75. Palladium-Catalyzed 'Metallo-Ene'-Type Cyclization/Vinylstannane Coupling of 1-Acetoxy-octa-2,7-dienes and 1-Acetoxy-oct-2-en-7-ynes

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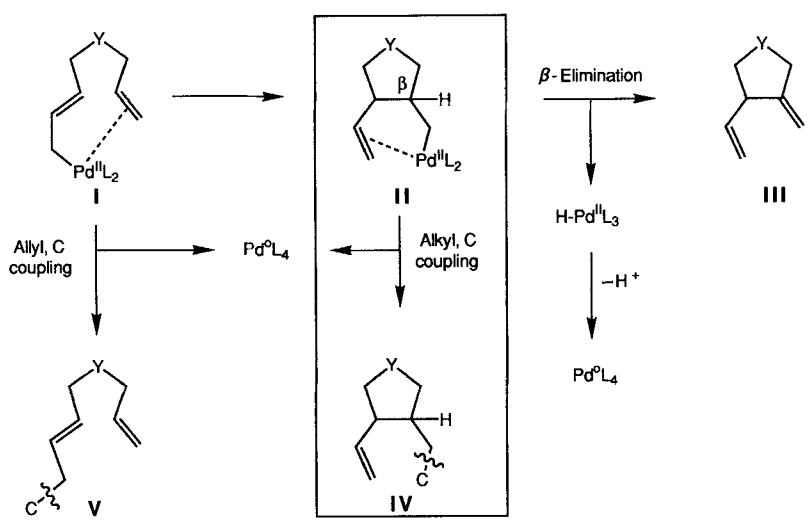
Palladiumbis(dibenzylideneacetone)/tri(2-furyl)phosphine-catalyzed cyclizations of dienyl acetates **2** in the presence of an (1-alkenyl)(tributyl)stannane and $ZnCl_2$ provided *trans*-substituted 3-alkenyl-4-vinylcyclopentanes **11** in good yields. Analogous intramolecular carbometallation/C,C-coupling of enynyl acetates **4**, **6**, and **8** furnished, stereospecifically, monocyclic trienes **19**, **20**, and **21**, respectively.

Introduction. – The recently discovered Pd^0(and Ni^0-)-catalyzed intramolecular tandem alkene allylation/β-elimination reactions **I** → **II** → **III** offer interesting perspectives for the stereocontrolled construction of various carbo- and heterocyclic systems (*Scheme 1*) [1].

Scheme 1



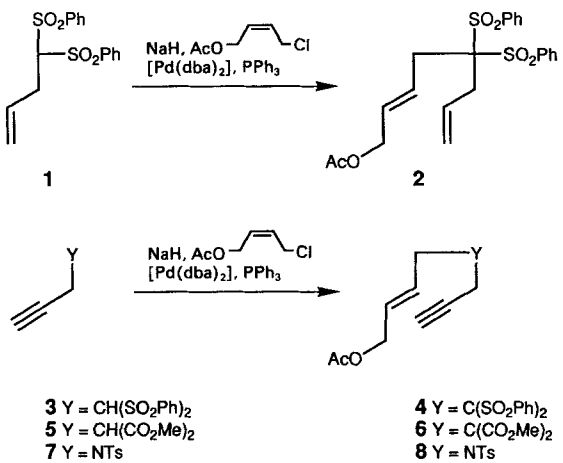
Particularly attractive is trapping of the transient σ-alkylpalladium species **II** by means of C,C-coupling reactions with simultaneous regeneration of the catalyst (**I** → **II** → **IV**). This requires not only that the trapping process **II** → **IV** is faster than β-elimination **II** → **III**, but also that the allylation step **I** → **II** prevails over allylic coupling **I** → **V**. Carbonylation reactions of intermediates **II** meet these requirements [2].

Of more limited scope are intramolecular *Heck*-type olefin insertions into Pd complexes **II** as these depend critically on a rigid conformation of **II** enforcing proximity of the C–metal and C=C bonds [3].

An alternative bimolecular C,C-coupling process linked with the 'metallo-ene'-type cyclization could be the interception of σ-palladium complexes **II** with vinylmetal reagents[1]).

Results. – Acyclic dienyl acetate precursor **2** was easily prepared by a Pd-catalyzed allylation of deprotonated gem-disulfone **1** with (*Z*)-4-chlorobut-2-enyl acetate (*Scheme 2*).

Scheme 2

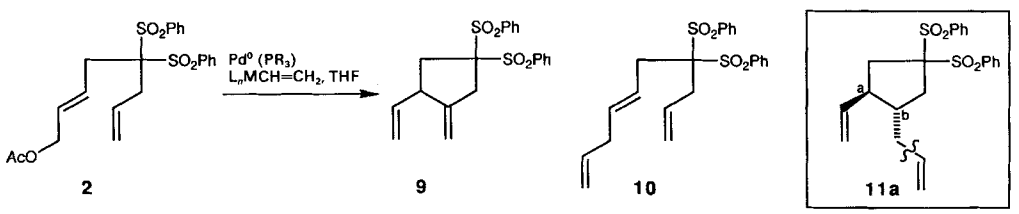


The corresponding enyne substrates **4**, **6**, and **8** were routinely obtained by analogous allylation of acetylene derivatives **3**, **5**, and **7**, respectively.

Treatment of dienyl acetate **2** with $[Pd(PPh_3)_4]$ (0.15 mol-equiv.) and (tributyl)-(vinyl)stannane (1.2 mol-equiv.) in THF at 40° afforded, to our disappointment, the cyclized β-elimination product **9** in 69% yield (*Scheme 3*; *Table 1*, *Entry 1*).

Equally discouraging was the $[Pd(dba)_2]$/tri(2-furyl)phosphine-catalyzed[2]) reaction of **2** with divinylzinc which furnished the acyclic, allylic coupling product **10** in 71% yield

Scheme 3



[1]) For Pd-catalyzed C,C-coupling reactions of vinylmetal reagents, see [4].

[2]) Tri(2-furyl)phosphine has been described as a superior ligand to Ph_3P in Pd^0-catalyzed coupling reactions of 1-alkenylstannanes [5]. For the beneficial effect of $ZnCl_2$, see [5b].

Table 1. *Pd-Catalyzed Reactions of 5,5-Bis(phenylsulfonyl)octa-2,7-diene* (**2**) *with Vinylmetal Reagents in THF.* Competition between cyclization (*β*-elimination (**2** → **9**)), allyl/vinyl coupling (**2** → **10**), and cyclization/vinyl coupling (**2** → **11**) (*Scheme 3*).

Entry	$[Pd^0L_4]$	PR_3	$L_nMCH{=}CH_2$ ([mol-equiv.])	Additive ([mol-equiv.])	Temp. [°C]	Time [h]	Product	Yield [%]
1	$[Pd(PPh_3)_4]$	–	$Bu_3SnCH{=}CH_2$ (1.2)	–	40	6	**9**	69
2	$[Pd(dba)_2]$		$Zn(CH{=}CH_2)_2$ (2.3)	–	0	96	**10**	71
3	$[Pd(dba)_2]$		$Bu_3SnCH{=}CH_2$ (2)	$ZnCl_2$ (2)	reflux	1	**11a**	76

(*Entry 2*). However, using the same catalyst but employing (tributyl)(vinyl)stannane and $ZnCl_2$[2]) in THF at reflux the desired cyclization/coupling product **11a** was obtained in 76% yield (*Entry 3*).

