Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Cat. Sci. Technol.

RSCPublishing

ARTICLE

Desulfitative Pd-catalysed coupling reaction using benzenesulfonyl chlorides and enones as the coupling partners

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

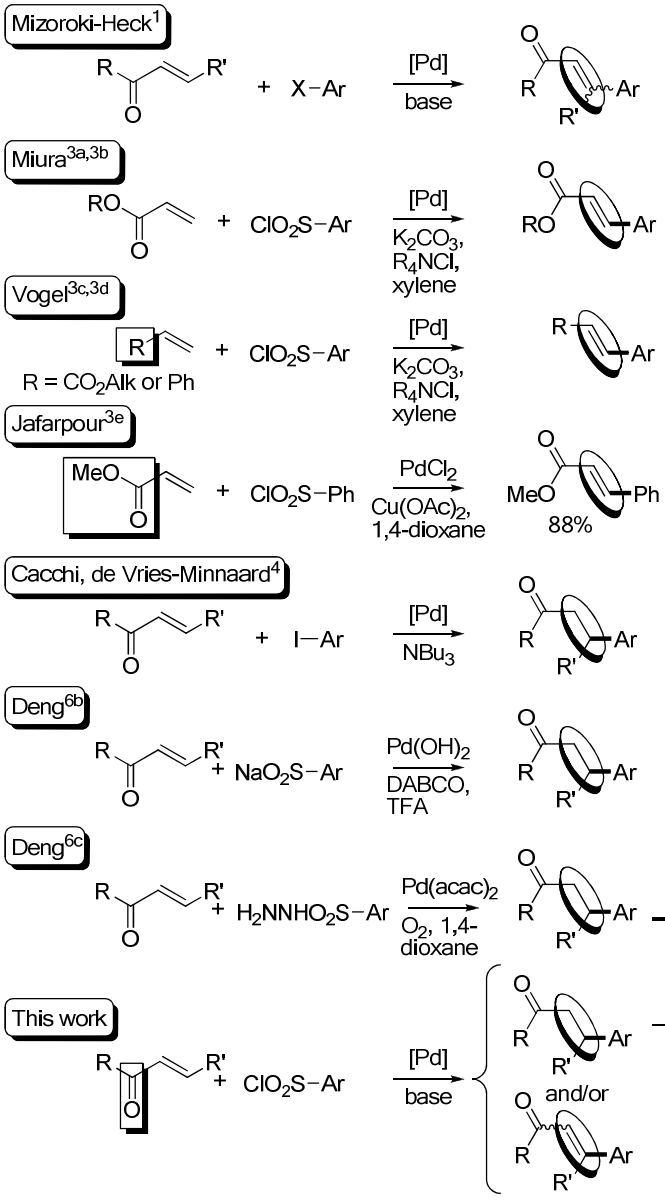
Kedong Yuan, Rui Sang, Jean-François Soulé and Henri Doucet*

The reaction of benzenesulfonyl chlorides with enones was investigated. β-Ionone and benzalacetone in the presence of a palladium catalyst were found to afford the conjugate addition products instead of the expected Heck type products. The reaction tolerates a wide variety of substituents on the benzenesulfonyl chloride. It should be noted that no cleavage of the C-Br and C-I bonds was observed in the course of the reactions with 4-bromo- or 4-iodo-benzenesulfonyl chlorides, allowing further transformations. For example, using 4-bromobenzenesulfonyl chloride as the central unit, consecutive conjugate addition followed arylations allowed the access to substituted bi(hetero)aryls.

Introduction

Mizoroki-Heck reaction is certainly one of the most powerful method for the preparation of styrene derivatives and proceeds with a variety of alkenes including enones.[1,2] For such reactions a variety of coupling partners such as aryl halides or aryl triflates can be employed, and in recent years the reactivity of benzenesulfonyl derivatives was also studied. For example, Miura and co-workers reported the coupling of acrylates with benzenesulfonyl chlorides for access to 3-aryl-2-propenoates (Scheme 1, top).[3a,3b] Then, Vogel extended the reaction to styrene and substituted acrylates.[3c,3d] Jafarpour et al. also reported recently that the reaction of benzenesulfonyl chloride with methylacrylate in the presence of $PdCl_2$ and $Cu(OAc)_2$ as catalytic system also affords the Heck type product (Scheme 1, middle).[3e] On the other hand, the Pd-catalysed conjugate addition of aryl halides with enones has attracted less attention. Cacchi and more recently de Vries and Minnaard reported conditions allowing such conjugate addition using aryl halides as the coupling partners (Scheme 1, middle).[4,5] The palladium-catalysed desulfitative conjugate addition of phenylazo sulfones,[6a] sodium sulfinates[6b] or arylsulfonyl hydrazides[6c] with α,β-unsaturated carbonyl compounds has also been described (Scheme 1, bottom). On the other hand, to our knowledge, the conjugate addition using enones and benzenesulfonyl chlorides as reaction partners has not been described (Scheme 1, bottom). Advantages of benzenesulfonyl chlorides as reactants are that many of them are commercially available at an affordable cost, and they can be easily prepared from sulfonic acids or sulfur substrates by chlorination. Moreover, for some desulfitative Pd-catalysed reactions, the use of halo-substituted $ArSO_2R$ derivatives affords coupling products without cleavage of the Ar-Br or Ar-I bonds allowing further transformations.[7-9] Therefore, the reaction outcome using such coupling partners in the presence of palladium catalysts needed to be investigated.

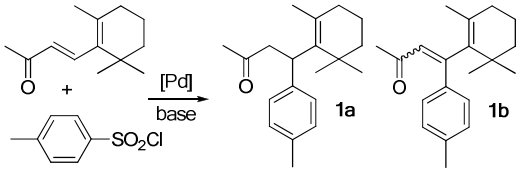
Herein, we describe the selectivity of the reactions using benzenesulfonyl chlorides and enones as the coupling partners in the presence of a palladium catalyst (Scheme 1, bottom). The influence of functional groups on the benzenesulfonyl chloride and sequential C-C bonds formation are also reported.



Scheme 1

Results and discussion

Based on our previous results on the Pd-catalysed desulfitative coupling with heteroarene derivatives,[7a,7b] We first examined the influence of several reaction conditions, using 5 mol% $PdCl_2(MeCN)_2$ catalyst and Li_2CO_3 as the base, on the product formation (Scheme 2, Table 1). Unexpectedly, the reaction of 1 equiv. of β-ionone and 1.2 equiv. of 4-methylbenzenesulfonyl chloride at 140 °C during 24 h, without addition of reductant, led regioselectively to the conjugate addition product **1a** with complete selectivity and in 72% yield (Table 1, entry 1). No formation of the expected Mizoroki-Heck reaction type product **1b** was observed. A lower reaction temperature of 130 °C also gave selectively **1a**, but in lower yield (Table 1, entry 2). Then, we investigated the influence of the nature of the solvent. DMF, ethylbenzene, diethylcarbonate and pentan-1-ol were completely ineffective, as in all cases with these solvents no formation of products **1a** or **1b** was observed. The reaction performed in CPME gave **1a** as trace amount (Table 1, entries 3-7). A mixture of 1,4-dioxane and H_2O afforded **1a** in a lower yield of 27% and a mixture 1,4-dioxane/TFA without base was ineffective (Table 1, entries 8 and 9). The use of 5 mol% $Pd(OAc)_2$, $PdCl_2$ or $Pd(TFA)_2$ also afforded product **1a**, although in low yields of 21-35%; whereas, a reaction performed in absence of catalyst gave no product (Table 1, entries 10-13). Then, the influence of several additives was investigated (Table 1, entries 14-19). Bu_4NCl, NEt_3 and DABCO gave no coupling products; whereas both CuBr and $Cu(OAc)_2$ had no significant influence on the selectivity and yields as **1a** was isolated in 69% and 67% yields, respectively.



