

Guiding the Nitrogen Nucleophile to the Middle: Palladium-Catalyzed Decarboxylative Cyclopropanation of 2-Alkylidenetrimethylene Carbonates with Isocyanates

Ryo Shintani,* Kohei Moriya, and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University,
Sakyo, Kyoto 606-8502, Japan

Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

THF and Et₂O were purified by passing through neutral alumina columns under nitrogen. CH₂Cl₂ was distilled over CaH₂ under nitrogen. Triethylamine was distilled over KOH under nitrogen.

1,3-Diacetoxyacetone (TCI), triphosgene (Wako Chemicals), allyl acetate (Wako Chemicals), benzyl isocyanate (TCI), 4-methoxybenzyl isocyanate (Aldrich), 4-chlorobenzyl isocyanate (Aldrich), ethyl isocyanate (TCI), cyclohexyl isocyanate (TCI), phenyl isocyanate (Wako Chemicals), *N*-benzylbenzamide (Aldrich), ethylenediamine (Wako Chemicals), MeOH (Wako Chemicals), *n*-BuLi (Kanto Chemicals; 1.65 M solution in hexane), NaH (Kanto Chemicals; 60 wt% in mineral oil), LiAlH₄ (Wako Chemicals), K₂CO₃ (Wako Chemicals), tris(4-methoxyphenyl)phosphine (Alfa Aesar), triphenylphosphine (Wako Chemicals), tris(4-fluorophenyl)phenylphosphine (Wako Chemicals), and tris(4-trifluoromethylphenyl)phosphine (Aldrich or Wako Chemicals) were used as received.

Benzyl(triphenyl)phosphonium bromide ¹ and PdCp(η³-C₃H₅) ² were synthesized following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

II. Synthesis of Substrates

Representative Procedure: Preparation of 2-Benzylidenetrimethylene Carbonate (1a) (CAS 172877-23-5)

n-BuLi (4.24 mL, 7.00 mmol; 1.65 M solution in hexane) was added to a solution of benzyl(triphenyl)phosphonium bromide (3.25 g, 7.50 mmol) in THF (73 mL) at -78 °C, and the mixture was stirred for 3 min at 0 °C. This was cooled to -78 °C and a solution of 1,3-diacetoxyacetone (871 mg, 5.00 mmol) in THF (17 mL) was added dropwise. The resulting mixture was stirred for 3 h at -78 °C and the precipitate was filtered off with Et₂O. The Et₂O solution was washed with saturated NH₄Cl aq, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5 to afford 2-benzylidenepropane-1,3-diyl diacetate as a yellow oil (1.16 g, 4.67 mmol; 93%

¹ Amsharov, K. Y.; Kabdulov, M. A.; Jansen, M. *Eur. J. Org. Chem.* **2009**, 6328.

² (a) Shaw, B. L. *Proc. Chem. Soc.* **1960**, 247. (b) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muettterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, 83, 1601.

yield).

^1H NMR (CDCl_3): δ 7.36 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.29 (tt, $^3J_{\text{HH}} = 7.3$ Hz and $^4J_{\text{HH}} = 2.1$ Hz, 1H), 7.25 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 6.85 (s, 1H), 4.79 (s, 2H), 4.76 (d, $^4J_{\text{HH}} = 1.1$ Hz, 2H), 2.11 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (CDCl_3): δ 170.8, 170.7, 135.4, 134.4, 131.2, 128.9, 128.5, 128.0, 66.4, 60.8, 21.03, 20.95. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4$: C, 67.73; H, 6.50. Found: C, 67.44; H, 6.54.

A mixture of 2-benzylidenepropane-1,3-diyl diacetate (1.16 g, 4.67 mmol) and K_2CO_3 (3.87 g, 28.0 mmol) in MeOH (145 mL) was stirred for 1 h at room temperature. The precipitate was filtered off and the resulting solution was concentrated under vacuum. NH_4Claq was added to it and this was extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 3/1 to afford 2-benzylidenepropane-1,3-diol as a white solid (662 mg, 4.03 mmol; 86% yield).

^1H NMR (CDCl_3): δ 7.35 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 7.29-7.25 (m, 3H), 6.66 (s, 1H), 4.46 (s, 2H), 4.42 (s, 2H), 2.15 (bs, 2H). ^{13}C NMR (CDCl_3): δ 139.4, 136.3, 129.9, 129.0, 128.4, 127.5, 67.6, 60.7. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.40.

A solution of triphosgene (1.48 g, 4.99 mmol) in CH_2Cl_2 (50 mL) was slowly added to a solution of 2-benzylidenepropane-1,3-diol (411 mg, 2.50 mmol) and triethylamine (3.48 mL, 25.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C over 30 min. The resulting mixture was stirred for 2 h while gradually raising the temperature to 20 °C. The reaction was quenched with NH_4Claq and this was extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 2/3 and the solid thus obtained was washed with hexane to afford compound **1a** as a white solid (377 mg, 1.98 mmol; 79% yield).

