

# **Supporting Information**

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# Rhodium-catalyzed, three-component reaction of diazo compounds with amines and azodicarboxylates

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# **Supporting Information**

General methods: Melting points are uncorrected. NMR spectra were recorded on a Bruker-300 MHz spectrometer. MS (EI) Mass spectra were recorded on VG7070E. Elemental analyses were performed on a Carlo Erba-1106 instrument. Dichloromethane was distilled over calcium hydride. Toluene was distilled over sodium benzophenone ketyl.

General procedure for the reaction of ethyl diazoacetate with aniline and DEAD:

To a 10 mL CH<sub>2</sub>Cl<sub>2</sub> solution of Rh<sub>2</sub>(OAc)<sub>4</sub> (3.6 mg, 0.0081 mmol), aniline **2b** (82.8 mg, 0.89 mmol) and DEAD **3a** (154.8 mg, 0.89 mmol) was added ethyl diazoacetate **1a** (92.2 mg, 0.81 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> under argon atmosphere via a syringe pump over 1 h under refluxing. After completed the addition, the reaction mixture was cooled to room temperature. Solvent was removed and a portion of the crude mixture was subjected to <sup>1</sup>H NMR analysis for determination of the product ratio. The crude product was purified by flash chromatography on silica gel by using 10 % EtOAc-light petroleum ether as eluent to give **4b** as a solid. Single crystal **4b** was grown in hexane and ethyl acetate solution. Products **4a~4h** and **6a** were obtained by the same procedure.

# Ethyl [N,N'-bis(ethoxycarbonyl)hydrazino]-4-methoxy phenylamino- acetate 4a:

 $R_f = 0.23$  (30% EtOAc/ light petroleum); mp = 79.1-80.5°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) & 6.76 (d, J = 8.9Hz, 2H), 6.69 (d, J = 8.9Hz, 2H), 6.26 (s, 1H), 6.17 (br, 1H), 4.81 (s, 1H), 4.28-4.80 (m, 4H), 4.17 (& J = 7.1Hz, 2H), 3.73 (s, 3H), 1.39 (t, J = 7.1Hz, 3H), 1.22-1.30 (m, 6H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 167.8, 155.7 (two C=O carbons), 153.4, 137.6, 115.3, 115.0, 66.5, 63.1, 62.6, 62.3, 55.8, 14.6, 14.3, 14.1; EIMS (70 eV) m/z (rel intensity) 383 [M<sup>+</sup>, 5], 310 [(M-COOEt)<sup>-+</sup>, 5], 208 [C<sub>11</sub>H<sub>14</sub>O<sub>3</sub><sup>+</sup>, 58], 134 [C<sub>8</sub>H<sub>8</sub>NO<sup>+</sup>, 100]; Anal. Calcd for C<sub>17</sub>H<sub>25</sub>N<sub>3</sub>O<sub>7</sub>: C, 53.26; H, 6.57; N, 10.96. Found: C, 53.09; H, 6.53; N, 10.68.

# Ethyl [N,N'-bis(ethoxycarbonyl)hydrazino]-phenylaminoacetate 4b:

 $R_f = 0.35$  (30% EtOAc/ light petroleum); mp = 97.8-98.9°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 7.21 (m, 2H), 6.81 (m, 1H), 6.74 (m, 2H), 6.21 (br, 2H), 5.03 (s, 1H), 4.33 (m, 4H), 4.14 (q, J = 7.1Hz, 2H), 1.34 (t, J = 7.1Hz, 3H), 1.25 (m, 6H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 167.8, 155.7 (two C=O carbons), 143.7, 129.6, 119.5, 113.9, 67.1, 63.2, 62.7, 62.4, 14.6, 14.4, 14.2; EIMS (70 eV) m/z (rel intensity) 353 [M<sup>+</sup>, 4], 280 [(M-COOEt)<sup>-+</sup>, 7], 178 [C<sub>10</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>, 84], 104 [C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>, 100], 77 [C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 89]; Anal. Calcd for C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>O<sub>6</sub>: C, 54.38; H, 6.56; N, 11.89. Found: C, 54.34; H, 6.57; N, 11.88.

