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Stereo-Selective and Atom-Economic Alkenyl C-H Allylation/ Alkenylation in Aqueous Media by Iridium Catalysis

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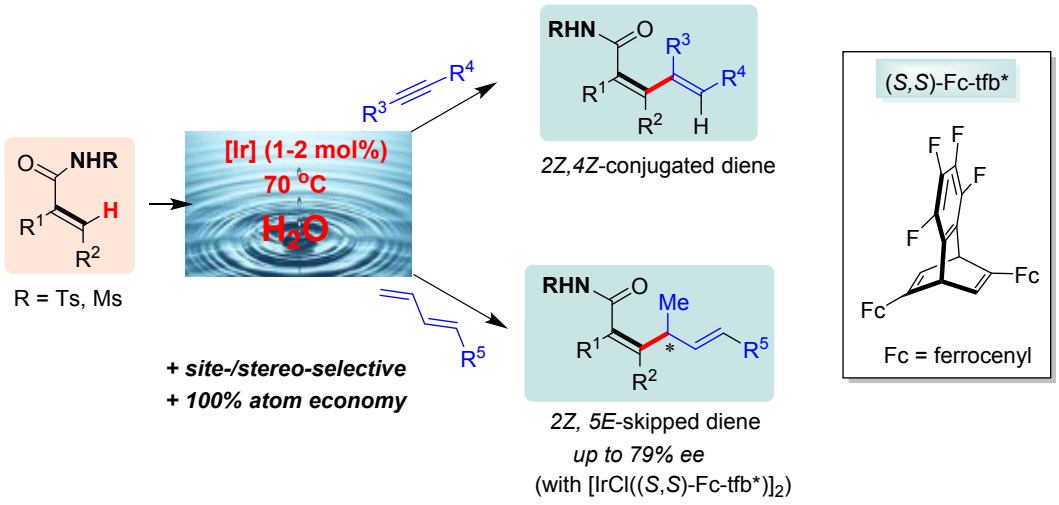


Abstract: A practical and atom economic protocol for the stereo-selective preparation of various 1,4- and 1,3-diene skeletons through iridium-catalyzed directed olefinic C–H allylation and alkenylation of NH-Ts acrylamides in water was developed. This reaction tolerated a wide scope of substrates under simple reaction conditions and enabled successful gram-scaled preparation.

Furthermore, an asymmetric variant of this reaction giving enantioenriched 1,4-dienes was achieved employing a chiral diene-iridium complex as the catalyst.

Introduction

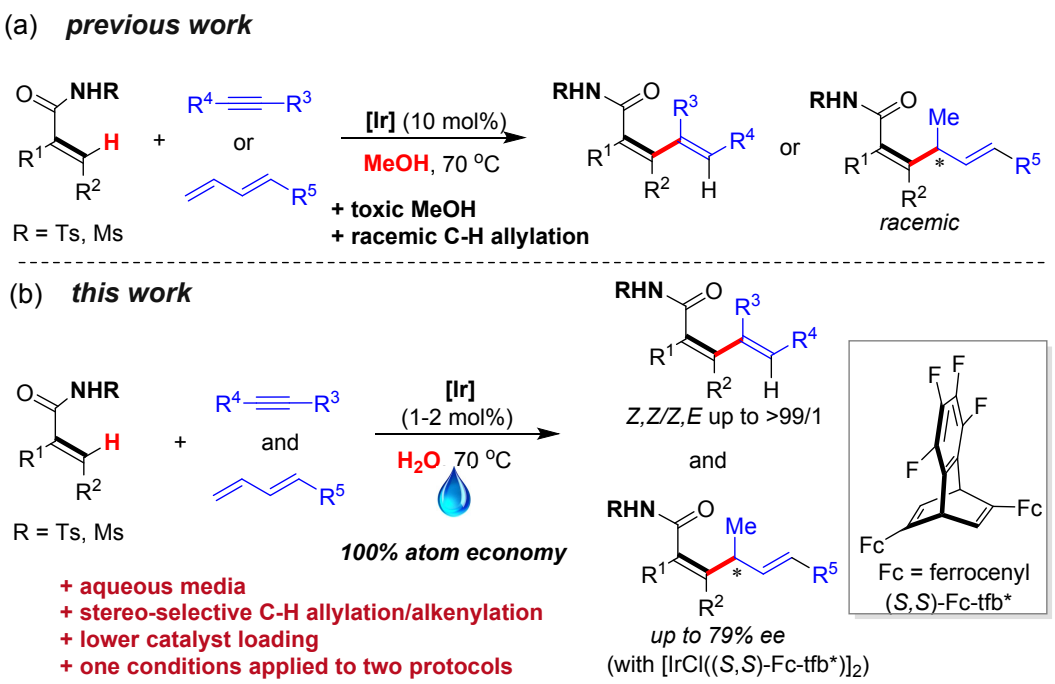
Cross-coupling reaction represents one of the most powerful methods to construct carbon-carbon bond for the synthesis of complex molecules.[1] Recently, remarkable progress has been made on C-H/C-H cross-couplings between two (hetero) arenes and/or alkenes, leading to valuable biaryl, stryene and 1,3-diene products.[2] However, quantitative amount of metal oxidants such as silver and copper salts are commonly required, which greatly reduce the functional compatibility and atom efficacy of the reaction. Notably, C-H alkylation and alkenylation reactions through the addition of a C−H bond across an unactivated alkene or alkyne are particularly important due to the attractive features such as by-product free, atom-economic synthesis and the more readily availability and lower price of starting materials than the corresponding alkyl and alkenyl halides.[3,4]

Chemistry has been driven to minimize chemical waste in order to be in line with the principles of Green Chemistry.[5] Organic solvents used in traditional chemical process are the main consumption of petroleum hydrocarbons, which account for 80–90% of mass utilization in a pharmaceutical/fine chemical process.[6] In this context, reactions in aqueous media represent the ideal strategy to solve this problem. Water, termed as a “green” solvent, is economical and safe, and it is neither flammable, potentially explosive, mutagenic, nor carcinogenic. Moreover, the term “green” also shows a “green workup”, avoiding high efforts and costs for purification and extraction methods.[7] Moreover, the largest proportions of biochemical conversions in living

cells proceed in water, and there is a high requirement for synthetic methodologies which can be applied in such polar, aqueous and protic media.[8]

Simultaneously with the development of cross-coupling reaction, a trend towards universal water as a solvent has been evolving for several decades.[9] Although the C-H allylation and alkenylation reactions exhibit great importance, there is still no report on addition of an olefinic C−H bond across an unactivated 1,3-diene or alkyne in highly polar aqueous media.[2,10] With our ongoing interest in directed olefinic C-H activation/functionalization,[10] herein, we demonstrated the first atom efficient and stereo-selective approaches to construct 1,3- and 1,4-dienes under aqueous catalytic conditions with wide functional group tolerance, and an asymmetric variant of this reaction giving enantioenriched 1,4-dienes (Scheme 1b).

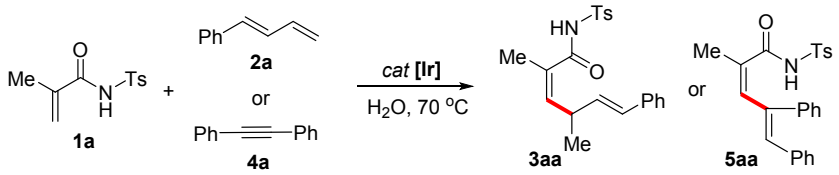
Scheme 1. Atom Economic Synthesis of 1,3/1,4-dienes by Alkenyl C-H Allylation and Alkenylation



Results and Discussion

At the beginning, the aqueous reaction of N-Ts acrylamide **1a** with 1,3-diene **2a** was chosen as the model reaction, providing 1,4-diene **3aa** as the product in 54% yield in 16 h using 5 mol% $[IrOMe(cod)]_2$ (Table 1, entry 1). To our delight, the product yield increased to 90% with 2 mol% catalyst loading in longer reaction time (entry 2). Notably, complex $[IrCl(cod)]_2$ exhibited comparable catalytic activity (entry 3), but Ir(III) complex $[IrCp^*Cl_2]_2$ led to no product (entry 4). The C-H allylation led to moderate yields using 1 mol% $[IrOMe(cod)]_2$ or one equiv. of **2a** (entries 5 and 6). Moreover, prolonged reaction time seemed to be disfavorable due to decomposition of the product under the catalytic aqueous conditions (entries 7 and 8).

