163. Rhodium(I)-Catalyzed 'Metallo-Ene' Cyclizations/β-Eliminations[1])

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Octadienyl carbonates **5** provide cyclic 1,4-dienes **6** when treated with Rh^I complexes (1–10 mol-%) at 80°. Similar cyclization of cyclohexenyl acetate **8** affords *cis*-fused hexahydroindene **9**. Analogous ring closures of nonadienyl carbonate **10** yield preferably the *cis*-divinylpyrrolidine **11** with Rh^I catalysis but the *trans*-isomer **12** when catalyzed by Pd^0. Azaoctadienyl carbonate **5a** undergoes elimination with $[RhH(PPh_3)_4]$ (5 mol-%, 80°) in MeCN giving acyclic triene **7**.

Introduction. – The intramolecular insertion of allyl-palladium und -nickel species into alkene and alkyne bonds ('metallo-ene' cyclization) has evolved into a synthetically powerful process [1] [2]. Most critically, this insertion process becomes part of a catalytic cycle when combined with oxidative addition and reductive elimination steps ($Pd^0 \rightleftharpoons Pd^{II}$, $Ni^0 \rightleftharpoons Ni^{II}$) to generate the allyl-metal intermediate and recover the metal catalyst, respectively. Pd- and Ni-ene reactions display useful stereochemical differences despite the close relationship of the d^{10}-metal catalysts [3]. On extending this concept to further transition metals, one could thus expect to find interesting selectivity changes.

We report here the first example of an efficient Rh-catalyzed metallo-ene cyclization/β-elimination tandem protocol **A**→**B**→**C**→**D** (involving the oxidation states $Rh^I \rightleftharpoons Rh^{III}$; *Scheme 1*).

At first, we examined the capacity of various Rh^I complexes to catalyze the transformation of dienyl carbonate **5a** into 3-methylidene-4-vinylpyrrolidine **6a** (*Scheme 2, Table 1*).

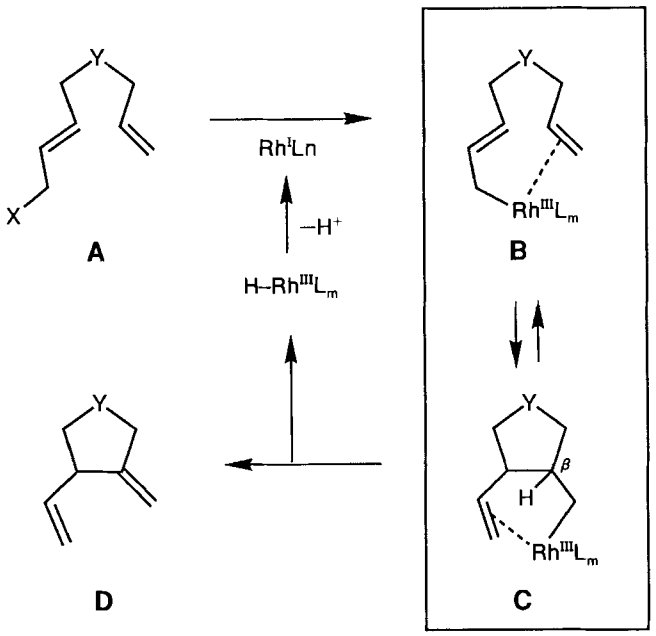
Most attempts were thwarted by the need of ≥ 0.25 mol-equiv. of Rh catalyst and high reaction temperatures (> 100°) which, furthermore, caused undesirable isomerizations of the 1,4-dienyl products to 1,3-dienes. Nevertheless, some encouraging results are summarized in *Table 1*.

For instance, heating **5a** with $[Rh(CO)_2(acac)]$/dppb (acac = acetylacetonate, dppb = 1,4-bis(diphenylphosphino)butane; 10 mol-% each) in AcOH at 70° for 6 h provided **6a** (79% by GC, *Entry 1*). More efficiently, $[Rh(cod)Cl]_2$ [4] (1 mol-%)/NEt_3 (10 mol-%, MeCN, 80°) led to 63% (GC) cyclization **5a**→**6a** (*Entry 2*)[2]). We then explored the potential of hydridotetrakis(triphenylphosphine)rhodium(I) as a catalyst for the

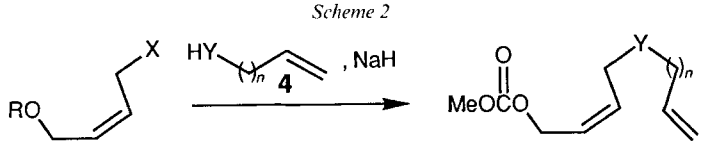
[1]) Presented by *W. O.* at the 2nd International Symposium 'Transision Metals in Organic Synthesis', Bristol, September 1992.

[2]) We assume that the NEt_3 deprotonates the relatively stable (compared to the Pd^{II}- and Ni^{II}-hydride complexes) Rh^{III}-hydride species, speeding up the recovery of the Rh^I catalyst.

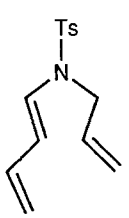
Scheme 1



Scheme 2



1 R = H, X = OH
2 R = CO_2Me, X = OH
3 R = CO_2Me, X = Br



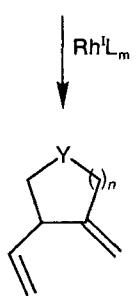


Table 1. *Rh[1]-Catalyzed Allyl-metal-Alkene Cyclizations/β-Eliminations* **5a**→**6a**: *Variation of the Catalyst System*

Entry	Series	Y	*n*	Rh Catalyst [mol.-equiv.]	Additive [mol.-equiv.]	Solvent	Temp. [°C]	Time [h]	Yield of **6a** [%]
1	**a**	NTs	*1*	$[Rh(CO)_2(acac)]$ (0.1)	dppb (0.1)	AcOH	70	6	79 (GC)
2	**a**	NTs	*1*	$[Rh(cod)Cl]_2$ (0.01)	NEt_3 (0.1)	MeCN	80	3	63 (GC)
3	**a**	NTs	*1*	$[RhH(PPh_3)_4]$ (0.5)	–	MeCN	80	0.5	0[a])
4	**a**	NTs	*1*	$[RhH(PPh_3)_4]$ (0.5)	–	AcOH	80	1.5	75 (GC)
5	**a**	NTs	*1*	$RhH(PPh_3)_4$ (0.02)	$P[Ph(MeO)_3]_3$ (0.04)	AcOH	80	1.5	80 (isol.)

