C-C Bond Forming Reactions *via* Pd-Mediated Decarboxylative α -Imino Anion Generation

Supporting Information

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Materials and Methods: All non-aqueous reactions were performed in oven or flame-dried glassware under an argon atmosphere with dry solvents and magnetic stirring, unless otherwise stated. All argon was purified by sequential passage through an OXICLEARTM deoxygenation column, Drierite, and NaOH. Anhydrous dichloromethane (CH₂Cl₂) and acetonitrile (MeCN), benzene (PhH), toluene (PhCH₃) and 1,4-dioxanes were used as received. Tetrahydrofuran (THF) was further dried over activated 4Å molecular sieves under argon. All liquid aldehydes were filtered through basic alumina (Al₂O₃), Brockman Activity I, prior to use with the exception of ethyl glyoxylate, purchased as a ca. 50% solution in PhCH₃ from Alfa Aesar. All other chemicals were used as received. Reaction progress was monitored by analytical TLC using 250 μ m thick Partisil[®] K6F 60Å silica gel plates (Whatman), with the exception of imine **1** formations (monitored by ¹H NMR *via* reaction aliquots). Developed TLC plates visualized by UV light (254 nm) and/or ninhydrin stain. All chromatography was performed with indicated solvents and Dynamic Adsorbents 230-400 mesh or Purasil (Whatman) 60Å 230-400 mesh silica gel, save for homoallylic amines **3e-g** and **4e-g** which were purified through basic Al₂O₃, Brockman Activity I. All yields refer to chromatographically and spectroscopically pure compounds, unless otherwise indicated. Melting points determined with a Mel-Temp[®] apparatus (Electrothermal) and are uncorrected. Infrared spectra were obtained from a Nicolet Avatar 330 FT-IR (Thermo) and reported in cm⁻¹ (%T). All ¹H NMR and ¹³C NMR taken on a Varian MercuryPlus 300 (75) or a Varian UnityNova 500 (125) at 300K, as indicated. Chemical shifts are reported in δ (ppm) units using residual solvent peak (CHCl₃) as a standard: ¹H NMR and ¹³C NMR peaks (7.26 and 77.0 ppm, respectively). All product ratios determined from ¹H NMR analysis of the crude reaction mixture. High resolution mass spectra obtained from the Mass Spectrometry Laboratory at the University of Illinois, Urbana-Champaign.

Other abbreviations: ethyl acetate (EtOAc), acetic acid (AcOH), diphenylglycine (D ϕ g), minutes (min), hours (h), diphenylphosphinoferrocene (dppf), dibenzylideneacetone (dba), room temperature (rt).

Experimental Procedures: Unless otherwise noted, the following experimentals describe conditions for the largest scale run for the reactions described in text. Therefore, the individual yields may differ from the reported average yields.

Z-D ϕ g-OH (N-Benzylcarbamatediphenylglycine) (6). Modified from literature: To a stirred slurry of D ϕ g (**5**, 5.183 g, 22.8 mmol) in acetone (10 mL) was added just enough 2N NaOH (≥ 2 eq) to dissolve the amino acid. Then benzylchloroformate (5 mL, 35.5 mmol) and 2N NaOH were added alternatively in a dropwise fashion so as to maintain a clear solution. The reaction was then stirred at rt overnight and quenched with 1N HCl until acidic, followed by extraction with EtOAc. The organic layer

was washed sequentially with 1N HCl and brine, then dried (MgSO₄), filtered, and concentrated in vacuo. Purified by flash chromatography (10% EtOAc/Hexanes to 30% EtOAc/Hexanes with 1% AcOH) to provide a clear colorless oil (8.796 g). Sample can then be recrystallized from ethyl acetate and petroleum ether in order to remove 4-methyl-4-hydroxy-2-pentanone and provided a white solid, however recrystallization proved unnecessary and the crude oil can be carried on directly to the next step. Characteristic data coincides with reported literature.¹ ¹H NMR (CDCl₃, 300MHz) δ 7.51-7.23 (m, 15H, ArH), 6.55 (s, 1H, -NH), 5.03 (s, 2H, benzylic-CH₂).

Z-Dφg-O-allyl (N-benzylcarbamate-O-allyldiphenylglycine) (7a). To a stirred solution of crude Z-Dφg-OH (**6**, 8.796 g, 24.4 mmol) in CH₂Cl₂ (10 mL) was added NEt₃ (3.8 mL, 27.4 mmol) followed by allyl bromide (2.4 mL, 27.6 mmol), and the resulting solution was stirred for 24 hrs. Reaction mixture then diluted with CH₂Cl₂ and washed sequentially with 1N HCl and brine, then dried (MgSO₄), filtered, and concentration in vacuo. Purified by flash chromatography (10% EtOAc/Hexanes to 30% EtOAc/Hexanes with 1% AcOH) to afford a clear colorless oil (3.630 g, 9.05 mmol). *Note: optimized conditions when carrying on “crude” calls for at least 2 equivalents of NEt₃ and allyl bromide, depending on 4-methyl-4-hydroxy-2-pentanone content. R_f = 0.63 (30% EtOAc/Hexanes with 1% AcOH); IR (CDCl₃) 3409 (br), 3062 (m), 3031 (m), 1727 (s), 1494 (s), 1249 (s), 1011 (m), 753 (m), 733 (m), 698 (s); ¹H NMR (CDCl₃, 300MHz) δ 7.40 (m, 15H, ArH), 6.56 (s, 1H, NH), 5.75 (tdd, *J* = 16.33, 11.09, 5.59, Hz, 1H, allyl-CH), 5.14 (ddt, *J* = 10.58, 2.49, 1.22 Hz, 1H, CH=CH(*H*)_{cis}), 5.03 (ddt, *J* = 17.11, 2.91, 1.47 Hz, 1H, CH=CH(*H*)_{trans}), 5.01 (s, *J* = 5.09 Hz, 2H, benzylic-CH₂), 4.64 (d, *J* = 5.08 Hz, 2H, allyl-OCH₂); ¹³C NMR (CDCl₃, 75MHz) δ 171.3, 139.0, 130.9, 128.4, 128.0, 127.9, 118.7, 69.5, 66.8, 66.7; HRMS (ESI+) *m/z* 402.1715 [(M+H)⁺; calculated mass for C₂₅H₂₄NO₄⁺: 402.1705 amu].

Z-Dφg-O-2-Methylpropene (N-benzylcarbamate-O-2-Methylpropenediphenylglycine) (7b). To a stirred solution of crude Z-Dφg-OH (**6**, 18.8 mmol) in CH₂Cl₂ (10 mL) was added NEt₃ (5.2 mL, 37.6 mmol) followed by 2-methyl-3-bromopropene (2.7 mL, 26.8 mmol), and the resulting solution was stirred for 20 hrs. Reaction mixture then diluted with CH₂Cl₂ and washed sequentially with 1N HCl and brine, then dried (MgSO₄), filtered, and concentration in vacuo. Purified by flash chromatography (10% EtOAc/Hexanes to 30% EtOAc/Hexanes with 1% AcOH) to afford a clear colorless oil (3.590 g, 8.64 mmol). R_f = 0.50 (20% EtOAc/Hexanes); IR (CH₂Cl₂) 3408 (br), 3062 (m), 3032 (m), 2947 (m), 1731 (s), 1598 (m), 1495 (s), 1397 (m), 1257 (s), 1136 (m), 1008 (s), 912 (s), 731 (s), 698 (s), 649 (m); ¹H NMR (CDCl₃, 500MHz) δ 7.50-7.26 (m, 15H, ArH), 6.65 (s, 1H, -NH), 5.04 (s, 2H, benzylic-CH₂), 4.83 (s, 1H, CH=CH(*H*)), 4.77 (s, 1H, CH=CH(*H*)), 4.58 (s, 2H, allyl-OCH₂), 1.54 (s, 3H, -Me); ¹³C NMR (CDCl₃, 125MHz) δ 171.5, 139.1, 138.9, 128.6, 128.1, 128.0, 113.8, 69.7, 68.1, 66.7, 19.3; HRMS (ESI+) *m/z* 416.1848 [(M+H)⁺; calculated mass for C₂₆H₂₆NO₄⁺: 416.1862 amu].

