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Iridium/*N*-Heterocyclic Carbene Complex-Catalyzed Intermolecular Allylic Alkylation Reaction

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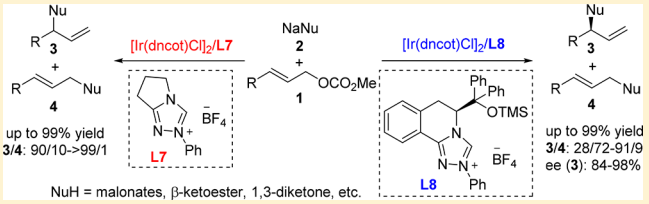
Supporting Information

ABSTRACT: *N*-Heterocyclic carbenes (NHCs) were found to be suitable ligands in Ir-catalyzed intermolecular allylic alkylation reaction. In the presence of a catalyst derived from $[Ir(dncot)Cl]_2$ (dncot = dinaphthocyclooctatetraene) and triazolium salt **L7**, the alkylation products from the reaction of aryl allyl carbonates with sodium dialkyl malonates could be obtained in 85−99% yields favoring the formation of branched products (90/10 → >99/1 b/l). In addition, chiral dihydroisoquinoline-type NHC (DHIQ-NHC) (**L8**) is successfully applied in Ir-catalyzed asymmetric allylic alkylation reactions. Excellent enantioselectivities and moderate regioselectivities were obtained for a wide range of substrates.



INTRODUCTION

Since the first report introduced by the group of Takeuchi, iridium-catalyzed allylic substitution reactions have developed into a reliable method to construct C−C (or C−X) bonds.[1−3] The emergence of privileged phosphoramidite ligands, such as Feringa[4] and Alexakis[5] (P/C) ligands and Carreira's bidentate (P/olefin) coordination ligand (Figure 1),[6] has contributed significantly to this field and allows numerous transformations in a highly regio- and enantioselective fashion. Meanwhile, our group developed a series of N-aryl phosphoramidites, in which the active species is formed through an Ir-mediated C−H bond insertion of the phenyl group. Further studies led to the observation that this C(sp²)−H activation mode renders the active iridacycle complex less sterically hindering in its three-dimensional structure, thus accommodating a wide range of substrates including those which were found to be challenging in previous studies.[7] Although great advances have been made within this domain, the development of new ligand types remains an important and challenging task.

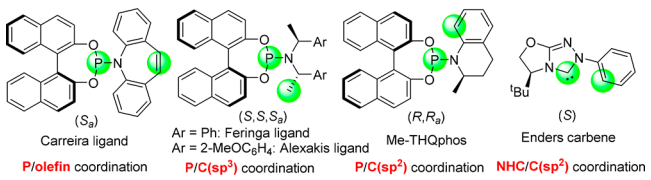
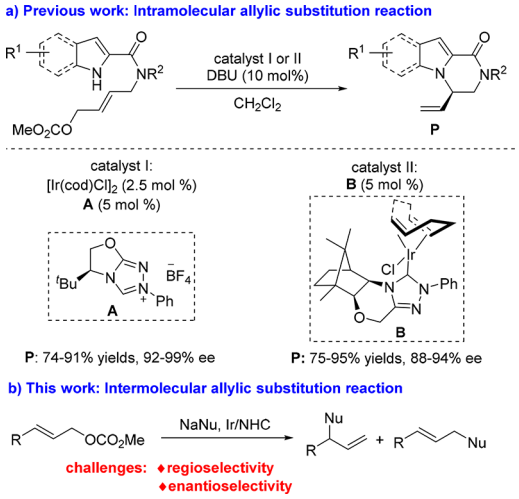


Figure 1. Selected ligands for Ir-catalyzed asymmetric allylic substitution reactions.

N-Heterocyclic carbenes (NHCs) have been well-established as organocatalysts[8] and chiral ligands[9] in the past years. However, their applications in transition-metal-catalyzed allylic substitution reaction have been less explored, with the exception of copper catalysis.[10] Recently, NHCs were found to be efficient ligands in Ir-catalyzed asymmetric allylic substitution reactions. In the presence of Ir-catalyst derived from the Enders NHC[11a] or D-camphor derived ones,[11b] intramolecular allylic amination reaction of indoles and pyrroles could be realized, providing facile access to the corresponding indolopiperazinones and piperazinones (Scheme 1a).[12] Interestingly, we found that the C(sp²)−H activation mode is also occurring with NHC ligands, in which an active five-membered cyclometalated complex is generated through C−H activation at the *ortho*-position of N-

Scheme 1. Ir/NHC-Catalyzed Allylic Substitution Reactions



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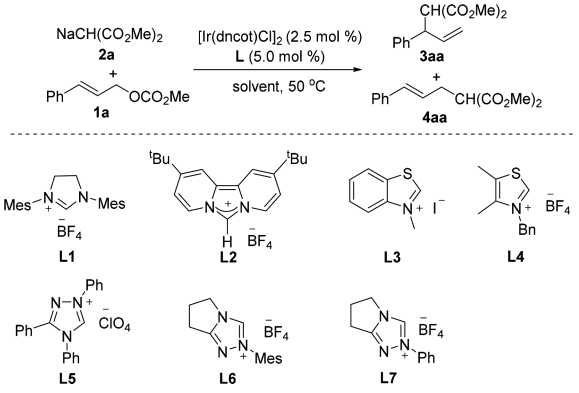
aryl group of the ligand. With these promising preliminary results in hand, we went on to explore the feasibility of Ir/NHC-catalyzed intermolecular variants (Scheme 1b). Control of regioselectivity in metal-catalyzed allylic substitutions employing NHC ligand remains a significant challenge. Accordingly, our efforts were devoted to the racemic versions at the very beginning, with the goal to achieve the reactions in a highly branched-selective fashion. Herein, we report our results from this study.

RESULTS AND DISCUSSION

Optimization of the Reaction Conditions. The initial attempt was launched with the reaction between cinnamyl carbonate (**1a**) and sodium dimethyl malonate (**2a**). With $[Ir(dncot)Cl]_2$ (dncot = dinaphthocyclooctatetraene)[13] as the iridium precursor and THF as the solvent, various NHCs including those derived from imidazolium, benzothiazolium, thiazolium, and triazolium salts were tested.[14] It was found that NHCs with different scaffolds have a profound effect on the reaction outcome and that triazolium salt **L7** gave the best reactivity and promising regioselectivity (**3aa**/**4aa** = 94/6, 96% yield, entry 7, Table 1). Switching the iridium precursor from $[Ir(dncot)Cl]_2$ to $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) led to a slight decrease in regioselectivity (**3aa**/**4aa** = 89/11, entry 8, Table 1). Further investigation of the solvents such as toluene, dioxane, CH_3CN, and CH_2Cl_2 showed that CH_2Cl_2 is optimal in terms of both yield and regioselectivity (entries 9–12, Table 1).