[a]) Acyclic triene **7** isolated in 75% yield.

cyclization of **5a**[3]). However, treatment of dienyl carbonate **5a** with $[RhH(PPh_3)_4]$ (5 mol-%) in MeCN (80°, 0.5 h) furnished rapidly and exclusively acyclic triene **7** (75%, *Entry 3*). By contrast, **5a** cyclized smoothly to **6a** (75%, GC) when heated with $[RhH(PPh_3)_4]$ (5 mol-%) in AcOH (80°, 1.5 h, *Entry 4*). Under identical conditions, but with 2 mol-% of $[RhH(PPh_3)_4]$ in the presence of the electron-donating ligand tris(2,4,6-trimethoxyphenyl)phosphine [7] (4 mol-%), **5a** afforded pyrrolidine **6a** even more efficiently (80% isolated yield, *Entry 5*). Employing the $[RhH(PPh_3)_4]/P[Ph(OMe)_3]_3$ catalyst system in AcOH various dienyl carbonates **5** were cyclized (63–88%) to vinylmethylidene pyrrolidines (*Table 2, Entries 5–7*) and cyclopentanes (*Entries 8–9*)[4]). Not unexpectedly,

Table 2. *$[RhH(PPh_3)_4]$/Tris(2,4,6-trimethoxyphenyl)phosphine-Catalyzed Allyl-metal-Alkene Cyclizations/β-Eliminations* (AcOH, 80°) **5**→**6**: *Variation of the Substrate*

Entry	Series	Y	*n*	$[RhH(PPh_3)_4]$ [mol.-equiv.]	Time [h]	Yield (isolated) of **6** [%]
5	**a**	NTs	*1*	0.02	1.5	80
6	**b**	$NCOCF_3$	*1*	0.02	6.5	83
7	**c**	NCO_2CH_2Ph	*1*	0.02	2.0	63
8	**d**	$C(CO_2Me)_2$	*1*	0.02	3.0	75
9	**e**	$C(SO_2Ph)_2$	*1*	0.02	7.5	88
10	**f**	NTs	*2*	0.08	6.5	65
11	**g**	$C(SO_2Ph)_2$	*2*	0.08	12.0	55

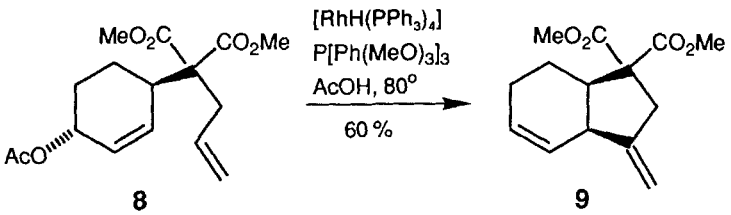
the analogous formation of six-membered rings proceeded more slowly and required more catalyst (8 mol-% Rh, *Entries 10* and *11*). Related cyclization of the *trans*-cyclohexenyl-propanedioate **8** provided *cis*-fused hexahydroindene **9** (60%, *Scheme 3*).

We then compared the relative allyl/alkene facilities of Rh- and Pd-ene cyclizations choosing nonadienylcarbonate **10** as substrate. Treatment of **10** with $[RhH(PPh_3)_4]/P[Ph(OMe)_3]_3$ in AcOH at 80° for 1 h gave an inseparable 86:14 mixture of *cis*/*trans*-isomers **11**/**12** (52%; *Scheme 4, Table 3, Entry 12*).

[3]) $[RhH(PPh_3)_4]$ is easily accessible [5] and, when modified with PBu_3, catalyzes the allylation of carbonucleophiles with allylic carbonates [6].

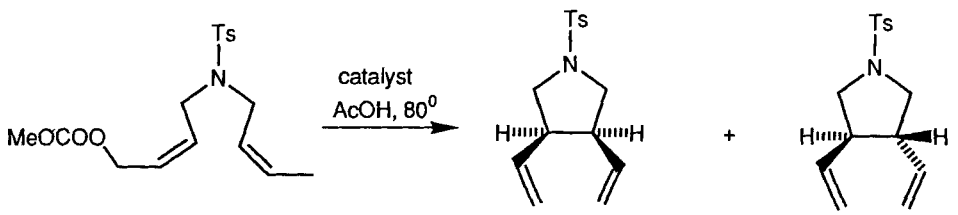
[4]) Five-membered cyclic products **6a** and **6d** were also obtained in 74 and 88% yield, respectively, by heating the corresponding acyclic dienyl acetates with $[RhH(PPh_3)_4]$ (5 mol-%)/$P[Ph(OMe)_3]_3$ (10 mol-%) in AcOH at 80°.

Scheme 3



8 **9**

Scheme 4



10 **11** **12**

Table 3. *Rh*^{I}- *and Pd*^{0}-*Catalyzed Allyl-metal-Alkene Cyclizations/β-Eliminations* (AcOH, 80°) **10**→**11** + **12**

Entry	Metal complex (mol-equiv.)	Additive [mol-equiv.]	Time [h]	Yield [%] **11** + **12**	Ratio **11**/**12**
12	$[RhH(PPh_3)_4]$ (0.02)	$[P[Ph(MeO)_3]_3]$ (0.04)	1	52	86:14
13	$[RhH(PPh_3)_4]$ (0.02)	$[P[Ph(MeO)_3]_3]$ (0.04)	12	70	77:23
14	$[Pd(dba)_2]$ (0.10)	PPh_3 (0.3)	1	60	20:80

Extending the reaction time to 12 h furnished **11**/**12** (70% yield) in a similar ratio (77:23) in favor of the *cis*-isomer (*Entry 13*). On the other hand, the *trans*-product **12** was favored by a factor of **11**/**12** 20:80 on $[Pd(dba)_2]$ (10 mol-%)/PPh^3 (30 mol-%)-catalyzed cyclization of **10** (*Entry 14*)[5].

In the light of these results, it is not unreasonable to expect that the 'Rh-ene' process may offer additional stereochemical perspectives owing to the octahedral hexacoordination of Rh^{III} complexes[6]. These and other aspects of transition-metal-mediated intramolecular alkene and alkyne allylations are presently pursued in our laboratory.

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[5] Pd^0-Catalyzed cyclization of a closely related azadienyl acetate also produced the *trans*-substituted pyrrolidine product under kinetic control [8]. For the assignment of *cis*- and *trans*-pyrrolidines **11** and **12**, see [8].

[6] *Cf.* [9]. Pd^{II}- and Ni^{II} complexes are usually planar-tetracoordinated [9].

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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, MeCN (CaH_2). '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*). GC: *Hewlett-Packard 5790 A*, integrator *HP 3390 A*, cap. column (fused silica, 0.2 mm i.d., 12 m), 10 psi H_2; t_R in min (area-%). M.p.: *Kofler* hot stage; uncorrected. IR: *Mattson Polaris*, 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 $CHCl_3$ ($\delta = 7.27$ ppm), J in Hz. MS: *Varian CH-4* or *Finnigan 4023* at 70 eV, *m/z* (rel.-%). HR-MS: *VG 7070-E*.

Preparation of Dienyl Carbonates. – *(Z)-(4-Hydroxybut-2-en-1-yl) Methyl Carbonate* (**2**). A soln. of methyl chloroformate (14.2 g, 149.8 mmol) in THF (50 ml) was slowly added to a soln. of (*Z*)-but-2-ene-1,4-diol (12 g, 136.2 mmol) and pyridine (16.2 g, 204.3 mmol) in THF (250 ml) at −5°. Stirring of the mixture at r.t. for 16 h, addition of 1N aq. HCl soln., extraction with AcOEt, washing of the combined org. phases with sat. aq. $NaHCO_3$ soln. and brine, drying, evaporation, and FC (hexane/AcOEt 3:2) gave **2** (oil, 13.5 g, 68%). IR: 3200–3600, 2900–3080, 1745, 1445, 1370, 1270, 1030, 950. ^{1}H-NMR (400 MHz): 5.90 (*dtt*, $J = 11, 7, 1, 1$ H); 5.66 (*dtt*, $J = 11, 7, 1, 1$ H); 4.74 (*dd*, $J = 7, 1, 2$ H); 4.26 (br. *d*, $J = 5, 2$ H); 3.78 (*s*, 3 H); 2.30 (br. *s*, 1 H). ^{13}C-NMR (50 MHz): 155.80 (*s*); 134.09 (*d*); 124.81 (*d*); 63.24 (*t*); 58.28 (*t*); 54.87 (*q*). MS: 128 (3, $[C_6H_{10}O_4 - H_2O]^{+\cdot}$), 116 (3), 112 (4), 84 (19), 77 (83), 70 (100), 59 (56).

