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Stereoselective Synthesis of Conjugated Alkenynes via Palladium-Catalyzed Coupling of Alkenyl Iodonium Salts with Terminal Alkynes

N. Sh. Pirguliyev [a], V. K. Brel [b*], N. S. Zefirov [a,b] and P.J. Stang [c]

[a]*Department of Chemistry, Moscow State University, Moscow 119899, Russia; FAX: +7(095) 939 0290*

[b]*Institute of Physiologically Active Compounds of Russian Academy of Sciences, 142432 Moscow Region, Chernogolovka, Russia; FAX: +7(095) 913 2113*

[c]*Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U.S.A; FAX: +1(801) 581-8433*

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Abstract: A novel method for stereospecific synthesis of conjugated alkenynes is suggested. The reaction of (E)-[β-(trifluoromethanesulfonyloxy)-1-alkenyl](phenyl) iodonium trifluoromethanesulfonate with terminal alkynes in the presence of catalytic amounts of dichloro(triphenylphosphine)palladium(II) and CuI in aqueous medium proceeds stereospecifically to give the corresponding enynes in good yields. A possible mechanism for these cross-coupling reactions is discussed.

Keywords: Alkynes, catalysis, hypervalent elements, palladium and compounds.

Introduction

The conjugated *enyne* framework, containing a di- or tri-substituted double bond,[1] is the typical structural fragment of many natural compounds, and especially pheromones.[2] There exist many synthetic approaches to this structural unit,[1,3-5] most of which include the coupling procedure of acetylenes and their derivatives with either vinyl halides[3d] or vinyl organometallic compounds, such as vinyl borates,[3a] vinyl cuprates[3b] as well as zinc,[3b] aluminium and magnesium derivatives.[3c] Although these methods have their own advantage, the scope of many of these reactions has still been limited by the nature of the organometallic involved or the procedure employed[3-5] and, hence, the development of novel (especially stereospecific) synthetic methods for enyne synthesis is of importance.

Among these procedures for conjugation of *ene* and *yne* fragments, we turned our attention to the vinyliodine(III) derivatives, stereospecific syntheses of which have been studied earlier.[6-8] Moreover, it was

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known that hypervalent iodine reagents can be used for carbon-carbon coupling.[9] Particularly, few articles have been reported regarding palladium-catalyzed reactions of alkenyliodonium salts with various compound.[8a,10-16] Moriarty and co-workers have developed a very mild and stereoselective procedure for palladium-catalyzed coupling of alkenyliodonium salts with various alkenes[10a] or alkenylstannanes.[10b] Recently, a similar procedure was employed in asymmetric Heck-type couplings of iodonium salts with 2,3-dihydrofuran.[11] Even better results are obtained in the palladium-catalyzed coupling of alkenyliodonium salts with organotin compounds.[8a,12] For example, palladium/copper-cocatalyzed coupling of the readily available trisubstituted alkenyl(phenyl)iodonium triflates with alkynyl- and alkenylstannanes proceeds under exceedingly mild conditions with retention of geometry of the alkenyl moiety of the iodonium salt.[8a] Alkenyliodonium salts can readily undergo palladium-catalyzed carbonylative coupling with terminal alkynes,[13] organofluorosilanes[14] and siloxy compouds[15] under extremely mild and aqueous conditions including short reaction times, ambient temperatures, and one atmosphere pressure of carbon monoxide. The palladium-[16a] and polymer-bound palladium-catalyzed[16b] cross-coupling reactions of allylic alcohols and organoboron compounds[16c] with alkenyliodonium salts to form carbon-carbon bonds was achieved at room temperature under extremely mild and aqueous conditions.

