A convenient synthesis of alkynylpyrazoles

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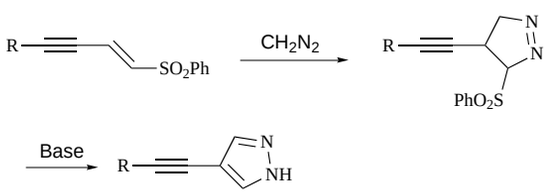
Diazomethane add to the enyne sulfones 1, 3, 4, 6–11 regio- and stereo-selectively to give the 4-alkynyl-5-phenylsulfonyl-4,5-dihydro-3*H*-pyrazoles 12–15 and 17–19, which are converted by MeLi into the 4-alkynyl-1*H*-pyrazoles 24, 25, 16, 26, 28, 30 in good yields. 4,5-Bis(alkynyl)-1*H*-pyrazoles 34, 37 are also obtained by the same procedure.

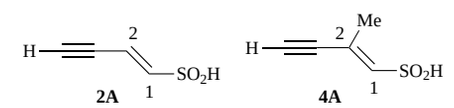
Whilst pyrazoles have been widely used as insecticides and herbicides,[1] much attention has been paid to alkynylpyrazoles which show cholesterol synthesis-inhibiting activity.[2] Several syntheses of these compounds have been reported. Thus, addition of diazoalkanes to conjugate enyne compounds affords a mixture of alkynyl- and alkenyl-pyrazoles,[3] whilst the reactions of trimethylsilyl- (TMS)-substituted aryl diynones and hydrazine give TMS-ethynylpyrazoles in good yields; this method is applicable only to aryl-substituted derivatives.[4] Decarboxylation of the pyrazolopropiolic acids resulted in low yields of such products.[5]



Scheme 1

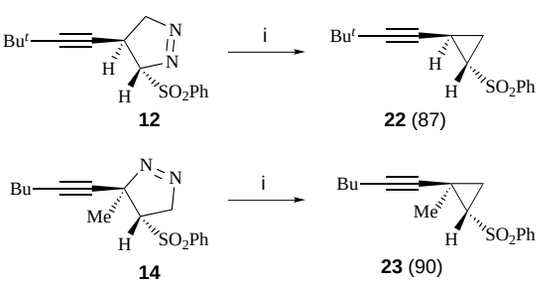
Recently, we reported the syntheses and the dehydrosulfonylation of conjugate enyne sulfones by MeLi.[6] If the cycloadditions of diazomethane and conjugate enyne sulfones proceed regioselectively to give 5-sulfonyl-substituted 4-alkynyl-4,5-dihydro-3*H*-pyrazoles, we thought that dehydrosulfonylation of these would give alkynyl pyrazoles (Scheme 1). We now report such a convenient synthesis of 4-alkynyl-1*H*-pyrazoles.

Cycloaddition of diazomethane to a conjugate enyne sulfone **1** afforded the pyrazoline† **12** regio- and stereo-selectively. The structure of **12** was assigned on the basis of IR and ^{1}H and ^{13}C NMR spectral results and an elemental analysis. The IR spectrum showed the acetylene absorption at 2225 cm^{-1} and those for the sulfonyl group at 1300 and 1150 cm^{-1}. The olefinic protons of the enyne sulfone **1** at δ 6.59, 6.78 disappeared in the ^{1}H NMR spectrum and new proton resonances due to the pyrazoline at δ 3.50–3.58 (5-H), 4.98–5.02 (3-H) and 5.41 (dt, *J* 7 and 2 Hz, 4-H) were observed. The ^{13}C NMR results and the elemental analysis were satisfied by structure **12**. The stereochemistry of the product **12** was determined after the cyclopropanation of the compound. Upon photoirradiation, denitrogenation of **12** proceeded easily[7] to give the cyclopropane **22** as a single *trans*-isomer with the repeated *trans*-coupling constant at *J* 4 Hz (Scheme 2). The Ph-substituted enyne sulfone **3** gave 1*H*-pyrazoline **13**; however, the butyl-substituted



LUMO	C1 = 0.62568 a.u.	C1 = 0.63000 a.u.
	C2 = –0.57799 a.u.	C2 = –0.55888 a.u.

Fig. 1

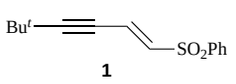
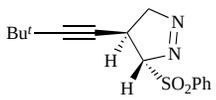
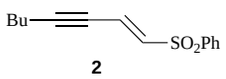
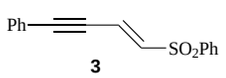
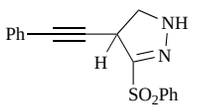
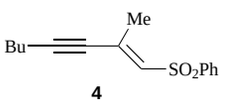
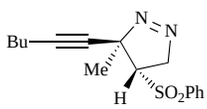
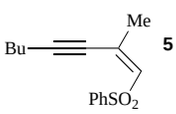
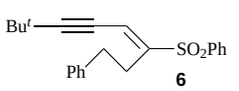
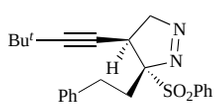
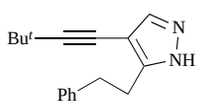
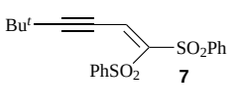
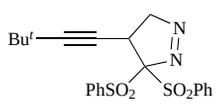
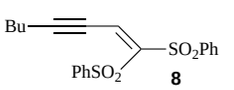
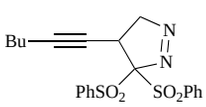
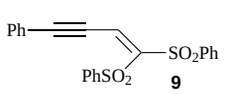
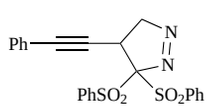
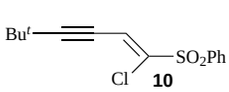
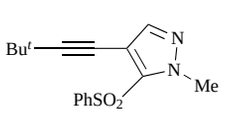
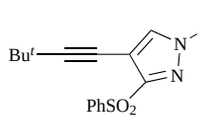
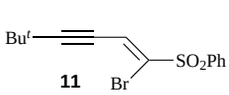


