48. Palladium-Catalysed Intramolecular Cyclisations of Olefinic Propargylic Carbonates and Application to the Diastereoselective Synthesis of Enantiomerically Pure (−)-α-Thujone

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Intramolecular $[Pd_2(dba)_3]$/tri(2-furyl)phosphine-catalysed (dba = dibenzylideneacetone, PhCH=CHCOCH=CHPh) cyclisations of olefinic propargylic carbonates **I** provided alk-1-enyl-(3-aza)bicyclo[3.1.0]-hexanes **VIII** in good yields. A palladium cascade sequence **I** → **II** → **III** → **IV** → **VII** → **VIII** is proposed. Furthermore, chiral propargylic carbonates such as **23**, **24** and **25** allowed diastereoselective formation of bicyclo[3.1.0]hexanes **29**, **30** and **31**, respectively. The first diastereoselective synthesis of the monoterpene, (−)-α-thujone **40** illustrates the potential of the method.

Introduction. – In connection with our previous studies of the intramolecular Pd-catalysed cyclisation of olefinic allylic acetates [1], we envisaged the extension of this chemistry to the analogous intramolecular Pd-catalysed cyclisations of olefinic propargylic carbonates (*Scheme 1*) [2]. Insertion of Pd into propargyl carbonate of type **I** to form allenylpalladium(II) species **III** [3] and Pd-catalysed cyclisation was expected to yield the transient σ-alkylpalladium species **IV**, which would either undergo β-elimination to give **V** or C,C-coupling to give **VI**, with concommitant regeneration of the Pd^0 catalyst.

Results and Discussion. – The cyclisation precursors were readily prepared from sulfonamide **1** [4] and bis-sulfone **2** [5]. Propargylation to provide enynes **3** and **4**, followed by deprotonation with LiHMDS and trapping sequentially with acetone and methyl chloroformate yielded gem-dimethyl propargylic carbonates **5** and **6**, respectively. Alkylation of **1** and **2** with propargyl bromide **9** [6] gave the parent olefinic propargylic carbonates **7** and **8**, respectively (*Scheme 2*).

Initial treatment of olefinic propargylic carbonate **5** with a catalytic amount of $[Pd_2(dba)_3]/PPh_3$ (dba = dibenzylideneacetone, PhCH=CHCO=CHPh) in AcOH at 80°, conditions that had previously been applied olefinic allylic carbonates, afforded a complex mixture of products from which 3-azabicyclo[3.1.0]hexane derivative **10** could be isolated in 15% yield. The expected allenyl-methylidene-pyrrolidine **V** was notably absent (*Scheme 3*). Rationalisation of the formation of **10** suggests that instead of the expected β-elimination across the σ-alkylpalladium (**IV** → **V**, *Scheme 1*), rapid intra-

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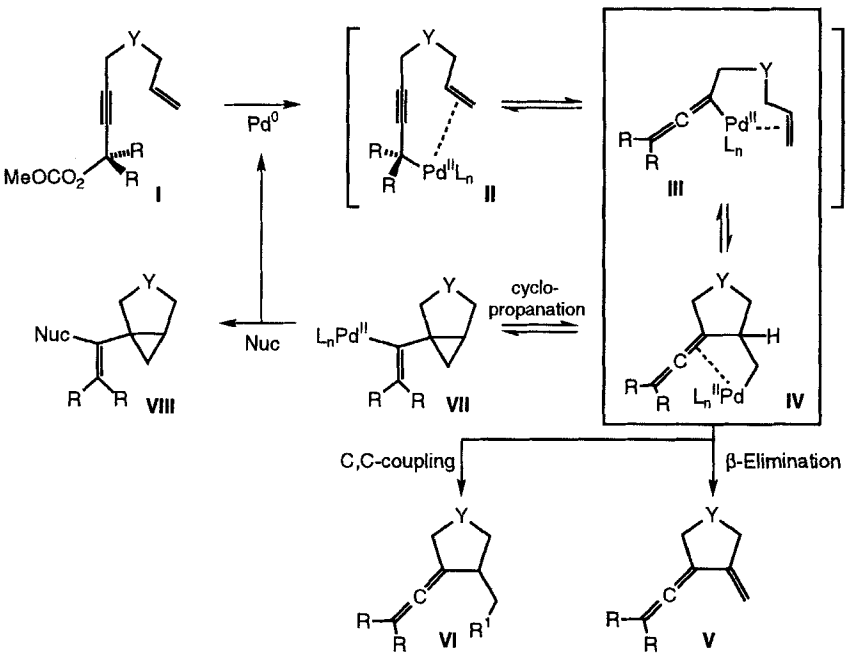
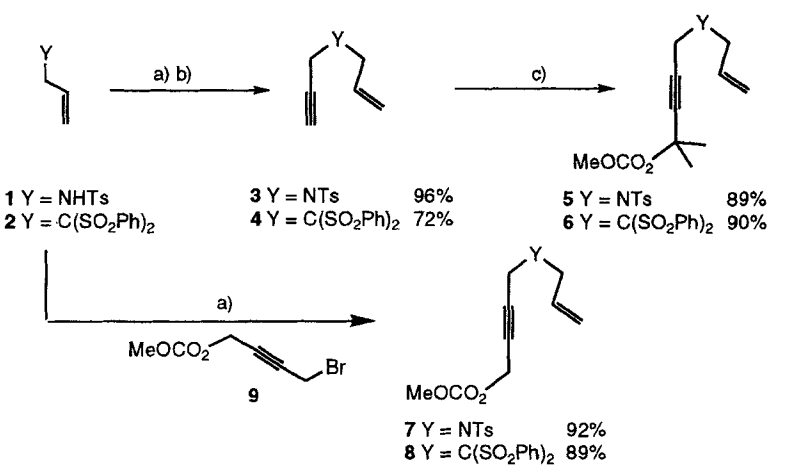
Scheme 1



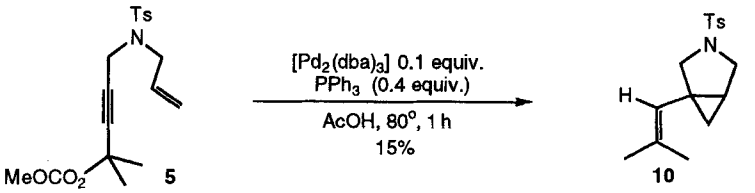
Scheme 2



a) NaH, DMF. b) Propargyl bromide. c) *i*) LiHMDS, THF, −78°; *ii*) acetone; *iii*) MeOC(O)Cl, −78° to r.t.

molecular carbopalladation of the allene function [7] had occurred to provide the 3-aza-bicyclo[3.1.0]hexane **VIII** *via* a vinylpalladium(II) intermediate **VII**, which had apparently been trapped by a hydride source (**VII** → **VIII**, *Scheme 1*).

Scheme 3



Scheme 4

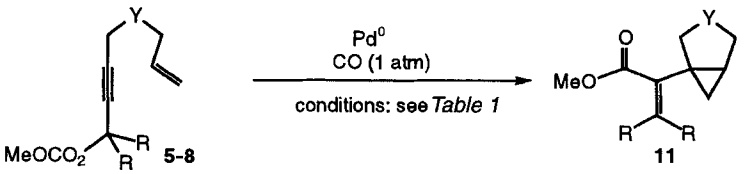


Table 1. *Pd-Catalysed Double Cyclisation/CO Insertion of Olefinic Propargylic Carbonates* **5–8** → **11** (*Scheme 4*)

Entry	Enyne			Conditions[a])	Time [h]	Product **11**	Yield [%]
		Y	R				
1	**7**	NTs	H	*A*	4	**11a**	10
2	**5**	NTs	Me	*A*	1	**11b**	65
3	**7**	NTs	H	*B*	1	**11a**	93
4	**5**	NTs	Me	*B*	1	**11b**	93
5	**8**	$C(SO_2Ph)_2$	H	*B*	3	**11c**	70
6	**6**	$C(SO_2Ph)_2$	Me	*B*	20	**11d**	70

[a]) *A*:*i*) $[Pd_2(dba)_3]$ (0.025 equiv.), PPh_3 (0.1 equiv.), CO, AcOH, 45°; *ii*) CH_2N_2, CH_2Cl_2, r.t. *B*:*i*) $[Pd_2(dba)_3]$ (0.025 equiv.), P(furyl)$_3$ (0.1 equiv.), CO, MeOH, 45°; *ii*) CH_2N_2, CH_2Cl_2, r.t.

Heating **5** under CO (1 atm) with $[Pd_2(dba)_3]/PPh_3$ in AcOH at 45° for 1 h and subsequent esterification with CH_2N_2 furnished the azabicyclo[3.1.0]hexane **11b** in 65% yield (*Scheme 4; Table 1, Entry 2*). Under the same reaction conditions, the parent precursor **7** gave the azabicyclo[3.10]hexane **11a** in a lower yield (10% yield; *Table 1, Entry 1*). Optimisation led to the $[Pd_2(dba)_3]$/tri(2-furyl)phosphine-catalysed-CO/MeOH protocol [8], which provided both vinylogous esters **11a** and **11b** in 93% yield (*Table 1, Entries 3* and *4*). Subjecting the gem-bis-sulfone precursors **8** and **6** to the same Pd-catalysed reaction conditions yielded the respective vinylogous esters **11c** and **11d** in 70% yield (*Table 1, Entries 5* and *6*). The absence of products derived from uncyclised or monocyclised olefinic propargylic carbonates indicates insertion of CO after the tandem double cyclisation.

In an attempt to intercept intermediates of the cyclisation process, we envisaged a transmetallation of the Pd intermediate **III** or **IV** (*Scheme 1*) with a organometallic reagent [9]. However, Pd-catalysed reaction of olefinic propargylic carbonates **5–8** in the presence of Me_2Zn afforded (aza)bicyclo[3.1.0]hexanes **12a–d** as the only products (*Scheme 5, Table 2*).

Scheme 5

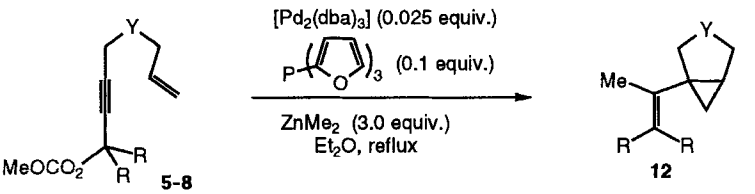


Table 2. *Pd-Catalysed Double Cyclisation/$ZnMe_2$ Coupling of Olefinic Propargylic Carbonates* **5–8** → **12** (*Scheme 5*)

Entry	Enyne			Time [h]	Product **12**	Yield [%]
		Y	R			
1	**7**	NTs	H	12	**12a**	58
2	**5**	NTs	Me	3	**12b**	85
3	**8**	$C(SO_2Ph)_2$	H	3	**12c**	58
4	**6**	$C(SO_2Ph)_2$	Me	7	**12d**	85

Similarly, reaction of carbonate **5** in the presence of triphenylborane or tris[(*E*)-(*tert*-butyl)alkenyl] borane led to **13a** or **13b** (*Scheme 6; Table 3, Entries 1* and *2*) [10]. On the other hand, reagents with β-H-atoms such as BEt and $ZnEt_2$ afforded a mixture of reduced and Et-coupled products (*Table 3, Entries 3* and *4*). It is interesting to note that exclusive reduction of the vinylpalladium intermediate **VII** occurred when i-PrOH was used both as reagent and solvent to give the azabicyclohexane **10** (85% yield; *Table 3, Entry 5*).

Scheme 6

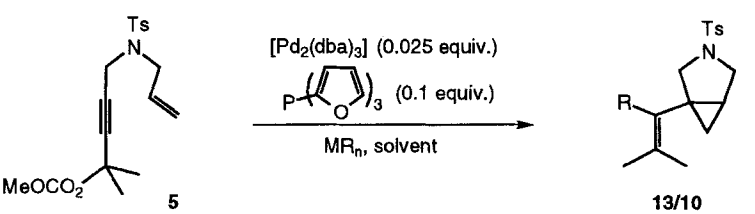


Table 3. *Pd-Catalysed Double Cyclisation/MR_n Coupling of Olefinic Propargylic Carbonates* **5–10**, **5** → **13** (*Scheme 6*)

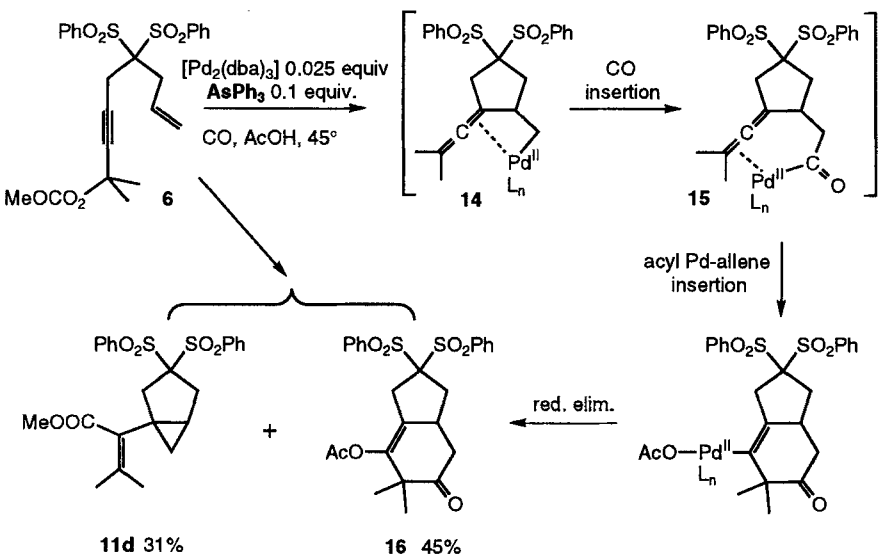
Entry	MR_n (mol-equiv.)	Solvent	Time [h]	Product **13**		
					R	Yield [%]
1	BPh_3 (1.1)	Et_2O	2	**13a**	Ph	77
2	(*E*)-(*t*-BuCH=CH)$_3$B (1.1)	Et_2O	20	**13b**	(*E*)-(*t*-BuCH=CH)	45
3	BEt_3 (3.0)	Et_2O	18	**13c**	Et:H[a])	60[c])
4	$ZnEt_2$ (3.0)	Et_2O	2	**13d**	Et:H[b])	65[c])
5	–	i-PrOH	4	**10**	H	85

[a]) 10:1 Ratio. [b]) 3:1 Ratio. [c]) Ratio and yields determined by GC.

