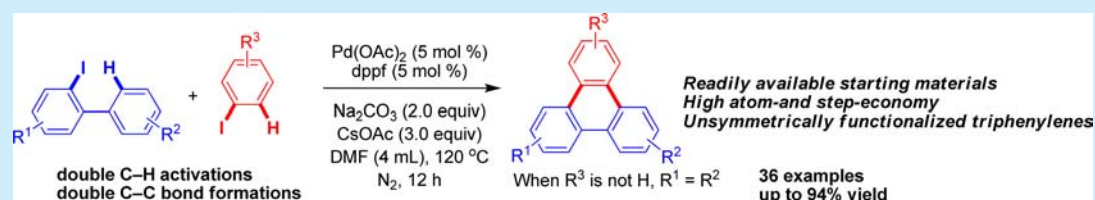


# Synthesis of Triphenylenes Starting from 2-Iodobiphenyls and Iodobenzenes via Palladium-Catalyzed Dual C–H Activation and Double C–C Bond Formation

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**S** Supporting Information



**ABSTRACT:** A novel and facile approach for the synthesis of triphenylenes has been developed via palladium-catalyzed coupling of 2-iodobiphenyls and iodobenzenes. The reaction involves dual palladium-catalyzed C–H activations and double palladium-catalyzed C–C bond formations. A range of unsymmetrically functionalized triphenylenes can be synthesized with the reaction. The approach features readily available starting materials, high atom- and step-economy, and access to various unsymmetrically functionalized triphenylenes.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of organic molecules due to their widespread applications in various fields.<sup>1</sup> Among these, triphenylenes are particularly interesting. As the smallest example of all-benzenoid polycyclic aromatic hydrocarbons, triphenylene has the same fundamental skeleton as many other PAHs and can act as a precursor to synthesize these PAHs.<sup>2</sup> More importantly, triphenylenes have great application potentials in supramolecular and materials chemistry.<sup>3</sup> Triphenylenes have been employed to make functional organic materials such as discotic liquid crystals and organic light-emitting diodes.<sup>4</sup>

Over the past decades, interest in the chemistry of triphenylenes has increased continuously, and the synthesis of triphenylenes has attracted considerable attention.<sup>5</sup> To date, a variety of synthetic strategies for triphenylenes have been developed. One of the common strategies involves the cyclization of *o*-terphenyls.<sup>6</sup> A second popular approach for the synthesis of triphenylenes is the trimerization of arynes.<sup>7</sup> This approach is primarily limited to the synthesis of symmetrical triphenylenes. Furthermore, a variety of other interesting synthetic means are available.<sup>8</sup> More recently, palladium catalysis based methods have gained great attention as they offer facile and efficient strategies for the synthesis of triphenylenes. Miura and co-workers found that *o*-dibromobenzenes could undergo Pd-catalyzed coupling reaction with *o*-phenylbenzyl alcohols to form triphenylenes.<sup>9</sup> The Larock group disclosed a novel method for the synthesis of substituted triphenylenes via the palladium-catalyzed annulation of *o*-iodobiphenyls with arynes.<sup>10</sup> The Cheng group developed the carbocyclization of arynes with aryl iodides,<sup>11</sup> and the Zhang

group realized the coupling of arynes with 1-(2-bromophenyl)-1*H*-indole.<sup>12</sup> Nishihara and co-workers reported the annulation of *o*-iodobiphenyls with *o*-bromobenzyl alcohols under palladium catalysis, providing an efficient method for the synthesis of highly substituted triphenylenes.<sup>4d,13</sup> Other palladium-catalyzed examples include double cross-coupling of 9-stannafuorenes with 1,2-dibromoarenes,<sup>14</sup> double cross-coupling of 1,2-bis(pinacolatoboryl)arenes with 2,2'-dibromobiaryls,<sup>15</sup> and the intramolecular cyclization of terarylsulfonium salts obtained from dibenzothiophenes.<sup>16</sup> Although these reactions offer versatile methods for the synthesis of triphenylenes, it is still desirable to develop general and facile methods starting from readily available substrates for the synthesis of triphenylenes, particularly substituted ones, which play important roles in materials chemistry.<sup>3a–c</sup>

