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Free-radical Carbo-alkenylation of Olefins. Scope, Limitations and Mechanistic Insights

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Abstract: The 3-component free-radical carbo-alkenylation of electron-rich olefins has been studied, varying the substitution pattern in the alkene, in the radical precursor and in the final acceptor. New vinylsulfones were also prepared and their reactivity investigated. The scope and limitations of the process was established, and the reaction mechanism clarified using selected dienes as radical clocks. It was thus recognised that the reversible addition onto the olefin of the released sulfonyl group is an important event, which should not be overlooked when using such multicomponent carbo-alkenylation reactions.

Introduction

Olefins are readily available feedstock, the functionalization of which offers an easy access to a variety of important building blocks for organic synthesis. The addition of carbon fragments across the olefinic π -system has thus attracted a considerable interest and is still the subject of an intense research nowadays.¹ Transition-metal carbo-functionalization of olefins is a straightforward option to elaborate olefinic precursors.² Freeradical processes are also receiving a constant attention due to mild reaction conditions and the large variety of substituents, which can be added onto the olefinic backbone.^{1,3} The addition of an alkyl radical onto a C=C bond is energetically favorable. However, intermolecular radical additions to olefins often suffer from low rates and are slowed down by steric hindrance and often plagued by competing processes.³ Intramolecular radical reactions onto unsaturated systems are in contrast much faster and largely employed in synthetic sequences, including complex radical cascades.⁴ Intermolecular addition to activated olefins (acrylates and more generally electron-poor olefins), as in the Giese reaction, have however been developed successfully and found many useful applications in the synthesis of complex substrates.⁵ The addition of electron-deficient radical species onto electron-rich unsaturated systems, has also been investigated and is currently receiving an increasing interest.⁶ The addition of

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fluorinated alkyl radicals,7 has for instance enjoyed recently a strong growth, using photocatalytic processes promoted by visible light.8 Polarity effects are important in such transformations, and consequently the nature of the added radical and that of the olefin greatly influences the outcome of the reaction.9 Electron-poor radical species, such as fluorinated alkyl radicals, but also alkyl radicals flanked by electron-withdrawing substituents (CN, CO₂R, PO(OR)₂,....) have been shown to add efficiently to electron-rich olefins (Figure 1).9d Electron-releasing substituents on the olefinic backbone are also critical in these additions as to ensure high rates. Consequently, enol ethers and thioethers, but also enamine enamides^{8j,k} and strained olefins are substrates of choice for these reactions. Addition of the first radical onto the olefin can then be followed by the reaction of the resulting nucleophilic radical with a radical trap (e.g. A-X) or simply oxidized into a carbocation which may eventually be trapped in situ with a nucleophile (Figure 1).8i,k Both outcome have been reported and give access to a broad range of functionalities in a single pot operation. Amongst A-X reagents, allyl-, vinyl- and alkynylsulfones are reagents of choice, which have been studied extensively.10



Figure 1. Free-radical addition onto electron-rich olefins.

In this context, our laboratory has developed three-component radical functionalization of olefins, relying on the addition of two carbon fragments across the olefinic skeleton, providing adducts with two new C-C bonds along with two additional functional groups.¹¹ Carbo-alkynylation, carbo-oximation and carbo-aminomethylation were thus devised, using various sulfones **III** to trap the radical species issued from the addition of the radical precursor **I** onto the olefinic partner **II** (Figure 2).¹² More recently, we extended this chemistry to the development of a one-pot carbo-alkenylation of olefins including useful enamides and ene-carbamates.¹³ We report here further studies in this context, which not only expand notably the scope of the carbo-alkenylation reaction, varying the nature of the olefinic pattern and that of the sulfonyl acceptor, but also provide additional insights into the mechanism of the process. Some functionalizations of the

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obtained radical adducts are also described showing the utility of this one-pot process for synthetic purposes.



Figure 2. Three-component radical functionalization processes.

