Organocatalytic and Direct Asymmetric Vinylogous Michael Addition of α, α-dicyanoolefins to α, β-Unsaturated Aldehydes

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Supplementary Information

1. General Methods:

NMR spectra were recorded with tetramethylsilane as the internal standard. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. Optical rotations were measured at 589 nm at 25°C. TLC was performed on glass-backed silica plates. Enantiomeric excess was determined by HPLC analysis on Chiralpak AS and OD columns. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997).

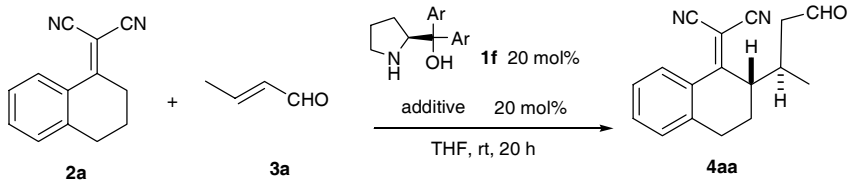
Catalysts **1b**, **1d** and **1f** were commercially available and used as received. Catalysts **1c**, **1e and 1g-1k** were prepared according to literature procedures.[1]

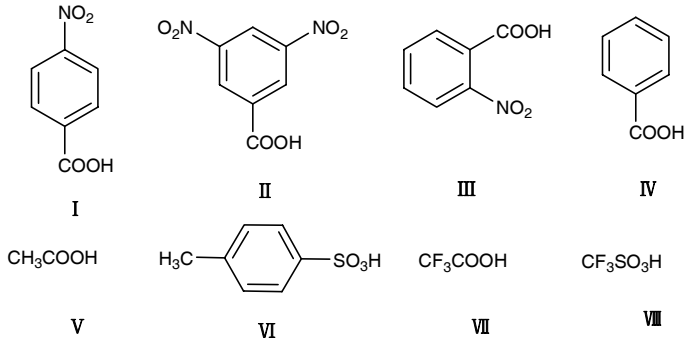
Reference:

1. C.-Y. Ho, Y.-C. Chen, M.-K. Wong and D. Yang, *J. Org. Chem.*, 2005, **70**, 898.

2. Screening of reaction conditions for the organocatalytic vinylogous Michael addition of α,α-dicyanoolefin 2a to crotonaldehyde 3a

2.1 Effects of Acid additives on the vinylogous Michael addition[a]

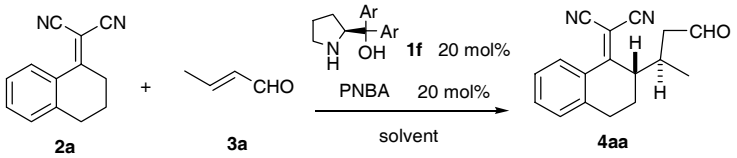




entry	additive	yield[b] (%)	ee[c] (%)
1	I	89	85.0
2	II	85	85.3
3	III	83	84.4
4	IV	50	80.0
5	V	50	75.3
6	VI	30	85.1
7	VII	65	83.0
8	VIII	15	76.8

[a] Reactions performed with 0.1 mmol **2a**. Method: 2.0 equiv. **3a**, **1f** (20 mol%), additive (20 mol%), in 1 mL THF at room temperature for 20 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

2.2 Effects of solvent on the vinylogous Michael reaction[a]



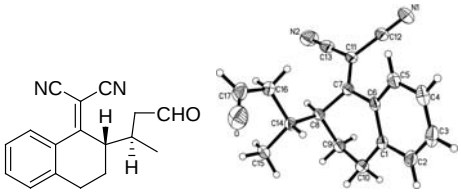
2a 3a 4aa

entry	solvent	cat. (mol %)/t (h)	T（°C）	yield[b] (%)	ee[c] (%)
1	THF	20/20	rt	89	85.0
2	DCM	20/20	rt	69	77.3
3	Et_2O	20/20	rt	66	78.0
4	toluene	20/20	rt	67	83.1
5	$MeOBu^t$	20/20	rt	91	85.4
6	CH_3CN	20/20	rt	89	84.3
7	MeOH	20/20	rt	No Reaction	-
8	**THF**	**20/96**	**-50**	**61**	**94.6**
9	$MeOBu^t$	20/96	-50	28	94.0
10	THF	30/96	-50	51	94.5

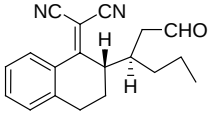
[a] Reactions performed with 0.1 mmol **2a**. Method: 2.0 equiv. **3a**, in 1 mL solvent. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

3. Spectra data of Michael addition products

General procedure for the vinylogous Michael addition: 19.2 mg (0.1 mmol) **2a,** 32 μL **3a** (0.2 mmol), **1f** 5.1mg (0.02 mol) and PNBA 3.4mg (0.02 mol) were stirred in 1mL THF at –50 °C for 96 h. Then the reaction was quenched by adding 0.5 mL 1M HCl. The mixture was extracted with EtOAc, dried with anhydrous sodium sulfate. The solvent was removed and flash chromatography on silica gel (10% ethyl acetate/petroleum ether) gave **4aa** as a white solid (16 mg, 61%). The structure of enantiopure **4aa** was confirmed by X-ray analysis.

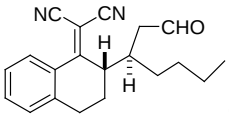


4aa, 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.63 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.36-7.26 (m, 2H), 3.13-3.10 (m, 1H), 2.90-2.88 (m, 2H), 2.41-2.34 (m, 2H), 2.29-2.10 (m, 3H), 1.04 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.3, 177.3, 140.1, 133.6, 129.4, 129.1, 128.2, 126.9, 113.4, 113.2, 80.7, 48.5, 47.0, 28.7, 24.8, 24.4, 17.2; IR (KBr) 2977, 2847, 2227, 1716, 1599, 1572, 1555, 775, 742 cm^{-1}; ESI-HRMS: calcd. for $C_{17}H_{16}N_2O$+Na 287.1155, found 287.1157; $[\alpha]^{25}_D$ = -371.3 (C 0.16, CH_2Cl_2), 95% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 12.840 min, t_{major} = 17.315 min.

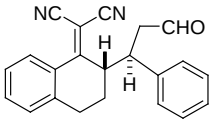


4ab, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.60 (s, 1H),

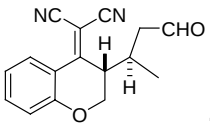
7.89 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36-7.26 (m, 2H), 3.27-3.23 (m, 1H), 3.20-2.69 (m, 2H), 2.48-2.47 (m, 1H), 2.29-2.14 (m, 4H), 1.41-1.32 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.5, 177.5, 140.1, 133.6, 129.4, 129.3, 128.4, 126.9, 113.4, 113.2, 81.0, 45.9, 45.3, 33.2, 32.9, 25.1, 24.5, 18.8, 14.2; ESI-HRMS: calcd. for $C_{19}H_{20}N_2O$+Na 315.1468, found 315.1463; IR (film) 2958, 2933, 2872, 2726, 2225, 1722, 1651, 1601, 1572, 1553, 772, 737 cm^{-1}; $[\alpha]^{25}_D$ = -201.2 (C 0.08, CH_2Cl_2), 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 10.615 min, t_{major} = 12.815 min.



4ac, 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.60 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36-7.26 (m, 2H), 3.27-3.23 (m, 1H), 2.90-2.71 (m, 2H), 2.50-2.40 (m, 1H), 2.48-2.14 (m, 4H), 1.44-1.25 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.5, 177.5, 140.1, 133.6, 129.4, 129.3, 128.4, 126.9, 113.4, 113.2, 80.9, 45.9, 45.2, 33.2, 30.3, 27.6, 25.1, 24.5, 22.9, 13.8; IR (film) 2931, 2870, 2225, 1723, 1601, 1572, 1553, 772, 736 cm^{-1}; ESI-HRMS: calcd. for $C_{20}H_{22}N_2O$-H 305.1648, found 305.1665; $[\alpha]^{25}_D$ = -254.2 (C 0.12, CH_2Cl_2), 93% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-PrOH/hexane, 1 mL/min), t_{minor} = 9.740 min, t_{major} = 11.523 min.