(Z)-(4-Bromobut-2-en-1-yl) Methyl Carbonate (**3**). A soln. of PPh_3 (13.46 g, 51.3 mmol) in CH_2Cl_2 (50 ml) was added at −5° to a soln. of **2** (7.5 g, 51.3 mmol) and *N*-bromosuccinimide (9.13 g, 51.3 mmol) in CH_2Cl_2 (150 ml). Stirring of the mixture at r.t. for 16 h, evaporation, trituration of the residue with pentane/Et_2O (6:1), evaporation, and FC (hexane/AcOEt 4:1) afforded **3** (oil, 7.17 g, 67%). IR: 2900–3050, 1750, 1445, 1360, 1280, 970. ^{1}H-NMR (200 MHz): 5.96 (*dtt*, $J = 11, 7, 1, 1$ H); 5.70 (*dt*, $J = 11, 7, 1$ H); 4.73 (*dd*, $J = 7, 1, 2$ H); 4.00 (*d*, $J = 8, 2$ H); 3.78 (*s*, 3 H). ^{13}C-NMR (50 MHz): 155.54 (*s*); 130.34 (*d*); 127.42 (*d*); 62.40 (*t*); 54.97 (*q*); 25.45 (*t*). MS: 135 (17), 132 (18), 129 (60, $[C_6H_9BrO_3 - HBr]^{+\cdot}$), 85 (100), 59 (61), 53 (83).

Dimethyl 2-(Prop-2-enyl)propanedioate (**4d**). NaH (60% in mineral oil, 2.0 g, 50 mmol) was added portionwise at 0° to a soln. of dimethyl malonate (5.7 ml, 50 mmol) in DMF (200 ml). Stirring of the mixture at 0° for 1 h, then at r.t. for 1 h, addition of allyl bromide (4.5 ml, 53 mmol) stirring at r.t. for 16 h, workup (AcOEt), and FC (hexane/AcOEt 15:1) provided **4d** (oil, 5.0 g, 58%). GC (80°): 3.13. IR: 3050–2950, 1740, 1732, 1435, 1342, 1272, 1243, 1197, 1160, 930. ^{1}H-NMR (200 MHz): 5.23 (*ddt*, $J = 17, 10, 7, 1$ H); 5.15–4.47 (2 H); 3.70 (*s*, 6 H); 3.43 (*t*, $J = 7.5, 1$ H); 2.71 (br. *t*, $J = 7, 2$ H). ^{13}C-NMR (50 MHz): 169.22 (*s*); 133.87 (*d*); 117.60 (*t*); 52.45 (*q*); 51.34 (*d*); 32.81 (*t*). MS: 172 (5, $[C_8H_{12}O_4]^{+\cdot}$), 141 (11), 140 (14), 113 (96), 112 (98), 111 (28), 109 (77), 108 (36), 97 (24), 84 (37), 81 (100), 71 (32), 59 (52).

(Z)-N-(But-2-en-1-yl)-p-toluenesulfonamide. TsCl (7.84 g, 41.13 mmol) was added to a stirred soln. of (*Z*)-crotylamine hydrochloride [10] (2.95 g, 27.42 mmol) and pyridine (5 ml) in CH_2Cl_2 (50 ml). Stirring of the mixture at r.t. for 16 h, addition of an aq. sat. $NaHCO_3$ soln., vigorous stirring for 0.5 h, washing of the org. phase (*i*) 10% aq. HCl soln., *ii*) H_2O), drying, evaporation, and FC (hexane/AcOEt 9:2) gave *(Z)-N-(but-2-en-1-yl)-p-toluenesulfonamide* (4.94 g, 80%) which was crystallized from EtOH. M.p. 40–41°. IR: 3400, 3250–3350, 2880–3080, 1600, 1400, 1330, 1160, 1195. ^{1}H-NMR (200 MHz): 7.77–7.73 (2 H); 7.30–7.26 (2 H); 5.51 (*m*, 1 H); 5.28 (*dtq*, $J = 11, 6.5, 1, 1$ H); 4.74 (br. *t*, $J = 6.5, 2$ H); 3.58 (*td*, $J = 6.5, 1, 2$ H); 2.41 (*s*, 3 H); 1.51 (*dt*, $J = 6.5, 1, 3$ H). ^{13}C-NMR (50 MHz): 143.35 (*s*); 136.84 (*s*); 129.61 (*d*); 128.62 (*d*); 127.15 (*d*); 124.69 (*d*); 39.75 (*t*); 21.45 (*q*); 12.80 (*q*). MS: 226 (3, $[C_{11}H_{15}NO_2S]^{+\cdot}$), 225 (2, $M^{+\cdot}$), 172 (4), 155 (14), 139 (6), 107 (6), 91 (75), 70 (100).

1,1-Bis(phenylsulfonyl)but-3-ene (**4g**). A soln. of bis(phenylsulfonyl)methane (10 g, 33.7 mmol) in DMF (20 ml) was added dropwise (30 min) to a suspension of NaH (55% in mineral oil, 1.54 g, 35.4 mmol) in DMF (20 ml) at 0°. Stirring the mixture at 0° for 1 h, then at r.t. 2 h, addition of buten-3-yl bromide (5.0 g, 37.11 mmol) in DMF (30 ml) at 0°, stirring at r.t. for 16 h, workup (AcOEt), and FC (hexane/AcOEt 65:35) afforded **4g** (oil, 7.5 g, 64%). ^{1}H-NMR (200 MHz): 8.0–7.85 (4 H); 7.80–7.50 (6 H); 5.55 (*m*, 1 H); 5.04 (*dd*, $J = 10, 1, 1$ H); 5.01 (*dd*, $J = 17, 1, 1$ H); 4.25 (br. *t*, $J = 5, 1$ H); 2.40–2.20 (4 H).

