Tetrahedron Letters xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and use of *ortho*-(branched alkoxy)-*tert*-butoxybenzenes

Slavko Rast, Michel Stephan *, Barbara Mohar *

National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 29 August 2012
Revised 21 September 2012
Accepted 2 October 2012
Available online xxxx

Keywords:
Dialkoxyarene
tert-Butoxyarene
o-Bromo-*tert*-butoxyarene
DMF di-*tert*-butyl acetal
Phosphine

ABSTRACT

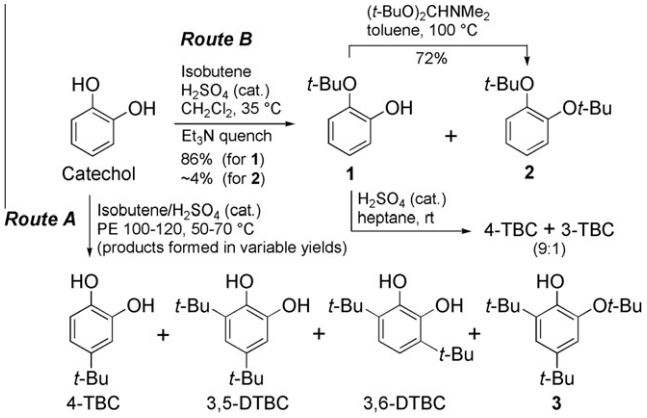
A series of sterically hindered *o*-(branched alkoxy)-*tert*-butoxybenzenes was efficiently prepared in good yields owing to a new practical and simple preparation of *o*-*tert*-butoxyphenol starting from catechol and isobutene. Use of DMF di-*tert*-butyl acetal reagent instead of isobutene/H_2SO_4 (cat.) for *O*-*tert*-butylation was very convenient in case of *ortho* bulky phenols affording the corresponding *tert*-butyl ethers in high yield and purity. This general route proved to be useful since no reliable access was available to *o*-di-*t*-BuO-substituted arenes. Application to the synthesis of congested phosphorus-based compounds is presented.

Despite the availability of a variety of simple-to-perform synthetic routes toward *tert*-butoxyarenes,[1–3] still access to *ortho* congested ones represents a particular challenge in organic chemistry.[4] Among the devised strategies to the former class of compounds, the acid-catalyzed addition of phenols to isobutene is the most economical and practical.[2] By contrast, a comprehensive literature survey revealed only a very limited number of poorly characterized *o*-di-*t*-BuO-substituted arenes; as for example, the fully peralkoxylated hexa-*tert*-butoxybenzene and a densely substituted 2,3-di-*tert*-butoxynaphthalene which were prepared though via aromatic cyclization reactions.[5]

Pursuing our study of bulky P-based compounds,[6] we aimed to increase the vicinal steric crowding of the appended *P*-*o*-RO-Ph groups wherein R represents a branched alkyl. Therefore, it was of special interest to prepare a series of *o*-(branched alkoxy)-*tert*-butoxybenzenes.[7]

To the best of our knowledge, the preparation of *o*-di-*tert*-butoxybenzene and its further use in phosphines' synthesis has been only reported by Horner and Simons in 1983.[8] They have also described therein the *para* isomer claiming their both preparations via the H_2SO_4-catalyzed addition of the corresponding diphenol to isobutene at 70 °C. However, our repetitive attempts to prepare the requisite *o*-di-*tert*-butoxybenzene according to their published procedure were consistently unsuccessful as a variety of ring *tert*-butylated catechols (variable yields) was being formed instead in our hands (Scheme 1, *Route A*). A closer look at their published data revealed that the corresponding ^{1}H NMR[9] does not match with the expected compound profile compared to a well-known series of *o*-dialkoxybenzenes.[7,10] Facing this discrepancy,[11] we ventured to synthesize the symmetric *o*-di-*tert*-butoxybenzene and its closely related *o*-(branched alkoxy)-*tert*-butoxybenzenes which results are presented herein.

We initiated our investigation by studying the reaction of catechol with isobutene under milder conditions (rt to 35 °C) employing a catalytic amount of H_2SO_4 in an aprotic solvent (PE 100–120, heptane, or CH_2Cl_2) (Scheme 1, *Route B*). Such conditions were



Scheme 1. *O*-*tert*-Butylation of catechol under various conditions.

