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Brief Communication

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Independence from the Sequence of Single-Electron Transfer of Photoredox Process in Redox-Neutral Asymmetric Bond-Forming Reaction

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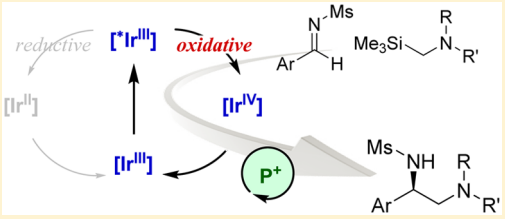
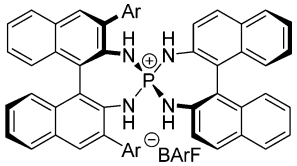
Supporting Information

ABSTRACT: A catalytic cycle initiated by the oxidative quenching of the excited photosensitizer ($Ir^*(ppy)_3$) is established for the enantioselective coupling between (*N*-arylamino)methanes and (*N*-methanesulfonyl)-aldimines catalyzed by Ir-based photosensitizer and a chiral (arylamino)-phosphonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate under visible light irradiation. This achievement clearly demonstrates the insensitivity of this redox-neutral asymmetric reaction to the sequence of the key redox events involved in the synergistic catalysis.



The photoredox activation of organic molecules with a catalytic amount of photosensitizers under visible light irradiation has recently emerged as a powerful strategy for generating reactive radical species under very mild conditions.[1,2] The distinctive feature of the photoredox catalysis is that it could facilitate unique bond cleavage and formation reactions, which are not possible within conventional methodological frameworks. The catalytic process is generally initiated by a single-electron transfer (SET) between a photoexcited sensitizer and an electron-donor/acceptor substrate to afford the corresponding transient redox-active intermediate and an ion-radical species. This intermediate generated from the sensitizer subsequently experiences another SET event, regenerating the parent, ground-state photosensitizer. By considering the number of incoming or outgoing electrons during the overall transformation, the photoredox process can be categorized as a net-oxidative, net-reductive, or redox-neutral system.[3−5] Among these, the redox-neutral reaction, wherein both oxidants and reductants to the sensitizer are incorporated into a desired product without any unproductive wastes, is particularly intriguing.[5] Another important characteristic of this system is its insensitivity to the sequence of redox events. Namely, the photocatalyst can engage in SET processes with both electron-donors and acceptors at the appropriate points in the catalytic cycle because both exist in the same reaction vessel. Therefore, in principle, an optimal sensitizer could be identified for either oxidative or reductive initiation of the redox-neutral reactions. However, little attention has been paid to constructing pairs of complementary, productive catalytic systems, although such an endeavor may provide meaningful insights into the mechanism of these redox-neutral reactions.[6]

Recently, we have developed an enantioselective redox-neutral α-coupling of (*N*-arylamino)methanes with *N*-sulfonylaldimines by utilizing the synergistic catalysis of an Ir-pyridylphenyl complex and chiral ionic Brønsted acid **1**·HBArF (Figure 1),[7−10] which is initiated by the reductive quenching of the visible-light-exited Ir^{III} complex with the aminomethanes.[11−13] On the basis of the successful establishment of the reductive quenching system for this redox-neutral coupling reaction, we were interested in the possibility of developing a complementary oxidative quenching system with a view of deepening the knowledge of the photoredox process. Herein, we describe the details of our study on closing the loop of a redox cycle initiated by SET from an exited Ir−pyridylphenyl complex to the imine.



1·HBArF
(Ar = 2-Ph-4-$CF_3C_6H_3$)

Figure 1. *P*-Spiro chiral (arylamino)phosphonium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borates **1**·HBArF. BArF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B$.

At the outset, we designed a new catalytic cycle starting with SET from an excited photosensitizer to *N*-sulfonylimine **3** (Figure 2). This oxidative quenching system requires an appropriate photosensitizer with an extremely high exited state

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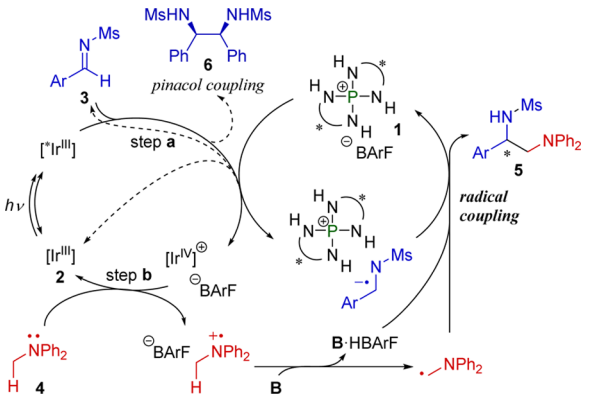
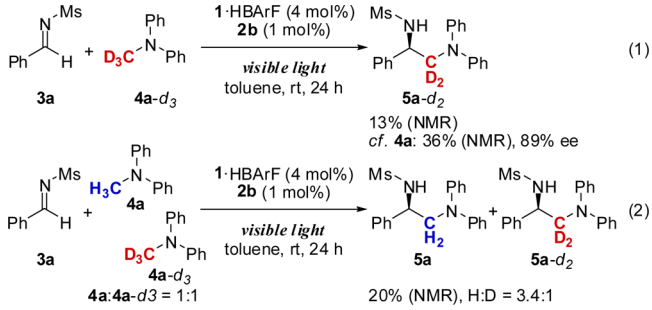


