*Supplementary Material*

# PINDY: A Novel, Pinene-Derived Bipyridine Ligand and its Application in Asymmetric, Copper(I)-Catalyzed Allylic Oxidation

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**General Methods.** Melting points were determined on a Kofler block and are uncorrected. Optical rotations were recorded in $CHCl_3$ at 25 °C unless otherwise indicated with an error of <±0.1. The NMR spectra were recorded in $CDCl_3$, $^1H$ at 250 MHz and $^{13}C$ at 62.9 MHz with chloroform-$d_1$ (δ 7.26, $^1H$; δ 77.0, $^{13}C$) as internal standard. Various 2D-techniques and DEPT experiments were used to establish the structures and to assign the signals. The IR spectra were recorded for $CHCl_3$ solutions. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. The GC-MS analysis was performed with RSL-150 column (25 m × 0.25 mm). All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware twice evacuated and filled with the nitrogen. Experiments involving copper complexes were carried out under the atmosphere of argon. Solvents and solutions were transferred by syringe-septum and cannula techniques. All solvents for the reactions were of reagent grade and were dried and distilled immediately before use as follows: diethyl ether from lithium aluminum hydride, tetrahydrofuran (THF) from sodium/benzophenone; dichloromethane from calcium hydride. Standard workup of an ethereal solution means washing 3 × with 5% HCl (aqueous), water, and 3 × with 5% $KHCO_3$ (aqueous) and drying with $MgSO_4$. Petroleum ether refers to the fraction boiling in the range of 40-60 $^oC$. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior. (1*S*)-(-)-β-Pinene was purchased from Aldrich and had $[\alpha]_D$ –21 (neat).

**(4*S*,6*R*)-(−)-5,5-Dimethyl-4,6-methano-(*N*-methylacetamido)-cyclohexene (−)-(4).** Nopinone oxime **3**[16] (10.0 g, 65.3 mmol) was dissolved in toluene (20 mL) and iron powder (36.4 g, 652 mmol) was added. The mixture was cooled to 0 ºC and a solution of acetic anhydride (18.6 mL, 196 mmol) and acetic acid (11.3 mL, 196 mmol) was added dropwise under mechanical stirring over a period of 10 min; the reaction was instantaneous. The residual iron powder was then filtered off and washed with ethyl acetate (4 × 100 mL). The combined organic solutions were washed with 2M NaOH (2 × 100 mL), dried ($MgSO_4$), and evaporated to give (-)-**4** as a white solid (10.5 g, 90%) that was pure enough for the next step: mp 66-68 ºC; $[\alpha]_D$ –61.6 (*c* 2.18, $CHCl_3$); $^1H$ NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.49 (s, 3 H), 1.52 (d, *J* = 8.7 Hz, 1 H), 2.22 (s, 3 H), 2.35-2.2 (m, 2 H), 2.55-2.45 (m, 1 H), 2.65-2.55 (m, 1 H), 6.11 (br s, 1 H), 7.20 (br s, 1 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$) δ 21.38, 24.76, 26.41, 29.76, 31.56, 38.80, 41.15,

47.56, 105.46, 141.04, 168.88, IR ($CHCl_3$) $\nu_{max}$ 3425, 3000, 2930, 2840, 1685, 1605, 1505, 1370 $cm^{-1}$; HRMS (FAB) 180.13892 ($C_{11}H_{18}NO$ requires 180.13884).

**(6*R*,8*R*)-(–)-2-Chloro-5,6,7,8,-tetrahydro-7,7-dimethyl-[6,8-methanoquinoline] (–)-(5).** Phosphoryl chloride (59.9 g, 390 mmol) was added dropwise to a DMF solution (12.9 mL, 167 mmol) of **4** (10.0 g, 55.8 mmol) at 0 ºC and the mixture was stirred at the same temperature for 1 h. Water (100 mL) was then carefully added (**CAUTION!** This reaction is strongly exothermic; temperature must be kept below 5 ºC). Aqueous NaOH solution was then added to reach pH 13 and the mixture was extracted with ethyl acetate (4 × 200 mL). The combined organic layers were washed with brine (1 × 100 mL), dried ($MgSO_4$), and evaporated to give crude **5** as an oil (10.3 g) that was purified *via* chromatography on silica gel (200 g), first with hexane, than a hexane-ethyl acetate mixture (9:1) to afford pure (-)-**5** (8.08 g, 70%) as a white solid: mp 80-82 ºC; $[\alpha]_D$ –18.6 (*c* 1.9, $CHCl_3$); $^1$H NMR (250 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 1.27 (d, *J* = 9.8 Hz, 1 H), 1.41 (s, 3 H), 2.3-2.4 (m, 1 H), 2.71 (ddd, *J* = 6.0, 5.5, and 9.8 Hz, 1 H), 2.91 (d, *J* = 2.7 Hz, 1 H), 2.98 (dd, *J* = 6.0 and 5.5, Hz, 1 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$) δ 21.58, 26.29, 30.94, 31.09, 39.46, 40.33, 50.40, 121.63, 129.20, 138.18, 147.29, 167.72; IR ($CHCl_3$) $\nu_{max}$ 2980, 2960, 2945, 1580, 1565, 1470, 1420, 1130 $cm^{-1}$; HRMS (FAB) 208.08921 ($C_{12}H_{15}ClN$ requires 208.08930).

