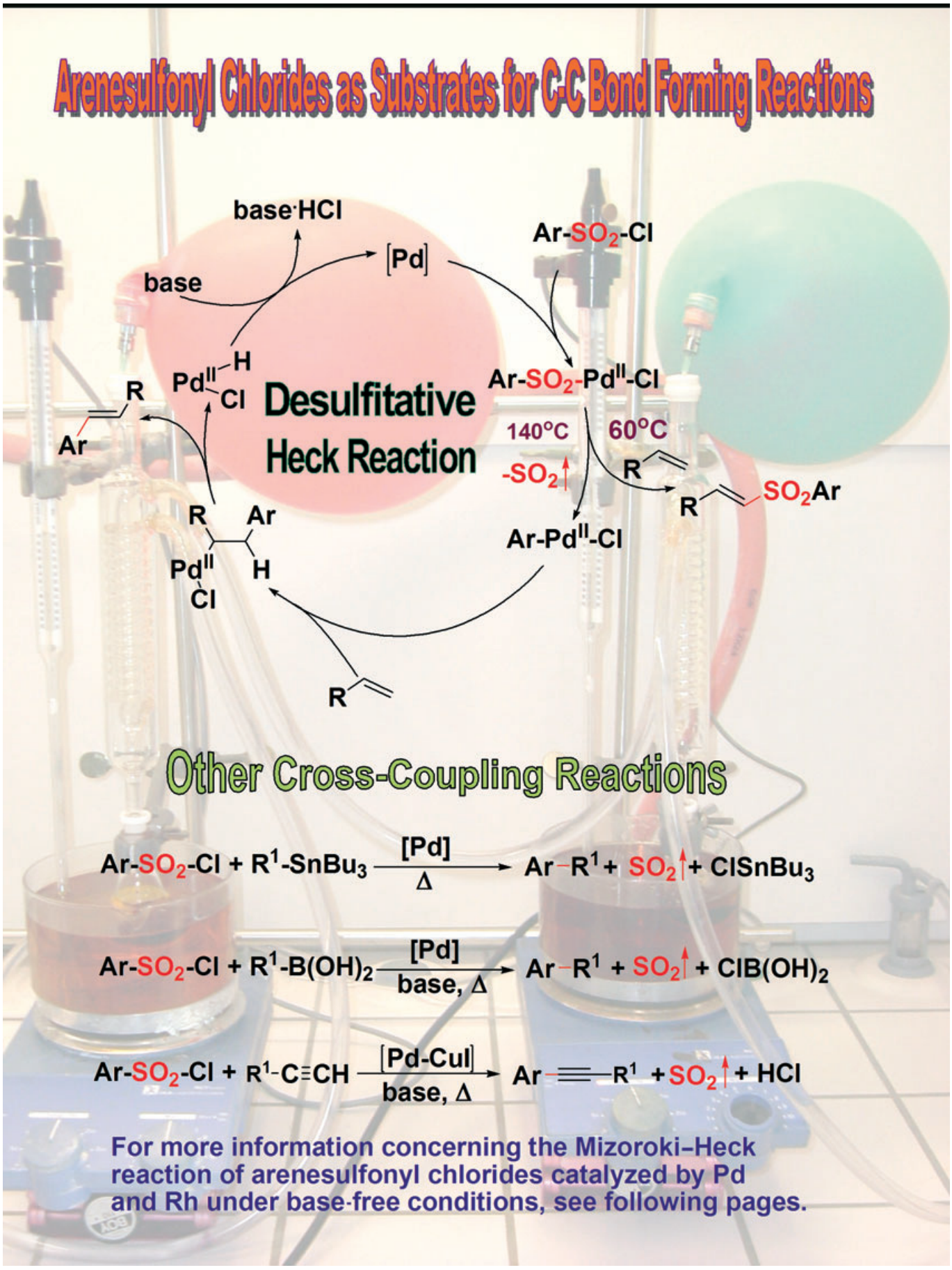

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Palladium-Catalyzed Desulfitative Mizoroki–Heck Couplings of Sulfonyl Chlorides with Mono-and Disubstituted Olefins: Rhodium-Catalyzed Desulfitative Heck-Type Reactions under Phosphine- and Base-Free Conditions

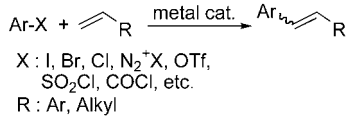
Srinivas Reddy Dubbaka and Pierre Vogel*[a]

Abstract: New conditions have been found for the desulfitative Mizoroki–Heck arylation and trifluoromethylation of mono- and disubustituted olefins with arenesulfonyl and trifluoromethanesulfonyl chlorides. Thus (*E*)-1,2-disubstituted alkenes with high stereoselectivity and 1,1,2-disubstituted alkenes with 12:1 to 21:1 *E*/*Z* steroselectivity can be obtained. Herrmann's palladacycle at 0.1 mol% is sufficient to catalyze these reactions, for which electron-rich or electron-poor sulfonyl chlorides and alkenes are suitable. If phosphine- and base-free conditions are required, 1 mol% $[RhCl(C_2H_4)_2]$ catalyzes the desulfitative cross-coupling reactions. Contrary to results reported for $[RuCl_2(PPh_3)_2]$-catalyzed coupling reactions with sulfonyl chlorides, the palladium and rhodium desulfitative Mizoroki–Heck coupling reactions are not inhibited by radical scavenging agents. Possible sulfones arising from the sulfonylation of alkenes at 60 °C are not desulfitated at higher temperatures in the presence of the Pd or Rh catalysts.

Keywords: alkenes · Mizoroki–Heck reaction · palladium · phase-transfer catalysis · rhodium

Introduction

Transition-metal-catalyzed C–C bond-forming reactions are among the most powerful methods of organic synthesis.[1,2] In recent years, new conditions (ligands, additives) have been developed that permit cross-coupling of a large variety of reactants (Scheme 1).[2] A search for more economical procedures has implied reduction or suppression of co-products and side products and the use of inexpensive starting materials.[3] We have shown that the readily available sulfonyl chlorides (RSO_2Cl, R = aryl, alkenyl, methallyl, benzyl) undergo desulfitative and carbonylative Stille,[4] Suzuki–Miyaura,[5] and Sonogashira–Hagihara[6] cross-coupling reactions. The sulfonyl chlorides are generally more reactive than the corresponding bromides and chlorides.[4,5] The Mizoroki–Heck arylation of alkenes is very useful for syntheses.[1,2] Aroyl chlorides and alkenes can be coupled under decarbonylative conditions.[7] With $[\{RhCl(alkene)_2\}_2]$ as catalyst the reactions can be carried out under phosphine- and base-free conditions.[8] From further exploration of the potential of sulfonyl chlorides as reactants in transition-metal-catalyzed reactions, we have now extended their application in the Mizoroki–Heck reaction using Pd and Rh catalysts.[9,10] We have found conditions under which desulfitative Mizoroki–Heck cross-coupling can be carried out with sulfonyl chlorides under phosphine- and base-free conditions.



