Electronic Supplementary Material (ESI) for Chemical Science

Chemoselective Cobalt-Catalyzed Biaryl Coupling Reactions

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General

Analytical Thin-Layer Chromatography

TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F_{254}). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdatophosphoric 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, H_2 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, H_2 as carrier gas). Standard heating program: 50°C (2 min), 25°C/min -> 300°C (5 min).

NMR Spectroscopy

^{1}H and ^{13}C 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 $[K(dme)_2\{Co(C_{14}H_{10})_2\}]$ (Figure 4) were recorded on a Bruker Avance 400 (400 MHz).

^{1}H-NMR: The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C-APT-NMR (Attached Proton Test) and ^{13}C-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; CH_{Ar}, aromatic CH; -CH=, α-vinyl carbon; =CH_2, β-vinyl carbon, CH, aliphatic CH group; CH_2, aliphatic CH_2

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 specta 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.

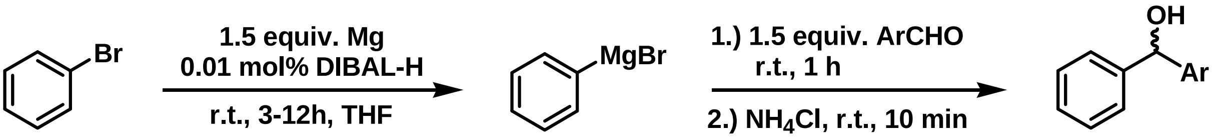
Chemicals

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_2O) 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-2*H*-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. Appukkuttan, 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:



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.

According to: F. M. Piller, P. Appukkuttan, A. Gavryushin, M. Helm, P. Knochel, *Angew. Chem. Int. Ed.* **2008**, *47*, 6802.

b) Iodine-Magnesium Exchange with *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 *i*-PrI were evaporated (to near dryness) at 0°C and the residue dissolved in dry THF (2.5 mL).

Slightly modified from: L. Boymond, M. Rottländer, G. Cahiez, P. Knochel, *Angew. Chem. Int. Ed.* **1998**, *37*, 1701.

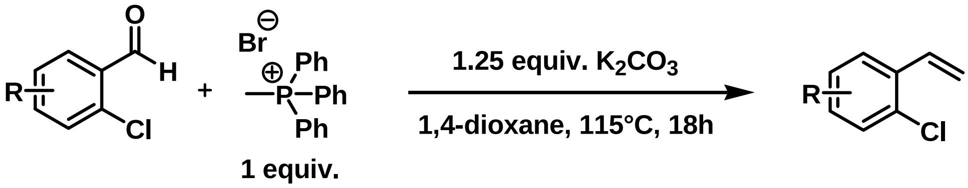
All other arylmagnesium bromides were prepared in similar manner from the corresponding aryl bromides. For commercial Grignard reagents, see General Part above.

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 NH_4Cl was added, and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The concentration of the resulting benzylalcohol was determined by ^{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.

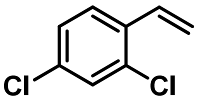
Synthesis of Styrenes



The respective benzaldehyde (20 mmol), K_2CO_3 (3.45 g, 25 mmol) and methyl-triphenylphosphonium 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 (Na_2SO_4), concentrated in vacuo, and purified by SiO_2 column chromatography.

According to: M. Ogata, H. Matsumoto, S. Shimizu, S. Kida, M. Shiro, K. Tawara, *Eur. J. Med. Chem.* **1989**, *24*, 137.

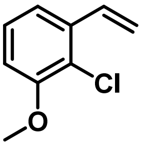
1,3-Dichloro-4-vinylbenzene



	$C_8H_6Cl_2$ (171.98 g/mol)
Yield	85%
GC-MS	R_t 6.13 min
	m/z 172[M], 159, 148, 137, 123, 113, 102, 87, 75, 63, 50.
^{1}H-NMR	(300 MHz, $CDCl_3$), δ 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).
^{13}C-APT-NMR	(75 MHz, $CDCl_3$), δ 134.4 (Q), 134.0 (Q), 133.8 (Q), 132.3 (-CH=), 129.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 117.2 ($=CH_2$).

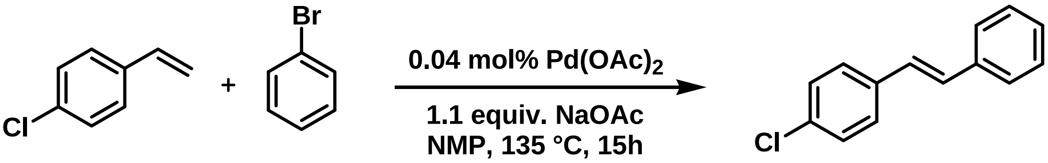
Analytical data in accordance with literature data: A. L. L. Hansen, A. Murray, D. Tanner, *Org. Biomol. Chem.* **2006**, *4*, 4497

2-Chloro-1-methoxy-3-vinylbenzene



	C_9H_9ClO (168.03 g/mol)
Yield	75%
GC-MS	R_t 6.81 min
	m/z 168[M], 153, 138, 125, 114, 103, 89, 77, 63, 50.
^{1}H-NMR	(300 MHz, $CDCl_3$), δ 7.28-7.08 (m; 3H), 6.84 (t; 1H, 4.7 Hz), 5.73 (d; 1H, 17.5 Hz), 5.38 (d; 1H, 11.0 Hz), 3.89 (s; 3H).
^{13}C-APT-NMR	(75 MHz, $CDCl_3$), δ 155.4 (Q), 137.4 (Q), 133.5 (-CH=), 127.0 (CH_{Ar}), 121.8 (Q), 118.6 (CH_{Ar}), 117.0 (=CH_2), 111.0 (CH_{Ar}), 56.4 (CH_3).

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



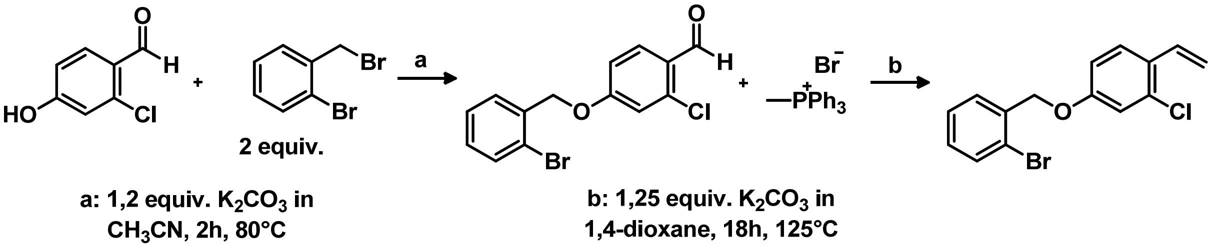
Under an inert atmosphere, a two-necked flask was charged with NaOAc (0.90 g, 11 mmol), bromobenzene (1.05 mL, 10 mmol), and *N*-methylpyrrolidone (NMP, 14 mL). In a separate flask, a stock solution of $Pd(OAc)_2$ (10 mg) in NMP (100 mL) was prepared. An aliquot (9 mL, 0.04 mol% Pd with respect to bromobenzene) 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_2O (75 mL), and extracted with toluene (2 x 75 mL). The combined organic layers were washed with H_2O (3 x 50 mL) and brine (50 mL), dried (Na_2SO_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%).

According to: A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Hendrickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285.

	$C_{14}H_{11}Cl$ (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}).

Analytical data in accordance with literature data: 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.

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



2-Chloro-4-hydroxybenzaldehyde (0.5g, 3.2 mmol), K_2CO_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_2CO_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_2SO_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)

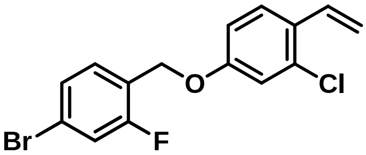
m/z 324[M], 243, 182, 169, 165, 153, 139, 125, 102, 89, 76, 63, 51.

^{1}H-NMR (300 MHz, $CDCl_3$), δ 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, $CDCl_3$), δ 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) 1/λ [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



$C_{15}H_{11}BrClFO$ (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 R_t 11.15 min (Standard heating procedure)

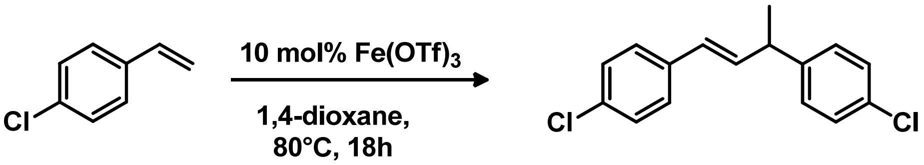
m/z 342[M], 262, 225, 185, 173, 153, 139, 125, 108, 89, 76, 63, 51.

^{1}H-NMR (300 MHz, $CDCl_3$), δ 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, $CDCl_3$), δ 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) 1/λ [cm^{-1}] 3086 (w), 2928 (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)

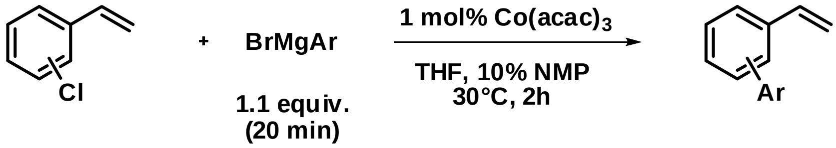


Under an inert atmosphere, a flask was charged with $Fe(OTf)_3$ (0.5 mmol, 10 mol%) and treated with 1,4-dioxane (4 mL) and 4-chlorostyrene (5 mmol, 620 μL). The mixture was stirred at 80°C for 18 h. Then, saturated aqueous $NaHCO_3$ was added, and the mixture extracted with *n*-pentane. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. Silica gel column chromatography (*n*-pentane) afforded the pure product as colorless oil (1.1 g, 85%).

According to: J. R. Cabrero-Antonino, A. L.-Perez, A. Corma, *Adv. Synth. Catal.* **2010**, *352*, 1571-1576.

	$C_{16}H_{14}Cl_2$ (276.05 g/mol)
Yield	85%
TLC	R_f 0.51 (SiO_2, *n*-pentane)
GC-MS	R_t 11.00 min (Standard heating program) m/z 276[M], 261, 241, 226, 212, 191, 165, 149, 129, 115, 101, 89, 77, 63, 51.
^{1}H-NMR	(300 MHz, $CDCl_3$), 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).
^{13}C-NMR	(75 MHz, $CDCl_3$), 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 (CH_3).
FT-IR	(ATR film) 1/λ [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_2SO_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 hydrogencarbonate 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 NaHCO$_3$ 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 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 Scheme4):

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.

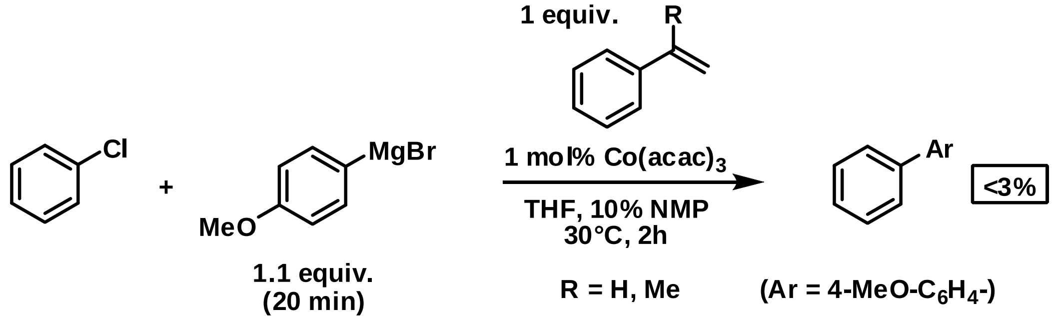
Chemoselectivity Study with Aryl Bromides (see Table 5):

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 hydrogencarbonate was added, the mixture extracted with ethyl acetate and 275 µl (1mmol) *n*-pentadecane was added as internal standard. The combined organic phases were dried (Na$_2$SO$_4$) 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:

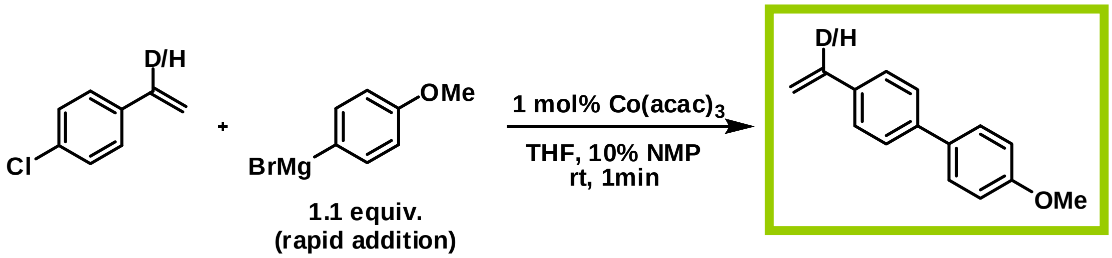


For R = H and R = Me, low conversions (of PhCl) were observed under standard conditions when employing chlorobenzene as electrophilic coupling partner.

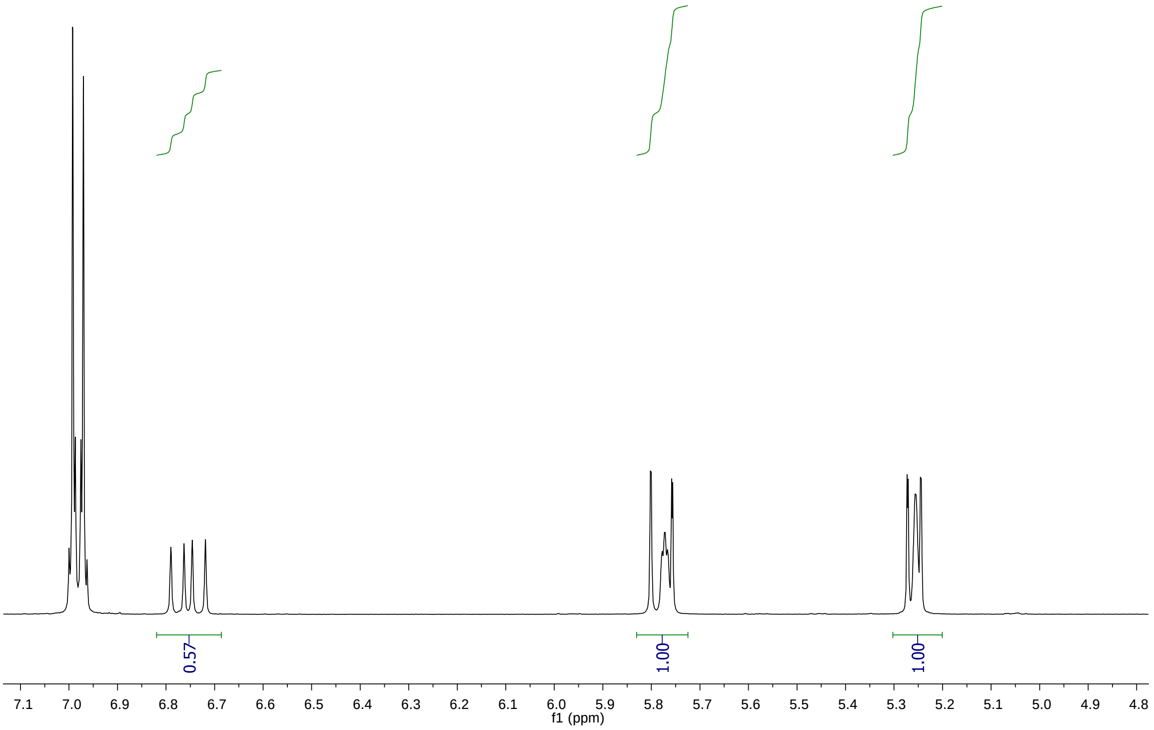
Secondary Kinetic Isotope Effect (see Scheme 5):

Preparation of d_1-**3**: A 50 mL flask was charged with $LiAlD_4$ (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 Na_2SO_4, 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 d_1-**3** as a colorless liquid in 66% yield (912 mg).
Preparation of d_1-**3** according to: (a) 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.

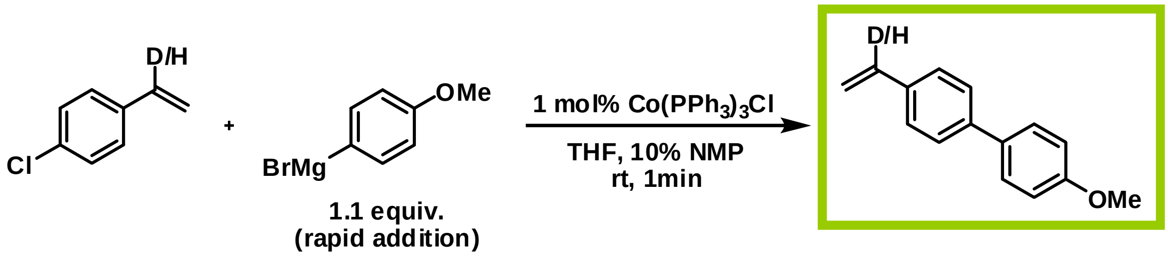
Cross-coupling reaction: An equimolar mixture of **3** and d_1-**3** (50% D content by ^1H NMR) was reacted under slightly modified standard conditions (rapid addition of 0.5 M 4-anisylmagnesium bromide solution over 2 s, 1 min reaction time, 18°C, $Co(acac)_3$ or complex **7** as pre-catalysts). Careful ^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).

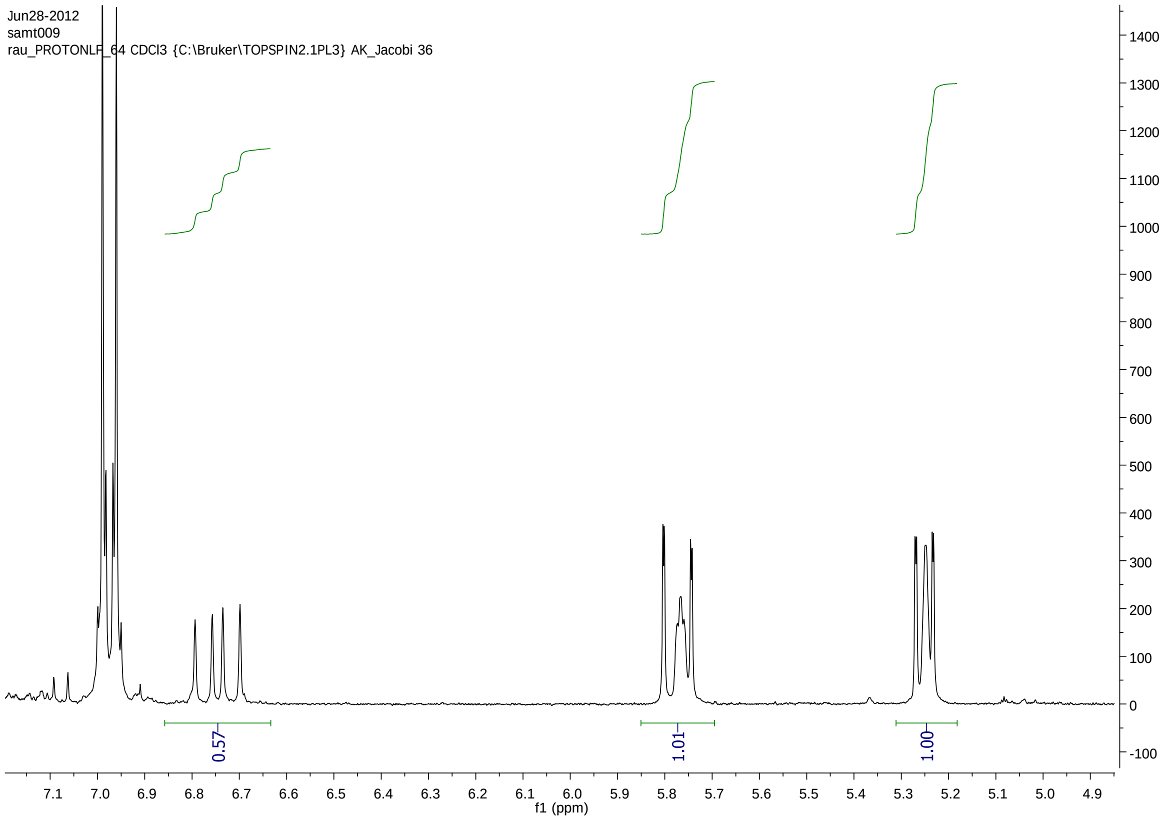


XGuel001
Guelak, sagk802 (10mg/0.8ml CDCl3) Ref.: TMS ext.
@rau_h1 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} puk06221 5



An identical procedure was followed for (Ph$_3$P)$_3$CoCl (**7**) as pre-catalyst.



