Synthesis of *o*-Dialkenylbenzenes and Indenes Using Heck and Oxypalladation Reactions☆

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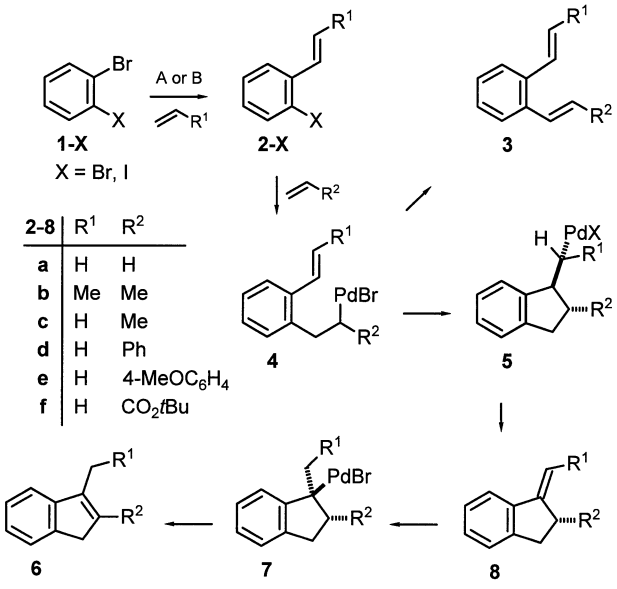
o-Bromostyrenes **2-Br** react with various alkenes in the presence of palladium catalysts to give either substituted indene **6** or *o*-diethenylbenzene derivatives **3**, depending on the reaction conditions. Under oxidative conditions the latter can be cyclized to indene derivatives as well.

Palladium-catalyzed reactions have attracted a steadily increasing interest in the past ten years[1]. Since the pioneering work of Heck et al.[2], the alkenylation of aryl and alkenyl halides has rapidly[3] become a powerful tool in organic synthesis[4]. In the standard reaction, the rather facile β-hydride elimination, which the intermediate alkylpalladium halide undergoes after the alkene insertion into the initially formed aryl- or alkenylpalladium species, leads to the stereospecific formation of a new double bond. However, as we have recently found, when an *o*-ethenyl substituent is present on the (β-phenylalkyl)palladium halide, intramolecular trapping can occur simultaneously with ring closure to an indane skeleton[5]; this is followed by reductive elimination which restores the palladium in the zero oxidation state.

During the course of our research focussing on ethylene as a coupling partner for haloarenes in the synthesis of styrenes and stilbenes[6], we observed, that 1,2-dibromobenzene (**1-Br**) could be converted to 3-methylindene (**6a**) and 1,2-diethenylbenzene (**3a**)[7][8], depending on the reaction conditions (Scheme 1). These observations encouraged us to study the factors that control the outcome of palladium-catalyzed coupling reactions of *o*-dibromobenzene (**1-Br**) and *o*-bromostyrene (**2a-Br**) with various alkenes.

Using the original experimental conditions reported by Heck[2] [A: $Pd(OAc)_2$, P(*o*-Tol)$_3$, NEt_3, DMF, 8 bar ethylene], 3-methylindene (**6a**) was obtained from **1-Br** in 16% yield along with **3a** (57%) (Table 1, entry 1), whereas the yield of **6a** rose to 74% when the modified conditions of Jeffery[8] [B: $Pd(OAc_2)$, LiCl, $KHCO_3$, NBu_4Br, 8 bar ethylene, entry 2] were used. In a control experiment 1,2-diethenylbenzene (**3a**) was treated with the same catalytic system (B), but no reaction took place. However, **6a** was obtained in 59% yield when 1-bromo-2-ethenylbenzene (**2a-Br**) was treated with ethylene (Table 1, entry 3). These observations corroborate that the formation of indenes is largely dependent on the rate of β-hydride elimination in intermediate **4**, the formation of which itself is influenced by the nature of the catalytic system.

Scheme 1. A: $Pd(OAc)_2$, PR_3, NEt_3; B: $Pd(OAc)_2$, PTC, base; for details see Table 1



2-8	R^1	R^2
a	H	H
b	Me	Me
c	H	Me
d	H	Ph
e	H	4-MeOC$_6$H$_4$
f	H	CO_2tBu

The twofold Heck coupling of **1-Br** with propene using Jeffery's conditions, produced pure (*E,E*)-1,2-bis(prop-1-enyl)benzene (**3b**) in 79% yield, and no cyclization products were observed (Table 1, entry 5). This result compares favorably with the result of the twofold Wittig olefination of phthalaldehyde, which gives a mixture of all three diastereomers [(*E,E*)/(*E,Z*)/(*Z,Z*) = 0.3:1:1][9]. Once more,

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Table 1. Palladium-catalyzed coupling reactions of *o*-halostyrenes with alkenes (see Schemes 1 and 2)

Entry	Aryl halide	Alkene	Solvent[a]/*T* [°C]/*t* [h]	Conditions[b]	Diethenylbenzene derivatives yield (%)	yield (%)	Indane derivatives yield (%)	yield (%)
1	**1-Br**	ethene	MeCN/125/48	A [P(*o*-Tol)$_3$]	**3a**: 57	–	**6a**: 16	**8a**: 0
2	**1-Br**	ethene	NMP/100/96	B ($KHCO_3$, LiCl)	**3a**: 7	–	**6a**: 74	**8a**: 0
3	**2a-Br**	ethene	NMP/100/48	B ($KHCO_3$, LiCl)	**3a**: 12	–	**6a**: 59	**8a**: 0
4	**2a-Br**	propene	NMP/100/96	B ($KHCO_3$, LiCl)	**3c**: 38	–	**6c**: 13	**8c**: 0
5	**1-Br**	propene	NMP/100/96	B ($KHCO_3$, LiCl)	**3b**: 79	–	**6b**: 0	**8b**: 0
6	**2a-Br**	styrene	NMP/90/24	A [P(*o*-Tol)$_3$]	**3d**: 35	–	**6d**: 0	**8d**: 0
7	**2a-Br**	styrene	NMP/100/48	B ($KHCO_3$, LiCl)	**3d**: 12	–	**6d**: 2	**8d**: 53
8	**2a-Br**	styrene	DMF/90/48	B ($KHCO_3$)	**3d**: 0	–	**6d**: 0	**8d**: 0
9	**2a-Br**	styrene	DMF/90/48	B (K_2CO_3)	**3d**: 25	–	**6d**: 0	**8d**: 0
10	**2a-I**	styrene	NMP/60/24	A [P(*o*-Tol)$_3$]	**3d**: 36	–	**6d**: 0	**8d**: 0
11	**2a-I**	styrene	NMP/60/24	B ($KHCO_3$, LiCl)	**3d**: 0	–	**6d**: 0	**8d**: 38
12	**2a-Br**	4-methoxy-styrene	NMP/100/48	B ($KHCO_3$, LiCl)	**3e**: 17	–	**6e**: 0	**8e**: 34
13	**2a-Br**	ethyl vinyl ether	NMP/80/48	B (K_2CO_3, LiCl)	–	–	**10**: 49	**9**: 9
14	**2a-Br**	**11**	NMP/80/48	B (K_2CO_3, LiCl)	–	–	**12**: 41	–
15	**2a-Br**	**11**	NMP/80/48	A [P(*o*-Tol)$_3$]	**13**: 30	**14**: 12	**12**: 3	–
16	**2a-Br**	**15**	NMP/100/48	B ($KHCO_3$, LiCl)	–	–	**20**: 37	–