Scheme 2

Table 1. Influence of the conditions on the Pd-catalysed reaction of β-ionone and 4-methylbenzenesulfonyl chloride (Scheme 2)

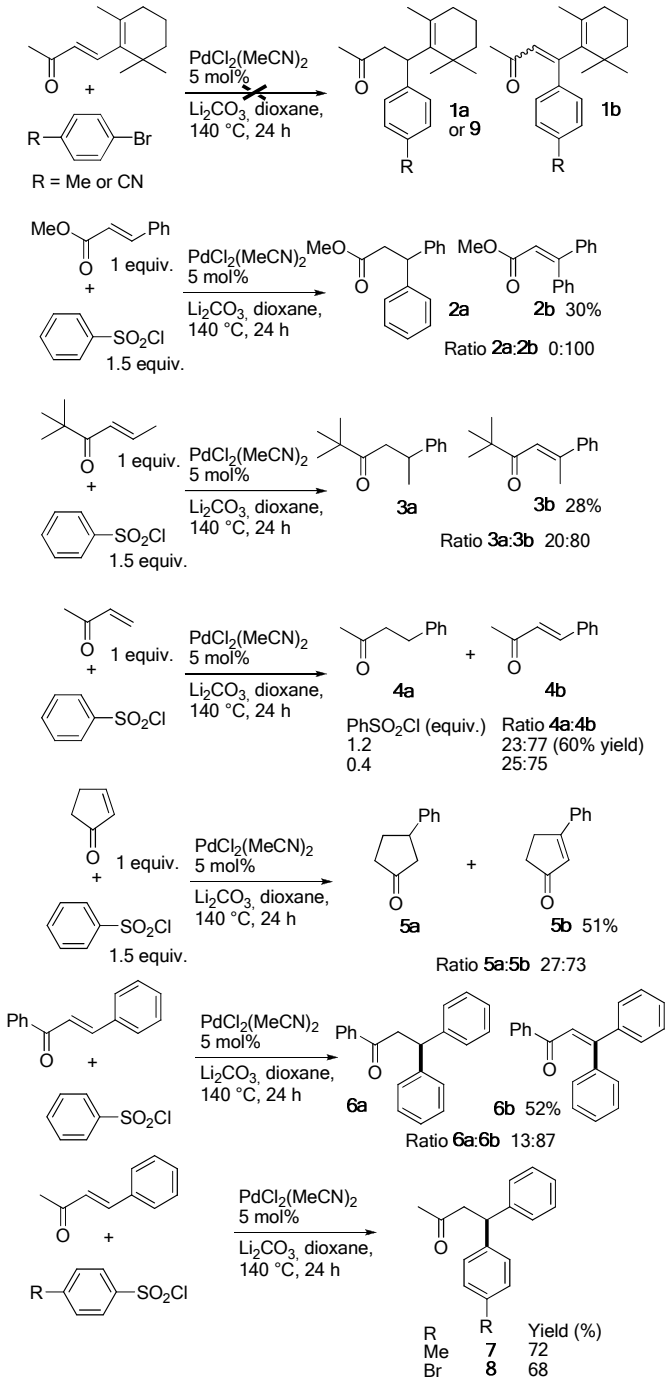
Entry	Catalyst	Solvent	Temp (°C)	Yield in **1a** (%)
1	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	77 (72)
2	$PdCl_2(CH_3CN)_2$	1,4-dioxane	130	40
3	$PdCl_2(CH_3CN)_2$	DMF	150	0
4	$PdCl_2(CH_3CN)_2$	Ethylbenzene	150	0
5	$PdCl_2(CH_3CN)_2$	CPME[a]	150	trace
6	$PdCl_2(CH_3CN)_2$	Diethylcarbonate	150	0
7	$PdCl_2(CH_3CN)_2$	Pentan-1-ol	150	0
8	$PdCl_2(CH_3CN)_2$	1,4-dioxane / H_2O (9:1)	140	27
9	$PdCl_2(CH_3CN)_2$	1,4-dioxane / TFA (9:1)	140	<5[b]
10	$Pd(OAc)_2$	1,4-dioxane	140	21
11	$PdCl_2$	1,4-dioxane	140	35
12	$Pd(TFA)_2$	1,4-dioxane	140	23
13	-	1,4-dioxane	140	0

14	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	69[c]
15	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	67[d]
16	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	<5[e]
17	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	<5[f]
18	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	<5[g]
19	$PdCl_2(CH_3CN)_2$	1,4-dioxane	140	33[h]

Condition: [Pd] 5 mol%, 4-methylbenzenesulfonyl chloride (1.5 equiv.), β-ionone (1 equiv.), Li_2CO_3 (3 equiv.), yield determined by GC and crude ^1H NMR, 24 h, yield in parenthesis is isolated. [a] CPME: cyclopentyl methyl ether. [b] No base. [c] CuBr as additive (2 equiv.). [d] $Cu(OAc)_2$ as additive (2 equiv.). [e] Bu_4NCl as additive (2 equiv.). [f] NEt_3 as additive (2 equiv.). [g] DABCO as additive (2 equiv.). [h] MS4Å as additive.

Under the same reactions conditions, but using 4-bromotoluene and β-ionone as the coupling partners, no formation of products **1a** and **1b** was detected (Scheme 3, top). A similar result was obtained using 4-bromobenzonitrile as arylation partner. On the other hand, a mixture of methyl cinnamate and benzenesulfonyl chloride in the presence of 5 mol% $PdCl_2(MeCN)_2$ catalyst affords exclusively the Heck type product **2b**. This selectivity is similar to the one observed by Miura and Vogel using K_2CO_3, R_4NCl, xylene as the reaction conditions.[3] Then, the selectivity of the coupling of a mixture of (*E*)-2,2-dimethylhex-4-en-3-one and benzenesulfonyl chloride was examined. The Heck type product **3b** was obtained in 80% selectivity together with 20% of conjugate addition product **3a**. The reaction of 1 equiv. of but-1-en-3-one with 0.4 or 1.2 equiv. of benzenesulfonyl chloride under the same reaction conditions also affords a mixture of conjugate addition product **4a** and Heck type product **4b** in a similar ratio of 23:77. The use of cyclopent-2-enone and chalcone also led to mixtures of conjugate addition and Heck type products **5a** and **5b** in 27:73 ratio and **6a** and **6b** in 13:87 ratio, respectively.

