OL Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Iodide-Mediated or Iodide-Catalyzed Demethylation and Friedel–Crafts C–H Borylative Cyclization Leading to Thiophene-Fused 1,2-Oxaborine Derivatives

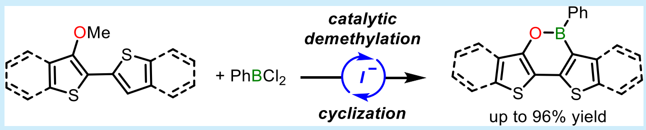
Keisuke Shigemori,[†] Momoka Watanabe,[†] Julie Kong,[†,#] Koichi Mitsudo,[*,†] Atsushi Wakamiya,[‡] Hiroki Mandai,[†] and Seiji Suga[*,†]

[†]Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan

[‡]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Supporting Information

ABSTRACT: The first synthesis of dithieno-1,2-oxaborine derivatives was achieved via iodide-mediated or iodide-catalyzed demethylation of 3-methoxy-2,2′-bithiophene and subsequent C–H borylation. A wide variety of thiophene-fused oxaborines could be synthesized by the procedure.



Organoboranes have played key roles in the field of organic chemistry as synthetic building blocks[1] and in organic materials.[2] Since the pioneering study by Dewar,[3] oxaborines, which are benzene derivatives containing boron and oxygen atoms, have gained focus because of their unique properties.[4] In particular, π-extended oxaborine compounds have attracted increased attention in recent years as active components of organic materials.[5] For instance, Hatakeyama and co-workers recently reported polycyclic aromatic compounds containing the 1,4-oxaborine skeleton, which could be used as a host material for organic light-emitting diodes and a thermally activated delayed fluorescence emitter (Figure 1a).[5a] In 2016, Hatakeyama[5b] and Müllen[5c] independently reported the syntheses of double helicenes having the oxaborine skeleton. Hatakeyama reported the ambipolar semiconductor characteristics of these species, and Müllen found that these compounds could be transformed to O–B-doped nanographenes.

Furthermore, incorporating thiophene moieties into acene derivatives has proven to be a powerful tool for conferring interesting properties, and these species have been the focus of research as promising compounds for the synthesis of organic materials.[6] Currently, boron-containing thienoacenes, such as thienoazaborines, are also highly topical research targets.[7] For instance, Perepichka reported terthiophenes fused with 1,2-azaborine units and applied them to fluorescence emitters (Figure 1b).[7a] Zhang and He reported angular-type thienoazaborines with high quantum yields, and used them to host materials for blue organic light-emitting diodes.[7k] Wang, Yuan, and Pei reported the use of B–N bond incorporated naphthotetrathiophene derivatives as p-type organic field effect transistors.[7d] Although there have been several reports on the synthesis and properties of thienoacenes containing 1,2-azaborines, to the best our knowledge, there has been no report on the synthesis of thienoacenes containing 1,2-oxaborines, although the latter should also be potential candidates for the synthesis of organic materials (Figure 1c).