Scheme 2 *Reagent:* i, *hv*

enyne sulfone **2** gave a complex mixture. The cycloaddition of diazomethane and (*E*)-2-methyl-substituted enyne derivative **4** proceeded in a different orientation to give 5-(hex-1-ynyl)-5-methyl-4-phenylsulfonyl-3*H*-pyrazoline **14** in good yield. The stereochemistry of the pyrazoline **14** was also determined by a DNOE experiment after cyclopropanation of the compound. Irradiation of the methyl group on the cyclopropane ring increased the intensity of the *ortho*-protons of the $PhSO_2$ group not the intensity of the α-hydrogen to the sulfonyl group. This orientation of the addition of diazomethane was confirmed from the coupling pattern of ^{1}H NMR spectral data, which exhibited a broad triplet δ 3.71 (*J* 8 Hz) due to the α-hydrogen to the sulfonyl group and two doublets δ 4.77 (*J* 8 and 18 Hz) and δ 4.88 (*J* 8 and 18 Hz) due to the 3-methylene protons. The different orientations were difficult to understand. Molecular orbital calculations for compounds **2A** and **4A** by the PM3 method were performed (see Fig. 1) with MOPAC Ver. 6.01. The value of the LUMO orbitals of **4A** and **2A** were almost the same. However, the steric hindrance or the conformation of compound **4** would strongly affect the orientation of the addition. On the other hand, the *Z*-isomer **5** gave a complex mixture; α-phenethyl derivative **15** was obtained, accompanied by the dehydrosulfonylated product **16** (entry 6). The 1,1-bis(phenylsulfonyl) enynes **7**–**9** afforded the adducts **17**–**19**, respectively (entries 7–9). The α-halogen enyne sulfones **10** and **11** gave the *N*-methylpyrazoles **20** and **21** but

† For convenience, the name pyrazoline is used to refer to the 4,5-dihydro-3*H*-pyrazole system.

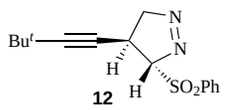
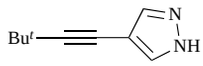
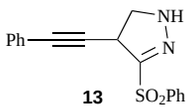
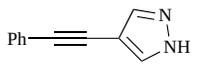
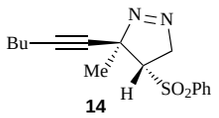
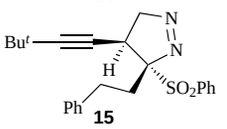
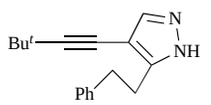
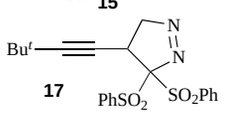
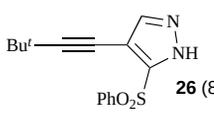
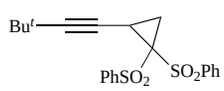
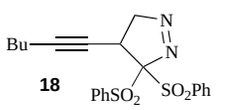
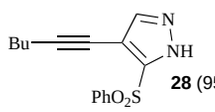
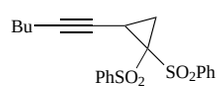
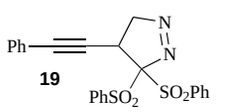
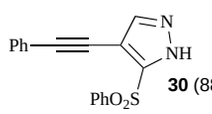
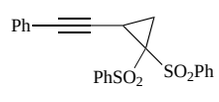
Table 1 Cycloadditions of enyne sulfones with CH_2N_2

Entry	Enyne sulfone	Products (% yield)	
1	 **1**		**12** (87)
2	 **2**	—	
3	 **3**		**13** (84)
4	 **4**		**14** (79)
5	 **5**	—	
6	 **6**		**15** (46)  **16** (17)
7	 **7**		**17** (59)
8	 **8**		**18** (52)
9	 **9**		**19** (86)
10	 **10**		**20** (21)  **21** (16)
11	 **11**	**20** (34)	**21** (17)

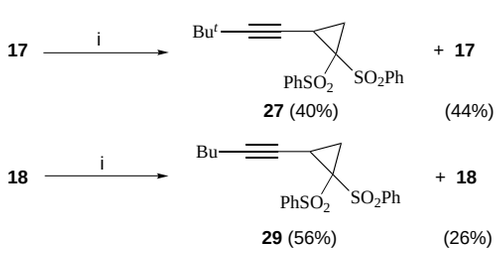
not the pyrazolines (entries 10 and 11). The positions of the *N*-methyl group were determined by the DNOE enhancement between the N-Me and the *ortho* protons of the sulfonyl group. Irradiation of the N-Me group of **20** increased the intensity of the *ortho* protons of the sulfonyl group; however, that of **21** did not show DNOE enhancement. The regioselectivity for the cycloadditions of diazomethane is accounted for by the Frontier MO theory that attachment of the sulfonyl group lowers the energy of the LUMO and thereby enhances the addition at the vinyl part of the enyne sulfones.[8]