However extension of these reaction, to (E)-[β-((trifluoromethanesulfonyl)oxy)-1-alkenyl](phenyl)iodonium trifluoromethanesulfonates and terminal alkynes is novel and of considerable synthetic potential. Recently we synthesized the title compounds by the reaction of terminal alkynes with fluoro(phenyl)iodonium triflates, generated *in situ via* oxidation of iodobenzene with xenon fluorotriflate at –78°C in dichloromethane.[7a] Consequently, if such alkenyl iodonium salts react with alkynes or alkynylsilanes, these reactions provide direct and convenient synthetic procedures for stereodefined conjugated alkenynes. In a continuation of our investigations on (E)-[β-((trifluoromethanesulfonyl)oxy)-1-alkenyl](phenyl)iodonium trifluoromethanesulfonates (**1**), we decided to study the cross-coupling reactions of these compounds with terminal alkynes; these couplings were performed in the presence of palladium catalyst in aqueous medium.

Results and Discussion

The coupling reactions of (E)-[β-((trifluoromethanesulfonyl)oxy)-1-alkenyl](phenyl)iodonium trifluoromethanesulfonates **1a-d** with either acetylenes or alkynylsilanes were performed in the presence of $PdCl_2(PPh_3)_2$, CuI, Et_3N and K_2CO_3 in DMF:H_2O (6:1) at 30-40 °C to give high yields of enynes (see data in the **Table I**). The reactions were monitored by the disappearance of iodonium triflates by TLC, and in most cases the reactions appeared to be complete. In no case did the reactions proceed in the absence of palladium catalyst, indicating that these reactions are truly catalytic

In all cases the couplings proceed stereospecifically to give the cross-coupling products **2a-n** with E-configuration. Assignment for the compouds **2e-h** was made on the basis of the values (J = 12.8 –13.1 Hz)[17] of

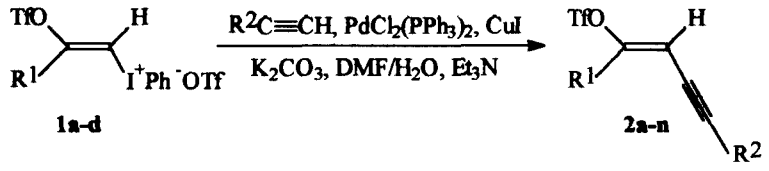

Table I. Alkenyliodonium Salt-Alkyne Palladium-Catalyzed Coupling: K_2CO_3 (2eq.), Et_3N (2eq.), CuI (3 mmol %), $PdCl_2(PPh_3)_2$ (2 mmol %), DMF : H_2O = 6:1

Entry	Alkenyl iodonium salt	R^1	R^2	Time h	Tempe-rature, °C	Product	Yield %
1	**1a**	n-Bu	n-C_8H_{17}	3	30	**2a**	77
2	**1a**	n-Bu	Ph	3	30	**2b**	78
3	**1a**	n-Bu	CH_2OMe	3	35	**2c**	72
4	**1a**	n-Bu	$SiMe_3$	3	30	**2d(R^2=H)**	70
5	**1b**	H	n-C_8H_{17}	4	40	**2e**	68
6	**1b**	H	Ph	4	40	**2f**	71
7	**1b**	H	CH_2OMe	4	40	**2g**	65
8	**1b**	H	$SiMe_3$	4	40	**2h(R^2=H)**	66
9	**1c**	CH_2OMe	n-C_8H_{17}	4	30	**2I**	68
10	**1c**	CH_2OMe	Ph	4	40	**2j**	62
11	**1c**	CH_2OMe	$SiMe_3$	4	40	**2k(R^2=H)**	65
12	**1d**	Ph	n-C_3H_7	4	30	**2l**	68
13	**1d**	Ph	CH_2Cl	4	40	**2m**	59
14	**1d**	Ph	$SiMe_3$	4	40	**2n(R^2=H)**	61

the coupling constant of the olefinic protons in the ^1H NMR spectrum and by the presence of a band at 950-980 cm^{-1} due to the out-of plane C-H bending vibration of the *trans* structure in the IR spectrum. The absorptions for the covalently bonded triflates appear near 640-650, 1210-1225, and 1415-1431 cm^{-1}. The vinyl C=C stretching mode is too weak to be observed even in neat samples due to the abundance of other absorptions.

