

Oxidative Coupling of 2-Naphthol to (R)/(S)-BINOL by MCM-41 Supported Mn-Chiral Schiff Base Complexes

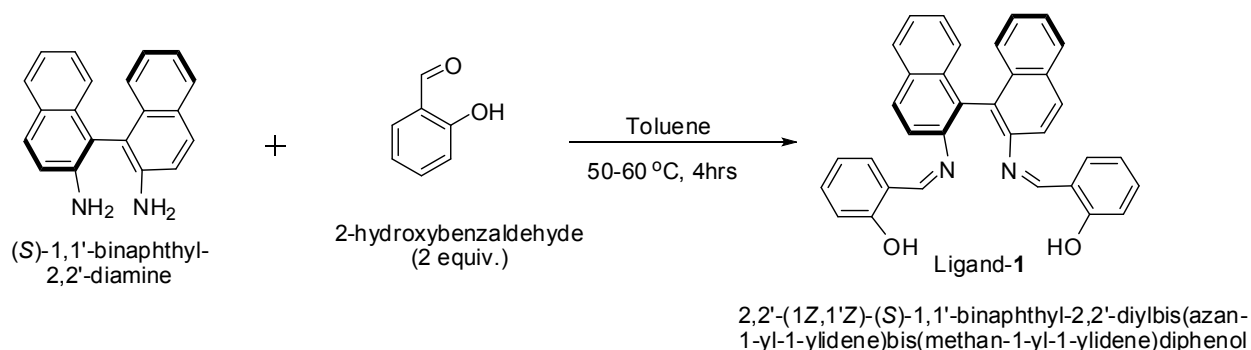
Kusum K. Bania,^{a*} G.V. Karunakar,^b Lanka Satyanarayana^c

^aDepartment of Chemical Sciences, Tezpur University, Napaam, Assam, India, 784028

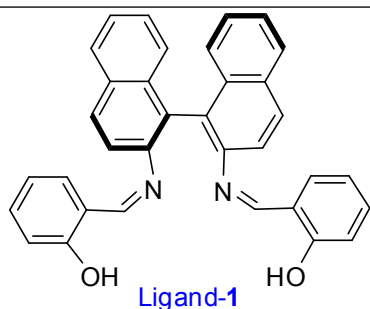
^bDivision of Crop Protection Chemicals, Indian Institute of Chemical Technology, Uppal Road, Hyderabad, Andhra Pradesh, India, 500607.

^cCenter for NMR and Structural Chemistry. Indian Institute of Chemical Technology, Uppal Road, Hyderabad, Andhra Pradesh, India, 500607.

Experimental procedure for the synthesis of **Ligands 1-3**:

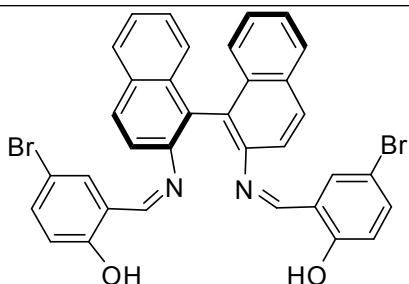


In a 5 mL round-bottomed two-neck flask compound (S)-1,1'-binaphthyl-2,2'-diamine (200 mg, 0.704 mmol, 1 equiv.) dissolved in 4mL of toluene and 2-hydroxybenzaldehyde was added (171 mg, 1.4 mmol, 2 equiv.). To this reaction mixture catalytic amount of *p*-toluenesulfonic acid (13mg, 0.07mmol, 0.1 equiv.) was added and the reaction mixture was stirred at 50-60 °C for 4 hours. The reaction mixture colour was changed to yellow; this reaction mixture was cooled to room temperature. Toluene was removed under reduced pressure. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent (10/3) to give pure chiral (S) ligand-**1**. The similar procedure was followed for the synthesis of ligands **2** and **3**.