Under analogous reaction conditions, dienyl acetate **2** was cyclized in the presence of various (1-alkenyl)(tributyl)stannanes to give a series of functionalized 1-vinyl-2-(2′-alkenyl)cyclopentane products **11** (*Scheme 4*, *Table 2*).

Scheme 4

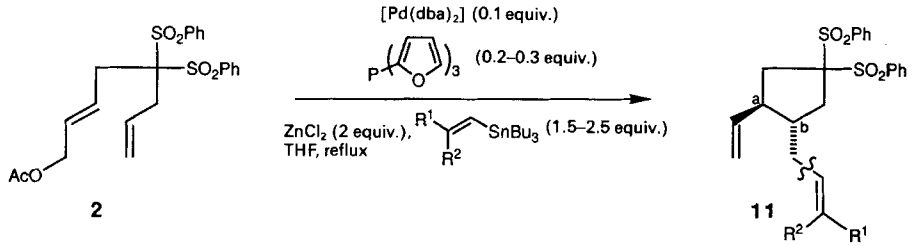
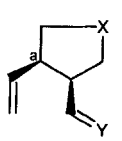


Table 2. *Pd-Catalyzed Octa-2,7-dienyl Acetate Cyclization/Vinylstannane Coupling* **2** → **11** (*Scheme 4*)

Entry	Vinylstannane		Time [h]	Product **11**	
	R^1	R^2			Yield [%]
3	H	H	1	**11a**	76
4	$SiMe_3$	H	2	**11b**	85
5	CO_2Et	H	2	**11c**	77
6	H	CO_2Et	4	**11d**	67
7	CH_2OTHP	H	2	**11e**	75
8	$CH_2NH(Fmoc)$	H	2	**11f**	65

The (*E*/*Z*)-integrity is preserved (*Entries 5* and *6*), and the two substituents in **11** are predominantly *trans*-related (94 to > 99%). This *trans*-substitution pattern of products **11** was readily assigned by comparing the chemical shifts of the ^{13}C-NMR signals of C(a) (δ = 49.23 to 49.76 ppm) with those of *trans*-cyclopentanes and *trans*-pyrrolidines **13**



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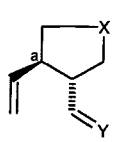

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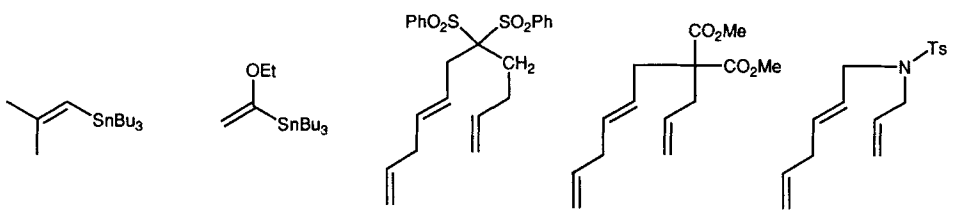
Table 3. *^{13}C-NMR Chemical Shifts of C(a) in* cis/trans-*Vicinally Substituted Vinylcyclopentanes and Vinylpyrrolidines* **12** *and* **13** [6b]

X	Y	δ(C(a)) [ppm] **12** (*cis*)	δ (C(a)) [ppm] **13** (*trans*)
CTs_2	CH_2	47.39	49.41
$NCOCF_3$	CH_2	46.35	48.46
$C(CO_2Me)_2$	H, CO_2Me	45.7	50.1
NTs	H, CO_2Me	44.9	48.8

(δ = 48.46 to 50.1 ppm). C(a) in *cis*-isomers **12** resonate at higher fields (δ = 44.9 to 47.39 ppm; *Table 3*) [6].

Nevertheless, two limitations deserve to be mentioned. Attempted cyclization/coupling of **2** with the sterically more demanding (1-alkenyl)stannanes **14** [7] and **15** [8] gave only the cyclized β-elimination product **9**.



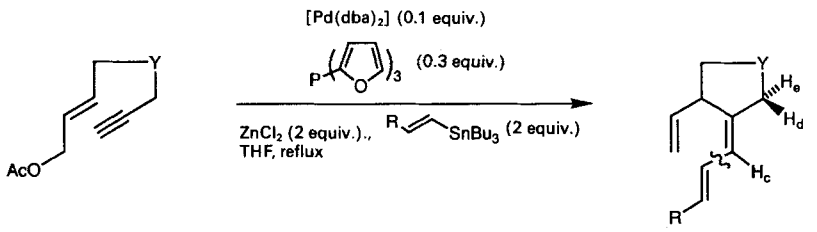
14 **15** **16** **17** **18**

The other limiting factor is the relatively small rate difference between cyclization (**I** → **II**) and allylic coupling (**I** → **V**): dienyl acetates in which the $C(SO_2Ph)_2$ moiety of **2** was replaced by a $C(SO_2Ph)_2CH_2$, $C(CO_2Me)_2$, or NTs group gave mainly non-cyclized allylic coupling products **16**, **17**, or **18**, respectively.

'Metallo-ene'-type cyclizations usually proceed faster with alkyne 'enophiles' (as compared to alkene 'enophiles') and do not pose the problem of β-elimination. They should, therefore, offer wider possibilities when combined with such a C,C-coupling protocol.

Indeed, [Pd(dba)$_2$]/tri(2-furyl)phosphine-catalyzed cyclization of enynyl acetates **4**, **6**, and **8** in the presence of $ZnCl_2$ and an (1-alkenyl)(tributyl)stannane afforded the expected products **19**, **20**, and **21** (61–83% yield; *Scheme 5*, *Table 4*), respectively.

Scheme 5



4 Y = $C(SO_2Ph)_2$
6 Y = $C(CO_2Me)_2$
8 Y = NTs

19 Y = $C(SO_2Ph)_2$
20 Y = $C(CO_2Me)_2$
21 Y = NTs

Table 4. *Pd-Catalyzed Oct-2-en-7-ynyl Acetate Cyclization/Vinylstannane Couplings* **4** → **19**, **6** → **20a**, *and* **8** → **21a** (*Scheme 5*)

Entry	Enyne		Vinylstannane R	Time [h]	Product	
		Y				Yield [%]
9	**4**	$C(SO_2Ph)_2$	H	1	**19a**	76
10	**4**	$C(SO_2Ph)_2$	CO_2Et	1	**19c**	74
11	**4**	$C(SO_2Ph)_2$	CH_2OTHP	4	**19e**	61
12	**6**	$C(CO_2Me)_2$	H	0.5	**20a**	72
13	**8**	NTs	H	1	**21a**	83

The 1,3-diene configurations of **19**, **20**, and **21** were assigned based on strong NOE interactions $H_c \leftrightarrow H_d$ and $H_c \leftrightarrow H_e$ in the NOESY spectrum of product **21a**.

