Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Titanium-catalysed deoxygenation of benzylic alcohols and lignin model compounds

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1 General Information

1.1 Chemicals and General Techniques

Bis(cyclopentadienyl)titanium(IV) dichloride, was supplied by Sigma-Aldrich and was stored in the Glovebox (GS MEGA E-Line, Glovebox Systemtechnik). Mn dust (Mash 325) was obtained from Alfa Aesar and stored in the Glovebox. The silanes were supplied by Acros, Sigma-Aldrich and Alfa Aesar and stored under Ar in Schlenk tubes. The alcohols, aldehydes, ketones and all other chemicals used in the optimization and substrates screening were purchased from TCI, Sigma-Aldrich, BLD Pharm, Fluorochem, Alfa Aesar and ABCR and used without any further purification. The dry (either distilled or purchased) and degassed solvents were stored under Ar over Molecular Sieves (3Å). All catalytical reactions were carried out under Ar atmosphere in under vacuum flame-dried Schlenk pressure tubes (maxiumum pressure 5 bar).

1.2 Chromatography and Analytical Techniques

Column chromatography and TLC

Column chromatography was carried out manually using gravity flow under isocratic conditions. All the solvents used for chromatography were distilled prior to use. The silica gel (0.04–0.063 mm) was purchased from Machery&Nagel.

Thin-Layer Chromatography (TLC) was performed aluminum plates coated with silica gel 60 F254 (layer thickness: 0.2 mm) and analyzed under UV-light (254 nm).

Gas chromatography (GC)

GC-FID analysis was carried out on an Agilent 7820A system with G4567A injector by using dry hydrogen as carrier gas and an Agilent 19091J-431 column (30 m, 320 µm, 0.25 µm). Two programs were used: heating from 50 °C to 280 °C with a 20 °C/min heating rate (**M_{FID}1**) and heating from 35 °C to 280 °C with a 10 °C/min heating rate (**M_{FID}2**).

The internal standard used for quantitative GC was *n*-pentadecane. The samples for the calibration lines used for determining the GC- yields were prepared by using defined amounts of substrate and internal standard. The obtained data was used to plot the ration of peak areas against the mass ratio and resulting slope, which is equivalent to the response factor (R), was used to quantify unknown samples by using following equation. y-Intercepts are not considered.

$$\frac{m(substrate)}{m(standard)} \times R = \frac{A(substrate)}{A(standard)}$$

GC-MS analysis was performed on an Agilent 7820A GC-system with G4513A injector coupled with an Agilent 5977B MSD by using hydrogen as carrier gas (Method: Heating from 50 °C to 280 °C with a 20 °C/min heating rate - **M_{MS}1**), an Agilent 8890 GC-system with G4513A injector coupled with an Agilent 5977B MSD by using helium as carrier gas (Method: Heating from 40 °C to 300 °C with a 10 °C/min heating rate – **M_{MS}2**) and Agilent 7820A GC-system with G4513A injector coupled with an Agilent 5977B MSD by using hydrogen as carrier gas (Method: Heating from 35 °C to 280 °C with a 10 °C/min heating rate - **M_{MS}3**).

For the identification of volatile compounds (SI, section 5.2) the obtained GC-MS chromatograms (Red) were compared with the existing chromatograms in NIST GC-MS Database (Blue). As a quality parameter Match Factor (MF) and Reverse Match Factor were considered (900 or greater - excellent match; 800–900 - a good match; 700–800 - fair match. Less then 600 - very poor match.)[1]

Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were recorder using a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C:101 MHz) or Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz). All NMR measurements were performed at ambient temperature. Chemical shifts (δ) are reported in ppm (parts per million) relative to the residual NMR solvent signals (^{1}H: $CDCl_3$: d = 7.26 ppm, ^{13}C: $CDCl_3$: d = 77.16). Coupling constants *J* are reported in Hz (Hertz) and the splitting patters in ^{1}H NMR spectra are described as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Infrared spectroscopy

FT-IR spectra were recorded using an Agilent Cary 630 FTIR.

2 General Procedures

GP1. Reduction of aldehydes and ketones to benzylic alcohols

The benzylic alcohols were synthesized by reduction with $NaBH_4$ following a modified literature procedure.[2] In a 100 mL round bottom flask the respective aldehyde or ketone (5.00 mmol, 1 equiv.) was dissolved in methanol (10 mL) and cooled in an ice bath. Then, $NaBH_4$ (10.0 mmol, 2 equiv.) was added in portions. After the addition, the solution was allowed to warm to ambient temperature and was stirred until the completion of the reaction was confirmed by TLC. The solution was cooled in an ice bath and quenched with ice and water. Then, methanol was removed under reduced pressure and the mixture was extracted with DCM (3 × 10 mL). The collected organic phases were washed with brine (3 × 10 mL), dried over Na_2SO_4 and filtered. The solvent was evaporated, and the respective alcohol was obtained and used without further purification except if otherwise stated.

GP2. Deoxygenation of benzylic alcohols

A flame-dried Schlenk-tube equipped with a stirring bar was charged in the glovebox with Cp_2TiCl_2 (24.9 mg, 0.100 mmol, 0.1 equiv.) and Mn (54.9 mg, 1.00 mmol, 1 equiv.). Then, the vessel was taken out of the glovebox and the benzylic alcohol (1.00 mmol, 1 equiv.) was added to the mixture. The components were dissolved in 2 mL 2-MeTHF and stirred at 50 °C for 2.5 h. Diethoxymethylsilane (0.480 mL, 3.00 mmol, 3 equiv.) was added and the reaction was heated to 100 °C and stirred for 16h. After the completion of the reaction the mixture was cooled to 0 °C and quenched with Lewatit.

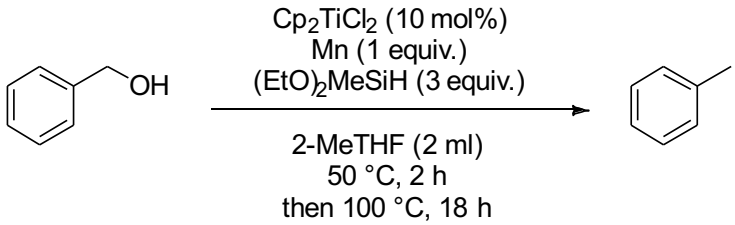
For NMR analysis: 1M HCl (5 ml) was added to the crude mixture and stirred for 24 h. Then, the reaction was extracted with DCM or EtOAc (3 × 10 mL) and the collected organic phases were washed with brine (3 × 10 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the crude product was purified by column chromatography (Solvent mixture stated for every reaction).

For GC-FID and GC-MS analysis: A 0.10 mL sample from the crude reaction mixture was diluted with DCM and passed through a Celite, Alumina and $MgSO_4$ column. For analysis *via* GC-FID, *n*-pentadecane was used as internal standard.

3 Optimization of the Catalytic Reaction

3.1 Control reactions

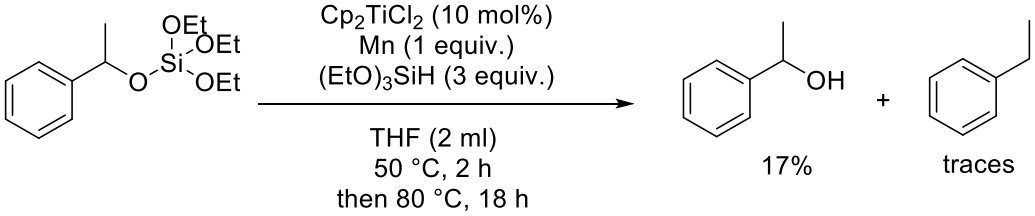
Table S1. Control reactions



Entry[a]	Deviation	Yield (%)[b]
1	Without $HSiMe(OEt)_2$	-
2	Without Cp_2TiCl_2	-
3	Without Mn	3

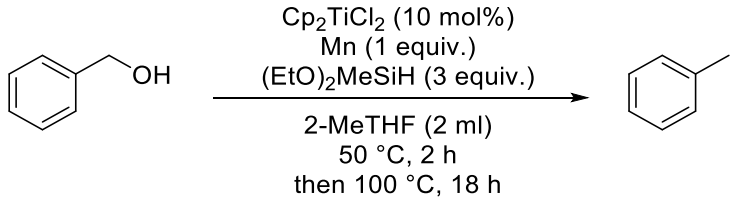
[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

Conversion of silyl ether:



3.2 Optimization Reactions

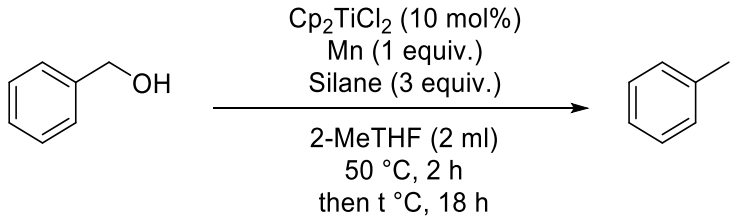
Table S2. General optimization



Entry[a]	Deviation	Yield (%)[b]
1	1.5 equiv. Mn	65
2	Zn instead of Mn	52
3	No activation	63
4	No further pressure release after silane addition	96
5	2 h activation at RT	25
6	4 h activation at 50°C	43
7	2.2 equiv. $HSiMe(OEt)_2$	53
8	4 equiv. $HSiMe(OEt)_2$	62

[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

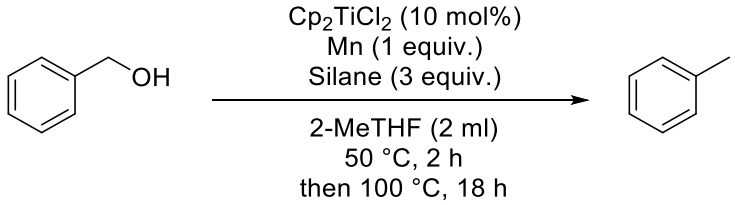
Table S3. Temperature screening



Entry[a]	Temperature (°C)	Yield (%)[b]
1	50	-
2	60	-
3	70	18
4	80	82
5	100	96

[a] Reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

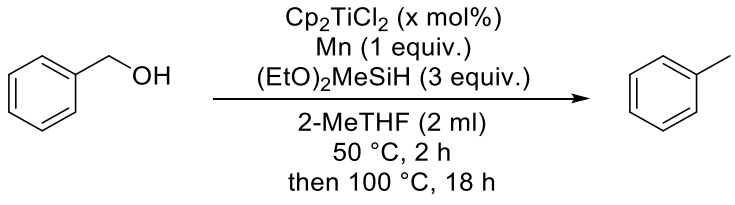
Table S4. Silane screening



Entry[a]	Silane	Yield (%)[c]
1	Et_3SiH	-
2	$PhSiH_3$	18
3	Ph_2SiH_2	4
4	TMS_3SiH	26
5	$TMSO_3SiH$	57
6	$Me(EtO)_2SiH$	96
7[b]	$(EtO)_3SiH$	99
8	$[(CH_3)_2SiH]_2O$	37

[a] Reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then silane (3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Reaction at 80 °C. [c] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

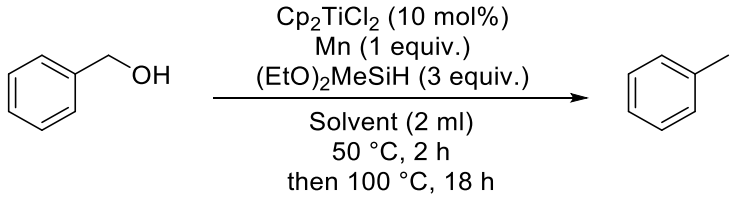
Table S5. Catalyst loading screening



Entry[a]	Ti loading (mol%)	Yield (%)[b]
1	5	77
2	8	81
3	10	99
4	12	97

[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (x mmol), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

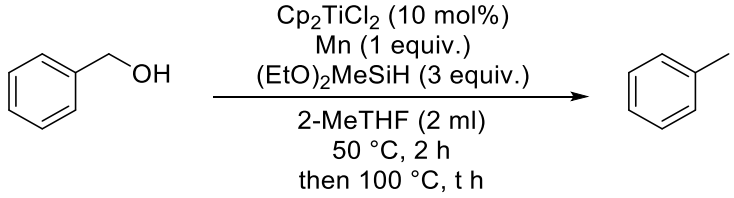
Table S6. Solvent screening



Entry[a]	Solvent	Yield (%)[c]
1[b]	THF	82
2	2-MeTHF	96
3	Toluene	-
4	THF:Toluene 1:1	16
5	$CHCl_3$	-

[a] Reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in solvent (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Reaction at 80 °C. [c] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

Table S7. Reaction time optimization

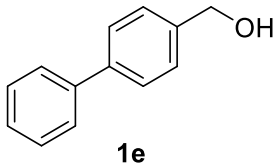


Entry[a]	Time (h)	Yield (%)[c]
1	0.5	4
2	1	9
3	2	15
4	4	28
5	16	96
6	48	92
7	48[b]	90

[a] Reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), t h, 100 °C in a Schlenk pressure tube. [b] with pressure release before 100 °C. [c] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

4 Substrate Synthesis and Analytical Data

[1,1′-biphenyl]-4-methanol (1e)



1e

According to **GP1**, [1,1′-biphenyl]-4-methanol **(1e)** was synthesized from [1,1′-biphenyl]-4-carboxaldehyde (911 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 4 h. The product was afforded as a colorless solid (801 mg, 4.34 mmol, 87%). Analytical data was in accordance with the literature.[3]

$C_{13}H_{12}O$ (184.09 g/mol)

R_f: 0.42 (5:1 Hex:EtOAc)

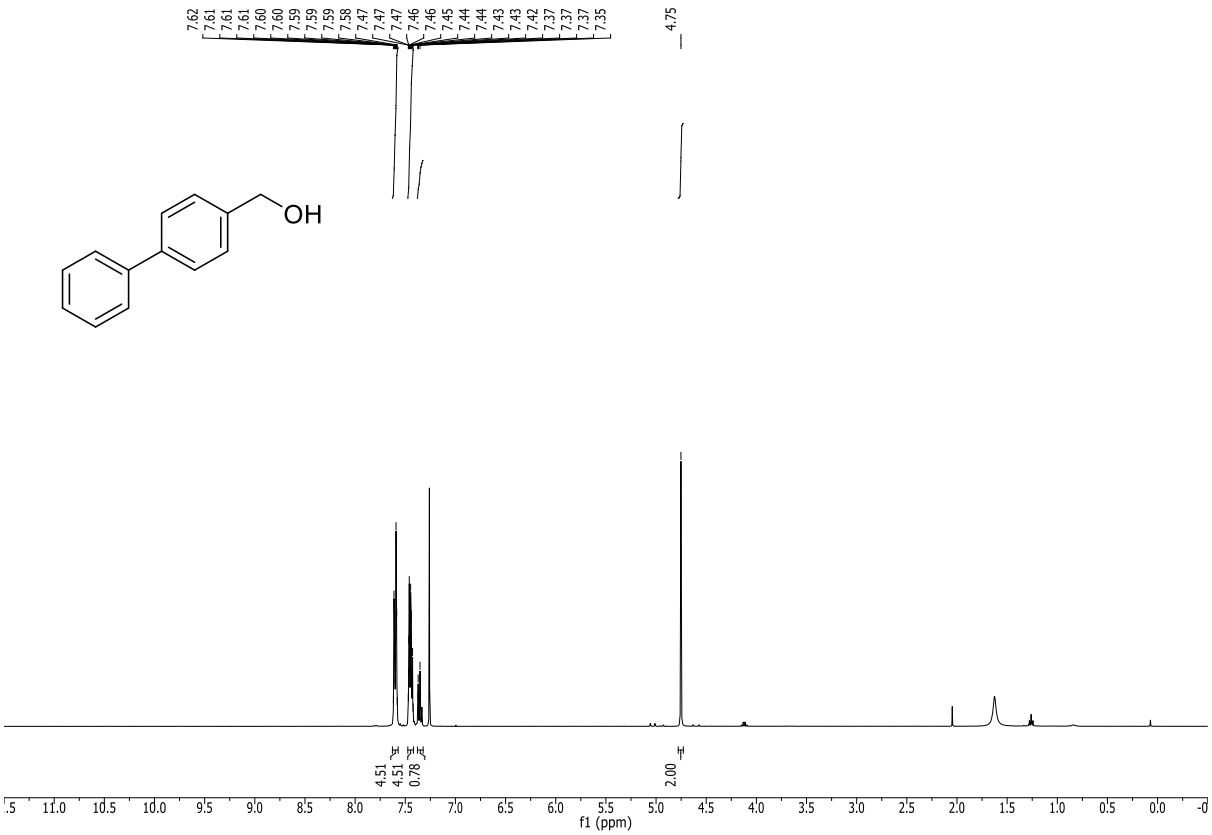
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.62 – 7.58 (m, 4H), 7.47 – 7.43 (m, 4H), 7.39 – 7.32 (m, 1H), 4.75 (s, 2H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm 140.9, 140.8, 140.0, 128.9, 127.6, 127.5, 127.5, 127.2, 65.3.

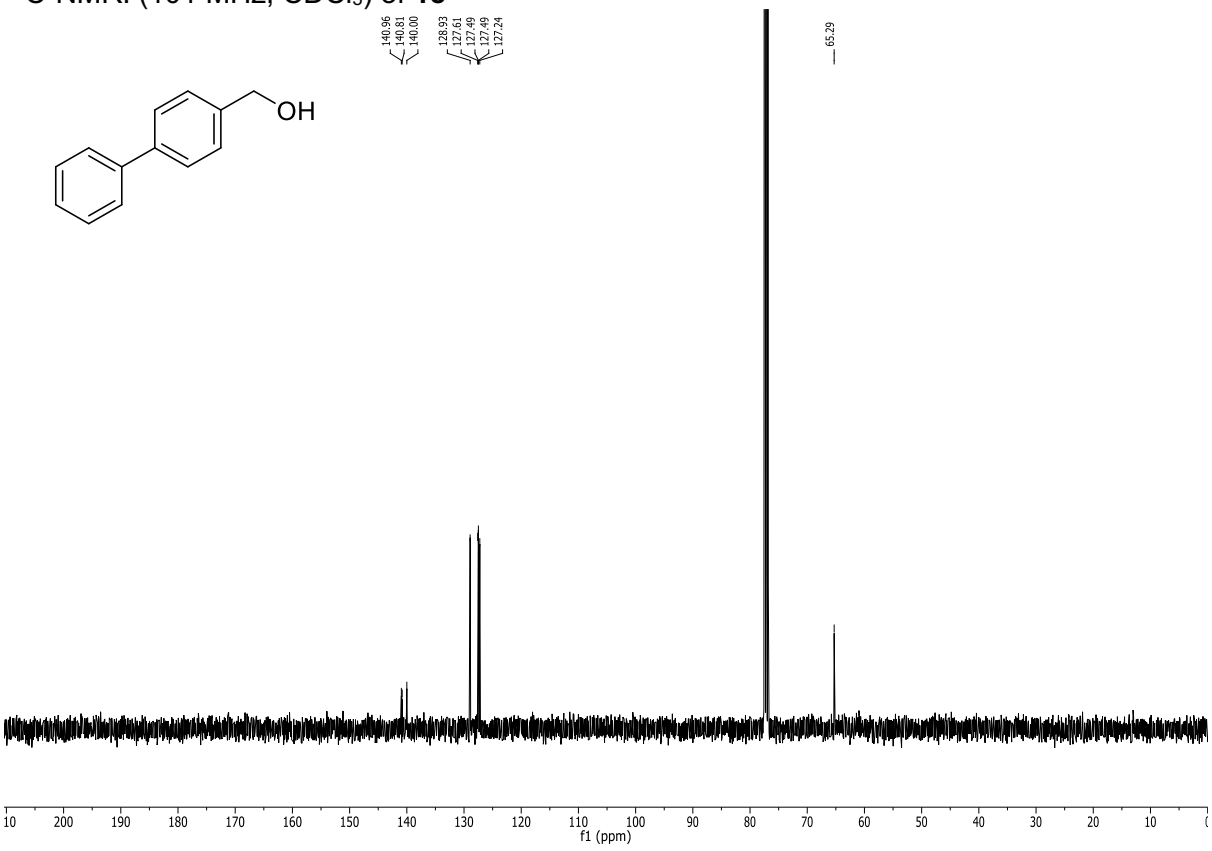
GC-MS: (EI): m/z = 184.1 (100, [$M^{+\bullet}$]), [$M^{+\bullet}$]-[$OH^{\bullet}$]), 167.1 (51, [$M^{+\bullet}$]-[$OH^{\bullet}$]), 155.1 (66, [$M^{+\bullet}$]-[$OH^{\bullet}$]-[$CH_2^{\bullet}$]), 77.1 (66, [$C_6H_5^{\bullet}$]),

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3445 (w), 3426 (w), 2987 (m), 2837 (m), 1483 (m), 1373 (w), 1108 (m), 1046 (s), 991 (s), 816 (s), 749 (s), 708 (s), 673 (m)

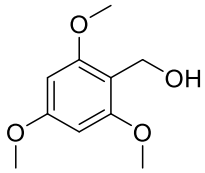
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1e**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1e**



(2,4,6-trimethoxyphenyl)methanol (1l)



1l

According to **GP1**, (2,4,6-trimethoxyphenyl)methanol **(1l)** was synthesized from 2,4,6-trimethoxybenzaldehyde (981 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 5 h. The product was afforded as a colorless solid (809 mg, 4.08 mmol, 82%). Analytical data was in accordance with the literature.[4]

$C_{10}H_{14}O_4$ (198.22 g/mol)

R_f: 0.42 (1:1 Hex:EtOAc)

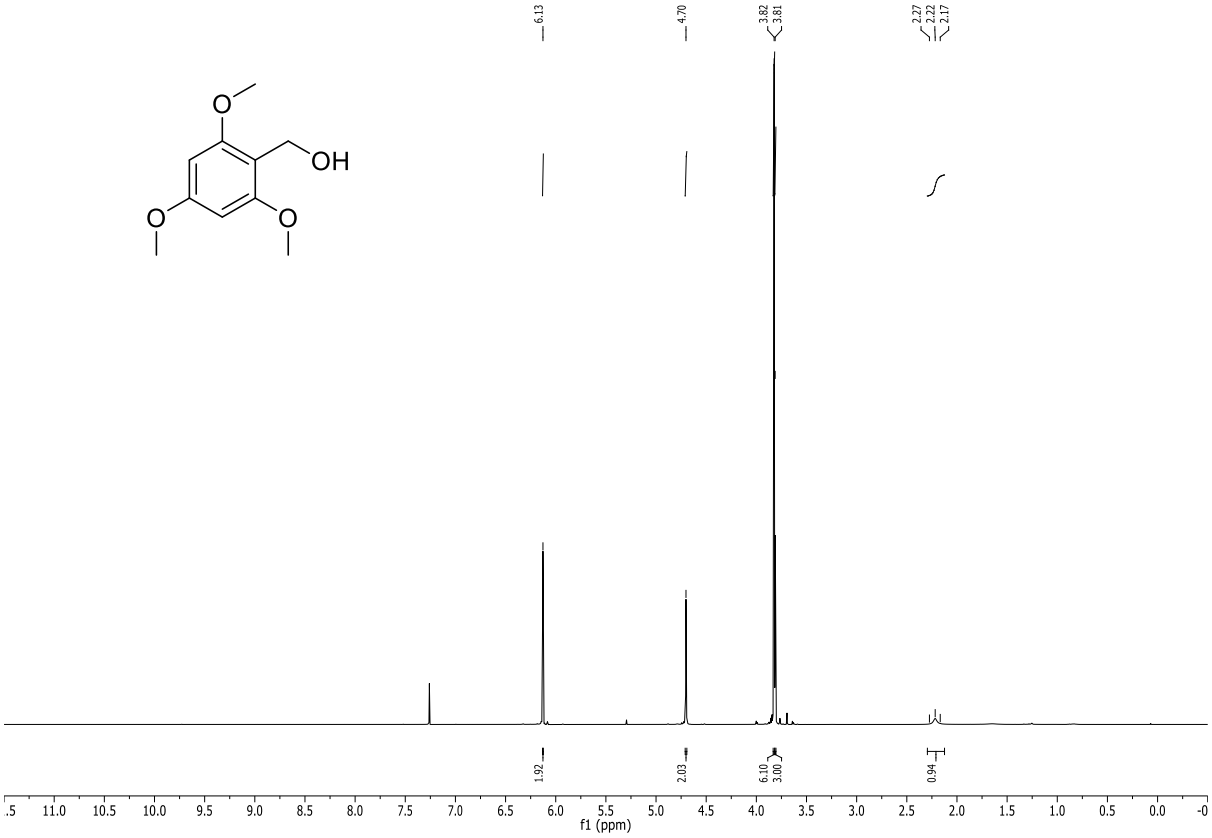
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.13 (s, 2H), 4.70 (s, 2H), 3.82 (s, 6H), 3.81 (s, 3H), 2.22 (bs, 1H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm 161.1, 159.2, 109.9, 90.5, 55.7, 55.4, 54.4

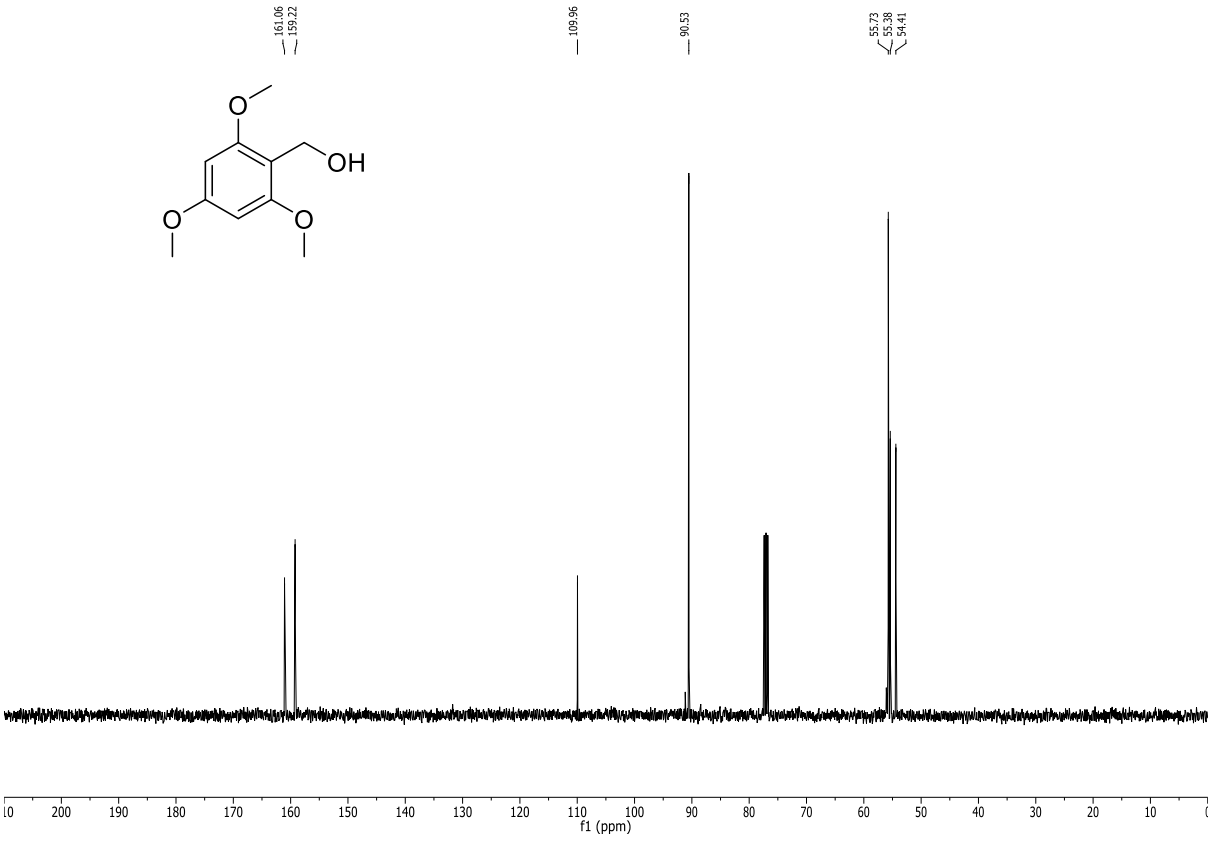
GC-MS: (EI): m/z = 198.1 (82, $[M^{+\bullet}]$), 181.1 (100, $[M^{+}]$-$[OH^{\bullet}]$), 167.1 (25, $[M^{+\bullet}]$-$[OCH_3^{\bullet}]$), 136.1 (24, $[M^{+\bullet}]$-$[OCH_3^{\bullet}]$-$[OCH_3^{\bullet}]$)

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3444 (w), 2997 (w), 2937 (w), 2840 (w), 1592 (s), 1498 (m), 1454 (s), 1338 (w), 1200 (s), 1118 (s), 1036 (m), 992 (s), 947 (s), 813 (s), 731 (m)

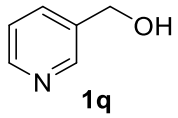
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1l**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1l**



pyridine-3-ylmethanol (1q)



1q

According to **GP1**, pyridine-3-ylmethanol (**1q)** was synthesized from 3-pyridinecarboxaldehyde (0.469 mL, 536 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 16 h. The product was afforded as a colorless oil (213 mg, 90% purity, 1.75 mmol, 35%). Analytical data was in accordance with the literature.[5]

C_6H_7NO (109.13 g/mol)

R_f: 0.19 (EtOAc)

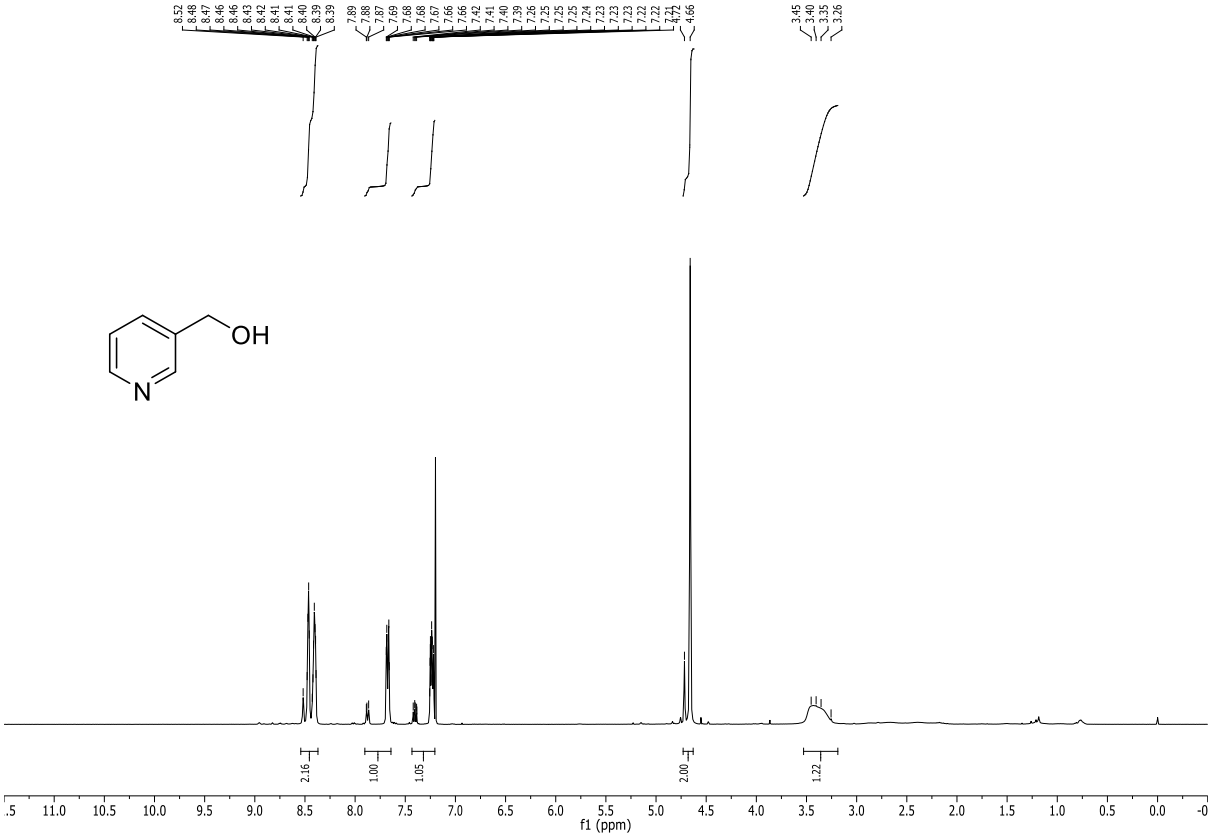
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 8.52 – 8.47 (m, 2H), 7.75 – 7.73 (m, 1H), 7.31 – 7.28 (m, 1H,), 4.72 (s, 2H), 3.47 (bs, 1H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 148.6, 148.2, 135.3, 123.8, 124.2, 62.6

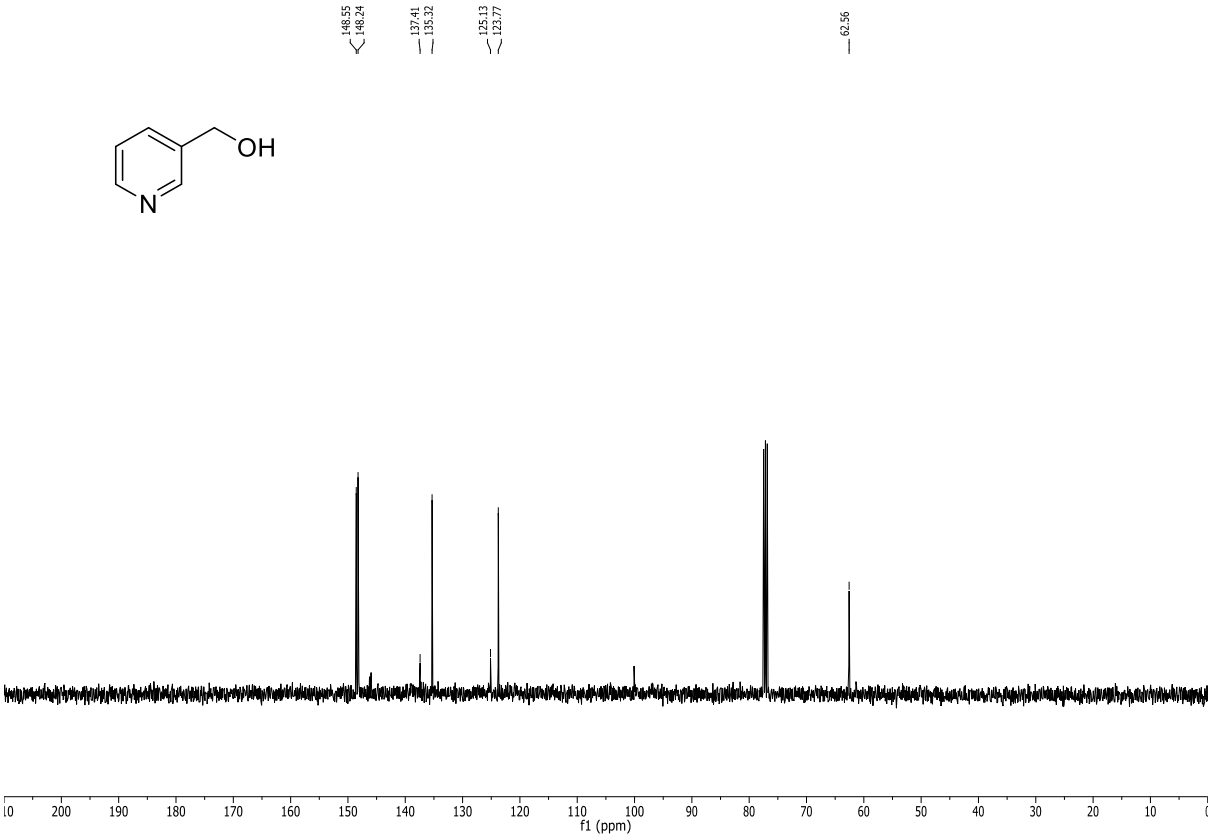
GC-MS: (EI): m/z = 109.0 (58, [$M^{+\bullet}$]), 79.9 (100, [$M^{+\bullet}$]-[$OH^{\bullet}$]-[$CH_2^{\bullet}$])

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3206 (w), 2922 (w), 2855 (w), 1480 (w), 1424 (m), 1364 (w), 1126 (w), 1163 (w), 1215 (w), 1021 (s), 790 (s), 708 (s)

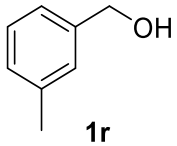
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1q**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1q**



(3-methylphenyl)methanol (1r)



1r

According to **GP1**, (3-methylphenyl)methanol **1r** was synthesized from 3-methylbenzaldehyde (0.59 mL, 601 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 1.5 h. The product was afforded as a colorless oil (531 mg, 4.35 mmol, 87%). Analytical data was in accordance with the literature.[6]

$C_8H_{10}O$ (122.17 g/mol)

R_f: 0.25 (5:1 Hex:EtOAc)

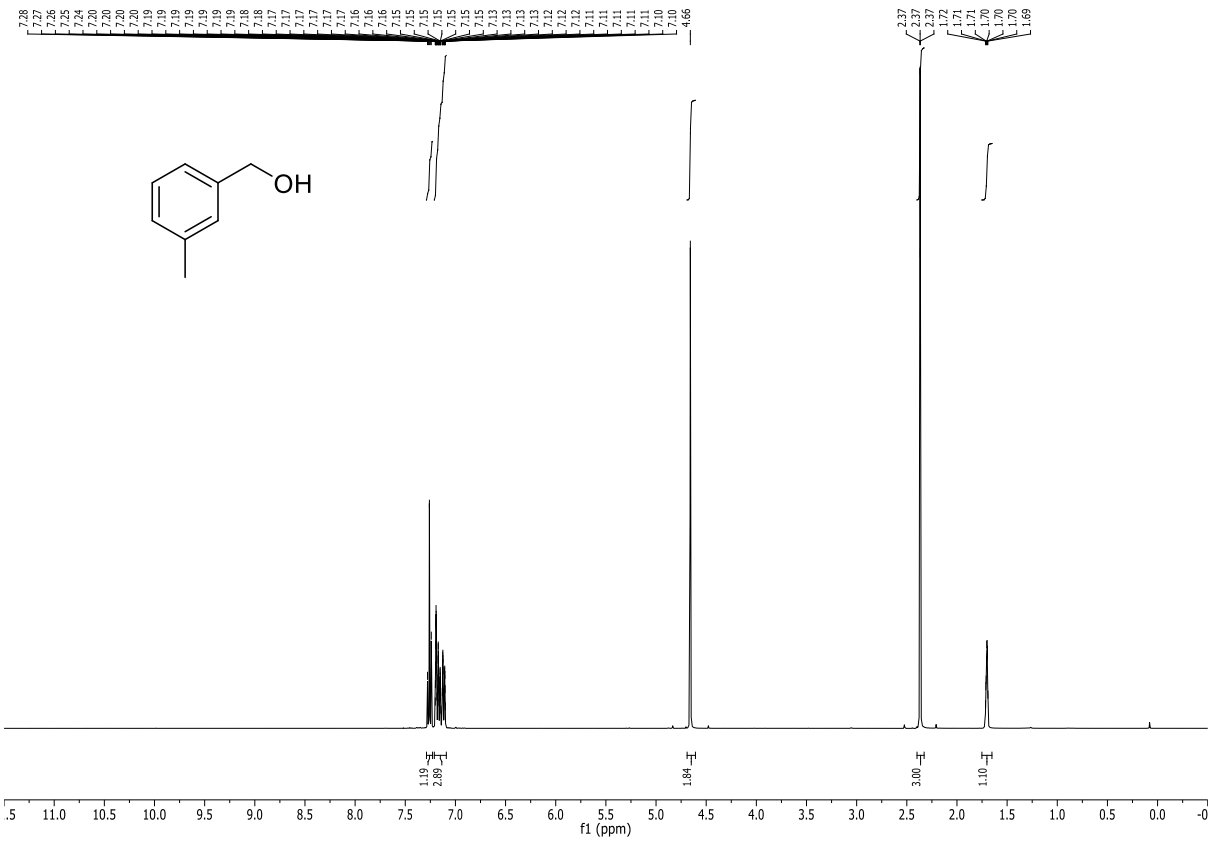
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.28 – 7.24 (m, 1H), 7.19 – 7.11 (m, 3H), 4.66 (s, 2H), 2.37 (s, 3H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 140.9, 138.4, 128.5, 127.9, 124.2, 65.6, 21.5.

