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Thianthrenation-Enabled α-Arylation of Carbonyl Compounds with Arenes

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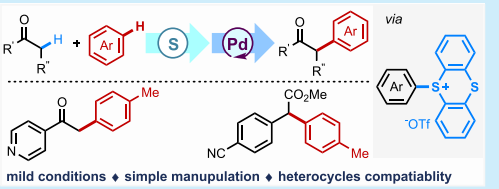
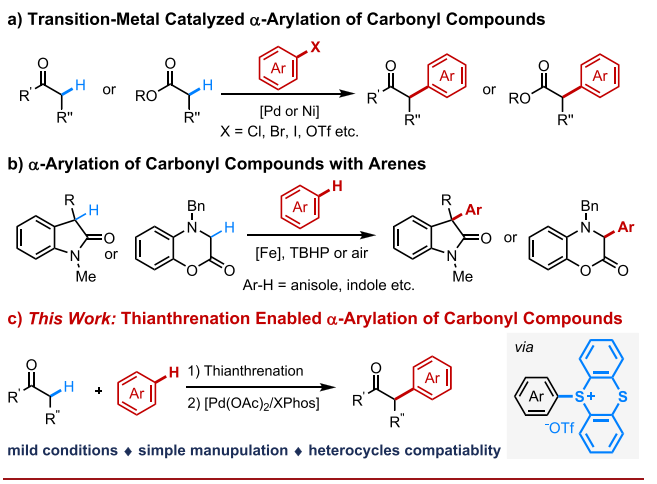
ABSTRACT: The Pd-catalyzed α-arylation of carbonyl compounds with simple arenes enabled by site-selective thianthrenation has been demonstrated. This one-pot process using thianthrenium salts as the traceless arylating reagents features mild conditions and a broad substrate scope. In addition, this protocol could also tolerate the heterocyclic carbonyl compounds and complex bioactive molecules, which is appealing for medicinal chemistry.



The transition-metal-catalyzed α-arylation of carbonyl compounds with aryl halides and their variants is one of the useful and powerful approaches for the construction of the carbon−carbon bond[1,2] and has been found widespread application in the synthesis of pharmaceuticals and complex natural products since the independent developments by Buchwald,[2a] Hartwig,[2b] and Miura.[2c] However, an alternate appealing approach with simple arenes as the arylating reagent for α-C(sp^3)−H of carbonyl compounds remains a paramount challenge, probably due to both the low activities and the low regioselectivity of simple arenes in the preactivation step.[3] Certainly, the α-arylation of carbonyl compounds with simple arenes via the cross coupling of α-C(sp^3)−H and C(sp^2)−H is highly attractive and synthetically useful. In this context, the Kündig[4a] and Taylor[4b] groups independently demonstrated a Cu-mediated intramolecular α-C(sp^3)-radical addition process to access oxindole derivatives in 2009. Alternatively, Liu and Li[4c] and Huo[4d] reported the elegant intermolecular Fe-catalyzed coupling of three-substituted oxindoles and 3,4-dihydro-1,4-benzoxazin-2-ones with electron-rich aromatics via a dehydrogenative coupling strategy, respectively. With our continuous interest in the transient mediator approach for the functionalization of arenes,[6] we envisioned that in-situ-generated aryl sulfonium salts could serve as an efficient arylating reagent, thus enabling the formal α-arylation of carbonyl compounds with simple arenes. Herein we present the site-selective thianthrenation-enabled α-arylation of carbonyl compounds with simple arenes with a broad substrate scope and heterocycle compatibility. This process also represents the first example of the Pd-catalyzed α-arylation of carbonyl compounds using an aryl sulfonium salt as an arylating reagent. Furthermore, this protocol provides an alternative strategy for the synthesis of α-arylated carbonyl compounds with high efficiency in comparison with the known methods with aryl halides (Scheme 1c).

Recently, the site-selective sulfonium salt formation and the sequent transformation have been demonstrated as a versatile strategy for the regioselective functionalization of simple arenes and complex bioactive molecules,[5−7] in which the thianthrenation[5b,6a] and phenoxathiination[6a] of simple arenes are noteworthy due to the remarkable regioselectivity gain in the sulfonium formation process.[5,6] Unlike aryl halides, normally accessed via an electrophilic process with low functional group tolerance and poor regioselectivity,[8] the aryl thianthrenium salts could be in situ generated in a highly regioselective manner under milder conditions. Thianthrene or phenoxathiine could be readily recovered after the reaction, which is different fromaryl halides.

