Synthesis H. Li et al. Paper

Kinetic Resolution of 5-Substituted Cyclohexenols by Palladium-Catalyzed Asymmetric Redox-Relay Heck Reaction

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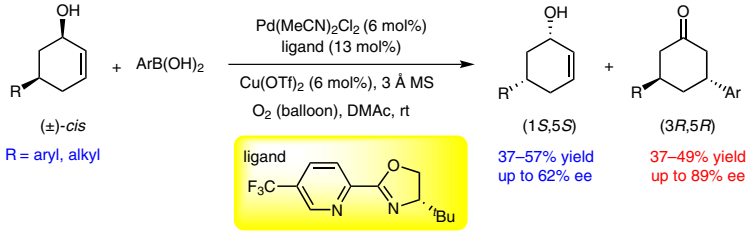
This paper is dedicated to Professor Dieter Enders



Received: 15.07.2016
Accepted: 22.07.2016
Published online: 09.09.2016
DOI: 10.1055/s-0035-1562620; Art ID: ss-2016-z0498-op

Abstract The kinetic resolution of 2-substituted-cyclohexenols via palladium-catalyzed asymmetric redox-relay Heck reaction was realized, providing optically active 2-substituted cyclohexenols and *trans*-3,5-disubstituted cyclohexan-1-ones in high yield and good enantioselectivities with an *S* factor up to 22.

Key words palladium, Heck reaction, kinetic resolution, cyclohexenol, cyclohexanone

Catalytic kinetic resolution, which provides a simple and efficient way to access both products and recovered starting materials in optical form, is one of the most useful protocols in asymmetric synthesis.[1] Classical kinetic resolution usually does not form a new chiral center in the products; however, recently, some reports have appeared that involve the creation of multiple new chiral centers in products by catalytic kinetic resolution.[2] Clearly, the development of this type of kinetic resolution is highly desirable.

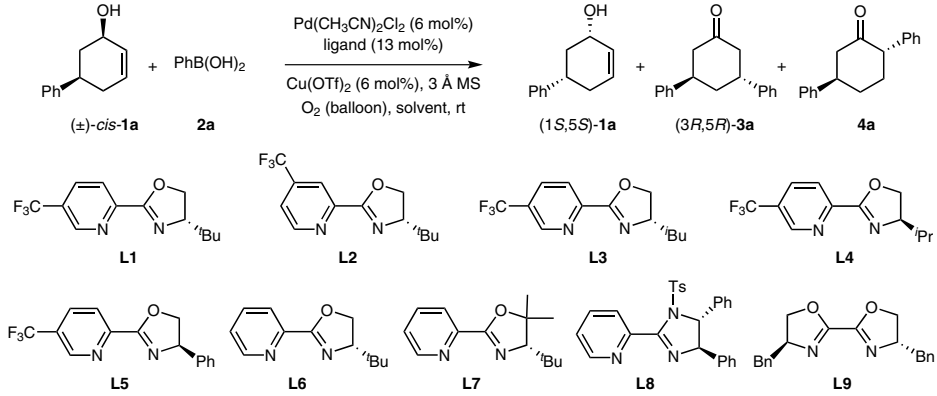
The Heck reaction is an important C–C bond-formation reaction that is widely used in the synthesis of natural products, medicines, and functional materials.[3] The Pd-catalyzed asymmetric intermolecular Heck reaction between cyclic olefins and aryl electrophiles, so called Mizoroki–Heck reaction, is well developed.[4] Recent developments have also revealed that acyclic substrates are suitable in the reaction.[5] Despite these significant developments, the substrate scope of the asymmetric intermolecular Heck reaction remains limited; furthermore, few examples for kinetic resolution via asymmetric Heck reaction have been reported.[3,4] Our group has succeeded in the application of kinetic resolution in asymmetric catalysis[6] and asymmetric Heck reaction.[7] We also realized the first example of kinetic resolution through Heck reaction, affording 2-substituted 2,3-dihydrofurans and *trans*-2,5-disubstituted dihydrofurans in high yield and with good enantioselectivities.[7f] As part of our effort to explore further applications of this protocol in organic synthesis, herein, we report the kinetic resolution of 5-substituted cyclohexenols by Pd-catalyzed enantioselective redox-relay Heck reaction. This kinetic resolution reaction delivers both optically enriched arylated products and starting materials bearing two stereocenters in high efficiency.

Initially, *cis*-5-phenyl-cyclohexenol (**1a**) was adopted as substrate in the reaction with phenylboronic acid (**2a**) using $Pd(MeCN)_2Cl_2$ and PyrOx (**L1**) as the catalyst in *N*,*N*-dimethylformamide (DMF) with $Cu(OTf)_2$ and 3 Å MS as additive at room temperature (Table 1, entry1).[5f,5j] The Heck reaction product **3a** was afforded in 43% yield with 84% ee, whereas **1a** was recovered in 57% yield with 38% ee. Byproduct **4a** was also observed, with the ratio of **3a**/**4a** being 94:6. Encouraged by these results, the impact of the reaction parameters including palladium sources, solvents, ligands, and reaction temperature on the efficiency of kinetic resolution was investigated (Table 1). The screening of solvents including DMF, DMSO, MeOH, MeCN, DCE, toluene and THF revealed that dimethylacetamide (DMAc) was the best choice (entries 2–8). When DMAc was used as solvent, **3a** was isolated in 49% yield with 82% ee and **1a** was recovered in 48% yield with 52% ee (entry 2). Different chiral *N*,*N*-

ligands were examined (entries 9–16). Among the pyridine oxazoline ligands, 4-CF_3 variant **L2** afforded similar results to those obtained using **L1** (entry 9), whereas other ligands **L3–7** gave unsatisfactory enantioselectivity (entries 10–14). Other *N*,*N*-ligands including **L8** and **L9** were also examined; however, very low ee value of recovered **1a** was acquired (entries 15 and 16). The effect of additives on the reaction was also examined. Of note, removing either oxygen or 3 Å MS had little effect on the reaction, whereas no significant reaction was observed in the absence of $Cu(OTf)_2$ (data not shown). These results indicated the critical role of $Cu(OTf)_2$ in the reaction. Surprisingly, a variety of other cupric salts, such as CuO, $CuCl_2$, $Cu(OAc)_2$, $CuBr_2$, CuF_2, $CuSO_4$, $Cu_2(OH)_2CO_3$ did not promote the reaction (data not shown). Changing the ratio of Pd to ligand from 6:13 to 6:3 had a detrimental effect on the kinetic resolution (data not shown).