2,2'-(1Z,1'Z)-(S)-1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol

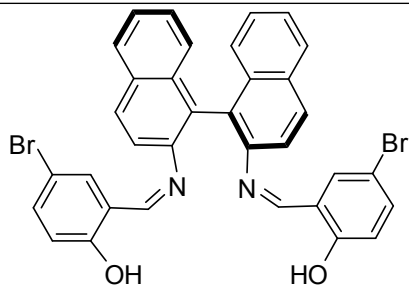
R_f : 0.5; Hexane: Ethyl acetate mixture(10:3); Yield: 92%; yellow solid; Melting point: 220-222°C; ^1H NMR (500 MHz, CDCl_3): δ 12.03 (brs, 1H), 8.56 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.8 Hz 1H), 7.37-7.32 (m, 1H), 7.18-7.16 (m, 2H), 7.09-7.04 (m, 2H), 6.67-6.63 (m, 1H), 6.60 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.7, 159.7, 142.6, 132.1, 131.6, 131.4, 131.1, 128.9, 128.5, 127.2, 125.9, 125.3, 124.8, 118.2, 117.5, 115.9, 115.8.



Ligand-2

2,2'-(1Z,1'Z)-(S)-1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)

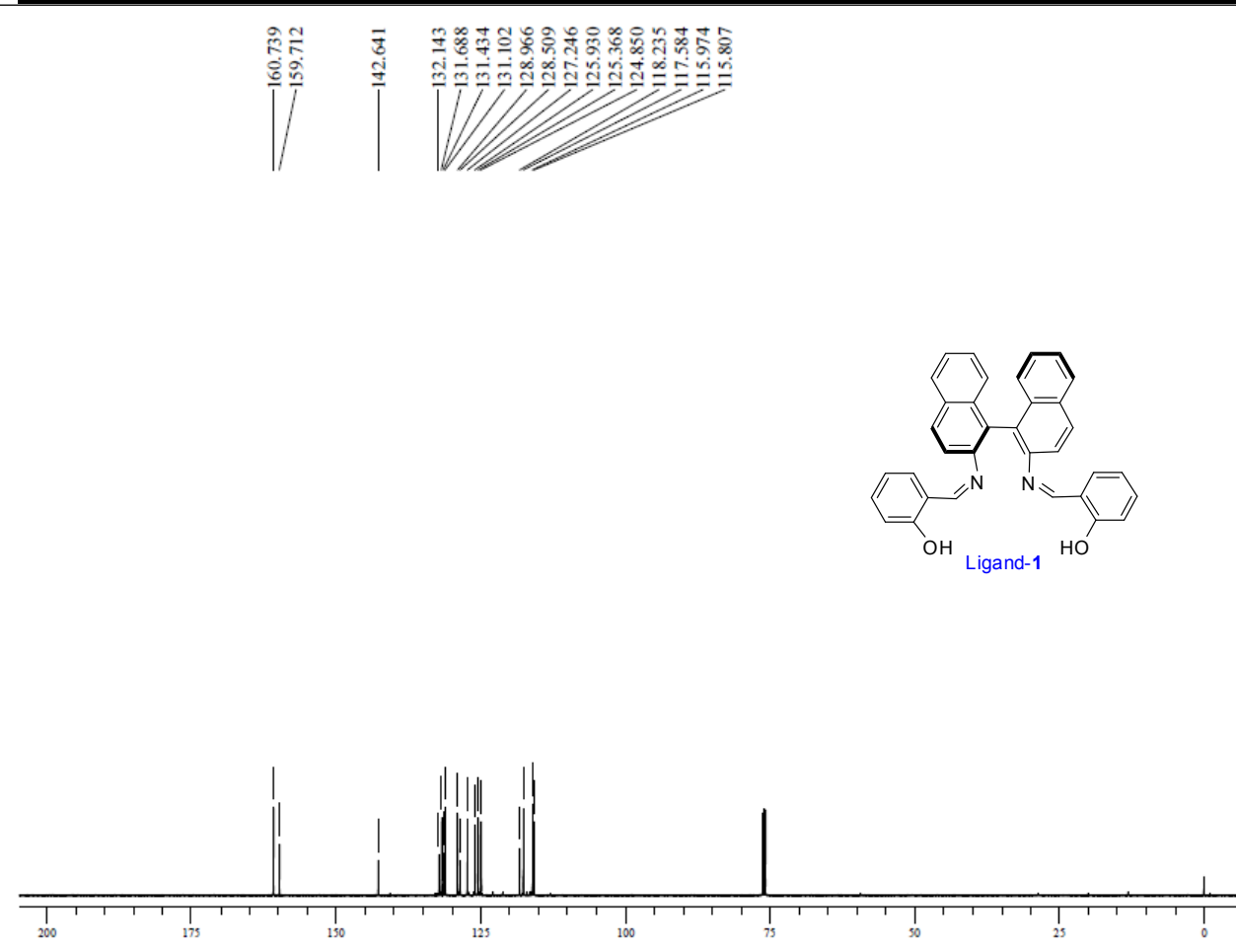
R_f: 0.4; Hexane: Ethyl acetate mixture(10:3); Yield: 93%; Orange colour solid; Melting point: 110-112°C; ¹H NMR (500 MHz, CDCl₃): δ 12.08 (brs, 1H), 8.58 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.8 Hz 1H), 7.62 (d, *J* = 8.8 Hz 1H), 7.49-7.44 (m, 1H), 7.31-7.26 (m, 2H), 7.25-7.21 (m, 2H), 6.58 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 160.2, 159.7, 143.0, 135.3, 134.0, 133.0, 132.6, 130.2, 129.8, 128.3, 127.1, 126.3, 126.2, 120.5, 119.0, 116.4, 110.1.