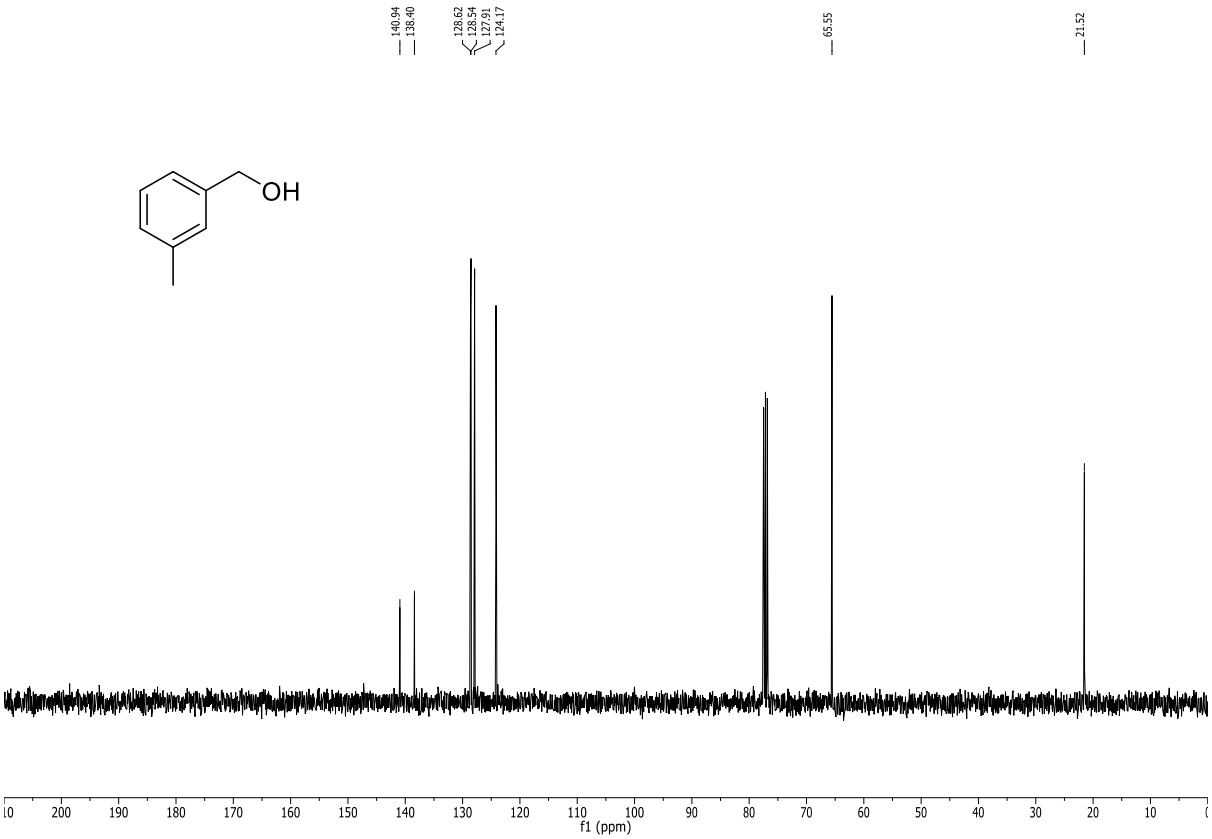
GC-MS: (EI): m/z = 122.0 (100, $[M^{+\bullet}]$), 107.0 (71, $[M^{+\bullet}]$-$[CH_3^{\bullet}]$), 91.0 (55, $[M^{+\bullet}]$-$[CH_3^{\bullet}]$-$[OH^{\bullet}]$)

IR: (ATR, $\tilde{\nu}$, $[cm^{-1}]$): 3317 (w), 2919 (w), 2866 (w), 1487 (w), 1457 (w), 1156 (w), 1014 (w), 883 (w), 775 (s), 738 (s), 693 (s)

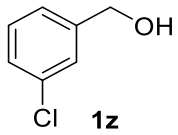
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1r**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1r**



(3-chlorophenyl)methanol (1z)



1z

According to **GP1**, (3-chlorophenyl)methanol **(1z)** was synthesized from 3-chlorobenzaldehyde (0.566 mL, 703 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 2 h. The product was afforded as a colorless oil (692 mg, 4.85 mmol, 97%). Analytical data was in accordance with the literature.[7]

$C_8H_7F_3O$ (176.14 g/mol)

R_f: 0.33 (5:1 Hex:EtOAc)

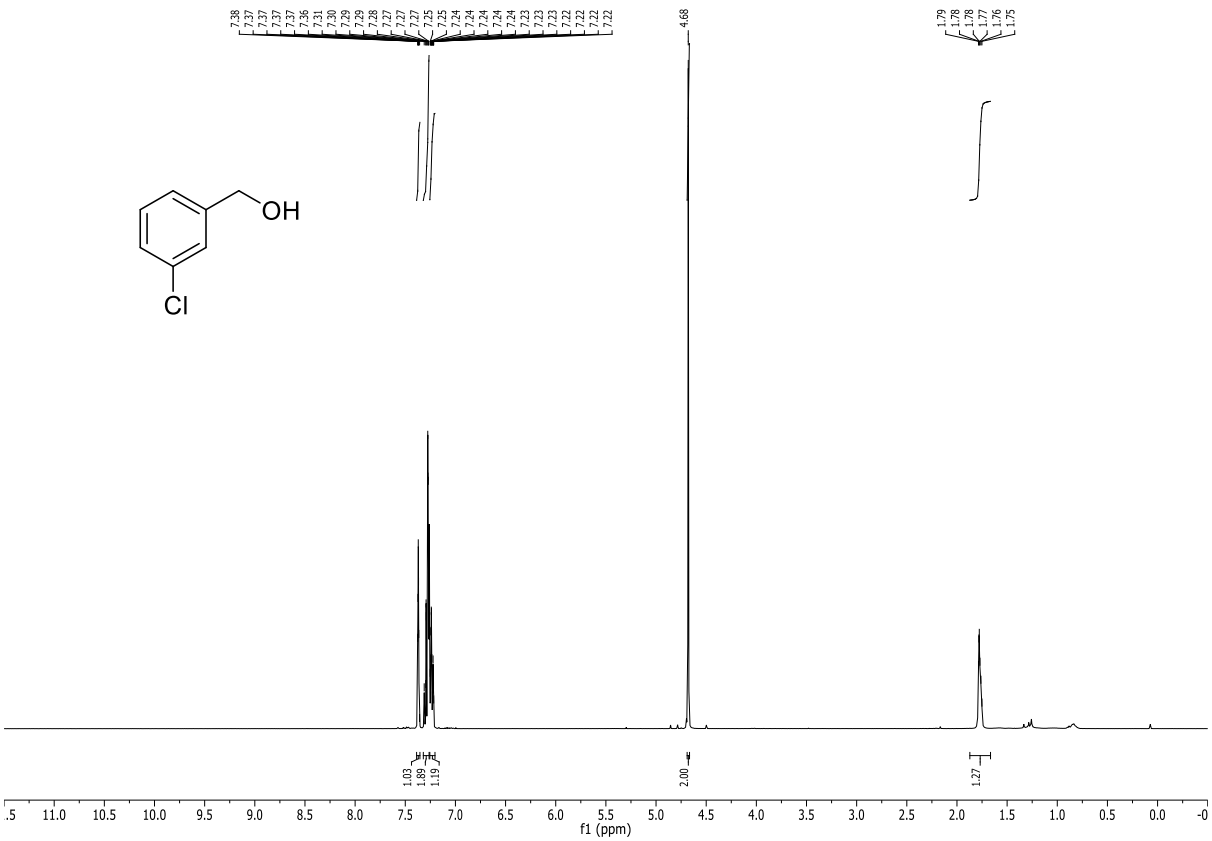
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.37 (s, 1H), 7.31 – 7.23 (m, 3H) 4.68 (s, 2H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 142.9, 134.6, 130.0, 127.9, 127.1, 125.0, 64.7.

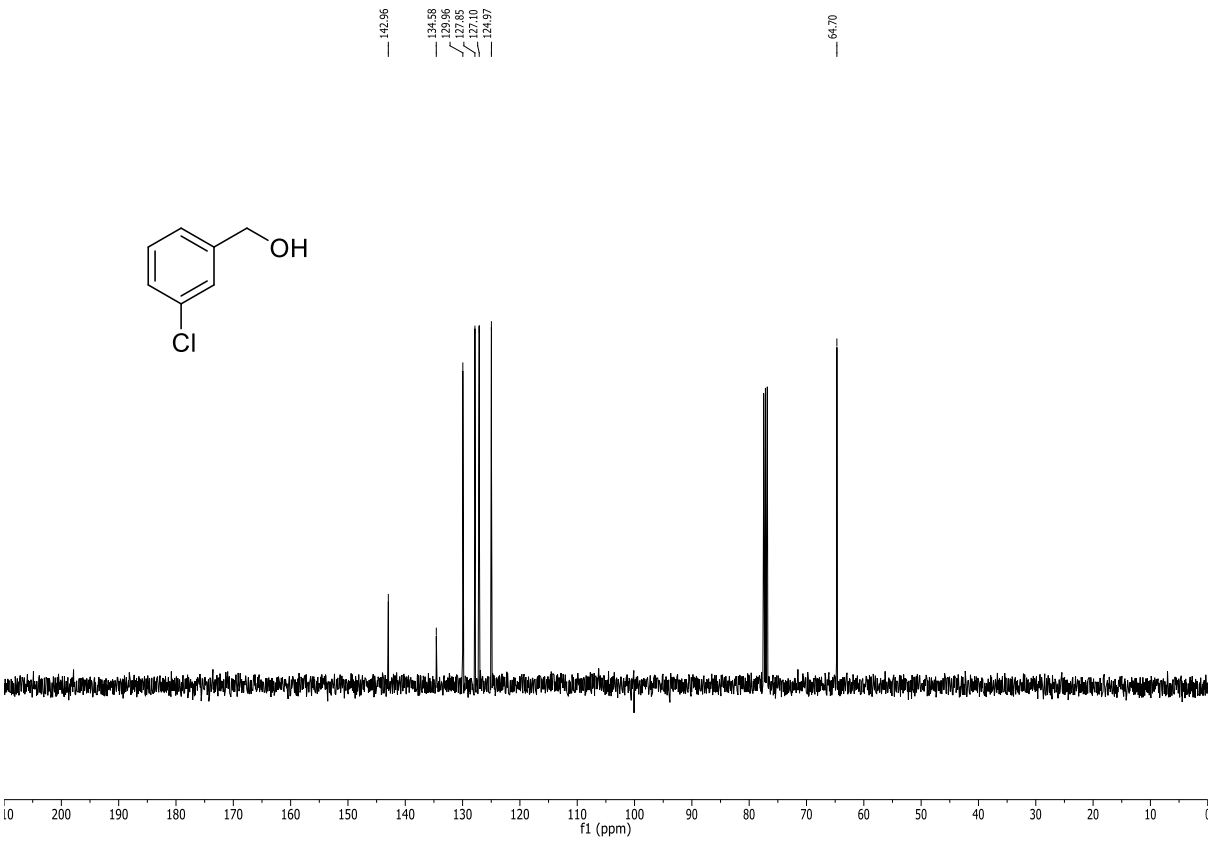
GC-MS: (EI): m/z = 142.0 (100, $[M^{+\bullet}]$), 107.1 (100, $[M^{+\bullet}]$-$[Cl^{\bullet}]$)

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3288 (m), 2926 (w), 2874 (w), 1599 (w), 1476 (m), 1431 (m), 1360 (w), 1200 (m), 1096 (m), 1014 (s), 861 (m), 775 (s), 678 (s)

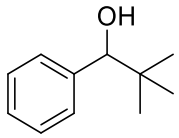
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1z**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1z**



2,2-dimethyl-1-phenylpropan-1-ol (1af)



1af

According to **GP1**, 2,2-dimethyl-1-phenylpropan-1-ol **(1af)** was synthesized from 2,2-dimethyl-1-phenyl-1-propanone (1.04 mL, 6.16 mmol, 1.00 equiv.) and $NaBH_4$ (466 mg, 12.3 mmol, 2.00 equiv.) over 3 h. The product was afforded as a colorless oil (836 mg, 5.09 mmol, 83%). Analytical data was in accordance with the literature.[2]

$C_{11}H_{16}O$ (164.25 g/mol)

R_f: 0.67 (5:1 Hex:EtOAc)

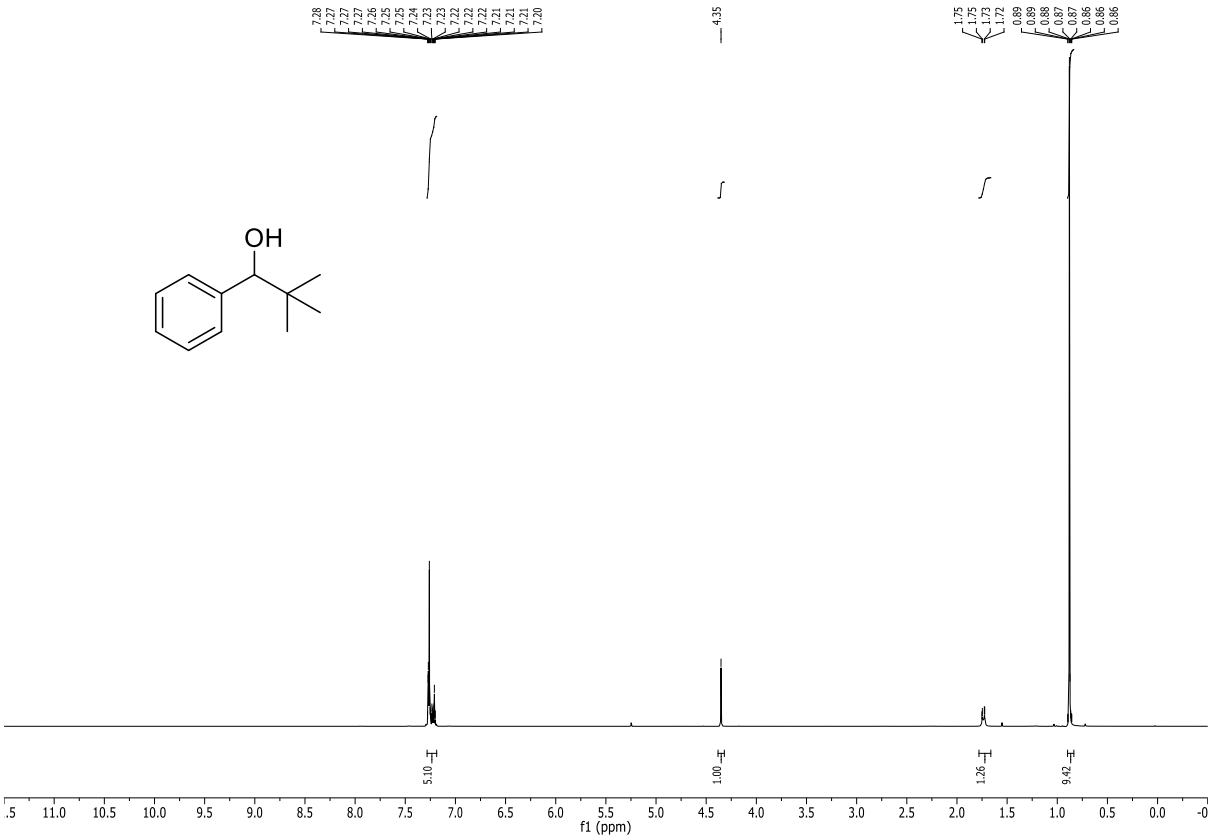
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.27 – 7.21 (m, 5H), 4.35 (s, 1H), 0.88 (s, 9H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 142.3, 127.8, 127.7, 127.4, 35.8, 26.1.

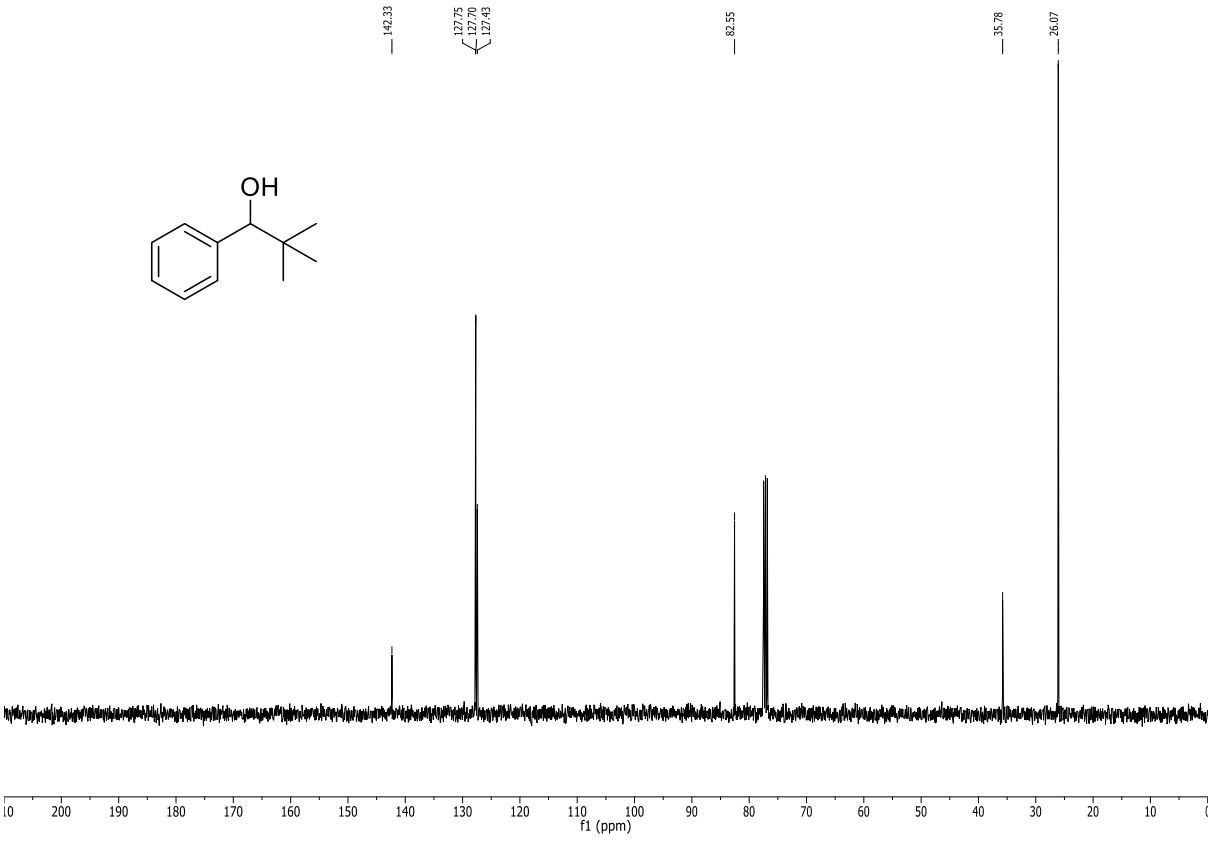
GC-MS: (EI): m/z = 164.1 (10, $[M^{+\bullet}]$), 131.1 (31, $[M^{+\bullet}]$-$[OH^{\bullet}]$-$[CH_3^{\bullet}]$) 107.1 (100, $[M^{+\bullet}]$-$[C(CH_3)_3^{\bullet}]$), 77.1 (39, $[M^{+\bullet}]$-$[C(CH_3)_3^{\bullet}]$-$[CHOH^{\bullet}]$)

IR: (ATR, $\tilde{\nu}$, $[cm^{-1}]$): 3440 (w), 2952 (m), 2904 (w), 2866 (w), 1480 (m), 1454 (m), 1364 (m), 1234 (w), 1178 (w), 1081 (w), 1044 (m), 1006 (s), 898 (w), 783 (w), 731 (s), 701 (s)

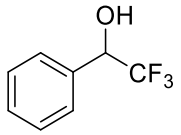
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1af**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1af**



2,2,2-trifluoro-1-phenylethanol (1ag)



1ag

According to **GP1**, 2,2,2-trifluoro-1-phenylethanol **(1ag)** was synthesized from 2,2,2-trifluoro-1-phenylethanone (0.70 mL, 871 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 17 h. The product was afforded as a colorless oil (838 mg, 4.76 mmol, 95%). Analytical data was in accordance with the literature.[8]

$C_8H_7F_3O$ (176.14 g/mol)

R_f: 0.64 (5:1 Hex:EtOAc)

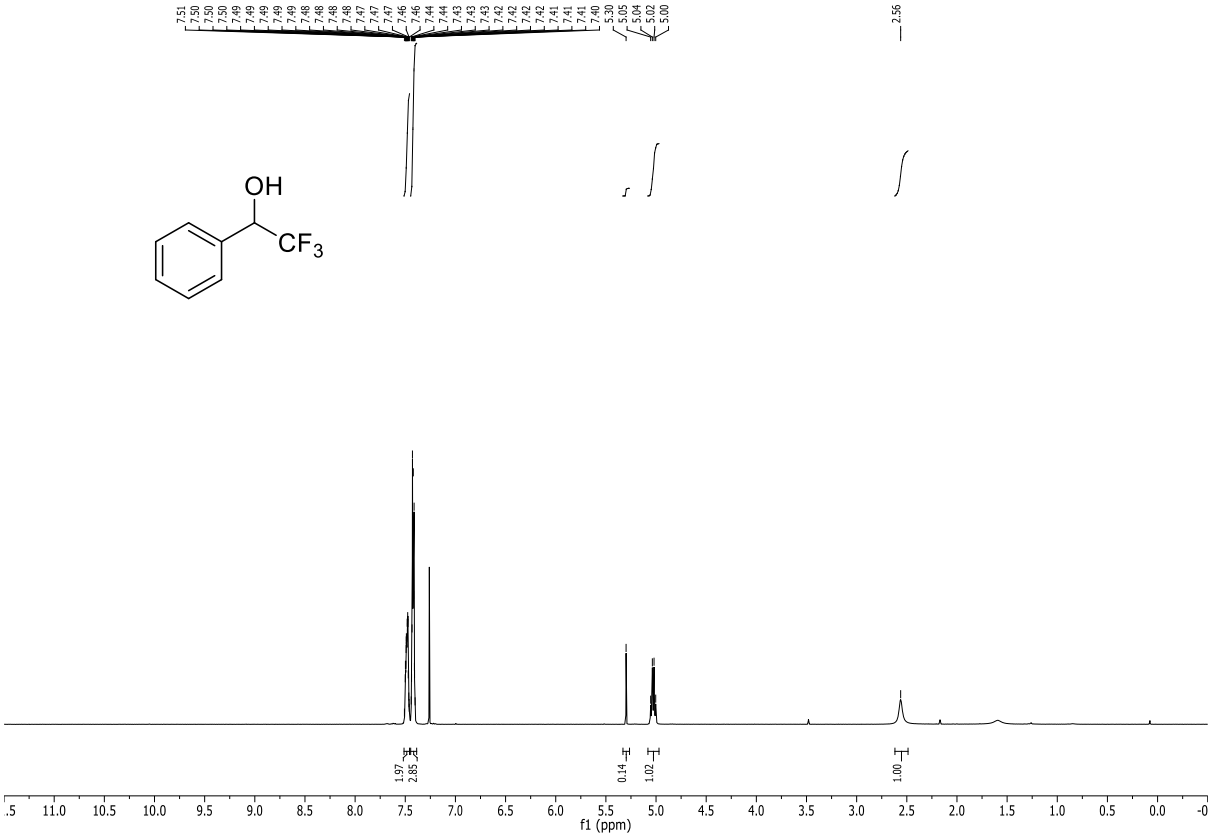
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.50 – 7.47 (m, 2H), 7.43 – 7.41 (m, 3H), 5.03 (q, *J* = 5.0 Hz, 1H), 2.56 (s, 1H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 134.1, 129.7, 128.8, 127.6, 124.4 (q, *J* = 280 Hz), 72.9 (q, *J* = 31.6).

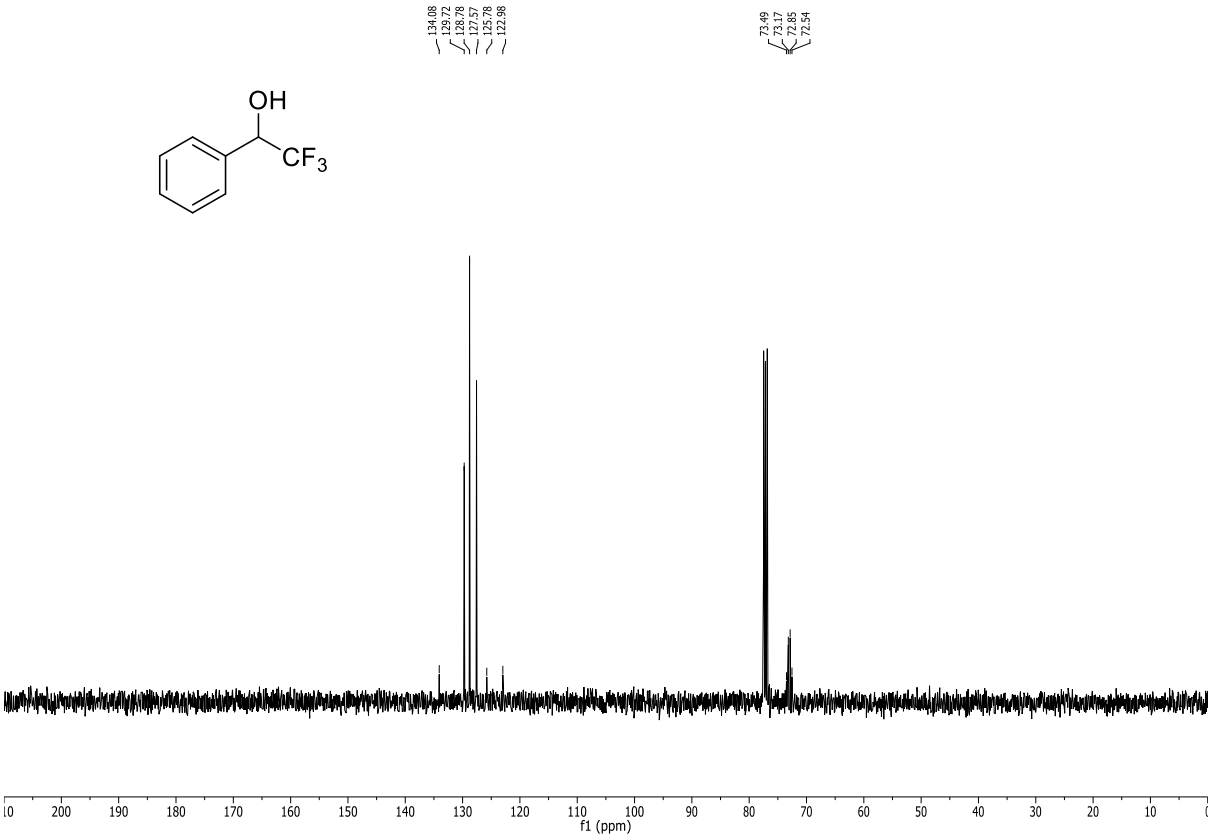
GC-MS: (EI): m/z = 176.0 (41, [$M^{+\bullet}$]), 107.0 (100, [$M^{+\bullet}$]-[$CF_3^\bullet$]), 77.0 (72, [$M^{+\bullet}$]-[$CF_3^\bullet$]-[$CHOH^\bullet$])

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3384 (w), 1457 (w), 1357 (w), 1264 (m), 1167 (s), 1122 (s), 1059 (m), 865 (w), 835 (w), 760 (w), 701 (s)

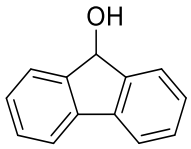
^{1}H-NMR: (400 MHz, $CDCl_3$) of **1ag**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1ag**



9*H*-fluoren-9-ol (1ai)



1ai

According to **GP1**, 9*H*-fluoren-9-ol **(1ai)** was synthesized from fluorenone (900 mg, 5.00 mmol, 1.00 equiv.) and $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv.) over 17 h. The MeOH was removed through filtration instead of distillation. The product was afforded as a colorless solid (836 mg, 4.59 mmol, 92%). Analytical data was in accordance with the literature.[9]

$C_{11}H_{16}O$ (182.22 g/mol)

R_f: 0.45 (5:1 Hex:EtOAc)

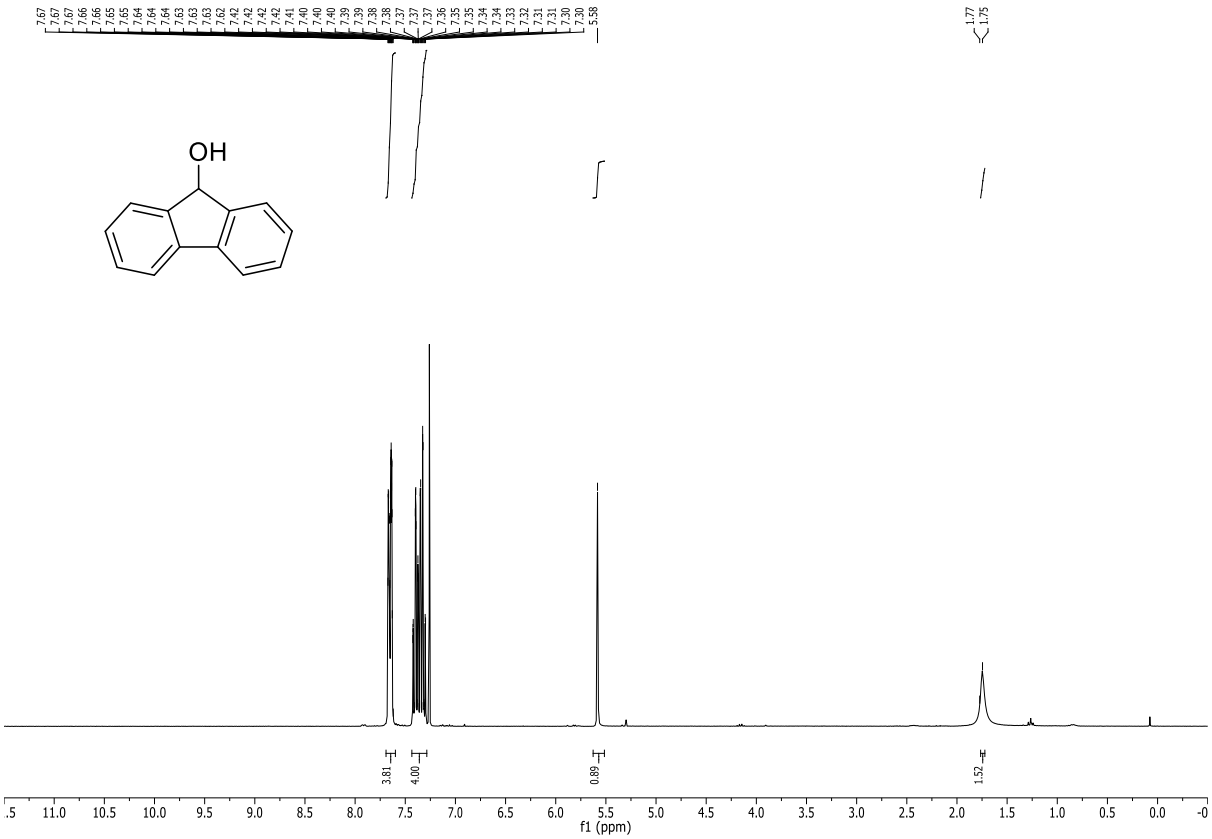
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.67 – 7.63 (m, 4H), 7.42 – 7.30 (m, 4H), 5.58 (s, 1H)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 145.8, 140.2, 129.2, 128.0, 125.3, 120.1, 75.4.

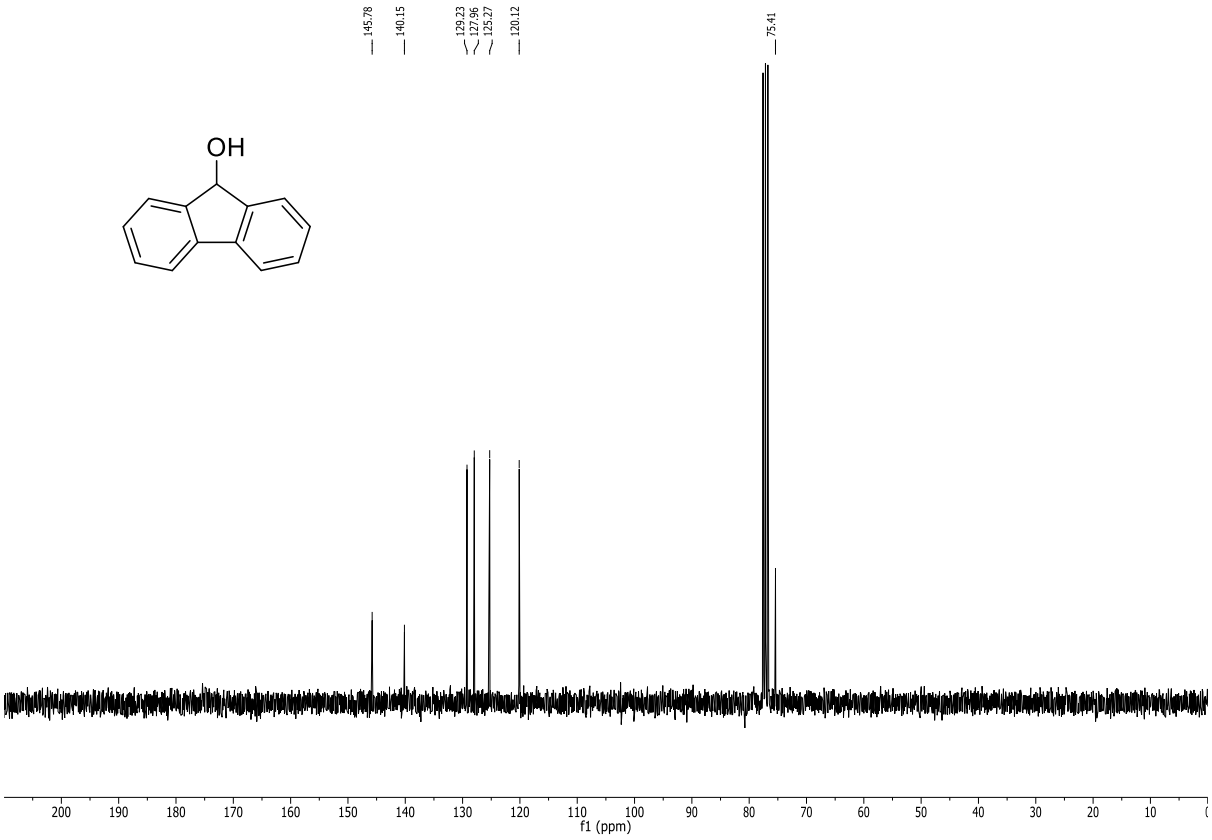
GC-MS: (EI): m/z = 182.1 (100, $[M^{+\bullet}]$), 165.1 (47, $[M^{+\bullet}]$-$[OH^{\bullet}]$), 152.1 (65, $[M^{+\bullet}]$-$[CHOH^{\bullet}]$), 76.0 (16, $[M^{+\bullet}]$-$[CHOH^{\bullet}]$-$[C_6H_4^{\bullet}]$)

IR: (ATR, $\tilde{\nu}$, $[cm^{-1}]$): 3284 (m), 3064 (m), 3038 (m), 1450 (m), 1305 (m), 1185 (m), 1096 (w), 1021 (s), 943 (m), 846 (w), 764 (m), 734 (s), 671 (m)

^{1}H-NMR: (400 MHz, $CDCl_3$) of **1ai**



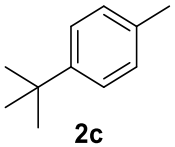
^{13}C-NMR: (101 MHz, $CDCl_3$) of **1ai**



5 Deoxygenation of Benzylic Alcohols: Analytical Data of Products

5.1 Isolated Compounds

1-(*tert*-butyl)-4-methylbenzene (2c)



2c

According to **GP2**, 1-(tert-butyl)-4-methylbenzene **(2c)** was synthesized from 4-*tert*-butylbenzyl alcohol (0.170 mL, 164 mg, 1.00 mmol, 1.00 equiv.), over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 4:1) and was afforded as a colorless oil (130 mg, 0.88 mmol, 88%, 92% determined by GC-FID). Analytical data was in accordance with the literature.[10]

$C_{11}H_{16}$ (148.25 g/mol)

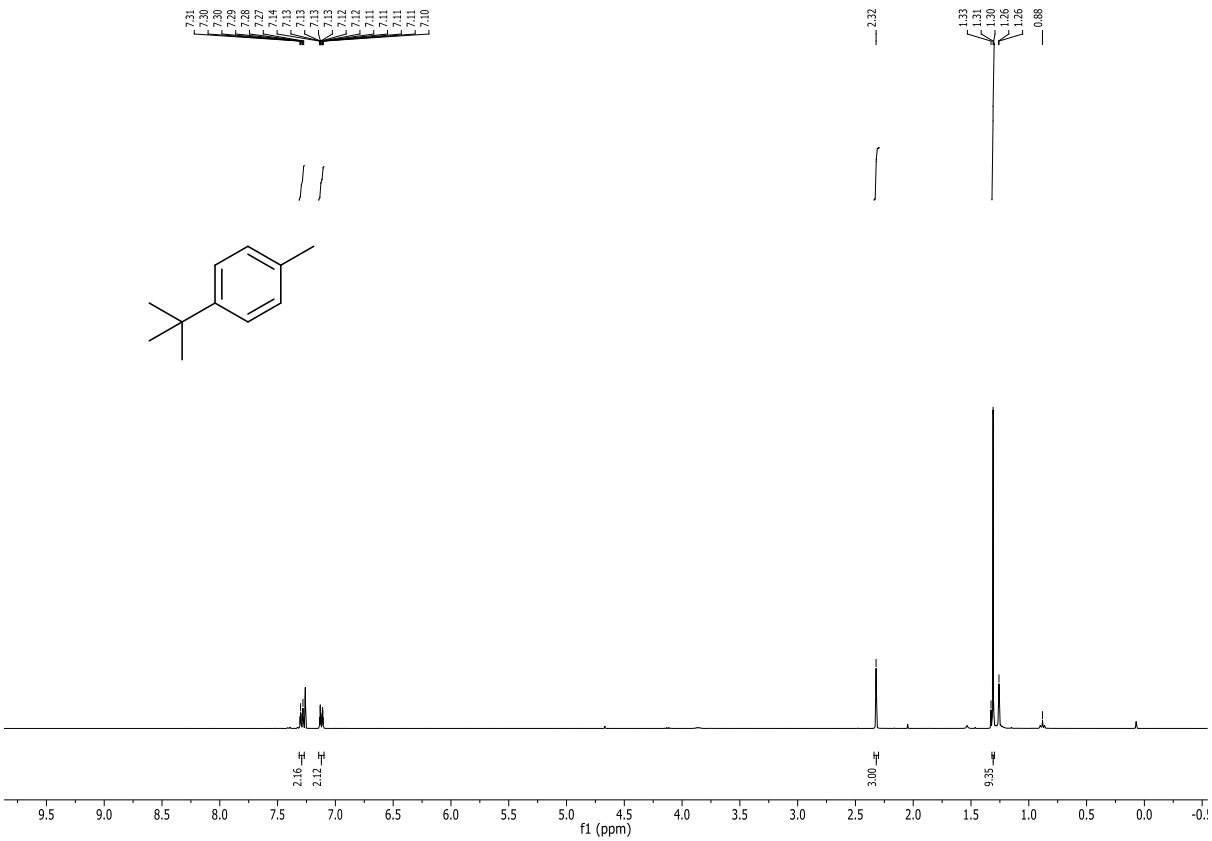
R_f: 0.88 (4:1 Hex:EtOAc)

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H/ppm: 7.31 – 7.27 (m, 2H), 7.14 – 7.10 (m, 2H), 2.32 (s, 3H), 1.31 (s, 9H); Impurity – Pentadecane (internal standard)

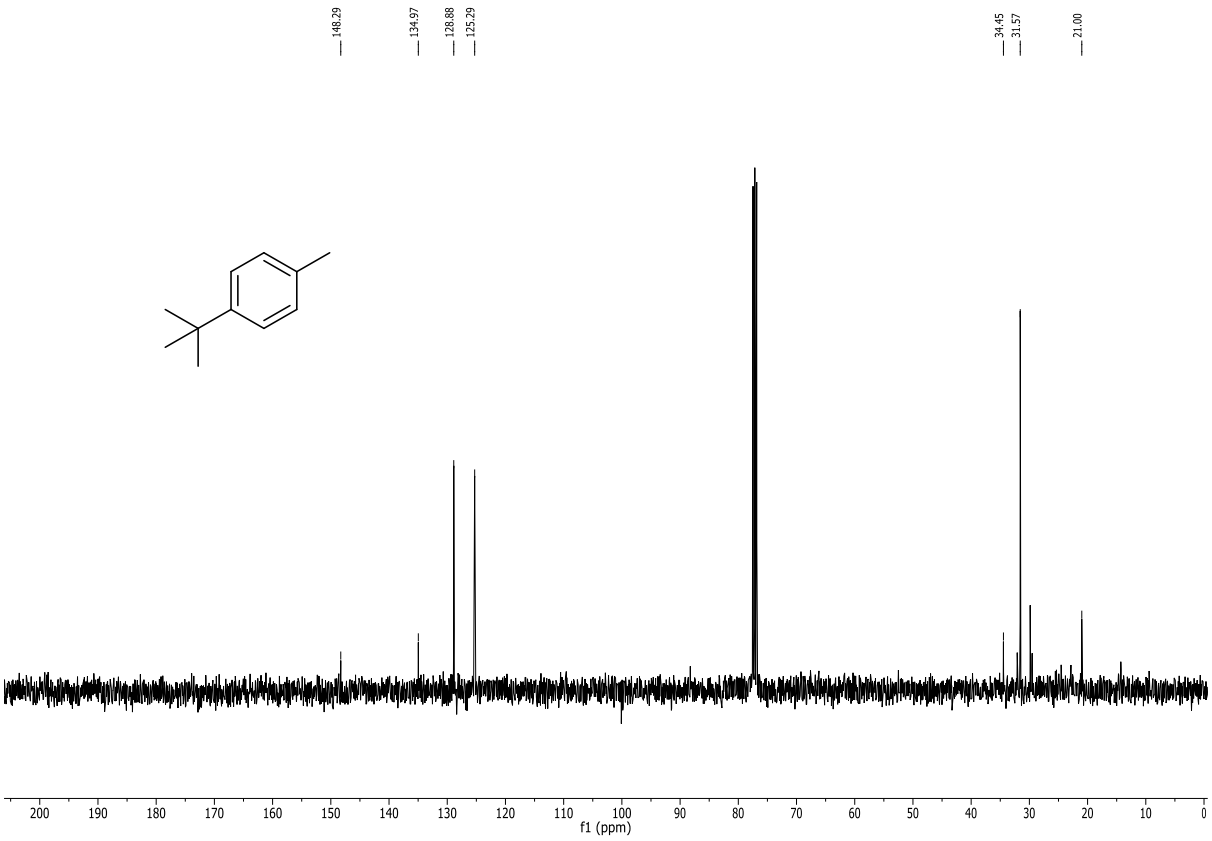
^{13}C-NMR (100 MHz, $CDCl_3$) δ_C/ppm: 148.3, 134.9, 128.9 (2), 125.3 (2), 34.5, 31.6, 21.0.

