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Copper(I) catalysis: Synthesis of *N,N′*-diarylated and *N*-aryl,*N′*-formylated chiral C_2-symmetric diamines

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ABSTRACT

Chiral *N,N′*-diaryl C_2-symmetric diamines and *N*-aryl,*N′*-formyl-*trans*-(1*R*,2*R*)-diaminocyclohexane are readily accessed by copper catalyzed *N,N′*-diarylation and *N*-aryl,*N′*-formylation of *trans*-(1*R*,2*R*)-diaminocyclohexane with aryl bromides. *N,N′*-diarylation using (*R*)-1,1′-binaphthyl-2,2′-diamine and iodobenzene gave the corresponding (*R*)-*N,N′*-diphenyl-1,1′-binaphthyl-2,2′-diamine derivative in 83% yield.

1. Introduction

Ligands derived from certain C_2-symmetric enantiopure diamines have been widely employed in asymmetric transformations including epoxidation [1], allylic substitution [2] and hydrogenation reactions [3]. Especially, the chiral *trans*-1,2-diaminocyclohexane and its derivatives were widely used in asymmetric synthesis as chiral reagents, scaffolds and as ligands in many organic transformations [4]. It was observed in this laboratory that *N,N′*-diphenylation of *trans*-(1*R*,2*R*)-diaminocyclohexane with bromobenzene using sodium metal in THF gave the diamine in poor yield (10%) besides biphenyl. Therefore, we were looking for a convenient alternative method for *N*-arylation of diamines [5]. Though carbon–nitrogen bond forming reactions employing primary amines and aryl halides as coupling partners using both palladium [6] and copper [7] catalyst systems have been reported, a mild, economic and efficient catalytic system is desirable for *N,N′*-diarylation of chiral C_2-symmetric diamines. Herein, we report convenient methods for copper(I) catalyzed *N,N′*-diarylation of chiral C_2-symmetric diamines **4** and **7** to obtain the corresponding *N,N′*-dirayl-1,2-diaminocyclohexane **6a–d**, (*R*)-*N,N′*-diphenyl-1,1′-binaphthyl-2,2′-diamine (**8**) and *N*-aryl,*N′*-formylation of *trans*-(1*R*,2*R*)-diaminocyclohexane (**4**) to obtain *N*-formyl,*N′*-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**9**).

2. Results and discussion

We have screened the ligands **1**, **2** and **3** for the *N,N′*-diarylation of *trans*-(1*R*,2*R*)-diaminocyclohexane under copper(I) catalysis (see Fig. 1). We have observed that the *N,N′*-diarylation of *trans*-(1*R*,2*R*)-diaminocyclohexane gave the corresponding *N,N′*-diphenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**6a**) (Scheme 1 and Table 1).

The catalytic systems using *rac*-BINOL **3** gave better results in the diarylation (Table 1). Accordingly we have examined the diarylation of *trans*-(1*R*,2*R*)-diaminocyclohexane (**4**) with various aryl bromides using this reagent (Table 2, entries 1–4). The % ee of starting *trans*-(1*R*,2*R*)-diaminocyclohexane is >98% ee. Since the reaction does not involve changes in the asymmetric centers, the ee of the product should be the same (Table 2, entries 1–4). Indeed, the % ee of the product was found to be >98% in the case of product **6a** by HPLC analysis. The yields are better in reactions using aryl bromides containing electron donating substituents (Table 2 entries 2 and 3).

