Chemoselective Cobalt-Catalyzed Biaryl Coupling Reactions

Samet Gülak, a,b Ondrej Stepanek, b,c Jennifer Malberg, d Babak Rezaei Rad, d Martin Kotora, c Robert Wolf, d and Axel Jacobi von Wangelin a,b,*

a Institute of Organic Chemistry, University of Regensburg, Universitaetsstr. 31, 93053 Regensburg, Germany
Tel: +49 (0)941 943 4802, Fax: +49 (0)941 943 4617, E-mail: axel.jacobi@ur.de
b Department of Chemistry, University of Cologne, Germany
c Department of Organic and Nuclear Chemistry, Charles University, Prague, Czech Republic
d Institute of Inorganic Chemistry, University of Regensburg, Germany
General

**Analytical Thin-Layer Chromatography**
TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdophosphoric acid in ethanol or a solution of potassium permanganate in water.

**Column Chromatography**
Flash column chromatography with silica gel 60 from KMF (0.040-0.063 mm). Mixtures of cyclohexane / ethyl acetate or n-pentane / ethyl acetate were used as solvents.

**Gas Chromatography with FID**
Yields of optimization and kinetic experiments were determined by GC/FID (n-pentadecane as internal reference) with analytically pure samples on an HP6890 with 7683B injector (HP-5MS column, 30m × 0.25 mm × 0.25, 5% phenylmethylsiloxane, H₂ as carrier gas). Standard heating program: 50°C (2 min), 25°C/min -> 300°C (5 min).

**Gas Chromatography with Mass-Selective Detector**
For GC/MS analysis of crude samples, an Agilent 6890N system with 5975 MS detector was used (HP-5MS column, 30m × 0.25 mm × 0.25, 5% phenylmethylsiloxane, H₂ as carrier gas). Standard heating program: 50°C (2 min), 25°C/min -> 300°C (5 min).

**NMR Spectroscopy**
¹H and ¹³C nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (300 MHz). Kinetic isotope effects with deuterated materials (see Scheme 5) were determined on a Bruker Avance III 600 (600 MHz). The NMR spectra of the bis(anthracene) cobaltate [K(dme)₂{Co(C₁₄H₁₀)₂}] (Figure 4) were recorded on a Bruker Avance 400 (400 MHz).
¹H-NMR: The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ¹³C-APT-NMR (Attached Proton Test) and ¹³C-CPD-NMR (Composite Pulse Decoupling): d (doublet) was used to indicate a C-F fluorine coupling. The carbon signals were assigned as: Q, quarternary carbon; CHAr, aromatic CH; -CH=, α-vinyl carbon; =CH₂, β-vinyl carbon, CH, aliphatic CH group; CH₂, aliphatic CH₂
group; CH$_3$, methyl group; OCH$_2$, methylenoxy group; OCH$_3$, methoxy group; Ar-CH$_2$, benzylic CH$_2$; Ar-CH, benzylic CH; Ar-CH$_3$, benzylic CH$_3$; NCH$_3$, N-methyl group; C=O, carbonyl group.

**IR Spectroscopy**

IR spectra of pure samples were measured by the ATR technique on a Thermo Nicolet 380 FT-IR. Intensities are given as: s = strong, m = medium, w = weak.

**High Resolution Mass Spectrometry (HRMS)**

Mass spectra were recorded on a Finnigan MAT 900s (EI) and given as m/z values.

**Melting Point**

Melting points were determined on a Büchi apparatus after Dr. Tottoli and are uncorrected.

**Chemicals**

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. THF was distilled over sodium and benzophenone under an argon atmosphere. N-Methyl-2-pyrrolidone (NMP) from Acros Organics (99.5%, anhydrous) was stored over 4 Å molecular sieves. CDCl$_3$ (0.03 % TMS, 0.01 % H$_2$O) from Eurisotop was stored over 4 Å molecular sieves. Co(acac)$_3$ (>98%) from Merck and CoCl$_2$ (98%) from Aldrich were stored and handled in a glove box. 2-Chlorostyrene (98%, Alfa Aesar), 4-chloro-α-methylstyrene (96%, Acros Organics), and 4-chlorostyrene (99%, Aldrich) were used without further purification. α-Deutero-4-chlorostyrene was prepared according to literature procedures: Reduction of 4-chloroacetophenone with LiAlD$_4$: H.-S. Choi, R. L. Kuczkowski, *J. Org. Chem.* 1985, 50, 901; (b) Dehydration of the resultant alcohol: G. Vassilikogiannakis, M. Hatzimarinaki, M. Orfanopoulos, *J. Org. Chem.* 2000, 65, 8180.

All other substituted chlorostyrenes were synthesized by Wittig olefination (according to: M. Ogata, H. Matsumoto, S. Shimizu, S. Kida, M. Shiro and K. Tawara, *Eur. J. Med. Chem.* 1989, 24, 137) or Heck reaction (according to: A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* 2003, 5, 3285, see also below). Commercial PhMgCl (25% in THF, from Chemetall), EtMgCl (2 M in THF, from Acros), 3,4-(methylenedioxy)phenylmagnesium bromide (1 M in PhMe/THF, from Aldrich), and 4-(2-tetrahydro-2H-pyranoxy)phenylmagnesium bromide (0.5 M in THF, from Aldrich) were
used as received. Isopropylmagnesium chloride/LiCl (1:1, 1.2 M in THF) was obtained as a gift from Chemetall. Other arylmagnesium bromides were freshly prepared from aryl bromide and magnesium and their concentration determined by reaction with benzaldehyde and quantitative GC-FID analysis (see also: F. M. Piller, P. Appukuttan, A. Gavryushin, M. Helm, P. Knochel, Angew. Chem. Int. Ed. 2008, 47, 6802). 2-Allylchlorobenzene was purchased from Rieke Metals.
Preparation of Arylmagnesium Bromides

a) Direct Magnesiation:

\[ \text{ArBr} + 1.5 \text{ equiv. Mg} \xrightarrow{0.01 \text{ mol\% DIBAL-H}} \text{ArMgBr} \]

A 30 mL flask was placed in a water bath (r.t.), charged with magnesium turnings (363 mg, 15 mmol), fitted with a rubber septum, and purged with argon. Dry THF (18.95 mL) was added via syringe followed by a solution of DIBAL-H in THF (0.1 mL, 1 M in THF, 0.001 mmol). The mixture was stirred at r.t. for 5 min. Then, 1.05 mL (10 mmol) bromobenzene was added and the reaction stirred for 3 h at r.t.


b) Iodine-Magnesium Exchange with \textit{iso}-PrMgCl:

A 30 mL flask was placed in a cooling bath (-20°C), charged with ethyl 4-iodobenzoate (375 mg, 1.3 mmol) in THF (1.5 mL), fitted with a rubber septum, and purged with argon. Then, a solution of isopropylmagnesium chloride / LiCl in THF (1.23 M, 1.05 mL, 1.3 mmol) was added dropwise (over 5 min) via a syringe. The mixture was stirred at -20°C for 30 min. Then, the solvent and \textit{i}-PrI were evaporated (to near dryness) at 0°C and the residue dissolved in dry THF (2.5 mL).


All other arylmagnesium bromides were prepared in similar manner from the corresponding aryl bromides. For commercial Grignard reagents, see General Part above.

Yield Determination:

A sample of 2 mL containing 1 mmol of the arylmagnesium bromide in THF (0.5 M) was treated with 151 µL (1.5 mmol) benzaldehyde under an atmosphere of argon. After 1 h at r.t., saturated aqueous NH₄Cl was added, and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na₂SO₄) and concentrated in vacuo. The concentration of the resulting benzylalcohol was determined by \textsuperscript{1}H NMR (referenced to...
hexamethyldisiloxane as internal standard) and quantitative GC-FID (referenced to \(n\)-pentadecane as internal standard).
If not noted otherwise, the yields of all prepared arylmagnesium halides were \(> 90\%\) by NMR.

**Synthesis of Styrenes**

\[
\begin{array}{c}
\text{C} & \text{H} & \text{O} & \text{Cl} & \text{H} & \text{Br} \\
\end{array} 
\begin{array}{c}
\text{\textsuperscript{1}equiv. K}_2\text{CO}_3 \\
\text{1,4-dioxane, 115°C, 18h}
\end{array}
\begin{array}{c}
\text{C} & \text{H} & \text{Cl} & \text{H} \\
\end{array} 
\]

The respective benzaldehyde (20 mmol), \(\text{K}_2\text{CO}_3\) (3.45 g, 25 mmol) and methyltriphenylphosphonium bromide (7.1 g, 20 mmol) were loaded into a flask and treated with 20 mL of 1,4-dioxane. The mixture was heated to reflux and stirred for 18 h. The mixture was then cooled, filtered, concentrated in vacuum, washed with \(n\)-pentane and filtered again. The combined organic phases were dried (\(\text{Na}_2\text{SO}_4\)), concentrated in vacuo, and purified by SiO\(_2\) column chromatography.


**1,3-Dichloro-4-vinylbenzene**

\[
\begin{array}{c}
\text{C} & \text{H} & \text{Cl} & \text{H} & \text{Cl} \\
\end{array} 
\]

Yield 85%

**GC-MS**

\[
m/z \begin{array}{c}
172[M], 159, 148, 137, 123, 113, 102, 87, 75, 63, 50.
\end{array}
\]

**\(^{1}\text{H-NMR}\)**

\[
\begin{array}{c}
\delta 7.55-7.16 (m; 3H), 7.01 (dd; 1H, 10.9/6.5 Hz), 5.71 (d; 1H, 17.5 Hz), 5.39 (d; 1H, 10.9 Hz).
\end{array}
\]

**\(^{13}\text{C-APT-NMR}\)**

\[
\begin{array}{c}
\delta 134.4 (Q), 134.0 (Q), 133.8 (Q), 132.3 (\text{-CH=}), 129.5 (\text{CH}_2\text{Ar}), 127.5 (\text{CH}_2\text{Ar}), 127.4 (\text{CH}_2\text{Ar}), 117.2 (\text{=CH}_2).
\end{array}
\]

2-Chloro-1-methoxy-3-vinylbenzene

\[
\text{C}_9\text{H}_9\text{ClO} \quad (168.03 \text{ g/mol})
\]

**Yield** 75%

**GC-MS**

\[ R_t \ 6.81 \text{ min} \]

\[ m/z \ 168[M], 153, 138, 125, 114, 103, 89, 77, 63, 50. \]

**\(^1\)H-NMR**

\( (300 \text{ MHz, CDCl}_3), \delta \ 7.28-7.08 \text{ (m; 3H)}, 6.84 \text{ (t; 1H, 4.7 Hz)}, 5.73 \text{ (d; 1H, 17.5 Hz)}, 5.38 \text{ (d; 1H, 11.0 Hz)}, 3.89 \text{ (s; 3H)} \)

**\(^{13}\)C-APT-NMR**

\( (75 \text{ MHz, CDCl}_3), \delta \ 155.4 \text{ (Q)}, 137.4 \text{ (Q)}, 133.5 \text{ (-CH=)}, 127.0 \text{ (CHAr)}, 121.8 \text{ (Q)}, 118.6 \text{ (CHAr)}, 117.0 \text{ (=CH2)}, 111.0 \text{ (CHAr)}, 56.4 \text{ (CH3)} \)

\((E)-1\)-Chloro-4-styrylbenzene

Under an inert atmosphere, a two-necked flask was charged with NaOAc (0.90 g, 11 mmol), bromobenzene (1.05 mL, 10 mmol), and N-methylpyrrolidone (NMP, 14 mL). In a separate flask, a stock solution of Pd(OAc)\(_2\) (10 mg) in NMP (100 mL) was prepared. An aliquot (9 mL, 0.04 mol% Pd with respect to bromobenzene) was added with a syringe to the flask containing the bromobenzene. The reaction was heated to 120 °C, then 4-chlorostyrene (1.89 mL, 15 mmol) was added, and stirring continued at 135 °C for 15 h. The mixture was then cooled, poured into H\(_2\)O (75 mL), and extracted with toluene (2 x 75 mL). The combined organic layers were washed with H\(_2\)O (3 x 50 mL) and brine (50 mL), dried (Na\(_2\)SO\(_4\)), and filtered through a small plug of celite. The filtered inorganic material was washed with toluene and the combined filtrates concentrated to give a white solid (1.9 g, 90%).

