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A concise synthesis of 2-diarylphosphino-2′-methoxy-1,1′-binaphthalenes (MOPs) by simple resolution

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Abstract—A practical synthesis of 2-diarylphosphino-2′-methoxy-1,1′-binaphthalene (MOPs) was provided by employing the etherification of 1,1′-bi-2,2′-naphthol on zeolite; the ring opening of the ether with lithium; the reaction with chlorodiaryl phosphine and the resolution with (1*S*)-(+)-10-camphorsulfonyl chloride as the key steps.

To develop new chiral ligands that might realize high enantioselectivity in asymmetric catalytic reactions is an important area in current research. Based on the chiral structure of 1,1′-binaphthalenyl-2,2′-diol, a chiral monophosphine ligand 2′-diphenylphosphanyl-1,1′-binaphthalenyl-2-ol was reported by Morgans and co-workers.[1] Later, Hayashi and co-workers[2] reported an improved synthesis enroute to substituted chiral monophosphine ligands (MOPs) that are efficient for several types of palladium-catalyzed asymmetric reactions including asymmetric hydrosilylation of olefins,[3] asymmetric 1,4-hydroboration of 1,3-enynes to form allenyl boranes,[4] and asymmetric reduction of allylic esters with formic acid.[5] In these reactions, the use of MOP-type ligands is crucial for obtaining high catalytic reactivity and regioselectivity as well as high enantioselectivity. Moreover, once the parent structure of chiral MOP-type ligands was established, it was expanded into other useful ligands, such as PHEST,[6] BINAPHOS,[7] BIPPHOS,[7] BIPNITE[7] etc., which now have been utilized in Pd-catalyzed asymmetric allylic substitution,[6a] Rh-catalyzed highly enantioselective hydroformylation of olefins.[7] Besides that the hydroxy group can also be converted into the thiol to produce another bidentate ligand 2′-diphenylphosphanyl-1,1′-binaphthalenyl-2-thiol.[8]

Another method provided by Miyano et al.[9] to prepare 2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol involves a nucleophilic aromatic substitution reaction of 1-methoxy-2-(diphenylphosphino)naphthalene with Grignard reagent. However, the monophosphine ligands made by this method were racemic.

Heinicke and co-workers[10] reported a facile route to synthesize biaryl racemic monophosphine ligands from either dibenzofuran or dinaphthofuran by lithium-mediated ring opening and a subsequent reaction with chlorodiphenylphosphine. However, attempts to resolve the racemic 2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol with camphorsulfonyl chloride failed, with only oxidized product being obtained.

It could be envisioned that the oxidized product could undergo further reaction with a chiral acid to form an ester, and the pair of diastereoisomers would have significantly different physical properties that would let them be separated from each other.

According to the literature procedure,[10] we prepared the dinaphthofuran in high yield by employing HY zeolite with a SiO_2/Al_2O_3 ratio of about 14. The ring opening of the dinaphthofuran with lithium at rt in Et_2O afforded the intermediate dilithium salt **3**. The dilithium salt **3** was then quenched with chlorodiphenyl phosphine oxide instead of chlorodiphenyl phosphine to give the racemic hydroxy phosphine oxide **4**, which served as the precursor to be resolved (Scheme 1).

Treatment of 2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol **4** with (1*S*)-(+)-10-camphorsulfonyl chloride in the presence of triethylamine as a base and dichloromethane

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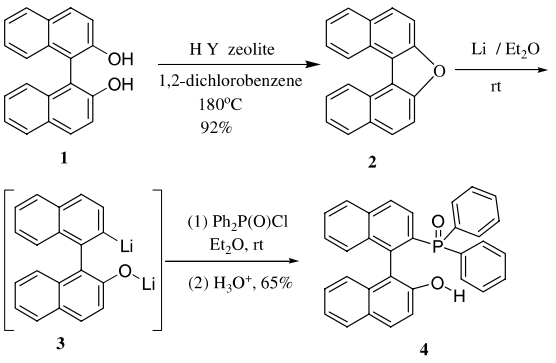
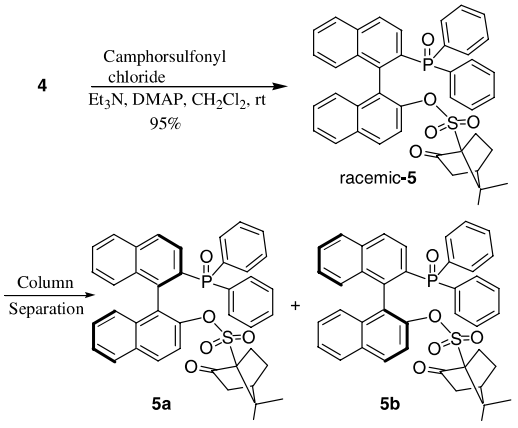