Scheme 1. Transition-Metal-Catalyzed α-Arylation of Carbonyl Compounds



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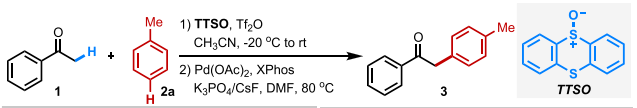
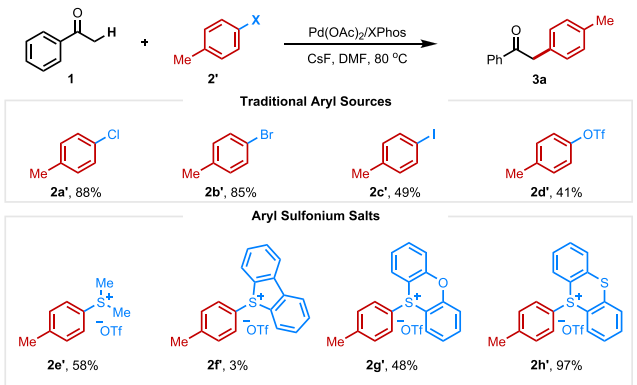
Scheme 2. Evaluation of Reaction Parameters[a,b]



Entry	Deviation from optimal conditions	Yield[b] (%)	Entry	Deviation from optimal conditions	Yield[b] (%)
1	none	99	9	Na_2CO_3 was used instead of K_3PO_4	86
2	without Pd/XPhos	-	10	KF was used instead of CsF	52
3	without K_3PO_4	67	11	Cs_2CO_3 was used instead of CsF	65
4	without CsF	51	12	$PdCl_2$ was used instead of $Pd(OAc)_2$	53
5	K_3PO_4 and CsF were added in one portion	81	13	$Pd(TFA)_2$ was used instead of $Pd(OAc)_2$	70
6	THF was used instead of DMF	72	14	$Pd(acac)_2$ was used instead of $Pd(OAc)_2$	8
7	1,4-dioxane was used instead of DMF	71	15	POSO was used instead of TTSO	71[c]
8	K_2CO_3 was used instead of K_3PO_4	87	16	DCM was used instead of CH_3CN	27

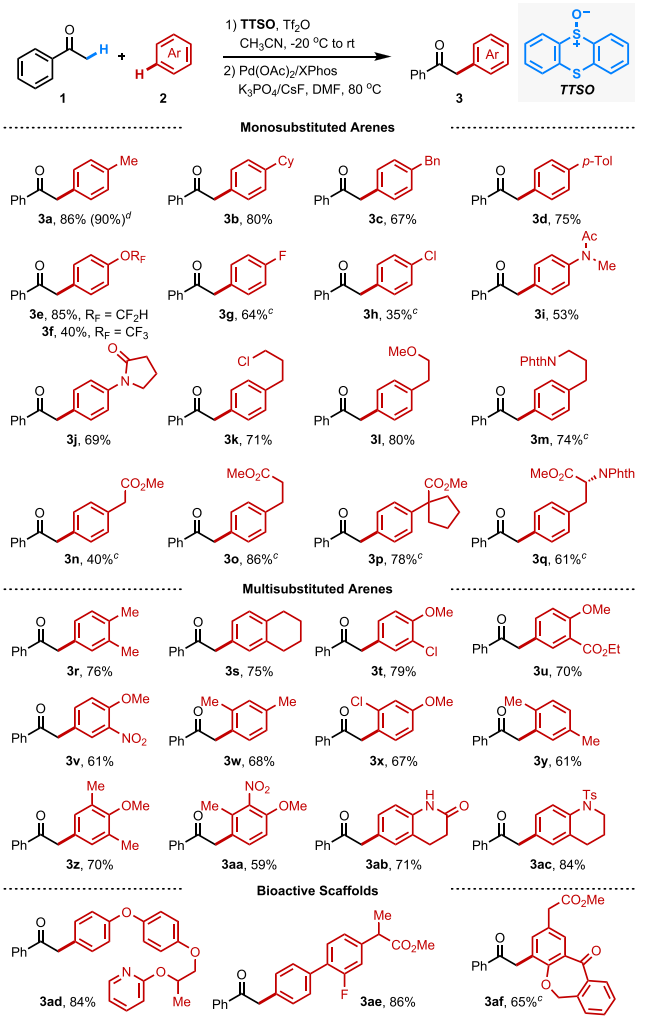
[a]Reaction conditions: (a) **2a** (0.2 mmol), **TTSO** (0.24 mmol), Tf_2O (0.24 mmol), CH_3CN (0.5 mL), N_2; −20 °C for 20 min, then rt for another 20 min. (b) K_3PO_4 (2.0 equiv) for 2 h, then $Pd(OAc)_2$ (10 mol %), XPhos (15 mol %), CsF (3.0 equiv), **1** (3.0 equiv), DMF (0.5 mL), 80 °C, 11 h. [b]Yields were determined by ^1H NMR using CH_2Br_2 as the internal standard. [c]Phenoxathiine 10-oxide (POSO) was used instead of TTSO.