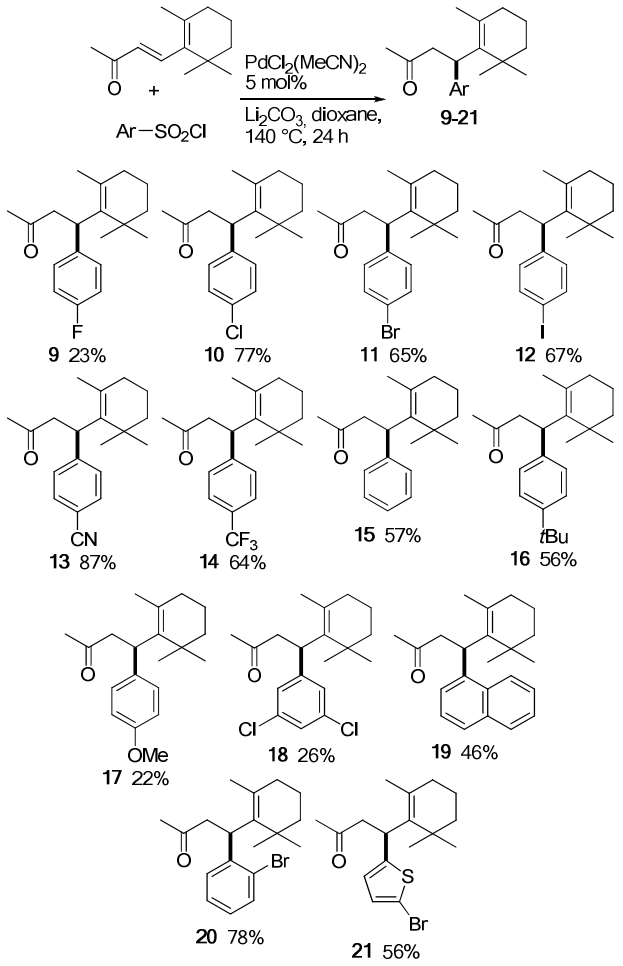
Then, the reaction using benzalacetone as partner was investigated. Minnaard and de Vries have recently reported that the Pd-catalysed reaction of benzalacetone with aryl iodides using an amine as base affords the conjugate addition product; whereas, CsOPiv base led to Heck type product.[4g] From both 4-methyl- and 4-bromo-benzenesulfonyl chlorides and benzalacetone as reaction partners using again 5 mol% $PdCl_2(MeCN)_2$ catalyst and Li_2CO_3 as base in dioxane, the conjugate addition products **7** and **8** were selectively obtained (Scheme 3, bottom). No formation of Heck type products was detected, and the C-Br bond of **8** was not cleaved.



Scheme 3

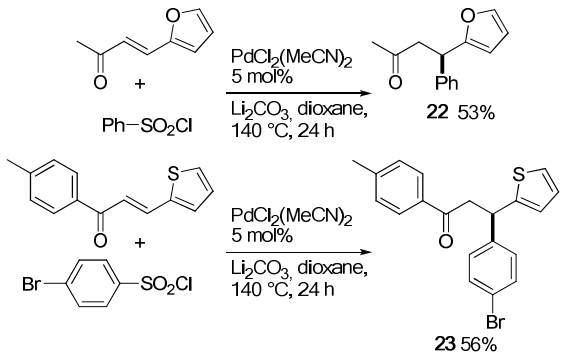
The scope of the reaction of β-ionone using a variety of benzenesulfonyl chlorides was investigated (Scheme 4). 4-fluorobenzenesulfonyl chloride afforded the reductive addition products **9** in only 23% yield. Higher yields were obtained for the coupling of 4-chloro-, 4-bromo and 4-iodo-benzenesulfonyl chlorides, as the desired products **10-12** were isolated in 65-77%. It should be noted that for these reactions, no cleavage of the C-Halo bonds was observed allowing further transformations. The reaction also tolerates 4-cyano and 4-trifluoromethyl substituents on the benzenesulfonyl chloride, as **13** and **14** were formed in 87%

and 64% yields. Similar yields of 57% and 56% in **15** and **16** were obtained in the presence of benzene sulfonylchloride and 4-*tert*-butylbenzene sulfonylchloride. A poor yield of 22% in **17** was obtained in the presence of electron-rich 4-methoxybenzenesulfonyl chloride; whereas congested, 2-bromobenzenesulfonyl chloride affords **20** in 78% yield. Even 5-bromothiophene-2-sulfonyl chloride could be employ to give **21** in 56% yield without cleavage of the thienyl C-Br bond.



Scheme 4

The reactivity of two enones substituted by an heteroarene was also investigated (Scheme 5). Is is known that the arylation of furans and thiophene via palladium-catalysed desulfitative arylation proceeds nicely.[11r] However, from both (*E*)-4-(furan-2-yl)but-3-en-2-one and (*E*)-3-(thiophen-2-yl)-1-(*p*-tolyl)prop-2-en-1-one the selective formation of **22** and **23** from conjugate addition was observed. No arylation on the heteroarene rings was observed on the ^{1}H NMR analysis of the crude mixture.



Scheme 5

Although the mechanism is not yet elucidated, we assume that in the first step an oxidative addition of $ArSO_2Cl$ to Pd(II) affords a Pd(IV) species (Figure 1). Such oxidative addition on Pd(II) have been found to proceed even at room temperature.[10] Then, after elimination of SO_2, the coordination of the enone might afford a Pd-O intermediate with transfer of the Ar group at the α-position to R substituent of the enone. However, the nature of the reductant in this process remains unclear.

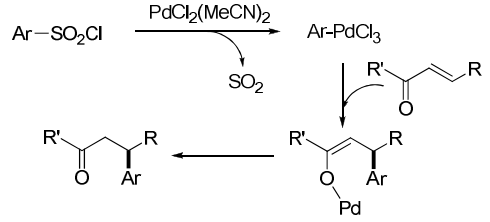
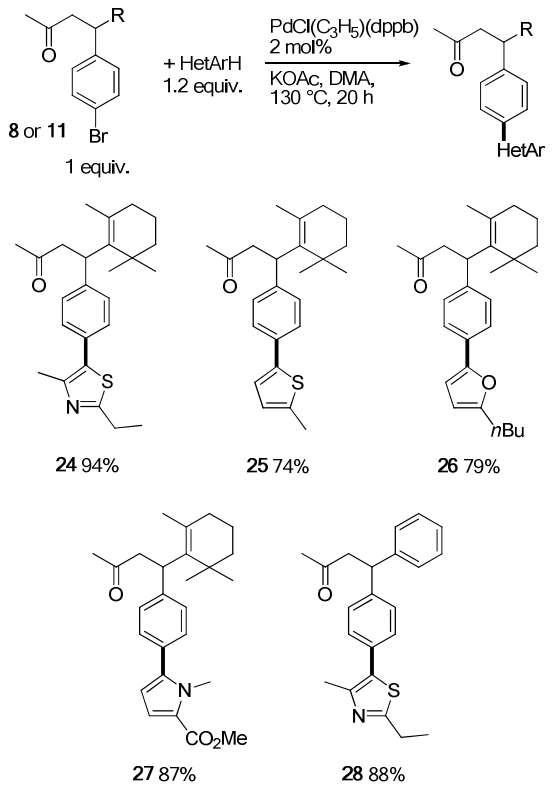