Scheme 1. Preparation of racemic 2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol.

as solvent at room temperature, formed the racemic ester **5** in high yield (Scheme 2).



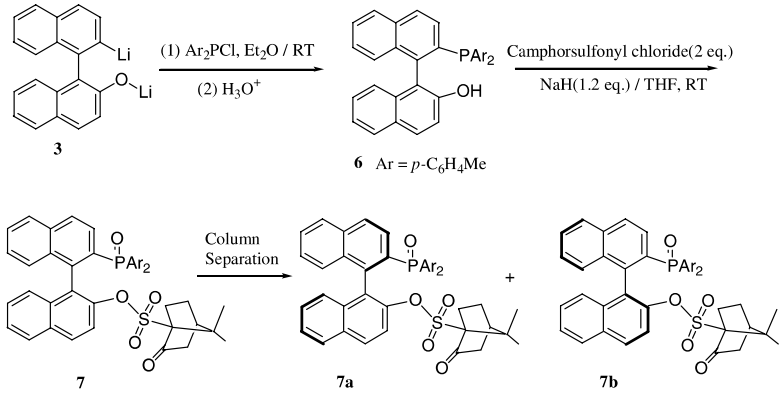
Scheme 2. Resolution of 2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol.

After extensive screening of the common solvents, we found that the diastereoisomers of **5** could be separated by chromatography on silica gel with diethyl ether and diisopropyl ether (5:1) as an eluent. Thus, **5a** and **5b** were obtained in decent yields with good diastereomeric purity (de: $\geqslant 95\%$). Both **5a** and **5b** were easily hydrolyzed to (*R*)- or (*S*)-2′-diphenylphosphinoyl-1,1′-binaphthalenyl-2-ol, respectively, in quantitative yield with the same conditions reported.[2] Therefore, chiral MOPs oxides could easily be derived from the common starting materials **5a** and **5b**, and the MOPs oxides obtained thus conveniently upgraded to >99% ee by simple recrystallization. The absolute configuration of the two diasteroisomers can simply be determined by converting one of them into an identified ligand, 2-diphenylphosphinoyl-2′-methoxyl-1,1′-binaphthalenes according to literature.[2] For example, **5b** was converted into 2-diphenylphosphinoyl-2′-methoxyl-1,1′-binaphthalene with 99% yield upon hydrolysis and methyl protection. The stereochemistry was determined to be (*R*)- for the naphthalene moiety after comparing the sign of specific rotation and spectroscopic data with a reported sample.[2]

We also made 2′-diphenylphosphanyl-1,1′-binaphthalenyl-2-ol and investigated the direct esterification reaction of it with (1*S*)-(+)-10-camphorsulfonyl chloride in the presence of NaH in THF. It was found that no esterification occurred and that only the oxidized product **4** could be detected apart from the starting material. This result is the same as the literature.[10]

However, when the same strategy was applied to resolve 2′-di(*p*-tolyl)phosphinoyl-1,1′-binaphthalenyl-2-ol, no esterification product could be detected and the starting material was recovered. The reaction also failed to give product when NaH was used as base and DMF as solvent.

