Highly Regioselective Allylic Substitution Reactions Catalyzed by an Air-Stable (π-Allyl)iridium Complex Derived from Dinaphthocyclooctatetraene and a Phosphoramidite Ligand

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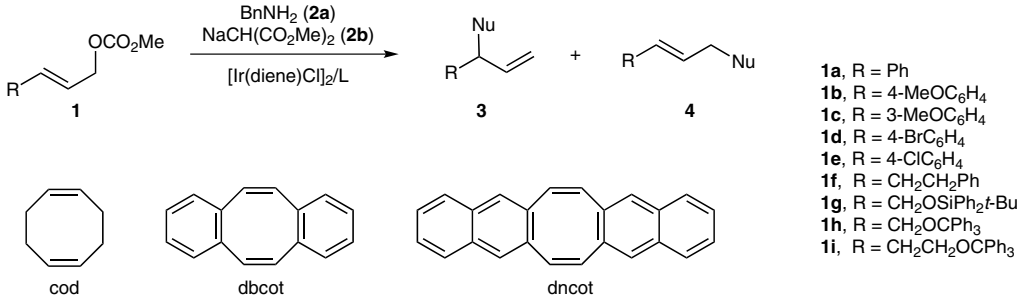
Abstract: An air-stable (π-allyl)iridium complex derived from dinaphthocyclooctatetraene and a phosphoramidite ligand has been synthesized and found to be highly efficient in iridium-catalyzed allylic substitution reactions. This catalyst features excellent regioselectivity and high stability. When $NaCH(CO_2Me)_2$ was used as the nucleophile, the catalyst loading in allylic alkylation reactions can be as low as 0.01 mol%.

Key words: (π-allyl)iridium complex, allylic substitution, enantioselectivity, regioselectivity, dinaphthocyclooctatetraene

Transition metal-catalyzed allylic substitution reactions represent one of the most powerful methods to construct C–C and C–X (X = N, O, S, etc.) bonds.[1] Among the various metals used, iridium catalyst features invariably high regio- and enantioselectivity control with a broad scope of monosubstituted substrates.[2,3] The bulk of the work on Ir-catalyzed allylic substitution reactions focused on catalysts derived from $[Ir(cod)Cl]_2$ and a phosphoramidite ligand, which consists of a cyclometalated iridium-phosphoramidite core chelated by cycloocta-1,5-diene (cod). In general, the reaction catalyzed by these air-sensitive iridium intermediates should be performed under an inert atmosphere in anhydrous solvents. In addition, the catalyst loading of the known Ir-catalytic system is far from satisfactory in the industrial viewpoint as generally more than 4 mol% Ir precatalyst was employed. This catalyst system also suffers from low regioselectivity with certain allylic substrates such as **1f–i** (Scheme 1).[4]

By taking the advantage of strong binding affinity to iridium of dibenzo[*a*,*e*]cyclooctatetraene (dbcot),[5] Helmchen and co-workers developed a modified catalyst derived from $[Ir(dbcot)Cl]_2$ and a phosphoramidite ligand and found the resulting catalyst could enable the reaction being run under air or in the presence of water.[6,7] As part of our ongoing research interest on Ir-catalyzed allylic substitution reactions,[8] we envisaged that $[Ir(dncot)Cl]_2$, prepared from dinaphthocyclooctatetraene (dncot), might be a good precursor given the strong binding of dncot with iridium. Herein, we report our results on allylic substitution reactions using a well-defined (π-allyl)Ir complex derived from $[Ir(dncot)Cl]_2$ and a phosphoramidite ligand.

