## **Electron Supplementary Information**

## A Multicomponent Formal [1+2+1+2]-Cycloaddition for the Synthesis of Dihydropyridines

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### **General Experimental**

All the starting materials including solvents were used as received without further purification, unless otherwise stated. All reactions were performed under air unless otherwise specified. Reactions were monitored by TLC analysis carried out on Polygram SIL G/UV<sub>254</sub> plastic backed silica gel plates, and were visualised under a UV lamp operating at short and long wavelength ranges. Visualisation was aided by dipping plates into an alkaline potassium permanganate solution. Flash column chromatography was carried out on Davisil Silica gel, 60-200 mesh. Molecular sieves were activated by heating to 150 °C. Concentration of the reaction mixture in vacuo is the removal of solvent under reduced pressure. <sup>1</sup>H NMR spectra were recorded on either Varian Mercury-400, Varian-Mercury 500 or Varian VNMRS 700 MHz spectrometers, operating at ambient probe temperature, unless otherwise stated. Deuterated chloroform CDCl<sub>3</sub> and DMSO were used as the deuterated solvents for all the spectra run. Peaks are reported as singlet (s), doublet (d), triplet (t), quartet (q), broad (br), some combinations of these, or multiplet (m). All chemical shifts are reported in parts per million (ppm) relative to residual protiated signals of the solvent, and coupling constants (J) in hertz (Hz). <sup>13</sup>C NMR spectra were recorded on Varian Mercury-400, Varian Mercury-500 or Varian VNMRS 700 instruments at frequencies of 101, 126 or 176 MHz unless otherwise stated. Standard abbreviations used were singlet (s), doublet (d), triplet (t), and quartet (q). Mass spectra for liquid chromatography mass spectrometry (LCMS) were obtained using a Waters LCT spectrometer, and accurate mass spectrometry obtained on a Finnigan LTQ-FT using the electrospray in positive ion mode (ES+) to generate ions, unless otherwise stated. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Melting points were measured, where appropriate, with a Gallenkamp Variable Heater melting point apparatus and are uncorrected.

# General Procedure for the scandium(III) triflate catalyed formal [1+2+2+1]-cycloaddition reaction

To amine (1 mmol) in  $CH_2Cl_2$  was added 4-methoxy-3-buten-2-one (0.204 mL, 2 mmol), aldehyde (1 mmol) and  $Sc(OTf)_3$  (0.049 g, 0.1 mmol), and the reaction mixtures were left to stir at rt for the times as reported in Table 1 (main paper). The reaction mixtures were purified as outlined as follows:

#### 1,1'-(1-Benzyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1, petroleum ether:diethyl ether to 1:1, diethyl ether:CH<sub>2</sub>Cl<sub>2</sub>, as eluent) afforded **4a** as a yellow solid (0.322 g, 86 %): m.p. 184-185 °C; R<sub>f</sub>. 0.16 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.03-8.01 (m, 2H), 7.48-7.45 (m, 2H), 7.44-7.41 (m, 3H), 7.32-7.29 (m, 2H), 7.24 (s, 2H), 5.29 (s, 1H), 4.72 (s, 2H), 2.13 (s, 6H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  194.4, 153.0, 146.4, 139.0, 135.4, 129.6, 129.2, 129.1, 127.3, 123.5, 119.0, 58.8, 35.8, 25.2; IR (thin film) 1651, 1624, 1573, 1368, 1349 cm<sup>-1</sup>; LRMS (TOF ES+), 399.236 (100%) [M+Na]+, 377.280 (25%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>, 377.14958; observed 377.14939; *Anal.* calcd: C, 70.20, H, 5.36, N, 7.44, found: C, 70.13, H, 5.37, N, 7.48.

