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A Highly Efficient and Practical Method for Catalytic Asymmetric Vinylogous Mannich (AVM) Reactions

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General. Infared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry was preformed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College and at the University of Illinois Mass Spectrometry Laboratories (Urbana, Illinois). Elemental microanalyses were performed at Robertson Microlit Laboratories (Madison, NJ). Enantiomeric ratios were determined by chiral HPLC analysis (Chiral Technologies Chiralcel OD column, 25 cm x 0.46 cm) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out under an air atmosphere using reagent grade solvents. Reagent grade THF containing 250 ppm BHT, was purchased from Aldrich and used without purification. Fisherbrand HPLC grade 2-propanol was used without further purification. CH_2Cl_2 and Et_2O were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system; CH_2Cl_2 and Et_2O were purged with Ar and purified by being passed through two alumina columns. All work-up and purification procedures were carried out with reagent solvents in air. All solvents were purchased from Doe and Ingalls. 2-(Trimethylsilyloxy)furan and AgOAc were purchased from Aldrich and used as received. $PhI(OAc)_2$ was purchased from Acros and used as received. 4-Methyl-2-(trimethylsilyloxy)furan and 3-methyl-2-(trimethylsilyloxy)furan were prepared from the respective furanones (purchased from TCI America and Aldrich) by established methods.[1] EDC•HCl, HOBt•H_2O, Boc-protected amino acids, *p*-anisidine, and 2-(diphenylphosphino)benzaldehyde were purchased from commercial sources (Advanced Chemtech, Nova Biochem, Aldrich) and used without purification. Unless otherwise stated, substrates were synthesized from commercially available starting materials through previously reported protocols.

Representative experimental procedure for the synthesis of phosphine amino acid-based ligands. Boc-L-Ile-OH (4.98 g, 20.0 mmol) was dissolved in 100 mL of CH_2Cl_2, and HOBt•H_2O (3.37 g, 22.0 mmol), EDC•HCl (4.22 g, 22.0 mmol) and *p*-anisidine (7.39 g, 60.0 mmol) were added successively at 22 °C. The resulting solution was allowed to stir at 22 °C for 4 h. Citric acid (50 mL of a 10 wt. % aqueous solution) was added and the two layers separated. The

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[1] G. Casiraghi, G. Rassu, *Synthesis* **1995**, 607–626.

aqueous layer was washed twice with 50 mL of CH_2Cl_2 and the combined organic layers were washed with 50 mL 10 wt. % aqueous citric acid and 50 mL of saturated aqueous $NaHCO_3$, followed by 50 mL of a saturated solution of NaCl. The organic layer was dried over $MgSO_4$ before removal of the volatiles in vacuo to afford a light brown solid (5.60 g, 16.8 mmol, 84% yield). Trifluoroacetic acid was added drop-wise to the solid (0.900 g, 2.69 mmol) until complete dissolution was achieved. The resulting solution was allowed to stir for 45 min. H_2O (10 mL) and CH_2Cl_2 (10 mL) were added and the solution cooled to 0 °C. NaOH (1.0 N solution) was added drop-wise until pH = >10 is achieved, after which the aqueous solution was washed with EtOAc (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the free amine as red oil (0.57 g, 2.5 mmol, 91% yield). The amine was dissolved in CH_2Cl_2 (20 mL), followed by the addition of 2-(diphenylphosphino)benzaldehyde (0.71 mg, 2.5 mmol) and $MgSO_4$. The resulting solution was allowed to stir for 16 h at 22 °C, after which $MgSO_4$ was removed by filtration and the organic filtrate was concentrated *in vacuo* to afford a light brown oil that was purified by silica gel column chromatography (4:1 hexanes:EtOAc) to deliver 808 mg (1.60 mmol, 65% yield) of **1a** as a light yellow solid.

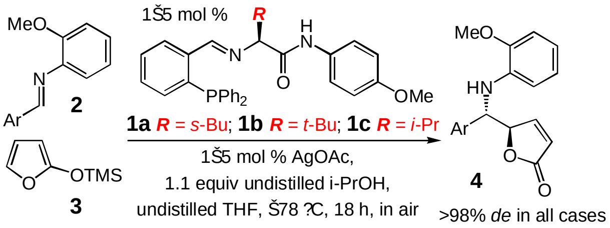
(*S,S*)-(+)-2-[2-(Diphenylphosphinobenzylidene)-amino]-3-methylpentanoic acid (4-methyoxyphenyl)-amide (1a). mp = 120 °C. IR (neat): 3263 (b), 2967 (m), 1690 (s), 1514 (s), 1476 (m), 1444 (m), 1306 (m), 1243 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.57 (1H, d, *J* = 5.6 Hz), 8.40 (1H, d, *J* = 2.8 Hz), 7.74-7.66 (3H, m), 7.47 (1H, td, *J* = 7.2, 1.2 Hz), 7.37-7.23 (9H, m), 7.17-7.13 (2H, m), 6.91 (1H, dd, *J* = 7.6, 4.4 Hz), 6.84 (2H, dt, *J* = 8.8, 2.0 Hz), 3.77 (3H, s), 3.72 (1H, dd, *J* = 4.0, 1.6 Hz), 1.92-1.87 (1H, m), 1.11-1.05 (1H, m), 0.64 (3H, d, *J* = 6.8 Hz), 0.56 (3H, t, *J* = 7.6 Hz), 0.30-0.22 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 162.4, 156.3, 138.6, 138.4, 138.1, 137.9, 137.1, 136.9, 136.8, 135.0, 134.8, 133.3, 133.1, 132.4, 132.0, 130.7, 129.3, 129.0, 129.0, 128.9, 128.7, 128.7, 128.6, 121.5, 121.4, 114.2, 81.3, 55.7, 39.6, 23.8, 15.9, 12.0. Anal Calcd for $C_{32}H_{33}N_2O_2P$: C, 75.57%; H, 6.54%; N, 5.51%; Found C, 75.81%; H, 6.29%; N, 5.41%. Optical rotation: $[\alpha]_D^{20}$ +127.2 (*c* = 1.470, $CHCl_3$).

(*S*)-(+)-2-[2-Diphenylphosphinobenzylidene)-amino]-N-(4-methoxyphenyl)-3,3-dimethyl-butyramide (1b). 1b was obtained as a white solid. mp = 150-151 °C. IR (neat): 3269 (b), 2955 (m), 1683 (s), 1520 (s), 1476 (m), 1444 (m), 1306 (m), 1255 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.23 (1H, d, *J* = 4.4 Hz), 8.43 (1H, d, *J* = 2.8 Hz), 7.73 (1H, ddd, *J* = 7.6, 3.6, 1.2 Hz), 7.58 (2H, dt, *J* = 6.8, 2.0 Hz), 7.46 (1H, td, *J* = 7.2, 1.2 Hz), 7.36-7.24 (9H, m), 7.18-7.14 (2H, m), 6.91 (1H, dd, *J* = 7.6, 4.4 Hz), 6.83 (2H, dt, *J* = 8.8, 2.0 Hz), 3.77 (3H, s), 3.52 (1H, d, *J* = 1.6 Hz), 0.72 (9H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 162.3, 162.2, 156.2, 138.8, 138.6, 137.9, 137.1, 136.8, 135.1, 134.9, 134.8, 133.4, 133.2, 132.3, 131.8, 130.8, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 121.8, 121.7, 113.2, 85.9, 55.7, 35.6, 27.2. Anal Calcd for $C_{32}H_{33}N_2O_2P$: C, 75.57%; H, 6.54%; N, 5.51%; Found C, 75.55%; H, 6.29%; N, 5.38%. Optical rotation: $[\alpha]_D^{20}$ +123.4 (*c* = 0.4700, $CHCl_3$).

(*S*)-(+)-2-[2-Diphenylphosphinobenzylidene)-amino]-N-(4-methoxyphenyl)-3-methyl-butyramide (1c). 1c was obtained as a yellow solid. mp = 118-119 °C. IR (neat): 3263 (b), 2955 (m), 1683 (s), 1526 (s), 1432 (m), 1249 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.45 (1H, d, *J* = 4.4 Hz), 8.42 (1H, d, *J* = 2.8 Hz), 7.74 (1H, dd, *J* = 6.8, 3.6 Hz), 7.62 (2H, dt, *J* = 6.8, 2.0 Hz), 7.47 (1H, td, *J* = 7.6, 1.2 Hz), 7.36-7.22 (9H, m), 7.18-7.13 (2H, m), 6.93 (1H, ddd, *J* = 7.6, 4.4, 1.2 Hz), 6.84 (2H, dt, *J* = 8.8, 1.6 Hz), 3.73 (3H, s), 3.67 (1H, dd, *J* = 4.4, 1.6 Hz), 2.20-2.16 (1H, m), 0.69 (3H, d, *J* = 6.8 Hz), 0.37 (3H, d, *J* = 6.8 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 170.4, 162.5, 162.4, 156.3, 138.4, 135.0, 134.9, 134.7, 133.4, 133.2, 132.3, 132.2, 131.9, 130.7, 129.3, 129.0, 128.9, 128.8, 128.8, 128.7, 121.7, 121.6, 114.2, 81.5, 55.7, 32.9, 19.5, 16.9. Anal Calcd for $C_{31}H_{31}N_2O_2P$: C, 75.28%; H, 6.32%; N, 5.66%; Found C, 75.27%; H, 6.12%; N, 5.56%. Optical rotation: $[\alpha]_D^{20}$ +152.4 (*c* = 0.5000, CHCl$_3$).

(*S,R*)-(+)-3-*tert*-Butoxy-2-[(2-diphenylphosphinobenzylidene)amino]-N-(4-methoxyphenyl)-butyramide (1d). 1d was obtained as a light yellow solid. mp = 68-70 °C. IR (neat): 3288 (b), 2974 (m), 1677 (s), 1514 (s), 1469 (m), 1438 (m), 1255 (s), 1193 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.00 (1H, bs), 8.64 (1H, d, *J* = 4.0 Hz), 7.91 (1H, ddd, *J* = 7.6, 4.0, 1.2 Hz), 7.53 (2H, dt, *J* = 8.8, 2.0 Hz), 7.44 (1H, td, *J* = 7.6, 1.2 Hz), 7.34-7.22 (11H, m), 6.94 (1H, ddd, *J* = 7.6, 4.4, 0.8 Hz), 6.83 (2H, dt, *J* = 8.8, 2.0 Hz), 3.91 (1H, dd, *J* = 6.4, 4.4 Hz), 3.77 (3H, s), 3.70 (1H, d, *J* = 4.0 Hz), 0.99 (9H, s), 0.90 (3H, d, *J* = 6.0 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.3, 162.9, 162.8, 156.2, 138.6, 138.0, 137.2, 136.4, 134.5, 134.3, 134.2, 134.0, 131.7, 130.8, 130.1, 129.1, 129.1, 129.0, 128.9, 128.8, 128.7, 121.5, 114.2, 81.7, 74.1, 69.3, 55.7, 28.8, 20.3. Anal Calcd for $C_{34}H_{37}N_2O_3P$: C, 73.89%; H, 6.75%; N, 5.07%; Found C, 73.66%; H, 6.79%; N, 4.82%. Optical rotation: $[\alpha]_D^{20}$ +35.5 (*c* = 0.670, CHCl$_3$).

Table 1: Ag-Catalyzed AVM with Siloxyfuran **3**.



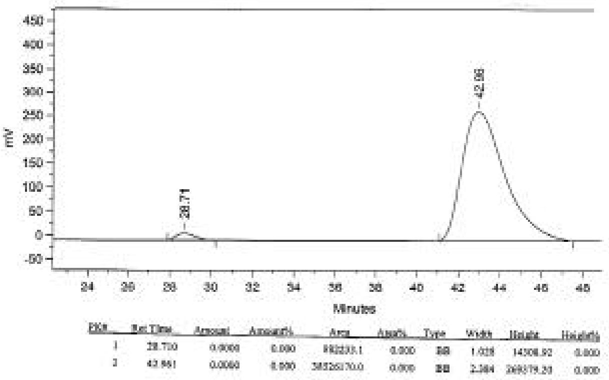
Ar		ligand (mol %)	Conv. [%][a]	Yield [%][b]	*ee* [%][b]
Ph	**a**	**1a**, 1	91	82	95
Ph	**a**	**1b**, 1	94	82	96
Ph	**a**	**1c**, 1	85	77	92
p-OMeC$_6$H$_4$	**b**	**1a**, 1	85	76	93
p-OMeC$_6$H$_4$	**b**	**1b**, 1	90	85	97
p-NO$_2$C$_6$H$_4$	**c**	**1a**, 1	>98	98	91
p-NO$_2$C$_6$H$_4$	**c**	**1b,** 1	>98	96	96
p-ClC$_6$H$_4$	**d**	**1a**, 1	94	89	93
p-ClC$_6$H$_4$	**d**	**1b**, 1	96	91	96
p-ClC$_6$H$_4$	**d**	**1c**, 1	98	86	92
m-NO$_2$C$_6$H$_4$	**e**	**1a**, 1	94	75	93
m-NO$_2$C$_6$H$_4$	**e**	**1b**, 1	93	76	94
2-napth	**f**	**1a**, 1	96	94	98
2-napth	**f**	**1b**, 1	>98	94	>98
o-MeC$_6$H$_4$	**g**	**1a**, 5	86	73	93
o-MeC$_6$H$_4$	**g**	**1b**, 5	73	65	94
o-BrC$_6$H$_4$	**h**	**1a**, 3	89	60	93
o-BrC$_6$H$_4$	**h**	**1b**, 3	98	62	95
2-furyl	**i**	**1a**, 1	98	77	84
2-furyl	**i**	**1b**, 1	98	78	90

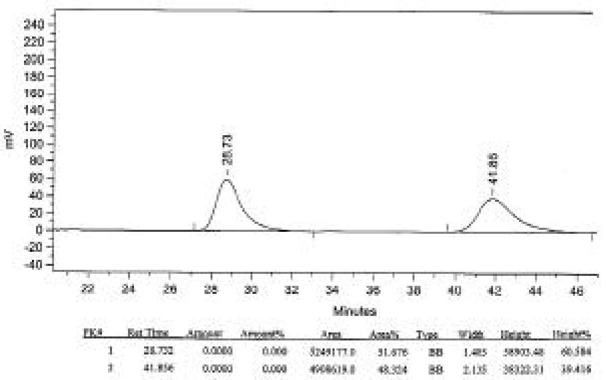
[a]Conversions determined by 400 MHz ^{1}H NMR analysis. [b]Isolated yields of purified products. [c]Determined by chiral HPLC analysis (see SI for details).

Representative experimental procedure for Ag-catalyzed asymmetric vinylogous Mannich reaction with 2-(trimethylsilyloxy)furans. Chiral phosphine **1a** (2.0 mg, 0.0040 mmol) and AgOAc (0.7 mg, 0.004 mmol) were weighed into a 13x100 mm test tube. The contents were dissolved in THF (0.5 ml) and allowed to stir for 5 min at 22 °C. A solution of imine **2a** (84 mg, 0.40 mmol) in THF (1.5 mL) was added followed by addition of *i*-PrOH (34 µL, 0.44 mmol) and the test tube capped with a septum. The mixture was allowed to cool to –78 °C before the addition of trimethylsiloxyfuran **3** (74 µL, 0.44 mmol), and allowed to stir at –78 °C for 18 h. At this time, the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (0.4 mL). The mixture was allowed to warm to 22 °C with vigorous stirring for 10 min. The mixture was filtered through silica gel and washed with 1:1 hexanes:Et_2O (50 mL) followed by 95:5 CH_2Cl_2:MeOH (50 mL). The filtrate was concentrated to afford a yellow solid that was purified by silica gel column chromatography (7:3 hexanes:Et_2O) to deliver 97 mg (0.33 mmol, 82% yield) of **4a** as a white solid.

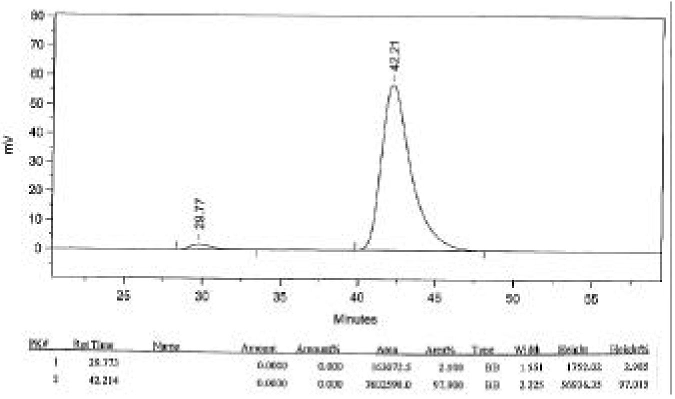
(*R*)-(+)-5-[(*S*)-(2-Methoxyphenyl)amino]-phenylmethyl]furan-2(5*H*)-one (4a) (Table 1, entry 1). mp = 141-143 °C. IR (neat): 3420 (b), 1753 (s), 1602 (m), 1513 (s), 1457 (m), 1350 (m), 1243 (s), 1224 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (1H, dd, *J* = 5.6, 1.6 Hz), 7.32-7.25 (5H, m), 6.75 (1H, dd, *J* = 7.2, 1.6 Hz), 6.72-6.63 (2H, m), 6.37 (1H, dd, *J* = 7.2, 1.6 Hz), 6.08 (1H, dd, *J* = 5.6, 2.0 Hz), 5.44 (1H, ddd, *J* = 4.0, 1.6, 1.6 Hz), 4.90 (1H, bs), 4.83 (1H, d, *J* = 4.4 Hz), 3.86 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.5, 153.3, 147.3, 137.4, 136.2, 129.0, 128.5, 127.4, 123.4, 121.2, 117.9, 111.5, 109.8, 85.7, 59.5, 55.8. Anal Calcd for $C_{18}H_{17}NO_3$: C, 73.20%; H, 5.80%; N, 4.74%; Found C, 72.98%; H, 5.46%; N, 4.59%. Optical rotation: $[\alpha]_D^{20}$ +101.8 (*c* = 1.000, CHCl$_3$) for a 95% ee sample.

