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Authors: Hong-Xi Li, Da-Liang Zhu, Qi Wu, Hai-Yan Li, and Jian-Ping Lang

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Hantzsch Ester as a Visible-light Photoredox Catalyst for Transition-Metal-Free Coupling of Arylhalides and Arylsulfinates

Da-Liang Zhu, Qi Wu, Hai-Yan Li, Hong-Xi Li,* and Jian-Ping Lang

Abstract: We firstly use diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5dicarboxylate (HEH) as a visible-light photoredox catalyst for cross coupling of arylhalides and arylsulfinates without transition-metal, sacrificial agent and mediator. This method is compatible with various functional groups and provides diaryl sulfones in good to high yields. Mechanistic studies indicate that this reaction undergoes the stepwise light irradiation of HE⁻, single electron transfer (SET) in donor–acceptor complex (DAC) from *HE⁻ to arylhalide, trapping of aryl radical with sulfinate, SET oxidation of sulfone radical anion by HE⁻ to sulfone via the DAC method.

Hantzsch esters (HEs) are bio-inspired hydride donors and have been widely employed as terminal proton sources and electron donors in transfer hydrogenations^[1] and in photoredox catalysis.^[2-4] 4-Alkyl- or acyl-Hantzsch esters can be used as alkyl and acyl radical precursors in C–C formations.^[5,6] Recently, the excited-state of HEs have also been identified as strong photoreductants $[E_{ox}(*HEH) = -2.28V$ vs. SCE; HEH = 2,6dimethyl-1,4-dihydropyridine-3,5-dicarboxylate].[7a] Under photoirradiation, the excited HEs have acted as electron and hydride donors in reduction of phenacyl onium salts,^[8] debromination of alkyl bromides^[7] and vicinal dibromo compounds,^[9] reductive cleavage of C-P bond in difluorinated phosphonium salts,^[10] reduction of cyanopyridines^[11] and aryl tri-/difluoroethanones.^[12] After the single-electron-, or hydrogen-, alkyl-transfer, the resulting radicals or radical cations are highly active and readily aromatized into pyridine derivatives (Scheme 1(a)).^[13] So HEs in cases above were used in stoichiometric or excess amounts. To date, the utilizing of HEs as photoredox catalysts remains unexplored. In this context, we report the first example of visible-light-induced HEH-catalyzed C-S formation.

Diaryl sulfones are not only highly important organic complexes, but also widely exist in natural products, bioactive and pharmaceutical molecules.^[14] Various protocols have been developed to synthesize these scaffolds.[15,16] Palladium- and copper-catalyzed coupling of sulfinates with aryl halides or oxidation of diarylsulfides at high temperature have been well investigated (Scheme 1(b)).^[17,18] In recent years, visible-light photoredox catalysis has emerged as a versatile platform for various transformations.^[19] Although progress has been made in the field of visible-light-mediated C-S bond formation,^[20] few references reported arylations of sulfinates using aryl halides as arvlating reagents.^[21] In 2018, Rueping, Manolikakes, Molander independently demonstrated Ru- or groups Ir-based photosensitizer facilitated nickel-catalyzed cross-couplings of sulfinates with (hetero)aryl and vinyl iodides/bromides.^[22] These

[*] D. L. Zhu, Q. Wu, Prof. H. Y. Li, Prof. Dr. H. X. Li, Prof. Dr. J. P. Lang College of Chemistry, Chemical Engineering and Materials Science Soochow University Suzhou 215123, China E-mail: lihx@suda.edu.cn Supporting information for this article is given via a link at the end of the document. above methods necessitate expensive Ir/Ru organometallic complexes and transition-metal catalysts, which bring about some limitations, such as toxicity and metal contamination. Very recently, ultraviolet (UV) light-induced-coupling of sulfinates and arylhalides was reported.^[23] The high-energy UV light is incompatible with some functional groups and leads to side reactions. Therefore, the strategy for the systhesis of sulfones under nonmetallic catalysis and greener conditions is still a challenging and fascinating project. Herein we report the first discovery of HEH as a visible-light photoredox catalyst for coupling of arylsulfinates and arylhalides to sulfones in absence of transition-metal, mediator and sacrificial reductant.



