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Photoreductive Coupling of Aldimines. Synthesis of C_2 Symmetrical Diamines

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Abstract—The photoreductive coupling of pyridine-, arene- and alkynecarboxaldimines is a very convenient procedure for the preparation of vicinal diamines in good to excellent yields. The usual trend gave an excess of *meso* diamine, which enhances the usefulness of this method. The procedure tolerates bulky groups such as *tert*-butyl and diphenylmethyl on the nitrogen atom.

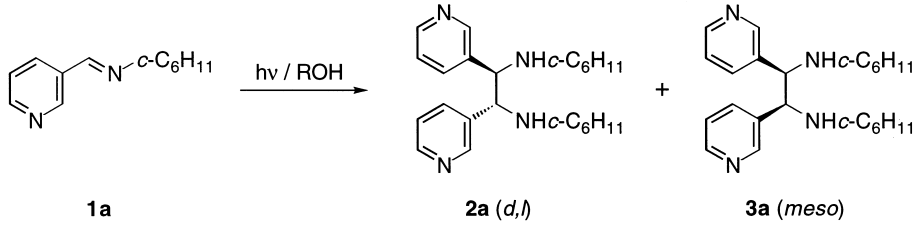
Introduction

The 1,2-diamine functionality can be found in many natural products, especially peptides, with valuable biological and therapeutic properties.[1] In recent years, several synthetic diamine derivatives have also been employed as medicinal agents, in particular in chemotherapy.[1] Moreover, enantiomerically pure vicinal diamines are also used increasingly in stereoselective organic synthesis as chiral auxiliaries or as metal ligands in catalytic asymmetric synthesis.[1,2] Given the significance of 1,2-diamines, a large number of methods for the synthesis of these derivatives have been developed. In principle, the reductive coupling of imines seems a simple way to prepare symmetric vicinal diamines and, thus, several procedures that make use of a metal or a metallic complex have been reported.[1–5] However, despite the high versatility shown by the imines in the coupling reaction, their photoreduction has not been extensively studied. In fact, only one example of photoreductive coupling of aryl *N*-alkylimines is described in the literature.[6]

In previous papers we have described the photochemical behavior of several conjugated imines and their usefulness in the synthesis of different heterocyclic compounds.[7,8] Our experience in the photochemistry of imines and the growing importance of 1,2-diamines, promted us to study the photoreduction of heterocyclic aldimines. Herein, we wish to report our results in this field.

Results and Discussion

First, we prepared the 3-pyridinecarboxaldehyde *N*-cyclohexylimine **1a** by a condensation of 3-pyridinecarboxaldehyde with cyclohexylamine. The absorption spectrum of **1a** in methanol showed bands at 202, 238 and 272 nm ($\epsilon \approx 168{,}000$, 155,000, and 55,000 $M^{-1}\,cm^{-1}$, respectively). Based on this spectrum, we carried out the irradiation of **1a** through quartz of a 2×10^{-2} M alcoholic solution of this compound with a 450 W medium-pressure mercury lamp. The reaction was monitored by ^1H NMR spectroscopy. Complete consumption of the starting material occurred after 6 h. The reaction occurred with formation of a large amount of polymeric material. After purification by column chromatography, we noted the formation of the corresponding D,L **2a** and *meso* **3a** 1,2-diamines (combined yield 45%),



1a **2a** (*d,l*) **3a** (*meso*)

Scheme 1.

Keywords: imines; photoreductive coupling; diamines.

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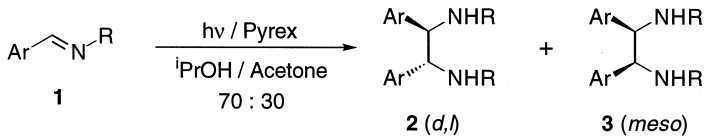
Table 1.