# Ethyl [N,N'-bis(ethoxycarbonyl)hydrazino]- 4-chloroy phenylamino acetate 4c:

 $R_f = 0.34$  (30% EtOAc/ light petroleum); mp = 85.6-86.4°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 7.15 (d, J = 8.9Hz, 2H), 6.68 (d, J = 8.9Hz, 2H), 6.21 (s, 1H), 6.11 (s, 1H), 5.06 (s, 1H), 4.27-4.38 (m, 4H), 4.16 (a), J = 7.1Hz, 2H), 1.34 (t, J = 7.1Hz, 3H), 1.23-1.27 (m, 6H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 167.6, 155.6 (two C=O carbons), 142.6, 129.4, 124.3, 115.2, 65.9, 63.4, 62.9, 62.4, 14.6, 14.3, 14.2; EIMS (70 eV) m/z (rel intensity) 387 [M<sup>+</sup>, 6], 280 [(M-C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>)<sup>-+</sup>, 99], 140 [C<sub>7</sub>H<sub>6</sub>NCl<sup>+</sup>, 100]; Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>3</sub>O<sub>6</sub>Cl: C, 49.55; H, 5.72; N, 10.84. Found: C, 49.48; H, 5.87; N, 10.83.

# Ethyl [N,N'-bis(ethoxycarbonyl)hydrazino]-4-nitrophenylamino acetate 4d:

 $R_f = 0.25$  (30% EtOAc/ light petroleum); mp = 148.2-149.2°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 8.12 (d, J = 9.1Hz, 2H), 6.78 (d, J = 9.1Hz, 2H), 6.35 (s, 1H), 6.30 (s, 1H), 5.75 (s, 1H), 4.34 (m, 4H), 4.20 (m, 2H), 1.24-1.38 (m, 9H); <sup>13</sup>C NMR (75MHz,CDCl<sub>3</sub>) d 167.1, 155.7 (two C=O carbons), 149.9, 140.1, 126.2, 113.0, 65.8, 63.7, 63.3, 62.5, 14.5, 14.4, 14.2; EIMS (70 eV) m/z (rel intensity) 398 [M<sup>+</sup>, 2], 223 [(M-C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>)·<sup>+</sup>, 32], 176 [C<sub>10</sub>H<sub>10</sub>NO<sub>2</sub>+, 28], 148 [C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>+, 100]; Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>O<sub>8</sub>: C, 48.24; H, 5.57 N, 14.06. Found: C, 48.13; H, 5.54; N, 13.96.

Ethyl [*N,N'*-bis(ethoxycarbonyl)hydrazino]-2,4-dinitrophenylamino acetate 4e:  $R_f = 0.25$  (30% EtOAc/ light petroleum); mp = 155.4-157.6°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)?d 9.35 (d, J = 7.4Hz, 1H), 9.16 (d, J = 2.6Hz, 1H), 8.35 (q,  $J_I = 7.4$ Hz,  $J_2 = 2.6$ Hz, 1H), 7.26 (s, 1H), 6.41 (br, 2H), 4.31-4.45 (m, 4H**?**, 4.06 (m, 2H), 1.17-1.58 (m, 9H); <sup>13</sup>C NMR(75MHz, CDCl<sub>3</sub>) d 165.9, 156.1 (two

C=O carbons), 146.4, 138.2, 132.3, 130.4, 123.8, 116.1, 66.2, 64.2, 63.9, 62.8, 14.5, 14.3, 14.2; EIMS (70 eV) m/z (rel intensity) 443 [M<sup>+</sup>, 1], 29 [C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 100]; Anal. Calcd for C<sub>16</sub>H<sub>21</sub>N<sub>5</sub>O<sub>10</sub>: C, 43.34; H, 4.77; N, 15.80. Found: C, 43.22; H, 4.84; N, 15.42.

#### Ethyl [N,N'-bis(isopropoxycarbonyl)hydrazino]-phenylaminoacetate 4f:

 $R_f = 0.43$  (30% EtOAc/ light petroleum); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 7.19 (m, 2H), 6.76-6.83 (m, 3H), 6.26 (s, 1H), 6.16 (s, 1H), 5.05 (m, 2H), 4.86 (s, 1H), 4.19-4.32 (m, 2H), 1.25-1.37 (m, 15H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 167.8, 155.3 (two C=O carbons), 143.9, 129.4, 119.2, 113.9, 70.8, 69.9, 66.9, 62.5, 21.9, 21.7, 14.1; EIMS (70 eV) m/z (rel intensity) 381 [M<sup>+</sup>, 6], 280 [(M-COOEt)<sup>-+</sup>, 5], 178 [C<sub>10</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>, 86], 104 [C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>, 100], 77 [C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 29]; Anal. Calcd for C<sub>18</sub>H<sub>27</sub>N<sub>3</sub>O<sub>6</sub>: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.32; H, 7.11; N, 10.90.

