Organic LETTERS

Letter

pubs.acs.org/OrgLett

Diaceno[*a*,*e*]pentalenes from Homoannulations of *o*-Alkynylaryliodides Utilizing a Unique Pd(OAc)$_2$/*n*-Bu$_4$NOAc Catalytic Combination

Junjian Shen,[†,§,∥] Dafei Yuan,[†,∥] Yan Qiao,[‡] Xingxing Shen,[†] Zhongbo Zhang,[†] Yuwu Zhong,[§]
Yuanping Yi,*,[†] and Xiaozhang Zhu*,[†]

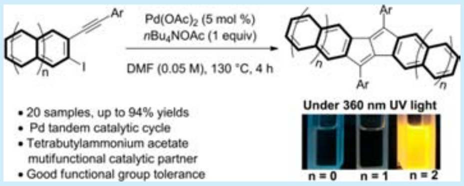
[†]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[‡]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi Province 030001, P. R. China

[§]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

Supporting Information

ABSTRACT: A heterogeneous catalytic system, Pd(OAc)$_2$/*n*-Bu$_4$NOAc, for the efficient synthesis of diaceno[*a*,*e*]pentalenes via a tandem Pd catalytic cycle is reported. The catalytic partner *n*-Bu$_4$NOAc played indispensable and versatile roles, acting as both the media for recovering active Pd(0) species and their stabilizer. A series of new diaceno[*a*,*e*]pentalenes were obtained in moderate to high yields, among which the octacyclic dianthracenopentalene was found to be highly emissive.



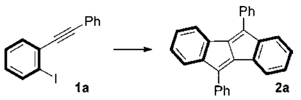
- 20 samples, up to 94% yields
- Pd tandem catalytic cycle
- Tetrabutylammonium acetate mutifunctional catalytic partner
- Good functional group tolerance

Dibenzo[*a*,*e*]pentalenes[1] have been known for over 100 years as distinctive polycyclic conjugated hydrocarbons with compatibly 4n π-electrons and a stable planar structure.[2] They have recently attracted considerable interest because of intriguing properties, such as high electron affinity derived from the aromatization tendency of cyclopentadiene by accepting one electron.[3] Although the construction of a dibenzo[*a*,*e*]pentalene framework comprising fused 6−5−5−6 carbocycles was highly challenging,[4] transition-metal-catalyzed synthesis of dibenzo[*a*,*e*]pentalenes initiated by Youngs et al.[5] has recently made significant progress. The Kawase,[6] Tilley[7] and Itami[8] groups developed tandem synthesis of dibenzo[*a*,*e*]pentalenes by the homocoupling of *o*-alkynylaryl bromides or arylacetylenes catalyzed by Ni or Pd catalysts. Jin et al. reported the cross annulations of *o*-alkynylaryl chlorides and diarylacetylenes leading to the unsymmetrical dibenzo[*a*,*e*]pentalenes.[9] However, because of the intrinsic limitations of the Pd(0, II) or Ni(0, II) catalytic cycle, these tandem reactions only operated with the help of the external strong reductant, oxidant, base, or even equivalent amount of the catalyst, which narrowed substrate scope and was thus less compatible for the synthesis of high-order diaceno[*a*,*e*]pentalenes (pentalene-containing acene analogues) that are very enticing for advanced applications in organic electronics.[10] Initially, we considered that the Pd four-valence-state catalytic cycle[11] might be applicable for the synthesis of diaceno[*a*,*e*]pentalenes. We report herein a heterogeneous catalytic system, Pd(OAc)$_2$/*n*-Bu$_4$NOAc, for the efficient construction of diaceno[*a*,*e*]pentalene frameworks. The catalytic partner tetrabutylammonium acetate (*n*-Bu$_4$NOAc) exhibits binary effects, as follows. First, the acetate anion could act as the media for recovering active Pd(0) species;[12] Second, the *n*-tetrabutylammonium group may contribute to stabilizing Pd nanoparticles.[13] In addition, *n*-Bu$_4$NOAc is neutral and a nonreductive reagent and is thus compatible with sensitive functional groups. A series of new diaceno[*a*,*e*]pentalenes were synthesized in moderate to high yields, among which we found that the high-order dianthraceno[*a*,*e*]pentalene **2t** showed unusually intensive emission, which is an exceptional example for antiaromatic pentalene derivatives.

