Electronic Supplementary Material (ESI) for RSC Advances.

Brønsted Acid-Catalyzed Hydroarylation of Activated Olefins

Ivana Fleischer and Jola Pospech*

Supporting Information

1. Analytical Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR) and for CD_2Cl_2 5.32 ppm (^{1}H-NMR) and 54.0 ppm (^{13}C-NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210 Time-of-Flight LC/MS (Agilent) with electrospray ionization (ESI). The data are given as mass units per charge (*m/z*) and intensities of signals are given in brackets. For GC analyses, HP 6890 chromatograph with a 30 m HP5 column was used. The enantiomeric excess was determined by HPLC (HP 1100 equipped with diode array detector) using Whelk-O 1 (*S*,*S*) column.

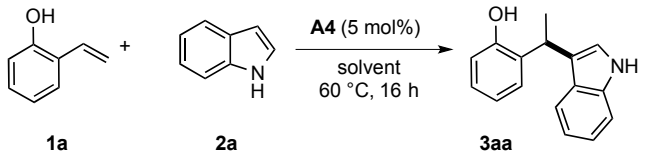
2. Materials and Methods

All commercial reagents were purchased from Acros Organics, Alfa Aesar, Aldrich or Strem. Dry solvents were prepared according to standard procedures.[1] Air- and moisture-sensitive syntheses were performed under argon atmosphere in heating gun vacuum dried glassware. Catalytic reactions were performed in screw cup equipped glass pressure tubes.

3. Experimental Procedures and Analytical Data

3.1. Additional Tables

Table SI1. Optimization: solvents at 60 °C with **A4**.[a]

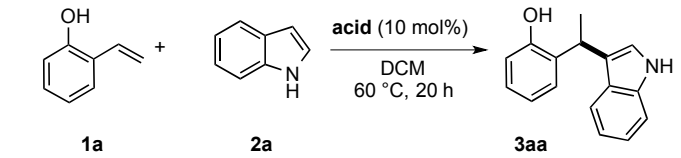


1a **2a** **3aa**

Entry [a]	Solvent	Conv. 1a (%)[b]	Yield 3aa (%)[b]
1	DCM	57	57
2	MeOH	10	7
3	MeCN	12	10
4	Toluene	49	46
5	THF	1	1
6	H_2O	76	60
7	DMF	0	0
8	DMSO	0	0
9	DCE	56	55
10[c]	H_2O	75	63
11[c]	DCM	82	80
12[d]	DCM	60	57
13	DCM	56	55
14[e]	H_2O	93	60 (55)[f]
15[e]	DCM	94	93 (88)[f]

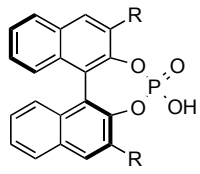
[a]Reaction conditions: **1a** (60.1 mg, 0.500 mmol), **2a** (64.4 mg, 0.550 mmol), **A4** (6.2 mg, 25 μmol) in DCM (1 mL), 60 °C, 16 h. [b]Determined by GC with isooctane as internal standard. [c]20 h. [d]0.5 mL solvent. [e]80 °C. [f]Isolated yields are given in brackets.

Table SI2. Chiral acids.[a]

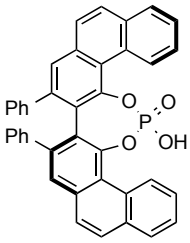


1a **2a** **3aa**

Acids:



A7 R = 3,5-$(CF_3)_2C_6H_3$
A8 R = $SiPh_3$
ent-**A9** R = 9-phenantrenyl
A10 R = 2,4,6-$^{i}Pr_3C_6H_2$



A11

Entry	**Acid**	**Yield 3aa (%)**[b]	***e.r.* 3aa (*R*/*S*)**[c]
1	**A7**	69	48:52
2	**A8**	83	46:53
3	**A9**	72	57:43
4	**A10**	76	48:52
5	**A11**	74	50:50
6[d]	**A9**	61	56:44

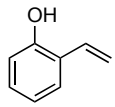
[a]Reaction conditions: **1a** (30.0 mg, 0.250 mmol), **2a** (32.2 mg, 0.275 mmol), **acid** (25 µmol) in DCM (1 mL), 60 °C, 20 h (with **1a**, **2a** stock solution). [b]Isolated yield. [c]Determined by HPLC on a chiral stationary phase. [d]Performed with 125 µmol **1a** at 30-35 °C, 87 h.

3.2. General Procedure for the Synthesis of Substrates[2]

Alkyltriphenylphosphonium bromide (2.46 g, 6.90 mmol) was added to a 250 mL 3-necked flask under argon and suspended in THF (10 mL). A solution of potassium *tert*-butoxide (784 mg, 6.99 mmol) in THF (5 mL) was added and the reaction mixture was stirred at ambient temperature for 4 h. The resulting orange solution was cooled down to -78 °C and a THF solution (2 mL) of the aldehyde (3.00 mmol) was added drop wise. The reaction mixture was allowed to warm to ambient temperature overnight. A saturated solution of NH_4Cl (5 mL) was added, the mixture was diluted with Et_2O (10 mL), washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography.

3.3. Characterization of the Substrates

2-Vinylphenol (1a)



According to the general procedure, **1a** was prepared from methyltriphenylphosphonium bromide (13.5 g, 37.7 mmol), potassium *tert*-butoxide (4.29 g, 38.2 mmol) and salicyl aldehyde (2.00 g, 16.4 mmol). The crude thick yellow oil was purified by column chromatography (silica, Et_2O/pentane 10:90-20:80) to yield the product as a pale yellow oil, which solidified upon standing below room temperature (1.85 g, 89%, 95% purity). The analytical data were in accordance with the literature.[3]

C_8H_8O (120.15 g/mol)

$\boldsymbol{R_f}$ = 0.28 (silica, EA/heptane 1:5).

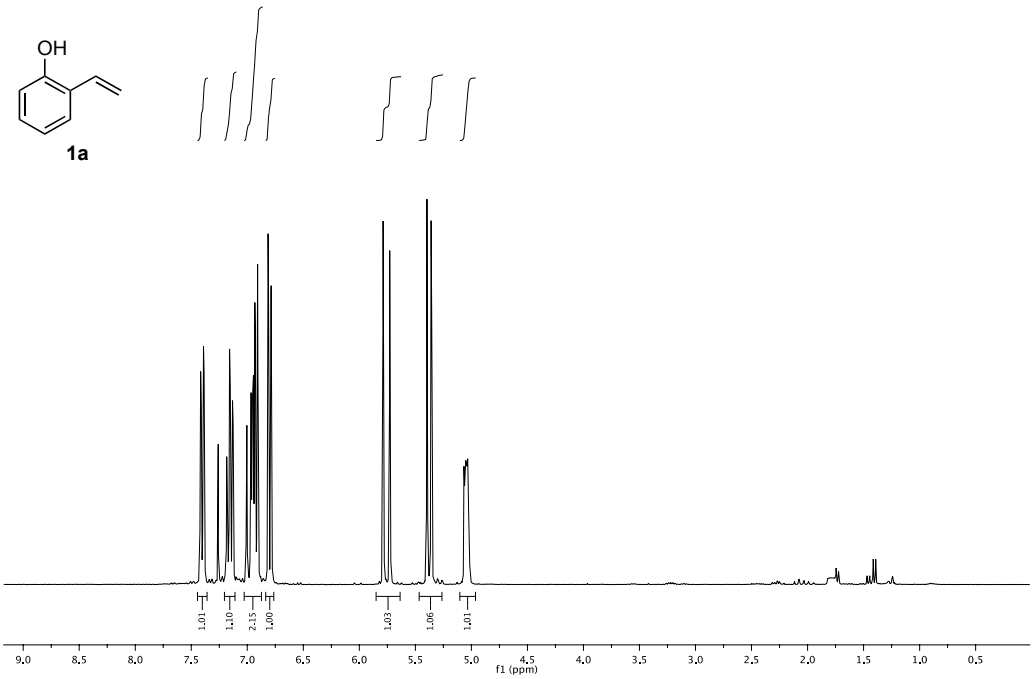
M.p.: ambient temperature

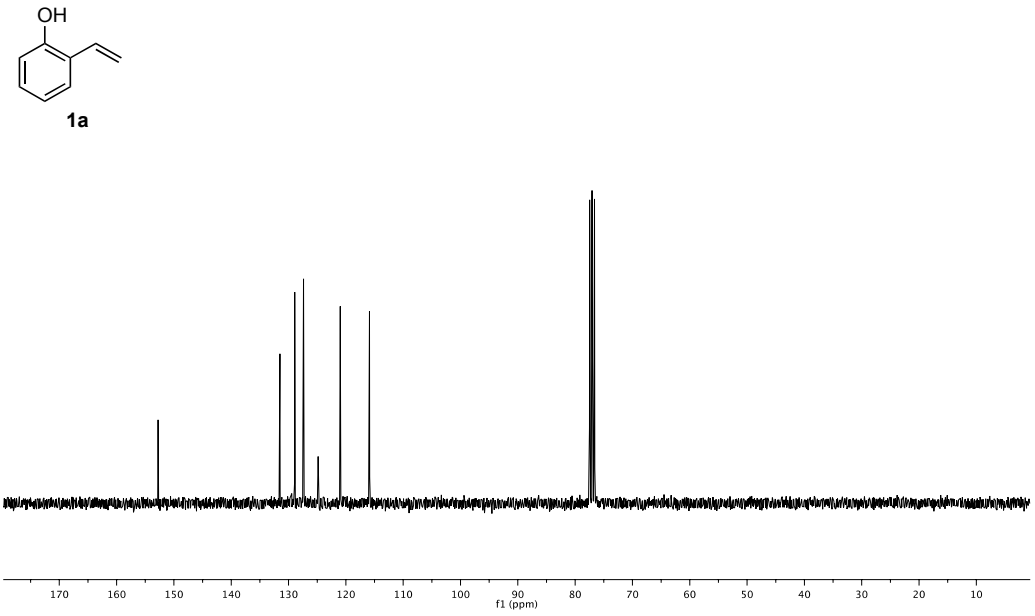
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.40 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 3-*H*), 7.15 (ddd, $^3J_{HH}$ = 8.0, 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 5-*H*), 7.03 – 6.88 (m, 2H, 4-*H*, C*H*=CH_2), 6.80 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 6-*H*), 5.76 (dd, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 5.37 (dd, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 5.12 (br. s, 1H, OH).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 152.9 (*C*-1), 131.6 (*C*H=CH_2), 129.0 (*C*-3), 127.5 (*C*-5), 124.9 (*C*-2), 121.1 (*C*-4), 116.03 (*C*-6), 115.98 (CH=*C*H_2).

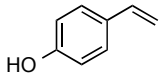
GC MS (EI) *m/z* (%): 120 (64, M^+), 91 (100, $C_7H_7^+$), 77 (4, $C_6H_5^+$), 65 (4, $C_5H_5^+$), 51 (8, $C_4H_3^+$), 39 (11, $C_3H_3^+$).

GC (HP5 30 m, 35 °C/10 min/10 °C/min/285 °C/5 min, DCM)**:** t_R = 20.3 min.


OH
1a
1.01
1.10
2.15
1.00
1.03
1.06
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


OH
1a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

4-Vinylphenol (1b)

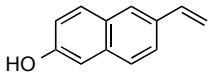


4-Vinylphenyl acetate (500 mg, 3.08 mmol) was dissolved in THF (5 mL) and treated with an aqueous sodium hydroxide solution (5 m, 3 mL, 15 mmol). The reaction mixture was stirred at ambient temperature and monitored by TLC. After 30 minutes, the mixture was neutralized by 1 M HCl and extracted with DCM (3 × 10 mL). The organic phase was separated using Whatmann® phase separator and concentrated *in vacuo* to desired concentration (for standard conditions 0.5 M) and directly used in the next step.

C_8H_8O (120.15 g/mol)

$\boldsymbol{R_f}$ = 0.20 (silica, EA/heptane 1:4).

6-Vinylnaphthalen-2-ol (1d)



According to the general procedure, **1d** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and 6-hydroxy-2-naphthaldehyde (516 mg, 3.00 mml). The crude thick yellow oil was purified by column chromatography (silica, Et_2O/pentane 10:90) to yield the product as a colorless solid (382 mg, 75%).

$C_{12}H_{10}O_2$ (170.21 g/mol)

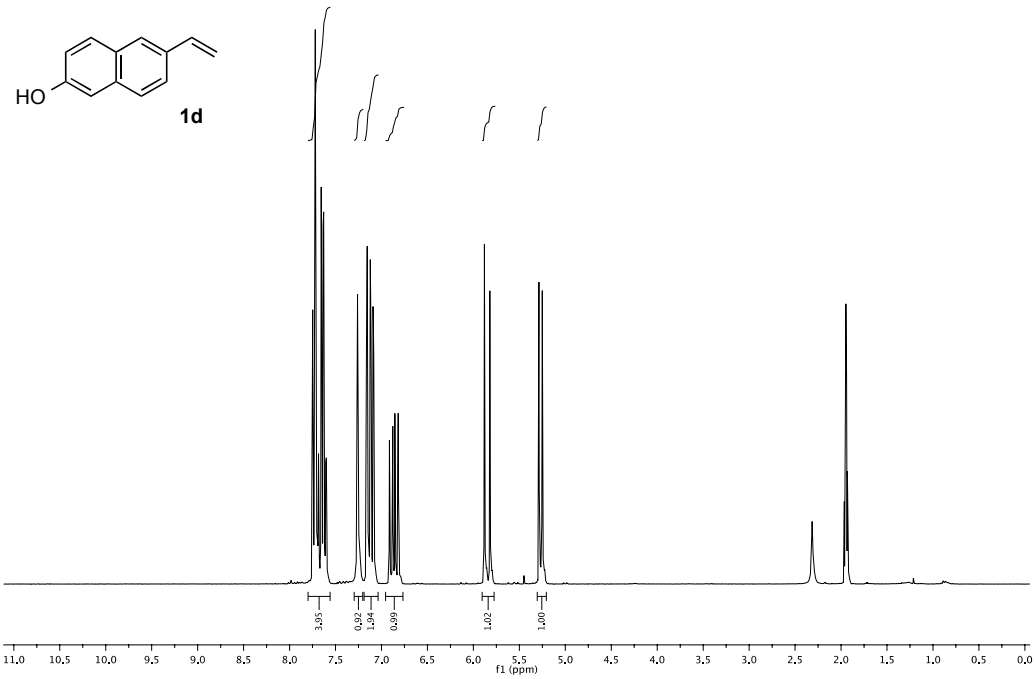
$\boldsymbol{R_f}$ = 0.26 (silica, EA/heptane 1:4).

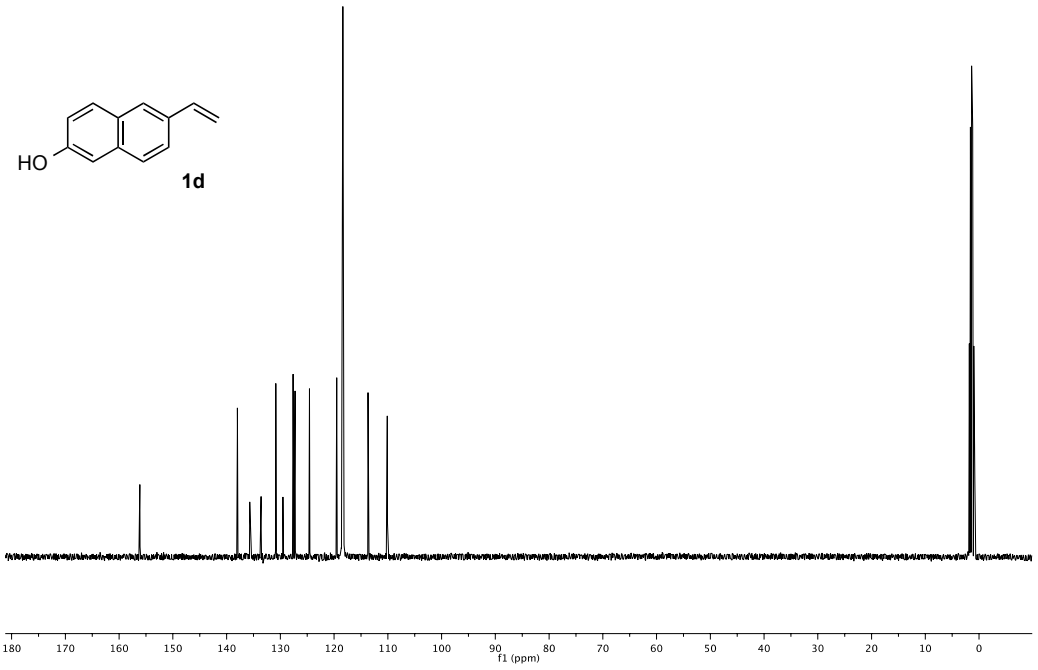
^{1}H NMR (300 MHz, CD_3CN) δ/ppm: 7.80-7.54 (m, 4H, Ar*H*), 7.25 (s, 1H, OH), 7.18-7.02 (m, 2H, Ar*H*), 6.86 (dd, $^3J_{HH}$ = 17.6 and 10.9 Hz, 1H, C*H*=CH_2), 5.84 (dd, $^3J_{HH}$ = 17.6 Hz, $^2J_{HH}$ = 1.0 Hz, 1H, CH=C$H_A$$H_B$), 5.26 (dd, $^3J_{HH}$ = 10.9 Hz, $^2J_{HH}$ = 1.0 Hz, 1H, CH=C$H_A$$H_B$). **^{13}C NMR** (75 MHz, CD_3CN) δ/ppm: 156.0 (*C*-2), 137.9 (*C*H=CH_2), 135.6 (*Ar*C), 133.5 (*Ar*C), 130.7 (*Ar*H), 129.4 (*Ar*C), 127.5 (*Ar*H), 127.1 (*Ar*H), 124.5 (*Ar*H), 119.4 (*Ar*H), 113.6 (CH=*C*H_2), 110.0 (*Ar*H).

MS (EI) *m/z* (%): 170 (100, M^+), 153 (6, $[M\text{-}OH]^+$), 141 (25, $[M\text{-}CHO]^+$), 115 (15, $C_9H_7^+$), 84 (7), 72 (5), 63 (3).

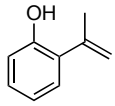
HRMS (EI) m/z (%): calculated for $C_{12}H_{10}O_2$ $[M]^+$ 170.07262; found 170.07253.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3256m (OH), 3087w, 3000w, 1816w, 1628m, 1576m, 1510m, 1480m, 1353m, 1270m, 1226m, 1160m, 992m, 907m, 902m, 892s (Ar), 868s (Ar), 809s (Ar), 624m.


HO
1d
3.95
0.92
1.94
0.99
1.02
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


HO
1d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-(Prop-2-en-2-yl)phenol (1h)



According to the general procedure, **1h** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and 2-hydroxyacetophenone (408 mg, 3.00 mmol). The crude product was purified by column chromatography (silica, Et_2O/pentane 5:95) to yield the product as a pale yellow oil (210 mg, 83%, 90% purity). The analytical data were in accordance with the literature.[2]

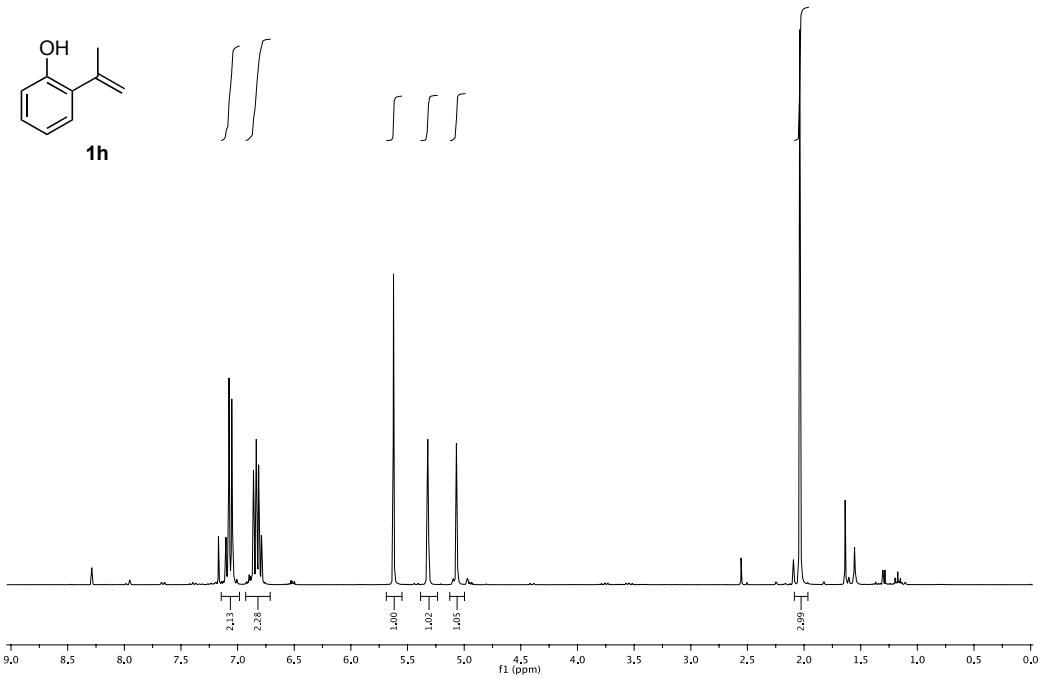
$C_9H_{10}O$ (134.18 g/mol)

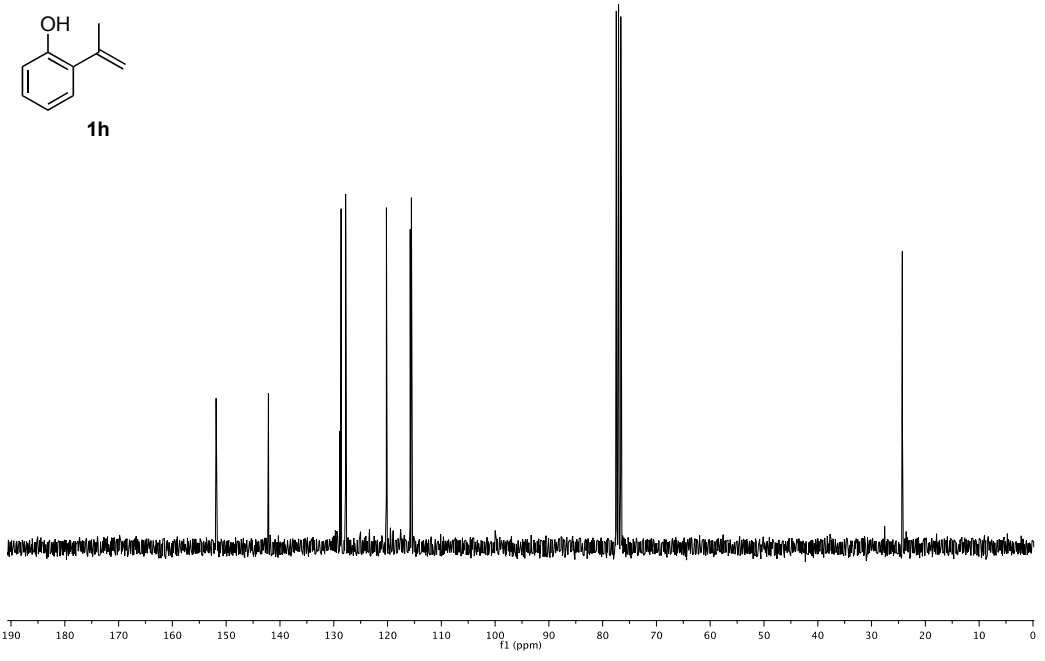
$\boldsymbol{R_f}$ = 0.35 (silica, EA/heptane 1:4).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.17-7.14 (m, 2H, Ph*H*), 6.97 – 6.88 (m, 2H, Ph*H*), 5.72 (s, 1H, OH), 5.40-5.42 (m, 1H, C=CH_AH$_B$), 5.17-5.15 (m, 1H, C=CH$_A$$H_B$), 2.13 (s, 3H, CH_3).

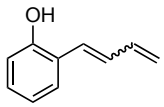
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 152.0 (*C*-1), 142.2 (*C*=CH_2), 129.0 (*C*-2), 128.7 (*Ar*H), 127.9 (*Ar*H), 120.3 (*Ar*H), 115.9 (*C*-6), 115.7 (C=*C*H_2), 24.4 (*C*H_3).

GC MS (EI) *m/z* (%): 134 (85, M^+), 119 (46, $[M\text{-}CH_3]^+$), 115 (16), 105 (17), 91 (100, $C_7H_7^+$), 77 (17, $C_6H_5^+$), 65 (14, $C_5H_5^+$), 51 (12, $C_4H_3^+$), 39 (14, $C_3H_3^+$).


OH
1h
2.13
2.28
1.00
1.02
1.05
2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
1h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-(Buta-1,3-dien-1-yl)phenol (1i)[4]



n-Butyllithium (3.7 mL of 1.6 M solution in hexanes, 5.9 mmol) was added to a solution of allyltriphenylphosphonium bromide (2.33 g, 6.09 mmol) in THF (10 mL) at -18 °C. The mixture was stirred for 30 minutes at -18 °C, then a THF (5 mL) solution of salicyladehyde (369 mg, 3.02 mmol) was added dropwise. The reaction mixture was stirred at -18 °C for an additional hour and was let to warm to ambient temperature overnight. A saturated solution of NH_4Cl (5 mL) was added, the mixture was diluted with Et_2O (10 mL), washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude orange product was purified by column chromatography (silica, Et_2O/pentane 3:97-15:85) to yield **1i** as a yellow oil, which solidified upon standing (308 mg, 70%). The analytical data were in accordance with the literature.[4]

$C_{10}H_{10}O$ (146.19 g/mol)

$\boldsymbol{R_f}$ = 0.24 (silica, EA/heptane 1:4).