The transformation was also examined using the (*R*)-1,1′-binaphthyl-2,2′-diamine (**7**). The corresponding (*R*)-*N,N′*-diphenyl-1,1′-binaphthyl-2,2′-diamine (**8**) was obtained in 19–83% yield (Scheme 2, Table 2). We have observed that partial racemization of the product **8** takes place under the reaction conditions and the (*R*)-*N,N′*-diphenyl-1,1′-binaphthyl-2,2′-diamine (**8**) was obtained in 13% to 91% ee indicating partial racemization during the *N*-arylation (Table 2, entries 5–8). It is well-known that optically active isomers containing 1,1′-binaphthyl moiety interconvert at high

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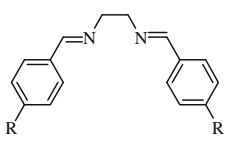
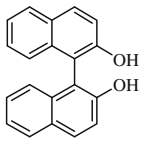


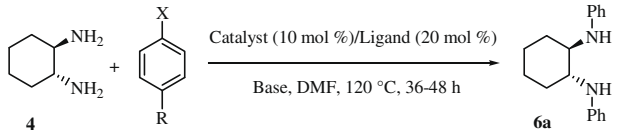
1, R = H, *N,N′*-dibenzylidineethane-1,2-diamine

2, R = OMe, *N,N′*-bis (4-methoxybenzylidine) ethane-1,2-diamine



3, (±)-Bi-2-naphthol (*rac* - BINOL)

Fig. 1. Ligands examined for *N*-arylation of chiral C_2-symmetric diamines.



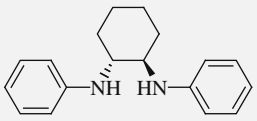
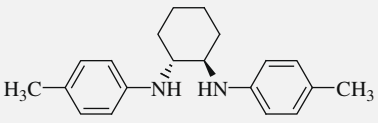
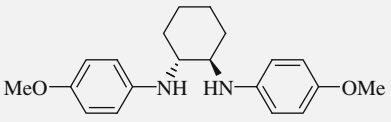
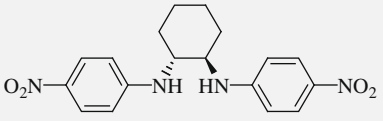
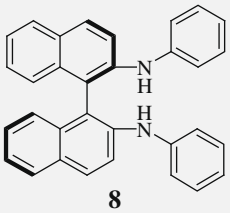
Scheme 1. Coupling of *trans*-(1*R*,2*R*)-diaminocyclohexane (**4**) and halobenzene in the presence of copper(I) catalyst.

Table 1
N,N′-diarylation of *trans*-(1*R*,2*R*)-diaminocyclohexane **4** with various catalysts.[a]

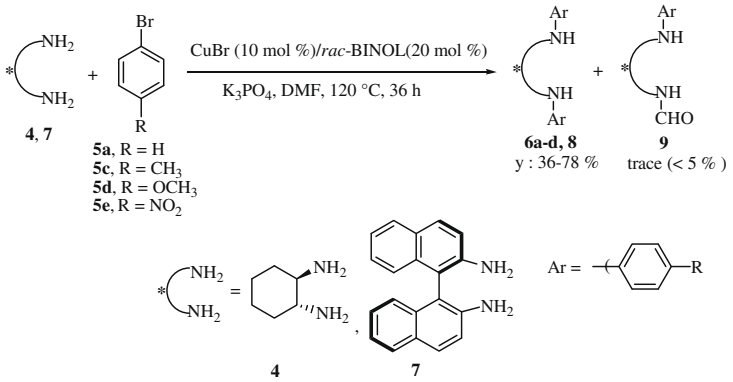
Entry	Catalyst	Halo benzenes	Ligand	Base	Time (h)	Yield (%)[b]
1	CuBr	**5a**	**1**	K_2CO_3	48	10
2	CuBr	**5a**	**1**	K_3PO_4	48	17
3	CuBr	**5a**	**2**	K_3PO_4	48	34
4	CuBr	**5a**	**3**	K_2CO_3	48	50
5	CuBr	**5a**	**3**	K_3PO_4	36	78
6	CuBr	**5b**	**3**	K_3PO_4	36	94
7	CuI	**5a**	**3**	K_3PO_4	48	56
8	CuBr	**5b**	–	K_3PO_4	48	5[c]
9	CuBr/Fe_2O_3	**5b**	**3**	K_3PO_4	36	84
10	CuBr/Fe_2O_3	**5a**	**3**	K_3PO_4	36	76
11	CuBr/ZnO	**5b**	**3**	K_3PO_4	36	73
12	CuO/NiBr	**5b**	**3**	K_3PO_4	48	15

