The Journal of Organic Chemistry

University of Sussex

Subscriber access provided by University of Sussex Library

Article

A Metal-free Approach to 1,2-Diamines via Visible Light-driven Reductive Coupling of Imines with Perylene as a Photoredox Catalyst

Shusuke Okamoto, Risako Ariki, Hiroki Tsujioka, and Atsushi Sudo

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b01838 • Publication Date (Web): 24 Aug 2017

Downloaded from http://pubs.acs.org on August 25, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

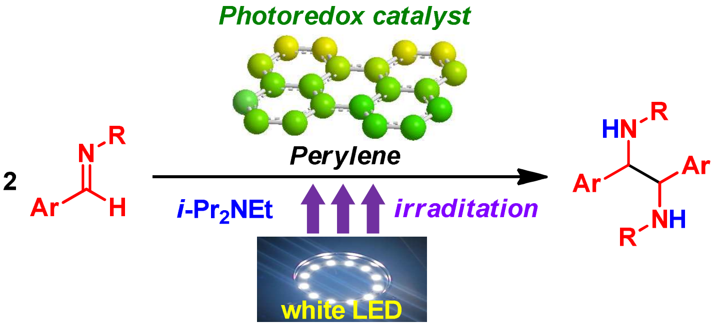
Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

A Metal-free Approach to 1,2-Diamines via Visible Light-driven Reductive Coupling of Imines with Perylene as a Photoredox Catalyst

Shusuke Okamoto, Risako Ariki, Hiroki Tsujioka and Atsushi Sudo*

Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, Kowakae 3-4-1, Higashi Osaka, Osaka 577-8502, Japan.

E-mail: asudo@apch.kindai.ac.jp



Abstract

A simple, metal-free, and versatile approach to 1,2-diamines has been developed based on reductive coupling reactions of various imines, where perylene, an aromatic hydrocarbon, was used as a photoredox catalyst under visible light irradiation using a white LED. The use of 1 mol% perylene enabled almost complete conversion of the imines, leading to the formation of their corresponding 1,2-diamines, which were isolated in good yields. The ratios between *dl* and *meso* diamines ranged from 31:69 to 82:18 depending on the substituents of the imines.

Introduction

Reductive coupling reaction of imines is a straightforward approach to obtain 1,2-diamines,[1a-g] which are highly valuable as precursors for ligands and chiral auxiliaries.[2a-c] These reactions have been achieved using metals, low-valent metal species, and metal alloys such as magnesium,[1a,b] samarium(II),[1c-e] titanium(III)-magnesium,[1f] and zinc-copper alloys.[1g] From these metal species with high reduction potentials, one electron can be transferred efficiently to imines to transform them into the corresponding radical anions, which then readily undergo coupling reactions to give 1,2-diamines. Due to a lack of other efficient methods, existing protocols have been frequently used. However, the consumption of stoichiometric amounts of precious metals such as those listed above is becoming more problematic in recent years from both economic and environmental perspectives. Therefore, the development of alternative catalytic method that avoid the utilization of large amounts of metal species is desired.

The requirement for greener and more sustainable alternative methods may be fulfilled by utilizing visible light as an energy source to drive the reaction. Currently, various reactions that can be promoted under irradiation of visible light have been developed.[3] In these reactions, photoredox catalysts are excited by visible light and mediate reactions *via* electron transfer processes. Among the various photoredox catalysts developed so far, ruthenium(II) and iridium(III) complexes have been the most extensively investigated. The applications of these metal complexes include dehalogenation,[4] C-C bond forming,[5] and C-heteroatom bond forming reactions.[6]

Nakajima *et al*. reported reductive coupling of *N*-benzylimines under irradiation of visible light using iridium(II) complexes as photoredox catalysts, allowing for the efficient synthesis of a variety of 1,2-diamines.[7] Fava *et al*. have reported the use of an iridium complex for visible light-driven reductive coupling of imines and *N*-methylaniline derivatives.[8] In addition, Rono *et al*. have reported the intramolecular coupling of ketohydrazone under the irradiation of visible light using iridium(II) complexes as a photoredox catalyst.[9]

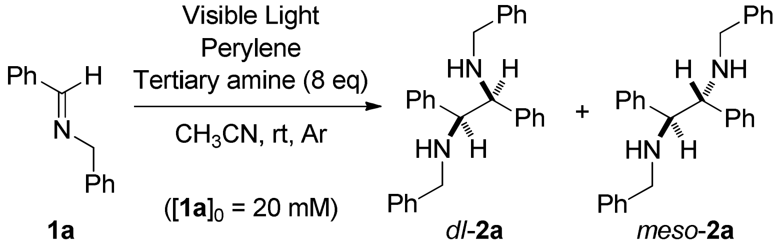
Besides such metal complexes, organic dyes with extended π-conjugated systems are also attractive candidates for photoredox catalysts, due to their structural diversity and lower cost and their non-dependence of the utilization of precious metals.[10] Recently, perylene, a commercially available polycyclic aromatic hydrocarbon, has been attracted attention as a photoredox catalyst that mediates controlled radical polymerizations.[11] We reported reductive coupling reactions of aromatic aldehydes and ketones, where perylene acted as a photoredox catalyst effectively.[12] In the mechanism postulated therein, perylene is excited (P*) upon irradiation with visible light. The excited perylene, P*, then abstracts one electron from a sacrificial tertiary amine, affording a perylene radical anion ($P^{\cdot -}$). Then, single electron transfer from $P^{\cdot -}$ to aldehydes and ketones converts them into the corresponding ketyl radicals, which readily undergo homo-coupling reactions to afford 1,2-diols.

In this study, we expanded the scope of metal-free photocatalysis using perylene for the reductive coupling reaction of imines under visible light irradiation. Reductive coupling reactions of *N*-arylmethyl-, *N*-*tert*-butyl-, and *N*-aryl-substituted imines derived from aromatic aldehydes were performed to demonstrate the versatility of this photocatalytic system.

