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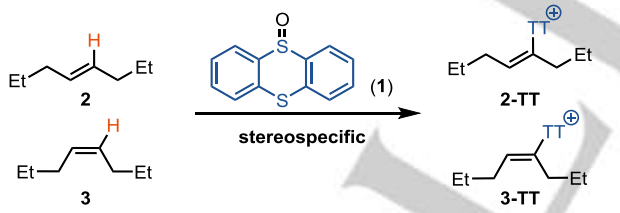
Regio- and Stereoselective Thianthrenation of Olefins to Access Versatile Alkenyl Electrophiles

Junting Chen, Jiakun Li, Matthew B. Plutschack, Florian Berger, and Tobias Ritter*

Abstract: Here we report a regioselective alkenyl electrophile synthesis from unactivated olefins via a direct and regioselective C–H thianthrenation reaction. The selectivity is proposed to arise from an unusual inverse electron demand hetero Diels-Alder reaction. The alkenyl sulfonium salts can serve as electrophiles for palladium and ruthenium catalyzed cross-coupling reactions to make alkenyl C–C, C–Cl, C–Br and C–SCF_3 bonds stereo-retentively.

Olefins are among the most useful building blocks in organic synthesis, but the direct synthesis of alkenyl electrophiles from olefins is an unsolved problem.[1] While olefins display C(sp^2)–H bonds like arenes, their reactivity is distinct from arenes when treated with electrophiles: arenes undergo electrophilic C(sp^2)–H substitution, while olefins typically undergo addition reactions like dihalogenation to generate dihaloalkanes.[2] Despite the synthetic utility of alkenyl electrophiles, general direct and regioselective functionalization of olefins via C(sp^2)–H substitution to access them is not yet known.[3] Herein, we report a regio- and stereoselective method to afford alkenyl electrophiles directly from unactivated alkenes by C(sp^2)–H substitution (Scheme 1). The high stereoselectivity may be the consequence of an unusual inverse electron demand hetero Diels-Alder reaction with a previously unused dicationic aromatic thianthrene dication. The resulting alkenyl sulfonium salts are versatile electrophiles for palladium- and ruthenium-catalyzed cross-coupling reactions.



Scheme 1. Stereoselective C(sp^2)–H thianthrenation of olefins; TT=thianthrenium.

Alkenyl halides, especially alkenyl bromides and iodides, are widely used alkenyl electrophiles for cross-coupling and other reactions.[4] Their syntheses often require multi-step sequences, for instance, dibromination of alkenes followed by the elimination of HBr under harsh conditions,[5] or the prior synthesis of alkenyl nucleophiles, such as alkenyl boronates,[6] alkenyl silanes,[7] or other metal species,[8] followed by treatment with electrophilic halogen sources. Methods starting from alkynes can afford alkenyl halides in one step, although they are less widely used considering the smaller availability of alkynes when compared to alkenes.[8] Other frequently used methods like the Takai- and Wittig olefination reactions often give *E*/*Z* mixtures starting from aldehydes or ketones.[9] It is desirable to access alkenyl (pseudo)halides directly from widely available alkenes, but functionalizations of alkenes commonly deliver hydrofunctionalized or vicinal difunctionalized alkanes.[10] Modern olefin metathesis catalysts can sometimes access the *Z* isomers of alkenyl halides through cross metathesis,[3e] and also *E* alkenyl halides in some cases when bulky substituents are present in the starting material.[11] Alkenyl nucleophiles are available directly from C(sp^2)–H functionalization of alkenes, such as alkenyl silane[12] and boronate.[13] Michael acceptors such as nitroolefin[14] and alkenyl nitrile[15] can also be synthesized from alkenes. Procter disclosed the synthesis of alkenyl sulfoniums via an interrupted Pummerer approach, but the reaction is limited to styrene-like substrates.[16] Carreira reported a directed C(sp^2)–H functionalization to make alkenyl iodides that bear a picolinamide directing group.[17] The direct synthesis of versatile alkenyl electrophiles from simple olefins via C(sp^2)–H functionalization is as of yet unknown.[12-16,18] Here we fill this gap, and showcase the utility of the alkenyl sulfonium electrophiles in several cross-coupling reactions. The chemistry differs conceptually from prior art due to an unusual mechanism of olefin functionalization that sets the chemistry apart from arene thianthrenation and other syntheses of alkenyl sulfoniums.

