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Iridium-Catalyzed Intramolecular Oxidative Cyclization of Alkenyl Amides and Alkenoic Acids

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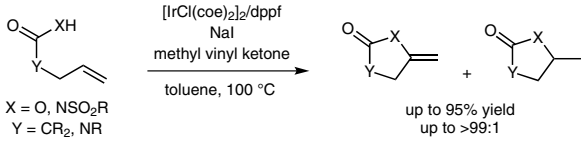

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Abstract An iridium/dppf complex efficiently catalyzed the oxidative cyclization of *N*-sulfonyl alkenyl amides and alkenoic acids. Electron-deficient alkenes were effective as sacrificial hydrogen acceptors. High selectivity of the oxidative cyclization over the competing addition reaction has been realized by the use of NaI as an additive.

Key words iridium, oxidative functionalization, alkenes, amides, carboxylic acids

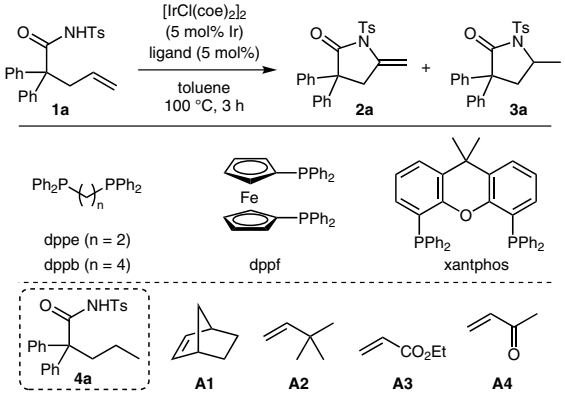
Direct functionalization of readily available alkenes has attracted considerable attention from the aspect of atom and step economy. Additions of heteroatom nucleophiles to alkenes[2] are an important class of transformations as they afford highly valuable building blocks such as enamines and vinyl ethers as a result of oxidative functionalization,[3–7] or alkylamines and ethers as a consequence of the formal addition of heteroatom–hydrogen bond.[8] Late transition-metal catalysts have contributed much to the development of efficient protocols for oxidative functionalization.[3–6] In particular, there have been numerous reports on palladium catalysis: Wacker-type oxidation,[2a,b,e,3] which involves β-hydride elimination as a key step, has been successfully extended to oxidative functionalization of alkenes with various nucleophiles to form carbon–heteroatom bonds. Rhodium complexes have also been studied as versatile catalysts for functionalization of alkenes.[4] Jiménez, Pérez-Torrente, and co-workers reported that cationic rhodium complexes containing flexible hemilabile phosphine ligands exhibit high catalytic activity toward *anti*-Markovnikov oxidative amination.[4d–f] Copper-catalyzed oxidative amination reactions via radical mechanism have also been reported.[5]

Recently we studied iridium-catalyzed hydrofunctionalization reactions of alkenes such as asymmetric cyclization of alkenoic acids and *N*-sulfonyl alkenyl amides leading to chiral γ-lactones and γ-lactams.[9] Although iridium complexes have emerged as effective catalysts for hydrofunctionalization of alkenes,[10] there have been only few reports on oxidative functionalization with heteroatom nucleophiles. Hartwig and co-workers reported iridium-catalyzed amination and etherification of aliphatic alkenes, where oxidative functionalization was competitive with hydrofunctionalization.[10e,f] Herein, we report the iridium-catalyzed intramolecular oxidative functionalization of alkenes with *N*-sulfonyl amides and carboxylic acids.

Treatment of *N*-tosyl-2,2-diphenyl-4-pentenamide (**1a**) in the presence of $[IrCl(coe)_2]_2$ (5 mol% of Ir, coe = cyclooctene) and a bisphosphine ligand (5 mol%) in toluene at 100 °C for 3 hours gave the corresponding cyclization products as a mixture of oxidative amination product **2a** and hydroamination product **3a**, along with **4a** formed by hydrogenation of **1a** (Table 1). The reaction in the presence of an iridium/dppe complex gave hydroamination product **3a** predominantly in low yield (Table 1, entry 1). Dppb and dppf complexes exhibited higher catalytic activity toward cyclization and increased the ratio of oxidative amination product **2a** to 28% and 45%, respectively (entries 2 and 3). By using xantphos, the selectivity of **2a** was improved but the yield of cyclization products was only 12% (entry 4). Norbornene (**A1**) and 3,3-dimethylbut-1-ene (**A2**) were ineffective to decrease the undesirable formation of **4a**, although they have been used as sacrificial hydrogen acceptors for several iridium-catalyzed dehydrogenative functionalization reactions (entries 5 and 6).[11] In contrast, electron-deficient alkenes such as ethyl acrylate (**A3**) and methyl vinyl ketone (MVK, **A4**) successfully suppressed the formation of **4a** (entries 7 and 8). Surprisingly, the reaction

in the presence of NaI (50 mol%) dramatically improved the selectivity of **2a** by up to 97% (entry 9). KI and *n*-Bu_4NI had little effect on the selectivity (entries 10 and 11).

Table 1 Screening Conditions[a]

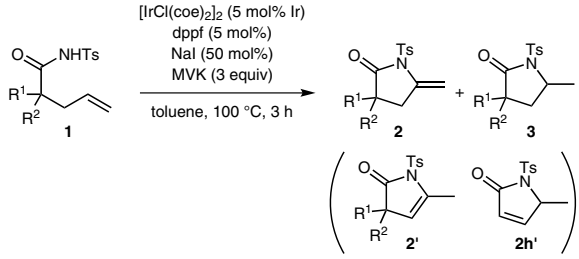


Entry	Ligand	Hydrogen acceptor	Additive	Yield (%) **2a** + **3a**	**2a**/**3a**	Yield (%) **4a**
1	dppe	–	–	15	3/97	0
2	dppb	–	–	66	28/72	17
3	dppf	–	–	62	45/55	24
4	xantphos	–	–	12	73/27	5
5	dppf	**A1**	–	70	53/47	18
6	dppf	**A2**	–	68	51/49	21
7	dppf	**A3**	–	88	70/30	0
8	dppf	**A4**	–	66	82/18	0
9	dppf	**A4**	NaI	99 (92)[b]	97/3	0
10	dppf	**A4**	KI	54	86/14	0
11	dppf	**A4**	*n*-Bu_4NI	83	88/12	0

[a] Reaction conditions: **1a** (0.10 mmol), $[IrCl(coe)_2]_2$ (5 mol% Ir), ligand (5 mol%), hydrogen acceptor (3 equiv), and additive (50 mol%) in toluene (0.40 mL) at 100 °C for 3 h.
[b] Isolated yield in parentheses.

The results obtained for the iridium-catalyzed oxidative cyclization of *N*-sulfonyl alkenyl amides are summarized in Table 2. Amides **1b–e** bearing aryl, *n*-hexyl, and benzyl groups participated in the reaction to give **2b–e** in high yields with high selectivity (Table 2, entries 1–4). The reactions of **1f** and **1g** bearing sterically less bulky cyclic pentamethylene and dimethyl groups proceeded at 120 °C to give the corresponding cyclization products in good yields (entries 5 and 6). Unsubstituted pentenamide **1h** participated in the reaction at 135 °C to give **2h′** in 27% yield (entry 7). In the reaction of amide **1i**, which bears both a terminal- and an internal alkene moiety, cyclization occurred only at the terminal alkene (entry 8). Not only *N*-tosylamides but also *N*-mesylamide **1j** reacted to give the cyclization products in 95% yield with 97% selectivity of **2j** (entry 9).

