### Synthesis and Optoelectronic Properties of 2,6-Bis(2anilinoethynyl)pyridine Scaffolds

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**General Methods.** Compounds **6-9** were prepared according to the previously published literature reports.<sup>1-5</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Varian 300 MHz spectrometer (<sup>1</sup>H 299.95 Hz, <sup>13</sup>C 75.43 Hz), Inova 500 MHz spectrometer (<sup>1</sup>H 500.10 MHz, <sup>13</sup>C 125.75 MHz) or Varian 600 MHz spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm from solvent signal using non-deuterated solvent present in the bulk deuterated solvent (DMSO-d6: <sup>1</sup>H 2.5 ppm, <sup>13</sup>C 39.52 ppm). Unless otherwise specified, solvents were obtained from distillation using published literature procedures directly before use. Mass spectra were acquired Waters LCT Premier ESI-MS in positive mode in MeCN solvent. UV-Vis spectra were acquired with a Hewlett-Packard 8453 UV-Visible spectrophotometer equipped with a 250 nm cutoff filter. Fluorescence data was acquired with a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer equipped with an integrating sphere. Absolute photoluminescence quantum yields were taken in triplicate in O<sub>2</sub>- containing (no inert gas purging) MeCN.

**General TMS Deprotection Procedure A.** To a solution of 4-substituted-2-(trimethylsilylethynyl)aniline (**6-9**, 1 equiv) in 2:1 MeOH/Et<sub>2</sub>O (0.1 M) was added K<sub>2</sub>CO<sub>3</sub> (5 equiv) at room temperature. After stirring for 30 min, the reaction mixture was diluted with water and extracted with  $CH_2Cl_2$ . The organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to give the desilylated product which was used without further purification.

**General Cross Coupling Procedure B.** To an Ar degassed solution of 2,6dibromopyridine (1 equiv) in 1:1 THF/DIPA (0.05 M) were added Cul (0.2 equiv) and  $Pd(PPh_3)_4$  (0.1 equiv) at room temperature. The solution was degassed with Ar for an additional 30 min and then heated to 50 °C. To this solution a second degassed solution

of 2-ethynyl-4-substituted aniline (2.2 equiv) in THF (20 mL) was cannula transferred. After stirring for 16 h, the reaction mixture was cooled, diluted with CH<sub>2</sub>Cl<sub>2</sub>, and filtered through a 4 cm pad of silica. The filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel to give the desired dianiline product.

**General Urea Formation Procedure C.** To a stirred solution of 2,6-bis(2anilinoethynyl)pyridine (6-9, 1 equiv) in dry toluene (0.01 M) was added the appropriate phenylisocyanate reagent (3-10 equiv). The reaction was stirred at rt-80 °C for 3 h- 2 d. The resulting suspension was diluted in hexanes and the solid precipitate was collected via vacuum filtration. The solid was redissolved in a minimal amount of 10:1 acetone/TFA and hexanes was added until the solution became cloudy. The resulting suspension was cooled and the precipitate was collected via vacuum filtration affording the desired product.

*t*-Butyl dianiline 6: Aniline 10<sup>1,2</sup> (3.88 g, 15.8 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.62 g, 6.85 mmol), Cul (150 mg, 0.78 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **6** (2.19 g, 76%) as a yellow solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (t, J = 7.8 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.21 (dd, J = 8.5, 1.8 Hz, 2H), 6.68 (d, J = 8.5 Hz, 2H), 4.31 (s, 4H), 1.28 (s, 18H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  146.43, 144.10, 140.88, 136.51, 129.47, 128.21, 125.89, 114.54, 106.15, 93.37, 87.61, 34.07, 31.51. UV-vis

(MeCN)  $\lambda_{max}$  360 nm (17225 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (EI+) calcd for C<sub>29</sub>H<sub>31</sub>N<sub>3</sub><sup>•+</sup> [M<sup>•+</sup>] 421.2513, found 421.2511.

Ester dianiline 7<sup>3</sup>: Benzoate 11 (2.13 g, 11.3 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.21 g, 5.13 mmol), Cul (150 mg, 0.79 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give 7 (1.50 g, 64%) as a yellow solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, J = 1.9 Hz, 2H), 7.85 (dd, J = 8.5, 1.9 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H), 6.70 (d, J = 8.5 Hz, 2H), 4.85 (s, 4H), 4.33 (q, J = 7.1 Hz, 4H), 1.38 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  166.09, 152.20, 143.77, 136.77, 135.19, 132.45, 126.36, 119.95, 113.60, 105.66, 93.93, 85.90, 60.71, 14.56. UV-vis (MeCN)  $\lambda_{max}$  354 nm (23149 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (EI+) calcd for C<sub>27</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>] 454.1761, found 454.1745.

