A Novel Asymmetric Synthesis of Atropisomeric 6-Aryl Pyrazinones via an Unusual Chirality Transfer Process.

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Structural, Analytical and Medicinal Chemistry

Kalamazoo, MI 49001-0199

Supporting Information

X-Ray Crystallography

Single crystal X-ray analysis of **4** (see Figure S1) established the absolute configuration as being (*aS*) about the aryl-heteroaryl bond. Similarly, the relative and absolute stereochemistry of **11a** and **12a** (Figures S2 and S3) were established as (*aR,R*) and (*aS,R*), respectively.

Spectroscopic and Elemental Analyses

(*aR,R*)-6-(2-α-Chlorophenyl)-3-[(1-phenylethyl)amino]-5-chloro-1-(1-furylmethyl)-2(1H)-pyrazinone (4): Mp 137.9-140.0 °C; $[I]_D$ -7° (*c* 0.7611, $CHCl_3$); FTIR (mineral oil mull) 3379, 3079, 3060, 3031, 1660, 1595, 1566, 1502, 1431, 1426, 1318, 1223, 1149, 1010, 773, 744, 735, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.52-7.24 (m, 10 H), 6.66 (d, 1 H, *J* = 10.0 Hz), 6.22-6.21 (m, 1 H), 5.92 (d, 1 H, *J* = 3.3 Hz), 5.31 (d, 1 H, *J* = 15.1 Hz), 5.30-5.25 (m, 1 H), 4.46 (d, 1 H, *J* = 15.2 Hz), 1.61 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 150.8, 148.5, 148.2, 142.7, 142.2, 135.4, 133.5, 131.0,

130.7, 129.5, 128.6, 127.4, 127.1, 126.9, 126.3, 120.5, 110.3, 109.2, 50.1, 42.3, 21.8; MS *m/z* (EI) 441, 439 (M+·), 358, 254, 105, 81. Anal. calcd for $C_{23}Cl_2H_{19}N_3O_2$: C, 62.74; H, 4.35; N, 9.54. Found: C, 62.45; H, 4.40; N, 9.44. HRMS (EI) calcd for $C_{23}Cl_2H_{19}N_3O_2$ (M+·): 439.0854; found: 439.0829.

(*R,R*)- α-[(1-Phenylethyl)amino]- α -(2-bromophenyl)acetonitrile hydrochloride 7b: Mp 141.5-157.0 °C; $[I]_D$ +120° (*c* 0.8917, EtOH); FTIR (mineral oil mull) 2632, 2612, 2586, 2565, 2544, 2524, 2489, 2443, 2414, 2400, 2380, 1557, 1475, 1027, 779, 770, 749, 702 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 7.97 (dd, 1 H, *J* = 7.8, 1.6 Hz), 7.72 (dd, 1 H, *J* = 8.0, 1.2 Hz), 7.63-7.54 (m, 6 H), 7.48 (m, 1 H), 5.39 (s, 1 H), 4.76 (q, 1 H, *J* = 6.8 Hz), 1.81 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 135.6, 135.2, 134.6, 132.3, 131.8, 131.0, 130.4, 129.5, 129.3, 125.4, 114.6, 60.7, 51.3, 19.9; MS *m/z* (EI) 314 (M+· - HCl), 299, 287, 194, 105. Anal. calcd for $C_{16}BrClH_{16}N_2$: C, 54.65; H, 4.59; N, 7.97; Br, 22.72; Cl, 10.08. Found: C, 54.62; H, 4.65; N, 7.96; Br, 22.34; Cl, 10.00. HRMS (FAB) calcd for $C_{16}BrH_{16}N_2$ (M+· - Cl): 315.0497, found: 315.0492.

(*S,R*)- α -[(1-Phenylethyl)amino]- α -(2-bromophenyl)acetonitrile hydrochloride 6b: Mp 144.0-146.8 °C; $[I]_D$ +53° (*c* 1.0148, MeOH); FTIR (mineral oil mull) 2783, 2740, 2699, 2688, 2655, 2619, 2590, 2555, 2514, 2402, 1565, 1553, 1479, 1441, 1029, 770, 759, 701 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 7.87-7.80 (m, 2 H), 7.60-7.49 (m, 7 H), 5.97 (s, 1 H), 4.65 (q, 1 H, *J* = 6.8 Hz), 1.83 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 136.4, 135.4, 134.5, 131.7, 131.4, 130.8, 130.4, 129.2, 128.0, 115.0, 61.0, 51.3, 19.6; MS *m/z* (EI) 316, 314 (M+· - HCL) 299, 237, 194, 120, 105. Anal. calcd for $C_{16}BrClH_{16}N_2$: C, 54.65; H, 4.59; N, 7.80; Br, 22.72; Cl, 10.08. Found: C, 54.53; H, 4.64; N, 7.86; Br, 22.73; Cl, 10.14.

(*S,S*)- α -[(1-Phenylethyl)amino]- α -(2-iodophenyl)acetonitrile 5a: Mp 103.4-105.5 °C; $[I]_D$ -151° (*c* 0.8758, EtOH); FTIR (mineral oil mull) 3306, 3058, 3030, 3023, 3003, 1476, 1451, 1438, 1433, 1114, 1015, 929, 771, 750, 707, 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.84 (dd, 1 H, *J* = 7.9, 1.2 Hz), 7.64 (dd, 1 H, *J* = 7.8, 1.6 Hz), 7.52-7.29 (m, 6 H), 7.06 (ddd, 1 H, *J* = 9.2, 7.6, 1.6 Hz), 4.58 (s,

1 H), 4.23 (q, 1 H, J = 6.5 Hz), 1.67 (s, 1 H), 1.46 (d, 3 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) L 141.9, 140.3, 137.9, 130.6, 129.0, 128.7, 128.6, 127.9, 127.6, 118.6, 98.5, 56.9, 56.8, 24.1; MS *m/z* (EI) 362 (M+·), 347, 285, 242, 105. Anal. calcd for $C_{16}H_{15}IN_2$: C, 53.06; H, 4.17; N, 7.73. Found: C, 53.21; H, 4.22; N, 7.59. HRMS (EI) calcd for $C_{16}H_{15}IN_2$ (M+·): 362.0282; found: 362.0270.

(*R,R*)- α -[(1-Phenylethyl)amino]- α -(2-iodophenyl)acetonitrile hydrochloride 7a: mp 142.0-157.0 °C; $[I]_D$ +50° (*c* 0.9849, EtOH); FTIR (mineral oil mull) 2636, 2611, 2586, 2566, 2546, 2524, 2484, 2441, 2413, 2399, 2381, 1557, 1016, 777, 770, 747, 702 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.99 (dd, 1 H, J = 8.0, 1.2 Hz), 7.94 (dd, 1 H, J = 7.9, 1.5 Hz), 7.65-7.54 (m, 6 H), 7.28 (dt, 1 H, J = 7.9, 1.5 Hz), 5.27 (s, 1 H), 4.76 (q, 1 H, J = 6.8 Hz), 1.81 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 142.2, 135.5, 134.3, 132.7, 131.9, 131.6, 131.2, 131.1, 129.7, 114.8, 101.1, 60.7, 56.4, 19.8; MS *m/z* (FAB) 363 (M· + 2 H), 336, 242, 232, 105. Anal. calcd for $C_{16}ClH_{16}IN_2$: C, 48.20; H, 4.04; N, 7.03; Cl, 8.89. Found: C, 48.23; H, 4.06; N, 7.06; Cl, 8.92.

(*S,S*)- α -[(1-Phenylethyl)amino]- α -(2-bromophenyl)acetonitrile 5b: Mp 107.4-109.5 °C; $[I]_D$ -175° (*c* 1.0021, $CHCl_3$); FTIR (mineral oil mull) 3310, 3065, 3033, 3025, 3006, 1495, 1473, 1437, 1342, 1114, 1059, 1027, 930, 836, 787, 772, 751, 707, 633 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) L 7.64-7.21 (m, 9 H), 4.67 (s, 1 H), 4.23 (q, 1 H, J = 6.5 Hz), 1.57 (br s, 1 H), 1.45 (d, 3 H, J = 6.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 142.1, 134.6, 133.6, 130.6, 129.2, 128.6, 128.1, 127.9, 127.3, 123.1, 118.4, 56.8, 52.4, 24.3; MS *m/z* (EI) 314 (M+·), 299, 194, 105, 77. Anal. calcd for $C_{16}BrH_{15}N_2$: C, 60.97; H, 4.80; N, 8.89; Br, 25.35. Found: C, 61.01; H, 4.75; N, 8.69; Br, 25.29. HRMS (EI) calcd for $C_{16}BrH_{15}N_2$ (M+·): 314.0419; found: 314.0405.

(*R,S*)- α -[(1-Phenylethyl)amino]- α -(2-bromophenyl)acetonitrile hydrochloride 8b: Mp 134.8-137.0 °C; $[I]_D$ -16° (*c* 0.8829, MeOH); FTIR (mineral oil mull) 2783, 2700, 2687, 2655, 2618, 2590, 2556, 2514, 2471, 2402, 2386, 1565, 1553, 1479, 1441, 1029, 770, 759, 701 cm-1; 1H NMR (300 MHz, CD_3OD) L 7.86-7.80 (m, 2 H), 7.62-7.50 (m, 7 H), 5.97 (s, 1 H), 4.65 (q, 1 H, J = 6.8 Hz), 1.85

(d, 3 H, J = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 136.9, 135.4, 134.4, 131.6, 131.3, 130.8, 130.4, 129.6, 129.1, 125.6, 115.2, 60.9, 51.6, 19.7; MS *m/z* (EI) 287 ($M^{\cdot}$ - HCl, HCN), 272, 105. Anal. calcd for $C_{16}BrClH_{16}N_2$: C, 54.65; H, 4.59; N, 7.80; Br, 22.72; Cl, 10.08. Found: C, 54.81; H, 4.63; N, 7.99; Br, 22.72; Cl, 9.87. HRMS (FAB) calcd for $C_{16}BrH_{15}N_2$ ($M^{\cdot}$ - HCl): 315.0497; found: 315.0492.

(*R,R*)- α -[(1-Phenylethyl)amino]- α -(2-chlorophenyl)acetonitrile 7c: Mp 149.8-160.0 °C (dec); $[I]_D$ +121° (*c* 0.9765, MeOH); FTIR (mineral oil mull) 2617, 2587, 2553, 2538, 2504, 2453, 2401, 2359, 2307, 1553, 1479, 1423, 1029, 778, 771, 766, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) L 7.61-7.58 (m, 1 H), 7.48-7.31 (m, 8 H), 4.67 (s, 1 H), 4.24 (q, 1 H, J = 6.5 Hz), 1.77 (br s, 1 H), 1.44 (d, 3 H, J = 6.5 Hz); MS *m/z* (FAB) 273, 271 ($M^{\cdot}$ + H), 244, 150, 140, 105. Anal. calcd for $C_{16}ClH_{15}N_2$: C, 62.55; H, 5.25; N, 9.12; Cl 23.08. Found: C, 62.16; H, 5.21; N, 9.00; Cl, 22.74.

(*S,S*)- α -[(1-Phenylethyl)amino]- α -(2-fluorophenyl)acetonitrile hydrochloride 5d: Mp 130.0-133.2 °C; $[I]_D$ -58° (*c* 1.0225, MeOH); FTIR (mineral oil mull) 2693, 2617, 2586, 2558, 2541, 2506, 2470, 2451, 2409, 2372, 2351, 2309, 1556, 1497, 1240, 772, 765, 703 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.78-7.26 (m, 9 H), 5.43 (s, 1 H), 4.70 (q, 1 H, J = 6.9 Hz), 1.76 (d, 3 H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 163.2, 159.9, 136.2, 135.4, 135.2, 131.6, 131.5, 131.0, 128.8, 126.9, 126.8, 117.7, 117.5, 117.2, 114.5, 60.4, 45.7, 45.6, 20.3; MS *m/z* (EI) 254 ($M^{\cdot}$ - HCl), 239, 227, 134, 105. Anal. calcd for $C_{16}ClFH_{16}N_2$: C, 66.09; H, 5.55; N, 9.63. Found: C, 65.84; H, 5.68; N, 9.24.

(*R,R*)- α -[(1-phenylethyl)amino]- α -(2-fluorophenyl)acetonitrile hydrochloride 7d: Mp 131.5-132.7 °C; $[I]_D$ +61° (*c* 0.9549, MeOH); FTIR (mineral oil mull) 2618, 2586, 2558, 2542, 2506, 2470, 2451, 2409, 2371, 2350, 2309, 1556, 1497, 1240, 772, 765, 755, 708, 703 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.76-7.26 (m, 9 H), 5.43 (s, 1 H), 4.70 (q, 1 H, J = 6.8 Hz), 1.75 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 163.2, 159.9, 136.1, 135.4, 135.3, 131.8, 131.5, 131.0, 128.9, 126.9, 126.8, 117.7, 117.4, 117.1, 114.4, 60.5, 45.5, 45.5, 20.3; MS *m/z* (EI) 254 ($M^{\cdot}$ - HCl), 239, 177, 149,

134, 105, 77. Anal. calcd for $C_{16}ClFH_{16}N_2$: C, 66.09; H, 5.55; N, 9.63; Cl, 12.19. Found: C, 65.88; H, 5.74; N, 9.24; Cl, 11.81. HRMS (EI) calcd for $C_{15}FH_{15}N_2$ (M· - HCl): 254.1219; found: 254.1205.

(*S,S*)- α -[(1-Phenylethyl)amino]- α-(2-methylphenyl)acetonitrile 5e: Mp 121.2-124.5 °C; $[I]_D$ -202° (*c* 0.8528, $CHCl_3$); FTIR (mineral oil mull) 3301, 1494, 1473, 1462, 1453, 1443, 1358, 1114, 1107, 962, 922, 840, 792, 769, 756, 708, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.59-7.16 (m, 9 H), 4.39 (br s, 1 H), 4.24 (q, 1 H, *J* = 6.5 Hz), 2.13 (s, 3 H), 1.56 (br s, 1 H), 1.43 (d, 3 H, *J* = 6.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 142.5, 136.2, 133.3, 131.0, 129.0, 128.6, 127.9, 127.2, 126.5, 119.0, 56.8, 50.1, 24.2, 18.5; MS *m/z* (EI) 250 (M+·), 235, 223, 173, 145, 130, 119, 105, 77. Anal. calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.62; H, 7.23; N, 11.03.

