Brønsted Acid Activation of α-Diazo Imides: A Highly *syn*-Selective Glycolate Mannich Reaction

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S-I-X

Experimental Section

All glassware used for reactions was flame-dried under vacuum. All reagents and solvents were commercial grade and purified prior to use when necessary. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), were dried by passage through a column of activated alumina as described by Grubbs.[1] All other solvents were distilled from calcium hydride before use or are otherwise indicated differently. All organic extracts were dried over $MgSO_4$ unless otherwise indicated.

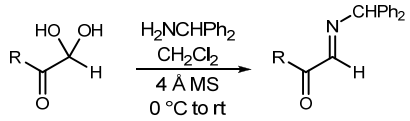
Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μm) plates and flash chromatography utilized 230–400 mesh silica. Products were visualized using UV light, and either ceric ammonium molybdate, potassium permanganate, ninhydrin, *p*-anisaldehyde, phosphomolybdic acid, or potassium iodoplatinate solutions.

Melting points were recorded on a Laboratory Devices Mel-Temp capillary melting point apparatus or a Stanford Research Systems OptiMelt MPA100 and are reported uncorrected. IR spectra were recorded on a Nicolet Avatar 360 or a Thermo Electron (Nicolet) IR100/IR200 spectrophotometer and are reported in wavenumbers (cm^{-1}). Liquids and oils were analyzed as neat films on a NaCl plate (transmission), whereas solids were applied to a diamond plate (ATR) if a thin film could not be prepared. Nuclear magnetic resonance spectra (NMR) were acquired on either a Varian instrument: INOVA-400 (400 MHz), VXR-400 (400 MHz) or Bruker instrument: AV-400 (400 MHz), DRX-500 (500 MHz), or AVII-600 (600 MHz). Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$) for ^1H and ^{13}C, respectively. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q) or combinations thereof while higher coupling patterns are not abbreviated. Mass spectra were obtained by use of chemical ionization (CI) or electrospray ionization (ESI) at Indiana University. Atlantic Microlabs, GA, performed all combustion analyses.

Benzhydrylimino acetic acid methyl ester (**1a**),[2] *p*-acetamidobenzenesulfonyl azide,[3] *N*-(4-nitrobenzylidene)benzhydrylamine (**1p**),[4] *N*-(4-fluorobenzylidene)benzhydrylamine (**1r**),[5] *N*-(4-trifluoromethoxybenzylidene)benzhydrylamine (**1s**),[6] *N*-(4-bromobenzylidene)benzhydrylamine (**1u**),[6] *N*-(4-chlorobenzylidene)-

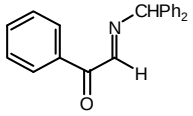
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15,* 1518-1520.
[2] Williams, A. L.; Johnston, J. N., *J. Am. Chem. Soc.* **2004**, *126,* 1612-1613.
[3] Davies, H. M. L.; Cantrell, W. R., Jr.; Romines, K. R.; Baum, J. S., Synthesis of furans via rhodium(II) acetate-catalyzed reaction of acetylenes with a-diazocarbonyls: ethyl 2-methyl-5-phenyl-3-furancarboxylate. In *Org. Synth.*, Wiley&Sons: New York, 1998; Vol. 9, pp 422-425.
[4] a) Antilla, J. C.; Wulff, W. D., *J. Am. Chem. Soc.* **1999**, *121,* 5099-5100; b) Antilla, J. C.; Wulff, W. D., *Angew. Chem. Int. Ed.* **2000**, *39,* 4518-4521.
[5] Brunner, B.; Stogaitis, N.; Lautens, M., *Org. Lett.* **2006**, *8,* 3473-3476.
[6] Green, D. S. C.; Gruss, U.; Hägele, G.; Hudson, H. R.; Lindblom, L.; Pianka, M., *Phosphorous, Sulfur Silicon Relat.Elem.* **1996**, *113,* 179 - 207.

benzhydrylamine (**1v**),[7] *N*-(4-acetoxybenzylidene)benzhydrylamine (**1x**),[6] *N*-(4-cyanobenzylidene)benzhydrylamine (**1y**),[8] were prepared according to literature procedures.



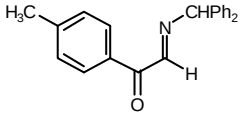
General procedure for the synthesis of imines 1b-1n. Imines were prepared by condensation of the corresponding hydrate[9] with diphenylmethylamine (1 equiv) using 4 Å MS in dichloromethane at 0 °C and warmed to rt. Solution was filtered through Celite and concentrated. Unless otherwise stated the imine was recrystallized from toluene/petroleum ether.

2-(Benzhydrylimino)-1-phenylethanone (1b). The hydrate (3.80 g, 5.00 mmol) was treated with



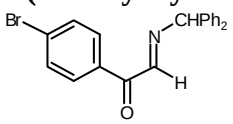
diphenylmethylamine (4.3 mL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (4.975 g, 66%). Mp 92.8-93.5 °C; IR (neat) 3061, 3027, 2862, 1662, 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.2 Hz, 2H), 8.24 (s, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.51 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.34-7.33 (m, 8H), 7.32 (dd, *J* = 6.8, 6.8 Hz, 2H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 190.6, 159.6, 142.1, 135.0, 133.5, 130.7, 128.6, 128.2, 127.5, 127.4, 78.6; HRMS (ESI): Exact mass calcd for $C_{21}H_{17}NaNO$ $[M+Na]^+$ 322.1208, found 322.1197.

2-(Benzhydrylimino)-1-(4-methylphenyl)ethanone (1c). The hydrate (839 mg, 5.00 mmol) was treated with



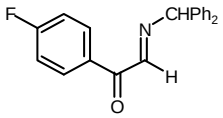
diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (1.059, 68%). Mp 71.0-72.0 °C; IR (neat) 3061, 3028, 2861, 1658, 1604, 1492, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 8.19 (s, 1H), 7.40-7.34 (m, 8H), 7.30-7.27 (m, 4H), 5.66 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 190.3, 159.8, 144.5, 142.2, 132.6, 130.8, 129.1, 128.7, 127.6, 127.4, 78.6, 21.7; HRMS (ESI): Exact mass calcd for $C_{22}H_{19}NaNO$ $[M+Na]^+$ 336.1364, found 336.1352.

2-(Benzhydrylimino)-1-(4-bromophenyl)ethanone (1d). The hydrate (1.15 g, 5.00 mmol) was treated with



diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (1.183 g, 63%). Mp 101.5-102.5 °C; IR (neat) 3061, 3028, 2863, 1663, 1584, 1492, 1290 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 8.19 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.41-7.31 (m, 10H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 189.5, 159.4, 141.9, 133.7, 132.2, 131.6, 128.9, 128.7, 127.5, 127.4, 78.6; HRMS (ESI): Exact mass calcd for $C_{21}H_{16}BrNaNO$ $[M]^+$ 400.0313, found 400.0333.

2-(Benzhydrylimino)-1-(4-fluorophenyl)ethanone (1e). The hydrate (851 mg, 5.00 mmol) was treated with



diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (731 mg, 43%). Mp 107.1-107.6 °C; IR (neat) 3062, 3028, 2864, 1663, 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.0, 5.8 Hz, 2H), 8.18 (s, 1H), 7.39-7.30 (m, 10H), 7.16 (t,

[7] Lautens, M.; Tayama, E.; Nguyen, D., *Org. Lett.* **2004**, *6,* 345-347.
[8] Siu, T.; Li, W.; Yudin, A. K., *J. Comb. Chem* **2001**, *3,* 554-558.
[9] (a) Fuson, R. C.; Gray, H.; Gouza, J. J., *J. Am. Chem. Soc.* **1939**, *61,* 1937-1940. (b) Ihmels, H.; Maggini, M.; Prato, M.; Scorrano, G., *Tetrahedron Lett.* **1991**, *32,* 6215-6218.

