

Supporting Information

Reaction of Ortho Oxazolinyl Phenyllithium with Carbon Monoxide.

Carbonylative Cyclization via an Aroyllithium Intermediate

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General Information. ^1H -NMR and ^{13}C -NMR were recorded on a JEOL JNM-EX270 (^1H at 270 MHz, ^{13}C at 67.5 MHz) spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Column chromatography was performed using Kiesegel 60 (230-400 mesh, Merck 9385). Infrared spectra (IR) were recorded on a Hitachi 270-50 infrared spectrometer as neat or KBr pellets; absorption peaks are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), w (weak) or br (broad). Mass spectra (MS) were obtained on a Shimadzu GCMS-QP5000 spectrometer with ionization voltages of 70 eV. The preparative HPLC separations were carried out with a LC-908 HPLC (Japan Analytical Industry Co., Ltd.) apparatus using preparative JAIGEL-1H (20 $\times$ 600 mm) and JAIGEL-2H (20 $\times$ 600 mm) column with chloroform as a mobile phase. Melting points were determined on a Yamato Scientific Co., Ltd. micro melting point apparatus and were uncorrected. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-12A gas chromatography, equipped with a flame ionization detector.

Materials. THF was distilled from sodium benzophenone ketyl immediately prior to use. A hexane solution of BuLi and an ether solution of MeLi were purchased from Nakalai Tesque, Inc. and Kanto Chemical Co., Inc., respectively. Phenylloxazoline **4** was purchased from Aldrich Chemical Co. and substituted phenylloxazoline **10**¹, **12**¹, and pyridinyloxazoline **14**² were prepared according to literature procedures. All reagents were used after distillation or recrystallization.

General Procedure for the Preparation of 3,3-Dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (9). A 30 mL round-bottomed flask equipped with a magnetic stirring bar, a

three-way stopcock, and a nitrogen line was flame-dried under a stream of nitrogen. In the reaction flask was placed 10 mL of dry THF and 350 mg (2.0 mmol) of phenyloxazoline **4**, and the solution was then cooled to -45°C with a dry ice/ CH_3CN bath. To the stirred solution was added 1.6 mL of a hexane solution of BuLi (1.5 M, 2.4 mmol) via a syringe. After stirring for 1.5 h, the three-way stopcock was then connected to a vacuum line (10 mmHg) and also to a balloon filled with carbon monoxide through a glass column packed with anhydrous calcium sulfate. After two cycles of evacuation of the nitrogen and filling with carbon monoxide, the reaction mixture was stirred under an atmospheric pressure of carbon monoxide, and gradually warmed to -30°C over a 2 h period. To the mixture was added 2 mL of saturated aqueous NH_4Cl and the resulting mixture was allowed to cool to room temperature. To the mixture was added 30 mL of Et_2O , and the layers were separated. The aqueous layer was extracted with Et_2O (10 mL $\times$ 3). The organic layers were combined and dried over anhydrous MgSO_4 . The solvents were removed under reduced pressure to give a green oil, which was subjected to column chromatography on silica gel to give 3,3-dimethyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9*bH*)-one (**9**) (370 mg, 91% yield) as a colorless oil.

3,3-Dimethyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9*bH*)-one (9**).** 91% yield, colorless oil, $R_f = 0.14$ (hexane/ $\text{EtOAc} = 5/1$): $^1\text{H-NMR}$ (CDCl_3) δ 1.53 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 4.06 (d, $J = 8.4$ Hz, 1H, OCHH), 4.15 (d, $J = 8.4$ Hz, 1H, OCHH), 5.92 (s, 1H, NCH), 7.53-7.59 (c, 3H, ArH), 7.77 (d, $J = 6.9$ Hz, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 23.0 (CH_3), 26.4 (CH_3), 58.9 ($\text{NC}(\text{CH}_3)_2$), 84.4 (OCH_2), 91.7 (NCH), 123.3 (Ar), 123.6 (Ar), 130.0 (Ar), 132.0 (Ar), 134.8 (Ar), 141.0 (Ar), 169.4 (C=O); IR (cm^{-1}) (neat) 2974 m, 2936 m, 2872 m, 1713 s, 1618 w, 1469 m, 1397 s, 1371 m, 1319 m, 1295 m, 1270 w, 1214 m, 1144 w, 1122 w, 1045 m, 989 w, 809 w, 795 w, 746 m; MS m/z (relative intensity) 203 (M^+ , 4), 173 (100), 160 (21), 145 (18), 144 (53), 132(13), 130 (35), 104 (26), 103 (12), 79 (14), 77 (35), 76 (21), 65 (24), 63 (13), 55 (15), 51 (30), 50 (25); Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.65; H, 6.46; N, 6.90.