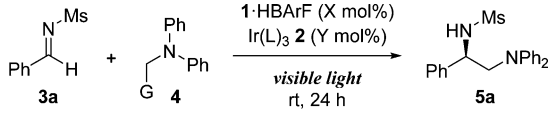
Figure 2. Working hypothesis for the redox-neutral coupling reaction via oxidative quenching process.

oxidation potential (step **a**); this is necessitated by the relatively high reduction potential of *N*-Ms-benzaldimine (**3a**) (E^{red} = −1.45 V vs SCE). Tris(2-(2-pyridyl)phenyl)iridium [Ir(ppy)$_3$ (**2a**)] was found to have a sufficiently high reducing ability in its excited state (E^{ox} of Ir*(ppy)$_3$ = −1.73 V).[14] However, an initial trial in the reaction of **3a** with Ph_2NMe (**4a**) under the influence of **1**·HBArF in toluene at ambient temperature showed that **2a** was not suitable for our purposes (Table 1, entry 1). Careful reinvestigation of the designed redox cycle revealed a mismatch of redox potential at the amine oxidation stage (step **b**), where the reduction potential of $Ir^{IV}(ppy)_3^+$ (E^{red} = +0.77 V) is slightly lower than that of Ph_2NMe (**4a**) (E^{ox} = +0.86 V).[15] Since the reduction potential of these Ir complexes is known to be increased by introducing electron-withdrawing groups to the phenyl moiety of the ppy ligand, the iridium complex bearing 5-fluoro-2-(2-pyridyl)phenyl (Fppy) groups was used as a sensitizer.[16] In the presence of Ir(Fppy)$_3$ (**2b**) (E^{red} = +0.97 V), the coupling took place as expected, albeit with low conversion (36% yield determined by ^{1}H NMR with mesitylene as an internal standard), to give the diamine product **5a** in 24% isolated yield with 93% ee (entry 2). This unsatisfactory conversion is presumably because the back-electron transfer from the anion-radical of the imine to the transient Ir^{IV} complex (dashed arrow in Figure 2) or the cation-radical of the amine competes with the desired downstream steps. With this in mind, we attempted the reaction with deuterated aminomethane **4a**-d_3 to assess any possible rate difference stemming from the kinetic isotope effect (KIE) for assigning the rate-determining step.[17] After 24 h of irradiation, ^{1}H NMR analysis of a crude aliquot indicated that the corresponding **5a**-d_2 was formed in only 13% yield (KIE = 2.8:1) (eq 1). Furthermore, subjecting an equimolar mixture of



4a and **4a**-d_3 to the standard conditions resulted in the formation of **5a** and **5a**-d_2 in a ratio of 3.4:1 (eq 2). These experiments suggest that the deprotonation of the cation-radical of the amine **4a** is the rate-determining step. In other words, if we could accelerate the generation of the aminomethyl radical, the efficiency of the entire catalytic cycle could be improved. This hypothesis prompted us to employ $Ph_2NCH_2SiMe_3$ (**4b**)[13,18] instead of **4a**, expecting rapid generation of the carbon radical via spontaneous release of a trimethylsilylium ion from the initially generated cation-radical of **4b**. Indeed, the conversion of the starting substrates was markedly improved by using **4b** as the amine component under otherwise similar conditions, but the chemical yield of the product **5a** was decreased with concomitant production of various byproducts (entry 3). After considering the oxidation potential of **4b** (E^{ox} = +0.60 V), we applied **2a** to the reaction with **4b**, which delivered a considerable increase in the isolated yield of **5a**, probably due to the attenuated oxidation ability of the transient $Ir^{IV}(ppy)_3^+$ (entry 4). We then pursued further optimization of the reaction parameters (entries 5−8). In regard to the stoichiometry of the coupling partners, using **4b** in slight excess enhanced the chemical yield, although the addition of 2 equiv of **3** was beneficial in our previous study.[7] This observation corroborates the importance of rapid generation of the aminomethyl radical for overall reaction

