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Chiral P,O-ligands derived from *N*,*O*-phenylene prolinols for palladium-catalyzed asymmetric allylic alkylation

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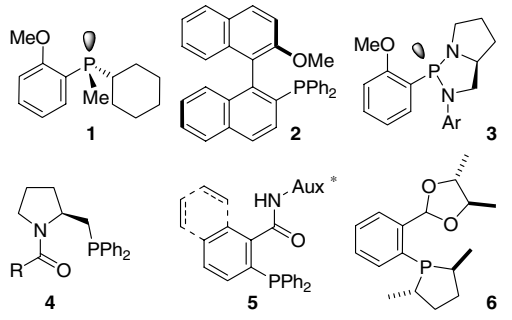
Abstract—CuI-catalyzed N,O-arylation of (*S*)-prolinols and 1-bromo-2-iodobenzene afforded cyclic *N*,*O*-(1,2-phenylene)prolinols, and subsequent *ortho*-lithiation and phosphination provided a new type of chiral P,O-ligands. Their palladium-complex-catalyzed asymmetric allylic alkylation of dimethyl malonate with 1,3-diphenyl 2-propenyl acetate gave high yields and good enantioselectivities.

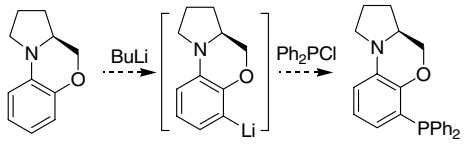
The development of effective and versatile chiral P,N-ligands with sterically and electronically unsymmetric nature for transition metal catalysis has been a fruitful endeavor,[1] while the exploration for chiral P,O-ligands has received much less attention.[2] The oxygen functionality in a P,O-ligand was often regarded as the spectator or a hemilabile coordinating site.[3] For example, CAMP **1**, MOP **2** and semi-ESPHOS **3** were used as chiral mono-phosphine ligands with the methoxy groups being nonchelating bystanders.[4] In particular, X-ray studies revealed that the palladium-complex of MOP-type ligands showed unique C–Pd σ-bonding, η^2-binding, or diene-bridging modes rather than the P,O-bidentate coordination.[5]



Exceptionally, some mixed phosphine–phosphine oxides[6] and phosphinocarboxylic acids[7] as ligands were reported working in P,O-chelating mode. A few other types of hemilabile bidentate P,O-ligands were also documented. Examples are (*S*)-prolinol-derived amido-mono-phosphine ligand **4** for a Rh-catalyzed addition reaction,[8] ligand **5** with a chiral amine auxiliary for a Pd–catalyzed allylic alkylation,[9] and semi-DuPHOS-type ligand **6** for a Ni-catalyzed hydrovinylation.[10]

Recently, we reported an interesting compound of the *N*,*O*-(1,2-phenylene)prolinol structure.[11] We wonder that *ortho*-lithiation of this compound, followed by phosphination, would produce a chiral P,O-ligand for asymmetric catalysis (Scheme 1). Our interest in (*S*)-prolinol-derived chiral ligands promoted us to try the CuI-catalyzed coupling of (*S*)-prolinols with 1-bromo-2-iodobenzene.[12] However, an unexpected intramolecular N,O-arylation was observed in addition to the normal N-arylation (Scheme 2).[13]

The results are shown in Table 1. In the presence of 2.5 mol % CuI and 2 equiv of NaOH, mixing of **7a**



Scheme 1.

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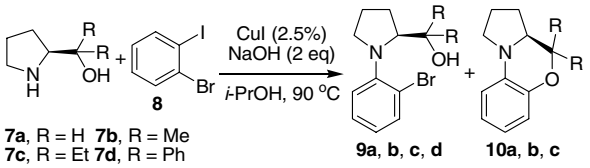


Scheme 2.