Scheme 1. Applications of Hantzsch Esters and Synthesis of Sulfones.

With the strong photoredox potential of excited *HEH^[7a] in mind, we hypothesized that *HEH might undergo single-electron reduction of aryl halides to deliver aryl radical and HEH^{*+}. The complementary single electron transfer (SET) from sulfinate (E_{ox} = +0.45 V vs. SCE for 4-methylbenzenesulfinate in MeCN)^[22a] to HEH^{*+} (E_{red} = +0.79 V vs. SCE in DMF)^[7a] affords sulfonyl radical. The radical-radical coupling would yield a sulfone. To demonstrate our hypothesis, we carried out a preliminary investigation of reaction conditions using 4-bromobenzonitrile

Table 1. Optimization of reaction conditions.^[a]

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(1a) and sodium benzenesulfinate (2a) as model substrates in DMSO under 10 W blue light-emitting diodes (LEDs) (λ = 435-455 nm) at ambient temperature (Table 1 and S1). The combination of HEH (20 mol%) provided the desired product 4-(phenylsulfonyl)benzonitrile (3aa) in 20% yield (Table 1, entry 1). Fortunately, the addition of Cs₂CO₃ led to a full conversion of 1a and could deliver 3aa in a good yield of 84% (entry 2). Other applied bases (entries 2-7) and solvents (entries 8-15) did not improve this coupling further. Performing the reaction in air led to much lower yield (entry 16). Upon 445-465 nm, 455-480 nm, 460-485 nm, or 495-550 nm LEDs irradiation, the same reaction afforded 3aa in 88%, 90% and 93%, and 89% yields (entries 17-20). Only trace of 3aa was detected in absence of HEH (entry 21). No desired product was observed when the reaction was carried out in dark (entry 22). A temperature of 60 °C did not promote this reaction in the dark (entry 23).

delivered Bromobenzonitrile 3ja in 63% yield. 2-(2-bromophenyl)(phenyl)methanone Bromobenzonitrile or reacted with 2a to afford 3ka and 3la in 51% and 63% yields. Aryl bromides containing groups at 3,5- or 3,4-positions of phenyl rings gave 3ma-3pa in 82-89% yields. 2-Bromonaphthalene underwent this coupling to offer 3qa in 60% yield. The current photoredox catalytic conditions tolerated heteroaryl halides, and 47-85% yields of 3ra-3xa were obtained. Noteworthy, inexpensive and less toxic aryl chlorides participated in the reaction efficiently to give 3aa, 3ea, 3ga, 3la, and 3va in 40-83% yields. Treatment of 8-chloro-3-iodoquinoline (1y) with 2a gave 8-chloro-3-(phenylsulfonyl)quinoline (3ya) in 83% yield. The subsequent Pd-catalyzed amination with piperazine would afford the medicinal molecule 3-(phenylsulfonyl)-8-(piperazin-1-yl)quinoline, which has а potential application in treatment of Alzheimer's disease.^[22a]