C$_{14}$H$_{11}$Cl (214.05 g/mol)

**Yield** 90%

**GC-MS**

R$_t$ 9.66 min

m/z 214[M], 199, 179, 165, 152, 139, 127, 114, 102, 89, 76, 63, 51.

**$^{1}H$-NMR**

(300 MHz, CDCl$_3$), δ 7.55-7.26 (m; 9H), 7.05 (s; 2H).

**$^{13}C$-APT-NMR**

(75 MHz, CDCl$_3$), δ 137.1 (Q), 136.0 (Q), 133.3 (Q), 129.4 (CH$_{Ar}$), 129.0 (CH$_{Ar}$), 128.9 (CH$_{Ar}$), 128.0 (=CH-), 127.8 (CH$_{Ar}$), 127.5 (=CH-), 126.7 (CH$_{Ar}$).


4-((2-Bromobenzyl)oxy)-2-chloro-1-vinylbenzene

2-Chloro-4-hydroxybenzaldehyde (0.5g, 3.2 mmol), K$_2$CO$_3$ (0.53 g, 3.8 mmol) and 2-bromobenzyl bromide (1.6 g, 6.4 mmol) were treated with 10 mL acetonitrile. The mixture was heated to 60 °C and stirred for 3 h before it was cooled, filtered, and concentrated in vacuum. The resulting crude product was dissolved in 20 mL 1,4-dioxane. Then, K$_2$CO$_3$ (0.56 g, 4 mmol) and methyltriphenylphosphonium bromide (1.4 g, 4 mmol) were added and the reaction heated to 125 °C for 18 h. The mixture was then cooled, filtered, concentrated in vacuum, washed with n-pentane and filtered again. The combined organic phases were dried (Na$_2$SO$_4$), concentrated in vacuo, and purified by SiO$_2$ column chromatography to give a white solid (0.6 g, 58%).

C$_{15}$H$_{12}$BrClO (321.98 g/mol)

**Yield** 58% over two steps

**TLC** R$_f$ 0.31 (SiO$_2$, n-pentane)

**Melting point** 74°C

**GC-MS** R$_t$ 11.19 min (Standard heating procedure)
m/z 324[M], 243, 182, 169, 165, 153, 139, 125, 102, 89, 76, 63, 51.

$^1$H-NMR (300 MHz, CDCl$_3$), $\delta$ 7.60 (dd; 1H, 7.9/1.1 Hz), 7.60-7.49 (m; 2H), 7.34 (td; 1H, 7.6/1.1 Hz), 7.20 (td; 1H, 7.8/1.7 Hz), 7.08-7.00 (m; 2H), 6.88 (dd; 1H, 8.7/2.6 Hz), 5.63 (dd; 1H, 17.5/1.0 Hz), 5.28 (dd; 1H, 11.0/1.1 Hz), 5.12 (s; 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 158.6 (Q), 135.8 (Q), 133.9 (Q), 132.9, 132.6, 129.6, 129.1, 129.0 (Q), 127.8, 127.4, 122.5, 115.7, 114.8, 114.2, 69.8 (Ar-CH$_2$).

FT-IR (ATR film) $\nu$ [cm$^{-1}$] 3086 (w), 2926 (w), 2857 (w), 1602 (s), 1490 (s), 1292 (s), 1244 (s), 1057 (s), 1029 (s), 747 (s).

4-Bromo-1-((3-chloro-4-vinylphenoxy)methyl)-2-fluorobenzene

![Chemical Structure Image]

C$_{15}$H$_{11}$BrClFO (339.97 g/mol)

Yield 70% over two steps

TLC $R_f$ 0.50 (SiO$_2$, $n$-pentane/ethyl acetate (95:5))

Melting point 69°C

GC-MS $t_R$ 11.15 min (Standard heating procedure)
m/z 342[M], 262, 225, 185, 173, 153, 139, 125, 108, 89, 76, 63, 51.

$^1$H-NMR (300 MHz, CDCl$_3$), $\delta$ 7.50 (d; 1H, 8.7 Hz), 7.42-7.27 (m; 3H), 7.10-6.93 (m; 2H), 6.86 (dd; 1H, 8.7/2.6 Hz), 5.63 (dd; 1H, 17.5/1.1 Hz), 5.29 (dd; 1H, 11.0/1.1 Hz), 5.06 (s; 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 160.2 (Q; d; 252 Hz), 158.3 (Q), 133.9, 132.6, 130.8 (d; 4.6 Hz), 129.2, 127.8 (d; 3.7 Hz), 127.4, 122.9 (d; 14.4 Hz), 122.5 (d; 9.4 Hz), 119.3 (d; 24.4 Hz), 115.6, 114.9, 114.2, 63.6 (Ar-CH$_2$; d; 4.1 Hz).

FT-IR (ATR film) $\nu$ [cm$^{-1}$] 3086 (w), 2926 (w), 2886 (w), 1728 (w), 1601 (s), 1487 (s), 1283 (s), 1238 (s), 1040 (s), 912 (s), 877 (s).

(E)-4,4'-(But-1-ene-1,3-diyl)bis(chlorobenzene)
Under an inert atmosphere, a flask was charged with Fe(OTf)₃ (0.5 mmol, 10 mol%) and treated with 1,4-dioxane (4 mL) and 4-chlorostyrene (5 mmol, 620 μL). The mixture was stirred at 80°C for 18 h. Then, saturated aqueous NaHCO₃ was added, and the mixture extracted with n-pentane. The combined organic phases were dried (Na₂SO₄) and concentrated in vacuo. Silica gel column chromatography (n-pentane) afforded the pure product as colorless oil (1.1 g, 85%).


C₁₆H₁₄Cl₂ (276.05 g/mol)

**Yield** 85%

**TLC** Rₜ 0.51 (SiO₂, n-pentane)

**GC-MS** Rₜ 11.00 min (Standard heating program)

**¹H-NMR** (300 MHz, CDCl₃), δ 7.33-7.16 (m; 8H), 7.40-7.24 (m; 2H), 3.62 (qd; 1H, 7.0/4.8 Hz), 1.45 (d; 3H, 7.0 Hz).

**¹³C-NMR** (75 MHz, CDCl₃), δ 143.9 (Q), 136.0 (Q), 135.5, 132.9 (Q), 132.1 (Q), 128.8, 128.8, 128.8 (partially obscured), 127.9, 127.5, 42.1 (Ar-CH), 21.2 (CH₃).

**FT-IR** (ATR film) 1/ν [cm⁻¹] 3027 (w), 2967 (w), 2928 (w), 2871 (w), 1647 (w), 1485 (s), 1089 (s), 1005 (s), 966 (s), 800 (s), 537 (m).
General Procedure

3.5 mg (1 mol%, 0.01 mmol) Co(acac)$_3$ were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dry THF and NMP (10/1 v/v). The resulting green solution was transferred to a water bath at 30°C and treated with 1 mmol of the chlorostyrene followed by 0.1 mmol of the freshly prepared arylmagnesium bromide (0.5 M in THF). Another 1.00 mmol ArMgBr was slowly added by syringe pump over a period 20 min, after which the mixture was stirred at 30°C for another 60 min. Then, saturated aqueous sodium hydrogencarbonate was added and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na$_2$SO$_4$) and concentrated in vacuo. Silica gel column chromatography (n-pentane/ethyl acetate) afforded the pure hetero-biaryl products.

Reaction Rates of Co- and Fe-Catalyzed Reactions (see Figure 1):

0.01 mmol (1 mol%) of M(acac)$_3$ (M = Fe, Co) were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dry THF and NMP (10/1, v/v). The resulting solution was put in a water bath at 30°C and treated with 1 mmol of 2-chlorostyrene and 1 mmol of n-pentadecane (internal GC reference). After 1 min, an aliquot (0.05 mL) was taken from the mixture, quenched with saturated aqueous NaHCO$_3$, extracted with ethyl acetate (1 mL) and analyzed by quantitative GC/FID.

4-Methoxyphenylmagnesium bromide (0.5 M in THF) was added rapidly (over 2 s). After stirring for 30 sec, 60 sec, 90 sec, 120 sec, and 180 sec, an aliquot (0.05 mL) was again collected and analyzed as described above. The concentration of all organic components were determined using n-pentadecane as an internal GC standard.

Representative Procedure for Initial Optimization Experiments (see Table 1):

**Entry 1:** 17.5 mg (5 mol%, 0.05 mmol) Co(acac)$_3$ were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dried THF and
NMP (10/1 v/v). The resulting green solution was put in a water bath at 30°C and treated with 1 mmol of 2-chlorostyrene (1) followed by 1.5 mmol of the freshly prepared 4-methoxyphenylmagnesium bromide solution (0.5 M in THF). The mixture was stirred at 30°C for 3h. Then, saturated aqueous sodium hydrogen carbonate was added, the mixture extracted with ethyl acetate and 275 µl (1mmol) n-pentadecane was added as internal standard. The yields of 2 were determined by GC-FID.

**Arylations of o-, m-, p-Chlorostyrenes (see Tables 2, 3, and 4):**

3.5 mg (1 mol%, 0.01 mmol) Co(acac)₃ were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dried THF and NMP (10/1, v/v). The resulting green solution was put in a water bath at 30°C and treated with 1 mmol of 2-chlorostyrene (1) followed by 0.1 mmol of the freshly prepared 4-methoxyphenylmagnesium bromide solution (0.5 M in THF). The remaining 1.00 mmol ArMgBr was slowly added by syringe pump over a period 20 min (or 40 min for α-substituted chlorostyrenes). The mixture was then stirred at 30°C for another 40 min. Then, saturated aqueous NaHCO₃ was added, and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na₂SO₄) and concentrated in vacuo. Silica gel column chromatography (n-pentane/ethyl acetate) afforded the pure biaryl products.

**Fe- vs. Co-Catalyzed Arylation of 4-Chlorostyrene (see Scheme 2):**

See General Procedure above. GPC analyses of the crude product mixtures were performed by Prof. Bernd Tieke, Institute of Physical Chemistry, University of Cologne.

**Unreactive Substrates (see Scheme 3):**

See General Procedure above.

**Chemoselectivity Study (see Table 3):**

See above. Addition of 1 equiv. of the additive immediately after the addition of 2-chlorostyrene (1). Product analysis by quantitative GC/FID (vs. n-pentadecane as internal reference).

**Arylations of 4-Chlorostyrene (see Table 4):**

See above.
Competitive Halostyrene Arylations (see Scheme 4):
See General Procedure above, but with 0.5 mmol 2-chlorostyrene and 0.5 mmol 2-bromostyrene. Slow addition (over 20 min) of 1 equiv. (1 mmol) 4-anisylmagnesium bromide in THF. After another 10 min at 30°C, work-up and product analysis according to the General Procedure. The reaction rates were determined from the conversions of 2-chlorostyrene and 2-bromostyrene by quantitative GC/FID.