(*R,R*)- α -[(1-Phenylethyl)amino]- α-(2-methylphenyl)acetonitrile hydrochloride 7e: Mp 121.2-135.0 °C; $[I]_D$ +80° (*c* 0.9418, MeOH); FTIR (mineral oil mull) 2694, 2627, 2588, 2544, 2511, 2466, 2453, 2407, 2372, 1557, 773, 767, 704, 700 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 7.78-7.31 (m, 9 H), 5.14 (s, 1 H), 4.74 (q, 1 H, *J* = 6.8 Hz), 1.92 (s, 3 H), 1.78 (d, 3 H, *J* = 6.9 Hz); MS *m/z* (FAB) 251 (M· - HCl + 2 H), 235, 224, 173, 145, 130, 120, 105. Anal. calcd for $C_{17}ClH_{19}N_2$: C, 71.19; H, 6.68; N, 9.77; Cl, 12.36. Found: C, 69.42; H, 6.60; N, 9.41; Cl, 12.30. HRMS (FAB) calcd for $C_{17}H_{19}N_2$ (M· - Cl): 251.1548; found, 251.1555.

(*R,R*)- α-[(1-Phenylethyl)amino]- α-(2-trifluoromethylphenyl)acetonitrile hydrochloride 7f: Mp 143.1-146.0 °C; $[I]_D$ +57° (*c* 0.9832, MeOH); FTIR (mineral oil mull) 2621, 2590, 2561, 2548, 2508, 2466, 2451, 2405, 2366, 1558, 1317, 1168, 1124, 1037, 787, 775, 768, 705, 667 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 8.18 (d, 1 H, *J* = 7.9 Hz), 7.91-7.77 (m, 3 H), 7.54 (br s, 5 H), 5.01 (s, 1 H), 4.73 (q, 1 H, *J* = 6.8 Hz), 1.80 (d, 3 H, *J* = 6.9 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 135.7, 135.2, 133.3, 132.4, 131.7, 131.0, 129.3, 128.5, 128.4, 128.0, 114.7, 61.0, 47.5, 19.9; MS *m/z* (EI) 304 (M· - HCl), 289, 277, 262, 184, 105. Anal. calcd for $C_{17}ClF_3H_{16}N_2$: C, 59.92; H, 4.73; N, 8.22. Found: C, 59.64; H, 4.77; N, 8.04.

(*S,S*)- α-[(1-Phenylethyl)amino]- α-(2-methoxyphenyl)acetonitrile hydrochloride 5g: Mp 139.0-142.7 °C; $[\Pi]_D$ -95° (*c* 0.8691, EtOH); FTIR (mineral oil mull) 2635, 2612, 2596, 2559, 2542, 2524, 2495, 2444, 2411, 1604, 1496, 1259, 773, 764, 759, 752, 703 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 7.64 (dd, 1 H, *J* = 8.0, 1.7 Hz), 7.59-7.49 (m, 6 H), 7.14-7.09 (m, 2 H), 5.40 (s, 1 H), 4.65 (q, 1 H, *J* = 6.8 Hz), 3.78 (s, 3 H), 1.76 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 158.2, 136.1, 134.7, 131.4, 131.1, 130.8, 129.1, 122.5, 116.9, 114.9, 112.9, 60.3, 56.4, 46.7, 20.1; MS *m/z* (EI) 266 ($M^{\cdot}$ - HCl), 251, 161, 146, 134, 119, 105. Anal. calcd for $C_{17}ClH_{19}N_2O$: C, 67.43; H, 6.32; N, 9.25; Cl, 11.71. Found: C, 66.76; H, 6.42; N, 9.09; Cl, 11.44. HRMS (EI) calcd for $C_{16}H_{18}N_2O$ ($M^{\cdot}$ - HCl): 266.1419; found: 266.1410.

(*R,R*)- α-[(1-Phenylethyl)amino]- α-(2-methoxyphenyl)acetonitrile hydrochloride 7g: Mp 139.0-142.9 °C; $[\Pi]_D$ +91° (*c* 0.9703, EtOH); FTIR (mineral oil mull) 2636, 2612, 2596, 2558, 2542, 2526, 2495, 2455, 2440, 2409, 1604, 1552, 1496, 1259, 773, 764, 758, 752, 702 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) L 7.63 (dd, 1 H, *J* = 8.0, 1.7 Hz), 7.58-7.52 (m, 6 H), 7.14-7.10 (m, 2 H), 5.40 (s, 1 H), 4.64 (q, 1 H, *J* = 6.9 Hz), 3.78 (s, 3 H), 1.75 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 158.2, 136.1, 134.7, 131.4, 131.1, 130.8, 129.2, 122.5, 116.9, 114.9, 112.9, 60.3, 56.4, 46.7, 20.1; MS *m/z* (EI) 266 ($M^{\cdot}$ - HCl), 251, 224, 146, 105. Anal. calcd for $C_{17}ClH_{19}N_2O$: C, 67.43; H, 6.32; N, 9.25; Cl, 11.71. Found: C, 67.14; H, 6.34; N, 9.42; Cl, 11.82. HRMS (EI) calcd for $C_{16}H_{18}N_2O$ ($M^{\cdot}$ - HCl): 266.1419; found: 266.1409.

(*S,S*)- α-[(1-Phenylethyl)amino]- α-(2,3-difluorophenyl)acetonitrile hydrochloride 5h: MP 130°C; ^1H NMR (300 MHz, CD_3OD) L 7.76 (dd, 1 H, *J* = 5.2, 1.5 Hz), 7.66-7.64 (m, 2H), 7.48-7.46 (m, 3 H), 7.18 (m, 3 H), 4.85 (s, 1 H), 4.49 (q, 1 H, *J* = 6.8 Hz), 1.37 (d, 3 H, *J* = 6.7 Hz); MS *m/z* (Es) 272.2 (M+1).

(*R,R*)- α-[(1-Phenylethyl)amino]- α-(3-methylphenyl)acetonitrile hydrochloride 7i: ^{1}H NMR (300 MHz, CD_3OD) L 7.53-7.37 (m, 9 H), 5.26 (s, 1H), 4.90 (s, 1 H), 4.63 (q, 1 H, J = 6.8 Hz), 2.40 (s, 3H), 1.75 (d, 3 H, J = 6.7 Hz)

(*R,R*)- α-[(1-Phenylethyl)amino]- α-(1-napthyl)acetonitrile hydrochloride 7j: ^{1}H NMR (300 MHz, CD_3OD) L 7.53-7.37 (m, 9 H), 5.26 (s, 1H), 4.90 (s, 1 H), 4.63 (q, 1 H, J = 6.8 Hz), 2.40 (s, 3H), 1.75 (d, 3 H, J = 6.7 Hz); MS *m/z* (Es) 287.2 (M+1).

(*S,S*)- α-[(1-Phenylethyl)amino]- α-(1-thienyl)acetonitrile hydrochloride 5k: Mp 164.2-166.0 °C; $[I]_D$ -46° (*c* 0.9006, MeOH); FTIR (mineral oil mull) 2764, 2742, 2716, 2661, 2627, 2591, 2566, 2536, 2480, 2436, 2425, 2403, 2369, 1436, 1388, 775, 700, 601 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.76 (dd, 1 H, J = 5.2, 1.5 Hz), 7.52-7.46 (m, 6 H), 7.18 (dd, 1 H, J = 5.2, 3.7 Hz), 5.81 (s, 1 H), 4.56 (q, 1 H, J = 6.8 Hz), 1.74 (d, 3 H, J = 6.7 Hz); ^{13}C NMR (75.5 MHz, CD_3OD) L 136.3, 133.5, 132.0, 131.4, 131.0, 129.7, 129.2, 129.0, 114.8, 59.6, 46.1, 19.8; MS *m/z* (FAB) 485 ($2M^+$ + H), 243 (M + H), 216, 122, 112, 105. Anal. calcd for $C_{14}ClH_{15}N_2S$: C, 60.31; H, 5.42; N, 10.05; Cl, 12.72; S, 11.50. Found: C, 59.92; H, 5.52; N, 9.86; Cl, 12.71; S, 11.21.

(*R,R*)- α-[(1-phenylethyl)amino]- α-(1-thienyl)acetonitrile hydrochloride 7k: Mp 164.8-166.9 °C; $[I]_D$ +46° (*c* 0.7689, MeOH); FTIR (mineral oil mull) 2764, 2742, 2716, 2660, 2625, 2591, 2566, 2535, 2480, 2436, 2424, 2402, 2369, 1436, 1388, 775, 722, 700 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.76 (dd, 1 H, J = 5.2, 1.5 Hz), 7.52-7.47 (m, 6 H), 7.18 (dd, 1 H, J = 4.1, 2.6 Hz), 5.84 (s, 1 H), 4.57 (q, 1 H, J = 6.8 Hz), 1.76 (d, 3 H, J = 6.8 Hz); MS *m/z* (FAB) 485 ($2M^+$ + H), 243 (M + H), 227, 216, 122, 112, 105, 77. Anal. calcd for $C_{14}ClH_{15}N_2S$: C, 60.31; H, 5.42; N, 10.05; Cl, 12.72; S, 11.50. Found: C, 60.23; H, 5.55; N, 9.93; Cl, 12.99; S, 11.15.

(*R,S*)- α-[(1-Phenylethyl)amino]- α-(1-thienyl)acetonitrile hydrochloride 8k: Mp 142.3-145.2 °C; $[I]_D$ +2° (*c* 1.0229, MeOH); FTIR (mineral oil mull) 2746, 2713, 2629, 2617, 2583, 2466, 2415, 2387, 2369, 1433, 1426, 985, 704 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) L 7.78 (dd, 1 H, J = 5.1,

0.8 Hz), 7.51-7.48 (m, 5 H), 7.44 (dd, 1 H, J = 3.6, 2.0 Hz), 7.19 (dd, 1 H, J = 5.2, 3.7 Hz), 6.10 (s, 1 H), 4.73 (q, 1 H, J = 6.8 Hz), 1.71 (d, 3 H, J = 6.9 Hz); MS *m/z* (FAB) 243 ($M^{\cdot}$ + H), 216, 139, 122, 105. Anal. calcd for $C_{14}ClH_{15}N_2S$: C, 60.31; H, 5.42; N, 10.05. Found: C, 60.13; H, 5.50; N, 9.90.

(*aS,S*) 6-(2-α-Iodophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9a): Mp 160.0-166.8 °C; $[I]_D$ -84° (*c* 1.0159, $CHCl_3$); FTIR (mineral oil mull) 3064, 3049, 3029, 3000, 1679, 1560, 1498, 1450, 1433, 1367, 1343, 1157, 1146, 1031, 939, 817, 766, 757, 741, 697, 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 8.03 (d, 1 H, J = 8.1 Hz), 7.47-7.21 (m, 8 H), 5.23 (br s, 1 H), 1.83 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.8, 147.8, 140.1, 139.5, 137.0, 135.5, 131.7, 130.2, 128.7, 127.7, 125.0, 99.5, 60.6, 16.3; MS *m/z* (EI) 469 ($M^{+\cdot}$), 365, 105. Anal. calcd for $C_{18}Cl_2H_{13}IN_2O$: C, 45.89; H, 2.78; N, 5.95; Cl, 15.05. Found: C, 45.90; H, 2.86; N, 5.67; Cl, 15.15. HRMS (EI) calcd for $C_{18}Cl_2H_{13}IN_2O$ ($M^{+\cdot}$): 469.9451, found: 469.9463.

(*aR,R*) 6-(2-α-Iodophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11a): Mp 162.2-164.0 °C; $[I]_D$ +89° (*c* 0.986, EtOH); FTIR (mineral oil mull) 3000, 1679, 1560, 1450, 1433, 1367, 1271, 1157, 1147, 1031, 939, 817, 766, 757, 742, 697, 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 8.03 (d, 1 H, J = 7.4 Hz), 7.47-7.21 (m, 8 H), 5.23 (br s, 1 H), 1.83 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.6, 147.8, 140.1, 139.5, 137.0, 135.5, 131.8, 130.2, 128.7, 128.1, 127.8, 127.7, 125.0, 99.5, 60.6, 16.3; MS *m/z* (EI) 470 ($M^{+\cdot}$), 366, 105. Anal. calcd for $C_{18}Cl_2H_{13}IN_2O$: C, 45.89; H, 2.78; N, 5.95; Cl, 15.05. Found: C, 45.87; H, 2.85; N, 5.75; Cl, 15.04. HRMS (EI) calcd for $C_{18}Cl_2H_{13}IN_2O$ ($M^{+\cdot}$): 469.9451, found: 469.9443.

(*aS,R*) 6-(2-α-Iodophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (12a): Mp 155.3-156.9 °C; $[I]_D$ +80° (*c* 0.9890, $CHCl_3$); FTIR (mineral oil mull) 1675, 1587, 1566, 1499, 1450, 1344, 1144, 1028, 1018, 942, 818, 767, 759, 755, 744, 701, 603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 8.05 (dd, 1 H, J = 8.5, 1.6 Hz), 7.53 (dt, 1 H, J = 7.5, 1.1 Hz), 7.36-7.19 (m, 7 H), 4.94 (q, 1 H, J = 6.9 Hz), 2.06 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.4, 148.3, 140.0, 140.0, 137.7, 136.1,

131.9, 130.3, 129.0, 128.4, 127.8, 126.6, 124.5, 98.5, 61.8, 17.0; MS *m/z* (EI) 470 (M+·), 366, 105. Anal. calcd for $C_{18}Cl_2H_{13}IN_2O$: C, 45.89; H, 2.78; N, 5.95; Cl, 15.05. Found: C, 45.82; H, 2.77; N, 5.88; Cl, 14.84. HRMS (EI) calcd for $C_{18}Cl_2H_{13}IN_2O$ (M+·): 469.9451, found: 469.9450.