Results and Discussion

Coupling reaction of imine 1a using perylene as a photoredox catalyst

First, using imine **1a** obtained by the condensation of benzaldehyde and benzylamine, conditions for the reductive coupling reaction of imines **1** were optimized (Scheme 1, Table 1). Acetonitrile was selected as the solvent, since it has been reported that photosensitized oxidation of tertiary amines using perylene was successfully performed in acetonitrile.[13] In addition, successful photoredox catalysis of the reductive coupling reaction of aromatic aldehydes in acetonitrile was successfully demonstrated in our previous report.[12]



Scheme 1. Reductive coupling of imine **1a**

Initially, the reaction was performed under the same optimized conditions developed for the visible light-driven reductive coupling reaction of benzaldehyde reported in our previous work (entry 1): upon irradiating an acetonitrile solution of **1a**, perylene (12 mol%), and *N*,*N*-diisopropylethylamine (i-Pr_2NEt; 8 eq.) with visible light using an 8.5 W white LED for 16 h, imine **1a** was consumed completely to yield the corresponding diamine **2a**. Diamine **2a** was isolated by preparative TLC in 66% yield. The structure of **2a** was confirmed by comparing its ^{1}H- and ^{13}C-NMR data with reported spectra.[7] The spectra clarified that diamine **2a** was obtained as a diastereomeric mixture with a *dl*:*meso* ratio of 65:35.

Table 1. Optimization of the reaction conditions for the reductive coupling of *N*-benzylimine **1a**

Entry	Tertiary Amine	Amount of perylene /mol%	Reaction time/h	Yield of **2a** /%[a]	*dl* : *meso*[b]	Yield of DBA /%[c]
1	*i*-Pr$_2$NEt	12	16	66	65:35	N.D.[d]
2	*i*-Pr$_2$NEt	4	16	58	71:29	5
3	*i*-Pr$_2$NEt	1	16	68	67:33	6
4	*i*-Pr$_2$NEt	1	4	25	89:11	N.D.[d]
5	Et$_3$N	1	16	46	74:26	N.D.[d]
6[e]	*i*-Pr$_2$NEt	1	16	0	-	-
7	*i*-Pr$_2$NEt	0	16	0	-	-
8	None	1	16	0	-	-

[a] Yield of **2a** isolated by preparative TLC. [b] Determined by the ^{1}H NMR analysis of **2a** isolated by preparative TLC. [c] Determined by the ^{1}H NMR analysis of crude **2a** before isolation. [d] Not determined. [e] Without irradiation.

Next, the influence of the amount of added perylene on the reaction efficiency was investigated (Table 1, entries 2 and 3). Remarkably, even when the amount of perylene was decreased to 1 mol%, the reaction proceeded efficiently to give **2a** with good yields.

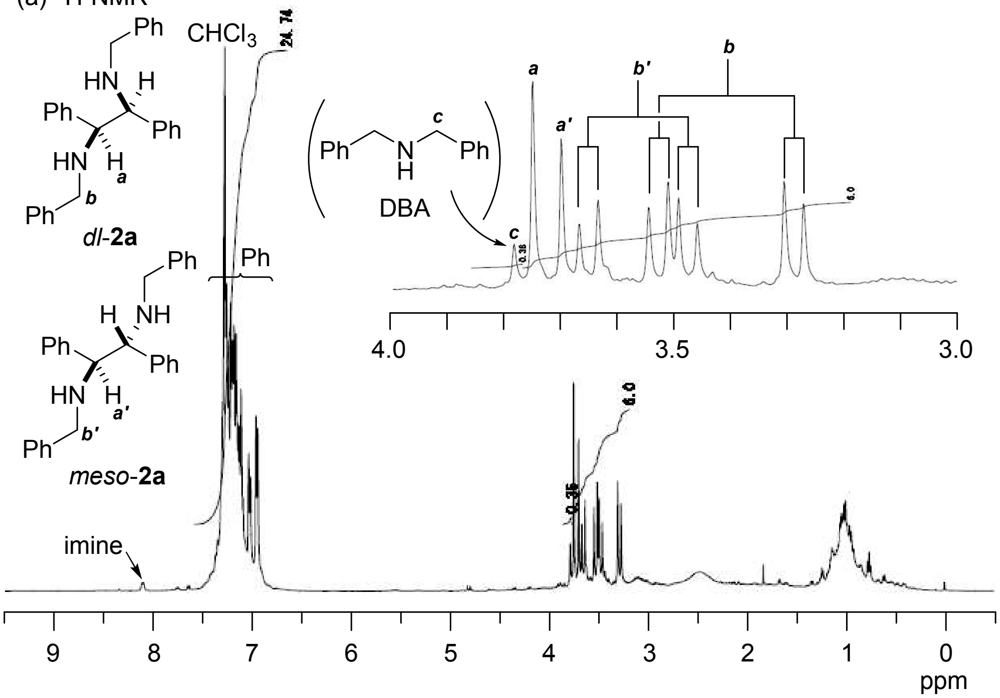
The crude product obtained by the experiment in entry 3 was analyzed by ^{1}H-NMR. The spectrum is shown in Figure 1. All the major signals were attributable to the protons of **2a**, implying a high conversion of imine **1a** to diamine **2a**. Besides, broad and multiple signals at around 1 ppm were attributable to alkyl groups of unidentified compounds derived from *i*-Pr$_2$NEt. A weak signal at 8.1 ppm was observed to confirm the presence of a small amount of unconsumed imine **1a**.

The ^{13}C-NMR spectrum of the crude product is also shown in Figure 1. The spectrum confirmed that diamine **2a** was fairly pure when the unidentified *i*-Pr$_2$NEt-derived compounds were neglected.

The reduction of **1a** into dibenzylamine (DBA) can compete with the reductive coupling reaction of **1a** into the diamine **2a**. In the ^{1}H-NMR spectrum of the crude mixture (Figure 1), a singlet signal was observed at 3.8 ppm, confirming the presence of DBA. The presence of DBA was also confirmed by ^{13}C-NMR analysis of the crude mixture. A weak signal attributable to the methylene carbons of DBA was observed at 53 ppm. Based on the ^{1}H-NMR analysis, the yields of DBA in entries 2 and 3 were calculated to be 5 and 6%, respectively.

In the experiment denoted by entry 4, irradiation of visible light was stopped at 4 h. As a result, the yield of **2a** dropped to 25%. For the experiment denoted by entry 5, triethylamine (Et$_3$N) was used in place of *i*-Pr$_2$NEt. The yield of **2a** decreased to 46% without influencing the diastereoselectivity. For the runs summarized in entries 6–8, the reaction was carried out without irradiation, in the absence of perylene, and in the absence of tertiary amine, respectively. In these cases, the reaction barely proceeded, indicating that the presence of all of these factors were indispensable for efficient progress of the reaction.