Chemoselectivity Study with Aryl Bromides (see Table 5):
See above. Addition of 1 equiv. of the aryl bromide immediately after the addition of 2-chlorostyrene (1). Product analysis by quantitative GC/FID (vs. n-pentadecane as internal reference).

Substituent Effects (see Table 6):
3.5 mg (1 mol%, 0.01 mmol) Co(acac)₃ were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dried THF and NMP (10/1 v/v). The resulting green solution was put in a water bath at 30°C and treated with 1 mmol of the aryl chloride followed by 1.1 mmol of the freshly prepared arylmagnesium bromide solution (0.5 M in THF, rapid addition over 2 s). The mixture was stirred at 30°C for 1h. Then, saturated aqueous sodium hydrogen carbonate was added, the mixture extracted with ethyl acetate and 275 μl (1 mmol) n-pentadecane was added as internal standard. The combined organic phases were dried (Na₂SO₄) and concentrated in vacuo. Product analysis by quantitative GC/FID (vs. n-pentadecane as internal reference) or isolation of pure biaryls by silica gel column chromatography (n-pentane/ethyl acetate).

Addition of (external) styrene:

For R = H and R = Me, low conversions (of PhCl) were observed under standard conditions when employing chlorobenzene as electrophilic coupling partner.
Secondary Kinetic Isotope Effect (see Scheme 5):
Preparation of d1-3: A 50 mL flask was charged with LiAlD₄ (200 mg, 4.7 mmol) and diethylether (10 mL), cooled to 0 °C. Then, a solution of 4-chloroacetophenone (1.54 g, 10 mmol) in diethylether (5 mL) was slowly added at 0°C upon which hydrogen gas evolved. The reaction was warmed to r.t., and after 1 h was quenched by dropwise addition of water (3 mL) and aqueous HCl (3 mL, 10%). The mixture was extracted with ethyl acetate (3x3 mL), the organic phases washed with water (2x10 mL), dried over Na₂SO₄, and the solvent removed in vacuum. The residue was dissolved in toluene (10 mL), p-toluenesulfonic acid monohydrate (75 mg) was added, and the reaction heated to reflux for 8 h (TLC monitoring). Then, the solvent was removed in vacuum, and the crude product subjected to silica gel flash chromatography (cyclohexane) to give d1-3 as a colorless liquid in 66% yield (912 mg).

Cross-coupling reaction: An equimolar mixture of 3 and d1-3 (50% D content by ¹H NMR) was reacted under slightly modified standard conditions (rapid addition of 0.5 M 4-anisylmagnesium bromide solution over 2 s, 1 min reaction time, 18°C, Co(acac)₃ or complex 7 as pre-catalysts). Careful ¹H NMR analysis of the crude reactions and the isolated product mixtures documented an erosion of deuterium content in the biaryl coupling product (from 50% to ~43% D, with Co(acac)₃ and 7, average of two runs for each pre-catalyst).
1 mol% Co(acac)$_3$ THF, 10% NMP rt, 1 min

1.1 equiv. (rapid addition)
An identical procedure was followed for $(\text{Ph}_3\text{P})_3\text{CoCl}$ (7) as pre-catalyst.
Preparation of [K(dme){Co(C_{14}H_{10})_2}] (4):

All manipulations were performed under an atmosphere of dry argon using standard Schlenk and glovebox techniques. Compound 4 was prepared by modification of the literature procedures for [K([18]crown-6)(thf)_2][Co(C_{14}H_{10})_2] and [K([2.2.2]cryptand)][Co(C_{14}H_{10})_2]: W. W. Brennessel, V. G. Young, Jr., J. E. Ellis, Angew. Chem. Int. Ed. 2002, 41, 1211.

A suspension of anhydrous CoBr_2 (5.455 g, 25.00 mmol) in 1,2-dimethoxyethane (DME, 350 mL, –78°C) was added by cannula to a freshly-prepared, deep blue solution of KC_{14}H_{10} (75.00 mmol) in DME (300 mL, –78°C). The reaction mixture turned deep red during the transfer and was allowed to warm to room temperature overnight. After filtration, n-heptane (150 mL) was added and the solvent was concentrated in vacuo until the deep red mixture became turbid and a dark precipitate began to form. Then diethyl ether (ca. 450 mL) was added, whereupon a dark solid precipitated. Recrystallization from DME/diethyl ether (1:3) afforded dark red, X-ray quality crystals of [K(dme)_2{Co(C_{14}H_{10})_2}] (4). Upon drying in high vacuum, 7.89 g (15.62 mmol, 63% based on CoBr_2) of 4 have been obtained.

M.p. 104-107 °C. ¹H NMR (400.03 MHz, [d_8]THF, 300 K): δ 3.05 (br s, 4H, H_{1,4} of anthracene), 3.27 (s, 12H, DME, OCH_3), 3.43 (s, 8H, DME, OCH_2), 5.05 (br s, 4H, H_{2,3} of anthracene), 6.27 (br s, 4H, H_{9,10} of anthracene), 6.73 (br s, 4H, H_{5,8} or H_{6,7} of anthracene), 6.93 (br s, 4H, H_{6,7} or H_{6,8} of anthracene). ¹³C{¹H} NMR (100.63 MHz, [d_8]THF, 300 K): δ 54.2 (br, C_{1,4} of anthracene), 58.8 (s, DME, OCH_3), 72.6 (s, DME, OCH_2), 74.8 (br, C_{2,3} of anthracene), 109.4 (s, C_{9,10} of anthracene), 122.0 (s, C_{5,8} or C_{6,7} of anthracene), 124.9 (s, C_{5,8} or C_{6,7} of anthracene), 133.5 (C_{13,14} of anthracene), 145.7 (C_{11,12} of anthracene).
Single Crystal X-ray Structure Determination of [K(dme)$_2${Co(C$_{14}$H$_{10}$)$_2$}] (4):

X-ray diffraction data for 4 were collected on an Oxford Diffraction SuperNova diffractometer at 123(1) K using a copper microfocus X-ray source with mirror optics ($\lambda = 1.54178$ Å) and a CCD area detector. A semi-empirical absorption correction from equivalents was applied: SCALE3 ABSPACK, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52, 2009.

Structure solutions were obtained with the SHELXS-97 package using the direct method and were refined with SHELXL-97 against $F^2$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms (G. M. Sheldrick, Acta Cryst. 2008, A64, 112). Some of the hydrogen atoms on the anthracene ligands were localized on the Fourier difference map and freely refined. The remaining hydrogens were generated with idealized geometries and isotropically refined using a riding model.

The structure displays two crystallographically independent molecules of 4 in the asymmetric unit. The oxygen atoms of all DME molecules bound to the potassium cations (K1 and K2) were disordered. The atoms affected by the disorder were refined over split positions with isotropic adp's. EADP and SADI instructions were used in order to obtain reasonable geometries and temperature factors.
Table. Crystal Data and Structure Refinement of 4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₃₆H₄₀CoKO₄</td>
</tr>
<tr>
<td>( M_r ) [g mol⁻¹]</td>
<td>634.71</td>
</tr>
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<td>dimension [mm³]</td>
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<td>grey rod</td>
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<tr>
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<tr>
<td>( c ) [Å]</td>
<td>21.0264(4)</td>
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<tr>
<td>( \beta ) [°]</td>
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<tr>
<td>( \gamma ) [°]</td>
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<td>( V ) [Å³]</td>
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<td>( Z )</td>
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<td>( T ) [K]</td>
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<tr>
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<td>residual density [e Å⁻³]</td>
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<td>GOF</td>
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<tr>
<td>( R_1 ) [I&gt;3σ(I)]</td>
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</tr>
<tr>
<td>( wR_2 ) (all data)</td>
<td>0.1800</td>
</tr>
<tr>
<td>CCDC</td>
<td>884015</td>
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</table>
Stoichiometric Studies of 4 with Aryl Chlorides (see Scheme 6):

With 2-chlorostyrene (1):
In a glovebox, 54 mg (0.85 equiv., 0.085 mmol) of 4 were weighed into a 10 mL-flask under an atmosphere of argon and treated with 4 mL dry THF at 22°C. Then, 12.6 µL (0.1 mmol) 2-chlorostyrene and 27.5 µL (0.1 mmol) of n-pentadecane were added. After 120 min, the reaction was removed from the glovebox, saturated aqueous NaHCO₃ was added, and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na₂SO₄), concentrated in vacuo, and analyzed by GC/FID.

With 4-chloro-α-methylstyrene:
As above. 14.2 µL (0.1 mmol) 4-chloro-α-methylstyrene.

With 2-chloronaphthalene:
As above. 13 µL (0.1 mmol) 2-chloronaphthalene.

Comparison of [Co] Pre-Catalysts (see Table 7):

Synthetic procedures as described in the General Procedure above, but reactions were performed at room temperature (22°C).

Kinetic Studies of Initial Reaction Rates (see Figure 3, bottom):
(Ar'-'Ar') was not observed. All other electron transfer processes operating under the reaction conditions must be related to redox process of the cobalt species (mono-anionic acetylacetonate is stable under the reaction conditions). The model reaction was performed on doubled scale (2 mmol) in the presence of n-pentadecane as internal reference. 4-Anisylmagnesium bromide (1.1 equiv., 0.5 M in THF) was added in small portions every 30 sec (2 mol%, 2 mol%, 2 mol% 4 mol%, 10 mol%, 10 mol%, 20 mol%, 60 mol%). Aliquots were always taken 10 sec after addition, quenched (NaHCO₃/H₂O), dried (Na₂SO₄), and analyzed by quantitative GC/FID.

Model reaction (see General procedure above):

![Model reaction diagram]

The model reaction was performed on doubled scale (2 mmol) with 5 mol% pre-catalyst loading and in the presence of n-pentadecane as internal reference. 4-Anisylmagnesium bromide (1.1 equiv., 0.5 M in THF) was added in small portions every 30 sec (2 mol%, 2 mol%, 2 mol% 4 mol%, 10 mol%, 10 mol%, 20 mol%, 60 mol%). Aliquots were always taken 10 sec after addition, quenched (NaHCO₃/H₂O), dried (Na₂SO₄), and analyzed by quantitative GC/FID. In the following, the concentrations of all organic materials (except for the quenched Grignard species ArH) and the electrons transferred (to/from the catalyst species) are given in [%].