^1H NMR (CDCl_3): δ 7.41 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.35 (tt, $^3J_{\text{HH}} = 7.3$ Hz and $^4J_{\text{HH}} = 2.2$ Hz, 1H), 7.13 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 6.73 (s, 1H), 5.21 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H), 4.94 (d, $^4J_{\text{HH}} = 1.1$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 150.0, 134.3, 129.6, 129.0, 128.84, 128.75, 125.3, 71.7, 68.5. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3$: C, 69.46; H, 5.30. Found: C, 69.57; H, 5.28.

Analytical Data for Other Substrates:

2-(4-Methylbenzylidene)trimethylene Carbonate (**1b**)

^1H NMR (CDCl_3): δ 7.21 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.02 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 6.69 (s, 1H), 5.21 (d, $^4J_{\text{HH}} = 1.2$ Hz, 2H), 4.92 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (CDCl_3): δ 150.1, 138.9, 131.4, 129.63, 129.55, 128.8, 124.3, 71.8, 68.6, 21.4. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92. Found: C, 70.45; H, 6.12.

2-(4-Chlorobenzylidene)trimethylene Carbonate (**1c**)

^1H NMR (CDCl_3): δ 7.38 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 7.07 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 6.67 (s, 1H), 5.17 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H), 4.93 (d, $^4J_{\text{HH}} = 1.1$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 149.8, 134.9, 132.7, 130.1, 129.3, 128.2, 126.2, 71.5, 68.3. Anal. Calcd for $\text{C}_{11}\text{H}_9\text{ClO}_3$: C, 58.81; H, 4.04. Found: C, 58.74; H, 4.11.

2-(2-Methylbenzylidene)trimethylene Carbonate (**1d**)

^1H NMR (CDCl_3): δ 7.27-7.23 (m, 2H), 7.20 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 6.90 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 6.83 (s, 1H), 5.03 (d, $^4J_{\text{HH}} = 1.4$ Hz, 2H), 4.98 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3): δ 149.8, 136.9, 133.1, 130.7, 129.2, 129.1, 128.6, 126.1, 125.4, 71.7, 68.2, 19.9. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92. Found: C, 70.28; H, 6.20.

2-(2-Naphthylmethylidene)trimethylene Carbonate (1e)

^1H NMR (CDCl_3): δ 7.87 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 7.86-7.83 (m, 2H), 7.57 (s, 1H), 7.55-7.52 (m, 2H), 7.27 (dd, $^3J_{\text{HH}} = 8.4$ Hz and $^4J_{\text{HH}} = 1.8$ Hz, 1H), 6.88 (s, 1H), 5.30 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H), 5.00 (d, $^4J_{\text{HH}} = 1.2$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 150.0, 133.2, 133.1, 131.7, 129.6, 128.8, 128.4, 128.3, 127.9, 127.1, 127.0, 126.2, 125.6, 71.8, 68.6. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_3$: C, 74.99; H, 5.03. Found: C, 74.91; H, 4.80.

2-Methylidenetrimethylene Carbonate (1f) (CAS 3775-32-4)

^1H NMR (CDCl_3): δ 5.31 (quint, $^4J_{\text{HH}} = 1.3$ Hz, 2H), 4.86 (t, $^4J_{\text{HH}} = 1.3$ Hz, 4H). ^{13}C NMR (CDCl_3): δ 149.4, 132.6, 114.5, 70.8. Anal. Calcd for $\text{C}_5\text{H}_6\text{O}_3$: C, 52.63; H, 5.30. Found: C, 52.80; H, 5.31.

5-Methylene-3-tosyl-1,3-oxazinan-2-one (5)

^1H NMR (CDCl_3): δ 7.94 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 7.34 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 5.32 (s, 1H), 5.27 (quint, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 4.67 (s, 2H), 4.51 (t, $^4J_{\text{HH}} = 1.6$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (CDCl_3): δ 149.6, 145.5, 134.8, 132.7, 129.7, 129.1, 115.2, 70.5, 49.9, 21.8. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$: C, 53.92; H, 4.90. Found: C, 53.79; H, 4.91.

III. Catalytic Reactions and Derivatization Reactions

General Procedure for Tables 1 and 2.

A solution of $\text{PdCp}(\eta^3\text{-C}_3\text{H}_5)$ (2.1 mg, 10 μmol), PAr_3 (20 μmol), carbonate **1** (0.20 mmol), and isocyanate **2** (0.24 mmol) in CH_2Cl_2 (0.50 mL) was stirred for 6 h at 40 $^\circ\text{C}$. The reaction mixture was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC to afford compounds **3/4**.

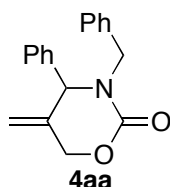


Table 1, Entry 2. Colorless oil. 27% yield.

^1H NMR (CDCl_3): δ 7.41 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 7.36 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 7.34-7.26 (m, 3H), 7.25 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 7.20 (d, $^3J_{\text{HH}} = 6.7$ Hz, 2H), 5.30 (d, $^2J_{\text{HH}} = 15.2$ Hz, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 4.83 (s, 1H), 4.72 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1H), 4.55 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1H), 3.63 (d, $^2J_{\text{HH}} = 15.2$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 154.8, 139.1, 138.6, 136.4, 129.2, 128.8, 128.5, 128.3, 127.8, 126.8, 114.5, 68.2, 63.0, 50.0. HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 302.1151, found 302.1160.

