Supporting Information

Pd(OAc)₂-Catalyzed Carbonylation of Amines

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General. All melting points were uncorrected. Mass spectrometric data were obtained by electron ionization at 70 eV. ^1H NMR spectra (270 MHz) were obtained in CDCl_3 using TMS as an internal reference.

General Procedure for Preparation of Ureas 1a-1p and 2cs-2rt. A stirred suspension of $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), $\text{Cu}(\text{OAc})_2$ (18.1 mg, 0.1 mmol) and a primary amine (0.2 mmol) in toluene (2 mL) in an atmosphere of CO gas (ca. 1~1.5 L) containing air (6 mL, corresponding to 0.05 mmol of O_2) delivered from a toy balloon was gently refluxed in an oil bath at 120 °C for 2 h. Precipitates were removed by filtration through a powdered MgSO_4 pad, and the solvent was evaporated to afford the crude product, which was purified by crystallization from the appropriate solvents to give the corresponding symmetrical urea (**1a-1p**).

For preparation of unsymmetrical trisubstituted ureas (**2cs-2rt**), a secondary amine (0.24 or 0.4 mmol), pyrrolidine, piperidine or dipropylamine, and air (12 mL) were added into the reaction mixture.

***N,N'*-Dibutylurea (1a):** mp 67-68.8 °C (hexane) (lit.¹ mp 65-68 °C; lit.^{2a} mp 67-69 °C, lit.³ mp 72-73 °C; lit.⁴ mp 73 °C); IR (Nujol) 3326, 1618, 1580 cm^{-1} ; ^1H NMR δ 0.91 (t, J = 7.3 Hz, 6H), 1.30-1.55 (m, 8H), 3.15 (q, J = 6.0 Hz, 4H), 4.57 (br. s, 2H); EI-MS m/z (relative intensity) 172 (M^+ , 100), 157 (9.6), 143 (14.4), 130 (29.6), 101 (25.6), 87 (19.2), 74 (28.0), 57 (36.0), 44 (80.0).

1,3-Dihexylurea (1b): colorless crystals (87%), mp 73.5-74 °C (hexane) (lit.^{2a} mp 73-74 °C); IR (Nujol) 3330, 1588, 1509 cm^{-1} ; ^1H NMR δ 0.88 (t, J = 6.6 Hz, 6H), 1.28-1.34 (m, 12H), 1.43-1.50 (m, 4H), 3.10-3.18 (m, 4H), 4.50 (br. s, 2H); EI-MS m/z (relative intensity) 228 (M^+ , 100), 199 (45.5), 185 (56.7), 171 (15.4), 158 (39.9), 145 (9.9), 128 (25.6), 115 (17.9), 102 (29.9), 87 (12.1), 74 (17.2).

1,3-Dibenzylurea (1c): colorless crystals (94%); mp 166-169 °C (CH₂Cl₂-Et₂O) (lit.³ mp 169-170 °C; lit.^{2a} mp 169-171 °C; lit.⁵ mp 170 °C; lit.⁷ mp 171-171.5 °C); IR (Nujol) 3322, 1625, 1579 cm⁻¹; ¹H NMR δ 4.40 (d, *J* = 5.9 Hz, 4H), 4.56 (br. s, 2H), 7.30 (m, 10H); EI-MS *m/z* (relative intensity) 240 (M⁺, 42.8), 149 (29.7), 106 (100).

1,3-Bis[3,4-(methylenedioxy)benzyl]urea (1d): colorless crystals (82%); mp 227-228 °C (dioxane) (lit.⁸ mp 219-220 °C); IR (Nujol) 3306, 1623, 1575, 1505 cm⁻¹; ¹H NMR (CDCl₃-DMSO-D₆) δ 4.28, 4.30 (each s, each 2H), 4.51 (br. s, 2H), 5.94 (s, 4H), 6.70-6.79 (m, 6H); EI-MS *m/z* (relative intensity) 328 (M⁺, 29.3), 193 (47.0), 150 (100).

1,3-Bis(phenethyl)urea (1e): colorless crystals (90%); mp 132-134 °C (MeOH) (lit.⁹ mp 139 °C; lit.¹⁰ mp 140-41 °C); IR (Nujol) 3336, 1616, 1576 cm⁻¹. ¹H NMR δ 2.79 (t, *J* = 6.6 Hz, 4H), 3.41 (q, *J* = 6.6 Hz, 4H), 4.14 (br. s, 2H), 7.16-7.30 (m, 10H); EI-MS *m/z* (relative intensity) 268 (M⁺, 15.0), 177 (54.2), 147 (11.3), 120 (8.7), 104 (42.3), 91 (100).

1,3-Bis[3,4-(methylenedioxy)phenethyl]urea (1f): colorless crystals (82%); mp 205-206 °C (CH₂Cl₂-MeOH); IR (Nujol) 3330, 1611 cm⁻¹; ¹H NMR δ 2.70 (t, *J* = 6.9 Hz, 4H), 3.36 (t, *J* = 6.9 Hz), 5.93 (br. s, 4H), 6.61 (dd, *J* = 7.9, 6.3 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 2H); EI-MS *m/z* (relative intensity) 350 (M⁺, 5.6), 208 (5.4), 191 (8.2), 148 (100), 135 (68.6). Anal. Calcd for C₁₉H₂₀N₂O₅: C, 64.04; H, 5.66; N, 7.86. Found: C, 63.94; H, 5.68; N, 7.71.

1,3-Bis[2-bromo-4,5-(methylenedioxy)phenethyl]urea (1g): colorless crystals (79%); mp 223-225 °C (CH₂Cl₂); IR (Nujol) 3306, 1607 cm⁻¹; ¹H NMR δ 2.86 (t, *J* = 6.9 Hz, 4H), 3.38 (q, *J* = 6.6 Hz, 4H), 4.28 (br. s, 2H), 5.95 (s, 4H), 6.72 (s, 2H), 6.99 (s, 2H); EI-MS *m/z* (relative intensity) 513 (M⁺, 0.3), 226 (63.0), 213 (100), 164 (60.0). Anal. Calcd for C₁₉H₁₈Br₂N₂O₅: C, 44.38; H, 3.53; Br, 31.08; N, 5.45. Found: C, 44.53; H, 3.58; Br, 30.87; N, 5.33.

1,3-Bis(2-bromo-3,4-dimethoxyphenethyl)urea (1h): colorless crystals (70%); mp 154-156 °C (CH₂Cl₂-MeOH); IR (Nujol) 3326, 1618, 1584 cm⁻¹; ¹H NMR δ 2.91 (t, *J* = 6.9 Hz, 6H), 3.40 (q, *J* = 6.6 Hz, 4H), 3.84 (s, 6H), 3.86 (s, 6H), 4.27 (br, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz); EI-MS *m/z* (relative intensity) 546 (M⁺, 2.2), 467 (45.8), 285 (17.8), 242 (84.3), 229 (100), 215 (10.5), 180 (34.4), 164 (29.7). Anal. Calcd for C₂₁H₁₉Br₂N₂O₅: C, 46.17; H, 4.80; Br, 29.26; N, 5.13. Found: C, 46.04; H, 5.00; Br, 29.37; N, 5.06.

1,3-Dicyclohexylurea (1i): colorless crystals (76%); mp 235-236 °C (MeOH) (lit.^{2a} mp 229-230 °C; lit.¹¹ mp 232-233 °C); IR (Nujol) 3326, 1628, 1576, 1537 cm⁻¹; ¹H NMR δ 1.00-1.25 (m, 4H), 1.25-2.15 (m, 4H), 1.55-1.75 (m, 4H), 1.85-2.00 (m, 4H), 3.40-3.55 (m, 2H), 4.04, 4.07 (each br. s, each 1H). EI-MS *m/z* (relative intensity) 224 (M⁺, 43), 143 (35.6), 99 (52.9), 56 (100).

1,3-Di(2-adamantyl)urea (1j): colorless crystals (74%); mp >300 °C (hexane); IR (Nujol) 3358, 1620, 1561 cm⁻¹; ¹H NMR δ 1.57-1.59 (m, 6H), 1.65 (m, 4H), 1.74-1.84 (m, 14H), 1.93 (m, 4H), 3.78-3.81 (m, 2H), 4.60-4.65 (m, 2H); EI-MS *m/z* (relative intensity) 328 (M⁺, 37.3),

150 (100), 135 (24.1). Anal. Calcd for $C_{21}H_{32}N_2O$: C, 76.78, H, 9.82; N, 8.53. Found: C, 76.56; H, 9.82; N, 8.44.

1,3-Di-*t*-butylurea (1k): colorless crystals (34%); mp 245 °C (hexane) (lit.³ mp 238-239 °C; lit.¹² mp 243 °C; lit.^{2a} mp 245 °C; lit.⁴ mp 248 °C); IR (Nujol) 3350, 1639, 1544 cm^{-1} ; 1H NMR δ 1.32 (s, 18H), 3.99 (br. s, 2H); EI-MS m/z (relative intensity) 172 (M^+ , 3.5), 157 (6.8), 84 (12.8), 58 (100).

1,3-Di(1-adamantyl)urea (1l): colorless crystals (43%); mp > 300 °C (MeOH- CH_2Cl_2) (lit.¹³ mp 312 °C); IR (Nujol) 3344, 1625, 1555 cm^{-1} ; 1H NMR δ 1.64 (d, J = 2.6 Hz, 12H), 1.91 (dd, J = 17.2, 9.6 Hz, 12H), 2.05-2.09 (m, 6H), 3.83 (br. s, 2H); EI-MS m/z (relative intensity) 328 (M^+ , 34.2), 177 (15.0), 151 (100).

1,3-Diphenylureas (1m): colorless crystals (14%); mp 238 °C (MeOH) (lit.^{2b} mp 234-235 °C; lit.¹⁴ 234-236 °C; lit.^{4,15,16} mp 238-239 °C; lit.¹¹ mp 239-241 °C; lit.³ mp 240-241 °C); IR (Nujol) 3326, 1651, 1596, 1563 cm^{-1} ; 1H NMR δ 6.40 (br. s, 2H), 7.35 (s, 4H), 7.36 (6H, s); EI-MS m/z (relative intensity) 212 (M^+ , 12.3), 119 (8.8), 93 (100), 77 (8.0).