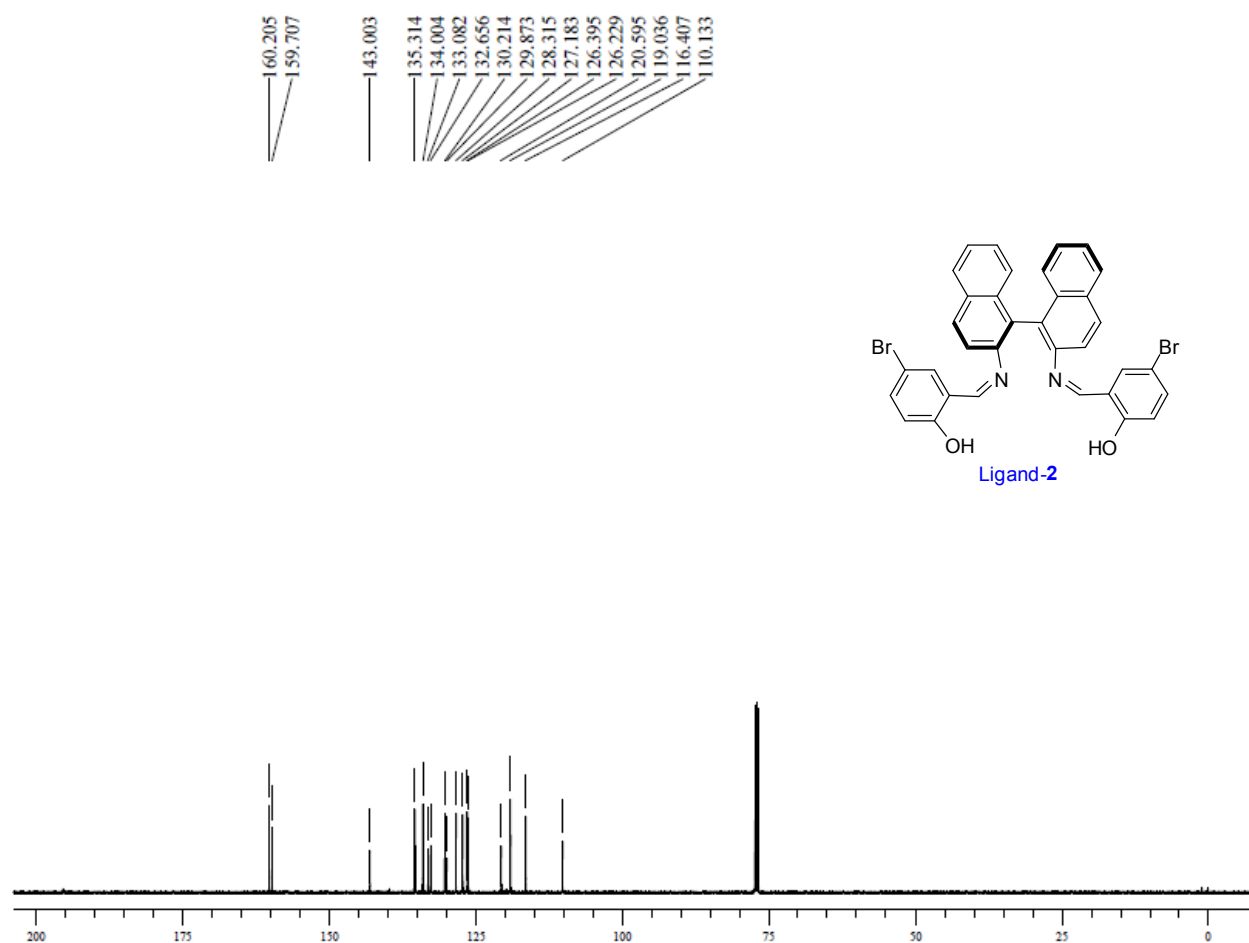
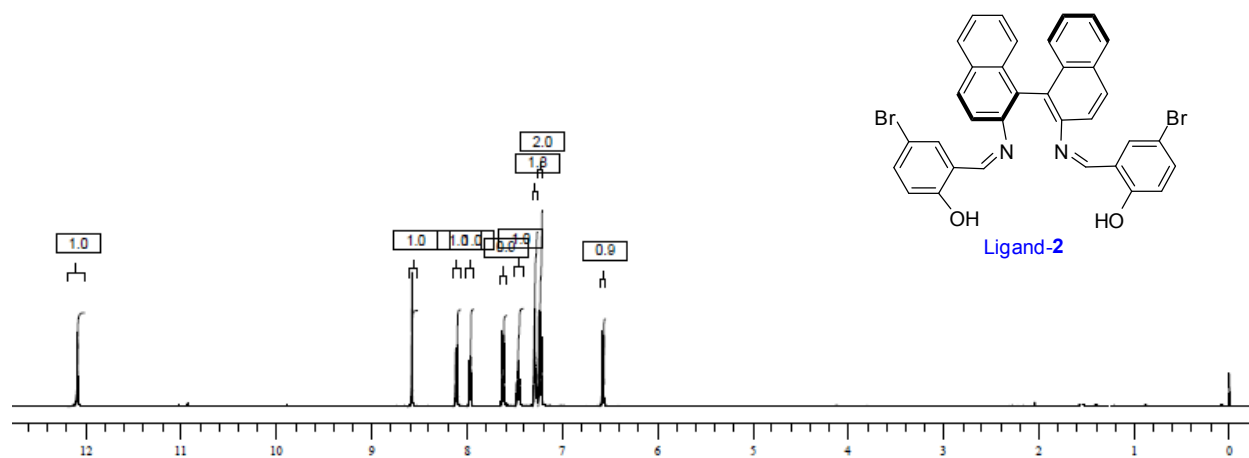
Ligand-3