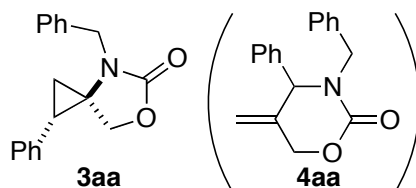


Table 1, Entry 4. White solid. 84% combined yield (**3aa/4aa** = 92/8, dr of **3aa** = 96/4). The

relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3aa**: ^1H NMR (CDCl_3): δ 7.38 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.33-7.30 (m, 3H), 7.28 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.21 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 6.90 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 4.50 (d, $^2J_{\text{HH}} = 15.8$ Hz, 1H), 4.33 (d, $^2J_{\text{HH}} = 16.2$ Hz, 1H), 4.09 (d, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 3.93 (d, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 2.38 (dd, $^2J_{\text{HH}} = 10.3$ Hz and $^3J_{\text{HH}} = 7.3$ Hz, 1H), 1.46 (dd, $^2J_{\text{HH}} = 10.4$ Hz and $^3J_{\text{HH}} = 7.4$ Hz, 1H), 1.05 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.3, 137.2, 135.1, 129.0, 128.8, 127.9, 127.6, 127.1, 126.9, 66.2, 45.8, 43.8, 22.5, 10.9. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$: C, 77.40; H, 6.13. Found: C, 77.14; H, 6.19.

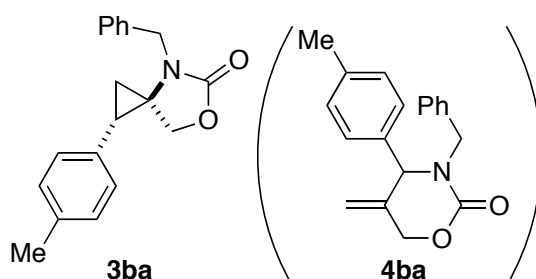


Table 2, Entry 2. White solid. 89% combined yield (**3ba/4ba** = 91/9, dr of **3ba** = 98/2). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ba**: ^1H NMR (CDCl_3): δ 7.37 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.33-7.29 (m, 3H), 7.08 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 6.79 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 4.47 (d, $^2J_{\text{HH}} = 16.3$ Hz, 1H), 4.32 (d, $^2J_{\text{HH}} = 16.2$ Hz, 1H), 4.07 (d, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 3.93 (d, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 2.34 (dd, $^2J_{\text{HH}} = 10.4$ Hz and $^3J_{\text{HH}} = 7.3$ Hz, 1H), 2.30 (s, 3H), 1.43 (dd, $^2J_{\text{HH}} = 10.4$ Hz and $^3J_{\text{HH}} = 7.4$ Hz, 1H), 1.01 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.4, 137.3, 136.7, 132.0, 129.5, 129.0, 127.9, 127.6, 127.1, 66.3, 45.7, 43.9, 22.2, 21.1, 11.0. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$: C, 77.79; H, 6.53. Found: C, 77.94; H, 6.59.

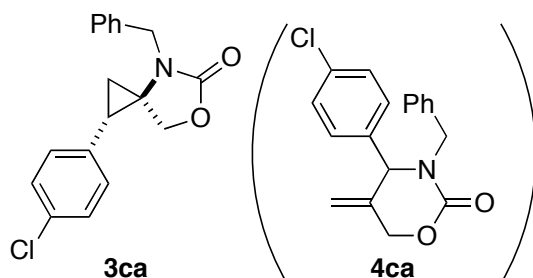


Table 2, Entry 3. White solid. 91% combined yield (**3ca/4ca** = 93/7, dr of **3ca** = 98/2). The relative configuration was determined by X-ray crystallographic analysis after recrystallization from THF/pentane.

Major diastereomer of **3ca**: ^1H NMR (CDCl_3): δ 7.38 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 7.34-7.29 (m, 3H), 7.25 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 6.82 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 4.49 (d, $^2J_{\text{HH}} = 16.2$ Hz, 1H), 4.31 (d, $^2J_{\text{HH}} = 16.4$ Hz, 1H), 4.08 (d, $^2J_{\text{HH}} = 8.9$ Hz, 1H), 3.89 (t, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 2.33 (dd, $^2J_{\text{HH}} = 10.4$ Hz and $^3J_{\text{HH}} = 7.5$ Hz, 1H), 1.49 (dd, $^2J_{\text{HH}} = 10.4$ Hz and $^3J_{\text{HH}} = 7.6$ Hz, 1H), 1.02 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.3, 137.2, 133.7, 132.9, 129.07, 129.05, 128.0, 127.1, 66.1, 45.9, 44.0, 22.1, 11.1. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_2$: C, 68.90; H, 5.14. Found: C, 68.65; H, 5.28.