On the basis of the above reaction parameters investigation, the substrate scope of the kinetic resolution of 5-substituted cyclohexenol **1** with arylboronic acid **2** was examined (Table 2). Generally, the reactions provided Heck products **3** with *trans*-stereoselectivity and recovered **1** in high yields with good enantioselectivities. The *S*-factor was up to 22. The presence of electron-donating substituents on

Table 1 Optimization of Reaction Parameters for Kinetic Resolution of *cis*-5-Phenyl-cyclohexenol[a]



Entry	Solvent	Ligand	**1a**		**3a**		**3a**/**4a**[d]	*S*[e]
			Yield (%)[b]	ee (%)[c]	Yield (%)[b]	ee (%)[c]		
1	DMF	**L1**	57	–38	43	84	94:6	17
2	DMAc	**L1**	48	–52	49	82	94:6	17
3	DMSO	**L1**	89	–8	11	70	98:2	6
4	MeOH	**L1**	55	–13	26	72	97:3	7
5	MeCN	**L1**	81	–7	18	76	96:4	8
6	DCE	**L1**	90	4	5	44	96:4	3
7	toluene	**L1**	53	9	27	26	98:2	2
8	THF	**L1**	40	–24	40	43	95:5	3
9	DMAc	**L2**	56	–49	40	85	98:2	20
10	DMAc	**L3**	49	–27	41	28	96:4	2
11	DMAc	**L4**	48	30	49	–22	97:3	2
12	DMAc	**L5**	65	12	26	–51	93:6	3
13	DMAc	**L6**	43	–57	48	68	96:4	9
14	DMAc	**L7**	47	–55	47	51	96:4	5
15	DMAc	**L8**	78	10	21	–43	98:2	3
16	DMAc	**L9**	80	–15	18	67	100:0	6

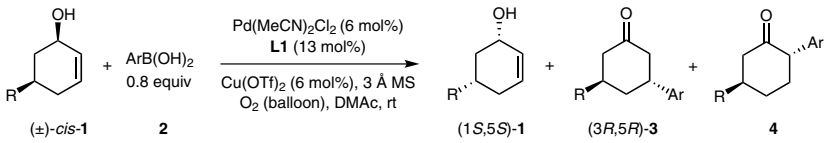
[a] Reaction conditions: molar ratio of **1a**/**2a**/Pd catalyst/ligand/$Cu(OTf)_2$ = 100:80:6:13:6.
[b] Isolated yield.
[c] Determined by chiral HPLC and GC. A minus symbol means the opposite sign of optical rotation of the product.
[d] Determined by GC analysis.
[e] Calculated by the method describe by Kagan. $S = \ln[(1-C/100)(1-ee/100)]/\ln[(1-C/100)(1+ee/100)]$ ($C = ee/ee+ee'$, *ee* = enantiomeric excess of recovered substrate, *ee'* = enantiomeric excess of product).

the aryl ring of phenylboronic acid had a detrimental effect on the enantioselectivity of Heck products **3** (entries 2–6). In addition, the enantioselectivity of the recovered cyclohexenol **1** was greatly affected by the position of the substituent on the aryl ring of phenylboronic acid (entries 2–4). The recovered **1a** was a racemate when the 2-tolylboronic acid (**2b**) was used (entry 2). When an electron-withdrawing substituent was introduced at the *para*-position of the phenyl ring of boronic acid **2**, Heck products **6** were furnished with excellent ee (entries 7 and 8).

The electron-donating and -withdrawing substituents on the aryl group of cyclohexenol **1** had a limited effect on the enantioselectivity of Heck products **3** and recovered cyclohexenol **1**, as its enantioselectivity was consistently good (Table 2, entries 10 and 11). Notably, alkyl-substituted cyclohexenols **1**, such as *cis*-5-methyl-cyclohexenol (**1d**) and *cis*-5-isopropyl-cyclohexenol (**1e**), were also suitable substrates to produce the corresponding products in high yield and with good enantioselectivity (entries 12–16). The *cis*-5-methyl-cyclohexenol (**1d**) could react with several arylboronic acid derivatives, and Heck products **3** were also obtained with over 64% enantioselectivity with 1-naphthyl boronic acid, 2-naphthyl boronic acid and 4-methoxyphenyl boronic acid. The *ee* of recovered cyclohexenol **1d** was greatly affected by the nature of the arylboronic acid (entries 13–15).

