Highly stereoselective construction of adjacent tetrasubstituted carbon stereogenic centres via organocatalytic Mukaiyama-aldol reaction of monofluorinated silyl enol ethers to isatins

Yun-Lin Liu, Fu-Min Liao, Yan-Fei Niu, Xiao-Li Zhao and Jian Zhou*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663N Zhongshan Road, Shanghai 200062, China, *E-mail: jzhou@chem.ecnu.edu.cn*

(Part I)

Content **Page**

^{1}H, ^{13}C, ^{19}F NMR and HPLC spectra are provided in Part II and III

General: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ or $(CD_3)_2SO$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Anhydrous CH_3CN was prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous THF were prepared by distillation over sodium-benzophenone ketyl. Anhydrous acetone and ethyl acetate were prepared by distillation over Ca_2SO_4 and 4 Å MS. Anhydrous methanol was prepared over Na_2SO_4 and magnesium prior to use. All the chiral (thio)urea catalysts were prepared using literature procedures.[1] All the isatins were commercially available or easily prepared using literature procedures.[2] The *N*-methyl protected isatins were prepared according to a literature method.[3] The monofluorinated silyl enol ethers were prepared according to the literature report.[4]

---

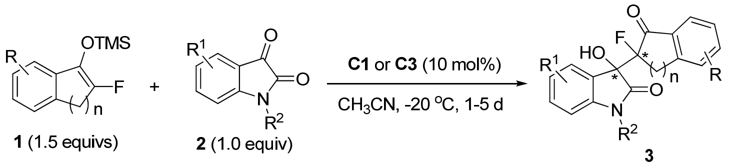
[1] a) Berkessel, A.; Mukherjee, S.; Müller, T. N.; Cleemann, F.; Roland, K.; Brandenburg, M.; Neudörfl, J.-M.; Lex, J. *Org. Biomol. Chem.* **2006**, *4*, 4319; b) Tárkányi, G.; Király, P.; Varga, S.; Vakulya, B.; Soós, T. *Chem. Eur. J.* **2008**, *14*, 6078; c) Vakulya, B.; Varga, S.; Soós, T. *J. Org. Chem.* **2008**, *73*, 3475; d) Peschiulli, A.; Quigley, C.; Tallon, S.; Gun'ko, Y. K.; Connon, S. J. *J. Org. Chem.* **2008**, *73*, 6409; e) Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org. Lett.* **2005,** *7*, 1967.

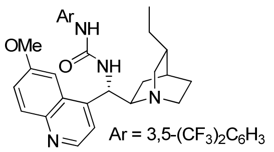
[2] For a review on the synthesis of isatins, see: da Silva, J. F. M.; Garden, S. J.; Pinto, A. C. *J. Braz. Chem. Soc.* **2001**, *12*, 273.

[3] Overman, L. E; Peterson, E. A. *Tetrahedron* **2003**, *59*, 6905.

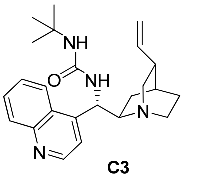
[4] Bélanger, É.; Cantin, K.; Messe, O.; Tremblay, M.; Paquin, J.-F. *J. Am. Chem. Soc.* **2007**, *129*, 1034.

1) Experimental data for products 3.



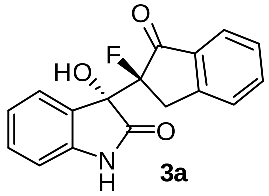


C1



C3

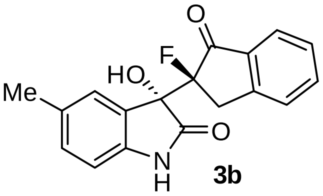
General procedure: To a 10 mL vial were added catalyst **C1** or **C3** as indicated in Table 2 (0.025 mmol) and isatins **2** (0.25 mmol), followed by 5.0 mL of anhydrous CH_3CN (8.0 mL of solvent was used when isatins have a poor solubility in CH_3CN, indicated below). The reaction mixture was stirred at room temperature until the full dissolution of isatins **2**, and then cooled to -20 °C for about 15 minutes before the freshly prepared monofluorinated silyl enol ethers **1** (0.375 mmol) was added. The reaction was kept at -20 °C untill the completion of isatins **2** by TLC analysis. The reaction mixture was quenched through a short column chromatograph to remove the chiral catalyst, and the solvent was removed under vacuum. The residue was subjected to flash column chromatography using CH_2Cl_2/ethyl acetate (from 10:1 to 1:1) as the eluent, affording the desired products **3**. The diastereoselectivity was determined by ^{1}H NMR analysis of the crude reaction mixture after a short column chromatography to remove the chiral catalyst, which was further confirmed by HPLC analysis of the product obtained by preparative TLC.



3a

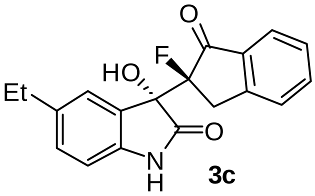
The reaction was run for 3 days, affording product **3a** in 95% yield as a white solid (m.p. 166-168 °C), (dr = 15:1); HPLC analysis [Chiralcel ODH-ODH, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; major diastereomer: τ_R = 31.71 min (major enantiomer), τ_R = 49.15 min (minor enantiomer); minor diastereomer: τ_R = 40.81 min (major enantiomer), τ_R = 62.99 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 94% ee, minor diastereomer: 5% ee; $[\alpha]^{25}_D$= 92.7 (c = 0.15, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.14 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.23 (dd, *J* = 18.4, 10.4 Hz, 1H), 6.65-6.66 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.86-6.90 (m, 1H), 7.20-7.28 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 10.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.23 (d, *J* = 18 Hz), 175.72 (d, *J* = 2 Hz), 150.83 (d, *J* = 5

Hz), 142.53, 136.28, 134.49 (d, *J* = 2 Hz), 129.88, 127.98, 126.99, 126.98, 126.51 (d, *J* = 2 Hz), 123.68, 121.12, 109.56, 98.16 (d, *J* = 193 Hz), 76.56 (d, *J* = 27 Hz), 34.90 (d, *J* = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -167.68 (s, 1 F); IR (neat): 3301, 2958, 2852, 1720, 1614, 1586, 1468, 1431, 1182, 928, 747; HRMS (ESI): Exact mass calcd for $C_{17}H_{13}FNO_3$ $[M+H]^+$: 298.0874, Found: 298.0880.



3b

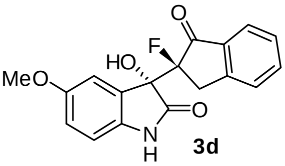
The reaction was run for 4 days, affording product **3b** in 70% yield as a white solid (m.p. 187-189 °C), (dr = 13:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 25.87 min (major enantiomer), τ_R = 46.06 min (minor enantiomer); minor diastereomer: τ_R = 31.20 min (major enantiomer), τ_R = 43.38 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 94% ee, minor diastereomer: 23% ee; $[\alpha]^{25}_D$ = 143.6 (c = 0.25, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.18 (s, 3H), 3.13 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.17 (dd, *J* = 18.0, 10.4 Hz, 1H), 6.60 (s, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.41-7.44 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 10.37 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.29 (d, *J* = 18 Hz), 175.70 (d, *J* = 2 Hz), 150.78 (d, *J* = 5 Hz), 140.05, 136.21, 134.59 (d, *J* = 1 Hz), 130.05, 129.94, 127.99, 127.24, 127.13, 126.47, 123.72, 109.32, 98.18 (d, *J* = 193 Hz), 76.83 (d, *J* = 28 Hz), 34.99 (d, *J* = 23 Hz), 20.66; ^{19}F NMR (376 MHz, DMSO-d_6): δ -167.98 (s, 1 F); IR (neat): 3286, 2923, 2854, 1713, 1624, 1604, 1488, 1468, 1025, 790, 735; HRMS (ESI): Exact mass calcd for $C_{18}H_{18}FN_2O_3$ $[M+NH_4]^+$: 329.1296, Found: 329.1303.



3c

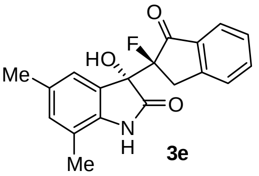
The reaction was run for 3 days, affording product **3c** in 72% yield as a white solid (m.p. 140-142 °C), (dr = 9:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 22.17 min (major enantiomer), τ_R = 42.78 min (minor enantiomer); minor diastereomer: τ_R = 30.05 min (major enantiomer), τ_R = 33.21 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 88% ee, minor diastereomer: 6% ee; $[\alpha]^{25}_D$ = 95.7 (c = 0.19, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.02 (t, *J* = 7.6 Hz, 3H), 2.44 (q, *J* = 7.6 Hz, 2H), 3.15 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.23 (dd, J_1 = 18.4, 10.4 Hz, 1H), 6.62-6.63 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.57-7.61 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 10.37 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.27 (d, *J* = 18 Hz), 175.68 (d, *J* = 3

Hz), 150.89 (d, J = 5 Hz), 140.26, 136.58, 136.25, 134.58 (d, J = 1 Hz), 129.02, 127.96, 126.94 (d, J = 2 Hz), 126.48, 126.05, 123.73, 109.35, 98.44 (d, J = 194 Hz), 76.69 (d, J = 27 Hz), 35.09 (d, J = 23 Hz), 27.91, 15.91; ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.97 (s, 1 F); IR (neat): 3419, 2965, 2931, 1723, 1624, 1490, 1378, 1050, 1025, 824, 759; HRMS (ESI): Exact mass calcd for $C_{19}H_{20}FN_2O_3$ [M+NH$_4$]$^+$: 343.1452, Found: 343.1455.