These results show that the double cyclisation process (**III** → **VII**) proceeds faster than the trapping of Pd intermediate **III** or **IV**, and that the formation of the reduced product is consistent with the formation and the reductive elimination of an alkenylpalladium hydride species [11].

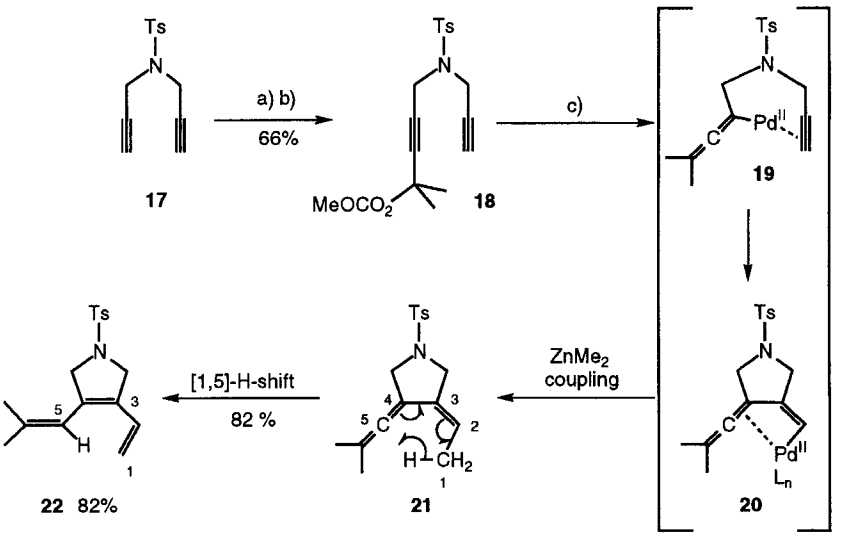
Changing the ligand from PPh_3 or tri(2-furyl)phosphine to $AsPh_3$ now gave carbonylation of the primary insertion product leading to **16** (45%) as well as to the usually observed doubly cyclised product **11d** (31%; *Scheme 7*) [12]. The formation of the major indenone product **16** can be explained by CO insertion into the (allenyl)(σ-alkyl)palladium intermediate **14** giving the acylpalladium complex **15**, followed by allene-insertion and reductive elimination.

Scheme 7



We then investigated the insertion of an allenylpalladium intermediate such as **19** into an alkyne to give a vinylpalladium insertion product **20**, which should neither form a strained cyclopropene nor undergo β-elimination. This should allow its interception by Me_2Zn. The key precursor carbonate **18** was easily prepared by dipropargylation of $TsNH_2$ to give dialkyne **17**, followed by monoalkylation with acetone and protection of the resulting tertiary alcohol as its carbonate. Now the stage was set to test the crucial Pd-catalysed cyclisation. Thus, the carbonate **18** was treated with the $[Pd_2(dba)_3]$/tri-(2-furyl)phosphine-catalyst system in the presence of Me_2Zn and gave the 1,3,5-triene **22** in 82% yield (*Scheme 8*).

The formation of **22** can be explained by the interception of a vinylpalladium intermediate such as **20** with Me_2Zn. The resulting triene **21** is now ideally positioned for a [1,5]-H-shift and gives *in situ* the more stable 1,3,5-triene **22**. We then looked at the possibility of transfer of chirality by using chiral propargylic carbonates. To study this idea, we prepared precursors **23**, **24** and **25** (*Scheme 9*).



a) LiHMDS, acetone, THF, −78°. b) LiHMDS, MeOC(O)Cl, THF, −78°. c) $[Pd_2(dba)_3]$ (0.025 equiv.), P(2-furyl)$_3$ (0.2 equiv.), $ZnMe_2$, Et_2O, reflux, 20 h.

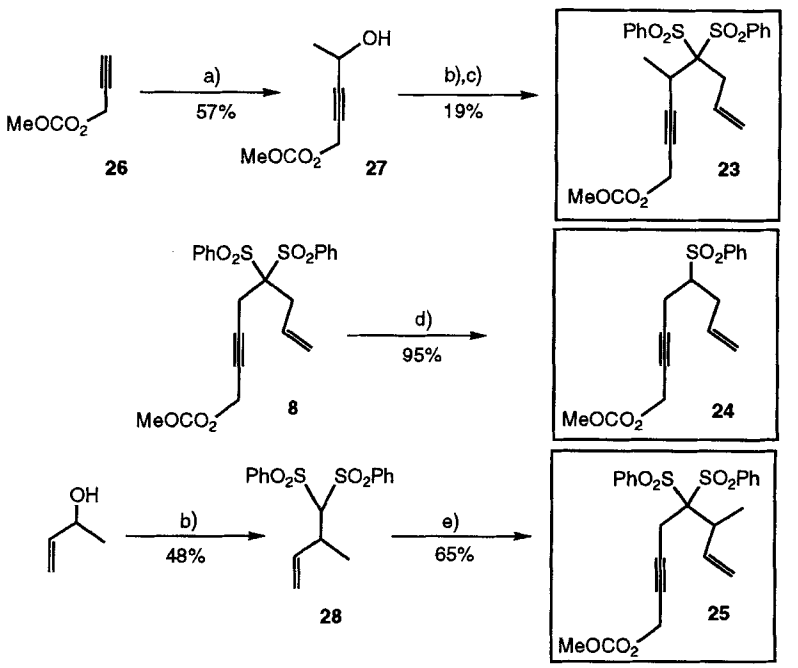
Trapping of the anion of propargyl carbonate **26** with MeCHO [13] gave alcohol **27**. *Mitsunobu* reaction of **27** with methylene bis-sulfone [14] followed by allylation afforded olefinic propargylic carbonate **23** in 19% overall yield. Al/Hg Reduction of the previously prepared bissulfone **8** gave olefinic propargylic carbonate **24** in 95% yield [5]. Finally, *Mitsunobu* reaction of but-3-en-2-ol with methylene bis-sulfone gave products from both the S_N2 (**28**) and S_N2' reaction (3:2 ratio). The S_N2 product **28** was propargylated with bromide **9** to leave olefinic propargylic carbonate **25** in 31% overall yield.

We examined the ring closure of these olefinic propargylic carbonates **23**–**25** under the Me_2Zn trapping protocol (*Scheme 10*). Pd-Catalysed cyclisation of carbonate **23** gave a modest 3:1 ratio of diastereoisomers, which was simply crystallised to leave the pure *cis*-isomer **29** in 54% yield. Carbonate **24** again afforded a 3:1 mixture of diastereoisomers **30** (configuration not determined). We were pleased to note, however, that cyclisation of carbonate **25** product exclusively diastereoisomer **31** in which the isopropenyl and the Me group are in a *cis*-relationship, in 83% yield. Bicyclo[3.1.0]hexanes **29** and **31** exhibited a strong NOE between H_a and H_b.

We propose that the excellent stereocontrol in the formation of **31** arises from the difference in the energies between transition states **A** and **B**. The *exo*-transition state **B** suffers two 1,3-pseudoaxial interactions as compared to only one in the favoured *endo*-transition state **A**. Thus, the C(4) stereogenic center controls the configuration at C(5) in the primary insertion product, which in turn dictates the configuration at C(1) in the second insertion product.

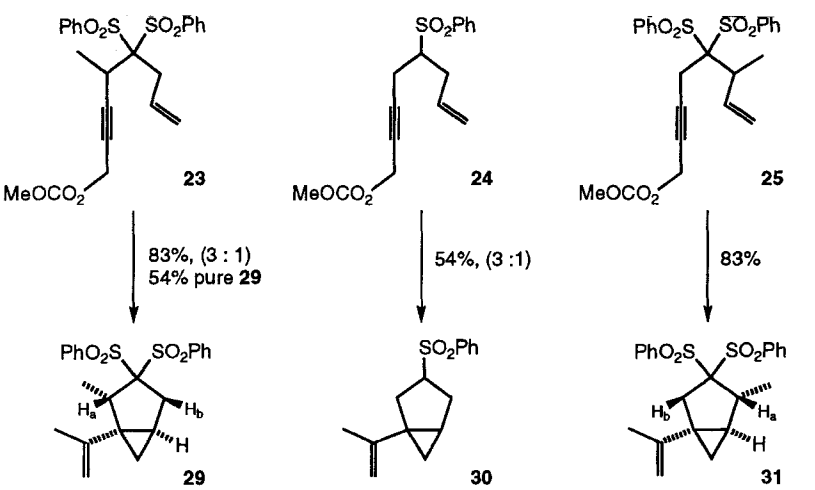
Finally, we looked at exploiting the high topological control in the Pd-catalysed cyclisation of olefinic propargylic carbonate **25** in the first enantiospecific synthesis of (1*S*,4*R*,5*R*)-1-isopropyl-4-methylbicyclo[3.1.0]hexan-3-one, *i.e.*, (−)-α-thujone **40** [15].

Scheme 9

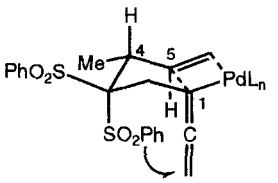


a) LiHMDS, acetaldehyde, THF, −78°. b) PPh_3, $EtO_2CN{=}C{=}NCO_2Et$, $CH_2(SO_2Ph)_2$. c) NaH, allyl bromide, DMF, 55°. d) Al/Hg, THF/H_2O. e) NaH, propargyl bromide **9**.

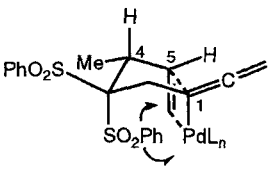
Scheme 10



Conditions: $[Pd_2(dba)_3]$ (0.025 equiv.), P(2-furyl)$_3$ (0.1 equiv.), $ZnMe_2$ (3 equiv.), Et_2O, reflux.



A *endo*-favoured

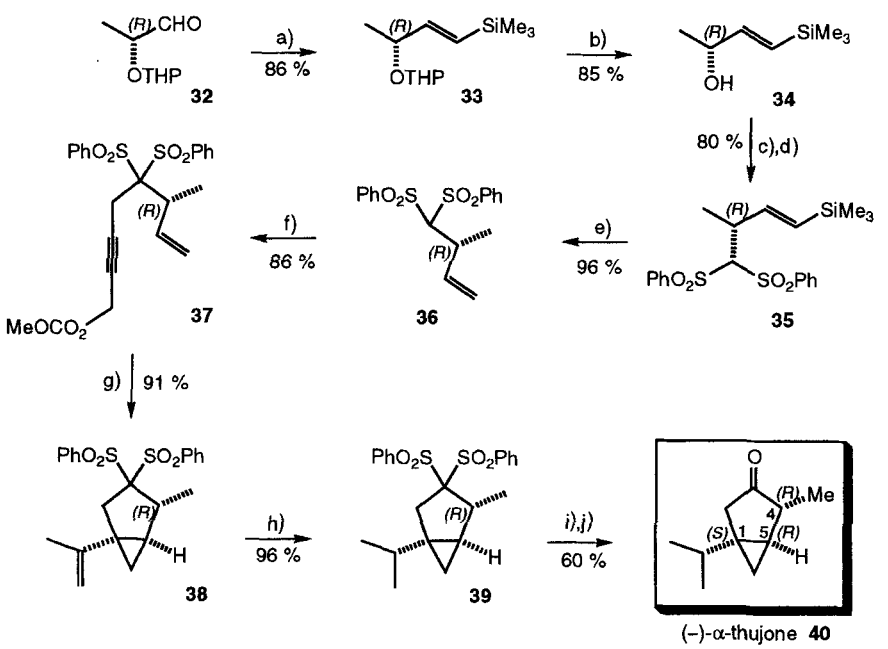


B *exo*-disfavoured

Thujone is a naturally occurring bicyclic monoterpenoid, comprised of two difficult to separate stereoisomers, α- and β-thujone [16]. The proportion of α/β-thujone depends upon the source from which it is isolated (*e.g.*, *Thuja occidentalis*, 77%:9% mixture, *Tanacetum vulgare* L., 4%:60%).

Our synthesis started with the known (+)-(*R*)-2-(tetrahydropyran-2-yloxy)propanal (**32**) (*Scheme 11*) [17]. *Takai* olefination with $Me_3SiCHBr_2/CrCl_2$ [18] gave tetrahydropyran-2-yl-protected allyl alcohol **33**, which was hydrolysed to leave allyl alcohol **34** in 73% overall yield. Alcohol **34** was carbonylated with methyl chloroformate, and the resulting allyl carbonate was displaced regiospecifically with methylene bis-sulfone under Pd catalysis with retention of configuration to leave vinylsilane **35** (80% yield) [19]. The Me_3Si moiety, used to direct the introduction of the methylene bissulfone, was removed with

Scheme 11



a) $CrCl_2$, $CHBr_2TMS$, THF. b) TsOH, MeOH. c) MeOC(O)Cl, Py, CH_2Cl_2, 0°. d) $[Pd_2(dba)_3]$, 1,2-bis(diphenylphosphino)ethane, $(PhSO_2)_2CHNa$, THF. e) $TsOH.H_2O$, MeCN, reflux. f) Propargyl bromide **9**, K_2CO_3, DMF, 60°. g) $[Pd_2(dba)_3]$, Me_2Zn, Et_2O, reflux. h) PtO_2 H_2 AcOEt, AcOH, 50°. i) Al/Hg, THF, H_2O, j) LDA, MoOPh, THF, −78°.