Table 1. Optimization of the Reaction Conditions[a]



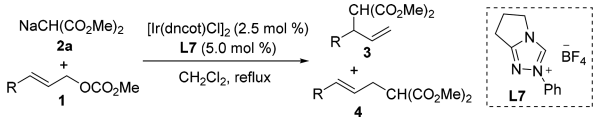
entry	L	solvent	t (h)	**3aa**/**4aa**[b]	yield (**3aa** + **4aa**) (%)[c]
1	**L1**	THF	11	59/41	10
2	**L2**	THF	12	57/43	57
3	**L3**	THF	11	84/16	26
4	**L4**	THF	16	72/28	63
5	**L5**	THF	11	40/60	4
6	**L6**	THF	11	52/48	5
7	**L7**	THF	12	94/6	100 (96)
8[d]	**L7**	THF	12	89/11	97 (93)
9	**L7**	toluene	14	91/9	100 (98)
10	**L7**	dioxane	14	92/8	100 (95)
11	**L7**	CH_3CN	14	94/6	100 (99)
12[e]	**L7**	CH_2Cl_2	11	96/4	100 (98)

[a]Reaction conditions: $[Ir(dncot)Cl]_2$ (2.5 mol %), **L** (5.0 mol %), **1a** (0.4 mmol), and **2a** (0.8 mmol) in solvent (2.0 mL) at 50 °C or reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^1H NMR of the crude reaction mixture. [c]^1H NMR yield with CH_2Br_2 as an internal standard. Unless otherwise noted, the isolated yield was shown in parentheses. [d]$[Ir(cod)Cl]_2$ (2.5 mol %) was used. [e]Reflux.

Finally, the optimal conditions were confirmed as follows: The catalyst derived from $[Ir(dncot)Cl]_2$ (2.5 mol %) and **L7** (5.0 mol %) was prepared via Et_3N activation, followed by the addition of substrates and CH_2Cl_2 under reflux.

Substrate Scope. With the optimal conditions in hand, the reaction scope was then explored. Various allylic substrates were allowed to react with sodium dimethyl malonate (**2a**). The reactions of allylic carbonates bearing an electron-donating group (−Me, −OMe, and −^{i}Bu) on different positions of the aromatic ring, including previously unfavorable *ortho*-substituted cinnamyl carbonates (**1b** and **1e**),[7b,f] all gave good regioselectivity and yields (**3**/**4** = 90/10 → 99/1, 90–99% yields, entries 2–7, Table 2). Substrates bearing an electron-withdrawing group, such as −Br or $-CF_3$, at the *para*-position on the phenyl ring (**1h**, **1i**) were also compatible with this protocol, leading to the desired products in 92/8 b/l, 99% yield, and 90/10 b/l, 85% yield, respectively (entries 8–9, Table 2).

Table 2. Scope of the Allylic Substrates[a]



entry	**1**, R	t (h)	**3**/**4**[b]	yield (**3** + **4**) (%)[c]
1	**1a**, Ph	11	**3aa**/**4aa**, 96/4	98
2	**1b**, 2-MeC_6H_4	12	**3ba**/**4ba**, 98/2	98
3	**1c**, 3-MeC_6H_4	13	**3ca**/**4ca**, 95/5	99
4	**1d**, 4-MeC_6H_4	15	**3da**/**4da**, 96/4	90
5	**1e**, 2-MeOC_6H_4	15	**3ea**/**4ea**, 90/10	94
6	**1f**, 4-MeOC_6H_4	15	**3fa**/**4fa**, > 99/1	99
7	**1g**, 4-^{i}BuC_6H_4	21	**3ga**/**4ga**, 99/1	99
8	**1h**, 4-BrC_6H_4	22	**3ha**/**4ha**, 92/8	99
9	**1i**, 4-$CF_3C_6H_4$	15	**3ia**/**4ia**, 90/10	85
10	**1j**, 2,4-$(CH_3)_2C_6H_3$	12	**3ja**/**4ja**, > 99/1	99
11	**1k**, 3,5-$(CH_3)_2C_6H_3$	18	**3ka**/**4ka**, 96/4	93
12	**1l**, 3,4-(methylenedioxy)C_6H_3	17	**3la**/**4la**, 95/5	99
13	**1m**, 3,4-$(MeO)_2C_6H_3$	14	**3ma**/**4ma**, > 99/1	99
14	**1n**, 1-naphthyl	13	**3na**/**4na**, 96/4	99
15	**1o**, 2-naphthyl	16	**3oa**/**4oa**, 99/1	99
16	**1p**, 2-furanyl	13	**3pa**/**4pa**, 94/6	91
17	**1q**, 2-thienyl	13	**3qa**/**4qa**, 98/2	99
18	**1r**, cyclohexyl	17	**3ra**/**4ra**, 18/82	84
19	**1s**, Et	13	**3sa**/**4sa**, 57/43	81

[a]Reaction conditions: $[Ir(dncot)Cl]_2$ (2.5 mol %), **L7** (5.0 mol %), **1** (0.4 mmol), and **2a** (0.8 mmol) in CH_2Cl_2 (2.0 mL) under reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^1H NMR of the crude reaction mixture. [c]Isolated yield.

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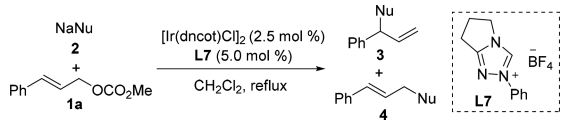
Additionally, the reaction conditions display a good tolerance of aromatic allylic carbonates bearing multi substituents [2,4-$(CH_3)_2C_6H_3$−, 3,5-$(CH_3)_2C_6H_3$−, 3,4-(methylenedioxy)-C_6H_3−, and 3,4-$(MeO)_2C_6H_3$−] on the phenyl ring. In all cases, good regioselectivity and yields were obtained (**3**/**4** = 95/5 → >99/1, 93−99% yields, entries 10−13, Table 2). Reactions of naphthyl-, furanyl- and thienyl-substituted allylic carbonates with sodium dimethyl malonate also proceeded smoothly, resulting in the corresponding alkylation products in satisfying results (**3**/**4** = 94/6−99/1, 91−99% yields, entries 14−17, Table 2). To our disappointment, only moderate regioselectivity (**3**/**4** = 18/82−57/43) was observed when aliphatic allylic carbonates [cyclohexyl− (**1r**), Et− (**1s**)] were employed.

Moreover, various nucleophiles were investigated. In addition to sodium dimethyl malonate, the corresponding sodium salt derived from diethyl malonate (**2b**), diisopropyl malonate (**2c**), *β*-ketoester (**2d**), and 1,3-diketone (**2e**) were also proved to be suitable nucleophiles. Uniformly high levels of regioselectivity and good yields were obtained (**3**/**4** = 95/5−97/3, 95−99% yields, entries 2−5, Table 3). Notably, the diastereoselectivity in **3ad** was confirmed as about 1:1 when an additional stereocenter was incorporated.

Table 3. Scope of the Nucleophiles[a]



entry	**2**, NaNu	*t* (h)	**3**/**4**[b]	yield (**3** + **4**) (%)[c]
1	**2a**, NaCH(CO_2Me)$_2$	11	**3aa**/**4aa**, 96/4	98
2	**2b**, NaCH(CO_2Et)$_2$	18	**3ab**/**4ab**, 97/3	95
3	**2c**, NaCH($CO_2{}^iPr$)$_2$	11	**3ac**/**4ac**, 97/3	99
4[d]	**2d**, NaCH(COMe)CO_2Et	10	**3ad**/**4ad**, 96/4	96
5	**2e**, NaCH(COMe)$_2$	19	**3ae**/**4ae**, 95/5	99

[a]Reaction conditions: [Ir(dncot)Cl]$_2$ (2.5 mol %), **L7** (5.0 mol %), **1a** (0.4 mmol), and **2** (0.8 mmol) in CH_2Cl_2 (2.0 mL) under reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^{1}H NMR of the crude reaction mixture. [c]Isolated yield. [d]The dr value for **3ad** was determined as 49/51 by ^{1}H NMR.