The synthesis of dibenzo[*a*,*e*]pentalene **2a** from substrate **1a** was investigated under several catalytic combinations. Initially, homocoupling of substrate **1a** solely using 5 mol % of Pd(OAc)$_2$ as the catalyst in DMF at 100 °C afforded dibenzo[*a*,*e*]pentalene **2a** in a trace amount with a large amount of unreacted starting materials, which indicated the feasibility of the potential Pd(0, II, IV) catalytic cycle (cf. Table 1. entry 1).[11] On the other hand, we ascribed low yield to the hindered catalytic cycle at the PdI$_2$ stage. As per our deduction, the yield was significantly improved by addition of acetate salts in order to recover active Pd(0) species (entries 2−6).[12] In particular, compound **2a** was obtained with a good (76%) yield using 1 equiv of *n*-Bu$_4$NOAc, a neutral salt (entry 6). The yield was further improved to excellent (94%) under higher reaction temperature (130 °C) together with a significantly reduced reaction time (4 h),[6−9] which may partly be ascribed to the stabilization effect of tetrabutylammonium cation upon Pd(0)

Received: August 17, 2014
Published: September 5, 2014

Table 1. Effect of Additives and Temperature on the Homocoupling of Compound 1a.[a]



entry	catalytic partner	temp (°C)	yield[b] (%)
1		100	trace
2	LiOAc (1.0 equiv)	100	34
3	NaOAc (1.0 equiv)	100	40
4	KOAc (1.0 equiv)	100	56
5	CsOAc (1.0 equiv)	100	54
6	$n\mathrm{Bu_4NOAc}$ (1.0 equiv)	100	76
7[c]	$n\mathrm{Bu_4NOAc}$ (1.0 equiv)	130	94
8[c,d]	$n\mathrm{Bu_4NOAc}$ (1.0 equiv)	130	75

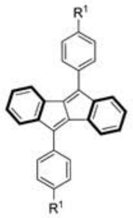
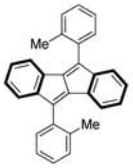
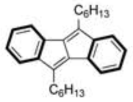
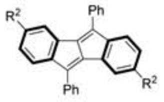
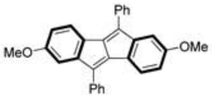
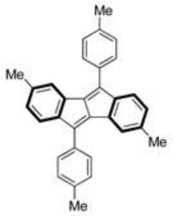
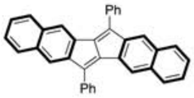
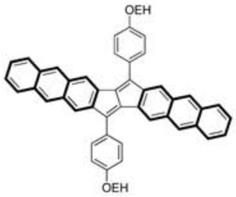
[a] Reaction conditions: **1a** (0.40 mmol), $\mathrm{Pd(OAc)_2}$ (5 mol %), catalytic partner, *N*,*N*-dimethylformide (DMF) (0.05 M) under N_2 atmosphere for 24 h. [b] Isolated yield. [c] Reaction time was 4 h. [d] The reaction was performed in air.

nanoparticles (entry 7).[14] Finally, we were pleased to observe that the reaction could even be performed under ambient conditions, and it gave compound **2a** with a good (75%) yield (entry 8).

The scope of the tandem reaction is illustrated under the optimized reaction conditions as shown in Table 2. Various R^1 groups including sensitive chloride (entry 6), aldehyde (entry 9), and ester (entry 10) groups could be tolerated. Both the electron-donating and the weak electron-withdrawing groups could give the corresponding products with moderate to high yields (entries 2−6). Substrates with electron-donating groups smoothly gave the corresponding products with 73−94% yield (entries 1−4). The electron-withdrawing groups slowed the reaction rates and gave relatively low yields between 40 and 78% (entries 5, 6, and 8−10). Compound **2g** with the trifluoromethyl groups was obtained with excellent (92%) yield using 10 mol % of $\mathrm{Pd(OAc)_2}$ (entry 7). The reaction was insensitive to the steric hindrance of the substrate as compound **2k** could equally be obtained at 83% yield (entry 11). The substrate 1-iodo-2-octynylbenzene **1l** can also proceed to give hexyl-substituted dibenzo[*a*,*e*]pentalene **2l** in moderate 40% yield. Similar substituent effects were observed for substrates with different R^2 groups (entries 13−17). For the fluoride-substituted substrate **1o**, the reaction can only proceed at high temperature, 145 °C (entry 15). The tetra-substituted compound **2r** was synthesized smoothly with 74% yield (entry 18). The dinaphtho[*a*,*e*]pentalene and dianthraceno[*a*,*e*]pentalene derivatives **2s** and **2t**, promising organic semiconductors,[10,15] could easily be obtained with similar 80% yields (entries 19 and 20). Despite of 32 π-electrons that are comparable to those of hepta- or octacene, dianthraceno[*a*,*e*]pentalene **2s** is bench-stable for months. Upon UV irradiation (360 nm, 4 W) of air-saturated solution, more than 50% of **2t** can survive after 28 h, which indicates the considerably higher stability of **2t** than that of TIPS-pentacene.[16]