Recently, our group disclosed that dibenzopalladacyclopentadienes have intriguing reactivities and have been exploited to develop facile and practical synthetic methods.<sup>17</sup> During the research on the synthesis of tetraphenylenes, we isolated a small amount of triphenylene when iodobenzene was added.<sup>17a</sup> Unfortunately, in spite of our great efforts, we failed to improve the yield of triphenylene. Dibenzopalladacyclopentadienes can also be generated from 2-iodobiphenyls under basic conditions,<sup>17b,c</sup> so we envisioned that triphenylenes could be formed by the coupling of 2-iodobiphenyl with iodobenzene under the basic conditions. Herein, we report a new method for the synthesis of triphenylenes starting from readily available

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substrates 2-iodobiphenyls and iodobenzenes under palladium catalysis.

We initiated our research by investigating the coupling reaction of 2-iodobiphenyl and iodobenzene. After extensive screening, we obtained the desired triphenylene in 38% yield when the reaction was carried out in DMF in the presence of Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, and KOAc under N<sub>2</sub> atmosphere (Table 1,

**Table 1. Optimization of Reaction Conditions for the Pd-Catalyzed Formation of Triphenylene from 2-Iodobiphenyl and Iodobenzene**

entry	base 1 (2 equiv)	base 2 (3 equiv)	ligand (mol %)	solvent (4 mL)	yield <sup>a</sup> (%)
1 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc		DMF	38
2 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc	PPh <sub>3</sub> (20)	DMF	41
3 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc	L1 (10)	DMF	48
4 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc	L2 (10)	DMF	46
5 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc	L3 (10)	DMF	49
6 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	KOAc	dppf (10)	DMF	60
7	K <sub>2</sub> CO <sub>3</sub>	KOAc	dppf (5)	DMF	63
8	Na <sub>2</sub> CO <sub>3</sub>	KOAc	dppf (5)	DMF	63
9	Na <sub>2</sub> CO <sub>3</sub>	NaOAc	dppf (5)	DMF	45
10	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF	71 (70) <sup>c</sup>
11	Na <sub>2</sub> CO <sub>3</sub>		dppf (5)	DMF	43
12		CsOAc	dppf (5)	DMF	35
13	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	NMP	50
14	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMSO	41
15	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	<i>t</i> -BuOH	4
16	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	THF	6
17	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF <sup>d</sup>	55
18	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF	10 <sup>e</sup>
19	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF	52 <sup>f</sup>
20	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF	47 <sup>g</sup>
21	Na <sub>2</sub> CO <sub>3</sub>	CsOAc	dppf (5)	DMF	64 <sup>h</sup>

<sup>a</sup>The yields were determined by <sup>1</sup>H NMR analysis of the crude reaction mixtures using CHCl<sub>3</sub>CHCl<sub>2</sub> as the internal standard.

<sup>b</sup>Pd(OAc)<sub>2</sub> (10 mol %). <sup>c</sup>Isolated yield. <sup>d</sup>2 mL. <sup>e</sup>100 °C. <sup>f</sup>140 °C.

<sup>g</sup>1 equiv of PhI. <sup>h</sup>2 equiv of PhI. L1: PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>. L2: PPh<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>. L3: bis(dicyclohexylphosphino)ferrocene. dppf: 1, 1'-bis(diphenylphosphino)ferrocene.

entry 1). However, further efforts failed to improve the yield, so we sought the aid of ligands. While PPh<sub>3</sub> gave a similar yield (entry 2), the use of a bidentate phosphine ligand led to a slight increase in yield (entries 3–5). The yield was improved to 60% when dppf was employed (entry 6). Notably, the yield remained almost unchanged when the loadings of Pd(OAc)<sub>2</sub> and the ligand were reduced to 5 mol % (entry 7). Next, we examined the impact of bases on the reaction. We found that replacing K<sub>2</sub>CO<sub>3</sub> with Na<sub>2</sub>CO<sub>3</sub> resulted in an identical yield (entry 8). However, while a combination of Na<sub>2</sub>CO<sub>3</sub> and NaOAc gave a lower yield (entry 9), a 71% yield was obtained in the presence of Na<sub>2</sub>CO<sub>3</sub> and CsOAc (entry 10). Furthermore, the absence of Na<sub>2</sub>CO<sub>3</sub> or CsOAc led to a much lower yield (entries 11 and 12). The reason remains to be investigated. The effect of solvents was also examined. The reactions in NMP or DMSO were lower yielding, and only a

small amount of triphenylene was observed for the reactions in *t*-BuOH or THF (entries 13–16). In addition, the reaction in 2 mL of DMF was less effective (entry 17), and the yields decreased when the reaction was carried out at a higher or lower temperature (entries 18 and 19). Finally, the use of 1 or 2 equiv of PhI resulted in lower yields (entries 20 and 21).