Table 1. Optimization of the Reaction Conditions[a]



entry	L (2)[b]	G (4)	3a:4	X, Y	solvent	yield[c] (%)	ee[d] (%)
1	ppy (**2a**)	H (**4a**)	2:1	4, 1	toluene	0	
2	Fppy (**2b**)	H (**4a**)	2:1	4, 1	toluene	24	93
3	Fppy (**2b**)	Me_3Si (**4b**)	2:1	4, 1	toluene	15	88
4	ppy (**2a**)	Me_3Si (**4b**)	2:1	4, 1	toluene	45	86
5	ppy (**2a**)	Me_3Si (**4b**)	1:1.5	4, 1	toluene	71	91
6	ppy (**2a**)	Me_3Si (**4b**)	1:1.5	4, 1	Et_2O	79	92
7	ppy (**2a**)	Me_3Si (**4b**)	1:1.5	4, 1	CPME[e]	79	93
8	ppy (**2a**)	Me_3Si (**4b**)	1:1.5	3, 0.5	CPME[e]	80	93

[a]The reactions were performed with 0.10 mmol of a yield determining reagent (**3a** or **4b**) with **1**·HBArF and **2** at ambient temperature for 24 h under argon atmosphere with visible light irradiation (15 W white LED). [b]ppy = 2-(2-pyridyl)phenyl, Fppy = 5-fluoro-2-(2-pyridyl)phenyl. [c]Isolated yield. [d]Enantiomeric excesses were determined by chiral stationary-phase HPLC. [e]CPME = cyclopentyl methyl ether.

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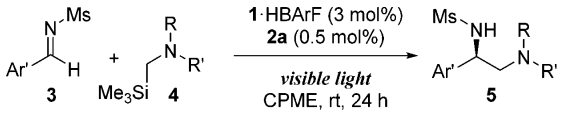
Table 2. Substrate Scope[a]



entry	Ar′ (3)	R, R′ (4)	yield[b] (%)	ee[c] (%)	prod
1	4-MeC$_6$H$_4$ (**3b**)	Ph, Ph (**4b**)	71	97	**5b**
2	4-FC$_6$H$_4$ (**3c**)	Ph, Ph (**4b**)	70	91	**5c**
3	4-ClC$_6$H$_4$ (**3d**)	Ph, Ph (**4b**)	64	87	**5d**
4	4-MeSC$_6$H$_4$ (**3e**)	Ph, Ph (**4b**)	50	96	**5e**
5	3-MeC$_6$H$_4$ (**3f**)	Ph, Ph (**4b**)	67	91	**5f**
6	3-MeOC$_6$H$_4$ (**3g**)	Ph, Ph (**4b**)	72	78	**5g**
7	2-MeC$_6$H$_4$ (**3h**)	Ph, Ph (**4b**)	59	93	**5h**
8[d]	3-thiophenyl (**3i**)	Ph, Ph (**4b**)	36	96	**5i**
9	2-naphthyl (**3j**)	Ph, Ph (**4b**)	40	93	**5j**
10	Ph (**3a**)	1-naphthyl, Ph (**4c**)	28	91	**5k**
11[d]	Ph (**3a**)	3-MeC$_6$H$_4$, Ph (**4d**)	78	87	**5l**
12[d]	Ph (**3a**)	4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$ (**4e**)	83	81	**5m**
13[d,e]	Ph (**3a**)	4-BrC$_6$H$_4$, 4-BrC$_6$H$_4$ (**4f**)	54	89	**5n**
14	Ph (**3a**)	^{i}Pr, Ph (**4g**)	66	90	**5o**
15[d]	4-MeC$_6$H$_4$ (**3b**)	^{i}Pr, Ph (**4g**)	86	97	**5p**
16	4-MeC$_6$H$_4$ (**3b**)	^{n}Hex, Ph (**4h**)	62	91	**5q**

[a]Unless otherwise noted, reactions were performed with 0.10 mmol of **3** and 0.15 mmol of **4** with **1**·HBArF (3.0 mol %) and **2a** (0.5 mol %) in 0.5 mL of CPME under argon atmosphere with visible light irradiation (15 W white LED). [b]Isolated yield. [c]Enantiomeric excesses were determined by chiral stationary-phase HPLC. [d]1.0 mL of toluene was used as solvent. [e]Ir(Fppy)$_3$ (**2b**) was used instead of Ir(ppy)$_3$ (**2a**).

efficiency (entry 5). It should be noted that the desired process was consistently accompanied by the formation of a pinacol-type coupling product **6** from the anion-radical of **3a**, inevitably reducing the yield of **5a**. Evaluation of the solvent effect in terms of reactivity and selectivity revealed that ethereal solvents were effective and cyclopentyl methyl ether (CPME) in particular was found to be optimal (entries 6 and 7).[19] Finally, the loading of sensitizer **2a**, which was not completely soluble in CPME under the reaction conditions, was reduced with a slight change in the ratio to **1**·HBArF to ensure maximum efficiency of excitation under visible light irradiation (entry 8).