Results and Discussion

The scope of the carbo-alkenylation was first extended to a series of olefins 2, using xanthates, iodides and bromides 1a-e as radical precursors in DCE, tBuON=NOtBu (DTBHN) as an initiator and (Bu₃Sn)₂ to sustain the radical chain. Results are summarized in Scheme 1 and 2. Simple esters and ketones were shown to be efficient radical precursors, adding smoothly to olefins. We observed little difference in reactivity between xanthates, iodides and bromides. In most reactions, 4 equivalents of olefins were required, but up to 10 equivalents were needed with less reactive olefins (1-octene for instance). 1.2 Equivalents of disulfone 3-E was used, whatever the nature of the olefin. Generally good vields were obtained with allylsilanes as shown with the formation of sulfone 4a. Functional groups in olefins 2, such as ketone, nitrile. phosphonate or acetal were found to be compatible with reaction conditions (i.e. 4b-e). Norbornene also reacted as expected providing 4f. albeit with no diastereocontrol. Addition onto 1.1disubstituted olefins provided sulfones with an allylic all-carbon quaternary center as in 4g and 4o. Electron-rich enol ethers were found to be reactive with the electrophilic radical issued from 1a, allowing additions onto 1,2-disubstituted double bonds as illustrated with the formation of 4h-l. If one except the case of 4j and 4k, which were formed as single trans isomers, low stereocontrol was generally observed with prochiral enol ethers as for example in 4h, 4i and 4l. Similarly, thioenol ethers also reacted to give thioethers 4m and 4n in good yields. Other classes of olefins, containing useful amino substituents, were also studied. Enamides and ene-carbamates were shown to be reactive under above conditions, as exemplified with the preparation of 4p-s in moderate to excellent yields. As above for enol ethers, Addition onto 1,2-disubstituted electron-rich olefins is not an issue as shown with the preparation of 4p-q from the corresponding enecarbamates. Monoprotected allylamine and fully protected aminoolefins were also found to react, affording the desired adducts 4tv in reasonable yields.



Scheme 1. Carbo-alkenylation of olefins using disulfone 3-E.

Readily available bromides are also potent radical precursors as illustrated below with some reactions using α -bromonitrile **5a** or fluorinated α -bromo esters **5c-d**¹⁴ (Scheme 2). Reactions were performed using conditions above and **3-Z** as the sulfone acceptor, leading exclusively to *E*-vinylsulfones **6a-i** in reasonable yields. This is in good agreement with previous studies,¹⁵ which

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established that the *E*-olefin was always obtained, irrespective of the geometry of the starting sulfone (*vide infra*). Slightly lower yields were obtained with fluoro or difluoroesters, while precusor **5e** led to the 3-component adducts **6h-i** in excellent yields. Aryl iodides were also reacted under similar conditions, but all our efforts to obtain useful amount of product were unsuccessful.¹⁶



Scheme 2. Carbo-alkenylation using bromide precursors 5a-e.

β-Pinene **7** was also treated under the same conditions than above and afforded, after rearrangement,¹⁷ sulfone **8** in moderate yield (Scheme 3), indicating that ring opening is faster than the intermolecular trapping of the secondary radical by disulfone **3** (*vide infra*).





Extension of the three-component carbo-alkenylation to dienes led to important observations from a mechanistic point of view. Regioselective addition of the radical precursor to the 1,1-disubstituted double bond of limonene **9** led to the sulfone **10**, the subsequent cyclization onto the endocyclic double bond being unfavored (Scheme 4). Norbornadiene **11** led to **12** as a mixture of two diastereomers after cyclization of the radical resulting from the addition of xanthate **1a**.¹⁸



Scheme 4. Carbo-alkenylation of limonene 9 and norbornadiene 11.

Dienes 13 and 17 behaved somewhat differently from simple alkenes and produced a mixture of products, depending on the ratio between the olefin and the tin mediator (Scheme 5). For instance, treatment of an excess of diene 13 (4 eq.) as above, led to a mixture of 14, 15 and 16. The former results from the addition of the electrophilic phenylsulfonyl radical onto one of the C=C bond of 13,¹⁹ while 15 and 16 are issued from the trapping of the final primary radical, respectively by the xanthate 1a and sulfone 3-E. Similarly, cycloocta-1,5-diene 17, which has been used previously as a radical clock,20 also afforded a mixture of bicyclo[3.3.0]octane systems 18 and 19 depending on the ratio between 17 and (Bu₃Sn)₂. In both cases, an excess of olefin was shown to favor the addition of the PhSO₂ radical. The best results were finally obtained when the three components and the tin mediator were present in a (quasi) equimolar ratio. In each case, a major diastereomer was formed, the structure and relative configuration of which were assigned using ¹H NMR and X-ray diffraction studies (for X-ray of 18, see supporting information).



Scheme 5. Carbo-alkenylation of diene 13 and cyclocta-1,5-diene 17.