M.p.: ambient temperature

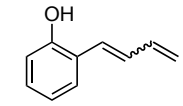
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.43 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 3-*H*), 7.12 (ddd, $^3J_{HH}$ = 8.1 and 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 5-*H*), 6.92 (ddd, $^3J_{HH}$ = 7.4 and 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 4-*H*), 6.86-6.72 (m, 3H, 6-H, 1'-*H*, 2'-*H*), 6.65-6.47 (m, 1H, 3'-*H*), 5.34 (dd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 1.7 Hz, 1H, CH=CH_AH$_B$), 5.19 (dd, $^3J_{HH}$ = 10.0 Hz, $^2J_{HH}$ = 1.7 Hz, 1H, CH=CH$_A$$H_B$), 5.00 (br. s, 1H, OH).

^{13}C NMR (75 MHz, CD_3CN) δ/ppm: 152.9 (*C*-1), 137.6 (*C*H=CH$_2$), 131.1 (*C*H), 128.7 (*C*H), 127.2 (*C*H), 127.1 (*C*H), 124.4 (*C*H), 121.1 (*C*H), 117.62 (CH=*C*H$_2$), 115.9 (*C*H).

MS (EI) *m/z* (%): 146 (75, M^+), 145 (100, $[M-H]^+$), 131 (82, $[M-CH_3]^+$), 127 (38, $[M-H_3O]^+$), 117 (22, $[M-CHO]^+$), 91 (7, $C_7H_7^+$), 77 (9, $C_6H_5^+$), 51 (5, $C_4H_3^+$), 39 (5, $C_3H_3^+$).

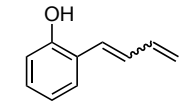
HRMS (EI) m/z (%): calculated for $C_{10}H_{10}O$ $[M]^+$ 146.07262; found 146.07237.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3386m (OH), 3037w, 2914w, 1595m, 1484m, 1453s, 1328m, 1299m, 1228s, 1174m, 1089m, 1004m, 971m, 899m, 853w, 748s (Ar).

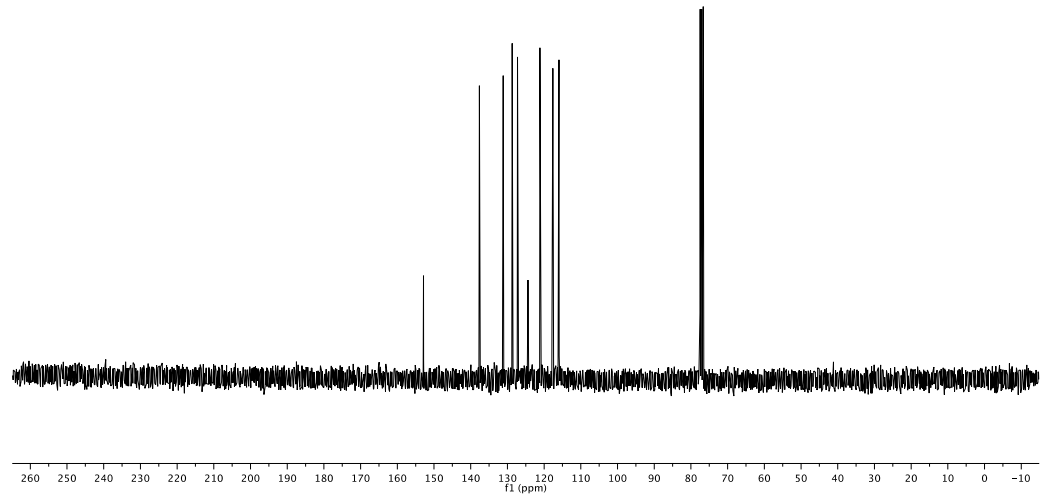

OH

1i

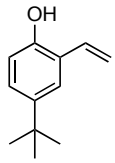
1.08
1.39
1.46
3.01
1.13
1.17
1.00
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH

1i


260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

4-*tert*-Butyl-2-vinylphenol (1k)



According to the general procedure, **1k** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and 2-hydroxy-5-*tert*-butylbenzaldehyde (516 mg, 2.90 mmol). The crude thick yellow oil was purified by column chromatography (silica, Et_2O/pentane 10:90) to yield the product as a pale yellow oil (450 mg, 88%).

$C_{12}H_{16}O$ (176.25 g/mol)

$\boldsymbol{R_f}$ = 0.35 (silica, EA/heptane 1:4).

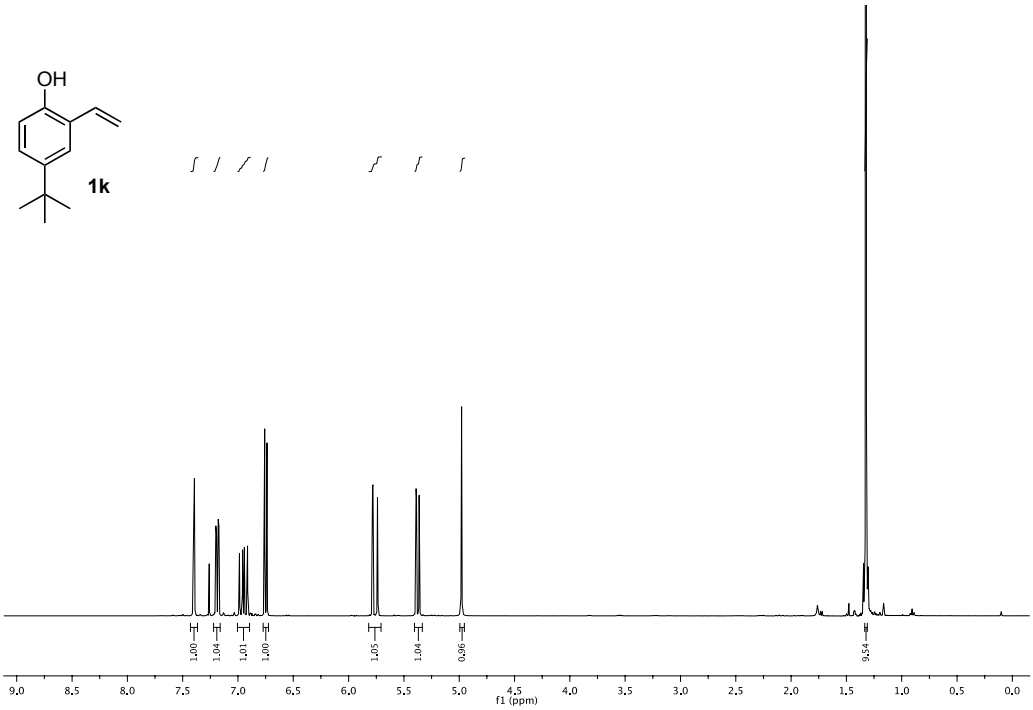
^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.40 (d, $^4J_{HH}$ = 2.5 Hz, 1H, 3-*H*), 7.19 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, 5-*H*), 6.95 (dd, $^3J_{HH}$ = 17.8 and 11.2 Hz, 1H, C*H*=CH_2), 6.75 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 6-*H*), 5.76 (dd, $^3J_{HH}$ = 17.8 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 5.37 (dd, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 4.98 (s, 1H, OH), 1.32 (s, 9H, C(CH_3)$_3$).

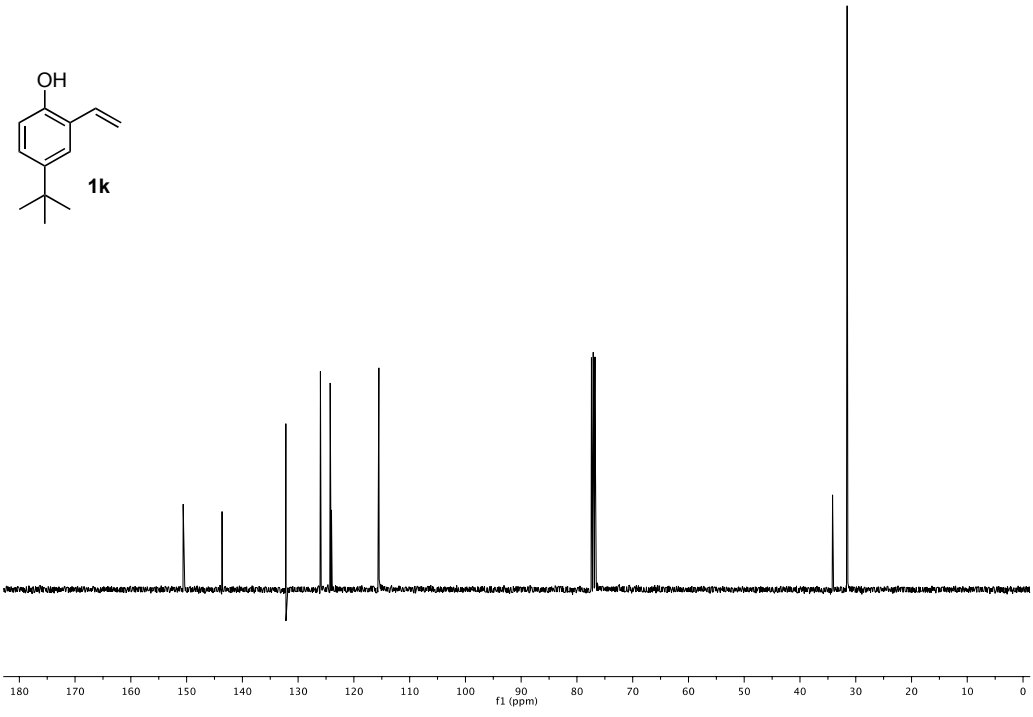
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 150.7 (*C*-1), 143.7 (*C*-4), 132.3 (*C*H=CH_2), 126.1 (Ar*H*), 124.3 (Ar*H*), 124.1 (*C*-2), 115.7 (CH=*C*H_2), 115.6 (*C*-6), 34.2 (*C*(CH_3)$_3$), 31.6 (C(*C*H_3)$_3$).

GC MS (EI) *m/z* (%): 176 (23, M^+), 161 (100, [M-CH_3]$^+$), 133 (16, [M-CO-CH_3]$^+$), 91 (79, $C_7H_7^+$), 77 (26, $C_6H_5^+$), 63 (10), 51 (17, $C_4H_3^+$), 39 (10, $C_3H_3^+$).

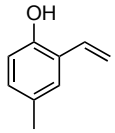
HRMS (EI) m/z (%): calculated for $C_{12}H_{16}O$ $[M]^+$ 176.11957; found 176.11945.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3406m (OH), 2960s (CH_3), 2903m, 2868m, 1626m, 1607w, 1496s, 1418m, 1363m, 1268s, 1234m, 1179m, 1124m, 1090m, 994m, 905m, 817s (Ar), 679m.


OH
1k
1.00
1.04
1.01
1.00
1.05
1.04
0.86
9.54
f1 (ppm)


OH
1k
f1 (ppm)

4-Methyl-2-vinylphenol (1l)



According to the general procedure W2, **1l** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and 2-hydroxy-5-methylbenzaldehyde (408 mg, 3.00 mmol). The crude thick yellow oil was purified by column chromatography (silica, Et_2O/pentane 20:80) to yield the product as a pale yellow oil (374 mg, 91%, 98% purity).

$C_9H_{10}O$ (134.18 g/mol)

$\boldsymbol{R_f}$ = 0.26 (silica, EA/heptane 1:4).

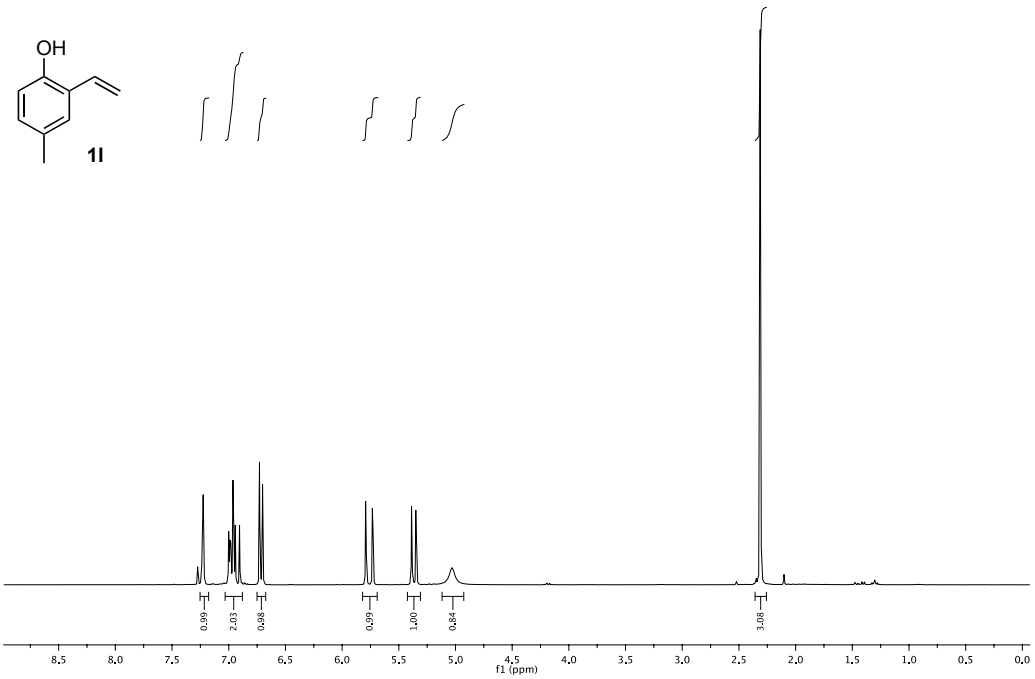
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.21 (d, $^4J_{HH}$ = 2.2 Hz, 1H, 3-*H*), 7.00-6.88 (m, 2H, 5-*H*, C*H*=CH_2), 6.70 (d, $^3J_{HH}$ = 8.1 Hz, 1H, 6-*H*), 5.75 (dd, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 5.35 (dd, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.4 Hz, 1H, CH=C$H_A$$H_B$), 5.02 (br. s, 1H, OH), 2.30 (s, 3H, CH_3).

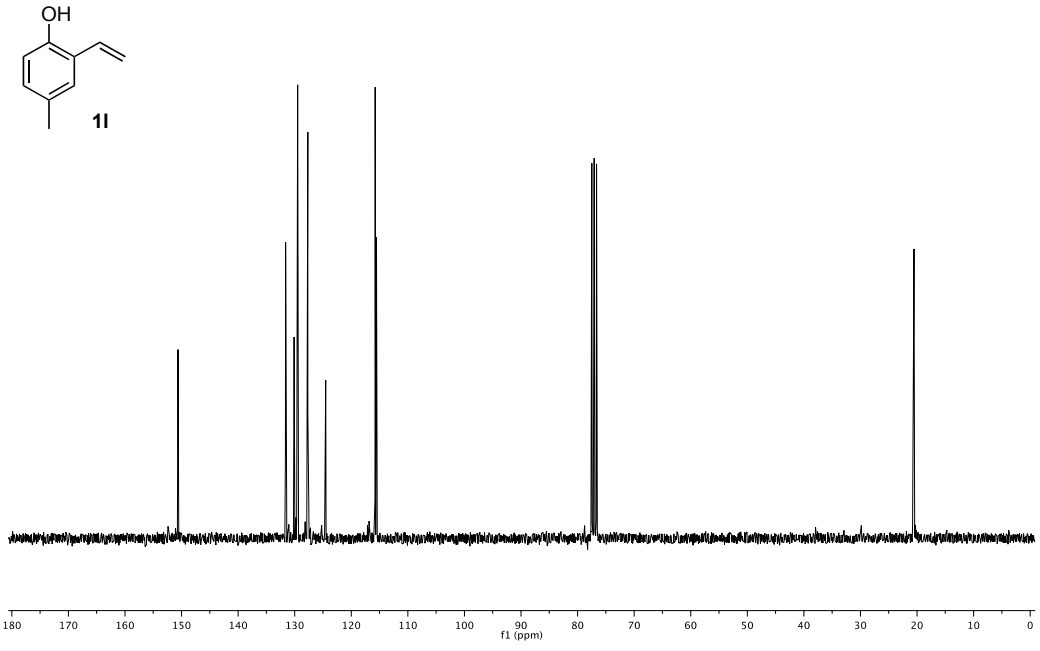
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 150.7 (*C*-1), 131.7 (*C*H=CH_2), 130.2 (*C*-4), 129.6 (*C*-5), 127.8 (*C*-3), 124.6 (*C*-2), 115.9 (*C*-6), 115.6 (CH=*C*H_2), 20.6 (*C*H_3).

GC MS (EI) *m/z* (%): 134 (100, M^+), 119 (12, $[M\text{-}CH_3]^+$), 105 (31, $[M\text{-}CHO]^+$), 91 (79, $C_7H_7^+$), 77 (26, $C_6H_5^+$), 63 (10), 51 (17, $C_4H_3^+$), 39 (10, $C_3H_3^+$).

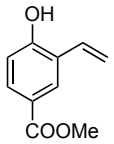
HRMS (EI) m/z (%): calculated for $C_9H_{10}O$ $[M]^+$ 134.07262; found 134.07244.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3393m (OH), 3020w, 2921w, 1624m, 1495s, 1417m, 1341m, 1253s, 1204s, 1101m, 994m, 908m, 807s (Ar), 780m.


OH
1l
0.99
2.03
0.88
0.99
1.00
0.84
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
1l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 4-hydroxy-3-vinylbenzoate (1m)



According to the general procedure, **1m** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and methyl 3-formyl-4-hydroxybenzoate (540 mg, 3.00 mmol). The crude product was purified by column chromatography (silica, Et_2O/pentane 20:80) to yield the product as a colorless solid (481 mg, 74%).

$C_{10}H_{10}O_3$ (178.18 g/mol)

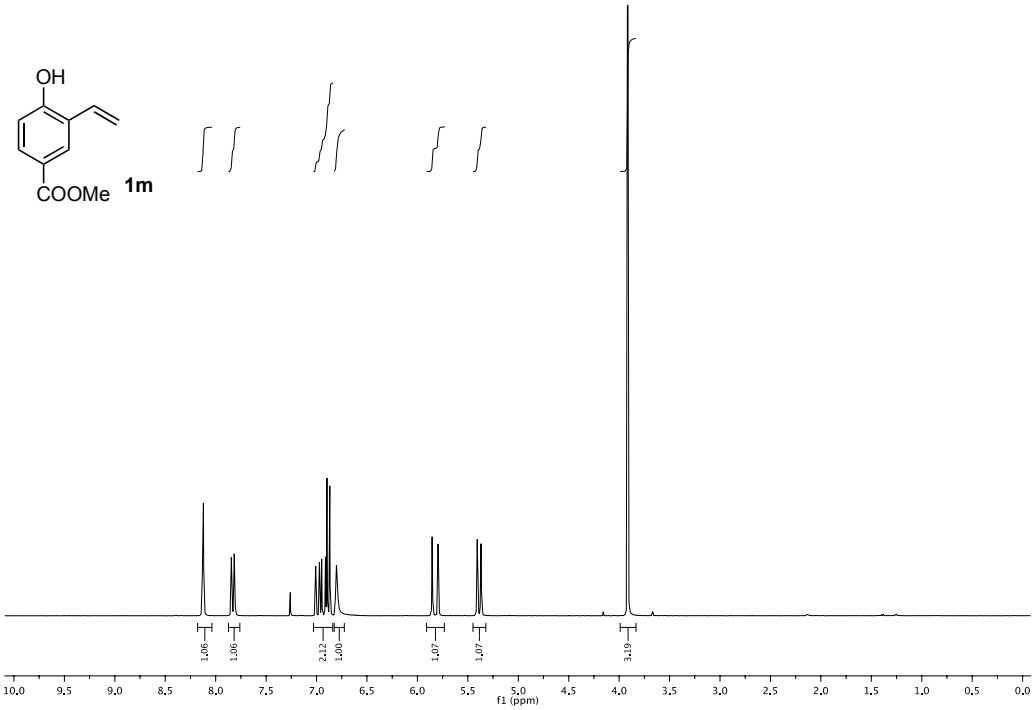
$\boldsymbol{R_f}$ = 0.46 (silica, EA/heptane 1:1).

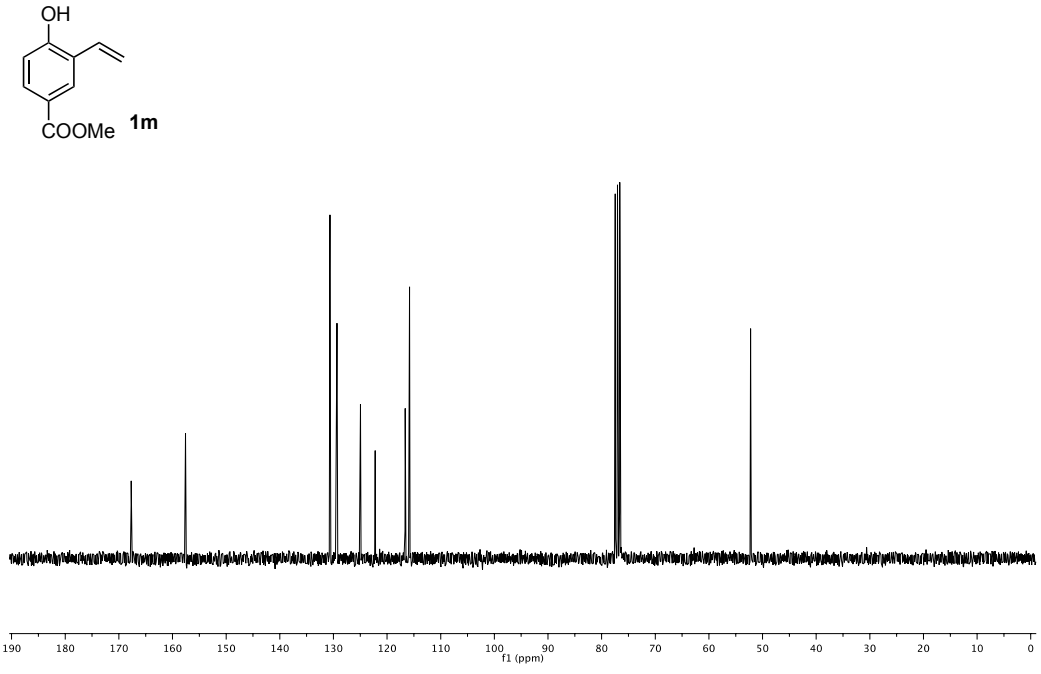
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.12 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 2-*H*), 7.83 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, 6-*H*), 6.96 (dd, $^3J_{HH}$ = 17.7 and 11.2 Hz, 1H, C*H*=CH_2), 6.88 (d, $^3J_{HH}$ = 8.5 Hz, 1H, 5-*H*), 6.80 (br s, 1H, OH), 5.82 (dd, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, CH=C$H_A$$H_B$), 5.39 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, CH=C$H_A$$H_B$), 3.92 (s, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 167.8 (*C*OCH_3), 157.7 (*C*-4), 130.7 (C*H*), 129.4 (C*H*), 125.1 (C_{quart}), 122.3 (C_{quart}), 116.7 (CH=*C*H_2), 115.9 (*C*-5), 52.3 (*C*H_3).

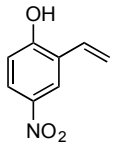
GC MS (EI) *m/z* (%): 178 (41, M^+), 147 (100, $[M\text{-}OCH_3]^+$), 119 (5, $[M\text{-}COOCH_3]^+$), 91 (21, $C_7H_7^+$), 65 (12), 51 (5, $C_4H_3^+$), 39 (4, $C_3H_3^+$).

HRMS (EI) m/z (%): calculated for $C_{10}H_{10}O_3$ $[M]^+$ 178.06245; found 178.06234.
IR (ATR) $\tilde{\nu}$/cm^{-1}: 3361m (OH), 2956w, 1888w, 1807w, 1678s, 1601s, 1505m, 1430m, 1358m, 1263s, 1223s, 1133s, 1093m, 1004m, 979m, 898s, 832m, 753s (Ar), 635s.


