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Asymmetric allylation of aldehydes with allyltrichlorosilane using aza-paracyclophane-oxazoline-*N*-oxide catalysts

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Abstract—Novel aza-paracyclophane-oxazoline catalysts **4**, **5** were produced from Vögtle's R_p-2-cyano-aza-paraclycophane and amino alcohols reacted with zinc chloride followed by *m*-chloroperbenzoic acid. 4′-Benzyl and *tert*-butyl-*S* and *R*-oxazoline variants were produced and explored as catalysts for asymmetric allylation of aldehydes using trichloroallylsilane. With R_p,*S*-**4a** (R = *tert*-butyl) (1.5 mol %) aromatic aldehydes reacted with high yields and selectivities, as with benzaldehyde (95%, 93% ee). R_p,*S*-**4b** (R = benzyl) was superior with dihydrocinnamaldehyde (77%, 85% ee).

Asymmetric aldehyde allylation to access secondary homo-allylic alcohols is a strategic transformation that plays a pivotal role in target directed synthesis.[1] Various stoichiometric and catalytic approaches have been reported based on boron,[2] silicon,[3] and tin reagents that have become mainstays in natural product applications.[4] A particularly appealing variation involves the use of trichloroallylsilane reacted with multi-dentate amine-oxide catalysts[5] following the lead of Nakajima et al.[6] Recently, we reported the development of a new class of bis-paracyclophane-imidazolium *N*-heterocylic carbene ligands for the asymmetric rhodium-catalyzed conjugate addition and ketone hydrosilylation.[7] To extend the approach to silane reagents, we now report the synthesis and application of novel aza-paracyclophane-*N*-oxide-oxazolines together with their application to aldehyde allylation with trichloroallylsilane.

Paracyclophanes (PCP) are rigid platforms that have recently been explored for catalysis. The reported [2.2]PCP ligands include diphosphines,[8] oxazoline-phosphines,[9] oxazoline-imidazolium,[10] oxazoline-selenides,[11] oxazoline-alcohols,[12] and Schiff base-phenols for hydrogenation, allylic substitution, and organozinc addition reactions.[13] Chiral aza-[2.2]PCP compounds are rare and their use as catalysts has not been developed. Vögtle and co-workers reported the synthesis of a novel bipyridyl-paracyclophane ligand, together with a chiral-HPLC based resolution of a key precursor, and its preliminary use as a copper complex for cyclopropanation.[14] In three steps from 2,5-bis-(bromomethyl)pyridine, R_p-2-cyano-aza-paraclycophane **1** ($[\alpha]_D$ −157.2) was reproduced following the reported procedure (Scheme 1).[14] *R* and *S*-amino alcohols were reacted with **1** with zinc chloride heated at reflux in chlorobenzene to give the aza-PCP-oxazolines **3** in moderate yields.[15] The corresponding *N*-oxides were then generated using *m*-chloroperbenzoic acid.[16] R_p,*S*-Products **4** were generated, with *tert*-butyl and benzyl side chains, along with the R_p,*R*-diastereomers **5** in good yields. The enantiopurity of **4** and **5** was established by chiral HPLC to be >99% ee at this point. The variations (R) of R_p,*S*-**4** were also made at this time including methyl, *i*-propyl, and phenyl with similar results.

The variations were explored to optimize the new catalysts **4**, **5** for aldehyde allylation with trichloroallylsilane (Table 1). It was found that 1.5 mol % of R_p,*S*-**4a** (R = *t*-Bu) was sufficient for a good reactivity using *i*-Pr_2NEt (2 equiv) in THF at −40 °C (6 h) for *p*-methoxybenzaldehyde **6** giving product **7** in 83% yield (entry 1).[17] In this case unlike previous pyridyl oxides and other ligands, no added tetraalkylammonium halide was