TsOH in MeCN to give bis-sulfone **36**, which was alkylated with propargyl bromide **9** to leave the cyclisation precursor **37** in 86% yield. The key stereospecific Pd-catalysed cyclisation/cross-coupling of carbonate **37** with Me_2Zn in refluxing Et_2O gave bicyclo[3.1.0]hexane **38** in an excellent 91% yield. An NOE analysis of **38** shows that the isopropenyl and Me group have the desired *cis*-relationship. The alkene was hydrogenated over Pt at 50° to introduce the i-Pr moiety of bicyclohexane **39** in 96% yield. Cleavage of one sulfone group with Al/Hg [5] yielded a mixture of C(3)-epimers (2.6:1), which were oxidised with MoOPh [20] to the desired (−)-α-thujone (**40**) in 60% isolated yield. ^{1}H-NMR, ^{13}C-NMR, IR, MS, $[\alpha]_D^{19.5}$ were comparable with authentic material. GC analysis with a chiral column (*Lipodex E*) indicates an e.e. > 99.2%.

In summary, the Pd-catalysed intramolecular cyclisations of olefinic propargylic carbonates afford intermediate palladium(alkenyl)bicyclo[3.1.0]hexanes, which can be trapped by hydride donor or carbonylated or cross-coupled with organometallic reagents. The potential of the tandem double cyclisation/cross-coupling is demonstrated by its application towards the first enantiospecific synthesis of (−)-α-thujone **40**.

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Experimental Part

General. All reactions were carried out under Ar with magnetic stirring, unless otherwise specified. Solvents are dried by distillation from drying agents as follows: Et_2O, THF and toluene (Na), CH_2Cl_2 and DMF (CaH_2), acetone (K_2CO_3). $Me_3SiCHBr_2$ [21], and MoOPh [20] were synthesised according to lit. methods. Workup denotes: Water was added, the mixture was extracted with Et_2O (dried on $MgSO_4$) and concentrated *in vacuo*; unless otherwise specified. Flash column chromatography (FC): SiO_2 (*Merck 9385*); M.p.: *Kofler* hot stage: uncorrected. $[\alpha]_D$: *Perkin-Elmer 241* polarimeter. IR: *Matteson Instruments Polaris* FT spectrometer, in $CHCl_3$ unless otherwise specified (cm^{-1}). NMR: *Bruker AMX 400*; ^{1}H-NMR at 400 MHz in $CDCl_3$, *J* in Hz, standard TMS ($\delta = 0$ ppm) and $CHCl_3$ ($\delta = 7.27$ ppm); ^{13}C-NMR at 100 MHz in $CDCl_3$, unless otherwise specified. MS: *Varian CH-4* or *Finnigan 4023* at 70 eV, *m/z* (rel.-%). HR-MS: *VG 7070-E*.

*4-Methyl-*N*-(prop-2-enyl)-*N*-(prop-2-ynyl)benzenesulfonamide* (**3**). To *4-methyl-*N*-(prop-2-enyl)benzenesulfonamide* (**1**, 1.50 g, 7.17 mmol) in DMF (10 ml) was added NaH (55% suspension in oil, 400 mg, 9.17 mmol), and the mixture was stirred at r.t. for 30 min. Propargyl bromide (1.0 ml, 11.82 mmol) was added and the mixture stirred for 1 h. Workup and FC eluting with Et_2O/hexane 1:5 gave **3** (1.72 g, 96%). M.p. 62–63° (Et_2O/pentane). IR: 3307, 3025, 2926, 1763, 1720, 1598, 1443, 1348, 1162. ^{1}H-NMR: 2.00(*t*, *J* = 2, 1 H); 2.43(*s*, 3 H); 3.83(*d*, *J* = 6.5, 2 H); 4.09(*d*, *J* = 2, 2 H); 5.23(*dm*, *J* = 10, 1 H); 5.29(*dm*, *J* = 17, 1 H); 5.72(*ddt*, *J* = 17, 10, 6.5, 1 H); 7.29 (*d*, *J* = 8, 2 H); 7.73 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.5(*s*); 136.4(*s*); 131.9(*d*); 129.5(2*d*); 27.8(2*d*); 119.9(*t*); 77.0(*s*); 73.6(*s*); 49.0(*t*); 35.8(*t*); 21.5(*q*). MS: 249(2, $[C_{13}H_{15}NO_2S]^+$), 184(7), 155(23), 139(6), 94(93), 91(100), 67(41), 65(55), 54(10).

N-*Allyl-4-methyl-*N*-[4-methyl-4-(methoxycarbonyloxy)pent-2-yn-1-yl]benzenesulfonamide* (**5**). To **3** (500 mg, 2.01 mmol) in THF (4 ml) at −79° was added LiHMDS (1.0M in THF, 2.3 ml, 2.3 mmol). After 1 h, dry acetone (0.15 ml, 2.04 mmol) was added followed 15 min later by methyl chloroformate (0.25 ml, 3.25 mmol). The mixture was warmed to r.t. and stirred for 1 h. Workup and FC (Et_2O/hexane 1:2) gave **5** (650 mg, 89%). M.p. 52–53°. IR: 3026, 2992, 2957, 2853, 1752, 1599, 1495, 1348, 1162. ^{1}H-NMR: 1.43(*s*, 6 H); 2.42(*s*, 3 H); 3.72(*s*, 3 H); 3.83(*d*, *J* = 6.5, 2 H); 4.14(*s*, 2 H); 5.23(*dd*, *J* = 10, 1, 1 H); 5.32(*dd*, *J* = 17, 1, 1 H); 5.74(*ddt*, *J* = 17, 10, 6.5, 1 H); 7.29(*d*, *J* = 8, 2 H); 7.72(*d*, *J* = 8, 2 H). ^{13}C-NMR: 153.3(*s*); 143.4(*s*); 136.2(*s*); 132.0(*d*); 129.5(2*d*); 127.7(2*d*); 119.9(*t*); 88.1(*s*); 77.5(*s*); 73.7(*s*); 54.2(*q*); 48.9(*t*); 36.0(*t*); 28.5(2*q*). MS: 365(1, $C_{18}H_{23}NO_5S^{+\cdot}$), 290(40), 224(7), 210(14), 184(4), 155 (15), 139(10), 134(100), 107(37), 94(19), 91(70), 80(49), 77(15), 65(37), 59(21), 53(17). HR-MS: 290.1205($[C_{18}H_{23}NO_5S - C_2H_3O_3]^{+\cdot}$; calc. 290.1215).

4,4-Bis(phenylsulfonyl)hept-1-en-6-yne (**4**). To *1,1-bis(phenylsulfonyl)but-3-ene* (**2**; 0.83 g, 2.47 mmol) in DMF (5 ml) at + 5° was added NaH (55% in oil, 113 mg, 2.6 mmol) portionwise, and the mixture was stirred

for 1 h. Propargyl bromide (0.21 ml, 2.8 mmol) was added and the mixture stirred for 1 h. Workup and FC (Et_2O/hexane 1:1) gave **4** (0.67 g, 72%). M.P. 148–149° (EtOH). IR: 3307, 3072, 3026, 1638, 1584, 1478, 1448, 1435, 1334, 1313, 1227, 1149, 1077, 1000, 932, 838. ^{1}H-NMR: 2.09 (*t*, *J* = 3, 1 H); 3.11 (*d*, *J* = 7, 2 H); 3.18 (*d*, *J* = 3, 2 H); 5.31 (*dd*, *J* = 10, 2, 1 H); 5.32 (*dd*, *J* = 17, 2, H); 6.08 (*dd*, *J* = 17, 10, 7, 1 H); 7.59 (*dd*, *J* = 7, 7, 4 H); 7.72 (*dd*, *J* = 7, 7, 2 H); 8.12 (*d*, *J* = 7, 4 H). ^{13}C-NMR: 136.5 (*s*); 134.8 (2*d*); 131.7 (4*d*); 129.5 (*d*); 128.6 (4*d*); 121.2 (*t*); 88.8 (*s*); 75.8 (*d*); 74.4 (*s*); 33.3 (*t*); 20.8 (*t*). MS: 375 (2, $[C_{19}H_{18}O_4S_2]^{+\cdot}$), 233 (11), 141 (15), 125 (20), 97 (12), 91 (45), 79 (10), 78 (16), 77 (100), 65 (25), 51 (50). HR-MS: 374.0648 ($[C_{19}H_{18}O_4S_2]^{+\cdot}$; calc. 374.0647).

4,4-Bis(phenylsulfonyl)-8-methyl-8-(methoxycarbonyloxy)non-1-en-6-yne (**6**). Following the procedure for **5**, **4** (680 mg, 1.82 mmol) was treated sequentially with LiHMDS (1.0M in THF, 2.91 ml, 2.91 mmol), acetone (0.21 ml, 2.91 mmol) and methyl chloroformate (0.28 ml, 3.63 mmol). Workup and FC (Et_2O/hexane 1:1) gave **6** (0.80 g, 90%). M.p. 80–82° (MeOH). IR: 3029, 2992, 2956, 1753, 1584, 1448, 1333, 1312, 1289, 1193, 1149, 1099, 1078, 1000, 949. ^{1}H-NMR: 1.63 (*s*, 6 H); 3.11 (*d*, *J* = 7, 2 H); 3.18 (*s*, 2 H); 3.75 (*s*, 3 H); 5.31 (*dd*, *J* = 17, 2, 1 H); 5.34 (*dd*, *J* = 10, 2, 1 H); 6.18 (*ddt*, *J* = 17, 10, 7, 1 H); 7.59 (*dd*, *J* = 7, 7, 4 H); 7.71 (*dd*, *J* = 7, 7, 2 H); 8.13 (*d*, *J* = 7, 4 H). ^{13}C-NMR: 153.5 (*s*); 136.6 (*s*); 134.7 (2*d*); 131.6 (4*d*); 129.7 (2*d*); 128.6 (2*d*); 121.0 (*t*); 89.1 (*s*); 86.3 (*s*); 76.9 (*s*); 74.1 (*s*); 54.3 (*q*); 33.1 (*t*); 28.6 (2*q*); 21.0 (*t*). MS: 415 (1, $[C_{24}H_{26}O_7S_2 - C_2H_3O_3]^{+\cdot}$), 272 (12), 147 (10), 132 (19), 131 (56), 125 (54), 117 (14), 166 (11), 115 (16), 105 (17), 97 (12), 91 (39), 79 (18), 78 (19), 77 (100), 65 (17). HR-MS: 415.1119 ($[C_{24}H_{26}O_7S_2 - C_2H_3O_3]^{+\cdot}$; calc. 415.1137).

4-Methyl-N-(prop-2-enyl)-N-[4-(methoxycarbonyloxy)but-2-yn-1-yl]benzenesulfonamide (**7**). NaH (55% in oil, 0.37 g, 8.48 mmol) was added to a soln. of **1** (1.50 g, 7.09 mmol) in DMF (30 ml), and the mixture was stirred at r.t. for 30 min. *1-Bromo-4-(methoxycarbonyloxy)but-2-yne* (**9**; 1.80 g, 8.70 mmol) was added, and the mixture was stirred for 30 min. Workup and FC (hexane/AcOEt 4:1) gave **7** (2.20 g, 92%). M.p. 50° (Et_2O/pentane). IR: 3025, 3011, 2958, 2859, 1753, 1598, 1445, 1374, 1162. ^{1}H-NMR: 2.43 (*s*, 3 H); 3.79 (*s*, 2 H); 3.80 (*s*, 3 H); 4.12 (*t*, *J* = 1.5, 2 H); 4.44 (*t*, *J* = 2, 2 H); 5.23 (*dm*, *J* = 10, 1 H); 5.28 (*dm*, *J* = 17, 1 H); 5.73 (*ddt*, *J* = 17, 10, 6, 1 H); 7.30 (*d*, *J* = 8, 2 H); 7.73 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 155.5 (*s*); 143.6 (*s*); 135.9 (*s*); 131.9 (*d*); 129.5 (2*d*); 127.8 (2*d*); 120.0 (*t*); 80.4 (*s*); 79.0 (*s*); 55.2 (*q* and *t*); 49.2 (*t*); 36.9 (*t*); 21.4 (*q*). MS: 338 (3, $[C_{16}H_{19}NO_5S + H]^{+\cdot}$), 262 (21), 182 (54), 155 (21), 139 (19), 106 (85), 91 (100), 79 (43), 65 (41). HR-MS: 262.0872 ($[C_{16}H_{19}NO_5S - C_2H_3O_3]^{+\cdot}$; calc. 262.0902).

4,4-Bis(phenylsulfonyl)-8-(methoxycarbonyloxy)oct-1-en-6-yne (**8**). Following the procedure for **7**, **2** (0.67 g, 2.00 mmol) in DMF (4 ml) was treated sequentially with NaH (55% in oil, 89 mg, 2.05 mmol) and **9** (400 mg, 1.93 mmol). Workup and FC (Et_2O/hexane 1:1) gave **8** (0.82 g, 89%). M.p. 80–81° (MeOH). IR: 3029, 2958, 1753, 1638, 1584, 1447, 1374, 1334, 1312, 1275, 1226, 1206, 1150, 1077, 955. ^{1}H-NMR: 3.06 (*d*, *J* = 7, 2 H); 3.23 (*t*, *J* = 2, 2 H); 3.81 (*s*, 2 H); 4.55 (*t*, *J* = 2, 2 H); 5.25–5.34 (*m*, 2 H); 6.06 (*ddt*, *J* = 17, 10, 7, 1 H); 7.59 (*dd*, *J* = 7, 7, 4 H); 7.71 (*dd*, *J* = 7, 7, 2 H); 8.10 (*d*, *J* = 7, 4 H). ^{13}C-NMR: 155.1 (*s*); 136.7 (2*s*); 134.8 (2*d*); 131.6 (4*d*); 129.5 (*d*); 128.6 (4*d*); 121.1 (*t*); 88.8 (*s*); 79.8 (*s*); 79.4 (*s*); 55.5 (*t*); 55.1 (*q*); 33.7 (*t*); 21.2 (*t*). MS: 463 (1, $[C_{22}H_{22}O_7S_2 + H]^{+\cdot}$), 387 (11), 125 (43), 104 (12), 103 (34), 97 (11), 91 (16), 79 (17), 78 (19), 77 (100), 59 (14). HR-MS: 462.0836 ($[C_{22}H_{22}O_7S_2]^{+\cdot}$; calc. 462.0807).

