OL Organic Letters

pubs.acs.org/OrgLett Letter

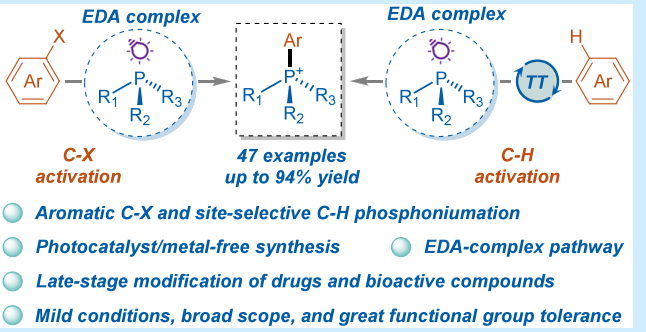
Photoinduced Phosphoniumation of Aryl Halides and Arylthianthrenium Salts via an Electron Donor–Acceptor Complex

Ziyu Gan, Jiajin Chen, Han Wang, Zhiyan Xue, Ziyang Chen, Yongqiang Zhang, Lifang Wang, Hui Zi, Shuyang Liu, Lei Shi, and Yunhe Jin*

Cite This: *Org. Lett.* 2024, 26, 7751–7756 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Owing to their remarkable practicality and utility, phosphonium salts have attracted substantial interest and are widely applied in critical areas, such as medicine, materials science, and catalysis. Herein, we developed a facile and photocatalyst/metal-free synthetic strategy for the preparation of phosphonium salts utilizing aryl halides/arylthianthrenium salts as aryl radical precursors. This approach is disclosed to undergo an efficient light-induced electron donor–acceptor pathway, facilitating the synthesis of a structurally diverse range of phosphonium salts.

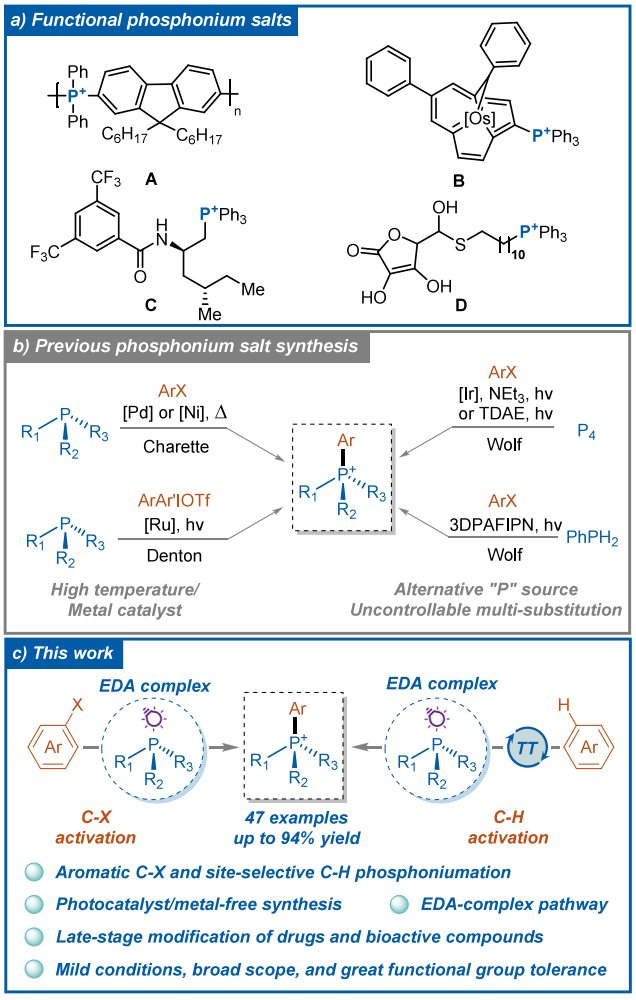


Quaternary phosphonium salts, characterized by a central phosphorus atom bonded covalently to four organic groups, exhibit remarkable structural tunability and functionality due to the extensive range of possible organic substituents encompassing alkyl, aryl, and heterocyclic moieties. This diversity not only facilitates the design and synthesis of tailor-made molecules for specific applications but also provides a rich chemical landscape for the exploration of novel materials and pharmaceuticals. Quaternary phosphonium salts can serve as polyelectrolytes **A**,[1] photothermal materials **B**,[2] chiral bifunctional catalysts **C**,[3] and mitochondria-targeted drugs **D**[4] (Scheme 1a), finding applications across various fields, including pharmaceuticals,[5] catalysis,[6] and materials science.[7] In addition, phosphonium salts are also versatile reagents for a variety of organic reactions in synthetic chemistry.[8] Therefore, the development of mild and environmentally friendly methods for their synthesis is a valuable as well as challenging task.