				0,0	
	NC-Br +		H, Base, Solvent		
	1a	2a) W LEDS, NV	NC 3aa	
En	try Base	Solvent	<i>hv</i> (nm)	Conversion	Yield
1		DMSO	435-455	27%	20%
2	Cs_2CO_3	DMSO	435-455	>99%	84%
3	Na ₂ CO ₃	DMSO	435-455	79%	70%
4	K ₂ CO ₃	DMSO	435-455	82%	75%
5	K ₃ PO ₄	DMSO	435-455	90%	76%
6	K ₂ HPO ₄	DMSO	435-455	55%	37%
7	NaOAc	DMSO	435-455	52%	44%
8	Cs_2CO_3	DMF	435-455	80%	65%
9	Cs_2CO_3	MeCN	435-455	43%	36%
10	Cs_2CO_3	Toluene	435-455	<5%	<5%
11	Cs_2CO_3	<i>n</i> -pentane	435-455	<5%	<5%
12	Cs_2CO_3	CHCI ₃	435-455	<5%	<5%
13	Cs_2CO_3	MeOH	435-455	<5%	<5%
14	Cs_2CO_3	THF	435-455	<5%	<5%
15	Cs_2CO_3	1,4-dioxane	435-455	<5%	<5%
16 [[]	^{b]} Cs ₂ CO ₃	DMSO	435-455	62%	53%
17	Cs_2CO_3	DMSO	445-465	>99%	88%
18	Cs_2CO_3	DMSO	455-480	>99%	90%
19	Cs_2CO_3	DMSO	460-485	>99%	93%
20	Cs_2CO_3	DMSO	495-550	>99%	89%
21 [[]	^{c]} Cs ₂ CO ₃	DMSO	460-485	<5%	<5%
22 [[]	^{d]} Cs ₂ CO ₃	DMSO	in dark	<5%	0
23 [[]	^{e]} Cs ₂ CO ₃	DMSO	🗼 in dark	<5%	<5%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), HEH (0.04 mmol), Cs_2CO_3 (0.3 mmol), solvent (1 mL), N_2 , 10 W LEDs with cooling by fan for 24 h. HPLC conversion and yield. [b] In air. [c] Without HEH. [d] At room temperature. [e] At 60 °C.

The established photocatalytic protocol was then tested for a family of reactions of various arylhalides and **2a**. As shown in Table 2, arylbromides substituted with electron-withdrawing groups at *para*-position of phenyl (**3aa-3ga**) were suitable substrates, giving expected products in good to excellent yields (60-92%). 1-Bromo-4-methylbenzene (**1h**), 1-bromo-4-methoxybenzene (**1i**) gave rise to **3ha** and **3ia** in 37-40% yields. Their yields could be enhanced to 65-76% using 1-iodo-4-methoxybenzene and 1-iodo-4-methylbenzene as partners. 3-



[a] Reaction conditions: 1 (0.2 mmol), 2 (0.4 mmol), HEH (0.04 mmol), Cs₂CO₃ (0.3 mmol), in 1 mL DMSO, 10 W LEDs (λ = 460–485 nm) with cooling by fan, in N₂, for 24 h and isolated yield.

3ak (39%)

We further examined the arylation of various sulfinates with 1a. Electron-deficient aryl sulfinates were more active than electronrich ones. Reactions of sulfinates 2b, 2c, 2i and 2j with 1a proceeded with high yields of 78-89%. The moderate yields were observed for sulfinates (2d-2h and 2k) with electron-

donating methyl, methoxyl, phenyl, tert-butyl groups. 2-Naphthyl sulfonate was compatible with the cross-coupling in 57% yield (**3al**). The photoreaction of **1a** and **2a** could also be performed under sunlight (the maximum power density is about 8.14 mW·cm⁻²) for 8 h to give **3aa** in 98% HPLC yield. The preparative-scale experiment was carried out using 1.09 g of **1a** and 1.97 g of **2a**. Satisfactorily, the yields of 75% under the irradiation of a blue LED soft rope light ($\lambda = 435-455$ nm) and 80% under sunlight were achieved (Figure S1).

