ORGANIC
LETTERS

2012
Vol. 14, No. 15
3882–3885

Short Synthesis of Alkyl-Substituted Acenes Using Carbonyl-Directed C−H and C−O Functionalization

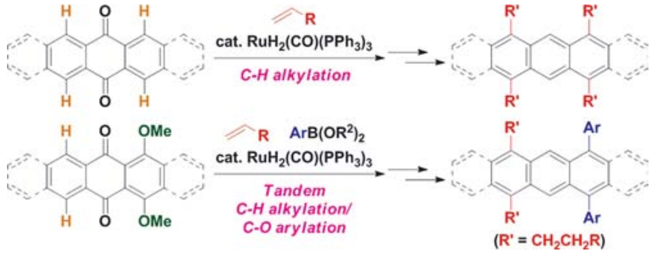
Daiki Matsumura,[†] Kentaroh Kitazawa,[†] Seiya Terai,[†] Takuya Kochi,[†] Yutaka Ie,[‡] Masashi Nitani,[‡] Yoshio Aso,[‡] and Fumitoshi Kakiuchi*,[†]

*Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa, 223-8522, Japan,
and The Institute of Science and Industrial Research (ISIR), Osaka University,
8-1,7 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

kakiuchi@chem.keio.ac.jp

Received June 11, 2012

ABSTRACT



A convenient method for the synthesis of tetraalkylanthracenes and -pentacenes by means of ruthenium-catalyzed regioselective C−H alkylation of the corresponding acenequinones was developed. Dialkyldiarylpentacene was also synthesized using chemoselective tandem C−H alkylation/C−O arylation of dimethoxypentacenequinone. It was suggested that a tetraalkylpentacene is stable under air in the dark and possesses an appropriate HOMO level as active material for p-type organic field-effect transistors (OFETs).

Linear acenes have widely received much attention due to their remarkable potential as organic semiconducting materials.[1] In particular, pentacene shows high charge mobility and is considered as one of the most promising materials.[2] Semiconducting properties of pentacene fabricated by vapor deposition have been extensively studied, but its poor solubility in almost all common organic solvents made it difficult to prepare OFET devices by solution processes such as spin-coating. In this context, a variety of substituents have been introduced to the pentacene framework to improve its solubility in organic solvents,[3−7] and some of the pentacene derivatives actually displayed OFET properties.[4]

While convenient methods are available for some pentacene derivatives with aryl[5] and alkynyl[6] groups, pentacenes bearing alkyl groups on the central three rings are

---

[†] Keio University.

[‡] Osaka University.

(1) (a) Anthony, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (b) Yamashita, Y. *Sci. Technol. Adv. Mater.* **2009**, *10*, 024313. (c) Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Soc. Rev.* **2010**, *39*, 2577.

(2) (a) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87. (b) Kelley, T. W.; Muyres, D. V.; Baude, P. F.; Smith, T. P.; Jones, T. D. *Mater. Res. Soc. Symp. Proc.* **2003**, *771*, 169. (c) Lee, S.; Koo, B.; Shin, J.; Lee, E.; Park, H.; Kim, H. *Appl. Phys. Lett.* **2006**, *88*, 162109/1–162109/3.

(3) A review on syntheses of acene derivatives: Qu, H.; Chi, C. *Curr. Org. Chem.* **2010**, *14*, 2070.

(4) (a) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090. (b) Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. *Adv. Mater.* **2003**, *15*, 2009. (c) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340. (d) Li, Y.; Wu, Y.; Liu, P.; Prostran, Z.; Gardner, S.; Ong, B. S. *Chem. Mater.* **2007**, *19*, 418. (e) Park, S. K.; Jackson, T. N.; Anthony, J. E.; Mourey, D. A. *Appl. Phys. Lett.* **2007**, *91*, 063514. (f) Park, S. K.; Anthony, J. E.; Jackson, T. N. *IEEE Electron Device Lett.* **2007**, *28*, 877. (g) Qu, H.; Cui, W.; Li, J.; Shao, J.; Chi, C. *Org. Lett.* **2011**, *13*, 924.

