

The efficient synthesis of unsymmetrical oligo(phenylenevinylenes)

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Abstract—Selective DDQ oxidation of 2,5-bis(methylmethoxy)-1,4-di(octyloxy)benzene generates an unsymmetrical subunit suitable for the preparation of substituted tetrameric oligo(phenylenevinylenes) in good to excellent yields.
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1. Introduction

Probing the characteristics of well-defined π conjugated systems has been an active area of research over the past few years.¹ The synthesis of unsymmetrically substituted oligo(phenylenevinylenes) (OPVs) may have uses in LED devices,² organic photovoltaics,³ and NLO applications.⁴ To efficiently prepare unsymmetrical oligo(phenylenevinylenes), the facile synthesis of an unsymmetrical central subunit that can be produced in high yields is highly desirable. The most common method for the production of unsymmetrical subunits involves di-iodination of 1,4-di(octyloxy)benzene followed by monoformylation with *n*-BuLi and DMF,⁵

from which a growing oligomeric chain can then be constructed. Unfortunately, monoformylation reactions are often plagued with unwanted byproducts and low to moderate yields. As part of an ongoing program to prepare novel unsymmetrical OPVs, we sought a more selective and synthetically simpler method of producing these oligomers (Chart 1). Such a facile and versatile synthesis is described in this Letter.

2. Results and discussion

The selective oxidation of substituted methyl benzyl ethers with DDQ to their corresponding mono-aldehydes has previously been described.⁶ The rate at which the oxidation occurs was found to depend on both the reaction concentration and the substitution pattern on the aromatic ring. In particular, the presence of electron donating substituents on the ring was found to accelerate the direct conversion of dimethyl benzyl ethers to mono-aldehydes in excellent yields (~99% isolated). This method appeared ideal for the preparation of an unsymmetrical subunit useful for OPV synthesis (Scheme 1).

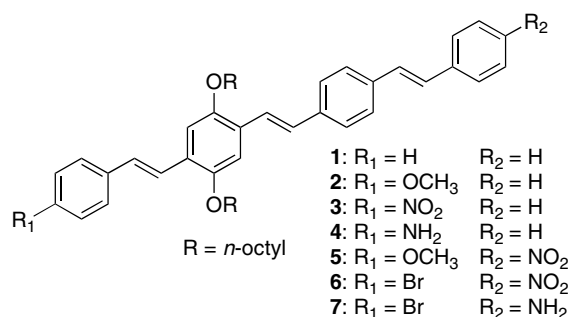
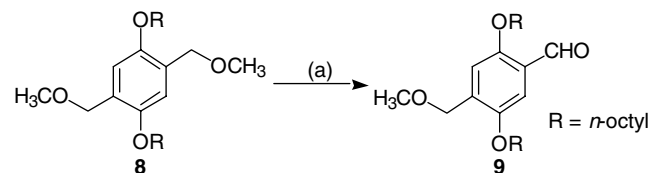


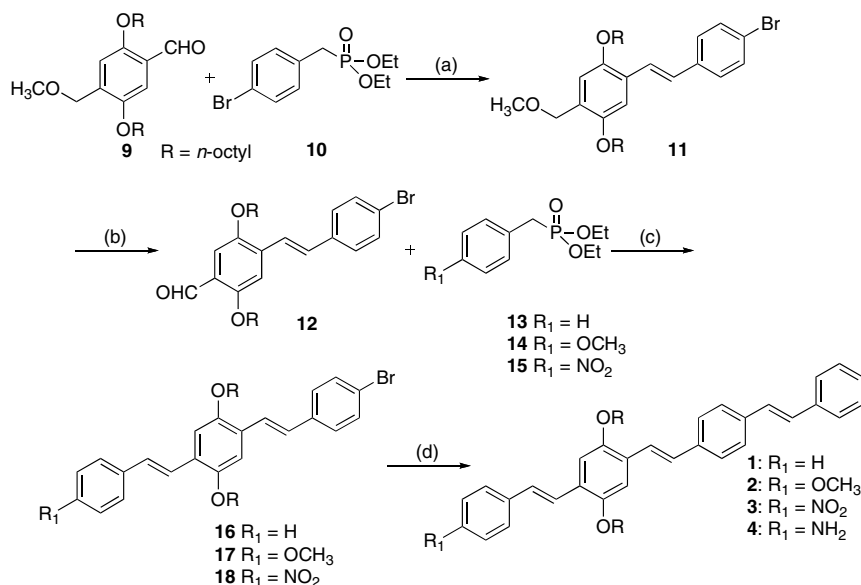
Chart 1. Unsymmetrical OPVs 1–7.