We performed the optimization of the reaction conditions for the model reaction of **1a** with phenylacetylene. Comparison of different solvents (DMF, THF, heptane and benzene) under various conditions demonstrated that the solvent choice appears to play an important role in obtaining higher yields of the enynes: high yields were obtained only in DMF. High yields of the enyne are obtained when relatively strong bases such as diethylamine, triethylamine or tri-n-propylamine are used, whereas more hindered base tri-n-butylamine is not effective in attaining high yields of the cross-coupling products. In all these cases the stereoselectivity does not change. All the palladium complexes examined were found to be effective but those having triphenylphosphine as a ligand were recognized to be most effective and to give the alkenynes with high stereoselectivity. The yields of the enynes were generally lower when less than 2 mmol % of the catalyst was used in a DMF solution.

It is well known that the reaction of (E)-alkenyl(phenyl)iodonium salts with acetylenes in the presence of copper (I) iodide is accelerated. However the detailed mechanism of the reaction or the exact role of copper (I) iodide has yet to be determined. CuI being inexpensive and readily available, we also investigated the effect of stoichiometric amount of the catalyst on this reaction (CuI may preferably be recrystallized and stored in a vial covered with aluminum foil).[18] It was found that as the percentage of CuI was increased from 1 mmol% to 3 mmol %, the yields of desired product increased and then decreased at 4 mmol %. The optimum $PdCl_2(PPh_3)_2$/CuI ratio was found to be 2/3. We have found that the mixture of K_2CO_3 with triethylamine as a base and a mixture DMF : H_2O (6:1) as a solvent gave a turnover of the catalyst. The decrease of yields with increasing of amount of water may be due to the heterogeneous character of the reaction mixture.

The principal features of the present cross-coupling reaction, which are important for delineating the mechanism, are as follows: (a) only catalytic amounts of palladium complexes (2 mmol %) are required to obtain the cross-coupling products; (b) the coupling reactions are stereospecific and take place while retaining the original configuration of alkenyl(phenyl)iodonium salts; (c) a base is required to carry out a successful coupling.

The mechanism of the present cross coupling reaction between alkenyl(phenyl) iodonium salts and terminal alkynes catalyzed by palladium complexes as well as bases, which accommodates all the above features of the reaction, is outlined in **Figure I** by two catalytic cycles:

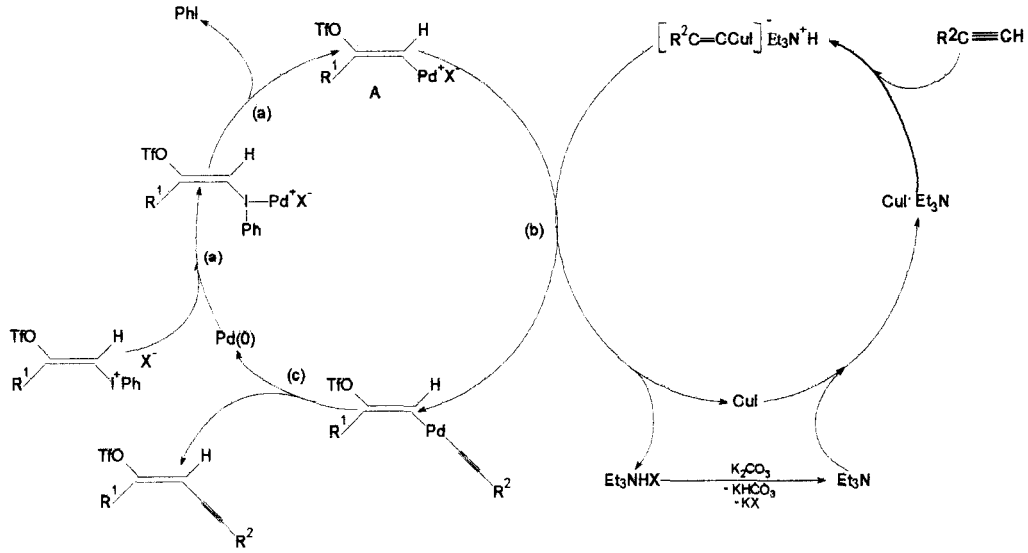

Figure I. Catalytic cycles for the cross-coupling reaction of alkenyl iodonium salts with alkynes.