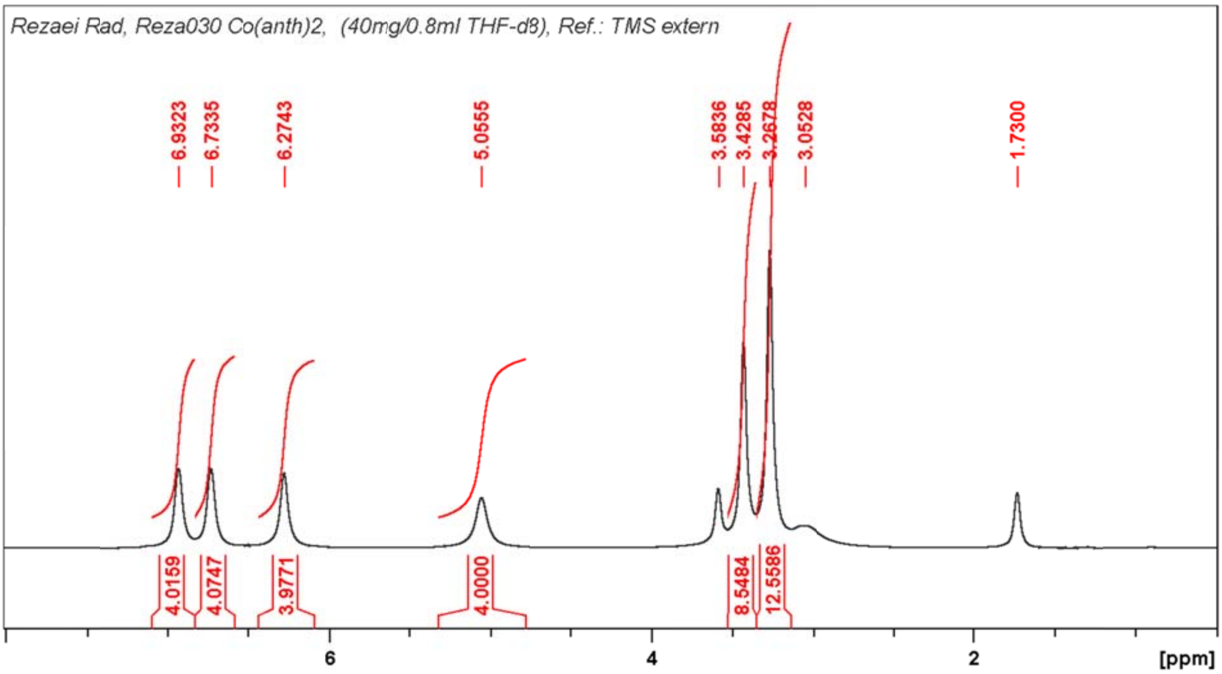


Preparation of [K(dme){Co($C_{14}H_{10}$)$_2$}] (4):

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. ^{1}H 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 $H_{5,8}$ of anthracene). ^{13}C{^{1}H} 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 (λ = 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**.

	4
formula	$C_{36}H_{40}CoKO_4$
M_r [g mol^{-1}]	634.71
dimension [mm^3]	0.04x0.09x0.34
color, habit	grey rod
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	15.4085(3)
b [Å]	20.2602(3)
c [Å]	21.0264(4)
α [°]	90
β [°]	102.870(2)
γ [°]	90
V [Å^3]	6399.1(2)
Z	8
T [K]	123(1)
ρ_c [g cm^{-3}]	1.318
F(000)	2672
λ, Å	1.54178 (CuK_α)
μ [mm^{-1}]	5.661
reflections collected	27567
reflections unique	10081
index ranges	$16 \leq h \leq 17, -23 \leq k \leq 17, -23 \leq l \leq 24$
R_{int}	0.040
reflection obs. [F>2σ(F)]	7024
residual density [e Å^{-3}]	–0.37, 1.30
parameters	777
GOF	1.03
R_1 [I>3σ(I)]	0.0631
wR_2 (all data)	0.1800
CCDC	884015

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 $NaHCO_3$ was added, and the mixture extracted with ethyl acetate. The combined organic phases were dried (Na_2SO_4), 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):

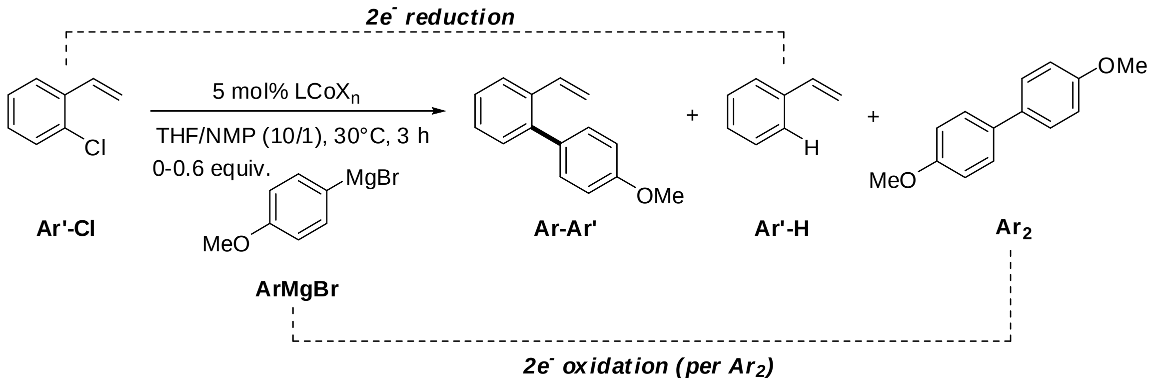
Synthetic procedures as described in the **General Procedure** above, but reactions were performed at **room temperature** (22°C).

Kinetic Studies of Initial Reaction Rates (see Figure 3, bottom):

Following literature procedures (For similar kinetic studies and mechanistic interpretations, see: (a) Kleimark, J.; Larsson, P.-F.; Emamy, P.; Hedström, A.; Norrby, P.-O. *Adv. Synth. Catal.* **2012**, *354*, 448. (b) Hedström, A.; Bollmann, U.; Bravidor, J.; Norrby, P.-O. *Chem. Eur. J.* **2011**, *17*, 11991. (c) Kleimark, J.; Hedström, A.; Larsson, P.-F.; Johansson, C.; Norrby, P.-O. *ChemCatChem* **2009**, *1*, 152.), we have performed time-resolved quantification of all organic materials (starting materials, products, by-products) by GC/FID. The operating redox reactions can be deduced from the analysis of the formed organic oxidation and reduction products. Formation of homo-biaryl is a two-electron oxidation (from 2 ArMgBr), while the formation of styrene is a two-electron reduction (from **1**). Anisole (ArH) and hetero-biaryl (Ar-Ar’) are formed via non-redox processes. The generation of dimerized styrene

(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 ($NaHCO_3/H_2O$), dried (Na_2SO_4), and analyzed by quantitative GC/FID.

Model reaction (see General procedure above):



L = $C_{14}H_{10}$, PPh_3; X = acac, Cl; n = 0,1,3

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 ($NaHCO_3/H_2O$), dried (Na_2SO_4), 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, $(Ph_3P)_3CoCl$ (**7**):

+ArMgBr	**Ar'-Cl**	**Ar-Ar'**	**Ar'-H**	**Ar$_2$**	**Ar total**	**Ar' total**	**electrons**
0 %	99 %	**0 %**	0 %	0 %	0 %	99 %	0 %
2	99	**1**	0	0	1	100	0
4	97	**2.5**	1	0.4	3	100	+1
6	96	**3**	1	0.6	4	100	+1
10	93	**6**	2	1	8	101	+2

20	84	**13.5**	2.5	2.5	18.5	100	0
40	62	**31.5**	4	5.5	42	98	-3
60	40	**51**	5	7	65	96	-4

5 mol% Co(-I) pre-catalyst, K(dme)$_2$ [(C$_{14}$H$_{10}$)$_2$Co] (**4**):

+ArMgBr	**Ar‘-Cl**	**Ar-Ar‘**	**Ar‘-H**	**Ar$_2$**	**Ar total**	**Ar‘ total**	**electrons**
0 %	96 %	0 %	**4 %**	0 %	0 %	100 %	+8 %
1	96	0	**4**	0	0	100	+8
2	95	0	**4.5**	0	0	100	+9
3	95	0	**4.5**	0	0	100	+9
4	95	0	**5**	0	0	100	+10
5	93	0	**5.5**	0	0	99	+11
6	92	0	**5.5**	0.5	1	98	+10
10	90	3	**6**	0.6	4	99	+11
20	80	13	**7**	1.7	16	100	+11
40	59	33	**7**	4	41	99	+6
60	37	54	**8**	6	66	99	+2

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

+ ArMgBr	**Ar‘-Cl**	**Ar-Ar‘**	**Ar‘-H**	**Ar$_2$**	**Ar total**	**Ar‘ total**	**electrons**
0 %	99 %	0 %	0 %	**0 %**	0 %	99 %	0 %
1	99	0	0	**0**	0	99	0
2	99	0	0	**0**	0	99	0
3	98	0.4	0	**0**	0.4	98	0
4	98	0.6	0	**0.5**	1.6	99	-1
5	98	0.7	0	**1**	2.7	99	-2
6	98	0.9	0	**1**	2.9	99	-2
10	98	1	0	**1.8**	4.6	99	-3.6
20	94	4	1	**5.5**	15	99	-9
40	77	19	2	**7.5**	34	98	-11
60	54	40	3	**10**	60	97	-14

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 Ar_2 and reduction product Ar'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.

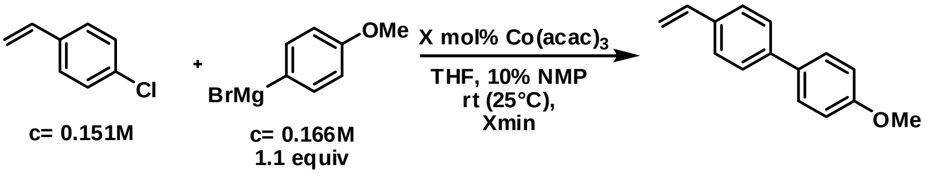
Stoichiometric Reactions with Complex 7 (see Scheme 7):

Scheme 7, **top**: 440.5 mg (100 mol%, 0.5 mmol) $(Ph_3P)_3CoCl$ (**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 *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_2SO_4) and analyzed by quantitative GC/FID.

Scheme 7, **bottom**: 440.5 mg (100 mol%, 0.5 mmol) $(Ph_3P)_3CoCl$ (**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 *n*-pentadecane followed by 63 µL (0.5

mmol) 2-chlorostyrene (**1**). After 10 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 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 $NaHCO_3$ was added and the mixture extracted with ethyl acetate (3x5 ml). The combined organic phases were dried (Na_2SO_4) and analyzed by quantitative GC/FID.

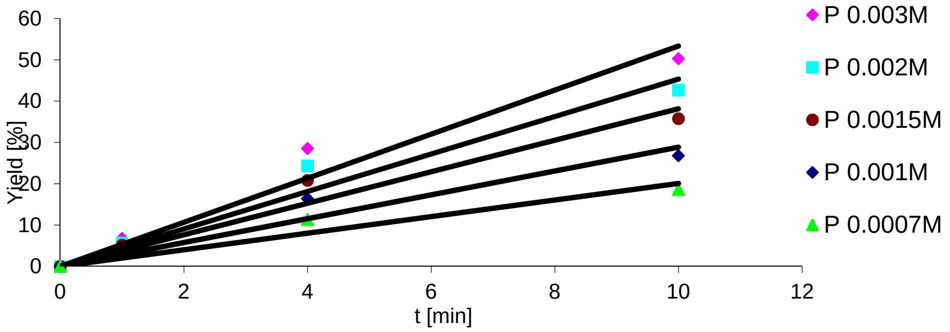
Determination of reaction order in [Co] (see Scheme 8, bottom left):



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 1, 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:

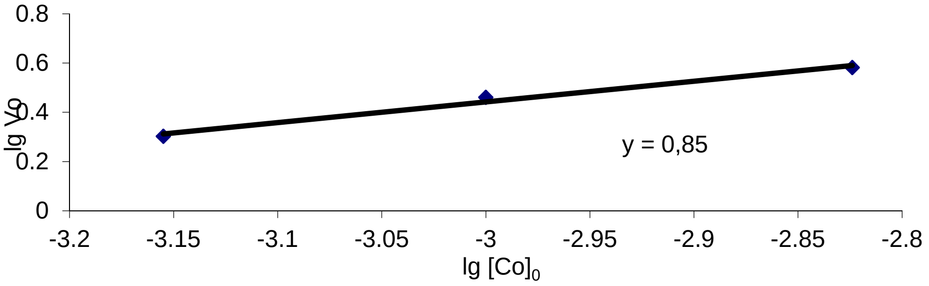
[Co]$_0$ dependent yield-time plot:



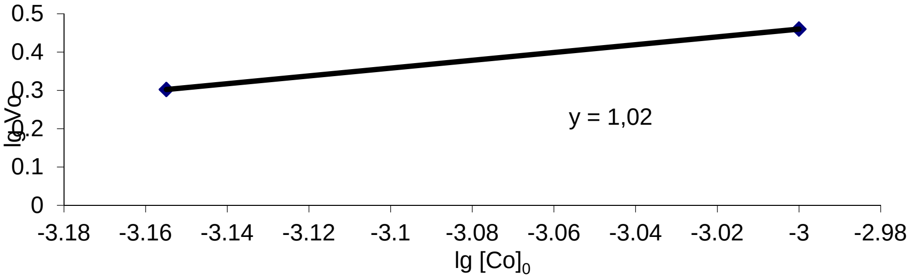
[Co]$_0$: catalyst concentration employed
v$_0$: initial reaction rate (i.e. increase of product yield)

[Co]$_0$	v$_0$	lg [Co]$_0$	lg v$_0$
0,003 mmol	5,3327	-2,5228	0,7269
0,002 mmol	4,5324	-2,6989	0,6563
0,0015 mmol	3,8154	-2,823	0,5815
0,001 mmol	2,8858	-3	0,4602
0,0007 mmol	2,006	-3,154	0,3023

Reaction order in catalyst for [Co]$_0$ = 0.0015-0.0007 M: <u>0.85</u>

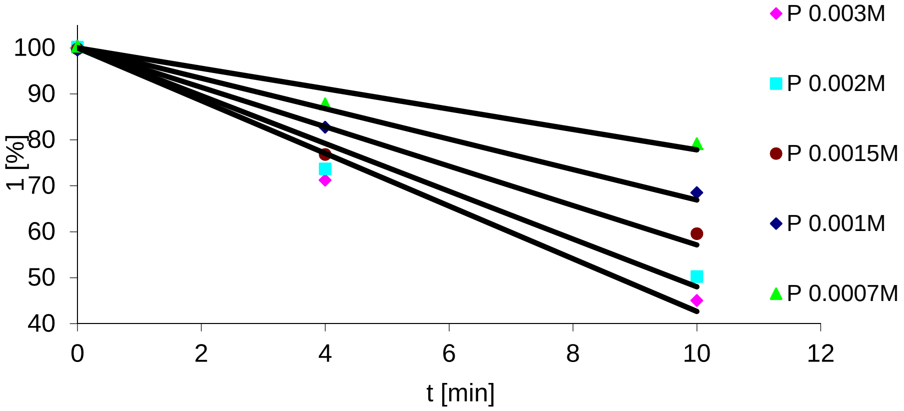


Reaction order in catalyst for $[Co]_0$ = 0.001-0.0007 M: <u>1.02</u>



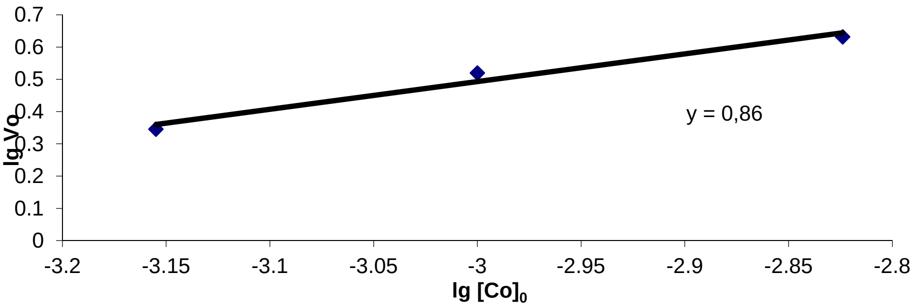
Determination of reaction order based on chlorostyrene (1) concentration:

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

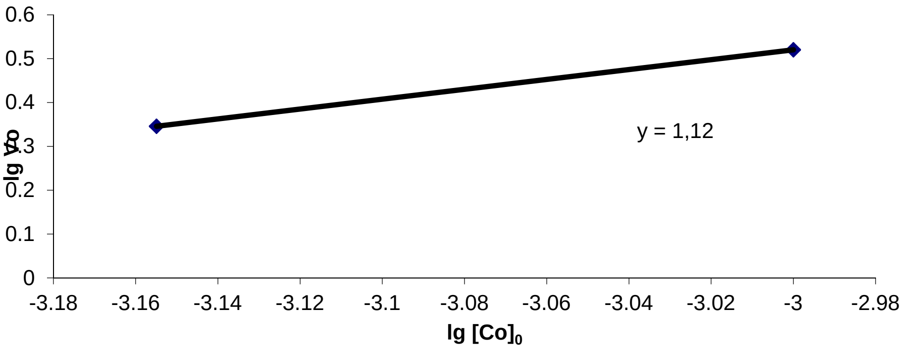


$[Co]_0$	v_0	lg $[Co]_0$	lg v_0
0,003	5,7324	-2,5228	0,7583
0,002	5,196	-2,6989	0,7156
0,0015	4,2836	-2,823	0,6318
0,001	3,3115	-3	0,5200
0,0007	2,2174	-3,154	0,3458

Reaction order in catalyst for $[Co]_0$ = 0.0015-0.0007 M: <u>0.86</u>



Reaction order in catalyst for $[Co]_0$ = 0.001-0.0007 M: <u>1.12</u>



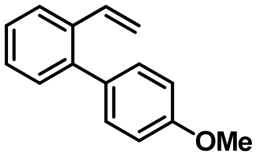
Biaryl Products

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)

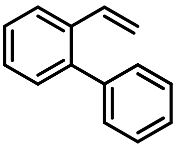
Colorless oil.



	$C_{15}H_{14}O$ (210.10 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}H-NMR	(300 MHz, $CDCl_3$), δ 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}C-APT-NMR	(75 MHz, $CDCl_3$), δ 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) 1/λ [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.



$C_{14}H_{12}$ (180.09 g/mol)

Yield 80% (88%)

TLC R_f 0.36 (SiO_2, cyclohexane)

GC-MS R_t 9.46 min (Standard heating procedure)
m/z 180[M], 165, 151, 129, 115, 89, 63.

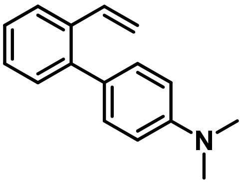
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.70-7.60 (m; 1H), 7.48-7.26 (m; 8H), 6.71 (dd; 1H, 11.0/6.5 Hz), 5.69 (d; 1H, 17.5 Hz), 5.18 (d; 1H, 10.9 Hz).

^{13}C-APT-NMR (75 MHz, $CDCl_3$), δ 141.0 (Q), 136.7 (Q), 136.0 (-CH=), 135.9 (Q), 130.2 (CH_{Ar}), 128.1 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.1 (CH_{Ar}), 125.8 (CH_{Ar}), 114.8 (=CH_2).

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.



$C_{16}H_{17}N$ (223.14 g/mol)

Yield 81% (93 %)

TLC R_f 0.5 (SiO_2, *n*-pentane/ethyl acetate (9:1))

GC-MS R_t 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}H-NMR (300 MHz, CDCl$_3$), δ 7.67-7.60 (m; 1H), 7.35-7.20 (m; 5H), 6.90-6.75 (m; 3H), 5.70 (dd; 1H, 17.5/1.1 Hz), 5.19 (dd; 1H, 11.0/1.1 Hz), 3.0 (s; 6H).