During recent decades, several catalytic approaches were successively established for the synthesis of multi-aryl phosphonium salts (Scheme 1b). Early in 2008, Marcoux and Charette reported Pd- or Ni-catalyzed cross-coupling reactions of haloarenes and triarylphosphines under high-temperature conditions.[9] A few years later, Detton and co-workers utilized hypervalent iodine salts as arylation reagents to synthesize a series of phosphonium salts under mild conditions with a ruthenium photocatalyst.[10] Recently, capitalizing on the unique single-electron transfer (SET) progress in photocatalytic reactions, white phosphorus and aryl phosphine hydrides were pioneeringly applied as alternative "P" sources for assembling phosphonium salts with aryl halides by the Wolf group.[11] Among these outstanding works, some challenges, such as strong conditions, expensive and complex metals or photocatalysts, and uncontrollable selectivity, still exist. In recent years, the light-induced electron donor–acceptor (EDA) pathway was demonstrated as a selective and sustainable radical generation strategy via intracomplex SET, bypassing the need for transition metals or dyes.[12] Because triarylphosphine with a delocalized lone pair is well-known as a typical electron donor, it is of great possibility to construct tetraarylphosphonium salts through an EDA complex consisting of triarylphosphine and an electron acceptor. Besides the widely used acceptor and arylation agent haloarenes,[13] aryl thianthrenium salt, which was innovatively developed as a key intermediate for site-specific aromatic C–H activation,[14] also exhibited wonderful activity as an electron acceptor in photocatalytic systems.[15] According to these thoughts and our continued interest in photodriven reactions,[16] we herein develop a facile method for the photoinduced synthesis of phosphonium salts through arene C–X and C–H bond activation under mild conditions (Scheme 1c). Photoactive EDA complexes are proposed to form between aryl thianthrenium salts/aryl halides and triarylphosphine, rendering the system with photocatalyst/metal-free conditions, a

Received: August 7, 2024
Revised: August 30, 2024
Accepted: September 3, 2024
Published: September 5, 2024

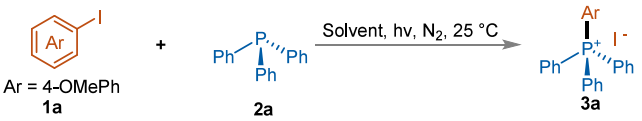
Scheme 1. Approaches for Phosphonium Salt Construction



broad scope, great compatibility with various functional groups, and wide application in late-stage modification.

The model reaction between aryl halide **1a** and triarylphosphine **2a** was first investigated under various metal/photocatalyst-free conditions (Table 1). As an initial attempt, the model reaction pleasingly provided the desired product **3a** in 41% yield with ethyl acetate as the solvent under 365 nm irradiation (entry 1). Then, we tuned the experimental parameters to obtain the best conditions. Other solvents, including dichloroethane, *o*-xylene, tetrahydrofuran, and acetonitrile, were screened (entries 2−5), and CH_3CN was shown to be the best candidate, affording a yield of 90% (entry 5). The following comparison of light sources with diverse wavelengths presented that 365 nm was still identified as the most favorable choice (entries 6 and 7). Finally, the control experiment revealed that light irradiation and inert gas protection were indispensable for the successful transformation (entries 8 and 9).

Table 1. Optimization of Reaction Conditions[a]



entry	solvent	wavelength (nm)	yield (%)[b]
1	EtOAc	365	41
2	DCE	365	trace
3	*o*-xylene	365	22
4	THF	365	trace
5	MeCN	365	90
6	MeCN	405	24
7	MeCN	455	0
8	MeCN	dark	0
9[c]	MeCN	365	14

