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SUPPORTING INFORMATION

For

An Efficient and Metal Free Synthesis of Benzylpyridines Using HI through Deoxygenation Reaction

S. Chandrasekar, I. Karthikeyan and G. Sekar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai -600 036, Tamil Nadu India

E-mail: gsekar@iitm.ac.in

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Synthesis of secondary alcohols (1a-1r):

Magnesium turnings were placed in a oven dried two neck 50 mL round bottom flask and the flask was further dried by hot air gun with applying vacuum. Then the setup was allowed to room temperature, refilled with nitrogen. Under nitrogen flow, a catalytic amount of iodine was added, followed by freshly distilled THF. The reaction mixture was cooled to 0 °C followed by corresponding aryl halide was added by drop wise. After the disappearance of the iodine color, the reaction was allowed to stir at room temperature for 2 hours. Once all the magnesium turnings were dissolved, the reaction mixture was cooled to 0 °C then pyridine-2-aldehyde (dissolved in THF) was added dropwise to the Grignard reagent. The reaction was monitored by TLC and the reaction mixture was quenched by *aqueous* NH₄Cl and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated under vacuum. The residue was purified by column chromatography with ethyl acetate/hexanes solvents to provide pure products (**1a-1r**).



Synthesis of primary and secondary alcohols (5a-5e):

Commercially available 2,6-pyridine-di-carboxylic **A** was esterified with catalytic amount of acid in ethanol as solvent to provide ester **B** in 83% yield.¹ This diester **B** was reduced to 2,6-pyridine-dimethanol **C** using sodium borohydride and calcium chloride in ethanol using literature procedure.² The mono aldehyde **D** was prepared using selenium dioxide, by oxidation of compound **C** in 1,4dioxane.³ The resulting monoaldehyde was converted to di-alcohol (**5a-5e**) having primary and secondary alcohol group using corresponding aryl magnesium bromide (2 equivalents).



Reference:

- 1. X. Li, C. Zhan, Y. Wang and J. Yao, Chem. Commun., 2008, 2444-2446.
- 2. X. Wu, Y. He and C. Wu, Wuhan Univ. J. Nat. Sci., 1996, 1, 105-106.
- N. M. Shavaleev, R. Scopelliti, F. Gumy and J.-C. G. Bunzli, *Inorg. Chem.*, 2009, 48, 6178-6191.



400 MHz ¹HNMR spectrum of **2a** in CDCl₃

	— 161.08			128.70	- 121.36			77.48 77.16	76.84							
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 190 180 17	70 160	150	140	130 12	20 110	100	90	80	70	60	50	40	30	20	 10	0 ppm

100 MHz 13 C NMR spectrum of **2a** in CDCl₃



400 MHz ¹H NMR spectrum of **2b** in CDCl₃

100 MHz 13 C NMR spectrum of **2b** in CDCl₃





400 MHz ¹HNMR spectrum of 2c in CDCl₃

			136.86	136.36 129.71 127.31	123.26				77.48 77.16	76.84					16 24	t V.O	
																	SCH ₃
 ₁ 70	_. 160	150	 140	130	 120	110	100	90	 80		60	50	40	30	 20	10	0 ppm

100 MHz 13 C NMR spectrum of **2c** in CDCl₃



400 MHz ¹H NMR spectrum of **2d** in CDCl₃

					138.07	132.36	121.55				77.48 77.16	76.84					N		CI
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190	180	170	160	150	140	130	120	110	100	90	 80	70	60	50	 40	30	20	10	0 ppm

100 MHz ¹³CNMR spectrum of **2d** in CDCl₃



400 MHz ¹H NMR spectrum of 2e in CDCl₃

				136.86	- 136.04 					77.48 77.16	76.84					Z		CH ₃
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							*	n the state of the	161			1091-923-923-0-02,0-14	5		1001-11-101-101-101-101-101-101-101-101			
 190 180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	 30	20	10	0 ppm

100 MHz ¹³CNMR spectrum of **2e** in CDCl₃



400 MHz ¹H NMR spectrum of **2f** in CDCl₃



100 MHz ¹³C NMR spectrum of **2f** in CDCl₃



400 MHz ¹HNMR spectrum of **2g** in CDCl₃



100 MHz ¹³C NMR spectrum of **2g** in CDCl₃



400 MHz $^1\!\mathrm{H}$ NMR spectrum of 2h in CDCl_3

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100 MHz ¹³C NMR spectrum of **2h** in CDCl₃



