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C–H-Alkenylation of Arenes in a One-pot VNS – Julia-Kocienski Reaction

Rafał Loska*

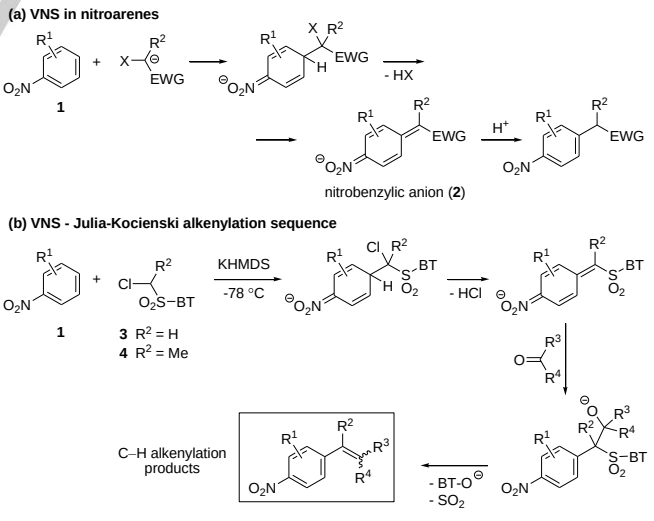
Abstract: A one-pot reaction sequence is reported that enables direct introduction of alkenyl substituents into C–H positions of electron-poor aromatic compounds under transition metal free conditions. The process incorporates vicarious nucleophilic substitution of hydrogen with carbanion of benzotriazolyl chloromethyl sulfone, followed by Julia-Kocienski olefination with aliphatic or aromatic aldehydes or trifluoromethyl ketones. The resulting nitrostyrene derivatives are usually formed with very high *E*/*Z* selectivity.

Introduction

Development of synthetic methods that enable selective functionalization of C–H bonds by transforming them into desired functional groups, without the need for substrate pre-functionalization, is a prevalent theme of modern organic synthesis.[1] C–H-alkenylation of aromatic compounds using alkene substrates that do not contain any activating substituents began with the Pd-catalysed Fujiwara-Moritani process already in the 1960s.[2] Discovery of similar, more selective and robust reaction protocols has been pursued very actively in recent years, relying mostly upon Rh(III) catalysis and substrates bearing directing groups in the aromatic ring.[3] Another general approach to arene C–H-alkenylation is hydroarylation of alkynes.[4]

Vicarious nucleophilic substitution of hydrogen is a well-established and robust method of functionalizing the rings of electron-deficient arenes, particularly nitroarenes (**1**).[5] In its most common, carbon-carbon bond forming variant, the aromatic ring is attacked by a carbanion stabilised by an electron-withdrawing group (EWG) and bearing a good leaving group at the anionic α-carbon (Scheme 1(a), X = leaving group). Consequently, the newly introduced group has the general structure of an EWG-substituted alkyl. Moderately successful attempts have been made to perform VNS with EWG groups (CF_3SO_2) playing also the role of leaving groups, thus enabling VNS alkylation of nitroarenes.[6] In recent years, a new approach to introduce further molecular complexity to the VNS reaction products has been attracting attention. This concept is based upon reactions of the intermediate nitrobenzylic anions **2** produced in the VNS process with various electrophiles, instead of simple protonation. Apart from alkylation of such anions,[7] efficient one-pot processes have been developed that involve initial VNS reactions with halogenated carbanions to form α-halosubstituted nitrobenzylic carbanions (**2,** R^2 = halogen), followed by in situ reaction with aldehydes and Michael acceptors to form nitroaryl oxiranes[8] and cyclopropanes,[9] respectively, via nucleophilic addition and intramolecular nucleophilic substitution.

A VNS reaction of a chloromethyl heteroaryl sulfone would result in the formation of a nitrobenzyl carbanion **2** containing a heteroaryl sulfonyl group (EWG = $HetSO_2$, Het = heteroaryl) at the anionic centre. With an appropriate heteroaryl moiety, such as benzothiazolyl (BT), 2-pyrimidynyl (PY) or phenyltetrazolyl (PT), such anion would be an appropriate partner for a Julia-Kocienski (J-K) olefination process,[10] assuming that it is capable of undergoing addition to a carbonyl compound, followed by a heterocyclic moiety transfer from sulfur to oxygen and subsequent SO_2 and $HetO^-$ elimination. Overall, such a tandem process would be a means of introducing an alkenyl moiety into an aromatic ring *directly* at the position occupied by hydrogen, in a transition metal-free reaction (Scheme 1(b)). The $HetSO_2$ moiety would therefore play a dual role: an EWG enabling deprotonation and carbanion formation necessary for the VNS step, and elimination of oxygen from the intermediate aldol adduct in the Julia-type process. Examples of the above concept exploiting phosphorous chemistry have been already described in the literature, but they were all two-step processes and involved preparation of benzylphosphonyl intermediates in a VNS reaction, followed by condensation with aromatic aldehydes as a separate step.[11]



Scheme 1. (a) A general scheme of the VNS reaction, (b) one-pot VNS – Julia-Kocienski olefination of arenes (for clarity, only attack *para* to NO_2 has been shown).

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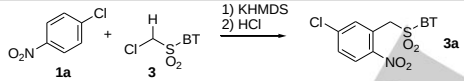
Herein, successful realization of the one-pot nitroarene alkenylation is described, using sulfur chemistry and resulting in the development of a fairly general method of synthesis of both nitrostyrenes and nitrostilbenes. Such nitroarenes are versatile synthetic intermediates.[12] In particular, their *ortho* isomers have been reported to be very useful as starting materials for the synthesis of indoles.[13]

Results and Discussion

The development of the VNS – J-K alkenylation methodology began with investigation of the VNS reaction between chloromethyl benzothiazolyl sulfone **3** and a simple nitroarene, 4-chloronitrobenzene (**1a**). The results of the reactions of **1a** with slight excess of **3** (1.2 – 1.4 equiv.) under basic conditions are summarised in Table 1. Potassium bis(trimethylsilyl) amide (KHMDS) has been chosen as the base required for VNS, as it has been reported to be efficient in other VNS reactions described in the literature[9b,14] and also because it is very convenient to use as a commercially available 1M solution in THF. Too short reaction time (Table 1, entry 1) or too low temperature (entry 3) resulted in poor or moderate yields of the expected VNS product **3a**. Increasing excess of the reagents and extending the reaction time, while performing it at intermediate temperature (-30 °C, entry 4) gave the highest yield of **3a** (82%). Exchanging the base for a sodium or lithium amide (NaHMDS, LiHMDS) resulted in lower yield (entry 5), as did performing the reaction in THF alone instead of DMF (entry 7). Clearly, the VNS reaction can be efficient only when carbanions $\mathbf{3}^-$ do not form tight ion pairs with metal counterions since such interactions prevent nucleophilic addition of $\mathbf{3}^-$ to the aromatic ring of nitroarene.