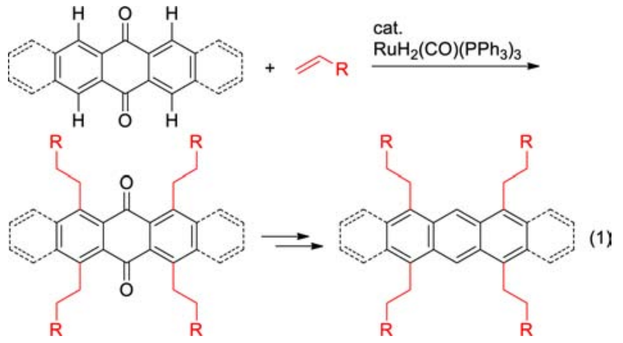
(5) (a) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253. (b) Hart, H.; Lai, C.-y.; Nwokogu, G. C.; Shamouilian, S. *Tetrahedron* **1987**, *43*, 5203. (c) Vets, N.; Diliën, H.; Toppet, S.; Dehaen, W. *Synlett* **2006**, 1359. (d) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274. (e) Kuninobu, Y.; Seiki, T.; Kanamaru, S.; Nishina, Y.; Takai, K. *Org. Lett.* **2010**, *12*, 5287.

(6) (a) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1969**, *34*, 1734. (b) Hanhela, P. J.; Paul, D. B. *Aust. J. Chem.* **1981**, *34*, 1701. (c) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (d) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15. (e) Jiang, J.; Kaafarani, B. R.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 2155. (f) Schmidt, R.; Göttling, S.; Leusser, D.; Stalke, D.; Krause, A.-M.; Würthner, F. *J. Mater. Chem.* **2006**, *16*, 3708. (g) Benard, C. P.; Geng, Z.; Heuft, M. A.; VanCrey, K.; Fallis, A. G. *J. Org. Chem.* **2007**, *72*, 7229.

10.1021/ol301608m

more difficult to prepare.[7] For example, Takahashi and co-workers have developed systematic methods using zirconacyclopentadienes to install alkyl groups at desired positions during multistep construction of the pentacene cores,[7b−g] but more efficient methods for preparation of alkyl-substituted pentacenes are still desired.

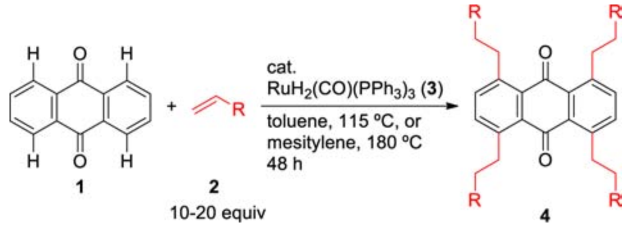
Recently, we reported a short synthesis of tetraarylated anthracenes using catalytic C−H arylation of anthraquinone with arylboronates.[8,9] We envisioned that tetraalkylacenes can also be prepared in a few steps, if the ruthenium-catalyzed C−H/olefin coupling developed by our group,[10] instead of the C−H arylation, is used for acenequinones, common starting materials for acene syntheses (eq 1).



Herein we report a short synthesis of tetraalkylated anthracenes and pentacenes using ruthenium-catalyzed C−H alkylation of acenequinones with olefins. Catalytic chemoselective tandem C−H alkylation/C−O arylation[11] of dimethoxypentacenequinone was also successfully applied for synthesis of a pentacene with two alkyl and two aryl groups. Optical and electronic properties of the pentacene products were also investigated.

First, we examined tetraalkylation of anthraquinone (**1**) with olefins (Table 1). When the reaction of **1** with 10 equivalents (2.5 equiv to each ortho C−H bond) of triethylvinylsilane (**2a**) was carried out at 115 °C in toluene using $RuH_2(CO)(PPh_3)_3$ (**3**) as a catalyst, tetraalkylated anthraquinone **4a** was obtained in 78% isolated yield (entry 1). However, the coupling using trimethylvinylsilane (**2b**) at 115 °C afforded the tetraalkylation product **4b** only in 21% yield (entry 2). Conduction of the reaction at 180 °C in an autoclave improved the yield to 82% (entry 3).[12] The high-temperature condition was also effective for the coupling with other olefins **2c**−**e**. Allyltrimethylsilane (**2c**) reacted with **1** to give **4c** in 89% yield (entry 4). Both aliphatic (entry 5) and aromatic olefins (entry 6) can be used for the tetraalkylation reaction. In these cases, the coupling products were isolated in excellent yields, but the alkylation proceeded with 96:4 linear/branch selectivity.

