SUPPORTING INFORMATION

Organocatalysis in Conjugate Amine Additions. Synthesis of β -Amino Acid Derivatives

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General Experimental Procedures. Anhydrous α,α,α -Trifluorotoluene was purchased from Aldrich Chemicals. Anhydrous 2-methyl-2-propanol was purchased from Lancaster Synthesis. Acetonitrile was dried over SOLV-TEK SPS purchased from SOLV-TEK, Inc., prior to use. Methylene chloride and pyridine were distilled from calcium hydride prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Methyl alcohol and ethyleneglycol dimethyl ether were used without further purification. Sodium hydride was purchased from Lancaster Synthesis. Diethylphosphonoacetic acid, oxalyl chloride, samarium trifluoromethanesulfonate, *O*-(*tert*-butyldimethylsilyl)hydroxylamine and benzoyl chloride were purchased from Aldrich Chemicals. Aldehydes were purchased commercially. *O*-Diphenylmethylhydroxylamine was prepared by previously reported methods.¹ *O*-Benzylhydroxylamine was purchased from Lancaster Synthesis. Powdered molecular sieves 4Å (MS 4Å) was purchased from Aldrich Chemical and dried at 300 °C under vacuum before use. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh).

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a METTLER-TOLEDO REACT-IR 4000. ¹H NMR was recorded on a Varian Unity/Inova-500 NB (500 MHz), or a Varian Mercury-400 (400 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl₃ (7.27 ppm) or DMSO-*d*₆ (2.49 ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sep = septet, dd = doublets of doublets, dt = doublets of triplets, dq = doublets of quartets, m = multiplet, br = broad, AB sys = AB system), coupling constant(s) and integration. ¹³C NMR was recorded on a Varian Unity/Inova-500 NB (125 MHz) or a Varian Mercury-400 (100 MHz) spectrometers using broad band proton decoupling. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of CDCl₃ (77.23 ppm) or DMSO-*d*₆ (39.7 ppm) as an internal standard. HPLC analyses were carried out on Waters 515 HPLC pump and a 2487 dual λ absorbance detector connected to a PC with millennium workstation. Rotations were recorded on a JASCO-DIP-370 instrument. High-resolution mass spectra (HRMS) [EI⁺ or FAB] were obtained from the Mass Spectrometry Laboratory, Ohio State University, Columbus, Ohio. Elemental analyses were performed in house on a Perkin Elmer Series II CHNS/O Analyzer 2400.

I. Preparation of chiral thiourea catalysts

To a solution of chiral amino alcohol (10.6 mmol) in THF (15 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (10.6 mmol) at 0 °C. The reaction mixture was allowed to warm to rt and stirred for overnight. THF was removed in *vacuo* and the residue was purified by FC (silica gel, hexane/ethyl acetate = 4:1 ~ 1:1) to provide chiral thiourea catalyst (Yield = 80 ~ 99 %).²

Catalyst 6a:

Colorless solid; mp 148 °C; $[\alpha]_D^{25} = +15.9$ (*c* 1.09, CHCl₃); IR (neat, cm⁻¹) ν 683, 702, 746, 887, 962, 1046, 1131, 1175, 1277, 1343, 1383, 1472, 1530, 2948, 3047, 3074, 3276 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.83 (app d, *J* = 16.2 Hz, 1H), 3.12 (dd, *J* = 4.3, 16.2 Hz, 1H), 4.55 (q, *J* = 4.3 Hz, 1H), 5.46 (d, *J* = 4.3 Hz, 1H), 5.80-5.83 (m, 1H), 7.15-7.31 (m, 4H), 7.75 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.40 (s, 2H), 10.56 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 62.0, 72.5, 116.7, 122.8, 123.7 (q, *J* = 273.3 Hz), 124.9, 125.0, 125.7, 126.9, 128.1, 130.8 (q, *J* = 32.1 Hz), 141.2, 142.2, 142.7, 181.3; HRMS calcd. for C₁₈H₁₄F₆N₂OSNa⁺ is 443.0623 and Observed = 443.0609.

Catalyst 6b:

Colorless solid; mp 226 °C; $[\alpha]_D^{25} = -26.2$ (*c* 1.05, MeOH); IR (neat) ν 685, 702, 737, 752, 889, 955, 1050, 1066, 1127, 1171, 1262, 1279, 1385, 1470, 1567, 1642, 2856, 2927, 2950, 3095, 3334 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.81 (app d, *J* = 16.2 Hz, 1H), 3.10 (dd, *J* = 4.5, 16.2 Hz, 1H), 4.45-4.48 (m, 1H), 5.10-5.12 (m, 1H), 5.33 (d, *J* = 4.1 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 7.15-7.24 (m, 4H), 7.54 (s, 1H), 8.07 (s, 2H), 9.61 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 62.0, 72.5, 113.9, 117.62, 117.64, 124.0 (q, *J* = 273.3 Hz), 124.7, 125.5, 126.9, 127.8, 131.5 (q, *J* = 131.5), 141.1, 143.2, 143.3, 155.6; HRMS calcd. for C₁₈H₁₄F₆N₂O₂Na⁺ is 427.0851 and Observed = 427.0860.