Scheme 3. Reactivities of Aryl Sulfonium Salts



We started our investigation using toluene-derived thianthrenium salt **2h′** as an arylating reagent for the α-arylation of acetophenone (Scheme 2). After systematically evaluating the reaction parameters, we were glad to find that an 86% yield of the desired monoarylated product could be obtained in the presence of $Pd(OAc)_2$ (5.0 mol %) and XPhos (5.0 mol %) in DMF using CsF (3.0 equiv) as a base. However, the further application of those conditions to the one-pot process led to only a 10% yield using DCM as the solvent in the thianthrenation step. After a quick investigation of the one-pot process, a 99% yield of the desired product was obtained using CH_3CN as the solvent for the sulfonium salt formation step and K_3PO_4 as the base to adjust the pH value of the reaction system. Control experiments unveiled that all reaction parameters are crucial to the formal α-arylation of ketone with sample arenes. The reaction did not proceed in the absence of palladium acetate and phosphine ligand. Both K_3PO_4 and CsF are important for the high efficiency of this transformation. The addition of K_3PO_4 and CsF in one portion also slightly decreased the efficiency. Other solvents (entries 6 and 7), bases (entries 8−11), and catalysts (entries 12−14) all led to the drop in the yields. Notably, phenoxathiine 10-oxide (POSO) was also an efficient mediator for this process with high regioselectivity, albeit with a lower yield (entry 15). Although DCM could be tolerated in several Pd-catalyzed TTSO-mediated late-stage functionalizations of simple arenes

Scheme 4. Scope of Arenes[a,b]



[a]Reaction conditions: (a) **2** (0.2 mmol), TTSO (0.24 mmol), Tf_2O (0.24 mmol), CH_3CN (0.5 mL), N_2; −20 °C for 20 min, then rt for another 20 min. (b) K_3PO_4 (2.0 equiv) was added for 2 h; then $Pd(OAc)_2$ (10 mol %), XPhos (15 mol %), CsF (3.0 equiv), **1** (3.0 equiv), DMF (0.5 mL), 80 °C, 11 h. [b]Isolated yield. [c]CH_3CN (0.2 mL) was used. [d]Gram scale.

in one pot, this solvent showed insufficient compatibility with our newly developed process (entry 16).

To gain more information regarding the reactivities of aryl sulfonium salts in the Pd-catalyzed α-arylation of carbonyl compounds, the control experiments with various aryl halides, aryl triflates, and aryl sulfonium salts under our optimal conditions were conducted (Scheme 3). Surprisingly, thianthrenium salt **2h′** gave the best outcome, in which aryl chloride **2a′** and aryl bromide **2b′** gave slightly lower yields along with the formation of a small amount of homocoupling byproducts. Aryl iodide **2c′**, normally a highly active coupling partner, showed high activity for the homocoupling side reaction. Aryl triflate **2d′** and phenoxathiinium salt **2g′** showed similar reactivities, resulting in moderate yields. With regard to the thianthrenium salt **2h′**, the dimethyl-thioether-derived sulfonium salt **2e′** provided the desired α-arylated product in moderate yield and the demethylation byproduct methyl *p*-tolyl sulfide in 29% yield. Interestingly, dibenzothiophene-