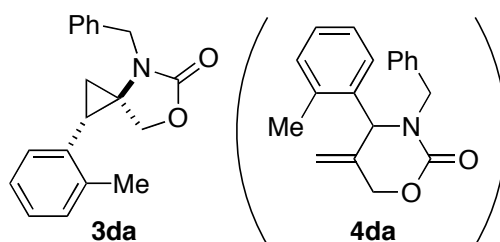


Table 2, Entry 4. The reaction was conducted with 1.5 equiv of **1d** and 1.0 equiv of **2a**. White solid. 63% combined yield (**3da/4da** = 98/2, dr of **3da** = 93/7). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3da**: ^1H NMR (CDCl_3): δ 7.38-7.33 (m, 4H), 7.30 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 1H), 7.14-7.08 (m, 3H), 6.83 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 1H), 4.61 (d, $^2J_{\text{HH}}$ = 15.9 Hz, 1H), 4.26 (d, $^2J_{\text{HH}}$ = 15.8 Hz, 1H), 3.97 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 3.63 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 2.26 (dd, $^2J_{\text{HH}}$ = 10.1 Hz and $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 1.99 (s, 3H), 1.55 (dd, $^2J_{\text{HH}}$ = 10.1 Hz and $^3J_{\text{HH}}$ = 7.4 Hz, 1H), 1.07 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.5, 138.5, 137.5, 133.8, 130.2, 129.0, 128.1, 127.8, 127.3, 126.7, 126.2, 66.3, 45.8, 44.4, 21.6, 19.7, 10.1. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$: C, 77.79; H, 6.53. Found: C, 77.53; H, 6.58.

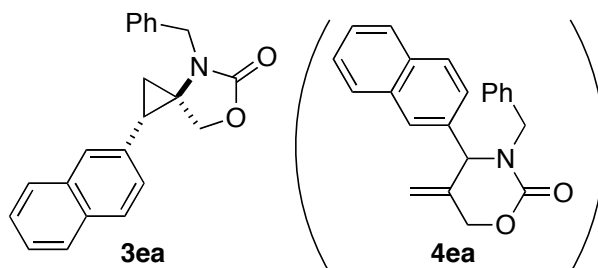


Table 2, Entry 5. White solid. 77% combined yield (**3ea/4ea** = 88/12, dr of **3ea** = 98/2). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ea**: ^1H NMR (CDCl_3): δ 7.81-7.72 (m, 3H), 7.49-7.43 (m, 2H), 7.41 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 2H), 7.37-7.32 (m, 3H), 7.31 (s, 1H), 7.05 (dd, $^3J_{\text{HH}}$ = 8.4 Hz and $^4J_{\text{HH}}$ = 1.7 Hz, 1H), 4.53 (d, $^2J_{\text{HH}}$ = 16.1 Hz, 1H), 4.38 (d, $^2J_{\text{HH}}$ = 16.2 Hz, 1H), 4.11 (d, $^2J_{\text{HH}}$ = 8.9 Hz, 1H), 3.91 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 2.53 (dd, $^2J_{\text{HH}}$ = 10.2 Hz and $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 1.54 (dd, $^2J_{\text{HH}}$ = 10.3 Hz and $^3J_{\text{HH}}$ = 7.6 Hz, 1H), 1.21 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.4, 137.3, 133.5, 132.8, 132.5, 129.1, 128.7, 128.0, 127.8, 127.5, 127.2, 126.6, 126.4, 126.0, 125.7, 66.3, 46.1, 44.0, 22.8, 11.0. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2$: C, 80.22; H, 5.81. Found: C, 79.99; H, 5.73.

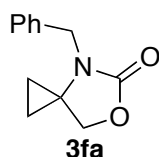


Table 2, Entry 6. White solid. 93% yield.

^1H NMR (CDCl_3): δ 7.32 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 2H), 7.28-7.24 (m, 3H), 4.30 (s, 2H), 4.23 (s, 2H), 0.92 (t, $^3J_{\text{HH}}$ = 7.0 Hz, 2H), 0.54 (t, $^3J_{\text{HH}}$ = 7.0 Hz, 2H). ^{13}C NMR (CDCl_3): δ 158.7, 137.3, 128.8, 127.7, 127.1, 69.9, 43.6, 41.1, 6.8. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; H, 6.45. Found: C, 70.78; H, 6.49.

