141. New Ethylzinc Reagents with Remarkable Properties in Palladium-Catalyzed Zinc-Ene Reactions

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Pd-Catalyzed Zn-ene allylic olefinations with the new ethylzinc reagents Et–Zn–OSO_2CF_3 (**4**) and Et–Zn–OC(O)CF(MeO)CF_3 (**5**) in CH_2Cl_2 showed an unexpected *trans*-selectivity in the ring closure to cyclopentane derivatives (see *Scheme 2* and *Table 1*). This strong *trans*-selectivity is in contrast with the corresponding known Zn-ene reaction using Et_2Zn in Et_2O which shows a high *cis*-selectivity (*Table 1*). The probable radical origin of the observed *trans*-selectivity is discussed. The Zn-ene reaction products of the type R–Zn–OSO_2CF_3 could be derivatized by the known protonation, iodination, and cyanation yielding **8**–**10** (*Scheme 4* and *Table 2*); these derivatizations could furthermore be extended by allylation and oxidation reaction (→ **13**, **15**, and **16**; see *Scheme 5*).

Introduction. – The development of metallo-ene reactions by *Oppolzer* and his coworkers in the last decade has not only resulted in a powerful tool for synthesizing functionalized hetero- and carbacycles [1], it remains one of the most esthetic and appealing topics of organometallic chemistry [2]. In this context, the recently developed intramolecular allylzincation protocol using the system diethylzinc/[Pd(PPh_3)$_4$] [3] showed an interesting potential for the stereocontrolled synthesis of functionalized *cis*-disubstituted cyclopentanes and pyrrolidines [4] (see *Scheme 1*, X = Et). The fate of the Zn ligands during the proposed catalytic cycle in these Et_2Zn/[Pd(PPh_3)]-promoted transformations remained undefined [4]. Therefore, it was our intention to substantiate this catalytic cycle. Furthermore, we wanted to enhance the scope of the derivatization of the final cyclic Zn-ene-reaction products.

To reach these goals, we focused our attention upon nonsymmetrical ethylzinc reagents of the type EtZnX with X = halides, alkoxides, sulfonates, or carboxylates. Indeed, to maintain the catalytic cycle, the substituent X of these reagents (and contrary to Et_2Zn) would now have to be firmly attached to Zn during the transformation (otherwise β-elimination cannot occur), whereas the Et group has to be transferred to the Pd-atom (*Scheme 1*). Bis(phenylsulfonyl)alkadienyl acetate [5] yielding the already known Zn-ene-reaction products **2** and **3** [4] (see also *Exper. Part*) was chosen as a model substrate (*Scheme 2*).

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[2]) Present address: Postfach 2743, D-72717 Reutlingen. *F.S.* wants to thank Prof. *Wolfgang Oppolzer* and his group. His vivid and clearcut style of sporty fairness will guide modern European research as a positive model.

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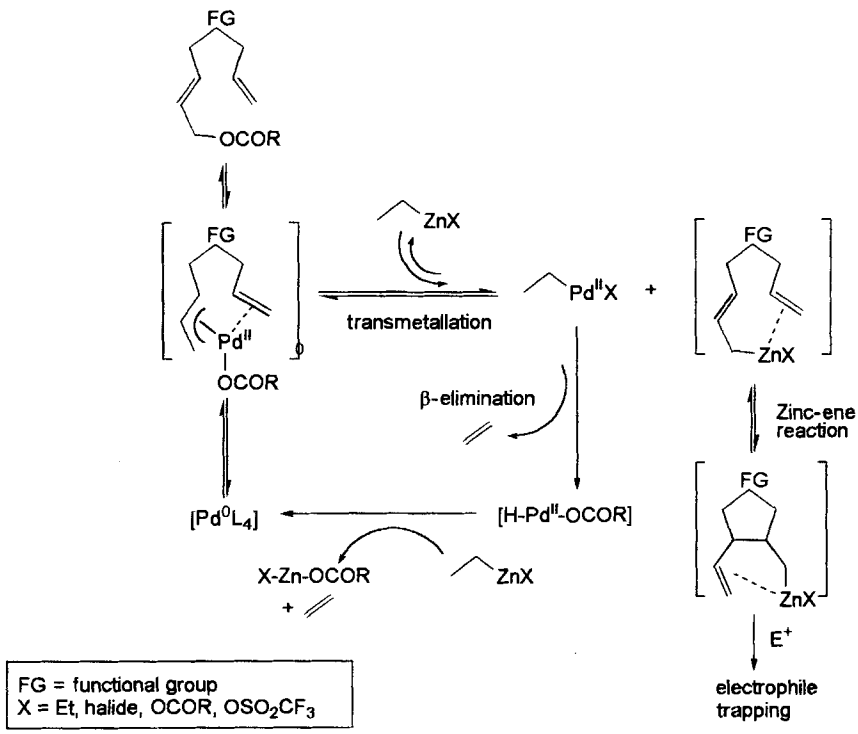
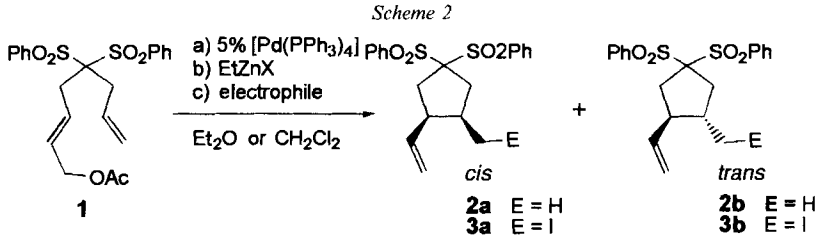
Scheme 1



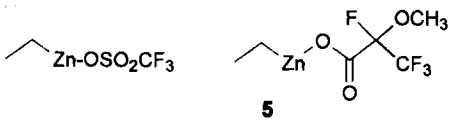
Scheme 2



Results and Discussion. – *Nonsymmetrical Ethylzinc Reagents.* Ethylzinc halides in CH_2Cl_2 were prepared as described in [6]. Ethylzinc alcoholates, carboxylates, and sulfonates EtZnX were easily synthesized by adding the acidic component HX in an appropriate solvent under Ar at $-78°$ to Et_2Zn. The concentration of these ethylzinc solutions were checked by I_2 titration of a small sample. The question if really a monomer of formula EtZnX or any kind of a higher complex is generated is, even after controversial discussions and NMR investigations [7], not quite solved.

The nonsymmetrical ethylzinc reagents **4** and **5** have not been used as reagents in organic synthesis so far. The non-foaming ethylzinc 2,3,3,3-tetrafluoro-2-methoxypropanoate (**5**) was smoothly prepared by the above procedure from 2,3,3,3-tetrafluoro-2-

methoxy propanoic acid [8] and Et_2Zn. Addition of trifluoromethansulfonic acid to Et_2Zn in CH_2Cl_2 yielding reagent **4** was, even at −78°, much more vigorous.



4 **5**

Stereocontrol of Ring Closure in the Presence of Nonsymmetrical Ethylzinc Reagents. The so far exploited Pd-catalyzed Zinc-ene ring closures with Et_2Zn in Et_2O have been uniformely *cis*-selective [4]. The results in *Table 1* show that the diastereoselectivity of the cyclization is depending on the nature of the zinc reagent; *e.g.*, whereas Et_2Zn led to the *cis*-products **2a** or **3a** (*Entries 1* and *2*) [4], this diastereoselectivity was entirely reversed with the new ethylzinc reagents **4** and **5** (*Entries 3* and *6*).

