Supporting Information

Tandem Acid/Pd-Catalyzed Reductive Rearrangement of Glycol Derivatives

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1. General Information

1.1. Chemicals
All chemicals including solvents were purchased from several commercial suppliers (abcr, Acros, Alfa Aeser, Fluka, Riedel-de Häen, Sigma-Aldrich, TCI) and were used without further purification. Solvents in technical grade were distilled before use. Phenylacetaldehyde was freshly distilled via kugelrohr before use.

L1 was purchased from abcr and stored in a glove box under an atmosphere of dry argon. L2–8 were obtained from Aldrich, L9 from Fluka. Pd(acac)2 and Pd(dba)2 were purchased from Aldrich, Pd(OAc)2 from abcr, PdCl2 from TCI and Pd(CF3COO)2 from Alfa Aeser. For the catalytic reaction, methanesulfonic acid (≥ 99 %) from Sigma-Aldrich, formic acid (for synthesis) from Merck and chloroform (99.9 %, extra dry over molecular sieves, stabilized) from Acros was used.

1.2. General Techniques
When necessary, reactions were carried out under an inert atmosphere of dry argon in flame-dried glassware using standard Schlenk technique and dry solvents. For storage and further manipulations under an argon atmosphere, a glove box from Glovebox Systemtechnik was used. NMR tube experiments were carried out under an atmosphere of dry argon either in a glove box or using Schlenk technique. Chloroform-δ was dried over P2O5, degassed (freeze–pump–thaw) and stored over molecular sieves (3 Å) in a glove box. The reaction tubes used for reaction progress analysis were oven-dried and transferred into a glove box where they were equipped with magnetic stir bars and subsequently sealed with septa.

Flash column chromatography (CC) was carried out using silica gel (60 Å) as stationary phase with the indicated solvent systems either under manual elution or using an automated flash purification system Interchim PuriFlash XS420 with UV-detection. Thin-layer chromatography (TLC) was run on aluminum plates coated with silica gel Merck 60 F254 (layer thickness: 0.2 mm). The plates were analyzed under UV-light (254 nm) or stained with a KMnO4 or Ce(SO4)2/(NH4)2MoO4 solution.

1.3. Analytical Techniques
NMR spectra were acquired on a Bruker Avance III HD 300 NanoBay, HD 400, HDX 400 or HDX 700 spectrometer between 300 and 700 MHz at 295 K. Chemical shifts (δ) in ppm are referenced to tetramethylsilane as primary reference in the unified scale. Coupling constants (J) are reported in Hz with the following multiplet designations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). For some compounds, 13C DEPT-135 spectra were measured for further structural elucidation but are not noted explicitly in the experimental data.

IR spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer, equipped with an ATR module. Absorption bands are reported in wave numbers (ν) in cm⁻¹.

Melting points (m.p.) were determined using a melting point meter MPM-HV3 and are uncorrected (heating rate: 1 °C/min).
High resolution (HR) mass spectra were recorded on a Bruker maXis (APCI/ESI-HRMS) and a Finnigan MAT 95 (EI-HRMS) instrument at the mass spectrometry facility of the Institute of Organic Chemistry at the University of Tübingen.

Gas chromatography–mass spectrometry (GC-MS) analyses were carried out on an Agilent Technologies 7820A system with an Agilent Technologies 5977B EI-quadrupole mass selective detector and an Agilent Technologies 190915-433UI column using dry hydrogen as carrier gas (program: 50 °C, 0 min / 20 °C/min / 280 °C, 3.5 min).

GC-FID analyses were carried out using an Agilent Technologies 7820A system in combination with an Agilent Technologies 19091J-431 column and dry hydrogen as carrier gas (program: 50 °C, 0 min / 25 °C/min / 280 °C, 0.5 min). For quantification, pentadecane was added as internal standard. For calibration, four samples with different mass ratios $m_x/m_{st}$ between substrate and standard (approximately 1:8, 1:2, 1:1 and 3:2) were measured, and the obtained data were used to plot the peak area ratio $A_x/A_{st}$ against $m_x/m_{st}$. The slope obtained by linear regression is equivalent to the response factor $R$, which can be used to quantify unknown samples:

$$A_x/A_{st} = R \cdot m_x/m_{st}.$$
2. General Procedures

2.1. GP1a: Catalytic Reaction of 1ab under Initial Conditions
A flame-dried glass pressure tube reactor was charged with Pd(acac)$_2$ (1.14 mg, 3.75 µmol, 0.75 mol%) and L1 (5.92 mg, 15.0 µmol, 3 mol%) in a glove box. Outside the glove box, model substrate 1ab (76.1 mg, 500 µmol, 1 equiv), degassed chloroform (1 ml), methanesulfonic acid (6.5 µl, 100 µmol, 20 mol%) and formic acid (189 µl, 5.00 mmol, 10 equiv) were added. The pressure tube was sealed and kept in a pre-heated heating block at 100 °C for 4 h. Afterwards, the reaction mixture was allowed to cool down to room temperature. QuadraSil MP and pentadecane (standard, 50 µl) were added to the reaction mixture, which was filtered through a pad of basic Al$_2$O$_3$ and Celite before subjecting it to GC analysis.

2.2. GP1b: Catalytic Reaction of 1ab under Optimized Conditions
A flame-dried glass pressure tube reactor was charged with Pd(acac)$_2$ (1.14 mg, 3.75 µmol, 0.75 mol%) and L1 (5.92 mg, 15.0 µmol, 3 mol%) in a glove box. Outside the glove box, model substrate 1ab (76.1 mg, 500 µmol, 1 equiv) and dry and degassed chloroform (1 ml) were added. The resulting solution was treated with methanesulfonic acid (6.5 µl, 100 µmol, 20 mol%) and stirred at room temperature for 30 min before formic acid (189 µl, 5.00 mmol, 10 equiv) was added. Subsequently, the pressure tube was sealed, and the reaction mixture was placed in a pre-heated heating block and stirred at 100 °C for 4 h. Afterwards, the reaction mixture was allowed to cool down to room temperature. QuadraSil MP and pentadecane (standard, 50 µl) were added to the reaction mixture, which was filtered through a pad of basic Al$_2$O$_3$ and Celite before subjecting it to GC analysis.

2.3. GP2: Catalytic Reaction under Optimized Conditions
A flame-dried glass pressure tube reactor was charged with Pd(acac)$_2$ (2.28 mg, 7.50 µmol, 0.75 mol%) and L1 (11.8 mg, 30.0 µmol, 3 mol%) in a glove box. Outside the glove box, the respective substrate (1.00 mmol, 1 equiv) and dry and degassed chloroform (2 ml) were added. The resulting solution was treated with methanesulfonic acid (13.0 µl, 200.0 µmol, 20 mol%) and stirred at room temperature for 30 min before formic acid (377 µl, 10.0 mmol, 10 equiv) was added. Thereafter, the pressure tube was sealed, and the reaction mixture was placed in a pre-heated heating block and stirred at 100 °C for 4 h. Afterwards, the reaction mixture was allowed to cool down to room temperature. For quantitative GC analysis, QuadraSil MP and pentadecane (standard, 100 µl) were added to the reaction mixture, which was filtered through a pad of basic Al$_2$O$_3$ and Celite before subjecting it to GC analysis. If the product of the transformation was meant to be isolated, the reaction mixture was washed with water (3×1 ml), and the combined aqueous phases were extracted with DCM (3 ml). The combined organic phases were dried over MgSO$_4$ and filtered before the solvent was evaporated under reduced pressure, and the product was purified by means of flash CC.

2.4. GP3: Catalytic Reaction of 1ab in the Presence of an Additive
A flame-dried glass pressure tube reactor was charged with Pd(acac)$_2$ (1.14 mg, 3.75 µmol, 0.75 mol%) and L1 (5.92 mg, 15.0 µmol, 3 mol%) in a glove box. Outside the glove box, model substrate 1ab (76.1 mg, 500 µmol, 1 equiv), dry and degassed chloroform (1 ml) and the
respective additive A1–3 (500 µmol, 1 equiv) were added. The resulting solution was treated with methanesulfonic acid (6.5 µl, 100 µmol, 20 mol%) and stirred at room temperature for 30 min before formic acid (189 µl, 5.00 mmol, 10 equiv) was added. Subsequently, the pressure tube was sealed, and the reaction mixture was placed in a pre-heated heating block and stirred at 100 °C for 4 h. Afterwards, the reaction mixture was allowed to cool down to room temperature. QuadraSil MP and pentadecane (standard, 50 µl) were added to the reaction mixture, which was filtered through a pad of basic Al₂O₃ and Celite before subjecting it to GC analysis.

2.5. GP4: Nucleophilic Substitution at 2-Bromoacetophenone

Following a modified literature procedure. Over 15 min, a solution of 2-bromoacetophenone (4.98 g, 25.0 mmol, 1 equiv) in acetone (75 ml) was added dropwise to a mixture of the respective nucleophile (27.5 mmol, 1.1 equiv) and K₂CO₃ (5.18 g, 37.5 mmol, 1.5 equiv) in acetone (75 ml). The reaction mixture was refluxed overnight, allowed to cool down to room temperature and filtered. The filtrate was evaporated under reduced pressure yielding an orange solid. The product was purified by flash CC or recrystallization.

2.6. GP5a: Preparation of 2-Methoxy-1-arylethan-1-ones Using Grignard Reagents

**Preparation of Grignard Reagents:**

THF (15 ml) was added to magnesium turnings (1.09 g, 45.0 mmol, 1.5 equiv.) and iodine (152 mg, 600 µmol, 2 mol %). After cooling to 0 °C, the respective aryl bromide (30.0 mmol, 1 equiv.) was added dropwise, and the reaction mixture was stirred at room temperature for at least 1.5 h.

**Addition of Grignard Reagents to Methoxyacetonitrile:**

Following an adapted literature procedure, Grignard reagent (10.8 ml, 21.6 mmol, 1.8 equiv.) was added to a solution of 2-methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv.) in THF (24 ml). Directly after the addition, CuBr or CuCl (480 µmol, 4 mol %) was added. The reaction mixture was heated to reflux for 2–4 h and then cooled to 0 °C. Water (4 ml) was added, followed by 15 % H₂SO₄ (24 ml). The reaction mixture was refluxed for 1–1.5 h, cooled to room temperature and extracted with diethyl ether (3×20 ml). The combined extracts were dried over MgSO₄, filtered and evaporated under reduced pressure. The product was purified by flash CC on silica gel.

2.7. GP5b: Preparation of 2-Methoxy-1-arylethan-1-ones Using Lithium Organyls

A diethylether (10 ml) solution of the respective aryl bromide (15.0 mmol, 1.5 equiv) was treated dropwise with n-buthyllithium (2.5 M in hexane, 6.0 ml, 15 mmol, 1.5 equiv) at 0 °C and stirred for 20 min before a solution of methoxyacetonitril (744 µl, 10.0 mmol, 1 equiv) in diethylether (5 ml) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The crude product was hydrolyzed in a separation funnel by addition of aqueous HCl solution (6 M, pH adjusted to 1–2) and subsequently neutralized by addition of saturated
aqueous K$_2$CO$_3$ solution. The aqueous phase was separated and extracted with diethyl ether. The combined extracts were dried over MgSO$_4$, filtered and evaporated under reduced pressure. Purification by flash CC on silica gel afforded the respective 2-methoxy-1-aryl ethan-1-ones.

2.8. GP6: Reduction of Ketones with NaBH$_4$

Following an adapted literature procedure,[3] A solution of the respective ketone (5.00 mmol, 1 equiv) in methanol (20 ml) was treated with NaBH$_4$ (378 mg, 10.0 mmol, 2 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2.5–4 h. Then, the solvent was removed under reduced pressure. The residue was taken up in water (20 ml) and extracted with DCM ($6\times10$ ml). The combined extracts were dried over MgSO$_4$, filtered and evaporated in vacuo. The product was used without further purification if not stated otherwise.

2.9. GP7: Addition of Phenyllithium to Ketones

A solution of the respective ketone (2.50 mmol, 1 equiv) in diethyl ether (7.9 ml) was treated with phenyllithium (nominally 1.9 M in dibutyl ether, 7.9 ml, 15 mmol, 2 equiv) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding saturated aqueous NH$_4$Cl solution (5 ml) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with DCM ($3\times10$ ml). The combined organic phases were dried over MgSO$_4$ and filtered. The solvent was evaporated in vacuo, and the residue was purified by flash CC on silica gel.

2.10. GP8: Addition of Grignard Reagents to 2-Methoxyacetophenone

To a THF (6 ml) solution of 2-methoxyacetophenone (901 mg, 6.00 mmol, 1 equiv), Grignard reagent (nominally 2.0 M in THF; 15.0 ml, 30.0 mmol, 5 equiv) was added dropwise, and the reaction mixture was heated to reflux overnight. After cooling to 0 °C, the reaction was quenched by addition of water (5 ml) followed by saturated aqueous NH$_4$Cl solution (25 ml). The organic phase was separated, and the aqueous phase was extracted with diethyl ether ($3\times30$ ml). The combined organic phases were dried over MgSO$_4$ and filtered. The solvent was evaporated in vacuo, and the product was purified by flash CC on silica gel.