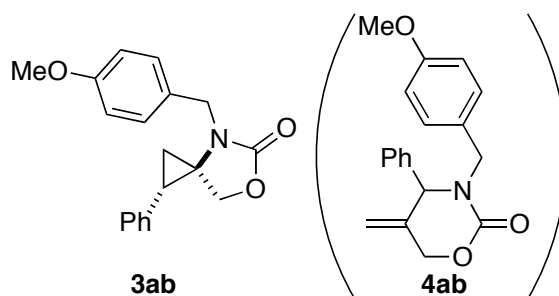


Table 2, Entry 7. The reaction was conducted with 1.5 equiv of **2b**. Colorless oil. 95% combined yield (**3ab/4ab** = 93/7, dr of **3ab** = 97/3). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ab**: ^1H NMR (CDCl_3): δ 7.28 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 2H), 7.24 (d, $^3J_{\text{HH}}$ = 8.6 Hz, 2H), 7.21 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 6.92-6.89 (m, 4H), 4.42 (d, $^2J_{\text{HH}}$ = 16.0 Hz, 1H), 4.28 (d, $^2J_{\text{HH}}$ = 16.0 Hz, 1H), 4.06 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 3.90 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 3.82 (s, 3H), 2.40 (dd, $^2J_{\text{HH}}$ = 10.3 Hz and $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 1.47 (dd, $^2J_{\text{HH}}$ = 10.2 Hz and $^3J_{\text{HH}}$ = 7.4 Hz, 1H), 1.04 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 1H). ^{13}C NMR (CDCl_3): δ 159.4, 158.4, 135.2, 129.3, 128.9, 128.5, 127.8, 127.0, 114.4, 66.2, 55.5, 45.9, 43.5, 22.6, 11.0. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.19. Found: C, 73.56; H, 6.28.

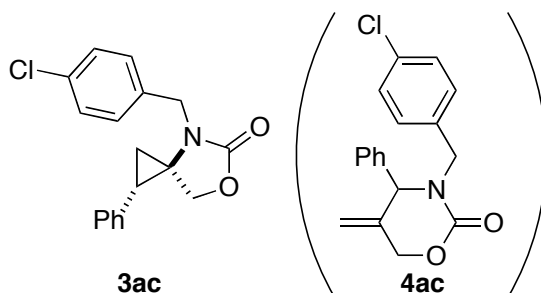


Table 2, Entry 8. Colorless oil. 67% combined yield (**3ac/4ac** = 84/16, dr of **3ac** > 99/1). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ac**: ^1H NMR (CDCl_3): δ 7.35 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 7.30 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 2H), 7.26 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 2H), 7.22 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 1H), 6.92 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 2H), 4.42 (d, $^2J_{\text{HH}}$ = 16.5 Hz, 1H), 4.30 (d, $^2J_{\text{HH}}$ = 16.4 Hz, 1H), 4.09 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 3.93 (d, $^2J_{\text{HH}}$ = 8.9 Hz, 1H), 2.37 (dd, $^2J_{\text{HH}}$ = 10.4 Hz and $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 1.44 (dd, $^2J_{\text{HH}}$ = 10.5 Hz and $^3J_{\text{HH}}$ = 7.6 Hz, 1H), 1.08 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 1H). ^{13}C NMR (CDCl_3): δ 158.3, 135.8, 134.9, 133.8, 129.2, 128.9, 128.5, 127.7, 127.1, 66.3, 45.7, 43.2, 22.6, 11.0. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_2$: C, 68.90; H, 5.14. Found: C, 68.71; H, 5.28.

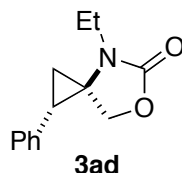


Table 2, Entry 9. Yellow oil. 73% yield (dr of **3ad** = 88/12). The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ad**: ^1H NMR (CDCl_3): δ 7.33 (t, $^3J_{\text{HH}}$ = 7.4 Hz, 2H), 7.25 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 1H), 7.05 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 2H), 4.05 (d, $^2J_{\text{HH}}$ = 8.8 Hz, 1H), 3.88 (d, $^2J_{\text{HH}}$ = 8.6 Hz, 1H), 3.14 (dq, $^2J_{\text{HH}}$ = 14.6 Hz and $^3J_{\text{HH}}$ = 7.1 Hz, 1H), 3.09 (dq, $^2J_{\text{HH}}$ = 14.6 Hz and $^3J_{\text{HH}}$ = 7.1 Hz, 1H), 2.48 (dd, $^2J_{\text{HH}}$ = 10.2 Hz and $^3J_{\text{HH}}$ = 7.2 Hz, 1H), 1.54 (dd, $^2J_{\text{HH}}$ = 10.2 Hz and

$^3J_{\text{HH}} = 7.4$ Hz, 1H), 1.24 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 1.18 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 157.7, 135.2, 128.9, 127.8, 127.1, 66.1, 45.3, 34.7, 23.4, 14.6, 11.8. Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.87; H, 6.96. Found: C, 71.82; H, 7.01.

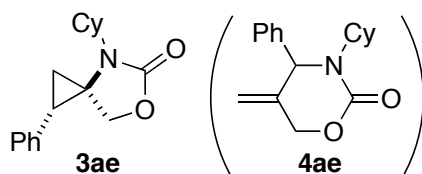


Table 2, Entry 10. Pale yellow solid. **3ae/4ae** = 93/7, dr of **3ae** = 84/16. 70% yield of major diastereomer of **3ae**. The relative configuration was assigned by analogy with Table 2, entry 3.

Major diastereomer of **3ae**: ^1H NMR (CDCl_3): δ 7.33 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.24 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.05 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 4.00 (d, $^2J_{\text{HH}} = 8.8$ Hz, 1H), 3.83 (d, $^2J_{\text{HH}} = 8.6$ Hz, 1H), 2.56 (tt, $^3J_{\text{HH}} = 12.1$ and 3.8 Hz, 1H), 2.42 (dd, $^2J_{\text{HH}} = 10.2$ Hz and $^3J_{\text{HH}} = 7.3$ Hz, 1H), 2.28-2.15 (m, 2H), 1.90-1.80 (m, 2H), 1.74-1.60 (m, 3H), 1.49 (dd, $^2J_{\text{HH}} = 10.3$ Hz and $^3J_{\text{HH}} = 7.5$ Hz, 1H), 1.31-1.20 (m, 3H), 1.13 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 156.7, 135.3, 128.9, 127.9, 127.0, 65.6, 51.8, 45.3, 29.9, 26.3, 25.1, 23.8, 12.0. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$: C, 75.25; H, 7.80. Found: C, 75.19; H, 7.93.

