A Novel Three-Component Reaction Catalyzed by Dirhodium(II) Acetate: Decomposition of Phenyldiazoacetate with Arylamine and Imine for Highly Diastereoselective Synthesis of 1,2-Diamines

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Supporting Information

General methods. NMR spectra were recorded on a Brucker-300MHz spectrometer. HRMS (ESI) Mass spectra were recorded on BRUCKER FT-MS. Dichloromethane was distilled over calcium hydride.

Procedure for Reaction of Phenyldiazoacetate with aniline and Imine. To a 10 mL CH_2Cl_2 solution of $Rh_2(OAc)_4$ (2.7mg, 0.0061mmol), imine **3** (152mg, 0.67mmol) and aniline **2a** (624mg, 0.67mmol) was added methyl phenyl diazoacetate **1** (107mg, 0.61mmol) in 4 mL of CH_2Cl_2 via a syringe pump over 1 h under refluxing. After completed addition, the reaction mixture was cooled to room temperature. Solvent was removed, and a portion of crude product was subjected to ^1H 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 as eluent to give **4a** and **5a**, total yield 68%. Single crystal **5a** was grown in hexanes and ethyl acetate solution.

Phenyl phenylamino acetic acid methyl ester (4a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 4.96 (br,1H), 5.08 (s, 1H), 6.55-6.58 (m, 2H), 6.67-6.73 (m, 1H), 7.10-7.15 (m, 2H), 7.33-7.36 (m, 3H), 7.49-7.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 60.7, 113.4, 118.1, 127.2, 128.3, 128.9, 129.2, 137.6, 145.9, 172.3; MS (m/z) 241 (M^+).

3-(4-Nitro-phenyl)-2-phenyl-2,3-bis-phenylamino-propionic acid methyl ester (5a, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 3 H), 5.22 (d, *J* = 10.6 Hz, 1 H), 5.40 (d, *J* = 10.6 Hz, 1 H), 5.52 (s, 1 H), 6.47-6.73 (m, 6 H), 7.00-7.13 (m, 4 H), 7.19 (d, *J* = 8.7 Hz, 2 H), 7.25-7.37 (m, 5 H), 8.03 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.7, 65.0, 70.6, 114.2, 116.2, 118.9, 119.1, 123.1, 128.3, 128.4, 128.6, 128.8, 129.4, 129.8, 136.3, 144.6, 145.4, 145.5, 147.6, 172.3; HRMS (ESI) calcd for $C_{28}H_{26}N_3O_4$ (M+H) 468.1923, Found: 468.1928.

3-(4-Nitro-phenyl)-2-phenyl-2,3-bis-phenylamino-propionic acid methyl ester (5a, threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3 H), 4.96 (s, 1 H), 5.00 (d, *J* = 6.5 Hz, 1 H), 5.49 (d, *J* = 6.4 Hz, 1 H), 6.36-6.46 (m, 4 H), 6.68-6.73 (m, 2 H), 7.00-7.11 (m, 4 H), 7.19 (d, *J* = 8.7 Hz, 2 H), 7.25-7.36 (m, 5 H), 8.02 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1, 62.5, 71.0, 113.8, 115.6, 118.7, 119.0, 123.1, 128.2, 128.5, 128.9, 129.0, 129.4, 129.5, 135.3, 144.2, 145.4, 145.8, 147.6, 172.3; HRMS (ESI) calcd for $C_{28}H_{26}N_3O_4$ (M+H) 468.1923, Found: 468.1910.

(4-Fluoro-phenylamino)-phenyl-acetic acid methyl ester (4b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 3H), 4.85 (d, J = 6.0 Hz, 1 H), 5.01 (d, J = 6.0 Hz, 1 H), 6.46-6.51 (m, 2 H), 6.80-6.86 (m, 2 H), 7.31-7.39 (m, 3 H), 7.47-7.49 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 61.2, 114.3, 115.7(d, $^{2}J_{CF}$ = 22.3 Hz), 127.2, 128.4, 128.9, 137.4, 142.2, 156.1(d, $^{1}J_{CF}$ = 234.4 Hz) ; MS (m/z) 259 (M^{+}).