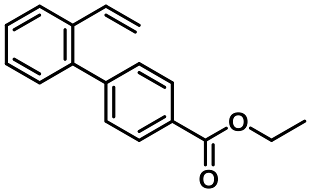
^{13}C-APT-NMR (75 MHz, CDCl$_3$), δ 149.7 (Q), 141.1 (Q), 136.7 (-CH=), 135.9 (Q), 130.7 (CH$_{Ar}$), 130.2 (CH$_{Ar}$), 128.9 (Q), 127.7 (CH$_{Ar}$), 126.8 (CH$_{Ar}$), 125.9 (CH$_{Ar}$), 114.1 (=CH$_2$), 112.1 (CH$_{Ar}$), 40.7 (CH$_3$).

FT-IR (ATR film) 1/λ [cm^{-1}] 3020 (m), 2882 (m), 2358 (w), 1819 (w), 1820 (w), 1677 (m), 1609 (m), 1520 (w), 1347 (m), 1165 (m), 1057 (m), 819 (m), 759 (m).

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

Colorless oil.

General Procedure (20 min)



$C_{17}H_{16}O_2$ (252.11 g/mol)

Yield 70%

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

GC-MS R$_t$ 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

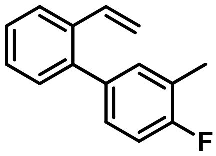
^{1}H-NMR (300 MHz, CDCl$_3$), δ 8.14-8.04 (m; 2H), 7.66 (dd; 1H; 7.3/1.9 Hz), 7.47-7.27 (m; 5H), 6.66 (dd; 1H, 17.5/6.6 Hz), 5.72 (dd; 1H, 17.5/1.3 Hz), 5.21 (dd; 1H, 11.0/1.2 Hz), 4.42 (q; 2H; 7.1 Hz), 1.42 (t; 3H, 7.1 Hz).

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

FT-IR (ATR film) 1/λ [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

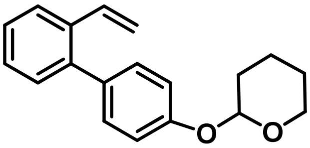
Colorless oil.



	$C_{15}H_{13}F$ (212.10 g/mol)
Yield	73%
TLC	R_f 0.34 (SiO_2, *n*-pentane)
GC-MS	R_t 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
^{1}H-NMR	(300 MHz, $CDCl_3$), 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).
^{13}C-APT-NMR	(75 MHz, $CDCl_3$), 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 (CH_{Ar}; d; 5.1 Hz), 130.2 (CH_{Ar}), 128.8 (CH_{Ar}; d; 7.9 Hz), 127.7 (CH_{Ar}; d; 12.5 Hz), 125.8 (CH_{Ar}), 124.5 (Q; d; 18 Hz), 115.4 (CH_{Ar}; d; 23 Hz), 114.9 (=CH_2), 114.7 (CH_{Ar}; d; 22 Hz), 14.8 (Ar-CH_3).
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-2*H*-pyran

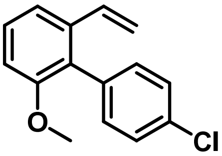
Colorless oil.



	$C_{19}H_{20}O_2$ (280.15 g/mol)
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, $CDCl_3$), δ 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, $CDCl_3$), δ 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/λ [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.



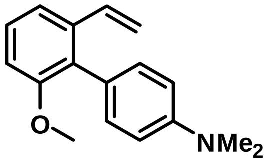
	$C_{15}H_{13}ClO$ (244.07 g/mol)
Yield	84%
GC-MS	R_t 8.78 min (Standard heating procedure) m/z 244], 228, 209, 193, 183, 165, 139, 115, 99, 82, 63.
HRMS	(EI, 70 eV, m/z): 244.066, calcd 244.0655

^{1}H-NMR (300 MHz, $CDCl_3$), 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).

^{13}C-NMR (75 MHz, $CDCl_3$), 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 (OCH_3).

FT-IR (ATR-Film) 1/λ [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



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.

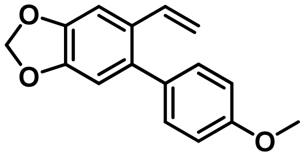
HRMS (EI, 70 eV, m/z): 253.146, calcd 253.1467

^{1}H-NMR (300 MHz, $CDCl_3$), 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).

^{13}C-APT-NMR (75 MHz, $CDCl_3$), δ 152.4 (Q), 149.5 (Q), 138.2 (Q), 136.4 (-CH=), 131.7 (CH_{Ar}), 130.4 (Q), 127.7 (CH_{Ar}), 124.0 (Q), 117.8 (CH_{Ar}), 114.3 (=CH_2), 111.9 (CH_{Ar}), 110.1 (CH_{Ar}), 56.0 (OCH_3), 40.7 (NCH_3).

FT-IR (ATR film) 1/λ [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.

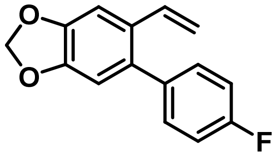
HRMS (EI, 70 eV, m/z): 254.093, calcd 254.0943

^{1}H-NMR (300 MHz, $CDCl_3$), 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).

^{13}C-NMR (75 MHz, $CDCl_3$), δ 147.3 (Q), 135.7, 135.1, 134.7, 131.1, 129.9, 113.6, 112.7 (=CH_2), 110.6, 110.1, 105.3, 104.4, 101.3 (OCH_2), 55.5 (OCH_3).

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)

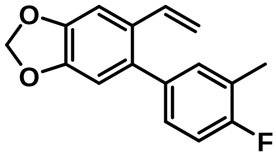
m/z 242[M], 211, 183, 157, 133, 112, 91, 63, 39.

^{1}H-NMR (300 MHz, $CDCl_3$), 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).

^{13}C-NMR (75 MHz, $CDCl_3$), 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 (=CH_2), 110.0, 105.4, 101.4 (OCH_2).

FT-IR (ATR film) 1/λ [cm^{-1}] 2889 (w), 1602 (w), 1499 (s), 1477 (s), 1351 (w), 1211 (s), 1156 (w), 1043 (m), 912 (s), 830 (m).

5-(4-Fluoro-3-methylphenyl)-6-vinylbenzo[*d*][1,3]dioxole



$C_{16}H_{13}FO_2$ (256.09 g/mol)

Yield 77%

GC-MS R_t 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

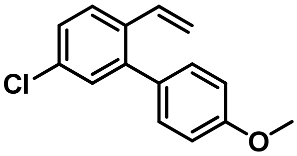
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.15-6.99 (m; 4H), 6.71 (s; 1H), 6.57 (dd; 1H, 10.9/6.5 Hz), 5.99 (s; 2H), 5.54 (dd; 1H, 17.4/1.0 Hz), 5.07 (dd; 1H, 11.0/1.0 Hz), 2.30 (s; 3H).

^{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/λ [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.



$C_{15}H_{13}ClO$ (244.07 g/mol)

Yield 76%

GC-MS R_t 8.66 min (Standard heating procedure)
m/z 244[M], 208, 179, 165, 139, 115, 87, 63.

HRMS (EI, 70 eV, m/z): 244.065, calcd 244.0655

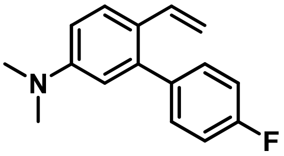
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.54 (d; 1H, 9.1 Hz), 7.29-7.23 (m; 4H), 6.96-6.93 (m; 2H), 6.65 (dd; 1H, 11.0/6.5 Hz), 5.66 (dd; 1H, 17.5/1,0 Hz), 5.20 (dd; 1H, 11.0/1.0 Hz), 3.85 (s; 3H).

^{13}C-NMR (75 MHz, $CDCl_3$), δ 159.3 (Q), 142.1 (Q), 135.2 (-CH=), 134.5 (Q), 133.3 (Q), 132.0 (Q), 130.9, 130.0, 127.3, 127.3, 115.1 (=CH_2), 113.8, 55.5 (OCH_3).

FT-IR (ATR film) 1/λ [cm^{-1}] 2933 (w), 2832 (w), 1607 (s), 1512 (s), 1462 (m), 1243 (s), 1176 (m), 1040 (m), 831 (s).

4'-Fluoro-3-*N*,*N*-dimethylamino-6-vinylbiphenyl

Yellow oil.



$C_{16}H_{16}FN$ (241.13 g/mol)

Yield 74%

TLC R_f 0.53 (SiO_2, *n*-pentane/ethyl acetate (9:1))

GC-MS R_t 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

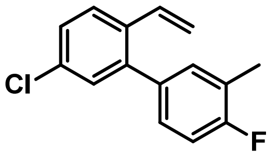
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.56 (d; 1H, 8.7 Hz), 7.28-7.36 (m; 2H), 7.06 (m; 2H), 6.75 (dd; 1H, 8.8/2.7 Hz), 6.50-6.62 (m; 2H), 5.50 (dd; 1H, 17.5/1.3 Hz), 4.98 (dd; 1H, 11/1.3 Hz), 2.99 (s; 6H).

^{13}C-APT-NMR (75 MHz, $CDCl_3$), δ 162.2 (Q; d; 246 Hz), 150.0 (Q), 140.9 (Q), 137.8 (Q), 135.3 (-CH=), 131.4 (CH_{Ar}; d; 7.7 Hz), 126.6 (CH_{Ar}), 124.5 (Q), 114.9 (CH_{Ar}; d; 21 Hz), 113.6 (CH_{Ar}), 112.2 (CH_{Ar}), 110.9 (=CH_2), 40.6 (NCH_3).

FT-IR (ATR-Film) 1/λ [cm^{-1}] 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.

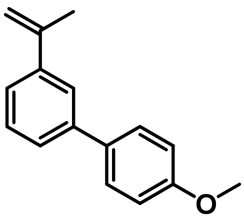


	$C_{15}H_{12}ClF$ (246.06 g/mol)
Yield	71%
GC-MS	R_t= 8,42 min (Standard heating procedure) m/z= 246[M], 196, 170, 133, 105, 77, 39.
HRMS	(EI, 70 eV, m/z): 246.061, calcd 246.0612
^{1}H-NMR	(300 MHz, $CDCl_3$), δ= 7.54 (d; 1H, 8.4 Hz), 7.35-7.00 (m; 5H), 6.60 (dd; 1H, 11.0/6.5 Hz), 5.66 (dd; 1H, 17.5/1.0 Hz), 5.20 (dd; 1H, 11.0/1.0), 2.31 (d; 3H, 1.8 Hz).
^{13}C-NMR	(75 MHz, $CDCl_3$), 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_2), 114.8 (d; 22.4 Hz), 14.7 (Ar-CH_3; d; 3.3 Hz).
FT-IR	(ATR film) in [cm^{-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).



	$C_{16}H_{16}O$ (224.12 g/mol)
Yield	78%
TLC	R_f 0.31 (SiO_2, hexanes/ethyl acetate (95:5))
Melting point	47 °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, $CDCl_3$), δ 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).

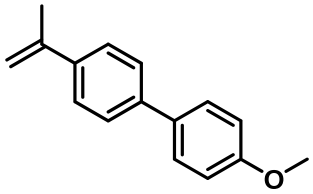
^{13}C-NMR (75 MHz, $CDCl_3$), δ 159.3 (Q), 143.5 (Q), 141.9 (Q), 141.0 (Q), 134.0 (Q), 128.8, 128.4, 126.1, 124.3, 124.1, 114.3, 112.8 (=CH_2), 55.5 (OCH_3), 22.1 (CH_3).

FT-IR (ATR film) 1/λ [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-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 (SiO_2, cyclohexane/ethyl acetate (98:2))

Melting Point 151°C

GC-MS R_t 9.99 min (Standard heating procedure)

m/z 224[M], 209, 194, 181, 165, 152, 141, 128, 115, 91, 77, 63.

HRMS (EI, 70 eV, m/z): 224.1199, calcd 224.1201

^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.60-7.50 (m; 6H), 6.97 (d; 2H, 8.3 Hz), 5.42 (s; 1H), 5.10 (s; 1H), 3.85 (s; 3H), 2.19 (s; 3H).

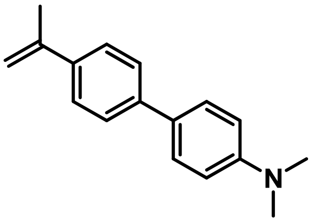
^{13}C-NMR (75 MHz, $CDCl_3$), δ 159.3 (Q), 142.9 (Q), 139.9 (Q), 139.6 (Q), 133.4 (Q), 128.1, 126.6, 126.0, 114.4, 112.3 (=CH_2), 55.5 (OCH_3), 21.9 (CH_3).

FT-IR (ATR film) 1/λ [cm^{-1}] 3080 (w), 3033 (w), 3000 (w), 2953 (m), 2833 (m), 2353 (w), 2053 (w), 1890 (w), 1790 (w), 1656 (w), 1602 (s), 1497 (s), 1254 (s), 1036 (s), 895 (s), 826 (s).

4-*N*,*N*-Dimethyl-4'-(prop-1-en-2-yl)biphenyl

White solid.

General Procedure (ArMgBr addition over 40 min).

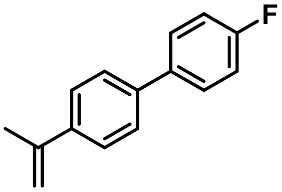


	$C_{17}H_{19}N$ (237.15 g/mol)
Yield	69%
TLC	R_f 0.18 (SiO_2, hexanes/ethyl acetate (95:5))
Melting point	182 °C
GC-MS	R_t 11.08 min (Standard heating procedure) m/z 237[M], 221, 206, 194, 178, 165, 152, 139, 117, 89, 77, 63, 51.
HRMS	(EI, 70 eV, m/z): 237.1515, calcd 237.1517
^{1}H-NMR	(300 MHz, $CDCl_3$), δ 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}C-NMR	(75 MHz, $CDCl_3$), δ 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) 1/λ [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).



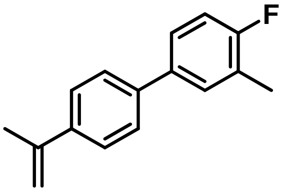
	$C_{15}H_{13}F$ (212.10 g/mol)
Yield	76%

TLC	R_f 0.29 (SiO_2, *n*-pentane)
Melting point	126.6 °C
GC-MS	R_t 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
^{1}H-NMR	(300 MHz, $CDCl_3$), 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).
^{13}C-APT-NMR	(75 MHz, $CDCl_3$), δ 162.6 (Q; d; 246 Hz), 142.8 (Q), 140.3 (Q), 139.3 (Q), 137.0 (Q), 128.6 (CH_{Ar}; d; 8.0 Hz), 126.9 (CH_{Ar}), 126.1 (CH_{Ar}), 115.8 (CH_{Ar}; d; 21.4 Hz), 112.7 (=CH_2), 21.9 (CH_3).
FT-IR	(ATR film) 1/λ [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).



$C_{16}H_{15}F$ (226.12 g/mol)

Yield	77%
TLC	R_f 0.55 (SiO_2, cyclohexane)
Melting point	83°C
GC-MS	R_t 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
^{1}H-NMR	(300 MHz, $CDCl_3$), 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).
^{13}C-APT-NMR	(75 MHz, $CDCl_3$), 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 (CH_{Ar}), 130.1 (CH_{Ar}), 126.9 (CH_{Ar}),

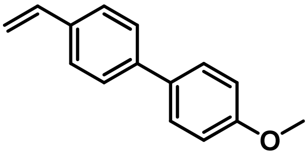
126.0 (CH_{Ar}), 125.9 (CH_{Ar}), 124.6 (Q; d; 17.0 Hz), 112.6 (=CH_2), 21.9 (CH_3), 14.8 (Ar-CH_3).

FT-IR (ATR film) 1/λ [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.



$C_{15}H_{14}O$ (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_t 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

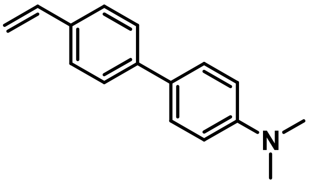
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.59-7.24 (m; 6H), 7.10-6.93 (m; 2H), 6.75 (dd; 1H, 10.9/6.6 Hz), 5.78 (dd; 1H, 17.6/0.9 Hz), 5.26 (dd; 1H, 10.9/0.9 Hz), 3.86 (s; 3H).

^{13}C-NMR (75 MHz, $CDCl_3$), δ 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) 1/λ [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.



$C_{16}H_{17}N$ (223.14 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

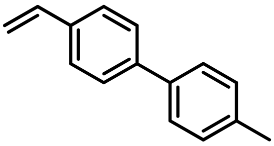
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.60-7.43 (m; 6H), 6.85-6.70 (m; 3H), 5.78 (dd; 1H, 17.6/1.0 Hz), 5.25 (dd; 1H, 10.9/0.9 Hz), 3.01 (s; 6H).

^{13}C-NMR (75 MHz, $CDCl_3$), δ 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/λ [cm^{-1}] 3050 (w), 2920 (w), 2364 (w), 1610 (m), 1504 (w), 1265 (m), 814 (s), 735 (s).

4-Methyl-4'-vinylbiphenyl

White solid.



$C_{15}H_{14}$ (194.11 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.

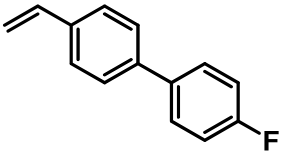
HRMS (EI, 70 eV, m/z): 194.1099, calcd 194.1096

^{1}H-NMR (300 MHz, $CDCl_3$), δ 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}C-NMR	(75 MHz, $CDCl_3$), δ 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 (=CH_2), 21.3 (Ar-CH_3).
FT-IR	(ATR film) 1/λ [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

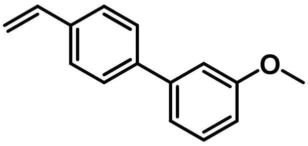
White solid.



	$C_{14}H_{11}$ (198.08 g/mol)
Yield	(97%)
TLC	R_f 0.25 (SiO_2, hexanes)
Melting Point	127°C
GC-MS	R_t 8.54 min (Standard heating procedure) m/z 198[M], 183, 170, 159, 151, 143, 133, 120, 107, 98, 85, 75, 63.
HRMS	(EI, 70 eV, m/z): 198.0841, calcd 198.0845
^{1}H-NMR	(300 MHz, $CDCl_3$), δ 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).
^{13}C-NMR	(75 MHz, $CDCl_3$), δ 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 (=CH_2; d; 21.4 Hz), 114.1.
FT-IR	(ATR film) 1/λ [cm^{-1}] 3089 (w), 3005 (w), 2920 (w), 2360 (w), 1598 (m), 1494 (m), 1240 (w), 99s (m), 909 (m), 824 (s), 665 (m).

3-Methoxy-4'-vinylbiphenyl

Colorless Oil.



$C_{15}H_{14}O$ (210.10 g/mol)

Yield 96%

TLC R_f 0.26 (SiO_2, hexanes/ethyl acetate (95:5))

GC-MS R_t 9.74 min (Standard heating procedure)

m/z 210[M], 197, 179, 165, 152, 139, 128, 115, 102, 89, 77, 63.

HRMS (EI, 70 eV, m/z): 210.1045, calcd 210.1046

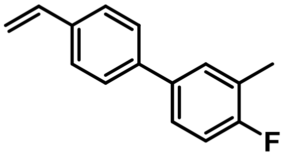
^{1}H-NMR (300 MHz, $CDCl_3$), δ 7.61-7.47 (m; 4H), 7.38 (t; 1H, 7.4 Hz), 7.25-7.14 (m; 2H), 6.95-6.90 (m; 1H), 6.78 (dd; 1H, 10.9/6.6 Hz), 5.82 (dd; 1H, 17.6/0.9 Hz), 5.30 (dd; 1H, 10.9/0.9 Hz), 3.88 (s; 3H).

^{13}C-NMR (75 MHz, $CDCl_3$), δ 160.1 (Q), 142.4 (Q), 140.6 (Q), 136.9 (Q), 136.5 (-CH=), 129.9, 127.4, 126.7, 119.6, 114.09, 112.9, 112.8 (=CH_2), 55.4 (OCH_3).

FT-IR (ATR film) 1/λ [cm^{-1}] 3082 (w), 3003 (w), 2835 (w), 1917 (w), 1563 (s), 1480 (s), 1294 (s), 1213 (s), 1035 (m), 837 (s), 778 (s), 695 (s).

4-Fluoro-3-methyl-4'-vinylbiphenyl

White solid.



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

Yield 85%

TLC R_f 0.21 (SiO_2, hexanes)

Melting Point 61°C

GC-MS R_t 9.05 min (Standard heating procedure)

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

HRMS (EI, 70 eV, m/z): 212.1001, calcd 212.0999

^{1}H-NMR (300 MHz, $CDCl_3$), 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).