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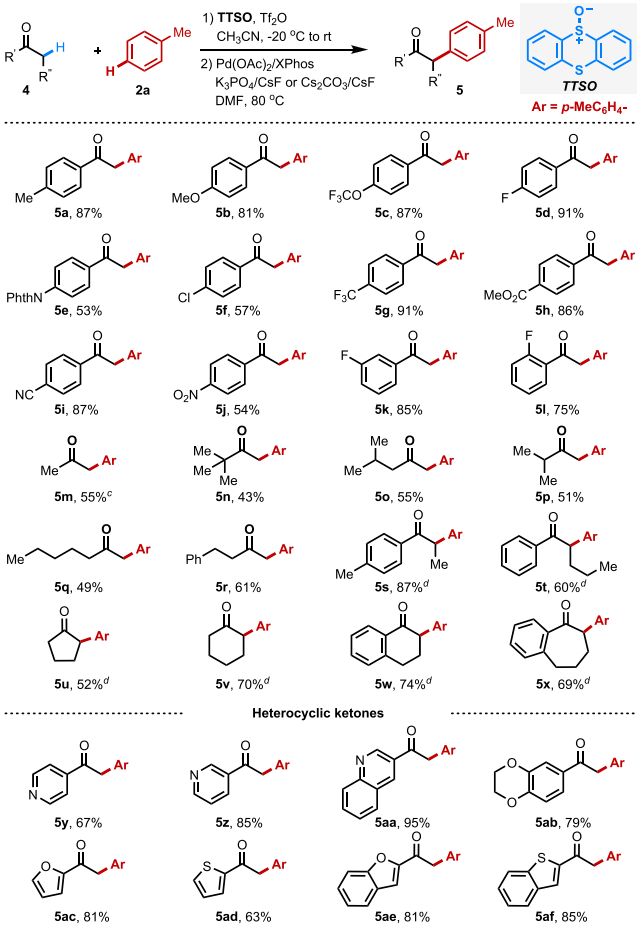
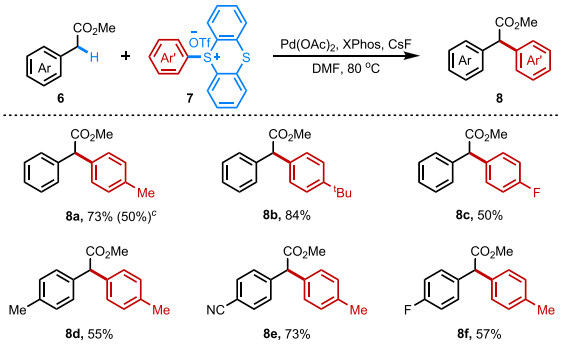
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 5. Scope of Ketones[a,b]



[a]Reaction conditions: (a) **2a** (0.2 mmol), TTSO (0.24 mmol), Tf_2O (0.24 mmol), CH_3CN (0.5 mL), N_2; −20 °C for 20 min, then rt for another 20 min. (b) K_3PO_4 (2.0 equiv) was added for 2 h, then $Pd(OAc)_2$ (10 mol %), XPhos (15 mol %), CsF (3.0 equiv), **4** (3.0 equiv), DMF (0.5 mL), 80 °C, 11 h. [b]Isolated yield. [c]21% yield of diarylated product (**5m′**) was obtained. [d]Cs_2CO_3 (2.0 equiv) was used instead of K_3PO_4.

Scheme 6. α-Arylation of Phenylacetate Derivatives[a,b]



[a]Reaction conditions: **6** (0.2 mmol), **7** (3.0 equiv), $Pd(OAc)_2$ (10 mol %), XPhos (15 mol %), CsF (5.0 equiv), DMF (1.0 mL), N_2, 80 °C, 11 h. [b]Isolated yield. [c]Reaction was conducted in one pot.

derived sulfonium salt **2f′** was less efficient under our standard conditions.