In contrast to usual cross-coupling RM with R'X catalyzed by Pd-catalyst, in this case, metalloorganic compounds are generated *in situ* likely to be heterocuprate $[RC{\equiv}CCuI]^- R_3NH^+$ in catalytic amounts from terminal acetylenes under the effect of base and CuI. Further, the high reactive heterocuprate goes into the catalytic cycle with alkenyl(phenyl)iodonium salts. Like other related reactions that are catalyzed by transition metals, this catalytic cycle should involve (a) addition of highly electrophilic alkenyl (phenyl) iodonium salt to the catalytic species Pd(0). In this case I(III) gets reduced to I(I); (b) addition of the alkenyl-palladium intermediate to the heterocuprate; (c) reductive elimination of Pd (0) and the formation of the coupled product. Alternatively, it is possible that the initial step is a transmetallation between the alkenyl iodonium salt and the palladium(II) catalyst which would also yield an alkenyl-palladium intermediate similar to A. In fact, similar transmetallations are proposed for palladium-catalyzed coupling reactions of organothallium(III)[19] and organomercury(II)[20] compounds.

So, the cross-coupling reaction may be presumed to proceed on the palladium complex without phosphine ligands, while the starting $PdCl_2(PPh_3)_2$ is the precursor of the catalyst and provides the "mild" conversion of $PdCl_2(PPh_3)_2$ to the more reactive "Pd" species.

Conclusion: The palladium-catalyzed cross-coupling reaction of alkenyl(phenyl)iodonium triflates in aqueous medium in the presence of amine base, K_2CO_3, and CuI proceed readily and stereospecifically to give conjugated alkenynes in good yields. The process reported herein may be regarded as a valuable supplement to the Stille cross-coupling due to its mild conditions, the range of structural types available and ease of operation. The demonstration of the versatility of the present method by the stereospecific synthesis of natural products bearing conjugated alkenynes structures is under investigation.

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Experimental Section

All the experiments were carried out under argon atmosphere. 1-Hexyne, 1-decyne, 3-methoxypropyn-1, phenylacetylene, and trimethylsilylethyne were used after distillation of the commercial reagents. Solvents and amines were purified by distillation prior to use.[22] Alkenyl(phenyl)iodonium sulfonates were prepared via the reaction of $[PhI^+F\ ^-OTf]$ with terminal acetylenes.[7a] The palladium(II)diacetate and palladium(II)dichloride used were commercial products. Dichlorobis(triphenylphosphine)palladium(II)[23] and tetrakis(triphenylphosphine)palladium(0)[24] were prepared according to the reported procedures. IR spectra were recorded with a UR-20 spectrometer. ^1H and ^{13}C NMR spectra were taken on a Varian VXR-400 at 400

MHz and 100 MHz, respectively. Chemical shifts (δ) are reported in $CDCl_3$ relative to the residual $CHCl_3$ proton signal at 7.24 ppm and the $CDCl_3$ carbon ^{13}C triplet at 77.0 ppm.

General procedure for the synthesis of Enynes. The following procedure for the preparation of (E)-1-butyl-4-phenyl-1-buten-3-ynyl trufluoromethanesulfonate is representative.

To a mixture of (E)-[β-(trifluoromethanesulfonyloxy)-1-hexenyl](phenyl) iodonium trifluoromethane sulfonate (1 mmol), $PdCl_2(PPh_3)_2$ ($2\cdot10^{-2}$ mmol), CuI ($3\cdot10^{-2}$ mmol), K_2CO_3 (2 mmol) was added phenylacetylene (1.1 mmol) in DMF:H_2O (14 mL, 6:1) and Et_3N (2 mmol) under argon atmosphere. The solution was mechanically stirred for 3 hrs at 30 °C. After completion of the reaction, the black reaction mixture was quenched with saturated aqueous solution of NH_4Cl (30 mL). The reaction mixture was extracted with ether or hexane (3x20 mL). The combined ethereal or hexane extracts were dried over potassium carbonate. The dried extracts were filtered through a plug of aluminia (pentane eluent) and concentrated under reduced pressure. The remaining liquid was purified by column chromatography by using hexane-ethyl acetate (3:2). Removal of solvents provided 0.259 g (78%) of **2b**.