They are consistent with a suprafacial (*syn*-)carbometallation of the 'enophilic' acetylene unit. Coupling with (*E*)-2-substituted (1-alkenyl)stannanes gave products **19c** and **19e** with preservation of the stereochemical integrity (*Entries 10* and *11*).

In summary, the synthetic potential of Pd-catalyzed intramolecular alkene and alkyne allylations can be further extended to encompass (1-alkenyl)stannane coupling reactions.

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Experimental Part

General. All reactions were carried out under Ar with magnetic stirring, unless otherwise specified. Solvents were dried by distillation from drying agents as follows: Et_2O, THF, toluene (Na), DMF, CH_2Cl_2 (CaH_2), CCl_4 (P_2O_5), MeOH (Mg). 'Workup' denotes extraction with an org. solvent, drying ($MgSO_4$), and evaporation *in vacuo*. Column flash chromatography (FC): SiO_2 (*60*, 0.04–0.06 mm, *Merck 9385*). M.p.: *Kofler* hot stage; uncorrected. IR: *Polaris Matteson*, in $CHCl_3$, unless otherwise specified. ^{1}H-NMR in $CDCl_3$, unless otherwise specified; ^{13}C-NMR in $CDCl_3$, unless otherwise specified; standard $CDCl_3$ (δ = 7.27 ppm), *J* in Hz. MS: *Varian CH-4* or *Finnigan 4023* at 70 eV, *m/z* (rel.-%). HR-MS: *VG 7070-E*.

Preparation of Acyclic Acetoxydienes and Acetoxyenynes. – *4,4-Bis(phenylsulfonyl)but-1-yne* (**3**). NaH (60% in mineral oil; 485 mg, 12 mmol) was added portionwise at 0° to a soln. of bis(phenylsulfonyl)methane (3.0 g, 10.12 mmol) in DMF (50 ml). After stirring the mixture at r.t. for 1 h, propargyl bromide (1.26 g, 10.6 mmol) was added dropwise. The mixture was stirred at r.t. for 16 h and then poured into ice-water. Extraction (AcOEt), washing of the extracts with H_2O and sat. aq. NaCl, drying ($MgSO_4$), evaporation, and chromatography of the residue (hexane/AcOEt 3:2) gave **3** (2.30 g, 68%). ^{1}H-NMR (200 MHz): 1.93 (*t*, *J* = 3, 1 H); 3.12 (*dd*, *J* = 6, 3, 2 H); 4.59 (*t*, *J* = 6, 1 H); 7.5–7.8 (6 H); 7.95–8.05 (4 H). ^{13}C-NMR: 137.54 (*s*); 134.86 (*d*); 129.8 (*d*); 129.34 (*d*); 129.16 (*d*); 128.82 (*d*); 81.91 (*d*); 76.78 (*s*); 72.16 (*d*); 16.56 (*t*).

N-*(Prop-2-ynyl)*-p-*toluenesulfonamide* (**7**). TsCl (5.0 g, 26.23 mmol) and pyridine (2.3 ml, 28.4 mmol) were added at 0° under Ar to a stirred soln. of propargylamine (1.2 g, 21.8 mmol) in CH_2Cl_2 (30 ml). Stirring of the mixture at 0° for 20 min then at r.t. for 20 min, followed by workup and chromatography (hexane/AcOEt 7:3) and crystallization (EtOH) furnished **7** (3.8 g, 84%). M.p. 74–75°. IR: 3400, 3300, 3000, 1400, 1320, 1150. ^{1}H-NMR (200 MHz): 2.09 (*t*, *J* = 3, 1 H); 2.42 (*s*, 3 H); 3.82 (*dd*, *J* = 6, 3, 2 H); 4.70 (*t*, *J* = 3, 1 H); 7.29–7.35 (2 H); 7.72–7.82 (2 H).

5,5-Bis(phenylsulfonyl)octa-2,7-dienyl Acetate (**2**). NaH (60%, 0.92 g, 22.9 mmol) was added portionwise at 0° to a soln. of **1** [9] (7.0 g, 20.8 mmol) in THF (90 ml). After stirring the mixture at 0° for 1 h, then at r.t. for 1 h, $[Pd(dba)_2]$ [10] (0.60 g, 1.04 mmol) and PPh_3 (1.09 g, 4.15 mmol) followed by a soln. of (*Z*)-4-chlorobut-2-enyl acetate [11] (3.10 g, 20.9 mmol) in THF (50 ml) were added under Ar. Stirring of the mixture for 16 h, pouring into H_2O, extraction (Et_2O), washing, and drying of the extracts, followed by chromatography of the residue (hexane/AcOEt 4:1→7:3) provided **2** (6.34 g, 68%). M.p. 67–68°. IR: 2950–3100, 1720, 1450, 1320, 1300, 1230, 1150.

^{1}H-NMR (400 MHz): 2.07 (*s*, 3 H); 2.98–3.04 (4 H); 4.52 (*dd*, *J* = 7, 2, 2 H); 5.17 (*dd*, *J* = 17, 2, 1 H); 5.23 (*dd*, *J* = 10, 2, 1 H); 5.68 (*m*, 1 H); 5.92 (*m*, 1 H); 6.0 (*ddt*, *J* = 17, 10, 7, 1 H); 7.56–7.60 (4 H); 7.69–7.73 (2 H); 8.04–8.06 (4 H). ^{13}C-NMR (100 MHz): 170.61 (*s*); 136.75 (*s*); 134.68 (*d*); 131.53 (*d*); 129.95 (*d*); 129.83 (*d*); 128.60 (*d*); 126.39 (*d*); 120.80 (*t*); 90.01 (*s*); 64.25 (*t*); 33.94 (*t*); 32.48 (*t*); 20.90 (*q*). MS: 389 (9, $[C_{22}H_{24}S_2O_6 - CH_3COO]^+$), 247 (15), 246 (10), 143 (23), 125 (100), 105 (85), 91 (22), 77 (90).

5,5-Bis(phenylsulfonyl)oct-2-en-7-ynyl Acetate (**4**). Employing the reaction conditions described for the preparation of **2**, **3** (1.893 g, 5.66 mmol) was treated successively with NaH (60%, 0.25 g), $[Pd(dba)_2]$ [10] (0.2 g), PPh_3 (0.3 g) and (*Z*)-4-chlorobut-2-enyl acetate [11] (0.84 g) giving **4** (oil, 2.3 g, 91%). IR (CH_2Cl_2): 3300, 1750, 1450, 1340, 1317, 1240, 1150, 1080. ^{1}H-NMR (360 MHz): 2.01 (*s*, 4 H); 3.09 (*dd*, *J* = 7, 1, 2 H); 3.14 (*d*, *J* = 3, 2 H); 4.55 (*dd*, *J* = 6, 1.2, 2 H); 5.79 (*m*, 1 H); 5.98 (*m*, 1 H); 7.5–7.65 (4 H); 7.65–7.75 (2 H); 8.05–8.15 (4 H). ^{13}C-NMR (50 MHz): 170.60 (*s*); 136.32 (*s*); 134.89 (*d*, 2 C); 131.4 (*d*, 2 C); 130.52 (*d*); 128.64 (*d*, 2 C); 125.84 (*d*); 88.43 (*s*); 75.65 (*s*); 74.54 (*s*); 64.25 (*t*); 32.11 (*t*); 20.91 (*t*). MS: 304 (20, $[C_{22}H_{22}O_6S_2 - C_6H_6SO_2]^+$), 141 (10), 125 (31), 97 (9), 91 (11), 77 (100). HR-MS: 262.0685 ($[C_{22}H_{22}O_6S_2 - C_8H_8O_3S]^+$, calc. 262.0663).