Table 2 Oxidative Cyclization of Alkenyl Amides[a]

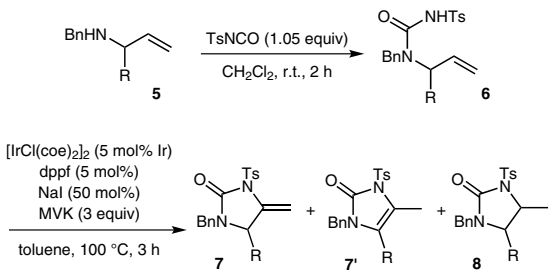


Entry	R^1, R^2	Yield (%) **2** + **3**	**2**/**3**
1	$R^1 = R^2$ = 4-$MeOC_6H_4$ (**1b**)	89	91/9
2[b]	$R^1 = R^2$ = 4-ClC_6H_4 (**1c**)	92	95/5
3[b]	$R^1 = R^2$ = *n*-hexyl (**1d**)	81	>99/1
4	$R^1 = R^2$ = benzyl (**1e**)	89	97/3
5[c]	$R^1 = R^2 = -(CH_2)_5-$ (**1f**)	72	99/1[d]
6[c]	$R^1 = R^2$ = Me (**1g**)	81	97/3[e]
7[f]	$R^1 = R^2$ = H (**1h**)	27	92/8[g]
8	R^1 = Ph, R^2 = cinnamyl (**1i**)	83	98/2
9[h]	$R^1 = R^2$ = Ph (**1j**)	95	97/3

[a] Reaction conditions: **1** (0.20 mmol), $[IrCl(coe)_2]_2$ (5 mol% Ir), dppf (5 mol%), MVK (3 equiv), and NaI (50 mol%) in toluene (0.80 mL) at 100 °C for 3 h.
[b] At 80 °C for 6 h.
[c] Ethyl vinyl ketone instead of MVK in *p*-xylene at 120 °C for 12 h.
[d] **2f**/**2f′** = 23:77.
[e] **2g**/**2g′** = 24:76.
[f] Ethyl vinyl ketone instead of MVK in *p*-xylene at 135 °C for 12 h.
[g] **2h**/**2h′** = 0:100.
[h] *N*-Mesylamide instead of *N*-tosylamide.

Allylamines can be transformed into imidazolidinone derivatives by a one-pot operation. Treatment of allylamines with tosyl isocyanate gave the corresponding *N*-allyl-*N′*-tosylureas, which were subjected to the present catalytic conditions without purification to give the cyclization products. It was found that allylic substituents had a significant effect on the selectivity of the reaction (Table 3). The reaction of an alkenyl urea generated from allylamine (**5a**) gave the cyclization product in moderate yield with 96% selectivity of **7a** (Table 3, entry 1). However, the reaction of allylamine **5b** bearing a methyl group at the allylic position gave the cyclization product as a mixture of **7b** and **8b** in a ratio of 12:88 (entry 2). A sterically bulky cyclohexyl group in **5c** completely suppressed the formation of **7c** and the hydroamination product **8c** was obtained in high yield (entry 3). These results indicate that β-hydride elimination leading to the oxidative cyclization product is inhibited by the steric repulsion between the allylic substituents and the iridium center.

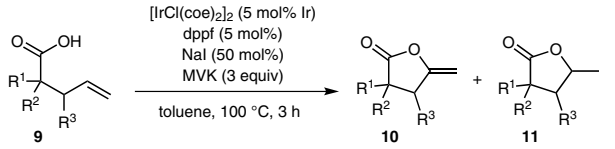
Table 3 Cyclization of Alkenyl Ureas in Situ Generated from Allylamines[a]



Entry	R	Yield (%) **7** + **8**	**7**/**8**
1	H (**5a**)	66	96/4[b]
2	Me (**5b**)	78	12/88
3	Cy (**5c**)	86	<1/99

[a] Reaction conditions for urea formation: **5** (0.20 mmol) and TsNCO (0.21 mmol) in CH_2Cl_2 (0.50 mL) at r.t. for 2 h. Reaction conditions for iridium-catalyzed cyclization: $[IrCl(coe)_2]_2$ (5 mol% Ir), dppf (5 mol%), MVK (3 equiv), and NaI (50 mol%) in toluene (0.80 mL) at 100 °C for 3 h.
[b] **7a**/**7a'** = 10/90.

Table 4 Oxidative Cyclization of Alkenoic Acids[a]



Entry	R^1–R^3	Yield (%) **10** + **11**	**10**/**11**
1	$R^1 = R^2$ = Ph, R^3 = H (**9a**)	95	97/3
2	$R^1 = R^2$ = 4-MeC_6H_4, R^3 = H (**9b**)	95	98/2
3	$R^1 = R^2$ = 4-$MeOC_6H_4$, R^3 = H (**9c**)	93	99/1
4	$R^1 = R^2$ = 4-FC_6H_4, R^3 = H (**9d**)	90	98/2
5[b]	$R^1 = R^2$ = 4-ClC_6H_4, R^3 = H (**9e**)	90	98/2
6	$R^1 = R^2$ = Bn, R^3 = H (**9f**)	83	99/1
7[c]	$R^1 = R^2$ = Me, R^3 = H (**9g**)	59	>99/1
8	R^1 = Ph, R^2 = cinnamyl, R^3 = H (**9h**)	91	99/1
9	$R^1 = R^2$ = Ph, R^3 = Me (**9i**)	84	90/10

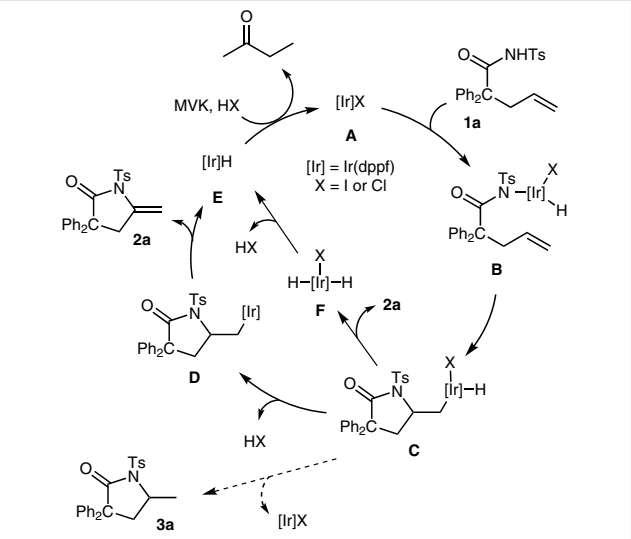
[a] Reaction conditions: **9** (0.20 mmol), $[IrCl(coe)_2]_2$ (5 mol% Ir), dppf (5 mol%), MVK (3 equiv), and NaI (50 mol%) in toluene (0.80 mL) at 100 °C for 3 h.
[b] For 12 h.
[c] Ethyl vinyl ketone instead of MVK in *p*-xylene at 135 °C for 12 h.

The same catalyst system can also be applied to the cyclization of alkenoic acids leading to γ-lactones (Table 4). The reactions of alkenoic acids **9a–e** bearing electron-rich and electron-poor aryl groups gave the cyclization products in high yields with over 97% selectivity of **10a–e** (Table 4, entries 1–5). Alkyl-substituted alkenoic acids **9f** and **9g** also participated in the reaction to give **10f** and **10g**, respectively, with high selectivity (entries 6 and 7). The internal alkene moiety in **9h** did not participate in the reaction (entry 8). A methyl group at β-position in **9i** slightly decreased the selectivity of oxidative cyclization (entry 9).

Hartwig and co-workers reported an iridium-catalyzed addition of benzamides to alkenes,[10e] where it was proposed that the reaction proceeds via N–H oxidative addition and alkene insertion into the Ir–N bond of the resulting amidoiridium(III) species. The formation of a hydridoiridium(III) carboxylate via oxidative addition of carboxylic acid was also confirmed by Mashima and co-workers.[12] Thus, the present reaction might involve oxidative addition of acidic N–H and O–H bonds as the first step. A stoichiometric reaction of $[IrCl(coe)_2]_2$, dppf, and **1h** in benzene-d_6 at room temperature resulted in the formation of hydridoiridium(III) complexes as a mixture of five isomers. These hydridoiridium(III) species showed double doublet or virtual triplet peaks at δ = –22.4, –23.7, –27.4, –27.7, and –29.5 in the ^{1}H NMR spectra, which were assigned to the hydrides at the *cis*-position to two phosphorous atoms.