Table 1. CuI-catalyzed N-arylation and N,O-arylation

Entry	Prolinol	Time (h)	Yield of **9**[a] (%)	Yield of **10**[a] (%)
1	**7a**	12	23	62
2	**7a**	24	5	78
3[b]	**7a**	12	57	13
4	**7b**	24	36	31
5	**7c**	24	50	3
6	**7c**	50	—[c]	25
7	**7d**	3	60	None
8	**7d**	20	75	None

[a] Isolated yields.
[b] NaOH (1 equiv).
[c] Debromation occurred.

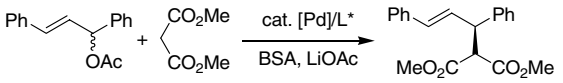
and **8** in *i*-PrOH with heating for 12 h afforded the normal N-arylation product **9a** in 23% yield along with 62% yield of a cyclic compound **10a** (entry 1).[14] As expected, the yield of **10a** was increased after longer reaction time, while a shorter duration and using less base decreased the N,O-arylation (entries 2 and 3). The N,O-arylation product **10b** was obtained in 31% yield (entry 4). Despite the hindrance of cyclization to **10c**, a 25% yield could be attained with prolonged reaction time, albeit debromation occurred in the meantime (entries 5 and 6). The N-arylation of **7d** was much rapid, affording 60% yield in 3 h, but the diphenyl substituted tertiary alcohol was totally inert toward intramolecular O-arylation (entries 7 and 8).

Next we performed *ortho*-lithiation and phosphination of the cyclic *N*,*O*-(1,2-phenylene)prolinols. It was known that the alkyloxy substituent on the aromatic ring (ROAr) was a superior directing group than an alkylamino moiety (R_2NAr).[15] The oxygen-directed *ortho*-lithiation of **10a–c** with *n*-BuLi/TMEDA, followed by addition of Ph_2PCl, afforded the phosphination products **11a** and **11b** in 34% and 44% yields, respectively, with 40–50% recovery of **10a** and **10b** (Scheme 3).[16] Unfortunately, the lithiation and phosphination of **10c** were unsuccessful. Only the starting material was recovered upon quenching the reaction.[17]

With **11a** and **11b** in hand, we set out to investigate their application as chiral P,O-ligands in Pd-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetates **12** with **13** in the presence of BSA/LiOAc.[18] The details are shown in Table 2.[19] It is noteworthy that comparable results (quantitative yields and 56–58% ees) were obtained in THF regardless of 2:1 or 4:1 ratios for the phosphine to the dimeric palladium source, albeit reaction under the latter conditions was slightly accelerated (entries 1 and 2). It is probable that the catalyst formed in situ worked in a 1:1 bidentate P,O-ligand to palladium coordination mode. Thus, a 1.5:1 ratio was used in the rest of our study. The reaction carried out in CH_2Cl_2 gave 99% yield with somewhat lowered 51% ee (entry 3). Inferior results were obtained in PhMe and MeCN (entries 4 and 5). Much rapid conversion was observed in ether, but the enantioselectivity was only 41% ee (entry 6). The optical yield was increased to 66% ee after an 8 h reaction time at 0 °C (entry 7). Switching the ligand to **11b**, a quantitative yield and 83% ee for **14** were attained in 3 h at rt, and it took 48 h to achieve 93% yield with 90% ee in THF at 0 °C (entries 8 and 9).

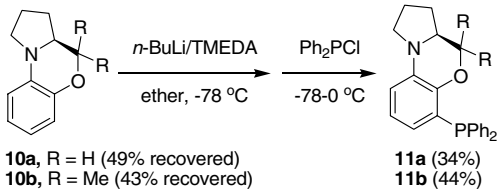
All products are determined as (*R*)-configuration by optical rotation measurement and chiral HPLC analysis.[20] On the basis of this output, a plausible mechanism is proposed (Scheme 4). The P,O-ligand **11b** has a relatively rigid conformation. Upon analysis of the stereoelectronics, the phenolic ether oxygen has two discriminable lone pairs of electrons. The axial-oriented lone pair tends to be in conjunction with the benzene

Table 2. Pd-catalyzed asymmetric allylic alkylation[a]