Dimethyl 2-(4-Acetoxybut-2-enyl)-2-(prop-2-ynyl)propanedioate (**6**). Employing analogous reaction conditions as described for the preparation of **2**, *dimethyl 2-(prop-2-ynyl)propanedioate* [12] (**5**; 180 mg, 1.4 mmol) was treated successively with NaH (71 mg, 1.7 mmol), $[Pd(PPh_3)_4]$ (161 mg, 0.14 mmol) and (*Z*)-4-chlorobut-2-enyl acetate [11] (251 mg, 1.7 mmol) for 4 h at r.t., giving **6** (oil, 321 mg, 82%). IR: 3300, 3020, 2970, 1740, 1450, 1370, 1250, 1200, 1030, 970. ^{1}H-NMR (200 MHz): 1.98 (*s*, 3 H); 1.98 (*m*, 1 H); 2.65–2.75 (4 H); 3.75 (*s*, 6 H); 4.40 (*d*, *J* = 6, 2 H); 5.40–5.70 (2 H). ^{13}C-NMR (50 MHz): 170.45 (*s*); 169.78 (*s*); 129.21 (*d*); 128.37 (*d*); 78.42 (*s*); 71.71 (*d*); 64.26 (*t*); 59.95 (*s*); 56.67 (*t*); 52.77 (*q*); 52.68 (*q*); 34.90 (*t*); 20.75 (*q*).

N-*(4-Acetoxybut-2-enyl)*-N-*(prop-2-ynyl)*-p-*toluenesulfonamide* (**8**). Employing analogous reaction conditions as described for the preparation of **2**, **7** (1.9 g, 9 mmol) was treated successively with NaH (55%, 419 mg, 9.5 mmol), $[Pd(PPh_3)_4]$ (200 mg, 0.17 mmol), and (*Z*)-4-chlorobut-2-enyl acetate [11] (1.5 g, 10 mmol) for 4 h at r.t., giving **8** (oil, 2.6 g, 90%). IR: 3300, 3000, 2950, 1740, 1600, 1460, 1450, 1360, 1250, 1160. ^{1}H-NMR (200 MHz): 2.00 (*m*, 1 H); 2.02 (*s*, 3 H); 2.42 (*s*, 3 H); 3.80 (*d*, *J* = 6, 2 H); 4.05 (*d*, *J* = 4, 2 H); 4.52 (*d*, *J* = 5, 2 H); 5.61 (*dt*, *J* = 15.5, 6, 1 H); 5.79 (*dt*, *J* = 15.5, 6, 1 H); 7.25 (*d*, *J* = 8, 2 H); 7.7 (*d*, *J* = 8, 2 H). ^{13}C-NMR (50 MHz): 170.47 (*s*); 143.60 (*s*); 135.74 (*s*); 129.46 (*d*); 129.39 (*d*); 127.61 (*d*); 127.46 (*d*); 76.30 (*s*); 73.97 (*d*); 63.61 (*t*); 47.59 (*t*); 35.85 (*t*); 21.46 (*q*); 20.75 (*q*). MS: 262 (5, $[C_{16}H_{19}NO_4S - C_2H_4O_2]^+$), 261 (8), 248 (12), 166 (15), 155 (44), 106 (55), 91 (100), 79 (21). HR-MS: 261.0778 ($[C_{16}H_{19}NO_4S - C_2H_4O_2]^+$, calc. 261.0823).

Attempted Cyclization/Coupling Procedures. – *1,1-Bis(phenylsulfonyl)-3-methylidene-4-vinylcyclopentane* (**9**). A mixture of **2** (270 mg, 0.6 mmol), $[Pd(PPh_3)_4]$ (104 mg, 0.09 mmol), (tributyl)(vinyl)stannane (0.22 ml, 0.75 mmol), and THF (3 ml) was stirred at 40° for 6 h. Dilution with Et_2O, washing with sat. aq. NaCl soln., drying, evaporation, and chromatography (hexane/AcOEt 3:2) furnished **9** (161 mg, 69%). M.p. 113–114° (EtOH). IR: 3100–2950, 1450, 1330, 1310, 1150, 1070. ^{1}H-NMR (400 MHz): 2.48 (*dd*, *J* = 15, 10.5, 1 H); 2.75 (*dd*, *J* = 15, 8.2, 1 H); 3.25–3.40 (3 H); 4.75 (*q*, *J* = 2.3, 1 H); 4.88 (*q*, *J* = 2.3, 1 H); 5.10 (*ddd*, *J* = 17, 1.5, 1, 1 H); 5.15 (*dd*, *J* = 10.5, 1.5, 1 H); 5.55 (*ddd*, *J* = 17, 10.5, 8.2, 1 H); 7.55–7.80 (6 H); 8.0–8.13 (4 H). ^{13}C-NMR (100 MHz): 148.37 (*s*); 137.67 (*d*); 134.67 (*d*); 134.56 (*d*); 131.31 (*d*); 131.22 (*d*); 128.79 (*d*); 128.75 (*d*); 117.53 (*d*); 108.64 (*t*); 91.79 (*s*); 48.04 (*d*); 38.15 (*t*); 37.70 (*t*). MS: 248 (10), 247 (42, $[C_{20}H_{20}O_4S_2 - C_6H_5O_2S]^+$), 246 (64), 245 (15), 125 (64), 121 (25), 105 (100), 77 (72). HR-MS: 246.06813 ($[C_{20}H_{20}O_4S_2 - C_6H_6O_2S]^+$, calc. 246.07145).

(E)-7,7-Bis(phenylsulfonyl)deca-1,4,9-triene (**10**). A 2.3M soln. of distilled divinylzinc [13] in THF (0.13 ml, 0.3 mmol) was added at 0° to a mixture of **2** (127 mg, 0.284 mmol) and $[Pd(PPh_3)_4]$ (16 mg, 0.014 mmol). Stirring the mixture at 0° for 4 days, dilution with Et_2O, washing with sat. aq. NH_4Cl soln., drying, evaporation, and chromatography (hexane/AcOEt 10:1) gave **10** (oil, 84 mg, 71%). IR: 3073, 3018, 2926, 2854, 1448, 1330, 1311, 1149, 1077. ^{1}H-NMR (360 MHz): 2.7–2.8 (2 H); 2.96–3.05 (4 H); 5.00–5.08 (2 H); 5.18 (*dd*, *J* = 17, 2, 1 H); 5.23 (*dd*, *J* = 10, 2, 1 H); 5.55–5.62 (2 H); 5.78 (*ddt*, *J* = 17, 10, 7, 1 H); 6.02 (*ddt*, *J* = 17, 10, 7, 1 H); 7.54–7.62 (4 H); 7.65–7.75 (2 H); 8.03–8.12 (4 H). ^{13}C-NMR (100 MHz): 136.95 (*s*); 135.96 (*d*); 134.49 (*d*); 134.34 (*d*); 131.52 (*d*); 130.03 (*d*); 128.46 (*d*); 122.16 (*d*); 120.36 (*t*); 115.69 (*t*); 90.44 (*s*); 36.66 (*t*); 33.68 (*t*); 32.60 (*t*). MS: 275 (23, $[C_{22}H_{24}O_4S_2 - C_6H_5SO_2]^+$), 279 (21), 233 (7), 219 (6), 210 (6), 143 (27), 133 (99), 125 (76), 117 (25), 105 (42), 91 (82), 80 (65), 77 (100), 67 (43), 55 (33).

