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Development of Biisoquinoline-Based Chiral Diaminocarbene Ligands: Enantioselective S_N2' Allylic Alkylation Catalyzed by Copper−Carbene Complexes

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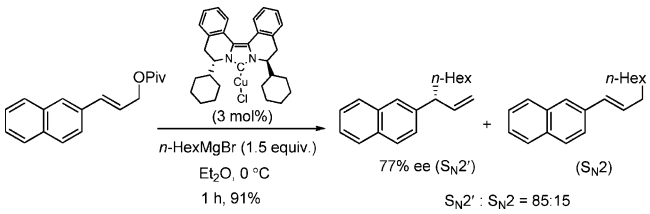

Chiral biisoquinoline-based diaminocarbene ligands (BIQ) were designed to create a chiral environment extended toward the metal center, which was confirmed by an X-ray structure. The concise ligand synthesis is highlighted by a modified Bischler−Napieralski cyclization of bisamides prepared from readily available chiral phenethylamines, and allows easy variation of the stereodifferentiating groups. The cyclohexyl-BIQ−copper complex is an efficient catalyst for enantioselective S_N2' allylic alkylation with Grignard reagents showing S_N2' regioselectivity higher than 5:1 and enantioselectivity in the range of 68−77% ee.

Since the discovery and isolation of several types of stable singlet carbenes, tremendous research efforts have been made to develop N-heterocyclic carbene (NHC) ancillary ligands.[1] NHCs are powerful σ-donating and weak π-accepting ligands, and their metal complexes generally show better air and thermal stability than phosphine complexes. Nevertheless, the development of *chiral* carbene ligands is still in its early stages.[2] Structural diversity in the chiral carbene ligands has not been fully explored. The chiral Ru complex (**1**) developed by Grubbs and co-workers represents one of the best "monodentate" designs, accounting for over 90% ee in asymmetric ring closing metathesis reactions (Figure 1).[3] However, a substrate dependence on enantioselectivity in these reactions[3b] might suggest that the chiral space created by the ligand is remote from the metal center, and therefore less discriminating for less sterically demanding substrates. In addition, the X-ray crystal structure shows that the aryl groups on the nitrogens are pointing orthogonal to the plane of NHC−Ru.[3b] Therefore, it would be interesting to *extend and reposition the stereodifferentiating groups more toward the metal center*. We envisioned that this possibility could be explored through the tricyclic biisoquinoline-based chiral carbene **2** featuring stereogenic centers at the positions α to the nitrogen atoms (Figure 1). Related *tricyclic* carbene structures have been reported.[4] During the course of our study, Herrmann reported a phenyl-substituted *biisoquinoline*-based carbene ligand and its Rh and Ir complexes.[4a,5] Herein we report a concise synthesis of chiral biisoquinoline-based carbene ligands (BIQ) and our results on enantioselective allylic alkylation catalyzed by Cu−carbene complexes.

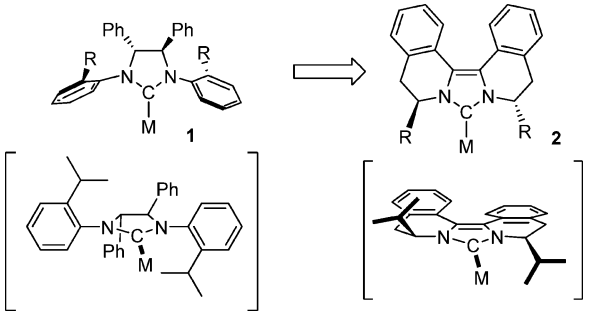

FIGURE 1. Design of tricyclic carbene ligands featuring an extended chiral pocket around the metal center.

Tricyclic biisoquinoline-based carbene ligands (BIQ) were synthesized from chiral phenethylamines (**3**) which were readily prepared by modifications of reported procedures[6,7] (Scheme 1). Chiral phenethylamines were converted to bisamides (**4**) which then were subjected to modified Bischler−Napieralski cyclization conditions (PCl_5 and $Zn(OTf)_2$) to afford 3,3′-disubstituted tetrahydrobiisoquinolines (**5**) in good yield. It is noteworthy that the biisoquinoline compounds (**5**) are also

(1) Recent reviews on NHC−metal complexes: (a) *N-heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Topics in Organometallic Chemistry, Vol. 21; Springer-Verlag: New York, 2007. (b) *N-heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany 2006. (c) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768−2813.