GC-MS (EI): 148.11 (100, $[M^{+\bullet}]$), 133.12 ($[M^{+\bullet}]$-$[CH_3^\bullet]$), 115.05 ($[M^{+\bullet}]$-2$[CH_3^\bullet]$), 105.05 ($[M^{+\bullet}]$-3$[CH_3^\bullet]$), 93.07 ($[M^{+\bullet}]$-3$[CH_3^\bullet]$-$[CH_3^\bullet]$), 91.07 ($[M^{+\bullet}]$-$[C_4H_9^\bullet]$), 77.04 ($[M^{+\bullet}]$-$[C_4H_9^\bullet]$-$[CH_3^\bullet]$)

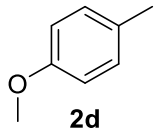
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2c**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2c**



4-methylanisole (2d)



2d

According to **GP2**, 4-methylanisole **(2d)** was synthesized from 4-methoxybenzyl alcohol (0.127 mL, 138 mg, 1.00 mmol, 1.00 equiv.), over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 4:1) and was afforded as a colorless oil (56 mg, 0.46 mmol, 46%, 92% determined by GC-FID). Analytical data was in accordance with the literature.[11]

$C_8H_{10}O$ (122.07 g/mol)

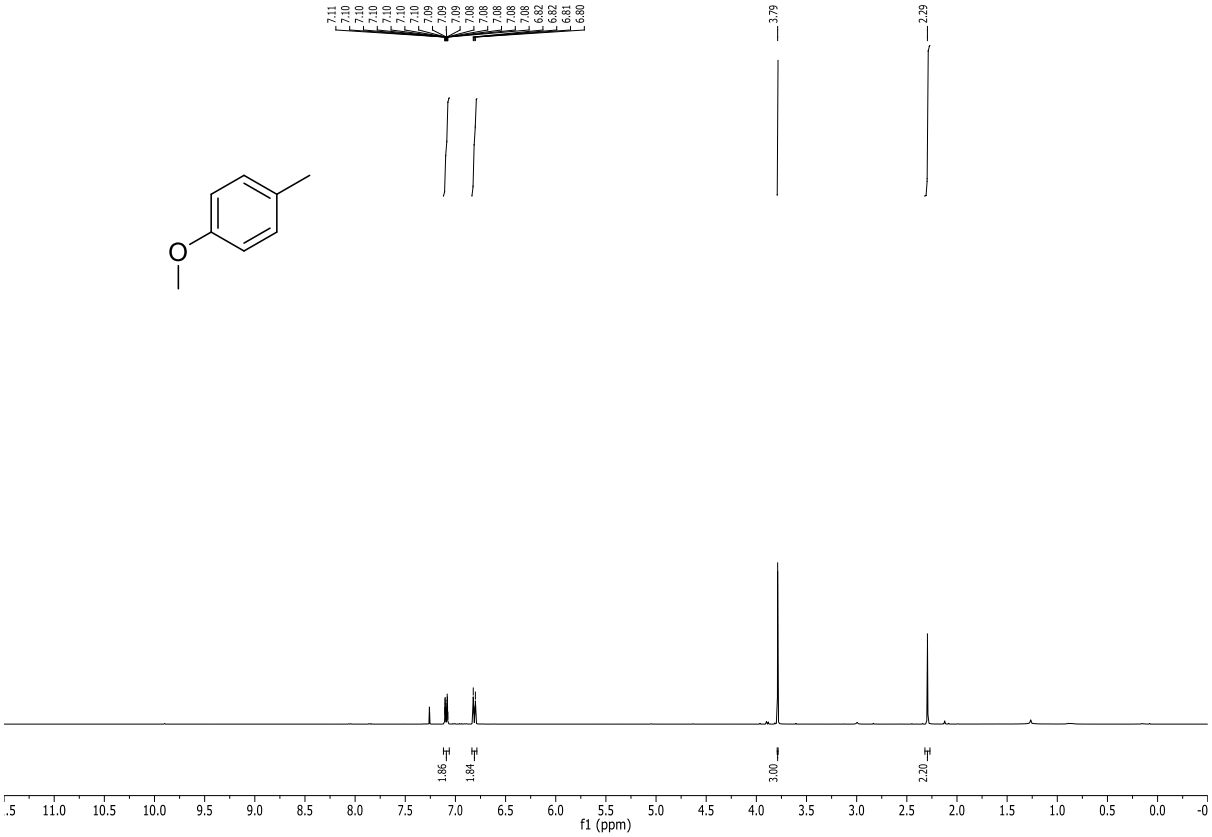
R_f: 0.74 (4:1 Hex:EtOAc)

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H/ppm: 7.13 – 7.04 (m, 2H), 6.85 – 6.76 (m, 2H), 3.78 (s, 3H), 2.29 (s, 3H).

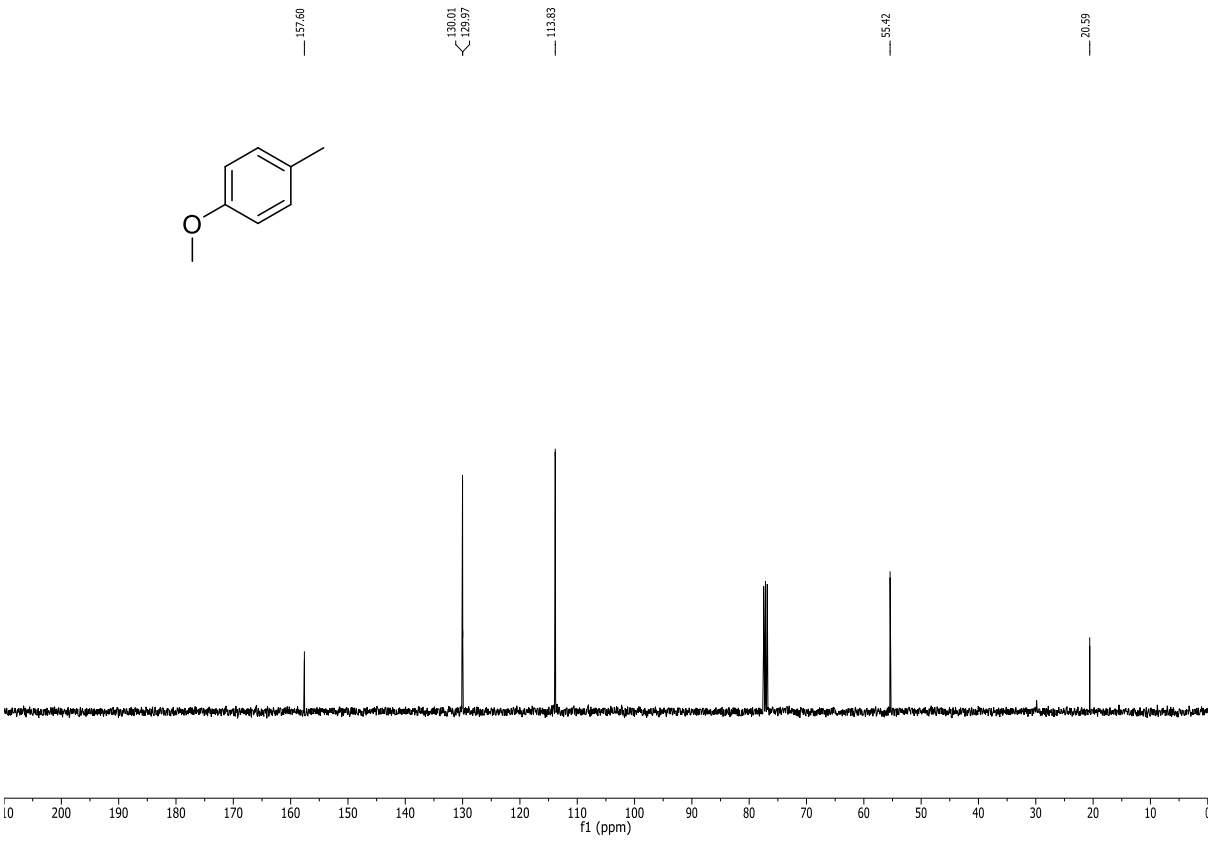
^{13}C-NMR (100 MHz, $CDCl_3$) δ_C/ppm: 157.6, 130.0, 113.8, 55.4, 20.6.

GC-MS (EI): 122.09 (100, $[M^{+\bullet}]$), 107.05 ($[M^{+\bullet}]$-$[CH_3^\bullet]$), 91.06 ($[M^{+\bullet}]$-$[OCH_3^\bullet]$), 77.04 ($[M^{+\bullet}]$-$[CH_3^\bullet]$-$[OCH_3^\bullet]$)

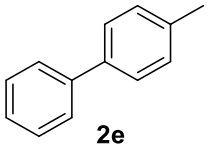
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2d**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2d**



4-methylbiphenyl (2e)



2e

According to **GP2**, 1-methylnaphtalene **(2e)** was synthesized from 1,1-Biphenyl-4-methanol (184 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 4:1) and was afforded as a colorless solid (138 mg, 0.82 mmol, 82%, 89% determined by GC-FID). Analytical data was in accordance with the literature.[12]

$C_{13}H_{12}$ (168.09 g/mol)

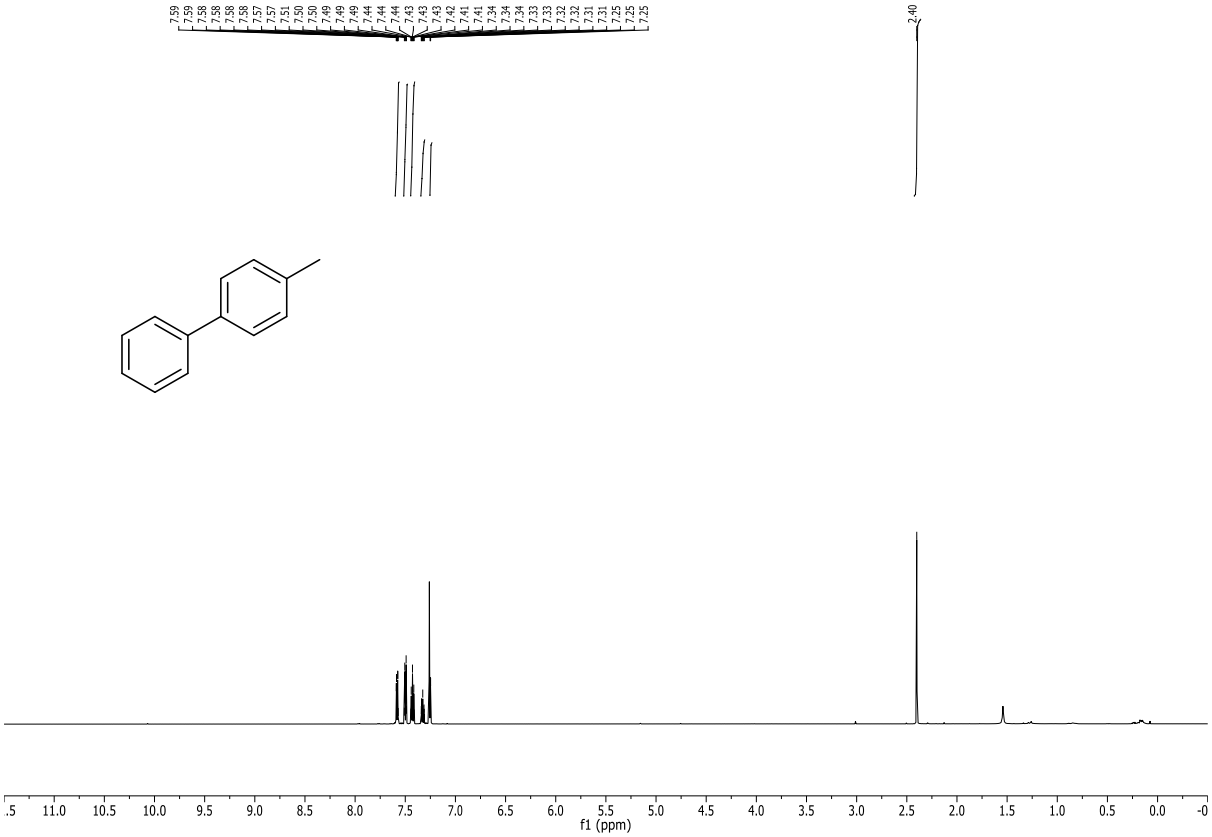
R_f: 0.83 (4:1 Hex:EtOAc)

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H/ppm: 7.60 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 2H), 7.34 – 7.31 (m, 1H), 7.27-7,23 (m, 1H), 2.40 (s, 3H).

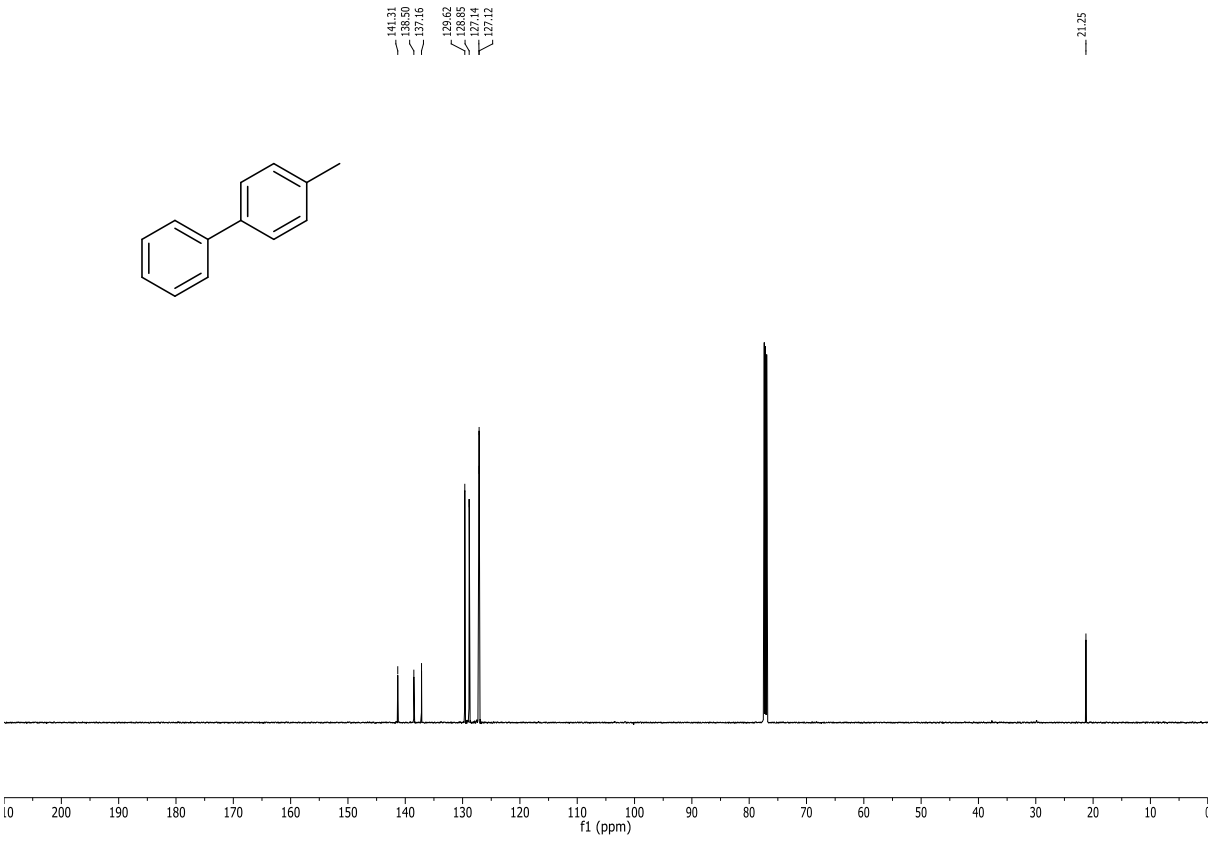
^{13}C-NMR (100 MHz, $CDCl_3$) δ_C/ppm: 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 127.1, 21.3.

GC-MS (EI): 168.1 (100, $[M^{+\bullet}]$), 152.1 (32, $[M^{+\bullet}]$-$[CH_3^\bullet]$), 91.0 (8, $[M^{+\bullet}]$-$[C_6H_5^\bullet]$)

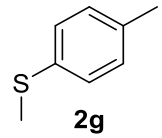
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2e**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2e**



1-methyl-4-methylsulfanylbenzene (2g)



2g

According to **GP2**, 1-methyl-4-methylsulfanylbenzene **(2g)** was synthesized from 4-(methylthio)benzyl alcohol (0.127 mL, 138 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless solid (48 mg, 0.35 mmol, 35%, 48% determined by GC-FID). Analytical data was in accordance with the literature.[13]

$C_8H_{10}S$ (138.23 g/mol)

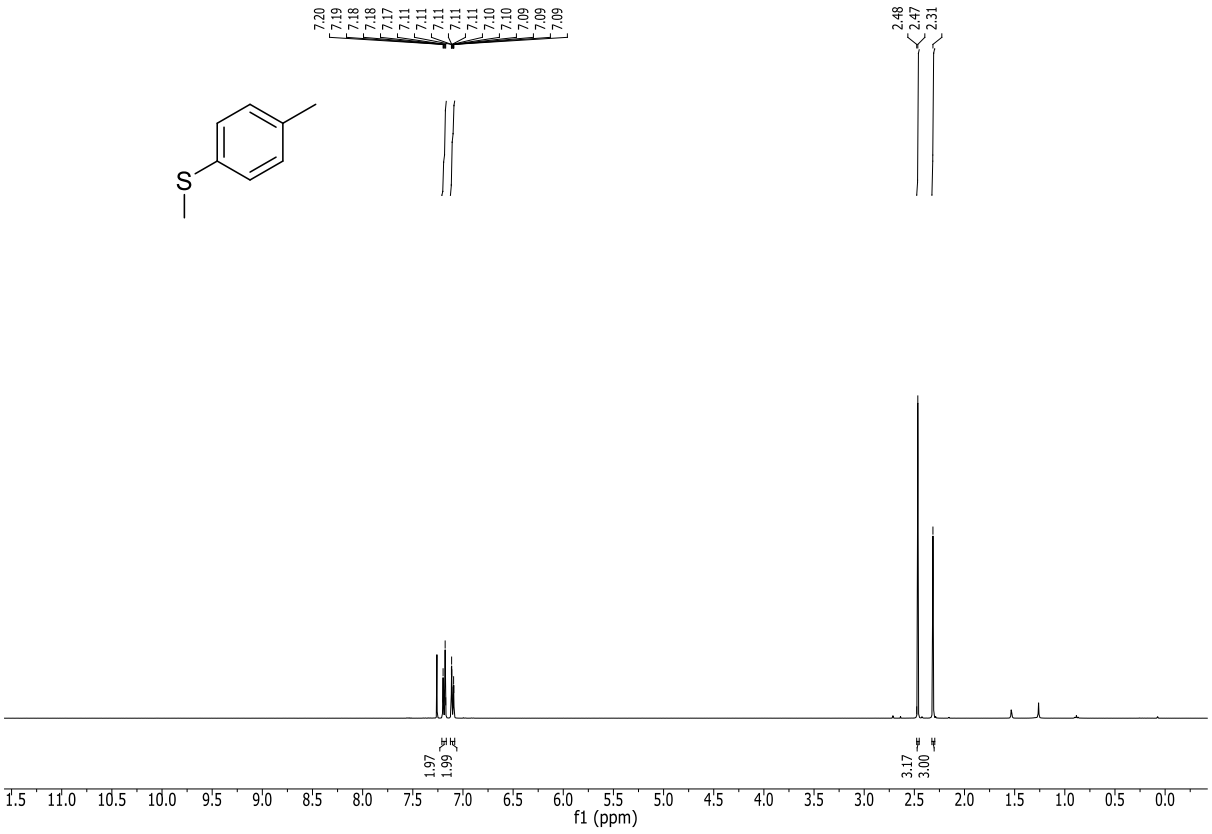
R_f: 0.50 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.20 – 7.17 (m, 2H), 7.11 – 7.09 (m, 2H), 2.46 (s, 3H), 2.31 (s, 3H)

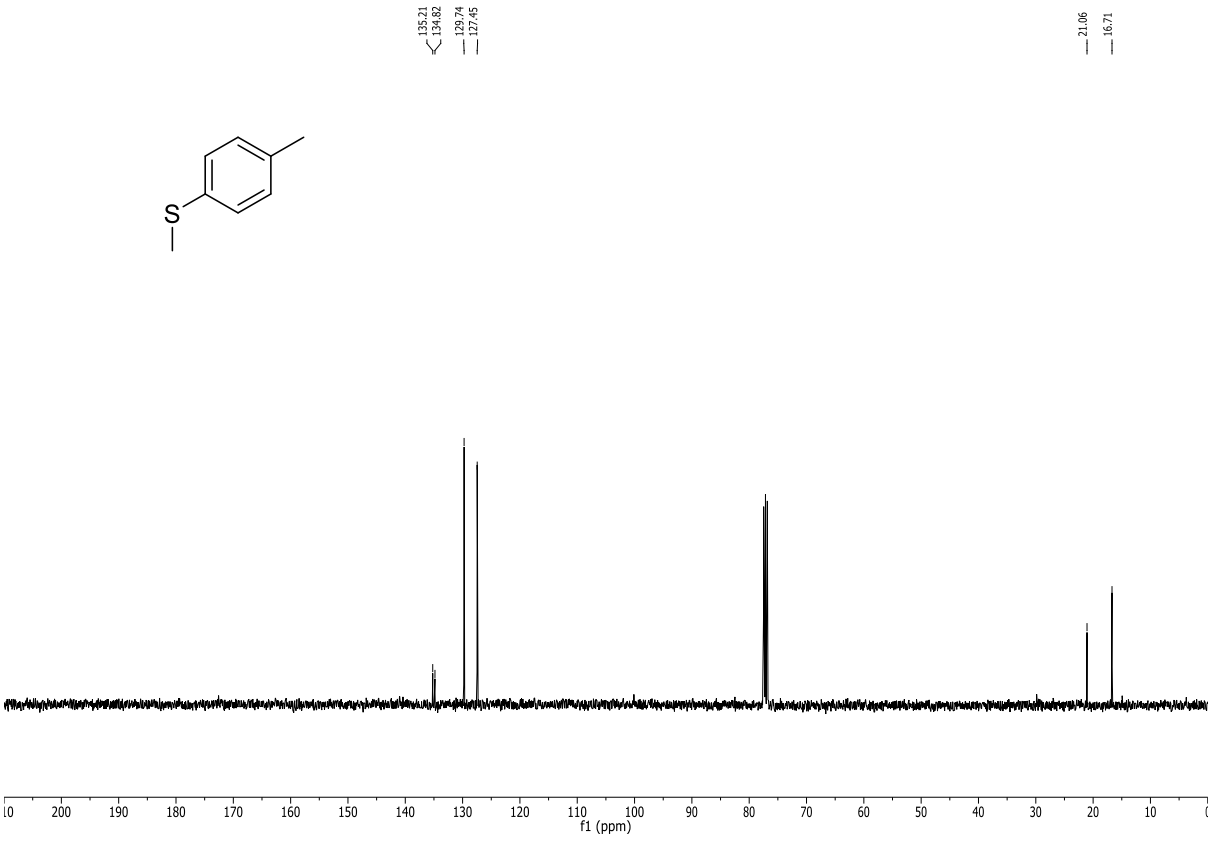
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 135.2, 134.8, 129.7, 127.5, 21.1, 16.7.

GC-MS: (EI): m/z = 138.0 (100, $[M^{+\bullet}]$), 123.0 (29, $[M^{+\bullet}]$-$[CH_3^\bullet]$), 91.1 (60, $[M^{+\bullet}]$-$[SCH_3^\bullet]$)

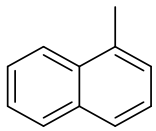
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2g**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2g**



1-methylnaphtalene (2j)



2j

According to **GP2**, 1-methylnaphtalene **(2j)** was synthesized from 1-naphthalenemethanol (158 mg, 1.00 mmol, 1.00 equiv.), over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 4:1) and was afforded as a colorless oil (134 mg, 0.94 mmol, 94%, 97% determined by GC-FID). Analytical data was in accordance with the literature.[11]

$C_{11}H_{10}$ (142.20 g/mol)

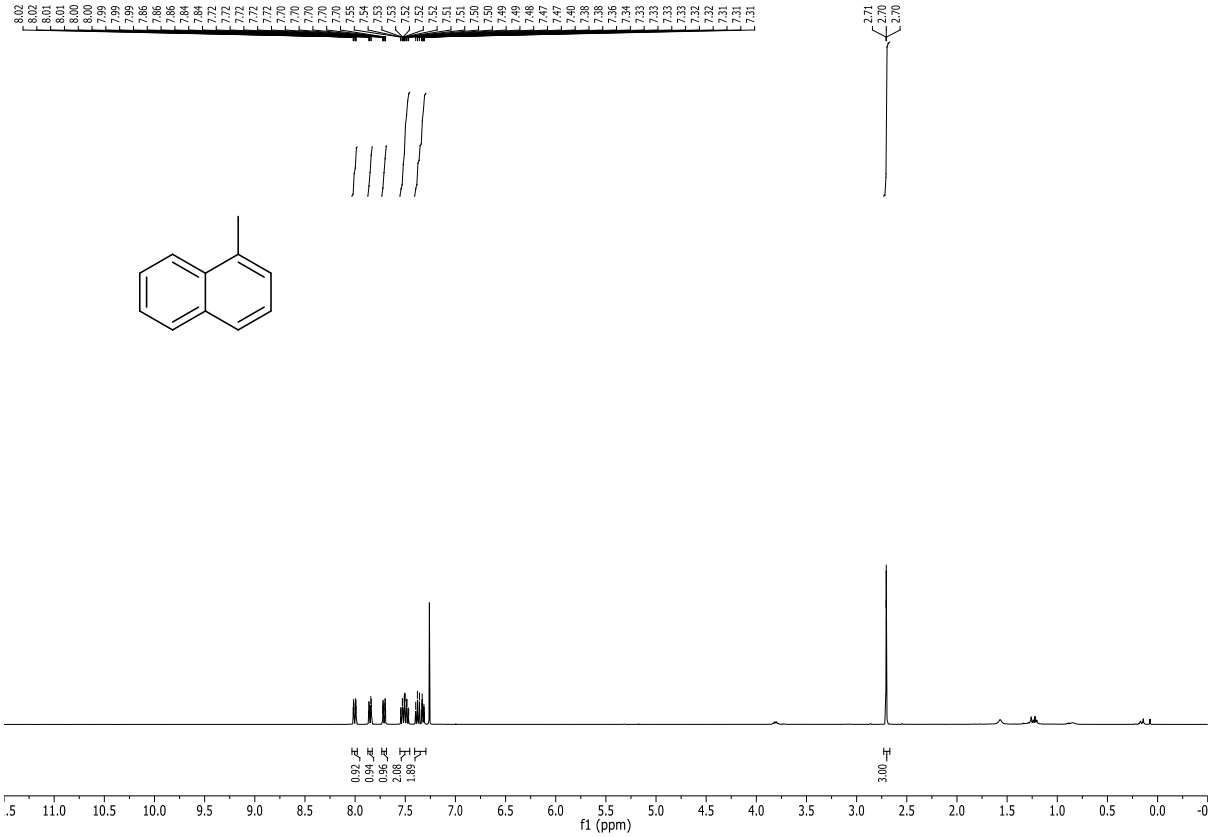
R_f: 0.91 (4:1 Hex:EtOAc)

^{1}H-NMR (400 MHz, Chloroform-d, δ_H/ppm) 8.03 – 7.98 (m, 1H), 7.87 – 7.83 (m, 1H), 7.77 – 7.71 (m, 1H), 7.55 – 7.46 (m, 2H), 7.41 – 7.29 (m, 2H), 2.70 (s, 3H).

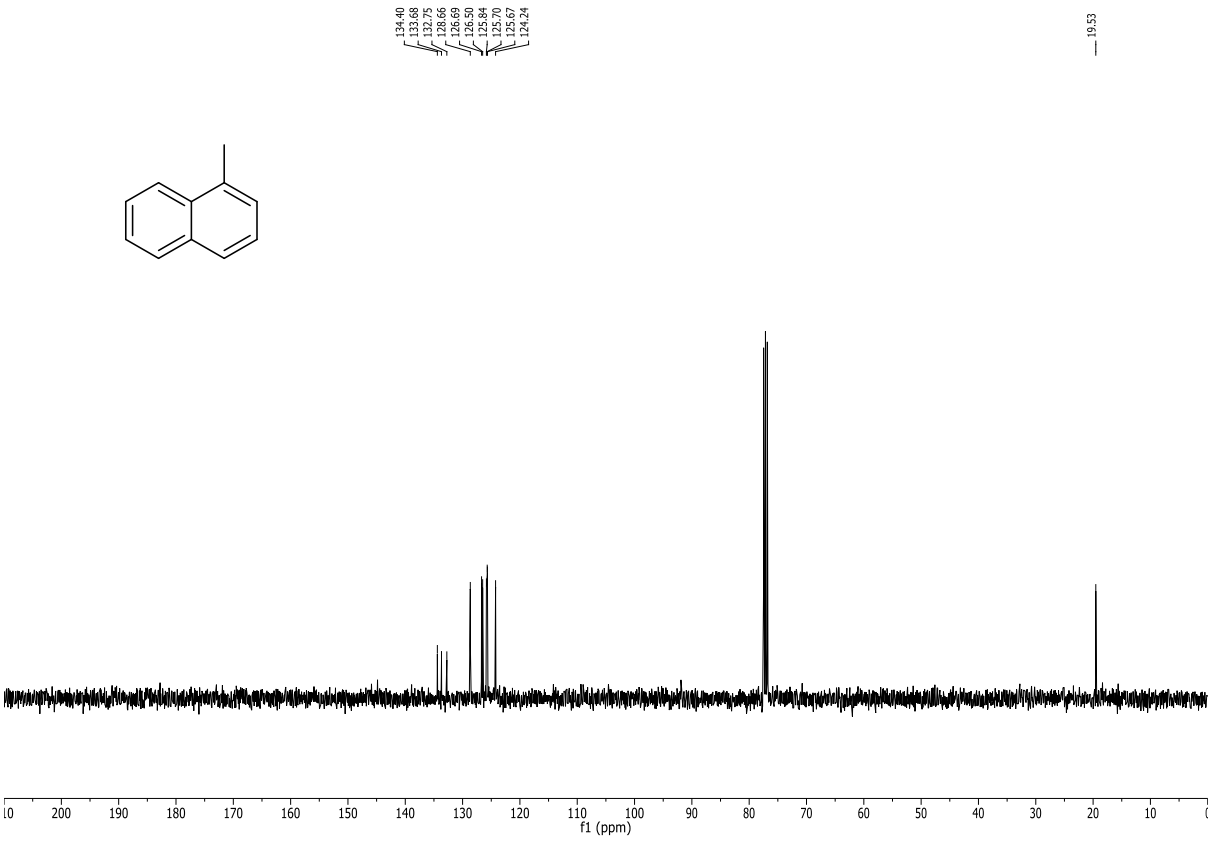
^{13}C-NMR (100 MHz, $CDCl_3$, δ_C/ppm) 134.40, 133.7, 132.8, 128.7, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 19.5.

GC-MS (EI): 142.1 (100, [$M^{+\bullet}$]), 126.0 ([M+•]-[CH_3]), 115.0 ([M+•]-[CH_3]), 102.0 ([M+•]-[$CCHCH_3$])

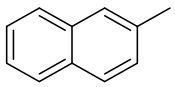
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2j**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2j**



2-methylnaphtalene (2k)



2k

According to **GP2**, 2-methylnaphtalene **(2k)** was synthesized from 2-naphthalenemethanol (158 mg, 1.00 mmol, 1.00 equiv.), over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 4:1) and was afforded as a colorless solid (128 mg, 0.90 mmol, 90%, 95% determined by GC-FID). Analytical data was in accordance with the literature.[14]

$C_{11}H_{10}$ (142.20 g/mol)

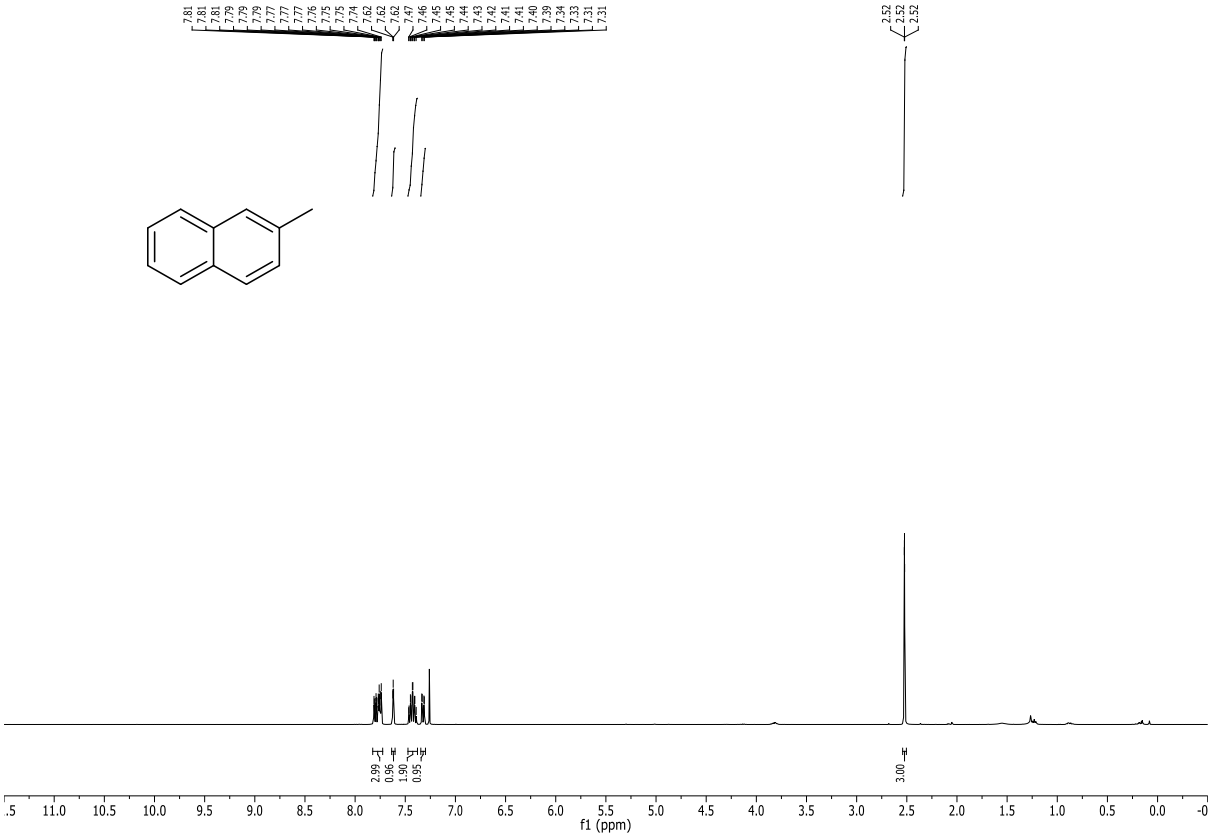
R_f: 0.89 (4:1 Hex:EtOAc)

^{1}H-NMR (400 MHz, Chloroform-d, δ_H/ppm) 7.82 – 7.73 (m, 3H), 7.64 – 7.60 (m, 1H), 7.47 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.4, 1.7 Hz, 1H), 2.52 (s, 3H)

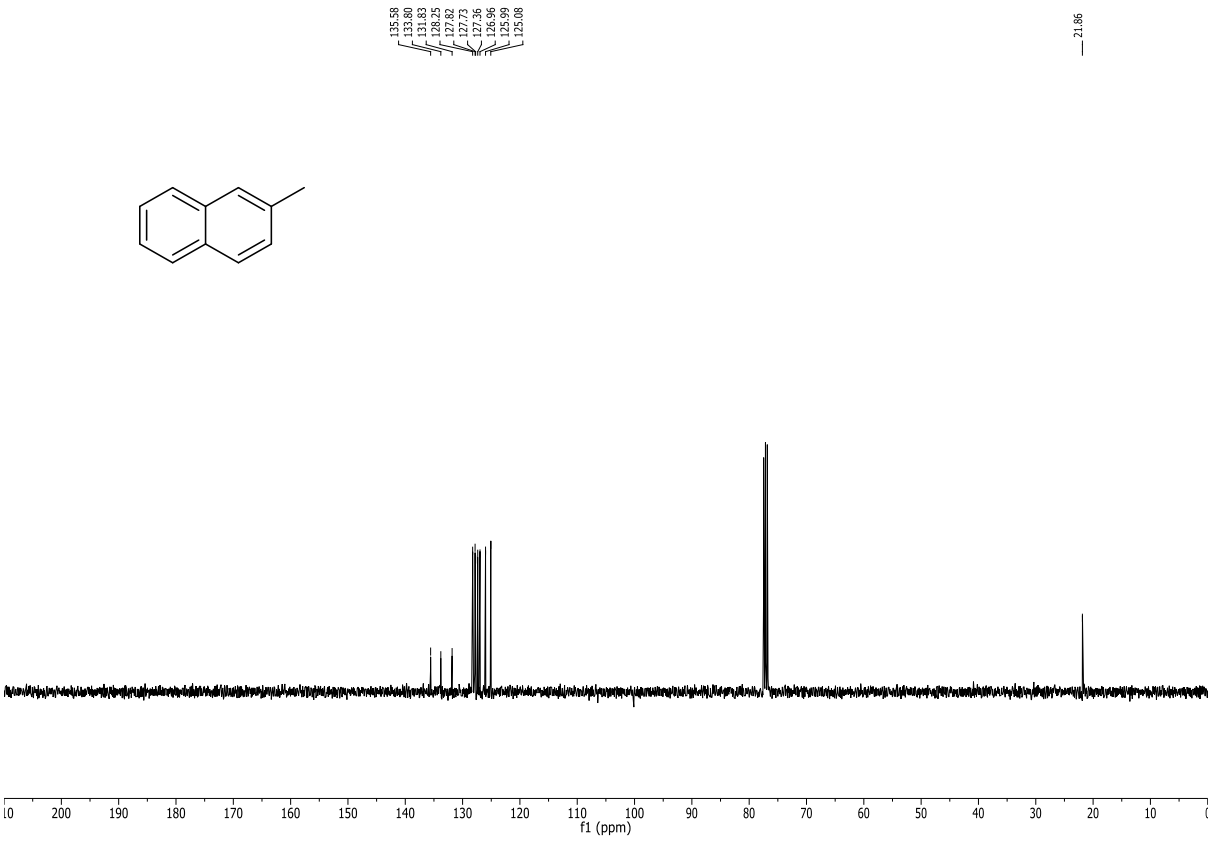
^{13}C-NMR (100 MHz, $CDCl_3$, δ_C/ppm) 135.6, 133.8, 131.8, 128.3, 127.8, 127.7, 127.4, 126.9, 126.0, 125.1, 21.9.