With the optimized reaction conditions in hand, the substrate generality of the oxidative quenching system was investigated. As is evident from the representative results summarized in Table 2, good to high enantioselectivities were generally observed, although the chemical yields were case-sensitive. With respect to the aromatic imine component **3**, the electronic and steric properties of the substituted phenyl groups affected the reaction profile subtly (entries 1−7); however, the conversion of 3-thiophenylaldimine **3i** was low, and the formation of many unidentified aromatic byproducts was detected in the case of 2-naphthylaldimine **3j** (entries 8 and 9). The problem associated with the incorporation of a naphthyl unit seemed to be inherent, as became apparent when a 1-naphthyl group was appended to the amine coupling partner (entry 10). With other (*N*-arylamino)methanes **4**, variation in the aromatic substituents was possible, and more dilute conditions were essential for avoiding precipitation of the less soluble amines or their coupling products to ensure light irradiation efficiency (entries 11 and 12). Interestingly, electron-deficient amine **4f** underwent very sluggish reaction, probably because of its higher oxidation potential; thus, **2b** was employed as the requisite photosensitizer (entry 13). The scope of the reaction was extended from (*N*,*N*-diarylamino)-methanes to (*N*-alkyl-*N*-arylamino)methanes, which also selectively reacted at the methyl carbon. This allowed access to a range of diamines **5** with an alkyl chain in moderate yields and with excellent enantioselectivities (entries 14−16).

In conclusion, we have demonstrated the feasibility of establishing a reverse catalytic cycle that initiates with the oxidative quenching of the excited photosensitizer for the asymmetric coupling reaction between (*N*-arylamino)methanes and *N*-Ms-arylaldimines under the synergistic catalysis of Ir(ppy)$_3$ and chiral (arylamino)phosphonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **1**·HBArF. This study sheds light on the insensitivity of redox-neutral transformations to the sequence of redox events, revealing new aspects of these photoredox reactions. Further efforts are being made to achieve a precise and deeper understanding of the reaction mechanism.

EXPERIMENTAL SECTION

General Information. Infrared (IR) spectra were recorded on film as absorption wavenumbers (cm^{-1}). ^{1}H NMR spectra were recorded at ambient temperature on a 400 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane (0.00 ppm) resonance as the internal standard (CDCl$_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded at ambient temperature on a 151 MHz FT-NMR spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl$_3$; 77.16 ppm). The high-resolution mass spectra (HRMS) were conducted on an FT-ESI mass analyzer. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40−50 μm; Kanto Chemical Co., Inc.), silica gel 60 (Merck 1.09385.9929, 230−400 mesh). Enantiomeric excesses were determined by HPLC analysis using chiral columns (ϕ 4.6 mm × 250 mm, DAICEL CHIRALPAK AD-3 (AD3) and CHIRALCEL OD-3 (OD3)) with hexane (H), and 2-propanol (IPA) as eluent. Toluene, diethyl ether (Et$_2$O), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc., as "dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Cyclo-

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pentyl methyl ether (CPME) was kindly supplied by Zeon Corp. Other simple chemicals were purchased and used as such.

Preparation of (Trimethylsilyl)methylamines. *Procedure for the Synthesis of $Ph_2NCH_2SiMe_3$ (**4b**).*[13] Synthesis of the title compound was performed by following the literature procedure with slight modifications. To a solution of diphenylamine (1.69 g, 10.0 mmol) in THF (20.0 mL) was added *n*-butyllithium (2.6 M in *n*hexane, 4.60 mL, 12.0 mmol) dropwise at 0 °C. After being stirred for 20 min at 0 °C, (iodomethyl)trimethylsilane (1.60 mL, 11.5 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched by addition of saturated aqueous solution of NH_4Cl and the aqueous phase was extracted with Et_2O twice. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (H/EA = 1:0−150:1 as eluent). The resulting liquid was further purified by distillation to give **4b** (0.891 g, 3.49 mmol, 35%) as a colorless liquid. *N*-Phenyl-*N*-((trimethylsilyl)methyl)aniline (**4b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (4H, t, J = 7.7 Hz), 6.98 (4H, d, J = 7.7 Hz), 6.91 (2H, t, J = 7.7 Hz), 3.30 (2H, s), −0.06 (3H, s). Other physical data were identical in all respects to those previously reported.[13]

*N-Phenyl-N-((trimethylsilyl)methyl)naphthalen-1-amine (**4c**):* 0.329 g, 39% as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (1H, d, J = 8.0 Hz), 7.80 (1H, d, J = 8.0 Hz), 7.75 (1H, d, J = 8.0 Hz), 7.51 (1H, t, J = 8.0 Hz), 7.46 (1H, t, J = 8.0 Hz), 7.40 (1H, d, J = 8.0 Hz), 7.38 (1H, t, J = 8.0 Hz), 7.11 (2H, t, J = 8.0 Hz), 6.66 (1H, t, J = 8.0 Hz), 6.57 (2H, d, J = 8.0 Hz), 3.38 (2H, s), −0.17 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 144.7, 135.4, 131.9, 128.9, 128.6, 127.1, 127.0, 126.3, 126.2, 124.5, 116.8, 113.6, 44.4, −1.2; IR (film) 3057, 2951, 1595, 1574, 1497, 1395, 1354, 1294, 1248, 1207 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}NSi^+$ ([M + H]$^+$) 306.1673, found 306.1671.