2,2'-(1Z,1'Z)-(R)-1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)

R_f: 0.4; Hexane: Ethyl acetate mixture(10:3); Yield: 92%; orange colour solid; Melting point: 125-127°C; ¹H NMR (500 MHz, CDCl₃): δ 12.08 (brs, 1H), 8.57 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz 1H), 7.48-7.44 (m, 1H), 7.30-7.26 (m, 2H), 7.24-7.21 (m, 2H), 6.57 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 160.2, 159.7, 143.0, 135.3, 134.0, 133.0, 132.6, 130.2, 129.8, 128.3, 127.1, 126.3, 126.2, 120.5, 119.0, 116.4, 110.1

[illegible]

2,2'-(1Z,1'Z)-(S)-1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)-**Ligand-2**



2,2'-(1Z,1'Z)-(R)-1,1'-binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)-**Ligand-3**

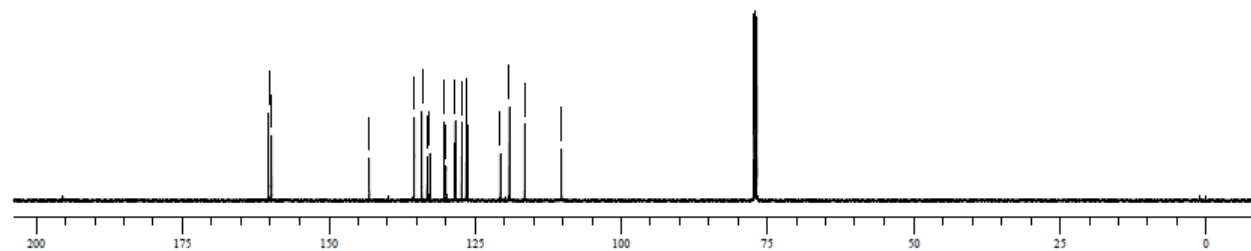
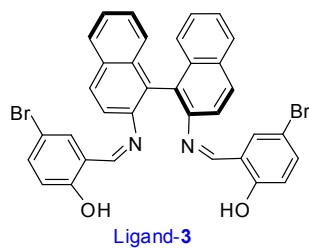
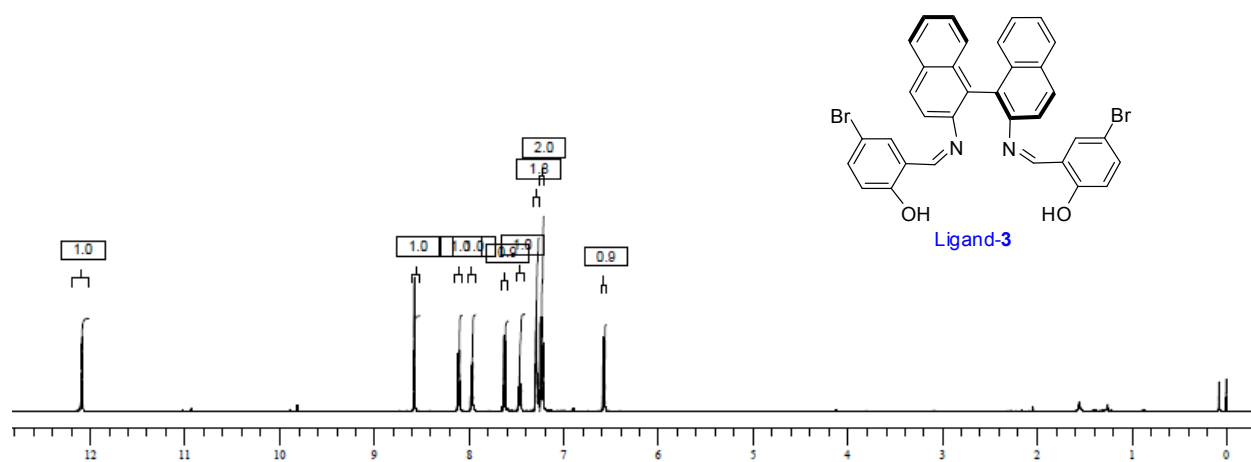


Table S1. Catalytic activity of the heterogeneous catalysts after 2nd, 3rd, 4th and 5th run.

Catalyst	Time (h)	Conv.(%) ^a	Yield(%) ^b	% ee ^c
<u>2nd RUN</u>				
