Stereocontrolled synthesis of trifluoromethylated (*E*)- or (*Z*)-ynenyl sulfones *via* sequential transformations

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Received (in Cambridge, UK) 3rd November 2000, Accepted 8th January 2001
First published as an Advance Article on the web 8th February 2001

Diethyl 1-(phenylsulfonyl)ethylphosphonate **1** was treated with *n*-butyllithium in tetrahydrofuran (THF) at −78 °C and the resulting carbanion **2** reacted with trifluoroacetic anhydride to give the trifluoroacylated phosphonate **3**. Without isolation, **3** was attacked by lithium acetylides and elimination of phosphate anion afforded trifluoromethylated (*Z*)-ynenyl sulfones (***Z*-4**) in 57–76% yields, while treatment of **3** with acetylenic Grignard reagents gave trifluoromethylated (*E*)-ynenyl sulfones (***E*-4**) in 45–54% yields. The configuration of the products could be ascertained on the basis of the crystal structure. A possible mechanism for the explanation of stereochemical results is proposed.

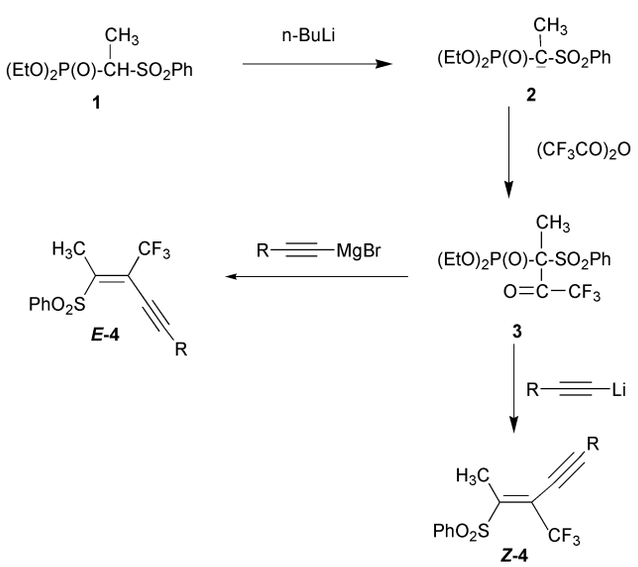
Introduction

In the past twenty years the use of sulfones in organic synthesis has increased significantly and they have been employed in a variety of versatile synthetic methodologies[1–3] enabling the synthesis of many functionalized compounds, particularly of naturally occurring products. A variety of sulfone-containing synthons are known, and among them, sulfone 1,3-dienes have attracted particular interest.[4] They are useful intermediates in cycloaddition reactions and Michael-type conjugate additions, and can undergo many synthetic transformations.[4] Similarly, ynenyl sulfones are also useful intermediates in the synthesis of diacetylenes which show antibacterial or antifungal activity,[5] but effective methods for their preparation are still limited. Recently it has been reported that ynenyl sulfones have been prepared *via* the pyrolysis of 4-aryl-1,2,3-selenadiazol-5-yl *p*-tolylvinyl sulfones, prepared in turn from phenacylsulfanylacetic acid.[6] An alternative route is by the ring-opening of oxanorborennic derivative with alkynyllithium, followed by reduction and isomerisation.[7] Enyne systems have attracted much attention from synthetic organic chemists as enynes show interesting chemical and biological reactivities.[8a] The introduction of trifluoromethyl groups into organic compounds may change their biological activity.[8b,c] Thus the synthesis of trifluoromethylated ynenyl sulfones may attract further interest. Control of the stereochemistry is very important in the synthesis of unsaturated natural products with biological activity.[9] Sequential transformations have emerged in recent years as a powerful methodology for their operational simplicity and efficient entry to complex compounds by including two or more transformations in a single operation to increase the complexity of a substrate starting from commercially available relatively simple precursors.[10]

Results and discussion

Very recently monofluoroenynes have been prepared by the Horner–Wadsworth–Emmons reaction but monofluoroacetylenic phosphonates had to be prepared in advance.[11] However to the best of our knowledge trifluoromethylated ynenyl sulfones have not been reported previously. Therefore to develop an effective method for their preparation would be valuable. Herein we report a stereocontrolled one-pot synthesis of trifluoromethylated (*E*)- or (*Z*)-ynenyl sulfones starting from easily available substances.