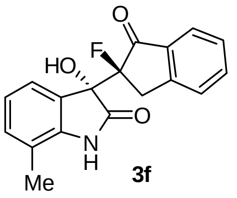
3d

The reaction was run for 4 days, affording product **3d** in 88% yield as a white solid (m.p. 195-197 °C), (dr = 14:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 35.89 min (major enantiomer), τ_R = 72.78 min (minor enantiomer); minor diastereomer: τ_R = 53.52 min (major enantiomer), τ_R = 59.53 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 92% ee, minor diastereomer: 24% ee; $[\alpha]^{25}_D$ = 97.1 (c = 0.20, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.14 (dd, J = 25.6, 18.4 Hz, 1H), 3.64 (s, 3H), 4.21 (dd, J = 18.4, 10.4 Hz, 1H), 6.67-6.71 (m, 2H), 6.78-6.81 (m, 1H), 6.90-6.91 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 10.31 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.28 (d, J = 18 Hz), 175.52 (d, J = 2 Hz), 154.34, 150.84 (d, J = 5 Hz), 136.29, 135.73, 134.56 (d, J = 2 Hz), 128.21, 128.03, 126.52, 123.76, 114.73, 113.59, 109.94, 98.17 (d, J = 194 Hz), 77.01 (d, J = 28 Hz), 55.47, 34.97 (d, J = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.83 (s, 1 F); IR (neat): 3403, 2963, 2924, 1719, 1664, 1606, 1490, 1468, 915, 895, 794, 736; HRMS (ESI): Exact mass calcd for $C_{18}H_{18}FN_2O_4$ [M+NH$_4$]$^+$: 345.1245, Found: 345.1250.



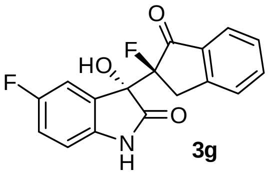
3e

The reaction was run in 8.0 mL of CH_3CN for 4 days , affording product **3e** in 98% yield as a white solid (m.p. 189-191 °C), (dr = 7:1); HPLC analysis [Chiralcel AY-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 21.48 min (major enantiomer), τ_R = 59.03 min (minor enantiomer); minor diastereomer: τ_R = 29.99 min (major enantiomer), τ_R = 15.15 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 91% ee, minor diastereomer: 9% ee; $[\alpha]^{25}_D$ = 127.0 (c = 0.10, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.14 (s, 3H), 2.16 (s, 3H), 3.13 (dd, J = 25.6, 18.4 Hz, 1H), 4.10 (dd, J = 18.4, 10.4 Hz, 1H), 6.53-6.54 (m, 1H), 6.86 (s, 1H), 6.94 (s, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.27 (d, J = 18 Hz), 176.11 (d, J = 3 Hz), 150.62 (d, J = 5 Hz), 138.59, 136.17, 134.69 (d, J = 2 Hz), 131.51, 129.96, 128.01, 126.94, 126.50, 124.50, 123.74, 118.54, 98.22 (d, *J* = 194 Hz), 77.22 (d, *J* = 27 Hz), 35.17 (d, *J* = 23 Hz), 20.61, 16.21; ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -168.21 (s, 1 F); IR (neat): 3448, 2932, 2851, 1718, 1630, 1608, 1482, 1418, 1218, 814, 707; HRMS (ESI): Exact mass calcd for $C_{19}H_{17}FNO_3$ [M+H]$^+$: 326.1187, Found: 326.1192.



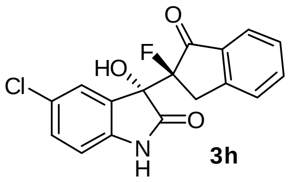
3f

The reaction was run for 4 days, affording product **3f** in 54% yield as a white solid (m.p. 102-104 °C), (dr = 12:1); HPLC analysis [Chiralcel IE, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 67.25 min (major enantiomer), τ_R = 55.20 min (minor enantiomer); minor diastereomer: τ_R = 28.93 min (major enantiomer), τ_R = 23.70 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 84% ee, minor diastereomer: 6% ee; $[\alpha]^{25}_D$ = 84.8 (c = 0.13, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.18 (s, 3H), 3.14 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.16 (dd, *J* = 18.4, 10.4 Hz, 1H), 6.60-6.61 (m, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.71 (td, *J* = 7.6, 0.8 Hz, 1H), 10.53 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.24 (d, *J* = 18 Hz), 176.18 (d, *J* = 3 Hz), 150.73 (d, *J* = 4 Hz), 141.09, 136.27, 134.61 (d, *J* = 2 Hz), 131.14, 128.03, 126.80 (d, *J* = 1 Hz), 126.56, 123.82, 123.74, 121.20, 118.85, 98.27 (d, *J* = 193 Hz), 76.92 (d, *J* = 28 Hz), 35.09 (d, *J* = 23 Hz), 16.29; ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.88 (s, 1 F); IR (neat): 3323, 2926, 2911, 1712, 1626, 1604, 1466, 1200, 698; HRMS (ESI): Exact mass calcd for $C_{18}H_{18}FN_2O_3$ [M+NH$_4$]$^+$: 329.1296, Found: 329.1302.



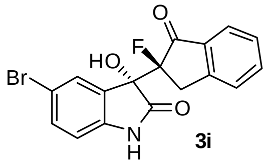
3g

The reaction was run for 2 days, affording product **3g** in 75% yield as a white solid (m.p. 180-182 °C), (dr = 5:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 20.02 min (major enantiomer), τ_R = 38.85 min (minor enantiomer); minor diastereomer: τ_R = 25.19 min (major enantiomer), τ_R = 33.37 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 81% ee, minor diastereomer: 9% ee; $[\alpha]^{25}_D$ = 58.0 (c = 0.22, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.15 (dd, *J* = 26.0, 18.4 Hz, 1H), 4.32 (dd, *J* = 18.8, 10.8 Hz, 1H), 6.80-6.83 (m, 1H), 6.87 (s, 1H), 7.07-7.15 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.72-7.76 (m, 1H), 10.55 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.40 (d, *J* = 18 Hz), 175.89, 157.47 (d, *J* = 235 Hz), 151.12 (d, *J* = 5 Hz), 138.84, 136.52, 134.46 (d, *J* = 2 Hz), 128.78 (d, *J* = 8 Hz), 128.12, 126.61, 123.91, 116.30 (d, *J* = 23 Hz), 114.50 (d, *J* = 25 Hz), 110.43 (d, *J* = 8 Hz), 97.92 (d, *J* = 193 Hz), 76.79 (d, *J* = 28 Hz), 34.73 (d, *J* = 22 Hz); ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -122.14 (s, 1 F), -167.21 (s, 1 F); IR (neat): 3672, 2987, 2901, 1725, 1608, 1483, 1406, 1066, 756; HRMS (ESI): Exact mass calcd for $C_{17}H_{15}F_2N_2O_3$ $[M+NH_4]^+$: 333.1045, Found: 333.1049.



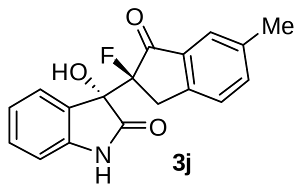
3h

The reaction was run for 1 days, affording product **3h** in 98% yield as a white solid (m.p. 176-178 ^{o}C), (dr = 5:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 20.52 min (major enantiomer), τ_R = 44.01 min (minor enantiomer); minor diastereomer: τ_R = 24.73 min (major enantiomer), τ_R = 34.39 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 86% ee, minor diastereomer: 20% ee; $[\alpha]^{25}_D$ = 82.6 (c = 0.12, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.15 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.33 (dd, *J* = 18.4, 10.8 Hz, 1H), 6.82-6.84 (m, 1H), 6.87-6.88 (m, 1H), 7.29-7.32 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 10.65 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.38 (d, *J* = 17 Hz), 175.69, 151.14 (d, *J* = 5 Hz), 141.52, 136.53, 134.42, 129.71, 129.04, 128.10, 126.92, 126.56, 125.20, 123.91, 111.08, 97.79 (d, *J* = 193 Hz), 76.54 (d, *J* = 29 Hz), 34.63 (d, *J* = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.05 (s, 1 F); IR (neat): 3339, 2988, 2925, 1726, 1616, 1477, 1435, 1103, 718; HRMS (ESI): Exact mass calcd for $C_{17}H_{15}ClFN_2O_3$ $[M+NH_4]^+$: 349.0750, Found: 349.0749.

