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Synergistic Catalysis of Ionic Brønsted Acid and Photosensitizer for a Redox Neutral Asymmetric α-Coupling of *N*-Arylaminomethanes with Aldimines

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Supporting Information

ABSTRACT: A redox neutral, highly enantioselective coupling between *N*-arylaminomethanes and *N*-sulfonyl aldimines was developed by harnessing the efficient catalysis of *P*-spiro chiral arylaminophosphonium barfate and a transition-metal photosensitizer under visible light irradiation. This mode of synergistic catalysis provides a powerful strategy for controlling the bond-forming processes of reactive radical intermediates.

Inarguably, radical-based transformations are fundamental synthetic tools, which are often compatible with various functional groups and have immense potential to enable unconventional bond cleavages and constructions.[1] Accordingly, numerous efforts have been devoted to the development of synthetically useful and selective radical reactions.[2,3] In particular, significant advances have been made in the arena of photoredox catalysis, providing a number of otherwise unachievable modes of molecular transformations.[4,5] However, precise absolute stereocontrol in light-driven photochemical reactions still constitutes a formidable challenge.[6−9] For addressing this important problem, several dual catalytic systems based on the combined use of transition-metal photosensitizer and stereocontroller[5a,10−13] have been successfully introduced, leading to the establishment of highly stereoselective protocols for the assembly of chiral molecules through unique bond formations. In seeking to make our own contribution in this emerging field, we became interested in the viability of dictating the selectivity of ion-radicals, which are always involved in photoredox processes of organic substrates and are considered to exhibit ambiphilic character as radicals and ions.[14] Specifically, in conjunction with our research program for developing novel asymmetric ion-pair catalysis, we hypothesized that the catalytic ion-pairing of a chiral tetraaminophosphonium ion of type **1**·H (Figure 1) with an anion-radical would allow this reactive intermediate to engage in subsequent bond formations with rigorous selectivity control by the structurally modifiable chiral cation.[15−17] As an initial step in this pursuit, we communicate herein the development of a redox neutral, highly enantioselective α-coupling of *N*-arylaminomethanes with *N*-sulfonyl aldimines under the catalysis of **1**·H and Ir-centered photosensitizer with visible light irradiation.

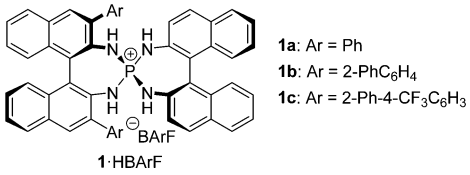

Figure 1. *P*-Spiro chiral arylaminophosphonium barfates **1**. BArF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B$.

At the outset of our study, we sought to develop a previously unknown carbon−carbon bond-forming reaction as a platform for substantiating our hypothesis. From this standpoint, we adopted *N*-sulfonyl imines **2** [E^{red} = −1.45 V vs a saturated calomel electrode (SCE) for **2a**] as the precursors of anion-radicals with a prospective affinity to the hydrogen (H)-bond-donor catalyst and envisioned their enantioselective coupling with the aminomethyl radical generated from *N*,*N*-diphenylaminomethane (Ph_2NMe).[18,11c] A catalytic cycle we postulated based on the use of an Ir(II) species as a strong reductant [$E^{II\rightarrow III}$ = −1.40 V vs SCE for $Ir^{II}(ppy)_2(bpy)$][19,20] for the generation of an anion-radical from **2** is illustrated in Figure 2. Initially, Ir(III) complexes such as $[Ir(ppy)_2(bpy)]$BArF (**3a**) are reversibly