Scheme 1. Substrates for general Mizoroki–Heck-type reactions.

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Results and Discussion

Palladium-catalyzed desulfitative Mizoroki–Heck-type coupling with sulfonyl chlorides: In continuation of work by Kasahara[9a,b] and Miura [9c,d] and their respective co-workers, we investigated whether catalysts other than $[PdCl_2(PhCN)_2]$, $Pd(OAc)_2$, $PdCl_2$, Pd black, and

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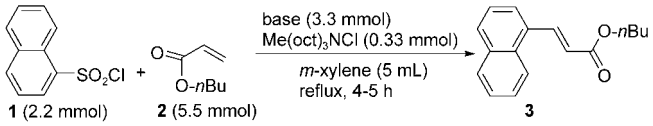
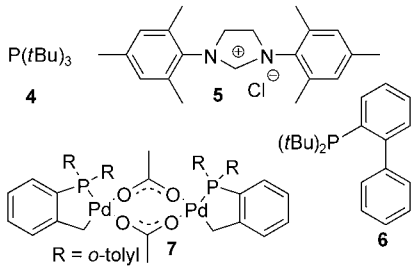
$[PdCl_2(PPh_3)_2]$ would improve the yield of the desulfitative vinylations. Our exploratory experiments started with the coupling of 1-naphthalenesulfonyl chloride (**1**; 2 mmol) and butyl acrylate (**2**; 5.5 mmol) in the presence of $[PdCl_2(PhCN)_2]$ (3 mol%), $Me(oct)_3NCl$ (15 mol%), and K_2CO_3 (4 mmol) in *m*-xylene. After 4 h at 140°C a 53% yield of coupling product **3** was obtained (Table 1, entry 1).[9d] It is known that phase-transfer catalysts can be beneficial to Mizoroki–Heck-type reactions.[11–14] By screening various phase-transfer catalysts we have found that the bulky trioctylmethylammonium chloride leads to better results than the smaller tetrabutyl- or tetraethylammonium chloride (Table 1, entry 1 versus 2). Bulky organic bases were not suitable in our examples, whereas an inorganic base such as K_2CO_3 led to higher yields (Table 1, entry 1 versus 3 and 4). Addition of electron-rich ligands such as **4**,[15] **5**,[16a] and **6**[16b] increased the yields. The best results were obtained by using the palladacycle **7**,[17] developed by Herrmann et al., as catalyst (Table 1, entries 5, 8–10). When using low boiling polar solvents, the yields were lower than in boiling *m*-xylene (Table 1, entries 6 and 7).

Table 1. Catalyst, bases, and PTC screening.



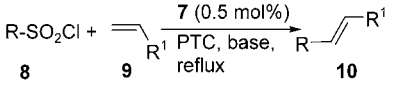
Entry	Pd source (Concn. [mol%])	Base	Yield [%][a]
1	$[PdCl_2(PhCN)_2]$ (3)	K_2CO_3	53
2	$[PdCl_2(PhCN)_2]$ (3)	K_2CO_3	15[b,c]
3	$[PdCl_2(PhCN)_2]$ (3)	Et_3N	30
4	$[PdCl_2(PhCN)_2]$/**4** (3/6)	Cy_2NMe	<20
5	$[PdCl_2(PhCN)_2]$/**4** (3/6)	K_2CO_3	78
6	$[PdCl_2(PhCN)_2]$/**4** (3/6)	K_2CO_3	45[d]
7	$[Pd_2dba_3]$/**4** (1.5/6)	K_2CO_3	54[d]
8	$[PdCl_2(PhCN)_2]$/**5** (3/6)	K_2CO_3	80
9	$[PdCl_2(PhCN)_2]$/**6** (3/6)	K_2CO_3	78
10	palladacycle **7** (0.1)	K_2CO_3	90[e]

[a] Yields of coupling products determined after flash chromatography. [b] Bu_4NCl was used instead of $Me(oct)_3NCl$. [c] Yield was 5 mol% when Et_4NCl was used instead of $Me(oct)_3NCl$. [d] The mixture was refluxed in THF instead of *m*-xylene, starting material and side product were observed after 24 h. [e] Yield was also 90% with 0.4 mol% of palladacycle **7**.



We applied these optimized conditions to the desulfitative coupling of electron-rich, electron-neutral, and electron-poor sulfonyl chlorides with a wide variety of olefins. For good yields of Mizoroki–Heck-type products **10** from the reaction of sulfonyl chlorides (**8**) (Table 2) with butyl acrylate, styrene, 1-hexene, and phenylvinylsulfone (**9**), the reaction temperature must be higher than 120°C (Table 2, entry 5). In most cases the reaction is over after 4–5 h, except when unreactive olefins such as 1-hexene are used. In the latter case, the reaction with 4-acetylbenzenesulfonyl chloride

Table 2. The palladium-catalyzed desulfitative Mizoroki–Heck type of reaction of various sulfonyl chlorides with terminal alkenes.



Entry	R	R^1	Yield [%][a]
1	1-naphthyl	COO*n*Bu	90[b]
2	1-naphthyl	Ph	83
3	4-methylphenyl	COO*n*Bu	76
4	4-methylphenyl	Ph	80[c]
5	4-acetylphenyl	COO*n*Bu	74[d]
6	4-acetylphenyl	*n*Bu	51[e,f]
7	4-trifluorophenyl	COO*n*Bu	72
8	4-fluorophenyl	COO*n*Bu	70[g]
9	4-methoxyphenyl	COO*n*Bu	75
10	3-cyanophenyl	COO*n*Bu	73[h]
11	4-nitrophenyl	COO*n*Bu	78
12	4-trifluorophenyl	SO_2Ph	49
13	4-(pyrazol-1-yl)phenyl	COO*n*Bu	40
14	2,4,6-trimethylphenyl	COO*n*Bu	45[i]
15	trifluoromethyl	Ph	50[j]
16	trifluoromethyl	COO*n*Bu	32[j]

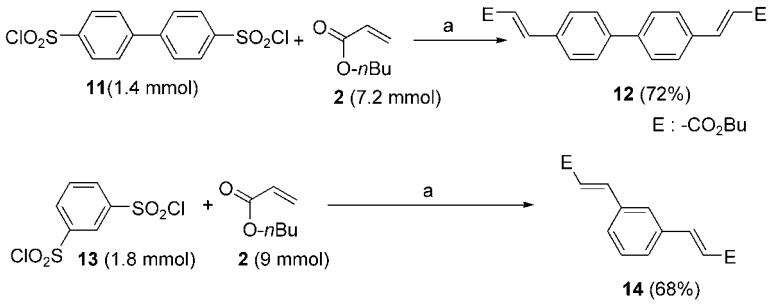
[a] Yields of coupling products determined after flash chromatography. [b] Yield 53% according to ref. [9d]. [c] Yield 75% with 3% $[PdCl_2(PhCN)_2]$, 6% ligand **5** instead of palladacycle **7**. [d] Yield 35% in THF under reflux. [e] In *p*-xylene under reflux, 21 h and with five equivalents of alkene. [f] Yield 51% in THF under reflux with 3% $[PdCl_2(PhCN)_2]$, 6% ligand **5** instead of palladacycle **7**. [g] Yield 64% with 3% $[PdCl_2(PhCN)_2]$, 6% ligand **5** instead of palladacycle **7**. [h] Under reflux for 13 h. [i] Under reflux for 24 h. [j] Using a microwave oven at 150°C for 10 h and with five equivalents of alkene.

