DOI: 10.1002/chem.200701982

Chiral Bidentate Bis(N-Heterocyclic Carbene)-Based Palladium Complexes Bearing Carboxylate Ligands: Highly Effective Catalysts for the Enantioselective Conjugate Addition of Arylboronic Acids to Cyclic Enones

Tao Zhang[a] and Min Shi*[a, b]

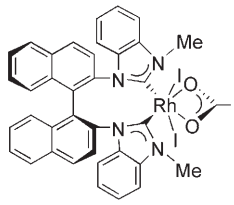
Abstract: Axially chiral *cis*-chelated bidentate bis(N-heterocyclic carbene)–palladium(II) complexes with two weakly coordinating carboxylate ligands are effective catalysts for the asymmetric conjugate addition of arylboronic acids to cyclic enones, producing the corresponding adducts in moderate-to-high yields and with good-to-high enantioselectivities, in most cases under mild conditions.

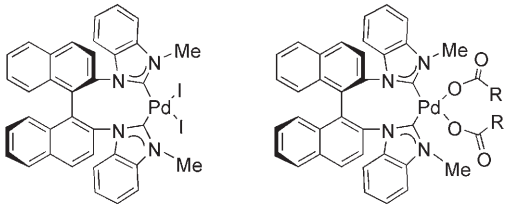
Keywords: asymmetric catalysis · boronic acids · carbenes · Michael addition · palladium

Introduction

Catalytic asymmetric conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds is an efficient method for the construction of chiral enantioenriched compounds by using achiral precursors.[1] Among the numerous methods to achieve this, rhodium-catalyzed asymmetric conjugate addition to enones with organoboron reagents (aryl- and alkenylboronic acids) has attracted much attention because of their stability towards air and moisture, functional group tolerance, as well as easy availability and broad scope.[2–4] However, compared with asymmetric conjugate addition catalyzed by chiral rhodium complexes, successful examples of chiral palladium-complex-catalyzed asymmetric conjugate addition of aryl- and alkenylboronic acids to α,β-unsaturated ketones are rare.[5,6] Therefore, the search for efficient chiral palladium complexes in asymmetric conjugate addition is still a formidable challenge in asymmetric catalysis.

N-Heterocyclic carbenes (NHCs)[7] represent a growing class of ligands that can be used in place of phosphine ligands in transition-metal catalysis, which provide more effective metal complexes owing to their stability to air and moisture and their strong σ-donor and poor π-acceptor properties.[8] Significantly, Pd–NHC complexes have emerged as effective catalysts for a variety of coupling reactions.[9] Unfortunately, to date, the promise of a highly active and enantioselective Pd–NHC catalyst has not been fulfilled, even though many palladium-mediated transformations, such as enolate arylation,[10] π-allyl alkylation,[11] and various ring-closing reactions with carbopalladation,[12] have opened up the possibility of the development of enantioselective catalysis. Previously, we reported the synthesis of a novel *cis*-chelated bidentate bis(NHC) ligand and its rhodium(III) complex (Scheme 1),[13a] as well as its pallad-





1 2: R = Me, 3: R = CF_3

Scheme 1. Structures of NHC–Rh^{III} and NHC–Pd^{II} complexes **1**, **2**, and **3**.

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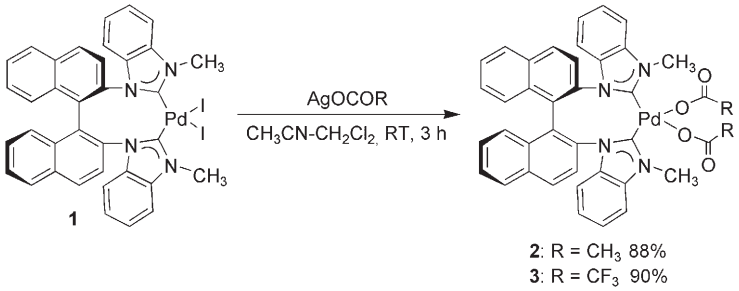
ium(II) complex **1**,[13b] and their application in both Suzuki–Miyaura and Heck coupling reactions as well as asymmetric hydrosilylation of methyl ketones and aerobic oxidative kinetic resolution of alcohols.[13c] As chiral C_2-symmetric *cis*-chelated bidentate NHC ligands remain scarce, we have continued to seek out more efficient chiral NHC–Pd^{II} complexes for asymmetric catalysis.[13,14] Herein, we report an interesting first example of the asymmetric conjugate addition of arylboronic acids to cyclic enones catalyzed by chiral *cis*-chelated bidentate bis(NHC)–palladium(II) complexes **2** and **3** with two weakly coordinating carboxylate ligands (Scheme 1).