1,3-Bis(4-methoxyphenyl)urea (1n): colorless crystals (18%); mp 141-143 °C (CH_2Cl_2 -MeOH) (lit.^{3,14} mp 240-241 °C); IR (Nujol) 3294, 1631, 1608, 1561, 1510 cm^{-1} ; 1H NMR δ

3.89 (s, 6H), 7.00 (dd, $J = 6.93, 4.6$ Hz, 2H), 7.88 (dd, $J = 6.93, 4.6$ Hz, 2H); EI-MS m/z (relative intensity) 272 (M^+ , 22.4), 149 (53.6), 134 (34.4), 123 (94.4), 108 (100).

1,3-Bis(3,4-dimethoxyphenyl)urea (1o): colorless crystals (20%); mp 211-212 °C (CH_2Cl_2 -MeOH) (lit.¹⁷ mp 209-210 °C); IR (Nujol) 3292, 1626, 1606, 1556, 1518 cm^{-1} ; ^1H NMR δ 3.88 (s, 6H), 3.89 (s, 6H), 6.25 (br, 2H), 6.76 (dd, $J = 8.57$ Hz, 2H), 6.82 (s, 2H), 7.04 (s, 2H); EI-MS m/z (relative intensity) 332 (M^+ , 37.3), 179 (70.2), 164 (40.3), 153 (89.3), 138 (100).

1,3-Bis(3,4,5-trimethoxyphenyl)urea (1p): colorless crystals (25%); mp 199-200 °C (CH_2Cl_2 -MeOH) (lit.¹⁸ mp 200-202 °C); IR (Nujol) 3310, 1645, 1604, 1568 cm^{-1} ; ^1H NMR δ 4.83 (s, 6H), 4.85 (s, 12H), 6.63 (s, 4H), 6.55 (br. s, 2H); EI-MS m/z (relative intensity) 392 (M^+ , 34.7), 209 (67.7), 194 (76.6), 183 (49.1), 168 (100).

1-[(N'-Benzyl)carbamoyl]-2,3,4,5-tetrahydropyrrole (2cs): colorless crystals [82% (93% with 2 equiv of piperidine)]; mp 121-123 °C (CH_2Cl_2 -MeOH) (lit.¹⁹ mp 115-118 °C); IR (Nujol) 3286, 1620, 1541 cm^{-1} ; ^1H NMR δ 1.89 (m, 4H), 3.34 (t, $J = 6.6$ Hz, 4H), 4.42, 4.44 (1:2, each s, 2H), 4.50 (br. s, 1H), 7.23-7.34 (m, 5H); EI-MS m/z (relative intensity) 204 (M^+ , 59.9), 113 (25.0), 106 (39.5), 106 (39.5), 98 (18.7), 91 (46.2), 70 (100).

N-Benzyl-N',N'-1,5-pentamethylenediylurea (2ct): colorless crystals [86% (87% with 2 equiv of piperidine)]; mp 100-101 °C (MeOH) (lit.²⁰ mp 98-99 °C); IR (Nujol) 3370, 3322,

1612, 1546 cm^{-1} ; ^1H NMR δ 1.56 (m, 4H), 2.17 (s, 2H), 3.32–3.36 (m, 4H), 4.43 (d, $J = 5.3$ Hz, 2H), 4.68 (br. s, 1H), 7.30–7.34 (m, 5H); EI-MS m/z (relative intensity) 218 (M^+ , 51.7), 127 (37.9), 106 (29.6), 91 (43.2), 84 (100).

N-Benzyl-*N'*,*N'*-dipropylurea (2cu): colorless crystals [77% (87% with 2 equiv of piperidine)]; mp 43–44 °C (hexane); 3316, 1626, 1537 cm^{-1} ; ^1H NMR δ 0.90 (t, $J = 7.6$ Hz, 6H), 1.59 (six, $J = 7.6$ Hz, 4H), 3.17 (t, $J = 7.6$ Hz, 4H), 4.44 (d, $J = 5.6$ Hz, 2H), 4.61 (br s, 1H), 7.23–7.36 (m, 5H); EI-MS m/z (relative intensity) 234 (M^+ , 5.4), 106 (5.4), 91 (27.0), 72 (100.0). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}$: C, 71.76; H, 9.46; N, 11.95. Found: C, 71.74; H, 9.46; N, 11.92.

N-Benzyl-*N'*,*N'*-dibutylurea (2cv): colorless needles [66% (84% with 2 equiv of Bu_2NH)]; mp 56.5–57 °C (hexane); IR (Nujol) 3320, 1625, 1540, 1493; ^1H NMR δ 0.92 (t, $J = 7.3$ Hz, 6H), 1.32 (sextet, $J = 7.3$ Hz, 4H), 1.48–1.59 (m, 4H), 3.20 (t, $J = 7.3$ Hz, 4H), 4.44 (br. s, 2H), 7.26–7.34 (m, 5H); EI-MS m/z (relative intensity) 262 (M^+ , 28.0), 219 (6.6), 91 (22.2), 86 (100), 57 (7.4). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}$: C, 73.24; H, 9.99; N, 10.68. Found: C, 73.28; H, 10.06; N, 10.50.

N-Hexyl-*N'*,*N'*-1,5-pentamethylenediylurea (2bt): a colorless oil (80%) [R_f 0.54, 1:1 hexane–EtOAc]; IR (neat) 3334, 1623, 1540 cm^{-1} ; ^1H NMR δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.2–1.40 (m, 6H), 1.40–1.65 (m, 8H), 3.22 (dt, $J = 7.3, 7.3, 1.7$ Hz, 2H), 3.31 (t, $J = 5.6$ Hz, 4H), 4.45 (br. s, 2H); EI-MS m/z (relative intensity) 212 (M^+ , 33.1), 128 (40.8), 112 (100.0), 100 (10.5), 84 (98.4); HRMS calcd for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}$ 212.1889, found 212.1959.

***N*-(2-Adamantyl)-*N'*,*N'*-1,5-pentamethylenediylurea (2jt):** colorless crystals (81%), mp 180-181 °C (Et₂O-CH₂Cl₂); IR (Nujol) 3356, 1616 cm⁻¹; ¹H NMR δ 1.54-1.58 (m, 6H), 1.66, 1.74 (each m, each 2H), 1.79-1.84 (m, 4H), 1.92 (m, 2H), 3.32-3.35 (m, 4H), 4.76 (br. s, 1H); EI-MS *m/z* (relative intensity) 262 (M⁺, 34.4), 150 (100). Anal. Calcd for C₁₂H₂₄N₂O: C, 73.73; H, 9.99; N, 10.68. Found: C, 73.28; H, 9.68; N, 10.49.

***N*-(2-Methyl-2-propyl)-*N'*,*N'*-1,5-pentamethylenediylurea (2kt):** colorless crystals (43%); mp 142-143 °C (hexane) (lit.² mp 142-144 °C); IR (Nujol) 3368, 1628, 1542 cm⁻¹; ¹H NMR δ 1.35 (s, 9H), 1.51-1.58 (m, 6H), 3.25-3.28 (m, 4H), 4.29 (br. s, 1H); EI-MS *m/z* (relative intensity) 184 (M⁺, 44.9), 169 (19.9), 128 (17.9), 11.2 (67.3), 84 (100).

***N*-(1-Adamantyl)-*N'*,*N'*-1,5-pentamethylenediylurea (2lt):** colorless crystals [69% (87% with 2 equiv of piperidine)]; mp 189-190 °C (Et₂O-CH₂Cl₂); IR (Nujol) 3354, 1620 cm⁻¹; ¹H NMR δ 1.55 (m, 6H), 1.75 (m, 6H), 1.99 (m, 6H), 2.06 (m, 6H), 3.26 (m, 4H), 4.18 (br. s, 1H); EI-MS *m/z* (relative intensity) 262 (M⁺, 100), 205 (36.0), 84 (88). Anal. Calcd for C₁₆H₂₆N₂O: C, 73.24; H, 9.99; N, 10.68. Found: C, 73.98; H, 9.88; N, 10.43.

***N*-Phenyl-*N'*,*N'*-1,5-pentamethylenediylurea (2mt):** colorless crystals (79%); mp 169-171 °C (MeOH-Et₂O) (lit.²¹ mp 167-169 °C; lit.¹⁶ mp 169-170 °C; lit.²² mp 167-171 °C; lit.²³ mp

171 °C; lit.¹⁵ mp 171-172 °C); IR (Nujol) 3280, 1631, 1598 cm⁻¹; ¹H NMR δ 1.60-1.63 (m, 6H), 3.44-3.47 (m, 4H), 6.37 (br. s, 1H), 6.99-7.26 (dd, *J* = 8.6, 3.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz); EI-MS *m/z* (relative intensity) 204 (M⁺, 53.0), 160 (10.2), 119 (11.3), 112 (100), 84 (14.9).

***N*-(3,4,5-Trimethoxyphenyl)-*N*',*N*'-1,5-pentamethylenediylurea (2pt):** colorless crystals (70%); mp 135-136 °C (MeOH-Et₂O); IR (Nujol) 3388, 1667, 1603, 1536, 1508 cm⁻¹; ¹H NMR δ 1.54-1.71 (m, 6H), 3.38-3.53 (m, 4H), 3.80 (s, 3H), 3.84 (s, 6H), 6.33 (br. s, 1H), 6.68 (s, 2H); EI-MS *m/z* (relative intensity) 294 (M⁺, 9.5), 209 (19.7), 194 (18.2), 182 (4.4), 166 (12.6), 112 (100.0), 84 (31.8), 69 (82.8). Anal. Calcd for C₁₅H₂₂N₂O₄: C, 62.32; H, 7.84; N, 9.08. Found: C, 62.24; H, 7.72; N, 9.29.