Abstract in French: *De nouvelles conditions sont rapporteés pour les couplages désulfitants du type Mizoroki–Heck des chlorures d'arènesulfonyles et trifluorométhanesulfonyle avec des oléfines mono- et disubstitueés. La méthode permet la synthèse de (E)-alcènes 1,2-disubstitués avec haute stéréosélectivité et d'alkènes 1,1,2-trisubstitués avec des stéréosélectivités E/Z variant de 12:1 à 21:1. La palladacycle de Herrmann à 0.1 mol% est suffisant pour catalyser ces reactions qui peuvent engager des chlorures de sulfonyles et des alcènes soit riches ou pauvres en électron. Si des conditions sans phosphine et sans base sont requises, 1 mol% de $[RhCl(C_2H_4)_2]$ est un excellent catalyseur pour ces couplages désulfitants. Contrairement à ce qui est rapporté pour des réactions analogues catalysées par $[RuCl_2(PPh_3)_2]$ et qui impliquent des intermédiaires radicalaires, les couplages du type Mizoroki–Heck désulfitants catalysés par des complexes de palladium ou de rhodium ne sont pas inhibés par des pièges à radicaux. De plus, les sulfones qui peuvent se former par sulfonylation des alcènes (60°C) ne sont pas désulfitées à plus haute température en présence des catalyseurs au Pd ou au Rh.*

gave 51% yield of the product of desulfitative Mizoroki–Heck coupling after 24 h, and only one isomer was isolated. The crude reaction mixture did not show evidence of the presence of isomeric products, apart from polymeric material. The lower yield might be attributed to the presence of an excess of alkene. It is known from previous work on Heck reactions that an increased concentration of olefin significantly reduces the catalyst efficiency. With phenylvinylsulfone the yield was also moderate (Table 2, entry 12). Heterocyclic compounds were also applied successfully in the reaction, but led only to moderate yields (Table 2, entry 13). Sterically hindered substrates required longer reaction times (see, for example, Table 2, entry 14). The reaction of trifluoromethanesulfonyl chloride with an excess of styrene (5 equiv) in a sealed tube or microwave oven at 150 °C in *m*-xylene gave the desired desulfitative Mizoroki–Heck coupling product ((*E*)-3,3,3-trifluoro-1-phenylprop-1-ene) in about 10 h (Table 2, entry 15).[10e] With butyl acrylate, the same reaction produced butyl (*E*)-4,4,4-trifluorobut-2-enoate in 32% yield (Table 2, entry 16).

Double desulfitative Mizoroki–Heck couplings have also been realized. The reaction between butyl acrylate **2** with biphenyl-4,4′-disulfonyl chloride **11** and with 1,3-benzenedisulfonyl chloride **13** produced the important polymer precursors[18] **12** and **14** respectively, in good yields (Scheme 2).

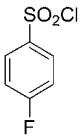
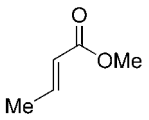
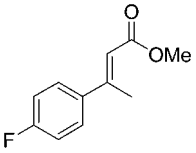
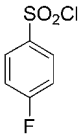
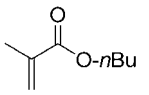
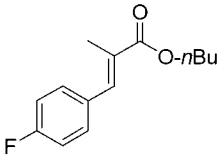
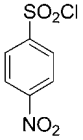
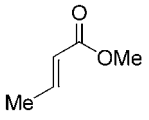
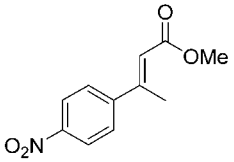
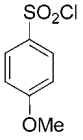
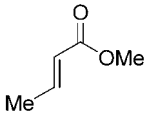
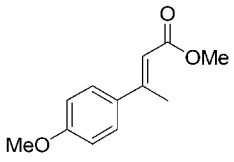
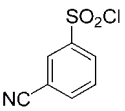
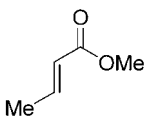
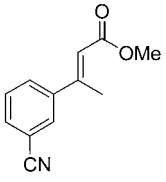
There are very few reports on Mizoroki–Heck-type arylation of disubstituted olefins with aryl halides. Buchwald and Gürtler have presented a general procedure for the Mizoroki–Heck arylation of disubstituted olefins with heteroaryl bromides using bulky amines as bases and a phase-transfer catalyst under phosphine-free conditions.[13] Moreno-Mañas and co-workers have reported Heck arylations of disubstituted olefins that require expensive aryl iodides.[19] Littke and Fu showed that cheaper aryl chlorides can react with mono- and disubstituted olefins under palladium-catalyzed conditions using electron-rich ligands.[15e] We have found that arenesulfonyl chlorides can react with disubstituted olefins under our conditions, with high stereoselectivity (Table 3). Both electron-rich and electron-poor sulfonyl chlorides can be coupled with methyl crotonate and butyl methacrylate with acceptable yields (Table 3).



Scheme 2. The reactions of *n*-butyl acrylate with disulfonyl dichlorides. a) K_2CO_3 (5.7 mmol), $Me(oct)_3NCl$ (0.43 mmol), palladacycle **7** (1 mol%) and *m*-xyxlene (5 mL) under reflux for 4–7 h.

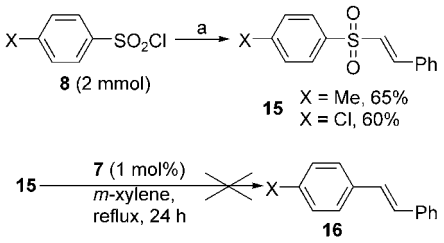
Preparation of α,β-unsaturated sulfones: mechanism of the palladium-catalyzed desulfitative Mizoroki–Heck coupling: We have found that the reaction of arenesulfonyl chlorides

Table 3. Palladium-catalyzed synthesis of trisubstituted olefins.

Entry	Sulfonyl chloride	Olefin	Product	(*E*)/(*Z*) ratio[a]	Yield [%][b]
1				20:1	40
2				14:1	40
3				12:1	52
4				21:1	47
5				15:1	60

[a] *E*/*Z* isomer ratio of product of the second desulfitative Mizoroki–Heck reaction as determined after flash chromatography. [b] Yield of all known products. We have verified their structures by NOE ^{1}H NMR experiments.