IR/NHC-CATALYZED INTERMOLECULAR ASYMMETRIC ALLYLIC ALKYLATION REACTION

Optimization of the Reaction Conditions. Next, we switched our efforts to asymmetric Ir-catalyzed allylic alkylation reactions with the introduction of chiral NHCs. The studies commenced with the investigation of different chiral NHCs derived from triazolium or imidazolium salts.[15] As shown in Table 4, the model reaction performed in the presence of dihydroisoquinoline-type NHC (DHIQ-NHC) (**L8**) gave the desired products with modest regioselectivity (**3aa**/**4aa** = 53/47). Gratifyingly, the ee value for the branched product **3aa** was determined as 93% (entry 1, Table 4). Further examinations by varying the aryl group on the triazolium core or deprotecting the hydroxyl group in DHIQ-NHCs were conducted, merely leading to a decreased regioselectivity or enantioselectivity for **3aa** (entries 2−4, Table 4). It is worth noting that the reaction gave poor yield without any asymmetric induction when **L12** was used, further demonstrating NHC/C(sp^2)−H bidentate coordination mode is responsible for both reactivity and enantioselectivity (entry 5, Table 4). Amino-indanol-derived triazolium salts **L13**−**L15**, camphor-derived triazolium salts **L16**−**L18**, phenylalaninol-derived triazolium salt **L19**, trimethylalaninol-derived triazolium salt **L20**, and (1*R*,2*R*)-DPEN-derived triazolium salt **L21** (DPEN = 1,2-diphenylethylenediamine) were subsequently tested, but none of them gave improved results (entries 6−14, Table 4). Finally, Enders triazolium salt **L22** offered promising enantioselectivity albeit with a low branched selectivity (95% ee, **3aa**/**4aa** = 29/71, entry 15, Table 4). Other triazolium salts such as **L23** and **L24** also gave satisfying results (entries 16 and 17, Table 4). However, chiral imidazolium salts **L25** and **L26** afforded low asymmetric induction (entries 18 and 19, Table 4). The utilization of other iridium precursors including [Ir(cod)Cl]$_2$ and [Ir(dbcot)Cl]$_2$[16] (dbcot = dibenzocyclooctatetraene) led to poor results (entries 20 and 21, Table 4). Further investigations on solvents verified that dichloromethane is the optimal solvent (**3aa**/**4aa** = 63/37, 90% yield, 95% ee, entry 24, Table 4).

Substrate Scope. Accordingly, our subsequent efforts were devoted to the substrate scope for Ir/NHC-catalyzed asymmetric allylic alkylation reactions. As shown in Table 5, the cinnamyl derived carbonates containing an electron-donating group at different positions of the phenyl ring (2-Me, 3-Me, 4-Me, 2-MeO, 4-MeO, 4-^{i}Bu) gave excellent enantioselectivity for the branched products (**3aa**−**3ga**, 91−98% ee, entries 1−7, Table 5). Notably, these reactions typically proceeded with a slight favoring of branched products (**3**/**4** = 55/45−79/21) except for *ortho*-methoxyl substituted substrate **1e** (**3ea**/**4ea** = 34/66). When introducing an electron-withdrawing substituent (4-Br, 4-CF_3) on the phenyl ring of cinnamyl carbonates **1h** and **1i**, selectivity for the corresponding linear products was observed (**3**/**4** = 28/72−36/64). Moreover, the multisubstituted cinnamyl carbonates [(2,4-$(CH_3)_2C_6H_3$−, 3,5-$(CH_3)_2C_6H_3$−, 3,4-(methylenedioxy)C_6H_3−, and 3,4-$(MeO)_2C_6H_3$−)] were also compatible with the reaction, leading to the alkylated products in moderate to good regioselectivity, excellent yields and enantioselectivity (**3**/**4** = 59/41−84/16, 97−99% yields, **3ja**-**3ma**: 95−98% ee, entries 10−13, Table 5). The allylic carbonates based on other aromatic rings including 1-naphthyl-, 2-naphthyl-, 2-furanyl-, and 2-thienyl proceeded smoothly under the optimized conditions. In all cases, excellent enantioselectivity and moderate to good regioselectivity were obtained for the branched products (**3**/**4** = 58/42−91/9, 90−98% yields, **3na**−**3qa**: 94−98% ee, entries 14−17, Table 5). In agreement with the previous racemic reactions, the aliphatic allylic carbonates (**1r** and **1s**) predominantly formed linear products (**3**/**4** = 21/79 to <1/99).

The asymmetric allylic alkylation reactions of diethyl malonate (**2b**), diisopropyl malonate (**2c**), *β*-ketoester (**2d**), and 1,3-diketone (**2e**) with cinnamyl carbonate **1a** all gave the desired products in reasonable to good regioselectivity, excellent yields and ee values for the branched product (**3**/**4** = 63/37−74/26, 91−98% yields, **3ab**−**3ae**: 95−98% ee, entries 2−5, Table 6).

Mechanistic Studies. [Ir(dncot)Cl]$_2$ was subjected to **L8** in the presence of Et_3N, which resulted in the formation of iridium(I)-NHC complex **Ir1**, an air- and moisture-stable solid, in 98% yield (Scheme 2a). Notably, the structure of its analog **Ir2**, which was generated from [Ir(cod)Cl]$_2$ and **L8**, has been confirmed by X-ray crystallographic analyses.[17] With complex **Ir1** as the catalyst, the model reaction proceeded smoothly with the assistance of Et_3N to afford the desired products in comparable yield and selectivity to those obtained when using

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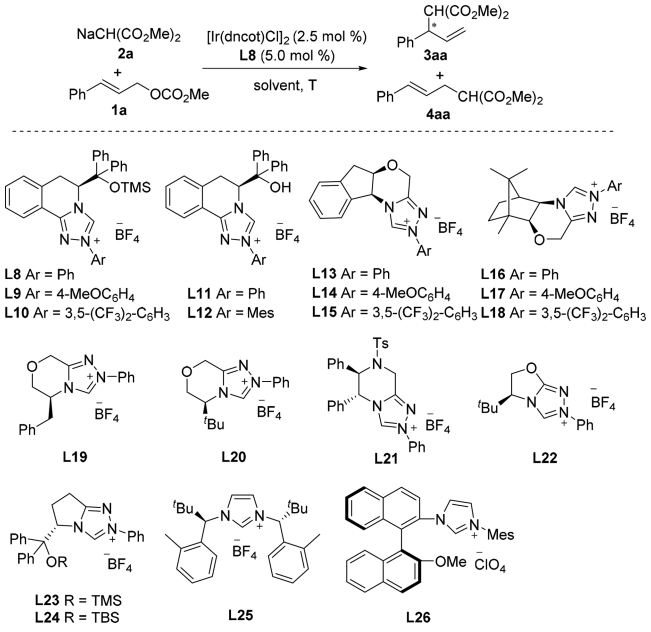
Table 4. Optimization of the Reaction Conditions[a]