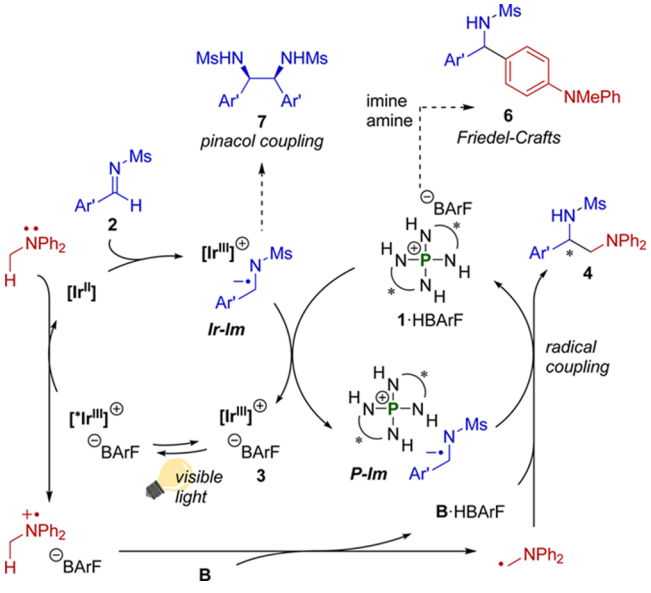

Figure 2. Working hypothesis.

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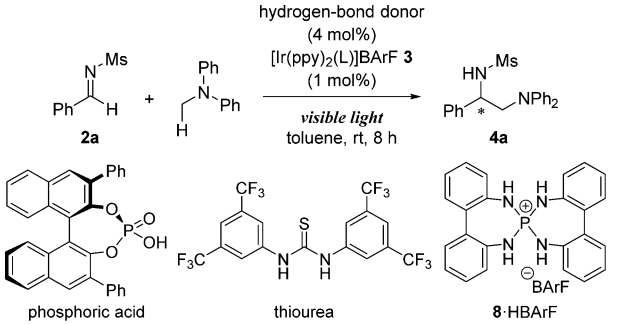
promoted to their excited state, [*Ir(ppy)$_2$(bpy)]BArF, under visible light irradiation. Subsequent reductive quenching of the *Ir(III) species with Ph$_2$NMe would result in the requisite, electronically neutral Ir(II) complex and the cation-radical of Ph$_2$NMe accompanying the negatively charged counterion, BArF$^-$. The resulting Ir(II) species could transfer an electron to imine **2** to form the corresponding anion-radical that should be spontaneously paired with the positively charged Ir(III) complex (***Ir-Im***).[21,22] ***Ir-Im*** would undergo prompt ion exchange with the aminophosphonium ion **1**·H, featuring double H-bond-donor ability, to afford a key chiral ion pair ***P-Im*** with concomitant regeneration of the parent photosensitizer. Concurrently with this process, an aminomethyl radical is formed via deprotonation of the Ph$_2$NMe cation-radical by a basic species (**B**).[23] Then, a coupling reaction between the imine anion-radical and the aminomethyl radical would take place under the guidance of **1**·H to enantioselectively produce the 1,2-diamine derivative **4**.

In the initial experiments to examine this possibility, achiral tetraaminophosphonium barfate, (4-CF$_3$C$_6$H$_4$NH)$_4$P·BArF (**5**·HBArF), was employed as the H-bond donor. Visible light irradiation (15 W household white LED lamp) of a toluene solution of benzaldehyde-derived *N*-sulfonyl imine **2a** and Ph$_2$NMe in the presence of **5**·HBArF (4 mol %) and the photosensitizer **3a** (1 mol %) led to the formation of diamine **4a** in 21% yield (Table 1, entry 1). The photoredox conditions were crucial for this bond connection, given that **4a** could not be obtained upon conducting the reaction in the absence of the sensitizer or irradiation.[24] Instead, a Friedel–Crafts-type adduct **6a** (Ar′ = Ph, Figure 2) was detected from the ^{1}H NMR analysis of the crude aliquots (~12%, entries 2 and 3), suggesting that **5**·HBArF simply acted as a Brønsted acidic activator of **2a**. More importantly, an attempted reaction in the absence of **5**·HBArF gave a pinacol-type coupling product *meso*-**7a** (Ar′ = Ph, Figure 2), a homodimer of **2a**, in ~30% yield along with a trace amount of **4a** (entry 4). This indicates the participation of the anion-radical of **2a**, and its reactivity seems to be attenuated by the aminophosphonium ion **5**·H.[25,26] Because the efficiency of the one-electron reduction of **2a** to the anion-radical would be associated with the oxidation potential of the transient Ir(II) species, we pursued the modification of the photosensitizer at this stage with respect to the structure of the bipyridine ligand. We found that the Ir(III) complex **3c**, bearing neocuproine (2,9-dimethyl-1,10-phenanthroline, Me$_2$phen), to be an optimal sensitizer,[27] thus allowing the isolation of **4a** in 79% yield (entries 5 and 6). These profiles are consistent with the proposed radical coupling mechanism.[25] However, we recognize that the addition of the aminomethyl radical to **2a** coordinated by **5**·H, followed by one-electron reduction of the resulting nitrogen-centered radical, is also feasible and cannot be ruled out.[28,29]