(a) ^{1}H-NMR



(b) ^{13}C-NMR

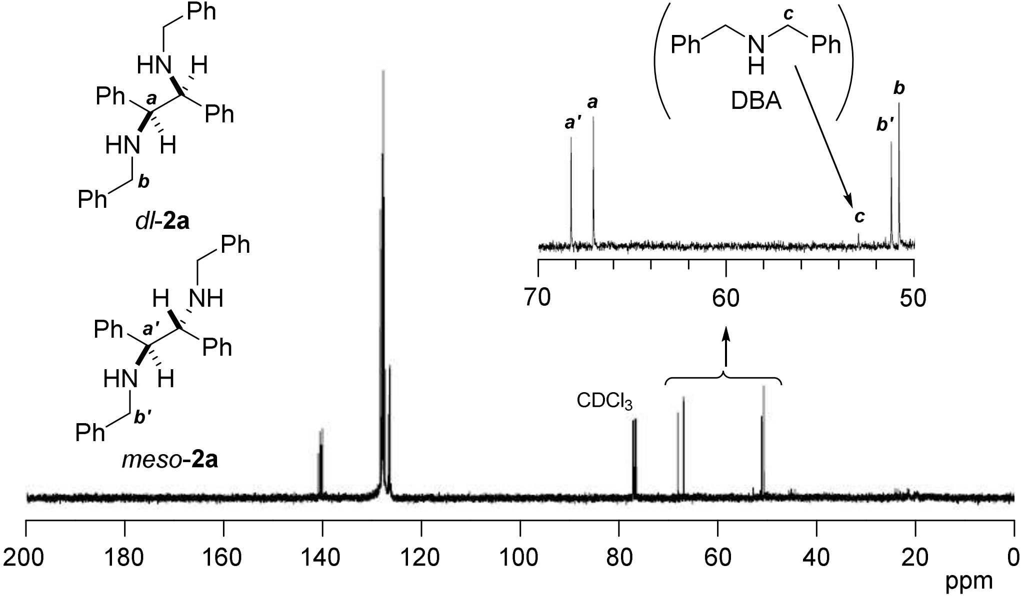


Figure 1. ^{1}H- and ^{13}C-NMR spectra of crude diamine **2a**

Reductive coupling reactions of imines 1b-m

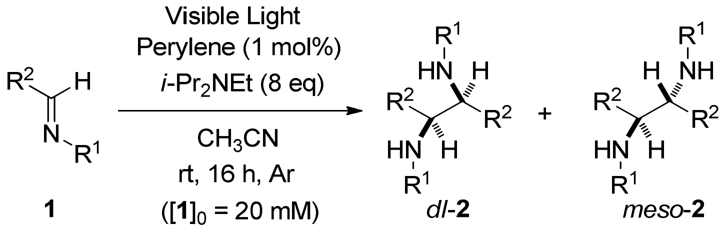
Under the optimized conditions for the reductive coupling reaction of **1a**, those of the other imines **1b**–**1m** were performed to expand the substrate scope of the photoredox catalyst under study (Scheme 2, Table 2). Imine conversion was determined by ^{1}H-NMR analysis of reaction mixtures before isolation of the corresponding diamines.

The reactions of *N*-(arylmethyl)imines **1b–1g** gave the corresponding diamines **2b–2g** in moderate to good yields. Diamines **2b**–**2g** were obtained as mixtures of *dl*- and *meso*-diastereomers and their ratios were determined by ^{1}H-NMR. It is noteworthy that the coupling reaction of imine **1c** bearing a 4-methoxyphenyl group gave diamine **2c** with a higher yield of its *dl*-diastereomer over that of its *meso*-diastereomer (Table 2, entry 3). Such a dominant formation of the *dl*-diastereomer was observed also in the reductive pinacol coupling reaction of 4-methoxybenzaldehyde.[12]

The protocol using perylene as the photoredox catalyst was extended to the reductive coupling reactions of several *N*-(*tert*-butyl)imines **1h–1k** (Table 2, entries 8–11). In all cases, excellent reactivity was revealed by ^{1}H-NMR analysis of the crude reaction product. Figure S2 shows the ^{1}H- and ^{13}C-NMR spectra of the crude product obtained by the coupling reaction of imine **1h**, demonstrating the high efficiency of the reaction.

In these reactions, the amounts of *meso* isomers were slightly higher than those of *dl* isomers. *N*-aryl-type imines **1l** and **1m** were also converted into the corresponding diamines **2l** and **2m**. In these reactions, higher *meso*-selectivity was observed than in the reactions of *N*-(*tert*-butyl)imines **1h–1k**.

The conversions of imines **1c** and **1m** bearing a 4-methoxyphenyl group were lower than those of the other imines. The lower reaction efficiencies may be due to the higher electron densities of these substrates, which can hinder the approach of a radical anion of perylene to the substrates.



Scheme 2. Reductive coupling of imines **1**

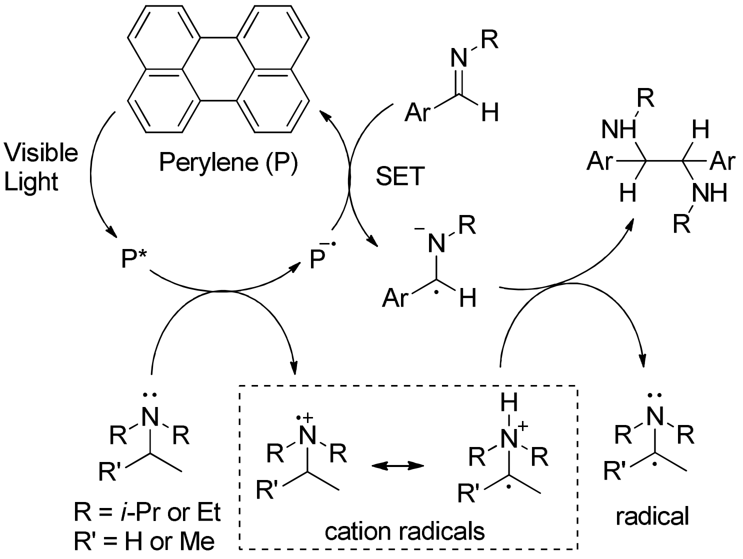
Table 2. Reductive coupling reactions of imines

