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Pinki Sihag and Masilamani Jeganmohan*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

E-mail: mjeganmohan@iitm.ac.in

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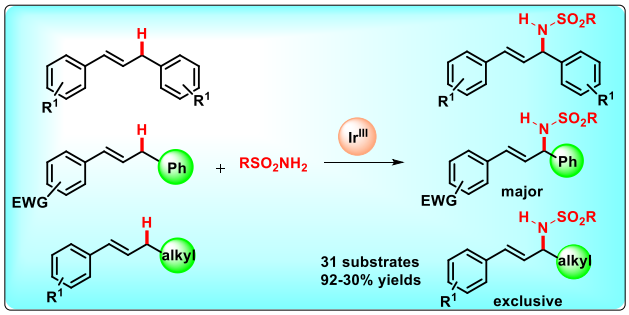


Abstract

The Ir(III)-catalyzed direct allylic C-H amidation of substituted internal alkenes with substituted sulfonamides without having directing group is demonstrated. The present protocol provides substituted allylic amines in a highly atom- and step-economical manner. The reaction was compatible with symmetrical and unsymmetrical internal alkenes as well as substituted sulfonamides. It is interesting to note that in the reaction of aryl-alkyl alkenes, the amidation selectively takes place at the alkyl substituted allylic carbon. Meanwhile, the better selectivity was also observed in the unsymmetrical aryl-aryl alkenes having electron-withdrawing substituent at one of the aryl groups. A possible reaction mechanism involving π-allyl iridium intermediate was proposed and supported by the deuterium labelling studies. The deuterium labelling study clearly reveals that in reaction mechanism, the initial C-H activation step via deprotonation pathway is reversible and nucleophile prefers to attack at the more electrophilic carbon of π-allyl iridium intermediate.

Introduction

The transition-metal-catalyzed allylic C-H functionalization of alkenes with nucleophiles has gained tremendous attention in organic synthesis for the past few years.[1] By employing this

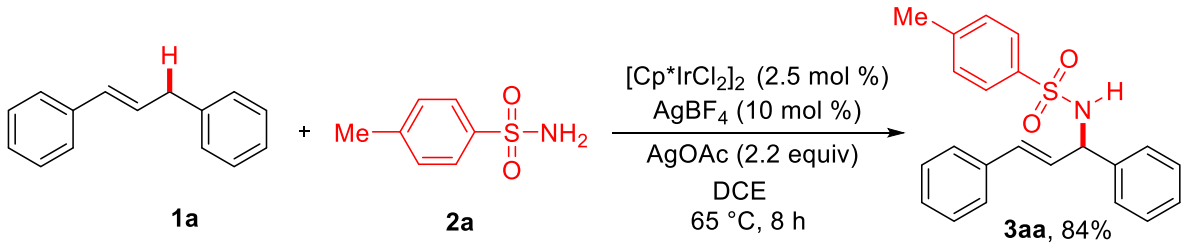
strategy, various chemical bonds such as C-O, C-N, and C-C can be constructed very effectively.[2-4] The allylic C-H bond of terminal alkenes can be activated very effectively in the presence of a palladium catalyst via π-allyl mechanism.[5] However, internal alkenes were not compatible for this type of reaction. The allylic C-H functionalization of internal alkene is very challenging as compared with the terminal alkene due to the high thermodynamic stability of internal alkene. The recent studies clearly reveal that the high valent Ru(II), Rh(III) and Ir(III) complexes can isomerizes the double bond of alkenes *via* π-allyl mechanism.[6-9] Recently, Blakey's group has reported a Rh(III)-catalyzed intermolecular C-H amination and etherification of internal alkenes with N and O nucleophiles.[7a-b] Subsequently, Glorius's group has reported a Rh(III)-catalyzed allylic C-C bond formation of internal alkenes with carbon nucleophiles.[7c-d] The low valent Iridium complexes are well known for carrying out various allylic substitution reactions. However, this type of allylic functionalization requires a labile leaving group at the allylic position.[8] Very recently, Rovis, Glorius and Blakey have independently reported Ir(III)-catalyzed intermolecular allylic amidation of terminal alkenes with substituted dioxazolones was reported.[9] However, internal alkenes are not very effective for this type of reaction due to the high thermodynamic stability. Herein, we report the Ir(III)-catalyzed intermolecular allylic C(sp^3)-H amidation of highly challenging unactivated internal alkenes with sulphonamides. The reaction was compatible with symmetrical and unsymmetrical internal alkenes as well as substituted sulfonamides. It is interesting to note that in the reaction of aryl-alkyl alkenes, the amidation selectively takes place at the alkyl substituted allylic carbon selectively. Meanwhile, the better selectivity was also observed in the unsymmetrical aryl-aryl alkenes having electron-withdrawing substituent at one of the aryl groups. The amidation reaction proceeds *via* π-allyl intermediate and the proposed mechanism was supported by the deuterium labelling studies.

Results and Discussion

Treatment of *trans* 1,3-diphenylpropene (**1a**) with *p*-toluenesulfonamide**2a** (2.5 equiv) in the presence of $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgBF_4$ (10 mol %) and AgOAc (2.2 equiv) in $ClCH_2CH_2Cl$ (DCE) for 8 h at 65 °C gave the expected allylic C-H amidation product **3aa** in 84% yield (Scheme 1). Initially, the amidation reaction was examined with various acetate sources (2.2 equiv) such as LiOAc, NaOAc, $Cu(OAc)_2$ and AgOAc (Table 1, entries 1-4). Among them, AgOAc was very effective, yielding product **3aa** in 84% yield (entry 4). $Cu(OAc)_2$ was partially effective, giving product **3aa** in moderate 45% yield (entry 3).

LiOAc and NaOAc were not effective for the reaction (entries 1 and 2). The reaction was examined with other silver based oxidants such as Ag_2CO_3 and Ag_2O. Ag_2CO_3 was equally effective as like AgOAc, yielding product **3aa** in 77% yield (entry 5). Ag_2O yielded only product **3aa** in 15% yield (entry 6). Further, the effect of counter ion such as $AgBF_4$, AgOTf, $AgSbF_6$ and KPF_6 were examined (entries 7-9). Among them, $AgBF_4$ was very effective, giving product **3aa** in 84% yield (entry 4). AgOTf was partially effective, giving product **3aa** in 75% yield (entry 9). $AgSbF_6$ and KPF_6 were ineffective for the reaction (entries 7 and 8). The reaction was further examined with solvents such as toluene, CH_2Cl_2, $ClCH_2CH_2Cl$, 1,4-dioxane, DMF, THF and MeOH. Among them, $ClCH_2CH_2Cl$ was very effective, giving product **3aa** in 84% yield (entry 5). Other solvents were not effective for the reaction. The product **3aa** was not formed in the absence of AgOAc (entry 10). This result clearly reveals that the metal oxidant is needed for the reaction. Meanwhile, the reaction was examined without $AgBF_4$ (entry 11). However, in this reaction also product **3aa** was not observed. The optimization studies clearly reveal that the $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgBF_4$ (10 mol %) and AgOAc (2.2 equiv) in $ClCH_2CH_2Cl$ is the best conditions for the amidation reaction.

Scheme 1. Iridium-Catalyzed Allylic C-H Amidation



1a 2a **3aa**, 84%

Table 1. Optimization of Allylic Amidation Reaction[a]

Entry	Solvent	Base	additive	yield (%)[b]
1	DCE	LiOAc	$AgBF_4$	NR
2	DCE	NaOAc	$AgBF_4$	NR
3	DCE	$Cu(OAc)_2$	$AgBF_4$	45
4	DCE	AgOAc	$AgBF_4$	84
5	DCE	Ag_2CO_3	$AgBF_4$	77

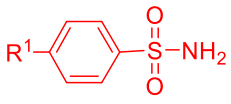
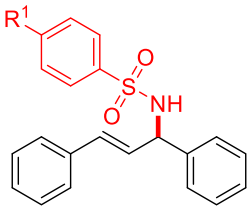
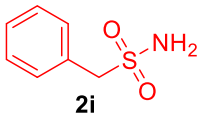
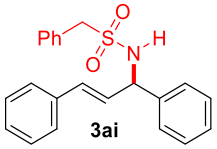
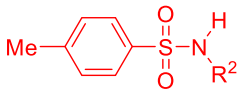
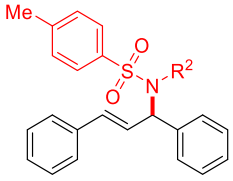
6	DCE	Ag_2O	$AgBF_4$	15
7	DCE	AgOAc	$AgSbF_6$	NR
8	DCE	AgOAc	KPF_6	NR
9	DCE	AgOAc	AgOTf	75
10	DCE	-	$AgBF_4$	NR
11	DCE	AgOAc	-	NR

[a]All reactions were carried out using **1a** (50 mg), **2a** (2.5 equiv) in the presence of $[Cp^*IrCl_2]_2$(2.5 mol %), base (2.2 equiv), additive (10 mol %) in solvent (2.0 mL) under N_2 at 65 °C for 8 h. [b]Isolated yield.

The scope of allylic amidation reaction was examined with various substituted sulfonamides under the optimized reaction conditions (Table 2). The reaction was examined with electron-donating group such as 4-methoxy **2b** and 4-*tert*-butyl **2c** phenyl sulfonamides. In the reaction, the expected allylic amidation products **3ab** and **3ac** were observed in 66% and 65% yields, respectively (entries 1 and 2). Phenyl sulfonamide was also effectively involved in the reaction, giving product **3ad** in 77% yield (entry 3). Halogen such as 4-Br, 4-Cl and 4-F substituted phenyl sulfonamides**2e-g** also efficiently participated in the reaction, giving the expected products **3ae-ag** in good to excellent 70%, 86%, 92% yields, respectively (entries 4-6). The reaction of electron-deficient 4-nitro phenyl sulfonamide (**2h**) with **1a** yielded product **3ah** in 30% yield (entry 7). Benzenemethanesulfonamide (**2i)** reacted efficiently with **1a** providing product **3ai** in 56% yield (entry 8). The reaction was further examined with secondary sulfonamides**2j-k**. *N*-methyl (**2i**) and *N*-benzyl (**2j**) substituted *p*-toulene sulphonamides reacted with **1a** yielding products **3aj** and **3ak** in moderate 58% and 34% yields, respectively (entries 9 and 10). However, ditosylamine (**2l**) provided product **3aa** with the loss of one of the tosyl group in 70% yield (entry 11). In the substrates **2h** and **2k**, the yield of product was not increased for the longer reaction time. The reaction of **1a** with ethylamine as nucleophile did not give the desired product under the optimized reaction conditions.