(2) Reviews on chiral NHC ligands: (a) Gade, L. H.; Bellemin-Laponnaz, S. *Top. Organomet. Chem.* **2007**, *21*, 117−157. (b) Perry, M. C.; Burgess, K. *Tetrahedron*: *Asymmetry* **2003**, *14*, 951−961.

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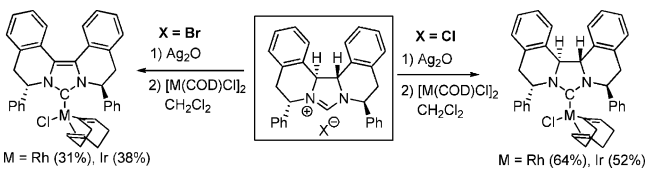
(4) (a) Baskakov, D.; Herrmann, W. A.; Herdtweck, E.; Hoffmann, S. D. *Organometallics* **2007**, *26*, 626−632. (b) Herrmann, W. A.; Baskakov, D.; Herdtweck, E.; Hoffmann, S. D.; Bunlaksananusorn, T.; Rampf, F.; Rodefeld, L. *Organometallics* **2006**, *25*, 2449−2456. (c) Cavell, K. J.; Elliott, M. C.; Nielsen, D. J.; Paine, J. S. *Dalton Trans.* **2006**, 4922−4925. (d) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704−2705.

(5) Herrmann reported that during the preparation of the *saturated* NHC−Rh or −Ir complexes via transmetalation, the *unsaturated* NHC−metal complexes were unexpectedly formed in moderate yields when bromide was counterion in the imidazolium salt.[4a]



(6) Nenajdenko, V. G.; Karpov, A. S.; Balenkova, E. S. *Tetrahedron*: *Asymmetry* **2001**, *12*, 2517−2527.

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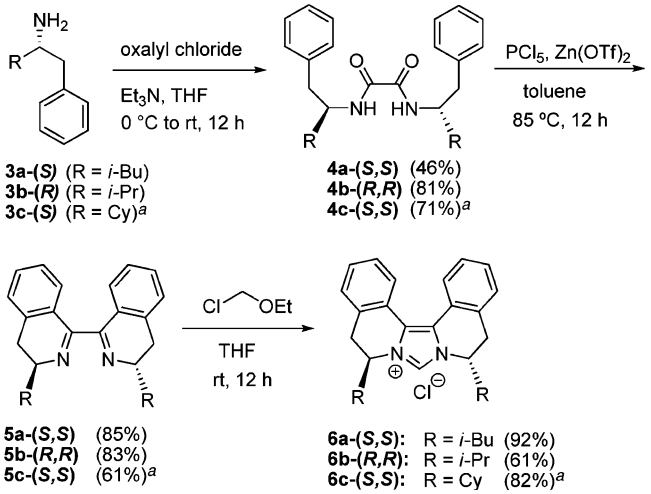
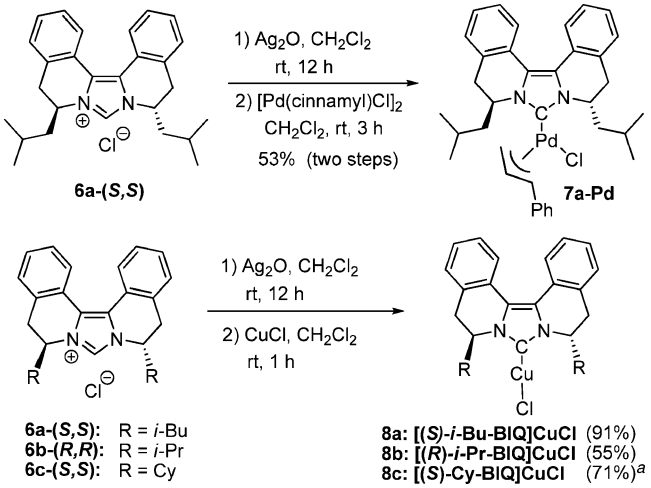
SCHEME 1. Synthesis of Chiral Imidazoliums



[a] Opposite enantiomer shown for compounds **3c**, **4c**, **5c**, and **6c.**

SCHEME 2. Synthesis of Metal−Carbene Complexes



[a] Opposite enantiomer shown for compounds **6c** and **8c**.

potentially interesting C_2-symmetric chiral bisimine ligands. Standard reaction of the bisimines (**5**) with chloromethyl ethyl ether smoothly produced the C_2-symmetric imidazolium salts (**6**) in excellent yield.[8]

Palladium(II) and copper(I) complexes were successfully synthesized from the chiral imidazoliums (**6**) via a transmetalation route[9] (Scheme 2) and single crystals of carbene−Pd(II) complex (**7a-Pd**) suitable for X-ray diffraction were easily obtained.[10] The X-ray structure of **7a-Pd** confirmed our design hypothesis showing that the stereodifferentiating groups (*i*-Bu) are projected toward the Pd metal center in this C_2-symmetric ligand structure (Figure 2).