Entry	**1**	R^1	R^2	Conversion of **1**/%^{a}	**2**	Yield /%^{b}	*dl* : *meso*^{c}
1	**1a**	$PhCH_2$	Ph	98	**2a**	68	67 : 33
2	**1b**	$PhCH_2$	4-MeC_6H_4	100	**2b**	69	69 : 31
3	**1c**	$PhCH_2$	4-$MeOC_6H_4$	53	**2c**	32	82 : 18
4	**1d**	$PhCH_2$	4-$CF_3C_6H_4$	100	**2d**	80	54 : 46
5	**1e**	$PhCH_2$	4-ClC_6H_4	100	**2e**	70	65 : 35
6	**1f**	(4-$MeOC_6H_4$)CH_2	Ph	100	**2f**	55	66 : 34
7	**1g**	(4-$CF_3C_6H_4$)CH_2	Ph	100	**2g**	75	59 : 41
8	**1h**	*t*-Bu	Ph	100	**2h**	64	45 : 55
9	**1i**	*t*-Bu	4-MeC_6H_4	100	**2i**	77	41 : 59
10	**1j**	*t*-Bu	4-FC_6H_4	100	**2j**	73	48 : 52
11	**1k**	*t*-Bu	4-$CF_3C_6H_4$	100	**2k**	75	44 : 56
12	**1l**	Ph	Ph	99	**2l**	70	39 : 61
13	**1m**	4-$MeOC_6H_4$	Ph	67	**2m**	41	31 : 69

[a] Determined by ^{1}H-NMR analysis of crude product. [b] Isolated by silica gel column chromatography. [c] Determined by ^{1}H-NMR of isolated product.

Reaction mechanism

In our previous report, a plausible mechanism for the photoredox catalysis of reductive coupling reactions of aromatic aldehydes and ketones by perylene was postulated,[12] based on the ability of perylene to mediate the oxidation of tertiary amines by absorbing visible light.[13] By analogy, a mechanism for the present photoredox catalysis of the reductive coupling reaction of imines was postulated (Scheme 3).



Scheme 3. Plausible mechanism for the reductive coupling using perylene as the photoredox catalyst

First, excited perylene (P*) generated by the irradiation of perylene (P) with visible light abstracts one electron from a tertiary amine. Second, single electron transfer (SET) from the resulting radical anion of perylene ($P^{\cdot -}$) to imine **1** takes place to convert **1** into the corresponding radical anion. Third, the radical anions undergo a homo-coupling reaction to achieve carbon-carbon bond formation. Finally, target diamine **2** can be obtained via abstraction of protons from proton donors such as the radical cation of the tertiary amine. Another possibility is that the radical anions abstract protons, and then the formed radicals undergo coupling reactions to form the corresponding diamines.

Because the important step in this reaction is SET from $P^{\cdot-}$ to imine, density functional theory (DFT) calculations were conducted to estimate the SOMO energy level of the perylene radical anion ($P^{\cdot-}$) and the LUMO energy level of imine **1a** (Figure 2). For comparison, the LUMO energy level of benzaldehyde was calculated in a similar manner. The LUMO energy level of **1a** (–1.21 eV) was higher than that of benzaldehyde (–1.73 eV) and thus closer to the SOMO level of $P^{\cdot-}$ (–0.69 eV), implying that the SET from $P^{\cdot-}$ to **1a** would be less exothermic and less efficient than that to benzaldehyde. On the other hand, the amount of perylene required for the efficient reductive coupling of imine **1a** was 1 mol%, while the amount of perylene required for the coupling reaction of benzaldehyde was 12 mol%,[12] implying that the efficiency of the SET from $P^{\cdot-}$ to **1a** would be higher than that of the SET to benzaldehyde. The combination of these two considerations leads to an assumption that the interactions of the SOMO of $P^{\cdot-}$ and the LUMO of an acceptor (imine or aldehyde) govern the SET process to some extent. Because perylene is an aromatic compound with high planarity that allows π-π interaction with the substrates, such SOMO-LUMO interactions can be significantly enhanced.

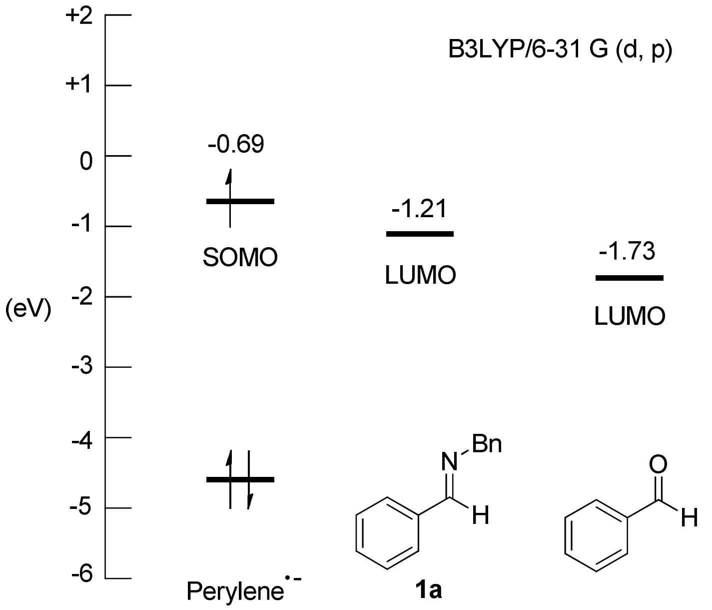


Figure 2. Energy levels of SOMO and HOMO of the perylene radical anion, LUMO of imine **1a**, and LUMO of benzaldehyde

Conclusions

A highly efficient visible light-driven system for reductive coupling reactions to transform imines to their corresponding 1,2-diamines has been developed using perylene, a simple polycyclic aromatic hydrocarbon, as a photoredox catalyst. The coupling reactions gave the corresponding 1,2-diamines as mixtures of their *dl*- and *meso*-diastereomers, and the selectivity depended on the substituents on the nitrogen atom of imines. 1) Coupling reactions of *N*-arylmethyl imines gave the corresponding diastereomeric mixtures of diamines, where the *dl*-diastereomers dominated over the *meso*-diastereomers. 2) In coupling reactions of *N*-*tert*-butyl imines, no clear diastereoselectivity was observed. 3) In coupling reactions of *N*-aryl imines, the formation of *meso*-diamines dominated over that of *dl*-diamines. The present photoredox catalytic method using perylene under irradiation of visible light allows for the synthesis of 1,2-diamines without the use of stoichiometric amounts of precious metal reagents and is thus considered to be more cost effective and environmentally friendly.

EXPERIMENTAL SECTION

General methods and materials

Acetonitrile was distilled from calcium hydride and stored over 4 Å molecular sieves in an argon atmosphere. The aldehydes were also distilled under an argon atmosphere. The primary amines and diisopropylethyamine were distilled and stored over sodium hydroxide in argon. NMR spectra (400 MHz for ^{1}H; 100 MHz for ^{13}C) were recorded with a JEOL NMR spectrometer (JNM-AL400) as solutions in $CDCl_3$ using TMS as the internal standard. Chemical shifts, δ, and coupling constants, J, are expressed in ppm and Hz, respectively. IR spectra were obtained using a JASCO FT/IR-470 spectrometer, and wavenumbers, v, are given in cm^{-1}. High-resolution mass spectroscopic analyses were performed using a JEOL mass spectrometer (JMS-T100LP AccuTOF LC-plus) in a direct analysis in real time (DART) mode and detected by the time-of-flight (TOF) method. For irradiation, a HOZAN LED (model L–711) was used.

