Supporting Informations

Chiral DBFOX/Ph Complexese Catalyzed Enantioselective Nitronc Cycloadditions to α,β -Unsaturated Aldehydes

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General procedures:

Proton NMR spectra were recorded on JEOL LA 395 NMR spectrometer (395 MHz). Chemical shifts were reported in parts per million downfield (δ) relative to internal tetramethylsilane (TMS, δ 0.00) or with the solvent reference as the internal standard (CDCl_3 , δ 7.26). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, o = octet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. Carbon NMR spectra were recorded on JEOL LA 395 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in parts per million downfield (δ) relative to internal TMS with the respective solvent reference as the internal standard (CDCl_3 , δ 77.0). NMR data were collected at 27 °C unless otherwise stated. Elemental analyses were performed with Hitachi 026 CHN analyzer. Infrared (IR) spectra were recorded on SHIMADZU FTIR-8300 spectrophotometer, $\square_{\text{max}}$ in cm^{-1} . Mass spectra were recorded with JEOL-JMS-70 spectrometer operating at ionization energy of 70 eV. Enantiomer ratios were determined by chiral high performance liquid chromatography (HPLC) analysis (SHIMADZ LC-10Avp) attached by Daicel Chiral Cell AD, OD, ADH and ODH in comparison with authentic materials. Specific rotations were recorded with Horiba SEPA-200 polarimeter. Melting points were recorded on Yanagimoto melting point apparatus JANACO MP. Frash chromatography was performed using Silica Gel 60 (63-210 microns, spherical, neutral) from Kanto Chemicals, Inc.

Solvents and materials:

Dry dichloromethane is commercially available. Nitrones were prepared from *N*-phenylhydroxylamine and the corresponding aldehydes. α -Bromoacrolein was prepared from acrolein and bromine, followed by dehydrobromination with tertiary amines.

In situ Generation of the DBFOX/Ph • ZnI(ClO₄) complex

DBFOX/Ph • ZnI(ClO₄) complex

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol) and ZnI₂ (0.016 g, 0.05 mmol) and AgClO₄ (0.010 g, 0.05 mmol) in CH₂Cl₂ (2 ml) was stirred at rt for 3h.

DBFOX • Mg(ClO₄)₂ complex

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol) and Mg(ClO₄)₂ (0.011 g, 0.05 mmol) in CH₂Cl₂ (2 ml) was stirred at rt for 3h.

DBFOX • Co(ClO₄)₂ • 6H₂O comolex

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol) and Mg(ClO₄)₂ (0.018 g, 0.05 mmol) in CH₂Cl₂ (2 ml) was stirred at rt for 3h.

Isolation of DBFOX/Ph • ZnI(ClO₄) complex

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol) and ZnI₂ (0.016 g, 0.05 mmol) and AgClO₄ (0.010 g, 0.05 mmol) in CH₂Cl₂ (2 ml) was stirred at rt for 3h. The precipitate was removed off by filtration and the solvent was evaporated in vacuo to give a colorless solid of the DBFOX/Ph • ZnI(ClO₄) complex. This complex isolated was stored in open air for 3 weeks and used in the following reaction. Other complexes similarly prepared, DBFOX/Ph • ZnI(BF₄) and DBFOX/Ph • Zn(BF₄)₂, could be stored in open air and employed in the same reaction as shown below.

condition : Isolated complex (10 mol% each), MS 4A (500 mg/mmol), CH₂Cl₂, rt

Entry	Complex	Time (h)	Yield (%)	endo/exo	%ee
1	DBFOX/Ph • ZnI(ClO ₄)	0.5	86	99/1	96/79
2	DBFOX/Ph • ZnI(BF ₄)	1	87	98/2	96/86
3	DBFOX/Ph • Zn(BF ₄) ₂	3	77	87/13	84/72

5-Methyl-2,3-diphenylisoxazolidine-5-carbaldehyde (3) and

5-methyl-2,3-diphenylisoxazolidine-5-methanol (4):

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol) and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.018 g, 0.05 mmol) in CH_2Cl_2 (2 ml) was stirred at rt for 3 h. To the resulting suspension were added a solution of methacrolein (0.0434 ml, 0.5 mmol) in CH_2Cl_2 (3 ml), MS 4A (500 mg/mmol), and *N*-benzylidenaniline *N*-oxide (0.099 g, 0.5 mmol) in this order. After stirring was continued for 48 h at room temperature, the reaction mixture was poured into saturated aqueous ammonium chloride, and extracted three times with CH_2Cl_2 (15 ml x 3). The combined organic extracts were dried over MgSO_4 and evaporated. The residue was purified by column chromatography over silica gel with hexane: AcOEt = 6:1 v/v to give 5-methyl-2,3-diphenylisoxazolidine-5-carbaldehyde (**3**) as colorless solid (0.10 g, 73%).

3: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **3** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 78 °C; IR (KBr) ν = 3089, 3066, 3035, 2989, 2950, 2812, 2715, 1724, 1593, 1485, 1458, 1373, 1311, 1296, 1280, 1242, 1203, 1107, 1080, 1029, 941, 918, 879, 852, and 659 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.48 (3H, s, Me), 2.27 (1H, dd, J_{gem} = 12.6 and J_{4-3} = 7.2 Hz, one of H-4), 3.26 (1H, dd, J_{gem} = 12.6 and J_{4-3} = 7.9 Hz, the other of H-4), 4.75 (1H, t, J_{3-4} = 7.9, 7.2 Hz, H-3), 6.86-7.43 (10H, m, Ph), and 9.66 (1H, s, CHO); ^{13}C NMR (CDCl_3) δ = 18.74 (Me), 46.19, 68.56, 87.13 (each isoxazolidine), 114.84, 121.61, 126.59, 127.57, 128.65, 128.79, 141.06, 149.98 (each Ph), and 201.35 (CHO); Mass (EI, relative intensity, %) m/z 268 (M^+ , 20), 267 (base peak), 249 (30), 233 (13), 224 (15), 220 (16), 196 (33), 194 (10), 182 (33), 181 (19), 180 (32), 146 (25), 145 (19), 131 (31), 121 (45), 119 (10), 104 (20), 103 (31), 93 (21), 91 (17), 77 (44), and 58 (16). Anal. by HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: m/z 267.1259 (M^+). Found m/z 267.1261.

This compound **3** (0.1 g, 0.37 mmol) was treated with sodium borohydride (0.042 g, 1.11 mmol) in THF at room temperature for 0.5 h and then the mixture was poured into saturated NH_4Cl aq.. The product was extracted with diethyl ether (15 ml x 2). The combined organic layers were dried over magnesium sulfate and evaporated to give the corresponding primary alcohol **4** (0.08 g, 82%) which was purified through silica gel column chromatography with hexane : AcOEt = 6:1 v/v to give colorless solid of 5-methyl-2,3-diphenylisoxazolidine-5-methanol (**4**).

4: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The residue obtained by evaporation of the fraction in vacuo solidified on standing); mp: 58 °C; $[\alpha]_{\text{D}}^{25}$ = +155.6 (c = 1.0, CHCl_3); IR (KBr) ν = 3340, 3085, 3062, 3028, 2977, 2908, 2869, 1596, 1488, 1454, 1415, 1369, 1311, 1272, 1226, 1191, 1145, 1056, 979, 948, 894, 952, 813, 779, and 756 cm^{-1} ; ^1H NMR (CDCl_3) δ = 1.47 (3H, s, Me), 1.93 (1H, appt, J_{OHCH_2} = 6.5 z, OH), 2.23 (1H, dd, J_{gem} = 12.3, J_{4-3} = 8.2 Hz, one of H-4), 2.94 (1H, dd, J_{gem} = 12.3, and J_{4-3} = 8.2 Hz, the other of H-4), 3.48 (1H, dd, J_{gem} = 11.8 and $J_{\text{CH}_2\text{-OH}}$ = 6.5 Hz, one of CH_2OH), 3.57 (1H, dd, J_{gem} = 11.8 and $J_{\text{CH}_2\text{-OH}}$ = 5.8 Hz, the other of CH_2OH), 4.62 (1H, t, J_{3-4} = 8.2 Hz, H-3), and 6.88-7.46 (10H, m, Ph); ^{13}C NMR (CDCl_3) δ = 22.47 (Me), 48.46 (CH_2OH), 67.04, 69.68, 83.31 (each isoxazolidine), 114.89, 121.59, 126.56, 127.46, 128.76, 128.86, 141.80, and 150.93 (each Ph); Mass

(FAB, relative intensity/%) m/z 270 ($M^+ + 1$, 39), 269 (M^+ , base peak), and 91 (10). Anal. by HRMS (FAB): Calcd for $C_{17}H_{19}NO_2$: m/z 269.1416 (M^+). Found: m/z 269.1416.

**4-Bromo-2,3-diphenylisoxazolidine-4-carbaldehyde (6) and
4-bromo-2,3-diphenylisoxazolidine-4-methanol (7):**

A mixture of (*R,R*)-DBFOX/Ph (0.023 g, 0.05 mmol), ZnI_2 (0.018 g, 0.05 mmol), and $AgClO_4$ (0.010 g, 0.05 mmol) in CH_2Cl_2 (2 ml) was stirred at rt for 3 h. To the resulting suspension were added a solution of α -bromoacrolein (0.135 g, 0.5 mmol) in CH_2Cl_2 (3 ml), MS 4A (500 mg/mmol), and *N*-benzylidenaniline *N*-oxide (0.099 g, 0.5 mmol) in this order. After stirring was continued for 30 min. at room temperature, the reaction mixture was poured into saturated aqueous ammonium chloride, and extracted three times with CH_2Cl_2 (15 ml x 3). The combined organic extracts were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography over silica gel with hexane: AcOEt = 6:1 v/v to give 4-bromo-2,3-diphenylisoxazolidine-4-carbaldehyde (**6**) as colorless solid (0.18 g, 94%):

6: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 65 °C; IR (KBr) ν = 3066, 3031, 2850, 1724, 1596, 1488, 1454, 1346, 1330, 1303, 1261, 1145, 1080, 1026, 999, 952, 921, 891, 756, 694, 663, and 628 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 4.52 (1H, d, J_{gem} = 10.0 Hz, one of H-5), 4.71 (1H, d, J_{gem} = 10.0 Hz, the other of H-5), 5.05 (1H, s, H-3), 6.96 - 8.01 (10 H, m, Ph), and 9.50 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) δ = 71.67, 73.99, 74.61 (each isoxazolidine), 116.45, 123.39, 128.46, 128.61, 128.66, 128.83, 138.03, 149.30 (each Ph), and 189.20 (CHO); Mass (FAB, relative intensity, %) m/z 333 ($M^+ + 2$, 26), 331 (M^+ , 26), 197 (13), 181 (10), 180 (11), 155 (23), 153 (20), 152 (11), 149 (29), 139 (11), 138 (27), 137 (56), 124 (10), 120 (13), 117 (17), 115 (14), 108 (10), 106 (34), 105 (22), 90 (17), 89 (29), and 78 (13). Anal. by HRMS (FAB): Calcd for $C_{16}H_{14}BrNO_2$: m/z 331.0208. Found: m/z 331.0211.