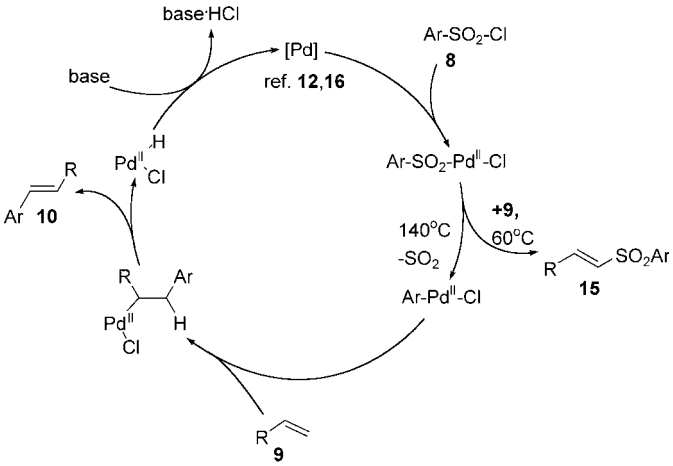
8 (X = Me, Cl) with styrene in the presence of a catalytic amount of $PdCl_2$ or tetrakis(triphenylphosphine)palladium(0) in benzene or in THF at 60 °C and in the presence of K_2CO_3 or NEt_3 produces the corresponding α,β-unsaturated sulfones **15** in good yields (Scheme 3). Kamigata and co-



Scheme 3. Preparation of sulfones. a) styrene (3 mmol), $[Pd(PPh_3)_4]$ (4 mol%), Et_3N (2.4 mmol) in PhH at 60 °C for 70 h.

workers[10c] have reported that $[RuCl_2(PPh_3)_2]$ catalyzes the addition of sulfonyl chlorides to alkenes with formation of the corresponding sulfones. These reactions imply radical intermediates of the $RSO_2^{\bullet}$ type that add to the alkenes, generating alkyl radical intermediates that are then quenched with the sulfonyl chlorides, giving the corresponding β-chlorosulfones. In the presence of Et_3N the latter eliminate HCl and form the corresponding α,β-unsaturated sulfones. We have therefore investigated whether our palladium-catalyzed nondesulfitative coupling reactions, **8** + styrene→HCl + **15** (Scheme 3), also involve radical intermediates. Whereas the Ru-catalyzed reactions[10c,g] are inhibited by the galvinoxyl free radical, we found that our reactions catalyzed by $[Pd(PPh_3)_4]/Et_3N$ were inhibited neither by the same inhibitor nor by the 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO). Similarly, the desulfitative Mizoroki–Heck coupling reaction of tosyl chloride (2 mmol) and styrene (5.00 mmol) catalyzed by palladacycle **7** (0.2 mol%) was inhibited neither by the galvinoxyl free radical nor by TEMPO. When sulfones **15** were heated in boiling xylene in the presence of 1 mol% Herrmann's catalyst **7** or 1 mol% $[RhCl(C_2H_4)_2]$, no traces of desulfitation products **16** were detected after 24 h. This demonstrates that sulfones **15** are not intermediates in our palladium-catalyzed desulfitative Mizoroki–Heck coupling reactions.

These observations can be interpreted as follows (Scheme 4). The metal is inserted into the SO_2–Cl bond first. At 60 °C, elimination of SO_2 does not occur and the alkene insertion generates the corresponding sulfone **15**. At a higher temperature (140 °C), desulfitation is rapid and an Ar–Pd–Cl complex is formed into which the olefin is then inserted, similarly to aryl halides or triflates in Mizoroki–Heck coupling reactions.[1,2] Alternatively, palladium may be inserted first into the C–S bond of the sulfonyl chlorides, giving intermediates of the Ar–Pd–SO_2Cl type. The latter cannot generate sulfones **15** at 60 °C, but at higher temperatures desulfitative Heck coupling products can be formed. This does not prove that Ar–Pd–SO_2Cl species are never formed, as the alkenes might be inserted too slowly with respect to

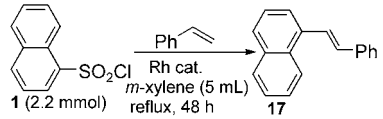


Scheme 4. Probable catalytic cycle for sulfone synthesis and desulfitative Mizoroki–the Heck type of reaction between sulfonyl chlorides and olefins catalyzed by **7**.

their equilibrium with Ar–SO_2Pd–Cl species and/or desulfitation into Ar–Pd–Cl intermediates.

Rhodium-catalyzed desulfitative Heck-type reactions with arenesulfonyl chlorides under phosphine- and base-free conditions: Decarbonylative Mozoroki–Heck coupling of aroyl chlorides and alkenes[7] is possible with $[\{RhCl(alkene)_2\}_2]$ as catalyst and under phosphine- and base-free conditions.[8] As arenesulfonyl chlorides are inexpensive reagents, we explored whether the latter conditions could be extended to their desulfitative Mizoroki–Heck coupling reactions. In an initial attempt, 1-naphthalenesulfonyl chloride (**1**) was treated with styrene in the presence of $[\{RhCl(C_2H_4)_2\}_2]$ (1 mol%), P*t*Bu$_3$ (2 mol%), and K_2CO_3 (1.5 equiv) in refluxing *m*-xylene. After 48 h, the arylation product **17** was formed in only trace amounts (Table 4, entry 1). Interestingly, the reaction proceeded much more smoothly in the absence of the phosphane ligand and base (Table 4, entries 2 and 3 versus 4). As a result, **17** was obtained in 72% yield (Table 4, entry 4). The yield did not increase when the reac-

Table 4. Reaction of 1-naphthalenesulfonyl chloride with styrene.



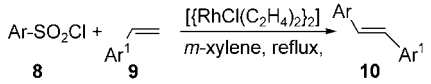
Entry	Rh source (1 mol%)	Yield [%][a]
1	$[\{RhCl(C_2H_4)_2\}_2]$/P*t*Bu$_3$/K_2CO_3	traces
2	$[\{RhCl(C_2H_4)_2\}_2]$/P*t*Bu$_3$	<10
3	$[\{RhCl(C_2H_4)_2\}_2]$/K_2CO_3	<3
4	$[\{RhCl(C_2H_4)_2\}_2]$	72
5	$[\{RhCl(C_2H_4)_2\}_2]$	72[b]
6	$[\{RhCl(cod)_2\}_2]$	20

[a] Yields of coupling products determined after flash chromatography for the reaction of **1** (2.2 mmol) with styrene (3.5 mmol) in *m*-xylene (5 mL) at reflux and under an argon atmosphere. [b] Under a slow stream of N_2.

tion was carried out under a slow stream of N_2 to remove the HCl and SO_2 evolved. Under the same conditions, $[\{RhCl(cod)_2\}_2]$ (cod = 1,5-cyclooctadiene) was a less effective catalyst (Table 4, entry 6).