NH₂-Dφg-O-allyl (O-allyldiphenylglycine) (8a). To a solution of **7a** (3.470 g, 8.65 mmol) in CH₂Cl₂ (20 mL) at rt was added TMSI (1.54 mL, 12.07 mmol). An immediate yellowing of solution was noted. The reaction mixture was stirred for 2 h, then quenched with MeOH (40 mL). Volatiles were removed in vacuo. The resulting residue was dissolved in 30% aqueous AcOH and washed with Et₂O until the yellow color was removed. The aqueous layer was then neutralized with 2N NaOH and extracted with EtOAc. The combined EtOAc extract was washed with brine, dried (Na₂SO₄), filtered and concentrated in vacuo to afford a clear colorless oil (2.28 g, 8.54 mmol, 99%). *Note: lyophilization of the aqueous layer after Et₂O wash but prior to neutralization allows the generation of the acetate salt for extended storage. R_f = 0.48 (30% EtOAc/Hexanes w/ 1% Et₃N); IR (CDCl₃) 3424 (br), 1728 (s), 1645 (s), 1416 (m), 1217 (m), 988 (w); ¹H NMR (CDCl₃, 500MHz) δ 7.49-7.45 (m, 4H,

(1) Crisma, M.; Valle, G.; Bonora, G. M.; De Menego, E.; Toniolo, C.; Lelj, F.; Barone, V.; Fraternali, F. Biopolymers. 1990, 30, 1

ArH), 7.41-7.31 (m, 6H, ArH), 5.92 (ddt, $J = 17.05, 10.85, 5.59$ Hz, 1H, allyl-CH), 5.27-5.20 (m, 2H, allyl-CH=CH₂), 4.74 (d, $J = 5.56$ Hz, 2H, allyl-O-CH₂), 2.40 (s, 2H, NH₂); ¹³C NMR (CDCl₃, 125MHz) δ 173.8, 143.3, 131.0, 127.5, 127.3, 127.3, 127.1, 126.9, 117.7, 67.8, 65.5; HRMS (ESI+) m/z 268.1350 [(M+H)⁺; calculated mass for C₁₇H₁₈NO₂⁺: 268.1338 amu].