This compound **6** (0.18 g, 0.54 mmol) was treated with sodium borohydride (0.062 g, 1.62 mmol) in THF at room temperature for 0.5 h and then the mixture was poured into saturated NH_4Cl aq.. The product was extracted with diethyl ether (15 ml x 2). The combined organic layers were dried over magnesium sulfate and evaporated to give the corresponding primary alcohol **7** (0.14 g, 82%) which was purified through silica gel column chromatography with hexane : AcOEt = 6:1 v/v to give colorless solid of 4-bromo-2,3-diphenylisoxazolidine-4-methanol (**7**).

7: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **7** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 85 °C; $[\alpha]_D^{25}$ = -135.4 (c = 1.0, $CHCl_3$); IR (KBr) ν = 3510, 3425, 3058, 3035, 2985, 2935, 2873, 2854,

2808, 2360, 2333, 1596, 1488, 1454, 1342, 1261, 1153, 1026, 999, 752, and 698 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.12 - 2.15 (1H, m, OH), 3.92 (1H, dd, J_{gem} = 12.6 and $J_{\text{CH}_2\text{-OH}}$ = 6.8 Hz, one of CH_2OH), 3.98 (1H, dd, J_{gem} = 12.6 and $J_{\text{CH}_2\text{-OH}}$ = 7.0 Hz, the other of CH_2OH), 4.43 (1H, d, J_{gem} = 9.7 Hz, one of H-5), 4.50 (1H, s, H-3), 4.50 (1H, d, J_{gem} = 9.7 Hz, the other of H-5), and 6.93 - 7.50 (10H, m, Ph); ^{13}C NMR (CDCl_3) δ = 68.15, 75.26, 76.35, 78.26 (each isoxazolidine, CH_2OH), 115.50, 122.59, 128.23, 128.44, 128.81, 139.91, 140.81, 150.27 (each Ph); Mass (EI, relative intensity, %) m/z 335 ($\text{M}^+ + 2$, 14), 333 (M^+ , 14), 196 (10), 182 (13), 181 (27), 180 (28), 117 (21), 116 (15), 105 (17), 104 (17), 91 (base peak), 78 (14), and 77 (81). Anal. by HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{16}\text{BrNO}_2$: m/z 333.0364. Found: m/z 333.0365.

4-Bromo-3-(4-methylphenyl)-2-phenylisoxazolidine-4-carbaldehyde (6b) and 4-bromo-3-(4-methylphenyl)-2-phenylisoxazolidine-4-methanol (7b):

6b: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); IR (NaCl) ν = 3379, 3028, 2923, 2858, 1724, 1685, 1643, 1600, 1492, 1450, 1307, 1215, 1168, 1022, 810, 756, and 694 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.38 (3H, s, Me), 4.50 (1H, d, J_{gem} = 9.9 Hz, one of H-5), 4.70 (1H, d, J_{gem} = 9.9 Hz, the other of H-5), 4.99 (1H, s, H-3), 6.64 - 7.41 (9H, m, Ar), and 9.49 (1H, s, CHO); ^{13}C NMR (CDCl_3) δ = 21.25 (Me), 71.65, 73.95, (each isoxazolidine, overlapping), 116.49, 123.34, 128.35, 128.79, 129.32, 134.94, 138.50, 149.36 (each Ar), and 189.34 (CHO); MS (EI, relative intensity, %) m/z 347 ($\text{M}^+ + 2$), 345 (M^+), 211 (59), 210 (40), 195 (29), 183 (14), 182 (21), 131 (20), 119 (23), 91 (base peak), and 77 (16); Anal. by HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{16}\text{BrNO}_2$: m/z 345.0364. Found: m/z 345.0360.

7b: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6b** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 67 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = -139.1 (c = 0.78, CHCl_3); IR (KBr) ν = 3571, 3035, 2923, 2846, 1593, 1512, 1488, 1450, 1342, 1299, 1265, 1180, 1114, 1080, 1029, 894, 860, 810, 771, 756, 694, and 659 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.14 (1H, t, $J_{\text{OH-CH}_2}$ = 6.0, 7.5 Hz, OH), 2.38 (3H, s, Me), 3.91 (2H, dd, J_{gem} = 12.1 and $J_{\text{CH}_2\text{-OH}}$ = 7.7 Hz, one of CH_2OH), 3.97 (2H, dd, J_{gem} = 12.1 and $J_{\text{CH}_2\text{-OH}}$ = 6.0 Hz, one of CH_2OH), 4.42 (1H, d, J_{gem} = 9.7 Hz, H-5), 4.45 (1H, s, H-3), 4.49 (1H, d, J_{gem} = 9.7 Hz, the other of H-5), and 6.93 - 7.38 (9H, m, Ar); ^{13}C NMR (CDCl_3) δ = 21.26 (Me), 68.03, 75.12, 76.34, 78.54 (each isoxazolidine, CH_2OH), 115.486, 122.52, 128.08, 128.78, 129.15, 135.97, 138.20, and 150.38 (each Ar); MS (EI, relative intensity, %) m/z 349 ($\text{M}^+ + 2$, 8), 347 (M^+ , 8), 210 (11), 196 (16), 195 (42), 194 (44), 131 (23), 130 (17), 129 (17), 128 (14), 119 (17), 116 (14), 115 (22), 105 (11), 104 (19), 92 (13), 91 (94), 78 (14), and 77 (base peak). Anal. by HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{18}\text{BrNO}_2$: m/z 347.0521. Found: m/z 347.0523.

4-Bromo-3-(4-bromophenyl)-2-phenylisoxazolidine-4-carbaldehyde (6c) and 4-bromo-3-(4-bromophenyl)-2-phenylisoxazolidine-4-methanol (7c):

6c: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); IR (NaCl) ν = 3425, 3070, 3031, 2923, 2854, 1724, 1593, 1488, 1454, 1407, 1338, 1249, 1180, 1153, 1103, 1072, 1033, 1010, 941, 891, 852, 813, 752, and 694 cm^{-1} ; ^1H NMR (CDCl_3) δ = 4.50 (1H, d, J_{gem} = 9.9 Hz, one of H-5), 4.68 (1H, d, J_{gem} = 9.9 Hz, the other of H-5), 5.04 (1H, s, H-3), 6.93 - 7.55 (9H, m, Ar), and 9.48 (1H, s, CHO); ^{13}C NMR (CDCl_3) δ = 70.94, 74.08 (each isoxazolidine, overlapping), 116.57, 122.12, 122.73, 123.70, 128.91, 130.13, 131.81, 148.95 (each Ar), and 188.92 (CHO); Mass (EI, relative intensity, %) m/z 412 ($\text{M}^+ + 3$, 14), 410 ($\text{M}^+ + 1$, 29), 408 ($\text{M}^+ - 1$, 15), 277 (20), 276 (12), 275 (22), 261 (14), 260 (10), 259 (14), 116 (20), 115 (13), 91 (base peak), and 77 (18). Anal. by HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{NO}_2$: m/z 410.9293 ($\text{M}^+ + 2$). Found: m/z 410.9287.

7c: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6c** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 132 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ = -141.7 (c = 1.0, CHCl_3); IR (KBr) ν = 3564, 3055, 2923, 2864, 1593, 1488, 1450, 1400, 1338, 1288, 1261, 1110, 1080, 1029, 1010, 894, 856, 810, 775, 756, 694, and 659 cm^{-1} . ^1H NMR (CDCl_3) δ = 2.14 - 2.17 (1H, m, OH), 3.92 (1H, dd, J_{gem} = 11.1 and $J_{\text{CH}_2\text{-OH}}$ = 5.3 Hz, one of CH_2OH), 3.96 (1H, dd, J_{gem} = 11.1 and $J_{\text{CH}_2\text{-OH}}$ = 6.5 Hz, the other of CH_2OH), 4.41 (1H, d, J_{gem} = 9.7 Hz, one of H-5), 4.48 (1H, d, J_{gem} = 9.7, the other of H-5), 4.49 (1H, s, H-3), and 6.91 - 7.54 (9H, m, Ar); ^{13}C NMR (CDCl_3) δ = 68.16, 74.68, 76.32, 77.64 (each isoxazolidine, CH_2OH), 115.51, 122.39, 122.84, 128.89, 129.90, 131.61, 138.12, and 149.91 (each Ar); Mass (EI, relative intensity, %) m/z 415 ($\text{M}^+ + 4$, 14), 413 ($\text{M}^+ + 2$, 42), 412 ($\text{M}^+ + 1$, 4), 411 (M^+ , 21), 277 (18), 276 (12), 275 (18), 274 (11), 262 (14), 261 (21), 260 (31), 259 (20), 258 (17), 146 (13), 116 (22), 115 (28), 104 (14), 91 (base peak), and 77 (40). Anal. by HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{15}\text{Br}_2\text{NO}_2$: m/z 412.9450 ($\text{M}^+ + 2$). Found: m/z 412.9450.