*3-Methyl-N-phenyl-N-((trimethylsilyl)methyl)aniline (**4d**):* 0.329 g, 39% as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (2H, t, J = 7.3 Hz), 7.13 (1H, t, J = 7.7 Hz), 6.96 (2H, d, J = 7.3 Hz), 6.90 (1H, t, J = 7.3 Hz), 6.81 (1H, s), 6.79 (1H, d, J = 7.7 Hz), 6.75 (1H, d, J = 7.7 Hz), 3.28 (2H, s), 2.28 (3H, s), −0.05 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 149.7, 139.0, 129.2, 129.1, 122.2(2), 122.2(0), 121.0, 120.8, 118.7, 43.9, 21.8, −1.1; IR (film) 2953, 1593, 1493, 1429, 1354, 1248, 1206, 1169, 854 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}NSi^+$ ([M + H]$^+$) 270.1673, found 270.1671.

*4-Chloro-N-(p-tolyl)-N-((trimethylsilyl)methyl)aniline (**4e**):* 0.543 g, 52% as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (2H, d, J = 8.0 Hz), 7.10 (2H, d, J = 9.2 Hz), 6.97 (2H, d, J = 8.0 Hz), 6.72 (2H, d, J = 9.2 Hz), 3.22 (2H, s), 2.32 (3H, s), −0.06 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 146.5, 133.2, 130.2, 128.8, 124.6, 123.4, 118.7, 44.1, 21.0, −1.2; IR (film) 2953, 1591, 1510, 1489, 1431, 1356, 1248, 1190, 1096, 841, 812 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{23}N^{35}ClSi^+$ ([M + H]$^+$) 304.1283, found 304.1280.

*4-Bromo-N-(4-bromophenyl)-N-((trimethylsilyl)methyl)aniline (**4f**):* 0.782 g, 66% as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (4H, d, J = 9.0 Hz), 6.84 (4H, d, J = 9.0 Hz), 3.24 (2H, s), −0.03 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 132.2, 122.8, 113.8, 44.1, −1.1; IR (film) 2953, 1578, 1483, 1433, 1356, 1248, 1188, 1072, 1009, 841, 810 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}N^{79}Br_2Si^+$ ([M + H]$^+$) 411.9726, found 411.9728.

Procedure for the Synthesis of [(*N*-Alkyl-*N*-phenylamino)-methyl]trimethylsilane. This protocol is a modified literature procedure.[13] To a solution of *N*-*n*-hexylaniline (1.25 g, 7.04 mmol) in THF (14.0 mL) and hexamethylphosphoric triamide (2.80 mL) was added *n*-butyllithium (2.6 M in *n*hexane, 3.25 mL, 8.45 mmol) dropwise at 0 °C. After being stirred for 30 min at 0 °C, (iodomethyl)trimethylsilane (1.20 mL, 8.61 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 d. The reaction was then quenched by the addition of saturated aqueous solution of NH_4Cl, and the aqueous phase was extracted with Et_2O twice. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (H/EA = 160:1−120:1 as eluent) to give **4h** (0.99 g, 3.76 mmol, 53%) as a colorless liquid. [(*N*-*n*-Hexyl-*N*-phenylamino)methyl]trimethylsilane (**4h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, dd, J = 7.1, 8.8 Hz), 6.60 (2H, d, J = 8.8 Hz), 6.57 (1H, t, J = 7.1 Hz), 3.26−3.21 (1H, m), 2.81 (2H, s), 1.60−1.51 (2H, m), 1.38−1.22 (6H, m), 0.89 (3H, t, J = 7.0 Hz), 0.07 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 129.1, 114.7, 112.0, 52.8, 41.9, 31.9, 27.0, 25.9, 22.9, 14.2, −0.9; IR (film) 2953, 2928, 1599, 1504, 1456, 1364, 1248, 1225, 1119, 989, 841 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{30}NSi^+$ ([M + H]$^+$) 264.2142, found 264.2135.