Table 1. Optimization of the VNS reaction between 4-chloronitrobenzene **1a** and chloromethyl sulfone **3** (BT = 2-benzothiazolyl)[a]



	Amount of **3** (mmol)	Amount of base (mmol)	Time, temperature	**3a** isolated yield
1	0.6	1.25	15 min, -20 °C	52%
2	0.6	1.25	30 min, -45 °C	55%
3	0.6	1.25	30 min, -78 °C	<20%
4	**0.75**	**1.4**	**45 min, -30 °C**	**82%**
5	0.75	1.4[b]	45 min, -30 °C	57%
6	0.75	1.4[c]	45 min, -30 °C	<5%
7	0.6	1.25	45 min, -30 °C	<5%[d]

[a] To KHMDS (1M in THF) a solution of **1a** (0.5 mmol).and **3** in DMF (the same volume as KHMDS solution) was added dropwise under inert atmosphere and quenched with 2M HCl after time indicated. [b] NaHMDS (1M in THF) used instead of KHMDS. [c] LiHMDS (0.5M in toluene) used instead of KHMDS. [d] THF instead of DMF for dissolving **1a** and **3**.

With the optimal conditions of the VNS step in hand, attempts were undertaken to couple this reaction with a J-K-type alkenylation process by adding carbonyl compounds to the reaction mixture instead of quenching it with strong acid.

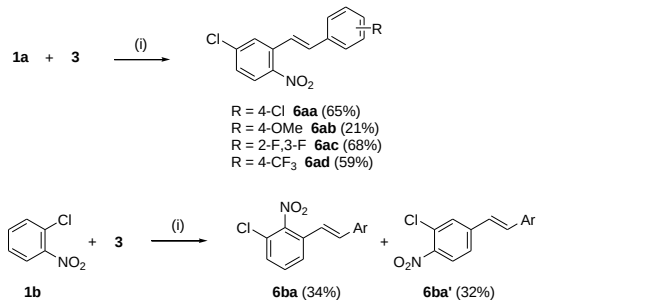
When studying a model reaction between **1a** and **3** in the presence of KHMDS, followed by addition of 4-chlorobenzaldehyde **5a** as a carbonyl reaction partner, it was quickly established that due to poor nucleophilicity of α-sulfonylnitrobenzylic carbanions with potassium or sodium counterions, the equilibrium of their addition to 4-chlorobenzaldehyde was strongly shifted towards the starting materials. In consequence, the J-K olefination step failed to occur at any noticeable rate. Fortunately, this problem could be averted by addition of excess of lithium salts to the reaction mixture together with aldehyde after the VNS step, specifically 3 equiv. of LiCl as a 0.5M solution in THF. Larger excess of lithium salts had little effect on the final yield of nitrostilbene. After extensive optimization of the tandem process leading from **1a**, **3** and **5a** to 4-chloro-2-[2-(4-chlorophenyl)ethenyl]nitrobenzene (**6aa**)[7a] it was found that the optimal conditions were the following: **1a** (0.5 mmol) and **3** (0.65 mmol) in DMF were added to KHMDS (1.15 mmol, 1M in THF) at -30 °C, then after 40 min the reaction mixture (deep violet owing to the presence of carbanions **2**) was cooled to -60 °C and aldehyde (1.5 mmol) and LiCl (1.5 mmol, 3 mL of 0.5M THF solution) were slowly added. The reaction mixture was then allowed to reach slowly the room temperature. Under these conditions, nitrostilbene **6aa** could be obtained in 65%, as *E* isomer exclusively. With respect to the conditions established for the VNS reaction alone, excess of **3** and of KHMDS had to be diminished slightly to inhibit formation of side products that result from the J-K reaction between aldehyde and sulfone **3**, leading to chlorostilbenes.[15]

The highest yield of the alkenylation product **6aa** obtained after optimization was still rather moderate, but it has to be noted that both stages of the reactions are in fact multistep processes.

A two-step alkenylation reaction in the absence of any metal cations but using DBU as base instead, provided no products of reaction between **1b**, **3** and **5a**. Concerning other sulfones typically used in the J-K olefination processes, 2-pyrimidynyl or phenyltetrazolyl chloromethyl sulfones gave poor results already at the VNS step (low conversion and formation of unidentified numerous side products). Another approach to VNS-based alkenylation of arenes has also been attempted which was based upon an innovative sulfone-based olefination protocol developed recently by the Barbasiewicz group.[16] Unlike the J-K and similar olefination reactions, this reaction is based upon addition of deprotonated sulfonyl esters to carbonyl compounds, followed by sulfaoxetane formation in a manner resembling the mechanism of the Wittig reaction. A VNS reaction between *o*-chloronitrobenzene and appropriate sulfonyl ester (2,2,2-trifluoroethyl chloromethanesulfonate) could be achieved but, unfortunately, the intermediate nitrobenzylsulfonyl anion failed to

react further with aldehydes even in the presence of lithium salts, probably due to its low nucleophilicity.

The crucial role of Li^+ cations for the one-pot alkenylation protocol can be probably explained by their coordination to the intermediate carbanions of the type **2** (EWG = $BTSO_2$) and exchange of K^+ counterions, accompanied by Lewis-acidic activation of the aldehyde carbonyl group and facilitating the nucleophilic addition step. Moreover, the Li^+ cation probably stabilizes the aldol adduct and thus enables the BT moiety transfer and further elimination. The whole one-pot protocol cannot be simplified by using a lithium base at the VNS step since lithiated carbanions of sulfones fail to attack nitroarene rings.



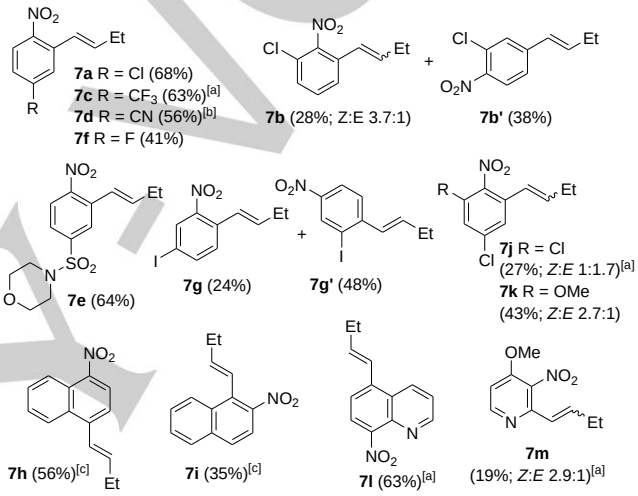
Scheme 2. Synthesis of nitrostilbenes in a one-pot VNS-J-K olefination reaction. (i) 1) KHMDS, 2) aldehyde **5a-d**, LiCl

The optimized synthetic procedure has been next applied to the synthesis of nitrostilbenes. As demonstrated by the examples shown in Scheme 2, the reaction proceeds with both electron-poor and electron-rich benzaldehydes: 4-methoxy (**5b**), 2,3-difluoro (**5c**) and 4-trifluoromethyl (**5d**). The yield of the reaction with **5b** was lower, though, probably due to its lower electrophilicity resulting in less efficient reaction with the nitrobenzylic carbanions **2**. 2-Chloronitrobenzene, which displays two non-equivalent positions activated by the nitro group, gave two isomeric products **6ba**, **6ba'** in nearly equal amounts.