OH
COOMe
1m
1.06
1.06
2.12
1.00
1.07
1.07
3.19
f1 (ppm)


OH
COOMe
1m
f1 (ppm)

4-Nitro-2-vinylphenol (1n)



According to the general procedure, **1n** was prepared from methyltriphenylphosphonium bromide (2.46 g, 6.90 mmol), potassium *tert*-butoxide (784 mg, 6.99 mmol) and 5-nitro-2-hydroxybenzaldehyde (501 mg, 3.00 mmol). The crude product was purified by column chromatography (silica, Et_2O/pentane 20:80) to yield the product as a yellow solid (367 mg, 74%). The analytical data were in accordance with the literature.[5]

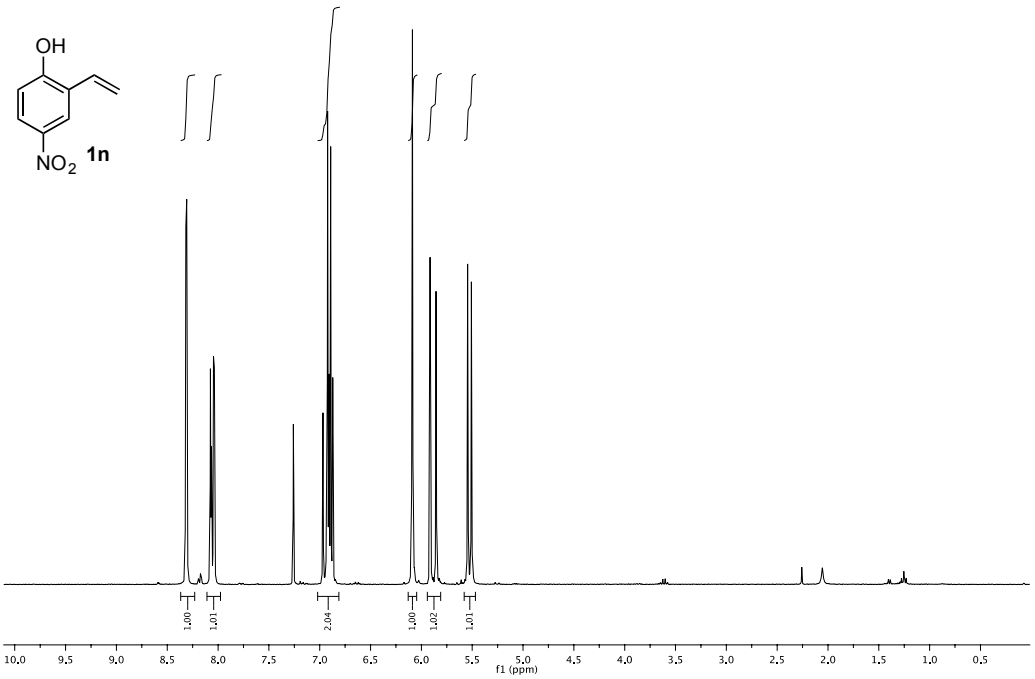
$C_8H_7NO_3$ (165.15 g/mol)

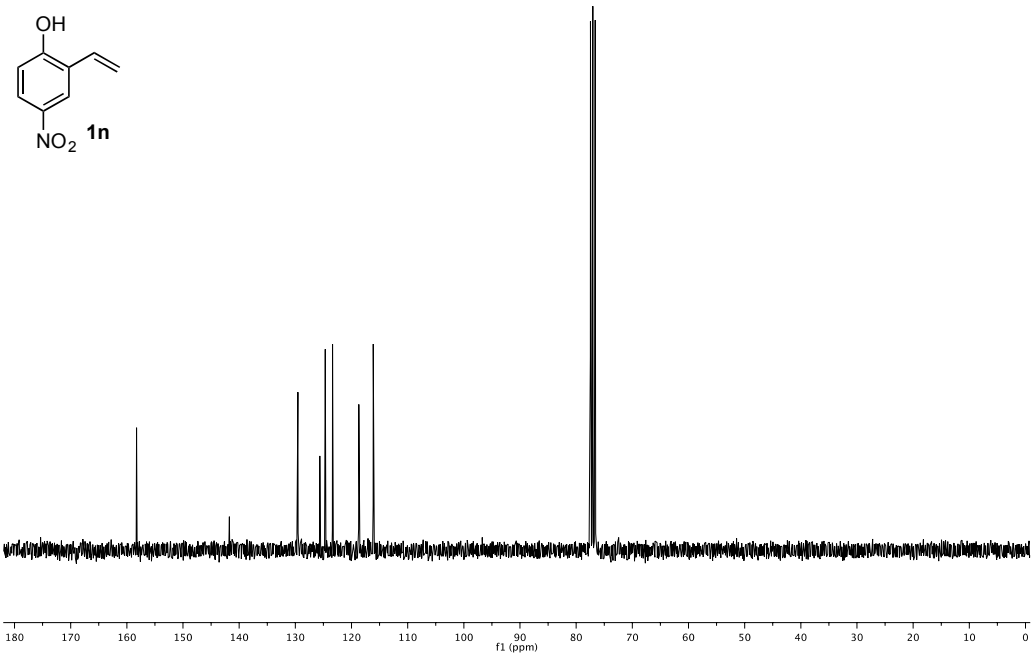
$\boldsymbol{R_f}$ = 0.46 (silica, EA/heptane 1:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.31 (d, $^4J_{HH}$ = 2.7 Hz, 1H, 3-*H*), 8.06 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, 5-*H*), 7.00 – 6.82 (m, 2H, 6-*H*, C*H*=CH_2), 6.09 (s, 1H, OH), 5.88 (dd, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 0.9 Hz, 1H, CH=C$H_A$$H_B$), 5.53 (dd, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 0.9 Hz, 1H, CH=$CH_A$$H_B$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 158.7 (*C*-1), 141.7 (*C*-4), 129.7 (*C*H=CH_2), 125.8 (*C*-2), 124.8 (*Ar*H), 123.4 (*Ar*H), 118.6 (CH=*C*H_2), 116.2 (*C*-6).

GC MS (EI) *m/z* (%): 165 (100, M^+), 135 (37, $[M\text{-}CH_2O]^+$), 107 (14), 91 (54, $C_7H_7^+$), 77 (23, $C_6H_5^+$), 65 (49), 51 (16, $C_4H_3^+$), 39 (18, $C_3H_3^+$).


OH
NO2
1n
1.00
1.01
2.04
1.00
1.02
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

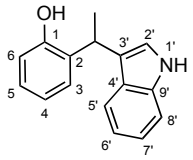

OH
NO2
1n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3.4. General Procedure for the Hydroarylation

The alkene (500 μmol), nucleophilic aromatic compound (550 μmol) and diphenyl phosphate (6.2 mg, 25 μmol) were placed in a pressure tube under air and dissolved in DCM (1 mL). The pressure tube was sealed and heated to 80 °C for 16 h. After cooling down, the crude reaction mixture was adsorbed on silica gel and purified by column chromatography.

3.5. Characterization of the Hydroarylation Products

2-(1-(1*H*-Indol-3-yl)ethyl)phenol (3aa)



The compound **3aa** was prepared according to the general procedure for hydroarylation from 2-vinylphenol (60.1 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 85:15) and obtained as yellow solid (105 mg, 88%). Crystals for X-ray analysis were obtained from heptane/ethanol. The analytical data were in accordance with the literature.[3]

$C_{16}H_{15}NO$ (237.30 g/mol)

R_f = 0.16 (silica, EA/heptane 1:5).

M.p.: 102-103°C

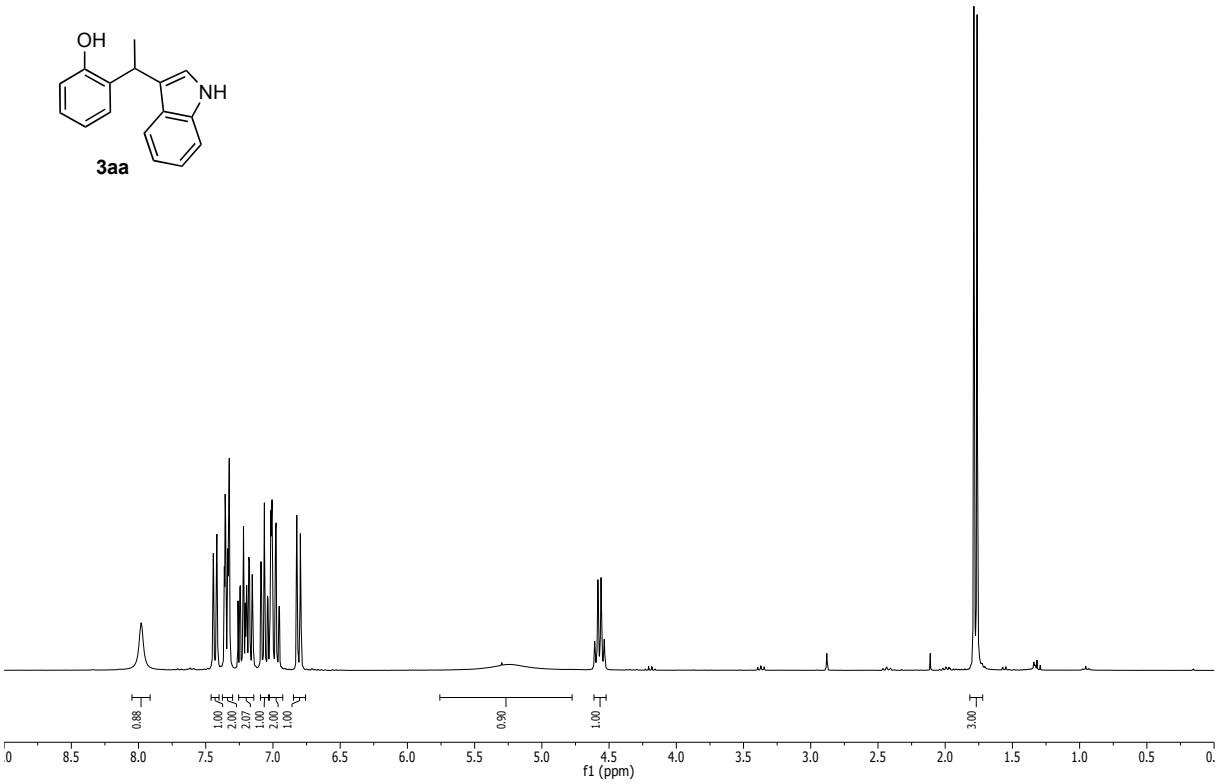
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.98 (br. S, H, NH), 7.41 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, 5'-*H*), 7.34 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, 8'-*H*), 7.33 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 3-*H*), 7.21 (ddd, $^3J_{HH}$ = 8.1 and 6.0 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, 7'-*H*), 7.16 (ddd, $^3J_{HH}$ = 7.8 and 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 5-*H*), 7.05 (ddd, $^3J_{HH}$ = 8.0 and 6.0 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, 6'-*H*), 7.03 (s, 1H, 2'-*H*), 6.96 (ddd, $^3J_{HH}$ = 7.8 and 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 4-*H*), 6.80 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, 6-*H*), 5.24 (br. S, 1H, OH), 4.56 (q, $^3J_{HH}$ = 7.1 Hz, 1H, C*H*CH_3), 1.76 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CHC*H*$_3$).

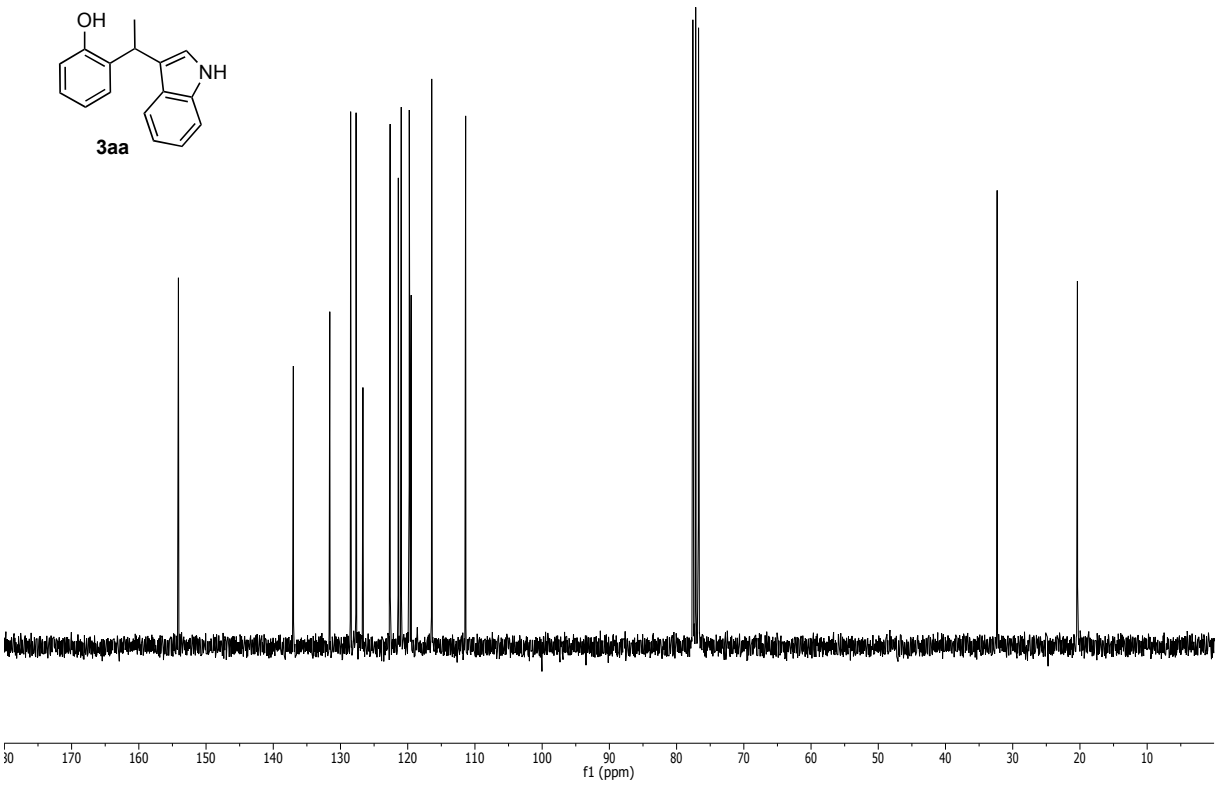
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 154.1 (*C*-1), 137.0 (*C*-9'), 131.6 (*C*-2), 128.5 (*C*-3), 127.7 (*C*-5), 126.7 (*C*-4'), 122.6 (*C*-7'), 121.4 (*C*-2'), 121.0 (*C*-4), 119.8 (*C*-5'), 119.7 (*C*-6'), 119.5 (*C*-3'), 116.4 (*C*-6), 111.4 (*C*-8'), 32.3 (*C*HCH_3), 20.4 (*C*H$_3$).

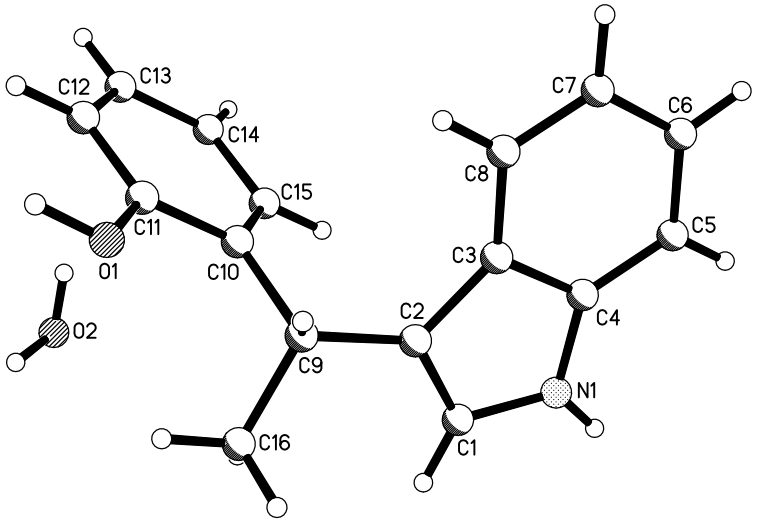
GC MS (EI) *m/z* (%): 237 (65, M^+), 222 (100, $[M\text{-}CH_3]^+$), 204 (7), 194 (5), 165 (9), 144 (7, $[M\text{-}C_6H_5O]^+$), 117 (97, $C_8H_7N^+$), 91 (13, $C_7H_7^+$), 77 (6, $C_6H_5^+$), 63 (5), 51 (3), 39 (3).

GC (HP5 30 m, 35 °C/10 min/10 °C/min/285 °C/5 min, DCM)**:** t_R = 32.3 min.

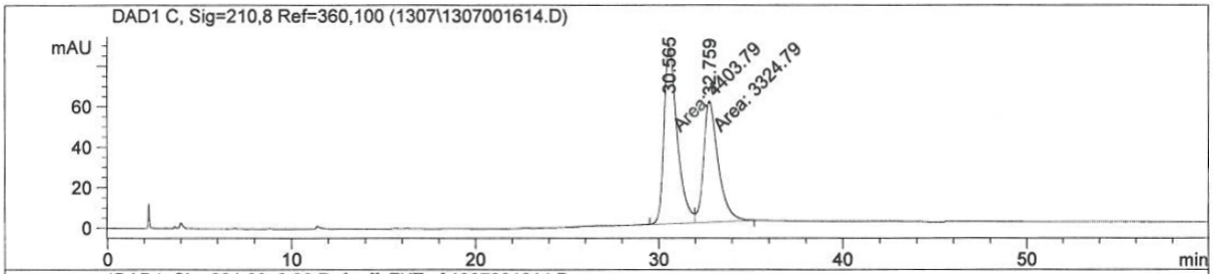
HPLC: Whelk-O 1 (*S*,*S*), heptane/ethanol 98:2, 1.0 mL/min, t_R = 30.6 min (*R*), 32.8 min (*S*).


OH
NH
3aa
0.88
1.00
2.00
2.07
1.00
2.00
1.00
0.90
1.00
3.00
f1 (ppm)

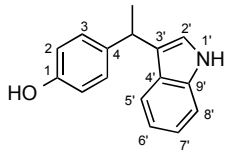

OH
NH
3aa
f1 (ppm)



HPLC trace of the enantiomerically enriched product (e.r. 57:43 *R*/*S*)



4-(1-(1*H*-Indol-3-yl)ethyl)phenol (3ba)



The compound **3ba** was prepared according to the general procedure for hydroarylation from 4-vinylphenol (60.1 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10-80:20) and obtained as yellow solid (81 mg, 68%). The analytical data were in accordance with the literature. [3]

$C_{16}H_{15}NO$ (237.30 g/mol)

$\boldsymbol{R_f}$ = 0.09 (silica, EA/heptane 1:4).

M.p.: 148-149°C

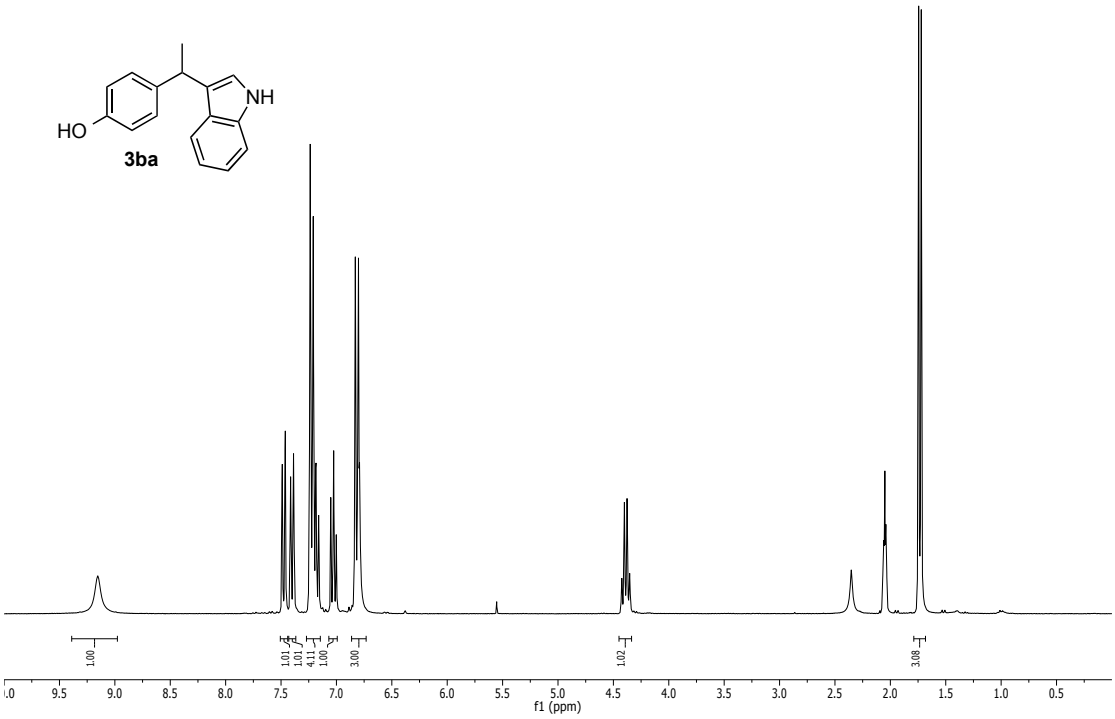
^{1}H NMR (300 MHz, CD_3CN) δ/ppm: 9.04 (br. S, H, N*H*), 7.36 (d, $^3J_{HH}$ = 8.1 Hz, 1H, 5'-*H*), 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 1H, 8'-*H*), 7.15 – 6.98 (m, 4H, Ar*H*), 7.00 – 6.83 (m, 1H, Ar*H*), 6.72-6.68 (m, 3H, OH, 2-*H*), 4.28 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*CH_3), 1.62 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CHC*H*$_3$).

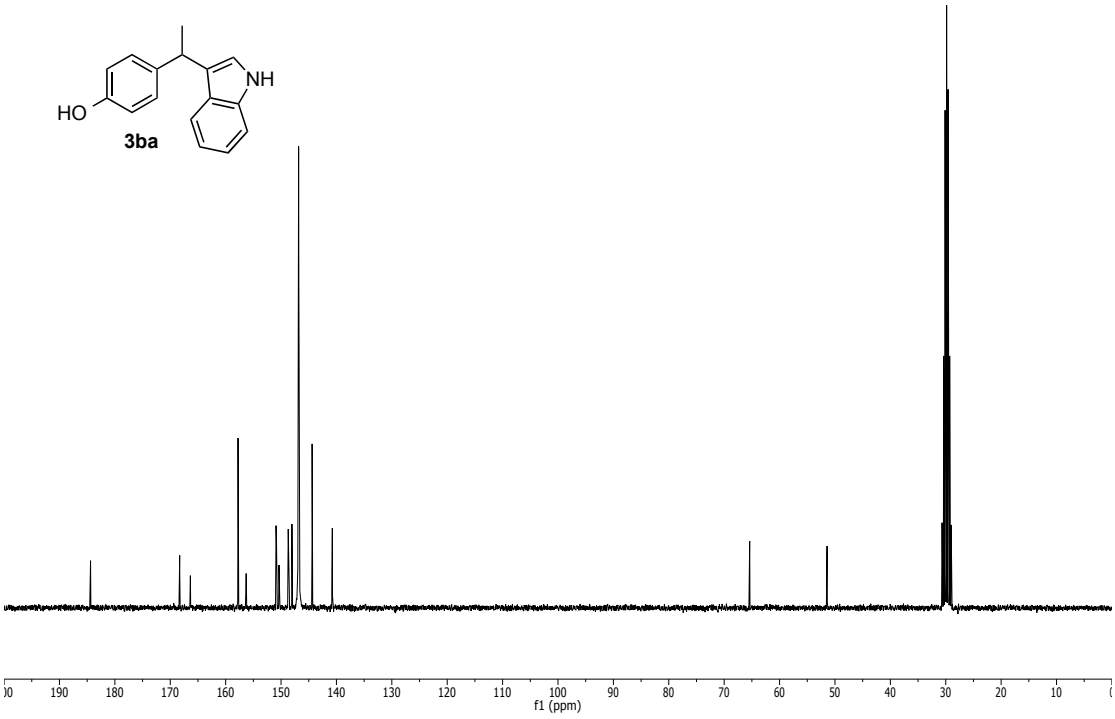
^{13}C NMR (75 MHz, CD_3CN) δ/ppm: 155.8 (*C*-1), 139.8 (C_{quart}), 137.8 (C_{quart}), 129.2 (*C*-3), 127.8 (*C*-4'), 122.4 (Ar*H*), 122.3 (Ar*H*), 121.9 (*C*-3'), 120.2 (Ar*H*), 119.5 (Ar*H*), 115.9 (*C*-2), 112.2 (*C*-8'), 36.9 (*C*HCH_3), 22.9 (*C*H_3).

GC MS (EI) *m/z* (%): 237 (31, M^+), 222 (100, $[M\text{-}CH_3]^+$), 204 (4), 192 (6), 165 (7), 144 (4, $[M\text{-}C_6H_5O]^+$), 117 (5), 77 (3, $C_6H_5^+$), 63 (2), 51 (2), 39 (2).

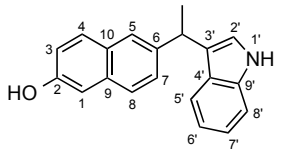
HRMS (EI) m/z (%): calculated for $C_{16}H_{14}NO$ $[M\text{-}H]^+$ 236.10809; found 236.10823.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3423m (OH), 3050w, 2963w, 2854w, 1613w, 1510m, 1455m, 1410m, 1331m, 1256m, 1183m, 1168m, 1091m, 1009m, 961w, 825s, 744s, 608m.


HO
NH
3ba
1.00
1.01
1.01
4.11
1.00
3.00
1.02
3.08
f1 (ppm)


HO
NH
3ba
f1 (ppm)

6-(1-(1*H*-Indol-3-yl)ethyl)naphthalen-2-ol (3da):



The compound **3da** was prepared according to the general procedure for hydroarylation from 6-vinylnapthtalen-2-ol (85.1 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 95:5-80:20) and obtained as purple oil (63 mg, 43%).