Representative Procedure for the Asymmetric Coupling between *N*-Ms Imine 3 and (Trimethylsilyl)methylamines 4. In a dried test tube were weighted *N*-sulfonylimine **3a** (18.8 mg, 0.10 mmol), **1**·HBArF (5.74 mg, 0.003 mmol), and Ir(ppy)$_3$ (**2a**, 0.33 mg, 0.0005 mol) under Ar. Then CPME (0.50 mL) was introduced at room temperature. After addition of $Ph_2NCH_2SiMe_3$ (0.15 mmol, 39.0 μL), evacuation of the tube followed by refilling with Ar was conducted three times. The test tube was placed in a water bath and illuminated with 15 W white LED (approximate distance was 2 cm from the light source) for 24 h. After the specified time had elapsed, the reaction mixture was concentrated. The residue was subjected to the purification by column chromatography on silica gel (H/CH_2Cl_2/EA = 6:2:1, then H/EA = 4:1 to 2:1 as eluent) to afford **5a** (29.2 mg, 0.080 mmol, 80%). The enantiomeric excess of **5a** was determined to be 93% by HPLC analysis. (*R*)-*N*-(2-(Diphenylamino)-1-phenylethyl)methanesulfonamide (**5a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (5H, m), 7.26 (4H, t, J = 7.8 Hz), 6.99 (2H, t, J = 7.8 Hz), 6.92 (4H, d, J = 7.8 Hz), 5.19 (1H, d, J = 5.8 Hz), 4.77 (1H, dt, J = 8.7, 5.8 Hz), 4.04 (1H, dd, J = 14.6, 8.7 Hz), 3.89 (1H, dd, J = 14.6, 5.8 Hz), 2.55 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 13.9 min (minor), 28.3 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(p-tolyl)ethyl)methanesulfonamide (**5b**):* 27.7 mg, 71%, 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (4H, td, J = 8.7, 7.3 Hz), 7.21 (2H, d, J = 8.2 Hz), 7.16 (2H, d, J = 8.2 Hz), 7.00 (2H, td, J = 7.3, 0.9 Hz), 6.94 (4H, dd, J = 8.7, 0.9 Hz), 5.08 (1H, d, J = 5.5 Hz), 4.73 (1H, dt, J = 9.2, 5.5 Hz), 4.01 (1H, dd, J = 15.1, 9.2 Hz), 3.87 (1H, dd, J = 15.1, 5.5 Hz), 2.54 (3H, s), 2.34 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.8 min (minor), 16.1 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(4-fluorophenyl)ethyl)methanesulfonamide (**5c**):* 25.9 mg, 70%, 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, dd, J = 8.7, 5.5 Hz), 7.27 (4H, td, J = 7.3, 0.9 Hz), 7.04 (2H, t, J = 8.7 Hz), 7.00 (2H, t, J = 7.3 Hz), 6.92 (4H, dd, J = 7.3, 0.9 Hz), 5.26 (1H, d, J = 5.7 Hz), 4.76 (1H, dt, J = 9.2, 5.7 Hz), 4.01 (1H, dd, J = 15.1, 9.2 Hz), 3.87 (1H, dd, J = 15.1, 5.7 Hz), 2.56 (3H, s); HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.3 min (minor), 14.4 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(1-(4-Chlorophenyl)-2-(diphenylamino)ethyl)methanesulfonamide (**5d**):* 26.0 mg, 64%, 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 8.7 Hz), 7.31−7.24 (6H, m), 7.02 (2H, tt, J = 7.3, 0.9 Hz), 6.93 (4H, d, J = 7.3 Hz), 5.16 (1H, d, J = 5.6 Hz), 4.75 (1H, dt, J = 9.2, 5.6 Hz), 3.98 (1H, dd, J = 15.1, 9.2 Hz), 3.88 (1H, dd, J = 15.1, 5.6 Hz), 2.58 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.8 min (minor), 30.6 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(4-(methylthio)phenyl)ethyl)-methanesulfonamide (**5e**):* 19.9 mg, 50%, 96% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.19 (8H, m), 7.00 (2H, t, J = 7.8 Hz), 6.93 (4H, d, J = 7.8 Hz), 5.13 (1H, d, J = 5.5 Hz), 4.73 (1H, dt, J = 9.2, 5.5 Hz), 4.00 (1H, dd, J = 15.1, 9.2 Hz), 3.87 (1H, dd, J = 15.1, 5.5 Hz), 2.55 (3H, s), 2.47 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 29.0 min (minor), 42.4 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(m-tolyl)ethyl)methanesulfonamide (**5f**):* 24.8 mg, 67%, 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.21 (5H, m), 7.15−7.09 (3H, m), 7.00 (2H, t, J = 7.8 Hz), 6.94 (4H, d, J =

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J. Org. Chem. 2016, 81, 6953−6958