Entry	Imine **1**	Ar	R	*t* (h)[a]	Yield (%)[b]	Ratio **2**/**3**[c]
1	**1a**	3-Pyridyl	*c*-Hex	4	85	52/48
2	**1b**	3-Pyridyl	*t*-Bu	4	80	38/62
3	**1c**	2-Pyridyl	*n*-Hex	3	50	43/57
4	**1d**	2-Pyridyl	*c*-Pr	5	80	37/63
5	**1e**	2-Pyridyl	*c*-Hex	3	70	48/52
6	**1f**	2-Pyridyl	Ph_2CH	6	45	50/50
7	**1g**	4-Pyridyl	*c*-Hex	3	75	44/56
8	**1h**	Phenyl	*t*-Bu	3	>95	45/55
9	**1i**	Phenyl	*c*-Hex	3	75	58/42
10	**1j**	2-Naphthyl	*t*-Bu	10	65	49/51
11	**1k**	2-Naphthyl	*c*-Hex	10	21	5/95

[a] Irradiation time through Pyrex, for 1 mmol of imine **1**.
[b] Isolated yield of isomer mixture after column chromatography.
[c] As determined by 300 MHz ^{1}H NMR analysis of the crude products. Isomer structures were determined by analogy to other reported vicinal diamines.[10]

as elucidated by its spectroscopic data (^{1}H and ^{13}C NMR) and mass spectrometry (Scheme 1).

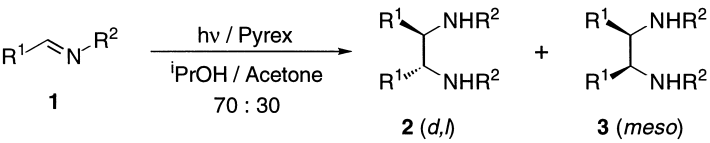
We next investigated some mechanistic aspects of this photoreduction reaction. We observed that the presence of triplet quenchers (i.e. bubbling oxygen) inhibited the formation of the diamine. On the contrary, irradiation of the imine in the presence of acetone (as triplet sensitizer) increased the reaction rate. Both effects could indicate that the reaction involves the formation of a triplet species. According to these results, we irradiated **1a** in the presence of acetone through Pyrex glass (where imine absorption is almost null). Under these experimental conditions, the polymer percentage was drastically reduced. Concerning the solvent, those without hydrogen donor capability, such as *tert*-butyl alcohol or *n*-hexane, were ineffective in the photoreduction coupling procedure, whereas the best results were obtained in isopropyl alcohol. These results indicate that hydrogen abstraction is essential for the development of the reaction.

The previous approach was extended to the irradiation of 2- and 4-pyridinecarboxaldimines. The results are given in Table 1. Some interesting points should be highlighted. The usual trend gave a slight excess of *meso* diamine (entries 2–5 and 7), in contrast to other methods reported in the literature.[1,3,4a] This *meso*-selectivity has been recently described for the first time.[5,9] The procedure tolerates bulky groups such as *tert*-butyl and diphenylmethyl on the nitrogen atom (entries 2 and 6). In all cases, good to excellent yields of the corresponding 1,2-diamines were obtained (45–85%). In all the cases tested, some polymeric material was obtained and the *meso* and D,L products needed to be purified by column chromatography on silica gel.

In order to explore the generality of the method, we undertook the extension of this methodology to include the irradiation of other aryl-, alkenyl- and alkynyl-based imines with different *N*-substituents. We have verified the feasibility of this reaction in the synthesis of 1,2-diamines from phenyl and naphthyl aldimines (Table 1, entries 8–11). The irradiation of benzenecarboxaldimine **1h** led to the formation of symmetrical diamines in quantitative yields (entry 8). Interestingly, the irradiation of naphthyl derivative **1k** gave the *meso* isomer **3k** in high ratio (entry 11). The D,L diamine **2k** could not be isolated.

The irradiation of alkenecarboxaldimines gave only polymeric material (the diamines could only be detected by electrospray mass spectra). On the contrary, the photoreaction of alkynyl-based imines yielded the corresponding diamines with *meso*-selectivity (Table 2, entries 1 and 2). The D,L diamine **2m** was obtained in very low yield and could not be isolated.

Table 2.