7-Methoxy-3,3-dimethyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9*bH*)-one (11**).** In a manner similar to that described for oxazolo[2,3-*a*]isoindolinone **9**, phenyloxazoline **10** in place of **4** was used.; 84% yield, colorless solid, mp $98-99^{\circ}\text{C}$, $R_f = 0.17$ (hexane/ $\text{EtOAc} = 3/1$): $^1\text{H-NMR}$ (CDCl_3) δ 1.52 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 4.03 (d, $J = 8.4$ Hz, 1H, OCHH), 4.15 (d, $J = 8.4$ Hz, 1H, OCHH), 5.86 (s, 1H, NCH), 7.10 (dd, $J = 8.3$ Hz, $J = 2.3$ Hz, 1H, ArH), 7.23 (d, $J = 2.3$ Hz, 1H, ArH) 7.46 (d, $J = 8.3$ Hz, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 23.1 (CH_3), 26.4 (CH_3),

55.4 (OCH₃), 58.9 (NC(CH₃)₂), 84.5 (OCH₂), 91.5 (NCH), 106.7 (Ar), 119.8 (Ar), 124.2 (Ar), 133.3 (Ar), 136.6 (Ar), 161.4 (Ar), 169.4 (C=O); IR (cm⁻¹) (KBr) 2974 w, 2936 w, 2852 w, 1690 s, 1620 w, 1496 w, 1393 m, 1331 m, 1279 m, 1216 w, 1202 w, 1131 w, 1115 w, 1087 w, 1040 w, 1017 m, 985 m, 933 m, 826 m, 772 m, 700 w; MS *m/z* (relative intensity) 233 (M⁺, 25), 232 (21), 204 (15), 203 (100), 190 (31), 178 (15), 175 (22), 174 (38), 162 (11), 160 (73), 135 (12), 134 (18), 102 (12), 91 (10), 77 (17), 65 (10), 63 (22), 55 (24), 51 (13), 50 (15); Anal. Calcd for C₁₃H₁₅NO₃: C, 66.94; H, 6.48; N, 6.01. Found: C, 66.76; H, 6.55; N, 6.04.

7-Chloro-3,3-dimethyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9*bH*)-one (13). In a manner similar to that described for **9**, phenyloxazoline **12** in place of **4** was used.; 86% yield, colorless solid, mp 84-85 °C, *R_f* = 0.20 (hexane/EtOAc = 4/1): ¹H-NMR (CDCl₃) δ 1.51 (s, 3H, CH₃), 1.63 (s, 3H, CH₃), 4.03 (d, *J* = 8.6 Hz, 1H, OCHH), 4.14 (d, *J* = 8.6 Hz, 1H, OCHH), 5.88 (s, 1H, NCH), 7.48-7.55 (c, 2H, ArH), 7.70-7.75 (m, 1H, ArH); ¹³C-NMR (CDCl₃) δ 23.2 (CH₃), 26.4 (CH₃), 59.3 (NC(CH₃)₂), 84.6 (OCH₂), 91.3 (NCH), 123.9 (Ar), 124.7 (Ar), 132.2 (Ar), 136.5 (Ar), 136.8 (Ar), 139.3 (Ar), 167.9 (C=O); IR (cm⁻¹) (KBr) 2984 w, 2882 w, 1696 s, 1424 m, 1408 m, 1327 m, 1219 m, 1042 m, 988 w, 962 w, 826 w, 774 m, 727 m; MS *m/z* (relative intensity) 237 (M⁺, 6), 209 (37), 208 (10), 207 (100), 194 (25), 180 (19), 179 (20), 178 (50), 166 (19), 164 (27), 144 (11), 139 (13), 138 (17), 111 (12), 102 (19), 76 (13), 75 (35), 74 (13), 64 (20), 62 (12), 57 (17), 56 (11), 55 (28), 51 (13), 50 (17); Anal. Calcd for C₁₂H₁₂NO₂Cl: C, 60.64; H, 5.09; N, 5.89. Found: C, 60.35; H, 5.05; N, 5.86.