Table 1. Optimization of Reaction Conditions[a]

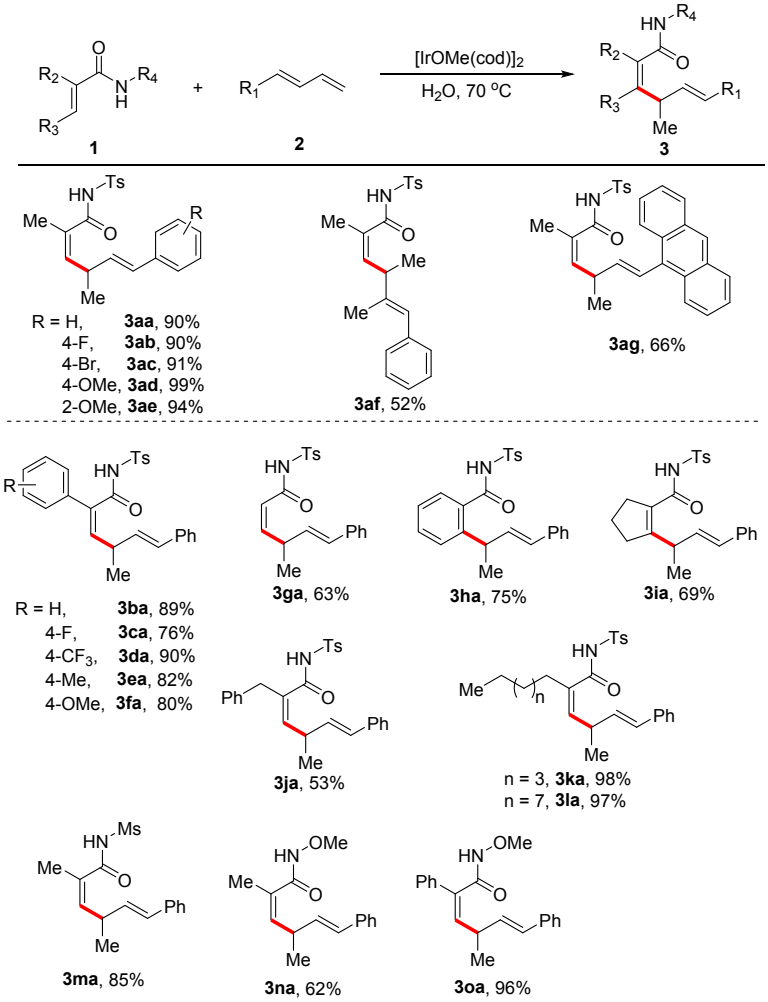


entry	catalyst (mol%)	substrate	time(h)	yield (%)[b]
1	$[IrOMe(cod)]_2$ (5)	**2a**	16	54
2	**$[IrOMe(cod)]_2$** (2)	**2a**	**24**	**90**
3	$[IrCl(cod)]_2$ (2)	**2a**	24	90
4	$[IrCp^*Cl_2]_2$ (2)	**2a**	24	0
5	$[IrOMe(cod)]_2$ (1)	**2a**	24	59
6[c]	$[IrOMe(cod)]_2$ (2)	**2a**	24	53
7	$[IrOMe(cod)]_2$ (2)	**2a**	36	69
8	$[IrOMe(cod)]_2$ (2)	**2a**	48	52
9	$[IrCl(cod)]_2$ (2)	**4a**	16	73
10	$[IrCl(cod)]_2$ (1)	**4a**	24	84
11	**$[IrOMe(cod)]_2$** (1)	**4a**	**24**	**92**
12	$[IrCp^*Cl_2]_2$ (1)	**4a**	24	0
13	$[IrOMe(cod)]_2$ (0.5)	**4a**	24	68
14[c]	$[IrOMe(cod)]_2$ (1)	**4a**	24	73
15	$[IrOMe(cod)]_2$ (1)	**4a**	36	87
16	$[IrOMe(cod)]_2$ (1)	**4a**	48	86

[a] Unless otherwise noted, the reactions were carried out using acrylamide (**1a**) (0.20 mmol), diene (**2a**) (0.24 mmol) or alkyne (**4a**) (0.3 mmol), [Ir] (2-4 mol%) in H_2O (0.2 M, 1.0 mL) under an argon atmosphere (1 atm). [b] The yields indicated in the table are isolated yields. [c] One equiv of **2a** or **4a** used.

Next, we turned to examine the olefinic C-H alkenylation using N-Ts acrylamide **1a** and diphenyl acetylene **4a**. This reaction led to **5aa** in 73% yield in 16 h (entry 9). To our pleasure, the product yield increased to 84% by simply prolonging the reaction time to 24 h with 1 mol% catalyst loading (entry 10). Using complex $[IrOMe(cod)]_2$ instead further improved the reaction to 92% yield, and excellent stereoselectivity (*Z,Z/Z,E* > 99/1) was achieved due to a directed oxidative addition of the vinylic C−H bond and a following *syn*-insertion of alkyne (entry 11). Complex $[IrCp^*Cl_2]_2$ still showed no catalytic activity in such alkenylation (entry 12). Reducing either catalyst loading or amount of alkyne **4a** led to decreased yields (entries 13 and 14). Similarly, longer reaction time led to slightly decreased yields (entries 15 and 16).

Table 2. Substrate Scope of C-H Allylation[a]

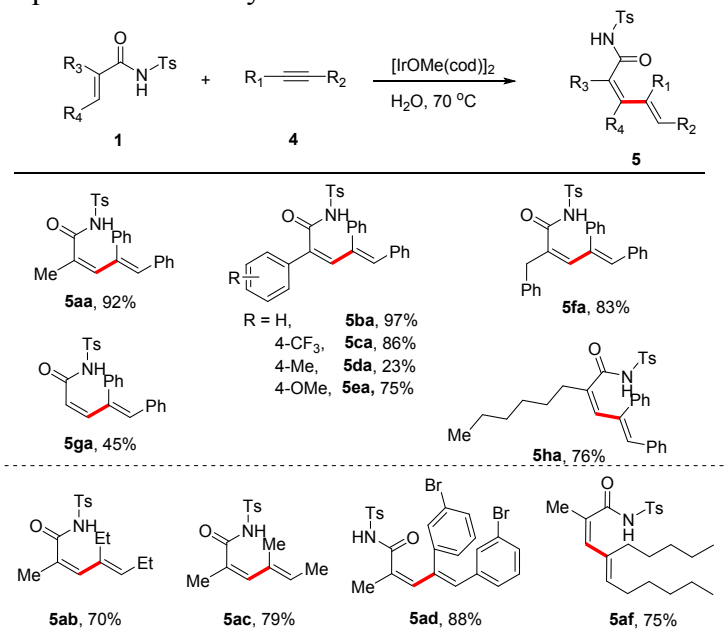


[a] Unless otherwise noted, the reactions were carried out using acrylamide **1** (0.2 mmol), diene **2** (0.24 mmol), $[IrOMe(cod)]_2$ (2 mol%), in H_2O (1.0 mL) at 70 °C for 24 h under an argon atmosphere (1 atm). The yields indicated in the table are isolated yields.

With the optimized reaction conditions in hand, we turned to examine the substrate scope of the alkenyl C-H allylation reaction (Table 2). 1-Aryl-1,3-butadienes (**1b-1e**) bearing F, Br and OMe were smoothly converted, leading to quantitative yields. 1-Phenyl-2-methyl-1,3-butadiene also reacted to provide corresponding 1,4-diene in 52% yield (**3af**). Introduction of anthracene ring into the diene also led to **3ag** in 66% yield. Various acrylamides were examined to react with diene **2a**. Aromatic N-Ts acrylamides bearing sensitive F, CF_3, Me, and OMe gave the corresponding 1,4-diene products in 76–90% yields, thus exhibiting good functional-group

compatibility (**3ba–3fa**). Interestingly, plain acrylamide, which usually showed limited reactivity in directed alkenyl C-H functionalization by Ru- or Rh-catalysis,[2,10] also reacted well with diene **2a** to provide 1,4-diene **3ga** in good yield. N-Ts benzamide also produced **3ha** in 75% yield. Moreover, acrylamide embedded with a cyclopentenyl unit produced 1,4-diene **3ia** in 69% yield. However, α-alkyl substituted acrylamides showed good reactivities (**3ja**, **3ka** and **3la**). Differently N-substituted acrylamides such as N-Ms and N-OMe acrylamides were investigated, and all of them were efficiently converted, leading to 1,4-dienes in 62-96% yields (**3ma**, **3na** and **3oa**).

Table 3. Substrate Scope of C-H Alkenylation[a]

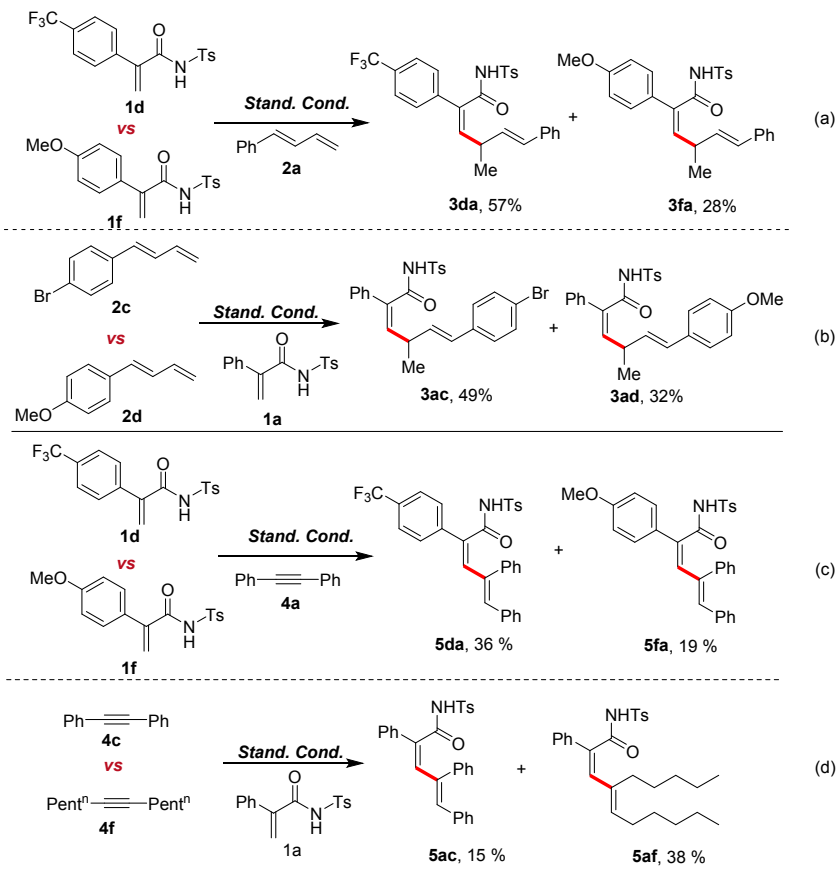


[a] Unless otherwise noted, the reactions were carried out using acrylamide **1** (0.2 mmol), alkyne **4** (0.24 mmol), $[IrOMe(cod)]_2$ (1 mol%), in H_2O (1.0 mL) at 70 °C for 24 h under an argon atmosphere (1 atm). The yields indicated in the table are isolated yields. Configuration of the 1,3-dienes was determined by ^1H NMR to be *Z,Z/Z,E* > 99/1 in all of the cases.