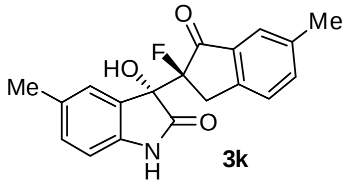


3i

The reaction was run for 3 days, affording product **3i** in 91% yield as a white solid (m.p. 193-195 ^{o}C), (dr = 5:1); HPLC analysis [Chiralcel IE, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 36.63 min (major enantiomer), τ_R = 24.90 min (minor enantiomer); minor diastereomer: τ_R = 11.86 min (major enantiomer), τ_R = 18.18 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 85% ee, minor diastereomer: 9% ee; $[\alpha]^{25}_D$ = 57.4 (c = 0.12, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.15 (dd, *J* = 26.0, 18.4 Hz, 1H), 4.33 (dd, *J* = 18.4, 10.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.87-6.88 (m, 1H), 7.42-7.47 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.73-7.77 (m, 1H), 10.67 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.40 (d, *J* = 18 Hz), 175.58 (d, *J* = 1 Hz), 151.14 (d, *J* = 4 Hz), 141.93, 136.55, 134.42 (d, *J* = 2 Hz), 132.56, 129.66, 129.43, 128.11, 126.57, 123.93, 112.90, 111.63, 97.81 (d, *J* = 193 Hz), 76.53 (d, *J* = 29 Hz), 34.64 (d, *J* = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.04 (s, 1 F); IR (neat): 3213, 2926, 2865, 1713, 1617, 1609, 1479, 1444, 1175, 727; HRMS (ESI): Exact mass calcd for $C_{17}H_{15}BrFN_2O_3$ $[M+NH_4]^+$: 393.0245, Found: 393.0248.

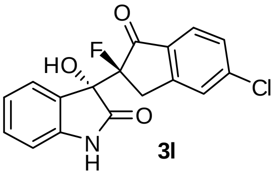

3j

The reaction was run for 3 days, affording product **3j** in 97% yield as a white solid (m.p. 162-164 ^{o}C), (dr = 10:1); HPLC analysis [Chiralcel ODH-ODH, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; major diastereomer: τ_R = 30.99 min (major enantiomer), τ_R = 46.93 min (minor enantiomer); minor diastereomer: τ_R = 40.61 min (major enantiomer), τ_R = 65.37 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 92% ee, minor diastereomer: 73% ee; $[\alpha]^{25}_{D}$ = 105.2 (c = 0.25, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.34 (s, 3H), 3.08 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.17 (dd, *J* = 18.0, 10.4 Hz, 1H), 6.65-6.66 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.45-7.46 (m, 2H), 7.52-7.54 (m, 1H), 10.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.25 (d, *J* = 18 Hz), 175. 85 (d, *J* = 2 Hz), 148.27 (d, *J* = 5 Hz), 142.64, 137.66, 137.45, 134.73 (d, *J* = 2 Hz), 129.95, 127.16, 126.58, 126.27, 123.54, 121.24, 109.66, 98.49 (d, *J* = 194 Hz), 76.70 (d, *J* = 28 Hz), 34.72 (d, *J* = 23 Hz), 20.58; ^{19}F NMR (376 MHz, DMSO-d$_6$): δ -167.29 (s, 1 F); IR (neat): 3367, 2987, 2922, 1723, 1618, 1472, 1407, 1050, 1026, 760; HRMS (ESI): Exact mass calcd for $C_{18}H_{18}FN_2O_3$ $[M+NH_4]^+$: 329.1296, Found: 329.1296.

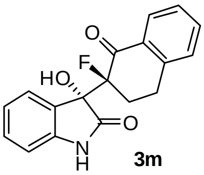

3k

The reaction was run for 4 days, affording product **3k** in 54% yield as a white solid (m.p. 156-158 ^{o}C), (dr = 7:1); HPLC analysis [Chiralcel IE, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 48.20 min (major enantiomer), τ_R = 62.19 min (minor enantiomer); minor diastereomer: τ_R = 31.68 min (major enantiomer), τ_R = 28.65 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 90% ee, minor diastereomer: 16% ee; $[\alpha]^{25}_{D}$ = 137.1 (c = 0.10, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.19 (s, 3H), 2.35 (s, 3H), 3.05 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.08 (dd, *J* = 18.4, 10.4 Hz, 1H), 6.55-6.56 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.44-7.46 (m, 2H), 7.53-7.55 (m, 1H), 10.36 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 198.24 (d, *J* = 18 Hz), 175. 73 (d, *J* = 3 Hz), 148.12 (d, *J* = 5 Hz), 140.08, 137.60, 137.31, 134.77, 130.06, 129.95, 127.23, 126.19, 123.49, 109.33, 98.40 (d, *J* = 194 Hz), 76.91 (d, *J* =

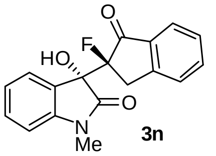
27 Hz), 34.71 (d, J = 23 Hz), 20.69, 20.55; ^{19}F NMR (376 MHz, DMSO-d_6): δ -167.65 (s, 1 F); IR (neat): 3357, 2919, 2850, 1718, 1624, 1490, 1423, 1005, 757; HRMS (ESI): Exact mass calcd for $C_{19}H_{20}FN_2O_3$ $[M+NH_4]^+$: 343.1452, Found: 343.1455.


3l

The reaction was run for 3 days, affording product **3l** in 98% yield as a white solid (m.p. 195-198 ^{o}C), (dr = 5:1); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 50.19 min (major enantiomer), τ_R = 47.31 min (minor enantiomer); minor diastereomer: τ_R = 58.36 min (major enantiomer), τ_R = 63.23 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 76% ee, minor diastereomer: 23% ee; $[\alpha]^{25}_{D}$ = 44.0 (c = 0.25, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.17 (dd, J = 24.8, 18.4 Hz, 1H), 4.23 (dd, J = 18.4, 9.2 Hz, 1H), 6.73-6.74 (m, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.88-6.92 (m, 1H), 7.22-7.28 (m, 2H), 7.47-7.49 (m, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 10.52 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.09 (d, J = 18 Hz), 175. 70 (d, J = 3 Hz), 152.66 (d, J = 5 Hz), 142.60, 141.14, 133.35 (d, J = 2 Hz), 130.05, 128.59, 126.93 (d, J = 1 Hz), 126.65, 126.57, 125.39, 121.28, 109.73, 98.32 (d, J = 194 Hz), 76.69 (d, J = 27 Hz), 34.75 (d, J = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -167.76 (s, 1 F); IR (neat): 3344, 2934, 2919, 1717, 1617, 1598, 1576, 1183, 767, 680; HRMS (ESI): Exact mass calcd for $C_{17}H_{15}ClFN_2O_3$ $[M+NH_4]^+$: 349.0750, Found: 349.0751.

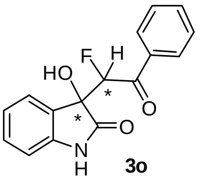

3m

The reaction was run for 5 days, affording product **3m** in 37% yield as a white solid (m.p. 132-134 ^{o}C), (dr = 5:1); HPLC analysis [Chiralcel IE, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 67.78 min (major enantiomer), τ_R = 73.31 min (minor enantiomer); minor diastereomer: τ_R = 59.47 min (major enantiomer), τ_R = 35.75 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 82% ee, minor diastereomer: 31% ee; $[\alpha]^{25}_{D}$ = 106.0 (c = 0.10, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.25-2.36 (m, 1H), 2.91-3.03 (m, 2H), 3.55-3.61 (m, 1H), 6.49-6.50 (m, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.92 (td, J = 7.6, 0.8 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.23 (td, J = 7.6, 1.2 Hz, 1H), 7.35-7.40 (m, 2H), 7.59 (td, J = 7.6, 1.2 Hz, 1H), 7.89-7.91 (m, 1H), 10.47 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.45 (d, J = 17 Hz), 176.18, 144.60, 142.59, 133.82, 132.81, 129.73, 128.76, 128.41, 126.79, 126.52, 125.86, 121.11, 109.53, 95.29 (d, J = 184 Hz), 77.78 (d, J = 31 Hz), 29.61 (d, J = 22 Hz), 26.06 (d, J = 11 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.26 (s, 1 F); IR (neat): 3674, 2967, 2924, 1718, 1697, 1620, 1601, 1471, 1393, 1064, 735; HRMS (ESI): Exact mass calcd for $C_{18}H_{15}FNO_3$ $[M+H]^+$: 312.1030, Found: 312.1032.