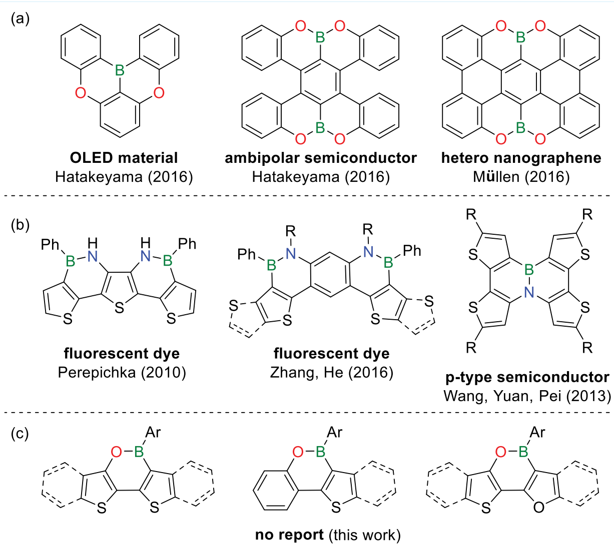


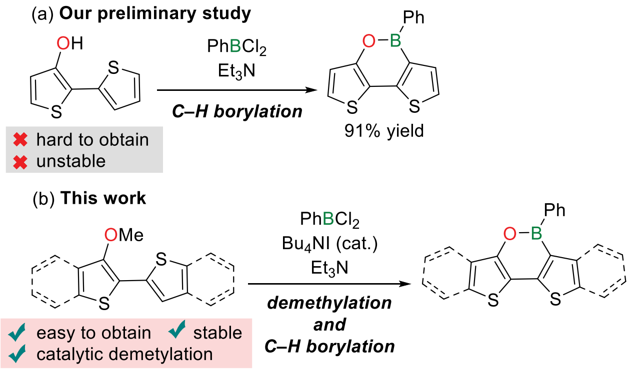
Figure 1. (a) Representative examples of previously reported 1,2-and 1,4-oxaborines, and (b) previously reported thiophene-fused 1,2-azaborines. (c) Dithieno-1,2-oxaborines, benzothieno-1,2-oxaborines, and thienofuro-1,2-oxaborines (this work).

We have been interested in the synthesis of π-extended thienoacenes,[8] and recently reported the synthesis and properties of thiophene-fused 1,4-azaborine derivatives.[8a] In this study, we turn our attention to the first and efficient synthesis of dithieno-1,2-oxaborine derivatives (DTOBs). We first considered that DTOBs could be derived from precursors

Received: February 5, 2019

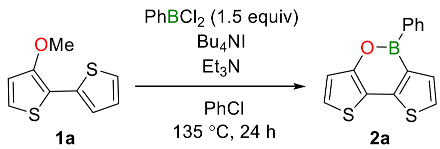
having a hydroxy group on their thiophene ring by Friedel–Crafts-type C–H borylation (Scheme 1a). Although the desired DTOB was obtained in excellent yield, synthesis of the precursors required several steps and the precursor species were relatively unstable.[9] In contrast, methoxy-group-substituted thiophene derivatives are stable and easy to handle, and a wide variety of derivatives can be easily obtained via coupling reactions. Therefore, methoxythiophene derivatives were selected as precursors for DTOBs from the synthesis point of view. We herein report the first synthesis of DTOBs via tandem reactions involving iodide-mediated or iodide-catalyzed demethylation and subsequent intramolecular Friedel–Crafts-type C–H borylation (Scheme 1b).

Scheme 1. Present Synthetic Strategy for Dithieno-1,2-oxaborines (DTOBs): (a) Preliminary Study and (b) This Work



First, **1a** was selected as a model substrate and subjected to demethylation and subsequent C–H borylation (Table 1).

Table 1. Synthesis of Dithienooxaborine 2a by Demethylation and Subsequent C–H Borylation under Various Conditions[a]



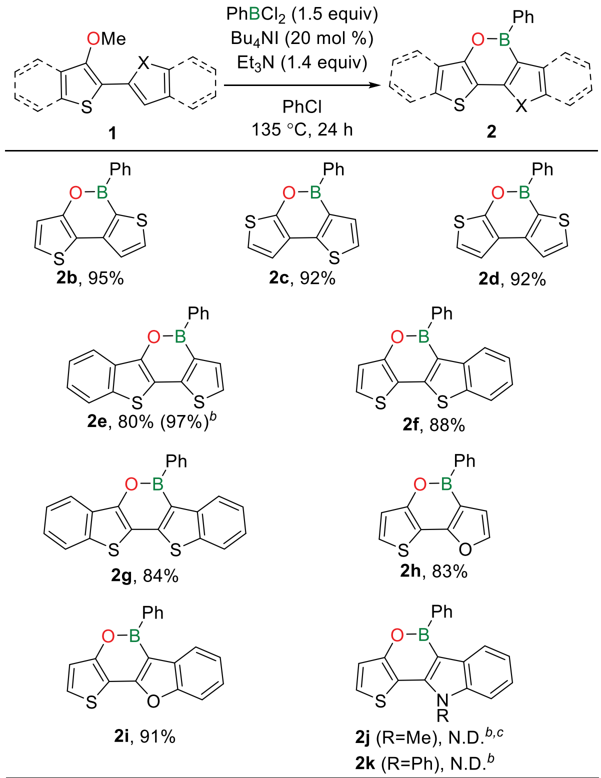
entry	Bu_4NI (equiv)	Et_3N (equiv)	yield[b] (%)
1	0	0	0
2	1.2	0	71
3	1.2	1.0	>99 (96)[c] (N.D.)[d]
4	0.2	1.0	90
5	0.2	1.4	>99 (93)[c]
6	0.2	1.4	82[c,e]