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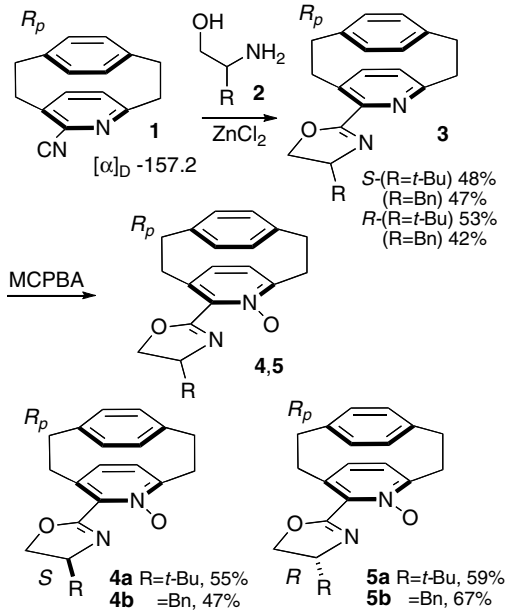
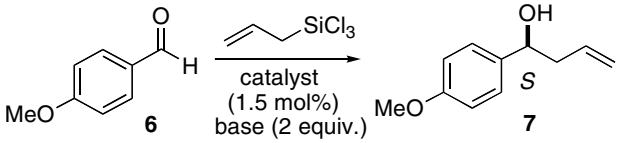


Scheme 1.

Table 1. Allyl addition catalyzed by aza-PCP-*N*-oxides



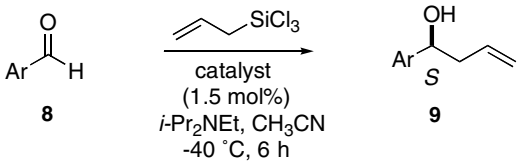
Entry	Catalyst	Base	Solvent	Yield (%)	ee (%)
1	**4a**	*i*-Pr_2NEt	THF	83[a]	47[b]
2	**4a**	*i*-Pr_2NEt	Tol.	61	48
3	**4a**	*i*-Pr_2NEt	CH_2Cl_2	82	86
4	**4a**	*i*-Pr_2NEt	CH_3CN	91	90
5	**4a**	Et_3N	CH_3CN	67	38
6	**4b**	*i*-Pr_2NEt	CH_3CN	83	75
7	**5a**	*i*-Pr_2NEt	CH_3CN	92	37[c]
8	**5b**	*i*-Pr_2NEt	CH_3CN	85	43[c]

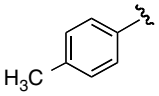
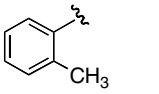
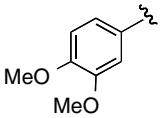
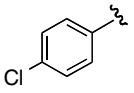
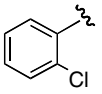
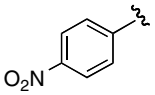
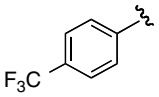
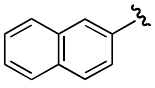
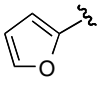
[a] All yields are for isolated, purified materials.
[b] Enantiomeric excesses were determined by chiral HPLC.
[c] The corresponding *R*-enantiomer was formed.

needed.[5,6] The enantiomeric excess, however, was modest at 47% ee. With methylene chloride or acetonitrile as a solvent (entries 3 and 4), the selectivities were significantly improved to 86% ee and 90% ee. Other bases, including Et_3N (entry 5), pyridine, and sodium carbonate, were inferior. Temperature changes gave lower (−20 °C) selectivity (68% ee) or comparable (−60 °C) selectivity (12 h, 90% ee). R_p,*S*-**4 b** (R = Bn) was less selective (75% ee, entry 6). R_p,*R*-**5a** and **5b** while showing a high reactivity, gave greatly reduced selectivities (37% ee, 43% ee).

The process using *i*-Pr_2NEt in acetonitrile (−40 °C, 6 h) was then extended to other aryl aldehydes with comparable success (Table 2). Catalyst **4a** again proved to be superior giving a high reactivity and selectivity as with benzaldehyde (entry 1, 93% ee). *p*-and *o*-methylbenzaldehyde (entries 2 and 3) were less selective (88%, 85% ee), while dimethoxy (entry 4) and the chlorobenzaldehydes (entries 5 and 6) gave an excellent results (96%, 91%, 93% ee). *p*-Nitro (entry 7) and 2-naphthaldehyde and 2-fufural (entries 9 and 10) were less selective (87%, 87%, 72% ee). *p*-Trifluoromethylbenzaldeyde (entry 8) in contrast gave excellent selectivity (96% ee).