J = 8.7 Hz, 2H), 5.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 188.9, 167.4, 164.8, 159.7, 142.0, 133.6, 133.5, 131.4, 128.7, 127.6, 127.5, 115.6, 115.4, 78.6; HRMS (ESI): Exact mass calcd for $C_{21}H_{16}FNaNO$ $[M+Na]^+$ 340.1114, found 340.1127.

2-(Benzhydrylimino)-1-(4-methoxyphenyl)ethanone (1f). The hydrate (911 mg, 5.00 mmol) was treated with diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (948 mg, 58%). Mp 91.5-92.5 °C; IR (neat) 3061, 3027, 2934, 2840, 1655, 1597, 1572, 1259 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.9 Hz, 2H), 8.19 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 4H), 7.38 (dd, *J* = 7.7, 7.7 Hz, 4H), 7.30 (t, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 5.66 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 188.9, 164.0, 160.0, 142.3, 133.1, 128.6, 128.0, 127.6, 127.4, 113.6, 78.6, 55.4; HRMS (ESI): Exact mass calcd for $C_{22}H_{19}NaNO_2$ $[M+Na]^+$ 352.1313, found 352.1305.

2-(Benzhydrylimino)-1-(4-phenylphenyl)ethanone (1g). The hydrate (1.14 g, 5.00 mmol) was treated with diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (731 mg, 31%). Mp 122.1-123.1 °C; IR (neat) 3059, 3029, 2862, 1659, 1602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 6.8 Hz, 2H), 8.27 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 6.0 Hz, 2H), 7.54-7.29 (m, 14H), 5.74 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 190.1, 159.8, 146.1, 142.1, 139.8, 133.8, 131.3, 128.9, 128.7, 128.2, 127.54, 127.47, 127.2, 126.9, 78.6; HRMS (ESI): Exact mass calcd for $C_{27}H_{21}NaNO$ $[M+Na]^+$ 398.1521, found 398.1533.

2-(Benzhydrylimino)-1-(4-trifluoromethoxyphenyl)ethanone (1h). The hydrate (2.362 g, 10.00 mmol) was treated with diphenylmethylamine (1.7 mL, 10 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (2.648, 70%). Mp 50.5-51.5 °C; IR (neat) 3063, 3029, 2866, 1670, 1642, 1325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.0 Hz, 2H), 8.21 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.41-7.31 (m, 10H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 189.7, 159.3, 141.9, 137.8, 134.5 (q, *J* = 32.7 Hz), 131.1, 128.8, 127.6, 127.5, 125.2 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.8 Hz), 78.6; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}F_3NaNO_2$ $[M+Na]^+$ 406.1031, found 406.1024.

2-(Benzhydrylimino)-1-(4-acetoxyphenyl)ethanone (1i). The hydrate (1.05 g, 5.00 mmol) was treated with diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (613 mg, 34%). Mp 97.7-98.7 °C; IR (neat) 3062, 3028, 2865, 1762, 1662, 1598, 1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.6 Hz, 2H), 8.18 (s, 1H), 7.38-7.27 (m, 10H), 7.23 (d, *J* = 8.7 Hz, 2H), 5.67 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 189.2, 168.7, 159.6, 154.7, 142.1, 132.6, 132.5, 128.7, 127.5, 121.5, 78.7, 21.1; HRMS (ESI): Exact mass calcd for $C_{23}H_{19}NaNO_3$ $[M+Na]^+$ 380.1263, found 380.1266.

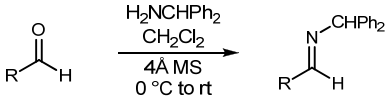
2-(Benzhydrylimino)-1-(4-trifluoromethylphenyl)ethanone (1j). The hydrate (1.10 g, 5.00 mmol) was treated with diphenylmethylamine (860 μL, 5.0 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized to give colorless crystals (830 mg, 45%). Mp 95.5-96.4 °C; IR (neat) 3063, 3029, 2865, 1666, 1601, 1259, 1222, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.9 Hz, 2H), 8.20 (s, 1H), 7.41-7.32 (m, 12H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 189.0, 159.6, 152.9, 141.9, 133.2, 132.9, 128.7, 127.6, 127.5, 119.9, 119.3 (q, *J* = 258.9 Hz), 78.7; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}F_3NaNO$ $[M+Na]^+$ 390.1082, found 390.1091.

2-(benzhydrylimino)-1-(thiophen-2-yl)ethanone (1k). The hydrate (1.25 mg, 7.90 mmol) was treated with diphenylmethylamine (1.36 mL, 1.91 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to light yellow oil. Column chromatography (SiO_2, 20% ethyl acetate in hexanes) of the residue provided the title compound as light brown solid which was recrystallized from hexanes. Brown crystals (1.66 g, 69%). Mp 71–74 °C, IR (film) 3085, 3061, 3027, 2867, 1632, 1599 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 3.8, 1.0 Hz, 1H), 8.07 (s, 1H), 7.76 (dd, *J* = 5.0, 1.0, 1H), 7.44–7.43 (m, 4H), 7.40–7.35 (m, 4H), 7.31–7.28 (m, 2H), 7.18 (dd, *J* = 4.8, 4.0 Hz, 1H), 5.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 182.2, 142.2, 138.5, 136.7, 136.0, 128.7, 128.5, 127.7, 127.5, 78.2; HRMS (ESI): Exact mass calcd for $C_{19}H_{15}NNaOS$ $[M+Na]^+$ 328.0772, found 328.0772.

1-(benzhydrylimino)-3,3-dimethylbutan-2-one (1l). The hydrate (1.00 g, 7.57 mmol) was treated with diphenylmethylamine (1.3 mL, 7.6 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil (2.09 g, 99%) and used without further purification. IR (film) 3298, 3061, 3028, 2968, 2879, 1683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.35 (d, *J* = 4.4 Hz, 8H), 7.30–7.24 (m, 2H), 5.49 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 205.7, 158.8, 142.5, 128.6, 127.3, 78.6, 43.8, 26.7; HRMS (CI): Exact mass calcd for $C_{19}H_{21}NO$ $[M+H]^+$ 280.1705, found 280.1696.

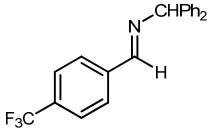
2-(benzhydrylimino)-1-cyclopropylethanone (1m). The hydrate (670 mg, 5.8 mmol) was treated with diphenylmethylamine (1.0 mL, 5.8 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to clear oil and recrystallized from hexanes to give colorless crystals (990 mg, 65%). Mp 64–66 °C, IR (film) 2085, 3061, 3027, 3007, 2865, 1683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.37–7.27 (m, 10H), 5.66 (s, 1H), 3.14 (dddd, *J* = 4.8, 4.7, 1.1, 1.0, 1H), 1.20–1.16 (m, 2H), 1.08–1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 201.2, 159.8, 142.1, 128.6, 127.6, 127.4, 77.4, 15.7, 12.6; HRMS (CI): Exact mass calcd for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1388, found 264.1395.