Table 2. Scope of Sulphonamides 2b-k with 1a[a]

Entry	**2**	product **3**	yield (%)[b]

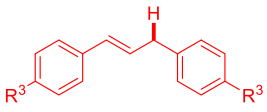
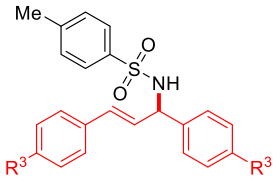
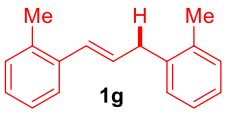
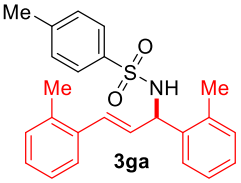
			
1	**2b**: R^1 = OMe	**3ab**: R^1 = OMe	66
2	**2c**: R^1 = *tert*-Bu	**3ac**: R^1 = *tert*-Bu	65
3	**2d**: R^1 = H	**3ad**: R^1 = H	77
4	**2e**: R^1 = Br	**3ae**: R^1 = Br	70
5	**2f**: R^1 = Cl	**3af**: R^1 = Cl	86
6	**2g**: R^1 = F	**3ag**: R^1 = F	92
7	**2h**: R^1 = NO_2	**3ah**: R^1 = NO_2	30
8	 **2i**	 **3ai**	56
			
9	**2j**: R^2 = Me	**3aj**: R^1 = Me	58
10	**2k**:R^2=CH_2Ph	**3ak**: R^1 = CH_2Ph	34
11	**2l**: R^2 = Tosyl	**3aa**: R^1 = H	70

[a]All reactions were carried out using **1a** (50 mg), **2b-l** (2.5 equiv), $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgBF_4$ (10 mol %) and AgOAc (2.2 equiv) in DCE (2.0 mL) under N_2 at 65 °C for 8 h.[b]Isolated yield.

The reaction was further examined with symmetrical aryl-aryl internal alkenes (Table 3). The reaction of alkenes with electron-donating OMe and Me substituent on the aromatic ring of **1b** and **1c** with **2a** provided products **3ba** and **3ca** in moderate 42% and 56% yields, respectively (entries 1 and 2). Similarly, alkenes with halogen group Br, Cl and F substituent on the aromatic ring of **1d**, **1e** and **1f** effectively participated in reaction, yielding products **3da**, **3ea** and **3fa** in excellent 94%, 91% and 92% yields, respectively (entries 3-5). Alkene with Methyl substituent at the *ortho* position of phenyl group **1g** reacted with **2a** producing product **3ga** in moderate 56% yield (entry 6).

Table 3. Scope of Symmetrical Aryl-Aryl Alkenes 1[a]

Entry	**1**	product **3**	yield (%)[b]

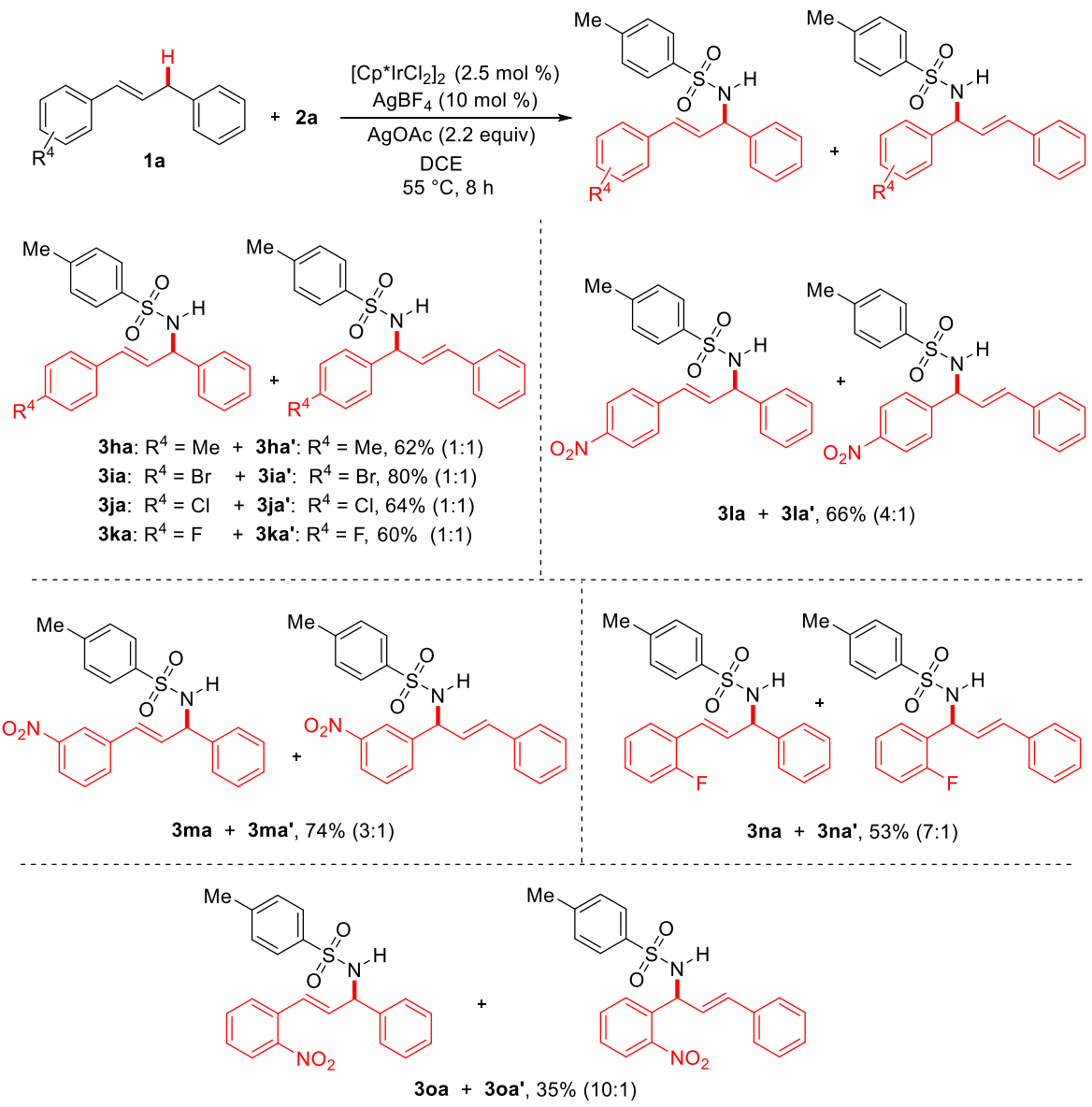
			
1	**1b**: R^3 = OMe	**3ba**: R^1 = Me	42
2	**1c**: R^3 = Me	**3ca**: R^1 = H	56
3	**1d**: R^3 = Br	**3da**: R^1 = Br	94
4	**1e**: R^3 = Cl	**3ea**: R^1 = Cl	91
5	**1f**: R^3 = F	**3fa**: R^1 = F	92
6	 **1g**	 **3ga**	56

[a]All reactions were carried out using **1b-g** (50 mg), **2a** (50 mg), $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgBF_4$ (10 mol %) and AgOAc (2.2 equiv) in DCE (2.0 mL) under N_2 at 65 °C for 8 h.[b]Isolated yield.

The scope of allylic amidation reaction was further examined with unsymmetrical aryl-aryl internal alkenes **1h-o** having substituent at one of the phenyl rings (Scheme 2). Alkene with methyl group at the *para* position of one of the phenyl rings of internal alkene **1h** reacted with **2a** giving 1:1 inseparable regioisomeric mixtures of **3ha** and **3ha'** in 62% combined yield. Similarly, alkenes containing halogen group such as Br, Cl and F at the *para* position of one of the phenyl rings of alkenes **1i-k** reacted with **2a**providing1:1 inseparable regioisomeric mixtures of **3ia-ka** and **3ia'-ka'** products in 80%, 64% and 60%combined yields, respectively. Alkene with electron-withdrawing NO_2substituentatthe *para* position of one of the phenyl rings**1l**provided products **3la** and **3la'** in 66% combined yields with 4:1 regioisomeric ratios. Similarly, alkenes having nitro at the *meta* position of one of the phenyl rings **1m** reacted with **2a** giving expected products **3ma** and **3ma'** in combined 74% yield with 3:1 regioisomeric ratios. To know the better selectivity, the reaction was examined with *ortho* F and NO_2 substituents at one of the phenyl groups **1n** and **1o** of alkenes. In the reaction of **1n** with **2a**, products **3na** and **3na'** were observed in 53% yields in 7:1 ratios. It is important to note that in the reaction of **1o** with **2a**, products **3oa** and **3oa'** were observed in 35% yields with 10:1 ratios. These results observed in the reaction of **1l-o** with **2a** clearly demonstrate that the amidation takes place majorly at the allylic carbon of Phenyl substituent rather than the electron-withdrawing group substituted aryl moiety. In the reaction of

unsymmetrical aryl-aryl internal alkenes with **2**, the expected product was not formed on increasing the reaction temperature above 60°C.

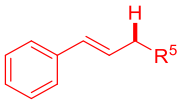
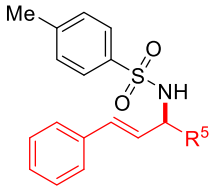
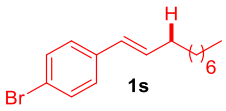
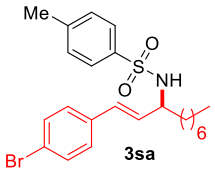
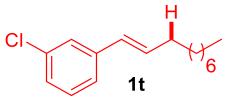
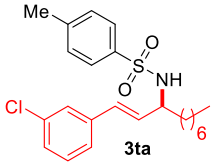
Scheme 2. Scope of Unsymmetrical Aryl-Aryl Alkenes



The reaction was also examined with various unsymmetrical aryl-alkyl alkenes **1p-t** (Table 4). It is very interesting to note that the reaction is highly regioselective and only a single regioisomeric product was observed out of the two possible regioisomeric products. In the reaction, the nucleophile attacks at the allylic sp^3-carbon atom. The reaction of aryl-alkyl alkenes **1p-r** having a longer alkyl chain such as heptyl, pentyl and propyl with **2a** provided products **3pa**, **3qa** and **3ra** in 40%, 45% and 56% yields, respectively, in a highly regioselective manner. Similarly, the reaction of alkenes with Br and Cl substituent on the

aryl ring, **1s** and **1t** with **2a** gave products **3sa** and **3ta** in 67% and 48% yields, respectively. In the preset iridium-catalyzed reaction, the amidation selectively takes place at the allylic sp^3-carbon atom. However, in the unsymmetrical aryl-alkyl alkenes, the mixture of products was observed in the presence of rhodium complex. Under the optimized reaction conditions, conjugated alkene such as 1,3-butadiene was not compatible for the reaction.