NH₂-Dpg-O-2-Methylpropene (O-2-Methylpropenediphenylglycine) (8b). To a solution of **7b** (884 mg, 2.20 mmol) in CH₂Cl₂ (8 mL) at rt was added TMSI (0.50 mL, 4.02 mmol). An immediate yellowing of solution was noted. The reaction mixture was stirred for 1.5 h, then quenched with MeOH (15 mL). Volatiles were removed in vacuo. The resulting residue was dissolved in 30% aqueous AcOH and washed with Et₂O until the yellow color was removed. The aqueous layer was then neutralized with 2N NaOH and extracted with EtOAc. The combined EtOAc extract was washed with brine, dried (Na₂SO₄), filtered and concentrated in vacuo to afford a clear pale yellow oil (541 mg, 1.92 mmol, 90%). *Note: lyophilization of the aqueous layer after Et₂O wash but prior to neutralization allows the generation of the acetate salt for extended storage. $R_f = 0.40$ (20% EtOAc/Hexanes); IR (CDCl₃) 3389 (br), 3060 (m), 3027 (m), 2975 (m), 2941 (m), 1732 (s), 1655 (m), 1600 (m), 1493 (m), 1447 (m), 1214 (s), 1004 (m), 909 (m), 834 (m), 754 (s), 699 (s); ¹H NMR (CDCl₃, 500MHz) δ 7.49-7.27 (m, 10H, ArH), 4.90-4.82 (m, 2H, allyl-CH=CH₂), 4.64 (s, 2H, allyl-O-CH₂), 2.44 (s, 2H, -NH₂), 1.63 (s, 3H, -Me); ¹³C NMR (CDCl₃, 125MHz) δ 174.8, 144.1, 139.6, 128.7, 128.4, 128.3, 128.0, 127.8, 113.7, 69.2, 68.8, 68.7, 68.6, 68.5, 68.4, 68.3, 68.2, 68.1, 68.0, 67.9, 67.8, 67.7, 67.6, 67.5, 67.4, 67.3, 67.2, 67.1, 67.0, 66.9, 66.8, 66.7, 66.6, 66.5, 66.4, 66.3, 66.2, 66.1, 66.0, 65.9, 65.8, 65.7, 65.6, 65.5, 65.4, 65.3, 65.2, 65.1, 65.0, 64.9, 64.8, 64.7, 64.6, 64.5, 64.4, 64.3, 64.2, 64.1, 64.0, 63.9, 63.8, 63.7, 63.6, 63.5, 63.4, 63.3, 63.2, 63.1, 63.0, 62.9, 62.8, 62.7, 62.6, 62.5, 62.4, 62.3, 62.2, 62.1, 62.0, 61.9, 61.8, 61.7, 61.6, 61.5, 61.4, 61.3, 61.2, 61.1, 61.0, 60.9, 60.8, 60.7, 60.6, 60.5, 60.4, 60.3, 60.2, 60.1, 60.0, 59.9, 59.8, 59.7, 59.6, 59.5, 59.4, 59.3, 59.2, 59.1, 59.0, 58.9, 58.8, 58.7, 58.6, 58.5, 58.4, 58.3, 58.2, 58.1, 58.0, 57.9, 57.8, 57.7, 57.6, 57.5, 57.4, 57.3, 57.2, 57.1, 57.0, 56.9, 56.8, 56.7, 56.6, 56.5, 56.4, 56.3, 56.2, 56.1, 56.0, 55.9, 55.8, 55.7, 55.6, 55.5, 55.4, 55.3, 55.2, 55.1, 55.0, 54.9, 54.8, 54.7, 54.6, 54.5, 54.4, 54.3, 54.2, 54.1, 54.0, 53.9, 53.8, 53.7, 53.6, 53.5, 53.4, 53.3, 53.2, 53.1, 53.0, 52.9, 52.8, 52.7, 52.6, 52.5, 52.4, 52.3, 52.2, 52.1, 52.0, 51.9, 51.8, 51.7, 51.6, 51.5, 51.4, 51.3, 51.2, 51.1, 51.0, 50.9, 50.8, 50.7, 50.6, 50.5, 50.4, 50.3, 50.2, 50.1, 50.0, 49.9, 49.8, 49.7, 49.6, 49.5, 49.4, 49.3, 49.2, 49.1, 49.0, 48.9, 48.8, 48.7, 48.6, 48.5, 48.4, 48.3, 48.2, 48.1, 48.0, 47.9, 47.8, 47.7, 47.6, 47.5, 47.4, 47.3, 47.2, 47.1, 47.0, 46.9, 46.8, 46.7, 46.6, 46.5, 46.4, 46.3, 46.2, 46.1, 46.0, 45.9, 45.8, 45.7, 45.6, 45.5, 45.4, 45.3, 45.2, 45.1, 45.0, 44.9, 44.8, 44.7, 44.6, 44.5, 44.4, 44.3, 44.2, 44.1, 44.0, 43.9, 43.8, 43.7, 43.6, 43.5, 43.4, 43.3, 43.2, 43.1, 43.0, 42.9, 42.8, 42.7, 42.6, 42.5, 42.4, 42.3, 42.2, 42.1, 42.0, 41.9, 41.8, 41.7, 41.6, 41.5, 41.4, 41.3, 41.2, 41.1, 41.0, 40.9, 40.8, 40.7, 40.6, 40.5, 40.4, 40.3, 40.2, 40.1, 40.0, 39.9, 39.8, 39.7, 39.6, 39.5, 39.4, 39.3, 39.2, 39.1, 39.0, 38.9, 38.8, 38.7, 38.6, 38.5, 38.4, 38.3, 38.2, 38.1, 38.0, 37.9, 37.8, 37.7, 37.6, 37.5, 37.4, 37.3, 37.2, 37.1, 37.0, 36.9, 36.8, 36.7, 36.6, 36.5, 36.4, 36.3, 36.2, 36.1, 36.0, 35.9, 35.8, 35.7, 35.6, 35.5, 35.4, 35.3, 35.2, 35.1, 35.0, 34.9, 34.8, 34.7, 34.6, 34.5, 34.4, 34.3, 34.2, 34.1, 34.0, 33.9, 33.8, 33.7, 33.6, 33.5, 33.4, 33.3, 33.2, 33.1, 33.0, 32.9, 32.8, 32.7, 32.6, 32.5, 32.4, 32.3, 32.2, 32.1, 32.0, 31.9, 31.8, 31.7, 31.6, 31.5, 31.4, 31.3, 31.2, 31.1, 31.0, 30.9, 30.8, 30.7, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.4, 28.3, 28.2, 28.1, 28.0, 27.9, 27.8, 27.7, 27.6, 27.5, 27.4, 27.3, 27.2, 27.1, 27.0, 26.9, 26.8, 26.7, 26.6, 26.5, 26.4, 26.3, 26.2, 26.1, 26.0, 25.9, 25.8, 25.7, 25.6, 25.5, 25.4, 25.3, 25.2, 25.1, 25.0, 24.9, 24.8, 24.7, 24.6, 24.5, 24.4, 24.3, 24.2, 24.1, 24.0, 23.9, 23.8, 23.7, 23.6, 23.5, 23.4, 23.3, 23.2, 23.1, 23.0, 22.9, 22.8, 22.7, 22.6, 22.5, 22.4, 22.3, 22.2, 22.1, 22.0, 21.9, 21.8, 21.7, 21.6, 21.5, 21.4, 21.3, 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 20.6, 20.5, 20.4, 20.3, 20.2, 20.1, 20.0, 19.9, 19.8, 19.7, 19.6, 19.5, 19.4, 19.3, 19.2, 19.1, 19.0, 18.9, 18.8, 18.7, 18.6, 18.5, 18.4, 18.3, 18.2, 18.1, 18.0, 17.9, 17.8, 17.7, 17.6, 17.5, 17.4, 17.3, 17.2, 17.1, 17.0, 16.9, 16.8, 16.7, 16.6, 16.5, 16.4, 16.3, 16.2, 16.1, 16.0, 15.9, 15.8, 15.7, 15.6, 15.5, 15.4, 15.3, 15.2, 15.1, 15.0, 14.9, 14.8, 14.7, 14.6, 14.5, 14.4, 14.3, 14.2, 14.1, 14.0, 13.9, 13.8, 13.7, 13.6, 13.5, 13.4, 13.3, 13.2, 13.1, 13.0, 12.9, 12.8, 12.7, 12.6, 12.5, 12.4, 12.3, 12.2, 12.1, 12.0, 11.9, 11.8, 11.7, 11.6, 11.5, 11.4, 11.3, 11.2, 11.1, 11.0, 10.9, 10.8, 10.7, 10.6, 10.5, 10.4, 10.3, 10.2, 10.1, 10.0, 9.9, 9.8, 9.7, 9.6, 9.5, 9.4, 9.3, 9.2, 9.1, 9.0, 8.9, 8.8, 8.7, 8.6, 8.5, 8.4, 8.3, 8.2, 8.1, 8.0, 7.9, 7.8, 7.7, 7.6, 7.5, 7.4, 7.3, 7.2, 7.1, 7.0, 6.9, 6.8, 6.7, 6.6, 6.5, 6.4, 6.3, 6.2, 6.1, 6.0, 5.9, 5.8, 5.7, 5.6, 5.5, 5.4, 5.3, 5.2, 5.1, 5.0, 4.9, 4.8, 4.7, 4.6, 4.5, 4.4, 4.3, 4.2, 4.1, 4.0, 3.9, 3.8, 3.7, 3.6, 3.5, 3.4, 3.3, 3.2, 3.1, 3.0, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.0; HRMS (ESI+) m/z 282.1503 [(M+H)⁺; calculated mass for C₁₇H₁₈NO₂⁺: 282.1494 amu].

General Procedures for Imine Formation (1)

Conditions A: To a flame-dried flask equipped with a Dean-Stark trap was added amine (**8a** or **8b**, 1 eq.) and aldehyde (0.98 eq.) dissolved in PhH (0.2M). The reaction mixture was heated to reflux and stirred at that temperature until completion, as determined by ¹H NMR analysis of reaction aliquots. Concentration in vacuo and purification by flash chromatography with the indicated eluent or recrystallization from the indicated solvent.

Conditions B: To a solution of amine **8a** (1 eq) dissolved in CH₂Cl₂ (0.1M) was added imine (1 eq), which was generated by bubbling ammonia gas through a solution of the corresponding aldehyde in PhH. After stirring at rt for the indicated time (monitored by ¹H NMR), the reaction mixture was concentrated in vacuo and purified by flash chromatography with the indicated eluent.

Conditions C: To a solution of the amine **8a** (1.0 eq) in PhCH₃ (0.1M) with 4Å molecular sieves was added a 50% solution of ethyl glyoxylate in PhCH₃ (ca. 1.0 eq). After stirring at rt for 24h, the reaction mixture was concentrated in vacuo and purified by flash chromatography (5-10% EtOAc/Hexanes gradient with 1-2% Et₃N).

O-Allyl-2-(benzylideneamino)-2,2-diphenylacetate (1a). Conditions A, 33 hrs, Eluent: 5% EtOAc/Hexanes with 1% Et₃N; White solid (95%): $R_f = 0.65$ (20% EtOAc/Hexanes with 1% Et₃N); mp = 62-65°C; IR (CDCl₃) 3085 (m), 3061 (m), 2925 (m), 1732 (m), 1645 (s), 1492 (s), 1448 (s), 1219 (s), 1032 (m), 758 (m), 696 (m); ¹H NMR (CDCl₃, 500MHz) δ 8.02 (s, 1H, N=CH), 7.92 (dd, $J = 6.62, 2.98$ Hz, 2H, benzylimine), 7.56-7.34 (m, 13H, ArH), 5.94 (tdd, $J = 17.04, 10.72, 5.38$ Hz, 1H, allyl-CH), 5.33-5.16 (m, 2H, allyl-CH=CH₂), 4.79 (td, $J = 5.37, 1.13$ Hz, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 171.8, 163.2, 142.4, 136.3, 131.1, 129.2, 128.7, 128.5, 127.9, 127.5, 127.3, 127.0, 118.2, 79.4, 66.1; HRMS (ESI+) m/z 356.1650 [(M+H)⁺; calculated mass for C₂₄H₂₂NO₂⁺: 356.1651 amu].