5 mol% Co(I) pre-catalyst, (Ph₃P)₃CoCl (7):

<table>
<thead>
<tr>
<th>+ArMgBr</th>
<th>Ar'-Cl</th>
<th>Ar-Ar'</th>
<th>Ar'-H</th>
<th>Ar₂</th>
<th>Ar total</th>
<th>Ar' total</th>
<th>electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
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<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
<td>99 %</td>
<td>0 %</td>
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<tr>
<td>2</td>
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<td>0</td>
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<td>1</td>
<td>0.4</td>
<td>3</td>
<td>100</td>
<td>+1</td>
</tr>
<tr>
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<td>4</td>
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<td>+1</td>
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<tr>
<td>10</td>
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<td>2</td>
<td>1</td>
<td>8</td>
<td>101</td>
<td>+2</td>
</tr>
</tbody>
</table>
5 mol% Co(-I) pre-catalyst, K(dme)$_2$ [(C$_{14}$H$_{10}$)$_2$Co] (4):

<table>
<thead>
<tr>
<th>+ArMgBr</th>
<th>Ar$^+$-Cl</th>
<th>Ar-Ar$^+$</th>
<th>Ar$^+$-H</th>
<th>Ar$_2$</th>
<th>Ar total</th>
<th>Ar$^+$ total</th>
<th>electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>96 %</td>
<td>0 %</td>
<td>4 %</td>
<td>0 %</td>
<td>100 %</td>
<td>0 %</td>
<td>+8 %</td>
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<tr>
<td>1</td>
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<td>4</td>
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<td>+8</td>
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<td>8</td>
<td>6</td>
<td>66</td>
<td>99</td>
<td>+2</td>
</tr>
</tbody>
</table>

5 mol% Co(III) pre-catalyst, Co(acac)$_3$:

<table>
<thead>
<tr>
<th>+ArMgBr</th>
<th>Ar$^+$-Cl</th>
<th>Ar-Ar$^+$</th>
<th>Ar$^+$-H</th>
<th>Ar$_2$</th>
<th>Ar total</th>
<th>Ar$^+$ total</th>
<th>electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>99 %</td>
<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
<td>99 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>99</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>99</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>99</td>
<td>0</td>
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</tr>
<tr>
<td>3</td>
<td>98</td>
<td>0.4</td>
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<td>98</td>
<td>0</td>
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</tr>
<tr>
<td>4</td>
<td>98</td>
<td>0.6</td>
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<tr>
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<td>1</td>
<td>5.5</td>
<td>99</td>
<td>-9</td>
<td></td>
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<tr>
<td>40</td>
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<td>2</td>
<td>7.5</td>
<td>98</td>
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<tr>
<td>60</td>
<td>54</td>
<td>40</td>
<td>3</td>
<td>10</td>
<td>97</td>
<td>-14</td>
<td></td>
</tr>
</tbody>
</table>

The amount of the quenched Grignard species ArMgBr, anisole (Ar-H), was not determined. The amount of added ArMgBr was not included into the calculation of “total Ar” content. The
mol% electrons being transferred were calculated from the observed oxidation product \( \text{Ar}_2 \) and reduction product \( \text{Ar}’\text{H} \) (each 2e-processes per 1 mole generated). Any other operating redox process must relate to the catalyst species, so that an electron excess (+ x%) results from the oxidation of the employed cobalt species (mostly by the penetration of air into the system), while an electron deficiency (- x%) is a consequence of pre-catalyst reduction (by reduction with the Grignard species). For complex 4, oxidation can also occur under strict exclusion of air with chlorostyrene acting as oxidant. Dehalogenative styrene dimerization (another potential oxidation process) was not observed. The formations of anisole, polymer, and cross-coupling product are not redox processes. The general trend of more reductive processes of the cobalt species operating with increased amounts of ArMgX added mirrors the penetration of air into the system by repetitive sampling with microliter syringes. This results in unwanted catalyst oxidation which requires reduction by ArMgBr again.

**Stoichiometric Reactions with Complex 7 (see Scheme 7):**

Scheme 7, **top**: 440.5 mg (100 mol%, 0.5 mmol) \((\text{Ph}_3\text{P})_3\text{CoCl} \) (7) were loaded into a 25 mL-flask under an atmosphere of argon and treated with 8.8 mL of a solvent mixture containing dry THF and NMP (10/1, v/v). The resulting green solution was put in a water bath at 30°C and treated with 137.5 μL (0.5 mmol) of \( \text{n-pentadecane} \) followed by 1 mL (0.5 mmol) 4-methoxyphenylmagnesium bromide (0.5 M in THF). After 5 min, an aliquot (0.05 mL) was taken from the mixture, quenched with a saturated NaHCO\(_3\) solution (1 mL), filtered through a small silica plug, diluted with ethyl acetate (1 mL) and analyzed by quantitative GC/FID. After addition of 63 μL (0.5 mmol) 2-chlorostyrene (1) and 5 min stirring, an aliquot (0.05 mL) was collected and analyzed as described above. Then, 1 mL (0.5 mmol) 4-methoxyphenylmagnesium bromide (0.5 M in THF) was added to the reaction. After 10 min, saturated aqueous NaHCO\(_3\) was added and the mixture extracted with ethyl acetate (3x5 ml). The combined organic phases were dried (Na\(_2\)SO\(_4\)) and analyzed by quantitative GC/FID.

Scheme 7, **bottom**: 440.5 mg (100 mol%, 0.5 mmol) \((\text{Ph}_3\text{P})_3\text{CoCl} \) (7) were loaded into a 25 mL-flask under an atmosphere of argon and treated with 8.8 mL of a solvent mixture containing dry THF and NMP (10/1, v/v). The resulting green solution was put in a water bath at 30°C and treated with 137.5 μL (0.5 mmol) of \( \text{n-pentadecane} \) followed by 63 μL (0.5
mmol) 2-chlorostyrene (I). After 10 min, an aliquot (0.05 mL) was taken from the mixture, quenched with a saturated NaHCO₃ solution (1 mL), filtered through a small silica plug, diluted with ethyl acetate (1 mL) and analyzed by quantitative GC/FID. After addition of 1 mL (0.5 mmol) 4-methoxyphenylmagnesium bromide (0.5 M in THF) and 5 min stirring, an aliquot (0.05 mL) was collected and analyzed as described above. Then, 1 mL (0.5 mmol) 4-methoxyphenylmagnesium bromide (0.5 M in THF) was added to the reaction. After 10 min, saturated aqueous NaHCO₃ was added and the mixture extracted with ethyl acetate (3x5 ml). The combined organic phases were dried (Na₂SO₄) and analyzed by quantitative GC/FID.
Determination of reaction order in [Co] (see Scheme 8, bottom left):

The reaction order with respect to the catalyst [Co] was determined by changing the concentration of the pre-catalyst Co(acac)$_3$ (0.0007-0.003 M, i.e. 0.5-1.9 mol%) with constant reactant concentrations (0.151 M I, 0.166 M ArMgBr) of the reaction. The reaction order in [Co] is 1.02 for highly diluted catalyst concentrations (≤0.001 M or ≤0.7 mol%). This value slightly decreased to 0.85 when considering [Co]$_0$ of ≤0.0015 M (or ≤1 mol%) as a consequence of catalyst aggregation.

Determination of reaction order based on product concentration:

[Co]$_0$ dependent yield-time plot:

<table>
<thead>
<tr>
<th>[Co]$_0$</th>
<th>$v_0$</th>
<th>$\lg [Co]_0$</th>
<th>$\lg v_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003 mmol</td>
<td>5.3327</td>
<td>-2.5228</td>
<td>0.7269</td>
</tr>
<tr>
<td>0.002 mmol</td>
<td>4.5324</td>
<td>-2.6989</td>
<td>0.6563</td>
</tr>
<tr>
<td>0.0015 mmol</td>
<td>3.8154</td>
<td>-2.823</td>
<td>0.5815</td>
</tr>
<tr>
<td>0.001 mmol</td>
<td>2.8858</td>
<td>-3</td>
<td>0.4602</td>
</tr>
<tr>
<td>0.0007 mmol</td>
<td>2.006</td>
<td>-3.154</td>
<td>0.3023</td>
</tr>
</tbody>
</table>

Reaction order in catalyst for [Co]$_0$ = 0.0015-0.0007 M: 0.85
Reaction order in catalyst for $[\text{Co}]_0 = 0.001-0.0007 \text{ M}$: $y = 0.85$

Reaction order in catalyst for $[\text{Co}]_0 = 0.001-0.0007 \text{ M}$: $y = 1.02$
Determination of reaction order based on chlorostyrene (1) concentration:

[Co]₀ dependent concentration-time plot:

<table>
<thead>
<tr>
<th>[Co]₀</th>
<th>v₀</th>
<th>lg [Co]₀</th>
<th>lg v₀</th>
</tr>
</thead>
<tbody>
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<td>0,003</td>
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<td>0,002</td>
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<td>0,0015</td>
<td>4,2836</td>
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<td>0,001</td>
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<tr>
<td>0,0007</td>
<td>2,2174</td>
<td>-3,154</td>
<td>0,3458</td>
</tr>
</tbody>
</table>

Reaction order in catalyst for [Co]₀ = 0.0015-0.0007 M: 0.86

Reaction order in catalyst for [Co]₀ = 0.001-0.0007 M: 1.12
Biaryl Products

For the general procedure and details on spectroscopic methods see General part above. Isolated yields are given (GC yields in parentheses).

Biaryls from Table 2:

4’-Methoxy-2-vinylbiphenyl (2)
Colorless oil.

\[
\text{C}_{15}\text{H}_{14}\text{O} \quad (210.10 \text{ g/mol})
\]

Yield 87%

TLC \( R_f = 0.45 \) (SiO\(_2\), \( n \)-pentane/ethyl acetate (95:5))

GC-MS \( R_t = 8.36 \) min (Standard heating procedure)
\[m/z \ 210[M], 194, 179, 165, 152, 139, 127, 115, 102, 89, 75, 63, 52.\]

HRMS (EI, 70 eV, m/z): 210.105, calcd: 210.1045

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)), \( \delta \) 7.70-7.60 (m; 1H), 7.40-7.20 (m; 5H), 6.96 (d; 2H, 8.7 Hz), 6.74 (dd; 1H, 10.9/6.4 Hz), 5.70 (dd; 1H, 17.5/1.1 Hz), 5.19 (dd; 1H, 11.0/1.1 Hz), 3.86 (s; 3H).

\(^{13}\text{C-APT-NMR}\) (75 MHz, CDCl\(_3\)), \( \delta \) 158.9 (Q), 140.6 (Q), 136.2 (-CH=), 135.9 (Q), 133.3 (Q), 131.0 (CH\(_{Ar}\)), 130.2 (CH\(_{Ar}\)), 127.7 (CH\(_{Ar}\)), 127.2 (CH\(_{Ar}\)), 125.8 (CH\(_{Ar}\)), 114.6 (=CH\(_2\)), 113.6 (CH\(_{Ar}\)), 55.4 (OCH\(_3\)).

FT-IR (ATR film) \( \nu \) [cm\(^{-1}\)] 3056 (m), 2952 (m), 2832 (m), 2533 (w), 2046 (w), 1890 (w), 1820 (w), 1686 (w), 1608 (s), 1513 (s), 1474 (s), 1240 (s), 1175 (s).
2-Vinylbiphenyl

Colorless oil.

![Structure of 2-Vinylbiphenyl]

C₁₄H₁₂ (180.09 g/mol)

**Yield** 80% (88%)

**TLC** Rₚ 0.36 (SiO₂, cyclohexane)

**GC-MS** Rₜ 9.46 min (Standard heating procedure)

m/z 180[M], 165, 151, 129, 115, 89, 63.

**¹H-NMR** (300 MHz, CDCl₃), δ 7.70-7.60 (m; 1H), 7.48-7.26 (m; 8H), 6.71 (dd; 1H, 11.0/6.5 Hz), 5.69 (d; 1H, 17.5 Hz), 5.18 (d; 1H, 10.9 Hz).

**¹³C-APT-NMR** (75 MHz, CDCl₃), δ 141.0 (Q), 136.7 (Q), 136.0 (-CH=), 135.9 (Q), 130.2 (CH₆), 128.1 (CH₆), 127.8 (CH₆), 127.6 (CH₆), 127.1 (CH₆), 125.8 (CH₆), 114.8 (=CH₂).

**FT-IR** (ATR film) 1/λ [cm⁻¹] 3058 (m), 3010 (m), 2885 (s), 2774 (m), 2496 (w), 2285 (w), 2033 (w), 1953 (w), 1922 (w), 1829 (m), 1623 (m), 1605 (m), 1500 (s), 1472 (s), 1336 (s), 1195 (s), 1095 (s), 993 (s), 812 (s), 771 (s), 721 (m).

4-N,N-Dimethylamino-2'-vinylbiphenyl

Yellow oil.