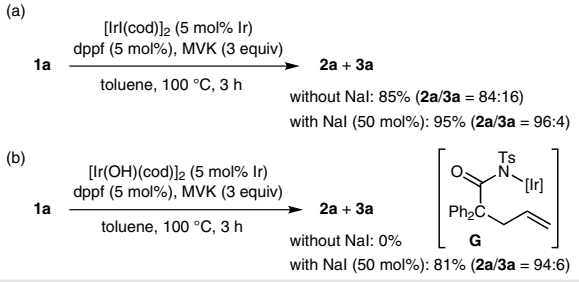
A plausible catalytic cycle of the present reaction is shown in Scheme 1. Oxidative addition of amide **1a** to the iridium/dppf complex **A** generates hydridoiridium(III) species **B**, and alkene insertion into the Ir–N bond generates alkylhydridoiridium(III) species **C**.[13] One possible pathway involves elimination of HX from the intermediate **C** to form alkyliridium(I) species **D**, which undergoes β-hydride elimination to give oxidative cyclization product **2a** and hydridoiridium(I) species **E**. The reaction of **E** with methyl vinyl ketone in the presence of HX gives ethyl methyl ketone and regenerates the iridium catalyst **A**. An alternative pathway involves β-hydride elimination from intermediate **C** to give iridium(III) dihydride **F**, and elimination of HX generates **E** which reacts with MVK. The inefficiency of norbornene and 3,3-dimethylbut-1-ene as hydrogen acceptors implies that the iridium(III) dihydride species is not likely to be directly involved in the hydrogenation of sacrificial alkenes.[11] Instead, the hydrogen transfer would proceed via conjugate addition of the iridium(I) hydride to electron-deficient alkenes and sequential protonation. The key role of sodium iodide might be the halide exchange on the iridium to facilitate the elimination of HX to give the iridium(I) species.

To gain further insight into the reaction mechanism, the effect of counterions of the iridium catalyst was investigated. By using $[IrI(cod)]_2$ as a catalyst precursor, the reaction of **1a** in the absence of NaI gave the cyclization products in 85% yield with 84% selectivity of **2a**. In contrast, the reaction in the presence of NaI (50 mol%) increased the selectivity of **2a** to 96% (Scheme 2a). These results indicate that the excess amount of iodide is essential for the high selectivity of **2**. The reaction of **1a** was also conducted in the presence of $[Ir(OH)(cod)]_2$ as a catalyst precursor, which is expected to react with **1a** to form an amidoiridium(I) species **G** (Scheme 2b). The cyclization products were not obtained in the absence of NaI. This result implies that alkene insertion



Scheme 1 Plausible catalytic cycle

into Ir(I)–N bond does not take place[13] and that the amidoiridium(I) is inactive toward oxidative addition of another molecule of **1a** to form hydridoiridium(III) species. The presence of NaI (50 mol%) prompted the reaction to give the cyclization products in 81% yield with 94% selectivity of **2a**. This is presumably because the catalytically active iodoiridium(I) species was generated from the amidoiridium(I) in the presence of excess NaI.



Scheme 2 Mechanistic studies

In summary, we have developed the oxidative cyclization of *N*-sulfonyl alkenyl amides and alkenoic acids catalyzed by an iridium/dppf complex in the presence of methyl vinyl ketone and NaI. The efficiency of electron-deficient alkenes as sacrificial hydrogen acceptors indicates that an iridium(I) hydride species is involved in the catalytic cycle. The presence of NaI was found to be important to suppress the competing addition reaction.

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried N_2. NMR spectra were recorded on JEOL JNM ECA-600 spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C) and JEOL JNM ECZ-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to the residual peaks of $CDCl_3$ (δ 7.26) for ^{1}H NMR, and $CDCl_3$ (δ 77.00) for ^{13}C NMR. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer. Preparative TLC was performed with Silica Gel 60 PF_{254} (Merck).

Iridium complexes, $[IrCl(coe)_2]_2$,[14] $[IrI(cod)]_2$,[13] and $[Ir(OH)(cod)]_2$[15] were prepared according to the reported procedures. Compounds **1a** (CAS: 1799905-43-3), **1f** (CAS: 1310538-68-1), **1g** (CAS: 1310538-67-0), **1h** (CAS: 413188-48-4), and **1j** (CAS: 1993425-86-7) were prepared from the corresponding carboxylic acids according to the reported procedure.[16] Allyl amines **5b** (CAS: 37857-30-0) and **5c** (CAS: 1826073-73-7) were prepared according to the reported procedure.[17] Compounds **9a** (CAS: 6966-03-6), **9b** (CAS: 138952-03-1), **9c** (CAS: 1803403-23-7), **9d** (CAS: 1397711-73-7), **9e** (CAS: 1803403-24-8), **9f** (CAS: 1803403-25-9), **9g** (CAS: 16386-93-9), and **9i** (CAS: 175879-58-0) were prepared according to the reported procedures.[18,19]

N-Sulfonyl Alkenyl Amides 1; General Procedure[16]

To a solution of alkenoic acid **9** (1.0 equiv) in THF (0.33 M) was added *p*-toluenesulfonyl isocyanate (1.0 equiv), and the mixture was stirred at r.t. for 10 min. To the solution was added Et_3N (1.0 equiv) and the mixture was stirred at r.t. for 6 h. Aq HCl was added to the mixture, and the resulting mixture was extracted with EtOAc (3 ×). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated on a rotary evaporator. The residue was subjected to short column chromatography on silica gel with EtOAc/hexane (1/2) as eluent and recrystallized from EtOAc and hexane to give **1**.

2,2-Bis(4-methoxyphenyl)-*N*-tosylpent-4-enamide (1b)

This compound was prepared from 2,2-bis(4-methoxyphenyl)pent-4-enoic acid (**9c**, CAS: 1803403-23-7) according to the general procedure; yield: 885.4 mg (1.90 mmol, 95%); white solid.

^{1}H NMR ($CDCl_3$): δ = 7.79 (br s, 1 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.04 (d, *J* = 8.9 Hz, 4 H), 6.81 (d, *J* = 8.9 Hz, 4 H), 5.51 (ddt, *J* = 16.9, 10.4, 7.0 Hz, 1 H), 4.88 (d, *J* = 10.4 Hz, 1 H), 4.86 (d, *J* = 16.9 Hz, 1 H), 3.81 (s, 6 H), 2.99 (d, *J* = 7.0 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 171.9, 158.8, 144.9, 135.1, 133.6, 132.2, 129.9, 129.4, 128.4, 118.8, 114.0, 60.2, 55.3, 42.9, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{28}NO_5S$: 466.1683; found: 466.1702.

2,2-Bis(4-chlorophenyl)-*N*-tosylpent-4-enamide (1c)

This compound was prepared from 2,2-bis(4-chlorophenyl)pent-4-enoic acid (**9e**, CAS: 1803403-24-8) according to the general procedure; yield: 339.2 mg (0.72 mmol, 72%); white solid.

^{1}H NMR ($CDCl_3$): δ = 7.80 (br s, 1 H), 7.75 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 8.1 Hz, 4 H), 7.03 (d, *J* = 8.1 Hz, 4 H), 5.47 (ddt, *J* = 17.3, 10.2, 7.0 Hz, 1 H), 4.95 (d, *J* = 10.2 Hz, 1 H), 4.91 (d, *J* = 17.3 Hz, 1 H), 3.01 (d, *J* = 7.0 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.4, 145.3, 138.3, 134.6, 134.0, 132.4, 130.0, 129.4, 128.9, 128.4, 120.1, 60.6, 42.5, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}{}^{35}Cl_2NO_3S$: 474.0692; found: 474.0675.

2-Allyl-2-hexyl-*N*-tosyloctanamide (1d)

This compound was prepared from 2-allyl-2-hexyloctanoic acid (CAS: 1803403-26-0) according to the general procedure; yield: 382.3 mg (0.91 mmol, 91%); white solid.

^{1}H NMR ($CDCl_3$): δ = 8.16 (br s, 1 H), 7.93 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 5.53 (ddt, *J* = 17.0, 10.2, 7.3 Hz, 1 H), 5.05–4.99 (m, 2 H), 2.43 (s, 3 H), 2.22 (d, *J* = 7.3 Hz, 2 H), 1.47–1.41 (m, 2 H), 1.38–1.32 (m, 2 H), 1.26–1.19 (m, 4 H), 1.19–1.13 (m, 8 H), 1.09–1.00 (m, 2 H), 1.00–0.91 (m, 2 H), 0.86 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR ($CDCl_3$): δ = 174.3, 144.9, 135.5, 132.7, 129.4, 128.5, 119.0, 50.0, 37.4, 35.1, 31.5, 29.6, 23.4, 22.5, 21.6, 14.0.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{40}NO_3S$: 422.2723; found: 422.2723.