#### 1,1'-(1-Benzyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (diethyl ether, as eluent) afforded **4b** as a yellow solid (0.194 g, 59 %): m.p. 136-137 °C (lit. 136-137 °C)<sup>1</sup>; R<sub>f</sub>. 0.23 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.42 (m, 2H), 7.41-7.38 (m, 1H), 7.30-7.27 (m, 4H), 7.22-7.19 (m, 2H), 7.19 (s, 2H), 7.13-7.10 (m, 1H), 5.19 (s, 1H), 4.68 (s, 2H), 2.12 (s, 6H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  195.3, 145.7, 138.2, 135.8, 129.5, 128.8, 128.4, 128.4, 127.3, 126.6, 119.7, 58.8, 35.9, 25.7; IR (thin film) 1628, 1565, 1453, 1412, 1366 cm<sup>-1</sup>; LRMS (TOF ES+), 354.3 (100%) [M+Na]+, 332.3 (30%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub>, 332.16451; observed 332.16440; *Anal.* calcd: C, 79.73, H, 6.39, N, 4.23, found: C, 78.84, H, 6.32, N, 4.08.

#### 1,1'-(1-Benzyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1, petroleum ether:diethyl ether to diethyl ether, as eluent) afforded **4c** as a yellow solid (0.212 g, 59 %): m.p. 172-173 °C; R<sub>f</sub>. 0.21 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.42 (m, 2H), 7.40-7.37 (m, 1H), 7.30-7.27 (m, 2H), 7.20-1.18 (m, 2H), 7.18 (s, 2H), 6.75-

<sup>&</sup>lt;sup>1</sup>G. Inouye, Nippon Kagaku Zasshi, 1959, 80, 1061.

6.72 (m, 2H), 5.13 (s, 1H), 4.66 (s, 2H), 3.73 (s, 3H), 2.12 (s, 6H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  195.3, 158.2, 138.3, 138.0, 135.8, 129.4, 129.3, 128.8, 127.3, 119.8, 113.7, 58.7, 55.3, 35.0, 25.7; IR (thin film) 1630, 1565, 1511, 1412, 1366 cm<sup>-1</sup>; LRMS (TOF ES+), 384.3 (100%) [M+Na]+, 254.3 (30%); HRMS (TOF ES+), calculated for C<sub>23</sub>H<sub>24</sub>NO<sub>3</sub>, 362.17507; observed 362.17507; *Anal.* calcd: C, 76.43, H, 6.41, N, 3.88, found: C, 75.38, H, 6.35, N, 3.75.

# 1,1'-(1-Benzyl-4-ethyl-1,4-dihydropyridine-3,5-diyl)diethanone and (*E*)-4-(Benzylamino)but-3-en-2-one



Purification by silica gel chromatography (1:1, petroleum ether:diethyl ether to diethyl ether, to EtOAc, as eluent) afforded a mixture **4d** as a yellow oil (0.036 g, 13 %): R<sub>f</sub>. 0.22 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42-7.39 (m, 2H), 7.37-7.34 (m, 1H), 7.24-7.22 (m, 2H), 7.11 (s, 2H), 4.58 (2, 2H), 4.16 (t, *J* = 4.9 Hz, 1H), 2.22 (s, 6H), 1.37 (qd, *J* = 7.5, 4.9 Hz, 2H), 0.69 (t, *J* = 7.5 Hz, 3H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  195.6, 139.7, 135.9, 129.4, 128.6, 127.2, 118.7, 58.6, 30.3, 28.1, 25.4, 9.1; IR (thin film) 1632, 1567, 1384 cm<sup>-1</sup>; LRMS (TOF ES+), 306.324 (100%) [M+Na]+, 284.332 (25%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>, 284.16451; observed 284.16442.