entry	L	solvent	t (h)	3aa/4aa[b]	yield (3aa + 4aa) (%)[c]	ee (3aa) (%)[d]
1	**L8**	THF	15	53/47	47	93
2	**L9**	THF	60	23/77	72	83
3	**L10**	THF	60	49/51	11	12
4	**L11**	THF	17	53/47	86	88
5	**L12**	THF	17		4	0
6	**L13**	THF	17	59/41	62	17
7	**L14**	THF	10	66/34	71	16
8	**L15**	THF	24	39/61	52	10
9	**L16**	THF	10	42/58	79	35
10	**L17**	THF	10	36/64	58	58
11	**L18**	THF	40	40/60	24	0
12	**L19**	THF	19	68/32	99	2
13	**L20**	THF	11.5	59/41	93	63
14	**L21**	THF	10	79/21	65	51
15	**L22**	THF	14	29/71	63	95
16	**L23**	THF	16	43/57	67	95
17	**L24**	THF	16	53/47	43	85
18	**L25**	THF	60	39/61	53	0
19	**L26**	THF	38	64/36	59	4
20[e]	**L8**	THF	18	43/57	48	13
21[f]	**L8**	THF	16	34/66	43	47
22	**L8**	1,4-dioxane	60	32/68	87	87
23[g]	**L8**	Et_2O	57	54/46	69	94
24[g]	**L8**	CH_2Cl_2	19	63/37	90	95
25	**L8**	$ClCH_2CH_2Cl$	34.5	26/74	75	85
26	**L8**	1,2-dichlorobenzene	33	45/55	30	90
27	**L8**	toluene	39	25/75	38	79
28	**L8**	MeCN	34	39/61	94	88
29	**L8**	EtOAc	58	16/84	22	62

[a]Reaction conditions: $[Ir(dncot)Cl]_2$ (2.5 mol %), **L8** (5.0 mol %), **1a** (0.4 mmol), and **2a** (0.8 mmol) in solvent (2.0 mL) at 50 °C or reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^1H NMR of the crude reaction mixture. [c]Isolated yield. [d]Determined by HPLC analysis. [e]$[Ir(cod)Cl]_2$ (2.5 mol %) was used. [f]$[Ir(dbcot)Cl]_2$ (2.5 mol %) was used. [g]Reflux.

the *in situ* prepared catalyst. These results are consistent with our previous studies (Scheme 2b).[12a,b] On the basis of these observations, we proposed that the catalytically active iridium complex might also involve C(sp^2)−H activation of the *N*-aryl group of the ligand.

CONCLUSION

In conclusion, we have developed an iridium/NHC complex-catalyzed intermolecular allylic alkylation reaction. With $[Ir(dncot)Cl]_2$ as the iridium precursor and triazolium salt **L7** as the NHC precursor, the alkylation reactions between aryl allyl

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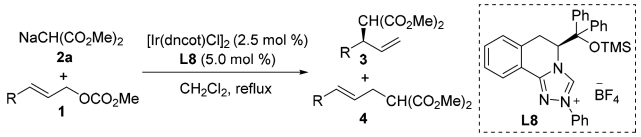
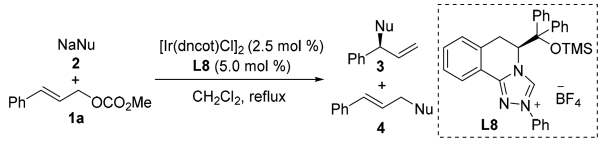
Table 5. Scope of the Allylic Substrates in Asymmetric Reaction[a]



entry	1, R	t (h)	3/4[b]	yield (3 + 4) (%)[c]	ee (3) (%)[d]
1	**1a**, Ph	19	**3aa/4aa**, 63/37	90	95
2	**1b**, 2-MeC_6H_4	12	**3ba/4ba**, 55/45	93	97
3	**1c**, 3-MeC_6H_4	13	**3ca/4ca**, 59/41	99	98
4	**1d**, 4-MeC_6H_4	35	**3da/4da**, 67/33	94	98
5	**1e**, 2-MeOC_6H_4	15	**3ea/4ea**, 34/66	98	96
6	**1f**, 4-MeOC_6H_4	16	**3fa/4fa**, 79/21	93	97
7	**1g**, 4-^{i}BuC_6H_4	43	**3ga/4ga**, 74/26	91	91
8	**1h**, 4-BrC_6H_4	21.5	**3ha/4ha**, 36/64	94	95
9	**1i**, 4-$CF_3C_6H_4$	39	**3ia/4ia**, 28/72	95	84
10	**1j**, 2,4-$(CH_3)_2C_6H_3$	12	**3ja/4ja**, 84/16	99	98
11	**1k**, 3,5-$(CH_3)_2C_6H_3$	42	**3ka/4ka**, 59/41	99	95
12	**1l**, 3,4-(methylenedioxy)C_6H_3	17	**3la/4la**, 66/34	97	96
13	**1m**, 3,4-$(MeO)_2C_6H_3$	13	**3ma/4ma**, 82/18	98	97
14	**1n**, 1-naphthyl	47	**3na/4na**, 85/15	97	97
15	**1o**, 2-naphtyl	15	**3oa/4oa**, 58/42	95	94
16	**1p**, 2-furanyl	47	**3pa/4pa**, 74/26	90	98
17	**1q**, 2-thienyl	47	**3qa/4qa**, 91/9	98	96
18	**1r**, cyclohexyl	41	**3ra/4ra**, < 1/99	94	
19	**1s**, Et	68	**3sa/4sa**, 21/79	49	

[a]Reaction conditions: $[Ir(dncot)Cl]_2$ (2.5 mol %), **L8** (5.0 mol %), **1** (0.4 mmol), and **2a** (0.8 mmol) in CH_2Cl_2 (2.0 mL) under reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^1H NMR of the crude reaction mixture. [c]Isolated yield. [d]Determined by HPLC analysis.

Table 6. Scope of the Nucleophiles in Asymmetric Reaction[a]

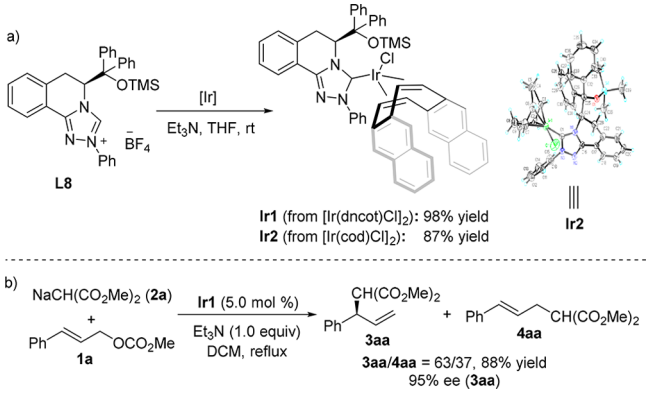


entry	2, NaNu	t (h)	3/4[b]	yield (3 + 4) (%)[c]	ee (3) (%)[d]
1	**2a**, $NaCH(CO_2Me)_2$	19	**3aa/4aa**, 63/37	90	95
2	**2b**, $NaCH(CO_2Et)_2$	19	**3ab/4ab**, 63/37	92	98
3	**2c**, $NaCH(CO^iPr)_2$	19	**3ac/4ac**, 74/26	96	97
4[e]	**2d**, NaCH(COMe)CO_2Et	62	**3ad/4ad**, 72/28	98	96, 96
5	**2e**, $NaCH(COMe)_2$	21	**3ae/4ae**, 65/35	91	95

[a]Reaction conditions: $[Ir(dncot)Cl]_2$ (2.5 mol %), **L8** (5.0 mol %), **1a** (0.4 mmol), and **2** (0.8 mmol) in CH_2Cl_2 (2.0 mL) under reflux. Catalyst was prepared via Et_3N activation. [b]Determined by ^1H NMR of the crude reaction mixture. [c]Isolated yield. [d]Determined by HPLC analysis. [e]The dr value for **3ad** was determined as 49/51 by ^1H NMR.

carbonates and sodium dialkyl malonates could be achieved in high yields and excellent branched selectivity. Meanwhile, the employment of dihydroisoquinoline-type chiral triazolium NHC (DHIQ-NHC) (**L8**) could enable the corresponding asymmetric reactions with excellent enantioselectivity and moderate regioselectivity. Future studies will focus on the development of NHCs with other novel scaffolds and their applications in diverse asymmetric allylic substitution reactions.