Mn-L1-MCM-41+Air	27	94	88	91 (S)
Mn-L2-MCM-41+Air	34	89	87	87 (R)
Mn-L3-MCM-41+Air	34	88	87	85 (S)
<u>3rd RUN</u>				
Mn-L1-MCM-41+Air	27	92	86	89 (S)
Mn-L2-MCM-41+Air	34	86	85	85 (R)
Mn-L3-MCM-41+Air	34	85	85	82 (S)
<u>4th RUN</u>				
Mn-L1-MCM-41+Air	27	69	48	51 (S)
Mn-L2-MCM-41+Air	34	54	47	47 (R)
Mn-L3-MCM-41+Air	34	48	37	45 (S)
<u>5th RUN</u>				
Mn-L1-MCM-41+Air	27	39	28	19 (S)
Mn-L2-MCM-41+Air	34	24	15	17 (R)
Mn-L3-MCM-41+Air	34	25	12	15 (S)

^aReaction conditions: Recovered catalyst ~20 mg, 2-naphthol 5 mmol, solvent 10 ml at -10 °C. ^b Determined by GC, Conversion (%) = [moles of reactant converted]×100/ [moles of reactant in feed]. ^c Isolated yield. ^d Determined by chiral HPLC analysis.

Table S2. % Mn loading determined from ICP and AAS in the recovered heterogeneous catalyst after 2nd, 3rd, 4th and 5th run

Compound	%Mn-Loading (mg/100mg)			
	2 nd Run	3 rd Run	4 th Run	5 th Run
Mn-L1-MCM-41	7.75 (7.79)	7.61(7.46)	3.45(2.89)	2.12(1.90)
Mn-L2/Mn-L3/MCM-41	6.35 (6.41)	6.12(6.21)	2.89(2.65)	1.78(1.10)