Optical purity of **4a** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R$_t$(minor) = 28.71 min, R$_t$(major) = 42.96 min).

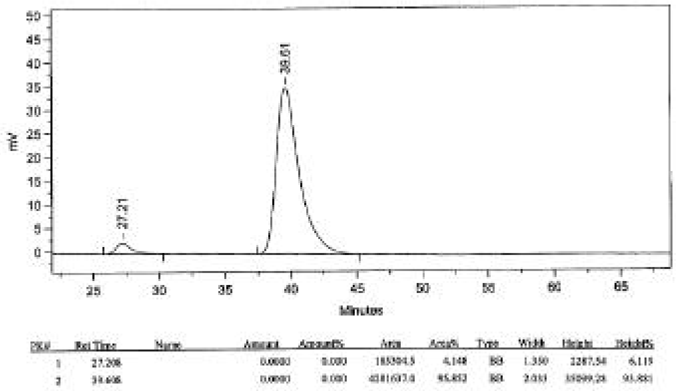




(*R*)-(+)-5-[(*S*)-(2-Methoxyphenyl)amino]-phenylmethyl]furan-2(5*H*)-one (4a) (Table 1, entry 2). Optical purity of **4a** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R$_t$(minor) = 29.77 min, R$_t$(major) = 42.21 min), 96% ee.

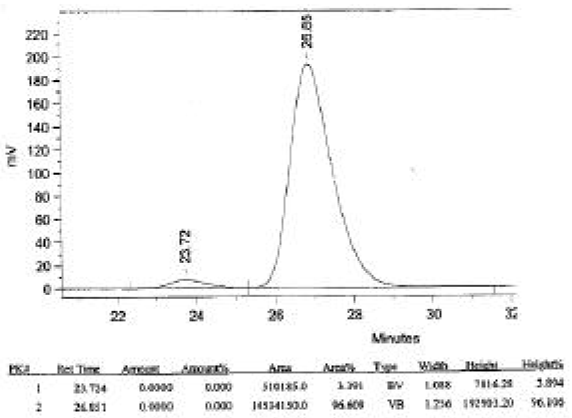


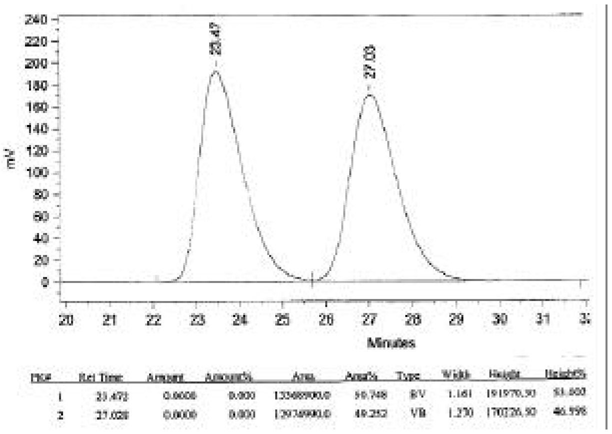
(*R*)-(+)-5-[(*S*)-(2-Methoxyphenyl)amino]-phenylmethyl]furan-2(5*H*)-one (4a) (Table 1, entry 3). Optical purity of **4a** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 27.21 min, R_t(major) = 39.61 min), 92% ee.



(*R*)-(+)-5-[(*S*)-(4-Methoxyphenyl)-(2-methoxyphenylamino)methyl]furan-2(5*H*)-one (4b) (Table 1, entry 4). 4b was obtained as a white solid. mp = 112-114 °C. IR (neat): 3427 (b), 1759 (s), 1602 (m), 1514 (s), 1451 (m), 1243 (s), 1218 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (1H, dd, *J* = 5.6, 1.6 Hz), 7.22 (2H, ddd, *J* = 9.6, 2.8, 2.8 Hz), 6.82 (2H, ddd, J = 9.6, 2.8, 2.8 Hz), 6.75 (1H, dd, *J* = 7.6, 1.6 Hz), 6.72-6.63 (2H, m), 6.38 (1H, dd, *J* = 7.6, 1.6 Hz), 6.06 (1H, dd, *J* = 5.6, 2.0 Hz), 5.41 (1H, ddd, *J* = 4.0, 2.0, 2.0 Hz), 4.70 (1H, bs), 4.78 (1H, d, *J* = 4.4 Hz), 3.84 (3H, s), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.6, 159.6, 153.4, 147.3, 136.2, 129.1, 128.5, 123.4, 121.2, 117.9, 114.4, 111.6, 109.8, 85.8, 59.0, 55.7, 55.4. Anal Calcd for $C_{19}H_{19}NO_4$: C, 70.14%; H, 5.89%; N, 4.31%; Found C, 70.28%; H, 5.79%; N, 4.17%. Optical rotation: $[\alpha]_D^{20}$ +131.6 (*c* = 1.000, $CHCl_3$) for a 93% ee sample.

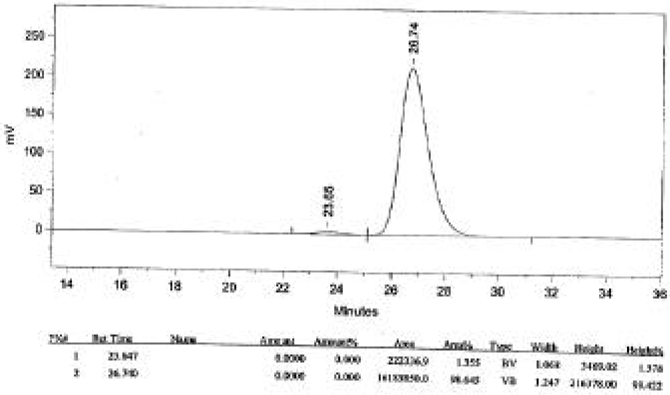
Optical purity of **4b** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 23.72 min, R_t(major) = 26.85 min).





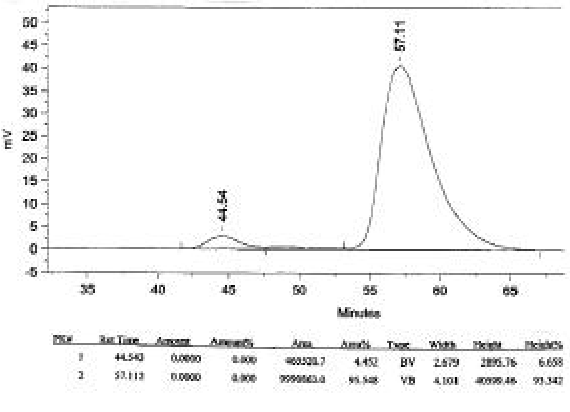
(*R*)-(+)-5-[(*S*)-(4-Methoxyphenyl)-(2-methoxyphenylamino)methyl]furan-2(5*H*)-one (4b) (Table 1, entry 5). Optical purity of **4b** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 23.65

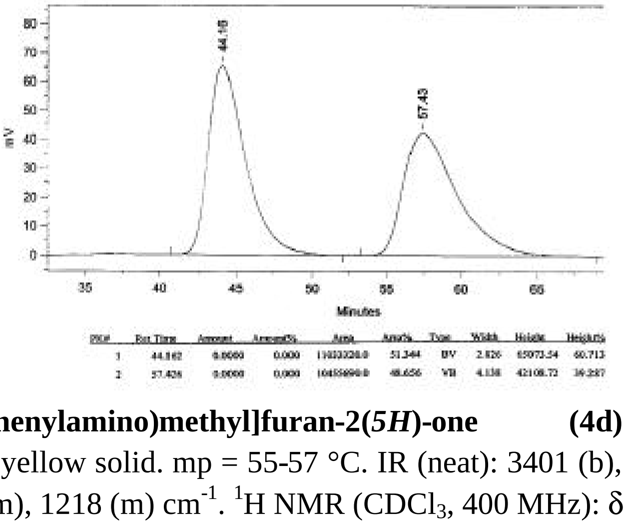
min, R$_t$(major) = 26.74 min), 97% ee.



(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)-(4-nitrophenyl)methyl]furan-2(*5H*)-one (4c) (Table 1, entry 6). 4c was obtained as a yellow solid. mp = 62-65 °C. IR (neat): 3402 (b), 1759 (s), 1602 (m), 1514 (s), 1463 (m), 1350 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.15 (2H, ddd, *J* = 8.8, 2.4, 2.4 Hz), 7.49 (2H, ddd, *J* = 8.8, 2.4, 2.4), 7.42 (1H, dd, *J* = 5.6, 1.6 Hz), 6.79-6.77 (1H, m), 6.71-6.67 (2H, m), 6.29-6.27 (1H, m), 6.10 (1H, dd, *J* = 5.6, 1.6 Hz), 5.48 (1H, ddd, *J* = 4.0, 2.0, 2.0 Hz), 5.15 (1H, bs), 4.90 (1H, d, *J* = 4.0 Hz), 3.88 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.8, 152.6, 148.1, 147.3, 144.8, 135.3, 128.6, 124.1, 123.9, 121.2, 118.8, 111.5, 110.1, 84.7, 59.4, 55.8. Anal Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52%; H, 4.74%; N, 8.23%; Found C, 63.37%; H, 4.92%; N, 7.97%. Optical rotation: $[\alpha]_D^{20}$ +102.2 (*c* = 1.000, CHCl$_3$) for a 91% ee sample.

Optical purity of **4c** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R$_t$(minor) = 44.54 min, R$_t$(major) = 57.11 min).

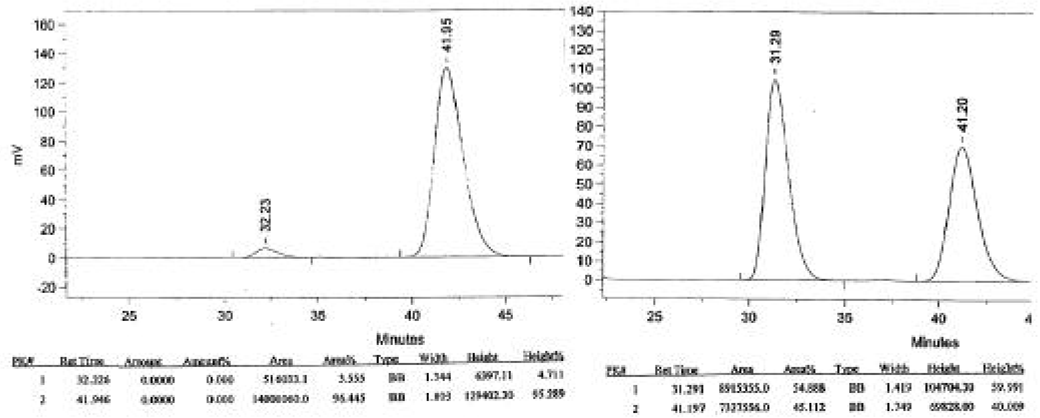




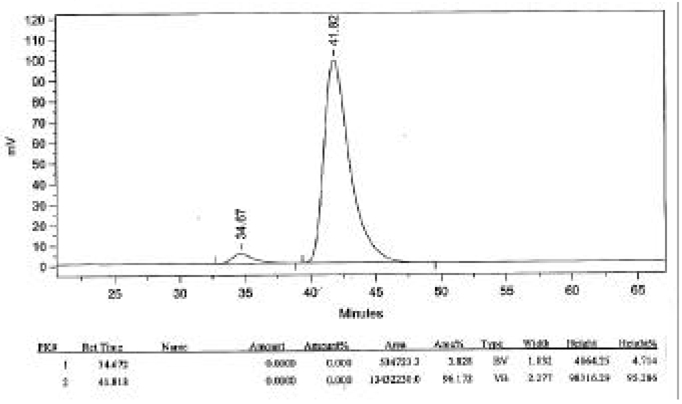
(*R*)-(+)-5-[(*S*)-(4-Chlorophenyl)-2-methoxyphenylamino)methyl]furan-2(*5H*)-one (4d) (Table 1, entry 7). 4d was obtained as a light yellow solid. mp = 55-57 °C. IR (neat): 3401 (b), 1759 (s), 1602 (m), 1514 (s), 1451 (m), 1243 (m), 1218 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.37 (1H, dd, *J* = 5.6, 1.6 Hz), 7.29-7.23 (4H, m), 6.76 (1H, dd, *J* = 7.2, 2.0 Hz), 6.71-6.65 (2H, m), 6.31 (1H, dd, *J* = 7.2, 1.6 Hz), 6.09 (1H, dd, *J* = 6.0, 2.0 Hz), 5.42 (1H, ddd, *J* = 4.0, 2.0, 2.0 Hz), 4.89 (1H, bs), 4.78 (1H, d, *J* = 4.0 Hz), 3.86 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.2, 152.9, 147.3, 135.8, 134.3, 129.2, 128.8, 123.7, 121.2, 118.3, 111.6, 109.9, 85.3, 59.1, 55.8. Anal

Calcd for $C_{18}H_{16}ClNO_3$: C, 65.56%; H, 4.89%; N, 4.25%; Found C, 65.69%; H, 4.90%; N, 4.06%. Optical rotation: $[\alpha]_D^{20}$ +102.4 (*c* = 1.000, $CHCl_3$) for a 93% ee sample.

Optical purity of **4d** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 32.23 min, R_t(major) = 41.95 min).



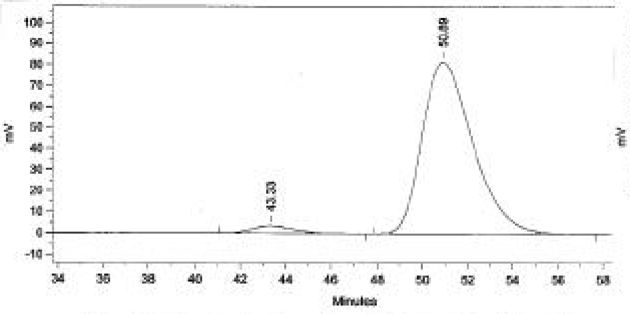
(*R*)-(+)-5-[(*S*)-(4-Chlorophenyl)-2-methoxyphenylamino)methyl]furan-2(*5H*)-one (4d) (Table 1, entry 8). Optical purity of **4d** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 34.67 min, R_t(major) = 41.82 min), 92% ee.



(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)-(3-nitrophenyl)methyl]furan-2(*5H*)-one (4e) (Table 1, entry 9). 4e was obtained as a yellow solid. mp = 154-155 °C. IR (neat): 3408 (b), 1759 (s), 1602 (m), 1526 (s), 1457 (m), 1350 (m), 1249 (m) 1218 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.17 (1H, t, *J* = 2.0 Hz), 8.12 (1H, ddd, *J* = 8.4, 2.0, 0.8 Hz), 7.68 (1H, d, *J* = 8.0 Hz), 7.49 (1H, t, *J* = 8.0 Hz), 7.46 (1H, dd, *J* = 5.6, 2.0 Hz), 6.79-6.77 (1H, m), 6.72-6.67 (2H, m), 6.34-6.31 (1H, m), 6.11 (1H, dd, *J* = 5.6, 2.0 Hz), 5.48 (1H, ddd, *J* = 4.4, 2.0, 2.0 Hz), 5.07 (1H, bs), 4.90 (1H, d, *J* = 4.4 Hz), 3.89 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.9, 152.8, 148.6, 147.4, 139.8, 135.3, 133.7, 130.1, 123.9, 123.6, 122.6, 121.2, 118.8, 111.6, 110.1, 84.8, 59.4, 55.8. Anal

Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52%; H, 4.74%; N, 8.23%; Found C, 63.59%; H, 4.91%; N, 8.03%. Optical rotation: $[\alpha]_D^{20}$ +56.2 (*c* = 1.00, $CHCl_3$) for a 93% ee sample.

Optical purity of **4e** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 43.33 min, R_t(major) = 50.89 min).