3n

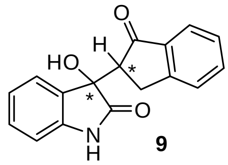
The reaction was run for 4 days, affording product **3n** in 56% yield as a white solid (m.p. 174-176 ^{o}C), (dr = 8:1); HPLC analysis [Chiralcel IE-H, ^{i}PrOH/hexane = 30/70, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 60.29 min (major enantiomer), τ_R = 47.18 min (minor enantiomer); minor diastereomer: τ_R = 17.26 min (major enantiomer), τ_R = 21.99 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 70% ee, minor diastereomer: 1% ee; $[\alpha]^{25}_D$ = 40.0 (c = 0.10, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.11 (s, 3H), 3.17 (dd, *J* = 25.6, 18.4 Hz, 1H), 4.31 (dd, *J* = 18.4, 10.8 Hz, 1H), 6.78-6.79 (m, 1H), 6.93-7.00 (m, 2H), 7.30-7.34 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.58-7.63 (m, 2H), 7.71-7.74 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.21 (d, *J* = 18 Hz), 174.09 (d, *J* = 1 Hz), 151.07 (d, *J* = 5 Hz), 144.01, 136.47, 134.40 (d, *J* = 2 Hz), 130.12, 128.08, 126.59, 126.25 (d, *J* = 2 Hz), 126.11, 123.80, 121.86, 108.53, 98.35 (d, *J* = 194 Hz), 76.27 (d, *J* = 28 Hz), 34.98 (d, *J* = 23 Hz), 26.10; ^{19}F NMR (376 MHz, DMSO-d_6): δ -167.00 (s, 1 F); IR (neat): 3367, 2988, 2921, 1715, 1653, 1610, 1558, 1540, 1491, 1350, 727; HRMS (ESI): Exact mass calcd for $C_{18}H_{15}FNO_3$ $[M+H]^+$: 312.1030, Found: 312.1034.



3o

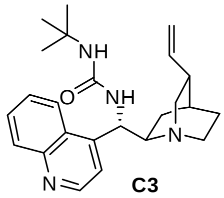
The reaction was run for 3 days, affording product **3o** in 46% yield as a white soild, (m.p. 102-106 ^{o}C); HPLC analysis [Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 11.43 min (major enantiomer), τ_R = 16.63 min (minor enantiomer); minor diastereomer: τ_R = 18.03 min (major enantiomer), τ_R = 23.15 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 81% ee, minor diastereomer: 71% ee; $[\alpha]^{25}_D$ = -1.8 (c = 0.17, THF); The two diastereoisomers could not be isolated by column chromatograph. ^{1}H NMR of the mixture (400 MHz, $CDCl_3$): δ 4.66 (s, 0.5H), 4.75 (s, 1H), 5.83 (d, *J* = 46.8 Hz, 0.5H), 5.95 (d, *J* = 46.0 Hz, 1H), 6.82-6.85 (m, 1.5H), 6.94-6.99 (m, 1.5H), 7.18-7.26 (m, 2.8H), 7.35-7.45 (m, 3.5H), 7.50-7.59 (m, 1.5H), 7.80-7.82 (m, 1H), 7.96-7.98 (m, 2H), 8.63 (s, 0.5H), 8.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.62 (d, *J* = 21 Hz), 195.28 (d, *J* = 19 Hz), 176.78, 176.52 (d, *J* = 5 Hz), 141.56, 141.50, 135.14, 134.75, 134.72, 134.34, 133.97, 130.71, 130.55, 129.48, 129.44, 129.38, 129.32, 128.59, 128.40, 126.85, 126.08, 125.80, 125.25, 123.12, 123.01, 110.94, 110.79, 95.02 (d, *J* = 195 Hz), 91.16 (d, *J* = 190 Hz), 34.98 (d, *J* = 23 Hz), 76.84, 76.47; ^{19}F NMR (376 MHz, $CDCl_3$): δ -192.98 (s, 1F),

-197.52 (s, 0.5F); IR (neat): 3271, 2927, 2852, 1720, 1714, 1620, 1596, 1471, 1448, 1334, 1222, 1184, 753; HRMS (ESI): Exact mass calcd for $C_{16}H_{13}FNO_3$ $[M+H]^+$: 286.0874, Found: 286.0877.



9

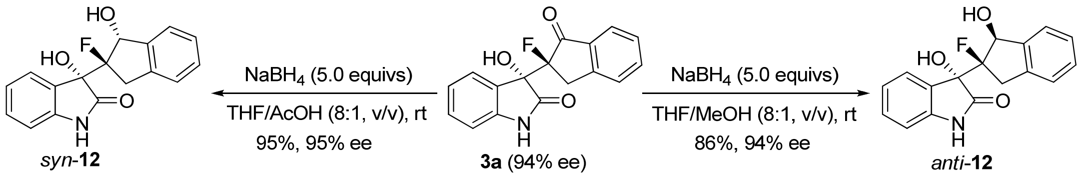
The reaction was run for 3 days, affording product **9** in 48% yield as a white solid (m.p. 160-162 °C), (dr = 7:1); HPLC analysis [Chiralcel IE, ^{i}PrOH/hexane = 30/70, 1.0 mL/min, 230 nm; major diastereomer: τ_R = 35.29 min (major enantiomer), τ_R = 31.29 min (minor enantiomer); minor diastereomer: τ_R = 18.75 min (major enantiomer), τ_R = 22.32 min (minor enantiomer)] gave the isomeric composition of major diastereomer: 94% ee, minor diastereomer: 37% ee; $[\alpha]^{25}_D$ = -2.0 (c = 0.10, THF); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.33-3.44 (m, 2H), 3.57-3.62 (m, 1H), 6.31 (s, 1H), 6.67 (td, *J* = 7.6, 0.8 Hz, 1H), 6.74-6.76 (m, 1H), 7.07-7.11 (m, 2H), 7.29-7.33 (m, 1H), 7.38-7.39 (m, 1H), 7.61-7.66 (m, 2H), 10.39 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 203.53, 177.97, 154.03, 142.56, 136.42, 134.93, 129.31, 129.23, 127.30, 126.80, 124.08, 123.01, 121.19, 109.63, 75.30, 53.18, 28.33; IR (neat): 3276, 2931, 2921, 1730, 1698, 1618, 1470, 1347, 741; HRMS (ESI): Exact mass calcd for $C_{17}H_{13}NNaO_3$ $[M+Na]^+$: 302.0788, Found: 302.0788.



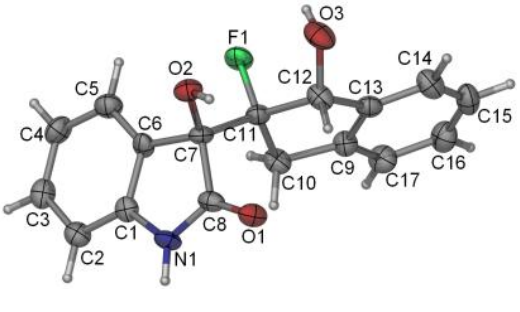
C3

According to reference 1, catalyst **C3** was obtained in 64% yield for 2 steps as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85-0.91 (m, 1H), 1.13 (s, 9H), 1.17-1.21 (m, 1H), 1.49-1.58 (m, 3H), 2.18 (brs, 1H), 2.48-2.52 (m, 1H), 2.58-2.63 (m, 1H), 2.87-2.88 (m, 1H), 3.03-3.09 (m, 2H), 4.80-4.87 (m, 3H), 5.16 (s, 1H), 5.52-5.61 (m, 1H), 6.05-6.06 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.40, 149.84, 148.30, 140.98, 130.00, 128.81, 127.20, 126.37, 123.45, 119.38, 114.32, 60.45, 55.48, 49.97, 40.50, 39.26, 29.34, 29.18, 27.48, 27.12, 25.55; IR (neat): 3644, 3616, 3073, 2945, 2864, 1740, 1724, 1679, 1657, 1649, 1588, 1554, 1391, 758; HRMS (ESI): Exact mass calcd for $C_{24}H_{33}N_4O$ $[M+H]^+$: 393.2649, Found: 393.2646.