General procedure for the preparation of imines 1

To a solution of an aldehyde (5.0–20.0 mmol) and a primary amine (1.0–1.3 eq) in dichloromethane (10–40 mL), molecular sieves 4 Å (1.0–4.0 g) were added. The resulting mixture was stirred vigorously at room temperature for 16 h. The mixture was passed through a Celite pad, and the filtrate was concentrated under reduced pressure and dried under vacuum to obtain the corresponding imines. The imines were purified by Kugelrohr distillation.

N-Benzylbenzaldimine (1a)

According to the general procedure, **1a** was obtained as a colourless oil (1.11 g, 57% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[14] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}N$ 196.1126; Found: 196.1132.

N-Benzyl-4-methylbenzaldimine (1b)

According to the general procedure, **1b** was obtained as a pale yellow oil (604 mg, 58% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[14] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}N$ 210.1283; Found: 210.1277.

N-Benzyl-4-methoxybenzaldimine (1c)

According to the general procedure, **1c** was obtained as a pale yellow oil (629 mg, 56% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[14] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}NO$ 226.1228; Found: 226.1232.

N-Benzyl-4-trifluoromethylbenzaldimine (1d)

According to the general procedure, **1d** was obtained as a white solid (2.45 g, 93% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[15] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_3N$ 264.1000; Found: 264.0994.

N-Benzyl-4-chlorobenzaldimine (1e)

According to the general procedure, **1e** was obtained as a colourless oil (2.10 g, 92% yield). Its ^{1}H-NMR data agreed with those reported.[16] ^{13}C-NMR ($CDCl_3$, r.t.) δ 160.7, 139.2, 136.8, 134.7, 129.6, 129.0, 128.7, 128.4, 128.1, 127.2, 65.1. IR: 3061, 3028, 2839, 1644, 751, 697 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}ClN$ 230.0737; Found: 230.0736.

N-Benzylidene-4-methoxybenzylamine (1f)

According to the general procedure, **1f** was obtained as a white solid (1.86 g, 83% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[17] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}NO$ 226.1232; Found: 226.1230.

N-Benzylidene-4-trifluoromethylbenzylamine (1g)

According to the general procedure, **1g** was obtained as pale a pale yellow oil (2.53 g, 96% yield): ^{1}H-NMR ($CDCl_3$, r.t.) δ 8.40 (s, 1H), 7.78 (d, J = 5.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.46-7.41 (m, 5H), 4.84 (s, 2H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 162.8, 143.7, 136.0, 131.1, 129.5, 129.2, 128.8, 128.4, 128.2, 125.8, 125.6, 125.5, 125.5, 125.4, 123.1, 64.5; IR (KBr) v 3064, 3029, 2846, 1646, 761, 693 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}F_3N$ 264.1000; Found: 264.0996.

N-*tert*-Butylbenzaldimine (1h)

According to the general procedure, **1h** was obtained as a colourless oil (2.43 g, 75% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[18] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}N$ 162.1283; Found: 162.1269.

N-*tert*-Butyl-4-methylbenzaldimine (1i)

According to the general procedure, **1i** was obtained as a colourless oil (1.30 g, 74% yield). Its ^{1}H-NMR data agreed with those reported.[19] ^{13}C-NMR ($CDCl_3$, r.t.) δ 155.2, 140.4, 129.3, 128.0, 114.0, 57.2, 29.9, 21.6. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}N$ 176.1439; Found: 176.1422.

N-tert-Butyl-4-fluorobenzaldimine (1j)

According to the general procedure, **1j** was obtained as a colourless oil (0.77 g, 43% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[18] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}FN$ 180.1189; Found: 180.1170.

N-tert-Butyl-4-trifluoromethylbenzaldimine (1k)

According to the general procedure, **1k** was obtained as a colourless oil (0.85 g, 74% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[18] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}F_3N$ 230.1157; Found: 230.1152.

N-Phenylbenzaldimine (1l)

According to the general procedure, **1l** was obtained as a pale yellow oil (1.68 g, 93% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[14] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}N$ 182.0970; Found: 182.0962.

N-(4-Methoxyphenyl)benzaldimine (1m)

According to the general procedure, **1m** was obtained as a brown solid (2.09 g, 99% yield). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[20] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1075; Found: 212.1074.

General Procedure for the reductive coupling reaction of imines

Imine **1** (1.00 mmol), perylene (2.5 mg; 10 μmol), *i*-Pr_2EtN (1.40 mL, 8.00 mmol), and acetonitrile (50 mL) were added to a 100 mL flask under argon. The resulting solution was irradiated using a LED light under stirring at room temperature. After 16 h, the solution was concentrated under reduced pressure. The resulting residue was purified by a silica gel column chromatography (eluent: hexane / ethyl acetate / triethylamine = 400~1000 / 50 / 1) and preparative TLC (eluent: hexane / ethyl acetate /

triethylamine = 500~1000 : 50 : 1) to afford the corresponding diamine **2** as a mixture of *dl*- and *meso*-diastereomers.

1,2-Diphenyl-*N,N′*-bis(phenylmethyl)-1,2-ethanediamine (2a)

According to the general procedure, **2a** was obtained as a pale yellow solid (133 mg, 68%, *dl* : *meso* = 67 : 33). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[7,12] HRMS (DART) m/z: [M+H]$^+$ Calcd for $C_{28}H_{29}N_2$ 393.2331; Found: 393.2314.