Table 1. cis/trans-*Diastereoselectivities of Some Ethylzinc Reagents*

Entry	Ethylzinc reagent ([mol-equiv.])	Reaction conditions	Trapping agent ([mol-equiv.])	Ratio *cis*/*trans*	Yield [%][b])
1	Et–Zn–Et (5)	1.5 h, Et_2O, r.t.	I_2 (7)	**3a**/**3b** 83:17	66
2	Et–Zn–Et (5)	1.5 h, Et_2O, r.t.	NH_4Cl	**2a**/**2b** 84:16	79
3	Et–Zn–OSO_2CF_3 (**4**, 2.5)	2 h, CH_2Cl_2, 40°	I_2 (1.5)	**3a**/**3b** 2:98	70
4	Et–Zn–OC(O)Ad[a]) (5)	3.5 h, Et_2O, r.t.	NH_4Cl	**2a**/**2b** 89:11	90
5	Et–Zn–OC(O)Ph (5)	4 h, Et_2O, r.t.	NH_4Cl	**2a**/**2b** 89:11	72
6	Et–Zn–OC(O)CF(MeO)CF_3 (**5**; 2.5)	1.5 h, CH_2Cl_2, 35°	I_2 (1.5)	**3a**/**3b** 3:97	74

[a]) Prepared from adamantane-1-carboxylic acid. [b]) Diastereoisomer mixture, ratio and yield before crystallization.

Ethylzinc halides [7] induced in CH_2Cl_2 a *cis*/*trans*-selectivity of *ca.* 20:80, but reacted comparatively slow (10–30 h) and with low yields (20–50%). Their generation was tedious and not very reproducible. The reagent Et–Zn–OSO_2CF_3 (**4**) in CH_2Cl_2 was by far superior concerning yield, selectivity, and rate of the cyclization (*Entry 3*); contrary to the ethylzinc halides (strong precipitates), with the new reagent **4**, the reaction was homogeneous until electrophile trapping.

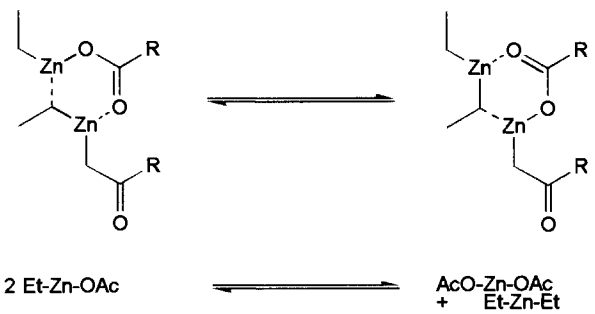
Ethylzinc alkoxides [9] reacted as sluggish as the ethylzinc halides but *cis*-selective. Several ethylzinc carboxylates in Et_2O (*Table 1*, *Entries 4* and *5*), however, improved even yield and *cis*-selectivity of the cyclization as compared to Et_2Zn [4] (*Table 1*, *Entries 1* and *2*).

Ethylzinc carboxylates with strong electron-withdrawing substituents reversed the diastereoselectivities from *cis* to *trans*. Several achiral and chiral carboxylic acids like camphanic acid, pentafluorobenzoic acid or *Mosher*'s acid (α-methoxy-α-(trifluoromethyl)benzeneacetic acid) [10] were transformed into the corresponding ethylzinc carboxylates in CH_2Cl_2, but they promoted the cyclization with only moderate yields (30–50%) and low *trans*-selectivities (*cis*/*trans ca.* 30:70). Replacing the Ph group of the *Mosher* derivative by an F-atom, however, led to the by far superior ethylzinc carboxy-

late **5**, with a *cis/trans*-selectivity of 3:97 (*Entry 6*). The diastereoselectivity, rate, and yield of the ring closure employing **5** were comparable to those obtained with ethylzinc trifluoromethansulfonate (**4**; *Entry 3*).

The question now arises why the *cis/trans*-selectivity of the carboxylates depends on the electron-withdrawing properties of the carboxylic substituents. If one takes into account the equilibration depicted in *Scheme 3*, it is highly probable that not ethylzinc adamantane-1-carboxylate and ethylzinc benzoate (*Table 1*, *Entries 4* and *5*) but free diethylzinc (see [4]) is responsible for the high *cis*-selectivity. Disproportionation of ethylzinc carboxylates with strong electron-withdrawing substituents (*Table 1*, *Entries 3* and *6*), however, would be hindered by the lower electron density, lower complexing ability, and lower nucleophilicity of the carbonyl O-atom (*Scheme 3*). In fact it has been stated by *Coates* and *Ridley* [9] that ethylzinc acetate undergoes disproportionation at much lower temperatures than ethylzinc alkoxides, amines, or halides. Furthermore, the complexing ability of carbonyl groups to ethylzinc reagents as well as Zn–C–Zn transition states have been propagated for diethylzinc-aldehyd additions under α-amino-alcohol catalysis [11].

Scheme 3



Intramolecular 'metallo-ene reactions' would be *trans*-selective if a *retro*-ene reaction is possible (usually at temperatures > 80° [1a]) or if the cyclization proceeds *via* an allylic free radical transfer cyclization [12]. In both cases, the thermodynamically favoured *trans*-product is formed by a *cis/trans* equilibration *via* the ring-opened intermediate. Evidence for a radical mechanism at low temperatures has been found for intramolecular metallo-ene reactions (allylic iodides, $[Ru_3(CO)_{12}]$/dppb, CH_2Cl_2, 40°, 12 h, 77%) in the *Oppolzer* group [13]. For the above described *trans*-selective cyclizations, there are three facts consistent with a radical mechanism:

1) In all of the described Zn-ene reactions, Et_2O as the solvent increased the *cis/trans* ratio, the same reaction in CH_2Cl_2 decreased it (the solvent CH_2Cl_2, however, has a profound impact on the ligand sphere of the ethylzinc reagent).

2) No asymmetric induction was observed by employing enantiomerically pure ethylzinc reagent (*R*)- or (*S*)-**5** under the conditions described for the reaction of the corresponding racemic ethylzinc reagent **5** (prepared from enantiomerically pure 2,3,3,3-tetrafluoro-2-methoxypropanoic acid [14]). In this case, the protonated *trans*-carbacycle **2b** (E = H, 84%); proved to the racemic (determined with *Pirkle*'s, reagent and ^{1}H-NMR [15]).

3) A further substituent at the bis(phenylsulfonyl)alkadienyl acetate as in substrate **7** led, under $[Pd(PPh_3)_4]$ catalysis in presence of $EtZnOSO_2CF_3$ (**4**) and after derivatization, to the thermodynamically favoured *trans,trans*-carbacycles **8**–**10** (*Scheme 4*, *Table 2*). Substrate **7** was synthesized *via* Pd-catalyzed allylation of precursor **6** [16] with (*Z*)-4-chlorobut-2-enyl acetate [17].