Having developed an efficient procedure for the synthesis of triphenylene, we next investigated the substrate scope of this transformation. We first examined the performance of a range of 2-iodobiphenyls under the optimized reaction conditions. Therefore, as shown in Table 2, 2-iodobiphenyls bearing a methoxy group at the 3' or 4' position coupled with iodobenzene (entries 1 and 2). It is noted that the reaction selectively occurred at the less hindered position for **1c**, so the reactions of **1b** and **1c** formed the same product **3ba**. The substrate bearing 2'-methoxy group was also suitable, albeit in a lower yield (entry 3). The substrates bearing a methyl or phenyl group were also reactive (entries 4–6). A range of electron-withdrawing substituents were then examined. The trifluoromethyl group was well-tolerated, and triphenylenes were formed in good or excellent yields (entries 7 and 8). However, other electron-withdrawing groups including ester, carbonyl, and nitro gave much lower yields (entries 9–11). In these reactions, a portion of 2-iodobiphenyls was recovered. The reason could be that it is difficult to cleave the C–H bonds of the electron-deficient benzene. Both fluoro and chloro groups, on the iodo-containing benzene ring or the other phenyl group, were well-tolerated under the standard conditions (entries 12–15). 2-Iodobiphenyl bearing two methyl groups was also reactive (entry 16). Furthermore, symmetrically substituted substrates, containing phenyl or trifluoromethyl groups, underwent the double coupling reaction, albeit in lower yields (entries 17 and 18). It is noted that unsymmetrically substituted 2-iodobiphenyls were suitable, affording unsymmetrically functionalized triphenylenes (entries 19 and 20).

Next, the iodobenzene scope was examined. The methoxy groups at the *para* and *meta* positions were compatible, and the reactions afforded methoxylated triphenylene in 91% or 74% yield (entries 21 and 22). It should be mentioned that the reaction for **2c** took place at the less hindered position, forming the same product as that for **2b**. In a similar way, iodobenzenes containing a *m*- or *p*-methyl group formed the same product **3ea** (entries 23 and 24). The chloro and fluoro groups were tolerated in the reaction (entries 25–27), and the reactions of **2g** and **2h** formed the same product **3pa**. 4-Iodobiphenyl and 1-(difluoromethoxy)-4-iodobenzene were also suitable (entries 28 and 29). The reactions of iodobenzenes bearing electron-withdrawing groups such as trifluoromethyl and ester were low yielding (entries 30 and 31). The major reason was that these electron-deficient iodobenzenes tended to undergo homocoupling to form biphenyl byproducts. Bromobenzene was also reactive, albeit in a low yield (entry 32). To obtain multiple substituted triphenylene derivatives, we also examined the reaction of substituted iodobenzenes and 2-iodobiphenyls.

4-Iodoanisole reacted with symmetrically substituted 2-iodobiphenyls to afford multiply substituted triphenylenes in moderate yields (entries 33–35). When unsymmetrically substituted 2-iodobiphenyls were used, two regioisomers were formed (entry 36).