[a] All the reactions were carried out with each metal catalyst (10 mol%), ligand (20 mol%), *trans*-(1*R*,2*R*)-diaminocyclohexane **4** (1 mmol), halobenzene (4 mmol) and DMF (5 mL) at 120 °C.
[b] Product was identified by ^{1}H NMR, ^{13}C NMR and mass spectral data.
[c] Reaction was carried out without employing any ligand.

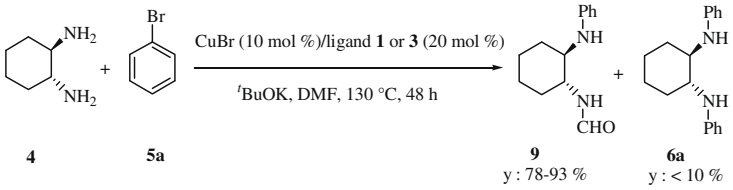
Table 2
Synthesis of *N,N′*-diaryl-*trans*-(1*R*,2*R*)-diaminocyclohexane **6a–d** and (*R*)-*N,N′*-diphenyl-1,1′-binaphthyl-2,2′-diamine (**8**).[a]

Entry	Aryl halide	Product	Time (h)	Yield (%)[b]	ee (%)[e]
1	**5a**	 **6a**	36	78	>98
2	**5c**	 **6b**	36	61	>98
3	**5d**	 **6c**	36	71	>98
4	**5e**	 **6d**	36	49	>98
5[c]	**5b**	 **8**	36	83	13[d]
6	**5b**	**8**	24	36	59
7	**5b**	**8**	12	19	91
8[f]	**5b**	**8**	48	39	58

[a] Unless noted otherwise, all the reactions were carried out with copper bromide (10 mol%), *rac*-BINOL **3** (20 mol%), *trans*-(1*R*,2*R*)-diaminocyclohexane **4** (1 mmol), aryl bromide (4 mmol), K_3PO_4 (3 mmol), DMF (5 mL) at 120 °C.
[b] All the products were identified by ^{1}H NMR, ^{13}C NMR and mass spectral data.
[c] (*R*)-1,1′-binaphthyl-2,2′-diamine **7** was used as substrate diamine.
[d] *Bis*-phenylation of *rac*-BINOL **3** was also observed (up to 20%).
[e] Since the reaction does not involve changes in the asymmetric centers the ee of the product should be the same and was confirmed by using chiral HPLC for product **6a:** on Daicel Chiralcel OD-H (elution hexane:isopropanol, 95/5, flow rate:1 mL/min UV detection at 254 nm) showed >98% ee (t_S = 10.5 min) and ee of product **8** was determined by using chiral HPLC on Daicel Chiral Pak AD-H (elution hexane–ethanol 19:1, flow rate:1 mL/min UV detection at 256 nm) showed 13–91% ee (t_S = 4.3 min, t_R = 5.8 min).
[f] Reaction was carried out at 100 °C.



Scheme 2. Synthesis of *N*,*N*′-diaryl chiral C_2-symmetric diamines.



Scheme 3. Synthesis of *N*-formyl,*N*′-phenyl- *trans*-(1*R*,2*R*)-diaminocyclohexane **9**.