Successful Cyclization/Coupling Procedures. – trans-*1,1-Bis(phenylsulfonyl)-3-(prop-2-enyl)-4-vinylcyclopentane* (**11a**). To a soln. of **2** (318 mg, 0.71 mmol) in THF (5 ml) was added successively $ZnCl_2$ (dried *in vacuo* at 130° for 16 h, 200 mg, 1.47 mmol), (tributyl)(vinyl)stannane (450 mg, 1.42 mmol), $[Pd(dba)_2]$ [10] (41 mg, 0.07 mmol), and tri(2-furyl)phosphine [14] (33 mg, 0.14 mmol). Heating the mixture under reflux for 1 h, dilution with Et_2O (20 ml), washing with sat. aq. NH_4Cl soln., sat. aq. KF soln. (4×), H_2O and sat. aq. NaCl soln., drying,

evaporation, and chromatography (hexane/AcOEt 15:1) gave **11a** (oil, 224 mg, 76%). IR: 3030–2900, 1650, 1600, 1450, 1290, 1260, 1200, 1150, 1050. ^{1}H-NMR: 1.72 (*m*, 1 H); 1.85 (*m*, 1 H); 2.15–2.30 (2 H); 2.25 (*dd*, *J* = 15, 11, 1 H); 2.40 (*dd*, *J* = 15, 11, 1 H); 2.68 (*dd*, *J* = 15, 8, 2 H); 4.96–5.10 (4 H); 5.55 (*ddd*, *J* = 17, 9, 8, 1 H); 5.60–5.72 (1 H); 7.56–7.62 (4 H); 7.65–7.75 (2 H); 8.05–8.12 (4 H). ^{13}C-NMR: 138.08 (*d*); 136.34 (*s*); 135.42 (*d*); 134.58 (*d*); 131.33 (*d*); 131.26 (*d*); 128.71 (*d*); 117.37 (*t*); 116.76 (*t*); 91.45 (*s*); 49.23 (*d*); 44.47 (*d*); 38.35 (*t*); 37.40 (*t*); 35.88 (*t*). MS: 416 (30, $C_{22}H_{24}O_4S_2^{+\cdot}$), 356 (65), 274 (60), 143 (20), 133 (100), 105 (45), 91 (86), 77 (95). HR-MS: 416.1112 ($C_{22}H_{24}O_4S_2^{+\cdot}$, calc. 416.1116).

trans-*1,1-Bis(phenylsulfonyl)-3-[(*E*)-3-(trimethylsilyl)prop-2-enyl]-4-vinylcyclopentane* (**11b**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **2** (268 mg, 0.6 mmol) was treated with $ZnCl_2$ (465 mg, 2 mol-equiv.), (*E*)-(tributyl)[2-(trimethylsilyl)vinyl]stannane [15] (465 mg, 2 mol-equiv.), [Pd(dba)$_2$] [10] (35 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (42 mg, 0.3 mol-equiv.) to give **11b** (oil, 248 mg, 85%). IR: 3030–2950, 1650, 1625, 1590, 1450, 1320, 1300, 1250, 1150, 1070, 970. ^{1}H-NMR: 0.05 (*s*, 9 H); 1.67 (*m*, 1 H); 1.87 (*m*, 1 H); 2.10–2.45 (4 H); 2.55–2.75 (2 H); 4.95–5.12 (2 H); 5.50 (*ddd*, *J* = 16.5, 10.5, 8, 1 H); 5.62 (*d*, *J* = 18.5, 1 H); 5.83 (*dt*, *J* = 18.5, 6, 1 H); 7.50–7.80 (6 H); 7.98–8.15 (4 H). ^{13}C-NMR: 143.57 (*d*); 138.19 (*d*); 136.42 (*s*); 136.31 (*d*); 134.64 (*d*); 132.62 (*d*); 131.38 (*d*); 131.32 (*d*); 128.79 (*d*); 128.73 (*d*); 117.37 (*t*); 91.55 (*s*); 49.51 (*d*); 44.42 (*d*); 39.13 (*t*); 38.36 (*t*); 37.54 (*t*); −1.16 (*q*). MS: 488 (0.75, $C_{25}H_{32}O_4S_2Si^{+\cdot}$), 347 (25), 331 (81), 215 (48), 199 (30), 135 (56), 125 (45), 91 (29), 77 (44), 73 (100), 59 (38). HR-MS: 347.1509 ([$C_{25}H_{32}O_4S_2Si - C_6H_5O_2S$]$^{+\cdot}$, calc. 347.1501).

*Ethyl (*E*)-4-[*trans-*4,4-Bis(phenylsulfonyl)-2-vinylcyclopentyl]but-2-enoate* (**11c**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **2** (310 mg, 0.69 mmol) was treated with $ZnCl_2$ (190 mg, 2 mol-equiv.), ethyl (*E*)-3-(tributylstannyl)propenoate [16] (540 mg, 2 mol-equiv.), [Pd(dba)$_2$] [10] (40 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (33 mg, 0.2 mol-equiv.) to give **11c** (oil, 260 mg, 77%). IR: 3070–2900, 1715, 1675, 1450, 1325, 1150, 1050, 1020, 900. ^{1}H-NMR: 1.30 (*t*, *J* = 8, 3 H); 1.75 (*m*, 1 H); 1.95 (*m*, 1 H); 2.05–2.30 (2 H); 2.30–2.45 (2 H); 2.60–2.80 (2 H); 4.20 (*q*, *J* = 8, 2 H); 4.95–5.15 (2 H); 5.48 (*ddd*, *J* = 17, 10, 7, 1 H); 5.76 (*dd*, *J* = 16, 2, 1 H); 6.75 (*dt*, *J* = 16, 8, 1 H); 7.50–7.80 (6 H); 7.98–8.15 (4 H). ^{13}C-NMR: 166.06 (*s*); 145.55 (*d*); 137.58 (*d*); 136.10 (*s*); 136.06 (*s*); 134.70 (*d*); 131.26 (*d*); 128.82 (*d*); 123.16 (*d*); 117.96 (*t*); 91.34 (*s*); 60.28 (*t*); 49.62 (*d*); 43.93 (*d*); 38.20 (*t*); 37.47 (*t*); 34.34 (*t*); 14.26 (*q*). MS: 488 (0.28, $C_{25}H_{28}O_6S)_2^{+\cdot}$), 205 (14), 159 (43), 141 (14), 131 (68), 125 (100), 91 (65), 77 (99). HR-MS: 301.0881 ($C_{17}H_{17}O_3S^{+\cdot}$, 301.0898). Anal. calc. for $C_{25}H_{28}O_6S_2$: C 61.47, H 5.73, S 13.11; found: C 61.69, H 5.68, S 12.87.