Keywords: Oligomers; Phenylene vinylene; Asymmetric synthesis; Photovoltaic; Wittig; Horner–Wadsworth–Emmons; Mono-formylated; Coupling.

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Scheme 1. Reagents and conditions: (a) DDQ, CH₂Cl₂/H₂O, rt, 99%.



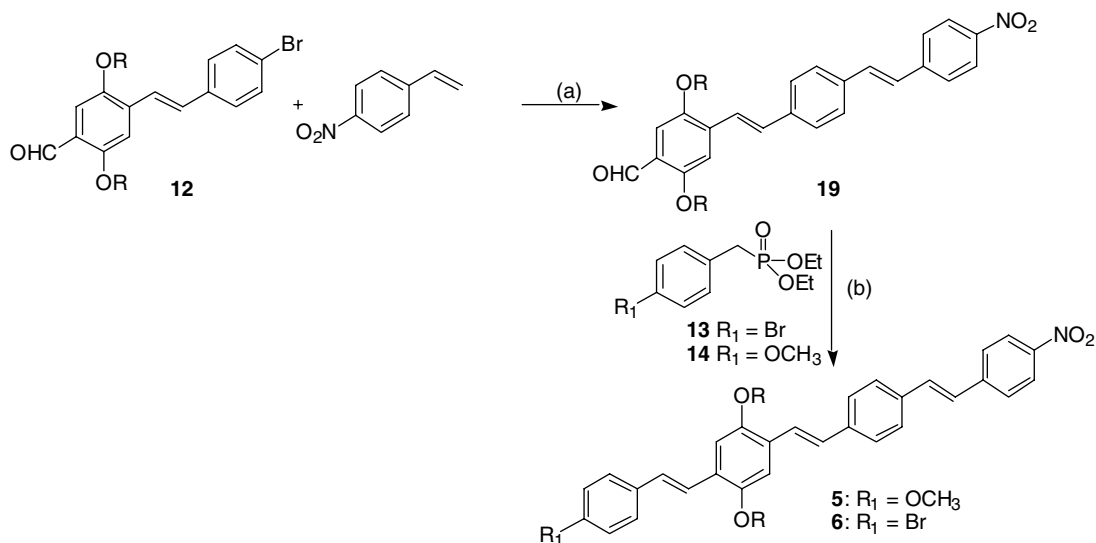
Scheme 2. Reagents and conditions: (a) *t*BuOK, THF, rt, 12 h, 92%; (b) DDQ, CH₂Cl₂/H₂O, rt, 96%; (c) *t*BuOK, THF, rt, 12 h, 74–84%; (d) Styrene, Pd(OAc)₂, K₃PO₄, DMA, 140 °C, 19 h, 50–75%.

The synthesis of unsymmetrical OPVs using mono-aldehyde **9** is shown in [Scheme 2](#). Dimethyl ether **8** was prepared from the corresponding dibromide by reaction with sodium methoxide in dry methanol in 96% yield. The selective oxidation of **8** to **9** was found to proceed best using a 0.02 M solution of **8** and DDQ in a 10:1 mixture of methylene chloride and water at room temperature. The conversion to mono-aldehyde **9** was found by TLC to occur quantitatively (99%) in 15 min. Purification of **9** was accomplished by washing the organic layer with satd NaHCO₃ and removing the organic solvent under reduced pressure. The intermediate dimeric bromide **11** was prepared using a Horner–Wadsworth–Emmons (HWE) coupling reaction of **9** with aryl phosphonate ester **10**, and then converted to **12** in 96% yield with DDQ. To demonstrate the versatility of the syn-

thetic approach presented here, we used two different reaction pathways to prepare tetramers **1–4** ([Scheme 2](#)) and **5–7** ([Scheme 3](#)) from this precursor.

