12. Found: C, 47.78; H, 5.48; N, 14.28.



**Complex 11:** PdCl<sub>2</sub>(PhCN)<sub>2</sub> (76.3 mg, 0.2 mmol) was dissolved in DCM, to which a solution of triazene **6** (104.0 mg, 0.4 mmol) in DCM was added (5 mL total volume). It was stirred overnight, forming a yellow precipitate, which was filtered and washed with a small amount of dichloromethane and pentane. The yellow solid was dried under vacuum, after which it was taken out of the glovebox for analysis. Yield (yellow solid): 103 mg (74%). <sup>1</sup>H NMR (600 MHz,CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  10.16 (hept, *J* = 6.6 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 8.00–7.91 (m, 2H, Ph), 7.63 (ddt, *J* = 8.7, 7.2, 1.3 Hz, 1H, Ph), 7.55–7.47 (m,

2H, Ph), 4.35 (hept, J = 6.4 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.73 (d, J = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (d, J = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  192.46, 177.70, 135.15, 133.17, 129.71, 129.52, 55.98, 55.76, 54.20, 54.02, 53.84, 53.66, 53.48, 22.86, 19.97. IR (v<sub>max</sub>, cm<sup>-1</sup>): 1728 (w, C=O stretch), 1682 (m, C=O stretch). HRMS (ESI/QTOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>6</sub>NaO<sub>4</sub>Pd<sup>+</sup> 721.1259; Found 721.1257. Anal. Calcd for C<sub>28</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>4</sub>Pd: C, 48.05; H, 5.47; N, 12.01. Found: C, 48.18; H, 5.33; N, 11.48.

# 7. NMR Spectra



Figure S7-1. <sup>1</sup>H NMR spectrum of 4(HOTf) (600 MHz, CD<sub>3</sub>CN).



Figure S7-2. <sup>13</sup>C NMR spectrum of 4(HOTf) (101 MHz, CD<sub>3</sub>CN).



Figure S7-3. <sup>1</sup>H-<sup>15</sup>N HSQC NMR spectrum of 4(HOTf) (-80 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-4. <sup>1</sup>H-<sup>15</sup>N HMBC NMR spectrum of 4(HOTf) (-80 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-5. <sup>1</sup>H NMR spectrum of 5(HOTf) (600 MHz, CD<sub>3</sub>CN).



Figure S7-6. <sup>13</sup>C NMR spectrum of 5(HOTf) (101 MHz, CD<sub>3</sub>CN).



Figure S7-7. <sup>1</sup>H NMR spectrum of 6(HOTf) (600 MHz, CD<sub>3</sub>CN).



Figure S7-8. <sup>13</sup>C NMR spectrum of 6(HOTf) (101 MHz, CD<sub>3</sub>CN).



Figure S7-9. <sup>1</sup>H NMR spectrum of 8 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-10. <sup>13</sup>C NMR spectrum of 8 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-11. <sup>1</sup>H NMR spectrum of 9 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-12. <sup>13</sup>C NMR spectrum of 9 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S7-13.** <sup>1</sup>H NMR spectrum of complex **10** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, *298K*).



Figure S7-14. <sup>13</sup>C NMR spectrum of complex 10 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, *298K*).



**Figure S7-15.** <sup>1</sup>H NMR spectrum of complex **10** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, *200K*).



Figure S7-16. <sup>13</sup>C NMR spectrum of complex 10 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, *200K*).



Figure S7-17. <sup>1</sup>H NMR spectrum of 11, small amount of free ligand (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-18. <sup>13</sup>C NMR spectrum of 11 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-19. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of 11 (CD<sub>2</sub>Cl<sub>2</sub>).



Figure S7-20. <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of 11 (CD<sub>2</sub>Cl<sub>2</sub>).

# 8. IR spectra



Figure S8-1. IR spectra of 4 and 4(HOTf).



Figure S8-2. IR spectra of 5 and 5(HOTf).



Figure S8-3. IR spectra of 6, 6(HOTf) and complex 11.

### 9. Crystallographic data

Bragg-intensities of **2(HOTf)**, **5(HOTf)**, **6(HOTf)**, **8**, **9**, **10** and **11** were collected at low temperature (See Table S9.1) using Cu*K* $\alpha$  radiation. A Rigaku SuperNova dual system diffractometer with an Atlas CCD detector was used for compounds **2(HOTf)**, **6(HOTf)**, **8**, **9** and **11**, and one equipped with an Atlas S2 CCD detector for compounds **5(HOTf)** and **10**. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis*<sup>Pro.3</sup>

The solutions and refinements of the structures were performed by the latest available version of ShelXT<sup>4</sup> and *ShelXL*.<sup>5</sup> All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on  $|F|^2$ . The hydrogen atoms were placed at calculated positions by means of the "riding" model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{eq}$  of its parent C-atom (1.5  $U_{eq}$  for the methyl groups), but in the structures **2(HOTf)**, **5(HOTf)** and **6(HOTf)** the hydrogen atom bound to nitrogen (N1) was found in a difference map and refined freely.