and **5a** as an orange oil (0.049 g, 28%): <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  10.07 (br s, 1H, N*H*), 7.37-7.34 (m, 2H), 7.30-7.28 (m, 1H), 7.26-7.25 (m, 2H), 6.71 (dd, *J* = 12.7, 7.4 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 4.38 (d, *J* = 6.1 Hz, 2H), 2.08 (s, 3H) ppm (addition of D<sub>2</sub>O caused the signal at  $\delta$  10.07 to disappear); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 152.4, 138.1, 128.9, 127.7, 127.2, 94.5, 52.5, 29.1; IR (thin film) 3262, 3029,1637, 1562, 1486 cm<sup>-1</sup>; LRMS (TOF ES+), 176.5 (100%) [M<sup>+</sup>+H<sup>+</sup>], 134.2 (90%); HRMS (TOF ES+), calculated for C<sub>11</sub>H<sub>14</sub>NO, 176.10699; found 176.10685.

#### 1,1'-(1-Benzyl-4-(dimethoxymethyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1, diethyl ether:EtOAc, as eluent) afforded **4e** as a yellow solid (0.137 g, 42%): R<sub>f</sub>. 0.28 (EtOAc, as eluent); m.p. 142-144 °C; <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.39-7.37 (m, 2H), 7.34-7.32 (m, 1H), 7.28-7.27 (m, 2H), 7.16 (d, *J* = 0.8 Hz, 2H), 4.65 (s, 2H), 4.49 (dt, *J* = 3.8, 0.8 Hz), 3.99 (d, *J* = 3.8 Hz, 1H), 3.34 (s, 6H), 2.25 (s, 6H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  195.8, 140.4, 136.2, 129.2, 128.4, 127.0, 114.9, 107.3, 58.7, 56.0, 33.1, 25.3; IR (thin film) 1643, 1569 cm<sup>-1</sup>; LRMS (TOF ES+), 352.2 (100%) [M<sup>+</sup>+Na<sup>+</sup>], 298.3 (80%); HRMS (TOF ES+), calculated for C<sub>19</sub>H<sub>23</sub>NO<sub>4</sub>+Na<sup>+</sup>, 352.1525; found 352.1526.

1,1'-(4-(4-Nitrophenyl)-1-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone and 1,1'-(2-Methoxy-4-(4-nitrophenyl)-1-phenyl-1,2,3,4-tetrahydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (diethyl ether, as eluent) afforded **4f** as a yellow solid (0.113 g, 31%):  $R_f$ . 0.34 (2:1, EtOAc:hexane as eluent); m.p. 217-218 °C; <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  8.11-8.09 (m, 2H), 7.57 (s, 2H), 7.57-7.53 (m, 4H), 7.44-7.41 (m, 1H), 7.38-7.36 (m, 2H), 5.35 (s, 1H), 2.23 (s, 6H) ppm; <sup>13</sup>C NMR

 $(176 \text{ MHz}, \text{CDCl}_3) \delta 194.6, 152.7, 146.7, 143.2, 137.5, 130.5, 129.4, 127.7, 123.7, 121.8, 120.4, 36.1, 25.4; IR (thin film) 1644, 1594, 1572, 1512, 1495, 1345 cm<sup>-1</sup>; LRMS (TOF ES+), 385.3 (53%) [M+Na]+, 363.3 (15%), [M+H]+; HRMS (TOF ES+), calculated for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>, 363.13393; observed 363.13485.$ 

and **6** as a yellow solid (0.105 g, 27%):  $R_f$ . 0.26 (2:1, EtOAc:hexane as eluent); m.p. 195-198 °C; <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  8.14-8.12 (m, 2H), 7.84 (s, 1H), 7.44-7.41 (m, 4H), 7.32-7.31 (m, 2H), 7.28-7.26 (m, 1H), 5.22-5.21 (m, 1H), 4.71 (br s, 1H), 3.41-3.40 (m, 1H), 2.80 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  205.2, 194.0, 150.6, 146.5, 145.8, 144.0, 130.0, 128.6, 126.2, 123.5, 121.7, 111.5, 87.2, 55.0, 53.9, 35.4, 28.3, 24.6; IR (thin film) 1709, 1613, 1591, 1512, 1494, 1323 cm<sup>-1</sup>; LRMS (TOF ES+), 417.2 (100%) [M+Na]+, 363.395.2 (18%), [M+H]+; HRMS (TOF ES+), calculated for C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O<sub>5</sub>, 395.1607; observed 395.1620.