High-quality crystals of compound **2t** can be readily obtained and characterized by single-crystal X-ray analysis under ambient conditions, which revealed a planar molecular structure with obvious single- and double-bond alternation indicating the absence of aromaticity (Figure 1). Because of its extended conjugated framework, highly ordered $\pi-\pi$ stacking interactions with a distance of 3.39 Å and quite large overlapped π-

Table 2. Synthesis of Diaceno[*a*,*e*]pentalenes by Pd-Catalyzed Homocoupling of *o*-Alkynylaryl Iodides[a]

entry	product		yield (%)[b]
1		**2a** (R^1 = H)	94
2		**2b** (R^1 = Me)	84
3		**2c** (R^1 = *t*-Butyl)	78
4		**2d** (R^1 = OMe)	73
5[c]		**2e** (R^1 = F)	65
6[c]		**2f** (R^1 = Cl)	78
7[d]		**2g** (R^1 = CF_3)	92
8[c]		**2h** (R^1 = CN)	53
9[c]		**2i** (R^1 = CHO)	56
10[c]		**2j** (R^1 = COOMe)	40
11		**2k**	83
12[c]		**2l**	40
13		**2m** (R^2 = Me)	71
14		**2n** (R^2 = *t*-Butyl)	72
15[c,e]		**2o** (R^2 = F)	42
16[c]		**2p** (R^2 = COMe)	32
17		**2q**	80
18		**2r**	74
19		**2s**	80 (20)[g]
20[d]		**2t**[f]	80 (7)[h]

[a] General reaction condition: **1a** (0.40 mmol), $\mathrm{Pd(OAc)_2}$ (5 mol %), *n*-$\mathrm{Bu_4NOAc}$ (0.40 mmol), DMF (0.05 M) under N_2 atmosphere at 130 °C for 4 h. [b] Isolated yield. [c] The reaction time was 12 h. [d] $\mathrm{Pd(OAc)_2}$ (10 mol %) was used. [e] The reaction temperature was 145 °C. [f] EH: 2-ethylhexyl. [g] Obtained from ref 15a. [h] Under Tilley's conditions.[7]

area could be clearly observed (Figure S2, Supporing information), which is unprecedented for the smaller dibenzo[*a*,*e*]pentalene (**2c**, **2e**, **2l**, see the Supporting Information) and

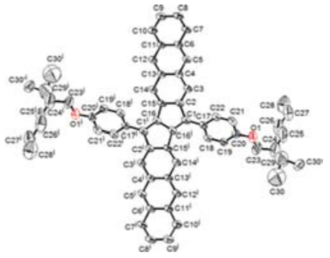
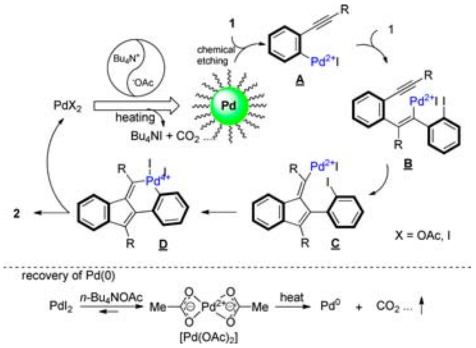


Figure 1. Single-crystal structure of compound **2t**.

dinaphtho[*a*,*e*]pentalene[15a] congeners and is a favorable hint for the upcoming applications in organic electronics.