3,3-Dimethyl-2,3-dihydrooxazolo[3',2':1,5]pyrrolo[3,4-*c*]pyridin-5(9*bH*)-one (15). In a manner similar to that described for **9**, ortho lithiation was carried out under a following condition.²: To a THF solution of pyridinyloxazoline **14** was added at -78 °C 2.2 mL of a pentane solution of MeLi (1.1 M; 2.4 mmol), and the reaction mixture was stirred at the same temperature for 1 h and allowed to warm to 0 °C for 1 h. Under an atmospheric pressure of CO the mixture was stirred at 0 °C for 2 h.; 74% yield, colorless solid, mp 102-103 °C, *R_f* = 0.26 (hexane/EtOAc = 1/3): ¹H-NMR (CDCl₃) δ 1.52 (s, 3H, CH₃), 1.63 (s, 3H, CH₃), 4.03 (d, *J* = 8.6 Hz, 1H, OCHH), 4.13 (d, *J* = 8.6 Hz, 1H, OCHH), 5.91 (s, 1H, NCH), 7.52 (d, *J* = 5.0 Hz, 1H, ArH), 8.81 (d, *J* = 5.0 Hz, 1H, ArH), 9.01 (s, 1H, ArH); ¹³C-NMR (CDCl₃) δ 22.9 (CH₃), 26.2 (CH₃), 59.3 (NC(CH₃)₂), 84.4 (OCH₂), 91.0 (NCH), 118.2 (Ar), 130.2 (Ar), 145.7 (Ar), 148.9 (Ar), 152.3 (Ar), 167.3 (C=O); IR (cm⁻¹) (KBr) 2980 w, 2888 w, 1712 s, 1611 m, 1476 m, 1387 s, 1367 w, 1319 m, 1272 w, 1252 w, 1206 m,

1189 w, 1140 w, 1123 w, 1045 m, 990 w, 975 w, 939 w, 897 w, 834 m, 810 m, 767 m, 716 w; MS m/z (relative intensity) 204 (M^+ , 3), 174 (23), 131 (11), 105 (10), 92 (16), 91 (24), 88 (20), 86 (24), 81 (10), 77 (10), 73 (18), 71 (18), 70 (38), 69 (11), 65 (11), 61 (37), 59 (12), 58 (30), 57 (100), 56 (61), 55 (31), 51 (19), 50 (14); Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.66; H, 5.97; N, 13.66.

The Reaction of the Cyclic Dienolate 8 with Alkylating Agents. Preparation of 3,3,9b-Trimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (16). To a THF solution of the cyclic dienolate 8, prepared from the reaction of lithium phenyloxazoline 6 with carbon monoxide *vide supra*, was added 1.25 mL (20 mmol) of methyl iodide at $-30\text{ }^\circ\text{C}$ and the mixture was stirred at $20\text{ }^\circ\text{C}$ for 12 h. After aqueous workup, 3,3,9b-Trimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (16) was isolated as a colorless solid by column chromatography on silica gel.

3,3,9b-Trimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (16). 84% yield, colorless solid, mp $102\text{--}103\text{ }^\circ\text{C}$, $R_f = 0.20$ (hexane/EtOAc = 5/1): $^1\text{H-NMR}$ (CDCl_3) δ 1.57 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.74 (s, 3H, OCCH_3), 4.12 (d, $J = 8.9\text{ Hz}$, 1H, OCHH), 4.28 (d, $J = 8.9\text{ Hz}$, 1H, OCHH), 7.49–7.57 (c, 3H, ArH), 7.73 (d, $J = 6.6\text{ Hz}$, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 23.5 (CH_3), 24.2 (CH_3), 27.8 (CH_3), 59.3 ($\text{NC}(\text{CH}_3)_2$), 83.2 (OCH_2), 99.9 (NCO), 121.5 (Ar), 123.8 (Ar), 129.7 (Ar), 132.5 (Ar), 133.2 (Ar), 147.0 (Ar), 170.3 (C=O); IR (cm^{-1}) (KBr) 2978 w, 2888 w, 1701 s, 1614 w, 1465 m, 1357 s, 1344 m, 1315 m, 1013 m, 771 m; MS m/z (relative intensity) 217 (M^+ , 2), 202 (29), 149 (27), 148 (12), 130 (20), 91 (11), 88 (17), 73 (17), 71 (18), 70 (68), 61 (100), 60 (11), 58 (10), 57 (49), 56 (21), 55 (31); Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.65; H, 7.00; N, 6.44.