With the optimal conditions, we first examined the generality of arenes using acetophenone as the model substrate. Predictably, the remarkable site selectivity for simple arenes was dominated by electronics thanks to the regioselective thianthrenation via the highly electrophilic thianthrenium dication intermediate[5e,6a] (Scheme 4). Both electron-rich and electron-deficient arenes were suitable substrates for this protocol, albeit the electron-deficient aromatics provided the desired products in relatively lower yields (**2a−q**). This protocol could also apply to a wide range of disubstituted (**2r−y**) and trisubstituted arenes (**2z**, **2aa**), heterocyclic arenes (**2ab**, **2ac**), and complex bioactive molecules (**2ad−af**) with remarkable regioselectivities. It is noteworthy that the scalability of this process has been demonstrated using acetophenone as the model substrate, providing the desired product **3a** in 90% yield.

Next, the scope of ketones was evaluated to further check the breadth of this method. As depicted in Scheme 5, the electronic properties of the substituents on aromatic ring of acetophenone derivatives did not significantly affect the reaction outcomes (**5a−j**). Substrates with the fluoro group at the ortho, meta, or para position were all compatible with this one-pot protocol, in which *ortho*-fluoro-substituted acetophenone gave a slightly lower yield (**5l** vs **5d**, **5k**). In addition, the reaction with dialkyl ketones could proceed at the less steric hindrance site, providing the corresponding arylated products in moderate yields (**5m−r**). The aryl alkyl ketones (**4s−t**) and cyclic ketones (**4u−x**), containing a methylene group, could also be arylated under our standard conditions in moderate to good yields. Most importantly, heterocycle-containing acetyl arenes, including pyridine, quinoline, 1,4-benzodioxan, furan, thiophene, benzofuran, and benzothiophene, were all tolerated with this protocol. The compatibility with heterocycles demonstrates that this methodology is highly valuable in medicinal chemistry.

The generality of this protocol was further demonstrated by the Pd-catalyzed α-arylation of phenylacetate derivatives using aryl thianthrenium salts as the arylating reagent (Scheme 6). Despite the fact that the one-pot process with arenes gave only moderate yields (see the Supporting Information), the direct arylation with the isolated aryl sulfonium salts could tolerate both the electron-rich and electron-deficient phenylacetate derivatives in moderate to good yields.

In summary, a Pd-catalyzed α-arylation of carbonyl compounds with arenes via in-situ-generated sulfonium salts was demonstrated for the first time. A series of ketones and phenylacetate derivatives are tolerated with high efficiency. This protocol is also compatible with heterocyclic substrates and complex bioactive molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02913.

Experimental procedures, complete characterization data, and copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected reviews on the α-arylation of carbonyl compounds, see: (a) Lloyd-Jones, G. C. Palladium-Catalyzed α-Arylation of Esters: Ideal New Methodology for Discovery Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 953−956. (b) Culkin, D. A.; Hartwig, J. F. Palladium-Catalyzed α-Arylation of Carbonyl Compounds and Nitriles. *Acc. Chem. Res.* **2003**, *36*, 234−245. (c) Bellina, F.; Rossi, R. Transition Metal-Catalyzed Direct Arylation of Substrates with Activated sp^3-Hybridized C−H Bonds and Some of Their Synthetic Equivalents with Aryl Halides and Pseudohalides. *Chem. Rev.* **2010**, *110*, 1082−1146. (d) Johansson, C. C. C.; Colacot, T. J. Metal-Catalyzed α-Arylation of Carbonyl and Related Molecules: Novel Trends in C−C Bond Formation by C−H Bond Functionalization. *Angew. Chem., Int. Ed.* **2010**, *49*, 676−707. (e) Novak, P.; Martin, R. Pd-catalyzed α-Arylation of Carbonyl and Related Compounds: Recent Developments and Perspectives. *Curr. Org. Chem.* **2011**, *15*, 3233−3262. (f) Mazet, C. Challenges and Achievements in the Transition-Metal-Catalyzed Asymmetric α-Arylation of Aldehydes. *Synlett* **2012**, *23*, 1999−2004. (g) Sivanandan, S. T.; Shaji, A.; Ibnusaud, I.; Seechurn, C. C. C. J.; Colacot, T. J. Palladium-Catalyzed α-Arylation Reactions in Total Synthesis. *Eur. J. Org. Chem.* **2015**, *2015*, 38−49. (h) Vargová, D.; Némethová, I.; Plevová, K.; Šebesta, R. Asymmetric Transition-Metal Catalysis in the Formation and Functionalization of Metal Enolates. *ACS Catal.* **2019**, *9*, 3104−3143. (i) Hao, Y.-J.; Hu, X.-S.; Zhou, Y.; Zhou, J.; Yu, J.-S. Catalytic Enantioselective α-Arylation of Carbonyl Enolates and Related Compounds. *ACS Catal.* **2020**, *10*, 955−993.