(Z)-N-{4-[(Methoxycarbonyl)oxy]but-2-enyl}-N-(prop-2-enyl)-p-toluenesulfonamide (**5a**). NaH (60% in mineral oil, 454 mg, 11.36 mmol) was added portionwise at r.t. to a stirred soln. of *N*-(prop-2-enyl)-*p*-toluenesul-

fonamide [11] (2.00 g, 9.47 mmol) and **3** (2.97 g, 14.2 mmol) in DMF (60 ml). Stirring of the mixture at r.t. for 4 h, workup (AcOEt), and FC (hexane/AcOEt 9:2) afforded **5a** (colorless crystals, 2.67 g, 83%). M.p. 44–45°. IR: 2850–3100, 1750, 1600, 1450, 1350, 1270, 940. ^{1}H-NMR (400 MHz): 7.71–7.69 (2 H); 7.32–7.30 (2 H); 5.49–5.71 (3 H); 5.17 (*dq*, *J* = 17, 1, 1 H); 5.15 (*dq*, *J* = 10, 1, 1 H); 4.62 (*dd*, *J* = 7, 1, 2 H); 3.88 (*dd*, *J* = 7, 1, 2 H); 3.79 (*d*, *J* = 6, 2 H); 3.78 (*s*, 3 H); 2.44 (*s*, 3 H). ^{13}C-NMR (100 MHz): 155.58 (*s*); 143.44 (*s*); 137.09 (*s*); 132.82 (*d*); 129.86 (*d*); 127.20 (*d*); 126.70 (*d*); 119.16 (*t*); 62.95 (*t*); 54.88 (*q*); 50.00 (*t*); 43.62 (*t*); 21.53 (*q*). MS: 282 (0.2, $[C_{16}H_{21}NSO_5 - 57]^+$), 235 (2), 222 (6), 184 (7), 173 (6), 155 (25), 128 (10), 108 (44), 96 (12), 91 (100), 81 (59), 55 (50).

*(Z)-*N*-{4-[(Methoxycarbonyl)oxy]but-2-enyl}-*N*-(prop-2-enyl)trifluoroacetamide* (**5b**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) *N*-*(prop-2-enyl)trifluoroacetamide* (**4b**) [12] (1.00 g, 6.53 mmol) was alkylated with **3** (1.43 g, 6.84 mmol) in DMF (30 ml) at r.t. for 12 h. Workup and FC (hexane/AcOEt 9:1) afforded **5b** (oil, 0.96 g, 52%). IR: 2900–3050, 1750, 1695, 1450, 1370, 1280, 1190, 1150, 950. ^{1}H-NMR (400 MHz, rotamers): 5.72–5.86 (2 H); 5.62 (*m*, 1 H); 5.27–5.33 (2 H); 4.74 (*dd*, *J* = 7, 1, 1.4 H); 4.67 (*dd*, *J* = 7, 1, 0.6 H); 4.12 (*d*, *J* = 7, 2 H); 4.01 (*d*, *J* = 7, 2 H); 3.81, 3.80 (*s*, 3 H). ^{13}C-NMR (100 MHz, rotamers): 156.76 (*q*, *J*(C,F) = 36.4); 156.54 (*q*, *J*(C,F) = 35.5); 155.54 (*s*); 131.72 (*d*); 130.86 (*d*); 129.03 (*d*); 127.98 (*d*); 127.80 (*d*); 127.72 (*d*); 119.42 (*t*); 118.99 (*t*); 116.37 (*q*, *J*(C,F) = 286); 62.87 (*t*); 62.54 (*t*); 54.90 (*q*); 54.80 (*q*); 49.55 (*t*); 49.52 (*t*); 48.33 (*t*); 43.56 (*t*); 42.94 (*t*). MS: 281 (1, $[C_{11}H_{14}F_3NO_4]^+$), 206 (44), 205 (38), 177 (20), 164 (48), 136 (16), 128 (18), 93 (18), 80 (20), 54 (100).

*Benzyl (Z)-*N*-{4-[(Methoxycarbonyl)oxy]but-2-enyl}-*N*-(prop-2-enyl)carbamate* (**5c**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) benzyl *N*-*(prop-2-enyl)carbamate* (**4c**) [13] (1.00 g, 5.23 mmol) was alkylated with **3** (1.64 g, 7.84 mmol) in DMF (20 ml) at r.t. for 45 min. Workup and FC (hexane/AcOEt 9:1) afforded **5c** (oil, 1.34 g, 83%). IR: 2900–3100, 1750, 1700, 1450, 1430, 1370, 1275, 1250, 1150, 940. ^{1}H-NMR (200 MHz, rotamers): 7.33 (br. *s*, 5 H); 5.60–5.80 (3 H); 5.10–5.20 (2 H); 5.13 (*s*, 2 H); 4.55–4.75 (2 H); 3.85–4.0 (4 H); 3.75 (*s*, 3 H). ^{13}C-NMR (50 MHz, rotamers): 155.86 (*s*); 155.59 (*s*); 136.61 (*s*); 133.46 (*d*); 130.80 (*d*); 128.48 (*d*); 128.22 (*d*); 127.98 (*d*); 127.90 (*d*); 126.03 (*d*); 125.90 (*d*); 125.63 (br. *d*); 117.1 (br. *t*); 67.28 (*t*); 63.05 (*t*); 54.81 (*q*); 49.4 (br. *t*); 48.9 (br. *t*); 43.2 (br. *t*). MS: 243 (2, $[C_{17}H_{21}NO_5 - 64]^+$), 170 (1), 158 (3), 108 (6), 91 (100), 65 (10), 54 (10).

Dimethyl 2-{4-[(Methoxycarbonyl)oxy]but-2-enyl}-2-(prop-2-enyl)propanedioate (**5d**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) **4d** (1.50 g, 8.71 mmol) was alkylated with **3** (2.37 g, 11.32 mmol) in DMF (60 ml) at r.t. for 12 h. Workup and FC (hexane/AcOEt 4:1) gave **5d** (oil, 2.20 g, 84%). IR: 2950–3050, 1750, 1730, 1440, 1280, 950. ^{1}H-NMR (200 MHz): 5.41–5.80 (3 H); 5.10 (*m*, 1 H); 5.03 (*m*, 1 H); 4.71 (*dd*, *J* = 6, 1, (*E*)-isomer); 4.62 (*dd*, *J* = 6, 1, 2 H, (*Z*)-isomer; (*E*)/(*Z*) = 1:4); 3.74 (*s*, 3 H); 3.73 (*s*, 3 H); 3.68 (*s*, 3 H); 2.65 (*d*, *J* = 7, 2 H); 2.61 (*dd*, *J* = 6, 1, 2 H). ^{13}C-NMR (50 MHz): 170.91 (*s*); 155.61 (*s*); 132.00 (*d*); 128.35 (*d*); 126.80 (*d*); 119.43 (*t*); 63.34 (*t*); 57.34 (*s*); 54.74 (*q*); 52.51 (*q*); 37.13 (*t*); 30.56 (*t*).