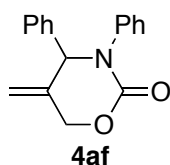
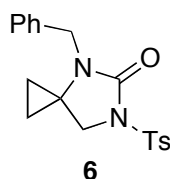


Table 2, Entry 11. White solid. 82% yield.

^1H NMR (CDCl_3): δ 7.39-7.28 (m, 5H), 7.26 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.22-7.19 (m, 2H), 7.17 (tt, $^3J_{\text{HH}} = 7.3$ Hz and $^4J_{\text{HH}} = 1.3$ Hz, 1H), 5.38 (s, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 4.86 (d, $^2J_{\text{HH}} = 12.7$ Hz, 1H), 4.74 (d, $^2J_{\text{HH}} = 12.7$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 153.4, 141.9, 139.5, 138.5, 129.2, 129.0, 128.4, 127.1, 126.74, 126.68, 114.0, 68.8, 68.3. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2$: C, 76.96; H, 5.70. Found: C, 76.80; H, 5.97.

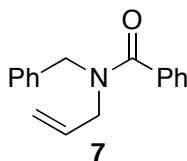
Procedure for Equation 3.



A solution of $\text{PdCp}(\eta^3\text{-C}_3\text{H}_5)$ (2.1 mg, 10 μmol), $\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$ (9.6 mg, 20 μmol ; 97% purity), carbamate **5** (53.5 mg, 0.200 mmol), and isocyanate **2a** (49.4 μL , 0.400 mmol) in CH_2Cl_2 (0.50 mL) was stirred for 6 h at 40 $^\circ\text{C}$. The reaction mixture was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 3/5 and then with EtOAc/ C_6H_6 = 1/20 to afford compound **6** as a white solid (44.7 mg, 0.125 mmol; 63% yield).

^1H NMR (CDCl_3): δ 7.98 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 7.36 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 7.25-7.19 (m, 3H), 7.07-7.03 (m, 2H), 4.11 (s, 2H), 3.83 (s, 2H), 2.46 (s, 3H), 0.86 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 0.54 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 154.5, 144.9, 137.2, 135.1, 129.8, 128.8, 128.3, 127.7, 127.1, 51.1, 42.8, 38.8, 21.8, 7.7. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$: C, 64.02; H, 5.66. Found: C, 64.27; H, 5.76.

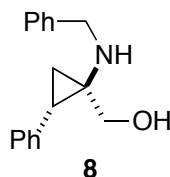
Procedure for Equation 4.



A mixture of *N*-benzylbenzamide (63.4 mg, 0.300 mmol) and NaH (16.8 mg, 0.420 mmol; 60 wt% in mineral oil) in THF (0.30 mL) was stirred for 1 h at room temperature to generate sodium benzoyl(benzyl)amide. Separately, a solution of PdCp(η^3 -C₃H₅) (3.2 mg, 15 μ mol) and P(4-CF₃C₆H₄)₃ (14.0 mg, 30 μ mol) in THF (0.20 mL) was stirred for 5 min at room temperature. Allyl acetate (38.8 μ L, 0.360 mmol) and the sodium benzoyl(benzyl)amide prepared above were successively added to it with the aid of additional THF (0.50 mL), and the resulting mixture was stirred for 24 h at 50 °C. This was then passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/3 to afford compound **7** (CAS: 210347-84-5) as a pale yellow solid (44.3 mg, 0.176 mmol; 59% yield).

¹H NMR (CDCl₃, 60 °C): δ 7.47-7.44 (m, 2H), 7.40-7.33 (m, 6H), 7.28 (t, ³*J*_{HH} = 7.2 Hz, 2H), 5.79 (bs, 1H), 5.23 (dq, ³*J*_{HH} = 10.4 Hz and *J*_{HH} = 1.4 Hz, 1H), 5.15 (dq, ³*J*_{HH} = 17.1 Hz and *J*_{HH} = 1.4 Hz, 1H), 4.67 (bs, 2H), 3.90 (bs, 2H). ¹³C NMR (CDCl₃, 60 °C): δ 172.1, 137.3, 136.7, 133.2, 129.7, 128.8, 128.5, 128.0, 127.6, 126.8, 117.9, 50.7, 47.7.

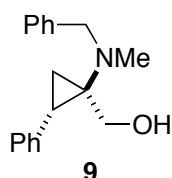
Procedure for Equation 5.