(2) For selected examples on the transition-metal-catalyzed α-arylation of carbonyl compounds with aryl halides or their variants, see: (a) Palucki, M.; Buchwald, S. L. Palladium-Catalyzed α-Arylation of Ketones. *J. Am. Chem. Soc.* **1997**, *119*, 11108−11109. (b) Hamann, B. C.; Hartwig, J. F. Palladium-Catalyzed Direct α-Arylation of Ketones. Rate Acceleration by Sterically Hindered Chelating Ligands and Reductive Elimination from a Transition Metal Enolate Complex. *J. Am. Chem. Soc.* **1997**, *119*, 12382−12383. (c) Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. Palladium-Catalyzed Regioselective Mono- and Diarylation Reactions of 2-Phenylphenols and Naphthols with Aryl Halides. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740−1742. (d) Åhman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. Asymmetric Arylation of Ketone Enolates. *J. Am. Chem. Soc.* **1998**, *120*, 1918−1919. (e) Satoh, T.; Inoh, J.-i.; Kawamura, Y.; Kawamura, Y.; Miura, M.; Nomura, M. Regioselective Arylation Reactions of Biphenyl-2-ols, Naphthols, and Benzylic Compounds with Aryl Halides under Palladium Catalysis. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2239−2246. (f) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. Well-Defined, Air-Stable (NHC)Pd(Allyl)Cl (NHC = *N*-Heterocyclic Carbene) Catalysts for the Arylation of Ketones. *Org. Lett.* **2002**, *4*, 4053−4056. (g) Spielvogel, D. J.; Buchwald, S. L. Nickel-BINAP Catalyzed Enantioselective α-Arylation of α-Substituted γ-Butyrolactones. *J. Am. Chem. Soc.* **2002**, *124*, 3500−3501. (h) Liao, X.; Weng, Z.; Hartwig, J. F. Enantioselective α-Arylation of Ketones with Aryl Triflates Catalyzed by Difluorphos Complexes of Palladium and Nickel. *J. Am. Chem. Soc.* **2008**, *130*, 195−200. (i) Ge, S.; Hartwig, J. F. Nickel-Catalyzed Asymmetric α-Arylation and Heteroarylation of Ketones with Chloroarenes: Effect of Halide on Selectivity, Oxidation State, and Room-Temperature Reactions. *J. Am. Chem. Soc.* **2011**, *133*, 16330−16333. (j) Cornella, J.; Jackson, E. P.; Martin, R. Nickel-Catalyzed Enantioselective C−C Bond Formation through C−O Cleavage in Aryl Esters. *Angew. Chem., Int. Ed.* **2015**, *54*, 4075−4078. (k) Jiao, Z.; Beiger, J. J.; Jin, Y.; Ge, S.; Zhou, J. S.; Hartwig, J. F. Palladium-Catalyzed Enantioselective α-Arylation of α-Fluoroketones. *J. Am. Chem. Soc.* **2016**, *138*, 15980−15986. (l) Xu, Y.; Su, T.; Huang, Z.; Dong, G. Practical Direct α-Arylation of Cyclopentanones by Palladium/Enamine Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55*, 2559−2563. (m) Rao, X.; Li, N.; Bai, H.; Dai, C.; Wang, Z.; Tang, W. Efficient Synthesis of (−)-Corynoline by Enantioselective Palladium-Catalyzed α-Arylation with Sterically Hindered Substrates. *Angew. Chem., Int. Ed.* **2018**, *57*, 12328−12332.

(3) (a) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. Beyond Directing Groups: Transition-Metal-Catalyzed C−H Activation of Simple Arenes. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236−10254. (b) Hartwig, J. F.; Larsen, M. A. Undirected, Homogeneous C−H Bond Functionalization: Challenges and Opportunities. *ACS Cent. Sci.* **2016**, *2*, 281−292. (c) Wedi, P.; van Gemmeren, M. Arene-Limited Nondirected C−H Activation of Arenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 13016−13027.