Next, we examined the dehydrosulfonylations of the pyrazolines by MeLi (see Table 2). The pyrazoline **12** underwent β-elimination by MeLi to give the 4-alkynyl-1*H*-pyrazole **24** (80%), the spectral data and the elemental analysis for which satisfied the assigned structure. Substituted enyne sulfone **13** gave the 4-alkynylpyrazole **25** quantitatively. The enyne **14**, which has no prop-2-ynylic hydrogen at the β-position of the sulfonyl group, failed to undergo dehydrosulfonylation. The α-phenethyl derivative **15** afforded the 4-alkynyl-5-phenethylpyrazole **16** in good yield. The 5,5-bis(sulfonyl)pyrazole **17** gave

Table 2 Reaction of pyrazolines with MeLi

Entry	Alkynylpyrazoline	Products (% yields)		
1	 **12**		**24** (80)	
2	 **13**		**25** (99)	
3	 **14**	—		
4	 **15**		**16** (66)	
5	 **17**		**26** (84)	 **27** (trace)
6	 **18**		**28** (95)	 **29** (trace)
7	 **19**		**30** (88)	 **31** (6)

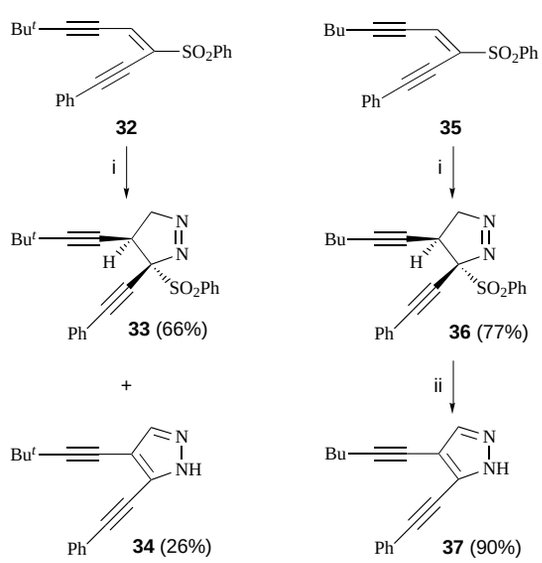
the 4-alkynyl-5-phenylsulfonylpyrazole **26**, accompanied by a trace of the alkynylcyclopropane **27** (entry 5). The cyclopropane derivatives were found to be easily obtained because of the denitrogenation of the pyrazolines under room light (Scheme 3). Thus, the pyrazolines **17** and **18** were stirred in



Scheme 3 *Reagent:* i, room light, $CHCl_3$

$CHCl_3$ for 12 h at room temperature to afford the cyclopropane derivatives **27** and **29**, respectively. The purified 4-(hex-1-ynyl)pyrazoline **18** also gave the pyrazole **28** in high yield. 4-(2-Phenylethynyl)pyrazole **19** gave the pyrazole **30**, accompanied by a trace of the cyclopropane **31** (entry 8). We also performed the desulfonylation of the pyrazolines with other bases such as LDA, NaH, Bu^{t}OK, Bu_4NF; however, the yields of the pyrazoles were rather low by comparison with MeLi.

The reactions of (*Z*)-enediyne sulfones **32** and **35** with diazomethane gave the bis(alkynyl)-substituted 3*H*-pyrazoles **33** and **36**, accompanied by the 1*H*-bis(alkynyl)pyrazole **34** (Scheme 4). The dehydrosulfonylation of **36** gave the 4,5-bis(alkynyl)-pyrazole **37**.



Scheme 4 *Reagents:* i, CH_2N_2; ii, MeLi–THF

Experimental

Mps were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were obtained for solution in $CDCl_3$ on a JEOL GX-270 (270 MHz) or a Varian Gemini 2000 (200 MHz) spectrometer with tetramethylsilane as an internal standard, unless otherwise indicated. ^{13}C NMR spectra and NOE measurements were run on a JEOL EX-270 spectrometer. *J* Values are given in Hz. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. All exact mass determinations were obtained on a JMA 2000 on-line system. Molecular orbital calculations

were carried out using MOPAC Ver. 6, J. J. Stewart, QCPE Bull. 9, 10 (1989); revised as Ver. 6.01 by Tsuneo Hirano, University of Tokyo, for HITAC and UNIX machines, JCPE Newsletter, 1, 10 (1989). All enyne sulfones were prepared according to our previous report.[9] Ether refers to diethyl ether.