***N*-(4-Chlorophenyl)-*N*',*N*'-1,5-pentamethylenediylurea (2qt):** colorless crystals (92%); mp 184-186 °C (benzene-hexane) (lit.²⁴ mp 181-182 °C); IR (Nujol) 3304, 1636, 1591, 1496 cm⁻¹; ¹H NMR δ 1.50-1.75 (m, 6H), 3.35-3.50 (m, 4H), 6.35 (br. s, 1H), 7.23, 7.31 (AB type, *J* = 9.2 Hz, each 2H); EI-MS *m/z* (relative intensity) 238 (M⁺, 42.7), 153 (6.1), 127 (3.3), 112 (100).

***N*-(4-Nitrophenyl)-*N*',*N*'-1,5-pentamethylenediylurea (2rt):** colorless crystals [64% (96% with 2 equiv of piperidine for 24 h)]; mp 165-166 °C (benzene-hexane) (lit.²⁵ mp 164 °C); IR (Nujol) 3304, 1640, 1611, 1602, 1535, 1504 cm⁻¹; ¹H NMR δ 1.50-1.75 (m, 6H), 3.40-3.50 (m,

4H), 7.01 (br. s, 1H), 7.55, 8.14 (AB type, $J = 9.5$ Hz, each 2H); EI-MS m/z (relative intensity) 249 (M^+ , 26.3), 164 (7.3), 134 (2.6), 112 (100).

General Procedure for Preparation of *Secondary Amines 3, 5, 7, 10, 13, 14, 15, 25, and 29.*

Method A. A mixture of an aldehyde (10 mmol), an amine (11 mmol) and Na_2SO_4 in CH_2Cl_2 (20 mL) was stirred for 2 h. The formed precipitates were removed by filtration, and the filtrate was concentrated. The residue (imine) was dissolved in MeOH (20 mL), and treated with $NaBH_4$ (5 mmol) at rt for 1 h. The mixture was concentrated, and the residue was dissolved in CH_2Cl_2 (30 mL), washed with water (3 x 15 mL), and dried (Na_2SO_4). The CH_2Cl_2 solution was concentrated, and the residue was subjected to valve-to-valve distillation.

Method B. A mixture of an alkyl chloride (10 mmol), an amine (11 mmol), and K_2CO_3 (20 mmol) in DMF (20 mL) was stirred until the chloride disappeared being monitored by TLC. The reaction mixture was dissolved in Et_2O (50 mL) and water (50 mL). The Et_2O layer was separated, and washed with water (3 x 20 mL) and saturated brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was distilled under reduced pressure to give an amine.

Method C. A mixture of a phenethylamine (10 mmol) and propionic acid (12 mmol) was heated at 200 °C for 2 h, and distilled under reduced pressure to give an amide, which was treated with $LiAlH_4$ (10 mmol) in dry boiling THF (20 mL) for 4 h. The excess hydride reagent was decomposed by addition of THF containing water. The mixture was filtered under reduced pressure to remove precipitates, and the filtrate was dried over K_2CO_3 and distilled under reduced pressure to give an amine.

For characterization of secondary amines, **3a,c,e, 5a, 7b, 10, 13a-d,f, 14a-f, 15a-f, 25a-c, and 29a-c**, see the Supporting Information of our preliminary report.²⁶

General Procedure for $Pd(OAc)_2$ -Catalyzed Carbonylation of Benzylic Amines 5a,b, 7a-d, 10, 13a-d,f 14a-f, 15a-i, 20a-c, and Phenethylamines 3a-d, 23a-c, Dibenzylamines

25c,f, 29a-e, N-Benzylphenethylamines 25a,d, and Diphenethylamines 25b,e. A stirred mixture of a freshly prepared appropriate *secondary* amine (0.2 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), and Cu(OAc)₂ (18.1 mg, 0.1 mmol) in toluene (2 mL) was refluxed in an oil bath at 120 °C in an atmosphere of CO gas (ca. 1~1.5 L) containing air (12 mL, corresponding to 0.1 mmol of O₂) delivered from a toy balloon for 2 h. The reaction mixture was cooled to rt, and filtered through a thin pad of powdered MgSO₄. Toluene was removed in a rotary evaporator. The residue was crystallized from the appropriate solvents or subjected to preparative TLC on silica gel to afford the corresponding benzolactam. For characterization of benzolactams, **4a,c,e, 6a, 8b, 9b, 11, 12, 16a-d,f, 17a-e, 18a-f, 19a-f, 26a-c, 27a-c, 28c, 30a-c, and 31a-c**, see the Supporting Information of our preliminary report.²⁶

N-Methyl-3,4-(methylenedioxy)phenethylamine (3b). Prepared by treatment of *N*-[3,4-(methylenedioxy)phenethyl]formamide with LiAlH₄ in boiling THF (Method C); a colorless oil (82%); bp 118 °C /14 mmHg (lit.²⁷ bp 99-101 °C/3 mmHg); IR (neat) 3316, 1609 cm⁻¹; ¹H NMR δ 2.44 (s, 3H), 2.71-2.83 (m, 4H), 5.91 (s, 2H), 6.65 (AB type, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.73 (AB type, *J* = 7.9 Hz, 1H); EI-MS *m/z* (relative intensity), 179 (M⁺, 100), 135 (90.2), 44 (100).

2-Methyl-7,8-(methylenedioxy)-3,4-dihydroisoquinolin-1(2H)-one (4b): a colorless oil (42%); *R_f* 0.40 (3% MeOH-CH₂Cl₂); IR (neat) 1662 cm⁻¹; ¹H NMR δ 2.91 (t, *J* = 6.3 Hz, 2H), 3.13 (s, 3H), 3.50 (t, *J* = 6.3 Hz, 2H), 6.09(s, 2H), 6.60, 6.81 (each d, *J* = 7.6 Hz, each 1H); EI-MS *m/z* (relative intensity) 205 (M⁺, 86.2), 162 (100), 134 (91.4); HRMS calcd for C₁₁H₁₁NO₃ 205.0739, found 205.0716.

3,4-(Methylenedioxy)-*N*-nonylphenethylamine (3d). Prepared by treatment of *N*-2-[3,4-(methylenedioxy)phenethyl]nonamide, mp 81-83 °C (MeOH), with LiAlH₄ in boiling THF (Method C); a colorless oil (76%); bp 160-175 °C/0.35 mmHg; IR (neat) 3302, 1653, 1610 cm⁻¹; ¹H NMR δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.22-1.48 (m, 14H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.66-2.74 (m, 4H), 5.92 (s, 2H), 6.65 (AB type, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.73 (AB type, *J* = 7.9 Hz, 1H); EI-MS *m/z* (relative intensity) 291 (M⁺, 3.5), 178 (1.8), 149 (7.6), 156 (100), 136 (12.5). Anal. Calcd for C₁₈H₂₉NO₂: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.27; H, 10.26; N, 4.71.

7,8-(Methylenedioxy)-2-nonyl-3,4-dihydroisoquinolin-1(2*H*)-one (4d): a colorless oil (63%); *R_f* 0.60 (1:1 hexane/AcOEt); IR (neat) 1650, 1599 cm⁻¹; ¹H NMR δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.20-1.40 (m, 12H), 1.50-1.70 (br. t, *J* = 7.6 Hz, 2H), 2.88, 3.48 (t, *J* = 6.3 Hz, each 2H), 3.53 (t, *J* = 7.3 Hz, 2H), 6.09 (s, 2H), 6.60, 6.81 (each d, *J* = 7.9 Hz, each 1H); EI-MS *m/z* (relative intensity) 317 (M⁺, 63.6), 205 (100), 204 (91.6), 148 (65.8); HRMS calcd for C₁₉H₂₇NO₃ 317.19907, found 317.19732.

***N*-Isopropylbenzylamine (5b).** Prepared from benzaldehyde and isopropylamine (Method A); a colorless oil (75%); bp 90 °C/5 mmHg; IR (neat) 3314 cm⁻¹; ¹H NMR δ 1.10 (d, *J* = 6.3 Hz, 6H), 2.89 (heptet, *J* = 6.3 Hz, 1H), 3.78 (s, 2H), 7.22-7.34 (m, 5H); EI-MS *m/z* (relative intensity) 149 (M⁺, 3.4), 134 (37.6), 91 (100), 65 (16.1). Anal. Calcd for C₁₀H₁₅N: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.59; H, 10.17; N, 9.19.

2-Isopropylisoindolin-1-one (6b): a colorless oil (72%); *R_f* 0.55 (1:1 hexane/AcOEt) (lit.²⁸ bp 125-133 °C/2 mmHg, mp 101-101.5 °C); IR (neat) 1682, 1649 cm⁻¹; ¹H NMR δ 1.29 (s, 3H), 1.31 (s, 3H), 4.34 (s, 2H), 4.69 (heptet, *J* = 6.6 Hz, 1H), 7.42-7.56 (m, 3H), 7.85 (d, *J* = 8.2 Hz,

1H); EI-MS m/z (relative intensity) 175 (M^+ , 12.9), 160 (100), 132 (15.8), 119 (16.0), 91 (19.6).

N-Methyl-3,4-(methylenedioxy)benzylamine (7a). Prepared by treatment of piperonal with methylamine in Et₂O with MgSO₄ powder at rt for 12 h, followed by reduction of the resultant imine with NaBH₄ in MeOH (Method A); a colorless oil (79%); bp 75 °C/0.15 mmHg (lit.²⁹ bp 98-100 °C/3 mmHg); IR (neat) 3304 cm⁻¹; ¹H NMR δ 2.43 (s, 3H), 3.65 (s, 2H), 5.92 (s, 2H), 6.76 (s, 2H), 6.83 (s, 1H); EI-MS m/z (relative intensity) 166 (M^+ , 8.7), 135 (100), 121 (7.6).

2-Methyl-6,7-(methylenedioxy)-2,3-dihydroisoindolin-1-one (8a): a colorless oil (42%); R_f 0.47 (2% MeOH-CH₂Cl₂); IR (neat) 1684 cm⁻¹; ¹H NMR δ 3.15 (s, 3H), 4.33, 6.12 (each s, each 2H), 6.84, 6.95 (each d, J = 7.9 Hz, each 1H); EIMS m/z (relative intensity) 191 (M^+ , 100), 162 (24.0), 135 (12.8); HRMS calcd for C₁₀H₉NO₃ 191.0573, found 191.0582.