A plausible reaction mechanism that involves a heterogeneous catalytic process via the Pd(0, II, IV) cycle[11,17] was proposed in Scheme 1. Accordingly, the key reference reactions include the following (see Table S1, Supporting Information). (1) The TEM image of the reaction mixture revealed a large quantity of Pd nanoparticles with ∼3 nm size (Figure S1, Supporting Information). Accordingly, adding liquid Hg to the reaction system[18] sharply decreased the yield to 15%. (2) Using 0.5 equiv of *n*-Bu_4NOAc only gave a 38% yield that agreed well with our assumption, i.e., an equivalent amount of *n*-Bu_4NOAc was necessary to continuously promote the catalytic cycle. However, an additional 1 equiv of *n*-Bu_4NOAc significantly inhibited the reaction and gave a rather low yield, 10%. We deduced that an excessive amount of tetrabutylammonium cations would cause the surface of the Pd nanoparticles to become overcrowded,[19] which is in disfavor with the catalytic process. (3) The changes of the acetate anion to bromide and of tetrabutylammonium to the ammonium cation could only give compound **2a** at low yields of 17% and 3%, respectively, which means that both the tetrabutylammonium cation and the acetate anion play complementary effects in this kind of transformation. Thus, the Pd(0) nanoparticles were formed in situ from $Pd(OAc)_2$ by thermolysis and were stabilized by the tetrabutylammonium cations. By chemical etching, arylpalladium(II) **B** was formed and proceeded with inter- and intramolecular alkyne carbopalladation to afford the intermediate **C**. Intramolecular oxidative addition of aryl iodide to Pd(II) delivered palladabenzocyclohexadiene **D**,[11,20] which subsequently underwent reductive elimination to afford dibenzo[*a*,*e*]penalenes **2** and PdI_2. The Pd(0) species was further regenerated in the presence of *n*Bu_4NOAc to push forward the catalytic cycle.[21]

Scheme 1. Proposed Catalytic Cycle



The photophysical properties of the representative diaceno-[*a*,*e*]pentalenes **2a**, **2s**, and **2t** were examined in diluted dichloromethane solution as summarized in Table 3, which indicates disparate fluorescence property with increasing π-conjugation. All of the compounds showed structured absorption that bathochromically shifted from 448 to 556 nm (Figure 2). In sharp contrast to dibenzo[*a*,*e*]pentalene **2a** and dinaphtho[*a*,*e*]pentalene **2s**, dianthraceno[*a*,*e*]pentalene **2t** exhibited strong yellow emission at 574 nm with a promisingly high quantum yield, 35%, and a small Stokes shift, 0.08 eV.[22] To illustrate the origin of such an unusual phenomenon, we performed calculations on the excited-state electronic properties of these compounds by means of time-dependent density functional theory (TDDFT) at the B3LYP/6-31G* level. As indicated previously,[6,15a] the longest absorption of compounds **2a** and **2s** originated from the second excited state (S_2), and the S_1 excitation was found to be symmetry-forbidden. As shown in Figure 2, all the compounds showed the LUMO (L, lowest

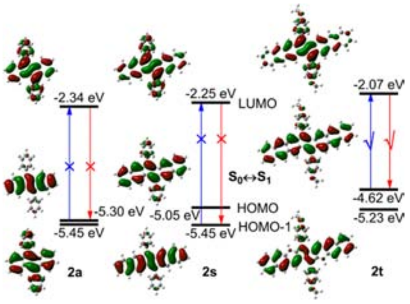


Figure 2. DFT-calculated orbital energy diagram and pictorial representation of HOMO-1, HOMO, and LUMO for diaceno[*a*,*e*]-pentalenes **2a**, **2s**, and **2t**. In calculations, the 2-ethylhexyloxy groups of **2t** were simplied to methoxy ones. [Blue and red arrows represent the lowest excitation and fluorescence (S_0↔S_1): ×, symmetry-forbidden; √, symmetry-allowed.]