2.11. GP9: Addition of Grignard Reagents to Methyl Methoxyacetate

A THF (6 ml) solution of methyl methoxyacetate (594 µl, 6.00 mmol, 1 equiv) was treated with the respective Grignard reagent (2.0 M in THF; 7.5 ml, 15 mmol, 2.5 equiv) at 0 °C. The reaction mixture was heated to reflux for 4 h. After cooling to 0 °C, the reaction was quenched by adding saturated aqueous NH$_4$Cl solution (10 ml). Aqueous HCl solution (1 M) was added until the precipitate that had formed during quenching went into solution. The aqueous layer was separated and extracted with DCM ($3\times20$ ml). The combined organic phases were dried over MgSO$_4$, filtered and evaporated in vacuo. The product was isolated by flash CC on silica gel or kugelrohr distillation.
2.12. GP10: Formylation of Alcohols

Following an adapted literature procedure,[4] A mixture of formic acid (1.13 ml, 30.0 mmol, 12 equiv) and acetic anhydride (2.12 ml, 22.5 mmol, 9 equiv) was stirred at 60 °C for 1.5 h. Subsequently, it was cooled to room temperature, and NaHCO₃ (420 mg, 5.00 mmol, 2 equiv) and the respective alcohol (2.50 mmol, 1 equiv) were added. The reaction mixture was stirred at room temperature for 6 h. Then, the reaction was quenched by addition of water (10 ml), and the aqueous solution was extracted with DCM (3×10 ml). The combined extracts were washed with saturated aqueous Na₂CO₃ solution (2×10 ml) and water (2×10 ml) before they were dried over MgSO₄, filtered and evaporated in vacuo yielding the respective formic ester. The product was purified by flash CC on silica gel or used without further purification.
3. Substrate Synthesis

Scheme S1: Preparation of 1ah and 1ak starting from 1aa.

Scheme S2: Preparation of 1ab, 1ac and 1ai via 6.

Scheme S3: Preparation of 1af, 1aj, 1al and 1am from diol 1ag.
Scheme S4: Synthesis of 1ad, 1ae and 1ao starting from 2-bromoacetophenone.

Scheme S5: Synthesis of substrates 1b–q by addition of metal organyls to methoxyacetonitrile.

Scheme S6: Synthesis of non-benzylic alcohols using Grignard reagents.
Scheme S7: Preparation of unsymmetric non-benzylic alcohol 1s.

Scheme S8: Synthesis of 1v from cyclohexanone.

Scheme S9: Preparation of compounds 1x and 1y bearing two different vicinal oxygen substituents.

Scheme S10: Preparation of 3a–c.

Scheme S11: Preparation of 3d by methylation of 3e.
Scheme S12: Preparation of deuterated substrates.
2-phenoxycetophenone (S1aa)

The title compound was synthesized from 2-bromoacetophenone (4.98 g, 25.0 mmol, 1 equiv) and phenol (2.59 g, 27.5 mmol, 1.1 equiv) in acetone (150 ml) in the presence of K₂CO₃ (5.18 g, 37.5 mmol, 1.5 equiv) according to general procedure GP4. It was isolated by recrystallization from methanol as a white solid (3.33 g, 15.7 mmol, 63 %). Analytical data was in accordance with the literature.\[1\]

m.p. = 74 °C

Rf = 0.23 (hexane/ethyl acetate 9:1)

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.95–7.91 (m, 2H), 7.7–7.52 (m, 1H), 7.45–7.40 (m, 2H), 7.24–7.17 (m, 2H), 6.93–6.85 (m, 3H), 5.20 (s, 2H).

\(^13\)C\(^{1}\)H NMR (101 MHz, CDCl₃): δ 194.6, 158.0, 134.6, 133.9, 129.6, 128.9, 128.2, 121.7, 114.8, 70.8.

GC-MS (EI): m/z 212, 105, 91, 77, 65, 51.

IR (ATR): \(\tilde{\nu}\) 3109, 3064, 3004, 2900, 2844, 2747, 1703, 1595, 1498, 1431, 1387, 1334, 1301, 1249, 1092, 1029, 973, 872, 749, 686.

2-(2-methoxyphenoxy)-1-phenylethan-1-one (S1ae)

The title compound was synthesized from 2-bromoacetophenone (1.99 g, 10.0 mmol, 1 equiv) and 2-methoxyphenol (1.37 g, 11.0 mmol, 1.1 equiv) in acetone (60 ml) in the presence of K₂CO₃ (2.07 g, 15.0 mmol, 1.5 equiv) according to general procedure GP4. It was isolated by flash CC on silica gel (petroleum ether/ethyl acetate 9:1) as an orange solid (2.36 g, 9.74 mmol, 97 %). Analytical data was in accordance with the literature.\[1\]

Rf = 0.12 (petroleum ether/ethyl acetate 9:1)

\(^1\)H NMR (400 MHz, CDCl₃): δ 8.01 (d, \(J = 9.8\) Hz, 2H), 7.65–7.56 (m, 1H), 7.53–7.45 (m, 2H), 7.01–6.90 (m, 2H), 6.88–6.82 (m, 2H), 5.35 (s, 2H), 3.88 (s, 3H).

\(^13\)C\(^{1}\)H NMR (101 MHz, CDCl₃): δ 194.5, 149.7, 147.5, 134.6, 133.7, 128.8, 128.1, 122.4, 120.7, 114.8, 112.1, 72.1, 55.9.

GC-MS (EI): m/z 242, 224, 120, 105, 77.
2-(heptylthio)-1-phenylethan-1-one (S1ao)

The title compound was synthesized from 2-bromoacetophenone (995 mg, 5.00 mmol, 1 equiv) and heptanethiol (728 mg, 5.50 mmol, 1.1 equiv) in acetone (20 ml) in the presence of K₂CO₃ (5.18 g, 37.5 mmol, 1.5 equiv) according to general procedure GP4 providing it as a yellow oil (1.18 g, 4.71 mmol, 94 %).

^1H NMR (400 MHz, CDCl₃): δ 7.93–7.89 (m, 2H), 7.53–7.37 (m, 3H), 3.71 (s, 2H), 2.49 (m, 2H), 1.56–1.47 (m, 2H), 1.33–1.13 (m, 8H), 0.80 (t, J = 6.9 Hz, 3H).

^13C(^1H) NMR (101 MHz, CDCl₃): δ 194.6, 135.3, 133.3, 128.8, 128.7, 37.1, 32.4, 31.7, 29.0, 28.8, 28.7, 22.6, 14.1.

GC-MS (EI): m/z 250, 132, 120, 105, 77.

1-(4-(tert-butyl)phenyl)-2-methoxyethan-1-one (S1b)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (4-(tert-butyl)phenyl)magnesium bromide (nominally 2 m in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuBr (68.9 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 3.5 h followed by acidic hydrolysis and overnight stirring at room temperature, it was isolated by flash CC on silica gel (hexane/ethyl acetate 85:15) as an orange oil (1.18 g, 5.72 mmol, 48 %). Analytical data was in accordance with the literature. Rᵣ = 0.24 (hexane/ethyl acetate 9:1)

^1H NMR (400 MHz, CDCl₃): δ 7.83–7.78 (m, 2H), 7.43–7.29 (m, 2H), 4.62 (s, 2H), 3.44 (s, 3H), 1.27 (s, 9H).

^13C(^1H) NMR (101 MHz, CDCl₃): δ 195.8, 157.4, 132.3, 127.8, 125.7, 75.3, 59.5, 35.2, 31.1.

GC-MS (EI): m/z 191, 176, 161, 146, 118, 117, 105, 91, 77, 57.

IR (ATR): ν 3056, 2960, 2870, 2822, 1696, 1603, 1566, 1461, 1409, 1364, 1409, 1290, 1234, 1193, 1129, 1029, 984, 924, 831, 716.
2-methoxy-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S1c)

![Chemical structure](image)

The title compound was synthesized from 4-bromobenzotrifluoride (2.1 ml, 15 mmol, 1.5 equiv) and methoxyacetonitrile (744 µl, 10.0 mmol, 1 equiv) according to general procedure GP5b. Purification by flash CC on silica gel (hexane/ethyl acetate 9:1) afforded the title compound as yellow crystals (1.14 g, 5.22 mmol, 52%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56–7.52 (m, 2H), 7.46–7.42 (m, 2H), 4.88 (dd, $J$ = 8.6, 3.2 Hz, 1H), 3.52–3.31 (m, 5H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 195.5, 128.4, 125.8 (q, $J$ = 3.6 Hz), 75.6, 59.5.

$^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ –62.5.

GC-MS (EI): m/z 218, 199, 188, 173, 145, 125, 109.

2-methoxy-1-(4-methoxyphenyl)ethan-1-one (S1d)

![Chemical structure](image)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (4-methoxyphenyl)magnesium bromide (nominally 2 M in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuCl (47.5 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 3.5 h followed by acidic hydrolysis and refluxing for 1 h, it was isolated after extraction with ethyl acetate and purification by flash CC on silica gel (hexane/diethyl ether 1:1) as an orange solid (1.17 g, 5.49 mmol, 54 %). Analytical data was in accordance with the literature.$^{[5]}$

m.p. = 39 °C

$R_t$ = 0.29 (hexane/diethyl ether 1:1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88–7.83 (m, 2H), 6.89–6.84 (m, 2H), 4.58 (s, 2H), 3.80 (s, 3H), 3.43 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 194.7, 163.8, 130.2, 128.0, 113.9, 75.2, 59.4, 55.5.

GC-MS (EI): m/z 150, 135, 121, 107, 92, 77.

IR (ATR): $\tilde{\nu}$ 3071, 2930, 2825, 1689, 1595, 1510, 1461, 1420, 1364, 1308, 1238, 1170, 1126, 1021, 980, 954, 921, 831, 772.
2-methoxy-1-(4-(methylthio)phenyl)ethan-1-one (S1e)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (4-(methylthio)phenyl)magnesium bromide (nominally 2 M in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuBr (138 mg, 960 µmol, 8 mol%) according to general procedure GP5a. After refluxing for 3 h followed by acidic hydrolysis and refluxing for 1.5 h, it was isolated after extraction with ethyl acetate and purification by flash CC on silica gel (hexane/ethyl acetate 9:1→8:2) as a yellow solid (1.64 g, 8.36 mmol, 68%).

m.p. = 60 °C

$R_F = 0.22$ (hexane/ethyl acetate 4:1)

$^1H$ NMR (400 MHz, CDCl$_3$): δ 7.79–7.75 (m, 2H), 7.21–7.17 (m, 2H), 4.50 (s, 2H), 3.42 (s, 3H), 2.45 (s, 3H).

$^{13}C$($^1H$) NMR (101 MHz, CDCl$_3$): δ 195.2, 146.6, 131.1, 128.3, 125.0, 75.2, 59.4, 14.7.

GC-MS (EI): m/z 196, 166, 151, 137, 123, 108, 79, 77.

HRMS (APCI$^+$): m/z calcld. for C$_{10}$H$_{13}$O$_2$S ([M+H]$^+$) 197.06308, found 197.06337.

IR (ATR): ν 3079, 2989, 2922, 2896, 2833, 1681, 1584, 1491, 1424, 1398, 1364, 1323, 1282, 1234, 1185, 1122, 1092, 1006, 977, 917, 839, 813, 708.

1-(4-fluorophenyl)-2-methoxyethan-1-one (S1f)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (4-fluorophenyl)magnesium bromide (nominally 2 M in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuBr (68.9 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 4 h followed by acidic hydrolysis and refluxing for 1.5 h, it was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1) as a brown oil (703 mg, 4.18 mmol, 35%). Analytical data was in accordance with the literature.$^{[6]}$

$R_F = 0.34$ (hexane/ethyl acetate 4:1)

$^1H$ NMR (400 MHz, CDCl$_3$): δ 7.94–7.88 (m, 2H), 7.11–7.04 (m, 2H), 4.59 (s, 2H), 3.43 (s, 3H).

$^{13}C$($^1H$) NMR (101 MHz, CDCl$_3$): δ 194.8, 166.0 (d, J = 255.4 Hz), 130.7 (d, J = 9.4 Hz), 115.9 (d, J = 22.0 Hz), 75.3, 59.5.

$^{19}F$ NMR (377 MHz, CDCl$_3$): δ −104.1 (m).

GC-MS (EI): m/z 138, 123, 109, 95, 75.