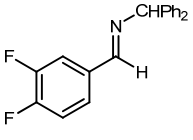
2-(benzhydrylimino)-1-cyclohexylethanone (1n). The hydrate (298 mg, 1.88 mmol) was treated with diphenylmethylamine (325 mL, 1.89 mmol) according to the general procedure. The reaction was stirred for 1 h and concentrated to light yellow solid and recrystallized from hexanes to give colorless crystals (397 mg, 65%). Mp 50–51 °C, IR (film) 3061, 2930, 2854, 1691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.37–7.27 (m, 10H), 5.60 (s, 1H), 3.49 (br, 1H), 1.88 (m, 2H), 1.82 (m, 2H), 1.44–1.33 (m, 4H), 1.27–1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 204.8, 159.0, 142.2, 128.7, 127.5, 127.5, 77.5, 44.4, 28.5, 25.9, 25.6; HRMS (CI): Exact mass calcd for $C_{21}H_{22}NO$ $[M-H]^+$ 304.1701, found 304.1682.

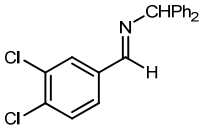


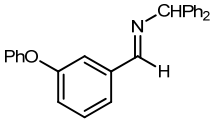
General Procedure for aldimine synthesis. All imines were prepared according to the procedure reported by Jacobsen.[10] Imines **1o, 1q, 1t** and **1w** were prepared by condensation of the aldehyde (1 equiv) with diphenylmethylamine (1 equiv) using 4 Å MS in dichloromethane at 0 °C and warmed to rt. Solution was filtered through Celite and concentrated. Unless otherwise stated the imine was recrystallized from toluene/petroleum ether.

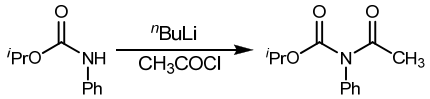
[10] Joly, G. D.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 4102.

N-(4-Trifluorobenzylidene)benzhydrylamine (1o). Colorless crystals (933 mg, 55%). Mp 82.4-82.7 °C; IR  (neat) 3062, 3027, 2848, 1643, 1493, 1323 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 4H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 4H), 7.29 (t, *J* = 6.9 Hz, 2H), 5.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 159.3, 143.5, 139.4, 132.3 (q, *J* = 32.5 Hz), 128.6, 128.5, 127.6, 127.2, 125.5 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.3 Hz), 77.9; HRMS (ESI): Exact mass calcd for $C_{21}H_{16}F_3N$ $[M]^+$ 339.1229, found 339.1217.

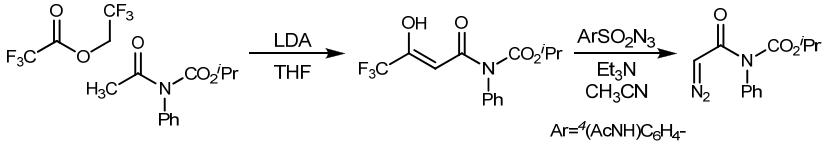
N-(3,4-Difluorobenzylidene)benzhydrylamine (1q). Colorless crystals (1.215, 79%). Mp 75.4-75.9 °C; IR  (neat) 3061, 3027, 2850, 1645, 1606, 1515, 1282 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.81 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.53-7.49 (m, 1H), 7.43 (d, *J* = 6.7, 4H), 7.37 (dd, *J* = 7.2, 7.2 Hz, 4H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.22 (dd, *J* = 17.6, 8.5 Hz, 1H), 5.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 158.3, 152.6 (dd, *J* = 138.9, 13.0 Hz), 150.1 (dd, *J* = 135.0, 13.1 Hz), 143.5, 133.5 (dd, *J* = 5.2, 3.7 Hz), 128.5, 127.6, 127.1, 125.2 (dd, *J* = 6.7, 3.4 Hz), 117.3 (d, *J* = 17.8 Hz), 116.4 (d, *J* = 17.9 Hz), 77.7; HRMS (CI): Exact mass calcd for $C_{20}H_{15}F_2N$ $[M]^+$ 307.1167, found 307.1172.

N-(3,4-Dichlorobenzylidene)benzhydrylamine (1t). Colorless crystals (1.334, 76%). Mp 84.0-84.6 °C; IR  (neat) 3061, 3026, 2849, 1642, 1557, 1471 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.01 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.47-7.27 (m, 10H), 5.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 158.2, 143.4, 136.1, 134.7, 133.0, 130.5, 129.7, 128.5, 127.5, 127.1, 77.8; HRMS (CI): Exact mass calcd for $C_{20}H_{15}Cl_2N$ $[M]^+$ 339.0582, found 339.0560.

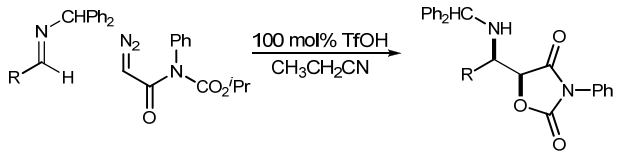
N-(3-Phenoxybenzylidene)benzhydrylamine (1w). Colorless crystals (1.696 g, 93%). Mp 109.3-109.9 °C; IR  (neat) 3060, 3026, 2848, 1643, 1580, 1489, 1256 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.34-7.33 (m, 11H), 7.26 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 5.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 160.0, 157.4, 157.1, 143.8, 138.3, 129.83, 129.78, 128.4, 127.6, 127.0, 123.4, 123.3, 121,2, 118.8, 118.7, 77.9; HRMS (ESI): Exact mass calcd for $C_{26}H_{22}NO$ $[M+H]^+$ 364.1701, found 364.1705.



Isopropyl N-(acetyl)-N-(phenyl)carbamate (S1). To a cold (-78 °C) solution of isopropyl *N*-(phenyl)carbamate (54.9 g, 312 mmol) in tetrahydrofuran (375 mL) was added *n*-butyllithium (132 mL, 330 mmol, 2.5M in hexanes) via addition funnel. The solution was stirred at -78 °C for 45 min after which acetic anhydride (34 mL, 380 mmol) was added via syringe over 5 min. Solution was allowed to warm to rt and was stirred for 3 h and then transferred to 1000 mL separatory funnel containing 250 mL of water and 250 mL of diethyl ether. Layers were separated and aqueous was extracted with diethyl ether. Combined organic extracts were washed with satd $NaHCO_3$, brine, dried and concentrated to light yellow solid. (69.8 g, 99%). Mp 84.5-85.5 °C; R_f = 0.38 (20% EtOAc/hexanes); IR (neat) 2983, 1738, 1711, 1262 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 4.97 (sept, *J* = 6.3 Hz, 1H), 2.60 (s, 3H), 1.16 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 172.9, 153.7, 138.3, 129.0, 128.2, 128.0, 71.1, 26.5, 21.5; HRMS (ESI): Exact mass calcd for $C_{12}H_{15}NaNO_3$ $[M+Na]^+$ 244.0950, found 244.0954. Anal. calcd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.84; N, 6.33. Found: C, 65.10; H, 6.87; N, 6.21.