Catalyst 6c:

Colorless solid; mp 75 °C; $[\alpha]_D^{25} = -26.2$ (*c* 1.10, CHCl₃); IR (neat) ν 752, 847, 941, 1046, 1160, 1179, 1229, 1273, 1343, 1403, 1513, 1540, 1563, 2950, 3027, 3047, 3074, 3271 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.82 (app d, *J* = 16.2 Hz, 1H), 3.10 (dd, *J* = 4.5, 16.2 Hz, 1H), 4.55 (q, *J* = 4.5 Hz, 1H), 5.46 (d, *J* = 4.5 Hz, 1H), 5.73-5.76 (m, 1H), 7.18-7.27 (m, 4H), 7.81-7.89 (m, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 9.57 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 63.0, 72.4, 105.4 (t, *J* = 23.6 Hz), 120.6 (t, *J* = 15.0 Hz), 124.7, 125.7, 126.9, 128.1, 141.1, 142.4, 143.1 (d, *J* = 13.4 Hz), 145.1 (app t, *J* = 13.4 Hz), 147.0 (dt, *J* = 3.2, 13.4 Hz), 183.8; HRMS calcd. for C₁₆H₁₂F₄N₂OSNa⁺ is 379.0498 and Observed = 379.0511.

Catalyst 6d:

Colorless solid; mp 137 °C; $[\alpha]_D^{25} = +140.2$ (*c* 1.51, CHCl₃); IR (neat) ν 698, 708, 748, 885, 957, 1129, 1181, 1273, 1346, 1383, 1470, 1530, 3053, 3247 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ

2.76 (dd, $J = 7.1, 15.4$ Hz, 1H), 3.16 (dd, $J = 6.9, 15.4$ Hz, 1H), 4.37-4.39 (m, 1H), 5.38 (d, $J = 4.7$ Hz, 1H), 5.73 (br s, 1H), 7.19-7.30 (m, 4H), 7.72 (s, 1H), 8.28 (s, 2H), 8.64 (d, $J = 7.3$ Hz, 1H), 10.04 (s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 66.5, 78.1, 116.6, 122.8, 123.9 (q, $J = 273.3$ Hz), 125.0, 125.1, 125.4, 127.2, 128.5, 134.5 (q, $J = 32.1$ Hz), 140.6, 141.8, 142.6, 182.0; HRMS calcd. for $\text{C}_{18}\text{H}_{14}\text{F}_6\text{N}_2\text{OSNa}^+$ is 443.0623 and Observed = 443.0612.

Catalyst 6e:

Yellow solid; mp 135 °C; $[\alpha]_D^{25} = +45.5$ (c 1.40, CHCl_3); IR (neat) ν 681, 702, 744, 768, 887, 955, 1109, 1177, 1277, 1343, 1383, 1470, 1530, 2858, 2970, 3047, 3244 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 1.91-1.93 (m, 1H), 2.48-2.56 (m, 2H), 2.81-2.87 (m, 1H), 2.93-2.98 (m, 1H), 5.88 (br d, $J = 6.5$ Hz, 1H), 7.19-7.28 (m, 3H), 7.38 (d, $J = 6.7$ Hz, 1H), 7.72 (s, 1H), 8.26 (s, 2H), 8.63 (br d, $J = 6.5$ Hz, 1H), 9.96 (s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 30.3, 33.3, 59.5, 116.4, 122.6, 123.9 (q, $J = 273.3$ Hz), 124.8, 125.3, 126.9, 128.3, 130.9 (q, $J = 33.6$ Hz), 142.7, 143.6, 143.8, 181.2; HRMS calcd. for $\text{C}_{18}\text{H}_{14}\text{F}_6\text{N}_2\text{SNa}^+$ is 427.0674 and Observed = 427.0672.

Catalyst 6f:

Colorless solid; mp 128 °C; $[\alpha]_D^{25} = +20.9$ (c 1.19, CHCl_3); IR (neat) ν 698, 740, 766, 847, 976, 1023, 1131, 1173, 1227, 1277, 1329, 1382, 1468, 1459, 1546, 2975, 3037, 3232 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 1.48 (d, $J = 6.9$ Hz, 3H), 5.54 (br s, 1H), 7.23-7.26 (m, 1H), 7.33-7.38 (m, 4H), 7.69 (s, 1H), 8.21 (s, 2H), 8.68 (br s, 1H), 9.94 (br s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 22.1, 53.4, 116.3, 122.4, 123.9 (q, $J = 273.3$ Hz), 126.9, 127.5, 128.9, 130.9 (q, $J = 32.0$ Hz), 142.7, 144.0, 180.5; HRMS calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{N}_2\text{SNa}^+$ is 415.0674 and Observed = 415.0663.

Catalyst 6g:

Colorless solid; mp 62 °C; $[\alpha]_D^{25} = +112.0$ (c 1.12, CHCl_3); IR (neat) ν 700, 849, 887, 959, 1001, 1055, 1109, 1131, 1173, 1275, 1345, 1382, 1455, 1470, 1519, 3035, 3066, 3091, 3271, 3340 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 5.11 (t, $J = 4.1$ Hz), 5.63-5.65 (m, 1H), 5.83 (d, $J = 4.1$ Hz, 1H), 7.08-7.23 (m, 10H), 7.71 (s, 1H), 8.26 (s, 2H), 8.69 (d, $J = 8.5$ Hz, 1H), 10.32 (s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 63.6, 74.9, 116.4, 122.1, 123.9 (q, $J = 271.6$ Hz), 127.1, 127.5, 127.6, 127.9, 128.2, 129.4, 131.0 (q, $J = 32.0$ Hz), 138.7, 142.7, 142.8, 180.4; HRMS calcd. for $\text{C}_{23}\text{H}_{18}\text{F}_6\text{N}_2\text{OSNa}^+$ is 507.0936 and Observed = 507.0935.