4-Bromo-3-(4-nitrophenyl)-2-phenylisoxazolidine-4-carbaldehyde (6d) and **4-bromo-3-(4-nitrophenyl)-2-phenylisoxazolidine-4-methanol (7d):**

6d: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); IR (NaCl) ν = 3514, 3074, 3024, 2927, 2854, 2360, 1936, 1728, 1596, 1519, 1488, 1454, 1346, 1218, 1176, 1145, 1107, 1033, 852, 756, and 694 cm^{-1} ; ^1H NMR (CDCl_3) δ = 4.52 (1H, d, J_{gem} = 10.2 Hz, one of H-5), 4.69 (1H, d, J_{gem} = 10.2 Hz, the other of H-5), 5.25 (1H, s, H-3), 6.93 - 8.26 (9H, m, Ar), and 9.49 (1H, s, CHO); ^{13}C NMR (CDCl_3) δ = 70.45, 73.64, 74.21 (each isoxazolidine), 116.45, 123.74, 123.95, 128.99, 129.36, 145.20, 147.92, 148.48 (each Ar), and 188.41 (CHO); Mass (EI, relative intensity, %) m/z 378 ($\text{M}^+ + 2$, 3), 376 (M^+ ,

3), 226 (13), 116 (13), 115 (17), 104 (11), 91 (base peak), 77 (64). Anal. by HRMS (EI): Calcd for $C_{16}H_{13}BrN_2O_4$: m/z 376.0059 (M^+). Found: m/z 376.0056.

7d: Pale yellow solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6d** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 76 °C; $[\alpha]_D^{25} = -146.3$ ($c = 1.0$, $CHCl_3$); IR (KBr) $\nu = 3317, 2943, 2858, 1596, 1519, 1488, 1454, 1346, 1315, 1272, 1107, 1083, 1014, 871, 852, 825, 783, 752, 694$, and 659 cm^{-1} ; 1H NMR ($CDCl_3$) $\delta = 2.21$ (1H, br, OH), 3.98 (2H, br, CH_2OH), 4.43 (1H, d, $J_{gem} = 9.7$ Hz, one of H-5), 4.51 (1H, d, $J_{gem} = 9.7$ Hz, the other of H-5), 4.72 (1H, s, H-3), and 6.89 - 8.28 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) $\delta = 68.36, 74.52, 76.48, 76.68$ (each isoxazolidine, CH_2OH), 115.47, 123.18, 123.67, 129.04, 129.18, 146.51, and 149.49 (each Ar, overlapping). Mass (EI, relative intensity, %) m/z 380 ($M^+ + 2$, 49), 378 (M^+ , 49), 242 (15), 227 (41), 226 (58), 225 (21), 181 (13), 180 (11), 179 (32), 116 (16), 115 (27), 107 (11), 104 (18), 91 (base peak), and 77 (50). Anal. by HRMS (EI): Calcd for $C_{16}H_{15}BrN_2O_4$: m/z 378.0215 (M^+). Found: m/z 378.0212.

4-Bromo-3-(2-furyl)-2-phenylisoxazolidine-4-carbaldehyde (6e) and 4-bromo-3-(2-furyl)-2-phenylisoxazolidine-4-methanol (7e):

6e: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6e** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 96 °C; IR (KBr) $\nu = 3429, 3143, 3071, 3039, 2985, 2939, 2877, 2842, 2781, 2723, 1724, 1593, 1492, 1454, 1334, 1299, 1269, 1230, 1188, 1149, 1068, 1049, 1010, 960, 937, 918, 898, 883, 829, 802, 756$, and 694 cm^{-1} ; 1H NMR ($CDCl_3$) $\delta = 4.49$ (1H, d, $J_{gem} = 9.7$ Hz, one of H-5), 4.68 (1H, d, $J_{gem} = 9.7$ Hz, the other of H-5), 5.13 (1H, s, H-3), 6.39 - 7.47 (8H, m, Ar), and 9.46 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) $\delta = 66.76, 71.42, 73.27$ (each isoxazolidine), 110.53, 116.24, 123.67, 128.84, 143.03, 148.96, 150.38 (each Ar), and 188.60 (CHO); Mass (EI, relative intensity, %) m/z 323 ($M^+ + 2$, 10), 321 (M^+ , 11), 187 (37), 171 (33), 170 (18), 158 (10), 135 (34), 115 (10), 107 (12), 104 (13), 91 (89), 79 (16), 78 (19), and 77 (base peak). Anal. by HRMS (EI): Calcd for $C_{14}H_{12}BrNO_3$: m/z 321.0001 (M^+). Found: m/z 320.9999.

7e: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); $[\alpha]_D^{25} = -159.2$ ($c = 1.0$, $CHCl_3$); IR (NaCl) $\nu = 3417, 3124, 3062, 3035, 2927, 2873, 1944, 1596, 1488, 1454, 1388, 1253, 1149, 1114, 1072, 1029, 1006, 941, 883, 752$, and 694 cm^{-1} ; 1H NMR ($CDCl_3$) $\delta = 2.27$ (1H, dd, $J_{OH-CH_2} = 7.7$ and 6.0 Hz, OH), 3.92 (1H, dd, $J_{gem} = 12.3$ and $J_{CH_2-OH} = 7.7$ Hz, one of CH_2OH), 4.00 (1H, dd, $J_{gem} = 12.3$ and $J_{CH_2-OH} = 6.0$ Hz, the other of CH_2OH), 4.38 (1H, d, $J_{gem} = 9.7$ Hz, H-5), 4.48 (1H, d, $J_{gem} = 9.7$ Hz, the other of H-5), 4.62 (1H, s, H-3), and 6.41 - 7.50 (8H, m, Ar); ^{13}C NMR ($CDCl_3$) $\delta = 67.82, 70.19, 76.03, 76.46$ (each isoxazolidine, CH_2OH), 109.48, 110.53, 115.39, 122.95, 128.88, 142.53, 150.08, and 151.80

(each Ar); Mass (EI, relative intensity, %) m/z 325 ($M^+ + 2$, 35), 323 (M^+ , 38), 187 (37), 172 (17), 171 (17), 170 (15), 159 (10), 158 (13), 137 (24), 107 (10), 104 (15), 91 (77), 81 (15), 77 (base peak), and 65 (12). Anal. by HRMS (EI): Calcd for $C_{14}H_{14}BrNO_3$: m/z 323.0157 (M^+). Found: m/z 323.0157.

4-Bromo-3-(1-naphthyl)-2-phenylisoxazolidine-4-carbaldehyde (6f) and

4-bromo-3-(1-naphthyl)-2-phenylisoxazolidine-4-methanol (7f):

6f: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); IR (NaCl) ν = 3421, 3058, 2920, 2846, 2727, 1940, 1855, 1724, 1596, 1512, 1488, 1454, 1396, 1377, 1269, 1230, 1149, 1056, 1026, 914, 883, 802, 775, 756, 690, and 651 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 4.56 (1H, d, J_{gem} = 9.7 Hz, one of H-5), 4.74 (1H, d, J_{gem} = 9.7 Hz, the other of H-5), 5.93 (1H, s, H-3), 6.84 - 8.42 (12H, m, Ar), and 9.56 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) δ = 66.02, 72.72, 73.78 (each isoxazolidine), 116.11, 122.73, 123.05, 125.43, 125.83, 126.50, 126.74, 128.75, 128.94, 129.11, 131.13, 133.68, 134.14, 148.93 (each Ar), and 189.90 (CHO); Mass (FAB, relative intensity, %) m/z 384 (19), 383 ($M^+ + 2$, 46), 382 ($M^+ + 1$, 19), 381 (M^+ , 44), 273 (10), 248 (15), 247 (42), 246 (26), 244 (10), 231 (10), 230 (20), 219 (13), 195 (15), 167 (32), 166 (25), 165 (28), 155 (30), 153 (24), 152 (22), 139 (16), 138 (27), 137 (52), 128 (11), 127 (10), 120 (14), 115 (10), 106 (10), 105 (11), 104 (12), 91 (22), 90 (16), 89 (25), and 78 (11). Anal. by HRMS (FAB): Calcd for $C_{20}H_{16}BrNO_2$: m/z 381.0364 (M^+). Found: m/z 381.0367.

7f: Colorless liquid (purified by column chromatography with hexane : AcOEt = 6:1 v/v); $[\alpha]_D^{25}$ = -37.5 (c = 1.0, $CHCl_3$); IR (NaCl) ν = 3440, 3058, 3012, 2927, 2873, 1994, 1596, 1512, 1488, 1454, 1396, 1338, 1257, 1230, 1114, 1083, 1029, 802, 779, 756, and 694 cm^{-1} ; 1H NMR ($CDCl_3$) δ = 2.31 (1H, br, OH), 4.01 (1H, dd, J_{gem} = 11.6 and J_{CH_2-OH} = 5.8 Hz, one of CH_2OH), 4.10 (1H, dd, J_{gem} = 11.6 and J_{CH_2-OH} = 3.1 Hz, the other of CH_2OH), 4.52 (2, s, H-5), 5.46 (1H, s, H-3), and 6.86-8.20 (12H, m, Ar); ^{13}C NMR ($CDCl_3$) δ = 68.25, 69.59, 75.59, 76.93 (each isoxazolidine, CH_2OH), 114.95, 122.24, 122.44, 125.55, 125.61, 126.47, 126.95, 128.85, 128.87, 129.30, 131.17, 133.71, 134.97, and 150.08 (each Ar); Mass (EI, relative intensity, %) m/z 385 ($M^+ + 2$, 9), 383 (M^+ , 9), 246 (10), 231 (17), 230 (31), 179 (13), 167 (26), 166 (18), 165 (40), 154 (12), 153 (23), 152 (27), 141 (11), 139 (11), 128 (25), 127 (41), 126 (16), 115 (11), 107 (15), 104 (13), 91 (23), 78 (12), and 77 (base peak). Anal. by HRMS (EI): Calcd for $C_{20}H_{18}BrNO_2$: m/z 383.0521 (M^+). Found: m/z 383.0516.