**(6*R*,6*R*',8*R*,8*R*')-(+)-5,5',6,6',7,7',8,8'-Octahydro-6,6',7,7'-tetramethylbi(6,8-methanoquinoline) (+)-(6).** Zinc powder (0.990 g, 15.2 mmol) was added to a solution of $NiCl_2$•$6H_2O$ (3.53 g, 14.6 mmol) and $PPh_3$ (15.3 g, 58.5 mmol) in degassed DMF (100 mL). The mixture was heated at 60 ºC for 2 h, during which period the color changed from blue to the red. Then a solution of (-)-**5** (3.00 g, 14.44 mmol) in DMF (10 mL) was added. The mixture was heated for a further 18 h and then poured into 10% aqueous $NH_3$ (50 mL). The resulting suspension was extracted with $CH_2Cl_2$ (4 × 200 mL), dried ($MgSO_4$), and evaporated to give a brown solid. This solid was dissolved in ethyl acetate (200 mL) and extracted with 6N HCl (5 × 100 mL). The combined aqueous layers were extracted twice with ethyl acetate, adjusted to pH 13 with a conc. aqueous NaOH solution, and extracted with ethyl acetate (5 × 200mL). The combined organic layers were extracted with brine (1 × 100 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a viscose yellowish oil (2.20 g). This oil was heated under vacuum (0.3 torr) to 200 ºC for 1 h to remove the reduction product **7** (0.80 g, 32%): $^1$H NMR (250 MHz, $CDCl_3$) δ 0.66 (s, 3 H), 1.38 (d, *J* = 9.6 Hz, 1 H), 1.41 (s, 3 H), 2.3-2.4 (m, 1 H), 2.71 (ddd, *J* =9.6, 5.8, and 5.8 Hz, 2 H), 2.97 (m, 2 H), 7.18 (m, 1 H), 7.52 (m, 1H), 8.32 (m, 1 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$) δ 21.5 (Me), 26.4 (Me), 31.1 ($CH_2$), 31.6 ($CH_2$), 39.4 (C), 40.4(CH), 50.6 (CH), 121.6 (CH), 130.3 (C), 135.4 (CH), 145.6 (C), 166.5 (C); MS (ES) 274 ($M+H^+$). The resulting solid was purified *via* chromatography on silica gel, first with hexane, then with a hexane-ethyl acetate mixture (9:1) to give compound (+)-**6** (1.25 g, 50%). Alternatively, the crude product was crystallized from a methanol-water mixture to afford (+)-**6** as a white solid (0.73 g, 33%): mp 142-144 ºC; $[\alpha]_D$ +35.8 (*c* 2.10, $CHCl_3$); $^1$H NMR (250 MHz, $CDCl_3$) δ 0.67 (s, 6 H), 1.34 (d, *J* = 9.6 Hz, 2 H), 1.42 (s, 6 H), 2.3-2.4 (m, 2 H), 2.73 (ddd, *J* =9.6, 5.8, and 5.8 Hz, 2 H), 2.96 (d, *J* = 2.5 Hz, 4 H), 3.08 (dd, *J* = 5.8 and 5.8, Hz, 2 H) 7.48 (d, *J* = 7.9 Hz, 2 H), 8.07 (d, *J* = 7.9 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$) δ 21.6, 26. 5, 31.29, 3.63, 39.6, 40.6, 50.9, 119.2, 130.2, 136.3, 153.1, 166.1; IR ($CHCl_3$) $\nu_{max}$ 2960, 2880, 2840, 1590, 1565, 1470, 1440, 1420, 1390, 1365; $cm^{-1}$; HRMS (FAB) 345.23312 ($C_{24}H_{29}N_2$ requires 345.23307).

**(6*R*,6*R*',8*R*,8*R*')-[5,5',6,6',7,7',8,8'-Octahydro-6,6',7,7'-tetramethylbi(6,8-methanoquinoline)] Copper(II) Chloride Complex (8).** A solution of copper(II) chloride dihydrate (97 mg, 0.57 mmol) in EtOH (5 mL) was added to a solution of (+)-**6** (200 mg, 0.58

mmol) in $CH_2Cl_2$ (5 mL); the color of the solution instantaneously changed from green to deep red. The mixture was refluxed for 12 h to ensure completion of the complexation reaction. The solvent was evaporated and the resulting red solid was recrystallized from a chloroform-hexane mixture to give the copper complex **8** (245 mg, 75%): mp dec. >250 $^{o}$C without melting. Calcd for $C_{24}H_{28}Cl_2N_2Cu\bullet CH_2Cl_2$: C, 53.25; H, 5.36; N, 4.97. Found: C, 52.91; H, 5.58; N, 4.71. Crystallographic data for **8**: $C_{24}H_{28}Cl_2N_2Cu\bullet CH_2Cl_2$, $M$ = 563.85. Crystals were obtained from a solution of the complex in $CH_2Cl_2$, covered by hexane and left at –18 $^{o}$C for two days. They are orthorhombic, space group $P2_12_12_1$, $a$ = 10.3637(1), $b$ =3.6592(2), $c$ = 17.9777(2) Å, $V$ = 2544.92(5) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.472 g cm$^{-3}$, $\mu$ = 1.295 mm$^{-1}$. Data were collected at 183 K on a Siemens SMART CCD diffractometer using Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å), a graphite monochromator, and $\omega$ scan mode at four different $\phi$ orientations, covering thus the entire reciprocal sphere up to 0.65 Å resolution. A total of 30160 reflections were measured, from which 9036 were unique ($R_{int}$ = 0.0198), with 8590 observed data having $I > 2\sigma_I$. All reflections were used in the structure refinement based on $F^2$ by full-matrix least-squares technique with hydrogen atoms calculated into theoretical positions, riding during refinement on the respective pivot atom (328 parameters). Final $R_F$ = 0.0332 for the observed data and w$R(F^2)$ = 0.0973 for all data. The estimated error in C-C bond-lengths is in the range of 0.002-0.003 Å. The absolute configuration determined with Flack factor = 0.003(7).