Figure 1 Suggested mechanism

In recent years, palladium-catalysed direct arylation of heteroaromatics with aryl halides *via* a C–H bond activation has become a popular method for generating carbon-carbon bonds.[11-13] As the desulfitative conjugate addition tolerates C-Br bonds to afford **8** and **11** in good yields, consecutive couplings using 4-bromobenzenesulfonyl chloride as the central unit was also studied (Scheme 6). Using 2 mol% $PdCl(C_3H_5)_2(dppb)$[14] catalyst in the presence of KOAc in DMA, **11** was coupled with a variety of heteroarenes to afford **24**-**27** in 74-94% yields. It should be mentioned that the reaction in the presence of methyl 1-methylpyrrole-2-carboxylate proceed without decarboxylation to afford **27** in 87% yield. From 4-(4-bromophenyl)-4-phenylbutan-2-one **8** and 2-ethyl-4-methylthiazole, under the same conditions, the desired product **28** was also obtained in a yield of 88%. In all cases, a regioselective arylation at carbon C5 on the heteroarene was observed.



Scheme 6

Conclusion

In summary, we report here the first palladium-catalysed conjugate addition using benzenesulfonyl chlorides and enones as the coupling partners. The selectivity of the reaction depends on the enone derivative. Benzalacetone and β-ionone only affords conjugate addition products; whereas, (*E*)-2,2-dimethylhex-4-en-3-one or but-3-en-2-one afforded mixtures of Heck and conjugate addition products. The reaction was found to proceeds with easily accessible ligand-free $Pd(MeCN)_2Cl_2$ catalyst and Li_2CO_3 as base. Moreover, this procedure tolerates a variety of substituents on the benzenesulfonyl chloride. It should be noted that even bromo- and iodo-benzenesulfonyl chlorides were successfully coupled without cleavage of the C-Br or C-I bonds, allowing further transformations. At present, it remains unclear why a conjugate addition via reduction takes place instead of the expected Heck type reaction. However, due to the wide availability of diversely functionalized benzenesulfonyl chlorides at an affordable cost, such simple reaction conditions (no expensive base and ligand) should be very attractive to synthetic chemists for access to 4-arylbutanones. Finally, from a 4-(4-bromophenyl)butanone, a palladium-catalysed C-H bond functionalization using heteroarenes as coupling partners allows the synthesis of a variety of heteroarylated 4-arylbutanones.

Acknowledgements

We thank the ministère de la recherche for a fellowship to K. Y. and the Centre National de la Recherche Scientifique and "Rennes Metropole" for providing financial support.

Experimental section

General Remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. Dioxane analytical grade was not distilled before use. Li_2CO_3 (>99%) was used. Commercial enones and benzenesulfonyl chlorides were used without purification. The reactions were followed by GC and NMR. ^1H and ^{13}C spectra were recorded with a Bruker 400 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

General procedure

In a typical experiment, the enone or acrylate derivative (1 mmol), benzenesulfonyl chloride derivative (1.5 mmol), Li_2CO_3 (0.222 g, 3 mmol) and $PdCl_2(MeCN)_2$ (12.9 mg, 0.05 mmol), were dissolved in 1,4-dioxane (2 mL) under an argon atmosphere. The reaction mixture was stirred at 140°C for 24 h. After evaporation of the solvent, the product was purified by silica gel column chromatography.

4-*p*-Tolyl-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (1a)[15]

From β-ionone (0.192 g, 1 mmol) and 4-methylbenzenesulfonyl chloride (0.285 g, 1.5 mmol), product **1a** was obtained in 72% (0.204 g) yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 4.33 (d, J = 8.3 Hz, 1H), 3.30 (dd, J = 17.1, 8.4 Hz, 1H), 2.80 (d, J = 17.1 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.30 (s, 3H), 1.06 (s, 3H), 1.03 (s, 3H).

Methyl 3,3-diphenylacrylate (2b)[16]

From methyl cinnamate (0.162 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol), product **2b** was obtained in 30% (0.072 g) yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.17 (m, 10H), 6.38 (s, 1H), 3.65 (s, 3H).

2,2-Dimethyl-5-phenylhexan-3-one (3a)[17] and (*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-one (3b)[18]

From (*E*)-2,2-dimethylhex-4-en-3-one (0.126 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol), a mixture of products **3a** and **3b** was obtained in a 20:80 ratio and product **3b** was isolated in 28% (0.056 g) yield.

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 2H), 7.29-7.25 (m, 3H), 6.74 (s, 1H), 2.50 (s, 3H), 1.21 (s, 9H).

4-Phenylbutan-2-one (4a) and (*E*)-4-phenylbut-3-en-2-one (4b)[19]

From but-3-en-2-one (0.070 g, 1 mmol) and benzenesulfonyl chloride (0.211 g, 1.2 mmol), a mixture of products **4a** and **4b** was obtained in a 23:77 ratio and in 60% yield (0.088 g) yield.

4a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 2.90 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.15 (s, 3H).

4b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.49 (m, 3H), 7.42-7.35 (m, 3H), 6.72 (d, J = 16.4 Hz, 1H), 2.39 (s, 3H).

3-Phenylcyclopentanone (5a)[20a] **and 3-phenylcyclopent-2-enone (5b)**[20b]

From cyclopent-2-enone (0.082 g, 1 mmol) and benzenesulfonyl chloride (0.211 g, 1.2 mmol), a mixture of products **5a** and **5b** was obtained in a 27:73 ratio and product **5b** was isolated 51% yield (0.080 g) yield.

5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 5H), 3.43-3.32 (m, 1H), 2.65 (dd, J = 7.0, 8.0 Hz, 1H), 2.50-2.20 (m, 4H), 2.00-1.85(m, 1H).

5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.50-7.35 (m, 3H), 6.55 (d, J = 1.0 Hz, 1H), 3.05-2.95 (m, 2H), 2.63-2.50 (m, 2H).

1,3,3-Triphenylpropan-1-one (6a)[21a] **and 1,3,3-triphenylprop-2-en-1-one (6b)**[21b]

From (*E*)-chalcone (0.208 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol), a mixture of products **6a** and **6b** was obtained in a 13:87 ratio and product **6b** was isolated in 52% (0.147 g) yield.

6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 3.0 Hz, 2H), 7.60-7.12 (m, 13H), 4.85 (t, J = 7.4 Hz, 1H), 3.75 (d, J = 7.5 Hz, 2H).

6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 1.5, 7.0 Hz, 2H), 7.52–7.44 (m, 1H), 7.42–7.34 (m, 7H), 7.30–7.22 (m, 3H), 7.20–7.16 (m, 2H), 7.11 (s, 1H).