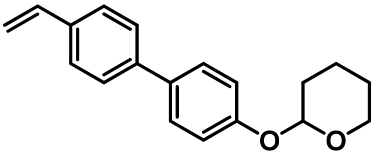
^{13}C-NMR (75 MHz, $CDCl_3$), δ 161.2 (Q; d; 244.9 Hz), 139.9 (Q), 136.7 (Q; d; 3.5 Hz), 136.6 (Q), 136.5 (-CH=), 130.2 (d; 5.2 Hz), 127.2, 126.8, 125.9 (d;

8.0 Hz), 125.2 (Q; d; 17.5 Hz), 115.4 (d; 22.5 Hz), 114.0 (=CH_2), 14.8 (Ar-CH_3; d; 3.5 Hz).

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

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

White solid.



$C_{19}H_{20}O_2$ (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 R_t 11.94 min (Standard heating procedure)
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, $CDCl_3$), δ 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, $CDCl_3$), δ 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).

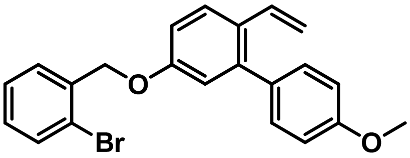
FT-IR (ATR film) 1/λ [cm^{-1}] 3086 (w), 2948 (m), 2870 (m), 1603 (m), 1497 (s), 1245 (s), 1110 (s), 1021 (m), 967 (s), 822 (s).

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 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, $CDCl_3$), δ 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).

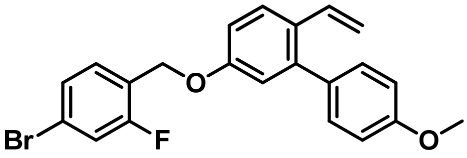
^{13}C-NMR (75 MHz, $CDCl_3$), δ 159.0, 158.0, 142.0, 136.3, 135.5, 133.1, 132.8, 130.9, 129.4, 129.3, 129.1, 127.7, 127.2, 122.5, 116.1, 114.1, 113.6, 112.9, 69.6 (Ar-CH), 55.4 (OCH_3).

FT-IR (ATR film) 1/λ [cm-1] 3063 (w), 3002 (w), 2935 (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 412[M], 382, 355, 333, 281, 257, 225, 186, 165, 139, 108, 81, 63.

^{1}H-NMR (300 MHz, $CDCl_3$), δ 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, $CDCl_3$), δ 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).

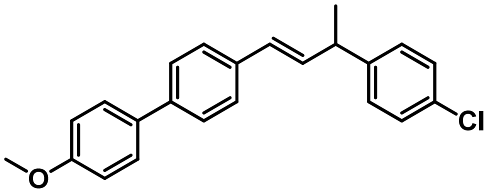
HRMS (EI, 70 eV, m/z):, 412.0469 calcd 412.0474

FT-IR (ATR film) 1/λ [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.



$C_{23}H_{21}ClO$ (348.13 g/mol)

Yield 66%

TLC R_f 0.24 (SiO_2, *n*-pentane/ethyl acetate (95:5))

Melting point 144°C

GC-MS R_t 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.

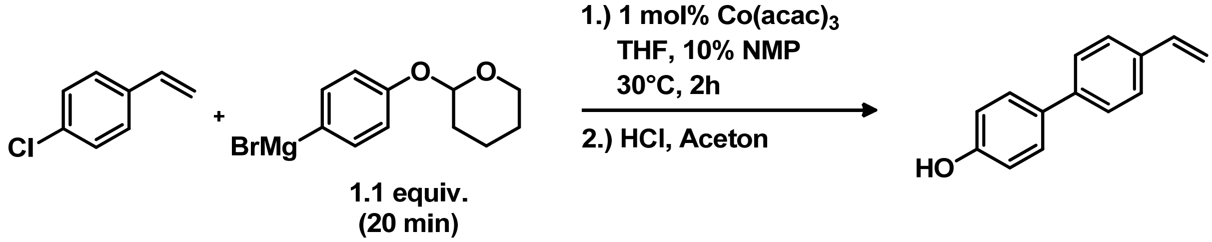
HRMS (EI, 70 eV, m/z): 348.1277, calcd 348.1281

^{1}H-NMR (300 MHz, $CDCl_3$), δ 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, $CDCl_3$), δ 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) 1/λ [cm-1] 2963 (w), 2929 (w), 2873 (w), 1728 (w), 1603 (w), 1494 (m), 1251 (m), 1013 (m), 808 (s).

4'-Vinyl-[1,1'-biphenyl]-4-ol



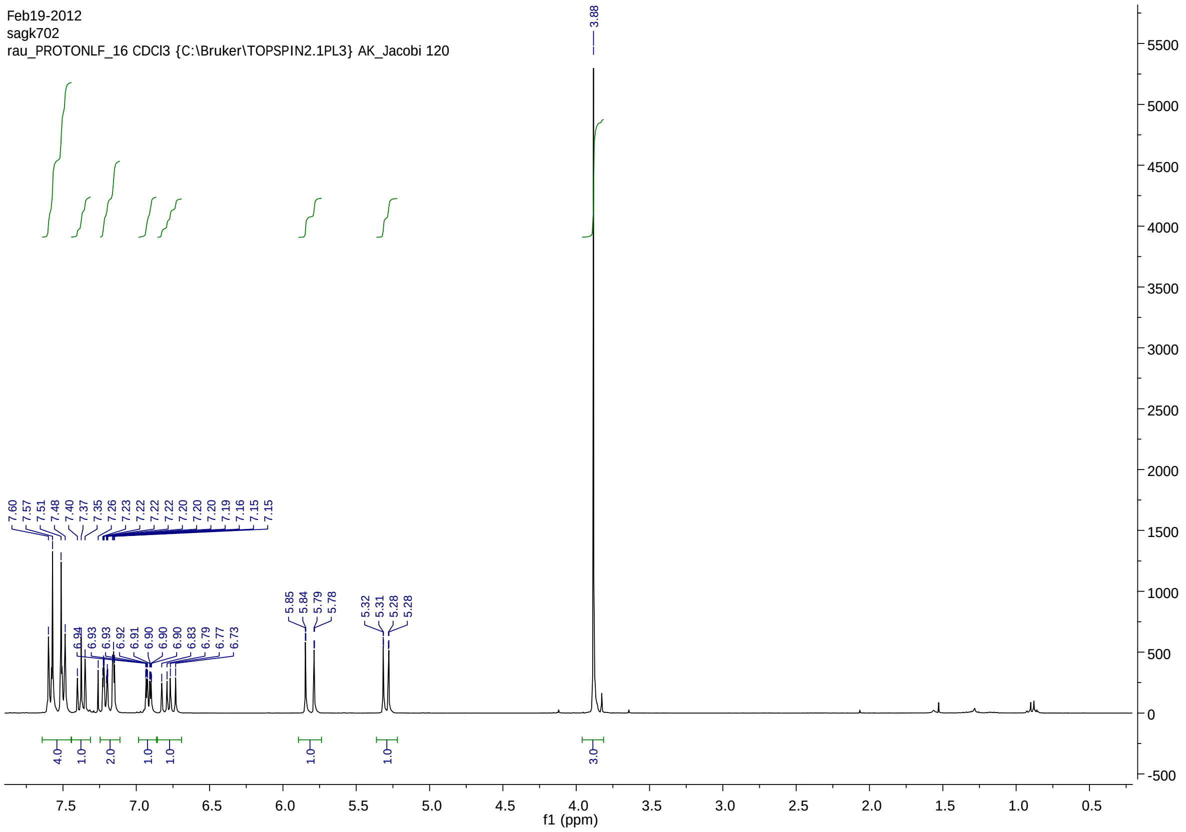
3.5 mg (1 mol%, 0.01 mmol) Co(acac)$_3$ were loaded into a 25 mL-flask under an atmosphere of argon and treated with 4.4 mL of a solvent mixture containing dried THF and NMP (10/1, v/v). The resulting green solution was put in a water bath at 30°C and treated with 1 mmol of the 4-chlorostyrene followed 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$_2$SO$_4$) and concentrated in vacuo. Silica gel column chromatography (*n*-pentane/ethyl acetate) afforded the pure product as white solid (180 mg, 92%).

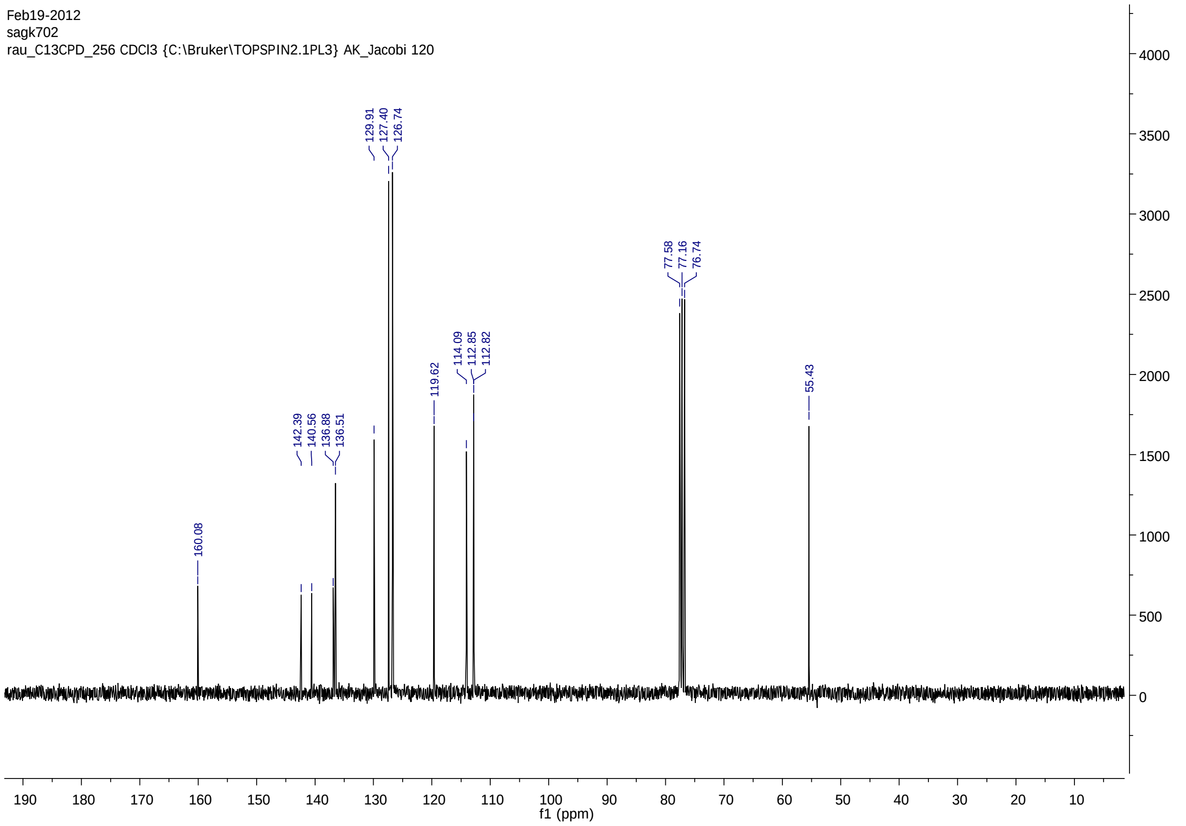
	$C_{14}H_{12}O$ (196.09 g/mol)
Yield	92%
TLC	R_f 0.15 (SiO$_2$, *n*-pentane/ethyl acetate (9:1))
Melting point	143°C
GC-MS	R_t 10.10 min (Standard heating procedure) m/z 196[M], 181, 165, 152, 139, 128, 115, 101, 89, 77, 63, 51.
^{1}H-NMR	(300 MHz, CDCl$_3$), δ 7.56-7.42 (m; 7H), 6.95-6.86 (m; 2H), 6.75 (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$_2$).

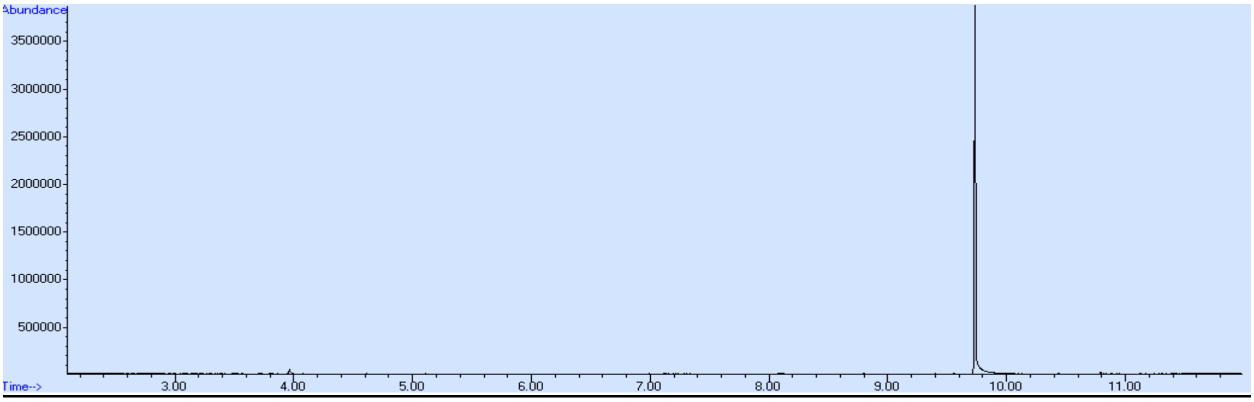
Analytical data in accordance with literature data: H. A. Zayas, M. C. Bowyer, C. P. Gordon, I. C. Holdsworth, A. McCluskey, *Tetrahedron Letters* **2009**, *50*, 5894-5895.

Selected Spectra

3-Methoxy-4'-vinylbiphenyl (2)



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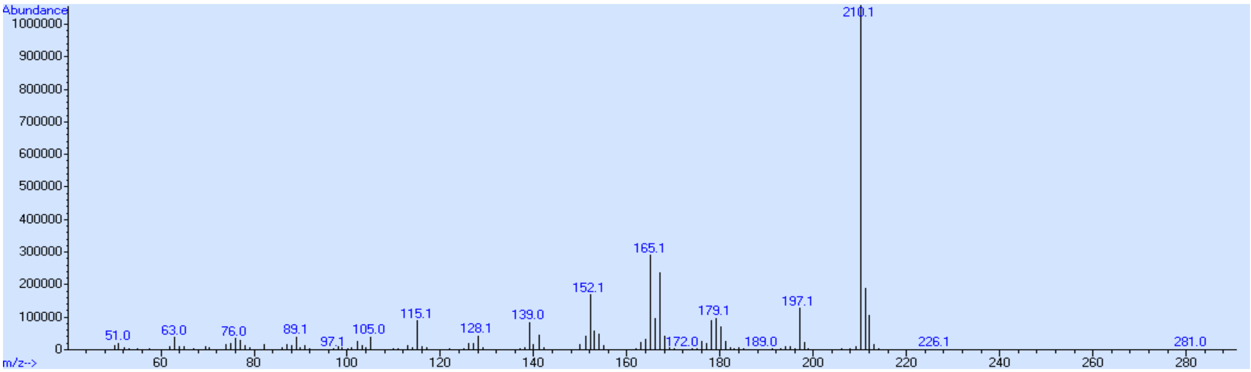
9.00
10.00
11.00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m/z-->
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160
180
200
220
240
260
280
210.1
165.1
152.1
197.1
179.1
115.1
139.0
128.1
105.0
89.1
63.0
76.0
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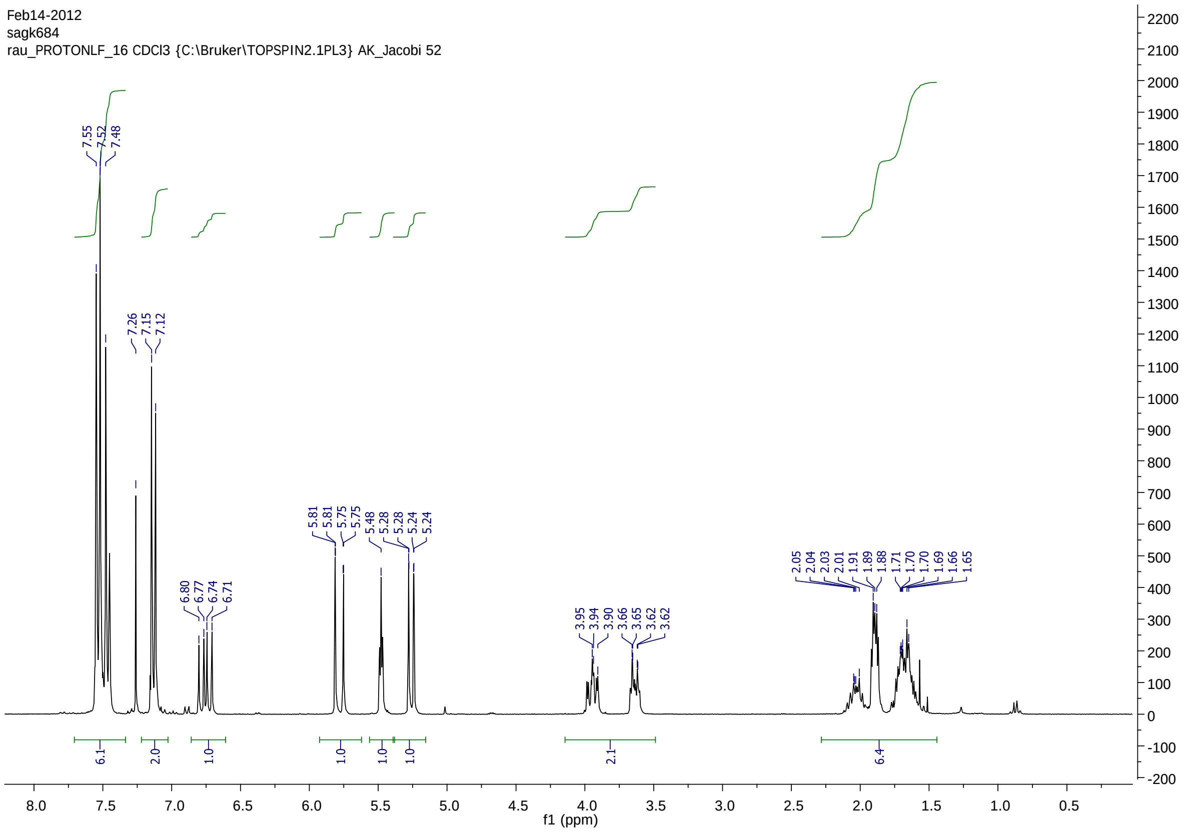
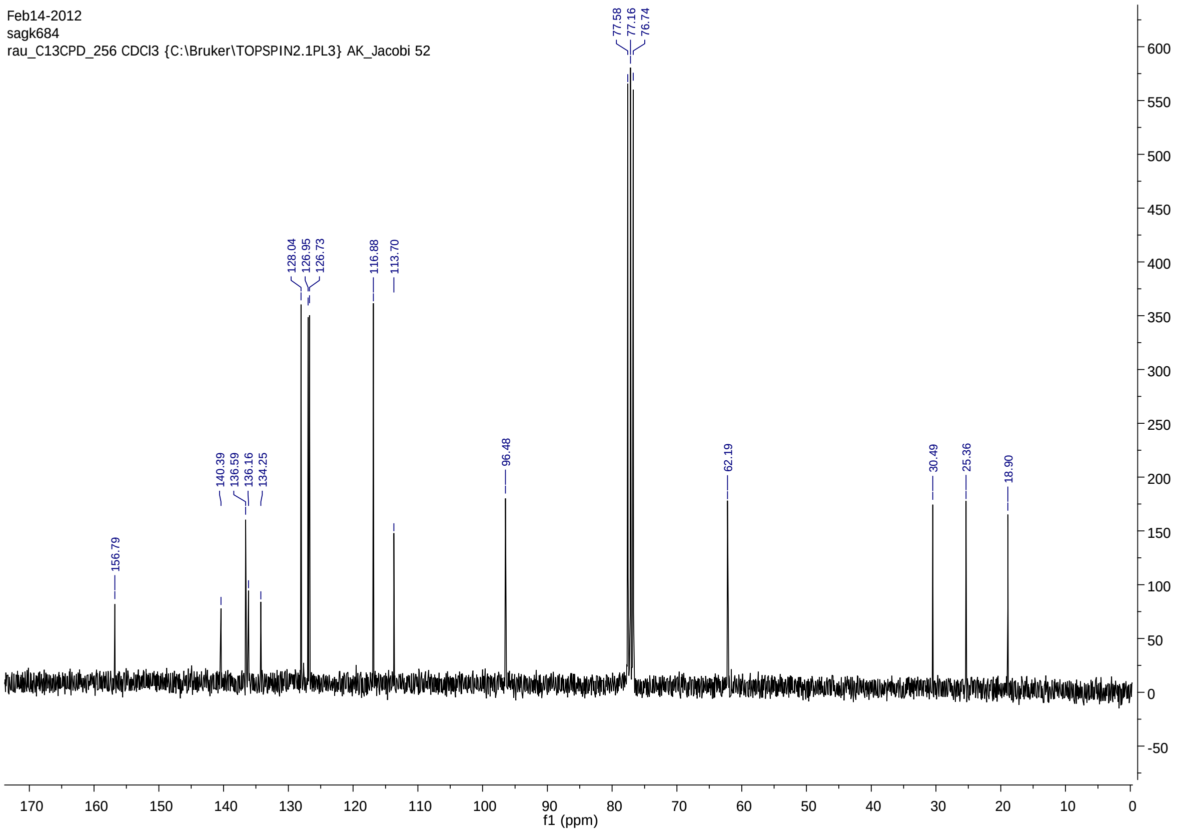
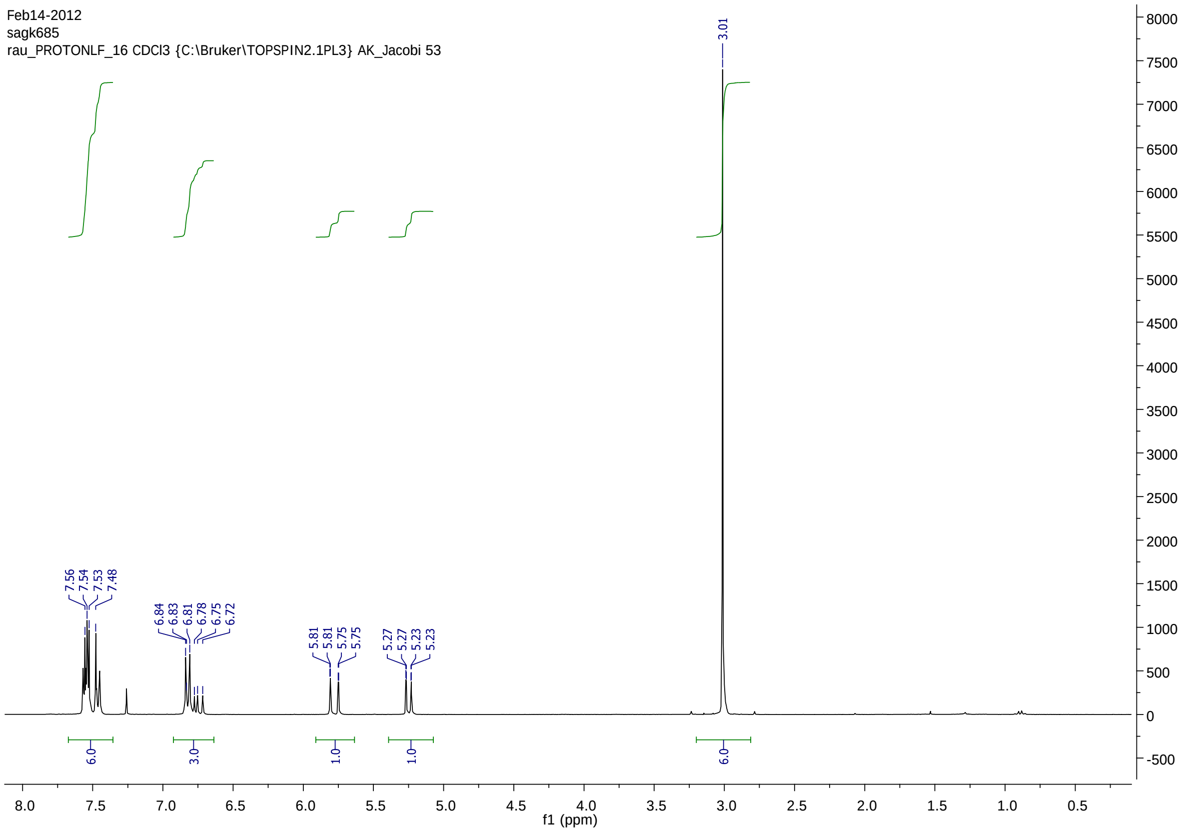
226.1
281.0