Table 4. Scope of Unsymmetrical Aryl-Alkyl Alkenes[a]

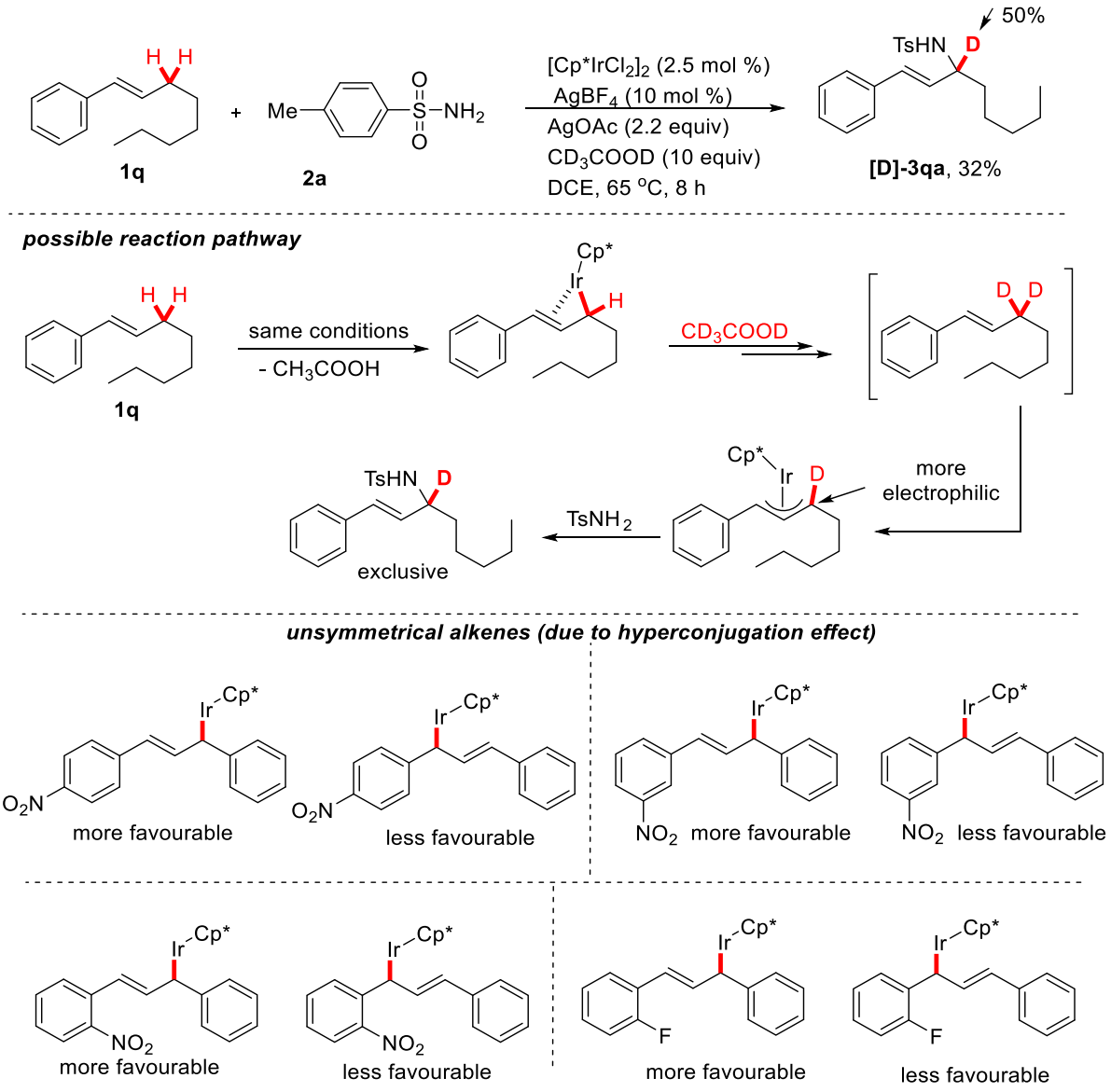
Entry	**1**	product **3**	yield (%)[b]
			
1	**1p**: R^5 =heptyl	**3pa**: R^5 = heptyl	40
2	**1q**: R^5 = pentyl	**3qa**: R^5 = pentyl	46
3	**1r**: R^5 = propyl	**3ra**: R^5 = propyl	56
4	 **1s**	 **3sa**	67
5	 **1t**	 **3ta**	48

[a]All reactions were carried out using **1p-t** (50 mg), **2a** (50 mg), $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgBF_4$ (10 mol %) and AgOAc (2.2 equiv) in DCE(2.0 mL) under N_2 at 65 °C for 8 h.[b]Isolated yield.

To understand the reaction mechanism, the deuterium labelling reaction was performed (Scheme 3). Treatment of **1q** with **2a** in the presence of CD_3COOD (10 equiv) under the optimized reaction conditions gave product **[D]-3qa** in 32% yield with the 50% of deuterium incorporation at the allylic carbon. This result clearly reveals that the initial C-H activation step *via* deprotonation pathway is reversible in nature which is in contrast with a Rh(III)-catalyzed reaction.[7a] It is important to mention that no deuterium incorporation was observed at the allylic carbon in the reaction of **1q** with CD_3COOD under the optimized reaction conditions. Meanwhile, the above observation shows that the deuterium incorporation occurs only at the alkyl substituted allylic carbon of π-allyl intermediate which explains the involvement of π-allyl intermediate in the reaction. It is also strongly believed

that the alkyl substituted carbon of π-allyl intermediate is more electrophilic in nature as compared with aryl substituted carbon. Thus, the nucleophile very selectively attacks at the alkyl substituted carbon of π-allyl intermediate. The better selectivity was also observed in the unsymmetrical aryl-aryl alkenes having electron-withdrawing substituent at one of the aryl groups **1l-o** (Scheme 3). It is expected that the phenyl substituted carbon of π-allyl intermediate is more electrophilic in nature as compared with electron-deficient aryl moiety due to the hyperconjugation effect.

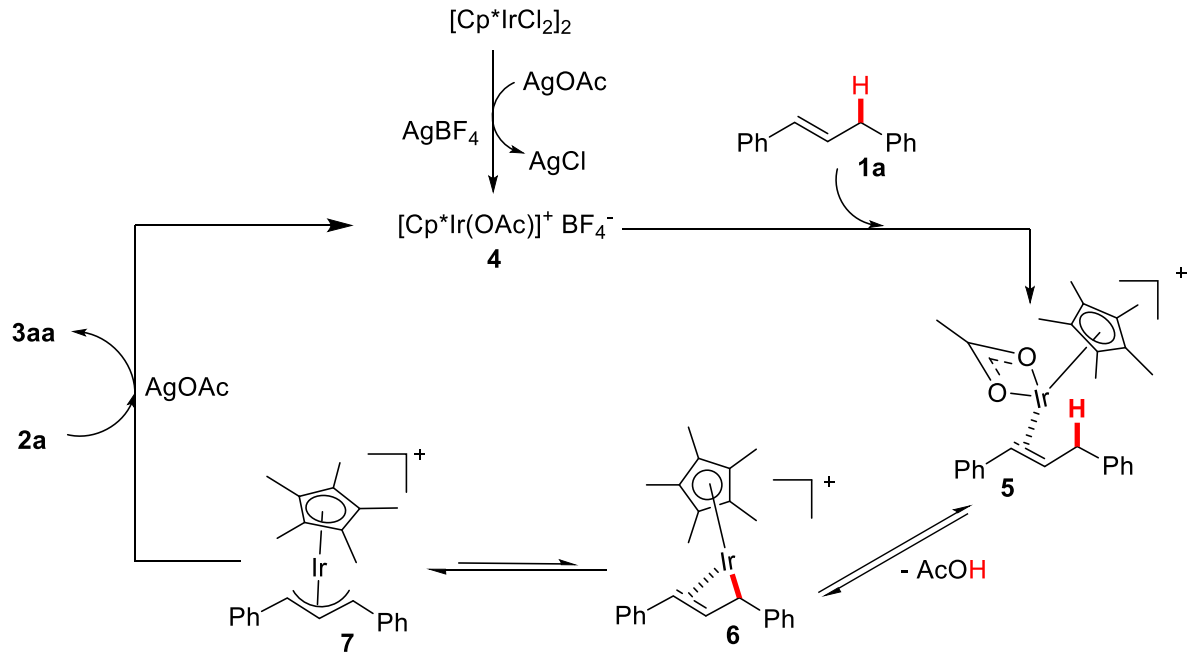
Scheme 3. Mechanistic Investigations



A plausible mechanism is proposed to account for the present allylic amidation reaction in Scheme 4.[5-9] The reaction of $[Cp^*IrCl_2]_2$ with AgOAc and $AgBF_4$ provides the active cationic

complex [Cp*Ir(OAc)][BF_4] **4**. The coordination of double bond of alkene **1** with the iridium complex **4** gives complex **5**. The allylic C-H bond of alkene is deprotonated by an acetate group of complex **5** affords σ-allyl iridium complex **6**. Intermediate **6** undergoes allylic isomerization to give π-allyl iridium complex **7**. The nucleophilic addition of nitrogen atom of sulfonamide**2**with complex **7**gives product **3aa** and the active catalyst Ir(III) complex **4**is regenerated in the presence of AgOAc for the next cycle.

Scheme 4. Proposed Mechanism



Conclusion

In conclusion, we have successfully demonstrated Ir(III)-catalyzed direct allylic C-H amidation of unactivated substituted internal alkenes with substituted sulphonamides. The reaction provides substituted allylic amines in a highly atom- and step-economical manner. The reaction was compatible with symmetrical and unsymmetrical internal alkenes as well as substituted sulfonamides. It is interesting to note that in the reaction of in the unsymmetrical alkenes, the amidation preferably takes place at the more electrophilic carbon of π-allylic intermediate due to the hyperconjugation effect. A possible reaction mechanism involves π-allyl intermediate was proposed and also strongly supported by deuterium labelling study. The deuterium labelling study clearly reveals that the reversibility of initial C-H activation step via deprotonation pathway as well as more preference of nucleophile to attack at the more electrophilic carbon of π-allyl intermediate.

Experimental Section

General information: All reactions were carried out under the N_2 atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents are used for the reaction. Column chromatographical purifications were performed using SiO_2 (120- 200 mesh ASTM) from Merck if not indicated otherwise. Abbrevations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; DCE, 1,2-Dichloroethane; DTBP, Di-tert-butyl peroxide; DCM, Dichloromethane; DMF, Dimethylformamide; MeCN, Acetonitrile. Starting Materials: alkenes, **1**[10a-d] and sulphonamides, **2**[10e-g] were prepared according to the literature procedures. Commercially available metal salts and acids were purchased from Sigma-Aldrich and Spectrochem. Pvt. Ltd., India and used without further purification.

General Procedure for the Synthesis of Allylic Amidation product 3:

A 15ml schlenk tube with septum containing sulphonamide **2a** (110 mg, 0.6 mmol) and $[Cp^*IrCl_2]_2$ (5 mg, 2.5 mol %) was evacuated and purged with nitrogen gas three times. In the glove box, $AgBF_4$ (5 mg, 10 mol %) and AgOAc (95 mg, 0.5 mmol) was added to the schlenk tube. Followed by, alkene **1a** (50 mg, 0.25 mmol) was dissolved in 1,2-dichloroethane (2 mL) was added *via* syringe and the reaction mixture was evacuated and purged with nitrogen gas three times. Then rubber septum was taken out and screw cap was used to cover the tube. The reaction mixture was allowed to stir at 65 ^oC (in oil bath) for 8 h. Then the reaction mixture was allowed to reach ambient temperature and diluted with CH_2Cl_2, followed by filteration through celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent to give pure **3aa** in 84% isolated yield. The yield of product was calculated based on alkene **1a.** The reaction was also examined in 1 mmol scale of **1a** (0.194 mg, 1 mmol), **2a** (0.425 mg, 2.5mmol), $[Cp^*IrCl_2]_2$ (0.020 mg, 2.5 mol %), $AgBF_4$ (0.20 mg, 10 mol %) and AgOAc (0.367 mg, 2.2 mmol) in 1,2-dichloroethane (12 mL). In the reaction, product **3aa** was observed in 83% yield (303 mg).