To gain some mechanistic information, the UV-vis absorption and emission spectra of HEH solution were recorded at room temperature. HEH in DMSO shows strong absorption in the UV region, but weak visible-light absorption tailing to 400-435 nm regions. The addition of Cs₂CO₃ deepened the color (Figure S2). A new broad peak (420-550 nm) centred at 475 nm is observed. Similar peaks appear with the addition of other strong or weak bases (Figure S3). This new peak is attributed to the absorption of HE⁻ anion. The hardly absorption of HEH/Cs₂CO₃ solutions in other solvents at $\lambda = 475$ nm is due to the low solubility of Cs₂CO₃ in toluene, *n*-pentane, CHCl₃, THF, 1,4-dioxane or the difficulty of HE⁻ formation in MeOH (Figure S3c). HEH shows no photocatalytic activity in these solvents (Table 1, entries 10-15). Upon excitation at 383 nm, the DMSO solution of HEH displays an emission at 450 nm (Figure S4a). The broad band at λ_{max} = 538 nm arises from luminescence of HE⁻ solution in DMSO excited at 469 nm (Figure S4b). The photoluminescence lifetimes and quantum yields of HEH and HE⁻ in DMSO are 0.419 ns/0.031, and 4.8 ns/0.325, respectively (Figure S5). The quantum yield of reaction system was decreased to 0.012. As discussed above (Table 1, entries 2, 17-20), the yield of 3aa is related to the spectral overlap between the radiation light and the absorbance of HE⁻ to a certain extent, which means more overlap would cause higher yield (Figure S2). These results suggest that HE⁻ anion plays a key role in the cross coupling. The electrochemical properties of HEH and HE anion were measured by cyclic voltammetry (CV). Two irreversible redox waves of HEH in DMSO at E = +0.882, -1.202 V vs. SCE are assigned to HEH⁺/HEH and H⁺/H₂ couples. The two other irreversible peaks are observed at -0.173, -2.379 V vs. SCE, in which HE^{-} is oxidized to HE^{+} and reduced to HE^{2-} (Figure S6a). The CV of HE⁻ contains two waves at E = -0.186 V and -2.372V vs. SCE, being assumed to one electron oxidation and reduction of HE⁻ ion (Figure S6b). The wave at E = -2.004 V belongs to the reduction of diethyl 2,6-dimethylpyridine-3,5dicarboxylate (Figure S6c). Based on the electrochemical and spectroscopic data, the redox potentials of excited-states *HEH and *HE are estimated to be +1.554/-1.874 V and -0.067/-2.490 V vs. SCE. So HE2- dianion, *HEH, *HE are powerful reductants (Table S2).

The luminescence responses of HEH or HE⁻ ion in DMSO to substrates were investigated. As shown in Figures S7 and S8, the addition of **1a** or **2a** into the HEH solution did not cause significant variations in the emission spectra ($\lambda_{ex} = 383$ nm). In contrast, **1a** did reduce the photoluminescent intensity ($\lambda_{ex} = 469$ nm) of the HE⁻ solution (Figure S9). Under photocatalytic conditions, the reduction potential of *HE⁻ (-2.490 V vs. SCE) is large enough to reduce **1a** [-2.043 V vs. SCE (Figures S6e)]. The relationship between E_{ox}(**2a**) [+0.540 V vs. SCE in DMSO (Figure S6d)] and E_{red}(*HE⁻) definitively excludes the possibility

of reductive quenching via SET from 2a to *HE⁻. As predicted, no obvious changes in the emission spectra were observed when 2a was added into HE⁻ solution (Figure S10). The ¹H NMR titration experiments have been performed between HE⁻ and 1a or 2a (Figure S11). When 1a or 2a is added, the resonance of HE⁻ protons at δ 3.98, 2.03 and 1.15 ppm shows remarkable downfield shifts. So an electron donor-acceptor (EDA) complex is formed between HE⁻ and arylhalide (or arylsulfinate) in photocatalytic process.^[24] The light on/off experiments showed that a smooth transformation under the light irradiation, but no further conversion was observed when the mixture was kept in dark (Figure S12). The coupling reactions is carried out at 100 °C to result in the formation of 3aa in about 25% yield with or without 2,2'-azobis(2-methylpropionitrile) (AIBN) (Table S1, entries 1 and 2). Taken together, the coupling reaction does proceed through a photoredox catalytic pathway.

The addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (2 equiv.) under optical conditions largely inhibited the model reaction, giving 3aa in 2% vield, Reaction of 1a, HEH (1 equiv.). and TEMPO (2 equiv.) with Cs₂CO₃ (1.5 equiv.) under optical conditions gave aryl-TEMPO adduct 4-((2.2.6.6tetramethylpiperidin-1-yl)oxy)benzonitrile in 29% isolated yield coupled with diethyl 2,6-dimethylpyridine-3,5-dicarboxylate in 79% HPLC yield (details in supporting information). These results demonstrated the involvement of aryl radical species in this photocatalytic coupling system. The SET from *HE to 1a gives aryl radical (Ar) and HE. The SET from 2a to HE is excluded due to that Eox(2a) of +0.540 V vs. SCE is higher than Eox(HE) of -0.186 vs. SCE. The subsequent coupling of aryl radical with 2a affords sulfone radical anion (3aa-), which can transfer one electron to HE' [$E_{red}(3aa)$ = -1.566 V vs. SCE (Figure S6i)]. In addition, Ered(1a) is lower than Ered(3aa). So the SET process from 3aa⁻ to 1a is unfavorable (Scheme S1).

Based on all above data, the proposed catalytic cycle via oxidative quenching progress is proposed in Scheme 2. First, the EDA complex [HE⁻...ArX] (I) is excited by visible light to provide [*HE⁻...ArX] (II) species. The SET occurs in II to yield aryl radical (Ar') and HE^{*} [E(HE'/*HE') = -2.490 V vs. SCE in DMSO, E(Ar-X) \approx -2.0 V vs. SCE^[25]]. Then, carbon radical Ar' reacts with **2** to form EDA intermediate III, which undergoes an SET to offer **3** along with regeneration of HE⁻. [E_{red}(**3aa**) = -1.566 V; E(HE'/HE⁻) = -0.186 V vs. SCE in DMSO].



Scheme 2. Proposed mechanism

In summary, we have developed the new application of cheap, commercially available Hantzsch ester (HEH) as a visible-light photoredox catalyst for the synthesis of sulfones. This transformation allows the cross-coupling of various sodium sulfinates with a wide range of aryl and heteroaryl bromides, iodides and chlorides. This conversion does not need transition metal, external oxidant, sacrificial reductant or mediator under blue LEDs or sunlight. This newly developed photoredox catalysis based on Hantzsch ester is also applicable to new C-X (X = C, N, O, S) bond transformations, which are currently under investigation in our laboratory.

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Keywords: Hantzsch ester • transition-metal-free • C-S bond formation • arylhalides • arylsulfinates