Interestingly, the alkenylation process turned out to be efficient also with aliphatic, enolizable aldehydes, which generally tend to be problematic in reactions performed under basic conditions. Under the same conditions as those established above for aromatic aldehydes, propionaldehyde provided a series of ethylvinyl derivatives of various nitroarenes in moderate or good yields (Scheme 3). These reactions were also much cleaner than those of benzaldehydes. Only traces of side products formed in Knoevenagel-like condensation of propanal with sulfone **3** were detected in some cases, whereas excess of propanal and its J-K olefination product (1-chlorobutene) were easily removed during evaporation. Nitroarenes with *para* position blocked with substituents such as Cl, afforded products of *ortho* substitution exclusively in *E* configuration, in moderate to good yields. No *Z* isomers could be detected by ^1H NMR of crude reaction mixtures nor by TLC analysis. Efficient substitution *ortho* to the NO_2 group indicates that the sterical requirements of carbanion $\mathbf{3}^-$ are moderate, unlike some other nucleophiles employed in one-pot processes involving VNS, for example $PhCCl_2^-$.[9b] A serious limitation of those processes was inability to achieve efficient substitution *ortho* to the nitro group.

Nitroarenes with more than one C–H position activated for nucleophilic attack give mixtures of regioisomers. For example, 3-iodonitrobenzene reacted at the *para* and the less hindered *ortho* position, in both cases with complete *E* selectivity.

Interestingly, with nitroarenes substituted *ortho* to NO_2 with Cl or OMe the reaction proceeded with lower *E/Z* selectivity, usually with marked preference for *Z* isomers (**7b**, **7k**, **7m**). Moreover, this effect occurred only for alkenylation *ortho* to the nitro group, as product **7b'** was obtained as *E* isomer only (Scheme 3, top).



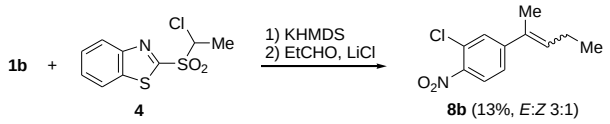
Scheme 3. Alkenylation of nitroarenes and nitroheterocycles. [a] VNS time: 15 min. [b] VNS time: 5 min. [c] VNS time: 10 min.

The yields of alkenylation obtained for some strongly electrophilic arenes are moderate (**7d**, **j**, **h**, **m**), although such substrates should be excellent partners for nucleophilic attack. It seems that high electrophilicity of the aromatic ring associated with good delocalisation of negative charge results in low nucleophilicity of the intermediate benzotriazolylsulfonyl nitrobenzyl anions **2**, which results in less efficient addition to aldehyde and overall lower yield of the two-step process. For these reasons alkenylation of 3-nitropyridine or nitropyrrole and nitrothiazole derivatives failed altogether, although nucleophilic addition of $\mathbf{3}^-$ evidently proceeded well, as evidenced by strong coloration of the reaction mixtures. On the other hand, a minimum electrophilic character of the starting arene is required, as nitroanisoles fail to react with $\mathbf{3}^-$ carbanion. The presence of additional weakly activating substituents such as Cl is already sufficient for the VNS of *o*-nitroanisole to proceed (**7k** formed in 43% yield).

Generally, nucleophilic attack is strongly preferred at ring positions activated by NO_2 and occupied by hydrogen atoms.[5] Accordingly, alkenylation of 4-fluoronitrobenzene proceeded selectively *ortho* to the nitro group to give nitrostyrene **7f**. On the other hand, with increasing electrophility of the ring classical

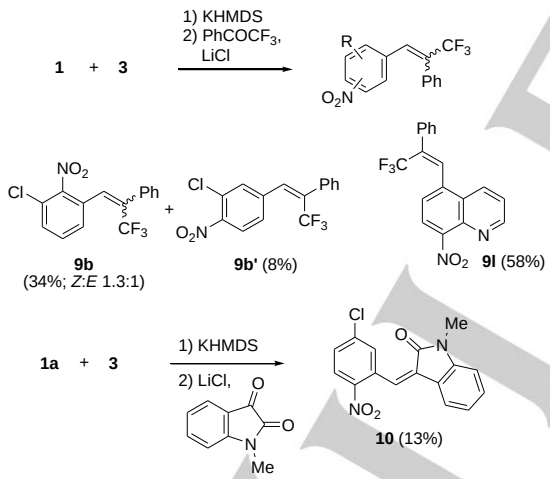
S_NAr substitution of fluorine becomes predominant as observed in the reaction of ethyl 4-fluoro-3-nitrobenzoate, which resulted in an inseparable mixture of product of H and F substitution in very low yield.

A benzothiazolyl sulfone bearing a branched chloroalkyl chain should in principle provide nitroaryl alkenes with higher degree of substitution at the double bond. Indeed, the reaction of sulfone **4** with **1b** and propanal gave alkenes *E,Z*-**8b**, but in low yield probably due to higher steric hindrance as compared to the standard reagent **3** (Scheme 4).



Scheme 4. Synthesis of a trisubstituted alkene from sulfone **4**

Simple enolizable ketones such as acetone fail to give alkenylation products, obviously due to concurrent enolisation and lower electrophilic character compared to aldehydes. However, more electrophilic trifluoromethyl phenyl ketone turned out to be a viable substrate, providing a method of synthesis of trifluoromethylvinyl-substituted nitroarenes.[17] Another electrophilic ketone capable of reacting with nitrobenzylic anions **2** was *N*-methylisatin which yielded the expected alkene **10** as a single stereoisomer, but in low yield (Scheme 5).



Scheme 5. Synthesis of trisubstituted alkenes from ketones

From the examples of olefination with both aldehydes and ketones described above it is evident that loss of stereoselectivity in the newly formed double bond occurs only when the nitro group becomes flanked by two substituents at its ortho, ortho' positions (**7b**, **7j**, **7k**, **7m**, **9b**), with one exception of stilbene **6ba**. An extensive computational study is probably necessary to explain this phenomenon, but it is reasonable to assume that it may result from a significant deviation of the NO_2 group from the plane of the aromatic ring in aldol-type adducts formed from nitrobenzylic carbanions **2** and carbonyl compounds. If one of the NO_2 oxygen atoms participates in coordination of Li^+ cation together with the anionic aldol oxygen, than the abovementioned deviation from planarity can certainly influence the energy of diastereoselective aldol adducts and/or of the transition states that lead to them. That in turn affects the ratio of *Z* and *E* isomers of the final alkene.

Conclusions

A one-pot VNS – Julia-Kocienski reaction sequence has been developed that allows for direct substitution of hydrogen of an electron-deficient aromatic ring with an alkenyl group, often with high *E* selectivity. Importantly, although the reaction involves basic conditions, it tolerates simple, enolizable aliphatic aldehydes that lead to alkylvinyl products. Ketones are generally poor substrates, but trifluoromethylketones provide trifluoromethylalkenes efficiently. Both homo- and heterocyclic aromatic nitro compounds can be thus transformed selectively into nitrostyrenes containing alkyl, aryl and trifluoromethyl substituents. The success of this two-step transformation depends upon meeting the specific requirements of the both reactions regarding the kind of metal cations present in the reaction mixture.