Catalyst 6h:

Colorless solid; mp 87 °C; $[\alpha]_D^{25} = +276.0$ (c 1.06, CHCl_3); IR (neat) ν 698, 733, 752, 850, 889, 1054, 1135, 1173, 1277, 1382, 1449, 1470, 1515, 3035, 3064, 3280, 3363 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 6.33 (d, $J = 8.7$ Hz, 1H), 6.40 (s, 1H), 7.00-7.10 (m, 11H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.66 (s, 1H), 7.68 (s, 2H), 8.77 (d, $J = 8.7$ Hz, 1H), 10.3 (s, 1H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 63.9, 81.5, 116.4, 121.6, 123.8 (q, $J = 273.3$ Hz), 126.9, 127.0, 127.1, 127.2,

127.50, 127.54, 128.0, 128.6, 130.2, 131.0 (q, $J = 33.8$ Hz), 139.3, 142.6, 145.6, 147.0, 180.0; HRMS calcd. for $C_{29}H_{22}F_6N_2OSNa^+$ is 583.1249 and Observed = 583.1239.

Catalyst 6i:

Colorless solid; mp 65 °C; $[\alpha]_D^{25} = +91.3$ (c 1.12, $CHCl_3$); IR (neat) ν 700, 887, 980, 1109, 1133, 1175, 1277, 1383, 1470, 1530, 2889, 2954, 3301 cm^{-1} ; 1H NMR (500 MHz, $DMSO-d_6$) δ 3.49-3.57 (m, 2H), 4.43-4.45 (m, 1H), 4.97 (t, $J = 4.9$ Hz, 1H), 5.07 (br s, 1H), 5.90 (d, $J = 4.1$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 7.3$ Hz, 2H), 7.67 (s, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 8.29 (s, 2H), 10.38 (s, 1H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 60.0, 61.2, 69.4, 116.2, 121.5, 123.8 (q, $J = 273.4$ Hz), 126.7, 127.4, 128.5, 130.8 (q, $J = 33.8$ Hz), 142.6, 144.2, 180.9; HRMS calcd. for $C_{18}H_{16}F_6N_2O_2SNa^+$ is 461.0728 and Observed = 461.0715.

II. Preparation of intermediates and substrates

General Procedure for (*E*)-3-substitued-2-alkenoyl chlorides: Under dry nitrogen, sodium hydride (163 mmol) was added to a solution of diethylphosphonoacetic acid (81.6 mmol) in ethyleneglycol dimethyl ether (210 mL) and the resulting suspension was stirred at rt until the evolution of hydrogen ceased. A solution of aldehyde (81.6 mmol) in ethyleneglycol dimethyl ether (50 mL) was added and stirring was continued at room temperature overnight. The reaction mixture was poured into ice water (150 mL) and extracted with diethyl ether (150 mL x 4). The combined aqueous extracts were acidified by hydrochloric acid (12 M) and extracted with diethyl ether (300 mL x 3). The combined extracts were washed with brine, dried over magnesium sulfate and evaporated in vacuo to give (*E*)-3-substitued-2-alkenoic acid. Under dry nitrogen, oxalyl chloride (122 mmol) and dry DMF (one drop) were added to a dichloromethane solution (81.6 mL) of (*E*)-3-substitued-2-alkenoic acid at 0 °C. The reaction mixture was allowed to warm to rt and stirred overnight. Dichloromethane and excess oxalyl chloride were removed by distillation to give the crude acid chloride. The crude residue was purified by distillation under reduced pressure (aspirator was used) to give pure (*E*)-3-substitued-2-alkenoyl chlorides.³ (*E*)-3-(*p*-Methoxyphenyloxymethyl)-2-propenoic acid was prepared by previous reported method.⁴ (*E*)-3-(*p*-Methoxyphenyloxymethyl)-2-propenoic chloride was used without purification.

General Procedure for 4-bromo-3,5-dimethylpyrazole and 4-bromo-3,5-diphenylpyrazole:

Bromine (0.39 mol) was slowly added over 1 h to a solution of 3,5-dimethylpyrazole or 3,5-diphenylpyrazole (0.26 mol) in anhydrous dichloromethane (520 mL) at -78 °C. After the addition was complete, the resulting solution was allowed to warm to 0 °C and treated with a saturated aqueous solution of sodium thiosulfate pentahydrate. When the brown color of bromine had disappeared, the reaction mixture was neutralized with a saturated aqueous solution of sodium hydrogen carbonate and then extracted with dichloromethane (500 mL x 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo to give 4-bromo-3,5-dimethylpyrazole (quantitative) or 4-bromo-3,5-diphenylpyrazole (52%), which was used for the following reactions without further purification.

4-Bromo-3,5-dimethylpyrazole:

White solid; mp 101 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 6H), 11.80 (br s, 1H); ¹³C NMR (CDCl₃) δ 11.4, 94.3, 142.9.

4-Bromo-3,5-dimethylpyrazole:

White solid; mp 195 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.48 (m, 6H), 7.78 (app d, J = 7.4 Hz, 4H), 10.48 (br s, 1H).

General procedure for the acylation of pyrazoles:

To a solution of crotonoyl chloride (4.41 mL, 54.6 mmol) in dichloromethane (90 mL) was added dropwise at 0 °C under nitrogen, a solution of 3,5-dimethylpyrazole (5 g, 52 mmol) in dichloromethane (90 mL) and pyridine (4.41 mL, 54.6 mmol). After stirring at 0 °C for 3 h, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane (100 mL x 3). The combined extracts were washed with brine, dried with magnesium sulfate, and evaporated in *vacuo*. The residue was purified by FC (silica gel, hexane/diethyl ether = 19:1) to provide analytically pure (*E*)-1-(2-butenoyl)-3,5-dimethylpyrazole (**6a**) (7.2 g, 84%).⁵

(*E*)-1-(2-Butenoyl)-3,5-dimethylpyrazole (5a**)⁵**

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (dd, J = 6.5 and 1.2 Hz, 3H), 2.01 (s, 3H), 2.25 (d, J = 0.7 Hz, 3H), 5.97 (s, 1H), 7.16 - 7.34 (m, 2H); ¹³C NMR (CDCl₃) δ 13.6, 14.5, 18.3, 110.0, 122.5, 144.2, 146.4, 151.5, 164.9.