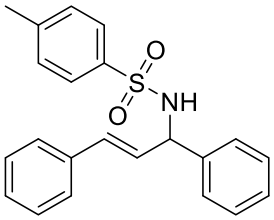
Mechanistic Studies

Deuterium labelling studies: A 15ml schlenk tube with septum containing sulphonamide **2a** (110 mg, 0.6 mmol) and $[Cp^*IrCl_2]_2$ (5 mg, 2.5 mol %) was evacuated and purged with nitrogen gas three times. In the glove box, $AgBF_4$ (5 mg, 10 mol %), AgOAc (95 mg, 0.5

mmol) and CD_3COOD (10 equiv) was added to the schlenk tube. Followed by, alkene **1q** (50 mg, 0.2 mmol) was dissolved in 1,2-Dichloroethane (2 mL) was added *via* syringe and the reaction mixture was evacuated and purged with nitrogen gas three times. Then rubber septum was taken out and screw cap was used to cover the tube. The reaction mixture was allowed to stir at 65 ^oC (in oil bath) for 8 h. Then the reaction mixture was allowed to reach ambient temperature and diluted with CH_2Cl_2, followed by filteration through celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent to give pure **[D]-3qa** in 32% isolated yield. The yield of product was calculated based on alkene **1q.** **^{1}H NMR(400 MHz, $CDCl_3$)**:δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.22 (m, 7H), 7.11 (d, *J* = 7.0 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 5.71 (dd, *J* = 15.9, 6.0 Hz, 1H), 4.54 (s, 1H), 3.98 – 3.84 (m, 0.5H), 2.30 (s, 3H), 1.56 – 1.43 (m, 2H), 1.34 – 1.15 (m, 6H), 0.84 (t, *J* = 6.8Hz, 3H).

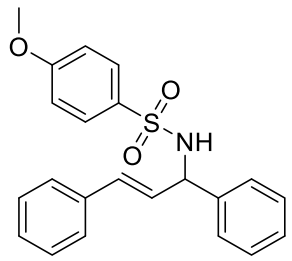
Spectral Data of All Compounds:

(*E*)-*N*-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide(3aa):



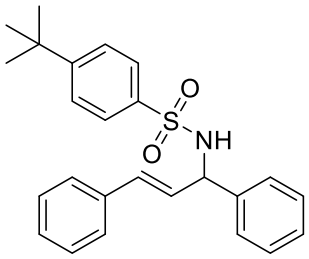
Prepared according to general procedure for the reaction of **1a** with **2a**; white solid; eluent (10 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 84% (81 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.34 – 6.85 (m, 6H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 6.5 Hz, s1H), 5.12 – 4.85 (m, 1H), 2.24 (s, 1H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$):** δ 143.3, 139.6, 137.7, 136.0, 132.1, 129.4, 128.7, 128.4, 128.1, 127.9, 127.3, 127.0, 126.5, 59.7and 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{21}NO_2SNa$ 386.1191, Found 386.1194.

(*E*)-*N*-(1,3-Diphenylallyl)-4-methoxybenzenesulfonamide (3ab):



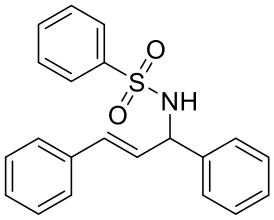
Prepared according to general procedure for the reaction of **1a** with **2b**; white solid; eluent (15 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 66% (65 mg); Mp: 90-91 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.9 Hz, 2H), 7.27 – 7.15 (m, 10H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.27 (d, *J* = 7.9 Hz, 1H), 5.09 (t, *J* = 7.0 Hz, 1H), 3.73 (s, 3H). **^{13}C {1H} NMR (126 MHz, $CDCl_3$):** δ 162.7, 139.7, 136.1, 132.3, 132.0, 129.4, 128.7, 128.4, 128.3, 127.8, 127.8, 127.0, 126.5, 113.9, 59.8and 55.5. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{21}NO_3SNa$ 402.1140; Found 402.1145.

(*E*)-4-(*tert*-Butyl)-N-(1,3-diphenylallyl)benzenesulfonamide (3ac):



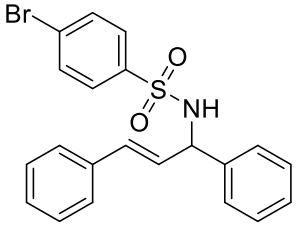
Prepared according to general procedure for the reaction of **1a** with **2c**; white solid; eluent (8 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 65% (68 mg)); Mp: 148-150 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.68 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.12 (m, 10H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.39 – 5.24 (m, 1H), 5.15 (t, *J* = 7.1 Hz, 1H), 1.24 (s, 9H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**:δ 156.1, 139.6, 137.6, 136.0, 132.1, 128.6, 128.4, 128.2, 127.8, 127.8, 127.1, 127.0, 126.5, 125.7, 59.7, 34.9and 31.0. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{25}H_{31}N_2O_2S$ 423.2106; Found 423.2109.

(*E*)-*N*-(1,3-Diphenylallyl)benzenesulfonamide (3ad):



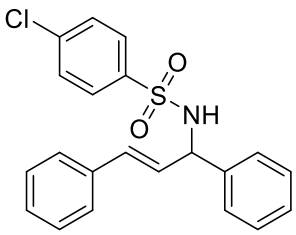
Prepared according to general procedure for the reaction of **1a** with **2d**; white solid; eluent (10 % ethyl acetate in hexane);**1a** was taken in 50 mg; yield is 77% (70 mg); Mp: 100-104 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.13 (m, 7H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.32 (s, 1H), 5.15 (t, *J* = 6.4 Hz, 1H). **^{13}C {1H} NMR (101 MHz, $CDCl_3$)**:δ 140.6, 139.5, 136.0, 132.4, 132.1, 128.8, 128.7, 128.4, 128.2, 127.9, 127.9, 127.2, 127.0, 126.5 and 59.8. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{21}H_{19}NO_2SNa$ 372.1034, Found 372.1035.

(*E*)-4-Bromo-*N*-(1,3-diphenylallyl)benzenesulfonamide (3ae):



Prepared according to general procedure for the reaction of **1a** with **2e**; white solid; eluent (12 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 70% (77 mg); Mp: 106-108 °C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.23 (m, *J* = 10H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.39 – 5.20 (m, 1H), 5.14 (t, *J* = 6.9 Hz, 1H). **^{13}C {1H} NMR (126 MHz, $CDCl_3$)**: δ 139.8, 139.2, 135.8, 132.5, 132.0, 128.8, 128.8, 128.6, 128.0, 128.0, 127.8, 127.3, 127.0, 126.5, 60.0. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{21}H_{18}NO_2SBrNa$ 450.0139;Found 450.0120.

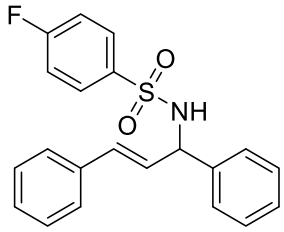
(E)-4-Chloro-N-(1,3-diphenylallyl)benzenesulfonamide (3af):



Prepared according to general procedure for the reaction of **1a** with **2f**; white solid; eluent (12 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 86% (85 mg); Mp: 109-111 °C.

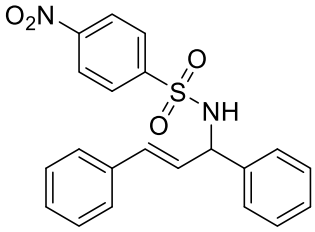
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.04 (m, 12H), 6.28 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.45 (s, 1H), 5.06 (t, *J* = 7.1 Hz, 1H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**:δ 139.2, 139.2, 138.8, 135.8, 132.3, 129.0, 128.7, 128.6, 128.5, 128.0, 127.9, 127.9, 127.0, 126.5, 59.9. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{21}H_{18}NO_2SClNa$ 406.0644; Found 406.0641.

(*E*)-*N*-(1,3-Diphenylallyl)-4-fluorobenzenesulfonamide (3ag):



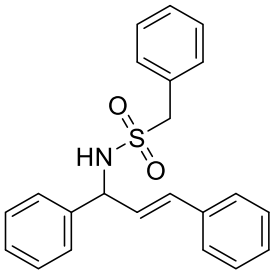
Prepared according to general procedure for the reaction of **1a** with **2g**; white solid; eluent (12 % ethyl acetate in hexane);**1a** was taken in 50 mg; yield is 95% (90 mg); Mp: 99-101 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (m, 2H), 7.21 – 7.01 (m, 10H), 6.88 (t, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.03 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.29 (broad peak, 1H), 5.07 (t, *J* = 6.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 165.0 (d, J=253 Hz), 139.2, 136.8(d, J=3 Hz), 135.9, 132.3, 129.9 (d, J=10 Hz), 128.0(d, J=5 Hz), 128.0 (d, J=4 Hz), 127.0, 126.5 116.0, 115.7, 59.9. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -105.63. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{21}H_{18}NO_2SFNa$ 390.0940;Found 390.0940.

(*E*)-*N*-(1,3-Diphenylallyl)-4-nitrobenzenesulfonamide (3ah):



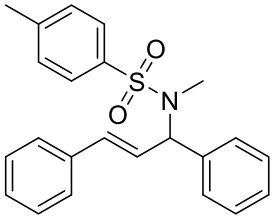
Prepared according to general procedure for the reaction of **1a** with **2h**; white solid; eluent (20 % ethyl acetate in hexane);**1a** was taken in 50 mg; yield is 30 % (28 mg); Mp: 140-142 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.08 (m, 10H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.02 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.18 (t, *J* = 6.7 Hz, 1H), 5.05 (d, *J* = 6.8 Hz, 1H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 149.6, 146.7, 138.6, 135.4, 133.1, 128.9, 128.7, 128.5, 128.3, 127.3, 127.0, 126.5, 123.9and 60.3. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{21}H_{22}N_3O_4S$ 412.1331; Found 412.1311.

(*E*)-*N*-(1,3-Diphenylallyl)-1-phenylmethanesulfonamide(3ai):



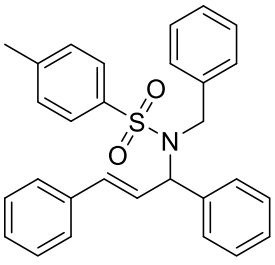
Prepared according to general procedure for the reaction of **1a** with **2i**; yellow sticky solid; eluent (8 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 56% (55 mg). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.45 – 7.23 (m, 13H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.23 (t, *J* = 6.8 Hz, 1H), 4.75 (broad peak, 1H), 4.11 (s, 1H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 140.1, 138.2, 135.9, 132.3, 130.8, 129.0, 128.7, 128.6, 128.2, 128.2, 127.2, 126.6, 60.1 and 59.9. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{21}NO_2SNa$ 386.1191; Found 386.1190.