(E)-1-n-Butyl-1-dodecen-3-ynyl trifluoromethanesulfonate 2a: The *title compound* **2a** (yield 77 %) was obtained by the general procedure as a colourless oil; [Found: C, 55.39; H, 7.38. $C_{17}H_{27}F_3O_3S$ requires C, 55.43; H, 7.34 %]; R_f (hexane/EtOAc 3:2) 0.35; ν_{max} (neat) 3080, 2260, 1645, 1418, 1225, 955, 641 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 5.6 Hz, C<u>H</u>$_3$-octyl), 1.05 (3 H, t, *J* 5.6 Hz, C<u>H</u>$_3$-butyl), 1.28 (10 H, m, 5C<u>H</u>$_2$-octyl), 1.39 (2 H, m, C<u>H</u>$_2$-butyl), 1.45 (2 H, m, C<u>H</u>$_2$-octyl), 1.50 (2 H, m, C<u>H</u>$_2$-butyl), 2.78 (2 H, m, allylic-C<u>H</u>$_2$-octyl), 2.84 (2 H, m, allylic-C<u>H</u>$_2$-butyl), 5.74 (1 H, s, =C<u>H</u>); δ_C NMR (100 MHz, $CDCl_3$) 13.8, 14.1, 20.6, 22.9, 23.7, 27.6, 29.7, 30.4, 30.6, 31.2, 32.7, 33.6, 78.4, 89.1, 103.3, 119.4, 147.3.

(E)-1-n-Butyl-4-phenyl-1-buten-3-ynyl trifluoromethanesulfonate 2b: The *title compound* **2b** (yield 78 %) was obtained by the general procedure as a colourless oil; [Found: C, 54.20, H, 4.58. $C_{15}H_{15}F_3O_3S$ requires C, 54.22, H, 4.52 %]; R_f (hexane/EtOAc 3:2) 0.41; ν_{max} (neat) 3100, 2245, 1650, 1415, 1220, 950, 640 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 1.05 (3 H, t, *J* 5.6 Hz, C<u>H</u>$_3$), 1.35 (2 H, m, C<u>H</u>$_2$), 1.46 (2 H, m, C<u>H</u>$_2$), 2.86 (2 H, m, allylic-C<u>H</u>$_2$), 5.68 (1 H, s, =C<u>H</u>), 7.19 (2 H, d, *J* 8.0 Hz, <u>H</u>$_{ortho}$), 7.32 (2 H, t, *J* 8.0 Hz, <u>H</u>$_{mctha}$), 7.75 (1 H, t, *J* 8.0 Hz, <u>H</u>$_{para}$); δ_C NMR (100 MHz, $CDCl_3$) 13.9, 22.8, 31.3, 32.7, 78.5, 88.4, 104.7, 119.5, 122.7, 128.8, 129.2, 132.5, 147.1.

(E)-1-n-Butyl-5-methoxy-1-penten-3-ynyl trifluoromethanesulfonate 2c: The *title compound* **2c** (yield 72 %) was obtained by the general procedure as a colourless oil; [Found: C, 44.04, H, 4.98. $C_{11}H_{15}F_3O_4S$ requires: C, 44.00, H, 5.00 %]; R_f (hexane/EtOAc 3:2) 0.39; ν_{max} (neat) 3078, 2255, 1648, 1415, 1223, 957,

645 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 1.05 (3 H, t, *J* 5.6 Hz, $C\underline{H}_3$), 1.39 (2 H, m, $C\underline{H}_2$), 1.50 (2 H, m, $C\underline{H}_2$), 2,86 (2 H, m, allylic-$C\underline{H}_2$), 3.65 (3 H, s, $C\underline{H}_3O$), 4.37 (2H, s, $OC\underline{H}_2$), 5.73 (1H, s, =C<u>H</u>); δ_C NMR (100 MHz, $CDCl_3$) 13.8, 22.8, 31.1, 32.4, 57.3, 63.8, 79.3, 89.5, 102.6, 119.7, 147.4.