The limitation of the acrylamide and alkyne coupling was also examined (Table 3). Representative aliphatic and aryl substituted acrylamides were all reacted well with diphenylacetylene **4a** (**5aa**-**5ha**). Aromatic CF_3 and OMe were both well tolerated (**5ca** and **5ea**).

In contrast, acrylamides bearing *para*-methyl phenyl ring led to low conversion due to poor solubility in water (**5da**). Notably, plain acrylamide led to moderate yield (**5ga**). Dialkylacetylene **4b**, **4c** and **4f** all reacted well with acrylamide **1a** to give the *Z,Z*-configured products in 70%-79% yields. Diphenylacetylenes bearing *meta*-Br substituent proceeded smoothly to give the product **5ad** in excellent yields. Notably, this protocol exhibited excellent site- and stereo-selectivities in all of the cases (*Z,Z/Z,E* > 99/1).

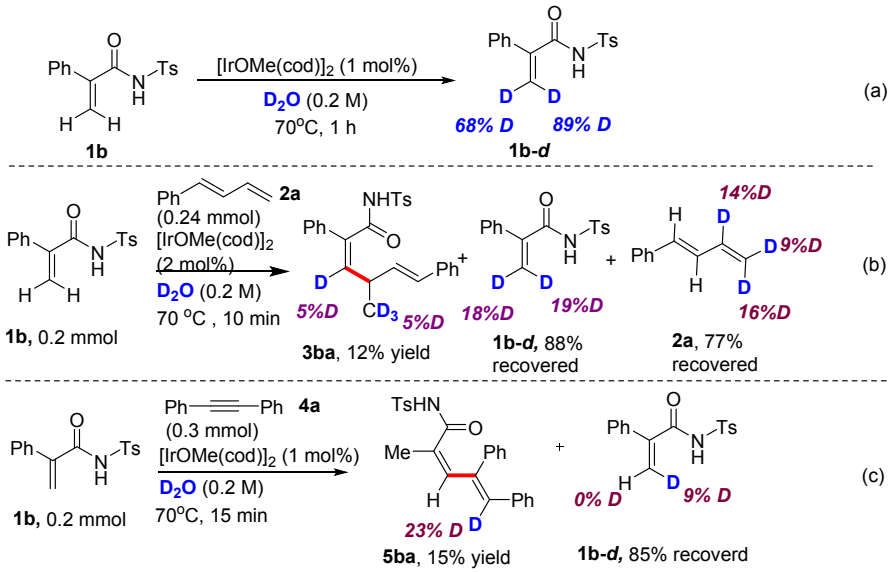
Considering the high efficacy of the aqueous iridium-catalyzed olefinic C-H alkenylation, we next attempted to obtain preliminary insight of the mechanisms by conducting some competition experiments. Competition reactions between acrylamides **1d** and **1f** with diene **2a** or alkyne **4a** demonstrated the electron-deficient substrate to be more reactive (Scheme 2a and 2c). Intermolecular competition experiments between dienes **2c** and **2d** also highlighted the electron-deficient one to be converted firstly (Scheme 2b). Moreover, competition experiments between alkynes **4c** and **4f** showed the alkylalkynes to be more reactive (Scheme 2d). These results are consistent with previous results in ruthenium- and rhodium-catalyzed olefinic C-H activations, as well as the Ir-catalyzed C–H alkenylation reactions.[10]



Scheme 2. Competitive Reactions.

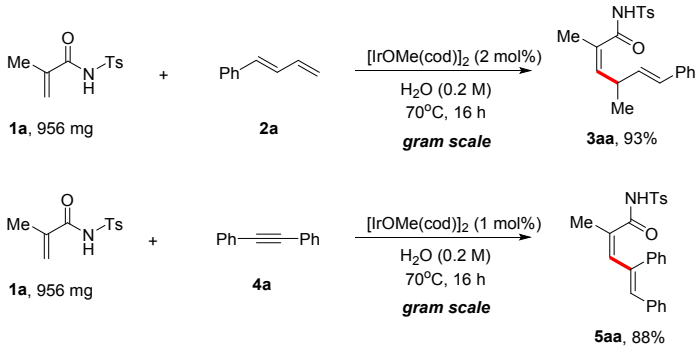
Deuterium-labelling experiments were also conducted to get mechanistic insights (Scheme 3). If **1b** was treated with D_2O under standard conditions, deuterium incorporation was observed at alkenyl C–H bond, exhibiting a reversible C-H activation event (Scheme 3a). Reaction of acrylamide **1b** with diene **2a** in D_2O for 10 min produced **3ba** in 12% yield, where deuterium incorporation was observed for product and recovered substrates, showing C–H activation and hydro-metalation steps to be fast and reversible (Scheme 3b). We also performed the deuterium incorporation experiment under the optimal conditions using acrylamide **1b** and alkyne **2a**. While 9% deuterium (*cis*-olefinic) incorporation to recovered acrylamide **1b** suggested that the alkenylation step is competitive with reversibility of the C−H activation step, 23% deuterium

incorporation to the product **3ba** exhibited a fast H/D exchange on hydridoiridium intermediate (Scheme 3c).

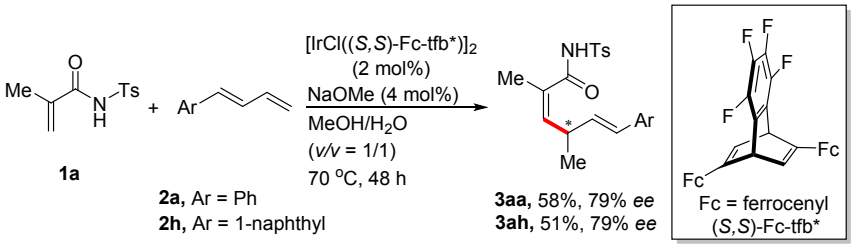


Scheme 3 Deuterium Labelled Experiments.

The gram-scale cross-coupling reaction also proceeded well even with 1-2 mol % catalyst loading, as illustrated by the preparation of **3aa** and **5aa** to demonstrate the robustness of the protocol (Scheme 4).



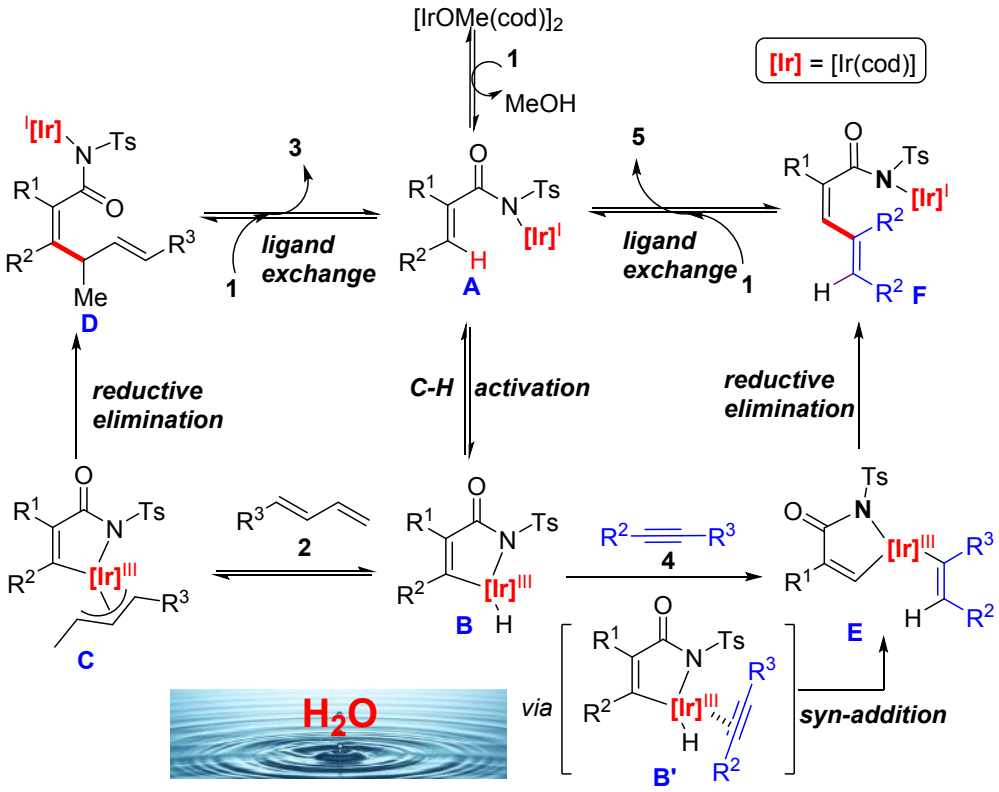
Scheme 4 Gram Scale Synthesis.