Table 3
Synthesis of *N*-formyl,*N*′-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**9**).[a]

Entry	Catalyst	Ligand	Base	Yield (%)[b]
1	CuBr	**1**	^{t}BuOK	78
2	CuBr	**3**	^{t}BuOK	93
3[c]	CuBr	–	^{t}BuOK	76
4	CuBr	**3**	K_3PO_4	Trace

[a] Unless noted otherwise, all the reactions were carried out with CuBr (10 mol%), ligand **1** or **3** (20 mol%), *trans*-(1*R*,2*R*)-diaminocyclohexane **4** (1 mmol), bromobenzene **5a** (1.2 mmol), ^{t}BuOK (2.5 mmol) and DMF (5 mL) at 130 °C for 48 h.
[b] Product **9** was identified by ^{1}H NMR, ^{13}C NMR and mass spectral data, X-ray crystal structure analysis.
[c] Reaction was carried out without employing any ligand.

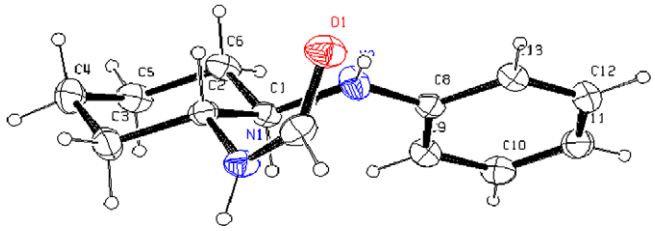


Fig. 2. ORTEP diagram of *N*-formyl,*N*′-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**9**) (thermal ellipsoids are drawn at 35% probability and all the hydrogen atoms were unlabled for clarity).

temperatures in long time reactions [8]. Accordingly, this partial racemization in the high temperature reactions is not entirely unexpected.

In all experiments with *trans*-(1*R*,2*R*)-diaminocyclohexane, the *N*-aryl,*N*′-formyl-*trans*-(1*R*,2*R*)-diaminocyclohexane was obtained in trace amount (<5%). Interestingly, when ^{t}BuOK was used in combination with the CuBr/*rac*-BINOL system, the mono phenyl and mono formyl product **9** was obtained in good to excellent yields (Scheme 3 and Table 3, entries 1 and 2). This transformation may be attributed to increased solubility and basicity of the ^{t}BuOK. It may be of interest to note that formylation of certain amines has reported in reactions with CH_3ONa and DMF [9].

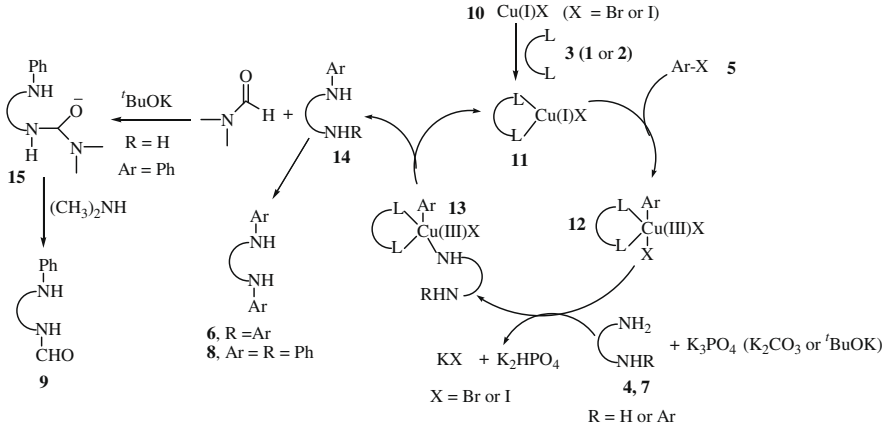
Interestingly, the compound **9** was isolated in 76% yield, even in the absence of ligand (Table 3, entry 3). We thought that the initially formed *N*-formyl,*N*′-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**9**) itself is acting as ligand to give product **9**. In order to examine this possibility, we have used the compound **9** in the *N*,*N*′-diphenylation of *trans*-(1*R*,2*R*)-diaminocyclohexane (**4**). In this run, the corresponding *N*,*N*′-diphenyl derivative **6a** was obtained in 40% yield. The structure of the *N*-formyl,*N*′-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (**9**) was further confirmed by X-ray crystal structure analysis. The ORTEP diagram is shown in Fig. 2.