The reaction sequences are shown in Scheme 1.



Scheme 1

Diethyl 1-(phenylsulfonyl)ethylphosphonate **1** was treated with *n*-butyllithium in tetrahydrofuran (THF) at −78 °C and the resulting carbanion **2** reacted with trifluoroacetic anhydride to form the trifluoroacylated phosphonate **3**. Without isolation, **3** was attacked by lithium acetylides and elimination of phosphate anion afforded trifluoromethylated (*Z*)-ynenyl sulfones (***Z*-4**) in 57–76% yields, while treatment of **3** with acetylenic Grignard reagents gave trifluoromethylated (*E*)-ynenyl sulfones (***E*-4**) in 45–54% yields.

The results are summarized in Table 1.

To assign the configuration of products, we carried out the X-ray crystallographic analysis of **4a** (Method A). Fortunately the crystal of **4a** could be grown from hexane. X-Ray crystallographic analysis showed that the trifluoromethyl group is *cis* with respect to the phenylsulfonyl group (see Fig. 1). The configuration of **4a** (from method A) could be assigned as the *Z*-isomer. The chemical shift of CF_3 of **4a**

DOI: 10.1039/b008849h

Table 1 Preparation of trifluoromethylated ynenyl sulfones

Compound	R	Method	Yield[a] (%)	$Z:E$[b]
***Z*-4a**	4-$CH_3C_6H_4$	A	56	100:0
***E*-4a**	4-$CH_3C_6H_4$	B	45	0:100
***Z*-4b**	C_6H_5	A	73	100:0
***E*-4b**	C_6H_5	B	45	0:100
***Z*-4c**	n-C_4H_9	A	76	100:0
***E*-4c**	n-C_4H_9	B	46	0:100
***Z*-4d**	CH_3OCH_2	A	57	100:0
***E*-4d**	CH_3OCH_2	B	53	0:100
***Z*-4e**	4-ClC_6H_5	A	57	100:0
***E*-4e**	4-ClC_6H_5	B	54	0:100
***Z*-4f**	n-C_7H_{15}	A	63	100:0
***E*-4f**	n-C_7H_{15}	B	51	0:100

[a] Isolated yields. [b] The ratio of *E*- and *Z*-isomers is estimated on the basis of NMR spectra and TLC data. (No other isomer was detectable from the NMR spectra and the TLC data showed that the ratios are >98:2.)