Table 3. Photophysical and Electrochemical Properties of the Representative Diaceno[*a*,*e*]pentalene Derivatives[a]

cpd.	λ_{abs} (nm) (ε, $M^{-1} \cdot cm^{-1}$)[a]	calcd excited states[b] (nm) (origin,[c] f[d])	λ_{em} (nm) (Φ)[e]	calcd emission wavelength[b] (nm) (f)[d]	$E_{red}^{1/2}$[f] (V)	E_g^{opt}[g] (eV)
2a	424, 448 (15400)	568 (S_1, H→L, 0.00) 440, (S_2, H-1→L, 0.31)	*h*	1054 (0.00)	−1.68	2.61
2s	468, 498 (19800)	496 (S_1, H-1→L, 0.00) 493, (S_2, H→L, 0.37)	*h*	735 (0.00)	−1.78	2.32
2t	516, 556 (36500)	543 (S_1, H→L, 0.50) 513, (S_2, H→L+1, 0.00)	578, 622 (0.35)	624 (0.51)	−1.87	2.13
3[i]	336, 352 (13900)	318 (S_1, H→L, 0.56)	385 (0.98)	*j*	*h*	3.40

[a] Measured in dichloromethane. [b] TDDFT-calculated vertical excitation or emission wavelengths. [c] It should be noted that except for the dominant excitation configurations listed above, there were very small contributions (<10%) from other configurations, such as H → L+1 for S_2 of **2a**, H-1 → L+1 for S_2 of **2s**, and H-1 or H-2 → L+1 for S_1 of **2t**. [d] Oscillator strengths. [e] Fluorescence quantum yield was determined by absolute method. [f] Cyclic voltammetry on a carbon electrode with *n*Bu_4NClO_4 in dichloromethane (0.1 M, vs Fc^+/Fc). [g] $E_g^{opt.} = 1240/\lambda_{onset}$ (eV). [h] Not detected. [i] Extracted from ref 24 (**3**: indenoindene). [j] Not examined.

unoccupied molecular orbital) orbitals of the same centro antisymmetry. The symmetry-allowed orbitals for the lowest optical excitation were HOMO-1 for compound **2a** and HOMO (H, highest unoccupied molecular orbital) for compounds **2s** and **2t**. Interestingly, only for compound **2t**, the S_1 excitation channel was opened and attributed to the HOMO−LUMO transition. It was shown by our calculations that the optimal S_0 and S_1 geometries presented a same nature for the molecular levels and lowest excited states. Thus, the emission channel from S_1 to S_0 was switched on for compound **2t**. To the best of our knowledge, compound **2t** was the first example among pentalene derivatives that showed intensive fluorescence.[23]

In summary, we developed a unique catalytic system, Pd(OAc)$_2$/*n*-Bu$_4$NOAc, for the efficient synthesis of diaceno[*a*,*e*]pentalenes. This catalytic combination showed good functional group tolerance and gave a series of diaceno[*a*,*e*]-pentalenes at moderate to excellent yields, among which the octacyclic dianthraceno[*a*,*e*]pentalene **2t** was found to be a distinctive example of pentalene derivatives featured by the unprecedented strong fluorescence and compact $\pi-\pi$ stacking in solution or solid states. The cheap catalytic partner, *n*-Bu$_4$NOAc, and the easy manipulation without need of sensitive and expensive phosphine ligands are noteworthy, making this catalytic combination promising for the mass preparation of pentalene-type organic semiconductors, especially based on high-order diaceno[*a*,*e*]pentalenes aimed at applications in organic electronics.[10,25]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental details, physical properties, and X-ray data for compounds **2c,e,l,t** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ypyi@iccas.ac.cn.
*E-mail: xzzhu@iccas.ac.cn.

Author Contributions

‖These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (91333113), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12010200), and the National Basic Research Program of China (973 Program) (No. 2014CB643500) for the financial support.

■ REFERENCES

(1) Brand, K. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3071.

(2) Hopf, H. *Angew. Chem., Int. Ed.* **2013**, *52*, 12224.

(3) (a) Wood, J. D.; Jellison, J. L.; Finke, A. D.; Wang, L.; Plunkett, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 15783. (b) Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong, Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. *J. Am. Chem. Soc.* **2012**, *134*, 10349. (c) Shimizu, A.; Kishi, R.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Hisaki, I.; Miyata, M.; Tobe, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 6076 and references cited therein.

(4) (a) Saito, M. *Symmetry* **2010**, *2*, 950. For selected recent examples, see: (b) London, G.; von Wantoch Rekowski, M.; Dumele, O.; Schweizer, W. B.; Gisselbrecht, J.-P.; Boudon, C.; Diederich, F. *Chem. Sci.* **2014**, *5*, 965. (c) Chen, C.; Harhausen, M.; Liedtke, R.; Bussmann, K.; Fukazawa, A.; Yamaguchi, S.; Petersen, J. L.; Daniliuc, C. G.; Fröhlich, R.; Kehr, G.; Erker, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 5992. (d) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 555. (e) Li, H.; Wei, B.; Xu, L.; Zhang, W.-X.; Xi, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 10822.