Reactions of the enyne sulfones 1–11 with diazomethane

Typical procedure. An ether (10 cm^3) solution of diazomethane [generated from *N*-methylnitrosourea[10] (2.0 g, 0.02 mol) and 50% aq. NaOH] was added dropwise to an ether (2 cm^3) solution of 5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne **1** (0.25 g, 1.0 mmol) at 0 °C. The resulting precipitate was filtered off and washed with a small amount of ether. The almost pure (4*S**,5*R**)-4-(3,3-dimethylbut-1-ynyl)-5-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole **12** (0.25 g, 87%) was obtained as colourless needles after recrystallization from $CHCl_3$–Et_2O; mp 124–126 °C (decomp.); ν_{max}/cm^{-1} 2225 (acetylene) and 1300 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.04 (9 H, s, CH_3 × 3), 3.50–3.58 (1 H, m, 5-H), 4.98–5.02 (2 H, m, 3-H), 5.41 (1 H, dt, *J* 7 and 2, 4-H), 7.60–7.65 (2 H, m, ArH), 7.70–7.76 (1 H, m, ArH) and 7.90–7.94 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.3 (s), 30.5 (q × 3), 64.3 (d), 71.2 (s), 76.6 (t), 80.8 (d), 97.9 (s), 128.4 (d × 2), 129.7 (d × 2), 134.5 (d) and 138.1 (s); *m/z* 290 (M^+) and 93 (base) (Found: C, 61.94; H, 6.25; N, 9.68. $C_{15}H_{18}N_2O_2S$ requires C, 62.04; H, 6.25; N, 9.65%).

4-(2-Phenylethynyl)-3-phenylsulfonyl-4,5-dihydro-1*H*-pyrazole 13. Colourless prisms (from $CHCl_3$–Et_2O), mp 120–121 °C; ν_{max}/cm^{-1} 3375 (NH), 2200 (acetylene) and 1300 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 3.95 (1 H, t, *J* 12, 4-H), 4.35 (1 H, dd, *J* 4 and 12, 5-H), 4.61 (1 H, dd, *J* 4 and 12, 5-H), 7.29–7.43 (5 H, m, ArH), 7.48–7.54 (2 H, m, ArH), 7.61–7.66 (1 H, m, ArH) and 8.00–8.03 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 50.4 (t), 72.1 (d), 81.3 (s), 95.2 (s), 121.7 (s), 128.2 (s), 128.3 (d × 2), 128.9 (d × 2), 129.1 (d), 129.4 (d × 2), 131.7 (d × 2), 134.3 (d) and 137.1 (s); *m/z* 308 ($M^+ - 2$) and 83 (base) (Found: C, 65.76; H, 4.53; N, 8.93. $C_{17}H_{14}N_2O_2S$ requires C, 65.79; H, 4.55; N, 9.03%).

(4*S,5*R**)-5-(Hex-1-ynyl)-5-methyl-4-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole 14.** A colourless oil; ν_{max}/cm^{-1} 2250 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.87 (3 H, t, *J* 7, CH_3), 1.27–1.42 (4 H, m, CH_2CH_2), 1.81 (3 H, s, CH_3), 2.12 (2 H, t, *J* 7, 3′-H), 3.71 (1 H, t, *J* 8, 4-H), 4.73–4.93 (2 H, m, 3-H), 7.60–7.90 (3 H, m, ArH) and 7.91–7.92 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.3 (q), 18.1 (t), 20.4 (q), 21.6 (t), 30.0 (t), 65.5 (d), 76.5 (t), 78.3 (s), 85.7 (s), 88.2 (s), 127.8 (d × 2), 129.3 (d × 2), 134.0 (d) and 139.3 (s) [Found (FABMS): $(M + 1)^+$, 305.1331. $C_{16}H_{20}N_2O_2S$ requires *M* + 1, 305.1324].

(4*R,5*S**)-4-(3,3-Dimethylbut-1-ynyl)-5-phenethyl-5-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole 15.** Colourless needles (from $CHCl_3$–Et_2O), mp 106–107 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1310 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.45 (9 H, s, CH_3 × 3), 2.26 (1 H, dt, *J* 6 and 12, $PhCH_2CH_2$), 2.52–2.61 (2 H, m, $PhCH_2CH_2$), 2.78 (1 H, dt, *J* 6 and 12, $PhCH_2CH_2$), 3.79 (1 H, dd, *J* 7 and 10, 4-H), 4.54 (1 H, dd, *J* 7 and 18, 3-H), 5.09 (1 H, dd, *J* 10 and 18, 3-H), 7.06–7.08 (2 H, m, ArH), 7.12–7.26 (3 H, m, ArH), 7.52–7.62 (2 H, m, ArH), 7.70–7.72 (1 H, m, ArH) and 7.96–7.98 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.4 (d), 27.5 (s), 29.1 (t), 30.9 (q × 3), 32.2 (t), 73.1 (s), 85.5 (t), 93.9 (s), 112.7 (s), 126.3 (d), 128.0 (d × 2), 128.5 (d × 2), 129.2 (d × 2), 130.6 (d × 2), 134.6 (d), 135.3 (s) and 140.2 (s); *m/z* 393 ($M^+ - 1$) and 252 (base) (Found: C, 69.86; H, 6.72; N, 6.97. $C_{23}H_{26}N_2O_2S$ requires C, 70.07; H, 6.65; N, 7.10%).

4-(3,3-Dimethylbut-1-ynyl)-5-phenethyl-1*H*-pyrazole 16. Colourless needles (from CH_2Cl_2–hexane), mp 107–110 °C; ν_{max}/cm^{-1} 3170 and 3130 (NH); δ_H(270 MHz, $CDCl_3$) 1.32 (9 H, s, CH_3 × 3), 3.01 (4 H, s, CH_2CH_2), 7.19–7.21 (2 H, m, ArH), 7.26–7.29 (3 H, m, ArH) and 7.52 (1 H, s, 3-H); δ_C(67.5 MHz, $CDCl_3$) 28.0 (t), 28.1 (s), 31.2 (q × 3), 34.7 (t), 69.6 (s), 101.2 (s), 102.2 (s), 126.2 (d × 2), 128.4 (d × 2), 128.5 (d × 2), 136.7 (s) and 141.2 (s); *m/z* 252 (M^+, base) (Found: C, 80.71; H, 7.90; N, 11.04. $C_{17}H_{20}N_2$ requires C, 80.91; H, 7.99; N, 11.10%).