Entry	Imine **1**	R^1	R^2	*t* (h)[a]	Yield (%)[b]	Ratio **2**/**3**[c]
1	**1l**	Ph-C≡C	*t*-Bu	4	65	35/65
2	**1m**	Ph-C≡C	*c*-Hex	4	12	5/95

[a] Irradiation time through Pyrex, for 1 mmol of imine **1**.
[b] Isolated yield of isomer mixture after column chromatography.
[c] As determined by 300 MHz ^{1}H NMR analysis of the crude products. Isomer structures were determined by analogy to other reported vicinal diamines.[10]

Conclusions

We have proven that the photoreductive coupling of pyridine-, arene- and alkynecarboxaldimines is a very convenient procedure for the preparation of vicinal diamines in good to excellent yields. Moreover, the anomalous *meso*-selectivity observed enhances the usefulness of this method. Further studies to elucidate the mechanism and to extend the scope of this reaction are planned.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ with TMS as internal standard. Electrospray mass spectra were obtained on an HP 5989 B apparatus with an HP 59987 A interface, in positive-ion mode with methanol–water–acetic acid (60:35:5) as the mobile phase. IR spectra were obtained on a Perkin–Elmer 1000 spectrophotometer. Elemental analyses were made using a CE Instrument Model 1110. All solvents were purified by standard procedures and freshly distilled prior to use. Reagents were of commercial grades (Aldrich). Aldimines were prepared by condensation of the corresponding aldehyde with the amine according to a literature procedure.[9]

Typical procedure for the irradiation of aldimines

A solution of the corresponding aldimines (1 mmol) in a mixture of isopropyl alcohol and acetone (100 mL, 70:30) was bubbled with argon and irradiated through Pyrex, at room temperature under an Ar atmosphere, using a medium-pressure mercury lamp (450 W) until complete consumption of the starting material had occurred (monitored by ^{1}H NMR spectroscopy, see Table 1). The solvent was evaporated under reduced pressure and the residue was treated with $NaHCO_3$ (25 mL, 10% aq solution) and extracted with Et_2O (3×25 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The resulting products were separated and/or purified by column chromatography (silica gel, MeOH/CH_2Cl_2). The yields (see Tables 1 and 2) described refer to isomer mixture isolated products, relative to the starting imine. The structures of **2h**, **3h**, **2i**, and **3i** were determined by comparison of spectral data with those of the authentic samples reported.

(*R,*R**)-*N*,*N*′-Dicyclohexyl-1,2-di(3-pyridyl)-1,2-ethylenediamine 2a.** Yellow oil; IR (CH_2Cl_2): ν=3300, 2933, 2856, 1695, 1590, 1450, 1426, 1025, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.37 (dd, *J*=4.8, 1.8 Hz, 2H), 8.21 (d, *J*=1.8 Hz, 2H), 7.41 (d, *J*=7.8 Hz, 2H), 7.11 (dd, *J*=7.8, 4.8 Hz, 2H), 3.76 (s, 2H), 2.19 (m, 2H), 0.80–2.00 (m, 22H); ^{13}C NMR ($CDCl_3$) δ 149.4, 148.3, 137.2, 135.0, 122.9, 63.7, 53.6, 34.7, 32.4, 25.9, 24.8, 24.4; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.25, H: 9.01, N: 14.74.

(*R,*S**)-*N*,*N*′-Dicyclohexyl-1,2-di(3-pyridyl)-1,2-ethylenediamine 3a.** Yellow solid, mp 123–125°C; IR (CH_2Cl_2): ν=2962, 2932, 2855, 1623, 1577, 1450, 1097, 1013, 864, 807 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.48 (dd, *J*=4.8, 1.8 Hz, 2H), 8.35 (d, *J*=1.8 Hz, 2H), 7.40 (d, *J*=7.8 Hz, 2H), 7.19 (dd, *J*=7.8, 4.8 Hz, 2H), 4.01 (s, 2H), 2.12 (m, 2H), 0.96–1.99 (m, 22H); ^{13}C NMR ($CDCl_3$) δ 149.8, 148.7, 136.3, 135.5, 123.1, 62.0, 53.1, 34.4, 32.5, 25.8, 24.8, 24.5; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.03, H: 9.10, N: 14.87.