2,2-Dibenzyl-*N*-tosylpent-4-enamide (1e)

This compound was prepared from 2,2-dibenzylpent-4-enoic acid (**9f**, CAS: 1803403-25-9) according to the general procedure; yield: 327.0 mg (0.75 mmol, 75%); white solid.

^{1}H NMR ($CDCl_3$): δ = 7.92 (d, *J* = 8.2 Hz, 2 H), 7.81 (br s, 1 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.19 (t, *J* = 7.5 Hz, 2 H), 7.13 (t, *J* = 7.5 Hz, 4 H), 6.95 (d, *J* = 7.5 Hz, 4 H), 5.90 (ddt, *J* = 17.0, 10.6, 6.8 Hz, 1 H), 5.27 (d, *J* = 10.6 Hz, 1 H), 5.15 (d, *J* = 17.0 Hz, 1 H), 3.09 (d, *J* = 14.0 Hz, 2 H), 2.76 (d, *J* = 14.0 Hz, 2 H), 2.51 (s, 3 H), 2.17 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 173.4, 145.0, 135.9, 135.4, 132.4, 130.2, 129.4, 129.0, 128.4, 126.9, 120.4, 52.0, 42.3, 35.6, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{28}NO_3S$: 434.1784; found: 434.1795.

(*E*)-2-Allyl-2,5-diphenyl-*N*-tosylpent-4-enamide (1i)

This compound was prepared by the reaction of (*E*)-2-allyl-2,5-diphenylpent-4-enoic acid (**9h**) according to the general procedure; yield: 341.5 mg (0.77 mmol, 77%); white solid.

^{1}H NMR ($CDCl_3$): δ = 7.82 (d, *J* = 7.3 Hz, 2 H), 7.69 (br s, 1 H), 7.37–7.30 (m, 3 H), 7.28–7.23 (m, 4 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 7.13 (d, *J* = 7.3 Hz, 2 H), 7.11 (d, *J* = 7.3 Hz, 2 H), 6.29 (d, *J* = 14.4 Hz, 1 H), 5.64 (dt, *J* = 14.4, 7.5 Hz, 1 H), 5.42–5.35 (m, 1 H), 5.01 (d, *J* = 10.2 Hz, 1 H), 5.00 (d, *J* = 17.0 Hz, 1 H), 2.77 (d, *J* = 7.5 Hz, 2 H), 2.68 (dd, *J* = 14.8, 8.0 Hz, 1 H), 2.64 (dd, *J* = 14.8, 8.0 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 172.5, 145.0, 139.7, 136.9, 135.3, 134.4, 132.0, 129.4, 129.2, 128.5, 128.4, 128.1, 127.4, 127.0, 126.2, 123.4, 119.7, 55.0, 39.1, 38.3, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}NO_3S$: 446.1784; found: 446.1792.

Alkenoic Acids 9a–h; General Procedure[18]

To a solution of *i*-Pr_2NH (2.5 equiv) in THF (4.0 M) at 0 °C was slowly added *n*-BuLi (1.63 M in hexane, 2.5 equiv), and the mixture was stirred at 0 °C for 1 h. To the solution was added the appropriate α,α-disubstituted acetic acid (1.0 equiv) in THF (0.8 M), and the mixture was stirred at 45 °C for 1.5 h. Allyl bromide (2.0 equiv) was added to the solution and the mixture was stirred at 45 °C overnight. H_2O was added to the mixture and the aqueous layer was washed with Et_2O. The aqueous layer was acidified with aq HCl, and the mixture was extracted with Et_2O (3 ×). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated on a rotary evaporator. The solid residue was recrystallized from $CHCl_3$ and hexane to give **9**.

(*E*)-2-Allyl-2,5-diphenylpent-4-enoic Acid (9h)

This compound was prepared from (*E*)-2,5-diphenylpent-4-enoic acid (CAS: 351207-71-1) according to the general procedure; yield: 649.0 mg (2.2 mmol, 55%); white solid.

^{1}H NMR ($CDCl_3$): δ = 7.39–7.34 (m, 4 H), 7.31–7.24 (m, 5 H), 7.22–7.18 (m, 1 H), 6.23 (d, *J* = 14.3 Hz, 1 H), 5.91 (dt, *J* = 14.3, 7.3 Hz, 1 H), 5.62 (ddt, *J* = 17.5, 10.1, 7.3 Hz, 1 H), 5.13 (d, *J* = 17.5 Hz, 1 H), 5.10 (d, *J* = 10.1 Hz, 1 H), 2.98 (dd, *J* = 13.9, 7.3 Hz, 1 H), 2.92 (dd, *J* = 13.9, 7.3 Hz, 1 H), 2.88 (dd, *J* = 13.9, 7.3 Hz, 1 H), 2.82 (dd, *J* = 13.9, 7.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 180.1, 140.9, 137.3, 133.9, 133.1, 128.54, 128.46, 127.2, 126.5, 126.1, 124.7, 119.0, 53.7, 38.8, 38.0.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}O_2$: 293.1536; found: 293.1546.

Ir-Catalyzed Oxidative Cyclization (Tables 1, 2, and 4)

Additive (50 mol%), dppf (5 mol%), and $[IrCl(coe)_2]_2$ (5 mol% of Ir) were placed in a Schlenk tube under N_2. Toluene (0.25 M) and hydrogen acceptor (3.0 equiv) were added and the mixture was stirred at r.t. for 10 min. *N*-Sulfonyl alkenyl amide **1** or alkenoic acid **9** (1.0 equiv) was added to the Schlenk tube and the tube was capped with a glass stopper and heated at 100 °C for 3 h with stirring. The mixture was passed through a short plug of silica gel with EtOAc as eluent and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel to give the corresponding cyclization products.

Ir-Catalyzed Oxidative Cyclization of *N*-Sulfonyl Alkenyl Ureas Generated in Situ (Table 3)

To a solution of amine **5** (0.20 mmol) in CH_2Cl_2 (0.50 mL) was added *p*-toluenesulfonyl isocyanate (32.1 μL, 0.21 mmol), and the mixture was stirred at r.t. for 2 h. The solvent was removed under vacuum at r.t. To the mixture were added NaI (15.0 mg, 50 mol%), dppf (5.5 mg, 5 mol%), $[IrCl(coe)_2]_2$ (4.5 mg, 0.010 mmol of Ir), toluene (0.80 mL), and methyl vinyl ketone (50 μL, 0.60 mmol) under N_2. The Schlenk tube was capped with a glass stopper and heated at 100 °C for 3 h with stirring. The mixture was passed through a short plug of silica gel with EtOAc as an eluent and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel to give the corresponding cyclization products.

5-Methylene-3,3-diphenyl-1-tosylpyrrolidin-2-one (2a) and 5-Methyl-3,3-diphenyl-1-tosylpyrrolidin-2-one (3a)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2a** and **3a** (97/3) in 92% yield (37.1 mg, 0.092 mmol).

Compound 2a

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.83 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 7.22–7.19 (m, 6 H), 7.11–7.08 (m, 4 H), 5.58–5.57 (m, 1 H), 4.67–4.66 (m, 1 H), 3.34–3.33 (m, 2 H), 2.43 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 174.0, 145.4, 140.7, 138.4, 134.8, 129.4, 128.4, 128.0, 127.5, 127.4, 94.6, 57.2, 42.5, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}NO_3S$: 404.1315; found: 404.1309.

Compound 3a (CAS: 2019142-42-6)

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.83 (d, *J* = 8.7 Hz, 2 H), 7.26–7.13 (m, 10 H), 7.07 (d, *J* = 8.7 Hz, 2 H), 4.29–4.23 (m, 1 H), 3.05 (dd, *J* = 13.3, 6.8 Hz, 1 H), 2.43 (s, 3 H), 2.41 (dd, *J* = 13.3, 7.5 Hz, 1 H), 1.52 (d, *J* = 6.1 Hz, 3 H).

3,3-Bis(4-methoxyphenyl)-5-methylene-1-tosylpyrrolidin-2-one (2b) and 3,3-Bis(4-methoxyphenyl)-5-methyl-1-tosylpyrrolidin-2-one (3b)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2b** and **3b** (91/9) in 89% yield (82.8 mg, 0.178 mmol).