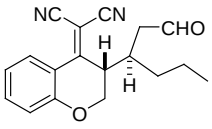


4ad, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.40 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.40-7.26 (m, 7H), 3.59-3.55 (m, 1H), 3.18-3.16 (m, 1H), 3.16-2.86 (m, 3H), 2.58-2.50 (m, 1H), 2.58-2.51 (m, 1H), 1.80-1.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.5, 176.4, 139.9, 139.8 , 134.1, 129.9, 129.2, 128.7, 128.3, 127.8, 127.0, 113.4, 80.7, 48.0, 47.2, 40.4, 25.2, 24.2; IR (KBr) 2953, 2886, 2842, 2689, 2214, 1753, 1652, 1528, 1449, 1423, 1318, 1215, 755, 743 cm^{-1}; ESI-HRMS: calcd. for $C_{22}H_{18}N_2O$-H 325.1335, found 325.1335; $[\alpha]^{25}_D$ = -173.3 (C 0.12, CH_2Cl_2), 89% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{major} = 16.634 min, t_{minor} = 24.687 min.

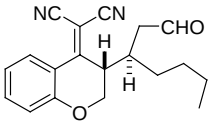


4ba, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.63 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.67 (dd, *J* = 1.6, 12.6 Hz, 1H), 4.26 (dd, *J* = 2.3, 12.6 Hz, 1H), 2.85 (d, *J* = 9.8 Hz, 1H), 2.49-2.35 (m, 3H), 1.19 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz,

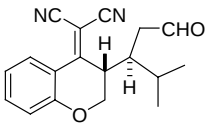
$CDCl_3$) δ (ppm) 199.9, 167.9, 156.1, 136.8, 127.7, 121.7, 118.0, 115.6, 113.2, 78.4, 66.2, 47.9, 44.4, 27.7, 17.8; IR (KBr) 2986, 2916, 2226, 1713, 1603, 1571, 1561, 1259, 1216, 771 cm^{-1}; ESI-HRMS: calcd. for $C_{16}H_{14}N_2O_2$+Na 289.0947, found 289.0954; $[\alpha]^{25}_D$ = -492.5 (C 0.16, CH_2Cl_2), 95% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (35% 2-propanol/hexane, 1 mL/min), t_{minor} = 13.298 min, t_{major} = 17.832 min.



4bb, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.57 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.65 (d, *J* = 12.6 Hz, 1H), 4.24 (dd, *J* = 2.2, 12.6 Hz, 1H), 3.00 (d, *J* = 9.8 Hz, 1H), 2.52-2.32 (m, 3H), 1.61-1.54 (m, 2H), 1.34-1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz,, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.9, 168.1, 156.2, 136.8, 127.9, 121.8, 118.0, 115.8, 113.2, 78.6, 66.4, 45.3, 42.7, 33.4, 31.8 , 18.8, 14.2; IR (film) 2959, 2933, 2873, 2831, 2224, 1722, 1606, 1572, 1555, 1479, 1466, 1327, 1260, 1217, 769, 749 cm^{-1}; ESI-HRMS: calcd. for $C_{18}H_{18}N_2O_2$-H 293.1285, found 293.1299; $[\alpha]^{25}_D$ = -402.5 (C 0.2, CH_2Cl_2), 95% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 9.965 min, t_{major} = 12.865 min.

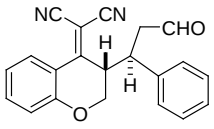


4bc, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.58 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.8 Hz,, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 2.99 (d, *J* = 10.1 Hz, 1H), 2.60-2.50 (m, 1H), 2.37-2.31 (m, 2H), 1.67-1.57 (m, 2H), 1.29 (br.s, 4H), 0.88 (t, *J* = 8.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.9, 168.1, 156.1, 136.8, 127.9, 121.8, 118.0, 115.8, 113.2, 78.5, 66.4, 45.2, 42.6, 31.8, 30.8, 27.5, 22.8, 13.8; IR (film) 2938, 2870, 2826, 2225, 1717, 1608, 1570, 1551, 1254, 1216, 775, 745 cm^{-1}; ESI-HRMS: calcd. for $C_{19}H_{20}N_2O_2$-H 307.1441, found 307.1426; $[\alpha]^{25}_D$ = -398.0 (C 0.16, CH_2Cl_2), 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 9.515 min, t_{major} = 11.382 min.

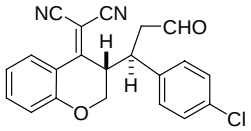


4be, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.42 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H,), 4.66 (dd, *J* = 1.5, 12.6 Hz, 1H), 4.22 (dd, *J* = 2.2, 12.6 Hz, 1H), 3.00 (d, *J* = 10.0 Hz, 1H), 2.48-2.17 (m, 4H), 0.95-0.91 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$)

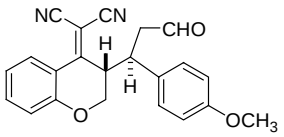
δ (ppm) 199.9, 168.2, 156.1, 136.7, 128.3, 121.7, 117.8, 115.9, 113.2, 113.1, 78.5, 66.3, 42.0, 41.4, 36.1, 27.7, 21.2, 15.8; IR (film) 2963, 2935, 2879, 2224, 1722, 1607, 1572, 1260, 1218, 767, 733 cm^{-1}; ESI-HRMS: calcd. for $C_{18}H_{18}N_2O_2$-H 293.1285, found 293.1271; $[\alpha]^{25}_D$ = -276.7 (C 0.12, CH_2Cl_2), 98% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 9.982 min, t_{major} = 12.598 min.



4bd, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.47 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.62-7.57 (m, 1H), 7.45-7.40 (m, 2H), 7.37-7.31 (m, 3H), 7.14 (t, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.11-4.09 (m, 2H), 3.46-3.44 (m, 1H), 3.28-3.22 (m, 1H), 3.17-3.07 (m, 1H), 2.69-2.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.2, 167.0, 156.2, 139.2, 137.2, 129.3, 128.1, 127.9, 122.0, 118.3, 115.2, 113.4, 113.1, 78.6, 66.5, 46.7, 45.1, 39.5; IR (KBr) 2946, 2887, 2832, 2732, 2223, 1718, 1610, 1548, 1478, 1452, 1329, 1216, 766, 742 cm^{-1}; ESI-HRMS: calcd. for $C_{21}H_{16}N_2O_2$+Na 351.1104, found 351.1107; $[\alpha]^{25}_D$ = -224.5 (C 0.2, CH_2Cl_2), 92% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 15.190 min, t_{major} = 17.223 min.

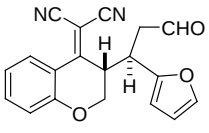


4bf, 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.46 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 4.13-4.00 (m, 2H), 3.42-3.38 (m, 1H), 3.20-3.03 (m, 2H), 2.67-2.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 198.6, 166.7, 156.1, 137.8, 137.3, 133.9, 129.5, 127.9, 122.1, 118.3, 115.1, 113.4, 113.0, 78.7, 66.4, 46.7, 44.9, 38.7; IR (KBr) 2916, 2880, 2772, 2763, 2218, 1716, 1609, 1550, 1455, 1450, 1328, 1205, 769, 732 cm^{-1}; ESI-HRMS: calcd. for $C_{21}H_{15}N_2O_2Cl$-H 361.0738, found 361.0751; $[\alpha]^{25}_D$ = -58.8 (C 0.24, CH_2Cl_2), 90% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 16.248 min, t_{major} = 18.115 min.