Results and Discussion

Chiral NHC–Pd^{II} complex **1** was prepared from axially chiral binaphthyl-2,2′-diamine (BINAM) according to a literature procedure.[13] NHC–Pd^{II} complexes **2** and **3** were then synthesized by treating **1** with AgO_2CCH_3 and AgO_2CCF_3, respectively, in a mixed solvent system of CH_2Cl_2 and CH_3CN at room temperature. These two NHC–Pd^{II} complexes were isolated as white solids in 88 and 90% yields, respectively (Scheme 2). They are fairly stable towards air and moisture in solution and in the solid state.



Scheme 2. Preparation of **2** and **3**.

Single crystals of **2** and **3** that were suitable for X-ray diffraction studies were grown from a mixed solvent system of hexane/CH_2Cl_2. The molecular structure of **3** is shown in Figure 1.[15] As can be seen from Figure 1, the palladium center is coordinated by the two carbene moieties of the axially chiral bidentate bis(NHC) ligand and two trifluoroacetate counterions in this interesting NHC–Pd^{II} complex.

Initial examination of the asymmetric addition of phenylboronic acid (**5a**) to 2-cyclohexenone (**4a**) in the presence of **1**, **2**, or **3** (3 mol%) failed to give the desired product after 48 h at room temperature (20°C) in THF/H_2O (10:1). Premixing **2** or **3** with KOH (40 mol% of **5a**) followed by the addition of **4a** and **5a** afforded the desired product **6aa** in 95% yield along with 93% enantiomeric excess (*ee*) and 97% yield along with 94% *ee*, respectively, after 36 h at room temperature (20°C) (Table 1, entries 2 and 3). However, complex **1** was ineffective as the catalyst under identical conditions (Table 1, entry 1). These results suggest that the two weakly coordinating carboxylate ligands play a very important role in this reaction. Interestingly, this asymmetric conjugate addition reaction catalyzed by (*R*)-bis(NHC)–Pd^{II}

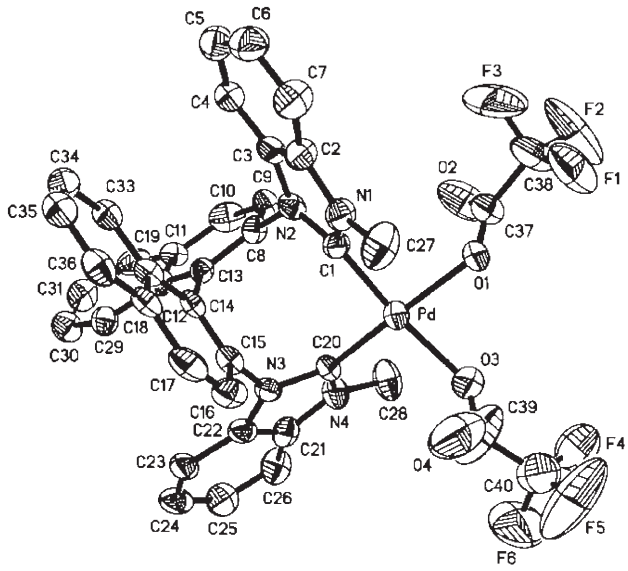
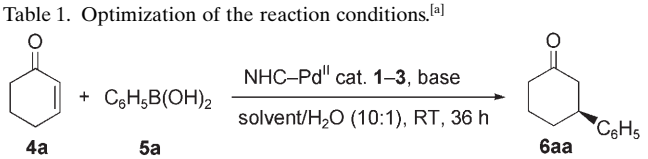


Figure 1. X-ray structure of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and water have been omitted for clarity.

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Base (equiv to **4a**)	Yield[b] [%]	*ee*[c] [%]
1	**1**	THF	KOH (0.4)	<5	n.d.[d]
2	**2**	THF	KOH (0.4)	95	93 (*S*)
3	**3**	THF	KOH (0.4)	97	94 (*S*)
4	**3**	THF	KOH (0.07)	46	80 (*S*)
5	**3**	THF	KOH (0.5)	85	90 (*S*)
6	**3**	THF	KOH (1.0)	22	78 (*S*)
7	**3**	THF	K_2CO_3 (0.4)	94	91 (*S*)
8	**3**	IPA	KOH (0.4)	99	74 (*S*)
9	**3**	MeCN	KOH (0.4)	8	n.d.[d]
10[e]	**3**	toluene/THF	KOH (0.4)	96	80 (*S*)
11[f]	**3**	THF	KOH (0.4)	97	96 (*S*)
12[f,g]	**3**	THF	KOH (0.4)	39	94 (*S*)
13[f,h]	**3**	THF	KOH (0.4)	32	96 (*S*)
14[f,i]	**3**	THF	KOH (0.4)	65	94 (*S*)
15[f,j]	**3**	THF	KOH (0.4)	97	96 (*S*)