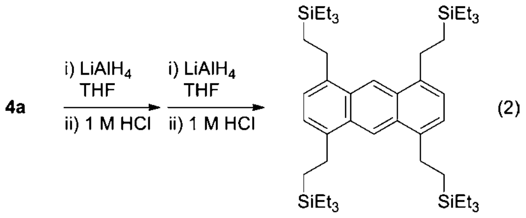
Table 1. Reaction of Anthraquinone with Olefins[a]



entry	2	R	4	isolated yield (%)
1	**2a**	Et_3Si	**4a**	78
2	**2b**	Me_3Si	**4b**	21
3[b]	**2b**	Me_3Si	**4b**	82
4[b,c]	**2c**	Me_3SiCH_2	**4c**	89
5[b,c]	**2d**	C_4H_9	**4d**	92[d]
6[b]	**2e**	*o*-MeC_6H_5	**4e**	quant[d]

[a] Reaction conditions: anthraquinone (**1**) (1 mmol), olefin (10 mmol), $RuH_2(CO)(PPh_3)_3$ (**3**) (0.1 mmol), toluene (1 mL), 115 °C, 48 h. [b] Performed in mesitylene (1 mL) at 180 °C. [c] 20 equiv of olefin was used. [d] Linear/branch = 96:4.

Anthraquinone derivative **4a** was converted to the corresponding tetraalkylated anthracene **5a** by repeating the cycle of reduction with $LiAlH_4$ and treatment with hydrochloric acid twice.[13] Tetraalkylated anthracene **5a** was obtained in 68% isolated yield (eq 2).



5a 68%

Next, we applied the C−H alkylation/aromatization strategy to the synthesis of tetraalkylpentacenes. The reaction of pentacenequinone (**6**) with **2a** at 115 °C gave the tetraalkylated pentacenequinone **7a** in 36% isolated yield (Scheme 1). The low yield of **7a** compared to that of anthraquinone **5a** may be attributed to the poor solubility of **6** in toluene. The reaction was also attempted at 180 °C, but significant dehydrogenative C−H alkenylation was

---

(7) (a) Clar, E. *Chem. Ber.* **1949**, *82*, 495. (b) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (c) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-i. *J. Org. Chem.* **2006**, *71*, 7967. (d) Takahashi, T.; Li, Y.; Hu, J.; Kong, F.; Nakajima, K.; Zhou, L.; Kanno, K.-i. *Tetrahedron Lett.* **2007**, *48*, 6726. (e) Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K.-i. *J. Am. Chem. Soc.* **2007**, *129*, 15752. (f) Li, S.; Li, Z.; Nakajima, K.; Kanno, K.-i.; Takahashi, T. *Chem. Asian. J.* **2009**, *4*, 294. (g) Zhou, L.; Nakajima, K.; Kanno, K.-i.; Takahashi, T. *Tetrahedron Lett.* **2009**, *50*, 2722.

(8) Kitazawa, K.; Kochi, T.; Sato, M.; Kakiuchi, F. *Org. Lett.* **2009**, *11*, 1951.

(9) Use of catalytic C−H arylation for synthesis of acene derivatives: (a) Yasukawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 12680. (b) Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2011**, *76*, 2867. (c) Mochida, K.; Kawasumi, K.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 10716. See also ref 4g.

(10) (a) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (b) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826.