Ethyl [*N,N'*-bis(*tert*-butoxycarbonyl)hydrazino]-phenylaminoacetate **4g:**  $R_f = 0.57 (30\% \text{ EtOAc/ light petroleum}); {}^{1}\text{H NMR} (300 \text{ MHz, CDCl}_3) d 7.09-7.30 (m, 2H), 6.74-6.82 (m, 3H), 6.21 (s, 1H), 6.11 (s, 1H), 5.02 (s, 1H), 4.22-4.29 (m, 2H), 1.16-1.48 (m, 21H); {}^{13}\text{C NMR} (75\text{MHz, CDCl}_3) d 167.9, 155.3 (two C=O carbons), 144.0, 129.5, 119.2, 113.9, 82.3, 81.4, 67.5, 62.5, 28.2, 28.0, 14.1; EIMS (70 eV) <math>m/z$  (rel intensity) 409 [M<sup>+</sup>, 3], 178 [C<sub>10</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>, 48], 104 [C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>, 33], 77 [C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 17], 57 [C<sub>4</sub>H<sub>9</sub><sup>+</sup>, 100]; Anal. Calcd for C<sub>20</sub>H<sub>31</sub>N<sub>3</sub>O<sub>6</sub>: C, 58.66; H, 7.63; Found: C, 58.46; H, 7.63.

# Ethyl [N,N'-bis(ethoxycarbonyl)hydrazino]-a-(benzeamino)-phenyl ethanone 4h:

 $R_f = 0.40 \ (30\% \ EtOAc/ \ light petroleum); mp = 105.3-106.4°C; ^1H NMR \ (300 \ MHz, CDCl_3) d 8.21, (m, 2H), 7.62 (m, 1H), 7.50 (m, 2H), 7.22 (m, 2H), 6.84 (m, 3H), 6.72 (s, 1H), 6.25 (s, 1H); 5.48 (s, 1H), 4.03-4.15 (m, 4H), 1.19-1.28 (m, 6H); <math>^{13}C$  NMR  $(75MHz, CDCl_3)$  d  $^{1}90.9$ , 155.8 (two C=O carbons), 143.8, 143.5, 134.3, 129.7, 129.3, 128.9, 119.3, 114.2, 66.8, 63.3, 62.2, 14.5, 13.4; EIMS  $(70 \ eV) \ m/z$  (rel intensity) 385 [M<sup>+</sup>, 1], 280 [(M-PhCO)<sup>-+</sup>, 64], 105 [PhCO<sup>+</sup>, 100], 77 [C<sub>6</sub>H<sub>5</sub> <sup>+</sup>, 100]; Anal.Calcd for  $C_{20}H_{23}N_3O_5$ : C, 62.33; H, 6.01; N, 10.90. Found: C, 62.13; H, 6.06; N, 10.86.

#### Methyl 2-phenyl-2-phenyliminoacetate 6a:

 $R_f = 0.71 \ (10\% \ EtOAc/ \ light petroleum); \ ^1H \ NMR \ (300 \ MHz, CDCl_3) \ d 7.87 \ (m, 2H), 7.48 \ (m, 3H), 7.34 \ (m, 2H), 7.14 \ (m, 1H), 6.96 \ (m, 2H); 3.63 \ (s, 3H); \ ^{13}C \ NMR \ (75MHz, CDCl_3) \ d 165.6, 160.1, 150.2, 131.9, 129.9, 129.3, 129.1, 128.6, 125.1, 119.6, 52.0. EIMS \ (70 \ eV) \ m/z \ (rel intensity) \ 239 \ [M^+, 52], 180 \ [(M-COOMe)^{-+}, 100], 77 \ [C_6H_5^+, 100]; \ Anal. \ Calcd \ for \ C_{15}H_{13}NO_2?1/4H_2O: C, 73.92; H, 5.59; N, 5.75. Found: C, 73.88; H, 5.73; N, 5.61.$ 