3-(4-Methylphenylsulfonyl)-1-(2-methylprop-1-en-1-yl)-3-azabicyclo[3.1.0]hexane (**10**). Carbonate **5** (105 mg, 0.29 mmol), $[Pd_2(dba)_3]$ (16 mg, 0.028 mmol) and PPh_3 (32 mg, 0.12 mmol) were dissolved in glacial acetic acid (2 ml) under Ar and stirred at 80° for 1 h. Evaporation of the solvent and FC (hexane/AcOEt 50:1) gave **10** (13 mg, 15%). IR: 2927, 2855, 1652, 1622, 1598, 1495, 1450, 1377, 1344, 1164, 1105, 1028, 815. ^{1}H-NMR: 0.68 (*dd*, *J* = 8, 5, 1 H); 0.82 (*dd*, *J* = 5, 4, 1 H); 1.27 (*ddd*, *J* = 8, 4, 4, 1 H); 1.62 (*dd*, *J* = 5, 1, 6 H); 2.44 (*s*, 3 H); 2.84 (*d*, *J* = 9, 1 H); 3.11 (*dd*, *J* = 9, 4, 1 H); 3.52 (*d*, *J* = 9, 1 H); 3.57 (*d*, *J* = 9, 1 H); 5.16 (*s*, 1 H); 7.32 (*d*, *J* = 8, 2 H); 7.67 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.3 (*s*); 138.9 (*s*); 129.5 (2*d*); 128.8 (*s*); 127.6 (2*d*); 122.0 (*d*); 53.2 (*t*); 50.0 (*t*); 26.3 (*s*); 25.3 (*q*); 23.1 (*d*); 21.5 (*q*); 18.9 (*q*); 15.3 (*t*). MS: 292 (21, $[C_{16}H_{21}NO_2S + H]^{+\cdot}$), 235 (11), 234 (10), 136 (40), 135 (27), 120 (15), 111 (18), 109 (49), 108 (94), 107 (14), 103 (10), 99 (11), 97 (27), 96 (11), 95 (16), 94 (24), 93 (97), 91 (58). HR-MS: 291.1286 ($[C_{16}H_{21}NO_2S]^{+\cdot}$; calc. 291.1293).

General Catalyst Formation. Tris(dibenzylideneacetone)dipalladium ($[Pd_2(dba)_3]$; 3.8 mg, 0.0041 mmol, 0.025 mol-equiv.), and tri(2-furyl)phosphine (3.8 mg, 0.016 mmol, 0.1 mol-equiv.) or PPh_3 (4.2 mg, 0.016 mmol, 0.1 mol-equiv.) or $AsPh_3$ (4.9 mg, 0.016 mmol, 0.1 mol-equiv). were stirred in degassed Et_2O or AcOH (2 ml) at r.t. for 0.5 h to form a homogeneous yellow catalyst. For catalyst formation in degassed MeOH or i-PrOH (4 ml), a time of 1–2 h was required, and the catalyst was orange coloured.

Methyl 2-[3-(4-Methylphenylsulfonyl)-3-azabicyclo[3.1.0]hex-1-yl]prop-2-enoate (**11a**). Carbonate **7** (150 mg, 0.45 mmol) was stirred with the $[Pd_2(dba)_3]$/PPh_3/AcOH catalyst system under 1 atm of CO gas at 45° for 4 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (2 ml), cooled to 0° and treated with excess CH_2N_2 soln. in Et_2O. Evaporation of the solvent and FC (Et_2O/hexane 1:1) afforded **11a** (22 mg, 10%).

M.p. 123–124° (Et_2O/pentane). IR: 3024, 3016, 2953, 2862, 1721, 1598, 1438, 1346, 1165. ^{1}H-NMR: 0.87 (*m*, 2 H); 1.61 (*dt*, *J* = 7.5, 4.5, 1 H); 2.44 (*s*, 3 H); 3.08 (*d*, *J* = 9, 1 H); 3.23 (*dd*, *J* = 9, 4, 1 H); 3.58 (*d*, *J* = 9, 1 H); 3.60 (*s*, 3 H); 3.64 (*d*, *J* = 9, 1 H); 5.59 (*d*, *J* = 1, 1 H); 6.22 (*d*, *J* = 1, 1 H); 7.33 (*d*, *J* = 8, 2 H); 7.68 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 166.3 (*s*); 143.5 (*s*); 139.1 (*s*); 133.7 (*s*); 129.6 (2*d*); 127.6 (2*d*); 127.6 (*t*); 52.9 (*t*); 51.8 (*q*); 49.9 (*t*); 29.6 (*s*); 23.1 (*d*); 21.5 (*q*); 14.8 (*t*). MS: 321 (1, $[C_{16}H_{19}NO_4S]^{+\cdot}$), 166 (100), 155 (11), 134 (16), 106 (58), 91 (50), 79 (30), 77 (13), 65 (14). HR-MS: 321.1052 ($[C_{16}H_{19}NO_4S]^{+\cdot}$; calc. 321.1035).

Methyl 3-Methyl-2-[3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]hex-1-yl]but-2-enoate (**11b**). Carbonate **5** (63 mg, 0.17 mmol) was stirred with the $[Pd_2(dba)_3]$/PPh_3/AcOH catalyst system under 1 atm of CO gas at 45° for 1 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (2 ml), cooled to 0° and treated with excess CH_2N_2 soln. Et_2O. Evaporation of the solvent and FC (Et_2O/hexane 1:1) afforded **11b** (39 mg, 65%). M.p. 120–122° (Et_2O/pentane). IR: 3024, 3016, 2950, 2863, 1712, 1598, 1435, 1345, 1165. ^{1}H-NMR: 0.73 (*dd*, *J* = 8, 5 H); 0.97 (*dd*, *J* = 5, 4, 1 H); 1.34 (*dt*, *J* = 8, 4, 1 H); 1.85 (*s*, 3 H); 1.95 (*s*, 3 H); 2.44 (*s*, 3 H); 3.03 (*d*, *J* = 9, 1 H); 3.16 (*dd*, *J* = 9, 4, 1 H); 3.46 (*s*, 3 H); 3.55 (*d*, *J* = 9, 1 H); 3.60 (*d*, *J* = 9, 1 H); 7.34 (*d*, *J* = 8, 2 H); 7.69 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 166.8 (*s*); 150.4 (*s*); 143.4 (*s*); 133.2 (*s*); 129.5 (2*d*); 127.7 (2*d*); 125.3 (*s*); 53.1 (*t*); 50.9 (*q*); 50.1 (*t*); 27.6 (*s*); 24.3 (*d*); 22.8 (*q*); 22.6 (*q*); 21.5 (*q*); 16.6 (*t*). MS: 349 (1, $[C_{18}H_{23}NO_4S]^{+\cdot}$), 318 (3), 194 (65), 162 (37), 155 (8), 134 (78), 119 (11), 107 (38), 91 (100), 79 (21), 77 (21), 65 (45), 59 (12). HR-MS: 349.1348 ($[C_{18}H_{23}NO_4S]^{+\cdot}$; calc. 349.1348).

Compound **11a**. Carbonate **7** (30 mg, 0.082 mmol) was stirred with the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/MeOH catalyst system under 1 atm of CO gas at r.t. for 1 h. Workup and FC eluting with Et_2O/hexane 1:1 gave **11a** (27 mg, 93%). For spectral data, see **11a** above.

Compound **11b**. Carbonate **5** (30 mg, 0.08 mmol) was stirred with the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/MeOH catalyst system under 1 atm of CO gas at r.t. for 1 h. Workup and FC eluting with Et_2O/hexane 1:1 gave **11b** (26 mg, 93%). For spectral data, see **11b** above.

Methyl 2-[3,3-Bis(phenylsulfonyl)bicyclo[3.1.0]hex-1-yl]prop-2-enoate (**11c**). Carbonate **8** (30 mg, 0.045 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/MeOH catalyst system was stirred under 1 atm of CO gas at r.t. for 3 h. Workup and FC (Et_2O/hexane 1:1) gave **11c** (20 mg, 70%). IR: 2952, 1720, 1448, 1327, 1311, 1226, 1219, 1147, 1079, 909. ^{1}H-NMR: 0.79 (*dd*, *J* = 8, 4, 1 H); 1.04 (*dd*, *J* = 4, 4, 1 H); 1.77 (*m*, 1 H); 2.71 (*dd*, *J* = 16, 16, 2 H); 3.09 (*dd*, *J* = 16, 7, 1 H); 3.12 (*d*, *J* = 16, 1 H); 3.79 (*s*, 3 H); 5.23 (*s*, 1 H); 6.00 (*s*, 1 H); 7.55–7.63 (*m*, 4 H); 7.65–7.74 (*m*, 2 H); 7.95–8.06 (*m*, 4 H). ^{13}C-NMR: 166.9 (*s*); 140.9 (*s*); 137.3 (*s*); 136.2 (*s*); 134.6 (*d*); 134.5 (*d*); 131.7 (2*d*); 131.3 (2*d*); 128.9 (2*d*); 128.8 (2*d*); 124.8 (*t*); 97.6 (*s*); 51.9 (*q*); 40.0 (*t*); 35.7 (*t*); 34.0 (*s*); 25.5 (*d*); 24.5 (*t*). MS: 447 (10, $[C_{22}H_{22}O_6S_2 + H]^{+\cdot}$), 243 (11), 163 (20), 131 (18), 125 (41), 104 (22), 103 (85), 97 (13), 91 (16), 85 (19), 82 (28), 79 (16), 78 (26), 77 (100). HR-MS: 447.0927 ($[C_{22}H_{22}O_6S_2 + H]^{+\cdot}$; calc. 447.0934).

Methyl 2-[3,3-Bis(phenylsulfonyl)bicyclo[3.1.0]hex-1-yl]-3-methylbut-2-enoate (**11d**). Carbonate **6** (56 mg, 0.12 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/MeOH catalyst system was stirred under 1 atm of CO gas at r.t. for 20 h. Workup and FC (Et_2O/hexane 1:1) gave **11d** (39 mg, 70%). M.p. 124–125° (MeOH). IR: 3020, 2951, 1712, 1585, 1448, 1434, 1311, 1232, 1146, 1079. ^{1}H-NMR: 0.88 (*dd*, *J* = 8, 4, 1 H); 1.45 (*dd*, *J* = 5, 5, 1 H); 1.85 (*s*, 3 H); 1.90 (*s*, 3 H); 1.84–1.89 (*m*, 1 H); 2.50 (*d*, *J* = 16, 1 H); 2.88 (*d*, *J* = 16, 1 H); 2.98 (*d*, *J* = 16, 1 H); 3.20 (*dd*, *J* = 16, 6, 1 H); 3.79 (*s*, 3 H); 7.60 (*dd*, *J* = 8, 8, 4 H); 7.71 (*dd*, *J* = 8, 8, 2 H); 8.02 (*d*, *J* = 7, 2 H); 8.12 (*d*, *J* = 7, 2 H). ^{13}C-NMR: 169.9 (*s*); 143.7 (*s*); 136.7 (*s*); 136.6 (*s*); 134.5 (*d*); 134.4 (*d*); 131.9 (2*d*); 131.4 (2*d*); 128.8 (*s*); 128.6 (2*d*); 128.5 (2*d*); 97.3 (*s*); 51.1 (*q*); 40.0 (*t*); 35.4 (*t*); 32.1 (*s*); 27.0 (*d*); 22.5 (*q*); 21.7 (*t*); 21.6 (*q*). MS: 475 (3, $[C_{24}H_{26}O_6S_2]^{+\cdot}$), 443 (22), 442 (16), 273 (11), 272 (22), 191 (11), 159 (44), 132 (25), 131 (100), 130 (15), 129 (14), 125 (13), 117 (24), 116 (17), 115 (24), 105 (13), 97 (12), 91 (50), 79 (13), 78 (18), 77 (88), 73 (29), 65 (13). HR-MS: 475.1256 ($[C_{24}H_{26}O_6S_2]^{+\cdot}$; calc. 475.1250).

1-(1-Methylethenyl)-3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (**12a**). Me_2Zn (2M in toluene; 0.14 ml, 0.28 mmol) was added to **7** (30 mg, 0.09 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system and the whole was stirred at 34° for 12 h. Workup and FC (Et_2O/hexane 1:6) gave **12a** (15 mg, 58%). IR: 3026, 2928, 2859, 1634, 1598, 1448, 1345, 1164, 1107, 1030, 1012, 884, 814. ^{1}H-NMR: 0.80 (*dd*, *J* = 5, 5, 1 H); 0.85 (*dd*, *J* = 8, 5, 1 H); 1.56 (*ddd*, *J* = 8, 4, 4, 1 H); 1.57 (*s*, 3 H); 2.44 (*s*, 3 H); 3.07 (*dd*, *J* = 9, 4, 1 H); 3.11 (*d*, *J* = 9, 1 H); 3.56 (*d*, *J* = 9, 1 H); 3.60 (*d*, *J* = 9, 1 H); 4.66 (*s*, 1 H); 4.78 (*s*, 1 H); 7.33 (*d*, *J* = 8, 2 H); 7.69 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.5 (*s*); 143.1 (*s*); 133.5 (*s*); 129.6 (2*d*); 127.6 (2*d*); 110.6 (*t*); 51.8 (*t*); 49.9 (*t*); 32.7 (*s*); 21.9 (*q*); 21.5 (*d*); 20.6 (*q*); 13.9 (*t*). MS: 278 (17, $[C_{15}H_{19}NO_2S + H]^{+\cdot}$), 277 (14, $[C_{15}H_{19}NO_2S]^{+\cdot}$), 155 (12), 122 (84), 121 (69), 120 (25), 107 (14), 106 (23), 95 (100), 94 (72), 93 (27), 92 (12), 91 (78), 81 (21), 80 (30), 79 (83), 77 (24), 67 (35), 65 (42). HR-MS: 277.1136 ($[C_{15}H_{19}NO_2S]^{+\cdot}$; calc. 277.1136).