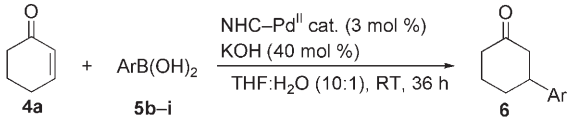
[a] All reactions were conducted with **4a** (0.25 mmol), **5a** (0.75 mmol), KOH (0.1 mmol), and catalyst **1**, **2**, or **3** (0.0075 mmol) in THF/H_2O (10:1, 1.1 mL) at 20°C for 36 h. [b] Yield of isolated product. [c] Determined by HPLC analysis using chiral stationary phase columns. The absolute configuration of **6aa** was determined by comparing the optical rotation $[\alpha]_D$ with the data in the literature. [d] n.d. = not determined. [e] Toluene/THF 1:1. [f] The reaction was conducted with 0.375 mmol of **5a**. [g] The reaction was carried out at 50°C for 10 h. [h] The reaction was carried out at room temperature (20°C) for 10 h. [i] The reaction was carried out at 50°C for 20 h. [j] The reaction was carried out at room temperature (20°C) for 20 h.

complex **2** or **3** gave **6aa** with an *S* configuration, which is a different outcome to that observed for the asymmetric conjugate addition reaction catalyzed by (*S*)-BINAP-rhodium in which **6aa** was also obtained with an *S* configuration.[3]

We next attempted to optimize further the reaction conditions and the results of these experiments are summarized in Table 1 (entries 4–11). Decreasing or increasing the amount of KOH lowered the yield and *ee* of **6aa** (Table 1, entries 4–6). Potassium carbonate (0.4 equiv K_2CO_3) is also an effective base in this reaction. Examination of solvent effects, reaction temperature, and the amount of **5a** employed revealed that the best reaction conditions involve the use of **3** (3 mol%) and KOH (40 mol%) with **5a** (1.5 equiv) in THF at room temperature, which gives **6aa** in high yield and high *ee* (Table 1, entry 11). Note, adduct **6aa** was obtained in a lower yield and with a high *ee* after 10 h at room temperature (20°C) and also when the reaction was carried out at 50°C for 10 h (Table 1, entries 12 and 13). After 20 h, **6aa** was obtained in good yield and high *ee* at room temperature (20°C) and in moderate yield and high *ee* at 50°C (Table 1, entries 14 and 15), which suggests that this asymmetric conjugate addition reaction is facilitated at room temperature.

With these optimized reaction conditions identified, by using 3 mol% of catalyst **2** or **3**, the generality of this interesting asymmetric conjugate addition reaction with various other arylboronic acids was examined and the results are shown in Table 2. We found that the adducts were obtained in high yields (78–99%) and excellent enantiomeric excesses (88–97% *ee*) with electron-rich arylboronic acids, which included easily hydrolyzed *p*-anisylboronic acid (Table 2, entry 5).[6d,16] With electron-poor *m*-chlorophenylboronic acid, the corresponding adduct (**6ah**) was produced in a slightly lower yield and a lower enantiomeric excess (Table 2, entry 9).

Table 2. Asymmetric conjugate addition of arylboronic acids to **4a**.[a]



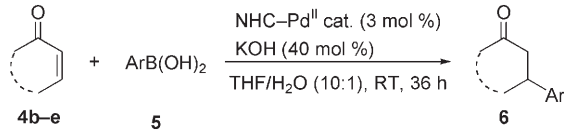
4a 5b–i 6

Entry	Ar	Catalyst	Yield [%][b]	*ee* [%][c]
1	3-MeC_6H_4 (**5b**)	**3**	97 (**6ab**)	97 (−)
2	4-MeC_6H_4 (**5c**)	**3**	89 (**6ac**)	92 (−)
3	3-MeOC_6H_4 (**5d**)	**3**	90 (**6ad**)	97 (−)
4	3-MeOC_6H_4 (**5d**)	**2**	92 (**6ad**)	94 (−)
5	4-MeOC_6H_4 (**5e**)	**3**	82 (**6ae**)	94 (−)
6	2-naphthyl (**5f**)	**3**	99 (**6af**)	97 (−)
7	2-naphthyl (**5f**)	**2**	98 (**6af**)	96 (−)
8	4-$C_6H_5C_6H_4$ (**5g**)	**3**	97 (**6ag**)	93 (−)
9	3-ClC_6H_4 (**5h**)	**3**	78 (**6ah**)	88 (−)
10	3,5-$Me_2C_6H_3$ (**5i**)	**3**	90 (**6ai**)	92 (−)

[a] All reactions were conducted with **4a** (0.25 mmol), **5** (0.375 mmol), KOH (0.1 mmol), and NHC–Pd^{II} catalyst **2** or **3** (0.0075 mmol) in THF/H_2O (10:1, 1.1 mL) at room temperature (20–25°C) for 36 h. [b] Yield of isolated product. [c] Determined by HPLC analysis with chiral stationary phase columns (Daicel Chiralcel OD-H, AD-H or AS-H). The signs of the optical rotations are indicated in parentheses.