Scheme 5 Asymmetric C-H Allylation of **1a** with **2a** and **2h**. Reaction conditions: **1a** (0.20 mmol), **2a** (or **2h**) (0.24 mmol), catalyst (2 mol%), NaOMe (4 mol %), H_2O (0.5 mL) and MeOH (0.5 mL), 70 °C, 48 h. The yields are isolated yields. The % ee was determined by HPLC on a chiral stationary phase column.

In attempt to achieve the asymmetric variant of this alkenyl C-H allylation (Scheme 5), we examined several types of chiral ligands. Neither chiral bisphosphine ligand such as binap, nor bisoxazole ligands[11] we examined showed enantioselectivity in this transformation. To our delight, the iridium complex coordinated with (*S,S*)-Fc-tfb*[12] displayed mild enantioselectivity towards the reaction of **1a** and **2a** (Ar = Ph), giving **3aa** in 58% with 79% ee. In order to improve the % ee, **2h** (Ar = 1-napthyl) with a bulky group was employed instead of **2a** under the same conditions, however **3ah** was obtained in 51% with the same enantioselectivity (79% ee). Although the enantioselectivity is not very high at this stage, the results show that the chiral diene ligands are promising for this type of reaction. To the best of our knowledge, this is the first example of the Ir-catalyzed asymmetric olefinic C-H allylation.

The possible catalytic cycle is proposed as described in Scheme 6.[10a-b] The methoxoiridium catalyst firstly reacts with N-Ts acrylamide **1** to form amidoiridium(I) species **A**, and the following oxidative addition of olefinic C-H bond gives hydridoiridium(III) intermediate **B**, which reacts with 1,3-diene **2** to generate π-allyliridium(III) species **C** by a branch-selective alkene insertion. Irreversible reductive elimination of allyliridium **C** and ligand exchange by acrylamide **1** gives the corresponding branched 1,4-diene **3** and regenerates catalytically active amidoiridium species **A**. In the reaction of alkynes, hydridoiridium(III) intermediate **B** generated from amidoiridium(I) species **A** reacts with alkyne **4** by *syn*-addition to generate the intermediate **E**. Reductive elimination and ligand exchange by amide **1** give the diene **5** and regenerate species **A**.



Scheme 6 Proposed Mechanisms.

In conclusion, we have developed a practical and atom economic protocol for the stereo-selective preparation of various 1,4- and 1,3-diene skeletons through iridium-catalyzed directed olefinic C–H allylation and alkenylation of NH-Ts acrylamides in water. This reaction tolerated a wide scope of substrates under simple aqueous conditions. The use of a chiral diene ligand enabled the asymmetric alkenyl C-H allylation with mild enantioselectivity (79% ee).

■Experimental Section

General considerations

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric

molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm-1). $[IrOMe(cod)]_2$ was purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.

Synthesis of Substrate N-Ts Acrylamides 1

To a solution of α-substituted acrylic acids (1 eq.) in THF (0.5 M) was added *p*-tosyl isocyanate (1 eq.). After stirring the resulting clear solution at rt for 10 min, triethyl amine (1 eq.) was added dropwise, with release of gas. The progress of the reaction was monitored using TLC. Once the acrylic acids disappeared, the mixture was diluted with EtOAc and washed with 2 M HCl (aq.). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was subjected to column chromatography on silica gel to deliver substrates **1**.[10]

Synthesis of Substrate Dienes 2

To a suspension of methyltriphenylphosphonium bromide (6.0 mmol) in THF (30 mL) was added n-BuLi (2.3 mL, 2.6 M in n-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 40 min, a cinnamaldehyde derivative (6.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat NH_4Cl aq. (10 mL) and extracted with EtOAc (10 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative **2**.[10b]

General Procedure for the C-H Allylation Using Dienes

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (2 mol%, 0.004 mmol, 2.7 mg) and H_2O (1 mL). Then, amide **1a** (1.0 equiv, 0.2 mmol, 47.8 mg) and butadiene **2a** (1.2 equiv, 0.24 mmol, 31.2 mg) were added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 24 h. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1).

General Procedure for the C-H Alkenylation Using Alkynes

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (1 mol%, 0.002 mmol, 1.4 mg) and H_2O (1 mL). Then, amide **1a** (1.0 equiv, 0.2 mmol, 47.8 mg) and butadiene **4a** (1.5 equiv, 0.3 mmol, 53.4 mg) were added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 24 h. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1).

Gram scaled synthesis

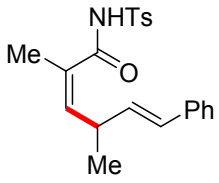
A screw-cap vial was charged with $[IrOMe(cod)]_2$ (2 mol %, 0.08 mmol, 53 mg) and H_2O (20 mL). Then, **1a** (1.0 equiv, 4.0 mmol, 956 mg) and **2a** (1.2 equiv, 4.8 mmol, 624 mg) (or **4a**, 1.5 equiv, 6.0 mmol, 1068 mg) were added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 8 h. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether

from 60/1 to 12/1). The desires product **3aa** was obtained as yellow liquid (1.38 g, 93%) (or **5aa**, 1.47 g, 88%).

Asymmetric synthesis of 3aa and 3ah

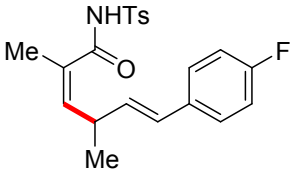
An screw-cap vial was charged with [IrCl((*S*,*S*)-Fc-tfb*)]$_2$ (2 mol%, 0.004 mmol, 5.6 mg), H_2O (0.5 mL) and MeOH (0.5 mL). Then, amide **1a** (1.0 equiv, 0.2 mmol, 47.8 mg) and butadiene **2a** (1.2 equiv, 0.24 mmol, 31.2 mg) (or **2h**, 1.2 equiv, 0.24 mmol, 43.2 mg) were added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 48 h. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) to give **3aa** (58%, 79% ee) (or **3ah** 51%, 79% ee). The ee% was measured by HPLC on a chiral stationary phase column.[11]

Characterization Data



3aa

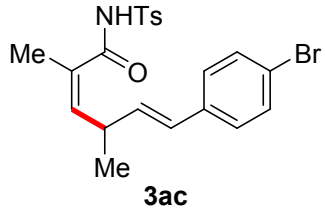
(2Z, 5E)-2, 4-dimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3aa): Following the general procedure, **3aa** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1)as a yellow liquid (67 mg, yield = 90%).^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 7.0 Hz, 3H), 1.87 (s, 3H), 2.41 (s, 3H), 3.56-3.49 (m, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.32-7.24 (m, 6H), 7.98 (d, *J* = 7.0 Hz, 2H), 8.56 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.2, 19.8, 20.7, 35.9, 125.2, 126.3, 126.9, 127.4, 127.5, 128.3, 128.6, 131.8, 134.6, 136.0, 141.5, 144.1, 165.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_3S$ 370.1471, found: 370.1475. FTIR (KBr, cm^{-1}): 3261, 2959, 1691, 1411, 1181, 1066, 660.



3ab

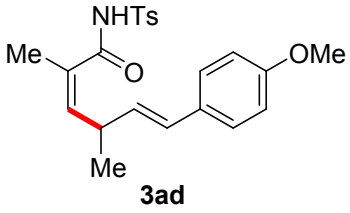
(2Z, 5E)-6-(4-fluorophenyl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3ab): Following the general procedure, **3ab** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 15/1) as a white liquid (70 mg, yield = 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.5 Hz, 3H), 1.87 (d, *J* = 1.0 Hz, 3H), 2.44 (s, 3H), 3.56-3.49 (m, 1H), 5.65 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 5.98 (dd, *J* = 16.0 Hz, *J* = 7.5 Hz,

1H), 6.35 (d, J = 16.0 Hz, 1H), 6.98 (t, J = 9.0 Hz, 1H), 7.35-7.29 (m, 4H), 7.98 (d, J = 8.0 Hz, 2H), 8.27 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.3, 19.9, 20.7, 36.1, 114.3, 114.5, 126.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 127.1, 127.4, 127.5, 128.6, 131.4 (d, $J_{C\text{-}F}$ = 1.3 Hz), 132.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 134.5, 141.4, 144.1, 161.2 (d, $J_{C\text{-}F}$ = 245.0 Hz), 164.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}FNO_3S$ 388.1377, found: 388.1377. FTIR (KBr, cm^{-1}): 3452, 2920, 1850, 1662, 1399.



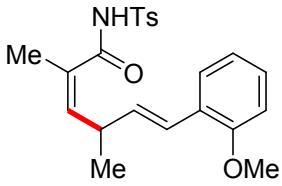
3ac

(2Z, 5E)-6-(4-fluorophenyl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3ac): Following the general procedure, **3ac** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white liquid (81 mg, yield = 91%). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, J = 7.0 Hz, 3H), 1.87 (d, J = 1.5 Hz, 3H), 2.43 (s, 3H), 3.58-3.50 (m, 1H), 5.63 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 6.05 (dd, J = 16.0 Hz, J = 7.5 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 8.39 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.3, 19.7, 20.7, 36.0, 120.1, 126.8, 127.1, 127.3, 127.5, 128.6, 130.6, 132.5, 134.5, 135.0, 141.4, 144.2, 164.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}BrNO_3S$ 448.0577, found: 448.0570. FTIR (KBr, cm^{-1}): 3552, 3416, 1630, 1609, 1412, 606.