This kinetic resolution proceeded smoothly on a 1 mmol scale. Treatment of 1.0 mmol of **1a** with 0.6 mmol of **2a** under optimized conditions afforded 37% yield of **3a** with 84% ee and 45% yield of **1a** with 40% ee. Finally, a se-

Table 2 Substrate Scope for the Kinetic Resolution of *cis*-5-Substituted Cyclohexnol[a]



(±)-*cis*-**1** **2** (1*S*,5*S*)-**1** (3*R*,5*R*)-**3** **4**

1a: R = Ph
1b: R = *p*-MeOC$_6$H$_4$
1c: R = *p*-ClC$_6$H$_4$
1d: R = Me
1e: R = ^{i}Pr

2a: Ar = Ph
2b: Ar = *o*-MeC$_6$H$_4$
2c: Ar = *m*-MeC$_6$H$_4$
2d: Ar = *p*-MeC$_6$H$_4$
2e: Ar = *p*-MeOC$_6$H$_4$

2f: Ar = *p*-FC$_6$H$_4$
2g: Ar = MeO$_2$CC$_6$H$_4$
2h: Ar = *p*-CHOC$_6$H$_4$
2i: Ar = *p*-BrC$_6$H$_4$
2j: Ar = 1-naphthyl
2k: Ar = 2-naphthyl

Entry	**1**	**2**	**1**		**3**		**3**/**4**[d]	*S*[e]
			Yield (%)[b]	ee (%)[c]	Yield (%)[b]	ee (%)[c]		
1	**1a**	**2a**	**1a**, 48	52	**3a**, 49	82	94:6	17
2	**1a**	**2b**	**1a**, 50	0	**3b**, 37	50	96:4	–
3	**1a**	**2c**	**1a**, 42	59	**3c**, 40	63	98:2	8
4	**1a**	**2d**	**1a**, 45	44	**3d**, 43	62	99:1	7
5	**1a**	**2e**	**1a**, 49	38	**3e**, 44	69	92:8	8
6	**1a**	**2f**	**1a**, 45	53	**3f**, 38	57	99.5:0.5	6
7	**1a**	**2g**	**1a**, 57	11	**3g**, 37	89	99.9:0.1	19
8	**1a**	**2h**	**1a**, 47	35	**3h**, 42	88	93:7	22
9	**1a**	**2i**	**1a**, 47	49	**3i**, 42	76	99.5:0.5	12
10	**1b**	**2a**	**1b**, 41	52	**3j**, 47	81	97:3	16
11	**1c**	**2a**	**1c**, 44	50	**3k**, 43	72	99.7:0.3	10
12	**1d**	**2a**	**1d**, 39	51	**3l**, 46	81	95:5	16
13	**1d**	**2j**	**1d**, 57	18	**3m**, 43	76	100:0	9
14	**1d**	**2k**	**1d**, 38	38	**3n**, 45	74	100:0	10
15	**1d**	**2e**	**1d**, 39	21	**3o**, 43	64	90:10	6
16	**1e**	**2a**	**1e**, 47	59	**3p**, 43	85	99:1	22

[a] Molar ratio of **1**/**2**/Pd(MeCN)$_2$Cl$_2$/**L1**/Cu(OTf)$_2$ = 100:80:6:13:6.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] Determined by GC analysis
[e] Calculated by the method describe by Kagan. $S = \ln[(1-C/100)(1-ee/100)]/\ln[(1-C/100)(1+ee/100)]$ ($C = ee/ee+ee'$, *ee* = enantiomeric excess of recovered substrate **1**, *ee*′ = enantiomeric excess of product **3**).

lection of other boronic acids, for example, methylboronic acid, benzylboronic acid, styrylboronic acid, and cyclohexylboronic acid, were subjected to the kinetic resolution; unfortunately, no reaction occurred (data not shown).

The absolute configuration of Heck product **3l** was determined to be 3*R*,5*R* by comparing its sign of optical rotation with that reported previously.[8] The *trans*-stereochemistry of product **3a** was also supported by its X-ray diffraction analysis (Figure 1). Accordingly, the absolute configuration of the recovered 5-phenylcyclohexenol (**1a**) was determined to be 1*S*,5*S*.

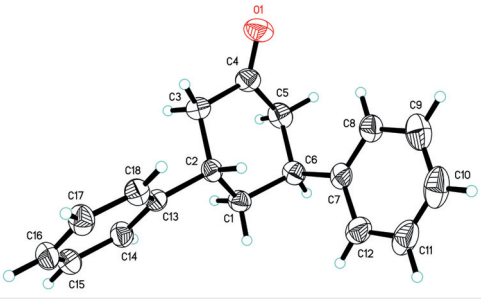


Figure 1 X-ray crystal structure of *rac*-**3a**

In conclusion, we have realized the kinetic resolution of *cis*-5-substituted cyclohexenol via palladium-catalyzed enantioselective redox relay Heck reaction, providing exclusively *trans*-3,5-disubstituted cyclohexanones in high yield and ee, and recovered *cis*-5-substituted cyclohexenol in high yields and with moderate to good enantioselectivities. The extension and application of the kinetic resolution in organic synthesis are underway in our group.

All solvents were purified and dried by using standard methods prior to use. Commercially available reagents were used without further purification. ^{1}H NMR spectra were recorded with an Agilent NMR instrument operated at 400 MHz. Chemical shifts are reported in parts per million (ppm) with the solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm). ^{13}C NMR spectra were recorded with a NMR instrument operated at 101 MHz, with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ = 77.1 ppm). Infrared spectra were recorded from thin films of pure samples. Mass and HRMS spectra were measured in EI or ESI mode and the mass analyzer of the HRMS was TOF. Thin-layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Enantiomer ratios were determined by chiral HPLC or GC analysis and compared with authentic racemic materials.