# **Dimethyl 2-phenyliminomalonate 6b:**

 $R_f = 0.43$  (10% EtOAc/ light petroleum); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 7.33, (m, 2H), 7.22 (m, 1H), 6.99 (m, 2H), 3.96 (m, 3H), 3.67 (s, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 162.8, 161.4, 151.6, 147.3, 129.1, 127.2, 119.6, 53.6, 52.6. EIMS (70 eV) m/z (rel intensity) 221 [M<sup>+</sup>, 30], 162 [(M-COOMe)<sup>+</sup>, 58], 118 [C<sub>8</sub>H<sub>8</sub>N<sup>+</sup>, 34], 77 [C<sub>6</sub>H<sub>5</sub>

<sup>+</sup>, 100]; Anal. Calcd for C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.63; H, 5.01; N, 6.31.

General procedure for the reaction of dimethyl diazomalonate with 4-nitrobenzenamine and DEAD: To a 8 mL toluene solution of Rh<sub>2</sub>(OAc)<sub>4</sub> (2.2 mg, 0.0049 mmol), 4-nitrobenzenamine 2d (75 mg, 0.54 mmol) and DEAD 3a (85.5 uL, 0.54 mmol) under argon atmosphere was added dimethyl diazomalonate 1c (78 mg, 0.49 mmol) in 5 mL of toluene via a syringe pump over 1 h under refluxing. After completed the addition, the reaction mixture was cooled to room temperature. Solvent was removed, and a portion of the crude mixture was subjected to <sup>1</sup>H NMR analysis for determination of the product ratio. The crude product was purified by flash chromatography on silica gel by using 15% EtOAc-light petroleum ether as eluent to give 7 as a white solid, yield 50%. Products 6b was obtained by the same procedure.

Dimethyl [N,N'-bis(ethoxycarbonyl)hydrazino]-4-nitrophenylamino malonate 7:

 $R_f = 0.23$  (30% EtOAc/ light petroleum); mp = 137.5-138.4°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) & 8.08 (q,  $J_I = 7.9$  Hz,  $J_2 = 2.0$  Hz, 2H), 6.96 (q,  $J_I = 7.9$ Hz,  $J_2 = 2.0$ Hz, 2H), 6.72 (s, 1H), 6.23 (s, 1H), 4.22-4.08 (m, 4H), 3.86 (s, 6H), 1.28-1.09 (m, 6H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 165.7 (two C=O carbons), 155.5, 155.2, 148.9, 140.2, 125.7, 114.5, 79.3, 63.9, 62.7, 54.5, 14.5, 14.3. EIMS (70 eV) m/z (rel intensity) 385 [(M+Na)<sup>+</sup>, 465]; Anal. Calcd for  $C_{17}H_{22}N_4O_{10}$ : C, 46.16; H, 5.01; N, 12.66. Found: C, 45.96; H, 4.96; N, 12.58.

**Dimethyl 2-(4-nitrophenylimino)-malonate 6c:** A toluene solution (8.0 mL) of **7** (40 mg. 0.09 mmol) was refluxed for 24 h. The reaction mixture was cooled to room temperature. Solvent was removed, and a portion of the crude mixture was

subjected to <sup>1</sup>H NMR analysis for determination of the conversion. The crude product was purified by flash chromatography on silica gel by using 15% EtOAc-light petroleum ether as eluent to give **6c** (23.4 mg, 0.088 mmol), yield 98%.

$$\begin{array}{c} \text{MeOOC} \\ \\ \text{MeOOC} \end{array} \hspace{-0.5cm} - \hspace{-0.5cm} \text{NO}_2 \\ \end{array}$$

# Dimethyl 2-(4-nitrophenylimino)-malonate 6c:

 $R_f = 0.53$  (30% EtOAc/ light petroleum); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) d 8.24 (m, 2H), 7.04 (m, 2H), 4.01 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) d 161.3, 160.8, 153.4, 152.9, 146.1, 125.0, 119.5, 54.1, 53.2. EIMS (70 eV) m/z (rel intensity) 266 [(M+1)<sup>+</sup>, 267]; Anal. Calcd for  $C_{11}H_{10}N_2O_6$ : C, 49.63; H, 3.79; N, 10.52. Found: C, 50.01; H, 3.95; N, 10.40.