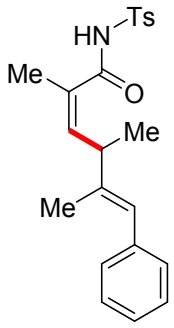
3ad

(2Z,5E)-6-(4-methoxyphenyl)-2,4-dimethyl-N-tosylhexa-2, 5-dienamide (3ad): Following the general procedure, **3ad** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 10/1) as a white liquid (80 mg, yield = 99%). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, J = 6.5 Hz, 3H), 1.86 (d, J = 1.5 Hz, 3H), 2.44 (s, 3H), 3.51-3.44 (m, 1H), 3.80 (s, 3H), 5.66 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 5.92 (dd, J = 16.0 Hz, J = 7.5 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 8.22 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.3, 20.2, 20.7, 36.2, 54.3, 113.0, 126.4, 127.1, 127.5, 128.1, 128.6, 128.7, 129.5, 134.7, 141.4, 144.1, 158.2, 164.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_4S$ 400.1577, found: 400.1578. FTIR (KBr, cm^{-1}): 3475, 3410, 2961, 2921, 1611, 1180.



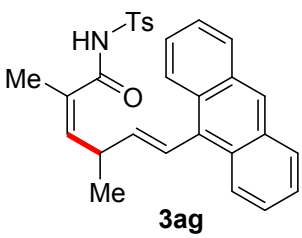
3ae

(2Z, 5E)-6-(2-methoxyphenyl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3ae): Following the general procedure, **3ae** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 10/1) as a yellow liquid (75 mg, yield = 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, *J* = 6.5 Hz, 3H), 1.88 (d, *J* = 1.0 Hz, 3H), 2.42 (s, 3H), 3.46-3.39 (m, 1H), 3.85 (s, 3H), 5.65 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.08 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 7.22-7.19 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.37 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.3, 20.0, 20.7, 36.4, 54.4, 109.8, 119.6, 123.3, 125.0, 125.8, 127.1, 127.5, 128.5, 132.6, 134.7, 141.0, 144.0, 155.5, 165.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_4S$ 400.1577, found: 400.1580. FTIR (KBr, cm^{-1}): 3546, 3461, 3420, 2921, 1621, 1167.



3af

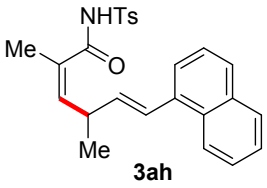
(2Z, 5E)-2, 4, 5-trimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3af): Following the general procedure, **3af** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white liquid (40 mg, yield = 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6.5 Hz, 3H), 1.82 (d, *J* = 1.0 Hz, 3H), 1.89 (d, *J* = 1.5 Hz, 3H), 2.42 (s, 3H), 3.36-3.30 (m, 1H), 5.78 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.33 (s, 1H), 7.26-7.20 (m, 3H), 7.35-7.31 (m, 4H), 7.98 (d, *J* = 8.0 Hz, 2H), 8.43 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 14.7, 19.0, 19.4, 20.7, 41.6, 124.7, 125.4, 127.1, 127.5, 127.9, 128.4, 128.6, 134.6, 136.5, 140.5, 140.8, 144.1, 165.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_3S$ 384.1628, found: 384.1638. FTIR (KBr, cm^{-1}): 3455, 2890, 2880, 1630, 1404, 1162, 721.



3ag

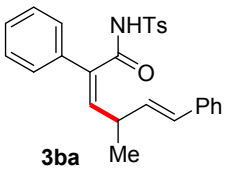
(2Z, 5E)-6-(anthracen-9-yl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3ag): Following the general procedure, **3ag** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1)as a yellow liquid (62 mg, yield = 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.0 Hz, 3H), 1.98 (d, *J* = 1.5 Hz, 3H), 2.31 (s, 3H), 3.92-3.85 (m, 2H), 5.90-5.85 (m, 2H), 6.98 (d, *J* = 16.5 Hz, 1H), 7.25 (d, *J* =

7.0 Hz, 1H), 7.48-7.44 (m, 4H), 8.00-7.98 (m, 4H), 8.18-8.16 (m, 2H), 8.21 (s, 1H), 8.37 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.5, 20.1, 20.6, 36.5, 124.1, 124.4, 124.8, 125.2, 127.0, 127.5, 127.6, 128.4, 128.5, 130.4, 131.5, 134.5, 140.3, 142.3, 144.2, 164.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}NO_3S$ 470.1784, found: 470.1780. FTIR (KBr, cm^{-1}):3415, 2930, 1628, 1400, 611.



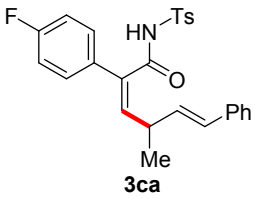
3ah

(R,2Z,5E)-4-methyl-6-(naphthalen-1-yl)-2-phenyl-N-tosylhexa-2,5-dienamide (3ah): Following the general procedure, **3ah** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (71 mg, yield = 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 7.0 Hz, 3H), 1.91 (d, *J* = 1.0 Hz, 3H), 2.37 (s, 3H), 3.72-3.64 (m, 1H), 5.74 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.08 (dd, *J* = 16.5 Hz, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 16.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.54-7.47 (m, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 8.30 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.3, 20.1, 20.6, 36.4, 122.7, 122.8, 124.5, 124.7, 125.0, 125.7, 126.8, 127.0, 127.4, 128.6, 130.1, 132.6, 133.8, 134.5, 135.1, 141.8, 144.1, 164.8. FTIR (KBr, cm^{-1}):3442, 2827, 1655, 1360, 650.



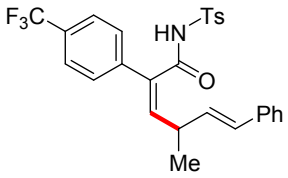
3ba

(2Z, 5E)-4-methyl-2, 6-diphenyl-N-tosylhexa-2, 5-dienamide (3ba): Following the general procedure, **3ba** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white solid (77 mg, yield = 89%), m.p.: 110.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.5 Hz, 3H), 2.46 (s, 3H), 3.64-3.57 (m, 1H), 6.00 (dd, *J* = 10.5 Hz, *J* = 0.5 Hz, 1H), 6.10 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 7.15-7.13 (m, 2H), 7.21 (t, *J* = 6.5 Hz, 1H), 7.36-7.27 (m, 9H), 7.94 (d, *J* = 7.0 Hz, 2H), 8.08 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.5, 20.7, 36.1, 125.2, 126.1, 126.3, 127.5, 127.5, 127.7, 128.0, 128.6, 131.3, 132.8, 134.5, 134.7, 136.1, 141.9, 144.2, 164.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}NO_3S$ 432.1628, found: 432.1634. FTIR (KBr, cm^{-1}): 3488, 3409, 2922, 1610, 1401.



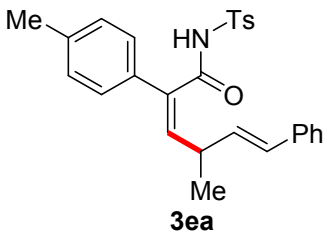
3ca

(2Z,5E)-2-(4-fluorophenyl)-4-methyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3ca): Following the general procedure, **3ca** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white solid (68 mg, yield = 76%), m.p.: 143.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 7.0 Hz, 3H), 2.47 (s, 3H), 3.60-3.52 (m, 1H), 5.96 (d, *J* = 10.0 Hz, 1H), 6.09 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.99 (t, *J* = 8.5 Hz, 2H), 7.15-7.11 (m, 2H), 7.22 (td, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.34-7.28 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.02 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.6, 20.7, 36.3, 115.0 (d, $J_{C\text{-}F}$ = 21.3 Hz), 125.2, 126.4, 127.5, 127.5, 127.9 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.6, 128.7, 130.8 (d, $J_{C\text{-}F}$ = 1.5 Hz), 131.1, 131.9, 134.4, 136.0, 141.5, 144.3, 161.8 (d, $J_{C\text{-}F}$ = 247.5 Hz), 163.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}FNO_3S$ 450.1534, found: 450.1533. FTIR (KBr, cm^{-1}): 3473, 2959, 2924, 2848, 1571, 1403.



3da

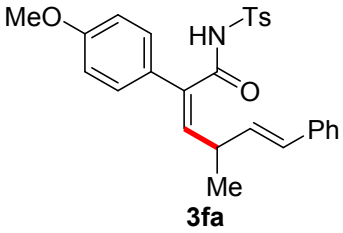
(2Z, 5E)-4-methyl-6-phenyl-N-tosyl-2-(4-(trifluoromethyl) phenyl) hexa-2, 5-dienamide (3da): Following the general procedure, **3da** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 10/1) as a white solid (90 mg, yield = 90%), m.p.: 173.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.5 Hz, 3H), 2.47 (s, 3H), 3.56-3.49 (m, 1H), 6.12-6.07 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.37-7.26 (m, 8H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 8.15 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.5, 20.7, 36.5, 122.8 (q, $J_{C\text{-}F}$ = 271.3 Hz), 124.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.2, 126.4, 127.5, 127.6, 128.7, 129.0, 129.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 130.7, 132.0, 134.2, 135.8, 138.0, 142.4, 144.5, 163.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{25}F_3NO_3S$ 500.1502, found: 500.1494. FTIR (KBr, cm^{-1}): 3445, 2960, 2924, 1648, 1398.