GC-MS (EI): 142.1 (100, [$M^{+\bullet}$]), 126.0 ([M+•]-[CH_3]), 115.0 ([M+•]-[CH_3]), 102.0 ([M+•]-[$CCHCH_3$])

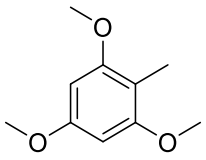
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2k**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2k**



1,2,3-trimethoxy-5-methylbenzene (2l)



2l

According to **GP2**, 1,3,5-trimethoxy-5-methylbenzene **(2l)** was synthesized from (2,4,6-trimethoxyphenyl)methanol (198 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless solid (124 mg, 0.68 mmol, 68%, 73% determined by GC-FID). Analytical data was in accordance with the literature.[15]

$C_{10}H_{14}O_3$ (182.22 g/mol)

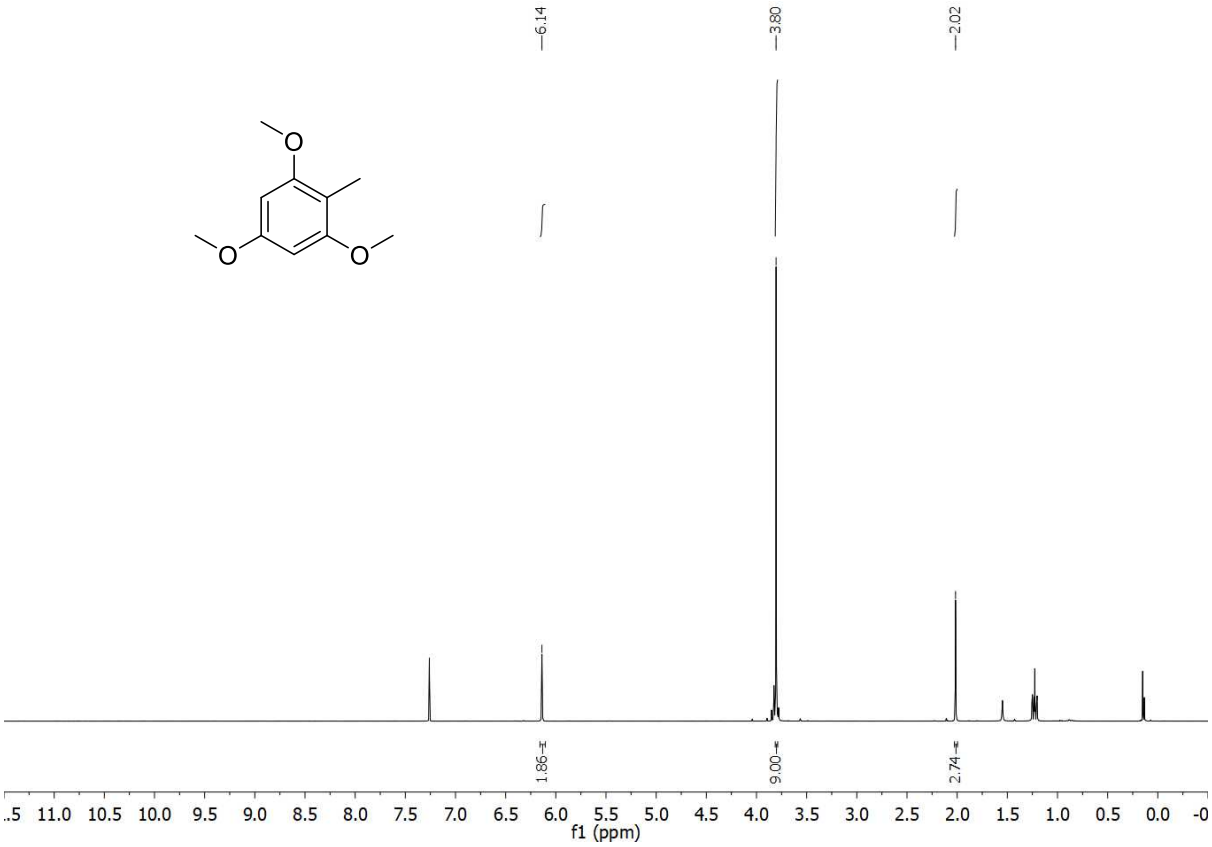
R_f: 0.36 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.14 (s, 2H), 3.80 (s, 9H), 2.02 (s, 3H); Impurity – ethyl acetate

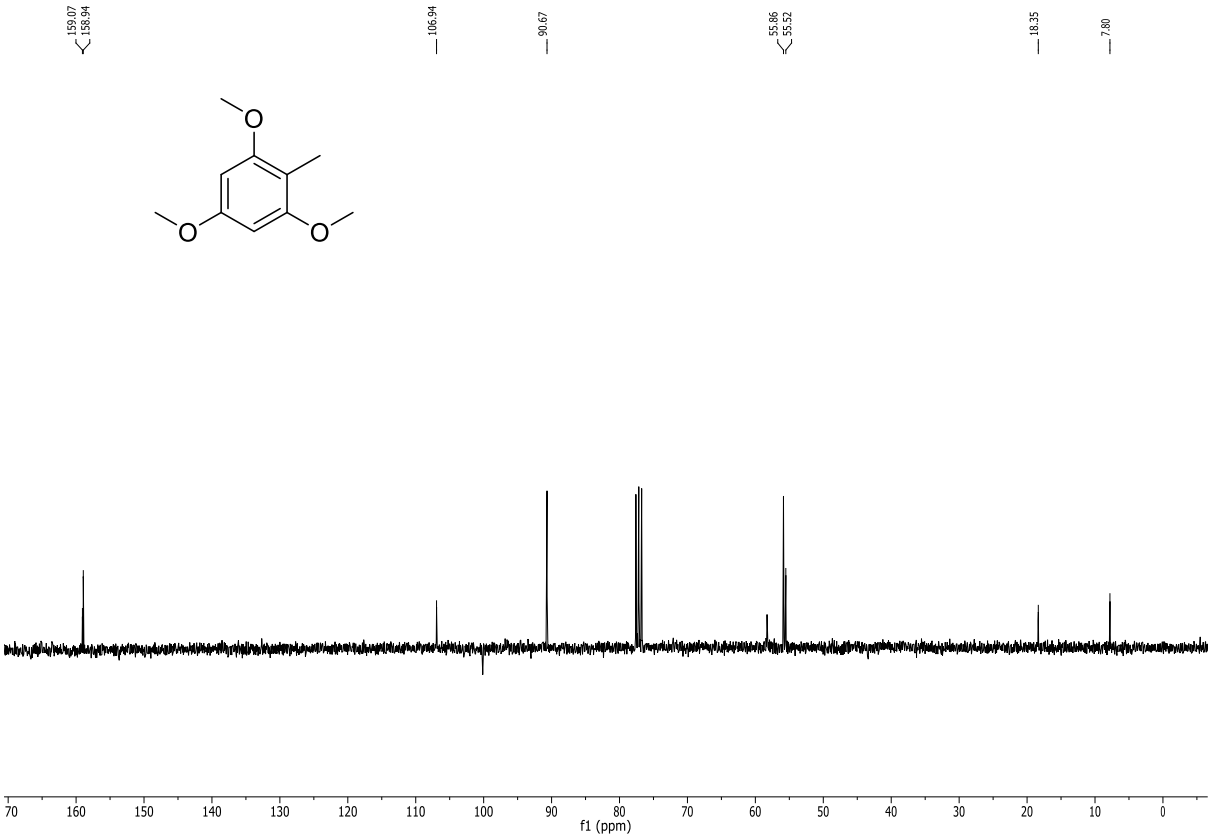
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 158.9, 106.9, 90.7, 58.3, 55.9, 18.4, 7.8.

GC-MS: (EI): m/z = 182.1 (100, $[M^{+\bullet}]$), 167.1 (28, $[M^{+\bullet}]$-$[CH_3^{\bullet}]$), 151.1 (33, $[M^{+\bullet}]$-$[OCH_3^{\bullet}]$)

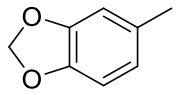
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2l**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2l**



5-methylbenzo[*d*][1,3]dioxole (2n)



2n

According to **GP2**, 5-methylbenzo[*d*][1,3]dioxole **(2n)** was synthesized from piperonyl alcohol (152 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless oil (38 mg, 0.28 mmol, 28%, 94% determined by GC-FID). Analytical data was in accordance with the literature.[16]

$C_8H_8O_2$ (136.15 g/mol)

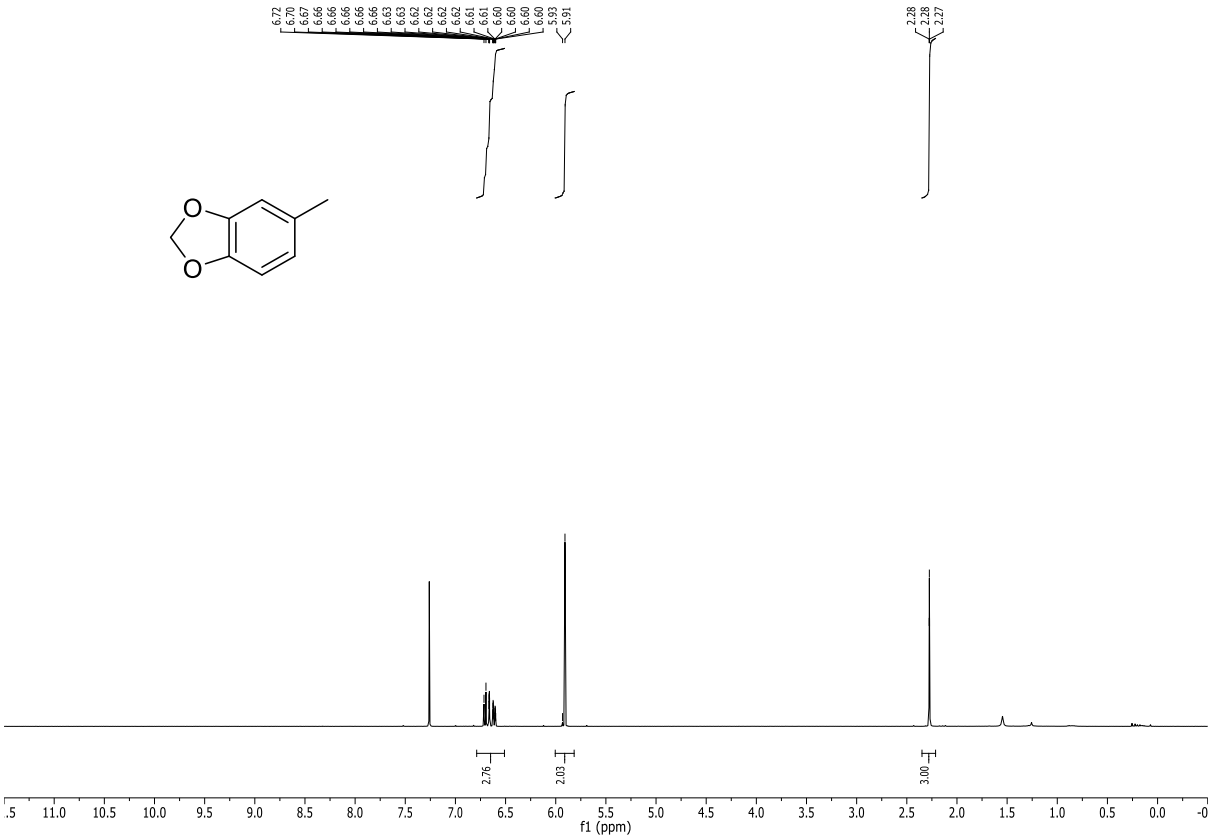
R_f: 0.49 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.72 – 6.70 (m, 1H), 6.67 – 6.66 (m, 1H), 6.63 – 6.60 (m, 1H), 5.91 (s, 2H), 2.28 (s, 3H)

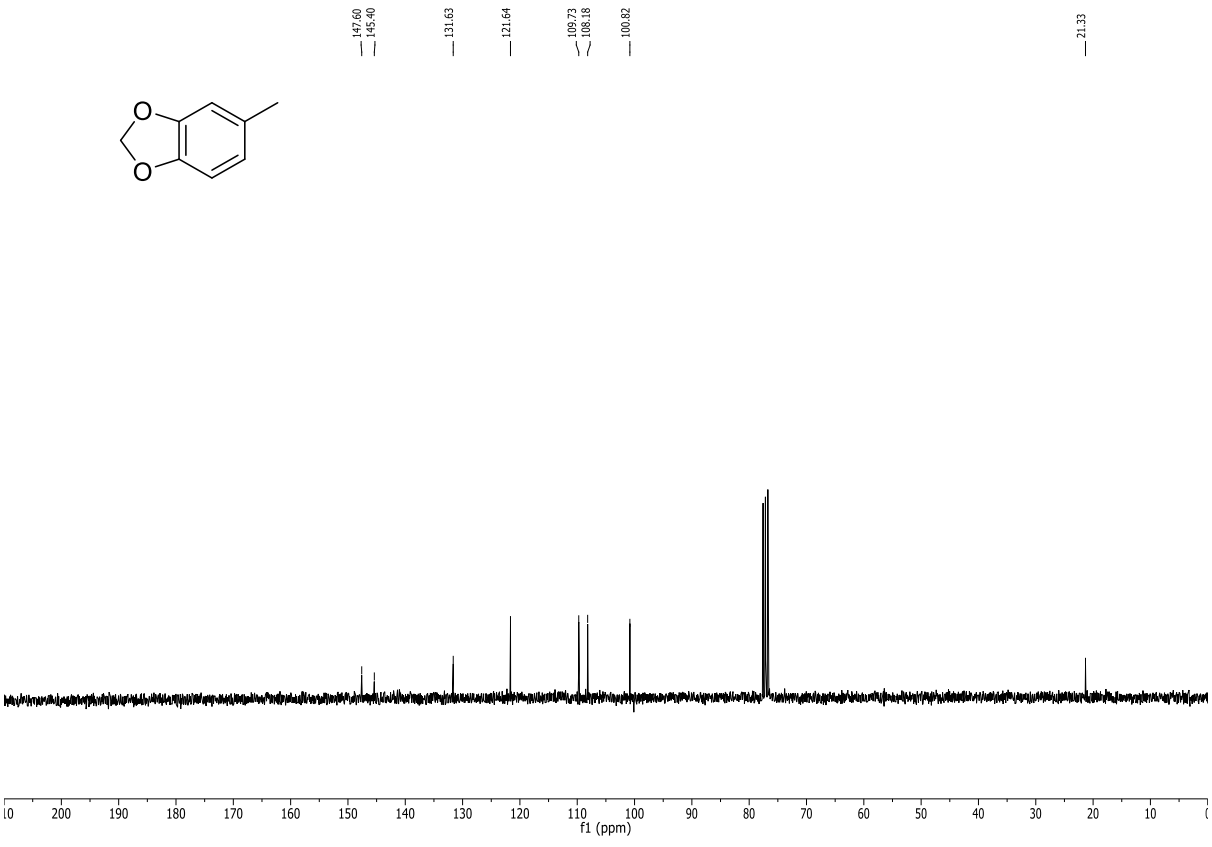
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 147.6, 131.4, 121.6, 109.7, 108.2, 100.8, 31.8, 21.3.

GC-MS: (EI): m/z = 136.0 (100, $[M^{+\bullet}]$), 121.0 (3, $[M^{+\bullet}]$-$[CH_3^\bullet]$), 77.0 (45, $[C_6H_5^\bullet]$)

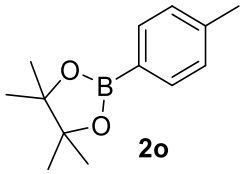
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2n**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2n**



4,4,5,5-tetramethyl-2-(4-methylphenyl)1,3,2-dioxoborolane (2o)



2o

According to **GP2**, 4,4,5,5-tetramethyl-2-(4-methylphenyl)1,3,2-dioxoborolane **(2o)** was synthesized from (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (234 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless solid (205 mg, 0.94 mmol, 94%, 99% determined by GC-FID). Analytical data was in accordance with the literature.[17]

$C_{13}H_{19}BO_2$ (218.10 g/mol)

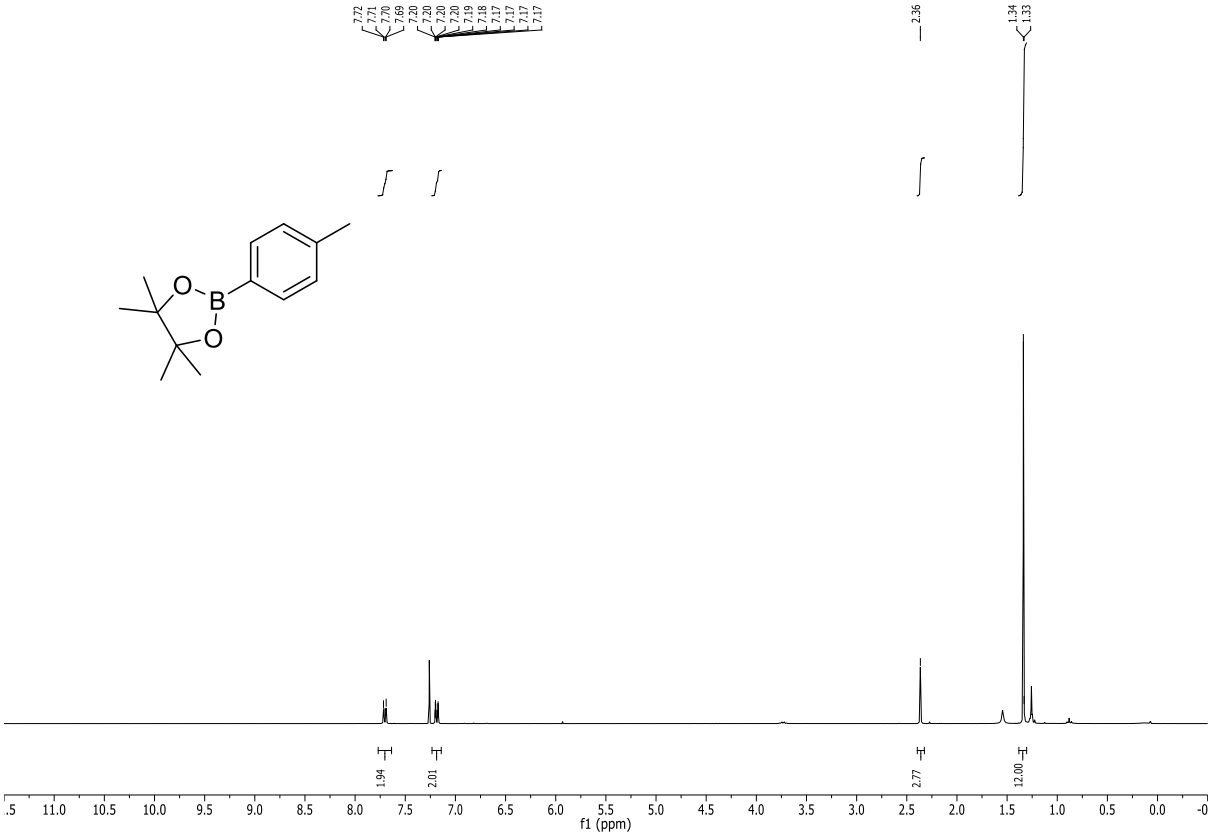
R_f: 0.44 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.70 (d, *J* = 7.5 Hz 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H); Impurity – Pentadecane (internal standard)

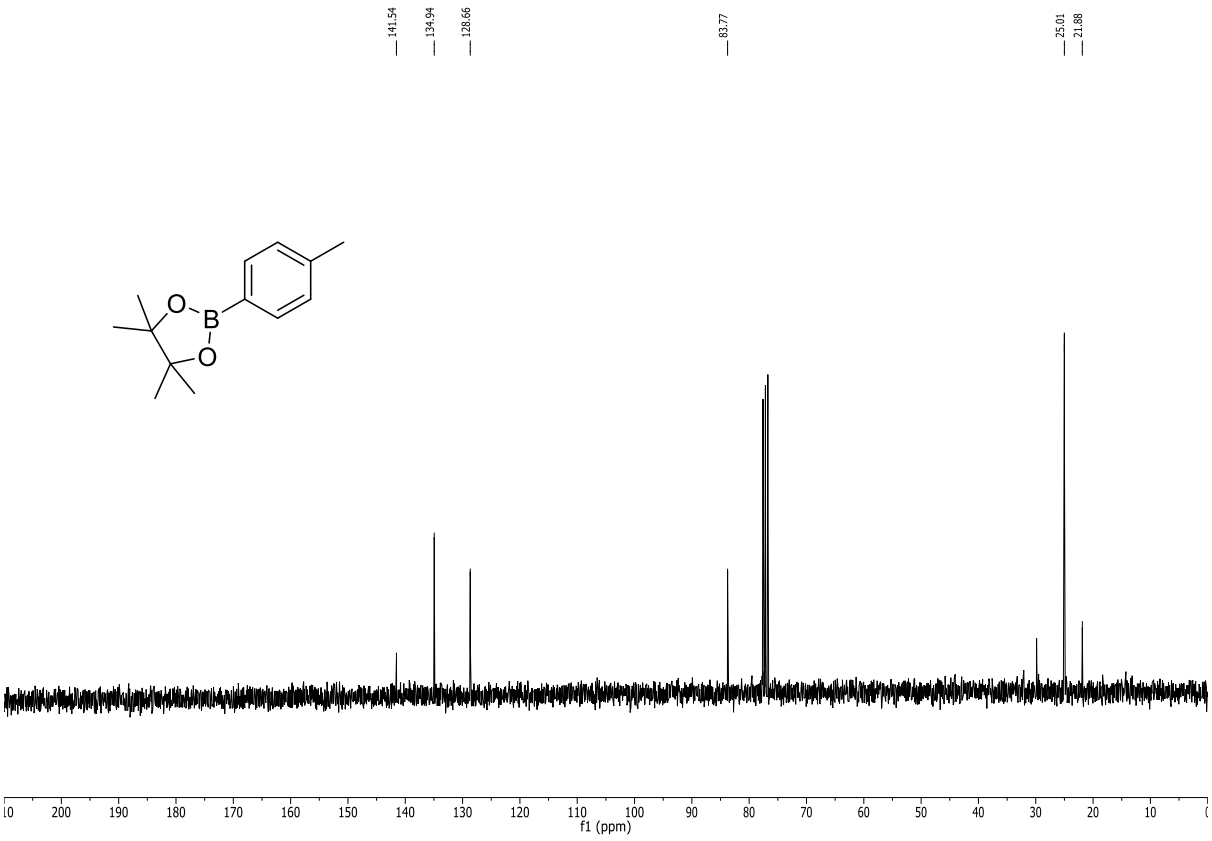
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 141.5, 135.0, 128.7, 83.8, 29.9, 25.0, 21.9.

GC-MS: (EI): m/z = 218.2 (40, $[M^{+\bullet}]$), 203.2 (52, $[M^{+\bullet}]$-$[CH_3^\bullet]$), 119.1 (100, $[M^{+\bullet}]$-$[CH_3^\bullet]$-$[C_2(CH_3)_4^\bullet]$), 91,1 (20, $[M^{+\bullet}]$-$[BO_2C_2(CH_3)_4^\bullet]$)

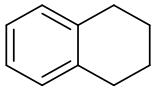
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2o**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2o**



1,2,3,4-tetrahydronaphtalene (2ae)



2ae

According to **GP2**, 1,2,3,4-tetrahydronaphtalene **(2ae)** was synthesized from 1-tetralol (0.136 mL, 148 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless liquid (88 mg, 0.60 mmol, 60%, 86% determined by GC-FID). Analytical data was in accordance with the literature.[18]

$C_{10}H_{12}$ (132.21 g/mol)

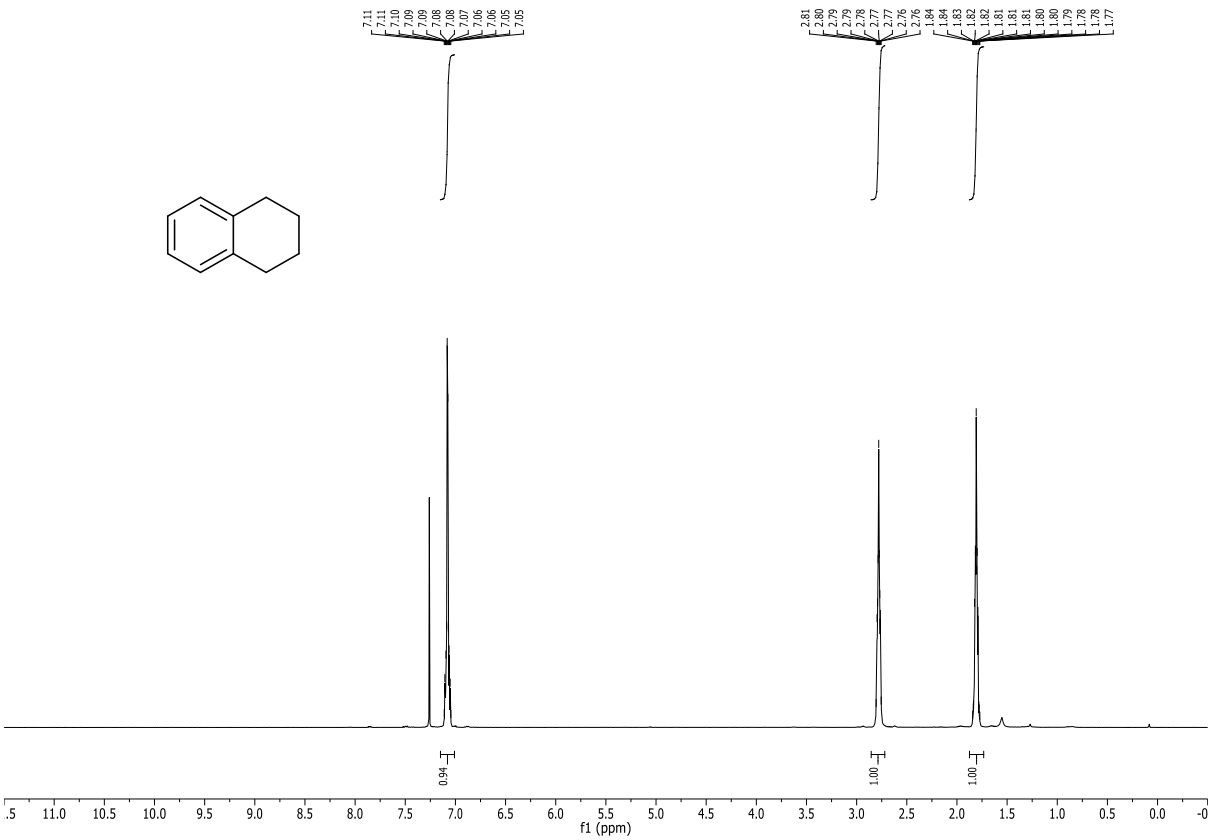
R_f: 0.85 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.09 – 7.06 (m, 4H), 2.81 – 2.76 (m, 4H), 1.84 – 1.77 (m, 4H)

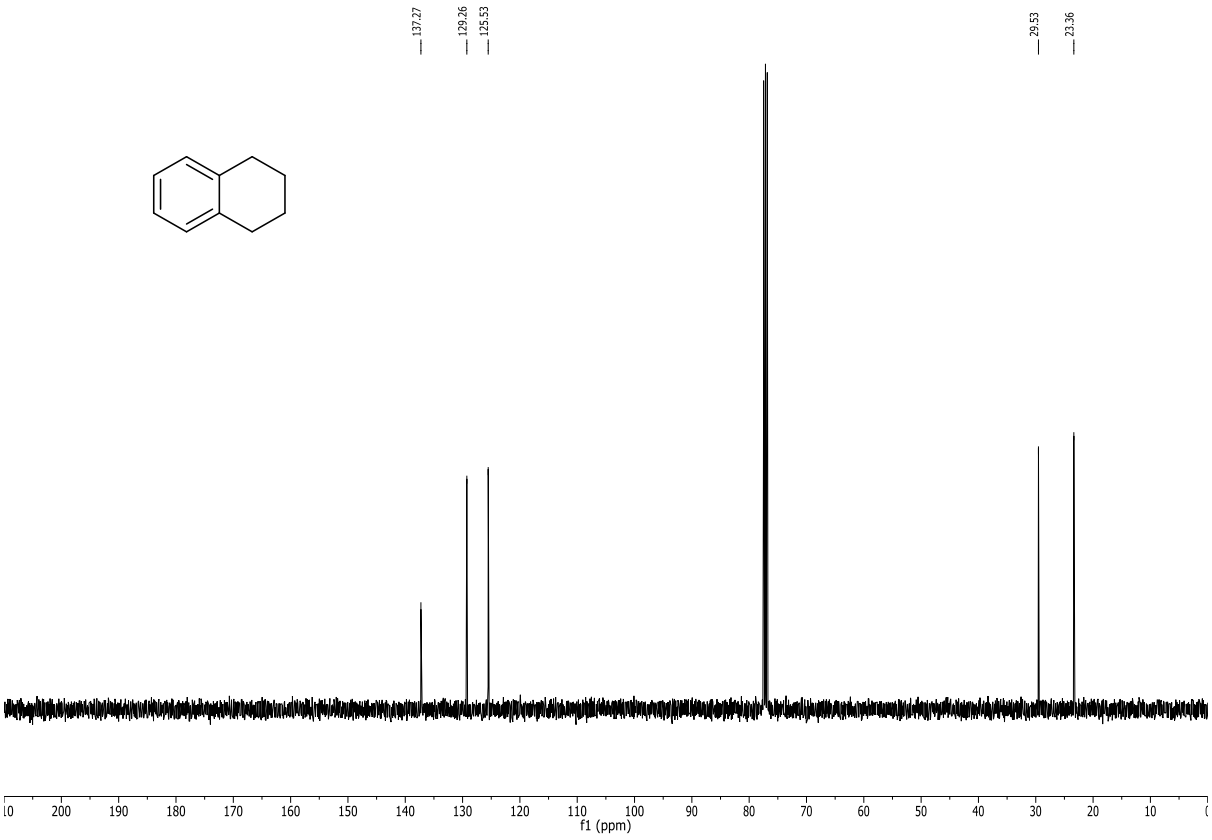
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 137.3, 129.3, 125.5, 29.5, 23.3.

GC-MS: (EI): m/z = 132.1 (43, $[M^{+\bullet}]$), 104.1 (100, $[M^{+\bullet}]$-$[C_2H_4^{\bullet}]$), 91.1 (40, $[M^{+\bullet}]$-$[C_3H_5^{\bullet}]$)

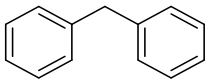
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2ae**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2ae**



diphenylmethane (2ah)



2ah

According to **GP2**, diphenylmethane **(2ah)** was synthesized from benzhydrol (183 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless oil (104 mg, 0.62 mmol, 62%, 75% by GC-FID). Analytical data was in accordance with the literature.[19]

$C_{13}H_{12}$ (168.26 g/mol)

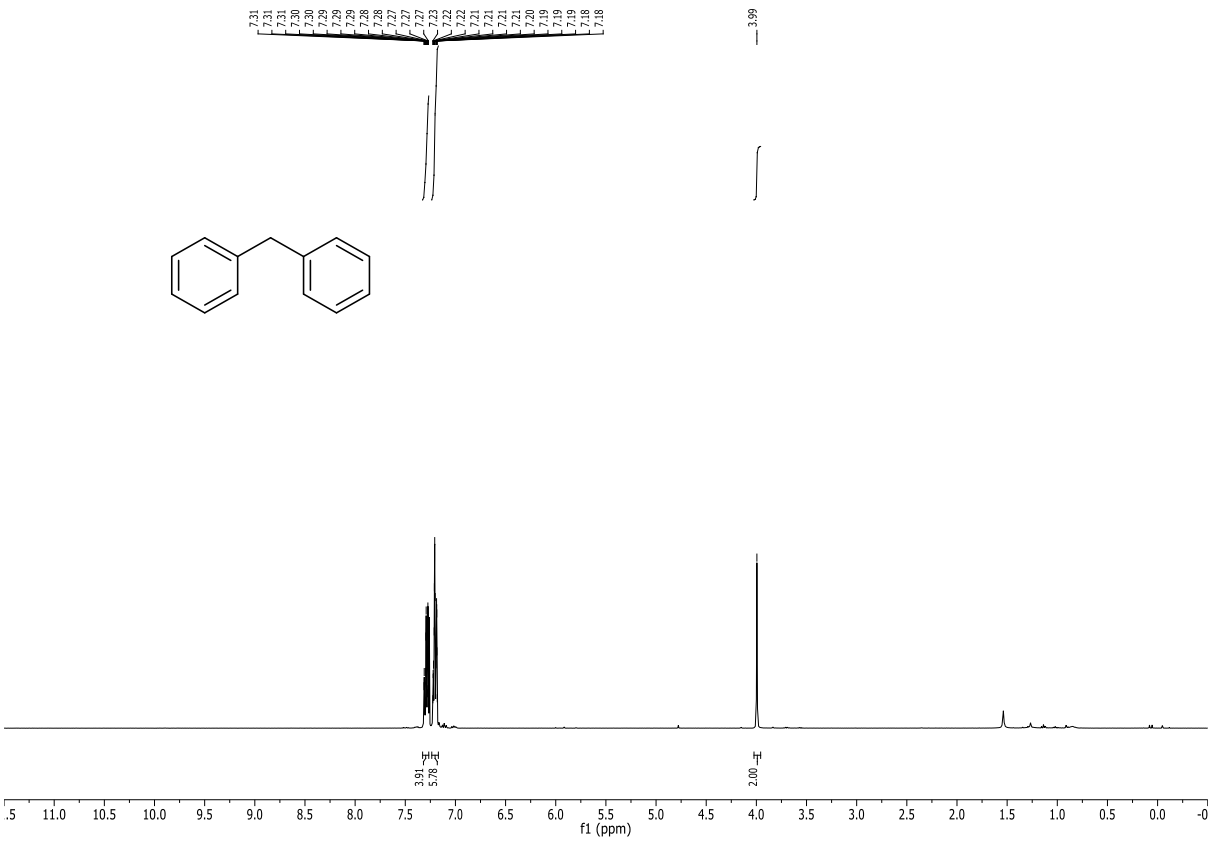
R_f: 0.66 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.31 – 7.27 (m, 4H), 7.22 – 7.19 (m, 6H), 3.99 (s, 2H)

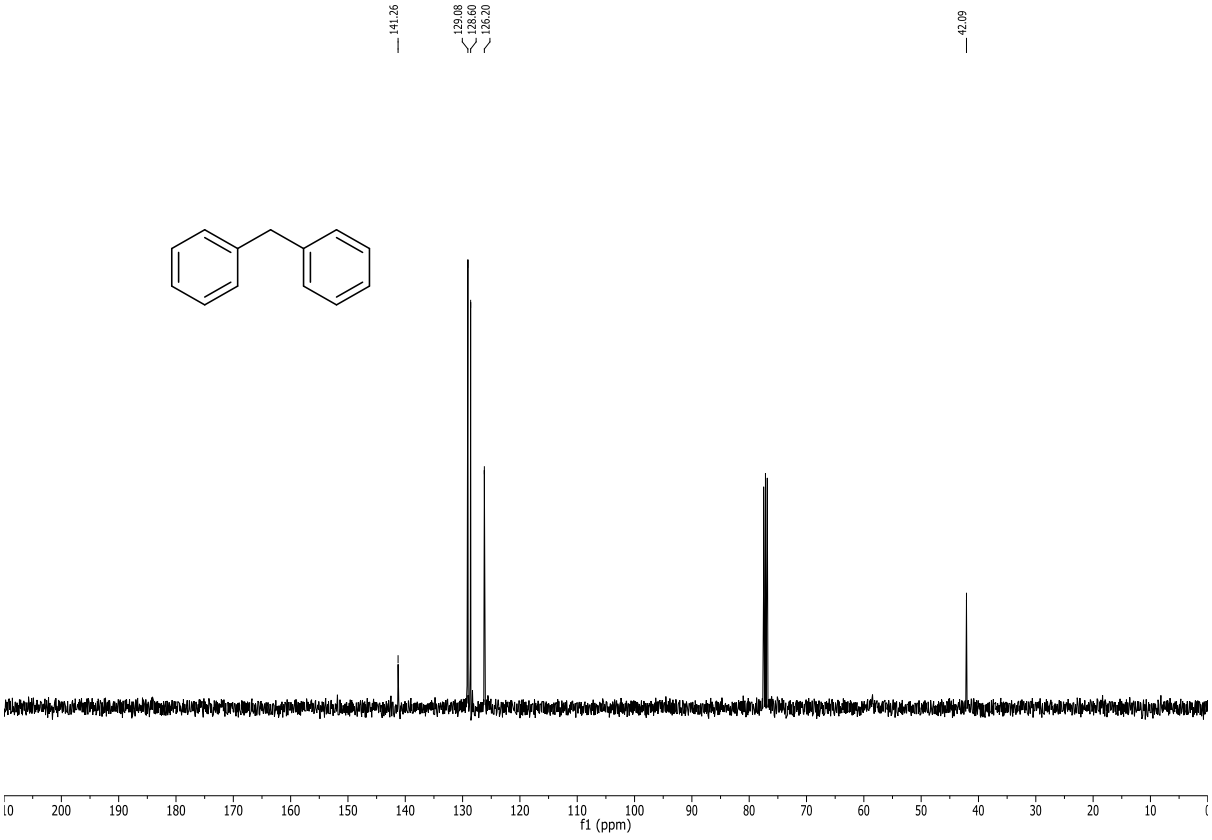
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 141.3, 129.1, 128.6, 126.2, 42.1.

GC-MS: (EI): m/z = 168.1 (100, $[M^{+\bullet}]$), 91.1 (29, $[M^{+\bullet}]$-$[C_6H_5^{\bullet}]$)

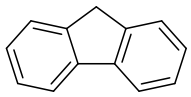
^{1}H-NMR: (400 MHz, $CDCl_3$) of **2ah**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2ah**



9*H*-fluorene (2ai)



2ai

According to **GP2**, 9*H*-fluorene **(2ai)** was synthesized from fluoren-9-ol (182 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless solid (115 mg, 0.69 mmol, 69%, 88% determined by GC-FID). Analytical data was in accordance with the literature.[20]

$C_{13}H_{10}$ (166.22 g/mol)

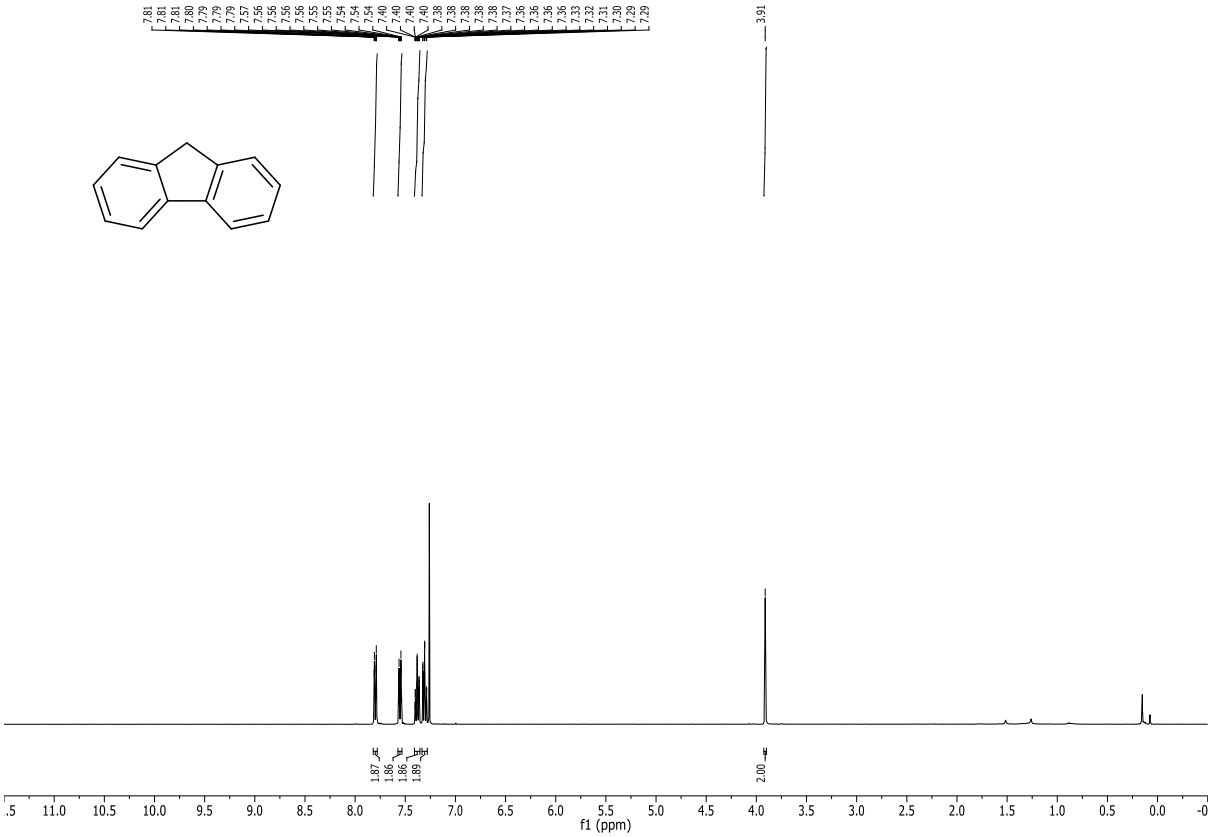
R_f: 0.55 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 7.80 (d, J = 7.7 Hz, 2H), 7.57 – 7.53 (m, 2H), 7.41 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 3.91 (s, 2H).