Scheme 4

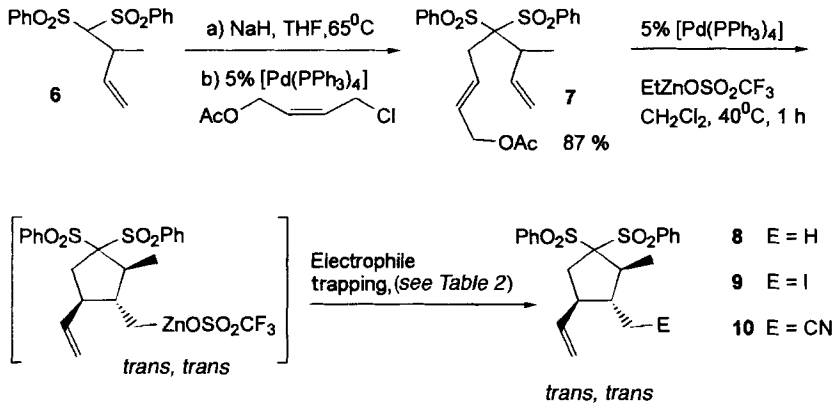


Table 2. *Pd-Catalyzed Zinc-ene Reactions of Substrate* **7** *and Derivatization*

Entry	Ethylzinc reagent ([mol-equiv.])	Trapping agent ([mol-equiv.])	Diastereoselectivity (A/B/C/D)[a])	Yield [%] (mixture of diastereoisomers)	Crystallization of *trans, trans*-product Yield [%] de [%][b])
7	Et–Zn–Et (5)	aq. NH_4Cl soln.	32:63:3:2	69%	
8	Et–Zn–OSO_2CF_3 (**4**; 2.5)	aq. NH_4Cl soln.	90:6:4	86%	**8**: 52% > 99%
9	Et–Zn–OSO_2CF_3 (**4**; 2.5)	I_2 (4)	99:1	74%	**9**: 66% > 99%
10	Et–$ZnOSO_2CF_3$ (**4**; 2.5)	$[CuCN(LiCl)_2]$ (1), then TosCN (5)	97:3	66%	**10**: 56% > 99%

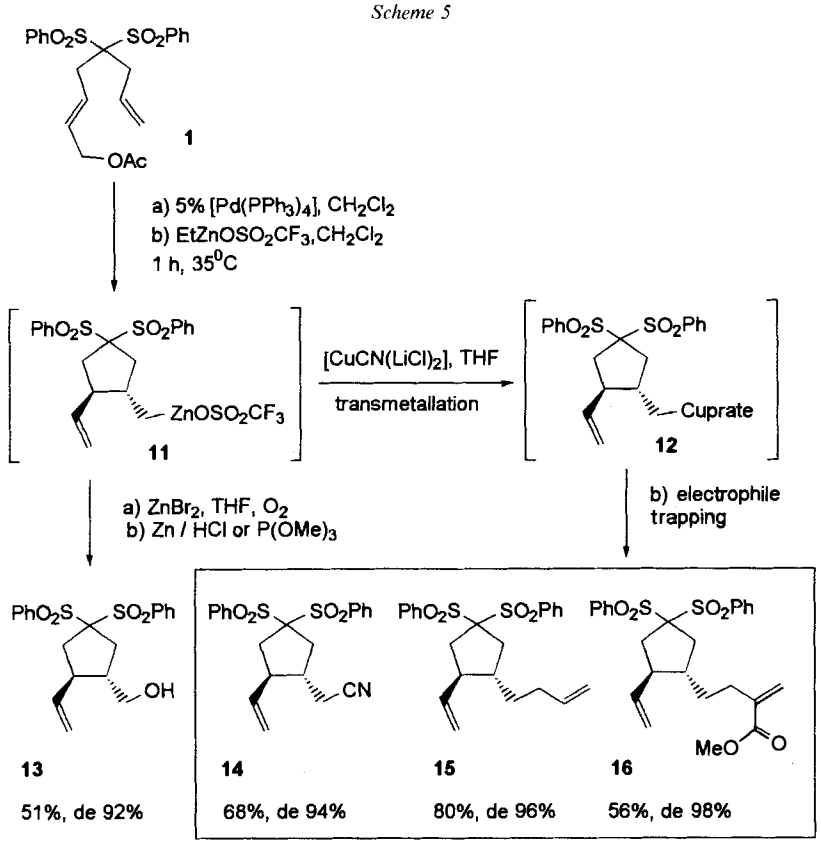
[a]) A = *trans,trans*-product (COSY, NOESY). Relative configuration of B, C, and D not determined. Ratio A/B/C/D of the crude product (GC). [b]) Determined by GC.

Derivatizations of the Zinc-Ene-Reaction Products. Dialkylzinc compounds and alkylzinc halides have been derivatized by a variety of methods [18]. The derivatization of alkylzinc triflate is described here for the first time (see also **7** → **8**–**10** in *Schemes 4* and *5*, *Table 2*).

Thus, the oxidation of cyclized intermediate **11** was achieved with 1 mol-equiv. of $ZnBr_2$ in THF and gaseous O_2 [19] followed by reduction of the hydroperoxide with $P(OMe)_3$ (one-pot procedure) to give alcohol **13** (*Scheme 5*). Allylation and cyanation of intermediate **11** were possible after transmetallation with equimolar amounts (with respect to **11**) of $[CuCN(LiCl)_2]$ following the procedure of *Knochel* [18] which led to an overall transmetallation sequence Pd → Zn → Cu. The transmetallated cuprate **12**, with

the most probable structure $[R-Cu(LiCl)_2] \cdot CF_3SO_3Zn(CN)$, was unstable above 30°. Subsequent cyanation of **12** with TosCN (5 mol-equiv.) furnished the *trans*-acetonitrile **14** (68%, de 94%) in essentially the same way ($EtZnOSO_2CF_3$ (**4**) instead of Et_2Zn) as the already known *cis*-acetonitrile [4]. Subsequent allylation of **12** with allyl bromide or methyl 2-(bromomethyl)acrylate yielded the derivatives **15** (80%, de 96%; after crystallization, 55%, de > 99%) and **16** (56%, de 98%), respectively (*Scheme 5*).

Scheme 5



Conclusion. – The new *trans*-selective ethylzinc reagents $EtZnOSO_2CF_3$(**4**) and $EtZnOC(O)CF(MeO)CF_3$ (**5**) could be successfully employed in Pd-catalyzed Zn-ene reactions. These ethylzinc reagents and the derivatization of the corresponding cyclic Zn-ene products have not been described so far. The Zn-ene products of type $R-Zn-OSO_2CF_3$ were derivatized by protonation, iodination, and cyanation similarly to the transformations described in [4]. Furthermore, these derivatizations were extended to allylation and oxidation.