*Ethyl (*Z*)-4-[*trans-*4,4-Bis(phenylsulfonyl)-2-vinylcyclopentyl]but-2-enoate* (**11d**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **2** (332 mg, 0.74 mmol) was treated with $ZnCl_2$ (205 mg, 2 mol-equiv.), ethyl (*Z*)-3-(tributylstannyl)propenoate [16] (578 mg, 2 mol-equiv.), [Pd(dba)$_2$] [10] (43 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (35 mg, 0.2 mol-equiv.) to give **11d** (oil, 245 mg, 67%). IR: 3030–2900, 1725, 1640, 1450, 1325, 1300, 1180, 1150, 1075, 900. ^{1}H-NMR: 1.30 (*t*, *J* = 8, 3 H); 1.60–1.90 (2 H); 2.10–2.45 (4 H); 2.60–2.80 (2 H); 4.20 (*q*, *J* = 8, 2 H); 4.96–5.10 (2 H); 5.54 (*ddd*, *J* = 16, 11, 8, 1 H); 5.80 (*dt*, *J* = 11.5, 2, 1 H); 6.10 (*dt*, *J* = 11.5, 8, 1 H); 7.50–7.80 (6 H); 7.98–8.15 (4 H). ^{13}C-NMR: 166.03 (*s*); 146.69 (*d*); 137.81 (*d*); 136.31 (*s*); 134.56 (*d*); 134.51 (*d*); 131.48 (*d*); 131.31 (*d*); 128.67 (*d*); 121.29 (*d*); 117.67 (*t*); 91.38 (*s*); 59.89 (*t*); 49.76 (*d*); 44.81 (*d*); 38.32 (*t*); 37.40 (*t*); 30.98 (*t*); 14.24 (*q*). MS: 488 (0.34, $C_{25}H_{28}O_6S_2^{+\cdot}$), 301 (16), 205 (14), 159 (77), 131 (52), 125 (100), 91 (65), 77 (96). HR-MS: 301.0895 ([$C_{25}H_{28}O_6S_2 - C_8H_{11}O_3S$]$^{+\cdot}$, calc. 301.0898).

*(*E*)-2-{{(4-[*trans-*4,4-Bis(phenylsulfonyl)-2-vinylcyclopentyl]but-2-enyl}oxy}tetrahydropyran* (**11e**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **2** (293 mg, 0.65 mmol) was treated with $ZnCl_2$ (200 mg, 2.25 mol-equiv.), tetrahydro-2-{[(*E*)-3-(tributylstannyl)prop-2-enyl]oxy}pyran [17] (704 mg, 2.5 mol-equiv.), [Pd(dba)$_2$] [10] (35 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (31 mg, 0.2 mol-equiv.) to give **11e** (oil, 263 mg, 75%). IR: 3050–2900, 1700, 1475, 1325, 1300, 1140, 1050. ^{1}H-NMR: 1.45–1.90 (8 H); 2.10–2.30 (3 H); 2.36 (*dd*, *J* = 15, 11.5, 1 H); 2.61–2.70 (2 H); 3.50 (*m*, 1 H); 3.82–3.95 (2 H); 4.18 (*m*, 1 H); 4.60 (*m*, 1 H); 4.96–5.15 (2 H); 5.50 (*ddd*, *J* = 17, 10, 8, 1 H); 5.55–5.6 (2 H); 7.55–7.62 (4 H); 7.65–7.75 (2 H); 8.05–8.10 (4 H). ^{13}C-NMR: 138.00 (*d*); 136.28 (*s*); 134.60 (*d*); 131.31 (*d*); 131.26 (*d*); 130.43 (*d*); 130.36 (*d*); 128.71 (*d*); 117.37 (*t*); 97.88 (*d*); 97.85 (*d*); 91.41 (*s*); 67.45 (*t*); 67.42 (*t*); 62.25 (*t*); 49.24 (*d*); 44.62 (*d*); 38.32 (*t*); 37.46 (*t*); 34.32 (*t*); 30.63 (*t*); 25.38 (*t*); 19.53 (*t*). MS: 286 (24, [$C_{28}H_{34}O_6S_2 - C_{11}H_{16}O_4S$]$^{+\cdot}$), 145 (45), 125 (100), 117 (23), 91 (66), 77 (83), 67 (22). HR-MS: 286.0989 ($C_{17}H_{18}O_2S^{+\cdot}$, calc. 286.1027).

trans-*1,1-Bis(phenylsulfonyl)-3-{(*E*)-4-[(fluoren-9-yl)methoxycarbonylamino]but-2-enyl}-4-vinylcyclopentane* (**11f**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **2** (150 mg, 0.335 mmol) was treated with $ZnCl_2$ (92 mg, 2 mol-equiv.), (*E*)-1-[(fluoren-9-yl)methoxycarbonylamino]-1-(tributylstannyl)propene [18] (290 mg, 1.5 mol-equiv.), [Pd(dba)$_2$] [10] (20 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (16 mg, 0.2 mol-equiv.) to give **11f** (solid, 143 mg, 65%). IR: 3400, 3050–2900, 1730, 1520, 1450, 1325, 1300, 1230, 1150, 1070. ^{1}H-NMR (200 MHz): 1.65–1.92 (2 H); 2.10–2.45 (4 H); 2.60–2.75 (2 H); 3.60–3.84 (2 H); 4.22 (*t*, *J* = 7,

1 H); 4.42 (*d*, *J* = 7, 2 H); 4.80 (*m*, 1 H); 4.94–5.12 (2 H); 5.38–5.60 (3 H); 7.20–7.45 (4 H); 7.50–7.85 (10 H); 7.95–8.15 (4 H). ^{13}C-NMR: 156.17 (*s*); 143.89 (*s*); 141.26 (*s*); 138.05 (*d*); 136.28 (*d*); 136.25 (*s*); 134.64 (*d*); 131.31 (*d*); 131.26 (*d*); 129.79 (*d*); 128.75 (*d*); 128.61 (*d*); 128.32 (*d*); 127.63 (*d*); 127.00 (*d*); 125.00 (*d*); 119.93 (*d*); 117.45 (*t*); 91.52 (*s*); 66.65 (*t*); 66.60 (*t*); 49.28 (*d*); 47.21 (*d*); 44.65 (*d*); 42.80 (*t*); 38.35 (*t*); 37.37 (*t*). MS: 286 (14, $[C_{38}H_{37}NO_6S_2 - C_{21}H_{19}NO_4S]^{+}$), 165 (100), 125 (35), 77 (32). Anal. calc. for $C_{38}H_{37}NO_6S_2$: C 68.36, H 5.54, N 2.09, S 9.59; found: C 68.11, H 5.47, N 2.33, S 9.48.