With these optimized reaction conditions in hand, we have examined the desulfitative Mozoroki–Heck-type reactions of 1-naphthalene-, 4-methylbenzene-, benzene-, 4-bromobenzene-, and (*E*)-2-phenylethenesulfonyl chloride with styrene and 4-chlorostyrene (Table 5). They all gave the desired products of coupling (**10**) with satisfactory yields.

Table 5. Rhodium-catalyzed desulfitative Mizoroki–Heck coupling reactions of sulfonyl chlorides with styrene and 4-chlorostyrene under base- and phosphine-free conditions.



8 9 10

Entry	Ar	Ar[1]	Yield [%][a]
1	1-naphthyl	Ph	72
2	1-naphthyl	4-ClC_6H_4	70
3	phenyl	Ph	54
4	4-methylphenyl	Ph	70
5	4-bromophenyl	Ph	70
6	(*E*)-PhCH=CH	Ph	58
7	(*E*)-PhCH=CH	4-ClC_6H_4	55

[a] Yield of coupling products determined after flash chromatography for reaction of sulfonyl chloride (2 mmol) with the olefin (3.0 mmol) in refluxing *m*-xylene under argon for 48–60 h; in general the reactions were not complete and some starting materials could be recovered.

The mechanisms of the $[\{Rh^{I}Cl(C_2H_4)_2\}_2]$-catalyzed desulfitative Mizoroki–Heck coupling reactions are probably similar to those for the Pd-catalyzed reactions (Scheme 4). We verified that the Rh-catalyzed reactions were not inhibited by radical scavenging agents such as the galvinoxyl free radical.

Conclusion

We have demonstrated for the first time that desulfitative Mizoroki–Heck-type arylation of alkenes can be performed by using sulfonyl chlorides in the presence of a rhodium catalyst under phosphine- and base-free conditions. We have also found Herrmann's palladacycle (**7**) to be an excellent catalyst for palladium-catalyzed desulfitative Mizoroki–Heck-type reactions of mono- and disubustituted olefins with arenesulfonyl chlorides at 140 °C. We have demonstrated that sulfones can also be obtained at 60 °C under conditions (alkene sulfonylation) that are otherwise the same. These reactions are not inhibited by radical scavenging agents.

Experimental Section

Materials and methods: Unless otherwise stated, reactions were conducted in flame-dried glassware under vacuum. Catalysts and ligands were purchased from Strem Chemical Inc. THF was distilled before use from sodium and benzophenone and *m*-xylene was received from Aldrich (Sure-Seal). Sulfonyl chlorides were purchased from Aldrich, Acros, Fluka, Lancaster, and Fluoro Chem. All olefins were purchased from Aldrich or Acros and used without further purification. TLC for reaction monitoring was performed on 60 F_{254} (Merck) with detection by UV light and charring with $KMnO_4$. Liquid/solid flash chromatography (FC): silica gel columns (0.040–0.63 mm, Merck No. 9385 silica gel 60, 240–400 mesh). ^1H and ^{13}C NMR spectra were recorded with a Bruker-DPX-400 or Bruker-ARX-400 spectrometer at 400 MHz and 100.6 MHz respectively and are reported relative to Me_4Si ($\delta = 0.0$ ppm) or to the solvent residual ^1H signal ($CDCl_3$, $\delta(H) = 7.27$ ppm). IR spectra were recorded on a Perkin-Elmer 1420 spectrometer. HRMS (MALDI-TOF) mass spectra were recorded on Kratos Analytical instruments.

Mizoroki–Heck reaction of sulfonyl chloridesGeneral procedure 1: desulfitative Pd-catalyzed reaction with monosubstituted olefins (Table 2): The sulfonyl chloride (1 equiv, 2.00 mmol), Herrmann's palladacycle **7** (0.1–0.5 mol %, 0.002–0.01 mmol), and K_2CO_3 (2 equiv, 4 mmol) were weighed in a glove box and placed in a round-bottom flask (dried under vacuum) under a nitrogen atmosphere. The flask was connected to a vacuum line, flushed three times with argon, then *m*-xylene (5 mL) was added under argon. $Me(oct)_3NCl$ (15 mol %, 0.3 mmol) and the olefin (2.5 equiv, 5.0 mmol) were added under argon. The reaction mixture was stirred at reflux for 4–5 h or longer (see footnotes to Table 2). After being cooled to room temperature, the mixture was diluted with ether and washed with water. The aqueous layer was extracted again three times with ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated to 5 mL under reduced pressure. The residue was purified by FC.

General procedure 2: Pd-catalyzed reaction with disubstituted olefins (Table 3): The preparation, extraction, and purification methods were similar to procedure 1, with sulfonyl chloride (1 equiv, 2.00 mmol), Herrmann's palladacycle **7** (0.5–1.0 mol %, 0.01–0.02 mmol), and K_2CO_3 (2 equiv, 4 mmol). Stirring at reflux was performed for 5–8 h.

General procedure 3: desulfitative Rh-catalyzed reaction under phosphine- and base-free conditions (Table 5): The sulfonyl chloride (1 equiv, 2.00 mmol) $[\{RhCl(C_2H_4)_2\}_2]$ (1 mol %, 0.02 mmol) were weighed in a glove box and placed in a round-bottom flask (dried under vacuum) under a nitrogen atmosphere. The flask was connected to a vacuum line, flushed three times with argon, and *m*-xylene (5 mL) was added under argon. Then the olefin (1.5–2.0 equiv, 3.0–4.0 mmol) was added under argon. This reaction mixture was stirred at reflux for 48–60 h. After being cooled to room temperature, the mixture was extracted and purified as in procedure 1.

Butyl (*E*)-3-(naphthalen-1-yl)acrylate:[20] See Table 2, entry 1. The product was obtained in 90 % yield by general procedure 1. FC (pentane/Et_2O, 15:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 16.0 Hz, 1H; ArCH=), 8.23 (d, J = 8.3 Hz, 1H; Ar), 7.90 (m, 2H; Ar), 7.78 (d, J = 7.0 Hz, 1H; Ar), 7.58 (m, 3H; Ar), 6.52 (d, J = 16.0 Hz, 1H; =$CHCO_2Bu$), 4.31 (t, J = 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.77 (tt, J = 6.8, 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.52 (qt, J = 7.3, 6.8 Hz, 2H; CH_2CH_3), 1.0 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.0, 141.6, 133.7, 131.8, 131.4, 130.5, 128.7, 126.9, 126.2, 125.5, 125.0, 123.4, 120.9, 64.5, 30.8, 19.3, 13.8 ppm; CI-MS (NH_3): 254 (31, $[M]^+$), 181 (25), 153 (100), 76 (15).

(*E*)-1-(Naphthalen-1-yl)-2-phenylethene:[21] See Table 2, entry 2. The product was obtained in 83 % yield by general procedure 1. FC (pentane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.19 (m, 13H; Ar, =C*H*Ar), 6.47 ppm (s, 1H; =C*H*Ar); CI-MS (NH_3): 230 (38, $[M]^+$), 208 (65), 193 (90), 178 (51), 115 (100), 91 (77).