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Experimental Part

General. All organometallic reactions were carried out under Ar and all reactions with ethylzinc reagents in degassed solvents, unless specified otherwise. Fresh $[Pd(PPh_3)_4]$ (*Aldrich*) should be green-yellow (not brown or red) and stored under Ar at −20°. Its purity was checked as follows: a suspension of $[Pd(PPh_3)_4]$ in abs. and degassed AcOEt was shaken and the supernatant soln. filtered through a capillary filled with cotton wool and SiO_2 and checked by GC: the ratio of PPh_3 (t_R 4.78) and $O{=}PPh_3$ (t_R 8.86) correlates with the purity of the catalyst. Solvents were dried by distillation from drying agents as follows: Et_2O, THF, and toluene (Na/benzophenone), CH_2Cl_2 (CaH_2), acetone (K_2CO_3), DMF (CaH_2, activated molecular sieves 3 Å). All solvents for chromatography were distilled before use. Workup denotes: H_2O was added, the mixture extracted with Et_2O, the extract dried ($MgSO_4$), and the filtrate evaporated, unless specified otherwise. Flash column chromatography (FC): SiO_2 (*Merck 9385*); M.p.: *Kofler* hot stage; uncorrected. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. GC: *Hewlett-Packard 5790a*, integrator *HP3390*, capillary column *OV-1*, 10 psi H_2 head pressure; GC conditions: initial temp./time 190°/min, gradient 100/min, final temp./time 270°/min, unless otherwise specified; t_R in min. IR: *Matteson-Instruments-Polaris-FT* spectrometer; in $CHCl_3$ unless specified otherwise in cm^{-1}. NMR: *Bruker AMX 400*; ^1H at 400 MHz in $CDCl_3$, *J* in Hz, $SiMe_4$ (δ 0 ppm) and $CHCl_3$ (δ 7.27 ppm); ^{13}C at 400 MHz in $CDCl_3$, unless specified otherwise; multiplicities by DEPT. MS: *Varian CH-4* or *Finnigan 4023* at 70 eV; *m/z* (rel. %). HR-MS: *VG 7070-E.*

General Procedure A: *Generation of Ethylzinc Alcoholates, Carboxylates, and Sulfonates EtZnX.* Neat Et_2Zn (0.4 ml, 4 mmol) was dissolved in degassed CH_2Cl_2 (6 ml) at r.t. under stirring and Ar. After cooling at −78°, compound HX (4.4 mmol), neat or dissolved, was added dropwise. The soln. was allowed to come to r.t. (slowly when strong acids were employed) and stirred for 1 h at r.t. The concentration of the EtZnX reagent was determined by I_2/THF (degassed) titration. For the synthesis of **4** and **5**, see below.

General Procedure B: *Pd-Catalyzed Zinc-Ene Reaction to (Cyclopentylmethyl)zinc Intermediates.* At r.t., **1** [5] was dissolved in Et_2O or CH_2Cl_2 (as indicated, 0.05M) under Ar and placed in a *Carius* tube filled with $[Pd(PPh_3)_4]$ (5 mol-%). The mixture was stirred vigorously for 1–4 min until the catalyst was dissolved. Immediately, the EtZnX (from *General Procedure A*) or Et_2Zn was added dropwise to the yellow soln. which turned colourless after several minutes. The tube was sealed and placed in a heating bath at elevated temp. under stirring. The end of the reaction (1–3 h) was easily recognized when the typical yellow colour reappeared. Then (10 min after yellowing), the mixture was treated according to the *General procedures C*, *D*, or *E*.

General Procedure C: *Proton Quenching.* The (cyclopentylmethyl)zinc soln. from *Procedure B* was quenched with an excess of sat. NH_4Cl soln. at 0° under stirring to give a two-phase system from which the protonated product **2** was extracted.

General Procedure D: *Trapping with Iodine.* The alkyzinc soln. described in *Procedure A* or *B* was titrated with I_2 (1M in degassed THF) at r.t. under stirring. In these titrations, I_2 was usually consumed in amounts of $y = x\text{-}1$, with y = mol-equiv. of I_2 and x = mol-equiv. of ethylzinc units. After reaching the titration point, an excess of I_2 was added, furnishing a dark violet soln. which was stirred vigourously for 15 min. When the dark colour persisted, sat. $Na_2S_2O_3$ soln. was added to give a two-phase system which was stirred for another 60 min.

General Procedure E: *Transmetallation with [CuCn(LiCl)$_2$] and Electrophile Trapping.* CuCN (1 mol-equiv.) and LiCl (2 mol-equiv.; dried for 3 h at 180° high vacuum) were stirred for 20 min in degassed THF and under Ar to give a 0.2M pale yellow soln. To the (cyclopentylmethyl)zinc soln. prepared according to *Procedure B* with ethylzinc trifluoromethanesulfonate (**4**) and cooled to −50° under stirring, the above soln. of $[CuCN(LiCl)_2]$ in THF was added dropwise *via* a syringe (→ yellow soln.). The cooling bath was removed and the temp. raised to 0° within 5 min (→ colourless soln.). After stirring at 0° for 1 min, the mixture was cooled to −78° and the electrophile added dropwise. After 1 h at −78° and 2 h at −30°, the flask was immersed in an ice bath and left like that overnight, having reached r.t. after several hours. After addition of an excess of sat. NH_4Cl soln. at 0° under stirring to give a two-phase system, the protonated products were extracted and purified by standard workup.

cis-3-Ethenyl-4-methyl-1,1-bis(phenylsulfonyl)cyclopentane (**2a**). Following *Procedure B*, with **1** (45 mg, 0.1 mmol), Et_2O (2 ml), $[Pd(PPh_3)_4]$ (6 mg, 5 mol-%), and neat Et_2Zn (50 µl, 0.5 mmol). Addition of 2 ml of sat. NH_4Cl soln. (*Procedure C*) and FC (hexane/AcOEt 4:1) yielded **2b** (31 mg, 79%; *cis/trans* 86:14). Colourless oil. GC: t_R 12.88. IR (KBr): 3080, 2960, 1640, 1580, 1450, 1310, 1140, 1080, 1000, 920, 760, 720, 600, 570, 540. ^1H-NMR: 0.9 (*d*, *J* = 7, 3 H); 2.36 (*dd*, *J* = 7.1, 15.2, 1 H); 2.43–2.53 (*m*, 1 H); 2.54–2.73 (3 H); 2.87–2.96 (*m*, 1 H); 4.88–5.04 (2 H); 5.68 (*ddd*, *J* = 8.7, 10.3, 16.9, 1 H); 7.6 (*t*, *J* = 8.1, 4 H); 7.69–7.75 (2 H); 8.05–8.09 (4 H). ^{13}C-NMR: 137.4 (*d*); 137.1 (*s*); 136.5 (*s*); 134.5 (*d*); 134.4 (*d*); 131.5 (*d*); 134.38 (*d*); 128.7 (*d*); 128.68 (*d*); 116.2 (*t*); 94.2 (*s*); 47.3 (*d*); 38.9 (*t*); 37.2 (*d*); 36.6 (*t*); 15.97 (*q*). MS: 390 (2, $C_{20}H_{22}O_4S_2$), 249

(5, $[C_{20}H_{22}O_4S_2 - C_6H_5SO_2]^+$), 248 (4, $[C_{20}H_{22}O_4S_2 - C_6H_5SO_2H]^+$), 125 (22), 107 (33), 77 (100). Anal. calc. for $C_{20}H_{22}O_4S_2$: C 61.52, H 5.68; found: C 61.37, H 5.72.