Compound 8:

Ethylenediamine (6.0 mL) and 2 M NaOH_{aq} (1.5 mL) were successively added to a solution of **3aa** (168 mg, 0.601 mmol) in THF (1.0 mL), and the mixture was stirred for 18 h at room temperature. The volatiles were removed under vacuum and the residue was diluted with water. This was neutralized with 1 M HCl_{aq} and then extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. This crude material was treated with HCl in Et₂O and extracted with water. The aqueous layer was washed with Et₂O, neutralized with 2 M NaOH_{aq}, and back-extracted with CH₂Cl₂. The organic layer thus obtained was dried over MgSO₄, filtered, and concentrated under vacuum to afford compound **8** as a yellow solid (126 mg, 0.498 mmol; 83% yield).

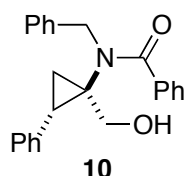
¹H NMR (CDCl₃): δ 7.39 (d, ³*J*_{HH} = 7.0 Hz, 2H), 7.35 (t, ³*J*_{HH} = 7.5 Hz, 2H), 7.31-7.26 (m, 3H), 7.21 (t, ³*J*_{HH} = 7.3 Hz, 1H), 7.19 (d, ³*J*_{HH} = 7.4 Hz, 2H), 3.96 (d, ²*J*_{HH} = 12.7 Hz, 1H), 3.91 (d, ²*J*_{HH} = 12.7 Hz, 1H), 3.39 (s, 2H), 2.41 (dd, ²*J*_{HH} = 9.2 Hz and ³*J*_{HH} = 6.8 Hz, 1H), 1.90 (bs, 2H), 1.17 (dd, ²*J*_{HH} = 9.1 Hz and ³*J*_{HH} = 5.6 Hz, 1H), 1.14 (dd, ³*J*_{HH} = 6.6 and 5.6 Hz, 1H). ¹³C NMR (CDCl₃): δ 140.6, 138.0, 128.7, 128.6, 128.5, 128.3, 127.2, 126.4, 62.0, 50.2, 46.9, 30.6, 16.7. Anal. Calcd for C₁₇H₁₉NO: C, 80.60; H, 7.56. Found: C, 80.38; H, 7.52.



Compound 9:

LiAlH₄ (15.2 mg, 0.400 mmol) was added to a solution of **3aa** (55.9 mg, 0.200 mmol) in Et₂O (2.0 mL), and the mixture was refluxed for 8 h. The reaction was quenched by the addition of water (15 μ L), 15% NaOH aq (15 μ L), and water (45 μ L), and the precipitate that formed was filtered off with THF. The solvent was removed under vacuum and the residue was purified by preparative TLC with EtOAc/hexane = 1/2 to afford compound **9** as a yellow oil (42.8 mg, 0.160 mmol; 80% yield).

¹H NMR (CDCl₃): δ 7.35-7.32 (m, 4H), 7.32-7.24 (m, 3H), 7.23-7.19 (m, 3H), 4.00 (d, ²J_{HH} = 13.4 Hz, 1H), 3.95 (d, ²J_{HH} = 13.4 Hz, 1H), 3.65 (d, ²J_{HH} = 12.6 Hz, 1H), 3.56 (d, ²J_{HH} = 12.6 Hz, 1H), 2.51 (dd, ²J_{HH} = 8.9 Hz and ³J_{HH} = 6.9 Hz, 1H), 2.42 (s, 3H), 1.28 (bs, 1H), 1.25 (dd, ²J_{HH} = 9.1 Hz and ³J_{HH} = 5.2 Hz, 1H), 1.22 (dd, ³J_{HH} = 6.7 and 5.2 Hz, 1H). ¹³C NMR (CDCl₃): δ 140.2, 138.1, 128.60, 128.59, 128.58, 128.4, 127.0, 126.5, 62.0, 59.5, 52.8, 38.6, 32.0, 17.9. HRMS (ESI-TOF) calcd for C₁₈H₂₂NO (M+H⁺) 268.1696, found 268.1701.

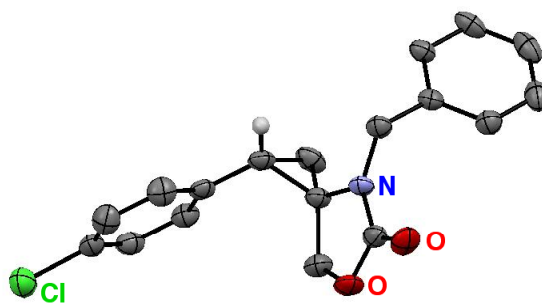


Compound 10:

Phenylmagnesium bromide (490 μ L, 1.03 mmol; 2.1 M solution in THF) was added to a solution of **3aa** (55.9 mg, 0.200 mmol) in THF (1.0 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. The reaction was quenched with NH₄Cl aq and this was extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/1 to afford compound **10** as a white solid (60.6 mg, 0.170 mmol; 85% yield).