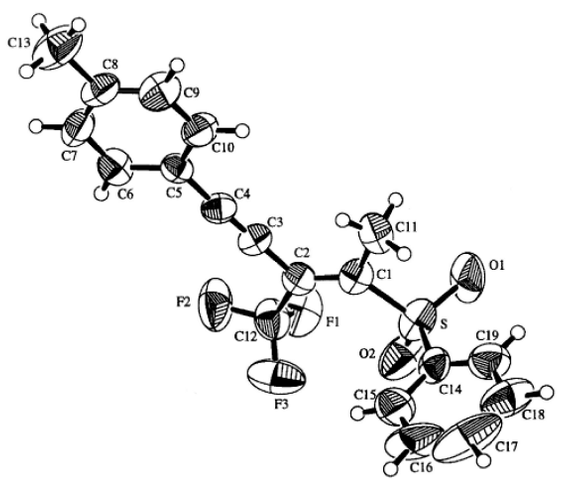


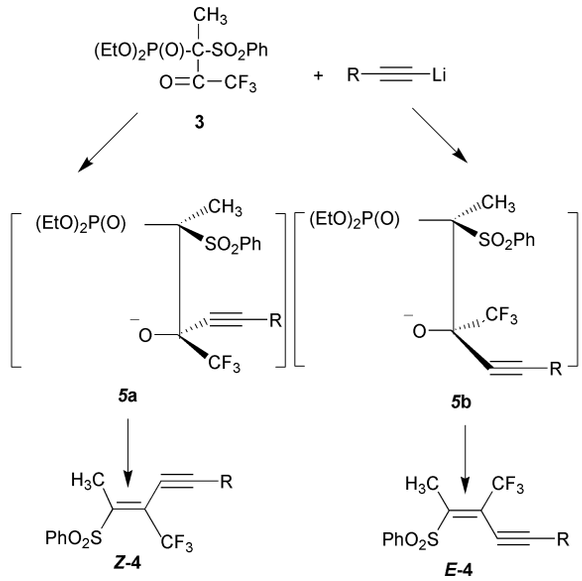
Fig. 1 The X-ray molecular structure of (*Z*) 4-(4-Methylphenyl)-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone) (***Z*-4b**).

(from method A) in the ^{19}F NMR spectra is −53.6 ppm, while that of **4a** (from method B) is −58.8 ppm. Thus the chemical shift of CF_3 of the product which appeared at low field is assigned as the *Z*-isomer while that which appeared at high field is assigned as the *E*-isomer. The stereochemical results are rationalized.

(1) The reaction of the lithium reagent with 3

The reaction was kinetically controlled since it was carried out at −78 °C. The mechanism for the formation of trifluoromethylated (*Z*)-ynenyl sulfones is analogous to that of the intramolecular Horner–Wadsworth–Emmons reaction[12] and is outlined in Scheme 2.

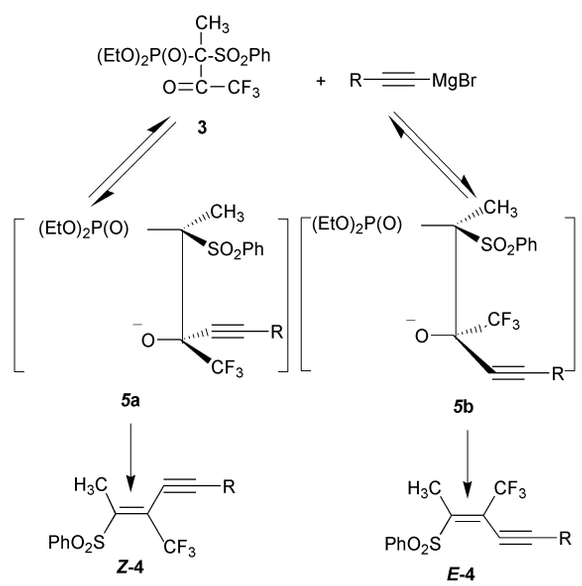
The reaction is initiated by nucleophilic attack of the lithium reagent on the carbon–oxygen double bond of the carbonyl group, and for the additions containing an asymmetric α-carbon, the Felkin-Anh model of asymmetric induction[13] predicts the predominant diastereomer. The incoming nucleophile preferentially attacks the less hindered side of the plane containing the C=O bond. Therefore the relative steric bulk of CH_3 and SO_2Ph plays an important role in the stereoselectivity. The relative bulk of CH_3 is smaller than that of SO_2Ph, and hence the attack is from the rear (the side of the plane containing the small group) of **3** forming the intermediate **5a**; the reverse is true for the attack from the front which leads to the formation of intermediate **5b**. Each of those intermediates decomposes *via* a *syn*-elimination, affording ***E*-4** or ***Z*-4**. In our case formation of **5a** will be favored over **5b** and the *Z*-isomer was obtained exclusively (see Table 1).