By using 2-cycloheptenone (**4b**) as the substrate with arylboronic acids **5a**, **5b**, **5d**, and **5f**, the corresponding adducts **6ba**, **6bb**, **6bd**, and **6bf** were produced in good yields and high enantiomeric excesses in the presence of catalyst **2** or **3** under the standard conditions (Table 3, entries 1–6). The

Table 3. Asymmetric conjugate addition of arylboronic acids to cyclic enones.[a]



4b–e 5 6

Entry	Substrate	Ar	Catalyst	Yield [%][b]	*ee* [%][c]
1	**4b**	C_6H_5 (**5a**)	**3**	88 (**6ba**)	91 (−)
2	**4b**	C_6H_5 (**5a**)	**2**	85 (**6ba**)	94 (−)
3	**4b**	4-MeC_6H_4 (**5b**)	**3**	90 (**6bb**)	91 (−)
4	**4b**	3-MeOC_6H_4 (**5d**)	**3**	86 (**6bd**)	96 (−)
5	**4b**	2-naphthyl (**5f**)	**3**	99 (**6bf**)	97 (−)
6	**4b**	2-naphthyl (**5f**)	**2**	84 (**6bf**)	96 (−)
7[d]	**4c**	C_6H_5 (**5a**)	**3**	53 (**6ca**)	81 (−)
8[d]	**4d**	2-naphthyl (**5f**)	**3**	62 (**6df**)	38 (+)
9	**4e**	C_6H_5 (**5a**)	**3**	58 (**6ea**)	32 (+)

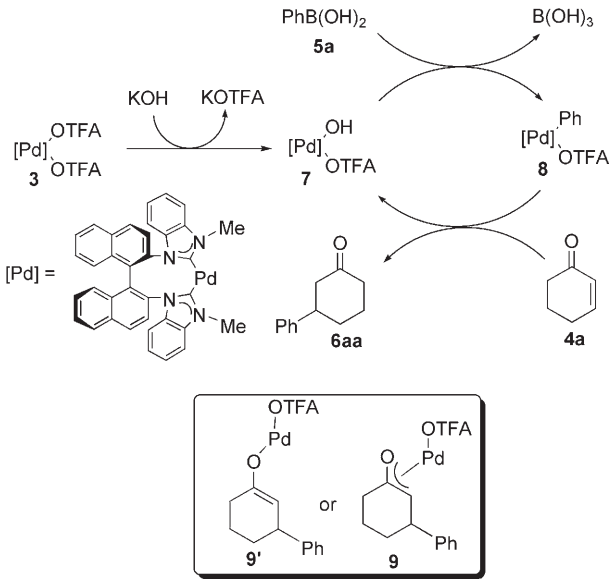
[a] All reactions were conducted with **4a** (0.25 mmol), **5** (0.375 mmol), KOH (0.1 mmol), and NHC–Pd^{II} catalyst **2** or **3** (0.0075 mmol) in THF/H_2O (10:1, 1.1 mL) at room temperature (20–25°C) for 36 h. [b] Yield of isolated product. [c] Determined by HPLC analysis with chiral stationary phase columns (Daicel Chiralcel OD-H, AD-H or AS-H). The signs of the optical rotations are indicated in parentheses. [d] The reaction was carried out at 50°C.

conjugate addition of **5a** to benzyl 2,3-dihydro-4-oxo-1*H*-pyridinecaboxylate (**4c**) and of **5f** to 5,6-dihydropyran-2-one (**4d**) afforded the corresponding products **6ca** in moderate yield along with good *ee* and **6df** in good yield along with a lower *ee* in the presence of **3** at 50°C, respectively (Table 3, entries 7 and 8). The asymmetric conjugate addition reaction of 2-cyclopentenone (**4e**) with **5a** afforded the corresponding adduct **6ea** in moderate yield and low *ee* under the standard conditions (Table 3, entry 9).

On the basis of previous mechanistic studies by Hayashi and co-workers,[3,4] a plausible catalytic cycle is outlined in Scheme 3. First, catalyst **3** reacts with KOH to afford the corresponding hydroxopalladium complex **7**, which readily undergoes transmetalation with **5a**[5a,6b,d,17] to produce a phenylpalladium species **8**. Insertion of the C–Pd bond of **8** into the C=C double bond of the cyclic enone substrate takes place to give π-oxaallylpalladium species **9** or the palladium enolate species **9′**. The resulting species is hydrolyzed by water to give product **6aa** and regenerate **7**.