Procedure for the preparation of 12 from 3a.[5]



The synthesis of *syn*-12: To a stirred solution of **3a** (59.4 mg, 0.20 mmol, 94% ee) in 4.5 mL of mixture solvent of THF/AcOH (8/1, v/v) was added $NaBH_4$ (38.0 mg, 1.0 mmol) at room temperature in two portions. The reaction mixture was stirred for 0.5 h until the completion of **3a** as indicated by TLC analysis. Then the reaction was quenched by the addition of 5.0 mL of saturated $NaHCO_3$ aqueous solution, the mixture was extracted with CH_2Cl_2 (10 mL × 3), the combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by silica gel column chromatography by using CH_2Cl_2/AcOEt (from 5:1 to 1:1) as the eluent to give desired product ***syn*-12** (56.8 mg) in 95% yield as white soild (m.p. = 115-117 ^{o}C). The relative configuration of product ***syn*-12** was determined by X-Ray analysis**.** HPLC analysis (Chiralcel IE, ^{i}PrOH/hexane = 30/70, 1.0 mL/min, 230 nm; t_r (major) = 10.29 min, t_r (minor) = 9.73 min) gave the isomeric composition of the product: 95% ee, $[\alpha]^{25}{}_{D}$ = 17.1 (c = 0.17, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.95 (dd, J = 24.8, 18.0 Hz, 1H), 3.49 (dd, J = 34.0, 18.4 Hz, 1H), 5.33 (d, J = 9.2 Hz, 1H), 5.67 (dd, J = 19.2, 9.6 Hz, 1H), 5.67-5.68 (m, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.96-7.00 (m, 1H), 7.20-7.27 (m, 4H), 7.31-7.33 (m, 1H), 7.56 (d, J = 7.6 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): 177.24 (d, J = 3 Hz), 143.31, 142.35, 137.23, 129.36, 128.78, 127.90, 127.09, 126.78, 124.55, 124.32, 121.20, 109.27, 104.58 (d, J = 192 Hz), 76.40 (d, J = 29 Hz), 73.78 (d, J = 18 Hz), 37.85 (d, J = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -175.68 (s, 1F); IR (ATR): 3189, 2919, 2850, 1718, 1659, 1619, 1471, 1423, 1194, 1047, 1022, 744; HRMS (ESI): Exact mass calcd for $C_{17}H_{18}FN_2O_3[M+NH_4]^+$: 317.1296, Found: 317.1299.



---

[5] P. Shanmugam, V. Vaithiyanathan and B. Viswambharan, *Aust. J. Chem.* **2007**, 60, 296.

The synthesis of *anti*-12: To a stirred solution of **3a** (59.4 mg, 0.20 mmol, 94% ee) in 4.5 mL of mixture solvent of THF/ MeOH (8/1, v/v) was added $NaBH_4$ (38.0 mg, 1.0 mmol) at room temperature in two portions. The resulting mixture was stirred until the completion of **3a** as indicated by TLC (1 h). The reaction was quenched by the addition of 0.5 mL of saturated NH_4Cl aqueous solution, and the resulting mixture was stirred at room temperature until the generation of gas ceased. Then the mixture was extracted with CH_2Cl_2 (10 mL × 3), the combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography by using CH_2Cl_2/AcOEt (from 5:1 to 1:1) as the eluent to give product *anti*-**12** (51.4 mg) in 86% yield as colourless oil. The relative configuration of product *anti*-**12** was determined by HPLC analysis. HPLC analysis (Chiralcel IE, ^{i}PrOH/hexane = 30/70, 1.0 mL/min, 230 nm; t_r (major) = 8.15 min, t_r (minor) = 8.74 min) gave the isomeric composition of the product: 94% ee, $[\alpha]^{25}_{D}$ = 56.4 (c = 0.11, THF); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.19 (dd, J = 21.6, 18.0 Hz, 1H), 3.94 (dd, J = 36.0, 20.0 Hz, 1H), 4.92 (dd, J = 12.0, 6.0 Hz, 1H), 6.09 (s, 1H), 6.21 (d, J = 5.8 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 7.03-7.07 (m, 1H), 7.21-7.31 (m, 3H), 7.34-7.40 (m, 2H), 7.86 (d, J = 8.0 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): 176.08, 143.14, 142.06, 141.19, 129.78, 129.31, 128.94, 126.93, 126.27, 125.45, 125.34, 121.90, 109.76, 104.56 (d, J = 176 Hz), 79.29 (d, J = 34 Hz), 77.19 (d, J = 31 Hz), 36.42 (d, J = 23 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -158.97 (s, 1F); IR (ATR): 3241, 2921, 2845, 1719, 1663, 1621, 1501, 1057, 756; HRMS (ESI): Exact mass calcd for $C_{17}H_{14}FNO_3Na$ $[M+Na]^+$: 322.0850, Found: 322.0852.

Determination of the absolute configuration.

The absolute configuration of product **3h** was determined to be (*S, S*) by X-ray analysis.[6] The configurations of other compounds were tentatively assigned by comparing the sign of their optical rotations to that of **3h**. Following the general procedure, compound **3h** was obtained in 98% yield with 85% ee as white solid. After a single recrystalization, the ee value of **3h** was enriched to 99%, and we obtained the homochiral single crystal of product **3h**.

Data intensity of this compound was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **3h**: $C_{17}H_{11}ClFNO_3$, M = 331.72, T = 296(2) K, λ = 0.71073 Å, Monoclinic, space group P2(1), a = 6.6455(2) Å, b = 14.0680(5) Å, c = 15.4102(5) Å, V = 1440.68(8) $Å^3$, z = 4, d_{calc} = 1.529 mg/m^3, 16806 reflections measured, 2522 unique [R(int) = 0.0416], R_1 = 0.0315, wR_2 = 0.0651 ($I > 2\sigma(I)$, final R_1 = 0.0426, wR_2 = 0.0712 (all data), GOF = 1.030, and 208 parameters.

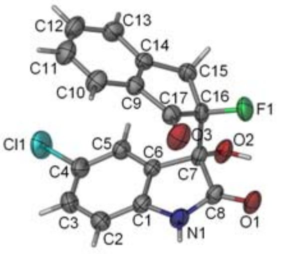


Table 1. Crystal data and structure refinement for z.

Identification code	z
Empirical formula	$C_{17}H_{11}ClFNO_3$
Formula weight	331.72
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)
Unit cell dimensions	a = 6.6455(2) A alpha = 90 deg.
	b = 14.0680(5) A beta = 90 deg.

---

[6] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 999612)

	c = 15.4102(5) A gamma = 90 deg.
Volume	1440.68(8) A^3
Z, Calculated density	4, 1.529 Mg/m^3
Absorption coefficient	0.291 mm^-1
F(000)	680
Crystal size	0.38 x 0.26 x 0.22 mm
Theta range for data collection	1.96 to 24.99 deg.
Limiting indices	-7<=h<=7, -16<=k<=16, -18<=l<=17
Reflections collected / unique	16806 / 2522 [R(int) = 0.0416]
Completeness to theta = 24.99	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9387 and 0.8974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2522 / 0 / 208
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0651
R indices (all data)	R1 = 0.0426, wR2 = 0.0712
Absolute structure parameter	-0.06(8)
Largest diff. peak and hole	0.135 and -0.182 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic, displacement parameters (A^2 x 10^3) for z. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	9634(1)	6756(1)	5120(1)	76(1)
O(1)	9206(2)	7732(1)	9890(1)	48(1)
O(2)	12336(2)	7484(1)	8563(1)	46(1)
C(17)	8626(3)	9440(2)	8020(1)	39(1)
F(1)	11197(2)	9330(1)	9108(1)	55(1)
N(1)	7234(3)	7318(1)	8731(1)	42(1)
C(1)	7501(3)	7179(1)	7836(1)	37(1)
C(2)	6174(4)	6807(2)	7240(1)	47(1)
C(3)	6844(4)	6685(2)	6397(2)	52(1)
C(4)	8787(4)	6930(2)	6175(1)	47(1)
C(5)	10112(3)	7325(1)	6770(1)	40(1)

C(6)	9437(3)	7454(1)	7605(1)	35(1)
C(7)	10440(3)	7884(1)	8392(1)	35(1)
C(8)	8909(3)	7650(2)	9113(1)	37(1)
C(9)	8853(3)	9731(1)	7115(1)	37(1)
C(10)	7380(4)	10028(2)	6542(1)	48(1)
C(11)	7930(4)	10240(2)	5705(2)	55(1)
C(12)	9926(4)	10181(2)	5459(2)	54(1)
C(13)	11398(4)	9888(2)	6030(1)	48(1)
C(14)	10854(3)	9650(1)	6873(1)	38(1)
C(15)	12154(3)	9278(2)	7599(1)	42(1)
C(16)	10634(3)	8982(1)	8295(1)	37(1)
O(3)	7191(3)	9531(1)	8496(1)	58(1)

Table 3. Bond lengths [A] and angles [deg] for z.