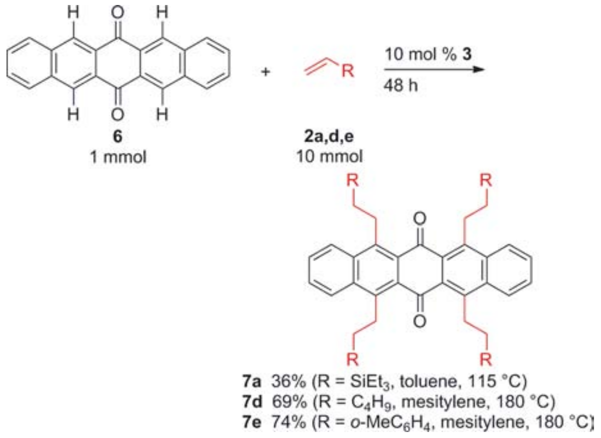
(11) Ueno, S.; Mizushima, E.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2006**, *128*, 16515.

(12) $RuH_2(CO)(PPh_3)_3$-catalyzed C−H/olefin coupling at high temperature: Nakazono, S.; Imazaki, Y.; Yoo, H.; Yang, J.; Sasamori, T.; Tokitoh, N.; Cedric, T.; Kageyama, H.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 7530.

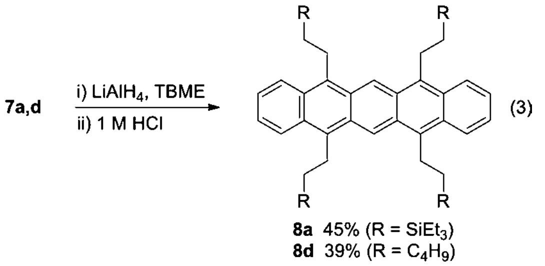
(13) Vets, N.; Smet, M.; Dehaen, W. *Tetrahedron Lett.* **2004**, *45*, 7287.

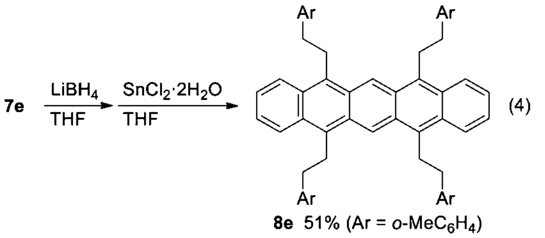
observed as a side reaction. The C–H alkylations of **6** with **2d** and **2e** at 180 °C gave the corresponding tetraalkylated pentacenequinones **7d** and **7e** in 69% and 74% isolated yields, respectively, and only linear isomers were observed.

Scheme 1. Regioselective Tetraalkylation of Pentacenequinone



Conversion of pentacenequinone derivatives **7** to tetraalkylpentacenes **8** were then investigated. When **7a** was reacted with $LiAlH_4$ in TBME and subsequently treated with hydrochloric acid, the desired pentacene **8a** was formed without repeating the reduction/dehydration cycle and isolated in 45% yield as a blue oil (eq 3). Tetrahexylpentacene **8d** was prepared in 39% yield in a similar manner as a blue solid. As we expected, the obtained tetraalkylpentacenes **8a,d** show high solubility in common organic solvents including hexane. In order to prepare pentacene derivative **8e**, the reduction of **7e** with $LiAlH_4$ was also attempted but did not proceed probably due to the low solubility of **7e** in TBME. After screening of various reaction conditions, it was found that reduction the carbonyls of **7e** with $LiBH_4$ in THF, followed by reductive aromatization using $SnCl_2 \cdot 2H_2O$ provides pentacene **8e** in 51% isolated yield over two steps as a deep blue solid (eq 4).[5e]



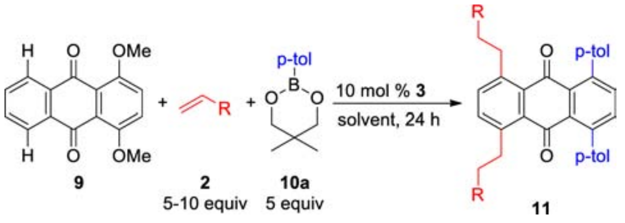


Previously, we reported ruthenium-catalyzed chemoselective tandem C–H alkylation/C–O arylation of 2′-methoxyacetophenones using olefins and organoboronates.[11] This reaction enables selective introduction of two different groups on aromatic rings in a single step. Therefore, we examined the tandem C–H alkylation/C–O arylation using dimethoxy-substituted acenequinones in order to prepare acenes bearing two different substituents in short sequences.