[a]Reaction conditions: **1a** (0.20 mmol), $PhBCl_2$ (1.5 equiv), Bu_4NI (0–1.2 equiv), Et_3N (0–1.4 equiv), PhCl (0.14 M), 135 °C, 24 h. [b]Determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [c]Isolated yield. [d]Performed with PhBpin, instead of $PhBCl_2$. N.D. = not detected. [e]Performed with 1.0 mmol of **1a**.

Treatment of **1a** with $PhBCl_2$ (1.5 equiv) in chlorobenzene at 135 °C for 24 h yielded no reaction (Table 1, entry 1). To promote demethylation of the methoxy group, various additives were employed, and Bu_4NI was found effective. In the presence of 1.2 equiv of Bu_4NI, **1a** was consumed completely and the desired oxaborine **2a** was obtained in 71% yield (Table 1, entry 2). Further optimization revealed that addition of Et_3N increased the yield of **2a**. With Et_3N (1.0 equiv), the reaction proceeded quantitatively (Table 1, entry 3; >99% NMR yield, 96% isolated yield). We also tried to use phenylboronic acid pinacol ester (PhBpin) instead of $PhBCl_2$, but **2a** was not obtained at all. Thereafter, the amount of Bu_4NI was reduced to catalytic quantities, where demethylation also proceeded upon decreasing the amount of Bu_4NI to 0.2 equiv to give **2a** in 90% yield (Table 1, entry 4). With 1.4 equiv of Et_3N, the yield of **2a** increased slightly to 93% (Table 1, entry 5). On the 1.0 mmol scale, **2a** was also obtained in good yield (Table 1, entry 6).

To clarify the scope of the iodide-catalyzed demethylation and subsequent C–H borylation, several thienooxaborines **2** were synthesized under the optimized conditions (Scheme 2).

Scheme 2. Synthesis of Thienooxaborines 2 by Iodide-Catalyzed Demethylation and C–H Borylation[a]



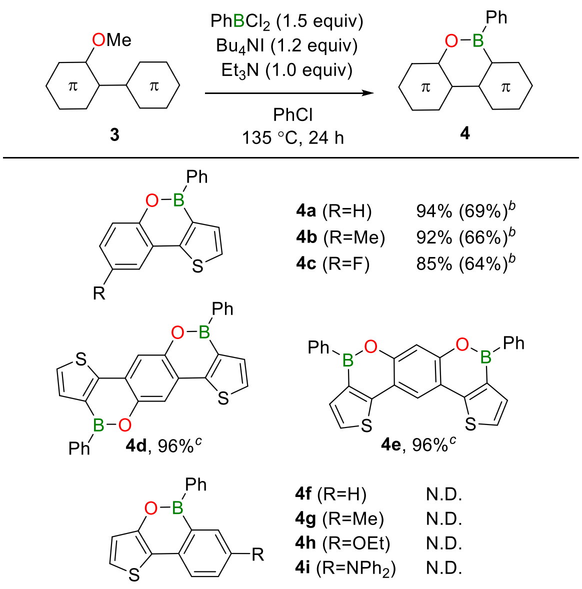
[a]Reaction conditions: **1** (0.20 mmol), $PhBCl_2$ (1.5 equiv), Bu_4NI (0.2 equiv), Et_3N (1.4 equiv), PhCl (0.14 M). Isolated yield. [b]Performed with Bu_4NI (1.2 equiv), Et_3N (1.0 equiv). [c]N.D. = not detected.