We have recently published a site-selective aromatic C(sp^2)–H functionalization reaction via *in situ* activation of thianthrene-*S*-oxides with trifluoroacetic anhydride.[19a] The formed aryl thianthrenium salts are used as aryl electrophiles to synthesize challenging bonds like aryl C–SCF_3,[19a] C–CF_3,[19b] C–N,[19c] C–O,[19d] and C–F[19e,f] bonds. Extension of aromatic substitution chemistry to olefins is generally not successful because olefins typically react with electrophiles by addition. Thianthrene radical cation addition to olefins has been explored.[20] In contrast to this addition chemistry and our previous arene substitution; we disclose here data that supports a distinct mechanism for alkene substitution that allows for the selective synthesis of alkenyl sulfonium salts from thianthrene-*S*-oxide.

The reaction is straightforward to execute: alkene (1.00 equiv.) and thianthrene-*S*-oxide (**1**) (1.03 equiv.) are dissolved in anhydrous acetonitrile under ambient atmosphere, followed by sequential addition of trifluoroacetic anhydride and trifluoromethanesulfonic acid with cooling. The reaction is complete within less than two hours. The products can be purified by column chromatography (Table 1).

[a] J. Chen, Dr. J. Li, Dr. M. B. Plutschack, Dr. F. Berger, Prof. Dr. T. Ritter
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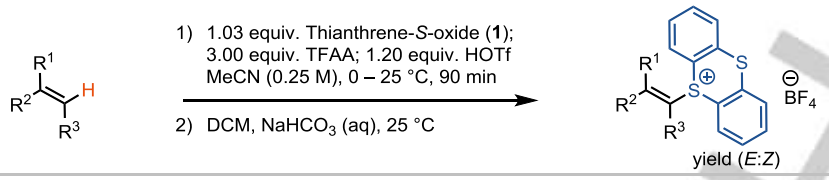
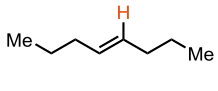
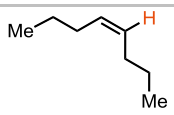
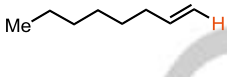
Supporting information for this article is given via a link at the end of the document.

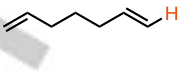
Table 1. Regioselective C(sp^2)–H Thianthrenation of Unactivated Alkenes.[a]

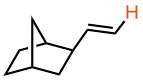



2, 95% (<1:50)


3, 98% (>49:1)[b]


4, 93% (20:1)[b]


5, 76% (17:1)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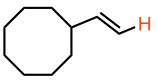
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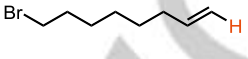
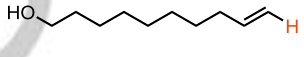
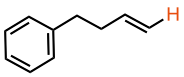

8, >99% (17:1)


9, 71% (16:1)[b,c]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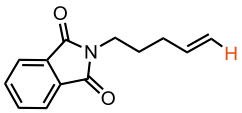
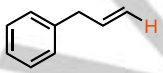

11, 72% (>50:1)[d,e]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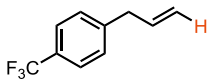
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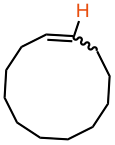
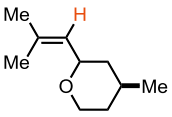
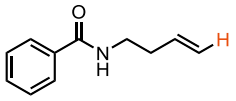
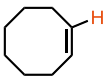
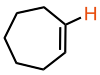

14, 68% (≈1:1)[f,h]


15, 75%[g]


16, 88%[g]

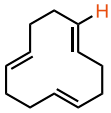

17, 68% (>50:1)

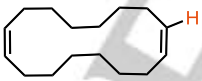

18, 74%[e,g,h]

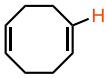

19, 75%[g]

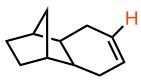

20, 60%[g,h]

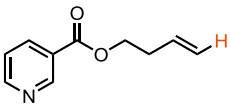

21, 74%[g,h]

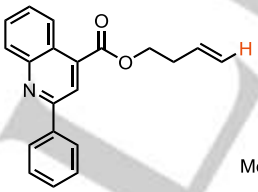

22, 68% (<1:50)[h]

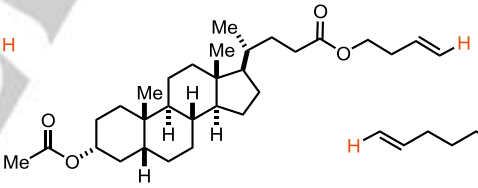

23, 61% (>50:1)