The tandem alkylation/arylation was first examined with 1,4-dimethoxyanthracene-9,10-dione (**9**) (Table 2). When the reaction of **9** with vinylsilane **2a** and *p*-tolylboronate **10a** was carried out using catalyst **3** under toluene refluxing conditions for 24 h, the methoxy groups and hydrogens at ortho positions of carbonyls were selectively converted to *p*-tolyl and 2-(triethylsilyl)ethyl groups, respectively, and the desired anthraquinone derivative **11a** was isolated in 74% yield (entry 1). Other olefins such as **2b**,**d**,**e** and 3,3-dimethyl-1-butene (**2f**) were also applicable to the C–H alkylation/C–O arylation, and the corresponding dialkyldiarylanthraquinones were obtained in 31–79% isolated yields (entries 2–5). The molecular structure of product **11f** was established by X-ray diffraction analysis, and an ORTEP drawing of **11f** is shown in Figure S1 (Supporting Information). The X-ray structure of **11f** clearly shows that two *p*-tolyl groups are introduced on one of the benzene rings, while the other benzene ring possesses two alkyl groups.

The chemoselective tandem C–C bond formation was applied to synthesize a dialkyldiarylpentacene using 5,14-dimethoxypentacene-6,13-dione (**12**) (Scheme 2). The reaction of **12** with **2a** and phenylboronate **10b** under toluene refluxing conditions proceeded chemoselectively to give the desired pentacenequinone **13** in 60% isolated yield. Aromatization of **13** using $LiAlH_4$ and HCl aq provided diphenyldialkylpentacene **14** in 42% isolated yield.

Table 2. Reaction of 1,4-Dimethoxyanthracene-9,10-dione (**9**) with *p*-Tolylboronate **10** and Olefins[a]

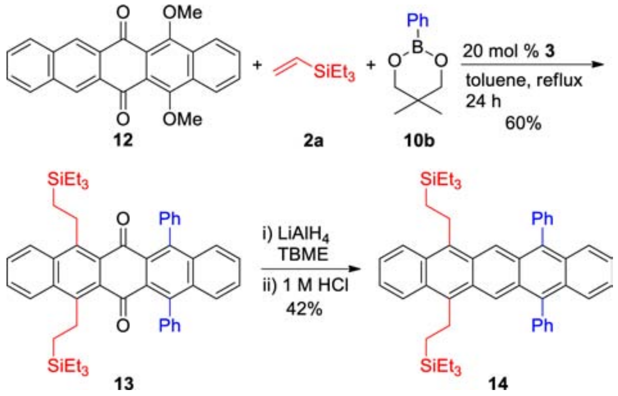


entry	2	R	11	isolated yield (%)
1	**2a**	Et_3Si	**11a**	74
2[b]	**2b**	Me_3Si	**11b**	51
3[b]	**2d**	C_4H_9	**11d**	31
4	**2e**	*o*-MeC_6H_5	**11e**	79
5[b]	**2f**	*t*-Bu	**11f**	58

[a] Reaction conditions: **9** (1 mmol), phenylboronate **10a** (5 mmol), olefin **2** (5 mmol), $RuH_2(CO)(PPh_3)_3$ (**3**) (0.1 mmol), toluene (2 mL), reflux, 24 h. [b] Performed with 10 mmol of **2** in mesitylene (2 mL) at 180 °C.

UV–vis absorption spectra of synthesized tetraalkylated pentacenes **8a**,**d**,**e** were measured in THF at room

Scheme 2. Synthesis of Dialkyldiarylpentacene **14**



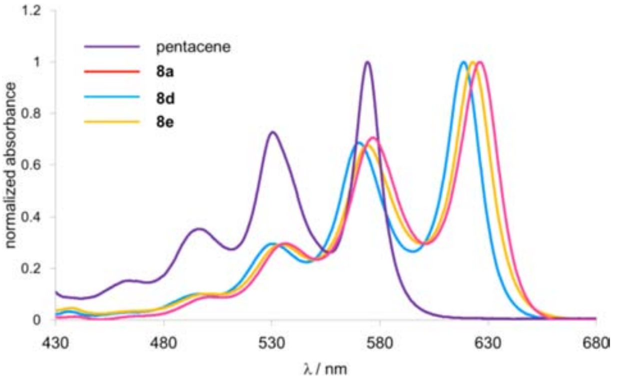


Figure 1. Normalized UV–vis spectra of tetraalkylpentacenes **8a**,**d**,**e** in THF.