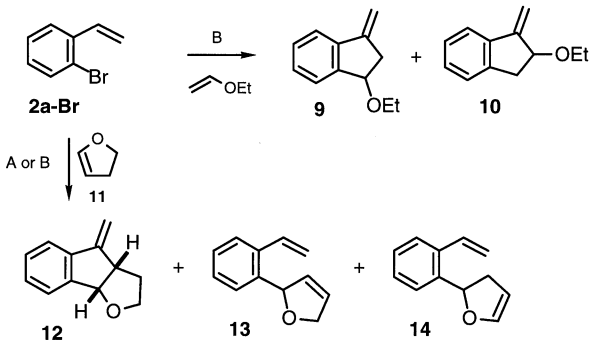
[a] NMP: *N*-Methylpyrrolidinone. – [b] A: Heck conditions: $Pd(OAc)_2$, PR_3, NEt_3; B: Jeffery conditions: $Pd(OAc)_2$, Bu_4NBr or Bu_4NCl, base.

these unequivocal results underline the superiority of the Heck reaction. The coupling of *o*-bromostyrene (**2a-Br**) with propene gave the open-chain product **3c** in 38% yield along with 13% of 2,3-dimethylindene (**6c**, Table 1, entry 4). In the reaction of *o*-bromostyrene (**2a-Br**) with styrene, the product distribution varies strongly with the reaction conditions (Table 1, entries 6 through 11). While the classical Heck conditions gave only *o*-ethenylstilbene (**3d**, 35%, entry 6), the Jeffery conditions B using the weaker base $KHCO_3$ gave the 1-methyleneindane **8d** (53%) along with the 3-methylindene (**6d**, 2%) and **3d** (12%). Apparently in the latter case, the reductive elimination of hydrogen bromide is slower and the hydridopalladium species of type **4** is more resistant to β-hydride elimination. Donor-substituted styrenes should be less reactive towards *syn* addition of the arylpalladium species, and the corresponding σ-alkylpalladium species should also be more stable. Indeed, reaction of *o*-bromostyrene (**2a-Br**) with *p*-methoxystyrene gave the methyleneindane **8e** in 34% yield, along with the stilbene **3e** (17%, entry 12). The influence of the conditions is even more apparent in the reaction of *o*-iodostyrene (**2a-I**) with styrene at 60°C. While the Heck conditions gave only *o*-ethenylstilbene (**3d**) in 36% yield (entry 10), the Jeffery conditions led exclusively to the methyleneindane **8d** (38%, entry 11).

Even electron-rich alkenes like alkenyl ethers could be used as coupling partners in this reaction of *o*-halostyrenes. Ethenyl ethyl ether and **2a-Br** gave a 1:6 mixture of the two regioisomeric ethoxy-1-methyleneindanes **9** and **10** in 58% yield, respectively. The major isomer **10** could be identified on the basis of the observed nuclear Overhauser effect between one of the olefinic methylene protons and the ethoxy methylene protons in the ^{1}H-NMR spectrum. Compound **10** corresponds to the typical regioisomer in enol ether coupling reactions with acceptor-substituted aryl halides[10].

2,3-Dihydrofuran (**11**) and **2a-Br** yielded 4-methylene-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-*b*]furan (**12**, 41%) under the Jeffery conditions. The *cis* configuration of **12** was established by means of a nuclear Overhauser effect measurement. Under the Heck conditions, the coupling of **2a-Br** and 2,3-dihydrofuran (**11**) gave mainly the noncyclized isomeric products **13** and **14** in 30 and 12% yield, respectively, and only 3% of the cyclized product **12**[11].

Scheme 2. A: $Pd(OAc)_2$, PR_3, NEt_3; B: $Pd(OAc)_2$, PTC, base; for details see Table 1



As methylenecyclopropanes have recently been proved to be particularly reactive in palladium-catalyzed cyclization and coupling reactions[12], the easily available nonvolatile 1-methylene-2,2-diphenylcyclopropane (**15**)[13] was also tested in the reaction with *o*-bromostyrene (**2a-Br**). Under Jeffery conditions for the Heck reaction, the cyclization product **20** was isolated (37% yield). Its constitution was proved by X-ray crystal-structure analysis[14].

The formation of **20** can be rationalized as resulting from the insertion of the double bond of **15** into the C–Pd bond of the *o*-styrylpalladium halide with a regioselectivity reverse of that observed with other methylenecyclopropanes[15]. The σ-cyclopropylpalladium species **16** apparently rearranges to the π-allyl complex **18**, in equilibrium with the σ complex **19**, that electrophilically attacks the ethenyl double bond in an intramolecular process, which results in 5-*exo*-*trig* ring closure and the indane skeleton of

Scheme 3. B: $Pd(OAc)_2$, $KHCO_3$, LiCl; for details see Table 1

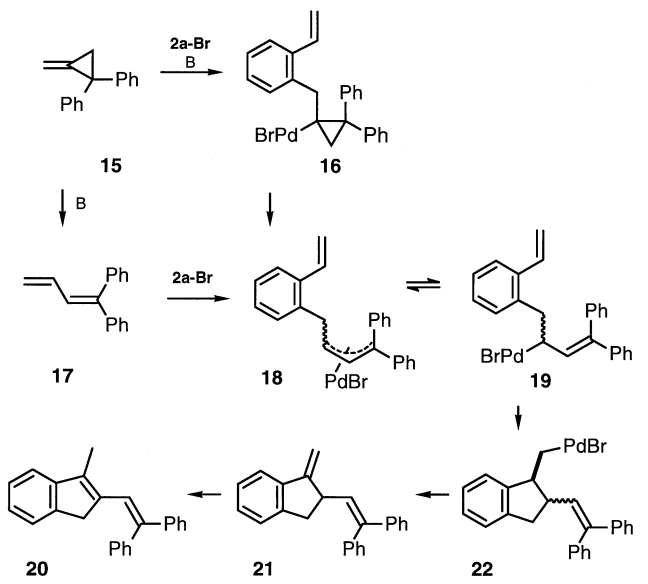
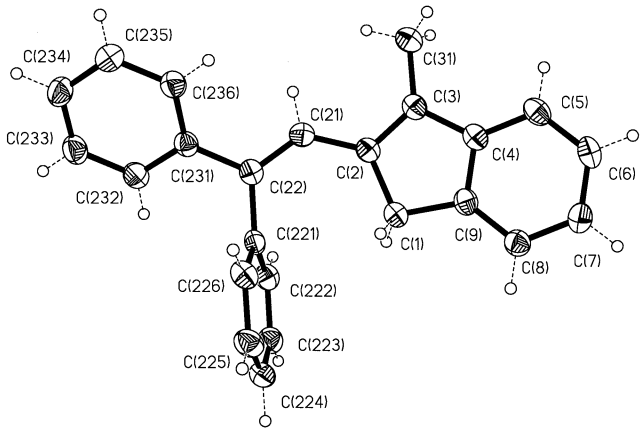


Figure 1. Structure of compound **20** in the crystal

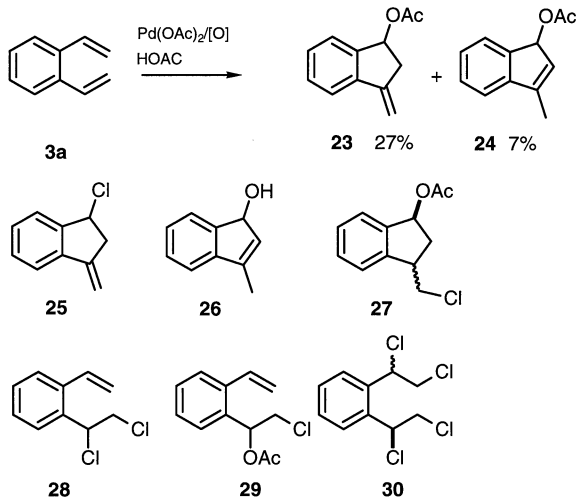


22. The indene **20** is obtained via the substituted methyleneindane **21** after β-hydride elimination and readdition/elimination. An alternative mechanism can be considered as well: A palladium-induced ring-opening of 2,2-diphenylmethylenecyclopropane (**15**) could lead to 1,1-diphenylbutadiene (**17**), which would form a π complex with the *o*-styrylpalladium bromide, and insertion of the terminal double bond of **17** into the carbon−palladium bond of the latter would lead to the same π-allylpalladium intermediate **18**.

