

Pd(II)-Catalyzed Direct Dehydrogenative Mono- and Diolefination of Selenophenes

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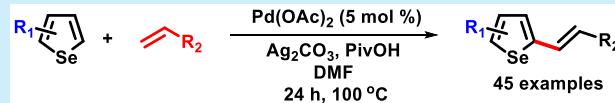
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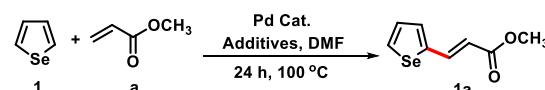
ABSTRACT: Pd(II)-catalyzed dehydrogenative Heck olefination of selenophenes with a broad olefinic substrate scope and high functional group tolerance is demonstrated. Carbonyl-substituted and phenyl-substituted olefins with electron-donating (D) and electron-accepting (A) groups can be regioselectively installed at C2 of the selenophene. The 2-olefinated selenophenes can subsequently undergo a second oxidative olefination to rapidly produce a new class of symmetrical D- π -D or unsymmetrical D- π -A 2,5-diolefinated selenophene materials.



Olefination of arenes or heteroarenes to extend π conjugation is an important transformation in synthesizing organic semiconducting materials and bioactive molecules.¹ Although the traditional palladium-catalyzed Heck reaction has been widely used to install carbon–carbon double bonds, the direct cross-dehydrogenative Heck reaction (DHR) coupling of an arene with an alkene, first discovered by Fujiwara and Moritani,² is the most powerful and cost-effective strategy, as it does not require the preparation of a halogenated arene.³ Thiophene is the most ubiquitous component in enormous conjugated molecules for organic optoelectronic applications.⁴ Selenophene in the chalcogenophene family has emerged as a promising alternative to traditional thiophene for property optimization. Selenophene has a higher polarizability and lower aromaticity than thiophene.⁵ Therefore, the selenophene-incorporated materials usually exhibit higher crystallinity and narrower band gaps, which are desirable characteristics for achieving high-performance semiconducting properties.⁶ As a result, π extension of selenophenes by C–H activation methodology has attracted increasing interest in recent years.⁷ DHR of heteroarenes, including C2 olefination of thiophene, has been previously described.⁸ Nevertheless, C–H arylation of selenophenes is more challenging, not to mention the DHR of selenophenes, which has not been well-explored. Herein we report the first palladium-catalyzed C2 direct cross-dehydrogenative alkenylation of selenophenes with a variety of vinyl olefins.

As an initial attempt, bare selenophene was reacted with electron-deficient methyl acrylate to afford 2-olefinated **1a**. The optimization of conditions is shown in Table 1. As shown in entries 1–4, using common catalysts such as Pd(PPh₃)₄, Pd₂(dba)₃, Pd(PhCN)₂Cl₂, and Pd(PPh₃)₂Cl₂ in the presence of Ag₂CO₃ as an oxidant in *N,N*-dimethylformamide (DMF) at 100 °C for 24 h resulted in only low yields of **1a**. Fortunately, when 5 mol % Pd(OAc)₂ was used as the catalyst, the yield of **1a** was dramatically improved to 70% (entry 5).

Table 1. Direct Olefination of Selenophene with Methyl Acrylate^a



entry	catalyst	oxidant	yield (%)
1	Pd(PPh ₃) ₄	Ag ₂ CO ₃	15
2	Pd ₂ (dba) ₃	Ag ₂ CO ₃	3
3	Pd(PhCN) ₂ Cl ₂	Ag ₂ CO ₃	25
4	Pd(PPh ₃) ₂ Cl ₂	Ag ₂ CO ₃	11
5	Pd(OAc) ₂	Ag ₂ CO ₃	70
6 ^b	Pd(OAc) ₂	Ag ₂ CO ₃	69
7		Ag ₂ CO ₃	0
8	Pd(OAc) ₂	Cu(OAc) ₂	5
9	Pd(OAc) ₂	Co(OAc) ₂	3
10	Pd(OAc) ₂		5
11	Pd(OAc) ₂	Ag ₂ O	31
12	Pd(OAc) ₂	AgOAc	32
13	Pd(OAc) ₂	AgOCOCF ₃	37
14	Pd(OAc) ₂	Ag ₂ CO ₃ + PivOH (30 mol %)	72
15	Pd(OAc) ₂	Ag ₂ CO ₃ + PivOH (60 mol %)	71
16 ^c	Pd(OAc) ₂	Ag ₂ CO ₃ + PPh ₃ + PivOH (30 mol %)	68