trans-*3-Ethenyl-4-methyl-1,1-bis(phenylsulfonyl)cyclopentane* (**2b**). Following *Procedure B*, with **1** (24 mg, 0.054 mmol), CH_2Cl_2 (2 ml), $[Pd(PPh_3)_4]$ (3 mg, 5 mol-%), and **4** (0.125 mmol) or **5** at 40° in 2.5 h. Addition of 2 ml of sat. NH_4Cl soln. (*Procedure C*) and FC (hexane/AcOEt 2:1, R_f 0.35) gave a colourless oil which could be crystallized from CH_2Cl_2/Et_2O/pentane 1:1:1: **2b** (15 mg, 71%; de 88%). Colourless crystals. GC: t_R 12.45. M.p. 173–174°. IR (KBr): 3025, 1448, 1327, 1311, 1208, 1149, 1077, 924. ^{1}H-NMR: 0.94 (*d*, J = 6.6, 3 H); 1.7–1.8 (*m*, 1 H); 2.02–2.13 (*m*, 1 H); 2.17 (*dd*, J = 11.5, 15.0, 1 H); 2.37 (*dd*, J = 11.4, 15.3, 1 H); 2.69 (*ddd*, J = 7.1, 12.2, 15.3, 2 H); 4.99–5.06 (2 H); 5.53 (*ddd*, J = 8.3, 10.3, 16.9, 1 H); 7.58–7.63 (4 H); 7.70–7.75 (2 H); 8.05–8.08 (4 H). ^{13}C-NMR: 138.24 (*d*); 136.57 (*s*); 134.54 (*s*); 131.4 (*d*); 131.36 (*d*); 128.72 (*d*); 128.64 (*d*); 116.93 (*t*); 91.94 (*s*); 51.57 (*d*); 40.1 (*d*); 40.06 (*t*); 38.57 (*t*); 16.79 (*q*). MS: 390 (5, $C_{20}H_{22}O_4S_2^+$), 249 (76, $[C_{20}H_{22}O_4S_2 - C_6H_5SO_2]^+$), 125 (78), 107 (100). HR-MS: 390.09717 ($C_{20}H_{22}O_4S_2^+$; calc. 390.09595).

cis-*4-Ethenyl-3-iodomethyl-1,1-bis(phenylsulfonyl)cyclopentane* (**3a**). Following *Procedure B*, with **1** (25 mg, 0.05 mmol) Et_2O (2 ml), $[Pd(PPh_3)_4]$ (3 mg, 5 mol-%), and neat Et_2Zn (21 µl, 0.2 mmol). After I_2 titration (0.35 mmol, *Procedure D*) and FC (hexane/AcOEt 4:1), the yellow resin (*cis*/*trans* 83:17, GC) was crystallized from CH_2Cl_2/Et_2O/hexane at −20°; **3a** (16 mg, 62%; de > 95%). White powder. M.p. 160°. IR (KBr): 3070, 2950, 2920, 1450, 1310, 1140, 1080, 1000, 910, 750, 720, 690, 630, 580, 570. ^{1}H-NMR: 2.58–2.66 (2 H); 2.71–2.84 (3 H); 3.03 (*m*, 1 H); 3.09–3.16 (2 H); 5.1–5.18 (2 H); 5.79 (*ddd*, J = 9.1, 10.3, 16.9, 1 H); 7.63 (*t*, J = 8.1, 4 H); 7.73 (*dt*, J = 1.1, 7.5, 2 H); 8.04–8.13 (4 H). ^{13}C-NMR: 136.66 (*s*); 135.78 (*s*); 135.23 (*s*); 134.77 (*d*); 134.66 (*d*); 131.43 (*d*); 128.86 (*d*); 128.76 (*d*); 117.97 (*t*); 93.01 (*s*); 46.95 (*d*); 46.13 (*d*); 37.73 (*t*); 36.27 (*t*); 6.87 (*t*). MS: 516 (3, $C_{20}H_{21}IO_4S_2^+$), 389 (3, $[C_{20}H_{21}IO_4S_2 - HI]^+$), 375 (6, $[C_{20}H_{21}IO_4S_2 - CH_2I]^+$), 247 (14), 125 (100). HR-MS: 389.0869 ($[C_{20}H_{21}IO4S_2 - HI]^+$; calc. 389.0881).

trans-*4-Ethenyl-3-(iodomethyl)-1,1-bis(phenylsulfonyl)cyclopentane* (**3b**). Following *Procedure B* with **1** (45 mg, 0.1 mmol), CH_2Cl_2 (2 ml), $[Pd(PPh_3)_4]$ (6 mg, 5 mol-%), and **4** (0.25 mmol) at 40° for 2 h. I_2 Titration (0.15 mmol; *Procedure D*) and FC (hexane/AcOEt 4:1) gave a colourless oil (36 mg, 70%; de 96%). IR (KBr): 3030, 1327, 1311, 1147, 1077, 980. ^{1}H-NMR: 1.6–1.72 (*m*, 1 H); 2.3–2.42 (2 H); 2.42–2.54 (*dd*, J = 11.4, 15.1, 1 H); 2.65–2.75 (*dd*, J = 6.6, 15.0, 1 H); 2.75–2.83 (*dd*, J = 7.7, 15.1, 1 H); 3.05–3.13 (*dd*, J = 6.6, 10.7, 1 H); 3.28–3.33 (*dd*, J = 3.0, 10.3, 1 H); 5.1–5.17 (2 H); 5.44–5.55 (*ddd*, J = 8.4, 9.9, 18.0, 1 H); 7.63 (*t*, J = 8.1, 4 H); 7.73 (*dt*, J = 1.1, 7.5, 2 H); 8.04–8.13 (4 H). ^{13}C-NMR: 136.65 (*s*); 136.14 (*s*); 136.08 (*s*); 134.76 (*d*); 134.73 (*d*); 131.55 (*d*); 131.44 (*d*); 128.87 (*d*); 128.85 (*d*); 118.45 (*t*); 90.69 (*s*); 49.42 (*d*); 45.63 (*d*); 39.01 (*t*); 38.22 (*t*); 8.76 (*t*). MS: 516 (2, $C_{20}H_{21}IO_4S_2^+$), 389 (2, $[C_{20}H_{21}IO_4S_2 - HI]^+$), 375 (4, $[C_{20}H_{21}IO_4S_2 - CH_2I]^+$), 247 (12), 125 (100). HR-MS: 389.0871 ($[C_{20}H_{21}IO_4S_2 - HI]^+$; calc. 389.0881).

Ethylzinc Trifluoromethanesulfonate (**4**) *in* CH_2Cl_2. Neat Et_2Zn (0.4 ml, 4 mmol) was dissolved in degassed CH_2Cl_2 (6 ml) at r.t. under stirring and Ar. After cooling to −78°, neat trifluoromethanesulfonic acid (0.39 ml, 4.4 mmol) was added dropwise. The drops were freezing immediately. The two-phase mixture was carefully warmed up to −50 to −40° when suddenly vigourous fouming occurred. At the first sign of reaction, stirring was stopped and the flask cooled to −60° (→ colourless viscous gel). Then the cooling bath was removed and the flask warmed to r.t. under slight bubbling of dissolved ethane. The gel-like content liquefied near r.t. and became a cloudy soln. (just a little bit more viscous then Et_2Zn in CH_2Cl_2). Samples were removed under strong stirring. The soln. of **4** in CH_2Cl_2 was 0.7M as indicated by I_2/THF titration. Reagent **4** in CH_2Cl_2 was transferred *via* syringe.