Dithienooxaborine isomers **2b–2d** were obtained from the corresponding precursors in excellent yields. Precursors having a 3-methoxybenzo[*b*]thienyl group were effective for this reaction and the *π*-expanded thienooxaborine derivatives **2e–2g** were obtained in good yields. The yield of **2e** increased to 97% with 1.2 equiv of Bu_4NI. Furan-fused thienooxaborines could also be obtained by this reaction. The iodide-catalyzed demethylation and C–H borylation proceeded smoothly to give the corresponding thienofuro-1,2-oxaborine derivatives **2h** and **2i** in the respective yields of 83% and 91%. In contrast, indole-fused thienooxaborines **2j** and **2k** were not obtained. The demethylation process proceeded, but the desired oxaborines **2j** and **2k** were not obtained, probably because of their instability.

DOI: 10.1021/acs.orglett.9b00485
Org. Lett. XXXX, XXX, XXX–XXX

The demethylation and C−H borylation of precursors **3** having a 2-phenylthiophene skeleton were then performed (Scheme 3). Treatment of precursor **3a**, having a methoxy group on the benzene skeleton, under catalytic conditions gave oxaborine **4a** in moderate yield (69%) with 21% of the starting material. Re-examination of the reaction conditions revealed that the addition of a stoichiometric amount Bu_4NI was essential for the substrate. With 1.2 equiv of Bu_4NI, the yield of **4a** was 94%. Both precursors, bearing electron-donating or electron-withdrawing groups, could be used for the reaction. Both **4b** and **4c** were obtained in high yields (**4b**, 92%; **4c**, 85%). This strategy could also be applied to the construction of highly π-expanded thienooxaborine derivatives. The demethylation and C−H borylation proceeded smoothly to give the corresponding ladder-type thienooxaborines **4d** and **4e** in 96% yield. In contrast, benzene-fused thienooxaborines **4f**−**4i** having an oxygen atom on their thiophene rings were unfortunately not obtained, possibly because of the lower nucleophilicity of the benzene ring of the precursors.

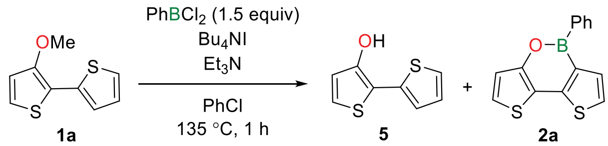
Scheme 3. Synthesis of Benzene-Fused Thienooxaborines 4[a]



[a]Reaction conditions: **3** (0.20 mmol), $PhBCl_2$ (1.5 equiv), Bu_4NI (1.2 equiv), Et_3N (1.0 equiv), PhCl (0.14 M), 135 °C, 24 h. Isolated yield. [b]Performed with Bu_4NI (0.2 equiv) and Et_3N (1.4 equiv). [c]Performed with $PhBCl_2$ (3.0 equiv), Bu_4NI (2.4 equiv), and Et_3N (2.0 equiv) in PhCl (0.07 M). N.D. = not detected.

To obtain further insight into the reaction mechanism, the products of the early stage of the reaction were examined (Table 2). The model substrate **1a** was treated with 1.2 equiv of Bu_4NI and 1.0 equiv of Et_3N under the established reaction conditions for 1 h. At this stage, the demethylation product **5** and the desired product **2a** were obtained in respective yields of 64% and 28%. This result suggests that the demethylation step may be very fast, and the intramolecular C−H borylation step would be slower than the demethylation step. Without Bu_4NI or Et_3N, demethylation was very slow, and more than 80% of the starting material **1a** was recovered (Table 2, entries 2 and 3). In contrast, with 20 mol % of Bu_4NI and 1.0 equiv of Et_3N, the catalytic demethylation proceeded smoothly to afford the demethylation product **5** in 54% yield and the cyclization product **2a** in 13% yield (Table 2, entry 4). The addition of 20 mol % of methyl iodide also promoted the reaction (Table 2, entry 5). The use of Bu_4NCl instead of Bu_4NI was not effective (Table 2, entry 6), indicating that the presence of I^- is essential for the reaction.