**Chiral HPLC Analysis of the Products of Allylic Oxidation (11a-c). 11a:** Chiralcel OD-H, hexane-isopropyl alcohol (99.8:0.2), flow rate 0.5 mL/min, $t_s$ = 30.2 min (major), $t_R$ = 38.3 min (minor), UV detection at 220 nm. **11b:** Chiralpak AD, hexane-isopropyl alcohol (99.6:0.4), flow rate 1 mL/min, $t_R$ = 12.6 min (minor), $t_S$ = 13.8 min (major), UV detection at 220 nm. **11c:** Chiralcel OJ, hexane-isopropyl alcohol (99.7:0.3), flow rate 0.5 mL/min, $t_R$ = 23.7 min (minor), $t_S$ = 25.7 min (major), UV detection at 220 nm.

Table 1. Crystal data and structure refinement for **8**•$CH_2Cl_2$.

| | | |
|---|---|---|
| Empirical formula | C25 H30 Cl4 Cu N2 | |
| Formula weight | 563.85 | |
| Temperature | 183(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 10.36370(10) Å | α= 90°. |
| | b = 13.6592(2) Å | β= 90°. |
| | c = 17.9777(2) Å | γ = 90°. |
| Volume | 2544.92(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.472 $Mg/m^3$ | |
| Absorption coefficient | 1.295 $mm^{-1}$ | |
| F(000) | 1164 | |
| Crystal size | 0.56 x 0.40 x 0.35 $mm^3$ | |
| Theta range for data collection | 1.87 to 32.97°. | |
| Index ranges | -15<=h<=15, -20<=k<=18, -26<=l<=27 | |
| Reflections collected | 30160 | |
| Independent reflections | 9036 [R(int) = 0.0198] | |
| Completeness to theta = 32.97° | 96.3 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.6600 and 0.5309 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9036 / 0 / 328 | |
| Goodness-of-fit on $F^2$ | 1.085 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0332, wR2 = 0.0954 | |
| R indices (all data) | R1 = 0.0356, wR2 = 0.0973 | |
| Absolute structure parameter | 0.003(7) | |
| Largest diff. peak and hole | 1.550 and -0.921 e.$Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **8**•$CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cu(1) | 2661(1) | 8096(1) | 1742(1) | 20(1) |
| Cl(1) | 4658(1) | 7546(1) | 1576(1) | 36(1) |
| Cl(2) | 2509(1) | 8306(1) | 2968(1) | 34(1) |
| Cl(3) | 5785(1) | 10116(1) | 3125(1) | 70(1) |
| Cl(4) | 6106(1) | 8648(1) | 4276(1) | 53(1) |
| N(1) | 866(1) | 7677(1) | 1432(1) | 18(1) |
| N(1') | 2459(1) | 9009(1) | 879(1) | 20(1) |
| C(2) | 435(2) | 8156(1) | 815(1) | 20(1) |
| C(3) | -805(2) | 8020(2) | 543(1) | 26(1) |
| C(4) | -1646(2) | 7402(2) | 933(1) | 29(1) |
| C(4A) | -1214(2) | 6911(1) | 1555(1) | 24(1) |
| C(5) | -2086(2) | 6273(2) | 2035(1) | 31(1) |
| C(6) | -1324(2) | 5844(1) | 2687(1) | 28(1) |
| C(7) | -495(2) | 6644(1) | 3084(1) | 23(1) |
| C(8) | 521(2) | 6470(1) | 2445(1) | 22(1) |
| C(8A) | 81(2) | 7043(1) | 1781(1) | 20(1) |
| C(9) | -44(2) | 5417(1) | 2375(1) | 32(1) |
| C(10) | -1024(2) | 7680(2) | 3183(1) | 29(1) |
| C(11) | 8(2) | 6291(2) | 3840(1) | 35(1) |
| C(2') | 1349(2) | 8860(1) | 484(1) | 19(1) |
| C(3') | 1097(2) | 9390(1) | -161(1) | 25(1) |
| C(4') | 1974(2) | 10099(1) | -389(1) | 26(1) |
| C(4A') | 3066(2) | 10282(1) | 27(1) | 26(1) |
| C(5') | 4054(2) | 11058(2) | -173(1) | 35(1) |
| C(6') | 5109(2) | 11120(2) | 420(1) | 35(1) |
| C(7') | 5651(2) | 10071(2) | 609(1) | 31(1) |
| C(8') | 4432(2) | 9972(1) | 1132(1) | 26(1) |
| C(8A') | 3279(2) | 9716(1) | 671(1) | 22(1) |
| C(9') | 4457(2) | 11115(2) | 1199(1) | 34(1) |
| C(10') | 5841(2) | 9333(2) | -18(1) | 37(1) |
| C(11') | 6898(2) | 10115(2) | 1062(2) | 46(1) |
| C(12) | 5813(3) | 8851(2) | 3328(2) | 47(1) |