(*R,*R**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(3-pyridyl)-1,2-ethylenediamine 2b.** Yellow solid, mp 78–80°C; IR (CH_2Cl_2): ν=3653, 3287, 2969, 1690, 1577, 1476, 1425, 1390, 1365, 1214, 1089, 1025, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.36 (dd, *J*=4.8, 1.8 Hz, 2H), 8.31 (d, *J*=1.8 Hz, 2H), 7.55 (d, *J*=7.8 Hz, 2H), 7.05 (dd, *J*=7.8, 4.8 Hz, 2H), 3.68 (s, 2H), 1.70–2.00 (br, 2H), 0.89 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 149.3, 148.0, 140.2, 135.0, 122.8, 61.8, 51.0, 30.0; ESMS *m*/*z* 327 (MH^+). Anal. Calcd for $C_{20}H_{30}N_4$: C: 73.56, H: 9.27, N: 17.17. Found: C: 73.70, H: 9.21, N: 17.09.

(*R,*S**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(3-pyridyl)-1,2-ethylenediamine 3b.** Yellow solid, mp 72–74°C; IR (CH_2Cl_2): ν=3663, 3290, 3042, 2971, 1674, 1590, 1577, 1477, 1425, 1390, 1365, 1216, 1092, 1025, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.43 (dd, *J*=4.8, 1.8 Hz, 2H), 8.42 (d, *J*=1.8 Hz, 2H), 7.50 (d, *J*=7.8 Hz, 2H), 7.15 (dd, *J*=7.8, 4.8 Hz, 2H), 3.81 (s, 2H), 1.80–2.20 (br, 2H), 0.82 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 149.7, 148.3, 139.6, 135.6, 122.8, 60.9, 51.0, 29.9; ESMS *m*/*z* 327 (MH^+). Anal. Calcd for $C_{20}H_{30}N_4$: C: 73.56, H: 9.27, N: 17.17. Found: C: 73.40, H: 9.34, N: 17.26.

(*R,*R**)-*N*,*N*′-Dihexyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 2c.** Yellow oil; IR (CH_2Cl_2): ν=3657, 3324, 2930, 2858, 1673, 1591, 1570, 1469, 1434, 1378, 1148, 1048, 996, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.48 (d, *J*=4.8 Hz, 2H), 7.34 (dd, *J*=7.8, 7.5 Hz, 2H), 7.05 (dd, *J*=7.5, 4.8 Hz, 2H), 6.89 (d, *J*=7.8 Hz, 2H), 3.85 (s, 2H), 2.40–2.70 (br, 2H), 2.39 (t, *J*=6.0 Hz, 4H), 1.00–1.50 (m, 16H), 0.85 (t, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 161.2, 149.1, 135.4, 123.0, 121.7, 68.9, 47.8, 31.2, 29.9, 26.8, 22.3, 13.9; ESMS *m*/*z* 383 (MH^+). Anal. Calcd for $C_{24}H_{38}N_4$: C: 75.33, H: 10.02, N: 14.65. Found: C: 75.45, H: 9.97, N: 14.58.

(*R,*S**)-*N*,*N*′-Dihexyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 3c.** Yellow oil; IR (CH_2Cl_2): ν=3617, 3437, 2970, 2876, 1736, 1712, 1502, 1466, 1392, 1367, 1238, 1159, 1062, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.49 (d, *J*=4.8 Hz, 2H), 7.48 (dd, *J*=7.8, 7.5 Hz, 2H), 7.07 (dd, *J*=7.5, 4.8 Hz, 2H), 7.01 (d, *J*=7.8 Hz, 2H), 4.10 (s, 2H), 2.40–2.70 (br, 2H), 2.38 (t, *J*=6.9 Hz, 4H), 1.00–1.50 (m, 16H), 0.85 (t, *J*=6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 160.9, 149.0, 135.4, 123.0, 122.0, 67.4, 47.5, 31.5, 29.8, 26.7, 22.5, 13.9; ESMS *m*/*z* 383 (MH^+). Anal. Calcd for $C_{24}H_{38}N_4$: C: 75.33, H: 10.02, N: 14.65. Found: C: 75.20, H: 10.08, N: 14.72.