Isopropyl N-(diazoacetyl)-N-(phenyl)carbamate (2). To a cold (-78 °C) solution of the carbamate (1.086 g, 4.908 mmol) in THF (20 mL) was added a freshly prepared solution of lithium diispropylamide in THF (13.5 mL, 6.08 mmol, 0.45 M). The solution was stirred at -78 °C for 30 m at which time trifluoroethyl trifluoroacetate (1.40 mL, 10.5 mmol) was added in one portion. The solution was stirred 15 m and then quenched with satd aq NH_4Cl and extracted with Et_2O. The combined organic layers were washed with 50% acetic acid in water and brine, dried, and concentrated to a brown oil. To a solution of the brown oil in acetonitrile (3.4 mL) was added *p*-ABSA (1.172 g, 5.136 mmol) and then triethylamine (1.0 mL, 7.2 mmol). The reaction was stirred at ambient temperature for 1 h and then diluted in dichloromethane, filtered through a pad of Celite, and condensed to a brown oil that was purified by silica gel flash chromatography (15% ethyl acetate in hexanes) at 0 °C to afford the diazoacetyl carbamate as a light yellow solid (425 mg, 35%). Mp 61.5-62.5 °C; R_f = 0.38 (20% EtOAc/hexanes); IR (neat) 2983, 2115, 1729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41-7.35 (m, 3H), 7.13-7.10 (m, 2H), 6.61 (s, 1H), 4.94 (sept, *J* = 6.0 Hz, 1H). 1.14 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 166.9, 153.4, 137.6, 129.0, 128.9, 128.6, 128.1, 71.2, 51.8, 21.5; HRMS (ESI): Exact mass calcd for $C_{12}H_{13}NaN_3O_3$ $[M+Na]^+$ 270.0855, found 270.0859. Anal. calcd for $C_{12}H_{13}N_3O_3$: C, 58.28; H, 5.30; N, 17.00. Found: C, 58.35; H, 5.22; N, 16.82.



General procedure for the *syn*-Glycolate Mannich reaction. To a cold (-78 °C) solution of imine (1.0 equiv) and α-diazo imide (1.2 equiv) in propionitrile (1.0 mL) was added dry TfOH (1.0 equiv), and the solution was stirred at -78 °C. The reaction was quenched with satd aq $NaHCO_3$ and extracted with ethyl acetate. The organic layers were dried, concentrated, and the resulting solid was purified by silica gel flash chromatography.

***syn*-Methyl 2-(benzhydrylamino)-2-(2,4-dioxo-3-phenyloxazolidin-5-yl)acetate (3a).** Imine (39 mg, 150 μmol) was treated with α-diazo imide (44.5 mg, 180 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (15% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (50.1 mg, 76%). Mp 120.5-121.5 °C; R_f = 0.07 (10% EtOAc/hexanes); IR (film) 3323, 3028, 2954, 1820, 1749, 1503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55-7.34 (m, 5H), 7.34-7.22 (m, 10H), 5.27 (d, *J* = 1.9 Hz, 1H), 5.00 (d, *J* = 3.4 Hz, 1H), 3.98 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.82 (s, 3H), 2.70 (dd, *J* = 10.9, 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.4, 169.5. 153.9, 142.9, 141.0, 130.8, 129.5, 129.4, 129.1, 129.0, 128.7, 128.6, 127.73, 127.68, 127.6, 127.2, 125.6, 125.5, 80.1, 65.5, 58.2, 53.0; HRMS (CI): Exact mass calcd for $C_{25}H_{23}N_2O_5$ $[M+H]^+$ 431.1607, found 431.1608. Anal Calcd for $C_{25}H_{22}N_2O_5$: C, 69.76; H, 5.15; N, 6.51. Found: C, 69.70; H, 5.16; N, 6.48. Relative stereochemistry determined by X-ray diffraction of a crystal grown from toluene in a chamber containing petroleum ether.

***syn*-5-(1-(Benzhydrylamino)-2-oxo-2-phenylethyl)-3-phenyloxazolidine-2,4-dione (3b).** Imine (46 mg, 150 μmol) was treated with α-diazo imide (47.4 mg, 192 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (15% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (54 mg, 77%). Mp 133-133.5 °C; R_f = 0.089 (10% EtOAc/hexanes); IR (film) 3312, 3062, 1823, 1749, 1686 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4

Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.55-7.45 (m, 8H), 7.35-7.20 (m, 9H), 5.13 (d, *J* = 2.1 Hz, 1H), 4.88-4.87 (m, 2H), 3.24 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 196.3, 169.9, 153.8, 142.7, 141.6, 134.4, 134.1, 130.8, 129.4, 129.1, 129.0, 128.9, 128.62, 128.57, 128.4, 127.6, 127.5, 127.3, 125.7, 78.9, 65.5, 60.1; HRMS (ESI): Exact mass calcd for $C_{30}H_{24}N_2NaO_4$ $[M+Na]^+$ 499.1634, found 499.1645. Anal Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.25; H, 5.04; N, 5.85.

***syn*-5-(1-(Benzhydrylamino)-2-oxo-2-p-tolylethyl)-3-phenyloxazolidine-2,4-dione (3c).** Imine (50.4 mg, 161 μmol) was treated with α-diazo imide (47.3 mg, 191 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred at 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (59 mg, 79%). Mp 138.5-139.5 °C; R_f = 0.091 (10% EtOAc/hexanes); IR (film) 3311, 3061, 3026, 1823, 1751, 1685 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.31-7.21 (m, 11H), 5.12 (d, *J* = 2.2 Hz, 1H), 4.87-4.85 (m, 2H), 3.24 (br s, 1H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 195.7, 170.0, 153.9, 145.4, 142.9, 141.7, 131.9, 130.9, 129.8, 129.5, 129.1, 128.7, 128.6, 127.7, 127.6, 127.5, 127.3, 125.7, 79.2, 65.5, 59.9, 21.8; HRMS (ESI): Exact mass calcd for $C_{31}H_{27}N_2O_4$ $[M+H]^+$ 491.1965, found 491.1967.

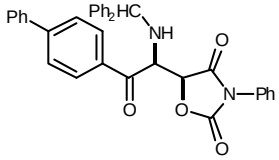
***syn*-5-(1-(Benzhydrylamino)-2-(4-bromophenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3d)**. Imine (59.3 mg, 157 μmol) was treated with α-diazo imide (44.9 mg, 182 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless oil (60 mg, 69%). R_f = 0.11 (10% EtOAc/hexanes); IR (film) 3307, 3061, 3024, 1822, 1749, 1686 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (dd, *J* = 7.9, 7.6 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.31-7.22 (m, 9H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.88 (s, 1H), 4.82 (br s, 1H), 3.21 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 195.4, 170.0, 153.8, 142.5, 141.5, 133.1, 132.5, 130.8, 129.9, 129.6, 129.5, 129.1, 128.72, 128.69, 127.8, 127.7, 127.6, 127.4, 125.7, 78.4, 65.6, 60.0; HRMS (ESI): Exact mass calcd for $C_{30}H_{24}BrN_2O_4$ $[M+H]^+$ 555.0914, found 555.0908.

***syn*-5-(1-(Benzhydrylamino)-2-(4-fluorophenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3e).** Imine (48 mg, 150 μmol) was treated with α-diazo imide (46.8 mg, 189 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (59 mg, 81%). Mp 146.5-147 °C; R_f = 0.091 (5% EtOAc/hexanes); IR (film) 3309, 3063, 3024, 1824, 1750, 1688 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.54 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.47 (dd, *J* = 7.4, 7.4 Hz, 1H) 7.33 (d, *J* = 7.2 Hz, 2H), 7.31-7.27 (m, 7H), 7.22 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 5.10 (d, *J* = 2.3 Hz, 1H), 4.88 (br s, 1H), 4.84 (dd, *J* = 6.0, 2.3 Hz, 1H), 3.23 (br d, *J* = 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 194.7, 170.0, 167.2, 165.4, 153.8, 142.6, 141.6, 131.3, 131.2, 130.8, 129.5, 129.1, 128.70, 128.67, 127.7, 127.64, 127.61, 127.4, 125.7, 116.4 (d), 78.5, 65.5, 59.9; HRMS (ESI): Exact mass calcd for $C_{30}H_{24}FN_2O_4$ $[M+H]^+$ 495.1715, found 495.1719.