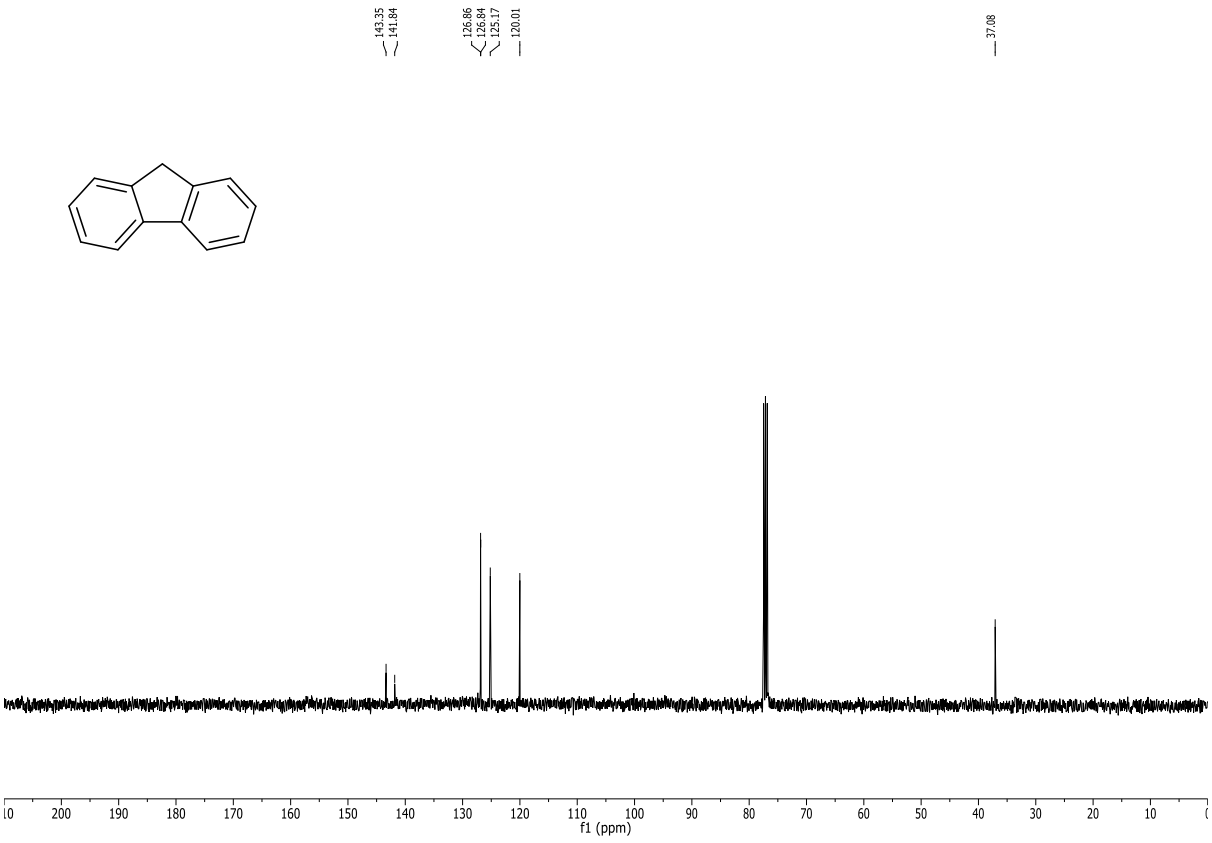
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 143.4, 141.8, 126.9, 126.8, 125.2, 120.0, 37.1.

GC-MS: (EI): m/z = 166.1 (100, $[M^{+\bullet}]$), 165.1 (88, $[M^{+\bullet}]$-$[H^{\bullet}]$)

^{1}H-NMR: (400 MHz, $CDCl_3$) of **2ai**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **2ai**



5.2 Non-Isolated Compounds

toluene (2a)

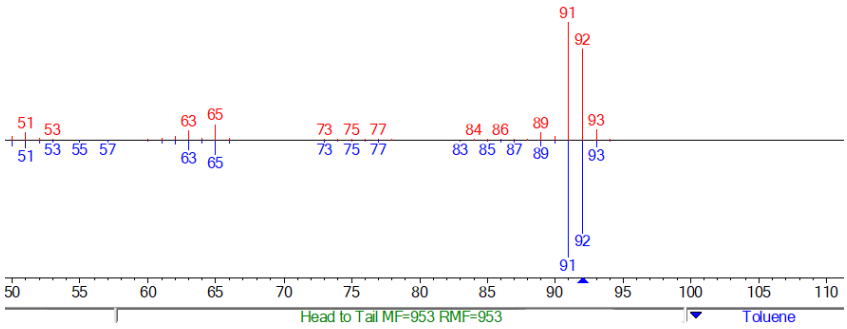
2a

According to **GP2**, toluene (**2a**) was synthesized from benzyl alcohol (0.104 mL, 108 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 97% yield determined by GC-FID.

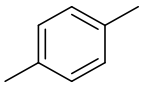
C_7H_8 (92.14 g/mol)

GC-FID: R_t = 3.052 **(M_{FID}1)**; R_t = 4.254 **(M_{FID}2)**

GC-MS: (EI): m/z = 92.1 (70, [$M^{+\bullet}$]), 91.1 (100, [$M^{+\bullet}$]-[$H^{\bullet}$]); R_t = 5.014 **(M_{MS}2)**



***p*-xylene (2b)**



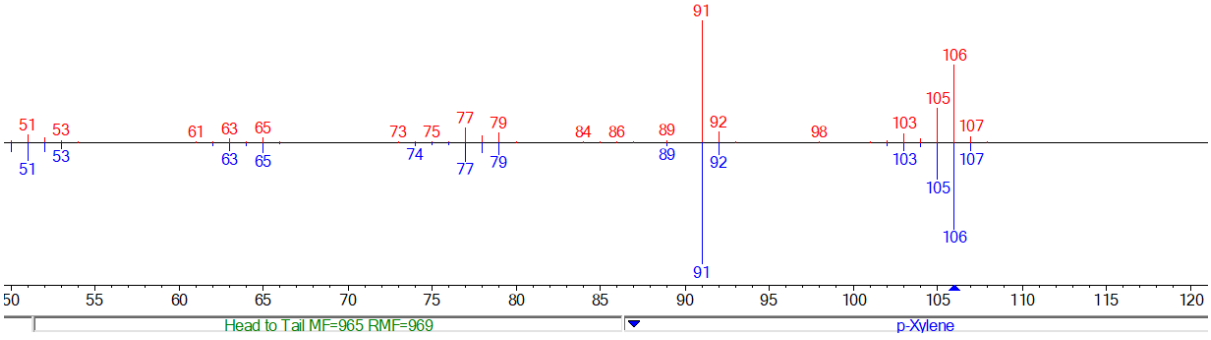
2b

According to **GP2**, *p*-xylene (2b) was synthesized from 4-methylbenzyl alcohol (0.12 mL, 122 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 95% yield determined by GC-FID.

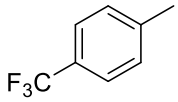
C_8H_{10} (106.17 g/mol)

GC-FID: R_t = 3.617 **(M_{FID}1)**

GC-MS: (EI): m/z = 106.0 (59, [$M^{+\bullet}$]), 91.0 (100, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t = 7.106 **(M_{MS}2)**



1-methyl-4-(trifluoromethyl)benzene (2f)



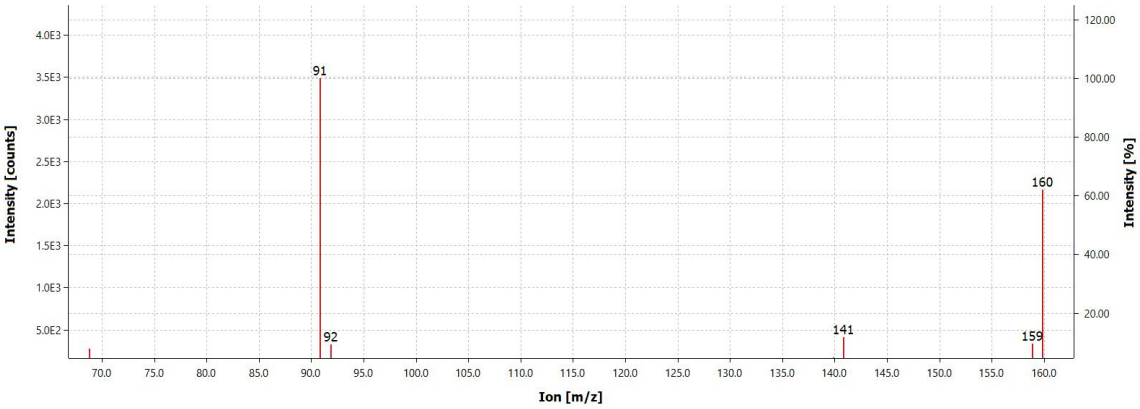
2f

According to **GP2**, 1-methyl-4-(trifluoromethyl)benzene **(2f)** was synthesized from 4-(trifluoromethyl)benzenemethanol (0.137 mL, 176.2 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 86% yield determined by GC-FID.

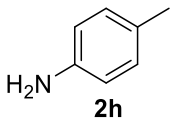
$C_8H_7F_3$ (160.14 g/mol)

GC-FID: R_t = 3.279 **(M_{FID}1)**

GC-MS: (EI): m/z = 159.9 (62, [$M^{+\bullet}$])140.9 (12, [$M^{+\bullet}$]-[$F^{\bullet}$]), 90.9 (100, [$M^{+\bullet}$]-[$CF_3^{\bullet}$]); R_t = 3.757 **(M_{MS}2)**



4-methylaniline (2h)



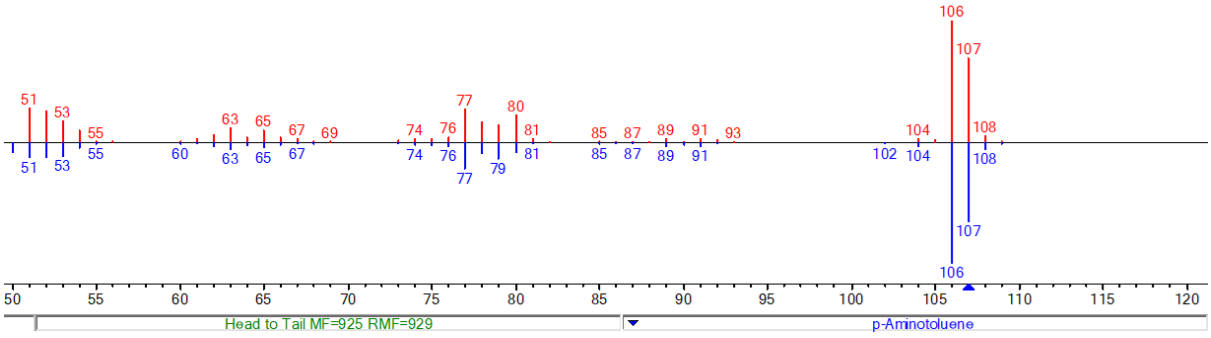
2h

According to **GP2**, 4-methylaniline **(2h)** was synthesized from 4-aminobenzyl alcohol (123.2 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 60% yield determined by GC-FID.

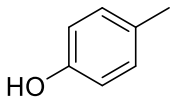
C_7H_9N (107.16 g/mol)

GC-FID: R_t = 5.067 **(M_{FID}1)**

GC-MS: (EI): m/z = 107.0 (70, [$M^{+\bullet}$]), 106.0 [100, $M^{+\bullet}$], 77.0 [26, $M^{+\bullet}$]; R_t = 3.362 **(M_{MS}1)**



***p*-cresol (2i)**



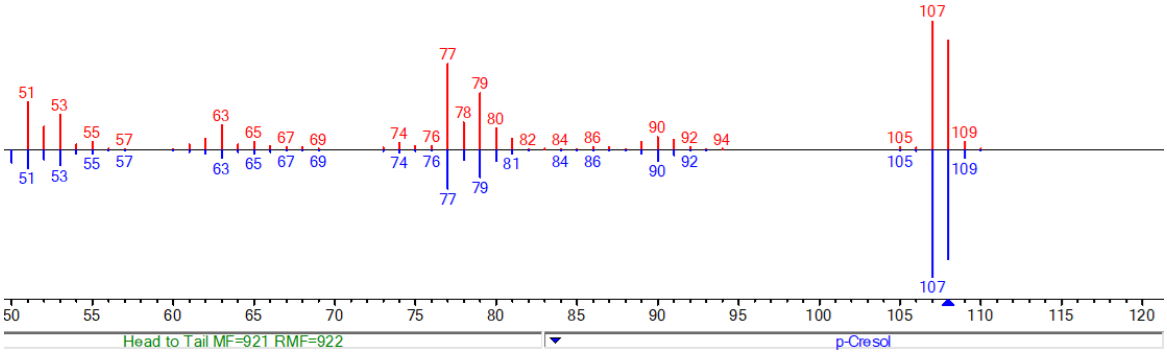
2i

According to **GP2**, *p*-cresol **(2i)** was synthesized from 4-hydroxybenzyl alcohol (124.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 78% yield determined by GC-FID after workup with 1M HCl.

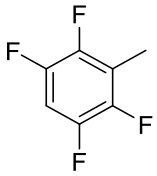
C_7H_8O (108.14 g/mol)

GC-FID: R_t = 5.030 **(M_{FID}1)**

GC-MS: (EI): m/z = 108 (86, $[M^{+\bullet}]$), 107 (100, $[M^{+\bullet}]$-$[H^{\bullet}]$), 90 (11, $[M^{+\bullet}]$-$[OH^{\bullet}]$), 77.0 (66, $[M^{+\bullet}]$-$[CH_3^{\bullet}]$); R_t = 3.316 **(M_{MS}1)**



1,2,4,5-tetrafluoro-3-methylbenzene (2m)



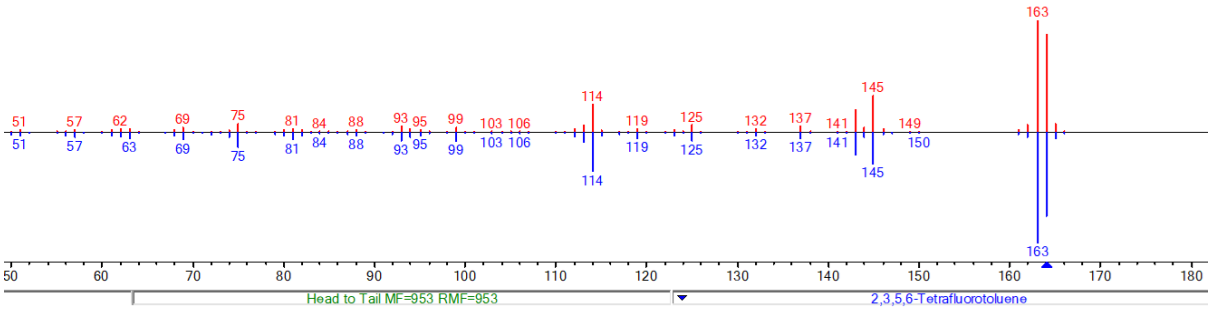
2m

According to **GP2**, 1,2,4,5-tetrafluoro-3-methylbenzene **(2m)** was synthesized from 2,3,5,6-tetrafluorobenzyl alcohol (0.120 mL, 180 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 95% yield determined by GC-FID.

$C_8H_7F_4$ (164.02 g/mol)

GC-FID: R_t = 3.074 **(M_{FID}1)**

GC-MS: (EI): m/z = 164.0 (88, $[M^{+\bullet}]$), 163.0 (100, $[M^{+\bullet}]$-$[H^{\bullet}]$), 145.0 (37, $[M^{+\bullet}]$-$[F^{\bullet}]$); R_t = 5.228 **(M_{MS}2)**



2-methylpyridine (2p)

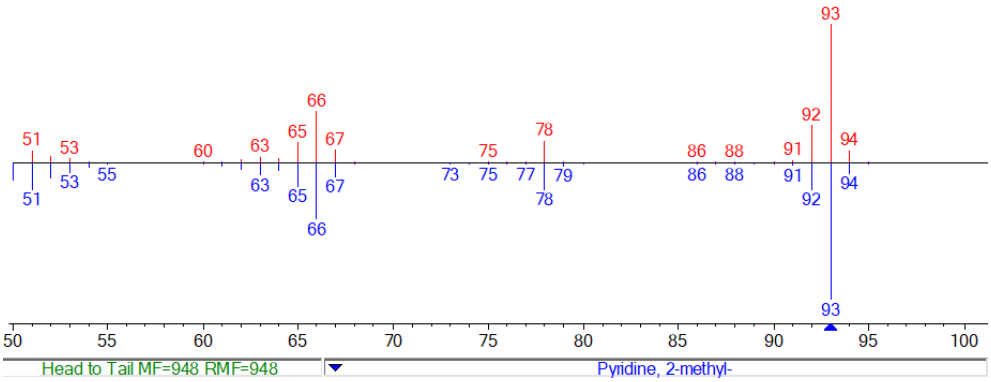
2p

According to **GP2**, 2-methylpyridine **(2p)** was synthesized from pyridine-2-ylmethanol (0.096 mL, 109.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 37% yield determined by GC-FID.

C_6H_7N (93.13 g/mol)

GC-FID: R_t = 3.335 **(M_{FID}1)**

GC-MS: (EI): m/z = 93.0 (100, [$M^{+\bullet}$]), 78.0 (12, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t = 9.562 **(M_{MS}2)**



3-methylpyridine (2q)

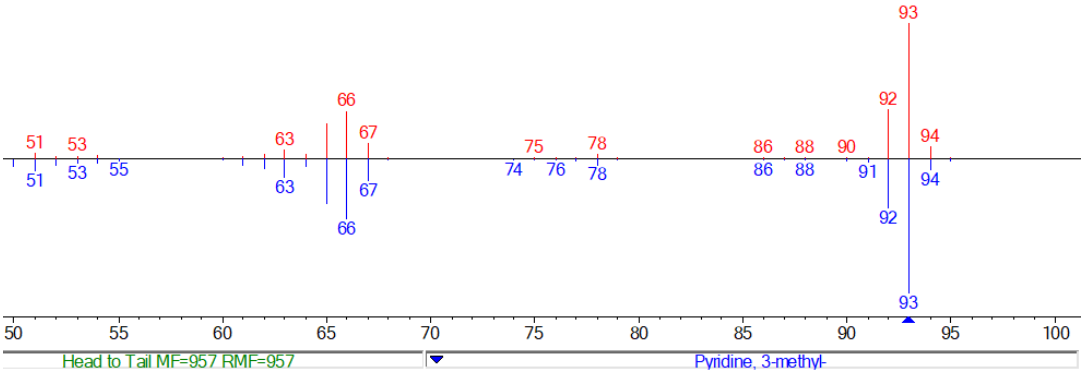
2q

According to **GP2**, 3-methylpyridine **(2q)** was synthesized from pyridine-3-ylmethanol **(1q)** (0.097 mL, 109 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 37% yield determined by GC-FID.

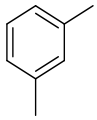
C_6H_7N (93.13 g/mol)

GC-FID: R_t = 3.551 **(M_{FID}1)**

GC-MS: (EI): m/z = 93.0 (100, [$M^{+\bullet}$]), 78.0 (3, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t = 9.847 **(M_{MS}2)**



m-xylene (2r)



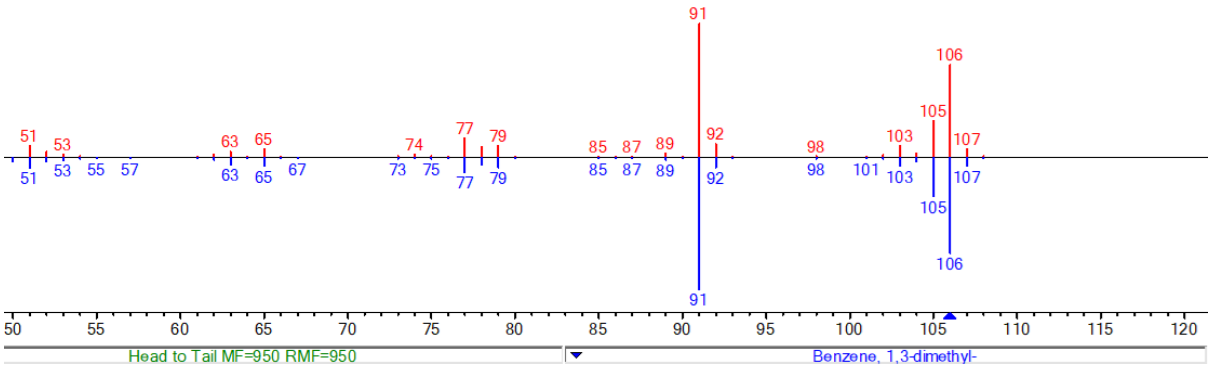
2r

According to **GP2**, m-xylene **(2r)** was synthesized from 3-methylbenzyl alcohol **(1r)** (0.120 mL, 122.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 85% yield determined by GC-FID

C_8H_{10} (106.17 g/mol)

GC-FID: R_t = 3,665 **(M_{FID}1)**

GC-MS: (EI): m/z = 106.0 (56, [$M^{+\bullet}$]), 91.0 (100, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t = 7.158 **(M_{MS}2)**



o-xylene (2s)

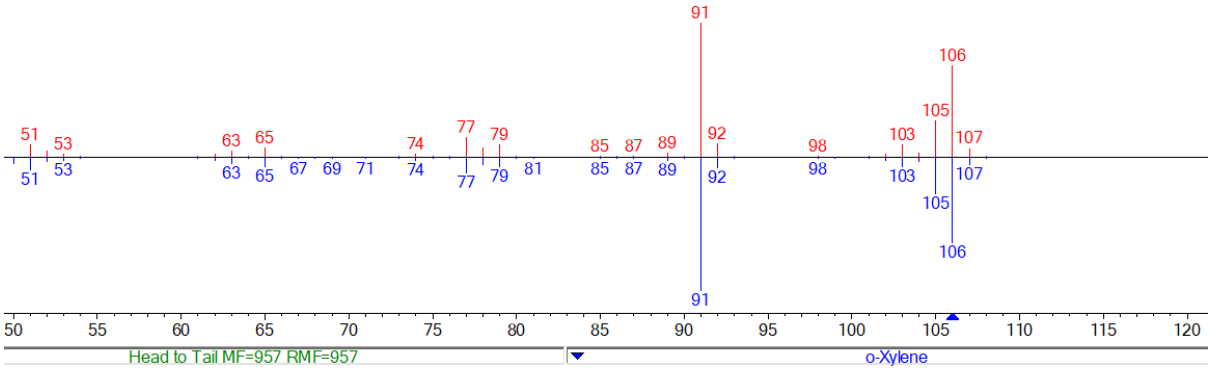
2s

According to **GP2**, o-xylene **(2s)** was synthesized from 2-methylbenzyl alcohol (0.120 mL, 122.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 90% yield determined by GC-FID.

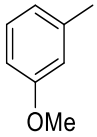
C_8H_{10} (106.17 g/mol)

GC-FID: R_t = 3.790 **(M_{FID}1)**

GC-MS: (EI): m/z = 106.1 (68, [$M^{+\bullet}$]), 91.1 (100, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t = 7.635 **(M_{MS}2)**



3-methylanisole (2t)



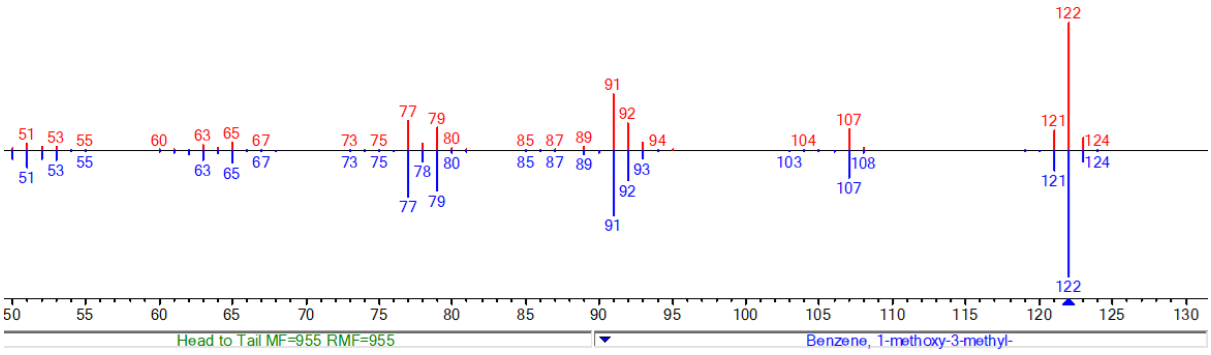
2t

According to **GP2**, 3-methylanisole **(2t)** was synthesized from 3-methoxybenzyl alcohol (0.110 mL, 138.1 mg, 1 mmol, 1 equiv.) over 16 h. The product was afforded in 85% yield determined by GC-FID.

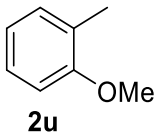
$C_8H_{10}O$ (122.07 g/mol)

GC-FID: R_t = 4.667 **(M_{FID}1)**

GC-MS: (EI): m/z = 122.1 (100, [$M^{+\bullet}$]), 107.0 (45, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]), 91.0 (31, [$M^{+\bullet}$]-[$OCH_3^{\bullet}$]); R_t = 9.961 **(M_{MS}2)**



2-methylanisole (2u)



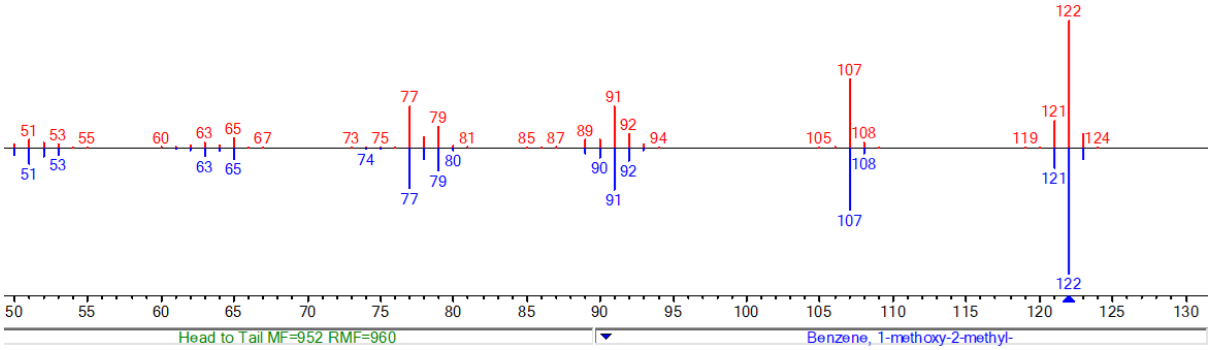
2u

According to **GP2**, 2-methylanisole **(2u)** was synthesized from 2-methoxybenzyl alcohol (0.110 mL, 138.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 90% yield determined by GC-FID.

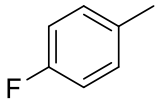
$C_8H_{10}O$ (122.07 g/mol)

GC-FID: R_t = 4.591 **(M_{FID}1)**

GC-MS: (EI): m/z = 122.1 (100, [$M^{+\bullet}$]), 107.0 (53, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]), 91.0 (33, [$M^{+\bullet}$]-[$OCH_3^{\bullet}$]); R_t = 9.884 **(M_{MS}2)**



4-fluorotoluene (2v)



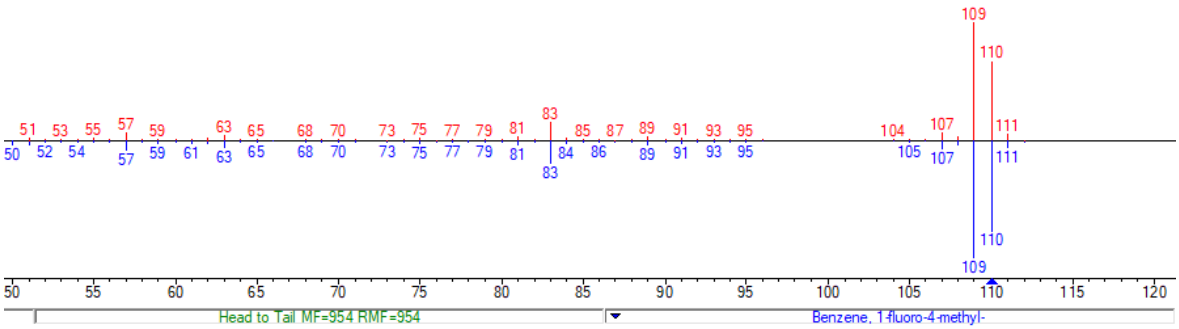
2v

According to **GP2**, 4-fluorotoluene **(2v)** was synthesized from 4-fluorobenzyl alcohol (0.107 mL, 126.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 95% yield determined by GC-FID.

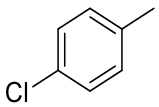
C_7H_7F (110.13 g/mol)

GC-FID: R_t = 3.122 **(M_{FID}1)**

GC-MS: (EI): m/z = 110.0 (63, [$M^{+\bullet}$]), 109.1 [100, [$M^{+\bullet}$]-[$H^{\bullet}$])]; R_t = 5.092 **(M_{MS}2)**



4-chlorotoluene (2w)



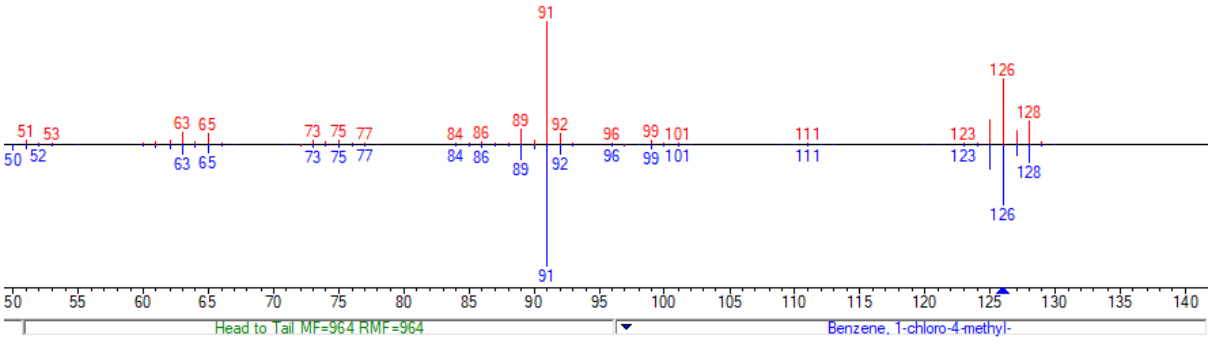
2w

According to **GP2**, 4-chlorotoluene **(2w)** was synthesized from 4-chlorobenzyl alcohol (142.5 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 56% yield determined by GC-FID.

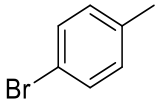
C_7H_7Cl (126.58 g/mol)

GC-FID: R_t = 4.232 **(M_{FID}1)**

GC-MS: (EI): m/z = 128.0 (17, [$M^{+\bullet}$]), 126.0 [50, $M^{+\bullet}$], 91.1 (100, [$M^{+\bullet}$]-[$Cl^{\bullet}$]); R_t = 8.835 **(M_{MS}2)**



4-bromotoluene (2x)



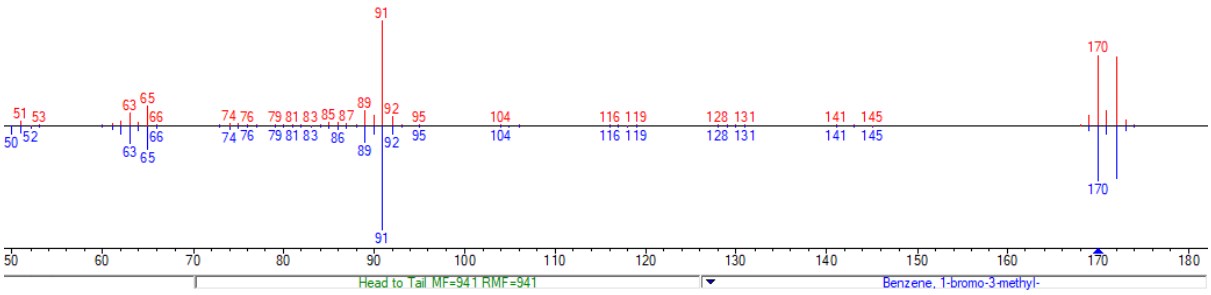
2x

According to **GP2**, 4-bromotoluene **(2x)** was synthesized from 4-bromobenzyl alcohol (176 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 56% yield determined by GC-FID.

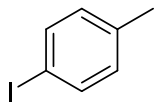
C_7H_7Br (171.04 g/mol)

GC-FID: R_t = 4.873 **(M_{FID}1)**

GC-MS: (EI): m/z = 172.0 (64, [$M^{+\bullet}$]), 170.0 (63, [$M^{+\bullet}$]), 91.1 (100, [$M^{+\bullet}$]-[$Br^{\bullet}$]); R_t = 10.458 **(M_{MS}2)**



4-iodotoluene (2y)



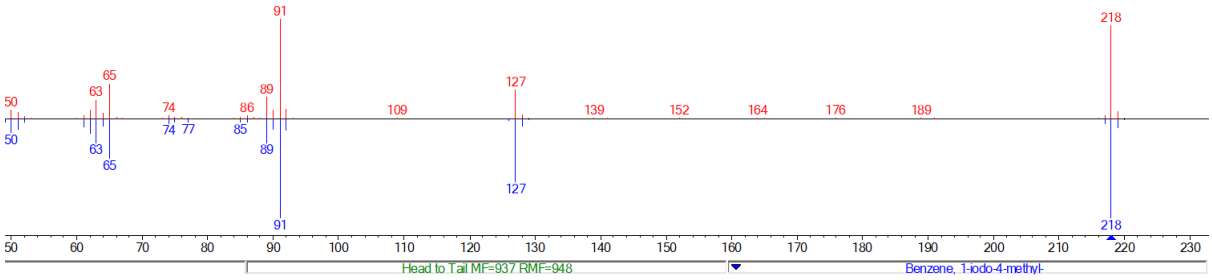
2y

According to **GP2**, 4-iodotoluene **(2y)** was synthesized from 4-iodobenzyl alcohol (234 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 41% yield determined by GC-FID.

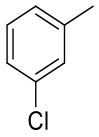
C_7H_7I (218.04 g/mol)

GC-FID: R_t = 9.763 **(M_{FID}2)**

GC-MS: (EI): m/z = 217.9.0 (93, [$M^{+\bullet}$]), 126.8 [27, [$I^{\bullet}$]-[$M^{+\bullet}$]], 91.0 (100, [$M^{+\bullet}$]-[$I^{\bullet}$]); R_t = 3.934 **(M_{MS}1)**



1-chloro-3-methylbenzene (2z)



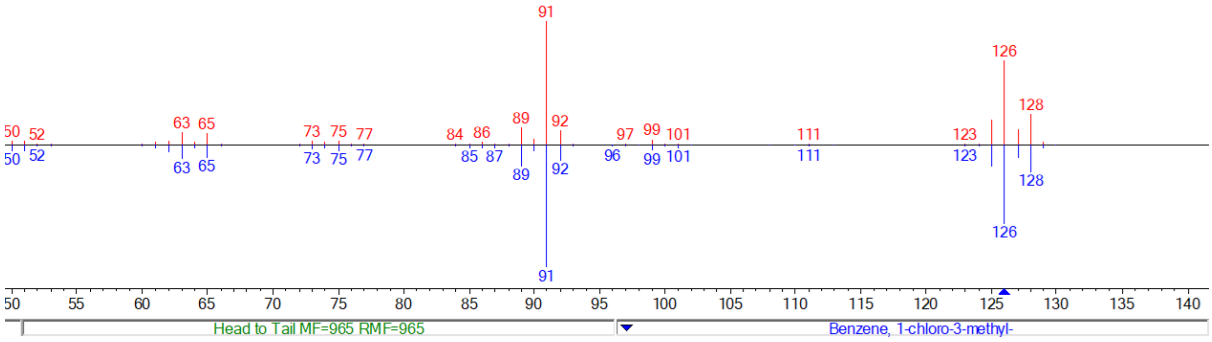
2z

According to **GP2**, 1-chloro-3-methylbenzene **(2z)** was synthesized from 3-chlorobenzyl alcohol **(1z)** (142.5 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 85% yield determined by GC-FID.

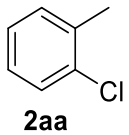
C_7H_7Cl (126.58 g/mol)

GC-FID: R_t = 4.218 **(M_{FID}1)**

GC-MS: (EI): m/z = 128.0 (19, [$M^{+\bullet}$]), 126.0 [56, $M^{+\bullet}$], 91.0 ([$M^{+\bullet}$]-[$Cl^{\bullet}$]); R_t = 8.704 **(M_{MS}2)**



1-chloro-2-methylbenzene (2aa)



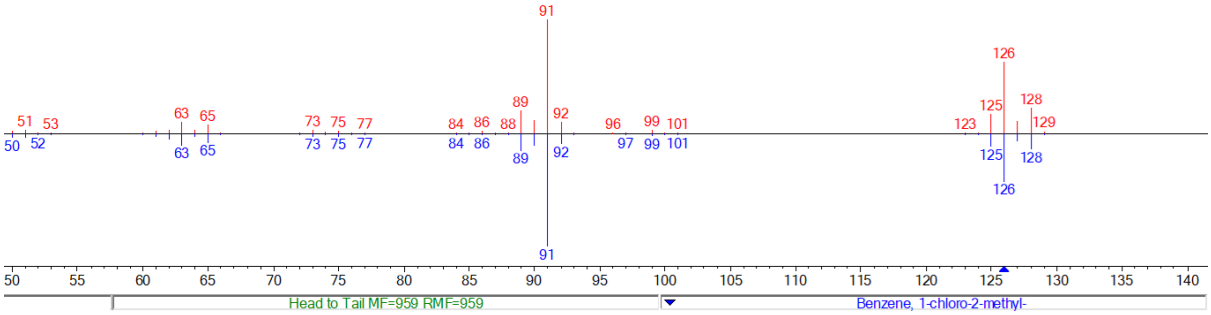
2aa

According to **GP2**, 1-chloro-2-methylbenzene **(2aa)** was synthesized from 2-chlorobenzyl alcohol (142.5 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 85% yield determined by GC-FID.