The *N*,*N*′-diarylation and *N*-aryl,*N*′-formylation transformations may be rationalized by the tentative mechanisms outlined in Scheme 4 considering reports on copper(I) catalyzed *N*-arylations [10].

Initially, the copper(I) halide **10** coordinates with bidentate ligand **3** (**1** or **2**) to form the metal–ligand complex **11** (Scheme 4). Subsequent, oxidative addition of aryl halide **5** would give the copper(III) complex **12**. Then, the deprotonated amine **4** or **7** would react with the diamine to form the complex **13**, which on reductive elimination would give the product **14** and the copper(I) that could participate in the catalytic cycle again. The product **14** could react with DMF in the presence of ^{t}BuOK to yield *N*′-formylated compound **9** through the intermediate **15**.

3. Conclusion

In summary, we have developed inexpensive and convenient methods for *N*,*N*′-diarylation and *N*-formylation of chiral C_2-symmetric diamines. The products are expected to be useful ligands for developing new catalyst systems for application in asymmetric transformations. Especially, the unsymmetrical nature of the *N*-formyl,*N*′-phenyl-*trans*-(1*R*,2*R*)-diaminocyclohexane should be helpful in designing of new unsymmetrical diamine ligands. The *N*-aryl amine derivatives are also useful in several material science applications [11]. Therefore, the methods for *N*-arylation and



Scheme 4. Copper(I) catalyzed *N*,*N*′-diarylation and *N*-aryl,*N*′-formylation of diamines.

N-aryl,*N*′-formylation of diamines described here have considerable potential for further synthetic exploitations.

4. Experimental

Infrared spectra were recorded on JASCO FT-IR spectrophotometer Model 5300. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV-400 spectrometers with chloroform-*d* as a solvent and TMS as the reference (δ = 0 ppm). Coupling constants *J* are in Hz. Elemental analyses were carried out on a Flash EA 1112 series analyzer. Optical rotations were measured in an AUTOPOL-IV automatic polarimeter (readability ±0.001). HPLC analysis performed on SCL-10ATVP Shimadzu instrument. Chromatography was carried out using Acme's silica gel (100–200 mesh and 230–400 mesh). Solvents were dried using the standard procedures. The commercial reagents were used without further purification. The commercial *cis*/*trans* mixture of 1,2-diaminocyclohexane was resolved to obtain the *trans*-(1*R*,2*R*)-diaminocyclohexane in >98% ee following a reported procedure [12].

4.1. General procedure for the synthesis of N-aryl chiral diamines **6a–d** and **8**

In a 25 mL two necked flask equipped with air condenser protected by a mercury trap, CuBr (10 mol%, 14.3 mg), *rac*-BINOL (20 mol%, 57.2 mg), K_3PO_4 (3 mmol, 636 mg) and DMF (5 mL) were placed under nitrogen. The contents were stirred for 20–30 min at 25 °C. To this, chiral diamine (1 mmol, 114.2 mg) and aryl halide (4 mmol, 628 mg) were added and stirring was continued for 36 h at 120 °C. The reaction mixture was brought to 25 °C, diluted with 10 mL of ethyl acetate and 5 mL of water and stirred for 10 min at 25 °C. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extract was washed with water and brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (silica gel 100–200 mesh, hexanes/ethyl acetate) to yield the desired product.