Table 2. Effect of the Amount of Bu_4NI and Et_3N at the Start of the Reaction[a]



entry	Bu_4NI (equiv)	Et_3N (equiv)	**5** (%)	**2a** (%)
1	1.2	1.0	64	28
2	0	1.0	6	2
3	0.2	0	7	1
4	0.2	1.0	54	13
5[b]	0.2	1.0	36	12
6[c]	1.2	1.0	3	<2

[a]Reaction conditions: **1a** (0.20 mmol), $PhBCl_2$ (1.5 equiv), Bu_4NI (0−1.2 equiv), Et_3N (0−1.0 equiv), PhCl (0.14 M), 135 °C, 1 h. Isolated yield. [b]Methyl iodide was used in place of Bu_4NI. [c]Bu_4NCl was used in place of Bu_4NI.

Based on the results presented above, a plausible mechanism for the reaction is illustrated in Figure 2. First, **1** reacts with $PhBCl_2$ to afford complex **A**. Thereafter, I^- attacks the methyl group of **A**, where demethylation affords the intermediate **B**, iodomethane, and triethylmethylammonium chloride ($MeEt_3NCl$) which would be in equilibrium with triethylamine and chloromethane (MeCl).[10] Subsequently, in the presence of Et_3N, intramolecular Friedel−Crafts-type C−H borylation furnishes **2** and $Et_3N{\cdot}HCl$. The iodomethane generated in situ reacts with Et_3N to regenerate $MeEt_3NI$.

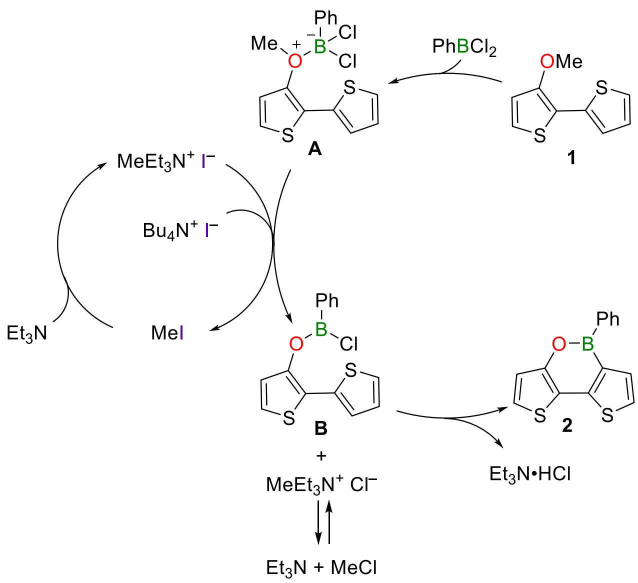
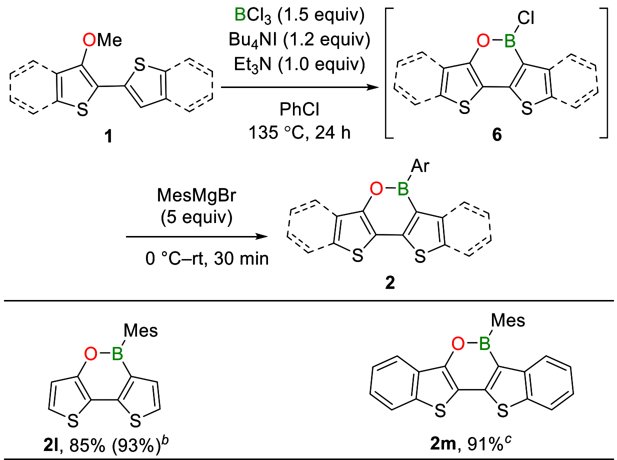


Figure 2. Plausible mechanism for the synthesis of DTOB.