While the detailed mechanism of the reaction remains to be investigated and other reaction pathways cannot be ruled out, based on our previous works, a tentative mechanism can be

Table 2. Substrate Scope with Respect to 2-Iodobiphenyls

entry	substrate	product <sup>a</sup>	entry	substrate	product <sup>a</sup>	entry	substrate	product <sup>a</sup>	entry	substrate	product <sup>a</sup>
1	1b: R <sup>1</sup> = H R <sup>2</sup> = 4'-OMe 2a: R <sup>3</sup> = H	3ba, 76%	10	1k: R <sup>1</sup> = H R <sup>2</sup> = 4'-COCH <sub>3</sub> 2a: R <sup>3</sup> = H	3ka, 32%	19	1t: R <sup>1</sup> = 4-Cl R <sup>2</sup> = 4'-Me 2a: R <sup>3</sup> = H	3ta, 73%	28	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2i: R <sup>3</sup> = 4-Ph	3ga, 60%
2	1c: R <sup>1</sup> = H R <sup>2</sup> = 3'-OMe 2a: R <sup>3</sup> = H	3ba, 81%	11	1l: R <sup>1</sup> = H R <sup>2</sup> = 3'-NO <sub>2</sub> 2a: R <sup>3</sup> = H	3la, 32%	20	1u: R <sup>1</sup> = 5-Me R <sup>2</sup> = 4'-Me 2a: R <sup>3</sup> = H	3ua, 77%	29	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2j: R <sup>3</sup> = 4-OCHF <sub>2</sub>	3aj, 50%
3	1d: R <sup>1</sup> = H R <sup>2</sup> = 2'-OMe 2a: R <sup>3</sup> = H	3da, 60%	12	1m: R <sup>1</sup> = H R <sup>2</sup> = 3'-Cl 2a: R <sup>3</sup> = H	3ma, 71%	21	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2b: R <sup>3</sup> = 4-OMe	3ba, 91%	30	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2k: R <sup>3</sup> = 4-CF <sub>3</sub>	3ha, 44%
4	1e: R <sup>1</sup> = H R <sup>2</sup> = 3'-Me 2a: R <sup>3</sup> = H	3ea, 76%	13	1n: R <sup>1</sup> = 5-Cl R <sup>2</sup> = H 2a: R <sup>3</sup> = H	3ma, 55%	22	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2c: R <sup>3</sup> = 3-OMe	3ba, 74%	31	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2l: R <sup>3</sup> = 4-CO <sub>2</sub> Me	3ja, 32%
5	1f: R <sup>1</sup> = H R <sup>2</sup> = 2'-Me 2a: R <sup>3</sup> = H	3fa, 66%	14	1o: R <sup>1</sup> = H R <sup>2</sup> = 2'-F 2a: R <sup>3</sup> = H	3oa, 72%	23	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2d: R <sup>3</sup> = 4-Me	3ea, 72%	32	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2m: 1-Bromo-4-chlorobenzene	3ma, 19%
6	1g: R <sup>1</sup> = H R <sup>2</sup> = 4'-Ph 2a: R <sup>3</sup> = H	3ga, 62%	15	1p: R <sup>1</sup> = 5-F R <sup>2</sup> = H 2a: R <sup>3</sup> = H	3pa, 65%	24	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2e: R <sup>3</sup> = 3-Me	3ea, 67%	33	1v: R <sup>1</sup> = 4-Me R <sup>2</sup> = 4'-Me 2b: R <sup>3</sup> = 4-OMe	3vb, 56%
7	1h: R <sup>1</sup> = H R <sup>2</sup> = 4'-CF <sub>3</sub> 2a: R <sup>3</sup> = H	3ha, 94%	16	1q: R <sup>1</sup> = H R <sup>2</sup> = 3'-Me, 4'-Me 2a: R <sup>3</sup> = H	3qa, 79%	25	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2f: R <sup>3</sup> = 4-Cl	3ma, 44%	34	1w: R <sup>1</sup> = 4-Cl R <sup>2</sup> = 4'-Cl 2b: R <sup>3</sup> = 4-OMe	3wb, 66%
8	1i: R <sup>1</sup> = H R <sup>2</sup> = 3'-CF <sub>3</sub> 2a: R <sup>3</sup> = H	3ha, 81%	17	1r: R <sup>1</sup> = 5-Ph R <sup>2</sup> = 3'-Ph 2a: R <sup>3</sup> = H	3ra, 57%	26	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2g: R <sup>3</sup> = 4-F	3pa, 55%	35	1x: R <sup>1</sup> = 4-OMe, 5-OMe R <sup>2</sup> = 3'-OMe, 4'-OMe 2b: R <sup>3</sup> = 4-OMe	3xb, 55%
9	1j: R <sup>1</sup> = H R <sup>2</sup> = 4'-CO <sub>2</sub> Me 2a: R <sup>3</sup> = H	3ja, 56%	18	1s: R <sup>1</sup> = 5-CF <sub>3</sub> R <sup>2</sup> = 3'-CF <sub>3</sub> 2a: R <sup>3</sup> = H	3sa, 46%	27	1a: R <sup>1</sup> = H R <sup>2</sup> = H 2h: R <sup>3</sup> = 3-F	3pa, 50%	36	1t: R <sup>1</sup> = 4-Cl R <sup>2</sup> = 4'-Me 2b: R <sup>3</sup> = 4-OMe 3tb-A R <sup>4</sup> = H, R <sup>5</sup> = OMe 3tb-B R <sup>4</sup> = OMe, R <sup>5</sup> = H	3tb, 62% <sup>b</sup>