4.1.1. Synthesis of trans-(1R,2R)-N,N′-diphenylcyclohexane-1,2-diamine (**6a**)

Synthesized following the above general procedure: Yield: 0.207 g, 78% as yellow oil; $\alpha_D^{25} = +66.3^\circ$ (*c* = 0.58, benzene), *lit.* [13a] $\alpha_D^{25} = +64.1^\circ$ (*c* = 0.95, benzene); FTIR (neat) ν_{max} (cm^{-1}): 3391, 3051, 2930, 1601, 1500; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21–1.24 (m, 2H), 1.32–1.47 (m, 2H), 1.76–1.79 (m, 2H), 2.33–2.36 (m, 2H), 3.17–3.21 (m, 2H), 3.89 (brs, 2H, NH), 6.61–6.63 (m, 4H), 6.69–6.73 (m, 2H), 7.15–7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 32.6, 57.3, 113.5, 117.6, 129.3, 147.8; LCMS (*m*/*z*): 267 (M+1); HPLC analysis: Daicel Chiralcel OD-H (elution hexane–isopropanol, 95:5, flow rate: 1 mL/min UV detection at 254 nm) showed the product with >98% ee (t_R = 10.5 min, for (1*R*,2*R*)) [13b].

4.1.2. Synthesis of trans-(1R,2R)-N,N′-di-p-tolylcyclohexane-1,2-diamine (**6b**)

Synthesized following the above general procedure: Yield: 0.180 g, 61% as gummy; $\alpha_D^{25} = +85.7^\circ$ (*c* = 0.58, benzene), *lit.* [13a] $\alpha_D^{25} = +101.5^\circ$ (*c* = 0.98, benzene); FTIR (neat) ν_{max} (cm^{-1}): 3385, 3018, 2928, 1616, 1516, 1300, 808; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19–1.21 (m, 2H), 1.37–1.40 (m, 2H), 1.75–1.77 (m, 2H), 2.22–2.24 (d, 6H), 2.31–2.34 (m, 2H), 3.13–3.15 (m, 2H), 3.75 (brs, 2H, NH), 6.53–6.56 (m, 4H), 6.96–7.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 24.6, 32.6, 57.68, 113.9, 126.9, 129.8, 145.5; LCMS (*m*/*z*): 295 (M−1).

4.1.3. Synthesis of trans-(1R,2R)-N,N′-bis-(4-methoxyphenyl)-cyclohexane-1,2-diamine (**6c**)

Synthesized following the above general procedure: Yield: 0.231 g, 71% as gummy; $\alpha_D^{25} = +29.2^\circ$ (*c* = 0.24, $CHCl_3$); FTIR (neat) ν_{max} (cm^{-1}): 3354, 3030, 2993, 1616, 1510, 1037, 819; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.4 (m, 2H), 1.76–1.78 (m, 2H), 2.30–2.33 (m, 2H), 3.07–3.09 (m, 2H), 3.68 (brs, 2H, NH), 3.75–3.76 (d, 6H), 6.61–6.64 (m, 4H), 6.78–6.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 32.6, 55.8, 58.5, 114.9, 115.5.3, 141.9, 152.4; LCMS (*m*/*z*): 327 (M+1).

4.1.4. Synthesis of trans-(1R,2R)-N,N′-bis-(4-nitrophenyl)-cyclohexane-1,2-diamine (**6d**)

Synthesized following the above general procedure: Yield: 0.174 g; 49% as yellow solid; m.p: 200–202 °C; *lit.* [14] m.p: 204–206 °C; $\alpha_D^{25} = +904.5^\circ$ (*c* = 0.34, methanol), *lit.* [14] $\alpha_D^{25} = +875^\circ$ (*c* = 0.192, methanol); FTIR (KBr) ν_{max} (cm^{-1}): 3356, 3084, 2930, 1595, 1527, 1298, 1111, 831; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.26–1.33 (m, 2H), 1.36–1.45 (m, 2H), 1.84 (m, 2H), 2.25–2.28 (m, 2H), 3.42 (m, 2H), 5.63 (brs, 2H, NH), 6.53–6.55 (m, 4H), 7.93–7.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 32.1, 56.3, 111.1, 126.4, 136.9, 153.3; LCMS (*m*/*z*): 357 (M+1).