From the synthesis point of view, introduction of another substituent on the B atom of DTOB has a significant impact. As an example, introduction of the mesityl group on the DTOB skeleton is demonstrated in Scheme 4. Precursor **1** was treated with BCl_3 to generate chlorinated DTOB **6** in situ, and

DOI: 10.1021/acs.orglett.9b00485
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 4. Introduction of a Mesityl Group on Boron Atom[a]



[a]Reaction conditions: **1** (0.2 mmol), BCl_3 (1.5 equiv), Bu_4NI (1.2 equiv), Et_3N (1.0 equiv), PhCl (0.14 M), 135 °C, 24 h, followed by MesMgBr (5 equiv), 0 °C, 30 min. Isolated yield. [b]Performed with 1.0 mmol of **1**. [c]Performed at room temperature.

6 was then reacted with the mesityl Grignard reagent (MesMgBr, 5 equiv) to give DTOB **2l** and **2m** in high yields (**2l**, 93%; **2m**, 91%).

The fundamental physical properties of the thus-obtained DTOB and other related derivatives were explored. Notably, all the DTOBs have low HOMO−LUMO levels, and are easy to handle. [Here, HOMO represents highest occupied molecular orbital and LUMO represents the lowest unoccupied molecular orbital.] In particular, highly π-expanded oxaborine **4d** and **4e** exhibited good fluorescence properties.[11]

In conclusion, we achieved the syntheses of DTOB and related derivatives via iodide-mediated or iodide-catalyzed demethylation and subsequent intramolecular C−H borylation. π-Expanded ladder-type oxaborines were also readily constructed by this method. The fundamental physical properties of the products were also studied. Further investigations of these derivatives are ongoing 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.9b00485.

Experimental details, photophysical and electrochemical properties of **2a−2m** and **4a−4e**, spectral data for all new compounds, data of theoretical calculations (PDF)

Accession Codes

CCDC 1895523 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: mitsudo@okayama-u.ac.jp (K. Mitsudo).

*E-mail: suga@cc.okayama-u.ac.jp (S. Suga).

ORCID

Koichi Mitsudo: 0000-0002-6744-7136

Atsushi Wakamiya: 0000-0003-1430-0947

Hiroki Mandai: 0000-0001-9121-3850

Seiji Suga: 0000-0003-0635-2077

Present Address

#Faculty of Science and Engineering, Sorbonne Université, 4 place Jussieu 75005 Paris, France.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by JSPS KAKENHI Grant Nos. JP16K05695 and JP16K05777, Okayama Foundation for Science and Technology, the Collaborative Research Program of Institute for Chemical Research, Kyoto University (Grant No. 2018-42), and JST, ACT-C, Japan. J.K. thanks LABEX MICHEM Sorbonne Universités and Association des Anciens Boursiers Francophones de la JSPS for their financial support.

■ REFERENCES

(1) (a) Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722. (b) Biffis, A.; Centomo, P.; Del Zotto, A.; Zecca, M. *Chem. Rev.* **2018**, *118*, 2249. (c) Xu, L.; Zhang, S.; Li, P. *Chem. Soc. Rev.* **2015**, *44*, 8848. (d) Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270. (e) Tobisu, M.; Chatani, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 3565. (f) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275.

(2) (a) Ji, L.; Griesbeck, S.; Marder, T. B. *Chem. Sci.* **2017**, *8*, 846. (b) Yang, X.; Zhou, G.; Wong, W.-Y. *Chem. Soc. Rev.* **2015**, *44*, 8484. (c) Wakamiya, A.; Yamaguchi, S. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1357. (d) Dogru, M.; Bein, T. *Chem. Commun.* **2014**, *50*, 5531. (e) Li, D.; Zhang, H.; Wang, Y. F. *Chem. Soc. Rev.* **2013**, *42*, 8416. (f) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584. (g) Elbing, M.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 834. (h) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (i) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927.

(3) (a) Dewar, M. J. S.; Dietz, R. *J. Chem. Soc.* **1960**, 1344. (b) Dewar, M. J. S.; Poesche, W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2253. (c) Dewar, M. J. S.; Rogers, H. *J. Am. Chem. Soc.* **1962**, *84*, 395. (d) Davis, F. A.; Dewar, M. J. S. *J. Org. Chem.* **1968**, *33*, 3324.