**Trifluoromethyl dianiline 8:** Aniline **12**<sup>4</sup> (0.631 g, 3.41 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (0.337 g, 1.55 mmol), Cul (59 mg, 0.31 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (179 mg, 0.16 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give 8 (0.48 g, 70%) as an off-white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 4H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  151.14, 143.59, 136.87, 130.28 (q, *J* = 3.9 Hz), 127.66 (q, *J* = 3.6 Hz),

126.48, 124.38 (d, J = 270.7 Hz), 119.93 (q, J = 33.2 Hz), 114.08, 105.90, 94.29, 85.47. UV-vis (MeCN)  $\lambda_{max}$  351 nm (23078 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (EI+) calcd for C<sub>23</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub><sup>•+</sup> [M<sup>•+</sup>] 445.1008, found 445.1014.

**Methoxy dianiline 9:** Aniline **13**<sup>5</sup> (1.46 g, 9.91 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.118 g, 4.72 mmol), Cul (150 mg, 0.79 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **9** (1.50 g, 86%) as a light brown solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 2.9 Hz, 2H), 6.81 (dd, *J* = 8.8, 2.9 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.15 (s, 4H), 3.75 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 151.90, 143.93, 143.13, 136.59, 126.10, 118.88, 116.27, 116.08, 107.08, 93.66, 87.02, 55.97. UV-vis (MeCN) λ<sub>max</sub> 373 nm (17226 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (EI+) calcd for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub><sup>\*+</sup> [M<sup>\*+</sup>] 369.1472, found 369.1477.

**Bis-urea 2a:** Dianiline **6** (100 mg, 0.238 mmol) and 4-methoxyphenyl isocyanate (88.6 mg, 0.594 mmol) were reacted at 80 °C for 16 h using general procedure C to afford the desired product **2a** (160 mg, 93%) as an yellow solid<sup>1</sup>H NMR (600 MHz, DMSO-d6)  $\delta$  9.27 (s, 2H), 8.22 (s, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 2.3 Hz, 2H), 7.47 (dd, *J* = 8.8, 2.3 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 4H), 6.87 (d, *J* = 9.0 Hz, 4H), 3.71 (s, 6H), 1.29 (s, 18H). <sup>13</sup>C NMR (151 MHz, DMSO-d6)  $\delta$  154.61, 152.36, 144.51, 142.82, 138.46, 137.41, 132.42, 129.02, 127.59, 127.25, 120.16, 119.88, 114.04, 109.99, 93.46, 85.87, 55.14, 33.95, 30.97. UV-

vis (MeCN)  $\lambda_{max}$  336 nm (22541 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>45</sub>H<sub>46</sub>N<sub>5</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>] 720.3544, found 720.3550.

**Bis-urea 2b:** Dianiline **6** (100 mg, 0.238 mmol) and 4-nitrophenyl isocyanate (97.5 mg, 0.594 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (166 mg, 93%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 10.12 (s, 2H), 8.53 (s, 2H), 8.19 (d, J = 9.2 Hz, 4H), 8.02 – 7.96 (m, 3H), 7.82 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 9.2 Hz, 4H), 7.57 (d, J = 2.3 Hz, 2H), 7.51 (dd, J = 8.8, 2.3 Hz, 2H), 1.30 (s, 18H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 151.78, 146.08, 145.58, 142.75, 141.16, 137.49, 129.20, 127.68, 127.38, 125.15, 120.52, 117.56, 111.02, 93.55, 85.67, 34.04, 30.93. UV-vis (MeCN) λ<sub>max</sub> 337 nm (37271 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>43</sub>H<sub>40</sub>N<sub>7</sub>O<sub>6</sub><sup>+</sup> [MH<sup>+</sup>] 750.3035, found 750.2986.