Ethylzinc 2,3,3,3-Tetrafluoro-2-methoxypropanoate (**5**) *in* CH_2Cl_2 was prepared according to *Procedure A* from neat Et_2Zn (4 mmol) in CH_2Cl_2 (5 ml) and 2,3,3,3-tetrafluoro-2-methoxypropanoic acid [8] (4.2 mmol) in CH_2Cl_2 (1 ml) to yield smoothly a colourless, clear and non-foaming soln. of **5** (0.8–0.9M as indicated by I_2/THF titration). Reagent **5** in CH_2Cl_2 was transferred *via* syringe.

(E)-6-Methyl-5,5-bis(phenylsulfonyl)octa-2,7-dien-1-yl Acetate (**7**). To a soln. of 3-methyl-4,4-bis(phenylsulfonyl)but-1-ene [16] (203 mg, 0.58 mmol) in THF (2.5 ml), NaH (48 mg, 1.2 mmol; 60% in mineral oil) was added. The mixture was refluxed for 3 h. After cooling to r.t. $[Pd(PPh_3)_4]$ (34 mg, 5 mol-%) and (*Z*)-4-chlorobut-2-en-1-yl acetate [17] were added, and the mixture was stirred at r.t. for 2.5 h. After quenching the reaction with conc. NH_4Cl soln., extraction with Et_2O, standard workup, and FC (hexane/AcOEt 2:1), **7** (234 mg, 87%) was obtained. Colourless oil. IR (KBr): 3030, 1736, 1447, 1333, 1311, 1240, 1142, 1077. ^{1}H-NMR: 1.18 (*d*, J = 7.4, 3 H); 2.07 (*s*, 3 H); 2.92–2.98 (*m*, 1 H); 3.02–3.08 (*m*, 1 H); 3.32 (*dq*, J = 7.4, 1 H); 4.47 (*d*, J = 5.5, 2 H); 5.02–5.06 (2 H); 5.54–5.61 (*m*, 1 H); 5.87–5.94 (*m*, 1 H); 6.04 (*ddd*, J = 7.9, 9.7, 17.5, 1 H); 7.56–7.60 (*m*, 4 H); 7.68–7.72 (*m*, 2 H); 8.14–8.16 (4 H). ^{13}C-NMR: 170.61 (*s*); 138.86 (*s*); 138.62 (*s*); 136.88 (*d*); 134.57 (*d*); 131.84 (*d*); 131.79 (*d*); 129.74 (*d*); 128.51 (*d*); 126.36 (*d*); 117.71 (*t*); 94.37 (*s*); 64.31 (*t*); 40.75 (*d*); 34.48 (*t*); 20.92 (*q*); 16.80 (*q*). MS: 403 (10, $[C_{23}H_{26}O_6S_2 - OAc]^+$), 321 (6, $[C_{23}H_{26}O_6S_2 - C_6H_5O_2S]^+$), 261 (11, $[C_{23}H_{26}O_6S_2 -$

$C_6H_5O_2S - OAc]^+$), 143 (16), 141 (812), 137 (16), 125 (80), 119 (100). HR-MS: 403.1044 ($[C_{23}H_{26}O_6S_2 - OAc]^+$; calc. 403.1037).

t-*4-Ethenyl-1,1-bis(phenylsulfonyl)*-r-*2*,t-*3-dimethylcyclopentane* (**8**). Following *Procedure B*, with **7** (20 mg, 0.043 mmol), CH_2Cl_2 (2 ml), $[Pd(PPh_3)_4]$ (2.5 mg, 5 mol-%), and **4** (0.11 mmol, 2.5 mol-equiv.) at 35° in 2 h. Addition of 2 ml of sat. NH_4Cl soln. (*Procedure C*) and FC (hexane/AcOEt 2:1, R_f 0.45) gave a colourless oil (de 80%) which could be crystallized from CH_2Cl_2/Et_2O/pentane: **8** (9 mg, 52%; de > 99%). Colourless crystals. M.p. 171°. GC: t_R 11.51. IR (KBr): 3020, 1447, 1327, 1311, 1147, 1077. ^{1}H-NMR: 0.95 (*d*, *J* = 6.6, 3 H); 1.01 (*d*, *J* = 7.0, 3 H); 1.85–1.95 (*m*, 1 H); 2.13–2.22 (*m*, 1 H); 2.32 (*dd*, *J* = 11, 15.1, 1 H); 2.35–2.43 (*m*, 1 H); 2.65 (*dd*, *J* = 7.2, 14.9, 1 H); 5.07–5.11 (*m*, 1 H); 7.57–7.76 (6 H); 8.12–8.16 (4 H). ^{13}C-NMR: 138.94 (*d*); 138.44 (*s*); 136.33 (*s*); 134.5 (*d*); 134.21 (*d*); 132.09 (*d*); 131.81 (*d*); 128.62 (*d*); 128.28 (*d*); 116.99 (*t*); 93.56 (*s*); 50.89 (*d*); 50.7 (*d*); 46.0 (*d*); 38.16 (*t*); 15.69 (*q*); 12.55 (*q*). MS: 404 (0.3, $C_{21}H_{24}O_4S_2^+$), 263 (3, $[C_{21}H_{24}O_4S_2 - C_6H_5SO_2]^+$), 121 (100, $[C_{21}H_{24}O_4S_2 - C_{12}H_{11}O_4S_2]^+$), 93 (25), 79 (13), 77 (30). HR-MS: 404.11094 ($C_{21}H_{24}O_4S_2^+$; calc. 404.11160).

t-*4-Ethenyl*-t-*3-(iodomethyl)*-r-*2-methyl-1,1-bis(phenylsulfonyl)cyclopentane* (**9**). Following *Procedure B*, with **7** (26 mg, 0.056 mmol), CH_2Cl_2 (2 ml), $[Pd(PPh_3)_4]$ (3.2 mg, 5 mol-%), and **4** (0.14 mmol, 2.5 mol-equiv.) at 35° in 2 h. Addition of 2 ml of sat. NH_4Cl soln. (*Procedure C*) and FC (hexane/AcOEt 2:1, R_f 0.45) gave a colourless oil (de 80%), which was crystallized from CH_2Cl_2/Et_2O/pentane: **8** (9 mg, 52%; de > 99%). Colourless crystals. M.p. 222°. GC: t_R 14.78. IR ($CHCl_3$): 2921, 2856, 1447, 1327, 1311, 1147, 1077. ^{1}H-NMR: 0.9 (*d*, *J* = 7.0, 3 H); 1.25–1.3 (*m*, 1 H); 2.35–2.45 (2 H); 2.6–2.74 (2 H); 3.28–3.42 (2 H); 5.16–5.52 (2 H); 5.57 (*ddd*, *J* = 8.2, 10.2, 16.8, 1 H); 7.58–7.77 (6 H); 8.13–8.21 (2 H). ^{13}C-NMR: 138.04 (*s*); 137.34 (*d*); 135.53 (*s*); 134.63 (*d*); 134.41 (*d*); 132.14 (*d*); 131.89 (*d*); 128.77 (*d*); 128.34 (*d*); 118.51 (*t*); 92.56 (*s*); 48.43 (*d*); 48.31 (*d*); 47.15 (*d*); 37.14 (*t*); 11.7 (*q*); 11.37 (*t*). MS: 530 (1.3, $C_{21}H_{23}IO_4S_2^+$), 389 (4, $[C_{21}H_{23}IO_4S_2 - C_6H_5SO_2]^+$), 261 (11, $[C_{21}H_{23}IO_4S_2 - C_6H_5SO_2 - HI]^+$), 247 (100, $[C_{21}H_{23}IO_4S_2 - C_{12}H_{11}S_2O_4]^+$), 143 (9), 125 (34), 120 (60, $[C_{21}H_{23}IO_4S_2 - C_{12}H_{10}S_2O_4 - HI]^+$). HR-MS: 389.00801 ($[C_{21}H_{23}IO_4S_2 - C_6H_5SO_2]^+$; calc. 389.00723).