Scheme 2. (a) Synthesis of Iridium/NHC Complexes and (b) Ir1-Catalyzed Asymmetric Allylic Alkylation Reaction



EXPERIMENTAL SECTION

General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^1H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 and 100 MHz, respectively) or an Agilent instrument (600 and 150 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

General Procedure for Ir/L7(L8)-Catalyzed Allylic Alkylation Reaction. A flame-dried 10 mL tube was cooled to room temperature and charged with NaH (19.2 mg, 0.8 mmol, 2.0 equiv, without oil). The

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tube was evacuated and backfilled with argon. To the flask were added freshly distilled CH_2Cl_2 (1.0 mL) and malonate (0.8 mmol, 2.0 equiv), and the resultant solution was stirred for 1 min to afford nucleophile **2**.

A flame-dried 10 mL tube was cooled to room temperature and charged with $[Ir(dncot)Cl]_2$ (10.6 mg, 0.01 mmol, 2.5 mol %) and NHC precursor **L7** (5.5 mg, 0.02 mmol, 5 mol %) [or **L8** (11.8 mg, 0.02 mmol, 5 mol %)]. The tube was evacuated and backfilled with argon. To the flask were added freshly distilled THF (0.5 mL) and triethylamine (80 μL), and the resultant solution was stirred for 30 min at 50 °C. Then, the solvent was removed under reduced pressure to afford a yellow solid. The freshly distilled CH_2Cl_2 (1.0 mL), allylic substrate **1** (0.4 mmol, 1.0 equiv), and the above prepared nucleophile **2** in 1.0 mL CH_2Cl_2 were added. The resultant solution was stirred under reflux. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered through Celite and the filtrate was concentrated by rotary evaporation. The ratio of **3**/**4** was determined by ^{1}H NMR of the crude reaction mixture. Then the combined crude product was purified by silica gel column chromatography (PE/EtOAc = 30/1−5/1) to afford desired product **3**.

3aa.[18] Pale yellow oil, 109.4 mg, 98% yield, **3aa**/**4aa** = 96/4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.28 (m, 2H), 7.23−7.21 (m, 3H), 5.99 (ddd, J = 18.0, 10.0, 8.8 Hz, 1H), 5.14−5.07 (m, 2H), 4.11 (dd, J = 10.8, 8.0 Hz, 1H), 3.87 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.48 (s, 3H).

3ba.[7b] Pale yellow oil, 122.1 mg, 98% yield, **3ba**/**4ba** = 98/2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.09 (m, 4H), 5.89−5.81 (m, 1H), 5.08−5.03 (m, 2H), 4.39 (dd, J = 11.6, 8.4 Hz, 1H), 3.97 (d, J = 11.6 Hz, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 2.42 (s, 3H).

3ca. Pale yellow oil, 104.2 mg, 99% yield, **3ca**/**4ca** = 95/5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 1H), 7.03−7.01 (m, 3H), 6.02−5.93 (m, 1H), 5.14−5.06 (m, 2H), 4.06 (dd, J = 12.0, 9.2 Hz, 1H), 3.86 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.9, 139.9, 138.3, 138.0, 128.7, 128.6, 128.0, 124.8, 116.6, 57.4, 52.7, 52.5, 49.8, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 3010, 2953, 2845, 1735, 1639, 1606, 1489, 1434, 1309, 1258, 1192, 1145, 1067, 1026, 994, 923, 785, 706, 673, 443. HRMS-ESI calcd for $C_{15}H_{22}NO_4$ [M + NH_4]$^+$: 280.1543. Found: 280.1545.

3da.[18] Pale yellow oil, 94.7 mg, 90% yield, **3da**/**4da** = 96/4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11−7.10 (m, 4H), 6.02−5.93 (m, 1H), 5.13−5.05 (m, 2H), 4.10−4.05 (m, 1H), 3.85 (d, J = 11.2 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 2.30 (s, 3H).

3ea.[19] Pale yellow oil, 126.0 mg, 94% yield, **3ea**/**4ea** = 90/10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.15 (m, 2H), 6.90−6.84 (m, 2H), 6.18−6.09 (m, 1H), 5.14−5.03 (m, 2H), 4.34 (dd, J = 9.6, 9.2 Hz, 1H), 4.19 (d, J = 10.8 Hz, 1H), 3.85 (s, 3H), 3.72 (s, 3H), 3.49 (s, 3H).

3fa.[18] Pale yellow oil, 106.3 mg, 99% yield, **3fa**/**4fa** > 99/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.98 (ddd, J = 18.4, 10.4, 8.0 Hz, 1H), 5.12−5.05 (m, 2H), 4.06 (dd, J = 11.2, 10.0 Hz, 1H), 3.82 (d, J = 11.2 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.50 (s, 3H).

3ga. Pale yellow oil, 119.1 mg, 99% yield, **3ga**/**4ga** = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 5.99 (ddd, J = 18.0, 9.6, 7.6 Hz, 1H), 5.14−5.06 (m, 2H), 4.10−4.05 (m, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.47 (s, 3H), 2.42 (d, J = 7.2 Hz, 2H), 1.87−1.77 (m, 1H), 0.87 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.0, 140.6, 138.0, 137.09, 137.07, 129.4, 127.7, 116.4, 57.5, 52.6, 52.4, 49.53, 49.46, 45.1, 30.2, 22.4. IR (thin film): ν_{max} (cm^{-1}) = 3008, 2954, 2956, 2869, 2846, 2365, 1759, 1737, 1639, 1512, 1434, 1384, 1315, 1256, 1194, 1161, 1143, 1066, 1024, 990, 951, 921, 841, 793, 733, 667, 542, 416. HRMS-ESI calcd for $C_{18}H_{28}NO_4$ [M + NH_4]$^+$: 322.2013. Found: 322.2012.

3ha.[20] Pale yellow oil, 129.4 mg, 99% yield, **3ha**/**4ha** = 92/8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.41 (m, 2H), 7.12−7.09 (m, 2H), 5.99−5.90 (m, 1H), 5.13−5.08 (m, 2H), 4.08 (dd, J = 10.0, 9.2 Hz, 1H), 3.82 (d, J = 11.2 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H).

3ia.[21] Pale yellow oil, 106.9 mg, 85% yield, **3ia**/**4ia** = 90/10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.96 (ddd, J = 18.4, 10.4, 8.4 Hz, 1H), 5.16−5.12 (m, 2H), 4.18 (dd, J = 10.8, 8.0 Hz, 1H), 3.88 (d, J = 11.2 Hz, 1H), 3.75 (s, 3H), 3.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6.