![Structure of 4-N,N-Dimethylamino-2'-vinylbiphenyl]

C₁₆H₁₇N (223.14 g/mol)

**Yield** 81% (93 %)

**TLC** Rₚ 0.5 (SiO₂, n-pentane/ethyl acetate (9:1))

**GC-MS** Rₜ 9.18 min (Standard heating procedure)

m/z 233[M], 223, 207, 193, 178, 165, 152, 139, 128, 110, 105, 89, 77, 63, 51.

**HRMS** (EI, 70 eV, m/z): 223.136, calcd 223.1361
\[ ^1\text{H-NMR} \ (300 \text{ MHz, CDCl}_3), \delta \ 7.67-7.60 \ (m; 1\text{H}), 7.35-7.20 \ (m; 5\text{H}), 6.90-6.75 \ (m; 3\text{H}), 5.70 \ (dd; 1\text{H}, 17.5/1.1 \text{ Hz}), 5.19 \ (dd; 1\text{H}, 11.0/1.1 \text{ Hz}), 3.0 \ (s; 6\text{H}). \]

\[ ^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3), \delta \ 149.7 \ (Q), 141.1 \ (Q), 136.7 \ (-\text{CH=}), 135.9 \ (Q), 130.7 \ (\text{CH}_2), 130.2 \ (\text{CH}_2), 128.9 \ (Q), 127.7 \ (\text{CH}_2), 126.8 \ (\text{CH}_2), 125.9 \ (\text{CH}_2), 114.1 \ (=\text{CH}_2), 112.1 \ (\text{CH}_2), 40.7 \ (\text{CH}_3). \]

\[ \text{FT-IR} \ (\text{ATR film}) \ \lambda/\text{cm}^{-1} \ 3020 \ (m), 2882 \ (m), 2358 \ (w), 1819 \ (w), 1820 \ (w), 1677 \ (m), 1609 \ (m), 1520 \ (m), 1165 \ (m), 1057 \ (m), 819 \ (m), 759 \ (m). \]

**Ethyl 2'-vinyl-[1,1'-biphenyl]-4-carboxylate**

Colorless oil.

**General Procedure (20 min)**

\[ \text{C}_{17}\text{H}_{16}\text{O}_2 \ (252.11 \text{ g/mol}) \]

**Yield** 70%

**TLC** R\(_f\) 0.34 (SiO\(_2\), n-pentane/ethyl acetate (95:5))

**GC-MS** R\(_f\) 10.30 min (Standard heating procedure)

m/z 252[M], 223, 207, 179, 165, 152, 139, 126, 115, 103, 89, 76, 63, 51.

**HRMS** (EI, 70 eV, m/z): 252.1152, calcd 252.1150

\[ ^1\text{H-NMR} \ (300 \text{ MHz, CDCl}_3), \delta \ 8.14-8.04 \ (m; 2\text{H}), 7.66 \ (dd; 1\text{H}; 7.3/1.9 \text{ Hz}), 7.47-7.27 \ (m; 5\text{H}), 6.66 \ (dd; 1\text{H}, 17.5/6.6 \text{ Hz}), 5.72 \ (dd; 1\text{H}, 17.5/1.3 \text{ Hz}), 5.21 \ (dd; 1\text{H}, 11.0/1.2 \text{ Hz}), 4.42 \ (q; 2\text{H}, 7.1 \text{ Hz}), 1.42 \ (t; 3\text{H}, 7.1 \text{ Hz}). \]

\[ ^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3), \delta \ 166.7 \ (O=\text{C}), 145.6 \ (Q), 139.9 \ (Q), 135.9 \ (Q), 135.6 \ (-\text{CH=}), 132.9 \ (Q), 130.0 \ (\text{CH}_2), 129.9 \ (\text{CH}_2), 129.4 \ (\text{CH}_2), 128.2 \ (\text{CH}_2), 127.9 \ (\text{CH}_2), 126.1 \ (\text{CH}_2), 115.5 \ (=\text{CH}_2), 61.1 \ (\text{OCH}_2), 14.5 \ (\text{CH}_3). \]

**FT-IR** (ATR film) 1/\(\lambda\) [cm\(^{-1}\)] 3063 (w), 2983 (w), 2935 (w), 2906 (w), 1713 (s), 1609 (m), 1284 (s), 1177 (m), 1098 (s), 1021 (m), 749 (s), 708 (s).
4'-Fluoro-3'-methyl-2-vinylbiphenyl

Colorless oil.

![Chemical Structure](image)

C₁₅H₁₃F (212.10 g/mol)

**Yield** 73%

**TLC** Rₜ 0.34 (SiO₂, n-pentane)

**GC-MS** Rt 7.55 min (Standard heating procedure)

m/z 212[M], 197, 177, 173, 152, 133, 115, 98, 83, 63.

**HRMS** (EI, 70 eV, m/z): 212.100, calcd 212.1001

**¹H-NMR** (300 MHz, CDCl₃), δ 7.71-7.61 (m; 1H), 7.40-7.05 (m; 6H), 6.70 (dd; 1H, 10.9/6.5 Hz), 5.71 (dd; 1H, 17.5/1.1 Hz), 5.20 (dd; 1H, 11.0/1.1 Hz), 2.33 (s; 3H).

**¹³C-APT-NMR** (75 MHz, CDCl₃), δ 161.1 (Q; d; 245 Hz), 160.8 (Q; d; 249 Hz), 140.2 (Q), 136.6 (Q; d; 3.4 Hz), 135.9 (-CH=), 132.9 (CH₃Ar; d; 5.1 Hz), 130.2 (CH₂Ar), 128.8 (CH₃Ar; d; 7.9 Hz), 127.7 (CH₃Ar; d; 12.5 Hz), 125.8 (CH₃Ar), 124.5 (Q; d; 18 Hz), 115.4 (CH₃Ar; d; 23 Hz), 114.9 (=CH₂), 114.7 (CH₃Ar; d; 22 Hz), 14.8 (Ar-CH₃).

**FT-IR** (ATR film) 1/λ [cm⁻¹] 3060 (m), 3020 (m), 2924 (m), 2853 (m), 1923 (w), 1876 (w), 1816 (w), 1690 (m), 1593 (m), 1493 (s), 1228 (s), 1118 (s), 823 (s), 762 (s).
2-(2'-Vinylbiphenyl-4-yloxy)tetrahydro-2H-pyran

Colorless oil.

\[
\begin{align*}
\text{C}_{19}\text{H}_{20}\text{O}_{2} \ (280.15 \ g/mol)
\end{align*}
\]

**Yield** 83%

**TLC** \( R_f \) 0.20 (SiO\(_2\), cyclohexane/ethyl acetate (98:2))

**HRMS** (EI, 70 eV, m/z): 280.146, calcd 280.1463

**GC-MS** \( R_t \) 7.74 min (Standard heating procedure)

\[ m/z \ 280[M], \ 196, \ 179, \ 165, \ 139, \ 115, \ 101, \ 85, \ 69, \ 55. \]

**\( ^1\)H-NMR** (300 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) 7.66-7.58 (m; 1H), 7.36-7.26 (m; 4H), 7.13-6.93 (m; 3H), 6.74 (dd; 1H, 11.0/6.5 Hz), 5.68 (d; 1H, 17.5 Hz), 5.46 (t; 1H, 5.46 Hz), 5.12 (d; 1H, 11.0 Hz), 4.05-3.54 (m; 2H), 2.13-1.58 (m; 6H).

**\( ^{13}\)C-APT-NMR** (75 MHz, CD\(_2\)Cl\(_2\)), \( \delta \) 156.4 (Q), 140.6 (Q), 136.2 (-CH=), 135.9 (Q), 134.2 (Q), 131.0 (CH\(_Ar\)), 130.2 (CH\(_Ar\)), 127.7 (CH\(_Ar\)), 127.3 (CH\(_Ar\)), 125.8 (CH\(_Ar\)), 116.0 (CH\(_Ar\)), 114.5 (=CH\(_2\)), 96.5 (CH), 62.2 (CH\(_2\)), 30.5 (CH\(_2\)), 25.4 (CH\(_2\)), 19.0 (CH\(_2\)).

**FT-IR** (ATR film) 1/\( \lambda \) [cm\(^{-1}\)] 3080 (m), 3056 (m), 2940 (s), 2871 (s), 2848 (m), 2461 (w), 2354 (w), 2918 (w), 1823 (w), 1607 (s), 1512 (s), 1445 (s), 1355 (s), 1258 (s), 1175 (s), 1109 (s), 997 (s), 834 (s), 757 (s), 691 (m).

4'-Chloro-2-methoxy-6-vinylbiphenyl

Colorless oil.

\[
\begin{align*}
\text{C}_{15}\text{H}_{13}\text{ClO} \ (244.07 \ g/mol)
\end{align*}
\]

**Yield** 84%

**GC-MS** \( R_t \) 8.78 min (Standard heating procedure)

\[ m/z \ 244], \ 228, \ 209, \ 193, \ 183, \ 165, \ 139, \ 115, \ 99, \ 82, \ 63. \]

**HRMS** (EI, 70 eV, m/z): 244.066, calcd 244.0655
**1H-NMR** (300 MHz, CDCl3), δ 7.39-7.16 (m; 6H), 6.89 (dd; 1H, 7.7/1.2 Hz), 6.40 (dd; 1H, 11.0/6.5 Hz), 5.64 (dd; 1H, 17.5/1.1 Hz), 5.13 (dd; 1H, 11.0/1.2 Hz), 3.72 (s; 3H).

**13C-NMR** (75 MHz, CDCl3), δ 156.9 (Q), 137.9 (Q), 135.4 (-CH=), 135.0 (Q), 133.0, 132.3, 128.8 (Q), 128.7, 128.2, 117.9, 115.4, 110.1, 55.9 (OCH3).

**FT-IR** (ATR-Film) 1/\(\tilde{\nu}\) [cm\(^{-1}\)] 2926 (m), 2826 (m), 2360 (m), 1569 (s), 1465 (s), 1254 (s), 1068 (s), 1002 (s), 827 (s), 743 (s).

---

**2'-Methoxy-4-N,N-dimethylamino-6'-vinylbiphenyl**

![Chemical structure](image)

White solid.

C\(_{17}\)H\(_{19}\)NO (253.15 g/mol)

**Yield** 72%

**TLC** R\(_f\) 0.18 (SiO\(_2\), cyclohexane/ethyl acetate (95:5))

**Melting point** 110°C

**GC-MS** R\(_t\) 10.40 min (Standard heating procedure)
m/z 253[M], 237, 222, 209, 178, 165, 152, 139, 127, 115, 104, 84, 63, 51.

**HRMS** (EI, 70 eV, m/z): 253.146, calcd 253.1467

**1H-NMR** (300 MHz, CDCl3), δ 7.20-7.32 (m; 2H), 7.12 (d; 2H, 8.1 Hz), 6.87 (t; 1H, 4.3 Hz), 6.78 (d; 2H, 8.1 Hz), 6.54 (dd; 1H, 10.6/6.7 Hz), 5.62 (d; 1H, 17.5 Hz), 5.09 (d; 1H, 10.9 Hz), 3.73 (s; 3H), 2.99 (s; 6H).

**13C-APT-NMR** (75 MHz, CDCl3), δ 152.4 (Q), 149.5 (Q), 138.2 (Q), 136.4 (-CH=), 131.7 (CHAr), 130.4 (Q), 127.7 (CHAr), 124.0 (Q), 117.8 (CHAr), 114.3 (=CH\(_2\)), 111.9 (CHAr), 110.1 (CHAr), 56.0 (OCH\(_3\)), 40.7 (NCH\(_3\)).