General Experimental Procedure

Under a dry argon atmosphere, to a dry, 10 mL Schlenk flask equipped with a stir bar, $Pd(MeCN)_2Cl_2$ (3.11 mg, 0.012 mmol, 6.0 mol%), $Cu(OTf)_2$ (4.34 mg, 0.012 mmol, 6.0 mol%), **L1** (7.08 mg, 0.026 mmol, 13.0 mol%), 3Å molecular sieves (30.0 mg, 150 mg/mmol) and dimethylacetamide (2 mL) were added. A three-way adaptor fitted with a balloon of O_2 was added, and the flask was evacuated by using a house vacuum and refilled with O_2 three times while stirring. The resulting mixture was stirred for 30 min, then *cis*-5-substituted cycloalcohol **1** (0.2 mmol) and corresponding boronic acid **2** (0.16 mmol, 0.8 equiv) were added by using a syringe. The resulting mixture was stirred until boronic acid **2** was fully consumed (reaction monitored by TLC) at r.t. (23–25 °C). The mixture was diluted with diethyl ether (10 mL) and water (2 mL), the aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organic layers were washed with water (3 × 2 mL) and brine (2 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was directly subjected to flash chromatography on silica gel (petroleum ether–EtOAc), to provide the recovered starting material **1** and Heck product **3**.

(1*S*,5*S*)-5-Phenyl-2-cyclohexenol (1a; Table 2, Entry 1)[9]

Yield: 16.6 mg (42%); white solid; mp 43.0–43.7 °C; 52% ee; $[\alpha]_D^{26}$ = 1.2 (*c* 0.64, $CHCl_3$); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 95:5; 0.7 mL/min; 214 nm): t_R = 14.83 (minor), 16.13 (major) min.

IR (film): 3302.00, 3080.45, 2916.93, 1450.05, 1034.25, 911.73, 760.25, 733.44, 699.90, 676.82 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 7.26–7.20 (m, 3 H), 5.87–5.83 (m, 1 H), 5.77–5.75 (m, 1 H), 4.51–4.46 (m, 1 H), 2.96–2.88 (m, 1 H), 2.32–2.25 (m, 2 H), 2.19–2.10 (m, 1 H), 1.78–1.70 (m, 1 H), 1.59 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.56, 131.06, 128.70, 126.76, 126.36, 68.52, 39.53, 39.25, 33.76.

GC-MS (EI): *m*/*z* = 174.1, 1561.1, 130.1, 151.1, 104.1, 91.1, 70.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1048.

(1*S*,5*S*)-5-(4-Methoxyphenyl)-2-cyclohexenol (1b; Table 2, Entry 10)[9]

Yield: 16.6 mg (41%); white solid; mp 76.9–78.0 °C; 52% ee; $[\alpha]_D^{26}$ = 1.3 (*c* 0.91, $CHCl_3$); HPLC (Chiralpak ID-3; 4.6 mm × 250 mm; hexane/*i*-PrOH, 92:8; 0.7 mL/min; 214 nm): t_R = 8.94 (minor), 10.36 (major) min.

IR (film): 3351.61, 3288.55, 2937.29, 2882.13, 2838.17, 1510.56, 1247.46, 1177.87, 1028.68, 908.49, 827.59, 808.81, 727.57 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.13 (m, 2 H), 6.88–6.85 (m, 2 H), 5.86–5.82 (m, 1 H), 5.77–5.73 (m, 1 H), 4.48–4.45 (m, 1 H), 3.78 (s, 3 H), 2.90–2.83 (m, 1 H), 2.30–2.22 (m, 2 H), 2.14–2.05 (m, 1 H), 2.05–1.65 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.01, 137.78, 131.01, 128.75, 127.64, 113.80, 68.54, 55.27, 39.81, 38.38, 33.94.

GC-MS (EI): *m*/*z* = 204.3, 186.2, 147.2, 134.2, 119.2, 103.1, 91.1, 77.1, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1151.

(1*S*,5*S*)-5-(4-Chlorophenyl)-2-cyclohexenol (1c;Table 2, Entry 11)[9]

Yield: 18.2 mg (44%); white solid; mp 75.7–76.3 °C; 50% ee; $[\alpha]_D^{27}$ = 6.2 (*c* 1.35, $CHCl_3$); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 95:5; 0.7 mL/min; 214 nm): t_R = 13.54 (minor), 14.61 (major) min.

IR (film): 3271.61, 3023.78, 2921.36, 1490.31, 1302.18, 1278.04, 1032.01, 912.79, 814.79, 693.55 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.14 (m, 2 H), 7.30–7.26 (m, 2 H), 5.85–5.82 (m, 1 H), 5.77–5.74 (m, 1 H), 4.50–4.44 (m, 1 H), 2.95–2.55 (m, 1 H), 2.30–2.23 (m, 2 H), 2.13–2.05 (m, 1 H), 1.74–1.65 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.99, 131.95, 131.12, 128.66, 128.54, 128.40, 128.12, 68.33, 39.38, 38.67, 33.68.

GC-MS (EI): *m*/*z* = 210.2, 208.2, 190.1, 140.1, 138.1, 125.1, 103.0, 89.1, 70.0, 51.1.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}OCl$: 208.0655; found: 208.0652.

(1*S*,5*S*)-5-Methyl-2-cyclohexenol (1d; Table 2, Entry 12)[9]

Yield: 8.8 mg (39%); colorless oil; 51% ee; $[\alpha]_D^{25}$ = –7.3 (*c* 0.59, $CHCl_3$); Chiral GC {RESTEK Rt-βDEXcst column (30 m × 0.25 mm × 0.25 μm); carrier gas: nitrogen; injector temperature: 300 °C; split ratio: 60; constant column flow: 10 psi; column temperature: 50 °C (2 min), 50–150 °C (3 °C/min, 5 min), 150–180 °C (5 °C /min); FID detector temperature: 300 °C}: t_R = 29.17 (major), 29.73 (minor) min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77–5.73 (m, 1 H), 5.67–5.65 (m, 1 H), 4.31 (s, 1 H), 2.07–2.02 (m, 2 H), 1.80–1.59 (m, 3 H), 1.18–1.10 (m, 1 H), 0.99 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 130.91, 128.84, 69.15, 41.47, 33.69, 28.10, 21.96.