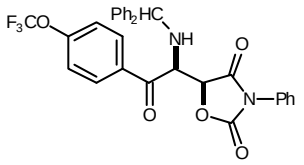
***syn*-5-(1-(Benzhydrylamino)-2-(4-methoxyphenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3f).** Imine (50 mg, 150 μmol) was treated with α-diazo imide (45.1 mg, 182 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (52 mg, 70%). Mp 126-127 °C; R_f = 0.056 (10% EtOAc/hexanes); IR (film) 3307, 3027, 2933, 1823, 1751, 1678 cm^{-1}; ^{1}H NMR

(600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.1 Hz, 2H), 7.54 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.31-7.24 (m, 7H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 9.1 Hz, 2H), 5.12 (d, *J* = 2.3 Hz, 1H), 4.85 (d, *J* = 1.4 Hz, 1H), 4.83 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.88 (s, 3H), 3.24 (dd, *J* = 10.1, 2.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 194.4, 170.1, 164.4, 153.9, 142.9, 141.7, 130.9, 129.5, 129.0, 128.63, 128.59, 127.7, 127.6, 127.5, 127.3, 127.2, 125.7, 114.3, 79.2, 65.5, 59.6, 55.6; HRMS (ESI): Exact mass calcd for $C_{31}H_{27}N_2O_5$ $[M+H]^+$ 507.1914, found 507.1922.

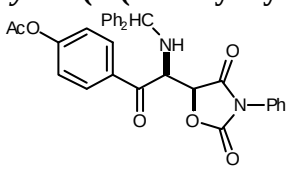
***syn*-5-(1-(Benzhydrylamino)-2-(biphenyl-4-yl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3g).** Imine (57 mg, 150 μmol) was treated with α-diazo imide (45.1 mg, 182 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (66 mg, 81%). Mp 181.5-183 °C; R_f = 0.11 (10% EtOAc/hexanes); IR (film) 3309, 3029, 1823, 1750, 1685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.50-7.47 (m, 5H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.33-7.27 (m, 7H), 7.22 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.18 (d, *J* = 2.2 Hz, 1H), 4.92 (dd, *J* = 10.5, 2.0 Hz, 1H), 4.91 (d, *J* = 4.1 Hz, 1H), 3.27 (dd, *J* = 10.5, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 195.8, 170.0, 153.9, 147.0, 142.8, 141.7, 139.4, 133.0, 130.9, 129.5, 129.09, 129.06, 128.7, 128.64, 128.60, 127.7, 127.6, 127.4, 127.3, 125.8, 79.0, 65.6, 60.1; HRMS (ESI): Exact mass calcd for $C_{36}H_{29}N_2O_4$ $[M+H]^+$ 553.2122, found 553.2123.



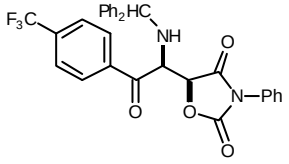
***syn*-5-(1-(Benzhydrylamino)-2-(4-trifluormethoxyphenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3h).** Imine (59.7 mg, 153 μmol) was treated with α-diazo imide (45.0 mg, 182 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (55 mg, 64%). Mp 148-150 °C; R_f = 0.095 (10% EtOAc/hexanes); IR (film) 3324, 3064, 2924, 2853, 1824, 1750, 1692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.54 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.49-7.45 (m, 3H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.31-7.22 (m, 10H), 5.10 (d, *J* = 2.2 Hz, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.85 (dd, *J* = 10.5, 1.9 Hz, 1H), 3.23 (dd, *J* = 10.5, 3.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 195.0, 169.9, 153.8, 153.3, 142.5, 141.5, 132.6, 130.8, 130.6, 129.5, 129.4 129.1, 128.72, 128.69, 127.8, 127.7, 127.6, 127.4, 125.7, 120.8 78.3, 65.6, 60.1; HRMS (ESI): Exact mass calcd for $C_{31}H_{23}F_3N_2NaO_5$ $[M+Na]^+$ 583.1457, found 583.1445. Anal Calcd for $C_{31}H_{23}F_3N_2O_5$: C, 66.43; H, 4.14; N, 5.00. Found: C, 66.03; H, 4.20; N, 4.89.



***syn*-5-(1-(Benzhydrylamino)-2-(4-acetoxyphenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3i).** Imine (53 mg, 150 μmol) was treated with α-diazo imide (44.9 mg, 182 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (15% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (52 mg, 66%). Mp 98-100 °C; R_f = 0.023 (10% EtOAc/hexanes); IR (film) 3308, 3063, 3028, 2925, 1823, 1752, 1688 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.54 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.31-7.24 (m, 7H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 5.12 (d, *J* = 2.3 Hz, 1H), 4.87 (br s, 1H), 4.85 (br d, *J* = 9.4 Hz, 1H), 3.23 (br d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 195.0, 169.9, 168.6, 155.2, 153.8, 142.7, 141.6, 131.9, 130.9, 130.2, 129.5, 129.1, 128.70, 128.66, 127.71, 127.66, 127.6, 127.3, 125.7, 122.4, 78.7, 65.6, 60.0, 21.1; HRMS (ESI): Exact mass calcd for $C_{32}H_{27}N_2O_6$ $[M+H]^+$ 535.1864, found 535.1872.

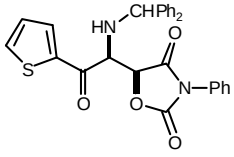


***syn*-5-(1-(Benzhydrylamino)-2-(4-trifluormethylphenyl)-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3j).**



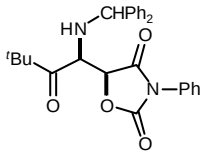
Imine (58 mg, 160 μmol) was treated with α-diazo imide (45.6 mg, 184 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (58 mg, 72%). Mp 160.5-161 °C; R_f = 0.11 (10% EtOAc/hexanes); IR (film) 3314, 3064, 3029, 1824, 1751, 1696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.49-7.46 (m, 3H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.31-7.27 (m, 7H), 7.24 (t, *J* = 7.1 Hz, 1H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.92 (br s, 1H), 4.87 (br d, *J* = 8.0 Hz, 1H), 3.22 (br d, *J* = 6.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 195.8, 169.9, 153.7, 142.4, 141.5, 137.3, 135.4 (d), 130.8, 129.5, 129.2, 128.83, 128.76, 128.7, 127.82, 127.77, 127.6, 127.4, 126.2 (d), 125.7, 78.0, 65.6, 60.5; HRMS (ESI): Exact mass calcd for $C_{31}H_{24}F_3N_2O_4$ $[M+H]^+$ 545.1683, found 545.1680. Anal calcd for $C_{31}H_{23}F_3N_2O_4$: C, 68.38; H, 4.26; N, 5.14. Found: C, 68.12; H, 4.26; N, 4.99.

***syn*-5-(1-(Benzhydrylamino)-2-oxo-2-(thiophen-2-yl)ethyl)-3-phenyloxazolidine-2,4-dione (3k).** Imine



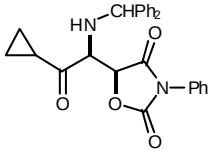
(46 mg, 150 μmol) was treated with α-diazo imide (44 mg, 180 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (15-25% ethyl acetate in hexanes) to afford the oxazolidine dione as colorless oil (57 mg, 80%). R_f = 0.14 (20% EtOAc/hexanes); IR (film) 3063, 3027, 2926, 1824, 1750, 1711, 1665, 1597 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 4.1, 0.9 Hz, 1H), 7.61 (dd, *J* = 3.9, 0.8 Hz, 1H), 7.59–7.54 (m, 2H), 7.54–7.48 (m, 3H), 7.39–7.11 (m, 10H), 7.17 (dd, *J* = 4.8, 3.9 Hz, 1H), 5.21 (d, *J* = 2.4 Hz, 1H), 4.90 (d, *J* = 3.8 Hz, 1H), 4.71 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.24 (dd, *J* = 11.2, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 188.8, 169.8, 153.8, 142.7, 141.4, 141.1, 135.8, 133.1, 130.8, 129.4, 129.3, 129.0, 129.0, 128.6, 128.6, 128.5, 127.7, 127.6, 127.5, 127.2, 125.7, 125.5, 79.1, 67.6, 65.3, 61.0; HRMS (CI): Exact mass calculated for $C_{28}H_{23}N_2O_4S$ $[M+H]^+$ 483.1373, found 483.1368.