5,5-Bis(phenylsulfonyl)-4-(3,3-dimethylbut-1-ynyl)-4,5-dihydro-3*H*-pyrazole 17. Colourless needles (from $CHCl_3$–Et_2O), mp 97–98 °C (decomp.); ν_{max}/cm^{-1} 2260 (acetylene) and 1350 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.05 (9 H, s, CH_3 × 3), 3.69 (1 H, t, *J* 9, 4-H), 4.67 (1 H, dd, *J* 9 and 18, 3-H), 5.24 (1 H, dd, *J* 9 and 18, 3-H), 7.51–7.61 (4 H, m, ArH), 7.67–7.75 (2 H, m, ArH), 7.92–7.95 (2 H, m, ArH) and 8.04–8.07 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.3 (s), 30.4 (q × 3), 31.5 (d), 65.8 (s), 67.8 (s), 84.6 (t), 95.5 (s), 128.5 (d × 2), 128.9 (d × 2), 131.4 (d × 2), 131.6 (d × 2), 134.9 (d), 135.1 (d), 135.6 (s) and 137.0 (s); *m/z* 430 (M^+) and 125 (base) (Found: C, 58.52; H, 5.47; N, 6.20. $C_{21}H_{22}N_2O_4S_2$ requires C, 58.59; H, 5.15; N, 6.51%).

5,5-Bis(phenylsulfonyl)-4-(hex-1-ynyl)-4,5-dihydro-3*H*-pyrazole 18. Yellow powder (from $CHCl_3$–Et_2O), mp 96–97 °C (decomp.); ν_{max}/cm^{-1} 2250 (acetylene) and 1330 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.86 (3 H, t, *J* 7, CH_3), 1.24–1.43 (4 H, m, CH_2CH_2), 2.08 (2 H, dt, *J* 2 and 7, 3′-H), 3.75 (1 H, tt, *J* 2 and 9, 4-H), 4.65 (1 H, dd, *J* 9 and 18, 3-H), 5.21 (1 H, dd, *J* 9 and 18, 3-H), 7.48–7.54 (4 H, m, ArH), 7.64–7.70 (2 H, m, ArH), 7.87–7.91 (2 H, m, ArH) and 7.99–8.03 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.5 (q), 18.4 (t), 21.7 (t), 30.2 (t), 31.1 (d), 69.2 (s), 84.5 (t), 88.0 (s), 120.0 (s), 128.4 (d × 2), 128.9 (d × 2), 131.2 (d × 2), 131.4 (d × 2), 134.8 (d), 135.1 (d), 135.5 (s) and 137.2 (s); *m/z* 430 (M^+) and 125 (base) (Found: C, 58.42; H, 5.18; N, 6.74. $C_{21}H_{22}N_2O_4S_2$ requires C, 58.59; H, 5.15; N, 6.51%).

5,5-Bis(phenylsulfonyl)-4-phenylethynyl-4,5-dihydro-3*H*-pyrazole 19. Colourless prisms (from $CHCl_3$–Et_2O), mp 104–106 °C (decomp.); ν_{max}/cm^{-1} 1350 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 4.00 (1 H, t, *J* 9, 4-H), 4.77 (1 H, dd, *J* 9 and 18, 3-H), 5.31 (1 H, dd, *J* 9 and 18, 3-H), 7.22–7.35 (5 H, m, ArH), 7.46–7.57 (4 H, m, ArH), 7.63–7.71 (2 H, m, ArH), 7.89–7.93 (2 H, m, ArH) and 8.03–8.06 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 31.4 (d), 79.3 (s), 84.4 (t), 87.0 (s), 120.8, (s), 122.2 (s), 128.2 (d × 2), 128.5 (d × 2), 128.6 (d), 129.0 (d × 2), 131.3 (d × 2), 131.5 (d × 2), 131.7 (d × 2), 135.0 (d), 135.3 (d), 135.5 (s) and 137.1 (s); *m/z* 422 ($M^+ - N_2$) and 281 (base) (Found: C, 61.29; H, 4.03; N, 6.21. $C_{23}H_{18}N_2O_4S_2$ requires C, 61.32; H, 4.03; N, 6.22%).

4-(3,3-Dimethylbut-1-ynyl)-1-methyl–5-phenylsulfonylpyrazole 20. A yellow oil; ν_{max}/cm^{-1} 2250 (acetylene) and 1340 and 1140 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.34 (9 H, s, CH_3 × 3), 4.14 (3 H, s, CH_3), 7.47 (1 H, s, 3-H), 7.53–7.57 (2 H, m, ArH), 7.63–7.66 (1 H, m, ArH) and 8.05–8.07 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.2 (s), 30.6 (q × 3), 40.0 (q), 68.0 (s), 104.7 (s), 109.3 (s), 127.3 (d × 2), 129.2 (d × 2), 134.0 (d), 139.4 (s), 141.0 (s) and 141.2 (d) (Found: M^+, 302.1077. $C_{16}H_{18}N_2O_2S$ requires *M*, 302.1089).