t-*5-Ethenyl*-t-*2-methyl-3,3-bis(phenylsulfonyl)cyclopentane-1-acetonitrile* (**10**). Following *Procedure B* with **7** (22 mg, 0.048 mmol) CH_2Cl_2 (2 ml), $[Pd(PPh_3)_4]$ (2.8 mg, 5 mol-%), and **4** (0.12 mmol, 2.5 mol-equiv.) at 35° in 2 h. After transmetallation (*Procedure E*) with $[CuCN(LiCl)_2]$ (13 mg, 0.07 mmol), TsCN (68 mg, 0.38) in THF (0.5 ml) was added dropwise according to *Procedure E*. Quenching with NH_4Cl, standard workup, and purification by FC (hexane/AcOEt 2:1, R_f 0.24) furnished a colourless residue (13.5 mg, 66%; de 94%). Crystallization from CH_2Cl_2/Et_2O/pentane gave pure **10** (11.5 mg, 56%, de > 99%). Colourless crystals. M.p. 219°. GC: t_R 13.48. IR ($CHCl_3$): 3019, 1447, 1327, 1311, 1147, 1071. ^{1}H-NMR: 1.08 (*d*, *J* = 7.0, 3 H); 2.16 (*tdd*, *J* = 4.3, 11.4, 11.4, 1 H); 2.34 (*dd*, *J* = 11.0, 14.7, 1 H); 2.42–2.47 (*m*, 1 H); 2.51 (*d*, *J* = 4.4, 2 H); 2.72 (*dd*, *J* = 7.0, 14.3, 1 H); 2.69–2.79 (*m*, 1 H); 5.2–5.25 (*m*, 2 H); 5.61 (*ddd*, *J* = 8.6, 9.9, 17.1, 1 H); 7.59–7.78 (6 H); 8.13–8.19 (4 H). ^{13}C-NMR: 137.83 (*s*); 136.91 (*d*); 135.52 (*s*); 134.82 (*d*); 134.54 (*d*); 132.16 (*d*); 131.81 (*d*); 128.94 (*d*); 128.41 (*d*); 119.24 (*t*); 116.29 (*s*); 92.2 (*s*); 47.34 (*d*); 46.99 (*d*); 46.21 (*d*); 37.58 (*t*); 17.32 (*t*); 12.27 (*q*). MS: 429 (1, $C_{22}H_{23}NO_4S_2^+$), 288 (11, $[C_{22}H_{23}NO_4S_2 - C_6H_5SO_2]^+$), 146 (100, $[C_{21}H_{23}IO_4S_2 - C_{12}H_{11}S_2O_4]^+$), 143 (41), 125 (45), 105 (25). HR-MS: 429.10714 ($C_{22}H_{23}NO_4S_2^+$; calc. 429.10684).

trans-*2-Ethenyl-4,4-bis(phenylsulfonyl)cyclopentane-1-methanol* (**13**). Following *Procedure B*, with **1** (45 mg, 0.1 mmol), CH_2Cl_2 (4 ml), $[Pd(PPh_3)_4]$ (6 mg, 5 mol-%), and **4** (0.25 mmol) at 40° in 2.5 h. Degassed THF (5 ml) and $ZnBr_2$ (51 mg, 2.3 mmol; dried for 3 h at 100° high vacuum) were added, and dry O_2 was bubbled through the mixture for 2 h at 0° (the corresponding hydroperoxide could be isolated as well: 47%, de 90%). The flask was allowed to warm up to r.t. and Ar was bubbled through the mixture for 15 min. To reduce the zinc peroxides $P(OMe)_3$ (0.15 ml) was added and the mixture stirred for 30 min. Standard workup and purification by FC (hexane/AcOEt 1:1, R_f 0.18) gave **13** (20.5 mg, 51%; de 92%). IR ($CHCl_3$): 3600–3300, 3030, 1447, 1327, 1311, 1147, 1077, 924. ^{1}H-NMR: 1.4 (br., 1 H); 1.97–2.04 (*m*, 1 H); 2.39–2.45 (3 H); 2.65–2.75 (2 H); 3.52 (*dd*, *J* = 5.8, 10.8, 1 H); 3.67 (*dd*, *J* = 3.7, 11, 1 H); 5.4–5.08 (2 H); 5.6 (*ddd*, *J* = 7.7, 10.6, 16.5, 1 H); 7.59–7.63 (4 H); 7.71–7.75 (2 H); 8.06–8.09 (4 H). ^{13}C-NMR: 138.3 (*d*); 136.58 (*s*); 136.45 (*s*); 134.57 (*d*); 131.43 (*d*); 131.39 (*d*); 128.74 (*d*); 117.32 (*t*); 91.84 (*s*); 62.72 (*t*); 47.41 (*d*); 46.25 (*d*); 38.5 (*t*); 35.8 (*t*). MS: 406 (0.5, $C_{20}H_{22}O_5S_2^+$), 388 (3, $[C_{20}H_{22}O_5S_2 - H_2O]^+$), 265 (27, $[C_{20}H_{22}O_5S_2 - C_6H_5O_2S]^+$), 245 (24), 143 (24), 125 (100). HR-MS: 265.08984 ($[C_{20}H_{22}O_5S_2 - C_6H_5O_2S]^+$; calc. 265.08810).

trans-*2-Ethenyl-4,4-bis(phenylsulfonyl)cyclopentane-1-acetonitrile* (**14**). Following *Procedure B*, with **1** (45 mg, 0.1 mmol), CH_2Cl_2 (4 ml), $[Pd(PPh_3)_4]$ (6 mg, 5 mol-%), and **4** (0.25 mmol, 2.5 mol-equiv.) at 40° in 2.5 h. After transmetallation (*Procedure E*) with $[CuCN(LiCl)_2]$ (26 mg, 0.15 mmol), TsCN (136 mg, 0.75 mmol) in degassed THF (2 ml) was added dropwise according to *Prodedure E*. Quenching with NH_4Cl, standard workup, and purification by FC (hexane/AcOEt 2:1, R_f 0.16) gave **14** (23.3 mg, 61%; de 94%). Colourless oil. GC: t_R 13.16. IR (KBr): 3030, 1147, 1327, 1311, 1147, 1077, 908. ^{1}H-NMR: 2.07–2.15 (*m*, 1 H); 2.24–2.53 (5 H); 2.72