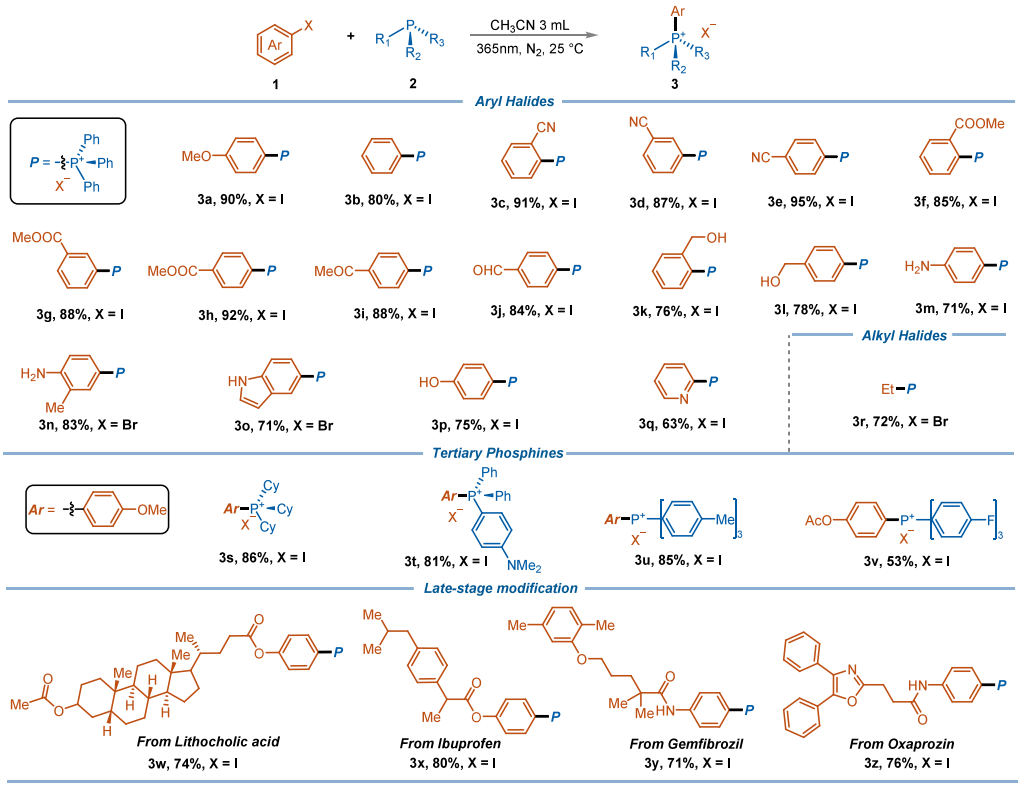
[a]Reaction conditions: compound **1a** (0.2 mmol), compound **2a** (0.4 mmol), and solvent (3.0 mL) under N_2 and irradiation of 30 W light-emitting diodes (LEDs) for 18 h. [b]Isolated yield. [c]Air atmosphere.

With the optimal conditions in hand, we explored the substrate scope. As outlined in Scheme 2, various aryl halides bearing electron-withdrawing groups or electron-donating groups proceeded effectively with triarylphosphines under irradiation of 365 nm, giving the corresponding products in good to excellent yields (**3a**−**3p**). Altering the substituted positions of cyano and ester groups at the *ortho*, *meta*, or *para* sites of halide brought little influence on the reaction efficiency (**3c**−**3e** and **3f**−**3h**). Halobenzenes bearing reactive functional groups (−NH_2 and −OH) were also suitable substrates and afford the phosphonium salts in good yields (**3k**−**3n**), thus providing opportunities for further transformation. In addition, the bioactive indole and phenol motifs were involved and proved to be compatible with this system (**3o** and **3p**). 2-Iodopyridine and bromoethane could also react in this system to yield products **3q** and **3r** with good efficiency. Besides, other trialkylphosphine and triarylphosphine could also participate in this protocol, and the corresponding phosphonium salts were obtained in good yields (**3s**−**3v**). Significantly, this facile and simple method efficiently realized the phosphoniumation of several complex substrates derived from lithocholic acid, ibuprofen, gemfibrozil, and oxaprozin (**3w**−**3z**), exhibiting valuable application potential in the late-stage modification of bioactive molecules and drugs.

Besides aryl halides, multitudinous aryl thianthrenium salts as another type of electron acceptors were next tested to accomplish tandem C−H functionalization, and the findings demonstrated the employed visible-light-driven methodology to be a broadly applicable and effective technique for synthesizing phosphonium tetrafluoroborates (Scheme 3). Arenes featuring ester, phenyl, cyano, and chloroalkyl groups have all been effectively utilized as starting materials, yielding satisfactory results (**5b**−**5f**). *tert*-Butyl, cyclohexyl, and benzyl groups did not impair the reaction efficiency, despite their considerable steric hindrance (**5h**−**5j**). Fortunately, the heterocyclic and amide-assembled thianthrenium salts were also tolerated under standard conditions with high reaction efficiency (**5l** and **5m**). Furthermore, tertiary phosphines bearing diverse aryl groups all exhibited desirable reactivity with over 75% yields (**5n**−**5q**). Notably, an array of biologically significant compounds, including pyriproxyfen, sildenafil, flurbiprofen, and pyriproxyfen, demonstrated excellent compatibility within the described reaction process, delivering the structurally modified end products with yields ranging from moderate to high (**5r**−**5u**). These outcomes underscore the potential of our methodology as a powerful instrument for the late-stage hydrophilic modification of drug entities and intricate bioactive frameworks, thereby enhancing the scope of molecular tailoring in pharmaceutical and biochemical research.