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1	43.333	0.0000	0.000	429304.8	3.275	BB	2.015	3483.01	4.094
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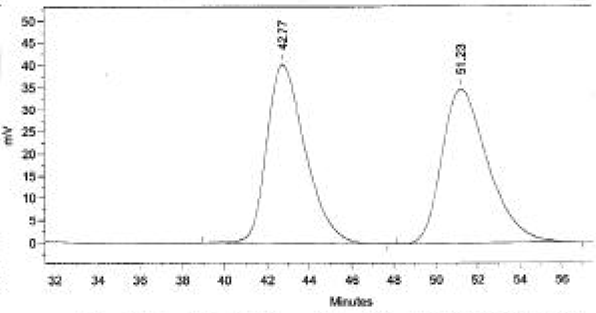
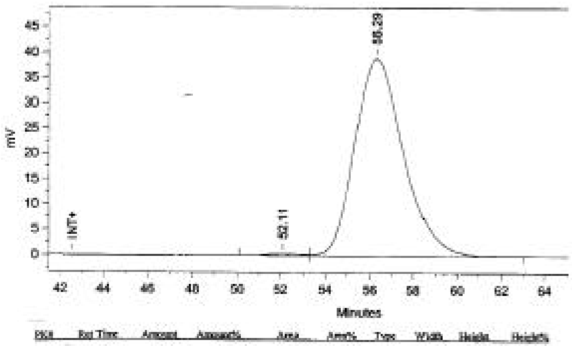


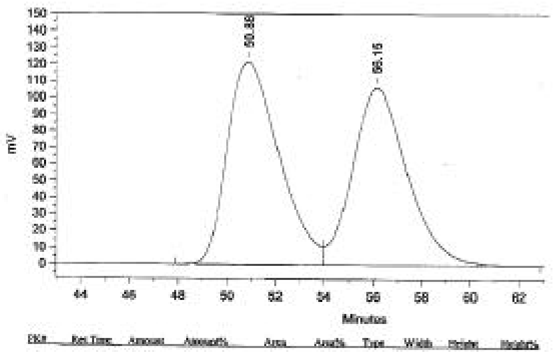
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	42.772	0.0000	0.000	5129052.0	49.170	BB	2.120	40309.42	53.745
2	51.226	0.0000	0.000	5301159.0	50.830	BB	2.347	34682.33	46.255

(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)naphthalene-2-yl-methyl]furan-2(*5H*)-one (4f) (Table 1, entry 10). 4f was obtained as a white solid. mp = 75-78 °C. IR (neat): 3415 (b), 1753 (s), 1602 (m), 1507 (s), 1457 (m), 1243 (m), 1218 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.78 (4H, m), 7.49-7.43 (3H, m), 7.41 (1H, dd, *J* = 5.6, 1.6 Hz), 6.77-6.75 (1H, m), 6.68-6.63 (2H, m), 6.41-6.39 (1H, m), 6.08 (1H, dd, *J* = 5.6, 2.0 Hz), 5.54 (1H, ddd, *J* = 4.0, 2.0, 2.0 Hz), 5.10 (1H, bs), 5.00 (1H, d, *J* = 4.0 Hz), 3.88 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.5, 153.2, 147.3, 136.3, 134.9, 133.5, 133.4, 129.0, 128.2, 127.9, 126.6, 126.5, 124.9, 123.5, 121.2, 118.1, 111.7, 109.8, 85.7, 59.8, 55.8. Anal Calcd for $C_{22}H_{19}NO_3$: C, 76.50%; H, 5.54%; N, 4.06%; Found C, 76.50%; H, 5.45%; N, 3.97%. Optical rotation: $[\alpha]_D^{20}$ +131.6 (*c* = 1.000, $CHCl_3$) for a 98% ee sample.

Optical purity of **4f** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 52.11 min, R_t(major) = 56.29 min).



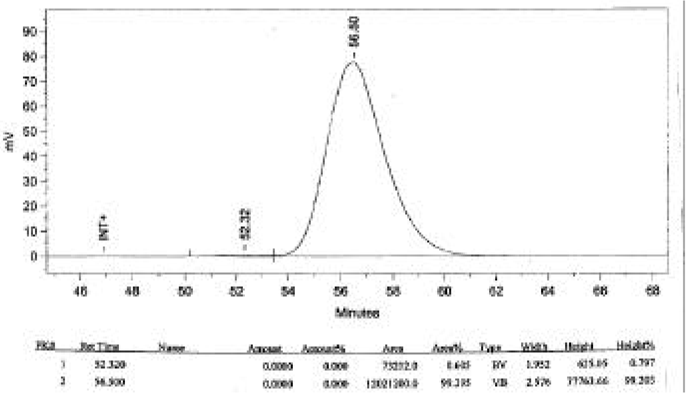
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	52.110	0.0000	0.000	41852.8	0.697	BV	1.944	358.89	0.913
2	56.287	0.0000	0.000	5964899.0	99.303	VB	2.553	38947.35	99.087



PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	50.880	0.0000	0.000	18051540.0	52.156	BV	2.467	121947.60	53.410
2	56.150	0.0000	0.000	16559430.0	47.844	VB	2.594	106375.40	46.590

(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)naphthalene-2-yl-methyl]furan-2(*5H*)-one (4f) (Table 1, entry 11). Optical purity of **4f** was established by chiral HPLC analysis (Chiral

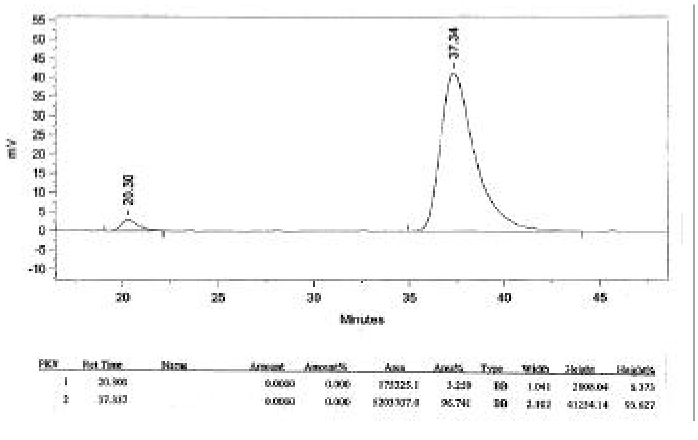
Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 52.32 min, R_t(major) = 56.50 min), >98% ee.



Pk#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	52.320		0.0000	0.000	75272.0	0.615	BV	1.952	615.05	0.797
2	56.500		0.0000	0.000	12021280.0	99.385	VB	2.576	77361.66	99.203

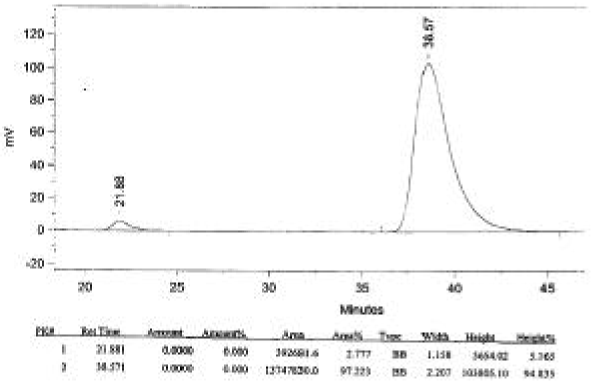
(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)-2-tolyl-methyl]furan-2(*5H*)-one (4g) (Table 1, entry 12). **4g** was obtained as a white solid. mp = 138-140 °C. IR (neat): 3415 (b), 1759 (s), 1602 (m), 1514 (s), 1457 (m), 1249 (m), 1224 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.44 (1H, dd, *J* = 5.6, 1.6 Hz), 7.38 (1H, ddd, *J* = 4.4, 2.0, 2.0 Hz), 7.20-7.17 (3H, m), 6.74 (1H, dd, *J* = 7.6, 1.6 Hz), 6.70 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz), 6.65 (1H, ddd, *J* = 7.2, 7.2, 1.6 Hz), 6.26 (1H, dd, *J* = 7.6, 1.6 Hz), 6.19 (1H, dd, *J* = 5.6, 1.6 Hz), 5.35 (1H, ddd, *J* = 3.6, 1.6, 1.6 Hz), 5.02 (1H, dd, *J* = 6.0, 6.0 Hz), 4.69 (1H, d, *J* = 6.4 Hz), 3.84 (3H, s), 2.47 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.5, 153.2, 147.3, 136.4, 135.9, 135.6, 131.2, 128.2, 127.0, 126.4, 123.7, 121.3, 117.9, 111.1, 109.8, 84.8, 55.8, 55.7, 19.6. Anal Calcd for $C_{19}H_{19}NO_3$: C, 73.77%; H, 6.19%; N, 4.53%; Found C, 73.60%; H, 6.06%; N, 4.54%. Optical rotation: $[\alpha]_D^{20}$ +125.4 (*c* = 1.000, CHCl$_3$) for a 93% ee sample.

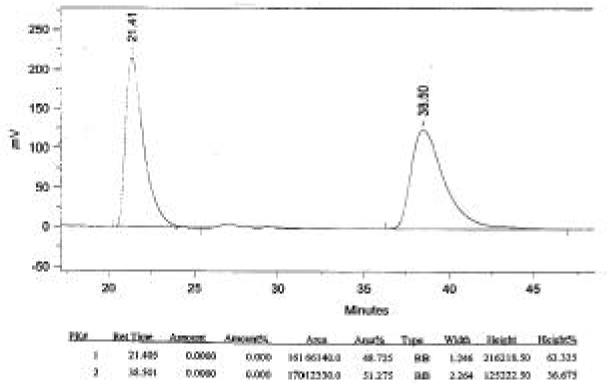
Optical purity of **4g** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 20.30 min, R_t(major) = 37.34 min).



Pk#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	20.300		0.0000	0.000	173225.1	3.259	BB	1.041	2308.04	5.373
2	37.337		0.0000	0.000	5203707.0	96.741	BB	2.102	41234.14	94.627

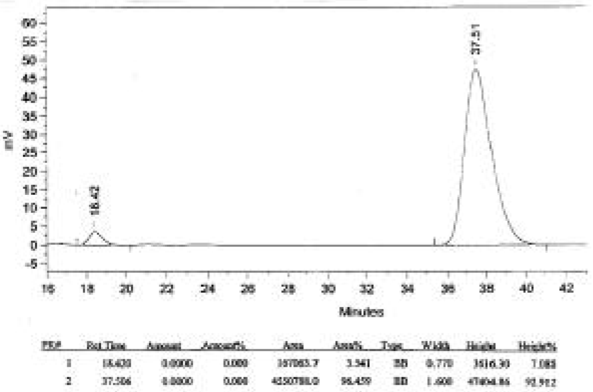
(*R*)-(+)-5-[(*S*)-2-Methoxyphenylamino)-2-tolyl-methyl]furan-2(*5H*)-one (4g) (Table 1, entry 13). Optical purity of **4g** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 80/20 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 21.88 min, R_t(major) = 38.57 min), 94% ee.

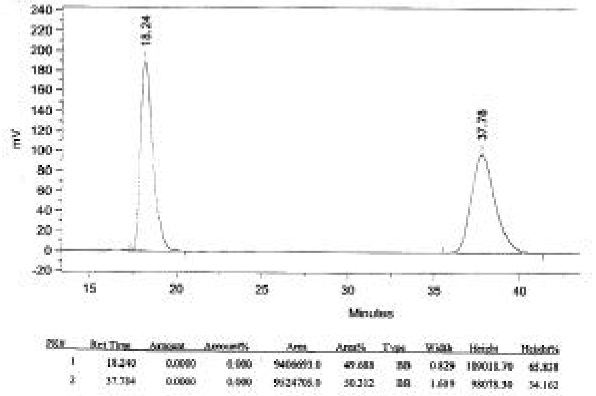




(*R*)-(+)-5-[(*S*)-(2-Bromophenyl)-2-methoxyphenylamino)methyl]furan-2(*5H*)-one (4h) (Table 1, entry 14). 4h was obtained as a light yellow solid. mp = 60-63 °C. IR (neat): 3415 (b), 1766 (s), 1602 (m), 1513 (s), 1457 (m), 1249 (m), 1237 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.57 (1H, dd, *J* = 5.6, 1.6 Hz), 7.51 (1H, dd, *J* = 8.0, 1.2 Hz), 7.36 (1H, dd, *J* = 8.0, 1.6 Hz), 7.21 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.10 (1H, ddd, *J* = 7.6, 7.6, 2.0 Hz), 6.76-6.63 (3H, m), 6.32 (1H, dd, *J* = 7.6, 1.6 Hz), 6.02 (1H, dd, *J* = 5.6, 2.0 Hz), 5.56 (1H, ddd, *J* = 4.0, 1.6, 1.6 Hz), 5.40 (1H, d, *J* = 3.6 Hz), 5.20 (1H, bs), 3.86 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.4, 152.4, 147.3, 135.7, 135.6, 133.1, 130.0, 129.2, 128.3, 124.1, 123.5, 121.3, 118.1, 111.4, 109.8, 84.6, 57.9, 55.7. Anal Calcd for $C_{18}H_{16}BrNO_3$: C, 57.77%; H, 4.31%; N, 3.74%; Found C, 58.02%; H, 4.25%; N, 3.66%. Optical rotation: $[\alpha]_D^{20}$ +1.80 (*c* = 1.00, CHCl$_3$) for a 93% ee sample.

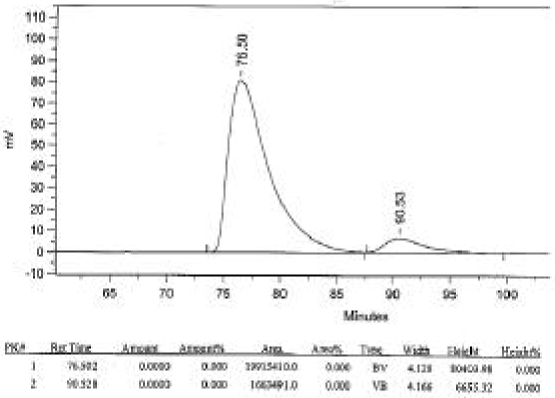
Optical purity of **4h** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 83/17 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 18.42 min, R_t(major) = 37.51 min).

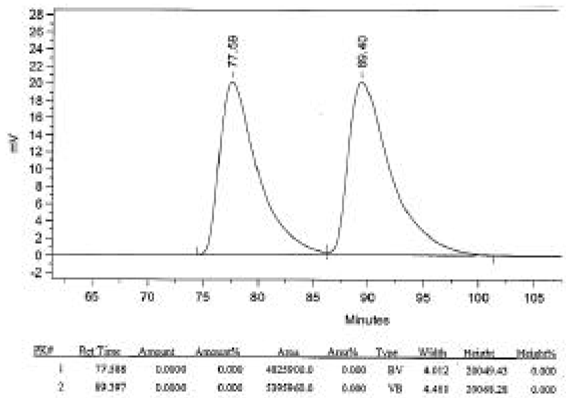




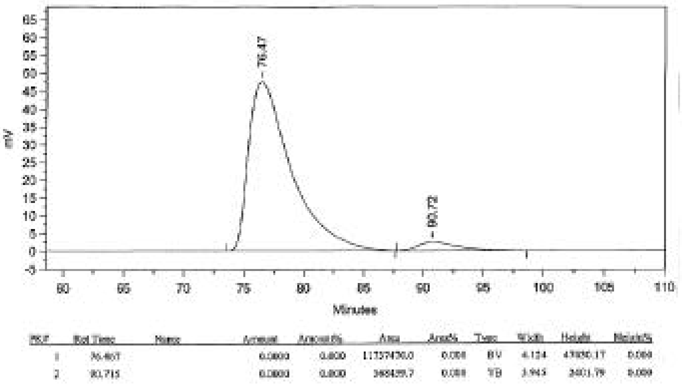
(*R*)-(+)-5-[(*S*)-(Furan-2-yl)-2-methoxyphenylamino)methyl]furan-2(*5H*)-one (4i) (Table 1, entry 15). 4i was obtained as a white solid. mp = 93-95 °C. IR (neat): 3402 (b), 1759 (s), 1602 (m), 1514 (s), 1457 (m), 1249 (m), 1224 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.48 (1H, dd, *J* = 6.0, 1.6 Hz), 7.33 (1H, dd, *J* = 2.0, 1.2 Hz), 6.81-6.68 (3H, m), 6.56 (1H, dd, *J* = 7.6, 1.6 Hz), 6.28-6.25 (2H, m), 6.12 (1H, dd, *J* = 5.6, 2.0 Hz), 5.47 (1H, ddd, *J* = 3.6, 1.6, 1.6 Hz), 4.92 (1H, bs), 4.78 (1H, bs), 3.83 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.6, 153.3, 150.9, 147.4, 142.5, 136.0, 123.3, 121.3, 118.5, 111.5, 110.8, 110.1, 108.5, 84.1, 55.7, 54.2. Anal Calcd for $C_{16}H_{15}NO_4$: C, 67.36%; H, 5.30%; N, 4.91%; Found C, 67.33%; H, 5.38%; N, 4.77%. Optical rotation: $[\alpha]_D^{20}$ +153.0 (c = 1.000, $CHCl_3$) for an 84% ee sample.

Optical purity of **4i** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 92/8 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(major) = 76.50 min, R_t(minor) = 90.53 min).





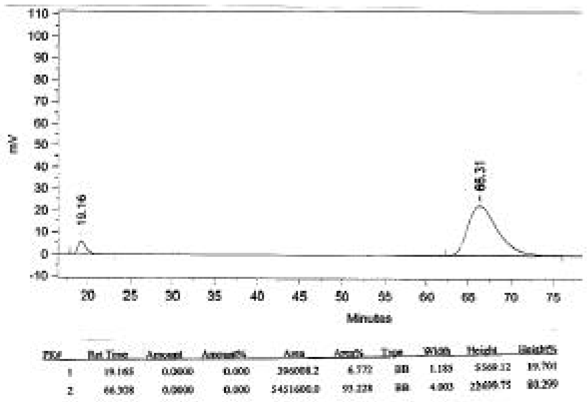
(*R*)-(+)-5-[(*S*)-(Furan-2-yl)-2-methoxyphenylamino)methyl]furan-2(*5H*)-one (4i) (Table 1, entry 16). Optical purity of **4i** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 92/8 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(major) = 76.47 min, R_t(minor) = 90.72 min), 90% ee.