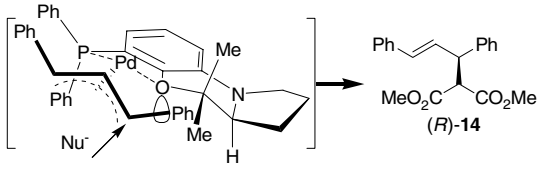


Entry	Solvent	Temperature	Time (h)	Yield[b] (%)	ee[c] (%)
1[d]	THF	rt	3	99	56
2[e]	THF	rt	1	99	58
3	CH_2Cl_2	rt	3	99	51
4	PhMe	rt	24	75	43
5	MeCN	rt	24	86	37
6	Et_2O	rt	0.5	98	41
7	THF	0 °C	8	99	66
8[f]	THF	rt	3	99	83
9[f]	THF	0 °C	48	93	90

[a] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/**11a**/LiOAc/**12**/**13**/BSA = 2:6:4:100:300:300.
[b] Isolated yields.
[c] Determined by chiral HPLC, and all the products are (*R*)-configuration.
[d] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/**11a** = 2:4.
[e] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/**11a** = 2:8.
[f] Compound **11b** as ligand.



Scheme 3.



Scheme 4.

backbone, while the quasi-equatorial lone pair might exhibit distinct donating and coordinating characteristics. Assuming a bidentate chelating mode, the preferential attack of deprotonated malonate *trans* to the phosphorous atom at a W-type 1,3-diphenyl allyl complex would lead to an (*R*)-product.

To conclude, the chiral P,O-ligands have been derived from *N*,*O*-(1,2-phenylene)prolinols, which have been generated by the N,O-arylation of (*S*)-prolinols and 1-bromo-2-iodo-benzene with CuI-catalysis. Their use in Pd-catalyzed asymmetric allylic alkylation of malonate with 1,3-dipenyl 2-propenyl acetate has been demonstrated, and a P,O-bidentate working mode is proposed to rationale the stereochemical outcome.

Acknowledgement

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13. *Compound* **9b**: $[\alpha]_D^{20}$ +75 (*c* 0.70, $CHCl_3$). IR: 3464, 2972, 2871, 1584, 1473, 1301, 1157, 1134, 1112, 1027, 952, 755 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, 1H, $J = 1.0$, 7.6 Hz), 7.28–7.23 (m, 2H), 6.94–6.89 (m, 1H), 3.78 (dd, 1H, $J = 6.6$, 8.1 Hz), 3.69–3.61 (m, 1H), 2.83–2.75 (m, 1H), 2.67 (s, 1H), 2.10–1.78 (m, 4H), 1.14 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (75 MHz): δ 151.7, 133.4, 128.2, 124.8, 123.8, 122.6, 72.7, 69.3, 57.7, 29.1, 28.0, 25.9, 25.2. EIMS: 284 ($[M+H]^+$, 10.2%), 286 (8.6%), 224 (83%), 226 (100%); HRMS: $[M+H]^+$ calcd for $C_{13}H_{19}NOBr^+$ 284.0645, found 284.0648. *Compound* **9c**: $[\alpha]_D^{20}$ +56.5 (*c* 0.99, $CHCl_3$). IR: 3481, 2968, 1584, 1472, 1302, 1130, 1027, 959, 755 cm^{-1}. ^1H NMR: δ 7.57 (d, 1H, $J = 7.8$ Hz), 7.26–7.22 (m, 2H), 6.95–6.89 (m, 1H), 3.88 (t, 1H, $J = 7.5$ Hz), 3.62–3.54 (m, 1H), 2.81–2.74 (m, 1H), 2.76 (s, 1H), 2.08–2.00 (m, 2H), 1.88–1.74 (m, 2H), 1.63–1.53 (m, 1H), 1.40–1.33 (m, 1H), 1.25–1.01 (m, 2H), 0.85 (t, 3H, $J = 7.5$ Hz), 0.62 (t, 3H, $J = 7.6$ Hz). ^{13}C NMR: δ 152.0, 133.3, 128.0, 124.8, 123.7, 122.8, 76.2, 65.9, 58.0, 29.3, 27.3, 25.9, 25.7, 7.9, 7.7. EIMS: 312 ($[M+H]^+$, 1.9%), 314 (1.8%), 224 (85%), 226 (100%); HRMS: $[M+H]^+$ calcd for $C_{15}H_{23}NOBr^+$ 312.0958, found 312.0970. *Compound* **9d**: Mp: 155–156 °C. $[\alpha]_D^{20}$ +112.5 (*c* 1.07, $CHCl_3$). IR: 3385, 3057, 2841, 1659, 1599, 1587, 1493, 1473, 1449, 1373, 1027, 704, 695 cm^{-1}. ^1H NMR: δ 7.59–7.56 (m, 2H), 7.36–7.29 (m, 4H), 7.24–7.13 (m, 2H), 7.09 (d, 1H, $J = 7.5$ Hz), 6.98 (t, 1H, $J = 7.6$ Hz), 6.86 (t, 2H, $J = 7.8$ Hz), 6.78–6.68 (m, 2H), 4.94 (dd, 1H, $J = 4.4$, 8.9 Hz), 4.64 (s, 1H), 3.64–3.59 (m, 1H), 2.79 (m, 1H), 2.17–2.12 (m, 1H), 1.97–1.82 (m, 3H). ^{13}C NMR: δ 148.86, 145.96, 145.72, 132.40, 130.03,