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These last results led us reconsidering the radical chain mechanism, by including the addition of the released PhSO₂ radical onto the olefin component, a crucial step in the process. Figure 3 below summarizes a reasonable radical chain mechanism, incorporating the reversible phenylsulfonyl addition. The tin radical, generated through reaction of (Bu₃Sn)₂ with DTBHN, abstracts the xanthate or the halogen atom from I to form the electrophilic radical A, which adds to the olefin II. The new nucleophilic radical B may then react with the sulfonyl derivative **III** (*i.e.* **3**) to afford the final product. Depending on the nature of the olefin, the atom transfer product may also be isolated.²¹ Usually, it is further consumed in the reaction medium by adding an additional amount of the initiator (DTBHN) as long as sufficient ditin reagent is present. With electron-rich enamides, the atom transfer product is not formed under these conditions, the nucleophilic radical **B** (α to nitrogen) reacting faster with the electron-deficient disulfone 3.13 The released PhSO₂ radical then sustains the radical chain by reacting with ditin to furnish PhSO₂SnBu₃ and a new tin radical. The addition of the PhSO₂ radical onto the olefin also occurs, generating radical C, whatever the nature of the olefin, but this step is reversible and β fragmentation of the β -sulfonyl radical is known to be fast with most olefins.²² With dienes such as 13 or 17, 5-exo-trig cyclization of the β -sulfonyl radical **C** competes with β -fragmentation, thus generating radical D. Rate constants for such cyclizations are estimated to be in the range 10⁵ s⁻¹ and 10⁶ s⁻¹ respectively.²³ As a comparison, β -fragmentation rate constants are in the range of 10⁵ s⁻¹.²² The cyclization step leading to radical **D** is irreversible and leads to products 14 or 18, depending on the relative reactivity between xanthate 1a and sulfone 3. Using an excess of olefin thus favors, in these cases, the addition of the electrophilic sulfonyl radical and leads to an increase of the concentration of radical C. We already observed a similar phenomenon during our study on carboalkynylation of olefins, using vinyl pivalate as an olefin. In this case, the β-fragmentation was reported to be slow and large amount of sulfonyl addition intermediate C was formed.12b





The study on dienes was also extended to systems having electronically differentiated C=C bonds, as for instance in 20 and 24a-b (Scheme 6). In the former, addition of xanthate 1a occurred preferentially onto the electron-richer ene-carbamate moiety to provide a nucleophilic radical which was trapped by disulfone 3-E, thus underlining the importance of polar effects in such processes. Interestingly, when sulfonyloxime 22 was used instead of 3-E, the addition of 1a was followed by a 5-exo-trig cyclization and final trapping of the primary C-centered radical by 22. This clearly indicates that 3-E is a very efficient radical trap, as addition of primary alkyl radicals onto 22 is known to proceed with a rate constant of 9.6 x 10⁵ M⁻¹s⁻¹ (25 °C).²⁴ The high reactivity of 3-E was further supported by the absence of 5-exo-trig cyclization products during addition of 1a onto dienes 24a-b, which afforded instead 25a-b, resulting from the addition onto the enamide moiety. Interestingly, we also observed the formation of by-products 26a-b, resulting from the addition of the tBuO radical generated from DTBHN. The addition of this radical onto the olefin in these 3-component processes has never been observed before but is not so surprising considering the electrophilic nature of the alkoxy radicals.25,26



Scheme 6. Carbo-alkenylation of dienes 20 and 24a-b.

Finally, while most electron-rich olefins reacted efficiently under the above conditions, such was not the case with allylic alcohols and ethers (Scheme 7). Unprotected allylic alcohols did not react at all.²⁷ Protection of the alcohol function as in allylic ethers **27** restored the desired reactivity, but led to the expected compound **28** in low yield and no stereocontrol. Phenylallyl ethers **29a-b** reacted under the standard conditions, but furnished in both cases the corresponding phenols as main isolable products, likely as a result of the β -fragmentation of the phenoxy radical.²⁸ Recent

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studies by Zard *et al.* have shown that related allylic ethers are efficient allylating agents.²⁹



Scheme 7. Carbo-alkenylation of allylic ethers 27 and 29a-b.