<sup>a</sup>Yields are those of purified and isolated products. <sup>b</sup>The ratio of the two isomers is 1:2.44.

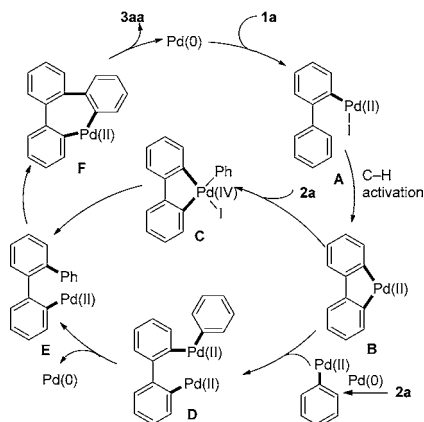
proposed as shown in Scheme 1. Therefore, the catalytic cycle should begin with the oxidative addition of 2-iodobiphenyl to Pd(0) to form complex A. Intramolecular C–H activation yields palladacycle B. Next, B undergo oxidative addition with iodobenzene to give Pd(IV) complex C. The subsequent reductive elimination generates Pd(II) complex E. At this stage, an alternative pathway for the formation of E from B cannot be ruled out. Complex B could undergo transmetalation-type exchange of aryl ligands with the phenylpalladium(II) species, which is formed by the oxidative addition of iodobenzene to

Pd(0) to afford dinuclear arylpalladium complex D.<sup>18</sup> The reductive elimination of complex D leads to complex E.

In conclusion, a novel and facile approach for the synthesis of triphenylenes has been developed. The starting materials 2-iodobiphenyls and iodobenzenes are readily available. The reaction involves two palladium-catalyzed C–H activations and two palladium-catalyzed C–C bond formation steps, which makes the reaction atom- and step-economic. A range of unsymmetrically functionalized triphenylenes can be synthesized with this method. Therefore, the approach features readily



**Scheme 1. Proposed Mechanism for the Pd-Catalyzed Formation of Triphenylene from 2-Iodobiphenyl and Iodobenzene<sup>a</sup>**



<sup>a</sup>Complex E undergo a second intramolecular C–H activation to give complex F.<sup>19</sup> The final reductive elimination generates triphenylene and releases a Pd(0) species to initiate a second catalytic cycle.

available starting materials, atom- and step-economy, and comparatively broad substrate scope. A tentative mechanism involved in the reaction has been proposed. Further studies aimed at elucidating the detailed mechanism and improving the reaction are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02071.

Detailed experimental procedures, spectroscopic data, and characterization of products (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley–VCH: Weinheim, 1997. (b) Boorum, M. M.; Scott, L. T. *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley–VCH: Weinheim, 2002; pp20–31. (c) Harvey, R. G. *Curr. Org. Chem.* **2004**, *8*, 303. (d) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994. (e) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (f) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (g) Feng, X.; Pisula, W.; Müllen, K. *Pure Appl. Chem.* **2009**, *81*, 2203. (h) Zhang, H.; Wu, D.; Hua Liu, S.; Yin, J. *Curr. Org. Chem.* **2012**, *16*, 2124.
- (2) Wei, J.; Jia, X.; Yu, J.; Shi, X.; Zhang, C.; Chen, Z. *Chem. Commun.* **2009**, 4714.