4-Phenyl-4-*p*-tolylbutan-2-one (7)[22]

From (*E*)-4-phenylbut-3-en-2-one (0.146 g, 1 mmol) and 4-methylbenzenesulfonyl chloride (0.285 g, 1.5 mmol), product **7** was obtained in 72% (0.171 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.12 (m, 5H), 7.08 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 4.52 (t, J = 7.6 Hz, 1H), 3.13 (d, J = 7.6 Hz, 2H), 2.26 (s, 3H), 2.04 (s, 3H).

4-(4-Bromophenyl)-4-phenylbutan-2-one (8)[4g]

From (*E*)-4-phenylbut-3-en-2-one (0.146 g, 1 mmol) and 4-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol), product **8** was obtained in 68% (0.206 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.20 (m, 7H), 7.13 (d, J = 8.2 Hz, 2H), 4.59 (t, J = 7.6 Hz, 1H), 3.18 (d, J = 7.6 Hz, 2H), 2.11 (s, 3H).

4-(4-Fluorophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (9)

From β-ionone (0.192 g, 1 mmol) and 4-flurobenzenesulfonyl chloride (0.292 g, 1.5 mmol), product **9** was obtained in 23% (0.066 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.00 (m, 2H), 6.90 (t, J = 8.6 Hz, 2H), 4.30 (d, J = 8.3 Hz, 1H), 3.29 (dd, J = 17.1, 8.4 Hz, 1H), 2.82 (d, J = 17.1 Hz, 1H), 2.25 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.26 (s, 3H), 1.04 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 160.7 (d, J = 243.2 Hz), 140.9, 140.8 (d, J = 3.2 Hz), 130.5, 128.3 (d, J = 7.9 Hz), 114.6 (d, J = 20.7 Hz), 51.8, 39.9, 36.1, 33.5, 30.1, 28.4, 28.1, 22.3, 19.4.

$C_{19}H_{25}FO$ (288.40): Calcd C 79.13, H 8.74; Found C 79.00, H 8.89.

4-(4-Chlorophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (10)

From β-ionone (0.192 g, 1 mmol) and 4-chlorobenzenesulfonyl chloride (0.316 g, 1.5 mmol), product **10** was obtained in 77% (0.234 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 4.30 (d, J = 8.3 Hz, 1H), 3.27 (dd, J = 17.1, 8.4 Hz, 1H), 2.82 (d, J = 17.1 Hz, 1H), 2.24 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.26 (s, 3H), 1.04 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 143.8, 140.7, 130.8, 130.7, 128.3, 128.1, 51.7, 39.9, 36.2, 36.1, 33.5, 30.0, 28.4, 28.1, 22.4, 19.4.

$C_{19}H_{25}ClO$ (304.85): Calcd C 74.86, H 8.27; Found C 74.99, H 8.37.

4-(4-Bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (11)

From β-ionone (0.192 g, 1 mmol) and 4-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol), product **11** was obtained in 65% (0.227 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 4.28 (d, J = 8.3 Hz, 1H), 3.26 (dd, J = 17.1, 8.4 Hz, 1H), 2.80 (d, J = 17.1 Hz, 1H), 2.23 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 144.4, 140.6, 131.0, 130.7, 128.8, 118.9, 51.6, 39.9, 36.3, 36.1, 33.5, 30.0, 28.4, 28.1, 22.4, 19.4.
$C_{19}H_{25}BrO$ (349.31): Calcd C 65.33, H 7.21; Found C 65.24, H 7.01.

4-(4-Iodophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (12)

From β-ionone (0.192 g, 1 mmol) and 4-iodobenzenesulfonyl chloride (0.454 g, 1.5 mmol), product **12** was obtained in 67% (0.265 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.28 (d, J = 8.3 Hz, 1H), 3.27 (dd, J = 17.1, 8.4 Hz, 1H), 2.80 (d, J = 17.1 Hz, 1H), 2.23 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 145.1, 140.5, 136.9, 130.7, 129.1, 90.2, 51.5, 39.8, 36.2, 36.0, 33.5, 30.0, 28.4, 28.0, 22.4, 19.3.
$C_{19}H_{25}IO$ (396.31): Calcd C 57.58, H 6.36; Found C 57.77, H 6.20.

4-(3-Oxo-1-(2,6,6-trimethylcyclohex-1-enyl)butyl)benzonitrile (13)

From β-ionone (0.192 g, 1 mmol) and 4-cyanobenzenesulfonyl chloride (0.303 g, 1.5 mmol), product **13** was obtained in 87% (0.256 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 4.35 (d, J = 8.3 Hz, 1H), 3.28 (dd, J = 17.1, 8.4 Hz, 1H), 2.84 (d, J = 17.1 Hz, 1H), 2.25 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 151.2, 140.2, 131.8, 131.1, 127.6, 119.1, 108.9, 51.1, 39.6, 36.8, 36.0, 33.3, 29.9, 28.3, 27.9, 22.3, 19.2.
$C_{20}H_{25}NO$ (295.42): Calcd C 81.31, H 8.53; Found C 81.73, H 8.29.

4-(4-(Trifluoromethyl)phenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (14)

From β-ionone (0.192 g, 1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (0.366 g, 1.5 mmol), product **14** was obtained in 64% (0.216 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 4.38 (d, J = 8.3 Hz, 1H), 3.31 (dd, J = 17.1, 8.4 Hz, 1H), 2.85 (d, J = 17.1 Hz, 1H), 2.26 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.23 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 149.5, 140.5, 130.9, 127.5 (q, J = 32.6 Hz), 127.2, 124.9 (q, J = 4.0 Hz), 124.4 (q, J = 271.0 Hz), 51.5, 39.8, 36.6, 36.1, 33.4, 30.0, 28.4, 28.0, 22.4, 19.3.
$C_{20}H_{25}F_3O$ (338.41): Calcd C 70.98, H 7.45; Found C 71.24, H 7.25.

4-Phenyl-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (15)[23]

From β-ionone (0.192 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol), product **15** was obtained in 57% (0.154 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.6 Hz, 2H), 7.12 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 4.36 (d, J = 8.3 Hz, 1H), 3.30 (dd, J = 17.1, 8.4 Hz, 1H), 2.80 (d, J = 17.1 Hz, 1H), 2.25 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 145.2, 140.8, 130.3, 128.0, 126.8, 125.1, 51.7, 39.9, 36.7, 36.1, 33.6, 30.0, 28.5, 28.1, 22.3, 19.4.

4-(4-*tert*-Butylphenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (16)

From β-ionone (0.192 g, 1 mmol) and 4-*tert*-butylbenzenesulfonyl chloride (0.349 g, 1.5 mmol), product **16** was obtained in 56% (0.182 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 4.32 (d, J = 8.3 Hz, 1H), 3.33 (dd, J = 18.7, 8.8 Hz, 1H), 2.80 (d, J = 18.7 Hz, 1H), 2.25 (s, 3H), 1.98-1.90 (m, 2H), 1.70-1.55 (m, 4H), 1.29 (s, 9H), 1.28 (s, 3H), 1.09 (s, 3H), 1.03 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 147.7, 141.9, 140.9, 130.2, 126.5, 124.8, 51.6, 40.0, 36.4, 36.1, 34.2, 33.6, 31.4, 30.1, 28.5, 28.2, 22.4, 19.5.
$C_{23}H_{34}O$ (326.52): Calcd C 84.60, H 10.50; Found C 84.79, H 10.22.