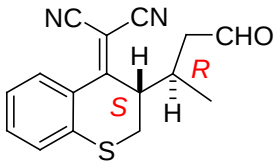


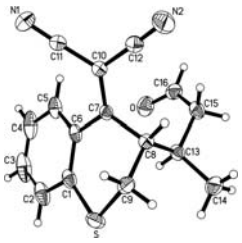
4bg, 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.44 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 6.7 Hz, 2H), 4.08 (d, *J* = 1.9 Hz, 2H), 3.81 (s, 3H), 3.38-3.36 (m, 1H), 3.20-3.15 (m, 1H), 3.09-3.03 (m, 1H), 2.62-2.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.4, 167.2, 159.2, 156.2, 137.2, 130.9, 129.2, 127.9, 122.0, 118.3, 115.2, 114.7, 113.4, 113.2, 78.5, 66.5, 55.3, 46.8, 45.4,

38.8; IR (KBr) 2985, 2930, 2221, 1719, 1603, 1571, 1558, 1513, 1260, 1215, 826, 768 cm^{-1}; ESI-HRMS: calcd. for $C_{22}H_{18}N_2O_3$+Na 381.1210, found 381.1204; $[\alpha]^{25}_D$ = -46.4 (C 0.11, CH_2Cl_2), 92% ee; The enantiomeric excess was determined by HPLC using a Chiralpak OD column (10% 2-propanol/hexane, 1 mL/min) after converted to the alcohol, t_{minor} = 17.761 min, t_{major} = 26.292 min.

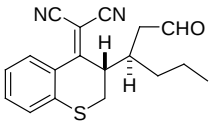


4bh, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.51 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 13.6 Hz, 2H), 4.21 (br.s, 2H), 3.60-3.51 (m, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 3.11 (dd, *J* = 10.4, 17.3 Hz, 1H), 2.56 (dd, *J* = 4.3, 17.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 198.6, 166.3, 156.0, 151.3, 142.6, 137.1, 127.8, 121.9, 118.3, 115.0, 113.1, 113.0, 110.5, 109.2, 78.9, 66.8, 44.5, 42.8, 33.2; IR (KBr) 2925, 2221, 1718, 1607, 1569, 1551, 1479, 1451, 1450; ESI-HRMS: calcd. for $C_{19}H_{14}N_2O_3$+CH_3OH+Na 373.1159, found 373.1159; $[\alpha]^{25}_D$ = -333.7 (C 0.24, CH_2Cl_2), 95% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AS column (10% 2-propanol/hexane, 1 mL/min) after converted to the alcohol, t_{minor} = 44.947 min, t_{major} = 50.296 min.



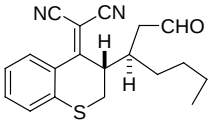


4ca, 91% yield. Its absolute configuration was determined to be (*C_8S, C_{13}R*) by X-ray analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.59 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.5 Hz, 1H), 7.24-7.17 (m, 2H), 3.48-3.42 (m, 1H), 3.27-3.21 (m, 2H), 2.44-2.27 (m, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.8, 173.3, 138.2, 133.8, 130.2, 127.1, 125.6, 124.9, 113.0, 112.6, 82.5, 48.0, 43.9, 28.4, 27.8, 17.5; IR (KBr) 2976, 2919, 2850, 2749, 2228, 1717, 1563, 1585, 1548, 1463, 775, 745 cm^{-1}; ESI-HRMS: calcd. for $C_{16}H_{14}N_2OS$-H 281.0743, found 281.0736; $[\alpha]^{25}_D$ = -547.5 (C 0.2, CH_2Cl_2), 92% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (35% 2-propanol/hexane, 1 mL/min), t_{minor} = 16.382 min, t_{major} = 29.398 min.

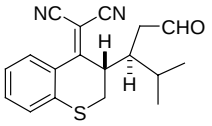


4cb, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.54 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 3.47-3.41 (m, 2H), 3.25-3.20 (m, 1H), 2.45-2.41 (m, 2H), 2.24-2.23 (m, 1H), 1.55-1.52 (m, 2H),

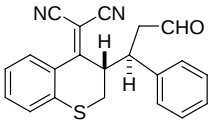
1.32-1.26 (m, 2H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.9, 173.4, 138.1, 133.7, 130.3, 127.0, 125.8, 124.9, 113.0, 112.5, 82.7, 45.2, 42.1, 33.0, 31.9, 29.6, 28.5, 18.7, 14.2; IR (film) 2958, 2931, 2225, 1722, 1588, 1562, 769, 735 cm^{-1}; ESI-HRMS: calcd. for $C_{18}H_{18}N_2OS$-H 309.1056, found 309.1066; $[\alpha]^{25}_D$ = -499.5 (C 0.22, CH_2Cl_2), 93% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 12.532 min, t_{major} = 18.432 min.



4cc, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.54 (s, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 3.46-3.41 (m, 2H), 3.23-3.20 (m, 1H), 2.46-2.41 (m, 2H), 2.24-2.23 (m, 1H), 1.60-1.56 (m, 1H), 1.33-1.25 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.9, 173.4, 138.1, 133.7, 130.4, 127.1, 125.8, 124.9, 113.0, 112.5, 82.7, 45.1, 42.0, 31.9, 30.4, 28.5, 27.5, 22.8, 13.9; IR (film) 2936, 2843, 2210, 1734, 1609, 1532, 1455, 795, 762 cm^{-1}; ESI-HRMS: calcd. for $C_{19}H_{20}N_2OS$-H 323.1213, found 323.1230; $[\alpha]^{25}_D$ = -643.5 (C 0.2, CH_2Cl_2), 92% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 11.415 min, t_{major} = 16.257 min.

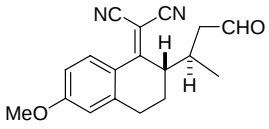


4ce, 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.35 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.26-7.16 (m, 2H), 3.48-3.36 (m, 2H), 3.23-3.18 (m, 1H), 2.49-2.43 (m, 2H), 2.16-2.09 (m, 2H), 0.91 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.9, 173.0, 138.0, 133.8, 131.0, 126.9, 125.6, 124.7, 113.0, 112.7, 82.5, 41.8, 41.2, 35.9, 28.6, 27.6, 21.4, 15.5; IR (film) 2960, 2933, 2225, 1721, 1588, 1561, 1547, 910, 734 cm^{-1}; ESI-HRMS: calcd. for $C_{18}H_{18}N_2S$-H 309.1056, found 309.1059; $[\alpha]^{25}_D$ = -318.3 (C 0.16, CH_2Cl_2), 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 11.557 min, t_{major} = 15.740 min.

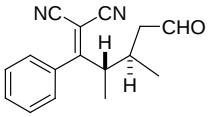


4cd, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.36 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.38-7.20 (m, 7H), 3.67-3.62 (m, 1H), 3.51-3.50 (m, 1H), 3.28 (dd, J = 3.3, 13.9 Hz, 1H), 2.97-2.96 (m, 1H), 2.62 (dd, J = 3.2, 13.9 Hz, 1H), 2.46 (dd, J = 1.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.1, 172.1, 138.9, 138.3, 134.1, 130.4, 129.2, 128.1, 127.9, 127.2, 125.0, 124.7, 113.0, 112.8, 82.7, 46.9, 44.0, 39.3, 28.6; IR (KBr) 2938, 2879, 2846, 2698, 2213,

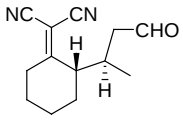
1736, 1620, 1543, 1472, 1446, 1326, 1219, 769, 517 cm^{-1}; ESI-HRMS: calcd. for $C_{21}H_{16}N_2OS$-H 343.0900, found 343.0896; $[\alpha]^{25}_D$ = -871.7 (C 0.12, CH_2Cl_2), 86% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 18.465 min, t_{major} = 22.332 min.