9b-Benzyl-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (17). Benzyl bromide (0.26 mL, 2.2 mmol) was added as the alkylating agent.; 90% yield, colorless oil, $R_f = 0.20$ (hexane/EtOAc = 4/1): $^1\text{H-NMR}$ (CDCl_3) δ 1.60 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 3.19 (d, $J = 13.5\text{ Hz}$, 1H, PhCHH), 3.49 (d, $J = 13.5\text{ Hz}$, 1H, PhCHH), 4.21 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 4.44 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 6.95–7.05 (c, 2H, ArH), 7.05–7.20 (c, 4H, ArH), 7.33–7.47 (c, 2H, ArH), 7.53–7.58 (m, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 24.2 (CH_3), 27.4 (CH_3), 42.1 (PhCH_2), 59.6 ($\text{NC}(\text{CH}_3)_2$), 83.0 (OCH_2), 102.1 (NCO), 122.4 (Ar), 123.3 (Ar), 126.5 (Ar), 127.6 (Ar), 130.2 (Ar), 131.7 (Ar), 133.9 (Ar), 134.5 (Ar), 145.3 (Ar), 170.4 (C=O); IR (cm^{-1}) (neat) 3034 w, 2976 m, 2932 w, 2878 w, 1709 s, 1614 w, 1499 w, 1468 m, 1457 m, 1366 s, 1304 m, 1205 m, 1124 m, 1055 m, 1032 m, 1008

m, 911 m, 888 m, 767 m, 754 m, 733 m, 704 s; MS m/z (relative intensity) 293 (M^+ , 0.06), 203 (13), 202 (100), 160 (27), 148 (35), 130 (60), 102 (11), 86 (37), 84 (57), 55 (31); Anal. Calcd for $C_{19}H_{18}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.50; H, 6.57; N, 4.71.

9b-Allyl-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (18). Allyl bromide (0.19 mL, 2.2 mmol) was added as the alkylating agent.; 86% yield, colorless oil, R_f = 0.20 (hexane/EtOAc = 5/1): 1H -NMR ($CDCl_3$) δ 1.58 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.80 (dd, J = 13.5 Hz, J = 7.4 Hz, 1H, $CH_2=CHCHH$), 2.91 (dd, J = 13.5 Hz, J = 7.4 Hz, 1H, $CH_2=CHCHH$), 4.15 (d, J = 8.6 Hz, 1H, $OCHH$), 4.31 (d, J = 8.6 Hz, 1H, $OCHH$), 4.91-5.00 (c, 2H, $CH_2=CH$), 5.36-5.54 (m, 1H, $CH_2=CH$), 7.44-7.59 (c, 3H, ArH), 7.69-7.74 (m, 1H, ArH); ^{13}C -NMR ($CDCl_3$) δ 24.3 (CH_3), 27.5 (CH_3), 40.2 ($CH_2=CHCH_2$), 59.2 ($NC(CH_3)_2$), 83.3 (OCH_2), 101.4 (NCO), 119.4 ($CH_2=CH$), 122.0 (Ar), 123.5 (Ar), 129.6 (Ar), 130.8 ($CH_2=CH$), 132.2 (Ar), 134.0 (Ar), 145.3 (Ar), 170.3 ($C=O$); IR (cm^{-1}) (neat) 3080 w, 2978 m, 2880 m, 1714 s, 1644 w, 1614 w, 1468 m, 1388 m, 1365 s, 1303 m, 1265 m, 1231 m, 1202 m, 1139 m, 1087 m, 1057 m, 1033 m, 1010 m, 920 m, 764 m, 734 m, 717 m; MS m/z (relative intensity) 229 (M^+ , 0.2), 203 (13), 202 (100), 160 (32), 148 (43), 130 (74), 102 (13), 76 (10); 58 (11), 55 (29); Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.65; H, 7.15; N, 5.94.