$C_{20}H_{17}NO$ (287.36 g/mol)

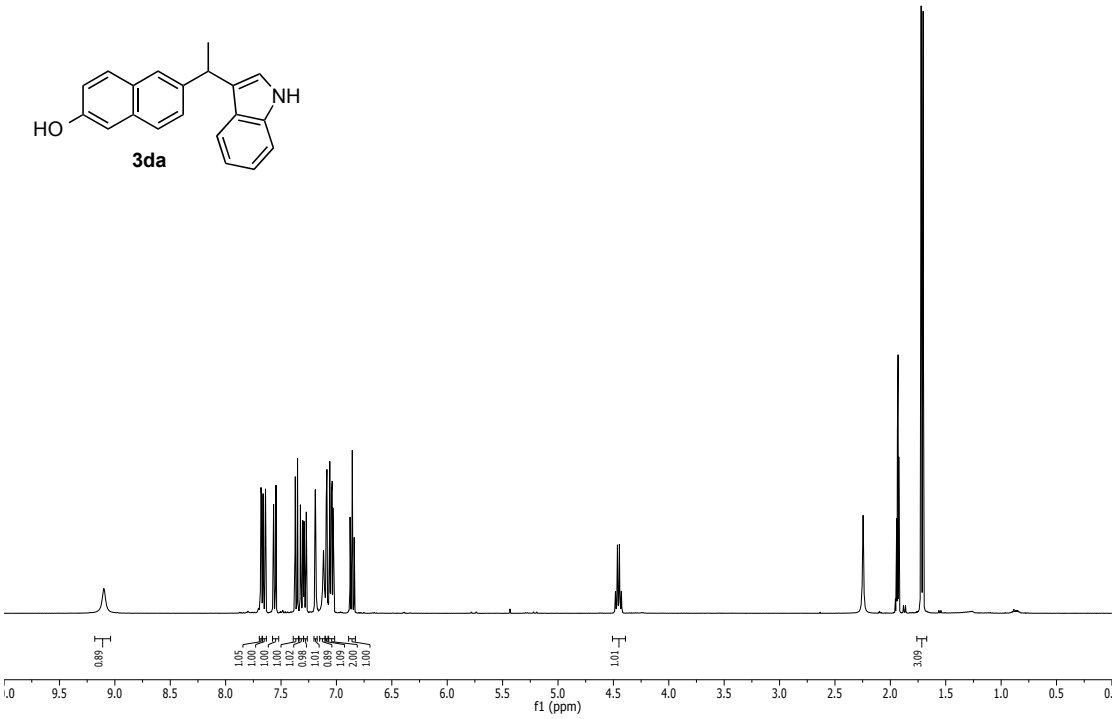
R_f = 0.08 (silica, EA/heptane 1:4).

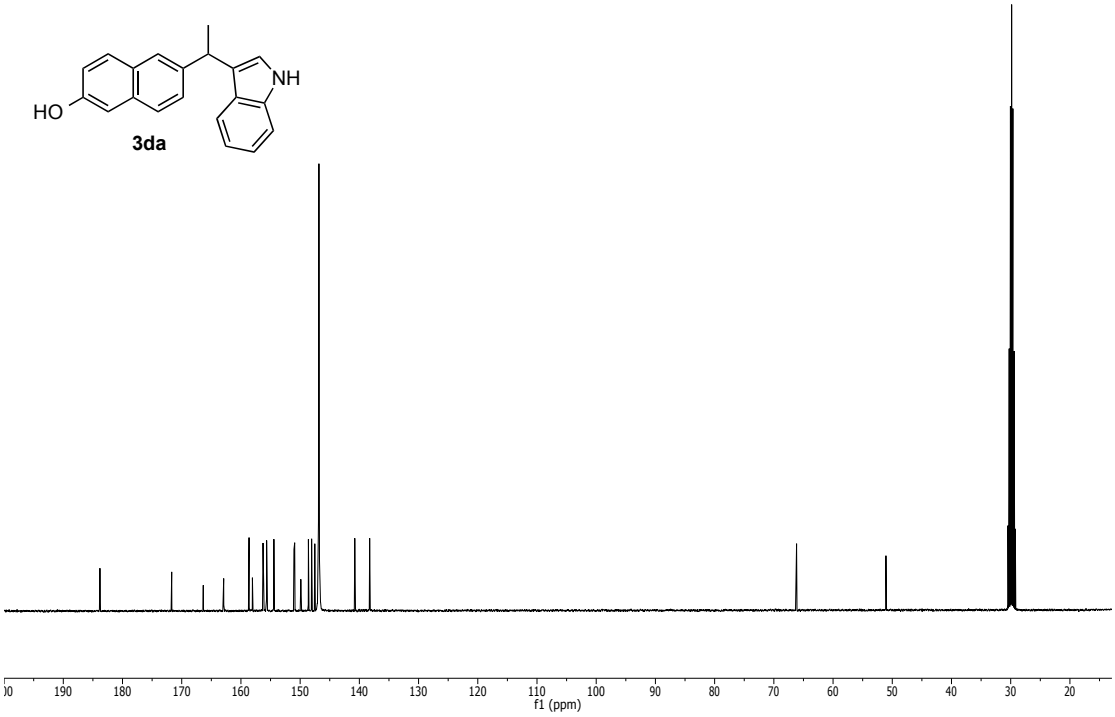
^{1}H NMR (400 MHz, CD_3CN) δ/ppm: 9.11 (br. S, H, NH), 7.69 (d, $^4J_{HH}$ = 1.2 Hz, 1H, 5-*H*), 7.66 (d, $^3J_{HH}$ = 8.7 Hz, 1H, 4-*H*), 7.57 (d, $^4J_{HH}$ = 8.5 Hz, 1H, 8-*H*), 7.37 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, 8'-*H*), 7.32 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.2 Hz, 1H, 7-*H*), 7.29 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, 5'-*H*), 7.20 (dd, $^3J_{HH}$ = 2.5 Hz, $^5J_{HH}$ = 1.0 Hz, 1H, 2'-*H*), 7.13 (br. s, H, OH), 7.10 (d, $^4J_{HH}$ = 2.2 Hz, 1H, 1-*H*), 7.10-7.01 (m, 2H, 3-*H*, 7'-*H*), 6.87 (ddd, $^3J_{HH}$ = 8.0 and 7.0 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, 6'-*H*), 4.46 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*CH_3), 1.72 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CHC*H*$_3$).

^{13}C NMR (101 MHz, CD_3CN) δ/ppm: 155.3 (*C*-2), 143.2 (*C*-6), 137.8 (*C*-9'), 134.4 (*C*-9), 130.1 (*C*-4), 129.5 (*C*-10), 127.78 (*C*-4'), 127.75 (*C*-7), 127.1 (*C*-8), 125.9 (*C*-5), 122.5 (*C*-2'), 122.4 (*C*-7'), 121.4 (*C*-3'), 120.1 (*C*-5'), 119.5 (*C*-6'), 119.0 (*C*-3), 112.2 (*C*-8'), 109.7 (*C*-1), 37.6 (*C*HCH_3), 22.6 (*C*H_3).

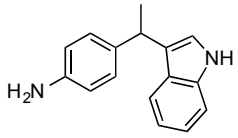
GC MS (EI) *m/z* (%): 287 (35, M^+), 272 (100, $[M\text{-}CH_3]^+$), 242 (6), 215 (3), 144 (5, $C_{10}H_{10}N^+$), 136 (5), 115 (6, $C_9H_7^+$).

HRMS (EI) m/z (%): calculated for $C20H_{17}NO$ $[M]^+$ 287.13047; found 287.13040.


HO
NH
3da
0.89
1.05
1.00
1.00
1.00
1.02
0.98
1.01
0.89
1.09
2.00
1.00
1.01
3.09
f1 (ppm)


HO
NH
3da
f1 (ppm)

4-(1-(1H-indol-3-yl)ethyl)aniline (3ea)



The compound **3ea** was prepared according to the general procedure for hydroarylation from 4-vinylaniline (62.0 mg, 520 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10-80:20) and obtained as pale yellow solid (79 mg, 64%).

$C_{16}H_{15}N_2$ (236.32 g/mol)

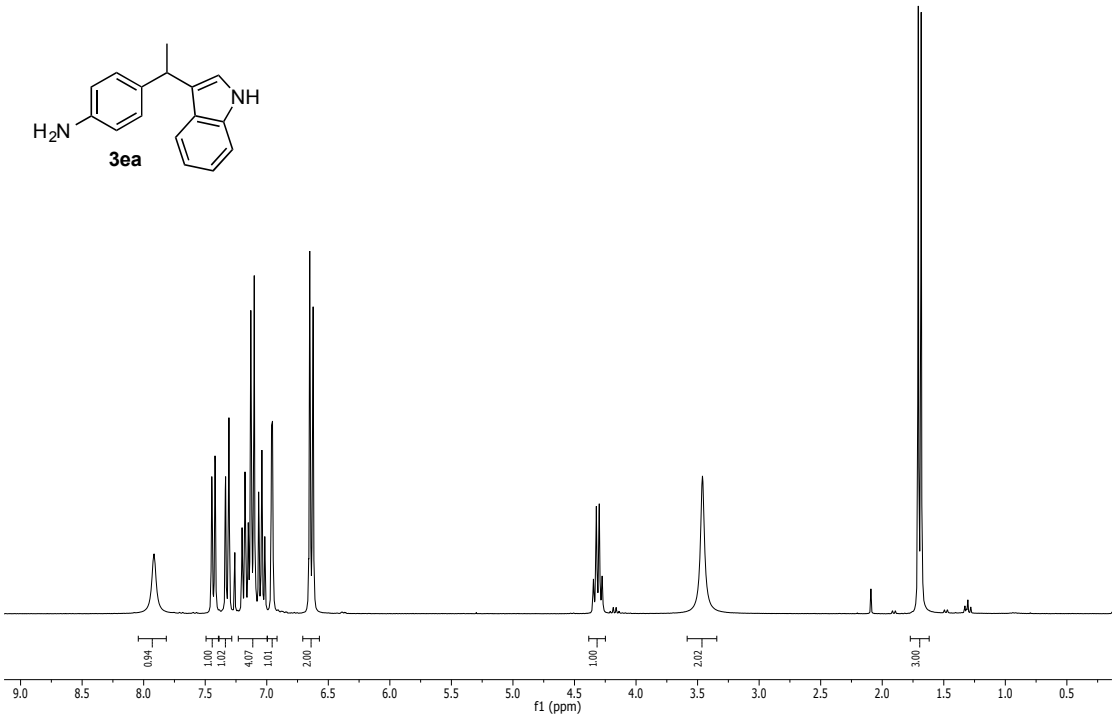
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.92 (s, 1H, N*H*), 7.43 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.32 (dt, *J* = 8.2, 1.0 Hz, 1H, Ar*H*), 7.23 – 7.00 (m, 4H), 6.96 (dd, *J* = 2.3, 1.1 Hz, 1H), 6.72 – 6.54 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 1H, C*H*), 3.46 (s, 2H, NH_2), 1.70 (d, *J* = 7.4 Hz, 3H, CH_3).

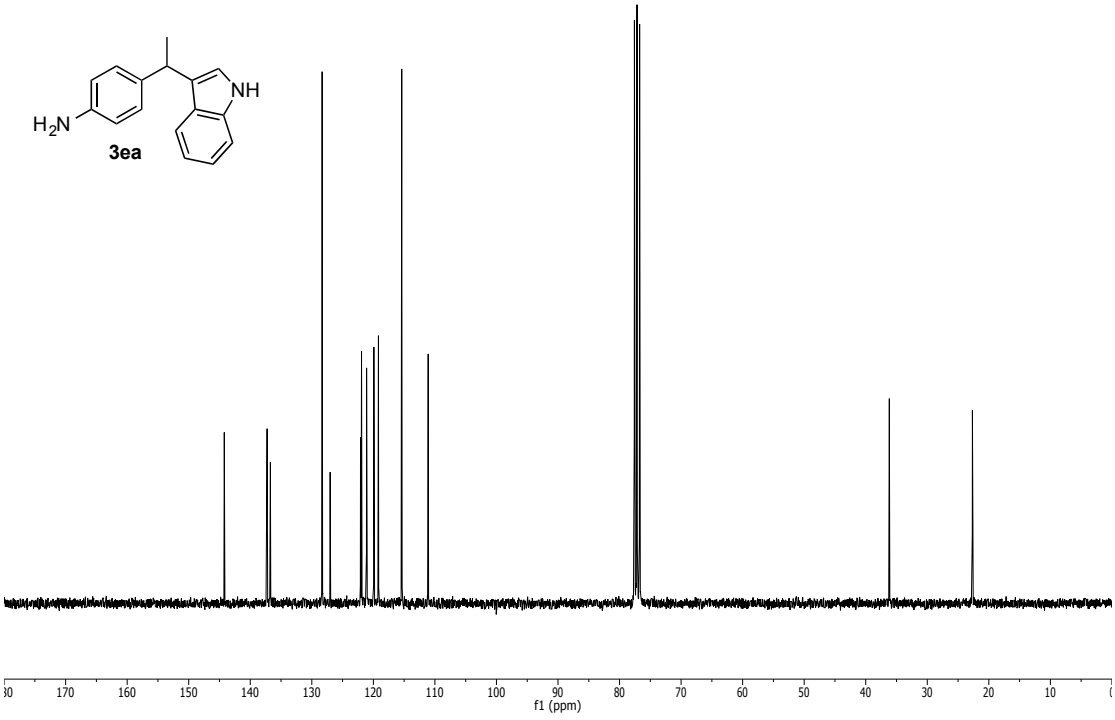
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 144.2 (C_q), 137.3 (C_q), 136.7 (C_q), 128.3 (CH), 127.0 (C_q), 122.1 (C_q), 121.9 (CH), 121.1 (CH), 119.9 (CH), 119.2 (CH), 115.4 (CH), 111.1 (CH), 36.2 (CH), 22.7 (CH_3).

GC MS (EI) *m/z* (%): 236 (29, M^+), 221 (100), 204 (7), 192 (3), 165 (3), 110 (8).

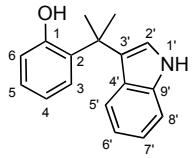
HRMS (EI) m/z (%): calculated for $C_{16}H_{16}N$ $[M+H]^+$ 237.1387; found 237.1386.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3413m (OH), 3324 (w), 3180 (bw), 2969 (w), 1615 (w), 1510 (m), 1337 (m), 1224 (m), 1108 (w), 821 (s), 742 (s), 543 (s).


NH
H_2N
3ea
0.94
1.00
1.02
4.07
1.01
2.00
1.00
2.02
3.00
f1 (ppm)


NH
H_2N
3ea
f1 (ppm)

2-(2-(1H-indol-3-yl)propan-2-yl)phenol (3ha)



The compound **3ha** was prepared according to the general procedure for hydroarylation from 2-(prop-2-en-2-yl)phenol (76.8 mg, 544 µmol, 95% purity), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol) at 80 °C. The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10) and obtained as a pale purple foamy solid (133 mg, 97%).

$C_{17}H_{17}NO$ (251.33 g/mol)

M.p.: 118-119°C

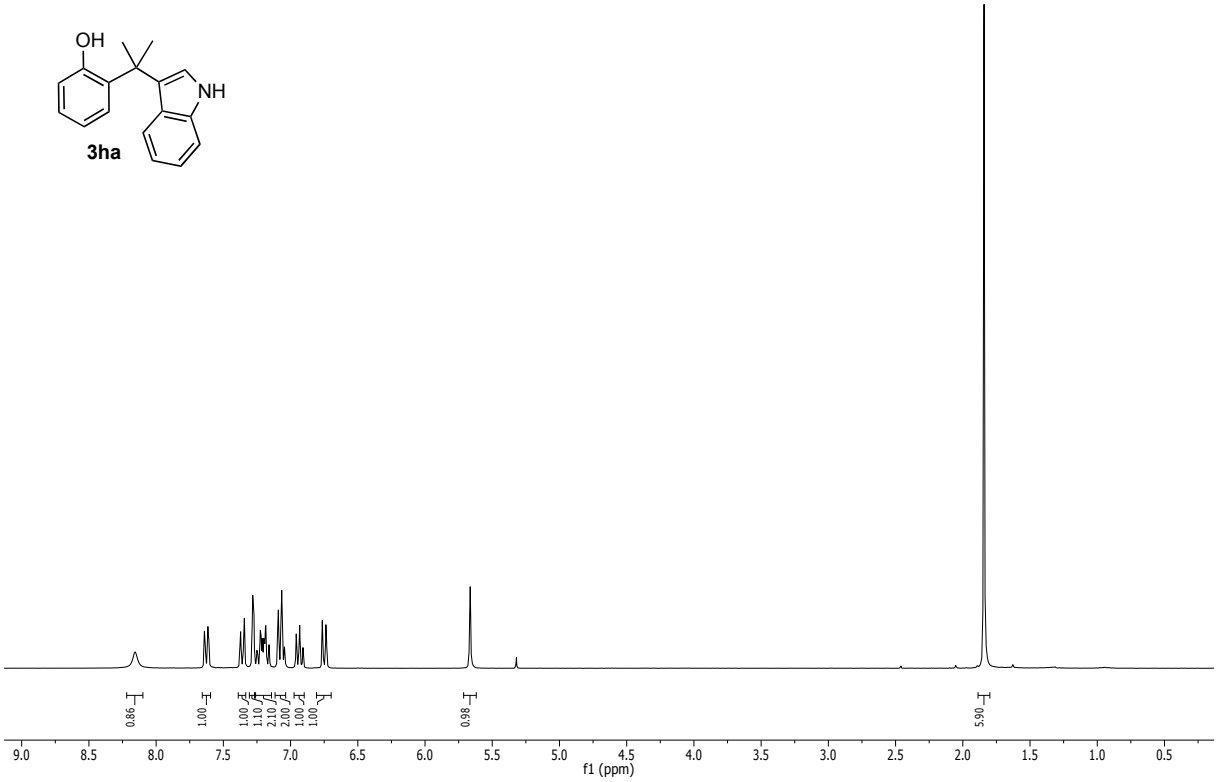
R_f = 0.30 (silica, EA/heptane 1:4).

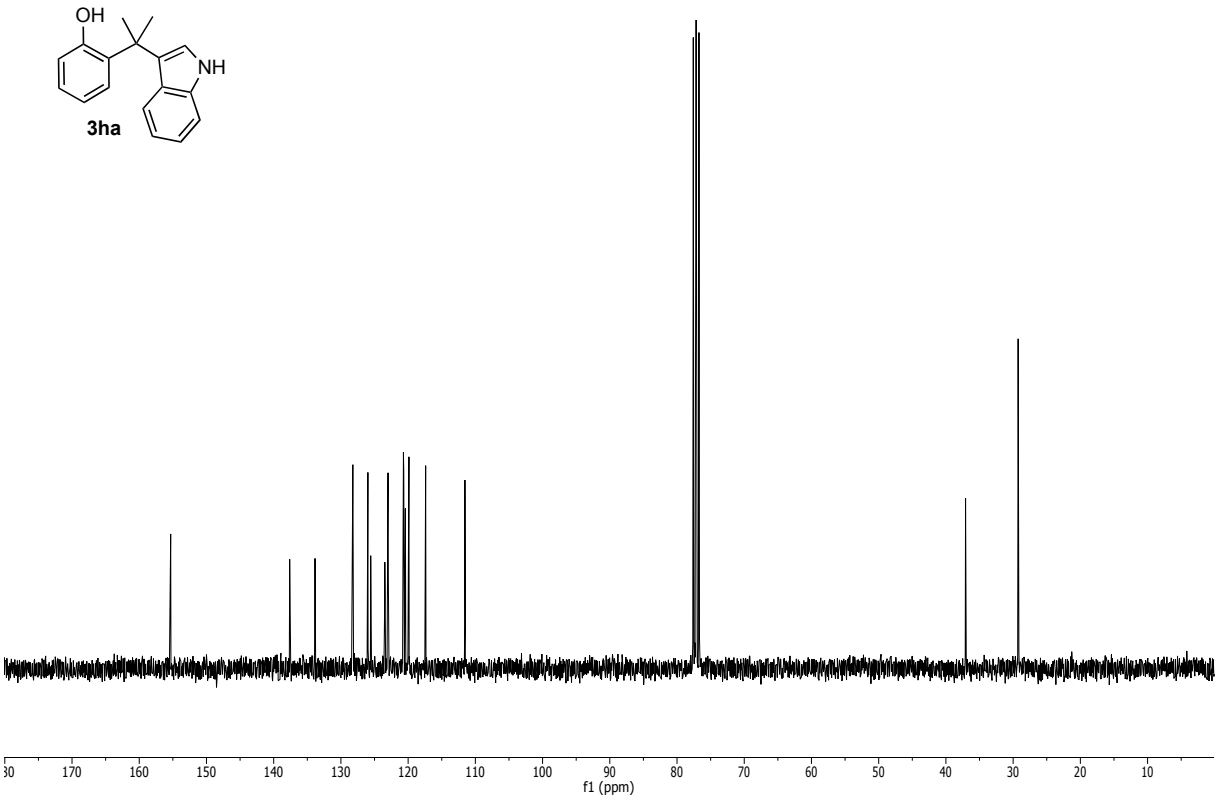
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.14 (br. S, H, NH), 7.61 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 5'-*H*), 7.35 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, 8'-*H*), 7.27 (s, 1H, 2'-*H*), 7.24-7.14 (m, 2H, Ar*H*), 7.10-7.01 (m, 2H, Ar*H*), 6.92 (ddd, 3JHH = 8.0 and 7.0 Hz, 4JHH = 1.3 Hz, 1H, 4-*H*), 6.74 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 6-*H*), 5.65 (s, 1H, OH), 1.83 (s, 6H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 155.3 (*C*-1), 137.6 (*C*-9'), 133.9 (*C*-2), 128.2 (*Ar*H), 126.0 (*Ar*H), 125.6 (*Ar*C), 123.5 (*Ar*C), 123.0 (*Ar*H), 120.7 (*Ar*H), 120.7 (*Ar*H), 120.4 (*Ar*H), 120.9 (*Ar*H), 117.4 (*Ar*H), 111.6 (*Ar*H), 37.1 ($C(CH_3)_2$), 29.3 (CH_3).

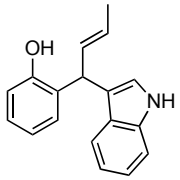
GC MS (EI) *m/z* (%): 251 (63, M^+), 236 (90, $[M\text{-}CH_3]^+$), 220 (11), 158 (10), 117 (100, $C_8H_7N^+$), 91 (30, $C_7H_7^+$), 77 (7, $C_6H_5^+$).

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3331m (OH), 3034w, 2972w, 1575w, 1486m, 1453m, 1341wm, 1285w, 1221m, 1154m, 1105m, 1040m, 1012m, 967w, 830m, 767m, 747s (Ar), 612m.


OH
NH
3ha
0.86
1.00
1.00
1.10
2.10
2.00
1.00
1.00
0.98
5.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


OH
NH
3ha
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(*E*)-2-(1-(1H-indol-3-yl)but-2-en-1-yl)phenol (3ia)



The compound **3ia** was prepared according to the general procedure for hydroarylation from (*E*)-2-(buta-1,3-dien-1-yl)phenol (71 mg, 487 µmol), indole (65 mg, 550 µmol) and diphenyl phosphate (6.3 mg, 25 µmol) at 80 °C. The product was purified by column chromatography (silica, pentane/ethyl acetate 7:1 – 5:1) and obtained as colorless oil (69 mg, 54%).