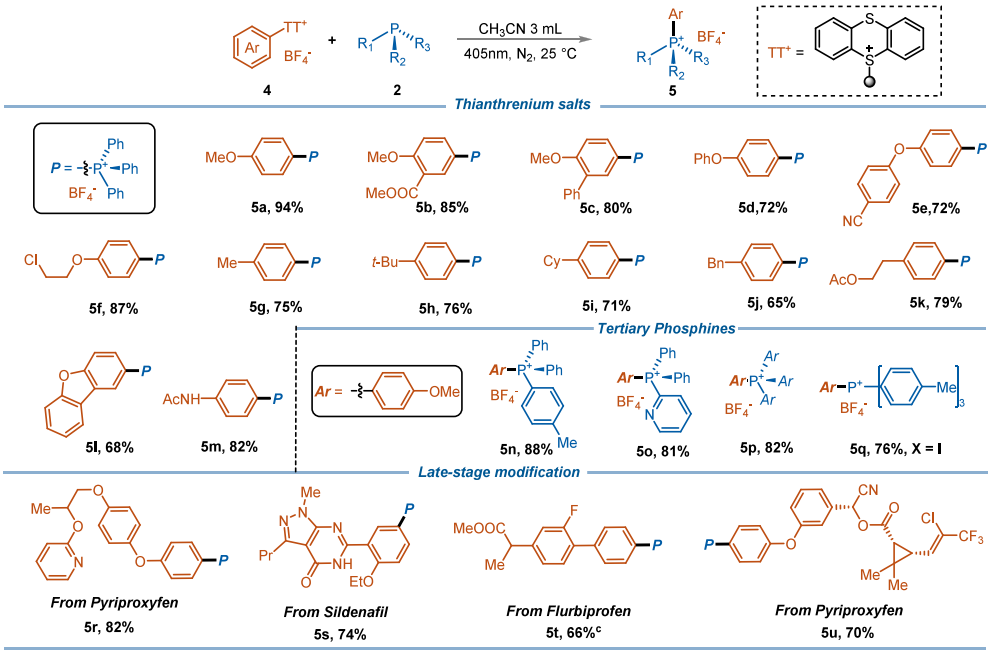
https://doi.org/10.1021/acs.orglett.4c02909
Org. Lett. 2024, 26, 7751−7756

Scheme 2. Scope for Aryl Halide Phosphoniumation[a,b]



[a]Reaction conditions: compound **1** (0.2 mmol), compound **2** (0.4 mmol), and CH_3CN (3 mL) under N_2 and irradiation of 30 W 365 nm LEDs for 18 h. [b]Isolated yield.

Scheme 3. Scope for Arene Phosphoniumation[a,b]

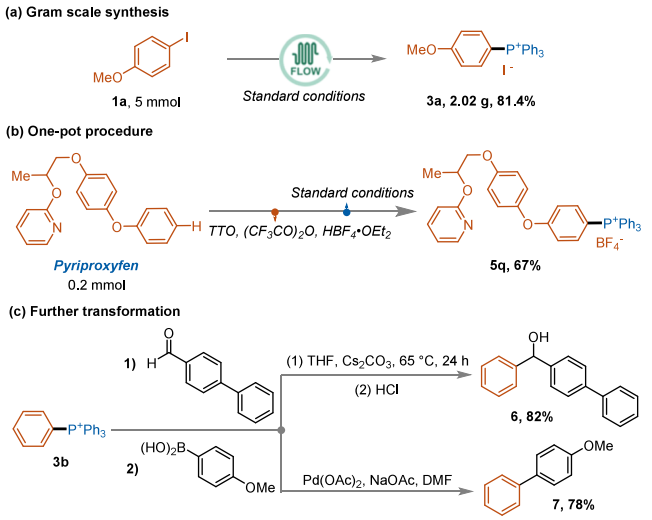


[a]Reaction conditions: compound **4** (0.2 mmol), compound **2** (0.4 mmol), and CH_3CN (3 mL) under N_2 and irradiation of 30 W 405 nm LEDs for 12 h. [b]Isolated yield. [c]The anion is TfO^-.

To demonstrate the broad applicability of this mild phosphoniumation protocol, several synthetic applications were explored (Scheme 4). The scale-up feasibility of conducting this reaction was investigated using a well-designed continuous-flow reactor (Scheme 4a). Encouragingly, the reaction proceeded smoothly and generated 2.02 g of product **3a** in 81.4% yield after purification, affirming the practicability and user-friendliness of our photocatalyst/metal-free proce-