(Z)-5,5-Bis(phenylsulfonyl)octa-2,7-dienyl Methyl Carbonate (**5e**). NaH (880 mg, 22.0 mmol) was added portionwise to a soln. of *1,1-bis(phenylsulfonyl)but-3-ene* (**4e**) [14] (6.73 g, 20.0 mmol) in THF (100 ml) at 0°, and the mixture was stirred for 1 h at r.t. Addition of $[Pd(dba)_2]$ (575 mg, 5 mol-%) and PPh_3 (1.05 g, 20 mol-%), then dropwise addition of a soln. of (*Z*)-1-[(1-chlorotetrahydropyran-4-yl)oxy]butene [15] (4.00 g, 21.0 mmol) in THF (60 ml), stirring for 16 h at r.t., workup (Et_2O), and FC (hexane/AcOEt 3:2) afforded the expected alkylation product (oil, 6.00 g, 62%), which was stirred with $TsOH \cdot H_2O$ (10 mg) in MeOH (100 ml) at 50° for 3 h. Addition of solid $NaHCO_3$, evaporation, stirring of the residue with pyridine (1.60 g, 20 mmol) and methyl chloroformate (1.90 g, 20.0 mmol) in CH_2Cl_2 (70 ml) at 0° for 1 h, workup and FC (hexane/AcOEt 1:1) afforded **5e** (oil, 3.31 g, 74%; overall yield: 46%). IR: 2950–3100, 1750, 1455, 1330, 1320, 1270, 1150, 1080. ^{1}H-NMR (200 MHz): 7.50–8.10 (10 H); 5.88–6.09 (2 H); 5.68 (*dtt*, *J* = 15, 6, 1, 1 H); 5.23 (*dq*, *J* = 10, 1, 1 H); 5.15 (*dq*, *J* = 16, 1, 1 H); 4.56 (*dd*, *J* = 6, 1, 2 H); 3.80 (*s*, 3 H); 3.01 (*t*, *J* = 4.5, 4 H). ^{13}C-NMR (50 MHz): 155.38 (*s*); 136.59 (*s*); 134.66 (*d*); 131.49 (*d*); 129.69 (*d*); 129.33 (*d*); 128.56 (*d*); 127.31 (*d*); 120.85 (*t*); 89.84 (*s*); 67.59 (*t*); 54.81 (*q*); 33.78 (*t*); 32.31 (*t*). MS: 389 (4, $[C_{22}H_{24}O_7S_2 - CH_3OCO_2]^+$), 247 (10), 181 (5), 143 (12), 141 (12), 125 (81), 121 (10), 107 (9), 106 (18), 105 (100), 97 (17), 91 (30), 79 (48), 78 (23), 77 (96), 65 (12), 59 (22), 51 (29).

*N-[(Z)-But-2-en-1-yl]-*N*-{[4-(Methoxycarbonyl)oxy]but-2-enyl}-*p*-toluenesulfonamide* (**5f**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) *N*-(but-3-enyl)-*p*-toluenesulfonamide [16] (1.22 g, 5.33 mmol) was alkylated with **3** (1.12 g, 5.36 mmol) in DMF (20 ml) at r.t. for 16 h. Workup and FC (hexane/AcOEt 2:1) furnished **5f** (oil, 1.48 g, 79%). IR: 2880–3100, 1750, 1600, 1450, 1350, 1270, 1160, 1090, 940. ^{1}H-NMR (200 MHz): 7.72–7.62 (2 H); 7.32–7.22 (2 H); 5.80–5.49 (3 H); 5.10–4.98 (2 H); 4.63 (*dd*, *J* = 6, 1, 2 H); 3.90 (*d*, *J* = 6, 2 H); 3.76 (*s*, 3 H); 3.18 (*dd*, *J* = 8, 6, 2 H); 2.41 (*s*, 3 H); 2.28 (br. *q*, *J* = 6, 2 H). ^{13}C-NMR (50 MHz): 155.54 (*s*); 143.31 (*s*); 136.82 (*s*); 134.55 (*d*); 130.57 (*d*); 129.69 (*d*); 127.10 (*d*); 126.33 (*d*); 117.12 (*t*); 62.71 (*t*); 54.86 (*q*); 47.26 (*t*); 44.84 (*t*); 33.06 (*t*); 21.45 (*q*). MS: 315 (0.7, $[C_{17}H_{23}NO_5S - 39]^+$), 312 (79), 236 (4), 155 (42), 129 (52), 91 (100), 85 (33), 82 (51), 55 (79).

(Z)-5,5-Bis(phenylsulfonyl)nona-2,8-dienyl Methyl Carbonate (**5g**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) *1,1-bis(phenylsulfonyl)pent-4-ene* (**4g**) (1.00 g, 2.85 mmol) was alkylated with **3** (0.895 g, 4.28 mmol) in DMF (15 ml) at r.t. for 4 h. Workup and FC (hexane/AcOEt 9:2) gave **5g** (oil, 1.21 g, 89%). IR: 2900–3100, 1750, 1450, 1330, 1320, 1280, 1150, 1080, 910. ^{1}H-NMR (200 MHz): 8.1–8.0 (4 H); 7.79–7.65 (2 H); 7.65–7.53 (4 H); 5.95 (*td*, *J* = 11, 6, 1 H); 5.59–5.83 (2 H); 5.04 (*dd*, *J* = 17, 1, 1 H); 5.01 (*dd*, *J* = 10, 1, 1 H); 4.61 (*dd*, *J* = 6, 1, 2 H); 3.79 (*s*, 3 H); 3.06 (*dd*, *J* = 6, 1, 2 H); 2.23–2.48 (4 H). ^{13}C-NMR (50 MHz): 155.52 (*s*); 136.31 (*s*); 136.17 (*d*); 134.66 (*d*); 131.29 (*d*); 128.64 (*d*); 127.21 (*d*); 125.88 (*d*); 115.94 (*t*); 90.27 (*s*); 63.17 (*t*); 54.90 (*q*); 27.56 (*t*); 27.42 (*t*); 26.78 (*t*). MS: 403 (0.5, $[C_{23}H_{26}O_7S_2 - CH_3OCO_2]^+$), 261 (5), 157 (3), 143 (14), 135 (4), 126 (6), 125 (67), 119 (63), 117 (15), 97 (12), 91 (64), 77 (100).

trans-*Dimethyl 2-(4-Acetoxycyclohex-2-enyl)-2-(prop-2-enyl)propanedioate* (**8**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) **4d** (503 mg, 2.92 mmol) was alkylated with *cis*-4-chlorocyclohex-2-en-1-yl acetate [17] (535 mg, 1.05 mmol) in DMF (4 ml) at r.t. for 24 h. Workup and FC (hexane/AcOEt 4:1) provided **8** (oil, 655 mg, 72%). GC (100°/3 min, 10°/min→270°): 12.2. IR: 3040, 2980, 1730, 1640, 1440, 1380, 1250. ^{1}H-NMR (360 MHz): 5.92 (*dq*, *J* = 11, 2, 1 H); 5.75 (*ddt*, *J* = 17, 10, 7, 1 H); 5.68 (*m*, 1 H); 5.32 (*m*, 1 H); 5.2–5.1 (2 H); 3.77 (*s*, 3 H); 3.74 (*s*, 3 H); 3.00 (*m*, 1 H); 2.72 (*d*, *J* = 7, 2 H); 2.18 (*m*, 1 H); 2.09 (*s*, 3 H); 1.92 (*m*, 1 H); 1.65–1.45 (3 H). ^{13}C-NMR (50 MHz): 170.73 (*s*); 170.68 (*s*); 170.30 (*s*); 132.57 (*d*); 131.64 (*d*); 128.19 (*d*); 118.85 (*t*); 69.68 (*d*); 61.16 (*s*); 52.19 (*q*); 52.04 (*q*); 38.92 (*d*); 37.02 (*t*); 28.33 (*t*); 22.47 (*t*); 21.23 (*q*). MS: 279 (0.5, $[C_{16}H_{22}O_6 - CH_3O]^+$), 218 (12), 190 (22), 131 (100), 113 (31), 108 (33), 91 (35), 78 (94).