^aConditions: **1** (0.5 mmol, 1 equiv), **a** (1.2 equiv), oxidant (2 equiv), catalyst (5 mol %), DMF (1 mL). ^b10 mol % Pd(OAc)₂. ^c20 mol % PPh₃ was added.

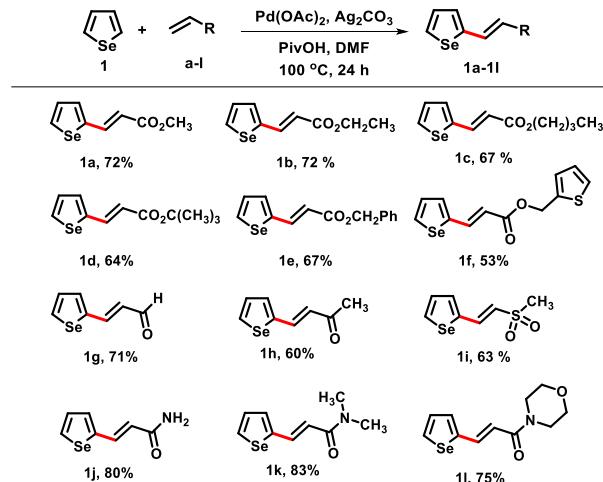
Increasing the amount of Pd(OAc)₂ to 10 mol % gave a similar yield of 69%. The reaction completely failed when no

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palladium catalyst was added (entry 7). The optimization of the conditions by changing the solvent, temperature, and reaction time is shown in Table S1. Using other oxidants, including $\text{Cu}(\text{OAc})_2$ and $\text{Co}(\text{OAc})_2$ (entry 8 and 9), or no oxidant (entry 10) resulted in poor yields of less than 5%, indicating that both $\text{Pd}(\text{OAc})_2$ and Ag_2CO_3 are crucial for the reaction to proceed. Combination of $\text{Pd}(\text{OAc})_2$ with other silver salts such as Ag_2O , AgOAc , and AgOCOCF_3 gave lower yields of 31–37% (entries 11–13). Furthermore, with 30 mol % pivalic acid as an additive, the yield was improved to 72% (entry 14). Introducing PPh_3 (20 mol %) as a ligand slightly decreased the yield to 68%. The substrate scope of alkenes for the direct mono-olefination of selenophene was explored using the optimized conditions (Table 1, entry 14).

The DHR of selenophene can be successfully achieved with various alkenes having ester, keto, aldehyde, sulfone, and amide substituents (Scheme 1). Ester-substituted olefins **a–f** with

Scheme 1. Direct Olefination of Selenophene (**1**) with Carbonyl-Substituted Olefins^{a,b}



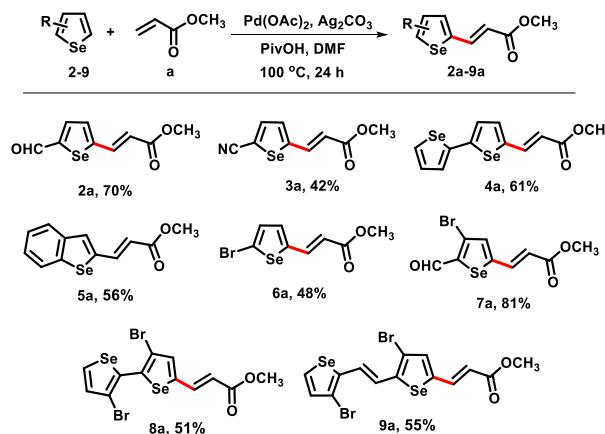
^aConditions: **1** (0.5 mmol, 1 equiv), **a–l** (1.2 equiv), Ag_2CO_3 (2 equiv), $\text{Pd}(\text{OAc})_2$ (5 mol %), PivOH (30 mol %), DMF (1 mL).