#### 1,1'-(1-Allyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1 to 4:1, EtOAc:Hexane, as eluent) afforded **4g** as a yellow solid (0.201 g, 62%): m.p. 106-107 °C; R<sub>f</sub>. 0.28 (EtOAc, as eluent); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  8.06-8.04 (m, 2H), 7.47-7.45 (m, 2H), 7.16 (s, 2H), 6.00 (ddt, *J* = 17.1, 10.3, 5.6 Hz, 1H), 5.43-5.41 (m, 1H), 5.38 (dtd, *J* = 17.1, 1.6, 0.8 Hz, 1H), 5.27 (s, 1H), 4.15 (dt, *J* = 5.6, 1.6 Hz, 2H), 2.15 (s, 6H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  194.4, 153.2, 146.4, 138.9, 132.2, 129.2, 123.5, 119.9, 118.8, 57.4, 35.9, 25.2; IR (thin film) 1632, 1597, 1513, 1368, 1341 cm<sup>-1</sup>; LRMS (TOF ES+), 349.2 (100%) [M+Na]+, 327.3 (40%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>, 327.13393; observed 327.13509.

#### 1,1'-(1-Allyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone



4h

Purification by silica gel chromatography (1:9, EtOAc:hexane, to 1:9, EtOAc:diethyl ether as eluent) afforded **4h** as a yellow solid (0.135 g, 48%): m.p. 118-119 °C; R<sub>f</sub>. 0.18 (1:9, EtOAc:diethyl ether as eluent); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d, J = 7.7 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.14-7.11 (m, 1H), 7.13 (s, 2H), 5.94 (ddt, J = 17.0, 10.5, 5.6 Hz, 1H), 5.38 (dtd, J = 10.5, 1.6, 0.9 Hz, 1H), 5.36 (dtd, J = 17.0, 1.6, 0.9 Hz, 1H), 5.18 (s, 1H), 4.10 (dt, J = 5.6, 1.6 Hz, 2H), 2.15 (br s, 6H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  195.2, 145.9, 138.0, 132.5, 128.3, 128.3, 126.6, 119.6, 119.5, 57.3, 35.9, 25.7; IR (thin film) 1633, 1566 cm<sup>-1</sup>; LRMS (TOF ES+), 304.3 (100%) [M<sup>+</sup>+Na<sup>+</sup>], 282.3 (35%) [M<sup>+</sup>+H<sup>+</sup>], 176.2 (20%), 146.2 (20%); HRMS (TOF ES+), calculated for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>+H<sup>+</sup>, 282.1494; found 282.1495; *Anal.* Calcd: C, 76.84, H, 6.81, N, 4.98, found: C, 76.65, H, 6.84, N, 4.94.

1,1'-(1-Allyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1 to 4:1, EtOAc:Hexane, as eluent) afforded **4i** as a yellow oil (0.107 g, 34%):  $R_f$ . 0.35 (EtOAc, as eluent); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.22-7.20 (m, 2H), 7.11 (s, 2H), 6.77-6.75 (m, 2H), 5.93 (ddt, J = 17.1, 10.3, 5.6 Hz, 1H), 5.39-5.37 (m, 1H), 5.35 (dtd, J = 17.1, 1.6, 0.8 Hz), 5.11 (s, 1H, *Hf*), 4.08 (dt, J = 5.6, 1.6 Hz, 2H)3.73 (s, 3H), 2.14 (s, 6H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  195.3, 158.2, 138.4, 137.8, 132.5, 129.3, 119.7, 119.5, 113.7, 57.3, 55.3, 35.0, 25.7; IR (thin film) 1638, 1568, 1508, 1370 cm<sup>-1</sup>; LRMS (TOF ES+), calculated for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>Na, 334.14136; observed 334.14133.