This last example (Table 1, entry 16) again demonstrates the possibility to form indenes under the modified conditions for the Heck reaction. Apparently, the (*o*-styrylalkyl)palladium intermediate of type **19** must be more long-lived under the Jeffery conditions so that it can more efficiently undergo the 5-*exo*-*trig* ring closure to yield **22**.

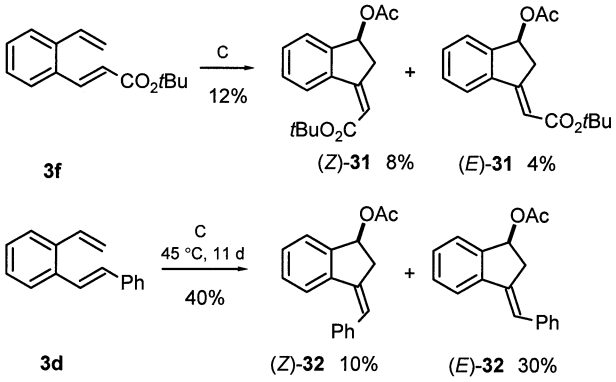
This cyclization to a five-membered ring resembles that previously observed for various 1,5-hexadienes and *cis*-diethenylcyclohexane under oxidative conditions (MnO_2/benzoquinone or $CuCl_2$) in the presence of palladium acetate to give 1-acetoxy-3-methylenecyclopentenes[16][17] and 7-acetoxybicyclo[4.3.0]non-1(9)ene[18]. The chemical behavior of *o*-dialkenylarenes under such experimental conditions was tested for comparison. When *o*-diethenylbenzene (**3a**) was treated with $Pd(OAc)_2$, MnO_2 and benzoquinone in acetic acid[19], the indene derivatives **23** and **24** were obtained in 27 and 7% yield, respectively (Table 2). Under the conditions developed by Waegell et al. ($PdCl_2$, $CuCl_2$, NaOAc)[18], a mixture of **23**, **25**−**30** (Table 2) was formed. In the presence of additional lithium chloride the tetrachlorinated product **30** could also be isolated. Apparently, the low yields observed for these cyclizations of *o*-diethenylbenzene are due to the instability and polymerization of **3a** under these reaction conditions.

Scheme 4. For details see Table 2



Unfortunately, the cyclization of *ortho*-substituted alkenylbenzenes like *tert*-butyl *o*-ethenylcinnamate (**3f**) and *o*-ethenylstilbene (**3d**) did not proceed much better. The cyclized products (*E*)-**31** and (*Z*)-**31** obtained from **3f** were isolated in low yields (4 and 8%, respectively). The cyclization yields were somewhat higher with **3d**, from which the diastereomeric benzylideneindanes (*E*)-**32** and (*Z*)-**32** were obtained in 30 and 10% yield, respectively.

Scheme 5. C: $Pd(OAc)_2$, benzoquinone, MnO_2 in HOAc



In conclusion, indane derivatives can be prepared in a palladium-catalyzed domino reaction of an *o*-halostyrene and an alkene under appropriate conditions. An attempted

Table 2. Oxidative cyclization of 1,2-diethenylbenzene (**3a**)[a]

Entry	Method[b]	*T* [°C]	Time [d]	**3a**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	Naphthalene
1	C[b]	40	10	8	28	24	–	–	–	–	–	–	8(4[c])
2	C	50	5	–	20	20	–	–	–	–	–	–	32[c]
3	C[d]	45	1	–	27[c]	7[c]	–	–	–	–	–	–	32[c]
4	D	40	10	–	12	–	8	16	20	10	12	–	–
5	D	40	14	12	–	–	–	–	–	47	–	9	–
6	D	50	14	–	–	–	–	–	–	50(16[c])	–	16(6[c])	–

[a] Yields determined by GC MS. – [b] C: $Pd(OAc)_2$/benzoquinone/MnO_2; D: $PdCl_2/CuCl_2$/NaOAc. – [c] Isolated yield. – [d] Excess of MnO_2.

oxidative cyclization of *o*-dialkenylarenes, however, gave only poor yields in comparison to the known oxidative cyclization of 1,2-divinylcyclohexane. In the latter case, the electron density at the vinylic positions is somewhat higher, and the flexibility of the aliphatic ring probably permits for coordination with palladium, which apparently is essential for an oxidative cyclization.

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Experimental Section

General: ^{1}H- and ^{13}C-NMR spectra were recorded with Bruker AW 250 or WM 500 instruments at 250 MHz or 500 MHz and 62.9 MHz or 125 MHz, respectively. Chemical shifts in $CDCl_3$ or [D_6]benzene are reported in δ values relative to tetramethylsilane (TMS), chloroform or benzene as internal reference unless otherwise stated. – IR spectra were registered with a Perkin Elmer 1720 FTIR or a Bruker IFS 66. – Low-resolution EI mass spectra were obtained with a Varian MAT CH-7 with Varian Aerograph 1740 with an ionizing voltage of 70 eV. High-resolution mass spectra were obtained with a VG-70-250S. – Elemental analyses were performed by the Mikroanalytisches Laboratorium der Universität Göttingen, Germany. – Melting points are uncorrected. – Flash chromatography was performed using Merck Kieselgel 60 (200–400 mesh). – Analytical gas chromatography (GC) was performed using a Siemens Sichromat 4 equipped with a 25-m capillary column coated with CP-Sil-55-5B. – Solvents for extraction and chromatography were technical grade and distilled before use. Organolithium compounds were titrated by the method of Suffert[20]. All reactions were carried out under dry nitrogen or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solutions of NH_4Cl and $NaHCO_3$ are satd. aqueous solutions. Tetrahydrofuran and diethyl ether were distilled from potassium benzophenone ketyl, and CH_2Cl_2 was distilled from CaH_2.

1-Bromo-2-ethenylbenzene (**2a-Br**)[21]: A solution of 0.90 g (30.0 mmol) of NaH (80% in mineral oil) and 2.40 g (30.7 mmol) of dimethyl sulfoxide in 50 ml of THF was heated at 80°C for 1 h, cooled to 0°C, treated with 10.7 g (30.0 mmol) of methyltriphenylphosphonium bromide and stirred for 10 min at room temp. *o*-Bromobenzaldehyde (5.55 g, 30.0 mmol) was added, and the solution was stirred at 80°C for 1 h. After cooling to room temp., 150 ml of pentane was added and the mixture was extracted with water (5 × 20 ml). The organic phase was dried ($MgSO_4$), the solvent was removed in vacuo and the residue chromatographed on silica gel (column 60 × 3 cm, pentane) to give 3.25 g (59%) of **2a-Br** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.40 (dd, ^3J = 8.0, ^2J = 1.0 Hz, 1 H, vinyl), 5.75 (dd, ^3J = 16.0, ^2J = 1.0 Hz, 1 H, vinyl), 7.20 (dd, ^3J = 8.0, ^3J = 16.0 Hz, 1 H, vinyl), 7.30–7.52 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 116.50 (–, vinyl), 123.60 (C_{quat}, CBr), 126.73 (+, Ar-C), 127.41 (+, Ar-C), 129.00 (+, Ar-C), 132.83 (+, Ar-C), 135.79 (+, vinyl), 137.45 (C_{quat}, Ar-C).