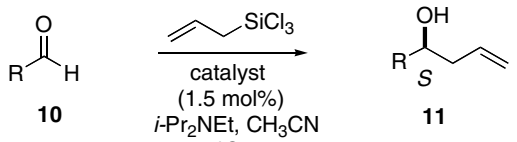
Table 2. Allyl addition to aryl aldehydes



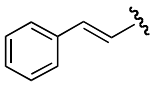
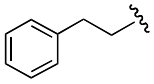
Entry	Ar	Catalyst	Yield (%)	ee (%)
1	Ph–	**4a**	95	93
		4b	90	87
		5a	93	47
		5b	89	53
2		**4a**	87	88
		4b	91	67
		5a	84	36
		5b	85	41
3		**4a**	88	85
		5a	86	31
4		**4a**	93	96
		5a	90	12
5		**4a**	91	91
		4b	90	82
		5a	88	27
		5b	?	?
6		**4a**	89	93
		4b	92	83
7		**4a**	96	87
		4b	89	91
8		**4a**	91	96
		4b	88	74
9		**4a**	92	87
		4b	84	71
10		**4a**	73	72
		4b	73	51

Additions were also explored using non-benzaldehyde substrates (Table 3). With cyclohexanecarboxaldehyde (entry 1), catalyst R_p,*S*-**4b** (R = Bn) was found to be

Table 3. Allylation with non-aromatic aldehydes



10 **11**

Entry	R=	Catalyst	Yield (%)	ee (%)
1	*c*-Hexyl	**4a**	72	48
		4b	78	67
		5a	71	7[a]
		5b	73	21[a]
2		**4b**	82	81
		5a	67	0
		5b	73	29[a]
3		**4a**	69	45
		4b	77	85
		5a	59	0

[a] The corresponding *R*-enantiomer was formed.

most effective (78%, 67% ee). The *tert*-butyl aza-PCP-*N*-oxide **4a** was less selective (48% ee). Cinnamaldehyde (entry 2) reacted with **4b** giving product **11** with a good selectivity (81% ee), with all other catalysts being less effective. Remarkably, dihydrocinnamaldehyde (entry 3) with **4b** also provided product with a surprisingly high selectivity (85% ee).

In summary, a new class of organo-catalytic aza-paracyclophane *N*-oxides was developed. This new template allows for a simple amino alcohols variation and direct synthesis from a resolved aza-PCP azide **1**. These new catalysts show a high reactivity at a low catalyst load (1.5 mol %) and produce high selectivities with aryl and non-aryl aldehyde substrates. Applications to other transformations following these promising results are currently under investigation.

Acknowledgment

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15. General preparation of **3**: Zinc chloride (68 mg, 0.5 mmol) was fused under high vacuum in a 50 mL Schlenk flask and cooled under nitrogen. After cooling to rt, chlorobenzene (30 mL) was added followed by **1** (10 mmol), and either the *R*-amino alcohol or *S*-amino alcohol **2** (13 mmol). The reaction mixture was heated at reflux for 48 h. The solvent was removed under reduced pressure and the resultant mixture solid was dissolved in CH_2Cl_2 (100 mL). The solution was stirred for 2 h and water (50 mL) was added. The CH_2Cl_2 layer was separated and washed by Na_2CO_3 (satd, 30 mL × 2), brine (30 mL), and dried with sodium sulfate. The solvent was removed and

the product was purified by flash chromatography on silica gel (methanol/CH_2Cl_2: from 2% to 10%). Data for the product compounds **3** was obtained:

R_p,*S*-**3**-(R = *t*-Bu): Yield: 53%; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9H), 2.91–3.13 (m, 3H), 3.15–3.31 (m, 4H), 3.37–3.45 (m, 1H), 4.07 (dd, 1H, $J = 7.6$, $J = 10.1$), 4.25 (t, 1H), 4.35 (dd, 1H, $J = 7.6$, $J = 10.1$), 6.40 (m, 1H), 6.42 (m, 1H), 6.63 (d, 1H, $J = 7.6$), 6.72 (m, 1H), 6.86 (d, 1H, $J = 7.6$), 6.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 33.7, 34.7, 34.9, 37.5, 68.3, 76.1, 116.3, 116.5, 123.6, 125.7, 127.5, 128.5, 129.8, 130.8, 131.0, 132.3, 133.7, 134.2, 137.5, 138.1, 162.9; MS (M+): 335.5; $[\alpha]_D$ −126.8 (*c* 0.085, MeOH).