4-(3,3-Dimethylbut-1-ynyl)-1-methyl–3-phenylsulfonylpyrazole 21. Colourless prisms (from CH_2Cl_2–hexane), mp 103–104 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1320 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.37 (9 H, s, CH_3 × 3), 3.83 (3 H, s, CH_3), 7.48–7.52 (2 H, m, ArH), 7.56–7.58 (1 H, m, ArH), 7.86 (1 H, s, 5-H) and 8.00–8.02 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 29.2 (s), 30.9 (q × 3), 38.3 (q), 65.8 (s), 113.6 (s), 125.4 (s), 128.0 (d × 2), 128.2 (s), 129.5 (d × 2), 133.6 (d), 139.4 (d) and 143.1 (s); *m/z* 302 (M^+, base) (Found: C, 63.35; H, 6.01; N, 9.29. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.00; N, 9.26%).

(4*S,5*S**)-4-(3,3-Dimethylbut-1-ynyl)-5-phenylethynyl-5-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole 33.** Colourless prisms (from $CHCl_3$–hexane), mp 113–117 °C; ν_{max}/cm^{-1} 2210 (acetylene) and 1325 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.11 (9 H, s, CH_3 × 3), 3.83 (1 H, dd, *J* 5 and 9, 4-H), 4.85 (1 H, dd, *J* 5 and 18, 3-H), 5.14 (1 H, dd, *J* 9 and 18, 3-H), 7.29–7.36 (5 H, m, ArH), 7.57–7.62 (2 H, m, ArH), 7.71–7.74 (1 H, m, ArH) and 8.06–8.09 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.3 (s), 29.9 (t), 30.8 (q × 3), 73.6 (s), 78.1 (s), 86.3 (d), 94.0 (s), 95.4 (s), 100.6 (s), 121.0 (s), 128.3 (d × 2), 128.8 (d × 2), 129.5 (d), 130.9

(d × 2), 131.7 (d × 2), 134.8 (d) and 135.2 (s); *m/z* 362 (M^+), 362 (base) (Found: C, 70.87; H, 5.75; N, 7.27. $C_{23}H_{22}N_2O_2S$ requires C, 70.74; H, 5.69; N, 7.17%).

4-(3,3-Dimethylbut-1-ynyl)-5-phenylethynyl-1*H*-pyrazole 34. Colourless prisms (from CH_2Cl_2–hexane), mp 139–141 °C; ν_{max}/cm^{-1} 3150 (NH) and 2200 (acetylene); δ_H(270 MHz, $CDCl_3$) 1.34 (9 H, s, CH_3 × 3), 7.32–7.34 (3 H, m, ArH), 7.52–7.54 (2 H, m, ArH) and 7.66 (1 H, s, 3-H); δ_C(67.5 MHz, $CDCl_3$) 28.2 (s), 31.0 (q × 3), 68.9 (s), 78.8 (s), 94.8 (s), 102.4 (s), 108.0 (s), 122.4 (s), 128.3 (d × 2), 128.7 (d), 131.7 (d × 2), 133.5 (s) and 135.1 (d); *m/z* 248 (M^+) and 233 (base) (Found: C, 82.42; H, 6.61; N, 11.23. $C_{17}H_{16}N_2$ requires C, 82.22; H, 6.49; N, 11.28%).

(4*S,5*S**)-4-(Hex-1-ynyl)-5-phenylethynyl–5-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole 36.** Colourless prisms (from CH_2Cl_2–hexane), mp 67–68 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.78 (3 H, t, *J* 7, CH_3), 1.24–1.43 (4 H, m, CH_2CH_2), 2.15 (2 H, dt, *J* 2 and 7, 3′-H), 3.82–3.87 (1 H, m, 4-H), 4.86 (1 H, dd, *J* 5 and 18, 3-H), 5.15 (1 H, dd, *J* 9 and 18, 3-H), 7.26–7.38 (5 H, m, ArH), 7.55–7.63 (2 H, m, ArH), 7.73–7.77 (1 H, m, ArH) and 8.08–8.10 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.5 (q), 18.5 (t), 21.9 (t), 30.1 (d), 30.7 (t), 75.0 (s), 78.1 (s), 86.0 (s), 86.0 (t), 95.8 (s), 109.5 (s), 121.1 (s), 128.4 (d × 2), 128.9 (d × 2), 129.6 (d), 131.0 (d × 2), 131.8 (d × 2), 134.9 (d) and 135.3 (s); *m/z* 390 (M^+) and 178 (base) (Found: C, 70.75; H, 5.74; N, 7.21. $C_{23}H_{22}N_2O_2S$ requires C, 70.74; H, 5.69; N, 7.17%).

Cyclopropanations of the pyrazoles 12 and 14

We performed the cyclopropanations of **12** and **14** by the general procedure described by Padwa.[7]

(1*S,2*R**)-2-(3,3-Dimethylbut-1-ynyl)-1–phenylsulfonylcyclopropane 22.** Colourless needles (from CH_2Cl_2–hexane), mp 99–100 °C; ν_{max}/cm^{-1} 2225 (acetylene) and 1325 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.13 (9 H, s, Me × 3), 1.24 (1 H, ddd, *J* 5 and 9 and 10, 3-H), 1.58 (1 H, ddd, *J* 6 and 9 and 10, 3-H), 2.25 (1 H, ddd, *J* 4 and 6 and 9, 2-H), 2.65 (1 H, ddd, *J* 4 and 5 and 9, 1-H), 7.54–7.59 (2 H, m, ArH), 7.62–7.66 (1 H, m, ArH) and 7.88–7.91 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 8.8 (d), 14.8 (t), 27.1 (s), 30.8 (q × 3), 40.7 (d), 75.6 (s), 87.7 (s), 127.5 (d × 2), 129.2 (d × 2), 133.5 (d) and 140.1 (s); *m/z* 262 (M^+) and 93 (base) (Found: C, 68.65; H, 6.95. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.92%).