(*dd*, J = 7.0, 15.1, 1 H); 2.83 (*dd*, J = 7, 15.1, 1 H); 5.1–5.17 (2 H); 5.52 (*ddd*, J = 8.6, 10.1, 16.9, 1 H); 7.62–7.65 (4 H); 7.73–7.77 (2 H); 8.07–8.1 (4 H). ^{13}C-NMR: 136.22 (*d*); 135.97 (*s*); 134.89 (*d*); 131.42 (*d*); 131.35 (*d*); 129.03 (*d*); 128.87 (*d*); 119.25 (*t*); 117.06 (*s*); 90.8 (*s*); 49.06 (*d*); 41.04 (*d*); 37.92 (*t*); 37.02 (*t*); 19.06 (*t*). MS: 415 (2, $V_{21}H_{21}NO_4S_2^+$), 274 (38, $[C_{21}H_{21}NO_4S_2 - C_6H_5SO_2]^+$), 143 (21), 141 (27, $C_6H_5SO_2^+$), 132 (57, $[C_{21}H_{21}NO_4S_2 - C_{12}H_{11}S_2O_4]^+$), 125 (98), 105 (19), 97 (13), 91 (33), 77 (100). HR-MS: 415.0912 ($C_{21}H_{21}NO_4S_2^+$; calc. 415.0912).

trans-*3-(But-3-enyl)-4-ethenyl-1,1-bis(phenylsulfonyl)cyclopentane* (**15**). Following *Procedure B* with **1** (94 mg, 0.21 mmol), CH_2Cl_2 (8 ml), $[Pd(PPh_3)_4]$ (13 mg, 5 mol-%), and **4** (0.52 mmol, 2.5 mol-equiv.) at 40° in 2.5 h. After transmetallation (*Prodedure E*) with $[CuCN(LiCl)_2]$ (55 mg, 0.32 mmol), allyl bromide (0.25 ml, 3 mmol) in degassed THF (2 ml) was added dropwise according to *Prodedure E*. Quenching with NH_4Cl, standard workup, and purification by FC (hexane/AcOEt 4:1, R_f 0.21) gave crude product (80%; de 96%) which was recrystallized from CH_2Cl_2/Et_2O/pentane; **15** (50 mg, 55%; de > 99%). Colourless crystals. M.p. 159°. GC: t_R 13.16. IR ($CHCl_3$): 3030, 2936, 1147, 1327, 1311, 1147, 1077, 924. ^{1}H-NMR: 1.11–1.21 (*m*, 1 H); 1.54–1.65 (2 H); 1.88–1.97 (*m*, 1 H); 2.0–2.05 (*m*, 1 H); 2.13–2.23 (2 H); 2.35 (*dd*, J = 11.4, 1 H); 2.66 (*dd*, J = 7.4, J = 15.1, 1 H); 2.73 (*dd*, J = 6.8, 15.3, 1 H); 4.94–5.05 (2 H); 5.5 (*ddd*, J = 8.5, 10.3, 16.9, 1 H); 5.72 (*tdd*, J = 6.6, 10.3, 16.9, 1 H); 7.58–7.64 (4 H); 7.7–7.75 (2 H); 8.03–8.09 (4 H). ^{13}C-NMR: 138.42 (*d*); 138.06 (*d*); 136.56 (*s*); 136.44 (*s*); 134.58 (*d*); 131.39 (*d*); 131.33 (*d*); 128.77 (*d*); 128.74 (*d*); 117.16 (*t*); 114.93 (*t*); 91.85 (*s*); 50.31 (*d*); 44.63 (*d*); 38.44 (*t*); 37.97 (*t*); 31.99 (*t*); 31.8 (*t*). MS: 430 (0.5, $C_{23}H_{26}O_4S_2^+$), 288 (34, $[C_{23}H_{26}O_4S_2 - C_6H_5SO_2]^+$), 233 (16), 147 (98, $[C_{23}H_{26}O_4S_2 - C_{12}H_{11}S_2O_4]^+$), 125 (100), 119 (26), 91 (69), 77 (89). HR-MS: 430.1303 ($C_{23}H_{26}O_4S_2^+$; calc. 430.1272).

Methyl trans-*2-Ethenyl-α-methylidene-4,4-bis(phenylsulfonyl)cyclopentane-1-butanoate* (**16**). Following *Procedure B*, with **1** (44 mg, 0.1 mmol), CH_2Cl_2 (4 ml), $[Pd(PPh_3)_4]$ (6 mg, 5 mol-%), and **4** (0.25 mmol, 2.5 mol-equiv.) at 40° in 2.5 h. After transmetallation (*Prodedure E*) with $[CuCN(LiCl)_2]$ (0.32 mmol), methyl 2-(bromomethyl)prop-2-enoate (190 mg, 1 mmol) in degassed THF (2 ml) was added dropwise according to *Prodedure E*. Quenching with NH_4Cl, standard workup, and purification by FC (hexane/AcOEt 4:1, R_f 0.13) gave **16** (28 mg, 56%; de 98%). Colourless oil. GC: t_R 16.29. IR (KBr): 3030, 1714, 1147, 1327, 1311, 1147, 1077. ^{1}H-NMR: 1.24–1.27 (*m*, 1 H); 1.59–1.69 (2 H); 2.16–2.39 (5 H); 2.67 (*dd*, J = 7, 15.1, 1 H); 2.77 (*dd*, J = 6.8, 15.2, 1 H); 3.75 (*s*, 1 H); 5.0–5.06 (2 H); 5.5 (*s*, 1 H); 5.47–5.56 (*m*, 1 H); 6.13 (*s*, 1 H); 7.59–7.64 (4 H); 7.71–7.75 (2 H); 8.04–8.08 (4 H). ^{13}C-NMR: 167.39 (*s*); 140.17 (*s*); 138.34 (*d*); 136.6 (*s*); 134.54 (*d*); 131.4 (*d*); 128.74 (*d*); 124.85 (*t*); 117.2 (*t*); 91.94 (*s*); 51.76 (*q*); 50.18 (*d*); 44.76 (*d*); 38.5 (*t*); 37.98 (*t*); 31.4 (*t*); 30.12 (*t*). MS: 488 (1, $C_{25}H_{28}O_6S_2^+$), 456 (3, $[C_{25}H_{28}O_6S_2 - CH_4O]^+$), 347 (18, $[C_{25}H_{28}O_6S_2 - C_6H_5SO_2]^+$), 315 (25, $[C_{25}H_{28}O_6S_2 - C_6H_5SO_2 - CH_4O]^+$), 314 (25), 286 (12), 205 (42, $[C_{25}H_{28}O_6S_2 - C_{12}H_{11}S_2O_4]^+$), 173 (86, $[C_{25}H_{28}O_6S_2 - C_{12}H_{11}S_2O_2 - CH_4O]^+$), 145 (90, $[C_{25}H_{2806}S_2 - C_{12}H_{11}S_2O_4 - C_2H_4O_2]^+$), 125 (100). HR-MS: 347.13171 ($[C_{25}H_{28}O_6S_2 - C_6H_5SO_2]^+$; calc. 347.13521), 315.10175 ($[C_{25}H_{28}O_6S_2 - C_6H_5SO_2 - CH_4O]^+$), calc. 315.10175).

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