Conclusion

We have developed a novel type of effective axially chiral *cis*-chelated bidentate bis(NHC)–palladium(II) catalyst for the asymmetric conjugate addition of arylboronic acids to cyclic enones, which affords the corresponding adducts in



Scheme 3. Proposed catalytic cycle for the conjugate addition of **5a** to **4a** by catalysis with **3**.

moderate-to-high yields and with good-to-high enantioselectivities, in most cases under mild conditions. To the best of our knowledge, this is the first example of the use of chiral *cis*-chelated bidentate bis(NHC)–palladium(II) catalysts in the asymmetric conjugate addition of arylboronic acids to cyclic enones. Further studies on substrate scope, the mechanistic details of the catalytic system, and the use of palladium complexes **2** and **3** as catalysts in other asymmetric C–C bond-forming reactions are in progress.

Experimental Section

General methods: Melting points are uncorrected (Yanagimoto micro melting apparatus). ^{1}H and ^{13}C NMR spectra were recorded by using a Varian Mercury vx 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard at 300 and 75 MHz, respectively. Mass spectra were recorded by using an HP-5989 instrument by EI/ESI/MALDI methods. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained by using a Carlo Erba 1106 analyzer. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin–Elmer 341 MC digital polarimeter; $[\alpha]_D$ values are given with units of $10\,cm^2\,deg^{-1}\,g^{-1}$. Chiral HPLC was performed by using a SHIMADZU SPD-10A vp series instrument with chiral columns (Chiralpak AS-H, OD-H, and AD-H columns, 4.6×250 mm, Daicel Chemical). Commercially obtained reagents were used without further purification. All reactions were monitored by TLC by using Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure.

Synthesis of 2: Complex **1** (174 mg, 0.20 mmol) was suspended in a mixture of CH_2Cl_2 (15 mL) and CH_3CN (5 mL). AgOAc (70 mg, 0.42 mmol) was added and the mixture was stirred at room temperature for 3 h. The resulting suspension was filtered from the precipitated AgI through Celite and the solvent was removed under reduced pressure to give **2** as a white powder (131 mg, 88%). Crystals that were suitable for X-ray diffraction study were grown from solutions in CH_2Cl_2/hexane (2:1). M.p. 268°C (decomp); $[\alpha]_D^{20}=52.0$ ($c=0.12$ in DMSO); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=1.88$ (br s, 6H; CH_3), 3.90 (s, 6H; CH_3), 6.70–6.73 (m, 2H; ArH), 6.83–6.92 (m, 10H; ArH), 7.20–7.26 (m, 2H; ArH), 7.71 (d, $J=8.4$ Hz, 2H; ArH), 8.05 (d, $J=8.4$ Hz, 2H; ArH), 8.15 ppm (d, $J=8.4$ Hz, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=23.7$, 35.0, 109.1, 112.4, 123.1, 123.4, 124.9, 126.4, 126.9, 127.5, 130.1, 131.2, 132.5, 132.7, 133.1, 135.1, 135.8, 171.6, 177.3 ppm; IR (KBr): $\tilde{\nu}=3408$, 3053, 2924, 2847, 1580, 1510, 1385, 751 cm^{-1}; MS (MALDI): m/z: 620.2.0 [$M^+-2\,O_2CCH_3$]; elemental analysis calcd (%) for $C_{40}H_{32}N_4O_4Pd\cdot1.5\,H_2O$ requires: C 62.71, H 4.60, N 7.31; found: C 62.75, H 4.62, N 7.30%.

Synthesis of 3: Complex **1** (174 mg, 0.20 mmol) was suspended in a mixture of CH_2Cl_2 (15 mL) and CH_3CN (5 mL). $AgOCOCF_3$ (93 mg, 0.42 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The resulting suspension was filtered from the precipitated AgI through Celite and the solvent was removed under reduced pressure to give **3** as a white powder (153 mg, 90%). Crystals that were suitable for diffraction study were grown from solutions in CH_2Cl_2/hexane (1:1). M.p. 248°C (decomp); $[\alpha]_D^{20}=49.0$ ($c=0.55$ in DMSO); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=3.88$ (s, 6H; CH_3), 6.75–6.78 (m, 2H; ArH), 6.83–6.97 (m, 10H; ArH), 7.22–7.27 (m, 2H; ArH), 7.73 (d, $J=8.1$ Hz, 2H; ArH), 8.09 ppm (s, 4H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=34.9$, 109.4, 112.6, 115.9 (q, $J=287.9$ Hz, CF_3), 123.8, 124.0, 124.4, 126.8, 127.3, 127.7, 130.5, 131.1, 132.5, 132.8, 133.0, 134.6, 135.7, 161.7 (q, $J=36.7$ Hz, CO), 166.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): $\delta=-74.9$ ppm; IR (KBr): $\tilde{\nu}=3558$, 2924, 1680, 1510, 1393, 745 cm^{-1}; MS (MALDI): m/z: 515.2 [$M^+-2\,OCOCF_3-Pd$]; elemental analysis calcd (%) for $C_{40}H_{26}F_6N_4O_4Pd\cdot H_2O$ requires: C 55.54, H 3.26, N 6.48; found: C 55.64, H 3.11, N 6.27%.