* Corresponding authors. Present address: PhosPhoenix SARL, 115, rue de l'Abbé Groult, F-75015 Paris, France (M.S.). Tel.: +386 1 4760250; fax: +386 1 4760300.
E-mail addresses: mstephan@phosphoenix.com (M. Stephan), barbara.mohar@ki.si (B. Mohar).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.10.010

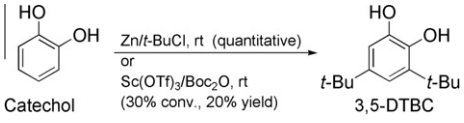
already recommended by Stevens back in 1955 for the preparation of mono *tert*-butoxyarenes.[12]

While the rt reaction in CH_2Cl_2 of PhOH with excess isobutene in the presence of a trace of H_2SO_4 (performed in a glass pressure-bottle) led in our hands to the major formation of 4-*tert*-butyl- and 2,4-di-*tert*-butylphenol mixture wherein Friedel–Crafts C-alkylation had taken place,[12] interestingly enough starting from catechol (reaction in CH_2Cl_2 at 35 °C) and neutralizing H_2SO_4 with Et_3N after 3 h, furnished *o*-*tert*-butoxyphenol (**1**) in 92% (86% isolated yield) accompanied by 8% of the targeted *O*,*O*′-di-*tert*-butylated product **2** (by ^1H NMR analysis). In the literature, **1** has been prepared in 23–33% overall yield via a protection–etherification–deprotection sequence from catechol.[13] We have noticed that a reaction equilibrium exists during *O*-*tert*-butylation of **1** (protection of catechol remaining free OH group) as prolonging reaction time did not lead to a significant yield increase of *O*,*O*′-di-*tert*-butylcatechol (**2**), but to isobutene polymerization. Advantageously, neutralizing H_2SO_4 prior to reaction workup proved to prevent *C*-*tert*-butylation as well as de-*O*-*tert*-butylation. Our study showed that **1** rearranges readily into isomeric 4-*tert*-butyl- and 3-*tert*-butylcatechols (4-TBC/3-TBC 9:1 ratio) in heptane at rt in the presence of a trace of H_2SO_4. Also, employing CH_2Cl_2 instead of heptane or petroleum ethers was beneficial for reaction rate due to a better catechol solubilization. Further on, instead of the acid-catalyzed *O*-*tert*-butylation of phenols using isobutene, the non-acidic working conditions (toluene at 80–110 °C) provided by the commercially available DMF di-*tert*-butyl acetal reagent[14] (~8 equiv) permitted finally the formation of *o*-di-*tert*-butoxybenzene (**2**) from **1** in 72% isolated yield. Thus, following the above optimized protocols, *o*-*tert*-butoxyphenol (**1**) and *o*-di-*tert*-butoxybenzene (**2**) were efficiently prepared from catechol on multigram-scale (up to 20 g).

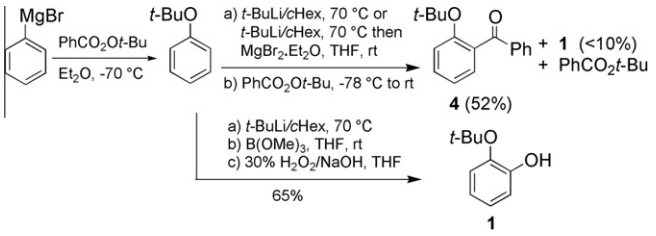
In parallel, alternative strategies to *o*-di-*tert*-butoxybenzene (**2**) from catechol were explored but to no avail. Applying Bandgar's conditions (Zn in *t*-BuCl, rt)[2f] or Bartoli's conditions (5 mol% $Sc(OTf)_3$ in excess Boc_2O, rt)[2g,2h] resulted in the exclusive formation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in quantitative isolated yield within 1 day for the former and in ~20% isolated yield (30% total conversion) after 2 days for the latter (Scheme 2).

Another potential stepwise route to *o*-di-*tert*-butoxybenzene (**2**) was attempted inspired from the preparation of *tert*-butoxybenzene via PhMgBr addition to $PhCO_2Ot$-Bu.[3a] Surprisingly, the *ortho*-metallated *tert*-butoxybenzene (metal = Li or MgBr) reacted with $PhCO_2Ot$-Bu to yield 2-*tert*-butoxy-benzophenone (**4**) in 52% isolated yield with concomitant formation of *o*-*tert*-butoxyphenol (**1**) and $PhCO_2t$-Bu (Scheme 3). Nevertheless, *o*-*tert*-butoxyphenol could be prepared in 65% yield via *o*-*tert*-butoxyphenyllithium addition to $B(OMe)_3$ followed by oxidation.