1-(1,2-Dimethylprop-1-enyl)-3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (**12b**). Me_2Zn (2M in toluene; 0.21 ml, 0.42 mmol) was added to **5** (50 mg, 0.14 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system and the whole was stirred at 34° for 3 h. Workup and FC (Et_2O/hexane 1:6) gave **12b** (30 mg, 85%). IR: 3020,

2925, 1343, 1224, 1164, 1098, 1030, 929, 792. ^{1}H-NMR: 0.67 (*dd*, *J* = 8, 5, 1 H); 0.81 (*dd*, *J* = 4, 4, 1 H); 1.35 (*ddd*, *J* = 8, 4, 4, 1 H); 1.52 (*s*, 3 H); 1.62 (*d*, *J* = 1, 3 H); 2.42 (*d*, *J* = 10, 2 H); 2.84 (*d*, *J* = 10, 2 H); 3.15 (*dd*, *J* = 9, 4, 1 H); 3.52 (*d*, *J* = 10, 1 H); 3.54 (*d*, *J* = 9, 1 H); 7.32 (*d*, *J* = 8, 2 H); 7.67 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.3 (*s*); 131.5 (*s*); 129.5 (2*d*); 128.4 (*s*); 127.2 (2*d*); 124.3 (*s*); 52.3 (*t*); 50.3 (*t*); 32.0 (*s*); 22.7 8*q*); 21.5 (*d*); 21.0 (*q*); 20.6 (*q*); 17.5 (*q*); 16.0 (*t*). MS: 305 (6, $[C_{17}H_{23}NO_2S]^{+\cdot}$), 155 (12), 150 (46), 149 (13), 134 (18), 123, (23), 122 (72), 121 (20), 109 (14), 108 (26), 107 (100), 105 (10), 96 (13), 95 (11), 94 (14), 91 (66), 81 (23), 80 (12), 79 (18), 77 (17), 67 (17), 65 (26). HR-MS: 305.1457 ($[C_{17}H_{23}NO_2S]^{+\cdot}$; calc. 305.1450).

3,3-Bis(phenylsulfonyl)-1-(1-methylethenyl)bicyclo[3.1.0]hexane (**12c**). Me_2Zn (2M in toluene; 0.65 ml, 1.30 mmol) was added to **8** (200 mg, 0.43 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 3 h. Workup and FC (Et_2O/hexane 1:3) gave **12c** (101 mg, 58%). M.p. 45–46°. IR: 3009, 1585, 1448, 1331, 1311, 1145, 1078. ^{1}H-NMR: 0.86 (*dd*, *J* = 8, 4, 1 H); 0.93 (*dd*, *J* = 5, 4, 1 H); 1.15–1.57 (*m*, 1 H); 1.44 (*s*, 3 H); 2.65 (*d*, *J* = 16, 1 H); 2.88 (*d*, *J* = 16, 1 H); 2.98 (*d*, *J* = 16, 1 H); 3.01 (*dd*, *J* = 16, 6, 1 H); 4.56 (*s*, 1 H); 4.68 (*s*, 1 H); 7.56–7.64 (*m*, 4 H); 7.65–7.75 (*m*, 2 H); 8.01 (*d*, *J* = 8, 2 H); 8.07 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 144.9 (*s*); 137.3 (*s*); 136.1 (*s*); 134.6 (*d*); 134.4 (*d*); 131.6 (2*d*); 131.3 (2*d*); 128.8 (2*d*); 128.7 (2*d*); 110.3 (*t*); 97.4 (*s*); 38.5 (*t*); 37.3 (*s*); 35.9 (*t*); 25.8 (*q*); 21.6 (*t*); 20.2 (*d*). MS: 403 (1, $[C_{21}H_{22}O_4S_2]^{+\cdot}$), 261 (29), 260 (14), 259 (20), 125 (20), 120 (11), 119 (100), 118 (13), 117 (12), 105 (11), 91 (31), 79 (15), 78 (12), 77 (50). HR-MS: 402.1001 ($[C_{21}H_{22}O_4S_2]^{+\cdot}$; calc. 402.0960).

3,3-Bis(phenylsulfonyl)-1-(1,2-dimethylprop-1-enyl)bicyclo[3.1.0]hexane (**12d**). Me_2Zn (2M in toluene; 0.09 ml, 0.012 mmol) was added to **6** (30 mg, 0.061 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 7 h. Workup and FC (Et_2O/hexane 1:3) gave **12d** (22 mg, 85%). M.p. 111–112°. IR: 3020, 2924, 2859, 1584, 1478, 1448, 1373, 1325, 1310, 1145, 1078, 1024, 999, 956. ^{1}H-NMR: 0.71 (*dd*, *J* = 8, 4, 1 H); 0.88 (*dd*, *J* = 5, 4, 1 H); 1.15 (*m*, H); 1.55 (*s*, 3 H); 1.72 (*s*, 3 H); 1.73 (*s*, 3 H); 2.58 (*d*, *J* = 16, 1 H); 2.69 (*d*, *J* = 16, 1 H); 2.91 (*d*, *J* = 16, 1 H); 3.14 (*dd*, *J* = 16, 6, 1 H); 7.58–7.62 (*m*, 4 H); 7.69–7.73 (*m*, 2 H); 8.03–8.08 (*m*, 4 H). ^{13}C-NMR: 137.9 (*s*); 136.4 (*s*); 134.5 (*d*); 134.4 (*d*); 131.8 (2*d*); 131.4 (2*d*); 130.2 (*s*); 128.7 (2*d*); 128.6 (2*d*); 127.9 (*s*); 97.4 (*s*); 39.9 (*t*); 36.4 (*s*); 36.1 (*t*); 25.5 (*q*); 22.1 (*t*); 23.1 (*q*); 20.7 (*q*); 16.7 (*d*). MS: 430 (1, $[C_{23}H_{26}O_4S_2]^{+\cdot}$, 148 (14), 147 (100), 131 (11), 119 (14), 105 (19), 91 (18), 77 (30). HR-MS: 430.1273 ($[C_{23}H_{26}O_4S_2]^{+\cdot}$; calc. 430.1289).

1-(2-Methyl-1-phenylprop-1-en-1-yl)-3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]hexane (**13a**). BPh_3 (24 mg, 0.098 mmol) was added to **5** (30 mg, 0.082 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 12 h. Workup and FC (Et_2O/hexane 1:10) gave **13a** (23 mg, 77%). IR: 2925, 2855, 1598, 1492, 1441, 1347, 1166, 1094, 1029, 912, 814, 733, 703, 666. ^{1}H-NMR: 0.68 (*dd*, *J* = 8, 5, 1 H); 0.77 (*dd*, *J* = 5, 5, 1 H); 1.22 (*ddd*, *J* = 8, 4, 4, 1 H); 1.51 (*s*, 3 H); 1.78 (*s*, 3 H); 2.45 (*s*, 3 H); 3.11 (*dd*, *J* = 9, 4, 1 H); 3.14 (*d*, *J* = 9, 1 H); 3.47 (*d*, *J* = 9, 1 H); 3.73 (*d*, *J* = 9, 1 H); 6.81 (*dd*, *J* = 9, 1, 2 H); 7.12–7.22 (*m*, 3 H); 7.32 (*d*, *J* = 8, 2 H); 7.68 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.3 (*s*); 142.6 (*s*); 135.3 (*s*); 133.6 (*s*); 132.3 (*s*); 129.5 (2*d*); 128.5 (2*d*); 128.0 (2*d*); 127.5 (2*d*); 53.7 (*t*); 50.2 (*t*); 31.5 (*s*); 29.7 (*s*); 24.4 (*d*); 22.4 (*q*); 21.5 (*q*); 21.1 (*q*); 16.6 (*t*). MS: 367 (16, $[C_{22}H_{25}NO_2S]^{+\cdot}$), 367 (16), 212 (52), 211 (52), 196 (10), 185 (21), 184 (64), 183 (20), 170 (20), 169 (62), 155 (10), 143 (16), 141 (16), 129 (20), 128 (17), 105 (13), 92 (10), 91 (100), 77 (16), 65 (19), 55 (1). HR-MS: 367.1610 ($[C_{22}H_{25}NO_2S]^{+\cdot}$; calc. 367.1610).

1-[(E)-4,4-Dimethyl-1-(1-methylethylidene)pent-2-enyl]-3-(4-methylphenylsulfonyl)-3-azabicyclo[3.1.0]-hexane (**13b**). Tris(3,3-dimethylbut-1-en-1-yl)borane (synthesised *in situ* from 3,3-dimethylbut-1-yne (0.03 ml, 0.246 mmol) and boranedimethylsulphide complex (10M; 0.008 ml, 0.08 mmol), 0°, 1 h, Et_2O) was added to **5** (30 mg, 0.082 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 20 h. Workup and FC (Et_2O/hexane 1:10) gave **13b** (14 mg, 45%). M.p. 143–144°. IR: 3028, 2959, 2863, 1598, 1494, 1478, 1461, 1345, 1228, 1165, 1102, 1029, 970, 815. ^{1}H-NMR: 0.70 (*dd*, *J* = 8, 5, 1 H); 0.85 (*s*, 9 H); 0.99 (*dd*, *J* = 5, 5, 1 H); 1.38 (*ddd*, *J* = 4, 4, 4, 1 H); 1.74 (*s*, 3 H); 1.75 (*s*, 3 H); 2.41 (*s*, 3 H); 2.86 (*d*, *J* = 9, 1 H); 3.23 (*dd*, *J* = 9, 4, 1 H); 3.55 (*d*, *J* = 9, 1 H); 3.63 (*d*, *J* = 9, 1 H); 5.24 (*d*, *J* = 16, 1 H); 6.06 (*d*, *J* = 16, 1 H); 7.32 (*d*, *J* = 8, 2 H); 7.70 (*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.5 (*s*); 140.7 (*d*); 135.6 (*s*); 132.5 (*s*); 129.5 (2*d*); 128.4 (*s*); 127.7 (2*d*); 121.2 (*d*); 42.9 (*t*); 50.5 (*t*); 33.1 (*s*); 29.5 (3*q*); 28.1 (*s*); 24.0 (*d*); 22.2 (*q*); 21.5 (*q*); 20.6 (*q*); 16.8 (*t*). MS: 374 (10, $[C_{22}H_{31}NO_2S+H]^{+\cdot}$), 373 (20, $[C_{22}H_{31}NO_2S]^{+\cdot}$), 316 (18), 218 (20), 162 (23), 160 (15), 155 (15), 145 (17), 133 (28), 121 (14), 120 (15), 119 (22), 107 (12), 105 (26), 93 (16), 92 (16), 91 (100), 85 (16), 83 (25), 57 (82). HR-MS: 273.2118 ($[C_{22}H_{31}NO_2S]^{+\cdot}$; calc. 373.2078).

Compound **10**. Carbonate **5** (30 mg, 0.082 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/i-PrOH catalyst system was stirred at 34° for 4 h. Workup and FC (Et_2O/hexane 1:6) gave **10** (20 mg, 85%). For spectral data, see **10** above.

[8,8-Bis(phenylsulfonyl)-3,3-dimethyl-4-oxobicyclo[4.3.0]non-1-en-2-yl] Ethanoate (**16**). Carbonate **6** (120 mg, 0.24 mmol) in the $[Pd_2(dba)_3]$/$AsPh_3$/AcOH catalyst system was stirred under 1 atm of CO gas for 1.5 h. Workup and FC (Et_2O/hexane 1:1) gave **16** (53 mg, 45%) and *methyl 2-[3,3-bis(phenylsulfonyl)bicyclo-[3.1.0]hex-1-yl]-3-methylbut-2-enoate* (**11d**; 27 mg, 31%).

Data of **16**. M.p. 153–154° (MeOH). IR: 3027, 1732, 1709, 1665, 1448, 1367, 1329, 1312, 1228, 1146, 1077. ^{1}H-NMR: 1.60(*s*, 3 H); 1.70(*s*, 3 H); 1.98(*s*, 3 H); 2.17(*dd*, *J* = 11, 8, 1 H); 2.18(*dd*, *J* = 14, 7, 1 H); 2.65(*dd*, *J* = 18, 6, 1 H); 2.87(*dd*, *J* = 14, 8, 1 H); 3.15–3.22(*m*, 1 H); 3.43(*d*, *J* = 19, 1 H); 3.80(*d*, *J* = 19, 1 H); 7.61–7.68(*m*, 4 H); 7.76–7.78(*m*, 2 H); 8.05–8.13(*m*, 4 H). ^{13}C-NMR: 204.9(*s*); 171.9(*s*); 169.6(*s*); 140.4(*s*); 135.9(*s*); 135.4(*s*); 135.1(*d*); 135.0(*d*); 131.5(2*d*); 131.4(2*d*); 129.0(2*d*); 129.0(2*d*); 93.6(*s*); 79.9(*s*); 42.6(*t*); 42.2(*q*); 36.5(*t*); 33.7(*t*); 26.4(*q*); 25.0(*q*); 22.0(*d*). MS: 301(32, $[C_{25}H_{26}O_7S_2 - C_8H_9O_4S]^{+\cdot}$), 300(32, $[C_{25}H_{26}O_7S_2 - C_8H_{10}O_4S]^{+\cdot}$), 175(14), 159(42), 158(12), 132(10), 131 (55), 129(11), 126(10), 125(80), 117(21), 116(18), 115(27), 105(16), 97(15), 91(48), 79(20), 78(28), 77(100), 65(18). HR-MS: 300.0810($[C_{25}H_{26}O_7S_2 - C_8H_{10}O_4S]^{+\cdot}$; calc. 300.0820).