IR (ATR): ν 3071, 2989, 2930, 2825, 1700, 1595, 1506, 1454, 1409, 1364, 1297, 1226, 1197, 1156, 1126, 1010, 984, 924, 835, 738, 686.
1-(4-chlorophenyl)-2-methoxyethan-1-one (S1g)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (4-chlorophenyl)magnesium bromide (nominally 2 M in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuBr (68.9 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 3 h followed by acidic hydrolysis and refluxing for 1.5 h, it was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1) as a colorless solid (1.46 g, 7.91 mmol, 66 %). Analytical data was in accordance with the literature.[5]

\[ R_f = 0.28 \text{ (hexane/ethyl acetate 4:1)} \]

\[ ^1H\text{ NMR} (400 MHz, CDCl}_3): \delta 7.83–7.79 (m, 2H), 7.40–7.35 (m, 2H), 4.58 (s, 2H), 3.42 (s, 3H). \]

\[ ^{13}C\{^1H\} \text{ NMR} (101 MHz, CDCl}_3): \delta 195.2, 140.0, 133.1, 129.4, 129.1, 75.4, 59.5. \]

\[ \text{GC-MS (EI)}: m/z 154, 141, 139, 113, 111, 75. \]

\[ \text{IR (ATR)}: \tilde{\nu} 3090, 3034, 2986, 2930, 2881, 2818, 2743, 1931, 1812, 1696, 1588, 1469, 1398, 1308, 1238, 1193, 1126, 1088, 1025, 951, 828, 712. \]

2-methoxy-1-(3-methoxyphenyl)ethan-1-one (S1h)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and (3-methoxyphenyl)magnesium bromide (nominally 2 M in THF, 10.8 ml, 21.6 mmol, 1.8 equiv) in THF (24 ml) in presence of CuCl (47.5 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 2.5 h followed by acidic hydrolysis and refluxing for 1 h, it was isolated by flash CC on silica gel (hexane/ethyl acetate 9:1→8:2) as a yellow liquid (1.03 g, 5.69 mmol, 48 %). Analytical data was in accordance with the literature.[5]

\[ R_f = 0.32 \text{ (hexane/ethyl acetate 4:1)} \]

\[ ^1H\text{ NMR} (400 MHz, CDCl}_3): \delta 7.44–7.39 (m, 2H), 7.30 (t, J = 7.9 Hz, 1H), 7.08–7.03 (m, 1H), 4.63 (s, 2H), 3.79 (s, 3H), 3.44 (s, 3H). \]

\[ ^{13}C\{^1H\} \text{ NMR} (101 MHz, CDCl}_3): \delta 195.9, 159.9, 136.1, 129.7, 120.3, 120.1, 112.1, 75.3, 59.5, 55.5. \]

\[ \text{GC-MS (EI)}: m/z 180, 150, 135, 121, 107, 92, 77, 63. \]

\[ \text{IR (ATR)}: \tilde{\nu} 3071, 2930, 2825, 1700, 1580, 1484, 1454, 1431, 1364, 1331, 1260, 1193, 1126, 1025, 992, 928, 872, 768, 686. \]
2-methoxy-1-(o-tolyl)ethan-1-one (S1i)

![Structure S1i](image)

The title compound was synthesized from methoxyacetonitrile (892 µl, 12.0 mmol, 1 equiv) and o-tolylmagnesium chloride (nominally 1 M in THF, 21.6 ml, 21.6 mmol, 1.8 equiv) in THF (12 ml) in presence of CuBr (68.9 mg, 480 µmol, 4 mol%) according to general procedure GP5a. After refluxing for 4 h followed by acidic hydrolysis and refluxing for 1 h, it was isolated after extraction with DCM and purification by flash CC on silica gel (hexane/ethyl acetate 9:1) as a yellow liquid (1.12 g, 6.82 mmol, 57 %). Analytical data was in accordance with the literature.\[7\]

$R_f = 0.19$ (hexane/ethyl acetate 9:1)

$^1H$ NMR (400 MHz, CDCl$_3$): δ 7.51–7.47 (m, 1H), 7.35–7.29 (m, 1H), 7.21–7.15 (m, 2H), 4.48 (s, 2H), 3.41 (s, 3H), 2.44 (s, 3H).

$^{13}C(^1H)$ NMR (101 MHz, CDCl$_3$): δ 200.3, 138.6, 135.3, 132.1, 131.8, 128.1, 125.7, 76.6, 59.4, 21.1.

GC-MS (EI): m/z 119, 91, 65.

IR (ATR): ν 3064, 2930, 2822, 1696, 1599, 1572, 1453, 1379, 1293, 1223, 1193, 1118, 1018, 973, 924, 820, 757, 723.

2-methoxy-1-(2-methoxyphenyl)ethan-1-one (S1j)

![Structure S1j](image)

The title compound was synthesized from 0-bromoanisole (1.9 ml, 15 mmol, 1.5 equiv) and methoxyacetonitrile (744 µl, 10.0 mmol, 1 equiv) according to general procedure GP5b. Purification by flash CC on silica gel (hexane/ethyl acetate 9:1) afforded the title compound as a yellow oil (0.97 g, 5.38 mmol, 54 %).

$R_f = 0.2$ (hexane/ethyl acetate 9:1)

$^1H$ NMR (400 MHz, CDCl$_3$): δ 7.84 (dd, J = 7.8, 1.7 Hz, 1H), 7.46–7.40 (m, 1H), 6.99–6.98 (m, 2H), 4.58 (s, 2H), 3.86 (s, 3H), 3.43 (s, 3H).

$^{13}C(^1H)$ NMR (101 MHz, CDCl$_3$): δ 197.5, 259.2, 134.3, 130.8, 125.4, 121.0, 111.5, 79.1, 59.3, 55.5.

GC-MS (EI): m/z 180, 164, 150, 135, 121, 105, 92, 77
1-methoxypentan-2-one (S1s)

Following a literature procedure. Methoxyacetonitrile (1.5 ml, 20 mmol, 1 equiv) was added to \( n \)-propylmagnesium chloride (2 M in THF, 10.0 ml, 20.0 mmol, 1 equiv) at 0 °C over 30 min. The reaction mixture was allowed to warm to room temperature and stirred overnight and then quenched by addition of 1 M aqueous HCl (5 ml). The organic layer was separated, washed with sat. aqueous Na₂CO₃ solution (5 ml), dried over MgSO₄, filtered and evaporated \textit{in vacuo}. Kugelrohr distillation yielded the title compound as a colorless liquid (610 mg, 5.25 mmol, 27 %). Spectral data was in accordance with the literature. \([G]\)

\[ R_f = 0.52 \text{ (hexane/ethyl acetate 85:15)} \]

\( ^1H \) NMR (300 MHz, CDCl₃): \( \delta \) 3.99 (s, 2H), 3.40 (s, 3H), 2.40 (t, \( J = 7.3 \) Hz, 2H), 1.68–1.54 (m, 2H), 0.91 (t, \( J = 7.4 \) Hz, 3H).

\( ^13C\{^1H\} \) NMR (75 MHz, CDCl₃): \( \delta \) 208.6, 77.6, 59.2, 40.6, 16.8, 13.7.

1-oxaspiro[2.5]octane (S1v)

Following a literature procedure. To a solution of dibromomethane (838 \( \mu l \), 12.0 mmol, 1.2 equiv) and cyclohexanone (1.04 ml, 10.0 mmol, 1 equiv) in THF (40 ml), butyllithium (2.5 M in hexane, 4.2 ml, 10.5 mmol, 10.5 equiv) was added drowise at \(-78 \) °C. The reaction mixture was allowed to warm to room temperature, stirred over night and then quenched with sat. aqueous NH₄Cl solution (25 ml). The aqueous phase was separated and extracted with diethylether (2×20 ml). The combined organic phases were dried over MgSO₄, filtered and evaporated under reduced pressure. Kugelrohr distillation afforded the title compound as a colorless oil (502 mg, 4.48 mmol, 45 %). The spectral data was in accordance with the literature. \([J]\)

\[ R_f = 0.7 \text{ (hexane/ethyl acetate 99:1)} \]

\( ^1H \) NMR (300 MHz, CDCl₃): \( \delta \) 2.59 (s, 2H), 1.80–1.67 (m, 2H), 1.63–1.44 (m, 8H).

\( ^13C\{^1H\} \) NMR (75 MHz, CDCl₃): \( \delta \) 59.0, 54.5, 33.6, 25.2, 24.9.
1-methoxy-3-phenoxypropan-2-one (S1x)

\[ \text{PhO} \overset{\text{O}}{\longrightarrow} \text{OMe} \]

S1x

The title compound was synthesized by Swern oxidation of 1-methoxy-3-phenoxypropan-2-ol (1x, 1.72 g, 9.45 mmol) according to a reported procedure.\[m\] It was obtained as a white crystalline solid (480 mg, 2.66 mmol, 27%). Analytical data was in accordance with the literature.\[n\]

m.p. = 50 °C

\[ R_f = 0.2 \text{ (hexane/ethyl acetate 4:1) } \]

\[^1H\text{ NMR (300 MHz, CDCl}_3\text{): } \delta \text{ 7.37–7.23 (m, 2H), 7.05–6.97 (m, 1H), 6.93–6.88 (m, 2H), 4.74 (s, 2H), 4.33 (s, 2H), 3.46 (s, 3H).} \]

\[^{13}C\text{(^1H) NMR (75 MHz, CDCl}_3\text{): } \delta \text{ 204.2, 157.6, 129.7, 121.8, 114.5, 76.2, 71.6, 59.5.} \]

\text{GC-MS (EI): } m/z 180, 162, 138, 107, 94, 77.

2-methoxy-1-phenylpropan-1-one (S3a)

\[ \text{Ph} \overset{\text{O}}{\longrightarrow} \text{OMe} \]

S3a

Sodium hydride (57–63 % in mineral oil, 1.05 g, 26.3 mmol, 1.05 equiv) was added to a solution of 2-methoxyacetophenone (3.76 g, 25.0 mmol, 1 equiv) in THF (25 ml) cooled to 0 °C. After 10 min of stirring, methyl iodide (1.56 ml, 25.0 mmol, 1 equiv) was added, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched at 0 °C by addition of water (5 ml) and saturated aqueous NH\textsubscript{4}Cl solution (10 ml). The organic layer was separated, and the aqueous phase was extracted with DCM (3×15 ml). The combined organic phases were dried over MgSO\textsubscript{4}, filtered and evaporated under reduced pressure. The residue was purified by flash CC on silica gel (hexane/ethyl acetate 9:1) yielding the title compound as a yellow liquid (2.58 g, 14.5 mmol, 58 %). Analytical data was in accordance with the literature.\[n\]

\[ R_f = 0.33 \text{ (hexane/ethyl acetate 9:1) } \]

\[^1H\text{ NMR (400 MHz, CDCl}_3\text{): } \delta \text{ 7.99–7.95 (m, 2H), 7.53–7.47 (m, 1H), 7.42–7.36 (m, 2H), 4.56 (q, } J = 6.9 \text{ Hz, 1H), 3.31 (s, 3H), 1.41 (d, } J = 6.9 \text{ Hz, 3H).} \]

\[^{13}C\text{(^1H) NMR (101 MHz, CDCl}_3\text{): } \delta \text{ 200.5, 134.8, 133.4, 128.7, 128.7, 80.2, 57.3, 18.5.} \]

\text{GC-MS (EI): } m/z 134, 105, 77, 59, 51.

\text{IR (ATR): } \tilde{\nu} 3064, 2982, 2933, 2825, 1692, 1595, 1446, 1372, 1338, 1305, 1267, 1208, 1111, 1014, 962, 865, 790, 749, 697.
2-methoxy-2-methyl-1-phenylpropan-1-one (S3b)

Sodium hydride (57–63 % in mineral oil, 799 mg, 20.0 mmol, 3 equiv) was added to a solution of 2-methoxyacetophenone (1.00 g, 6.66 mmol, 1 equiv) in THF (20 ml) cooled to 0 °C. After 15 min of stirring, methyl iodide (1.24 ml, 20.0 mmol, 3 equiv) was added, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched at 0 °C by addition of water (5 ml) and saturated aqueous NH₄Cl solution (10 ml). The organic layer was separated, and the aqueous phase was extracted with DCM (3×15 ml). The combined organic phases were dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by flash CC on silica gel (hexane/ethyl acetate 95:5) yielding the title compound as a colorless liquid (681 mg, 3.82 mmol, 57 %). Analytical data was in accordance with the literature.[12]

Rf = 0.40 (hexane/ethyl acetate 95:5)

¹H NMR (400 MHz, CDCl₃): δ 8.22–8.18 (m, 2H), 7.49–7.44 (m, 1H), 7.39–7.34 (m, 2H), 3.12 (s, 2H), 1.45 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 203.6, 134.9, 312.8, 129.8, 128.3, 83.4, 52.5, 24.7.

GC-MS (EI): m/z 105, 77, 73, 51.

IR (ATR): ν 3068, 2986, 2933, 2825, 1677, 1595, 1446, 1379, 1271, 1167, 1070, 1003, 939, 902, 813, 712.

2-phenoxy-1-phenylethanol-1-ol (1aa)

The title compound was synthesized from 2-phenoxyacetophenone (S1ad, 1.06 g, 5.00 mmol, 1 equiv) and NaBH₄ (378 mg, 10.0 mmol, 2 equiv) in methanol (20 ml) according to general procedure GP6. After 2 h at room temperature, it was isolated as a colorless solid (1.04 g, 4.85 mmol, 97 %). Analytical data was in accordance with the literature.[11]

m.p. = 63 °C

Rf = 0.64 (hexane/diethylether 1:1)

¹H NMR (400 MHz, CDCl₃): δ 7.40–7.17 (m, 7H), 6.92–6.82 (m, 3H), 5.05 (dd, J = 8.8, 3.1 Hz, 1H), 4.06–3.90 (m, 2H), 2.73 (s, 1H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 158.4, 139.7, 129.6, 128.6, 128.2, 126.3, 121.3, 114.7, 73.3, 72.6.

GC-MS (EI): m/z 196, 108, 107, 94, 91, 79, 77, 65, 51.

IR (ATR): ν 3247, 3060, 3030, 2933, 2878, 1584, 1495, 1454, 1387, 1342, 1290, 1238, 1096, 1066, 1040, 917, 861, 749, 690.

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2-methoxy-1-phenylethan-1-ol (1ab)

The title compound was synthesized from 2-methoxyacetophenone (1.50 g, 10.0 mmol, 1 equiv) and NaBH₄ (757 mg, 20.0 mmol, 2 equiv) in methanol (40 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1–1:1) as a colorless liquid (1.40 g, 9.21 mmol, 92%). Analytical data was in accordance with the literature.[1]

*RF* = 0.22 (hexane/ethyl acetate 4:1)

^1H NMR (400 MHz, CDCl₃): δ 7.32–7.18 (m, 5H), 4.81 (dd, *J* = 8.9, 3.2 Hz, 1H), 3.48–3.32 (m, 2H), 3.35 (s, 3H).

^13C{^1H} NMR (101 MHz, CDCl₃): δ 140.3, 128.4, 127.9, 126.2, 78.2, 72.6, 59.0.