O-Allyl-2-(4-fluorobenzylideneamino)-2,2-diphenylacetate (1b). Conditions A, 24 h, Eluent: 5% EtOAc/Hexanes with 1% Et₃N; Clear off-white oil (88%): $R_f = 0.77$ (30% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3060 (m), 2927 (m), 1735 (s), 1645 (m), 1601 (s), 1508 (s), 1447 (w), 1231 (s), 836 (s), 757 (m), 701 (s); ¹H NMR (CDCl₃, 300MHz) δ 7.87 (s, 1H, N=CH), 7.84 (dd, $J = 8.70, 5.58$ Hz, 2H, FC=CH), 7.45-7.27 (m, 10H, ArH), 7.11 (dd, $J = 8.65, 8.65$ Hz, 2H, -C_{ipso}=CH), 5.86 (ddt, $J =$

17.38, 10.66, 5.39 Hz, 1H, allyl-CH), 5.22-5.13 (m, 2H, allyl-CH=CH₂), 4.71 (td, *J* = 5.38, 1.24 Hz, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃, 75MHz) δ 161.9, 142.3, 131.5, 130.7, 130.6, 129.2, 128.0, 127.6, 118.2, 115.8, 115.5, 79.3, 66.2; HRMS (ESI+) *m/z* 374.1558 [(M+H)⁺; calculated mass for C₂₄H₂₁FNO₂⁺: 374.1556 amu].

O-Allyl-2-(4-cyanobenzylideneamino)-2,2-diphenylacetate (1c). Conditions A, 21 h Eluent: 5% EtOAc/Hexanes with 1% Et₃N; Clear off-white solid (96%): R_f = 0.46 (20% EtOAc/Hexanes with 1% Et₃N); mp = 97-99°C; IR (CDCl₃) 3060 (w), 3025 (w), 2933 (w), 2228 (m), 1733 (s), 1646 (m), 1492 (m), 1447 (m), 1411 (m), 1219 (s), 1033 (m), 1012 (m), 981 (m), 835 (m), 750 (m), 701 (m), 553 (m); ¹H NMR (CDCl₃, 500MHz) δ 7.94 (d, *J* = 8.12 Hz, 2H, aromatic-C=CH-CCN), 7.93 (s, 1H, -CH=N), 7.71 (d, *J* = 8.37 Hz, 2H, -C_{ipso}-CH=CH-), 7.43-7.29 (m, 10H, ArH), 5.92 (ddt, *J* = 16.71, 10.90, 5.40 Hz, 1H, allyl-CH), 5.17 (dd, *J* = 16.67, 1.44 Hz, 1H, allyl-CH=CH₂(*trans*)), 5.17 (dd, *J* = 11.21, 1.38 Hz, 1H, allyl-CH=CH₂(*cis*)), 4.72 (td, *J* = 5.41, 1.50, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 171.1, 161.5, 143.6, 141.7, 139.9, 132.3, 131.2, 129.1, 129.0, 128.0, 127.7, 127.5, 118.4, 118.3, 114.1, 79.6, 66.2; HRMS (ESI+) *m/z* 381.1587 [(M+H)⁺; calculated mass for C₂₅H₂₁N₂O₂⁺: 381.1603 amu].

O-Allyl-2-(furan-2-carbimine)-2,2'-diphenylacetate (1d). Conditions B, 19 h, Eluent: 8% EtOAc/Hexanes with 1% Et₃N; Clear colorless oil (69%): R_f = 0.58 (20% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3060 (s), 2935 (s), 1732 (s), 1651 (s), 1484 (s), 1393 (m), 1221 (s), 1083 (m), 1016 (s), 923 (s), 814 (m), 751 (s), 595 (s); ¹H NMR (CDCl₃, 500MHz) δ 7.68 (s, 1H, N=CH), 7.57 (d, *J* = 1.73 Hz, 1H, -O-CH=), 7.43-7.29 (m, 10H, ArH), 6.80 (dd, *J* = 3.44, 0.69 Hz, 1H, -C_{ipso}=CH-), 6.48 (dd, *J* = 3.43, 1.77 Hz, 1H, -CH=CH-CH=), 5.87 (ddt, *J* = 17.20, 10.63, 5.48 Hz, 1H, allyl-CH), 5.18 (ddt, *J* = 16.16, 2.75, 1.35 Hz, 1H, CH=CH(*H*)_{trans}), 5.15 (ddt, *J* = 9.64, 2.93, 1.45 Hz, 1H, CH=CH(*H*)_{cis}), 4.71 (td, *J* = 5.58, 1.40 Hz, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 171.7, 151.9, 145.3, 141.9, 131.5, 129.4, 128.0, 127.7, 118.4, 115.5, 111.9, 79.6, 66.4; HRMS (ESI+) *m/z* 346.1454 [(M+H)⁺; calculated mass for C₂₂H₂₀NO₃⁺: 346.1443 amu].

O-Allyl-2-(4-methoxybenzylideneamino)-2,2-diphenylacetate (1e). Conditions A, 48 h, Eluent: 10% EtOAc/Hexanes with 1% Et₃N; Clear off-white oil (94%): R_f = (20% EtOAc/Hexanes with 1-2% Et₃N); IR (CDCl₃) 3060 (m), 3023 (m), 2935 (m), 2838 (m), 1733 (s), 1640 (s), 1605 (s), 1512 (s), 1446 (m), 1309 (m), 1254 (s), 1217 (s), 1165 (s), 1031 (m), 931 (m), 833 (m), 757 (m), 701 (m), 607 (m); ¹H NMR (CDCl₃, 300MHz) δ 7.85 (s, 1H, CH=N), 7.79 (d, *J* = 8.78 Hz, 2H, CH=COMe), 7.48-7.25 (m, 10H, ArH), 6.94 (d, *J* = 8.79 Hz, 2H, C_{ipso}=CH-), 5.86 (tdd, *J* = 17.13, 10.65, 5.38 Hz, 1H, allyl-CH), 5.18 (ddt, *J* = 17.26, 3.11, 1.56 Hz, 1H, CH=CH(*H*)_{trans}), 5.15 (ddt, *J* = 10.43, 2.67, 1.31 Hz, 1H, CH=CH(*H*)_{cis}), 4.71 (td, *J* = 5.37, 1.45 Hz, 2H, allyl-O-CH₂), 3.85 (s, 3H, O-CH₃); ¹³C NMR (CDCl₃, 75MHz) δ 172.0, 162.5, 162.0, 142.6, 131.5, 130.3, 129.2, 127.9, 127.4, 118.1, 113.9, 79.2, 66.1, 55.3; HRMS (ESI+) *m/z* 386.1758 [(M+H)⁺; calculated mass for C₂₅H₂₄NO₃⁺: 386.1756 amu].