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Table 3. Bond lengths [Å] and angles [°] for **8**•$CH_2Cl_2$.

| | |
|---|---|
| Cu(1)-N(1') | 2.0004(13) |
| Cu(1)-N(1) | 2.0244(14) |
| Cu(1)-Cl(1) | 2.2227(5) |
| Cu(1)-Cl(2) | 2.2294(5) |
| Cl(3)-C(12) | 1.766(3) |
| Cl(4)-C(12) | 1.753(3) |
| N(1)-C(8A) | 1.343(2) |
| N(1)-C(2) | 1.364(2) |
| N(1')-C(8A') | 1.340(2) |
| N(1')-C(2') | 1.367(2) |
| C(2)-C(3) | 1.387(2) |
| C(2)-C(2') | 1.475(2) |
| C(3)-C(4) | 1.401(3) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(4A) | 1.380(3) |
| C(4)-H(4) | 0.9500 |
| C(4A)-C(8A) | 1.414(2) |
| C(4A)-C(5) | 1.523(3) |
| C(5)-C(6) | 1.530(3) |
| C(5)-H(5A) | 0.97(3) |
| C(5)-H(5B) | 1.05(5) |
| C(6)-C(9) | 1.554(3) |
| C(6)-C(7) | 1.563(3) |
| C(6)-H(6) | 1.0000 |
| C(7)-C(10) | 1.528(3) |
| C(7)-C(11) | 1.534(3) |
| C(7)-C(8) | 1.577(2) |
| C(8)-C(8A) | 1.497(2) |
| C(8)-C(9) | 1.558(3) |
| C(8)-H(8) | 1.0000 |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |
| C(11)-H(111) | 0.9800 |
| C(11)-H(112) | 0.9800 |

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|---|---|
| C(11)-H(113) | 0.9800 |
| C(2’)-C(3’) | 1.392(2) |
| C(3’)-C(4’) | 1.390(3) |
| C(3’)-H(3’) | 0.9500 |
| C(4’)-C(4A’) | 1.380(3) |
| C(4’)-H(4’) | 1.0800 |
| C(4A’)-C(8A’) | 1.409(2) |
| C(4A’)-C(5’) | 1.518(3) |
| C(5’)-C(6’) | 1.529(3) |
| C(5’)-H(5’1) | 0.9900 |
| C(5’)-H(5’2) | 0.9900 |
| C(6’)-C(9’) | 1.555(3) |
| C(6’)-C(7’) | 1.576(3) |
| C(6’)-H(6’) | 1.0000 |
| C(7’)-C(10’) | 1.525(3) |
| C(7’)-C(11’) | 1.529(3) |
| C(7’)-C(8’) | 1.581(3) |
| C(8’)-C(8A’) | 1.496(3) |
| C(8’)-C(9’) | 1.566(3) |
| C(8’)-H(8’) | 1.0000 |
| C(9’)-H(9’1) | 0.9900 |
| C(9’)-H(9’2) | 0.9900 |
| C(10’)-H(10D) | 0.9800 |
| C(10’)-H(10E) | 0.9800 |
| C(10’)-H(10F) | 0.9800 |
| C(11’)-H(11A) | 1.0162 |
| C(11’)-H(11B) | 1.0162 |
| C(11’)-H(11C) | 1.0162 |
| C(12)-H(12A) | 1.0228 |
| C(12)-H(12B) | 1.0228 |

| | |
|---|---|
| N(1’)-Cu(1)-N(1) | 82.38(6) |
| N(1’)-Cu(1)-Cl(1) | 101.77(5) |
| N(1)-Cu(1)-Cl(1) | 136.31(4) |
| N(1’)-Cu(1)-Cl(2) | 132.79(4) |
| N(1)-Cu(1)-Cl(2) | 104.08(4) |
| Cl(1)-Cu(1)-Cl(2) | 104.01(2) |
| C(8A)-N(1)-C(2) | 119.41(14) |
| C(8A)-N(1)-Cu(1) | 127.63(11) |