Crystallographic and refinement data are summarized in Table S9.1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and correspond to the following codes: **2(HOTf)** (1966935), **5(HOTf)** (1966936), **6(HOTf)** (1966937), **8** (1967012), **9** (1966938), **10** (1963420), and **11** (1966939). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

In the structure **8**, an isopropyl and a tert-butyl groups are disordered over two positions found in a difference map and which were refined anisotropically imposing distance and similarity restraints (SADI and SIMU) for the least-squares refinement, yielding site occupancies of 0.654(8)/0.346(8).

In the structure 9, one of the isopropyl groups is disordered over two orientations each, found in a difference map. These were anisotropically refined imposing distance and similarity restraints (SADI and SIMU) for the least-squares refinement which yielded site occupancies of 0.706(17)/0.294(17).

Table S9.1.	Crystall	ographic	and refinem	ent data.
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Compound	2(HOTf)	5(HOTf)	6(HOTf)	8	9	10	11
Formula	C <sub>13</sub> H <sub>20</sub> F <sub>3</sub> N <sub>3</sub> O <sub>3</sub> S	C <sub>13</sub> H <sub>24</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub> S	C <sub>15</sub> H <sub>20</sub> F <sub>3</sub> N <sub>3</sub> O <sub>5</sub> S	C <sub>30</sub> H <sub>23</sub> BF <sub>15</sub> N <sub>3</sub>	$C_{30}H_{19}BF_{15}N_3$	C <sub>22</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>6</sub> Pd	C <sub>28</sub> H <sub>38</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>4</sub>
$D_{1}/2$ am <sup>-3</sup>	1 262	1 229	1 409	1 566	1 505	1 522	Pd
$D_{calc.}$ g cm	1.302	1.556	1.408	1.300	1.393	1.355	1.439
μ/mm <sup>-1</sup>	2.095	2.013	2.033	1.404	1.439	8.423	6.588
Formula	355.38	375.41	411.40	721.32	717.29	555.82	699.94
Weight							
Colour	clear colourless	clear colourless	clear colourless	clear colourless	clear colourless	clear intense orange	clear intense orange
Shape	prism	prism	needle	needle	irregular	prism	prism
Size/mm <sup>3</sup>	0.21×0.11×0.07	0.66×0.44×0.37	0.27×0.08×0.04	0.43×0.11×0.09	0.31×0.14×0.13	0.36×0.13×0.10	0.55×0.12×0.08
T/K	150.01(10)	139.98(11)	140.00(10)	100.00(10)	140.00(10)	140.00(10)	150.01(10)
Crystal System	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	triclinic	triclinic
Space Group	$P2_{1}/n$	$P2_{1}/n$	$P\overline{1}$	Pbca	Pbca	PĪ	PĪ
a/Å	8.0352(3)	11.05100(19)	8.8991(5)	19.1659(5)	18.9040(6)	9.2984(10)	8.1628(4)
b/Å	25.0842(6)	10.81512(18)	10.8721(10)	18 1081(5)	16 3612(6)	12 1013(13)	8 4628(4)
 	8 6190(3)	15 9625(3)	11 4526(9)	35 2711(11)	19 3108(5)	12.1015(13)	12 1951(6)
	90	90	117.321(9)	90	90	82.298(9)	98,576(4)
	94.100(3)	102.2766(16)	91.458(6)	90	90	68.456(10)	106.738(4)
	90	90	97.837(6)	90	90	70 100(10)	90 520(4)
$\frac{\gamma}{V/\lambda^3}$	1732 76(10)	1864 18(5)	970 37(15)	12241 1(6)	5072 7(3)	1204 3(2)	796 52(7)
	4	4	2	16	8	2	1
<u> </u>	1	1	1	2	1	1	0.5
Wavelength/Å	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	CuKa	CuKa	CuKa	CuKa	CuKa	CuKa	CuKa
<u> </u>	5.439	4.457	4.367	3.584	4.244	3.884	3.833
$\Theta$	76.837	76.004	73 411	76 291	72.428	66 580	76 558
Measured Refl	16441	16719	6582	91492	15890	7530	6988
Independent	3623	3844	3768	12733	5770	4181	3299
Refl.	5025	5011	5700	12,55	5770	1101	5277
Reflections	2746	3730	2904	8559	4910	3447	3206
with $I > 2(I)$							
R <sub>int</sub>	0.0526	0.0312	0.0340	0.0816	0.0355	0.0640	0.0285
Parameters	216	231	252	949	468	282	191
Restraints	0	0	0	128	43	0	0
Largest Peak/e Å <sup>-3</sup>	0.331	0.416	0.351	0.442	0.646	2.430	1.208
Deepest Hole/e	-0.397	-0.358	-0.405	-0.256	-0.291	-1.475	-0.518
A-5	1.046	1.0/0	1.022	1.016	1.056	1.004	1.061
	1.046	1.068	1.033	1.016	1.056	1.094	1.061
$\frac{WK_2 \text{ (all data)}}{WK_2 \text{ (all data)}}$	0.1240	0.1265	0.1230	0.1222	0.1510	0.2614	0.0937
$\frac{WK_2}{D(-11, 1, 1, 1)}$	0.1104	0.1256	0.1093	0.0054	0.1445	0.2469	0.0926
$\frac{K_{l} \text{ (all data)}}{P}$	0.0637	0.0490	0.0627	0.0854	0.0643	0.1062	0.0365
	1066025	0.04/8	1066027	0.0532	0.0554	0.0935	1066020
CCDC code	1900933	1200230	190093/	190/012	1900938	1903420	1900939