(*aS,S*) 6-(2-α-Bomophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9b): Mp 42.0-149.1 °C; $[I]_D$ -153° (*c* 1.0393, $CHCl_3$); FTIR (mineral oil mull) 3068, 1679, 1587, 1560, 1499, 1451, 1437, 1425, 1157, 1148, 1030, 941, 818, 766, 758, 742, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.79-7.76 (m, 1 H); 7.42-7.26 (m, 7 H); 7.13 (br s, 1 H), 5.27 (br s, 1 H), 1.82 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.5, 148.0, 137.1, 133.7, 132.0, 131.7, 130.6, 128.2, 128.0, 127.8, 127.4, 125.0, 124.0, 60.5, 15.9; MS *m/z* (EI) 422 (M+·), 318, 289, 105. Anal. calcd for $C_{18}BrCl_2H_{13}N_2O$: C, 50.98; H, 3.09; N, 6.60; Br, 18.84; Cl, 16.72. Found: C, 51.13; H, 3.14; N, 6.58; Br, 18.85; Cl, 16.27. HRMS (EI) calcd for $C_{18}BrCl_2H_{13}N_2O$ (M+.): 421.9589, found: 421.9589.

(*aR,S*) 6-(2-α-Bromophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (10b): Mp 121.8-122.9 °C; $[I]_D$ -84° (*c* 1.0062, $CHCl_3$); FTIR (mineral oil mull) 1675, 1590, 1569, 1500, 1451, 1426, 1345, 1156, 1144, 1027, 944, 819, 768, 756, 746, 702, 603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.79 (d, 1 H, J = 7.5 Hz), 7.54-7.20 (m, 8 H), 4.98 (q, 1 H, J = 6.9 Hz), 2.02 (d, 3 H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.4, 148.3, 137.5, 137.4, 133.7, 132.2, 132.1, 131.0, 128.4, 127.8, 126.7, 124.5, 123.6, 61.7, 16.5; MS *m/z* (EI) 422 (M+·), 320, 105. Anal. calcd for $C_{18}BrCl_2H_{13}N_2O$: C, 50.98; H, 3.09; N, 6.60; Br, 18.84; Cl, 16.72. Found: C, 51.46; H, 3.19; N, 6.31; Br, 18.36; Cl, 16.57. HRMS (EI) calcd for $C_{18}BrCl_2H_{13}N_2O$ (M+.): 421.9589, found: 421.9586.

(*aR,R*) 6-(2-α-Bromophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11b): Mp 143.8-149.0 °C; $[I]_D$ +154° (*c* 1.0068, $CHCl_3$); FTIR (mineral oil mull) 3068, 1679, 1587, 1560, 1499, 1451, 1436, 1425, 1157, 1148, 1030, 941, 818, 766, 758, 742, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.80-7.76 (m, 1 H), 7.42-7.26 (m, 8 H), 5.26 (br s, 1 H), 1.82 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.5, 147.9, 137.1, 137.0, 133.7, 132.0, 131.7, 130.6, 128.2, 128.0, 127.8, 127.4, 125.0,

124.0, 60.6, 15.9; MS *m/z* (EI) 422 (M+·), 318, 105. Anal. calcd for $C_{18}BrCl_2H_{13}N_2O$: C, 50.98; H, 3.09; N, 6.60; Br, 18.84; Cl, 16.72. Found: C, 50.84; H, 3.13; N, 6.59; Br, 18.55; Cl, 16.85. HRMS (EI) calcd for $C_{18}BrCl_2H_{13}N_2O$ (M+.): 421.9589, found: 421.9593.

(*aS,R*) 6-(2-α-Bromophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (12b): Mp 120.6-121.8 °C; $[I]_D$ +85° (*c* 1.0402, $CHCl_3$); FTIR (mineral oil mull) 1675, 1590, 1569, 1500, 1450, 1426, 1345, 1156, 1144, 1027, 944, 819, 768, 756, 746, 702, 603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.80 (dd, 1 H, *J* = 7.9, 1.3 Hz), 7.55-7.20 (m, 8 H), 4.98 (q, 1 H, *J* = 6.9 Hz), 2.02 (d, 3 H, *J* = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.4, 148.3, 137.5, 137.4, 133.7, 132.2, 132.1, 131.0, 128.4, 127.8, 126.7, 124.5, 123.6, 61.7, 16.5; MS *m/z* (EI) 422 (M+·), 318, 289, 105. Anal. calcd for $C_{18}BrCl_2H_{13}N_2O$: C, 50.98; H, 3.09; N, 6.60; Br, 18.84; Cl, 16.72. Found: C, 50.94; H, 3.20; N, 6.57; Br, 18.49; Cl, 16.37. HRMS (EI) calcd for $C_{18}BrCl_2H_{13}N_2O$ (M+·): 421.9589, found: 421.9579.

(*aR,R*) 6-(2-α-Chlorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11c): Mp 160.4-161.9 °C; $[I]_D$ +180° (*c* 0.9959, $CHCl_3$); FTIR (mineral oil mull) 1678, 1592, 1560, 1499, 1449, 1431, 1349, 1158, 1145, 1054, 1029, 942, 816, 761, 744, 730, 698, 603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.62-7.15 (m, 9 H), 5.23 (br s, 1 H), 1.82 (d, 3 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.5, 148.0, 137.0, 135.7, 134.1, 132.0, 130.5, 130.4, 129.8, 128.2, 127.8, 127.5, 127.2, 125.1, 60.5, 15.7; MS *m/z* (EI) 378 (M+·), 274, 105, 77. Anal. calcd for $C_{18}Cl_3H_{13}N_2O$: C, 56.94; H, 3.45; N, 7.38; Cl, 28.01. Found: C, 57.00; H, 3.52; N, 7.34; Cl, 27.89.

(*aS,S*) 6-(2-α-Fluorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9d) and (*aR,S*) 6-(2-α-Fluorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (10d): Mp 130.2-132.5 °C; $[I]_D$ -145° (*c* 0.9841, $CHCl_3$); FTIR (mineral oil mull) 1676, 1564, 1500, 1482, 1450, 1351, 1228, 1159, 1152, 1140, 1104, 1028, 820, 807, 760, 755, 742, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.57-7.04 (m, 9 H), 5.37 (br s, 0.5 H), 5.25 (br s, 0.5 Hz), 1.93 (d, 1.5 H, *J* = 7.0 Hz), 1.82 (d, 1.5 Hz, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 161.1, 161.0, 157.8, 157.6, 151.5, 148.3, 148.1, 137.1, 133.1,

133.0, 132.9, 131.1, 130.3, 128.3, 127.8, 127.8, 126.9, 126.8, 125.2, 125.2, 125.1, 125.0, 118.9, 118.7, 116.8, 116.7, 116.5, 116.4, 60.9, 60.3, 15.3; MS *m/z* (EI) 362 (M+·), 258, 105. Anal. calcd for $C_{18}Cl_2FH_{13}N_2O$: C, 59.52; H, 3.61; N, 7.71; Cl, 19.52. Found: C, 59.50; H, 3.62; N, 7.59; Cl 19.19. HRMS (EI) calcd for $C_{18}Cl_2FH_{13}N_2O$ (M+·): 362.0389, found: 362.0393.

(*aR,R*) 6-(2-α-Fluorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11d) and (*aS,R*) 6-(2-α-Fluorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (12d): Mp 133.8-138.9 °C; $[\Gamma]_D$ +143° (*c* 0.9901, $CHCl_3$); FTIR (mineral oil mull) 1676, 1564, 1482, 1450, 1351, 1152, 1140, 1104, 1028, 940, 820, 760, 754, 742, 696, 605 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.57-7.17 (m, 9 H), 5.39 (br s, 0.5 H), 5.25 (br s, 0.5 H), 1.93 (d, 1.5 H, *J* = 7.0 Hz), 1.82 (d, 1.5 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 161.1, 161.0, 157.8, 157.6, 151.5, 151.4, 148.4, 148.1, 137.1, 133.1, 133.0, 132.9, 131.1, 130.3, 128.3, 127.8, 127.8, 126.9, 126.8, 125.2, 125.1, 125.0, 125.0, 118.9, 118.7, 116.7, 116.5, 116.4, 60.9, 60.3, 15.4, 15.3; MS *m/z* (EI) 362 (M+·), 258, 105. Anal. calcd for $C_{18}Cl_2FH_{13}N_2O$: C, 59.52; H, 3.61; N, 7.71; Cl, 19.52. Found: C, 59.56; H, 3.59; N, 7.65; Cl, 19.52.

(*aS,S*) 6-(2-α-Methylphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9e): Mp 136.7-138.7 °C; $[\Gamma]_D$ -118° (*c* 1.0218, $CHCl_3$); FTIR (mineral oil mull) 1672, 1560, 1500, 1482, 1450, 1367, 1341, 1216, 1144, 1113, 936, 812, 765, 752, 739, 694, 604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.46-7.16 (m, 9 H), 5.29 (br s, 1 H), 2.30 (s, 3 H), 1.85 (d, 3 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.9, 147.4, 138.2, 137.4, 137.0, 131.2, 131.0, 130.7, 130.2, 129.1, 128.5, 128.3, 127.7, 127.1, 126.7, 126.6, 124.4, 61.1, 19.7, 16.3; MS *m/z* (EI) 358 (M+·), 254, 219, 105. Anal. calcd for $C_{19}Cl_2H_{16}N_2O$: C, 63.52; H, 4.49; N, 7.80; Cl, 19.74. Found: C, 63.45; H, 4.56; N, 7.71; Cl, 19.81. HRMS (EI) calcd for $C_{19}Cl_2H_{16}N_2O$ (M+·): 358.0640, found: 358.0648.

(*aR,R*) 6-(2-α-Methylphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11e): Mp 122.8-131.1 °C; $[\Gamma]_D$ +106° (*c* 1.0328, $CHCl_3$); FTIR (mineral oil mull) 3002, 1672, 1560, 1450, 1367, 1341, 1216, 1144, 1113, 1028, 935, 812, 765, 752, 739, 694, 604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L

7.48-7.16 (m, 9 H), 5.18 (br s, 1 H), 2.30 (s, 3 H), 1.89 (d, 1.5 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.9, 147.4, 138.1, 137.4, 137.0, 136.7, 131.2, 131.0, 130.7, 130.7, 130.2, 129.1, 128.5, 128.3, 128.3, 127.8, 127.7, 127.1, 126.7, 126.6, 61.1, 60.7, 19.6, 19.5, 16.6, 16.2; MS *m/z* (EI) 358 (M+·), 254, 219, 105. Anal. calcd for $C_{19}Cl_2H_{16}N_2O$: C, 63.52; H, 4.49; N, 7.80; Cl, 19.74. Found: C, 63.50; H, 4.60; N, 7.76; Cl, 19.24. HRMS (EI) calcd for $C_{19}Cl_2H_{16}N_2O$ (M+·): 358.0640, found: 358.0648.

(*aR,R*) 6-(2-α-Trifluromethylphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11f): Mp 152.1-155.9 °C; $[I]_D$ +160° (*c* 0.9519, $CHCl_3$); FTIR (mineral oil mull) 1680, 1563, 1446, 1315, 1291, 1273, 1176, 1158, 1145, 1134, 1114, 1055, 1036, 819, 774, 737, 644, 604 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) L 7.85 (d, 1 H, J = 8.7 Hz), 7.71-7.69 (m, 2 H), 7.28-7.26 (m, 3 H), 7.13-7.12 (m, 3 H), 5.27 (br s, 1 H), 1.78 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.6, 148.0, 136.9, 135.7, 132.4, 131.1, 130.8, 129.7, 129.3, 128.2, 128.0, 127.9, 127.7, 126.5, 125.1, 124.6, 121.5, 60.6, 16.6; MS *m/z* (EI) 414, 412 (M+·), 308, 105. Anal. calcd for $C_{19}Cl_2F_3H_{13}N_2O$: C, 55.23; H, 3.17; N, 6.78; Cl, 17.16. Found: C, 55.25; H, 3.17; N, 6.75; Cl, 17.51.

(*aS,S*) 6-(2-α-Methoxyphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9g): Mp 180.9-183.0 °C; $[I]_D$ -102° (*c* 0.943, $CHCl_3$); FTIR (mineral oil mull) 1666, 1601, 1564, 1500, 1481, 1450, 1433, 1284, 1259, 1245, 1156, 1145, 1113, 1043, 1024, 821, 790, 765, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) L 7.56-7.50 (m, 1 H), 7.32-7.04 (m, 8 H), 5.18 (s, 1 H), 3.87 (s, 3 H), 1.80 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 156.5, 151.6, 146.9, 137.6, 136.3, 132.3, 129.9, 128.0, 127.4, 126.8, 124.8, 121.2, 119.7, 111.6, 60.6, 55.5, 15.2; MS *m/z* (EI) 374 (M+·), 270, 235, 105. Anal. calcd for $C_{19}Cl_2H_{16}N_2O_2$: C, 60.81; H, 4.30; N, 7.47; Cl, 18.90. Found: C, 60.68; H, 4.33; N, 7.43; Cl, 18.77. HRMS (EI) calcd for $C_{19}Cl_2H_{16}N_2O_2$ (M+·): 374.0589, found: 374.0589.

(*aR,R*) 6-(2-α-Methoxyphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11g): Mp 180.9-184.1 °C; $[I]_D$ +115° (*c* 1.0018, $CHCl_3$); FTIR (mineral oil mull) 1669, 1602, 1561, 1499,

1482, 1451, 1435, 1367, 1282, 1142, 1 117, 1027, 812, 764, 759, 753, 744, 733, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl^3$) L 7.55-7.50 (m, 1 H), 7.37-7.04 (m, 8 H), 5.19 (br s, 1 H), 3.86 (s, 3 H), 1.80 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 156.4, 151.4, 146.7, 137.5, 136.1, 132.2, 130.7, 129.7, 127.4, 126.8, 126.7, 121.1, 119.6, 111.4, 60.5, 55.3, 15.1; MS *m/z* (EI) 376, 374 (M+), 270, 235, 105. Anal. calcd for $C_{19}Cl_2H_{16}N_2O_2$: C, 60.81; H, 4.30; N, 7.47; Cl, 18.90. Found: C, 60.48; H, 4.36; N, 7.37; Cl, 18.74.