https://doi.org/10.1021/acs.orglett.4c02909
Org. Lett. 2024, 26, 7751−7756

Scheme 4. Synthetic Application

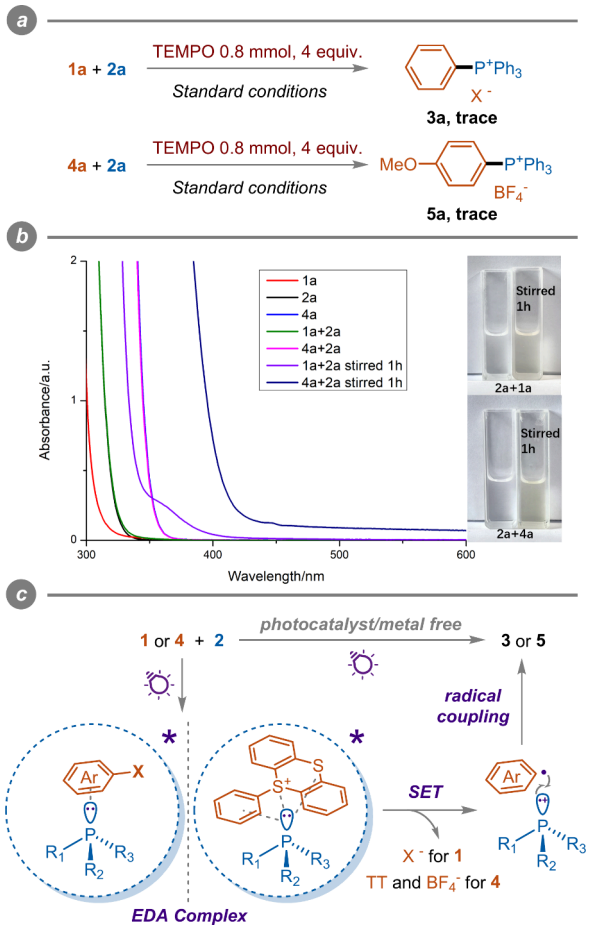


dure. Moreover, the valuable late-stage C−H phosphoniumation of pyriproxyfen utilizing a one-pot strategy was successfully achieved, giving the corresponding product **5q** in a respectable two-step yield (Scheme 4b). To reinforce the method's practical viability, further transformation of the phosphonium salts was executed (Scheme 4c). Applying product **3b** as a shelf-stable and easily handled nucleophile, the hydroarylation of carbonyl was acquired in an 82% yield.[8c] Additionally, a valuable C−C coupling reaction was also conducted, giving biphenyl **7** in good efficiency.[17]

To verify whether the reaction underwent an EDA complex pathway as we designed, some mechanistic studies were carried out. 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO) as a universal radical scavenger was subjected to the two standard reaction conditions, respectively, and the desired reaction processes were both inhibited almost entirely, indicating that radical processes are probably involved (Scheme 5a). The light on−off experiments were performed next, presenting that continuous irradiation is essential for these systems (Figures S2 and S3 of the Supporting Information). To further elucidate the formation of EDA complexes, we conducted measurements of the ultraviolet−visible (UV−vis) absorption spectra for substrates (**1a**, **2a**, and **4a**) and their combined mixture. As depicted in Scheme 5b, compounds **1a**, **2a**, and **4a** exhibited no absorbance within the light spectrum over 365 nm individually. No obvious variation was observed in the spectra of the immediate mixtures of compounds **2a** + **1a** or compounds **2a** + **4a**. Strikingly, after stirring the mixtures for 1 h, the resulting solutions manifested pronounced red shifts, commonly referred to as the charge transfer band.[12,13,15] This spectral alteration served as evidence for the successful assembly of EDA complexes between compounds **1a**/**4a** and **2a**. On the basis of these experimental outcomes, a proposed mechanism was outlined in Scheme 5c. Photoactive EDA complexes between compounds **1**/**4** and **2** formed initially *in situ* and were excited under light irradiation. The following intracomplex SET spontaneously took place, generating an aryl radical and a P-centered radical cation. Finally, the cross-coupling of the two radicals constructed the C−P bonds and provided the quaternary phosphonium salts.

To summarize, we herein develop a convenient synthetic route that commences with aromatic C−X or C−H bonds and

Scheme 5. Mechanistic Study



aims to construct C(sp^2)−P bonds via the EDA complex mechanism. This methodology offers straightforward and photocatalyst/metal-free access to a diverse array of phosphonium salts and wide utility in the late-stage functionalization of biorelevant molecules and drugs with operational ease. This novel procedure circumvents the conventional dependence upon precious metals, unstable phosphorus sources, and reductive reagents, thereby harmonizing with the goals of sustainable and environmentally benign chemistry.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c02909.

Mechanism investigations, synthetic procedures, characterization data, and ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectra of these synthesized compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yunhe Jin − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian,*

https://doi.org/10.1021/acs.orglett.4c02909
Org. Lett. 2024, 26, 7751−7756

Liaoning 116024, People's Republic of China; orcid.org/0000-0003-0626-4587; Email: jinyh18@dlut.edu.cn

Authors

Ziyu Gan – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China;* orcid.org/0009-0005-0226-0572

Jiajin Chen – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Han Wang – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Zhiyan Xue – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Ziyang Chen – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Yongqiang Zhang – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Lifang Wang – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Hui Zi – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China*

Shuyang Liu – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China;* orcid.org/0009-0001-8246-4970

Lei Shi – *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, People's Republic of China;* orcid.org/0000-0002-2644-1168

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.4c02909

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the assistance of Professor Shengyang Tao and Professor Lijing Zhang in the School of Chemistry at Dalian University of Technology (DUT) for their great help in flow chemistry. The authors acknowledge the assistance of Dr. Huihui Wan in DUT Instrumental Analysis Center for her great help in high-resolution mass spectrometry (HRMS) analysis. The authors acknowledge the support of the National Natural Science Foundation of China (21901032 and 22171036), the Fundamental Research Funds for the Central Universities (DUT21LK13), and the Open Research Fund of the School of Chemistry and Chemical Engineering, Henan Normal University (2020YB03).