**FT-IR** (ATR film) 1/\(\tilde{\nu}\) [cm\(^{-1}\)] 3073 (m), 3006 (m), 2926 (m), 2828 (m), 2353 (w), 2126 (w), 1963 (w), 1920 (w), 1876 (w), 1823 (w), 1743 (w), 1611 (s), 1565 (s), 1463 (s), 1355 (s), 1252 (s), 1066 (s), 994 (s), 750 (s).
5-(4-Methoxyphenyl)-6-vinylbenzo[d][1,3]dioxole

C_{16}H_{14}O_{3} (254.09 g/mol)

Yield 89%

GC-MS R_t 9.84 min (Standard heating procedure)
m/z 254[M], 223, 195, 153, 127, 98, 63, 39.

HRMS (EI, 70 eV, m/z): 254.093, calcd 254.0943

1H-NMR (300 MHz, CDCl₃), δ 7.23-7.20 (m; 2H), 7.11 (s; 1H), 6.94-6.91 (m; 2H), 6.74 (s; 1H), 6.59 (dd; 1H, 10.9/6.6 Hz), 5.99 (s; 2H), 5.54 (dd; 1H, 17.4/0.9 Hz), 5.07 (dd; 1H, 10.9/1.0 Hz).

13C-NMR (75 MHz, CDCl₃), δ 147.3 (Q), 135.7, 135.1, 134.7, 134.7, 131.1, 129.9, 113.6, 112.7 (=CH₂), 110.6, 110.1, 105.3, 104.4, 101.3 (OCH₂), 55.5 (OCH₃).

FT-IR (ATR film) 1/λ [cm⁻¹] 2896 (w), 1607 (w), 1499 (m), 1474 (s), 1241 (s), 1210 (s), 1175 (m), 1043 (m), 935 w), 827 (s).

5-(4-Fluorophenyl)-6-vinylbenzo[d][1,3]dioxole

C_{15}H_{11}FO_{2} (242.07 g/mol)

Yield 85%

HRMS (EI, 70 eV, m/z): 242.073, calcd 242.0743

GC-MS R_t 8.76 min (Standard heating procedure)
m/z 242[M], 211, 183, 157, 133, 112, 91, 63, 39.

1H-NMR (300 MHz, CDCl₃), δ 7.30-7.20 (m; 2H), 7.15-7.00 (m; 3H), 6.71 (s; 1H), 6.55 (dd; 1H, 10.9/6.4 Hz), 5.99 (s; 2H), 5.55 (dd; 1H, 17.4/0.9 Hz), 5.08 (dd; 1H, 10.9/0.9 Hz).

13C-NMR (75 MHz, CDCl₃), δ 162.2 (Q; d; 123 Hz), 147.5 (Q; d; 11.0 Hz), 147.4, 136.7 (Q), 135.4 (-CH=), 134.3 (Q), 131.6 (d; 8.0 Hz), 129.9 (Q), 115.1 (d; 21 Hz), 113.2 (=CH₂), 110.0, 105.4, 101.4 (OCH₂).
5-(4-Fluoro-3-methylphenyl)-6-vinylbenzod[1,3]dioxole

\[
\text{C}_{16}\text{H}_{13}\text{FO}_{2} \text{ (256.09 g/mol)}
\]

**Yield** 77%

**GC-MS** Rt 9.15 min (Standard heating procedure)

m/z 256[M], 241, 211, 183, 157, 133, 98, 63, 39.

**HRMS** (EI, 70 eV, m/z): 256.090, calcd 256.0900

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)), \(\delta\) 7.15-6.99 (m; 4H), 6.71 (s; 1H), 6.57 (dd; 1H, 10.9/6.5 Hz), 5.99 (s; 2H), 5.54 (dd; 1H, 17.4/1.0 Hz), 5.07 (dd; 1H, 11.0/1.0 Hz), 2.30 (s; 3H).

**\(^{13}\)C-NMR** (75 MHz, CDCl\(_3\)), 160.7 (Q; d; 244 Hz), 147.4 (Q), 147.3 (Q), 136.4 (Q), 135.4 (Q), 134.6, 133.0, 129.9 (Q), 128.9 (d; 7.8 Hz), 124.5 (Q; d; 17 Hz), 114.6 (d; 22 Hz), 113.0 (=CH\(_2\)), 110.1, 105.2, 101.4 (OCH\(_2\)), 14.8 (Ar-CH\(_3\)).

**FT-IR** (ATR film) 1/\(\lambda\) [cm\(^{-1}\)] 2889 (w), 1499 (s), 1477 (s), 1427 (w), 1354 (w), 1239 (s), 1060 (m), 1118 (m), 1045 (m), 936 (m), 820 (m).

5-Chloro-4'-methoxy-2-vinylbiphenyl

Colorless oil.

\[
\text{C}_{15}\text{H}_{13}\text{ClO} \text{ (244.07 g/mol)}
\]

**Yield** 76%

**GC-MS** Rt 8.66 min (Standard heating procedure)

m/z 244[M], 208, 179, 165, 139, 115, 87, 63.
**4'-Fluoro-3-N,N-dimethylamino-6-vinylbiphenyl**

Yellow oil.

C<sub>16</sub>H<sub>16</sub>FN (241.13 g/mol)

**Yield** 74%

**TLC** R<sub>f</sub> 0.53 (SiO<sub>2</sub>, n-pentane/ethyl acetate (9:1))

**GC-MS** R, 9.02 min (Standard heating procedure)

m/z 240[M], 225, 211, 197, 183, 165, 144, 119, 98, 75, 51.

**HRMS** (EI, 70 eV, m/z): 241.126, calcd 241.1267

**1H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.56 (d; 1H, 8.7 Hz), 7.28-7.36 (m; 2H), 7.06 (m; 2H), 6.75 (dd; 1H, 8.8/2.7 Hz), 6.50-6.62 (m; 2H), 5.50 (dd; 1H, 17.5/1.3 Hz), 4.98 (dd; 1H, 11/1.3 Hz), 2.99 (s; 6H).

**13C-APT-NMR** (75 MHz, CDCl<sub>3</sub>), δ 162.2 (Q; d; 246 Hz), 150.0 (Q), 140.9 (Q), 137.8 (Q), 135.3 (-CH=), 131.4 (CH<sub>Ar</sub>; d; 7.7 Hz), 126.6 (CH<sub>Ar</sub>), 124.5 (Q), 114.9 (CH<sub>Ar</sub>; d; 21 Hz), 113.6 (CH<sub>Ar</sub>), 112.2 (CH<sub>Ar</sub>), 110.9 (=CH<sub>2</sub>), 40.6 (NCH<sub>3</sub>).

**FT-IR** (ATR-Film) 1/λ [cm<sup>-1</sup>] 3073 (m), 2973 (m), 2880 (m), 2799 (m), 2020 (w), 1960 (w), 1890 (w), 1790 (w), 1601 (s), 1496(s), 1358 (s), 1217 (s), 1156 (s), 1125 (s), 957 (s).
5-Chloro-4'-fluoro-3'-methyl-2-vinylbiphenyl

Colorless Oil.

![Structure of 5-Chloro-4'-fluoro-3'-methyl-2-vinylbiphenyl]

C\textsubscript{15}H\textsubscript{12}ClF (246.06 g/mol)

Yield 71%

GC-MS

R\textsubscript{t} = 8.42 min (Standard heating procedure)

m/z = 246[M], 196, 170, 133, 105, 77, 39.

HRMS

(El, 70 eV, m/z): 246.061, calcld 246.0612

\textsuperscript{1}H-NMR

(300 MHz, CDCl\textsubscript{3}), \(\delta = 7.54\) (d; 1H, 8.4 Hz), 7.35-7.00 (m; 5H), 6.60 (dd; 1H, 11.0/6.5 Hz), 5.66 (dd; 1H, 17.5/1.0 Hz), 5.20 (dd; 1H, 11.0/1.0), 2.31 (d; 3H, 1.8 Hz).

\textsuperscript{13}C-NMR

(75 MHz, CDCl\textsubscript{3}), 161.1 (Q; d; 245 Hz), 141.6 (Q), 135.4 (Q), 134.9 (-CH=), 134.5 (Q), 133.3 (Q), 132.8 (d; 5.2 Hz), 130.0, 128.7 (d; 8.0 Hz), 127.7, 127.2, 124.8 (Q; d; 17.4 Hz), 115.4 (=CH\textsubscript{2}), 114.8 (d; 22.4 Hz), 14.7 (Ar-CH\textsubscript{3}; d; 3.3 Hz).

FT-IR

(ATR film) in [cm\textsuperscript{-1}]= 3010 (w), 2920 (w), 1820 (w), 1589 (m), 1503 (s), 1469 (s), 1228 (s), 1118 (s), 1097 (m), 991 (m), 911 (s), 880 (m), 824 (s), 752 (s), 726 (s).

4'-Methoxy-3-(prop-1-en-2-yl)biphenyl

White solid.

General Procedure (ArMgBr addition over 40 min).

![Structure of 4'-Methoxy-3-(prop-1-en-2-yl)biphenyl]

C\textsubscript{16}H\textsubscript{16}O (224.12 g/mol)

Yield 78%

TLC

R\textsubscript{t} 0.31 (SiO\textsubscript{2}, hexanes/ethyl acetate (95:5))

Melting point 47 °C
4-Methoxy-4′-(prop-1-en-2-yl)biphenyl

White solid.

General Procedure (ArMgBr addition over 40 min).

C_{16}H_{16}O (224.12 g/mol)

Yield 80%

TLC R_f 0.30 (SiO₂, cyclohexane/ethyl acetate (98:2))

Melting Point 151°C

GC-MS R_t 10.02 min (Standard heating procedure)
m/z 224[M], 209, 194, 181, 165, 152, 139, 115, 89, 76, 63, 51.

HRMS (EI, 70 eV, m/z): 224.1198, calcd 224.1201

\(^{1}\)H-NMR (300 MHz, CDCl₃), \(\delta\) 7.70-7.36 (m; 6H), 6.99 (d; 2H, 8.9 Hz), 5.43 (dd; 1H, 1.5/0.8 Hz), 5.13 (d; 1H, 1.5 Hz), 3.86 (s; 3H), 2.21 (dd; 3H, 1.4/0.8 Hz).

\(^{13}\)C-NMR (75 MHz, CDCl₃), \(\delta\) 159.3 (Q), 143.5 (Q), 141.9 (Q), 141.0 (Q), 134.0 (Q), 128.8, 128.4, 126.1, 124.3, 124.1, 114.3, 112.8 (=CH₂), 55.5 (OCH₃), 22.1 (CH₃).

FT-IR (ATR film) 1/\(\nu\) [cm\(^{-1}\)] 2953 (w), 2927 (w), 2841 (w), 2044 (w), 1610 (m), 1515 (s), 1245 (s), 1080 (m), 891 (m), 833 (s), 797 (m).
4-N,N-Dimethyl-4'-((prop-1-en-2-yl)biphenyl
White solid.

General Procedure (ArMgBr addition over 40 min).

\[
\text{C}_{17}\text{H}_{19}\text{N} \quad (237.15 \text{ g/mol})
\]

**Yield** 69%

**TLC** \( R_f 0.18 \) (SiO\(_2\), hexanes/ethyl acetate (95:5))

**Melting point** 182 °C

**GC-MS** \( R_t 11.08 \) min (Standard heating procedure)

\( m/z \ 237[M], 221, 206, 194, 178, 165, 152, 139, 117, 89, 77, 63, 51. \)

**HRMS** (EI, 70 eV, m/z): 237.1515, calcd 237.1517

\( ^{1}\text{H-NMR} \) (300 MHz, CDCl\(_3\)), \( \delta \) 7.60-7.52 (m; 6H), 6.83 (d; 2H, 8.8 Hz), 5.42 (d; 1H, 0.8 Hz), 5.09 (s; 1H), 3.01 (s; 6H), 2.19 (s; 3H).