1,2-Bis(4-methylphenyl)-*N,N'*-bis(phenylmethyl)-1,2-ethanediamine (2b)

According to the general procedure, **2b** was obtained as a pale yellow solid (146 mg, 69% yield, *dl* : *meso* = 69 : 31): ^{1}H-NMR (CDCl$_3$, r.t.) δ 7.30-7.12 (m, 28H), 6.97-6.93 (m, 8H), 3.69 (s, 2H, *dl*), 3.67 (s, 2H, *meso*), 3.64 (d, *J* = 13.7 Hz, 2H, *meso*), 3.52 (d, *J* = 14.2 Hz, 2H, *dl*), 3.47 (d, *J* = 13.7 Hz, 2H, *meso*), 3.28 (d, *J* = 13.7 Hz, 2H), 2.35 (s, 6H, *dl*), 2.25 (s, 6H, *meso*), 1.92 (brs, 4H, *dl* and *meso*); ^{13}C-NMR (CDCl$_3$, r.t.) δ 140.6, 140.6, 137.9, 137.3, 129.3, 129.3, 128.8, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 126.8, 126.7, 68.0, 67.1, 51.4, 51.0, 21.3, 21.3. IR (KBr) *v* 3308, 3061, 2963, 2922, 2825, 1454, 738, 695. cm^{-1}. HRMS (DART) m/z: [M+H]$^+$ Calcd for $C_{30}H_{33}N_2$ 421.2644; Found: 421.2631.

1,2-Bis(4-methoxyphenyl)-*N,N'*-bis(phenylmethyl)-1,2-ethanediamine (2c)

According to the general procedure, **2c** was obtained as a pale yellow solid (72.7 mg, 32% yield, *dl* : *meso* = 82 : 18). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[7] HRMS (DART) m/z: [M+H]$^+$ Calcd for $C_{30}H_{33}N_2O_2$ 453.2542; Found: 453.2527.

1,2-Bis(4-trifluoromethylphenyl)-*N,N'*-bis(phenylmethyl)-1,2-ethanediamine (2d)

According to the general procedure, **2d** was obtained as a pale yellow solid (211 mg, 80% yield, *dl* : *meso* = 54 : 46): ^{1}H-NMR (CDCl$_3$, r.t.) 7.55 (d, *J* = 7.8 Hz, 4H), 7.43 (d, *J* = 8.3 Hz, 4H), 7.30 (d, *J* = 8.3 Hz, 4H), 7.27-7.18 (m, 16H), 7.14 (d, *J* = 7.8 Hz, 4H), 7.01 (d, *J* = 7.8 Hz, 4H), 3.85 (s, 2H, *dl*), 3.75 (s, 2H, *meso*), 3.65 (d, *J* = 13.2 Hz, 2H, *dl*), 3.56 (d, *J* = 13.7 Hz, 2H, *meso*), 3.46 (d, *J* = 13.7 Hz, 2H, *dl*), 3.32 (d, *J* = 13.7 Hz, 2H, *meso*), 2.03 (brs, 4H, *dl* and *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ145.2, 144.6, 140.0, 139.9, 130.6, 130.3, 129.9, 129.8, 129.6, 129.5, 129.0, 128.6, 128.5, 128.3, 128.2, 128.0, 127.2, 127.2, 125.7, 125.6, 125.4, 125.4, 125.3, 125.3, 125.2, 125.2, 123.0, 122.9, 67.9, 66.6, 51.4, 51.2. IR (KBr) ν 3274, 3020, 2927, 2861, 1327, 1121, 748, 699 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}F_6N_2$ 529.2078; Found: 529.2053.

1,2-Bis(4-chlorophenyl)-*N*,*N*'-bis(phenylmethyl)-1,2-ethanediamine (2e)

According to the general procedure, **2e** was obtained as a pale yellow solid (162 mg, 70% yield, *dl* : *meso* = 65 : 35): ^{1}H-NMR ($CDCl_3$, r.t.) 7.31-7.17 (m, 16H), 7.14 (d, *J* = 8.3 Hz, 8H), 7.00 (d, *J* = 6.3 Hz, 8H), 6.94 (d, *J* = 8.3 Hz, 4H), 3.72 (s, 2H, *dl*), 3.65-3.61 (m, 4H, *dl* and *meso*), 3.55 (d, *J* = 13.7 Hz, 2H, *dl*), 3.46 (d, *J* = 13.7 Hz, 2H, *meso*), 3.30 (d, *J* = 13.7 Hz, *dl*), 1.80 (brs, 4H, *dl* and *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ140.3, 140.1, 139.6, 139.0, 133.7, 133.4, 130.1, 130.0, 129.4, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.1, 127.0, 126.9, 67.7, 66.4, 51.4, 51.1. IR (KBr) ν 3279, 3062, 3026, 2961, 2859, 1455, 747, 697 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}Cl_2N_2$ 461.1551; Found: 461.1530.

***N*,*N*'-Bis[(4-methoxyphenyl)methyl]-1,2-diphenyl-1,2-ethanediamine (2f)**

According to the general procedure, **2f** was obtained as a pale yellow solid (125 mg, 55% yield, *dl* : *meso* = 66 : 34): ^{1}H-NMR ($CDCl_3$, r.t.) 7.33-7.25 (m, 12H), 7.15-7.11 (m, 8H), 7.03 (d, *J* = 6.8 Hz, 4H), 6.88 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.3 Hz, 4H), 6.74 (d, *J* = 8.8 Hz, 4H), 3.78 (s, 6H, *meso*), 3.76 (s, 6H, *dl*), 3.73 (s, 2H, *dl*), 3.68 (s, 2H, *meso*), 3.58 (d, *J* = 12.7 Hz, 2H), 3.46 (d, *J* = 13.7 Hz, 2H), 3.40 (d, *J* = 13.2 Hz, 2H), 3.23 (d, *J* = 13.2 Hz, 2H), 1.92 (brs, 4H, *dl* and *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ158.6, 158.5, 141.4, 141.0, 132.9, 132.6, 129.4, 129.1, 128.7, 128.4, 128.1, 128.0, 127.7, 127.0, 113.8, 113.7, 68.3, 67.2, 55.4, 55.3, 50.8, 50.4. IR (KBr) ν 3446, 3029, 2954, 2834, 1457, 753, 702 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_2$ 453.2542; Found: 453.2520.

N,N'-Bis[(4-trifluoromethylphenyl)methyl]-1,2-diphenyl-1,2-ethanediamine (2g)

According to the general procedure, **2g** was obtained as a pale yellow solid (198 mg, 75% yield, *dl* : *meso* = 59: 41): ^{1}H-NMR ($CDCl_3$, r.t.) 7.52 (d, *J* = 7.8 Hz, 8H), 7.44 (d, *J* = 7.8 Hz, 8H), 7.36-7.29 (m, 12H), 7.21-7.14 (m, 8H), 7.05 (d, *J* = 7.8 Hz, 8H), 3.73-3.70 (m, 6H), 3.56 (t, *J* = 13.7 Hz, 4H), 3.35 (d, *J* = 14.2 Hz, 2H), 2.02 (brs, 4H, *dl* and *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ144.7, 144.6, 140.8, 140.6, 129.4, 129.3, 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 125.8, 125.7, 125.4, 125.3, 125.3, 125.2, 125.2, 125.2, 123.1, 123.0, 68.4, 67.5, 50.9, 50.5. IR (KBr) ν 3278, 3061, 2854, 2825, 1454, 1119, 753, 697 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}F_6N_2$ 529.2078; Found: 529.2054.