(*aS,S*) 6-(2,3-α-Difluorophenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9h): Mp 181.2-183.8 °C; $[I]_D$ -154° (*c* 0.9756, $CHCl_3$); FTIR (mineral oil mull) 1681, 1568, 1497, 1482, 1449, 1354, 1278, 1215, 1160, 1149, 1035, 1025, 989, 820, 802, 793, 765, 744, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.40-7.17 (m, 7 H), 6.84 (br s, 1 H), 5.39 (br s, 1 H), 1.83 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, CDCl3) L 152.4, 151.4, 149.6, 149.5, 149.2, 148.7, 146.3, 146.2, 136.9, 131.3, 128.4, 127.9, 126.8, 125.4, 125.3, 125.2, 125.1, 120.9, 120.7, 120.2, 120.0, 60.3, 15.4; MS *m/z* (EI) 382, 380 (M+), 276, 105. Anal. calcd for $C_{18}Cl_2F_2H_{12}N_2O$: C, 56.71; H, 3.17; N, 7.35; Cl, 18.60. Found: C, 56.64; H, 3.17; N, 7.29; Cl, 18.29.

(*aR,R*) 6-(3-α-Methylphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11i) and (*aS,R*) 6-(3-α-Methylphenyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (12i): Mp 141.9-143.8 °C; $[I]_D$ +112° (*c* 1.0052, $CHCl_3$); FTIR (mineral oil mull) 3030, 1676, 1670, 1585, 1559, 1497, 1479, 1350, 1153, 1138, 964, 836, 816, 793, 763, 741, 710, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.44-7.00 (m, 9 H), 5.36 (br s, 0.5 H), 5.21 (br s, 0.5 H), 2.43 (s, 1.5 H), 2.39 (s, 1.5 H), 1.85 (d, 1.5 H, J = 7.0 Hz), 1.84 (d, 1.5 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.4, 147.2, 147.0, 139.4, 139.3, 138.8, 138.8, 137.6, 137.5, 131.1, 130.8, 130.8, 129.5, 129.3, 129.1, 128.9, 128.2, 128.2, 127.6, 126.8, 126.7, 126.2, 125.4, 124.2, 124.0, 60.4, 60.0, 21.4, 21.3, 15.7, 15.6; MS *m/z* (EI) 358 (M+), 254, 105. Anal. calcd for $C_{19}Cl_2H_{16}N_2O$: C, 63.52; H, 4.49; N, 7.80. Found: C, 62.81; H, 4.55; N, 7.74.

(*aR,R*) 6-(α-Napthyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11j): Mp 200-210 °C (dec.); $[\Gamma]_D$ +78° (*c* 1.0190, $CHCl_3$); FTIR (mineral oil mull) 1679, 1579, 1557, 1498, 1451, 1341, 1251, 1227, 1162, 1155, 1148, 1030, 821, 806, 798, 782, 766, 740, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl^3$) L 8.06 (d, 1 H, *J* = 8.3 Hz), 8.01-7.97 (m, 1 H), 7.73-7.58 (m, 4 H), 7.44 (m, 1 H), 7.19-7.10 (m, 5 H), 5.06 (br s, 1 H), 1.80 (d, 3 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.8, 147.9, 137.0, 136.8, 133.6, 131.1, 130.3, 128.9, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.2, 125.2, 124.5, 61.0, 15.8; MS *m/z* (EI) 394 (M+·), 290, 105, 77. Anal. calcd for $C_{22}H_{16}N_2OCl_2$: C, 66.85; H, 4.08; N, 7.09. Found: C, 66.65; H, 4.14; N, 7.06.

(*aS,S*) 6-(1-Thienyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (9k): Mp 101.5-103 °C; $[\Gamma]_D$ -111° (*c* 0.9990, $CHCl_3$), FTIR (mineral oil mull) 3116, 3111, 3090, 1665, 1563, 1497, 1448, 1314, 1253, 1154, 1125, 1113, 849, 810, 764, 741, 733, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.62 (d, 1 H, *J* = 6.1 Hz), 7.34-7.19 (m, 7 H), 5.41 (br s, 1 H), 1.89 (d, 3 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) L 151.2, 148.9, 137.3, 131.9, 130.9, 130.2, 129.9, 128.3, 127.9, 127.7, 126.9, 126.5, 60.3, 15.5; MS *m/z* (EI) 350 (M+·), 246, 105, 77. Anal. calcd for $C_{16}Cl_2H_{12}N_2OS$: C, 54.71; H, 3.44; N, 7.97; Cl, 20.19; S, 9.13. Found: C, 54.72; H, 3.48; N, 7.91; Cl, 20.07; S, 9.08.

(*aR,R*) 6-(1-Thienyl)-3,5-dichloro-1-(1-phenylethyl)-2(1H)-pyrazinone (11k): Mp 102.2-104.7 °C; $[\Gamma]_D$ +114° (*c* 1.0426, $CHCl_3$); FTIR (mineral oil mull) 3306, 3111, 3089, 3074, 3065, 3029, 3004, 1665, 1660, 1563, 1496, 1448, 1154, 1125, 810, 741, 732, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) L 7.63 (d, 1 H, *J* = 5.8 Hz), 7.32-7.18 (m, 7 H), 5.42 (br s, 1 H), 1.89 (d, 3 H, *J* = 7.0 Hz); MS *m/z* (EI) 352, 350 (M+·), 335, 246, 105. Anal. calcd for $C_{16}Cl_2H_{12}N_2OS$: C, 54.71; H, 3.44; N, 7.97; Cl, 20.19; S, 9.13. Found: C, 54.82; H, 3.40; N, 8.02; Cl, 20.08; S, 9.13.

Reaction Kinetics Simulation

The mechanism derived from explorations of the reaction potential surfaces using the AM1 method has been examined in a simulation of the kinetics of the process **15b**+HCl→...→**19b/20b**. All of the exaggerated AM1 barriers have been scaled down so that the reaction completes within the 24h time span of the experiment. Rate constants (Table S1) have been determined from considerations of absolute reaction-rate theory.[1] The use of the CHEMKIN II program[2] to simulate actual experiments serves as a powerful tool to examine the validity of estimated rate constants. Although CHEMKIN II has been designed for gas-phase kinetics, it may be appropriately used in constant temperature studies with rate constants determined for condensed fluids. Validation of the model is provided by comparison of the results of computer the simulation (Fig. S4) with experimentally observed product yields. The capability of following reactive intermediates that are unobserved experimentally is an advantage of the procedure.

The rate constant is expressed as:

$$k = A'T^m \exp\left[-(E' + u)/RT\right]$$

where R is the gas constant, T is the absolute temperature, $E' = \alpha\Delta H_f^{\ddagger}$ is the estimated reaction barrier, and u is the desolvation energy (bimolecular ≈ 0.2 and unimolecular=0 kcal mol^{-1}). Except for the cases involving formation of weak HCl complexes with **15b**, **17b**, and **17b'**, where α=1, a scale factor of 0.65 is employed to obtain estimates of E' from the calculated AM1 barriers. The pre-exponential term in a bimolecular reaction is obtained from order-of-magnitude estimates of the partition functions for the

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[1]Frost, A.A.; Pearson,R.G. *Kinetics and Mechanism*, 2nd edn., Wiley, New York, 1961, pp 77-102.

[2] Kee, R.J.; Rupley, F.M.; Miller, J.A. *CHEMKIN II: A Fortran Package for the Analysis of Gas Phase Chemical Kinetics*, Sandia National Laboratories, Livermore, Calif. report SAND 89-8009.

reactants and transition-state complex. The following entropic factors contribute most to the value of A : 1) loss of the translational and rotational degrees of freedom of the HCl molecule upon forming the transition-state complex; 2) a term $100V/V_M$ accounting for the free volume of the condensed medium, where V (5 mL) is the total volume and V_M ($\approx$ 0.1L) is the molar volume of toluene. In the cyclization reaction, there is also a factor $(0.01T)^{-3}$ arising from the loss of rotational freedom in three single bonds of **16b** when the transition-state complex is formed.

The reaction,which proceeds at 350K, is initiated with 0.2M oxoamide intermediate **15b** and 0.1M HCl in 5mL toluene. Saturation with HCl is maintained through rapid exchange with HCl vapor at 1 atm pressure above the system. Henry's law is used to estimate the concentration of HCl in the toluene solvent. At completion of the simulated 24h reaction period, the following product yields are found: **19b** (0.126M, 63%), **20b** (2.6mM, 1.3%), and intermediate **18b′** (1.8mM, 0.9%). Only 34.5% of the initial reactant **15b** (69mM) remains at termination of the experiment. Since **19b**→**11b**, the large calculated ratio (**19b**:**20b**=48.5:1) of the atropisomeric intermediates is consistent with the observation that **11b** is the sole final product in the reaction initiated with **7b**. Also in agreement with experiment are the low levels of the intermediates **16b**, **17b**, **17b′**, **18b**, and **18b′** in the pathway.

Table S1

Rate constants[a] from absolute reaction rate theory and scaled AM1 barriers[b]

Reaction	Pre-exponential Terms in Rate Constant		Scaled Barrier	AM1 Barrier
	A'	m	$E'+u$	$\Delta H_f^{\ddagger}$
15b + HCl → **15b**·HCl	6.27E+13	-1.5	0.2	0.0
15b + HCl ← **15b**·HCl	2.08E+12	0.0	1.8	1.8
15b·HCl + HCl → **16b** + HCl	6.27E+13	-1.5	18.5	28.1
16b + HCl → **17b** + 2HCl	6.27E+19	-4.5	12.7	19.2
16b + HCl → **17b'** + 2HCl	6.27E+19	-4.5	9.9	14.8
17b + HCl → **17b**·HCl	6.27E+13	-1.5	0.2	0.0
17b + HCl ← **17b**·HCl	2.08E+12	0.0	2.8	2.8
17b' + HCl → **17b'**·HCl	6.27E+13	-1.5	0.2	0.0
17b' + HCl ← **17'**·HCl	2.08E+12	0.0	2.8	2.8
17b·HCl + HCl → **18b** + HCl	6.27E+13	-1.5	11.6	17.5
17'·HCl + HCl ← **18b'** + HCl	6.27E+13	-1.5	12.1	18.3
18b + HCl → **19b** + 2HCl	6.27E+13	-1.5	16.8	25.4
18b' + HCl → **20b** + 2HCl	6.27E+13	-1.5	22.4	34.1
17b → **17b'**	2.08E+10	1.0	5.6	8.6
17b ← **17b'**	2.08E+10	1.0	6.8	10.4
18b → **18b'**	2.08E+10	1.0	9.3	14.3
18b ← **18b'**	2.08E+10	1.0	12.2	18.7

(*a*) *The units for bimolecular and unimolecular rate constants are* $M^{-1}\,s^{-1}$ *and* s^{-1}, *respectively.*

(*b*) *Energy barriers are expressed in kcal* mol^{-1}.

Figure Captions

Figure S1. X-ray crystal structure of **4** revealing *aS* configuration about the aryl-heteroaryl bond.

Figure S2. The (*aR,R*) stereochemistry of pyrazinone **11a** established by X-ray analysis.

Figure S3. The X-ray structure of pyrazinone **12a** exhibits (*aS,R*) stereochemistry.

Figure S4. Computer simulation of the reactions from formation of the Pinner salt **16b** to the production of the dione intermediates **19b** and **20b** using the mechanism outlined in the text and estimates of rate constants based on the AM1 calculations.

Figure S1

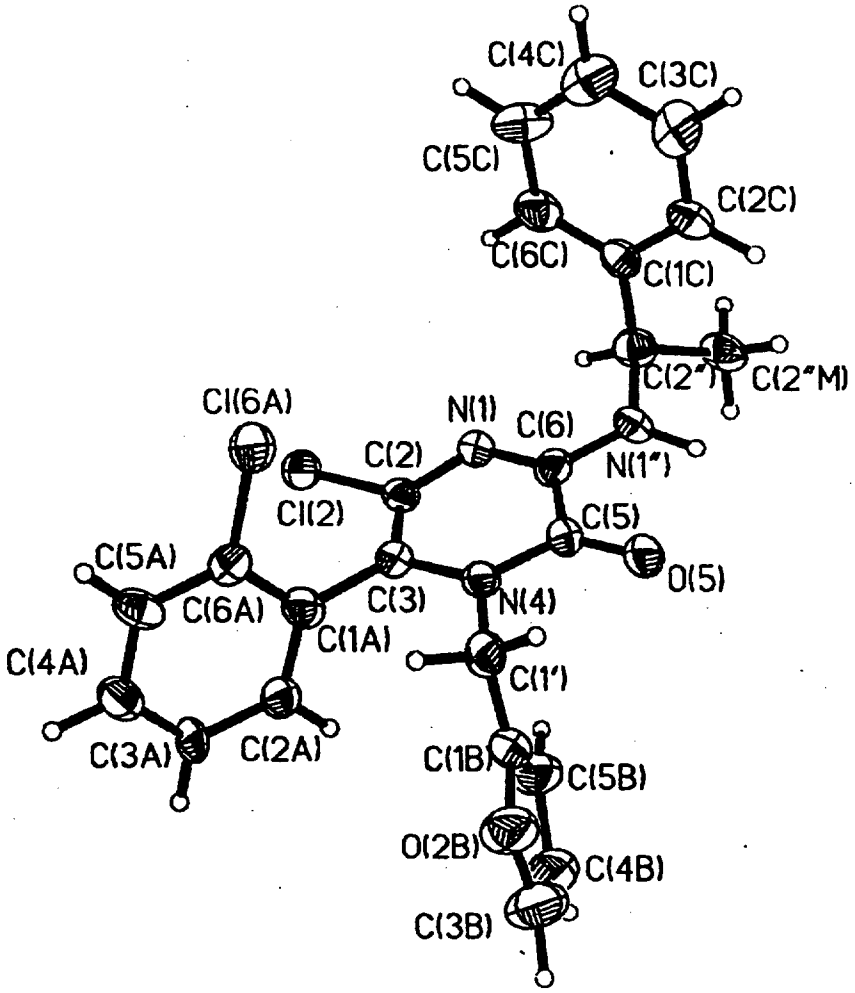

C(4C)
C(3C)
C(5C)
C(2C)
C(6C)
C(1C)
C(2")
C(2"M)
Cl(6A)
N(1)
C(6)
C(2)
N(1")
Cl(2)
C(5)
C(5A)
O(5)
C(6A)
C(3)
N(4)
C(1A)
C(4A)
C(1')
C(3A)
C(2A)
C(1B)
C(5B)
O(2B)
C(4B)
C(3B)