Compound 2b

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.80 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.00 (d, *J* = 8.1 Hz, 4 H), 6.72 (d, *J* = 8.1 Hz, 4 H), 5.56 (d, *J* = 1.4 Hz, 1 H), 4.64 (d, *J* = 1.4 Hz, 1 H), 3.76 (s, 6 H), 3.26 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 174.4, 158.7, 145.3, 138.6, 134.8, 132.8, 129.4, 128.6, 127.9, 113.8, 94.4, 56.0, 55.2, 42.8, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{26}NO_5S$: 464.1526; found: 464.1544.

Compound 3b

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.81 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.05 (d, *J* = 8.9 Hz, 2 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 6.76 (d, *J* = 8.9 Hz, 2 H), 6.70 (d, *J* = 8.9 Hz, 2 H), 4.25–4.19 (m, 1 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 2.97 (dd, *J* = 13.3, 6.8 Hz, 1 H), 2.42 (s, 3 H), 2.32 (dd, *J* = 13.3, 7.5 Hz, 1 H), 1.52 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 174.9, 158.7, 158.4, 144.7, 135.3, 134.4, 132.0, 129.2, 128.8, 128.4, 128.3, 113.8, 113.7, 56.7, 55.2, 53.6, 42.5, 22.0, 21.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{28}NO_5S$: 466.1683; found: 466.1687.

3,3-Bis(4-chlorophenyl)-5-methylene-1-tosylpyrrolidin-2-one(2c) and 3,3-Bis(4-chlorophenyl)-5-methyl-1-tosylpyrrolidin-2-one (3c)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2c** and **3c** (95/5) in 92% yield (87.0 mg, 0.184 mmol).

Compound 2c

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 2 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.17 (d, *J* = 8.8 Hz, 4 H), 7.01 (d, *J* = 8.8 Hz, 4 H), 5.61 (d, *J* = 1.4 Hz, 1 H), 4.69 (d, *J* = 1.4 Hz, 1 H), 3.26 (s, 2 H), 2.44 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 173.3, 145.7, 138.6, 137.8, 134.2, 133.8, 129.4, 128.8, 128.7, 127.9, 95.0, 56.3, 42.1, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{20}{}^{35}Cl_2NO_3S$: 472.0535; found: 472.0533.

Compound 3c

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.78 (d, *J* = 8.8 Hz, 2 H), 7.24–7.20 (m, 4 H), 7.14 (d, *J* = 8.8 Hz, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 4.26–4.20 (m, 1 H), 2.99 (dd, *J* = 13.4, 6.8 Hz, 1 H), 2.44 (s, 3 H), 2.31 (dd, *J* = 13.4, 7.8 Hz, 1 H), 1.54 (d, *J* = 5.4 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 173.8, 145.2, 140.3, 137.7, 134.7, 133.7, 133.4, 129.3, 129.0, 128.8, 128.7, 128.2, 56.9, 53.6, 41.9, 22.2, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}{}^{35}Cl_2NO_3S$: 474.0692; found: 474.0707.

3,3-Dihexyl-5-methylene-1-tosylpyrrolidin-2-one (2d)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give **2d** in 81% yield (33.9 mg, 0.081 mmol) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.93 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 2 H), 5.50 (d, *J* = 2.1 Hz, 1 H), 4.53 (d, *J* = 1.4 Hz, 1 H), 2.52 (s, 2 H), 2.42 (s, 3 H), 1.45–1.33 (m, 4 H), 1.22–1.16 (m, 4 H), 1.15–1.05 (m, 10 H), 0.84 (t, *J* = 7.5 Hz, 6 H), 0.86–0.78 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 178.2, 145.2, 139.8, 135.4, 129.4, 128.0, 93.4, 47.3, 37.2, 37.1, 31.5, 29.5, 23.7, 22.4, 21.7, 14.0.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{38}NO_3S$: 420.2567; found: 420.2563.

3,3-Dibenzyl-5-methylene-1-tosylpyrrolidin-2-one (2e) and 3,3-Dibenzyl-5-methyl-1-tosylpyrrolidin-2-one (3e)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2e** and **3e** (97/3) in 89% yield (77.2 mg, 0.178 mmol) as colorless oils.

Compound 2e

^{1}H NMR ($CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.18 (t, *J* = 7.5 Hz, 2 H), 7.11 (t, *J* = 7.5 Hz, 4 H), 6.94 (d, *J* = 7.5 Hz, 4 H), 5.10 (s, 1 H), 4.22 (s, 1 H), 3.08 (d, *J* = 13.3 Hz, 2 H), 2.63 (d, *J* = 13.3 Hz, 2 H), 2.50 (s, 2 H), 2.49 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 177.0, 145.1, 138.7, 135.7, 135.3, 130.2, 129.4, 128.33, 128.27, 126.8, 94.0, 50.4, 42.6, 34.2, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{26}NO_3S$: 432.1628; found: 432.1635.

Compound 3e

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.24–7.18 (m, 3 H), 7.14 (d, *J* = 8.1 Hz, 1 H), 7.07 (t, *J* = 8.1 Hz, 2 H), 7.03 (d, *J* = 8.1 Hz, 2 H), 6.94 (d, *J* = 8.1 Hz, 2 H), 3.56–3.49 (m, 1 H), 3.20 (d, *J* = 13.6 Hz, 1 H), 3.12 (d, *J* = 13.6 Hz, 1 H), 2.57 (d, *J* = 10.2 Hz, 1 H), 2.55 (d, *J* = 10.2 Hz, 1 H), 2.50 (s, 3 H), 2.22 (dd, *J* = 13.6, 9.5 Hz, 1 H), 1.54 (dd, *J* = 13.6, 5.4 Hz, 1 H), 0.78 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 177.5, 144.6, 136.8, 136.3, 136.0, 130.4, 130.2, 129.2, 128.6, 128.4, 128.3, 126.9, 126.8, 53.0, 51.5, 44.8, 44.0, 33.0, 22.2, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{28}NO_3S$: 434.1784; found: 434.1795.

3-Methylene-2-tosyl-2-azaspiro[4.5]decan-1-one (2f), 3-Methyl-2-tosyl-2-azaspiro[4.5]dec-3-en-1-one (2f′), and 3-Methyl-2-tosyl-2-azaspiro[4.5]decan-1-one (3f)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2f**, **2f′**, **3f** (23/76/1) in 72% yield (51.7 mg, 0.162 mmol). Compound **2f** could not be separated from compound **2f′**.

Compound 2f

Colorles oil.

^{1}H NMR ($CDCl_3$): δ = 7.89 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.48 (d, *J* = 1.4 Hz, 1 H), 4.56 (d, *J* = 1.4 Hz, 1 H), 2.52 (s, 2 H), 2.41 (s, 3 H), 1.70–1.20 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 178.3, 145.2, 139.2, 135.4, 129.5, 127.8, 94.4, 44.9, 38.2, 32.0, 25.0, 21.6.

Compound 2f′

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 5.38 (s, 1 H), 2.42 (s, 3 H), 2.29 (s, 3 H), 1.72–1.52 (m, 4 H), 1.36–1.22 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 180.6, 144.8, 137.4, 136.2, 129.6, 127.7, 113.5, 50.0, 32.9, 25.2, 22.0, 21.6, 16.8.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{22}NO_3S$: 320.1315; found: 320.1305.

Compound 3f

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 4.32–4.26 (m, 1 H), 2.42 (s, 3 H), 2.23 (dd, *J* = 12.9, 8.2 Hz, 1 H), 1.54 (d, *J* = 6.1 Hz, 3 H), 1.70–1.52 (m, 5 H), 1.43–1.37 (m, 2 H), 1.29–1.20 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 178.6, 144.7, 136.1, 129.4, 128.2, 53.3, 45.5, 38.2, 33.6, 33.0, 25.1, 23.4, 21.7, 21.63, 21.57.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{24}NO_3S$: 322.1471; found: 322.1478.

3,3-Dimethyl-5-methylene-1-tosylpyrrolidin-2-one (2g), 3,3,5-Trimethyl-1-tosyl-1,3-dihydro-2*H*-pyrrol-2-one (2g′), and 3,3,5-Trimethyl-1-tosylpyrrolidin-2-one (3g)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2g**, **2g′**, and **3g** (23/74/3) in 81% yield (40.0 mg, 0.144 mmol).

Compound 2g (CAS: 1875033-08-1)

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.92 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 5.52 (d, *J* = 2.0 Hz, 1 H), 4.58 (d, *J* = 2.0 Hz, 1 H), 2.47 (s, 2 H), 2.44 (s, 3 H), 1.09 (s, 6 H).