■ REFERENCES

(1) Wan, W.; Yang, X.; Smith, R. C. Convenient route to tetraarylphosphonium polyelectrolytes via metal-catalysed P–C coupling polymerisation of aryl dihalides and diphenylphosphine. *Chem. Commun.* **2017**, *53*, 252–254.

(2) Zhu, C.; Yang, C.; Wang, Y.; Lin, G.; Yang, Y.; Wang, X.; Zhu, J.; Chen, X.; Lu, X.; Liu, G.; Xia, H. CCCCC pentadentate chelates with planar Möbius aromaticity and unique properties. *Sci. Adv.* **2016**, *2*, No. e1601031.

(3) Xia, X.; Zhu, Q.; Wang, J.; Chen, J.; Cao, W.; Zhu, B.; Wu, X. Direct Asymmetric Vinylogous Mannich Addition of 3,5-Disubstituted-4-nitroisoxazoles to Isatin-Derived Imines Catalyzed by a Bifunctional Phase-Transfer-Catalyst. *J. Org. Chem.* **2018**, *83*, 14617–14625.

(4) Zielonka, J.; Joseph, J.; Sikora, A.; Hardy, M.; Ouari, O.; Vasquez-Vivar, J.; Cheng, G.; Lopez, M.; Kalyanaraman, B. Mitochondria-targeted triphenylphosphonium-based compounds: Syntheses, mechanisms of action, and therapeutic and diagnostic applications. *Chem. Rev.* **2017**, *117*, 10043–10120.

(5) Alfei, S. Shifting from Ammonium to Phosphonium Salts: A Promising Strategy to Develop Next-Generation Weapons against Biofilms. *Pharmaceutics* **2024**, *16*, 80.

(6) (a) Li, H.; Liu, H.; Guo, H. Recent advances in phosphonium salt catalysis. *Adv. Synth. Catal.* **2021**, *363*, 2023–2036. (b) Noroozi-Shad, N.; Gholizadeh, M.; Sabet-Sarvestani, H. Quaternary phosphonium salts in the synthetic chemistry: Recent progress, development, and future perspectives. *J. Mol. Struct.* **2022**, *1257*, 132628. (c) Hughes, D. L. Highlights of the recent patent literature: Focus on asymmetric organocatalysis. *Org. Process Res. Dev.* **2022**, *26*, 2224–2239. (d) Liu, S.; Kumatabara, Y.; Shirakawa, S. Chiral quaternary phosphonium salts as phase-transfer catalysts for environmentally benign asymmetric transformations. *Green Chem.* **2016**, *18*, 331–341.

(7) Xue, Y.; Xiao, H.; Zhang, Y. Antimicrobial polymeric materials with quaternary ammonium and phosphonium salts. *Int. J. Mol. Sci.* **2015**, *16*, 3626–3655.

(8) (a) Liu, Q.; Zhang, B.-B.; Zhang, C.-S.; Han, J.-N.; Wang, Z.-X.; Chen, X.-Y. Pnictogen Bonding Enabled Photosynthesis of Chiral Selenium-Containing Pyridines from Pyridylphosphonium Salts. *Fundam. Res.* **2023**, DOI: 10.1016/j.fmre.2023.03.013. (b) Tang, S.; Liu, Z.; Zhang, J.; Li, B.; Wang, B. Copper-Catalyzed C4-selective Carboxylation of Pyridines with CO_2 via Pyridylphosphonium Salts. *Angew. Chem.* **2024**, *136*, No. e202318572. (c) Deng, Z.; Lin, J.-H.; Xiao, J.-C. Nucleophilic arylation with tetraarylphosphonium salts. *Nat. Commun.* **2016**, *7*, 10337.

(9) (a) Marcoux, D.; Charette, A. B. Nickel-catalyzed synthesis of phosphonium salts from aryl halides and triphenylphosphine. *Adv. Synth. Catal.* **2008**, *350*, 2967–2974. (b) Marcoux, D.; Charette, A. B. Palladium-catalyzed synthesis of functionalized tetraarylphosphonium salts. *J. Org. Chem.* **2008**, *73*, 590–593.

(10) Fearnley, A.; An, J.; Jackson, M.; Lindovska, P.; Denton, R. Synthesis of quaternary aryl phosphonium salts: Photoredox-mediated phosphine arylation. *Chem. Commun.* **2016**, *52*, 4987–4990.