4-Bromo-3-(2-naphthyl)-2-phenylisoxazolidine-4-carbaldehyde (6g) and

4-bromo-3-(2-naphthyl)-2-phenylisoxazolidine-4-methanol (7g):

6g: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **6g** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 118 °C; IR (KBr) ν = 3749, 3733, 3058, 3024, 2931, 2850, 1720, 1651, 1596, 1488, 1454, 1369, 1330, 1265, 1145, 1126, 1041, 1022, 956, 914, 875, 821, 756, and 694 cm^{-1} ; ^1H NMR (CDCl_3) δ = 4.58 (1H, d, J_{gem} = 9.9 Hz, one of the H-5), 4.75 (1H, dd, J_{gem} = 9.9 and $J_{5\text{-CHO}}$ = 0.7 Hz, the other of H-5), 5.23 (1H, s, H-3), 6.97 - 7.94 (12H, m, Ar), and 9.55 (1H, d, $J_{\text{CHO-5}}$ = 0.7 Hz, CHO); ^{13}C NMR (CDCl_3) δ = 71.87, 74.15, 74.59 (each isoxazolidine), 116.45, 123.42, 125.96, 126.43, 126.53, 127.71, 127.78, 128.24, 128.36, 128.85, 133.14, 133.42, 135.55, 149.33 (each Ar), and 189.78 (CHO); Mass (FAB, relative intensity, %) m/z 383 ($\text{M}^+ + 2$, 6), 381 (M^+ , 5), 166 (11), 165 (10), 155 (25), 153 (13), 152 (11), 139 (11), 138 (28), 137 (55), 91 (11), and 90 (12). Anal. by HRMS (FAB): Calcd for $\text{C}_{20}\text{H}_{16}\text{BrNO}_2$: m/z 383.0346 (M^+). Found: m/z 381.0366.

7g: Colorless solid (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **7g** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); mp: 157 °C; $[\alpha]_{\text{D}}^{25}$ = -139.1 (c = 1.0, CHCl_3); IR (KBr) ν = 3564, 3066, 3031, 2923, 2881, 2846, 1593, 1485, 1450, 1365, 1334, 1288, 1265, 1164, 1080, 1029, 956, 910, 894, 825, 763, 694, and 663 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.20 (1H, br, OH), 3.99 (1H, d, J_{gem} = 12.1 Hz, one of CH_2OH), 4.05 (1H, d, J_{gem} = 12.1 Hz, the other of CH_2OH), 4.48 (1H, d, J_{gem} = 9.7 Hz, one of H-5), 4.56 (1H, d, J_{gem} = 9.7 Hz, the other of H-5), 4.68 (1H, s, H-3), and 6.93-7.94 (12H, m, Ar); ^{13}C NMR (CDCl_3) δ = 68.24, 75.48, 76.43, 78.12 (each isoxazolidine and CH_2OH), 115.52, 122.63, 126.04, 126.30, 126.33, 127.30, 127.77, 128.11, 128.19, 128.83, 130.64, 133.34, and 136.64 (each Ar, overlapping); Mass (EI, relative intensity, %) m/z 385 ($\text{M}^+ + 2$, 15), 383 (M^+ , 15), 247 (16), 246 (10), 232 (17), 231 (44), 230 (38), 179 (12), 167 (23), 165 (28), 153 (17), 152 (19), 153 (17), 152 (19), 144 (10), 141 (11), 139 (12), 128 (25), 127 (33), 126 (14), 115 (12), 104 (22), 91 (30), 78 (11), and 77 (base peak). Anal. by HRMS (EI): Calcd for $\text{C}_{20}\text{H}_{18}\text{BrNO}_2$: m/z 383.0521 (M^+). Found: m/z 383.0518.

2,3-Diphenylisoxazolidine-5-methanol (**13**) and 2,3-diphenylisoxazolidine-4-methanol (**13'**):

13: Colorless oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **13** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_{\text{D}}^{25}$ = 125.71 (c = 0.28, CHCl_3); IR (NaCl) ν = 3367, 3069, 3026, 2935, 2877, 1647, 1596, 1488, 1450, 1427, 1045, 752 and 698 cm^{-1} ; ^1H NMR (CDCl_3) δ = 2.38 (1H, ddd, J_{gem} = 12.1, J_{4-3} = 6.0, J_{4-5} = 5.8 Hz, one of H-4), 2.67 (1H, ddd, J_{gem} = 12.1, J_{4-3} = 8.7, J_{4-5} = 3.6 Hz, the other of H-4), 3.64 (1H, dd, J_{gem} = 12.1, $J_{5'-5}$ = 5.8 Hz, one of H-5'), 3.81 (1H, dd, J_{gem} = 12.1, $J_{5'-5}$ = 3.1 Hz, the other of H-5'), 4.50 (1H, eighth, J_{5-4} = 5.8, 3.6, J_{5-5} = 5.8, 3.1 Hz, H-5), 4.59 (1H, dd, J_{3-4} = 8.7, 6.0 Hz, H-3) and 6.89-7.51 (10H, m, Ar). ^{13}C NMR (CDCl_3)

δ = 60.38, 63.31, 68.93, 78.32 (each isoxazolidine and CH₂OH), 115.43, 121.95, 126.62, 127.26, 127.48, 128.11, 128.64, 128.77 (each Ar); Mass (EI, relative intensity, %) m/z 256 ($M^+ + 1$, 18), 255 (M^+ , base peak), 194 (14), 182 (16), 181 (10), 147 (15), 129 (41), 105 (12), 104 (19), 91 (76) and 77 (33). Anal. by HRMS (EI): Calcd for C₁₆H₁₇BrNO₂: m/z 255.1259 (M^+). Found: m/z 255.1252.

13': Colorless oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **13** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_D^{25}$ = -64.83(c = 0.6, CHCl₃); IR (NaCl) ν = 3421, 3064, 3026, 1654, 1647, 1637, 1629, 1596, 1488, 1217, 1072, 1029, 754, 698 and 667 cm⁻¹; ¹H NMR (CDCl₃) δ = 2.87 (1H, m, H-4), 3.69 (1H, dd, J_{gem} = 10.6, $J_{4'-4}$ = 67.2 Hz, one of H-4'), 3.76 (1H, dd, J_{gem} = 10.6, $J_{4'-4}$ = 6.2 Hz, the other of H-4'), 3.95 (1H, dd, J_{gem} = 7.5, J_{5-4} = 6.0 Hz, one of H-5), 4.30 (1H, dd, J_{gem} = 7.5, J_{5-4} = 7.0 Hz, the other of H-5), 4.34 (1H, d, J_{3-4} = 5.6 Hz, H-3) and 6.89-7.52 (10 H, m, Ar). ¹³C NMR (CDCl₃) δ = 56.72, 62.74, 69.30, 72.15 (each isoxazolidine and CH₂OH), 114.712, 121.63, 126.58, 127.49, 128.76, 128.85 (each Ar, overlapping); Mass (FAB, relative intensity, %) m/z 256 ($M^+ + 1$, 38), 255 (M^+ , base peak), 182 (17), 181 (10), 180 (15), 178 (10), 117 (32), 104 (11) and 91 (27). Anal. by HRMS (FAB): Calcd for C₁₆H₁₇NO₂: m/z 255.1259 (M^+). Found: m/z 255.1260.

5-Ethyl-2,3-diphenylisoxazolidine-5-methanol (**14**):

14: Colorless oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **14** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_D^{25}$ = 168.31 (c = 0.303, CHCl₃); IR (NaCl) ν = 3421, 3060, 3026, 2968, 2939, 2879, 1596, 1488, 1452, 1263, 1051, 754 and 698 cm⁻¹; ¹H NMR (CDCl₃) δ = 1.01 (3H, t, J_{Me-CH_2} = 7.5 Hz, Me), 1.78 (1H, app. sextet, J_{gem} = 14.0, J_{CH_2-Me} = 7.5 Hz, one of CH₂Me), 1.94 (1H, app. sextet, J_{gem} = 14.0, J_{CH_2-Me} = 7.5 Hz, the other of CH₂Me), 2.26 (1H, dd, J_{gem} = 12.3, J_{4-3} = 8.5 Hz, one of H-4), 2.82 (1H, dd, J_{gem} = 12.3, J_{4-3} = 8.5 Hz, the other of H-4), 3.48 (1H, d, J_{gem} = 11.8 Hz, one of CH₂OH), 3.61 (1H, J_{gem} = 11.8 Hz, the other of CH₂OH), 4.60 (1H, t, J_{3-4} = 8.5 Hz, H-3) and 6.87-7.46 (10H, m, Ar). ¹³C NMR (CDCl₃) δ = 8.59 (Me), 28.13 (CH₂Me), 46.74, 64.87, 69.44, 85.82 (each isoxazolidine and CH₂OH), 114.93, 121.54, 126.51, 127.46, 128.75 and 128.88 (each Ar, overlapping); Mass (EI, relative intensity, %) m/z 284 ($M^+ + 1$, 20), 283 (M^+ , base peak), 198 (33), 196 (13), 182 (13), 181 (14), 180 (19), 129 (10), 104 (11), 91 (55), 77 (19), 58 (27) and 57 (12). Anal. by HRMS (EI): Calcd for C₁₈H₂₁BrNO₂: m/z 283.1572 (M^+). Found: m/z 283.1571.

5-Phenyl-2,3-diphenylisoxazolidine-5-methanol (**15**) :

15: Yellow oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product was obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_D^{25} = 32.4$ ($c = 1.0$, CHCl_3); IR (NaCl) $\nu = 3411, 3060, 3026, 2925, 2869, 1639, 1598, 1488, 1263, 1170, 1039, 786, 758$ and 700 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 2.66$ (1H, dd, $J_{\text{gem}} = 12.3 \text{ Hz}$, $J_{4-3} = 7.7 \text{ Hz}$, one of the H-4), 3.45 (1H, dd, $J_{\text{gem}} = 12.3$ and $J_{4-3} = 8.9 \text{ Hz}$, the other of H-4), 3.69 (1H, dd, $J_{\text{gem}} = 12.1$, $J_{5'-\text{OH}} = 9.4 \text{ Hz}$, one of H-5'), 3.81 (1H, dd, $J_{\text{gem}} = 12.1 \text{ Hz}$, $J_{5'-\text{OH}} = 9.4 \text{ Hz}$, the other of H-5'), 4.60 (1H, dd, $J_{3-4} = 8.9, 7.7 \text{ Hz}$, H-3) and 6.93-7.54 (15H, m, Ph), ^{13}C NMR (CDCl_3) $\delta = 64.29, 67.64, 70.06, 85.91$ (each isoxazolidine, overlapping), 116.24, 122.22, 123.96, 125.39, 125.46, 126.79, 127.38, 127.40, 128.30, 128.43, 128.73 (each Ar) Mass (EI, relative intensity, %) m/z 332 ($\text{M}^+ + 1, 22$), 331 ($\text{M}^+, 91$), 205 (24), 198 (25), 197 (13), 196 (15), 182 (24), 181 (17), 180 (17), 195 (base peak), 104 (14), 92 (11), 91 (91), 78 (10) and 77 (63). Anal. by HRMS (EI): Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2$: m/z 331.1572 (M^+). Found: m/z 331.1566.