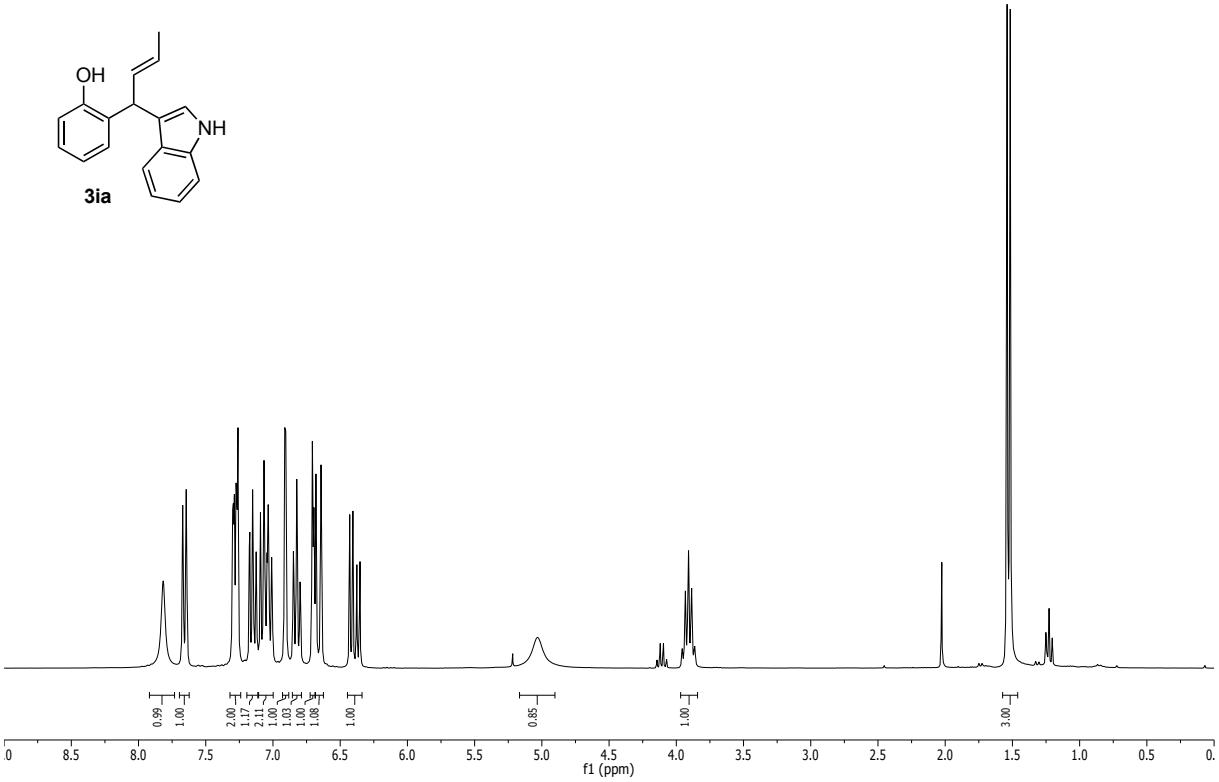
$C_{18}H_{17}NO$ (263.34 g/mol)

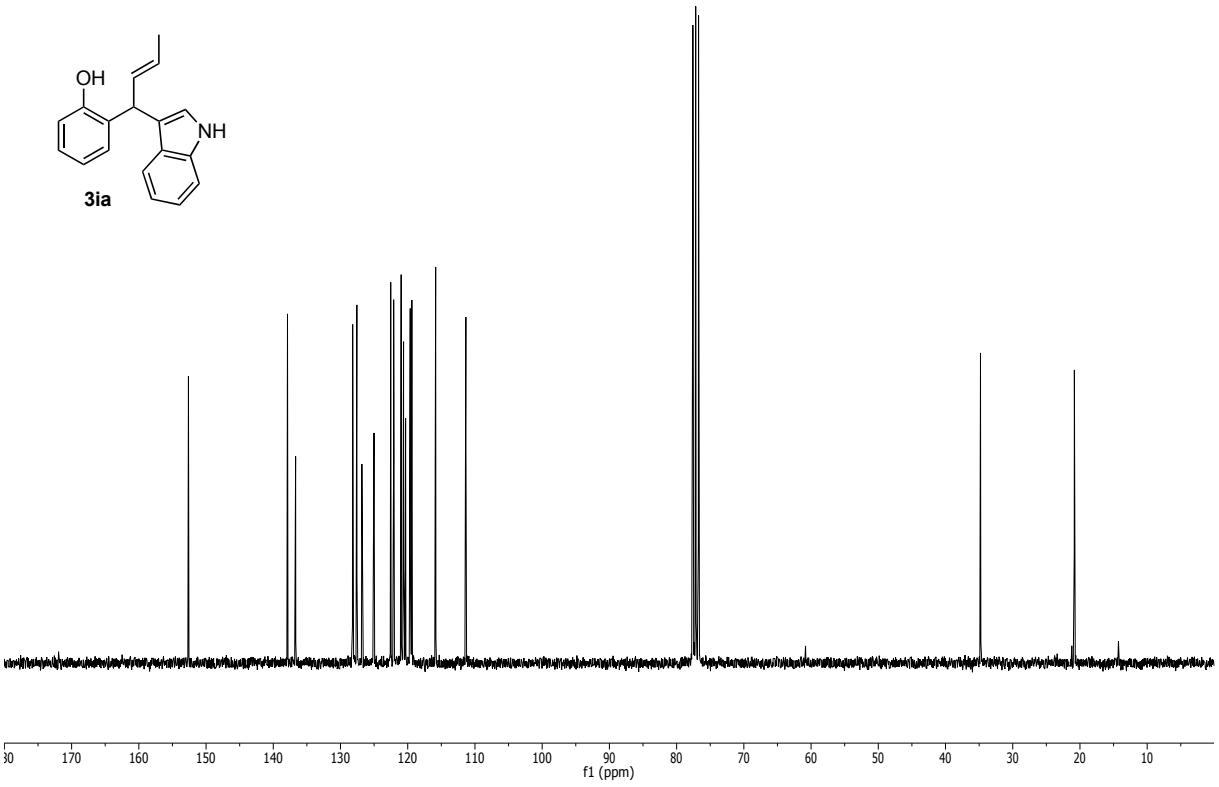
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.82 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 2H), 7.19 – 7.11 (m, 1H), 7.11 – 7.00 (m, 2H), 6.91 (dd, *J* = 2.3, 1.1 Hz, 1H), 6.82 (td, *J* = 7.5, 1.2 Hz, 1H), 6.70 (dd, *J* = 3.3, 1.2 Hz, 1H), 6.68 (s, 1H), 6.39 (ddd, *J* = 15.9, 7.0, 1.0 Hz, 1H), 5.03 (s, 1H), 3.91 (dq, *J* = 7.o, 2.3 Hz, 1H), 1.53 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 152.6 (C_q), 137.9 (CH), 136.7 (C_q), 128.2 (CH), 127.6 (CH), 126.8 (C_q), 125.0 (C_q), 122.5 (CH), 122.1 (CH), 121.0 (CH), 120.6 (CH), 120.3 (C_q), 119.6 (CH), 119.4 (CH), 115.8 (CH), 111.4 (CH), 34.8 (CH), 20.8 (CH_3).

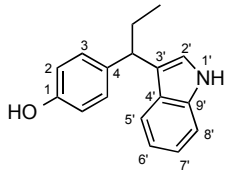
HRMS (EI) m/z (%): calculated for $C_{18}H_{17}NO$ $[M-H]^+$ 263.1305; found 263.1302.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3406 (m), 2964 (w), 1499 (m), 1455 (m), 1337 (w), 1096 (m), 811 (m), 737 (s).


OH
NH
3ia
0.99
1.00
2.00
1.17
2.11
1.00
1.03
1.00
1.08
1.00
0.85
1.00
3.00
f1 (ppm)


OH
NH
3ia
f1 (ppm)

2-(1-(1*H*-Indol-3-yl)propyl)phenol (3ja)



The compound **3ja** was prepared according to a modified general procedure for hydroarylation from 2-(prop-2-enyl)phenol (67.1 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (12.5 mg, 50.0 µmol) at 100 °C. The product was purified by column chromatography (silica, heptane/ethyl acetate 85:15) and obtained as a purple oil (113 mg, 90%).

$C_{17}H_{17}NO$ (251.32 g/mol)

$\boldsymbol{R_f}$ = 0.19 (silica, EA/heptane 1:4).

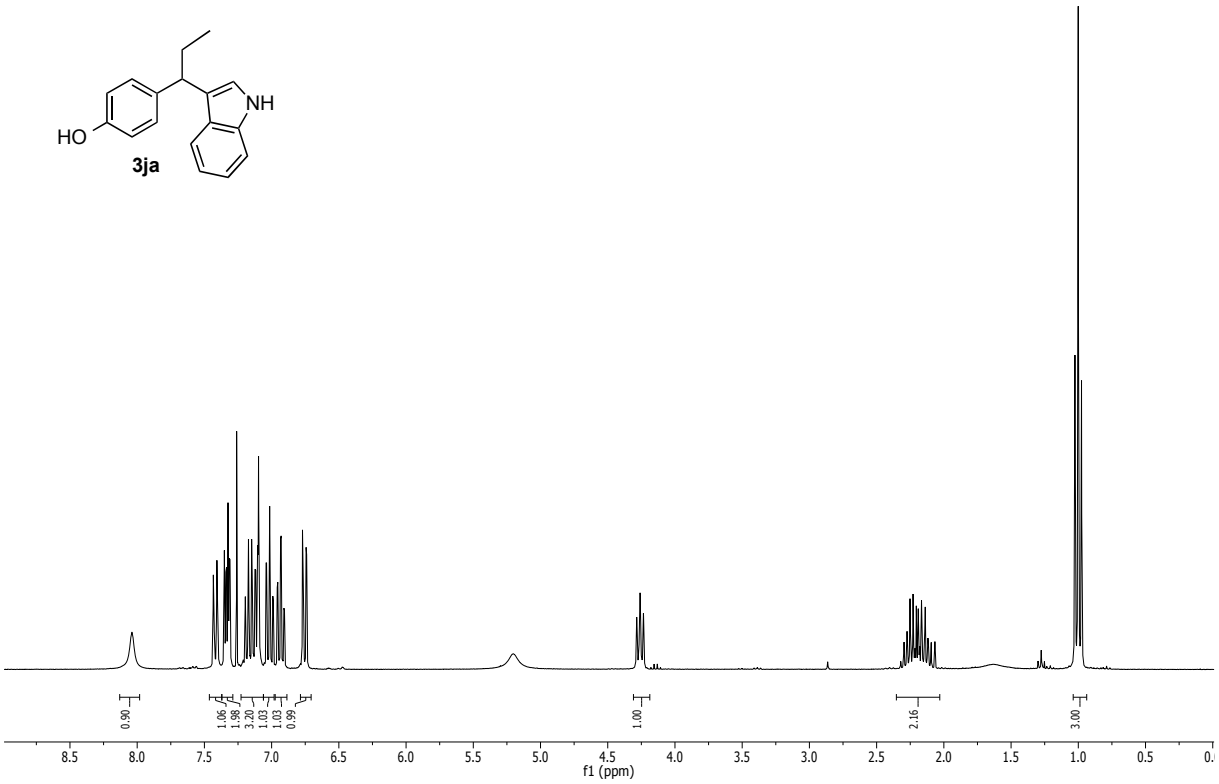
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.04 (br. S, H, NH), 7.44-7.40 (m, 1H, 5'-*H*), 7.34 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, 8'-*H*), 7.32 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 3-*H*), 7.20-7.09 (m, 3H, 7'-*H*, 5-*H*, 2'-*H*), 7.01 (ddd, $^3J_{HH}$ = 8.0 and 6.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, 6'-*H*), 6.93 (ddd, $^3J_{HH}$ = 7.5 and 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 4-*H*), 6.80 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 6-*H*), 5.20 (br. S, 1H, OH), 4.26 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C*H*CH_2), 2.35-2.03 (m, 2H, CHCH_2), 1.00 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3).

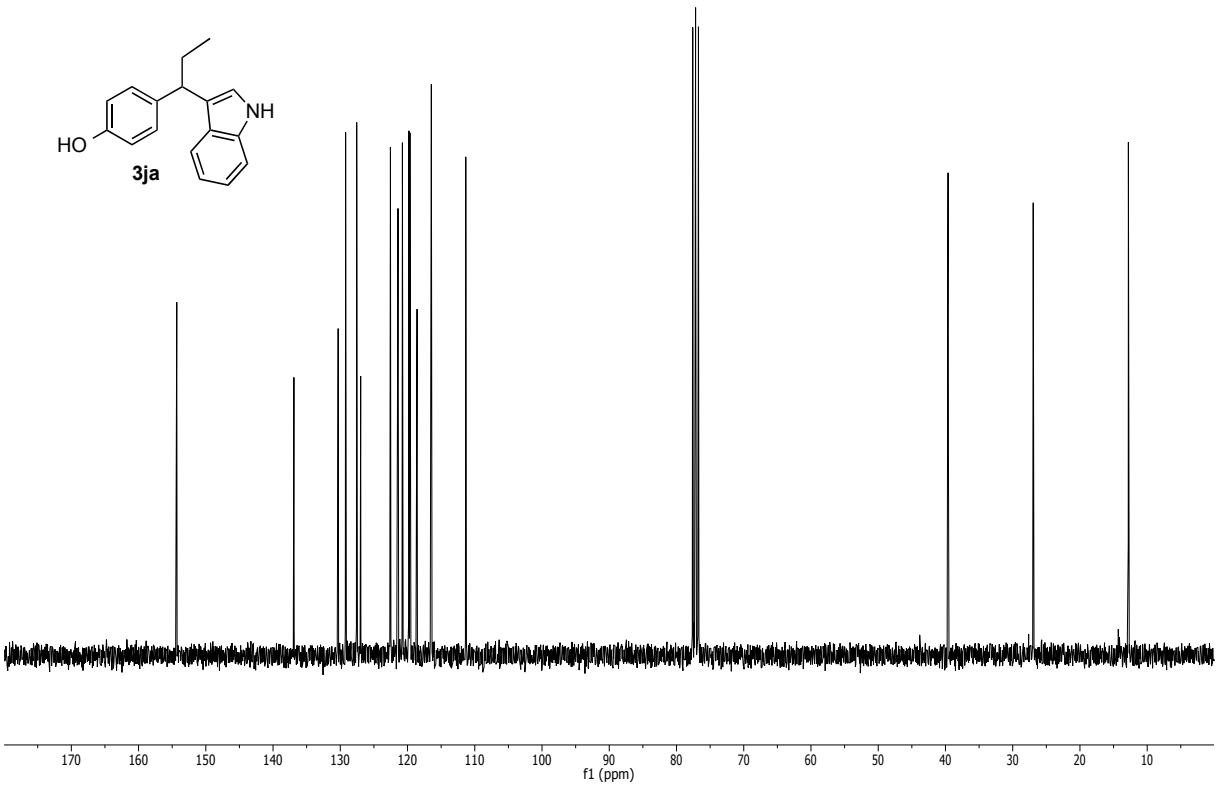
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 154.3 (*C*-1), 136.9 (*C*-9'), 130.3 (*C*-2), 129.2 (*C*-3), 127.6 (*C*-5), 127.0 (*C*-4'), 122.6 (*C*-7'), 121.4 (*C*-2'), 120.8 (*C*-4), 119.8 (*C*-5'), 119.6 (*C*-6'), 118.6 (*C*-3'), 116.5 (*C*-6), 111.3 (*C*-8'), 39.6 (*C*HCH_2), 27.0 (CH*C*H_2), 20.4 (*C*H_3).

GC MS (EI) *m/z* (%): 251 (22, M^+), 222 (100, $[M\text{-}CH_2CH_3]^+$), 204 (4), 165 (6), 117 (10, $C_8H_7N^+$), 77 (3, $C_6H_5^+$).

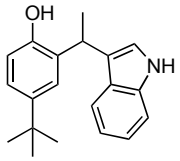
HRMS (EI) m/z (%): calculated for $C_{17}H_{17}NO$ $[M]^+$ 251.13047; found 251.13067.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3407m (OH), 3057w, 2961w, 2929w, 2871w, 1583w, 1487m, 1453s, 1337m, 1217m, 1095m, 1038m, 1010m, 907m, 845w, 799m, 737s (Ar).


HO
NH
3ja
0.90
1.06
1.98
3.20
1.03
1.03
0.99
1.00
2.16
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


HO
NH
3ja
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2-(1-(1*H*-indol-3-yl)ethyl)-4-(*tert*-butyl)phenol (3ka)



The compound **3ka** was prepared according to the general procedure for hydroarylation from 24-(tert-butyl)-2-vinylphenol (88.4 mg, 502 µmol), indole (65 mg, 550 µmol) and diphenyl phosphate (6.4 mg, 25 µmol) at 80 °C. The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10) and obtained as a brownish solid (133 mg, 91%).

$C_{20}H_{23}NO$ (293.41 g/mol)

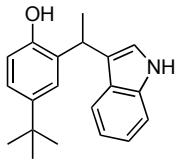
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.03 (s, 1H), 7.44 – 7.33 (m, 3H), 7.23 – 7.12 (m, 2H), 7.08 – 6.97 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 1H), 4.49 (q, *J* = 7. 1 Hz, 1H), 1.77 (d, *J* = 7.1 Hz, 3H), 1.33 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 151.9 (C_q), 143.5 (C_q), 137.1 (C_q), 130.5 (C_q), 126.7 (C_q), 125.5 (C_q), 124.4 (CH), 122.7 (CH), 121.3 (CH), 119.8 (CH), 119.7 (CH), 119.7 (CH), 116.0 (CH), 111.4 (CH), 34.3 (C_q), 33.2 (CH), 31.8 (CH_3), 20.4 (CH_3).

GC MS (EI) *m/z* (%): 293 (41, M^+), 278 (41), 262 (7), 161 (16), 117 (100).

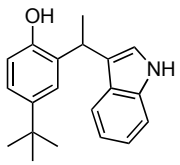
HRMS (EI) m/z (%): calculated for $C_{20}H_{23}NO$ $[M]^+$ 293.1774; found 293.1779.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3401 (w), 3346 (w), 2960 (w), 1501 (m), 1216 (m), 1109 (m), 1021 (m), 823 (m), 747 (s).


OH
NH

3ka

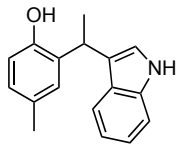
0.92
2.98
2.00
2.00
1.00
0.84
1.01
3.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
NH

3ka

70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2-(1-(1*H*-indol-3-yl)ethyl)-4-methylphenol (3la)



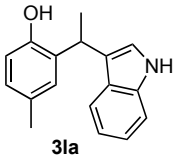
The compound **3la** was prepared according to the general procedure for hydroarylation from 4-(tert-butyl)-2-vinylphenol (88.4 mg, 502 µmol), indole (65 mg, 550 µmol) and diphenyl phosphate (6.4 mg, 25 µmol) at 80 °C. The product was purified by column chromatography (silica, pentane/ethyl acetate 60:10) and obtained as a brownish solid (112 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.04 (s, 1H), 7.41 (dq, *J* = 8.0, 0.9 Hz, 1H), 7.36 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.18 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 – 6.98 (m, 3H), 6.93 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 4.97 (s, 1H), 4.48 (q, *J* = 7.4 Hz, 1H), 2.29 (s, 3H), 1.73 (d, *J* = 7.1 Hz, 3H).

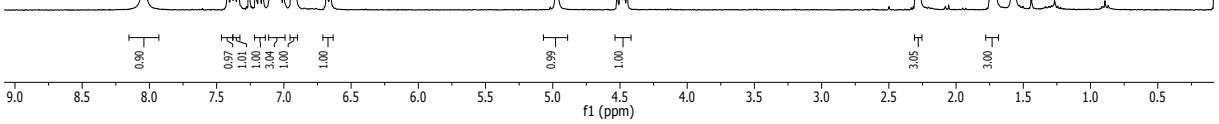
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 151.9, 137.1, 131.2, 130.0, 129.0, 128.1, 126.8, 122.7, 121.3, 119.9, 119.8, 116.3, 111.3, 32.4, 20.9, 20.5.

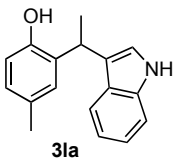
HRMS (EI) m/z (%): calculated for $C_{17}H_{17}NO$ $[M-H]^+$ 252.1383; found 252.1383.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3406 (m), 2964 (w), 1499 (m), 1455 (m), 1337 (w), 1096 (m), 811 (m), 737 (s).


OH
NH

3la

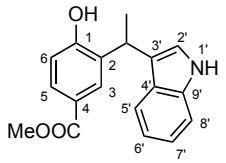

0.90
0.97
1.01
1.00
3.04
1.00
1.00
0.99
1.00
3.05
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


OH
NH

3la

70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Methyl 3-(1-(1*H*-indol-3-yl)ethyl)-4-hydroxybenzoate (3ma)



The compound **3ma** was prepared according to the general procedure for hydroarylation from methyl 4-hydroxy-3-vinylbenzoate (89.1 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.3 mg, 25 µmol). The product was purified by column chromatography (silica, *n*-pentane/Et_2O 5:1-1:1). The title compound was obtained as colorless solid (144 mg, 98%).

$C_{18}H_{17}NO_3$ (295.34 g/mol)

$\boldsymbol{R_f}$ = 0.09 (silica, EA/heptane 1:2).

M.p.: 156°C

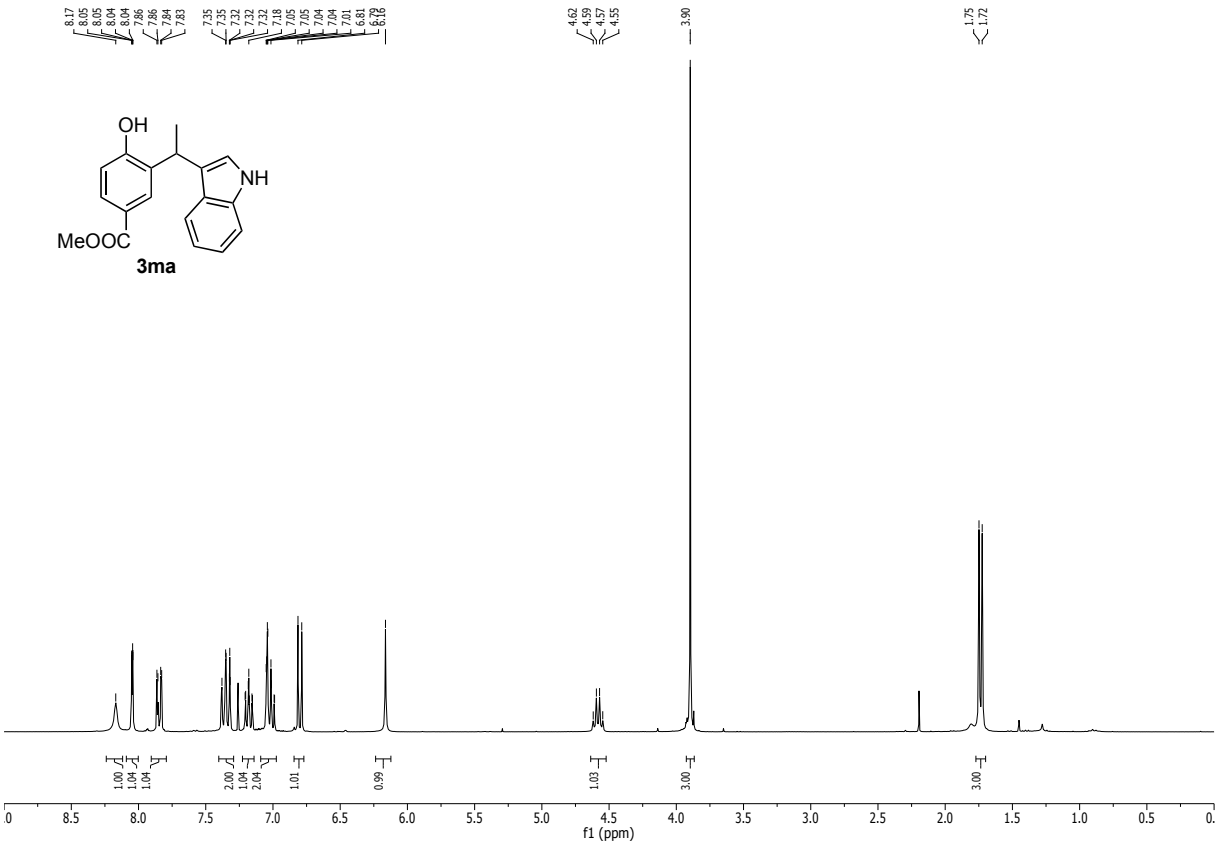
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.15 (s, 1H, N*H*), 8.05 (d, $^3J_{HH}$ = 1.8 Hz, 1H, 3-*H*), 7.85 (dd, $^3J_{HH}$ = 8.4, 1.8 Hz, 1H, 5-*H*), 7.36 (dd, $^3J_{HH}$ = 8.0, 1.2 Hz, 1H), 7.35 (dd, $^3J_{HH}$ = 8.4, 1.1 Hz, 1H), 7.35 (m, 2H, Ar*H*), 7.19 (ddd, $^3J_{HH}$ = 8.4, 7.0, 1.2 Hz, 1H), 7.07 (s, 1H, 2'-*H*), 7.02 (ddd, $^3J_{HH}$ = 8.0, 7.0, 1.1 Hz, 1H), 6.79 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 6-*H*), 6.00 (s, 1H, O*H*), 4.56 (q, $^3J_{HH}$ = 7.1 Hz, 1H, C*H*CH_3), 3.90 (s, 3H, CO_2C*H*$_3$), 1.75 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CHC*H*$_3$).

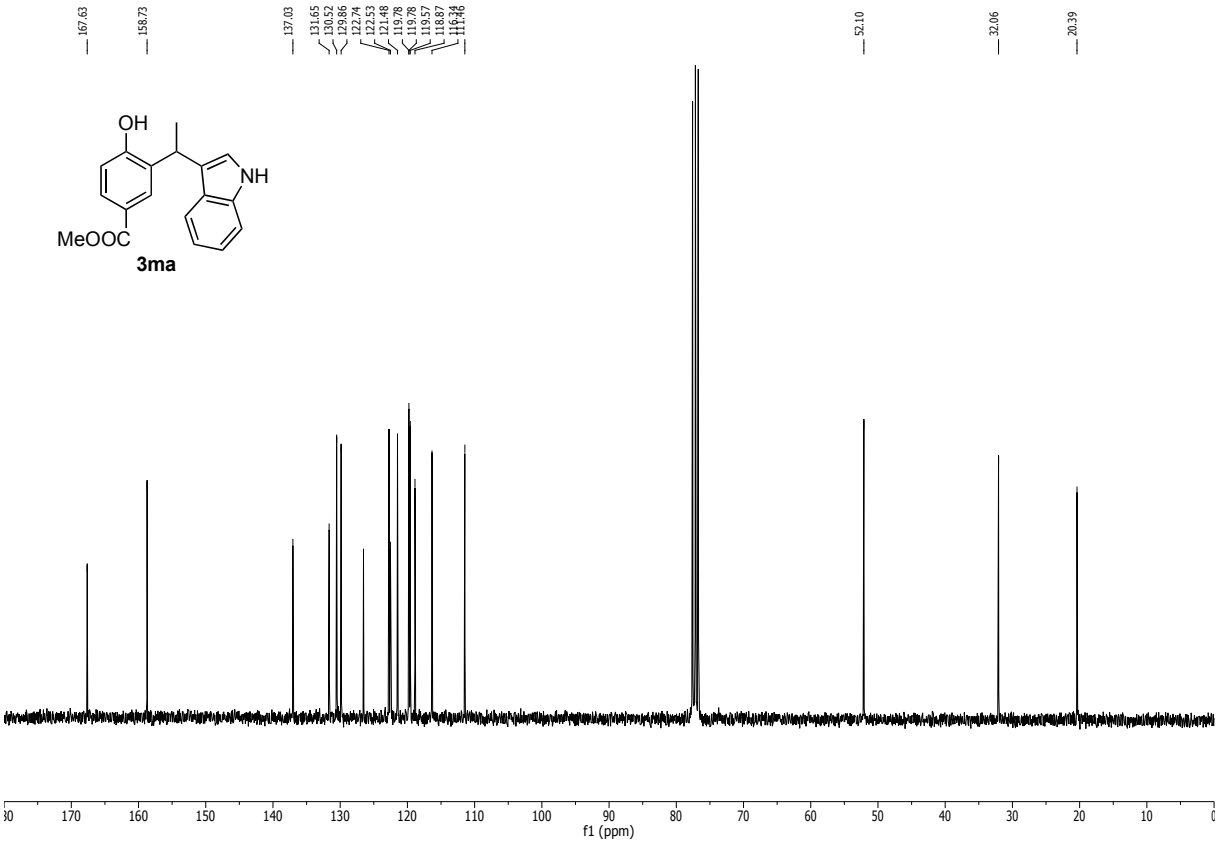
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 167.5 (C_q), 158.7 (C_q), 137.1 (C_q), 131.5 (C_q), 130.5 (Ar*H*), 129.9 (Ar*H*), 126.5 (C_q), 122.8 (Ar*H*), 122.7 (Ar*H*), 121.4 (Ar*H*), 119.9 (Ar*H*), 119.6 (Ar*H*), 118.9 (C_q), 116.4 (Ar*H*), 111.5 (Ar*H*), 52.1 (CO_2C*H*$_3$), 32.3 (C*H*CH_3), 20.4 (C*H*$_3$).