(11) (a) Lennert, U.; Arockiam, P. B.; Streitferdt, V.; Scott, D. J.; Rödl, C.; Gschwind, R. M.; Wolf, R. Direct catalytic transformation of white phosphorus into arylphosphines and phosphonium salts. *Nat. Catal.* **2019**, *2*, 1101–1106. (b) Arockiam, P. B.; Lennert, U.; Graf, C.; Rothfelder, R.; Scott, D. J.; Fischer, T. G.; Zeitler, K.; Wolf, R. Versatile Visible-Light-Driven Synthesis of Asymmetrical Phosphines and Phosphonium Salts. *Chem. - Eur. J.* **2020**, *26*, 16374–16382. (c) Till, M.; Streitferdt, V.; Scott, D. J.; Mende, M.; Gschwind, R. M.; Wolf, R. Photochemical transformation of chlorobenzenes and white phosphorus into arylphosphines and phosphonium salts. *Chem. Commun.* **2022**, *58*, 1100–1103.

(12) (a) Lima, C. G. S.; de M. Lima, T.; Duarte, M.; Jurberg, I. D.; Paixão, M. W. Organic synthesis enabled by light-irradiation of EDA complexes: Theoretical background and synthetic applications. *ACS Catal.* **2016**, *6*, 1389–1407. (b) Crisenza, G. E.; Mazzarella, D.; Melchiorre, P. Synthetic methods driven by the photoactivity of electron donor–acceptor complexes. *J. Am. Chem. Soc.* **2020**, *142*, 5461–5476. (c) Wortman, A. K.; Stephenson, C. R. EDA photochemistry: Mechanistic investigations and future opportunities. *Chem.* **2023**, *9*, 2390–2415. (d) Leifert, D.; Studer, A. The persistent radical effect in organic synthesis. *Angew. Chem., Int. Ed.* **2020**, *59*, 74–108.

(e) Wang, C.; Qi, R.; Xue, H.; Shen, Y.; Chang, M.; Chen, Y.; Wang, R.; Xu, Z. Visible-Light-Promoted C(sp^3)−H Alkylation by Intermolecular Charge Transfer: Preparation of Unnatural α-Amino Acids and Late-Stage Modification of Peptides. *Angew. Chem., Int. Ed.* **2020**, *59*, 7461−7466.

(13) (a) Piedra, H. F.; Valdés, C.; Plaza, M. Shining light on halogen-bonding complexes: A catalyst-free activation mode of carbon−halogen bonds for the generation of carbon-centered radicals. *Chem. Sci.* **2023**, *14*, 5545−5568. (b) Tian, Y.-M.; Hofmann, E.; Silva, W.; Pu, X.; Touraud, D.; Gschwind, R. M.; Kunz, W.; König, B. Enforced Electronic-Donor−Acceptor Complex Formation in Water for Photochemical Cross-Coupling. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202218775. (c) Zhu, C.; Zhumagazy, S.; Yue, H.; Rueping, M. Metal-free C−Se cross-coupling enabled by photoinduced intermolecular charge transfer. *Chem. Commun.* **2021**, *58*, 96−99. (d) Pan, L.; Deckert, M. M.; Cooke, M. V.; Bleeke, A. R.; Laulhé, S. Solvent anions enable photoinduced borylation and phosphonation of aryl halides via EDA complexes. *Org. Lett.* **2022**, *24*, 6466−6471. (e) Pan, P.; Liu, S.; Lan, Y.; Zeng, H.; Li, C. J. Visible-light-induced cross-coupling of aryl iodides with hydrazones via an EDA-complex. *Chem. Sci.* **2022**, *13*, 7165−7171.

(14) Berger, F.; Plutschack, M. B.; Riegger, J.; Yu, W.; Speicher, S.; Ho, M.; Frank, N.; Ritter, T. Site-selective and versatile aromatic C−H functionalization by thianthrenation. *Nature* **2019**, *567*, 223−228.