Figure S2

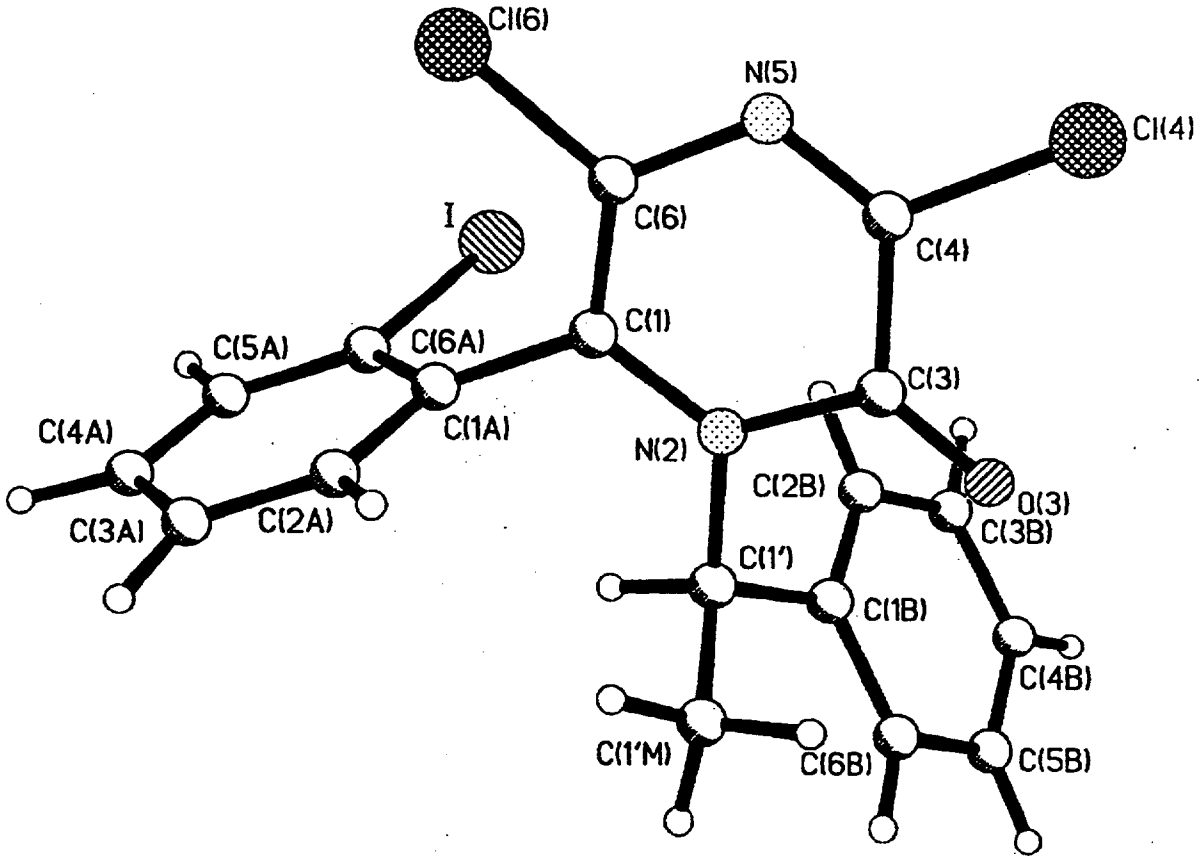


Figure S3

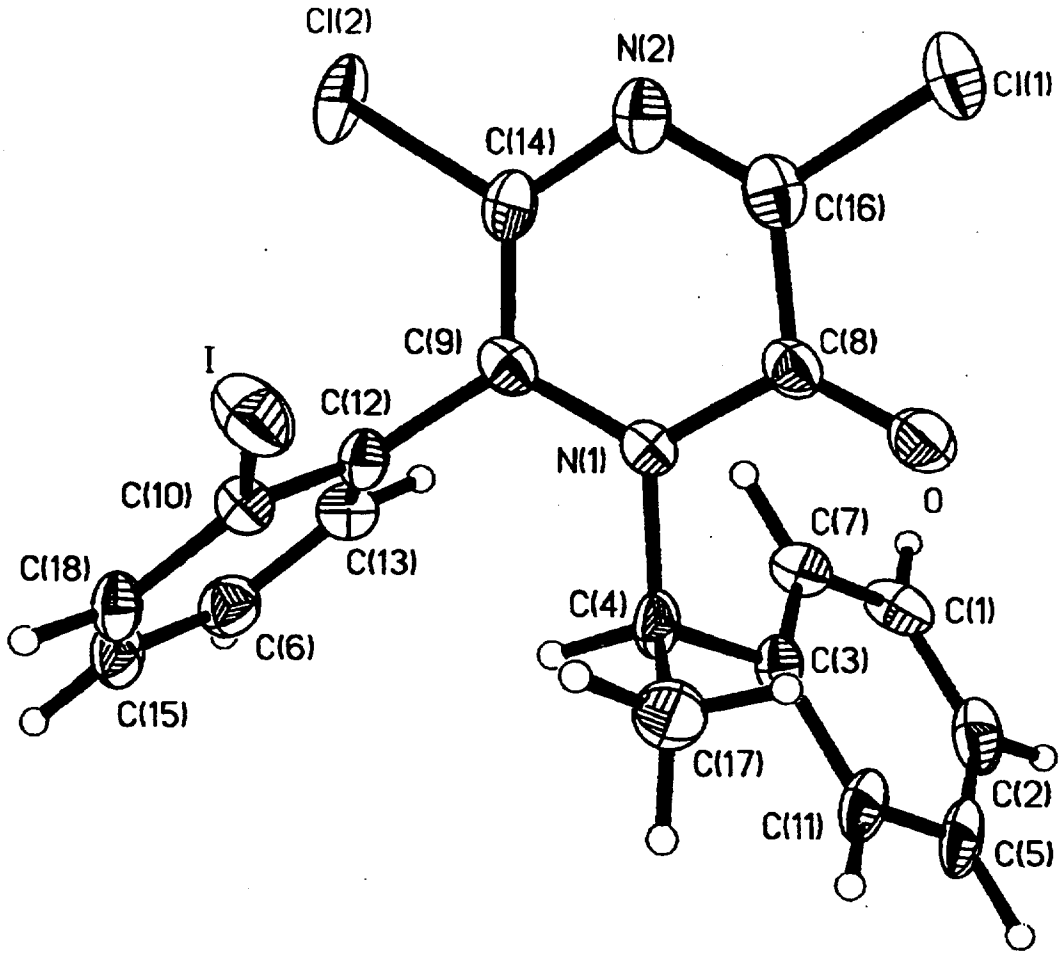
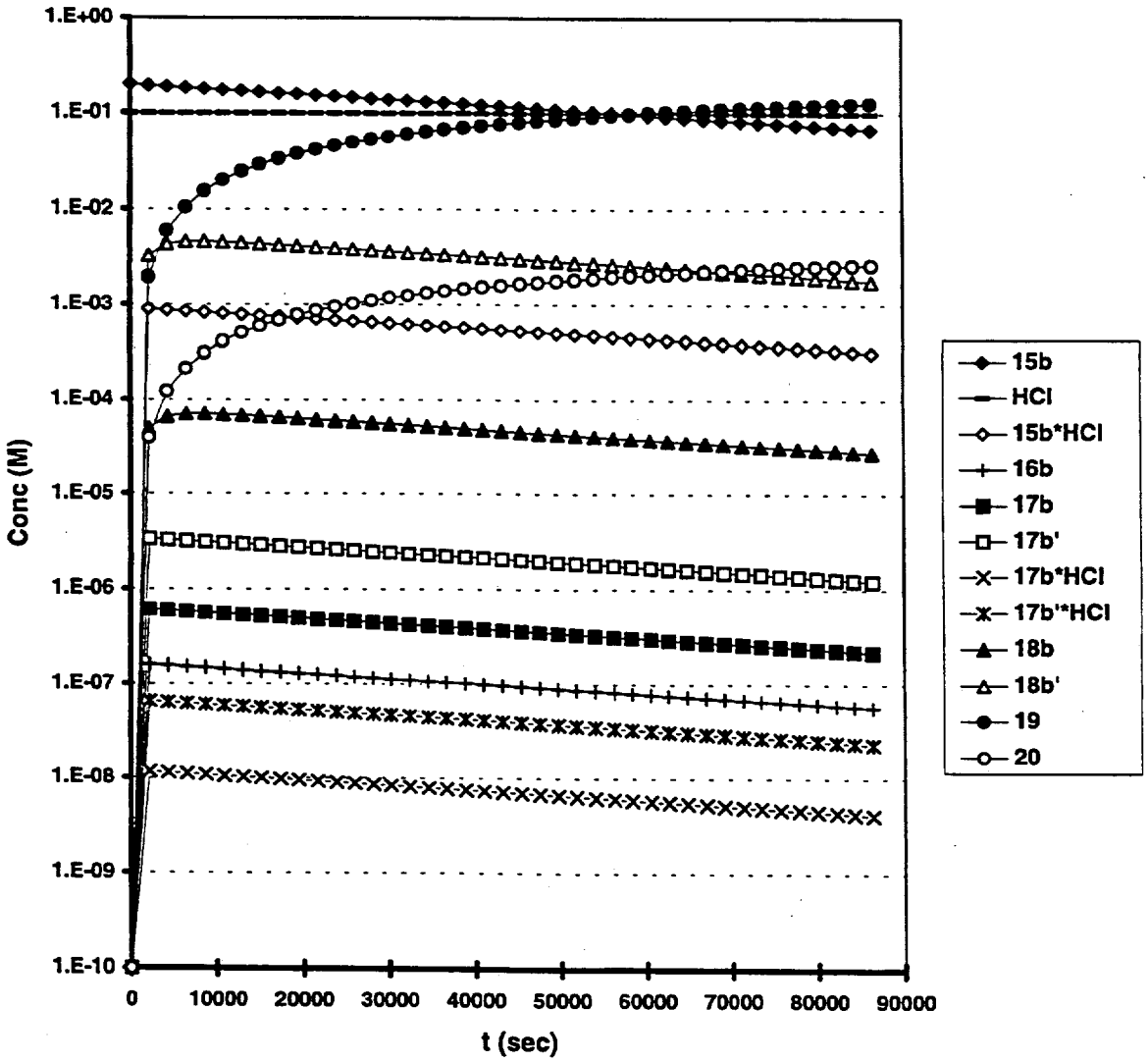


Figure S4



A Novel Asymmetric Synthesis of Atropisomeric 6-Aryl Pyrazinones via an Unusual Chirality Transfer Process.

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Crystal Data

11a: $C_{18}H_{13}N_2OCl_2I$, $M_r = 471.12$, monoclinic, $P2_1$, $a = 8.081(1)$, $b = 11.502(11)$, $c = 9.936(3)$Å, $\beta = 102.55$, $V = 901.5(8)$Å^3, $Z = 2$, $D_x = 1.735$ g cm^{-3}, $\cdot = 163.2$ cm^{-1}, S=5.58, $wR = 0.189$ for 1355 reflections [$R = 0.074$ for $F^2 > 3\sigma(F^2)$]. **12a**: $C_{18}H_{13}N_2OCl_2I$, $M_r = 471.12$, orthorhombic, $P2_12_12_1$, $a = 7.900(1)$, $b = 12.510(1)$, $c = 18.120(1)$Å, $V = 1848.5(1)$Å^3, $Z = 4$, $D_x = 1.693$ g cm^{-3}, $\cdot = 159.2$ cm^{-1}, S=7.31, $wR = 0.152$ for 1770 reflections [$R = 0.060$ for $F^2 > 3\sigma(F^2)$]. **4**: $C_{23}H_{19}N_3O_2C1_2$, $M_r = 440.33$, tetragonal, $P4_3$ $a = b = 10.073(1)$, $c = 20.647(1)$Å, $V = 1931.5(1)$Å^3, $Z = 8$, $D_x = 1.39$ g cm^3, $\cdot = 2.88$ cm^{-1}, S=2.68, $wR = 0.103$ for 1546 inflections [$R = 0.043$ for $F^2 > 3\sigma(F^2)$]. **9k**: $C_{16}H_{12}N_2OSC1_2$, $M_r = 351.25$, monoclinic, $P2_1$, $a = 8.887(1)$, $b = 10.665(1)$, $c = 17.107(1)$Å, $\beta = 101.75(2)$., $V = 1931.5(2)$Å^3, $Z = 4$, $D_x = 1.469$ g cm^{-3}, $\cdot = 4.84$ cm^{-1}, S=2.16, $wR = 0.078$ for 2225 reflections [$R = 0.032$ for $F^2 > 3\sigma(F^2)$].

Experimental

The four compounds were crystallized by slow evaporation from a variety of organic solvents ranging from methylene chloride/hexane to ethanol. The crystals used in this study were of similar size and shape with approximately 0.2 x 0.2 x 0.2 mm as their average dimensions. The crystals were each mounted with glue on the end of a glass fiber affixed in a Supper XYZ goniometer head. All of the data collections were maintained at 143 K by an LT-2 system from Siemens Corporation.

