Geometric control of ground state spin in a copper(I) bis(verdazyl) complex)

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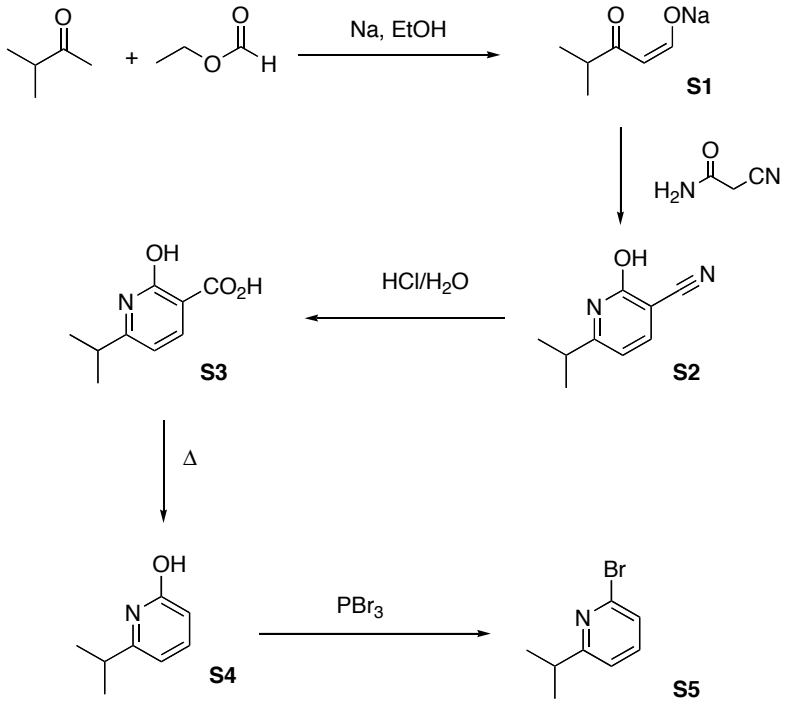
Supporting Information



Scheme S1: Synthesis of 6-isopropyl-2-bromopyridine (**S5**)

4-methyl-3-oxopentanal sodium salt (S1)

A mixture of ethyl formate (74 g, 1 mol) and 3-methyl-2-butanone (86 g, 1 mol) was added dropwise to a suspension of metallic sodium (23 g, 1 mol) in 500 mL ether. Addition was continued at a rate required to maintain a gentle reflux. After 5h the sodium had been completely consumed and the product precipitate was removed by filtration. Cooling of the filtrate at 4˚C for two days resulted in a second crop of product giving a total yield of 85g (0.62 mol, 62%). The product was not purified but used directly in the next step.

3-cyano-2-hydroxy-6-isopropylpyridine (S2)[1]

To 85 g (0.62 mol) of 4-methyl-3-oxopentanal sodium salt (**S1**) dissolved in 300 mL water was added 52.2 g (0.62 mol) cyanoacetamide. The solution was heated under reflux for 4h and allowed to cool overnight. The precipitated solids were removed by filtration and a second crop isolated after acidification with conc. HCl. The combined solids were stirred with 200 mL dichloromethane, filtered and the solution evaporated to give 3-cyano-2-hydroxy-6-isopropylpyridine as a yellow solid that was recrystallized from toluene. Yield 45.2 g (0.28 mol, 45 %). m.p. 201-204˚C (lit.[2] 203-204˚C) Spectroscopic properties were identical to literature values.[1]

2-hydroxy-6-isopropylpyridine-3-carboxylic acid (S3)

3-cyano-2-hydroxy-6-isopropylpyridine (**S2**) (45 g, 0.28 mol) was dissolved in 200 mL conc. HCl and heated under reflux for 3h. Upon cooling, crystals of the product were formed and isolated by filtration. A second crop was obtained by dilution of the filtrate with 500 mL H_2O. The combined solids were redissolved in dichloromethane, the solution dried with $MgSO_4$, filtered and evaporated to give the product as a cream solid, yield 46 g (0.254 mol, 92%), m.p. 182-184 ˚C (lit[2-3] 185-186˚C) ^{1}H NMR ($CDCl_3$) 13.69 (bs, 1H), 13.07 (bs, 1H), 8.54 (d, 1H, J=8.7 Hz), 6.54 (d, 1H, J, =8.7 Hz), 3.01 (septet , 1H, J=5.1 Hz), 1.38 (d, 6H, J=5.3). ^{13}C NMR ($CDCl_3$) 166.1, 165.3, 162.1, 148.1, 115.2, 106.7, 33.2, 21.5. IR (NaCl plate) 2917 cm^{-1}(broad, CO_2H) 1746 cm^{-1} (C=O)