The carbene−copper(I) complexes (**8a**−**c**) were tested in asymmetric allylic alkylation (AAA) reactions[11] (Table 1). Cu-

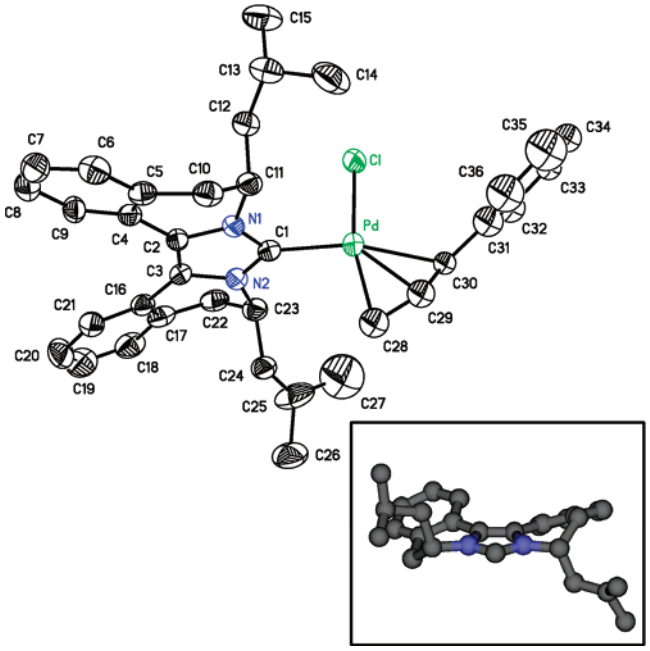


FIGURE 2. X-ray structure of Pd−carbene complex **7a-Pd**. Thermal ellipsoids are drawn at the 50% probability level. The inserted structure ($PdClC_9H_9$ omitted) shows the front view of the tricyclic carbene ligand.

catalyzed asymmetric allylic alkylations[12] allow the use of hard nucleophiles such as Grignard reagents[13,14,15] or dialkyl zinc[16,17] and usually proceed with high S_N2'-selectivity, creating new tertiary or quaternary stereogenic centers from simple linear allylic substrates. The new BIQ carbene−copper catalysts favor the γ-alkylation product (S_N2'),[18] which has been observed with

(8) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523−14534.

(9) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(10) Attempts to grow single crystals of BIQ−copper(I) complexes (**8a**−**c**) for X-ray diffraction were unsuccessful.

(11) Pfaltz, A.; Lautens, M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, Germany, 1999; Vol. II, pp 833−884.

(12) Reviews: (a) Alexakis, A.; Malan, C.; Louise, L.; Tissot-Croset, K.; Polet, D.; Falciola, C. *Chimia* **2006**, *60*, 124−130. (b) Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4435−4439. (c) Hoveyda, A. H.; Hird, A. W.; Kacprzynski, M. A. *Chem. Commun.* **2004**, 1779−1785.

(13) (P,N) or (S,N) ligands: (a) Carosi, L.; Hall, D. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5913−5915. (b) Falciola, C. A.; Alexakis, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2619−2622. (c) Geurts, K.; Fletcher, S. P.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 15572−15573. (d) López, F.; van Zijl, A. W.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2006**, 409−411. (e) Falciola, C. A.; Tissot-Croset, K.; Alexakis, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 5995−5998. (f) Tissot-Croset, K.; Polet, D.; Alexakis, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2426−2428. (g) Alexakis, A.; Croset, K. *Org. Lett.* **2002**, *4*, 4147−4149. (h) Meuzelaar, G. J.; Karlström, A. S. E.; van Klaveren, M.; Persson, E. S. M.; del Villar, A.; van Koten, G.; Bäckvall, J-E. *Tetrahedron* **2000**, *56*, 2895−2903.