Catalyst preparation is of crucial importance for Ir-catalyzed allylic substitution reaction for ligands that undergo C–H activation at the Me or aryl group generating the cyclometalated iridium intermediate. Certain additives (such as TBD,[9] *n*-propylamine,[10] DABCO,[10] DBU,[11] etc.) have been used to induce the formation of the active catalyst by C–H activation. The air-sensitive character of this intermediate makes the preactivation process inconvenient. The mechanistic studies revealed that the cyclometalated iridium-phosphoramidite complex is the active catalytic species in Ir-catalyzed allylic substitution reactions.[12] Helmchen and co-workers have demonstrated that the corresponding isolated (π-allyl)Ir complex exhibited much higher catalytic activity than the catalyst prepared in situ in Ir-catalyzed allylic hydroxylation reaction.[7d] The direct use of (π-allyl)Ir complex as catalyst precursor would greatly simplify the operation procedure.



Scheme 1 Ir-catalyzed allylic substitutions

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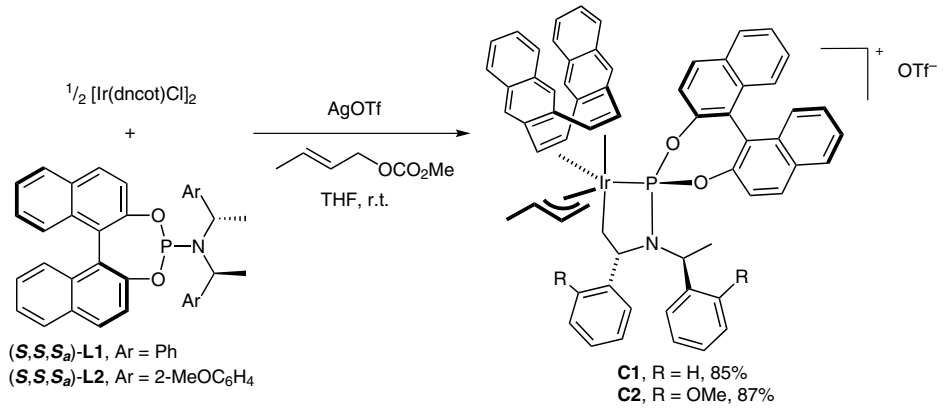


Scheme 2 Preparation of (π-allyl)Ir complexes

The dncot ligand can be conveniently synthesized in gram-scale via a [2+2+2+2] cycloaddition of diynes developed by Wender and co-workers.[13] The preparation of $[Ir(dncot)Cl]_2$ is also straightforward following the known procedure.[13c] The (π-allyl)Ir complexes **C1** and **C2** can be directly synthesized using a one-pot procedure developed by Helmchen and co-workers,[12b] as depicted in Scheme 2. Similar to $[Ir(dbcot)Cl]_2$, the (π-allyl)Ir complexes derived from $[Ir(dncot)Cl]_2$ could be subjected to silica gel column chromatography for purification. These complexes are not sensitive to oxygen and moisture. They could be stored under ambient atmosphere for more than six months without detectable loss of catalytic activity.

With these (π-allyl)Ir complexes in hand, their catalytic performance in allylic substitution reactions was examined next. With 2 mol% catalyst loading, the reaction of $BnNH_2$ with cinnamyl methyl carbonate occurred smoothly at room temperature furnishing the allylic amination products with excellent regio- and enantioselectivities (Table 1, entries 1, 2). The reaction with (π-allyl)Ir complex **C2** provided higher yield and ee (90% yield, **3aa**/**4aa** >97:3, 98% ee for **3aa**). Prolonged reaction time was needed in the presence of 1 mol% catalyst and the reaction time could be shortened by running the reaction at 50 °C without decrease of enantioselectivity (entries 3, 4). The reaction with the new catalyst was generally slower than those with $[Ir(cod)Cl]_2$ and $[Ir(dbcot)Cl]_2$ probably due to the steric hindrance and strong binding affinity to iridium of dncot. Allylic substitution reactions with the new catalyst proceeded smoothly under aerobic conditions as a proof of its air-insensitive character (entry 5). The allylic amination reactions catalyzed by (π-allyl)Ir complex **C2** are general for substituted cinnamyl methyl carbonates bearing either an electron-donating (**1b**, **1c**) or an electron-withdrawing group (**1d**, **1e**). In all cases, excellent regio- and enantioselectivities were obtained (entries 6–9). When $NaCH(CO_2Me)_2$ was used as a nucleophile, the allylic alkylation reaction proceeded much faster than the allylic amination reaction and the desired alkylation product was obtained with excellent results (91% yield, **3ba**/**4ba** >97:3, 98% ee for **3ba**, entry 10). The high catalytic activity of (π-allyl)Ir complex **C2** with $NaCH(CO_2Me)_2$ prompted us to further explore the lower catalyst loading. It was found that good results could also be obtained with 0.1 mol% catalyst in four hours (Table 1, entry 11). No deleterious effect of regio- and enantioselectivities was observed even with 0.01 mol% catalyst although a longer reaction time was needed and a lower yield resulted (entry 12).