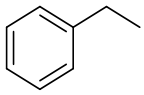
C_7H_7Cl (126.58 g/mol)

GC-FID: R_t = 4.191 **(M_{FID}1)**

GC-MS: (EI): m/z = 128.0 (16, [$M^{+\bullet}$]) 126.0 (49, [$M^{+\bullet}$]), 91.0 (100, [$M^{+\bullet}$]-[$Cl^{\bullet}$]); R_t = 8.704 **(M_{MS}2)**



ethylbenzene (2ac)



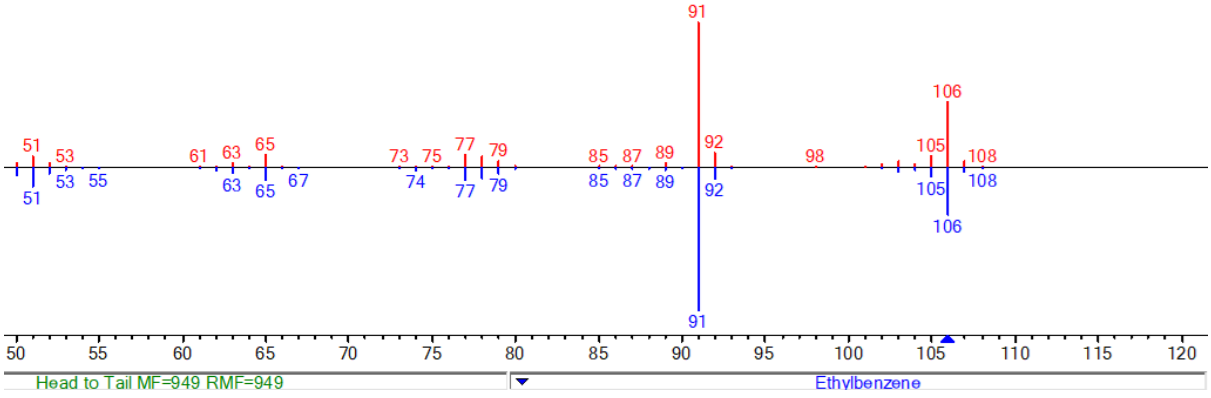
2ac

According to **GP2**, ethylbenzene **(2ac)** was synthesized from 1-phenylethanol (0.120 mL, 122.1 mg, 1.00 mmol, 1.00 equiv.) and from styrene (0.115 mL, 104.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 78% (from 1-phenylethanol) and 72% (from styrene) yield determined by GC-FID.

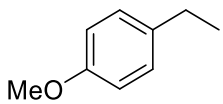
C_8H_{10} (106.17 g/mol)

GC-FID: R_t = 3.582 **(M_{FID}1)**

GC-MS: (EI): m/z = 106.1 (46, [$M^{+\bullet}$]), 91.1 (100, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]), 77.0 (10, [$M^{+\bullet}$]-[$C_2H_5^{\bullet}$]); R_t = 6.985 **(M_{MS}2)**



1-ethyl-4-methoxybenzene (2ad)



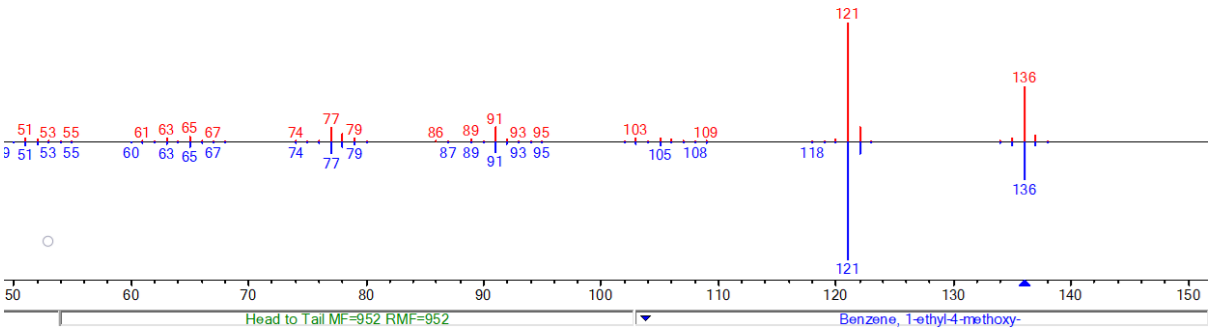
2ad

According to **GP2**, 1-ethyl-4-methoxybenzene **(2ad)** was synthesized from 1-(4-methoxyphenyl)ethanol (0.140 mL, 152 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 67% yield determined by GC-FID.

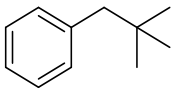
$C_9H_{12}O$ (122.07 g/mol)

GC-FID: R_t = 5.355 **(M_{FID}1)**

GC-MS: (EI): m/z = 136.1 (42, [$M^{+\bullet}$]), 121.1 (100, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]), 77.0 (11, [$M^{+\bullet}$]-[$OCH_3^{\bullet}$]); R_t =11.616 **(M_{MS}2)**



2,2-dimethylpropylbenzene (2af)



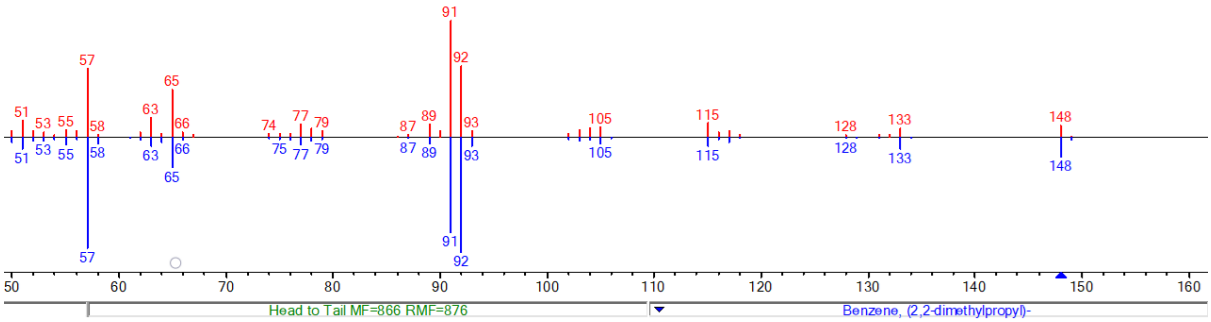
2af

According to **GP2**, 2,2-dimethylpropylbenzene **(2af)** was synthesized from 2,2-dimethyl-1-phenylpropan-1-ol **(1af)** (164.3 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 23% yield determined by GC-FID.

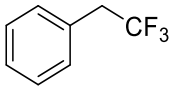
$C_{11}H_{16}$ (148.25 g/mol)

GC-FID: R_t = 4.963 **(M_{FID}1)**

GC-MS: (EI): m/z = 148.0 (10, [$M^{+\bullet}$]), 91.0 (100, [$M^{+\bullet}$]-[$C(CH_3)_3^{\bullet}$]), 77.0 (7, [$M^{+\bullet}$]-[$C(CH_3)_3^{\bullet}$]-[$CH_2^{\bullet}$]); R_t = 3.293 **(M_{MS}1)**



2,2,2-trifluoroethylbenzene (2ag)



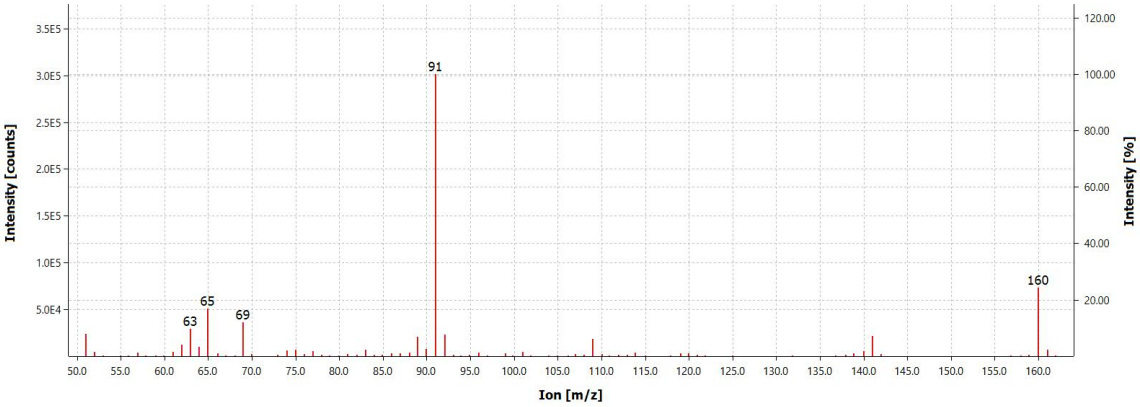
2ag

According to **GP2**, 2,2,2-trifluoroethylbenzene **(2ag)** was synthesized from 2,2,2-trifluoro-1-phenylethanol **(1ag)** (176.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 31% yield determined by GC-FID.

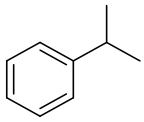
$C_8H_7F_3$ (160.14 g/mol)

GC-FID: R_t = 3.561 **(M_{FID}1)**

GC-MS: (EI): m/z = 160.0 (23, [$M^{+\bullet}$]), 141.0 (7, [$M^{+\bullet}$]-[$F^{\bullet}$]), 91.0 (100, [$M^{+\bullet}$]-[$CF_3^{\bullet}$]); R_t = 4.237 **(M_{MS}3)**



cumene (2aj)



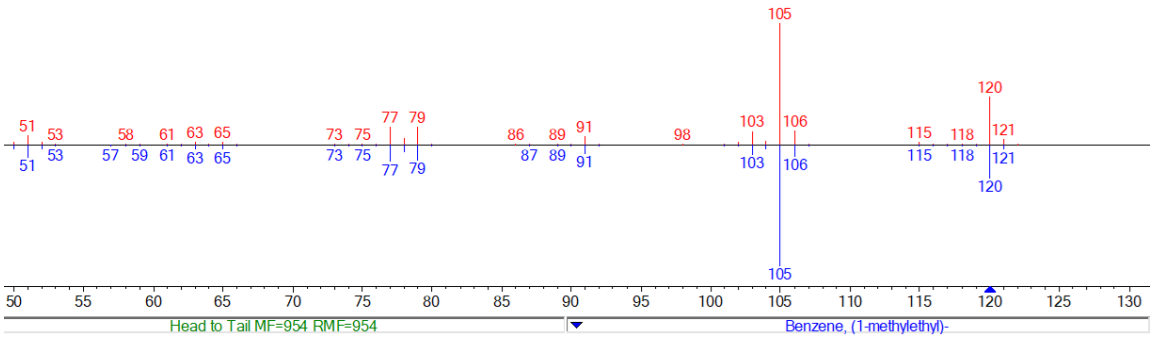
2ak

According to **GP2**, cumene **(2ak)** was synthesized from 2-phenyl-2-propanol (0.140 mL, 136.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 19% yield determined by GC-FID.

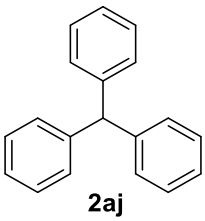
C_9H_{12} (120.09 g/mol)

GC-FID: R_t = 3.976 **(M_{FID}1)**

GC-MS: (EI): m/z = 120.1 (39, [$M^{+\bullet}$]), 105.1 (100, [$M^{+\bullet}$]-[$C_2H_5^{\bullet}$]), 77.0 (15, [$M^{+\bullet}$]-[$C_3H_7^{\bullet}$]); R_t = 8.248 **(M_{MS}2)**



triphenylmethane (2ak)



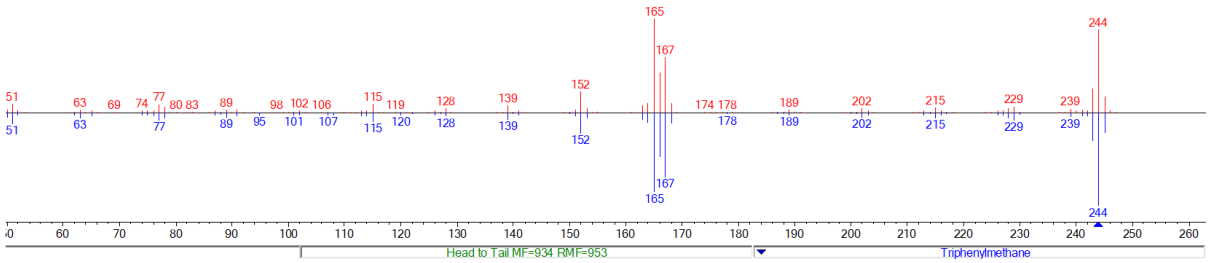
2aj

According to **GP2**, triphenylmethane **(2aj)** was synthesized from triphenylmethanol (260.1 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 32% yield determined by GC-FID.

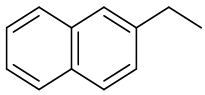
$C_{19}H_{16}$ (244.13 g/mol)

GC-FID: R_t = 10.681 **(M_{FID}1)**

GC-MS: (EI): m/z = 244.1 (65, [$M^{+\bullet}$]), 167.0 (58, [$M^{+\bullet}$]-[$C_6H_5^{\bullet}$]), 165.0 (100, [$M^{+\bullet}$]-[$C_6H_5^{\bullet}$]-[$H^{\bullet}$]), 77.0 (10, [$M^{+\bullet}$]-2[$C_6H_5^{\bullet}$]); R_t = 9.135 **(M_{MS}1)**



2-ethylnaphtalene (2al)



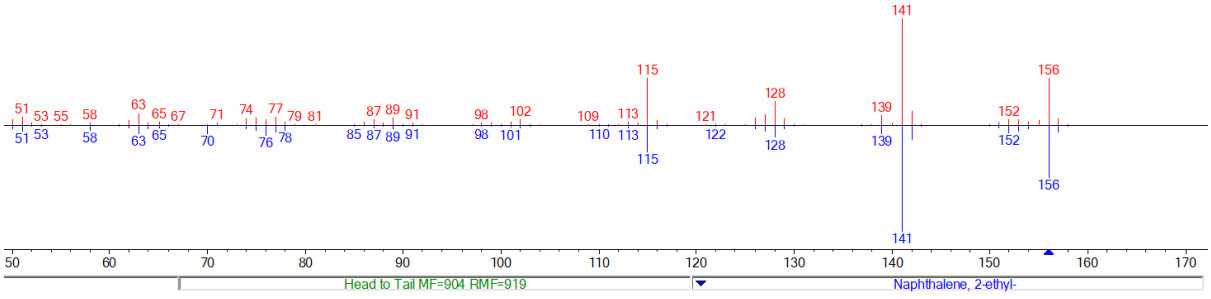
2al

According to **GP2**, 2-ethylnaphtalene **(2al)** was synthesized from 2-acetylnaphthalene (170 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 91% yield determined by GC-FID.

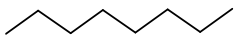
$C_{12}H_{12}$ (156.09 g/mol)

GC-FID: R_t = 7.331 **(M_{FID}1)**

GC-MS: (EI): m/z = 156.1 (100, [$M^{+\bullet}$]), 141.0 (48, [$M^{+\bullet}$]-[$CH_3^{\bullet}$]); R_t =5.651 **(M_{MS}1)**



n-octane (5b)



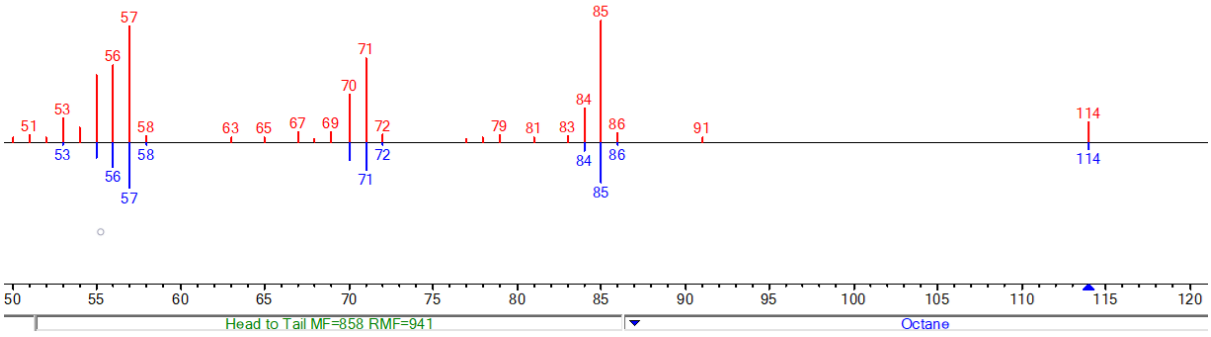
5b

According to **GP2**, n-octane **(6b)** was synthesized from 1-octene (0.156 mL, 112.2 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 87% yield determined by GC-FID.

C_8H_{18} (114.14 g/mol)

GC-FID: R_t = 3.172 **(M_{FID}1)**

GC-MS: (EI): m/z = 114.1 (17, [$M^{+\bullet}$]), 85.1 (100, [$M^{+\bullet}$]-[$C_2H_5^{\bullet}$]); 71.1 (68, [$M^{+\bullet}$]-[$C_3H_7^{\bullet}$]), 57.1 (95, [$M^{+\bullet}$]-[$C_4H_9^{\bullet}$]); R_t =3.303 **(M_{MS}3)**



5.3 Deoxygenation-Dehalogenations and Deoxygenation Reductions

a) Deoxygenation-Dehalogenations

Reactions on halogenated substrates were conducted following general method **GP2**. For GC-MS and GC-FID Data of the deoxygenated products see **Chapter 5.2**

Table S8. Deoxygenation and deoxygenation-dehalogenation products yields

1v - 1aa **2v - 2aa** **2a**

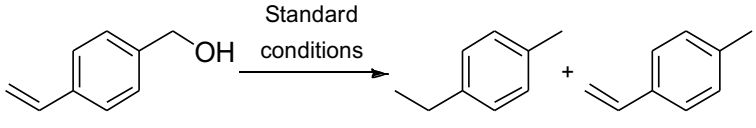
Entry	Substrate[a]	Deoxygenation Product	Deoxygenation Product Yield (%)[b]	Toluene Yield (%)[b]
1	X = 4-F; R = H	**2v**	95	-
2	X = 4-Cl; R = H	**2w**	83	6
3	X = 4-Br; R = H	**2x**	56	35
4	X = 4-I; R = H	**2y**	27	41
5	X = 3-Cl; R = H	**2z**	88	8
6	X = 2-Cl; R = H	**2aa**	85	7
7	X = 4-Cl; R = CH_3	**2ab**	traces	0

[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

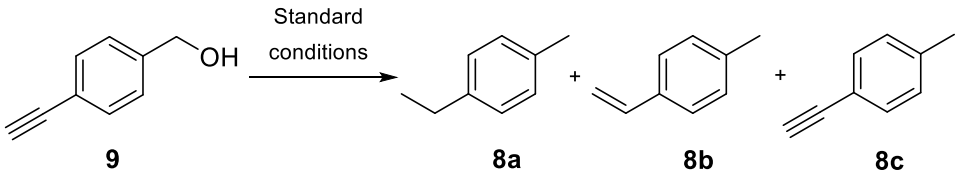
b) Deoxygenation-Hydrogenations

Reactions on unsaturated alcohols were conducted following general method **GP2**. Further investigations regarding the influence of the hydrosilane were conducted on substrate (**10**) by using 2 equiv. and 4 equiv. of $Me(EtO)_2SiH$. Results are shown in Table S9.

Conversion of 4-vinylbenzyl alcohol (7) and 4-ethynylbenzenemethanol (9)



7 **8a** **8b**



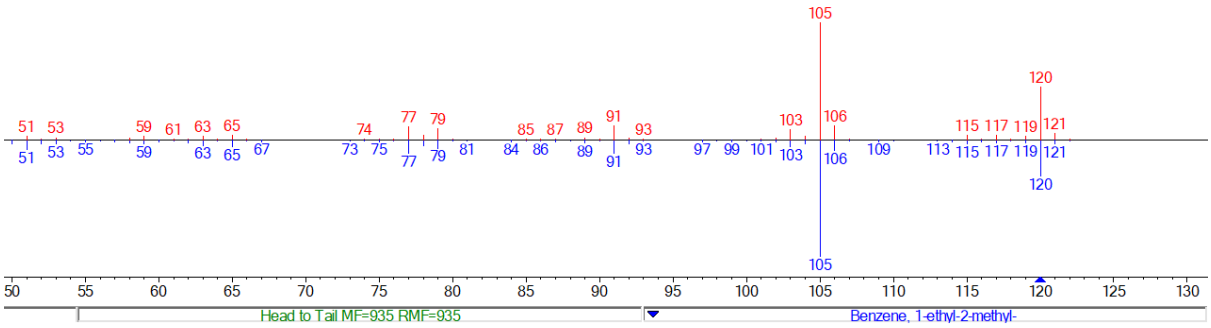
1-ethyl-4-methylbenzene (8a)

According to **GP2**, 1-ethyl-4-methylbenzene **(8a)** was synthesized from 4-vinylbenzyl alcohol (0.130 mL, 134 mg, 1.00 mmol, 1.00 equiv.) and 4-ethynylbenzenemethanol (0.122 mL, 132 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 45% (from 4-vinylbenzyl alcohol) and 15% (from 4-ethynylbenzenemethanol) yield determined by GC-FID.

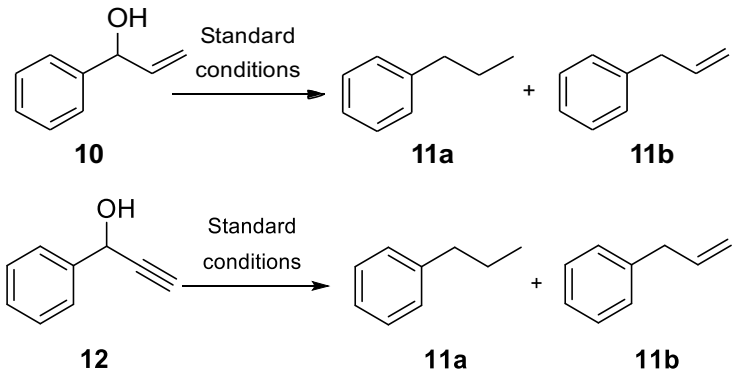
C_9H_{12} (120.20 g/mol)

GC-FID: R_t = 4.220 **(M_{FID}1)**

GC-MS: (EI): m/z = 120.1 (43, [$M^{+\bullet}$]), 105.1 (100, [$M^{+\bullet}$]-[$CH_3^\bullet$]), 91.0 (12, [$M^{+\bullet}$]-[$C_2H_5^\bullet$]), 77.0 (9, [$M^{+\bullet}$]-[$C_2H_5^\bullet$]-[$CH_3^\bullet$]); R_t = 8.978 **(M_{MS}2)**



Conversion of 1-phenyl-2-propen-1-ol (10) and 1-phenyl-2-propyn-1-ol (12)



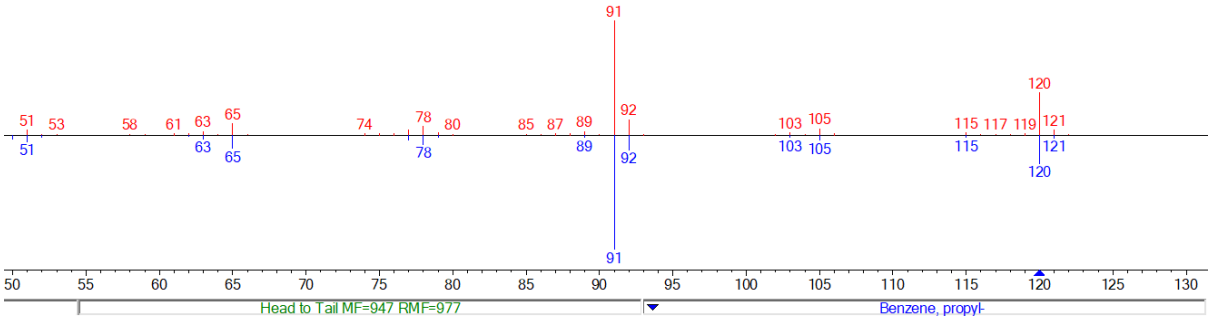
Propylbenzene (11a)

According to **GP2**, propylbenzene **(11a)** was synthesized from 1-phenyl-2-propen-1-ol (0.131 mL, 134.2 mg, 1.00 mmol, 1.00 equiv.) and 1-phenyl-2-propyn-1-ol (0.121 mL, 132.2 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 45% (from 1-phenyl-2-propen-1-ol) and 20% (from 1-phenyl-2-propyn-1-ol) yield determined by GC-FID.

C_9H_{12} (120.20 g/mol)

GC-FID: R_t = 4.171 **(M_{FID}1)**

GC-MS: (EI): m/z = 120.1 (37, [$M^{+\bullet}$]), 105.1 (9, [$M^{+\bullet}$]-[$C_2H_5^\bullet$]), 91.0 (100, [$M^{+\bullet}$]-[$C_2H_5^\bullet$]), 78.0 (14, [$M^{+\bullet}$]-[$C_3H_7^\bullet$]); R_t = 9.954 **(M_{MS}2)**



Allylbenzene (11b)

According to **GP2**, allylbenzene **(11b)** was synthesized from 1-phenyl-2-propen-1-ol (0.131 mL, 134.2 mg, 1.00 mmol, 1.00 equiv.) and 1-phenyl-2-propyn-1-ol (0.121 mL, 132.2 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 28% (from 1-phenyl-2-propen-1-ol) and 9% (from 1-phenyl-2-propyn-1-ol) yield determined by GC-FID.

C_9H_{10} (118.18 g/mol)

GC-FID: R_t = 4.657 **(M_{FID}1)**

GC-MS: (EI): m/z = 118.1 (53, [$M^{+\bullet}$]), 117.1 (100, [$M^{+\bullet}$]-[$H^{\bullet}$]), 105.1 (7, [$M^{+\bullet}$]-[$CH^{\bullet}$]), 91.0 (48, [$M^{+\bullet}$]-[$C_2H_3^{\bullet}$]), 77.0 (12, [$M^{+\bullet}$]-[$C_3H_5^{\bullet}$]); R_t = 12.008 **(M_{MS}2)**

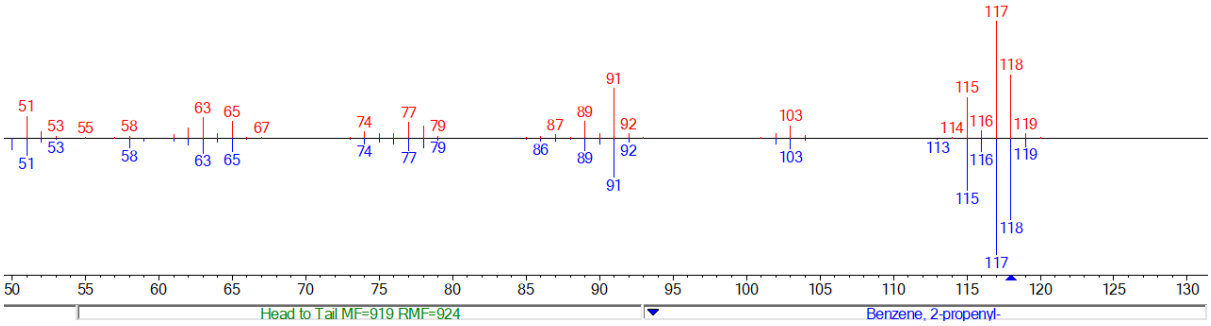


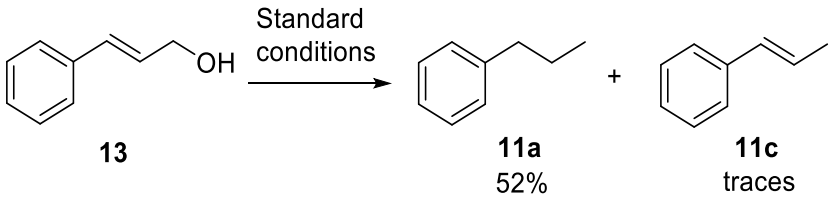
Table S9. Influence of hydrosilane equivalents on the deoxygenation-hydrogenation reaction of **10**

Entry	Silane (equiv.)[a]	Yield 11a[b]	Yield 11b[b]
1	2	43	27
2	3	45	28
3	4	54	24

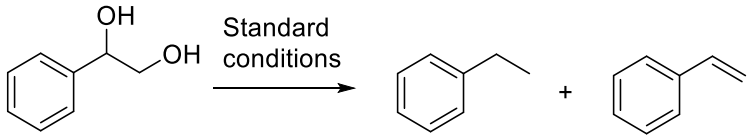
[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (x equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

Conversion of cinnamyl alcohol (13) and 1-phenyl-1,2-ethanediol (14)

The analytical data for the main products of the reduction of cinnamyl alcohol (**13**) can be found in this chapter (transformation of **10** and **12**) and for 1-phenyl-1,2-ethanediol (**14**) in **Chapter 5.2**.



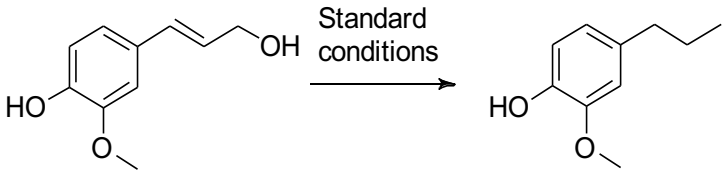
13 **11a** 52% **11c** traces



14 **2ac** 69% **5a** traces

6 Deoxygenation of Lignin Related Compounds

Deoxygenation of cofineryl alcohol (15)



15 **16**

4-Propylguaiacol (16)

According to **GP2**, 4-propylguaiacol **(16)** was synthesized from coniferyl alcohol (180 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless liquid (87 mg, 0.52 mmol, 52%, 76% determined by GC-FID). Analytical data was in accordance with the literature.[21]

$C_{10}H_{14}O_2$ (166.22 g/mol)

R_f: 0.48 (98:2 Hex:EtOAc)

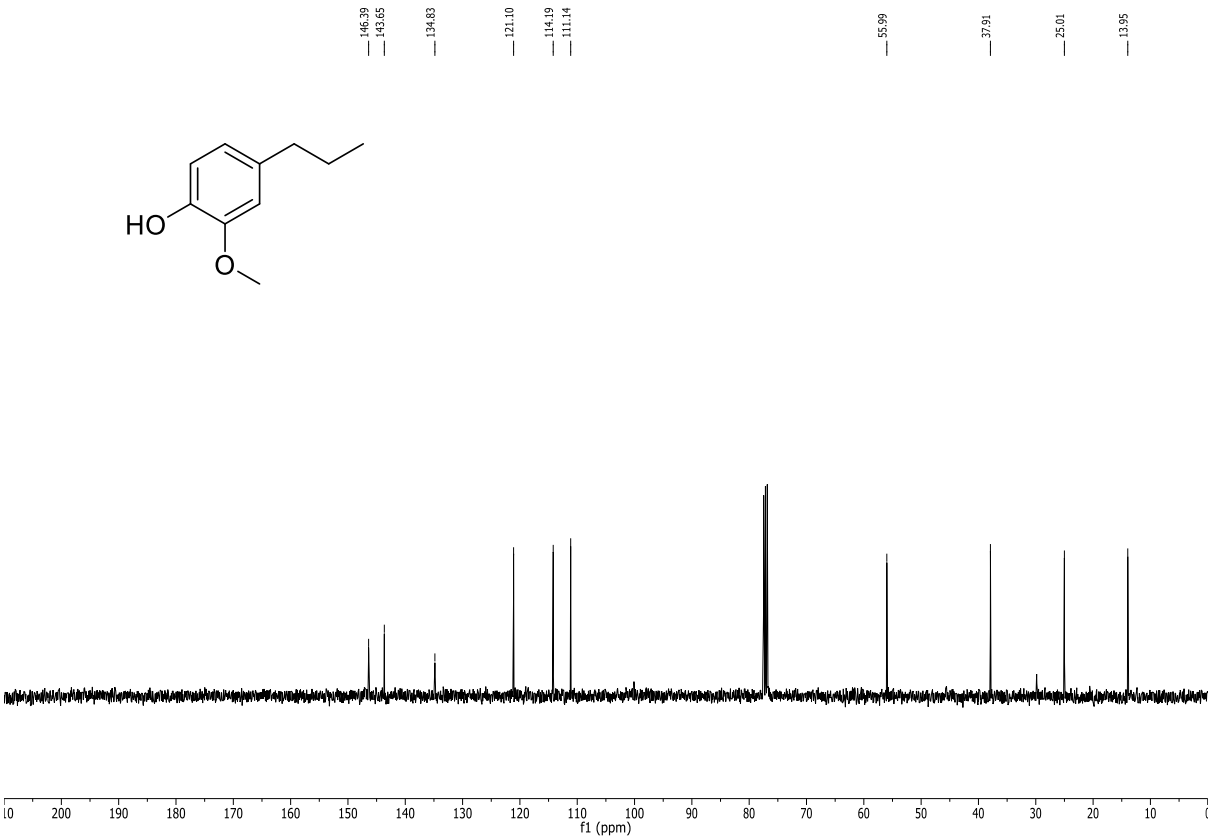
^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.83 (dd, J = 8.1, 0.9 Hz, 1H), 6.68 (m, 2H), 5.44 (s, 1H), 3.88 (s, 3H), 2.52 (t, J = 7.3, 2H), 1.68 – 1.55 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); (90% purity) Impurity – pentadecane

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 146.4, 143.7, 134.8, 121.1, 114.2, 111.1, 56.0, 37.9, 25.0, 13.9.

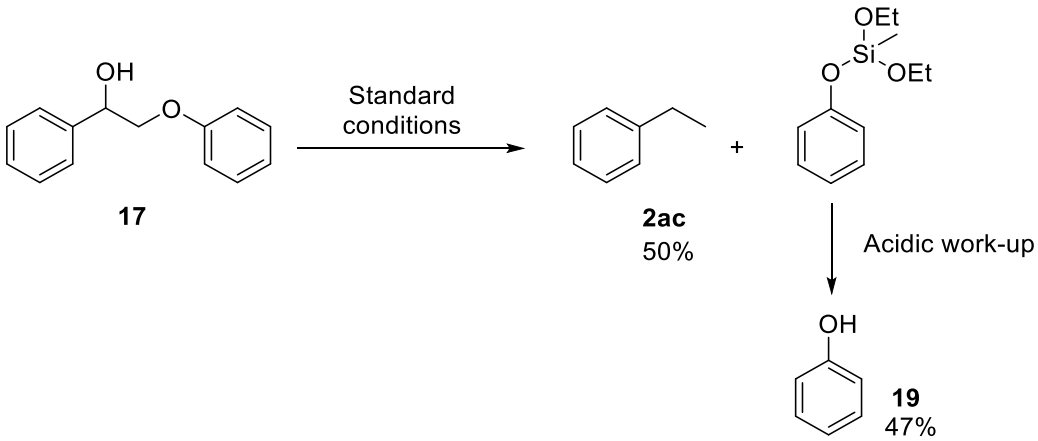
GC-MS: (EI): m/z = 166.1 (32, [$M^{+\bullet}$]), 137.1 (100, [$M^{+\bullet}$]-[$C_2H_5^\bullet$]), 122.1 (10, [$M^{+\bullet}$]-[$C_3H_7^\bullet$]), 77.0 (4, [$C_6H_5^\bullet$])

^{1}H-NMR: (400 MHz, $CDCl_3$) of **16**

^{13}C-NMR: (100 MHz, $CDCl_3$) of **16**



Deoxygenation of α-(Phenoxymethyl)benzenemethanol (17)



ethylbenzene (2ac)

The analytical data for ethylbenzene (**2ac**) are presented in **chapter 5.2**

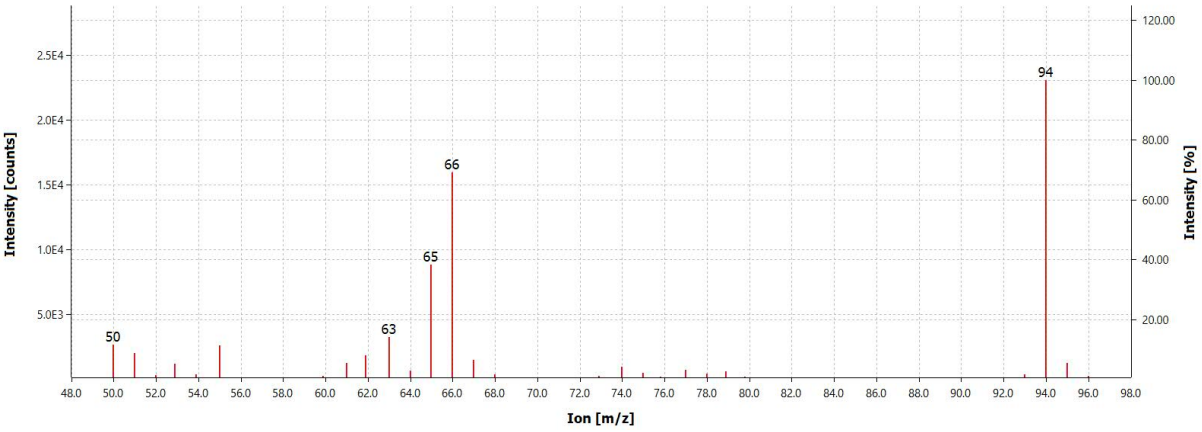
phenol (19)

According to **GP2**, phenol **(19)** was synthesized from α-(phenoxymethyl)benzenemethanol (214 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in 47% yield determined by GC-FID after workup with 1M HCl.