\( ^{13}\text{C-NMR} \) (75 MHz, CDCl\(_3\)), \( \delta \) 145.0 (Q), 143.0 (Q), 138.9 (Q), 131.1 (Q), 127.7 (Q), 127.7, 126.1, 125.9, 113.0, 112.0 (=CH\(_2\)), 40.8 (NCH\(_3\)), 22.0 (CH\(_3\)).

**FT-IR** (ATR film) \( \lambda [\text{cm}^{-1}] \) 2931 (w), 2804 (w), 2360 (m), 2268 (w), 1609 (w), 1508 (w), 1226 (w), 879 (w), 814 (m), 737 (w).

4-Fluoro-4'-((prop-1-en-2-yl)biphenyl
White solid.

General Procedure (ArMgBr addition over 40 min).

\[
\text{C}_{15}\text{H}_{13}\text{F} \quad (212.10 \text{ g/mol})
\]

**Yield** 76%
TLC  \( R_f \) 0.29 (SiO₂, n-pentane)

**Melting point**  126.6 °C

**GC-MS**  \( R_f \) 8.06 min (Standard heating procedure)

m/z 212[M], 197, 189, 183, 176, 151, 133, 115, 96, 89, 75, 63, 51.

**HRMS**  (EI, 70 eV, m/z): 212.101, calcd 212.1001

**¹H-NMR**  (300 MHz, CDCl₃), δ 7.60-7.50 (m; 6H), 7.14 (t; 2H, 8.7 Hz), 5.45 (s; 1H), 5.14 (s; 1H), 2.20 (s; 3H).

**¹³C-APT-NMR**  (75 MHz, CDCl₃), δ 162.6 (Q; d; 246 Hz), 142.8 (Q), 140.3 (Q), 139.3 (Q), 137.0 (Q), 128.6 (CHAr; d; 8.0 Hz), 126.9 (CHAr), 126.1 (CHAr), 115.8 (CHAr; d; 21.4 Hz), 112.7 (=CH₂), 21.9 (CH₃).

**FT-IR**  (ATR film) 1/\( \lambda \) [cm⁻¹] 3084 (m), 2973 (m), 2945 (m), 1915 (w), 1892 (w), 1801 (w), 1683 (w), 1622 (s), 1495 (s), 1397 (s), 894 (s), 823 (s), 754 (s).

---

4-Fluoro-3-methyl-4’-(prop-1-en-2-yl)biphenyl

White solid.

General Procedure (ArMgBr addition over 40 min).

![Chemical structure of 4-Fluoro-3-methyl-4’-(prop-1-en-2-yl)biphenyl](attachment:chemical_structure.png)

C₁₆H₁₅F (226.12 g/mol)

**Yield**  77%

**TLC**  \( R_f \) 0.55 (SiO₂, cyclohexane)

**Melting point**  83°C

**GC-MS**  \( R_f \) 9.22 min (Standard heating procedure)

m/z 226[M], 211, 196, 181, 165, 147, 133, 95, 79, 51.

**HRMS**  (EI, 70 eV, m/z): 226.116, calcd 226.1158

**¹H-NMR**  (300 MHz, CDCl₃), δ 7.52-7.26 (m; 6H), 7.10-7.01 (m; 1H), 5.42 (s; 1H), 5.11 (s; 1H), 2.33 (s; 3H), 2.18 (s; 3H).

**¹³C-APT-NMR**  (75 MHz, CDCl₃), δ 161.1 (Q; d; 245 Hz), 142.8 (Q), 140.1 (Q), 140.0 (Q), 136.6 (Q; d; 3.4 Hz), 130.2 (CHAr), 130.1 (CHAr), 126.9 (CHAr), 120.9 (CHAr).
126.0 (CH$_2$Ar), 125.9 (CH$_2$Ar), 124.6 (Q; d; 17.0 Hz), 112.6 (=CH$_2$), 21.9 (CH$_3$), 14.8 (Ar-CH$_3$).

**FT-IR** (ATR film) $\nu$ [cm$^{-1}$] 3083 (w), 3032 (w), 2923 (m), 2855 (m), 2359 (w), 1918 (w), 1792 (w), 1622 (m), 1493 (s), 1234 (s), 1122 (s), 890 (s), 819 (s), 753 (s).

**Products from Table 4:**

*4-Methoxy-4'-vinylbiphenyl*

White solid.

![Chemical structure](image)

C$_{15}$H$_{14}$O (210.10 g/mol)

**Yield** 81% (92%)

**TLC** $R_f$ 0.32 (SiO$_2$, hexanes/ethyl acetate 95:5)

**Melting Point** 143°C

**GC-MS** $R_s$ 9.83 min (Standard heating procedure)

m/z 210[M], 195, 178, 167, 152, 139, 128, 115, 102, 89, 76, 63.

**HRMS** (EI, 70 eV, m/z): 210.1045, calcd 210.1045

**$^1$H-NMR** (300 MHz, CDCl$_3$), $\delta$ 7.59-7.24 (m; 6H), 7.10-6.93 (m; 2H), 6.75 (dd; 1H, 10.9/6.6 Hz), 5.78 (dd; 1H, 17.6/0.9 Hz), 5.26 (dd; 1H, 10.9/0.9 Hz), 3.86 (s; 3H).

**$^{13}$C-NMR** (75 MHz, CDCl$_3$), $\delta$ 159.3 (Q), 140.3 (Q), 136.6 (-CH=), 136.1 (Q), 133.4 (Q), 128.1, 126.9, 126.8, 114.4, 113.7 (=CH$_2$), 55.5 (OCH$_3$).

**FT-IR** (ATR film) $\nu$ [cm$^{-1}$] 3086 (w), 3003 (w), 2959 (w), 2838 (w), 2362 (m), 2341 (m), 1603 (m), 1499 (s), 1289 (m), 1039 (m), 993 (m), 907 (m), 826 (s), 737 (m).
4-N,N-Dimethylamino-4'-vinylbiphenyl

White solid.

\[
\text{C}_{16}\text{H}_{17}\text{N} (223.14 \text{ g/mol})
\]

**Yield** 74 % (86%)

**TLC** \( R_f \) 0.18 (SiO\(_2\), hexanes/ethyl acetate (95:5))

**Melting Point** 170°C

**GC-MS** \( R_t \) 10.75 min (Standard heating procedure)

\[
m/\z 223[M], 207, 194, 178, 165, 152, 139, 128, 111, 89, 76, 63.
\]

**HRMS** (EI, 70 eV, m/z): 223.1361, calcd 223.1356

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)), \( \delta \) 7.60-7.43 (m; 6H), 6.85-6.70 (m; 3H), 5.78 (dd; 1H, 17.6/1.0 Hz), 5.25 (dd; 1H, 10.9/0.9 Hz), 3.01 (s; 6H).

**\(^13\)C-NMR** (75 MHz, CDCl\(_3\)), \( \delta \) 149.1 (Q), 139.8 (Q), 135.7 (-CH=), 134.4 (Q), 127.8 (Q), 126.7, 125.7, 125.4, 112.2, 111.9 (=CH\(_2\)), 39.7 (NCH\(_3\)).

**FT-IR** (ATR film) \( 1/\lambda [\text{cm}^{-1}] \) 3050 (w), 2920 (w), 2364 (w), 1610 (m), 1504 (w), 1265 (m), 814 (s), 735 (s).

4-Methyl-4'-vinylbiphenyl

White solid.

\[
\text{C}_{15}\text{H}_{14} (194.11 \text{ g/mol})
\]

**Yield** 91%

**TLC** \( R_f \) 0.14 (SiO\(_2\), hexanes)

**Melting Point** 119°C

**GC-MS** \( R_t \) 9.13 min (Standard heating procedure)

\[
m/\z 194[M], 178, 152, 137, 115, 89, 63.
\]

**HRMS** (EI, 70 eV, m/z): 194.1099, calcd 194.1096

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)), \( \delta \) 7.59-7.47 (m; 6H), 7.26 (m; 2H), 6.77 (dd; 1H,
10.9/6.5 Hz), 5.80 (dd; 1H, 17.5/0.9 Hz), 5.28 (dd; 1H, 10.9/0.9 Hz), 2.41 (s; 3H).

\[^{13}\text{C-NMR}\] \(75 \text{ MHz, CDCl}_3\), \(\delta\) 140.7 (Q), 138.0 (Q), 137.3 (Q), 136.6 (-CH=), 136.5 (Q), 129.7, 129.6, 127.2, 126.9, 113.8 (=CH2), 21.3 (Ar-CH3).

\[^{\text{FT-IR}}\] (ATR film) \(\nu\) [cm\(^{-1}\)] 3089 (w), 3028 (w), 2918 (w), 2855 (w), 2367 (w), 2052 (w), 1627 (w), 1499 (m), 1397 (m), 991 (m), 905 (m), 813 (s), 748 (m).

4-Fluoro-4'-vinylbiphenyl

White solid.

\[
\begin{align*}
\text{C}_{14}\text{H}_{11} &\text{ (198.08 g/mol)} \\
\text{Yield} &\text{ (97\%)} \\
\text{TLC} &\text{ Rf 0.25 (SiO}_2\text{, hexanes)} \\
\text{Melting Point} &\text{ 127°C} \\
\text{GC-MS} &\text{ R, 8.54 min (Standard heating procedure)} \\
&\text{m/z 198[M], 183, 170, 159, 151, 143, 133, 120, 107, 98, 85, 75, 63.} \\
\text{HRMS} &\text{ (EI, 70 eV, m/z): 198.0841, calcd 198.0845} \\
\text{\(^{1}\text{H-NMR}\)} &\text{ (300 MHz, CDCl}_3\text{), \(\delta\) 7.65-7.45 (m; 6H), 7.20-7.09 (m; 2H), 6.78 (dd; 1H, 17.6/6.6 Hz), 5.82 (dd; 1H, 17.6/0.9 Hz), 5.31 (dd; 1H, 10.9/0.9 Hz).} \\
\text{\(^{13}\text{C-NMR}\)} &\text{ (75 MHz, CDCl}_3\text{), \(\delta\) 162.6 (Q; d; 245.5 Hz), 139.7 (Q), 137.0 (Q; d; 3.3 Hz), 136.7 (Q), 136.4 (-CH=), 128.6 (d; 8.1 Hz), 127.2, 126.8, 115.8 (=CH2; d; 21.4 Hz), 114.1.} \\
\text{\(^{\text{FT-IR}}\)} &\text{ (ATR film) \(\nu\) [cm\(^{-1}\)] 3089 (w), 3005 (w), 2920 (w), 2360 (w), 1598 (m), 1494 (m), 1240 (w), 99s (m), 909 (m), 824 (s), 665 (m).}
\end{align*}
\]

3-Methoxy-4'-vinylbiphenyl

Colorless Oil.
4-Fluoro-3-methyl-4'-vinylbiphenyl

White solid.

C_{15}H_{13}F (212.10 g/mol)

Yield 85%

TLC R_f 0.21 (SiO2, hexanes)

Melting Point 61°C

GC-MS R_f 9.05 min (Standard heating procedure)

m/z 212[M], 196, 170, 152, 133, 109, 91, 77, 63.

HRMS (EI, 70 eV, m/z): 212.0999, calcd 212.0999

{sup}H-NMR (300 MHz, CDCl₃), δ 7.56-7.34 (m; 6H), 7.12-7.04 (m; 1H), 6.77 (dd; 1H, 10.9/6.6 Hz), 5.81 (dd; 1H, 17.6/0.9 Hz), 5.29 (dd; 1H, 10.9/0.9 Hz), 2.36 (d; 3H, 1.9 Hz).