24, 54%[g]


25, 53%[g,h]


26, 52% (20:1)[i]


27, 71% (>50:1)[i]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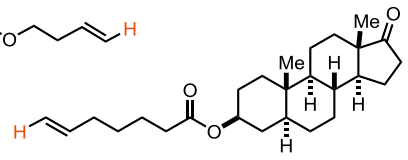
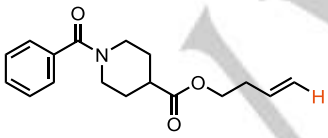
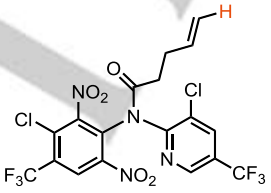
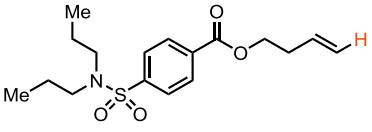
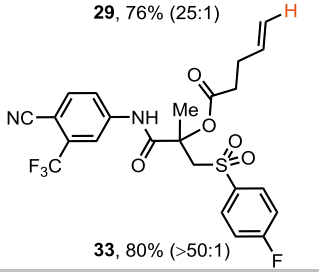

29, 76% (25:1)


30, 58% (>50:1)


31, 48% (>50:1)[i]

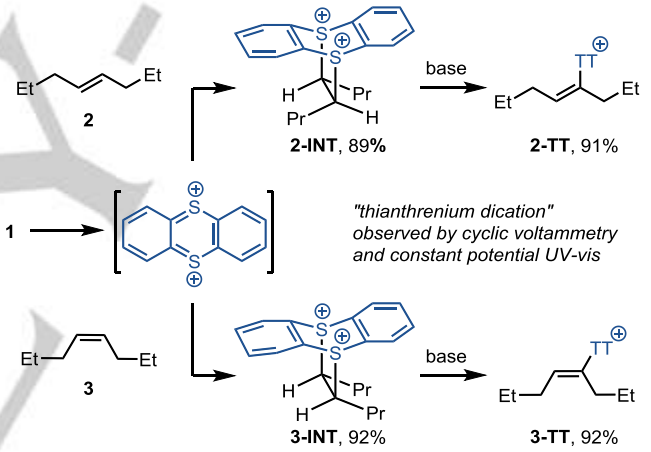

32, 69% (>50:1)


33, 80% (>50:1)

(a) 0.500 mmol scale, 1.03 equiv. thianthrene-*S*-oxide (**1**), 3.00 equiv. trifluoroacetic anhydride (TFAA), 1.20 equiv. trifluoromethanesulfonic acid (HOTf). Isolated yields. *E*/*Z* ratios were determined by ^{1}H-NMR. (b) 2.40 equiv. of HOTf was used to obtain better *E*/*Z* ratio. (c) The alcohol was partially acylated during the reaction (see Supporting Information). (d) 1.20 equiv. HBF_4•Et_2O instead of HOTf was used to obtain better *E*/*Z* ratio. (e) Reaction was performed on 3.00 mmol scale. (f) Cyclododecene starting material used as mixture of isomers (*E*/*Z* ≈ 1/2, see Supporting Information). (g) *E*/*Z* ratio is not applicable. (h) 1.20 equiv. HBF_4•Et_2O instead of HOTf was used to obtain higher yields. (i) 2.40 equiv. of HOTf was used to obtain higher yields.