^bIsolated yields are shown.

different carbon chains furnished the corresponding regioselective 2-olefinated selenophene products in good yields (53–72%). Acrolein (**g**), methyl vinyl ketone (**h**), and methyl vinyl sulfone (**i**) with increasing electron deficiency afforded the 2-olefinated selenophene products **1g** (71%), **1h** (60%), and **1i** (63%), respectively. Furthermore, olefins **j–l** bearing more electron-rich amide substituents also yielded the respective products **1j–l** in higher yields (75–83%). For clarification of the oxidative DHR, product **1k** was characterized by single-crystal X-ray diffraction analysis (Figure S1 and Table S2).

The substrate scope was further extended to mono- and disubstituted selenophenes (Scheme 2). Reaction of methyl acrylate with 2-formylselenophene (**2**) and 2-cyanoselenophene (**3**) having electron-withdrawing groups at the 2-position furnished the 5-olefinated products **2a** (70%) and **3a** (42%), respectively. Electron-rich 2,2'-biselenophene (**4**) and benzo[*b*]selenophene (**5**) also led to the corresponding products **4a** and **5a** in 61% and 56% yield. It was found that 2-bromoselenophene gave the 5-olefinated product **6a**, indicating that the DHR is more favorable than the traditional Heck-type reaction under the reaction conditions. Other

Scheme 2. Direct Olefination of Mono- and Disubstituted Selenophenes with Methyl Acrylate^{a,b}



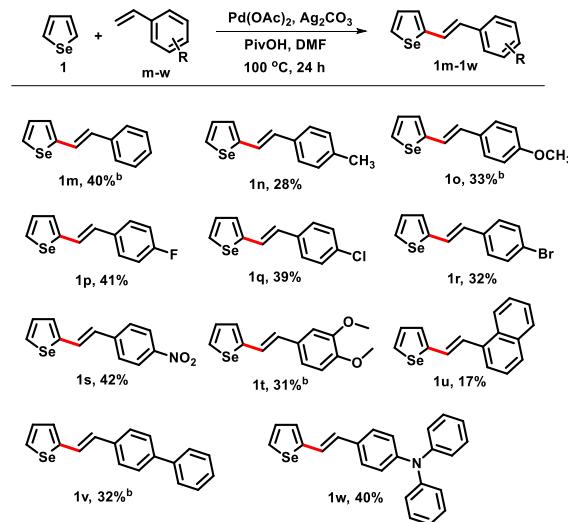
^aConditions: **2–9** (0.5 mmol, 1 equiv), **a** (1.2 equiv), Ag_2CO_3 (2 equiv), $\text{Pd}(\text{OAc})_2$ (5 mol %), PivOH (30 mol %), DMF (1 mL).

^bIsolated yields are shown.

brominated selenophene substrates **7–9** were also tested. Similarly, the regioselective olefination at CS rather than the debrominative Heck-type reaction was observed, generating **7a**, **8a**, and **9a** in moderate yields. The selectivity allows the intact bromo group to be further functionalized by a metal-catalyzed cross-coupling reaction for π extension.

In addition to the carbonyl-substituted olefin substrates, we also exploited phenyl-substituted olefins as coupling partners (Scheme 3). In some cases, $\text{Pd}_2(\text{dba})_3$ was used to improve the

Scheme 3. Direct Olefination of Selenophene (**1**) with Phenyl-Substituted Olefins^{a,c}