GC-MS (EI): *m/z* 152, 134, 107, 91, 79, 77, 51.

IR (ATR): *ν* 3425, 3064, 3030, 2982, 2889, 2825, 1957, 1882, 1812, 1700, 1603, 1491, 1454, 1405, 1371, 1323, 1193, 1115, 1062, 1029, 969, 902, 828, 757, 701.

2-ethoxy-1-phenylethan-1-ol (1ac)

Ethanol (2.3 ml, 40 mmol, 10 equiv) was added dropwise to sodium metal (115 mg, 5.00 mmol, 1.25 equiv), and the resulting mixture was heated to reflux for 45 min until all of the sodium metal had gone into solution. After cooling to room temperature, styrene oxide (457 µl, 4.00 mmol, 1 equiv) was added, and the resulting red solution was stirred under reflux for 2 h. The reaction mixture was cooled to 0 °C and quenched by addition of water (5 ml) and saturated aqueous NH₄Cl solution (10 ml). The resulting mixture was extracted with ethyl acetate (3×20 ml), and the combined extracts were dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by flash CC on silica gel (hexane/ethyl acetate 4:1) yielded the title compound as a yellow liquid (362 mg, 2.18 mmol, 54%).

*RF* = 0.34 (hexane/ethyl acetate 4:1)

^1H NMR (400 MHz, CDCl₃): δ 7.34–7.19 (m, 5H), 4.82 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.58–3.33 (m, 4H), 2.80 (s, 1H), 1.17 (t, *J* = 7.0 Hz, 3H).

^13C{^1H} NMR (101 MHz, CDCl₃): δ 140.3, 128.4, 127.8, 126.2, 76.2, 72.8, 66.8, 15.2.

GC-MS (EI): *m/z* 148, 120, 107, 91, 79, 77, 65, 59, 51.

HRMS (ESI^+): *m/z* calcd. for C₁₀H₁₄O₂Na ([M+Na]^+) 189.08860, found 189.08889.

IR (ATR): *ν* 3425, 3064, 3030, 2867, 1946, 1882, 1812, 1603, 1495, 1454, 1375, 1320, 1197, 1107, 1062, 1025, 906, 820, 757, 701.
2-(decyloxy)-1-phenylethan-1-ol (1ad)

1-Decanol (20.0 ml) was added to sodium metal (348 mg, 15.1 mmol, 2.1 equiv), and the resulting mixture was heated to 110 °C for 30 min. After cooling to room temperature, styrene oxide (822 µl, 7.20 mmol, 1 equiv) was added, and the resulting red solution was stirred at 110 °C for 2 h. The reaction was cooled to room temperature and quenched by addition of water (0.3 ml). Excess 1-decanol was removed by vacuum distillation, the residue was taken up in water (10 ml) and extracted with DCM (25 ml). The organic extract was washed with water (2×10 ml), dried over MgSO₄ and evaporated under reduced pressure. Purification by flash CC on silica gel (hexane/ethyl acetate 95:5) yielded the title compound as a colorless liquid (1.03 g, 3.71 mmol, 52 %).

Rₛ = 0.18 (hexane/ethyl acetate 95:5)

¹H NMR (400 MHz, CDCl₃): δ 7.33–7.18 (m, 5H), 4.81 (dd, J = 9.1, 3.1 Hz, 1H), 3.53–3.32 (m, 4H), 1.57–1.49 (m, 2H), 1.32–1.15 (m, 14H), 0.81 (t, J = 6.9 Hz, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 140.3, 128.4, 127.8, 126.2, 76.4, 72.8, 71.6, 31.9, 29.7, 29.6, 29.5, 29.3, 26.1, 22.7, 14.1.

GC-MS (EI): m/z 260, 171, 120, 107, 91, 79, 77, 57, 55.

HRMS (ESI⁺): m/z calcld. for C₉₅H₄₀OₙNa ([M+Na]⁺) 301.21380, found 301.21403.

IR (ATR): ν 3444, 3064, 3030, 2922, 2855, 1603, 1495, 1454, 1357, 1320, 1197, 1111, 1062, 910, 828, 753, 701.

2-(2-methoxyphenoxy)-1-phenylethan-1-ol (1ae)

The title compound was synthesized from 2-(2-methoxyphenoxy)-1-phenylethan-1-one (S1ae, 1.11 g, 4.58 mmol, 1 equiv) and NaBH₄ (347 mg, 9.16 mmol, 2 equiv) in methanol (18 ml) according to general procedure GP6. It was isolated as an orange oil (1.16 g, 4.75 mmol, 87 %). Analytical data was in accordance with the literature.[¹]

Rₛ = 0.41 (petroleum ether/ethyl acetate 4:1)

¹H NMR (400 MHz, CDCl₃): δ 7.39–7.21 (m, 5H), 6.96–6.80 (m, 4H), 5.04 (dd, J = 9.5, 2.8 Hz, 1H), 4.15–3.87 (m, 2H), 3.83 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 128.5, 128.0, 126.3, 122.7, 121.1, 116.2, 112.0, 72.3, 55.9.

GC-MS (EI): m/z 244, 226, 124, 104, 91, 77.
2-hydroxy-2-phenylethyl acetate (1af)

Following a literature procedure,[13] An acetonitrile (10 ml) solution of 1-phenylethan-1,2-diol (691 mg, 5.00 mmol, 1 equiv) and N,N-diisopropylethylamine (174 µl, 1.00 mmol, 20 mol%) was treated with acetic anhydride (520 µl, 5.50 mmol, 1.1 equiv) and stirred at 40 °C for 15 h. After removing the solvent under reduced pressure, the product was purified by flash CC on silica gel (hexane/ethyl acetate 75:25→60:40) yielding the title compound as a colorless liquid (483 mg, 2.68 mmol, 54 %). Analytical data was in accordance with the literature.[14]

\[ R_f = 0.21 \text{ (hexane/ethyl acetate 3:1)} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{)}: \delta 7.34–7.21 \text{ (m, 5H)}, 4.88 \text{ (dd, } J = 8.4, 3.3 Hz, 1H), 4.23–4.05 \text{ (m, 2H)}, 2.03 \text{ (s, 3H).} \]

\[ ^1^3C\text{(^1H) NMR (101 MHz, CDCl}_3\text{)}: \delta 171.2, 139.8, 128.6, 128.3, 126.2, 72.4, 69.4, 20.9. \]

\[ \text{GC-MS (EI): } m/z 162, 149, 134, 107, 91, 79, 77. \]

\[ \text{IR (ATR): } \tilde{\nu} 3437, 3064, 3030, 2948, 1722, 1495, 1454, 1375, 1226, 1029, 980, 902, 854, 820, 760, 701. \]

2-methoxy-1-phenylethyl formate (1ah)

The title compound was synthesized from 2-methoxy-1-phenylethan-1-ol (1aa, 300 mg, 1.97 mmol, 1 equiv) and formic acid (892 µl, 23.7 mmol, 12 equiv) in presence of acetic anhydride (1.7 ml, 18 mmol, 9 equiv) and NaHCO\textsubscript{3} (331 mg, 394 mmol, 2 equiv) according to general procedure GP10. It was isolated as a colorless liquid (342 mg, 1.90 mmol, 96 %).

\[ R_f = 0.52 \text{ (hexane/ethyl acetate 4:1)} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{)}: \delta 8.10 \text{ (s, 1H)}, 7.32–7.22 \text{ (m, 5H)}, 6.01–5.96 \text{ (m, 1H)}, 3.72–3.49 \text{ (m, 2H)}, 3.33 \text{ (s, 3H).} \]

\[ ^1^3C\text{(^1H) NMR (101 MHz, CDCl}_3\text{)}: \delta 160.3, 136.7, 128.6, 128.6, 126.8, 75.2, 74.2, 59.2. \]

\[ \text{GC-MS (EI): } m/z 134, 107, 91, 79, 77. \]

\[ \text{HRMS (ESI\textsuperscript{+}): } m/z \text{ calcd. for } C_{16}H_{12}O_3Na ([M+Na\textsuperscript{+}]^+) 203.06786, \text{ found 203.06822.} \]

\[ \text{IR (ATR): } \tilde{\nu} 3064, 2986, 2930, 2892, 2833, 1722, 1603, 1495, 1454, 1383, 1353, 1156, 1126, 1025, 973, 932, 865, 757, 701. \]
2-(decyloxy)-1-phenylethyl formate (1ai)

The title compound was synthesized from 2-decyloxy-phenylethanol (1ac, 380 mg, 1.37 mmol, 1 equiv) and formic acid (618 µl, 16.4 mmol, 12 equiv) in presence of acetic anhydride (1.16 ml, 12.3 mmol, 9 equiv) and NaHCO₃ (626 mg, 2.73 mmol, 2 equiv) according to general procedure GP10. It was purified by flash CC on silica gel (hexane/ethyl acetate 9:1) and isolated as a colorless liquid (337 mg, 1.10 mmol, 81 %).

Rᵣ = 0.39 (hexane/ethyl acetate 95:5)

¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1H), 7.32–7.22 (m, 5H), 5.99–5.94 (m, 1H), 3.73–3.52 (m, 2H), 3.47–3.34 (m, 2H), 1.53–1.44 (m, 2H), 1.28–1.15 (m, 14H), 0.81 (t, J = 6.9 Hz, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 160.4, 136.9, 128.6, 128.5, 126.8, 74.5, 73.4, 71.7, 31.9, 29.6, 29.6, 29.4, 29.3, 26.0, 22.7, 14.1.

GC-MS (El): m/z 260, 120, 91, 57, 55.

HRMS (ESI⁺): m/z calcld. for C₂₀H₃₀O₃Na ([M+Na]⁺) 329.20872, found 329.20933.

IR (ATR): ν 3064, 3034, 2922, 2855, 1730, 1603, 1495, 1454, 1375, 1163, 1126, 1025, 910, 865, 757, 697.
1-phenylethene-1,2-diyldiformate (1aj), 2-hydroxy-2-phenylethyl formate (S2a) and 2-hydroxy-1-phenylethyl formate (S2b)

A mixture of formic acid (1.36 ml, 36.0 mmol, 1.2 equiv) and acetic anhydride (2.84 ml, 30.0 mmol, 1 equiv) was stirred at 70 °C for 1.5 h. Subsequently, it was cooled to room temperature, and NaHCO₃ (2.52 g, 30.0 mmol, 1 equiv) and 1-phenylethanol-1,2-diol (4.14 g, 30.0 mmol, 1 equiv) were added. The reaction mixture was stirred at room temperature overnight. Then, the reaction was quenched by addition of water (40 ml), and the aqueous solution was extracted with DCM (3×20 ml). The combined extracts were dried over MgSO₄, filtered and evaporated in vacuo. Separation by flash CC on silica gel (hexane/ethyl acetate 4:1) provided 1aj (427 mg, 2.20 mmol, 7%) and an inseparable mixture of mono-O-formylated products S2a and S2b (2.56 g, 15.4 mmol, 51%) as colorless liquids.

**Analytical data for 1aj:**

\[ R_f = 0.63 \] (hexane/ethyl acetate 3:1)

\[ ^1H\text{NMR (400 MHz, CDCl}_3\text{): } \delta 8.07 \text{ (s, 1H), 7.99 } \text{ (s, 1H), 7.35–7.26 } \text{ (m, 5H), 6.14–6.05 } \text{ (m, 1H) 4.42–4.35 } \text{ (m, 2H).} \]

\[ ^{13}C\{^1H\}\text{NMR (101 MHz, CDCl}_3\text{): } \delta 160.3, 159.9, 135.4, 129.1, 128.9, 126.8, 72.8, 65.1. \]

**GC-MS (EI):** m/z 148, 135, 120, 107, 103, 91, 79, 77, 65, 51.

**IR (ATR):** \( \overline{\nu} \) 3064, 3034, 2945, 1715, 1495, 1454, 1375, 1316, 1141, 1025, 951, 913, 865, 757, 701.

**Analytical data for S2a and S2b:**

\[ R_f = 0.28 \] (hexane/ethyl acetate 3:1)

\[ ^1H\text{NMR (400 MHz, CDCl}_3\text{): mixture of regioisomers } \delta 8.09 \text{ (s, 0.2H), 8.02 } \text{ (s, 0.8H), 7.34–7.22 } \text{ (m, 5H), 5.86 } \text{ (dd, } J = 7.6, 4.0 \text{ Hz, 0.2H), 8.90 } \text{ (dd, } J = 8.3, 3.5 \text{ Hz, 0.8H), 4.32–4.14 } \text{ (m, 1.6H), 3.86–3.73 } \text{ (m, 0.4H).} \]

\[ ^{13}C\{^1H\}\text{NMR (101 MHz, CDCl}_3\text{): mixture of regioisomers } \delta 160.9, 160.5, 139.5, 136.3, 128.8, 128.7, 128.5, 126.7, 76.7, 72.1, 68.5, 65.7. \]

**GC-MS (EI):** m/z 120, 107, 104, 91, 79, 77, 65, 51.

**IR (ATR):** \( \overline{\nu} \) 3399, 3064, 3034, 2941, 1715, 1495, 1454, 1379, 1312, 1156, 1066, 1025, 947, 910, 831, 753, 701.
2-methoxy-1-phenylethyl acetate (1ak)

Following an adapted literature procedure.\[^{[5]}\] To a DCM (4 ml) solution of 1aa (304 mg, 2.00 mmol, 1 equiv) and 4-dimethylaminopyridine (12.2 mg, 100 µmol, 5 mol%), acetic anhydride (227 µl, 2.40 mmol, 1.2 equiv) was added. After stirring the reaction mixture at room temperature overnight, the reaction was quenched with water (10 ml), and the aqueous phase was separated and extracted with DCM (3×10 ml). The combined organic phases were dried over MgSO\(_4\), filtered and evaporated in vacuo yielding the title compound as a colorless liquid (384 mg, 1.98 mmol, 99%), which was used without further purification.