(E)-1-n-Butyl-1-buten-3-ynyl trifluoromethanesulfonate 2d: The *title compound* **2d** (yield 70 %) was obtained by the general procedure as a colourless oil; [Found: C, 42.16, H, 4.34. $C_9H_{11}F_3O_3S$ requires: C, 42.19, H, 4.30 %]; R_f (hexane/EtOAc 3:2) 0.42; ν_{max} (neat) 3090, 2140, 1645, 1420, 1220, 960, 647 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 1.05 (3 H, t, *J* 5.6 Hz $C\underline{H}_3$), 1.39 (2 H, m, $C\underline{H}_2$), 1.54 (2 H, m, $C\underline{H}_2$), 2.87 (2 H, m, allylic-$C\underline{H}_2$), 3.04 (1 H, s, ≡C<u>H</u>), 5.74 (1 H, s, =C<u>H</u>); δ_C NMR (100 MHz, $CDCl_3$) 13.8, 22.6, 31.3, 32.6, 78.1, 83.4, 94.3, 119.6, 147.3.

(E)-1-Dodecen-3-ynyl trifluoromethanesulfonate 2e: The *title compound* **2e** (yield 68 %) was obtained by the general procedure as a colourless oil; [Found: C, 49.96, H, 6.12. $C_{13}H_{19}F_3O_3S$ requires: C, 50.00, H, 6.10 %]; R_f (hexane/EtOAc 3:2) 0.45; ν_{max} (neat) 3100, 2200, 1644, 1428, 1218, 964, 649 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 5.6 Hz, $C\underline{H}_3$), 1.28 (10 H, m, $5C\underline{H}_2$), 1.68 (2 H, m, $C\underline{H}_2$), 2.79 (2H, m, allylic-$C\underline{H}_2$), 5.79 (1 H, d, *J* 12.8 Hz, C=C<u>H</u>-C≡C), 7.94 (1 H, d, *J* 12.8 Hz, OC<u>H</u>=C-C≡C); δ_C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.7, 20.9, 23.6, 27.3, 29.4, 30.6, 30.8, 78.9, 88.9, 103.6, 120.2, 150.4.

(E)-4-Phenyl-1-buten-3-ynyl trifluoromethanesulfonate 2f: The *title compound* **2f** (yield 71 %) was obtained by the general procedure as a colourless oil; [Found: C, 47.80, H, 2.56. $C_{11}H_7F_3O_3S$ requires: C, 47.83, H, 2.54 %]; R_f (hexane/EtOAc 3:2) 0.47; ν_{max} (neat) 3095, 2230, 1645, 1425, 1222, 955, 650 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 5.71 (1 H, d, *J* 12.9 Hz, =C<u>H</u>), 7.43 (2 H, t, *J* 8.0 Hz, $\underline{H}_{meta}$), 7.45 (2 H, d, *J* 8.0 Hz, $\underline{H}_{ortho}$), 7.65 (1 H, t, *J* 8.0 Hz, $\underline{H}_{para}$), 7.99 (1 H, d, *J* 12.9 Hz, OC<u>H</u>=C); δ_C NMR (100 MHz, $CDCl_3$) 78.4, 88.5, 104.4, 120.7, 121.8, 128.8, 129.6, 132.5, 150.1.

(E)-4-Methoxy-1-penten-3-ynyl trifluoromethanesulfonate 2g: The *title compound* **2g** (yield 65 %) was obtained by the general procedure as a colourless oil; [Found: C, 34.40, H, 2.83. $C_7H_7F_3O_4S$ requires: C, 34.43, H, 2.87 %]; R_f (hexane/EtOAc 3:2) 0.44; ν_{max} (neat) 3098, 2250, 1640, 1431, 1210, 955, 645 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 3.67 (3 H, s, $C\underline{H}_3O$), 4.28 (2 H, s, $OC\underline{H}_2$), 5.85 (1 H, d, *J* 13.1 Hz, =C<u>H</u>), 7.94 (1H, d, *J* 13.1 Hz, OC<u>H</u>=C); δ_C NMR (100 MHz, $CDCl_3$) 57.3, 63.2, 79.7, 88.5, 102.2, 120.2, 150.3.