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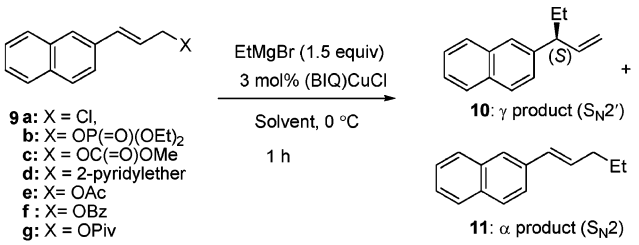
(15) Lewis base activation of Grignard reagents with NHC (Cu-free AAA): Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 15604−15605.

(16) NHC ligands: (a) Kacprzynski, M. A.; May, T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4554−4558. (b) Gillingham, D. G.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 3860−3864. (c) Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877−6882. (d) Larsen, A. O.; Leu, W.; Oberhuber, C. N.; Campbell, J. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 11130−11131.

(17) Other nitrogen or phosphine based ligands: (a) Kacprzynski, M. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 10676−10681. (b) Piarulli, U.; Daubos, P.; Claverie, C.; Roux, M.; Gennari, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 234−236. (c) Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1456−1460. (d) Malda, H.; van Zijl, A. W.; Arnold, L. A.; Feringa, B. L. *Org. Lett.* **2001**, *3*, 1169−1171. (e) Dübner, F.; Knochel, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 379−381.

TABLE 1. Optimization of Reaction Conditions



Entry	Leaving Group (X)	Solvent	Catalyst	Yield (%)[a]	γ : α [b]	% ee (config)[c]
1	Cl	CH_2Cl_2	**8a**	78	34: 66	44, (*S*)
2	Cl	Et_2O	**8b**	98	64: 36	35, (*S*)
3		Et_2O	**8a**	98	51: 49	45, (*S*)
4		Et_2O	**8a**	98	44: 56	55, (*S*)
5		Et_2O	**8a**	80	74: 26	46, (*S*)
6	OAc	Et_2O	**8a**	98	77: 23	70, (*S*)
7	OAc	Et_2O	**8b**	98	78: 22	62, (*S*)
8	OAc	Et_2O	**8c**	98	82: 18	73, (*R*)
9	OAc	Et_2O, -20 °C	**8a**	98	75: 25	69, (*S*)
10	OAc	Et_2O, -78 °C	**8a**	10	61: 39	74, (*S*)
11	OAc	CH_2Cl_2, -78 °C	**8a**	45	44: 56	72, (*S*)
12	OAc	MTBE	**8a**	61	81: 29	65, (*S*)
13	OAc	THF	**8a**	60	42: 58	38, (*S*)
14	OBz	Et_2O	**8a**	99	83: 17	58, (*S*)
15	OPiv	Et_2O	**8a**	68	87: 13	61, (*S*)
16	OPiv	Et_2O	**8c**	99	88: 12	72, (*R*)

[a] Isolated yield. [b] Determined by ^{1}H NMR. [c] Determined by chiral HPLC. Absolute configuration is determined by the optical rotation value (see the Supporting Information for details).

other reported copper catalysts.[12] The initial optimization of the reaction conditions was mostly performed with 3 mol % [(*S*)-*i*-Bu-BIQ]CuCl catalyst (**8a**) on naphthyl substrates (**9**). Interestingly, the BIQ−CuCl catalysts show better regioselectivity and enantioselectivity with ester leaving groups such as acetate (OAc) or pivaloate (OPiv) (entries 6, 14, and 15 vs entries 1−5). This is in contrast to the phosphoramidite ligands which typically use allylic halide substrates for Grignard reagent alkylations.[13] Diethyl ether was selected as the optimum solvent after a brief survey where changing the solvent to THF or CH_2Cl_2 significantly lowered regioselectivity and enantioselectivity (entries 1, 11, and 13). The enantioselectivity was rather insensitive to temperature; however, lower yields were obtained at −78 °C (entries 9 and 10). When the ligand structure is varied, the cyclohexyl complex (**8c**) gives the best regioselectivity (88:12) and enantioselectivity (72% ee).

(18) When a secondary alcohol pivaloate substrate was used, the linear substitution product was obtained as a major product. This result excludes the possible formation of an η^3-allyl Cu intermediate and implies that a S_N2'-type substitution mechanism is operative.