Cl(1)-C(4)	1.737(2)
O(1)-C(8)	1.220(2)
O(2)-C(7)	1.405(2)
O(2)-H(2B)	0.8200
C(17)-O(3)	1.210(2)
C(17)-C(9)	1.462(3)
C(17)-C(16)	1.541(3)
F(1)-C(16)	1.396(2)
N(1)-C(8)	1.343(3)
N(1)-C(1)	1.404(3)
N(1)-H(1A)	0.8600
C(1)-C(2)	1.377(3)
C(1)-C(6)	1.389(3)
C(2)-C(3)	1.383(3)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.380(3)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.387(3)
C(5)-C(6)	1.375(3)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.510(3)
C(7)-C(8)	1.542(3)
C(7)-C(16)	1.557(3)
C(9)-C(10)	1.384(3)
C(9)-C(14)	1.385(3)
C(10)-C(11)	1.373(3)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.382(3)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.379(3)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.390(3)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.507(3)

C(15)-C(16)	1.531(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(7)-O(2)-H(2B)	109.5
O(3)-C(17)-C(9)	129.1(2)
O(3)-C(17)-C(16)	124.1(2)
C(9)-C(17)-C(16)	106.84(18)
C(8)-N(1)-C(1)	111.94(18)
C(8)-N(1)-H(1A)	124.0
C(1)-N(1)-H(1A)	124.0
C(2)-C(1)-C(6)	121.9(2)
C(2)-C(1)-N(1)	128.8(2)
C(6)-C(1)-N(1)	109.25(19)
C(1)-C(2)-C(3)	117.8(2)
C(1)-C(2)-H(2A)	121.1
C(3)-C(2)-H(2A)	121.1
C(4)-C(3)-C(2)	120.2(2)
C(4)-C(3)-H(3A)	119.9
C(2)-C(3)-H(3A)	119.9
C(3)-C(4)-C(5)	122.0(2)
C(3)-C(4)-Cl(1)	120.00(19)
C(5)-C(4)-Cl(1)	118.00(19)
C(6)-C(5)-C(4)	117.7(2)
C(6)-C(5)-H(5A)	121.2
C(4)-C(5)-H(5A)	121.2
C(5)-C(6)-C(1)	120.3(2)
C(5)-C(6)-C(7)	131.31(19)
C(1)-C(6)-C(7)	108.38(18)
O(2)-C(7)-C(6)	112.69(17)
O(2)-C(7)-C(8)	111.74(16)
C(6)-C(7)-C(8)	101.59(16)
O(2)-C(7)-C(16)	109.94(17)
C(6)-C(7)-C(16)	110.98(16)
C(8)-C(7)-C(16)	109.65(16)
O(1)-C(8)-N(1)	126.7(2)
O(1)-C(8)-C(7)	125.50(19)

N(1)-C(8)-C(7)	107.79(17)
C(10)-C(9)-C(14)	122.1(2)
C(10)-C(9)-C(17)	128.4(2)
C(14)-C(9)-C(17)	109.4(2)
C(11)-C(10)-C(9)	118.5(2)
C(11)-C(10)-H(10A)	120.8
C(9)-C(10)-H(10A)	120.8
C(10)-C(11)-C(12)	120.0(2)
C(10)-C(11)-H(11A)	120.0
C(12)-C(11)-H(11A)	120.0
C(13)-C(12)-C(11)	121.6(2)
C(13)-C(12)-H(12A)	119.2
C(11)-C(12)-H(12A)	119.2
C(12)-C(13)-C(14)	118.9(2)
C(12)-C(13)-H(13A)	120.5
C(14)-C(13)-H(13A)	120.5
C(9)-C(14)-C(13)	118.8(2)
C(9)-C(14)-C(15)	112.30(19)
C(13)-C(14)-C(15)	128.9(2)
C(14)-C(15)-C(16)	103.63(17)
C(14)-C(15)-H(15A)	111.0
C(16)-C(15)-H(15A)	111.0
C(14)-C(15)-H(15B)	111.0
C(16)-C(15)-H(15B)	111.0
H(15A)-C(15)-H(15B)	109.0
F(1)-C(16)-C(15)	110.91(17)
F(1)-C(16)-C(17)	109.40(17)
C(15)-C(16)-C(17)	105.40(16)
F(1)-C(16)-C(7)	106.48(16)
C(15)-C(16)-C(7)	113.04(17)
C(17)-C(16)-C(7)	111.64(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	94(1)	98(1)	36(1)	-21(1)	9(1)	-22(1)
O(1)	42(1)	77(1)	26(1)	6(1)	4(1)	2(1)
O(2)	34(1)	72(1)	32(1)	9(1)	1(1)	13(1)
C(17)	40(1)	43(1)	34(1)	-4(1)	4(1)	1(1)
F(1)	62(1)	70(1)	33(1)	-10(1)	-7(1)	-11(1)
N(1)	34(1)	60(1)	32(1)	6(1)	7(1)	-3(1)
C(1)	38(1)	41(1)	34(1)	6(1)	2(1)	3(1)
C(2)	44(1)	50(1)	45(1)	3(1)	-3(1)	-7(1)
C(3)	58(2)	54(1)	43(1)	-2(1)	-10(1)	-11(1)
C(4)	59(2)	48(1)	33(1)	-4(1)	0(1)	-6(1)
C(5)	43(1)	46(1)	32(1)	0(1)	2(1)	-2(1)
C(6)	39(1)	37(1)	29(1)	4(1)	0(1)	0(1)
C(7)	31(1)	49(1)	25(1)	3(1)	0(1)	4(1)
C(8)	33(1)	50(1)	28(1)	6(1)	4(1)	6(1)
C(9)	41(1)	37(1)	33(1)	-2(1)	1(1)	3(1)
C(10)	48(1)	51(1)	44(1)	5(1)	2(1)	12(1)
C(11)	64(2)	58(2)	44(2)	8(1)	-8(1)	8(1)
C(12)	69(2)	60(1)	33(1)	5(1)	2(1)	0(1)
C(13)	48(1)	56(1)	40(1)	0(1)	10(1)	-4(1)
C(14)	43(1)	38(1)	32(1)	0(1)	1(1)	-6(1)
C(15)	36(1)	51(1)	38(1)	1(1)	0(1)	-8(1)
C(16)	37(1)	51(1)	24(1)	-4(1)	-3(1)	-4(1)
O(3)	51(1)	79(1)	44(1)	3(1)	16(1)	16(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(2B)	12557	7502	9086	69
H(1A)	6129	7203	9002	50
H(2A)	4869	6642	7398	56
H(3A)	5982	6437	5979	62
H(5A)	11411	7497	6610	48
H(10A)	6047	10082	6719	57
H(11A)	6959	10423	5304	66
H(12A)	10284	10343	4895	65
H(13A)	12734	9849	5853	58
H(15A)	13051	9768	7814	50
H(15B)	12949	8739	7408	50

Table 6.   Torsion angles [deg] for z.

C(8)-N(1)-C(1)-C(2)	176.4(2)
C(8)-N(1)-C(1)-C(6)	-1.4(2)
C(6)-C(1)-C(2)-C(3)	1.8(3)
N(1)-C(1)-C(2)-C(3)	-175.8(2)
C(1)-C(2)-C(3)-C(4)	0.3(4)
C(2)-C(3)-C(4)-C(5)	-1.7(4)
C(2)-C(3)-C(4)-Cl(1)	178.88(19)
C(3)-C(4)-C(5)-C(6)	1.1(3)
Cl(1)-C(4)-C(5)-C(6)	-179.50(16)
C(4)-C(5)-C(6)-C(1)	1.0(3)
C(4)-C(5)-C(6)-C(7)	-177.8(2)
C(2)-C(1)-C(6)-C(5)	-2.5(3)
N(1)-C(1)-C(6)-C(5)	175.55(18)
C(2)-C(1)-C(6)-C(7)	176.52(18)
N(1)-C(1)-C(6)-C(7)	-5.5(2)
C(5)-C(6)-C(7)-O(2)	-52.3(3)
C(1)-C(6)-C(7)-O(2)	128.89(17)
C(5)-C(6)-C(7)-C(8)	-172.0(2)
C(1)-C(6)-C(7)-C(8)	9.2(2)
C(5)-C(6)-C(7)-C(16)	71.5(3)
C(1)-C(6)-C(7)-C(16)	-107.32(19)
C(1)-N(1)-C(8)-O(1)	-170.8(2)
C(1)-N(1)-C(8)-C(7)	7.5(2)
O(2)-C(7)-C(8)-O(1)	48.0(3)
C(6)-C(7)-C(8)-O(1)	168.4(2)
C(16)-C(7)-C(8)-O(1)	-74.2(3)
O(2)-C(7)-C(8)-N(1)	-130.39(19)
C(6)-C(7)-C(8)-N(1)	-10.0(2)
C(16)-C(7)-C(8)-N(1)	107.45(19)
O(3)-C(17)-C(9)-C(10)	-12.6(4)
C(16)-C(17)-C(9)-C(10)	168.2(2)
O(3)-C(17)-C(9)-C(14)	168.9(2)
C(16)-C(17)-C(9)-C(14)	-10.3(2)
C(14)-C(9)-C(10)-C(11)	0.5(3)