**Bis-urea 2c:** Dianiline **6** (800 mg, 1.9 mmol) and phenyl isocyanate (679 mg, 5.7 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (1.15 g, 92%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.44 (s, 2H), 8.32 (s, 2H), 8.05 – 7.95 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 2.3 Hz, 2H), 7.51 – 7.43 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 2H), 1.30 (s, 18H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 152.22, 144.77, 142.82, 139.46, 138.24, 137.45, 129.07, 128.84, 127.61, 127.30, 122.05, 120.11, 118.29, 110.26, 93.46, 85.85, 33.98, 30.96. UV-vis (MeCN)  $\lambda_{max}$  334 nm (15310 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>43</sub>H<sub>42</sub>N<sub>5</sub>O<sub>2</sub><sup>+</sup> [MH<sup>+</sup>] 660.3333, found 660.3325.

**Bis-urea 2d:** Dianiline **6** (75.3 mg, 0.169 mmol) and pentafluorophenyl isocyanate (66  $\mu$ L, 0.507 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (115 mg, 81%). <sup>1</sup>H

NMR (600 MHz, DMSO-d6)  $\delta$  9.34 (s, 2H), 8.64 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 1.8 Hz, 2H), 7.49 (dd, *J* = 8.7, 11.8 Hz, 2H), 1.29 (s, 18H). <sup>13</sup>C NMR (151 MHz, dmso)  $\delta$  151.67, 145.48, 142.78, 143.64 – 141.64 (m), 139.36 – 137.49 (m), 137.67, 137.45, 138.20 – 136.16 (m), 129.17, 127.72, 127.33, 120.07, 113.84 – 113.42 (m), 110.77, 93.52, 85.59, 34.02, 30.92. UV-vis (MeCN)  $\lambda_{max}$  333 nm (14836 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>43</sub>H<sub>32</sub>F<sub>10</sub>N<sub>5</sub>O<sub>2</sub><sup>+</sup> [MH<sup>+</sup>] 840.2391, found 840.2435.

**Bis-urea 3a:** Dianiline **7** (43.3 mg, 0.095 mmol) and 4-methoxyphenyl isocyanate (120 μL, 0.96 mmol) were reacted at 80 °C for 16 h using general procedure C to afford the desired product **3a** (47.5 mg, 57%) as an orange solid. <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.56 (s, 2H), 8.57 (s, 2H), 8.36 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 1.9 Hz, 2H), 8.05 (t, J = 7.8 Hz, 1H), 7.98 (dd, J = 8.9, 1.9 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 8.9 Hz, 4H), 6.89 (d, J = 8.9 Hz, 4H), 4.31 (q, J = 7.1 Hz, 4H), 3.72 (s, 6H), 1.33 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 164.58, 154.96, 151.80, 144.88, 142.49, 137.60, 133.93, 131.84, 131.24, 127.90, 123.00, 120.50, 118.61, 114.10, 109.54, 94.51, 84.02, 60.71, 55.15, 14.16. UV-vis (MeCN)  $\lambda_{max}$  335 nm (13710 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>43</sub>H<sub>38</sub>N<sub>5</sub>O<sub>8</sub><sup>+</sup> [MH<sup>+</sup>] 752.2715, found 752.2681.

**Bis-urea 3b:** Dianiline **7** (89 mg, 0.196 mmol) and 4-nitrophenyl isocyanate (193 mg, 1.18 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (46.5 mg, 30%). <sup>1</sup>H NMR (300 MHz, DMSO-d6)  $\delta$  10.37 (s, 2H), 8.84 (s, 2H), 8.34 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 9.1 Hz, 4H), 8.14 (d, *J* = 1.9 Hz, 2H), 8.11 – 7.97 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 4H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz,

DMSO-d6)  $\delta$  164.98, 151.88, 146.05, 144.46, 142.91, 141.97, 138.14, 134.44, 131.77, 128.52, 125.64, 124.37, 119.70, 118.36, 110.90, 95.18, 84.36, 61.32, 14.63. UV-vis (MeCN)  $\lambda_{max}$  337 nm (53369 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>41</sub>H<sub>32</sub>N<sub>7</sub>O<sub>10</sub><sup>+</sup> [MH<sup>+</sup>] 782.2205, found 782.2221.