3ja. Pale yellow oil, 129.4 mg, 99% yield, **3ja**/**4ja** > 99/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02−6.96 (m, 3H), 5.83 (ddd, J = 18.0, 10.0, 8.0 Hz, 1H), 5.07−5.00 (m. 2H), 4.34 (dd, J = 11.2, 8.0 Hz, 1H), 3.95 (d, J = 11.2 Hz, 1H), 3.75 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.9, 137.8, 136.3, 135.1, 131.6, 127.0, 126.0, 116.3, 56.9, 52.6, 52.5, 44.8, 21.0, 19.6. IR (thin film): ν_{max} (cm^{-1}) = 3006, 2953, 2923, 1736, 1637, 1503, 14234, 1311, 1259, 1193, 1143, 1026, 990, 921, 813, 733, 662, 598, 559, 461. HRMS-ESI calcd for $C_{16}H_{24}NO_4$ [M + NH_4]$^+$: 294.1700. Found: 294.1699.

3ka. Pale yellow oil, 138.1 mg, 93% yield, **3ka**/**4ka** = 96/4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85−6.83 (m, 3H), 5.97 (ddd, J = 18.4, 12.0, 8.0 Hz, 1H), 5.14−5.04 (m, 2H), 4.02 (dd, J = 10.8, 8.4 Hz, 1H), 3.85 (d, J = 10.8 Hz, 1H), 3.73 (s, 3H), 3.52 (s, 3H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.0, 140.0, 138.2, 138.1, 128.9, 125.7, 116.5, 57.4, 52.7, 52.5, 49.8, 21.4. IR (thin film): ν_{max} (cm^{-1}) = 3011, 2953, 2919, 1739, 1603, 1437, 1252, 1150, 1027, 992, 921, 849, 805, 705, 653. HRMS-ESI calcd for $C_{16}H_{24}NO_4$ [M + NH_4]$^+$: 294.1700. Found: 294.1698.

3la.[22] Pale yellow oil, 115.2 mg, 99% yield, **3la**/**4la** = 95/5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74−6.67 (m, 3H), 5.98−5.90 (m, 3H), 5.13−5.06 (m, 2H), 4.06−4.01 (m, 1H), 3.79 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.55 (s, 3H).

3ma. Pale yellow oil, 122.1 mg, 99% yield, **3ma**/**4ma** > 99/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81−6.74 (m, 3H), 5.98 (ddd, J = 17.2, 10.4, 8.8 Hz, 1H), 5.14−5.07 (m, 2H), 4.08−4.03 (m, 1H), 3.86 (s, 3H), 3.85−3.82 (m, 4H), 3.74 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.9, 148.8, 148.0, 137.9, 132.3, 119.8, 116.4, 111.2, 57.5, 55.84, 55.80, 52.6, 52.5, 49.3. IR (thin film): ν_{max} (cm^{-1}) = 3001, 2954, 2837, 1757, 1735, 1591, 1515, 1462, 1435, 1236, 1193, 1142, 1026, 923, 856, 809, 763, 673, 622. HRMS-ESI calcd for $C_{16}H_{24}NO_6$ [M + NH_4]$^+$: 326.1598. Found: 326.1596.

3na.[18] Pale yellow oil, 118.7 mg, 99% yield, **3na**/**4na** = 96/4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.58−7.54 (m, 1H), 7.51−7.47 (m, 1H), 7.45−7.41 (m, 1H), 7.38 (d, J = 7.2 Hz, 1H), 6.08 (ddd, J = 17.2, 10.0, 8.0 Hz, 1H), 5.19−5.09 (m, 2H), 5.03 (dd, J = 10.8, 8.0 Hz, 1H), 4.16 (d, J = 10.8 Hz, 1H), 3.78 (s, 3H), 3.39 (s, 3H).

3oa.[19] Pale yellow oil, 117.9 mg, 99% yield, **3oa**/**4oa** = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.78 (m, 3H), 7.69 (s, 1H), 7.48−7.42 (m, 2H), 7.37 (d, J = 8.4 Hz, 1H), 6.12−6.03 (m, 1H), 5.19−5.11 (m, 2H), 4.29 (dd, J = 12.0, 9.6 Hz, 1H), 4.00 (d, J = 11.2 Hz, 1H), 3.77 (s, 3H), 3.45 (s, 3H).

3pa.[19] Pale yellow oil, 104.2 mg, 91% yield, **3pa**/**4pa** = 94/6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.32 (m, 1H), 6.28−6.27 (m, 1H), 6.11−6.10 (m, 1H), 6.01−5.92 (m, 1H), 5.21−5.15 (m, 2H), 4.22 (dd, J = 9.2, 8.8 Hz, 1H), 3.88 (d, J = 10.0 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H).

3qa.[18] Pale yellow oil, 147.5 mg, 99% yield, **3qa**/**4qa** = 98/2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 5.2 Hz, 1H), 6.93−6.91 (m, 1H), 6.88−6.87 (m, 1H), 6.06−5.97 (m, 1H), 5.21−5.12 (m, 2H), 4.41 (dd, J = 9.6, 9.2 Hz, 1H), 3.84 (d, J = 10.0 Hz, 1H), 3.73 (s, 3H), 3.61 (s, 3H).

3ra.[22] Pale yellow oil, 102.2 mg, 84% yield, **3ra**/**4ra** = 18/82. ^{1}H NMR (400 MHz, $CDCl_3$, the peaks for **4ra** were indicated by *) δ 5.72 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 5.46 (dd, J = 15.6, 6.8 Hz, 1H*), 5.30 (dt, J = 14.4, 7.2 Hz, 1H*), 5.08−5.01(m, 2H), 3.73 (s, 6H*), 3.72 (s, 3H), 3.68 (s, 3H), 3.63 (d, J = 8.8 Hz, 1H), 3.40 (dd, J = 7.6, 7.6 Hz, 1H*), 2.68−2.62 (m, 1H), 2.57−2.54 (m, 2H*), 2.08−2.00 (m, 1H), 1.92−1.84 (m, 1H*), 1.71−0.87 (m, 10H), 1.71−0.87 (m, 10H*).

3sa. Pale yellow oil, 64.1 mg, 81% yield, **3sa**/**4sa** = 57/43. ^{1}H NMR (400 MHz, $CDCl_3$, the peaks for **4sa** were indicated by *) δ 5.65−5.52 (m, 1H), 5.65−5.52 (m, 1H*), 5.32 (dt, J = 15.2, 6.8 Hz, 1H*), 5.10−5.06 (m, 2H), 3.71 (s, 6H*), 3.71 (s, 3H), 3.67 (s, 3H), 3.41−3.37 (m, 1H), 3.41−3.37 (m, 1H*), 2.70−2.63 (m, 1H), 2.58−2.54 (m, 2H*), 2.00−1.93 (m, 2H*), 1.69−1.42 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H*), 0.86 (t, J = 7.2 Hz, 3H).

3ab.[23] Pale yellow oil, 127.9 mg, 95% yield, **3ab**/**4ab** = 97/3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 2H), 7.24−7.19 (m, 3H), 5.99 (ddd, J = 18.0, 10.0, 7.2 Hz, 1H), 5.14−5.06 (m, 2H), 4.21 (q, J =

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7.8 Hz, 2H), 4.13−4.08 (m, 1H), 3.97−3.91 (m, 2H), 3.83 (d, J = 11.2 Hz, 1H), 1.27 (t, J = 7.2 H, 3H), 0.98 (t, J = 7.2 Hz, 3H).