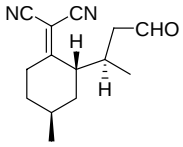
4da, 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.63 (s, 1H,), 7.98 (d, *J* = 8.9 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 3.86 (s, 3H), 3.06-2.87 (m, 3H), 2.42-2.07 (m, 5H), 1.05 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.5, 176.3, 163.9, 142.7, 130.5, 121.9, 114.3, 114.1, 113.9, 113.0, 77.7, 55.5, 48.6, 46.9, 28.6, 25.0, 24.4, 17.4; IR (KBr) 2935, 2879, 2746, 2223, 1718, 1605, 1568, 1561, 1546, 1496, 1279, 1243, 822 cm^{-1}; ESI-HRMS: calcd. for $C_{18}H_{18}N_2O_2$+Na 317.1260, found 317.1273; $[\alpha]^{25}_D$ = -180.0 (C 0.06, CH_2Cl_2), 95% ee; The enantiomeric excess was determined by HPLC on Chiralpak AS column (35% 2-propanol/hexane, 1 mL/min), t_{minor} = 16.640 min, t_{major} = 20.798 min.



4ea, 40 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.69 (s, 1H), 7.50-7.48 (m, 3H), 7.23-7.20 (m, 2H), 3.12-3.07 (m, 1H), 2.45-2.27 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.2, 184.2, 134.1, 131.0, 129.1, 126.9, 111.8, 88.0, 48.9, 47.0, 30.8, 29.6, 17.5, 16.7; IR (film) 2978, 2931, 2231, 1721, 1579, 1454 cm^{-1}; ESI-HRMS: calcd. for $C_{16}H_{16}N_2O$ +Na 275.1155, found 275.1166; $[\alpha]^{25}_D$ = -13.3 (C 0.1, CH_2Cl_2), 88% ee; The enantiomeric ratio was determined by HPLC on Chiralpak OD column (10% 2-propanol/hexane, 1 mL/min) after converted to the alcohol, t_{minor} = 10.015, t_{major} = 12.215 min.



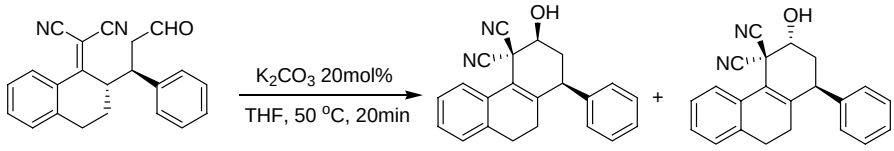
4fa, 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.74 (s, 1H), 2.92 (d, *J* = 13.9 Hz, 1H), 2.40 (d, *J* = 17.7 Hz, 1H), 2.36-2.33 (m, 1H), 2.28-2.26 (m, 2H), 2.22-2.20 (m, 3H), 1.65-1.52 (m, 4H), 1.08 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.2, 186.9, 110.6, 110.3, 82.8, 47.7, 47.7, 30.5, 28.8, 27.7, 27.0, 18.5, 16.9; IR (film) 2908, 2898, 1736, 1579, 1441 cm^{-1}; ESI-HRMS: calcd. for $C_{13}H_{16}N_2O$+Na 239.1155, found 239.1203; $[\alpha]^{25}_D$= -20.6 (C 0.32, CH_2Cl_2), 82%ee; The enantiomeric ratio was determined by HPLC on Chiracel OD column (5% 2-propanol/hexane, 1 mL/min) after converted to the alcohol, t_{minor} = 13.212 min, t_{major} = 15.988min.



4ga, 49% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.74 (s, 1H) 2.89-2.88 (m, 1H), 2.80-2.72 (m, 1H), 2.51-2.34 (m, 4H), 2.29-2.09 (m, 3H), 1.25-1.23 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H); 2D NMR and NOESY study determined the *trans*-configuration in the cyclohexyl ring structure; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ (ppm) 200.2 (CH), 187.7 (C), 111.7 (CN), 111.3 (CN), 82.8 (C), 49.0 (CH), 48.8 (CH_2), 37.9 (CH_2), 36.5 (CH_2), 31.5 (CH_2), 28.6 (CH), 25.8 (CH), 21.0 (CH_3), 18.0 (CH_3); IR (film) 2953, 2928, 1723, 1589, 1456, 1456 cm^{-1}; ESI-HRMS: calcd. for $C_{14}H_{18}N_2O$+Na 253.1311, found 253.1308; $[\alpha]^{25}_D$ = -47.0 (C 0.20, CH_2Cl_2), 68%ee; The enantiomeric ratio was determined by HPLC on Chiracel AS column (10% 2-propanol/hexane, 1 mL/min) after converted to the alcohol, t_{minor} = 7.373 min, t_{major} = 8.163min.

4. Spectra data of derived products

Intramolecular vinylogous aldol reaction



4ad 89% ee

5a 54% yield, 89% ee

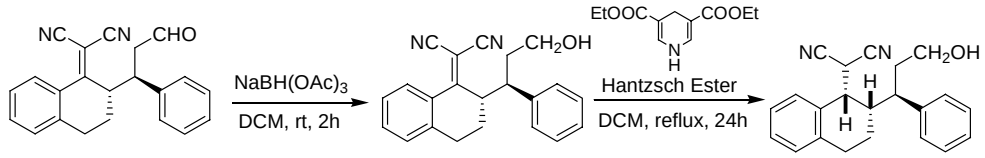
5b 18% yield, 89% ee

4ad 65.2mg (0.2 mmol) and K_2CO_3 5.5mg (0.04 mmol) were stirred in 5ml THF at 50 ^{o}C for 20 min. Then the solvent was removed and the residue was chromatographed on silica gel (10% ethyl acetate petroleum ether) to give pure **5a** 35.2 mg (54% yield) and **5b** 12mg (18% yield).

The structure of racemic **5a** has been confirmed by X-ray analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 7.8 Hz, 1H), 7.40-7.24 (m, 5H), 7.16-7.13 (m, 3H) 4.49-4.43 (m, 1H), 3.84-3.77 (m, 1H), 3.00 (d, *J* = 6.3 Hz, 1H), 2.69-2.48 (m, 3H), 2.21-2.16 (m, 1H), 1.95- 1.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.9, 140.3, 135.8, 133.7, 130.7, 129.8, 129.0, 128.3, 127.7, 127.6, 126.7, 126.3, 123.3, 121.3, 115.3, 114.0, 72.6, 47.8, 37.0, 28.5, 27.6; IR (KBr) 3535, 2939, 2930, 1630, 1600, 1490, 1451, 1113, 1067 cm^{-1}; ESI-HRMS: calcd. for $C_{22}H_{18}N_2O$ +Na 349.1311, found 349.1314; $[\alpha]^{25}_D$ = -29.0 (C 0.10, CH_2Cl_2), 89% ee; The enantiomeric ratio was determined by HPLC on Chiralpak OD column (30% 2-propanol/hexane, 1 mL/min), t_{minor} = 7.640, t_{major} = 23.176 min.

Compound **5b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.01 (d, *J* = 7.8 Hz, 1H), 7.39-7.21 (m, 5H), 7.14 (t, *J* = 6.5 Hz, 1H), 4.49 (m, 1H), 3.84-3.78 (m, 1H), 3.00 (d, *J* = 5.9 Hz, 1H), 2.69-2.50 (m, 3H), 2.21-2.17 (m, 1H), 1.95-1.90 (m, 2H); ESI-HRMS: calcd. for $C_{22}H_{18}N_2O$+Na349.1311, found 349.1314; The enantiomeric ratio (89% ee) was determined by HPLC on Chiralpak OD column (5% 2-propanol/hexane, 1 mL/min), t_{minor} = 42.061, t_{major} = 48.746