O-Allyl-2-(2,4-dimethoxybenzylideneamino)-2,2-diphenylacetate (1f). Conditions A, 48 h, Recrystallized from hexanes; White solid (79%): R_f = 0.32 (20% EtOAc/Hexanes with 1% Et₃N); mp = 85-87°C; IR (CDCl₃) 3022 (m), 2938 (m), 1732 (s), 1606 (s), 1504 (m), 1464 (s), 1273 (s), 1209 (s), 1160 (m), 1032 (s), 937 (m), 835 (m), 757 (m), 702 (s); ¹H NMR (CDCl₃, 300MHz) δ 8.36 (s, 1H, N=CH), 8.23 (d, *J* = 8.65 Hz, 1H, -C_{ipso}-CH=), 7.47-7.23 (m, 10H, ArH), 6.58 (dd, *J* = 8.65, 2.29 Hz, 1H, aromatic-C₅H-), 6.39 (d, *J* = 2.29 Hz, 1H, aromatic-C₃H-), 5.87 (tdd, *J* = 17.20, 10.61, 5.39 Hz, 1H, allyl-CH), 5.19 (ddd, *J* = 15.56, 2.96, 1.49 Hz, 1H, CH=CH(*H*)_{trans}), 5.14 (ddt, *J* = 8.97, 2.55, 1.24 Hz, 1H, , CH=CH(*H*)_{cis}), 4.71 (td, *J* = 5.39, 1.47 Hz, 2H, allyl-O-CH₂), 3.84 (s, 1H, -OCH₃), 3.71 (s, 1H, -OCH₃); ¹³C NMR (CDCl₃, 75MHz) δ 172.3, 163.4, 160.5, 158.6, 142.9, 131.6, 129.1, 128.8, 128.2, 127.8, 127.3, 118.4, 118.0, 105.4, 97.8, 79.4, 66.0, 55.4; HRMS (ESI+) *m/z* 416.1868 [(M+H)⁺; calculated mass for C₂₆H₂₆NO₄⁺: 416.1862 amu].

O-Allyl-2-(1,3-benzodioxole-5-carbimine)-2,2'-diphenylacetate (1g). Conditions A, 24 h, Eluent: 15-20% EtOAc/Hexanes with 1% Et₃N; Clear colorless oil (53%): R_f = 0.60 (20% EtOAc/Hexanes w/ 1-2% Et₃N); IR (CDCl₃) 3060 (m), 3023 (m), 2898 (m), 1733 (s), 1638 (m), 1603 (m), 1490 (m), 1448 (s), 1256 (s), 1200 (s), 1037 (s), 931 (m), 810 (m), 701 (m), 599 (m); ¹H NMR (CDCl₃ 500MHz) δ 7.82 (s, 1H, -CH=N), 7.61 (d, *J* = 1.52 Hz, 1H, -C_{ipso}=CH-CO), 7.48-7.27 (m, 10H, ArH), 7.09 (dd, *J* = 7.99, 1.56 Hz, 1H, -C_{ipso}-CH=CH), 6.82 (d, *J* = 7.96 Hz, 1H, -CH=CH-CO), 6.00 (s, 2H, -O-CH₂-O-), 5.87 (tdd, *J* = 17.20, 10.50, 5.29 Hz, 1H, allyl-CH), 5.19 (ddd, *J* = 17.46, 3.23, 1.68 Hz, 1H, CH=CH(*H*)_{trans}), 5.16 (ddd, *J* = 10.41, 1.31, 1.31 Hz, 1H, CH=CH(*H*)_{cis}), 4.72 (td, *J* = 5.36, 1.45, 1.45 Hz, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃ 125MHz) δ 172.2, 162.6, 150.5, 148.5, 142.8, 131.8, 131.6, 129.5, 128.2, 127.8, 125.7, 118.5, 108.2, 107.1, 101.7, 79.5, 66.4; HRMS (ESI+) *m/z* 400.1539 [(M+H)⁺]; calculated mass for C₂₅H₂₂NO₄⁺: 400.1549 amu].

O-Allyl-2-(3-pyridinalimine)-2,2'-diphenylacetate (1h). Conditions B, 48 h. Eluent: 20% EtOAc/Hexanes with 1% Et₃N; Yellow oil (83%): R_f = 0.10 (20% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3058 (m), 2925 (m), 1734 (s), 1646 (m), 1589 (w), 1447 (m), 1420 (m), 1220 (m), 1199 (m), 1028 (m), 933 (w), 756 (w), 702 (m); ¹H NMR (CDCl₃, 500MHz) δ 8.87 (d, *J* = 1.99 Hz, 1H, C_{ipso}=CH-N), 8.58 (dd, *J* = 4.78, 1.65 Hz, 1H, =CH-CH=N), 8.19 (td, *J* = 7.88, 1.85 Hz, 1H, C_{ipso}=CH-CH), 7.97 (s, 1H, N=CH), 7.48-7.20 (m, 11H, ArH), 5.79 (tdd, *J* = 16.99, 10.65, 5.34 Hz, 1H, allyl-CH), 5.17 (dd, *J* = 17.18, 1.51 Hz, 1H, CH=CH(*H*)_{trans}), 5.15 (dd, *J* = 10.52, 1.29 Hz, 1H, CH=CH(*H*)_{cis}), 4.66 (td, *J* = 5.28, 1.18 Hz, 2H, allyl-O-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 171.3, 160.6, 151.7, 150.6, 141.8, 134.8, 131.7, 131.2, 129.1, 127.9, 127.6, 123.5, 118.2, 79.5, 66.1; HRMS (ESI+) *m/z* 357.1615 [(M+H)⁺]; calculated mass for C₂₃H₂₁N₂O₂⁺: 357.1603 amu].

O-Allyl-2-(2-ethoxy-2-oxoethylideneamino)-2,2'-diphenylacetate (1i). Condition C; Eluent: 5-10% EtOAc/Hexanes with 1% Et₃N; Clear colorless oil (50%): R_f = 0.53 (30% EtOAc/Hexanes w/ 1% Et₃N); IR (CDCl₃) 3060 (m), 2983 (m), 1736 (s), 1650 (m), 1493 (m), 1447 (m), 1371 (m), 1346 (m), 1302 (s), 1201 (s), 1095 (m), 1033 (s), 935 (s), 750 (m), 699 (m); ¹H NMR (CDCl₃, 500MHz) δ 7.36-7.30 (m, 11H, ArH and CH=N), 5.85 (ddt, *J* = 17.13, 10.71, 5.46 Hz, 1H, allyl-CH), 5.23-5.13 (m, 2H, allyl-CH=CH₂), 4.70 (td, *J* = 5.50, 1.24 Hz, 2H, allyl-O-CH₂), 4.34 (q, *J* = 7.11 Hz, 2H, -CH₂-), 1.35 (t, *J* = 7.10 Hz, 3H, -CH₃); ¹³C NMR (CDCl₃, 125MHz) δ 170.2, 163.2, 155.9, 140.3, 131.1, 129.1, 128.1, 128.0, 127.5, 127.4, 118.6, 80.1, 66.5, 61.8, 14.1; HRMS (ESI+) *m/z* 352.1549 [(M+H)⁺]; calculated mass for C₂₁H₂₂NO₄⁺: 352.1549 amu].

O-2-Methylpropene-2-(benzylideneamino)-2,2'-diphenylacetate (1j).² Conditions A, 17 h, Eluent: 5-10% EtOAc/Hexanes gradient with 1% Et₃N; Clear colorless oil (99%). R_f = 0.46 (20% EtOAc/Hexanes w/ 1% Et₃N); IR (CDCl₃): $\bar{\nu}_{\text{max}}$ 3060 (m), 3026 (m), 1735 (s), 1643 (m), 1448 (m), 1197 (m), 1030 (m), 908 (w), 757 (m), 696 (s); ¹H NMR (CDCl₃ 500MHz) δ : 7.97 (s, 1H, -CH=N), 7.87 (dd, *J* = 7.49, 2.08 Hz, 2H, ArH), 7.50-7.31 (m, 13H, ArH), 4.86 (m, 2H, C=CH₂), 4.65 (s, 2H, -O-CH₂), 1.62 (s, 3H, -Me); ¹³C NMR (CDCl₃ 125MHz) δ : 171.7, 163.3, 142.4, 139.3, 136.4, 131.0, 129.3, 128.6, 128.5, 127.9, 127.5, 113.0, 79.4, 68.8, 19.3; HRMS (ES+) *m/z* 370.1804 [(M+H)⁺]; calculated mass for C₂₅H₂₄NO₂⁺: 370.1807 amu].