2-(4-Fluoro-phenylamino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5b, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.60 (s, 3 H), 5.14 (s, 1 H), 5.47 (br, 2 H), 6.41-6.47 (m, 2 H), 6.59-6.62 (m, 1 H), 6.69-6.76 (m, 3 H), 7.04-7.17 (m, 4 H), 7.27-7.38 (m, 7 H), 8.03 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6, 65.2, 71.1, 114.4, 115.2(d, $^{2}J_{CF}$ = 22.1 Hz), 117.6, 117.7, 119.2, 123.0, 128.3, 128.4, 128.7, 129.4, 129.8, 136.2, 140.8, 145.2, 145.4, 147.5, 156.6(d, $^{1}J_{CF}$ = 236.3 Hz), 172.3; HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_4$ (M+H) 486.1829, Found: 486.1836.

2-(4-Fluoro-phenylamino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5b, threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3 H), 4.84 (s, 1 H), 4.99 (d, J = 6.5 Hz, 1 H), 5.44 (d, J = 6.1 Hz, 1 H), 6.31-6.47 (m, 4 H), 6.68-6.77 (m, 3 H), 7.06-7.12 (m, 2 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.28-7.36 (m, 5 H), 8.03 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1, 62.8, 71.5, 113.8, 115.5 (d, $^{2}J_{CF}$ = 22.1 Hz), 117.1, 117.2, 118.8, 123.1, 128.2, 128.6, 128.9, 129.4, 129.6, 129.8, 135.1, 140.4, 145.4, 145.7, 147.6, 156.7(d, $^{1}J_{CF}$ = 236.5 Hz), 171.9; HRMS (ESI) calcd for $C_{28}H_{25}FN_3O_4$ (M+H) 486.1829, Found: 486.1824.

(4-Chloro-phenylamino)-phenyl-acetic acid methyl ester (4c): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H), 4.95 (s, 1 H), 6.39 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 7.22-7.40 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 60.7, 114.5, 127.2, 128.5, 128.9, 129.0, 129.2, 137.1, 144.4, 172.0; MS(m/z) 275 (M^+).

2-(4-Chloro-phenylamino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5c, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 3 H), 5.15 (s, 1 H), 5.38 (br, 1 H), 5.62 (br, 1 H), 6.42 (d, *J* = 8.9 Hz, 2 H), 6.58-6.75 (m, 3 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 7.09 -7.16 (m, 4 H), 7.27-7.32 (m, 5 H), 8.03 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.7, 65.4, 70.6, 114.4, 117.4, 119.3, 123.0, 128.4, 128.5, 128.6, 129.4, 129.8, 135.9, 143.1, 145.0, 145.3, 147.6, 172.1; HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_4$ (M+H) 502.1534, Found: 502.1527.

2-(4-Chloro-phenylamino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5c, threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3 H), 5.01 (br, 1 H), 5.46 (s, 1 H), 6.29 (d, *J* = 8.9 Hz, 2 H), 6.44-6.48 (m, 2 H), 6.69-6.74 (m, 1 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 7.07 -7.12 (m, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.29 -7.37 (m, 5 H), 8.05 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.3, 62.6, 70.9, 113.8, 116.6, 118.9, 123.2, 128.3, 128.7, 128.9, 129.4, 129.5, 134.7, 142.8, 145.2, 145.4, 147.7, 171.7; HRMS (ESI) calcd for $C_{28}H_{25}ClN_3O_4$ (M+H) 502.1534, Found: 502.1535.

Phenyl-(4-trifluoromethyl-phenylamino)-acetic acid methyl ester (4d): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H), 5.09 (s, 1 H), 5.35 (br, 1 H), 6.55 (d, *J* = 8.8 Hz, 2 H), 7.30-7.40 (m, 5 H), 7.46-7.49 (m, 2 H); MS (m/z) 309 (M^+).