Chemoselective reduction of Michael addition product 4ad

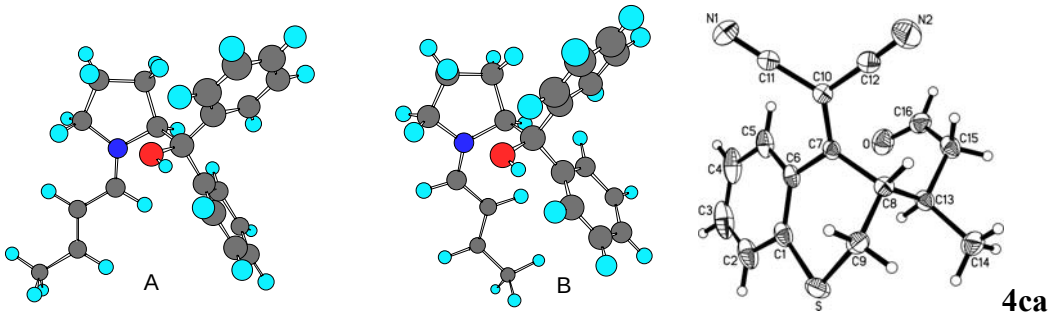


4ad 89% ee — **6** — 74% yield for two steps — **7** 89% ee

4ad 65.2mg (0.2 mmol) and $NaBH(OAc)_3$ 94mg (1 mmol) were stirred in 5ml DCM at room temperature for 2h. Then the mixture was washed with water, dried and concentrated. The residue was flash chromatographed on silica gel (20% ethyl acetate/petroleum ether) to give crude **6** (61mg, 98%) as white solid and direct used in the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 6.3 Hz, 1H), 7.38-7.22 (m, 7H), 3.59-3.54 (m, 1H), 3.41-3.35 (m, 1H), 2.85-2.83 (m, 2H), 2.72-2.71 (m, 1H), 1.93-1.88 (m, 2H), 1.75-1.67 (m, 3H); ESI-HRMS: calcd. for $C_{22}H_{20}N_2O$+Na 351.1468, found 351.1466.

Compound **6** 49 mg (0.15 mmol) and Hantzsch ester 202 mg (0.9 mmol) were refluxed in 5ml DCM for 24h. Then the solvent was removed and the residue was chromatographed on silica gel (40% ethyl acetate/petroleum ether) to give **7** as a white solid, 36mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.6 Hz, 1H), 7.40-7.19 (m, 8H), 4.44 (d, *J* = 2.0 Hz, 1H), 3.85 (br.s, 1H), 3.60-3.55 (m, 1H), 3.37-3.31 (m, 1H), 2.96 (dd, *J* = 6.8, 17.6 Hz, 1H), 2.84-2.78 (m, 1H), 2.76-2.66 (m, 1H), 2.32-2.25 (m, 2H), 2.19-2.12 (m, 1H), 1.85-1.69 (m, 2H), 1.57-1.47 (m, 1H); 2D NMR and NOESY study confirmed the *cis*-configuration in the ring structure; ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ (ppm) 142.2 (C), 136.9 (C), 133.1 (C), 129.6 (CH), 129.2 (CH), 128.8 (CH), 128.7 (CH), 128.1 (CH), 127.0 (CH), 126.1 (CH), 114.0 (CN), 112.3 (CN), 59.7 (CH_2), 44.7 (CH), 42.5 (CH), 42.2 (CH), 35.6 (CH_2), 27.9 (CH_2), 24.4 (CH), 21.9 (CH_2); ESI-HRMS: calcd. for $C_{22}H_{22}N_2O$+Na 353.1624, found 353.1636; IR (KBr) 3381, 2936, 1601, 1493, 1453, 1040, 703 cm^{-1}; $[\alpha]^{25}_D$ = -47 (C 0.2, CH_2Cl_2), 89% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AS column (5% 2-propanol/hexane, 1 ml/min), t_{minor} = 29.343 min, t_{major} = 36.390 min.

5. Preliminary calculation (PM3) study on the iminium transitional state of catalyst 1f and crotonaldehyde 3a



4ca

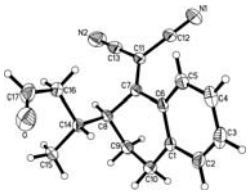
Optimized geometry of iminium transitional state

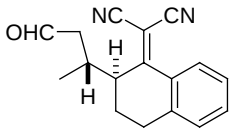
The activation of enal was proposed to be the formation of iminium salt of α,β-unsaturated aldehyde and secondary amine catalyst as shown above. The geometry of possible transitional **A** and **B** was optimized using semi-empirical method (PM3) performed on the Gaussian 98. The energy of transitional **A** was 3.6 kcal/mol lower than that of transitional **B**, indicating transitional **A** would be the preferred one in the Michael addition reaction. Therefore, attacking the *Re*-face of the transitional **A** leads to the formation of (*R*)-configuration at the β-position of crotonaldehyde **3a**, which is in fine accordance with what was observed in the X-ray analysis of chiral product **4ca** bearing a sulfur atom (see C13 in **4ca**).

6. X-ray data of enantiopure 4aa, 4ca and racemic 5a

Crystal data and structure of enantiopure 4aa

Table 1. Crystal data and structure refinement for 4aa.





enantiopure **4aa**

Identification code	4aa
Empirical formula	C17 H16 N2 O
Formula weight	264.32
Temperature	296(2) K
Wavelength	0.71073 A

Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 6.076(1) A alpha = 90 deg. b = 13.777(3) A beta = 90 deg. c = 17.439(3) A gamma = 90 deg.
Volume, Z	1459.74(51) A^3, 4
Density (calculated)	1.203 Mg/m^3
Absorption coefficient	0.076 mm^-1
F(000)	560
Crystal size	0.52 x 0.32 x 0.18 mm
Theta range for data collection	1.88 to 27.00 deg.
Limiting indices	0<=h<=7, 0<=k<=17, -1<=l<=22
Reflections collected	2014
Independent reflections	1903 [R(int) = 0.0093]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1903 / 0 / 183
Goodness-of-fit on F^2	0.905
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0722
R indices (all data)	R1 = 0.0663, wR2 = 0.0791
Absolute structure parameter	-3(3)
Extinction coefficient	0.039(2)
Largest diff. peak and hole	0.112 and -0.116 e.A^-3

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

	x	y	z	U(eq)
O	10901(4)	5384(2)	3706(1)	96(1)
N(1)	5422(5)	2678(2)	7038(1)	90(1)
N(2)	2025(4)	3162(2)	4918(1)	92(1)
C(1)	7507(4)	6078(2)	6477(1)	50(1)
C(2)	9051(5)	6431(2)	6994(1)	64(1)
C(3)	10566(5)	5837(2)	7338(1)	72(1)
C(4)	10621(5)	4865(2)	7163(1)	66(1)
C(5)	9094(4)	4488(2)	6664(1)	54(1)
C(6)	7496(4)	5075(1)	6323(1)	44(1)
C(7)	5833(4)	4687(1)	5793(1)	42(1)
C(8)	5084(4)	5373(1)	5174(1)	42(1)
C(9)	4187(4)	6260(2)	5606(1)	56(1)
C(10)	5939(5)	6759(2)	6087(1)	64(1)
C(11)	4899(4)	3801(1)	5872(1)	47(1)
C(12)	5255(5)	3181(2)	6523(1)	61(1)
C(13)	3307(5)	3450(2)	5339(2)	61(1)
C(14)	6917(4)	5602(1)	4590(1)	41(1)
C(15)	6150(4)	6371(1)	4016(1)	54(1)
C(16)	7582(4)	4678(1)	4170(1)	52(1)
C(17)	9530(5)	4773(2)	3673(2)	72(1)

Table 3. Bond lengths [A] and angles [deg] for 4aa.