9b-Butyl-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (19). Butyl bromide (0.24 mL, 2.2 mmol) was added as the alkylating agent.; 82% yield, colorless oil, R_f = 0.23 (hexane/EtOAc = 3/1): 1H -NMR ($CDCl_3$) δ 0.68-0.82 (m, 1H, $CH_3CH_2CH_2CHH$), 0.80 (t, J = 7.1 Hz, 3H, $CH_3CH_2CH_2CH_2$), 1.10-1.35 (c, 3H, $CH_3CH_2CH_2CHH$ and $CH_3CH_2CH_2CH_2$), 1.55 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.05-2.20 (c, 2H, $CH_3CH_2CH_2CH_2$), 4.12 (d, J = 8.6 Hz, 1H, $OCHH$), 4.28 (d, J = 8.6 Hz, 1H, $OCHH$), 7.45-7.60 (c, 3H, ArH), 7.73 (d, J = 7.59 Hz, 1H, ArH); ^{13}C -NMR ($CDCl_3$) δ 13.7 ($CH_3CH_2CH_2CH_2$), 22.5 ($CH_3CH_2CH_2CH_2$), 24.4 (CH_3), 25.7 ($CH_3CH_2CH_2CH_2$), 27.5 (CH_3), 35.2 ($CH_3CH_2CH_2CH_2$), 59.3 ($NC(CH_3)_2$), 83.4 (OCH_2), 102.6 (NCO), 121.6 (Ar), 123.7 (Ar), 129.7 (Ar), 132.4 (Ar), 134.2 (Ar), 145.7 (Ar), 170.6 ($C=O$); IR (cm^{-1}) (neat) 2962 s, 2876 s, 1714 s, 1615 m, 1468 s, 1369 s, 1319 m, 1300 m, 1265 m, 1229 m, 1203 m, 1143 m, 1109 m, 1085 m, 1058 m, 1032 m, 998 w, 966 w, 890 w, 852 w, 825 w, 802 w, 763 s, 705 s; MS m/z (relative intensity) 259 (M^+ , 1.1), 203 (13), 202 (100), 160 (28), 148 (33), 130 (50), 102 (10), 76 (10), 55 (36); Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.83; H, 8.14; N, 5.54.

The Reaction of the Cyclic Dienolate 8 with Aldehydes, Cyclohexanone, and Propylene Oxide. Preparation of **9b-(Hydroxyphenylmethyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (20)**. To a THF solution of the cyclic dienolate **8** was added 0.22 mL (2.2 mmol) of benzaldehyde at $-30\text{ }^{\circ}\text{C}$ and the mixture was stirred at $20\text{ }^{\circ}\text{C}$ for 12 h, followed by quenching with 2 mL of saturated aqueous NH_4Cl . After aqueous workup, **9b-(Hydroxyphenylmethyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (20)** was isolated by column chromatography on silica gel.