3ea

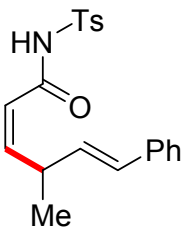
(2Z, 5E)-4-methyl-6-phenyl-2-(p-tolyl)-N-tosylhexa-2, 5-dienamide (3ea): Following the general procedure, **3ea** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white solid (73 mg, yield = 82%), m.p.: 135.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 7.0 Hz, 3H), 2.34 (s, 3H), 2.47 (s, 3H), 3.68-3.61 (m, 1H), 5.97 (d, *J* = 10.5 Hz, 1H), 6.10 (dd, *J* = 16.0 Hz, *J* = 7.0

Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.33-7.27 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.6, 20.1, 20.7, 36.0, 125.2, 126.2, 126.3, 127.5, 128.5, 128.6, 128.7, 131.5, 132.0, 132.5, 134.5, 136.2, 137.8, 141.8, 144.1, 164.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_3S$ 446.1784, found: 446.1776. FTIR (KBr, cm^{-1}): 3445, 2923, 1659, 1648, 1401.



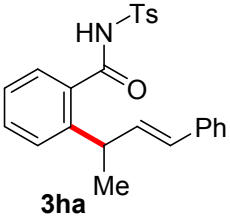
3fa

(2Z,5E)-2-(4-methoxyphenyl)-4-methyl-6-phenyl-N-tosylhexa-2,5-dienamide (3fa): Following the general procedure, **3fa** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (74 mg, yield = 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 7.0 Hz, 3H), 2.46 (s, 3H), 3.63-3.56 (m, 1H), 3.80 (s, 3H), 5.91 (d, *J* = 10.5 Hz, 1H), 6.10 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.33-7.27 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H) , 8.03 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.6, 20.7, 36.0, 54.4, 113.4, 125.2, 126.3, 127.2, 127.5, 127.5, 127.5, 128.4, 128.6, 131.6, 132.2, 134.5, 136.2, 140.7, 144.1, 158.9, 164.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_4S$ 462.1734, found: 462.1735. FTIR (KBr, cm^{-1}): 3439, 2923, 2853, 1712, 1513, 1260, 1088, 1022, 812.



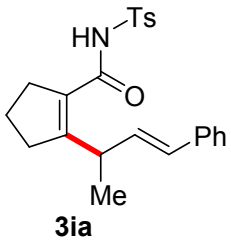
3ga

(2Z,5E)-4-methyl-6-phenyl-N-tosylhexa-2,5-dienamide (3ga): Following the general procedure, **3ga** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (45 mg, yield = 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 2.43 (s, 3H), 3.20 (m, 1H), 3.20 (d, *J* = 7.5 Hz, 2H), 5.63 (t, *J* = 7.5 Hz, 1H), 5.56 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.34-7.31 (m, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.32 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 11.8, 20.7, 35.3, 120.0, 125.5, 126.6, 127.5, 127.6, 127.8, 128.6, 131.0, 134.3, 136.0, 138.6, 144.3, 167.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_3S$ 356.1315, found: 356.1313. FTIR (KBr, cm^{-1}): 3439, 2923, 2853, 1712, 1513, 1260, 1088, 1022, 812.



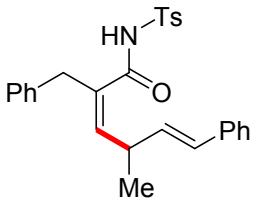
3ha

2-(4-phenylbut-3-en-2-yl)-N-tosylbenzamide (3ha): Following the general procedure, **3ha** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (61 mg, yield = 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 7.0 Hz, 3H), 2.43 (s, 3H), 4.03-3.98 (m, 1H), 6.25-6.24 (m, 2H), 7.23-7.17 (m, 2H), 7.27-7.25 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.36 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 2H), 7.42 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.69 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.1, 20.7, 36.7, 125.2, 125.3, 126.2, 126.3, 127.0, 127.4, 127.5, 128.1, 128.6, 130.8, 131.4, 133.4, 134.4, 136.2, 143.7, 144.1, 165.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_3S$ 406.1471, found: 406.1466. FTIR (KBr, cm^{-1}): 3439, 2923, 2853, 1712, 1513, 1260, 1088, 1022, 812.



3ia

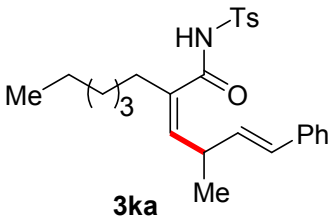
(E)**-2-(4-phenylbut-3-en-2-yl)-N-tosylcyclopent-1-ene-1-carboxamide (3ia):** Following the general procedure, **3ia** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (55 mg, yield = 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.5 Hz, 3H), 1.89-1.79 (m, 2H), 2.44 (s, 3H), 2.57-2.49 (m, 4H), 4.36-4.30 (m, 1H), 6.13 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.40 (d, *J* = 15.5 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.35-7.26 (m, 6H), 7.99 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$): δ = 17.3, 20.6, 20.7, 32.4, 32.9, 35.3, 125.2, 126.2, 127.5, 127.5, 128.5, 128.7, 130.7, 134.9, 136.2, 143.9, 161.5, 163.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{26}NO_3S$ 396.1628, found: 396.1632. FTIR (KBr, cm^{-1}): 3449, 2920, 1655, 1402, 1163.



3ja

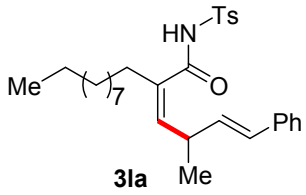
(2Z, 5E)-2-benzyl-4-methyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3ja): Following the general procedure, **3ja** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white solid (47 mg, yield = 53%), m.p.: 168.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 7.0 Hz, 3H), 2.43 (s, 3H), 3.54-3.44 (m, 3H), 5.66 (d, *J* = 10.0Hz, 1H), 6.09 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 7.03-7.01 (m, 2H), 7.26-7.19 (m, 6H), 7.36-7.29 (m, 4H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.99(s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ =20.0, 20.7, 36.3, 39.5, 125.3, 125.9, 126.5, 127.3, 127.5, 127.5, 127.9, 128.4, 128.7, 131.5, 131.8, 134.3, 135.9, 136.3, 140.5, 143.9, 164.7. HRMS (ESI) m/z:

[M+H]$^+$ Calcd for $C_{27}H_{28}NO_3S$ 446.1784, found: 446.1787. FTIR (KBr, cm^{-1}): 3444, 2952, 1640, 1400, 1269, 805.



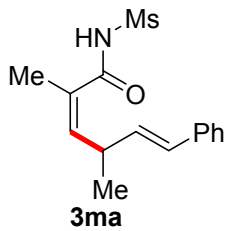
3ka

(Z)-2-((E)-2-methyl-4-phenylbut-3-en-1-ylidene)-N-tosyloctan amide (3ka): Following the general procedure, **3ka** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white liquid (86 mg, yield = 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H), 1.26-1.15 (m, 8H), 2.22-2.09 (m, 2H), 2.41 (s, 3H), 3.35-3.27 (m, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 6.06 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.34(d, *J* = 16.0 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.34-7.27 (m, 6H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.52 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 13.0, 20.0, 20.6, 21.4, 27.0, 27.6, 30.4, 33.3, 36.1, 125.2, 126.4, 127.4, 127.5, 128.3, 128.5, 131.9, 133.1, 134.6, 136.0, 137.7, 144.1, 165.8. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{26}H_{34}NO_3S$ 440.2254, found: 440.2253. FTIR (KBr, cm^{-1}): 3480, 3410, 2923, 1610, 1401, 1160, 1077.



3la

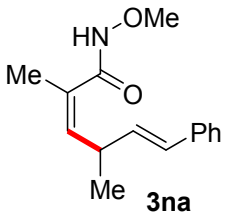
(Z)**-2-((E)-2-methyl-4-phenylbut-3-en-1-ylidene)-N-tosyldodecan amide (3la):** Following the general procedure, **3la** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a white liquid (96 mg, yield = 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.31-1.19 (m, 16H), 2.23-2.07 (m, 2H), 2.44 (s, 3H), 3.36-3.29 (m, 1H), 5.54 (d, *J* = 10.0 Hz, 1H), 6.07 (dd, *J* = 16.0 Hz, *J* = 7.5 Hz, 1H), 6.39 (d, *J* = 16.5 Hz, 1H), 7.25-7.22 (m, 1H), 7.36-7.30 (m, 6H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.14 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 13.1, 20.2, 20.7, 21.7, 27.2, 28.0, 28.3, 28.3, 28.5, 28.6, 30.9, 33.3, 36.4, 125.3, 126.5, 127.5, 127.6, 128.5, 128.6, 131.8, 133.2, 134.6, 135.9, 137.7, 144.1, 165.5. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{30}H_{42}NO_3S$ 496.2880, found: 496.2883. FTIR (KBr, cm^{-1}): 3551, 3420, 2919, 1621, 1401.



3ma

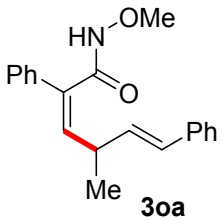
(2Z, 5E)-2, 4-dimethyl-N-(methylsulfonyl)-6-phenylhexa-2, 5-dienamide (3ma): Following the general procedure, **3ma** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 8/1) as a light yellow liquid (50 mg, yield = 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ =

1.22 (d, *J* = 6.5 Hz, 3H), 1.97 (d, *J* = 1.0 Hz, 3H), 3.34 (s, 3H), 3.78-3.71 (m, 1H), 5.80 (dd, *J* = 10.0 Hz, *J* = 1.0 Hz, 1H), 6.13 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.37-7.35 (d, *J* = 8.0 Hz, 1H), 8.18 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.4, 20.0, 36.2, 40.7, 125.2, 126.4, 126.5, 127.5, 128.7, 131.5, 135.9, 143.1, 166.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO_3S$ 294.1158, found: 294.1150. FTIR (KBr, cm^{-1}): 3449, 3218, 2921, 1641, 1395.