2-Ethenyl-1-iodobenzene (**2a-I**)[22]: Thionyl chloride (44.2 ml, 609 mmol), containing 1 drop of DMF, was added slowly to a 250-ml two-necked flask charged with 100.3 g (404 mmol) of *o*-iodobenzoic acid. The mixture was refluxed for 2 h, and then distilled to give 72.2 g (67%) of 2-iodobenzoyl chloride as a yellow solid, mp 34°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.14–7.30 (m, 1 H, Ar-H), 7.38–7.53 (m, 1 H, Ar-H), 7.91–8.09 (m, 2 H, Ar-H). – *tert*-Butyl alcohol (14.0 g, 189 mmol) was added to a solution of 2.37 g (62.5 mmol) of lithium aluminum hydride in 125 ml of dry diethyl ether. The solvent was decanted, 50 ml of diglyme was added, and the solution added to 15.0 g (56.3 mmol) of 2-iodobenzoyl chloride at –78°C. The mixture was slowly warmed to room temp. and added to 100 g of crushed ice. After filtration, the aqueous phase was extracted with ether (5 × 50 ml), the combined organic phases were washed with water (3 × 100 ml), dried ($MgSO_4$), and the solvent was removed in vacuo. Distillation afforded 12.5 g of a mixture of *o*-iodobenzyl alcohol and *o*-iodobenzaldehyde (1.8:1). A mixture of 2.57 g (64.2 mmol) of NaH (60% in mineral oil) and 10.03 g (128.4 mmol) of dimethyl sulfoxide in 50 ml of THF was heated to 80°C for 1 h, cooled to 0°C, treated with 19.11 g (53.5 mmol) of methyltriphenylphosphonium bromide in 200 ml of dimethyl sulfoxide and stirred for 10 min at room temp. *o*-Iodobenzaldehyde and *o*-iodobenzyl alcohol (12.48 g of 1:1.8 mixture) were added, and the solution was stirred for 1 h at 80°C. After cooling to room temp., the suspension was extracted with pentane (3 × 150 ml), the combined organic phases were washed with water (100 ml), and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue chromatographed on silica gel (column 40 × 3 cm, pentane) to give 3.25 g (73% based on *o*-iodobenzaldehyde) of 2-ethenyl-1-iodobenzene (**2a-I**) as a yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.35 (d, ^3J = 11.5 Hz, 1 H, vinyl), 5.65 (d, ^3J = 16.2 Hz, 1 H, vinyl), 6.98 (dd, ^3J = 11.5, ^3J = 16.2 Hz, 1 H, vinyl), 7.02–7.85 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 100.01 (Ar-C), 116.73 (vinyl), 126.37 (Ar-C), 128.36 (Ar-C), 129.22 (Ar-C),

130.22 (vinyl), 137.51 (Ar-C), 139.45 (Ar-C). − MS (70 eV); *m/z* (%): 230 (100) [M^+], 203 (8) [$M^+ - C_2H_3$], 179 (7), 153 (5), 103 (25) [$M^+ - I$], 77 (15) [$C_6H_5^+$].

General Procedure for the Heck Reaction of o-Halostyrenes **2a-X** *with Liquid Alkenes* (GP 1): In a screw-capped Pyrex bottle were placed $Pd(OAc)_2$ (18 mg, 0.08 mmol, 8 mol-% per halogen), nBu_4NCl (278 mg, 1.00 mmol), LiCl (42 mg, 1.0 mmol), and the base. DMF (20 ml) or NMP (20 ml) was added, and the resulting suspension was purged with N_2. To the stirred solution, the halostyrene **2a-X** (1.00 mmol) and the alkene (5.00 mmol) were added. The contents of the closed Pyrex bottle was heated with vigorous stirring for the stated time at 90 or 100°C. After the mixture had been cooled to room temp., it was poured into Et_2O and H_2O (50 ml each). The organic layer was washed three times with water and the aqueous layer was extracted with Et_2O (20 ml). The combined organic layers were dried ($MgSO_4$), concentrated in vacuo, and the residue was purified by column chromatography on silica gel and/or recrystallization.

General Procedure for the Heck Reaction of o-Halostyrenes **2a-X** *and o-Dibromobenzene* **1-Br** *with Gaseous Alkenes* (GP 2): In a 100-ml steel autoclave were placed $Pd(OAc)_2$ (5−22 mg, 0.02−0.10 mmol, 2−10 mol-%), nBu_4NBr (322 mg, 1.00 mmol) or nBu_4NCl (278 mg, 1.00 mmol), LiCl (42 mg, 1.0 mmol), and the base. Alternatively, a mixture of $Pd(OAc)_2$, P(*o*-Tol)$_3$ (61−244 mg, 0.04−0.16 mmol), NEt_3 (200 mg, 2.0 mmol) was used. The solvent, DMF (10−20 ml) or NMP (10−20 ml) or MeCN (10 ml) was added. To the stirred solution, the *o*-halostyrene **2a-X** or the *o*-dibromobenzene **1-Br** (1.00 mmol) and the alkene were added. The autoclave was heated and the contents vigorously stirred. The stated pressure of the alkene was applied for the stated time at 100°C. After the mixture had been cooled to room temp., it was poured into Et_2O and H_2O (50 ml each). The organic layer was washed three times with water, and the aqueous layer was extracted with Et_2O (20 ml). The combined organic layers were dried ($MgSO_4$), concentrated in vacuo, and the residue was purified by column chromatography on silica gel and/or recrystallization.

1,2-Diethenylbenzene (**3a**)[23] *and 3-Methylindene* (**6a**)[24]. − a) *From o-Dibromobenzene under Heck Conditions* (Table 1, entry 1): *o*-Dibromobenzene (**1-Br**, 1.18 g, 5.0 mmol) was treated with ethylene (8 bar) in the presence of palladium acetate (22 mg, 2 mol-%), tri-*o*-tolylphosphane (61 mg, 4 mol-%) and triethylamine (1.01 g, 10 mmol) in acetonitrile (50 ml) at 125°C for 2 d according to GP2. After work-up and evaporation of the solvent, 1.03 g of a yellow oil was obtained, containing 64% of **3a** and 25% of **6a** according to GLC. Column chromatography on silica gel (100 g, eluting with pentane) gave two fractions. − Fraction I: 371 mg (57%) of **3a** (R_f = 0.54) as a colorless oil. − ^{1}H NMR: (250 MHz, $CDCl_3$): δ = 5.23 (dd, ^3J = 12.5, ^2J = 1.2 Hz, 2 H, vinyl), 5.55 (dd, ^3J = 19.0, ^2J = 1.2 Hz, 2 H, vinyl), 6.94 (dd, ^3J = 12.5, ^3J = 19.0 Hz, 2 H, vinyl), 7.18 (m, 2 H, Ar-H), 7.39 (m, 2 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 116.27 (−, vinyl), 126.27 (+, Ar-C), 127.76 (+, Ar-C), 134.87 (+, vinyl), 136.09 (C_{quat}, Ar-C). − Fraction II: 107 mg (16%) of **6a** (R_f = 0.48) as a colorless oil. − IR (film): $\tilde{\nu}$ = 3064 cm^{-1}, 3018, 2966, 2925, 1242, 909, 771, 734. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02 (br. s, 3 H, CH_3), 3.15 (br. s, 2 H, CH_2), 6.03 (br. s, 1 H, CH), 7.00−7.32 (m, 4 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 12.92 (+, CH_3), 37.59 (−, CH_2), 118.78 (+, C-2), 123.53 (+, Ar-C), 124.41 (+, Ar-C), 126.00 (+, Ar-C), 128.62 (+, Ar-C), 139.89 (C_{quat}, C-3), 144.27 (C_{quat}, Ar-C), 146.07 (C_{quat}, Ar-C). − $C_{10}H_{10}$: calcd. 130.0782; found 130.0782 (MS).