The treatment of vinyltrifluoroborate 30 under the threecomponent reaction conditions in the presence of 1a and 3-E surprisingly and reproducibly (in 1,2-DCE or benzene) furnished the adduct 31 in moderate yield (Scheme 8). When the reaction was repeated with α -bromoacetate instead of **1a**, adduct **31** was again obtained, albeit in only 19% yield. Changing xanthate 1a for the benzoyl xanthate led to a complex mixture of products, but no trace of addition product. Interestingly, the formation of 31 in low amount was also observed during 3-component reaction between 1a, 3-E and unreactive olefins such as sterically hindered triacetyl-D-glucal, therefore indicating that 30 is not the olefinic partner during the formation of **31** in the reaction below. Although definitive conclusions cannot be drawn at that stage, it may be hypothesized that the formation of 31 is the result of the carboalkenylation of but-1-ene. The latter might be formed through β elimination of a β-stannylalkyl radical, generated from a Bu₃SnX species present in the medium. This radical might result from an abstraction, by a tbutoxy radical (DTBHN), of an hydrogen of one of the butyl chains in Bu₃SnX. β-elimination of such β-stannylalkyl radicals was invoked to explain the formation of but-1-ene during thermolysis of Bu₃SnCl at 200-300°C, occurring through disproportionation into Bu₂SnCl₂ and Bu₄Sn.³⁰ Although much milder conditions are used here, decomposition of Bu₃SnOt-Bu (formed during initiation, Figure 3) or/and Bu₃SnSO₂Ph might thus lead to sufficient concentration of but-1-ene to allow for the formation of 31. Interestingly, when the reaction was carried out using (Me₃Sn)₂ instead of (Bu₃Sn)₂, compound **31** was not formed, supporting the above hypothesis.



Scheme 8. Carbo-alkenylation of vinyltrifluoroborate 30.

In order to extend the scope of the carbo-alkenylation reaction, various acceptors were then studied.³¹ A survey on the effect of the substitution pattern on the vinyl acceptor was thus performed using allylsilane **2a** as a model olefin and xanthate **1a** as a radical

precursor in the presence of (Bu₃Sn)₂ and DTBHN in 1,2-DCE. Results are summarized in Table 1 below. Carbo-alkenylation generally occurs with high yields and in most cases with excellent stereocontrol, the E-isomer largely predominating. As shown above, E- and Z-acceptors 315a-c led selectively to adduct 33a with excellent yields and E-configuration (Entries 1-2, Table 1). Replacing one of the sulfonyl groups with an ester as in 32a-b (Entries 3-4) surprisingly led to much lower yields. Styrrylsulfone **32c**^{15a-c} (Entry 5) provided good yield of the sulfone adduct **33c**, while the silylsulfone analogue 32d proved unreactive (Entry 6). It is worth adding that 32c was however much less reactive than 3-E or 3-Z, requiring several additions of DTBHN to afford 33c. Chlorosulfone 32e reacted smoothly, giving vinyl chloride 33e, albeit with low stereocontrol (entry 7). Electronic effects were also studied using model acceptors 32f-i^{32,33} (entries 8-11). Reactions on these acceptors occurred on the less hindered site, providing adducts 33f-i in good yields and variable stereocontrol, depending on the nature of the para-substituent on the aromatic ring, but always favouring the retention of configuration.³³ Olefins 32j-n³⁴ proved to be excellent Michael acceptors, leading to adducts 33j-l in good yield, in fast reactions usually requiring a single addition of DTBHN. In good agreement with previous work by Russel et al.,15a-c chlorine and bromine were also shown to be good leaving groups in these reactions, as illustrated with the formation, in high yields, of addition products 33j-I from precursors 32j-n (Entries 12-16).^{15a-c} Finally, β-nitrostyrene³⁵ (Entry 18) was not reactive under our reaction conditions, only leading to traces of 33c.