**Bis-urea 3c:** Dianiline **7** (44.4 mg, 0.0979 mmol) and phenyl isocyanate (110 μL, 0.979 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (20.7 mg, 26%). <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 9.74 (s, 2H), 8.67 (s, 2H), 8.36 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 1.9 Hz, 2H), 8.05 (t, J = 7.8 Hz, 1H), 7.99 (dd, J = 8.9, 1.9 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.7 Hz, 4H), 7.31 (t, J = 7.7 Hz, 4H), 7.03 (t, J = 7.7 Hz, 2H), 4.32 (q, J = 7.1 Hz, 4H), 1.33 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 164.57, 151.70, 144.69, 142.49, 138.95, 137.63, 133.96, 131.25, 128.91, 127.96, 123.22, 122.56, 118.83, 118.60, 109.79, 94.54, 84.02, 60.75, 14.16. UV-vis (MeCN) λ<sub>max</sub> 340 nm (10677 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>41</sub>H<sub>34</sub>N<sub>5</sub>O<sub>6</sub><sup>+</sup> [MH<sup>+</sup>] 692.2504, found 692.2505.

**Bis-urea 3d:** Dianiline **7** (31.6 mg, 0.0697 mmol) and pentafluorophenyl isocyanate (50 μL, 0.42 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (52 mg, 76%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 10.05 (s, 2H), 9.18 (s, 2H), 8.29 (d, J = 8.9 Hz, 2H), 8.14 (d, J = 1.9 Hz, 2H), 8.08 – 8.01 (m, 3H), 7.99 (dd, J = 8.9, 1.9 Hz, 2H), 4.31 (q, J = 7.1 Hz, 4H), 1.33 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 164.50, 151.50, 144.09, 142.41, 137.45, 133.97, 131.27, 128.03, 123.86, 119.00, 110.37, 94.71, 83.78,

60.81, 14.11. UV-vis (MeCN)  $\lambda_{max}$  323 nm (11895 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>41</sub>H<sub>24</sub>F<sub>10</sub>N<sub>5</sub>O<sub>6</sub><sup>+</sup> [MH<sup>+</sup>] 872.1561, found 872.1612.

**Bis-urea 4a:** Dianiline **8** (29.6 mg, 0.067 mmol) and 4-methoxyphenyl isocyanate (90 μL, 0.67 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (9 mg, 16%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.54 (s, 2H), 8.58 (s, 2H), 8.42 (d, J = 8.9 Hz, 2H), 8.06 (t, J = 7.8 Hz, 1H), 7.94 (d, J = 1.5 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.77 (dd, J = 8.9, 1.5 Hz, 2H), 7.39 (d, J = 9.0 Hz, 4H), 6.89 (d, J = 9.0 Hz, 4H), 3.72 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 154.97, 151.89, 144.23, 142.39, 137.66, 131.82, 129.77, 128.09, 127.13, 124.77, 122.97, 122.14 (q, J = 32.4 Hz), 120.51, 119.35, 114.11, 110.06, 94.91, 83.64, 55.16. UV-vis (MeCN)  $\lambda_{max}$  332 nm (16404 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>39</sub>H<sub>28</sub>F<sub>6</sub>N<sub>5</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>] 744.2040, found 744.2059.

**Bis-urea 4b:** Dianiline **8** (102 mg, 0.023 mmol) and 4-nitrophenyl isocyanate (188 mg, 1.14 mmol) were reacted at 70 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (59.3 mg, 34%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 10.35 (s, 2H), 8.87 (s, 2H), 8.39 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 9.3 Hz, 4H), 8.07 (t, J = 7.8 Hz, 1H), 7.99 (s, 2H), 7.93 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 9.3 Hz, 4H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 151.48, 145.52, 143.36, 142.33, 141.54, 137.72, 129.89 (t, J = 6.1 Hz), 128.21, 127.24 (t, J = 6.6 Hz), 125.15, 124.05 (t, J = 407.7 Hz), 123.09 (q, J = 32.7 Hz), 120.03, 117.92, 111.04, 95.07, 83.50. UV-vis (MeCN) λ<sub>max</sub> 330 nm (9749 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>22</sub>F<sub>6</sub>N<sub>7</sub>O<sub>6</sub><sup>+</sup> [MH<sup>+</sup>] 774.1530, found 774.1553.

**Bis-urea 4c:** Dianiline **8** (22.7 mg, 0.051 mmol) and phenyl isocyanate (60 μL, 0.51 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (14.9 mg, 37%). <sup>1</sup>H NMR (300 MHz, DMSO-d6) δ 9.71 (s, 2H), 8.68 (s, 2H), 8.41 (d, J = 8.8 Hz, 2H), 8.07 (t, J = 7.8 Hz, 1H), 7.94 (m, 4H), 7.79 (dd, J = 8.9, 1.9 Hz, 2H), 7.49 (d, J = 7.5 Hz, 4H), 7.31 (t, J = 7.5 Hz, 4H), 7.03 (t, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 152.24, 144.51, 142.85, 139.39, 138.12, 130.28 (q, J = 3.8 Hz), 129.36, 128.59, 127.61 (q, J = 3.2 Hz), 124.30 (q, J = 271.1 Hz), 123.01, 122.82 (q, J = 32.6 Hz), 120.04, 119.05, 110.78, 95.39, 84.09. UV-vis (MeCN) λ<sub>max</sub> 329 nm (11661 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>24</sub>F<sub>6</sub>N<sub>5</sub>O<sub>2</sub><sup>+</sup> [MH<sup>+</sup>] 684.1829, found 684.1850.