***syn*-5-(1-(Benzhydrylamino)-3,3-dimethyl-2-oxobutyl)-3-phenyloxazolidine-2,4-dione (3l).** Imine (43 mg,



150 μmol) was treated with α-diazo imide (45 mg, 180 μmol) and dry TfOH (13μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes) to afford the oxazolidine dione as colorless oil (59.5 mg, 88%). R_f = 0.29 (20% EtOAc/hexanes); IR (film) 3308, 3028, 2967, 1824, 1771, 1708, 1598 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.21 (m, 15H), 5.11 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 5.6 Hz, 1H), 4.27 (dd, *J* = 9.9, 3.4 Hz, 1H), 2.88 (dd, *J* = 10.0, 5.6 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 211.4, 170.1, 154.3, 142.4, 141.8, 129.3, 129.0, 128.7, 128.6, 127.7, 127.6, 127.6, 127.3, 125.8, 77.1, 66.0, 60.2, 44.0, 26.9; HRMS (ESI): Exact mass calculated for $C_{28}H_{29}N_2O_4$ $[M+H]^+$ 457.2122, found 457.2067.

***syn*-5-(1-(Benzhydrylamino)-2-cyclopropyl-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3m).** Imine (132



mg, 500 μmmol) was treated with α-diazo imide (148 mg, 600 μmmol) and dry TfOH (44μL, 500 μmmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (10-20% ethyl acetate in hexanes) to afford the oxazolidine dione as colorless oil (215 mg, 98%) which was recrystallized from 10% EtOAc in hexanes to give colorless crystals (136.5 mg, 62%). Mp 167–168 °C; R_f = 0.23 (20% EtOAc/hexanes); IR (film) 3406, 3027, 2923, 1820, 1748, 1707, 1598 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57–7.49 (m, 2H), 7.49–7.43 (m, 3H), 7.37–7.20 (m, 10H), 5.34 (d, *J* = 1.6 Hz, 1H), 4.86 (d, *J* = 4.6 Hz, 1H), 4.17 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.99 (dd, *J* = 10.1, 4.7 Hz, 1H), 1.98 (m, 1H), 1.24–1.17 (m, 1H), 1.17–1.09 (m, 1H), 1.07–0.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 205.8, 170.1, 154.0, 142.7, 141.7, 130.8, 129.4, 129.0, 128.6, 128.5, 127.5, 127.3, 125.7, 78.5, 65.6, 64.8, 18.8, 12.6, 11.5; HRMS (CI): Exact mass calculated for $C_{27}H_{24}N_2O_4$ $[M]^+$ 440.1736, found 440.1756.

***syn*-5-(1-(Benzhydrylamino)-2-cyclohexyl-2-oxoethyl)-3-phenyloxazolidine-2,4-dione (3n).** Imine (46 mg, 150 μmol) was treated with α-diazo imide (44 mg, 180 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 1 h. Purified by silica gel flash chromatography (5-15% ethyl acetate in hexanes) to afford the oxazolidine dione as colorless oil (70.0 mg, 97%). R_f = 0.37 (20% EtOAc/hexanes); IR (film) 2930, 2854, 1820, 1750, 1712, 1598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 15H), 5.18 (d, *J* = 2.6 Hz, 1H), 4.81 (d, *J* = 4.8 Hz, 1H), 4.11 (d, *J* = 10.1 Hz, 1H), 3.06 (dd, *J* = 10.1, 5.7 Hz, 1H), 2.52 (m, 1H), 1.85–1.12 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 208.6, 170.2, 153.9, 142.4, 141.8, 130.8, 129.4, 129.0, 128.6, 128.5, 127.5, 127.5, 125.7, 78.0, 65.8, 62.7, 47.5, 28.8, 27.7, 25.5, 25.4, 25.1; HRMS (CI): Exact mass calculated for $C_{30}H_{31}N_2O_4$ $[M+H]^+$ 483.2278, found 483.2228.

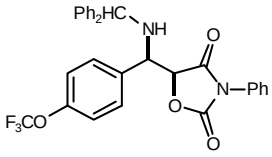
***syn*-5-(1-(Benzhydrylamino)(4-trifluoromethylphenyl)methyl))-3-phenyloxazolidine-2,4-dione (3o).** Imine (47 mg, 150 μmol) was treated with α-diazo imide (47 mg, 190 μmol) and dry TfOH (13 μL, 150 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (40 mg, 53%). Mp 173-174 °C; R_f = 0.14 (10% EtOAc/hexanes); IR (film) 3324, 3065, 3028, 1819, 1751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.58-7.45 (m, 5H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34-7.19 (m, 10H), 5.048 (d, *J* = 2.1 Hz, 1H), 4.63 (s, 1H), 4.35 (dd, *J* = 10.2, 2.1 Hz, 1H), 2.63 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.1, 154.1, 143.2, 141.4, 141.1, 131.1, 130.8, 130.7, 129.6, 129.2, 128.8, 128.1, 127.8, 127.6, 127.5, 126.8, 126.0 (t), 125.6, 82.4, 63.9, 58.9; HRMS (CI): Exact mass calcd for $C_{30}H_{23}F_3N_2NaO_3$ $[M+Na]^+$ 539.1558, found 539.1585. Anal Calcd for $C_{30}H_{23}F_3N_2O_3$: C, 69.76; H, 4.49; N, 5.42. Found: C, 69.47; H, 4.62; N, 5.15.

***syn*-5-(1-(Benzhydrylamino)(4-nitrophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3p).** Imine (48.4 mg, 153 μmol) was treated with α-diazo imide (44.8 mg, 181 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (52 mg, 69%). Mp 126.5-128 °C; R_f = 0.048 (10% EtOAc/hexanes); IR (film) 3324, 3062, 3028, 2927, 2853, 1817, 1750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 2H), 7.60-7.50 (m, 5H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.36-7.22 (m, 10H), 5.06 (d, *J* = 2.2 Hz, 1H), 4.60 (s, 1H), 4.42 (dd, *J* = 12.3, 1.8 Hz, 1H), 2.64 (d, *J* = 12.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 169.9, 154.0, 148.1, 144.8, 143.0, 140.8, 130.6, 129.6, 129.3, 128.9, 128.8, 128.7, 127.9, 127.7, 127.4, 126.8, 125.6, 124.3, 124.0, 82.0, 64.1, 58.8; HRMS (CI): Exact mass calcd for $C_{29}H_{24}N_3O_5$ $[M+H]^+$ 494.1716, found 494.1694. Anal Calcd for $C_{29}H_{23}N_2O_5$: C, 70.58; H, 4.70; N, 8.51. Found: C, 69.60; H, 4.69; N, 8.26.