General procedure for the palladium-catalyzed asymmetric conjugate addition of arylboronic acids to cyclic enones: The NHC–Pd^{II} catalyst (3 mol%, 7.5 mol) and KOH (40 mol%, 0.1 mmol, 5.6 mg) were dissolved in dry THF (1.0 mL) in a flame-dried Schlenk tube equipped with a septum and stirring bar and the mixture was stirred under argon at room temperature for 10 min. Arylboronic acid **5** (1.5 equiv, 0.375 mmol) was added followed by the addition of enone **4** (0.25 mmol). After the addition of H_2O (0.1 mL), the reaction mixture was stirred at room temperature for 36 h. Saturated aqueous solution of $NaHCO_3$ was then added. The organic phase was separated and the resulting aqueous layer was extracted with Et_2O. The combined organic phases were filtered through a plug of silica, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (eluent: EtOAc/petroleum ether) to yield the corresponding product **6**.

3-Phenylcyclohexanone (6aa):[3] Ketone **6aa** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 97% yield, 96% *ee*). The *ee* was determined by HPLC analysis (Chiralpak AD column, hexane/*i*PrOH 100:1, detection at 209 nm, retention times: 19.5 (major)/23.6 min (minor)). $[\alpha]_D^{25}=-20.4$ ($c=1.0$ in $CHCl_3$) (for 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=1.70$–1.92 (m, 2H), 2.06–2.18 (m, 2H;), 2.32–2.63 (m, 4H), 2.96–3.05 (m, 1H), 7.21–7.36 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=25.5$, 32.7, 41.1, 44.7, 48.9, 126.5, 126.6, 128.6, 144.3, 211.0 ppm.

3-(3-Methylphenyl)cyclohexanone (6ab):[3] Ketone **6ab** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 97% yield, 97% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 100:1, detection at 210 nm, retention times: 14.65 (major)/17.83 min (minor)). $[\alpha]_D^{25}=-20.8$ ($c=1.0$ in $CHCl_3$) (for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=1.78$–1.87 (m, 2H), 2.04–2.16 (m, 2H), 2.34 (s, 3H), 2.35–2.55 (m, 4H), 2.95–2.96 (m, 1H), 7.00–7.06 (m, 3H), 7.19–7.24 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=21.4$, 25.5, 32.7, 41.1, 44.7, 48.9, 123.5, 127.32, 127.34, 128.2, 138.2, 144.3, 211.1 ppm.

3-(4-Methylphenyl)cyclohexanone (6ac):[3] Ketone **6ac** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 89% yield, 92% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak AD column, hexane/*i*PrOH 150:1, detection at 209 nm, retention times: 8.11 (major)/8.77 min (minor)). $[\alpha]_D^{25}=-16.4$ ($c=0.5$ in $CHCl_3$) (for 92% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=$ 1.73–1.90 (m, 2H), 2.04–2.18 (m, 2H), 2.33 (s, 3H), 2.36–2.62 (m, 4H),

2.93–3.02 (m, 1H), 7.10–7.16 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.90, 25.5, 32.8, 41.1, 44.3, 49.0, 126.3, 129.2, 136.2, 141.3, 211.2 ppm.

3-(3-Methoxylphenyl)cyclohexanone (3ad):[5a,18] Ketone **3ad** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 90% yield, 97% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 42.95 (major)/49.80 min (minor)). $[\alpha]_D^{25} = -11.8$ (c = 1.1 in $CHCl_3$) (for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.73–1.88 (m, 2H), 2.06–2.18 (m, 2H), 2.34–2.63 (m, 4H), 2.95–3.02 (m, 1H), 3.80 (s, 3H), 6.77–6.83 (m, 3H), 7.22–7.28 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 25.5, 32.6, 41.2, 44.7, 48.9, 55.1, 111.7, 112.6, 118.8, 129.6, 145.9, 159.7, 211.1 ppm.

3-(4-Methoxylphenyl)cyclohexanone (6ae):[16] Ketone **6ae** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 20:1) in 82% yield and 94% *ee*. The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 100:1, detection at 210 nm, retention times: 30.50 (minor)/32.11 min (major)). $[\alpha]_D^{25} = -19.1$ (c = 0.35 in $CHCl_3$) (for 94% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.72–1.88 (m, 2H), 2.03–2.17 (m, 2H), 2.31–2.60 (m, 4H), 2.91–3.01 (m, 1H), 3.79 (s, 3H), 6.87 (d, J = 10.2 Hz, 2H), 7.18 ppm (d, J = 10.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 25.5, 33.0, 41.2, 43.9, 49.2, 55.2, 114.0, 127.5, 136.5, 158.2, 211.3 ppm.