2-Methyl-5,6-(methylenedioxy)-2,3-dihydroisoindolin-1-one (9a): a colorless oil (19%); R_f 0.38 (2% MeOH-CH₂Cl₂); IR (neat) 1678 cm⁻¹; ¹H NMR δ 3.16 (s, 3H), 4.25, 6.05 (each s, each 2H), 6.84, 6.94 (each s, each 1H); EIMS m/z (relative intensity) 191 (M^+ , 100), 162 (54.2), 135 (12.3); HRMS calcd for C₁₀H₉NO₃ 191.0582, found 191.0568.

N-Isopropyl-3,4-(methylenedioxy)benzylamine (7c). Prepared by treatment of piperonal with isopropylamine (Method A); a colorless oil (90%); bp 100 °C/0.6 mmHg (lit.³⁰ bp 95-100 °C/0.3 mmHg); IR (neat) 3302 cm⁻¹; ¹H NMR δ 1.08 (d, J = 6.3 Hz, 6H), 2.83 (heptet, J = 6.3

Hz, 1H), 3.68 (s, 2H), 5.93 (s, 2H), 6.76-6.87 (m, 3H); EI-MS m/z (relative intensity) 193 (M^+ , 6.1), 135 (100), 77 (18.1).

2-Isopropyl-6,7-(methylenedioxy)-2,3-dihydroisoindolin-1-one (8c): a colorless oil (52%); R_f 0.45 (1:1 hexane-AcOEt); IR (neat) 1682 cm^{-1} ; $^1\text{H NMR}$ δ 1.27 (d, $J = 6.9\text{ Hz}$, 6H), 4.30 (s, 2H), 4.64 (heptet, $J = 6.9\text{ Hz}$, 1H), 6.11 (s, 2H), 6.86 (d, $J = 7.9\text{ Hz}$, 1H), 6.95 (d, $J = 7.9\text{ Hz}$, 1H), EI-MS m/z (relative intensity) 219 (M^+ , 42.0), 204 (100), 176 (14.9), 163 (13.1); HRMS calcd $\text{C}_{12}\text{H}_{13}\text{NO}_3$ 219.0895, found 219.0898.

2-Isopropyl-5,6-(methylenedioxy)-2,3-dihydroisoindolin-1-one (9c): a colorless oil (12%); R_f 0.29 (1:1 hexane/AcOEt); IR (neat) 1670 cm^{-1} ; $^1\text{H NMR}$ δ 1.27 (d, $J = 6.9\text{ Hz}$, 6H), 4.22 (s, 2H), 4.62 (heptet, $J = 6.9\text{ Hz}$, 1H), 6.04 (s, 2H), 6.85 (s, 1H), 7.22 (s, 1H); EI-MS m/z (relative intensity) 219 (M^+ , 31.6), 204 (100), 176 (11.9), 163 (13.2); HRMS calcd $\text{C}_{12}\text{H}_{13}\text{NO}_3$ 219.0895, found 219.0896.

3,4-(Methylenedioxy)-N-nonylbenzylamine (7d). Prepared from piperonylamine and nonylaldehyde (Method A); a colorless oil (69 %); bp $114\text{ }^\circ\text{C}/0.15\text{ mmHg}$; IR (neat) 3324 cm^{-1} ; $^1\text{H NMR}$ δ 0.88 (t, $J = 6.6\text{ Hz}$, 3H), 1.26 (m, 15H), 1.49 (m, 2H), 2.59 (t, $J = 7.3\text{ Hz}$, 2H), 3.68 (s, 2H), 6.75 (d, $J = 1.0\text{ Hz}$, 2H), 6.83 (s, 1H); EI-MS m/z (relative intensity) 277 (M^+ , 4.5), 164 (16.7), 135 (100); HRMS calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_2$ 277.2042, found 277.2066. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.47; H, 9.74; N, 5.03.

6,7-(Methylenedioxy)-2-nonyl-2,3-dihydroisoindolin-1-one (8d): a colorless solid (48 %); mp 41-43 °C; R_f 0.33 (3:1 hexane/AcOEt); IR (neat) 1680 cm^{-1} ; ^1H NMR δ 0.85-0.90 (m, 3H), 1.26-1.33 (m, 12H), 1.53-1.57 (m, 2H), 3.53-3.58 (m, 2H), 4.33 (m, 2H), 6.12 (s, 2H), 6.85, 6.95 (each d, $J = 7.9$ Hz, each 1H); EI-MS m/z (relative intensity) 303 (M^+ , 49.6), 190 (100), 178 (7.1), 162 (11.1), 135 (15.0). Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_3$: C, 71.25; H, 8.31; N, 4.26. Found: C, 71.36; H, 8.45; N, 4.20.

5,6-(Methylenedioxy)-2-nonyl-2,3-dihydroisoindolin-1-one (9d): colorless crystals (9 %); mp 62-63 °C (Et_2O -hexane); R_f 0.39 (3:1 hexane-AcOEt); IR (Nujol) 1679 cm^{-1} ; ^1H NMR δ 0.87 (t, $J = 6.9$ Hz, 3H), 1.26-1.32 (m, 12H), 1.63 (quint, $J = 7.3$ Hz, 2H), 4.25 (s, 2H), 6.05 (s, 2H), 6.84, 7.22 (each s, each 1H); EI-MS m/z (relative intensity) 303 (M^+ , 49.6), 190 (100), 178 (7.1), 162 (11.1), 135 (15.0). Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_3$: C, 71.25; H, 8.31; N, 4.26. Found: C, 71.30; H, 8.40; N, 4.48.

N-Propyl-4-(trifluoromethyl)benzylamine (15g). Prepared by treatment of trifluoromethylbenzaldehyde with propylamine (Method A); a colorless oil (89%); bp 70 °C/0.4 mmHg; IR (neat) 3304 cm^{-1} ; ^1H NMR δ 0.93 (t, $J = 7.3$ Hz, 3H), 1.53 (heptet, $J = 7.3$ Hz, 2H), 2.59 (t, $J = 7.3$ Hz, 2H), 3.84 (s, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H); EI-MS m/z (relative intensity) 217 (M^+ , 4.2), 188 (51.6), 159 (100), 109 (15.6). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{N}$: C, 60.82; H, 6.50; F, 26.24; N, 6.45. Found: C, 60.27; H, 6.46; F, 26.40; N, 6.34.

N-Propyl-4-(trifluoromethyl)isoindolin-1-one (19g): a colorless oil (71%); R_f 0.66 (1:1 AcOEt/hexane); IR (neat) 1682, 1635, 1593 cm^{-1} ; ^1H NMR δ 1.00 (t, $J = 7.3$ Hz, 3H), 1.72 (sextet, $J = 7.3$ Hz, 2H), 3.61 (t, $J = 7.3$ Hz, 2H), 4.48 (s, 2H), 7.58 (d, $J = 7.9$, 1H), 7.57 (dd, J

= 7.9, 1.0 Hz, 1H), 7.13 (s, 1H); EI-MS m/z (relative intensity) 243 (M^+ , 32.7), 214 (100), 188 (21.3), 159 (42.2); HRMS calcd for $C_{12}H_{12}F_3NO$ 243.0871, found 243.0869.

N-Propyl-4-fluorobenzylamine (15h). Prepared by treatment of 4-fluorobenzaldehyde with propylamine (Method A); bp 63 °C/0.3 mmHg (86%); IR (neat) 3322 cm^{-1} ; 1H NMR δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.42 (br. s, 1H), 1.53 (sextet, $J = 7.3$ Hz, 2H), 2.58 (t, $J = 7.3$ Hz, 2H), 3.75 (s, 2H), 6.90-7.03 (m, 2H), 7.24-7.32 (m, 2H); EI-MS m/z (relative intensity) 167 (M^+ , 5.1), 138 (29.4), 109 (100), 83 (8.0); Anal. Calcd for $C_{10}H_{14}FN$: C, 71.82; H, 8.44; F, 11.36; N, 8.38. Found: C, 71.72; H, 8.40; F, 11.40; N, 8.33.

6-Fluoro-2-propylisoindolin-1-one (19h): a colorless oil (74%); R_f 0.57 (1:1 AcOEt/hexane); IR (neat) 1690, 1606 cm^{-1} ; 1H NMR δ 0.97 (t, $J = 7.3$ Hz, 3H), 1.70 (sextet, $J = 7.3$ Hz, 2H), 3.59 (t, $J = 7.3$ Hz, 2H), 4.35 (s, 2H), 7.23 [looked like dt, $J = 8.9$, (8.6), 2.6 Hz, 1H], 7.40 (dd, $J = 8.6$, 4.8 Hz, 1H), 7.51 (dd, $J = 7.3$, 2.6 Hz, 1H); EI-MS m/z (relative intensity) 193 (M^+ , 35.7), 164 (100), 109 (18.1); HRMS calcd for $C_{11}H_{12}FNO$ 193.0903, found 193.0911.

Methyl 4-(Propylaminomethyl)benzoate (15i). Prepared by treatment of methyl 4-formylbenzoate with propylamine (Method A); a colorless oil (89%); bp 125 °C/0.35 mmHg; IR (neat) 3328 cm^{-1} ; 1H NMR δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.53 (sextet, $J = 7.3$ Hz, 2H), 2.59 (t, $J = 7.3$ Hz, 2H), 3.85 (s, 2H), 3.91 (s, 3H), 7.40, 8.00 (AB type, $J = 8.3$ Hz, each 1H); EI-MS m/z (relative intensity) 207 (M^+ , 8.7), 178 (65.3), 149 (100), 121 (12.5), 90 (7.1), 74 (6.9). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.32; H, 8.27; N, 6.63.