- (3) (a) Buess, C. M.; Lawson, D. D. *Chem. Rev.* **1960**, *60*, 313. (b) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals*; Taylor and Francis: London, 1997. (c) Watson, M.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (d) Tschierske, C. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2001**, *97*, 191.
- (4) (a) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83. (b) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (c) Togashi, K.; Nomura, S.; Yokoyama, N.; Yasuda, T.; Adachi, C. *J. Mater. Chem.* **2012**, *22*, 20689. (d) Iwasaki, M.; Iino, S.; Nishihara, Y. *Org. Lett.* **2013**, *15*, 5326.
- (5) Pérez, D.; Guitián, E. *Chem. Soc. Rev.* **2004**, *33*, 274.
- (6) (a) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279. (b) Allemann, O.; Duttwyler, S.; Romanato, P.; Balbridge, K. K.; Siegel, J. S. *Science* **2011**, *332*, 574. (c) Amsharov, K. Y.; Merz, P. *J. Org. Chem.* **2012**, *77*, 5445. (d) Feng, C.; Tian, X.-L.; Zhou, J.; Xiang, S.-K.; Yu, W.-H.; Wang, B.-Q.; Hu, P.; Redshaw, C.; Zhao, K.-Q. *Org. Biomol. Chem.* **2014**, *12*, 6977. (e) Daigle, M.; Soligo, E.; Morin, J.-F. *Angew. Chem., Int. Ed.* **2016**, *55*, 2042.
- (7) (a) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (c) Cant, A. A.; Roberts, L.; Greaney, M. F. *Chem. Commun.* **2010**, 46, 8671. (d) Chen, L.; Zhang, C.; Wen, C.; Zhang, K.; Liu, W.; Chen, Q. *Catal. Commun.* **2015**, *65*, 81.
- (8) See ref 5 and references cited therein.
- (9) Terao, Y.; Wakui, H.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem.* **2003**, *68*, 5236.
- (10) (a) Liu, Z.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 15716. (b) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 223.
- (11) Jayanth, T. T.; Cheng, C.-H. *Chem. Commun.* **2006**, 894.
- (12) Xie, C.; Zhang, Y.; Huang, Z.; Xu, P. *J. Org. Chem.* **2007**, *72*, 5431.
- (13) Iwasaki, M.; Araki, Y.; Iino, S.; Nishihara, Y. *J. Org. Chem.* **2015**, *80*, 9247.
- (14) Nagao, I.; Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 7573.
- (15) Shimizu, M.; Nagao, I.; Tomioka, Y.; Kadowaki, T.; Hiyama, T. *Tetrahedron* **2011**, *67*, 8014.
- (16) Vasu, D.; Yorimitsu, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7162.
- (17) (a) Jiang, H.; Zhang, Y.; Chen, D.; Zhou, B.; Zhang, Y. *Org. Lett.* **2016**, *18*, 2032. (b) Chen, D.; Shi, G.; Jiang, H.; Zhang, Y.; Zhang, Y. *Org. Lett.* **2016**, *18*, 2130. (c) Shi, G.; Chen, D.; Jiang, H.; Zhang, Y.; Zhang, Y. *Org. Lett.* **2016**, *18*, 2958.
- (18) (a) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. (b) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. (c) Suzuki, Y.; Yagyu, T.; Yamamura, Y.; Mori, A.; Osakada, K. *Organometallics* **2002**, *21*, 5254. (d) Cárdenas, D. J.; Martín-Matute, B.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 5033.
- (19) Recent reviews on C–H functionalization: (a) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900. (b) Minami, Y.; Hiyama, T. *Acc. Chem. Res.* **2016**, *49*, 67. (c) Gandeevan, P.; Cheng, C.-H. *Chem. - Asian J.* **2016**, *11*, 448. (d) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (e) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007. (f) Su, B.; Cao, Z.-C.; Shi, Z.-J. *Acc. Chem. Res.* **2015**, *48*, 886. (g) Liu, B.; Hu, F.; Shi, B.-F. *ACS Catal.* **2015**, *5*, 1863. (h) Segawa, Y.; Maekawa, T.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 66. (i) Miao, J.; Ge, H. *Eur. J. Org. Chem.* **2015**, *2015*, 7859.