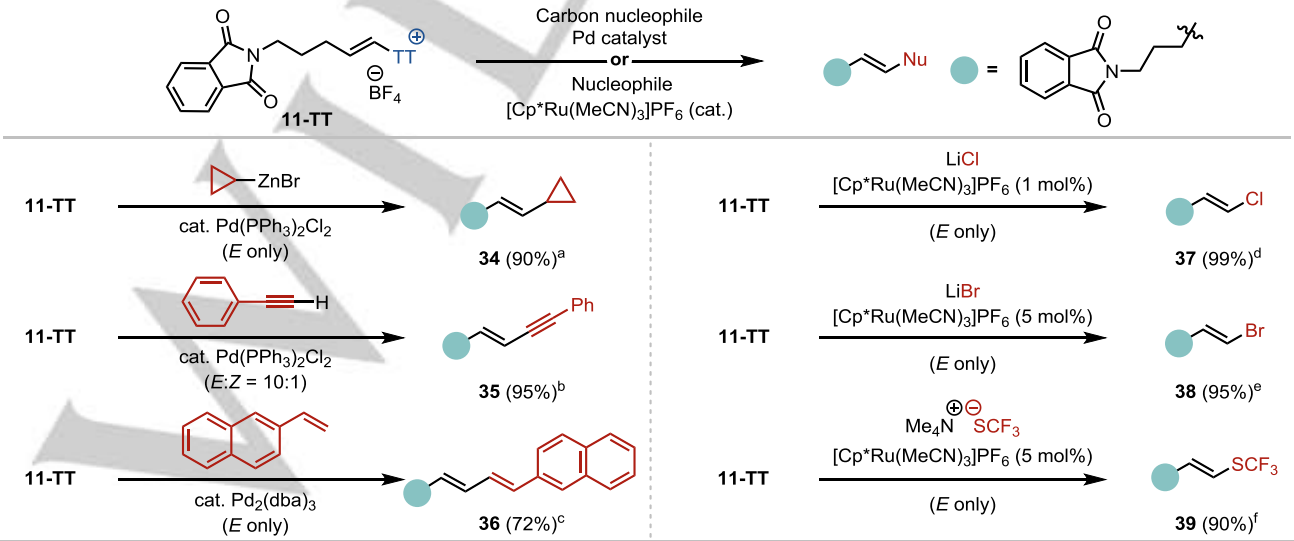
For all α-olefins, the *E*-alkenyl sulfonium salts were obtained as major products, often without detectable *Z* isomers, when analyzed by NMR spectroscopy. Functionalization of internal alkenes proceeded with retention of the double bond geometry for both *E* (**2**, **22**) and *Z* (**3**, **23**) olefins. Steric bulk in the allylic position does not interfere with productive functionalization (**6**, **7**). Functional groups like imides (**11**), primary alkyl bromides (**8**), alcohols (**9**), ethers (**15**, **16**), amides (**17**), esters (**26**–**33**), ketones (**29**) piperidine (**30**), nitro (**31**), sulfonamides (**32**), sulfones (**33**), and nitrile (**33**) are all tolerated. Electron rich arenes can undergo aromatic substitution,[19c] but electron-poor (**11**, **13**), electron-neutral (**12**) and six-membered heterocyclic arenes (**26**, **27**, **31**) are tolerated. Even bis-benzylic and allylic C(sp^3)–H bonds (**12**, **13**) are tolerated without double bond isomerization or allylic functionalization.[13b,18,21] Internal olefins that are electronically biased such as enol ethers (**16**) are functionalized regioselectively, as are all α-olefins, but the regioselectivity diminishes for other 1,2-disubstituted olefins.[22] Trisubstituted olefins (**15**) on the other hand are functionalized regioselectively. Cyclic olefins (**18**, **19**, **20**, **21**) participate well. Selective monofunctionalization is observed for dienes (**5**, **23**, **24**) and a triene (**22**), most likely due to the introduction of a cationic substituent in an electrophilic pathway.

To rationalize the selectivity, especially the unusually high selectivity with respect to double bond geometry such as in **2** and **3** (Scheme 2), we attempted to gain further insight into the reaction mechanism. When the work-up of the reaction (aqueous bicarbonate) was omitted, we were able to isolate and fully characterize the two diastereomeric intermediates **2-INT** and **3-INT** from *E*- and *Z*-4-octene, respectively. Both, the cycloadducts **2-INT** and **3-INT** as well as the high selectivity are consistent with an unusual [4+2] cycloaddition between olefin and the dicationic thianthrenium dication (see Supporting Information). To substantiate the viability of the unusual thianthenium dication as a reaction partner, we have observed it by cyclic voltammetry and recorded its UV-vis spectrum in an electrical cell at constant potential (see Supporting Information). We cannot rule out an addition of the thianthrene radical cation to the olefin, followed by single electron oxidation and subsequent cyclization to the bicyclic adducts, but oxidation and cyclization would need to occur faster than bond rotation around the C–C single bond to account for the observed selectivity. In addition, reaction of thianthrene radical cations with olefins can afford bis-adducts, with two thianthrene radical cations reacting with one olefin.[20] Attempts to thermally induce a cycloreversion of the cycloadduct **2-INT** was not successful, possibly due to its two formal positive charges that also prevented experiments such as flash-vacuum-pyrolysis. Treatment of either bicycle with mild base, such as bicarbonate, resulted in clean and high-yielding conversion to the corresponding alkenyl sulfonium salts **2-TT** and **3-TT**, respectively, with complete selectivity of olefin geometry. Stereoelectronic considerations dictate that the elimination cannot proceed by an E2 mechanism due to the geometry of the bicycles **2-INT** and **3-INT**, which prevent an antiperiplanar arrangement of leaving group and proton. An E1 mechanism cannot be excluded but is unlikely due to the near complete degree of fidelity of double bond geometry. Consistent with all data is an $E1cB_{irr}$ mechanism where rate-determining deprotonation is followed by a rapid elimination.[23]