¹H NMR (CDCl₃): δ 7.46 (d, ³J_{HH} = 6.7 Hz, 2H), 7.42-7.34 (m, 5H), 7.33-7.20 (m, 8H), 4.80 (d, ²J_{HH} = 15.6 Hz, 1H), 4.66 (d, ²J_{HH} = 15.9 Hz, 1H), 3.68 (bs, 1H), 3.29 (d, ²J_{HH} = 11.5 Hz, 1H), 3.25 (d, ²J_{HH} = 10.9 Hz, 1H), 2.73 (dd, ²J_{HH} = 8.8 Hz and ³J_{HH} = 7.9 Hz, 1H), 1.51-1.35 (m, 2H). ¹³C NMR (CDCl₃): δ 176.1, 137.8, 136.5, 136.3, 130.1, 129.0, 128.8, 128.6, 128.4, 127.7, 127.3, 127.1, 127.0, 64.9, 54.1, 47.3, 32.6, 16.6. Anal. Calcd for C₂₄H₂₃NO₂: C, 80.64; H, 6.49. Found: C, 80.39; H, 6.44.

IV. X-ray Crystal Structure of Compound 3ca



Data Collection

A colorless THF solution of compound **3ca** was prepared. Crystals suitable for X-ray analysis were obtained by diffusion of pentane at room temperature.

A colorless prism crystal of $C_{18}H_{16}ClNO_2$ having approximate dimensions of 0.50 x 0.40 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation.

Indexing was performed from 3 oscillations that were exposed for 60 seconds. The crystal-to-detector distance was 127.40 mm.

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

$$\begin{aligned} a &= 9.369(5) \text{ \AA} \\ b &= 16.869(9) \text{ \AA} \\ c &= 9.901(7) \text{ \AA} \\ V &= 1526.2(15) \text{ \AA}^3 \\ \beta &= 102.76(2)^\circ \end{aligned}$$

For $Z = 4$ and F.W. = 313.78, the calculated density is 1.366 g/cm³. The systematic absences of:

$$\begin{aligned} h0l: & h + l \pm 2n \\ 0k0: & k \pm 2n \end{aligned}$$

uniquely determine the space group to be:

$$P2_1/n \text{ (\#14)}$$

The data were collected at a temperature of -150 ± 1 °C to a maximum 2θ value of 55.0°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at $\chi = 45.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was 50.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at $\chi = 45.0^\circ$ and $\phi = 180.0^\circ$. The exposure rate was 50.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 14573 reflections that were collected, 3483 were unique ($R_{\text{int}} = 0.080$).

The linear absorption coefficient, μ , for Mo-K α radiation is 2.564 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.635 to 0.975. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³ and expanded using Fourier techniques.⁴ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement⁵ on F was based on 8816 observed reflections ($I > 2.00\sigma(I)$) and 215 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0691$$

$$R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.0871$$

The standard deviation of an observation of unit weight⁶ was 0.89. A Sheldrick weighting scheme was used. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.95 and $-1.63 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.⁷ Anomalous dispersion effects were included in F_{calc} ;⁸ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁹ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁰ All calculations were performed using the CrystalStructure^{11,12} crystallographic software package.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 802126). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

³ SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

⁴ DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1999).

⁵ Least Squares function minimized:

$$\Sigma w(|F_o| - |F_c|)^2 \quad \text{where } w = \text{Least Squares weights.}$$

⁶ Standard deviation of an observation of unit weight:

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

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

⁷ Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

⁸ Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

⁹ Creagh, D. C.; McAuley, W. J. "International Tables for Crystallography", Vol C, (Wilson, A. J. C., ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219–222 (1992).

¹⁰ Creagh, D. C.; Hubbell, J. H. "International Tables for Crystallography", Vol C, (Wilson, A. J. C., ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200–206 (1992).

¹¹ CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000–2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.

¹² CRYSTALS Issue 11: Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. Chemical Crystallography Laboratory, Oxford, UK (1999).

Experimental Details

A. Crystal Data

Empirical Formula	$C_{18}H_{16}ClNO_2$
Formula Weight	313.78
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.50 X 0.40 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 60.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	$a = 9.369(5) \text{ \AA}$ $b = 16.869(9) \text{ \AA}$ $c = 9.901(7) \text{ \AA}$ $\beta = 102.76(2)^\circ$ $V = 1526.2(15) \text{ \AA}^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.366 g/cm^3
F000	656.00
$\mu(\text{MoK}\alpha)$	2.564 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	44 exposures
ω oscillation Range ($\chi=45.0, \phi=0.0$)	130.0 - 190.0°
Exposure Rate	50.0 sec./°
ω oscillation Range ($\chi=45.0, \phi=180.0$)	0.0 - 160.0°
Exposure Rate	50.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\text{max}}$	55.0°
No. of Reflections Measured	Total: 14573 Unique: 3483 ($R_{\text{int}} = 0.080$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.635–0.975)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (F_o - F_c)^2$
Least Squares Weights	$1/[0.0010 F_o^2 + 3.0000 \sigma(F_o^2) + 0.5000]$
$2\theta_{\text{max}}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	8816
No. Variables	215
Reflection/Parameter Ratio	41.00
Residuals: R ($I > 2.00\sigma(I)$)	0.0691
Residuals: Rw ($I > 2.00\sigma(I)$)	0.0871
Goodness of Fit Indicator	0.886
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	$0.95 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-1.63 \text{ e}^-/\text{\AA}^3$

V. ^1H and ^{13}C NMR Spectra