(1*S,2*R**)-2-(Hex-1-ynyl)-2-methyl-1-phenylsulfonylcyclopropane 23.** A colourless oil; ν_{max}/cm^{-1} 2225 (acetylene) and 1310 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.87 (3 H, t, *J* 7, Me), 1.23–1.44 (4 H, m, alkyl H), 1.48 (1 H, dd, *J* 5 and 9, 3-H), 1.61 (1 H, dd, *J* 5 and 7, 3-H), 1.62 (3 H, s, Me), 2.06 (2 H, t, *J* 7, CH_2), 2.69 (1 H, dd, *J* 7 and 9, 1-H), 7.66–7.68 (3 H, m, ArH) and 7.90–7.94 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.5 (q), 18.1 (q), 18.1 (t), 21.5 (t), 21.8 (t), 30.6 (t), 45.4 (d), 78.5 (s), 82.7 (s), 127.2 (d × 2), 129.2 (d × 2), 133.3 (d) and 141.5 (s); *m/z* 135 (base) (Found: C, 69.66; H, 7.36. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%).

Dehydrosulfonylation of the pyrazolines 12–19 with MeLi

Typical procedure. An ether solution of MeLi (1 cm^3, 1.0 mmol) was added dropwise to a THF (2 cm^3) solution of the pyrazoline **12** (145 mg, 0.5 mmol) at −78 °C. The reaction mixture was stirred for 10 min after which saturated aqueous NH_4Cl was added to the mixture. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1:10) to give 4-(3,3-dimethylbut-1-ynyl)-1*H*-pyrazole **24** (59 mg, 80%) as colourless prisms after recrystallization from CH_2Cl_2–hexane; mp 160–163 °C; ν_{max}/cm^{-1} 3150 (NH) and 2250 (acetylene); δ_H(270 MHz, $CDCl_3$) 1.32 (9 H, s, CH_3 × 3), 6.37 (1 H, d, *J* 2, pyrazole H) and 7.54 (1 H, d, *J* 2, pyrazole H); δ_C(67.5 MHz, $CDCl_3$) 28.0 (s), 30.7 (q × 3), 69.5 (s), 101.5 (s), 129.2 (d), 129.3 (d) and 130.7 (s) (Found: M^+, 148.1003. $C_9H_{12}N_2$ requires *M*, 148.1001).

4-Phenylethynyl-1*H*-pyrazole 25. Colourless needles (from CH_2Cl_2–hexane), mp 99–101 °C; ν_{max}/cm^{-1} 3150 (NH); δ_H(270 MHz, $CDCl_3$) 6.55 (1 H, d, *J* 2, pyrazole H), 7.33–7.34 (3 H, m, ArH), 7.52–7.54 (2 H, m, ArH) and 7.63 (1 H, d, *J* 2, pyrazole H); δ_C(67.5 MHz, $CDCl_3$) 77.2 (s), 80.6 (s), 91.3 (s), 109.3 (d), 122.5 (s), 128.4 (d × 2), 128.6 (d), 131.6 (d × 2) and 132.5 (d); *m/z* 168 (M^+, base) (Found: C, 78.30; H, 4.89; N, 16.53. $C_{11}H_8N_2$ requires C, 78.55; H, 4.79; N, 16.65%).

4-(3,3-Dimethylbut-1-ynyl)-5-phenylsulfonyl-1*H*-pyrazole 26. Colourless needles (from $CHCl_3$–Et_2O), mp 170–172 °C; ν_{max}/cm^{-1} 3150 (NH), 2250 (acetylene) and 1340 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.34 (9 H, s, CH_3 × 3), 7.49–7.53 (2 H, m, ArH), 7.60–7.64 (1 H, m, ArH), 8.06–8.08 (2 H, m, ArH) and 8.16 (1 H, s, 3-H); δ_C(67.5 MHz, $CDCl_3$) 28.1 (s), 30.7 (q × 3), 67.1 (s), 103.8 (s), 104.6 (s), 127.9 (d × 2), 129.0 (d × 2), 133.7 (d), 136.2 (d), 140.3 (s) and 150.9 (s) (Found: M^+, 288.0922. $C_{15}H_{16}N_2O_2S$ requires *M*, 288.0932).

1,1-Bis(phenylsulfonyl)-2-(3,3-dimethylbut-1-ynyl)cyclopropane 27. Colourless prisms (from CH_2Cl_2–hexane), mp 119–121 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1320 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.24 (9 H, s, CH_3 × 3), 2.00 (1 H, dd, *J* 6 and 10, 3-H), 2.38 (1 H, dd, *J* 6 and 8, 3-H), 3.27 (1 H, dd, *J* 8 and 10, 2-H), 7.52–7.56 (4 H, m, ArH), 7.65–7.68 (2 H, m, ArH), 7.91–7.93 (2 H, m, ArH) and 8.27–8.29 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 18.3 (d), 20.7 (t), 27.6 (s), 30.5 (q × 3), 63.6 (s), 71.8 (s), 93.2 (s), 128.4 (d × 2), 128.8 (d × 2), 129.6 (d × 2), 129.7 (d × 2), 134.1 (d), 134.3 (d), 138.2 (s) and 139.1 (s) (Found: M^+, 402.0942. $C_{21}H_{22}O_4S_2$ requires *M*, 402.0960).