Scheme 2. Mechanism for regioselective thianthrenation of alkenyl C(sp^2)–H bonds.

Table 2. Derivatizations of Alkenyl Thianthrenium Salts.



(a) CyclopropylZnBr (3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (20 mol%) in THF (0.1 M). (b) Phenylacetylene (2.0 equiv.), N-methylmorpholine (2.0 equiv.), CuI (25 mol%), $Pd(PPh_3)_2Cl_2$ (10 mol%) in THF (0.1 M). (c) 2-Vinylnaphthalene (2.0 equiv.), K_2CO_3 (2.5 equiv.), $Pd_2(dba)_3$ (10 mol%) in DMF (0.1 M). (d) LiCl (1.5 equiv.), $[Cp^*Ru(MeCN)_3]PF_6$ (1 mol%) in THF (0.1 M). (e) LiBr (1.5 equiv.), $[Cp^*Ru(MeCN)_3]PF_6$ (5 mol%) in THF (0.1 M). (f) $[Me_4N^+][^-SCF_3]$ (1.2 equiv.), $[Cp^*Ru(MeCN)_3]PF_6$ (5 mol%) in THF (0.1 M).

As their aromatic counterparts,[19] the alkenyl thianthrenium salts serve as excellent electrophiles in follow up transformations and thus differ from other alkenyl sulfonium salts that have narrower reactivity (Table 2). Palladium-catalyzed cross coupling reactions generally proceed with retention of the double bond geometry (**34**, **35**, **36**, and see Supporting Information). The alkenyl thianthrenium salts also serve as suitable electrophiles for ruthenium-based catalysis, which enable the synthesis of alkenyl halides (**37**, **38**) and pseudohalides (**39**), also stereoselectively: For example, chlorination in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ as catalyst was performed successfully on gram-scale, and alkenyl trifluoromethyl thioether, which is difficult to access otherwise is readily obtained.[24] Although Ru(II) catalysts are often proposed to have slow oxidative addition to alkenyl halides,[25] $[Cp^*Ru(MeCN)_3]PF_6$ showed robust catalytic reactivity in the reactions using alkenyl thianthrenium salts as electrophiles. Retention of double bond geometry was observed for all cross coupling reactions; also those of trisubstituted olefins (see Supporting Information).

In conclusion, we have reported a synthesis of alkenyl electrophiles, directly from unactivated olefins, which proceeds regio- and stereoselectively for a large variety of olefin classes. Preliminary mechanistic studies suggest that thianthrenation could proceed via an unusual inverse electron demand cycloaddition reaction. The corresponding alkenyl sulfonium salts that can tolerate a large scope of functional groups are suitable electrophiles for Pd-catalyzed C–C cross coupling reactions and Ru-catalyzed C–X bonds formation reactions.

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Keywords: alkenes • regioselective • C–H functionalization • alkenyl electrophiles • cross-coupling reactions

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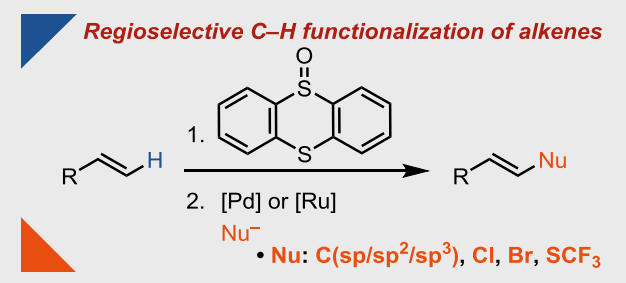

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Regio- and Stereoselective Thianthrenation of Olefins to Access Versatile Alkenyl Electrophiles

We report a regioselective synthesis of sulfonium-based alkenyl electrophiles directly through C–H functionalization of simple olefins. The alkenyl sulfonium salts participate in palladium catalyzed cross coupling and ruthenium catalyzed (pseudo)halogenation reactions.