(*E*)-4-Bromo-1-(2-butenoyl)-3,5-dimethylpyrazole (5b**)^{6a,b}**

Colorless solid; mp 65 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.91 (d, J = 5.2 Hz, 3H), 2.15 (s, 3H), 2.47 (s, 3H), 7.08-7.19 (m, 2H), 7.31 (d, J = 15.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 12.8, 13.6, 18.7, 102.2, 121.8, 141.5, 147.4, 150.2, 164.3.

(*E*)-1-(2-Butenoyl)-3,5-diphenylpyrazole (5c**)³**

Colorless solid; mp 102 °C; ¹H NMR (CDCl₃, 300 MHz) δ 2.05 (dd, J = 1.2, 6.9 Hz, 3H), 6.76 (s, 1H), 7.20-7.29 (m, 1H), 7.41-7.53 (m, 9H), 7.92-7.95 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 19.0, 110.2, 122.8, 126.5, 128.2, 129.0, 129.1, 129.2, 129.4, 131.6, 132.1, 147.8, 148.0, 153.5, 164.5; HRMS Exact mass Calcd for C₁₉H₁₆N₂O: 288.1257; Found: 288.1266.

(*E*)-4-Bromo-1-(2-butenoyl)-3,5-diphenylpyrazole (5d**)^{6a}**

Colorless solid; mp 115 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.02 (dd, J = 1.6, 6.9 Hz, 3H), 7.19-7.28 (m, 1H), 7.42-7.54 (m, 9H), 8.01-8.05 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 19.0, 101.0, 121.7, 128.3, 128.5, 128.7, 129.3, 129.6, 129.8, 130.1, 131.2, 144.9, 148.9, 151.4, 163.5.

(E)-1-[3-Ethoxycarbonyl-2-propenoyl]-3,5-dimethylpyrazole (5e)^{6d}

Colorless solid; mp 59 °C; ¹H NMR (CDCl₃, 400 MHz) δ 1.24 (t, J = 7.1 Hz, 3H), 2.14 (s, 3H), 2.46 (d, J = 0.9 Hz, 3H), 4.18 (q, J = 7.1 Hz, 2H), 5.91-5.92 (m, 1H), 6.87 (d, J = 15.7 Hz, 1H), 8.13 (d, J = 15.7 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 13.8, 14.2, 14.3, 61.3, 112.2, 133.6, 134.0, 144.5, 152.9, 163.7, 165.0.

(E)-3,5-Dimethyl-1-(2-pentenoyl) pyrazole (5f)³

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.08 (t, J = 7.5 Hz, 3H), 2.20 (s, 3H), 2.26-2.33 (m, 2H), 2.51 (s, 3H), 5.91 (s, 1H), 7.16-7.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.4, 13.9, 14.7, 26.0, 111.3, 120.3, 144.4, 151.8, 152.9, 165.4; Analysis Calcd for C₁₀H₁₄N₂O: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.20; H, 7.57; N, 15.62.

(E)-1-(2-Hexenoyl)-3,5-dimethylpyrazole (5g)^{6b,c}

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.3 Hz, 3H), 1.44-1.53 (m, 2H), 2.18 (s, 3H), 2.21-2.26 (m, 2H), 2.50 (d, J = 0.9 Hz, 3H), 5.89-5.90 (m, 1H), 7.09-7.25 (m, 2H); ¹³C NMR (CDCl₃) δ 13.8, 13.9, 14.7, 21.6, 34.8, 111.3, 121.4, 144.4, 151.5, 151.8, 165.3.

(E)-3,5-Dimethyl-1-(4-methyl-2-pentenoyl)pyrazole (5h)³

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.99 (d, J = 0.8 Hz, 3H), 1.01 (d, J = 0.8 Hz, 3H), 2.11 (s, 3H), 2.44-2.49 (m, 4H), 5.83 (s, 1H), 7.07-7.16 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 14.6, 21.3, 31.6, 111.1, 118.5, 144.2, 151.5, 157.4, 165.3; Analysis Calcd for C₁₁H₁₆N₂O: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.69; H, 8.26; N, 14.34.

(E)-1-(3-Cyclohexyl-2-propenoyl)-3,5-dimethylpyrazole (5i)^{6c}

Low-melting colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 1.08-1.30 (m, 5H), 1.59-1.78 (m, 5H), 2.20 (s, 3H), 2.20-2.26 (m, 1H), 2.50 (d, J = 0.9 Hz, 3H), 5.89-5.90 (m, 1H), 7.08 (dd, J = 6.8, 15.7 Hz, 1H), 7.19 (dd, J = 1.1, 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.7, 25.8, 26.1, 31.9, 41.2, 111.3, 118.9, 144.4, 151.7, 156.5, 165.7.