(1) Siemens Data

The Siemens data collection on structure **11a** was obtained from a $P2_1$ four-circle diffractometer with graphite-monochromatized Cu Kα radiation from a sealed tube controlled by a Harris computer. The step-scan technique was used with a scan rate of 4°/min, a scan width of 3.4°, and a $2\theta_{max}$=136°. Ten reflections periodically monitored showed no loss of intensity during the data collection. The unit cell parameters were determined accurately by a least squares fit of Cu $K\alpha_1$ 2θ values (λ(Cu $K\alpha_1$)=1.5402) for 25 high 2θ reflections.

(2) Marresearch Data

The Marresearch data collections on structures **12a**, **4** and **9k** were obtained from a MAR imaging-plate scanner (300 mm) with 5° oscillations, 100 mm crystal-to-detector distance and exposure times ranging fmm 60-120 seconds. A sealed tube with fine-focus Mo Kα graphitemonochromatized radiation was used as the source. The images were processed using the program *DENZO* (Orwinowski 1991); symmetry equivalent and Friedel pairs were merged during the data processing.

Structure determinations and refinements

The structure determinations were solved by direct methods using *MULTAN80* (Main P. *et al.,* 1980). They were refined by full-matrix least-squares with *CRYM*(Duchamp, 1984), minimizing $\Sigma w(F_o^2-F_c^2)^2$. The scattering factors were taken from Doyle & Tumer (1968), except, for hydrogens which were from Stewart, Davidson & Simpson (1965). The hydrogen positions found in difference Fourier maps were very close to the calculated positions, so the calculated positions were used. The two molecules in the asymmetric unit in structure **9k** are non-crystallographically related by 0, 0.65, 0.50.

Reterences

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Table 1. Fractional coordinates ($\times 10^4$) and B_{eq} ($Å^2$) for **11a**.

Estimated standard deviations are in parentheses.

$B_{eq}=4/3\ (a^2B_{11}+b^2B_{22},+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})$

	x	y	z	B_{eq}(Å)
C(1)	333(21)	-2684(16)	-7128(21)	1.5(6)
N(2)	9(16)	-1969(18)	-8256(13)	2.2(7)
C(3)	1272(21)	-1301(23)	-8685(22)	3.1(9)
0(3)	1081(16)	-828(17)	-9755(14)	2.9(6)
C(4)	2878(21)	-1340(22)	-7613(19)	2.6(9)
CL(4)	4428(6)	-424(7)	-7912(6)	3.56(24)
N(5)	3213(18)	-1967(18)	-6547(18)	2.6(7)
C(6)	1944(19)	-2701(17)	-6314(18)	1.2(6)
CL(6)	2468(6)	-3580(6)	-4897(5)	2.92(21)
C(1A)	-986(19)	-3447(17)	-6815(17)	1.3(6)
C(2A)	-1314(27)	-4542(26)	-7489(20)	3.1(10)
C(3A)	-2480(25)	-5305(30)	-7221(27)	4.2(11)
C(4A)	-3294(24)	-5130(24)	-6168(25)	3.0(9)
C(5A)	-3047(22)	-4068(23)	-5492(22)	2.3(7)
C(6A)	-1889(19)	-3276(18)	-5772(17)	1.4(6)
C(1')	-1719(19)	-1834(28)	-9170(18)	2.1(8)
C(1'M)	-1924(29)	-2605(22)	-10486(22)	2.8(9)
C(1B)	-2191(22)	-581(20)	-9390(24)	2.2(8)
C(2B)	-1788(21)	214(19)	-8337(19)	1.6(7)
C(3B)	-2286(25)	1337(25)	-8526(22)	3.0(9)
C(4B)	-3289(22)	1751(21)	-9807(22)	2.1(7)
C(5B)	-3721(28)	964(23)	-10876(27)	2.9(9)
C(6B)	-3161(24)	-205(21)	-10675(21)	2.2(7)
I	-1577(1)	-1682	-4710(1)	2.69(5)

N(5) C(6) CL(6)	116.0(11)	C(3B) C(4B) C(5B)	117.7(22)
C(1) C(1A) C(2A)	119.9(15)	C(4B) C(SB) C(6B)	119.5(22)
C(1) C(1A) C(6A)	126.3(17)	C(1B) C(6B) C(SB)	120.9(21)
C(2A) C(1A) C(6A)	113.4(16)		

C. Torsion angles (°)

C(6) C(1) N(2) C(3)	4.3(29)	C(4) N(5) C(6) C(1)	-5.7(28)
C(6) C(1) N(2) C(1')	-176.6(19)	C(4) N(5) C(6) CL(6)	177.5(16)
C(1A) C(1) N(2) C(3)	-173.6(19)	C(1) C(1A) C(2A) C(3A)	178.1(20)
C(1A) C(1) N(2) C(1')	5.5(28)	C(6A) C(1A) C(2A) C(3A)	4.8(28)
N(2) C(1) C(6) N(5)	4.2(27)	C(1) C(1A) C(6A) C(5A)	-176.3(17)
N(2) C(1) C(6) CL(6)	-179.2(14)	C(1) C(1A) C(6A) I	8.5(22)
C(1A) C(1) C(6) N(5)	-177.9(17)	C(2A) C(1A) C(6A) C(5A)	-3.5(24)
C(1A) C(1) C(6) CL(6)	-1.3(25)	C(2A) C(1A) C(6A) I	-178.7(12)
N(2) C(1) C(1A) C(2A)	82.7(22)	C(1A) C(2A) C(3A) C(4A)	-7.5(36)
N(2) C(1) C(1A) C(6A)	-104.9(22)	C(2A) C(3A) C(4A) C(5A)	8.2(34)
C(6) C(1) C(1A) C(2A)	-95.1(22)	C(3A) C(4A) C(5A) C(6A)	-6.9(31)
C(6) C(1) C(1A) C(6A)	77.2(23)	C(4A) C(5A) C(6A) C(1A)	4.9(29)
C(1) N(2) C(3) 0(3)	167.6(22)	C(4A) C(5A) C(6A) I	-180.0(15)
C(1) N(2) C(3) C(4)	-9.6(28)	N(2) C(1') C(1B) C(2B)	-39.2(19)
C(1') N(2) C(3) 0(3)	-11.5(33)	N(2) C(1') C(1B) C(6B)	144.7(14)
C(1') N(2) C(3) C(4)	171.3(19)	C(1'M) C(1') C(1B) C(2B)	-168.6(14)
C(1) N(2) C(1') C(1'M)	-98.3(20)	C(1'M) C(1') C(1B) C(6B)	15.4(20)
C(1) N(2) C(1') C(1B)	129.6(20)	C(1') C(1B) C(2B) C(3B)	-177.0(14)
C(3) N(2) C(1') C(1'M)	80.8(26)	C(6B) C(1B) C(2B) C(3B)	-0.9(22)
C(3) N(2) C(1') C(1B)	-51.3(21)	C(1') C(1B) C(6B) C(5B)	175.7(15)
N(2) C(3) C(4) CL(4)	-172.4(15)	C(2B) C(1B) C(6B) C(5B)	-0.5(23)
N(2) C(3) C(4) N(5)	8.4(32)	C(1B) C(2B) C(3B) C(4B)	1.7(24)
0(3) C(3) C(4) CL(4)	10.4(33)	C(2B) C(3B) C(4B) C(5B)	-1.2(24)
0(3) C(3) C(4) N(5)	-168.8(24)	C(3B) C(4B) C(5B) C(6B)	-0.2(23)
C(3) C(4) N(5) C(6)	-1.1(32)	C(4B) C(5B) C(6B) C(1B)	1.0(25)
CL(4) C(4) N(5) C(6)	179.7(14)		

Table 2. Bond lengths (Å), angles (°) and torsion angles (°) for **11a**.

A. Bond lengths (Å)

C(1) N(2)	1.368(25)	C(2A) C(3A)	1.356(35)
C(1) C(6)	1.376(20)	C(3A) C(4A)	1.366(30)
C(1) C(1A)	1.465(22)	C(4A) C(5A)	1.388(37)
N(2) C(3)	1.416(23)	C(5A) C(6A)	1.377(26)
N(2) C(1')	1.499(18)	C(6A) I	2.103(20)
C(3) 0(3)	1.174(27)	C(1') C(1'M)	1.559(32)
C(3) C(4)	1.490(23)	C(1') C(1B)	1.495(38)
C(4) CL(4)	1.711(19)	C(1B) C(2B)	1.374(31)
C(4) N(5)	1.260(28)	C(1B) C(6B)	1.413(30)
N(5) C(6)	1.386(21)	C(2B) C(3B)	1.355(35)
C(6) CL(6)	1.710(19)	C(3B) C(4B)	1.433(30)
C(1A) C(2A)	1.425(34)	C(4B) C(5B)	1.381(34)
C(1A) C(6A)	1.405(21)	C(5B) C(6B)	1.420(34)

B. Bond angles (°)

N(2) C(1) C(6)	118.6(14)	C(1A) C(2A) C(3A)	123.1(19)
N(2) C(1) C(1A)	121.0(14)	C(2A) C(3A) C(4A)	121.7(28)
C(6) C(1) C(1A)	120.4(17)	C(3A) C(4A) C(SA)	117.3(22)
C(1) N(2) C(3)	123.4(13)	C(4A) C(5A) C(6A)	121.1(17)
C(1) N(2) C(1')	123.1(14)	C(1A) C(6A) C(SA)	122.8(19)
C(3) N(2) C(1')	113.5(16)	C(1A) C(6A) I	117.8(13)
N(2) C(3) O(3)	124.2(15)	C(5A) C(6A) I	119.2(13)
N(2) C(3) C(4)	109.9(17)	N(2) C(1') C(1'M)	111.4(16)
O(3) C(3) C(4)	125.8(16)	N(2) C(1') C(1B)	111.3(19)
C(3) C(4) CL(4)	114.4(15)	C(1'M) C(1') C(1B)	116.7(18)
C(3) C(4) N(5)	127.8(17)	C(1') C(1B) C(2B)	121.3(19)
CL(4) C(4) N(5)	117.8(12)	C(1') C(1B) C(6B)	120.0(20)
C(4) N(5) C(6)	117.2(14)	C(2B) C(1B) C(6B)	118.6(20)
C(1) C(6) N(5)	122.2(17)	C(1B) C(2B) C(3B)	121.0(19)
C(1) C(6) CL(6)	121.7(13)	C(2B) C(3B) C(4B)	122.2(22)

Table 3. Fractional coordinates ($\times 10^4$) and B_{eq} ($Å^2$) for **12a**.

Estimated standard deviations are in parentheses.

$B_{eq}=4/3\ (a^2B_{11}+b^2B_{22},+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})$

	x	y	z	B_{eq}(Å)
I	2996(1)	593(1)	7174(1)	2.99(2)
CL(1)	777(2)	1288(1)	3883(1)	3.28(6)
CL(2)	914(2)	3317(1)	6370(1)	3.32(6)
0	-702(5)	-440(3)	4760(2)	2.38(15)
N(1)	-789(5)	452(3)	5860(2)	1.80(15)
N(2)	670(6)	2181(3)	5172(2)	2.43(18)
C(1)	-5822(6)	15(4)	5212(3)	2.58(21)
C(2)	-6499(7)	-995(5)	5173(3)	2.83(23)
Ct3)	-3335(6)	-664(4)	5827(2)	1.95(18)
C(4)	-1666(6)	-463(4)	6211(2)	2.03(19)
C(5)	-5593(7)	-1845(5)	5467(3)	2.78(23)
C(6)	-2596(7)	1474(4)	8100(3)	2.56(21)
C(7)	-4251(6)	191(4)	5538(3)	2.23(20)
C(8)	-424(6)	359(4)	5109(3)	1.96(19)
C(9)	-354(6)	1343(4)	6264(3)	1.96(19)
C(10)	569(6)	972(4)	7556(3)	1.97(18)
C(11)	-4038 (7)	-1682(4)	5787(3)	2.40(21)
C(12)	-666(6)	1328(3)	7072(3)	1.91(18)
C(13)	-2235(7)	1598(4)	7348(3)	2.38(20)
C(14)	340(7)	2174(4)	5904(3)	2.31(20)
C(15)	-1366(7)	1098(4)	8565(3)	2.36(21)
C(16)	305(7)	1331(4)	4806(3)	2.34(21)
C(17)	-502 (7)	-1423(4)	6286(3)	2.69(22)
C(18)	229(7)	855(4)	8305(2)	2.16(20)

Table 4. Bond lengths (Å), angles (°) and torsion angles (°) for **12a**.