5-Methyl-2,3-diphenylisoxazolidine-4-methanol (16):

16: Colorless oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **16** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_D^{25} = -109.10$ ($c = 0.747$, CHCl_3); IR (NaCl) $\nu = 3419, 3069, 3030, 2974, 2929, 2873, 1596, 1487, 1454, 754$ and 698 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 1.476$ (3H, d, $J_{\text{Me-5}} = 6.0 \text{ Hz}$, Me), 2.42 (1H, m, H-4), 3.72 (1H, dd, $J_{\text{gem}} = 10.8$, $J_{4'-4} = 6.3 \text{ Hz}$, one of H-4'), 3.79 (1H, dd, $J_{\text{gem}} = 10.8$, $J_{4'-4} = 5.3 \text{ Hz}$, the other of H-4'), 4.17 (1H, dq, $J_{5-\text{Me}} = 6.0$, $J_{5-4} = 3.6 \text{ Hz}$, H-5), 4.52 (1H, d, $J_{3-4} = 7.0 \text{ Hz}$, H-3) and 6.87-7.54 (10H, m, Ar). ^{13}C NMR (CDCl_3) $\delta = 17.72$ (Me), 61.38, 63.18, 73.43, 77.21 (each isoxazolidine and CH_2OH), 113.89, 121.11, 126.51, 127.41, 128.85 (each Ar, overlapping). Mass (EI, relative intensity, %) m/z 270 ($\text{M}^+ + 1, 18$), 269 (M^+ , base peak), 196 (10), 180 (12), 131 (13), 91 (58) and 77 (15). Anal. by HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: m/z 269.1416 (M^+). Found: m/z 269.1409.

2,3-Diphenylcyclopenta[d]isoxazolidine-3a-methanol (17):

17: Colorless oil (purified by column chromatography with hexane : AcOEt = 6:1 v/v. The purified product **17** obtained as viscous liquid by evaporation of the fraction in vacuo solidified on standing); $[\alpha]_D^{25} = -76.3$ ($c = 0.83$, CHCl_3); IR (NaCl) $\nu = 3427, 3087, 3027, 2957, 2873, 1710, 1598, 1488, 1250, 1075, 1042, 923, 752$ and 700 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 1.08$ -1.14 (1H, m), 2.03-2.06 (1H, m, H-5), 3.55 (2H, s, CH_2OH), 4.56-4.57 (1H, m, H-1), 4.89 (1H, s, H-4), and 6.87-7.45 (10H, m, Ph), ^{13}C NMR (CDCl_3) $\delta = 24.8, 31.1, 31.6$ (each *c*-penta), 31.6, 66.9, 67.5, 75.5, 86.8, 114.4, 121.1, 127.0, 127.3, 128.1, 128.7, 139.8,

and 151.1; Mass (FAB, relative intensity, %) m/z 296 ($M^+ + 1$, 44), 295 (M^+ , base peak), 182 (10), 180 (10) and 91 (21). Anal. by HRMS (EI): Calcd for $C_{19}H_{21}NO_2$; m/z 295.1572(M^+). Found: m/z 295.1566.

5-Methyl-2,3-diphenyl-5-isoxazolidinylmethyl 4-bromobenzoate (18):

5-Methyl-2,3-diphenylisoxazolidine-5-methanol (**4**, 0.16 g, 0.6 mmol) was treated with *p*-bromobenzoic acid (0.18 g, 0.9 mmol), 1,3-dicyclohexylcarbodiimide (0.15 g, 0.72 mmol), and 4-(dimethylamino)pyridene (0.04 g, 0.3 mmol) in CH_2Cl_2 at 0 °C for 5 min. The resulting solution was allowed to stir at room temperature for 13 h and then filtrated under a diminished pressure. The filtrate was washed with hydrochloric acid (0.5 M, 5 ml x 2) and saturated aqueous sodium hydrogencarbonate (5 ml x 2). The combined organic layers were dried over magnesium sulfate and evaporated to give 5-methyl-2,3-diphenyl-5-isoxazolidinylmethyl 4-bromobenzoate (**18**, 0.02 g, 13%) which was purified through silica gel column chromatography with hexane : AcOEt = 9:1 v/v.

18: Colorless solid (from *i*-PrOH - hexane); mp: 109 °C; $[\alpha]_D^{25} = +89.5$ ($c = 1.0$, $CHCl_3$); IR (KBr) $\nu = 3452, 3406, 3093, 3058, 3024, 2985, 2950, 2873, 1940, 1716, 1631, 1589, 1492, 1446, 1396, 1373, 1265, 1230, 1172, 1141, 1091, 1006, 945, 852, 756, 705$, and 690 cm^{-1} ; 1H NMR ($CDCl_3$) $\delta = 1.56$ (1H, s, Me), 2.36 (1H, dd, $J_{gem} = 12.7$ and $J_{4-3} = 8.2$ Hz, one of H-4), 2.92 (1H, dd, $J_{gem} = 12.7$ and $J_{4-3} = 8.2$ Hz, the other of H-4), 4.24 (1H, d, $J_{gem} = 11.6$ Hz, one of 5- CH_2), 4.32 (1H, d, $J_{gem} = 11.6$ Hz, the other of 5- CH_2), 4.73 (1H, t, $J_{3-4} = 8.2$ Hz, H-3), and 6.85 - 7.83 (14H, m, Ar); ^{13}C NMR ($CDCl_3$) $\delta = 22.83$ (Me), 49.12 (5- CH_2), 68.14, 69.85, 81.88 (each isoxazolidine), 114.53, 121.47, 126.50, 127.58, 128.32, 128.60, 128.66, 128.88, 131.14, 131.80, 141.65, 151.53 (each isoxazolidine), and 165.53 (CO); MS (EI, relative intensity, %) m/z 453 ($M^+ + 2$, 100), 451 (M^+ , 97), 198 (22), 196 (12), 194 (12), 185 (69), 183 (71), 182 (12), 181 (12), 180 (28), 157 (13), 155 (13), 144 (12), 143 (12), 129 (11), 104 (17), 91 (55), 77 (24), and 58 (14). Anal. by HRMS (EI): Calcd for $C_{24}H_{22}BrNO_3$; m/z 451.0783. Found: m/z 451.0781.

4-Bromo-2,3-diphenyl-4-isoxazolidinylmethyl 4-bromobenzoate (19):

4-Bromo-2,3-diphenylisoxazolidine-4-methanol (**7**, 0.2 g, 0.6 mmol) was treated with *p*-bromobenzoic acid (0.12 g, 0.6 mmol), 1,3-dicyclohexylcarbodiimide (0.15 g, 0.72 mmol), and 4-(dimethylamino)pyridene (0.04 g, 0.3 mmol) in CH_2Cl_2 at 0 °C for 5 min. The resulting solution was allowed to stir at room

temperature for 10 h and then the mixture was filtrated under a diminished pressure. The filtrate was washed with hydrochloric acid (0.5 M, 5 ml x 2) and saturated aqueous sodium hydrogencarbonate (5 ml x 2). The combined organic layers were dried over magnesium sulfate and evaporated to give the 4-bromo-2,3-diphenyl-4-isoxazolidinylmethyl 4-bromobenzoate (**19**, 0.30 g, 95%) which was purified through silica gel column chromatography with hexane : AcOEt = 9:1 v/v.

19: Colorless solid (from *i*PrOH - hexane); mp: 114 °C; $[\alpha]_D^{25} = -56.3$ (c= 1.0, CHCl₃); IR (KBr) ν = 3062, 3035, 2931, 2877, 2842, 1724, 1589, 1488, 1454, 1400, 1272, 1176, 1122, 1072, 1014, 840, 756, 705, and 655 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.51 (1H, d, J_{gem} = 9.7 Hz, one of H-5), 4.58 (1H, d, J_{gem} = 9.7 Hz, the other of H-5), 4.62 (1H, s, H-3), 4.69 (1H, d, J_{gem} = 12.1 Hz, one of 4-CH₂), 4.78 (1H, d, J_{gem} = 12.1 Hz, the other of 4-CH₂), and 6.94 - 7.74 (14H, m, Ar); ¹³C NMR (CDCl₃) δ = 67.62 (4-CH₂), 71.97, 75.99, 76.68 (each isoxazolidine), 115.35, 121.72, 122.75, 128.16, 128.50, 128.66, 128.93, 131.21, 131.94, 138.60, 147.24, 150.38 (each isoxazolidine), and 164.97 (CO); MS (FAB, relative intensity, %) m/z 519 ($M^+ + 4$, 2), 517 ($M^+ + 2$, 3), 515 (M^+ , 1), 155 (25), 153 (13), 139 (11), 138 (30), 137 (60), 120 (12), 105 (10), 91 (12), and 90 (14). Anal. by HRMS (FAB): Calcd for C₂₃H₁₉Br₂NO₃: m/z 516.9713 ($M^+ + 2$). Found: m/z 516.9706.

X-ray Structure Report / Compound 18 (C₂₄H₂₂BrNO₃)

Experimental

Data Collection

A colorless platelet crystal of C₂₄H₂₂BrNO₃ having approximate dimensions of 0.40 x 0.20 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation.