(E)-3,5-Dimethyl-1-[4-(p-methoxyphenoxy)butenoyl]pyrazole (5j)^{6c}

Colorless solid; mp. 64 °C, ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 3H), 2.55 (d, J = 0.9 Hz, 3H), 3.74 (s, 3H), 4.72 (dd, J = 1.9, 4.3 Hz, 2H), 5.96 (s, 1H), 7.25 (dt, J = 4.3, 15.7 Hz, 1H), 7.61 (dt, J = 1.9, 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.7, 55.7, 68.0, 111.7, 114.8, 116.0, 122.0, 144.5, 144.7, 152.2, 152.5, 154.4, 164.8.

(E)-1-Cinnamoyl-3,5-dimethylpyrazole (5k)³

Colorless solid; mp 69 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.30 (s, 3H), 2.63 (s, 3H), 6.02 (s, 1H), 7.41-7.42 (m, 3H), 7.67-7.69 (m, 2H), 7.91 (d, J = 16.0 Hz, 1H), 7.96 (d, J = 16.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.8, 14.6, 111.3, 117.8, 128.6, 128.7, 130.5, 134.71, 144.36, 146.09, 151.86, 165.40.

III. General procedure for the chiral thiourea catalyzed enantioselective conjugate addition of amines to α,β-unsaturated amides:

To a solution of α,β-unsaturated amide (1 equiv), chiral thiourea (1 equiv) and MS 4Å (500 mg/ 1 mmol of α,β-unsaturated amide) in anhydrous α,α,α-trifluorotoluene (0.075 M) was added dropwise at 0 °C under nitrogen, a solution of amine (1.2 equiv) in anhydrous α,α,α-trifluorotoluene and stirred for several days. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried with magnesium sulfate, and evaporated in vacuo. The residue was purified by FC (silica gel, hexane/diethyl ether = 8:1 ~ 4:1) to provide analytically pure adduct.

(3S)-3,5-Dimethyl-1-(3-benzyloxyaminobutanoyl)pyrazole (7a):

Low-melting colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; [α]_D²⁵ = -0.9 (c 3.03, CHCl₃) [86% ee estimated by chiral HPLC analysis on Daicel Chiral Cell OJ (0.46 cm x 25 cm), hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (minor) = 14.7 min, t_r (major) = 22.3 min. The absolute configuration of **7a** was determined by the retention time of chiral HPLC³]; IR (neat) ν 698, 748, 802, 1291, 1329, 1360, 1380, 1412, 1441, 1453, 1584, 1723, 2871, 2929, 2971, 3031, 3251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.21 (d, J = 6.4 Hz, 1H), 2.22 (s, 3H), 2.49 (s, 3H), 3.32 (dd, J = 5.1, 16.9 Hz, 1H), 3.40 (dd, J = 7.5, 16.9 Hz, 1H), 3.64-3.67 (m, 1H), 4.68 (s, 2H), 5.84 (br s, 1H), 5.93 (s, 1H), 7.23-7.32 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.7, 18.4, 39.5, 53.0, 76.7, 111.2, 127.8, 128.3, 128.4, 137.9, 144.1, 151.9, 172.7; HRMS calcd. for C₁₆H₂₁N₃O₂Na⁺ is 310.1525 and Observed = 310.1524.

(3S)-4-Bromo-3,5-Dimethyl-1-(3-benzyloxyaminobutanoyl)pyrazole (7b):

Colorless oil [silica gel column chromatography eluted by hexane/ethyl acetate = 8/1 (v/v)]; [α]_D²⁵ = +1.0 (c 1.59, CHCl₃) [61% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ODH (0.46 cm x 25 cm), hexane / 2-propanol (9:1 v/v), 1 mL/min, t_r (major) = 12.3 min, t_r (minor) = 13.5 min. The absolute configuration of **7b** was determined by the optical rotation after conversion to (3S)-methyl 3-benzyloxyaminobutanoate]; IR (neat) ν 698, 750, 945, 989, 1040, 1077, 1150, 1214, 1239, 1289, 1331, 1358, 1376, 1409, 1453, 1493, 1573, 1727, 2869, 2927, 3031, 3064, 3089, 3251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.18 (d, J = 6.5 Hz, 1H), 2.22 (s, 3H), 2.47 (s, 3H), 3.06 (dd, J = 5.1, 16.4 Hz, 1H), 3.37 (dd, J = 7.5, 16.4 Hz, 1H), 3.62-3.71 (m, 1H), 4.64 (s, 2H), 5.76 (br s, 1H), 7.22-7.31 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 12.9, 13.6, 18.4, 39.4, 53.2, 76.7, 102.3, 127.9, 128.3, 128.5, 137.9, 141.4, 150.6, 172.2; HRMS calcd. for C₁₆H₂₀BrN₃O₂Na⁺ is 388.0631 and Observed = 388.0647.

(3S)-1-(3-Benzyloxyaminobutanoyl)-3,5-diphenylpyrazole (7c):

Low-melting colorless solid [silica gel column chromatography eluted by hexane/ethyl acetate = 8/1 (v/v)]; $[\alpha]_D^{25} = -5.4$ (*c* 3.38, CHCl₃) [40% ee estimated by chiral HPLC analysis on Daicel Chiral Cell AD (0.46 cm x 25 cm), hexane / 2-propanol (9:1 v/v), 1 mL/min, *t_r* (major) = 13.9 min, *t_r* (minor) = 16.0 min, The absolute configuration of **7b** was determined by the optical rotation

after conversion to (3S)-methyl 3-benzyloxyaminobutanoate]; IR (neat) ν 694, 760, 769, 1027, 1204, 1277, 1287, 1336, 1403, 1441, 1463, 1488, 1739, 2871, 2925, 2971, 3031, 3062, 3269 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (d, *J* = 6.5 Hz, 1H), 3.31 (dd, *J* = 5.1, 16.4 Hz, 1H), 3.59 (dd, *J* = 7.3, 16.4 Hz, 1H), 3.68-3.76 (m, 1H), 4.70 (s, 2H), 5.84 (br s, 1H), 6.71 (s, 1H), 7.23-7.48 (m, 13H), 7.88-7.91 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 18.6, 40.2, 53.3, 76.8, 110.0, 126.5, 127.9, 128.1, 128.6, 128.9, 129.0, 129.2, 129.4, 131.3, 132.0, 138.0, 147.4, 153.5, 172.0; HRMS calcd. for C₂₆H₂₅N₃O₂Na⁺ is 434.1838 and Observed = 434.1839.