IR (film): 3322.69, 2951.43, 2909.32, 2874.21, 1453.69, 1086.38, 1064.90, 1021.73, 734.23, 675.36 cm^{-1}.

GC-MS (EI): *m*/*z* = 112.1, 97.1, 70.0, 69.0, 55.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_7H_{12}O$: 112.0888; found: 112.0893.

(1*S*,5*S*)-5-Isopropyl-2-cyclohexenol (1e; Table 2, Entry 16)[9]

Yield: 13.7 mg (47%); colorless oil; 59% ee; $[\alpha]_D^{26}$ = –0.3 (*c* 0.50, $CHCl_3$); Chiral GC {RESTEK Rt-βDEXcst column (30 m × 0.25 mm × 0.25 μm); carrier gas: nitrogen; injector temperature: 300 °C; split ratio: 60; constant column flow: 10 psi; column temperature: 50 °C (2 min), 50–150 °C (3 °C/min, 5 min), 150–180 °C (5 °C/min); FID detector temperature: 300 °C}: t_R = 37.67 (major), 38.22 (minor) min.

IR (film): 3321.43, 3025.63, 2956.68, 2924.49, 2871.45, 1464.98, 1385.87, 1023.94, 905.61, 729.58, 671.28 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80–5.75 (m, 1 H), 5.67–5.64 (m, 1 H), 4.33–4.27 (m, 1 H), 2.12–2.07 (m, 1 H), 2.04–1.97 (m, 1 H), 1.80–1.72 (m, 1 H), 1.60 (s, 1 H), 1.56–1.43 (m, 2 H), 1.16–1.08 (m, 1 H), 0.89 (dd, *J* = 4.4, 6.4 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.10, 129.04, 68.82, 39.17, 36.56, 32.22, 28.63, 19.60, 19.31.

GC-MS (EI): *m*/*z* = 139.1, 122.1, 97.0, 82.1, 69.0, 55.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{16}O$: 140.1201; found: 140.1199.

(3*R*,5*R*)-3,5-Diphenylcyclohexan-1-one (3a; Table 2, Entry 1)

Yield: 24.3 mg (49%); white solid; mp 64.2–65.1 °C; 82% ee; $[\alpha]_D^{28}$ = 11.7 (*c* 0.92, CH_2Cl_2).

HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 8.87 (major), 10.36 (minor) min.

IR (film): 3028.19, 2945.45, 1692.45, 1494.74, 1233.08, 1030.01, 756.00, 696.32 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 4 H), 7.24–7.17 (m, 6 H), 3.36–3.30 (m, 2 H), 2.79–2.69 (m, 4 H), 2.34 (t, *J* = 6.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.34, 143.81, 128.61, 127.01, 126.56, 46.58, 39.40, 38.82.

GC-MS (EI): *m*/*z* = 250.1, 232.1, 207.1, 193.1, 172.1, 146.1, 133.1, 118.1, 104.1, 91.1, 78.1, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}O$: 250.1358; found: 250.1361.

(3*R*,5*R*)-3-Phenyl-5-(*o*-tolyl)cyclohexan-1-one (3b; Table 2, Entry 2)

Yield: 19.5 mg (37%); 50% ee; colorless oil; $[\alpha]_D^{28}$ = –10.5 (*c* 0.55, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 8.65 (major), 9.65 (minor) min.

IR (film): 3061.08, 2950.19, 1707.26, 1491.73, 1451.58, 1231.61, 1029.35, 753.41, 699.44 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.29 (m, 2 H), 7.24–7.17 (m, 5 H), 7.14–7.11 (m, 2 H), 3.47–3.39 (m, 2 H), 2.81–2.66 (m, 4 H), 2.26–2.22 (m, 2 H), 2.04 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.85, 143.85, 135.33, 130.70, 128.76, 128.55, 127.13, 126.53, 126.44, 126.26, 125.72, 46.74, 46.02, 39.00, 28.42, 34.48, 18.92.

GC-MS (EI): *m*/*z* = 264.1, 246.1, 207.1, 186.1, 160.1, 145.1, 118.1, 104.1, 91.0, 78.0, 65.0, 51.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{19}H_{24}NO$: 282.1852; found: 282.1855.

(3*R*,5*R*)-3-Phenyl-5-(*m*-tolyl)cyclohexan-1-one (3c; Table 2, Entry 3)

Yield: 21.2 mg (40%); 63% ee; colorless oil; $[\alpha]_D^{24}$ = 12.3 (*c* 0.73, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 8.26 (major), 9.26 (minor) min.

IR (film): 3057.63, 2952.37, 2915.61, 1708.26, 1603.49, 1491.60, 1449.49, 1157.24, 783.63, 733.03, 698.27 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.28 (m, 2 H), 7.24–7.17 (m, 4 H), 7.03–6.96 (m, 2 H), 3.36–3.25 (m, 2 H), 2.78–2.68 (m, 4 H), 2.36–2.29 (m, 5 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.65, 143.87, 143.82, 138.23, 128.62, 128.51, 127.84, 127.33, 127.06, 126.55, 123.99, 46.71, 46.52, 39.35, 38.86, 38.73, 21.51.

GC-MS (EI): *m*/*z* = 264.1, 246.1, 172.1, 147.1, 132.2, 118.1, 105.1, 91.1, 77.0, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}O$: 264.1514; found: 264.1515.

(3*R*,5*R*)-3-Phenyl-5-(*p*-tolyl)cyclohexan-1-one (3d; Table 2, Entry 4)

Yield: 22.6 mg (43%); white solid; mp 59.0–59.8 °C; 62% ee; $[\alpha]_D^{24}$ = 23.8 (*c* 0.70, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 8.53 (major), 9.85 (minor) min.