b) *From o-Dibromobenzene under Jeffery Conditions* (Table 1, entry 2): *o*-Dibromobenzene (**1-Br**, 1.18 g, 5.0 mmol) was treated with ethylene (8 bar) in the presence of palladium acetate (22 mg, 2.0 mol-%), potassium hydrogen carbonate (2.00 g, 20.0 mmol), tetra-*n*-butylammonium bromide (3.22 g, 10.0 mmol), lithium chloride (2.12 g, 50.0 mmol) in NMP (50 ml) according to GP2. After work-up and evaporation of the solvent, 962 mg of a yellow oil was obtained, containing 7% of styrene, 7% of **3a** and 81% of **6a** according to GLC. Column chromatography on silica gel (60 g, eluting with pentane) gave 480 mg (74%) of pure **6a** as a light yellow oil. NMR data see above.

c) *From Bromostyrene under Jeffery Conditions* (Table 1, entry 3): 1-Bromo-2-ethenylbenzene (**2a-Br**, 183 mg, 1.00 mmol) was treated with ethylene (8 bar), lithium chloride (212 mg, 5.0 mmol), potassium hydrogen carbonate (400 mg, 4.0 mmol), tetrabutylammonium bromide (322 mg, 1.0 mmol) and palladium acetate (22 mg, 10 mol-%) in NMP (50 ml) for 2 d at 100°C according to GP 2. After work-up and evaporation of the solvent, 93 mg (71%) of a mixture was obtained, containing 17% of **3a** and 83% of **6a** according to GLC.

2-Ethenyl-1-propenylbenzene (**3c**) *and 2,3-Dimethylindene* (**6c**,[25] Table 1, entry 4): 1-Bromo-2-ethenylbenzene (**2a-Br**, 183 mg, 1.00 mmol) was treated with propene (8 bar), lithium chloride (212 mg, 5.0 mmol), potassium hydrogen carbonate (400 mg, 4.0 mmol), tetrabutylammonium bromide (322 mg, 1.0 mmol), and palladium acetate (22 mg, 10 mol-%) in NMP (50 ml) for 2 d at 100°C according to GP 2. After work-up and column chromatography, two fractions were obtained. − Fraction I: 55 mg (38%) of **3c** (R_f = 0.36) as a colorless oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.91 (dd, ^3J = 7.5, ^4J = 0.9 Hz, 3 H, CH_3), 5.32 (dd, ^3J = 10.5, ^2J = 0.7 Hz, 1 H, vinyl), 5.67 (dd, ^3J = 17.3, ^2J = 0.7 Hz, 1 H, vinyl), 6.11 (dt, ^3J = 7.5, ^3J = 15.8 Hz, 1 H, olefin), 6.70 (dd, ^3J = 15.8, ^4J = 0.9 Hz, 1 H, olefin), 7.11−7.59 (m, 4 H, Ar-H). − Fraction II: 19 mg (13%) of **6c** (R_f = 0.36) as a colorless oil.

trans,trans-1,2-Dipropenylbenzene (**3b**,[26] Table 1, entry 5): From 1,2-dibromobenzene (2.36 g, 10.0 mmol) in the presence of Bu_4NBr (6.45 g, 20 mmol), LiCl (4.24 g, 100 mmol) and $KHCO_3$ (4.00 g, 40 mmol) and propene was obtained 1.25 g (79%) of **3b** (R_f = 0.34). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93 (dd, ^3J = 6.6, ^4J = 1.7 Hz, 6 H, CH_3), 6.10 (dq, ^3J = 6.6, ^3J = 15.6 Hz, 2 H, olefin), 6.68 (dd, ^3J = 15.6, ^4J = 1.7 Hz, 2 H, olefin), 7.17 (m, 2 H, Ar-H), 7.39 (m, 2 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 18.72 (+, CH_3), 126.24 (+, Ar-C), 126.84 (+, Ar-C), 127.55 (+, olefin), 129.08 (olefin), 135.75 (C_{quat}, Ar-H).

1-Ethenyl-(E)-2-(2'-phenylethenyl)benzene (**3d**)[27], *3-Methyl-2-phenylindene* (**6d**),[28] *and 1-Methylene-2-phenylindane* (**8d**). − a) *From o-Bromostyrene* (**2a-Br**) *under Jeffery Conditions* (Table 1, entry 7): 1-Bromo-2-ethenylbenzene (**2a-Br**, 366 mg, 2.0 mmol) was treated with styrene (521 mg, 5.0 mmol), lithium chloride (424 mg, 10.0 mmol), potassium hydrogen carbonate (1.0 g, 10 mmol), tetrabutylammonium bromide (645 mg, 2.0 mmol), and palladium acetate (45 mg, 10 mol-%) in NMP (20 ml) for 2 d at 100°C according to GP 1. After work-up and column chromatography on silica gel, impregnated with silver nitrate (10%), three fractions were obtained. − Fraction I (R_f = 0.37): 218 mg (53%) of **8d** as a colorless oil. − IR (film): $\tilde{\nu}$ = 3058 cm^{-1}, 3019, 1387, 1331, 1029, 962, 765, 692. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (dd, ^3J = 6.8, ^2J = 15.8 Hz, 1 H, 3-H), 3.51 (dd, ^3J = 9.0, ^2J = 15.8 Hz, 1 H, 3-H), 4.18 (m, 1 H, 2-H), 4.78 (d, ^2J = 1.5 Hz, 1 H, olefin), 5.59 (d, ^2J = 1.5 Hz, 1 H, olefin), 7.18−7.42 (m, 8 H, Ar-H), 7.48−7.62 (m, 1 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 40.58 (−, C-3), 49.80 (+, C-2), 104.87 (−, olefin), 120.83 (+, Ar-C), 125.12 (+, Ar-C), 126.31 (+, Ar-C), 126.84 (+, Ar-C), 127.93 (+, Ar-C), 128.47 (+, Ar-C), 128.75 (+, Ar-C), 140.07 (C_{quat}, C-1), 144.53

(C_{quat}, Ar-C), 145.32 (C_{quat}, Ar-C), 154.60 (C_{quat}, Ar-C). − $C_{16}H_{14}$ (206.3): calcd. C 93.15, H 6.84; found C 93.06, H 6.89. − Fraction II (R_f = 0.21): 7 mg (2%) of **6d** as a colorless oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.32 (br. s, 3 H, CH_3), 3.77 (br. s, 2 H, CH_2), 7.06−7.61 (m, 9 H, Ar-H). − Fraction III (R_f = 0.08): 49 mg (12%) of **3d** as a colorless oil. − IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3026, 2926, 2854, 1419, 1375, 1328, 1156, 1028, 962 (*trans*-HC=CH), 910, 759, 735, 691, 531, 478. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.28 (dd, ^3J = 11.1, ^2J = 1.3 Hz, 1 H, vinyl), 5.56 (dd, ^3J = 17.4, ^2J = 1.3 Hz, 1 H, vinyl), 6.88 (d, ^3J = 16.2 Hz, 1 H, olefin), 7.00 (dd, ^3J = 11.1, ^3J = 17.4 Hz, 1 H, vinyl), 7.08 (m, 10 H, 9 Ar-H, 1 olefin). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 116.57 (−, vinyl), 126.30, 126.59, 127.66, 127.85, 128.67, 131.07, 135.03 (+, Ar-C, vinyl, olefin), 135.61 (C_{quat}, Ar-C), 136.52 (C_{quat}, Ar-C), 137.54 (C_{quat}, Ar-C), 3 C (+) are hidden. − MS (70 eV); *m/z* (%): 206 (100) [M^+], 178 (20) [$M^+ - C_2H_4$], 165 (13) [$M^+ - C_3H_5$], 77 (4) [$C_6H_5^+$].