A. Bond lengths (Å)

I C(10)	2.093(5)	C(3) C(7)	1.394(7)
CL(1) C(16)	1.714(5)	C(3) C(11)	1.391(7)
CL(2) C(14)	1.722(5)	C(4) C(17)	1.518(7)
O C(8)	1.204(6)	C(5) C(11)	1.373(8)
N(1) C(4)	1.481(6)	C(6) C(13)	1.400(7)
N(1) C(8)	1.396(6)	C(6) C(15)	1.370(7)
N(1) C(9)	1.376(6)	C(8) C(16)	1.453(7)
N(2) C(14)	1.352(7)	C(9) C(12)	1.486(7)
N(2) C(16)	1.286(7)	C(9) C(14)	1.345(7)
C(1) C(2)	1.374(8)	C(10) C(12)	1.385(7)
C(1) C(7)	1.392(7)	C(10) C(18)	1.391(6)
C(2) C(5)	1.388(8)	C(12) C(13)	1.378(7)
C(3) C(4)	1.512(7)	C(15) C(18)	1.379(8)

B. Bond angles (°)

C(4) N(1) C(8)	116.8(4)	N(1) C(9) C(14)	118.0(4)
C(4) N(1) C(9)	120.9(4)	C(12) C(9) C(14)	123.8(4)
C(8) N(1) C(9)	122.3 (4)	I C(10) C(12)	120.6 (3)
C(14) N(2) C(16)	117.2(4)	I C(10) C(18)	118.4(4)
C(2) C(1) C(7)	120.9 (5)	C(12) C(10) C(18)	121.0 (5)
C(1) C(2) C(5)	119.0 (5)	C(3) C(11) C(5)	121.0 (5)
C(4) C(3) C(7)	119.8(4j	C(9) C(12) C(10)	120.7(4)
C(4) C(3) C(11)	121.7(4)	C(9) C(12) C(13)	120.2(4)
C(7) C(3) C(11)	118.4 (5)	C(10) C(12) C(13)	118.9 (4)
N(1) C(4) C(3)	109.8(4)	C(6) C(13) C(12)	120.6(5)
N(1) C(4) C(17)	111.5(4)	CL(2) C(14) N(2)	115.2(4)
C(3) C(4) C(17)	115.9(4)	CL(2) C(14) C(9)	120.7(4)
C(2) C(5) C(11)	120.6 (5)	N(2) C(14) C(9)	124.1 (5)
C(13) C(6) C(15)	119.5(5)	C(6) C(15) C(18)	120.9(4)
C(1) C(7) C(3)	120.1 (5)	CL(1) C(16) N(2)	118.7 (4)

O C(8) N(1)	123.0(4)	CL(1) C(16) C(8)	115.4(4)
O C(8) C(16)	124.6(4)	N(2) C(16) C(8)	125.9(5)
N(1) C(8) C(16)	112.4(4)	C(10) C(18) C(15)	119.1(5)
N(1) C(9) C(12)	118.2(4)		

C. Torsion angles (°)

C(8) N(1) C(4) C(3)	-58.8(5)	C(7) C(3) C(ll) C(5)	0.3(7)
C(8) N(1) C(4) C(17)	71.1(5)	C(2) C(5) C(ll) C(3)	0.2(8)
C(9) N(1) C(4) C(3)	121.6(5)	C(15) C(6) C(13) C(12)	1.1(7)
C(9) N(1) C(4) C(17)	- 108.5(5)	C(13) C(6) C(15) C(18)	0.9(8)
C(4) N(1) C(8) O	-4.3(7)	O C(8) C(16) CL(1)	0.0(7)
C(4) N(1) C(8) C(16)	175.2(4)	O C(8) C(16) N(2)	-177.4(5)
C(9) N(1) C(8) O	175.3(5)	N(1) C(8) C(16) CL(1)	- 179.5(4)
C(9) N(1) C(8) C(16)	- 5.2(6)	N(1) C(8) C(16) N(2)	3.1(7)
C(4) N(1) C(9) C(12)	4.7 (7)	N(1) C(9) C(12) C(10)	90.7 (6)
C(4) N(1) C(9) C(14)	-175.8(5)	N(1) C(9) C(12) C(13)	- 84.6(6)
C(8) N(1) C(9) C(12)	-174.9(4)	C(14) C(9) C(12) C(10)	-88.7(6)
C(8) N(1) C(9) C(14)	4.6(7)	C(14) C(9) C(12) C(13)	95.9(6)
C(16) N(2) C(14) CL(2)	178.1(4)	N(l) C(9) C(14) CL(2)	179.9(4)
C(16) N(2) C(14) C(9)	- 0.7(8)	N(1) C(9) C(14) N(2)	-1.4(8)
C(14) N(2) C(16) CL(1)	- 177.5(4)	C(12) C(9) C(14) CL(2)	-0.6(7)
C(14) N(2) C(16) C(8)	-0.3(8)	C(12) C(9) C(14) N(2)	178.1(5)
C(7) C(1) C(2) C(5)	0.1(8)	I C(10) C(12) C(9)	6.4(6)
C(2) C(1) C(7) C(3)	0.4 (8)	I C(10) C(12) C(13)	-178.2 (3)
C(1) C(2) C(5) C(11)	-0.4(8)	C(18) C(10) C(12) C(9)	-173.5(4)
C(7) C(3) C(4) N(1)	_33.5(6)	C(18) C(10) C(12) C(13)	1.9(7)
C(7) C(3) C(4) C(17)	-161.0(4)	I C(10) C(18) C(15)	-179.8(4)
C(11) C(3) C(4) N(1)	150.0(4)	C(12) C(10) C(18) C(15)	0.1(7)
C(11) C(3) C(4) C(17)	22.5(6)	C(9) C(12) C(13) C(6)	172.9(4)
C(4) C(3) C(7) C(1)	-177.2(4)	C(10) C(12) C(13) C(6)	-2.5(7)
C(11) C(3) C(7) C(1)	-0.6(7)	C(6) C(15) C(18) C(10)	-1.5(7)
C(4) C(3) C(11) C (5)	176.9 (5)		

Table 5. Fractional coordinates ($\times 10^4$) and B_{eq} ($Å^2$) for **4**.

Estimated standard deviations are in parentheses.

$B_{eq}=4/3\ (a^2B_{11}+b^2B_{22},+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})$

	x	y	z	B_{eq}(Å)
N(1)	-6475(5)	2226(5)	-2692(2)	2.30(24)
C(2)	-6765(6)	1027(6)	-2931(3)	2.23(29)
CL(2)	-5718(2)	-240(2)	-2675	2.93(8)
C(3)	-7751(6)	717(6)	-3348(3)	2.5(3)
C(1A)	-7981(6)	-611(6)	-3624(3)	2.7(3)
C(2A)	-8906(7)	-1499(7)	-3350(3)	3.0(3)
C(3A)	-9059(7)	-2764(6)	-3592(4)	3.3(3)
C(4A)	-8318(7)	-3180(7)	-4108(4)	3.3(3)
C(5A)	-7407(7)	-2336(6)	-4397(3)	2.9(3)
C(6A)	-7247(6)	-1080(6)	-4159(3)	2.6(3)
CL(6A)	-6075(2)	-42(2)	-4510(1)	3.57(9)
N(4)	-8569(5)	1781(5)	-3542(3)	2.17(23)
C(1')	-9670(7)	1568(6)	-3977(3)	2.8(3)
C(1B)	-10876(7)	1285(6)	-3611(3)	2.9(3)
0(2B)	-11964(5)	953(5)	-3971(3)	4.60(28)
C(3B)	-12960(8)	743(9)	-3534(5)	5.6(4)
C(4B)	-12540(8)	924(9)	-2933(4)	4.7(4)
C(5B)	-11196(7)	1282(8)	-2977(4)	4.2(4)
C(5)	-8411(7)	3037(6)	-3303(3)	2.5(3)
0(5)	-9143(4)	3953(4)	-3445(2)	2.89(21)
C(6)	-7274(6)	3193(7)	-2873(3)	2.5(3)
N(1")	-7092 (5)	4446(5)	-2669(2)	2.48(25)
C(2")	-5903(6)	4878(6)	-2321(3)	2.8(3)
C(2"M)	-6285(7)	5981(7)	-1857(3)	3.3(3)
C(1C)	-4819(6)	5268(6)	-2784(3)	2.6(3)
C(2C)	-4908 (7)	6401(7)	-3151(3)	3.1(3)
C(3C)	-3897(8)	6766(7)	-3573(4)	4.0(3)
C(4C)	-2782(8)	5966(9)	-3637(4)	4.1(4)
C(5C)	-2691(7)	4825(9)	-3279(4)	4.1(3)
C(6C)	-3697(7)	4477(7)	-2860(3)	3.3(3)

Table 6. Bond lengths (Å), angles (°) and torsion angles (°) for **4**.

A. Bond lengths (Å)

N(1) C(2)	1.337(8)	C(1B) C(5B)	1.349(11)
N(1) C(6)	1.317(8)	0(2B) C(3B)	1.366(11)
C(2) CL(2)	1.738(6)	C(3B) C(4B)	1.324(13)
C(2) C(3)	1.350(9)	C(4B) C(5B)	1.404(11)
C(3) C(1A)	1.473(9)	C(5) 0(5)	1.217(8)
C(3) N(4)	1.410(8)	C(5) C(6)	1.457(9)
C(1A) C(2A)	1.409(9)	C(6) N(1")	1.343(8)
C(1A) C(6A)	1.410(9)	N(1") C(2")	1.462(8)
C(2A) C(3A)	1.377(9)	C(2") C(2"M)	1.517(9)
C(3A) C(4A)	1.367(10)	C(2") C(1C)	1.503(9)
C(4A) C(5A)	1.386(10)	C(1C) C(2C)	1.373(9)
C(5A) C(6A)	1.368(9)	C(1C) C(6C)	1.392(9)
C(6A) CL(6A)	1.736(7)	C(2C) C(3C)	1.390(10)
N(4) C(1')	1.442(8)	C(3C) C(4C)	1.389(11)
N(4) C(5)	1.369(8)	C(4C) C(5C)	1.369(12)
C(1') C(1B)	1.459(9)	C(5C) C(6C)	1.378(10)
C(1B) 0(2B)	1.367(9)		

B. Bond angles (°)

C(2) N(1) C(6)	115.5(5)	0(2B) C(1B) C(5B)	109.7(6)
N(1) C(2) CL(2)	114.7(4)	C(1B) 0(2B) C(3B)	105.5(6)
N(1) C(2) C(3)	127.2(6)	0(2B) C(3B) C(4B)	111.3(7)
CL(2) C(2) C(3)	118.1(5)	C(3B) C(4B) C(5B)	106.4(7)
C(2) C(3) C(1A)	124.9(6)	C(1B) C(5B) C(4B)	107.1(7)
C(2) C(3) N(4)	115.8(6)	N(4) C(5) 0(5)	122.9(6)
C(1A) C(3) N(4)	119.2(5)	N(4) C(5) C(6)	114.3(6)
C(3) C(1A) C(2A)	121.7(6)	0(5) C(5) C(6)	122.8(6)
C(3) C(1A) C(6A)	121.7(6)	N(1) C(6) C(5)	125.0(6)
C(2A) C(1A) C(6A)	116.6(6)	N(1) C(6) N(1~)	121.5(5)
C(1A) C(2A) C(3A)	121.1(6)	C(5) C(6) N(1")	113.5(5)
C(2A) C(3A) C(4A)	120.3(6)	C(6) N(1") C(2")	123.0(5)

C(3A) C(4A) C(5A)	120.6(6)	N(1") C(2") C(2"M)	108.7(5)
C(4A) C(5A) C(6A)	119.4(6)	N(1") C(2") C(1C)	111.1(5)
C(1A) C(6A) C(5A)	122.0(6)	C(2"M) C(2") C(1C)	113.2(5)
C(1A) C(6A) CL(6A)	118.8(5)	C(2") C(1C) C(2C)	121.4(6)
C(5A) C(6A) CL(6A)	119.1(5)	C(2") C(1C) C(6C)	120.8(6)
C(3) N(4) C(1')	120.9(5)	C(2C) C(1C) C(6C)	117.8(6)
C(3) N(4) C(5)	122.1(5)	C(1C) C(2C) C(3C)	121.2(6)
C(1') N(4) C(5)	116.9(5)	C(2C) C(3C) C(4C)	119.9(7)
N(4) C(1') C(1B)	110.3(5)	C(3C) C(4C) C(5C)	119.4(7)
C(1') C(1B) 0(2B)	115.7(6)	C(4C) C(5C) C(6C)	120.2(7)
C(1') C(1B) C(5B)	134.6(6)	C(1C) C(6C) C(5C)	121.5(7)

C. Torsion angles (°)

C(6) N(1) C(2) CL(2)	-178.8 (4)	C(2A) C(1A) C(6A) CL(6A)	-179.1 (5)
C(6) N(1) C(2) C(3)	2.2 (9)	C(1A) C(2A) C(3A) C(4A)	-0.6 (10)
C(2) N(1) C(6) C(5)	-0.1 (9)	C(2A) C(3A) C(4A) C(5A)	-0.1 (11)
C(2) N(1) C(6) N(1")	-179.8 (5)	C(3A) C(4A) C(5A) C(6A)	0.3 (10)
N(1) C(2) C(3) C(1A)	176.4 (6)	C(4A) C(5A) C(6A) C(1A)	0.2 (11)
N(1) C(2) C(3) N(4)	-0.9 (9)	C(4A) C(5A) C(6A) CL(6A)	178.5 (5)
CL(2) C(2) C(3) C(1A)	-2.5 (9)	C(3) N(4) C(1') C(1B)	90.9 (7)
CL(2) C(2) C(3) N(4)	-179.8 (4)	C(5) N(4) C(1') C(1B)	-85.5 (7)
C(2) C(3) C(1A) C(2A)	96.3 (8)	C (3) N (4) C (5) O (5)	-176.8 (6)
C(2) C(3) C(1A) C(6A)	-80.9 (9)	C(3) N(4) C(5) C(6)	4.4 (8)
N(4) C(3) C(1A) C(2A)	-86.5 (8)	C(1') N(4) C(5) 0(5)	-0.5 (9)
N(4) C(3) C(1A) C(6A)	96.3 (7)	C(1') N(4) C(5) C(6)	-179.3 (5)
C(2) C(3) N(4) C(1')	-178.9 (5)	N(4) C(1') C(1B) 0(2B)	-174.6 (5)
C(2) C (3) N(4) C(5)	-2.7 (9)	N(4) C(1') C(1B) C(5B)	6.2 (11)
C(1A) C(3) N(4) C(1')	3.6 (8)	C(1') C(1B) 0(2B) C(3B)	-179.6 (6)
C(1A) C(3) N(4) C(5)	179.8 (6)	C (5B) C (1B) O (2B) C (3B)	-0.2 (8)
C(3) C(1A) C(2A) C(3A)	-176.4 (6)	C(1') C(1B) C(5B) C(4B)	179.7 (7)
C(6A) C(1A) C(2A) C(3A)	1.0 (10)	O (2B) C (1B) C (5B) C (4B)	0.4 (8)
C(3) C(1A) C(6A) C(5A)	176.5 (6)	C (1B) O (2B) C (3B) C (4B)	- 0.2 (9)
C(3) C(1A) C(6A) CL(6A)	- 1.7 (9)	O(2B) C(3B) C(4B) C(5B)	0.4 (10)
C(2A) C(1A) C(6A) C(5A)	-0.8 (10)	C(3B) C(4B) C(5B) C(1B)	-0.5 (9)

N(4) C(5) C(6) N(1)	-3.0 (9)	C(2"M) C(2~) C(1C) C(2C)	-52.1 (8)
N(4) C(5) C(6) N(1")	176.7 (5)	C(2"M) C(2") C(1C) C(6C)	128.8 (7)
O(5) C(5) C(6) N(1)	178.2 (6)	C(2~) C(1C) C(2C) C(3C)	179.3 (6)
O(5) C(5) C (6) N(1")	-2.1 (9)	C(6C) C (1C) C (2C) C(3C)	-1.5 (10)
N(1) C(6) N(1") C(2")	9.8 (9)	C (2") C (1C) C (6C) C(5C)	-179.6 (6)
C(5) C(6) N(1") C(2")	-169.9 (5)	C(2C) C(1C) C(6C) C(5C)	1.2 (10)
C(6) N(1") C(2") C(2"M)	-148.5 (6)	C (1C) C(2C) C(3C) C(4C)	1.1 (11)
C(6) N(1") C(2") C(1C)	86.3 (7)	C(2C) C(3C) C(4C) C(5C)	-0.3(12)
N(1") C(2") C(1C) C(2C)	70.6 (8)	C(3C) C(4C) C(5C) C(6C)	-0.1 (12)
N(1") C(2") C(1C) C(6C)	-108.6 (7)	C(4C) C(5C) C(6C) C(1C)	-0.4 (11)

Table 7. Fractional coordinates ($\times 10^4$) and B_{eq} ($Å^2$) for **9k**.