However, when 2′-di(*p*-tolyl)phosphanyl-1,1′-binaphthalenyl-2-ol **6**, which was prepared by reaction of chlorodi(*p*-tolyl)phosphine with dilithium salt **3**, and (1*S*)-(+)-10-camphorsulfonyl chloride were employed as the starting materials (Scheme 3), the reaction proceeded in THF with NaH as the base to give the ester **7** in 50% yield, accompanied with the oxidized starting material, 2′-di(*p*-tolyl)phosphinoyl-1,1′-binaphthalenyl-2-ol and a little of unreacted **6**. It should be mentioned that **7** was not the direct esterification product; it was the oxidized product of the direct esterification product. No direct esterification product was isolated even if less than 1 mole equivalent of (1*S*)-(+)-10-camphorsulfonyl chloride was used, and the yield could not be improved upon, when more (1*S*)-(+)-10-camphorsulfonyl chloride was employed.



Scheme 3. Resolution of 2′-di(*p*-tolyl)phosphanyl-1,1′-binaphthalenyl-2-ol.

Ester **7** was also separated into **7a** and **7b** by chromatography on silica gel with Et_2O as eluent. Both **7a** and **7b** serve as key intermediates in monophosphine synthesis.[11]

In summary, we have provided a novel method for preparing chiral MOPs. This method involves the simple resolution of hydroxy monophosphines or their oxides bearing a naphthalene moiety. The enantiomerically pure form of **4** and **6** can allow the rapid construction of a series of chiral monophosphine ligands.