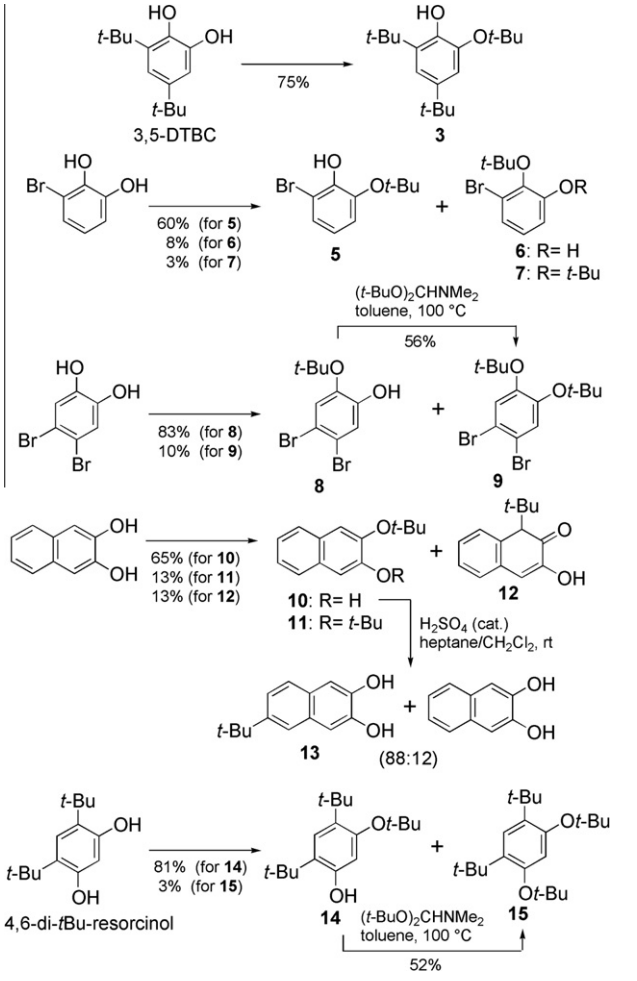
Next, we were interested to extend this study to other phenols. Thus, the mild *O*-*tert*-butylation conditions employing isobutene/H_2SO_4 (cat.) in CH_2Cl_2 at <40 °C (with low-temperature H_2SO_4 neutralization using Et_3N) were applied to *o*-*tert*-butylphenol, 3,5-di-*tert*-butylcatechol, 3-bromocatechol, 4,5-dibromocatechol, 2,3-dihydroxynaphthalene, 4,6-di-*tert*-butylresorcinol, and pyrogallol (Scheme 4). However, a complex mixture was obtained in the case of *o*-*tert*-butylphenol and pyrogallol.



Scheme 2. Attempts to *O*-*tert*-butylate catechol under selected literature conditions applied toward *tert*-butoxybenzene.



Scheme 3. Oxidation of *o*-*tert*-butoxyphenyllithium.



Scheme 4. *O*-*tert*-Butylation of selected dihydroxyarenes using isobutene/H_2SO_4 (cat.) in CH_2Cl_2 at 35–40 °C and low-temperature acid neutralization with Et_3N (after 0.5–7 days).

Similarly as noted in the case of catechol, an equilibrium was observed in the H_2SO_4-catalyzed addition of the examined series to isobutene, especially during the second *O*-*tert*-butylation; prolonging reaction time did not favor a significant yield increase of the *O*,*O*′-di-*tert*-butylated product. Fortunately, the latter could be obtained in good yield reverting to the DMF di-*tert*-butyl acetal reagent. Steric hindrance and electron-poor catechols had detrimental effect on *O*-*tert*-butylation using isobutene/H_2SO_4 in general, and on *O*,*O*′-di-*tert*-butylation in particular. For example, 3 h, 3 days and 12 h were necessary for a reasonable conversion to mostly mono *O*-*tert*-butylated products of catechol, 3-bromocatechol, and 4,5-dibromocatechol, respectively.

