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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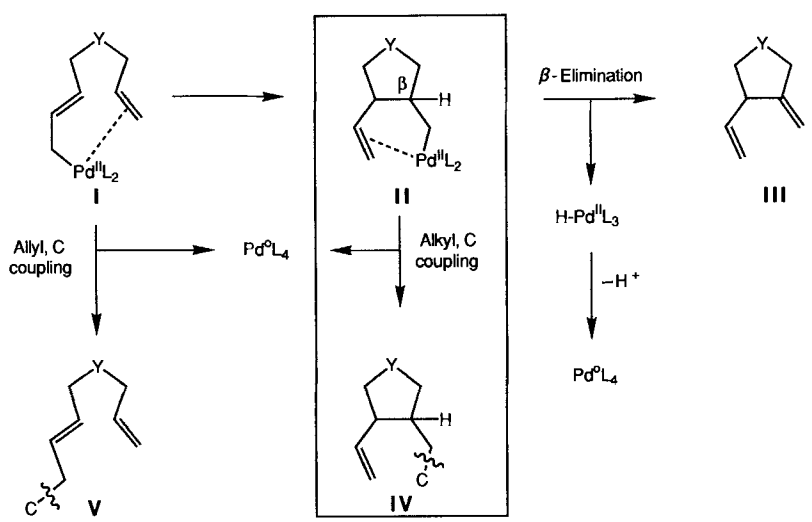
(11.II.93)

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



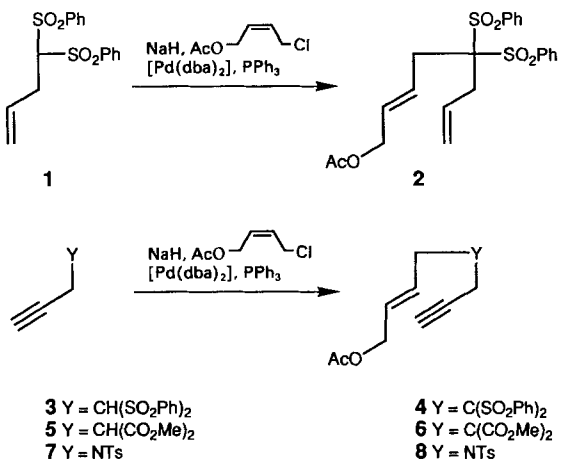
Particularly attractive is trapping of the transient σ-alkylpalladium species **II** by means of C,C-coupling reactions with simultaneous regeneration of the catalyst (**I** → **II** → **IV**). This requires not only that the trapping process **II** → **IV** is faster than β-elimination **II** → **III**, 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

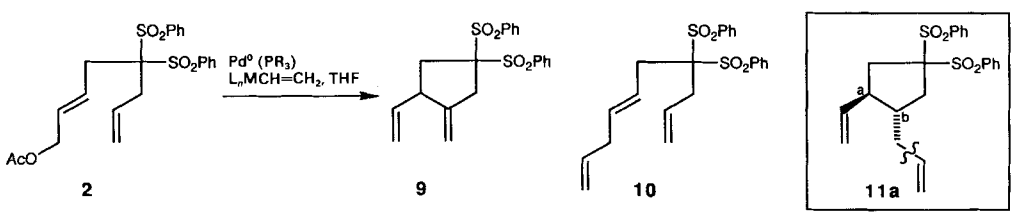


The corresponding enyne substrates **4**, **6**, and **8** were routinely obtained by analogous allylation of acetylene derivatives **3**, **5**, and **7**, respectively.

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

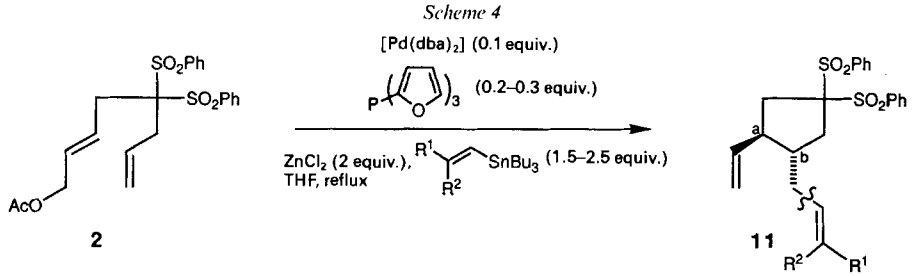
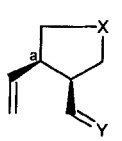


Table 2. *Pd-Catalyzed Octa-2,7-dienyl Acetate Cyclization/Vinylstannane Coupling* **2** → **11** (*Scheme 4*)

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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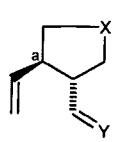


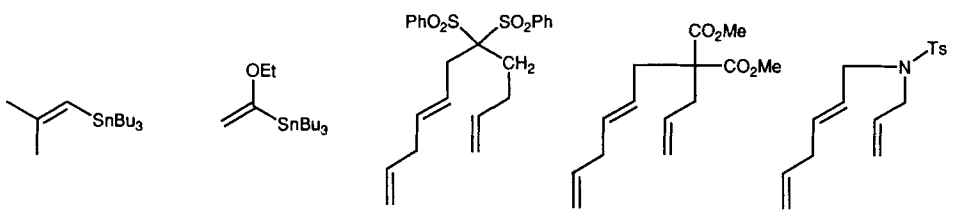
13

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**.



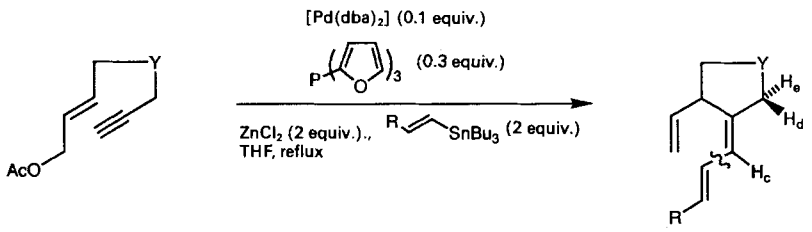
14 **15** **16** **17** **18**

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.

Financial support of this work by the *Swiss National Science Foundation*, *Sandoz Pharma Ltd.*, Basel, and *Givaudan-Roure AG*, Dübendorf, is gratefully acknowledged. We are grateful to Mr. *J. P. Saulnier*, Mr. *A. Pinto*, and Mrs. *C. Clément* for NMR and MS measurements.

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 ([$C_{25}H_{32}O_4S_2Si - C_6H_5O_2S$]$^+$, 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 ([$C_{25}H_{28}O_6S_2 - C_8H_{11}O_3S$]$^+$, 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).

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