| | |
|---|---|
| C(2)-N(1)-Cu(1) | 112.87(11) |
| C(8A')-N(1')-C(2') | 119.73(14) |
| C(8A')-N(1')-Cu(1) | 126.82(12) |
| C(2')-N(1')-Cu(1) | 113.45(11) |
| N(1)-C(2)-C(3) | 121.73(16) |
| N(1)-C(2)-C(2') | 115.50(14) |
| C(3)-C(2)-C(2') | 122.69(15) |
| C(2)-C(3)-C(4) | 118.75(16) |
| C(2)-C(3)-H(3) | 120.6 |
| C(4)-C(3)-H(3) | 120.6 |
| C(4A)-C(4)-C(3) | 119.76(17) |
| C(4A)-C(4)-H(4) | 120.1 |
| C(3)-C(4)-H(4) | 120.1 |
| C(4)-C(4A)-C(8A) | 118.65(16) |
| C(4)-C(4A)-C(5) | 123.05(16) |
| C(8A)-C(4A)-C(5) | 118.23(15) |
| C(4A)-C(5)-C(6) | 110.33(15) |
| C(4A)-C(5)-H(5A) | 114.4(17) |
| C(6)-C(5)-H(5A) | 110.4(17) |
| C(4A)-C(5)-H(5B) | 98(2) |
| C(6)-C(5)-H(5B) | 108(3) |
| H(5A)-C(5)-H(5B) | 115(3) |
| C(5)-C(6)-C(9) | 107.91(18) |
| C(5)-C(6)-C(7) | 111.40(16) |
| C(9)-C(6)-C(7) | 87.57(15) |
| C(5)-C(6)-H(6) | 115.5 |
| C(9)-C(6)-H(6) | 115.5 |
| C(7)-C(6)-H(6) | 115.5 |
| C(10)-C(7)-C(11) | 108.07(17) |
| C(10)-C(7)-C(6) | 120.24(16) |
| C(11)-C(7)-C(6) | 111.81(16) |
| C(10)-C(7)-C(8) | 117.67(14) |
| C(11)-C(7)-C(8) | 111.82(15) |
| C(6)-C(7)-C(8) | 85.91(13) |
| C(8A)-C(8)-C(9) | 107.69(15) |
| C(8A)-C(8)-C(7) | 107.38(14) |
| C(9)-C(8)-C(7) | 86.96(13) |
| C(8A)-C(8)-H(8) | 116.9 |
| C(9)-C(8)-H(8) | 116.9 |

| | |
|---|---|
| C(7)-C(8)-H(8) | 116.9 |
| N(1)-C(8A)-C(4A) | 121.50(15) |
| N(1)-C(8A)-C(8) | 121.62(14) |
| C(4A)-C(8A)-C(8) | 116.83(14) |
| C(6)-C(9)-C(8) | 86.90(14) |
| C(6)-C(9)-H(9A) | 114.2 |
| C(8)-C(9)-H(9A) | 114.2 |
| C(6)-C(9)-H(9B) | 114.2 |
| C(8)-C(9)-H(9B) | 114.2 |
| H(9A)-C(9)-H(9B) | 111.3 |
| C(7)-C(10)-H(10A) | 109.5 |
| C(7)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(7)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| C(7)-C(11)-H(111) | 109.5 |
| C(7)-C(11)-H(112) | 109.5 |
| H(111)-C(11)-H(112) | 109.5 |
| C(7)-C(11)-H(113) | 109.5 |
| H(111)-C(11)-H(113) | 109.5 |
| H(112)-C(11)-H(113) | 109.5 |
| N(1’)-C(2’)-C(3’) | 120.91(16) |
| N(1’)-C(2’)-C(2) | 115.35(14) |
| C(3’)-C(2’)-C(2) | 123.64(16) |
| C(2’)-C(3’)-C(4’) | 119.03(17) |
| C(2’)-C(3’)-H(3’) | 120.5 |
| C(4’)-C(3’)-H(3’) | 120.5 |
| C(4A’)-C(4’)-C(3’) | 120.14(16) |
| C(4A’)-C(4’)-H(4’) | 119.9 |
| C(3’)-C(4’)-H(4’) | 119.9 |
| C(4’)-C(4A’)-C(8A’) | 118.38(17) |
| C(4’)-C(4A’)-C(5’) | 123.45(17) |
| C(8A’)-C(4A’)-C(5’) | 118.17(18) |
| C(4A’)-C(5’)-C(6’) | 110.84(17) |
| C(4A’)-C(5’)-H(5’1) | 109.5 |
| C(6’)-C(5’)-H(5’1) | 109.5 |
| C(4A’)-C(5’)-H(5’2) | 109.5 |
| C(6’)-C(5’)-H(5’2) | 109.5 |

| | |
|---|---|
| H(5’1)-C(5’)-H(5’2) | 108.1 |
| C(5’)-C(6’)-C(9’) | 108.46(19) |
| C(5’)-C(6’)-C(7’) | 110.78(18) |
| C(9’)-C(6’)-C(7’) | 87.53(16) |
| C(5’)-C(6’)-H(6’) | 115.6 |
| C(9’)-C(6’)-H(6’) | 115.6 |
| C(7’)-C(6’)-H(6’) | 115.6 |
| C(10’)-C(7’)-C(11’) | 108.1(2) |
| C(10’)-C(7’)-C(6’) | 119.3(2) |
| C(11’)-C(7’)-C(6’) | 112.4(2) |
| C(10’)-C(7’)-C(8’) | 119.04(16) |
| C(11’)-C(7’)-C(8’) | 111.21(18) |
| C(6’)-C(7’)-C(8’) | 85.49(15) |
| C(8A’)-C(8’)-C(9’) | 106.76(17) |
| C(8A’)-C(8’)-C(7’) | 109.23(15) |
| C(9’)-C(8’)-C(7’) | 86.96(15) |
| C(8A’)-C(8’)-H(8’) | 116.6 |
| C(9’)-C(8’)-H(8’) | 116.6 |
| C(7’)-C(8’)-H(8’) | 116.6 |
| N(1’)-C(8A’)-C(4A’) | 121.69(17) |
| N(1’)-C(8A’)-C(8’) | 121.36(15) |
| C(4A’)-C(8A’)-C(8’) | 116.89(16) |
| C(6’)-C(9’)-C(8’) | 86.69(16) |
| C(6’)-C(9’)-H(9’1) | 114.2 |
| C(8’)-C(9’)-H(9’1) | 114.2 |
| C(6’)-C(9’)-H(9’2) | 114.2 |
| C(8’)-C(9’)-H(9’2) | 114.2 |
| H(9’1)-C(9’)-H(9’2) | 111.4 |
| C(7’)-C(10’)-H(10D) | 109.5 |
| C(7’)-C(10’)-H(10E) | 109.5 |
| H(10D)-C(10’)-H(10E) | 109.5 |
| C(7’)-C(10’)-H(10F) | 109.5 |
| H(10D)-C(10’)-H(10F) | 109.5 |
| H(10E)-C(10’)-H(10F) | 109.5 |
| C(7’)-C(11’)-H(11A) | 109.5 |
| C(7’)-C(11’)-H(11B) | 109.5 |
| H(11A)-C(11’)-H(11B) | 109.5 |
| C(7’)-C(11’)-H(11C) | 109.5 |
| H(11A)-C(11’)-H(11C) | 109.5 |