7.8 Hz), 5.05 (1H, d, J = 5.7 Hz), 4.73 (1H, dt, J = 9.2, 5.7 Hz), 4.01 (1H, dd, J = 15.1, 9.2 Hz), 3.89 (1H, dd, J = 15.1, 5.7 Hz), 2.56 (3H, s), 2.33 (3H, s); HPLC AD3, H/IPA = 10:1, flow rate =1.0 mL/min, λ = 210 nm, 9.0 min (minor), 9.5 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(3-methoxyphenyl)ethyl)-methanesulfonamide (**5g**):* 27.7 mg, 72%, 78% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.24 (5H, m), 7.00 (2H, t, J = 7.3 Hz), 6.97−6.91 (5H, m), 6.87−6.82 (2H, m), 5.04 (1H, d, J = 5.6 Hz), 4.74 (1H, dt, J = 9.2, 5.6 Hz), 4.02 (1H, dd, J = 15.1, 9.2 Hz), 3.90 (1H, dd, J = 15.1, 5.6 Hz), 3.78 (3H, s), 2.59 (3H, s); HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.5 min (minor), 15.6 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(o-tolyl)ethyl)methanesulfonamide (**5h**):* 21.7 mg, 59%, 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, dd, J = 6.9, 2.3 Hz), 7.28 (4H, t, J = 7.3 Hz), 7.22 (1H, dd, J = 7.3, 1.8 Hz), 7.20 (1H, td, J = 7.3, 1.8 Hz), 7.15 (1H, d, J = 7.3 Hz), 7.01 (2H, t, J = 7.3 Hz), 6.95 (4H, d, J = 7.3 Hz), 5.06 (1H, dt, J = 9.2, 5.0 Hz), 5.02 (1H, d, J = 5.0 Hz), 4.01 (1H, dd, J = 14.6, 9.2 Hz), 3.82 (1H, dd, J = 14.6, 5.0 Hz), 2.54 (3H, s), 2.26 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.9 min (minor), 19.8 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(thiophene-3-yl)ethyl)methanesulfonamide (**5i**):* 13.7 mg, 36%, 96% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, dd, J = 5.0, 3.2 Hz), 7.30−7.22 (5H, m), 7.07 (1H, dd, J = 5.0, 0.9 Hz), 7.00 (2H, td, J = 7.8, 0.9 Hz), 6.93 (4H, dd, J = 7.8, 0.9 Hz), 4.95−4.88 (2H, m), 4.10 (1H, dd, J = 14.6, 8.2 Hz), 3.95 (1H, dd, J = 14.6, 5.5 Hz), 2.60 (3H, s); HPLC OD3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.5 min (major), 24.3 min (minor). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Diphenylamino)-1-(naphthalen-2-yl)ethyl)-methanesulfonamide (**5j**):* 16.6 mg, 40%, 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (1H, d, J = 8.5 Hz), 7.84−7.79 (2H, m), 7.78 (1H, brs), 7.53−7.48 (2H, m), 7.46 (1H, dd, J = 8.5, 1.8 Hz), 7.27 (4H, t, J = 7.3 Hz), 7.00 (2H, t, J = 7.3 Hz), 6.97 (4H, d, J = 7.3 Hz), 5.21 (1H, d, J = 5.4 Hz), 4.95 (1H, dt, J = 9.2, 5.4 Hz), 4.11 (1H, dd, J = 15.1, 9.2 Hz), 3.98 (1H, dd, J = 15.1, 5.4 Hz), 2.53 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate =1.0 mL/min, λ = 210 nm, 19.5 min (minor), 24.3 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Naphthalen-1-yl(phenyl)amino)-1-phenylethyl)-methanesulfonamide (**5k**):* 10.9 mg, 28%, 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (1H, d, J = 8.4 Hz), 7.81 (1H, d, J = 8.4 Hz), 7.60 (1H, d, J = 8.4 Hz), 7.46 (2H, t, J = 8.4 Hz), 7.39−7.27 (6H, m), 7.23−7.12 (3H, m), 6.78 (1H, t, J = 8.4 Hz), 6.65 (2H, d, J = 8.4 Hz), 5.01−4.87 (2H, m), 4.19 (1H, dd, J = 15.2, 8.8 Hz), 3.97 (1H, dd, J = 15.2, 5.6 Hz), 2.49 (3H, s); HPLC AD3, H/IPA = 10:1, flow rate =1.0 mL/min, λ = 223 nm, 11.4 min (major), 13.0 min (minor). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(1-Phenyl-2-(phenyl(m-tolyl)amino)ethyl)methane-sulfonamide (**5l**):* 30.5 mg, 78%, 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.29 (5H, m), 7.26 (2H, t, J = 8.0 Hz), 7.17 (1H, t, J = 8.0 Hz), 6.98 (1H, tt, J = 8.0, 1.2 Hz), 6.92 (2H, dd, J = 8.0, 1.2 Hz), 6.84 (1H, d, J = 8.0 Hz), 6.75 (1H, d, J = 8.0 Hz), 6.73 (1H, s), 5.06 (1H, d, J = 5.6 Hz), 4.76 (1H, dt, J = 8.8, 5.6 Hz), 4.01 (1H, dd, J = 15.2, 8.8 Hz), 3.87 (1H, dd, J = 15.2, 5.6 Hz), 2.55 (3H, s), 2.28 (3H, s); HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.1 min (minor), 9.6 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-((4-Chlorophenyl)(p-tolyl)amino)-1-phenylethyl)-methanesulfonamide (**5m**):* 32.4 mg, 83%, 81% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.27 (5H, m), 7.15 (2H, d, J = 8.8 Hz), 7.10 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 6.73 (2H, d, J = 8.8 Hz), 5.14 (1H, d, J = 6.0 Hz), 4.73 (1H, dt, J = 8.8, 6.0 Hz), 4.00 (1H, dd, J = 15.2, 8.8 Hz), 3.80 (1H, dd, J = 15.2, 6.0 Hz), 2.57 (3H, s), 2.31 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 13.2 min (minor), 28.7 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Bis(4-bromophenyl)amino)-1-phenylethyl)methane-sulfonamide (**5n**):* 28.6 mg, 54%, 89% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.30 (7H, m), 7.26−7.22 (2H, m), 6.71 (4H, d, J = 9.2 Hz), 5.20 (1H, d, J = 7.6 Hz), 4.73 (1H, q, J = 7.6 Hz), 4.08 (1H, dd, J = 15.2, 7.6 Hz), 3.79 (1H, dd, J = 15.2, 7.6 Hz), 2.61 (3H, s); HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 21.2 min (minor), 40.9 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Isopropyl(phenyl)amino)-1-phenylethyl)methane-sulfonamide (**5o**):* 21.9 mg, 66%, 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (4H, d, J = 8.4 Hz), 7.33 (3H, t, J = 8.4 Hz), 7.08 (2H, d, J = 8.4 Hz), 7.00 (1H, t, J = 8.4 Hz), 5.27 (1H, br s), 4.47 (1H, ddd, J = 10.8, 4.8, 1.6 Hz), 3.76 (1H, sept, J = 6.8 Hz), 3.39 (1H, dd, J = 14.0, 4.8 Hz), 3.05 (1H, dd, J = 14.0, 10.8 Hz), 2.42 (3H, s), 1.23 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz); HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 8.9 min (minor), 10.7 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Isopropyl(phenyl)amino)-1-(p-tolyl)ethyl)methane-sulfonamide (**5p**):* 29.0 mg, 86%, 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, t, J = 7.6 Hz), 7.28 (2H, d, J = 7.6 Hz), 7.19 (2H, d, J = 7.6 Hz), 7.06 (2H, d, J = 7.6 Hz), 6.99 (1H, t, J = 7.6 Hz), 5.27 (1H, br s), 4.44 (1H, ddd, J = 10.8, 4.8, 2.0 Hz), 3.76 (1H, sept, J = 6.8 Hz), 3.36 (1H, dd, J = 14.0, 4.8 Hz), 3.04 (1H, dd, J = 14.0, 10.8 Hz), 2.42 (3H, s), 2.35 (3H, s), 1.23 (3H, d, J = 6.8 Hz), 0.95 (3H, d, J = 6.8 Hz); HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 10.9 min (minor), 13.1 min (major). The other physical data were identical in all respects to those previously reported.[7]