Experimental Section

Compound 3a: In a flame-dried Schlenk flask filled with argon a 1M THF solution of KHMDS (1.4 mmol, 1.4 mL) was placed and cooled to -30 °C. A solution of nitroarene (0.5 mmol) and sulfone **3** (0.75 mmol, 186 mg) in DMF (1.4 mL) was added dropwise with vigorous stirring. The stirring continued at -30 °C for 45 min and 2M $HCl_{(aq)}$ (0.75 mL) was then added, followed by brine (5 mL), water (2 mL) and Et_2O (5 mL). The mixture was then separated between Et_2O (25 mL) and brine (50 mL), the organic phase was washed with brine (3 x 40 mL), dried over anhydrous Na_2SO_4 and concentrated. Purification by column chromatography on silica gel using hexanes–AcOEt 2:1 gave **3a** as yellow solid in 152 mg (82%) yield. Crystallisation from heptane–CH_2Cl_2 gave yellow crystals. M.p. 146–148 °C . ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.35 (s, 2H, CH_2), 7.52 (m, 2H, H_{arom}), 7.62 (t, $^3J_{H,H}$ = 7.14 Hz, 1H, H_{arom}), 7.67 (t, $^3J_{H,H}$ = 7.14 Hz, 1H, H_{arom}), 8.00 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}), 8.03 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}), 8.22 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.8, 122.3, 123.8, 125.6, 127.2, 127.9, 128.4, 130.6, 134.3, 136.8, 139.9, 147.7, 152.4, 164.5 ppm. HRMS (ESI+) calcd for $C_{14}H_{10}ClN_2O_4S_2$ ($[M+H]^+$), 368.9771; found, 368.9775.

General procedure for alkenylation of nitroarenes. In a flame-dried Schlenk flask filled with argon a 1M THF solution of KHMDS (1.15 mmol, 1.15 mL) was placed and cooled to -30 °C. A solution of nitroarene (0.5 mmol) and sulfone **3** (0.65 mmol, 161 mg) in DMF (1.15 mL) was added dropwise with vigorous stirring. The stirring continued at -30 °C for 40 min (or, for some substrates, shorter time period indicated in Scheme 3). The reaction mixture was then cooled to -60 °C and benzaldehyde derivative (1.5 mmol), ketone (1.5 mmol) or propanal (2.0 mmol, 116 mg, 144 μL) was added dropwise, followed by LiCl (1.5 mmol, 3.0 mL of 0.5M

THF solution). The reaction was allowed to warm to RT and stirred for another 20 h. 2M $HCl_{(aq)}$ (0.75 mL) was then added, followed by brine (5 mL), water (2 mL) and Et_2O (5 mL). For amine products (**7m, 7n**), the water phase was neutralized at this point by dilution with saturated aqueous Na_2CO_3 (2 mL) and addition of solid Na_2CO_3. The mixture was then separated between Et_2O (25 mL) and brine (50 mL), the organic phase was washed with brine (3 x 40 mL), dried over anhydrous Na_2SO_4 and concentrated. The products were purified by column chromatography on silica gel using hexanes, hexanes–CH_2Cl_2 5:1 or hexanes–Et_2O 10:1 as eluent.

***(E)*-4-Chloro-2-[2-(4-chlorophenyl)ethenyl]nitrobenzene (6aa):**[7a] 96 mg (65%) yield, yellow crystals (heptane–CH_2Cl_2). M.p. 105–107 °C . ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, vinyl CH), 7.37 (m, 3H, H_{arom}), 7.47 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H_{arom}), 7.56 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, vinyl CH), 7.71 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}) ppm.

***(E)*-4-Chloro-2-[2-(4-methoxyphenyl)ethenyl]nitrobenzene (6ab):** 30 mg (21%) yield, yellow crystals (heptane–CH_2Cl_2). M.p. 78–79 °C. IR (KBr): ν_{max} = 3062, 2957, 2932, 2835, 1596, 1508, 1459, 1342, 1298, 1251, 1173, 1025, 921, 811 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 6.92 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, H_{arom}), 7.06 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, vinyl CH), 7.31 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.47 (m, vinyl CH, 3H, H_{arom}), 7.72 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.92 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 114.3, 120.0, 126.4, 127.4, 127.6, 128.7, 128.9, 134.8, 135.2, 139.4, 145.9, 160.4 ppm. MS (EI): *m/z* (%) = 289 (M^+, 56), 272 (54), 244 (39), 199 (32), 165 (58), 153 (63), 135 (100), 121 (77). HRMS (EI) calcd for $C_{15}H_{12}ClNO_3$ (M^+), 289.0506; found, 289.0492.

***(E)*-4-Chloro-2-[2-(2,3-difluorophenyl)ethenyl]nitrobenzene (6ac):** 100 mg (68%) yield, pale yellow crystals, (heptane–CH_2Cl_2). M.p. 116–118 °C. IR (KBr): ν_{max} = 3077, 1921, 1594, 1563, 1509, 1481, 1335, 1285, 1252, 1197, 1068, 983, 921, 848, 780, 715 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (m, 2H, H_{arom}), 7.19 (d, $^3J_{H,H}$ = 16.2 Hz, 1H, vinyl CH), 7.37 (m, 1H, H_{arom}), 7.40 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.66 (d, $^3J_{H,H}$ = 16.2 Hz, 1H, vinyl CH), 7.72 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.96 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 117.0, 117.3, 122.2 (m), 124.2 (dd, $J_{C,F}$ = 6.9 Hz, 4.6 Hz), 125.9 (m), 126.2 (m), 126.4, 128.3, 128.5, 134.5, 139.8, 146.0, 148.6 (dd, $^1J_{C,F}$ = 252.5 Hz, $^2J_{C,F}$ = 13.4 Hz), 150.9 (dd, $^1J_{C,F}$ = 248.0 Hz, $^2J_{C,F}$ = 12.6 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -142.66 (1F, dm, $^3J_{F,F}$ = 20.2 Hz), -137.90 (1F, dm, $^3J_{F,F}$ = 19.4 Hz) ppm. MS (EI): *m/z* (%) = 295 (M^+, 26), 278 (44), 250 (30), 212 (48), 201 (47), 153 (100), 141 (69), 127 (89). HRMS (EI) calcd for $C_{14}H_8F_2ClNO_2$ (M^+), 295.0212; found, 295.0206.