R_p,*S*-**3**-(R = benzyl): Yield: 42%; ^{1}H NMR ($CDCl_3$) δ 2.76 (d, 1H, $J = 9.2$ Hz), 2.90–3.07 (m, 3H), 3.13–3.26 (m, 5H), 3.37–3.45 (m, 1H), 4.16 (t, 1H, $J = 7.4$ Hz), 4.31 (t, 1H, $J = 8.6$ Hz), 4.61 (m, 1H), 6.38 (m, 1H), 6.43 (dd, 1H), 6.60 (d, 1H, $J = 7.8$), 6.78 (m, 1H), 6.85 (d, 1H, $J = 7.8$), 6.90 (m, 1H), 7.12–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.5, 34.2, 34.7, 37.7, 41.5, 67.9, 71.2, 116.4, 116.6, 123.7, 123.8, 126.3, 127.5, 128.4, 129.1, 130.9, 132.6, 137.6, 138.2, 139.3, 162.4; MS (M+): 369.5; $[\alpha]_D$ −153.7 (*c* 0.095, $CHCl_3$).

R_p,*R*-**3**-(R = *t*-Bu): Yield: 48%; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9H), 2.91–3.13 (m, 3H), 3.15–3.31 (m, 4H), 3.37–3.45 (m, 1H), 4.07 (dd, 1H, $J = 7.6$, $J = 10.1$), 4.25 (t, 1H), 4.35 (dd, 1H, $J = 7.6$, $J = 10.1$), 6.40 (m, 1H), 6.42 (m, 1H), 6.63 (d, 1H, $J = 7.6$), 6.72 (m, 1H), 6.86 (d, 1H, $J = 7.6$), 6.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 33.7, 34.7, 34.9, 37.5, 68.3, 76.1, 116.3, 116.5,123.6, 125.7, 127.5, 128.5, 129.8, 130.8, 131.0, 132.3, 133.7, 134.2, 137.5, 138.1, 162.9; MS (M+): 335.5; $[\alpha]_D$ +125.7 (*c* 0.082, MeOH).

R_p,*R*-**3**-(R = benzyl): Yield: 47%; ^{1}H NMR ($CDCl_3$) δ 2.76 (d, 1H, $J = 9.2$ Hz), 2.90–3.07 (m, 3H), 3.13–3.26 (m, 5H), 3.37–3.45 (m, 1H), 4.16 (t, 1H, $J = 7.4$ Hz), 4.31 (t, 1H, $J = 8.6$ Hz), 4.61 (m, 1H), 6.38 (m, 1H), 6.43 (dd, 1H), 6.60 (d, 1H, $J = 7.8$), 6.78 (m, 1H), 6.85 (d, 1H, $J = 7.8$), 6.90 (m, 1H), 7.12–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.5, 34.2, 34.7, 37.7, 41.5, 67.9, 71.2, 116.4, 116.6, 123.7, 123.8, 126.3, 127.5, 128.4, 129.1, 130.9, 132.6, 137.6, 138.2, 139.3, 162.4; MS (M+): 369.5; $[\alpha]_D$ +134.5 (*c* 0.010, $CHCl_3$).

16. General preparation of oxazoline-aza-PCP-*N*-oxides **4**, **5**: *m*-Chloroperoxybenzoic acid (70%, 122 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **3** (0.50 mmol) in CH_2Cl_2 (8 mL) under N_2 at −10 °C. The reaction mixture was stirred at this temperature for 75 min, and water (10 mL) was added and extracted with $CHCl_3$ (10×3 mL). The combined organic layer was washed with $NaHCO_3$ (satd), brine, and dried over anhydrous sodium sulfate. The solvent was removed and purified by flash chromatography on silica gel (methanol/CH_2Cl_2: from 5% to 20%) to produce products **4** and **5**. Purity was checked by Chiral HPLC (chiral OD-H, hexane/*i*PrOH, 95:5) and found to be above 99% ee. Data for the product compounds **4**, **5** was obtained:

Compound **4a**: Yield: 59%; ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 9H), 2.87–3.10 (m, 4H), 3.13–3.33 (m, 3H), 3.36–3.41 (m, 1H), 4.05 (m, 1H), 4.29 (m, 1H), 4.37 (m, 1H), 6.17 (m, 1H), 6.25 (m, 1H), 6.67 (d, 1H, $J = 7.6$), 6.73 (m, 1H), 6.96 (d, 1H, $J = 7.6$), 7.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.3, 37.0, 37.2, 38.3, 39.2, 68.7, 76.5, 116.2, 116.9, 123.3, 125.3, 127.2, 128.8, 129.7, 130.1, 131.8, 132.2, 133.6, 134.2, 137.3, 138.6, 141.2, 165.1; MS (M+): 351.5; Calcd for $C_{22}H_{26}N_2O_2$: C: 75.40, H: 7.48, N: 7.99, O: 9.13. Found: C: 75.21, H: 7.23, N: 7.72, O: 9.87; $[\alpha]_D$ −67.8 (*c* 0.08, $CHCl_3$).

Compound **4b**: Yield: 67%; ^{1}H NMR ($CDCl_3$) δ 2.77 (d, 1H, $J = 9.2$ Hz), 2.92–3.07 (m, 3H), 3.13–3.27 (m, 5H), 3.34–3.43 (m, 1H), 4.16 (t, 1H, $J = 7.4$ Hz), 4.32 (t, 1H, $J = 8.6$ Hz), 4.65 (m, 1H), 6.16 (m, 1H), 6.22 (dd, 1H), 6.68 (d, 1H, $J = 7.8$), 6.87 (m, 1H), 6.97 (d, 1H, $J = 7.8$), 7.10–7.32 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 32.3, 35.6, 35.7, 39.1, 41.6, 67.6, 71.3, 117.5, 117.6, 123.4, 123.6, 127.3, 127.7, 128.5, 129.7, 130.2, 133.6, 137.5, 138.0, 141.6, 167.1; MS (M+): 385.5; Calcd for $C_{25}H_{24}N_2O_2$: C: 78.10, H: 6.29, N: 7.29, O: 8.32. Found: C: 77.89, H: 6.07, N: 6.85, O: 8.87; $[\alpha]_D$ −79.2 (*c* 0.095, $CHCl_3$).

Compound **5a**: Yield: 55%; ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 9H), 2.87–3.10 (m, 4H), 3.13–3.33 (m, 3H), 3.36–3.41 (m, 1H), 4.05 (m, 1H), 4.29 (m, 1H), 4.37 (m, 1H), 6.17 (m, 1H), 6.25 (m, 1H), 6.67 (d, 1H, $J = 7.6$), 6.73 (m, 1H), 6.96 (d, 1H, $J = 7.6$), 7.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.3, 37.0, 37.2, 38.3, 39.2, 68.7, 76.5, 116.2, 116.9, 123.3, 125.3, 127.2, 128.8, 129.7, 130.1, 131.8,132.2, 133.6, 134.2, 137.3, 138.6, 141.2, 165.1; MS (M+): 351.5; Calcd for $C_{22}H_{26}N_2O_2$: C: 75.40, H: 7.48, N: 7.99, O: 9.13. Found: C: 75.21, H: 7.23, N: 7.72, O: 9.87; $[\alpha]_D$ +66.5 (*c* 0.08, $CHCl_3$).

Compound **5b**: Yield: 72%; ^{1}H NMR ($CDCl_3$) δ 2.77 (d, 1H, $J = 9.2$ Hz), 2.92–3.07 (m, 3H), 3.13–3.27 (m, 5H), 3.34–3.43 (m, 1H), 4.16 (t, 1H, $J = 7.4$ Hz), 4.32 (t, 1H, $J = 8.6$ Hz), 4.65 (m, 1H), 6.16 (m, 1H), 6.22 (dd, 1H), 6.68 (d, 1H, $J = 7.8$), 6.87 (m, 1H), 6.97 (d, 1H, $J = 7.8$), 7.10–7.32 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 32.3, 35.6, 35.7, 39.1, 41.6, 67.6, 71.3, 117.5, 117.6, 123.4, 123.6, 127.3, 127.7, 128.5, 129.7, 130.2, 133.6, 137.5, 138.0, 141.6, 167.1; MS (M+): 385.5; Calcd for $C_{25}H_{24}N_2O_2$: C: 78.10, H: 6.29, N: 7.29, O: 8.32. Found: C: 77.89, H: 6.07, N: 6.85, O: 8.87; $[\alpha]_D$ +80.2 (*c* 0.095, $CHCl_3$).