Butyl (*E*)-3-(4-methylphenyl)acrylate:[9d] See Table 2, entry 3. The product was obtained in 76 % yield by general procedure 1. FC (pentane/Et_2O, 9:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 16.0 Hz, 1H; ArC*H*=), 7.43 (d, J = 8.0 Hz, 2H; Ar), 7.19 (d, J = 8.0 Hz, 2H; Ar), 6.41 (d, J = 16.0 Hz, 1H; =*CH*CO_2Bu), 4.21 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 2.37 (s, 3H; Me) 1.70 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.52 (qt, J = 7.4, 6.7 Hz, 2H; CH_2CH_3), 1.0 ppm (t, J = 7.4 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.3, 144.6,

140.6, 131.8, 129.6, 128.1, 117.2, 64.4, 30.9, 21.5, 19.3, 13.8 ppm; CI-MS (NH_3): 218 (91, $[M]^+$), 162 (100), 145 (99), 115 (75), 91 (73).

(*E*)-1-(4-Methylphenyl)-2-phenylethene:[21] See Table 2, entry 4. The product was obtained in 80% yield by general procedure 1. FC (pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.4 Hz, 2H; Ar), 7.46 (d, J = 8.0 Hz, 2H; Ar), 7.39 (t, J = 7.36 Hz, 1H; Ar), 7.29 (d, J = 8.0 Hz, 2H; Ar), 7.21 (d, J = 8.0 Hz, 2H; Ar),7.12 (brs, 2H; ArC*H*=CHAr), 2.4 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 137.9, 135.0, 134.9, 129.8, 129.1, 129.0, 128.1, 127.8, 126.9, 126.8, 21.7 ppm; CI-MS (NH_3): 194 (100, $[M]^+$), 179 (84).

Butyl (*E*)-3-(4-acetylphenyl)acrylate:[22] See Table 2, entry 5. The product was obtained in 74% yield by general procedure 1. FC (pentane/Et_2O, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 2H; Ar), 7.67 (d, J = 16.0 Hz, 1H; ArC*H*=), 7.59 (d, J = 8.3 Hz, 2H; Ar), 6.51 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.21 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 2.60 (s, 3H; Me) 1.68 (tt, J = 6.8, 7.7 Hz, 2H; $CO_2CH_2CH_2$), 1.52 (qt, J = 7.7, 6.8 Hz, 2H; CH_2CH_3), 1.0 ppm (t, J = 7.7 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.3, 166.6, 143.0, 138.8, 137.9, 128.9, 128.1, 120.9, 64.7, 30.7, 26.7, 19.2, 13.8 ppm; CI-MS (NH_3): 246 (16, $[M]^+$), 231 (39), 190 (29), 175 (100), 102 (22).

(*E*)-1-[4-(Hex-1-enyl)phenyl]ethanone:[15a] See Table 2, entry 6. The product was obtained in 51% yield by general procedure 1. FC (pentane/Et_2O, 92:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.0 Hz, 2H; Ar), 7.41 (d, J = 8.3 Hz, 2H; Ar), 6.41 (brs, *2H;* ArCH=C*H*Bu), 2.59 (s, 3H; COMe), 2.25 (m, 2H), 1.49 (m, 2H), 1.39 (m, 2H), 0.95 ppm (t, J = 7.0 Hz, 3H;); CI-MS (NH_3): 202 (60, $[M]^+$), 187 (58), 131 (100), 115 (80), 91 (25).

Butyl (*E*)-3-(4-trifluoromethylphenyl)acrylate:[22] See Table 2, entry 7. The product was obtained in 72% yield by general procedure 1. FC (pentane/Et_2O, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 16.0 Hz, 1H; ArC*H*=), 7.55 (m, 4H; ArH), 6.43 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.15 (t, J = 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.62 (tt, J = 6.8, 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.36 (qt, J = 7.3, 6.8 Hz, 2H; CH_2CH_3), 0.89 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3).

Butyl (*E*)-3-(4-fluorophenyl)acrylate:[22] See Table 2, entry 8. The product was obtained in 70% yield by general procedure 1. FC (pentane/Et_2O, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.52 (dd, J = 8.6, 5.5 Hz, 2H; Ar), 7.08 (t, J = 8.6, 2H; Ar), 6.37 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.20 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.69 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.44 (qt, J = 7.3, 6.7 Hz, 2H; CH_2CH_3), 0.97 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.0, 164.0, 143.3, 130.8, 129.9, 118.1, 116.1, 64.5, 30.8, 19.3, 13.8 ppm; CI-MS (NH_3): 222 (25, $[M]^+$), 166 (100), 149 (92), 121 (30), 101 (59), 75 (40).

Butyl (*E*)-3-(4-methoxyphenyl)acrylate:[23] See Table 2, entry 9. The product was obtained in 75% yield by general procedure 1. FC (pentane/Et_2O, 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.48 (d, J = 8.9 Hz, 2H; Ar), 6.90 (d, J = 9.0 Hz, 2H; Ar), 6.32 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.21 (t, J = 6.8 Hz, 2H; $CO_2CH_2CH_2$), 3.84 (s, 3H; OMe), 1.70 (tt, J = 6.8, 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.44 (qt, J = 7.3, 6.8 Hz, 2H; CH_2CH_3), 0.97 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.8, 161.7, 144.6, 130.1, 127.6, 116.2, 114.7, 64.6, 33.7, 31.2, 19.6, 14.2 ppm.

Butyl (*E*)-3-(3-cyanophenyl)acrylate: See Table 2, entry 10. The product was obtained in 73% yield by general procedure 1, using FC (pentane/Et_2O, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (brs, 1H; Ar), 7.74 (d, J = 8.0 Hz, 1H; Ar), 7.65 (d, J = 8.0 Hz, 1H; Ar),7.62 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.51 (t, J = 8.0 Hz, 1H; Ar), 6.49 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.22 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.69 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.43 (qt, J = 7.3, 6.7 Hz, 2H; CH_2CH_3), 0.96 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.3, 141.8, 135.8, 133.2, 131.9, 131.3, 129.8, 121.1, 118.2, 113.4, 64.8, 30.7, 19.2, 13.8 ppm; IR (KBr): $\tilde{\nu}$ = 2960, 2934, 873, 2232, 1712, 1643, 1477, 1421, 1310, 1278, 1227, 1182, 980, 800 cm^{-1}; CI-MS (NH_3): 229 (16, $[M]^+$), 174 (58), 156 (100), 128 (43), 101 (25), 75 (25); HRMS (MALDI-TOF): calcd for $C_{14}H_{15}NO_2K^+$ 268.0745; found 268.0748.