IR (film): 3027.40, 2924.64, 1702.82, 1514.28, 1450.03, 1234.01, 808.51, 754.10, 696.43 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 2 H), 7.24–7.17 (m, 3 H), 7.13–7.06 (m, 4 H), 3.35–3.27 (m, 2 H), 2.77–2.67 (m, 4 H), 2.35–2.30 (m, 5 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.51, 143.89, 140.79, 136.11, 129.26, 128.59, 127.01, 126.88, 126.52, 46.66, 46.61, 39.47, 38.81, 38.45, 20.96.

GC-MS (EI): *m*/*z* = 264.1, 246.1, 207.1, 172.0, 132.1, 118.1, 105.1, 91.0, 78.0, 65.0, 51.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{19}H_{24}NO$: 282.1852; found: 282.1854.

(3*R*,5*R*)-3-(4-Methoxyphenyl)-5-phenylcyclohexan-1-one (3e; Table 2, Entry 5)

Yield: 24.8 mg (44%); white solid; mp 84.0–85.0 °C; 69% ee; $[\alpha]_D^{27}$ = 21.6 (*c* 1.09, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 11.31 (major), 13.06 (minor) min.

IR (film): 2950.34, 2913.44, 2886.69, 1698.14, 1510.29, 1236.67, 1178.53, 1030.52, 815.26, 758.27, 700.29 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 2 H), 7.23–7.17 (m, 3 H), 7.11–7.09 (m, 2 H), 6.85–6.83 (m, 2 H), 3.79 (s, 3 H), 3.34–3.27 (m, 2 H), 2.77–2.65 (m, 4 H), 2.30 (t, *J* = 5.6 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.48, 135.86, 128.59, 127.97, 127.73, 127.00, 126.53, 114.14, 113.92, 55.27, 46.76, 46.69, 39.60, 38.79, 38.10.

GC-MS (EI): *m*/*z* = 282.0, 250.1, 232.1, 172.0, 118.1, 104.1, 91.1, 78.1, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}O_2$: 280.1463; found: 280.1461.

(3*R*,5*R*)-3-(4-Fluorophenyl)-5-phenylcyclohexan-1-one (3f; Table 2, Entry 6)

Yield: 20.3 mg (38%); white solid; mp 75.0–76.2 °C; 57% ee; $[\alpha]_D^{26}$ = 8.0 (*c* 0.71, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 8.58 (minor), 7.79 (major) min.

IR (film): 3022.15, 2914.81, 2892.48, 2850.81, 1704.21, 1507.90, 1229.97, 1160.46, 816.87, 761.19, 701.93 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.29 (m, 2 H), 7.25–7.12 (m, 4 H), 7.01–6.90 (m, 2 H), 3.33–3.29 (m, 2 H), 2.96–2.70 (m, 4 H), 2.33–2.29 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.13, 143.64, 128.65, 128.50, 128.43, 126.97, 126.63, 115.49, 115.28, 46.69, 46.56, 39.54, 38.79, 38.19.

^{19}F NMR (400 MHz, $CDCl_3$): δ = –116.42.

GC-MS (EI): *m*/*z* = 268.1, 250.1, 211.1, 190.1, 164.0, 136.1, 122.1, 104.1, 91.0, 78.0, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}OF$: 268.1263; found: 268.1267.

Methyl 4-[(1*R*,5*R*)-3-Oxo-5-phenylcyclohexyl]benzoate (3g; Table 2, Entry 7)

Yield: 22.8 mg (37%); white solid; mp 79.1–80.3 °C; 89% ee; $[\alpha]_D^{25}$ = 39.7 (*c* 0.59, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 1.0 mL/min; 214 nm): t_R = 19.04 (minor), 22.93 (major) min.

IR (film): 2948.00, 2903.72, 1703.84, 1280.02, 1110.30, 758.99, 697.17 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.96 (m, 2 H), 7.33–7.29 (m, 2 H), 7.27–7.20 (m, 3 H), 7.18–7.16 (m, 2 H), 3.90 (s, 3 H), 3.41–3.28 (m, 2 H), 2.81–2.69 (m, 4 H), 2.35 (t, *J* = 6.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.72, 166.65, 143.50, 129.94, 128.68, 128.55, 127.09, 126.96, 126.69, 52.11, 46.47, 46.22, 39.21, 38.90, 36.71.

GC-MS (EI): *m*/*z* = 308.3, 230.2, 176.2, 145.2, 131.2, 118.2, 104.2, 91.1, 77.1, 59.0, 51.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{20}H_{24}NO_3$: 326.1751; found: 326.1751.

4-[(1*R*,5*R*)-3-Oxo-5-phenylcyclohexyl]benzaldehyde (3h; Table 2, Entry 8)

Yield: 23.1 mg (42%); colorless oil; 88% ee; $[\alpha]_D^{25}$ = 23.8 (*c* 0.71, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 34.89 (minor), 43.55 (major) min.

IR (film): 3028.04, 2949.14, 2738.53, 1695.76, 1604.40, 1210.13, 1168.32, 838.06, 757.28, 699.46 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1 H), 7.84–7.80 (m, 2 H), 7.36–7.29 (m, 4 H), 7.25–7.16 (m, 3 H), 3.44–3.29 (m, 2 H), 2.82–2.71 (m, 4 H), 2.37 (t, *J* = 6.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.55, 191.82, 150.88, 143.38, 134.98, 130.14, 128.72, 128.64, 127.76, 126.96, 126.76, 46.46, 46.13, 39.16, 39.11, 38.91.

GC-MS (EI): *m*/*z* = 278.1, 260.0, 249.0, 200.0, 146.1, 131.0, 115.1, 104.1, 91.0, 77.0, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1312.