***syn*-5-(1-(Benzhydrylamino)(3,4-difluorophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3q).** Imine (46.1 mg, 150 μmol) was treated with α-diazo imide (44.7 mg, 181 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (40 mg, 55%). Mp 143-143.5 °C; R_f = 0.12 (10% EtOAc/hexanes); IR (film) 3322, 3063, 3028, 2924, 1820, 1749, 1518 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.35-7.18 (m, 12H), 7.06-7.04 (m, 1H), 5.03 (d, *J* = 2.1 Hz, 1H), 4.63 (s, 1H), 4.25 (br d, *J* = 11.3 Hz, 1H), 2.50 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.1, 154.1, 150.6 (dd, *J* = 250, 41.8 Hz), 150.5 (dd, *J* = 250, 41.0 Hz) 143.2, 141.1, 134.6, 130.7, 129.6, 129.2, 128.8, 127.8, 127.6, 127.5, 126.8, 125.6, 123.8, 117.9 (d, *J* = 17.1 Hz), 116.7 (d, *J* = 17.4 Hz), 82.4, 63.9, 58.5; HRMS (CI): Exact mass calcd for $C_{29}H_{22}F_2N_2NaO_3$ $[M+Na]^+$ 507.1496, found 507.1476. Anal Calcd for $C_{29}H_{22}F_2N_2O_3$: C, 71.89; H, 4.51; N, 5.72. Found: C, 71.88; H, 4.51; N, 5.72.

***syn*-5-(1-(Benzhydrylamino)(4-fluorophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3r).** Imine (43.8 mg, 151 μmol) was treated with α-diazo imide (44.9 mg, 182 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (34 mg, 48%). Mp 147.5-148.5 °C; R_f = 0.13 (10% EtOAc/hexanes); IR (film) 3308, 3056, 3022, 2921, 1818, 1749, 1601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33-7.18 (m, 12H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 2H), 5.04 (d, *J* = 2.0 Hz, 1H), 4.62 (s, 1H), 4.25 (br s, 1H), 2.54 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.4, 154.2, 143.5, 141.3, 133.0, 130.8, 129.5, 129.43, 129.37, 129.1, 128.7, 127.7, 127.6, 127.5, 126.8, 125.6, 116.0 (d), 82.7, 63.8, 58.7; HRMS (CI): Exact mass calcd for $C_{29}H_{23}FN_2NaO_3$ $[M+Na]^+$ 489.1590, found 489.1581. Anal Calcd for $C_{29}H_{23}FN_2O_3$: C, 74.66; H, 4.97; N, 6.00. Found: C, 74.65; H, 4.91; N, 5.94.

***syn*-5-(1-(Benzhydrylamino)(4-trifluoromethoxyphenyl)methyl))-3-phenyloxazolidine-2,4-dione (3s)**.



Imine (53.3 mg, 150 μmol) was treated with α-diazo imide (44.6 mg, 180 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (41 mg, 51%). Mp 104.5-105.5 °C; R_f = 0.35 (20% EtOAc/hexanes); IR (film) 3323, 3063, 3027, 2924, 1818, 1749, 1504 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33-7.20 (m, 12H), 5.06 (d, *J* = 2.3 Hz, 1H), 4.65 (s, 1H), 4.31 (br d, *J* = 5.4 Hz, 1H), 2.59 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.2, 154.2, 143.3, 141.3, 136.0, 130.7, 129.6, 129.2, 128.8, 127.7, 127.5, 126.8, 125.6, 121.5, 82.5, 63.9, 58.7; HRMS (CI): Exact mass calcd for $C_{30}H_{24}F_3N_2O_4$ $[M+H]^+$ 533.1688, found 533.1664.

***syn*-5-(1-(Benzhydrylamino)(3,4-dichlorophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3t).** Imine (52.0 mg, 153 μmol) was treated with α-diazo imide (45.4 mg, 184 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (42 mg, 53%). Mp 105.5-106.5 °C; R_f = 0.33 (20% EtOAc/hexanes); IR (film) 3322, 3062, 3027, 2924, 1817, 1750, 1502 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.35-7.21 (m, 10H), 7.18 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.02 (d, *J* = 2.3 Hz, 1H), 4.62 (s, 1H), 4.25 (br s, 1H), 2.54 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.0, 154.1, 143.2, 141.0, 137.8, 133.4, 132.9, 131.1, 130.7, 129.6, 129.2, 128.81, 128.79, 127.8, 127.6, 127.5, 127.0, 126.8, 125.6, 82.3, 63.9, 58.4; HRMS (CI): Exact mass calcd for $C_{29}H_{23}Cl_2N_2O_3$ $[M+H]^+$ 517.1086, found 517.1096.

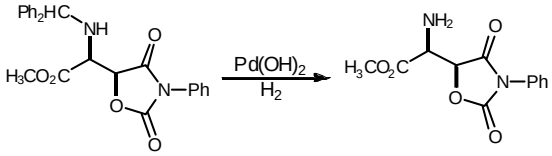
***syn*-5-(1-(Benzhydrylamino)(4-bromophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3u).** Imine (52.9 mg, 151 μmol) was treated with α-diazo imide (44.9 mg, 195 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 20 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (54 mg, 68%). Mp 139-139.5 °C; R_f = 0.35 (20% EtOAc/hexanes); IR (film) 3320, 3052, 3027, 2921, 2850, 1817, 1749, 1503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.5, 6.5 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.34-7.20 (m, 10H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 2.2 Hz, 1H), 4.63 (s, 1H), 4.25 (br s, 1H), 2.57 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.2, 154.2, 143.4, 141.2, 136.3, 132.2, 130.7, 129.6, 129.4, 129.2, 128.8, 127.7, 127.5, 126.8, 125.6, 122.7, 82.5, 63.8, 58.8; HRMS (CI): Exact mass calcd for $C_{29}H_{24}BrN_2O_3$ $[M+H]^+$ 527.0970, found 527.0968.

***syn*-5-(1-(Benzhydrylamino)(4-chlorophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3v).** Imine (45.2 mg, 148 μmol) was treated with α-diazo imide (44.9 mg, 182 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (42 mg, 59%). Mp 125-126 °C; R_f = 0.34 (20% EtOAc/hexanes); IR (film) 3322, 3059, 3027, 1817, 1749, 1492 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.33-7.18 (m, 12H), 5.04 (d, *J* = 2.1 Hz, 1H), 4.63 (s, 1H), 4.26 (br s, 1H), 2.57 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.3, 154.2, 143.4, 141.2, 135.8, 134.6, 130.7, 129.5, 129.3, 129.1, 129.0, 128.7, 128.2, 127.7, 127.5, 126.8, 125.6, 125.2, 82.5, 63.8, 58.7; HRMS (CI): Exact mass calcd for $C_{29}H_{24}ClN_2O_3$ $[M+H]^+$ 483.1475, found 483.1474. Anal Calcd for $C_{31}H_{23}F_3N_2O_4$: C, 68.38; H, 4.26; N, 5.14. Found: C, 68.12; H, 4.26; N, 4.99.