400 MHz ¹H NMR spectrum of **2i** in CDCl₃

				136.91	130.46 130.27 126.86	126.21	~121.17			77.48 77.16	76.84			42.47		— 19.81		
																		CH ₃
 180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

100 MHz ¹³C NMR spectrum of **2i** in CDCl₃



400 MHz ¹H NMR spectrum of **2j** in CDCl₃

			— 161.26	149.32	136.65	, 130,40 / 128.82 / 125.59					77.48 77 16	76.84							
																		<u>.</u>	
190	180	170	160	150	140	130	120	110	100	90	 80	70	60	50	40	30	20	10	0 ppm

100 MHz 13 C NMR spectrum of **2j** in CDCl₃



400 MHz ¹H NMR spectrum of 2k in CDCl₃



100 MHz ¹³C NMR spectrum of **2k** in CDCl₃



400 MHz ¹H NMR spectrum of **2l** in CDCl₃



100 MHz ¹³C NMR spectrum of **2l** in CDCl₃



400 MHz ¹HNMR spectrum of 2m in CDCl₃



100 MHz 13 C NMR spectrum of **2m** in CDCl₃

400 MHz ¹H NMR spectrum of **2n** in CDCl₃

100 MHz ¹³CNMR spectrum of **2n** in CDCl₃

400 MHz ¹H NMR spectrum of **20** in CDCl₃

			— 157.39		138.29	129.26	~126.71 — 118.77				77.48 77.16	76.84						N N	
		. .			.														
 190	180	170	160	150	₁₄₀	130	120	110	100	90	80	70	60	50	40	30	20	10	0 ppm

100 MHz 13 C NMR spectrum of **20** in CDCl₃

400 MHz ¹H NMR spectrum of **2p** in CDCl₃

100 MHz 13 C NMR spectrum of **2p** in CDCl₃

400 MHz 13 C NMR spectrum of **2q** in CDCl₃

100 MHz ¹³C NMR spectrum of **2q** in CDCl₃

150.14	— 138.87	129.08 128.78 156.73	124.26				77.48 77.16	76.84							
				an dia manjutri ya da katika		****		1.111.111.111.111.111.111.111.111.111.	110 gr. 2100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100 - 1100	An function of the state of the			61000, AL		
	140	130	120	110	100	 90	 80	 70	 60	50	 40	30	20	10	0 ppm

100 MHz ^{13}C NMR spectrum of 2r in CDCl_3

400 MHz ¹H NMR spectrum of 6a in CDCl₃

100 MHz ¹³C NMR spectrum of **6a** in CDCl₃

400 MHz 1 H NMR spectrum of **6b** in CDCl₃

100 MHz ¹³C NMR spectrum of **6b** in CDCl₃

400 MHz ¹H NMR spectrum of **6c** in CDCl₃

100 MHz ¹³C NMR spectrum of **6c** in CDCl₃

400 MHz ¹H NMR spectrum of **6d** in CDCl₃

100 MHz ¹³C NMR spectrum of **6d** in CDCl₃

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400 MHz ¹H NMR spectrum of **6e** in CDCl₃

100 MHz ¹³C NMR spectrum of **6e** in DMSO-d₆

100 MHz 13 C NMR spectrum of **8a** in CDCl₃

400 MHz ¹H NMR spectrum of **8b** in CDCl₃

100 MHz ^{13}C NMR spectrum of 8b in CDCl_3

400 MHz ¹H NMR spectrum of 8c in CDCl₃

100 MHz ^{13}C NMR spectrum of 8c in CDCl_3

400 MHz ¹H NMR spectrum of **8d** in CDCl₃

100 MHz ¹³C NMR spectrum of **8d** in CDCl₃

400 MHz ¹H NMR spectrum of 8e in CDCl₃

100 MHz ¹³C NMR spectrum of 8e in CDCl₃

400 MHz ¹H NMR spectrum of 8f in CDCl₃

100 MHz ¹³C NMR spectrum of **8f** in CDCl₃