***(E)*-4-Chloro-2-[2-(4-trifluoromethylphenyl)ethenyl]nitrobenzene (6ad):** 96 mg (59%) yield, pale yellow crystals, (heptane–CH_2Cl_2). M.p. 139–140 °C. IR (KBr): ν_{max} = 3079, 1563, 1519, 1328, 1159, 1113, 1068, 966, 864, 817 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, vinyl CH), 7.40 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.65 (m, vinyl CH, 5H, H_{arom}), 7.72 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.98 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.0 (q, $^1J_{C,F}$ = 272.1 Hz), 125.2, 125.8 (q, $^3J_{C,F}$ = 3.8 Hz), 126.5, 127.3, 128.2, 128.5, 130.6 (q, $^2J_{C,F}$ = 32.4 Hz), 133.3, 134.4, 139.4, 139.8, 146.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.68 (s, CF_3) ppm. MS (EI): *m/z* (%) = 327 (M^+, 18), 310 (47), 282 (30), 246 (22), 225 (24), 176 (46), 173 (51), 159 (52), 153 (100), 125 (81). HRMS (EI) calcd for $C_{15}H_9F_3ClNO_2$ (M^+), 327.0274; found, 327.0262.

***(E)*-2-Chloro-6-[2-(4-chlorophenyl)ethenyl]nitrobenzene (6ba):** 50 mg (34%) yield, colourless crystals (heptane–CH_2Cl_2). M.p. 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, vinyl CH), 7.12 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, vinyl CH), 7.34 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H_{arom}), 7.41 (m, 4H, H_{arom}), 7.65 (m, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.2, 124.7, 125.4, 128.3, 129.1, 129.2, 130.7, 131.2, 133.9, 134.2, 134.9, 148.4 ppm.

***(E)*-2-Chloro-4-[2-(4-chlorophenyl)ethenyl]nitrobenzene (6ba'):** 49 mg (32%) yield, yellow crystals (heptane–CH_2Cl_2). M.p. 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (d, $^3J_{H,H}$ = 16.3 Hz, 1H, vinyl CH), 7.17 (d, $^3J_{H,H}$ = 16.3 Hz, 1H, vinyl CH), 7.37 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, H_{arom}), 7.47 (m, 3H, H_{arom}), 7.63 (s, 1H, H_{arom}), 7.93 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.0, 125.6, 126.4, 128.0, 128.2, 129.2, 129.4, 132.7, 134.4, 134.8, 142.7, 146.1 ppm. MS (EI): *m/z* (%) = 293 (M^+, 100), 263 (25), 212 (83), 176 (73), 165 (41). HRMS (EI) calcd for $C_{14}H_9Cl_2NO_2$ (M^+), 293.0010; found, 293.0009.

***(E)*-2-(But-1-enyl)-4-chloronitrobenzene (7a):** 72 mg (68%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3099, 2968, 2932, 2875, 1600, 1563, 1522, 1461, 1343, 964, 909, 841 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.28 (m, 2H, CH_2), 6.29 (dt, $^3J_{H,H}$ = 15.6 Hz, 6.5 Hz, 1H, vinyl CH), 6.82 (d, $^3J_{H,H}$ = 15.7 Hz, 1H, vinyl CH), 7.27 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.54 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{arom}), 7.83 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 26.2, 123.2, 125.9, 127.3, 128.2, 135.3, 139.1, 139.7, 145.8 ppm. MS (EI): *m/z* (%) = 211 (M^+, 10), 194 (23), 182 (15), 166 (35), 154 (43), 138 (25), 126 (63), 115 (52), 99 (38), 75 (50), 57 (100). HRMS (EI) calcd for $C_{10}H_{10}ClNO_2$ (M^+), 211.0400; found, 211.0402. Anal. calcd for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76; N, 6.62; Cl, 16.75. Found: C, 56.97; H, 4.70; N, 6.53; Cl, 16.55.

***(E,Z)*-2-(But-1-enyl)-6-chloronitrobenzene (7b):** 30 mg (28%) yield, *Z*:*E* 3.7:1; pale yellow oil. IR (CH_2Cl_2): ν_{max} = 2969, 2876, 1538, 1461, 1367, 1187, 851, 790, 715 cm^{-1}. *Z*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.13 (m, 2H, CH_2), 5.88 (dt, $^3J_{H,H}$ = 11.4 Hz, 7.5 Hz, 1H, vinyl CH), 6.22 (m, 1H, vinyl CH), 7.24 (m, 1H, H_{arom}), 7.37 (m, 2H, H_{arom}) ppm. *E*:^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.24 (m, 2H, CH_2), 6.22 (m, 1H, vinyl CH), 6.38 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.4 Hz, 1H, vinyl CH), 7.33 (m, 2H, H_{arom}), 7.47 (m, 1H, H_{arom}) ppm. *E,Z*: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 13.9, 22.1, 26.2, 120.5, 120.7, 124.8, 124.9, 124.9, 127.9, 128.3, 128.7, 128.8, 130.2, 130.5, 131.8, 132.0, 140.0, 140.3. MS (EI): *m/z* (%) = 211 (M^+, 2), 194 (27), 179 (12), 166 (41), 154 (63), 125 (73), 115 (61), 90 (75), 75 (64), 57 (100). HRMS (EI) calcd for $C_{10}H_{10}ClNO_2$ (M^+), 211.0400; found, 211.0397.

***(E)*-4-(But-1-enyl)-2-chloronitrobenzene (7b'):** 40 mg (38%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 2968, 2933, 2875, 1650, 1590, 1523, 1345, 1046, 966, 837 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.28 (m, 2H, CH_2), 6.34 (d, $^3J_{H,H}$ = 15.9 Hz, 1H, vinyl CH), 6.46 (dt, $^3J_{H,H}$ = 15.8 Hz, 6.3 Hz, 1H, vinyl CH), 7.31 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 7.47 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 7.86 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 26.2, 124.5, 126.0, 126.2, 127.7, 128.9, 138.8, 143.7, 145.6 ppm.

***(E)*-2-(But-1-enyl)-1-nitro-4-trifluoromethylbenzene (7c):** 77 mg (63%) yield, colourless oil. IR (film): ν_{max} = 2971, 2878, 1532, 1328, 1176, 1137, 1096, 965, 916, 843 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.32 (m, 2H, CH_2), 6.39 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.5 Hz, 1H, vinyl CH), 6.80 (dt, $^3J_{H,H}$ = 15.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, vinyl CH), 7.58 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 1.7 Hz, 1H, H_{arom}), 7.84 (d, $^4J_{H,H}$ = 1.1 Hz, 1H, H_{arom}), 7.93 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 26.3, 122.6, 123.0 (q, $^1J_{C,F}$ = 272.8 Hz), 124.1 (q, $^3J_{C,F}$ = 3.5 Hz), 124.9, 125.5 (q, $^3J_{C,F}$ = 3.6 Hz), 133.9, 134.3 (q, $^2J_{C,F}$ = 33.3 Hz), 140.5, 149.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.26 (s, CF_3) ppm. MS (EI): *m/z* (%) = 245 (M^+, 3), 228 (13), 200 (22), 188 (30), 160

(40), 57 (100). HRMS (EI) calcd for $C_{11}H_{10}F_3NO_2$ (M^+), 245.0664; found, 245.0664.