In particular, *O*-*tert*-butylation of 3-bromocatechol led to a mixture of 2-bromo-6-*tert*-butoxyphenol (**5**), 3-bromo-2-*tert*-butoxyphenol

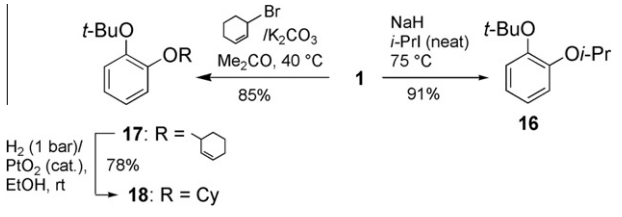
(**6**), and 2,3-di-*tert*-butoxy-bromobenzene (**7**) in 72:22:6 ratio, accompanied with an unreacted starting material. Noteworthy, forcing *O*-*tert*-butylation under the same conditions of 2-bromo-6-*tert*-butoxyphenol (**5**) (prepared via another route, vide infra) resulted in no conversion to the desired diether. Hence, it can be concluded that *O*,*O*′-di-*tert*-butylated product **7** is derived from **6**.

2,3-Dihydroxynaphthalene yielded after 7 days a mixture of 3-*tert*-butoxy-2-hydroxynaphthalene (**10**), 2,3-di-*tert*-butoxynaphthalene (**11**), and 3-*tert*-butoxy-1-*tert*-butylnaphthalen-2-one (**12**)[15] in 70:15:15 ratio. As H_2SO_4-catalyzed rearrangement of **10** gave 6-*tert*-butyl-2,3-dihydroxynaphthalene (**13**), the formation of **12** could stem either from a possible *C*-*tert*-butylation of a ketonic form of 2,3-dihydroxynaphthalene or a direct aromatic *C*-*tert*-butylation followed by enol-keto tautomerization to accommodate the bulky *tert*-butyl group.

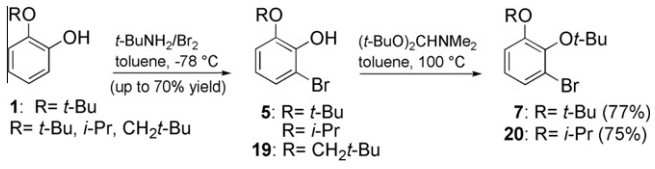
Pursuing the functionalization of *o*-*tert*-butoxyphenol (**1**), its Williamson's etherification in acetone using the reactive 3-bromocyclohexene or *i*-PrI and K_2CO_3, furnished after 2–3 days the targeted dissymmetric diethers in 85% and <5% yields, respectively (Scheme 5). Using NaH in excess with *i*-PrI as the solvent and performing the reaction in a glass pressure-tube at 75 °C for 2–3 days afforded the *o*-*tert*-butoxy-*iso*-propoxybenzene (**16**) in up to 91% yield. Further on, PtO_2-catalyzed hydrogenation of *o*-*tert*-butoxy-(2-cyclohexenyloxy)benzene (**17**) afforded *o*-*tert*-butoxy-cyclohexyloxybenzene (**18**) in 78% isolated yield.

The high yield generation of *ortho*-lithiated 1,2-dialkoxyarene species used in phosphines' synthesis, can be conveniently facilitated under mild conditions via bromine–lithium exchange. Moreover, regioselective arene bromination is crucial when utilizing unsymmetrical 1,2-dialkoxyarenes with two non-equivalent and competing free *ortho*-positions. Thus, the contiguous bromine atom-incorporated 2,3-di-*tert*-butoxybenzene **7** and analogue **20** (Scheme 6) were prepared in good yields by *O*-*tert*-butylation using excess DMF di-*tert*-butyl acetal of the *o*-bromo-hydroxyarenes derived in turn from *ortho*-regioselective ring bromination (*t*-$BuNH_2/Br_2$)[16] of *o*-(branched alkoxy)phenols. Unfortunately, 2-bromo-6-neopentoxyphenol (**19**) resisted *O*-*tert*-butylation under these standard conditions. Noteworthy, *O*-*tert*-butylation with DMF di-*tert*-butyl acetal of **1** or **5** proceeded with comparable reaction rates.

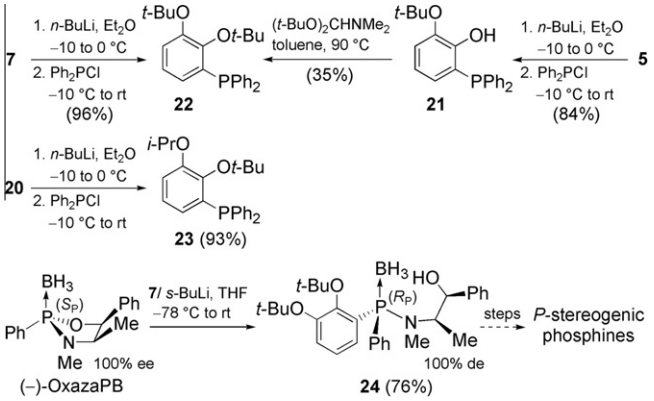
Finally, incorporation of the bulky 3-(α-branched alkoxy)-2-*tert*-butoxyphenyls onto P-based compounds was undertaken (Scheme 7). Starting from the corresponding 3-(α-branched alkoxy)-2-*tert*-butoxy-bromobenzenes **7** and **20**, (3-RO-2-*tert*-butoxyphenyl)diphenylphosphines **22** (R = *t*-Bu) and **23** (R = *i*-Pr) were



Scheme 5. Williamson's etherification of *o*-*tert*-butoxyphenol (**1**).



Scheme 6. Synthesis of 3-(branched alkoxy)-2-*tert*-butoxy-bromobenzenes.



Scheme 7. Preparation of congested P-based compounds calling upon *ortho*-(α-branched alkoxy)-*tert*-butoxybenzenes.

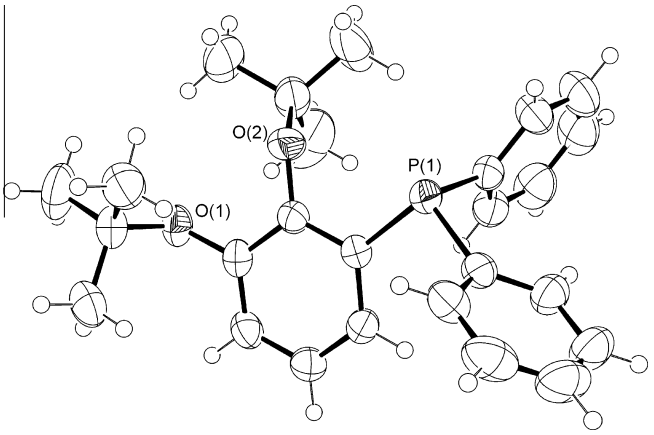


Figure 1. ORTEP drawing of **22** at the 50% probability level.

obtained in 93–96% yields. In another synthetic variant for **22** (29% overall yield), the diphenylphosphino group was first introduced starting from **5** followed by *O*-*tert*-butylation with DMF di-*tert*-butyl acetal. ^{1}H NMR of the *P*-(2,3-di-*tert*-butoxyphenyl)-substituted phosphine **22** is in utter disagreement with the corresponding one reported by Horner and Simons[8] bringing an additional proof against their misleading claim concerning preparation of both *o*-di-*tert*-butoxybenzene (**2**) and its P-derivative. Our characterization of **22** is backed up by its X-ray crystal structure determination (Fig. 1).[17] Progressing toward bulky *P*-stereogenic P-based compounds, we have prepared the stereomerically pure *P*-(2,3-di-*tert*-butoxyphenyl)-appended aminophosphine-*P*-borane **24** by ring-opening of enantiopure (–)-oxazaPB with preformed 2,3-di-*tert*-butoxyphenyllithium.[18,19] Such intermediate (**24**) serves as key-precursor in the Jugé–Stephan asymmetric route to *P*-stereogenic phosphines.[20] Preparation of derived bulky phosphines and their application in asymmetric catalysis will be presented elsewhere.

In summary, taking advantage of a new simple and straightforward preparation of *o*-*tert*-butoxyphenol, we have succeeded to prepare in high yields the elusive *o*-di-*tert*-butoxybenzene along with a series of congested *o*-RO-*tert*-butoxybenzenes wherein R = *i*-Pr, 2-cyclohexenyl, and Cy. In addition, the DMF di-*tert*-butyl acetal reagent proved to be quite effective for *O*-*tert*-butylation of a variety of congested phenols. Thus, starting from catechols, isobutene/H_2SO_4 (cat.) system can be applied for the preparation of *o*-*tert*-butoxyphenols (major mono *O*-*tert*-butylation), while when

targeting *o*-di-*tert*-butoxyarenes, DMF di-*tert*-butyl acetal reagent can be practical starting from *o*-*tert*-butoxyphenols. Moreover, successful use of the bulky *ortho*-(α-branched alkoxy)-*tert*-butoxybenzenes for the preparation of achiral and chiral P-based compounds was accomplished.

Acknowledgments

This work was supported by the Ministry of Higher Education, Science, and Technology of the Republic of Slovenia (Grant No. P1-242). We thank Barbara Modec, University of Ljubljana, for X-ray crystal structure determination on the Supernova diffractometer of EN-FIST Centre of Excellence, Slovenia.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.010. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Greene, T. W.; Wutz, P. G. M. *Protective Groups in Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1999; For a significant early achievement concerning *m*-cresol addition to isobutene in the presence of H_2SO_4, see: (b) Stevens, D. R. *J. Org. Chem.* **1955**, *20*, 1232–1236.
2. For *O*-*tert*-butylation of phenols, see: with *t*-BuBr/ZnO: (a) Ravindranath, B.; Srinivas, P. *Tetrahedron* **1984**, *40*, 1623–1628. with *t*-BuBr/pyridine:; (b) Masada, H.; Oishi, Y. *Chem. Lett.* **1978**, *1*, 57–58. with isobutene/TfOH (cat.), see:; (c) Holcombe, J. L.; Livinghouse, T. *J. Org. Chem.* **1986**, *51*, 111–113. with *t*-BuOH/acid, see:; (d) Shen, H.-Y.; Judeh, Z. M. A.; Ching, C. B.; Xia, Q.-H. *J. Mol. Catal. A: Chem.* **2004**, *212*, 301–308; (e) Wright, S. W.; Hageman, D. L.; Wright, A. S.; McClure, L. D. *Tetrahedron Lett.* **1997**, *38*, 7345–7348. with *t*-BuCl/Zn, see:; (f) Bandgar, B. P.; Kasture, S. P. *J. Chem. Res., Synop.* **2000**, 252–253. with Boc_2O/$Sc(OTf)_3$, see:; (g) Bartoli, G.; Bosco, M.; Carlone, A.; Dalpozzo, R.; Locatelli, M.; Melchiorre, P.; Sambri, L. *J. Org. Chem.* **2006**, *71*, 9580–9588; (h) Bartoli, G.; Bosco, M.; Locatelli, M.; Marcantoni, E.; Melchiorre, P.; Sambri, L. *Org. Lett.* **2005**, *7*, 427–430.
3. For the preparation of *tert*-butoxybenzene from PhMgBr/$PhCO_2Ot$-Bu, see: (a) *Org. Syn. Coll.* **1973**, *5*, 924; **1965,** *45*, 89; (b) Lawesson, S.-O.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 4230–4233; from PhBr/*t*-BuOK, see: (c) *Org. Syn. Coll.* **1973**, *5*, 926; **1961**, *41*, 91; (d) Cram, D. J.; Rickborn, B.; Knox, G. R. *J. Am. Chem. Soc.* **1960**, *82*, 6412–6413.
4. For 3,4-di-*t*-BuO-$PhCO_2H$ use (no preparation or characterization), see: (a) Rho, H. S.; Baek, H. S.; Lee, J. A.; Park, C. M.; Kim, D. H.; Chang, S.; Lee, S. WO2006118380, 2006; *Chem. Abstr.* **2006**, *145*, 489011; for attempts to prepare 2,3-di-tert-butoxynaphthalene from 2,3-naphthalenediol, see: (b) Font, J.; Messeguer, A.; Serratosa, F.; Sola, P.; Vilarrasa, L. *An. Quim.* **1976**, *72*, 247–253; for *O*-alkylation of phenols with $Me_2CClC{\equiv}CH$, see: (c) Kuemmerle, J.; Jiang, S.; Tseng, B.; Kasibhatla, S.; Drewe, J.; Cai, S. X. *Bioorg. Med. Chem.* **2008**, *16*, 4233–4241.
5. (a) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550–2552; (b) Serratosa, F. *Acc. Chem. Res.* **1983**, *16*, 170–176; (c) Enhsen, A.; Karabelas, K.; Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 1177–1185; (d) Causey, P. W.; Dubovyk, I.; Leznoff, C. C. *Can. J. Chem.* **2006**, *84*, 1380–1387.
6. (a) Stephan, M.; Mohar, B. FR2887253, 2005; WO2006136695, 2006 (http://www.cas.org/spotlight/rlist1q07p/rlist1q07p.html); *Chem. Abstr.* **2006**, *146*, 82028; (b) Stephan, M.; Šterk, D.; Mohar, B. *Adv. Synth. Catal.* **2009**, *351*, 2779–2786; (c) Zupančič, B.; Mohar, B.; Stephan, M. *Org. Lett.* **2010**, *12*, 1296–1299; (d) Zupančič, B.; Mohar, B.; Stephan, M. *Org. Lett.* **2010**, *12*, 3022–3025; (e) Stephan, M.; Šterk, D.; Zupančič, B.; Mohar, B. *Org. Biomol. Chem.* **2011**, *9*, 5266–5271.
7. For ^1H NMR spectra of bulky *o*-di-RO-benzenes wherein R = *i*-Pr, *i*-Bu, Cy, etc, see: Stephan, M.; Zupančič, B.; Mohar, B. *Tetrahedron* **2011**, *67*, 6308–6315.
8. Horner, L.; Simons, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1983**, *14*, 189–209.
9. The reported[8] ^1H NMR does not correspond to the one for *o*-di-*tert*-butoxybenzene.
10. For ^1H NMR spectra of *o*-di-RO-benzenes wherein R = Me and Et, see: Pouchert, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^1H *FT-NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1993.
11. For a similar discrepancy against Ref. 8 regarding their erroneous claim for *p*-di-*tert*-butoxybenzene preparation, see: Carman, R. M.; Kanizaj, N.; Taylor, R. J. K. *Aust. J. Chem.* **1997**, *50*, 515–516.
12. It was found at an early stage by Stevens[1b] that a low temperature and a catalytic amount of H_2SO_4 were crucial for the high yield formation of *m*-*tert*-butoxytoluene from *m*-cresol and isobutene. However, no yield or information was given about the reaction conditions of other listed phenols therein (ex. preparation of *tert*-butoxybenzene) which were supposedly prepared under the same reaction conditions.
13. *O*-*tert*-Butylation of *o*-benzoyloxyphenol was carried out using isobutene/TfOH (cat.) in CH_2Cl_2 at −50 °C. For this, see: (a) Beech, C. L.; Coope, J. F.; Fairley, G.; Gilbert, P. S.; Main, B. G.; Plé, K. *J. Org. Chem.* **2001**, *66*, 2240–2245; (b) Bredikhin, A. A.; Bredikhina, Z. A.; Zakharychev, D. V.; Konoshenko, L. V. *Tetrahedron: Asymmetry* **2007**, *18*, 1964–1970.
14. For *tert*-butyl aryl ethers synthesis using the *tert*-butyl-transfer reagent DMF di-*tert*-butyl acetal, see: Mohacsi, E. *Synth. Commun.* **1983**, *13*, 827–832.
15. Preparation of **12** was carried out by reaction of *t*-BuCl/NaH with 2,3-dihydroxynaphthalene. For this, see Ref. 4b.
16. For *ortho* bromination of phenols, see: Pearson, D. E.; Wysong, R. D.; Breder, C. V. *J. Org. Chem.* **1967**, *32*, 2358–2360.
17. Crystallographic data (excluding structure factors) for the structure (compound **22**) in this Letter has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 898217. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033; e-mail: deposit@ccdc.cam.ac.uk).
18. Surprisingly the ring-opening of oxazaPB with the bulky 2,3-di-*tert*-butoxyphenyllithium was not accompanied with a competitive attack on the ephedrine moiety as observed with other bulky organolithiums. For such study, see: Stephan, M. M. S.; Šterk, D.; Modec, B.; Mohar, B. *J. Org. Chem.* **2007**, *72*, 8010–8018.
19. For the ring-opening of oxazaPB with polymethoxy-substituted phenyllithiums, see: (a) Zupančič, B.; Mohar, B.; Stephan, M. *Adv. Synth. Catal.* **2008**, *350*, 2024–2032; (b) Zupančič, B.; Mohar, B.; Stephan, M. *Tetrahedron Lett.* **2009**, *50*, 7382–7384.
20. (a) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357–6360; (b) Stephan, M.; Modec, B.; Mohar, B. *Tetrahedron Lett.* **2011**, *52*, 1086–1089; (c) Grabulosa, A. *P-Stereogenic Ligands in Enantioselective Catalysis*, 1st ed.; RSC publishing: Cambridge, UK, 2011.