\( R_f = 0.35 \) (hexane/ethyl acetate 4:1)

\( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.30–7.20 (m, 5H), 5.89 (dd, \( J = 8.0 \) Hz, 3.8 Hz, 1H), 3.69–3.46 (m, 2H), 3.32 (s, 3H), 2.05 (s, 3H).

\( ^{13}C\)\( (^1H) \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 170.3, 137.6, 128.5, 128.3, 126.7, 75.4, 74.3, 59.2, 21.3.

GC-MS (EI): m/z 162, 149, 134, 107, 91, 79.

HRMS (ESI\(^+\)): m/z calcd. for C\(_{21}\)H\(_{34}\)O\(_3\) Na ([M+Na]\(^+\)) 217.08352, found 217.08392.

IR (ATR): \( \tilde{\nu} \) 3064, 3034, 2982, 2930, 2885, 2829, 1737, 1495, 1454, 1372, 1230, 1129, 1044, 973, 857, 760, 701.

1-phenylethane-1,2-diyl diacetate (1al)

Following an adapted literature procedure.\[^{[5]}\] To a DCM (12 ml) solution of 1-phenylethane-1,2-diol (829 g, 6.00 mmol, 1 equiv) and 4-dimethylaminopyridine (36.7 mg, 300 µmol, 5 mol%), acetic anhydride (1.36 ml, 14.4 mmol, 2.4 equiv) was added. After stirring the reaction mixture at room temperature for four days, the reaction was quenched with ice water (20 ml), and the aqueous phase was separated and extracted with DCM (2×20 ml). The combined organic phases were washed with brine (20 ml), dried over MgSO\(_4\), filtered and evaporated in vacuo yielding the title compound as a yellow liquid (1.20 g, 5.41 mmol, 90%), which was used without further purification.

\( R_f = 0.67 \) (hexane/ethyl acetate 1:1)

\( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.31–7.21 (m, 5H), 5.94 (dd, \( J = 7.9 \) Hz, 4.0 Hz, 1H), 4.29–4.18 (m, 2H), 2.05 (s, 3H), 1.98 (s, 3H).

\( ^{13}C\)\( (^1H) \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 170.6, 170.1, 136.5, 128.7, 128.6, 126.7, 73.3, 66.1, 21.1, 20.8.

GC-MS (EI): m/z 162, 149, 120, 107, 91, 89, 77.

HRMS (ESI\(^+\)): m/z calcd. for C\(_{22}\)H\(_{36}\)O\(_3\)Na ([M+Na]\(^+\)) 245.07843, found 245.07884.

IR (ATR): \( \tilde{\nu} \) 3064, 3034, 2952, 1737, 1495, 1454, 1368, 1215, 1040, 947, 876, 760, 701.
(1,2-dimethoxyethyl)benzene (1am)

Following a modified literature procedure. Sodium hydride (57–63 % in mineral oil, 720 mg, 18.0 mmol, 6 equiv) was added to a THF (40 ml) solution of 1-phenylethan-1,2-diol (415 mg, 3.00 mmol, 1 equiv) at 0 °C, and the reaction mixture was stirred at this temperature for 30 min before methyl iodide (467 µl, 7.50 mmol, 2.5 equiv) was added. After overnight stirring at room temperature and subsequent cooling to 0 °C, water (20 ml) was added and the reaction mixture was extracted with DCM (3×30 ml). The combined organic phases were washed with brine (30 ml), dried over MgSO₄, filtered and evaporated under reduced pressure. Flash CC on silica gel (hexane/ethyl acetate 9:1→3:1) yielded the title compound as a colorless liquid (283 mg, 1.70 mmol, 57 %). Analytical data was in accordance with the literature.

\[ R_f = 0.51 \] (hexane/ethyl acetate 4:1)

\[^1\text{H}\] NMR (400 MHz, CDCl₃): \( \delta \) 7.32–7.21 (m, 5H), 4.32 (dd, \( J = 8.3, 3.4 \) Hz, 1H), 3.55–3.31 (m, 5H), 3.22 (s, 3H).

\[^{13}\text{C}\{^1\text{H}\}] \text{NMR} (101 MHz, CDCl₃): \( \delta \) 138.8, 128.5, 128.1, 127.0, 83.0, 77.3, 59.2, 57.0.

\[^{13}\text{C}\{^1\text{H}\}] \text{NMR} (101 MHz, CDCl₃): \( \delta \) 142.6, 128.5, 127.8, 125.8, 71.5, 42.2, 32.2, 31.7, 29.7, 28.9, 28.8, 22.6, 14.1.

IR (ATR): \( \tilde{\nu} \) 3064, 3027, 2982, 2926, 2881, 2822, 1603, 1491, 1454, 1383, 1357, 1312, 1260, 1193, 1100, 1029, 973, 936, 865, 757, 701.

2-(heptylthio)-1-phenylethan-1-ol (1ao)

The title compound was synthesized from 2-(heptylthio)-1-phenylethan-1-one (S1ao, 1.18 g, 4.71 mmol, 1 equiv) and NaBH₄ (356 mg, 9.42 mmol, 2 equiv) in methanol (19 ml) according to general procedure GP6. It was isolated as a yellow oil (0.76 g, 3.01 mmol, 64 %).

\[^1\text{H}\] NMR (400 MHz, CDCl₃): \( \delta \) 7.33–7.19 (m, 5H), 4.67 (dd, \( J = 9.5, 3.6 \) Hz, 1H), 2.89–2.60 (m, 2H), 2.47 (t, \( J = 7.4 \) Hz, 2H), 1.57–1.48 (m, 2H), 1.35–1.17 (m, 8H), 0.82 (t, \( J = 6.9 \) Hz, 3H).

\[^{13}\text{C}\{^1\text{H}\}] \text{NMR} (101 MHz, CDCl₃): \( \delta \) 142.6, 128.5, 127.8, 125.8, 71.5, 42.2, 32.2, 31.7, 29.7, 28.9, 28.8, 22.6, 14.1.

\[^{13}\text{C}\{^1\text{H}\}] \text{NMR} (101 MHz, CDCl₃): \( \delta \) 154.8, 136.0, 129.0, 128.7, 126.8, 126.4, 125.1, 123.8, 122.7, 120.0, 112.3, 110.0, 106.3, 100.4, 98.8, 94.3, 93.0, 91.0, 88.7, 87.4, 86.1, 85.0, 83.7, 82.5, 81.3, 80.1, 78.9, 77.7, 76.5, 75.3, 74.1, 72.9, 71.7, 70.5, 69.3, 68.1, 66.9, 65.7, 64.5, 63.3, 62.1, 60.9, 59.7, 58.5, 57.3, 56.1, 54.9, 53.7, 52.5, 51.3, 50.1, 48.9, 47.7, 46.5, 45.3, 44.1, 42.9, 41.7, 40.5, 39.3, 38.1, 36.9, 35.7, 34.5, 33.3, 32.1, 30.9, 29.7, 28.5, 27.3, 26.1, 24.9, 23.7, 22.5, 21.3, 20.1, 18.9, 17.7, 16.5, 15.3, 14.1.

IR (ATR): \( \tilde{\nu} \) 3418, 3026, 2922, 2855, 1453, 1192, 1054, 1028, 726.
1-(4-(tert-butyl)phenyl)-2-methoxyethan-1-ol (1b)

The title compound was synthesized from 1-(4-(tert-butyl)phenyl)-2-methoxyethan-1-one (S1b, 1.03 g, 5.00 mmol, 1 equiv) and NaBH₄ (378 mg, 10.0 mmol, 2 equiv) in methanol (20 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as a yellow oil (1.01 g, 4.87 mmol, 97 %). Analytical data was in accordance with the literature.¹⁸

Rᵣ = 0.50 (hexane/ethyl acetate 2:1)

¹H NMR (400 MHz, CDCl₃): δ 7.33–7.22 (m, 4H), 4.80 (dd, J = 8.9, 3.2 Hz), 3.49–3.35 (m, 2H), 3.36 (s, 3H), 1.24 (s, 9H).

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 150.8, 137.2, 125.9, 125.4, 78.1, 72.5, 59.0, 34.6, 31.3.

GC-MS (EI): m/z 190, 175, 163, 145, 133, 117, 105, 91, 77, 57.

IR (ATR): ν 3425, 3056, 2960, 2900, 2825, 1614, 1513, 1461, 1402, 1364, 1323, 1267, 1193, 1111, 1074, 1018, 969, 902, 831, 697.

1-(4-(trifluoromethyl)phenyl)-2-methoxyethan-1-ol (1c)

The title compound was synthesized from 2-methoxy-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S1c, 709 mg, 3.25 mmol, 1 equiv) and NaBH₄ (246 mg, 6.50 mmol, 2 equiv) in methanol (13 ml) according to general procedure GP6. It was isolated as an orange oil (0.67 g, 3.04 mmol, 94 %).

Rᵣ = 0.11 (hexane/ethyl acetate 90:10)

¹H NMR (400 MHz, CDCl₃): δ 7.56–7.52 (m, 2H), 7.46–7.42 (m, 2H), 4.88 (dd, J = 8.6, 3.2 Hz, 1H), 3.52–3.31 (m, 2H), 3.37 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.3, 130.0 (q, J = 32.3 Hz), 126.4, 125.3 (q, J = 3.8 Hz), 124.1 (q, J = 272.0 Hz), 77.8, 72.1, 59.1.

¹⁹F NMR (377 MHz, CDCl₃): δ –62.5.

GC-MS (EI): m/z 220, 202, 175, 159, 145, 127, 91, 77.

IR (ATR): ν 3412, 2929, 2896, 1416, 1323, 1110, 1162, 969, 902, 760, 838.
2-methoxy-1-(4-methoxyphenyl)ethan-1-ol (1d)

The title compound was synthesized from 2-methoxy-1-(4-methoxyphenyl)ethan-1-one (S1d, 451 mg, 2.50 mmol, 1 equiv) and NaBH₄ (189 mg, 5.00 mmol, 2 equiv) in methanol (10 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as an orange liquid (453 mg, 2.49 mmol, 99 %). Analytical data was in accordance with the literature.[56]

\[ R_f = 0.46 \text{ (hexane/diethyl ether 1:2)} \]

\(^1\)H NMR (400 MHz, CDCl₃): $\delta$ 7.26–7.21 (m, 2H), 6.84–6.79 (m, 2H), 4.80–4.74 (m, 1H), 3.73 (s, 3H), 3.46–3.32 (m, 2H), 3.36 (s, 3H), 2.64, (d, $J = 2.1$ Hz).

\(^{13}\)C\(^{(1)}\)H NMR (101 MHz, CDCl₃): $\delta$ 159.3, 132.4, 127.4, 113.8, 78.2, 72.3, 59.0, 55.3.

GC-MS (EI): m/z 182, 164, 149, 137, 121, 109, 94, 91, 77, 65, 51.

HRMS (ESI⁺): m/z calcd. for C₁₀H₈O₃Na ([M+Na]⁺) 205.08352, found 205.08354.

IR (ATR): $\tilde{\nu}$ 3425, 2896, 2833, 1610, 1584, 1513, 1461, 1372, 1301, 1245, 1174, 1111, 1029, 969, 902, 828, 764.

2-methoxy-1-(4-(methylthio)phenyl)ethan-1-ol (1e)

The title compound was synthesized from 2-methoxy-1-(4-(methylthio)phenyl)ethan-1-one (S1e, 981 mg, 5.00 mmol, 1 equiv) and NaBH₄ (378 mg, 10.0 mmol, 2 equiv) in methanol (20 ml) according to general procedure GP6. After 2.5 h at room temperature, it was isolated as a yellow oil (971 mg, 4.90 mmol, 98 %). Analytical data was in accordance with the literature.[56]

\[ R_f = 0.52 \text{ (hexane/ethyl acetate 1:1)} \]

\(^1\)H NMR (400 MHz, CDCl₃): $\delta$ 7.34–7.14 (m, 4H), 4.77 (dd, $J = 8.8, 3.3$ Hz, 1H), 3.46–3.30 (m, 2H), 3.35 (s, 3H), 2.40 (s, 3H).

\(^{13}\)C\(^{(1)}\)H NMR (101 MHz, CDCl₃): $\delta$ 138.0, 137.2, 126.7, 126.7, 78.1, 72.3, 59.1, 15.9.

GC-MS (EI): m/z 198, 180, 165, 153, 150, 137, 118, 109, 91, 78, 77, 63, 51.

IR (ATR): $\tilde{\nu}$ 3422, 3019, 2982, 2919, 2885, 2822, 1599, 1566, 1491, 1435, 1320, 1282, 1193, 1115, 1070, 965, 902, 816, 723, 686.
1-(4-fluorophenyl)-2-methoxyethan-1-ol (1f)

The title compound was synthesized from 1-(4-fluorophenyl)-2-methoxyethan-1-one (S1f, 673 mg, 4.00 mmol, 1 equiv) and NaBH₄ (303 mg, 8.00 mmol, 2 equiv) in methanol (16 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as an orange liquid (662 mg, 3.89, 97%). Analytical data was in accordance with the literature.[18]

\[ R_{f} = 0.40 \text{ (hexane/ethyl acetate 2:1)} \]

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.31–7.25 (m, 2H), 7.00–6.92 (m, 2H), 4.80 (dd, \( J = 8.8, 3.2 \text{ Hz, 1H} \)), 3.47–3.29 (m, 2H), 3.36 (s, 3H).