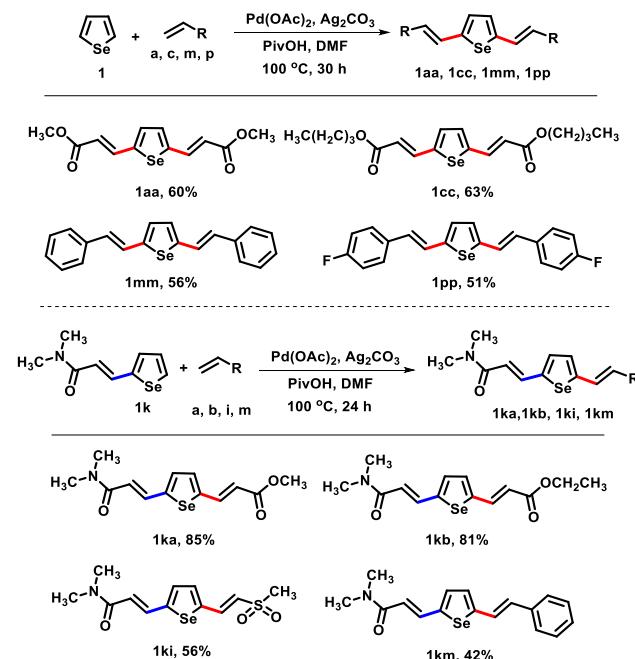
^aConditions: **1** (0.5 mmol, 1 equiv), **m–w** (1.2 equiv), Ag_2CO_3 (2 equiv), $\text{Pd}(\text{OAc})_2$ (5 mol %), PivOH (30 mol %), DMF (1 mL). ^b5 mol % $\text{Pd}_2(\text{dba})_3$ was used as the catalyst. ^cIsolated yields are shown.

reaction yield. The reaction of selenophene with styrene furnished the 2-olefinated product **1m** in 40% yield. 4-Methylstyrene, 4-methoxystyrene, and 3,4-dimethoxystyrene with electron-donating substituents at the *para* position resulted in lower yields of 28%, 33%, and 31%, respectively. However, 4-nitrostyrene and 4-fluorostyrene with electron-

withdrawing substituents at the *para* position slightly improved the yield to over 40%. 4-Chlorostyrene and 4-bromostyrene afforded the corresponding products **1q** and **1r** in moderate yields of 39% and 32%, respectively. 1-Vinylnaphthalene and 4-vinylbiphenyl also successfully generated the corresponding products **1u** and **1v**. Selenophene can be olefinated with electron-rich *N,N*-diphenyl-4-vinyylaniline (**w**) to afford donor- π -bridged conjugated material **1w**.

Symmetrical 2,5-diolefinated selenophenes can also be obtained when an excess amount (3 equiv) of the corresponding olefins is employed with increased catalyst amount and reaction time (Scheme 4). The four examples **1aa**,

Scheme 4. Symmetrical^a and Unsymmetrical^b Direct Diolefinations of Selenophene^c

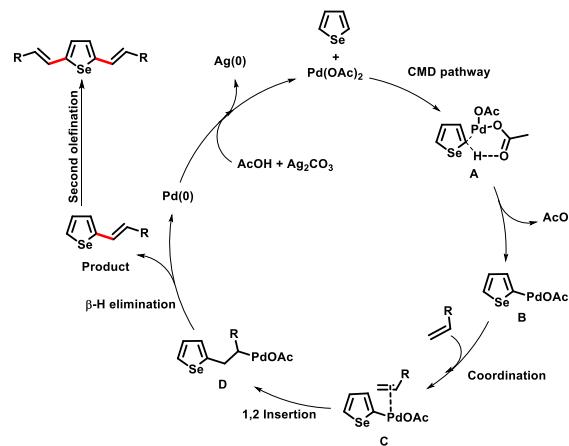


^aConditions: **1** (0.5 mmol, 1 equiv), olefin **a**, **c**, **m**, **p** (3 equiv), Ag_2CO_3 (3 equiv), $\text{Pd}(\text{OAc})_2$ (10 mol %), PivOH (60 mol %), DMF (1 mL). ^bConditions: **1k** (0.5 mmol, 1 equiv), olefin **a**, **b**, **i**, **m** (1.2 equiv), Ag_2CO_3 (2 equiv), $\text{Pd}(\text{OAc})_2$ (5 mol %), PivOH (30 mol %), DMF (1 mL). ^cIsolated yields are shown.