4-(Hex-1-ynyl)-5-phenylsulfonyl-1*H*-pyrazole 28. Colourless needles (from $CHCl_3$–Et_2O), mp 96–98 °C; ν_{max}/cm^{-1} 3100 (NH), 2200 (acetylene) and 1300 and 1100 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.96 (3 H, t, *J* 7, CH_3), 1.40–1.66 (4 H, m, CH_2CH_2), 2.44 (2 H, t, *J* 7, 3′-H), 7.48–7.54 (2 H, m, ArH), 7.59–7.65 (1 H, m, ArH), 8.03–8.06 (2 H, m, ArH) and 8.12 (1 H, s, 3-H) (Found: M^+, 288.0921. $C_{15}H_{16}N_2O_2S$ requires *M*, 288.0932).

1,1-Bis(phenylsulfonyl)-2-(hex-1-ynyl)cyclopropane 29. White prisms (from CH_2Cl_2–hexane), mp 68–71 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7, CH_3), 1.36–1.52 (4 H, m, CH_2CH_2), 2.01 (1 H, dd, *J* 6 and 10, 3-H), 2.17–2.21 (2 H, m, 3′-H), 2.39 (1 H, dd, *J* 6 and 8, 3-H), 3.23–3.27 (1 H, m, 2-H), 7.52–7.58 (4 H, m, ArH), 7.65–7.70 (2 H, m, ArH), 7.95–7.96 (2 H, m, ArH) and 8.23–8.25 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.5 (q), 18.2 (d), 18.7 (t), 20.9 (t), 21.9 (t), 30.3 (t), 63.0 (s), 72.6 (s), 85.6 (s), 128.3 (d × 2), 128.8 (d × 2), 129.8 (d × 2), 129.9 (d × 2), 134.2 (d), 134.4 (d), 138.4 (s) and 138.9 (s) (Found: M^+, 402.0945. $C_{21}H_{22}O_4S_2$ requires *M*, 402.0960).

4-Phenylethynyl-5-phenylsulfonyl-1*H*-pyrazole 30. Colourless needles (from $CHCl_3$–Et_2O), mp 178–180 °C; ν_{max}/cm^{-1} 3150 (NH), 2225 (acetylene) and 1320 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 7.38–7.40 (3 H, m, ArH), 7.49–7.56 (4 H, m, ArH), 7.60–7.64 (1 H, m, ArH), 8.10–8.12 (2 H, m, ArH) and 8.27 (1 H, s, 3-H); δ_C(67.5 MHz, $CDCl_3$) 77.2 (s), 94.8 (s), 104.1 (s), 122.6 (s), 128.1 (d × 2), 128.5 (d × 2), 128.8 (d), 129.2 (d × 2), 131.5 (d × 2), 134.0 (d), 136.3 (d), 140.0 (s) and 151.4 (s); *m/z* 308 (M^+, base) (Found: C, 66.02; H, 4.00; N, 9.04. $C_{17}H_{12}N_2O_2S$ requires C, 66.22; H, 3.92; N, 9.08%).

1,1-Bis(phenylsulfonyl)-2-phenylethynylcyclopropane 31. Yellow prisms (from CH_2Cl_2–hexane), mp 41–42 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 2.13 (1 H, dd, *J* 6 and 10, 3-H), 2.56 (1 H, dd, *J* 6 and 8, 3-H), 3.47 (1 H, dd, *J* 8 and 10, 2-H), 7.31–7.38 (3 H, m, ArH), 7.42–7.45 (4 H, m, ArH), 7.57–7.64 (3 H, m, ArH), 7.69–7.73 (1 H, m, ArH), 8.00–8.02 (2 H, m, ArH) and 8.24–8.26 (2 H, m, ArH) (Found: M^+, 422.0625. $C_{23}H_{18}O_4S_2$ requires *M*, 422.0646).

4-(Hex-1-ynyl)-5-phenylethynyl-1*H*-pyrazole 37. Colourless needles (from $CHCl_3$–Et_2O), mp 56–58 °C; ν_{max}/cm^{-1} 3175 (NH), 2225 (acetylene) and 1340 and 1150 (SO_2); δ_H(270 MHz,

$CDCl_3$) 0.93 (3 H, t, *J* 7, CH_3), 1.47–1.64 (4 H, m, CH_2CH_2), 2.45 (2 H, t, *J* 7, 3′-H), 7.32–7.35 (3 H, m, ArH), 7.53–7.55 (2 H, m, ArH) and 7.65 (1 H, s, 3-H); δ_C(67.5 MHz, $CDCl_3$) 13.6 (q), 19.3 (t), 21.9 (t), 30.8 (t), 70.3 (s), 78.5 (s), 94.2 (s), 94.9 (s), 108.0 (s), 122.3 (s), 128.3 (d × 2), 128.8 (d) and 131.8 (d × 3) and 136.2 (s); *m/z* 248 (M^+, base) (Found: C, 82.01; H, 6.41; N, 11.17. $C_{17}H_{16}N_2$ requires C, 82.22; H, 6.50; N, 11.28%).

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