b) *From o-Bromostyrene* (**2a-Br**) *under Heck Conditions* (Table 1, entry 6): 1-Bromo-2-ethenylbenzene (**2a-Br**, 1.30 g, 7.10 mmol) was treated with styrene (3.70 g, 35.5 mmol) in the presence of palladium acetate (159 mg, 10 mol-%), tri-*o*-tolylphosphane (432 mg, 20 mol-%) and triethylamine (1.43 g, 14.2 mmol) in *N*-methylpyrrolidinone (20 ml) at 90°C for 1 d according to GP1. After work-up and column chromatography on silica gel (100 g, eluting with petroleum ether) 0.51 g (35%) of pure **3d** (R_f = 0.46) was obtained as a colorless oil. Spectroscopic data as above.

c) *From o-Iodostyrene* (**2a-I**) *under Heck Conditions* (Table 1, entry 10): 2-Ethenyl-1-iodobenzene (1.15 g, 5.0 mmol) was treated with styrene (2.60 g, 25.0 mmol) in the presence of palladium acetate (22 mg, 10 mol-%), tri-*o*-tolylphosphane (304 mg, 20 mol-%) and triethylamine in NMP (20 ml) at 60°C for 24 h according to GP1. After work-up and column chromatography on silica gel (60 g, eluting with petroleum ether) 371 mg (36%) of **3d** was obtained. Spectroscopic data as above.

d) *From o-Iodostyrene* (**2a-I**) *under Jeffery Conditions* (Table 1, entry 11): 2-Ethenyl-1-iodobenzene (1.15 g, 5.0 mmol) was treated with styrene (2.60 g, 25.0 mmol) in the presence of palladium acetate (22 mg, 10 mol-%), tetra-*n*-butylammonium bromide (1.61 g, 5.0 mmol), potassium hydrogen carbonate (2.00 g, 20 mmol) and lithium chloride (210 mg, 5.0 mmol) in NMP (20 ml) at 60°C for 24 h according to GP1. After work-up and column chromatography on silica gel (60 g, eluting with petroleum ether) 392 mg (38%) of pure **8d** was obtained as a colorless oil. Spectroscopic data as above.

1-Ethenyl-(E)-2-[2′-(4′′-methoxyphenyl)ethenyl]benzene (**3e**) *and 2-(4′-Methoxyphenyl)-3-methyleneindane* (**8e**, Table 1, entry 12): 1-Bromo-2-ethenylbenzene (**2a-Br**, 183 mg, 1.0 mmol) was treated with 4-methoxystyrene (335 mg, 2.5 mmol), lithium chloride (212 mg, 5.0 mmol), potassium hydrogen carbonate (200 mg, 2.0 mmol) tetrabutylammonium bromide (322 mg, 1.0 mmol) and palladium acetate (22 mg, 10 mol-%) in NMP (20 ml) for 2 d at 100°C according to GP 1. After work-up, 120 mg (51%) of a 1:2 mixture of **3e** and **8e** was obtained. − **3e**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 5.36 (dd, ^2J = 10.96, ^3J = 1.35 Hz, 1 H, vinyl-H), 5.65 (dd, ^2J = 17.40, ^3J = 1.47 Hz, 1 H, vinyl-H), 6.80−7.58 (m, 8 H, Ar-H, 1 H, vinyl-H, 2 H, olefin). − **8e**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.05 (dd, ^3J = 6.8, ^2J = 15.6 Hz, 1 H, 3-H), 3.45 (dd, ^3J = 6.8, ^2J = 15.6 Hz, 1 H, 3-H), 3.83 (s, 3 H, OCH_3), 4.12 (m, 1 H, 2-H), 4.76 (d, ^2J = 1.5 Hz, 1 H, olefin), 5.56 (d, ^2J = 1.5 Hz, olefin), 7.02−7.63 (m, 8 H, Ar-H). − $C_{17}H_{16}O$ (236.3): calcd. C 86.41, H 6.83; found C 86.37, H 6.72.

1-Ethoxy-3-methyleneindane (**9**) *and 2-Ethoxy-1-methyleneindane* (**10**, Table 1, entry 13): 1-Bromo-2-ethenylbenzene (**2a-Br**, 732 mg, 4.0 mmol) was treated with ethenyl ethyl ether (1.44 g, 20.0 mmol), lithium chloride (848 mg, 20.0 mmol), potassium carbonate (6.91 g, 50.0 mmol), tetrabutylammonium bromide (3.22 g, 10.0 mmol) and palladium acetate (18 mg, 2 mol-%) in NMP (20 ml) for 2 d at 80°C according to GP 1. After work-up and column chromatography on silica gel (petroleum ether/diethyl ether, 100:1), 403 mg (58%) of a 1:6 mixture of **9** and **10** (R_f = 0.54) was obtained as a colorless oil. − **9** and **10**: IR (film): $\tilde{\nu}$ = 3072 cm^{-1}, 3023, 2974 (CH), 2928, 2870, 1395, 1321, 1253, 1209, 1173, 1122, 1082, 1021, 887, 731, 686. − MS (70 eV); *m/z* (%): 174 (8) [M^+], 145 (10) [$M^+ - C_2H_5$], 130 (100) [$M^+ - C_2H_4O$], 117 (63), 91 (11) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$]. − $C_{12}H_{14}O$: calcd. 174.1044; found 174.1044 (MS). − **9**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 6.7 Hz, 3 H, CH_3), 2.74 (dm, 1 H, CH_2), 3.03 (dm, 1 H, CH_2), 3.62 (dq, ^3J = 6.7, ^4J = 1.2 Hz, 2 H, OCH_2), 4.98 (dd, 1 H, HCO), 5.07 (t, 1 H, olefin), 5.50 (t, 1 H, olefin), 7.28 (m, 3 H, Ar-H), 7.50 (m, 1 H, Ar-H). − **10**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 6.7 Hz, 3 H, CH_3), 2.93 (dd, ^2J = 15.1, ^3J = 3.8 Hz, 1 H, CH_2), 3.21 (dd, ^2J = 15.1, ^3J = 7.6 Hz, 1 H, CH_2), 3.62 (dq, ^3J = 6.7, ^4J = 1.2 Hz, 2 H, OCH_2), 4.58−4.67 (m, 1 H, HCO), 5.29 (d, ^2J = 1.6 Hz, 1 H, olefin), 5.62 (d, ^2J = 1.6 Hz, 1 H, olefin), 7.14−7.23 (m, 3 H, Ar-H), 7.41−7.50 (m, 1 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 15.42 (+, CH_3), 37.73 (−, CH_2), 63.84 (−, OCH_2), 106.49 (−, olefin), 120.96 (+, Ar-C), 125.36 (+, Ar-C), 126.80 (+, Ar-C), 128.72 (+, Ar-C), 139.06 (C_{quat}, Ar-C), 142.88 (C_{quat}, Ar-C), 149.91 (C_{quat}, C-1). − $C_{12}H_{14}O$ (174.2): calcd. C 82.72; H 8.10; found C 82.54; H 8.12.