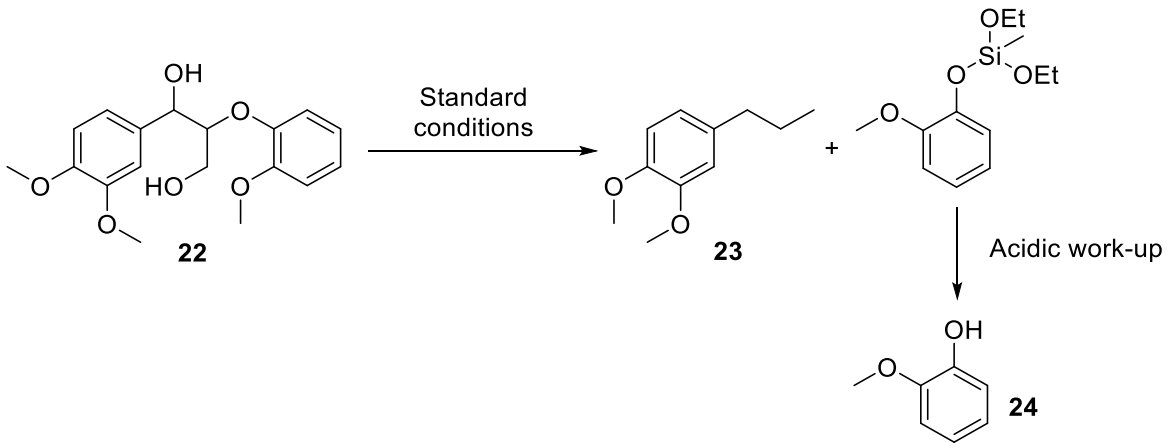
C_6H_6O (94.11 g/mol)

GC-FID: R_t = 4.335 **(M_{FID}1)**

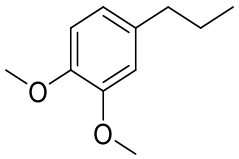
GC-MS: (EI): m/z = 94 (100, [$M^{+\bullet}$]), 66 (64, [$M^{+\bullet}$]-[HO-C$^{\bullet}$]); R_t = 11.258 **(M_{MS}2)**



Deoxygenation of adlerol (22)



1,2-dimethoxy-4-propylbenzene (23)



According to lower scale **GP2** (0.75 equiv.) 1,2-dimethoxy-4-propylbenzene **(23)** was synthesized from adlerol (250 mg, 0.75 mmol, 1.00 equiv.) over 16 h. The product was afforded as a colorless liquid (61 mg, 0.34 mmol, 45%, 67% determined by GC-FID). Analytical data was in accordance with the literature.[22]

$C_{11}H_{16}O_2$ (180.25 g/mol)

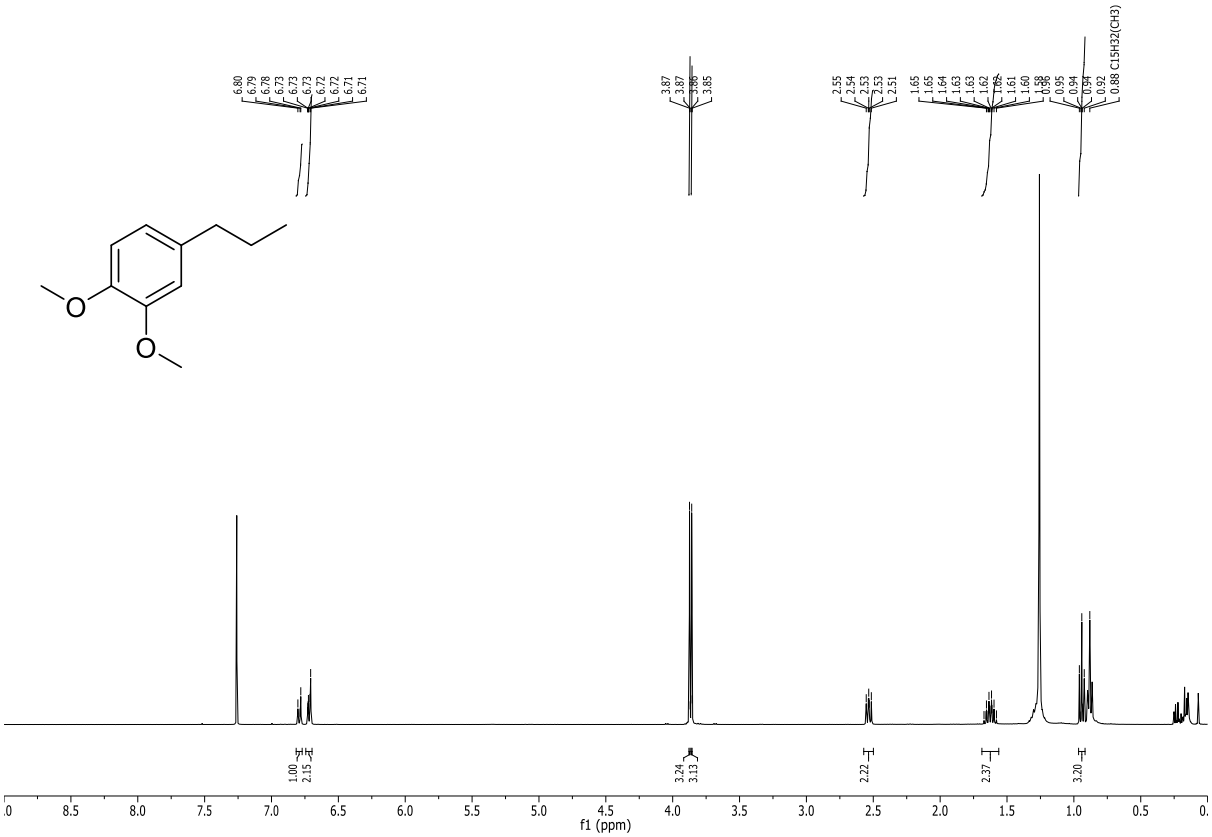
R_f: 0.76 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.79 (d, J = 8.7 Hz, 1H), 6.74 – 6.70 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.56 – 2.50 (m, 2H), 1.68 – 1.57 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) – 4:3 mixture product:pentadecane

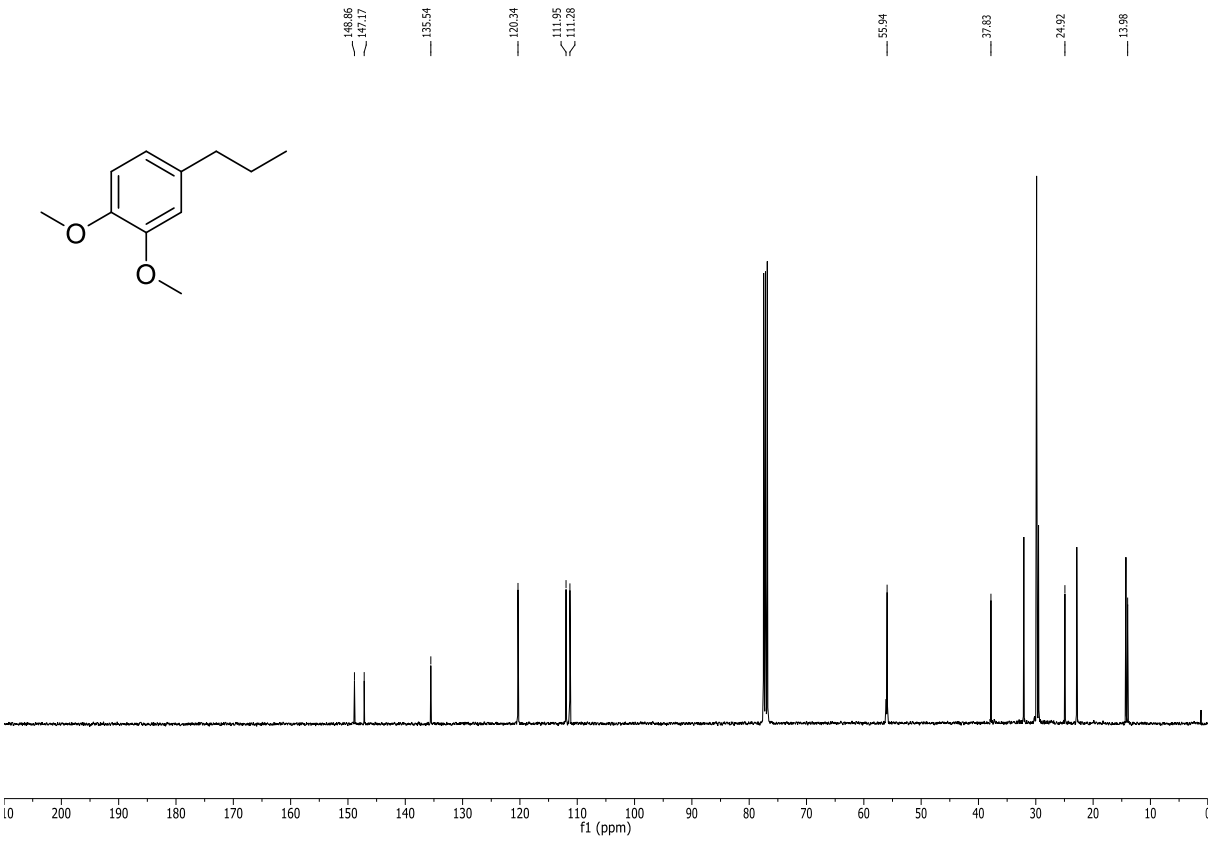
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 148.9, 147.2, 135.5, 120.3, 111.9, 111.3, 55.9, 37.8, 24.9, 13.9.

GC-MS: (EI): m/z = 180.1 (32, [$M^{+\bullet}$]), 151.1 (100, [$M^{+\bullet}$]-[$C_2H_5^{\bullet}$]), 91 (19, [$M^{+\bullet}$]-[$CH_3O^{\bullet}$]-[$C_2H_5^{\bullet}$]), 77.0 (21, [$C_6H_5^{\bullet}$])

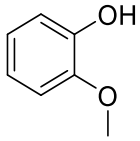
^{1}H-NMR: (400 MHz, $CDCl_3$) of **23**



^{13}C-NMR: (100 MHz, $CDCl_3$) of **23**



guaiacol (24)



According to lower scale **GP2** (0.75 equiv.), guaiacol **(24)** was synthesized from adlerol (250 mg, 0.75 mmol, 1.00 equiv.) over 16 h. The product was afforded as a colorless liquid (32 mg, 0.26 mmol, 34%, 41% determined by GC-FID). Analytical data was in accordance with the literature.[23]

$C_7H_8O_2$ (124.14 g/mol)

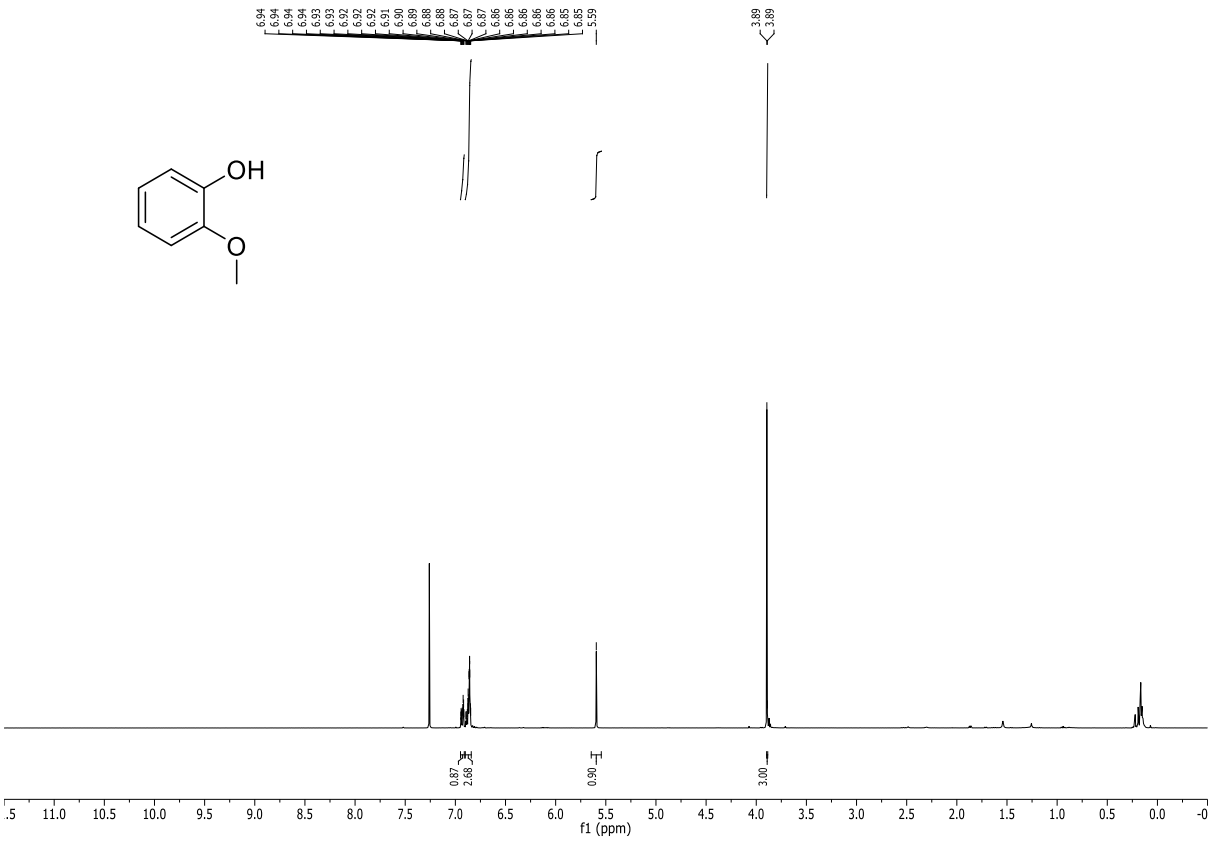
R_f: 0.51 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm = 6.95 – 6.91 (m, 1H), 6.90 – 6.83 (m, 3H), 5.59 (s, 1H), 3.89 (s, 3H)

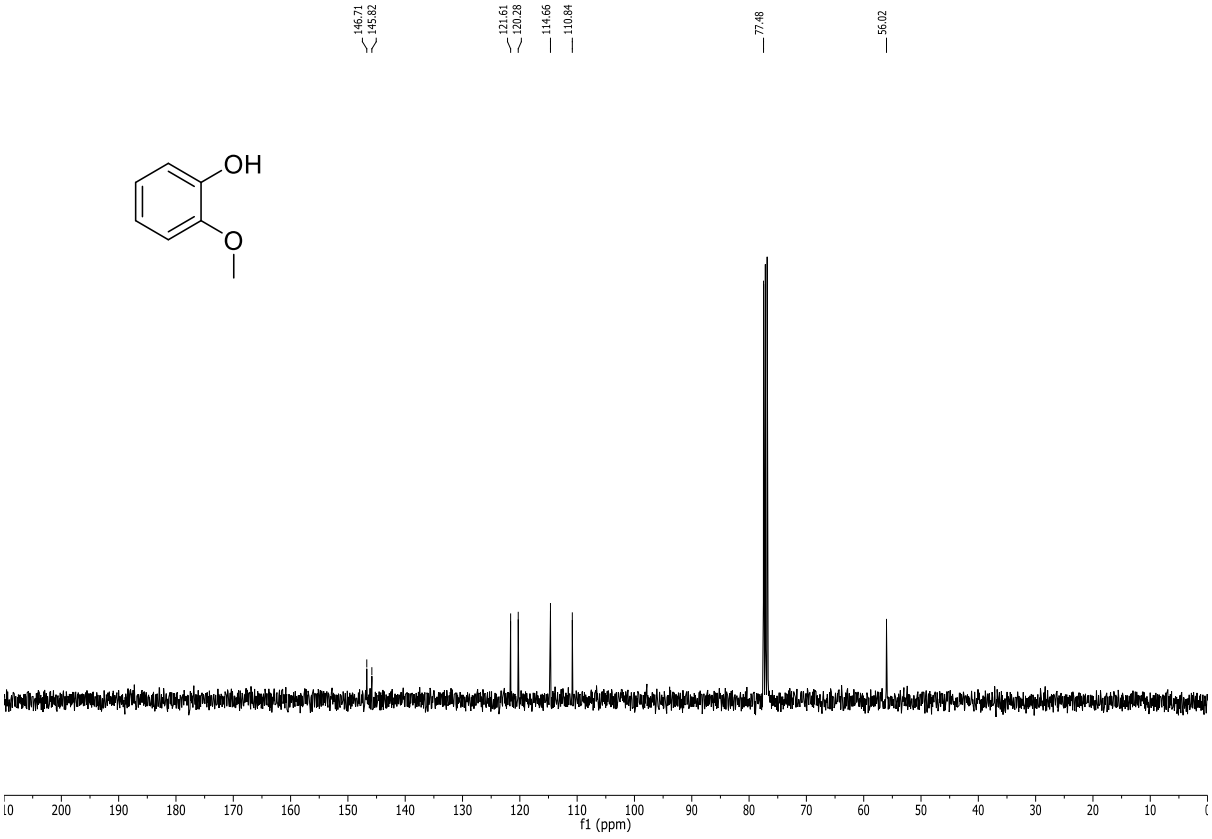
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 146.7, 145.8, 121.6, 120.3, 114.7, 110.8, 56.0.

GC-MS: (EI): m/z = 124.1 (29, $[M^{+\bullet}]$), 109.1 (40, $[M^{+\bullet}]$-$[CH_3^{\bullet}]$), 81.1 (100, $[M^{+\bullet}]$-)

^{1}H-NMR: (400 MHz, $CDCl_3$) of **23**

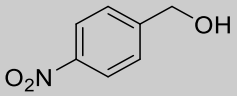
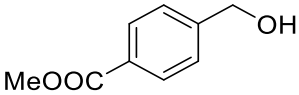
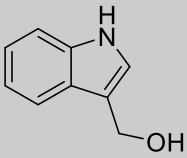
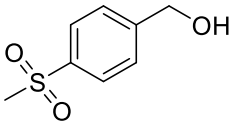
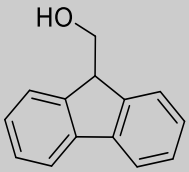
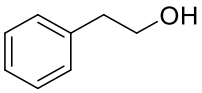
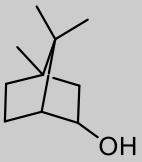
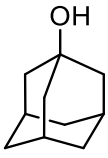


^{13}C-NMR: (100 MHz, $CDCl_3$) of **24**



7 Unsuccessful Substrates

Table S10. List of failed substrates

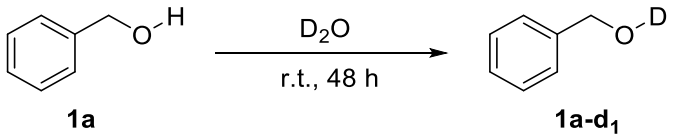
Entry	Substrate [a]	Deoxygenation Product Yield (%) [b]	Main Product
1		-	No reaction
2		traces	Transesterification product
3		traces	Polymer
4		traces	Corresponding silyl ether
5		traces	Corresponding silyl ether
6		-	Corresponding silyl ether
7		-	Corresponding silyl ether
8		-	Corresponding silyl ether

[a] Standard reaction conditions: benzyl alcohol (0.104 mL, 1.00 mmol, 1.00 equiv.), Cp_2TiCl_2 (25.0 mg, 10 mol%), Mn (54.9 mg, 1.00 mmol, 1.00 equiv.) in 2-MeTHF (2 mL), stirred for 2 h at 50 °C, then $(EtO)_2MeSiH$ (0.48 mL, 3.00 mmol, 3.00 equiv.), 18 h, 100 °C in a Schlenk pressure tube. [b] Yields determined *via* quantitative GC-FID with n-pentadecane as internal standard.

8 Mechanistical Studies

8.1 Synthesis of Deuterated Starting Materials

Benzenemethanol-*d* (1a-d_1)



1a **1a-d_1**

In a round-bottom flask benzyl alcohol (1.04 mL, 1.08 g, 10.0 mmol) were dissolved in 10 mL D_2O. The reaction was stirred under air at room temperature for 48 h. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL) and the organic phases were washed with brine (3 × 10 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure yielding the product in quantitative yield without any further purification needed. Analytical data was in accordance with the literature.[24]

C_7H_7DO (109,06 g/mol)

R_f: 0.27 (5:1 Hex:EtOAc)

^{1}H-NMR: (700 MHz, $CDCl_3$): δ/ppm = 7.38-7.36 (dd, *J* = 4.2, 1.1 Hz, 4H), 7.32 – 7.29 (m, 1H), 4.69 (s, 2H).

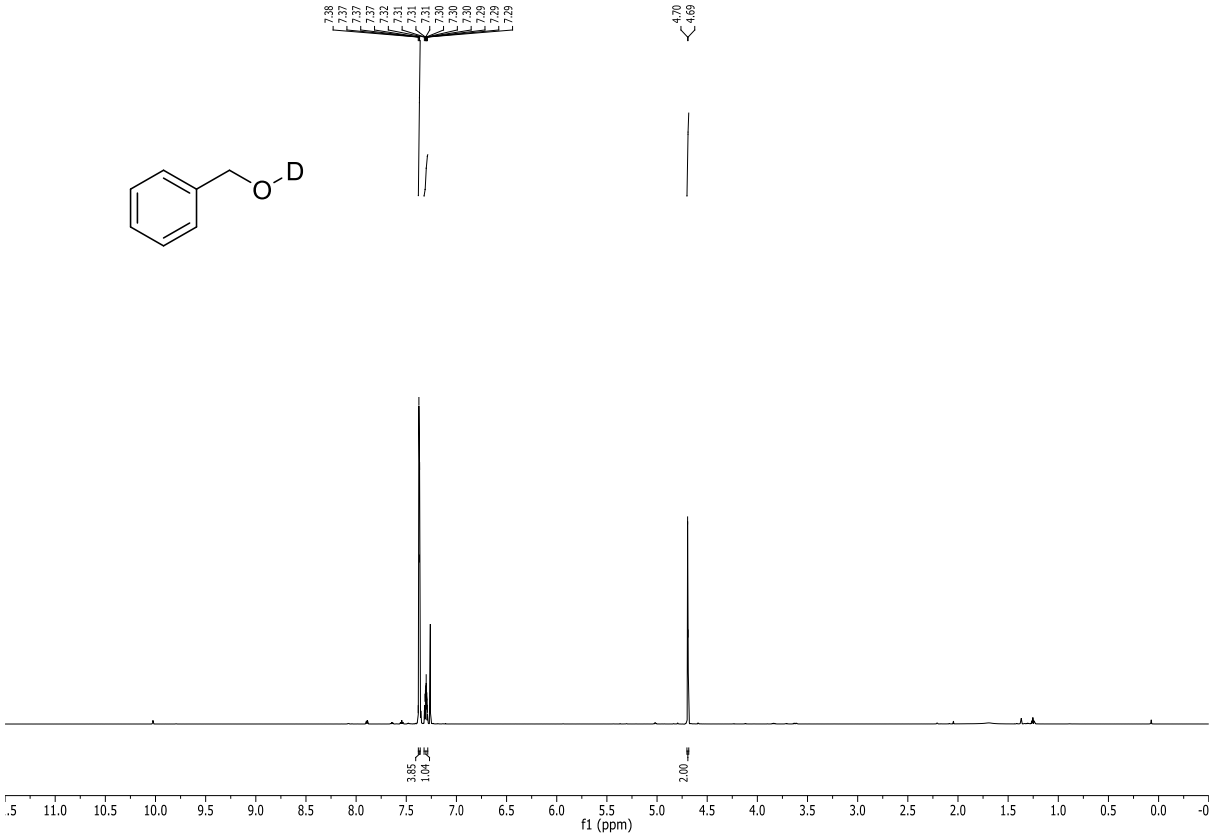
^{2}H-NMR: (107 MHz, $CDCl_3$): δ/ppm = 2.17 (bs)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 140.9, 128.1, 127.8, 127.1, 65.5

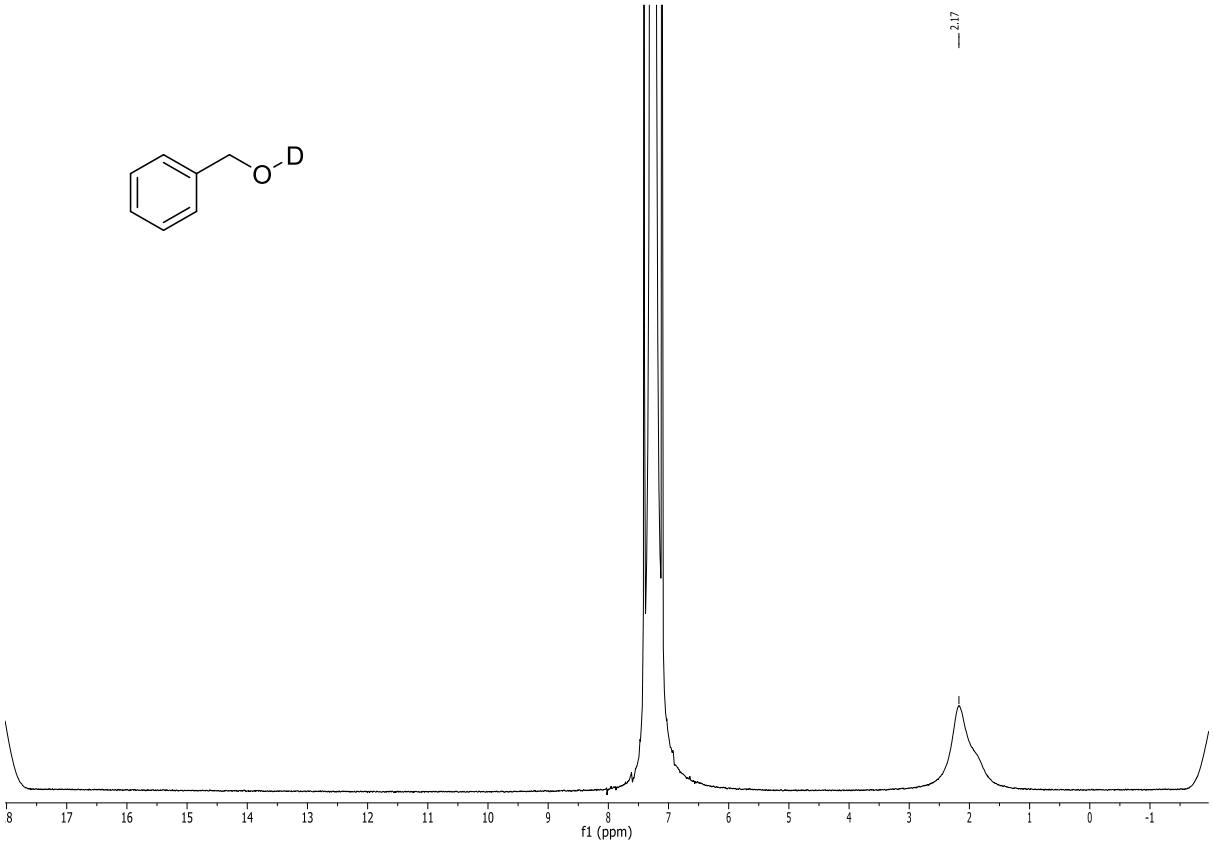
GC-MS: (EI): m/z =109.1 (92, [$M^{+\bullet}$]), 108.1 (100, [$M^{+\bullet}$]-[$H^{\bullet}$]), 80.1 (71, [$M^{+\bullet}$]-)

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3326 (w), 3030 (w), 3030 (m), 2870 (m), 2467 (s), 1494 (m), 1453 (s), 1371 (s), 1207 (m), 1006 (s), 846 (m), 730 (s), 693 (s)

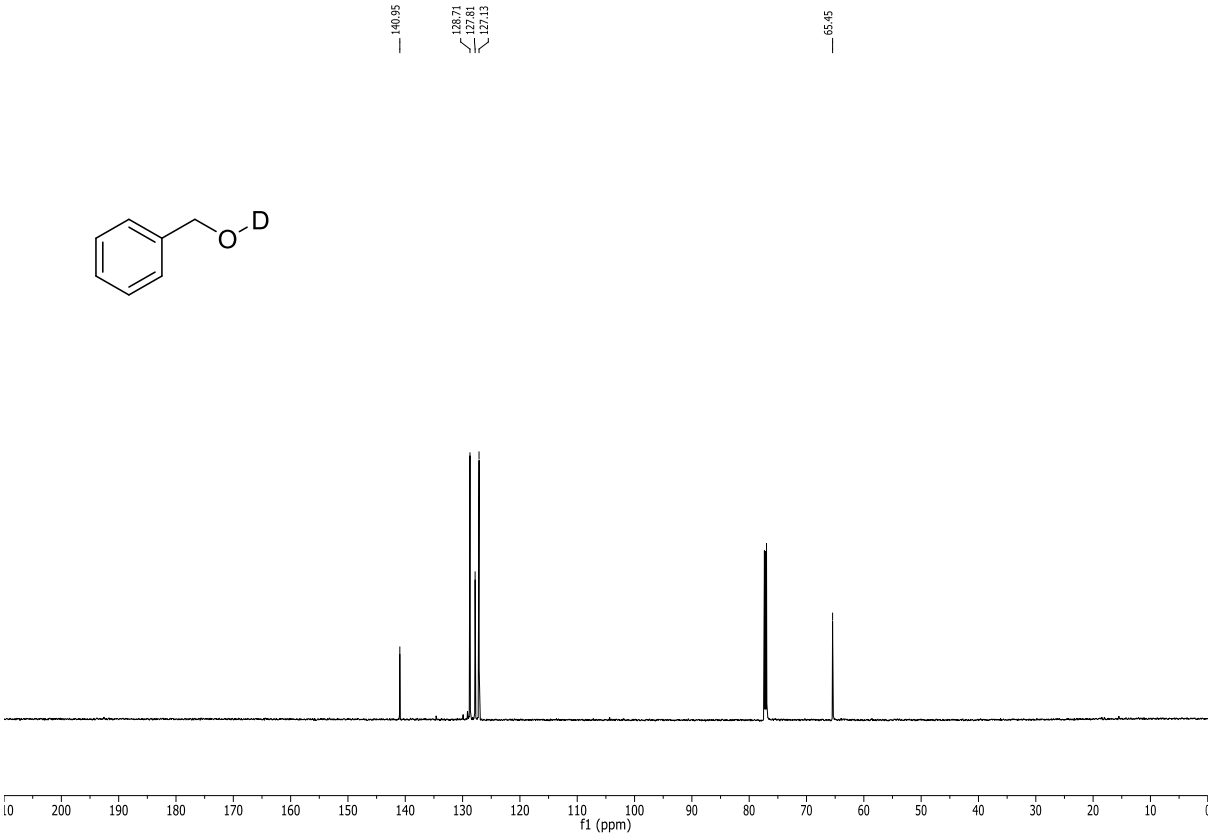
^{1}H-NMR: (700 MHz, $CDCl_3$) of **1a-d$_1$**



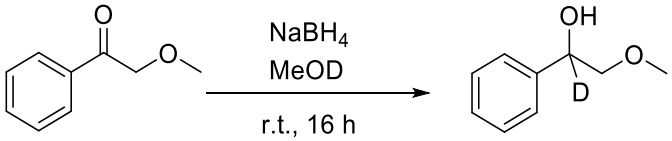
^{2}H-NMR: (107 MHz, $CDCl_3$) of **1a-d$_1$**



^{13}C-NMR: (101 MHz, $CDCl_3$) of **1a-d$_1$**



2-methoxy-1-phenylethan-1-*d*-1-ol (20-d_1)



20-ket **20-d_1**

In a 100 mL round bottom flask 2-methoxy-1-phenylethanone (**20-ket**) (751 mg, 5.00 mmol, 1 equiv.) was dissolved in methanol-*d* (20 mL) and cooled in an ice bath. Then $NaBD_4$ (418 mg, 10.0 mmol, 2 equiv.) was added in portions. Upon complete addition the solution was allowed to warm to ambient temperature and was stirred until the completion of the reaction was confirmed by TLC. After 16 h the solution was cooled in an ice bath and quenched with ice and water. Then, methanol was removed under reduced pressure and the mixture was extracted with DCM (3 × 10 mL). The collected organic phases were washed with brine (3 × 10 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the respective alcohol was obtained and used without further purification. Analytical data was in accordance with the literature.[25]

$C_9H_{11}DO_2$ (153,2 g/mol)

R_f: 0.23 (4:1 Hex:EtOAc)

^{1}H-NMR: (700 MHz, $CDCl_3$): δ/ppm 7.41 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 3.55 – 3.42 (m, 2H), 3.44 (s, 3H).

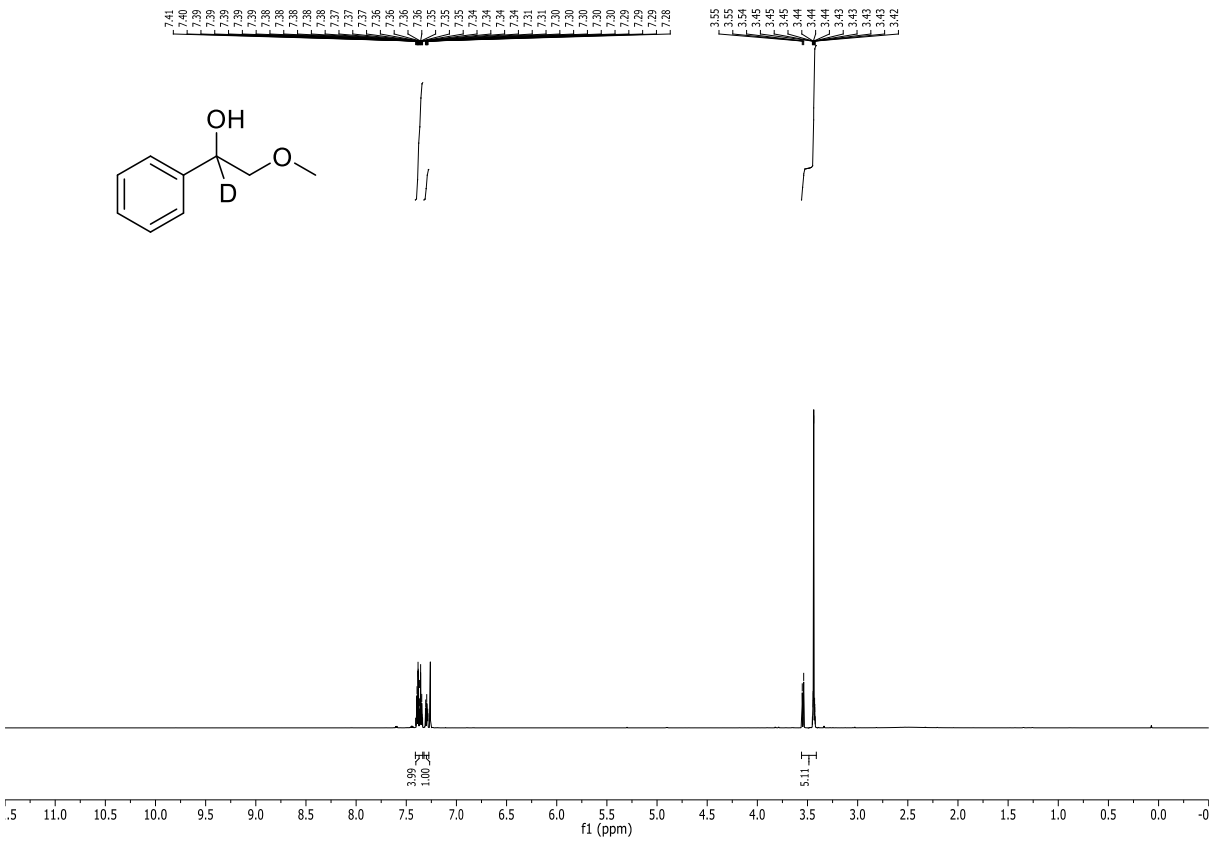
^{2}H-NMR: (107 MHz, $CDCl_3$): δ/ppm = 4.90 (s)

^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 140.3, 128.5, 128.0, 126.3, 78.2, 72.2 (t, *J* = 22.2 Hz), 59.2.

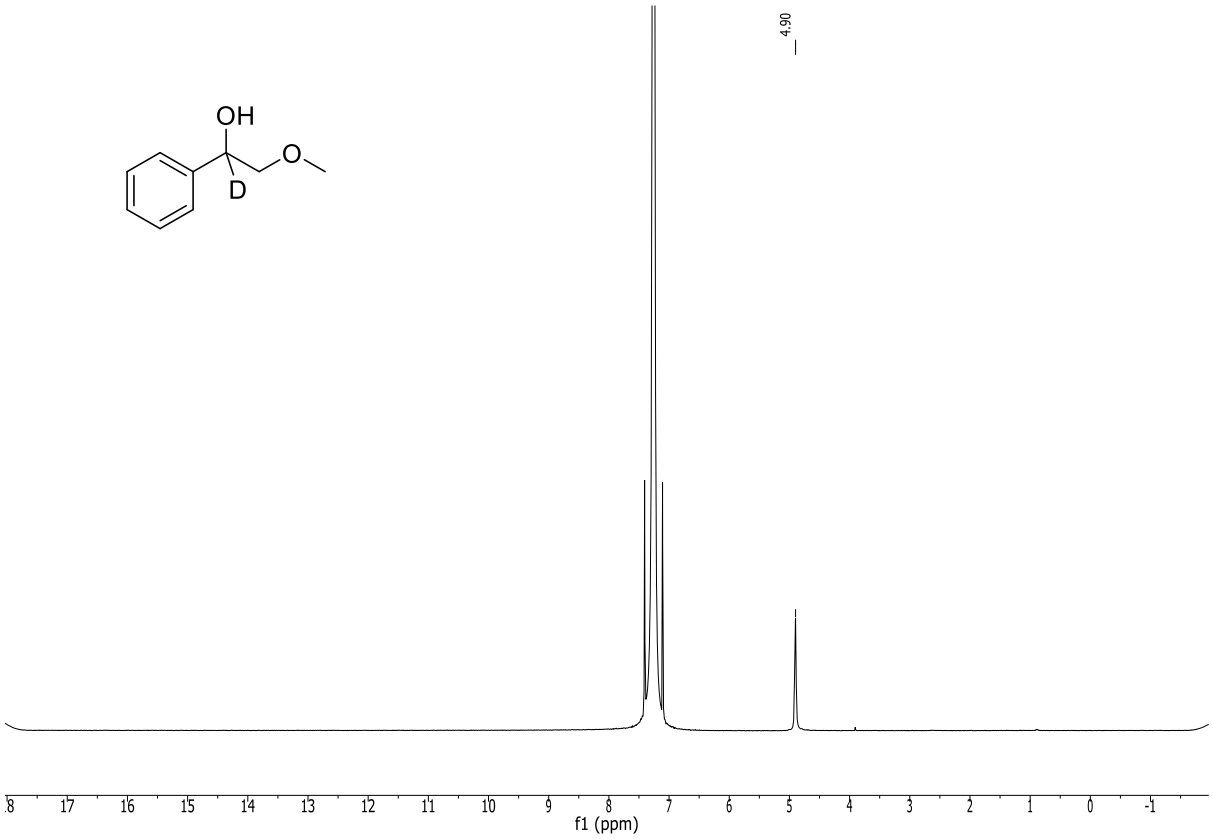
GC-MS: (EI): m/z =109.1 (92, $[M^{+\bullet}]$-$[H^\bullet]$), 108.1 (100, $[M^{+\bullet}]$-$[C_2H_5O^\bullet]$), 92.1 (71, $[M^{+\bullet}]$-$[C_2H_5O^\bullet]$-$[OH^\bullet]$)

IR: (ATR, $\tilde{\nu}$, [cm^{-1}]): 3421 (w), 2926 (w), 2885 (m), 2825 (w), 1490 (m), 1446 (s), 1196 (s), 1103 (s), 946 (s), 752 (s)

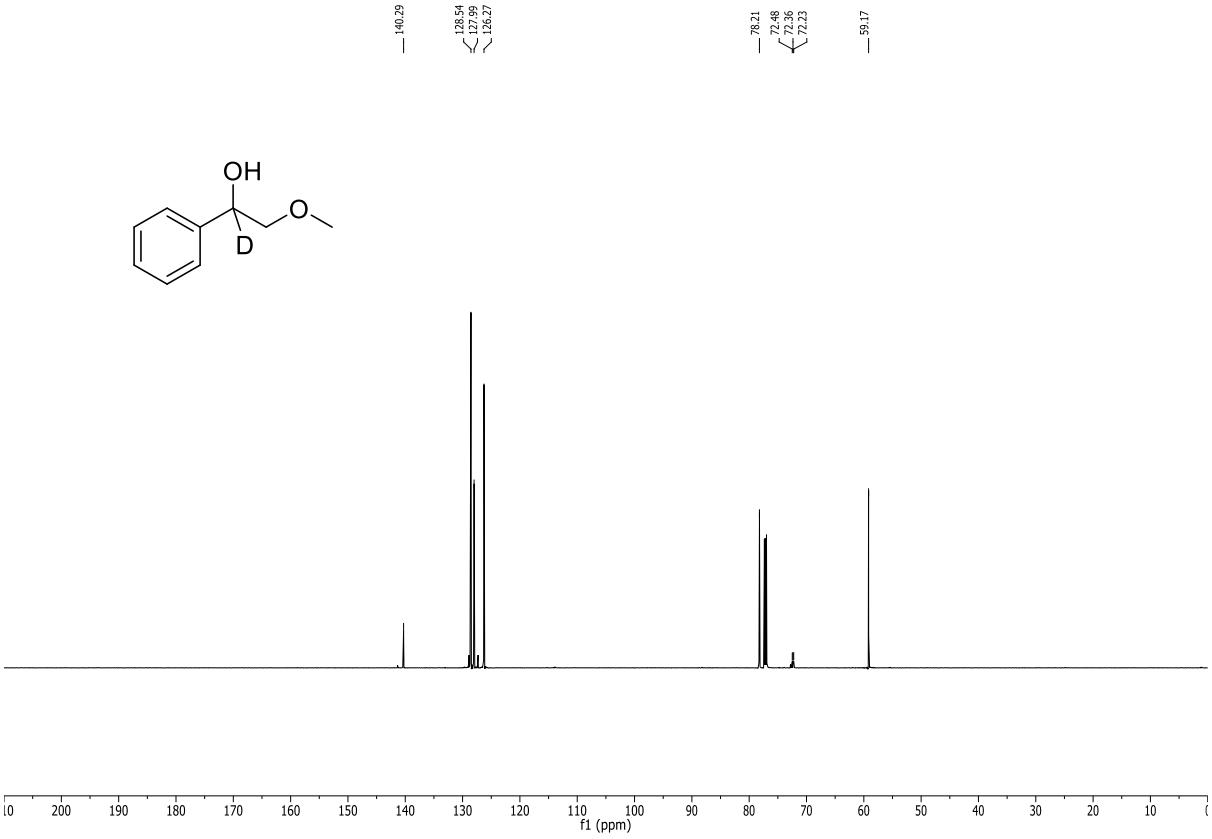
^{1}H-NMR: (700 MHz, $CDCl_3$) of **20-d_1**



^{2}H-NMR: (107 MHz, $CDCl_3$) of **20-d_1**



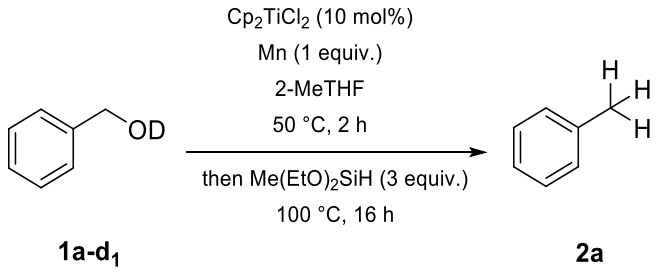
^{13}C-NMR: (101 MHz, $CDCl_3$) of **20-d_1**