GC MS (EI) *m/z* (%): 295 (61, M^+), 280 (100), 264 (7), 220 (13), 191 (9), 117 (82).

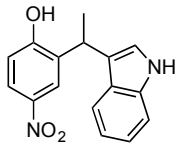
HRMS (EI) m/z (%): calculated for $C_{18}H_{17}O_3N$ $[M-H]^+$ 295.1203; found 295.1200.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3373 (m, OH), 1683 (s), 1603 (m), 1428 (m), 1230 (s), 1249 (m), 1133 (w), 1097 (w), 992 (w), 748 (s).


OH
NH
MeOOC
3ma
f1 (ppm)


OH
NH
MeOOC
3ma
f1 (ppm)

2-(1-(1*H*-Indol-3-yl)ethyl)-4-nitrophenol (3na)



The compound **3na** was prepared according to the general procedure for hydroarylation from 4-nitro-2-vinylphenol (82.6 mg, 500 µmol), indole (64.4 mg, 550 µmol) and diphenyl phosphate (6.3 mg, 25 µmol). The product was purified by column chromatography (silica, *n*-pentane/Et_2O 7:1-5:1). The title compound was obtained as colorless solid (85 mg, 63%).

$C_{16}H_{14}N_2O_3$ (295.34 g/mol)

M.p.: decomposition >200°C

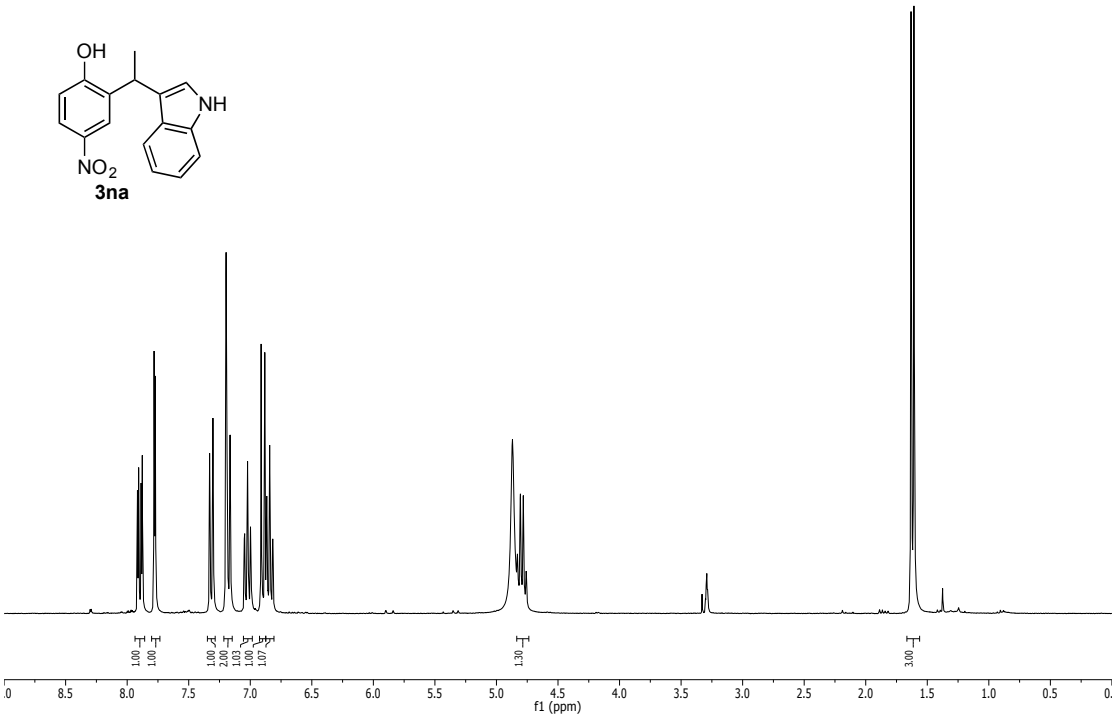
^{1}H NMR (300 MHz, d_4-MeOD) δ/ppm: 7.90 (dd, *J* = 8.9, 2.9 Hz, 1H), 7.78 (d, *J* = 2.8 Hz, 1H), 7.32 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.02 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.84 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.79 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H).

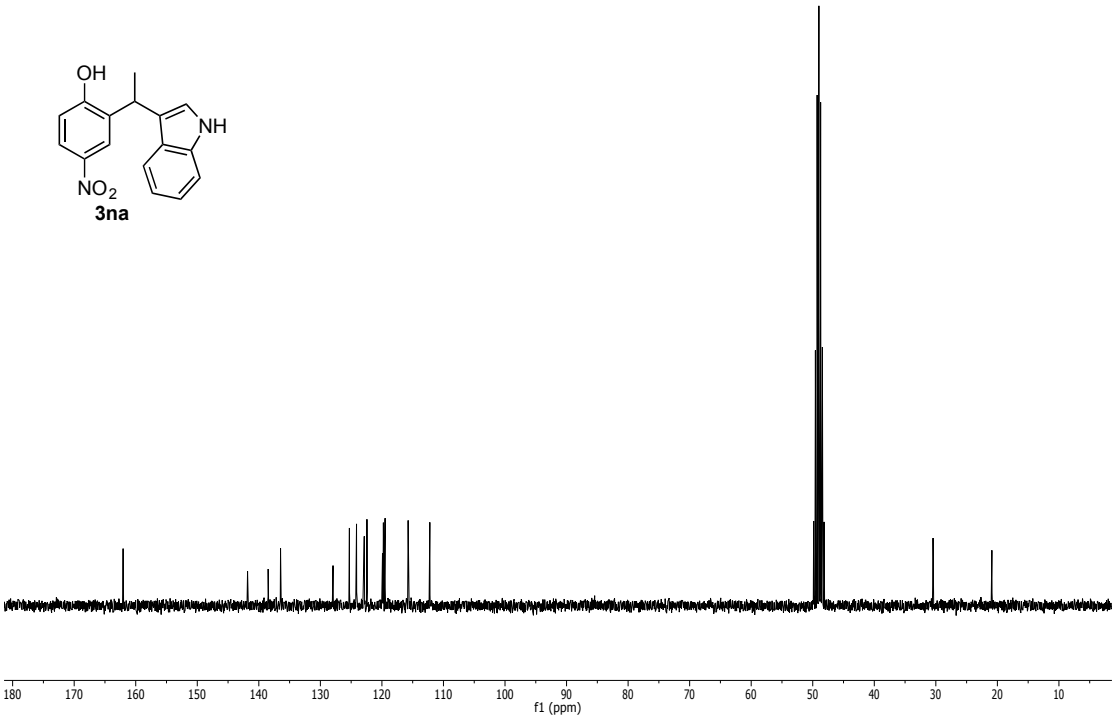
^{13}C NMR (75 MHz, d_4-MeOD) δ/ppm: 162.1 (C_q), 141.8 (C_q), 138.5 (C_q), 136.5 (C_q), 127.9 (C_q), 125.3 (CH), 124.1(CH) , 122.9 (CH), 122.4 (CH), 119.9 (C_q), 119.8 (CH), 119.5 (CH), 115.7 (CH), 112.2 (CH), 30.5 (CH), 20.9 (CH_3).

GC MS (EI) *m/z* (%): 282 (64, M^+), 267 (100, $[M]^+$), 264 (7), 221 (22), 191 (11), 144 (14), 117 (75).

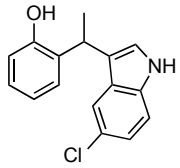
HRMS (EI) m/z (%): calculated for $C_{16}H_{14}O_3N_2$ $[M-H]^+$ 282.0999; found 282.1000.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3413 (w), 2534 (m), 1583 (m), 1481 (m), 1324 (s), 1272 (s), 1082 (m), 905 (m), 741 (s), 639 (m).


OH
NH
NO2
3na
1.00
1.00
1.00
2.00
1.03
1.00
1.07
1.30
3.00
f1 (ppm)


OH
NH
NO2
3na
f1 (ppm)

2-(1-(5-Chloro-1*H*-indol-3-yl)ethyl)phenol (3ab)



The compound **3ab** was prepared according to the modified general procedure for hydroarylation from 2-vinylphenol (60 mg, 500 µmol), 5-chloroindole (84.4 mg, 550 µmol) and diphenyl phosphate (12.6 mg, 60 µmol) in DCE at 100 °C. The product was purified by column chromatography (silica, *n*-pentane/Et_2O 7:1-5:1). The title compound was obtained as colorless solid (85 mg, 63%).

$C_{16}H_{14}ClNO$ (271.74 g/mol)

M.p.: 125°C

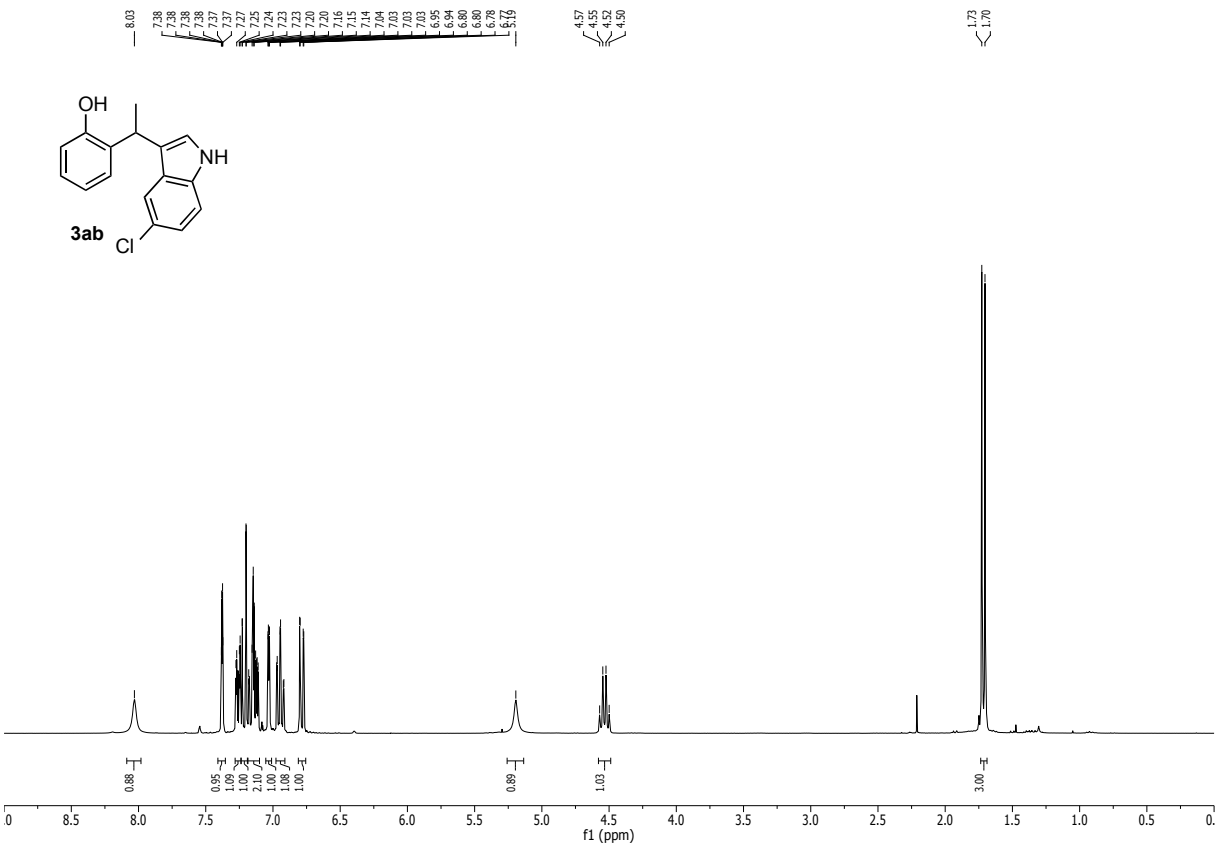
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.03 (s, 1H, N*H*), 7.38 (ddd, *J* = 1.9, 0.6 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (dd, *J* = 8.6, 0.6 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.03 (dd, *J* = 2.4, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.19 (s, 1H, O*H*), 4.53 (q, *J* = 7.1 Hz, 1H, C*H*), 1.72 (d, *J* = 7.1 Hz, 3H, CH_3).

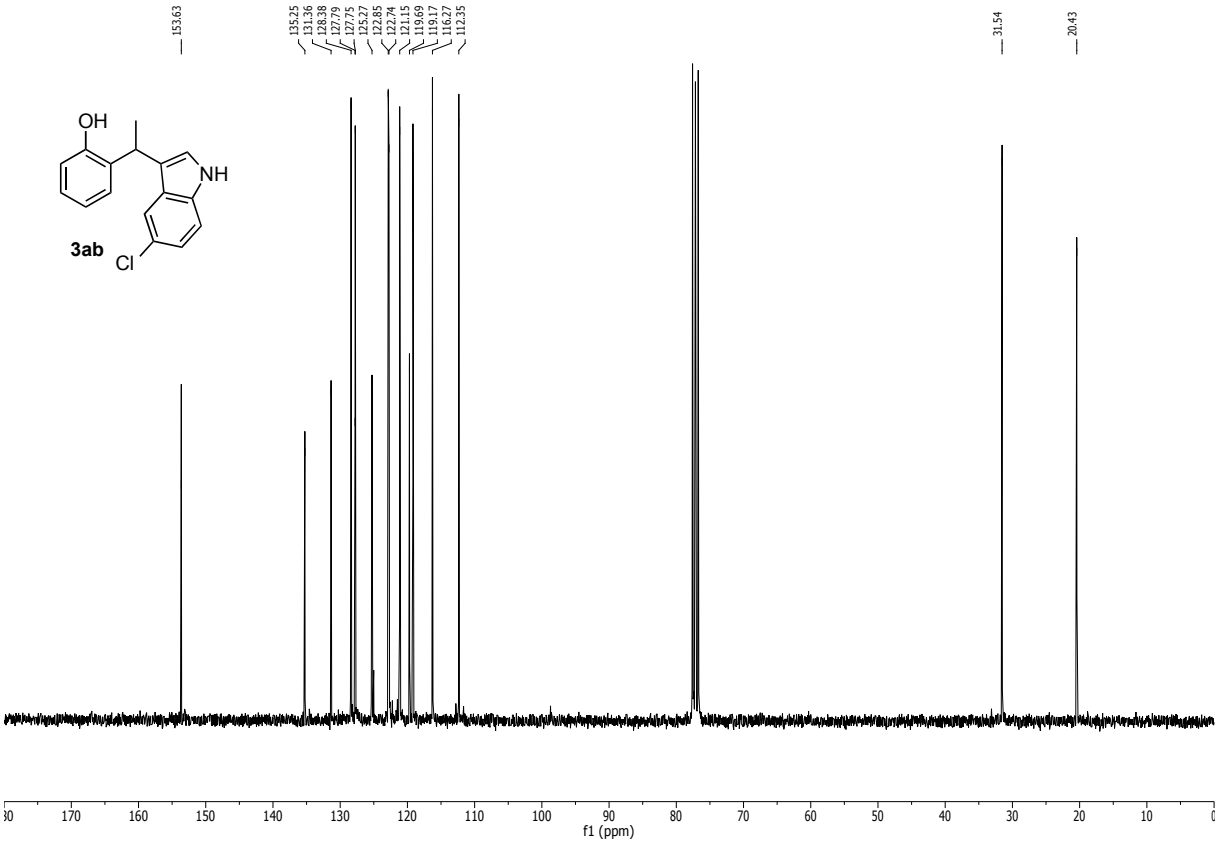
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 153.6 (C_q), 135.3 (C_q), 131.4 (C_q), 128.4 (Ar*H*), 127.8 (C_q), 127.7 (Ar*H*), 125.3 (C_q), 122.9 (Ar*H*), 122.7 (Ar*H*), 121.1 (Ar*H*), 119.7 (C_q), 119.2 (Ar*H*), 116.3 (Ar*H*), 112.4 (Ar*H*), 31.5 (C*H*CH_3), 20.4 (CH_3).

GC MS (EI) *m/z* (%): 271 (68, M^+), 256 (99), 220 (23), 165 (12), 151 (100), 115 (10), 91 (15).

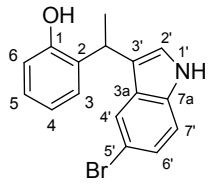
HRMS (EI) m/z (%): calculated for $C_{16}H_{14}ClNO$ $[M-H]^-$ 270.0691; found 270.0693.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3417 (m, OH), 1589 (w), 1451 (m), 1327 (w), 1217 (m), 1097 (m), 906 (m), 838 (w), 796 (s), 751 (s), 728 (s), 584 (m).


OH
NH
Cl
3ab
f1 (ppm)


OH
NH
Cl
3ab
f1 (ppm)

2-(1-(5-Bromo-1H-indol-3-yl)ethyl)phenol (3ac)



The compound **3ac** was prepared according to a modified general procedure for hydroarylation from 2-vinylphenol (60 mg, 500 µmol), 5-bromoindole (108 mg, 550 µmol) and diphenyl phosphate (12.6 mg, 60 µmol) in DCE at 100 °C. The product was purified by column chromatography (silica, *n*-pentane/Et_2O 7:1-5:1). The title compound was obtained as colorless solid (82 mg, 52%).

$C_{16}H_{14}BrNO$ (316.20 g/mol)

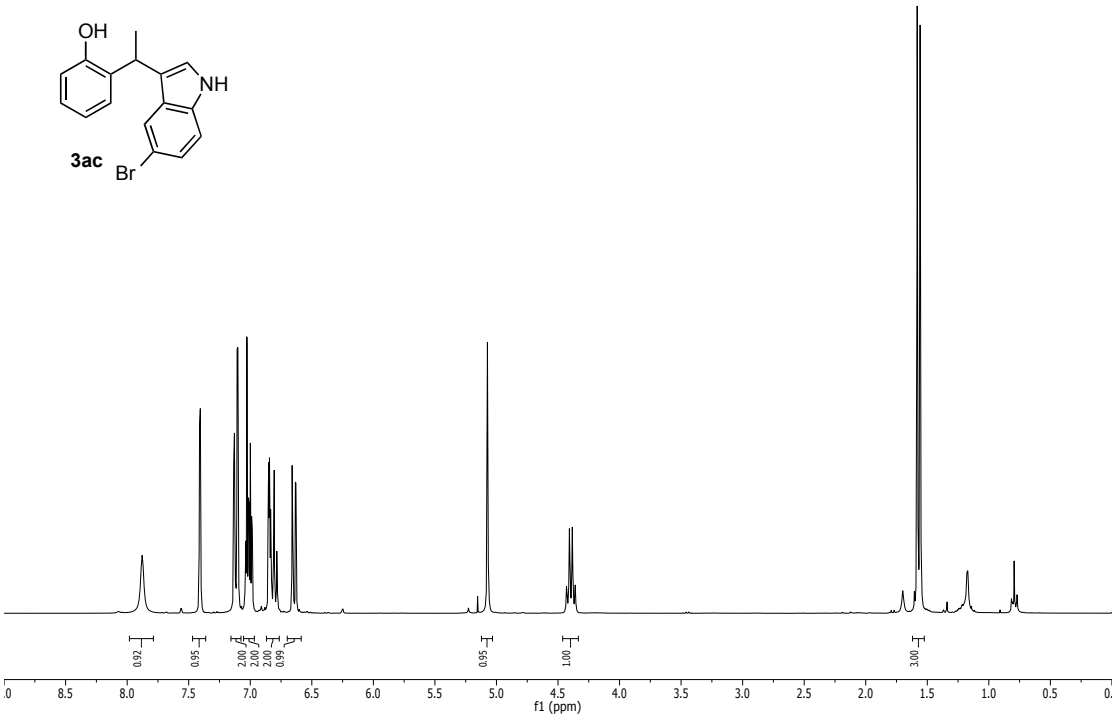
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.03 (s, 1H, N*H*), 7.38 (ddd, *J* = 1.9, 0.6 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (dd, *J* = 8.6, 0.6 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.03 (dd, *J* = 2.4, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.19 (s, 1H, O*H*), 4.53 (q, *J* = 7.1 Hz, 1H, C*H*), 1.72 (d, *J* = 7.1 Hz, 3H, CH_3).

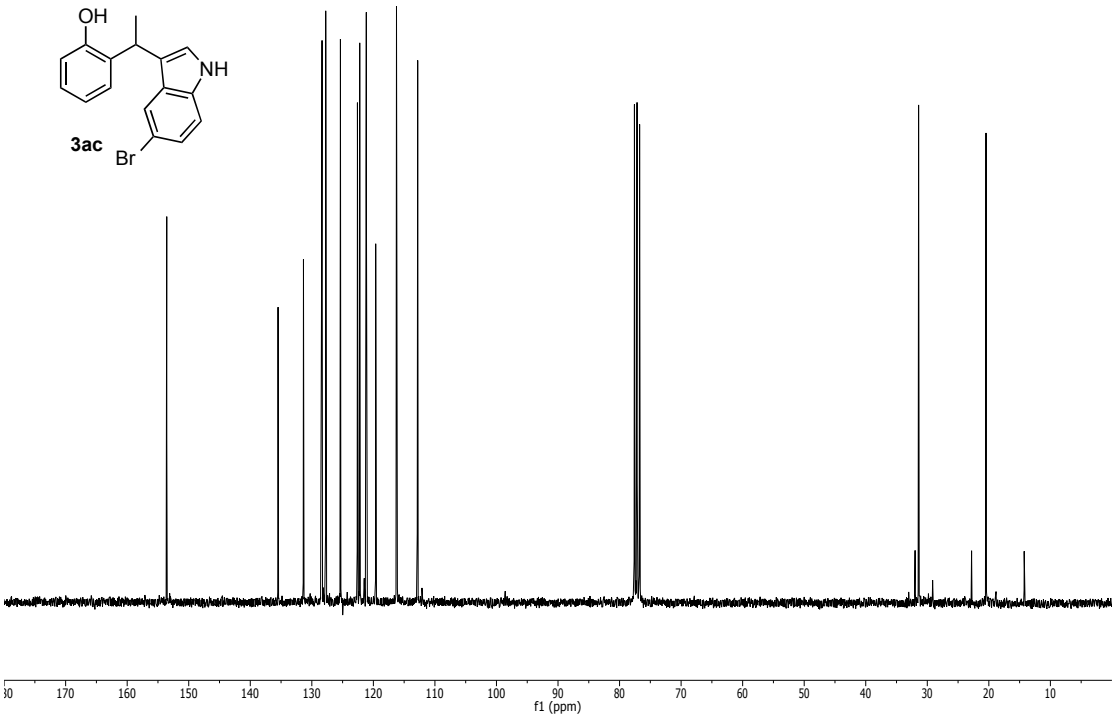
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 153.6 (C_q), 135.3 (C_q), 131.4 (C_q), 128.4 (Ar*H*), 127.8 (C_q), 127.7 (Ar*H*), 125.3 (C_q), 122.9 (Ar*H*), 122.7 (Ar*H*), 121.1 (Ar*H*), 119.7 (C_q), 119.2 (Ar*H*), 116.3 (Ar*H*), 112.4 (Ar*H*), 31.5 (C*H*CH_3), 20.4 (CH_3).

GC MS (EI) *m/z* (%): 315 (71, M^+), 300 (93), 220 (69), 197 (100), 165 (18), 143 (12), 116 (27), 91 (24).

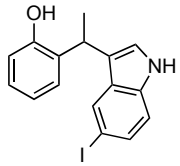
HRMS (EI) m/z (%): calculated for $C_{16}H_{14}BrNO$ $[M+H]^+$ 316.0332; found 316.0327.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3418 (m, OH), 1590 (w), 1453 (s), 1327 (w), 1220 (m), 1097 (m), 796 (m), 753 (s).