4-Methylene-3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan (**12**, Table 1, entry 14): 1-Bromo-2-ethenylbenzene (**2a-Br**, 732 mg, 4.0 mmol) was treated with 2,3-dihydrofuran (**11**, 1.40 g, 20.0 mmol), lithium chloride (848 mg, 20.0 mmol), potassium carbonate (6.91 g, 50.0 mmol), tetrabutylammonium bromide (3.22 g, 10.0 mmol), and palladium acetate (18 mg, 2 mol-%) in NMP (20 ml) for 2 d at 80°C according to GP 1. After work-up and column chromatography on silica gel (petroleum ether/ethyl acetate, 20:1), 280 mg (41%) of **12** was obtained as a yellow solid; mp 43°C. − IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1}, 2947, 2864, 1635, 1192, 1054, 987, 878, 509, 424. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.89 (dddd, ^2J = 11.1, ^3J = 5.5, ^3J = 5.0, ^3J = 3.5 Hz, 1 H, 3-H), 2.27 (dddd, ^2J = 11.1, ^3J = 8.7, ^3J = 7.1, ^3J = 9.2 Hz, 1 H, 3-H), 3.46 (ddd, ^2J = 9.0, ^3J = 8.7, ^3J = 5.5 Hz, 1 H, 2-H), 3.58 (dddd, ^3J = 9.2, ^3J = 7.0, ^3J = 5.0 Hz, 1 H, CH), 3.85 (ddd, ^2J = 9.0, ^3J = 7.1, ^3J = 3.5 Hz, 1 H, 2-H), 5.12 (d, ^2J = 2.0 Hz, 1 H, olefin), 5.45 (d, ^3J = 7.0 Hz, 1 H, 8b-H), 5.57 (d, ^2J = 2.0 Hz, 1 H, olefin), 7.27−7.33 (m, 2 H, Ar-H), 7.44−7.49 (m, 2 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 35.04 (−, C-3), 47.26 (+, C-3a), 66.77 (−, C-2), 84.09 (+, C-8b), 104.66 (−, olef-C), 120.19 (+, Ar-C), 126.08 (+, Ar-C), 128.82 (+, Ar-C), 129.21 (+, Ar-C), 140.80 (C_{quat}, Ar-C), 143.93 (C_{quat}, Ar-C), 152.09 (C_{quat}, C-4). − MS (70 eV); *m/z* (%): 172 (84) [M^+], 143 (100) [$M^+ - C_2H_5$], 141 (60) [$M^+ - OCH_3$], 128 (32), 115 (30), 77 (7) [$C_6H_5^+$]. − $C_{12}H_{12}O$: calcd. 172.0888; found 172.0888 (MS); calcd. C 83.69, H 7.02; found C 83.44, H 6.96.

4-Methylene-3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan (**12**), *2-(2′-Ethenylphenyl)-2,5-dihydrofuran* (**13**), *and 2-(2′-Ethenylphenyl)-2,3-dihydrofuran* (**14**, Table 1, entry 15): 1-Bromo-2-ethenylbenzene (**2a-Br**, 732 mg, 4.0 mmol) was treated with 2,3-dihydrofuran (**11**, 1.40 g, 20.0 mmol), triethylamine (810 mg, 8.0 mmol), tri-*o*-tolylphosphane (49 mg, 4 mol-%) and palladium acetate (18 mg, 2 mol-%) in NMP (20 ml) for 2 d at 80°C according to GP 1. After work-up and column chromatography on silica gel (petroleum ether/dichloromethane, 20:1), three fractions were obtained.

– Fraction I (R_f = 0.54): 80 mg (12%) of **14** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.50 (dddd, ^2J = 15.0, ^3J = 8.6, ^3J = 2.5, ^4J = 2.5 Hz, 1 H, 3-H), 3.08 (dddd, ^2J = 15.0, ^3J = 11.0, ^3J = 2.5, ^4J = 2.5 Hz, 1 H, 3-H), 4.94 (dd, ^3J = 5.1, ^3J = 2.5 Hz, 1 H, 4 H), 5.33 (dd, ^3J = 12.0, ^2J = 1.3 Hz, 1 H, vinyl), 5.64 (dd, ^3J = 16.9, ^2J = 1.3 Hz, 1 H, vinyl), 5.77 (dd, ^3J = 8.6, ^3J = 11.0 Hz, 1 H, 2-H), 6.48 (dd, ^3J = 5.1, ^4J = 2.5 Hz, 5-H), 6.92 (dd, ^3J = 12.0, ^3J = 16.9 Hz, 1 H, vinyl), 7.26–7.52 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 37.58 (–, C-3), 79.97 (+, C-2), 98.93 (+, C-4), 116.35 (–, vinyl), 125.17 (+, Ar-C), 126.18 (+, Ar-C), 127.54 (+, Ar-C), 127.92 (+, Ar-C), 134.17 (+, vinyl), 135.32 (C_{quat}, Ar-C), 140.00 (C_{quat}, Ar-C), 145.34 (+, C-5). – Fraction II (R_f = 0.38): 204 mg (30%) of **13** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.69–4.98 (m, 2 H, 5-H), 5.37 (dd, ^3J = 11.3, ^2J = 2.5 Hz, 1 H, vinyl), 5.68 (dd, ^3J = 16.6, ^2J = 2.5 Hz, 1 H, vinyl), 5.75–6.08 (m, 2 H, 3,4-H), 6.08–6.21 (m, 1 H, 2-H), 7.12 (dd, ^3J = 11.3, ^3J = 16.6 Hz, 1 H, vinyl), 7.18–7.62 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 76.60 (–, C-5), 84.56 (+, C-2), 116.42 (–, vinyl), 126.18 (+, 2 Ar-C), 126.63 (+, Ar-C), 127.69 [+, C-3(4)], 127.95 [+, C-4(3)], 129.35 (+, Ar-C), 134.16 (+, vinyl), 136.01 (C_{quat}, Ar-C), 138.94 (C_{quat}, Ar-C). – $C_{12}H_{12}O$ (172.2): calcd. C 83.69, H 7.02; found C 83.81, H 7.14. – Fraction III (R_f = 0.21): 20 mg (3%) of **12** as a colorless oil.

2-(2′,2′-Diphenylethenyl)-3-methylindene (**20**, Table 1, entry 13): 1-Bromo-2-ethenylbenzene (**2a-Br**, 366 mg, 2.0 mmol) was treated with 1-methylene-2,2-diphenylcyclopropane (**15**, 1031 mg, 5.0 mmol), lithium chloride (424 mg, 10.0 mmol), potassium hydrogen carbonate (400 mg, 4.0 mmol), tetrabutylammonium bromide (645 mg, 2.0 mmol), and palladium acetate (45 mg, 10 mol-%) in NMP (20 ml) for 2 d at 100°C according to GP 1. After work-up and column chromatography on silica gel (pentane), two fractions were obtained. – Fraction I (R_f = 0.32): 534 mg (52%) of **15**. – Fraction II (R_f = 0.16): 230 mg (37%) of **20** as colorless crystals, mp 79°C. – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 3019, 2850, 1598, 1488, 1457, 1383, 1174, 1072, 967, 755, 698. – UV (dichloromethane): λ_{max} (lg ε) = 348 nm (4.543). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.32 (br. s, 3 H, CH_3), 2.88 (br. s, 2 H, CH_2), 7.10–7.51 (m, 15 H, 14 Ar-H, 1 olefin). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 10.99 (+, CH_3), 39.36 (–, CH_2), 118.85 (+), 122.43 (+), 123.17 (+), 125.17 (+), 126.20 (+), 127.18 (+), 127.24 (+), 127.56 (+, 2 C), 128.27 (+, 2 C), 128.59 (+, 2 C), 130.52 (+, 2 C), 138.77 (C_{quat}), 140.14 (C_{quat}), 140.52 (C_{quat}), 141.22 (C_{quat}), 143.27 (C_{quat}), 143.36 (C_{quat}), 146.00 (C_{quat}). – MS (70 eV); *m/z* (%): 308 (3) [M^+], 206 (100) [$M^+ - C_8H_6$], 191 (73) [$M^+ - C_9H_9$], 165 (45) [$M^+ - C_{11}H_{11}$], 120 (34) [$C_9H_{12}^+$], 91 (43) [$C_7H_7^+$]. – $C_{24}H_{20}$: calcd. 308.1565; found 308.1565 (MS); calcd. C 93.46, H 6.54; found C 93.55, H 6.54.