The critical importance of the aminophosphonium ion in facilitating the desired coupling reaction prompted us to probe the essential elements required for the catalyst to exert effective performance. The use of tetrabutylammonium salt (Bu$_4$N·BArF), which lacks H-bond-donor ability, in place of **5**·HBArF under identical photoredox conditions with **3c** mainly yielded *meso*-**7a**. This outcome is similar to that observed in the reaction conducted without **5**·HBArF (entry 4 vs 7).

On the other hand, employment of the widely utilized nonionic Brønsted acids such as the phosphoric acid diester, benzoic acid, and the 3,3′-Ph$_2$-BINOL as H-bond donors turned out to be ineffective for selectively obtaining **4a**, and *meso*-**7a** was again isolated as the major product along with other unidentified side products (entries 8–10).[30] It was of interest that the use of *N*,*N*′-bis(3,5- bistrifluoromethyl phenyl)thiourea, one of the weak Brønsted acids, delivered slight improvement in the reaction profile (entry 11), and a notable enhancement in the yield of **4a** was attained when ionic triethylammonium and 2,6-lutidinium barfates were applied (entries 12 and 13). These results demonstrate that exploiting an ionic H-bond donor is a prerequisite for the present catalysis to be synergistically operative with the Ir(III) photosensitizer, and the aminophosphonium ion appeared to be particularly effective.

Table 1. Effect of Each Element of the Synergistic Catalysis[a]



entry	H-bond donor	L (**3**)[b]	yield (%)[c]	ee (%)[e]
1	**5**·HBArF	bpy (**3a**)	21	–
2	**5**·HBArF	none	0	–
3[d]	**5**·HBArF	**3a**	0	–
4	none	**3a**	6	–
5	**5**·HBArF	phen (**3b**)	46	–
6	**5**·HBArF	Me$_2$phen (**3c**)	79	–
7	Bu$_4$N·BArF	**3c**	7	–
8	phosphoric acid	**3c**	9	–
9	benzoic acid	**3c**	12	–
10	3,3′-Ph$_2$-BINOL	**3c**	11	–
11	thiourea	**3c**	21	–
12	Et$_3$N·HBArF	**3c**	40	–
13	2,6-lutidine·HBArF	**3c**	56	–
14	**8**·HBArF	**3c**	59	–
15	**1a**·HBArF	**3c**	56	53
16	**1b**·HBArF	**3c**	79	89
17	**1c**·HBArF	**3c**	89	94

[a]Unless otherwise indicated, the reactions were performed with 0.20 mmol of **2a** and 0.10 mmol of Ph$_2$NMe with a H-bond donor (4.0 mol %) and **3** (1.0 mol %) in 0.5 mL of toluene at ambient temperature for 8 h under argon atmosphere with visible light irradiation (15 W white LED). [b]bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline. [c]Isolated yield. [d]Under dark. [e]Enantiomeric excesses were determined by chiral HPLC.