O-C(17)	1.185(3)
N(1)-C(12)	1.138(3)
N(2)-C(13)	1.141(3)
C(1)-C(2)	1.389(3)
C(1)-C(6)	1.408(3)
C(1)-C(10)	1.500(3)
C(2)-C(3)	1.369(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.374(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.374(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.397(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.470(3)
C(7)-C(11)	1.352(3)
C(7)-C(8)	1.506(3)
C(8)-C(9)	1.535(3)
C(8)-C(14)	1.542(3)
C(8)-H(8)	0.9800
C(9)-C(10)	1.520(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(13)	1.426(3)
C(11)-C(12)	1.437(3)
C(14)-C(16)	1.523(3)
C(14)-C(15)	1.531(3)
C(14)-H(14)	0.9800
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(17)	1.473(3)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17)	0.9300
C(2)-C(1)-C(6)	118.1(2)
C(2)-C(1)-C(10)	120.3(2)

C(6)-C(1)-C(10)	121.6(2)
C(3)-C(2)-C(1)	122.0(2)
C(3)-C(2)-H(2)	119.0
C(1)-C(2)-H(2)	119.0
C(2)-C(3)-C(4)	120.1(3)
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(5)-C(4)-C(3)	119.5(3)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	121.4(2)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.9(2)
C(5)-C(6)-C(7)	122.34(18)
C(1)-C(6)-C(7)	118.7(2)
C(11)-C(7)-C(6)	123.56(18)
C(11)-C(7)-C(8)	120.8(2)
C(6)-C(7)-C(8)	115.48(18)
C(7)-C(8)-C(9)	104.77(15)
C(7)-C(8)-C(14)	112.54(18)
C(9)-C(8)-C(14)	114.71(17)
C(7)-C(8)-H(8)	108.2
C(9)-C(8)-H(8)	108.2
C(14)-C(8)-H(8)	108.2
C(10)-C(9)-C(8)	112.5(2)
C(10)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
C(1)-C(10)-C(9)	114.35(18)
C(1)-C(10)-H(10A)	108.7
C(9)-C(10)-H(10A)	108.7
C(1)-C(10)-H(10B)	108.7
C(9)-C(10)-H(10B)	108.7
H(10A)-C(10)-H(10B)	107.6
C(7)-C(11)-C(13)	121.6(2)
C(7)-C(11)-C(12)	123.6(2)
C(13)-C(11)-C(12)	114.5(2)
N(1)-C(12)-C(11)	176.4(3)
N(2)-C(13)-C(11)	179.3(3)
C(16)-C(14)-C(15)	110.22(16)
C(16)-C(14)-C(8)	109.78(17)

C(15)-C(14)-C(8)	110.68(18)
C(16)-C(14)-H(14)	108.7
C(15)-C(14)-H(14)	108.7
C(8)-C(14)-H(14)	108.7
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(14)	114.94(19)
C(17)-C(16)-H(16A)	108.5
C(14)-C(16)-H(16A)	108.5
C(17)-C(16)-H(16B)	108.5
C(14)-C(16)-H(16B)	108.5
H(16A)-C(16)-H(16B)	107.5
O-C(17)-C(16)	126.8(3)
O-C(17)-H(17)	116.6
C(16)-C(17)-H(17)	116.6

Symmetry transformations used to generate equivalent atoms:

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

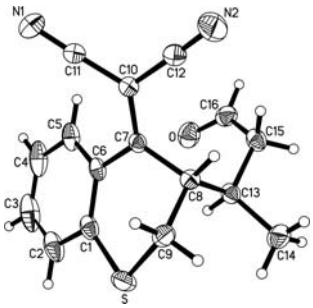
	U11	U22	U33	U23	U13	U12
O	73(1)	123(2)	94(2)	-11(1)	27(1)	-20(2)
N(1)	131(2)	67(1)	71(1)	26(1)	9(2)	-6(2)
N(2)	96(2)	73(2)	108(2)	-4(2)	-25(2)	-21(2)
C(1)	69(2)	49(1)	31(1)	1(1)	8(1)	-1(1)
C(2)	86(2)	68(2)	38(1)	-5(1)	9(2)	-22(2)
C(3)	72(2)	106(2)	37(1)	-2(1)	-1(2)	-19(2)
C(4)	61(2)	94(2)	43(1)	12(1)	-2(1)	-1(2)
C(5)	57(2)	62(1)	43(1)	6(1)	1(1)	6(2)
C(6)	52(1)	49(1)	30(1)	6(1)	4(1)	1(1)
C(7)	48(1)	42(1)	37(1)	1(1)	9(1)	8(1)
C(8)	46(1)	42(1)	38(1)	5(1)	1(1)	1(1)
C(9)	64(2)	55(1)	48(1)	10(1)	11(1)	17(2)
C(10)	96(2)	49(1)	48(1)	-4(1)	11(2)	9(2)
C(11)	58(2)	39(1)	43(1)	4(1)	5(1)	1(1)
C(12)	84(2)	44(1)	54(1)	6(1)	9(2)	-4(2)
C(13)	69(2)	47(2)	67(2)	6(1)	3(2)	-7(1)
C(14)	44(1)	44(1)	35(1)	1(1)	-3(1)	-4(1)
C(15)	70(2)	50(1)	42(1)	10(1)	2(1)	-7(1)
C(16)	60(2)	52(1)	45(1)	-1(1)	3(1)	-1(1)
C(17)	75(2)	83(2)	57(2)	-11(2)	19(2)	4(2)

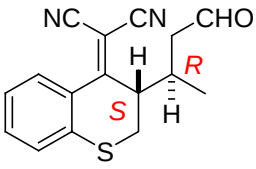
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 4aa.

	x	y	z	U(eq)
H(2)	9057	7089	7110	77
H(3)	11558	6093	7690	86
H(4)	11684	4465	7381	79
H(5)	9125	3829	6552	65
H(8)	3859	5068	4898	50
H(9A)	3597	6720	5238	67
H(9B)	2991	6055	5937	67
H(10A)	6774	7193	5759	77
H(10B)	5218	7152	6474	77
H(14)	8200	5852	4867	49
H(15A)	7236	6444	3620	65
H(15B)	5956	6979	4276	65
H(15C)	4779	6173	3792	65
H(16A)	7869	4176	4547	63
H(16B)	6351	4464	3859	63
H(17)	9703	4304	3294	86

Crystal data and structure of enantiopure 4ca

Table 1. Crystal data and structure refinement for 4ca.





enantiopure **4ca**

Identification code	4ca
Empirical formula	C16 H14 N2 O S
Formula weight	282.35
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 7.534(1) A alpha = 90 deg. b = 7.610(1) A beta = 97.25(1) deg. c = 12.685(1) A gamma = 90 deg.
Volume, Z	721.52(14) A^3, 2
Density (calculated)	1.300 Mg/m^3
Absorption coefficient	0.221 mm^-1
F(000)	296
Crystal size	0.58 x 0.48 x 0.16 mm
Theta range for data collection	1.62 to 27.00 deg.
Limiting indices	-9<=h<=9, -9<=k<=9, -16<=l<=16

Reflections collected	3788
Independent reflections	3158 [R(int) = 0.0126]
Absorption correction	Empirical
Max. and min. transmission	0.9960 and 0.9029
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3158 / 1 / 183
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0885
R indices (all data)	R1 = 0.0472, wR2 = 0.0924
Absolute structure parameter	0.05(8)
Extinction coefficient	0.035(5)
Largest diff. peak and hole	0.174 and -0.210 e.A^-3

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

	x	y	z	U(eq)
S	9545(1)	1427(1)	1120(1)	67(1)
O	4373(2)	4601(3)	2096(2)	75(1)
N(1)	5965(4)	-865(3)	4971(2)	96(1)
N(2)	9059(4)	3726(3)	5733(2)	95(1)
C(1)	7436(3)	723(3)	1384(2)	53(1)
C(2)	6423(5)	-241(3)	579(2)	81(1)
C(3)	4759(5)	-819(4)	686(3)	97(1)
C(4)	3998(4)	-441(3)	1610(3)	86(1)
C(5)	4960(3)	492(3)	2405(2)	60(1)
C(6)	6707(2)	1068(2)	2327(1)	43(1)
C(7)	7704(2)	2080(2)	3193(1)	36(1)
C(8)	9050(2)	3402(2)	2906(1)	38(1)
C(9)	10430(3)	2343(3)	2388(2)	51(1)
C(10)	7516(3)	1783(3)	4232(1)	46(1)
C(11)	6599(3)	309(3)	4615(2)	62(1)
C(12)	8391(3)	2881(3)	5060(2)	59(1)
C(13)	8233(3)	4964(2)	2237(2)	44(1)
C(14)	9699(3)	6115(3)	1873(2)	69(1)
C(15)	7023(3)	6055(3)	2870(2)	53(1)
C(16)	5088(3)	5629(3)	2725(2)	59(1)

Table 3. Bond lengths [A] and angles [deg] for 4ca.