3-(2-Naphthyl)cyclohexanone (6af):[3] Ketone **6af** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 99% yield, 97% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 40.42 (major)/49.07 min (minor)). $[\alpha]_D^{25} = -8.4$ (c = 1.0 in $CHCl_3$) (for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.80–1.98 (m, 2H), 2.15–2.22 (m, 2H), 2.41–2.47 (m, 2H), 2.64–2.68 (m, 2H), 3.17–3.20 (m, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.43–7.51 (m, 2H), 7.65 (s, 1H), 7.80–7.84 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 25.5, 32.7, 41.2, 44.8, 48.8, 124.7, 125.3, 125.6, 126.2, 127.57, 127.64, 128.3, 132.3, 133.5, 141.7, 211.0 ppm.

3-Biphenyl-4-ylcyclohexanone (6ag):[3] Ketone **6ag** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 20:1; 97% yield, 93% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50:1, detection at 209 nm, retention times: 25.25 (minor)/34.62 min (major)). $[\alpha]_D^{25} = -5.5$ (c = 0.5 in $CHCl_3$) (for 93% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.77–1.92 (m, 2H), 2.11–2.21 (m, 2H), 2.37–2.67 (m, 4H), 3.03–3.10 (m, 1H), 7.26–7.37 (m, 3H), 7.44 (t, J = 7.2 Hz, 2H), 7.55–7.60 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 25.5, 32.7, 41.2, 44.4, 48.9, 126.98, 126.99, 127.2, 127.4, 128.7, 139.6, 140.7, 143.4, 211.1 ppm.

3-(3-Chlorophenyl)cyclohexanone (6ah):[3] Ketone **6ah** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 78% yield, 88% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak AD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 16.06 (major)/18.28 min (minor)). $[\alpha]_D^{25} = -5.4$ (c = 1.0 in $CHCl_3$) (for 88% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.74–1.91 (m, 2H), 2.07–2.19 (m, 2H), 2.34–2.62 (m, 4H), 2.95–3.03 (m, 1H), 7.09–7.29 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.96, 25.6, 32.9, 41.2, 44.4, 49.1, 126.4, 129.3, 136.2, 141.4, 211.05 ppm.

3-(3,5-Dimethylphenyl)cyclohexanone (6ai): Ketone **6ai** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 90% yield, 92% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 13.08 (major)/20.12 min (minor)). $[\alpha]_D^{25} = -4.2$ (c = 0.8 in $CHCl_3$) (for 92% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.72–1.89 (m, 2H), 2.03–2.18 (m, 2H), 2.30 (s, 6H), 2.33–2.59 (m, 4H), 2.87–2.96 (m, 1H), 6.83 (s, 2H), 6.88 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.3, 25.6, 32.8, 41.2, 44.7, 49.0, 124.3, 128.3, 138.1, 144.3, 211.2 ppm.

3-Phenylcycloheptanone (6ba):[3] Ketone **6ba** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 88% yield, 91% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50/1, detection at 210 nm, retention times: 12.68 (major)/13.66 min (minor)). $[\alpha]_D^{25} = -50.8$ (c = 1.0 in $CHCl_3$) (for 91% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.41–1.48 (m, 1H), 1.64–1.80 (m, 2H), 1.96–2.10 (m, 3H), 2.57–2.66 (m, 3H), 2.85–2.96 (m, 2H), 7.16–7.32 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 24.1, 29.2, 39.2, 42.7, 43.9, 51.2, 126.3, 126.4, 128.6, 146.9, 213.5 ppm.

3-(4-Methylphenyl)cycloheptanone (6bb): Ketone **6bb** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 90% yield, 91% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 12.71 (major)/14.59 min (minor)). $[\alpha]_D^{25} = -51.4$ (c = 0.5 in $CHCl_3$) (for 91% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.47–1.51 (m, 1H), 1.67–1.76 (m, 2H), 1.98–2.09 (m, 3H), 2.33 (s, 3H), 2.57–2.65 (m, 3H), 2.87–2.98 (m, 2H), 7.06–7.14 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.9, 24.1, 29.1, 39.2, 42.2, 43.9, 51.3, 126.2, 129.2, 135.7, 143.9, 213.6 ppm.

3-(3-Methoxylphenyl)cycloheptanone (6bd): Ketone **6bd** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 25:1; 86% yield, 96% *ee*. The *ee* was determined by chiral HPLC analysis (Chiralpak AD column, hexane/*i*PrOH 50:1, detection at 210 nm, retention times: 28.67 (major)/32.28 min (minor)). $[\alpha]_D^{25} = -15.9$ (c = 0.4 in $CHCl_3$) (for 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.42–1.56 (m, 1H), 1.64–1.79 (m, 2H), 1.96–2.07 (m, 3H), 2.57–2.70 (m, 3H), 2.82–2.97 (m, 2H), 2.80 (s, 3H), 6.73–6.78 (m, 3H), 7.22 ppm (t, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 24.1, 29.2, 39.0, 42.7, 43.9, 51.1, 55.1, 111.3, 112.3, 118.7, 129.6, 148.6, 159.6, 213.5 ppm.