Indexing was performed from -842150451 stills which were exposed for -431602080.0 minutes. The crystal-to-detector distance was -431602080.00 mm. The detector swing angle was -431602080.00°. Readout was performed in the -431602080.000 mm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

$$\begin{array}{ll} a = 8.183(1) \approx & \alpha = 104.161(4)^\circ \\ b = 11.275(2) \approx & \beta = 94.974(3)^\circ \\ c = 5.736(1) \approx & \gamma = 94.356(7)^\circ \\ V = 508.7(1) \approx^3 & \end{array}$$

For $Z = 1$ and F.W. = 452.35, the calculated density is 1.48 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#1)

The data were collected at a temperature of $-50 \pm 1^\circ\text{C}$ to a maximum 2θ value of 55.0° . A total of -842150451 -431602080.00° oscillation images were collected, each being exposed for -431602080.0 minutes. The crystal-to-detector distance was -431602080.00 mm. The detector swing angle was -431602080.00°. Readout was performed in the -431602080.000 mm pixel mode.

Data Reduction

A total of 3499 reflections was collected.

The linear absorption coefficient, μ , for Mo-K α radiation is 20.5 cm⁻¹. was applied which resulted in transmission factors ranging from 0.71 to 1.19. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.314540).

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². The non-hydrogen

atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement³ on F^2 was based on 3403 observed reflections and 264 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.041$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2} = 0.107$$

The standard deviation of an observation of unit weight⁴ was 1.11. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.41 and -0.52 $e^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the teXsan⁹ crystallographic software package of Molecular Structure Corporation except for refinement, which was performed using SHELXL-97¹⁰.

References

(1) SHELX97: Sheldrick, G.M. (1997).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2 - F_c^2)^2 \text{ where}$$

$$w = 1 / [\sigma^2(F_o^2) + (0.0000 \cdot P)^2 + 0.0000 \cdot P]$$

$$P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$$

(4) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

- (6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).
- (7) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
- (9) teXsan for Windows version 1.06: Crystal Structure Analysis Package, Molecular Structure Corporation (1997-9).
- (10) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$\text{C}_{24}\text{H}_{22}\text{BrNO}_3$
Formula Weight	452.35
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.40 X 0.20 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	-842150451 stills @ -431602080.0 minutes
Detector Position	-431602080.00 mm
Detector Swing Angle	-431602080.00°
Pixel Size	-431602080.000 mm
Lattice Parameters	$a = 8.183(1) \text{ \AA}$ $b = 11.275(2) \text{ \AA}$ $c = 5.736(1) \text{ \AA}$ $\alpha = 104.161(4)^\circ$ $\beta = 94.974(3)^\circ$ $\gamma = 94.356(7)^\circ$ $V = 508.7(1) \text{ \AA}^3$
Space Group	P1 (#1)
Z value	1
D_{calc}	1.477 g/cm^3
F_{000}	232.00
$\mu(\text{MoK}\alpha)$	20.52 cm^{-1}

B. Intensity Measurements

Diffractometer	RAXIS-RAPID
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Detector Aperture	200 mm x 200 mm
Data Images	-842150451 exposures @ -431602080.0 minutes
Oscillation Range	-431602080.0 $^\circ$
Detector Position	-431602080.00 mm
Detector Swing Angle	-431602080.00 $^\circ$
Pixel Size	-431602080.000 mm
$2\theta_{\text{max}}$	55.0 $^\circ$
No. of Reflections Measured	Total: 3499
Corrections	Lorentz-polarization Absorption (trans. factors: 0.7124 - 1.1920) Secondary Extinction (coefficient: 3.14540e-001)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0000 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms

No. Observations ($I > 3.00\sigma(I)$)	3403
No. Variables	264
Reflection/Parameter Ratio	12.89
Residuals: R1; wR2	0.041 ; 0.107
Goodness of Fit Indicator	1.11
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.41 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.52 e ⁻ /Å ³

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B _{eq}
Br(1)	-0.7029	-0.9042	-0.5833	4.378
O(1)	-0.4212	-1.4677	0.2034	2.923
O(2)	-0.6998	-1.3793	-0.0532	3.450
O(3)	-0.9046	-1.4604	-0.3455	5.751
N(1)	-0.2862	-1.4282	0.0842	2.704
C(1)	-0.2880	-1.5236	-0.1410	2.729
C(2)	-0.4728	-1.5605	-0.2185	2.925
C(3)	-0.5459	-1.5467	0.0212	2.728
C(4)	-0.2875	-1.3022	0.0839	2.484
C(5)	-0.3462	-1.2211	0.2712	3.224
C(6)	-0.3301	-1.0957	0.2882	3.498
C(7)	-0.2579	-1.0496	0.1145	3.540
C(8)	-0.1997	-1.1303	-0.0734	3.545
C(9)	-0.2127	-1.2567	-0.0935	3.123
C(10)	-0.1919	-1.6278	-0.1026	2.726
C(11)	-0.1826	-1.7277	-0.2990	3.629
C(12)	-0.0896	-1.8232	-0.2762	4.081
C(13)	-0.0064	-1.8205	-0.0539	3.743
C(14)	-0.0161	-1.7233	0.1408	3.546
C(15)	-0.1079	-1.6268	0.1191	3.097
C(16)	-0.5698	-1.6676	0.0959	3.318
C(17)	-0.7080	-1.4901	0.0324	3.496
C(18)	-0.8036	-1.3770	-0.2424	3.271
C(19)	-0.7807	-1.2596	-0.3159	2.857
C(20)	-0.8797	-1.2458	-0.5142	3.506
C(21)	-0.8596	-1.1394	-0.5935	3.592
C(22)	-0.7388	-1.0479	-0.4704	3.273
C(23)	-0.6411	-1.0582	-0.2708	3.584
C(24)	-0.6618	-1.1654	-0.1934	3.466
H(1)	-0.2403	-1.4889	-0.2586	3.128

H(2A)	-0.5174	-1.5079	-0.3080	3.341
H(2B)	-0.4914	-1.6435	-0.3150	3.341
H(5)	-0.4014	-1.2511	0.3887	3.788
H(6)	-0.3692	-1.0408	0.4209	4.087
H(7)	-0.2482	-0.9630	0.1253	4.355
H(8)	-0.1508	-1.0992	-0.1933	4.211
H(9)	-0.1718	-1.3114	-0.2262	3.732
H(11)	-0.2384	-1.7303	-0.4524	4.285
H(12)	-0.0851	-1.8906	-0.4128	4.692
H(13)	0.0547	-1.8870	-0.0346	4.343
H(14)	0.0420	-1.7214	0.2927	4.173
H(15)	-0.1121	-1.5603	0.2568	3.758
H(16A)	-0.5687	-1.6500	0.2674	3.881
H(16B)	-0.6738	-1.7101	0.0227	3.881
H(16C)	-0.4847	-1.7170	0.0468	3.881
H(17B)	-0.7922	-1.5477	-0.0663	4.060
H(17A)	-0.7330	-1.4702	0.1945	4.060
H(20)	-0.9628	-1.3090	-0.5958	4.092
H(21)	-0.9275	-1.1305	-0.7304	4.174
H(23)	-0.5606	-0.9935	-0.1857	4.227
H(24)	-0.5940	-1.1746	-0.0567	4.052

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	0.0690	0.0441	0.0608	0.0134	0.0033	0.0267
O(1)	0.0444	0.0383	0.0288	-0.0050	0.0038	0.0120
O(2)	0.0426	0.0410	0.0526	0.0052	-0.0032	0.0239
O(3)	0.0809	0.0584	0.0743	-0.0251	-0.0322	0.0312
N(1)	0.0393	0.0307	0.0349	0.0020	0.0059	0.0124
C(1)	0.0396	0.0335	0.0316	0.0024	0.0046	0.0106
C(2)	0.0415	0.0393	0.0308	0.0029	-0.0033	0.0125
C(3)	0.0385	0.0339	0.0334	-0.0006	-0.0002	0.0154
C(4)	0.0312	0.0313	0.0322	0.0016	-0.0019	0.0111
C(5)	0.0433	0.0369	0.0409	0.0001	0.0010	0.0097
C(6)	0.0439	0.0378	0.0492	0.0043	0.0002	0.0089
C(7)	0.0478	0.0330	0.0514	0.0004	-0.0054	0.0110
C(8)	0.0522	0.0384	0.0475	-0.0033	0.0010	0.0214
C(9)	0.0458	0.0357	0.0395	0.0027	0.0086	0.0131
C(10)	0.0363	0.0313	0.0380	0.0017	0.0051	0.0128
C(11)	0.0457	0.0427	0.0462	0.0054	0.0003	0.0063
C(12)	0.0479	0.0377	0.0654	0.0064	0.0078	0.0043
C(13)	0.0444	0.0367	0.0652	0.0087	0.0107	0.0178
C(14)	0.0413	0.0457	0.0530	0.0049	0.0026	0.0233
C(15)	0.0399	0.0396	0.0380	0.0017	0.0019	0.0109
C(16)	0.0448	0.0367	0.0471	-0.0017	-0.0040	0.0202
C(17)	0.0442	0.0438	0.0532	0.0055	0.0072	0.0271
C(18)	0.0405	0.0414	0.0442	0.0032	-0.0001	0.0162
C(19)	0.0319	0.0401	0.0368	0.0043	-0.0004	0.0114
C(20)	0.0421	0.0431	0.0450	-0.0004	-0.0082	0.0112
C(21)	0.0481	0.0488	0.0412	0.0107	-0.0069	0.0166
C(22)	0.0434	0.0393	0.0465	0.0105	0.0073	0.0173
C(23)	0.0510	0.0405	0.0431	0.0007	-0.0052	0.0124
C(24)	0.0452	0.0430	0.0434	0.0039	-0.0100	0.0159

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table 3. Bond Lengths(≈)

atom	atom	distance	atom	atom	distance
Br1	C22	1.898(4)	O1	N1	1.446(4)
O1	C3	1.466(4)	O2	C18	1.326(5)
O2	C17	1.450(4)	O3	C18	1.201(6)
N1	C4	1.422(4)	N1	C1	1.463(5)
C1	C10	1.512(5)	C1	C2	1.534(5)
C2	C3	1.525(5)	C3	C17	1.515(5)
C3	C16	1.530(4)	C4	C5	1.377(6)
C4	C9	1.411(5)	C5	C6	1.388(5)
C6	C7	1.386(6)	C7	C8	1.375(7)
C8	C9	1.396(6)	C10	C15	1.389(6)
C10	C11	1.397(6)	C11	C12	1.389(6)
C12	C13	1.385(8)	C13	C14	1.372(7)
C14	C15	1.392(6)	C18	C19	1.488(5)
C19	C20	1.386(5)	C19	C24	1.388(6)
C20	C21	1.386(6)	C21	C22	1.382(6)
C22	C23	1.372(6)	C23	C24	1.390(5)