(4) (a) Jia, Y.-X.; Kündig, E. P. Oxindole Synthesis by Direct Coupling of C−H and C−H Centers. *Angew. Chem., Int. Ed.* **2009**, *48*, 1636−1639. (b) Perry, A.; Taylor, R. J. K. Oxindole Synthesis by Direct C−H, Ar−H Coupling. *Chem. Commun.* **2009**, 3249−3251. (c) Wu, H.-R.; Huang, H.-Y.; Ren, C.-L.; Liu, L.; Wang, D.; Li, C.-J. Fe^{III}-Catalyzed Cross-Dehydrogenative Arylation (CDA) between Oxindoles and Arenes under an Air Atmosphere. *Chem. - Eur. J.* **2015**, *21*, 16744−16748. (d) Huo, C.; Dong, J.; Su, Y.; Tang, J.; Chen, F. Iron-Catalyzed Oxidative sp^3 Carbon−Hydrogen Bond Functionalization of 3,4-Dihydro-1,4-benzoxazin-2-ones. *Chem. Commun.* **2016**, *52*, 13341−13344.

(5) For selected examples on the site-selective functionalization of arenes via sulfonium salts, see: (a) 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. (b) Engl, P. S.; Häring, A. P.; Berger, F.; Berger, G.; Pérez-Bitrián, A.; Ritter, T. C−N Cross-Couplings for Site-Selective Late-Stage Diversification via Aryl Sulfonium Salts. *J. Am. Chem. Soc.* **2019**, *141*, 13346−13351. (c) Ye, F.; Berger, F.; Jia, H.; Ford, J.; Wortman, A.; Börgel, J.; Genicot, C.; Ritter, T. Aryl Sulfonium Salts for Site-Selective Late-Stage Trifluoromethylation. *Angew. Chem., Int. Ed.* **2019**, *58*, 14615−14619. (d) Li, J.; Chen, J.; Sang, R.; Ham, W.-S.; Plutschack, M. B.; Berger, F.; Chabbra, S.; Schnegg, A.; Genicot, C.; Ritter, T. Photoredox catalysis with aryl sulfonium salts enables site-selective late-stage fluorination. *Nat. Chem.* **2020**, *12*, 56−62. (e) Chen, J.; Li, J.; Plutschack, M. B.; Berger, F.; Ritter, T. Regio- and Stereoselective Thianthrenation of Olefins to Access Versatile Alkenyl Electrophiles. *Angew. Chem., Int. Ed.* **2020**, *59*, 5616−5620. (f) Aukland, M. H.; Šiaučiulis, M.; West, A.; Perry, G. J. P.; Procter, D. J. Metal-free photoredox-catalysed formal C−H/C−H coupling of arenes enabled by interrupted Pummerer activation. *Nat. Catal.* **2020**, *3*, 163−169. (g) Selmani, A.; Gevondian, A. G.; Schoenebeck, F. Germylation of

Arenes via Pd(I) Dimer Enabled Sulfonium Salt Functionalization. *Org. Lett.* **2020**, *22*, 4802−4805. (h) Alvarez, E. M.; Plutschack, M. B.; Berger, F.; Ritter, T. Site-Selective C−H Functionalization−Sulfination Sequence to Access Aryl Sulfonamides. *Org. Lett.* **2020**, *22*, 4593−4596.

(6) (a) Wu, J.; Wang, Z.; Chen, X.-Y.; Wu, Y.; Wang, D.; Peng, Q.; Wang, P. Para-Selective Borylation of Monosubstituted Benzenes Using a Transient Mediator. *Sci. China: Chem.* **2020**, *63*, 336−340. (b) Chen, X.-Y.; Nie, X.-X.; Wu, Y.; Wang, P. Para-Selective Arylation and Alkenylation of Monosubstituted Arenes Using Thianthrene S-oxide as a Transient Mediator. *Chem. Commun.* **2020**, *56*, 5058−5061. (c) Chen, X.-Y.; Huang, Y.-H.; Zhou, J.; Wang, P. Pd-Catalyzed Site-Selective Borylation of Simple Arenes via Thianthrenation. *Chin. J. Chem.* **2020**, *38*, 1269−1272. (d) Wu, Y.; Huang, Y.-H.; Chen, X.-Y.; Wang, P. *Org. Lett.* **2020**, *22*, 6657−6661.