3-(4-Nitro-phenyl)-2-phenyl-3-phenylamino-2-(4-trifluoromethyl-phenylamino)-propionic acid methyl ester (5d, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3 H), 5.15 (d, *J* = 11.0 Hz, 1 H), 5.36 (d, *J* = 11.0 Hz, 1 H), 5.94 (s, 1H), 6.51 (d, *J* = 8.6 Hz, 2 H), 6.59-6.76 (m, 3 H), 7.09-7.14 (m, 4 H), 7.25-7.34 (m, 7 H), 8.02 (d, *J* = 8.5 Hz, 2 H); HRMS (ESI) calcd for $C_{29}H_{25}F_3N_3O_4$ (M+H) 536.1797, Found: 536.1784.

3-(4-Nitro-phenyl)-2-phenyl-3-phenylamino-2-(4-trifluoromethyl-phenylamino)-propionic acid methyl ester (5d, threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3 H), 4.86 (d, *J* = 7.6 Hz, 1 H), 5.38 (s, 1 H), 5.50 (d, *J* = 7.2 Hz, 1 H), 6.39 (d, *J* = 8.5 Hz, 2 H), 6.47-6.49 (m, 2 H), 6.71-6,76 (m, 1 H), 7.08-7.18 (m, 4 H), 7.24-7.39 (m, 3 H), 8.06 (d, *J* = 8.8 Hz, 2 H); HRMS (ESI) calcd for $C_{29}H_{25}F_3N_3O_4$ (M+H) 536.1797, Found: 536.1789.

(4-Nitro-phenylamino)-phenyl-acetic acid methyl ester (4e): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 5.40 (d, *J* = 5.6 Hz, 1 H), 5.86 (d, *J* = 5.5 Hz, 1 H), 6.50 (d, *J* = 9.2 Hz, 2 H), 7.30-7.47 (m, 5 H), 8.00 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.2, 59.8, 112.1, 126.1, 127.0, 128.8, 129.1, 135.9, 138.8, 150.8, 171.1; MS (m/z) 286 (M^+).

3-(4-Nitro-phenyl)-2-(4-nitro-phenylamino)-2-phenyl-3-phenylamino-propionic acid methyl ester (5e, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 3 H), 5.15 (s, 1 H), 6.46 (br, 1 H), 6.51 (d, *J* = 9.3 Hz, 2 H), 6.64-6.81 (m, 3 H), 7.11-7.42 (m, 8 H), 7.95 (d, *J* = 9.3 Hz, 2 H), 8.03 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.0, 66.1, 70.4, 114.7, 115.0, 120.0, 121.0,123.1, 125.4, 128.2, 128.8, 129.5, 129.8, 135.0, 139.4, 144.0, 145.1, 147.7, 150.1, 171.2; HRMS (ESI) calcd for $C_{28}H_{25}N_4O_6$ 513.1774 (M+H), Found: 513.1765.

3-(4-Nitro-phenyl)-2-(4-nitro-phenylamino)-2-phenyl-3-phenylamino-propionic acid methyl ester (5e, threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3 H), 4.78 (br, 1 H), 5.53 (d, *J* = 6.5 Hz, 1 H), 5.85 (s, 1 H), 6.36 (d, *J* = 9.0 Hz, 2 H), 6.49-6.77 (m, 3 H), 7.09-7.34 (m, 8 H), 7.93 (d, *J* = 9.0 Hz, 2 H), 8.07 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.7, 62.3, 70.5, 113.8,114.1, 119.4, 123.4, 125.8, 128.7, 128.8, 129.1, 129.3, 129.5, 133.5, 139.3, 144.6, 144.8, 147.9, 149.9, 171.1; HRMS (ESI) calcd for $C_{28}H_{25}N_4O_6$ 513.1774 (M+H), Found: 513.1773.