Estimated standard deviations are in parentheses.

$B_{eq}=4/3\ (a^2B_{11}+b^2B_{22},+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})$

	x	y	z	B_{eq}(Å)
N(1')	6387(4)	2873(4)	1647(2)	2.19(14)
C(2')	5166(4)	2309(4)	1285(2)	2.22(17)
CL(2')	3731(1)	2012(2)	1792(1)	3.11(5)
C(3')	4876(4)	1871(4)	465(2)	1.86(16)
0(3')	3737(3)	1304(3)	136(2)	2.25(11)
N(4')	6066(3)	2169(3)	76(2)	1.69(12)
C(5')	7376(4)	2796(4)	457(2)	1.88(15)
C(6')	7486(4)	3104(4)	1229(2)	2.26(17)
CL(6')	9089(1)	3853(2)	1756(1)	3.38(5)
C(7')	8575(4)	3109(4)	7(2)	2.06(16)
C(8')	8670(4)	4141(4)	-435(2)	2.29(17)
C(9')	10021(4)	4140(4)	-757(2)	2.50(17)
C(10')	10897(4)	3125(4)	-548(2)	2.54(18)
S(11')	10120(1)	2140(2)	38(1)	2.90(5)
C(12')	5910(4)	1712(4)	-757(2)	1.91(16)
C(12M)	6007(4)	295(4)	-756(2)	2.61(18)
C(13')	4535(4)	2299(4)	-1290(2)	1.89(16)
C(14')	4425(4)	3604(4)	-1325(2)	2.07(16)
C(15')	3216(4)	4185(4)	-1847(2)	2.62(18)
C(16')	2123(5)	3480(4)	-2336(2)	2.65(18)
C(17')	2224(4)	2194(5)	-2309(2)	2.80(18)
C(18')	3419(4)	1600(4)	-1789(2)	2.27(17)
N(1)	6359(4)	6344(4)	-3718(2)	2.84(16)
C(2)	5155(4)	5808(5)	-4119(2)	2.51(18)
CL(2)	3635(1)	5556	-3667(1)	3.32(5)
C(3)	4962(4)	5385(4)	-4936(2)	2.31(16)
0(3)	3870(3)	4786(3)	-5286(2)	2.94(13)
N(4)	6167(3)	5740(4)	-5290(2)	2.02(13)
C(5)	7476(4)	6339(4)	-4873(2)	2.27(17)

C(6)	7526(5)	6580(5)	-4087(2)	3.11(20)
CL(6)	9118(1)	7258(2)	-3501(1)	4.91(6)
C(7)	8704(4)	6745(4)	-5263(2)	2.15(16)
C(8)	8982(4)	7942(4)	-5454(2)	2.47(17)
C(9)	10336(5)	8056(5)	-5759(3)	2.92(19)
C(10)	11060(4)	6955(5)	-5782(2)	2.91(18)
S(11)	10106(1)	5754(2)	-5447(1)	3.29(5)
C(12)	6022(4)	5445(4)	-6156(2)	2.30(17)
C(12M)	6201(5)	4051(5)	-6265(3)	3.53(20)
C(13)	4627(4)	6081(4)	-6639(2)	2.32(18)
C(14)	4599(4)	7380(4)	-6662(2)	2.47(18)
C(15)	3397(5)	8019(5)	-7143(3)	3.23(20)
C(16)	2221(5)	7368(5)	-7600(3)	3.57(21)
C(17)	2234(5)	6087(6)	-7584(3)	3.91(23)
C(18)	3423(5)	5423(5)	-7104(3)	3.14(20)

Table 8. Bond lengths (Å), angles (°), and torsion angles (°) for **9k**.

A. Bond lengths (Å)

N(1') C(2')	1.285(5)	N(1) C(2)	1.281(5)
N(1') C(6')	1.346(4)	N(1) C(6)	1.344(5)
C(2') CL(2')	1.712(3)	C(2) CL(2)	1.709(3)
C(2') C(3')	1.451(5)	C(2) C(3)	1.445(6)
C(3') 0(3')	1.214(4)	C(3) 0(3)	1.213(5)
C(3') N(4')	1.395(4)	C(3) N(4)	1.387(4)
N(4') C(5')	1.384(4)	N(4) C(5)	1.390(5)
N(4') C(12')	1.486(5)	N(4) C(12)	1.495(5)
C(5') C(6')	1.345(5)	C(5) C(6)	1.360(6)
C(5') C(7')	1.474(4)	C(5) C(7)	1.456(5)
C(6') CL(6')	1.720(4)	C(6) CL(6)	1.718(4)
C(7') C(8')	1.347(6)	C(7) C(8)	1.353(6)
C(7') S(11')	1.711(4)	C(7) S(11)	1.711(4)
C(8') C(9')	1.419(4)	C(8) C(9)	1.411(5)
C(9') C(10')	1.339(6)	C(9) C(10)	1.343(7)
C(10') S(11')	1.693(4)	C(10) S(11)	1.699(5)
C(12') C(12M)	1.514(6)	C(12) C(12M)	1.511(7)
C(12') C(13')	1.504(5)	C(12) C(13)	1.504(5)
C(13') C(14')	1.395(6)	C(13) C(14)	1.387(7)
C(13') C(18')	1.388(5)	C(13) C(18)	1.386(6)
C(14') C(15')	1.395(5)	C(14) C(15)	1.387(6)
C(15') C(16')	1.370(6)	C(15) C(16)	1.361(6)
C(16') C(17')	1.374(7)	C(16) C(17)	1.367(8)
C(17') C(18')	1.391(5)	C(17) C(18)	1.392(6)

B. Bond angles (°)

C(2') N(1') C(6')	117.5(3)	C(2) N(1) C(6)	118.1(3)
N(1') C(2') CL(2')	119.0(3)	N(1) C(2) CL(2)	118.6(3)
N(1') C(2') C(3')	125.7(3)	N(1) C(2) C(3)	125.4(3)
CL(2') C(2') C(3')	115.3(2)	CL(2) C(2) C(3)	116.0(3)

C(2') C(3') 0(3')	125.0(3)	C(2) C(3) 0(3)	124.6(3)
C(2') C(3') N(4')	112.6(3)	C(2) C(3) N(4)	112.8(3)
O (3') C(3') N(4')	122.3 (3)	O(3) C(3) N(4)	122.6 (4)
C(3') N(4') C(5')	122.2(3)	C(3) N(4) C(5)	122.8(3)
C(3') N(4') C(12')	116.8(3)	C(3) N(4) C(12)	117.2(3)
C(5') N(4') C(12')	121.0(2)	C(5) N(4) C(12)	120.0(3)
N(4') C(5') C(6')	117.7(3)	N(4) C(5) C(6)	116.7(3)
N(4') C(5') C(7')	119.5(3)	N(4) C(5) C(7)	121.9(3)
C(6') C(5') C(7')	122.8(3)	C(6) C(5) C(7)	121.3(3)
N(1') C(6') C(5')	124.2(3)	N(1) C(6) C(5)	123.8(4)
N(1') C(6') CL(6')	114.8(3)	N(1) C(6) CL(6)	115.3(3)
C(5') C(6') CL(6')	121.0(3)	C(5) C(6) CL(6)	120.9(3)
C(5') C(7') C(8')	127.8(3)	C(5) C(7) C(8)	125.6(4)
C(5') C(7') S(11')	120.5 (3)	C 5) C(7) S(11)	122.9 (3)
C(8') C(7') S(11')	111.6 (2)	C(8) C(7) S(11)	111.2 (2)
C(7') C(8') C(9')	111.8(3)	C(7) C(8) C(9)	112.4(4)
C(8') C(9') C(10')	112.9(4)	C(8) C(9) C(10)	112.7(4)
C(9') C(10') S(11')	112.0(2)	C(9) C(10) S(11)	111.9(3)
C(7') S(11') C(10')	91.7(2)	C(7) S(11) C(10)	91.7(2)
N(4') C(12') C(12M)	109.4(3)	N(4) C(12) C(12M)	109.8(3)
N(4') C(12') C(13')	110.5(3)	N(4) C(12) C(13)	110.1(3)
C(12M) C(12') C(13')	117.1(3)	C(12M) C(12) C(13)	118.2(3)
C(12') C(13') C(14')	118.8(3)	C(12) C(13) C(14)	118.3(3)
C(12') C(13') C(18')	122.7(4)	C(12) C(13) C(18)	122.7(4)
C(14') C(13') C(18')	118.3 (3)	C(14) C(13) C(18)	118.8 (4)
C(13') C(14') C(15')	120.6 (3)	C(13) C(14) C(15)	121.0 (4)
C(14') C(15') C(16')	120.3(4)	C(14) C(15) C(16)	120.0(5)
C(15') C(16') C(17')	119.6(4)	C(15) C(16) C(17)	119.7(4)
C(16') C(17') C(18')	120.8(4)	C(16) C(17) C(18)	121.5(4)
C(13') C(18') C(17')	120.3(4)	C(13) C(18) C(17)	119.1(5)

C. Torsion angles (°)

C(6') N(1') C(2') CL(2')	- 179.3(3)	C(6) N(1) C(2) CL(2)	- 177.5(3)
C(6') N(1') C(2') C(3')	1.4(6)	C(6) N(1) C(2) C(3)	2.7(7)
C(2') N(1') C(6') C(5')	0.9(6)	C(2) N(1) C(6) C(5)	3.3(7)
C(2') N(1') C(6') CL(6')	- 179.6(3)	C(2) N(1) C(6) CL(6)	-178.2(4)
N(1') C(2') C(3') 0(3')	177.6(4)	N(1) C(2) C(3) 0(3)	173.5(4)
N(1') C(2') C(3') N(4')	- 2.2(6)	N(1) C(2) C(3) N(4)	-6.7(7)
CL(2') C(2') C(3') 0(3')	- 1.8(6)	CL(2) C(2) C(3) 0(3)	- 6.3(6)
CL(2') C(2') C(3') N(4')	178.4(3)	CL(2) C(2) C(3) N(4)	173.4(3)
C(2') C(3') N(4') C(5')	1.1(5)	C(2) C(3) N(4) C(5)	5.4(6)
C(2') C(3') N(4') C(12')	177.4(3)	C(2) C(3) N(4) C(12)	- 175.0(4)
0(3') C(3') N(4') C(5')	- 178.8(4)	0(3) C(3) N(4) C(5)	- 174.8(4)
0(3') C(3') N(4') C(12')	-2.5(6)	0(3) C(3) N(4) C(12)	4.8(6)
C(3') N(4') C(5') C(6')	0.8(6)	C(3) N(4) C(5) C(6)	-0.6(6)
C(3') N(4') C(5') C(7')	- 178.5(4)	C(3) N(4) C(5) C(7)	- 177.7(4)
C(12') N(4') C(5') C(6')	-175.4(4)	C(12) N(4) C(5) C(6)	179.8(4)
C(12') N(4') C(5') C(7')	5.3(5)	C(12) N(4) C(5) C(7)	2.7(6)
C(3') N(4') C(12') C(12M)	-67.0(4)	C(3) N(4) C(12) C(12M)	-71.9(4)
C(3') N(4') C(12') C(13')	63.3(4)	C(3) N(4) C(12) C(13)	59.9(5)
C(5') N(4') C(12') C(12M)	109.4(4)	C(5) N(4) C(12) C(12M)	107.7(4)
C(5') N(4') C(12') C(13')	- 120.3(4)	C(5) N(4) C(12) C(13)	- 120.5(4)
N(4') C(5') C(6') N(1')	-1.9(6)	N(4) C(5) C(6) N(1)	-4.2(7)
N(4') C(5') C(6') CL(6')	178.6(3)	N(4) C(5) C(6) CL(6)	177.3(3)
C(7') C(5') C(6') N(1')	177.4(4)	C(7) C(5) C(6) N(1)	172.9(4)
C(7') C(5') C(6') CL(6')	- 2.1(6)	C(7) C(5) C(6) CL(6)	-5.5(6)
N(4') C(5') C(7') C(8')	87.6(5)	N(4) C(5) C(7) C(8)	104.8(5)
N(4') C(5') C(7') S(11')	- 95.0(4)	N(4) C(5) C(7) S(11)	-81.9(5)
C(6') C(5') C(7') C(8')	-91.7(5)	C(6) C(5) C(7) C(8)	-72.2(6)
C(6') C(5') C(7') S(11')	85.7(5)	C(6) C(5) C(7) S(11)	101.1(5)
C(5') C(7') C(8') C(9')	177.8(4)	C(5) C(7) C(8) C(9)	174.5(4)
S(ll') C(7') C(8') C(9')	0.2(4)	S(ll) C(7) C(8) C(9)	0.5(4)
C(5') C(7') S(ll') C(10')	-177.9(3)	C(5) C(7) S(ll) C(10)	-174.2(3)
C(8') C(7') S(11') C(10')	-0.1 (3)	C(8) C(7) S(11) C(10)	-0.1 (3)