S-C(1)	1.749(3)
S-C(9)	1.802(2)
O-C(16)	1.196(3)
N(1)-C(11)	1.133(3)
N(2)-C(12)	1.134(3)
C(1)-C(2)	1.403(3)
C(1)-C(6)	1.403(3)
C(2)-C(3)	1.351(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.398(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.365(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.402(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.468(2)
C(7)-C(10)	1.362(2)
C(7)-C(8)	1.505(2)
C(8)-C(9)	1.528(3)
C(8)-C(13)	1.542(2)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.434(3)
C(10)-C(12)	1.436(3)
C(13)-C(14)	1.526(3)
C(13)-C(15)	1.533(3)
C(13)-H(13)	0.9800
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.481(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16)	0.9300
C(1)-S-C(9)	100.97(10)
C(2)-C(1)-C(6)	118.9(2)
C(2)-C(1)-S	116.4(2)
C(6)-C(1)-S	124.67(16)

C(3)-C(2)-C(1)	121.6(3)
C(3)-C(2)-H(2)	119.2
C(1)-C(2)-H(2)	119.2
C(2)-C(3)-C(4)	120.1(3)
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(5)-C(4)-C(3)	119.4(3)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	121.7(3)
C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
C(5)-C(6)-C(1)	118.28(19)
C(5)-C(6)-C(7)	120.47(17)
C(1)-C(6)-C(7)	121.18(17)
C(10)-C(7)-C(6)	122.05(16)
C(10)-C(7)-C(8)	120.05(16)
C(6)-C(7)-C(8)	117.80(15)
C(7)-C(8)-C(9)	105.50(15)
C(7)-C(8)-C(13)	114.46(14)
C(9)-C(8)-C(13)	114.58(15)
C(7)-C(8)-H(8)	107.3
C(9)-C(8)-H(8)	107.3
C(13)-C(8)-H(8)	107.3
C(8)-C(9)-S	113.11(14)
C(8)-C(9)-H(9A)	109.0
S-C(9)-H(9A)	109.0
C(8)-C(9)-H(9B)	109.0
S-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(7)-C(10)-C(11)	124.85(17)
C(7)-C(10)-C(12)	121.13(18)
C(11)-C(10)-C(12)	113.79(17)
N(1)-C(11)-C(10)	175.5(3)
N(2)-C(12)-C(10)	178.2(3)
C(14)-C(13)-C(15)	110.40(17)
C(14)-C(13)-C(8)	110.83(16)
C(15)-C(13)-C(8)	110.63(15)
C(14)-C(13)-H(13)	108.3
C(15)-C(13)-H(13)	108.3
C(8)-C(13)-H(13)	108.3
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(13)	117.25(19)
C(16)-C(15)-H(15A)	108.0
C(13)-C(15)-H(15A)	108.0
C(16)-C(15)-H(15B)	108.0
C(13)-C(15)-H(15B)	108.0
H(15A)-C(15)-H(15B)	107.2
O-C(16)-C(15)	125.4(2)
O-C(16)-H(16)	117.3
C(15)-C(16)-H(16)	117.3

Symmetry transformations used to generate equivalent atoms:

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

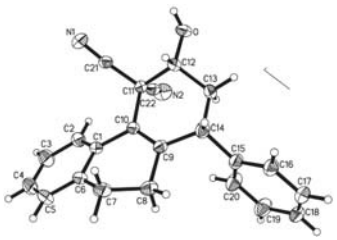
	U11	U22	U33	U23	U13	U12
S	94(1)	59(1)	54(1)	-2(1)	30(1)	16(1)
O	61(1)	67(1)	98(1)	3(1)	10(1)	-5(1)
N(1)	136(2)	72(1)	93(2)	3(1)	60(2)	-27(2)
N(2)	140(2)	88(2)	52(1)	-13(1)	-1(1)	-24(2)
C(1)	76(1)	35(1)	45(1)	0(1)	-7(1)	12(1)
C(2)	136(3)	47(1)	49(1)	-7(1)	-23(2)	11(2)
C(3)	122(3)	50(2)	99(2)	-9(2)	-69(2)	1(2)
C(4)	67(2)	43(1)	133(3)	1(2)	-42(2)	-1(1)
C(5)	49(1)	37(1)	89(2)	-3(1)	-9(1)	3(1)
C(6)	44(1)	30(1)	52(1)	-3(1)	-5(1)	6(1)
C(7)	36(1)	30(1)	43(1)	-1(1)	6(1)	6(1)
C(8)	37(1)	41(1)	35(1)	2(1)	1(1)	0(1)
C(9)	48(1)	46(1)	60(1)	9(1)	16(1)	7(1)
C(10)	53(1)	40(1)	46(1)	-2(1)	15(1)	-2(1)
C(11)	85(2)	51(1)	57(1)	-6(1)	33(1)	-6(1)
C(12)	84(2)	54(1)	41(1)	-3(1)	13(1)	-10(1)
C(13)	54(1)	38(1)	40(1)	1(1)	4(1)	6(1)
C(14)	91(2)	48(1)	73(1)	17(1)	27(1)	3(1)
C(15)	61(1)	40(1)	59(1)	-2(1)	6(1)	11(1)
C(16)	66(1)	51(1)	63(1)	12(1)	20(1)	10(1)

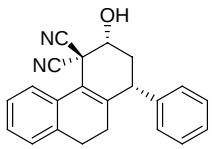
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 4ca.

	x	y	z	U(eq)
H(2)	6908	-489	-43	97
H(3)	4119	-1468	144	117
H(4)	2847	-822	1683	103
H(5)	4444	753	3015	72
H(8)	9659	3882	3572	46
H(9A)	10872	1396	2861	61
H(9B)	11434	3098	2293	61
H(13)	7502	4497	1606	53
H(14A)	10470	6533	2481	83
H(14B)	9164	7098	1478	83
H(14C)	10385	5439	1429	83
H(15A)	7462	5934	3618	64
H(15B)	7153	7281	2684	64
H(16)	4371	6209	3160	71

Crystal data and structure of racemic 5a

Table 1. Crystal data and structure refinement for 5a.





racemic **5a**

Identification code	5a
Empirical formula	C22 H18 N2 O
Formula weight	326.38
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 15.603(4) A alpha = 90 deg. b = 6.159(1) A beta = 97.72(2) deg. c = 18.040(4) A gamma = 90 deg.
Volume, Z	1717.96(73) A^3, 4
Density (calculated)	1.262 Mg/m^3
Absorption coefficient	0.078 mm^-1
F(000)	688
Crystal size	0.60 x 0.42 x 0.24 mm
Theta range for data collection	1.62 to 25.49 deg.
Limiting indices	0<=h<=18, 0<=k<=7, -21<=l<=21
Reflections collected	3776

Independent reflections	3203 [R(int) = 0.0250]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3203 / 0 / 228
Goodness-of-fit on F^2	0.966
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.0936
R indices (all data)	R1 = 0.0815, wR2 = 0.1033
Extinction coefficient	0.0204(15)
Largest diff. peak and hole	0.174 and -0.143 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 5a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O	4640(1)	6747(3)	5818(1)	56(1)
N(1)	4423(1)	8848(3)	3962(1)	59(1)
N(2)	3433(1)	2927(4)	4759(1)	69(1)
C(1)	2061(1)	8175(3)	3908(1)	39(1)
C(2)	2270(1)	6854(4)	3341(1)	51(1)
C(3)	1849(2)	7031(5)	2618(1)	67(1)
C(4)	1213(2)	8550(5)	2463(1)	74(1)
C(5)	991(1)	9883(5)	3015(1)	68(1)
C(6)	1403(1)	9722(4)	3745(1)	49(1)
C(7)	1162(1)	11083(4)	4374(1)	59(1)
C(8)	1185(1)	9704(4)	5074(1)	55(1)
C(9)	2058(1)	8618(3)	5258(1)	37(1)
C(10)	2479(1)	8005(3)	4694(1)	32(1)
C(11)	3412(1)	7149(3)	4850(1)	34(1)
C(12)	3833(1)	7785(3)	5653(1)	39(1)
C(13)	3237(1)	7083(4)	6199(1)	45(1)
C(14)	2393(1)	8358(3)	6078(1)	43(1)
C(15)	1729(1)	7315(3)	6515(1)	43(1)
C(16)	1594(1)	8115(4)	7203(1)	51(1)
C(17)	1017(1)	7137(4)	7617(1)	57(1)
C(18)	568(1)	5352(4)	7342(1)	59(1)
C(19)	692(2)	4517(4)	6659(1)	66(1)
C(20)	1274(1)	5492(4)	6251(1)	59(1)
C(21)	3961(1)	8079(3)	4322(1)	38(1)
C(22)	3432(1)	4761(4)	4786(1)	43(1)

Table 3. Bond lengths [A] and angles [deg] for 5a.