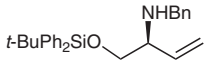
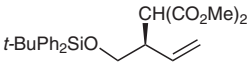
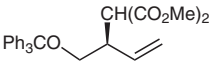
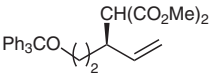
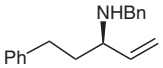
Table 1 Ir-Catalyzed Allylic Substitution Reactions[a]

Entry	Cat.	1	2	Temp (°C)	Time (h)	Product Yield (%)[b]	Ratio of 3/4[c]	ee (%)[d]
1[e]	**C1**	**1a**	**2a**	r.t.	24	**3aa** 82	>97:3	94
1[e]	**C2**	**1a**	**2a**	r.t.	24	**3aa** 90	>97:3	98
3	**C2**	**1a**	**2a**	r.t.	48	**3aa** 86	>97:3	98
4	**C2**	**1a**	**2a**	50	24	**3aa** 90	>97:3	98
5[f]	**C2**	**1a**	**2a**	50	24	**3aa** 89	>97:3	98
6	**C2**	**1b**	**2a**	50	24	**3ab** 88	>97:3	96
7	**C2**	**1c**	**2a**	50	24	**3ac** 93	>97:3	96
8	**C2**	**1d**	**2a**	50	24	**3ad** 95	>97:3	97
9	**C2**	**1e**	**2a**	50	24	**3ae** 81	>97:3	95
10	**C2**	**1a**	**2b**	50	1	**3ba** 91	>97:3	98
11[g]	**C2**	**1a**	**2b**	50	4	**3ba** 86	>97:3	98
12[h]	**C2**	**1a**	**2b**	50	48	**3ba** 52	>97:3	97

[a] Reaction conditions: **1**/**2**/cat. = 1:2:0.01, 0.4 mmol of **1** in 1.0 mL THF.
[b] Isolated yield.
[c] Determined by ^1H NMR analysis of the crude reaction mixture.
[d] Determined by HPLC analysis.
[e] Catalyst used: 2 mol%.
[f] Under air.
[g] Conditions: 0.8 mmol of **1a**, 0.1 mol% of **C2** in 2 mL THF.
[h] Conditions: 8 mmol of **1a**, 0.01 mol% of **C2** in 20 mL THF.

Despite the generally high regioselectivity control in Ir-catalyzed allylic substitution reactions, low regioselectivity was observed with certain allylic substrates. The re-

Table 2 Allylic Substitution Reactions of Challenging Substrates with Catalyst Derived from **L2**[a]

Entry	Product **3**	Diene	Temp (°C)	Time (h)	Yield (%)[b]	**3**/**4**[c]	ee (%)[d]
1	 **3ag**	cod	r.t.	2	68	73:27	97
		dbcot	50	2	87	>95:5	90
		dncot	50	24	89	>97:3	82
2	 **3bg**	cod	r.t.	8	85	76:24	98.5
		dbcot	50	4	91	94:6	92
		dncot	50	4	79	93:7	84
3	 **3bh**	cod	r.t.	18	90	82:18	99
		dbcot	50	2	88	94:6	94
		dncot	50	4	89	94:6	84
4	 **3bi**	cod	r.t.	18	90	74:26	92
		dbcot	50	1	93	93:7	96
		dncot	50	2	82	>97:3	95
5	 **3af**	cod	r.t.	2	65	85:15	95
		dbcot	r.t.	3.5	79	96:4	94
		dncot	50	24	68	>97:3	96