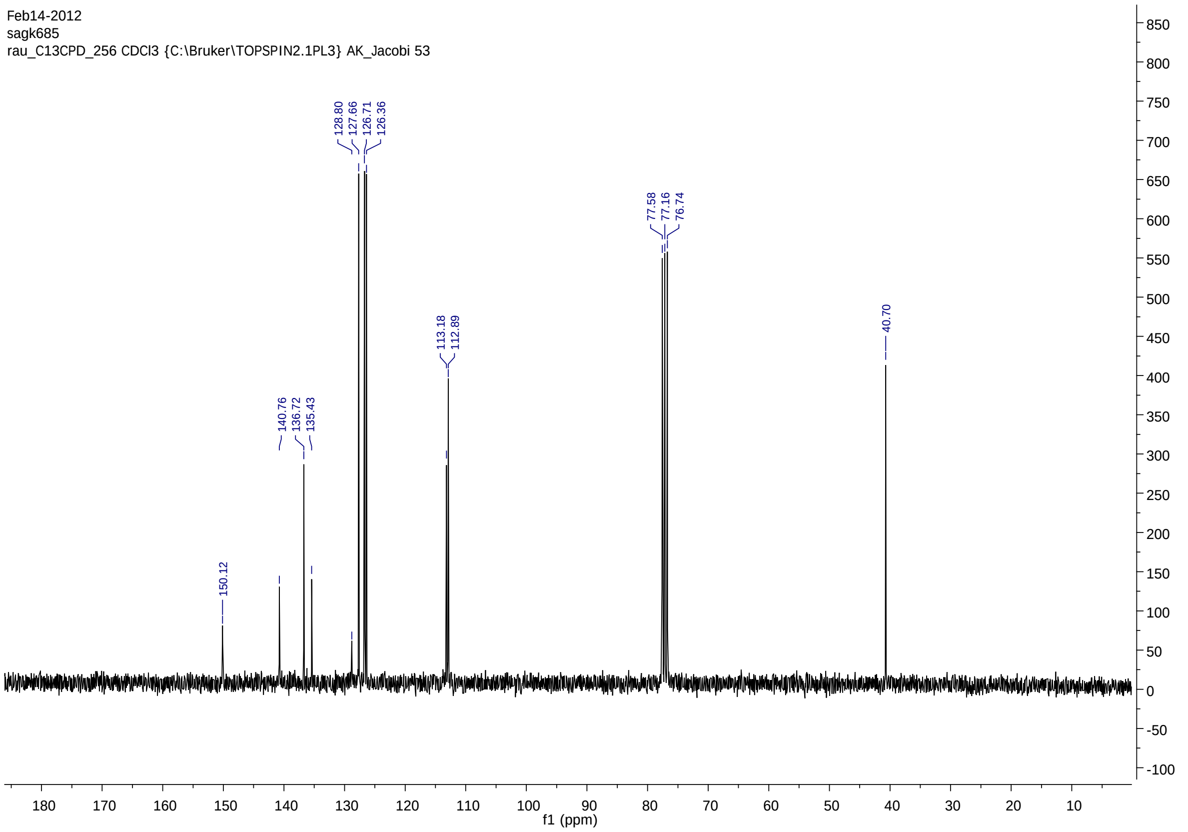
2-(4'-Vinylbiphenyl-4-yloxy)tetrahydro-2*H*-pyran

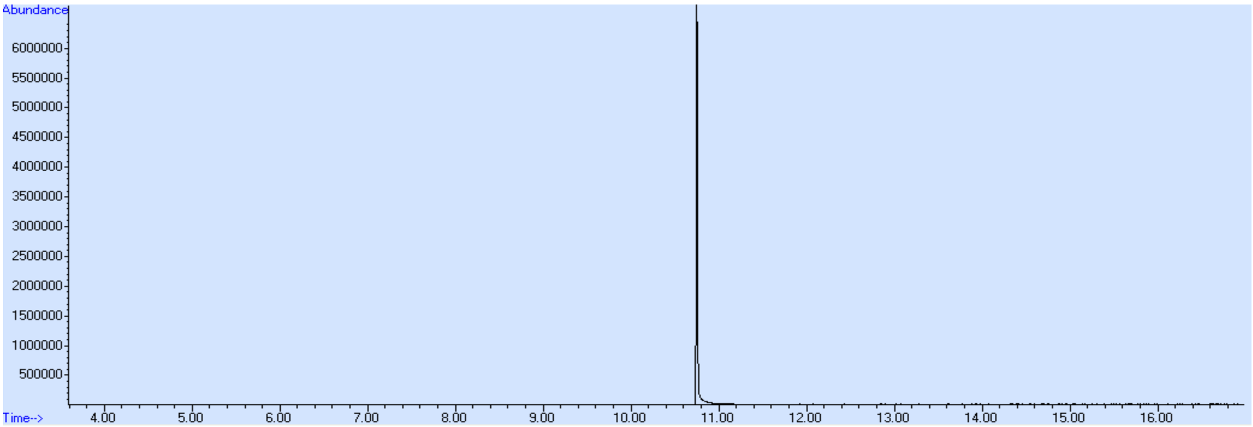




4-*N*,*N*-Dimethylamino-4'-vinylbiphenyl



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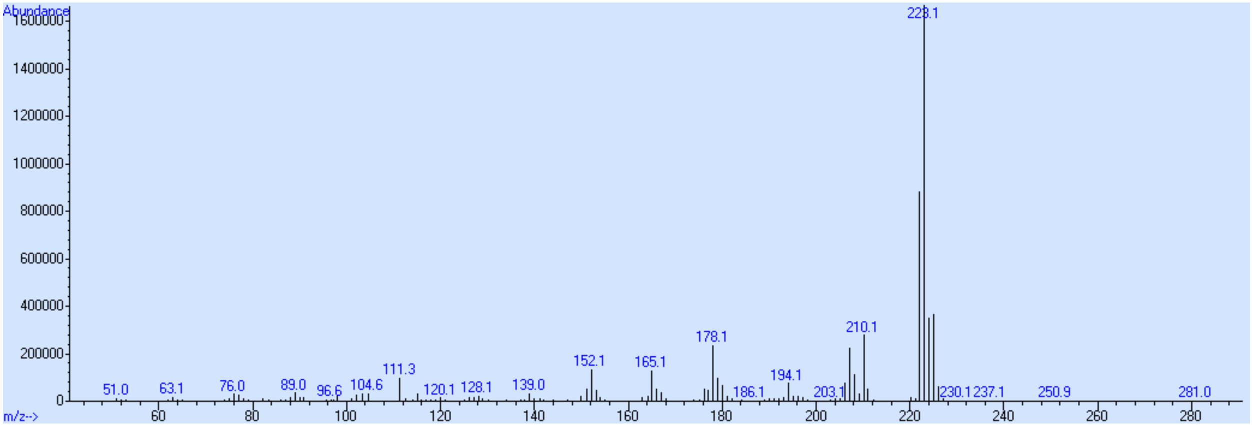
13.00
14.00
15.00
16.00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m/z-->
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180
200
220
240
260
280
223.1
210.1
178.1
152.1
165.1
111.3
194.1
51.0
63.1
76.0
89.0
96.6
104.6
120.1
128.1
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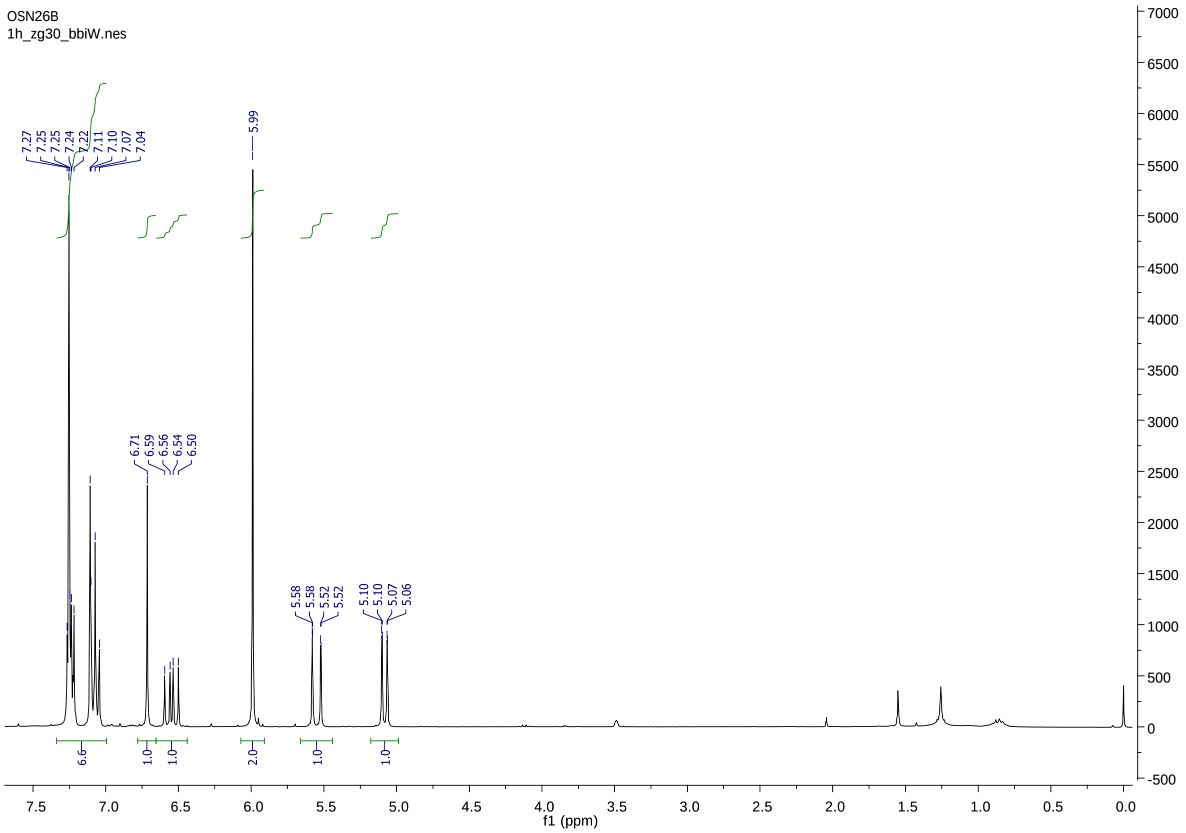
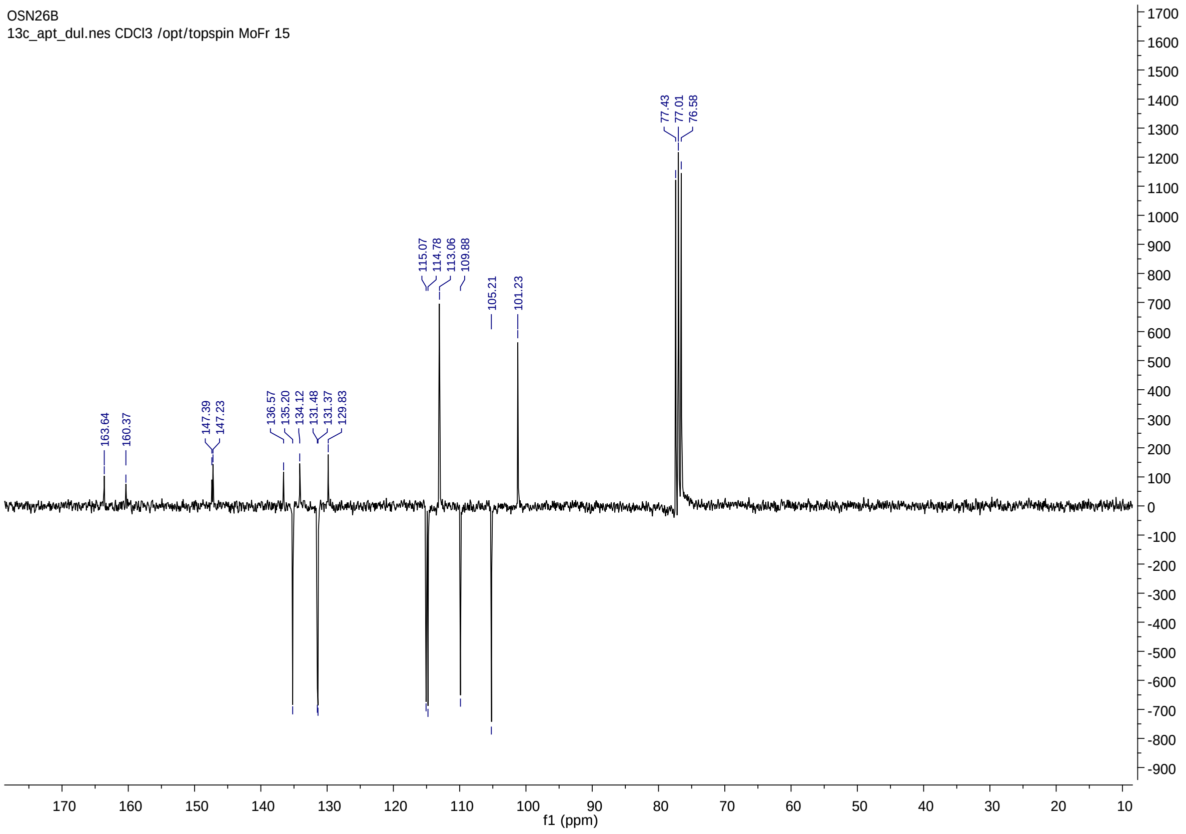
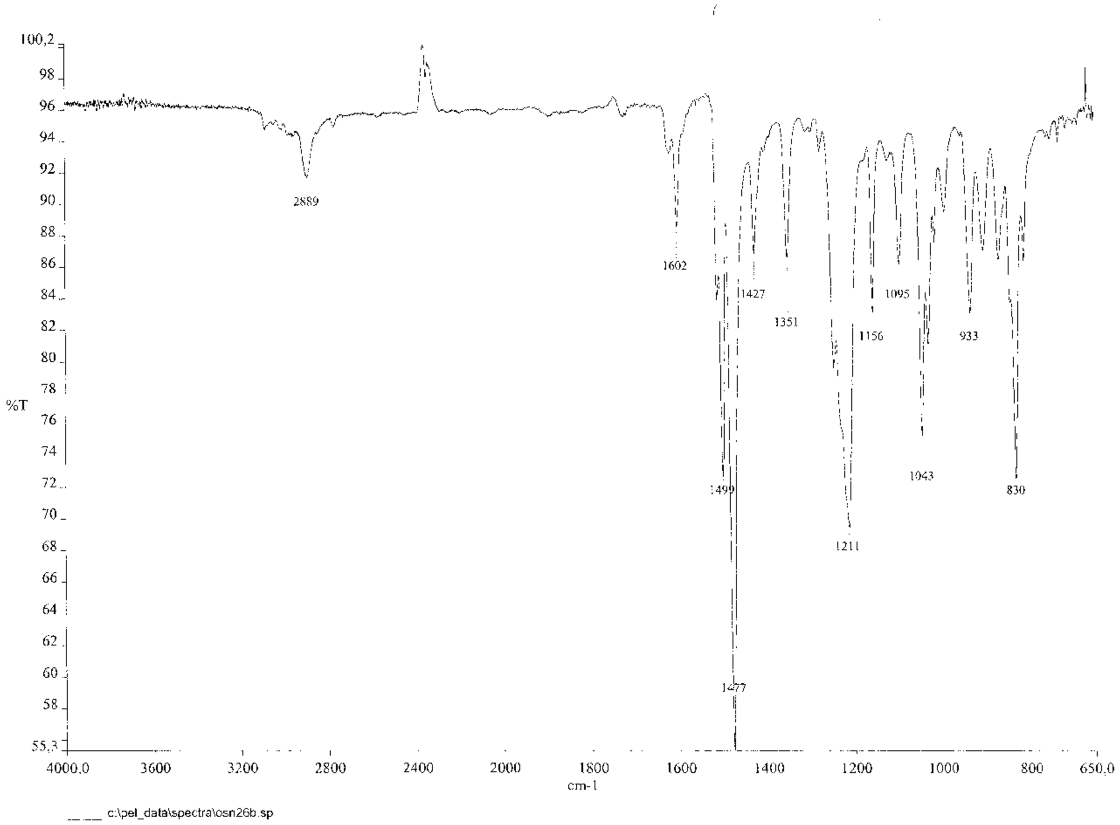
237.1
250.9
281.0