(15) (a) van Dalsen, L.; Brown, R. E.; Rossi-Ashton, J. A.; Procter, D. J. Sulfonium Salts as Acceptors in Electron Donor−Acceptor Complexes. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202303104. (b) Cabrera-Afonso, M. J.; Granados, A.; Molander, G. A. Sustainable thioetherification via electron donor−acceptor photoactivation using thianthrenium salts. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202202706. (c) Feng, Z.; Riemann, L.; Guo, Z.; Herrero, D.; Simon, M.; Golz, C.; Mata, R. A.; Alcarazo, M. Pentafluorocyclopropanation of (Hetero)-arenes Using Sulfonium Salts: Applications in Late-Stage Functionalization. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202306764. (d) Dang, X.; Li, Z.; Shang, J.; Zhang, C.; Wang, C.; Xu, Z. Photoinduced C(sp^3)−H Bicyclopentylation Enabled by an Electron Donor−Acceptor Complex-Mediated Chemoselective Three-Component Radical Relay. *Angew. Chem., Int. Ed.* **2024**, No. e202400494. (e) Sun, K.; Shi, A.; Liu, Y.; Chen, X.; Xiang, P.; Wang, X.; Qu, L.; Yu, B. A general electron donor−acceptor complex for photoactivation of arenes via thianthrenation. *Chem. Sci.* **2022**, *13*, 5659−5666. (f) Li, B.; Wang, K.; Yue, H.; Drichel, A.; Lin, J.; Su, Z.; Rueping, M. Catalyst-Free C(sp^2)−H Borylation through Aryl Radical Generation from Thiophenium Salts via Electron Donor−Acceptor Complex Formation. *Org. Lett.* **2022**, *24*, 7434−7439. (g) Xu, H.; Li, X.; Dong, Y.; Ji, S.; Zuo, J.; Lv, J.; Yang, D. Thianthrenium-Enabled Phosphorylation of Aryl C−H Bonds via Electron Donor−Acceptor Complex Photoactivation. *Org. Lett.* **2023**, *25*, 3784−3789. (h) Liu, W.; Hou, H.; Jing, H.; Huang, S.; Ou, W.; Su, C. Photoinduced Phosphination of Arenes Enabled by an Electron Donor-Acceptor Complex Using Thianthrenium Salts. *Org. Lett.* **2023**, *25*, 8350−8355. (i) Cai, Y.; Chatterjee, S.; Ritter, T. Photoinduced copper-catalyzed late-stage azidoarylation of alkenes via arylthianthrenium salts. *J. Am. Chem. Soc.* **2023**, *145*, 13542−13548.

(16) (a) Jin, Y. H.; Zhang, Q. Q.; Wang, L. F.; Wang, X. Y.; Meng, C. G.; Duan, C. Y. Convenient C(sp^3)−H bond functionalisation of light alkanes and other compounds by iron photocatalysis. *Green Chem.* **2021**, *23*, 6984−6989. (b) Zhang, Q. Q.; Jin, Y. H.; Ma, L.; Zhang, Y. Q.; Meng, C. G.; Duan, C. Chromophore-Inspired Design of Pyridinium-Based Metal−Organic Polymers for Dual Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202204918. (c) Zhang, Q. Q.; Liu, S. Y.; Lei, J. L.; Zhang, Y. Q.; Meng, C. G.; Duan, C. G.; Jin, Y. H. Iron-catalyzed photoredox functionalization of methane and heavier gaseous alkanes: Scope, kinetics, and computational studies. *Org. Lett.* **2022**, *24*, 1901−1906. (d) Zhang, Y. Q.; Jin, Y. H.; Wang, L. F.; Zhang, Q. Q.; Meng, C. G.; Duan, C. Y. Selective C(sp^3)−H activation of simple alkanes: Visible light-induced metal-free synthesis of phenanthridines with H_2O_2 as a sustainable oxidant. *Green Chem.* **2021**, *23*, 6926−6930. (e) Jin, Y. H.; Wang, L. F.; Zhang, Q. Q.; Zhang, Y. Q.; Liao, Q.; Duan, C. Y. Photo-induced direct alkynylation of methane and other light alkanes by iron catalysis. *Green Chem.* **2021**, *23*, 9406−9411. (f) Lei, J. L.; Li, M.; Zhang, Q. Q.; Liu, S. Y.; Li, H.; Shi, L.; Jiang, W. F.; Duan, C.; Jin, Y. Visible-Light-Induced Radical Cascade Cross-Coupling via C(sp^3)−H Activation and C−N/N−O Cleavage: Feasible Access to Methylenebisamide Derivatives. *Org. Lett.* **2023**, *25*, 2300−2305. (g) Chen, J. J.; Gan, Z. Y.; Zhang, Y. Q.; Chen, Z. Y.; Liu, S. Y.; Cui, R. Q.; Xue, Z. Y.; Sun, H. X.; Shi, L.; Jiang, W. F.; Jin, Y. H. Iron-Catalyzed Photoredox Alcohol α-C−H Alkylation and Tandem Intramolecular Cyclization: Facile Access to Multisubstituted 2,3-Dihydrofurans and γ-Butyrolactones. *Org. Lett.* **2024**, *26*, 5329−5334.

(17) Hwang, L. K.; Na, Y.; Lee, J.; Do, Y.; Chang, S. Tetraarylphosphonium Halides as Arylating Reagents in Pd-Catalyzed Heck and Cross-Coupling Reactions. *Angew. Chem., Int. Ed.* **2005**, *44*, 6166−6169.

https://doi.org/10.1021/acs.orglett.4c02909
Org. Lett. 2024, 26, 7751−7756