N-*[(Z)-But-2-enyl]*-N-{*(Z)-4-[(Methoxycarbonyl)oxy]but-2-enyl*}-p-*toluenesulfonamide* (**10**). Following the protocol, described for the preparation of **5a**, deprotonated (NaH) *N-[(Z)-but-2-enyl]*-p-*toluenesulfonamide* (1.00 g, 4.44 mmol) was alkylated with **3** (1.11 g, 5.33 mmol) in DMF (30 ml) at r.t. for 14 h. Workup and FC (hexane/AcOEt 9:2) furnished **10** (oil, 1.35 g, 86%). IR: 2850–3100, 1750, 1600, 1445, 1340, 1280, 1160, 1090. ^{1}H-NMR (400 MHz): 7.71–7.69 (2 H); 7.31–7.29 (2 H); 5.53–5.72 (3 H); 5.22 (*qtd*, *J* = 10, 6, 1, 1 H); 4.62 (*dd*, *J* = 6, 1, 2 H); 3.87 (*d*, *J* = 7, 2 H); 3.85 (*d*, *J* = 7, 2 H); 3.77 (*s*, 3 H); 2.43 (*s*, 3 H); 1.58 (*td*, *J* = 6, 1, 3 H). ^{13}C-NMR (100 MHz): 155.43 (*s*); 143.23 (*s*); 136.91 (*s*); 130.10 (*d*); 129.62 (*d*); 128.77 (*d*); 127.07 (*d*); 126.37 (*d*); 124.49 (*d*); 62.81 (*t*); 54.71 (*q*); 43.68 (*t*); 43.63 (*t*); 21.37 (*q*); 12.69 (*q*). MS: 354 (0.6, $[C_{17}H_{23}NO_5S + 1]^+$), 278 (5), 224 (10), 198 (16), 155 (23), 122 (37), 95 (22), 91 (80), 68 (82), 55 (100).

Cyclization Reactions. – *Tetrahydro-3-methylidene-1-(*p-*toluenesulfonyl)-4-vinylpyrrole* (**6a**). A soln. of **5a** (200 mg, 0.589 mmol), $[RhH(PPh_3)_4]$ (13.5 mg, 2 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (12.5 mg, 4 mol-%) in AcOH (5 ml) was heated under Ar at 80° for 1.5 h. Evaporation and FC (hexane/AcOEt 9:1) afforded **6a** (oil, 124 mg, 80%).

Analogous treatment of (*Z*)-*N*-(4-acetoxybut-2-enyl)-*N*-(prop-2-enyl)-*p*-toluenesulfonamide (100 mg, 0.309 mmol) with $[RhH(PPh_3)_4]$ (17.7 mg, 5 mol-%) and tris(2,4,6-trimethoxyphenyl)phosphine (16.5 mg, 10 mol-%) in AcOH (3.5 ml) at 80° for 2 h also gave **6a** (60 mg, 74%). GC (200°): 3.14. IR: 2850–3100, 1350, 1230, 1170, 1090. ^{1}H-NMR (400 MHz): 7.77–7.68 (2 H); 7.64–7.56 (2 H); 5.50 (*ddd*, *J* = 16.5, 10.5, 8, 1 H); 5.14 (*dd*, *J* = 10.5, 1, 1 H); 5.11 (*dd*, *J* = 16.5, 1, 1 H); 4.98 (*q*, *J* = 2.5, 1 H); 4.87 (*q*, *J* = 2.5, 1 H); 3.99 (*dq*, *J* = 14, 1, 1 H); 3.72 (*dq*, *J* = 14, 2, 1 H); 3.64 (*dd*, *J* = 9.2, 7.7, 1 H); 3.24 (br. *q*, *J* = 7.7, 1 H); 2.86 (*t*, *J* = 9.2, 1 H); 2.44 (*s*, 3 H). ^{13}C-NMR (100 MHz): 146.75 (*s*); 143.64 (*s*); 135.73 (*d*); 129.68 (*d*); 127.82 (*d*); 117.88 (*t*); 108.16 (*t*); 53.20 (*t*); 51.90 (*t*); 47.69 (*d*); 21.49 (*q*). MS: 263 (0.8, $[C_{14}H_{17}NO_2S]^+$), 155 (7), 108 (63), 107 (33), 91 (61), 81 (89), 79 (100). HR-MS: 263.0963 ($[C_{14}H_{17}NSO_2]^+$; calc. 263.0980).

Tetrahydro-3-methylidene-1-(trifluoroacetyl)-4-vinylpyrrole (**6b**). A soln. of **5b** (150 mg, 0.533 mmol), $[RhH(PPh_3)_4]$ (12.2 mg, 2 mol-%), and tris (2,4,6-trimethoxyphenyl)phosphine (11.3 mg, 4 mol-%) in AcOH (4 ml) was heated under Ar at 80° for 6.5 h. Addition of Et_2O (35 ml), washing with H_2O (15 ml), sat. aq. $NaHCO_3$ soln. (15 ml) and brine (10 ml), drying, evaporation, and FC (pentane/Et_2O 6:1) afforded **6b** (oil, 91 mg, 83%). GC (100°): 1.62. IR: 2870–3050, 1690, 1450, 1230, 1150. ^{1}H-NMR (400 MHz): 5.65 (*m*, 1 H); 5.19–5.27 (2 H); 5.15 (*m*, 1 H); 5.05 (*m*, 1 H); 4.16–4.37 (2 H); 4.02 (*m*, 1 H); 3.31–3.49 (2 H). ^{13}C-NMR (100 MHz, rotamers): 155.49 (*s*); 155.11 (*s*); 145.67 (*s*); 143.89 (*s*); 135.12 (*d*); 134.65 (*d*); 118.83 (*t*); 118.51 (*t*); 116.20 (*q*, *J*(C,F) = 286); 109.10 (*t*); 109.02 (*t*); 51.93 (*t*); 51.51 (*t*); 51.48 (*t*); 51.33 (*t*); 47.82 (*d*); 45.31 (*d*). MS: 206 (11, $[C_9H_{10}F_3NO + 1]^+$), 205 (M^+, 8), 190 (4), 136 (8), 108 (8), 93 (18), 92 (47), 91 (25), 79 (100). HR-MS: 205.0740 ($C_9H_{10}F_3NO^{+\cdot}$; calc. 205.0714).

Benzyl Tetrahydro-3-methylidene-4-vinylpyrrole-1-carboxylate (**6c**). A soln. of **5c** (200 mg, 0.651 mmol), $[RhH(PPh_3)_4]$ (15 mg, 2 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (13.8 mg, 4 mol-%) in AcOH (5 ml) was heated under Ar at 80° for 2 h. Evaporation and FC (hexane/AcOEt 9:1) provided **6c** (oil, 100 mg, 63%). GC (150° (0), 10°/min→270°): 4.47. IR: 2850–3100, 1700, 1430, 1365, 1110. ^{1}H-NMR (400 MHz): 7.25–7.38 (5 H); 5.65 (*ddd*, *J* = 17, 10, 7, 1 H); 5.12–5.20 (2 H); 5.14 (*s*, 2 H); 5.03 (*d*, *J* = 17, 1 H); 4.93 (*s*, 1 H); 4.18–4.00 (2 H); 3.83 (*ddd*, *J* = 11, 8, 7, 1 H); 3.32 (*m*, 1 H); 3.22 (*q*, *J* = 7, 1 H). ^{13}C-NMR (100 MHz, rotamers): 154.67 (*s*); 147.84 (*s*);

147.35 (*s*); 136.82 (*d*); 136.18 (*d*); 128.47 (*d*); 127.97 (*d*); 127.90 (*d*); 117.71 (*t*); 107.75 (*t*); 107.65 (*t*); 66.84 (*t*); 51.33 (*t*); 51.10 (*t*); 50.66 (*t*); 50.26 (*t*); 47.75 (*d*); 47.00 (*d*). MS: 243 (0.1, $[C_{15}H_{17}NO_2]^{+\cdot}$), 166 (1), 152 (10), 109 (4), 91 (100), 81 (4), 65 (14). HR-MS: 152.0703 ($[C_{15}H_{17}NO_2 - C_7H_7]^{+}$; calc. 152.0711). Further elution furnished **4c** (25 mg, 20%).