[a] Reaction conditions: **1**/**2**/**C2** = 1:2:0.01, 0.4 mmol of **1** in 1.0 mL THF. The data for $[Ir(cod)Cl]_2$ and $[Ir(dbcot)Cl]_2$ are taken from the literature.[6]
[b] Isolated yield.
[c] Determined by ^1H NMR analysis of the crude reaction mixture.
[d] Determined by HPLC analysis.

gioselectivity could be improved by utilizing $[Ir(dbcot)Cl]_2$ as shown previously by Helmchen et al.[6] When the new catalyst **C2** was used, regioselectivity of all reactions with those challenging substrates was considerably improved compared with that of the cod complex and slightly improved even when compared with that of the dbcot complex (Table 2). There is a general trend that the enantioselectivity was decreased while the regioselectivity was improved (**3ag**, **3bg**, **3bh**). We reasoned that the bulky substrates might retard the rate of nucleophilic attack at the (π-allyl)Ir center, which provided longer time for epimerization of the diastereomeric (π-allyl)Ir complexes leading to decreased enantioselectivity.[12d] It is worth noting that in the allylic alkylation of **1i** and allylic amination of **1f**, excellent regioselectivity and enantioselectivity could be obtained in both cases (Table 2, entries 4, 5).

In summary, well-defined catalysts derived from $[Ir(dncot)Cl]_2$ and phosphoramidite ligands have been synthesized and applied in allylic substitution reactions. These (π-allyl)Ir complexes have the following features: 1) They are air-stable and can be stored under ambient atmosphere over six months without loss of catalytic activity; 2) Very high regioselectivity was obtained even with some challenging substrates, and 3) The catalytic loading can be as low as 0.01 mol%. Further studies on extending the substrate scope are currently under way in our laboratory.

Unless stated otherwise, all reactions were carried out in flame-dried glassware under argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^1H NMR spectra were obtained at 300 MHz or 400 MHz and recorded relative to TMS signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 75 MHz or 100 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.0 ppm). Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (standard abbreviations were used to denote the signal multiplicities), coupling constant(s) in Hz, integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The phosphoramidite ligands[14] and the substituted allylic carbonates[4c,d,15] were prepared according to the known procedures.

Catalyst C1

In a flame-dried Schlenk tube under an argon atmosphere, a solution of $[Ir(dncot)Cl]_2$ (211.2 mg, 191 μmol) and (*S*,*S*,*S*$_a$)-L1 (215.7 mg, 400 μmol) in anhyd THF (10 mL) was stirred at r.t. for 1 h. (*E*)-But-2-en-1-yl methyl carbonate (104.0 mg, 800 μmol) and AgOTf (102.4 mg, 400 μmol) were added and the resulting suspension was stirred for 24 h at r.t. The resultant white precipitate was removed by filtration, and the solution was concentrated in vacuo. The residue was subjected to silica gel column chromatography (CH_2Cl_2–*i*-PrOH, 100:0 → 97:3) to yield **C1** (400.6 mg, 85%) as a light yellow powder; mp 195 °C (dec.).

^1H NMR (400 MHz, THF-d_8): δ = 0.59 (d, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 12.0 Hz, 1 H), 1.60 (dd, *J* = 8.4, 6.4 Hz, 3 H), 2.24 (dd, *J* = 11.0, 5.6 Hz, 1 H), 2.98 (d, *J* = 11.2 Hz, 2 H), 3.31 (t, *J* = 7.6 Hz, 1 H), 3.94 (dd, *J* = 16.4, 7.2 Hz, 1 H), 4.02 (dd, *J* = 11.6, 5.6 Hz, 1 H), 4.48 (dd, *J* = 9.2, 2.8 Hz, 1 H), 4.50–4.59 (m, 1 H), 4.71–4.82 (m, 1 H), 4.85 (d, *J* = 9.2 Hz, 1 H), 5.21 (dd, *J* = 8.8, 6.4 Hz, 1 H), 5.58 (br, 1 H), 6.32 (dd, *J* = 9.6, 7.2 Hz, 1 H), 6.39 (d, *J* = 8.0 Hz, 1 H), 6.49 (d, *J* = 8.8 Hz, 1 H), 6.85 (t, *J* = 6.8 Hz, 1 H), 6.97 (t, *J* = 7.2 Hz, 1 H), 7.00 (t, *J* = 8.4 Hz, 1 H), 7.08–7.13 (m, 1 H), 7.18–7.22