| | |
|---|---|
| H(11B)-C(11’)-H(11C) | 109.5 |
| Cl(4)-C(12)-Cl(3) | 111.01(15) |
| Cl(4)-C(12)-H(12A) | 109.4 |
| Cl(3)-C(12)-H(12A) | 109.4 |
| Cl(4)-C(12)-H(12B) | 109.4 |
| Cl(3)-C(12)-H(12B) | 109.4 |
| H(12A)-C(12)-H(12B) | 108.0 |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$)for **8**•$CH_2Cl_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Cu(1) | 17(1) | 25(1) | 17(1) | 3(1) | 0(1) | -1(1) |
| Cl(1) | 22(1) | 39(1) | 46(1) | 3(1) | 3(1) | 7(1) |
| Cl(2) | 36(1) | 47(1) | 19(1) | -4(1) | 0(1) | -11(1) |
| Cl(3) | 96(1) | 67(1) | 47(1) | 9(1) | 8(1) | 5(1) |
| Cl(4) | 68(1) | 47(1) | 43(1) | 1(1) | 9(1) | 18(1) |
| N(1) | 18(1) | 20(1) | 16(1) | 0(1) | 0(1) | 1(1) |
| N(1') | 20(1) | 22(1) | 17(1) | 2(1) | 2(1) | -1(1) |
| C(2) | 21(1) | 23(1) | 18(1) | -1(1) | 0(1) | 1(1) |
| C(3) | 25(1) | 32(1) | 22(1) | 3(1) | -6(1) | -4(1) |
| C(4) | 23(1) | 36(1) | 28(1) | 3(1) | -8(1) | -6(1) |
| C(4A) | 23(1) | 28(1) | 22(1) | 0(1) | -2(1) | -7(1) |
| C(5) | 27(1) | 38(1) | 29(1) | 5(1) | -3(1) | -14(1) |
| C(6) | 28(1) | 26(1) | 31(1) | 3(1) | 2(1) | -8(1) |
| C(7) | 21(1) | 26(1) | 22(1) | 2(1) | 1(1) | -3(1) |
| C(8) | 22(1) | 21(1) | 22(1) | 4(1) | 2(1) | -1(1) |
| C(8A) | 20(1) | 20(1) | 20(1) | 0(1) | 1(1) | -2(1) |
| C(9) | 37(1) | 19(1) | 41(1) | 0(1) | 6(1) | -2(1) |
| C(10) | 26(1) | 33(1) | 28(1) | -5(1) | 4(1) | 3(1) |
| C(11) | 29(1) | 49(1) | 26(1) | 12(1) | -1(1) | -3(1) |
| C(2') | 21(1) | 21(1) | 16(1) | 0(1) | 2(1) | 2(1) |
| C(3') | 27(1) | 29(1) | 19(1) | 3(1) | 1(1) | 3(1) |
| C(4') | 32(1) | 26(1) | 20(1) | 6(1) | 3(1) | 3(1) |
| C(4A') | 31(1) | 25(1) | 23(1) | 4(1) | 6(1) | -1(1) |
| C(5') | 43(1) | 32(1) | 30(1) | 9(1) | 6(1) | -10(1) |
| C(6') | 38(1) | 33(1) | 34(1) | 2(1) | 7(1) | -13(1) |
| C(7') | 25(1) | 35(1) | 32(1) | -3(1) | 4(1) | -10(1) |
| C(8') | 29(1) | 27(1) | 23(1) | 0(1) | 1(1) | -7(1) |
| C(8A') | 23(1) | 24(1) | 21(1) | 2(1) | 3(1) | -2(1) |
| C(9') | 40(1) | 29(1) | 31(1) | -3(1) | 6(1) | -9(1) |
| C(10') | 30(1) | 45(1) | 38(1) | -8(1) | 7(1) | -5(1) |
| C(11') | 28(1) | 62(2) | 47(1) | -5(1) | 0(1) | -16(1) |
| C(12) | 38(1) | 57(2) | 45(1) | -16(1) | -7(1) | 15(1) |