(*R,*R**)-*N*,*N*′-Dicyclopropyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 2d.** Yellow solid [obtained as a stereoisomeric mixture (DL/*meso*=37:63)]; IR (CH_2Cl_2): ν=3625, 3422, 2945, 2836, 2024, 1627, 1592, 1571, 1472, 1435, 1338, 1018, 793, 606 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.49 (d, *J*=4.8 Hz, 2H), 7.32 (dd, *J*=7.8, 7.5 Hz, 2H), 6.95 (dd, *J*=7.5, 4.8 Hz, 2H), 6.84 (d, *J*=7.8 Hz, 2H), 4.00 (s, 2H),

3.01 (bs, 2H), 1.86 (m, 2H), 0.26 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 161.4, 148.9, 135.5, 123.2, 121.6, 67.0, 28.3, 6.7, 6.2; ESMS *m*/*z* 295 (MH^+). Anal. Calcd for $C_{18}H_{22}N_4$: C: 73.42, H: 7.54, N: 19.04. Found: C: 73.59, H: 7.47, N: 18.94.

(*R,*S**)-*N*,*N*′-Dicyclopropyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 3d.** Yellow solid [obtained as a stereoisomeric mixture (*meso*/DL=63:37)]; IR (CH_2Cl_2): ν=3625, 3422, 2945, 2836, 2024, 1627, 1592, 1571, 1472, 1435, 1338, 1018, 793, 606 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.51 (d, *J*=4.8 Hz, 2H), 7.45 (dd, *J*=7.8, 7.5 Hz, 2H), 7.07 (dd, *J*=7.5, 4.8 Hz, 2H), 6.86 (d, *J*=7.8 Hz, 2H), 4.26 (s, 2H), 3.00 (s, 2H), 1.93 (m, 2H), 0.28 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 161.3, 149.1, 135.3, 123.8, 121.6, 68.7, 29.2, 6.9, 5.7; ESMS *m*/*z* 295 (MH^+). Anal. Calcd for $C_{18}H_{22}N_4$: C: 73.42, H: 7.54, N: 19.04. Found: C: 73.59, H: 7.47, N: 18.94.

(*R,*R**)-*N*,*N*′-Dicyclohexyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 2e.** Yellow oil; IR (CH_2Cl_2): ν=3287, 3045, 2969, 2869, 1682, 1589, 1577, 1476, 1450, 1424, 1390, 1365, 1214, 1089, 1025, 957, 816, 629, 592 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.45 (d, *J*=3.9 Hz, 2H), 7.38 (dd, *J*=7.8, 7.5 Hz, 2H), 6.95–7.03 (m, 4H), 4.02 (s, 2H), 3.50–3.80 (br, 2H), 2.23 (m, 2H), 1.89 (m, 2H), 1.00–1.85 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 161.5, 148.9, 135.5, 123.2, 121.6, 66.2, 54.7, 34.3, 32.6, 25.9, 24.8, 24.6; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.28, H: 9.00, N: 14.72.

(*R,*S**)-*N*,*N*′-Dicyclohexyl-1,2-di(2-pyridyl)-1,2-ethylenediamine 3e.** Yellow oil; IR (CH_2Cl_2): ν=3654, 2936, 2858, 1697, 1598, 1451, 1377, 1097, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.47 (d, *J*=4.2 Hz, 2H), 7.51 (dd, *J*=7.8, 7.5 Hz, 2H), 7.04–7.10 (m, 4H), 4.22 (s, 2H), 2.40–2.80 (br, 2H), 2.23 (m, 2H), 0.90–1.78 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 162.1, 148.5, 135.5, 122.9, 121.5, 64.4, 54.0, 34.0, 32.6, 25.9, 24.7, 24.5; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.01, H: 9.12, N: 14.87.

(*R,*R**)-*N*,*N*′-Di(diphenylmethyl)-1,2-di(2-pyridyl)-1,2-ethylenediamine 2f.** Yellow solid, mp 80–82°C; IR (CH_2Cl_2): ν=3433, 2930, 1715, 1657, 1591, 1570, 1493, 1471, 1453, 1434, 1158, 1027, 593, 552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.55 (d, *J*=4.2 Hz, 2H), 7.60 (dd, *J*=7.8, 7.5 Hz, 2H), 7.04–7.30 (m, 22H), 6.79 (m, 2H), 4.32 (s, 2H), 3.78 (s, 2H), 2.80–3.20 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 161.9, 149.2, 149.2, 144.7, 143.1, 135.3, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.9, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.7, 126.6, 124.7, 121.7, 65.4, 64.3; ESMS *m*/*z* 547 (MH^+). Anal. Calcd for $C_{38}H_{34}N_4$: C: 83.47, H: 6.27, N: 10.25. Found: C: 84.01, H: 6.10, N: 9.89.