*(R)-N-(2-(Hexyl(phenyl)amino)-1-(p-tolyl)ethyl)methane-sulfonamide (**5q**):* 24.5 mg, 62%, 91% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.23 (4H, m), 7.19 (2H, d, J = 8.0 Hz), 6.82 (2H, d, J = 8.0 Hz), 6.79 (1H, t, J = 8.0 Hz), 5.02 (1H, d, J = 5.6 Hz), 4.69 (1H, dt, J = 8.8, 5.6 Hz), 3.53 (1H, dd, J = 14.8, 8.8 Hz), 3.43 (1H, dd, J = 14.8, 5.6 Hz), 3.15 (2H, t, J = 7.8 Hz), 2.55 (3H, s), 2.36 (3H, s), 1.53−1.33 (2H, m), 1.32−1.18 (6H, m), 0.87 (3H, t, J = 7.2 Hz). HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.3 min (minor), 8.6 min (major). The other physical data were identical in all respects to those previously reported.[7]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00445.

Electro- and photochemical experiments and copies of spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(19) This result was a little surprising and is in contrast to the results obtained from the reductive quenching system.[7] We had assumed that the three-dimensional structure of the transition state in the carbon−carbon bond-forming step would be identical in both the reductive and oxidative quenching systems. Thus, the origin of the difference in the optimal reaction conditions remains open for further mechanistic investigation and discussion.

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