4-Methyl-N,N-*di(prop-2-ynyl)benzenesulfonamide* (**17**). Following the procedure for **3**, *p*-toluenesulfonamide (5.0 g, 29.2 mmol) in DMF (6 ml) was treated sequentially with NaH (55% in oil, 2.67 g, 61.3 mmol) and propargyl bromide (4.57 ml, 62.3 mmol). Workup and FC (Et_2O/hexane 1:4) gave **17**(4.48 g, 62%). IR: 3307, 3030, 2926, 1916, 1598, 1494, 1432, 1353, 1332, 1307, 1161, 1095, 955, 893, 814, 661, 639, 575, 542. ^{1}H-NMR: 2.15 (*t*, *J* = 2, 2 H); 2.43(*s*, 3 H); 4.17(*d*, *J* = 2, 4 H); 7.30(*d*, *J* = 8, 2 H); 7.72(*d*, *J* = 8, 2 H). ^{13}C-NMR: 144.0(*s*); 135.2(*s*); 129.6(2*d*); 127.9(2*d*); 76.2(2*d*); 74.0(2*s*); 36.2(2*t*); 21.6(*q*). MS: 247(3, $[C_{13}H_{13}NO_2S]^{+\cdot}$), 155(11), 92(72), 91(100), 90(14), 65(76), 64(15), 63(17), 52(10), 51(11). HR-MS: 247.0667($[C_{13}H_{13}NO_2S]^{+\cdot}$; calc. 247.0640).

N-*[4-(Methoxycarbonyloxy)-4-methylpent-2-yn-1-yl]-4-methyl*-N-*(prop-2-ynyl)benzenesulfonamide* (**18**). Following the procedure for **5**, **17**(2.50 g, 10.1 mmol) in THF (10 ml) was treated sequentially with LiHMDS (1.0M in THF; 11.1 ml, 11.1 mmol) and acetone (0.78 ml, 10.5 mmol). Workup and FC (Et_2O/hexane 2:1) gave the alcohol (2.33 g, 76%): N-*(4-Hydroxy-4-methylpent-2-yn-1-yl)-4-methyl*-N-*(prop-2-ynyl)benzenesulfonamide*. IR: 3510, 3412, 3287, 2981, 2930, 1598, 1438, 1351, 1237, 1163, 1095, 951, 897, 855, 815, 754, 660. ^{1}H-NMR: 1.34(*s*, 6 H); 172(*s*, 1 H); 2.17(*t*, *J* = 2, 1 H); 2.43(*s*, 3 H); 4.13(*d*, *J* = 2, 2 H); 4.19(*s*, 2 H); 7.31(*d*, *J* = 8, 2 H); 7.73(*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.9(*s*); 135.5(*s*); 129.6(2*d*); 128.0(2*d*); 90.6(*s*); 76.4(*d*); 74.3(*s*); 73.9(*s*); 65.9(*s*); 36.7(*t*); 36.3(*t*); 31.0(2*q*); 21.5(*q*). MS: 306(1, $[C_{16}H_{19}NO_3S]^{+\cdot}$), 155(27), 150(16), 139(20), 134(17), 133(10), 132(56), 117(14), 108(13), 107(19), 106(12), 105(17), 105(13), 94(11), 93(41), 92(41), 91(100), 90(11), 80(35), 79(19), 77(15), 65(54). HR-MS: 305.1086 ($[C_{16}H_{19}NO_3S]^{+\cdot}$; calc. 305.1083).

Following the procedure for **5**, the alcohol (1.15 g, 3.76 mmol) in THF (12 ml) was treated sequentially with LiHMDS (1.0M in THF, 4.51 ml, 4.51 mmol) and methyl chloroformate (0.34 ml, 4.89 mmol). Workup and FC (Et_2O/hexane 1:1) gave **18** (1.19 g, 87%). M.p. 54–55°. IR: 3285, 2989, 1754, 1598, 1441, 1352, 1277, 1165, 1138, 1096, 948, 895, 851, 816, 792, 754, 659. ^{1}H-NMR: 1.51(*s*, 6 H); 2.14(*t*, *J* = 2, 1 H); 2.42(*s*, 3 H); 3.73(*s*, 3 H); 4.16(*d*, *J* = 2, 2 H); 4.21(*s*, 2 H); 7.30(*d*, *J* = 8, 2 H); 7.71(*d*, *J* = 8, 2 H). ^{13}C-NMR: 153.3(*s*); 143.8(*s*); 135.3(*s*); 129.6(2*d*); 127.9(2*d*); 86.4(*s*); 77.1(*s*); 76.4(*d*); 73.7(*s*); 73.7(*s*); 54.3(*q*); 36.5(*t*); 36.2(*t*); 28.5(2*q*); 21.5(*q*). MS: 318(1, $[C_{18}H_{21}NO_5S - CO_2]^{+\cdot}$), 288(2), 287(2), 208(12), 155(23), 139(23), 133(10), 132(75), 117(17), 105(21), 94(12), 93(18), 92(18), 91(99), 81(13), 80(100), 79(39), 77(29), 67(18), 66(13), 65(51), 59(30), 53(20). HR-MS: 318.1137($[C_{18}H_{21}NO_5S - CO_2]^{+\cdot}$; calc. 318.1164).

3-Ethenyl-(4-Methylphenylsulfonyl)-4-(2-methylprop-1-enyl)-2,5-dihydropyrrole (**22**). Me_2Zn (2M in toluene, 0.17 ml, 0.33 mmol) was added to **18** (40 mg, 0.11 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 20 h. Workup and FC (Et_2O/hexane 1:10) gave **22**(27 mg, 82%). IR: 3514, 3027, 2980, 2929, 2872, 2254, 1919, 1728, 1668, 1598, 1494, 1450, 1344, 1306, 1290, 1166, 1094, 1018, 909, 815. ^{1}H-NMR: 1.69(*s*, 3 H); 1.82(*s*, 3 H); 2.43(*s*, 3 H); 4.23(*s*, 2 H); 4.33(*s*, 2 H); 4.98(*d*, *J* = 17, 1 H); 5.13(*d*, *J* = 10, 1 H); 5.82(*s*, 1 H); 6.47(*dd*, *J* = 17, 10, 1 H); 6.48(*d*, *J* = 10, 1 H); 7.32(*d*, *J* = 8, 2 H); 7.74(*d*, *J* = 8, 2 H). ^{13}C-NMR: 143.4(*s*); 138.7(*s*); 134.2(*s*); 132.6(*s*); 130.5(*s*); 129.7(2*d*); 128.3(*d*); 127.5(2*d*); 116.3(*d*); 115.5(*t*); 57.4(*t*); 27.3 – 21.5(*q*); 20.1(*q*). MS: 303(16, $[C_{17}H_{21}NO_2S]^{+\cdot}$), 155(11), 148(61), 147(57), 146(30), 133(17), 132(77), 131(15), 121(20), 120(10), 119(17), 117(12), 106(33), 105(29), 93(27), 92(15), 91(100). HR-MS: 302.1235($[C_{17}H_{21}NO_2S - H]^{+\cdot}$; calc. 302.1215).

5-(Methoxycarbonyloxy)pent-3-yn-2-ol (**27**). To **26** (1.0 g, 8.76 mmol) in THF (10 ml) at −78° was added LiHMDS (1.0M in THF; 9.2 ml, 9.2 mmol) and stirred for 30 min. MeCHO (0.62 ml, 11.04 mmol) was added and stirred for 10 min. Workup and FC (Et_2O/hexane 1:1) gave **27**(796 mg, 57%). IR: 3404, 2984, 2960, 1756, 1447, 1376, 1278, 1158, 1083, 1006, 950, 892, 792. ^{1}H-NMR: 4.74(*d*, *J* = 1, 2 H); 4.54–4.60(*m*, 1 H); 3.82(*s*, 3 H); 1.96(*d*, *J* = 7, 1 H); 1.46(*d*, *J* = 7, 3 H). ^{13}C-NMR: 155.2(*s*); 89.3(*s*); 77.4(*s*); 58.3(*d*); 55.6(*t*); 55.1(*q*); 23.9(*q*). MS: 158(1, $[C_7H_{10}O_4]^{+\cdot}$), 143(36), 141(22), 140(15), 99(100), 96(17), 95(29), 82(57), 81(84), 77(34), 71(39), 59(87). HR-MS: 158.0594($[C_7H_{10}O_4]^{+\cdot}$; calc. 158.0579).

4-4-Bis(phenylsulfonyl)-8-(methoxycarbonyloxy)-5-methyloct-1-en-6-yne (**23**). To **27** (0.20 g, 1.26 mmol), $CH_2(SO_2Ph)_2$ (425 mg, 1.26 mmol) and PPh_3 (498 mg, 1.90 mmol) in benzene (10 ml) at r.t. was added $EtO_2CN{=}C{=}NCO_2Et$ (0.30 ml, 1.90 mmol) dropwise (slight exotherm). The orange soln. was stirred for 1 h and

then absorbed onto silica. FC (Et_2O/hexane 2:1) gave crude bis-sulfone (279 mg, 51%), of which following the procedure for **3**, bis-sulfone (212 mg, 0.49 mmol) was dissolved in DMF (3 ml) and treated sequentially with NaH (55% in oil; 28 mg, 0.63 mmol) and allyl bromide (0.076 ml, 0.87 mmol) at 55° for 12 h. Workup and FC (Et_2O/hexane 1:2 to 1:1) gave **23** (85 mg, 37%; 19% yield for the two steps). IR: 3029, 2956, 1752, 1584, 1447, 1374, 1333, 1312, 1275, 1148, 1076, 951. ^{1}H-NMR: 1.53(*d*, *J* = 7, 3 H); 3.02(*ddd*, *J* = 8, 8, 7, 2 H); 3.77–3.80(*m*, 1 H); 3.79(*s*, 3 H); 4.33(*d*, *J* = 1, 2 H); 5.22(*dd*, *J* = 17, 1, 1 H); 5.27(*dd*, *J* = 10, 1, 1 H); 6.06(*ddd*, *J* = 17, 10, 1, 1 H); 7.55–7.61(*m*, 4 H); 7.67–7.72(*m*, 2 H); 8.12–8.22(*m*, 4 H). ^{13}C-NMR: 155.0(*s*); 138.6(*s*); 138.5(*s*); 134.6(*d*); 134.6(*d*); 131.9(2*d*); 131.9(2*d*); 129.2(*d*); 128.5(2*d*); 128.4(2*d*); 121.7(*t*); 92.6(*s*); 85.6(*s*); 78.7(*s*); 55.4(*t*); 55.0(*q*); 35.6(*t*); 28.4(*d*); 17.2(*q*). MS: 476(0.5, $[C_{23}H_{24}O_7S_2]^{+\cdot}$), 401(16), 335(23), 259(43), 258(23), 257(12), 195(10), 193(12), 125(100), 117(80), 91(49), 77(81). HR-MS: 401.0864($[C_{23}H_{24}O_7S_2 - C_2H_6O_3]^{+\cdot}$; calc. 401.0882).

8-(Methoxycarbonyloxy)-4-phenylsulfonyloct-1-en-6-yne (**24**). Al/Hg (25 mg, see procedure for **40**) was added to **8** (60 mg, 0.13 mmol) in THF/H_2O (19:1, 2 ml) at r.t. Stirring for 4 h followed by filtration through *Celite*, washing with Et_2O, adsorption onto silica and FC (Et_2O/hexane 1:6) gave **24** (40 mg, 95%). IR: 3646, 3070, 3005, 2957, 2244, 1747, 1643, 1585, 1446, 1372, 1265, 1147, 1085, 998, 948, 791, 734, 691. ^{1}H-NMR: 2.47–2.57(*m*, 1 H); 2.68–2.72(*m*, 1 H); 2.72–2.81(*m*, 1 H); 3.14–3.21(*m*, 1 H); 3.80(*s*, 3 H); 4.54(*d*, *J* = 2, 2 H); 5.15(*dd*, *J* = 9, 1, 1 H); 5.17(*dd*, *J* = 17, 1, 1 H); 5.79(*ddd*, *J* = 17, 10, 7, 1 H); 7.56–7.61(*m*, 2 H); 7.65–7.71(*m*, 1 H); 7.80–7.93(*m*, 2 H). ^{13}C-NMR: 155.5(*s*); 137.8(*s*); 134.0(*d*); 132.6(*d*); 129.2(2*d*); 129.1(2*d*); 119.1(*t*); 82.6(*s*); 76.8(*s*); 62.7(*d*); 55.6(*t*); 55.0(*q*); 31.6(*t*); 18.2(*t*). MS: 247(4, $[C_{16}H_{18}O_2S - C_2H_2O_3]^{+\cdot}$), 143(10), 125(10), 105(56), 104(100), 103(20), 91(11), 79(37), 78(17), 77(46), 65(11). HR-MS: 247.0799($[C_{16}H_{18}O_2S - C_2H_2O_3]^{+\cdot}$; calc, 247.0792).

4,4-Bis(phenylsulfonyl)-3-methylbut-1-ene (**28**). To 3-buten-2-ol (0.09 ml, 1.00 mmol), $CH_2(SO_2Ph)_2$ (337 mg, 1.00 mmol) and PPh_3 (395 mg, 1.51 mmol) in benzene (10 ml) at r.t. was added $EtO_2CN{=}C{=}NCO_2Et$ (0.24 ml, 1.51 mmol) dropwise. The resulting soln. was stirred for 1 h and then absorbed onto silica. FC (Et_2O/hexane 2:1) gave **28** (100 mg, 48%). M.p. 101–102° (MeOH). IR: 3034, 2958, 1585, 1448, 1334, 1312, 1153, 1079, 999, 928. ^{1}H-NMR: 1.37(*d*, *J* = 7, 3 H); 3.36(*ddq*, *J* = 7, 7, 1, 1 H); 4.57(*d*, *J* = 1, 1 H); 4,98(*d*, *J* = 17, 1 H); 5.01(*d*, *J* = 10, 1 H); 6.13(*ddd*, *J* = 17, 10, 7, 1 H); 7.51–7.59(*m*, 4 H); 7.64–7.71(*m*, 2 H); 7.89–7.97(*m*, 4 H). ^{13}C-NMR: 140.0(*s*); 138.9(*d*); 138.8(*s*); 134.5(*d*); 134.2(*d*); 129.7(2*d*); 129.3(2*d*); 129.1(2*d*); 129.0(2*d*); 116.5(*t*); 87.9(*d*); 38.1(*d*); 16.7(*q*). MS: 210(10, $[C_{17}H_{18}O_4S_2 - C_6H_4O_2S]^{+\cdot}$), 209(76), 142(15), 125(47), 97(12), 78(15), 77(100), 68(27), 51(30). HR-MS: 209.0630($[C_{17}H_{18}O_4S_2 - C_6H_4O_2S]^{+\cdot}$; calc. 209.0636).