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



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55,3
%T
2889
1602
1427
1351
1156
1095
933
1499
1043
830
1211
1477
4000,0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650,0
cm-1
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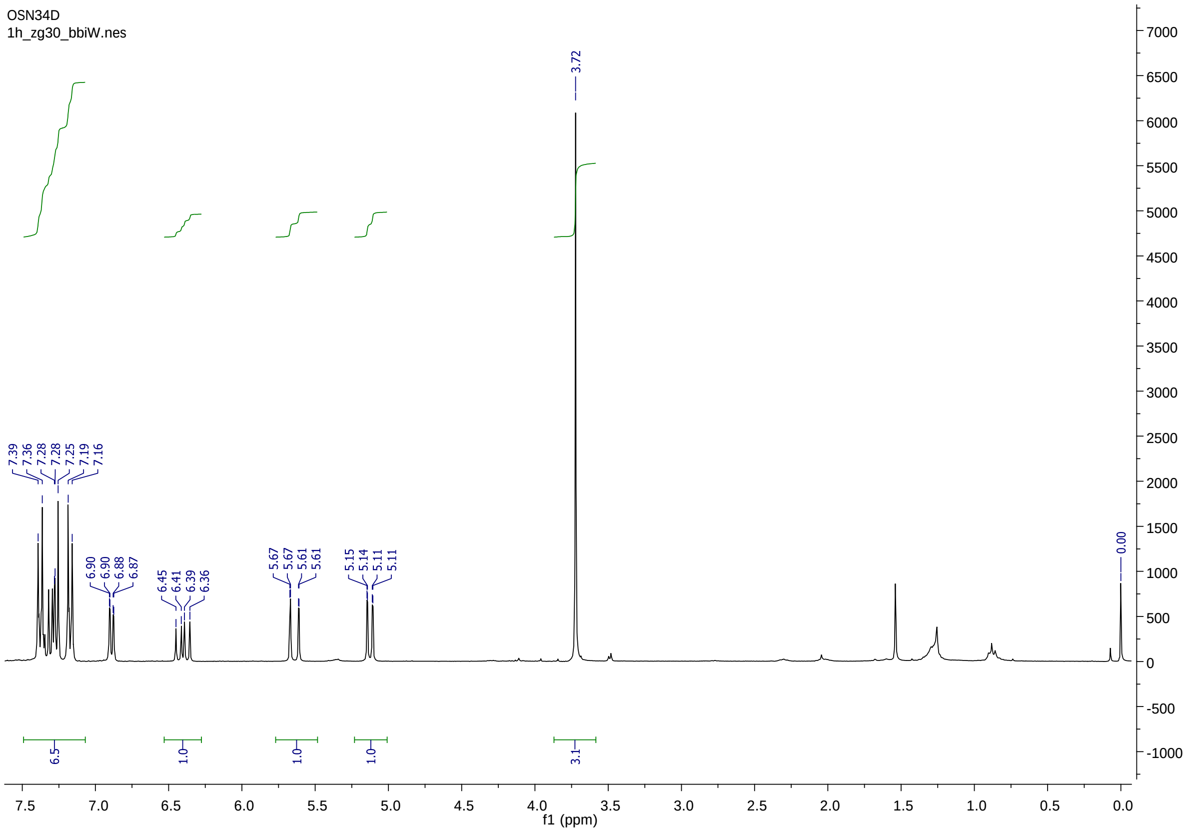
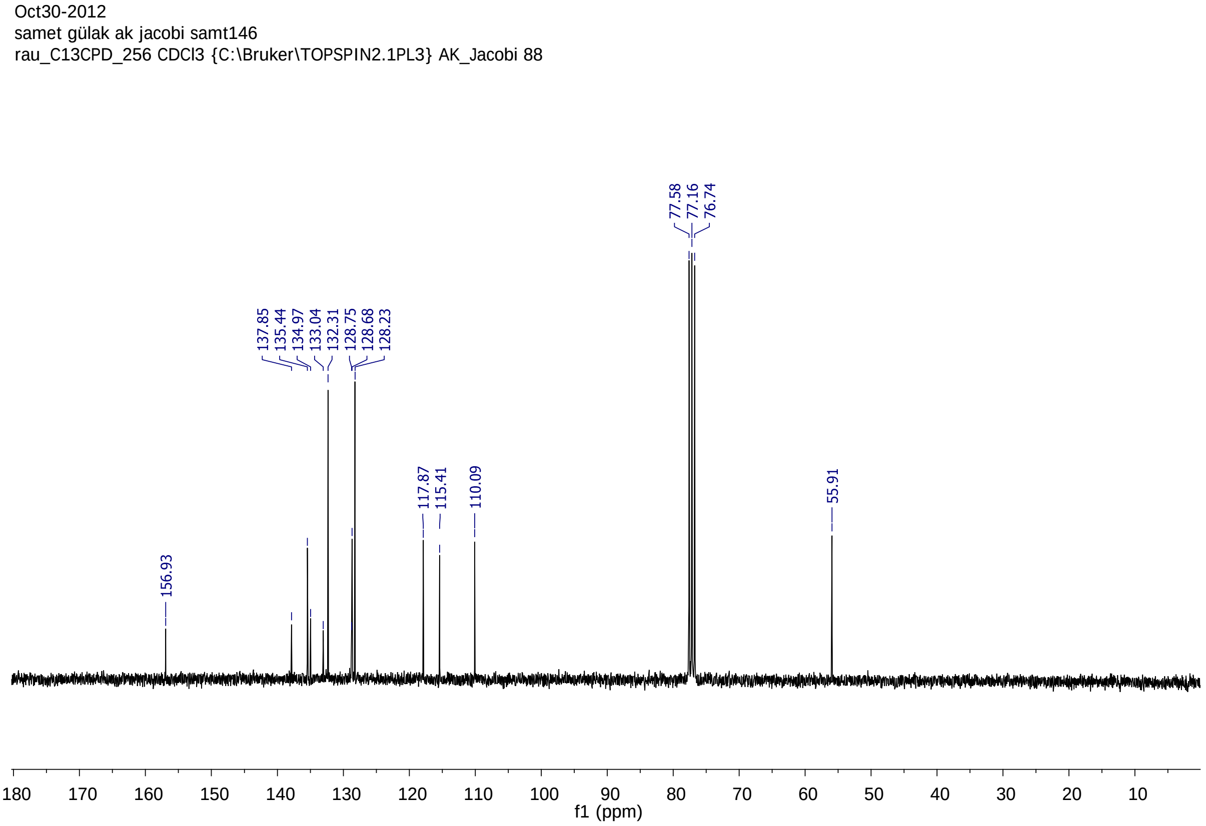
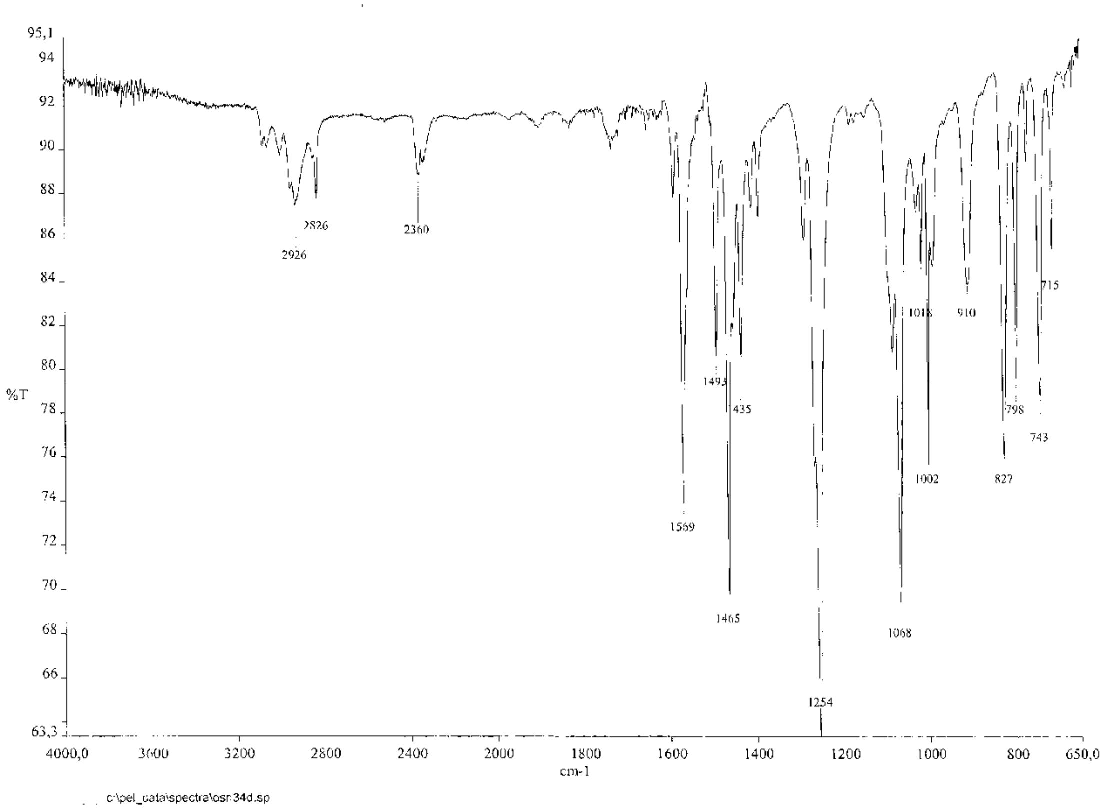
4'-Chloro-2-methoxy-6-vinylbiphenyl






95,1
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74
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70
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3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650,0
cm-1
2926
2826
2360
1569
1493
1465
435
1254
1068
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1002
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827
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743
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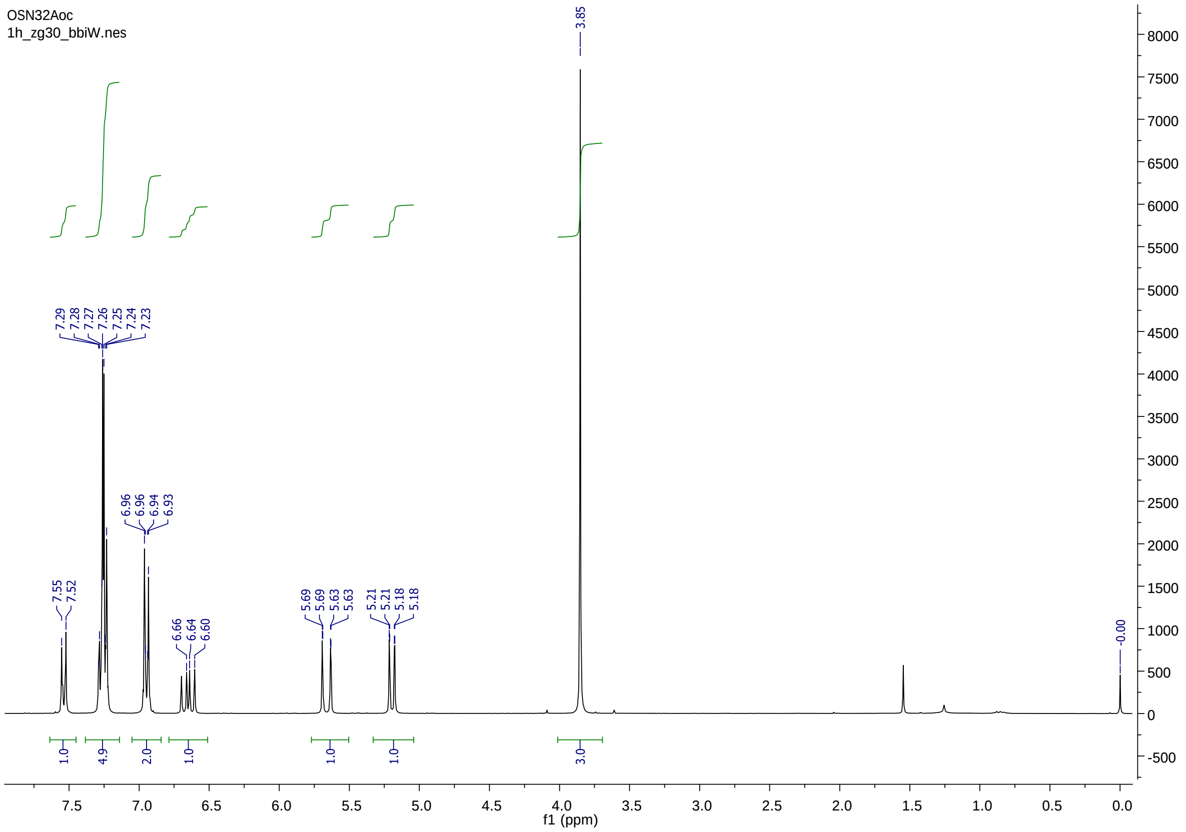
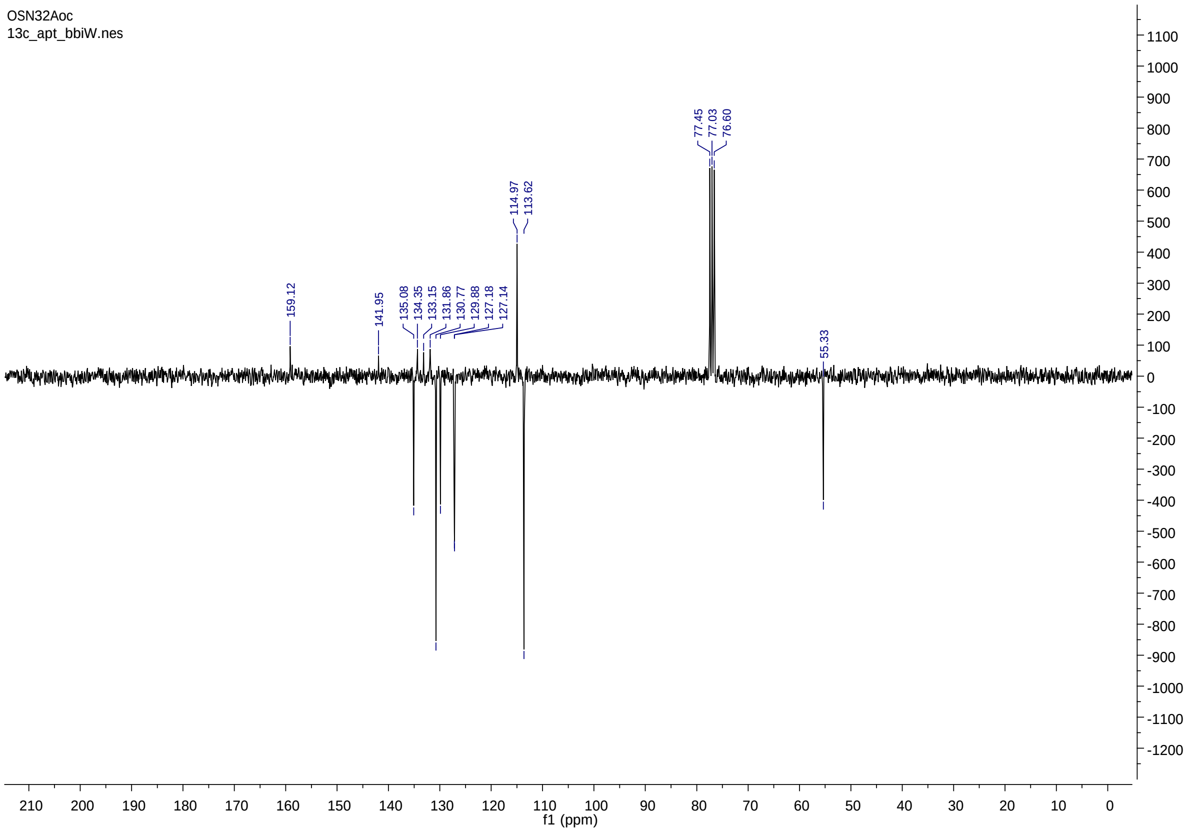
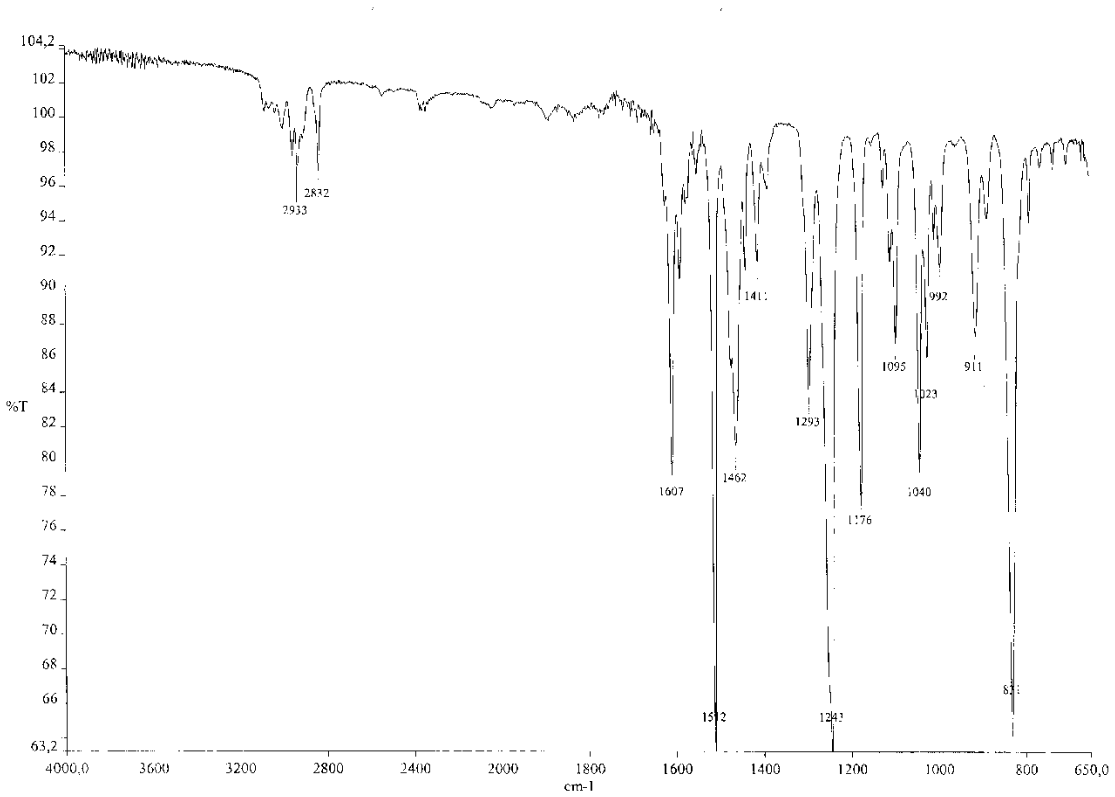
5-Chloro-4'-methoxy-2-vinylbiphenyl