(m, 4 H), 7.22–7.25 (m, 2 H), 7.29–7.33 (m, 4 H), 7.36–7.40 (m, 2 H), 7.43–7.49 (m, 3 H), 7.52–7.57 (m, 4 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.8 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 8.57 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, THF-d_8): δ = 15.1 (d, *J* = 4.1 Hz, 1 C), 19.6, 21.3 (d, *J* = 4.9 Hz, 1 C), 50.0, 61.1 (d, *J* = 5.3 Hz, 1 C), 66.6, 82.0 (d, *J* = 7.1 Hz, 1 C), 85.5 (d, *J* = 24.5 Hz, 1 C), 90.8 (d, *J* = 5.7 Hz, 1 C), 95.4, 104.6, 108.6, 121.8, 122.5, 122.8, 123.6, 125.3, 126.0, 126.6, 126.7, 126.8, 127.1, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.6, 128.7, 128.8, 129.1, 129.2, 129.4, 129.5, 129.8, 129.9, 130.0, 132.2, 132.3, 132.8, 133.2, 133.3, 133.4, 133.7, 134.2, 136.7, 139.7, 141.0, 141.6, 142.1, 143.7, 143.8, 148.4, 148.5, 149.7, 149.8.

^{31}P NMR (162 MHz, THF-d_8): δ = 115.2.

HRMS (ESI+): *m*/*z* calcd for [Ir(dncot)(*C*,*P*-L1)(crotyl)] = $C_{64}H_{52}IrNO_2P$: 1090.3365; found: 1090.3356.

Catalyst C2

In a flame-dried Schlenk tube under an argon atmosphere, a solution of $[Ir(dncot)Cl]_2$ (106.2 mg, 96 μmol) and (*S*,*S*,*S*$_a$)-L2 (123.5 mg, 206 μmol) in anhyd THF (5 mL) was stirred at r.t. for 1 h. (*E*)-But-2-en-1-yl methyl carbonate (48.7 mg, 374 μmol) and AgOTf (63.9 mg, 250 μmol) were added and the resulting suspension was stirred for 24 h at r.t. The resultant white precipitate was removed by filtration, and the solution was concentrated in vacuo. The residue was subjected to silica gel column chromatography (CH_2Cl_2–*i*-PrOH, 100:0 → 97:3) to yield **C2** (226.5 mg, 87%) as a light yellow powder; mp 205 °C (dec.).