4,4-Bis(phenylsulfonyl)-8-(methoxycarbonyloxy-3-methyl)oct-1-en-6-yne (**25**). Following the procedure for **8**, **28** (335 mg, 0.96 mmol) in DMF (10 ml was treated sequentially with NaH (55% in oil; 50 mg, 1.14 mmol) and **9** (300 mg, 1.45 mmol). Workup and FC (Et_2O/hexane 1:5 to 1:2) gave an inseparable mixture **25**, **28** (295 mg, 65%) in a 3:1 molar ratio. For spectral data, see **37**.

cis-3,3-Bis(phenylsulfonyl)-2-methyl-1-(1-methylethenyl)bicyclo[3.1.0]hexane (**29**). Me_2Zn (2M in toluene; 0.14 ml, 0.28 mmol) was added to the **23** (45 mg, 0.094 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_2$P/Et_2O catalyst system, and the whole was stirred at 34° for 21 h. Workup and FC (Et_2O/hexane 1:5) gave **29** (33 mg, 83%) as a 3:1 mixture of *cis*/*trans*-isomers. Recrystallisation gave pure *cis*-isomer **29** (22 mg, 54%). M.p. 217–218° (EtOH). IR: 3029, 2988, 2952, 1634, 1584, 1478, 1448, 1387, 1324, 1309, 1229, 1147, 1076, 1113, 1076, 999, 910. ^{1}H-NMR 0.69(*dd*, *J* = 4, 4, 4 H); 0.91(*dd*, *J* = 8, 4, 1 H); 1.11(*d*, *J* = 7, 3 H); 1.79(*s*, 3 H); 1.81–1.87(*m*, 1 H); 2.67(*dd*, *J* = 17, 1, 1 H); 2.81(*dd*, *J* = 17, 7, 1 H); 3.07(*q*, *J* = 7, 1 H); 5.00(*s*, 1 H); 5.11(*d*, *J* = 2, 1 H); 7.57–7.65(*m*, 4 H); 7.67–7.75(*m*, 2 H); 8.08–8.13(*m*, 2 H); 8.15–8.20(*m*, 2 H). ^{13}C-NMR: 143.4(*s*); 138.5(*s*); 136.8(*s*); 134.5(*d*); 134.2(*d*); 132.1(2*d*); 131.6(2*d*); 128.6(2*d*); 128.3(2*d*); 117.1(*t*); 101.5(*s*); 50.1(*q*); 40.7(*s*); 35.4(*t*); 27.1(*t*); 27.0(*q*); 22.8(*d*); 13.3(*d*). MS: 274(12, $[C_{22}H_{24}O_4S_2 - C_6H_6O_2S]^{+\cdot}$), 134(15), 133(100), 132(41), 125(25), 119(16), 117(26), 105(45), 91(49), 77(78). HR-MS: 274.1024($[C_{22}H_{24}O_4S_2 - C_6H_6O_2S]^{+\cdot}$; calc. 274.1028).

1-(1-Methylethenyl)-3-(phenylsulfonyl)bicyclo[3.1.0]hexane (**30**). Me_2Zn (2M in toluene; 0.16 ml, 0.33 mmol) was added to the **24** (35 mg, 0.11 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_2$P/Et_2O catalyst system, and the whole was stirred at 34° for 21 h. Workup and FC (Et_2O/hexane 1:4) gave **30** (15 mg, 54%) as a 3:1 mixture of diastereoisomers. IR: 2933, 2867, 1630, 1600, 1447, 1385, 1305, 1226, 1146, 1087, 908. ^{1}H-NMR: 0.44(*dd*, *J* = 3, 3, 0.5 H); 0.77(*dd*, *J* = 7, 7, 0.5 H); 0.97(*dd*, *J* = 8, 5, 0.5 H); 1.09(*dd*, *J* = 5, 5, 0.5 H); 1.50–1.58(*m*, 1 H); 1.59(*s*, 1.5 H); 1.62(*s*, 1.5 H); 1.95–2.10(*m*, 1 H); 2.20–2.47(*m*, 3 H); 3.20(*tt*, *J* = 10, 7, 0.5 H); 3.01(*tt*, *J* = 7, 5, 0.5 H); 4.69(*s*, 0.5 H); 4.72(*s*, 0.5 H); 4.75(*s*, 0.5 H); 4.78(*s*, 0.5 H); 7.52–7.59(*m*, 2 H); 7.61–7.68(*m*, 1 H); 7.85–7.91(*m*, 2 H). ^{13}C-NMR: 146.1(*s*); 145.4(*s*); 139.6(*s*); 133.6(*d*); 133.5(*d*); 129.2(2*d*); 129.2(2*d*); 129.1(*s*); 128.5(2*d*); 128.4(2*d*); 110.2(*t*); 109.5(*t*); 66.7(*d*); 61.0(*d*); 36.2(*s*); 33.5(*t*); 31.9(*t*); 30.4(*t*); 29.7(*s*); 29.2(*t*); 25.1(*q*); 23.0(*q*); 20.4(*d*); 20.1(*d*); 19.9(*t*); 13.8(*t*). MS: 143(13, $[C_{15}H_{18}O_2S - C_9H_{11}]^{+\cdot}$). HR-MS: 143.0204($[C_{15}H_{18}O_2S - C_9H_{11}]^{+\cdot}$; calc. 143.0167).

cis-3,3-Bis(phenylsulfonyl)-4-methyl-1-(1-methylethenyl)bicyclo[3.1.0]hexane (**31**). Me_2Zn (2M in toluene; 0.18 ml, 0.36 mmol) was added to the **28/25** (55 mg) in the $[Pd_2(dba)_3]/(2\text{-furyl})_3P/Et_2O$ catalyst system, and the whole was stirred at 34° for 4 h. Workup and FC (Et_2O/hexane 1:3) gave **31** (40 mg, 83%; 42% for two steps). M.p. 185–185.5°. IR: 2984, 2945, 1631, 1585, 1478, 1448, 1326, 1311, 1232, 1143, 1080, 999, 883. ^{1}H-NMR: 0.86 (*dd*, *J* = 4, 4, 1 H); 1.09 (*dd*, *J* = 8, 4, 1 H); 1.21 (*d*, *J* = 7, 3 H); 1.70 (*s*, 3 H); 1.75 (*ddd*, *J* = 8, 4, 3, 1 H); 2.75 (*d*, *J* = 16, 1 H); 2.81 (*dq*, *J* = 7, 3, 1 H); 2.97 (*d*, *J* = 16, 1 H); 4.89 (*s*, 1 H); 4.96 (*s*, 1 H); 7.55–7.63 (*m*, 4 H); 7.66–7.75 (*m*, 2 H); 8.07 (*m*, 2 H); 8.14–8.18 (*m*, 2 H). ^{13}C-NMR: 145.6 (*s*); 137.7 (*s*); 136.9 (*s*); 134.5 (*d*); 134.2 (*d*); 132.3 (2*d*); 131.5 (2*d*); 128.6 (2*d*); 128.2 (2*d*); 110.7 (*t*); 100.0 (*s*); 48.4 (*d*); 38.8 (*t*); 36.3 (*s*); 33.3 (*q*); 29.3 (*t*); 20.6 (*d*); 15.4 (*q*). MS: 274 (13, $[C_{22}H_{24}O_4S_2 - C_6H_6OS]^{+\cdot}$), 134 (15), 133 (100), 132 (33), 125 (11), 119 (10), 117 (15), 105 (30), 93 (14), 91 (32), 79 (13), 78 (11), 77 (50). HR-MS: 274.1026 ($[C_{22}H_{24}O_4S_2 - C_6H_6OS]^{+\cdot}$; calc. 274.1027).

(3R)-3-[(Tetrahydro-2H-pyran-2-yl)oxy]-1-(trimethylsilyl)but-3-ene (**33**). A soln. of *(2R)-2-[(tetrahydro-2H-pyranyl)oxy]propanal* (**32**) (959 mg, 6.07 mmol) and $Me_3SiCHBr_2$ (3.67 g, 12.1 mmol) in THF (35 ml) was added to a suspension of green $CrCl_2$ in THF (150 ml) under Ar at r.t. The resultant dark red/brown mixture was stirred for 16 h. Workup with FC (hexane/Et_2O 40:1) gave **33** as a clear liquid (mixture of diastereoisomers; 1.19 g, 86%). $[\alpha]_D^{19.5} = +43.21$, $[\alpha]_{578} = +45.05$, $[\alpha]_{546} = +51.28$, $[\alpha]_{436} = +87.44$, $[\alpha]_{365} = +137.69$ (*c* = 0.98). ^{1}H-NMR: 1.22 (*d*, *J* = 6.5, 3 H); 1.27 (*d*, *J* = 6.5, 3 H); 1.49–1.64 (*m*, 8 H); 1.71 (*m*, 2 H); 1.86 (*m*, 2 H); 3.48 (*m*, 2 H); 3.89 (*m*, 2 H); 4.25 (*m*, 2 H); 4.61 (*t*, *J* = 3, 1 H); 4.73 (*t*, *J* = 3, 1 H); 5.84 (*m*, 3 H); 6.11 (*dd*, *J* = 19, 5, 1 H). ^{13}C-NMR: 148.3; 147.3; 131.2; 128.6; 94.5; 96.1; 74.4; 73.0; 62.0; 62.4; 31.1; 30.9; 22.6; 22.5; 21.5; 19.8; 19.5; 19.4; −1.3. MS: 229 (0.4, $[C_{12}H_{24}O_2Si + H]^+$), 143 (4), 85 (100), 73 (44), 57 (40). Anal. calc. for $C_{12}H_{24}O_2Si$: C 63.10, H 10.59; found: C 63.29, H 10.61.

(2R)-4-(Trimethylsilyl)but-3-en-2-ol (**34**). To **33** (3.5 g, 15.5 mmol) in MeOH (60 ml) under Ar was added TsOH · H_2O (58.8 mg, 0.31 mmol), and the mixture was stirred at r.t. for 45 h. Workup and distillation (b.p. 72–74°/12 mmHg) gave **34** (1.90 g, 85%). $[\alpha]_D^{19.5} = -2.17$ (*c* = 1.15) [22]: $[\alpha]_D^{23} = -2.48$ (*c* = 1.13), $[\alpha]_{578} = -5.14$, $[\alpha]_{546} = -5.92$, $[\alpha]_{436} = -11.50$, $[\alpha]_{365} = -22.04$. IR: 3345, 2956, 2897, 1620, 1368, 1327, 1248, 1209, 1129, 1060, 989, 940, 869, 840, 739, 692. ^{1}H-NMR: 0.07 (*s*, 9 H); 1.27 (*d*, *J* = 7, 3 H); 1.61 (br. *s*, 1 H); 4.28 (*dq*, *J* = 7, 5, 1 H); 5.83 (*dd*, *J* = 19, 1, 1 H); 6.08 (*dd*, *J* = 19, 5, 1 H). ^{13}C-NMR: 149.6 (*d*); 128.2 (*d*); 70.5 (*d*); 22.9 (*q*); −1.35 (3*q*). MS: 144 (1, $[C_7H_{16}OSi]^{+\cdot}$), 129 (39), 75 (100), 73 (65), 61 (17). HR-MS: 129.0724 ($[C_7H_{16}OSi - CH_3]^{+\cdot}$; calc. 129.0736).

(3R)-4,4-Bis(phenylsulfonyl)-3-methyl-1-(trimethylsilyl)but-1-ene (**35**). Methyl chloroformate (1.50 g, 15.8 mmol) was added dropwise to **34** (1.90 g, 13.2 mmol) and pyridine (2.09 g, 26.4 mmol) in CH_2Cl_2 (20 ml) under Ar at 0°, and the mixture was stirred at r.t. for 20 h. Workup with HCl (2N) and FC (hexane/Et_2O 20:1) gave the carbonate as a clear liquid (2.33 g, 87%). $[\alpha]_D = +62.31$, $[\alpha]_{578} = +66.00$, $[\alpha]_{546} = +74.92$, $[\alpha]_{436} = +130.77$, $[\alpha]_{365} = +213.08$ (*c* = 0.65). IR: 2956, 1750, 1623, 1443, 1269, 1138, 1038, 989, 945, 870, 839, 792. ^{1}H-NMR: 0.07 (*s*, 9 H); 1.36 (*d*, *J* = 6, 3 H); 3.79 (*s*, 3 H); 5.19 (*ddq*, *J* = 6, 5, 1, 1 H); 5.90 (*dd*, *J* = 19, 1, 1 H); 6.01 (*dd*, *J* = 19, 5, 1 H). ^{13}C-NMR: 155.1 (*s*); 143.9 (*d*); 131.5 (*d*); 76.5 (*d*); 54.6 (*q*); 19.9 (*q*); −1.2 (3*q*). MS: 202 (1, $[C_9H_{18}O_3Si]^{+\cdot}$), 143 (44), 127 (16), 115 (16), 111 (20), 89 (71), 83 (11), 75 (29), 73 (100), 59 (41). HR-MS: 143.0900 ($[C_9H_{18}O_3Si - C_2H_3O_2]^{+\cdot}$; calc. 143.0892).