Scheme 2

(2) The reaction of the Grignard reagent with 3

The reaction was thermodynamically controlled since it was carried out at 25 °C. The mechanism for the formation of trifluoromethylated (*E*)-ynenyl sulfones is analogous to that of the bisphosphonate reported in the literature[14] and is outlined in Scheme 3.



Scheme 3

The reaction is initiated by nucleophilic attack of the Grignard reagent on the carbon–oxygen double bond of the carbonyl group, forming intermediates **5a** and **5b** (Scheme 3). The size of the reactive groups is $SO_2Ph > CF_3 > CH_3 > C{\equiv}CR$. Since the intermediate **5b** involves a synperiplanar (eclipsed) orientation of two pairs of 'small'/'large' substituents (C≡CR/SO_2Ph, CH_3/CF_3), this conformer should be favored relative to the stereoisomer **5a** which contains unfavorable 'large'/'large' (SO_2Ph/CF_3) non-bonding interactions. Therefore the stereoselectivity of olefination in our case is a function of the conformational equilibrium of the adducts. Each of these intermediates decomposes *via* a *syn*-elimination, affording alkene ***E*-4** or ***Z*-4**. In our case, formation of isomer **5b** will be favored over isomer **5a** and the *E*-isomer was obtained exclusively.

Finally the lithium and magnesium ions may play an import-

ant role in this reaction but there is no evidence to support this suggestion.

Experimental

Bps and mps are uncorrected. The IR spectra of liquid products as films and of solid products as KCl disk on a Digilab FTS-20E spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer (δ values are in ppm using tetramethylsilane as internal standard and $CDCl_3$ as solvent; J-values are given in Hz). ^{19}F NMR spectra were recorded on a Varian EM-360 (60 MHz) spectrometer (δ values are in ppm using trifluoroacetic acid as internal standard and $CDCl_3$ as solvent; positive values are for upfield shifts). The published ^{19}F NMR spectra were re-calculated using a standard chemical shift of reference δ_F (CF_3COOH) −76.5 ppm with respect to δ_F ($CFCl_3$) 0.00 ppm. Mass spectra were measured on a Finnigan GC-MS-4021 mass spectrometer. HRMS data were obtained on Finnigan-Mat 8430 high resolution mass spectrometer.

Diethyl (1-phenylsulfonyl)ethylphosphonate (1)

Compound **1** was prepared according to the known procedure.[15]

General procedure for the preparation of trifluoromethylated (*E*)- or (*Z*)-ynenyl sulfones (4)

Method A. *n*-Butyllithium (1.1 mmol in 0.7 mL hexane) was added dropwise over 10 minutes to a stirred solution of diethyl (1-phenylsulfonyl)ethylphosphonate (1 mmol) in absolute THF (20 mL) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 0.5 h and trifluoroacetic anhydride (1 mmol) was added to it in one portion. Stirring was continued at −78 °C for 1 h, after which lithium acetylide (1.3 mmol) was added dropwise to the mixture which was stirred for another 1 h. The reaction mixture was poured into dil. HCl (0.5 M, 15 mL) and the water layer was extracted with dichloromethane (4 × 20 mL). The combined organic layer was washed with water (2 × 10 mL) until neutral and dried over Na_2SO_4. Evaporation of the solvent gave a residue which was purified by column chromatography eluting with petroleum ether (60–90 °C)–ethyl acetate (98 : 2) to give the product **4**.

Method B. If Grignard reagent was used instead of lithium reagent, the reaction mixture was allowed to warm to 25 °C, and stirred for 4 h. Then it was worked up as for the lithium reagent.