OH
NH
Br
3ac
0.92
0.95
2.00
2.00
2.00
0.99
0.95
1.00
3.00
f1 (ppm)


OH
NH
Br
3ac
f1 (ppm)

2-(1-(5-Iodo-1H-indol-3-yl)ethyl)phenol (3ad)



The compound **3ad** was prepared according to a modified general procedure for hydroarylation from 2-vinylphenol (60 mg, 500 µmol), 5-iodoindole (133.8 mg, 550 µmol) and diphenyl phosphate (12.6 mg, 60 µmol) in DCE at 100 °C. The product was purified by column chromatography (silica, *n*-pentane/Et_2O 7:1-5:1). The title compound was obtained as reddish oil (105 mg, 58%).

$C_{16}H_{14}INO$ (363.20 g/mol)

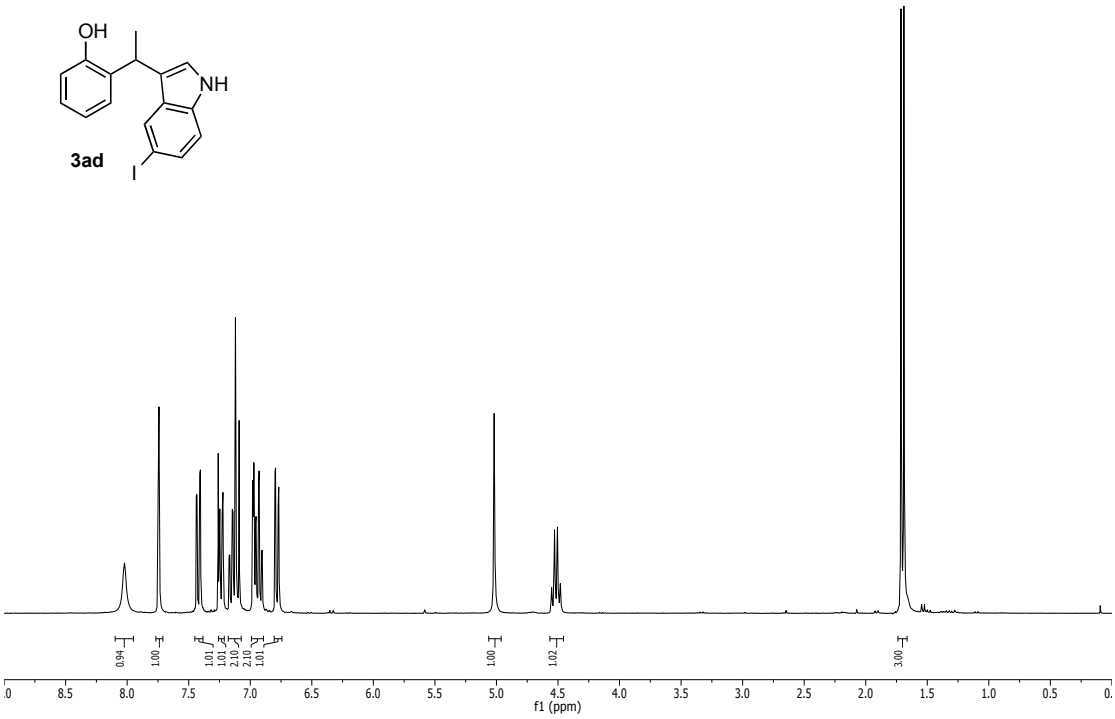
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.03 (s, 1H, N*H*), 7.38 (ddd, *J* = 1.9, 0.6 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (dd, *J* = 8.6, 0.6 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.03 (dd, *J* = 2.4, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.19 (s, 1H, O*H*), 4.53 (q, *J* = 7.1 Hz, 1H, C*H*), 1.72 (d, *J* = 7.1 Hz, 3H, CH_3).

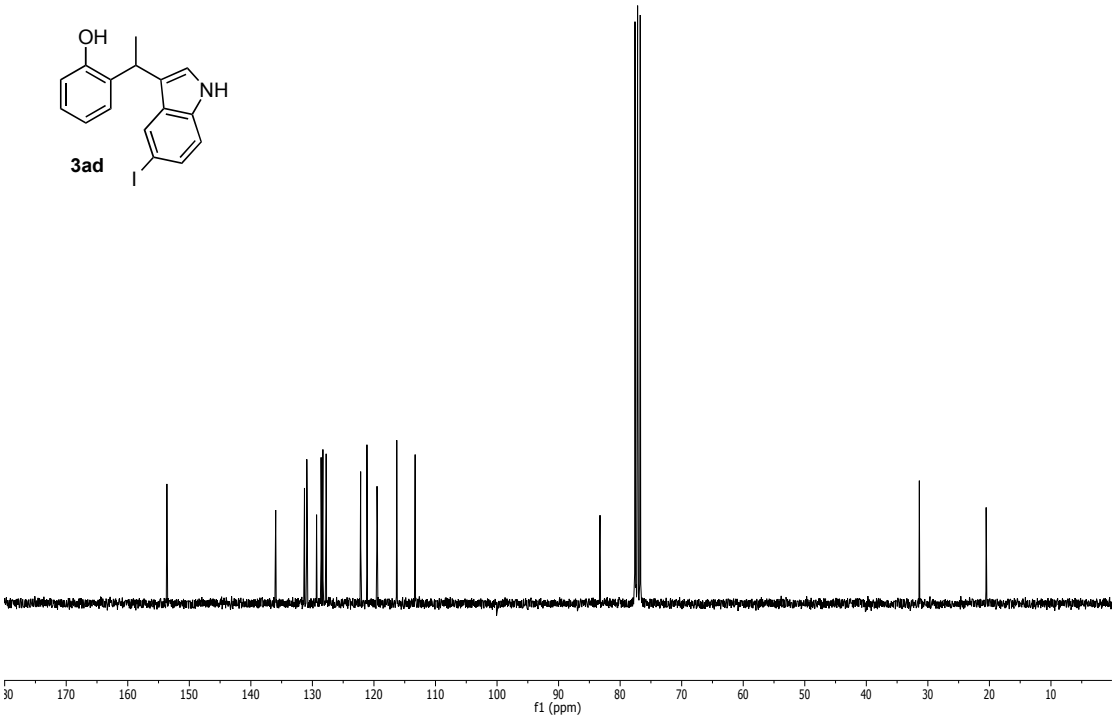
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 153.6 (C_q), 135.3 (C_q), 131.4 (C_q), 128.4 (Ar*H*), 127.8 (C_q), 127.7 (Ar*H*), 125.3 (C_q), 122.9 (Ar*H*), 122.7 (Ar*H*), 121.1 (Ar*H*), 119.7 (C_q), 119.2 (Ar*H*), 116.3 (Ar*H*), 112.4 (Ar*H*), 31.5 (C*H*CH_3), 20.4 (CH_3).

GC MS (EI) *m/z* (%): 315 (71, M^+), 300 (93), 220 (69), 197 (100), 165 (18), 143 (12), 116 (27), 91 (24).

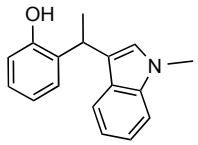
HRMS (EI) m/z (%): calculated for $C_{16}H_{14}INO$ $[M+H]^+$ 316.0332; found 316.0327.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3418 (m, OH), 1590 (w), 1453 (s), 1327 (w), 1220 (m), 1097 (m), 796 (m), 753 (s).


OH
NH
I
3ad
0.94
1.00
1.01
1.01
2.10
2.10
1.01
1.00
1.02
3.00
f1 (ppm)


OH
NH
I
3ad
f1 (ppm)

2-(1-(1-Methyl-1H-indol-3-yl)ethyl)phenol (3ae)



The compound **3ea** was prepared according to the general procedure for hydroarylation from 2-vinylphenol (60.1 mg, 500 µmol), 1-methylindole (72.1 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 95:5) and obtained as yellow oil (101 mg, 80%). The analytical data were in accordance with the literature.[3]

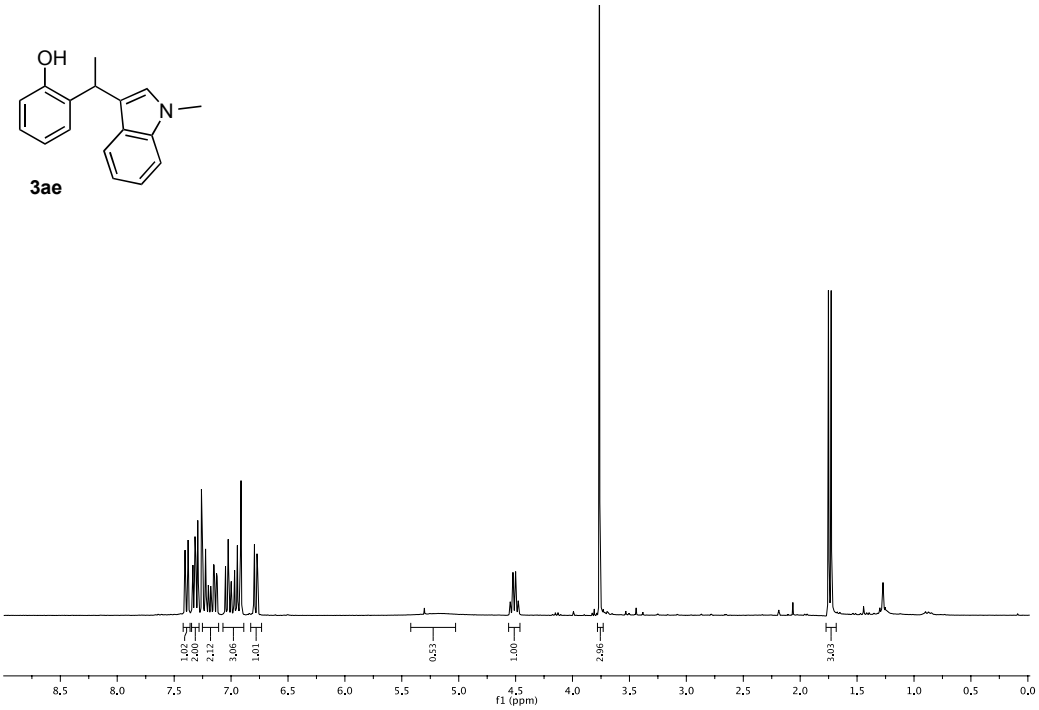
$C_{17}H_{17}NO$ (251.33 g/mol)

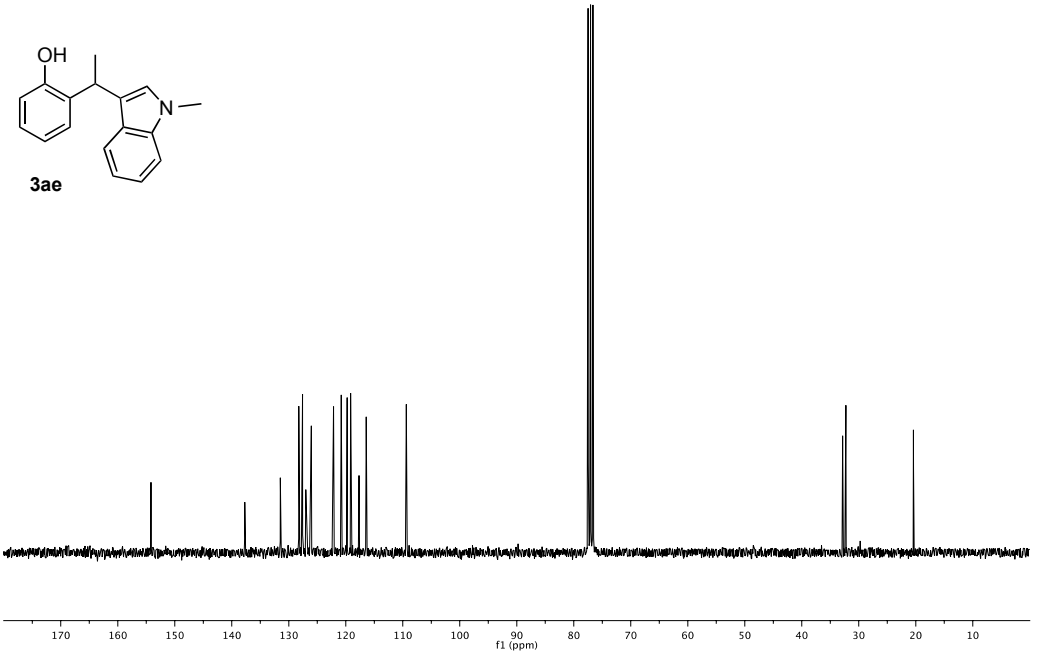
$\boldsymbol{R_f}$ = 0.32 (silica, EA/heptane 1:4).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.41 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.9 Hz, $^5J_{HH}$ = 1.0 Hz, 1H), 7.34-7.29 (m, 2H), 7.25-7.12 (m, 2H), 7.05-6.91 (m, 3H), 6.82 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 5.20 (br. S, 1H, OH), 4.51 (q, $^3J_{HH}$ = 7.1 Hz, 1H, C*H*CH_3), 3.76 (s, 3H, C*H*$_3$), 1.74 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CHC*H*$_3$).

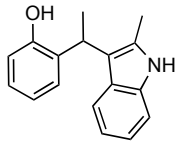
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 154.2 (C_q), 137.7 (C_q), 131.5 (C_q), 128.2 (*Ar*H), 127.6 (*Ar*H), 127.0 (C_q), 126.0 (*Ar*H), 122.2 (*Ar*H), 120.8 (*Ar*H), 119.8 (*Ar*H), 119.1 (*Ar*H), 117.7 (C_q), 116.4 (*Ar*H), 109.4 (*Ar*H), 32.8 (*C*H_3), 32.3 (*C*HCH_3), 20.4 (CH*C*H_3).

GC MS (EI) *m/z* (%): 251 (91, M^+), 236 (83, $[M\text{-}CH_3]^+$), 220 (22), 165 (25), 131 (100, $C_9H_{10}N^+$), 91 (51, $C_7H_7^+$), 77 (33, $C_6H_5^+$), 63 (24), 51 (21).


OH
N
3ae
1.02
2.00
2.12
3.06
1.01
0.53
1.00
2.96
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
N
3ae
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2-(1-(2-Methyl-1H-indol-3-yl)ethyl)phenol (3af)



The compound **3af** was prepared according to the general procedure for hydroarylation from 2-vinylphenol (60.1 mg, 500 µmol), 2-methylindole (72.1 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10) and obtained as orange oil (87 mg, 69%). The analytical data were in accordance with the literature.[3]

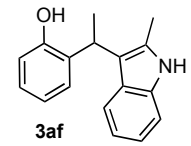
$C_{17}H_{17}NO$ (251.33 g/mol)

$\boldsymbol{R_f}$ = 0.23 (silica, EA/heptane 1:4).

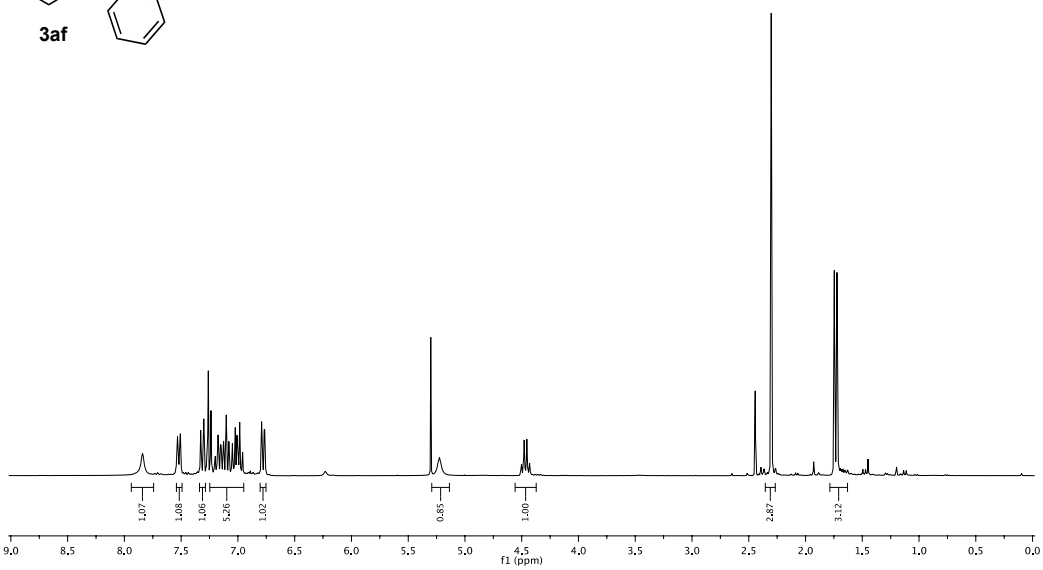
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.88 (br.s, 1H, N*H*), 7.56 (dd, $^3J_{HH}$ = 7.7 Hz, 1H), 7.35 (dd, $^3J_{HH}$ = 8.0 Hz, 1H), 7.30-7.00 (m, 5H), 6.81 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 5.26 (br. S, 1H, OH), 4.51 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*CH_3), 2.34 (s, 3H, CH_3), 1.77 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CHCH_3).

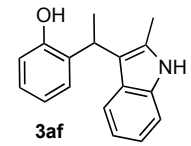
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 154.7 (C_q), 135.5 (C_q), 131.6 (C_q), 130.8 (C_q), 127.6 (*Ar*H), 127.1 (C_q), 126.9 (*Ar*H), 121.5 (*Ar*H), 120.6 (*Ar*H), 119.6 (*Ar*H), 118.7 (*Ar*H), 116.2 (*Ar*H), 112.7 (C_q), 110.5 (*Ar*H), 30.4 (*C*HCH_3), 19.7 ($CHCH_3$), 12.0 (*C*H_3).

GC MS (EI) *m/z* (%): 251 (49, M^+), 236 (60, $[M\text{-}CH_3]^+$), 165 (9), 131 (100, $C_9H_{10}N^+$), 91 (21, $C_7H_7^+$), 77 (15, $C_6H_5^+$), 63 (12), 51 (10).


OH
NH

3af

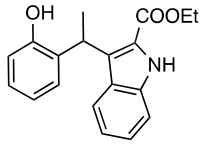

1.07
1.08
1.06
5.26
1.02
0.85
1.00
2.87
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
NH

3af

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 3-(1-(2-hydroxyphenyl)ethyl)-1*H*-indole-2-carboxylate (3ag)



The compound **3ag** was prepared according to the general procedure for hydroarylation from 2-vinylphenol (60.1 mg, 500 µmol), ethyl 1*H*-indole-2-carboxylate (104.1 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10) and obtained as orange oil (111 mg, 72%). The analytical data were in accordance with the literature.[3]

$C_{19}H_{19}NO_3$ (309.37 g/mol)

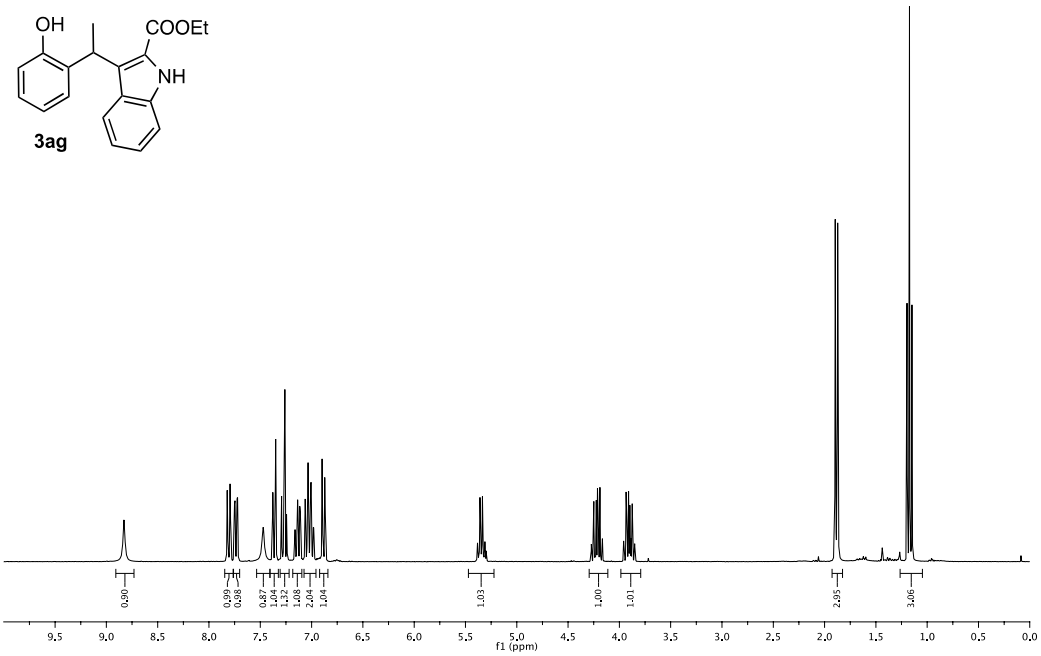
R_f = 0.20 (silica, EA/heptane 1:4).

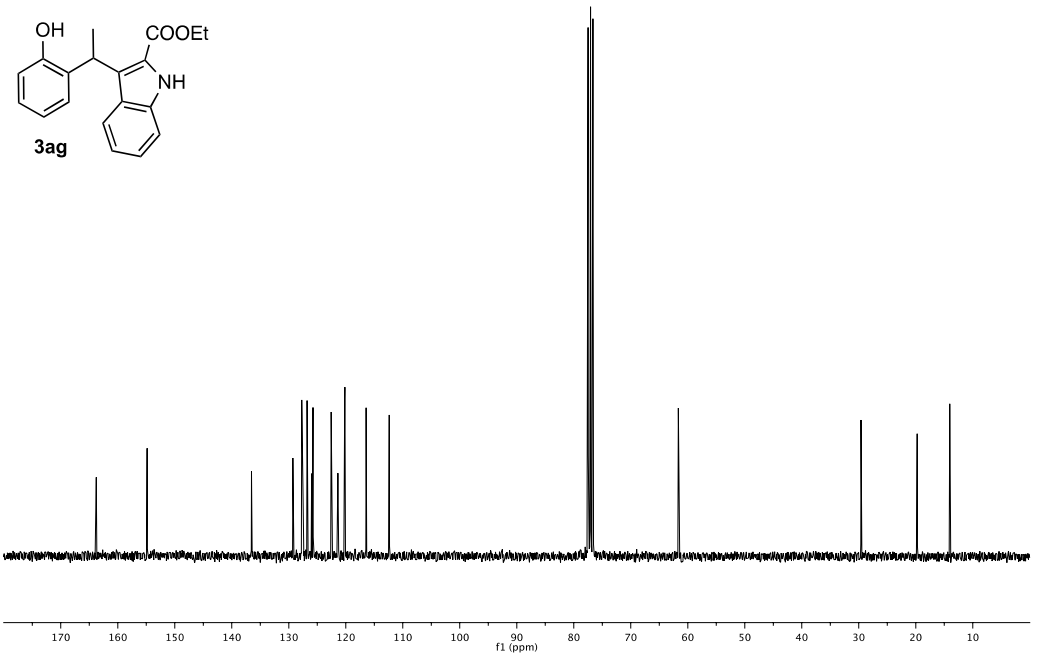
M.p.: 133-135°C

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.87 (br. S, H, NH), 7.84 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H), 7.77 (dd, $^3J_{HH}$ = 7.70 Hz, $^4J_{HH}$ = 1.6Hz, 1H), 7.51 (br. s, 1H, OH), 7.40 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 and 0.9 Hz, 1H), 7.33-7.28 (m, 1H), 7.18 (ddd, $^3J_{HH}$ = 7.6 and 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 7.11-7.02 (m, 2H), 6.92 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 5.39 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*CH_3), 4.27 and 3.95 (ABX, 2H, C*H*$_2CH_3$), 1.92 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CHC*H*$_3$), 1.21 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_2C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 163.8 (*C*OOEt), 154.9 (C_q), 136.5 (C_q), 129.3 (C_q), 127.7 (*Ar*H), 127.5 (C_q), 126.8 (*Ar*H), 126.0 (C_q), 125.7 (*Ar*H), 122.6 (*Ar*H), 121.4 (C_q), 120.19 (*Ar*H), 120.16 (*Ar*H), 116.4 (*Ar*H), 112.4 (*Ar*H), 61.7 (*C*H_2CH_3), 29.6 (*C*HCH_3), 19.7 (*C*H_3), 14.0 (*C*H_3).

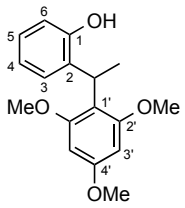
GC MS (EI) *m/z* (%): 263 (51, $[M\text{-}OEt]^+$), 248 (100, $[M\text{-}OEt\text{-}OH]^+$), 220 (62, $[M\text{-}COOEt\text{-}OH]^+$), 204 (9), 191 (15), 165 (19), 115 (6, $C_8H_5N^+$), 89 (6), 77 (6, $C_6H_5^+$), 63 (10), 51 (7).