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Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **8**•$CH_2Cl_2$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | -1078 | 8340 | 101 | 24(6) |
| H(4) | -2511 | 7322 | 769 | 43(8) |
| H(5A) | -2530(30) | 5760(20) | 1765(16) | 33(7) |
| H(5B) | -2680(50) | 6820(30) | 2250(30) | 78(14) |
| H(6) | -1821 | 5399 | 3024 | 39(8) |
| H(8) | 1453 | 6525 | 2583 | 20(6) |
| H(9A) | -106 | 5174 | 1858 | 47(9) |
| H(9B) | 373 | 4930 | 2704 | 25(6) |
| H(10A) | -1668 | 7683 | 3582 | 70(13) |
| H(10B) | -1427 | 7897 | 2718 | 27(7) |
| H(10C) | -317 | 8125 | 3312 | 34(7) |
| H(111) | -689 | 6322 | 4208 | 52 |
| H(112) | 722 | 6712 | 4001 | 52 |
| H(113) | 313 | 5615 | 3796 | 52 |
| H(3') | 336 | 9268 | -441 | 38(8) |
| H(4') | 1800(8) | 10508(18) | -890(20) | 81(15) |
| H(5'1) | 3621 | 11701 | -219 | 28(7) |
| H(5'2) | 4448 | 10898 | -660 | 63(11) |
| H(6') | 5773 | 11641 | 340 | 18(5) |
| H(8') | 4553 | 9593 | 1603 | 37(8) |
| H(9'1) | 3592 | 11423 | 1210 | 67(12) |
| H(9'2) | 5011 | 11365 | 1605 | 38(8) |
| H(10D) | 6559 | 9543 | -335 | 50(10) |
| H(10E) | 5051 | 9291 | -315 | 82(15) |
| H(10F) | 6036 | 8688 | 195 | 38(8) |
| H(11A) | 7039(4) | 9463(12) | 1323(5) | 29(7) |
| H(11B) | 6831(3) | 10657(10) | 1447(7) | 61(11) |
| H(11C) | 7654(14) | 10252(3) | 717(6) | 40(8) |
| H(12A) | 4950(30) | 8545(9) | 3184(5) | 88(15) |
| H(12B) | 6520(20) | 8520(10) | 3020(9) | 52(10) |

Table 6. Torsion angles [°] for **8**•$CH_2Cl_2$.

| | |
|---|---|
| N(1')-Cu(1)-N(1)-C(8A) | -174.36(14) |
| Cl(1)-Cu(1)-N(1)-C(8A) | 86.56(14) |
| Cl(2)-Cu(1)-N(1)-C(8A) | -42.06(14) |
| N(1')-Cu(1)-N(1)-C(2) | 2.14(11) |
| Cl(1)-Cu(1)-N(1)-C(2) | -96.94(12) |
| Cl(2)-Cu(1)-N(1)-C(2) | 134.44(11) |
| N(1)-Cu(1)-N(1')-C(8A') | 174.44(15) |
| Cl(1)-Cu(1)-N(1')-C(8A') | -49.73(15) |
| Cl(2)-Cu(1)-N(1')-C(8A') | 72.27(16) |
| N(1)-Cu(1)-N(1')-C(2') | -5.42(11) |
| Cl(1)-Cu(1)-N(1')-C(2') | 130.41(11) |
| Cl(2)-Cu(1)-N(1')-C(2') | -107.59(11) |
| C(8A)-N(1)-C(2)-C(3) | 1.2(2) |
| Cu(1)-N(1)-C(2)-C(3) | -175.63(14) |
| C(8A)-N(1)-C(2)-C(2') | 178.13(14) |
| Cu(1)-N(1)-C(2)-C(2') | 1.31(18) |
| N(1)-C(2)-C(3)-C(4) | 2.5(3) |
| C(2')-C(2)-C(3)-C(4) | -174.20(18) |
| C(2)-C(3)-C(4)-C(4A) | -2.8(3) |
| C(3)-C(4)-C(4A)-C(8A) | -0.4(3) |
| C(3)-C(4)-C(4A)-C(5) | 176.4(2) |
| C(4)-C(4A)-C(5)-C(6) | -179.2(2) |
| C(8A)-C(4A)-C(5)-C(6) | -2.4(3) |
| C(4A)-C(5)-C(6)-C(9) | -47.5(2) |
| C(4A)-C(5)-C(6)-C(7) | 47.1(2) |
| C(5)-C(6)-C(7)-C(10) | 37.9(2) |
| C(9)-C(6)-C(7)-C(10) | 146.17(17) |
| C(5)-C(6)-C(7)-C(11) | 166.18(17) |
| C(9)-C(6)-C(7)-C(11) | -85.53(18) |
| C(5)-C(6)-C(7)-C(8) | -81.94(17) |
| C(9)-C(6)-C(7)-C(8) | 26.36(14) |
| C(10)-C(7)-C(8)-C(8A) | -40.9(2) |
| C(11)-C(7)-C(8)-C(8A) | -166.83(16) |
| C(6)-C(7)-C(8)-C(8A) | 81.30(15) |
| C(10)-C(7)-C(8)-C(9) | -148.48(17) |
| C(11)-C(7)-C(8)-C(9) | 85.57(18) |
| C(6)-C(7)-C(8)-C(9) | -26.30(15) |