- a) C. Zheng, S.-L. You, *Chem. Soc. Rev.* 2012, *41*, 2498–2518; b) S. G. Ouellet, A. M. Walji, D. W. C. Macmillan, *Acc. Chem. Res.* 2007, *40*, 1327–1339; c) J. W. Yang, M. T. H. Fonseca, B. List, *Angew. Chem. Int. Ed.* 2004, *43*, 6660–6662; d) Q.-A. Chen, M.-W. Chen, C.-B. Yu, L. Shi, D.-S. Wang, Y. Yang, Y.-G. Zhou, *J. Am. Chem. Soc.* 2011, *133*, 16432–16435; e) A. M. F. Phillips, A. J. L. Pombeiro, *Org. Biomol. Chem.* 2017, *15*, 2307–2340.
- a) P.-Z. Wang, J.-R. Chen, W.-J. Xiao, Org. Biomol. Chem. 2019, 17, 6936–6951; b) K. N. Lee, Z. Lei, M.-Y. Ngai, J. Am. Chem. Soc. 2017, 139, 5003–5006.
- a) J. Zhang, Y. Li, F. Zhang, C. Hu, Y. Chen, *Angew. Chem. Int. Ed.* **2016**, 55, 1872–1875; b) L. J. Rono, H. G. Yayla, D. Y. Wang, M. F. Armstrong, R. R. Knowles, *J. Am. Chem. Soc.* **2013**, *135*, 17735–17738.
- [4] a) H.-H. Zhang, Q. Liu, K. Feng, B. Chen, C.-H. Tung, L.-Z. Wu, *Langmuir* 2012, *28*, 8224–8229; b) K. Cao, S. M. Tan, R. Lee, S. Yang, H. Jia, X. Zhao, B. Qiao, Z. Jiang, *J. Am. Chem. Soc.* 2019, *141*, 5437–5443; c) G. Park, S. Y. Yi, J. Jung, E. J. Cho, Y. You, *Chem. Eur. J.* 2016, *22*, 17790–17799.
- [5] a) G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang, Z. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 8432–8436; b) W. Chen, Z. Liu, J. Tian, J. Ma, X. Cheng, G. Li, *J. Am. Chem. Soc.* **2016**, *138*, 12312–12315; c) K. Nakajima, S. Nojima, Y Nishibayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 14106–14110; d) T. v. Leeuwen, L. Buzzetti, L. A. Perego, P. A. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 4953–4957.
- [6] a) G. Goti, B. Bieszczad, A. Vega-Penaloza, P. Melchiorre, Angew. Chem. Int. Ed. 2019, 58, 1213–1217; b) S. O. Badir, A. Dumoulin, J. K. Matsui, G. A. Molander, Angew. Chem. Int. Ed. 2018, 57, 6610–6613; c) H.-H. Zhang, S. Yu, J. Org. Chem. 2017, 82, 9995–10006; d) B. R. McDonald, K. A. Scheidt, Org. Lett. 2018, 20, 6877–6881.
- a) J. Jung, J. Kim, G. Park, Y. You, E. J. Cho, Adv. Synth. Catal. 2016, 358, 74–80; b) M. A. Emmanuel, N. R. Greenberg, d. G. Oblinsky, T. K. Hyster, Nature 2016, 540, 414–417; c) J. Zhang, M.-Z. Jin, W. Zhang, L. Yang, Z.-L. Liu, Tetrahedron Lett. 2002, 43, 9687–9689. d) S. Fukuzumi, K. Hironaka, T. Tanaka, J. Am. Chem. Soc. 1983, 105, 4722–4727.