N,N'-Bis(1,1-dimethylethyl)-1,2-diphenyl-1,2-ethanediamine (2h)

According to the general procedure, **2h** was obtained as a pale yellow solid (104 mg, 64% yield, *dl* : *meso* = 45 : 55). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[21] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{22}H_{33}N_2$ 325.2644; Found 325.2647.

N,N'-Bis(1,1-dimethylethyl)-1,2-bis(4-methylphenyl)-1,2-ethanediamine (2i)

According to the general procedure, **2i** was obtained as a pale yellow solid (135 mg, 77% yield, *dl* : *meso* = 41 : 59): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.26 (d, *J* = 5.9 Hz, 4H), 7.11-7.08 (m, 8H), 6.96 (d, *J* = 7.8 Hz, 4H), 3.65(s, 2H, *dl*), 3.64 (s, 2H, *meso*), 2.32 (s, 6H, *meso*), 2.25 (s, 6H, *dl*) 0.80 (s, 18H, *dl*), 0.69 (s, 18H, *meso*). ^{13}C-NMR ($CDCl_3$, r.t.) δ *dl*: 142.8, 142.0, 136.5, 135.5, 128.8, 128.5, 128.4, 127.7, 63.8, 63.7, 50.9, 50.9, 30.0, 30.0, 21.3, 21.2. IR (KBr) ν 3335, 2955, 2924, 2854, 1457, 758, 691 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{24}H_{37}N_2$ 353.2957; Found 353.2957.

_N,N_'-Bis(1,1-dimethylethyl)-1,2-bis(4-fluorophenyl)-1,2-ethanediamine (2j)

According to the general procedure, **2j** was obtained as a pale yellow solid (131 mg, 73% yield, *dl* : *meso* = 48 : 52): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.27 (m, 4H), 7.10 (m, 4H), 6.97 (t, *J* = 8.5 Hz, 4H), 6.84 (t, *J* = 8.5 Hz, 4H), 3.65 (s, 2H, *meso*), 3.61 (s, 2H, *dl*), 1.50 (brs, 4H, *dl* and *meso*), 0.83 (s, 18H, *dl*), 0.72 (s, 18H, *meso*). ^{13}C-NMR ($CDCl_3$, r.t.) δ 163.3, 162.8, 160.8, 160.3, 141.3, 141.3, 140.7, 140.6, 129.9, 129.8, 129.1, 129.0, 114.9, 114.7, 114.7, 114.5, 63.7, 63.1, 51.0, 51.0, 30.1, 30.0. IR (KBr) ν 3395, 3032, 2954, 2924, 2854, 1457, 758, 690 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{22}H_{31}F_2N_2$ 361.2455; Found: 361.2445.

_N,N_'-Bis(1,1-dimethylethyl)-1,2-bis(4-trifluoromethylphenyl)-1,2-ethanediamine (2k)

According to general procedure, the reductive coupling reaction of imine **1k** (1.00 mmol) was performed to obtain **2k** as a mixture of *meso*- and *dl*-diastereomers. IR (KBr) ν 3336, 3033, 2954, 2924, 2854, 1457, 758, 701 cm^{-1}. HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}F_6N_2$ 461.2391; Found: 461.2382.

Silica gel column chromatography (eluent: hexane / ethyl acetate / triethylamine = 2500 / 50 / 1) gave *meso*-**2k** as a pale yellow solid (96.5 mg; 42%) and *dl*-**2k** as a pale yellow solid (76.6 mg; 33%).

meso-**2k**: ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.51 (d, J = 7.81 Hz, 4H, *meso*), 7.35 (d, J = 8.3 Hz, 4H, *meso*), 3.81 (s, 2H, *meso*), 1.29 (brs, 2H, *meso*), 0.77 (s, 18H, *meso*). ^{13}C-NMR ($CDCl_3$, r.t.) δ 149.8, 149.0, 131.4, 129.5, 129.2, 129.1, 128.9, 128.8, 128.8, 128.5, 128.3, 128.0, 127.9, 126.7, 125.8, 125.6, 125.1, 124.9, 124.8, 124.5, 123.1, 123.0, 120.4, 63.9, 63.2, 51.2, 30.0, 30.0.

dl-**2k**: ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.42 (d, J = 7.8 Hz, 4 H, *dl*), 7.30 (d, J = 7.8 Hz, 4H, *dl*), 3.71 (s, 2H, *dl*), 1.83 (brs, 2H, *dl*), 0.82 (s, 18H, *dl*). ^{13}C-NMR ($CDCl_3$, r.t.) δ 149.7, 129.1, 128.8, 128.0, 128.0, 125.7, 124.9, 124.9, 124.8, 124.8, 123.0, 63.9, 51.2, 30.0.

N,N′-1,2-Tetraphenyl-1,2-ethanediamine (2l)

According to the general procedure, **2l** was obtained as a pale yellow solid (128 mg, 70% yield, *dl* : *meso* = 39 : 61). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[21] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2$ 365.2018; Found: 365.2017.

N,N′-Bis(4-methoxyphenyl)-1,2-diphenyl-1,2-ethanediamine (2m)

According to the general procedure, **2m** was obtained as a pale yellow solid (86 mg, 41% yield, *dl* : *meso* = 31 : 69). Its ^{1}H- and ^{13}C-NMR data agreed with those reported.[22] HRMS (DART) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}N_2O_2$ 425.2229; Found: 425.2211.

Acknowledgements

We gratefully acknowledge the financial support of the MEXT-supported Program for the Strategic Research Foundation at Private Universities 2014–2018 (no. 26410059), a subsidy from MEXT and Kindai University.

Supporting Information. Copies of ^{1}H- and ^{13}C-NMR spectra of crude diamine **2h**; copies of ^{1}H- and ^{13}C-NMR spectra of imines **1**; copies of ^{1}H- and ^{13}C-NMR spectra of isolated diamines **2**.