C(17)-C(9)-C(10)-C(11)	-177.8(2)
C(9)-C(10)-C(11)-C(12)	-1.8(4)
C(10)-C(11)-C(12)-C(13)	1.8(4)
C(11)-C(12)-C(13)-C(14)	-0.3(4)
C(10)-C(9)-C(14)-C(13)	0.9(3)
C(17)-C(9)-C(14)-C(13)	179.56(19)
C(10)-C(9)-C(14)-C(15)	-177.7(2)
C(17)-C(9)-C(14)-C(15)	0.9(2)
C(12)-C(13)-C(14)-C(9)	-1.0(3)
C(12)-C(13)-C(14)-C(15)	177.4(2)
C(9)-C(14)-C(15)-C(16)	8.8(2)
C(13)-C(14)-C(15)-C(16)	-169.7(2)
C(14)-C(15)-C(16)-F(1)	-132.53(18)
C(14)-C(15)-C(16)-C(17)	-14.2(2)
C(14)-C(15)-C(16)-C(7)	107.97(19)
O(3)-C(17)-C(16)-F(1)	-44.6(3)
C(9)-C(17)-C(16)-F(1)	134.63(17)
O(3)-C(17)-C(16)-C(15)	-163.9(2)
C(9)-C(17)-C(16)-C(15)	15.3(2)
O(3)-C(17)-C(16)-C(7)	73.0(3)
C(9)-C(17)-C(16)-C(7)	-107.78(19)
O(2)-C(7)-C(16)-F(1)	-66.1(2)
C(6)-C(7)-C(16)-F(1)	168.55(16)
C(8)-C(7)-C(16)-F(1)	57.1(2)
O(2)-C(7)-C(16)-C(15)	55.9(2)
C(6)-C(7)-C(16)-C(15)	-69.4(2)
C(8)-C(7)-C(16)-C(15)	179.14(17)
O(2)-C(7)-C(16)-C(17)	174.56(16)
C(6)-C(7)-C(16)-C(17)	49.2(2)
C(8)-C(7)-C(16)-C(17)	-62.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for z [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Determination of the configuration of *syn*-12.

The configuration of product *syn*-**12** was determined by X-ray analysis.[7] The configuration of *anti*-**12** was tentatively assigned by HPLC and NMR analysis. Data intensity of this compound was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for *syn*-**12**: $C_{17}H_{14}FNO_3$, M = 299.29, T = 173(2) K, λ = 0.71073 Å, Monoclinic, space group P2(1), a = 8.1719(15) Å, b = 6.8476(12) Å, c = 12.493(2) Å, V = 693.8(2) Å^3, z = 2, d_{calc} = 1.433 mg/m^3, 8012 reflections measured, 2321 unique [R(int) = 0.1057], R_1 = 0.0627, wR_2 = 0.1003 ($I > 2\sigma(I)$), final R_1 = 0.1336, wR_2 = 0.1250 (all data), GOF = 1.050, and 199 parameters.

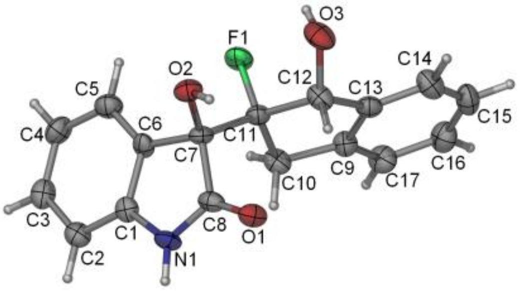


Table 1. Crystal data and structure refinement for z.

Identification code	z	
Empirical formula	C17 H14 F N O3	
Formula weight	299.29	
Temperature	173(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)	
Unit cell dimensions	a = 8.1719(15) A	alpha = 90 deg.
	b = 6.8476(12) A	beta = 97.076(7) deg.
	c = 12.493(2) A	gamma = 90 deg.
Volume	693.8(2) A^3	
Z, Calculated density	2, 1.433 Mg/m^3	
Absorption coefficient	0.107 mm^-1	
F(000)	312	

---

[7] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 999613)

Crystal size	0.28 x 0.07 x 0.05 mm
Theta range for data collection	1.64 to 24.97 deg.
Limiting indices	-9<=h<=9, -8<=k<=7, -14<=l<=14
Reflections collected / unique	8012 / 2321 [R(int) = 0.1057]
Completeness to theta = 24.97	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9946 and 0.9705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2321 / 1 / 199
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1003
R indices (all data)	R1 = 0.1336, wR2 = 0.1250
Absolute structure parameter	-0.5(19)
Largest diff. peak and hole	0.239 and -0.237 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic, displacement parameters (A^2 x 10^3) for z. U(eq) is defined as one third of the trace of the orthogonalized, Uij tensor.

	x	y	z	U(eq)
F(1)	7873(3)	8171(4)	7970(2)	34(1)
O(1)	10283(4)	11086(4)	5407(2)	29(1)
O(2)	7561(4)	8260(4)	5703(2)	30(1)
C(1)	6641(5)	12949(7)	6152(3)	24(1)
O(3)	10112(4)	5973(5)	7214(3)	42(1)
C(8)	8964(6)	11407(6)	5762(4)	26(1)
C(12)	10509(5)	7967(7)	7397(4)	30(1)
N(1)	8120(4)	13082(6)	5686(3)	28(1)
C(6)	6481(5)	11049(7)	6549(3)	26(1)
C(14)	12764(6)	7293(7)	9030(4)	36(1)
C(9)	10981(6)	10087(7)	8912(4)	28(1)
C(15)	13522(6)	7950(9)	10014(4)	39(1)
C(5)	5096(6)	10602(7)	7030(4)	33(1)
C(10)	9564(6)	10976(7)	8186(4)	30(1)
C(17)	11737(6)	10757(8)	9909(4)	35(1)
C(4)	3916(6)	12020(8)	7112(4)	36(1)

C(3)	4103(6)	13880(7)	6719(4)	32(1)
C(11)	8978(5)	9302(7)	7438(4)	25(1)
C(2)	5496(6)	14376(7)	6228(4)	30(1)
C(13)	11495(5)	8377(7)	8489(4)	28(1)
C(7)	8001(5)	9898(7)	6357(4)	25(1)
C(16)	13013(6)	9677(8)	10446(4)	38(1)

Table 3. Bond lengths [A] and angles [deg] for z.

F(1)-C(11)	1.416(5)
O(1)-C(8)	1.235(5)
O(2)-C(7)	1.408(5)
O(2)-H(2B)	0.8400
C(1)-C(2)	1.365(6)
C(1)-C(6)	1.405(7)
C(1)-N(1)	1.408(5)
O(3)-C(12)	1.416(6)
O(3)-H(3B)	0.8400
C(8)-N(1)	1.336(6)
C(8)-C(7)	1.544(6)
C(12)-C(13)	1.523(6)
C(12)-C(11)	1.556(6)
C(12)-H(12A)	1.0000
N(1)-H(1A)	0.8800
C(6)-C(5)	1.380(6)
C(6)-C(7)	1.515(6)
C(14)-C(15)	1.382(6)
C(14)-C(13)	1.382(6)
C(14)-H(14A)	0.9500
C(9)-C(13)	1.372(6)
C(9)-C(17)	1.398(6)
C(9)-C(10)	1.508(6)
C(15)-C(16)	1.385(7)
C(15)-H(15A)	0.9500
C(5)-C(4)	1.382(7)

C(5)-H(5A)	0.9500
C(10)-C(11)	1.519(6)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(17)-C(16)	1.383(6)
C(17)-H(17A)	0.9500
C(4)-C(3)	1.381(6)
C(4)-H(4A)	0.9500
C(3)-C(2)	1.399(7)
C(3)-H(3A)	0.9500
C(11)-C(7)	1.537(6)
C(2)-H(2A)	0.9500
C(16)-H(16A)	0.9500

C(7)-O(2)-H(2B)	109.5
C(2)-C(1)-C(6)	123.0(4)
C(2)-C(1)-N(1)	127.9(4)
C(6)-C(1)-N(1)	109.2(4)
C(12)-O(3)-H(3B)	109.5
O(1)-C(8)-N(1)	126.4(4)
O(1)-C(8)-C(7)	125.0(4)
N(1)-C(8)-C(7)	108.6(4)
O(3)-C(12)-C(13)	114.0(4)
O(3)-C(12)-C(11)	113.7(4)
C(13)-C(12)-C(11)	101.6(4)
O(3)-C(12)-H(12A)	109.1
C(13)-C(12)-H(12A)	109.1
C(11)-C(12)-H(12A)	109.1
C(8)-N(1)-C(1)	112.2(4)
C(8)-N(1)-H(1A)	123.9
C(1)-N(1)-H(1A)	123.9
C(5)-C(6)-C(1)	118.5(4)
C(5)-C(6)-C(7)	133.3(5)
C(1)-C(6)-C(7)	108.2(4)
C(15)-C(14)-C(13)	119.1(5)
C(15)-C(14)-H(14A)	120.4