1cc, **1mm**, and **1pp** were generated in good yields (51–63%) from the reaction of selenophene with **a**, **c**, **m**, and **p**, respectively. Likewise, it was envisaged that 2-olefinated selenophenes could undergo a subsequent regioselective direct olefination at C5 in a similar manner. We selected **1k** as a model substrate for the second olefination at C5. Accordingly, the diolefinated products **1ka** and **1kb** were synthesized from the corresponding ester-substituted olefins **a** and **b** in high yields (85% and 81%, respectively). The reactions of **1k** with methylsulfonyl-substituted olefin (**i**) and styrene (**m**) afforded the products **1ki** (56%) and **1km** (42%).

A plausible catalytic cycle is shown in Scheme 5.⁹ The reaction of selenophene and $\text{Pd}(\text{OAc})_2$ via a concerted metalation–deprotonation (CMD) process furnishes intermediate **A**, and subsequent elimination of acetic acid generates Pd–aryl species **B**. Afterward, the olefin coordinates to the palladium to afford **C**, which undergoes a 1,2-migratory insertion to form a C–C bond (**D**). The desired product and $\text{Pd}(0)$ are then generated by β -hydride elimination. $\text{Pd}(0)$ can

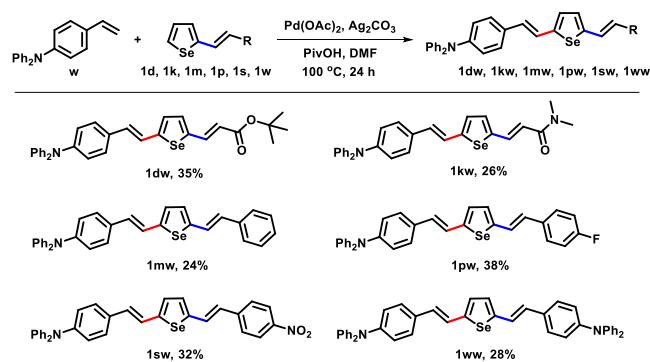
Scheme 5. Proposed Mechanism for the Direct Olefinations of Selenophene



be reoxidized to $\text{Pd}(\text{II})$ in the presence of Ag_2CO_3 and continue the catalytic cycle. Evidence for the reduction of $\text{Ag}(\text{I})$ to $\text{Ag}(0)$ was confirmed by the observation of a silver mirror after completion of the reaction. Subsequently, the second catalytic cycle generates the symmetrical 2,5-diolefinated product.

Utilizing the sequential C2 and C5 olefination of selenophene can facilitate the synthesis of a new class of unsymmetrical D– π –A-type or symmetrical D– π –D-type conjugated materials using divinyleneselenophene as the π bridge and the triphenylamino group as the donor. Thus, a series of 2,5-diolefinated selenophenes **1dw**, **1kw**, **1mw**, **1pw**, **1sw**, and **1ww** were synthesized in 24–38% yield by reacting mono-olefinated **1d**, **1k**, **1m**, **1p**, **1s**, and **1w** with **w** (Scheme 6). These new selenophene-based materials can be used as hole-transporting or light-emitting materials for organic optoelectronic applications.

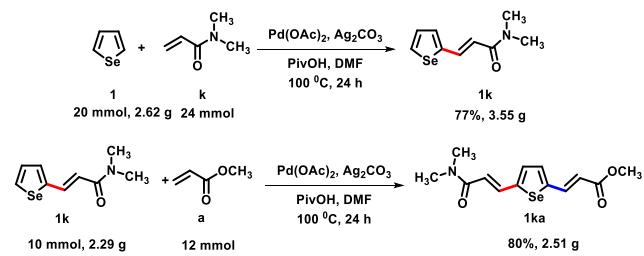
Scheme 6. Second Direct Olefination of Selenophenes with *N,N*-Diphenyl-4-vinyylaniline (w**)^{a,b}**



^aConditions: **w** (1.2 equiv), olefin **1d**, **1k**, **1m**, **1p**, **1s**, **1w** (1 equiv), $\text{Pd}(\text{OAc})_2$ (10 mol %), Ag_2CO_3 (2 equiv), PivOH (30 mol %), 24 h, 100 °C. ^bIsolated yields are shown.