Butyl (*E*)-3-(4-nitrophenyl)acrylate:[16c] See Table 2, entry 11. The product was obtained in 78% yield by general procedure 1. FC (pentane/Et_2O, 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.8 Hz, 2H; Ar), 7.66 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.65 (d, J = 8.8 Hz, 2H; Ar), 6.52 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.17 (t, J = 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.66 (tt, J = 6.8, 6.8 Hz, 2H; $CO_2CH_2CH_2$), 1.40 (qt, J = 7.3, 6.8 Hz, 2H; CH_2CH_3), 0.92 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3).

1-[(*E*)-2-Benzenesulfonylvinyl]-4-trifluoromethylbenzene:[24] See Table 2, entry 12. The product was obtained in 49% yield by general procedure 1. FC (pentane/Et_2O, 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.4 Hz, 2H; Ar), 7.72 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.69–7.55 (m, 7H; Ar), 6.97 ppm (d, J = 16.0 Hz, 1H; =C*H*SO_2Ph); CI-MS (NH_3): 313(3, $[M]^+$), 248(4), 151(13), 125(100), 102 (17).

Butyl (*E*)-3-[4-(1*H*-pyrazol-1-yl)phenyl]acrylate: See Table 2, entry 13. The product was obtained in 40% yield by general procedure 1. FC (pentane/Et_2O, 6:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, J = 16.0 Hz, J = 2.0 Hz, 1H; het. Ar), 7.88 (d, J = 8.9 Hz, 1H; Ar), 7.78 (d, J = 8.9 Hz, 1H; Ar), 7.74 (m, 1H), 7.68 (d, J = 16.0 Hz, 1H; ArC*H*H=), 7.61 (t, J = 8.6 Hz, 1H; Ar), 6.50 (dt, J = 10.8, 2.5 Hz, 1H; Ar) ; 6.44 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.21 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.68 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.42 (qt, J = 7.3, 6.7 Hz, 2H; CH_2CH_3), 0.95 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.5, 146.7, 143.3, 141.8, 129.1, 127.5, 124.3, 118.3, 108.5, 108.2, 64.8, 30.7, 19.2, 13.8 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 2872, 1735, 1457, 1393, 1166, 1064 cm^{-1}; CI-MS (NH_3): 270 (34, $[M]^+$), 214 (70), 197 (100), 149 (32), 84 (40); HRMS (MALDI-TOF): calcd for $C_{16}H_{18}N_2O_2Na^+$ 293.1271; found 293.1289.

Butyl (*E*)-3-(1,3,6-trimethylphenyl)acrylate:[14] See Table 2, entry 14. The product was obtained in 45% yield by general procedure 1. FC (pentane/Et_2O, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.00 (m, 3H; Ar, ArC*H*H=), 6.48 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.13 (t, J = 6.7 Hz, 2H; $CO_2CH_2CH_2$), 2.36 (s, 3H; Me), 1.63 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.39 (qt, J = 7.3, 6.7 Hz, 2H; CH_2CH_3), 0.95 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3).

(*E*)-3,3,3,-Trifluoro-1-phenylpropene:[10e] See Table 2, entry 15). The product was obtained in 50% yield by general procedure 1 (but in a sealed tube or microwave). FC (pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 5H; Ar), 6.87–7.25 (m, 1H; =C*H*Ar), 5.80–6.40 ppm (m, 1H; =C*H*CF_3).

Butyl (*E*)-4,4,4-trifluorobut-2-enoate:[10e] See (Table 2, entry 16. The product was obtained in 32% yield (crude NMR analysis) by general procedure 1 (but in a sealed tube or microwave).

Butyl (*E*)-3-[4′-(2-butoxycarbonylvinyl)biphenyl-4-yl] acryate: See Scheme 2 (**12**). Following general procedure 1 but using Herrmann's palladacycle **7** (0.2–1 mol%), K_2CO_3 (4 equiv), Me(oct)$_3$NCl (30 mol%) and olefin (5 equiv) were loaded. The product was isolated in 72% yield. FC (pentane/Et_2O, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 16.0 Hz, 2H; ArC*H*H=), 7.63 (d, J = 8.6 Hz, 4H; Ar), 7.61 (d, J = 8.6 Hz, 4H; Ar), 6.49 (d, J = 16.0 Hz, 1H; =C*H*CO_2Bu), 4.23 (t, J = 6.7 Hz, 4H; $CO_2CH_2CH_2$), 1.71 (tt, J = 6.7, 7.4 Hz, 4H; $CO_2CH_2CH_2$), 1.45 (qt, J = 7.7, 6.7 Hz, 4H; CH_2CH_3), 1.0 ppm (t, J = 7.4 Hz, 6H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.1, 143.9, 141.8, 134.0, 128.7, 127.5, 118.5, 64.5, 30.9, 19.3, 13.8 ppm; IR (KBr): $\tilde{\nu}$ = 2959, 2932, 2873, 2254, 1699, 1634, 1606, 1313, 1275, 1183, 983, 910, 817 cm^{-1}; CI-MS (NH_3): 408 (41, $[M+2]^+$), 407 (41, $[M+1]^+$), 406 (45, $[M]^+$), 350 (29), 333 (45), 294 (61), 277 (31), 202 (68), 134 (14); HRMS (MALDI-TOF): calcd for $C_{26}H_{30}O_4^+$ 406.2144; found 406.2149.

Butyl (*E*)-3-[3-(2-butoxycarbonylvinyl)phenyl]acrylate: See Scheme 2 (**14**). Following general procedure 1, but using Herrmann's palladacycle **7** (0.2–1 mol%), K_2CO_3 (4 equiv), Me(oct)$_3$NCl (30 mol%), and olefin (5 equiv) were loaded; the product was isolated in 68% yield. FC (pentane/Et_2O, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 16.0 Hz, 2H; ArC*H*H=), 7.65 (brs, 1H; Ar), 7.52 (d, J = 7.8 Hz, 2H; Ar), 7.40 (d, J = 7.8 Hz, 1H; Ar), 6.47 (d, J = 16.0 Hz, 2H; =C*H*CO_2Bu), 4.21 (t, J = 6.7 Hz, 4H; $CO_2CH_2CH_2$), 1.69 (tt, J = 6.7, 7.4 Hz, 4H; $CO_2CH_2CH_2$), 1.44 (qt, J = 7.4, 6.7 Hz, 4H; CH_2CH_3), 1.0 ppm (t, J = 7.4 Hz, 6H; CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.8, 143.6, 135.3, 129.5, 127.6, 119.4, 64.6, 30.8, 19.3, 13.8 ppm; IR (film): $\tilde{\nu}$ = 2958,

2872, 1731, 1638, 1309, 1286, 1166, 983, 860, 796, 674 cm^{-1}; CI-MS (NH_3): 408 (30, $[M+2]^+$), 407 (75, $[M+1]^+$), 406 (62, $[M]^+$), 311 (13), 273 (35), 257 (97), 200 (67), 183 (79), 155 (100), 126 (93); HRMS (MALDI-TOF): calcd for $C_{20}H_{26}O_4+K^+$) 369.1468; found 369.1408.