	SiMe ₂ Ph 2a R ¹ R ² X R ² 32a-o		1a (1 equiv) (Bu ₃ Sn) ₂ DTBHN 1,2-DCE 65°C	- EtO ₂ C SiMe ₂ Ph R ² R ¹ 33a-I			
Entry	Acceptor ^[a]	R¹	R ²	х	33	E/Z ^[b]	Yield [%] ^{[c}
1	3-E	SO₂Ph	Н	SO ₂ Ph	33a	95:5	88
2	3-2	H	SO ₂ Ph	SO ₂ Ph	33a	95:5	78
3	32a	CO ₂ Et		SO ₂ Pn	330	95:5	27
4	320		CO2EI	502P11	330	95.5	20
5	320	Pn Mo Si	н	SO ₂ Pn	33C 224	95:5	74
6	320	IVIE35I	н	SO ₂ Ph	330	-	-
6	32e 20f		П Dh	SO2PII	33e 22f	00.00	75
0	321		FII nTol	SO2F11	220	02.10	69
10	32y 32h		pT0 pMeOPh	SO ₂ Ph	33h	02.8	65
11	321			SO ₂ Ph	331	92.0	75
12	32i	CO ₂ Et	CO ₂ Et	SO ₂ Ph	33i	95.5	71
13	32k	CO ₂ Et	CO ₂ Et	CI	33i	95.5	73
14	321	CO ₂ Et	CO ₂ Et	Br	33i	95:5	79
15	32m	CN	CO ₂ Et	CI	33k	95:5	76
16	32n	SO ₂ Ph	CO ₂ Et	CI	331	95:5	56
17	320	Ph	Н	Br	33c	95:5	49
18	32n	Ph	н	NOa	330	_	trace

Table 1. Carbo-alkenylation of allylsilane 2a with acceptors 3 and 32a-p.

[a] *E/Z* ratio in acceptors 32a-p is > 95:5. [b] *E/Z* ratio estimated by ¹H NMR. [c] Yield of isolated products.

This study finally allowed us drawing a general picture to rationalize both the reactivity of these radical traps and the stereocontrol of the addition-elimination process (Figure 4). When

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using trisubstituted olefins, addition of the radical species occurs on the less sterically hindered position, β - to the acceptors, as shown with 32f-n. With disubstituted systems, the picture is less clear-cut and depends on the steric and electronic nature of both substituents and attacking radical species. For instance, stabilization of the radical intermediate is important as shown in 32c and 32o where a stabilized benzylic radical is formed upon radical addition. In systems having two conjugate acceptors acting in opposition as in 32a and 32b with PhSO₂ and CO₂Me substituents, the nucleophilic radical may add on both centers, explaining the low yield observed in this case. With chlorovinylsulfone **32e**, the addition occurs with high selectivity α to the sulfonyl group, yet the more powerful acceptor. This regioselectivity is in good agreement with pioneering studies by Russel et al.15c who showed that addition of secondary alkyl radicals occurred preferentially α to PhSO₂ (e.g. a 85:15 selectivity was observed with a cyclohexyl radical). This was explained by the interplay between steric factors and polar effects. Stabilization of the resulting radical by the α -chlorine atom may also explain this selectivity. Stereocontrol is another issue in this process. In most cases, the reaction proceeds with retention of configuration.^{15c} With trisubstituted sulfones 32f-i, retention of configuration was generally observed, with a level of stereocontrol depending on the nature of the para substituent of the aromatic moiety, and increasing in the order H < Me < OMe < CO₂Me. This order is consistent with the radical stabilizing effect of these substituents. Addition of a nucleophilic alkyl radical (R) onto these olefins generates a benzylic radical intermediate, eventually leading to conformations IVa-b in which the $\sigma_{C-SO2Ph}$ bond and the radical orbital are suitably aligned for β -elimination (Figure 4). Barrier to rotation ($IVa \leftrightarrow IVb$) is likely higher with more stabilizing substituents (X = CO_2Me) thus leading to more retention. In disubstituted systems, the radical intermediate is not stabilized by resonance. For instance, with disulfone 3-Z, interconversion between conformations such as IVa and IVb must be fast relative to β -elimination, the latter occurring from a conformation minimizing interactions between the attacking R group and the remaining PhSO₂ substituent.



Figure 4. Radical addition to acceptors (arrows indicates the regioselectivity of the process).

Based on the above observations, best acceptors were used varying the nature of olefins. Results of these investigations are summarized in Scheme 9 below. Vinylsulfone **32j** provided the desired adducts with yields similar to those obtained with the vinyl chloride analogue **32k**. As above, the reaction was compatible with a wide range of olefins. Noteworthy, reactions with these acceptors were fast processes, requiring the addition of smaller amount of initiator as compared to those needed for acceptors such as **3-***E* and **3-***Z* (0.15 to 0.3 equiv. of DTBHN).



Scheme 9. Carbo-alkenylation of olefins 2 with Michael acceptors 32j-k.

The reaction was also performed starting from α -bromo acylsilane^{12b} **35** and 2-methoxypropene, which led in the presence of Michael acceptor **32j**, to the corresponding unsaturated acylsilane **36** in good yield (Scheme 10).



Scheme 10. Carbo-alkenylation of 2-methoxypropene with α -bromo acylsilane 35.