(*Z*)-4-(4-Methylphenyl)-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*Z*-4a). Yield 56%; mp: 110–111 °C; IR (KBr): 2930, 2240, 1610, 1510, 1250, 1190, 1070 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.98–7.95 (m, 2H), 7.71–7.66 (m, 1H), 7.62–7.56 (m, 2H), 7.38 (d, 2H, J = 8.1 Hz), 7.17 (d, 2H, J = 8.0 Hz), 2.39 (q, 3H, J = 2.1 Hz), 2.38 (s, 3H) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$) δ −53.6 (s, 3F) ppm. MS: 364 (M^+, 15%), 345 (5), 316 (10), 300 (30), 285 (8), 211 (10), 192 (100). Anal. Calcd for $C_{19}H_{15}F_3O_2S$ (364.38): C, 62.63; H, 4.15. Found: C, 62.38; H, 4.11%.

(*E*)-4-(4-Methylphenyl)-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*E*-4b). Yield 45%; mp: 66–68 °C; IR (KBr): 2210, 1600, 1510, 1450, 1340, 1320, 1210, 1160, 1140 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 8.01–7.97 (m, 2H), 7.68–7.63 (m, 1H), 7.55–7.50 (m, 2H), 7.46 (d, 2H, J = 8.1 Hz), 7.21 (d, 2H, J = 7.7 Hz), 2.42 (q, 3H, J = 2.5 Hz), 2.41 (s, 3H) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −58.8 ppm. MS: 364 (M^+, 21%), 316 (11), 300 (35), 285 (7), 265 (3), 240 (8), 192 (100). Anal. Calcd for $C_{19}H_{15}F_3O_2S$ (364.38): C, 62.63; H, 4.15. Found: C, 62.75; H, 4.02%.

(*Z*)-4-Phenyl-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*Z*-4b). Yield 73%; mp: 93–94 °C; IR (KBr): 2210, 1580, 1490, 1440, 1340, 1330, 1130, 1160, 1130 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.98–7.95 (m, 2H), 7.71–7.66 (m, 1H), 7.62–7.56 (m, 2H), 7.50–7.47 (m, 2H), 7.42–7.33 (m, 3H), 2.39 (q, 3H, J = 1.9 Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −53.4 (s, 3F) ppm. MS: 350 (M^+, 10%), 331 (8), 302 (18), 286 (30), 271 (6), 245 (13), 197 (22), 178 (100). Anal. Calcd for $C_{18}H_{13}F_3O_2S$ (350.36): C, 61.71; H, 3.74. Found: C, 61.49; H, 3.62%.

(*E*)-4-Phenyl-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*E*-4b). Yield 45%; mp: 50–52 °C; IR (KBr): 2930, 2850, 2210, 1600, 1490, 1450, 1320, 1310 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 8.0–7.97 (m, 2H), 7.68–7.63 (m, 1H), 7.57–7.50 (m, 4H), 7.45–7.37 (m, 3H), 2.43–2.39 (q, 3H) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −59.0 (s, 3F) ppm. MS: 350 (M^+, 13%), 302 (20), 286 (30), 245 (16), 178 (100), 139 (33), 116 (23). Anal. Calcd for $C_{18}H_{13}F_3O_2S$ (350.36): C, 61.71; H, 3.74. Found: C, 61.86; H, 3.58%.

(*Z*)-2-Trifluoromethyl-1-methyloct-1-en-3-ynyl phenyl sulfone (*Z*-4c). Yield 76%; oil; IR (neat): 2960, 2940, 2220, 1680, 1590, 1450, 1340, 1310, 1170 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.94–7.91 (m, 2H), 7.70–7.64 (m, 1H), 7.60–7.55 (m, 2H), 2.45 (t, 2H, J = 7.0 Hz), 2.27 (q, 3H, J = 1.9 Hz), 1.58–1.55 (m, 2H), 1.45–1.37 (m, 2H), 0.91 (t, 3H, J = 7.2 Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −53.6 (s, 3F) ppm. MS: 330 (M^+, 26%), 310 (29), 273 (2), 261 (4), 223 (5), 125 (100). Anal. Calcd for $C_{16}H_{17}F_3O_2S$ (330.36): C, 58.17; H, 5.19. Found: C, 58.14; H, 5.26%.