\(^{13}\text{C} \)\(^{1}\text{H} \) \text{NMR} \) (101 MHz, CDCl₃): \( \delta \) 162.4 (d, \( J = 245.7 \text{ Hz, 136.0} \) (d, \( J = 3.0 \text{ Hz, 127.8} \) (d, \( J = 8.2 \text{ Hz, 115.3} \) (d, \( J = 21.4 \text{ Hz, 78.1, 72.0, 59.1.} \)

\(^{19}\text{F} \text{NMR} \) (377 MHz, CDCl₃): \( \delta \) –114.7 (m).

\text{GC-MS (EI): } m/z 152, 125, 109, 97, 77.

\text{IR (ATR): } \nu 3418, 3071, 2986, 2892, 2825, 1894, 1771, 1603, 1510, 1454, 1409, 1320, 1219, 1156, 1118, 1070, 969, 902, 835, 779, 719.

1-(4-chlorophenyl)-2-methoxyethan-1-ol (1g)

The title compound was synthesized from 1-(4-chlorophenyl)-2-methoxyethan-1-one (S1g, 923 mg, 5.00 mmol, 1 equiv) and NaBH₄ (378 mg, 10.0 mmol, 2 equiv) in methanol (20 ml) according to general procedure GP6. After 3 h at room temperature, it was isolated as a yellow liquid (902 mg, 4.83 mmol, 97%). Analytical data was in accordance with the literature.[18]

\[ R_{f} = 0.52 \text{ (hexane/ethyl acetate 2:1)} \]

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.25 (s, 4H), 4.79 (dd, \( J = 8.8, 3.3 \text{ Hz, 1H} \)), 3.47–3.28 (m, 2H), 3.35 (s, 3H).

\(^{13}\text{C} \)\(^{1}\text{H} \) \text{NMR} \) (101 MHz, CDCl₃): \( \delta \) 138.7, 133.6, 128.6, 127.5, 77.9, 72.0, 59.1.

\text{GC-MS (EI): } m/z 186, 168, 151, 143, 141, 125, 113, 103, 89, 77, 63, 51

\text{IR (ATR): } \nu 3407, 2982, 2889, 2825, 1901, 1782, 1651, 1595, 1491, 1454, 1402, 1320, 1223, 1193, 1118, 1085, 969, 902, 824, 738, 686.
2-methoxy-1-(3-methoxyphenyl)ethan-1-ol (1h)

The title compound was synthesized from 2-methoxy-1-(3-methoxyphenyl)ethan-1-one (S1h, 541 mg, 3.00 mmol, 1 equiv) and NaBH₄ (227 mg, 6.00 mmol, 2 equiv) in methanol (12 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as an orange liquid (518 mg, 2.84 mmol, 95%).

Rₚ = 0.26 (hexane/diethyl ether 1:1)

¹H NMR (400 MHz, CDCl₃): δ 7.19 (dd, J = 7.9, 7.9 Hz, 1H), 6.91–6.86 (m, 2H), 6.78–6.74 (m, 1H), 4.81 (dd, J = 8.9, 3.2 Hz, 1H), 3.74 (s, 3H), 3.50–3.33 (m, 2H), 3.36 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 159.8, 141.9, 129.4, 118.4, 113.4, 111.6, 78.1, 72.6, 59.0, 55.2.

GC-MS (EI): m/z 182, 164, 137, 121, 109, 105, 94, 91, 77, 65, 51.

HRMS (ESI⁺): m/z calcld. for C₁₀H₁₆O₃Na ([M+Na]⁺) 205.08352, found 205.08353.

IR (ATR): ν 3422, 2892, 2833, 1588, 1487, 1454, 1372, 1320, 1256, 1193, 1156, 1115, 1066, 1040, 969, 924, 876, 783, 749, 697.

2-methoxy-1-(o-tolyl)ethan-1-ol (1i)

The title compound was synthesized from 2-methoxy-1-(o-tolyl)ethan-1-one (S1i, 411 mg, 2.50 mmol, 1 equiv) and NaBH₄ (189 mg, 5.00 mmol, 2 equiv) in methanol (10 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as a colorless oil (400 mg, 2.41 mmol, 96%).

Rₚ = 0.36 (hexane/ethyl acetate 4:1)

¹H NMR (400 MHz, CDCl₃): δ 7.46–7.43 (m, 1H), 7.18–7.04 (m, 3H), 5.05 (dd, J = 9.0, 1.7 Hz, 1H), 3.45–3.28 (m, 2H), 3.36 (s, 3H), 2.27 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 138.2, 134.8, 130.3, 127.6, 126.3, 125.9, 77.1, 69.4, 59.0, 19.1.

GC-MS (EI): m/z 148, 121, 105, 93, 91, 77.

HRMS (ESI⁺): m/z calcld. for C₁₀H₁₄O₃Na ([M+Na]⁺) 189.08860, found 189.08893.

IR (ATR): ν 3422, 3064, 3023, 2922, 2889, 2822, 1607, 1457, 1320, 1193, 1111, 1066, 969, 902, 835, 753.
2-methoxy-1-(2-methoxyphenyl)ethan-1-ol (1j)

The title compound was synthesized from 2-methoxy-1-(2-methoxyphenyl)ethan-1-one (S1j, 640 mg, 3.55 mmol, 1 equiv) and NaBH₄ (269 mg, 7.10 mmol, 2 equiv) in methanol (15 ml) according to general procedure GP6. It was isolated as a red-brown oil (0.61 g, 3.35 mmol, 96 %, 80 % purity).

¹H NMR (400 MHz, CDCl₃): δ 7.41–7.38 (m, 1H), 7.22–7.16 (m, 1H), 6.94–6.89 (m, 1H), 6.81–6.78 (m, 1H), 5.14 (dd, J = 8.4, 3.1 Hz, 1H), 3.77 (s, 3H), 3.58–3.31 (m, 2H), 3.36 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 156.3, 128.6, 128.5, 127.0, 120.8, 110.2, 76.7, 68.2, 58.9, 55.3.

GC-MS (EI): m/z 182, 164, 137, 121, 107, 91, 77.

IR (ATR): ν 3429, 2922, 2836, 1602, 1490, 1312, 1237, 1110, 1066, 752, 685.

1-methoxy-2-phenylpropan-2-ol (1k)

A solution of 2-methoxyacetophenone (751 mg, 5.00 mmol, 1 equiv) in diethyl ether (15 ml) was treated with methyllithium (nominally 1.6 M in diethyl ether, 13.1 ml, 21.0 mmol, 4.2 equiv) at – 78 °C and stirred for 50 min. The reaction was quenched by adding saturated aqueous NH₄Cl solution (10 ml). The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3×10 ml). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash CC on silica gel (hexane/ethyl acetate 4:1) yielding the title compound as a colorless liquid (380 mg, 2.29 mmol, 46 %). Analytical data was in accordance with the literature.[¹⁶]

Rᵣ = 0.37 (hexane/ethyl acetate 4:1)

¹H NMR (400 MHz, CDCl₃): δ 7.42–7.37 (m, 2H), 7.31–7.25 (m, 2H), 7.21–7.15 (m, 1H), 3.53–3.39 (m, 2H), 3.31 (s, 3H), 1.44 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 145.5, 128.2, 126.9, 124.9, 80.8, 73.8, 59.4, 26.7.

GC-MS (EI): m/z 148, 121, 118, 105, 103, 91, 77, 51.

IR (ATR): ν 3455, 3060, 3027, 2978, 2930, 2889, 2825, 1700, 1603, 1495, 1446, 1375, 1334, 1282, 1193, 1103, 969, 917, 865, 764, 701.
The title compound was synthesized from 2-methoxyacetophenone (901 mg, 6.00 mmol, 1 equiv) and 1-hexylmagnesium chloride (nominally 2.0 M in THF, 15.0 ml, 30.0 mmol, 5 equiv) according to general procedure GP8. It was isolated by flash CC on silica gel (hexane/ethyl acetate 95:5→90:10) as a colorless oil (818 mg, 3.46 mmol, 58 %).

$R_f = 0.34$ (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36–7.32 (m, 2H), 7.29–7.24 (m, 2H), 7.19–7.13 (m, 1H), 3.54–3.43 (m, 2H), 3.27 (s, 3H), 1.80–1.62 (m, 2H), 1.29–1.05 (m, 7H), 0.99–0.86 (m, 1H), 0.75 (t, $J =$ 6.9 Hz, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 144.2, 128.1, 126.7, 125.3, 80.4, 76.2, 59.4, 39.3, 31.7, 29.7, 23.1, 22.6, 14.1.

GC-MS (EI): m/z 218, 191, 147, 129, 117, 115, 105, 103, 91, 77.

HRMS (ESI$^+$): m/z calcld. for C$_{16}$H$_{14}$O$_2$Na ([M+Na]$^+$) 259.16685, found 259.16723.

IR (ATR): $\tilde{v}$ 3567, 3489, 3060, 3027, 2926, 2855, 1603, 1495, 1446, 1379, 1312, 1193, 1107, 977, 906, 764, 701.

The title compound was synthesized from 2-methoxyacetophenone (901 mg, 6.00 mmol, 1 equiv) and benzylmagnesium chloride (nominally 2.0 M in THF, 15.0 ml, 30.0 mmol, 5 equiv) according to general procedure GP8. It was isolated by flash CC on silica gel (hexane/ethyl acetate 85:15) as a colorless oil (757 mg, 3.13 mmol, 52 %).

$R_f = 0.29$ (hexane/ethyl acetate 9:1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29–7.06 (m, 8H), 6.88–6.83 (m, 2H), 3.57–3.49 (m, 2H), 3.29 (s, 3H), 3.06–2.98 (m, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 143.8, 136.4, 130.7, 128.0, 127.9, 127.0, 126.4, 125.6, 78.5, 76.1, 59.4, 46.0.

GC-MS (EI): m/z 224, 192, 178, 165, 151, 119, 115, 105, 103, 91, 77, 65, 51.

HRMS (ESI$^+$): m/z calcld. for C$_{16}$H$_{16}$O$_2$Na ([M+Na]$^+$) 265.11990, found 265.12042.

IR (ATR): $\tilde{v}$ 3548, 3478, 3060, 3027, 2922, 2892, 2822, 1946, 1879, 1808, 1603, 1495, 1446, 1387, 1349, 1267, 1193, 1096, 1029, 954, 869, 772, 727.
2-methoxy-1,1-diphenylethan-1-ol (1n)

\[
\text{\( \text{OH} \quad \text{OMe} \)}
\]

The title compound was synthesized from 2-methoxyacetophenone (1.00 g, 6.66 mmol, 1 equiv) and phenyllithium (nominally 1.9 M in dibutyl ether, 21.0 ml, 40.0 mmol, 6 equiv) in diethylether (20 ml) according to general procedure GP7. After purification by flash CC on silica gel (hexane/ethyl acetate 85:15), it was isolated as a yellow oil (1.09 g, 4.78 mmol, 72%).

\[ R_f = 0.37 \text{ (hexane/ethyl acetate 9:1)} \]

\(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta 7.37–7.32 \text{ (m, 4H)}, 7.26–7.20 \text{ (m, 4H)}, 7.19–7.13 \text{ (m, 2H)}, 3.85 \text{ (s, 2H)}, 3.36 \text{ (s, 3H)}.\]

\(^{13}\text{C}(^1\text{H}) \text{ NMR} (101 \text{ MHz, CDCl}_3): \delta 144.4, 128.2, 127.2, 126.4, 78.9, 77.7, 59.4.\]

\(^1\text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3): \delta 7.51–7.45 \text{ (m, 4H)}, 7.34–7.29 \text{ (m, 2H)}, 7.28–7.22 \text{ (m, 2H)}, 7.20–7.15 \text{ (m, 1H)}, 3.89–3.21 \text{ (m, 2H)}, 3.37 \text{ (s, 3H)}.\]

\(^{19}\text{F NMR} (377 \text{ MHz, CDCl}_3): \delta −26.5.\]

**2-methoxy-1-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (1o)**

\[
\text{\( \text{OMe} \)}
\]

Mg turnings (438 mg, 18.0 mmol, 3 equiv) and dry LiCl (636 mg, 15.0 mmol, 2.5 equiv) were covered with THF (10 ml). At 0 °C, 4-(trifluoromethyl)bromobenzene (1.7 ml, 12.0 mmol, 2 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After cooling to 0 °C, a THF (6 ml) solution of 2-methoxyacetophenone (901 mg, 6.00 mmol, 1 equiv) was added, and the reaction mixture was heated to reflux for 3 h. The reaction was quenched at room temperature by addition of aqueous saturated NH\(_4\)Cl solution (20 ml). The organic phase was separated, and the aqueous phase was extracted with DCM (3×20 ml). The combined organic phases were dried over MgSO\(_4\), filtered and evaporated under reduced pressure. Flash CC on silica gel (hexane/ethyl acetate 85:15) provided the title compound as a yellow oil (1.14 g, 3.85 mmol, 64%).

\[ R_f = 0.42 \text{ (hexane/ethyl acetate 85:15)} \]

\(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta 7.51–7.45 \text{ (m, 4H)}, 7.34–7.29 \text{ (m, 2H)}, 7.28–7.22 \text{ (m, 2H)}, 7.20–7.15 \text{ (m, 1H)}, 3.89–3.21 \text{ (m, 2H)}, 3.37 \text{ (s, 3H)}.\]

\(^{13}\text{C}(^1\text{H}) \text{ NMR} (101 \text{ MHz, CDCl}_3): \delta 148.5, 143.6, 129.3 (q, J = 32.4 \text{ Hz}), 128.4, 127.6, 126.9, 126.3, 125.1 (q, J = 3.8 \text{ Hz}), 124.2 (q, J = 27.18 \text{ Hz}), 78.5, 77.5, 59.4.\]

\(^1\text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3): \delta −26.5.\]

\(^{19}\text{F NMR} (377 \text{ MHz, CDCl}_3): \delta −62.5.\]

**IR (ATR): \( \tilde{\nu} \) 3474, 3064, 3030, 2989, 2930, 2896, 2829, 1618, 1491, 1450, 1409, 1323, 1163, 1111, 1066, 1014, 932, 872, 764, 701.**
2-methoxy-1-(4-(methylthio)phenyl)-1-phenylethan-1-ol (1p)

The title compound was synthesized from 2-methoxy-1-(4-(methylthio)phenyl)ethan-1-one (S1e, 552 mg, 2.81 mmol, 1 equiv) and phenyllithium (nominally 1.9 M in dibutyl ether, 8.9 ml, 17 mmol, 6 equiv) in diethylether (8.5 ml) according to general procedure GP. After purification by flash CC on silica gel (hexane/ethyl acetate 4:1), it was isolated as a yellow oil (563 mg, 2.05 mmol, 73 %).