Three-component adducts may be elaborated further as illustrated below with the transformation of diester **34i** into the fused tetrahydrofuran **37** (Scheme 11). Treatment of **34i** with (tris(dimethylamino)sulfonium difluorotrimethylsilicate) (TASF) led to a tandem desilylation/oxa-Michael process affording **38** as a mixture of diastereomers. Deprotonation of **38** with NaH then triggered a Dieckmann-type cyclization, which was followed by the saponification of one of the ester group, then decarboxylation,

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to eventually give the fused tetrahydrofuran **37** in 41% overall yield. Formation of a single isomer of **37**, starting from a 72:28 mixture of **38** indicates that the oxa-Michael process is reversible. This was confirmed when the cyclisation of **34i** was carried out in a single pot, using dry TBAF, leading to **37** in 65% overall yield with complete diastereocontrol.



Scheme 11. Elaboration of diester 34i into fused tetrahydrofuran 37 through a desilylation/oxa-Michael/Dieckmann/saponification/decarboxylation process.

Michael addition was also performed using unsaturated sulfones as illustrated in Scheme 12.³⁶ For instance, pyrrolidine was able to initiate the intramolecular conjugate addition in **39**, leading to spiroketone **40** in good yield. Intramolecular Michael addition in **41** led similarly to cyclohexanone **42** as a single diastereoisomer. In the last case, it is worthy of note that the second cyclization onto the ester group does not take place under these conditions, and **43** can be isolated as a single *trans*-diastereoisomer.



Scheme 12. Pyrrolidine-catalyzed Michael additions onto vinyl sulfones $\mathbf{39},^{37}$ $\mathbf{41}^{37}$ and $\mathbf{4d}.$

Conclusions

In summary, we reported extensive investigations on the freeradical carbo-alkenylation of olefins. This process can be applied to a broad range of electron-rich olefins, with a few limitations such as allylic alcohols. The reaction is also effective with non-

conjugated dienes. In this case, the reaction only requires the use of an equimolar amount of diene and precursor 1a, as to avoid competing reactions such as the addition of the sulfonyl radical, released from the vinylsulfone acceptor. This addition occurs irrespective of the nature of the olefin, but is reversible, except with dienes where a fast 5-exo-trig cyclization competes. The study on dienes thus showed that the addition of the electrophilic sulfonyl radical is an important step which should not be overlooked when designing such 3-component carbo-alkenylation reactions. These studies allowed a better understanding of the reaction mechanism, which will however await for further kinetic studies regarding for instance addition onto sulfonyl acceptors, where kinetic data are scarce.²² Variation of the substitution pattern of these acceptors have led to the development of new Michael acceptors, which were elaborated further, demonstrating that useful intermediates for organic synthetic purposes may be assembled in no more than two steps in a straightforward manner.

Experimental Section

General procedure for the carbo-alkenylation of olefins. To a solution of xanthate, bromide or iodide **1** (1 equiv.) in dry 1,2-DCE (2.5 to 5 mL) were added olefin **2** (1 to 4 equiv.), sulfone **3** (1.2 equiv.) and di(tributyltin) (1 to 1.5 equiv.). The reaction mixture was degassed and then stirred at 65°C. Then 15 mol% of DTBHN was added and the reaction mixture stirred for 1.5 h. The reaction progress was monitored by TLC and further additions of DTBHN (15 mol %) were carried out (up to 3 times every 1.5 h) depending on the quantity of precursor **1** remaining. The yellow reaction mixture was then concentrated under reduced pressure and the residue purified by chromatography on silica gel (Petroleum Ether / EtOAc).

Full synthetic details and characterization data is available in the Supporting Information. The crystal structure of compound **18** was deposited at the Cambridge Crystallographic Data Centre. The data have been assigned to the following deposition number: CCDC 1508782.

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Radical and fast. Free-radical carboalkenylation of electron-rich olefins has been studied, varying the substitution pattern on the alkene, the radical precursor and on the final sulfonyl acceptor. The scope and limitations of the process was established, and the reaction mechanism precised using selected dienes as radical clocks. It was shown that the reversible addition of the released sulfonyl group onto the olefin is important and should not be overlooked when using such processes. R. Beniazza, V. Liautard, C. Poittevin, B. Ovadia, S. Mohammed, F. Robert, and Y. Landais*

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Free-radical Carbo-alkenylation of Olefins. Scope, Limitations and Mechanistic Insights