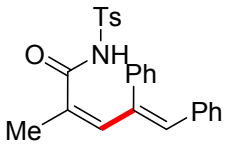
3na

(2Z, 5E)-N-methoxy-2, 4-dimethyl-6-phenylhexa-2, 5-dienamide (3na): Following the general procedure, **3na** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 8/1) as a light yellow liquid (31 mg, yield = 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.19 (d, *J* = 6.5 Hz, 3H), 1.94 (s, 3H), 3.47 (s, 1H), 3.82 (s, 3H), 5.52 (d, *J* = 9.5 Hz, 1H), 6.16 (dd, *J* = 16.0 Hz, *J* = 6.5 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 7.23-7.21 (m, 1H), 7.36-7.29 (m, 4H), 8.31 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.6, 20.2, 36.3, 63.6, 125.1, 126.4, 127.5, 127.8, 132.9, 136.0, 136.7. HRMS (ESI): m/z for $C_{15}H_{19}NO_2$ $[M+H]^+$: 246.1489, found: 246.1494. FTIR (KBr, cm^{-1}): 3444.99, 3192.65, 2951.53, 2362.75, 1663.42, 1401.08. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO_2$ 246.1489, found: 246.1498. FTIR (KBr, cm^{-1}): 3450, 3190, 2921, 2375, 1664, 1400.



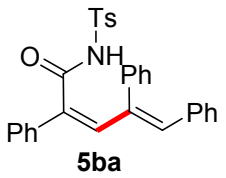
3oa

(2Z, 5E)-N-methoxy-4-methyl-2, 6-diphenylhexa-2, 5-dienamide (3oa): Following the general procedure, **3oa** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 8/1) as a light yellow liquid (59 mg, yield = 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (d, *J* = 6.5 Hz, 3H), 3.65-3.61 (m, 1H), 3.86 (s, 3H), 6.03 (d, *J* = 10.0 Hz, 1H), 6.22 (dd, *J* = 15.5 Hz, *J* = 7.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.41-7.28 (m, 9H), 8.30 (s, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.9, 36.7, 63.6, 125.2, 125.4, 126.3, 137.2, 127.5, 127.7, 128.2, 132.2, 132.5, 135.4, 136.1, 137.5, 165.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_2$ 308.1645, found: 308.1650. FTIR (KBr, cm^{-1}): 3475, 3405, 3200, 1622, 1398.



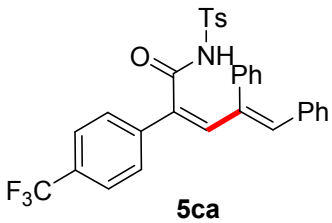
5aa

(2Z,4Z)-2-methyl-4,5-diphenyl-N-tosylpenta-2,4-dienamide (5aa): Following the general procedure, **5aa** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (77 mg, yield = 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.01(d, *J* = 1.5 Hz, 3H), 2.28 (s, 3H), 6.34 (t, *J* = 1.5 Hz, 1H), 6.40 (s, 1H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.18-7.10 (m, 5H), 7.25-7.24 (m, 2H), 7.42-7.35 (m, 1H), 7.68 (d, *J* = 7.0 Hz, 2H), 8.48 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.1, 20.6, 126.6, 127.1, 127.4, 127.8, 128.1, 128.2, 128.6, 131.0, 131.2, 133.8, 134.8, 135.3, 135.8, 136.7, 143.6, 166.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}NO_3S$ 418.1471, found: 418.1477. FTIR (KBr, cm^{-1}): 3845, 3443, 3400, 2910, 1670, 1410.



5ba

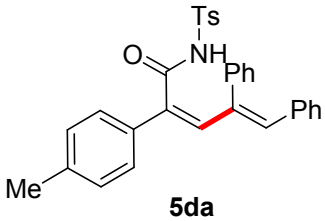
(2Z,4Z)-2,4,5-triphenyl-N-tosylpenta-2,4-dienamide (5ba): Following the general procedure, **5ba** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (93 mg, yield = 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23(s, 3H), 6.62 (s, 1H), 6.66 (d, *J* = 1.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.0 Hz, 2H), 7.12-7.10 (m, 1H), 7.21-7.15 (m, 5H), 7.29-7.26 (m, 5H), 7.69 (d, *J* = 8.5 Hz, 2H), 8.72 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.6, 125.6, 126.3, 126.5, 126.8, 127.0, 127.7, 127.9, 128.3, 128.3, 128.7, 131.7, 133.8, 134.0, 134.8, 134.9, 136.5, 137.0, 143.7, 165.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}NO_3S$ 480.1628, found: 480.1625. FTIR (KBr, cm^{-1}): 3851, 3573, 3399, 2992, 1641, 1385, 680.



5ca

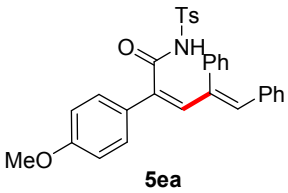
(2Z,4Z)-4,5-diphenyl-N-tosyl-2-(4-(trifluoromethyl)phenyl) penta -2,4-dienamide (5ca): Following the general procedure, **5ca** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (94 mg, yield = 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28(s, 3H), 6.68 (s, 1H), 6.78 (d, *J* = 1.0 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 2H), 7.19-7.14 (m, 4H), 7.25-7.24 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 8.50 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.6, 122.8 (d, J_{C-F} = 270.0 Hz), 124.7 (d, J_{C-F} = 3.75 Hz), 125.8, 126.3, 126.5, 126.8, 126.9, 127.3,

127.6, 127.8, 128.3, 128.4, 128.7, 128.8, 133.0, 133.4, 133.6, 134.6, 135.9, 136.2, 136.6, 138.3, 144.0, 164.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{25}F_3NO_3S$ 548.1502, found: 548.1549. FTIR (KBr, cm^{-1}): 3851, 3494, 3400, 2920, 1681, 1451, 1092.



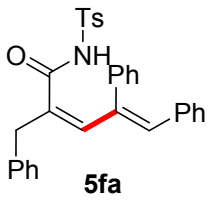
5da

(2Z,4Z)-4,5-diphenyl-2-(p-tolyl)-N-tosylpenta-2,4-dienamide (5da): Following the general procedure, **5da** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (23 mg, yield = 23%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.26(s, 3H), 2.33 (s, 3H), 6.60 (s, 1H), 6.65 (d, *J* = 1.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 7.12-7.05 (m, 5H), 7.25-7.15 (m, 7H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.38 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.2, 20.6, 125.5, 126.3, 126.8, 126.9, 127.3, 127.7, 128.2, 128.4, 128.5, 128.7, 131.3, 131.9, 133.1, 133.8, 134.9, 135.0, 136.6, 137.2, 137.8, 143.6, 165.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{28}NO_3S$ 494.1784, found: 494.1780. FTIR (KBr, cm^{-1}): 3850, 3415, 2390, 1680, 1420, 1370.



5ea

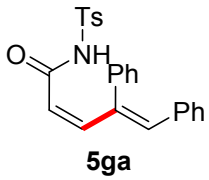
(2Z,4Z)-2-(4-methoxyphenyl)-4,5-diphenyl-N-tosylpenta-2,4-dienamide (5ea): Following the general procedure, **5ea** was obtained as a yellow liquid (76 mg, yield = 75%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.79 (s, 3H), 6.58-6.59 (m, 1H), 6.82-6.78 (m, 4H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 2H), 7.25-7.15 (m, 8H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.34-7.31 (m, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.39 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.6, 54.3, 113.3, 126.3, 126.8, 126.9, 127.0, 127.3, 127.4, 127.6, 128.2, 128.4, 128.7, 131.0, 132.1, 133.8, 134.6, 135.1, 136.7, 137.3, 143.7, 159.0, 165.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{28}NO_4S$ 510.1734, found: 510.1739. FTIR (KBr, cm^{-1}): 3849, 3424, 2404, 1700, 1416, 1388.



5fa

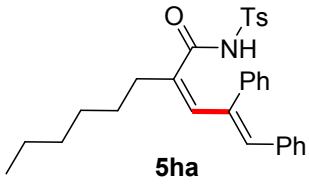
(2Z,4Z)-2-benzyl-4,5-diphenyl-N-tosylpenta-2,4-dienamide (5fa): Following the general procedure, **5fa** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a light yellow liquid (82 mg, yield = 83%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.30(s,

3H), 3.62 (s, 2H), 6.30 (d, J = 1.0 Hz, 1H), 6.50 (s, 1H), 6.87 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 7.0 Hz, 2H), 7.14-7.09 (m, 6H), 7.28-7.18 (m, 7H), 7.60 (d, J = 8.5 Hz, 2H), 8.05 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.6, 40.1, 125.8, 126.6, 127.0, 127.2, 127.3, 127.8, 127.9, 128.1, 128.0, 128.6, 131.6, 134.0, 134.8, 135.2, 135.3, 135.6, 136.3, 136.7, 143.5, 165.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{28}NO_3S$ 494.1784, found: 494.1793. FTIR (KBr, cm^{-1}): 3850, 3463, 3412, 2918, 1675, 1419, 1141.