Compound 2g′

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 7.2 Hz, 2 H), 7.32 (d, *J* = 7.2 Hz, 2 H), 5.07 (s, 1 H), 2.43 (s, 3 H), 2.26 (s, 3 H), 1.07 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 181.2, 144.9, 137.0, 136.0, 129.6, 127.7, 116.3, 45.2, 23.7, 21.6, 16.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{18}NO_3S$: 280.1002; found: 280.1005.

Compound 3g

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.92 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 4.33–4.27 (m, 1 H), 2.43 (s, 3 H), 2.13 (dd, *J* = 12.9, 8.2 Hz, 1 H), 1.55 (dd, *J* = 12.9, 6.8 Hz, 1 H), 1.55 (d, *J* = 6.1 Hz, 3 H), 1.14 (s, 3 H), 1.01 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 179.0, 144.8, 136.0, 129.4, 128.2, 53.1, 42.2, 41.2, 25.2, 23.0, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{20}NO_3S$: 282.1158; found: 282.1172.

5-Methyl-1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (2h′) and 5-Methyl-1-tosylpyrrolidin-2-one (3h)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2h′** and **3h** (92/8) in 27% yield (13.6 mg, 0.054 mmol) as colorless oils.

Compound 2h′ (CAS: 96013-62-6)

^{1}H NMR ($CDCl_3$): δ = 7.96 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.14 (dd, *J* = 6.0, 1.7 Hz, 1 H), 5.97 (dd, *J* = 6.0, 1.7 Hz, 1 H), 4.87 (qt, *J* = 6.3, 1.7 Hz, 1 H), 2.42 (s, 3 H), 1.58 (d, *J* = 6.3 Hz, 3 H).

Compound 3h (CAS: 118429-46-2)

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 4.55–4.50 (m, 1 H), 2.59–2.52 (m, 1 H), 2.43 (s, 3 H), 2.39–2.32 (m, 1 H), 2.31–2.23 (m, 1 H), 1.74–1.69 (m, 1 H), 1.47 (d, *J* = 6.1 Hz, 3 H).

3-Cinnamyl-5-methylene-3-phenyl-1-tosylpyrrolidin-2-one (2i) and 3-Cinnamyl-5-methyl-3-phenyl-1-tosylpyrrolidin-2-one (3i)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2i** and **3i** (98/2) in 83% yield (73.3 mg, 0.166 mmol).

Compound 2i

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.86 (d, *J* = 7.5 Hz, 2 H), 7.33–7.24 (m, 7 H), 7.23–7.18 (m, 3 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 6.31 (d, *J* = 14.4 Hz, 1 H), 5.75 (dt, *J* = 14.4, 7.4 Hz, 1 H), 5.52 (d, *J* = 1.3 Hz, 1 H), 4.62 (d, *J* = 1.3 Hz, 1 H), 3.07 (d, *J* = 14.0 Hz, 1 H), 2.99 (d, *J* = 14.0 Hz, 1 H), 2.77 (dd, *J* = 13.8, 7.4 Hz, 1 H), 2.71 (dd, *J* = 13.8, 7.4 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 175.3, 145.3, 139.3, 138.8, 136.7, 135.1, 134.6, 129.4, 128.7, 128.4, 127.9, 127.53, 127.50, 126.2, 126.1, 123.6, 94.7, 52.1, 42.0, 38.4, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{26}NO_3S$: 444.1628; found: 444.1625.

Compound 3i

Colorless oil; d.r. = 60:40.

^{1}H NMR ($CDCl_3$): δ = 7.94 [d, *J* = 8.2 Hz, 2 H (minor)], 7.75 [d, *J* = 8.2 Hz, 2 H (major)], 7.35–7.15 [m, 10 H (major) + 12 H (minor)], 7.10 [d, *J* = 8.2 Hz, 2 H (major)], 6.33 [d, *J* = 14.0 Hz, 1 H (major)], 6.30 [d, *J* = 14.0 Hz, 1 H (minor)], 5.87 [dt, *J* = 14.0, 7.6 Hz, 1 H (major)], 5.74 [dt, *J* = 14.0, 7.6 Hz, 1 H (minor)], 4.42–4.36 [m, 1 H (minor)], 4.11–4.05 [m, 1 H (major)], 2.74–2.62 [m, 3 H (major) + 2 H (minor)], 2.54 [dd, *J* = 14.0, 8.2 Hz, 1 H (minor)], 2.43 [s, 3 H (minor)], 2.42 [s, 3 H (major)], 2.24 [dd, *J* = 14.0, 2.7 Hz, 1 H (minor)], 1.90 [dd, *J* = 13.3. 9.2 Hz, 1 H (major)], 1.59 [d, *J* = 6.1 Hz, 3 H (major)], 1.25 [d, *J* = 6.1 Hz, 3 H (minor)].

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}NO_3S$: 446.1784; found: 446.1771.

1-Methanesulfonyl-5-methylene-3,3-diphenylpyrrolidin-2-one (2j) and 1-Methanesulfonyl-5-methyl-3,3-diphenylpyrrolidin-2-one (3j)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **2j** and **3j** (97/3) in 95% yield (62.2 mg, 0.190 mmol).

Compound 2j

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.36–7.28 (m, 10 H), 5.41 (d, *J* = 1.7 Hz, 1 H), 4.68 (d, *J* = 1.7 Hz, 1 H), 3.44 (s, 2 H), 3.29 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 175.3, 140.9, 138.0, 128.7, 127.7, 127.5, 95.1, 57.3, 42.8, 41.3.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}NO_3S$: 328.1002; found: 328.1010.

Compound 3j (CAS: 1993426-09-7)

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.36–7.31 (m, 8 H), 7.31–7.25 (m, 2 H), 4.31–4.25 (m, 1 H), 3.26 (s, 3 H), 3.13 (dd, *J* = 13.3, 6.8 Hz, 1 H), 2.56 (dd, *J* = 13.3, 6.1 Hz, 1 H), 1.43 (d, *J* = 6.1 Hz, 3 H).

1-Benzyl-4-methylene-3-tosylimidazolidin-2-one (7a), 1-Benzyl-4-methyl-3-tosyl-1,3-dihydro-2*H*-imidazol-2-one (7a′), and 1-Benzyl-4-methyl-3-tosylimidazolidin-2-one (8a)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **7a**, **7a′**, and **8a** (10/86/4) in 66% yield (45.2 mg, 0.132 mmol).

Compound 7a

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.96 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.32–7.27 (m, 3 H), 7.15–7.12 (m, 2 H), 5.51 (q, *J* = 2.3 Hz, 1 H), 4.43 (q, *J* = 2.3 Hz, 1 H), 4.36 (s, 2 H), 3.81 (t, *J* = 2.3 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 153.0, 145.1, 135.6, 134.9, 134.4, 129.6, 128.9, 128.2, 128.1, 127.9, 91.9, 47.3, 47.2, 21.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}N_2O_3S$: 343.1111; found: 343.1121.

Compound 7a′

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.99 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.32–7.27 (m, 3 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 5.80 (s, 1 H), 4.58 (s, 2 H), 2.44 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 150.9, 145.3, 135.6, 135.5, 129.7, 128.8, 128.13, 128.08, 128.0, 119.0, 110.1, 46.8, 21.7, 13.3.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}N_2O_3S$: 343.1111; found: 343.1112.

Compound 8a

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.96 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.31–7.26 (m, 3 H), 7.13 (d, *J* = 8.1 Hz, 2 H), 4.34 (dd, *J* = 14.7 Hz, 1 H), 4.37–4.31 (m, 1 H), 4.27 (d, *J* = 14.7 Hz, 1 H), 3.40 (t, *J* = 9.1 Hz, 1 H), 2.79 (dd, *J* = 9.1, 4.1 Hz, 1 H), 2.44 (s, 3 H), 1.44 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 153.8, 144.4, 136.4, 135.4, 129.4, 128.7, 128.2, 128.1, 127.9, 50.4, 49.1, 47.6, 21.9, 21.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{21}N_2O_3S$: 345.1267; found: 345.1284.

1-Benzyl-5-methyl-4-methylene-3-tosylimidazolidin-2-one (7b) and 1-Benzyl-*trans*-4,5-dimethyl-3-tosylimidazolidin-2-one (8b)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/2) to give a mixture of **7b** and **8b** (12/88) in 78% yield (55.5 mg, 0.156 mmol).