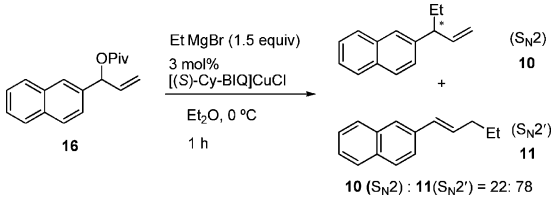
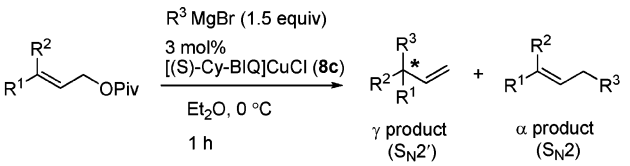
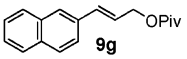
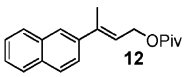
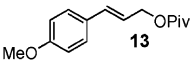
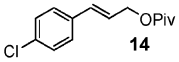
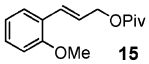


TABLE 2. Reaction Scope



Entry	Substrate	R^3MgBr	Yield (%)[a]	γ : α [b]	% ee[c]
1	 **9g**	Et	99	88: 12	72
2	**9g**	*n*-Hex	91	85: 15	77
3	**9g**	cyclopentyl	91	84: 16	68
4	**9g**	Ph	95	<2: 98	N/A
5	 **12**	Et	91	85: 15	76
6	 **13**	Et	66	86: 14	72
7	 **14**	*n*-Hex	60	77: 23	75
8	 **15**	*n*-Hex	77	75: 25	70

[a] Isolated yield. [b] Determined by ^{1}H NMR. [c] Determined by chiral HPLC (see the Supporting Information for details).

The reaction scope was studied under the optimized conditions (Table 2). Other alkyl Grignard reagents can be used without significantly decreasing reaction yield, regioselectivity, or enantioselectivity (entries 1−3). However, use of phenyl Grignard reagent affords the S_N2 product exclusively, implying a possible change in mechanism. The reaction was also effective for the formation of a quaternary chiral center (entry 5). The aryl substrates also tolerate electron-donating (entry 6) and electron-withdrawing substituents (entry 7), as well as ortho-substituents (entry 8).

In summary, we have synthesized chiral biisoquinoline-based tricyclic chiral diaminocarbene ligands (BIQ) and their Pd and Cu complexes. The chiral environment is created in close proximity to the metal center, which is confirmed by an X-ray crystal structure. The concise ligand synthesis allows easy variation of stereodifferentiating groups from readily accessible starting materials. The cyclohexyl-BIQ−copper complex is an efficient catalyst for enantioselective S_N2' allylic alkylation with Grignard reagents and the BIQ carbene ligands can be applied to other asymmetric catalyses. Application of BIQ carbene and imine ligands in other asymmetric transformations is currently in progress in our laboratory.

Experimental Section

***N*^{1},*N*^{2}-Bis((*S*)-1-cyclohexyl-2-phenylethyl)oxalamide, 4c-(*S*,*S*).** To a cooled, magnetically stirred solution of **3c** (0.458 g, 2.25 mmol) and triethylamine (0.350 mL, 2.53 mmol) in THF (28 mL)

under argon was added oxalyl chloride (0.096 mL, 1.1 mmol) dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 12 h. The reaction mixture was cooled to 0 °C before quenching with water (10 mL). The mixture was extracted with $CHCl_3$ (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 3:1 chloroform/hexane) to afford **4c** (0.349 g, 0.778 mmol, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.09 (m, 12H), 3.95 (m, 2H), 2.88 (dd, J = 5.6, 14 Hz, 2H), 2.66 (dd, J = 8.3, 14 Hz, 2H), 1.78−1.58 (m, 10H), 1.44 (m, 2H), 1.24−1.02 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 138.2, 129.3, 128.6, 126.6, 56.1, 41.0, 38.2, 30.3, 28.3, 26.5, 26.3, 26.2. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{30}H_{40}N_2O_2$ 461.3163, found 461.3164. $[\alpha]^{24}_D$ −24.4 (*c* 4.78, $CHCl_3$).

(3*S*,3′*S*)-3,3′-Dicyclohexyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinoline, 5c-(*S*,*S*). To a solution of **4c** (619 mg, 1.38 mmol) in toluene (60 mL) under nitrogen was added $Zn(OTf)_2$ (1.51 g, 4.14 mmol) and PCl_5 (1.72 g, 8.28 mmol). The reaction mixture was heated at 85 °C for 12 h and then was cooled to room temperature before quenching with a 30% aqueous NH_4OH solution (20 mL). The mixture was extracted with EtOAc (3 × 35 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, 7:1 hexanes/EtOAc) afforded **5c** (357 mg, 0.841 mmol, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.05 (m, 8H), 3.40 (m, 2H), 2.69 (m, 4H), 1.93−1.54 (m, 12H), 1.29−1.09 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 138.2, 130.9, 128.5, 127.8, 62.0, 42.9, 30.4, 29.2, 27.9, 26.8, 26.7, 26.6. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{30}H_{36}N_2$ 425.2951, found 425.2957. $[\alpha]^{24}_D$ +6.2 (*c* 2.64, $CHCl_3$).