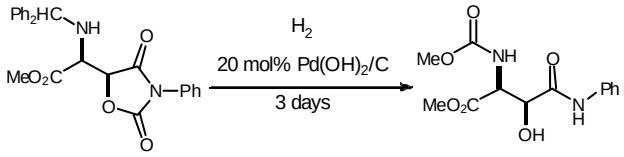
***syn*-5-(1-(Benzhydrylamino)(3-phenoxyphenyl)methyl))-3-phenyloxazolidine-2,4-dione (3w).** Imine (54.8 mg, 151 μmol) was treated with α-diazo imide (44.3 mg, 179 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (30 mg, 37%). Mp 164-165 °C; R_f = 0.32 (20% EtOAc/hexanes); IR (film) 3310, 3056, 3027, 2922, 1820, 1749, 1583 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.31-7.20 (m, 10H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 3H), 6.97 (s, 1H), 5.08 (d, *J* = 2.1 Hz, 1H), 4.70 (s, 1H), 4.23 (br s, 1H), 2.58 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 170.4, 158.0, 156.7, 154.2, 143.5, 141.3, 139.3, 130.8, 130.5, 129.9, 129.5, 129.1, 128.71, 128.68, 127.6, 127.5, 126.9, 125.7, 123.7, 122.0, 119.2, 118.7, 118.0, 82.6, 63.8, 59.1; HRMS (CI): Exact mass calcd for $C_{35}H_{28}N_2NaO_4$ $[M+Na]^+$ 563.1947, found 563.1921.

***syn*-5-(1-(Benzhydrylamino)(4-acetoxyphenyl)methyl))-3-phenyloxazolidine-2,4-dione (3x).** Imine (51.2 mg, 155 μmol) was treated with α-diazo imide (44.5 mg, 180 μmol) and dry TfOH (14.0 μL, 158 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (34 mg, 43%). Mp 171-171.5 °C; R_f = 0.16 (20% EtOAc/hexanes); IR (film) 3322, 3028, 2924, 2853, 1817, 1749 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.32-7.18 (m, 10H), 7.16 (d, *J* = 8.5 Hz, 2H), 5.05 (d, *J* = 2.2 Hz, 1H), 4.67 (s, 1H), 4.28 (br s, 1H), 2.57 (br s, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 170.4, 169.3, 154.3, 150.8, 143.5, 141.4, 134.8, 130.8, 129.5, 129.1, 128.7, 127.64, 127.58, 127.5, 126.8, 125.8, 122.2, 82.7, 63.7, 58.7, 29.7; HRMS (CI): Exact mass calcd for $C_{31}H_{26}N_2NaO_5$ $[M+Na]^+$ 529.1739, found 529.1722.

***syn*-5-(1-(Benzhydrylamino)(4-cyanophenyl)methyl))-3-phenyloxazolidine-2,4-dione (3y).** Imine (44.7 mg, 151 μmol) was treated with α-diazo imide (45.0 mg, 182 μmol) and dry TfOH (13.5 μL, 153 μmol) according to the general procedure and stirred for 15 h. Purified by silica gel flash chromatography (10% ethyl acetate in hexanes) to afford the oxazolidine dione as a colorless solid (26 mg, 36%). Mp 170-171 °C; R_f = 0.18 (20% EtOAc/hexanes); IR (film) 3305, 3062, 3026, 2923, 1817, 1749 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.57 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.35-7.21 (m, 10H), 5.04 (d, *J* = 2.2 Hz, 1H), 4.59 (s, 1H), 4.35 (d, *J* = 10.0, 1H), 2.60 (br d, *J* = 11.2, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) ppm 169.9, 154.0, 143.0, 142.8, 140.9, 132.8, 130.6, 129.6, 129.2, 128.8, 128.5, 127.9, 127.7, 127.4, 126.7, 125.5, 118.2, 112.7, 82.0, 64.0, 59.0; HRMS (CI): Exact mass calcd for $C_{30}H_{23}N_3NaO_3$ $[M+Na]^+$ 496.1637, found 496.1659.



***syn*-Methyl 2-amino(2,4-dioxo-3-phenyloxazolidin-5-yl)acetate (5)**. To a solution of oxazolidine dione (430 mg, 999 μmol) in ethanol (10.0 mL) and ethyl acetate (1.0 mL) was added $Pd(OH)_2$ (171 mg, 100 μmol, 20% on carbon, 50% H_2O). The flask was put under an atmosphere of hydrogen and the solution was stirred at ambient temperature for 5 h. The reaction was filtered through Celite, and concentrated, and the resulting solid was purified by silica gel flash chromatography (30% ethyl acetate in hexanes) to afford the amine as a colorless solid (235 mg, 89%). Mp 112.0-113.0 °C; R_f = 0.078 (30% EtOAc/hexanes); IR (film) 3400, 3338, 2956, 1817, 1746, 1410 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.44-7.41 (m, 3H), 5.34 (d, *J* = 1.7 Hz, 1H), 4.16 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 3H), 1.77 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 171.3, 170.3, 154.1, 130.8, 129.4, 129.1, 125.7, 80.3, 54.5, 53.2; HRMS (CI): Exact mass calcd for $C_{12}H_{13}N_2O_5$ $[M+H]^+$ 265.0819, found 265.0810.



***syn*-Methyl 3-hydroxy-2-(methoxycarbonylamino)-4-oxo-4-(phenylamino)butanoate (6).** Dione (100 mg, 232 μmmol) was suspended in methanol (2 mL) and palladium(II) hydroxide (20% wt on carbon, 33 mg, 23 μmmol) was added in one portion. The flask was put under an atmosphere of hydrogen and the solution was stirred at ambient temperature for 3 days and then filtered through Celite and concentrated. The residue was dissolved in ethyl acetate, washed with satd NH_4Cl, dried, concentrated, and resulting residue was purified using flash chromatography (SiO_2, 50% ethyl acetate in hexanes) to afford amido alcohol (30.9 mg 45%) as colorless solid. Mp 146–148 °C, R_f = 0.14 (50% EtOAc/ hexanes), IR (film) 3341, 2955, 2924, 2851, 1723, 1600, 1537, 1445 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.13 (dd, *J* = 7.6, 7.2 Hz, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 4.99 (br, 1H), 4.89 (dd, *J* = 9.4, 2.6 Hz, 1H), 4.72 (dd, *J* = 6.6, 2.6 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (150 MHz, CDCl3) ppm 170.9, 169.0, 157.7, 136.8, 129.0, 124.9, 120.0, 72.7, 56.5, 53.0, 52.9; HRMS (ESI): Exact mass calcd for $C_{13}H_{16}N_2NaO_6$ $[M+Na]^+$ 319.0901. Found 319.0895.

Determination of the Relative Configuration. A crystal of purified *syn*-oxazolidine dione *syn*-**3a** was grown from toluene and petroleum ether, and the relative stereochemistry was determined by X-ray crystallography. The crystallographic data (CCDC 734742) can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

compound	**3a**
crystals obtained from	Toluene/Light Petroleum Ether
color	colorless
formula	$C_{25}H_{22}N_2O_5$
formula weight	430.45
wavelength (Å)	0.71073
crystal size (mm^3)	0.30 x 0.23 x 0.22
crystal system	Monoclinic
space group	$P2_1/c$
unit cell dimensions	
a (Å)	10.0853(3)
b (Å)	16.6495(6)
c (Å)	13.6635(5)
α (deg)	90
β (deg)	109.0620(9)
γ (deg)	90
V ($Å^3$)	2168.50(13)
Z	4
density, calcd (Mg/m^3)	1.318
abs coeff μ (mm^{-1})	0.093
F (000)	904
T (K)	130(2)
θ range (ϖ scans)	2.00-27.54
index ranges	$-13 \le h \le 13$
	$-21 \le k \le 21$
	$-17 \le l \le 17$
no. reflections collected	33553
no. independent reflections	4997
no. of data/restr/parameters	4997/0/315
abs. corr	Semi-empirical from equivalents
Refinement method	Full matrix least squares on F^2
R(int)	0.0342
goodness-of-fit	1.020
R1/wR2 [$I>2\sigma(I)$]	0.0354, 0.0866
R1/wR2 (all data)	0.0439, 0.0940
extinction coefficient	
max/min peaks ($e/Å^3$)	0.300 and -0.184