To $CH_2(SO_2Ph)_2$ (806 mg, 2.72 mmol) in THF (10 ml) at r.t. was added NaH (55% in oil; 119 mg, 2.72 mmol) and the mixture was stirred for 1 h to leave a white suspension. Meanwhile $[Pd_2(dba)_3] \cdot CHCl_3$ complex (128 mg, 0.12 mmol) and $Ph_2P(CH_2)_2PPh_2$ (98 mg, 0.25 mmol) in THF were stirred at r.t. for 1 h to give an orange soln. To this was added the above carbonate (500 mg, 2.47 mmol), and then the whole was added to the above anion by syringe and stirred for 1.5 h. Workup and FC (Et_2O/hexane 1:7 to 1:4) gave **35** (951 mg, 91%). $[\alpha]_D = +51.44$, $[\alpha]_{578} = +53.84$, $[\alpha]_{546} = +61.82$, $[\alpha]_{436} = +110.77$, $[\alpha]_{365} = +185.90$ (*c* = 1.07). IR: 3067, 2954, 2809, 1611, 1585, 1479, 1448, 1338, 1248, 1155, 1080, 990, 874, 837, 750, 719. ^{1}H-NMR: 0.03 (*s*, 9 H); 1.36 (*d*, *J* = 7, 3 H); 3.40 (*ddq*, *J* = 7, 6, 2, 1 H); 4.61 (*d*, *J* = 2, 1 H); 5.62 (*dd*, *J* = 18, 2, 1 H); 6.17 (*dd*, *J* = 18, 6, 1 H); 7.51–7.60 (*m*, 4 H); 7.63–7.72 (*m*, 2 H); 7.88 (*m*, 2 H); 7.97–8.01 (*m*, 2 H). ^{13}C-NMR: 146.1 (*d*); 140.1 (*s*); 139.1 (*s*); 134.5 (*d*); 134.3 (*d*); 132.2 (*d*); 129.8 (2*d*); 129.5 (2*d*); 129.1 (2*d*); 129.0 (2*d*); 88.5 (*d*); 39.8 (*d*); 16.6 (*q*); −1.3 (3*q*). MS: 423 (0.5, $[C_{20}H_{26}O_4S_2Si + H^+]$), 407 (15), 282 (22), 281 (100), 199 (100), 199 (30), 135 (22), 125 (10). HR-MS: 408.0786 ($[C_{20}H_{26}O_4S_2Si - CH_4]^{+\cdot}$; calc. 408.0807).

(3R)-4,4-Bis(phenylsulfonyl)-3-methylbut-1-ene (**36**). Compound **35** (940 mg, 2.22 mmol) and TsOH · H_2O (210 mg, 1.10 mmol) in MeCN (10 ml) were heated at reflux for 5 h. Workup and FC (Et_2O/hexane 1:2) gave **36** (752 mg, 96%). M.p. 101–102° (MeOH). $[\alpha]_D = +23.39$, $[\alpha]_{578} = +24.19$, $[\alpha]_{546} = +27.58$, $[\alpha]_{436} = +45.81$, $[\alpha]_{3.56} = +69.03$ (*c* = 0.62). IR: 3034, 2958, 1585, 1448, 1334, 1312, 1153, 1079, 999, 928. ^{1}H-NMR: 1.37 (*d*, *J* = 7, 3 H); 3.36 (*ddq*, *J* = 7, 7, 1, 1 H); 4.57 (*d*, *J* = 1, 1 H); 4.98 (*d*, *J* = 17, 1 H); 5.01 (*d*, *J* = 10, 1 H); 6.13 (*ddd*, *J* = 17, 10, 7, 1 H); 7.51–7.59 (*m*, 4 H); 7.64–7.71 (*m*, 2 H); 7.89–7.97 (*m*, 4 H). ^{13}C-NMR: 140.0 (*s*); 138.9 (*d*); 138.8 (*s*); 134.5 (*d*); 134.2 (*d*); 129.7 (2*d*); 129.3 (2*d*); 129.1 (2*d*); 129.0 (2*d*); 116.5 (*t*); 87.9 (*d*); 38.1 (*d*); 16.7 (*q*). MS: 210 (10,

$[C_{17}H_{18}O_4S_2 - C_6H_4O_2S]^{+\cdot}$), 209(76), 142(15), 125(47), 97(12), 78(15), 77(100), 68(27), 51(30). HR-MS: 209.0630($[C_{17}H_{18}O_4S_2 - C_6H_5O_2S]^{+\cdot}$; calc. 209.0636).

(3R)-4,4-Bis(phenylsulfonyl)-8-(methoxycarbonyloxy)-3-methyloct-1-en-6-yne (**37**). To **36** (1.62 g, 4.64 mmol) and K_2CO_3 (673 mg, 4.87 mmol) in anh. DMF (2 ml) was added **9** (1.13 g, 5.10 mmol). The mixture was stirred at 60° for 16 h. Then, it was cooled to r.t., dissolved in CH_2Cl_2 (20 ml) and filtered through *Celite*. The solvent was removed *in vacuo* and FC (CH_2Cl_2/Et_2O 1.5:1) gave **37** as a white powder (1.15 g, 88%). M.p. 94–97° (MeOH). $[\alpha]_D^{22} = -11.42$, $[\alpha]_{578} = -12.36$, $[\alpha]_{546} = -14.42$, $[\alpha]_{436} = -27.34$, $[\alpha]_{365} = -50.75$ ($c = 1.01$). ^{1}H-NMR: 1.29(*d*, $J = 7$, 3 H); 3.03(*d*, $J = 18$, 1 H); 3.22(*d*, $J = 18$, 1 H); 3.58(*quint.*, $J = 7$, 1 H); 3.82(*s*, 3 H); 4.67(*dd*, $J = 4$, 2, 2 H); 5.09(*d*, $J = 10$, 1 H); 5.17(*d*, $J = 17$, 1 H); 6.10(*ddd*, $J = 17$, 10, 8, 1 H); 7.58(*m*, 4 H); 7.71(*m*, 2 H); 8.19(*m*, 4 H). ^{13}C-NMR (50 MHz): 155.19(*s*); 138.59(*s*); 137.97(*s*); 136.46(*d*); 134.78(*d*); 134.67(*d*); 131.86(2*d*); 131.75(2*d*); 128.59(2*d*); 128.49(2*d*); 118.07(*t*); 92.88(*s*); 80.19(*s*); 79.83(*s*); 55.61(*t*); 55.20(*q*); 40.36(*d*); 24.4(*t*); 16.46(*q*). MS: 401(12, $[C_{23}H_{24}O_7S_2 - C_2H_3O_3]^{+\cdot}$), 335(3), 259(16), 117(72), 91(48), 77(100), 64(4), 51(28). HR-MS 401.0871($[C_{23}H_{24}O_7S_2 - C_2H_3O_3]^{+\cdot}$; calc. 401.0881). Anal. calc. for $C_{23}H_{24}O_7S_2$: C 57.97, H 5.08, S 13.46; found: C 57.98, H 5.05, S 13.50.

(1R,4R,5R)-3,3-Bis(phenylsulfonyl)-4-methyl-1-(1-methylethenyl)-bicyclo[3.1.0]hexane (**38**). Me_2Zn (2M in toluene; 8.76 ml, 17.4 mmol) was added to **37** (2.78 g, 5.84 mmol) in the $[Pd_2(dba)_3]$/(2-furyl)$_3$P/Et_2O catalyst system, and the whole was stirred at 34° for 4 h. Workup and FC (Et_2O 3:1) gave **38**. White solid (2.22 g, 91%). M.p. 187–189° (AcOEt). $[\alpha]_D = -48.86$, $[\alpha]_{578} = -51.90$, $[\alpha]_{546} = -61.52$, $[\alpha]_{436} = -132.66$, $[\alpha]_{365} = -281.01$ ($c = 0.40$). IR: 3017, 2984, 1633, 1585, 1448, 1326, 1311, 1232, 1143, 1080, 999, 790–720. ^{1}H-NMR: 0.86(*dd*, $J = 4$, 4, 1 H); 1.09(*dd*, $J = 8$, 4, 1 H); 1.22(*d*, $J = 7$, 3 H); 1.70(*s*, 3 H); 1.76(*ddd*, $J = 8$, 4, 3, 1 H); 2.76(*d*, $J = 16$, 1 H); 2.81(*dq*, $J = 7$, 3, 1 H); 2.98(*d*, $J = 16$, 1 H); 4.90(*s*, 1 H); 4.97(*s*, 1 H); 7.55–7.63(*m*, 4 H); 7.66–7.75(*m*, 2 H); 8.07(*m*, 2 H); 8.14–8.18(*m*, 2 H). ^{13}C-NMR: 145.7(*s*); 137.9(*s*); 137.0(*s*); 134.5(*d*); 134.2(*d*); 132.3(2*d*); 131.6(2*d*); 128.6(2*d*); 128.2(2*d*); 110.7(*t*); 1003(*s*); 48.5(*d*); 39.0(*t*); 36.4(*s*); 33.4(*q*); 29.4(*t*); 20.6(*d*); 15.5(*q*). MS: 416(1, $[C_{22}H_{24}O_4S_2]^{+\cdot}$), 275(14), 274(39), 273(14), 133(100), 132(22), 105(27), 91(27), 77(38). HR-MS: 416.1134($[C_{22}H_{24}O_4S_2]^{+\cdot}$; calc. 416.1116).

(1R,4R,5R)-3,3-Bis(phenylsulfonyl)-4-methyl-1-(1-methylethyl)bicyclo[3.1.0]hexane (**39**). PtO_2 (303 mg, 1.33 mmol) was added to **38** (2.22 g, 5.33 mmol) dissolved in AcOEt/AcOH (1:1, 90 ml), and the mixture was hydrogenated at 50° for 2 d. The catalyst was filtered over *Celite*, and the filtrate was concentrated *in vacuo* to yield **39**. White solid (2.02 g, 96%). M.p. 219–220° (AcOEt). $[\alpha]_D = -62.54$, $[\alpha]_{578} = -66.43$, $[\alpha]_{546} = -78.08$, $[\alpha]_{436} = -160.24$, $[\alpha]_{365} = -318.93$ ($c = 0.52$). IR: 2961, 1448, 1322, 1149, 1076. ^{1}H-NMR: 0.44(*dd*, $J = 4$, 4, 1 H); 0.68(*d*, $J = 7$, 3 H); 0.89(*dd*, $J = 8$, 5, 1 H); 1.01(*d*, $J = 7$, 3 H); 1.19(*d*, $J = 7$, 3 H); 1.29(*ddd*, $J = 8$, 6, 4, 1 H); 2.15(*sept.* $J = 7$, 1 H); 2.56(*dd*, $J = 16$, 1, 1 H); 2.85(*d*, $J = 16$, 1 H); 2.87(*dq*, $J = 7$, 2, 1 H); 7.57–7.65(*m*, 4 H); 7.67–7.73(*m*, 2 H); 8.06–8.10(*m*, 2 H); 8.17–8.21(*m*, 2 H). ^{13}C-NMR (200 MHz): 138.2(*s*); 136.7(*s*); 134.5(*d*); 134.2(*d*); 132.2(2*d*); 131.5(2*d*); 128.6(2*d*); 128.3(2*d*); 99.9(*s*); 49.3(*d*); 39.8(*t*); 37.6(*s*); 31.3(*d*); 31.1(*d*); 21.3(*t*); 21.0(*q*); 18.3(*q*); –15.9(*q*). MS: 277(17, $[C_{22}H_{26}O_4S_2 - C_6H_6O_2S]^{+\cdot}$), 276(33), 143(16), 141(11), 136(12), 135(100), 134(27), 133(15), 125(32), 119(28), 107(18), 105(19), 93(50), 91(42), 77(41). HR-MS: 276.1175($[C_{22}H_{26}O_4S_2 - C_6H_6O_2S]^{+\cdot}$; calc. 276.1184).

(1S,4R,5R)-4-Methyl-1-(1-methylethyl)bicyclo[3.1.0]hexan-3-one (*(–)-α-Thujone*, **40**). Al/Hg (formed by submerging Al foil (50 mg) in a 2% aq. $HgCl_2$ soln., followed by successively washing the foil with EtOH and then Et_2O) was added to **39** (50 mg, 0.12 mmol) in THF/H_2O (19:1; 3 ml, and the mixture was stirred at r.t. for 5 h. The mixture was filtered through *Celite* and the filtrate concentrated *in vacuo*. Purification by FC (pentane/Et_2O 5:1) gave the monosulfones as a thick oil (33 mg, 995).

BuLi (2.7M; 3.22 ml, 8.7 mmol) was added to (i-Pr)$_2$NH (1.20 ml, 9.14 mmol) in THF (7.5 ml) under Ar at –78° and the mixture was stirred for 5 min, the cooling bath was removed for 10 min and then replaced. The above monosulfones (392 mg, 1.41 mmol) in THF (7.5 ml) were added dropwise, and a bright yellow colour formed. The mixture was stirred for 10 min. MoOPH (1.89 g, 4.36 mmol) in THF (60 ml) was added dropwise to give a deep red soln. and the mixture was stirred for 20 min. Aq. Na_2SO_3 (15 ml) was added; workup and FC (pentane/Et_2O 10:1) gave **40**. Volatile liquid, smelling of pine needles (104 mg, 60%). $[\alpha]_D^{19.5} = -21.26$ ($c = 1.00$). $[\alpha]_D^{23} = -20.5$, $[\alpha]_{578} = -22.58$, $[\alpha]_{546} = -27.16$, $[\alpha]_{436} = -63.28$, $[\alpha]_{365} = -170.80$ ($c = 1.0$). Chiral GC analysis (*Lipodex E*) indicated > 99.2% e.e. IR: 3020, 2961, 1733, 1602, 1455, 1219, 1096, 1014. ^{1}H-NMR: 0.12(*dd*, $J = 5.5$, 4, 1 H); 0.76(*ddd*, $J = 8$, 5.5, 2, 1 H); 0.95(*d*, $J = 7$, 3 H); 1.01(*d*, $J = 7$, 3 H); 1.09(*m*, 1 H); 1.16(*d*, $J = 7$, 3 H); 1.35(*sept.* $J = 7$, 1 H); 2.07(*d*, $J = 19$, 1 H); 2.22(*q*, $J = 7.4$, 1 H); 2.55(*ddd*, $J = 19$, 2, 1, 1 H). ^{13}C-NMR: 221.32(*s*); 47.36(*d*); 39.72(*t*); 32.90(*d*); 29.63(*s*); 25.52(*d*); 19.97(*q*); 19.70(*q*); 18.70(*t*); 18.70(*q*). ν_{max}($CHCl_3$)/cm^{-1}: 2996.4, 1733.6. MS: 151(1, $[C_{10}H_{16}O]^{+\cdot}$), 150(37), 149(45), 148(82), 147 (100), 133(41). HR-MS: 110.1093($[C_{10}H_{16}O - C_2H_2O]^{+\cdot}$; calc. 110.1095). Anal. calc. for $C_{10}H_{16}O$: C 78.90, H 10.59; found: C 78.78, H 10.55.

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