C(13)-C(14)-H(14A)	120.4
C(13)-C(9)-C(17)	120.1(5)
C(13)-C(9)-C(10)	111.2(4)
C(17)-C(9)-C(10)	128.7(4)
C(14)-C(15)-C(16)	120.1(5)
C(14)-C(15)-H(15A)	119.9
C(16)-C(15)-H(15A)	119.9
C(6)-C(5)-C(4)	119.6(5)
C(6)-C(5)-H(5A)	120.2
C(4)-C(5)-H(5A)	120.2
C(9)-C(10)-C(11)	103.0(4)
C(9)-C(10)-H(10A)	111.2
C(11)-C(10)-H(10A)	111.2
C(9)-C(10)-H(10B)	111.2
C(11)-C(10)-H(10B)	111.2
H(10A)-C(10)-H(10B)	109.1
C(16)-C(17)-C(9)	118.7(5)
C(16)-C(17)-H(17A)	120.6
C(9)-C(17)-H(17A)	120.6
C(3)-C(4)-C(5)	120.9(5)
C(3)-C(4)-H(4A)	119.6
C(5)-C(4)-H(4A)	119.6
C(4)-C(3)-C(2)	120.8(5)
C(4)-C(3)-H(3A)	119.6
C(2)-C(3)-H(3A)	119.6
F(1)-C(11)-C(10)	107.1(4)
F(1)-C(11)-C(7)	105.4(3)
C(10)-C(11)-C(7)	115.5(4)
F(1)-C(11)-C(12)	104.9(4)
C(10)-C(11)-C(12)	105.7(4)
C(7)-C(11)-C(12)	117.4(4)
C(1)-C(2)-C(3)	117.3(5)
C(1)-C(2)-H(2A)	121.3
C(3)-C(2)-H(2A)	121.3
C(9)-C(13)-C(14)	121.1(5)
C(9)-C(13)-C(12)	110.4(4)

C(14)-C(13)-C(12)	128.4(4)
O(2)-C(7)-C(6)	110.5(4)
O(2)-C(7)-C(11)	111.5(4)
C(6)-C(7)-C(11)	110.3(4)
O(2)-C(7)-C(8)	111.3(4)
C(6)-C(7)-C(8)	101.8(4)
C(11)-C(7)-C(8)	111.1(4)
C(17)-C(16)-C(15)	120.8(5)
C(17)-C(16)-H(16A)	119.6
C(15)-C(16)-H(16A)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	40(2)	36(2)	28(2)	12(2)	10(1)	-2(2)
O(1)	37(2)	26(2)	27(2)	-1(2)	14(2)	1(2)
O(2)	38(2)	27(2)	26(2)	-5(2)	8(1)	-6(2)
C(1)	30(3)	31(3)	12(3)	-4(2)	3(2)	2(3)
O(3)	60(2)	27(2)	36(2)	-5(2)	0(2)	7(2)
C(8)	39(3)	22(3)	18(3)	1(2)	2(2)	-3(2)
C(12)	41(3)	28(3)	19(3)	-5(2)	2(2)	5(3)
N(1)	37(2)	22(2)	26(2)	7(2)	10(2)	0(2)
C(6)	26(2)	33(3)	19(3)	7(3)	3(2)	3(2)
C(14)	42(3)	39(3)	28(3)	1(3)	10(3)	11(3)
C(9)	31(3)	32(3)	23(3)	-3(2)	4(2)	1(2)
C(15)	31(3)	52(4)	33(4)	10(3)	3(2)	7(3)
C(5)	39(3)	33(3)	28(3)	4(2)	7(2)	-4(2)
C(10)	42(3)	28(3)	22(3)	-5(2)	4(2)	3(3)
C(17)	44(3)	37(3)	25(3)	-7(3)	0(2)	-2(3)
C(4)	28(3)	46(3)	35(3)	-2(3)	11(2)	-5(3)
C(3)	31(3)	42(3)	24(3)	-11(3)	4(2)	4(2)

C(11)	28(3)	24(3)	25(3)	2(2)	7(2)	-3(2)
C(2)	38(3)	28(3)	25(3)	-4(2)	4(2)	1(2)
C(13)	33(3)	27(3)	25(3)	2(2)	9(2)	-3(2)
C(7)	29(3)	19(2)	27(3)	0(2)	6(2)	-4(2)
C(16)	37(3)	51(4)	26(3)	-2(3)	0(2)	-1(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(2B)	8315	8016	5323	36
H(3B)	9429	5622	7627	50
H(12A)	11147	8443	6814	35
H(1A)	8450	14145	5379	33
H(14A)	13112	6112	8728	43
H(15A)	14393	7216	10394	47
H(5A)	4955	9326	7303	40
H(10A)	9936	12096	7777	37
H(10B)	8681	11417	8606	37
H(17A)	11381	11933	10212	43
H(4A)	2963	11711	7444	43
H(3A)	3277	14835	6782	39
H(2A)	5638	15655	5959	37
H(16A)	13547	10125	11120	46

Table 6. Torsion angles [deg] for z.

O(1)-C(8)-N(1)-C(1)	178.5(4)
C(7)-C(8)-N(1)-C(1)	-0.5(5)
C(2)-C(1)-N(1)-C(8)	179.2(5)
C(6)-C(1)-N(1)-C(8)	-1.0(5)
C(2)-C(1)-C(6)-C(5)	0.5(7)
N(1)-C(1)-C(6)-C(5)	-179.3(4)
C(2)-C(1)-C(6)-C(7)	-178.1(4)

N(1)-C(1)-C(6)-C(7)	2.1(5)
C(13)-C(14)-C(15)-C(16)	-0.2(7)
C(1)-C(6)-C(5)-C(4)	-0.2(7)
C(7)-C(6)-C(5)-C(4)	178.0(5)
C(13)-C(9)-C(10)-C(11)	15.5(5)
C(17)-C(9)-C(10)-C(11)	-162.8(5)
C(13)-C(9)-C(17)-C(16)	0.7(7)
C(10)-C(9)-C(17)-C(16)	178.9(5)
C(6)-C(5)-C(4)-C(3)	0.0(7)
C(5)-C(4)-C(3)-C(2)	-0.1(8)
C(9)-C(10)-C(11)-F(1)	84.9(4)
C(9)-C(10)-C(11)-C(7)	-158.0(4)
C(9)-C(10)-C(11)-C(12)	-26.5(5)
O(3)-C(12)-C(11)-F(1)	37.5(5)
C(13)-C(12)-C(11)-F(1)	-85.5(4)
O(3)-C(12)-C(11)-C(10)	150.5(4)
C(13)-C(12)-C(11)-C(10)	27.5(5)
O(3)-C(12)-C(11)-C(7)	-79.1(5)
C(13)-C(12)-C(11)-C(7)	157.9(4)
C(6)-C(1)-C(2)-C(3)	-0.6(7)
N(1)-C(1)-C(2)-C(3)	179.2(4)
C(4)-C(3)-C(2)-C(1)	0.4(7)
C(17)-C(9)-C(13)-C(14)	-0.4(7)
C(10)-C(9)-C(13)-C(14)	-178.9(4)
C(17)-C(9)-C(13)-C(12)	-179.2(4)
C(10)-C(9)-C(13)-C(12)	2.3(5)
C(15)-C(14)-C(13)-C(9)	0.1(7)
C(15)-C(14)-C(13)-C(12)	178.7(4)
O(3)-C(12)-C(13)-C(9)	-141.4(4)
C(11)-C(12)-C(13)-C(9)	-18.6(5)
O(3)-C(12)-C(13)-C(14)	39.9(7)
C(11)-C(12)-C(13)-C(14)	162.7(5)
C(5)-C(6)-C(7)-O(2)	61.1(7)
C(1)-C(6)-C(7)-O(2)	-120.5(4)
C(5)-C(6)-C(7)-C(11)	-62.6(7)
C(1)-C(6)-C(7)-C(11)	115.8(4)

C(5)-C(6)-C(7)-C(8)	179.4(5)
C(1)-C(6)-C(7)-C(8)	-2.3(5)
F(1)-C(11)-C(7)-O(2)	-64.1(4)
C(10)-C(11)-C(7)-O(2)	177.9(4)
C(12)-C(11)-C(7)-O(2)	52.2(5)
F(1)-C(11)-C(7)-C(6)	59.1(4)
C(10)-C(11)-C(7)-C(6)	-59.0(5)
C(12)-C(11)-C(7)-C(6)	175.3(4)
F(1)-C(11)-C(7)-C(8)	171.2(3)
C(10)-C(11)-C(7)-C(8)	53.2(5)
C(12)-C(11)-C(7)-C(8)	-72.5(5)
O(1)-C(8)-C(7)-O(2)	-59.6(6)
N(1)-C(8)-C(7)-O(2)	119.4(4)
O(1)-C(8)-C(7)-C(6)	-177.4(4)
N(1)-C(8)-C(7)-C(6)	1.7(5)
O(1)-C(8)-C(7)-C(11)	65.2(6)
N(1)-C(8)-C(7)-C(11)	-115.7(4)
C(9)-C(17)-C(16)-C(15)	-0.8(7)
C(14)-C(15)-C(16)-C(17)	0.6(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for z [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)