6-Methoxycarbonyl-2-propylisoindolin-1-one (19i): a colorless oil (72%); R_f 0.52 (1:1 AcOEt/hexane); IR (neat) 1720, 1687, 1627, 1590, 1530 cm^{-1} ; ^1H NMR δ 0.97 (t, $J = 7.3$ Hz, 3H), 1.70 (sextet, $J = 7.3$ Hz, 2H), 3.60 (t, $J = 7.3$ Hz, 2H), 3.95 (s, 3H), 4.44 (s, 2H), 7.52 (dd, $J = 0.7, 7.9$ Hz, 1H), 8.23 (dd, $J = 1.7, 7.9$ Hz, 1H), 8.51 (d, $J = 1.0$ Hz, 1H); EI-MS m/z (relative intensity) 233 (M^+ , 32.9), 204 (100), 149 (14.0); HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ 233.1052, found 233.1057. Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: C, 66.94; H, 6.48; N, 6.00 Found: C, 69.82; H, 6.27; N, 6.13.

Preparation of Benzocyclic Compounds (20a,b,c). 1-(Benzylamino)indane (20a). To a stirred solution of 1-indanone (500 mg, 3.8 mmol) and benzylamine (38 mmol) at 0-5 $^{\circ}\text{C}$ was added a solution of TiCl_4 (2.3 mmol) in dry benzene (4 mL) over a period of 10 min. The mixture was stirred at rt for 3 days, and filtered to remove precipitates. The filtrate was concentrated, and the residue was dissolved in CH_2Cl_2 (20 mL), washed with water (20 mL), dried over Na_2SO_4 , and concentrated. The resultant solid was dissolved in dry CH_2Cl_2 (10 mL), and NaBH_4 (1.3 g, 7.6 mmol) was added in portions. After stirring at rt overnight, the mixture was concentrated, and the residue was subjected to preparative silica gel TLC with 3% $\text{MeOH}-\text{CH}_2\text{Cl}_2$ to give **20a** as a colorless oil (440 mg, 52%) (lit.³¹ bp 164 $^{\circ}\text{C}/2$ mmHg). IR (neat) 3326 cm^{-1} ; ^1H NMR δ 1.92 (1H, m), 2.43 (m, 1H), 2.82 (dt, $J = 16.5, 7.3, 7.3$, Hz, 1H), 3.00 (m, 1H), 3.82 (s, 1H), 3.88, 3.94 (AB type, $J = 13.2$ Hz, each 1H), 4.34 (t, $J = 6.6$ Hz, 1H), 7.20-7.42 (m, 9H).

2-(1-Indanyl)isoindolin-1-one (22a): a colorless oil [R_f 0.27 (3:1 hexane/EtOAc), 87%]; IR (Nujol) 1677, 1625 cm^{-1} ; ^1H NMR δ 2.03-2.16 (m, 1H), 2.59 (m, 1H), 2.92-3.20 (m, 2H), 3.08-3.17 (m, 1H), 4.06, 4.23 (AB type, $J = 17.2$ Hz, each 1H), 7.13-7.60 (m, 8H), 7.91 (dd, $J = 7.6,$

1.3 Hz, 1H); EI-MS m/z (relative intensity) 249 (M^+ , 52.6), 134 (100), 116 (70.5), 91 (21.8). HRMS Calcd for $C_{17}H_{15}NO$ 249.1154, found 249.1150.

1-(Benzylamino)tetraline (20b): a colorless oil (34%); IR (neat) 3344 cm^{-1} ; ^1H NMR δ 1.68-1.79 (m, 1H), 1.88-2.10 (m, 2H), 2.65-2.92 (m, 2H), 3.00 (br. s, 1H), 3.95, 3.83 (AB type, $J = 13.2\text{ Hz}$, each 1H), 3.85 (hiding, 1H), 7.06-7.42 (m, 9H). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.89; H, 8.04; N, 5.87.

2-(1,2,3,4-Tetrahydronaphthalen-1-yl)isoindolin-1-one (22b): a colorless oil (66%); R_f 0.26 (3:1 hexane/EtOAc); IR (Nujol) $1690, 1624\text{ cm}^{-1}$; ^1H NMR δ 1.92-2.08 (m, 4H), 2.85 (m, 1H), 4.09, 4.29 (AB type, $J = 17.2\text{ Hz}$, each 1H), 5.75 (br. t, $J = 6.9\text{ Hz}$, 1H), 6.98 (d, $J = 7.3\text{ Hz}$, 1H), 7.03-7.57 (m, 6H), 7.93 (dd, $J = 7.6, 1.3\text{ Hz}$, 1H); EI-MS m/z (relative intensity) 263 (M^+ , 0.38), 134 (0.38), 130 (100), 119 (0.28), 91 (0.33). HRMS calcd for $C_{18}H_{17}NO$ 263.1310, found 263.1299.

1-(Benzylamino)benzocycloheptane (20c). A colorless oil (56%); IR (neat) 3336 cm^{-1} ; ^1H NMR δ 1.59-1.65 (m, 2H), 1.68-1.85 (m, 3H), 2.76 (dt, $J = 14.2, 5.6, 5.6\text{ Hz}$, 1H), 3.07 (m, 1H), 3.69, 3.75 (AB type, $J = 13.1\text{ Hz}$, each 1H), 3.91 (t, $J = 4.3\text{ Hz}$, 1H), 7.08-7.21 (m, 4H), 7.23-7.38 (m, 5H). Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.85; H, 8.37; N, 5.38.

2-(6,7,8,9-Tetrahydro-5-benzocycloheptan-1-yl)-2,3-dihydroisoindolin-1-one (22c): a colorless oil (74%); R_f 0.25 (3:1 hexane/EtOAc); IR (Nujol) 1686, 1622 cm^{-1} ; ^1H NMR δ 1.42-1.60 (m, 2H), 1.80-2.25 (m, 4H), 2.85-23.03 (m, 2H), 4.52, 4.58 (AB type, $J = 10.1$ Hz, each 1H), 5.61 (d, $J = 8.6$ Hz, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 7.02-7.63 (m, 6H), 7.93 (dd, $J = 7.0$, 1.3 Hz, 1H); EI-MS m/z (relative intensity) 277 (M^+ , 100), 144 (0.84), 129 (0.39), 116 (0.20), 91 (0.17). HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$ 277.1537, found 277.1468.

Preparation of 2-Benzylpyrrolidine (23a). To a stirred solution of pyrrolidine-1-carboxylic acid *t*-butyl ester (1.87 g, 10 mmol) and TMEDA (3.31 mL, 22 mmol) in Et_2O (20 mL) at -78°C was added *sec*-BuLi (21.8 mL, 0.99 M solution in cyclohexane, 22 mmol) was added slowly. After 3.5 h, BnBr (2.05 g, 12 mmol) was added at -78°C . The mixture was then allowed to be stirred at rt overnight, and quenched with water (10 mL), and extracted with Et_2O (3 x 20 mL). The extracts were washed with a 0.5 N HCl (2 x 30 mL), a saturated NaHCO_3 solution (30 mL), and brine (30 mL), and dried (Na_2SO_4). Et_2O was evaporated, and the residue was dissolved in CH_2Cl_2 (10 mL) containing F_3CCOOH (8.5 mL), and stirred at rt for 3 h. The solvents were evaporated. The residue was dissolved in Et_2O (10 mL), washed with a 2N NaOH solution (10 mL), water (2 x 20 mL), and dried (MgSO_4), and concentrated. The residue was distilled under reduced pressure to give 2-benzylpyrrolidine (**23a**) as a colorless oil (0.56 g, 32%); bp $58\text{--}64^\circ\text{C}/0.1$ mmHg (lit.³² bp $96\text{--}97^\circ\text{C}/2$ mmHg); IR (neat) 3308 cm^{-1} ; ^1H NMR δ 1.46 (s, 9H), 1.81-1.86 (m, 4H), 3.28-3.33 (m, 4H).

Benz[*b*]indolizidine-5-one (24a): a colorless oil (83%, lit.³³ mp 98 °C, lit.³⁴ mp 108-108.5 °C); R_f 0.65 (1:1 hexane/EtOAc); IR (Nujol) 1632 cm^{-1} ; ^1H NMR δ 1.60-1.95 (m, 2H), 2.00-2.15 (m, 1H), 2.22-2.35 (m, 1H), 2.82 (t, J = 14.2 Hz, 1H), 3.02 (dd, J = 15.2, 4.0 Hz, 1H), 3.60-3.90 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 7.33 (dd, J = 7.6, 7.3 Hz, 1H), 7.40 (dt, J = 7.3, 7.3, 1.7 Hz, 1H).

Preparation of 2-Benzylpiperidine (23b). Methyl 2-oxocyclopentane carboxylate (4.26 g, 30 mmol) was slowly added to a stirred suspension of NaH [1.44 g, 60% dispersion in mineral oil, which was used after washing with hexane (3 x 10 mL), 36 mmol] in DMF (60 mL), and stirred at rt for 1 h. To this, BnBr (5.13 g, 30 mmol) was slowly added. After 18 h, the reaction mixture was diluted with Et₂O (100 mL) and water (50 mL). The organic layer was separated, and the water layer was extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with water (5 x 30 mL), dried (MgSO₄), and concentrated. The oily residue was dissolved in a 40% HBr solution (25 mL), and heated at reflux for 12 h. The reaction mixture was diluted with Et₂O (50 mL), washed with a 5% Na₂S₂O₃ solution (20 mL), water (2 x 20 mL), brine (20 mL) and dried with MgSO₄, concentrated. The crude product was purified by distillation under reduced pressure to give 2-benzylcyclopentanone as a colorless oil (2.87 g, 58%); bp 95 °C/0.4 mmHg; IR (neat) 1691 cm^{-1} ; ^1H NMR δ 1.47-1.81 (m, 2H), 1.89-2.15 (m, 3H), 2.16-2.40 (m, 2H), 2.49-2.58 (m, 1H), 3.15 (dd, J = 13.5, 4.0 Hz, 1H), 7.15-7.34 (m, 5H).