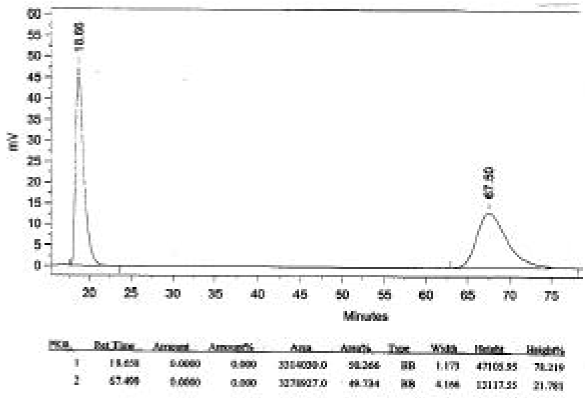
(*R*)-(+)-5-[(*S*)-(2-Methoxyphenylamino)phenylmethyl]-4-methylfuran-2(*5H*)-one (6a) (Table 2, entry 1). **6a** was obtained as a white solid. mp = 194-196 °C. IR (neat): 3427 (b), 1746 (s), 1595 (m), 1507 (s), 1451 (m), 1249 (m), 1218 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.20 (5H, m), 6.76-6.62 (3H, m), 6.45 (1H, dd, J = 8.0, 1.6 Hz), 5.62 (1H, dd, J = 1.6, 1.6 Hz), 5.36-5.35 (1H, m), 5.33-5.31 (1H, m), 4.82 (1H, bs), 3.89 (3H, s), 2.09 (3H, d, J = 0.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.7, 165.5, 147.4, 136.1, 136.0, 128.7, 128.4, 127.7, 121.1, 119.3, 117.9, 111.3, 109.9, 86.8, 58.7, 55.7, 14.8. Anal Calcd for $C_{19}H_{19}NO_3$: C, 73.77%; H, 6.19%; N, 4.53%; Found C, 73.60%; H, 6.06%; N, 4.54%. Optical rotation: $[\alpha]_D^{20}$ +18.2 (c = 1.00, $CHCl_3$) for an 87% ee sample.

Optical purity of **6a** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 0.95 mL/min, R_t(minor) = 19.16 min, R_t(major) = 66.31

min).



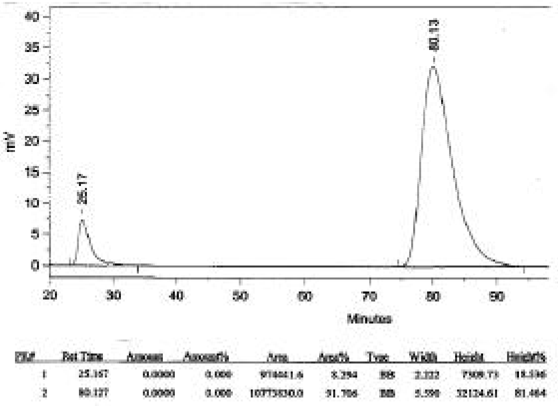
Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	19.165	0.0000	0.000	396008.2	6.772	BB	1.133	5569.12	19.701
2	66.308	0.0000	0.000	5451600.0	93.228	BB	4.003	22699.75	80.299



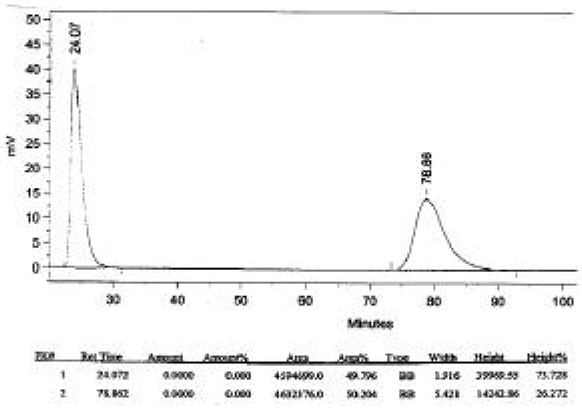
Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	18.658	0.0000	0.000	3314030.0	50.266	BB	1.173	47105.95	78.219
2	67.498	0.0000	0.000	3278927.0	49.734	BB	4.166	13117.55	21.781

(*R*)-(+)-5-[(*S*)-(4-Methoxyphenyl)-(2-methoxyphenylamino)methyl]-4-methylfuran-2(*5H*)-one (6b) (Table 2, entry 2). 6b was obtained as a white solid. mp = 134-135 °C. IR (neat): 3420 (b), 1759 (s), 1602 (m), 1507 (s), 1457 (m), 1249 (m), 1231 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (2H, d, *J* = 8.4 Hz), 6.77-6.69 (4H, m), 6.63 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 6.45 (1H, d, *J* = 7.6 Hz), 5.63 (1H, s), 5.33-5.24 (2H, m), 4.77 (1H, d, *J* = 2.4 Hz), 3.86 (3H, s), 3.72 (3H, s), 2.09 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.8, 165.5, 159.5, 147.4, 136.1, 128.8, 127.8, 121.1, 119.2, 117.8, 114.1, 111.4, 109.9, 86.9, 58.1, 55.7, 55.3, 14.8. Anal Calcd for $C_{20}H_{21}NO_4$: C, 70.78%; H, 6.24%; N, 4.13%; Found C, 70.61%; H, 5.99%; N, 3.93%. Optical rotation: $[\alpha]_D^{20}$ +45.0 (*c* = 1.00, $CHCl_3$) for an 83% ee sample.

Optical purity of **6b** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 0.95 mL/min, R_t(minor) = 25.17 min, R_t(major) = 80.13 min).



Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	25.167	0.0000	0.000	974441.6	8.294	BB	2.222	7309.73	18.536
2	80.127	0.0000	0.000	10773830.0	91.706	BB	5.590	32124.61	81.464

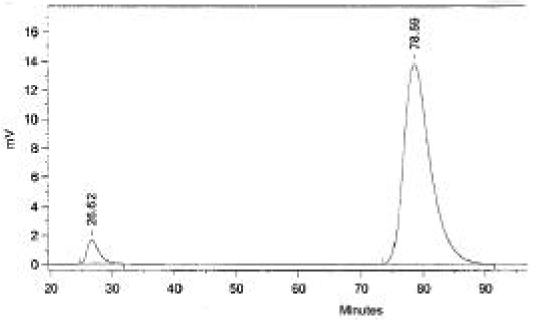


Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	24.072	0.0000	0.000	4594699.0	49.796	BB	1.916	39969.55	73.728
2	78.862	0.0000	0.000	4632176.0	50.204	BB	5.421	14242.86	26.272

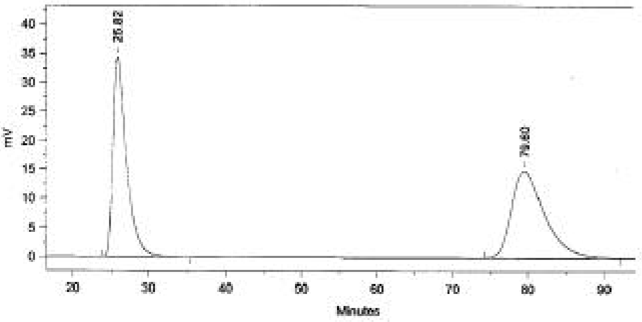
(*R*)-(+)-5-[(*S*)-(4-Chlorophenyl)-(2-methoxyphenylamino)methyl]-4-methylfuran-2(*5H*)-one (6d) (Table 2, entry 3). 6d was obtained as a light yellow solid. mp = 150-151 °C. IR (neat): 3415 (b), 1753 (s), 1602 (m), 1507 (s), 1457 (m), 1249 (m), 1218 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.20 (4H, m), 6.75 (1H, dd, *J* = 7.6, 1.6 Hz), 6.72-6.63 (2H, m), 6.39 (1H, dd, *J* = 7.6, 1.6 Hz), 5.65 (1H, s), 5.33 (2H, s), 4.79 (1H, d, *J* = 2.8 Hz), 3.86 (3H, s), 2.10

(3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 165.1, 147.4, 135.7, 134.6, 134.3, 129.1, 128.9, 121.1, 119.5, 118.2, 111.4, 109.9, 86.5, 58.2, 55.7, 14.8. Anal Calcd for $C_{19}H_{18}ClNO_3$: C, 66.38%; H, 5.28%; N, 4.07%; Found C, 66.38%; H, 5.18%; N, 3.94%. Optical rotation: $[\alpha]_D^{20}$ +33.8 (c = 1.00, $CHCl_3$) for a 90% ee sample.

Optical purity of **6d** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 0.95 mL/min, R_t(minor) = 26.62 min, R_t(major) = 78.59 min).



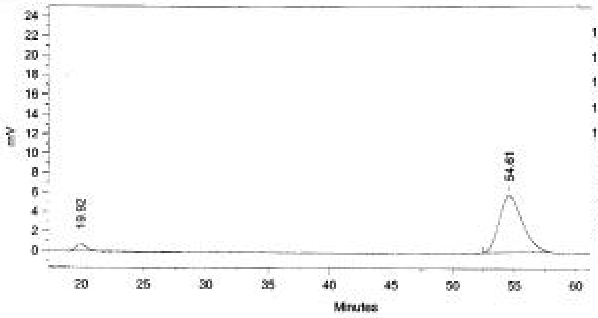
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	26.620	0.0000	0.000	222388.9	5.059	BB	2.254	1644.42	10.661
2	78.592	0.0000	0.000	4173947.0	94.941	BB	5.048	13780.45	89.339



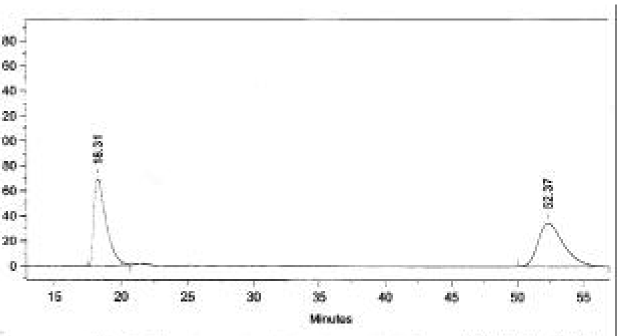
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	25.819	0.0000	0.000	4297114.0	48.507	BB	2.086	34326.28	69.835
2	79.605	0.0000	0.000	4561623.0	51.493	BB	3.127	14827.36	30.165

(*R*)-(-)-5-[(*S*)-(2-Bromophenyl)-(2-methoxyphenylamino)methyl]-4-methylfuran-2(*5H*)-one (6h) (Table 2, entry 4). 6h was obtained as a light yellow solid. mp = 204-206 °C. IR (neat): 3408 (b), 1772 (s), 1608 (m), 1520 (s), 1457 (m), 1432 (m), 1249 (m), 1224 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (2H, td, J = 9.2, 1.2 Hz), 7.24-7.20 (1H, m), 7.09 (1H, td, J = 7.6, 2.0 Hz), 6.76-6.75 (2H, m), 6.66 (1H, dt, J = 7.6, 1.6 Hz), 6.54-6.51 (1H, m), 5.75 (1H, t, J = 1.6 Hz), 5.43-4.42 (1H, m), 5.37 (1H, dd, J = 8.4, 3.6 Hz), 5.17 (1H, d, J = 8.0 Hz), 3.85 (3H, s), 2.15 (3H, d, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 166.3, 147.4, 136.0, 135.8, 133.3, 129.9, 129.8, 128.2, 124.0, 121.3, 119.4, 118.2, 111.8, 109.9, 86.2, 57.3, 55.8, 15.6. Anal Calcd for $C_{19}H_{18}BrNO_3$: C, 58.78%; H, 4.67%; N, 3.61%; Found C, 58.45%; H, 4.69%; N, 3.30%. Optical rotation: $[\alpha]_D^{20}$ –50.4 (c = 0.500, $CHCl_3$) for an 89% ee sample.

Optical purity of **6h** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 90/10 hexanes/*i*-PrOH eluent, 1.0 mL/min, R_t(minor) = 19.92 min, R_t(major) = 54.61 min).



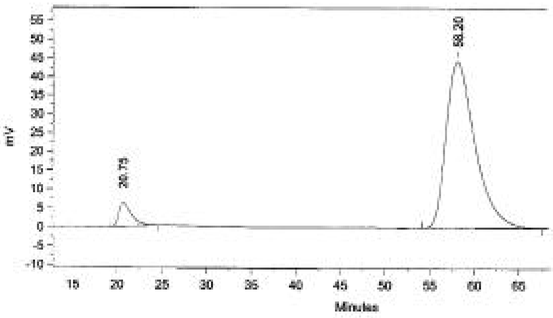
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	19.923	0.0000	0.000	43454.4	5.375	BB	0.981	738.53	11.279
2	54.608	0.0000	0.000	764957.2	94.625	BB	2.195	5809.33	88.721



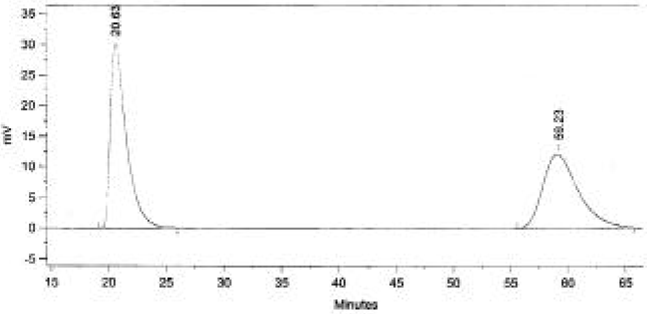
PK#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	18.312	0.0000	0.000	4359024.0	48.193	BB	1.053	68929.58	66.654
2	52.368	0.0000	0.000	4682582.0	51.807	BB	2.265	34484.73	33.346

(*R*)-(+)-5-[(*S*)-(4-Bromophenyl)-(2-methoxyphenylamino)methyl]-4-methylfuran-2(*5H*)-one (6j) (Table 2, entry 5). 6j was obtained as a white solid. mp = 162-163 °C. IR (neat): 3408 (b), 1759 (s), 1602 (m), 1514 (s), 1463 (m), 1432 (m), 1249 (m), 1224 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (2H, d, *J* = 8.4 Hz), 7.13 (2H, d, *J* = 8.4 Hz), 6.73 (1H, dd, *J* = 7.6, 1.6 Hz), 6.70-6.61 (2H, m), 6.37 (1H, dd, *J* = 7.6, 1.6 Hz), 5.64 (1H, t, *J* = 1.2 Hz), 5.32-5.28 (2H, m), 4.75 (1H, dd, *J* = 9.2, 2.8 Hz), 3.85 (3H, s), 2.08 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.3, 165.0, 147.3, 135.6, 135.0, 131.8, 129.3, 122.3, 121.0, 119.4, 118.1, 111.3, 109.9, 86.4, 58.2, 55.6, 14.7. Anal Calcd for $C_{19}H_{18}BrNO_3$: C, 58.78%; H, 4.67%; N, 3.61%; Found C, 58.98%; H, 4.76%; N, 3.52%. Optical rotation: $[\alpha]_D^{20}$ +33.2 (*c* = 0.500, $CHCl_3$) for a >98% ee sample.

Optical purity was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R_t(minor) = 20.75 min, R_t(major) = 58.20 min), 88% ee.



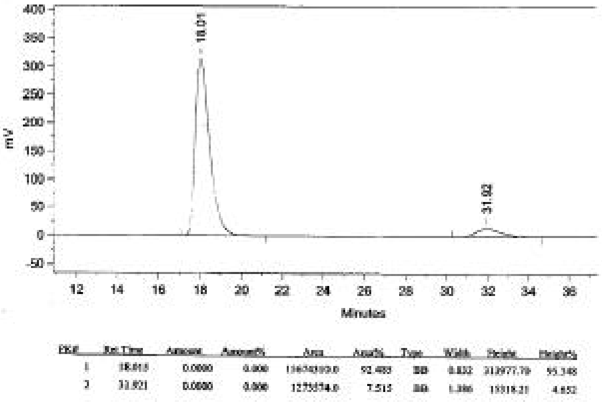
Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	20.747	0.0000	0.000	618614.4	5.885	BB	1.695	6082.73	12.057
2	58.195	0.0000	0.000	9892387.0	94.115	BB	3.716	44366.52	87.943

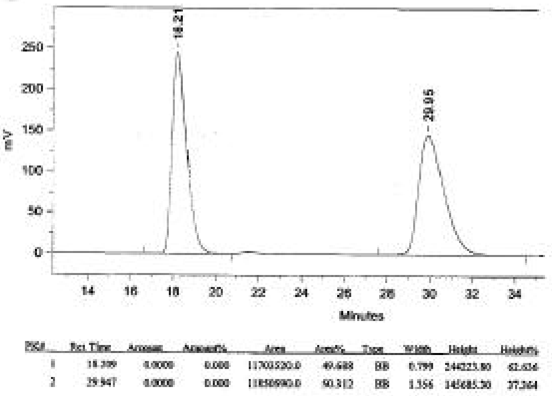


Pk#	Ret Time	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	20.629	0.0000	0.000	2955701.0	53.269	BB	1.638	30068.94	71.414
2	59.234	0.0000	0.000	2592979.0	46.731	BB	3.591	12036.81	28.586

(*R*)-(+)-5-[(*R*)-(2-Methoxyphenylamino)phenylmethyl]-3-methylfuran-2(*5H*)-one (8a) (Table 3, entry 1). 8a was obtained as a colorless oil. IR (neat): 3408 (b), 1765 (s), 1514 (m), 1451 (m), 1249 (m), 1224 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.41 (2H, m), 7.38-7.29 (3H, m), 6.83 (1H, dd, *J* = 1.6, 1.6 Hz), 6.76-6.73 (1H, m), 6.66-6.64 (2H, m), 6.34-6.32 (1H, m), 5.10 (1H, ddd, *J* = 6.8, 1.6, 1.6 Hz), 5.06 (1H, d, *J* = 4.4 Hz), 4.39 (1H, dd, *J* = 6.8, 4.4 Hz), 3.86 (3H, s), 1.86 (3H, t, *J* = 1.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.9, 147.4, 146.2, 138.9, 136.8, 131.5, 129.2, 128.5, 127.5, 121.1, 118.0, 111.9, 109.7, 83.8, 61.8, 55.7, 10.9. Anal Calcd for $C_{19}H_{19}NO_3$: C, 73.77%; H, 6.19%; N, 4.53%; Found C, 73.53%; H, 5.94%; N, 4.41%. Optical rotation: $[a]_D^{20}$ +103.8 (*c* = 0.5200, $CHCl_3$) for an 85% ee sample.