Rf = 0.46 (hexane/ethyl acetate 4:1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.35–7.09 (m, 9H), 3.85–3.78 (m, 2H), 3.36 (s, 3H), 2.36 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 144.3, 141.4, 137.3, 128.2, 127.3, 127.0, 126.4, 78.8, 77.5, 59.4, 15.8.

GC-MS (EI): m/z 256, 229, 213, 194, 178, 165, 151, 105, 77.

HRMS (ESI$^+$): m/z calcd. for C$_{16}$H$_{16}$O$_2$SNa ([M+Na$^+$]) 297.09197, found 297.09196.

IR (ATR): ν 3463, 3056, 3027, 2982, 2919, 2822, 1595, 1491, 1446, 1398, 1331, 1170, 1092, 969, 869, 764, 701.

1-(4-chlorophenyl)-2-methoxy-1-phenylethan-1-ol (1q)

The title compound was synthesized from 1-(4-chlorophenyl)-2-methoxylethan-1-one (S1g, 426 mg, 2.31 mmol, 1 equiv) and phenyllithium (nominally 1.9 M in dibutyl ether, 7.3 ml, 14 mmol, 6 equiv) in diethylether (7 ml) according to general procedure GP7. After purification by flash CC on silica gel (hexane/ethyl acetate 85:15), it was isolated as a yellow oil (432 mg, 1.65 mmol, 71 %).

Rf = 0.42 (hexane/ethyl acetate 85:15)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.33–7.14 (m, 9H), 3.84–3.77 (m, 2H), 3.36 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 143.9, 143.1, 133.1, 128.3, 128.0, 127.4, 126.3, 78.6, 77.4, 59.4.

GC-MS (EI): m/z 246, 244, 217, 203, 201, 179, 178, 166, 165, 139, 105 77, 51.

HRMS (ESI$^+$): m/z calcd. for C$_{15}$H$_{14}$O$_2$ClNa ([M+Na$^+$]) 285.06528, found 285.06559.

IR (ATR): ν 3545, 3463, 3056, 3027, 2986, 2922, 2892, 2825, 1599, 1491, 1446, 1402, 1334, 1267, 1170, 1088, 932, 869, 820, 764, 697.
7-(methoxymethyl)tridecan-7-ol (1r)

To a solution of methyl methoxyacetate (833 mg, 8.00 mmol, 1 equiv) in THF (8 ml), 1-hexylmagnesium chloride (nominally 2 m in THF, 24.0 ml, 48.0 mmol, 6 equiv) was added at 0 °C. The reaction mixture was heated to reflux for 10 h. After cooling down to 0 °C, the reaction was quenched by addition of saturated NH₄Cl solution (50 ml). The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3×50 ml). The combined organic phases were dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by flash CC on silica gel (hexane/ethyl acetate 98:2→95:5) provided the title compound as a colorless liquid (1.20 g, 4.90 mmol, 61 %).

Rᵣ = 0.26 (hexane/ethyl acetate 95:5)

1H NMR (400 MHz, CDCl₃): δ 3.30 (s, 3H), 3.16 (s, 2H), 1.43–1.16 (m, 20H), 0.81 (t, J = 6.8 Hz, 6H).

13C{1H} NMR (101 MHz, CDCl₃): δ 73.4, 73.8, 59.3, 36.5, 31.8, 30.0, 23.4, 22.6, 14.1.

GC-MS (EI): m/z 226, 199, 159, 155, 141, 123, 109, 97, 95, 85, 83, 61, 69, 67, 57, 55.

HRMS (ESI⁺): m/z calcd. for C₁₅H₃₂O₂Na ([M+Na]⁺) 267.22945, found 267.22989.

IR (ATR): ν 3466, 2922, 2855, 1457, 1402, 1379, 1338, 1193, 1115, 969, 809, 723.

2-benzyl-1-methoxypentan-2-ol (1s)

To a solution of 1-methoxypentan-2-one (S1s, 580 mg, 5.00 mmol, 1 equiv) in THF (5 ml), benzylmagnesium chloride (2 m in THF, 3.00 ml, 6.00 mmol, 1.2 equiv) was added dropwise at 0 °C over 15 minutes. The reaction mixture was stirred under reflux for 3 h. After cooling to room temperature, the reaction was quenched by addition of sat. aqueous NH₄Cl solution (20 ml), and 1 m aqueous HCl (5 ml) was added. The aqueous phase was separated and extracted with ethyl acetate (4×25 ml). The combined organic phases were dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was purified by flash CC on silica gel (hexane/ethyl acetate 9:1) providing it as a yellow oil (540 mg, 2.59 mmol, 52 %).

Rᵣ = 0.52 (hexane/ethyl acetate 9:1)

1H NMR (300 MHz, CDCl₃): δ 7.26–7.09 (m, 5H), 3.30 (s, 3H), 3.09 (s, 1H), 3.08 (s, 1H), 2.74 (s, 2H), 1.95 (s, 1H), 1.40–1.30 (m, 4H), 0.91–0.78 (m, 3H).

13C{1H} NMR (75 MHz, CDCl₃): δ 137.4, 130.4, 128.1, 126.3, 74.0, 59.0, 43.0, 38.8, 16.6, 14.6.

GC-MS (EI): m/z 208, 190, 163, 129, 117, 91.

HRMS (ESI⁺): m/z calcd. for C₁₃H₂₀O₂Na ([M+Na]⁺) 231.13555, found 231.13597.

IR (ATR): ν 3473, 2959, 2926, 2873, 1494, 1453, 961, 1107, 730, 700.
2-benzyl-1-methoxy-3-phenylpropan-2-ol (1t)

The title compound was synthesized according to general procedure GP9. It was purified by flash CC on silica gel (hexane/ethyl acetate 9:1) and isolated as a colorless oil (958 mg, 3.74 mmol, 62%).

\( R_f = 0.33 \) (hexane/ethyl acetate 9:1)

\( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.24–7.13 (m, 10H), 3.25 (s, 3H), 2.91 (s, 2H), 2.84–2.73 (m, 4H), 1.82 (br, 1H).

\( ^{13}C(\text{H}) \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 137.2, 130.7, 128.2, 126.5, 75.4, 74.0, 58.8, 43.7.

GC-MS (EI): m/z 238, 206, 165, 147, 133, 115, 105, 91, 65.

HRMS (ESI\(^+\)): m/z calcd. for C\(_{27}\)H\(_{38}\)O\(_2\)Na ([M+Na]\(^+\)) 279.13555, found 279.13595.

IR (ATR): \( \tilde{\nu} \) 3470, 3060, 3027, 2981, 2922, 2814, 1603, 1491, 1402, 1353, 1193, 1088, 969, 891, 753, 701.

4-(methoxymethyl)heptan-4-ol (1u)

The title compound was synthesized according to general procedure GP9. It was purified by kugelrohr distillation (100 °C at 120 mmHg) and isolated as a colorless oil (680 mg, 4.19 mmol, 70%).

\( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.36 (s, 3H), 3.22 (s, 2H), 2.08 (s, 1H), 1.47–1.40 (m, 4H), 1.36–1.26 (m, 4H), 0.90 (t, \( J = 7.2 \) Hz, 6H).

\( ^{13}C(\text{H}) \) NMR (75 MHz, CDCl\(_3\)): \( \delta \) 78.3, 73.8, 59.2, 38.8, 16.7, 14.7.

GC-MS (EI): m/z 159, 142, 115, 99, 85.

HRMS (ESI\(^+\)): m/z calcd. for C\(_{13}\)H\(_{20}\)O\(_2\)Na ([M+Na]\(^+\)) 183.13555, found 183.13587.

IR (ATR): \( \tilde{\nu} \) 3470, 2959, 2873, 1457, 1196, 1144, 1110, 961, 909, 745.
1-(methoxymethyl)cyclohexan-1-ol (1v)

Sodium methoxide (5 M in methanol, 5.0 ml, 24 mmol, 5.3 equiv) was added to 1-oxaspiro[2.5]octane (S1v, 500 mg, 4.46 mmol, 1 equiv), and the reaction mixture was refluxed for 45 minutes. The reaction was quenched with sat. aqueous NH₄Cl solution (20 ml) followed by addition of diethylether (20 ml). The phases were separated, and the aqueous layer was extracted with diethylether (2×20 ml). The combined organic phases were dried over Na₂SO₄, filtered and evaporated at 85 °C under atmospheric pressure yielding the title compound as a colorless oil (502 mg, 3.48 mmol, 43 %).

¹H NMR (300 MHz, CDCl₃): δ 3.32 (s, 3H), 3.17 (s, 2H), 2.00 (s, 1H), 1.63–1.11 (m, 10H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 80.3, 70.9, 59.4, 34.5, 25.9, 21.8.

GC-MS (EI): m/z 144, 126, 99, 81, 55.

3-(methoxymethyl)-2,4-dimethylpentan-3-ol (1w)

The title copound was synthesized from methyl methoxyacetate (437 mg, 4.00 mmol, 1 equiv) and isopropylmagnesium chloride (1 M in THF, 12.0 ml, 12.0 mmol, 3 equiv) according to general procedure GP9 yielding it in > 95 % purity (by NMR; 210 mg, 1.31 mmol, 32 %).

Note: The final product and the ketone (after single addition of isopropylmagnesium chloride) were obtained as a mixture. In the above synthesis, most of the ketone was taken off by rotary evaporation (50 °C at 30 mbar). The volatility of 1w lowers the yield furthermore.

¹H NMR (300 MHz, CDCl₃): δ 3.40–3.25 (m, 6H), 1.94–1.90 (m, 2H), 0.96 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 75.6, 73.7, 58.9, 32.9, 17.3, 17.1.

GC-MS (EI): m/z 142, 127, 117, 99, 85, 71.
1-methoxy-3-phenoxypropan-2-ol (1x)

\[
\begin{array}{c}
\text{PhO} \\
\overset{\text{OH}}{-} \\
\overset{\text{OMe}}{\text{Me}}
\end{array}
\]

The title compound was synthesized from 2-(phenoxymethyl)oxirane (1.50 g, 10.0 mmol, 1 equiv) and sodium methoxide following a procedure reported in the literature. Sodium methoxide was generated \textit{in situ} from sodium hydride (600 mg, 25.0 mmol, 2.5 equiv) and methanol (30 ml). It was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1) as a colorless oil (1.72 g, 9.45 mmol, 95 %). Analytical data was in accordance with the literature. \[ R_f = 0.26 \text{ (hexane/ethyl acetate 4:1) } \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.25–7.16 \text{ (m, 2H), 6.93–6.79 \text{ (m, 3H), 4.13–4.05 \text{ (m, 1H), 3.98–3.89 \text{ (m, 2H), 3.56–3.42 \text{ (m, 2H), 3.33 \text{ (s, 3H), 2.64 \text{ (s, 1H).} } }}] \]

\[ \text{C}^{13}\text{H NMR (101 MHz, CDCl}_3\text{): } \delta 158.5, 129.5, 121.1, 114.5, 73.5, 69.0, 68.8, 59.3. \]

\[ \text{GC-MS (EI): } m/z 182, 119, 108, 94, 77. \]

1-methoxy-3-phenoxy-2-phenylpropan-2-ol (1y)

\[
\begin{array}{c}
\text{PhO} \\
\overset{\text{OH}}{-} \\
\overset{\text{OMe}}{\text{Ph}}
\end{array}
\]

To a solution of 1-methoxy-3-phenoxypropan-2-one (480 mg, 2.66 mmol, 1 equiv) in THF (5 ml), phenylmagnesium bromide (1 M in THF, 4.0 ml, 4.0 mmol, 1.5 equiv) was added dropwise at 0 °C. The reaction mixture was heated to 65 °C for 4 h. The reaction mixture was allowed to attain room temperature, quenched by addition of sat. aqueous NH$_2$Cl solution (20 ml) and extracted with ethyl acetate (4×20 ml). The combined extracts were dried over MgSO$_4$, filtered and evaporated under reduced pressure. Flash CC on silica gel (hexane/ethyl acetate 85:15) afforded the title compound (270 mg, 1.04 mmol, 40 %).

\[ R_f = 0.35 \text{ (hexane/ethyl acetate 85:15) } \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.63–7.55 \text{ (m, 2H), 7.42–7.33 \text{ (m, 2H), 7.32–7.22 \text{ (m, 3H), 6.98–6.87 \text{ (m, 3H), 4.23–4.14 \text{ (m, 2H), 3.86–3.69 \text{ (m, 2H), 3.39 \text{ (s, 3H).} }}] } \]

\[ \text{C}^{13}\text{H NMR (101 MHz, CDCl}_3\text{): } \delta 158.5, 141.7, 129.4, 128.2, 127.5, 125.7, 121.1, 114.7, 76.6, 75.1, 71.9, 59.5. \]

\[ \text{GC-MS (EI): } m/z 258, 240, 213, 151, 119, 91, 77. \]
(±)-erythro-2-methoxy-1-phenylpropan-1-ol (3a)

The title compound was synthesized from 2-methoxy-1-phenylpropan-1-one (S2, 821 mg, 5.000 mmol, 1 equiv) and NaBH₄ (378 mg, 10.0 mmol, 2 equiv) in methanol (20 ml) according to general procedure GP6. After 4 h at room temperature, it was isolated as a colorless liquid (812 mg, 4.88 mmol, 98 %, d.r. (erythro/threo) = 70:30 by NMR). Analytical data was in accordance with the literature.[9]

Rᵣ = 0.37 (hexane/ethyl acetate 4:1)

¹H NMR (400 MHz, CDCl₃): mixture of diastereomers δ 7.30–7.15 (m, 5H), 4.82 (d, J = 3.6 Hz, 0.7H, erythro), 4.32 (d, J = 7.9 Hz, 0.3H, threo), 3.52–3.26 (m, 4H), 0.91 (d, J = 6.4 Hz, 2.1H, erythro), 0.90 (d, J = 6.2 Hz, 0.9H, threo).