(5) Chakraborty, M.; Tessier, C. A.; Youngs, W. J. *J. Org. Chem.* **1999**, *64*, 2947.

(6) Kawase, T.; Konishi, A.; Hiro, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem.—Eur. J.* **2009**, *15*, 2653.

(7) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796.

(8) Maekawa, T.; Segawa, Y.; Itami, K. *Chem. Sci.* **2013**, *4*, 2369.

(9) Zhao, J.; Oniwa, K.; Asao, N.; Yamamoto, Y.; Jin, T. *J. Am. Chem. Soc.* **2013**, *135*, 10222.

(10) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

(11) (a) Catellani, M.; Fagnola, M. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2421. (b) Catellani, M.; Motti, E.; Della Ca, N. *Acc. Chem. Res.* **2008**, *41*, 1512. (c) Malacria, M.; Maestri, G. *J. Org. Chem.* **2013**, *78*, 1323. (d) Kung, Y.-H.; Cheng, Y.-S.; Tai, C.-C.; Liu, W.-S.; Shin, C.-C.; Ma, C.-C.; Tsai, Y.-C.; Wu, T.-C.; Kuo, M.-Y.; Wu, Y.-T. *Chem.—Eur. J.* **2010**, *16*, 5909. (e) Wu, T.-C.; Chen, C.-H.; Hibi, D.; Shimizu, A.; Tobe, Y.; Wu, Y.-T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7059. (f) Lin, Y.-D.; Cho, C.-L.; Ko, C.-W.; Pulte, A.; Wu, Y.-T. *J. Org. Chem.* **2012**, *77*, 9979.

(12) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(13) (a) Reetz, M. T.; de Vries, J. G. *Chem. Commun.* **2004**, 1559. (b) Balanta, A.; Godard, C.; Claver, C. *Chem. Soc. Rev.* **2011**, *40*, 4973. (c) Deraedt, C.; Astruc, D. *Acc. Chem. Res.* **2014**, *47*, 494.

(14) (a) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165. (b) Jeffery, T. *J. Chem. Soc., Chem, Commun.* **1984**, 1287.

(15) (a) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 7728. (b) Nakano, M.; Osaka, I.; Takimiya, K.; Koganezawa, T. *J. Mater. Chem. C* **2014**, *2*, 64.

(16) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, K.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980.

(17) Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 6896.

(18) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(19) (a) Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921. (b) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938.

(20) (a) In the absence of reductant, a reductive-coupling mechanism involving a Pd(0)/Pd(II) cycle (ref 7) unlikely operated in our reaction.. (b) As the cross coupling between compound **1a** and di-*p*-tolylacetylene did not proceed under the optimized reaction conditions, a concerted metalation deprotonation (CMD) process can be excluded..

(21) The pyrolytic transformation from Pd(OAc)$_2$ to Pd(0) is elusive. (a) Reetz, M. T.; Masse, M. *Adv. Mater.* **1999**, *11*, 773. (b) Tano, T.; Esumi, K.; Meguro, K. *J. Colloid Interface Sci.* **1989**, *133*, 530. (c) Gallagher, P. K.; Gross, M. E. *J. Therm. Anal.* **1986**, *31*, 1231.

(22) Ouchi, Y.; Sugiyasu, K.; Ogi, S.; Sato, A.; Takeuchi, M. *Chem. Asian. J.* **2012**, *7*, 75.

(23) (a) Falchi, A.; Gellini, C.; Salvi, P. R.; Hafner, K. *J. Phys. Chem. A* **1998**, *102*, 5006. (b) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012.

(24) Zhu, X.; Tsuji, H.; Navarrete, J.; Casado, J.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, *134*, 19254.

(25) Watanabe, M.; Chang, Y. J.; Liu, S.-W.; Chao, T.-H.; Goto, K.; Islam, Md. M.; Yuan, C.-H.; Tao, Y.-T.; Shinmyozu, T.; Chow, T. J. *Nat. Chem.* **2012**, *4*, 574.