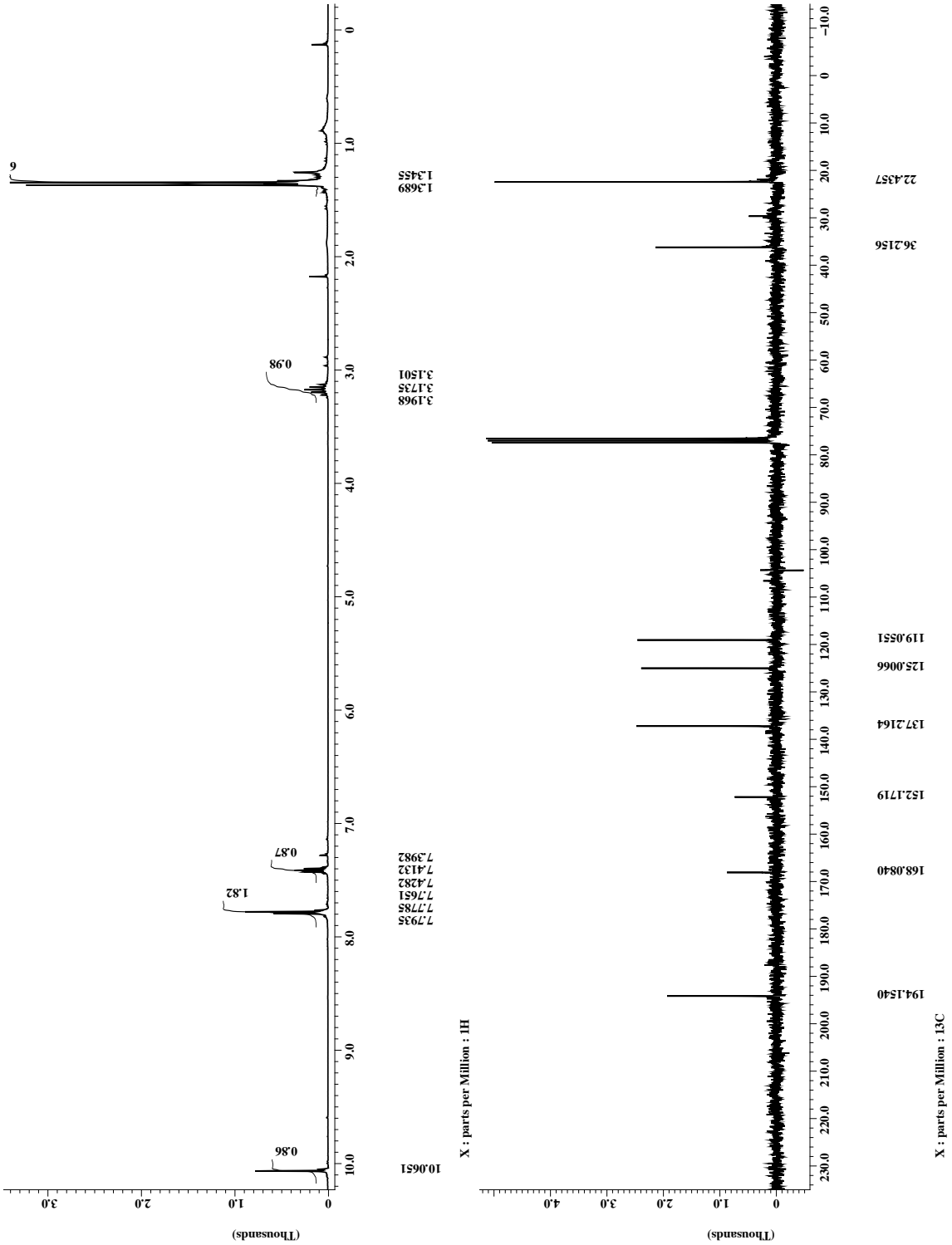
2-hydroxy-6-isopropylpyridine (S4)

2-hydroxy-6-isopropylpyridine-3-carboxylic acid (**S3**) (45 g, 0.25 mol) was added in small portions to a beaker heated to 300˚C in a sand bath. In between additions the beaker was covered with a cooled watch glass to minimize loss of product vapor. After 15 min, bubbling had ceased and the beaker was removed and allowed to cool. The tan colored residue was recrystallized from heptane to give 22 g (0.16 mol, 65%) of 2-hydroxy-6-isopropylpyridine as pale yellow crystals with m.p. 130-131˚C (lit[2] 129-130˚C) ^{1}H NMR 13.12 (bs, 1H), 7.37 (1H, dd, J=9.0, 7.5 Hz) 6.39 (d, 1H, J=9.), 6.05 (d, 1H, J=7.5) 2.90 (septet, 1H, J=6.9 Hz) 1.27 (d, 6H, J-6.9 Hz); ^{13}C NMR data identical to that reported by Overman.[4]