(E)-1-Buten-3-ynyl trifluoromethanesulfonate 2h: The *title compound* **2h** (yield 66 %) was obtained by the general procedure as a colourless oil; [Found: C, 30.06, H, 1.49. $C_5H_3F_3O_3S$ requires: C, 30.00, H, 1.50 %]; R_f (hexane/EtOAc 3:2) 0.41; ν_{max} (neat) 3305, 3091, 2135, 1644, 1428, 1219, 962, 645 cm^{-1}; δ_H NMR

(400 MHz, $CDCl_3$) 2.86 (1 H, s, ≡C<u>H</u>), 5.89 (1 H, d, *J* 12,9 Hz, C=C<u>H</u>-C≡C), 8.24 (1 H, d, *J* 12,9 Hz, C<u>H</u>=C-C≡C); δ_C NMR (100 MHz, $CDCl_3$) 78.5, 83.6, 94.0, 120.7, 150.8.

(E)-1-Methoxy-2-tridecen-4-ynyl trifluoromethanesulfonate 2i: The *title compound* **2i** (yield 68 %) was obtained by the general procedure as a colourless oil; [Found: C, 50.54, H, 6.47. $C_{15}H_{23}F_3O_4S$ requires: C, 50.56, H, 6.46 %]; R_f (hexane/EtOAc 3:2) 0.47; ν_{max} (neat) 3100, 2240, 1645, 1425, 1220, 955, 648 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 5.6 Hz, C<u>H</u>$_3$), 1.28 (10 H, m, 5C<u>H</u>$_2$), 1.47 (2 H, m, C<u>H</u>$_2$), 2.73 (2H, m, allylic-C<u>H</u>$_2$), 3.65 (3 H, s, C<u>H</u>$_3$O), 4.38 (2 H, s, OC<u>H</u>$_2$), 5.75 (1 H, s, C=C<u>H</u>-C≡C); δ_C NMR (100 MHz, $CDCl_3$) 14.1, 20.6, 23.6, 27.5, 29.8, 30.4, 30.6, 33.7, 60.3, 70.2, 78.3, 89.4, 102.9, 120.3, 146.8.

(E)-1-Methoxy-5-phenyl-2-penten-4-ynyl trifluoromethanesulfonate 2j: The *title compound* **2j** (yield 62 %) was obtained by the general procedure as a colourless oil; [Found: C, 48.72, H, 3.47. $C_{13}H_{11}F_3O_4S$ requires: C, 48.75, H, 3.44 %]; R_f (hexane/EtOAc 3:2) 0.43; ν_{max} (neat) 3095, 2255, 1640, 1428, 1224, 960, 649 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 3.30 (3H, s, C<u>H</u>$_3$O), 4.38 (2H, s, OC<u>H</u>$_2$), 5.79 (1H, s, =C<u>H</u>), 7.31 (2 H, t, *J* 8.0 Hz, <u>H</u>$_{meta}$), 7.31 (1 H, t, *J* 8.0 Hz, <u>H</u>$_{para}$), 7.32 (2 H, d, *J* 8.0 Hz, <u>H</u>$_{ortho}$); δ_C NMR (100 MHz, $CDCl_3$) 60.2, 70.2, 78.9, 88.6, 104.4, 120.3, 122.8, 128.9, 129.5, 132.7, 146.2.