2-(2,4-Dinitro-phenylamino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5f, erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3 H), 4.89 (d, *J* = 10.2 Hz, 1 H), 5.22 (d, *J* = 10.2 Hz, 1 H), 6.46-6.78 (m, 4 H), 7.08-7.15 (m, 4 H), 7.37-7.44 (m, 5 H), 7.94 (dd, *J* = 2.7, 9.6 Hz, 1 H), 8.03 (d, *J* = 8.6 Hz, 2 H), 9.14 (d, *J* = 2.7 Hz, 1 H), 10.11 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.4, 67.1, 71.3, 115.2, 118.0, 120.4, 123.2, 123.7, 128.1, 129.0, 129.2, 129.5, 129.6, 129.8, 132.3, 133.6,

137.3, 143.0, 144.8, 146.2, 147.9, 169.8; HRMS (ESI) calcd for $C_{28}H_{24}N_5O_8$ 558.1625 (M+H), Found: 558.1611.

(Methyl-phenyl-amino)-phenyl-acetic acid methyl ester (4g): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (s, 3H), 3.81 (s, 3H), 5.69 (s, 1 H), 6.83-6.91 (m, 3 H), 7.27-7.40 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.5, 52.0, 65.7, 113.5, 118.1, 119.5, 128.0, 128.1, 128.4, 128.7, 128.9, 129.3, 135.8, 149.9, 172.4; MS(m/z) 255 (M^+).

2-(Methyl-phenyl-amino)-3-(4-nitro-phenyl)-2-phenyl-3-phenylamino-propionic acid methyl ester (5g, erythro): δ 2.98 (s, 3 H), 3.83 (s, 3 H), 4.96 (br, 1 H), 5.18 (s, 1 H), 6.25-6.28 (m, 2 H), 6.57-6.62 (m, 1 H), 6.95-7.32 (m, 14 H), 7.87 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.7, 51.7, 60.0, 77.5, 113.3, 117.9, 122.2, 123.8, 125.0, 127.2, 128.2, 128.5, 128.9, 129.8, 131.0, 134.4, 145.5, 146.9, 147.0, 148.5, 170.7; HRMS (ESI) calcd for $C_{29}H_{28}N_3O_4$ 482.2080 (M+H), Found: 482.2075.

Procedure for Reaction of Phenyldiazoacetate with aniline and aldehyde. To a 8 mL CH_2Cl_2 solution of $Rh_2(OAc)_4$ (1.5mg, 0.0034mmol), 2-nitrobenzaldehyde(62mg, 0.41mmol) and O-anisidine(51mg, 0.41mmol) was added methyl phenyl diazoacetate(60mg, 0.34mmol) in 3 mL of CH_2Cl_2 via a syringe pump over 1 h under refluxing. After completed addition, the reaction mixture was cooled to room temperature. Solvent was removed and a portion of crude product was subjected to ^{1}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 as eluent to give **7-erythro** and **7-threo**, total yield 90%.

3-Hydroxy-2-(2-methoxy-phenylamino)-3-(2-nitro-phenyl)-2-phenyl-propionic acid methyl ester (7-erythro): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.58 (s, 3 H), 3.74 (d, *J* = 5.1 Hz, 1 H), 3.89 (s, 3 H), 5.74 (s, 1 H), 6.31-6.34 (m, 2 H), 6.55-6.80 (m, 4 H), 6.95 –6.98 (m, 1 H), 7.21-7.37 (m, 7 H), 7.80 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 55.8, 71.5, 71.6, 109.7, 114.1, 118.4, 120.3, 123.9, 127.6, 128.0, 128.5, 128.6, 130.3, 131.7, 133.1, 134.4, 134.8, 147.9, 149.4, 173.7; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_6$ (M+H) 423.1556, Found: 423.1553.

3-Hydroxy-2-(2-methoxy-phenylamino)-3-(2-nitro-phenyl)-2-phenyl-propionic acid methyl ester (7-threo): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3 H), 3.96 (s, 3 H), 4.18 (d, *J* = 3.1 Hz, 1 H), 6.08 (s, 1 H), 6.17-6.20 (m, 1 H), 6.51-7,51 (m, 11 H), 7.87 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6, 55.8, 71.3, 71.8, 109.5, 115.3, 118.0, 120.2, 123.5, 127.8, 128.0, 128.1, 128.4, 130.2, 131.8, 132.5, 134.1, 134.4, 148.1, 149.1,174.2; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_6$ (M+H) 423.1556, Found: 423.1552.