***(E)*-2-(But-1-enyl)-4-cyanonitrobenzene (7d):** 57 mg (56%) yield, white needles (heptane–CH_2Cl_2). M.p. 86–88 °C. IR (KBr): ν_{max} = 3077, 2970, 2882, 2231, 1649, 1573, 1518, 1362, 1267, 962, 901, 830, 736, 611 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.31 (m, 2H, CH_2), 6.38 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.5 Hz, 1H, vinyl CH), 6.74 (d, $^3J_{H,H}$ = 15.7 Hz, 1H, vinyl CH), 7.61 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 1H, H_{arom}), 7.89 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, H_{arom}), 7.91 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 26.3, 116.6, 116.9, 121.9, 125.1, 130.4, 132.4, 134.3, 141.3, 149.6 ppm. MS (EI): *m/z* (%) = 202 (M^+, 6), 185 (17), 157 (47), 145 (46), 117 (74), 57 (100). HRMS (EI) calcd for $C_{11}H_{10}N_2O_2$ (M^+), 202.0742; found, 202.0736. Anal. calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.23; H, 5.05; N, 13.69.

Sulfonamide 7e: 104 mg (64%) yield, pale yellow crystals (heptane–CH_2Cl_2). M.p. 107–108 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.14 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.33 (m, 2H, CH_2), 3.07 (m, 4H, NCH_2), 3.77 (m, 4H, OCH_2), 6.43 (dt, $^3J_{H,H}$ = 15.8 Hz, 6.4 Hz, 1H, vinyl CH), 6.78 (d, $^3J_{H,H}$ = 15.5 Hz, 1H, vinyl CH), 7.69 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.95 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 7.97 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.9, 26.3, 45.9, 66.0, 122.2, 125.2, 126.1, 127.6, 134.3, 139.3, 141.2, 149.8 ppm. MS (EI): *m/z* (%) = 151 (100), 123 (58), 96 (60).

***(E)*-2-(But-1-enyl)-4-fluoronitrobenzene (7f):** 40 mg (41%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3083, 2969, 2876, 1617, 1580, 1524, 1471, 1347, 1273, 1219, 1075, 964, 877, 843, 752, 607 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, 7.5 Hz, 3H, CH_3), 2.30 (m, 2H, CH_2), 6.29 (dt, 15.6 Hz, 6.5 Hz, 1H, vinyl CH), 6.88 (dm, 15.6 Hz, 1H, vinyl CH), 7.01 (ddd, $^3J_{H,H}$ = 9.2 Hz, $^3J_{H,F}$ = 7.3 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, H_{arom}), 7.25 ($^3J_{H,F}$ = 9.6 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H, H_{arom}), 7.96 (dd, $^3J_{H,H}$ = 9.1 Hz, $^4J_{H,F}$ = 5.2 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 26.2, 114.4 (d, $^2J_{C,F}$ = 23.7 Hz), 114.8 (d, $^2J_{C,F}$ = 24.1 Hz), 123.6, 127.3 (d, $^3J_{C,F}$ = 9.9 Hz), 136.9 (d, $^3J_{C,F}$ = 9.5 Hz), 139.6, 164.6 (d, $^1J_{C,F}$ = 255.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -104.75 (m) ppm. MS (EI): *m/z* (%) = 195 (M^+, 9) 178 (14), 150 (25), 138 (27), 133 (30), 109 (40), 83 (35), 75 (36), 57 (100). HRMS (EI) calcd for $C_{10}H_{10}FNO_2$ (M^+), 195.0696; found, 195.0698.

***(E)*-2-(But-1-enyl)-5-iodonitrobenzene (7g):** 36 mg (24%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 2965, 1642, 1523, 1465, 1345, 1269, 10176, 965, 872, 847, 818, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.27 (m, 2H, CH_2), 6.30 (dt, $^3J_{H,H}$ = 15.6 Hz, 6.5 Hz, 1H, vinyl CH), 6.75 (d, $^3J_{H,H}$ = 15.6 Hz, 1H, vinyl CH), 7.31 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}), 7.81 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.7 Hz, 1H, H_{arom}), 8.17 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 26.3, 90.4, 123.2, 129.7, 132.8, 132.9, 139.1, 141.6, 147.9 ppm. MS (EI): *m/z* (%) = 303 (M^+, 18), 246 (44), 218 (28), 159 (37), 131 (49), 115 (49), 91 (37), 57 (100). HRMS (EI) calcd for $C_{10}H_{10}INO_2$ (M^+), 302.9756; found, 302.9756.

***(E)*-4-(But-1-enyl)-3-iodonitrobenzene (7g'):** 72 mg (48%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3092, 2965, 1641, 1575, 1515, 1459, 1342, 1113, 963, 736 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.33 (m, 2H, CH_2), 6.36 (dt, $^3J_{H,H}$ = 15.6 Hz, 6.5 Hz, 1H, vinyl CH), 6.61 (d, $^3J_{H,H}$ = 15.6 Hz, 1H, vinyl CH), 7.55 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}), 8.13 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.3 Hz, 1H, H_{arom}), 8.66 (d, $^4J_{H,H}$ = 2.4 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 26.3, 97.8, 123.2, 126.0, 131.4, 134.5, 140.5, 146.4, 147.3 ppm. Anal. calcd for $C_{10}H_{10}INO_2$: C, 39.63; H, 3.33; N, 4.62. Found: C, 39.45; H, 3.39; N, 4.64.

***(E)*-4-(But-1-enyl)-1-nitronaphthalene (7h):** 64 mg (56%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3064, 2965, 2874, 1648, 1524, 1459, 1362, 960, 865, 813, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.30 (m, 2H, CH_2), 6.47 (d, $^3J_{H,H}$ = 15.9 Hz, 1H, vinyl CH), 6.53 (dt, $^3J_{H,H}$ = 15.8 Hz, 5.4 Hz, 1H, vinyl CH), 7.51 (m, 1H, H_{arom}), 7.58 (m, 1H, H_{arom}), 7.67 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, H_{arom}), 7.84 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 26.5, 121.6, 121.7, 122.9, 124.7, 126.9, 126.9, 127.9, 128.6, 130.2, 132.6, 139.5, 146.0 ppm. MS (EI): *m/z* (%) = 227 (M^+, 36), 210 (78), 182 (44), 170 (100), 165 (81), 141 (83), 127 (67), 115 (86), 57 (71). HRMS (EI) calcd for $C_{14}H_{13}NO_2$ (M^+), 227.0946; found, 227.0947. Anal. calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.74; H, 5.71; N, 6.13.

***(E)*-1-(But-1-enyl)-2-nitronaphthalene (7i):** 40 mg (35%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 2965, 2930, 2873, 1587, 1524, 1345, 967, 819, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.37 (m, 2H, CH_2), 5.91 (dt, $^3J_{H,H}$ = 16.1 Hz, 6.4 Hz, 1H, vinyl CH), 6.86 (dt, $^3J_{H,H}$ = 16.1 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, vinyl CH), 7.61 (m, 2H, H_{arom}), 7.81 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H_{arom}), 7.84 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H_{arom}), 7.89 (m, 1H, H_{arom}), 8.27 (m, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 26.4, 120.0, 121.4, 127.4, 127.8, 128.0, 128.2, 128.4, 132.0, 132.4, 134.8, 140.8, 146.2 ppm. MS (EI): *m/z* (%) = 227 (M^+, 53), 210 (70), 198 (45), 170 (100), 143 (70), 115 (100), 57 (76). HRMS (EI) calcd for $C_{14}H_{13}NO_2$ (M^+), 227.0946; found, 227.0941.