(Z)-1,1-Bis(phenylsulfonyl)-3-(prop-2-enylidene)-4-vinylcyclopentane (**19a**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **4** (335 mg, 0.747 mmol) was treated with $ZnCl_2$ (210 mg, 2 mol-equiv.), (tributyl)(vinyl)stannane (0.44 ml, 2 mol-equiv.), $[Pd(dba)_2]$ [10] (43 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (53 mg, 0.3 mol-equiv.) to give **19a** (235 mg, 76%). IR: 3050, 3000, 2950, 1650, 1600, 1450, 1330, 1320, 1250, 1150, 1070. ^{1}H-NMR (200 MHz): 2.58 (*dd*, *J* = 15.5, 7.5, 1 H); 2.90 (*ddd*, *J* = 15.5, 8.5, 2, 1 H); 2.86 (*d*, *J* = 17, 1 H); 3.48–3.64 (1 H); 3.63 (br. *d*, *J* = 17, 1 H); 4.95–5.15 (4 H); 5.74 (*ddd*, *J* = 17, 10, 8, 1 H); 5.88 (br. *d*, *J* = 10.5, 1 H); 6.40 (*dt*, *J* = 16.5, 10.5, 1 H); 7.50–7.80 (6 H); 7.90–8.15 (4 H). ^{13}C-NMR: 140.39 (*s*); 139.18 (*d*); 137.03 (*s*); 135.78 (*s*); 134.77 (*d*); 134.55 (*d*); 132.45 (*d*); 131.03 (*d*); 130.96 (*d*); 128.67 (*d*); 125.57 (*d*); 117.16 (*t*); 115.38 (*t*); 91.81 (*s*); 45.05 (*d*); 39.41 (*t*); 38.02 (*t*). MS: 414 (0.5, $C_{22}H_{22}O_4S_2^{+}$), 272 (26), 271 (11), 147 (12), 131 (100). HR-MS: 272.0852 ($[C_{22}H_{22}O_4S_2 - C_6H_6O_2S]^{+}$, calc. 272.0870). Anal. calc.: C63.76, H 5.31, S 15.45; found: C 63.53, H 5.33, S 15.42.

Ethyl (2E,4Z)-4-[4,4-Bis(phenylsulfonyl)-2-vinylcyclopentylidene]but-2-enoate (**19c**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **4** (286 mg, 0.64 mmol) was treated with $ZnCl_2$ (175 mg, 2 mol-equiv.), ethyl (*E*)-3-(tributylstannyl)propenoate [16] (500 mg, 2 mol-equiv.), $[Pd(dba)_2]$ [10] (37 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (45 mg, 0.3 mol-equiv.) to give **19c** (oil, 230 mg, 74%). IR: 3000–2950, 1700, 1625, 1600, 1425, 1320, 1300, 1270, 1150, 1050. ^{1}H-NMR: 1.25 (*t*, *J* = 8, 3 H); 2.62 (*dd*, *J* = 15, 8, 1 H); 2.89 (*ddd*, *J* = 15, 8, 2, 1 H); 2.95 (*d*, *J* = 18, 1 H); 3.68 (*d*, *J* = 18, 1 H); 3.76 (*m*, 1 H); 4.18 (*q*, *J* = 8, 2 H); 5.05–5.20 (2 H); 5.72 (*d*, *J* = 16, 1 H); 5.77 (*ddd*, *J* = 16, 8, 6, 1 H); 6.01 (*d*, *J* = 10, 1 H); 7.42 (*dd*, *J* = 16, 10, 1 H); 7.50–7.80 (6 H); 7.92–8.10 (4 H). ^{13}C-NMR: 166.80 (*s*); 149.86 (*s*); 139.45 (*d*); 136.99 (*d*); 136.74 (*s*); 135.49 (*s*); 134.94 (*d*); 134.71 (*d*); 131.01 (*d*); 130.97 (*d*); 128.80 (*d*); 128.75 (*d*); 122.65 (*d*); 121.12 (*d*); 116.25 (*t*); 91.59 (*s*); 60.27 (*t*); 45.57 (*d*); 39.85 (*t*); 37.80 (*t*); 14.20 (*q*). MS: $C_{25}H_{26}O_6S_2^{+}$ absent, 344 (25), 298 (17), 270 (21), 203 (12), 157 (31), 129 (100), 125 (41), 115 (21), 91 (25). HR-MS: 299.0767 ($[C_{25}H_{26}O_6S_2 - C_{18}H_{11}O_3S]^{+}$, calc. 299.0742).

2-{{(2E,4Z)-4-[4,4-Bis(phenylsulfonyl)-2-vinylcyclopentylidene]but-2-enyl}oxy}tetrahydropyran (**19e**). Employing the cyclization/coupling conditions described for the preparation of **11a**, acetoxyenyne **4** (172 mg, 0.386 mmol) was treated with $ZnCl_2$ (110 mg, 2 mol-equiv.), (*E*)-tetrahydro-2-(propenyloxy)-3-(tributylstannyl)-pyran [17] (340 mg, 2 mol-equiv.), $[Pd(dba)_2]$ [10] (23 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (27 mg, 0.3 mol-equiv.) to give **19e** (oil, 125 mg, 61%). IR: 3030–2900, 1450, 1325, 1300, 1150, 1075, 1000. ^{1}H-NMR: 1.40–1.95 (6 H); 2.56 (*dd*, *J* = 15, 7.5, 1 H); 2.75–2.96 (2 H); 3.43–3.72 (3 H); 3.86 (*m*, 1 H); 3.92 (*dd*, *J* = 13, 6.5, 1 H); 4.16 (*dd*, *J* = 13, 6.5, 1 H); 4.62 (*m*, 1 H); 4.98–5.16 (2 H); 5.55–5.85 (2 H); 5.84 (*d*, *J* = 11, 1 H); 6.34 (*ddd*, *J* = 15, 11, 2, 1 H); 7.50–7.80 (6 H); 7.90–8.15 (4 H). ^{13}C-NMR: 140.12 (*d*); 139.32 (*s*); 137.04 (*d*); 134.70 (*d*); 134.53 (*d*); 131.03 (*d*); 130.97 (*d*); 129.55 (*d*); 128.65 (*d*); 127.84 (*d*); 127.75 (*d*); 124.25 (*d*); 115.41 (*t*); 97.87 (*d*); 91.84 (*s*); 67.23 (*t*); 62.16 (*t*); 62.11 (*d*); 45.15 (*d*); 39.44 (*t*); 38.03 (*t*); 30.57 (*t*); 25.38 (*t*); 19.35 (*t*). MS: 286 (0.62, $[C_{28}H_{32}O_6S_2 - C_{11}H_{14}O_4S]^{+}$), 125 (11), 85 (20), 84 (66), 77 (27), 55 (100), 51 (21).