4-(4-Methoxyphenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (17)[24]

From β-ionone (0.192 g, 1 mmol) and 4-methoxybenzenesulfonyl chloride (0.311 g, 1.5 mmol), product **17** was obtained in 22% (0.066 g) yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 4.29 (d, J = 8.3 Hz, 1H), 3.76 (s, 3H), 3.27 (dd, J = 17.1, 8.4 Hz, 1H), 2.80 (d, J = 17.1 Hz, 1H), 2.23 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).

4-(3,5-Dichlorophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (18)

From β-ionone (0.192 g, 1 mmol) and 3,5-dichlorobenzenesulfonyl chloride (0.367 g, 1.5 mmol), product **18** was obtained in 26% (0.088 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 6.93 (s, 2H), 4.28 (d, J = 8.3 Hz, 1H), 3.27 (dd, J = 17.1, 8.4 Hz, 1H), 2.82 (d, J = 17.1 Hz, 1H), 2.25 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.25 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 149.1, 140.1, 134.5, 131.3, 125.6, 125.5, 51.4, 39.7, 36.3, 36.0, 33.4, 30.0, 28.3, 28.0, 22.4, 19.3.

$C_{19}H_{24}Cl_2O$ (339.30): Calcd C 67.26, H 7.13; Found C 67.04, H 7.34.

4-(Naphthalen-1-yl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (19)

From β-ionone (0.192 g, 1 mmol) and 1-naphthylsulfonyl chloride (0.340 g, 1.5 mmol), product **19** was obtained in 46% (0.147 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.39-7.23 (m, 3H), 4.98-4.92 (m, 1H), 3.20 (dd, J = 17.1, 8.4 Hz, 1H), 2.84 (d, J = 17.1 Hz, 1H), 2.10-1.90 (m, 2H), 2.06 (s, 3H), 1.74 (s, 3H), 1.65-1.25 (m, 4H), 0.95 (s, 3H), 0.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 139.6, 139.5, 134.3, 131.5, 130.6, 129.0, 126.9, 126.1, 125.4, 125.2, 125.0, 123.6, 50.4, 40.6, 36.6, 36.1, 34.3, 30.6, 28.8, 27.7, 23.9, 19.2.

$C_{23}H_{28}O$ (320.47): Calcd C 86.20, H 8.81; Found C 86.43, H 8.99.

4-(2-Bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (20)

From β-ionone (0.192 g, 1 mmol) and 2-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol), product **20** was obtained in 78% (0.272 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 4.37 (d, J = 8.3 Hz, 1H), 3.01 (dd, J = 17.1, 8.4 Hz, 1H), 2.87 (d, J = 17.1 Hz, 1H), 2.08 (s, 3H), 2.05-1.90 (m, 2H), 1.69 (s, 3H), 1.65-1.20 (m, 4H), 1.03 (s, 3H), 0.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 143.1, 137.6, 133.4, 131.1, 129.7, 127.6, 127.0, 124.8, 49.1, 40.9, 40.6, 36.2, 34.5, 29.9, 29.1, 27.6, 23.5, 19.1.

$C_{19}H_{25}BrO$ (349.31): Calcd C 65.33, H 7.21; Found C 65.35, H 7.42.

4-(5-Bromothiophen-2-yl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (21)

From β-ionone (0.192 g, 1 mmol) and 5-bromothiophene-2-sulfonyl chloride (0.391 g, 1.5 mmol), product **21** was obtained in 56% (0.199 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 3.7 Hz, 2H), 6.32 (d, J = 3.7 Hz, 2H), 4.33 (d, J = 8.3 Hz, 1H), 3.34 (dd, J = 17.1, 8.4 Hz, 1H), 2.72 (d, J = 17.1 Hz, 1H), 2.22 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.48 (s, 3H), 1.12 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 152.2, 140.9, 132.2, 128.9, 123.3, 108.9, 51.4, 39.7, 36.0, 34.2, 33.6, 30.0, 28.1, 22.3, 19.2.

$C_{17}H_{23}BrOS$ (355.33): Calcd C 57.46, H 6.52; Found C 57.69, H 6.31.

4-(Furan-2-yl)-4-phenylbutan-2-one (22)[25]

From (*E*)-4-(furan-2-yl)but-3-en-2-one (0.136 g, 1 mmol) and benzenesulfonyl chloride (0.264 g, 1.5 mmol), product **22** was obtained in 56% (0.120 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 6H), 6.26 (dd, J = 3.2, 2.0 Hz, 1H), 5.99 (d, J = 3.2 Hz, 1H), 4.60 (t, J = 7.4 Hz, 1H), 3.25 (dd, J = 16.8, 7.5 Hz, 1H), 3.00 (dd, J = 16.8, 7.3 Hz, 1H), 2.11 (s, 3H).

3-(4-Bromophenyl)-3-(thiophen-2-yl)-1-*p*-tolylpropan-1-one (23)

From (*E*)-3-(thiophen-2-yl)-1-(*p*-tolyl)prop-2-en-1-one (0.228 g, 1 mmol) and 4-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol), product **23** was obtained in 53% (0.204 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 5.2 Hz, 1H), 6.94 (dd, J = 3.4, 5.2 Hz, 1H), 6.88-6.86 (m, 1H), 5.07 (t, J = 7.2 Hz, 1H), 3.80-3.70 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 147.7, 144.1, 142.8, 134.2, 131.6, 129.4, 129.3, 128.1, 126.7, 124.2, 123.9, 120.5, 45.7, 41.0, 21.6.

$C_{20}H_{17}BrOS$ (385.32): Calcd C 62.34, H 4.45; Found C 62.56, H 4.65.

Preparation of the $PdCl(C_3H_5)$(dppb) catalyst:[14] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

General procedure for the synthesis of 24-28

In a typical experiment, 4-(4-bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one **7** (0.349 g, 1 mmol), heteroarene derivative (1.2 mmol), KOAc (0.196 g, 2 mmol) and $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol), were dissolved in DMA (4 mL) under an argon atmosphere. The reaction mixture was stirred at 130°C for 20 h. After evaporation of the solvent, the product was purified by silica gel column chromatography.

4-(4-(2-Ethyl-4-methylthiazol-5-yl)phenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (24)

From 4-(4-bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one **11** (0.349 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.152 g, 1.2 mmol), product **24** was obtained in 94% (0.371 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.38 (d, J = 8.3 Hz, 1H), 3.37 (dd, J = 17.1, 8.4 Hz, 1H), 3.00 (q, J = 7.8 Hz, 2H), 2.87 (d, J = 17.1 Hz, 1H), 2.46 (s, 3H), 2.28 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.40 (t, J = 7.8 Hz, 3H), 1.30 (s, 3H), 1.11 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 169.7, 146.6, 144.8, 140.7, 130.9, 130.6, 129.2, 128.7, 127.1, 51.5, 39.9, 36.5, 36.1, 33.6, 30.0, 28.5, 28.2, 26.9, 22.4, 19.4, 16.1, 14.3.