***(E,Z)*-1-(But-1-enyl)-3,5-dichloro-2-nitrobenzene (7j):** 34 mg (27%) yield. pale yellow oil, *Z*:*E* 1:1.7. IR (CH_2Cl_2): ν_{max} = 3078, 2969, 2934, 2875, 1540, 1363, 1135, 962, 861 cm^{-1}. *Z:* ^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.14 (m, 2H, CH_2), 5.92 (dt, $^3J_{H,H}$ = 11.5 Hz, 7.5 Hz, 1H, vinyl CH), 6.17 (m, 1H, vinyl CH), 7.22 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.40 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}) ppm. *E:* ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.25 (m, 2H, CH_2), 6.17 (m, 1H, vinyl CH), 6.40 (dt, $^3J_{H,H}$ = 15.6 Hz, 6.5 Hz, 1H, vinyl CH), 7.33 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.45 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}) ppm. *Z*, *E*: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 13.8, 22.1, 26.3, 119.7, 119.9, 125.0, 126.06, 126.07, 128.0, 128.5, 128.8, 133.1, 133.2, 135.9, 136.2, 141.3, 141.4 ppm. MS (EI): *m/z* (%) = 245 (M^+, 3), 228 (17), 200 (30), 188 (44), 159 (72), 124 (56), 57 (100). HRMS (EI) calcd for $C_{10}H_9Cl_2NO_2$ (M^+), 245.0010; found, 245.0018.

***(E)*-2-(But-1-enyl)-4-chloro-6-methoxynitrobenzene (7k):** 52 mg (43%) yield, pale yellow oil, *Z*:*E* 2.7:1. IR (CH_2Cl_2): ν_{max} = 2970, 2876, 1599, 1571, 1534, 1459, 1416, 1369, 1301, 1074, 891, 834 cm^{-1}. *Z:* ^1H NMR (400 MHz, $CDCl_3$): δ = 1.0 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.14 (m, 2H, CH_2), 3.88 (s, 3H, OMe), 5.85 (dt, $^3J_{H,H}$ = 11.4 Hz, 7.5 Hz, 1H, vinyl CH), 6.18 (m, 1H, vinyl CH), 6.87 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 6.91 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, H_{arom}) ppm. *E:* ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.23 (m, 2H, CH_2), 3.87 (s, 3H, OMe), 6.18 (m, 1H, vinyl CH), 6.37 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.5 Hz, 1H, vinyl CH), 6.84 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, H_{arom}), 7.11 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 13.9, 22.1, 26.2, 56.7, 111.0, 111.5, 117.9, 120.1, 120.2, 121.6, 132.4, 132.4, 136.1, 136.4, 138.6, 139.5, 140.2, 140.3, 151.4, 151.4 ppm. MS (EI): *m/z* (%) = 241 (M^+, 12), 224 (45), 196 (45), 184 (40), 161 (71), 140 (79), 127 (77), 115 (85), 102 (54), 75 (67), 57 (100). HRMS (EI) calcd for $C_{11}H_{12}ClNO_3$ (M^+), 241.0506; found, 241.0511. Anal. calcd for $C_{11}H_{12}ClNO_3$: C, 54.67; H, 5.00; N, 5.80; Cl, 14.76. Found: C, 54.62; H, 5.01; N, 5.78; Cl, 14.80.

***(E)*-5-(But-1-enyl)-8-nitroquinoline (7l):** 72 mg (63%) yield, pink crystals (heptane–CH_2Cl_2). M.p. 121–123 °C. IR (KBr): ν_{max} = 2976, 2915, 1649, 1529, 1379, 959, 874, 830, 797, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.29 (m, 2H, CH_2), 6.44 (d, $^3J_{H,H}$ = 15.8 Hz, 1H, vinyl CH), 6.37 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.5 Hz, 1H, vinyl CH), 6.58 (dt, $^3J_{H,H}$ = 15.7 Hz, 6.4 Hz, 1H, vinyl CH), 7.41 (dd, $^3J_{H,H}$ = 8.3

Hz, 4.3 Hz, 1H, H_{arom}), 7.70 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, H_{arom}), 7.79 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H_{arom}), 8.11 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, H_{arom}), 8.89 (dd, $^3J_{H,H}$ = 4.2 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 26.5, 121.0, 122.2, 123.5, 127.3, 129.1, 129.4, 135.5, 139.9,140.8, 146.1, 152.2 ppm. MS (EI): *m/z* (%) = 228 (M^+, 11), 211 (45), 199 (41), 183 (33), 171 (100), 154 (32), 142 (64), 128 (43), 116 (49), 57 (29). HRMS (EI) calcd for $C_{13}H_{12}N_2O_2$ (M^+), 228.0899; found, 228.0892. Anal. calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.27; H, 5.23; N, 12.04.

***(E,Z)*-2-(But-1-enyl)-4-methoxy-3-nitropyridine (7m):** 20 mg (19%) yield, pale yellow oil, *Z*:*E* 2.9:1. IR (CH_2Cl_2): ν_{max} = 2966, 2935, 2875, 1703, 1645, 1589, 1532, 1469, 1367, 1304, 1065, 854, 819 cm^{-1}. *Z*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.56 (m, 2H, CH_2), 3.94 (s, 3H, OCH_3), 6.03 (dt, $^3J_{H,H}$ = 11.7 Hz, 7.4 Hz, 1H, vinyl CH), 6.24 (dt, $^3J_{H,H}$ = 11.7 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, vinyl CH), 6.84 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, H_{arom}), 8.53 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.6, 56.4, 105.6, 119.7, 123.2, 144.5, 149.3, 151.2, 156.9 ppm. *E*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 2.29 (m, 2H, CH_2), 3.94 (s, 3H, OCH_3), 6.32 (dt, $^3J_{H,H}$ = 15.2 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, vinyl CH), 6.79 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, H_{arom}), 7.14 (dt, $^3J_{H,H}$ = 15.1 Hz, 6.7 Hz, 1H, vinyl CH), 8.46 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 26.0, 56.5, 105.5, 120.6, 126.4, 143.8, 148.0, 151.5, 159.6 ppm.