(*E*)-*N*-(1,3-Diphenylallyl)-N,4-dimethylbenzenesulfonamide (3aj):



Prepared according to general procedure for the reaction of **1a** with **2j**; yellow liquid; eluent (8 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 58% (56 mg). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.16 (m, 12H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.6 Hz, 1H), 5.83 (d, *J* = 7.6 Hz, 1H), 2.70 (s, 3H), 2.32 (s, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 143.1, 138.5, 136.5, 136.1, 134.7, 129.4, 128.5, 128.5, 128.0, 127.8, 127.7, 127.5, 126.4, 123.8, 62.3, 30.1 and 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{23}H_{23}NO_2SNa$ 400.1347; Found 400.1352.

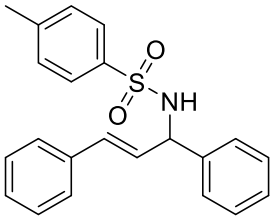
(*E*)-*N*-Benzyl-N-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (3ak):



Prepared according to general procedure for the reaction of **1a** with **2k**; yellow liquid; eluent (10 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 34% (40 mg). **^{1}H NMR (400**

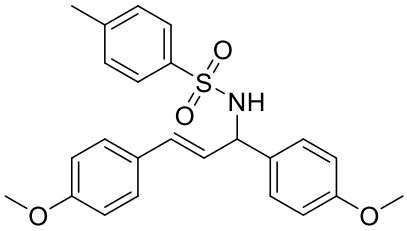
MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.06 (m, 19H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.76 (d, *J* = 8.0 Hz, 1H), 4.53 (d, *J* = 15.8 Hz, 1H), 4.30 (d, *J* = 15.8 Hz, 1H), 2.37 (s, 3H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 143.1, 138.5, 138.1, 137.5, 136.9, 133.8, 129.4, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.4, 127.2, 126.9, 126.1, 63.5, 49.2and 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{29}H_{27}NO_2SNa$ 476.1660; Found 476.1665.

(*E*)-*N*-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide (3al):



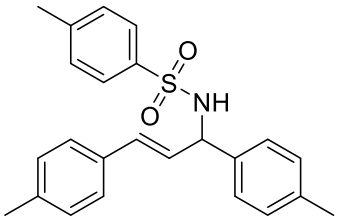
Prepared according to general procedure; white solid for the reaction of **1a** with **2l**;white solid; eluent (10 % ethyl acetate in hexane); **1a** was taken in 50 mg; yield is 70% (65 mg). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.39 – 6.98 (m, 12H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.11 (t, *J* = 6.8 Hz, 1H), 4.93 (d, *J* = 7.0 Hz, 1H), 2.33 (s, 3H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 143.1, 138.5, 138.1, 137.5, 136.3, 133.8, 129.4, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.4, 127.2, 126.5, 126.1, 63.5, 49.2 and 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{21}NO_2SNa$ 386.1191; Found 386.1190.

(*E*)-*N*-(1,3-Bis(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (3ba):



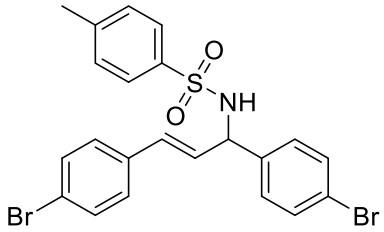
Prepared according to general procedure for the reaction of **1b** with **2a**; yellow solid; eluent (15 % ethyl acetate in hexane); **1b** was taken in 50 mg; yield is 42% (35 mg); Mp: 99-102 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.11 (m, 4H), 6.78 (m, 4H),6.27 (d, *J* = 15.5 Hz, 1H), 5.92 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.04 (t, *J* = 6.8 Hz, 1H), 4.95 – 4.91 (m, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.34 (s, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 159.4, 159.1, 143.1, 137.8, 132.0, 131.4, 129.4, 128.9, 128.3, 127.7, 127.3, 126.2, 114.0, 113.8, 59.3, 55.3 and 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{24}H_{25}NO_4SNa$ 446.1402, Found 446.1393.

(*E*)-*N*-(1,3-Di-*p*-tolylallyl)-4-methylbenzenesulfonamide (3ca):



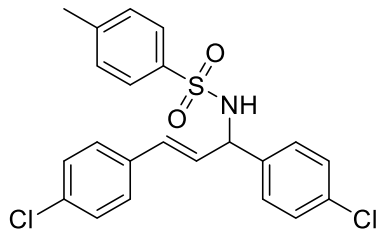
Prepared according to general procedure for the reaction of **1c** with **2a**; white solid; eluent (8 % ethyl acetate in hexane); **1c** was taken in 50 mg; yield is 56% (55 mg) Mp: 90-92°C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.02 (m, 8H), 6.29 (dd, *J* = 15.8, 1.0 Hz, 1H), 6.01 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.05 (t, *J* = 6.8 Hz, 1H), 4.92 (d, *J* = 7.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H). **^{13}C {1H} NMR (126 MHz, $CDCl_3$)**: δ 143.1, 137.8, 137.7, 137.6, 136.8, 133.3, 131.8, 129.4, 129.3, 129.1, 127.3, 127.0, 126.4, 59.6, 21.4, 21.2, and 21.0. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{24}H_{25}NO_2SNa$ 414.1504; Found 414.1512.

(*E*)-*N*-(1,3-*bis*(4-Bromophenyl)allyl)-4-methylbenzenesulfonamide (3da):



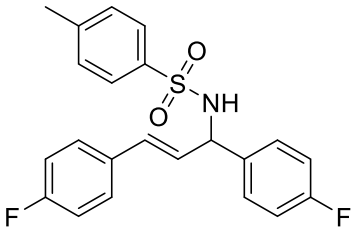
Prepared according to general procedure for the reaction of **1d** with **2a**; white solid; eluent (15 % ethyl acetate in hexane); **1d** was taken in 50 mg; yield is 94% (91 mg); Mp: 172-176 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.03 (m, 4H), 6.26 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.29 (broad doublet,1H), 5.04 (t, *J* = 7.0 Hz, 1H), 2.34 (s, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$):** δ 143.6, 138.3, 137.4, 134.7, 131.8, 131.6, 131.4, 129.5, 128.8, 128.3, 128.0, 127.2, 122.0, 59.1, and 21.4. **HRMS (ESI):** $(M+NH_4)^+$ Calcd for $C_{22}H_{23}Br_2N_2O_2S$ 536.9847; Found 538.9806.

(*E*)-*N*-(1,3-*bis*(4-Chlorophenyl)allyl)-4-methylbenzenesulfonamide (3ea):



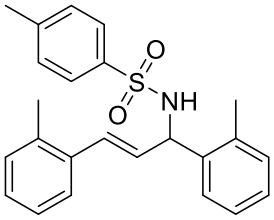
Prepared according to general procedure for the reaction of **1e** with **2a**; white solid; eluent (15 % ethyl acetate in hexane); **1e** was taken in 50 mg; yield is 91% (75 mg); Mp: 131-133°C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.12 (m, 4H), 7.07 – 6.99 (m, 6H), 6.19 (d, *J* = 15.8 Hz, 1H), 5.94 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 4.99 (s, 1H), 2.26 (s, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 143.5, 137.9, 137.5, 134.3, 133.8, 133.7, 131.2, 129.5, 128.8, 128.7, 128.5, 128.3, 127.7, 127.2, 59.1, 21.4. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{19}Cl_2NO_2SNa$ 454.0411;Found 454.0401.

(*E*)-*N*-(1,3-*bis*(4-Fluorophenyl)allyl)-4-methylbenzenesulfonamide (3fa):



Prepared according to general procedure for the reaction of **1f** with **2a**; white solid; eluent (15 % ethyl acetate in hexane); **1f** was taken in 50 mg; yield is 92% (80 mg); Mp: 128-130 °C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.15 (m,6H), 6.93 (m, 4H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 5.09 (d, *J* = 6.8 Hz, 1H), 2.33 (s, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 162.5 (d, J=247 Hz), 162.0 (d, J=247 Hz), 143.4, 137.7, 135.0 (d, J= 3 Hz), 132.4 (d, J=3 Hz), 131.2, 129.5, 129.0 (d, J=9), 128 (d, J=8), 127.7, 127.3, 115.6 (d, J=16 Hz), 115.5(d, J=16 Hz), 59.1, 21.4. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -113.56, -114.09. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{19}F_2NO_2SNa$ 422.1002; Found 422.0996.

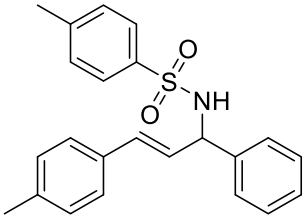
(*E*)-*N*-(1,3-Di-*o*-tolylallyl)-4-methylbenzenesulfonamide (3ga):



Prepared according to general procedure for the reaction of **1g** with **2a**; white solid; eluent (8 % ethyl acetate in hexane);**1g** was taken in 50 mg; yield is 56% (50 mg); Mp: 88-90 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.04 (m,10H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.89 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.28 (t, *J* = 6.4 Hz, 1H), 5.12 (broad peak,1H), 2.24 (s, 3H), 2.23 (s, 3H), 2.09 (s, 3H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 143.2, 137.8, 137.7, 135.5, 135.4, 135.2, 130.7, 130.1, 129.8, 129.4, 129.4, 127.7, 127.6, 127.1, 126.7, 126.3,

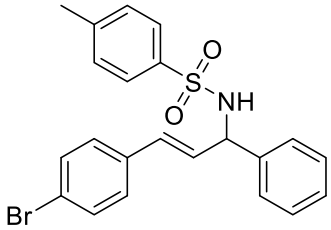
125.9, 125.7, 56.5, 21.4, 19.5, 19.2. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$Calcd for $C_{24}H_{25}NO_2SNa$ 414.1504; Found 414.1495.

(*E*)-4-Methyl-*N*-(1-phenyl-3-(*p*-tolyl)allyl)benzenesulfonamide (3ha+3ha'):



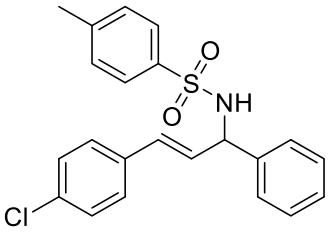
Prepared according to general procedure for the reaction of **1h** with **2a** at 55°C; yellow solid; eluent (8 % ethyl acetate in hexane);**1h** was taken in 50 mg; yield is 62% (56 mg) as 1:1 inseparable regioisomeric mixtures); Mp: 72-74 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (dd, *J* = 7.6, 3.6 Hz, 4H), 7.30 – 6.99 (m, 22H), 6.44 – 6.23 (m, 2H), 6.03 (td, *J* = 17.6, 6.4 Hz, 2H), 5.11 (m, 4H), 2.44 – 2.20 (m, 12H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 143.1, 139.8, 137.7, 137.6, 136.6, 136.1, 133.2, 132.0, 131.8, 129.4, 129.3, 129.1, 128.6, 128.4, 128.3, 127.8, 127.7, 127.3, 127.3, 127.1, 127.0, 126.9, 126.5, 126.4, 59.8, 59.5, 21.4, 21.1, 21.0. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{23}H_{23}NO_2SNa$ 400.1347; Found 400.1340.