- [8] D. M. Hedstrand, W. H. Kruizinga, R. M. Kellogg, *Tetrahedron Lett.* 1978, 19, 1225–1258.
- [9] W. Chen, H. Tao, W. Huang, G. Wang, S. Li, X. Cheng, G. Li, *Chem. Eur. J.* 2016, 22, 9546–9550.
- [10] L. I. Panferova, A. V. Tsymbal, V. V. Levin, M. I. Struchkova, A. D. Dilman, Org. Lett. 2016, 18, 996–999.
- [11] D. Chen, L. Xu, T. Long, S. Zhu, J. Yang; L. Chu, *Chem. Sci.* 2018, 9, 9012–9017.
- [12] X. Xu, Q.-Q. Min, N. Li, F. Liu, Chem. Commun. 2018, 54, 11017–11020.
- [13] a) Q.-Y. Meng, T. E. Schirmer, K. Katou, B. König, *Angew. Chem. Int. Ed.* **2019**, *58*, 5723–5728; b) X. Huang, S. Luo, O. Burghaus, R. D. Webster, K. Harms, E. Meggers, *Chem. Sci.* **2017**, *8*, 7126–7131.
- a) L. Kunkler, N. James, J. Maher, *Expert Rev. Anticancer Ther.* 2004, 4, 37–41; b) M. Ma, Y. Cheng, Z. Xu, P. Xu, H. Qu, Y. Fang, T. Xu, L. Wen, *Eur. J. Med. Chem.* 2007, 42, 93–98; c) G. L. Regina, A. Coluccia, A. Brancale, F. Piscitelli, V. Gatti, G. Maga, A. Samuele, C. Pannecouque, D. Schols, J. Balzarini, E. Novellino, R. Silvestri, *J. Med. Chem.* 2011, 54, 1587–1598.
- [15] a) N. W. Liu, S. Liang, G. Manolikakes, 2016, 48, 1939–1973; (b) G. Liu,
 C. Fan, J. Wu, Org. Biomol. Chem. 2015, 13, 1592–1599.
- [16] a) E. J. Emmett, B. R. Hayter, M. C. Willis, Angew. Chem. Int. Ed. 2013, 52, 12679–12683; b) D. H. Kim, J. Lee, A. Lee, Org. Lett. 2018, 20, 764–767; c) T. Jia, M. Zhang, H. Jiang, C. Y. Wang, P. J. Walsh, J. Am. Chem. Soc. 2015, 137, 13887–13893; d) Y. Jiang, T.-P. Loh, Chem. Sci. 2014, 5, 4939–4943; e) Y. Li, T. Miao, P. Li, L. Wang, Org. Lett. 2018, 20, 1735–1739.
- [17] a) J. M. Baskin, Z. Wang, Org. Lett. 2002, 4, 4423–4425; b) S. Cacchi,
 G. Fabrizi, A. Goggiamani, L. M. Parisi, R. Bernini, J. Org. Chem. 2004, 69, 5608–5614; c) W. Zhu, D. Ma, J. Org. Chem. 2005, 70, 2696–2700;
 d) G. Le Duc, E. Bernoud, G. Prestat, S. Cacchi, G. Fabrizi, A. Iazzetti,
 D. Madec, G. Poli, Synlett 2011, 2943–2946; e) M. Wang, S. Chen, X. Jiang, Org. Lett. 2017, 19, 4916–4919; f) A. Shavnya, S. B. Coffey, A. C. Smith, V. Mascitti, Org. Lett. 2013, 15, 6226–6229.
- [18] a) L. A. Smyth, E. M. Phillips, V. S. Chan, J. G. Napolitano, R. Henry, S. Shekhar, *J. Org. Chem.* **2016**, *81*, 1285–1294; b) D. C. Reeves, S. Rodriguez, L. Heewon, N. Haddad, D. Krishnamurthy, C. H. Senayake, *Tetrahedron Lett.* **2009**, *50*, 2870–2873; c) B. P. Bandgar, S. V. Bettigeri, J. Phopase, *Org. Lett.* **2004**, *6*, 2105–2108; d) A. Shavnya, K. D. Hesp, V. Mascitti, A. C. Smith, *Angew. Chem. Int. Ed.* **2015**, *54*, 13571–13575.
- [19] a) F. Teplý, Collect. Czech. Chem. Commun. 2011, 76, 859–917; b) C.
 K. Prier, D. A. Rankic, D. W. C. MacMillan, Chem. Rev. 2013, 113, 5322–5363; c) J. M. R. Narayanam, C. R. J. Stephenson, Chem. Soc. Rev. 2011, 40, 102–113; d) K. Zeitler, Angew. Chem. Int. Ed. 2009, 48, 9785–9789; e) T. P. Yoon, M. A. Ischay, J. Du, Nat. Chem. 2010, 2, 527–532; f) J. Xuan, W. J. Xiao, Angew. Chem. Int. Ed. 2012, 51, 6828–6838.
- [20] a) X. Wang, G. D. Cuny, T. Noël, Angew. Chem. Int. Ed. 2013, 52, 7860–7864; b) M. S. Oderinde, M. Frenette, D. W. Robbins, B. Aquila, J. W. Johannes, J. Am. Chem. Soc. 2016, 138, 1760–1763; c) M. Jiang, H. Li, H. Yang, H. Fu, Angew. Chem. Int. Ed. 2017, 56, 874–879; d) G. Zhang, C. Liu, H. Yi, Q. Meng, C. Bian, H. Chen, J.-X. Jian, L.-Z. Wu, A. Lei, J. Am. Chem. Soc. 2015, 137, 9273–9280; f) B. Liu, C.-H. Lim, G. M. Miyake, J. Am. Chem. Soc. 2017, 139, 13616–13619; g) S. K. Pagire, S. Paria, O. Reiser, Org. Lett. 2016, 18, 2106–2109.
- [21] a) I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* 2014, *346*, 725–728; b) B. J. Shields, A. G. Doyle, *J. Am. Chem. Soc.* 2016, *138*, 12719–12722; (c) S. M. Senaweera, A. Singh, J. D. Weaver, *J. Am. Chem. Soc.* 2014, *136*, 3002–3005; d) W.-J. Zhou, G.-M. Cao, G. Shen, X.-Y. Zhu, Y.-Y. Gui, J.-H. Ye, L. Sun, L.-L. Liao, J. Li, D.-G. Yu, *Angew. Chem. Int. Ed.* 2017, *56*, 15683–15687; e) H. Yin, P. J. Carroll, B. C. Manor, J. M. Anna, E. J. Schelter, *J. Am. Chem. Soc.* 2016, *138*, 5984–5993; f) A. M. Mfuh, V. T. Nguyen, B. Chhetri, J. E. Burch, J. D. Doyle, V. N. Nesterov, H. D. Arman, O. V. Larionov, *J. Am. Chem. Soc.* 2016, *138*, 8408–8411; g) A. J. Boyington, M.-L. Y. Riu, N. T. Jui, *J. Am.*