Encouraged by the comparable activity of the *P*-spiro-type aminophosphonium ion **8**·H (entry 14), we undertook the absolute stereocontrol of this new carbon–carbon bond-forming reaction by combined utilization of chiral aminophosphonium barfate **1a**·HBArF and **3c** under visible light irradiation. This trial afforded **4a** in good chemical yield with moderate enantioselectivity (entry 15). The introduction of 2-biphenyl groups into the 3,3′-positions of one of the two binaphthyl subunits (**1b**·HBArF) significantly improved the stereoselectivity (entry 16). Eventually, rigorous enantiocontrol was achieved with **1c**·HBArF, possessing a 2-phenyl-4-trifluoromethylphenyl substituent, and **4a** was obtained in 89% yield with 94% ee (entry 17). The three-dimensional molecular structure of **1c**·H was unambiguously determined by single-crystal X-ray diffraction (XRD) analysis, revealing its "*R*,*R*,*R*" configuration, and the

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pendant 2-phenyl group of the 3,3′-substituents contributed to the creation of a cavity over the ionic H-bonding site (Figure 3).

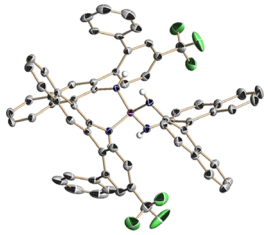
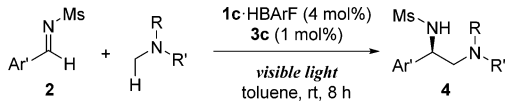


Figure 3. ORTEP diagram of **1c**·HCl. Chloride ion, calculated hydrogen atoms, and solvent molecules (methanol) are omitted for clarity. Gray, carbon; purple, phosphorus; blue, nitrogen; green, fluorine.

With the optimized catalyst combination in hand, the generality of this asymmetric coupling protocol was explored. As summarized in Table 2, the reaction proceeded smoothly with

Table 2. Substrate Scope[a]



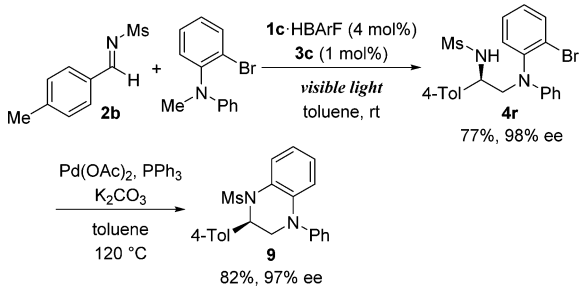
entry	Ar′ (**2**)	R, R′	yield (%)[b]	ee (%)[c]	prod
1	4-MeC_6H_4 (**2b**)	Ph, Ph	85	97	**4b**
2	4-FC_6H_4 (**2c**)	Ph, Ph	90	91	**4c**
3	4-ClC_6H_4 (**2d**)	Ph, Ph	85	91	**4d**
4	4-MeSC_6H_4 (**2e**)	Ph, Ph	72	96	**4e**
5	3-MeC_6H_4 (**2f**)	Ph, Ph	75	90	**4f**
6	3-MeOC_6H_4 (**2g**)	Ph, Ph	75	85	**4g**
7	2-MeC_6H_4 (**2h**)	Ph, Ph	77	94	**4h**
8	2-naphthyl (**2i**)	Ph, Ph	64	94	**4i**
9[d]	3-thiophenyl (**2j**)	Ph, Ph	60	95	**4j**
10	Ph (**2a**)	2-naphthyl, Ph	82	93	**4k**
11	Ph (**2a**)	3-MeC_6H_4, Ph	83	91	**4l**
12	Ph (**2a**)	4-MeC_6H_4, 4-ClC_6H_4	85	89	**4m**
13	Ph (**2a**)	4-BrC_6H_4, 4-BrC_6H_4	63	92	**4n**
14	Ph (**2a**)	^{i}Pr, Ph	73	91	**4o**
15	4-MeC_6H_4 (**2b**)	^{i}Pr, Ph	83	94	**4p**
16	4-MeC_6H_4 (**2b**)	^{n}Hex, Ph	65	91	**4q**