(*E*)-*N*-(3-(4-Bromophenyl)-1-phenylallyl)-4-methylbenzenesulfonamide (3ia+ 3ia'):



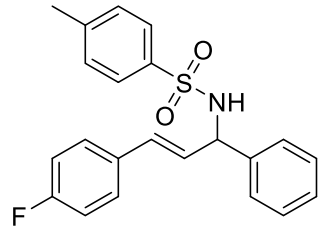
Prepared according to general procedure for the reaction of **1i** with **2a** at 55°C; white solid; eluent (10 % ethyl acetate in hexane);**1i** was taken in 50 mg; yield is 80% (65 mg) as 1:1 inseparable regioisomeric mixtures); Mp: 80-82°C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.64 (d, 8.5 Hz, 2H), 7.62 (d, 8.5 Hz, 2H), 7.34 (dd, *J* = 17.1, 8.4 Hz, 4H), 7.27 – 7.10 (m,14H), 7.04 (dd, *J* = 19.0, 8.4 Hz, 4H), 6.29 (d, *J* = 15.8 Hz, 2H), 6.06 (m, 1H), 6.06 (m, 1H), 5.39 (d, *J* = 7.0 Hz, 1H), 5.39 (d, *J* = 7.0 Hz, 1.0H), 5.07 (dt, *J* = 11.4, 7.0 Hz, 2H), 2.32 (s, 6H). **^{13}C {1H}NMR (101 MHz, $CDCl_3$)**: δ 143.1, 139.8, 137.7, 137.6, 136.7, 136.1, 133.2, 132.0, 131.8, 129.4, 129.3, 129.1, 128.6, 128.4, 128.3, 127.8, 127.7, 127.3, 127.3, 127.1, 127.0, 126.9, 126.5, 126.4, 59.8, 59.5, 21.4, 21.1, 21.0. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{22}H_{24}BrN_2O_2S$ 459.0742;Found 459.0738.

(*E*)-*N*-(3-(4-Chlorophenyl)-1-phenylallyl)-4-methylbenzenesulfonamide (3ja+3ja'):



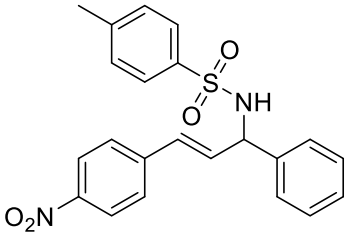
Prepared according to general procedure for the reaction of **1j** with **2a** at 55°C; white solid; eluent (10 % ethyl acetate in hexane); **1j** was taken in 50 mg; yield is 64% (56 mg) as 1:1 inseparable regioisomeric mixtures; Mp: 100-102 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (dd, *J* = 8.1, 2.8 Hz, 4H), 7.23 (m, 6H), 7.16 (m,10H), 6.92 (m, 4H), 6.31 (dd, *J* = 15.8, 5.8 Hz, 2Hz), 6.09 – 5.95 (m, 2H), 5.24 (broad peak, 2H), 5.09 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 6H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 143.4, 143.3, 139.4, 138.1, 137.6, 137.5, 135.8, 134.6, 133.6, 133.5, 132.5, 130.7, 129.4, 129.4, 128.9, 128.7, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.5, 127.3, 127.2, 127.0, 126.5, 59.7, 59.1, 21.4. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{22}H_{24}ClN_2O_2S$ 415.1247; Found 415.1216.

(*E*)-*N*-(3-(4-Fluorophenyl)-1-phenylallyl)-4-methylbenzenesulfonamide (3ka+3ka'):



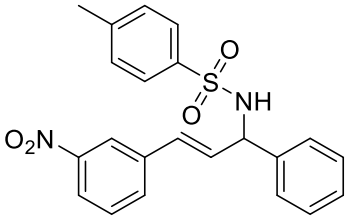
Prepared according to general procedure for the reaction of **1k** with **2a** at 55°C; white solid; eluent (10 % ethyl acetate in hexane); **1k** was taken in 50 mg; yield is 60% (54 mg) as 1:1 inseparable regioisomeric mixtures; Mp: 86-88 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (dd, *J* = 7.9, 2.1 Hz, 4H), 7.18 (ddd, *J* = 20.6, 12.4, 7.7 Hz, 19H), 6.99 – 6.85 (m, 4H), 6.32 (d, *J* = 5.1 Hz, 1H), 6.28 (d, *J* = 5.1 Hz, 1H), 6.11 – 5.95 (m, 2H), 5.39 (dd, *J* = 19.2, 6.9 Hz, 2H), 5.08 (t, *J* = 6.6 Hz, 2H), 2.31 (s, 6H). **^{13}C {1H} NMR (101 MHz, $CDCl_3$):** δ 163.3 (d, J=245 Hz), 162.0 (d, J=245 Hz), 143.3, 143.2, 139.5, 137.7, 137.6, 135.9, 135.5, 135.4, 132.2, 130.8, 129.4, 129.4, 128.8, 128.7, 128.7, 128.4, 128.1, 128.0, 128.0, 127.8, 127.8, 127.0, 126.5, 115.5, 115.4, 115.3, 115.2, 61.8, 59.7, 59.0, 21.4. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -113.87, -114.33. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{22}H_{24}FN_2O_2S$ 399.1543; Found 399.1537.

(*E*)-4-Methyl-*N*-(3-(4-nitrophenyl)-1-phenylallyl)benzenesulfonamide (3la+3la'):



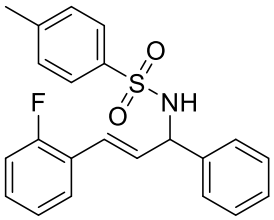
Prepared according to general procedure for the reaction of **1l** with **2a** at 55°C; white solid; eluent (20% ethyl acetate in hexane); **1l** was taken in 50 mg; yield is 66% (56 mg) as 4:1 inseparable regioisomeric mixtures; Mp: 122-124 °C.**^{1}H NMR (500 MHz, CDCl$_3$)**: δ 8.12 (d, *J* = 8.8 Hz, 2H), 8.09 (d, *J* = 8.7 Hz, 0.68H), 7.65 (m, 2.73H), 7.41 (d, *J* = 8.7 Hz, 0.94H), 7.33 (d, *J* = 8.8 Hz, 2.3H), 7.27 (m, 5H), 7.22 – 7.12 (m, 5H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.36 – 6.26 (m, 1.4H), 6.03 (dd, *J* = 15.8, 7.1 Hz, 0. 37H), 5.33 (d, *J* = 7.2 Hz, 1H), 5.33 (d, *J* = 7.2 Hz, 2.56H), 2.35 (s, 3H), 2.33 (s, 1.1H). **^{13}C {1H}NMR (126 MHz, CDCl$_3$)**: δ 147.1, 143.5, 142.5, 138.8, 137.5, 137.2, 135.3, 133.7, 133.3, 129.8, 129.6, 129.5, 129.0, 128.6, 128.5, 128.3, 128.0, 127.3, 127.2, 127.1, 127.0, 126.6, 126.3, 124.0, 123.8, 59.6, 59.2, 21.5. **HRMS (ESI- TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{22}H_{24}N_3O_4S$ 426.1488; Found 426.1486.

(*E*)-4-Methyl-*N*-(3-(4-nitrophenyl)-1-phenylallyl)benzenesulfonamide (3ma+3ma'):



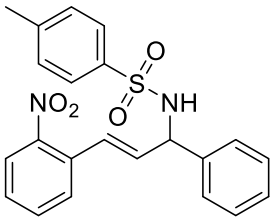
Prepared according to general procedure for the reaction of **1m** with **2a** at 55°C; yellow sticky solid; eluent (20% ethyl acetate in hexane); **1m** was taken in 50 mg; yield is 74% (63 mg) as 3:1 inseparable regioisomeric mixtures. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.06 (, *J* = 8.0 Hz, 1.25H), 7.97 (s, 1.27H), 7.68 (d, *J* = 8.2 Hz, 1.94H), 7.62 (d, *J* = 8.2 Hz, 0.97H), 7.50 (d, *J* = 7.7 Hz, 1.06 H), 7.42 (t, *J* = 8.0 Hz, 1.38H), 7.30 – 7.23 (m, 4H), 7.20 – 7.15 (m, 4.5H), 7.12 (d, *J* = 8.1 Hz, 0.6H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 0.3H), 6.25 (dd, *J* = 15.8, 6.4 Hz, 1H), 6.06 (dd, *J* = 15.8, 7.0 Hz, 0.3H), 5.58 (d, *J* = 7.2 Hz, 0.3H), 5.38 (d, *J* = 7.2 Hz, 1H), 5.20 (t, *J* = 7.0 Hz, 0.3H), 5.13 (t, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 1H). **^{13}C {1H}NMR (101 MHz, CDCl$_3$)**: δ 148.4, 148.2, 145.6, 143.7, 143.5, 141.77, 139.0, 138.0, 137.6, 137.2, 135.4, 133.5, 133.4, 132.4, 131.7, 129.7, 129.6, 129.5, 129.4, 129.0, 128.6, 128.4, 128.2, 127.3, 127.2, 127.0, 126.6, 126.5, 126.4, 122.6, 122.4, 122.0, 121.0, 59.5, 59.2, 21.4, 21.3. **HRMS (ESI-TOF) m/z:** $(M+NH_4)^+$ Calcd for $C_{22}H_{24}N_3O_4S$ 426.1488; Found 426.1481.

(*E*)-*N*-(3-(2-Fluorophenyl)-1-phenylallyl)-4-methylbenzenesulfonamide (3na+3na'):



Prepared according to general procedure for the reaction of **1n** with **2a** at 55°C; white solid; eluent (10 % ethyl acetate in hexane);**1a** was taken in 50 mg; yield is 86% (77 mg) as 7:1 inseparable regioisomeric mixtures; Mp: 135-139 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.67 (d, *J* = 8.0 Hz, 1.9H), 7.62 (d, *J* = 8.0 Hz, 1.26H), 7.34 – 6.80 (m, 18H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 0.7H), 6.23 – 6.08 (m, 1.67H), 5.50 (d, *J* = 8.3 Hz, 0.7H), 5.32 (d, *J* = 7.0 Hz, 1.65H), 5.09 (t, *J* = 6.8 Hz, 1H), 2.29 (s, 3H). **^{13}C {1H} NMR (101 MHz, $CDCl_3$)**: δ 160 (d, J=248 Hz), 160.0 (d, J=245 Hz), 143.3, 143.2, 139.4, 137.5, 137.4, 135.9, 132.0, 130.7, 130.0, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.4, 127.9, 127.8, 127.6, 127.5, 127.3, 127.1, 127.1, 127.0, 126.5, 124.5, 124.5, 124.4, 124.3, 123.9, 123.9, 123.9, 115.8, 115.7, 115.6, 115.5, 60.0, 55.3, 21.3. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -117.39, -117.41. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{22}H_{20}NO_2FSNa$404.1096; Found 404.1095.