(3*R*,5*R*)-3-(4-Bromophenyl)-5-phenylcyclohexan-1-one (3i; Table 2, Entry 9)

Yield: 27.5 mg (42%); white solid; mp 84.7–85.6 °C; 76% ee; $[\alpha]_D^{25}$ = 38.1 (*c* 0.55, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 9.10 (minor), 10.52 (major) min.

IR (film): 2942.54, 2917.76, 1699.47, 1486.22, 1260.97, 1097.29, 1007.08, 818.01, 796.62, 764.93, 701.31 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 2 H), 7.33–7.28 (m, 2 H), 7.24–7.20 (m, 1 H), 7.18–7.15 (m, 2 H), 7.06–7.03 (m, 2 H), 3.31–3.27 (m, 2 H), 2.78–2.36 (m, 4 H), 2.36–2.25 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.07, 143.55, 142.77, 132.40, 131.89, 128.80, 128.70, 126.97, 126.69, 120.40, 117.27, 46.55, 46.36, 39.32, 38.83, 38.42.

GC-MS (EI): *m*/*z* = 329.9, 311.9, 270.9, 249.0, 224.0, 197.9, 181.9, 133.1, 117.1, 104.0, 91.1, 77.1, 65.0, 50.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}OBr$: 328.0463; found: 328.0470.

(3*R*,5*R*)-3-(4-Methoxyphenyl)-5-phenylcyclohexan-1-one (3j; Table 2, Entry 10)

Yield: 26.6 mg (47%); white solid; mp 84.0–85.0 °C; 81% ee; $[\alpha]_D^{28}$ = 24.9 (*c* 1.11, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 11.87 (minor), 13.90 (major) min.

IR (film): 2950.34, 2913.44, 2886.69, 1698.14, 1510.29, 1236.67, 1178.53, 1030.52, 815.26, 758.27, 700.29 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.29 (m, 2 H), 7.24–7.17 (m, 3 H), 7.11–7.08 (m, 2 H), 6.86–6.83 (m, 2 H), 3.79 (s, 3 H), 3.34–3.27 (m, 2 H), 2.77–2.67 (m, 4 H), 2.30 (t, *J* = 6.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.57, 143.88, 135.63, 129.74, 128.59, 127.97, 127.00, 126.53, 113.92, 55.26, 46.76, 46.68, 39.59, 38.78, 36.10.

GC-MS (EI): *m*/*z* = 280.2, 223.2, 144.2, 134.2, 121.1, 104.1, 91.1, 78.0, 65.0, 51.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}O_2$: 280.1463; found: 280.1458.

(3*R*,5*R*)-3-(4-Chlorophenyl)-5-phenylcyclohexan-1-one (3k; Table 2, Entry 11)

Yield: 24.3 mg (43%); yellow solid; mp 59.0–59.8 °C; 72% ee; $[\alpha]_D^{28}$ = 21.2 (*c* 0.75, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 80:20; 0.7 mL/min; 214 nm): t_R = 9.11 (major), 10.65 (minor) min.

IR (film): 2896.67, 2871.23, 1704.32, 1491.41, 1242.67, 1090.26, 838.55, 818.52, 698.92 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–6.83 (m, 9 H), 3.33–3.28 (m, 2 H), 2.79–2.70 (m, 4 H), 2.33–2.29 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.94, 143.57, 142.24, 132.32, 128.72, 128.67, 128.39, 126.96, 126.66, 46.54, 46.39, 39.36, 38.80, 38.83.

MS (EI): *m*/*z* = 284, 266, 249, 227, 206, 152, 138, 133, 118, 104, 91, 77.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}OCl$: 284.0968; found: 284.0962.

(3*R*,5*R*)-3-Methyl-5-phenylcyclohexan-1-one (3l; Table 2, Entry 12)[8]

Yield: 17.1 mg (46%); colorless oil; 81% ee; $[\alpha]_D^{27}$ = –20.4 (*c* 0.50,CH_2Cl_2) {reported value of (3*R*,5*R*)-**3l**:[8] 81% ee; $[\alpha]_D$ = –22.3 (*c* 0.50, CH_2Cl_2)}; HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 98:2; 0.5 mL/min; 210 nm): t_R = 28.25 (major), 32.17 (minor) min.

IR (film): 2957.51, 2923.94, 1710.74, 1453.22, 1261.27, 1239.42, 1074.89, 1026.17, 799.82, 757.21, 701.24 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 6.8 Hz, 2 H), 7.24–7.20 (m, 3 H), 3.42–3.35 (m, 1 H), 2.65–2.53 (m, 3 H), 2.31–2.24 (m, 1 H), 2.18 (dd, *J* = 14.0, 6.4 Hz, 1 H), 2.11–2.04 (m, 1 H), 1.90–1.84 (m, 1 H), 1.04 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.60, 144.30, 128.56, 126.91, 126.47, 48.42, 47.16, 39.51, 39.30, 29.24, 20.26.

GC-MS (EI): *m*/*z* = 188.1, 173.1, 131.1, 118.1, 104.1, 91.1, 78.1, 56.1, 51.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}O$: 189.1274; found: 189.1274.

(3*R*,5*R*)-3-Methyl-5-(naphthalen-1-yl)cyclohexan-1-one (3m; Table 2, Entry 13)[8]

Yield: 20.4 mg (43%); colorless oil; 76% ee; $[\alpha]_D^{28}$ = –78.1 (*c* 0.44, CH_2Cl_2) {reported value of (3*R*,5*R*)-**3m**:[8] 87% ee; $[\alpha]_D$ = –19.7 (*c* 1.00, CH_2Cl_2)}; HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 95:5; 0.7 mL/min; 214 nm): t_R = 16.91 (major), 18.28 (minor) min.