General procedure for the synthesis of protected homoallylic amines via allylic alkylation. To a 0.1M solution of imine **1** in MeCN was added 10 mol% dppf and 10 mol% Pd(dba)₂, and the reaction mixture was stirred at room temperature unless otherwise indicated for the indicated time. The reaction mixture was then filtered through Celite, concentrated in vacuo, and purified by flash chromatography (0-5% EtOAc and hexanes w/ 1-2% Et₃N, unless otherwise noted).

(2) The 2-methylallylbromide we obtained from Acros contained an unidentified impurity (presumably the corresponding dibromide) in ca. 10%, as determined by ¹H NMR spectroscopy (δ 5.1 ppm, s). This impurity was carried through our entire reaction process up through homoallylic imine **3j**.

4-Diphenylimine-4-phenyl-1-butene (3a). Reaction time: 30 min. Experimental data for **3a** is in agreement with literature.³ ¹H NMR (CDCl₃, 300MHz) δ 7.68 (dd, J = 8.01, 1.68 Hz, 2H, ArH), 7.49-7.40 (m, 3H, ArHs), 7.40-7.19 (m, 8H, ArH), 7.10-7.05 (m, 2H, ArH), 5.66 (tdd, J = 17.23, 10.12, 7.11 Hz, 1H, allyl-CH), 5.11-4.86 (m, 2H, allyl-CH₂=CH), 4.44 (dd, J = 7.88, 5.48 Hz, 1H, -CH-), 2.71 (td, J = 14.92, 7.63 Hz, 1H, diastereotopic allyl-CH₂), 2.59 (td, J = 13.67, 6.79, 5.64, 1.08 Hz, 1H, diastereotopic allyl-CH₂); HRMS (ESI+) m/z 312.1756 [(M+H)⁺]; calculated mass for C₂₃H₂₂N⁺: 312.1752 amu].

4-Diphenylimine-4-(4-fluorophenyl)-1-butene (3b). Reaction time: 60 min. Experimental data for **3b** is in agreement with literature.² ¹H NMR (CDCl₃, 300MHz) δ 7.67 (d, J = 6.41 Hz, 2H, ArH), 7.49-7.22 (m, 8H, ArH), 7.10-7.03 (m, 2H, ArH), 6.98 (t, J = 8.78 Hz, 2H, ArH), 5.63 (tdd, J = 17.32, 10.22, 7.13 Hz, 1H, allyl-CH), 5.02-4.92 (m, 2H, allyl-CH₂=CH), 4.41 (dd, J = 7.57, 5.75 Hz, 1H, -CH-), 2.65 (td, J = 14.90, 7.50 Hz, 1H, diastereotopic allyl-CH₂), 2.54 (ddd, J = 13.57, 6.90, 5.69, 1.09 Hz, 1H, diastereotopic allyl-CH₂); HRMS (ESI+) m/z 330.1656 [(M+H)⁺]; calculated mass for C₂₃H₂₁NF⁺: 330.1658 amu].

4-Diphenylimine-4-(4-cyanophenyl)-1-butene (3c). Reaction time: 60 min. Clear colorless oil: R_f = 0.64 (20% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3060 (m), 2927 (m), 2227 (s), 1623 (s), 1607 (s), 1490 (m), 1446 (s), 1281 (s), 1179 (m), 993 (m), 918 (m), 838 (m), 781 (m), 697 (s), 564 (m); ¹H NMR (CDCl₃, 500MHz) δ 7.67 (dd, J = 8.19, 1.58 Hz, 2H, ArH), 7.59 (d, J = 8.46 Hz, 2H, ArH), 7.49-7.27 (m, 8H, ArH), 7.02 (dd, J = 6.53, 3.00 Hz, 2H, ArH), 5.62 (tdd, J = 17.89, 9.36, 7.14 Hz, 1H, allyl-CH), 5.06-4.87 (m, 2H, allyl-CH=CH₂), 4.47 (dd, J = 7.52, 5.66 Hz, 1H, -CH-), 2.65 (dddt, J = 13.72, 7.44, 7.44, 1.07 Hz, 1H, diastereotopic allyl-CH₂), 2.54 (dddt, J = 13.74, 6.97, 5.77, 1.19 Hz, 1H, diastereotopic allyl-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 167.8, 149.8, 139.5, 136.6, 134.6, 132.1, 130.2, 128.6, 128.5, 128.1, 127.9, 127.6, 119.1, 117.5, 110.5, 66.0, 43.7; HRSM (ESI+) m/z 337.1689 [(M+H)⁺]; calculated mass for C₂₄H₂₁N₂⁺: 337.1705 amu].

4-Diphenylimine-4-(2-furanyl)-1-butene (3d). Reaction time: 2 h. Clear colorless oil: R_f = 0.78 (20% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3060 (w), 2923 (m), 1623 (s), 1490 (m), 1446 (s), 1287 (m), 1148 (m), 1002 (s), 916 (s), 884 (w), 733 (m), 697 (s); ¹H NMR (CDCl₃, 300MHz) δ 7.66 (m, 2H, ArH), 7.49-7.25 (m, 9H, ArH), 6.31 (dd, J = 3.20, 1.85 Hz, 1H, -CH=CH-CH=), 6.15 (td, J = 3.18, 0.67 Hz, 1H, -C_{ipso}=CH-), 5.67 (tdd, J = 17.19, 10.12, 7.11 Hz, 1H, allyl-CH), 5.09-4.93 (m, 2H, allyl-CH₂=CH), 4.57 (t, J = 6.64 Hz, 1H, -CH-), 2.75-2.68 (m, 2H, overlapping diastereotopic allyl-CH₂); ¹³C NMR (CDCl₃, 75MHz) δ 168.6, 156.1, 141.5, 139.8, 136.7, 135.0, 132.4, 130.0, 128.7, 128.4, 128.2, 128.0, 128.0, 117.1, 110.0, 105.5, 60.2, 39.7; HRMS (ESI+) m/z 302.1553 [(M+H)⁺]; calculated mass for C₂₁H₂₀NO⁺: 302.1539 amu].

4-Diphenylimine-4-(4-methoxyphenyl)-1-butene (3e). Reaction time: 7 h. Clear colorless oil: R_f = 0.57 (20% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 3060 (m), 2935 (m), 1577 (s), 1640 (m), 1512 (s), 1512 (s), 1309 (m), 1254 (s), 1164 (s), 1031 (s), 833 (m), 757 (m), 701 (s); ¹H NMR (CDCl₃, 500MHz) δ 7.66 (d, J = 6.86 Hz, 2H, ArH), 7.44-7.40 (m, 2H, ArH), 7.39-7.28 (m, 4H, ArH), 7.23 (d, J = 8.41 Hz, 2H, ArH), 7.09-7.04 (m, 2H, -C_{ipso}=CH-), 6.84 (d, J = 8.79 Hz, 2H, -CH=C-O), 5.64 (tdd, J = 17.24, 10.17, 7.12 Hz, 1H, allyl-CH), 5.03-4.89 (m, 2H, allyl-CH₂=CH), 4.39 (dd, J = 7.85, 5.55 Hz, 1H, -CH-), 3.79 (s, 3H, -CH₃), 2.66 (td, J = 13.89, 7.58, 7.58, 1.16 Hz, 1H, diastereotopic allyl-CH₂), 2.56 (td, J = 13.72, 6.86, 5.54, 1.21 Hz, 1H, diastereotopic allyl-CH₂); ¹³C NMR (CDCl₃, 125MHz) δ 166.4, 158.3, 140.0, 137.1, 136.6, 135.8, 129.8, 128.5, 128.3, 128.2, 128.1, 127.9, 127.9, 116.6, 113.6, 65.8, 55.2, 43.9; HRMS (ESI+) m/z 386.1758 [(M+H)⁺]; calculated mass for C₂₅H₂₄NO₃⁺: 386.1756 amu].