(*R,*S**)-*N*,*N*′-Di(diphenylmethyl)-1,2-di(2-pyridyl)-1,2-ethylenediamine 3f.** Yellow oil; IR (CH_2Cl_2): ν=3310, 3028, 2928, 1687, 1659, 1591, 1570, 1492, 1453, 1434, 1186, 1094, 1028, 552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.45 (d, *J*=4.2 Hz, 2H), 7.46 (dd, *J*=7.8, 7.5 Hz, 2H), 7.04–7.30 (m, 22H), 6.87 (m, 2H), 4.48 (s, 2H), 3.93 (s, 2H), 2.50–3.30 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 161.1, 148.8, 144.7, 143.7, 143.2, 135.6, 135.3, 128.5, 128.4, 128.4, 128.2, 128.1, 127.6, 127.5, 127.0, 126.9, 126.8, 126.8, 126.6, 124.7, 123.5, 122.4, 121.7, 66.9, 64.3; ESMS *m*/*z* 547 (MH^+). Anal. Calcd for $C_{38}H_{34}N_4$: C: 83.47, H: 6.27, N: 10.25. Found: C: 82.96, H: 6.37, N: 10.67.

(*R,*R**)-*N*,*N*′-Dicyclohexyl-1,2-di(4-pyridyl)-1,2-ethylenediamine 2g.** White solid, mp 131–133°C; IR (CH_2Cl_2): ν=3298, 3049, 2931, 2855, 1598, 1562, 1450, 1414, 1371, 1118, 994, 615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.39 (d, *J*=4.5 Hz, 4H), 6.99 (d, *J*=4.5 Hz, 4H), 3.68 (s, 2H), 2.30–2.70 (br, 2H), 2.12–2.15 (m, 2H), 0.70–1.90 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 151.2, 149.4, 122.9, 65.0, 53.9, 34.7, 32.4, 25.9, 24.8, 24.4; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.31, H: 8.99, N: 14.70.

(*R,*S**)-*N*,*N*′-Dicyclohexyl-1,2-di(4-pyridyl)-1,2-ethylenediamine 3g.** Yellow solid, mp 139–141°C; IR (CH_2Cl_2): ν=3318, 3045, 2932, 2855, 1938, 1642, 1597, 1558, 1450, 1414, 1124, 993, 613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.47 (d, *J*=4.5 Hz, 4H), 6.98 (d, *J*=4.5 Hz, 4H), 3.97 (s, 2H), 2.30–2.70 (br, 2H), 2.13–2.15 (m, 2H), 0.75–1.90 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 150.0, 149.4, 123.2, 63.2, 53.3, 34.4, 32.5, 25.8, 24.8, 24.4; ESMS *m*/*z* 379 (MH^+). Anal. Calcd for $C_{24}H_{34}N_4$: C: 76.13, H: 9.06, N: 14.81. Found: C: 76.00, H: 9.11, N: 14.89.

(*R,*R**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(2-naphtyl)-1,2-ethylenediamine 2j.** White solid, mp 176–178°C; IR (CH_2Cl_2): ν=3686, 3166, 2778, 1602, 1496, 1391, 1363, 861, 826 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82–7.85 (m, 8H), 7.67 (d, *J*=8.4 Hz, 2H), 7.46–7.50 (m, 4H), 3.99 (s, 2H), 1.40–1.60 (br, 2H), 0.65 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 142.3, 133.0, 132.9, 127.9, 127.7, 127.7, 127.6, 127.6, 126.3, 125.8, 125.4, 63.6, 50.9, 29.8; ESMS *m*/*z* 425 (MH^+). Anal. Calcd for $C_{30}H_{36}N_2$: C: 84.85, H: 8.55, N: 6.60. Found: C: 84.68, H: 8.65, N: 6.67.