A mixture of the ketone (1.74 g, 10 mmol), NH₂OH·HCl (1.29 g, 20 mL), and a 6N NaOH solution (4 mL), in MeOH (20 mL) was stirred at rt for 4 h, and H₂O (40 mL) was added. The resulting precipitates were collected by filtration, washed with water, recrystallized from EtOH to give the oxime (1.82 g, 96%), mp 114-116 °C; IR (Nujol) 3264 cm^{-1} ; ^1H NMR δ 1.36-1.87 (m, 4H), 2.30-2.62 (m, 3H), 2.74-2.81 (m, 1H), 3.16 (dd, J = 13.5, 4.3 Hz, 1H), 7.16-7.32

(m, 5H); EI-MS m/z (relative intensity) 189 (M^+ , 30.0), 172 (42.1), 157 (29.8), 91 (100). Anal. Calcd for $C_{12}H_{15}NO$: C, 75.16; H, 7.99; N, 7.40. Found: C, 7.14; 8.01; N, 7.54.

Ice-cold solutions of the oxime (0.96 g, 5 mmol) in pyridine (2 mL) and *p*-TsCl (1.5 g) were mixed, and allowed to warm to rt. After the vigorously exothermic reaction subsided, the bright yellow solution was stirred overnight. It was then warmed to 100 °C for 30 min, poured into a mixture of conc. H_2SO_4 (3 mL) and ice (15 g), and extracted with Et_2O (3 x 10 mL). The extracts were washed with a 5% Na_2CO_3 solution (2 x 20 mL), water (20 mL), brine (20 mL), dried (Na_2SO_4), and concentrated. A solution of the resultant lactam in dry THF (10 mL) was added to a stirred suspension of $LiAlH_4$ (1.51 g, 20 mmol) in dry THF (20 mL), and refluxed for 4 h. Water (2 mL) was added, and the resulting mixture was filtered. The filtrate was concentrated, and the residue was dissolved in CH_2Cl_2 (20 mL), washed with water (3 x 20 mL), dried (Na_2SO_4), and concentrated. The residue was distilled to give **23b**, bp 75 °C /0.2 mmHg (HCl salt: lit.³⁵ mp 135-137 °C; lit.³⁶ mp 136.5-137 °C), as a colorless oil (0.887 g, 55%); IR (neat) 3250 cm^{-1} ; 1H NMR δ 1.06-1.80 (m, 7H), 2.22-2.75 (m, 2H), 3.00 (dd, J = 11.6, 4.0 Hz, 1H), 7.12-7.35 (m, 5H); EI-MS m/z (relative intensity) 175 (M^+ , 46.0), 158 (20.6), 117 (41.5), 91 (100). Anal. Calcd for $C_{12}H_{17}N$: C, 82.28; H, 9.78; N, 7.99. Found: 82.10; H, 9.78; N, 7.77.

Benzo[*b*]quinolizidin-5-one (24b): a colorless oil (17%, lit.³⁷ mp 92-93 °C, lit.³⁸ mp 95-97 °C, lit.³⁹ mp 101-102 °C); R_f 0.65 (1:1 hexane/EtOAc); IR (Nujol) 1637 cm^{-1} ; 1H NMR δ 1.43-1.62 (m, 3H), 1.74-1.99 (m, 3H), 2.64-2.70 (m, 1H), 2.72-2.88 (m, 1H), 3.01 (dd, J = 5.3, 15.8 Hz, 1H), 3.50-3.62 (m, 1H), 4.68-4.75 (m, 1H), 7.14 (d, J = 7.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.41 (dt, J = 7.6, 1.3 Hz, 1H), 8.11 (dd, J = 7.6, 7.6, 1.3 Hz, 1H).

Preparation of 2-Benzylhexahydroazepine (23c). 2-Benzylcyclohexanone bp 95 °C/0.4 mmHg, was prepared in a similar manner to that for 2-benzylcyclopentanone in 58% yield. The oxime, mp 125-127 °C (EtOH), was obtained in 97% yield; IR (Nujol) 3236, 1673 cm⁻¹; ¹H NMR δ 1.29-1.79 (m, 6H), 2.12-2.23 (m, 1H), 2.43-2.60 (m, 2H), 2.87-2.97 (m, 1H), 3.13 (dd, *J* = 12.9, 4.3 Hz, 1H), 6.87 (s, 1H), 7.13-7.31 (m, 5H); EI-MS *m/z* (relative intensity) 203 (M⁺, 23.4), 186 (40.4), 171 (37.0), 91 (100). Anal. Calcd for C₁₃H₁₇NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.70; H, 8.31; N, 6.86. 6-Benzylazepan-2-one was obtained as an oil (83%), which was treated with LiAlH₄ in the same manner as noted above for that of 2-benzylpiperidine to give **23c**, bp 115 °C/2 mmHg (lit.⁴⁰ bp 120 °C/1 mmHg), as a colorless oil (47%); IR (neat) 3250, 1624 cm⁻¹; ¹H NMR δ 1.13-1.86 (m, 9H), 2.52-2.76 (m, 2H), 2.73 (dd, *J* = 15.5, 5.3 Hz, 1H), 7.17-7.33 (m, 5H); EI-MS *m/z* (relative intensity) 205 (M⁺, 31.7), 176 (100), 153 (12.1), 121 (26.2).

8,9,10,11,11a,12-Hexahydro-7H-azepino[1,2-*b*]isoquinoline-5-one (24c): a colorless oil (7%, lit.³⁸ mp 77-78 °C); *R_f* 0.58 (1:1 hexane/EtOAc); IR (Nujol) 1644 cm⁻¹; ¹H NMR δ 1.43-1.62 (m, 3H), 1.74-1.99 (m, 3H), 2.67 (m, 1H), 2.80 (m, 1H), 3.01 (dd, *J* = 5.3, 15.8 Hz, 1H), 3.56 (m, 1H), 4.72 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.38 (dt, *J* = 7.6, 7.6, 1.3 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.3 Hz, 1H).

***N*-[3,4-(Methylenedioxy)benzyl]-4,5-(methylenedioxy)phenethylamine (25d).** Prepared by treatment of 3,4-(methylenedioxy)benzaldehyde with 3,4-(methylenedioxy)-phenethylamine (Method A); colorless crystals (86%); mp 48-49 °C (hexane-Et₂O) (lit.⁴¹ mp 51 °C); IR (Nujol) 3320 cm⁻¹; ¹H NMR δ 1.47 (br, s, 1H), 2.69-2.75 (m, 2H), 2.80-2.90 (m, 2H), 3.69 (s, 2H), 5.92 (s, 2H), 5.93 (s, 2H), 6.62-6.79 (m, 6H); EI-MS *m/z* (relative intensity) 299 (M⁺, 2.5), 164 (18.5), 135 (100).

2-[3,4-(Methylenedioxy)benzyl]-7,8-(methylenedioxy)-1-oxo-1,2,3,4-tetrahydroisoquinoline (26d): colorless crystals (5%); mp 171-172 °C (Et₂O-MeOH); *R_f* 0.47 (1:1 hexane/EtOAc); IR (Nujol) 1686, 1619, 1508 cm⁻¹; ¹H-NMR δ 2.84 (t, *J* = 6.3 Hz, 2H), 3.43 (t, *J* = 6.3 Hz, 2H), 4.66 (s, 2H), 5.94 (s, 2H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.82 (dd, *J* = 7.9, 3.3 Hz, 1H). EI-MS *m/z* (relative intensity) 325 (M⁺, 29.5), 190 (62.9), 148 (100), 135 (19.3). Anal. Calcd for C₁₈H₁₅NO₅: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.44; H, 4.82; N, 4.21.

2-[3,4-(Methylenedioxy)phenyl]ethylbenzyl-6,7-(methylenedioxy)-1-oxoisindoline (27d): colorless crystals (25%); mp 188-190 °C (Et₂O); *R_f* 0.40 (1:1 hexane/EtOAc); IR (Nujol) 1669 cm⁻¹; ¹H NMR δ 2.89 (t, *J* = 6.9 Hz, 2H), 3.77 (t, *J* = 6.9 Hz, 2H), 4.18 (s, 2H), 5.93 (s, 2H), 6.12 (s, 2H), 6.66 (dd, *J* = 8.2, 6.6 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 1.7 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H); EI-MS *m/z* (relative intensity) 325 (M⁺, 17.0), 190 (94.8), 148 (100). Anal. Calcd for C₁₈H₁₅NO₅: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.27; H, 4.58; N, 4.11.

2-[3,4-(Methylenedioxy)phenethyl]-5,6-(methylenedioxy)-1-oxoisindoline (28d): colorless crystals (0.8%); mp 184-185 °C (MeOH-Et₂O); *R_f* 0.44 (1:1 hexane/EtOAc); IR (Nujol) 1666, 1625 cm⁻¹; ¹H NMR δ 2.88 (t, *J* = 6.9 Hz, 2H), 3.77 (t, *J* = 7.3 Hz, 2H), 4.11 (s, 2H), 5.93 (s, 2H), 6.04 (s, 2H), 6.66 (dd, *J* = 7.9, 6.3 Hz, 1H), 6.71 (s, 1H), 6.72 (dd, *J* = 3.63, 1.3 Hz, 1H), 6.79 (s, 1H), 7.23 (s, 1H); EI-MS *m/z* (relative intensity) 325 (M⁺, 19.4), 190 (83.8), 148 (100), 135 (27.3). Anal. Calcd for C₁₈H₁₅NO₅: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.44; H, 4.78; N, 4.21.

Bis[3,4-(Methylenedioxy)phenethyl]amine (25e): prepared treatment of *N*-3,4-(methylenedioxy)phenethyl-3,4-(methylenedioxyphenylacetamide, mp 120-121 °C, with LiAlH₄ (Method C); colorless crystals (8%); mp 77-77.5 °C (Et₂O-CH₂Cl₂) (HCl salt: lit.⁴² mp 261-262 °C); IR (Nujol) 3310 cm⁻¹; ¹H NMR δ 2.69 (t, *J* = 6.3 Hz, 2H), 2.82 (t, *J* = 6.6 Hz, 2H), 5.92 (s, 4H), 6.61 (t, *J* = 9.2 Hz, 4H), 6.71 (d, *J* = 6.6 Hz, 2H), EI-MS *m/z* (relative intensity) 313 (M⁺, 6.1), 148 (100), 135 (6.9), 121 (10.7). Anal. Calcd for C₁₇H₁₅NO₅: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.89; H, 6.23; N, 4.45.