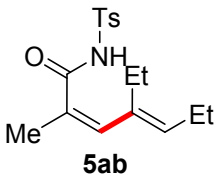
5ga

(2Z,4Z)-4,5-diphenyl-N-tosylpenta-2,4-dienamide (5ga): Following the general procedure, **5ga** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (36 mg, yield = 45%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 5.86 (d, J = 7.0 Hz, 1H), 6.66-6.64 (m, 2H), 6.94 (d, J = 7.0 Hz, 2H), 7.18-7.12 (m, 6H), 7.41-7.33 (m, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.34-7.31 (m, 1H), 7.40 (d, J = 7.0 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 8.25 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.6, 120.9, 125.8, 127.0, 127.1, 127.3, 127.4, 127.9, 128.1, 128.4, 128.7, 133.6, 134.4, 135.7, 136.1, 142.6, 143.8, 162.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}NO_3S$ 404.1315, found: 404.1315. FTIR (KBr, cm^{-1}): 3851, 3423, 3412, 2234, 1635, 1400.



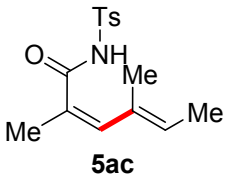
5ha

(Z)-2-((Z)-2,3-diphenylallylidene)-N-tosyloctanamide (5ha): Following the general procedure, **5ha** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (74 mg, yield = 76%). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.0Hz, 3H), 1.30-1.23 (m, 6H), 1.45-1.39 (m, 1H), 2.27 (s, 3H), 2.32 (t, J = 7.0Hz, 2H), 6.25 (d, J = 1.5 Hz, 1H), 6.40 (s, 1H), 6.84 (d, J = 7.5 Hz, 2H), 6.93 (d, J = 8.0 Hz, 1H), 7.15-7.09 (m, 5H), 7.27-7.24 (m, 3H), 7.69 (d, J = 8.5 Hz, 2H), 8.26 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 13.0, 20.6, 21.5, 27.1, 27.8, 30.5, 34.4, 126.5, 126.9, 127.1, 127.4, 127.8, 128.1, 128.2, 128.6, 130.8, 133.9, 133.9, 134.9, 135.8, 136.2, 137.0, 143.6, 166.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{34}NO_3S$ 488.2254, found: 488.2248. FTIR (KBr, cm^{-1}): 3677, 3402, 1646, 1395, 444.



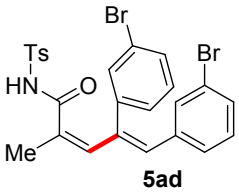
5ab

(2Z,4E)-4-ethyl-2-methyl-N-tosylhepta-2,4-dienamide (5ab): Following the general procedure, **5ab** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (45 mg, yield = 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02-0.98 (m, 6H), 1.88 (d, *J* = 1.5 Hz, 2H), 2.12-2.05 (m, 2H), 2.15 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 5.41 (t, *J* = 7.0 Hz, 1H), 6.31 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.61 (s, 1H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$): δ = 12.4, 12.7, 19.6, 20.3, 20.7, 22.5, 127.5, 128.5, 128.7, 133.8, 134.8, 136.4, 137.7, 143.9, 165.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NO_3S$ 322.1471, found: 322.1480. FTIR (KBr, cm^{-1}): 3844, 3472, 3995, 1661, 1396, 1093.



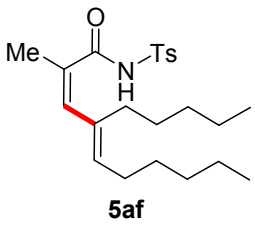
5ac

(2Z,4E)-2,4-dimethyl-N-tosylhexa-2,4-dienamide (5ac): Following the general procedure, **5ac** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (46 mg, yield = 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.64-1.62 (m, 6H), 1.87 (d, *J* = 1.5 Hz, 3H), 2.45 (s, 3H), 5.51-5.48 (m, 1H), 6.19 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.31 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 12.9, 14.4, 19.7, 20.7, 127.1, 127.5, 128.0, 128.5, 131.2, 134.5, 137.6, 144.0, 166.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO_3S$ 294.1158, found: 294.1160. FTIR (KBr, cm^{-1}): 3424, 3400, 2980, 1666, 1421, 1086.



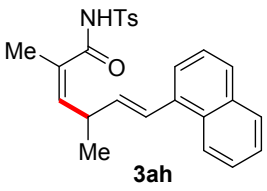
5ad

(2Z,4Z)-4,5-bis(3-bromophenyl)-2-methyl-N-tosylpenta-2,4-dienamide (5ad): Following the general procedure, **5ad** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (101 mg, yield = 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (d, *J* = 1.5 Hz, 3H), 2.32 (s, 3H), 6.22 (t, *J* = 1.5 Hz, 1H), 6.31 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 7.04-6.96 (m, 5H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.37 (dq, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.27 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.2, 20.7, 121.2, 121.8, 126.9, 126.9, 127.3, 128.3, 128.5, 129.3, 129.7, 129.7, 130.4, 130.9, 131.5, 132.6, 133.5, 133.7, 135.7, 136.5, 138.4, 144.0, 165.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}Br_2NO_3S$ 575.9838, found: 575.9848. FTIR (KBr, cm^{-1}): 3560, 3472, 3266, 3231, 1666, 1401, 479.



5af

(2Z,4E)-2-methyl-4-pentyl-N-tosyldeca-2,4-dienamide (5af): Following the general procedure, **5af** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (61 mg, yield = 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.5 Hz, 6H), 1.36-1.25 (m, 12H), 1.88 (d, *J* = 1.0 Hz, 3H), 2.02 (q, *J* = 7.0 Hz, 1H), 2.09 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 5.41 (t, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.58 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 13.0, 13.0, 19.6, 20.6, 21.4, 21.5, 27.2, 27.5, 27.8, 29.6, 30.6, 30.8, 127.5, 128.4, 128.4, 132.9, 134.8, 135.5, 138.1, 143.8, 165.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{36}NO_3S$ 406.2410, found: 406.2418. FTIR (KBr, cm^{-1}): 3535, 3415, 2921, 1630, 1410.



3ah

(R,2Z,5E)-4-methyl-6-(naphthalen-1-yl)-2-phenyl-N-tosylhexa-2,5-dienamide (3ah): Following the general procedure, **3ah** was obtained from a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) as a yellow liquid (71 mg, yield = 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 7.0 Hz, 3H), 1.91 (d, *J* = 1.0 Hz, 3H), 2.37 (s, 3H), 3.72-3.64 (m, 1H), 5.74 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.08 (dd, *J* = 16.5 Hz, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 16.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.54-7.47 (m, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 8.30 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 19.3, 20.1, 20.6, 36.4, 122.7, 122.8, 124.5, 124.7, 125.0, 125.7, 126.8, 127.0, 127.4, 128.6, 130.1, 132.6, 133.8, 134.5, 135.1, 141.8, 144.1, 164.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_3S$ 420.1628, found: 420.1633. FTIR (KBr, cm^{-1}): 3442, 2827, 1655, 1360, 650.

Ir-Catalyzed H/D Exchange of 1e:

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (1 mol %, 0.002 mmol, 1.4 mg) and D_2O (1 mL). Then, **1b** (1.0 equiv, 0.2 mmol, 60.2 mg) was added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 2 h. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1). The D% of **1b-d** was estimated by ^{1}H NMR.

KIE Experiment for Alkenyl C-H Allylation

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (2 mol %, 0.004 mmol, 2.7 mg) and H_2O (1 mL). Then, **2a** (2.0 equiv, 0.4 mmol, 52.1 mg), **1b** (1.0 equiv, 0.2 mmol, 60.2 mg) and **1b-d** (1.0 equiv, 0.2 mmol, 60.6 mg) was added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 15 min. After cooling down, the mixture was extracted and concentrated in vacuo and purified by column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) affording the product (8.8 mg) as yellow liquid. The ratio of **3ba/3ba-d** was determined by ^1H NMR to be 1.63.

KIE Experiment for Alkenyl C-H Alkenylation

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (1 mol %, 0.002 mmol, 1.4 mg) and H_2O (1 mL). Then, **4a** (2.0 equiv, 0.4 mmol, 71 mg), **1b** (1.0 equiv, 0.2 mmol, 60.2 mg) and **1b-d** (1.0 equiv, 0.2 mmol, 60.6 mg) was added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 15 min. After cooling down, the mixture was extracted and concentrated in vacuo and purified by column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1) affording the product (9.6 mg) as yellow liquid. The ratio of **5ba/5ba-d** was determined by ^1H NMR (500 MHz, $CDCl_3$) to be 2.56.

Deuterium Labelling Experiment for Alkenyl C-H Allylation

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (2 mol %, 0.004 mmol, 2.7 mg) and D_2O (1 mL). Then, **1b** (1.0 equiv, 0.2 mmol, 60.2 mg), **2a** (1.2 equiv, 0.24 mmol, 31.2 mg) was added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 11 min. After cooling down, the mixture was extracted first and then applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1).

Deuterium Labelling Experiment for Alkenyl C-H Alkenylation

A screw-cap vial was charged with $[IrOMe(cod)]_2$ (1 mol %, 0.002 mmol, 1.4 mg) and D_2O (1 mL). Then, **1b** (1.0 equiv, 0.2 mmol, 60.2 mg), **4a** (1.5 equiv, 0.3 mmol, 53.4 mg) was added into the solution in sequence. The vial was sealed under argon and heated in oil bath to 70 ℃ with stirring for 15 min. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether from 60/1 to 12/1).

■ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0000.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, HPLC charts, and deuterium labelled experiments (PDF)

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Notes

The authors declare no competing financial interest.

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