Acknowledgements

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11. Analytical data for **5a**, **5b**, **7a**, **7b**. **5a**: ^{1}H NMR (δ, ppm; $CDCl_3$): 8.18 (dd, 1H, $J = 8.4$, 2.1 Hz), 7.92 (d, 1H, $J = 8.1$ Hz), 7.83 (dd, 1H, $J = 11.4$, 8.4 Hz), 7.77–7.72 (m, 2H), 7.56–7.11 (m, 16H), 6.96 (d, 1H, $J = 8.7$ Hz), 2.86 (d, 1H, $J = 15.0$ Hz), 2.46 (d, 1H, $J = 15.0$ Hz), 2.28–2.19 (m, 1H), 2.04–1.94 (m, 2H), 1.24 (d, 2H, $J = 9.0$ Hz), 0.80 (s, 3H), 0.57 (s, 3H); ^{13}C NMR (δ, ppm; $CDCl_3$): camphor: 213.2, 57.6, 48.9, 47.4, 42.6, 42.1, 26.6, 24.9, 19.4, 19.3, aryl: 146.0–119.9; ^{31}P NMR (δ, ppm; $CDCl_3$): 29.4; IR (KBr; wavenumber, cm^{-1}): 3056 (m), 2959 (s), 1746 (vs), 1591 (m), 1509 (m), 1437 (s), 1371 (vs), 1198 (vs), 1168 (vs), 1116 (s), 964 (s), 941 (s), 819 (vs), 749 (s), 699 (vs), 539 (s), 524 (s); MS (ESI): m/z 685.2 [M+1], 686.2 [M+2], 707.1 [M+1]Na, 708.1 [M+2]Na; HRMS m/z calcd for $C_{42}H_{38}O_5SP$ $[M+1]^+$: 685.2174, found: 685.2172; De: 98%. **5b**: ^{1}H NMR (δ, ppm; $CDCl_3$): 8.16 (dd, 1H, $J = 8.4$, 2.1 Hz), 7.92 (d, 1H, $J = 8.1$ Hz), 7.84 (dd, 1H, $J = 11.4$, 8.4 Hz), 7.77–7.72 (m, 2H), 7.56–7.13 (m, 16H), 6.96 (d, 1H, $J = 8.4$ Hz), 3.1 (d, 1H, $J = 15.0$ Hz), 2.25–2.16 (m, 1H), 2.08 (d, 1H, $J = 15.0$ Hz), 1.97–1.88 (m, 2H), 1.82–1.75 (m, 2H), 1.37–1.20 (m, 2H), 0.68 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (δ, ppm; $CDCl_3$): camphor: 213.4, 57.4, 48.8, 47.4, 42.4, 42.1, 26.6, 24.3, 19.2, 19.0, aryl: 145.7–120.2; ^{31}P NMR (δ, ppm; $CDCl_3$): 29.4; IR (KBr; wavenumber, cm^{-1}): 3055 (m), 2959 (s), 1747 (vs), 1591 (m), 1509 (m), 1437 (s), 1362 (vs), 1199 (s), 1168 (vs), 1116 (s), 965 (s), 941 (s), 817 (vs), 749 (s), 699 (vs), 539 (s), 524 (s); MS (ESI): m/z 685.2 [M+1], 686.2 [M+2], 707.1 [M+1]Na, 708.1 [M+2]Na; HRMS m/z calcd for $C_{42}H_{38}O_5$ SP $[M+1]^+$: 685.2174, found: 685.2172; De: 95%. **7a**: ^{1}H NMR (δ, ppm; $CDCl_3$): 8.02 (dd, 1H, $J = 9.0$, 2.1 Hz), 7.94–7.87 (m, 2H), 7.74 (dd, 2H, $J = 11.1$, 8.7 Hz), 7.52 (dd, 2H, $J = 6.9$, 8.7 Hz), 7.38–7.25 (m, 7H), 7.17–7.11 (m, 2H), 7.01–6.94 (m, 2H), 6.89 (dd, 2H, $J = 7.8$, 2.4 Hz), 2.82 (d, 1H, $J = 15.0$ Hz), 2.4 (d, 1H, $J = 15.0$ Hz); 2.87 (s, 3H), 2.25 (s, 3.5H), 2.22–2.19 (m, 0.5H), 2.04–1.76 (m, 4H), 1.26–1.23 (m, 2H), 0.80 (s, 3H), 0.56 (s, 3H); ^{13}C NMR (δ, ppm; $CDCl_3$): 213.2, 57.6, 48.9, 47.4, 42.6, 42.2, 26.6, 25.0, 21.41, 21.40, 21.37, 21.36, 19.5, and 19.3, aryl: 146.0–120.0; ^{31}P NMR (δ, ppm; $CDCl_3$): 29.8. IR (KBr; wavenumber, cm^{-1}): 2958 (m), 1748 (vs), 1601 (m), 1369 (vs), 1216 (s), 1197 (s), 1168 (vs), 1114 (s), 965 (s), 941 (s), 810 (vs), 749 (s), 681 (s), 659 (s), 526 (vs); MS (ESI): m/z 713.2 [M+1]; 714.2 [M+2]; 735.2 [M+1]Na. HRMS calcd for $C_{44}H_{41}O_5SPNa$ $[M+1]Na^+$: 735.2341, found: 735.2304. De: 97%. **7b**: ^{1}H NMR (δ, ppm; $CDCl_3$): 8.00 (dd, 1H, $J = 8.7$, 2.1 Hz), 7.95–7.90 (m, 2H), 7.73 (dd, 2H, $J = 11.1$, 8.4 Hz), 7.52–7.45 (m, 2H), 7.38–7.24 (m, 6H), 7.15–7.12 (m, 2H), 7.03 (dd, 2H, $J = 8.1$, 2.4 Hz), 6.96 (d, 1H, $J = 13.8$ Hz), 6.90 (dd, 2H, $J = 7.8$, 2.4 Hz), 3.08 (d, 1H, $J = 15.0$ Hz), 2.3 (s, 3H), 2.26 (s, 3.5H), 2.19–2.18 (m, 0.5H), 2.06 (d, 1H, $J = 15.0$ Hz), 2.00–1.76 (m, 4H), 1.34–1.25 (m, 2H), 0.67 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (δ, ppm; $CDCl_3$): Camphor: 213.3, 57.4, 48.8, 47.4, 42.36, 42.1, 26.6, 24.3, 21.43, 21.41, 21.38, 21.36, 19.2, 19.0, aryl: 141.5–120.3; ^{31}P NMR (δ, ppm; $CDCl_3$): 29.8; IR (KBr; wave number, cm^{-1}): 2958 (m), 1748 (vs), 1601 (m), 1362 (vs), 1216 (s), 1197 (s), 1167 (vs), 1114 (s), 965 (s), 941 (s), 811 (vs), 774 (s), 749 (s), 681 (s), 660 (s), 526 (vs); MS (ESI) m/z 713.2 [M+1], 714.2 [M+2], 715.2 [M+3], 735.2 [M+1]Na; HRMS m/z calcd for $C_{44}H_{41}O_5SPNa$ $[M+1]Na^+$: 735.2328, found: 735.2304; De: 99%.