**Bis-urea 4d:** Dianiline **8** (24.5 mg, 0.055 mmol) and pentafluorophenyl isocyanate (72 μL, 0.55 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (40.3 mg, 75%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.65 (s, 2H), 9.00 (s, 2H), 8.35 (d, J = 8.9 Hz, 2H), 8.07 (t, J = 7.8 Hz, 1H), 7.98 (d, J = 1.6 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.80 (dd, J = 8.9, 1.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 151.41, 143.42, 143.65 – 141.64 (m), 142.34, 139.82 – 137.37 (m), 137.69, 137.23 (dt, J = 32.1, 19.1 Hz), 129.97 – 129.74 (m, J = 3.8 Hz), 128.14, 127.45 – 127.21 (m, J = 3.5 Hz), 123.74 (q, J = 271.2 Hz), 123.08 (q, J = 33.6 Hz), 119.61, 113.12 (t, J = 13.8 Hz), 110.85, 95.05, 83.40. UV-vis (MeCN) λ<sub>max</sub> 331 nm (9291 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>14</sub>F<sub>16</sub>N<sub>5</sub>O<sub>2</sub><sup>+</sup> [MH<sup>+</sup>] 864.0887, found 864.0952.

**Bis-urea 5a:** Dianiline **9** (116 mg, 0.314 mmol) and 4-methoxyphenyl isocyanate (121 µL, 0.94 mmol) were reacted at rt for 16 h using general procedure C. Purification

using general procedure C afforded the desired product (133 g, 64%). <sup>1</sup>H NMR (300 MHz, DMSO-d6) δ 9.17 (s, 2H), 8.15 (s, 2H), 8.04 – 7.95 (m, 1H), 7.92 (d, J = 9.1 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 9.0 Hz, 4H), 7.13 (d, J = 3.0 Hz, 2H), 7.04 (dd, J = 9.1, 3.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 4H), 3.77 (s, 6H), 3.71 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 154.55, 154.18, 152.62, 142.70, 137.48, 134.32, 132.55, 127.42, 122.40, 120.14, 117.18, 116.19, 114.03, 112.03, 93.47, 85.47, 55.46, 55.14. UV-vis (MeCN)  $\lambda_{max}$  342 nm (10529 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>39</sub>H<sub>34</sub>N<sub>5</sub>O<sub>6</sub><sup>+</sup> [MH<sup>+</sup>] 668.2504, found 668.2509.

**Bis-urea 5b:** Dianiline **9** (214 mg, 0.58 mmol) and 4-nitrophenyl isocyanate (285 mg, 1.74 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (0.346 g, 86%). <sup>1</sup>H NMR (300 MHz, DMSO-d6) δ 10.02 (s, 2H), 8.49 (s, 2H), 8.19 (d, J = 9.3 Hz, 4H), 7.99 (t, J = 7.8 Hz 1H), 7.88 (d, J = 9.1 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 9.3 Hz, 4H), 7.16 (d, J = 3.0 Hz, 2H), 7.08 (dd, J = 9.1, 3.0 Hz, 2H), 3.79 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 154.95, 152.03, 146.23, 142.63, 141.08, 137.58, 133.20, 127.51, 125.16, 123.21, 117.51, 117.11, 116.47, 113.33, 93.49, 85.32, 55.52. UV-vis (MeCN) λ<sub>max</sub> 341 nm (29956 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>28</sub>N<sub>7</sub>O<sub>8</sub><sup>+</sup> [MH<sup>+</sup>] 698.1994, found 698.2028.