[a]Unless otherwise noted, reactions were performed with 0.20 mmol of **2** and 0.10 mmol of RR′NMe with **1c**·HBArF (4.0 mol %) and **3c** (1.0 mol %) in 0.5 mL of toluene under argon atmosphere with visible light irradiation (15 W white LED). [b]Isolated yield. [c]Enantiomeric excesses were determined by chiral stationary phase HPLC. Absolute configuration of **4b** was determined by X-ray crystallographic analysis. [d]2.0 mL of toluene was used as solvent. Reaction time was 34 h.

a wide range of aromatic *N*-sulfonyl imines, irrespective of their electronic properties and substitution patterns, to give **4** with excellent enantioselectivities (entries 1−7). The absolute configuration of **4b** was assigned to be "*R*" based on the single-crystal XRD analysis (see SI). This system also tolerated fused aromatic and heteroaromatic imines, although a certain decrease in the chemical yield was observed (entries 8 and 9). In contrast, aliphatic imines with a lower reduction potential (E^{red}) remained intact under the present catalysis. With respect to the aminomethane component, significant variation in the substituents (R, R′) was possible with a comparable degree of reactivity and stereoselectivity (entries 10−16). Not only various *N*,*N*-diarylaminomethanes but also *N*-alkyl derivatives appeared to be good candidates for coupling partners and consistently reacted via the generation of the corresponding aminomethyl radicals. It is worth adding that the α-coupling did not occur in the reaction with *N*,*N*-diphenylaminoethane.

The immediate utility of this asymmetric direct coupling between aminomethanes and imines was highlighted by the rapid construction of chiral benzopiperazine frameworks, which are core structures of potent pharmaceutical motifs, such as active cholesteryl ester transfer protein inhibitors.[31] For instance, the reaction of **2b** and *N*-2-bromophenyl-*N*-phenylaminomethane under standard conditions produced the corresponding 1,2-diamine **4r** in 77% yield with 98% ee. The subsequent palladium-catalyzed intramolecular amination furnished the desired chiral benzopiperazine **9** as shown in Scheme 1.

Scheme 1. Preparation of Chiral Benzopiperazine 9



In conclusion, we have demonstrated the remarkable effectiveness of the synergistic catalysis of chiral arylaminophosphonium ions **1**·H and Ir(III) photosensitizer **3** for achieving a redox neutral, highly enantioselective α-coupling of *N*-arylaminomethanes with *N*-sulfonyl imines **2** under visible light irradiation. This study may have significant implications on the catalytic control of ion-radicals, and we believe that a judicious combination of chiral ionic Brønsted acid and photoredox catalysis offers a new opportunity for the development of an array of photoinduced stereoselective radical transformations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09329.

Experimental procedures and characterizations of compounds (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(20) The reaction initiated from the oxidative quenching of excited $Ir(ppy)_3$ derivatives was found to be less productive; see SI.

(21) While we presumed the electron transfer to free imine **2a** followed by the ion exchange with the H-bond-donor catalyst **1**·HBArF, intervention of the proton-coupled electron-transfer in forming the key chiral ion pair ***P-Im*** cannot be rigorously excluded because most of **1**·H would interact with **2a**.[11a] However, we confirmed that the quenching rate of an excited $Ir(ppy)_3$ derivative with **2a** was not enhanced upon addition of **8**·HBArF. For details, see SI.

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(23) As previously seen in the literatures,[18] an actual species that functions as a base is uncertain, and therefore it is not specified in the catalytic cycle. We anticipate that *N*,*N*-diphenylaminomethane itself, anion-radical of **2**, and/or conjugate base of **1**·H could play this role.

(24) We also confirmed that the product formed only during the period of constant irradiation. See "light/dark" experiment in SI.

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(26) Without such effect, we speculate that the coupling of the anion-radical ***Ir-Im*** with the aminomethyl radical might be inherently unfavorable. In addition, considering the level of enantioselectivity observed in this study, ion exchange between ***Ir-Im*** and **1**·HBArF would be fast enough to minimize the intervention of this racemic pathway.

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