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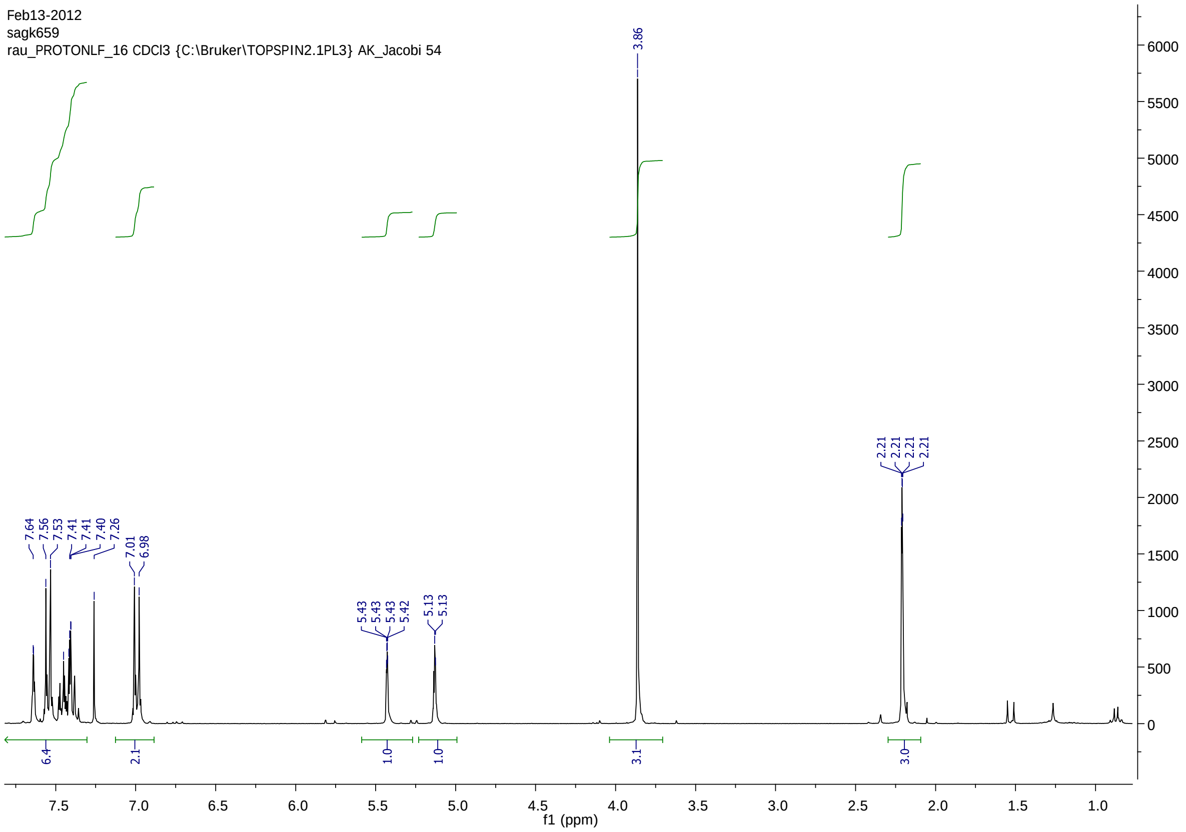
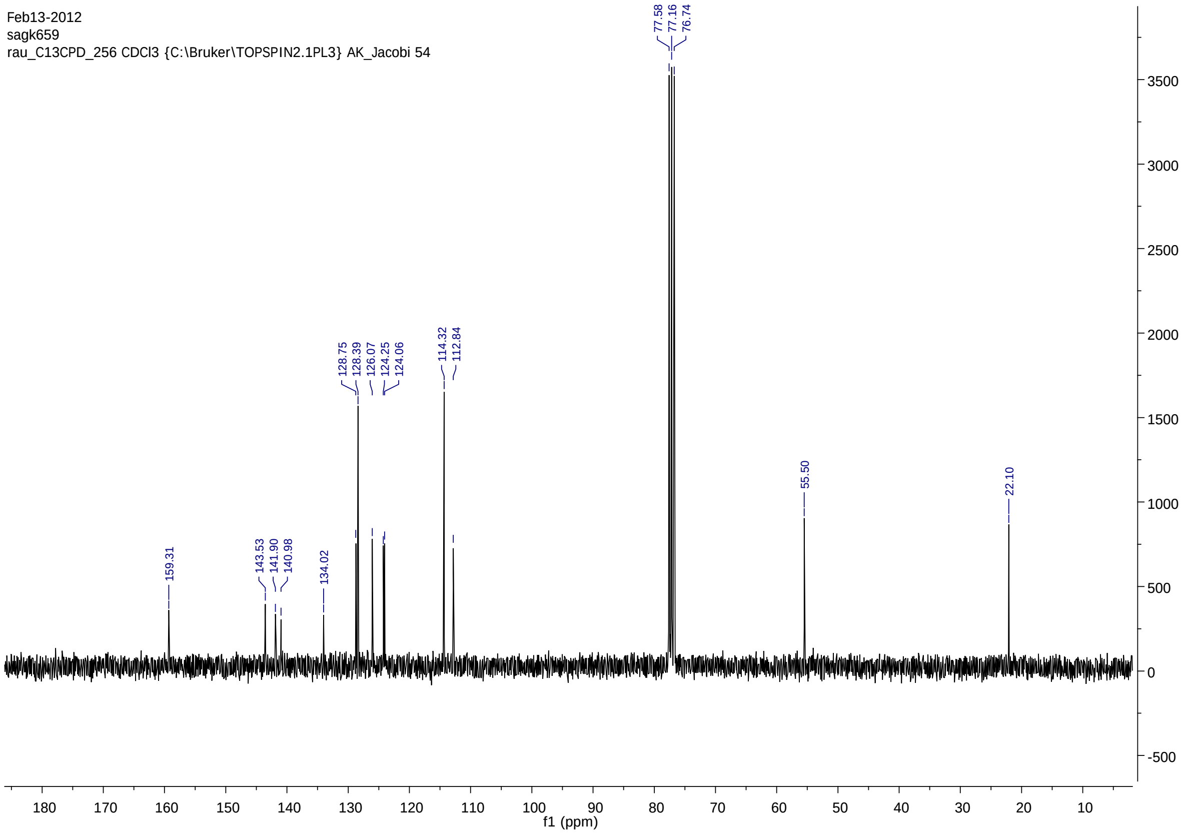
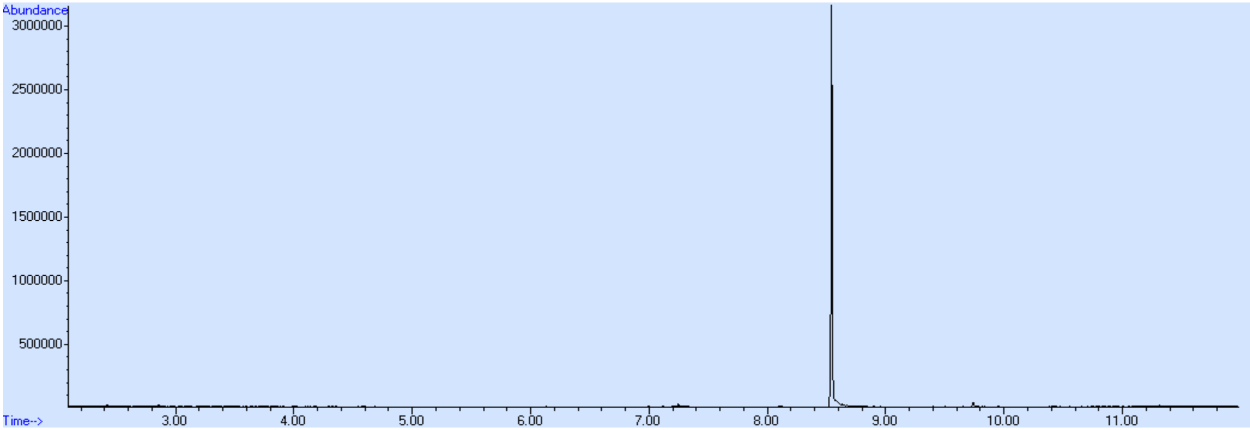
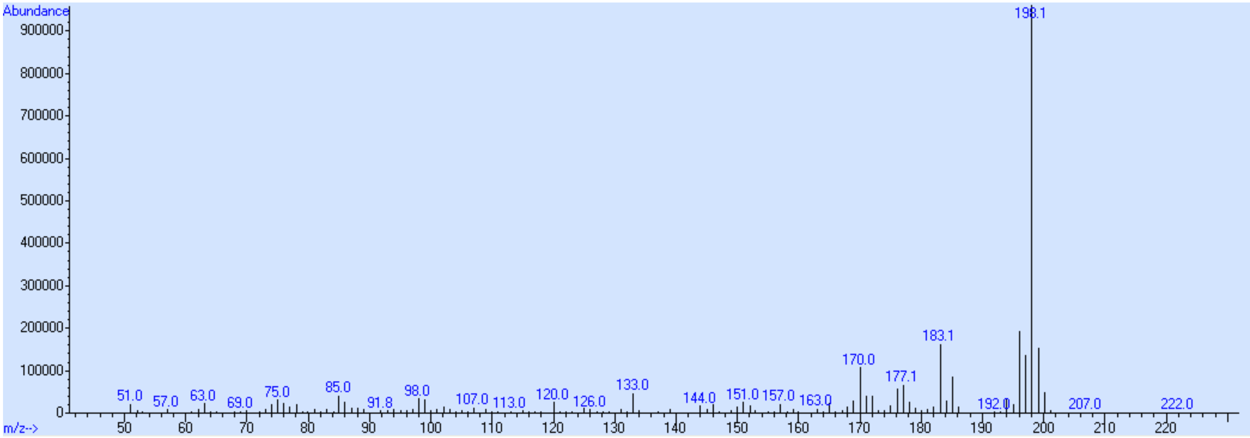
4'-Methoxy-3-(prop-1-en-2-yl)biphenyl

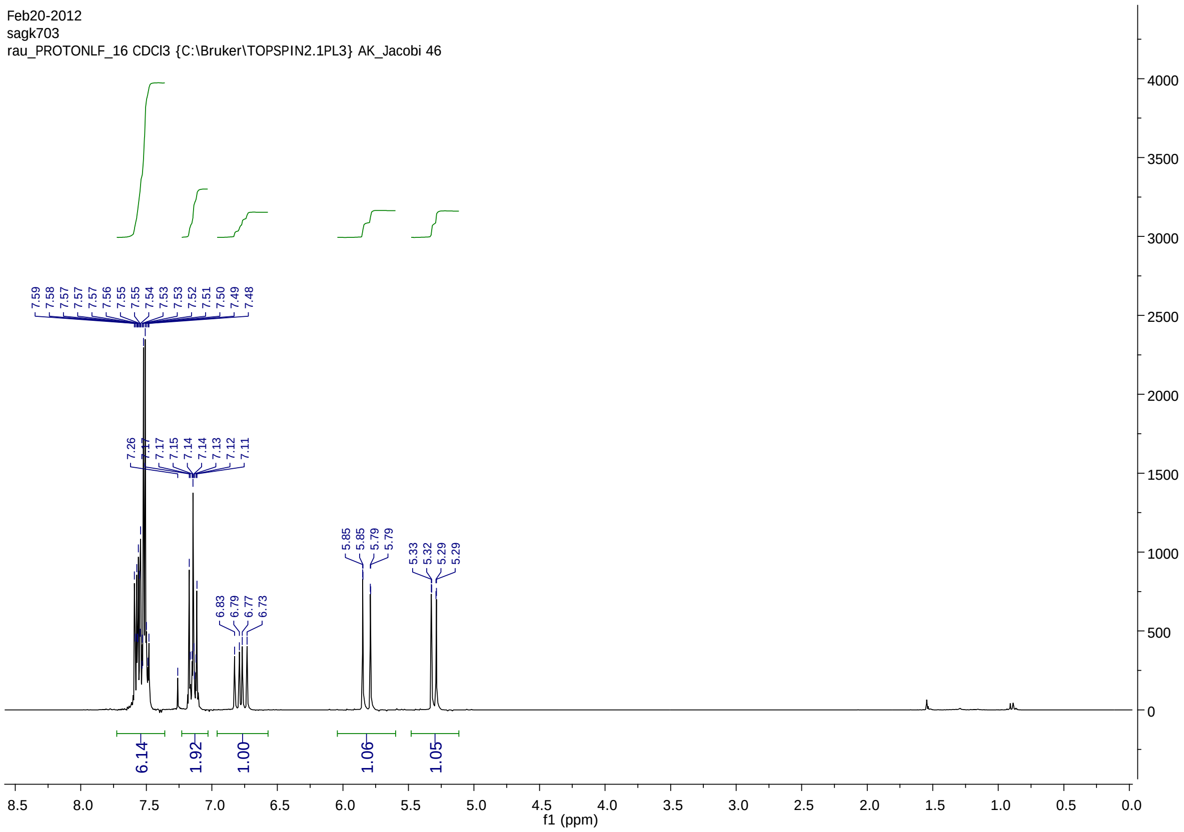


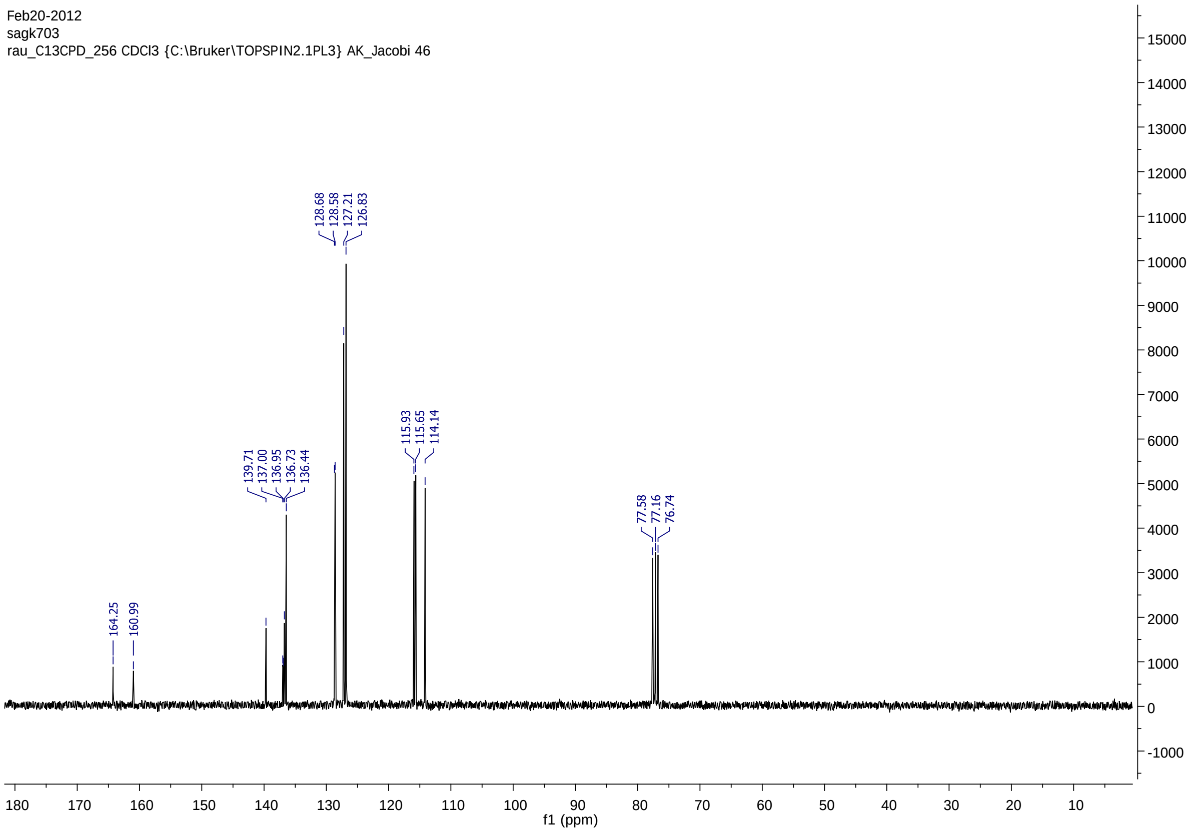


4-Fluoro-4'-vinylbiphenyl








Feb20-2012
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137.00
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136.73
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127.21
126.83
115.93
115.65
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77.58
77.16
76.74
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11000
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4000
3000
2000
1000
0
-1000
180
170
160
150
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20
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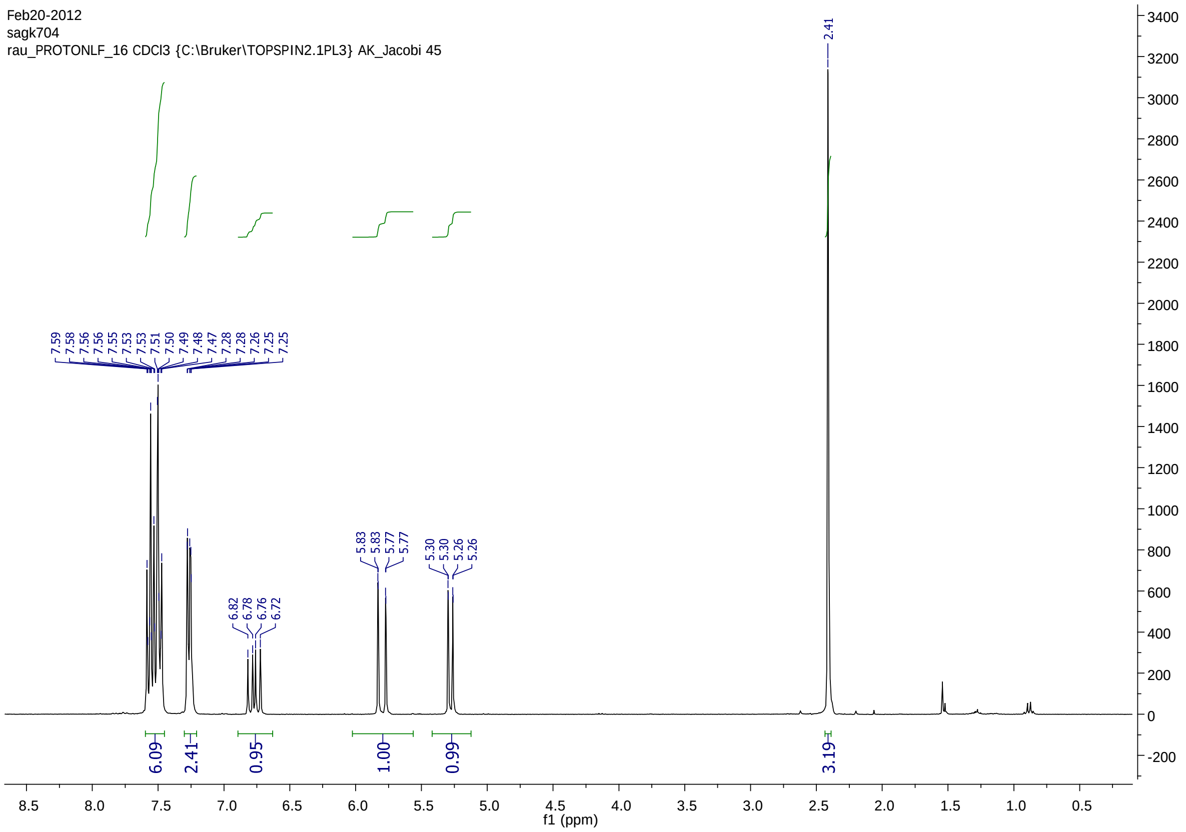
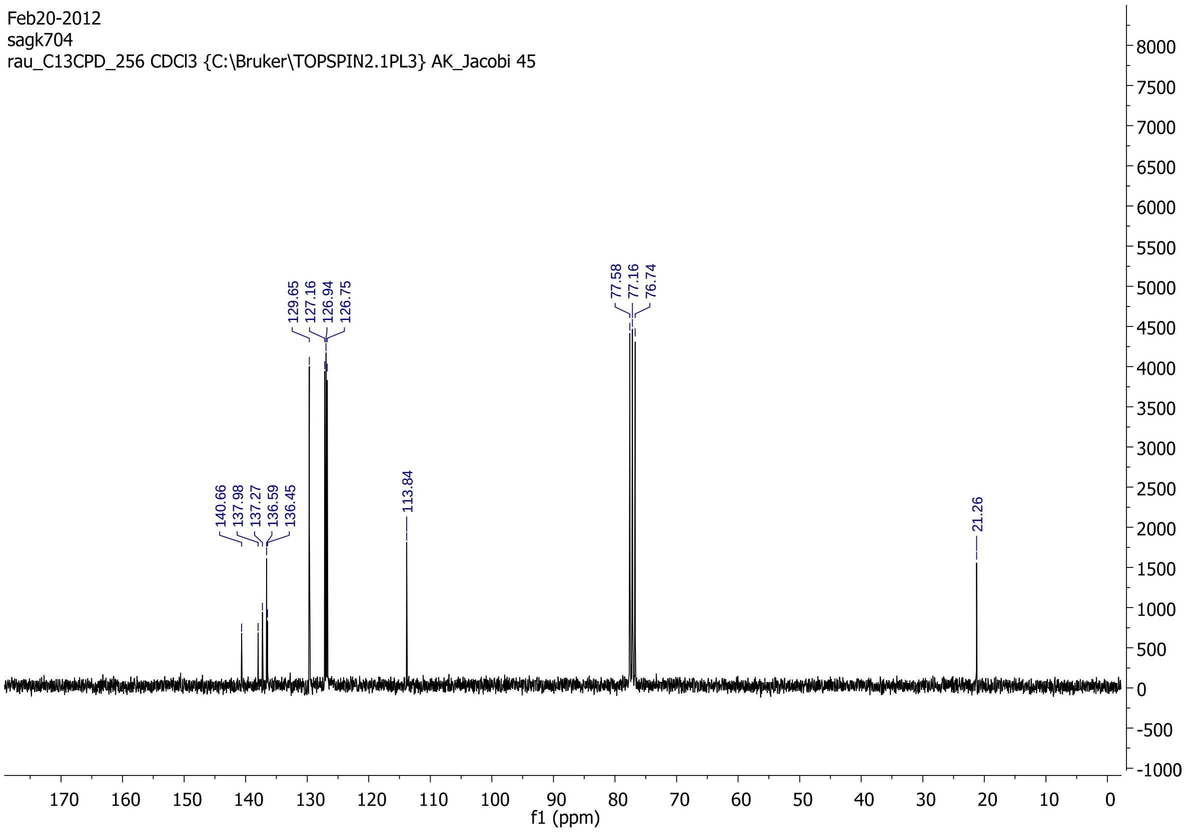
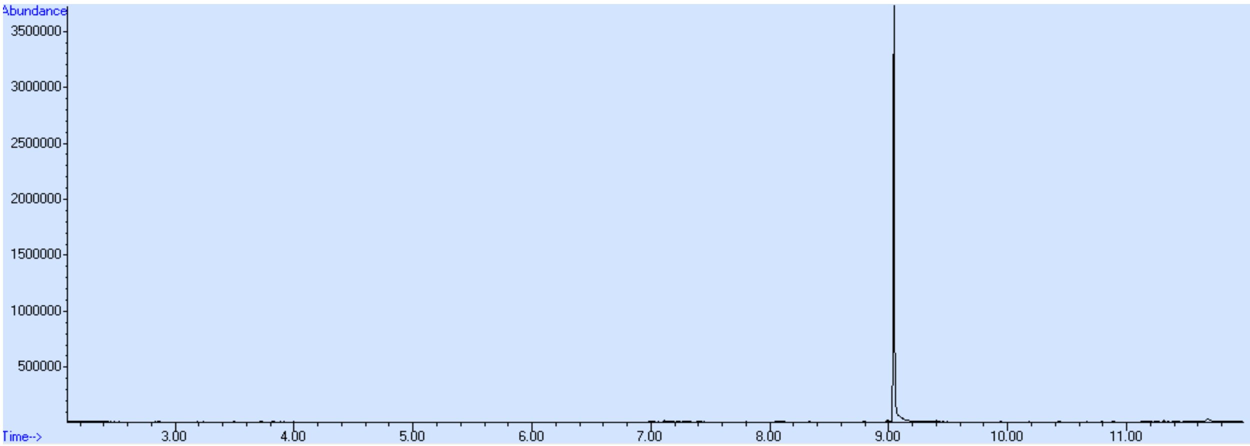
f1 (ppm)