^{1}H NMR (300 MHz, THF-d_8): δ = 0.46 (d, *J* = 7.5 Hz, 3 H), 0.97 (t, *J* = 11.1 Hz, 1 H), 1.64 (dd, *J* = 8.1, 5.7 Hz, 3 H), 2.38 (dd, *J* = 11.1, 4.5 Hz, 1 H), 2.94 (d, *J* = 10.5 Hz, 1 H), 3.24 (t, *J* = 6.9 Hz, 1 H), 3.55 (s, 3 H), 3.89 (s, 3 H), 4.40–4.67 (m, 5 H), 4.85 (d, *J* = 9.3 Hz, 1 H), 5.03 (t, *J* = 6.3 Hz, 1 H), 5.74 (br, 1 H), 6.37 (d, *J* = 8.1 Hz, 1 H), 6.43 (d, *J* = 8.7 Hz, 1 H), 6.49 (t, *J* = 8.4 Hz, 1 H), 6.80 (t, *J* = 6.9 Hz, 1 H), 6.85–6.99 (m, 4 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 7.08–7.16 (m, 2 H), 7.16–7.19 (m, 1 H), 7.20–7.26 (m, 4 H), 7.26–7.31 (m, 2 H), 7.31–7.36 (m, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H), 7.51–7.63 (m, 6 H), 7.73 (d, *J* = 8.7 Hz, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 8.12 (d, *J* = 9.0 Hz, 1 H), 8.17 (d, *J* = 8.7 Hz, 1 H), 8.28 (d, *J* = 8.1 Hz, 1 H), 8.54 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, THF-d_8): δ = 15.3, 18.6, 19.6, 49.7, 53.3, 55.4, 56.0, 60.7 (d, *J* = 34.8 Hz, 1 C), 82.2 (d, *J* = 7.6 Hz, 1 C), 84.6 (d, *J* = 26.7 Hz, 1 C), 91.2, 94.7, 104.0, 108.8, 111.4, 111.8, 121.6, 121.8, 121.9, 122.3, 123.1, 123.6, 124.2, 125.1, 125.3, 125.9, 126.5, 126.6, 126.7, 127.0, 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.8, 129.2, 129.4, 129.6, 130.0, 130.1, 130.3, 131.6, 131.7, 132.2, 132.8, 133.2, 133.3, 133.4, 133.6, 133.7, 134.0, 136.9, 139.7, 141.0, 142.2, 148.2, 148.3, 149.6, 149.8, 158.0, 158.1.

^{31}P NMR (162 MHz, THF-d_8): δ = 115.4.

HRMS (ESI+): *m*/*z* calcd for [Ir(dncot)(*C*,*P*-L2)(crotyl)] = $C_{66}H_{56}IrNO_4P$: 1150.3576; found: 1150.3569.

Ir-Catalyzed Allylic Amination Reaction; General Procedure

A suspension of **C2** (5.2 mg, 1 mol%), allylic carbonate **1** (0.4 mmol), and $BnNH_2$ (85.6 mg, 0.8 mmol) in THF (1 mL) was stirred at 50 °C until TLC monitoring (eluent: PE–EtOAc, 20:1) showed complete conversion. The solvent was removed in vacuo and the residue was subjected to silica gel column chromatography (eluent: eluent: PE–EtOAc, 20:1) to yield the amination products. The ratio of regioisomers was determined by ^{1}H NMR analysis of the crude product, and the enantiomeric excess was determined by HPLC on a chiral column.

3aa[16]

Yield: 83.2 mg (90%); colorless oil; $[\alpha]_D^{18.2}$ +6.2 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 9.31 min, t_R (major) = 10.25 min; 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (br, 1 H), 3.70 (AB, J_{AB} = 13.2 Hz, 1 H), 3.74 (BA, J_{BA} = 13.2 Hz, 1 H), 4.22 (d, *J* = 7.2 Hz, 1 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 5.22 (d, *J* = 17.2 Hz, 1 H), 5.94 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1 H), 7.19–7.27 (m, 2 H), 7.29–7.39 (m, 8 H).

3ab[16]

Yield: 89.1 mg (88%); colorless oil; $[\alpha]_D^{20.4}$ +0.8 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 12.63 min, t_R (major) = 16.40 min; 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (br, 1 H), 3.70 (s, 2 H), 3.77 (s, 3 H), 4.17 (d, *J* = 7.2 Hz, 1 H), 5.11 (d, *J* = 9.6 Hz, 1 H), 5.19 (d, *J* = 17.1 Hz, 1 H), 5.92 (ddd, *J* = 17.1, 9.9, 7.2 Hz, 1 H), 6.81–6.91 (m, 2 H), 7.18–7.35 (m, 7 H).