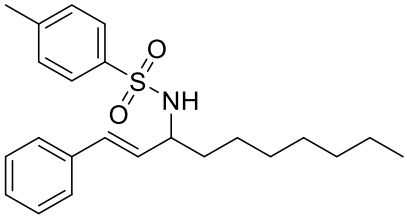
(*E*)-4-Methyl-*N*-(3-(2-nitrophenyl)-1-phenylallyl)benzenesulfonamide (3oa+3oa'):



Prepared according to general procedure for the reaction of **1o** with **2a** at 55°C; yellow solid; eluent (20% ethyl acetate in hexane); **1o** was taken in 50 mg; yield is 35% (30 mg) as 10:1 inseparable regioisomeric mixtures; Mp: 92-96°C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.92 (d, *J* = 8.1 Hz, 0.9H), 7.86 (d, *J* = 8.1 Hz, 0.1H), 7.70 (d, *J* = 8.1 Hz, 1.9H), 7.65 (d, *J* = 8.2 Hz, 0.18H), 7.58 – 7.48 (m, 1.4H), 7.38 (t, *J* = 8.4 Hz, 2.29H), 7.31 – 7.17 (m, 8.5H), 6.89 (d, *J* = 15.7 Hz, 0.9H), 6.27 (d, *J* = 16.1 Hz, 0.1H), 6.14 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.69 (t, *J* = 6.9 Hz, 0.08H), 5.53 (broad singlet, 0.08H), 5.20 – 4.99 (m, 1.8H), 4.92 (broad peak, *J* = 7.9 Hz, 0.1H), 2.36 (s, 3.17H). **^{13}C {1H} NMR (101 MHz, $CDCl_3$)**: δ 147.6, 143.5, 138.9, 137.3,

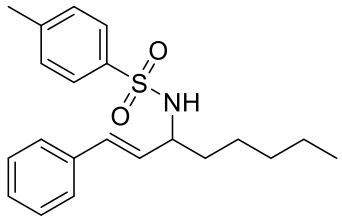
133.8, 133.0, 132.1, 129.6, 128.9, 128.8, 128.4, 128.2, 127.5, 127.3, 127.0, 124.6, 59.7, 21.5. **HRMS (ESI) m/z**: $(M+NH_4)^+$ Calcd for $C_{22}H_{24}N_3O_4S$ 426.1488; Found 426.1490.

(*E*)-4-Methyl-*N*-(1-phenyldec-2-en-1-yl)benzenesulfonamide (3pa):



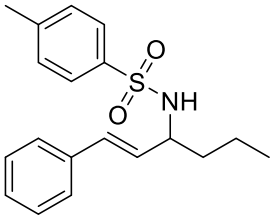
Prepared according to general procedure for the reaction of **1p** with **2a**; white solid; eluent (8% ethyl acetate in hexane);**1p** was taken in 50 mg; yield is 40% (36 mg); Mp: 89-93°C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.21 (m,5H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.20 (d, *J* = 16.0 Hz, 1H), 5.71 (dd, *J* = 16.0, 7.5 Hz, 1H), 4.75 (d, *J* = 8.0 Hz, 1H), 3.90 (p, *J* = 7.1 Hz, 1H), 2.29 (s, 3H), 1.59 – 1.47 (m, 2H), 1.29 – 1.18 (m, 10H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$) m/z**: δ 143.2, 138.2, 136.3, 131.3, 129.5, 129.0, 128.4, 127.6, 127.3, 126.3, 56.3, 35.9, 31.7, 29.1, 29.1, 25.4, 22.6, 21.4, 14.0. **HRMS (ESI-TOF)m/z**: $(M+Na)^+$ Calcd for $C_{23}H_{31}NO_2SNa$ 408.1973; Found 408.1977.

(*E*)-4-Methyl-*N*-(1-phenyloct-1-en-3-yl)benzenesulfonamide (3qa):



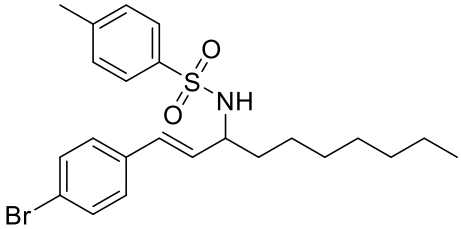
Prepared according to general procedure for the reaction of **1q** with **2a**; white solid; eluent (8% ethyl acetate in hexane); **1q** was taken in 50 mg; yield is 46% (44 mg); Mp: 90-92°C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.15 (m, 5H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.71 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.77 (t, *J* = 9.3 Hz, 1H), 3.90 (p, *J* = 7.2 Hz, 1H), 2.29 (s, 3H), 1.58 – 1.47 (m, 2H), 1.34 – 1.17 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H). **^{13}C {1H} NMR (126 MHz, $CDCl_3$)**: δ 143.2, 138.2, 136.3, 131.3, 129.4, 129.0, 128.3, 127.6, 127.3, 126.3, 56.3, 35.9, 31.3, 25.1, 22.4, 21.3 and 14.0. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{21}H_{27}NO_2SNa$ 380.1660; Found 380.1660.

(*E*)-4-Methyl-*N*-(1-phenylhex-1-en-3-yl)benzenesulfonamide (3ra):



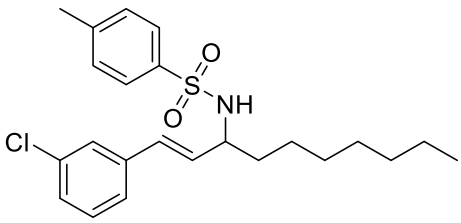
Prepared according to general procedure for the reaction of **1r** with **2a**; white solid; eluent (8 % ethyl acetate in hexane); **1r** was taken in 50 mg; yield is 56% (58 mg); Mp: 70-72°C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.07 (m, 5H), 7.01 (d, *J* = 7.3 Hz, 2H), 6.11 (d, *J* = 16.0 Hz, 1H), 5.62 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.80 (d, *J* = 7.8 Hz, 1H), 3.84 (p, *J* = 7.2 Hz, 1H), 2.21 (s, 1H), 1.55 – 1.38 (m, 2H), 1.30 – 1.20 (m, 2H), 0.78 (t, *J*= 7.2 Hz, 3H). **^{13}C {1H} NMR (126 MHz, $CDCl_3$)**: δ 143.2, 138.2, 136.3, 131.3, 129.4, 129.0, 128.3, 127.6, 127.3, 126.3, 56.3, 36.0, 31.3, 25.1, 22.4, 21.3, 13.9. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{19}H_{23}NO_2SNa$ 352.1347; Found 352.1350.

(*E*)-*N*-(1-(4-Bromophenyl)dec-1-en-3-yl)-4-methylbenzenesulfonamide (3sa):



Prepared according to general procedure for the reaction of **1s** with **2a**; white solid; eluent (10 % ethyl acetate in hexane); **1s** was taken in 50 mg; yield is 67% (53 mg); Mp: 108-109°C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.17 (d, *J* = 15.9 Hz, 1H), 5.72 (dd, *J* = 15.9, 7.4 Hz, 1H), 4.62 (d, *J* = 7.5 Hz, 1H), 3.90 (p, *J* = 7.1 Hz, 1H), 2.32 (s, 3H), 1.56 – 1.44 (m, 2H), 1.26 (m,10H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C {1H}NMR (126 MHz, $CDCl_3$)**: δ 143.2, 138.1, 135.2, 131.5, 130.1, 123.0, 129.5, 127.8, 127.3, 121.4, 56.2, 35.8, 31.7, 29.1, 29.1, 25.4, 22.6, 21.4, 14.0. **HRMS (ESI-TOF) m/z:** $(M+Na)^+$ Calcd for $C_{23}H_{30}NO_2SNa$ 486.1078;Found 486.1063.

(*E*)-*N*-(1-(3-Chlorophenyl)dec-1-en-3-yl)-4-methylbenzenesulfonamide (3ta):



Prepared according to general procedure for the reaction of **1t** with **2a**; white solid; eluent (10 % ethyl acetate in hexane); **1t** was taken in 50 mg; yield is 48% (35 mg); Mp: 130-132°C.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.03 (s, 1H), 6.99 (m, 1H), 6.15 (d, *J* = 16..0 Hz, 1H), 5.70 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.59 (s, 1H), 3.92 (p, *J* = 7.0 Hz, 1H), 2.33 (s, 1H), 1.53 (m, 2H), 1.23 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C {1H} NMR (101 MHz, $CDCl_3$)**: δ 143.4, 138.2, 130.7, 130.0, 129.6, 129.5, 127.6, 127.3, 126.1, 124.7, 56.2, 35.8, 31.7, 29.1, 25.4, 22.6, 21.4, 14.0. **HRMS (ESI-TOF) m/z:**$(M+Na)^+$ Calcd for $C_{23}H_{30}ClNO_2SNa$ 442.1583; Found 442.1600.

ASSOCIATED CONTENT

Supporting Information

All theNMR spectra data of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*mjeganmohan@iitm.ac.in

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References and note

1. (a) Graening, T.; Schmalz, H.-G. Pd-Catalyzed Enantioselective Allylic Substitution: New Strategic Options for the Total Synthesis of Natural Products. *Angew.Chem., Int. Ed*. **2003**, *42*, 2580−2584; *Angew.Chem*. **2003**, *115*, 2684−2688. (b) Trost, B. M.; Crawley, M. L. Asymmetric Transition-Metal-Catalyzed Allylic Alkylations: Applications in Total Synthesis. *Chem. Rev*. **2003**, *103*, 2921−2944. (c) Trost, B. M. Pd- and Mo-Catalyzed Asymmetric Allylic Alkylation. *Org. Process Res. Dev*. **2012**, *16*, 185−194. (d) Turnbull, B.

W. H.; Evans, P. A. Asymmetric Rhodium-Catalyzed Allylic Substitution Reactions: Discovery, Development and Applications to Target-Directed Synthesis**.** *J. Org. Chem.***2018**, *83*, 11463−11479. (e) Trost, B. M.; Bai, Y.; Bai, W.-J.; Schultz, J. E. Enantioselective Divergent Synthesis of C19-Oxo Eburnane Alkaloids via Palladium-Catalyzed Asymmetric Allylic Alkylation of an *N*-Alkyl-α,β-unsaturated Lactam. *J. Am. Chem. Soc.* **2019**, *141*, 4811 −4814.