4-Diphenylimine-4-(2,4-dimethoxyphenyl)-1-butene (3f). Reaction time: 5 h. Clear colorless oil: R_f = 0.53 (30% EtOAc/Hexanes with 1% Et₃N); IR (CDCl₃) 2930 (m), 1613 (s), 1504 (s), 1446 (m), 1287 (br), 1208 (s), 1181 (w), 1156 (m),

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1038 (m), 912 (m), 833 (m), 768 (m), 697 (s); ^1H NMR (CDCl_3 , 500MHz) δ 7.67 (d, J = 7.01 Hz, 2H, ArH), 7.57 (d, J = 8.46 Hz, 1H, $-\text{C}_{\text{ipso}}=\text{CH}-$), 7.42-7.30 (m, 6H, ArH), 7.03 (dd, J = 6.45, 2.92 Hz, 2H, ArH), 6.50 (dd, J = 8.48, 2.23 Hz, 1H, $-\text{COMe}=\text{CH}-\text{CH}=\text{CH}-$), 6.39 (d, J = 2.29 Hz, 1H, $-\text{COMe}=\text{CH}-\text{COMe}=\text{CH}-$), 5.71 (tdd, J = 16.93, 10.06, 7.00 Hz, 1H, allyl- $\text{CH}-$), 4.99 (ddd, J = 17.17, 2.17, 0.81 Hz, 1H, $\text{CH}=\text{CH}(\text{H})_{\text{trans}}$), 4.94 (ddd, J = 10.18, 2.13, 0.92 Hz, 1H, $\text{CH}=\text{CH}(\text{H})_{\text{cis}}$), 4.84 (dd, J = 7.69, 5.17 Hz, 1H, $-\text{CH}-$), 3.81 (s, 3H, $-\text{OCH}_3$), 3.62 (d, J = 0.49 Hz, 3H, $-\text{OCH}_3$), 2.66-2.53 (m, 2H, overlapping diastereotopic allyl- CH_2); ^{13}C NMR (CDCl_3 , 125MHz) δ 166.6, 156.9, 136.4, 129.6, 128.7, 128.5, 128.0, 127.9, 116.0, 104.2, 98.2, 58.5, 55.2, 42.6; HRMS (ESI+) m/z 372.1967 $[(\text{M}+\text{H})^+]$; calculated mass for $\text{C}_{25}\text{H}_{26}\text{NO}_2^+$: 372.1964 amu].

4-Diphenylimine-4-(1,3-benzodioxole-5-yl)-1-butene (3g). Reaction time 3 h. Clear colorless oil: R_f = 0.50 (20% EtOAc/Hexanes); IR (CDCl_3) 3060 (w), 2918 (m), 1622 (m), 1486 (s), 1446 (m), 1284 (m), 1246 (s), 1040 (s), 920 (m), 810 (m), 698 (s); ^1H NMR (CDCl_3 , 300MHz) δ 7.87-7.77 (m, 1H, ArH), 7.70-7.56 (m, 2H, ArH), 7.53-7.29 (m, 5H, ArH), 7.12-7.04 (m, 2H, ArH), 6.96 (d, J = 1.53 Hz, 1H, ArH), 6.73 (d, J = 7.93 Hz, 1H, ArH), 6.68 (dd, J = 8.12, 1.41 Hz, 1H, aromatics), 5.93 (ABq, J = 4.19, 1.44 Hz, 2H), 5.63 (tdd, J = 17.25, 10.15, 7.11 Hz, 1H, allyl- $\text{CH}-$), 5.03-4.92 (m, 2H, $-\text{CH}=\text{CH}_2$), 4.36 (dd, J = 7.63, 5.74 Hz, 1H, $-\text{CH}-$), 2.69-2.48 (m, 2H, allyl- CH_2); ^{13}C NMR (CDCl_3 , 75MHz) δ 166.7, 147.7, 146.4, 140.2, 138.7, 137.8, 137.3, 135.9, 132.7, 130.3, 130.1, 128.8, 128.6, 128.5, 128.2, 128.1, 120.3, 117.0, 108.2, 107.9, 101.0, 66.4, 44.2; HRMS (ESI+) m/z 356.1642 $[(\text{M}+\text{H})^+]$; calculated mass for $\text{C}_{25}\text{H}_{26}\text{NO}_2^+$: 356.1651 amu].

4-Diphenylimine-4-(3-pyridinyl)-1-butene (3h). Reaction time: 2.5 h; Eluent: 20% EtOAc/Hexanes with 1% Et_3N . Clear off-white oil: R_f = 0.23 (20% EtOAc/Hexanes with 1% Et_3N); IR (CDCl_3) 3057 (m), 2925 (m), 2853 (m), 1623 (s), 1575 (s), 1477 (m), 1425 (s), 1286 (s), 1180 (m), 1026 (s), 915 (s), 781 (s), 697 (s), 621 (m); ^1H NMR (CDCl_3 , 300MHz) δ 8.48 (dd, J = 4.70, 1.39 Hz, 1H, $-\text{N}=\text{CH}-\text{CH}=\text{CH}-$), 8.44 (d, J = 1.44 Hz, 1H, $-\text{N}=\text{CH}-\text{C}_{\text{ipso}}$), 7.76 (td, J = 7.86, 1.91 Hz, 1H, $-\text{C}_{\text{ipso}}=\text{CH}-\text{CH}=\text{CH}-$), 7.67 (dd, J = 8.13, 1.60 Hz, 2H, ArH), 7.50-7.28 (m, 6H, ArH), 7.24 (dd, J = 7.56, 4.55 Hz, 1H, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$), 7.05 (ddd, J = 5.62, 3.07, 1.62 Hz, 2H, ArH), 5.64 (tdd, J = 19.95, 9.60, 7.14 Hz, 1H, allyl- $\text{CH}-$), 5.04-4.93 (m, 1H, $\text{CH}_2=\text{CH}-$), 4.47 (dd, J = 7.56, 5.79 Hz, 1H, $-\text{CH}-$), 2.69 (dddt, J = 13.67, 7.47, 7.47, 0.98 Hz, 1H, diastereotopic allyl- CH_2), 2.57 (dddt, J = 13.72, 6.97, 5.80, 1.03 Hz, 1H, diastereotopic allyl- CH_2); ^{13}C NMR (CDCl_3 , 75MHz) δ 167.6, 148.8, 148.2, 139.6, 136.7, 134.8, 130.1, 128.5, 128.5, 128.0, 127.6, 123.4, 117.4, 64.1, 43.6, 29.7; HRMS (ESI+) m/z 313.1708 $[(\text{M}+\text{H})^+]$; calculated mass for $\text{C}_{22}\text{H}_{21}\text{N}_2^+$: 313.1705 amu].