2-[3,4-(Methylenedioxy)phenethyl]-7,8-(methylenedioxy)-1-oxo-1,2,3,4-tetrahydroisoquinoline (26e): colorless crystals (81%); *R_f* 0.67 (3:8 hexane/EtOAc); mp 151.5-152.2 °C (Et₂O); IR (Nujol) 1647, 1601 cm⁻¹; ¹H NMR δ 2.78 (t, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 7.9 Hz, 2H), 3.36 (t, *J* = 6.9 Hz, 2H), 3.71 (t, *J* = 7.6 Hz, 2H), 5.93 (s, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 13.2 Hz, 2H), 6.73 (s, 1H), 6.74 (d, *J* = 13.2 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H); EI-MS *m/z* (relative intensity) 339, (M⁺, 9.7), 325 (21.8), 190 (97.6), 148 (100). Anal. Calcd for C₁₉H₁₇NO₅: C, 67.25, H, 5.05; N, 4.13. Found: C, 67.17; H, 5.01; N, 4.07.

Bis[3,4-(Methylenedioxy)benzyl]amine (25f). Prepared by treatment of 3,4-(methylenedioxy)benzaldehyde with 3,4-(methylenedioxy)benzylamine (Method A); colorless crystals (78%); mp 66.5-67.7 °C (Et₂O-CH₂Cl₂) (lit.⁴³ mp 72-73 °C); IR (Nujol) 3310 cm⁻¹; ¹H NMR δ 1.54 (br. s, 1H), 3.41 (s, 2H), 5.93 (s, 4H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.90 (s, 2H); EI-MS *m/z* (relative intensity) 285 (M⁺, 2.9), 150 (6.4), 135 (100), 106 (4.6).

2-[3,4-(Methylenedioxy)benzyl]-6,7-(methylenedioxy)-1-oxoindoline (26f): colorless crystals (50%); R_f 0.56 (1:1 hexane/EtOAc); mp 171.5-172.5 °C (MeOH); IR (Nujol) 1686, 1610 cm^{-1} ; ^1H NMR δ 4.21 (s, 2H), 4.64 (s, 2H), 5.93 (s, 2H), 6.13 (s, 2H), 6.76 (s, 1H), 6.78 (d, $J = 7.9$ Hz, 3H), 6.93 (d $J = 7.9$ Hz, 1H); EI-MS m/z (relative intensity) 311 (M^+ , 87.0), 189 (10.6), 176 (11.3), 163 (81.2), 135 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_5$: C, 65.59; H, 4.21; N, 4.59. Found: C, 65.39; H, 4.44; N, 4.39.

2-[3,4-(Methylenedioxy)benzyl]-5,6-(methylenedioxy)-1-oxoindoline (27f): colorless crystals (5%); R_f 0.65 (1:1 hexane/EtOAc); mp 167-168 °C (MeOH); IR (Nujol) 1687, 1686, 1610 cm^{-1} ; ^1H NMR δ 4.14 (s, 2H), 4.66 (s, 2H), 5.94 (s, 2H), 6.05 (s, 2H), 6.76 (m, 5H); EI-MS m/z (relative intensity) 311 (M^+ , 93.6), 189 (21.1), 163 (81.2), 135 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_5$: C, 65.59; H, 4.21; N, 4.59. Found: C, 65.58; H, 4.11; N, 4.61.

2,3-(Methylenedioxy)-3-nitrodibenzylamine (29d). Prepared from 3-nitrobenzaldehyde and 2,3-(methylenedioxy)benzylamine [bp 85 °C/0.4 mmHg, obtained in 73% yield by reduction of 2,3-(methylenedioxy)benzaldehyde oxime, mp 128-129 °C, with $\text{NaBH}_4\text{-NiCl}_2\cdot 6\text{H}_2\text{O}$ in MeOH]⁴⁴ Method A); a colorless oil (82%), bp 200 °C /0.4 mmHg; IR(neat) 3336, 1527, 1349 cm^{-1} ; ^1H NMR δ 1.78 (br. s, 1H), 3.81 (s, 2H), 3.90 (s, 2H), 5.97 (s, 2H), 6.70-6.84 (m, 3H), 7.48 (t, $J = 7.9$ Hz, 1H), 7.68 (dd, $J = 7.6, 0.7$ Hz, 1H), 8.08-8.12 (m, 1H), 8.24 (d, $J = 1.7$ Hz, 1H); EI-MS m/z (relative intensity) 286 (M^+ , 7.8), 136 (100), 106 (21.7). Anal: Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.97; H, 5.09; N, 9.79.

2-(3-Nitrobenzyl)-4,5-methylenedioxyisoindolin-1-one (30d): colorless crystals (28%), mp 198.2-200.1 °C (EtOH-hexane); R_f 0.27 (1:1 EtOAc/hexane); IR (CHCl₃) 1676, 1524 cm⁻¹; ¹H NMR δ 4.28 (s, 2H), 4.87 (s, 2H), 5.97 (s, 2H), 6.96 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 8.15-8.18 (m, 2H); EI-MS m/z (relative intensity) 312 (M⁺, 45), 296 (19), 295 (94), 282 (7), 266 (20), 265 (100), 176 (18), 163 (42), 136 (18). Anal. Calcd for C₁₆H₁₂N₂O₅: C, 61.54; H, 3.87; N, 8.97. Found: C, 61.55; H, 4.05; N, 8.53.

2-[2,3-(Methylenedioxy)benzyl]-6-nitroisoindolin-1-one (31d): a colorless oil (17%); R_f 0.46 (1:1 EtOAc/hexane); IR (neat) 1697, 1530 cm⁻¹; ¹H NMR δ 4.45 (s, 2H), 4.83 (s, 2H), 5.98 (s, 2H), 6.80-6.83 (m, 3H), 8.02 (d, J = 8.3 Hz, 1H), 8.25-8.29 (m, 1H), 8.35 (dd, J = 8.3, 2.0 Hz, 1H); EI-MS m/z (relative intensity) 312 (M⁺, 45), 282 (11), 266 (5), 265 (11), 263 (9), 149 (11), 136 (100); HR-MS calcd for C₁₆H₁₂N₂O₅ 312.0746, found 312.0750.

2-Methyl-2',3'-(methylenedioxy)dibenzylamine (29e). Prepared from *o*-tolualdehyde and 2,3-methylenedioxybenzylamine (Method A); a colorless oil (85%), IR (neat) 3326 cm⁻¹; ¹H NMR δ 1.58 (br. s, 1H), 2.32 (s, 3H), 3.78 (s, 2H), 3.85 (s, 2H), 5.96 (s, 2H), 6.73-6.85 (m, 3H), 7.13-7.19 (m, 3H), 7.31 (m, 1H); EI-MS m/z (relative intensity) 255 (M⁺, 12), 150 (52), 149 (60), 136 (64), 135 (96), 120 (82), 105 (77), 104 (100); HR-MS calcd for C₁₆H₁₇NO₂ 255.1259, found 255.1251.

2-(2-Methylbenzyl)-4,5-(methylenedioxy)isoindolin-1-one (30e): a colorless oil (34 %), R_f 0.58 (1:1 EtOAc/hexane); IR(neat) 1690 cm^{-1} ; ^1H NMR δ 2.34 (s, 3H), 4.14 (s, 2H), 4.79 (s, 2H), 6.03 (s, 2H), 6.94 (d, $J = 7.9\text{ Hz}$, 1H), 7.12-7.23 (m, 4H), 7.44 (d, $J = 7.9\text{ Hz}$, 1H); EI-MS m/z (relative intensity) 281 (M^+ , 93), 266 (8), 190 (36), 176 (100), 163 (37), 105 (43), 104 (60), 91 (13); HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$ 281.1052, found 281.1041.

2-[2,3-(Methylenedioxy)benzyl]-4-methylisoindolin-1-one (31e): a colorless oil (45%), R_f 0.53 (1:1 EtOAc/hexane); IR (neat) 1687 cm^{-1} ; ^1H NMR δ 2.30 (s, 3H), 4.27 (s, 2H), 4.82 (s, 2H), 5.98 (s, 2H), 6.75-6.82 (m, 3H), 7.31 (d, $J = 7.5\text{ Hz}$, 1H), 7.38 (t, $J = 7.4\text{ Hz}$, 1H), 7.71 (d, $J = 7.3\text{ Hz}$, 1H); EI-MS m/z (relative intensity) 281 (M^+ , 100), 146 (20), 135 (32), 133 (11), 105 (8); HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$ 281.1052, found 281.1061.

General Procedure for Preparation of 2-Oxazolidinones (33a-f). A stirred mixture of an appropriate 2-aminoalcohol (0.2 mmol), $\text{Pd}(\text{OAc})_2$ (2.24 mg, 0.01 mmol), and $\text{Cu}(\text{OAc})_2$ (36.2 mg, 0.2 mmol) in toluene (2 mL) was refluxed in an oil bath at $120\text{ }^\circ\text{C}$ in an atmosphere of carbon monoxide (ca. 1~1.5 L) containing air (12 mL, corresponding to 0.1 mmol of O_2) delivered from a toy balloon for 2 h. The reaction mixture was cooled to rt, and filtered through a thin pad of powdered MgSO_4 . The filtrate was concentrated in a rotary evaporator. The residue was crystallized from benzene to afford colorless crystals of the corresponding 2-oxazolidinone. ^1H NMR spectra were compared with those reported by Dinsmore and Mercer.⁴⁵ Optical purities were measured on a HPLC system using a chiral column (0.46 x 150 mm) at $40\text{ }^\circ\text{C}$, and all the oxazolidinones gave single peaks except **33f**, which showed two peaks at 10.975 and 11.633 minutes in a 1:1 ratio, when eluted with 2:3 v/v $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at the rate of 0.25 mL/min. Carbonylation of the corresponding chiral amino alcohol resulted in the

formation of (5*R*)-5-phenyl-1,3-oxazolidin-2-one (75.1%) together with its (5*S*)-isomer (4.2%), probably being reflected by the optical purity of the commercially available (*R*)-(-)-2-amino-1-phenylethanol (90% purity) used, not by the isomerization.