9b-(Hydroxyphenylmethyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (20). 81% yield (74:26), each diastereomer was separated by column chromatography on silica gel. A major isomer, colorless solid, mp $158\text{--}159\text{ }^{\circ}\text{C}$, $R_f = 0.26$ ($\text{CH}_2\text{Cl}_2/\text{EtOAc} = 10/1$): $^1\text{H-NMR}$ (CDCl_3) δ 1.59 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 3.01 (d, $J = 1.7\text{ Hz}$, 1H, OH), 4.23 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 4.46 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 5.39 (d, $J = 1.7\text{ Hz}$, 1H, CHOH), 6.95–7.10 (c, 5H, ArH), 7.30–7.43 (c, 2H, ArH), 7.46–7.52 (m, 1H, ArH), 7.80 (d, $J = 7.6\text{ Hz}$, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 24.2 (CH_3), 27.4 (CH_3), 60.0 ($\text{NC}(\text{CH}_3)_2$), 74.1 (CHOH), 83.0 (OCH_2), 103.2 (NCO), 123.1 (Ar), 124.0 (Ar), 126.8 (Ar), 127.1 (Ar), 127.3 (Ar), 129.6 (Ar), 131.7 (Ar), 134.4 (Ar), 136.5 (Ar), 143.0 (Ar) 171.1 (C=O); IR (cm^{-1}) (KBr) 3352 br, 2974 w, 2912 w, 2886 w, 1681 s, 1614 w, 1377 s, 1342 w, 1088 m, 1065 m, 1007 w, 714 m, 703 m; MS m/z (relative intensity) 309 (M^+ , 0.07), 200 (22), 199 (100), 157 (37), 145 (41), 128 (51), 101 (13), 77 (20), 76 (10), 53 (49); Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.16; N, 4.53. Found: C, 73.79; H, 6.31; N, 4.53. A minor isomer, colorless solid, mp $212\text{--}213\text{ }^{\circ}\text{C}$, $R_f = 0.14$ ($\text{CH}_2\text{Cl}_2/\text{EtOAc} = 10/1$): $^1\text{H-NMR}$ (CDCl_3) δ 1.59 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.66 (d, $J = 2.6\text{ Hz}$, 1H, OH), 4.21 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 4.56 (d, $J = 8.6\text{ Hz}$, 1H, OCHH), 5.31 (d, $J = 2.6\text{ Hz}$, 1H, CHOH), 6.47 (d, $J = 7.3\text{ Hz}$, 1H, ArH), 7.25–7.44 (c, 7H, ArH), 7.64 (d, $J = 7.3\text{ Hz}$, 1H, ArH); $^{13}\text{C-NMR}$ (CDCl_3) δ 24.5 (CH_3), 27.8 (CH_3), 60.6 ($\text{NC}(\text{CH}_3)_2$), 73.7 (CHOH), 84.4 (OCH_2), 104.2 (NCO), 123.5 (Ar), 123.8 (Ar), 127.4 (Ar), 127.7 (Ar), 127.9 (Ar), 129.9 (Ar), 131.7 (Ar), 135.0 (Ar), 137.8 (Ar), 143.5 (Ar), 172.1 (C=O); IR (cm^{-1}) (KBr) 3336 br, 1687 s, 1380 m, 1326 w, 1314 w, 1263 w, 1058 m, 1009 w, 718 m, 701 w; MS m/z (relative intensity) 309 (M^+ , 0.08), 200 (22), 199 (100), 157 (30), 145 (39), 128 (45), 77 (14), 53 (34); Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.16; N, 4.53. Found: C, 73.63; H, 6.24; N, 4.57.

9b-(1-Hydroxy-2,2-Dimethylpropyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9b*H*)-one (21). Pivalaldehyde (0.24 mL, 2.2 mmol) was added. This product was purified by

recrystallization from hexane/EtOAc.; 83 % yield, colorless solid, mp 169-171 °C (hexane/EtOAc): ¹H-NMR (CDCl₃) δ 0.64 (s, 9H, C(CH₃)), 1.59 (s, 6H, NC(CH₃)), 2.83 (d, *J* = 1.8 Hz, 1H, OH), 4.05 (d, *J* = 1.8 Hz, 1H, CHOH), 4.13 (d, *J* = 8.9 Hz, 1H, OCHH), 4.32 (d, *J* = 8.9 Hz, 1H, OCHH), 7.45-7.55 (c, 2H, ArH), 7.70-7.80 (c, 2H, ArH); ¹³C-NMR (CDCl₃) δ 24.8 (CH₃), 27.7 (C(CH₃)₃), 27.8 (CH₃), 34.1 (C(CH₃)₃), 60.2 (NC(CH₃)₂), 77.8 (CHOH), 82.4 (OCH₂), 103.0 (NCO), 123.6 (Ar), 125.5 (Ar), 130.1 (Ar), 131.9 (Ar), 133.9 (Ar), 144.8 (Ar), 171.4 (C=O); IR (cm⁻¹) (KBr) 3438 br, 2982 w, 2884 w, 1686 s, 1615 w, 1468 w, 1392 m, 1316 m, 1268 w, 1229 w, 1201 w, 1151 w, 1130 w, 1078 m, 1063 w, 1040 m, 1024 w, 1009 w, 768 m, 729 w, 702 w; MS *m/z* (relative intensity) 289 (M⁺, 0.04), 203 (21), 202 (100), 160 (27), 148 (35), 130 (39), 55 (21); Anal. Calcd for C₁₇H₂₃NO₃: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.34; H, 8.09; N, 4.80.