#### 1,1'-(1-Allyl-4-(dimethoxymethyl)-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:9, EtOAc:diethyl ether to EtOAc as eluent) afforded **4j** as a dark orange oil (0.045 g, 20%):  $R_f$ . 0.15 (EtOAc as eluent); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.09 (s, 2H), 5.86 (ddt, J = 16.7, 10.2, 5.0 Hz, 1H), 5.33 (dtd, J = 16.7, 1.6, 0.9 Hz, 1H), 5.29 (dtd, J = 10.2, 1.6, 0.9 Hz, 1H), 4.45 (d, J = 4.0 Hz, 1H), 4.03 (dt, J = 5.0, 1.6 Hz, 2H), 3.97 (d, J = 4.0 Hz, 1H), 3.22 (br s, 6H), 2.26 (br s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  195.9, 139.9, 132.7, 118.8, 114.9, 107.3, 57.3, 55.9, 33.3, 25.5; IR (thin film) 1639, 1567 cm<sup>-1</sup>; LRMS (TOF ES+), 302.3 (100%) [M<sup>+</sup>+Na<sup>+</sup>], 280.3 (60%) [M<sup>+</sup>+H<sup>+</sup>], 176.2 (20%), 248.2 (30%); HRMS (TOF ES+), calculated for C<sub>15</sub>H<sub>21</sub>NO<sub>4</sub>+Na<sup>+</sup>, 302.1368; found 302.1382.

#### 1,1'-(4-Ethyl-1-methyl-1,4-dihydropyridine-3,5-diyl)diethanone



Purification by silica gel chromatography (1:1, EtOAc:hexane to EtOAc, as eluent) afforded **4k** as a yellow solid (0.057 g, 28 %): m.p. 182-183 °C; R<sub>f</sub>. 0.10 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02 (d, *J* = 0.5 Hz, 2H), 4.12 (t, *J* = 4.9 Hz, 1H), 3.24 (s, 3H), 2.25 (s, 6H), 3.53 (qd, *J* = 7.5, 4.9 Hz, 2H), 0.68 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  195.5, 140.3, 118.4, 41.9, 30.0, 28.2, 25.4, 9.0; IR (thin film) 2960, 1626, 1564, 1366 cm<sup>-1</sup>; LRMS (TOF ES+), 208.2 (90%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub>, 208.1338; *Anal.* calcd: C, 69.54, H, 8.27, N, 6.76, found: C, 69.64, H, 8.30, N, 6.62.

1,1'-(1-(*tert*-Butyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-diyl)diethanone and (*3Z*,5*Z*)-3,5-Bis((*tert*-butylamino)methylene)-4-(4-nitrophenyl)heptane-2,6dione



Purification by silica gel chromatography (4:1, hexane:EtOAc to 2:1, EtOAc:hexane, as eluent) afforded a mixture of **4I** as a yellow oil (0.103 g, 30%): R<sub>f</sub>. 0.23 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.06-8.04 (m, 2H), 7.51 (s, 2H), 7.43-7.40 (m, 2H), 5.27 (s, 1H), 2.18 (s, 6H), 1.55 (s, 9H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  194.6, 153.2, 146.4, 135.5, 129.0, 123.5, 118.8, 58.4, 36.0, 29.5, 25.3; IR (thin film) 1636, 1561, 1513, 1372, 1340 cm<sup>-1</sup>; LRMS (TOF ES+), 365.3 (100%) [M+Na]+, 343.3 (35%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Na, 365.1477; observed 365.1460.