We further evaluated the scalability of the DHR method. Gram-scale selenophene **1** was reacted with olefin **k** to form product **1k**, which was further coupled with **a** to generate the unsymmetrical diolefinated compound **1ka** (Scheme 7). Both reactions efficiently afforded the target products in good yields (77% and 80%, respectively) on a large scale.

Scheme 7. Gram-Scale Synthesis of Mono- and Diolefinated Selenophenes



The UV absorption and emission spectra of **1dw**, **1kw**, **1mw**, **1pw**, **1sw**, and **1ww** were measured in dichloromethane to investigate the photophysical properties of these 2,5-diolefinated selenophenes containing a triphenylamino group (Figure S2 and Table S3). The absorption λ_{max} of these materials was distributed in the range of 426–470 nm. The fluorescence color of the unsymmetrical 2,5-diolefinated selenophenes under irradiation at 365 nm can be fine-tuned by using different electron-accepting substituents (Figure 1). Notably, the emission of **1sw** was greatly quenched in the presence of the strong electron-withdrawing nitro group.¹⁰

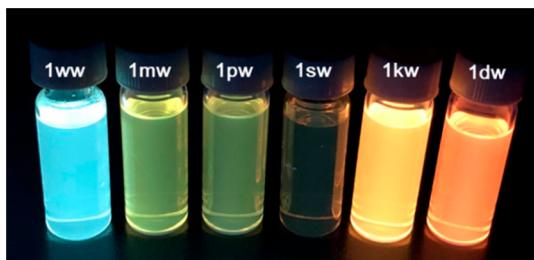


Figure 1. Fluorescence of **1dw**, **1kw**, **1mw**, **1pw**, **1sw**, and **1ww** under UV light (365 nm) in CH_2Cl_2 solution (10^{-5} M).

In summary, we have demonstrated an efficient palladium-catalyzed direct dehydrogenative C2 alkenylation of selenophenes with a broad olefinic substrate scope and high functional group tolerance. Carbonyl-based olefins with aldehyde, keto, ester, sulfone, and amide substituents and styrene derivatives with electron-rich or electron-deficient substituents at the *para* position can be regioselectively installed at the 2-position of selenophene. The 2-olefinated selenophenes can further undergo a second alkenylation at C5 to produce a new class of 2,5-diolefinated symmetrical D- π -D and unsymmetrical D- π -A semiconducting materials that are promising for various organic optoelectronic applications. This strategy provides a facile protocol to rapidly extend the π conjugation of selenophene.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c00506>.

Detailed synthetic procedures, single-crystal X-ray crystallographic data, photophysical properties, and NMR spectra (PDF)

Accession Codes

CCDC 1579528 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (a) Nielsen, C. B.; Holliday, S.; Chen, H.-Y.; Cryer, S. J.; McCulloch, I. *Acc. Chem. Res.* **2015**, *48*, 2803–2812. (b) Lin, Y.; Zhan, X. *Adv. Energy Mater.* **2015**, *5*, 1501063. (c) Chang, S.-L.; Cao, F.-Y.; Huang, W.-C.; Huang, P.-K.; Hsu, C.-S.; Cheng, Y.-J. *ACS Appl. Mater. Interfaces* **2017**, *9*, 24797–24803. (d) Wiesner, J.; Mitsch, A.; Altenkämper, M.; Ortmann, R.; Jomaa, H.; Schlitzer, M. *Pharmazie* **2003**, *58*, 854–856. (e) Mai, A.; Massa, S.; Ragno, R.; Cerbara, I.; Jesacher, F.; Loidl, P.; Brosch, G. *J. Med. Chem.* **2003**, *46*, 512–524. (f) Mitsch, A.; Altenkämper, M.; Sattler, I.; Schlitzer, M. *Arch. Pharm.* **2005**, *338*, 9–17.
- (a) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166–7169. (b) Moritani, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, *8*, 1119–1122.
- (a) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369–375. (b) Li, B.; Dixneuf, P. H. *Chem. Soc. Rev.* **2013**, *42*, 5744–5767. (c) Shang, X.; Liu, Z.-Q. *Chem. Soc. Rev.* **2013**, *42*, 3253–3260. (d) Kuhl, N.; Hopkinson, M. H.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236–10254. (e) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960–9009. (f) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936–946. (g) Gigant, N.; Bäckvall, J.-E. *Org. Lett.* **2014**, *16*, 1664–1667. (h) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. *Chem. Rev.* **2015**, *115*, 12138–12204. (i) Le Bras, J.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170–1214.
- (a) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868–5923. (b) Guo, X.; Facchetti, A.; Marks, T. J. *Chem. Rev.* **2014**, *114*, 8943–9021. (c) Planells, M.; Schroeder, B. C.; McCulloch, I. *Macromolecules* **2014**, *47*, 5889–5894.