3ac. Pale yellow oil, 125.0 mg, 99% yield, **3ac**/**4ac** = 97/3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.18 (m, 5H), 5.99 (ddd, J = 18.4, 10.4, 8.0 Hz, 1H), 5.13−5.04 (m, 3H), 4.83−4.74 (m, 1H), 4.09 (dd, J = 10.8, 8.0 Hz, 1H), 3.77 (d, J = 11.2 Hz, 1H), 1.27−1.23 (m, 6H), 1.03 (d, J = 6.4 Hz, 3H), 0.93 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 167.2, 140.3, 138.3, 128.6, 128.2, 127.1, 116.4, 69.2, 68.9, 57.7, 49.7, 21.8, 21.7, 21.5, 21.4. IR (thin film): ν_{max} (cm^{-1}) = 2981, 2937, 1726, 1455, 1260, 1174, 1099, 993, 912, 821, 761, 699, 523. HRMS-ESI calcd for $C_{18}H_{28}NO_4$ $[M + NH_4]^+$: 322.2013. Found: 322.2012.

3ad.[24] Pale yellow oil, 99.3 mg, 96% yield, **3ad**/**4ad** = 96/4, dr = 49/51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.28 (m, 4H), 7.23−7.19 (m, 6H), 6.00−5.86 (m, 2H), 5.13−5.06 (m, 4H), 4.20 (q, J = 7.2 Hz, 2H), 4.15−4.10 (m, 2H), 4.04−3.98 (m, 2H), 3.91 (q, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.99 (s, 3H), 1.27 (t, J = 6.8 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H).

3ae.[25] Pale yellow oil, 97.5 mg, 99% yield, **3ae**/**4ae** = 95/5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.24−7.18 (m, 3H), 5.87 (ddd, J = 18.0, 10.4, 8.0 Hz, 1H), 5.10−5.05 (m, 2H), 4.27 (d, J = 11.6 Hz, 1H), 4.17 (dd, J = 11.6, 7.6 Hz, 1H), 2.25 (s, 3H), 1.89 (s, 3H).

*(R)-**3aa***.[18] Pale yellow oil, 93.0 mg, 90% yield, (*R*)-**3aa**/**4aa** = 63/37, 95% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 90/10, v = 1.0 mL/min, λ = 224 nm, t (minor) = 15.85 min, t (major) = 17.42 min]; $[\alpha]_D^{25}$ + 18.5 (c = 1.0, $CHCl_3$).

*(R)-**3ba***.[76] Pale yellow oil, 123.4 mg, 93% yield, (*R*)-**3ba**/**4ba** = 55/45, 97% ee [Daicel Chiralpak OD-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t (major) = 5.90 min, t (minor) = 6.67 min]; $[\alpha]_D^{30}$ + 37.3 (c = 1.0, $CHCl_3$).

*(R)-**3ca***. Pale yellow oil, 103.0 mg, 99% yield, (*R*)-**3ca**/**4ca** = 59/41, 98% ee [Daicel Chiralpak OZ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 1.0 mL/min, λ = 224 nm, t (major) = 15.75 min, t (minor) = 17.78 min]; $[\alpha]_D^{30}$ + 21.4 (c = 1.0, $CHCl_3$).

*(R)-**3da***.[18] Pale yellow oil, 112.4 mg, 94% yield, (*R*)-**3da**/**4da** = 67/33, 98% ee [Daicel Chiralpak OZ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 1.0 mL/min, λ = 224 nm, t (major) = 10.29 min, t (minor) = 11.52 min]; $[\alpha]_D^{30}$ + 23.6 (c = 1.0, $CHCl_3$).

*(R)-**3ea***.[19] Pale yellow oil, 112.9 mg, 98% yield, (*R*)-**3ea**/**4ea** = 34/66, 96% ee [Daicel Chiralpak OD-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t (major) = 7.75 min, t (minor) = 9.03 min]; $[\alpha]_D^{29}$ + 13.3 (c = 1.0, $CHCl_3$).

*(R)-**3fa***.[18] Pale yellow oil, 102.3 mg, 93% yield, (*R*)-**3fa**/**4fa** = 79/21, 97% ee [Daicel Chiralpak OD-H (0.46 cm × 25 cm), hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 224 nm, t (major) = 12.84 min, t (minor) = 14.92 min]; $[\alpha]_D^{26}$ + 19.8 (c = 1.0, $CHCl_3$).

*(R)-**3ga***. Pale yellow oil, 130.3 mg, 91% yield, (*R*)-**3ga**/**4ga** = 74/26, 91% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 1.0 mL/min, λ = 224 nm, t (major) = 26.35 min, t (minor) = 29.76 min]; $[\alpha]_D^{26}$ + 19.1 (c = 1.0, $CHCl_3$).

*(R)-**3ha***.[20] Pale yellow oil, 122.5 mg, 94% yield, (*R*)-**3ha**/**4ha** = 36/64, 95% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 1.0 mL/min, λ = 224 nm, t (major) = 31.15 min, t (minor) = 38.43 min]; $[\alpha]_D^{30}$ + 5.7 (c = 1.0, $CHCl_3$).

*(R)-**3ia***.[21] Pale yellow oil, 119.6 mg, 95% yield, (*R*)-**3ia**/**4ia** = 28/72, 84% ee. [Daicel Chiralpak ID-3, hexane/2-propanol = 96/4, v = 0.7 mL/min, λ = 214 nm, t (minor) = 5.47 min, t (major) = 6.21 min]; $[\alpha]_D^{25}$ + 5.45 (c = 1.0, $CHCl_3$).

*(R)-**3ja***. Pale yellow oil, 126.3 mg, 99% yield, (*R*)-**3ja**/**4ja** = 84/16, 98% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t (minor) = 13.85 min, t (major) = 17.61 min]; $[\alpha]_D^{30}$ + 56.0 (c = 1.0, $CHCl_3$).

*(R)-**3ka***. Pale yellow oil, 107.5 mg, 99% yield, (*R*)-**3ka**/**4ka** = 59/41, 95% ee [Daicel Chiralpak OZ-H (0.46 cm × 25 cm), hexane/2-propanol = 99.5/0.5, v = 1.0 mL/min, λ = 224 nm, t (major) = 30.24 min, t (minor) = 34.23 min]; $[\alpha]_D^{29}$ + 21.2 (c = 1.0, $CHCl_3$).

*(R)-**3la***.[22] Pale yellow oil, 115.9 mg, 97% yield, (*R*)-**3la**/**4la** = 66/34, 96% ee [Daicel Chiralpak OZ-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t (major) = 14.89 min, t (minor) = 16.71 min]; $[\alpha]_D^{26}$ + 16.5 (c = 1.0, $CHCl_3$).

*(R)-**3ma***. Pale yellow oil, 117.6 mg, 98% yield, (*R*)-**3ma**/**4ma** = 82/18, 97% ee [Daicel Chiralpak IC (0.46 cm × 25 cm), hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 224 nm, t (minor) = 23.13 min, t (major) = 30.19 min]; $[\alpha]_D^{26}$ + 21.3 (c = 1.0, $CHCl_3$).

*(R)-**3na***.[18] Pale yellow oil, 119.3 mg, 97% yield, (*R*)-**3na**/**4na** = 85/15, 97% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 224 nm, t (minor) = 13.97 min, t (major) = 19.84 min]; $[\alpha]_D^{25}$ + 36.6 (c = 1.0, $CHCl_3$).

*(R)-**3oa***.[19] Pale yellow oil, 118.3 mg, 95% yield, (*R*)-**3oa**/**4oa** = 58/42, 94% ee [Daicel Chiralpak OZ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 0.8 mL/min, λ = 224 nm, t (major) = 20.95 min, t (minor) = 22.36 min]; $[\alpha]_D^{27}$ + 31.4 (c = 1.0, $CHCl_3$).