For the synthesis of tetramers **1–3** ([Scheme 2](#)), the intermediate bromide **12** was reacted with the *para*-substituted aryl phosphonates **13–15** under HWE coupling conditions to produce trimers **16–18**. The subsequent Heck coupling reactions with styrene produced tetramers **1–3**. Nitro-substituted tetramer **3** was converted to its amine-substituted analog **4** by reduction with SnCl₂ in ethanol (80 °C, 18 h) in 60% yield.

The procedure used to synthesize tetramers **5–6** is outlined in [Scheme 3](#). In this synthesis, **12** is reacted under Heck coupling conditions with *para*-nitrostyrene to give



Scheme 3. Reagents and conditions: (a) Pd(OAc)₂, NaOAc, tetramethylguanidine, DMA, 140 °C, 16 h, 50%; (b) *t*BuOK, THF, rt, 12 h, 67–69%.

the trimeric aldehyde **19** in ~50% crude yield. HWE coupling with either **13** or **14** provided the corresponding methoxy-nitro (**5**) and bromo-nitro-substituted (**6**) tetramers, which were subsequently purified by column chromatography. The bromo-nitro-substituted tetramer **6** was then converted to the amine-substituted analog **7** using SnCl₂ in ethanol in ~60% yield, similar to the conversion of **3** to **4**.

In summary, the selective oxidation of a methyl benzyl ether produces an intermediate we have used to synthesize unsymmetrical mono- and disubstituted OPVs. We believe this synthetic procedure is more versatile and simpler to work with than previous synthetic methods.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.11.073](https://doi.org/10.1016/j.tetlet.2007.11.073).

References and notes

1. Wong, M. S.; Li, Z. H.; Shek, M. F.; Kei, H. C.; Tao, Y.; D'Iorio, M. *J. Mater. Chem.* **2000**, *10*, 1805–1810; Würthner, F.; Chen, Z.; Hoeben, F. J. M.; Osswald, P.; You, C.-C.; Jonkheijm, P.; Herrikhuyzen, J. v.; Schenning, A. P. H. J.; van der Schoot, P. P. A. M.; Meijer, E. W.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611–10618; Summers, M. A.; Kemper, P. R.; Bushnell, J. E.; Robinson, M. R.; Bazan, G. C.; Bowers, M. T.; Buratto, S. K. *J. Am. Chem. Soc.* **2003**, *125*, 5199–5203; Murphy, A. R.; Fréchet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597; Jonkheijm, P.; Stutzmann, N.; Chen, Z.; de Leeuw, D. M.; Meijer, E. W.; Schenning, A. P. H. J.; Würthner, F. *J. Am. Chem. Soc.* **2006**, *128*, 9535–9540.
2. Tao, Y.; Donat-Bouillud, A.; D'Iorio, M.; Lam, J.; Gorjanc, T. C.; Py, C.; Wong, M. S.; Li, Z. H. *Thin Solid Films* **2000**, *363*, 298–301.
3. Sun, S.; Fan, Z.; Wang, Y.; Haliburton, J. *J. Mater. Sci.* **2005**, *40*, 1429–1443; Bundgaard, E.; Krebs, F. C. *Solar Energy Solar Cells* **2007**, *91*, 954–985.
4. Klärner, G.; Former, C.; Martin, K.; Räder, J.; Müllen, K. *Macromolecules* **1998**, *31*, 3571–3577.
5. Nierengarten, J.-F.; Gu, T.; Hadzioennou, G.; Tsamouras, D.; Krasnikov, V. *Helv. Chim. Acta* **2004**, *87*, 2948–2966; Gu, T.; Nierengarten, J.-F. *Tetrahedron Lett.* **2001**, *42*, 3175–3178.
6. Wang, W.; Li, T.; Attardo, G. *J. Org. Chem.* **1997**, *62*, 6598–6602.