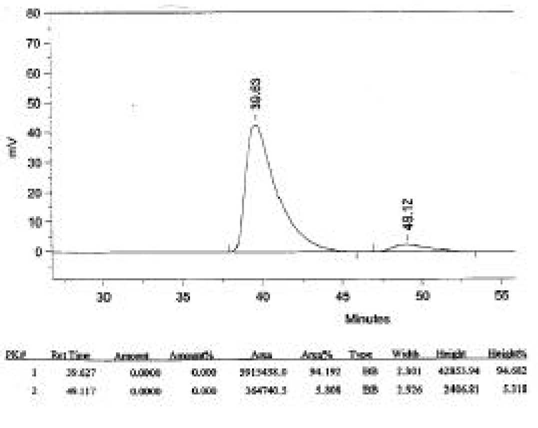
Optical purity of **8a** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 92/8 hexanes/*i*-PrOH eluent, 1.0 mL/min, R_t(major) = 18.01 min, R_t(minor) = 31.92 min).

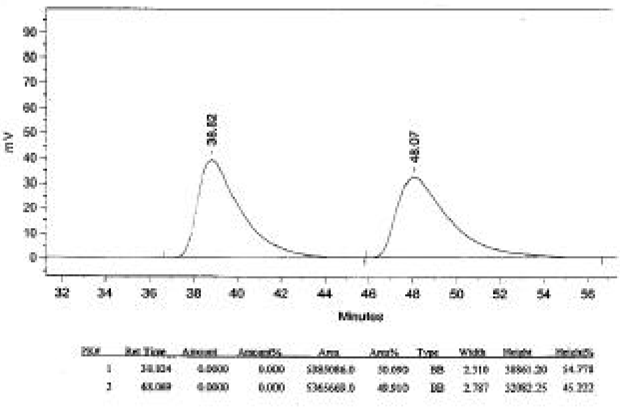




(R)-(+)-5-[(R)-(4-Methoxyphenyl)-(2-methoxyphenylamino)methyl]-3-methylfuran-2(5*H*)-one (8b) (Table 3, entry 2). 8b was obtained as a colorless oil. IR (neat): 3408 (b), 1772 (s), 1608 (m), 1507 (s), 1457 (m), 1249 (m), 1231 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.34-7.32 (2H, m), 6.90-6.86 (2H, m), 6.83 (1H, dd, *J* = 1.6, 1.6 Hz), 6.76-6.73 (1H, m), 6.67-6.64 (2H, m), 6.35-6.32 (1H, m), 5.06 (1H, ddd, *J* = 6.8, 1.6, 1.6 Hz), 5.02 (1H, d, *J* = 3.6 Hz), 4.33 (1H, dd, *J* = 6.8, 3.6 Hz), 3.86 (3H, s), 3.78 (3H, s), 1.86 (3H, t, *J* = 1.6 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 173.9, 159.7, 147.4, 146.3, 136.9, 131.5, 130.7, 128.6, 121.1, 118.0, 114.5, 111.9, 109.6, 83.9, 61.3, 55.7, 55.5, 11.0. Anal Calcd for $C_{20}H_{21}NO_4$: C, 70.78%; H, 6.24%; N, 4.13%; Found C, 70.51%; H, 6.14%; N, 3.91%. Optical rotation: $[\alpha]_D^{20}$ +97.8 (*c* = 0.370, CHCl$_3$) for an 88% ee sample.

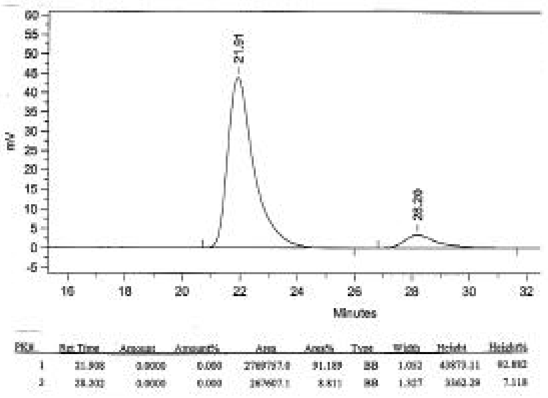
Optical purity of **8b** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 95/5 hexanes/*i*-PrOH eluent, 1.0 mL/min, R_t(major) = 39.63 min, R_t(minor) = 49.12 min).

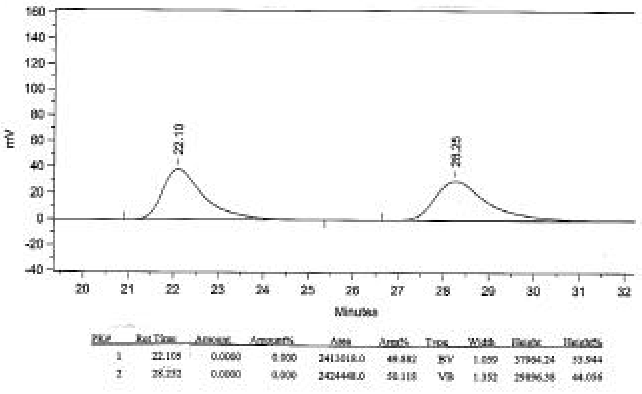




(R)-(+)-5-[(R)-(4-Chlorophenyl)-(2-methoxyphenylamino)methyl]-3-methylfuran-2(5*H*)-one (8d) (Table 3, entry 3). 8d was obtained as a colorless oil. IR (neat): 3408 (b), 1759 (s), 1602 (m), 1514 (s), 1457 (m), 1256 (m), 1224 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.37-7.31 (4H, m), 6.85 (1H, dd, *J* = 1.6, 1.6 Hz), 6.76-6.74 (1H, m), 6.67-6.65 (2H, m), 6.29-6.27 (1H, m), 5.08 (1H, ddd, *J* = 6.4, 1.6, 1.6 Hz), 4.98 (1H, d, *J* = 4.8 Hz), 4.41 (1H, dd, *J* = 6.4, 5.2 Hz), 3.86 (3H, s), 1.87 (3H, t, *J* = 1.6 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 173.6, 147.4, 145.7, 137.4, 136.4, 134.2, 131.9, 129.3, 128.9, 121.1, 118.3, 111.9, 109.7, 83.4, 60.9, 55.7, 10.9. Anal Calcd for $C_{19}H_{18}ClNO_3$: C, 66.38%; H, 5.28%; N, 4.07%; Found C, 66.66%; H, 4.99%; N, 3.87%. Optical rotation: $[\alpha]_D^{20}$ +95.0 (*c* = 1.00, $CHCl_3$) for an 83% ee sample.

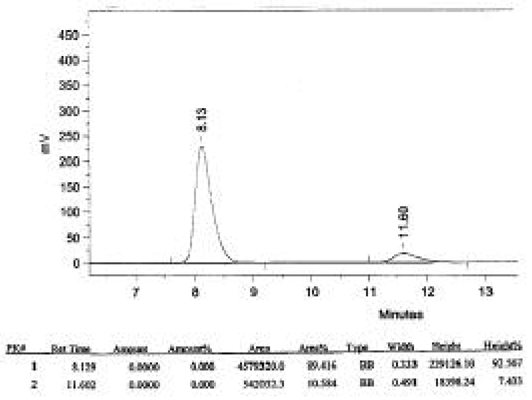
Optical purity of **8d** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 92/8 hexanes/*i*-PrOH eluent, 1.0 mL/min, R_t(major) = 21.91 min, R_t(minor) = 28.20 min).

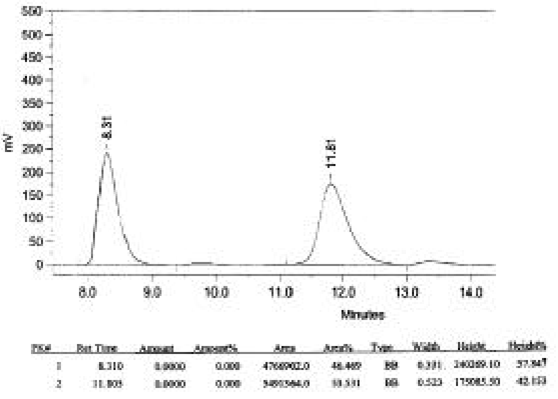




(*R*)-(+)-5-[(*R*)-(2-Bromophenyl)-(2-methoxyphenylamino)methyl]-3-methylfuran-2(*5H*)-one (8h) (Table 3, entry 4). 8h was obtained as colorless oil. IR (neat): 3408 (b), 1765 (s), 1608 (m), 1514 (s), 1457 (m), 1256 (m), 1224 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.59 (1H, dd, *J* = 7.6, 1.6 Hz), 7.51 (1H, dd, *J* = 7.6, 1.6 Hz), 7.28 (1H, td, *J* = 7.2, 1.2 Hz), 7.15 (1H, td, *J* = 8.0, 1.6 Hz), 6.94 (1H, t, *J* = 1.6 Hz), 6.74 (1H, dd, *J* = 7.2, 1.6 Hz), 6.71-6.63 (2H, m), 6.27 (1H, dd, *J* = 7.6, 2.0 Hz), 5.20-5.17 (1H, m), 5.00-5.07 (2H, m), 3.85 (3H, s), 1.92 (3H, t, *J* = 1.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.0, 147.3, 146.6, 137.9, 136.0, 133.2, 131.5, 129.9, 129.3, 128.5, 123.5, 121.3, 118.2, 111.8, 109.7, 82.9, 58.7, 55.7, 10.9. Anal Calcd for $C_{19}H_{18}BrNO_3$: C, 58.78%; H, 4.67%; N, 3.61%; Found C, 58.94%; H, 4.91%; N, 3.48%. Optical rotation: $[\alpha]_D^{20}$ +210.4 (*c* = 0.4600, $CHCl_3$) for a 79% ee sample.

Optical purity of **8h** was established by chiral HPLC analysis (Chiral Technologies Chiralcel OD, 254 nm, 85/15 hexanes/*i*-PrOH eluent, 1.0 mL/min, R_t(major) = 8.13 min, R_t(minor) = 11.60 min).





(5*R*,6*S*)-(+)-5-(Aminomethylphenyl)-furan-2(5*H*)-one (13) (Scheme 2). To a solution of PhI(OAc)$_2$ (23.35 g, 72.50 mmol) in MeOH (200 mL) under an atmosphere of N$_2$ at 0 °C was added a solution of **4a** (5.350 g, 18.12 mmol) in 1:1 MeOH:CH$_2$Cl$_2$ (100 mL) through a pressure-equalizing addition funnel over 30 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (270 mL) was added. The resulting solution was allowed to warm to 22 °C and allowed to stir for 1 h. The mixture was diluted with CH$_2$Cl$_2$ (150 mL) and the layers separated. The aqueous layer was washed with CH$_2$Cl$_2$ (3 x 100 mL) and the combined organic portions washed with 1.0 M aqueous HCl (100 mL). The combined aqueous layers were neutralized with solid Na$_2$CO$_3$ until a pH = 7 was obtained. CH$_2$Cl$_2$ (100 mL) was added, the layers were separated, and the aqueous layer was washed with CH$_2$Cl$_2$ (4 x 100 mL). The combined organic layers were washed with brine (100 mL), dried over MgSO$_4$, and concentrated in vacuo to deliver 2.61 g (13.8 mmol, 76%) of **15** as orange oil. IR (neat): 3377 (b), 3314 (b), 1753 (s), 1608 (m), 1495 (m), 1457 (m), 1168 (s), 1092 (m), 1029 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.39-7.30 (5H, m), 7.28 (1H, dd, *J* = 5.6, 1.6 Hz), 6.12 (1H, dd, *J* = 5.6, 1.6 Hz), 5.20 (1H, ddd, *J* = 4.4, 1.6, 1.6 Hz), 4.45 (1H, d, *J* = 4.4 Hz), 1.57 (2H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.9, 153.4, 139.6, 129.1, 128.4, 126.9, 123.5, 87.2, 57.2. Optical rotation: $[\alpha]_D^{20}$ +98.5 (*c* = 0.930, CHCl$_3$) for a 92% ee sample.

(+)-[(5-Oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid benzyl ester (14) (Scheme 2). To a solution of PhI(OAc)$_2$ (436 mg, 1.35 mmol) in MeOH (5 mL) under an atmosphere of nitrogen at 0 °C was added a solution of **4a** (100 mg, 0.340 mmol) in 1:1 MeOH:CH$_2$Cl$_2$ (5 mL) through a pressure-equalizing addition funnel over 15 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (5 mL) was added. The mixture was allowed to warm to 22 °C and allowed to stir for 1 h. The mixture was diluted with CH$_2$Cl$_2$ (20 mL) and the layers separated. The aqueous layer was washed with CH$_2$Cl$_2$ (3 x 15 mL) and the combined organic portions washed with 1.0 M aqueous HCl (10 mL). The combined aqueous layers were neutralized with solid Na$_2$CO$_3$ until a pH = 7 was obtained. CH$_2$Cl$_2$ (30 mL) was added, followed by CbzCl (0.190 mL, 1.35 mmol) and the biphasic mixture stirred vigorously for 4 h at 22 °C. After this time, the layers were separated and the aqueous layer was washed with CH$_2$Cl$_2$ (3 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO$_4$, and concentrated in vacuo to afford a yellow oil that product was purified by silica gel column chromatography (7:3 hexanes:Et$_2$O) to deliver 83 mg (0.26 mmol, 76%) of **13** as a white solid. mp = 106-107 °C. IR (neat): 3313 (b), 1765 (s), 1721 (s), 1533 (m), 1331 (w), 1249 (m), 1161 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.31-7.24 (9H, m), 7.19-7.17 (2H, m), 5.92 (1H, d, *J* = 4.4 Hz), 5.58 (1H, d, *J* = 8.0 Hz), 5.39 (1H, s), 5.14-5.03 (3H, m). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.4, 155.9, 152.9, 136.2, 135.5, 129.1, 128.9, 128.8, 128.6, 128.4, 127.4, 123.5, 84.5, 67.6, 57.1. Anal Calcd for $C_{19}H_{17}NO_4$: C, 70.58%; H, 5.30%; N, 4.33%; Found C, 70.31%; H, 5.30%; N, 4.20%. Optical rotation: $[\alpha]_D^{20}$ +62.4 (*c* = 0.500, CHCl$_3$) for a 92% ee sample.

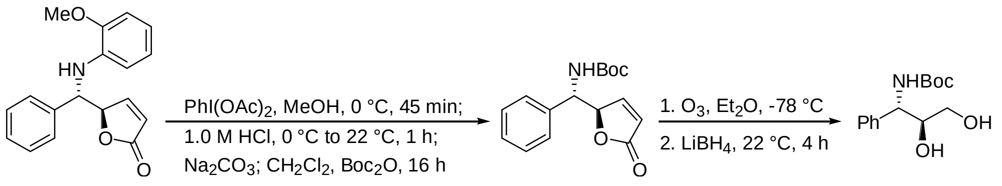
(+)-*N*-[(5-Oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-acetamide (extra data; not shown in text). To a solution of $PhI(OAc)_2$ (436 mg, 1.35 mmol) in MeOH (5 mL) under an atmosphere of N_2 at 0 °C was added a solution of **4a** (100 mg, 0.340 mmol) in 1:1 $MeOH:CH_2Cl_2$ (5 mL) through a pressure-equalizing addition funnel over 15 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (5 mL) was added. The resulting solution was allowed to warm to 22 °C and stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the layers separated. The aqueous layer was washed with CH_2Cl_2 (3 x 15 mL) and the combined organic portions were washed with 1.0 M aqueous HCl (10 mL). The combined aqueous layers were neutralized by addition of solid Na_2CO_3 until a pH = 7 was obtained. CH_2Cl_2 (30 mL) was added, followed by Ac_2O (0.13 mL, 1.35 mmol) and the biphasic mixture was allowed to stir vigorously for 2 h at 22 °C. After this time, the layers were separated and the aqueous layer was washed with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo to afford yellow oil that was purified by silica gel column chromatography (CH_2Cl_2 to 98:2 CH_2Cl_2:MeOH) to deliver 59 mg (0.26 mmol, 75%) of **14** as a white solid. mp = 164-165 °C. IR (neat): 3301 (b), 1790 (m), 1759 (s), 1658 (m), 1495 (m), 1161 (m), 1111 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.27 (4H, m), 7.22-7.19 (2H, m), 6.47 (1H, d, *J* = 8.0 Hz), 5.89 (1H, dd, *J* = 5.6, 2.0 Hz), 5.46-5.40 (2H, m), 2.04 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.6, 169.9, 153.3, 135.0, 129.1, 128.9, 127.6, 123.1, 84.5, 55.2, 23.5. Anal Calcd for $C_{13}H_{13}NO_3$: C, 67.52%; H, 5.67%; N, 6.06%; Found C, 67.27%; H, 5.52%; N, 5.94%. Optical rotation: $[\alpha]_D^{20}$ +136.4 (*c* = 0.5000, $CHCl_3$) for a 90% ee sample.

(5*R*,6*S*)-(–)-5-[(2-Methoxyphenylamino)-phenylmethyl]-dihydrofuran-2-one. To a solution of **4a** (300 mg, 1.01 mmol) in EtOAc (30 mL) was added 10% Pd(C) (30 mg, 10% w/w). The head space of the solution was purged with H_2 and the mixture allowed to stir at 22 °C under 1 atm of H_2 for 4 h. After this time, the mixture was filtered through celite and washed with EtOAc (50 mL) followed by MeOH (50 mL). The filtrate was concentrated *in vacuo* and the resulting yellow oil purified by silica gel column chromatography (7:3 hexanes/Et_2O) to deliver 285 mg (0.960 mmol, 95%) of 5-[(2-methoxyphenylamino)-phenylmethyl]-dihydrofuran-2-one as a white solid. mp = 101 °C. IR (neat): 3427 (b), 2955 (m), 2924 (m), 2854 (m), 1785 (s), 1602 (m), 1514 (s), 1463 (m), 1255 (m), 1224 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (5H, m), 6.75 (1H, dd, *J* = 7.6, 1.6 Hz), 6.70-6.60 (2H, m), 6.39 (1H, dd, *J* = 7.6, 1.6 Hz), 5.18 (1H, d, *J* = 6.0 Hz), 4.99-4.95 (1H, m), 4.52 (1H, dd, *J* = 6.0, 3.6 Hz), 3.86 (3H, s), 2.32-2.21 (2H, m), 2.11-2.05 (1H, m), 1.85-1.79 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.1, 147.3, 137.5, 136.3, 129.0, 128.4, 128.3, 121.2, 117.6, 111.5, 109.7, 82.4, 60.7, 55.7, 27.9, 24.1. Anal Calcd for $C_{18}H_{19}NO_3$: C, 72.71%; H, 6.44%; N, 4.71%; Found C, 72.89%; H, 6.35%; N, 4.58%. Optical rotation: $[\alpha]_D^{20}$ –18.8 (*c* = 0.500, $CHCl_3$) for a 92% ee sample.