IR (film): 3048.84, 2953.19, 2924.78, 1704.80, 1273.75, 1237.58, 774.16, 733.22 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 1 H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.57–7.41 (m, 3 H), 7.35–7.29 (m, 1 H), 4.33–4.22 (m, 1 H), 2.77 (d, *J* = 6.8 Hz, 1 H), 2.65–2.59 (m, 1 H), 2.25–2.16 (m, 3 H), 2.05–1.97 (m, 1 H), 1.07 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.22, 129.12, 127.63, 127.24, 126.14, 125.58, 125.39, 125.34, 1123.48, 122.89, 48.85, 46.71, 38.50, 34.89, 29.21, 20.56.

GC-MS (EI): *m*/*z* = 238.1, 181.1, 153.1, 128.1, 115.1, 76.0, 56.1.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1352.

(3*R*,5*R*)-3-Methyl-5-(naphthalen-2-yl)cyclohexan-1-one (3n; Table 2, Entry 14)[8]

Yield: 21.6 mg (45%); white solid; mp 82.4–84.7 °C; 74% ee; $[\alpha]_D^{28}$ = –9.4 (*c* 0.70, CH_2Cl_2) {reported value of (3R,5R)-3n:[8] 80% ee; $[\alpha]_D$ = –5.4 (*c* 0.70, CH_2Cl_2)}; HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 95:5; 0.7 mL/min; 214 nm): t_R = 18.73 (major), 19.61 (minor) min.

IR (film): 3054.59, 2953.79, 2923.90, 1703.92, 1204.92, 1217.52, 950.28, 900.69, 859.73, 814.31, 741.23 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.88 (m, 1 H), 7.81–7.79 (m, 3 H), 7.62 (s, 1 H), 7.54–7.43 (m, 1 H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 1 H), 3.59–3.52 (m, 1 H), 2.78–2.56 (m, 3 H), 2.31–2.24 (m, 1 H), 2.22–2.15 (m, 2 H), 1.97–1.91 (m,1 H), 1.05 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.59, 141.72, 128.51, 128.25, 127.73, 127.67, 127.52, 126.17, 125.71, 125.63, 125.13, 48.58, 46.98, 39.65, 39.23, 29.21, 20.38.

GC-MS (EI): *m*/*z* = 238.1, 181.1, 154.1, 141.1, 128.1, 115.1, 83.0, 56.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{22}NO$: 256.1696; found: 256.1698.

(3*R*,5*R*)-3-(4-Methoxyphenyl)-5-methylcyclohexan-1-one (3o; Table 2, Entry 15)[8]

Yield: 18.6 mg (43%); colorless oil; 64% ee; $[\alpha]_D^{28}$ = –8.7 (*c* 0.69, CH_2Cl_2) {reported value of (3*R*,5*R*)-**3o**:[8] 86% ee; $[\alpha]_D$ = –20.0 (*c* 0.30, CH_2Cl_2)}; HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 90:10; 0.5 mL/min; 280 nm): t_R = 23.68 (major), 26.03 (minor) min.

IR (film): 2954.81, 2922.48, 1707.25, 1611.17, 1511.89, 1458.52, 1246.93, 1179.68, 1033.26, 872.84, 830.64 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.11 (m, 2 H), 6.89–6.84 (m, 2 H), 3.79 (s, 3 H), 3.36–3.31 (m, 1 H), 2.58–2.52 (m, 3 H), 2.28–2.22 (m, 1 H), 2.18–2.13 (m, 1 H), 2.07–2.00 (m, 1 H), 1.87–1.81 (m, 1 H), 1.03 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.84, 158.09, 136.45, 127.88, 113.89, 55.26, 48.48, 47.45, 39.50, 38.77, 29.22, 20.31.

GC-MS (EI): *m*/*z* = 218.1, 161.1, 146.1, 134.2, 119.1, 103.1, 91.1, 77.0, 56.1.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{18}O_2$: 218.1307; found: 218.1302.

(3*R*,5*R*)-3-Isopropyl-5-phenylcyclohexan-1-one (3p; Table 2, Entry 16)

Yield: 18.4 mg (43%); colorless oil; 85% ee; $[\alpha]_D^{28}$ = –27.7 (*c* 0.80, CH_2Cl_2); HPLC (Chiralpak IC; 4.6 mm × 250 mm; hexane/*i*-PrOH, 98:2; 0.5 mL/min; 210 nm): t_R = 24.48 (major), 29.09 (minor) min.

IR (film): 2958.41, 2874.54, 1707.71, 1451.30, 1231.21, 759.13, 699.24 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 7.24–7.20 (m, 3 H), 3.43–3.37 (m, 1 H), 2.71–2.58 (m, 2 H), 2.48 (dd, *J* = 14.8, 4.8 Hz, 1 H), 2.36–2.30 (m, 1 H), 2.06–1.98 (m, 2 H), 1.73–1.64 (m, 1 H), 1.58–1.50 (m, 1 H), 0.89 (t, *J* = 6.0 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.28, 144.34, 128.55, 126.98, 126.41, 46.51, 44.63, 40.11, 39.38, 35.28, 30.49, 19.96, 19.92.

GC-MS (EI): *m*/*z* = 216.0, 201.1, 173.2, 159.2, 146.1, 131.1, 117.2, 104.1, 91.1, 69.1, 55.0.

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{20}O$: 216.1514; found: 216.1518.

Acknowledgment

We acknowledge financial support by National Natural Science Foundation of China (NSFC) (21532010, 21372242, 21472214, 21421091), the NSFC and the Research Grants Council of Hong Kong Joint Research Scheme (21361162001), the Chinese Academy of Sciences, the Technology Commission of Shanghai Municipality, and the Croucher Foundation of Hong Kong.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562620.

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