Methyl (*E*)-3-(4-fluorophenyl)-3-methylacrylate:[13] See Table 3, entry 1. The product was obtained in 40% yield by general procedure 2. FC (pentane/Et_2O, 95:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (dd, J = 8.6, 5.4 Hz, 2H; Ar), 7.06 (t, J = 8.6 Hz, 2H; Ar), 6.1 (s, 1H; =C*H*CO_2Me), 3.75 (s, 3H; OMe), 2.56 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.2, 163.4, 154.6, 138.2, 128.2, 116.7, 115.5, 51.2, 18.0 ppm; IR (KBr): $\tilde{\nu}$ = 2951, 2359, 1715, 1630, 1600, 1510, 1437, 1349, 1272, 1233, 1166, 834 cm^{-1}; CI-MS (NH_3): 194 (52, $[M]^+$), 163 (100), 135 (73), 115 (23); HRMS (MALDI-TOF): calcd for $C_{11}H_{11}FO_2H^+$ 195.0821; found 195.0828.

***n*-Butyl (*E*)-3-(4-fluorophenyl)-2-methylacrylate**:[13] See Table 3, entry 2. The product was obtained in 40% yield by general procedure 2. FC (pentane/Et_2O, 15:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 1H; =C*H*Ar), 7.39 (d, J = 8.0 Hz, 1H; Ar), 7.36 (d, J = 8.0 Hz, 1H; Ar), 7.09 (d, J = 8.0 Hz, 1H; Ar), 7.05 (d, J = 8.0 Hz, 1H; Ar), 4.21 (t, J = 6.0 Hz, 2H; $CO_2CH_2CH_2$), 2.09 (s, 3H; Me), 1.68 (tt, J = 6.7, 6.7 Hz, 2H; $CO_2CH_2CH_2$), 1.42 (qt, J = 7.3, 6.7 Hz, 2H; CH_2CH_3), 0.95 ppm (t, J = 7.3 Hz, 3H; CH_2CH_3).

Methyl (*E*)-3-(4-nitrophenyl)-3-methylacrylate:[25] See Table 3, entry 3. The product was obtained in 52% yield by general procedure 2. FC (pentane/Et_2O, 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.6 Hz, 2H; Ar), 7.06 (d, J = 8.6 Hz, 2H; Ar), 6.19 (s, 1H; =C*H*CO_2Me), 3.78 (s, 3H; OMe), 2.59 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.6, 153.2, 148.6, 148.0, 127.3, 123.9, 119.8, 51.5, 18.0 ppm; CI-MS (NH_3): 221 (68, M^+), 204 (83), 190 (100), 174 (23), 144 (46), 116 (69).

Methyl (*E*)-3-(3-methoxyphenyl)-3-methylacrylate:[13] See Table 3, entry 4. The product was obtained in 47% yield by general procedure 2. FC (pentane/Et_2O, 8:2); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H; Ar), 7.10 (dd, J = 7.5, 1.5 Hz, 1H; Ar), 6.96 (dd, J = 1.5, 1.5 Hz, 1H; Ar), 6.88 (dd, J = 7.5, 1.5 Hz, 1H; Ar), 6.1 (s, 1H; =C*H*CO_2Me), 3.79 (s, 3H; OMe), 3.72 (s, 3H; OMe), 2.56 ppm (s, 3H; Me).

Methyl (*E*)-3-(3-cyanophenyl)-3-methylacrylate: See Table 3, entry 5. The product was obtained in 60% yield by general procedure 2. FC (pentane/Et_2O, 7:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (brs, 1H; Ar), 7.69 (d, J = 7.7 Hz, 1H; Ar), 7.65(d, J = 7.7 Hz, 1H; Ar), 7.50 (t, J = 7.7 Hz, 1H; Ar), 6.14 (brs, 1H; =C*H*CO_2Me), 3.77 (s, 3H; OMe), 2.57 ppm (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.7, 153.1, 143.5, 132.3, 130.6, 130.1, 129.6, 118.8, 118.5, 113.1, 51.5, 19.9 ppm; IR (film): $\tilde{\nu}$ = 2951, 2231, 1715, 1633, 1436, 1349, 1281, 1196, 1162, 1036, 873, 800, 687 cm^{-1}; CI-MS (NH_3): 201 (43, $[M]^+$), 170 (100), 142 (41), 115 (34); HRMS (MALDI-TOF): calcd for $C_{12}H_{11}NO_2$+Na+2H) 226.0846; found 226.0840.

(*E*)-2-Phenyl-1-(4′-tolylsulfonyl)ethene:[24] See Scheme 3, **15** (X = Me). The sulfonyl chloride (1 equiv, 2.00 mmol) and $[Pd(PPh_3)_4]$ (4 mol%, 0.08 mmol) were weighed in a glove box and placed in a round-bottom flask (dried under vacuum) under a nitrogen atmosphere. The flask was connected to a vacuum line and flushed three times with argon, and benzene (5 mL) was added under argon. Then the Et_3N (1.2 equiv, 2.4 mmol) and olefin (2.5 equiv, 5.0 mmol) were added under argon. This reaction mixture was stirred at 60°C for 50–60 h. After being cooled to room temperature, the mixture was diluted with diethyl ether and washed with water. The aqueous layer was extracted again three times with diethyl ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by FC and the product was isolated in 65% yield. FC (pentane/EtOAc, 8:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.0 Hz, 2H; Ar), 7.67 (d, J = 15.4 Hz, 1H; =C*H*Ar), 7.49 (m, 2H; Ar), 7.41 (m, 3H; Ar), 7.35 (d, J = 8.0 Hz, 2H; Ar), 6.85 (d, J = 15.4 Hz, 1H; =C*H*SO_2Ar), 2.45 ppm (s, 3H; Me); CI-MS (NH_3): 258 (18, $[M]^+$), 179 (16), 139 (100), 102 (37), 91 (81).

(*E*)-1-(4′-Chlorophenylsulfonyl)-2-phenylethene:[24] See Scheme 3, **15** (X = Cl). The same procedure was used as for **16**. The product was isolated in 60% yield. FC (pentane/EtOAc 8:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 15.4 Hz, 1H; =C*H*Ar), 7.40–7.54 (m, 7H; Ar), 6.85 ppm (d, J = 15.4 Hz, 1H; =C*H*SO_2Ar).

(*E*,*E*)-1,4-Diphenyl-1,3-butadiene:[10d] See Table 5, entry 6. The product was obtained in 58% yield by general procedure 3. FC (pentane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 7.4 Hz, 4H; Ar), 7.37 (t, J = 1 Hz, 4H; Ar), 7.27 (t, J = 7.4 Hz, 2H; Ar), 7.0 (dd, J = 14.7, 7.04, 3.0 Hz, 2H; olefin), 6.71 ppm (dd, J = 14.7, 7.04, 3.0 Hz, 2H; olefin); CI-MS (NH_3): 206 (100, $[M]^+$), 128 (33), 91 (82), 77 (23).

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