9b-(1-Hydroxycyclohexyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (22). Cyclohexanone (0.23 mL, 2.2 mmol) was added.; 70 % yield, colorless solid, mp 180-182 °C, *R_f* = 0.13 (hexane/EtOAc = 4/1): ¹H-NMR (CDCl₃) δ 0.69-0.79 (m, 1H, CH₂ of Cy), 0.80-1.05 (m, 1H, CH₂ of Cy), 1.30-1.80 (c, 9H, CH₂ of Cy and CHOH), 1.45 (s, 3H, CH₃), 1.60 (s, 3H, CH₃), 4.05 (d, *J* = 7.9 Hz, 1H, OCHH), 4.55 (d, *J* = 7.9 Hz, 1H, OCHH), 7.44-7.70 (c, 3H, ArH), 7.73 (d, *J* = 6.9 Hz, 1H, ArH); ¹³C-NMR (CDCl₃) δ 20.9 (Cy), 21.2 (Cy), 24.7 (CH₃), 25.3 (Cy), 26.4 (CH₃), 30.3 (Cy), 33.6 (Cy), 61.4 (NC(CH₃)₂), 77.6 (CHOH), 85.0 (OCH₂), 107.0 (NCO), 123.0 (Ar), 123.8 (Ar), 129.5 (Ar), 132.3 (Ar), 134.5 (Ar), 147.8 (Ar), 174.4 (C=O); IR (cm⁻¹) (KBr) 3494 br, 2940 m, 2852 m, 1699 s, 1611 w, 1470 w, 1451 w, 1344 s, 1302 m, 1262 m, 1200 m, 1161 m, 1125 m, 1045 m, 1004 m, 992 m, 896 m, 764 s, 707 m; MS *m/z* (relative intensity) 301 (M⁺, 0.16), 203 (56), 202 (28), 160 (21), 149 (10), 148 (100), 130 (69), 102 (12), 81 (11), 76 (11), 56 (21), 55 (52); Anal. Calcd for C₁₈H₂₃NO₃: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.67; H, 7.71; N, 4.58.

9b-(2-Hydroxypropyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (23). Propylene oxide (0.15 mL, 2.2 mmol) was added as electrophile and the product **23** was obtained as a 51:49 mixture of diastereomers.; 53% yield, colorless solid, mp 126-129 °C, *R_f* = 0.10 (hexane/EtOAc = 1/1): The spectra data was obtained as a 51:49 mixture of diastereomers.: ¹H-NMR (CDCl₃) δ 1.05 (d, *J* = 6.3 Hz, 3H, CH₃CH(OH)CH₂), 1.18 (d, *J* = 6.3 Hz, 3H, CH₃CH(OH)CH₂), 1.59 (s, 6H, NC(CH₃)₂), 1.62 (s, 6H, NC(CH₃)₂), one diastereomer [1.87 (dd, *J* = 2.3 Hz, *J* = 14.5 Hz, 1H, CH₃CH(OH)CH₂), 2.22 (dd, *J* = 2.0 Hz, *J* = 14.5 Hz, 1H, CH₃CH(OH)CH₂)], the other diastereomer [2.42 (dd, *J* = 8.9 Hz, *J* = 12.2 Hz, 1H,