128.02, 127.76, 127.11, 126.28, 125.76, 125.57, 125.53, 125.48, 123.77, 78.6, 68.7, 58.0, 29.5, 25.5. EIMS: 389 ($[M-H_2O]^+$, 0.5%), 391 (0.4%), 224 (75%), 226 (100%). Anal. Calcd for $C_{23}H_{22}NOBr$: C, 67.65; H, 5.43; N, 3.43. Found: C, 67.86; H, 5.35; N, 3.11. *Compound* **10b**: $[\alpha]_D^{20}$ +27 (*c* 0.5, $CHCl_3$). IR: 2976, 2840, 1686, 1607, 1508, 1372, 1236, 1141, 740 cm^{-1}. ^1H NMR: δ 6.87–6.79 (m, 2H), 6.59 (t, 1H, $J = 7.5$ Hz), 6.49 (d, 1H, $J = 7.8$ Hz), 3.41–3.34 (m, 2H), 3.23 (dd, 1H, $J = 5.5$, 9.7 Hz), 2.09–1.95 (m, 3H), 1.57–1.50 (m, 1H), 1.38 (s, 3H), 1.05 (s, 3H). ^{13}C NMR: δ 141.9, 134.4, 121.1, 116.5, 116.0, 110.8, 74.2, 63.4, 46.9, 28.1, 26.0, 23.2, 19.0. HRMS: $[M+Na]^+$ calcd for $C_{13}H_{17}NONa^+$ 226.1202, found 226.1210. *Compound* **10c**: $[\alpha]_D^{20}$ −12 (*c* 0.90, $CHCl_3$). IR: 2974, 1602, 1512, 1463, 1269, 946, 750 cm^{-1}. ^1H NMR: δ 6.86–6.81 (m, 2H), 6.59 (t, 1H, $J = 7.6$ Hz), 6.48 (d, 1H, $J = 7.5$ Hz), 3.44–3.37 (m, 1H), 3.35–3.30 (m, 1H), 2.08–1.85 (m, 4H), 1.67–1.55 (m, 2H), 1.52–1.42 (m, 1H), 1.38–1.26 (m, 1H), 1.00 (t, 3H, J=7.6 Hz), 0.85 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR: δ 142.1, 121.0, 116.4, 116.1, 110.7, 77.2, 61.0, 46.6, 28.3, 27.5, 23.4, 22.4, 7.8, 6.7. HRMS: 231.1623 calcd for $C_{15}H_{22}NO^+$, found 231.1624.