| | |
|---|---|
| C(2)-N(1)-C(8A)-C(4A) | -4.6(2) |
| Cu(1)-N(1)-C(8A)-C(4A) | 171.72(13) |
| C(2)-N(1)-C(8A)-C(8) | 177.75(15) |
| Cu(1)-N(1)-C(8A)-C(8) | -5.9(2) |
| C(4)-C(4A)-C(8A)-N(1) | 4.2(3) |
| C(5)-C(4A)-C(8A)-N(1) | -172.76(17) |
| C(4)-C(4A)-C(8A)-C(8) | -178.04(18) |
| C(5)-C(4A)-C(8A)-C(8) | 5.0(2) |
| C(9)-C(8)-C(8A)-N(1) | -140.48(16) |
| C(7)-C(8)-C(8A)-N(1) | 127.14(16) |
| C(9)-C(8)-C(8A)-C(4A) | 41.8(2) |
| C(7)-C(8)-C(8A)-C(4A) | -50.63(19) |
| C(5)-C(6)-C(9)-C(8) | 85.05(17) |
| C(7)-C(6)-C(9)-C(8) | -26.67(14) |
| C(8A)-C(8)-C(9)-C(6) | -80.84(16) |
| C(7)-C(8)-C(9)-C(6) | 26.44(14) |
| C(8A')-N(1')-C(2')-C(3') | 4.2(2) |
| Cu(1)-N(1')-C(2')-C(3') | -175.90(13) |
| C(8A')-N(1')-C(2')-C(2) | -172.25(14) |
| Cu(1)-N(1')-C(2')-C(2) | 7.62(18) |
| N(1)-C(2)-C(2')-N(1') | -6.0(2) |
| C(3)-C(2)-C(2')-N(1') | 170.93(16) |
| N(1)-C(2)-C(2')-C(3') | 177.65(16) |
| C(3)-C(2)-C(2')-C(3') | -5.4(3) |
| N(1')-C(2')-C(3')-C(4') | -1.9(3) |
| C(2)-C(2')-C(3')-C(4') | 174.25(16) |
| C(2')-C(3')-C(4')-C(4A') | -1.0(3) |
| C(3')-C(4')-C(4A')-C(8A') | 1.7(3) |
| C(3')-C(4')-C(4A')-C(5') | -178.55(19) |
| C(4')-C(4A')-C(5')-C(6') | 176.8(2) |
| C(8A')-C(4A')-C(5')-C(6') | -3.4(3) |
| C(4A')-C(5')-C(6')-C(9') | -45.4(2) |
| C(4A')-C(5')-C(6')-C(7') | 49.1(2) |
| C(5')-C(6')-C(7')-C(10') | 39.2(3) |
| C(9')-C(6')-C(7')-C(10') | 147.99(19) |
| C(5')-C(6')-C(7')-C(11') | 167.14(19) |
| C(9')-C(6')-C(7')-C(11') | -84.0(2) |
| C(5')-C(6')-C(7')-C(8') | -81.76(18) |
| C(9')-C(6')-C(7')-C(8') | 27.06(15) |

| | |
|---|---|
| C(10’)-C(7’)-C(8’)-C(8A’) | -41.3(3) |
| C(11’)-C(7’)-C(8’)-C(8A’) | -167.87(19) |
| C(6’)-C(7’)-C(8’)-C(8A’) | 79.83(17) |
| C(10’)-C(7’)-C(8’)-C(9’) | -148.0(2) |
| C(11’)-C(7’)-C(8’)-C(9’) | 85.4(2) |
| C(6’)-C(7’)-C(8’)-C(9’) | -26.86(15) |
| C(2’)-N(1’)-C(8A’)-C(4A’) | -3.6(3) |
| Cu(1)-N(1’)-C(8A’)-C(4A’) | 176.58(13) |
| C(2’)-N(1’)-C(8A’)-C(8’) | 173.59(16) |
| Cu(1)-N(1’)-C(8A’)-C(8’) | -6.3(2) |
| C(4’)-C(4A’)-C(8A’)-N(1’) | 0.6(3) |
| C(5’)-C(4A’)-C(8A’)-N(1’) | -179.15(18) |
| C(4’)-C(4A’)-C(8A’)-C(8’) | -176.66(17) |
| C(5’)-C(4A’)-C(8A’)-C(8’) | 3.6(3) |
| C(9’)-C(8’)-C(8A’)-N(1’) | -132.99(18) |
| C(7’)-C(8’)-C(8A’)-N(1’) | 134.35(18) |
| C(9’)-C(8’)-C(8A’)-C(4A’) | 44.3(2) |
| C(7’)-C(8’)-C(8A’)-C(4A’) | -48.4(2) |
| C(5’)-C(6’)-C(9’)-C(8’) | 83.81(19) |
| C(7’)-C(6’)-C(9’)-C(8’) | -27.29(15) |
| C(8A’)-C(8’)-C(9’)-C(6’) | -81.97(18) |
| C(7’)-C(8’)-C(9’)-C(6’) | 27.21(16) |

Table 7. Hydrogen bonds for **8**•$CH_2Cl_2$ [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(4')-H(4')...Cl(2)#1 | 1.08 | 2.71 | 3.7082(18) | 154.2 |
| C(12)-H(12A)...Cl(2) | 1.02 | 2.58 | 3.563(3) | 161.8 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+2,z-1/2