**Bis-urea 5c:** Dianiline **9** (36.3 mg, 0.098 mmol) and phenyl isocyanate (110  $\mu$ L, 0.983 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (44.1 mg, 62%). <sup>1</sup>H NMR (600 MHz, DMSO-d6)  $\delta$  9.30 (s, 2H), 8.24 (s, 2H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* =

3.0 Hz, 2H), 7.05 (dd, J = 9.1, 3.0 Hz, 2H), 6.97 (t, J = 7.5 Hz, 2H), 3.78 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6)  $\delta$  154.36, 152.46, 142.70, 139.58, 137.50, 134.06, 128.81, 127.45, 122.65, 121.93, 118.25, 117.17, 116.24, 112.34, 93.45, 85.45, 55.47. UV-vis (MeCN)  $\lambda_{max}$  339 nm (7270 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>30</sub>N<sub>5</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>] 608.2292, found 608.2294.

**Bis-urea 5d:** Dianiline **9** (37 mg, 0.100 mmol) and pentafluorophenyl isocyanate (40 μL, 0.300 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (55.7 mg, 71%). <sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.17 (s, 2H), 8.56 (s, 2H), 8.01 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 9.1 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 2.6 Hz, 2H), 7.05 (dd, J = 9.1, 2.6 Hz, 2H), 3.78 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-d6) δ 155.30, 152.36, 144.32–141.92 (m), 143.12, 139.90–137.47 (m), 137.95, 138.72–136.48 (m), 133.88, 127.90, 123.19, 117.57, 116.88, 114.25 (t, J = 15.8 Hz), 113.53, 93.93, 85.67, 55.94. UV-vis (MeCN) λ<sub>max</sub> 342 nm (7945 cm<sup>-1</sup>M<sup>-1</sup>). HRMS (TOF MS ES+) calcd for C<sub>37</sub>H<sub>20</sub>F<sub>10</sub>N<sub>5</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>] 788.1350, found 788.1398

#### Discussion of 2-quinazolinone side-product:



**SCHEME S1.** Observed 6-*exo*-dig cyclization pathway (top); typical but unobserved 5*endo*-dig cyclization pathway (bottom).

While attempting to synthesize 4d a small amount of an unexpected 2quinazolinone was isolated and its crystal structure was solved. To our knowledge this is the first reported example of a 2-quinazolinone resulting from a 6-exo-dig cyclization pathway with an internal alkyne (Scheme S1) as typically a 5-endo-dig cyclization occurs. Additionally, the x-ray crystal structure shows that one of the resulting alkenes is in the *E* conformation, which the other is in a *Z* conformation, resulting in an unusual structure (Figure S1). CCDC-844849 twisted contains the supplementary crystallographic data for this molecule, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.



FIGURE S1. 2-Quinazolinone side product formed while attempting to synthesize 4d.

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- 5. D. B. Kimball, T. J. R. Weakley, and M. M. Haley, J. Org. Chem., 2002, 67, 6395.



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (t, J = 7.8 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.21 (dd, J = 8.5, 1.8 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 4.31 (s, 4H), 1.28 (s, 18H).





4.307

1.278

Compound 6	-146.435 -144.104 -144.104 -140.876	 		 — 34.071 — 31.512
	41 14 13 13 13	 	- 10	 

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 146.43, 144.10, 140.88, 136.51, 129.47, 128.21, 125.89, 114.54, 106.15, 93.37, 87.61, 34.07, 31.51.



















































f1 (ppm)











**Compound 7** 



-4.347 -4.335 -4.323 -4.323 -4.849

.387 .375 .363

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, J = 1.9 Hz, 2H), 7.85 (dd, J = 8.6, 1.9 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 4.85 (s, 4H), 4.33 (q, J = 7.1 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 6H).

































f1 (ppm)





-9.340





<sup>1</sup>H NMR (600 MHz, DMSO-d6)  $\delta$  9.34 (s, 2H), 8.64 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 1.8 Hz, 2H), 7.49 (dd, *J* = 8.7, 11.8 Hz, 2H), 1.29 (s, 18H).



-1.292



6





г4.329 г4.317 ч4.305 ч4.293 -3.722 -1.341 -1.330 -1.318

<sup>1</sup>H NMR (600 MHz, DMSO-d6) δ 9.56 (s, 2H), 8.57 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 1.9 Hz, 2H), 8.05 (t, J = 7.8 Hz, 1H), 7.98 (dd, J = 8.9, 1.9 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 8.9 Hz, 4H), 6.89 (d, J = 8.9 Hz, 4H), 4.31 (q, J = 7.1 Hz, 4H), 3.72 (s, 6H), 1.33 (t, J = 7.1 Hz, 6H).

















































0.0













f1 (ppm)