#### CCDC database analyses

To compare the bond lengths of the protonated triazenes with aryl triazenes, a CCDC database search was performed. For the search, the program ConQuest (v2.0.1, CCDC 2019) was used with a CCDC database (CSD version 5.40 (November 2018) + 2 updates).

R N2 N2 (R')

The query that was searched:

With the following additional requirements: R = any atom except H, R' = one or multiple substituents(*n*), Filter = only organics and must not contain:

The resulting 122 hits were analysed and taken out of the data set if:

- (1) The triazene is cyclic.
- (2) It contains any other atom than H, C, N, O, F, Cl, Br, S.
- (3) The amount of connected N atoms > 3.
- (4) R is another atom than C, or if R is C–O.
- (5) No coordinates are available in the database.
- (6) R > 9 atoms (excl. H).
- (7) (R') $_n > 21$  atoms (excl. H).

The resulting **30 hits** were analysed with Mercury (v3.10, CCDC 2001-2017) and the bond lengths were measured.

30 Structures from the CCDC database:

BOCYUO, BOCZAV, BOCZEZ, BOCZID, CMPDZB, DEHFUT, EMUDEX, FUZLUI, HAHQOZ, HOBXAY, IPUDEE, IPUDII, JANXAA, JANXEE, JANXII, JOLNED, JOWTOE, KUJXOC, LOXWOM, MIJDEP, MTZPCX, OFUBUO, OPAVUX, PIGRUT, PIGSAA, RUJQIX, UDINEC, VUYGEB, YUMWIO, ZIKQOZ.

Average bond lengths: N1-N2 = 1.276 Å; N2-N3 = 1.325 Å

To compare the bond lengths of the B–N dative bonds with  $B(C_6F_5)_3$ , a CCDC database search was performed. For the search, the program ConQuest (v2.0.1, CCDC 2019) was used with a CCDC database (CSD version 5.40 (November 2018) + 2 updates).

The query that was searched: 
$$R'^{N-B(C_6F_5)_3}$$

The resulting 184 hits were analysed and taken out of the data set if:

- (1) R, R' contains any other atom than C, H, N, (O).
- (2) The B–N adduct is charged.
- (3) No coordinates available.

The resulting **46 hits** were analysed with Mercury (v3.10, CCDC 2001-2017) and the bond lengths were measured.

## 46 Structures from the CCDC database:

AGASAF, BAZRIE, BUNXEO, DERGOZ, DERGUF, EKUBOB, EKUBUH, FEYHIB, GABQUW, GABRAD, HAFFAX, IFUFIA, IJOHAQ, IJOHEU, IJOHIY, IPAPIA, IPAPOG, JEGKUC, KECRUG, MIVLOS, MIVLUY, MIVMAF, MIVMEJ, MIVMIN, MOJVOX, NOWJEQ, OGACUX, PIKDAQ, PIKFAS, QEYSAO, RASQEI, RASQIM, RASQOS, RASQUY, RASRAF, SELTIO, TURPOM, UKITUF, WAWCEE, WAWCII, XERWIC, XERWOI, XUCCIH, YALTAJ, YALTOX, ZILXEA.

Average bond length: B-N = 1.626 Å

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