(*E*)-2-Trifluoromethyl-1-methyloct-1-en-3-ynyl phenyl sulfone (*E*-4c). Yield 46%; oil; IR (neat): 2960, 2930, 2220, 1600, 1450, 1330, 1310, 1210, 1170 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.97–7.93 (m, 2H), 7.71–7.66 (m, 1H), 7.60–7.55 (m, 2H), 2.42 (t, 2H, J = 7.1 Hz), 2.37 (q, 3H, J = 2.0 Hz), 1.61–1.49 (m, 2H), 1.47–1.26 (m, 2H), 0.93 (t, 3H, J = 7.2 Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −59.5 (s, 3F) ppm. MS: 331 (M^++1, 2%), 288 (25), 261 (100), 223 (37), 213 (5), 195 (7), 163 (52), 125 (73). Anal. Calcd for $C_{16}H_{17}F_3O_2S$ (330.36): C, 58.17; H, 5.19. Found: C, 58.12; H, 5.41%.

(*Z*)-5-Methoxy-2-trifluoromethyl-1-methylpent-1-en-3-ynyl phenyl sulfone (*Z*-4d). Yield 57%; oil; IR (neat): 3420, 2940, 1730, 1640, 1450, 1420, 1330, 1160 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.98–7.94 (m, 2H), 7.73–7.68 (m, 1H), 7.63–7.58 (m, 2H), 4.34 (s, 2H), 3.41 (s, 3H), 2.32 (q, 3H, J = 1.9 Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −54.1 (s, 3F) ppm. MS: 318 (M^+, 8%), 299 (11), 287 (7), 253 (4), 125 (100), 97 (8), 77 (46). HRMS: $C_{14}H_{13}F_3O_3S$ − F: Calcd: 299.0553. Found: 299.0576 (M − F).

(*E*)-5-Methoxy-2-trifluoromethyl-1-methylpent-1-en-3-ynyl phenyl sulfone (*E*-4d). Yield 53%; oil; IR (neat): 3410, 2930, 1730, 1690, 1660, 1450, 1150 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.99–7.95 (m, 2H), 7.73–7.69 (m, 1H), 7.68–7.55 (m, 2H), 4.31 (s, 2H), 3.43 (s, 3H), 2.37 (q, 3H, J = 2.2 Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −59.5 (s, 3F) ppm. MS: 317 (M^+ − 1, 2%), 287 (36), 239 (8), 223 (14), 193 (12), 163 (30), 125 (42). HRMS: $C_{14}H_{13}F_3O_3S$: Calcd 318.0537. Found: 318.0552.

(*Z*)-4-(4-Chlorophenyl)-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*Z*-4e). Yield 57%; mp: 114–115 °C; IR (KBr): 2210, 1570, 1490, 1450, 1340, 1240, 1180, 1150 cm^{-1}. ^{1}H NMR ($CDCl_3$–TMS): δ 7.97 (d, 2H, J = 7.7 Hz), 7.73–7.68 (m, 1H), 7.63-7.58 (m, 2H), 7.43–7.34 (m, 4H), 2.38 (q, 3H, J = 1.7 Hz) ppm. ^{19}F ($CDCl_3$–$CFCl_3$): δ −53.4 (s, 3F) ppm. MS: 384 (M^+, 5%), 336 (8), 320 (13), 285 (5), 259 (7), 212 (100), 173 (13). Anal. Calcd for $C_{18}H_{12}ClF_3O_2S$ (384.80): C, 56.18; H, 3.14. Found: C, 56.14; H 3.08%.