References

1. (a) Kitajima, K.; Nagatomo, R.; Fujimoto, T. *Tetrahedron.* **2015**, *71,* 977-981; (b) Aspinall, H. C.; Greeves, N.; Hin, S. L. F. *Tetrahedron Lett.* **2010**, *51,* 1558-1561; (c) Annunziata, R.; Benaglia, M.; Caporale, M.; Raimondi, L. *Tetrahedron: Asymmetry* **2002**, *13,* 2727-2734; (d) Machrouchi, F.; Namy, J.-L. *Tetrahedron Lett.* **1999**, *40*, 1315-1318; (e) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Tetrahedron Lett.* **1998**, *39,* 3333-3336; (f) Talukdar, S.; Banerji, A. *J. Org. Chem.* **1998**, *63,* 3468-3470; (g) Shimizu, M.; Iida, T.; Fujisawa, T. *Chem. Lett.* **1995**, *7,* 609-610.
2. (a) Wang, H.; Lu, G.; Sormunen, G. J.; Malik, H. A.; Liu, P.; Montgomery, J.; *J. Am. Chem. Soc*. **2017**, *139*, 9317-9324; (b) Rokade, B. V.; Guiry, P. J. *ACS. Catal.* **2017**, *7*, 2334-2338; (c) Lucet, D.; Gall, T. L.; Mioskowski, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 2580-2627.
3. (a) Meggers, E. *Chem. Commun*. **2015**, *51,* 3290-3301; (b) Peña-López, M.; Rosas-Hernández, A.; Beller, M. *Angew. Chem. Int. Ed.* **2015**, *54,* 5006-5008; (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113,* 5322-5363; (d) Xuan, J.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2012**, *51,* 6828-6838; (e) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102-113.
4. (a) Poelma, S. O.; Burnett, G. L.; Discekici, E. H.; Mattson, K. M.; Treat, N. J.; Luo, Y.; Hudson, Z. M.; Shankel, S. L.; Clark, P. G.; Kramer, J. W.; Hawker, C. J.; Alaniz,

J. R. *J. Org. Chem.* **2016**, *81,* 7155-7160; (b) Tapan, M.; Ananta, K.; Oliver, R. *J. Org. Chem.* **2011**, *76,* 736-739; (c) Narayanam, J. M. R.; Tucker, J. W.; Stephenson C. R. J. *J. Am. Chem. Soc.* **2009**, *131*, 8756-8757.

5. (a) Tomita, R.; Koike, T.; Akita, M. *Chem. Commun.* **2017**, *53*, 4681-4684. (b) Lin, R.; Sun, H.; Yang, C.; Shen, W.; Xia, W. *Chem. Commun.* **2015**, *51,* 399-401; (c) Wang, J.; Zheng, N. *Angew. Chem. Int. Ed.* **2015**, *54,* 11424-11427; (d) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. *Science* **2014**, *346*, 725-728; (e) Huo, H.; Shen, X.; Wang, C.; Zhang, L.; Röse, P.; Chen, L.-A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E. *Nature* **2014**, *515,* 100-103; (f) Wallentin, C.-J.; Nguyen, J. D.; Stephenson, C. R. J. *Chimia.* **2012**, *66*, 394-398; (g) Nicewicz, D. A.; MacMillan, D. W. C. *Science.* **2008**, *322,* 77-80.
6. (a) Qin, Q; Han, Y.-Y.; Jiao, Y.-Y.; He, Y.; Yu, S. *Org. Lett.* **2017**, *19,* 2909-2912; (b) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2016**, *45,* 2044-2056; (c) Oderinde, M. S.; Frenette, M.; Robbins, D. W.; Aquila, B., Johannes, J. W. *J. Am. Chem. Soc.* **2016**, *138,* 1760-1763; (d) Yoo, W.-J.; Tsukamoto, T.; Kobayashi, S. *Org. Lett.* **2015**, *17,* 3640-3642.
7. Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. *Angew. Chem. Int. Ed.* **2015**, *54,* 8828-8832.
8. Fava, E.; Millet, A.; Nakajima, M.; Loescher, S.; Rueping, M. *Angew. Chem. Int. Ed.* **2016**, *55,* 6776-6779.
9. Rono, L. J.; Yayla, H. G.; Wang, D. Y.; Armstrong, M. F.; Knowles, R. R. *J. Am. Chem. Soc.* **2013**, *135,* 17735-17738.
10. (a) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116,* 10075-10166; (b) Corrigan, N.; Shanmugam, S.; Xu, J.; Boyer, C. *Chem. Soc. Rev.* **2016**, *45,*

6165-6212; (c) Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Soc. Rev.* **2013**, *42,* 97-113; (d) Marin, M. L.; Santos-Juanes, L.; Arques, A.; Amat, A. M.; Miranda, M. A. *Chem. Rev.* **2012**, *112,* 1710-1750; (e) Hoffmann, N. *J. Photoch. Photobio. C.* **2008**, *9,* 43-60; (f) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A. *Chem. Rev.* **2007**, *107*, 2725-2756.

11. (a) Aydogan, C.; Kutahya, C.; Allushi, A.; Yilmaz, G.; Yagci, Y. *Polym. Chem*. **2017**, *8,* 2899-2903; (b) Miyake, G. M.; Theriot, J. C. *Macromolecules*, **2014**, *47,* 8255-8261.
12. Okamoto, S.; Kojiyama, K.; Tsujioka, H.; Sudo, A. *Chem. Commun.* **2016**, *52*, 11339-11342.
13. Bartholomew, R. F.; Brimage, D. R. G.; Davidson, R. S. *J. Chem. Soc*. **1971**, *(C),* 3482-3484.
14. Jiang, L.; Jin, L.; Tian, H.; Yuan, X.; Yu, X.; Xu, Q. *Chem. Commun.* **2011**, *47*, 10833-10835.
15. Seayad, A. M.; Ramalingam, B.; Yoshinaga, K.; Nagata, T.; Chai, C. L. L. *Org. Lett.* **2010***, 12*, 264-267.
16. Albert, J.; Cadena, J. M.; Granell, J.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **2004**, *689*, 4889-4896.
17. Cremonesi, G.; Croce, P. D.; Fontana, F.; Rosa, C. L. *Tetrahedron: Asymmetry* **2008**, *19* 554-561.
18. Guimond, N.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, 131, 12050-12051.
19. Krystian, K.; Elżbieta, K.; Jacek, M.; Ludwik, S. *Synthesis* **1987**, *12*, 1084-1087.
20. Kumar, A.; Samuelson, A. G. *J. Organomet. Chem*. **2010**, *695*, 338-345.
21. Mangeney, P.; Tejero, T.; Alexakis, A.; Grosjean, F.; Normant, J. *Synthesis* **1998**, *3*,

255-257.

22. Vellemäe, E.; Tšubrik, O.; Mäeorg, S.; Mäeorg, U. *J. Chem. Res.* **2006**, *3*, 149-150.