(E)-1-Methoxy-2-penten-4-ynyl trifluoromethanesulfonate 2k: The *title compound* **2k** (yield 65 %) was obtained by the general procedure as a colourless oil; [Found: C, 34.40, H, 2.84. $C_7H_7F_3O_4S$ requires: C, 34.43, H, 2.87 %]; R_f (hexane/EtOAc 3:2) 0.41; ν_{max} (neat) 3300, 3100, 2100, 1640, 1418, 1222, 965, 643 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 3.00 (1 H, s, ≡C<u>H</u>), 3.70 (3 H, s, C<u>H</u>$_3$O), 4.36 (2 H, s, OC<u>H</u>$_2$), 5.62 (1 H, s, =C<u>H</u>); δ_C NMR (100 MHz, $CDCl_3$) 60.8, 70.7, 79.0, 85.1, 96.5, 120.2, 146.9.

(E)-1-Phenyl-1-hepten-3-ynyl trifluoromethanesulfonate 2l: The *title compound* **2l** (yield 68 %) was obtained by the general procedure as a colourless oil; [Found: C, 52.79, H, 4.10. $C_{14}H_{13}F_3O_3S$ requires: C, 52.83, H, 4.09 %]; R_f (hexane/EtOAc 3:2) 0.45; ν_{max} (neat) 3090, 2250, 1645, 1430, 1220, 955, 643 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 1.02 (3 H, t, *J* 5,6 Hz, C<u>H</u>$_3$), 1.52 (2 H, m, C<u>H</u>$_2$), 2.70 (2H, m, allylic-C<u>H</u>$_2$), 5.60 (1 H, s, =C<u>H</u>), 7,61 (2 H, t, *J* 8.0 Hz, <u>H</u>$_{meta}$), 7.72 (1 H, t, *J* 8.0 Hz, <u>H</u>$_{para}$), 7.85 (2 H, d, *J* 8.0 Hz, <u>H</u>$_{ortho}$); δ_C NMR (100 MHz, $CDCl_3$) 13.2, 22.0, 22.5, 79.1, 88.7, 103.1, 120.1, 130.3, 131.1, 131.3, 137.5, 149.9.

(E)-1-Phenyl-5-chloro-1-penten-3-ynyl trifluoromethanesulfonate 2m: The *title compound* **2m** (yield 59 %) was obtained by the general procedure as a colourless oil; [Found: C, 44.36, H, 2.48. $C_{12}H_8ClF_3O_3S$ requires: C, 44.38, H, 2.47 %]; R_f (hexane/EtOAc 3:2) 0.47; ν_{max} (neat) 3100, 2244, 1640, 1415, 1220, 956, 647 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 4.65 (2 H, s, C<u>H</u>$_2$Cl), 5.70 (1 H, s, =C<u>H</u>), 7.62 (2 H,

t, *J* 8.0 Hz, $\underline{H}_{meta}$), 7.74 (1 H, t, *J* 8.0 Hz, $\underline{H}_{para}$), 7.82 (2 H, d, *J* 8.0 Hz, $\underline{H}_{ortho}$); δ_C NMR (100 MHz, $CDCl_3$) 32.9, 78.6, 85.1, 94.2, 120.3, 130.3, 130.9, 131.1, 137.5, 150.3.

(E)-1-Phenyl-1-buten-3-ynyl trifluoromethanesulfonate 2n: The *title compound* **2n** (yield 61 %) was obtained by the general procedure as a colourless oil; [Found: C, 47.86, H, 2.51. $C_{11}H_7F_3O_3S$ requires: C, 47.83, H, 2.54 %]; R_f (hexane/EtOAc 3:2) 0.41; ν_{max} (neat) 3300, 3090, 2130, 1645, 1430, 1215, 955, 643 cm^{-1}; δ_H NMR (400 MHz, $CDCl_3$) 3.16 (1 H, s, ≡C$\underline{H}$), 5.60 (1 H, s, =C$\underline{H}$), 7.61 (2 H, t, *J* 8.0 Hz, $\underline{H}_{meta}$), 7.72 (1 H, t, *J* 8.0 Hz, $\underline{H}_{para}$), 7.87 (2 H, d, *J* 8.0 Hz, $\underline{H}_{ortho}$); δ_C NMR (100 MHz, $CDCl_3$) 78.4, 84.8, 94.7, 120.1, 130.3, 131.0, 131.1, 138.0, 149.0.

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