(*E*)-4-(4-Chlorolphenyl)-2-trifluoromethyl-1-methylbut-1-en-3-ynyl phenyl sulfone (*E*-4e). Yield 54%; mp: 157–158 °C; IR (KBr): 2960, 2930, 2210, 1590, 1490, 1330, 1250, 1210, 1160 cm^{-1}. ^1H NMR ($CDCl_3$–TMS): δ 7.98–7.94 (m, 2H), 7.69–7.64 (m, 1H), 7.56–7.47 (m, 4H), 7.40–7.34 (m, 2H), 2.40 (q, 3H, $J = 2.1$ Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −59.2 (s, 3F) ppm. MS: 384 (M^+, 8%), 336 (8), 320 (15), 285 (5), 245 (11), 212 (100), 188 (6), 139 (42). Anal. Calcd for $C_{18}H_{12}ClF_3O_2S$ (384.36): C, 56.18; H, 3.14. Found: C, 56.26; H, 2.89%.

(*Z*)-2-Trifluoromethyl-1-methylundec-1-en-3-ynyl phenyl sulfone (*Z*-4f). Yield 63%; oil; IR (neat): 2960, 2930, 2860, 2220, 1450, 1340, 1200, 1160 cm^{-1}. ^1H NMR ($CDCl_3$–TMS): δ 7.98–7.92 (m, 2H), 7.71–7.66 (m, 1H), 7.60–7.52 (m, 2H), 2.45 (t, 2H, $J = 7.0$ Hz), 2.27 (q, 3H, $J = 1.7$ Hz), 1.62–1.27 (m, 10H), 0.87 (t, 3H, $J = 6.4$ Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −54.1 (s, 3F) ppm. MS: 373 ($M^+ + 1$, 2%), 353 (4), 261 (16), 231 (6), 189 (7), 175 (11), 125 (100). Anal. Calcd for $C_{19}H_{23}F_3O_2S$ (372.45): C, 61.29; H, 6.18. Found: C, 61.54; H, 6.42%.

(*E*)-2-Trifluoromethyl-1-methylundec-1-en-3-ynyl phenyl sulfone (*E*-4f). Yield: 51%; oil; IR (neat): 2960, 2930, 2860, 2220, 1450, 1330, 1310, 1210, 1160 cm^{-1}. ^1H NMR ($CDCl_3$–TMS): δ 7.95–7.92 (m, 2H), 7.70–7.65 (m, 1H), 7.59–7.53 (m, 2H), 2.40 (t, 2H, $J = 7.0$ Hz), 2.37 (q, 3H, $J = 2.2$ Hz), 1.61–1.26 (m, 10H), 0.89 (t, 3H, $J = 7.0$ Hz) ppm. ^{19}F NMR ($CDCl_3$–$CFCl_3$): δ −59.3 (s, 3F) ppm. MS: 373 ($M^+ + 1$, 3%), 261 (22), 223 (8), 195 (12), 179 (23), 165 (15), 149 (100). HRMS: $C_{19}H_{23}F_3O_2S$: Calcd: 372.1371. Found: 372.1344.

Crystal structure determination †

Crystal data for compound ***Z*-4b**. $C_{19}H_{15}F_3O_2S$, $M = 364.38$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 24.847(4)$, $b = 5.433(1)$, $c = 13.118(3)$ Å, $V = 1770(1)$ Å^3, $Z = 4$, $D_{calc} = 1.36$ g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, $\mu = 2.21$ cm^{-1}, $T = 293.0$ K, prismatic crystal, 0.20 × 0.20 × 0.30 mm.

Data correction and processing. Data were measured on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation using the ω 2θ scan technique to a maximun 2θ-value of 49.9°. 1806 reflections were collected. The data were corrected for Lorentz and polarization factors. A correction for secondary extinction was also applied.

Structure solution and refinement. The structure was resolved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 1071 observed reflections and 225 variable parameters. The final R and R_w values are 0.066 and 0.076, respectively. All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corporation. We did not use the Bijvoet technique to determine the absolute configuration by X-ray analysis but the relative configuration has been determined and we can assign the relative configuration of the products.

† CCDC reference number(s) 152496. See http://www.rsc.org/suppdata/p1/b0/b008849h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the National Natural Science Foundation of China, the Laboratory of Organometallic Chemistry and Academia Sinica for financial support.

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