O-C(12)	1.408(2)
O-H(0)	0.8200
N(1)-C(21)	1.137(2)
N(2)-C(22)	1.131(3)
C(1)-C(2)	1.380(3)
C(1)-C(6)	1.403(3)
C(1)-C(10)	1.482(2)
C(2)-C(3)	1.384(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.365(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.372(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.389(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.498(3)
C(7)-C(8)	1.518(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.513(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.337(2)
C(9)-C(14)	1.510(3)
C(10)-C(11)	1.538(2)
C(11)-C(22)	1.476(3)
C(11)-C(21)	1.480(2)
C(11)-C(12)	1.558(2)
C(12)-C(13)	1.506(2)
C(12)-H(12)	0.9800
C(13)-C(14)	1.524(3)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.526(2)
C(14)-H(14)	0.9800
C(15)-C(16)	1.377(3)
C(15)-C(20)	1.379(3)
C(16)-C(17)	1.383(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.360(3)

C(17)-H(17)	0.9300
C(18)-C(19)	1.374(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.380(3)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300

C(12)-O-H(0)	109.5
C(2)-C(1)-C(6)	118.96(18)
C(2)-C(1)-C(10)	123.40(18)
C(6)-C(1)-C(10)	117.61(18)
C(1)-C(2)-C(3)	121.5(2)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
C(4)-C(3)-C(2)	119.2(2)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	120.6(2)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	121.1(2)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	118.7(2)
C(5)-C(6)-C(7)	123.1(2)
C(1)-C(6)-C(7)	118.20(17)
C(6)-C(7)-C(8)	109.67(19)
C(6)-C(7)-H(7A)	109.7
C(8)-C(7)-H(7A)	109.7
C(6)-C(7)-H(7B)	109.7
C(8)-C(7)-H(7B)	109.7
H(7A)-C(7)-H(7B)	108.2
C(9)-C(8)-C(7)	110.47(16)
C(9)-C(8)-H(8A)	109.6
C(7)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8B)	109.6
C(7)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
C(10)-C(9)-C(14)	125.07(16)
C(10)-C(9)-C(8)	118.51(17)
C(14)-C(9)-C(8)	116.40(16)
C(9)-C(10)-C(1)	120.66(16)
C(9)-C(10)-C(11)	120.48(16)
C(1)-C(10)-C(11)	118.86(15)

C(22)-C(11)-C(21)	108.39(16)
C(22)-C(11)-C(10)	110.88(16)
C(21)-C(11)-C(10)	111.45(15)
C(22)-C(11)-C(12)	108.18(16)
C(21)-C(11)-C(12)	107.01(15)
C(10)-C(11)-C(12)	110.77(14)
O-C(12)-C(13)	110.18(15)
O-C(12)-C(11)	109.65(15)
C(13)-C(12)-C(11)	108.35(15)
O-C(12)-H(12)	109.5
C(13)-C(12)-H(12)	109.5
C(11)-C(12)-H(12)	109.5
C(12)-C(13)-C(14)	110.90(16)
C(12)-C(13)-H(13A)	109.5
C(14)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
C(14)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	108.0
C(9)-C(14)-C(13)	111.89(15)
C(9)-C(14)-C(15)	112.40(16)
C(13)-C(14)-C(15)	110.07(16)
C(9)-C(14)-H(14)	107.4
C(13)-C(14)-H(14)	107.4
C(15)-C(14)-H(14)	107.4
C(16)-C(15)-C(20)	117.97(19)
C(16)-C(15)-C(14)	120.76(19)
C(20)-C(15)-C(14)	121.20(18)
C(15)-C(16)-C(17)	121.3(2)
C(15)-C(16)-H(16)	119.3
C(17)-C(16)-H(16)	119.3
C(18)-C(17)-C(16)	119.7(2)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(17)-C(18)-C(19)	120.2(2)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(18)-C(19)-C(20)	119.8(2)
C(18)-C(19)-H(19)	120.1
C(20)-C(19)-H(19)	120.1
C(15)-C(20)-C(19)	121.0(2)
C(15)-C(20)-H(20)	119.5
C(19)-C(20)-H(20)	119.5
N(1)-C(21)-C(11)	174.9(2)
N(2)-C(22)-C(11)	177.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 5a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O	31(1)	74(1)	60(1)	17(1)	-6(1)	-1(1)
N(1)	47(1)	76(1)	55(1)	8(1)	18(1)	-9(1)
N(2)	67(1)	47(1)	93(2)	-1(1)	13(1)	3(1)
C(1)	30(1)	49(1)	37(1)	6(1)	2(1)	-4(1)
C(2)	47(1)	69(2)	38(1)	-1(1)	1(1)	-3(1)
C(3)	68(2)	92(2)	39(1)	-5(1)	-5(1)	-14(2)
C(4)	60(2)	114(2)	43(1)	17(2)	-16(1)	-18(2)
C(5)	41(1)	93(2)	65(2)	30(2)	-10(1)	4(1)
C(6)	29(1)	65(2)	52(1)	17(1)	2(1)	2(1)
C(7)	39(1)	67(2)	73(2)	18(1)	13(1)	20(1)
C(8)	40(1)	68(2)	60(1)	6(1)	17(1)	14(1)
C(9)	33(1)	41(1)	39(1)	1(1)	9(1)	1(1)
C(10)	27(1)	35(1)	35(1)	2(1)	3(1)	1(1)
C(11)	30(1)	38(1)	34(1)	3(1)	5(1)	0(1)
C(12)	31(1)	47(1)	38(1)	5(1)	-1(1)	-3(1)
C(13)	45(1)	57(1)	30(1)	5(1)	-1(1)	-7(1)
C(14)	47(1)	45(1)	37(1)	-5(1)	10(1)	-6(1)
C(15)	45(1)	48(1)	37(1)	0(1)	12(1)	-1(1)
C(16)	50(1)	64(2)	39(1)	-5(1)	12(1)	-4(1)
C(17)	53(1)	78(2)	43(1)	0(1)	17(1)	3(1)
C(18)	47(1)	77(2)	55(1)	19(1)	19(1)	2(1)
C(19)	68(2)	66(2)	68(2)	-1(1)	21(1)	-19(1)
C(20)	70(2)	62(2)	51(1)	-11(1)	25(1)	-17(1)
C(21)	30(1)	45(1)	39(1)	0(1)	4(1)	3(1)
C(22)	31(1)	49(2)	49(1)	2(1)	7(1)	3(1)

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

	x	y	z	U(eq)
H(0)	5028	7615	5771	67
H(2)	2705	5822	3447	62
H(3)	1996	6126	2242	81
H(4)	927	8682	1978	89
H(5)	557	10912	2900	82
H(7A)	587	11675	4238	71
H(7B)	1564	12283	4468	71
H(8A)	1073	10611	5490	66
H(8B)	736	8607	4997	66
H(12)	3913	9362	5683	47
H(13A)	3518	7310	6705	53
H(13B)	3114	5545	6135	53
H(14)	2514	9815	6284	51
H(16)	1897	9338	7393	61
H(17)	935	7698	8081	68
H(18)	177	4696	7618	70
H(19)	384	3299	6471	79
H(20)	1361	4910	5791	71

H-bond:
O H0 N1 0.82 2.37 3.082(2) 146.2 3_676