$C_{25}H_{33}NOS$ (395.60): Calcd C 75.90, H 8.41; Found C 76.14, H 8.33.

4-(4-(5-Methylthiophen-2-yl)phenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (25)

From 4-(4-bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one **11** (0.349 g, 1 mmol) and 2-methylthiophene (0.118 g, 1.2 mmol), product **25** was obtained in 74% (0.271 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 3.6 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 4.38 (d, J = 8.3 Hz, 1H), 3.35 (dd, J = 17.1, 8.4 Hz, 1H), 2.84 (d, J = 17.1 Hz, 1H), 2.52 (s, 3H), 2.28 (s, 3H), 1.98-1.90 (m, 2H), 1.65-1.55 (m, 4H), 1.33 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 144.2, 142.0, 140.7, 138.8, 131.6, 130.5, 127.3, 126.0, 125.1, 122.3, 51.5, 39.9, 36.6, 36.1, 33.6, 30.0, 28.5, 28.2, 22.4, 19.4, 15.4.

$C_{24}H_{30}OS$ (366.56): Calcd C 78.64, H 8.25; Found C 78.41, H 8.09.

4-(4-(5-*n*Butylfuran-2-yl)phenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (26)

From 4-(4-bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one **11** (0.349 g, 1 mmol) and 2-*n*-butylfuran (0.149 g, 1.2 mmol), product **26** was obtained in 79% (0.310 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 3.1 Hz, 1H), 6.02 (d, J = 3.1 Hz, 1H), 4.35 (d, J = 8.3 Hz, 1H), 3.33 (dd, J = 17.1, 8.4 Hz, 1H), 2.81 (d, J = 17.1 Hz, 1H), 2.66 (t, J = 7.8 Hz, 2H), 2.26 (s, 3H), 1.98-1.90 (m, 2H), 1.70-1.33 (m, 8H), 1.30 (s, 3H), 1.09 (s, 3H), 1.04 (s, 3H), 0.94 (t, J = 7.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 156.0, 152.2, 143.8, 140.7, 130.4, 128.3, 127.1, 123.1, 106.7, 104.9, 51.5, 40.0, 36.7, 36.1, 33.6, 30.2, 30.1, 28.5, 28.1, 27.8, 22.3, 22.2, 19.4, 13.8.

$C_{27}H_{36}O_2$ (392.57): Calcd C 82.61, H 9.24; Found C 82.79, H 9.37.

Methyl 1-methyl-5-(4-(3-oxo-1-(2,6,6-trimethylcyclohex-1-enyl)butyl)phenyl)-pyrrole-2-carboxylate (27)

From 4-(4-bromophenyl)-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one **11** (0.349 g, 1 mmol) and methyl 1-methylpyrrole-2-carboxylate (0.167 g, 1.2 mmol), product **27** was obtained in 87% (0.354 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 4.0 Hz, 1H), 6.19 (d, J = 4.0 Hz, 1H), 4.41 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.39 (dd, J = 17.1, 8.4 Hz, 1H), 2.87 (d, J = 17.1 Hz, 1H), 2.30 (s, 3H), 2.00-1.95 (m, 2H), 1.70-1.50 (m, 4H), 1.31 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 162.0, 145.4, 141.8, 140.8, 130.6, 129.0, 128.9, 127.0, 123.1, 117.7, 108.9, 51.5, 51.0, 39.9, 36.6, 36.1, 34.4, 33.6, 30.1, 28.5, 28.2, 22.4, 19.4.

$C_{26}H_{33}NO_3$ (407.55): Calcd C 76.62, H 8.16; Found C 76.39, H 8.00.

4-(4-(2-Ethyl-4-methylthiazol-5-yl)phenyl)-4-phenylbutan-2-one (28)

From 4-(4-bromophenyl)-4-phenylbutan-2-one **8** (0.303 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.152 g, 1.2 mmol), product **28** was obtained in 88% (0.307 g) yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.10 (m, 9H), 4.54 (t, J = 7.6 Hz, 1H), 3.13 (d, J = 7.6 Hz, 2H), 2.91 (q, J = 7.6 Hz, 2H), 2.36 (s, 3H), 2.03 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 170.3, 146.6, 143.5, 143.4, 130.6, 130.4, 129.3, 128.7, 128.0, 127.7, 126.6, 49.6, 45.7, 30.7, 26.8, 16.0, 14.3.

$C_{22}H_{23}NOS$ (349.49): Calcd C 75.61, H 6.63; Found C 75.48, H 6.87.

Notes and references

[a] Institut Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes "Organométalliques:

Matériaux et Catalyse", Campus de Beaulieu, 35042 Rennes, France. Fax: +33-(0)2-23-23-69-39; Tel: +33-(0)2-23-23-63-84.