4.1.5. Synthesis of (R)-N,N′-diphenyl-1,1′-binaphthyl-2,2′-diamine (**8**)

Synthesized following the above general procedure: Yield: 0.362 g, 83% as amorphous solid; $\alpha_D^{25} = +54.9^\circ$ (*c* = 0.15, THF) for 91% ee, *lit.* [15] $[\alpha]_D$ = +63. 4° (*c* = 0.4, THF) for 98% ee; FTIR (KBr) ν_{max} (cm^{-1}): 3395, 3051, 1936, 1732, 1612, 1591, 1494, 810, 738; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (brs, 2H), 6.81–6.97

(m, 6H), 7.12–7.24 (m, 7H), 7.29–7.42 (m, 4H), 7.67–7.89 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.4, 117.9, 120.0, 122.2, 123.5, 124.5, 127.1, 128.3, 129.1, 129.3, 129.4, 134.0, 140.4, 142.5; LCMS (*m*/*z*): 267 (M+1); 437 (M+1); HPLC on Daicel Chiral Pak AD-H (elution hexane–ethanol 19:1, flow rate:1 mL/min UV detection at 256 nm) showed 13–91% ee (t_S = 4.3 min, t_R = 5.8 min) [15].

4.2. Representative procedure for the synthesis of N-formyl,N′-phenyl-trans-(1R,2R)-diaminocyclohexane (**9**)

In a 25 mL two necked flask equipped with air condenser protected by a mercury trap, CuBr (10 mol%, 14.3 mg), *rac*-BINOL (20 mol%, 57.2 mg), ^{t}BuOK (3 mmol, 336 mg) and DMF (5 mL) were placed under nitrogen. The contents were stirred for 20–30 min at 25 °C. To this, *trans*-(1*R*,2*R*)-diaminocyclohexane (**4**) (1 mmol, 114.2 mg) and bromobenzene **5a** (1.2 mmol, 188.4 mg) were added and stirring was continued for 48 h at 130 °C. The reaction mixture was brought to 25 °C, diluted with 10 mL of ethyl acetate and 5 mL of water and stirred for 10 min at 25 °C. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extract was washed with water and brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate = 75/25) to yield the desired product.

4.3. Physical and spectral data for compound **9**

Yield: 0.203 g, 93% as colorless solid; m.p.: 106–108 °C; $\alpha_D^{25} = +39.4^\circ$ (*c* = 0.86, $CHCl_3$); FTIR (KBr) ν_{max} (cm^{-1}): 3400, 3333, 3022, 2924, 1635, 1604, 1523, 746, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12–1.27 (m, 2H), 1.30–1.43 (m, 2H), 1.66–1.76 (m, 2H), 2.07–2.10 (m, 1H), 2.24–2.28 (m, 1H), 3.07 (brs, 1H), 3.85–3 (m, 1H), 4.06 (brs, 1H), 5.56 (m, 2H, NH), 6.53–6.58 (m, 2H), 6.63–6.70 (m, 1H), 7.11–7.25 (m, 2H), 8.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 24.8, 32.5, 32.7, 51.8, 58.0, 112.6, 117.0, 129.3, 147.5, 161.8; LCMS (*m*/*z*): 219 (M+1). Elemental Anal. Calc. for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.46; H, 8.35; N, 12.91%.

4.4. Crystal data for compound **9**

Molecular formula: $C_{13}H_{18}N_2O$, *Mw* = 218.29, orthorhombic, space group: *P*2(1)2(1)2(1), *a* = 5.1335(4) Å, *b* = 7.7826(6) Å, *c* = 30.628(2) Å, α = 90.00, β = 90.00, γ = 90.00, *V* = 1223.66(16) Å, *Z* = 4, ρ_c = 1.185 mg m^{-3}, μ = 0.08 mm^{-1}, *T* = 298(2) K. Of the 12 650 reflections collected, 8389 were unique (R_{int} = 0.0311). Refinement on all data converged at R_1 = 0.0489, wR_2 = 0.1142.

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Appendix A. Supplementary material

CCDC 728374 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.002.

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