3ac[17]

Yield: 90.5 mg (93%); colorless oil; $[\alpha]_D^{22.4}$ +3.8 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 13.30 min, t_R (major) = 17.83 min; 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (br, 1 H), 3.71 (s, 2 H), 3.77 (s, 3 H), 4.18 (d, *J* = 7.2 Hz, 1 H), 5.10 (d, *J* = 9.9 Hz, 1 H), 5.22 (d, *J* = 17.1 Hz, 1 H), 5.92 (ddd, *J* = 17.7, 10.2, 7.2 Hz, 1 H), 6.94–6.82 (m, 1 H), 6.91–6.98 (m, 2 H), 7.16–7.34 (m, 6 H).

3ad[18]

Yield: 117.8 mg (95%); colorless oil; $[\alpha]_D^{24.1}$ –1.5 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 10.50 min, t_R (major) = 11.92 min; 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (br, 1 H), 3.66 (AB, J_{AB} = 13.8 Hz, 1 H), 3.71 (BA, J_{BA} = 13.5 Hz, 1 H), 4.17 (d, *J* = 7.2 Hz, 1 H), 5.11 (d, *J* = 9.3 Hz, 1 H), 5.20 (d, *J* = 17.1 Hz, 1 H), 5.87 (ddd, *J* = 16.8, 9.6, 6.9 Hz, 1 H), 7.19–7.36 (m, 7 H), 7.40–7.50 (m, 2 H).

3ae[17]

Yield: 83.2 mg (81%); colorless oil; $[\alpha]_D^{23.3}$ +0.1 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 10.27 min, t_R (major) = 11.55 min; 95% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60 (br, 1 H), 3.67 (AB, J_{AB} = 13.8 Hz, 1 H), 3.72 (BA, J_{BA} = 13.8 Hz, 1 H), 4.19 (d, *J* = 7.2 Hz, 1 H), 5.12 (d, *J* = 9.9 Hz, 1 H), 5.20 (d, *J* = 17.1 Hz, 1 H), 5.88 (ddd, *J* = 17.1, 9.9, 6.9 Hz, 1 H), 7.20–7.36 (m, 9 H).

3af[17]

Yield: 69.2 mg (68%); colorless oil; $[\alpha]_D^{23.4}$ +2.8 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (minor) = 17.97 min, t_R (major) = 19.74 min; 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (br, 1 H), 1.63–1.92 (m, 2 H), 2.50–2.73 (m, 2 H), 2.99–3.11 (m, 1 H), 3.62 (AB, J_{AB} = 13.5 Hz, 1 H), 3.82 (BA, J_{BA} = 13.2 Hz, 1 H), 5.14 (d, *J* = 18.0 Hz, 1 H), 5.19 (d, *J* = 12.0 Hz, 1 H), 5.57–5.77 (m, 1 H), 7.09–7.19 (m, 3 H), 7.20–7.35 (m, 7 H).

3ag[4d]

Yield: 168.0 mg (89%); colorless oil; $[\alpha]_D^{22.0}$ +34.2 (*c* 1.00, $CHCl_3$).

HPLC: Daicel Chiralpak AD-H, hexane–*i*-PrOH (90:10), v = 0.5 mL·min^{-1}, λ = 210 nm, t_R (minor) = 7.20 min, t_R (major) = 8.85 min; 82% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 2.18 (br, 1 H), 2.50–2.73 (m, 1 H), 3.63 (d, *J* = 6.0 Hz, 2 H), 3.66 (d, *J* = 14.7 Hz, 1 H),

3.89 (d, J = 13.8 Hz, 1 H), 5.15 (d, J = 9.9 Hz, 1 H), 5.16 (d, J = 18.6 Hz, 1 H), 5.62 (ddd, J = 18.0, 9.9, 7.8 Hz, 1 H), 7.19–7.46 (m, 11 H), 7.57–7.68 (m, 4 H).