3-(2-Naphthyl)cycloheptanone (6bf): Ketone **6bf** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 20:1; 99% yield, 97% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak AD column, hexane/*i*PrOH 100:1, detection at 210 nm, retention times: 31.10 (major)/35.80 min (minor)). $[\alpha]_D^{25} = -35.3$ (c = 0.8 in $CHCl_3$) (for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.70–1.81 (m, 2H), 2.00–2.13 (m, 2H), 2.29 (s, 3H), 2.30–2.55 (m, 4H), 2.89–2.96 (m, 1H), 7.06–7.22 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.96, 25.6, 32.9, 41.2, 44.4, 49.1, 126.4, 129.3, 136.2, 141.4, 211.05 ppm.

4-Oxo-2-phenylpiperidine-1-carboxylic acid benzyl ester (6ca):[5a] Ketone **6ca** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 4:1; 53% yield, 81% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OD column, hexane/*i*PrOH 90:10, detection at 210 nm, retention times: 29.24 (major)/34.59 min (minor)). $[\alpha]_D^{25} = -30.5$ (c = 0.9 in $CHCl_3$) (for 81% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.37 (d, J = 15.9 Hz, 1H), 2.49–2.60 (m, 1H), 2.86 (dd, J_1 = 15.6 Hz, J_2 = 6.6 Hz, 1H), 3.00 (d, J = 15.6 Hz, 1H), 3.19 (t, J = 11.1 Hz, 1H), 4.28 (br s, 1H), 5.19 (d, J = 12.6 Hz, 1H), 5.25 (d, J = 12.6 Hz, 1H), 5.84 (br s, 1H), 7.23–7.35 ppm (m, 10H).

4-(2-Naphthyl)tetrahydropyran-2-one (6df).[16] Ketone **6df** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 4:1; 62% yield, 38% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak AS column, hexane/*i*PrOH 90:10, detection at 210 nm, retention times: 49.85 (minor)/54.42 min (major). $[\alpha]_D^{25} = +12.9$ (c = 0.4 in $CHCl_3$) (for 38% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.14–2.32 (m, 2H), 2.76 (dd, J_1 = 17.7 Hz, J_2 = 10.5 Hz, 1H), 3.03 (dd, J_1 = 11.4 Hz, J_2 = 6.3 Hz, 1H), 3.36–3.47 (m, 1H), 4.40–4.57 (m, 2H), 7.34 (d, J = 8.7 Hz, 1H), 7.47–7.53 (m, 2H), 7.64 (s, 1H), 7.80–7.87 ppm (m, 3H).

3-Phenylcyclopentanone (6ea):[3] Ketone **6ea** was obtained after purification by flash chromatography (eluent: petroleum ether/Et_2OAc 20:1; 58% yield, 32% *ee*). The *ee* was determined by chiral HPLC analysis (Chiralpak OB column, hexane/*i*PrOH 99.5:0.5, detection at 210 nm, retention times: 39.93 (major)/42.78 min (minor)). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.94–2.02 (m, 1H), 2.26–2.48 (m, 4H), 2.62–2.71 (dd, J_1 = 7.8 Hz, J_2 = 18.0 Hz, 1H), 3.38–3.44 (m, 1H), 7.22–7.37 ppm (m, 5H).

Acknowledgements

Financial support from the Shanghai Municipal Committee of Science and Technology (04JC14083 and 06XD14005) and the National Natural Science Foundation of China (20472096, 203900502, 20672127 and 20732008) are gratefully acknowledged.

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[15] Crystal data for **2**: formula = $C_{40}H_{34}N_4O_5Pd$; M_r = 757.11; colorless; prismatic; crystal dimensions = 0.503 × 0.387 × 0.050 mm; orthorhombic; primitive; a = 9.5879(12), b = 16.684(2), c = 22.540(3) Å; α = 90, β = 90, γ = 90°; V = 3605.4(8) Å^3; space group = $P2_12_12_1$; Z = 4; ρ_{calcd} = 1.395 g cm^{-3}; F_{000} = 1552; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0556, 0.1079. Crystal data for **3**: formula = $C_{40}H_{28}F_6N_4O_5Pd$; M_r: 865.06; colorless; prismatic; crystal dimensions = 0.234 × 0.168 × 0.109 mm; orthorhombic; primitive; a = 9.6346(7), b = 17.2104(13), c = 22.7713(18) Å; α = 90, β = 90, γ = 90°; V = 3775.8(5) Å^3; space group = $P2_12_12_1$; Z = 4; ρ_{calcd} = 1.522 g cm^{-3}; F_{000} = 1744; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0536, 0.1018. CCDC-605041 (**2**) and CCDC-633231 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: December 17, 2007
Published online: February 28, 2008