Dimethyl 3-Methylidene-4-vinylcyclopentane-1,1-dicarboxylate (**6d**). A soln. of **5a** (100 mg, 0.333 mmol), $[RhH(PPh_3)_4]$ (7.6 mg, 2 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (7.1 mg, 4 mol-%) in AcOH (3 ml) was heated under Ar at 80° for 3 h. Evaporation and FC (hexane/AcOEt 9:1) gave **6d** (oil, 56 mg, 75%). GC (100° (5), 10°/min→200°): 6.69. IR: 2900–3080, 1740, 1450, 1280, 1200, 1180. ^{1}H-NMR (400 MHz): 5.64 (*dt*, *J* = 17, 9, 1 H); 5.09 (*d*, *J* = 15.5, 1 H); 5.06 (*d*, *J* = 10.5, 1 H); 4.99 (br. *s*, 1 H); 4.83 (br. *s*, 1 H); 3.75 (*s*, 3 H); 3.73 (*s*, 3 H); 3.17 (*m*, 1 H); 3.09 (*d*, *J* = 17, 1 H); 2.96 (*d*, *J* = 17, 1 H); 2.59 (*dd*, *J* = 12, 8, 1 H); 2.02 (*t*, *J* = 8, 1 H). ^{13}C-NMR (100 MHz): 172.15 (*s*); 171.96 (*s*); 150.44 (*s*); 139.12 (*d*); 115.93 (*t*); 108.04 (*t*); 58.60 (*s*); 52.68 (*t*); 47.64 (*t*); 40.36 (*q*). MS: 225 (1.2, $[C_{12}H_{16}O_4 + 1]^{+}$), 224 (0.7), 193 (3), 164 (26), 133 (6), 105 (100), 91 (18), 79 (24), 77 (23). HR-MS: 224.1039 ($[C_{12}H_{16}O_4]^{+\cdot}$; calc. 224.1049).

1,1-Bis(phenylsulfonyl)-3-methylidene-4-vinylcyclopentane (**6e**). A soln. of **5e** (290 mg, 0.625 mmol), $[RhH(PPh_3)_4]$ (14.3 mg, 2 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (13.3 mg, 4 mol-%) in AcOH (5 ml) was heated under Ar at 80° for 7.5 h. Evaporation and FC (hexane/AcOEt 7:3) provided **6e** (colorless crystals, 213 mg, 88%).

Analogous treatment of (*Z*)-5,5-bis(phenylsulfonyl)octa-2,7-dienyl acetate (100 mg, 0.223 mmol) with $[RhH(PPh_3)_4]$ (12.8 mg, 5 mol-%) and tris(2,4,6-trimethoxyphenyl)phosphine (11.9 mg, 10 mol-%) at 80° for 5.5 h also gave **6e** (76 mg, 88%). M.p. 113–114° (EtOH). GC (250°): 5.91. The IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectra are identical to those reported in [2].

4-Methylidene-1-(p-toluenesulfonyl)-5-vinylpiperidine (**6f**). A soln. of **5f** (100 mg, 0.283 mmol), $[RhH(PPh_3)_4]$ (25.8 mg, 8 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (23.9 mg, 16 mol-%) in AcOH (5 ml) was heated under Ar at 80° for 6.5 h. Evaporation and FC (hexane/AcOEt 15:1) afforded **6f** (oil, 51 mg, 65%). GC (200°): 3.73. IR: 2800–3100, 1650, 1600, 1360, 1300, 1170, 1100, 940. ^{1}H-NMR (400 MHz): 7.48–7.45 (2 H); 7.17–7.13 (2 H); 5.62 (*ddd*, *J* = 17, 11. 7, 1 H); 5.02 (*dd*, *J* = 11, 1.5, 1 H); 4.99 (*dt*, *J* = 17, 1, 1 H); 4.60 (br. *s*, 1 H); 4.54 (br. *s*, 1 H); 3.25–3.15 (2 H); 2.82 (*m*, 1 H); 2.58 (*ddd*, *J* = 11, 9, 4, 1 H); 2.47 (*dd*, *J* = 11, 9, 1 H); 2.26 (*s*, 3 H); 2.11–2.24 (2 H). ^{13}C-NMR (100 MHz): 145.62 (*s*); 143.48 (*s*); 136.37 (*d*); 129.62 (*d*); 127.58 (*d*); 117.51 (*t*); 110.01 (*t*); 51.42 (*t*); 47.54 (*t*); 46.07 (*d*); 33.16 (*t*); 21.46 (*q*). MS: 277 (17, $[_{15}H_{19}NO_2S]^{+\cdot}$), 184 (20), 155 (48), 122 (100), 91 (67). HR-MS: 277.1124 ($[C_{15}H_{19}NO_2S]^{+\cdot}$; calc. 277.1136).

1,1-Bis(phenylsulfonyl)-4-methylidene-5-vinylcyclohexane (**6g**). A soln. of **5g** (100 mg, 0.209 mmol), $[RhH(PPh_3)_4]$ (18.4 mg, 8 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (17 mg, 16 mol-%) in AcOH (3 ml) was heated under Ar at 80° for 12 h. Evaporation and FC (hexane/AcOEt 9:1) provided **6g** (colorless crystals, 46 mg, 55%). GC (200° (0), 10°/min→270°): 8.88. M.p. 134–135° (Et_2O). IR: 2900–3100, 1580, 1445, 1330, 1310, 1150, 1080. ^{1}H-NMR (400 MHz): 8.12–7.99 (4 H); 7.75–7.57 (6 H); 5.76 (*ddd*, *J* = 17, 11, 9, 1 H); 5.17 (*dd*, *J* = 11, 1, 1 H); 5.12 (*dd*, *J* = 17, 1, 1 H); 4.86 (*d*, *J* = 1, 1 H); 4.73 (*d*, *J* = 1, 1 H); 3.55 (*m*, 1 H); 2.92 (*m*, 1 H); 2.23–2.46 (5 H). ^{13}C-NMR (100 MHz): 146.22 (*s*); 138.42 (*s*); 136.46 (*s*); 136.14 (*s*); 134.62 (*d*); 134.49 (*d*); 131.55 (*d*); 131.13 (*d*); 128.64 (*d*); 128.57 (*d*); 116.88 (*t*); 109.53 (*t*); 87.95 (*s*); 41.93 (*d*); 32.62 (*t*); 30.74 (*t*); 27.60 (*t*). MS: 261 (6, $[C_{21}H_{22}O_4S - C_6H_5O_2S]^{+}$), 260 (9), 259 (6), 141 (4), 125 (29), 119 (100), 91 (98), 77 (77). HR-MS: 259.0783 ($[C_{21}H_{22}O_4S - C_6H_5O_2S]^{+}$; calc. 259.0793).