Compound 7b

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.30–7.25 (m, 3 H), 7.12–7.08 (m, 2 H), 5.55 (t, *J* = 2.2 Hz, 1 H), 4.80 (d, *J* = 15.3 Hz, 1 H), 4.42 (t, *J* = 2.2 Hz, 1 H), 3.97 (d, *J* = 15.3 Hz, 1 H), 3.94–3.90 (m, 1 H), 2.46 (s, 3 H), 1.21 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 152.6, 145.0, 141.1, 135.7, 135.3, 129.6, 128.8, 128.0, 127.94, 127.90, 91.8, 52.9, 44.7, 21.7, 19.7.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{21}N_2O_3S$: 357.1267; found: 357.1268.

Compound 8b

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 7.9 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.31–7.25 (m, 3 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 4.72 (d, *J* = 15.0 Hz, 1 H), 3.92 (d, *J* = 15.0 Hz, 1 H), 3.83 (qd, *J* = 6.1, 3.8 Hz, 1 H), 2.99 (qd, *J* = 6.1, 3.8 Hz, 1 H), 2.44 (s, 3 H), 1.39 (d, *J* = 6.1 Hz, 3 H), 1.07 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 153.3, 144.4, 136.3, 135.8, 129.5, 128.7, 128.1, 128.0, 127.8, 58.2, 55.7, 44.9, 21.6, 21.0, 18.1.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_3S$: 359.1424; found: 359.1423.

1-Benzyl-*trans*-5-cyclohexyl-4-methyl-3-tosylimidazolidin-2-one (8c)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/3) to give a mixture of **8c** in 86% yield (73.4 mg, 0.172 mmol) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 2 H), 7.34–7.26 (m, 5 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 4.82 (d, *J* = 14.9 Hz, 1 H), 4.09 (qd, *J* = 6.4, 2.9 Hz, 1 H), 3.86 (d, *J* = 14.9 Hz, 1 H), 2.79 (t, *J* = 2.9 Hz, 1 H), 2.43 (s, 3 H), 1.74 (br d, *J* = 12.9 Hz, 1 H), 1.68–1.58 (m, 2 H), 1.53–1.47 (m, 1 H), 1.33 (br d, *J* = 13.3 Hz, 1 H), 1.30 (d, *J* = 6.4 Hz, 3 H), 1.24 (br d, *J* = 13.3 Hz, 1 H), 1.21–1.12 (m, 1 H), 1.11–1.03 (m, 1 H), 1.03–0.93 (m, 2 H), 0.72–0.64 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 153.3, 144.4, 136.7, 135.9, 129.4, 128.7, 128.09, 128.07, 127.8, 64.0, 51.7, 45.2, 38.3, 28.0, 26.2, 26.1, 25.6, 24.9, 23.2, 21.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{31}N_2O_3S$: 427.2050; found: 427.2039.

5-Methylene-3,3-diphenyldihydrofuran-2(3*H*)-one (10a) and 5-Methyl-3,3-diphenyldihydrofuran-2(3*H*)-one (11a)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10a** and **11a** (97/3) in 95% yield (43.9 mg, 0.190 mmol).

Compound 10a (CAS: 137415-99-7)

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.36–7.33 (m, 8 H), 7.32–7.28 (m, 2 H), 4.82–4.80 (m, 1 H), 4.44–4.42 (m, 1 H), 3.57 (t, *J* = 1.7 Hz, 2 H).

Compound 11a (CAS: 1729-20-0)

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.38–7.21 (m, 10 H), 4.51–4.45 (m, 1 H), 3.06 (dd, *J* = 12.9, 4.8 Hz, 1 H), 2.59 (dd, *J* = 12.9, 10.2 Hz, 1 H), 1.46 (d, *J* = 6.1 Hz, 3 H).

3,3-Bis(4-methylphenyl)-5-methylenedihydrofuran-2(3*H*)-one (10b) and 3,3-Bis(4-methylphenyl)-5-methyldihydrofuran-2(3*H*)-one (11b)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10b** and **11b** (98/2) in 95% yield (52.9 mg, 0.190 mmol).

Compound 10b

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.21 (d, *J* = 8.1 Hz, 4 H), 7.14 (d, *J* = 8.1 Hz, 4 H), 4.79–4.77 (m, 1 H), 4.41–4.40 (m, 1 H), 3.53 (s, 2 H), 2.33 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 175.4, 152.9, 138.0, 137.4, 129.4, 127.2, 89.2, 56.6, 41.8, 21.0.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O_2$: 279.1380; found: 279.1392.

Compound 11b [CAS: 1803403-16-8 for (*R*)-11b]

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.25 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.16 (d, *J* = 8.1 Hz, 2 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 4.50–4.44 (m, 1 H), 3.02 (dd, *J* = 12.9, 4.8 Hz, 1 H), 2.55 (dd, *J* = 12.9, 10.2 Hz, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 1.46 (d, *J* = 6.1 Hz, 3 H).

3,3-Bis(4-methoxyphenyl)-5-methylenedihydrofuran-2(3*H*)-one (10c) and 3,3-Bis(4-methoxyphenyl)-5-methyldihydrofuran-2(3*H*)-one (11c)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/3) to give a mixture of **10c** and **11c** (99/1) in 93% yield (58.0 mg, 0.186 mmol).

Compound 10c

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.24 (d, *J* = 8.9 Hz, 4 H), 6.86 (d, *J* = 8.9 Hz, 4 H), 4.79–4.78 (m, 1 H), 4.42–4.41 (m, 1 H), 3.79 (s, 6 H), 3.50 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 175.7, 158.9, 152.9, 133.1, 128.4, 114.0, 89.2, 56.0, 55.3, 42.0.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; found: 311.1287.

Compound 11c [CAS: 1803403-17-9 for (*R*)-11c]

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.26 (d, *J* = 8.9 Hz, 2 H), 7.19 (d, *J* = 8.9 Hz, 2 H), 6.86 (d, *J* = 8.9 Hz, 2 H), 6.82 (d, *J* = 8.9 Hz, 2 H), 4.48–4.42 (m, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 2.99 (dd, *J* = 12.9, 4.8 Hz, 1 H), 2.51 (dd, *J* = 12.9, 10.2 Hz, 1 H), 1.44 (d, *J* = 6.1 Hz, 3 H).

3,3-Bis(4-fluorophenyl)-5-methylenedihydrofuran-2(3*H*)-one (10d) and 3,3-Bis(4-fluorophenyl)-5-methyldihydrofuran-2(3*H*)-one (11d)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10d** and **11d** (98/2) in 90% yield (26.1 mg, 0.090 mmol).

Compound 10d

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.29 (dd, *J* = 8.9, 4.8 Hz, 4 H), 7.04 (t, *J* = 8.9 Hz, 4 H), 4.84–4.82 (m, 1 H), 4.47–4.46 (m, 1 H), 3.52 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 174.9, 162.2 (d, $J_{F,C}$ = 248 Hz), 152.2, 136.4 (d, $J_{F,C}$ = 3 Hz), 129.1 (d, $J_{F,C}$ = 9 Hz), 115.7 (d, $J_{F,C}$ = 22 Hz), 89.9, 56.1, 41.8.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{13}F_2O_2$: 287.0878; found: 287.0891.

Compound 11d [CAS: 1803403-18-0 for (*R*)-11d]

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.33–7.29 (m, 2 H), 7.28–7.24 (m, 2 H), 7.04 (t, *J* = 8.7 Hz, 2 H), 6.99 (t, *J* = 8.7 Hz, 2 H), 4.49–4.43 (m, 1 H), 3.01 (dd, *J* = 12.9, 4.8 Hz, 1 H), 2.53 (dd, *J* = 12.9, 10.2 Hz, 1 H), 1.46 (d, *J* = 6.1 Hz, 3 H).

3,3-Bis(4-chlorophenyl)-5-methylenedihydrofuran-2(3*H*)-one (10e) and 3,3-Bis(4-chlorophenyl)-5-methyldihydrofuran-2(3*H*)-one (11e)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10e** and **11e** (98/2) in 90% yield (57.7 mg, 0.180 mmol).