(3S)- 4-Bromo-1-(3-Benzyloxyaminobutanoyl)-3,5-diphenylpyrazole (7d):

Colorless oil [silica gel column chromatography eluted by hexane/ethyl acetate = 8/1 (v/v)]; $[\alpha]_D^{25} = -0.9$ (*c* 1.18, CHCl₃) [31% ee estimated by chiral HPLC analysis on Daicel Chiral Cell OJ/OJ doubly connected column (0.46 cm x 25 cm), hexane / 2-propanol (4:1 v/v), 1 mL/min, *t_r* (major) = 129.6 min, *t_r* (minor) = 166.4 min]; IR (neat) ν 694, 771, 941, 980, 1028, 1152, 1245, 1304, 1324, 1366, 1453, 1744, 2871, 2966, 3031, 3062, 3251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.21 (d, *J* = 6.5 Hz, 1H), 3.23 (dd, *J* = 5.1, 16.5 Hz, 1H), 3.54 (dd, *J* = 7.4, 16.5 Hz, 1H), 3.65-3.73 (m, 1H), 4.66 (s, 2H), 5.79 (br s, 1H), 7.23-7.52 (m, 13H), 7.97-8.00 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 18.5, 39.6, 53.3, 76.8, 101.1, 127.9, 128.3, 128.5, 128.7, 129.4, 129.6, 129.8, 129.9, 131.1, 137.6, 144.5, 151.4, 171.1; HRMS calcd. for C₂₆H₂₄BrN₃O₂Na⁺ is 512.0944 and Observed = 512.0953.

Determination of the absolute configuration of 7b, 7c and 7d:

To a solution of **7a**, **7b**, **7c** or **7d** (0.21 mmol) in MeOH (3 mL) was added Sm(OTf)₃ (0.010 mmol) at rt. The reaction mixture was stirred for 15 min. MeOH was removed in vacuo and the residue was purified by FC (silica gel, hexane/diethyl ether = 8:1) to give (3S)-methyl 3-benzyloxyaminobutanoate (Yield = 84 ~ 94 %).⁷⁷

(3S)-Methyl 3-benzyloxyaminobutanoate:

Colorless oil [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_D^{25} = +7.5$ (*c* 1.15, CHCl₃), IR

3,5-Dimethyl-1-(3-diphenylmethoxyaminobutanoyl)pyrazole (7aa):

[illegible]CC1=CN(C)C(=C1)C(=O)NCC(C)NOSi(C)(C)C(C)(C)C

Determination of enantioselectivity of 7bb:

COC(=O)C(C)NOSi(C)(C)C(C)(C)C

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(s, 9H), 1.04 (d, $J = 6.5$ Hz, 1H), 2.28 (dd, $J = 5.9, 15.6$ Hz, 1H), 2.57 (dd, $J = 6.6, 15.9$ Hz, 1H), 3.29-3.34 (m, 1H), 5.08 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.28, -5.22, 17.9, 18.1, 26.4, 38.2, 51.5, 54.7, 172.9; HRMS calcd. for $\text{C}_{11}\text{H}_{25}\text{NO}_3\text{Na}^+$ is 270.1495 and Observed = 270.1495.

Methyl 3-*N*-benzoyl-*tert*-butyldimethylsiloxyaminobutanoate:

Colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 15/1 (v/v)]; mp. 43 °C; $[\alpha]_{\text{D}}^{25} = -0.7$ (c 0.67, CHCl_3) [94% ee estimated by chiral HPLC analysis on Daicel Chiral Cell OJ/OJ doubly connected column (0.46 cm x 25 cm), hexane / 2-propanol (99:1 v/v), 0.5 mL/min, t_{r} (major) = 33.7 min, t_{r} (minor) = 41.2 min]; IR (neat) ν 700, 785, 831, 947, 1005, 1023, 1073, 1088, 1179, 1198, 1250, 1287, 1364, 1382, 1447, 1582, 1650, 1670, 1739, 2858, 2896, 2931, 2954 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (s, 6H), 0.96 (s, 9H), 1.26 (d, $J = 6.6$ Hz, 1H), 2.39 (dd, $J = 6.0, 16.3$ Hz, 1H), 2.84 (dd, $J = 7.7, 16.3$ Hz, 1H), 4.31-4.39 (m, 1H), 7.26-7.44 (m, 3H), 7.54-7.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.05, -4.01, 18.7, 19.1, 26.4, 37.8, 51.8, 55.7, 127.9, 128.6, 130.8, 135.5, 171.4, 172.2; HRMS calcd. for $\text{C}_{18}\text{H}_{29}\text{NO}_4\text{SiNa}^+$ is 374.1758 and Observed = 374.1748.