{sup}13C-NMR (75 MHz, CDCl₃), δ 161.2 (Q; d; 244.9 Hz), 139.9 (Q), 136.7 (Q; d; 3.5 Hz), 136.6 (Q), 136.5 (-CH=), 130.2 (d; 5.2 Hz), 127.2, 126.8, 125.9 (d;
8.0 Hz), 125.2 (Q; d; 17.5 Hz), 115.4 (d; 22.5 Hz), 114.0 (=CH2), 14.8 (Ar-CH3; d; 3.5 Hz).

**FT-IR** (ATR film) $\nu$ [cm$^{-1}$] 3036 (w), 2925 (w), 2859 (w), 1494 (s), 1237 (s), 843 (s), 813 (s).

---

2-(4'-Vinylbiphenyl-4-yloxy)tetrahydro-2H-pyran

White solid.

![Structure](structure.png)

C$_{19}$H$_{20}$O$_2$ (280.15 g/mol)

**Yield** 81 % (93 %)

**TLC** $R_f$ 0.21 (SiO$_2$, hexanes/ethyl acetate (95:5))

**Melting Point** 105°C

**GC-MS** $m/z$ 280[M], 196, 181, 165, 139, 115, 98, 84, 69.

**HRMS** (EI, 70 eV, $m/z$): 280.1463, calcd 280.1467

**$^1$H-NMR** (300 MHz, CDCl$_3$), $\delta$ 7.59-7.43 (m; 6H), 7.19-7.09 (m; 2H), 6.75 (dd; 1H, 10.9/6.7 Hz), 5.78 (dd; 1H, 17.6/0.9 Hz), 5.48 (t; 1H, 3.2 Hz), 5.26 (dd; 1H, 10.9/0.9 Hz), 3.99-3.89 (m; 1H), 3.67-3.60 (m; 1H), 2.08-1.55 (m; 6H).

**$^{13}$C-NMR** (75 MHz, CDCl$_3$), $\delta$ 155.8 (Q), 139.4 (Q), 135.6 (-CH=), 135.2 (Q), 133.3 (Q), 127.0, 126.0, 125.7, 115.9, 112.7 (=CH$_2$), 95.5 (CH), 61.2 (CH$_2$), 29.5 (CH$_2$), 24.4 (CH$_2$), 17.9 (CH$_2$).

**FT-IR** (ATR film) $\nu$ [cm$^{-1}$] 3086 (w), 2948 (m), 2870 (m), 1603 (m), 1497 (s), 1245 (s), 1110 (s), 1021 (m), 967 (s), 822 (s).

---

**Products from Scheme 4:**

5-((2-Bromobenzyl)oxy)-4'-methoxy-2-vinyl-1,1'-biphenyl

Colorless Oil.

General Procedure (20 min), then 30 min reaction time, 0.9 equiv. ArMgBr.
C_{22}H_{19}BrO_2 (394.06 g/mol)

**Yield** 70%

**TLC** \( R_f 0.48 \) (SiO\(_2\), \( n \)-pentane/ethyl acetate (4:1))

**GC-MS** \( R_t \) 14.15 min (Standard heating procedure)

\[ m/z \text{ 396}[M], 365, 315, 283, 255, 225, 197, 169, 153, 139, 115, 90, 63. \]

**HRMS** (EI, 70 eV, m/z): 394.0564, calcd 394.0569

**\( ^1 \)H-NMR** (300 MHz, CDCl\(_3\)), \( \delta \) 7.60-7.52 (m; 3H), 7.35-7.24 (m; 3H), 7.17 (td; 1H, 7.8/1.8 Hz), 6.99-6.88 (m; 4H), 6.65 (dd; 1H, 17.5/6.6 Hz), 5.57 (dd; 1H, 17.5/1.4 Hz), 5.14 (s; 2H), 5.08 (dd; 1H, 11.0/1.3 Hz), 3.84 (s; 3H).

**\( ^{13} \)C-NMR** (75 MHz, CDCl\(_3\)), \( \delta \) 159.0, 158.0, 142.0, 136.3, 135.5, 133.1, 132.8, 130.9, 129.4, 129.3, 129.1, 127.7, 127.2, 122.5, 116.1, 114.1, 113.6, 112.9, 69.6 (Ar-CH), 55.4 (OCH\(_3\)).

**FT-IR** (ATR film) \( \lambda \) [cm\(^{-1}\)] 3063 (w), 3002 (w), 2935 (w), 2832 (w), 2357 (w), 2832 (w), 2357 (w), 1603 (s), 1488 (s), 1246 (s), 1204 (s), 1024 (s), 833 (s), 750 (s).

---

5-((4-Bromo-2-fluorobenzyl)oxy)-4'-methoxy-2-vinyl-1,1'-biphenyl

Colorless Oil.

General Procedure (20 min), then 20 min reaction time, 0.9 equiv. ArMgBr.

C_{22}H_{18}BrFO_2 (412.05 g/mol)

**Yield** 69%

**TLC** \( R_f 0.31 \) (SiO\(_2\), \( n \)-pentane/ethyl acetate (95:5))

**GC-MS** \( R_t \) 13.99 min (Standard heating procedure)

\[ m/z \text{ 412}[M], 382, 355, 333, 281, 257, 225, 186, 165, 139, 108, 81, 63. \]

**\( ^1 \)H-NMR** (300 MHz, CDCl\(_3\)), \( \delta \) 7.58 (d; 1H, 8.6 Hz), 7.45-7.23 (m; 5H), 7.01-6.86 (m; 4H), 6.65 (dd; 1H, 17.5/6.6 Hz), 5.59 (dd; 1H, 17.5/1.3 Hz), 5.14-
5.04 (m; 1H), 3.86 (s; 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$), $\delta$ 160.3 (d; 251.7 Hz), 159.0, 157.8, 142.0, 135.5, 133.1, 130.9, 130.8 (d; 4.7 Hz), 129.5, 127.8 (d; 3.7 Hz), 127.2, 123.5 (d; 14.4), 122.2 (d; 9.6 Hz), 119.2 (d; 24.7 Hz), 116.0, 114.0, 113.6, 113.0, 63.4 (Ar-CH; d; 3.9 Hz), 55.5 (OCH$_3$).

HRMS (EI, 70 eV, m/z): 412.0469 calcd 412.0474

FT-IR (ATR film) $\lambda$ [cm$^{-1}$] 3082 (w), 2956 (w), 2932 (w), 2838 (w), 1724 (w), 1602 (s), 1487 (s), 1244 (s), 1201 (s), 1175 (s), 1021 (s), 875 (s), 831 (s).

(E)-4-(3-(4-Chlorophenyl)but-1-en-1-yl)-4'-methoxy-1,1'-biphenyl

White solid.

General Procedure (20 min), then 30 min reaction time, 0.9 equiv. ArMgBr.

![Chemical structure](image)

C$_{23}$H$_{21}$ClO (348.13 g/mol)

Yield 66%

TLC Rf 0.24 (SiO$_2$, n-pentane/ethyl acetate (95:5))

Melting point 144°C

GC-MS Ret 15.16 min (Standard heating procedure)
m/z 348[M], 333, 313, 298, 283, 265, 239, 221, 195, 179, 165, 149, 125, 103, 77, 63.

HRMS (EI, 70 eV, m/z): 348.1277, calcd 348.1281

$^1$H-NMR (300 MHz, CDCl$_3$), $\delta$ 7.60-7.46 (m; 4H), 7.44-7.36 (m; 2H), 7.33-7.18 (m; 4H), 7.01-6.94 (m; 2H), 6.48-6.30 (m; 2H), 3.85 (s; 3H), 1.46 (d; 3H; 7.02 Hz).

$^{13}$C-APT-NMR (75 MHz, CDCl$_3$), $\delta$ 159.3, 144.2, 139.7, 135.9, 124.5, 133.4, 132.0, 131.0, 128.7, 128.6, 128.1, 126.9, 126.7, 114.3, 55.5 (Ar-CH), 42.1 (OCH$_3$), 21.3 (CH$_3$).

FT-IR (ATR film) $\lambda$ [cm$^{-1}$] 2963 (w), 2929 (w), 2873 (w), 1728 (w), 1602 (w), 1494 (m), 1251 (m), 1013 (m), 808 (s).
3.5 mg (1 mol%, 0.01 mmol) Co(acac)_3 were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dried THF and NMP (10/1, v/v). The resulting green solution was put in a water bath at 30°C and treated with 1 mmol of the 4-chlorostyrene followed by 0.1 mmol of the freshly prepared arylmagnesium bromide solution (0.5 M in THF). The remaining 1.00 mmol ArMgBr was slowly added by syringe pump over a period 20 min. The mixture was then stirred at 30°C for another 100 min. Then, 1mL of an aqueous 5% HCl solution and 2 ml acetone were added, and the reaction stirred for 1 h at rt. Then the mixture was extracted with ethyl acetate. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. Silica gel column chromatography (n-pentane/ethyl acetate) afforded the pure product as white solid (180 mg, 92%).

C_{14}H_{12}O (196.09 g/mol)

Yield 92%

TLC R_f 0.15 (SiO_2, n-pentane/ethyl acetate (9:1))

Melting point 143°C

GC-MS R_t 10.10 min (Standard heating procedure)
m/z 196[M], 181, 165, 152, 139, 128, 115, 101, 89, 77, 63, 51.

^1_H-NMR (300 MHz, CDCl_3), δ 7.56-7.42 (m; 7H), 6.95-6.86 (m; 2H), 6.75 (dd; 1H, 17.6/6.7 Hz), 5.78 (dd; 1H, 17.6/0.9 Hz), 5.25 (dd; 1H, 10.9/0.9 Hz).

^13_C-NMR (75 MHz, CDCl_3), δ 155.4 (Q), 140.3 (Q), 136.6, 136.1 (Q), 133.5 (Q), 128.3, 126.9, 126.8, 115.8, 113.7 (=CH_2).

Selected Spectra

3-Methoxy-4’-vinylbiphenyl (2)

Feb19-2012
sagk702
rau_PROTONLF_16 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} AK_Jacobi 120

Feb19-2012
sagk702
rau_C13CPD_256 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} AK_Jacobi 120
2-(4'-Vinylbiphenyl-4-yloxy)tetrahydro-2H-pyran

Feb14-2012
sagik684
rau_PROTONLF_16 CDCl3 (C:\Bruker\TOPSPIN2.1PL3) AK_Jacobi S2

Feb14-2012
sagik684
rau_C13CPD_256 CDCl3 (C:\Bruker\TOPSPIN2.1PL3) AK_Jacobi S2

Electronic Supplementary Material (ESI) for Chemical Science
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4-N,N-Dimethylamino-4'-vinylbiphenyl

Feb14-2012
sagk685
rau_PROTONLF_16 CDCl3 (C:\Bruker\TOPSPIN2.1PL3) AK_Jacobi 53

Feb14-2012
sagk685
rau_C13CPD_256 CDCl3 (C:\Bruker\TOPSPIN2.1PL3) AK_Jacobi 53
5-(4-Fluorophenyl)-6-vinylbenzo[d][1,3]dioxole

Electronic Supplementary Material (ESI) for Chemical Science
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5-Chloro-4'-methoxy-2-vinylbiphenyl

Electronic Supplementary Material (ESI) for Chemical Science
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4'-Methoxy-3-(prop-1-en-2-yl)biphenyl

Electronic Supplementary Material (ESI) for Chemical Science
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4-Methyl-4'-vinylbiphenyl

Electronic Supplementary Material (ESI) for Chemical Science
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4-Fluoro-3-methyl-4'-vinylbiphenyl
4-Methoxy-4'-vinylbiphenyl