(4) For recent representative examples, see: (a) Saito, H.; Nogi, K.; Yorimitsu, H. *Chem. Lett.* **2017**, *46*, 1122. (b) Yruegas, S.; Patterson, D. C.; Martin, C. D. *Chem. Commun.* **2016**, *52*, 6658. (c) Saito, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. *J. Am. Chem. Soc.* **2016**, *138*, 15315. (d) Budanow, A.; von Grotthuss, E.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Tetrahedron* **2016**, *72*, 1477. (e) Sumida, Y.; Harada, R.; Kato-Sumida, T.; Johmoto, K.; Uekusa, H.; Hosoya, T. *Org. Lett.* **2014**, *16*, 6240. (f) Mathew, S.; Crandall, L. A.; Ziegler, C. J.; Hartley, C. S. *J. Am. Chem. Soc.* **2014**, *136*, 16666. (g) Guo, R.; Li, K.-N.; Liu, B.; Zhu, H.-J.; Fan, Y.-M.; Gong, L.-Z. *Chem. Commun.* **2014**, *50*, 5451. (h) He, J.; Crase, J. L.; Wadumethrige, S. H.; Thakur, K.; Dai, L.; Zou, S.; Rathore, R.; Hartley, C. S. *J. Am. Chem. Soc.* **2010**, *132*, 13848. (i) Greig, L. M.; Slawin, A. M. Z.; Smith, M. H.; Philp, D. *Tetrahedron* **2007**, *63*, 2391. (j) Chen, J.; Bajko, Z.; Kampf, J. W.; Ashe, A. J., III. *Organometallics* **2007**, *26*, 1563. (k) Zhou, Q. J.; Worm, K.; Dolle, R. E. *J. Org. Chem.* **2004**, *69*, 5147.

(5) (a) Numano, M.; Nagami, N.; Nakatsuka, S.; Katayama, T.; Nakajima, K.; Tatsumi, S.; Yasuda, N.; Hatakeyama, T. *Chem. - Eur. J.* **2016**, *22*, 11574. (b) Katayama, T.; Nakatsuka, S.; Hirai, H.; Yasuda, N.; Kumar, J.; Kawai, T.; Hatakeyama, T. *J. Am. Chem. Soc.* **2016**, *138*, 5210. (c) Wang, X.-Y.; Narita, A.; Zhang, W.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2016**, *138*, 9021.

(6) (a) Li, L.; Zhao, C.; Wang, H. *Chem. Rec.* **2016**, *16*, 797. (b) Cinar, M. E.; Ozturk, T. *Chem. Rev.* **2015**, *115*, 3036.

(c) Takimiya, K.; Osaka, I.; Mori, T.; Nakano, M. *Acc. Chem. Res.* **2014**, *47*, 1493. (d) Takimiya, K.; Nakano, M.; Kang, M. J.; Miyazaki, E.; Osaka, I. *Eur. J. Org. Chem.* **2013**, *2013*, 217. (e) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347.