Chem. Soc. **2017**, *139*, 6582–6585; h) K. Shimomaki, K. Murata, R. Martin, N. Iwasawa, *J. Am. Chem. Soc.* **2017**, *139*, 9467–9470; i) J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nature Chem.* **2012**, *4*, 854–859; j) H. Zeng, Q. Dou, C.-J. Li, *Org. Lett.* **2019**, *21*, 1301–1305.

- [22] a) H. Yue, C. Zhu, M. Rueping, *Angew. Chem. Int. Ed.* 2018, *57*, 1371–1375; b) N. W. Liu, K. Hofman, A. Herbert, G. Manolikakes, *Org. Lett.* 2018, *20*, 760–763; c) M. J. Cabrera-Afonso, Z.-P. Lu, C. B. Kelly, S. B. Lang, R. Dykstra, O. Gutierrez, G. A. Molander, *Chem. Sci.* 2018, *9*, 3186–3191; d) R. Chawla, L. D. S. Yadav, *Org. Biomol. Chem.* 2019, *17*, 4761–4766.
- [23] L. Chen, J. Liang, Z.-Y. Chen, J. Chen, M. Yan, X.-J. Zhang, Adv. Synth. Catal. 2019, 361, 956–960.
- [24] J. Zhang, Y. Li, R. Xu, Y. Chen, Angew. Chem. Int. Ed. 2017, 56, 12619–12623.
- [25] a) I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, Acc. Chem. Res.
 2016, 49, 1566–1577; b) H. G. Roth, N. A. Romero, D. A. Nicewicz, Synlett 2016, 27, 714–723; c) L. Zeng, T. Liu, C. He, D. Shi, F. Zhang, C. Duan, J. Am. Chem. Soc. 2016, 138, 3958–3961.

Entry for the Table of Contents

COMMUNICATION



Hantzsch Ester as a Photocatalyst: We firstly use diethyl 2,6-dimethyl-1,4dihydropyridine-3,5-dicarboxylate (HEH) as a visible-light photoredox catalyst for coupling of aryl sulfinates and arylhalides without transition metal, external oxidant, sacrificial agent and mediator. Da-Liang Zhu, Qi Wu, Hai-Yan Li, Hong-Xi Li,* and Jian-Ping Lang

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Hantzsch Ester as a Visible-light Photoredox Catalyst for Transition-Metal-Free Coupling of Arylhalides and Arylsulfinates

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