(*R,*S**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(2-naphtyl)-1,2-ethylenediamine 3j.** White solid, mp 178–180°C; IR (CH_2Cl_2): ν=3167, 2779, 1600, 1506, 1391, 1363, 861, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64–7.75 (m, 8H), 7.37–7.42 (m, 6H), 4.02 (s, 2H), 1.80–2.10 (br, 2H), 0.82 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 143.0, 133.1, 132.4, 127.7, 127.4, 127.2, 126.3, 126.2, 125.5, 125.0, 63.8, 51.0, 29.8; ESMS *m*/*z* 425 (MH^+). Anal. Calcd for $C_{30}H_{36}N_2$: C: 84.85, H: 8.55, N: 6.60. Found: C: 84.75, H: 8.61, N: 6.64.

(*R,*S**)-*N*,*N*′-Dicyclohexyl-1,2-di(2-naphtyl)-1,2-ethylenediamine 3k.** White solid, mp 203°C (decomposes); IR (KBr): ν=3454, 2927, 1651, 1455, 1118, 480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78–7.85 (m, 8H), 7.50–7.55 (m, 6H), 4.17 (s, 2H), 2.07 (m, 2H), 1.80 (m, 2H), 0.63–1.42 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 139.4, 133.1, 133.0, 128.1, 127.8, 127.8, 127.6, 125.8, 125.8, 125.6, 65.0, 52.9, 34.6, 32.3, 25.9, 25.0, 24.6; ESMS *m*/*z* 477 (MH^+). Anal. Calcd for $C_{34}H_{40}N_2$: C: 85.67, H: 8.46, N: 5.87. Found: C: 85.72, H: 8.43, N: 5.85.

(*R,*R**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(phenylethynyl)-1,2-ethylenediamine 2l.** Brown oil; IR (CH_2Cl_2): ν=3427, 2971, 1760, 1598, 1490, 1433, 1390, 1366, 1288, 1175,

1093, 1029, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27–7.31 (m, 10H), 3.71 (s, 2H) 1.40–1.60 (br, 2H) 1.20 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 131.5, 131.4, 131.3, 128.1, 123.6, 91.8, 83.7, 53.7, 51.2, 51.0, 29.8; ESMS *m*/*z* 373 (MH^+). Anal. Calcd for $C_{26}H_{32}N_2$: C: 83.82, H: 8.66, N: 7.52. Found: C: 83.90, H: 8.62, N: 7.48.

(*R,*S**)-*N*,*N*′-Di-*tert*-butyl-1,2-di(phenylethynyl)-1,2-ethylenediamine 3l.** Brown oil [obtained as a stereoisomeric mixture (*meso*/DL=67:33)]; IR (CH_2Cl_2): ν=3331, 2967, 2200, 1952, 1883, 1808, 1674, 1598, 1490, 1443, 1390, 1365, 1227, 1100, 1028, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43–7.84 (m, 4H), 7.25–7.33 (m, 6H), 3.81 (s, 2H), 1.60–1.80 (br, 2H), 1.25 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 131.5, 131.4, 128.1, 127.5, 126.0, 91.9, 83.6, 51.1, 50.9, 50.6, 29.9; ESMS *m*/*z* 373 (MH^+). Anal. Calcd for $C_{26}H_{32}N_2$: C: 83.82, H: 8.66, N: 7.52. Found: C: 83.87, H: 8.64, N: 7.49.

(*R,*S**)-*N*,*N*′-Dicyclohexyl-1,2-di(phenylethynyl)-1,2-ethylenediamine 3m.** Brown oil; IR (CH_2Cl_2): ν=3420, 2932, 2856, 1686, 1598, 1490, 1451, 1116 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–7.40 (m, 10H), 3.97 (s, 2H), 2.87 (m, 2H), 2.10–2.25 (br, 2H), 1.05–1.95 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 131.8, 131.5, 128.2, 128.1, 128.0, 123.1, 88.3, 84.8, 52.1, 47.0, 34.3, 33.0, 32.4, 26.1, 25.3, 25.0, 24.7; ESMS *m*/*z* 425 (MH^+). Anal. Calcd for $C_{30}H_{36}N_2$: C: 84.85, H: 8.55, N: 6.60. Found: C: 85.06, H: 8.45, N: 6.49.

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