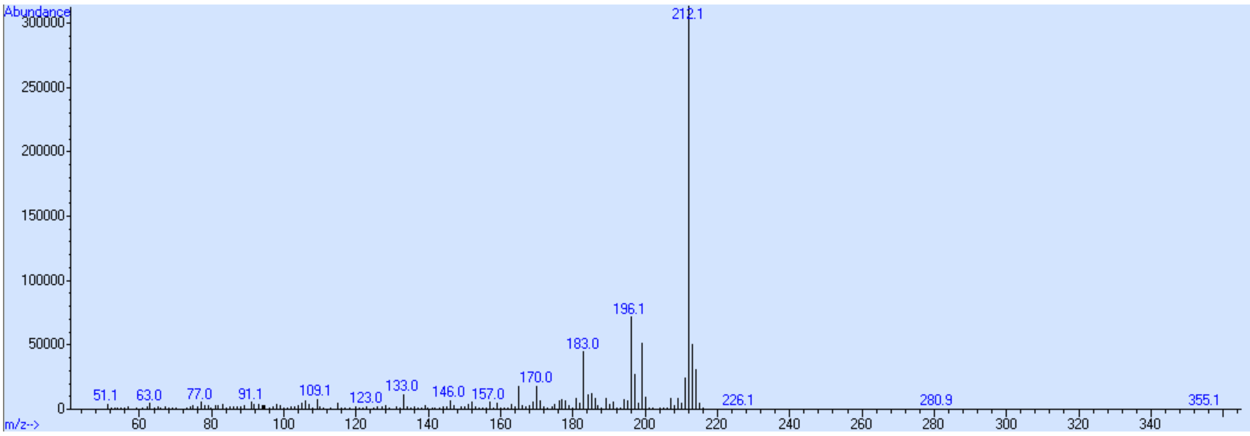
4-Methyl-4'-vinylbiphenyl

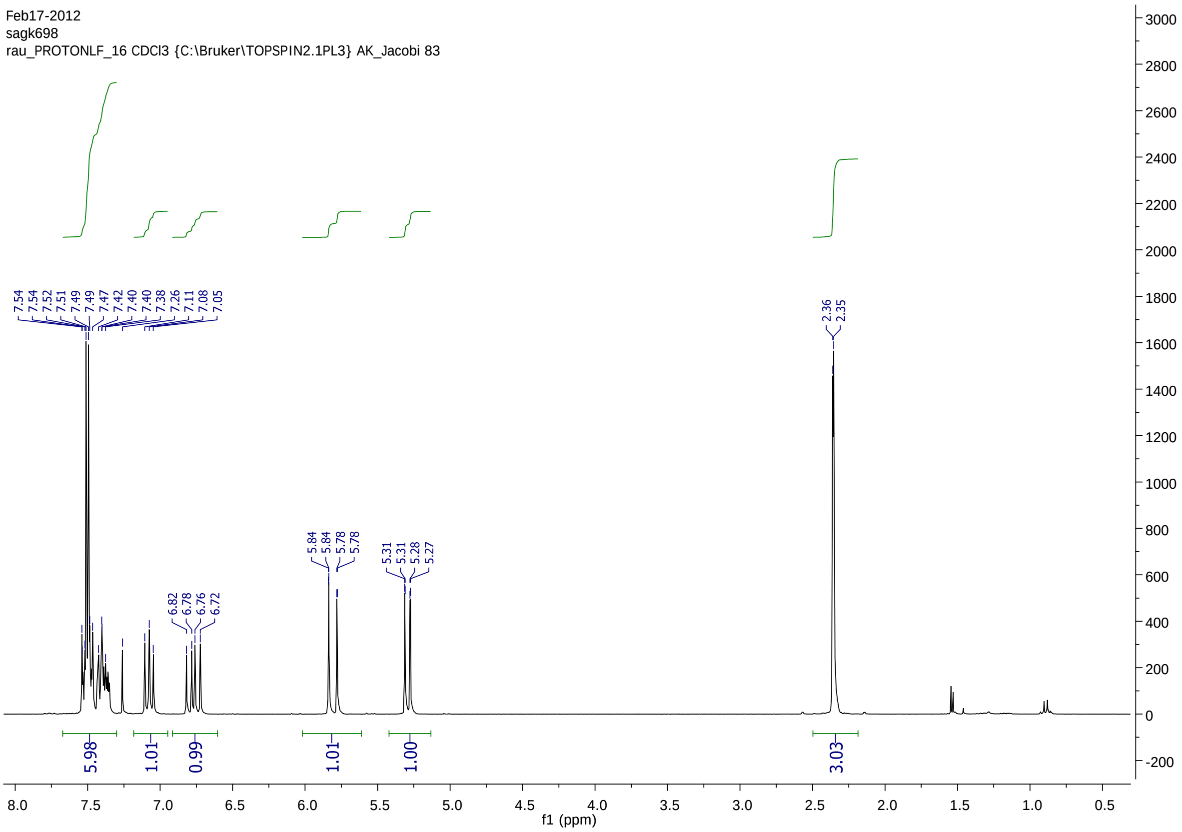


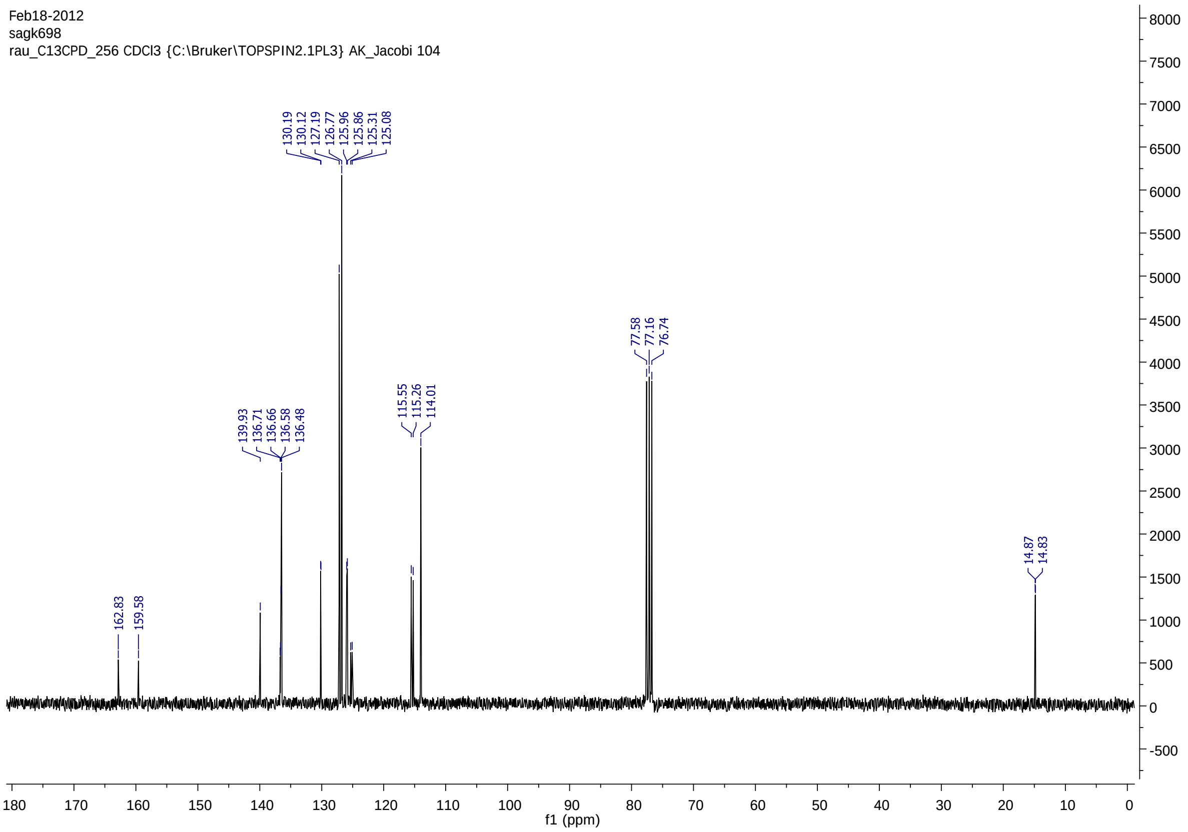


4-Fluoro-3-methyl-4'-vinylbiphenyl





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127.19
126.77
125.96
125.86
125.31
125.08
115.55
115.26
114.01
77.58
77.16
76.74
14.87
14.83
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
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70
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50
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30
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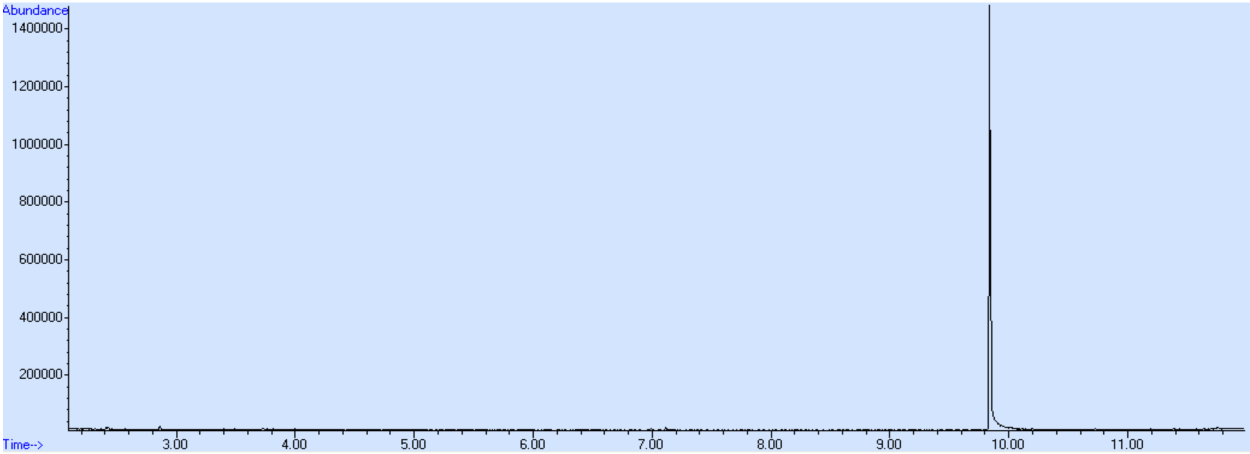
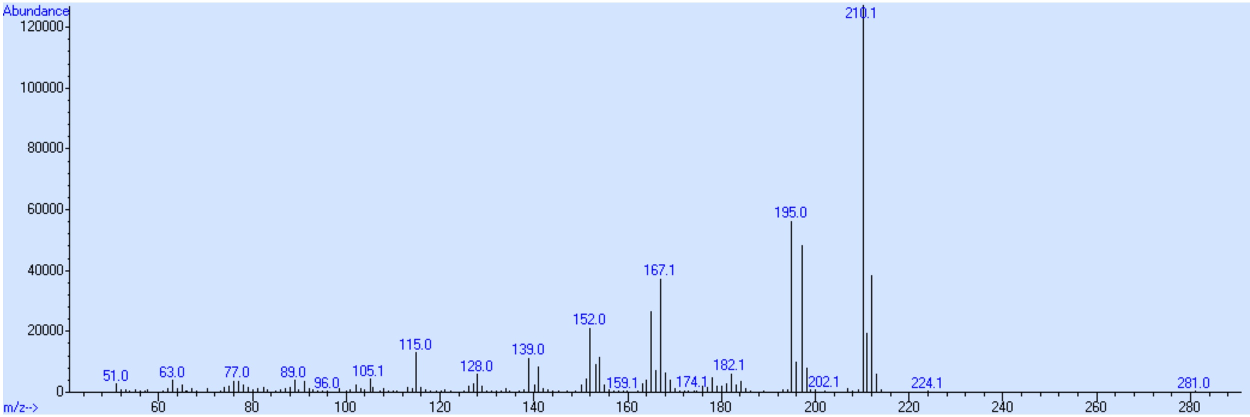
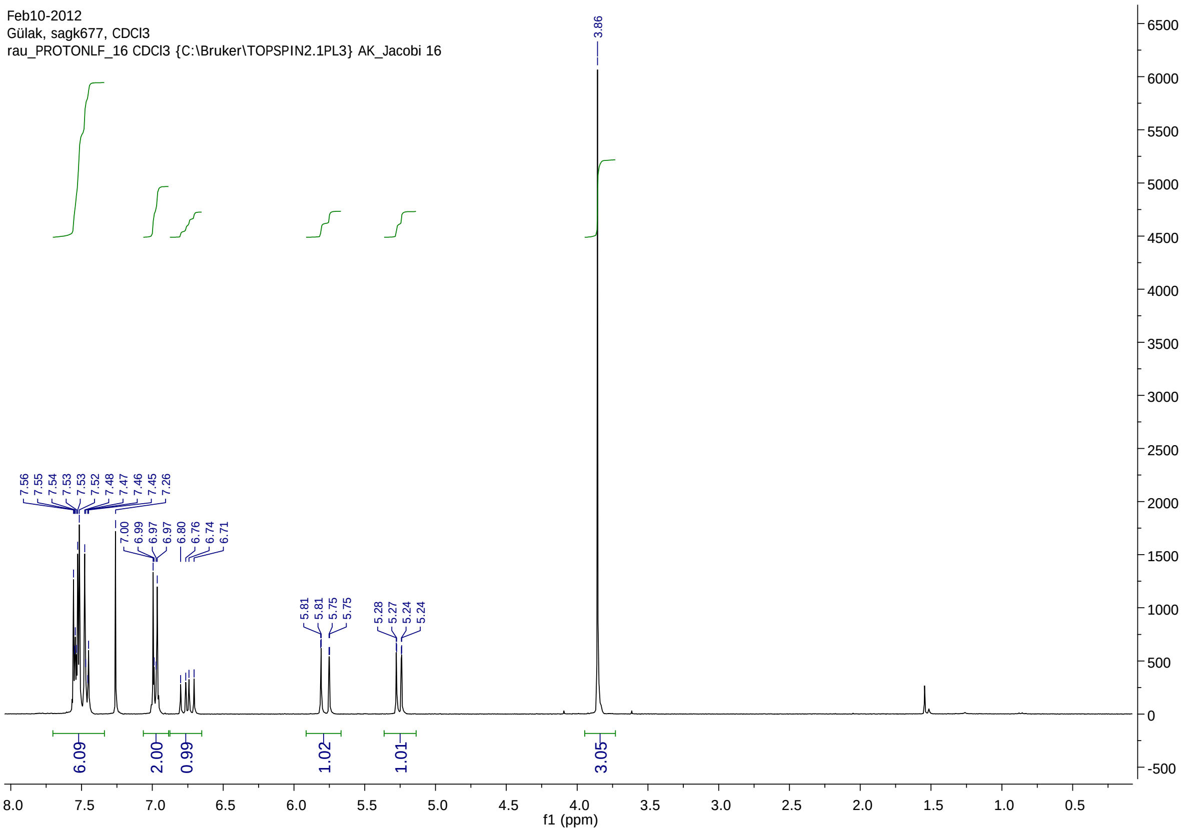
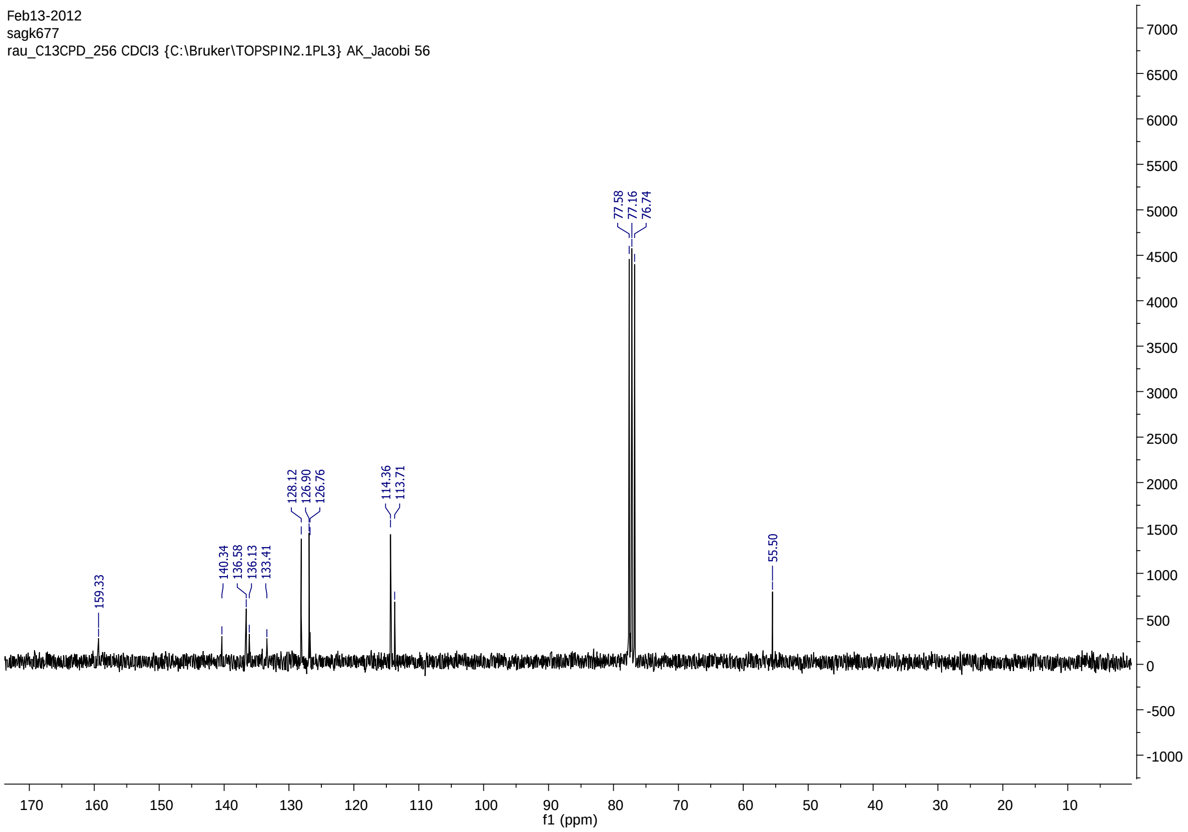
10
0
f1 (ppm)

4-Methoxy-4'-vinylbiphenyl








Feb13-2012
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77.16
76.74
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6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)