17. General allylation procedure: An oven-dried flask was charged with allytrichlorosilane (0.080 mL, 0.47 mmol), ligand (0.006 mmol), diisopropylethylamine (0.35 mL, 2.0 mmol), and aldehyde (0.40 mmol) with CH_3CN (2.0 mL) under nitrogen at −40 °C. The mixture was stirred at this temperature and followed by TLC. After the start material was consumed (6 h), the reaction was quenched with aqueous saturated $NaHCO_3$ (5.0 mL) and the aqueous layer was extracted with ethyl acetate (3×5 mL). The organic layers were combined, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate, 95:5) furnished the known products with isolated yields indicated that were characterized by the data shown:

(*S*)-4′-Methoxy-α-(2-propenyl) benzenemethanol: ^{1}H NMR ($CDCl_3$) δ 2.07–12 (broad, 1H), 2.48–2.55 (m, 2H), 3.80 (s, 3H), 4.76–4.79 (m, 1H), 5.09–5.19 (m, 2H), 5.79–5.88 (m, 1H), 6.90 (d, 2H, $J = 8.6$), 7.29 (d, 2H, $J = 8.6$); ^{13}C NMR ($CDCl_3$) δ 43.7, 56.1, 73.2, 113.7, 118.2, 127.1, 134.6, 135.9, 159.0; HRMS: 178.21; chiral HPLC (OD-H, hexane/*i*-PrOH, 19:1, 0.2 mL/min): t_R: 11.2 min, t_S: 12.7 min; $[\alpha]_D$ −48.1 ($CHCl_3$, 1.0).

(*S*)-4′-Chloro-α-(2-propenyl) benzenemethanol: ^{1}H NMR ($CDCl_3$) δ 1.61 (broad, 1H), 2.40–2.53 (m, 2H), 4.67–4.71 (m, 1H), 5.12–5.17 (m, 2H), 5.73–5.84 (m, 1H), 7.27–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 43.6, 46.7, 72.5, 118.7, 119.5, 126.9, 127.2, 128.2,128.5, 129.3, 132.9, 133.1, 133.9, 142.3; HRMS: 182.63; chiral HPLC (OD-H, hexane/*i*-PrOH, 19:1, 0.2 mL/min): t_R: 13.7 min, t_S: 15.1 min; $[\alpha]_D$ −60.7 (*c* 1.5, $CHCl_3$).

(*S*)-α-(2-Propenyl)-2-naphthalenemethanol: ^{1}H NMR ($CDCl_3$) δ 1.83–1.93 (broad, 1H), 2.47–2.56 (m, 2H), 4.83 (m, 1H), 5.11–5.19 (m, 2H), 5.63–5.82 (m, 1H), 7.41–7.57 (m, 3H), 7.72–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 42.8, 69.8, 118.2, 122.9, 121.1, 127.8, 128.2,128.6, 131.6,

133.2, 135.2; HRMS:198.17; chiral HPLC (OD-H, hexane/*i*-PrOH, 9:1, 0.2 mL/min): t_S: 12.6 min, t_R: 14.6 min; $[\alpha]_D$ −55.2 (*c* 1.10, $CHCl_3$).

(*S*)-α-(2-Propenyl)cyclohexanemethanol: ^1H NMR ($CDCl_3$) δ 0.98–1.32 (m, 4H), 1.60–1.71 (m, 1H), 1.75–1.77 (m, 1H), 1.82–2.01 (m, 4H), 2.15 (m, 1H), 2.30–2.38 (m, 2H), 3.40–3.51 (m, 1H), 5.15 (d, 1H, $J = 9.2$), 5.17 (d, 1H,$J = 9.2$ Hz), 5.19 (d, 1H, $J = 12.8$ Hz), 5.88–6.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.9, 26.3, 26.6, 27.9, 29.0, 38.9, 43.2, 74.7, 118.2, 135.6; HRMS: 154.29; chiral HPLC (OD, hexane/*i*-PrOH, 19:1, 0.2 mL/min): t_R: 26.5 min, t_S: 29.1 min; $[\alpha]_D$ −2.5 (*c* 0.6, benzene).