- (5) (a) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Chem. - Eur. J.* **2009**, *15*, 8613–8624. (b) Patra, A.; Bendikov, M. *J. Mater. Chem.* **2010**, *20*, 422–433. (c) Ashraf, R. S.; Meager, I.; Nikolka, M.; Kirkus, M.; Planells, M.; Schroeder, B. C.; Holliday, S.; Hurhangee, M.; Nielsen, C. B.; Sirringhaus, H.; McCulloch, I. *J. Am. Chem. Soc.* **2015**, *137*, 1314–1321.
- (6) (a) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabiny, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, *43*, 5061–5063. (b) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Chem. Mater.* **2011**, *23*, 896–906. (c) Lai, Y.-Y.; Tung, T.-C.; Liang, W.-W.; Cheng, Y.-J. *Macromolecules* **2015**, *48*, 2978–2988.
- (7) (a) Tamba, S.; Fujii, R.; Mori, A.; Hara, K.; Koumura, N. *Chem. Lett.* **2011**, *40*, 922–924. (b) Rampon, D. S.; Wessjohann, L. A.; Schneider, P. H. *J. Org. Chem.* **2014**, *79*, 5987–5992. (c) Skhiri, A.; Salem, R. B.; Soule, J.-F.; Doucet, H. *Chem. - Eur. J.* **2017**, *23*, 2788–2791. (d) Lu, T.-J.; Lin, P.-H.; Lee, K.-M.; Liu, C.-Y. *Eur. J. Org. Chem.* **2017**, *2017*, 111–123. (e) Chen, S.-Y.; Pao, Y.-C.; Sahoo, S. K.; Huang, W.-C.; Lai, Y.-Y.; Cheng, Y.-J. *Chem. Commun.* **2018**, *54*, 1517–1520. (f) Shi, X.; Mao, S.; Roisnel, T.; Doucet, H.; Soule, J.-F. *Org. Chem. Front.* **2019**, *6*, 2398–2403.
- (8) (a) Asano, R.; Moritani, I.; Fujiwara, Y.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 663–664. (b) Maehara, A.; Satoh, T.; Miura, M. *Tetrahedron* **2008**, *64*, 5982–5986. (c) Vasseur, A.; Muzart, J.; Le Bras, J. *Chem. - Eur. J.* **2011**, *17*, 12556–125560. (d) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068–5083. (e) Zhang, Y.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2012**, *14*, 226–229. (f) Gorsline, B. J.; Wang, L.; Ren, P.; Carrow, B. P. *J. Am. Chem. Soc.* **2017**, *139*, 9605–9614. (g) Zhao, J.; Huang, L.; Cheng, K.; Zhang, Y. *Tetrahedron Lett.* **2009**, *50*, 2758–2761. (h) Morita, T.; Satoh, T.; Miura, M. *Org. Lett.* **2015**, *17*, 4384–4387.
- (9) (a) Pawar, G. G.; Singh, G.; Tiwari, V. K.; Kapur, M. *Adv. Synth. Catal.* **2013**, *355*, 2185–2190. (b) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010**, *327*, 315–319. (c) Fujiwara, Y.; Asano, R.; Moritani, I.; Teranishi, S. *J. Org. Chem.* **1976**, *41*, 1681–1683.
- (10) (a) Ueno, T.; Urano, Y.; Setsukinai, K.; Takakusa, H.; Kojima, H.; Kikuchi, K.; Ohkubo, K.; Fukuzumi, S.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 14079–14085. (b) Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2006**, *128*, 10640–10641.