(7) (a) Lepeltier, M.; Lukoyanova, O.; Jacobson, A.; Jeeva, S.; Perepichka, D. F. *Chem. Commun.* **2010**, *46*, 7007. (b) Lukoyanova, O.; Lepeltier, M.; Laferriere, M.; Perepichka, D. F. *Macromolecules* **2011**, *44*, 4729. (c) Wang, X.; Zhang, F.; Liu, J.; Tang, R.; Fu, Y.; Wu, D.; Xu, Q.; Zhuang, X.; He, G.; Feng, X. *Org. Lett.* **2013**, *15*, 5714. (d) Wang, X.-Y.; Lin, H.-R.; Lei, T.; Yang, D.-C.; Zhuang, F.-D.; Wang, J.-Y.; Yuan, S.-C.; Pei, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 3117. (e) Wang, X.-Y.; Zhuang, F.-D.; Wang, R.-B.; Wang, X.-C.; Cao, X.-Y.; Wang, J.-Y.; Pei, J. *J. Am. Chem. Soc.* **2014**, *136*, 3764. (f) Wang, X.-Y.; Zhuang, F.-D.; Zhou, X.; Yang, D.-C.; Wang, J.-Y.; Pei, J. *J. Mater. Chem. C* **2014**, *2*, 8152. (g) Crossley, D. L.; Cade, I. A.; Clark, E. R.; Escande, A.; Humphries, M. J.; King, S. M.; Vitorica-Yrezabal, I.; Ingleson, M. J.; Turner, M. L. *Chem. Sci.* **2015**, *6*, 5144. (h) Wang, X.; Zhang, F.; Gao, J.; Fu, Y.; Zhao, W.; Tang, R.; Zhang, W.; Zhuang, X.; Feng, X. *J. Org. Chem.* **2015**, *80*, 10127. (i) Wang, X.-Y.; Yang, D.-C.; Zhuang, F.-D.; Liu, J.-J.; Wang, J.-Y.; Pei, J. *Chem. - Eur. J.* **2015**, *21*, 8867. (j) Wang, X.-Y.; Zhuang, F.-D.; Wang, J.-Y.; Pei, J. *Chem. Commun.* **2015**, *51*, 17532. (k) Zhang, W.; Zhang, F.; Tang, R.; Fu, Y.; Wang, X.; Zhuang, X.; He, G.; Feng, X. *Org. Lett.* **2016**, *18*, 3618. (l) Zhou, J.; Tang, R.; Wang, X.; Zhang, W.; Zhuang, X.; Zhang, F. *J. Mater. Chem. C* **2016**, *4*, 1159. (m) Zhang, W.; Fu, Y.; Qiang, P.; Hunger, J.; Bi, S.; Zhang, W.; Zhang, F. *Org. Biomol. Chem.* **2017**, *15*, 7106. (n) Li, G.; Chen, Y.; Qiao, Y.; Lu, Y.; Zhou, G. *J. Org. Chem.* **2018**, *83*, 5577. (o) Zhang, J.; Liu, F.; Sun, Z.; Li, C.; Zhang, Q.; Zhang, C.; Liu, Z.; Liu, X. *Chem. Commun.* **2018**, *54*, 8178.

(8) (a) Mitsudo, K.; Shigemori, K.; Mandai, H.; Wakamiya, A.; Suga, S. *Org. Lett.* **2018**, *20*, 7336. (b) Mitsudo, K.; Tanaka, S.; Isobuchi, R.; Inada, T.; Mandai, H.; Korenaga, T.; Wakamiya, A.; Murata, Y.; Suga, S. *Org. Lett.* **2017**, *19*, 2564. (c) Mitsudo, K.; Kurimoto, Y.; Mandai, H.; Suga, S. *Org. Lett.* **2017**, *19*, 2821. (d) Mitsudo, K.; Asada, T.; Inada, T.; Kurimoto, Y.; Mandai, H.; Suga, S. *Chem. Lett.* **2018**, *47*, 1044. (e) Kurimoto, Y.; Mitsudo, K.; Mandai, H.; Wakamiya, A.; Murata, Y.; Mori, H.; Nishihara, Y.; Suga, S. *Asian J. Org. Chem.* **2018**, *7*, 1635. (f) Mitsudo, K.; Murakami, T.; Shibasaki, T.; Inada, T.; Mandai, H.; Ota, H.; Suga, S. *Synlett* **2016**, *27*, 2327. (g) Mitsudo, K.; Sato, H.; Yamasaki, A.; Kamimoto, N.; Goto, J.; Mandai, H.; Suga, S. *Org. Lett.* **2015**, *17*, 4858. (h) Kamimoto, N.; Schollmeyer, D.; Mitsudo, K.; Suga, S.; Waldvogel, S. R. *Chem. - Eur. J.* **2015**, *21*, 8257. (i) Mitsudo, K.; Shimohara, S.; Mizoguchi, J.; Mandai, H.; Suga, S. *Org. Lett.* **2012**, *14*, 2702.

(9) For the detail, see the Supporting Information.

(10) A conversion of tributylmethylammonium chloride to tributylamine and methyl chloride under the similar condition was confirmed. For details, see the Supporting Information.

(11) For the detail of the physical properties of DTOB derivatives, see the Supporting Information.

DOI: 10.1021/acs.orglett.9b00485
Org. Lett. XXXX, XXX, XXX−XXX