OH
COOEt
NH
3ag
0.30
0.09
0.28
0.87
1.04
1.22
1.08
2.04
1.04
1.03
1.00
1.01
2.95
3.06
f1 (ppm)


OH
COOEt
NH
3ag
f1 (ppm)

2-(1-(2,4,6-Trimethoxyphenyl)ethyl)phenol (6aa)

The compound **6aa** was prepared according to the general procedure for hydroarylation from 2-vinylphenol (60.1 mg, 500 µmol), 1,3,5-trimethoxyphenol (92.5 mg, 550 µmol) and diphenyl phosphate (6.2 mg, 25 µmol). The product was purified by column chromatography (silica, heptane/ethyl acetate 95:5-90:10) and obtained as yellow solid (82 mg, 57%).



$C_{17}H_{20}O_4$ (288.34 g/mol)

$\boldsymbol{R_f}$ = 0.24 (silica, EA/heptane 1:4).

M.p.: 114-115°C

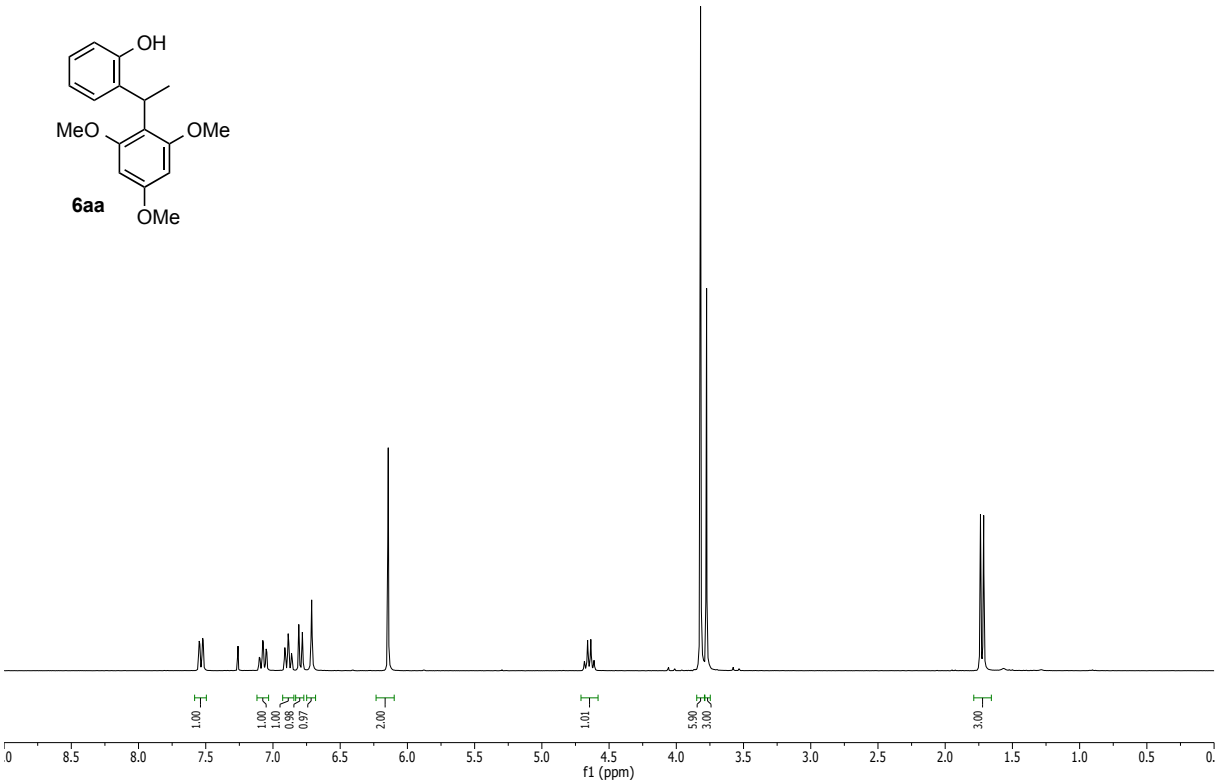
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.53 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 3-*H*), 7.08 (ddd, $^3J_{HH}$ = 8.0 and 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 5-*H*), 6.88 (ddd, $^3J_{HH}$ = 7.7 and 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 4-*H*), 6.79 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 6-*H*), 6.71 (s, 1H, OH), 6.14 (s, 2H, 3'-*H*), 4.65 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*CH_3), 3.82 (s, 6H, 2'-OCH_3), 3.77 (s, 3H, 4'-OCH_3), 1.73 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CHCH_3).

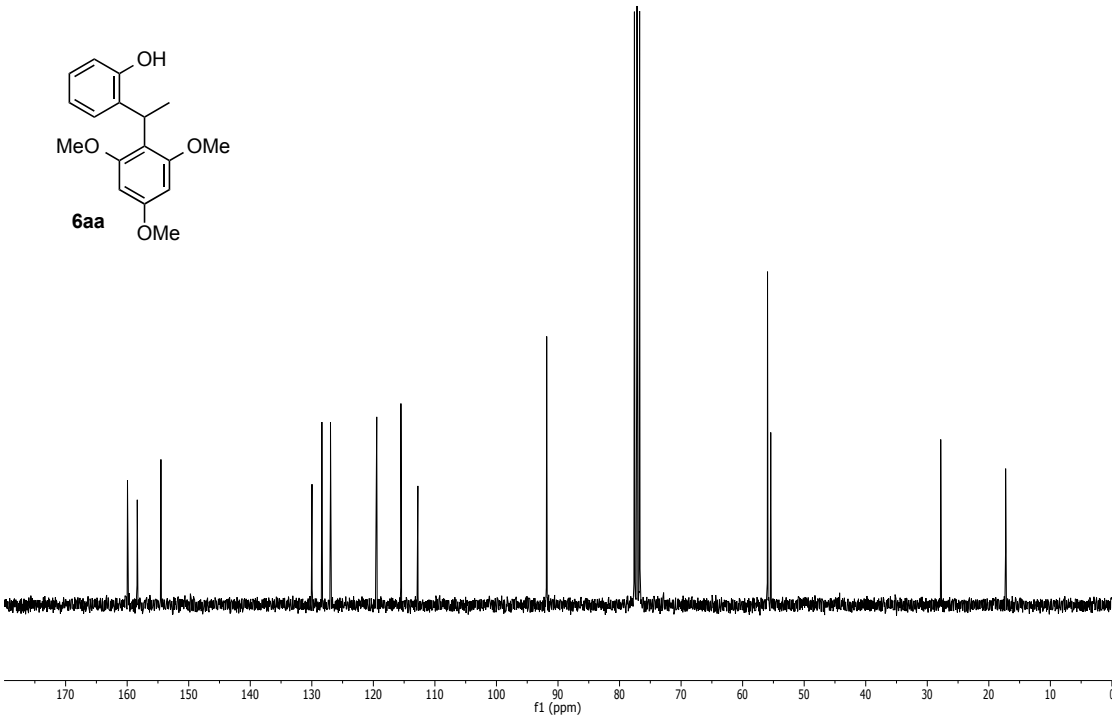
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 160.0 (*C*-2'), 158.4 (*C*-4'), 154.5 (*C*-1), 130.0 (*C*-2), 128.4 (*C*-3), 127.0 (*C*-5), 119.5 (*C*-4), 115.5 (*C*-6), 112.8 (*C*-1'), 91.8 (*C*-3'), 56.0 (2'-OCH_3), 55.4 (4'-OCH_3), 27.8 (*C*HCH_3), 17.3 (*C*H_3).

GC MS (EI) *m/z* (%): 288 (24, M^+), 204 (5), 168 (100, $C_9H_{12}O_3^+$), 139 (21), 121 (5), 107 (4), 91 (7, $C_7H_7^+$), 77 (5, $C_6H_5^+$), 51 (2), 39 (2).

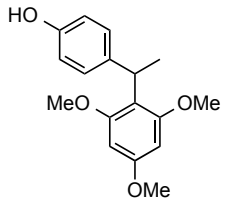
HRMS (EI) m/z (%): calculated for $C_{17}H_{21}O_4$ $[M+H]^+$ 289.14344; found 289.14345.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3410m (OH), 3003w, 2943w, 2844w, 1606m, 1586s, 1485m, 1463m, 1420m, 1350w, 1317w, 1230m, 1204s, 1147s, 1114s, 1098s, 1027m, 945m, 820m, 807m, 759s, 632m.


OH
MeO
OMe
OMe
6aa
1.00
1.00
1.00
0.98
0.97
2.00
1.01
5.90
3.00
3.00
f1 (ppm)


OH
MeO
OMe
OMe
6aa
f1 (ppm)

4-(1-(2,4,6-Trimethoxyphenyl)ethyl)phenol (6ca)



The compound **6ca** was prepared according to a modified general procedure for hydroarylation from freshly prepared 4-vinylphenol (601 mg, 5.00 mmol), 1,3,5-trimethoxyphenol (1.68 g, 10.0 mmol) and diphenyl phosphate (62.1 mg, 250 µmol) at 100 °C in DCE. The product was purified by column chromatography (silica, heptane/ethyl acetate 90:10-80:20) and obtained as colorless solid (1.31 g, 91%).

$C_{17}H_{20}O_4$ (288.34 g/mol)

$\boldsymbol{R_f}$ = 0.12 (silica, EA/heptane 1:4).

M.p.: 116-117°C

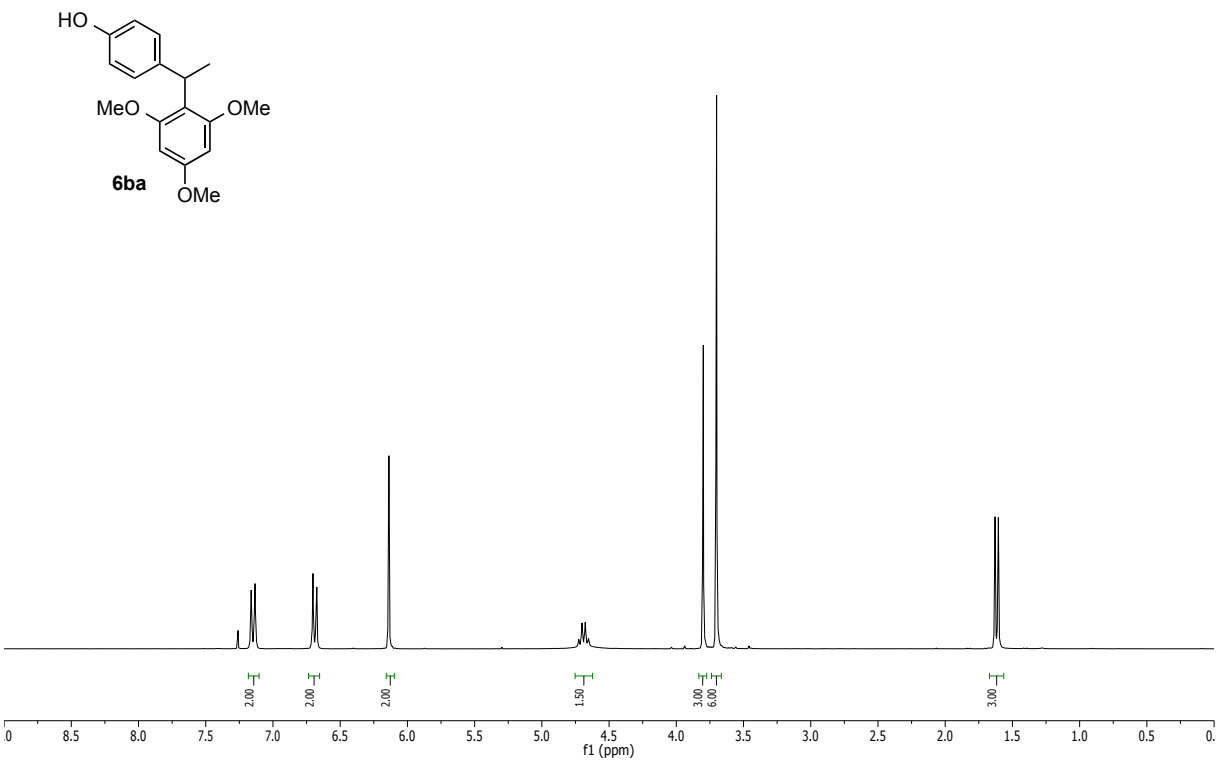
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.15 (d, $^3J_{HH}$ = 8.6 Hz, 2H, 3-*H*), 6.69 (d, $^3J_{HH}$ = 8.6 Hz, 2H, 2-*H*), 6.14 (s, 2H, 3'-*H*), 4.69 (q and br. s, $^3J_{HH}$ = 7.3 Hz, 2H, O*H*, C*H*CH_3), 3.80 (s, 3H, 4'-OC*H*$_3$), 3.70 (s, 6H, 2'-OC*H*$_3$), 1.62 (d, $^3J_{HH}$ = 7.3 Hz, 3H, CHC*H*$_3$).

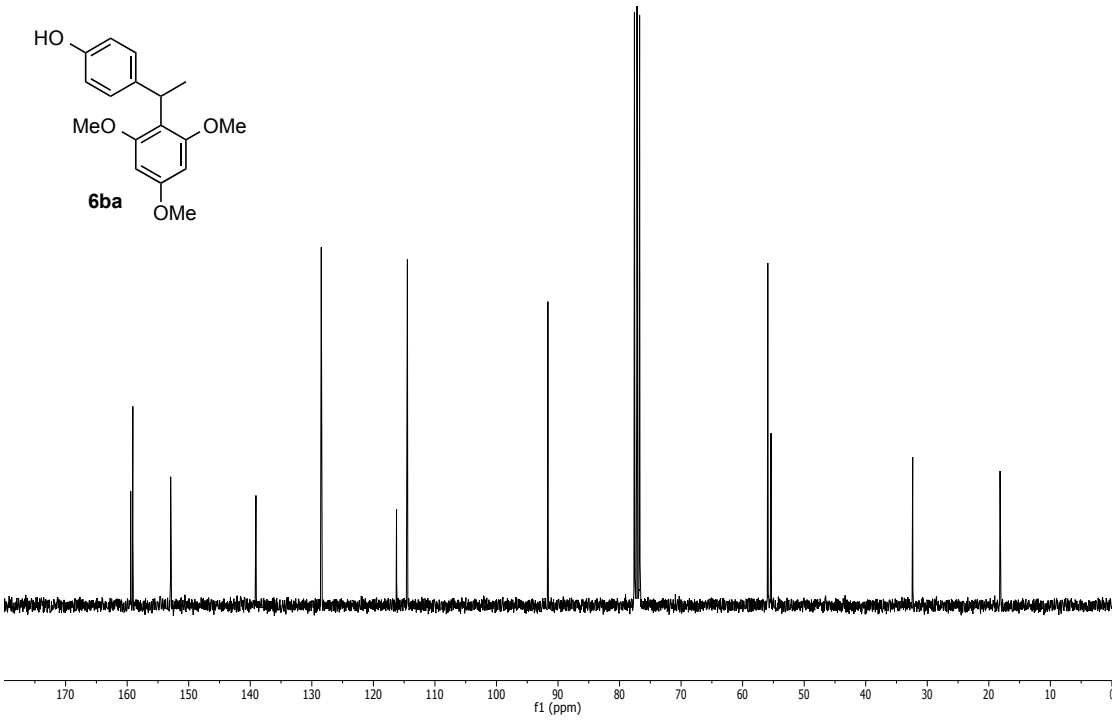
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 159.4 (*C*-4'), 159.1 (*C*-2'), 152.9 (*C*-1), 139.1 (*C*-4), 128.5 (*C*-3), 116.2 (*C*-1'), 114.5 (*C*-2), 91.6 (*C*-3'), 55.9 (2'-O*C*H_3), 55.4 (4'-O*C*H_3), 32.4 (*C*HCH_3), 18.2 (*C*H_3).

GC MS (EI) *m/z* (%): 288 (41, M^+), 273 (100, $[M\text{-}CH_3]^+$), 167 (100, $C_9H_{11}O_3^+$), 137 (6), 107 (15), 91 (5, $C_7H_7^+$), 77 (5, $C_6H_5^+$).

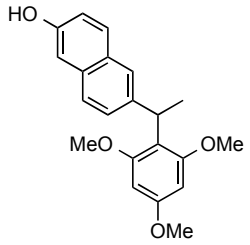
HRMS (EI) m/z (%): calculated for $C_{17}H_{21}O_4$ $[M+H]^+$ 289.14344; found 289.14318.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3372m (OH), 2998w, 2938m, 2837w, 1585m, 1511m, 1489w, 1455m, 1410m, 1350w, 1256w, 1219m, 1198m, 1122s, 1063m, 1037m, 939m, 835m, 801m, 778m, 629m.


HO
MeO
OMe
OMe
6ba
2.00
2.00
2.00
1.50
3.00
6.00
3.00
f1 (ppm)


HO
MeO
OMe
OMe
6ba
f1 (ppm)

6-(1-(2,4,6-Trimethoxyphenyl)ethyl)naphthalen-2-ol (6da)



The compound **6da** was prepared according to the modified general procedure for hydroarylation from 6-vinylnaphthalyl-2-ol (85.1 mg, 500 µmol), 1,3,5-trimethoxyphenol (168 mg, 1.00 mmol) and diphenyl phosphate (12.4 mg, 50 µmol, 10 mol%) at 100 °C in DCE. The product was purified by column chromatography (silica, *n*-pentane/ethyl acetate 5:1-4:1) and obtained as colorless solid (102 mg, 60%).

$C_{21}H_{22}O_4$ (338.40 g/mol)

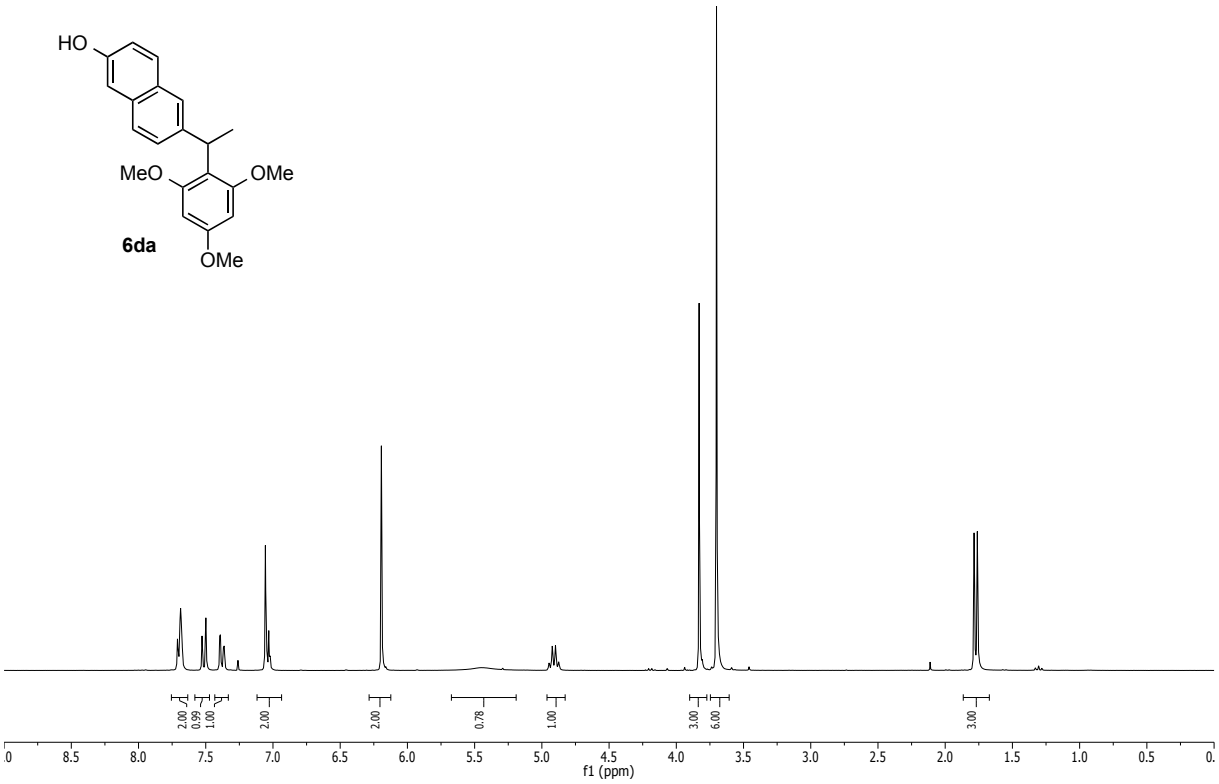
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.76 – 7.63 (m, 2H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.09 – 6.99 (m, 2H), 6.19 (s, 2H), 5.44 (s, 1H), 4.91 (q, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 6H), 1.77 (d, *J* = 7.2 Hz, 3H).

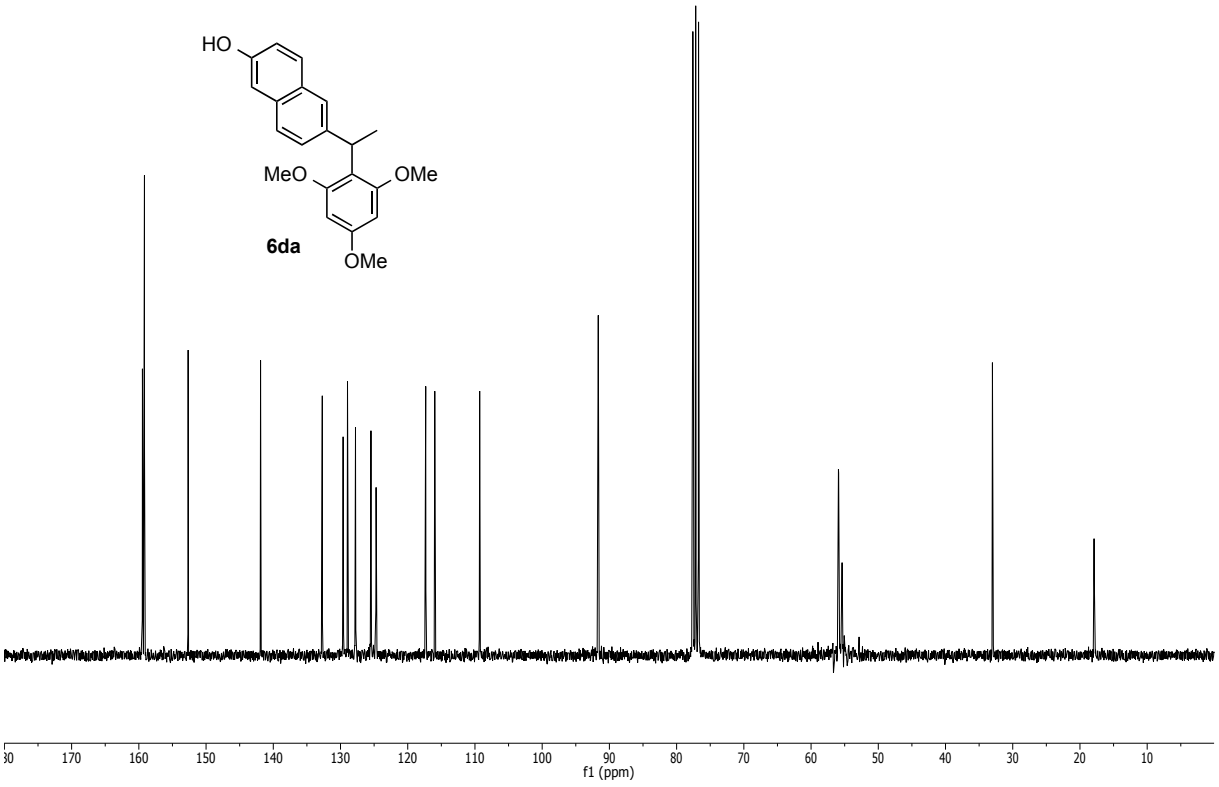
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 159.5 (C_q), 159.2 (C_q), 152.7 (C_q), 141.9 (C_q), 132.7 (C_q), 129.6 (CH), 129.0 (C_q), 127.8 (CH), 125.5 (CH), 124.7 (CH), 117.3 (CH), 116.0 (C_q), 109.3 (CH), 91.7 (CH), 55.9 (OCH_3), 55.4 (OCH_3), 33.0 (CH), 17.9 (CH_3).

GC MS (EI) *m/z* (%): 338 (53, M^+), 323 (100, $[M\text{-}CH_3]^+$), 307 (6), 195 (5), 167 (21), 157 (37), 115 (4).

HRMS (EI) m/z (%): calculated for $C_{21}H_{23}O_4$ $[M+H]^+$ 338.1512; found 338.1509.

IR (ATR) $\tilde{\nu}$/cm^{-1}: 3341m (OH), 2963w, 2936m, 2834w, 1588m, 1435m, 1197w, 1117m, 1031m, 938w, 891w, 587m, 822m, 659m, 606w, 469s.


HO
MeO
OMe
OMe
6da
2.00
0.99
1.00
2.00
2.00
0.78
1.00
3.00
6.00
3.00
f1 (ppm)


HO
MeO
OMe
OMe
6da
f1 (ppm)

[1] *Purification of Laboratory Chemicals* (Eds: Perrin, D. D.; Armarego, W. L. F.). Pergamon Press, Oxford, 1988 (3).

[2] Konishi, H.; Ueda, T.; Muto, T.; Manabe, K. *Org. Lett.* **2012**, *14*, 4722-4725.

[3] Pathak, T. P.; Sigman, M. S. *Org. Lett.* **2011**, *13*, 2774-2777.

[4] Pearson, E. L.; L. C. H. Kwan, C. I. Turner, G. A. Jones, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *J. Org. Chem.* **2006**, *71*, 6099-6109.

[5] L. Pérez-Serrano, J. Blanco-Urgoiti, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *J. Org. Chem.* **2000**, *65*, 3513-3519.