(7) For reviews on sulfonium salt chemistry, see: (a) Nenaidenko, V. G.; Balenkova, E. S. New Synthetic Capabilities of Sulfonium Salts. *Russ. J. Org. Chem.* **2003**, *39*, 291−330. (b) Tian, Z.-Y.; Hu, Y.-T.; Teng, H.-B.; Zhang, C.-P. Application of arylsulfonium salts as arylation reagents. *Tetrahedron Lett.* **2018**, *59*, 299−309. (c) Kaiser, D.; Klose, I.; Oost, R.; Neuhaus, J.; Maulide, N. Bond-Forming and -Breaking Reactions at Sulfur(IV): Sulfoxides, Sulfonium Salts, Sulfur Ylides, and Sulfinate Salts. *Chem. Rev.* **2019**, *119*, 8701−8780. Fan, R.; Tan, C.; Liu, Y.; Wei, Y.; Zhao, X.; Liu, X.; Tan, J.; Yoshida, H. A leap forward in sulfonium salt and sulfur ylide chemistry. *Chin. Chem. Lett.* **2020**, DOI: 10.1016/j.cclet.2020.06.003. (e) Kozhushkov, S. I.; Alcarazo, M. Synthetic Applications of Sulfonium Salts. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2486−2500. (f) Péter, Á.; Perry, G. J. P.; Procter, D. J. Radical C−C Bond Formation using Sulfonium Salts and Light. *Adv. Synth. Catal.* **2020**, *362*, 2135−2142. For selected examples, see: (g) Srogl, J.; Allred, G. D.; Liebeskind, L. S. Sulfonium salts. Participants par excellence in metal-catalyzed carbon−carbon bond-forming reactions. *J. Am. Chem. Soc.* **1997**, *119*, 12376−12377. (h) Cowper, P.; Jin, Y.; Turton, M. D.; Kociok-Köhn, G.; Lewis, S. E. Azulenesulfonium salts: accessible, stable, and versatile reagents for cross-coupling. *Angew. Chem., Int. Ed.* **2016**, *55*, 2564−2568. (i) Wang, S.-M.; Wang, X.-Y.; Qin, H.-L.; Zhang, C.-P. Palladium-catalyzed arylation of arylboronic acids with Yagupolskii−Umemoto reagents. *Chem. - Eur. J.* **2016**, *22*, 6542−6546. (j) Minami, H.; Nogi, K.; Yorimitsu, H. Palladium-catalyzed alkoxycarbonylation of arylsulfoniums. *Org. Lett.* **2019**, *21*, 2518−2522. (k) Minami, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. Palladium-catalyzed borylation of aryl sulfoniums with diborons. *ACS Catal.* **2018**, *8*, 579−583. (l) Aukland, M. H.; Talbot, F. J. T.; Fernández-Salas, J. A.; Ball, M.; Pulis, A. P.; Procter, D. J. An interrupted Pummerer/Nickel-catalysed cross-coupling sequence. *Angew. Chem., Int. Ed.* **2018**, *57*, 9785−9789. (m) Zhao, J.-N.; Kayumov, M.; Wang, D.-Y.; Zhang, A. Transition-metal-free aryl−heteroatom bond formation via C−S bond cleavage. *Org. Lett.* **2019**, *21*, 7303−7306. (n) Kafuta, K.; Korzun, A.; Böhm, M.; Golz, C.; Alcarazo, M. Synthesis, Structure, and Reactivity of 5-(Aryl)dibenzothiophe nium Triflates. *Angew. Chem., Int. Ed.* **2020**, *59*, 1950−1955.

(8) (a) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990. (b) de la Mare, P. B. *Electrophilic Halogenation*; Elmore, D. T., Leadbetter, A., Schofield, K., Eds.; Cambridge University Press: Cambridge, U.K., 1976; Chapter 5. (c) Olah, G. A. Aromatic Substitution. XXVIII. Mechanism of Electrophilic Aromatic Substitutions. *Acc. Chem. Res.* **1971**, *4*, 240−248.

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