***(E,Z)*-2-(3-Chloro-4-nitrophenyl)-2-pentene (8b):** 15 mg (13%), pale yellow oil, *E*:*Z* = 3:1. IR (CH_2Cl_2): ν_{max} = 2967, 2873, 1587, 1523, 1345, 1045, 859, 835 cm^{-1}. *E:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 2.02 (d, $^4J_{H,H}$ = 1.1 Hz, 3H, CH_3), 2.24 (m, 2H, CH_2), 5.94 (tq, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H, vinyl CH), 7.36 (dd, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.50 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, H_{arom}), 7.86 (d, $^3J_{H,H}$ = 8.6 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 15.2, 22.3, 124.3, 125.8, 127.3, 128.8, 131.6, 135.1, 145.6, 149.5 ppm. *Z:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, CH_3), 1.96 (m, 2H, CH_2), 2.01 (m, 3H), 5.58 (tq, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, vinyl CH), 7.19 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 7.34 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, H_{arom}), 7.87 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.5, 24.7, 125.6, 127.0, 127.2, 131.3, 132.4, 132.7, 145.1, 148.2 ppm.

***(E)*-1-(3-Chloro-2-nitrophenyl)-2-phenyl-3,3,3-trifluoropropene (*E*-9b):** 24 mg (14%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3064, 2891, 1538, 1365, 1294, 1270, 1169, 1128, 963, 850, 794, 706, 626 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, H_{arom}), 7.09 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, H_{arom}), 7.13 (d, $^4J_{H,F}$ = 1.4 Hz, 1H, vinyl CH), 7.23 (m, 2H, H_{arom}), 7.34 (m, 4H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8 (q, $^1J_{C,F}$ = 274.3 Hz), 125.5, 126.0 (q, $^3J_{C,F}$ = 6.1 Hz), 128.6, 128.7, 128.9, 129.1, 129.4, 129.6, 130.4, 130.8, 136.9 (q, $^2J_{C,F}$ = 30.4 Hz), 149.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.22 (s) ppm. MS (EI): *m/z* (%) = 327 (M^+, 11), 280 (13), 245 (21), 230 (57), 213 (36), 176 (42), 153 (100), 125 (83), 105 (47). HRMS (EI) calcd for $C_{15}H_9F_3ClNO_2$ (M^+), 327.0274; found, 327.0282.

***(Z)*-1-(3-Chloro-2-nitrophenyl)-2-phenyl-3,3,3-trifluoropropene (*Z*-9b):** 32 mg (20%) yield, colourless crystals (heptane–CH_2Cl_2). M.p. 75–77 °C. IR (KBr): ν_{max} = 3100, 3060, 2925, 2859, 1968, 1896, 1576, 1524, 1347, 1268, 1161, 1116, 923, 835, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, $^3J_{H,H}$ = 8.6 Hz, 1H, H_{arom}), 7.19 (m, 2H, H_{arom}), 7.25 (m, 2H, H_{arom}), 7.43 (m, 3H, H_{arom}), 7.65 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.0 (q, $^1J_{C,F}$ = 273.9 Hz), 125.4, 127.2, 128.5, 129.3, 129.4, 129.7, 129.7 (m), 131.1, 133.0, 135.2 (q, $^2J_{C,F}$ = 30.2 Hz), 139.1, 147.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.62 (s) ppm. MS (EI): *m/z* (%) = 327 (M^+, 100), 281 (51), 246 (66), 212 (68), 176 (46), 165 (35), 105 (20). HRMS (EI) calcd for $C_{15}H_9F_3ClNO_2$ (M^+), 327.0274; found, 327.0275.

***(Z)*-1-(3-Chloro-4-nitrophenyl)-2-phenyl-3,3,3-trifluoropropene (9b'):** 13 mg (8%) yield, pale yellow oil. IR (CH_2Cl_2): ν_{max} = 3063, 2928, 2858, 1577, 1527, 1350, 1283, 1172, 1123, 964, 907, 835, 765, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 1H, vinyl CH), 7.44 (m, 6H, H_{arom}), 7.56 (s, 1H, H_{arom}), 7.92 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8 (q, $^1J_{C,F}$ = 276.0 Hz), 125.5, 127.2, 127,6 (m), 128.0, 128.7, 129.2, 131.7 (m), 134.2 (q, $^4J_{C,F}$ = 3.2 Hz), 135.7 (q, $^2J_{C,F}$ = 30.3 Hz), 140.4, 147.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = 56.46 (s) ppm. MS (EI): *m/z* (%) = 327 (M^+, 100), 280 (42), 246 (46), 212 (68), 176 (45), 165 (39). HRMS (EI) calcd for $C_{15}H_9F_3ClNO_2$ (M^+), 327.0274; found, 327.0269.

***(E)*-1-(8-Nitroquinolin-5-yl)-2-phenyl-3,3,3-trifluoropropene (9l):** 100 mg (58%) yield, pink crystals (heptane–CH_2Cl_2). M.p. 140–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.95 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, H_{arom}), 7.34 (m, 6H, vinyl CH, Ph), 7.52 (dd, $^3J_{H,H}$ = 8.4 Hz, 4.3 Hz, 1H, H_{arom}), 7.58 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H_{arom}), 8.11 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, H_{arom}), 9.00 (dd, $^3J_{H,H}$ = 4.3 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, H_{arom}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 122.9 (q, $^1J_{C,F}$ = 274.3 Hz), 123.3, 124.6 (m), 125.9 (q, $^3J_{C,F}$ = 5.7 Hz), 126.6, 126.7, 128.3, 128.9, 128.9, 129.5, 129.8, 131.0, 135.6, 137.1 (q, $^2J_{C,F}$ = 31.0 Hz), 139.3, 152.7 ppm. Anal. calcd for $C_{18}H_{11}F_3N_2O_2$: C, 62.79; H, 3.22; N, 8.14. Found: C, 62.71; H, 3.18; N, 8.33.

Alkene 10: 21 mg (13%), orange oil. IR (CH_2Cl_2): ν_{max} = 3058, 2931, 1712, 1607, 1563, 1523, 1469, 1377, 1337, 1104, 914, 749 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.28 (s, 3H), 6.84 (m, 3H), 7.28 (m, 1H), 7.60 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,H}$ = 2.3 Hz, 1H), 7.68 (d, $^4J_{H,H}$ = 2.2 Hz, 1H), 7.98 (s, 1H), 8.27 (d, $^3J_{H,H}$ = 8.9 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.2, 108.6, 120.1, 122.1, 122.6, 126.9, 129.0, 130.0, 130.7, 130.8, 131.2, 133.2, 140.4, 144.7, 145.5, 167.2 ppm.

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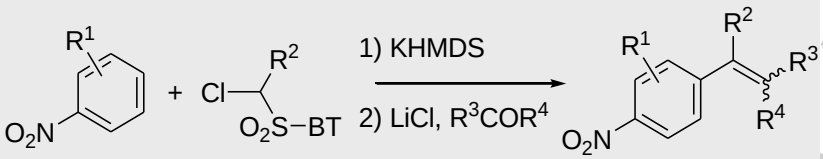

C–H Alkenylation

*Rafał Loska**

Page No. – Page No.

C–H-Alkenylation of Arenes in a One-pot VNS – Julia-Kocienski Reaction

C–H bonds in nitroarenes and heteroarenes can be efficiently functionalized with alkene moieties in a one-pot, two-step reaction sequence without the need for transition metal catalysis. The resulting two- or three-substituted double bonds are formed usually with complete *E* selectivity.