*(R)-**3pa***.[19] Pale yellow oil, 90.0 mg, 90% yield, (*R*)-**3pa**/**4pa** = 74/26, 98% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 97/3, v = 1.0 mL/min, λ = 224 nm, t (minor) = 21.74 min, t (major) = 23.54 min]; $[\alpha]_D^{30}$ + 23.5 (c = 1.0, $CHCl_3$).

*(R)-**3qa***.[18] Pale yellow oil, 92.4 mg, 98% yield, (*R*)-**3qa**/**4qa** = 91/9, 96% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t (minor) = 31.53 min, t (major) = 33.72 min]; $[\alpha]_D^{26}$ + 36.6 (c = 1.0, $CHCl_3$).

4ra.[22] Pale yellow oil, 93.5 mg, 94% yield, (*R*)-**3ra**/**4ra** < 1/99. ^{1}H NMR (400 MHz, $CDCl_3$) δ **4ra** 5.48−5.43 (m, 1H), 5.33−5.26 (dt, J = 14.4, 6.8 Hz, 1H), 3.71 (s, 6H), 3.40 (t, J = 7.6 Hz, 1H), 2.56 (dd, J = 7.2, 7.2 Hz, 2H), 1.90−1.85 (m, 1H), 1.69−1.61 (m, 5H), 1.27−1.10 (m, 3H), 1.05−0.96 (m, 2H).

*(R)-**3sa***. Pale yellow oil, 43.2 mg, 49% yield, (*R*)-**3sa**/**4sa** = 21/79.

*(R)-**3ab***.[23] Pale yellow oil, 119.0 mg, 92% yield, (*R*)-**3ab**/**4ab** = 63/37, 98% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 99/1, v = 1.0 mL/min, λ = 224 nm, t (minor) = 24.98 min, t (major) = 27.39 min]; $[\alpha]_D^{29}$ + 13.6 (c = 1.0, $CHCl_3$).

*(R)-**3ac***. Pale yellow oil, 120.4 mg, 96% yield, (*R*)-**3ac**/**4ac** = 74/26, 97% ee [Daicel Chiralpak IC (0.46 cm × 25 cm), hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 224 nm, t (minor) = 6.06 min, t (major) = 6.97 min]; $[\alpha]_D^{28}$ + 13.7 (c = 1.0, $CHCl_3$).

*(R)-**3ad***.[24] Pale yellow oil, 106.5 mg, 98% yield, (*R*)-**3ad**/**4ad** = 72/28, 96% ee, 96% ee, 49/51 dr [Daicel Chiralpak AD-H (0.46 cm × 25 cm), hexane/2-propanol = 98/2, v = 1.0 mL/min, λ = 224 nm, t_1 (minor) = 7.36 min, t_1 (major) = 8.29 min; t_2 (major) = 9.16 min, t_2 (minor) = 10.12 min]; $[\alpha]_D^{29}$ + 14.7 (c = 1.0, $CHCl_3$).

*(R)-**3ae***.[25] Pale yellow oil, 81.7 mg, 91% yield, (*R*)-**3ae**/**4ae** = 65/35, 95% ee [Daicel Chiralpak OJ-H (0.46 cm × 25 cm), hexane/2-propanol = 85/15, v = 1.0 mL/min, λ = 224 nm, t (minor) = 15.29 min, t (major) = 20.07 min]; $[\alpha]_D^{24}$ + 22.7 (c = 1.0, $CHCl_3$).

Procedure for the Synthesis of Iridium(I) Complex Ir1.[12a] Et_3N (227.7 mg, 2.25 mmol) was added in one portion to a mixture of $[Ir(dncot)Cl]_2$ (53.2 mg, 0.05 mmol) and chiral triazolium salt **L8** (59.0 mg, 0.10 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 16 h, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **Ir1**. Yellow solid, 101.2 mg, 98% yield, mp 213.9−215.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28−8.26 (m, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.75 (br s, 2H), 7.66−6.80 (m, 24H), 6.74 (s, 1H), 6.69−6.58 (m, 2H), 6.49 (d, J = 6.0 Hz, 1H), 5.93 (d, J = 8.8 Hz, 1H), 5.82 (d, J = 8.8 Hz, 1H), 3.61−3.41 (m, 1H), 3.31 (d, J = 16.4 Hz, 1H), 2.53 (d, J = 8.4 Hz, 1H), −0.36 and −0.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 151.6, 145.7, 145.3, 142.4, 142.2, 141.8, 141.03, 139.8, 138.7, 131.79, 131.76, 131.7, 131.6, 129.8, 18.8, 128.5, 128.2, 128.1, 127.8, 127.7, 127.4, 126.9, 126.5, 125.8, 125.3, 125.23, 125.17, 125.1, 125.0, 124.3, 123.7, 123.5, 123.1, 121.9, 86.3, 83.9, 83.2, 64.7, 57.0, 54.1, 31.0, 29.7, 1.4. Anal. Calcd for $C_{56}H_{47}N_3ClOSiIr$: C, 65.06; H, 4.58; N, 4.06. Found: C, 65.00; H, 4.80; N, 4.01. IR (thin film): ν_{max} (cm^{-1}) = 3052, 2951, 2920, 2850, 2361, 1596, 1498, 1473, 1249, 1099, 1074, 992, 974, 874, 837, 739, 727, 704, 691, 575, 474, 454.

Procedure for the Synthesis of Iridium(I) Complex Ir2.[12a] Et_3N (489.7 mg, 4.84 mmol) was added in one portion to a mixture of $[Ir(cod)Cl]_2$ (72.2 mg, 0.108 mmol) and chiral triazolium salt **L8** (126.7 mg, 0.215 mmol) in THF (6.5 mL). The reaction mixture was stirred at room temperature for 16 h, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **Ir2**. Yellow solid, 156.9 mg, 87% yield, mp 221.2−222.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 9.0 Hz, 3H), 7.66−7.19 (m, 10H), 7.09 (q, J = 9.0, 6.0

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Hz, 3H), 6.83−6.68 (m, 2H), 6.35 (d, J = 9.0 Hz, 1H), 4.75−4.63 (m, 2H), 3.42 (dd, J = 9.0, 6.0 Hz, 1H), 3.09 (d, J = 15.0 Hz, 1H), 2.29 (q, J = 9.0, 6.0 Hz, 2H), 1.92−1.78 (m, 2H), 1.53−1.41 (m, 2H), 1.27 (dd, J = 9.0, 9.0 Hz, 2H), 0.91−0.82 (m, 1H), −0.26 and −0.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.3, 151.6, 143.1, 142.7, 140.8, 139.5, 131.5, 129.9, 128.7, 128.6, 128.3, 128.2, 128.1, 127.8, 126.4, 126.1, 124.3, 122.4, 87.3, 85.8, 83.5, 64.7, 56.7, 51.9, 34.3, 32.2, 31.4, 30.0, 27.5, 1.6. Anal. Calcd for $C_{40}H_{43}N_3ClOSiIr$: C, 57.36; H, 5.18; N, 5.02. Found: C, 57.01; H, 4.93; N, 4.65. IR (thin film): ν_{max} (cm^{-1}) = 2955, 2912, 2883, 1589, 1564, 1471, 1418, 1327, 1249, 1080, 1040, 991, 973, 893, 835, 769, 728, 756, 739, 575.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and analysis data for all new compounds (PDF)

Accession Codes

CCDC 1873681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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