Ethyl 2-(diphenylmethyleneamino)pent-4-enoate (3i). Reaction time: 90 min. Clear colorless oil: R_f = 0.69 (30% EtOAc/Hexanes with 1% Et_3N); IR (CDCl_3) 3060 (m), 2980 (s), 2926 (m), 1738 (s), 1624 (m), 1446 (s), 1287 (s), 1182 (br), 1030 (m), 917 (m), 781 (m), 697 (s), 652 (w); ^1H NMR (CDCl_3 , 300MHz) δ 7.65 (d, J = 7.09 Hz, 2H, ArH), 7.53-7.23 (m, 6H, ArH), 7.18 (dd, J = 6.20, 2.64 Hz, 2H, ArH), 5.70 (tdd, J = 17.13, 9.94, 7.11 Hz, 1H, allyl- $\text{CH}-$), 5.07 (d, J = 17.71 Hz, 1H, $\text{CH}=\text{CH}(\text{H})_{\text{trans}}$), 5.03 (d, J = 10.79 Hz, 1H, $\text{CH}=\text{CH}(\text{H})_{\text{cis}}$), 4.32-3.98 (m, 3H, overlapping $-\text{CH}-$ and $-\text{O}-\text{CH}_2-$), 2.72 (dd, J = 13.81, 6.49 Hz, 1H, diastereotopic allyl- CH_2), 2.63 (dd, J = 14.00, 7.58 Hz, 1H, diastereotopic allyl- CH_2), 1.26 (t, J = 7.10 Hz, 3H, $-\text{CH}_3$); ^{13}C NMR (CDCl_3 , 75MHz) δ 171.7, 170.5, 139.5, 136.4, 134.3, 130.3, 128.8, 128.6, 128.4, 128.0, 127.9, 117.5, 65.3, 60.9, 38.1, 14.2; HRMS (ESI+) m/z 308.1654 $[(\text{M}+\text{H})^+]$; calculated mass for $\text{C}_{22}\text{H}_{21}\text{N}_2^+$: 308.1651 amu].

4-Diphenylimine-4-phenyl-2-methyl-1-butene (3j). Reaction time: 90 min at 40 °C. Experimental data for **3j** is in agreement with literature.² ^1H NMR (CDCl_3 , 300MHz) δ 7.68 (dd, J = 7.93, 1.62 Hz, 2H, ArH), 7.47-7.39 (m, 4H, ArH), 7.38-7.27 (m, 7H, ArH), 7.11-7.04 (m, 2H, ArH), 4.74-4.68 (m, 1H, $\text{CH}=\text{CH}(\text{H})$), 4.63 (s, 1H, $\text{CH}=\text{CH}(\text{H})$), 4.53 (dd, J = 8.42, 4.95 Hz, 1H, $-\text{CH}-$), 2.70 (dd, J = 13.06, 8.50 Hz, 1H, diastereotopic allyl- CH_2), 2.48 (dd, J = 13.29, 4.57 Hz, 1H,

diastereotopic allyl-CH₂), 1.51 (s, 3H, -CH₃); HRMS (ESI+) m/z 326.1901 [(M+H)⁺; calculated mass for C₂₄H₂₄N⁺: 326.1909 amu].

Density Functional Theory Calculations. α -Imino anion **14** and the corresponding protonated zwitterion **14-H** were analyzed computationally following a modification of reported procedures.⁴ The computational suite Spartan06 was used to generate conformations of **14** and **14-H** employing the semi-empirical method PM3 and then the RHF/3-21G "ab initio" SCF method. The resulting lowest energy conformations were then analyzed using the B3LYP/6-31G(d) model to predict overall molecular structure (Figure S1) and local atomic charge (Figure S2). The predicted shift in electron density within the α -imino anion upon protonation of the pyridine nitrogen (**14** $\rightarrow$ **14-H**) can be recognized by the effect on bond lengths and atomic charges in the system. Specifically, there is a lengthening in the C_b-N bond distance (Δ +0.036 Å) with a corresponding shortening of the C_b-Ar and C_a-N bond lengths (Δ -0.032 Å and Δ -0.043 Å, respectively) upon protonation of the pyridyl N. This structural shift is matched by an increased negative local atomic charge at C_b (Δ -0.016) and positive atomic charge at C_a (Δ +0.113 Å).

Figure S1. Key calculated bond distances in the α -imino anion **14** and zwitterion **14-H**

Figure S1. Key atomic charge calculations for α -imino anion **14** and zwitterion **14-H**

⁴ Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio, R. A., Jr.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S.; H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C.-P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Paters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L., III; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F., III; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, 27, 3172.

¹H NMR spectrum of 7a (CDCl₃, 300MHz)

¹³C NMR spectrum of 7a (CDCl₃, 75MHz)

¹H NMR spectrum of 7b (CDCl₃, 300MHz)

¹³C NMR spectrum of 7b (CDCl₃, 75MHz)

¹H NMR spectrum of 8a (CDCl₃, 500MHz)

¹³C NMR spectrum of 8a (CDCl₃, 125MHz)

¹H NMR spectrum of 8b (CDCl₃, 500MHz)

¹³C NMR spectrum of 8b (CDCl₃, 125MHz)

¹H NMR spectrum of 1a (CDCl₃, 500MHz)

¹³C NMR spectrum of 1a (CDCl₃, 125MHz)

¹H NMR spectrum of 1b (CDCl₃, 300MHz)

¹³C NMR spectrum of 1b (CDCl₃, 75MHz)

¹H NMR spectrum of 1c (CDCl₃, 500MHz)

¹³C NMR spectrum of 1c (CDCl₃, 125MHz)

¹H NMR spectrum of 1d (CDCl₃, 500MHz)

¹³C NMR spectrum of 1d (CDCl₃, 125MHz)

¹H NMR spectrum of 1e (CDCl₃, 300MHz)

¹³C NMR spectrum of 1e (CDCl₃, 75MHz)

¹H NMR spectrum of 1f (CDCl₃, 500MHz)

¹³C NMR spectrum of 1f (CDCl₃, 125MHz)

¹H NMR spectrum of 1g (CDCl₃, 300MHz)

¹³C NMR spectrum of 1g (CDCl₃, 75MHz)

¹H NMR spectrum of 1h (CDCl₃, 500MHz)

¹³C NMR spectrum of 1h (CDCl₃, 125MHz)

¹H NMR spectrum of 1i (CDCl₃, 500MHz)

¹³C NMR spectrum of 1i (CDCl₃, 125MHz)

CC(=C)COCC(=O)C(Ph)(Ph)N=Cc1ccccc1 CC(=C)COCC(=O)C(Ph)(Ph)N=Cc1ccccc1

¹H NMR spectrum of 3c (CDCl₃, 500MHz)

¹³C NMR spectrum of 3c (CDCl₃, 125MHz)

¹H NMR spectrum of 3d (CDCl₃, 300MHz)

¹³C NMR spectrum of 3d (CDCl₃, 125MHz)

¹H NMR spectrum of 3e (CDCl₃, 500MHz)

¹³C NMR spectrum of 3e (CDCl₃, 125MHz)

¹H NMR spectrum of 3f (CDCl₃, 500MHz)

¹³C NMR spectrum of 3f (CDCl₃, 125MHz)

¹H NMR spectrum of 3g (CDCl₃, 300MHz)

¹³C NMR spectrum of 3g (CDCl₃, 75MHz)

¹H NMR spectrum of 3h (CDCl₃, 300MHz)

¹³C NMR spectrum of 3h (CDCl₃, 75MHz)

¹H NMR spectrum of 3i (CDCl₃, 300MHz)

¹³C NMR spectrum of 3i (CDCl₃, 75MHz)