2. (a) Chen, M. S.; White, M. C. A Sulfoxide-Promoted, Catalytic Method for the Regioselective Synthesis of Allylic Acetates from Monosubstituted Olefins via C−H Oxidation. *J. Am. Chem. Soc.* **2004**, *126*, 1346−1347. (b) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. Serial Ligand Catalysis: A Highly Selective Allylic C−H Oxidation. *J. Am. Chem. Soc.* **2005**, *127*, 6970−6971. (c) Vermeulen, N. A.; Delcamp, J. H.; White, M. C. Synthesis of Complex Allylic Esters via C−H Oxidation vs C−C Bond Formation. *J. Am. Chem. Soc.* **2010**, *132*, 11323−11328. (d) Litman, Z. C.; Sharma, A., Hartwig, J. F. Oxidation of Hindered Allylic C–H Bonds with Applications to the Functionalization of Complex Molecules. *ACS Catal.* **2017,** *7*, 1998-2001. (e) Wang, P.-S.; Liu, P.; Zhai, Y.-J.; Lin, H.-C.; Han, Z.-Y.; Gong, L.-Z. Asymmetric Allylic C–H Oxidation for the Synthesis of Chromans**.** *J. Am. Chem. Soc.*,**2015 ,***137* , 12732-12735.

(3) (a) Reed, S. A.; White, M. C. Catalytic Intermolecular Linear Allylic C−H Amination via Heterobimetallic Catalysis. *J. Am. Chem. Soc.* **2008**, *130*, 3316−3318. (b) Ma, R.; White, M. C. C–H to C–N Cross-Coupling of Sulfonamides with Olefins. *J. Am. Chem. Soc.*, **2018**, *140*, 3202−3205. (c) Reed, S. A.; Mazzotti, A. R.; White, M. C. A Catalytic, Brønsted Base Strategy for Intermolecular Allylic C−H Amination**.** *J. Am. Chem. Soc.* **2009**, *131*, 11701− 11706. (d) Pattillo, C. C.; Strambeanu, I. I.; Calleja, P.; Vermeulen, N. A.; Mizuno, T.; White, M. C. Aerobic Linear Allylic C–H Amination: Overcoming Benzoquinone Inhibition. *J. Am. Chem. Soc.* **2016,** *138*, 1265-1272.

(4) (a) Young, A. J.; White, M. C. Catalytic Intermolecular Allylic C−H Alkylation. *J. Am. Chem. Soc.*, **2008**, *130*, 14090−14091. (b) Liu, W.; Ali, S. Z.; Ammann, S. E; White. M. C. Asymmetric Allylic C–H Alkylation via Palladium(II)/*cis*-ArSOX Catalysis**.** *J. Am. Chem. Soc.* **2018,** *140*, 10658-10662. (c) Young, A. J.; White, M. C. Allylic C-H Alkylation of Unactivated α-Olefins: Serial Ligand Catalysis Resumed. *Angew. Chem. Int. Ed.*, **2011**, *50*,

6824−6827. (d) Howell, J. M.; Liu, W.; Young, A. J.; White, M. C. General Allylic C–H Alkylation with Tertiary Nucleophiles. *J. Am. Chem. Soc.* **2014**, *136*, 5750−5754.

(5) (a) Timsina, Y. N.; Gupton, B. F.; Ellis, K. C. Palladium-Catalyzed C–H Amination of C(sp^2) and C(sp^3)–H Bonds: Mechanism and Scope for *N*-Based Molecule Synthesis. *ACS Catal.* **2018,** *8*, 5732-5776. (b) Park, Y.; Kim, Y.; Chang S. Transition Metal-Catalyzed C–H Amination: Scope, Mechanism, and Applications. *Chem. Rev.* **2017,** *117*, 9247-9301. (c) Yin, G.; Wu, Y.; Liu, G. Scope and Mechanism of Allylic C−H Amination of Terminal Alkenes by the Palladium/PhI(OPiv)$_2$-Catalyst System: Insights into the Effect of Naphthoquinone *J. Am. Chem. Soc.* **2010**, *132*, 11978−11987. (d) Gandeepan, P.; Cheng, C.-H. Allylic Carbon–Carbon Double Bond Directed Pd-Catalyzed Oxidative *ortho*-Olefination of Arenes. *J. Am. Chem. Soc.* **2012**, *134*, 5738−5741. (e) Gandeepan, P.; Cheng, C.-H. Transition-Metal-Catalyzed π-Bond-Assisted C−H Bond Functionalization: An Emerging Trend in Organic Synthesis. *Chem. Asian. J.* **2015**, *10*, 424−438.

(6) (a) Manikandan, R.; Madasamy, P.; Jeganmohan, M. Temperature-Controlled Redox-Neutral Ruthenium(II)-Catalyzed Regioselective Allylation Of Benzamides With Allylic Acetates. *Chem. Eur. J.* **2015**, *21*, 13934−7701. (b) Manikandan, R.; Jeganmohan, M. Ruthenium-Catalyzed Oxidant-Free Allylation of Aromatic Ketoximes with Allylic Acetates at Room Temperature. *Org. Biomol. Chem.* **2016**, *14*, 7691. (c) Jambu, S.; Tamizmani, M.; Jeganmohan, M. Ruthenium(II)-Catalyzed Cyclization of Aromatic Acids with Allylic Acetates via Redox-Free Two-Fold Aromatic/Allylic C−H Activations: Combined Experimental and DFT Studies. *Org. Lett*. **2018**, *20*, 1982. (d) Mishra, N. K.; Sharma, S.; Park, J.; Han, S.; Kim, I.-S. Recent Advances in Catalytic C(sp^2)–H Allylation Reactions. *ACS Catal*. **2017**, *7*, 2821−2847. (e) Trita, A. S.; Biafora, A.; Drapeau, M. P.; Weber, P.;Gooßen, L.J. Regiospecific *ortho*-C−H Allylation of Benzoic Acids. *Angew.Chem. Int. Ed*. **2018**, *57*, 14580−14584.(f) Hu, X.Q.; Hu, Z.; Trita, A.S.; Zhang.G.; Gooßen, L. J. Carboxylate-Directed C–H Allylation with Allyl Alcohols or Ethers. *Chem. Sci*. **2018**, *9*, 5289−5294.

(7) (a) Burman, J. S.; Blakey, S. B. Regioselective Intermolecular Allylic C-H Amination of Disubstituted Olefins via Rhodium/π-Allyl Intermediates. *Angew.Chem., Int. Ed*. **2017**, *56*, 13666−13669. (b) Nelson, T. A. F.; Blakey, S. B. Intermolecular Allylic C-H Etherification of Internal Olefins. *Angew.Chem., Int. Ed*., **2018**, *57*, 14911 –14915. (c) Lerchen, A.; Knecht,

T.; Koy, M.; Ernst, J. B.; Bergander, K.; Daniliuc, C. G.; Glorius, F. Non-Directed Cross-Dehydrogenative (Hetero)arylation of Allylic C(sp3)−H bonds enabled by C−H Activation. *Angew. Chem., Int. Ed.,* **2018**, *57*, 15248−15252. (d) Knecht, T.; Pinkert, T.; Dalton, T.; Lerchen, A.; Glorius, F. Cp*Rh(III)-Catalyzed Allyl–Aryl Coupling of Olefins and Arylboron Reagents Enabled by C(sp3)–H Activation. *ACS Catal.,* **2019**, *9*, 1253−1257.

(8) (a) Bai, X.-D.; Zhang, Q.-F.; He, Y. Enantioselective Iridium-catalyzed α-Alkylation of Azlactones by a Tandem Asymmetric Allylic Alkylation/Aza-Cope Rearrangement. *Chem. Commun.*, **2019,** *55*, 5547−5550. (b) Wang, Y.; Zhang, W.-Y.; You, S.-L. Ketones and Aldehydes as *O*-Nucleophiles in Iridium-Catalyzed Intramolecular Asymmetric Allylic Substitution Reaction. *J. Am. Chem. Soc.* **2019,** *141*, 2228−2232.(c) Rössler, S. L.; Petrone, D. A.; Carreira, E.M. Iridium-Catalyzed Asymmetric Synthesis of Functionally Rich Molecules Enabled by (Phosphoramidite,Olefin) Ligands. *Acc.Chem. Res.,* **2019**, DOI: 10.1021/acs.accounts.9b00209 and reference therein.(d) Cheng, Q.; Tu, H.-F.; Zheng, C.; Qu, J.-P.; Helmchen, G.; You, S.-L. Iridium-Catalyzed Asymmetric Allylic Substitution Reactions. *Chem. Rev.* **2019**, *119*, 1855−1969 and reference therein.

(9) (a) Knecht, T.; Mondal, S.; Ye, J.-H.; Das, M.; Glorius, F. Intermolecular, Branch-Selective, and Redox-Neutral Cp*Ir^{III}-Catalyzed Allylic C−H Amidation. *Angew. Chem. Int. Ed.*, **2019**, *58*, 7117 –7121. (b) Lei, H.; Rovis, T. Ir-Catalyzed Intermolecular Branch-Selective Allylic C–H Amidation of Unactivated Terminal Olefins. *J. Am. Chem. Soc.* **2019**, *141*, 2268−2273. (c) Burman, J. S.; Harris, R. J.; Farr, C. M. B.; Bacsa, J.; Blakey, S. B. Rh(III) and Ir(III)Cp* Complexes Provide Complementary Regioselectivity Profiles in Intermolecular Allylic C–H Amidation Reactions. *ACS Catal.* **2019**, *9*, 5474−5479.

(10) (a) Yuan, Q.; Yao, K.; Liu, D.; Zhang, W. Iridium-Catalyzed Allyl–Allyl Cross-Coupling Of Allylic Carbonates With (*E*)-1,3-Diarylpropenes. *Chem. Commun.*, **2015**, *51*, 11834-11836. (b) Liu, Y.; Yao, B.; Deng, C.-L.; Tang, R.-Y.; Zhang, X.-G.; Li J.-H. Palladium-Catalyzed Selective Heck-Type Diarylation of Allylic Esters with Aryl Halides Involving a β-OAc Elimination Process. *Org. Lett.,* **2011**, *13*, 1126-1129. (c) Luo, Z.; Han, X.; Fang, Y.; Liu, P.; Feng, C.; Lia, Z.; Xu, X. Copper-Catalyzed Decarboxylative And Oxidative Decarbonylative Cross-Coupling Between Cinnamic Acids And Aliphatic Aldehydes *Org. Chem. Front.*, **2018**, *5*, 3299–3305. (d) Werner, E. W.; Sigman, M. S**.** Operationally Simple and Highly (*E*)-Styrenyl-Selective Heck Reactions of Electronically

Nonbiased Olefins. *J. Am. Chem. Soc.*, **2011**, *133*, 9692-9695. (e) Kerr, W. J.; Reid, M.; Tuttle, T.Iridium-Catalyzed C–H Activation and Deuteration of Primary Sulfonamides: An Experimental and Computational Study. *ACS Catal*., **2015**, *5*, 402-411. (f) Witt et al Development of a Multi-Kilogram-Scale Synthesis of AZD1283: A Selective and Reversible Antagonist of the $P2Y_{12}$ Receptor. *Org. Process Res. Dev*. **2013**, *17*, 1543−1551(g) Dong, X.; Sang, R.; Wang, Q.; Tang, X.-Y.; Shi, M. Copper-Catalyzed Trifluoromethylation and Cyclization of Aromatic-Sulfonyl Group Tethered Alkenes for the Construction of 1,2-Benzothiazinane Dioxide Type Compounds. *Chem. Eur. J.*, **2013**, *19*, 16910 – 16915.