Ir-Catalyzed Allylic Alkylation Reaction; General Procedure

A suspension of **C2** (5.2 mg, 1 mol%), allylic carbonate **1** (0.4 mmol), and $NaCH(CO_2Me)_2$ (0.8 mmol) in THF (1 mL) was stirred at 50 °C until TLC monitoring (eluent: eluent: PE–EtOAc, 10:1) showed complete conversion. The reaction was quenched by sat. aq NH_4Cl (2.0 mL) and diluted with EtOAc (2.0 mL). The organic layer was separated, washed with brine (2.0 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was subjected to flash chromatography over silica gel (eluent: eluent: PE–EtOAc, 20:1) to yield the products. The ratio of regioisomers was determined by ^{1}H NMR of the crude product, the enantiomeric excess was determined by HPLC on a chiral column.

3ba[4c]

Yield: 94.1 mg (91%); colorless oil; $[\alpha]_D^{23.1}$ +31.1 (c 1.00, $CHCl_3$).

HPLC: Daicel Chiralcel OJ-H, hexane–*i*-PrOH (95:5), v = 1.0 mL·min^{-1}, λ = 230 nm, t_R (minor) = 24.71 min, t_R (major) = 27.16 min; 98% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 3.73 (s, 3 H), 3.87 (d, J = 11.1 Hz, 1 H), 4.10 (dd, J = 10.5, 8.7 Hz, 1 H), 5.08 (d, J = 9.6 Hz, 1 H), 5.12 (d, J = 16.5 Hz, 1 H), 5.99 (ddd, J = 18.0, 9.3, 8.1 Hz, 1 H), 7.15–7.24 (m, 3 H), 7.25–7.33 (m, 2 H).

3bg[4c]

Yield: 148.7 mg (79%); colorless oil; $[\alpha]_D^{18.0}$ +42.5 (c 1.00, $CHCl_3$).

HPLC: Daicel Chiralpak AD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (major) = 10.15 min, t_R (minor) = 11.17 min; 84% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 2.96–3.10 (m, 1 H), 3.67 (s, 3 H), 3.69 (s, 3 H), 3.69–3.76 (m, 2 H), 3.88 (d, J = 8.1 Hz, 1 H), 5.10 (d, J = 10.2 Hz, 1 H), 5.11 (d, J = 17.7 Hz, 1 H), 5.90 (dt, J = 16.8, 9.3 Hz, 1 H), 7.32–7.46 (m, 6 H), 7.57–7.66 (m, 4 H).

3bh[4c]

Yield: 168.8 mg (89%); colorless oil; $[\alpha]_D^{23.3}$ +29.4 (c 1.00, $CHCl_3$).

HPLC: Daicel Chiralpak AD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (major) = 14.79 min, t_R (minor) = 17.21 min; 84% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03–3.15 (m, 1 H), 3.15–3.24 (m, 2 H), 3.56 (s, 3 H), 3.62 (s, 3 H), 3.82 (d, J = 8.1 Hz, 1 H), 5.10 (d, J = 9.9 Hz, 1 H), 5.11 (d, J = 18.9 Hz, 1 H), 5.91 (dt, J = 17.1, 9.9 Hz, 1 H), 7.15–7.32 (m, 9 H), 7.35–7.47 (m, 6 H).

3bi[4c]

Yield: 180.8 mg (82%); colorless oil; $[\alpha]_D^{22.2}$ –2.3 (c 1.00, $CHCl_3$).

HPLC: Daicel Chiralpak AD-H, hexane–*i*-PrOH (98:2), v = 0.5 mL·min^{-1}, λ = 230 nm, t_R (major) = 12.72 min, t_R (minor) = 13.61 min; 95% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51–3.68 (m, 1 H), 1.78–1.92 (m, 1 H), 2.92–3.06 (m, 2 H), 3.07–3.17 (m, 1 H), 3.42 (d, J = 8.4 Hz, 1 H), 3.66 (s, 3 H), 3.72 (s, 3 H), 4.92 (d, J = 9.0 Hz, 1 H), 4.94 (d, J = 17.1 Hz, 1 H), 5.55 (dt, J = 17.1, 9.6 Hz, 1 H), 7.15–7.31 (m, 9 H), 7.38–7.46 (m, 6 H).

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