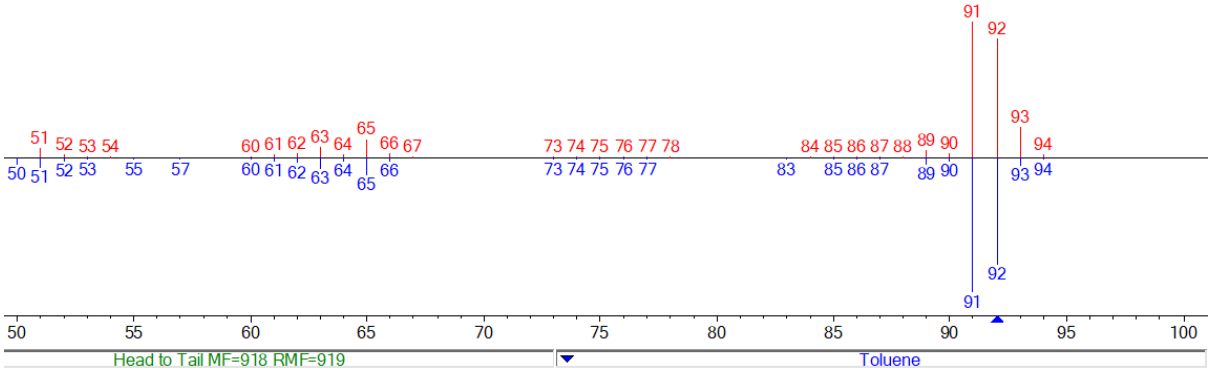
8.2 Deuteration Experiments

The deuteration mechanistical experiments were conducted under indicated conditions for each reaction, following modified general procedure **GP2**. The crude reaction mixture obtained was analyzed by GC-MS with method $\mathbf{M_{MS}2}$ (Heating from 40 °C to 300 °C with a 10 °C/min heating rate; Helium –carrier gas) and GC-FID with method $\mathbf{M_{FID}1}$ (35 °C to 280 °C with a 10 °C/min heating rate). Pentadecane was used as internal standard for the quantitative GC.[26, 27]

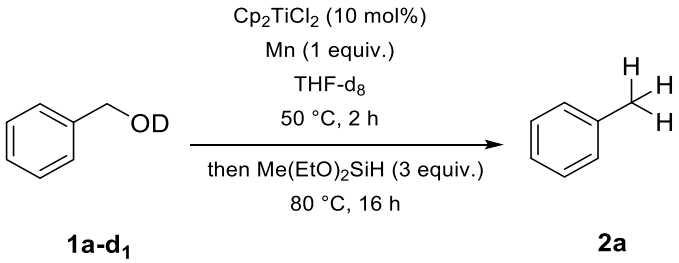
Deoxygenation of 1a-d_1 in 2-MeTHF



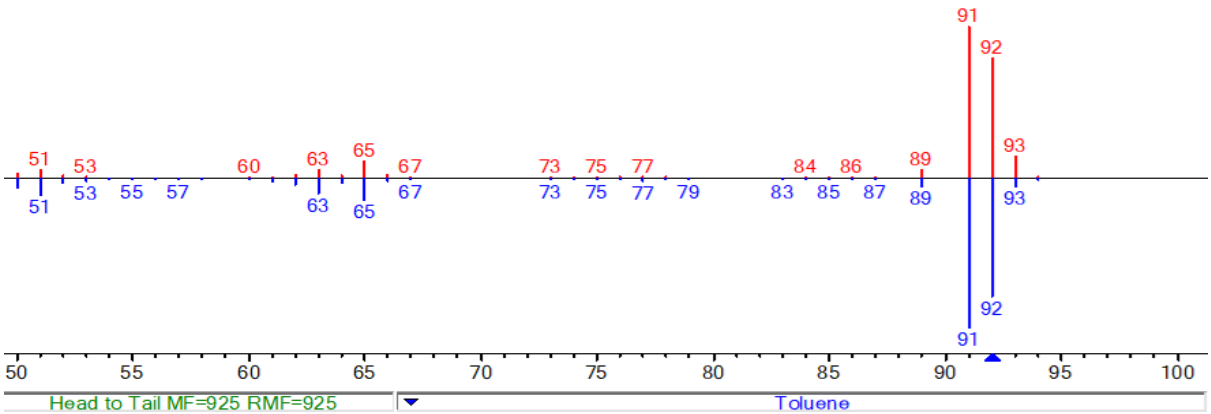
1a-d_1 **2a**



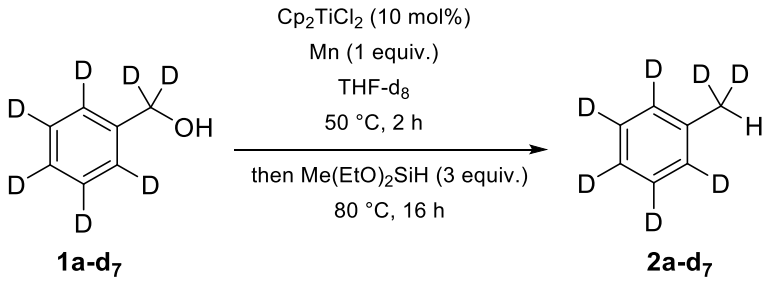
Deoxygenation of 1a-d_1 in THF-d_8



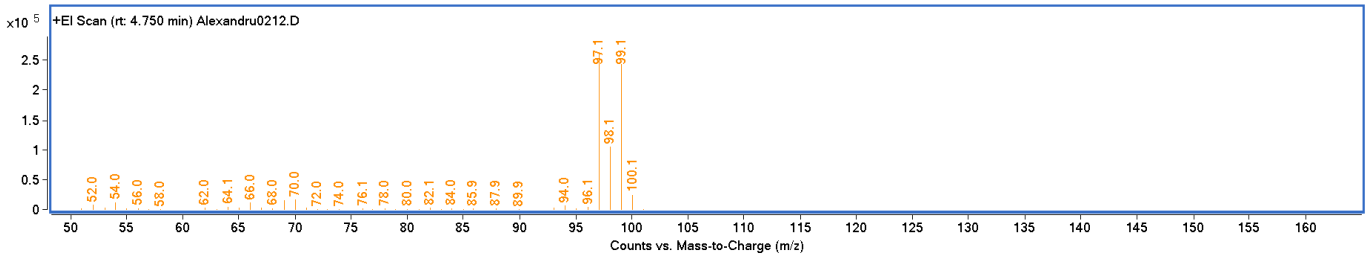
1a-d_1 **2a**

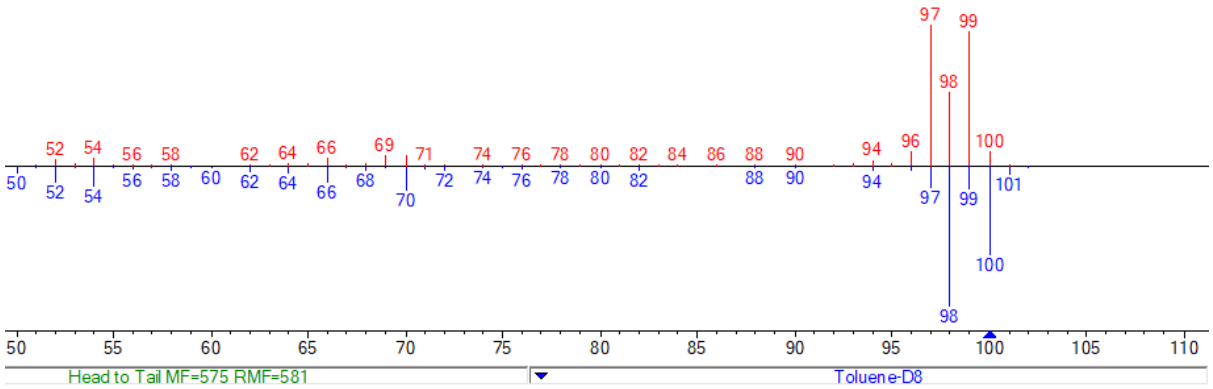


Deoxygenation of 1a-d_7 in THF-d_8

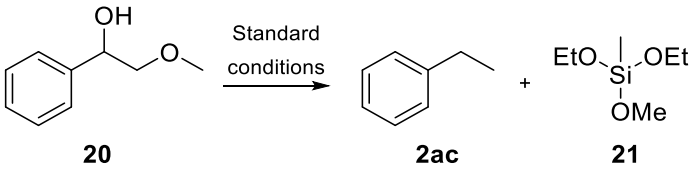


1a-d_7 **2a-d_7**

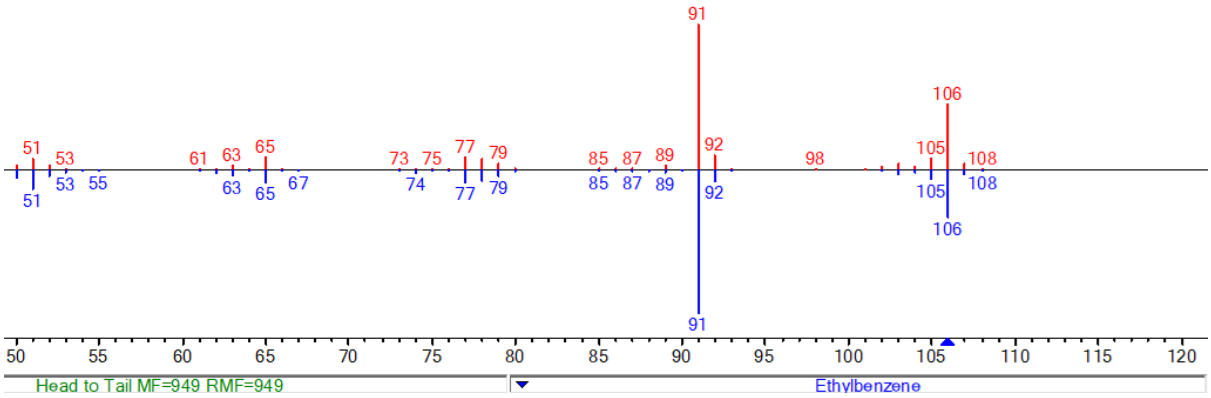


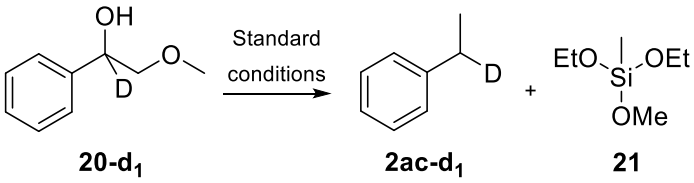


Deoxygenation of α-(methoxymethyl)benzenemethanol (20)

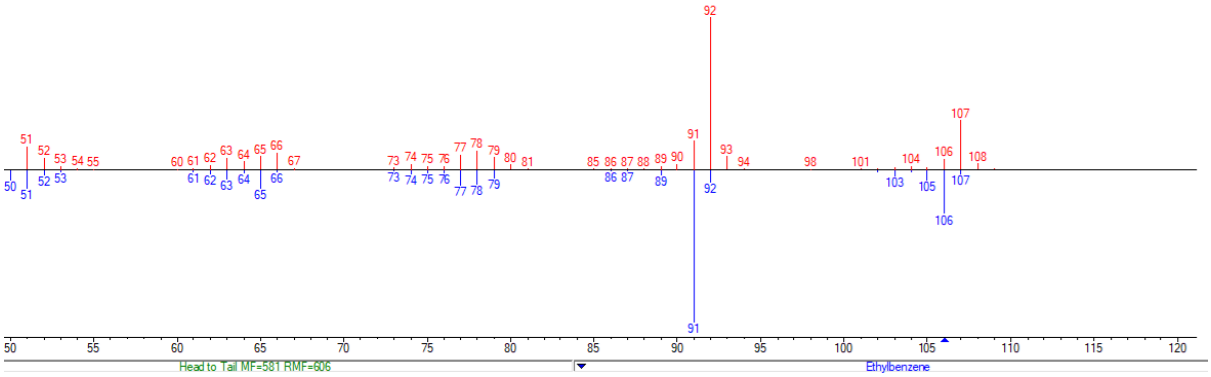


20 **2ac** **21**





20-d$_1$ **2ac-d$_1$** **21**

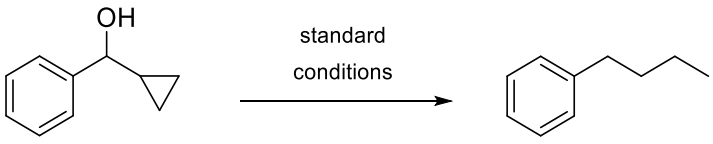


Comparing the chromatograms obtained from both **20** and **20-d$_1$** we concluded from the fragmentation patterns that the C-D bond was not cleaved during the reaction hinting that not a rearrangement is responsible for the obtained products.[28]

8.3 Radical Clock Experiments

Radical clock experiments were conducted following the general procedure **GP2**. The obtained crude reaction mixture was analyzed by GC-MS with method $\mathbf{M_{MS}2}$ (Heating from 40 °C to 300 °C with a 10 °C/min heating rate; Helium –carrier gas) and GC-FID with method $\mathbf{M_{FID}1}$ (35 °C to 280 °C with a 10 °C/min heating rate).[29]

Deoxygenation of α-cyclopropylbenzyl alcohol (27)



27 **28**

n-Butylbenzene (**28**) was synthesized from α-cyclopropylbenzyl alcohol (0,130 ml, 148 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was isolated by column chromatography (hexane/ethyl acetate 98:2) and was afforded as a colorless liquid (67 mg, 0.50 mmol, 50%, 69% determined by GC-FID). Analytical data was in accordance with the literature.[30]

n-Butylbenzene (**28**)

$C_{10}H_{14}$ (134.20 g/mol)

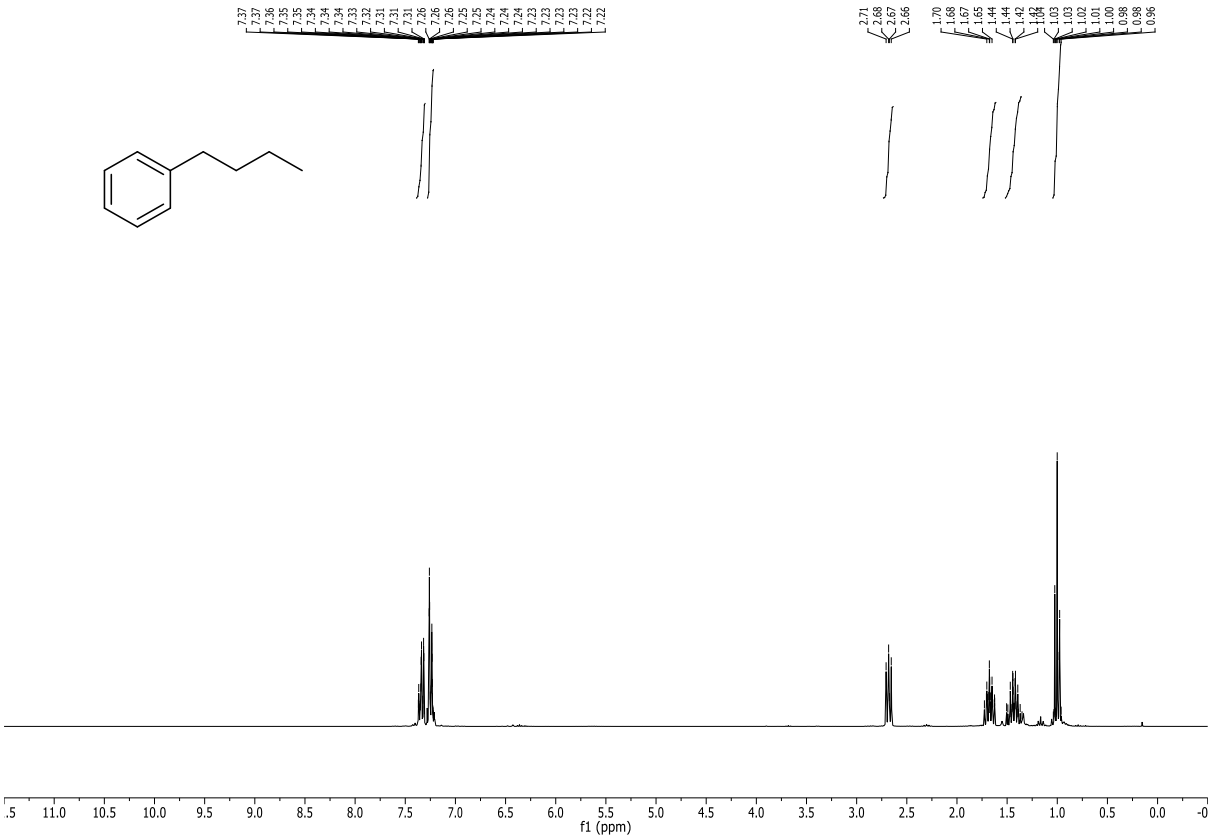
R_f: 0.78 (98:2 Hex:EtOAc)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ/ppm 7.39 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 2.69 (t, J = 7.3 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.44 – 1.36 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H)

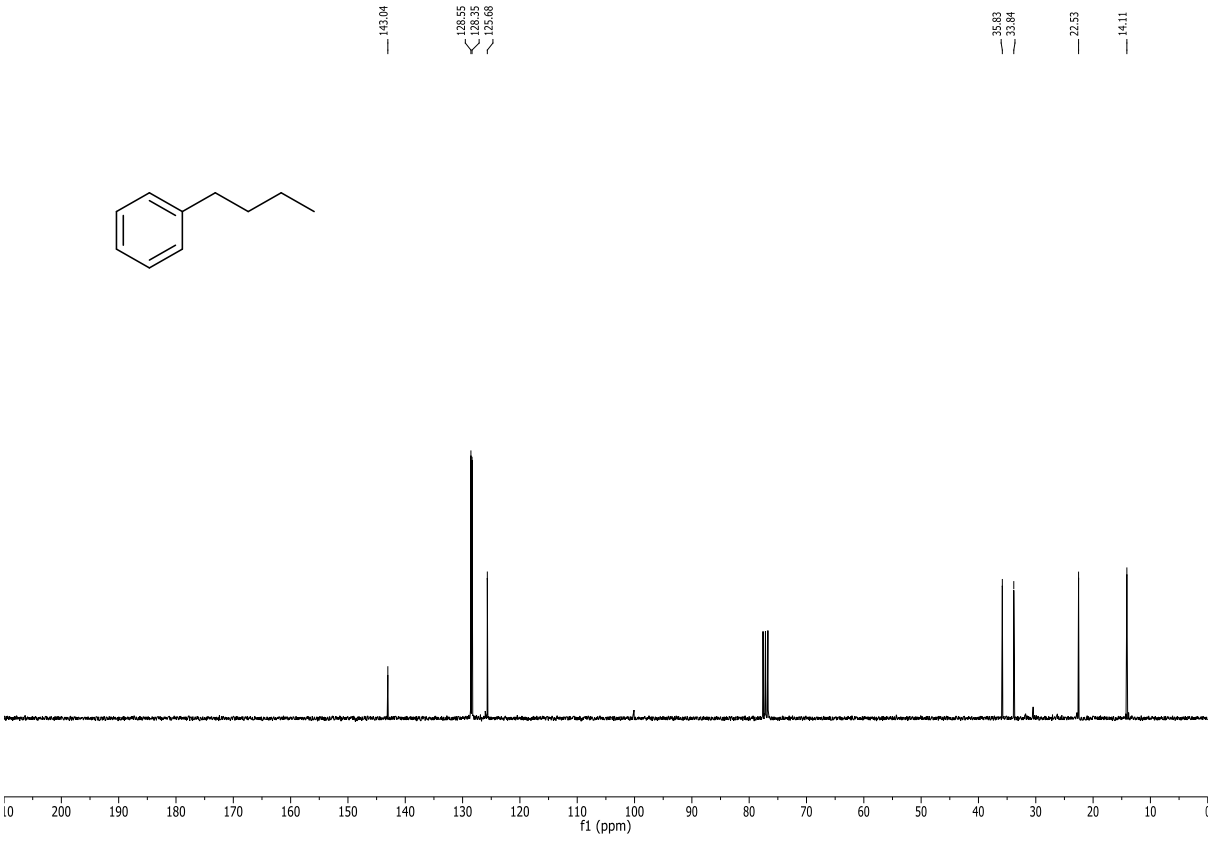
^{13}C-NMR: (101 MHz, $CDCl_3$): δ/ppm = 143.0, 128.6, 128.4, 125.7, 35.8, 33.8, 22.5, 14.1.

GC-MS: (EI): m/z =133.9 (92, [$M^{+\bullet}$]), 104.9 (100, [$M^{+\bullet}$]-[$C_2H_5^{\bullet}$]), 90.9 (71, [$M^{+\bullet}$]- $C_3H_7^{\bullet}$])

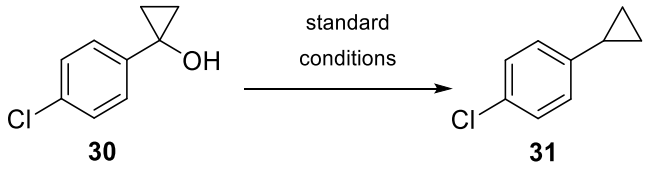
^{1}H-NMR: (400 MHz, $CDCl_3$) of **28**



^{13}C-NMR: (100 MHz, $CDCl_3$) of **28**



Deoxygenation of 1-(4-chlorophenyl)cyclopropanol (30)



30 **31**

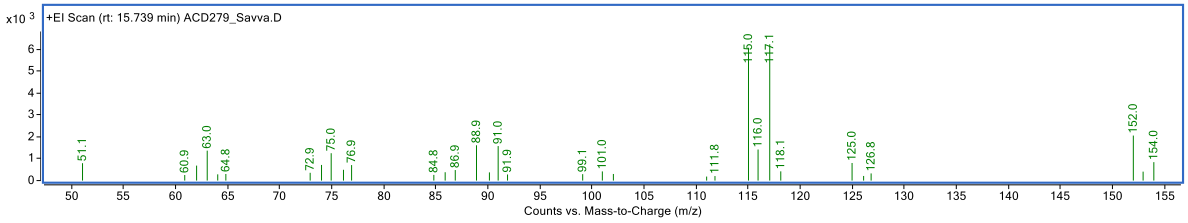
According to **GP2**, 1-chloro-4-cyclopropylbenzene **(31)** was synthesized from 1-(4-chlorophenyl)cyclopropanol (168 mg, 1.00 mmol, 1.00 equiv.) over 16 h. The product was afforded in traces determined by GC-FID.[31]

1-Chloro-4-cyclopropylbenzene **(31)**

C_8H_{18} (152.62 g/mol)

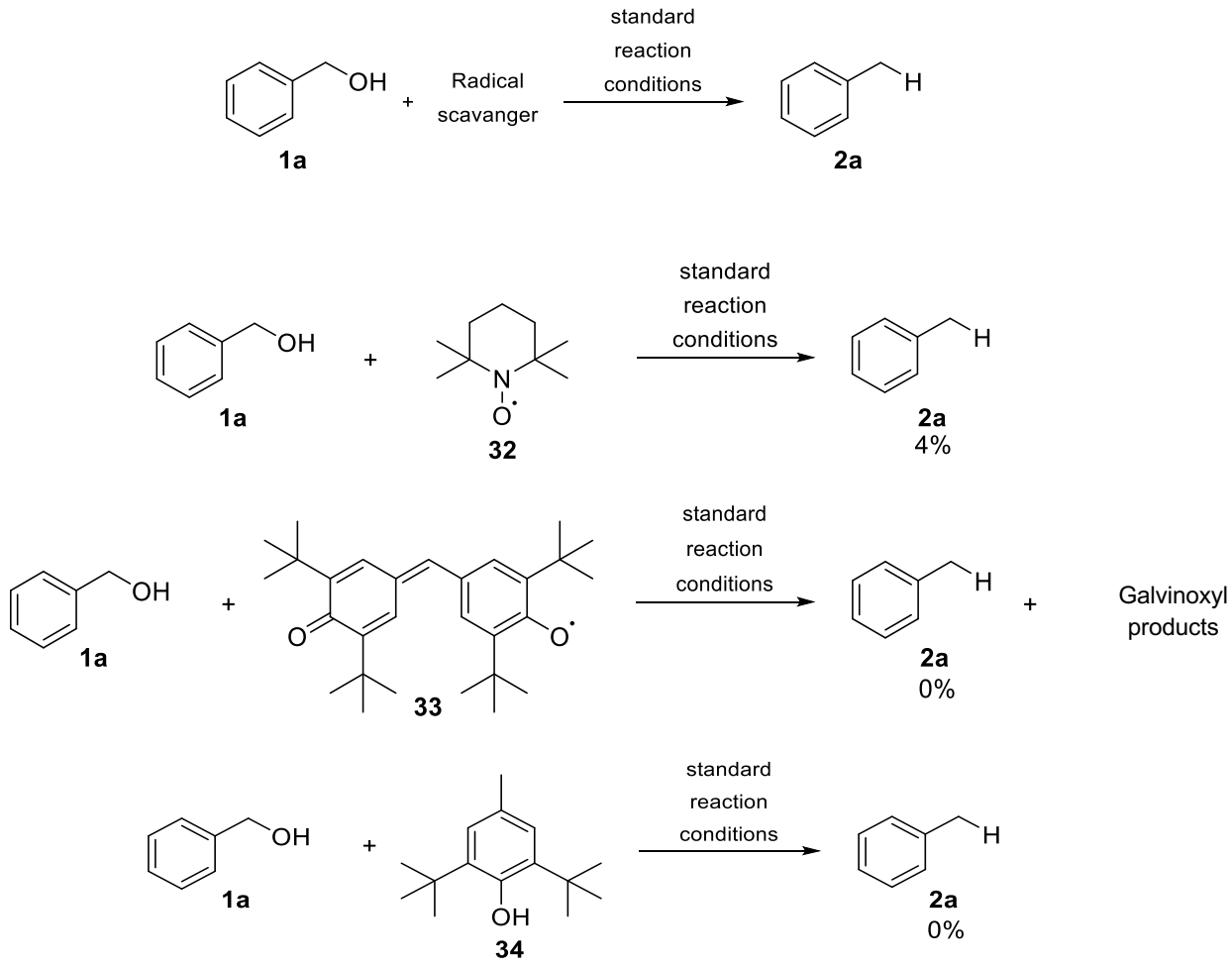
GC-FID: R_t = 8.469 **(M_{FID}1)**

GC-MS: (EI): m/z = 154.1 (12, [$M^{+\bullet}$]), 152.1 (37, [$M^{+\bullet}$]); 117.1 (100, [$M^{+\bullet}$]-[$Cl^{\bullet}$]), 115.1 (97, [$M^{+\bullet}$]-[$Cl^{\bullet}$]-2[$H^{\bullet}$]), 111.8 (97, [$M^{+\bullet}$]-[$C_3H_5^{\bullet}$]); R_t =15.739 **(M_{MS}3)**

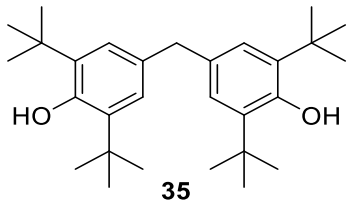


8.4 Radical Scavanger Experiments

Radical scavanger reactions were conducted under the standard conditions by which 2 equiv. of radical scavenger was added to the mixture. The obtained crude reaction mixture was analyzed by GC-MS with method **M_{MS}2** (Heating from 40 °C to 300 °C with a 10 °C/min heating rate; Helium –carrier gas) and GC-FID with method **M_{FID}1** (35 °C to 280 °C with a 10 °C/min heating rate).[32]

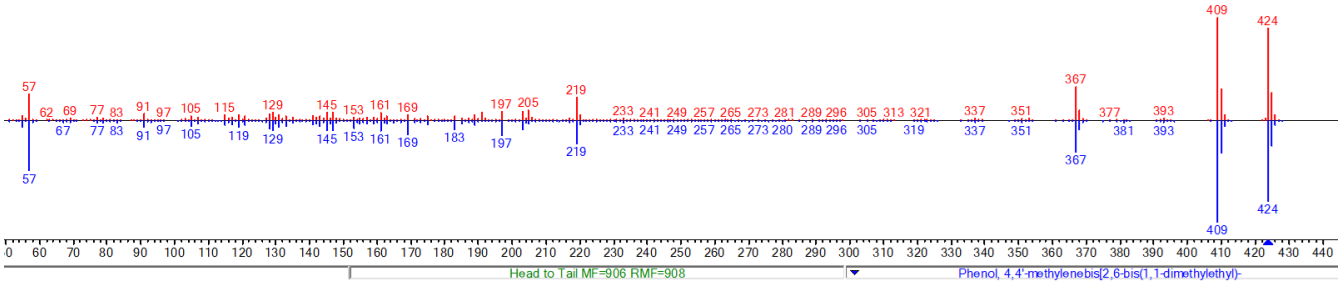


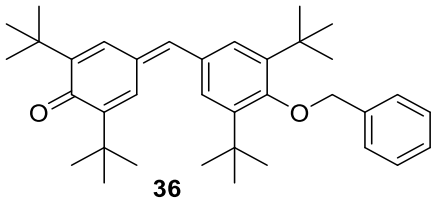
GC-MS detected products of the reaction with Galvinoxyl



Exact Mass: 424.33

GC-MS (EI): 424.34

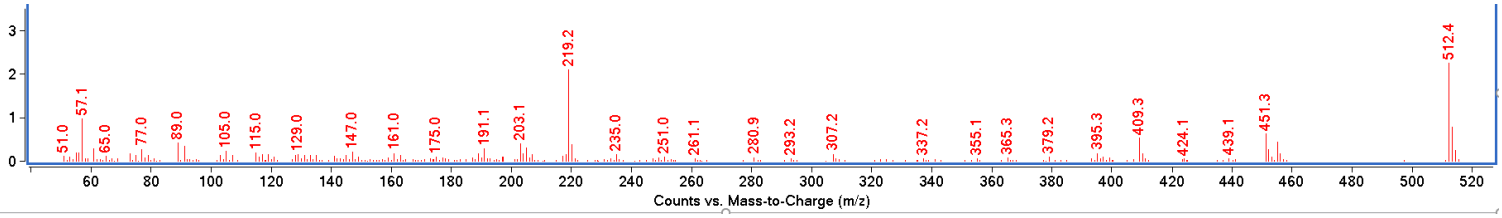




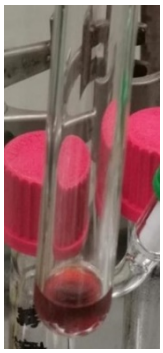
36

Exact Mass: 512.37

GC-MS (EI): 512.38

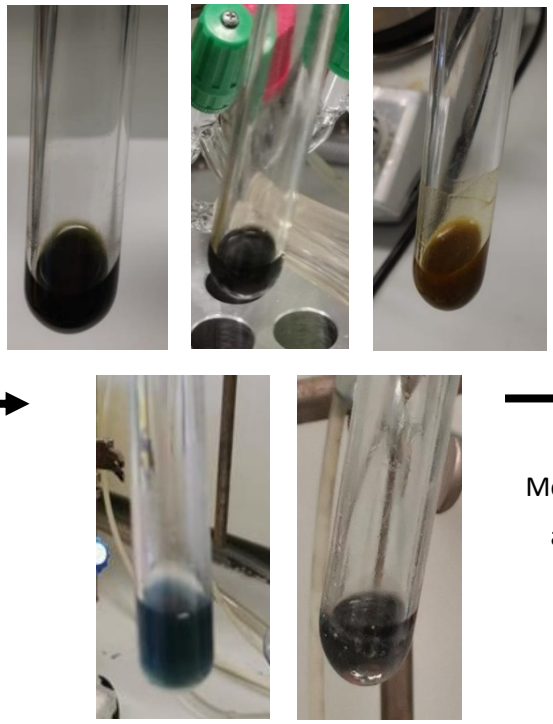


8.5 Color Evolution of the Reaction



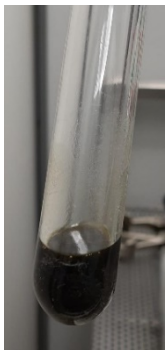
Cp_2TiCl_2 and Mn mixture before heating

Adding alcohol and heating to 50 °C



During the 2 h stirring at 50 °C. Color of the mixture varies among different alcohols

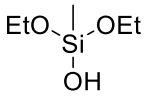
$Me(EtO)_2SiH$ addition

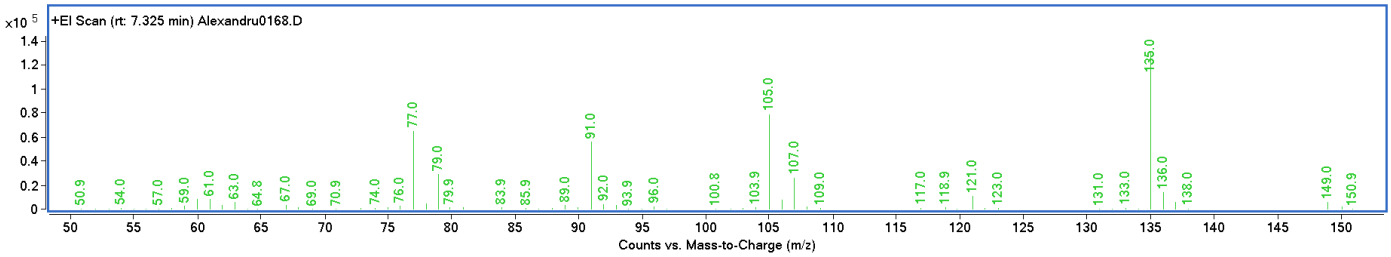


After $Me(EtO)_2SiH$ addition

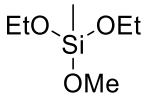
8.6 Analytical Data of Detected Silane By-products

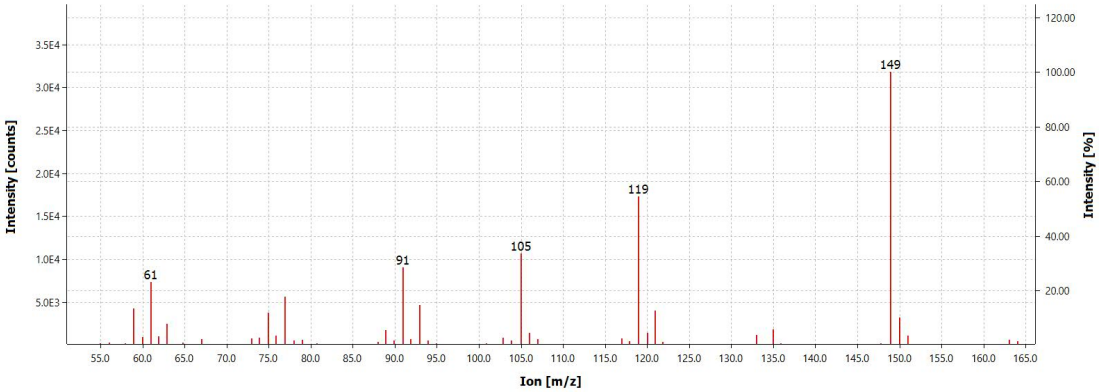
Diethoxymethylsilanol (38)



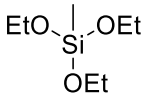


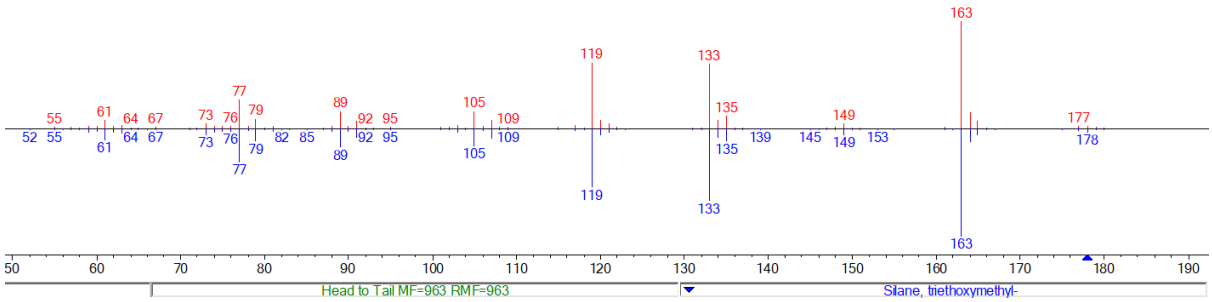
Diethoxymethoxymethylsilane (**21**)



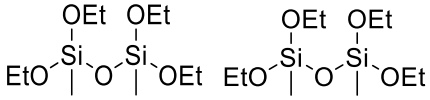


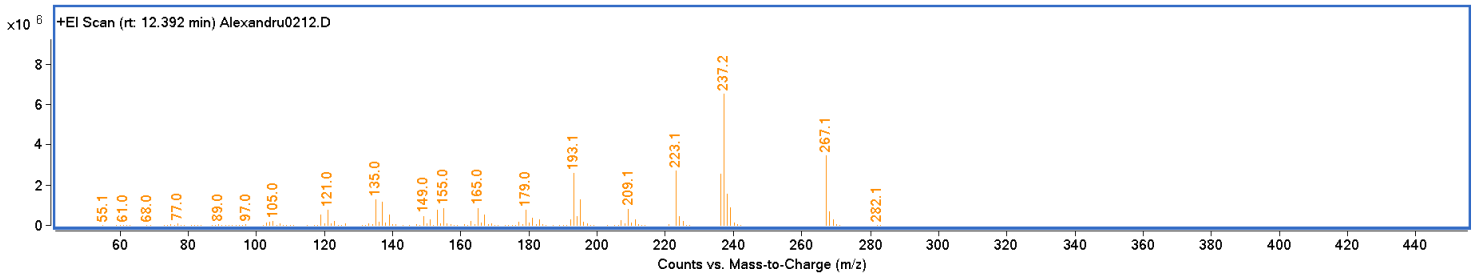
Triethoxymethylsilane (**39**)





1,1,3,3-Tetraethoxy-1,3-dimethyldisiloxane **(37)**



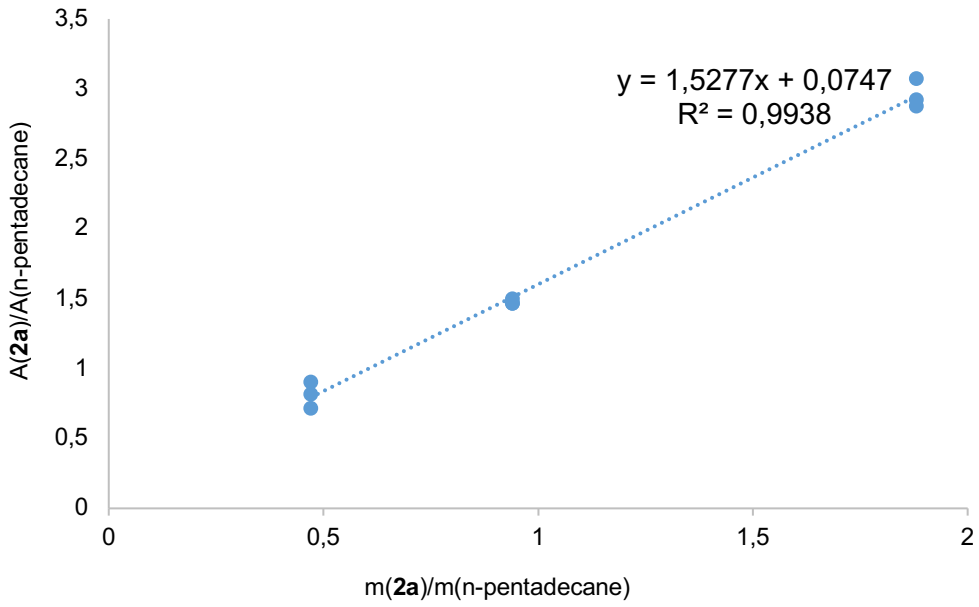


9 Calibration Data for GC-FID Analysis

GC calibration was performed by measuring samples with known amounts of analyte (here toluene) and internal standard (here n-pentadecane) (Table 8). Plotting of the area ratio of the two components versus the ratio of the respective masses leads to a calibration function which is used to calculate unknown amounts of analyte in samples taken from catalytic reactions.

Table S11. Calibration line for toluene **(2a)**

Sample	Mass (2a) (mg)	Mass (n-penatdecane) (mg)	Area (2a) (pAs)	Area (n-penatdecane) (pAs)
1.1 Tol	1.5	3.19	7077	7800
1.2 Tol	1.5	3.19	7321	8924
1.3 Tol	1.5	3.19	6350	8848
2.1 Tol	3	3.19	12762	8703
2.2 Tol	3	3.19	13314	8875
2.3 Tol	3	3.19	13363	9093
3.1 Tol	4.5	3.19	25018	8697
3.2 Tol	4.5	3.19	26627	9100
3.3 Tol	4.5	3.19	26372	8578



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