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
N1	O1	C3	109.2(3)	C18	O2	C17	117.7(3)
C4	N1	O1	111.1(3)	C4	N1	C1	121.2(3)
O1	N1	C1	105.4(3)	N1	C1	C10	111.3(3)
N1	C1	C2	102.9(3)	C10	C1	C2	114.3(3)
C3	C2	C1	103.4(3)	O1	C3	C17	109.5(3)
O1	C3	C2	105.2(3)	C17	C3	C2	114.8(3)
O1	C3	C16	105.9(3)	C17	C3	C16	107.7(3)
C2	C3	C16	113.3(3)	C5	C4	C9	119.2(3)
C5	C4	N1	120.1(3)	C9	C4	N1	120.3(3)
C4	C5	C6	120.6(4)	C7	C6	C5	120.8(4)
C8	C7	C6	118.7(4)	C7	C8	C9	121.6(4)
C8	C9	C4	118.9(4)	C15	C10	C11	118.4(4)
C15	C10	C1	122.7(4)	C11	C10	C1	118.9(4)
C12	C11	C10	121.3(4)	C13	C12	C11	119.6(4)
C14	C13	C12	119.6(4)	C13	C14	C15	121.2(4)
C10	C15	C14	120.0(4)	O2	C17	C3	111.3(3)
O3	C18	O2	124.2(4)	O3	C18	C19	123.3(4)
O2	C18	C19	112.6(3)	C20	C19	C24	119.7(3)
C20	C19	C18	118.6(3)	C24	C19	C18	121.7(3)
C21	C20	C19	120.6(4)	C22	C21	C20	118.5(4)
C23	C22	C21	122.1(4)	C23	C22	Br1	118.6(3)
C21	C22	Br1	119.2(3)	C22	C23	C24	119.0(4)
C19	C24	C23	120.1(4)				

X-ray Structure Report / Compound 19 (C₂₃H₁₉Br₂NO₃)

Experimental

Data Collection

A pale platelet crystal of C₂₃H₁₉Br₂NO₃ having approximate dimensions of 0.50 x 0.30 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation.

Indexing was performed from -842150451 stills which were exposed for -431602080.0 minutes. The crystal-to-detector distance was -431602080.00 mm. The detector swing angle was -431602080.00°. Readout was performed in the -431602080.000 mm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

$$\begin{array}{ll} a = 8.249(2) \text{ \AA} & \alpha = 103.648(2)^\circ \\ b = 10.929(2) \text{ \AA} & \beta = 95.74(1)^\circ \\ c = 6.0550(7) \text{ \AA} & \gamma = 92.710(3)^\circ \\ V = 526.4(1) \text{ \AA}^3 \end{array}$$

For $Z = 1$ and F.W. = 517.22, the calculated density is 1.63 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#1)

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ to a maximum 2θ value of 55.0° . A total of -842150451 -431602080.00° oscillation images were collected, each being exposed for -431602080.0 minutes. The crystal-to-detector distance was -431602080.00 mm. The detector swing angle was -431602080.00°. Readout was performed in the -431602080.000 mm pixel mode.

Data Reduction

A total of 3468 reflections was collected.

The linear absorption coefficient, μ , for Mo-K α radiation is 38.9 cm⁻¹. was applied which resulted in transmission factors ranging from 0.53 to 1.37. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.174750).

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix

least-squares refinement³ on F^2 was based on 3075 observed reflections and 264 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.048$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2} = 0.140$$

The standard deviation of an observation of unit weight⁴ was 1.11. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.61 and -0.47 $e^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the teXsan⁹ crystallographic software package of Molecular Structure Corporation except for refinement, which was performed using SHELXL-97¹⁰.

References

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(3) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2 - F_c^2)^2 \text{ where}$$

$$w = 1 / [\sigma^2(F_o^2) + (0.0000 \cdot P)^2 + 0.0000 \cdot P]$$

$$P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$$

(4) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

$$\text{where: } N_o = \text{number of observations}$$

$$N_v = \text{number of variables}$$

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

- (6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).
- (7) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
- (9) teXsan for Windows version 1.06: Crystal Structure Analysis Package, Molecular Structure Corporation (1997-9).
- (10) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$\text{C}_{23}\text{H}_{19}\text{Br}_2\text{NO}_3$
Formula Weight	517.22
Crystal Color, Habit	pale, platelet
Crystal Dimensions	0.50 X 0.30 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	-842150451 stills @ -431602080.0 minutes
Detector Position	-431602080.00 mm
Detector Swing Angle	-431602080.00 $^\circ$
Pixel Size	-431602080.000 mm
Lattice Parameters	$a = 8.249(2) \approx$ $b = 10.929(2) \approx$ $c = 6.0550(7) \approx$ $\alpha = 103.648(2)^\circ$ $\beta = 95.74(1)^\circ$ $\gamma = 92.710(3)^\circ$ $V = 526.4(1) \approx^3$
Space Group	P1 (#1)
Z value	1
D _{calc}	1.632 g/cm ³
F ₀₀₀	258.00
$\mu(\text{MoK}\alpha)$	38.86 cm ⁻¹

B. Intensity Measurements

Diffractometer	RAXIS-RAPID
Radiation	MoK α ($\lambda = 0.71069 \approx$) graphite monochromated
Detector Aperture	200 mm x 200 mm
Data Images	-842150451 exposures @ -431602080.0 minutes
Oscillation Range	-431602080.0 $^{\circ}$
Detector Position	-431602080.00 mm
Detector Swing Angle	-431602080.00 $^{\circ}$
Pixel Size	-431602080.000 mm
$2\theta_{\max}$	55.0 $^{\circ}$
No. of Reflections Measured	Total: 3468
Corrections	Lorentz-polarization Absorption (trans. factors: 0.5332 - 1.3701) Secondary Extinction (coefficient: 1.74750e-001)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0000 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	3075
No. Variables	264
Reflection/Parameter Ratio	11.65
Residuals: R1; wR2	0.048 ; 0.140
Goodness of Fit Indicator	1.11
Max Shift/Error in Final Cycle	0.06
Maximum peak in Final Diff. Map	0.61 $e^-/\approx^3$
Minimum peak in Final Diff. Map	-0.47 $e^-/\approx^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B _{eq}
Br(1)	0.4687	1.3187	-0.1246	5.071
Br(2)	0.6721	0.5154	0.5902	5.739
O(1)	0.3043	1.0119	-0.3760	4.865
O(2)	0.6031	1.0326	0.1697	4.157
O(3)	0.8562	1.0836	0.3425	7.099
N(1)	0.2243	1.0019	-0.1812	3.462
C(1)	0.2895	1.1092	0.0063	2.911
C(2)	0.4599	1.1502	-0.0617	3.390
C(3)	0.4711	1.0511	-0.2785	4.703
C(4)	0.2273	0.8784	-0.1420	3.434
C(5)	0.2816	0.7789	-0.2944	4.539
C(6)	0.2676	0.6590	-0.2573	5.515
C(7)	0.2024	0.6365	-0.0675	5.369
C(8)	0.1479	0.7360	0.0820	4.864
C(9)	0.1591	0.8577	0.0511	4.109
C(10)	0.1703	1.2113	0.0455	3.375
C(11)	0.0624	1.2279	-0.1337	3.870
C(12)	-0.0467	1.3215	-0.0964	4.805
C(13)	-0.0506	1.3981	0.1174	5.453
C(14)	0.0506	1.3800	0.2961	5.411
C(15)	0.1624	1.2854	0.2626	4.542
C(16)	0.6024	1.1556	0.1249	4.205
C(17)	0.7397	1.0095	0.2888	3.718
C(18)	0.7257	0.8845	0.3418	3.538
C(19)	0.8360	0.8627	0.5192	4.821
C(20)	0.8216	0.7552	0.5897	5.148
C(21)	0.6978	0.6651	0.4841	4.023
C(22)	0.5912	0.6803	0.3060	4.745
C(23)	0.6055	0.7920	0.2363	4.088
H(1)	0.3078	1.0805	0.1437	3.508
H(3A)	0.5265	0.9816	-0.2480	5.577
H(3B)	0.5286	1.0862	-0.3822	5.577
H(5)	0.3308	0.7930	-0.4231	5.562
H(6)	0.2990	0.5900	-0.3672	6.332
H(7)	0.1991	0.5533	-0.0410	6.527
H(8)	0.1030	0.7233	0.2144	5.854
H(9)	0.1208	0.9240	0.1588	5.002
H(11)	0.0650	1.1763	-0.2841	4.734
H(12)	-0.1202	1.3322	-0.2198	5.652
H(13)	-0.1259	1.4617	0.1433	6.381
H(14)	0.0483	1.4343	0.4448	6.677
H(15)	0.2298	1.2692	0.3907	5.728
H(16A)	0.5864	1.2173	0.2619	5.181
H(16B)	0.7032	1.1779	0.0762	5.181
H(19)	0.9244	0.9256	0.5884	5.847
H(20)	0.8952	0.7410	0.7129	6.158
H(22)	0.5082	0.6143	0.2321	5.787