3,5-Dimethyl-1-(3-diphenylmethoxyamino-3-ethoxycarbonylpropanoyl)pyrazole (7e):

Colorless oil [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_{\text{D}}^{25} = +10.1$ (c 0.81, CHCl_3) [94% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (4:1 v/v), 1 mL/min, t_{r} (minor) = 30.3 min, t_{r} (major) = 32.4 min]; IR (neat) ν 700, 742, 758, 810, 986, 1027, 1138, 1218, 1245, 1279, 1326, 1382, 1434, 1453, 1493, 1586, 1725, 2929, 2981, 3029, 3062, 3269 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.25 (t, $J = 7.1$ Hz, 1H), 2.19 (s, 3H), 2.47 (d, $J = 0.8$ Hz, 3H), 3.50 (dd, $J = 7.3, 17.1$ Hz, 3H), 3.58 (dd, $J = 5.9, 17.1$ Hz, 1H), 4.17-4.26 (m, 2H), 5.72 (s, 1H), 5.91 (s, 1H), 6.20 (br s, 1H), 7.18-7.37 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.3, 14.5, 35.6, 60.1, 61.5, 86.9, 111.4, 127.50, 127.53, 127.7, 128.4, 128.4, 141.4, 144.2, 152.3, 171.1, 172.0; HRMS calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_4\text{Na}^+$ is 444.1893 and Observed = 444.1899.

1-(3-*tert*-Butyldimethylsiloxyamino-3-ethoxycarbonylpropanoyl)-3,5-Dimethylpyrazole (7ee):

Low-melting colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 10/1 (v/v)]; $[\alpha]_{\text{D}}^{25} = +10.1$ (c 0.86, CHCl_3) [90% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ODH (1 cm x 25 cm), hexane / 2-propanol 99:1 v/v), 0.5 mL/min, t_{r} (major) = 53.7 min, t_{r} (minor) = 66.4 min]; IR (neat) ν 781, 835, 962, 1027, 1189, 1248, 1328, 1382, 1463, 1586, 1727, 2858, 2887, 2896, 2931, 2958, 3261 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.022 (s, 3H), 0.027 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 2.20 (s, 3H), 2.49 (d, $J = 0.9$ Hz, 3H), 3.38 (dd, $J = 6.3, 17.8$ Hz, 1H), 3.48 (dd, $J = 6.8, 17.8$ Hz, 1H), 4.07 (t, $J = 6.8$ Hz, 1H), 4.15-4.27 (m, 2H), 5.70 (br s, 1H), 5.92-5.93 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.48, -

5.45, 13.9, 14.3, 14.5, 18.1, 26.3, 35.5, 61.3, 61.8, 111.4, 144.2, 152.3, 170.9, 172.6; HRMS calcd. for $C_{17}H_{31}N_3O_4Na^+$ is 392.1976 and Observed = 392.1965.

3,5-Dimethyl-1-(3-diphenylmethoxyaminopentanoyl)pyrazole (7f):

Colorless oil [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_D^{25} = +14.1$ (c 1.46, $CHCl_3$) [91% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (19:1 v/v), 1 mL/min, t_r (minor) = 28.9 min, t_r (major) = 31.4 min]; IR (neat) ν 700, 742, 962, 1003, 1337, 1378, 1412, 1453, 1584, 1723, 2877, 2929, 2964, 3029, 3062, 3251 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.5 Hz, 3H), 1.48-1.58 (m, 1H), 1.62-1.73 (m, 1H), 2.20 (s, 3H), 2.42 (d, J = 0.9 Hz, 3H), 3.09-3.15 (m, 1H), 3.41-3.49 (m, 2H), 5.67 (s, 1H), 5.64 (s, 1H), 5.85 (br s, 1H), 5.89 (d, J = 0.9 Hz, 1H), 7.18-7.32 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 14.0, 14.7, 25.4, 38.0, 59.3, 86.8, 111.2, 127.2, 127.4, 127.52, 127.6, 128.4, 128.5, 141.9, 142.0, 144.2, 151.9, 173.2; HRMS calcd. for $C_{23}H_{27}N_3O_2Na^+$ is 400.1995 and Observed = 400.1987.

3,5-Dimethyl-1-(3-diphenylmethoxyaminohexanoyl)pyrazole (7g):

Colorless oil [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_D^{25} = +9.2$ (c 2.36, $CHCl_3$) [88% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (19:1 v/v), 1 mL/min, t_r (major) = 27.5 min, t_r (minor) = 30.3 min]; IR (neat) ν 700, 740, 802, 889, 962, 1023, 1140, 1170, 1331, 1378, 1412, 1453, 1493, 1584, 1723, 2873, 2931, 2958, 3029, 3062, 3087, 3250 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 1.36-1.51 (m, 3H), 1.60-1.65 (m, 1H), 2.23 (s, 3H), 2.41 (d, J = 0.9 Hz, 3H), 3.14 (dd, J = 3.9, 15.9 Hz, 1H), 3.46 (dd, J = 8.1, 15.9 Hz, 1H), 3.51-3.57 (m, 1H), 5.65 (s, 1H), 5.84 (br s, 1H), 5.88-5.89 (m, 1H), 7.17-7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.2, 14.7, 19.5, 34.7, 38.4, 57.7, 86.8, 111.2, 127.2, 127.46, 127.49, 127.5, 128.3, 128.4, 141.9, 142.0, 144.2, 151.8, 173.2; HRMS calcd. for $C_{24}H_{29}N_3O_2Na^+$ is 414.2151 and Observed = 414.2143.