and 7 as an orange solid (0.246 g, 59%): m.p. 151-153 °C; R<sub>f</sub>. 0.39 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.98-7.96 (m, 2H), 7.63 (d, *J* = 14.2 Hz, 2H), 7.13-7.11 (m, 2H), 5.54 (s, 1H), 2.18 (br s, 6H), 1.20 (br s, 18H) ppm; <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  193.7 (br), 149.5, 148.2, 145.5, 127.8, 122.9, 109.7, 52.8, 35.3, 30.0, 24.5 (br); IR (thin film) 2970, 1636, 1571, 1511, 1490, 1369,

1339, 1321 cm<sup>-1</sup>; LRMS (ASAP), 416.3 (62%) [M+H]+, 275.1 (100%), 142.1 (32%); HRMS (TOF ES+), calculated for C<sub>22</sub>H<sub>34</sub>N<sub>3</sub>O<sub>4</sub>, 416.2544; observed 416.2545.

(E)-4-(Phenylamino)but-3-en-2-one



To pivalaldehyde (0.086 g, 1 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (1 mL), was added 4-methoxy-3buten-2-one (0.204 mL, 2 mmol), aniline (0.091 mL, 1 mmol) and Sc(OTf)<sub>3</sub> (0.049 g, 0.1 mmol) and the RM was left to stir at rt for 14 d. Purification by silica gel chromatography (1:1, petroleum ether:diethyl ether to diethyl ether, as eluent) afforded **5b** as a beige solid (0.075 g, 45 %): R<sub>f</sub>. 0.44 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  11.58 (br s, 1H), 7.32-7.30 (m, 2H), 7.22 (dd, *J* = 12.3, 7.7 Hz, 1H), 7.06-7.02 (m, 3H), 5.30 (d, *J* = 7.7 Hz, 1H), 2.16 (s, 3H) ppm (addition of D<sub>2</sub>O caused the signal at  $\delta$  11.58 to disappear); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$ 199.0, 143.2, 140.5, 129.8, 123.5, 116.2, 97.6, 29.7; IR (thin film) 1639, 1596, 1568, 1477 cm<sup>-1</sup>; LRMS (TOF ES-), 160.2 (50%) [M-H]-, 149.0 (100%); HRMS (TOF ES-), calculated for C<sub>10</sub>H<sub>10</sub>NO, 160.07679; found 160.07690.

#### (E)-4-(tert-Butylamino)but-3-en-2-one



To propionaldehyde (0.058 g, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added 4-methoxy-3buten-2-one (0.204 mL, 2 mmol), *tert*-butylamine (0.105 mL, 1 mmol) and Sc(OTf)<sub>3</sub> (0.049 g, 0.1 mmol) and the RM was left to stir at rt for 17 d. Purification by silica gel chromatography (1:1, petroleum ether:diethyl ether to diethyl ether, to EtOAc, as eluent) afforded **5c** as a beige solid (0.141 g, 99%): R<sub>f</sub>. 0.44 (2:1, EtOAc:hexane as eluent); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.13 (br s, 1H, N*H*), 6.8 (dd, *J* = 13.3, 7.4 Hz, 1H), 4.98 (d, *J* = 7.4 Hz, 1H), 2.02 (s, 3H), 1.27 (s, 9H) ppm (addition of D<sub>2</sub>O caused the signal at  $\delta$  10.13 to disappear); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  1970, 148.2, 93.5, 51.9, 30.2, 29.1; IR (neat) 2971, 1631, 1555, 1484 cm<sup>-1</sup>; LRMS (TOF ES+), 164.2 (100%) [M+Na]+, 142.2 (34%) [M+H]+; HRMS (TOF ES+), calculated for C<sub>8</sub>H<sub>15</sub>NONa, 164.10459; observed 164.10442.

### Procedure for the mechanistic studies

The reagents were added in the order shown in Table 2 in  $\text{CDCl}_3$  (1 mL), where 1 equivalent of a reagent = 1 mmol. The reaction mixture was stirred at rt and monitored using <sup>1</sup>H NMR until it was certain that the reaction had gone to completion.

## <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds









































