(5*R*,6*S*)-(+)-5-(Aminophenylmethyl)-dihydrofuran-2-one. To a solution of PhI(OAc)$_2$ (390 mg, 1.21 mmol) in MeOH (5 mL) at 0 °C was added a solution of 5-[(2-methoxyphenylamino)-phenylmethyl]-dihydrofuran-2-one (90 mg, 0.30 mmol) in 1:1 MeOH:CH$_2$Cl$_2$ (5 mL) by a pressure-equalizing addition funnel over 15 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (5 mL) was added. The mixture was allowed to warm to 22 °C and stir for 1 h. The mixture was diluted with CH$_2$Cl$_2$ (20 mL) and the layers separated. The aqueous layer was washed with CH$_2$Cl$_2$ (3 x 15 mL) and the combined organic portions were washed with 1.0 M aqueous HCl (10 mL). The combined aqueous layers were neutralized with solid Na$_2$CO$_3$ until a pH = 7 was obtained. CH$_2$Cl$_2$ (30 mL) was added, the layers were separated, and the aqueous layer was washed with CH$_2$Cl$_2$ (4 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO$_4$ and concentrated in vacuo to deliver 41 mg (0.21 mmol, 71%) of 5-(aminophenylmethyl)-dihydrofuran-2-one as orange oil. IR (neat): 3364 (b), 3308 (b), 2936 (b), 1772 (s), 1658 (m), 1463 (m), 1174 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.35-7.28 (5H, m), 4.68 (1H, td, *J* = 7.2, 4.0 Hz), 4.34 (1H, d, *J* = 4.0 Hz), 2.45-2.30 (2H, m), 2.28-2.18 (1H, m), 1.99-1.91 (1H, m), 1.56 (2H, s). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 177.5, 140.0, 128.9, 128.2, 127.3, 84.0, 57.5, 28.8, 22.1. HRMS calcd for C$_{11}$H$_{13}$NO$_2$: 191.0946, Found: 191.0950. Optical rotation: $[\alpha]_D^{20}$ +22.0 (*c* = 0.500, CHCl$_3$) for a 92% ee sample.

(5*R*,6*S*)-(–)-5-Hydroxy-6-phenyl-piperidin-2-one (15) (Scheme 2). 5-(Aminophenylmethyl)-dihydrofuran-2-one (20.0 mg, 0.104 mmol) was dissolved in DBU (0.5 mL, 3.34 mmol) and heated to 120 °C for 18 h. The mixture was allowed to cool to 22 °C and the mixture purified by silica gel column chromatography (98:2 CH$_2$Cl$_2$/MeOH) to deliver 14 mg (0.073 mmol, 70%) of **16** as a white solid. mp = 173 °C. IR (neat): 3295 (b), 2917 (m), 1595 (m), 1576 (m), 1495 (m), 1457 (m), 1362 (m), 1338 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.39-7.30 (5H, m), 5.75 (1H, s), 4.33 (1H, d, *J* = 6.8 Hz), 3.84 (1H, ddd, *J* = 9.6, 6.8, 3.2 Hz), 2.64-2.57 (1H, m), 2.53-2.45 (1H, m), 2.16 (1H, s), 2.08-2.00 (1H, m), 1.93-1.84 (1H, m). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.7, 139.6, 129.3, 128.9, 127.3, 71.0, 64.3, 28.8, 27.1. HRMS calcd for C$_{11}$H$_{13}$NO$_2$: 191.0946, Found: 191.0953. Optical rotation: $[\alpha]_D^{20}$ –25.9 (*c* = 0.270, MeOH) for a 92% ee sample.

n **Proof of absolute stereochemistry.** For (*R*)-(+)-5-[(*S*)-(2-methoxyphenyl)amino]-phenylmethyl]furan-2(5*H*)-one (**4a**):

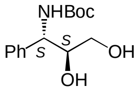


[(5-Oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester. To a solution of PhI(OAc)$_2$ (436 mg, 1.35 mmol) in MeOH (5 mL) under an atmosphere of N$_2$ at 0 °C was added a solution of **4a** (100 mg, 0.340 mmol) in 1:1 MeOH:CH_2Cl_2 (5 mL) through a pressure-equalizing addition funnel over 15 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (5 mL) was added. The mixture was allowed to warm to 22 °C and stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the layers separated. The aqueous layer was washed with CH_2Cl_2 (3x15 mL) and the combined organic portions washed with 1.0 M aqueous HCl (10 mL). The combined aqueous layers were neutralized with solid Na_2CO_3 until a pH = 7 was obtained. CH_2Cl_2 (30 mL) was added, followed by Boc_2O (295 mg, 1.35 mmol) and the biphasic mixture was allowed to stir vigorously for 16 h at 22 °C. After this time, the layers were separated, and the aqueous layer was washed with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford brown oil that was purified by silica gel column chromatography (80:20 hexanes:Et_2O) to deliver 25 mg (0.086 mmol, 26%) of [(5-oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester as white solid.

(2*S*,3*S*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1,2-propanediol. Ozone was bubbled through a solution of [(5-oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester (32 mg, 0.11 mmol) in Et_2O/CH_2Cl_2 (1:1, 10 mL) at –78 °C for 5 min. The flask was purged with N_2 before the addition of $LiBH_4$ (7.2 mg, 0.33 mmol). The resulting solution was allowed to warm to 22 °C and stir for 4 h. The reaction was quenched by the addition of 1.0 M aqueous HCl (5 mL), the layers were separated, and the aqueous portion washed with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to afford yellow oil that was purified by silica gel column chromatography (1:1 EtOAc/hexanes) to deliver 12 mg (0.045 mmol, 40%) of 3-(*tert*-butoxycarbonylamino)-3-phenyl-1,2-propanediol as white solid. mp = 107-108 °C. IR (neat): 3370 (b), 2986 (m), 2930 (m), 1696 (s), 1495 (m), 1400 (m), 1369 (m), 1161 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.26 (5H, m), 5.13 (1H, bs), 4.65 (1H, t, J = 8.0 Hz), 3.84-3.76 (1H, m), 3.66 (2H, bs), 3.04 (1H, bs), 2.40 (1H, d, J = 7.6 Hz), 1.40 (9H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.4, 136.9, 128.9, 128.1, 127.4, 80.5, 74.2, 63.0, 56.8, 28.3. HRMS calcd for $C_{14}H_{22}NO_4$ $(M+H^+)$: 268.1549, Found: 268.1556. Optical rotation: $[\alpha]_D^{20}$ +42.9 (c = 0.730, $CHCl_3$) for a >98% ee sample.

Comparison with authentic materials. The spectral data for (2*S*,3*S*)-3-(*tert*-butoxycarbonylamino)-3-phenyl-1,2-propanediol are fully consistent with those reported in the literature.[2] Moreover, as summarized in the table below, the optical rotation measurements correspond to the (2*S*,3*S*)-enantiomer being formed as the major isomer with chiral ligand **1a**.

study	product ee (%)	specific rotation ($[\alpha]_D$)	absolute configuration
Merino (ref 2a)	>98	+51 (c = 0.65, $CHCl_3$)	2*S*,3*S*
Matsuura (ref 2b)	>98	–42.4 (c = 1.02, $CHCl_3$)	2*R*,3*R*
this study	>98	+42.9 (c = 0.73, $CHCl_3$)	2*S*,3*S*



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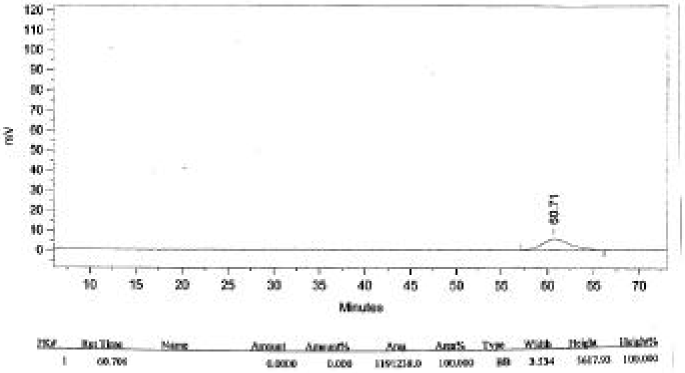
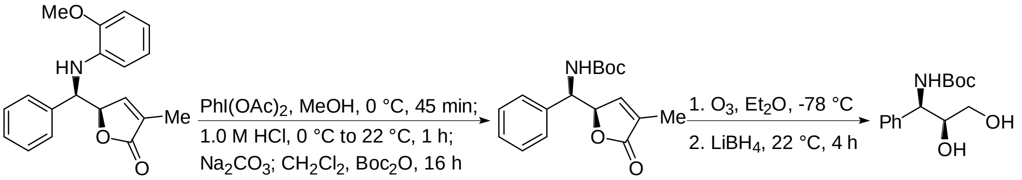
[2] (a) P. Merino, E. Castillo, S. Franco, F. L. Merchán, T. Tejero, *Tetrahedron* **1998**, *54*, 12301–12322. (b) F. Matsuura, Y. Hamada, T. Shiori, *Tetrahedron* **1993**, *49*, 8211–8222.

(*R*)-(+)-5-[(*S*)-(4-Bromophenyl)-(2-methoxyphenylamino)methyl]-4-methylfuran-2(*5H*)-one (6j) (Table 2, entry 5). AVM product **6j** (88% ee) was dissolved in hot Et_2O (5 mL) and hexanes added (1 mL) to yield upon cooling to 22 °C single crystals suitable for X-ray crystallography. The identity of the single crystal used for X-ray crystallography was established by chiral HPLC analysis as the major enantiomer (Chiral Technologies Chiralcel OD, 254 nm, 70/30 hexanes/*i*-PrOH eluent, 1 mL/min, R_t = 60.71 min).



Pk#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	60.706		0.0000	0.000	1191218.0	100.000	BB	3.534	5617.93	100.000

For (*R*)-(+)-5-[(*R*)-(2-Methoxyphenylamino)phenylmethyl]-3-methylfuran-2(*5H*)-one (**8a**)

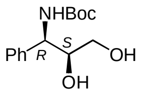


(*R,R*)-[(4-Methyl-5-oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester. To a solution of $PhI(OAc)_2$ (354 mg, 1.10 mmol) in MeOH (5 mL) under an atmosphere of N_2 at 0 °C was added a solution of **8a** (85 mg, 0.275 mmol) in 1:1 MeOH:CH_2Cl_2 (5 mL) through a pressure-equalizing addition funnel over 15 min. The mixture was allowed to stir at 0 °C for an additional 30 min upon which time a 1.0 M aqueous solution of HCl (5 mL) was added. The mixture was allowed to warm to 22 °C and stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the layers separated. The aqueous layer was washed with CH_2Cl_2 (3 x 15 mL) and the combined organic portions washed with 1.0 M aqueous HCl (10 mL). The combined aqueous layers were neutralized with solid Na_2CO_3 until a pH = 7 was obtained. CH_2Cl_2 (30 mL) was added, followed by Boc_2O (240 mg, 1.10 mmol) and the biphasic mixture was allowed to stir vigorously for 16 h at 22 °C. At this time, the layers were separated and the aqueous layer was washed with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and concentrated in vacuo to afford brown oil that was purified by silica gel column chromatography (80:20 hexanes:Et_2O) to deliver 24 mg (0.079 mmol, 29%) of [(4-methyl-5-oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester as white solid.

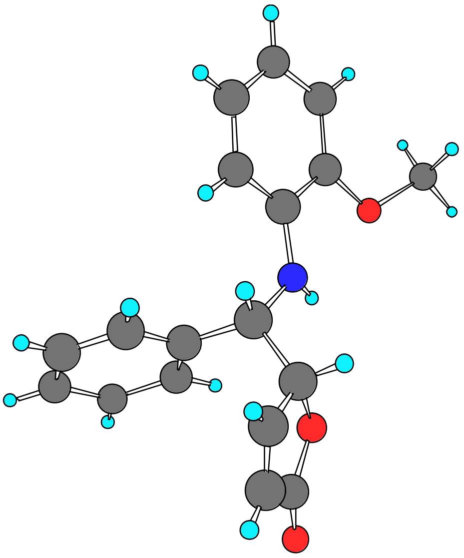
(2*S*,3*R*)-3-(*tert*-Butoxycarbonylamino)-3-phenyl-1,2-propanediol. Ozone was introduced through a solution of [(4-methyl-5-oxo-2,5-dihydrofuran-2-yl)-phenylmethyl]-carbamic acid *tert*-butyl ester (24 mg, 0.080 mmol) in Et_2O/CH_2Cl_2 (1:1, 10 mL) at –78 °C for 5 min. The flask was then purged with N_2 before the addition of $LiBH_4$ (5.2 mg, 0.24 mmol). The mixture was allowed to warm to room temperature and allowed to stir for 4 h. The reaction was quenched by the addition of 1.0 M aqueous HCl (5 mL), the layers separated, and the aqueous portion washed with CH_2Cl_2 (3x15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford yellow oil that was purified by silica gel column chromatography (1:1 Et_2O/hexanes) to deliver 6.0 mg (0.022 mmol, 28%) of 3-(*tert*-butoxycarbonylamino)-3-phenyl-1,2-propanediol as white solid. mp = 74 °C. IR (neat): 3389 (b), 2974 (m), 2923 (m), 1690 (s), 1495 (m), 1400 (m), 1369 (m), 1161 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.25 (5H, m), 5.13 (1H, d, *J* = 8.4 Hz), 4.80 (1H, bs), 3.93 (1H, bs), 3.58-3.50 (2H, m), 2.70-2.60 (2H, m), 1.41 (9H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.0, 139.6, 129.1, 128.0, 126.9, 80.6, 75.4, 63.9, 56.1, 28.5. HRMS calcd for $C_{14}H_{22}NO_4$ ($M+H^+$): 268.1549, Found: 268.1557. Optical rotation: $[\alpha]_D^{20}$ –19.99 (*c* = 0.4000, $CHCl_3$) for an 80% ee sample.

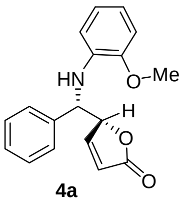
The spectral data for (2*S*,3*R*)-3-(*tert*-butoxycarbonylamino)-3-phenyl-1,2-propanediol are consistent with those reported in the literature.[2a] Moreover, as summarized in the table below, the optical rotation measurements correspond to the (2*S*,3*R*) enantiomer being formed as the major enantiomer with chiral ligand **1d**.

study	product ee (%)	specific rotation ($[\alpha]_D$)	absolute configuration
Merino (ref 2a)	>98	–23.4 (*c* = 0.82, $CHCl_3$)	2*S*,3*R*
this study	80	–19.99 (*c* = 0.40, $CHCl_3$)	2*S*,3*R*



X-ray crystal structure of Mannich product 4a.





4a

Table 1. Crystal data and structure refinement for **4a**

Identification code	ec01t	
Empirical formula	C18 H17 N O3	
Formula weight	295.33	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.6940(9) Å	α= 90°.
	b = 19.100(3) Å	β= 102.025(2)°
	c = 12.0820(16) Å	γ = 90°
Volume	1510.9(4) Å^3	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	624	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.72 to 28.35°	
Index ranges	–8<=h<=8, –13<=k<=25, –15<=l<=16	
Reflections collected	11365	
Independent reflections	5206 [R(int) = 0.0317]	
Completeness to theta = 28.35°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5206 / 1 / 407	
Goodness-of-fit on F^2	0.861	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0764	
R indices (all data)	R1 = 0.0466, wR2 = 0.0804	
Absolute structure parameter	–0.7(8)	
Largest diff. peak and hole	0.214 and –0.140 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for EC01t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6162(2)	539(1)	1393(1)	38(1)
O(4)	11500(2)	2940(1)	6953(1)	41(1)
C(23)	7923(3)	3230(1)	6142(1)	32(1)
N(1)	2802(2)	1530(1)	676(2)	45(1)
O(3)	3618(2)	2870(1)	855(1)	49(1)
N(2)	8246(2)	3974(1)	6285(1)	39(1)
O(2)	8780(2)	-151(1)	1218(1)	55(1)
C(12)	1200(3)	1990(1)	333(1)	32(1)
C(24)	7970(3)	2959(1)	4963(1)	33(1)
C(4)	4109(2)	441(1)	1563(1)	35(1)
O(5)	14108(2)	2252(1)	6760(2)	69(1)
C(5)	2544(2)	778(1)	606(1)	32(1)
C(1)	7084(3)	-93(1)	1387(1)	36(1)
C(22)	9415(2)	2842(1)	7069(1)	35(1)
C(30)	6802(3)	4451(1)	5741(1)	35(1)
C(25)	6388(3)	2549(1)	4391(2)	45(1)
O(6)	9400(2)	5271(1)	6152(1)	58(1)
C(3)	3922(3)	-326(1)	1675(1)	36(1)
C(6)	2601(2)	466(1)	-544(1)	30(1)
C(17)	1599(3)	2713(1)	456(1)	35(1)
C(11)	1013(3)	45(1)	-1077(2)	42(1)
C(29)	9551(3)	3124(1)	4440(2)	45(1)
C(13)	-801(3)	1780(1)	-91(1)	38(1)
C(21)	9164(3)	2068(1)	7056(1)	37(1)
C(7)	4202(3)	586(1)	-1079(2)	41(1)
C(14)	-2356(3)	2272(1)	-353(2)	43(1)
C(20)	10867(3)	1760(1)	6944(2)	40(1)
C(35)	7382(3)	5153(1)	5703(1)	39(1)
C(16)	53(3)	3193(1)	190(2)	41(1)
C(15)	-1940(3)	2970(1)	-209(2)	45(1)
C(2)	5658(3)	-631(1)	1598(1)	39(1)
C(19)	12368(3)	2302(1)	6872(2)	44(1)
C(34)	5994(3)	5658(1)	5247(2)	49(1)

C(10)	1041(4)	-258(1)	-2112(2)	56(1)
C(18)	4108(3)	3566(1)	1239(2)	51(1)
C(8)	4232(4)	279(1)	-2113(2)	55(1)
C(32)	3389(3)	4793(1)	4845(2)	60(1)
C(26)	6385(4)	2309(1)	3314(2)	67(1)
C(33)	3982(4)	5475(1)	4820(2)	61(1)
C(28)	9549(4)	2877(1)	3360(2)	62(1)
C(27)	7962(5)	2475(1)	2805(2)	70(1)
C(9)	2657(4)	-141(1)	-2626(2)	59(1)
C(31)	4787(3)	4279(1)	5294(2)	48(1)
C(36)	10055(4)	5976(1)	6323(2)	65(1)

Table 3. Bond lengths [Å] and angles [°] for EC01t.