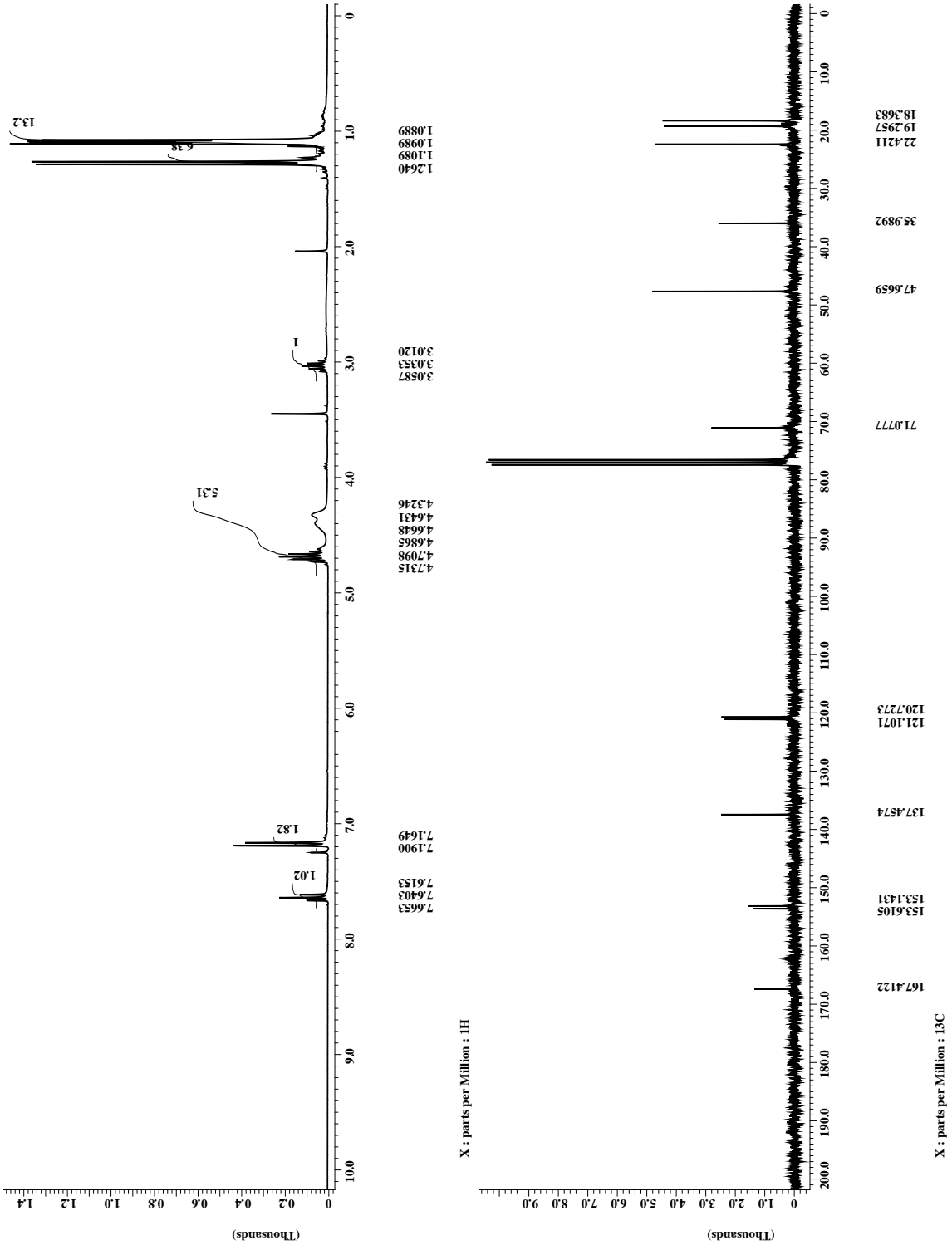
2-bromo-6-isopropylpyridine (S5)

2-hydroxy-6-isopropylpyridine (**S4**) (5.32 g, 0.04 mol) was combined with 40 mL phosphorus tribromide and heated under reflux for 1h. After cooling the biphasic mixture was poured onto ice. When hydrolysis was complete, the mixture was made basic (pH 12) with aqueous NaOH and extracted with dichloromethane. Drying ($MgSO_4$) and evaporation of the organic layer gave the crude product which was purified by vacuum distillation (b.p. 69 ˚C/0.8 mmHg) to give 4.64 g (0.023 mol, 58%) of 2-bromo-6-isopropylpyridine as a colorless oil. Though this compound was recently reported by Gaillard and co-workers[5] spectrocopic details were not provided and so are presented here. ^{1}H NMR ($CDCl_3$) 7.46 (t, 1H, J=7.5 Hz), 7.28 (d, 1H, J=7.5 Hz) 7.12 (d, 1H, J=7.5 Hz), 3.05 (septet, 1H, J=6.7 Hz) 1.29 (d, 6H, J=6.7 Hz); ^{13}C NMR ($CDCl_3$) 169.2, 141.4, 138.8, 125.3, 119.2, 36.1, 22.43; EIMS m/z (relative abundance), 199(M+, 30), 198 (M-H, 29), 184 (100) 171 (26), 104 (33).

^{1}H and ^{13}C NMR of compound 6-isopropylpyridine-2-carboxaldehyde (**5**)



^{1}H NMR and ^{13}C NMR of 1,3-diisopropyl-5-(6'-isopropylpyridyl)-tetrazane-2-one **(6)**



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