Dimethyl (Z)-3-(Prop-2-enylidene)-4-vinylcyclopentane-1,1-dicarboxylate (**20a**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **6** (224 mg, 0.795 mmol) was treated with $ZnCl_2$ (220 mg, 2 mol-equiv.), (tributyl)(vinyl)stannane (504 mg, 2 mol-equiv.), $[Pd(dba)_2]$ [10] (46 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (55 mg, 0.3 mol-equiv.) to give **20a** (oil, 145 mg, 72%). IR: 3070, 3050, 2990, 1730, 1650, 1640, 1630, 1430, 1280, 1170, 1100, 1050. ^{1}H-NMR: 2.04 (*dd*, *J* = 13, 7, 1 H); 2.69 (*ddd*, *J* = 13, 7, 2, 1 H); 2.86 (br. *d*, *J* = 16.5, 1 H); 3.12 (*d*, *J* = 16.5, 1 H); 3.59 (*m*, 1 H); 3.68 (*s*, 3 H); 3.69 (*s*, 3 H); 4.91–5.11 (4 H); 5.71 (*ddd*, *J* = 17, 10, 7, 1 H); 6.03 (*dd*, *J* = 10, 2, 1 H); 6.46 (*dt*, *J* = 17, 10.5, 1 H). ^{13}C-NMR: 171.69 (*s*); 171.63 (*s*); 142.65 (*s*); 139.86 (*d*); 133.20 (*d*); 125.08 (*d*); 115.95 (*t*); 114.62 (*t*); 58.84 (*s*); 52.75 (*q*); 52.65 (*q*); 44.27 (*d*); 41.89 (*t*); 40.73 (*t*). MS: 250 (7, $C_{14}H_{18}O_2^{+}$), 191 (13), 190 (37), 132 (12), 131 (100), 130 (32), 129 (15). HR-MS: 250.1197 ($C_{14}H_{18}O_4^{+}$, calc. 250.1205).

3-[(E)-Prop-2-enylidene]-1-(p-toluenesulfonyl)-4-vinylpyrrolidine (**21a**). Employing the cyclization/coupling conditions described for the preparation of **11a**, **8** (280 mg, 0.87 mmol) was treated with $ZnCl_2$ (240 mg, 2 mol-equiv.), (tributyl)(vinyl)stannane (504 mg, 2 mol-equiv.), $[Pd(dba)_2]$ [10] (50 mg, 0.1 mol-equiv.), and tri(2-furyl)phosphine [14] (61 mg, 0.3 mol-equiv.) to give **21a** (oil, 210 mg, 83%). IR: 3000–2900, 1650, 1350, 1160. ^{1}H-NMR: 2.41 (*s*, 3 H); 3.26 (*d*, *J* = 5.5, 2 H); 3.49 (*m*, 1 H); 3.70 (*d*, *J* = 15, 1 H); 3.95 (*d*, *J* = 15, 1 H); 4.98–5.18 (4 H); 5.68 (*ddd*, *J* = 17, 10, 7, 1 H); 5.96 (*dd*, *J* = 11, 2, 1 H); 6.37 (*dt*, *J* = 17, 10, 1 H); 7.35 (*d*, *J* = 8, 2 H); 7.70 (*d*, *J* = 8, 2 H). The NOESY spectrum shows significant NOE interactions between the signals at 5.96/3.95 ppm and

5.96/3.70 ppm. ^{13}C-NMR: 143.73 (*s*); 138.70 (*s*); 136.96 (*d*); 132.28 (*d*); 132.21 (*s*); 129.61 (*d*); 127.87 (*d*); 124.37 (*d*); 117.86 (*t*); 115.85 (*t*); 53.83 (*t*); 52.14 (*t*); 44.46 (*d*); 21.49 (*q*). MS: 289 (5, $C_{16}H_{19}NO_2S^{+\cdot}$), 222 (4), 155 (16), 134 (63), 91 (100). HR-MS: 134.0966 ($[C_{16}H_{19}NO_2S - C_7H_7O_2S]^{+\cdot}$, calc. 134.0970).

REFERENCES

[1] W. Oppolzer, *Angew. Chem.* **1989,** *101,* 39; *ibid. Int. Ed.* **1989,** *28,* 38; W. Oppolzer, *Pure Appl. Chem.* **1990,** *62,* 1941; W. Oppolzer, in 'Comprehensive Organic Synthesis', Ed. B.M. Trost, Pergamon, Oxford, 1991, Vol. 5, p. 29.

[2] W. Oppolzer, M. Bedoya-Zurita, C.Y. Switzer, *Tetrahedron Lett.* **1988,** *29,* 6433; W. Oppolzer, T.H. Keller, M. Bedoya-Zurita, C. Stone, *ibid.* **1989,** *30,* 5883; W. Oppolzer, H. Bienaymé, A. Genevois-Borella, *J. Am. Chem. Soc.* **1991,** *113,* 9660; R. Keese, R. Guidetti-Grept, B. Herzog, *Tetrahedron Lett.* **1992,** *33,* 1207; W. Oppolzer, A. Ando, *Chimia* **1992,** *46,* 122.

[3] W. Oppolzer, R.J. DeVita, *J. Org. Chem.* **1991,** *56,* 6256; R. Grigg, V. Sridharan, S. Sukirthalingam, *Tetrahedron Lett.* **1991,** *32,* 3855.

[4] J.K. Stille, *Pure Appl. Chem.* **1985,** *57,* 1771; D.W. Knight, in 'Comprehensive Organic Synthesis', Ed. B.M. Trost, Pergamon, Oxford, 1991, Vol. 3, p. 481.

[5] a) V. Farina, S.R. Baker, D.A. Benigni, C. Sapino, Jr., *Tetrahedron Lett.* **1988,** *29,* 5739; b) V. Farina, S.R. Baker, C. Sapino, Jr., *ibid.* **1988,** *29,* 6043.

[6] a) D.G. Hawthorne, S.R. Johns, R.I. Willing, *Aust. J. Chem.* **1976,** *29,* 315; b) W. Oppolzer, J.-M. Gaudin, M. Bedoya-Zurita, J. Hueso-Rodriguez, T.M. Raynham, C. Robyr, *Tetrahedron Lett.* **1988,** *29,* 4709; W. Oppolzer, J.-M. Gaudin, T. Keller, C. Stone, unpublished work.

[7] F.K. Sheffy, J.P. Godschalx, J.K. Stille, *J. Am. Chem. Soc.* **1984,** *106,* 4833.

[8] J.A. Soderquist, A. Hassner, *J. Am. Chem. Soc.* **1980,** *102,* 1577; J.A. Soderquist, G.J.-H. Hsu, *Organometallics* **1982,** *1,* 830.

[9] C. Herve Du Penhoat, M. Julia, *Tetrahedron* **1986,** *42,* 4807.

[10] M.F. Rettig, P.M. Maitlis, *Inorg. Synth.* **1990,** *28,* 110.

[11] J. Cologne, G. Poilane, *Bull. Soc. Chim. Fr.* **1955,** 953.

[12] K.H. Doetz, M. Popall, *Tetrahedron* **1985,** *41,* 5797.

[13] B. Bartocha, H.D. Kaesz, F.G.A. Stone, *Z. Naturforsch., B* **1959,** *14,* 352.

[14] E. Niwa, H. Aoki, H. Tanaka, F. Munakata, *Chem. Ber.* **1966,** *99,* 712; D.W. Allen, B.G. Hutley, M.T.J. Mellor, *J. Chem. Soc., Perkin Trans. 2* **1972,** 63.

[15] R.F. Cunico, F.J. Clayton, *J. Org. Chem.* **1976,** *41,* 1480.

[16] J.K. Stille, B.L. Groh, *J. Am. Chem. Soc.* **1987,** *109,* 813.

[17] E.J. Corey, R.H. Wollenberg, *J. Org. Chem.* **1975,** *40,* 2265.

[18] A.S. Kende, R.J. DeVita, *Tetrahedron Lett.* **1990,** *31,* 307.