O(1)-C(1)	1.356(2)
O(1)-C(4)	1.4434(19)
O(4)-C(19)	1.363(2)
O(4)-C(22)	1.443(2)
C(23)-N(2)	1.442(2)
C(23)-C(24)	1.523(2)
C(23)-C(22)	1.528(2)
C(23)-H(23)	1.0000
N(1)-C(12)	1.381(2)
N(1)-C(5)	1.447(2)
N(1)-H(2)	0.87(2)
O(3)-C(17)	1.370(2)
O(3)-C(18)	1.423(2)
N(2)-C(30)	1.390(2)
N(2)-H(1)	0.888(19)
O(2)-C(1)	1.200(2)
C(12)-C(13)	1.390(2)
C(12)-C(17)	1.409(2)
C(24)-C(25)	1.381(3)
C(24)-C(29)	1.377(2)
C(4)-C(3)	1.479(3)
C(4)-C(5)	1.531(2)
C(4)-H(4)	1.0000
O(5)-C(19)	1.204(2)
C(5)-C(6)	1.519(2)
C(5)-H(5)	1.0000
C(1)-C(2)	1.461(3)
C(22)-C(21)	1.486(3)
C(22)-H(22)	1.0000
C(30)-C(31)	1.384(3)
C(30)-C(35)	1.401(3)
C(25)-C(26)	1.380(3)
C(25)-H(25)	0.9500
O(6)-C(35)	1.365(2)

O(6)-C(36)	1.418(3)
C(3)-C(2)	1.321(3)
C(3)-H(3)	0.9500
C(6)-C(11)	1.381(2)
C(6)-C(7)	1.381(2)
C(17)-C(16)	1.369(3)
C(11)-C(10)	1.381(3)
C(11)-H(11)	0.9500
C(29)-C(28)	1.387(3)
C(29)-H(29)	0.9500
C(13)-C(14)	1.389(3)
C(13)-H(13)	0.9500
C(21)-C(20)	1.315(2)
C(21)-H(21)	0.9500
C(7)-C(8)	1.384(3)
C(7)-H(7)	0.9500
C(14)-C(15)	1.366(3)
C(14)-H(14)	0.9500
C(20)-C(19)	1.458(3)
C(20)-H(20)	0.9500
C(35)-C(34)	1.371(3)
C(16)-C(15)	1.388(3)
C(16)-H(16)	0.9500
C(15)-H(15)	0.9500
C(2)-H(37)	0.9500
C(34)-C(33)	1.383(3)
C(34)-H(34)	0.9500
C(10)-C(9)	1.374(3)
C(10)-H(10)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(8)-C(9)	1.366(3)
C(8)-H(8)	0.9500
C(32)-C(33)	1.364(3)
C(32)-C(31)	1.386(3)

C(32)-H(32)	0.9500
C(26)-C(27)	1.365(4)
C(26)-H(26)	0.9500
C(33)-H(33)	0.9500
C(28)-C(27)	1.368(4)
C(28)-H(28)	0.9500
C(27)-H(27)	0.9500
C(9)-H(9)	0.9500
C(31)-H(31)	0.9500
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800

C(1)-O(1)-C(4)	109.47(14)
C(19)-O(4)-C(22)	109.00(14)
N(2)-C(23)-C(24)	114.50(14)
N(2)-C(23)-C(22)	109.41(14)
C(24)-C(23)-C(22)	112.51(14)
N(2)-C(23)-H(23)	106.6
C(24)-C(23)-H(23)	106.6
C(22)-C(23)-H(23)	106.6
C(12)-N(1)-C(5)	122.53(15)
C(12)-N(1)-H(2)	116.5(15)
C(5)-N(1)-H(2)	117.5(15)
C(17)-O(3)-C(18)	117.56(15)
C(30)-N(2)-C(23)	121.14(15)
C(30)-N(2)-H(1)	112.4(13)
C(23)-N(2)-H(1)	117.1(14)
N(1)-C(12)-C(13)	123.76(17)
N(1)-C(12)-C(17)	118.24(16)
C(13)-C(12)-C(17)	117.96(16)
C(25)-C(24)-C(29)	118.89(17)
C(25)-C(24)-C(23)	119.83(16)
C(29)-C(24)-C(23)	121.27(16)
O(1)-C(4)-C(3)	104.04(14)
O(1)-C(4)-C(5)	111.09(14)

C(3)-C(4)-C(5)	115.36(14)
O(1)-C(4)-H(4)	108.7
C(3)-C(4)-H(4)	108.7
C(5)-C(4)-H(4)	108.7
N(1)-C(5)-C(6)	114.72(14)
N(1)-C(5)-C(4)	108.62(14)
C(6)-C(5)-C(4)	112.44(14)
N(1)-C(5)-H(5)	106.9
C(6)-C(5)-H(5)	106.9
C(4)-C(5)-H(5)	106.9
O(2)-C(1)-O(1)	122.06(18)
O(2)-C(1)-C(2)	129.82(19)
O(1)-C(1)-C(2)	108.12(15)
O(4)-C(22)-C(21)	103.77(15)
O(4)-C(22)-C(23)	111.30(14)
C(21)-C(22)-C(23)	114.82(14)
O(4)-C(22)-H(22)	108.9
C(21)-C(22)-H(22)	108.9
C(23)-C(22)-H(22)	108.9
C(31)-C(30)-N(2)	123.72(18)
C(31)-C(30)-C(35)	117.92(18)
N(2)-C(30)-C(35)	118.24(17)
C(24)-C(25)-C(26)	120.7(2)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(35)-O(6)-C(36)	117.67(17)
C(2)-C(3)-C(4)	109.77(16)
C(2)-C(3)-H(3)	125.1
C(4)-C(3)-H(3)	125.1
C(11)-C(6)-C(7)	118.38(17)
C(11)-C(6)-C(5)	119.47(16)
C(7)-C(6)-C(5)	122.16(15)
C(16)-C(17)-O(3)	125.31(17)
C(16)-C(17)-C(12)	120.91(17)
O(3)-C(17)-C(12)	113.78(15)
C(6)-C(11)-C(10)	120.8(2)

C(6)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(24)-C(29)-C(28)	120.2(2)
C(24)-C(29)-H(29)	119.9
C(28)-C(29)-H(29)	119.9
C(14)-C(13)-C(12)	120.54(18)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(20)-C(21)-C(22)	110.37(17)
C(20)-C(21)-H(21)	124.8
C(22)-C(21)-H(21)	124.8
C(6)-C(7)-C(8)	120.73(19)
C(6)-C(7)-H(7)	119.6
C(8)-C(7)-H(7)	119.6
C(15)-C(14)-C(13)	120.50(18)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.8
C(21)-C(20)-C(19)	108.10(18)
C(21)-C(20)-H(20)	125.9
C(19)-C(20)-H(20)	125.9
O(6)-C(35)-C(34)	125.12(19)
O(6)-C(35)-C(30)	113.75(17)
C(34)-C(35)-C(30)	121.13(19)
C(17)-C(16)-C(15)	120.09(19)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(14)-C(15)-C(16)	119.97(19)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(3)-C(2)-C(1)	108.54(18)
C(3)-C(2)-H(37)	125.7
C(1)-C(2)-H(37)	125.7
O(5)-C(19)-O(4)	121.04(19)
O(5)-C(19)-C(20)	130.2(2)
O(4)-C(19)-C(20)	108.75(15)
C(35)-C(34)-C(33)	119.9(2)

C(35)-C(34)-H(34)	120.1
C(33)-C(34)-H(34)	120.1
C(11)-C(10)-C(9)	120.1(2)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
O(3)-C(18)-H(18A)	109.5
O(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(9)-C(8)-C(7)	120.2(2)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(33)-C(32)-C(31)	120.6(2)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(27)-C(26)-C(25)	119.9(2)
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0
C(32)-C(33)-C(34)	119.9(2)
C(32)-C(33)-H(33)	120.1
C(34)-C(33)-H(33)	120.1
C(27)-C(28)-C(29)	120.0(2)
C(27)-C(28)-H(28)	120.0
C(29)-C(28)-H(28)	120.0
C(26)-C(27)-C(28)	120.3(2)
C(26)-C(27)-H(27)	119.9
C(28)-C(27)-H(27)	119.9
C(8)-C(9)-C(10)	119.78(19)
C(8)-C(9)-H(9)	120.1
C(10)-C(9)-H(9)	120.1
C(32)-C(31)-C(30)	120.6(2)
C(32)-C(31)-H(31)	119.7
C(30)-C(31)-H(31)	119.7
O(6)-C(36)-H(36A)	109.5

O(6)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
O(6)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for EC01t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	33(1)	36(1)	44(1)	-2(1)	5(1)	-7(1)
O(4)	34(1)	40(1)	47(1)	2(1)	3(1)	-8(1)
C(23)	33(1)	31(1)	34(1)	-4(1)	8(1)	-1(1)
N(1)	30(1)	26(1)	78(1)	-14(1)	8(1)	-2(1)
O(3)	41(1)	29(1)	73(1)	-12(1)	3(1)	-4(1)
N(2)	35(1)	32(1)	47(1)	-8(1)	5(1)	0(1)
O(2)	32(1)	65(1)	69(1)	0(1)	13(1)	-1(1)
C(12)	33(1)	30(1)	35(1)	-5(1)	10(1)	3(1)
C(24)	42(1)	26(1)	30(1)	3(1)	6(1)	4(1)
C(4)	33(1)	39(1)	35(1)	-9(1)	10(1)	-1(1)
O(5)	36(1)	75(1)	99(1)	20(1)	21(1)	6(1)
C(5)	29(1)	23(1)	45(1)	-8(1)	10(1)	-3(1)
C(1)	32(1)	41(1)	34(1)	-1(1)	3(1)	-2(1)
C(22)	36(1)	41(1)	30(1)	-4(1)	10(1)	-1(1)
C(30)	41(1)	35(1)	31(1)	-5(1)	11(1)	5(1)
C(25)	57(1)	35(1)	40(1)	-4(1)	-2(1)	1(1)
O(6)	58(1)	35(1)	76(1)	1(1)	1(1)	-6(1)
C(3)	36(1)	42(1)	30(1)	6(1)	7(1)	-7(1)
C(6)	36(1)	20(1)	35(1)	2(1)	6(1)	4(1)
C(17)	40(1)	32(1)	34(1)	-3(1)	11(1)	0(1)
C(11)	52(1)	30(1)	42(1)	1(1)	7(1)	-3(1)
C(29)	58(1)	40(1)	41(1)	8(1)	18(1)	3(1)
C(13)	34(1)	37(1)	43(1)	-6(1)	10(1)	-1(1)

C(21)	35(1)	41(1)	35(1)	9(1)	8(1)	-4(1)
C(7)	42(1)	39(1)	43(1)	9(1)	10(1)	6(1)
C(14)	33(1)	53(1)	43(1)	6(1)	9(1)	4(1)
C(20)	39(1)	36(1)	45(1)	7(1)	6(1)	2(1)
C(35)	50(1)	38(1)	32(1)	-2(1)	12(1)	4(1)
C(16)	53(1)	30(1)	43(1)	3(1)	14(1)	5(1)
C(15)	45(1)	45(1)	46(1)	13(1)	14(1)	14(1)
C(2)	41(1)	35(1)	40(1)	6(1)	2(1)	-1(1)
C(19)	36(1)	46(1)	48(1)	10(1)	7(1)	2(1)
C(34)	69(2)	37(1)	43(1)	7(1)	18(1)	10(1)
C(10)	86(2)	38(1)	40(1)	-8(1)	1(1)	-6(1)
C(18)	60(1)	28(1)	64(1)	-5(1)	11(1)	-8(1)
C(8)	66(1)	60(2)	43(1)	15(1)	22(1)	20(1)
C(32)	47(1)	65(2)	63(1)	8(1)	2(1)	13(1)
C(26)	102(2)	47(1)	42(1)	-10(1)	-11(1)	7(2)
C(33)	63(2)	60(2)	58(1)	16(1)	13(1)	26(1)
C(28)	96(2)	53(2)	48(1)	18(1)	37(1)	26(1)
C(27)	128(2)	49(2)	31(1)	2(1)	11(1)	30(2)
C(9)	98(2)	47(1)	30(1)	4(1)	12(1)	22(1)
C(31)	43(1)	47(1)	54(1)	0(1)	8(1)	3(1)
C(36)	79(2)	41(1)	68(2)	8(1)	3(1)	-13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for EC01t.

	x	y	z	U(eq)
H(23)	6522	3133	6272	39
H(4)	3995	665	2295	42
H(5)	1163	674	758	38
H(22)	9267	3024	7823	42
H(25)	5291	2430	4744	54
H(3)	2731	-564	1785	43
H(11)	-111	-38	-727	50
H(29)	10646	3408	4820	54

H(13)	-1107	1296	-203	45
H(21)	7947	1831	7119	44
H(7)	5294	882	-733	49
H(14)	-3721	2121	-634	51
H(20)	11082	1269	6915	48
H(16)	346	3679	278	50
H(15)	-3014	3303	-381	54
H(37)	5934	-1119	1669	47
H(34)	6415	6132	5224	59
H(10)	-60	-548	-2468	68
H(18A)	3699	3893	607	76
H(18B)	5583	3603	1534	76
H(18C)	3380	3680	1840	76
H(8)	5352	360	-2467	65
H(32)	2005	4669	4552	72
H(26)	5287	2029	2926	81
H(33)	3014	5824	4510	73
H(28)	10651	2987	3006	75
H(27)	7957	2311	2062	84
H(9)	2679	-350	-3336	70
H(31)	4358	3805	5294	57
H(36A)	9820	6220	5593	97
H(36B)	11514	5987	6670	97
H(36C)	9282	6208	6823	97
H(1)	9520(30)	4129(11)	6349(15)	45(6)
H(2)	4030(30)	1696(12)	709(17)	60(7)

Table 6. Torsion angles [°] for EC01t

C(24)-C(23)-N(2)-C(30)	68.4(2)
C(22)-C(23)-N(2)-C(30)	-164.24(15)
C(5)-N(1)-C(12)-C(13)	1.2(3)
C(5)-N(1)-C(12)-C(17)	178.78(16)
N(2)-C(23)-C(24)-C(25)	-128.63(18)
C(22)-C(23)-C(24)-C(25)	105.63(18)

N(2)-C(23)-C(24)-C(29)	50.3(2)
C(22)-C(23)-C(24)-C(29)	-75.4(2)
C(1)-O(1)-C(4)-C(3)	0.78(16)
C(1)-O(1)-C(4)-C(5)	-123.94(15)
C(12)-N(1)-C(5)-C(6)	83.6(2)
C(12)-N(1)-C(5)-C(4)	-149.60(16)
O(1)-C(4)-C(5)-N(1)	-67.37(18)
C(3)-C(4)-C(5)-N(1)	174.56(15)
O(1)-C(4)-C(5)-C(6)	60.69(18)
C(3)-C(4)-C(5)-C(6)	-57.4(2)
C(4)-O(1)-C(1)-O(2)	177.20(15)
C(4)-O(1)-C(1)-C(2)	-2.08(17)
C(19)-O(4)-C(22)-C(21)	0.46(17)
C(19)-O(4)-C(22)-C(23)	-123.57(15)
N(2)-C(23)-C(22)-O(4)	-65.70(18)
C(24)-C(23)-C(22)-O(4)	62.76(19)
N(2)-C(23)-C(22)-C(21)	176.79(15)
C(24)-C(23)-C(22)-C(21)	-54.8(2)
C(23)-N(2)-C(30)-C(31)	18.2(3)
C(23)-N(2)-C(30)-C(35)	-165.87(16)
C(29)-C(24)-C(25)-C(26)	-0.2(3)
C(23)-C(24)-C(25)-C(26)	178.80(18)
O(1)-C(4)-C(3)-C(2)	0.95(18)
C(5)-C(4)-C(3)-C(2)	122.90(16)
N(1)-C(5)-C(6)-C(11)	-126.57(17)
C(4)-C(5)-C(6)-C(11)	108.66(18)
N(1)-C(5)-C(6)-C(7)	53.8(2)
C(4)-C(5)-C(6)-C(7)	-70.9(2)
C(18)-O(3)-C(17)-C(16)	13.4(3)
C(18)-O(3)-C(17)-C(12)	-166.60(16)
N(1)-C(12)-C(17)-C(16)	-176.30(16)
C(13)-C(12)-C(17)-C(16)	1.4(3)
N(1)-C(12)-C(17)-O(3)	3.7(2)
C(13)-C(12)-C(17)-O(3)	-178.59(14)
C(7)-C(6)-C(11)-C(10)	0.9(3)
C(5)-C(6)-C(11)-C(10)	-178.71(17)