[6(*S*),8(*S*)-Dicyclohexyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[*c*,*g*]fluorenium] Chloride, 6c-(*S*,*S*). To a solution of **5c** (0.0822 g, 0.194 mmol) in THF (8 mL) was added chloromethyl ethyl ether (0.110 mL, 1.18 mmol). The reaction mixture was stirred for 12 h. Volatiles were removed at reduced pressure and the resulting sticky residue was purified by flash column chromatography (silica gel, 10:1 CH_2Cl_2/MeOH) to afford **6c** (0.0750 g, 0.159 mmol, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.92 (d, J = 7.2 Hz, 2H), 7.39−7.32 (m, 6H), 7.17 (m, 2H), 3.34 (dd, J = 5.5, 16.1 Hz, 2H), 3.20 (d, J = 15.9 Hz, 2H), 1.73−0.82 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 132.8, 130.7, 129.9, 127.9, 124.5, 124.1, 124.0, 60.1, 38.3, 31.6, 29.5, 29.4, 25.9, 25.7, 25.6. HRMS-ESI (m/z) $[M - Cl]^+$ calcd for $C_{31}H_{37}ClN_2$ 437.2957, found 437.2971. $[\alpha]^{25}_D$ +212.1 (*c* 2.44, $CHCl_3$).

[6(*S*),8(*S*)-Dicyclohexyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[*c*,*g*]fluoren-5-ylidene]chlorocopper(I), 8c. (a) A solution of **6c** (0.30 g, 0.63 mmol) and Ag_2O (0.088 g, 0.38 mmol) in CH_2Cl_2 (5 mL) was stirred for 12 h at room temperature under argon and then filtered through a pad of celite. The filtrate was concentrated under reduced pressure to afford the crude silver−carbene complex, which was used immediately in the next step without further purification. (b) A solution of the crude silver−carbene complex and CuCl (64 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was stirred for 2 h at room temperature under argon and then filtered through a pad of celite. The filtrate was concentrated under reduced pressure. The residue was purified quickly by flash column chromatography on silica gel (CH_2Cl_2) to yield **8c** (0.24 g, 0.45 mmol, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, J = 2.3, 6.2 Hz, 2H), 7.29−7.23 (m, 6H), 4.43 (m, 2H), 3.26 (dd, J = 5.0, 15.8 Hz, 2H), 3.16 (dd, J = 1.8, 15.6 Hz, 2H), 1.73−0.89 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.4, 129.4, 129.1, 127.3, 126.3, 124.1, 124.0, 61.7, 38.2, 32.7, 31.4, 30.0, 26.1, 26.0, 25.9. Anal. Calcd for $C_{31}H_{36}ClCuN_2$: C, 69.51; H, 6.77; N, 5.23. Found: C, 69.42; H, 6.75; N, 4.83. $[\alpha]^{23}_D$ +173.6 (*c* 0.78, $CHCl_3$).

Typical Procedure for Asymmetric Allylic Alkylation. A flame-dried Schlenk flask was charged with a substrate (0.5 mmol), a copper catalyst (0.015 mmol, 3 mol %), and a solvent (3 mL). To this solution under argon was added a Grignard reagent (0.75 mmol in Et_2O) via syringe at a specified temperature and the resulting reaction mixture was stirred for 1 h at the same temperature. Then the reaction was quenched with a saturated aqueous NH_4Cl solution (10 mL). The mixture was extracted with Et_2O (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silicagel, hexanes). The regioselectivity (S_N2':S_N2) was determined by ^{1}H NMR. The integration values of the olefinic proton signal of the two regioisomers were compared. The absolute configuration of the chiral center of 2-(pent-1-en-3-yl)naphthalene (**10**) was determined by comparing the $[\alpha]_D$ value of our product with the reported value.[17a] The values for enantiomeric excess of the chiral products were measured by chiral stationary phase HPLC analysis. (HPLC condition for **10**: Whelk-O1 column, 254 nm, 100% pentane, 0.2 mL/min, t_S = 25.5 min, t_R = 26.9 min.)

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Supporting Information Available: Detailed synthetic procedures and analytical data for new compounds (pdf) and X-ray crystallographic data for **7a-Pd** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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