X-ray Crystal-Structure Analysis of **20**[14]: Single crystal from pentane, 0.8 × 0.6 × 0.5 mm, T = 293 K, Siemens-Stoe AED2 diffractometer, Mo-K_α (graphite monochromator); λ = 71.073 pm, empirical formula $C_{24}H_{20}$, space group $P\bar{1}$; unit cell dimensions: a = 879.2 pm; b = 909.2 pm; c = 1210.3 pm; α = 107.920°, β = 105.990°, γ = 101.650°; $d_{calcd.}$ = 1.219 Mg/m^3, V = 0.8403 nm^3, Z = 2; μ(Mo-K_α) = 0.069 mm^{-1}; range for data collection: θ from 3.52 to 25.01°; index ranges: $-10 \le h \le 10$, $-10 \le k \le 10$, $-7 \le l \le 14$; 2977 reflections collected; 2960 independent reflections. Structure solution: Direct methods (SHELXS-90, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467); structure refinement (G. M. Sheldrick, *SHELXL-93, Programm for Crystal Structure Refinement*, University of Göttingen, **1993**): Full-matrix least-squares on F^2, R values: $R1$ = 0.0675, $wR2$ = 0.1381 (for all data with 217 parameters and no restrain); Goodness-of-Fit on F^2 = 1.062. Maximum and minimum 205 and –240 e nm^{-3}.

General Procedure for the Oxidative Cyclization of 1,2-Dialkenylbenzenes (GP 3): In a screw-capped Pyrex bottle were placed the arene (2.0 mmol), $Pd(OAc)_2$, (22 mg, 5 mol-%), *p*-benzoquinone (22 mg, 0.2 mmol), MnO_2 (522 mg, 6.0 mmol), and acetic acid (10 ml). The contents of the closed Pyrex bottle was heated with vigorous stirring for the stated time at the stated temp. After the mixture had been cooled to room temp., it was filtered through a silica-gel pad, and washed with pentane/dichloromethane (2:1). The organic layer was washed one time each with water, potassium hydrogen carbonate solution and water. The organic layer was dried ($MgSO_4$), concentrated in vacuo, and the residue was purified by column chromatography on silica gel and/or recrystallization.

1-Acetoxy-3-methylindene (**24**) *and 1-Acetoxy-3-methyleneindane* (**23**, Table 2, entry 3): 1,2-Diethenylbenzene (**3a**, 260 mg, 2.0 mmol) was treated with *p*-benzoquinone (22 mg, 0.2 mmol), MnO_2 (522 mg, 6.0 mmol), and palladium acetate (22 mg, 5 mol-%) in acetic acid (10 ml) for 24 h at 45°C according to GP 3. After work-up and column chromatography on silica gel (petroleum ether/ethyl acetate), 151 mg (40%) of a mixture of **23** and **24** was obtained. After column chromatography on 20 g of silica gel [impregnated with 10% (w/w) of silver nitrate, petroleum ether/ethyl acetate, 10:1], two fractions were obtained. – Fraction I (R_f = 0.29): 26 mg (7%) of **24**, colorless oil. – IR (film): $\tilde{\nu}$ = 3075 cm^{-1}, 3029, 2926, 2854, 2695, 1733 (C=O), 1646, 1473, 1425, 1373, 1343, 1228, 1114, 1045, 963, 876, 828, 782, 761, 739, 687, 606, 573, 547, 486, 424. – ^{1}H NMR (250 MHz, $CDCl_3$): 2.12 (d, ^4J = 1.7 Hz, 3 H, CH_3), 2.13 (s, 3 H, CH_3CO), 6.06 (dd, ^3J = 1.7, ^4J = 1.7 Hz, 1 H, 2-H), 6.18 (d, ^3J = 1.7 Hz, 1 H, 1-H), 7.12–7.49 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 12.71 (+, CH_3), 20.90 (+, CH_3CO), 76.54 (+, C-1), 119.17 (+, C-2), 123.89 (+, Ar-C), 126.09 (+, Ar-C), 127.85 (+, Ar-C), 128.63 (+, Ar-C), 171.18 (C_{quat}, CO_2). – MS (70 eV); *m/z* (%): 188 (8) [M^+], 146 (100) [$M^+ - H_2C_2O$], 131 (40) [$M^+ - C_3H_5O$], 128 (27) [$M^+ - C_2H_4O_2$], 115 (16) [$M^+ - C_3H_5O_2$], 77 (4) [$C_6H_5^+$]. – $C_{12}H_{12}O_2$: calcd. 188.0928; found 188.0837 (MS). – Fraction II (R_f = 0.22): 101 mg (27%) of **23**, colorless oil. – IR (film): $\tilde{\nu}$ = 3070 cm^{-1}, 3026, 2922, 2856, 1736 (C=O), 1626, 1438, 1370, 1289, 1237, 1170, 1036, 1020, 980, 919, 806, 762, 651, 537. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, CH_3CO), 2.76 (ddd, ^2J = 17.4, ^3J = 4.1, ^4J = 2.2 Hz, 1 H, 2-H), 3.26 (ddd, ^2J = 17.4, ^3J = 7.4, ^4J = 2.2 Hz, 1 H, 2-H), 5.12 (dd, ^2J = 2.4, ^4J = 2.2 Hz, 1 H, olefin), 5.57 (dd, ^2J = 2.4, ^4J = 2.2 Hz, 1 H, olefin), 6.22 (dd, ^3J = 7.4, ^3J = 4.1 Hz, 1 H, 1-H), 7.18–7.63 (m, 4 H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.00 (+, CH_3CO), 38.97 (–, C-2), 74.99 (+, C-1), 104.37 (–, olefin-CH_2), 120.52 (+, Ar-C), 125.96 (+, Ar-C), 128.74 (+, Ar-C), 129.14 (+, Ar-C), 141.06 (C_{quat}, Ar-C), 143.10 (C_{quat}, Ar-C), 145.90 (C_{quat}, C-3), 170.84 (C_{quat}, CO_2). – MS (70 eV); *m/z* (%): 188 (2) [M^+], 145 (5) [$M^+ - C_2H_3O$], 128 (100) [$M^+ - C_2H_4O_2$], 115 (2) [$M^+ - C_3H_5O_2$]. – $C_{12}H_{12}O_2$: calcd. 188.0837; found 188.0837 (MS); calcd. C 76.57, H 6.43; found C 76.55, H 6.48.

tert-Butyl 1-Acetoxyindan-3-ylacetate (**31**): The arene **3f** (299 mg, 1.3 mmol) was treated with *p*-benzoquinone (14 mg, 0.13 mmol), MnO_2 (226 mg, 2.6 mmol), and palladium acetate (29 mg, 10 mol-%) in acetic acid (5 ml) for 11 d at 45°C according to GP 3. After work-up and column chromatography on silica gel (petroleum ether/ethyl acetate), 43 mg (12%) of a mixture of (*E*)-**31** and (*Z*)-**31** was obtained. – (*Z*)-**31**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, CH_3CO), 2.81 (ddd, ^2J = 17.3, ^3J = 3.3, ^4J = 1.8 Hz, 1 H, 2-H), 3.25 (ddd, ^2J = 17.3, ^3J = 7.0, ^4J =

1.8 Hz, 1 H, 2-H), 5.91 (dd, ^3J = 1.8, ^3J = 1.8 Hz, 1 H, olefin), 6.14 (dd, ^3J = 7.0, ^3J = 3.3 Hz, 1 H, 1-H), 7.18−7.67 (m, 4 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 20.94 (+, CH_3CO), 28.24 [+, C(CH_3)$_3$], 42.72 (−, C-2), 73.59 (+, C-1), 80.19 −[C_{quat}, $C(CH_3)_3$], 114.87 (+, olefin), 125.49 (+, Ar-C), 128.55 (+, Ar-C), 129.25 (+, Ar-C), 130.87 (+, Ar-C), 137.61 (C_{quat}, Ar-C), 146.59 (C_{quat}, Ar-C), 152.97 (C_{quat}, C-3), 165.43 (C_{quat}, CO), 170.96 (C_{quat}, CH_3CO).

☆ Dedicated to Professor *Lars Skattebøl* on the occasion of his 70th birthday.

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