H(23) 0.5314 0.8055 0.1142 4.777

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	0.0482	0.0656	0.0967	0.0052	0.0077	0.0551
Br(2)	0.0693	0.0661	0.1019	0.0192	0.0177	0.0524
O(1)	0.0788	0.0727	0.0356	0.0113	-0.0009	0.0196
O(2)	0.0335	0.0536	0.0785	-0.0007	-0.0069	0.0375
O(3)	0.0612	0.0754	0.1409	-0.0163	-0.0395	0.0669
N(1)	0.0444	0.0476	0.0399	0.0029	-0.0031	0.0148
C(1)	0.0364	0.0413	0.0360	0.0029	0.0006	0.0168
C(2)	0.0395	0.0470	0.0512	0.0073	0.0058	0.0285
C(3)	0.0635	0.0706	0.0586	0.0162	0.0232	0.0346
C(4)	0.0381	0.0390	0.0511	0.0054	-0.0096	0.0121
C(5)	0.0513	0.0522	0.0609	0.0082	0.0006	-0.0009
C(6)	0.0521	0.0432	0.1033	0.0054	-0.0096	0.0031
C(7)	0.0603	0.0472	0.0912	-0.0067	-0.0161	0.0185
C(8)	0.0595	0.0544	0.0698	-0.0104	-0.0097	0.0227
C(9)	0.0510	0.0514	0.0536	-0.0006	0.0011	0.0154
C(10)	0.0356	0.0426	0.0504	-0.0005	0.0069	0.0118
C(11)	0.0382	0.0459	0.0637	0.0054	-0.0008	0.0173
C(12)	0.0449	0.0543	0.0909	0.0143	0.0054	0.0315
C(13)	0.0570	0.0494	0.1053	0.0143	0.0262	0.0186
C(14)	0.0602	0.0588	0.0793	0.0001	0.0235	-0.0032
C(15)	0.0500	0.0612	0.0569	0.0022	0.0068	0.0055
C(16)	0.0374	0.0521	0.0801	-0.0037	-0.0061	0.0423
C(17)	0.0390	0.0456	0.0582	0.0013	-0.0038	0.0199
C(18)	0.0339	0.0493	0.0538	0.0096	-0.0011	0.0190
C(19)	0.0450	0.0627	0.0790	0.0018	-0.0150	0.0339
C(20)	0.0510	0.0780	0.0745	0.0045	-0.0168	0.0442
C(21)	0.0473	0.0463	0.0651	0.0137	0.0097	0.0216
C(22)	0.0562	0.0539	0.0708	0.0049	-0.0056	0.0214
C(23)	0.0507	0.0531	0.0523	0.0066	-0.0102	0.0204

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(≈)

atom	atom	distance	atom	atom	distance
Br1	C2	1.966(7)	Br2	C21	1.904(8)

O1	N1	1.431(7)	O1	C3	1.445(10)
O2	C17	1.343(7)	O2	C16	1.433(8)
O3	C17	1.193(9)	N1	C4	1.425(8)
N1	C1	1.464(8)	C1	C10	1.514(8)
C1	C2	1.577(8)	C1	H1	0.958(6)
C2	C3	1.506(11)	C2	C16	1.536(8)
C3	H3A	0.949(7)	C3	H3B	0.961(7)
C4	C5	1.374(9)	C4	C9	1.407(10)
C5	C6	1.383(12)	C5	H5	0.954(8)
C6	C7	1.383(14)	C6	H6	0.946(8)
C7	C8	1.366(13)	C7	H7	0.961(9)
C8	C9	1.386(11)	C8	H8	0.952(8)
C9	H9	0.943(7)	C10	C15	1.381(9)
C10	C11	1.385(9)	C11	C12	1.389(9)
C11	H11	0.954(7)	C12	C13	1.370(13)
C12	H12	0.947(8)	C13	C14	1.358(13)
C13	H13	0.950(7)	C14	C15	1.410(11)
C14	H14	0.957(8)	C15	H15	0.964(8)
C16	H16A	0.962(9)	C16	H16B	0.950(7)
C17	C18	1.477(9)	C18	C23	1.374(9)
C18	C19	1.409(8)	C19	C20	1.345(11)
C19	H19	0.968(7)	C20	C21	1.378(11)
C20	H20	0.960(6)	C21	C22	1.369(10)
C22	C23	1.386(11)	C22	H22	0.964(8)
C23	H23	0.955(6)			

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
N1	O1	C3	103.0(4)	C17	O2	C16	115.4(5)
C4	N1	O1	112.0(5)	C4	N1	C1	118.3(5)
O1	N1	C1	106.9(5)	N1	C1	C10	111.4(4)
N1	C1	C2	104.6(5)	C10	C1	C2	115.4(5)
N1	C1	H1	108.6(5)	C10	C1	H1	107.9(5)
C2	C1	H1	108.7(5)	C3	C2	C16	113.6(6)
C3	C2	C1	101.6(6)	C16	C2	C1	113.4(5)
C3	C2	Br1	109.9(4)	C16	C2	Br1	105.1(5)
C1	C2	Br1	113.5(4)	O1	C3	C2	105.6(5)
O1	C3	H3A	110.8(8)	C2	C3	H3A	111.3(6)
O1	C3	H3B	110.2(6)	C2	C3	H3B	110.3(7)
H3A	C3	H3B	108.6(6)	C5	C4	C9	119.9(7)
C5	C4	N1	122.4(6)	C9	C4	N1	117.6(5)
C4	C5	C6	119.6(8)	C4	C5	H5	120.1(8)
C6	C5	H5	120.3(7)	C7	C6	C5	121.6(7)
C7	C6	H6	119.0(9)	C5	C6	H6	119.4(10)
C8	C7	C6	118.3(8)	C8	C7	H7	121.5(10)
C6	C7	H7	120.1(9)	C7	C8	C9	122.1(8)
C7	C8	H8	120.0(8)	C9	C8	H8	117.9(8)
C8	C9	C4	118.6(7)	C8	C9	H9	119.5(7)
C4	C9	H9	121.9(7)	C15	C10	C11	118.9(6)

C15	C10	C1	120.5(5)	C11	C10	C1	120.5(5)
C10	C11	C12	120.2(7)	C10	C11	H11	119.9(6)
C12	C11	H11	119.9(7)	C13	C12	C11	120.8(7)
C13	C12	H12	119.4(7)	C11	C12	H12	119.7(8)
C14	C13	C12	119.5(6)	C14	C13	H13	119.5(9)
C12	C13	H13	120.9(9)	C13	C14	C15	120.6(7)
C13	C14	H14	119.2(8)	C15	C14	H14	120.1(9)
C10	C15	C14	119.7(7)	C10	C15	H15	119.6(7)
C14	C15	H15	120.6(7)	O2	C16	C2	106.6(5)
O2	C16	H16A	109.8(6)	C2	C16	H16A	110.2(6)
O2	C16	H16B	110.8(6)	C2	C16	H16B	111.0(7)
H16A	C16	H16B	108.4(7)	O3	C17	O2	122.3(6)
O3	C17	C18	125.7(5)	O2	C17	C18	112.0(5)
C23	C18	C19	118.7(6)	C23	C18	C17	123.4(5)
C19	C18	C17	117.8(6)	C20	C19	C18	121.0(7)
C20	C19	H19	120.0(6)	C18	C19	H19	119.0(7)
C19	C20	C21	119.1(6)	C19	C20	H20	121.1(8)
C21	C20	H20	119.8(8)	C22	C21	C20	122.0(7)
C22	C21	Br2	118.7(6)	C20	C21	Br2	119.3(5)
C21	C22	C23	118.5(7)	C21	C22	H22	120.1(8)
C23	C22	H22	121.4(7)	C18	C23	C22	120.6(6)
C18	C23	H23	119.2(7)	C22	C23	H23	120.1(7)

Table 5. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C3	O1	N1	C4	-90.4(5)	C3	O1	N1	C1	40.6(6)
C4	N1	C1	C10	-129.6(5)	O1	N1	C1	C10	103.0(5)
C4	N1	C1	C2	105.1(5)	O1	N1	C1	C2	-22.3(5)
N1	C1	C2	C3	-3.5(6)	C10	C1	C2	C3	-126.3(6)
N1	C1	C2	C16	-125.8(6)	C10	C1	C2	C16	111.4(6)
N1	C1	C2	Br1	114.3(5)	C10	C1	C2	Br1	-8.5(7)
N1	O1	C3	C2	-42.8(6)	C16	C2	C3	O1	150.0(6)
C1	C2	C3	O1	27.9(6)	Br1	C2	C3	O1	-92.5(5)
O1	N1	C4	C5	-8.2(7)	C1	N1	C4	C5	-133.1(6)
O1	N1	C4	C9	177.2(5)	C1	N1	C4	C9	52.2(7)
C9	C4	C5	C6	0.5(9)	N1	C4	C5	C6	-174.1(6)
C4	C5	C6	C7	-1.1(10)	C5	C6	C7	C8	1.5(11)
C6	C7	C8	C9	-1.3(11)	C7	C8	C9	C4	0.7(10)
C5	C4	C9	C8	-0.3(9)	N1	C4	C9	C8	174.5(5)
N1	C1	C10	C15	147.7(6)	C2	C1	C10	C15	-93.3(7)
N1	C1	C10	C11	-29.3(8)	C2	C1	C10	C11	89.8(7)
C15	C10	C11	C12	2.9(10)	C1	C10	C11	C12	179.9(6)
C10	C11	C12	C13	-0.5(11)	C11	C12	C13	C14	-1.8(12)
C12	C13	C14	C15	1.7(13)	C11	C10	C15	C14	-3.0(10)
C1	C10	C15	C14	-180.0(6)	C13	C14	C15	C10	0.7(12)
C17	O2	C16	C2	165.4(6)	C3	C2	C16	O2	-57.9(8)

C1	C2	C16	O2	57.4(7)	Br1	C2	C16	O2	-178.1(4)
C16	O2	C17	O3	-4.0(11)	C16	O2	C17	C18	175.9(6)
O3	C17	C18	C23	-165.4(9)	O2	C17	C18	C23	14.7(9)
O3	C17	C18	C19	18.4(11)	O2	C17	C18	C19	-161.5(6)
C23	C18	C19	C20	-2.1(11)	C17	C18	C19	C20	174.3(8)
C18	C19	C20	C21	0.7(13)	C19	C20	C21	C22	1.5(13)
C19	C20	C21	Br2	-177.8(7)	C20	C21	C22	C23	-2.3(12)
Br2	C21	C22	C23	177.0(6)	C19	C18	C23	C22	1.2(10)
C17	C18	C23	C22	-174.9(7)	C21	C22	C23	C18	0.9(11)