Compound 10e

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.33 (d, *J* = 8.1 Hz, 4 H), 7.25 (d, *J* = 8.1 Hz, 4 H), 4.84 (q, *J* = 1.7 Hz, 1 H), 4.47 (q, *J* = 1.7 Hz, 1 H), 3.51 (t, *J* = 1.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 174.4, 152.0, 138.9, 134.1, 129.0, 128.7, 90.1, 56.3, 41.4.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{13}{}^{35}Cl_2O_2$: 319.0287; found: 319.0286.

Compound 11e [CAS: 1803403-19-1 for (*R*)-11e]

White solid.

^{1}H NMR ($CDCl_3$): δ = 7.32 (d, *J* = 8.8 Hz, 2 H), 7.29–7.22 (m, 6 H), 4.49–4.43 (m, 1 H), 2.99 (dd, *J* = 12.9, 4.8 Hz, 1 H), 2.53 (dd, *J* = 12.9, 10.9 Hz, 1 H), 1.46 (d, *J* = 6.1 Hz, 3 H).

3,3-Dibenzyl-5-methylenedihydrofuran-2(3*H*)-one (10f) and 3,3-Dibenzyl-5-methyldihydrofuran-2(3*H*)-one (11f)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10f** and **11f** (99/1) in 83% yield (46.8 mg, 0.166 mmol).

Compound 10f

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.31–7.24 (m, 6 H), 7.17 (d, *J* = 8.1 Hz, 4 H), 4.34 (q, *J* = 1.7 Hz, 1 H), 3.94–3.92 (m, 1 H), 3.21 (d, *J* = 13.5 Hz, 2 H), 2.81 (d, *J* = 13.5 Hz, 2 H), 2.71 (t, *J* = 1.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 178.5, 153.1, 135.7, 130.3, 128.5, 127.2, 88.3, 51.1, 42.9, 32.9.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O_2$: 279.1380; found: 279.1390.

Compound 11f [CAS: 1803403-20-4 for (*R*)-11f]

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.31–7.17 (m, 10 H), 3.41–3.35 (m, 1 H), 3.27 (d, *J* = 13.5 Hz, 1 H), 3.16 (d, *J* = 13.5 Hz, 1 H), 2.77 (d, *J* = 13.2 Hz, 1 H), 2.71 (d, *J* = 13.2 Hz, 1 H), 2.17 (dd, *J* = 13.2, 7.1 Hz, 1 H), 1.77 (dd, *J* = 13.2, 9.2 Hz, 1 H), 0.84 (d, *J* = 6.8 Hz, 3 H).

3,3-Dimethyl-5-methylenedihydrofuran-2(3*H*)-one (10g) (CAS: 86972-24-9)

The crude mixture was subjected to column chromatography on silica gel with Et_2O/pentane (1:4) to give a mixture of **10g** in 59% yield (22.5 mg, 0.177 mmol) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 4.75 (d, *J* = 1.9 Hz, 1 H), 4.32 (d, *J* = 1.9 Hz, 1 H), 2.69 (t, *J* = 1.9 Hz, 2 H), 1.30 (s, 6 H).

3-Cinnamyl-5-methylene-3-phenyldihydrofuran-2(3*H*)-one (10h) and 3-Cinnamyl-5-methyl-3-phenyldihydrofuran-2(3*H*)-one (11h)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/4) to give a mixture of **10h** and **11h** (99/1) in 91% yield (53.1 mg, 0.182 mmol).

Compound 10h

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.50 (d, *J* = 7.8 Hz, 2 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.30–7.27 (m, 4 H), 7.25–7.21 (m, 1 H), 6.48 (d, *J* = 14.4 Hz, 1 H), 6.00 (dt, *J* = 14.4, 7.5 Hz, 1 H), 4.76 (d, *J* = 1.9 Hz, 1 H), 4.36 (*J* = 1.9 Hz, 1 H), 3.25 (dt, *J* = 16.0, 1.9 Hz, 1 H), 3.21 (dt, *J* = 16.0, 1.9 Hz, 1 H), 2.91 (dd, *J* = 13.5, 7.5 Hz, 1 H), 2.88 (dd, *J* = 13.5, 7.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 176.4, 153.1, 139.2, 136.7, 135.1, 128.9, 128.5, 127.7, 127.6, 126.3, 126.1, 123.4, 89.2, 52.3, 42.7, 37.4.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{19}O_2$: 291.1380; found: 291.1381.

Compound 11h

Colorless oil; d.r. = 70:30.

^{1}H NMR ($CDCl_3$): δ = 7.56 [d, *J* = 7.5 Hz, 2 H (minor)], 7.45 [d, *J* = 7.5 Hz, 2 H (major)], 7.40–7.20 [m, 8 H (major) + 8 H (minor)], 6.45 [d, *J* = 16.3 Hz, 1 H (major)], 6.42 [d, *J* = 16.3 Hz, 1 H (minor)], 6.07–5.97 [m, 1 H (major) + 1 H (minor)], 4.68–4.62 [m, 1 H (minor)], 4.41–4.35 [m, 1 H (major)], 2.86–2.72 [m, 3 H (major) + 3 H (minor)], 2.32 [dd, *J* = 13.2, 7.8 Hz, 1 H (minor)], 2.12 [t, *J* = 12.2 Hz, 1 H (major)], 1.40 [d, *J* = 6.1 Hz, 3 H (major)], 1.34 [d, *J* = 6.1 Hz, 3 H (minor)].

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}O_2$: 293.1542; found: 293.1550.

4-Methyl-5-methylene-3,3-diphenyldihydrofuran-2(3*H*)-one (10i) and 4,5-Dimethyl-3,3-diphenyldihydrofuran-2(3*H*)-one (11i)

The crude mixture was subjected to preparative TLC on silica gel with EtOAc/hexane (1/5) to give a mixture of **10i** and **11i** (90/10) in 84% yield (44.0 mg, 0.168 mmol).

Compound 10i

White solid.

^{1}H NMR ($CDCl_3$): δ = 7.50 (d, *J* = 8.2 Hz, 2 H), 7.41–7.32 (m, 3 H), 7.30–7.24 (m, 3 H), 6.99–6.94 (m, 2 H), 4.86 (t, *J* = 2.4 Hz, 1 H), 4.38 (t, *J* = 2.4 Hz, 1 H), 3.93 (qt, *J* = 6.8, 2.4 Hz, 1 H), 0.97 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 175.1, 158.6, 139.1, 138.8, 128.4, 128.2, 127.8, 127.4, 88.9, 60.4, 41.8, 14.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{16}O_2Na$: 287.1048; found: 287.1039.

Compound 11i

Colorless oil.

^{1}H NMR ($CDCl_3$): δ = 7.45–7.41 (m, 2 H), 7.39–7.34 (m, 2 H), 7.33–7.25 (m, 4 H), 6.97–6.93 (m, 2 H), 4.14–4.06 (m, 1 H), 3.04–2.95 (m, 1 H), 1.49 (d, *J* = 6.0 Hz, 3 H), 0.90 (d, *J* = 6.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 177.7, 140.2, 138.7, 129.1–127.2 (br), 78.4, 61.3, 45.4 (br), 18.0 (br), 11.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}O_2Na$: 289.1205; found: 289.1214.

Stoichiometric Reaction of 1h with $[IrCl(coe)_2]_2$/dppf

Dppf (11.0 mg, 0.020 mmol) and $[IrCl(coe)_2]_2$ (5.1 mg, 0.020 mmol Ir) were placed in a Schlenk tube under N_2. C_6D_6 (0.60 mL) was added to the Schlenk tube and the mixture was stirred at r.t. for 15 min. Compound **1h** and 1,4-dimethoxybenzene (3.3 mg, 0.024 mmol as an internal standard) were added to the Schlenk tube and the mixture was stirred at r.t. for 30 min. The resulting solution was transferred to an NMR tube capped with a rubber septum by use of a syringe pump. The signal of the hydride was observed at δ = –29.5 (t, $J_{P,H}$ = 22 Hz), –27.7 (dd, $J_{P,H}$ = 27, 16 Hz), –27.4 (dd, $J_{P,H}$ = 29, 18 Hz), –23.7 (t, $J_{P,H}$ = 20 Hz), and –22.4 (t, $J_{P,H}$ = 22 Hz). The yield of the iridium hydride complex was estimated to be 3%, 23%, 9%, 10%, and 6%, respectively.

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Supporting Information

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