14. Optical comparisons of **9a**, **10a**, and debrominated **9a** with those obtained in Ref. 11 indicate there is no racemization for this technique.
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16. *Compound* **11a**: Mp: 50–60 °C. $[\alpha]_D^{20}$ +27.3 (*c* 0.50, $CHCl_3$). IR: 2975, 2869, 1735, 1584, 1472, 1434, 1365, 1321, 1203, 999, 696 cm^{-1}. ^1H NMR: δ 7.34–7.31 (m, 10H), 6.78 (t, 1H, $J = 7.9$ Hz), 6.59 (d, 1H, $J = 7.8$ Hz), 5.99 (t, 1H, $J = 6.3$ Hz), 4.35 (dd, 1H, $J = 3.0$, 9.9 Hz), 3.55–3.45 (m, 2H), 3.32–3.17 (m, 2H), 2.08–1.95 (m, 3H), 1.44–1.34 (m, 1H). ^{13}C NMR: δ 144.41 (d, $J = 16.6$ Hz), 137.11, 136.98, 136.85, 136.71, 134.52, 134.47, 133.89, 133.85, 133.63, 133.59, 128.31, 128.30, 128.19, 128.15, 128.10, 128.06, 123.48, 123.34, 121.83, 121.80, 120.19, 112.83, 68.3, 55.2, 47.8, 28.3, 23.7. ^{31}P NMR (121 MHz): δ −15.8. HRMS: $[M+H]^+$ calcd for $C_{23}H_{23}NOP^+$ 360.1512, found 360.1522. *Compound* **11b**: $[\alpha]_D^{20}$ +124 (*c* 0.95, $CHCl_3$). IR: 3005, 1714, 1589, 1477, 1437, 1363, 1223, 1093, 913, 734 cm^{-1}. ^1H NMR: δ 7.42–7.31 (m, 10H), 6.73 (t, 1H, $J = 7.6$ Hz), 6.49 (d, 1H, $J = 7.2$ Hz), 6.06–6.02 (m, 1H), 3.36 (dd, 2H, $J = 5.5$, 7.3 Hz), 3.20 (dd, 1H, $J = 5.5$, 9.7 Hz), 2.06–1.92 (m, 3H), 1.48–1.21 (m, 1H), 1.16 (s, 3H), 0.66 (s, 3H). ^{13}C NMR: δ 143.5 (d, $J = 14.9$ Hz), 137.34, 137.21, 137.14, 137.01, 134.40, 134.12, 133.98, 133.73, 128.39, 128.08, 128.06, 128.04, 127.99, 127.94, 123.99, 123.85, 120.86, 120.83, 120.34, 120.30, 111.48, 74.6, 63.3, 47.0, 27.9, 25.6, 23.3, 18.5. ^{31}P NMR: δ -14.9. HRMS: $[M+H]^+$ calcd for $C_{25}H_{27}NOP^+$ 388.1825, found 388.1822.
17. No racemization occurred in this process as evidenced by the optical purity measurement of the recovered **10a**–**c**.
18. (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393; (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361–4401; (c) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257–276; (d) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089–1122; (e) Reiser, O. *Angew. Chem., Int. Ed.* **1993**, *32*, 547–549; (f) Trost, B. M. *Acc. Chem. Res.* **1996**, *29*, 355–364; (g) Trost, B. M.; van Vruken, D. L. *Chem. Rev.* **1996**, *96*, 395–422; (h) Williams, J. M. J. *Synlett* **1996**, 705–710; (i) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689–1708; (j) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203–214; (k) Pfaltz, A. *Chimia* **2001**, *55*, 708–714; (l) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195–202; (m) Dai, L.-X.; Tu, T.; You, S.-L.; Deng, W.-P.; Hou, X.-L. *Acc. Chem. Res.* **2003**, *36*, 659–667; (n) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2944; (o) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813–5837.
19. Following the procedure described in Ref. 11.
20. Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315–6323.