(*R*)-(-)-4-Phenyl-2-oxazolidinone (33a): colorless crystals (84%); mp 136-138 °C (benzene) (lit.⁴⁶ mp 128-130 °C; lit.⁴⁷ 129.5-1130 °C; lit.⁴⁸ 130-131 °C; lit.⁴⁹ 131-132 °C; lit.⁵⁰ 131-133 °C; lit.^{51,52} 132-133 °C); IR (Nujol) 3278, 1723 cm⁻¹; ¹H NMR δ 4.19 (dd, *J* = 8.6, 6.9 Hz, 1H), 4.73 (t, *J* = 8.6 Hz, 1H), 5.96 (t, *J* = 7.6 Hz, 1H), 5.67 (br, s, 1H), 7.32-7.45 (m, H); EI-MS *m/z* (relative intensity) 163 (*M*⁺, 24.4), 107 (100), 79 (5.3).

3-Benzyl-2-oxazolidinone (33b): colorless crystals (59%); mp 78-80 °C (benzene) (lit.⁵² mp 80-81 °C); *R_f* 0.5 (2% MeOH-CH₂Cl₂); IR (Nujol) 1737 cm⁻¹; ¹H NMR δ 3.42 (t, *J* = 7.9 Hz, 2H), 4.30 (t, *J* = 7.9 Hz, each 1H), 4.43 (s, 2H), 5.62 (t, *J* = 8.3 Hz, 1H), 7.26-7.36 (m, 5H); EI-MS *m/z* (relative intensity) 177 (*M*⁺, 100), 104 (65.4), 78 (9.2).

(4*S*,5*R*)-(-)-cis-4,5-Diphenyl-2-oxazolidinone (33c): colorless crystals (67%); mp 230.5-234 °C (benzene) (lit.⁵⁰ mp 227-232 °C); IR (Nujol) 3280, 1751, 1717 cm⁻¹; ¹H NMR δ 5.17 (d, *J* = 8.3 Hz, 1H), 5.95 (t, *J* = 8.3 Hz, 1H), 6.93-7.12 (m, 10H); EI-MS *m/z* (relative intensity) 239 (*M*⁺, 5.4), 107 (100), 104 (22.6).

(4*R*,5*S*)-(+)-4-Methyl-5-phenyl-2-oxazolidinone (28d): colorless crystals (99%), mp 122.5-125.3 °C (benzene) (lit.⁵³ mp 117 °C; lit.⁵⁴ 117-8 °C; lit.^{55,56} 120-121 °C; lit.⁵⁷ 121-122 °C; lit.⁴⁹ 121-123 °C); R_f 0.5 (5% MeOH-CH₂Cl₂); IR (Nujol) 3260, 1750, 1727 cm⁻¹; ¹H NMR δ 0.81 (d, J = 6.6 Hz, 3H), 4.21 (q, J = 6.6 Hz, 1H), 5.59 (br. s, 1H), 5.72 (d, J = 7.9 Hz, 1H), 7.26-7.40 (m, 5H); EI-MS m/z (relative intensity) 177 (M⁺, 14.9), 107 (100), 79 (30.4).

(*S*)-(-)-4-Benzyl-2-oxazolidinone (33e): colorless crystals (88%); mp 89-90 °C (benzene) (lit.⁴⁷ mp 85-87 °C; lit.^{48,58} 87-88 °C; lit.⁵⁰ 89-91 °C); R_f 0.4 (5% MeOH-CH₂Cl₂); IR (Nujol) 3276, 1752, 1710 cm⁻¹; ¹H NMR δ 2.80-2.94 (m, 2H), 4.02-4.10 (m, 2H), 4.48 (t, J = 7.9 Hz, 1H), 5.10 (br. s, 1H), 7.33-7.45 (m, 5H); EI-MS m/z (relative intensity) 177 (7.1), 92 (100), 86 (78.6).

(±)-5-Phenyl-2-oxazolidinone (33f): colorless crystals (73%); mp 88-90 °C (benzene) (lit.⁵⁹ mp 88-90; lit.⁶⁰ 88.8-90.2 °C; lit.⁶¹ 89-90 °C; lit.⁴⁸ 90-91 °C); lit.⁵² 90-92 °C); R_f 0.2 (1% MeOH-CH₂Cl₂); IR (Nujol) 3282, 1750, 1723 cm⁻¹; ¹H NMR δ 3.54, 3.98 (each t, J = 8.6 Hz, each 1H), 5.62 (t, J = 8.3 Hz, 1H), 6.05 (br. s, 1H), 7.33-7.45 (m, 5H); EI-MS m/z (relative intensity) 163 (M⁺, 41.6), 104 (100), 77 (24.3).

General Procedure for Carbonylation of *Primary* Amine Hydrochlorides 34, 36, 38 to Ureas 35a-c and Carbamates 37, 39a,b. A stirred mixture of hydrochloride, **34a**, **b** or **c** (0.2 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), and Cu(OAc)₂ (36.2 mg, 0.2 mmol) in toluene (2 mL) was refluxed in an oil bath at 120 °C in an atmosphere of CO gas (ca. 1~1.5 L) containing air (6 mL, corresponding to 0.05 mmol of O₂) delivered from a toy balloon for 2 h. The reaction mixture was cooled to rt, and filtered through a thin pad of powdered MgSO₄. The filtrate was washed with 0.5 N HCl solution (2 mL) and water (2 mL), and dried over Na₂SO₄.

The solvent was removed in a rotary evaporator. The residue was crystallized from the appropriate solvent to give urea **35a**, **b** or **c**. The carbonylation of hydrochloride **36** or **38a,b** was carried out using 99.5% EtOH (2 mL) and air (12 mL) for 2 h under the same conditions, and EtOH was removed in a rotary evaporator. The residue was dissolved in CH₂Cl₂ (5 mL) and washed with 0.5 N HCl solution (2 mL) and water (2 mL), and dried over Na₂SO₄. The solvent was removed in a rotary evaporator. The residue was subjected to preparative silica gel TLC developed with 5% MeOH-CH₂Cl₂ for **37** and **39a** or 1:1 EtOAc/hexane for **39b**.

***N,N'*-Bis[(ethoxycarbonyl)methyl]urea (35a)**: colorless crystals (86%); mp 142-143.5 °C (CHCl₃) (lit.⁶² mp 143-145 °C; lit.⁶³ mp 147-148 °C); IR (Nujol) 3346, 1746, 1625 cm⁻¹; ¹H NMR δ 1.28 (t, *J* = 7.3 Hz, 3H), 3.99 (d, *J* = 5.3 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 5.04 (br. s, 1H).

***(S,S)*-N,N'-Bis[1-(ethoxycarbonyl)ethyl]urea (35b)**: colorless crystals (76%); mp 152-156 °C (CHCl₃) (lit.⁶³ mp 156 °C); IR (Nujol) 3350, 1744, 1636 cm⁻¹; ¹H NMR δ 1.28 (t, *J* = 7.3 Hz, 6H), 1.38 (d, *J* = 6.9 Hz, 6H), 4.20 (q, *J* = 7.3 Hz, 2H), 4.45 (quint, *J* = 7.4 Hz, 2H), 5.10 (d, *J* = 7.6 Hz, 2H).

***(S,S)*-N,N'-Bis[1-(ethoxycarbonyl)-2-phenylethyl]urea (35c)**: colorless crystals (80%); mp 143-144 °C (EtOH) (lit.⁶³ mp 147-148 °C); IR (Nujol) 3352, 1731, 1639 cm⁻¹; ¹H NMR δ 1.20 (t, *J* = 7.3 Hz, 6H), 3.03 (d, *J* = 5.9 Hz, 4H), 4.09 (m, 4H), 4.74, 4.77 (each t, *J* = 5.9 Hz, each 1H), 5.15, 5.18 (each s, each 1H), 7.31-7.08 (m, 10H). EI-MS *m/z* (relative intensity) 412 (M⁺, 8.2), 366 (25.2), 236 (29.9), 176 (832.8), 120 (79.5), 102 (100), 74 (10.0).

Ethyl Hexylcarbamate (37): a colorless oil (73%); R_f 0.9 (5% MeOH-CH₂Cl₂) (lit.⁶⁴ bp 91-93 °C/3 mmHg); IR (neat) 3332, 1700, 1536 cm⁻¹; ¹H NMR δ 0.83 (t, J = 6.9 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 1.27-1.41 (br. s, 6H), 1.48 (quint, J = 6.3 Hz, 2H), 3.17 (q, J = 6.6 Hz, 2H), 4.12 (q, J = 7.3 Hz, 2H), 4.61 (br. s, 1H).

Ethyl Benzylcarbamate (39a): a colorless oil (69%); R_f 0.9 (5% MeOH-CH₂Cl₂) (lit.⁶⁵ bp 115-120 °C/0.15 mmHg); IR (neat) 3326, 1693, 1517 cm⁻¹; ¹H NMR δ 1.24 (t, J = 7.3 Hz, 3H), 4.13 (q, J = 7.3 Hz, 2H), 4.33, 4.36 (each s, each 1H), 5.09 (br. s, 1H), 7.35-7.23 (m, 4H).

Ethyl 2-Phenylethylcarbamate (39b): colorless crystals (64%); R_f 0.8 (1:1 EtOAc/hexane); mp 34-34.5 °C (pet. ether) (lit.⁶⁶ bp 100-103 °C/0.16 mmHg); IR (Nujol) 3330, 1695, 1530 cm⁻¹; ¹H NMR δ 1.23 (t, J = 7.3 Hz, 3H), 2.81 (m, 2H), 3.45 (m, 2H), 4.12 (q, J = 7.3 Hz, 2H), 4.69 (br. s, 1H), 7.18-7.34 (m, 5H).

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