cis-*Dimethyl 9-Methylidenebicyclo[4.3.0]non-2-ene-7,7-dicarboxylate* (**9**). A soln. of **8** (60 mg, 0.193 mmol), $[RhH(PPh_3)_4]$ (11,1 mg, 5 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (10.3 mg, 10 mol-%) in AcOH (1 ml) was heated under Ar at 80° for 8 h. Evaporation and FC (hexane/AcOEt 9:1) provided **9** (oil, 29 mg, 60%). GC (150° (0), 10°/min→200° (5)): 2.64. IR: 2940–3050, 1730, 1440, 1270, 1250, 1160 ^{1}H-NMR (400 MHz): 5.86 (*m*, 1 H); 5.75 (*m*, 1 H); 4.98 (*q*, *J* = 1, 1 H); 4.84 (*q*, *J* = 1.5, 1 H); 3.74 (*s*, 3 H); 3.73 (*s*, 3 H); 3.33 (*dq*, *J* = 17, 3, 1 H); 3.22 (*m*, 1 H); 2.83–2.89 (2 H); 2.01–2.08 (2 H); 1.32 (*m*, 1 H); 1.15 (*m*, 1 H). ^{13}C-NMR (100 MHz): 172.30 (*s*); 170.25 (*s*); 151.11 (*s*); 126.49 (2*d*); 107.62 (*t*); 62.43 (*s*); 52.77 (*q*); 52.49 (*q*); 43.09 (*d*); 42.90 (*d*); 37.76 (*t*); 24.49 (*t*); 21.33 (*t*). MS: 250 (1, $[C_{14}H_{18}O_4]^{+\cdot}$), 219 (5), 190 (25), 145 (35), 131 (100), 91 (25). HR-MS: 250.1197 ($[C_{14}H_{18}O_4]^{+\cdot}$; calc. 250.1205).

cis/trans-*Tetrahydro-1-(p-toluenesulfonyl)-3,4-divinylpyrroles* (**11**/**12**). A soln. of **5g** (100 mg, 0.283 mmol), $[RhH(PPh_3)_4]$ (6.5 mg, 2 mol-%), and tris(2,4,6-trimethoxyphenyl)phosphine (6 mg, 4 mol-%) in AcOH (2 ml) was heated under Ar at 80° for 12 h. Evaporation and FC (hexane/AcOEt 9:1) provided a 77:23 mixture (GC) **11**/**12** (oil, 55 mg, 70%). For comparison, a soln. of **5g** (125 mg, 0.354 mmol), $[Pd(dba)_2]$ (20.3 mg, 10 mol-%), and PPh_3 (27.8 mg, 30 mol-%) in AcOH (2.5 ml) was heated under Ar at 80° for 1 h. Evaporation and FC (hexane/AcOEt 15:1) provided a 20:80 mixture (GC) **11**/**12** (oil, 59 mg, 60%). GC (200°): 3.67 (*trans*), 3.98 (*cis*). IR: 2850–3100, 1645, 1600, 1350, 1160, 925. ^{1}H-NMR (400 MHz, *cis*-isomer): 7.74–7.72 (2 H); 7.34–7.32 (2 H); 5.48 (*ddd*, *J* = 17,

10, 8, 2H); 5.02 (*dd*, *J* = 10, 1, 2H); 4.97 (*dd*, *J* = 17, 1, 2H); 3.44 (*dd*, *J* = 10, 6, 2H); 3.21 (*dd*, *J* = 10, 6, 2H); 2.80–2.70 (2H); 2.45 (*s*, 3H). ^{1}H-NMR (400 MHz, *trans*-isomer): 7.73–7.71 (2H); 7.34–7.32 (2H); 5.52 (*ddd*, *J* = 17, 10, 7, 2H); 5.05 (*dd*, *J* = 10, 1, 2H); 5.01 (*dd*, *J* = 17, 1, 2H); 3.56 (*dd*, *J* = 10, 7, 2H); 3.04 (*dd*, *J* = 9, 9, 2H); 2.45 (*s*, 3H); 2.42–2.35 (2H). ^{13}C-NMR (100 MHz, *cis*-isomer): 143.39 (*s*); 134.95 (*d*); 134.01 (*s*); 129.63 (*d*); 127.39 (*d*); 117.06 (*t*); 51.52 (*t*); 46.32 (*d*); 21.47 (*q*). ^{13}C-NMR (100 MHz, *trans*-isomer): 143.50 (*s*); 135.82 (*d*); 133.94 (*s*); 129.72 (*d*); 127.49 (*d*); 117.34 (*t*); 52.40 (*t*); 48.49 (*d*); 21.54 (*q*). MS: 278 (5, $[C_{15}H_{19}NO_2S + 1]^+$), 277 (3, M^+), 223 (7), 155 (9), 122 (100), 105 (14), 95 (48), 91 (90), 79 (50), 65 (61). HR-MS: 277.1141 ($[C_{15}H_{19}NO_2S]^+$; calc. 277.1136).

N-(Buta-1,3-dienyl)-N-(prop-2-enyl)-p-toluenesulfonamide (**7**). A soln. of **5a** (50 mg, 0.147 mmol) and $[RhH(PPh_3)_4]$ (8.1 mg, 5 mol-%) in MeCN (1 ml) was heated at 80° under Ar for 25 min. Addition of bipyridine (3 mg, to destroy the catalyst), evaporation, and FC (hexane/AcOEt 9:1) furnished **7** (oil, 29 mg, 75%). IR: 2900–3100, 1640, 1590, 1370, 1310, 1170, 1090. ^{1}H-NMR (400 MHz): 7.67–7.65 (2H); 7.30–7.26 (2H); 6.95 (*d*, *J* = 14, 1H); 6.28 (*td*, *J* = 16, 10, 1H); 5.64 (*ddt*, *J* = 6, 10, 17, 1H); 5.49 (*dd*, *J* = 10, 14, 1H); 5.19 (*d*, *J* = 17, 1H); 5.16 (*d*, *J* = 10, 1H); 5.02 (*d*, *J* = 16, 1H); 4.91 (*d*, *J* = 10, 1H); 4.03 (*d*, *J* = 6, 2H); 2.42 (*s*, 3H). ^{13}C-NMR (100 MHz): 143.99 (*s*); 134.79 (*d*); 131.52 (*d*); 129.86 (*d*); 129.76 (*d*); 127.00 (*d*); 117.97 (*t*); 113.70 (*t*); 112.29 (*d*); 48.10 (*t*); 21.55 (*q*). MS: 264 (5, $[C_{14}H_{17}NO_2S + 1]^+$, 263 (5), 224 (4), 155 (31), 110 (16), 108 (15), 91 (100). HR-MS: 263.1005 ($[C_{14}H_{17}NSO_2]^+$; calc. 263.0980).

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