3,5-Dimethyl-1-(3-diphenylmethoxyamino-4-methylpentanoyl)pyrazole (7h):

Colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; mp. 59 °C; $[\alpha]_D^{25} = +16.1$ (c 2.02, $CHCl_3$) [87% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (4:1 v/v), 1 mL/min, t_r (minor) = 24.5 min, t_r (major) = 28.6 min]; IR (neat) ν 700, 740, 758, 804, 914, 982, 1021, 1177, 1347, 1378, 1421, 1453, 1493, 1584, 1723, 2873, 2894, 2929, 2960, 3029, 3062, 3087, 3257 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.95-2.05 (m, 1H), 2.20 (s, 3H), 2.41 (s, 3H), 3.05-3.11 (m, 1H), 3.33-3.41 (m, 2H), 5.61 (s, 1H), 5.82 (br s, 1H), 5.88 (s, 1H), 7.14-7.27 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.7, 18.7, 19.5, 29.6, 35.4, 63.1, 86.6, 111.2, 127.2, 127.4, 127.5, 128.3, 142.0, 142.1, 144.24, 151.8, 173.5; HRMS calcd. for $C_{24}H_{29}N_3O_2Na^+$ is 414.2151 and Observed = 414.2140.

3,5-Dimethyl-1-(3-Cyclohexyl-3-diphenylmethoxyaminopropanoyl)pyrazole (7i):

Colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; mp. 67 °C; $[\alpha]_D^{25} = +18.7$ (*c* 0.71, CHCl₃) [89% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (19:1 v/v), 1.0 mL/min, *t_r* (minor) = 25.7 min, *t_r* (major) = 30.6 min]; IR (neat) ν 700, 742, 804, 891, 962, 1021, 2318, 1378, 1412, 1451, 1584, 1723, 2852, 2925, 3029, 3062, 3251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.95-1.26 (m, 5H), 1.59-1.85 (m, 6H), 2.21 (s, 3H), 2.42 (d, *J* = 0.9 Hz, 3H), 3.10-3.14 (m, 1H), 3.36-3.48 (m, 2H), 5.60 (s, 1H), 5.84 (br s, 1H), 5.88-5.89 (m, 1H), 7.18-7.28 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 14.7, 26.5, 26.7, 29.4, 29.9, 35.9, 39.7, 62.6, 86.6, 111.1, 127.2, 127.4, 127.5, 128.3, 142.0, 142.1, 144.2, 151.7, 173.6; HRMS calcd. for C₂₇H₃₃N₃O₂Na⁺ is 454.2464 and Observed = 454.2466.

1-[3-Diphenylmethoxyamino-4-(*p*-methoxyphenoxy)propanoyl]-3,5-dimethylpyrazole (7j):

Colorless oil [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_D^{25} = +12.5$ (*c* 1.19, CHCl₃) [98% ee estimated by chiral HPLC analysis on Daicel Chiral Cell ADH (1 cm x 25 cm), hexane / 2-propanol (4:1 v/v), 1 mL/min, *t_r* (major) = 39.8 min, *t_r* (minor) = 44.3 min]; IR (neat) ν 702, 744, 823, 962, 1040, 1231, 1343, 1380, 1509, 1584, 1723, 2834, 2929, 3029, 3062, 3269 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, 3H), 2.48 (d, *J* = 0.9 Hz, 3H), 3.36 (dd, *J* = 5.3, 16.8 Hz, 1H), 3.56 (dd, *J* = 7.6, 16.8 Hz, 1H), 3.75 (s, 3H), 3.93-4.00 (m, 1H), 4.06-4.15 (m, 2H), 5.70 (s, 1H), 5.92-5.93 (m, 1H), 6.14 (br s, 1H), 6.79-6.85 (m, 4H), 7.21-7.31 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 14.7, 35.4, 55.9, 57.0, 68.0, 887.0, 111.3, 114.8, 115.8, 127.3, 127.5, 127.6, 128.5, 141.73, 141.76, 144.2, 152.1, 153.0, 154.2, 172.3; HRMS calcd. for C₂₉H₃₁N₃O₄Na⁺ is 508.2206 and Observed = 508.2216.

3,5-Dimethyl-1-(3-diphenylmethoxyamino-3-phenylpropanoyl)pyrazole (7k):

Low-melting colorless solid [silica gel column chromatography eluted by hexane/diethyl ether = 8/1 (v/v)]; $[\alpha]_D^{25} = +16.2$ (*c* 1.3, CHCl₃) [68% ee estimated by chiral HPLC analysis on Daicel Chiral Cell OJ (0.46 cm x 25 cm), hexane / 2-propanol (9:1 v/v), 1 mL/min, *t_r* (minor) = 30.4 min, *t_r* (major) = 42.7 min]; IR (neat) ν 781, 835, 962, 1027, 1189, 1248, 1328, 1382, 1463, 1586, 1727, 2858, 2887, 2896, 2931, 2958, 3261 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, 3H), 2.46 (s, 3H), 3.47 (dd, *J* = 5.1, 16.9 Hz, 1H), 3.67 (dd, *J* = 8.3, 16.9 Hz, 1H), 4.56 (dd, *J* = 11.4, 16.0, 2H), 4.69 (dd, *J* = 5.1, 8.3 Hz, 1H), 5.92 (s, 1H), 6.08 (br s, 1H), 7.19-7.45 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.6, 39.7, 61.5, 76.7, 111.2, 111.3, 127.76, 127.84, 127.9, 128.3, 128.5, 137.7, 140.6, 144.1, 152.1, 172.0; Analysis Calcd for C₂₁H₂₃N₃O₂: C, 72.18; H, 6.63; N, 12.03. Found: C, 72.12; H, 6.71; N, 12.15; HRMS calcd. for C₂₁H₂₃N₃O₂Na⁺ is 372.1687 and Observed = 372.1701.

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