C(25)-C(24)-C(29)-C(28)	-0.4(3)
C(23)-C(24)-C(29)-C(28)	-179.33(18)
N(1)-C(12)-C(13)-C(14)	175.86(17)
C(17)-C(12)-C(13)-C(14)	-1.8(2)
O(4)-C(22)-C(21)-C(20)	-0.20(19)
C(23)-C(22)-C(21)-C(20)	121.50(16)
C(11)-C(6)-C(7)-C(8)	-1.3(3)
C(5)-C(6)-C(7)-C(8)	178.32(17)
C(12)-C(13)-C(14)-C(15)	0.7(3)
C(22)-C(21)-C(20)-C(19)	-0.1(2)
C(36)-O(6)-C(35)-C(34)	10.3(3)
C(36)-O(6)-C(35)-C(30)	-169.75(18)
C(31)-C(30)-C(35)-O(6)	-179.35(16)
N(2)-C(30)-C(35)-O(6)	4.5(2)
C(31)-C(30)-C(35)-C(34)	0.6(3)
N(2)-C(30)-C(35)-C(34)	-175.57(16)
O(3)-C(17)-C(16)-C(15)	179.99(16)
C(12)-C(17)-C(16)-C(15)	-0.1(3)
C(13)-C(14)-C(15)-C(16)	0.7(3)
C(17)-C(16)-C(15)-C(14)	-1.1(3)
C(4)-C(3)-C(2)-C(1)	-2.21(19)
O(2)-C(1)-C(2)-C(3)	-176.48(18)
O(1)-C(1)-C(2)-C(3)	2.72(19)
C(22)-O(4)-C(19)-O(5)	179.38(17)
C(22)-O(4)-C(19)-C(20)	-0.54(18)
C(21)-C(20)-C(19)-O(5)	-179.5(2)
C(21)-C(20)-C(19)-O(4)	0.4(2)
O(6)-C(35)-C(34)-C(33)	-179.72(18)
C(30)-C(35)-C(34)-C(33)	0.3(3)
C(6)-C(11)-C(10)-C(9)	-0.1(3)
C(6)-C(7)-C(8)-C(9)	0.9(3)
C(24)-C(25)-C(26)-C(27)	0.3(3)
C(31)-C(32)-C(33)-C(34)	-0.1(4)
C(35)-C(34)-C(33)-C(32)	-0.6(3)
C(24)-C(29)-C(28)-C(27)	0.8(3)
C(25)-C(26)-C(27)-C(28)	0.2(4)

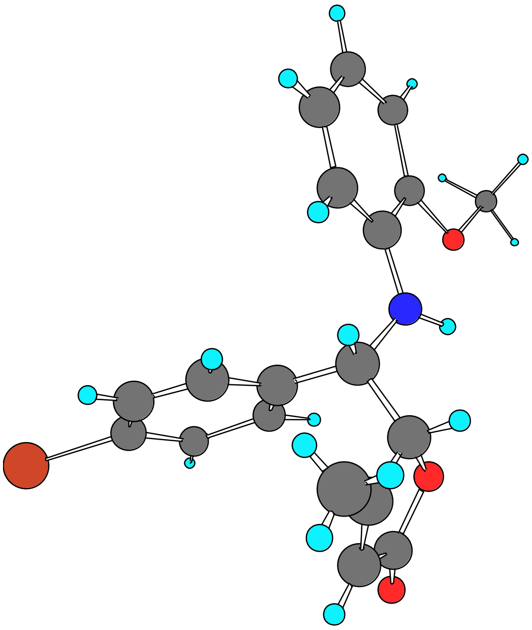
C(29)-C(28)-C(27)-C(26)	-0.7(3)
C(7)-C(8)-C(9)-C(10)	-0.1(3)
C(11)-C(10)-C(9)-C(8)	-0.3(3)
C(33)-C(32)-C(31)-C(30)	1.0(3)
N(2)-C(30)-C(31)-C(32)	174.66(18)
C(35)-C(30)-C(31)-C(32)	-1.3(3)

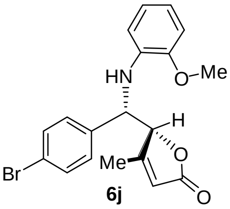
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for EC01t [Å and °]

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

X-ray crystal structure of Mannich product 6j.





6j

Table 7. Crystal data and structure refinement for **6j**

Identification code	ec106t
Empirical formula	C19 H18 Br N O3
Formula weight	388.25
Temperature	193(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.1751(16) Å	α= 90°
	b = 7.4936(16) Å	β= 92.840(4)°
	c = 16.863(4) Å	γ = 90°
Volume	905.6(3) Å^3	
Z	2	
Density (calculated)	1.424 mg/m^3	
Absorption coefficient	2.285 mm^{-1}	
F(000)	396	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.21 to 27.90°	
Index ranges	–9<=h<=5, –9<=k<=9, –22<=l<=21	
Reflections collected	6309	
Independent reflections	4143 [R(int) = 0.0224]	
Completeness to theta = 27.90°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8037 and 0.6579	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4143 / 1 / 219	
Goodness-of-fit on F^2	0.967	
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1513	
R indices (all data)	R1 = 0.0637, wR2 = 0.1621	
Absolute structure parameter	0.012(12)	
Largest diff. peak and hole	1.271 and –0.495 e.Å^{-3}	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ec106t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	3446(1)	9493(1)	-300(1)	103(1)
O(1)	7131(3)	4513(5)	2457(2)	63(1)
O(2)	4542(3)	4779(3)	3141(1)	39(1)
O(3)	3036(3)	9705(4)	4486(1)	46(1)
N(1)	1696(4)	7112(4)	3582(2)	35(1)
C(1)	5525(5)	4107(5)	2536(2)	43(1)
C(2)	4282(5)	2948(4)	2061(2)	41(1)
C(3)	2579(4)	3024(4)	2325(2)	34(1)
C(4)	2593(4)	4286(4)	3017(2)	33(1)
C(5)	853(5)	2088(4)	2025(2)	42(1)
C(6)	1440(4)	6000(4)	2874(2)	30(1)
C(7)	521(4)	8527(4)	3703(2)	33(1)
C(8)	-1299(5)	8643(5)	3391(2)	42(1)
C(9)	-2420(6)	10078(6)	3571(3)	55(1)
C(10)	-1732(6)	11411(6)	4080(3)	58(1)
C(11)	63(5)	11333(5)	4398(2)	45(1)
C(12)	1196(5)	9918(4)	4211(2)	38(1)
C(13)	3774(7)	11005(6)	5028(3)	57(1)
C(14)	1916(4)	6918(4)	2110(2)	29(1)
C(15)	3612(5)	7773(4)	2032(2)	36(1)
C(16)	4077(5)	8506(5)	1311(2)	46(1)
C(17)	2810(7)	8437(6)	676(2)	54(1)
C(18)	1104(7)	7640(6)	739(2)	57(1)
C(19)	691(5)	6863(5)	1451(2)	42(1)

Table 9. Bond lengths [Å] and angles [°] for ec106t

Br(1)-C(17)	1.901(4)
O(1)-C(1)	1.206(5)
O(2)-C(1)	1.366(5)
O(2)-C(4)	1.451(4)
O(3)-C(12)	1.387(4)
O(3)-C(13)	1.421(4)
N(1)-C(7)	1.376(4)
N(1)-C(6)	1.461(4)
N(1)-H(1)	0.8800
C(1)-C(2)	1.457(5)
C(2)-C(3)	1.323(5)
C(2)-H(2)	0.9500
C(3)-C(5)	1.490(4)
C(3)-C(4)	1.502(4)
C(4)-C(6)	1.541(4)
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(14)	1.513(4)
C(6)-H(6)	1.0000
C(7)-C(8)	1.386(5)
C(7)-C(12)	1.419(5)
C(8)-C(9)	1.386(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.391(6)
C(9)-H(9)	0.9500
C(10)-C(11)	1.372(6)
C(10)-H(10)	0.9500
C(11)-C(12)	1.382(5)
C(11)-H(11)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800

C(14)-C(19)	1.384(4)
C(14)-C(15)	1.387(5)
C(15)-C(16)	1.389(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.371(6)
C(16)-H(16)	0.9500
C(17)-C(18)	1.371(7)
C(18)-C(19)	1.380(6)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500

C(1)-O(2)-C(4)	109.2(2)
C(12)-O(3)-C(13)	117.0(3)
C(7)-N(1)-C(6)	120.5(3)
C(7)-N(1)-H(1)	119.8
C(6)-N(1)-H(1)	119.8
O(1)-C(1)-O(2)	121.4(3)
O(1)-C(1)-C(2)	130.7(4)
O(2)-C(1)-C(2)	107.8(3)
C(3)-C(2)-C(1)	109.8(3)
C(3)-C(2)-H(2)	125.1
C(1)-C(2)-H(2)	125.1
C(2)-C(3)-C(5)	129.1(3)
C(2)-C(3)-C(4)	108.6(3)
C(5)-C(3)-C(4)	122.3(3)
O(2)-C(4)-C(3)	104.0(2)
O(2)-C(4)-C(6)	108.4(2)
C(3)-C(4)-C(6)	114.8(2)
O(2)-C(4)-H(4)	109.8
C(3)-C(4)-H(4)	109.8
C(6)-C(4)-H(4)	109.8
C(3)-C(5)-H(5A)	109.5
C(3)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(3)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5

H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(14)	114.3(3)
N(1)-C(6)-C(4)	107.6(2)
C(14)-C(6)-C(4)	111.7(2)
N(1)-C(6)-H(6)	107.6
C(14)-C(6)-H(6)	107.6
C(4)-C(6)-H(6)	107.6
N(1)-C(7)-C(8)	124.4(3)
N(1)-C(7)-C(12)	117.5(3)
C(8)-C(7)-C(12)	118.0(3)
C(9)-C(8)-C(7)	120.7(3)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	120.0(4)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(11)-C(10)-C(9)	120.5(4)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(10)-C(11)-C(12)	119.7(3)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(11)-C(12)-O(3)	125.0(3)
C(11)-C(12)-C(7)	121.0(3)
O(3)-C(12)-C(7)	114.1(3)
O(3)-C(13)-H(13A)	109.5
O(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	117.5(3)
C(19)-C(14)-C(6)	120.6(3)
C(15)-C(14)-C(6)	121.8(3)
C(14)-C(15)-C(16)	121.1(3)
C(14)-C(15)-H(15)	119.5

C(16)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	119.3(3)
C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	121.1(4)
C(18)-C(17)-Br(1)	120.1(3)
C(16)-C(17)-Br(1)	118.8(3)
C(17)-C(18)-C(19)	118.8(4)
C(17)-C(18)-H(18)	120.6
C(19)-C(18)-H(18)	120.6
C(18)-C(19)-C(14)	122.1(4)
C(18)-C(19)-H(19)	118.9
C(14)-C(19)-H(19)	118.9

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters (Å^{2}x 10^3) for ec106t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	139(1)	116(1)	60(1)	47(1)	42(1)	42(1)
O(1)	32(1)	59(2)	99(2)	-22(2)	4(1)	-1(1)
O(2)	36(1)	37(1)	42(1)	-5(1)	-10(1)	4(1)
O(3)	53(1)	49(1)	36(1)	-14(1)	-4(1)	-6(1)
N(1)	40(1)	35(1)	28(1)	-9(1)	0(1)	3(1)
C(1)	34(2)	35(2)	60(2)	-7(2)	-3(2)	6(1)
C(2)	36(2)	30(1)	58(2)	-12(2)	10(2)	4(1)
C(3)	36(2)	25(1)	40(2)	-3(1)	1(1)	-1(1)
C(4)	39(2)	25(1)	33(1)	1(1)	2(1)	-1(1)
C(5)	36(2)	28(1)	63(2)	-11(2)	1(2)	-5(1)
C(6)	32(1)	31(1)	28(1)	-5(1)	5(1)	-2(1)
C(7)	38(2)	33(1)	28(1)	-1(1)	10(1)	-3(1)
C(8)	40(2)	40(2)	48(2)	-11(2)	10(2)	-5(1)
C(9)	41(2)	52(2)	71(3)	-11(2)	8(2)	5(2)
C(10)	64(3)	40(2)	73(3)	-16(2)	25(2)	7(2)
C(11)	63(2)	33(2)	40(2)	-9(1)	15(2)	-4(2)
C(12)	49(2)	35(2)	30(1)	-2(1)	14(1)	-4(1)
C(13)	75(3)	50(2)	45(2)	-13(2)	-17(2)	-7(2)
C(14)	32(1)	25(1)	29(1)	-4(1)	2(1)	5(1)
C(15)	39(2)	31(1)	38(2)	2(1)	2(1)	1(1)
C(16)	53(2)	33(2)	53(2)	6(2)	17(2)	3(2)
C(17)	80(3)	47(2)	35(2)	10(2)	16(2)	19(2)
C(18)	73(3)	63(2)	33(2)	1(2)	-6(2)	13(2)
C(19)	48(2)	43(2)	34(2)	-11(1)	-4(1)	6(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ec106t

	x	y	z	U(eq)
H(1)	2608	6875	3935	41
H(2)	4641	2242	1626	49
H(4)	2162	3651	3496	39
H(5A)	1148	1305	1583	64
H(5B)	-80	2970	1841	64
H(5C)	357	1374	2453	64
H(6)	95	5650	2822	36
H(8)	-1783	7728	3049	51
H(9)	-3658	10152	3347	66
H(10)	-2512	12383	4208	70
H(11)	525	12246	4745	54
H(13A)	3047	11008	5505	86
H(13B)	3706	12186	4778	86
H(13C)	5079	10719	5175	86
H(15)	4469	7858	2478	43
H(16)	5260	9050	1259	55
H(18)	222	7622	299	68
H(19)	-473	6272	1489	50

Table 12. Torsion angles [°] for ec106t

C(4)-O(2)-C(1)-O(1)	171.2(4)
C(4)-O(2)-C(1)-C(2)	-7.8(4)
O(1)-C(1)-C(2)-C(3)	-174.0(4)
O(2)-C(1)-C(2)-C(3)	4.9(4)
C(1)-C(2)-C(3)-C(5)	179.5(3)
C(1)-C(2)-C(3)-C(4)	0.0(4)
C(1)-O(2)-C(4)-C(3)	7.6(3)
C(1)-O(2)-C(4)-C(6)	-115.0(3)
C(2)-C(3)-C(4)-O(2)	-4.5(3)
C(5)-C(3)-C(4)-O(2)	176.0(3)
C(2)-C(3)-C(4)-C(6)	113.8(3)
C(5)-C(3)-C(4)-C(6)	-65.7(4)
C(7)-N(1)-C(6)-C(14)	70.1(4)
C(7)-N(1)-C(6)-C(4)	-165.2(3)
O(2)-C(4)-C(6)-N(1)	-60.9(3)
C(3)-C(4)-C(6)-N(1)	-176.7(3)
O(2)-C(4)-C(6)-C(14)	65.4(3)
C(3)-C(4)-C(6)-C(14)	-50.4(3)
C(6)-N(1)-C(7)-C(8)	26.0(5)
C(6)-N(1)-C(7)-C(12)	-157.0(3)
N(1)-C(7)-C(8)-C(9)	177.0(4)
C(12)-C(7)-C(8)-C(9)	0.0(5)
C(7)-C(8)-C(9)-C(10)	-0.9(6)
C(8)-C(9)-C(10)-C(11)	0.9(7)
C(9)-C(10)-C(11)-C(12)	0.0(6)
C(10)-C(11)-C(12)-O(3)	179.1(4)
C(10)-C(11)-C(12)-C(7)	-1.0(5)
C(13)-O(3)-C(12)-C(11)	2.9(5)
C(13)-O(3)-C(12)-C(7)	-177.0(3)
N(1)-C(7)-C(12)-C(11)	-176.2(3)
C(8)-C(7)-C(12)-C(11)	1.0(5)
N(1)-C(7)-C(12)-O(3)	3.7(4)
C(8)-C(7)-C(12)-O(3)	-179.1(3)
N(1)-C(6)-C(14)-C(19)	-130.9(3)

C(4)-C(6)-C(14)-C(19)	106.5(3)
N(1)-C(6)-C(14)-C(15)	51.9(4)
C(4)-C(6)-C(14)-C(15)	-70.6(4)
C(19)-C(14)-C(15)-C(16)	-1.6(5)
C(6)-C(14)-C(15)-C(16)	175.7(3)
C(14)-C(15)-C(16)-C(17)	2.3(5)
C(15)-C(16)-C(17)-C(18)	-0.7(6)
C(15)-C(16)-C(17)-Br(1)	178.6(3)
C(16)-C(17)-C(18)-C(19)	-1.5(6)
Br(1)-C(17)-C(18)-C(19)	179.1(3)
C(17)-C(18)-C(19)-C(14)	2.3(6)
C(15)-C(14)-C(19)-C(18)	-0.8(5)
C(6)-C(14)-C(19)-C(18)	-178.0(3)

Symmetry transformations used to generate equivalent atoms: