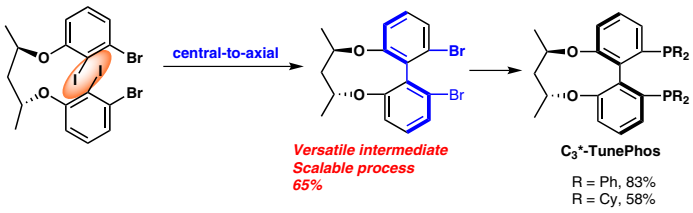
Synthesis X. Deng et al. Paper

An Efficient and Modular Route to C_3*-TunePhos-Type Ligands

Xu Deng[a,b]
Yu-Qing Guan[a]
Ning-Ning Huo[a]
Ya-Jing Wang[c]
Hui Lv*[a]
Xu-Mu Zhang*[a,d]

[a] College of Chemistry and Molecular Science, Wuhan University, Wuhan, Hubei 430072, P. R. of China
huilv@whu.edu.cn
xumu@whu.edu.cn
[b] College of Xiangya Pharmaceutical Sciences, Central South University, Changsha 410013, P. R. of China
[c] Hunan University of Chinese Medicine, Changsha 410208, China
[d] Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, P. R. of China



Received: 25.02.2017
Accepted after revision: 17.04.2017
Published online: 11.05.2017
DOI: 10.1055/s-0036-1588421; Art ID: ss-2017-h0115-op

Abstract An efficient and modular synthetic route to the bidentate C_3*-TunePhos was developed, which allowed tunable steric and electronic effects of the ligands. This novel chemical technology highlights a versatile C_3*-dibromodiphenyl intermediate that was accomplished by in situ Grignard exchange and subsequent Cu(II)-mediated intramolecular oxidative radical coupling process. It is worth noting that this advanced intermediate not only could be easily prepared by a diverse array of C_3*-TunePhos-type ligands, but also could be used to facile synthesis of other novel type of N,S-centered bidentate ligands.

Key words C_3*-TunePhos-type ligands, modular route, oxidative coupling

Given the tremendous success of BINAP in asymmetric catalysis,[1] design and synthesis of new efficient atropisomeric C_2-symmetric diphosphine ligands has been a constant research theme in asymmetric catalysis. In fact, both the aryl phosphorous substituents and the biaryl backbone are tunable parts in this ligand family.[2] Structure variations on the biaryl backbone led to a diverse set of atropisomeric C_2-symmetric diphosphine ligands in the past two decades, such as MeO-BIPHEP,[3] P-Phos,[4] SynPhos,[5] SegPhos,[6] DifluorPhos,[2] and other important biaryl phosphine ligands[7] (Figure 1), which found wide applications in asymmetric catalysis.[8] Subtle alterations of the electronic and steric properties of the phosphorous substituents on these C_2-symmetric ligands, such as replacing with bulkier aromatics (*p*-Tol-BINAP[9] and DTBM-SegPhos[6]), electronically modified substituents (*p*-F-BINAP, Cy-BINAP),[9,10] or heteroaromatics (α-furyl-MeO-BIPHEP),[3] also generated new, efficient ligands, all of which exhibited superior performance in asymmetric catalysis. Though great achievement has gained for C_2-symmetric ligands, highly modular ligands are still needed to counter the challenges posed by the asymmetric catalysis because no ligands is universally efficient for all types of substrates.[11] In 2000, Zhang et al. developed an efficient and tunable C_2-symmetric ligand, namely C_n-TunePhos. We not only investigated the effect of bite angle on the enantioselectivity, but also achieved the optimal ligand choice for a specific substrate by facile tuning of linking bridge.[12]

Initially, the synthesis of (*R*)-C_n-TunePhos was achieved through functional manipulations of the enantiopure precursor (*R*)-MeO-BIPHEP.[13] Later, Saito disclosed their de novo synthetic route to (*R*)-C_n-TunePhos starting from

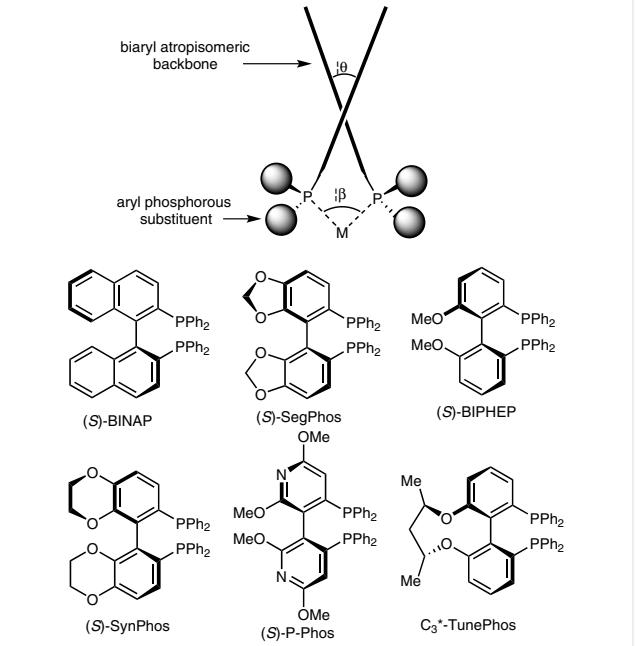
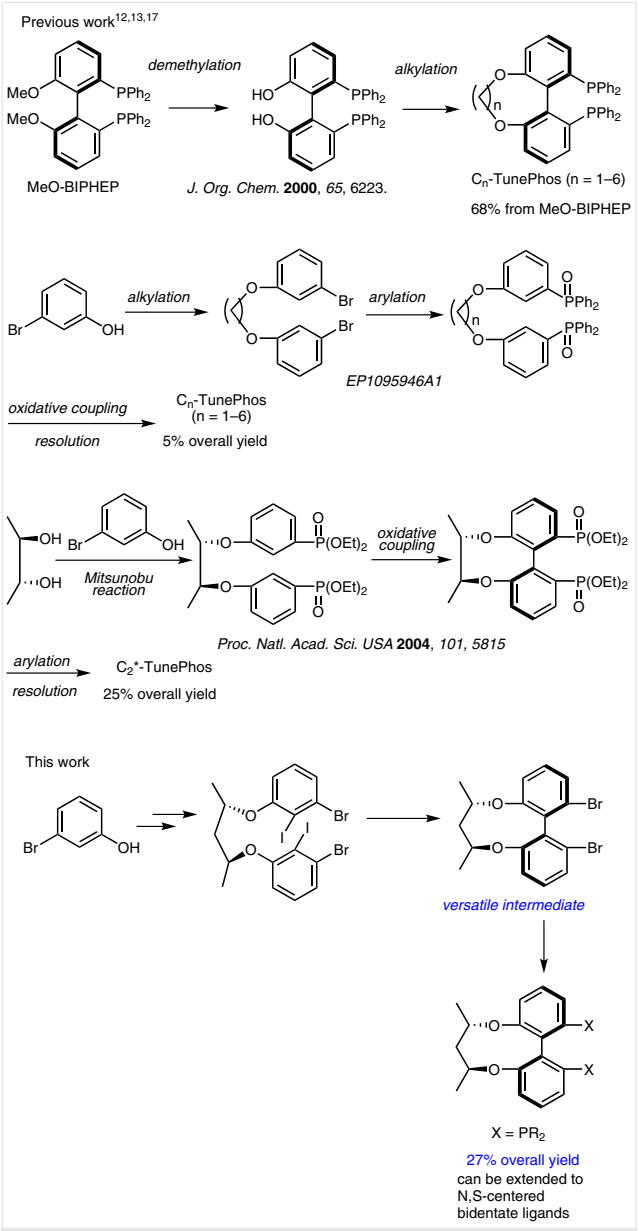


Figure 1 General stereoelectronic tunable features of a C_2-symmetric atropisomeric diphosphane and representative examples. M = transition-metal center, β = bite angle, θ = dihedral angle.

m-bromophenol, which features oxidative coupling as the key step.[13] Recently, Zhang[14,15] and Chan[16,17] have developed chiral-bridged atropisomeric diphosphine ligands through a remarkable central-to-axial chirality transfer strategy (Scheme 1). Though extensive studies have been directed to the efficient and practical synthesis of C_n-TunePhos, there were still problems to be circumvented. For instance, most of the synthetic processes towards atropisomeric C_2-symmetric ligands involved the tedious resolution procedure to obtain the enantiopure ligands, which is both time- and cost-consuming. And all of these processes involved diarylphosphonate as the key intermediate, which were proved to be quite inefficient for the subsequent arylation, especially for those with steric bulk and electron-poor substituents. Moreover, the flexibility of the processes remained to be improved. Thus, we wondered if we can develop an efficient and versatile synthetic route towards C_3-TunePhos and related bidentate ligands from a common intermediate. To this end, C_3*-dibromodiphenyl was an excellent choice since this versatile intermediate could be subjected to the subsequent arylation through a diverse set of methods, such as lithiation and cross-coupling reaction, which provides more possibilities for the synthesis of steric bulk and electron poor C_3-TunePhos, and even other related N,S-centered bidentate ligands. In turn, we envisaged that C_3*-dibromodiphenyl could be prepared by regioselective Grignard exchange[18] followed by oxidative coupling reaction using a similar center-to-axial chiral transfer strategy. Herein we present our efficient and modular synthesis of bidentate C_3*-TunePhos and related bidentate ligands using C_3*-dibromodiphenyl as the key intermediate.

Our synthetic endeavors towards C_3*-TunePhos commenced with the protection of commercially available 3-bromophenol (**1**) with *N*,*N*-diethylcarbamoyl chloride by deprotonation with NaH, giving the carbamate **2** in excellent yield. Subsequently, regiospecific lithiation with LDA followed by quenching with I_2 afforded the desired aryl iodide **3** in good yield.[19] Saponification of compound **3** delivered the phenol **4** smoothly, which was further converted to the coupling precursor (*R*,*R*)-**6** in high yield through Mitsunobu reaction by reacting with the enantiopure (*S*,*S*)-2,4-pentanediol (**5**) in the presence of DIAD and PPh_3. Up to this stage, the reactions proceeded uneventfully and we easily prepared the diiodide (*R*,*R*)-**6** on gram scale (Scheme 2).

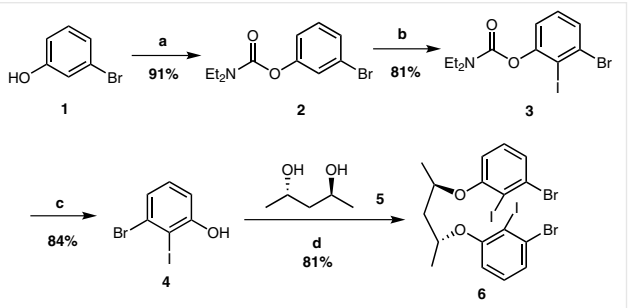
With the precursor (*R*,*R*)-**6** in hand, the key oxidative coupling reaction was then attempted (Table 1). First, several oxidants were examined. It was found that I_2 only afforded the desired product in 10% yield (Table 1 entry 1), while $Fe(acac)_3$, $FeCl_3$, and $CuCl_2$ also provided the dibromide (S_{ax},*RR*)-**7** in low yield (entries 2–4), albeit with minor improvements. It is elucidated that the main side product was the dehalogenated one, which might be attributed to low solubility of the oxidant in THF thus resulting in low conversion. The reaction outcomes dissected by way of introducing additives. Addition of TMEDA to $FeCl_3$ system resulted in negligible effects on the yield (entry 5), whereas the combination of $CuCl_2$ and TMEDA led to a significant improvement (entry 6), partially due to the enhancement of solubility of $CuCl_2$ in THF and subtle tuning of the oxidation state of $CuCl_2$. Further improvement was achieved by additional stabilizing agent, LiCl but not HMPA, delivering the desired product in acceptable yield (entry 8). In addition, the concentration also exerted some positive effects on the yield (entry 9). To this stage, the optimized reaction conditions were established. Notably, this versatile advanced intermediate (S_{ax},*RR*)-**7** could be prepared in gram scale under



Scheme 1 Synthetic endeavors towards C_n-TunePhos

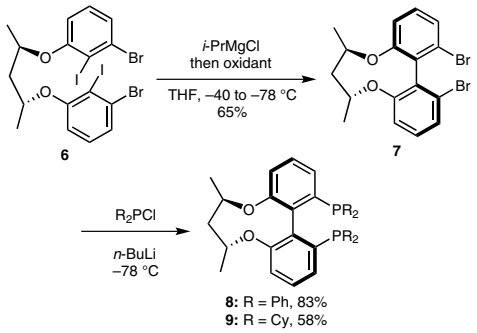
the optimal reaction conditions. Finally, the dibromide (S_{ax},*RR*)-**7** was subjected to Li–Br exchange by treatment with *n*-BuLi at low temperature, followed by quenching with R_2PCl to deliver the ligands (S_{ax},*RR*)-**8** and (S_{ax},*RR*)-**9** in moderate to good yields (Table 1). Both ligands (S_{ax},*RR*)-**8**[12] and (S_{ax},*RR*)-**9**[15] display generally very marked chiral recognition properties in asymmetric hydrogenation. The overall yield of ligand (S_{ax},*RR*)-**8** by this route is comparable to that by Chan's strategy[17] (Scheme 1).

In summary, we have developed an efficient and modular route to C_3*-TunePhos and related ligands, which highlights an efficient process involving Grignard exchange and subsequent Cu(II)-mediated oxidative coupling to give a versatile C_3*-dibromodiphenyl intermediate. It is worth noting that this advanced intermediate **7** could not only be the precursor to easily prepare a diverse array of C_3*-TunePhos type ligands, but also could be used to the facile synthesis of other novel type of N,S-centered ligands.



Scheme 2 *Reagents and conditions*: (a) *N*,*N*-diethylcarbamoyl chloride, NaH, THF, r.t., 24 h, 91%; (b) LDA, THF, then I_2, –78 °C, 0.5 h, 81%; (c) aq NaOH, THF, reflux, 24 h, 84%; (d) DIAD, PPh_3, THF, ultrasound, 0 °C, 1 h, 81%.

Table 1 Screening of the Coupling Reaction



Entry[a]	Oxidant	Additives	Conc. (mol/L)[b]	Yield (%)[c]
1	I_2	–	0.1	10
2	$Fe(acac)_3$	–	0.1	33
3	$FeCl_3$	–	0.1	30
4	$CuCl_2$	–	0.1	22
5	$FeCl_3$	TMEDA	0.1	28
6	$CuCl_2$	TMEDA	0.1	43
7	$CuCl_2$	TMEDA/HMPA	0.1	35
8	$CuCl_2$	TMEDA/LiCl	0.1	54
9	$CuCl_2$	TMEDA/LiCl	0.05	65

[a] Reactions were carried out in 1 mmol scale with the corresponding oxidant (2.5 equiv) and additive (2.5 equiv).
[b] The concentration of substrate **6** in THF.
[c] Isolated yields.

All reactions were carried out under an argon atmosphere using flame-dried glassware, unless otherwise noted. CH_2Cl_2 and 1,2-dichloroethane (DCE) were dried over CaH_2 and THF was distilled over Na metal. All reagents were commercially available and used without further purification, unless indicated otherwise. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by TLC carried out on GF254 plates (0.25 mm layer thickness) using UV light as visualizing agent and aq ammonium cerium nitrate/ammonium molybdate and H_2SO_4/EtOH solution (15%) as developing agents. Flash chromatography was performed with 300–400 mesh silica gel.

^1H and ^{13}C NMR spectra were recorded on a NMR spectrometer at ambient temperature. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from TMS (multiplicity, coupling constant, integration). Standard abbreviations are used to designate multiplicities. High-resolution mass spectra (HRMS) was taken on ESITOF (time of flight) mass spectrometer at a 4000 V emitter voltage.

3-Bromophenyl Diethylcarbamate (2)[19]

To a suspension of NaH (1.92 g, 80 mmol) in anhyd THF (100 mL) was added a solution of 3-bromophenol (**1**; 6.92 g, 40 mmol) in THF (10 mL) dropwise at 0 °C under argon. Upon completion of addition, the mixture was warmed to r.t. and was stirred at this temperature for another 3 h. Then, a solution of *N*,*N*-diethylcarbamoyl chloride in THF (10 mL) was added to the reaction mixture dropwise. The resulting suspension was stirred at r.t. overnight. The reaction was quenched with aq NH_4Cl and the mixture extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum. The crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (10:1) to afford the desired product as a white solid; yield: 9.68 g (91%); mp 157–158 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 1 H), 7.26 (d, *J* = 8.5 Hz, 1 H), 7.15 (t, *J* = 8.5 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 3.36–3.33 (m, 4 H), 1.18–1.14 (m, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 153.7, 152.4, 130.4, 128.3, 125.4, 122.2, 120.9, 42.6, 42.2, 14.5, 13.6.

3-Bromo-2-iodophenyl Diethylcarbamate (3)

To a solution of *i*-Pr_2NH (1.54 mL, 11 mmol) in anhyd THF (30 mL) at –78 °C under argon was added a solution of *n*-BuLi in THF (4.4 mL, 2.5 M in hexane) dropwise. The mixture was stirred at this temperature for 45 min. Then, a solution of 3-bromophenyl diethylcarbamate (**2**; 2.72 g, 10 mmol) in THF (10 mL) was added to the reaction mixture dropwise. The resulting solution was stirred at –78 °C for 0.5 h. Next, a solution of I_2 (3.05 g, 12 mmol) in THF (10 mL) was added dropwise

and the mixture was stirred at this temperature for another 0.5 h. Upon completion of the reaction (TLC monitoring), the reaction was quenched with sat. aq NH_4Cl and sat. aq Na_2SO_3. The aqueous layer was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum. The crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (10:1) to afford the desired product as a white solid; yield: 3.34 g (84%); mp 70–73 °C.

The spectral data of **3** were consistent with that reported in the literature.[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.22 (t, *J* = 8.1 Hz, 1 H), 7.08 (dd, *J* = 8.1, 1.5 Hz, 1 H), 3.52 (q, *J* = 7.1 Hz, 2 H), 3.38 (q, *J* = 7.1 Hz, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.22 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 152.8, 130.6, 130.0, 129.7, 121.8, 99.9, 42.5, 42.2, 14.5, 13.4.

3-Bromo-2-iodophenol (4)

To a solution of 3-bromo-2-iodophenyl diethylcarbamate (**3**; 3.96 g, 10 mmol) in EtOH (100 mL) was added powdered NaOH (4.0 g, 100 mmol) in two portions. The mixture was heated to reflux for 24 h. Upon completion of the reaction (TLC monitoring), the reaction was cooled to r.t. and quenched with aq 2 M HCl. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine and dried (anhyd Na_2SO_4). The solvent was evaporated off under vacuum. The crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (8:1) to afford the desired product as a white solid; yield: 2.66 g (89%); mp 85–87 °C.

The spectral data of compound **4** were consistent with that reported in the literature.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.12 (t, *J* = 8.1 Hz, 1 H), 6.92 (dd, *J* = 8.1, 1.5 Hz, 1 H), 5.54 (br s, 1 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.6, 130.8, 129.6, 125.0, 13.3, 94.4.

3,3′-(2*R*,4*R*)-Pentane-2,4-diylbis(oxy)bis(1-bromo-2-iodobenzene) (6)

To a solution of 3-bromo-2-iodophenol (**4**; 2.48 g, 8.3 mmol) in anhyd THF (40 mL) at 0 °C under argon were added (2*S*,4*S*)-2,4-pentanediol (**5**; 417 mg, 4.0 mmol) and PPh_3 (2.19 g, 8.3 mmol) successively. The mixture was stirred at this temperature for 15 min and then DIAD (1.63g, 8.3 mmol) was added to the reaction mixture dropwise. The resulting solution was ultrasonicated in ice-bath for 1 h. Upon completion of the reaction (TLC monitoring), Et_2O was added to dilute the suspension and the insolubles were filtered off. The filtrate was evaporated under vacuum and the crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (6:1) to afford the desired product as a white solid; yield: 2.34 g (88%); mp 71–73 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 8.0, 1.4 Hz, 2 H), 6.98 (t, *J* = 7.6 Hz, 2 H), 6.56 (dd, *J* = 8.2, 1.2 Hz, 2 H), 4.77 (m, 2 H), 2.09 (m, 2 H), 1.39 (d, *J* = 6.4 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 157.6, 129.9, 129.1, 124.1, 110.7, 95.1, 72.5, 44.0, 19.4.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}Br_2I_2O_2$ $[M + H]^+$: 666.7659; found: 666.7643.

(*S*)-[6,6′-(2*R*,4*R*-Pentadioxy)]-(2,2′)-dibromo-(1,1′)-biphenyl [(*S*$_{ax}$,*RR*)-7][18]

To a solution of **6** (1.332 g, 2.0 mmol) in anhyd THF (20 mL) and LiCl (0.127 g, 3 mmol) at –40 °C under argon were added a solution of isopropylmagnesium bromide in THF (2.5 mL, 2 M) dropwise. The mixture was stirred at this temperature for 4 h to give the corresponding Grignard reagent. The resulting mixture was added to another flask containing $CuCl_2$ (1.056 g, 8.0 mmol) and TMEDA (1.8 mL, 12 mmol) in THF (20 mL) at –78 °C dropwise. The mixture was stirred at this temperature for another 4 h. Upon completion of the reaction (TLC monitoring), the reaction was quenched with aq 2 M HCl and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine and dried (anhyd Na_2SO_4). The solvent was evaporated off under vacuum. The crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (80:1) to afford the dibromide as a white solid; yield: 0.52 g (60%); mp 157–160 °C.

The spectral data of (*S*$_{ax}$,*RR*)-**7** were consistent with that reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.0 Hz, 2 H), 7.25 (t, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 4.53 (m, 2 H), 1.79 (m, 2 H), 1.34 (d, *J* = 6.4 Hz, 6 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 158.6, 132.2, 130.2, 127.2, 125.0, 117.5, 76.7, 40.9, 22.4.

(*S*$_{ax}$)-[6,6′-(2*R*,4*R*-Pentadioxy)]-(2,2′)-bis(diphenylphosphino)-(1,1′)-biphenyl] [(*S*$_{ax}$,*RR*)-8]

To a solution of (*S*)-[6,6′-(2*R*,4*R*-pentadioxy)]-(2,2′)-dibromo-(1,1′)-biphenyl [(*S*$_{ax}$,*RR*)-**7**] (412 mg, 1.0 mmol) in anhydrous THF (20 mL) at –78 °C under argon was added a solution of *n*-BuLi in THF (1.25 mL, 2.5mmol) dropwise. The mixture was stirred at this temperature for 1 h. Then a solution of Ph_2PCl (550 mg, 2.5mmol) in THF (2 mL) was added to the mixture dropwise. The mixture was stirred at this temperature for another 2 h and then slowly warmed to the room temperature. Upon the completion of the reaction by TLC, the reaction was quenched with saturated aqueous NH_4Cl solution and was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. The crude mixture was purified by chromatography on silica gel eluting with PE/EtOAc (100:1), affording the title compound as a white foam; yield: 0.52 g (83%).

The spectral data were consistent with that reported in the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (d, *J* = 6.4 Hz, 6 H), 1.74 (t, *J* = 3.9 Hz, 2 H), 4.22–4.66 (m, 2 H), 6.67 (d, *J* = 7.4 Hz, 2 H), 6.92 (d, *J* = 8.0 Hz, 6 H), 7.05–7.21 (m, 12 H), 7.26–7.27 (m, 6 H), 7.44–7.46 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 40.9, 75.6, 118.6, 127.9, 128.1, 128.1, 128.2, 128.6, 128.6, 128.6, 129.1, 133.5, 133.7, 133.8, 133.9, 134.1, 134.2, 135.8, 136.0, 136.2, 137.7, 137.7, 137.8, 138.6, 138.6, 138.7, 138.8, 138.9, 139.0, 158.1, 158.2, 158.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –11.1.

(*S*$_{ax}$)-[6,6′-(2*R*,4*R*-Pentadioxy)]-(2,2′)-bis(dicyclhexylphosphino)-(1,1′)-biphenyl] [(*S*$_{ax}$,*RR*)-9]

The procedure described above for compound (*S*$_{ax}$,*RR*)-**8** but with Cy_2PCl as the chlorophoshine provide (*S*$_{ax}$,*RR*)-**9** as a white foam; yield: 0.57 g (58%).

The spectra data of (*S*$_{ax}$,*RR*)-**9** were in consistent with that reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 7.8 Hz, 2 H), 7.02 (d, *J* = 7.5 Hz, 2 H), 6.88 (d, *J* = 7.9 Hz, 2 H), 4.37 (dt, *J* = 6.4, 4.1 Hz, 2 H), 1.96 (d, *J* = 11.7 Hz, 2 H), 1.70–0.80 (m, 50 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 26.6, 27.0, 27.3, 27.8, 27.9, 28.6, 29.5, 30.2, 30.7, 32.2, 35.5, 40.6, 74.5, 116.9, 125.9, 126.6, 136.2, 157.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –11.4 (s).

Funding Information

We are grateful for the financial support by a grant from Wuhan University (203273463), '111' Project of the Ministry of Education of China and the National Natural Science Foundation of China (Grant No. 21302193, 21372179, 21432007, 21402145).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588421.

References

(1) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801.
(2) Jeulin, S.; Duprat de Paule, S.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Champion, N.; Dellis, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 320.
(3) Schmid, R. B.; Broger, E. A.; Cereghtti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Muller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131.
(4) Pai, C.-C.; Lin, C.-W.; Lin, C.-C.; Chen, C.-C.; Chan, A. S. C.; Wong, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 11513.
(5) Pai, C.-C.; Li, Y.-M.; Zhou, Z.-Y.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 2789.
(6) Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, *343*, 264.
(7) (a) Fernández-Pérez, H.; Mon, I.; Frontera, A.; Vidal-Ferran, A. *Tetrahedron* **2015**, *71*, 4490. (b) Vaquero, M.; Rovira, L.; Vidal-Ferran, A. *Chem. Commun.* **2016**, *52*, 11038.
(8) (a) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (b) Genet, J.-P.; Ayad, T.; Ratovelomanana-Vidal, V. *Chem. Rev.* **2014**, *114*, 2824. (c) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405.
(9) Mashima, K.; Kusano, K.-h.; Sato, N.; Matsumura, Y.-i.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T. *J. Org. Chem.* **1994**, *59*, 3064.
(10) Kumobayashi, H.; Miura, T.; Sayo, N.; Saito, T.; Zhang, X. *Synlett* **2001**, 1055.
(11) Zhang, X. *Enantiomer* **1999**, *4*, 541.
(12) Zhang, Z.; Qian, H.; Longmire, J.; Zhang, X. *J. Org. Chem.* **2000**, *65*, 6223.
(13) Yokozawa, T.; Sayo, N.; Saito, T.; Ishizaki, T. Patent EP1095946A1, **2001**.
(14) (a) Sun, X.; Zhou, L.; Li, W.; Zhang, X. *J. Org. Chem.* **2008**, *73*, 1143. (b) Wang, C.-J.; Wang, C.-B.; Chen, D.; Yang, G.; Wu, Z.; Zhang, X. *Tetrahedron Lett.* **2011**, *52*, 468.
(15) Zou, Y.; Geng, H.; Zhang, W.; Yu, S.; Zhang, X. *Tetrahedron Lett.* **2009**, *50*, 5777.
(16) Qiu, L.; Kwong, F. Y.; Wu, J.; Lam, W. H.; Chan, S.; Yu, W.-Y.; Li, Y.-M.; Guo, R.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2006**, *128*, 5955.
(17) Qiu, L.; Wu, J.; Chan, S.; Au-Yeung, T. T. L.; Ji, J.-X.; Guo, R.; Pai, C.-C.; Zhou, Z.; Li, X.; Fan, Q.-H.; Chan, A. S. C. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5815.
(18) Bailey, S. J.; Wales, S. M.; Willis, A. C.; Keller, P. A. *Org. Lett.* **2014**, *16*, 4344.
(19) Sanz, R.; Castroviejo, M. P.; Fernandez, Y.; Fananas, F. J. *J. Org. Chem.* **2005**, *70*, 6548.
(20) Sanz, R.; Castroviejo, M. P.; Guilarte, V.; Pérez, A.; Fañanás, F. J. *J. Org. Chem.* **2007**, *72*, 5113.