CH₃CH(OH)CH₂), 2.47 (dd, $J = 9.6$ Hz, $J = 12.2$ Hz, 1H, CH₃CH(OH)CH₂), 2.52 (s, 1H, OH), 2.79 (s, 1H, OH), 3.20-3.35 (m, 1H, CH₃CH(OH)CH₂), 4.05-4.20 (c, 3H, CH₃CH(OH)CH₂ and OCH₂), 4.27 (d, $J = 8.6$ Hz, 1H, OCH₂), 4.35 (d, $J = 8.6$ Hz, 1H, OCH₂), 7.47-7.66 (c, 6H, ArH), 7.77 (d, $J = 7.3$ Hz, 2H, ArH); ¹³C-NMR (CDCl₃) δ 23.5 (CH₃CH(OH)CH₂), 23.8 (CH₃CH(OH)CH₂), 24.2 (NC(CH₃)₂), 24.2 (NC(CH₃)₂), 27.3 (NC(CH₃)₂), 27.5 (NC(CH₃)₂), 43.8 (CH₃CH(OH)CH₂), 44.1 (CH₃CH(OH)CH₂), 59.3 (NC(CH₃)₂), 60.2 (NC(CH₃)₂), 63.7 (CHOH), 64.0 (CHOH), 82.8 (OCH₂), 82.9 (OCH₂), 101.4 (NCO), 101.4 (NCO), 122.1 (Ar), 122.4 (Ar), 123.8 (Ar), 129.8 (Ar), 130.0 (Ar), 132.3 (Ar), 132.9 (Ar), 133.2 (Ar), 133.4 (Ar), 145.5 (Ar), 145.6 (Ar), 170.2 (C=O), 171.5 (C=O); IR (cm⁻¹) (KBr) 3452 br, 2974 s, 2934 m, 2882 m, 1706 s, 1615 w, 1469 m, 1370 s, 1319 s, 1266 m, 1232 m, 1203 m, 1140 s, 1073 m, 1052 m, 1030 m, 996 w, 961 w, 944 w, 916 w, 890 w, 858 w, 829 w, 801 w, 763 s, 732 s, 710 s; MS m/z (relative intensity) 261 (M⁺, 0.42), 203 (15), 202 (100), 186 (10), 160 (34), 148 (38), 130 (61), 102 (14), 77(10), 76 (12), 55 (46); Anal. Calcd for C₁₅H₁₉NO₃: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.98; H, 7.23; N, 5.37.

The Reaction of the Cyclic Dienolate 8 with Pivaloyl Chloride. Preparation of 9b-(2,2-Dimethylpropionyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (24). To a THF solution of the cyclic dienolate 8 was added 0.27 mL (2.2 mmol) of pivaloyl chloride at -78 °C and the mixture was allowed to 20 °C for 3 h. The reaction mixture was filtered through a celite, and washed with pentane (20 mL $\times$ 2). The filtrate was evaporated under reduced pressure to give a brown oil. The ¹³C-NMR spectrum of the residue displayed a resonance at δ 208.6 ppm, which was regarded as a peak of ketone carbonyl. 9b-(2,2-Dimethylpropionyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (24) was isolated from the crude mixture by column chromatography on silica gel.

9b-(2,2-Dimethylpropionyl)-3,3-dimethyl-2,3-dihydrooxazolo[2,3-a]isoindol-5(9bH)-one (24). 80% yield, colorless oil, $R_f = 0.24$ (hexane/EtOAc = 4/1): ¹H-NMR (CDCl₃) δ 1.00 (s, 9H, C(CH₃)₃), 1.47 (s, 3H, CH₃), 1.60 (s, 3H, CH₃), 3.99 (d, $J = 8.6$ Hz, 1H, OCHH), 4.11 (d, $J = 8.6$ Hz, 1H, OCHH), 7.40-7.42 (m, 1H, ArH), 7.56-7.62 (c, 2H, ArH), 7.77-7.85 (m, 1H, ArH); ¹³C-NMR (CDCl₃) δ 23.9 (CH₃), 26.4 (CH₃), 28.1 (C(CH₃)₃), 44.3 (C(CH₃)₃), 60.6 (NC(CH₃)₂), 83.7 (OCH₂), 102.6 (NCO), 123.0 (Ar), 124.1 (Ar), 130.9 (Ar), 132.6 (Ar), 134.6 (Ar), 141.9 (Ar), 171.9 (N-C=O), 209.3 (C=O); IR (cm⁻¹) (neat) 2976 m, 2880 m, 1723 s, 1707 s, 1613 w, 1484 m, 1468 m, 1391 w, 1369 w, 1337 m, 1300 s, 1265 m, 1235 w, 1201 m, 1147 w, 1123 w, 1084 m, 1045 m, 914

m, 767 m, 706 m; MS m/z (relative intensity) 287 (M^+ , 0.04), 203 (14), 202 (100), 160 (30), 148 (34), 130 (57), 102 (12), 57 (16), 55 (26); Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.89; H, 7.47; N, 4.99.

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