1 (*a*) M. Oestreich, The Mizoroki–Heck Reaction, Wiley, New York, 2009; (*b*) J. Le Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170-1214.
2 For Heck type reactions with aryl sulfonyl hydrazides, aryl sulfinic acids or aryl sulfinates: (*a*) X. Zhou, J. Luo, J. Liu, S. Peng and G.-J. Deng, *Org. Lett.*, 2011, **13**, 1432-1435; (*b*) G.-W. Wang and T. Miao, *Chem. Eur. J.*, 2011, **17**, 5787-5790; (*c*) F.-L. Yang, X.-T. Ma and S.-K. Tian, *Chem. Eur. J.*, 2012, **18**, 1582-1585; (*d*) S. Hu, P. Xia, K. Cheng and C. Qi, *Appl. Organomet. Chem.*, 2013, **27**, 188-190.
3 For Heck type reaction with benzenesulfonyl chlorides: (*a*) M. Miura, H. Hashimoto, K. Itoh and M. Nomura, *Tetrahedron Lett.*, 1989, **30**, 975-976; (*b*) M. Miura, H. Hashimoto, K. Itoh and M. Nomura, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2207-2211; (*c*) S. R. Dubbaka and P. Vogel, *Chem. Eur. J.*, 2005, **11**, 2633-2641; (*d*) S. R. Dubbaka, D. Zhao, Z. Fei, C. M. R. Volla, P. J. Dyson and P. Vogel, *Synlett*, 2006, 3155-3157; (*e*) F. Jafarpour, M. B. A. Olia, H. Hazrati, *Adv. Synth. Catal.*, 2013, **355**, 3407-3412.
4 (*a*) S. Cacchi and G. Palmieri, *Tetrahedron*, 1983, **39**, 3373-3383; (*b*) S. Cacchi and A. Arcadi, *J. Org. Chem.*, 1983, **48**, 4236-4240; (*c*) S. Cacchi, F. Latorre and G. Palmieri, *J. Organomet. Chem.*,1984, **268**, C48-C51; (*d*) A. Amorese, A. Arcadi, E. Bernocchi, S. Cacchi, S. Cerrini, W. Fedeli and G. Ortar, *Tetrahedron* 1989, **45**, 813-828; (*e*) S. Cacchi, F. Gasparrini, P. Pace and C. Villani, *Synlett*, 2000, 650-652; (*f*) N. Miyaura, *Synlett*, 2009, 2039-2050; (*g*) A. L. Gottumukkala, J. G. de Vries and A. J. Minnaard, *Chem. Eur. J.*, 2011, **17**, 3091-3095.
5 A. Gutnov, *Eur. J. Org. Chem.*, 2008, 4547-4554.
6 (*a*) N. K. Kamigata, A. Satoh and M. Yoshida, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1989, **46**, 121-129; (*b*) W. Chen, X. Zhou, F. Xiao, J. Luo and G.-J. Deng *Tetrahedron Lett.*, 2012, **53**, 4347-4350; (*c*) W. Chen, H. Chen, F. Xiao, G.-J. Deng, *Org. Biomol. Chem.*, 2013, **11**, 4295-4298.
7 (*a*) K. Yuan and H. Doucet, *Chem. Sci.*, 2014, **5**, 392-396; (*b*) L. Loukotova, K. Yuan, H. Doucet, *ChemCatChem*, 2014, **6**, 1303-1309.
8 For a review on metal-catalysed desulfitative coupling: K. Yuan, J. F. Soulé and H. Doucet, *ACS Catal.*, 2015, **5**, 978-991.
9 For a review on transition-metal mediated C-S bond activation: L. Wang, W. He and Z. Yu, *Chem. Soc. Rev.*, 2013, **42**, 599-921.
10 X. Zhao and V. M. Dong, *Angew. Chem., Int. Ed.* 2011, **50**, 932-934.
11 For reviews on Pd-catalysed C-H functionalization: (*a*) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174-238; (*b*) T. Satoh and M. Miura, *Chem. Lett.*, 2007, **36**, 200-205; (*c*) B.-J. Li, S.-D. Yang and Z.-J. Shi, *Synlett*, 2008, 949-957; (*d*) F. Bellina and R. Rossi, *Tetrahedron*, 2009, **65**, 10269-10310; (*e*) L. Ackermann, R. Vincente and A. R. Kapdi, *Angew. Chem. Int. Ed.*, 2009, **48**, 9792-9826; (*f*) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem. Int. Ed.*, 2009, **48**, 5094-5115; (*g*) J. Roger, A. L. Gottumukkala and H. Doucet, *ChemCatChem*, 2010, **2**, 20-40; (*h*) L. Joucla and L. Djakovitch, *Adv. Synth. Catal.*, 2009, **351**, 673-714; (*i*) X.-F. Wu, P. Anbarasan, H. Neumann and M. Beller *Angew. Chem. Int. Ed.*, 2010, **49**, 7316-7319; (*j*) L. Ackermann, *Chem. Rev.*, 2011, **111**, 1315-1345; (*k*) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem. Int. Ed.*, 2012, **51**, 10236-10254; (*l*) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed.*, 2012, **51**, 8960-9009; (*m*) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936-946; (*n*) J. Wencel-Delord and F. Glorius, *Nature Chem.* 2013, **5**, 369-375; (*o*) S. I. Kuzhushkov, H. K. Potukuchi and L. Ackermann, *Catal. Sci. Technol.*, 2013, **3**, 562-571; (*p*) R. Rossi, F. Bellina, M. Lessi and C. Manzini, *Adv. Synth. Catal.*, 2014, **356**, 17-117; (*q*) M. He, J. F. Soulé and H. Doucet, *ChemCatChem*, 2014, **6**, 1824-1859; (*r*) K. Yuan, J. F. Soulé and H. Doucet, *ACS Catal.*, 2015, **5**, 978-991.
12 (*a*) Y. Akita, A. Inoue, K. Yamamoto, A. Ohta, T. Kurihara and M. Shimizu, *Heterocycles*, 1985, **23**, 2327-2333; (*b*) A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani and Y. Aoyagi, *Heterocycles*, 1990, **31**, 1951-1958; (*c*) Y. Aoyagi, A. Inoue, I. Koizumi, R. Hashimoto, A. Miyafuji, J. Kunoh, R. Honma, Y. Akita, A. Ohta, *Heterocycles*, 1992, **33**, 257-272.
13 For selected examples of Pd-catalysed direct arylations from our laboratory: (*a*) K. Beydoun, M. Zaarour, J. A. G. Williams, H. Doucet and V. Guerchais *Chem. Commun.*, 2012, **48**, 1260-1262; (*b*) H. Y. Fu, L. Chen and H. Doucet, *J. Org. Chem.*, 2012, **77**, 4473-4478; (*c*) L. Zhao, C. Bruneau and H. Doucet, *Chem. Commun.*, 2013, **49**, 5598-5600.
14 T. Cantat, E. Génin, C. Giroud, G. Meyer and A. Jutand, *J. Organomet. Chem.*, 2003, **687**, 365-376.
15 R. Itooka, Y. Iguchi and N. Miyaura, *J. Org. Chem.*, 2003, **68**, 6000-6004.
16 D. C. Reeves, S. Rodriguez, H. Lee, N. Haddad, D. Krishnamurthy and C. H. Senanayake, *Org. Lett.*, 2011, **13**, 2495-2497.
17 T. Bach, K. Joedicke, K. Kather and R. Froehlich, *J. Am. Chem. Soc.* 1997, **119**, 2437-2445.
18 T. R. Barbee and K. F. Albizati, *J. Org. Chem.*, 1991, **56**, 6764-6773.
19 D. J. Fox, D. S. Pedersen and S. Warren, *Org. Biomol. Chem.* 2006, **4**, 3102-3107.
20 (*a*) R. Lerebours and C. Wolf, *Org. Lett.* 2007, **9**, 2737-2740; (*b*) M. Shibuya, S. Ito, M. Takahashi and Y. Iwabuchi, *Org. Lett.* 2004, **6**, 4303-4306.

21 (*a*) S. Biswas, S. Maiti and U. Jana, *Eur. J. Org. Chem.*, 2010, 2861-2866; (*b*) M. Uyanik, R. Fukatsu and K. Ishihara, *Org. Lett.*, 2009, **11**, 3470-3473.
22 C. L. Stevens and W. Holland, *J. Org. Chem.*, 1958, **23**, 781-783.
23 W. Oroshnik, G. Karnas and R. A. Mallory, *J. Am. Chem. Soc.* 1954, **76**, 2325-2329.
24 A. Arcadi, F. Marinelli and S. Cacchi, *J. Organomet. Chem.*, 1986, **312**, C27-C32.
25 X. Zhang, X. Yu, X. Feng and M. Bao, *Synlett*, 2012, **23**, 1605-1608.

The reaction of benzenesulfonyl chlorides with some enones in the presence of a palladium catalyst affords the conjugate addition products instead of the expected Heck type products.

ABSTRACT