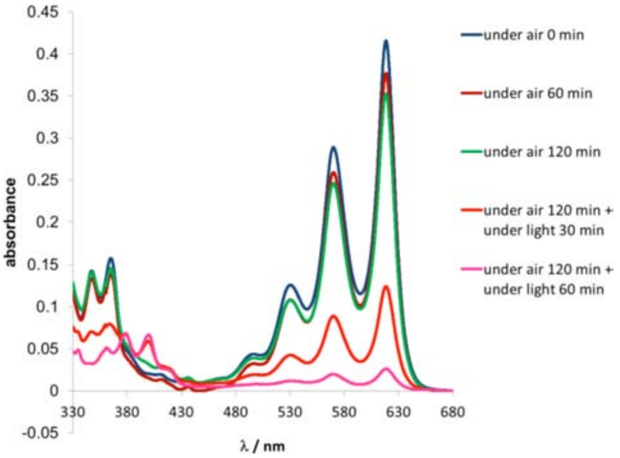


Figure 2. Absorbance change depending on exposing air in the dark or in the room light.

temperature under air (Figure 1). The absorption maxima of the pentacenes were observed at 626 (**8a**), 623 (**8e**), and 619 nm (**8d**). The observed absorption bands are highly red-shifted compared to that of parent pentacene in THF (λ_{max} = 574 nm),[14] but the substituents on the alkyl group only slightly affected the absorption behavior.

The stability of **8d** in THF under air was also evaluated by monitoring the UV–vis spectra (Figure 2). For the first 2 h, the absorption spectra was acquired in the dark, and the result suggested that most of **8d** remained undecomposed.[15] After 2 h, the solution was exposed to ambient light, and the absorption intensities of **8d** were significantly decreased within 60 min. These observations indicate that **8d** is somewhat stable under air in the dark. However, under ambient atmosphere and light, **8d** is easily photooxidized as was reported for 5,7,12,14-tetraphenylpentacene.[5d]

Cyclic voltammetry (CV) of **8d** was performed in dichloromethane containing 0.1 M n-Bu_4NPF_6. This molecule exhibited irreversible oxidation wave at +0.66 V. Based on this value, the highest occupied molecular orbital (HOMO) level of **8d** was estimated to be −5.46 eV, which is an appropriate level as active material for p-type OFETs.

In summary, we developed a new convenient method for the synthesis of alkyl-substituted acenes including pentacenes using our ruthenium-catalyzed C–H alkylation or tandem C–H alkylation/C–O arylation. The $RuH_2(CO)(PPh_3)_3$-catalyzed alkylations of anthraquinone and pentacenequinone with olefins afforded the corresponding tetraalkylated acenequinones in high yields.

The chemoselective tandem C–H alkylation/C–O arylation was applicable to acenequinones to give dialkyldiarylacenequinones. Conversion of tetrasubstituted pentacenequinones to the corresponding acene derivatives were achieved within two steps. CV analysis suggests that **8d** possesses an appropriate HOMO level as active material for p-type OFETs.

Acknowledgment. This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by The Science Research Promotion Fund, and by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices."

Supporting Information Available. Experimental procedures, characterization, and X-data/CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

---

(14) Debad, J. D.; Lee, S. K.; Qiao, X.; Pascal, R. A., Jr.; Bard, A. J. *Acta Chem. Scand.* **1998**, *52*, 45.

(15) (a) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980. (b) Palayangoda, S. S.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 6584. (c) De Angelis, F.; Gaspari, M.; Procopio, A.; Cuda, G.; Di Fabrizio, E. *Chem. Phys. Lett.* **2009**, *468*, 193.