¹³C{¹H} NMR (101 MHz, CDCl₃): mixture of diastereomers δ 140.6, 140.5, 128.4, 128.2, 128.0, 127.3, 126.3, 81.7, 80.8, 78.4, 74.5, 56.7, 56.7, 14.7, 12.6.

GC-MS (EI): m/z 107, 91, 79, 77, 59.

IR (ATR): ν 3433, 3064, 3030, 2978, 2930, 2878, 2825, 1603, 1491, 1454, 1379, 1323, 1230, 1193, 1137, 1088, 1025, 988, 906, 824, 749, 701.
(±)-erythro-3-methoxy-2-phenylbutan-2-ol (3b) and (±)-threo-3-methoxy-2-phenylbutan-2-ol (3b’)

To a solution of 2-methoxypropiophenone (985 mg, 6.00 mmol, 1 equiv) and N,N,N’,N’-tetramethylethylenediamine (1.8 ml, 12 mmol, 2 equiv) in diethyl ether (6 ml), methyllithium (nominally 1.6 M in diethyl ether, 22.5 ml, 36.0 mmol, 6 equiv) was added at 0 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched by adding saturated aqueous NH₄Cl solution (10 ml), the organic layer was separated, and the aqueous phase was extracted with DCM (3×10 ml). The combined organic phases were dried over MgSO₄, filtered and evaporated under reduced pressure. Flash CC on silica gel (hexane/ethyl acetate 9:1) yielded erythro-configured 3b (287 mg, 1.59 mmol, 27 %) and threo-configured 3b’ (254 mg, 1.41 mmol, 24 %, d.r. (threo/erythro) = 9:1 by NMR) as colorless liquids. Analytical data was in accordance with the literature.[20]

**Analytical data for 3b**:

$R_f = 0.36$ (hexane/ethyl acetate 9:1)

$^1$H NMR (400 MHz, CDCl₃): δ 7.36–7.31 (m, 2H), 7.28–7.23 (m, 2H), 7.18–7.13 (m, 1H), 3.35–3.31 (m, 4H), 1.51 (s, 3H), 0.82 (d, $J = 6.3$ Hz, 3H).

$^{13}$C{¹H} NMR (101 MHz, CDCl₃): δ 145.0, 128.0, 126.6, 125.3, 83.3, 76.2, 57.5, 27.4, 13.0.

GC-MS (EI): m/z 121, 105, 91, 77, 59.

IR (ATR): ν 3470, 3086, 3060, 3027, 2978, 2933, 2881, 2825, 1696, 1603, 1495, 1446, 1368, 1334, 1182, 1100, 1070, 1021, 932, 880, 820, 760, 701.

**Analytical data for 3b’:**

$R_f = 0.29$ (hexane/ethyl acetate 9:1)

$^1$H NMR (400 MHz, CDCl₃): δ 7.42–7.38 (m, 2H), 7.28–7.22 (m, 2H), 7.19–7.14 (m, 1H), 3.36 (q, $J = 6.3$ Hz, 1H), 3.22 (s, 3H), 1.40 (s, 3H), 0.98 (d, $J = 6.3$ Hz, 3H).

$^{13}$C{¹H} NMR (101 MHz, CDCl₃): δ 145.7, 128.0, 126.9, 125.8, 83.9, 76.4, 57.4, 23.0, 13.2.

GC-MS (EI): m/z 121, 105, 91, 77, 59.

IR (ATR): ν 3470, 3086, 3060, 3027, 2978, 2933, 2881, 2825, 1603, 1495, 1446, 1371, 1338, 1189, 1096, 1074, 1029, 999, 910, 883, 828, 760, 701.
2-methoxy-2-methyl-1-phenylpropan-1-ol (3c)

The title compound was synthesized from 2-methoxy-2-methylpropiophenone (S3, 622 mg, 3.49 mmol, 1 equiv) and NaBH₄ (264 mg, 6.98 mmol, 2 equiv) in methanol (14 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated as a colorless liquid (610 mg, 3.39 mmol, 97 %).

Rₜ = 0.27 (hexane/ethyl acetate 9:1)

¹H NMR (400 MHz, CDCl₃): δ 7.33–7.29 (m, 2H), 7.27–7.17 (m, 3H), 4.54 (s, 1H), 3.24 (s, 3H), 1.06 (s, 3H), 0.95 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 140, 127.8, 127.7, 127.5, 79.2, 78.1, 49.5, 21.1, 18.6.

GC-MS (EI): m/z 219, 105, 91, 77, 73.

HRMS (ESI⁺): m/z calcd. for C₁₅H₁₆O₂Na ([M+Na⁺]⁺) 203.10425, found 203.10455.

IR (ATR): ν 3448, 3064, 3030, 2974, 2937, 2829, 1949, 1886, 1812, 1603, 1495, 1454, 1379, 1327, 1230, 1185, 1141, 1051, 954, 869, 772, 731, 701.

(±)-erythro-2-methoxy-1,2-diphenylethan-1-ol (3d)

Following a modified literature procedure.[21] At room temperature, Ag₂O (695 mg, 3.00 mmol, 1 equiv) and methyl iodide (205 µl, 3.30 mmol, 1.1 equiv) were added to a solution of meso-1,2-diphenylethan-1,2-diol (3e, 643 mg, 3.00 mmol, 1 equiv) in DMF (6 ml). The reaction mixture was stirred at room temperature in the dark for 24 h. Then, it was filtered through a pad of Celite, which was subsequently washed with DCM (15 ml). The filtrate was reduced under reduced pressure, and the oily residue was taken up in ethyl acetate (6 ml) and washed with water (5×2 ml) and brine (2 ml) before it was dried over MgSO₄, filtered and evaporated in vacuo. The crude product was purified by flash CC on silica gel (hexane/ethyl acetate 98:2→75:25) yielding the title compound as a colorless solid (251 mg, 1.10 mmol, 37 %).

Analytical data was in accordance with the literature.[22]

m.p. = 102 °C

Rₜ = 0.25 (hexane/ethyl acetate 9:1)

¹H NMR (400 MHz, CDCl₃): δ 7.22–7.15 (m, 6H), 7.11–7.03 (m, 4H), 4.81 (d, J = 5.4 Hz, 1H), 4.27 (d, J = 5.4 Hz, 1H), 3.16 (s, 3H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 140.3, 137.3, 128.1, 128.0, 127.9, 127.6, 127.0, 87.6, 76.9, 57.2.

GC-MS (EI): m/z 210, 167, 165, 121, 105, 91, 77, 51.

IR (ATR): ν 3425, 3086, 3027, 2997, 2892, 2829, 2654, 1789, 1491, 1450, 1413, 1372, 1338, 1249, 1178, 1103, 1059, 977, 917, 839, 775, 749, 697.
styrene oxide (6)

Following a modified literature procedure. To a solution of styrene (5.73 ml, 50.0 mmol, 1 equiv) in DCM (150 ml), NaHCO₃ (8.40 g, 100 mmol, 2 equiv) was added. The reaction mixture was cooled to 0°C followed by addition of meta-chloroperbenzoic acid (≤ 77 %, 16.8 g, 75.0 mmol, 1.5 equiv). The reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, saturated aqueous Na₂CO₃ solution (50 ml) was added in order to dissolve a colorless precipitate formed in the reaction. The organic phase was separated and washed with saturated aqueous Na₂CO₃ solution (50 ml), saturated aqueous Na₂S₂O₅ solution (0×50 ml) and water (0×50 ml), dried over MgSO₄ and filtered. The solvent was removed under reduced pressure. Kugelrohr distillation afforded the title compound as a colorless liquid (6.0 g, 0.8 mmol, 51%). Analytical data was in accordance with the literature.

Rᵣ = 0.35 (hexane/ethyl acetate 9:1)

¹H NMR (400 MHz, CDCl₃): δ 7.30–7.17 (m, 5H), 3.77 (dd, J = 4.0 Hz, 2.6 Hz, 2H), 3.07 (dd, J = 4.0 Hz, 5.5 Hz, 1H), 2.73 (dd, J = 2.6 Hz, 5.5 Hz, 1H).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 137.6, 128.5, 128.2, 125.5, 52.4, 51.2.

GC-MS (EI): m/z 120, 91, 89, 65.

IR (ATR): ν 3034, 2989, 2911, 1953, 1882, 1812, 1700, 1607, 1476, 1454, 1387, 1312, 1254, 1200, 1126, 1074, 1025, 984, 872, 813, 757, 697.

2-methoxyacetophenone-2,2-d₂ (S1ab-[2,2-d₂])

Following an adapted literature procedure. To a solution of 2-methoxyacetophenone (1.50 g, 10.0 mmol, 1 equiv) in D₂O (8 ml) and methanol-d (2 ml), a 40 % NaOD solution in D₂O (338 mg, 3.30 mmol, 0.33 equiv) was added. The turbid mixture was stirred under reflux for 21 h. The reaction mixture was allowed to cool down to room temperature and extracted with diethyl ether (3×10 ml). The combined extracts were dried over MgSO₄ and filtered. The solvent was removed in vacuo yielding the title compound as a yellow liquid (1.44 g, 9.49 mmol, 95 %, >98 % atom D by ¹H NMR), which was reduced to ¹lab-[2,2-d₂] without further purification.

¹H NMR (400 MHz, CDCl₃): δ 7.89–7.85 (m 2H), 7.54–7.49 (m, 1H), 7.43–7.38 (m, 2H), 3.44 (s, 3H).

²H NMR (61 MHz, CHCl₃/CDCl₃): δ 4.66 (s).

¹³C(¹H) NMR (101 MHz, CDCl₃): δ 196.3, 134.9, 133.6, 128.7, 127.9, 59.4.

GC-MS (EI): m/z 122, 105, 93, 77, 51.

IR (ATR): ν 3060, 2989, 2930, 2822, 2121, 2065, 1696, 1595, 1446, 1320, 1267, 1208, 1152, 1096, 924, 865, 746, 690.
2-methoxy-1-phenylethan-2,2-d$_2$-1-ol (1ab-[2,2-d$_2$])

![Diagram of 2-methoxy-1-phenylethan-2,2-d$_2$-1-ol](image)

The title compound was synthesized from 2-methoxyacetophenone-2,2-d$_2$ (S1ab-[2,2-d$_2$], 1.40 g, 9.20 mmol, 1 equiv) and NaBH$_4$ (696 mg, 18.4 mmol, 2 equiv) in methanol (40 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1→1:1) as a yellow liquid (1.33 g, 8.59 mmol, 93 %). 

$R_t = 0.22$ (hexane/ethyl acetate 4:1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.32–7.18 (m, 5H), 4.81 (s, 1H), 3.35 (s, 3H).

$^2$H NMR (108 MHz, CHCl$_3$/CDCl$_3$): δ 2.54 (s, 1H), 2.44 (s, 1H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 140.3, 128.4, 127.9, 126.2, 72.5, 59.0.

GC-MS (EI): m/z 154, 135, 107, 92, 79, 77, 51.

IR (ATR): ν 3414, 3060, 3030, 2982, 2930, 2892, 2818, 2177, 2072, 1603, 1491, 1454, 1394, 1331, 1200, 1159, 1103, 1055, 973, 932, 835, 753, 701.

2-methoxy-1-phenylethan-1-d-1-ol (1ab-[1-d])

![Diagram of 2-methoxy-1-phenylethan-1-d-1-ol](image)

The title compound was synthesized from 2-methoxyacetophenone (751 mg, 5.00 mmol, 1 equiv) and NaBD$_4$ (419 mg, 10.0 mmol, 2 equiv) in methanol(d$_2$) (20 ml) according to general procedure GP6. After 3.5 h at room temperature, it was isolated by flash CC on silica gel (hexane/ethyl acetate 4:1→1:1) as a colorless liquid (695 mg, 4.54 mmol, 91 %, > 99 % atom D by $^1$H NMR).

$R_t = 0.22$ (hexane/ethyl acetate 4:1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.33–7.19 (m, 5H), 3.48–3.34 (m, 5H).

$^2$H NMR (61 MHz, CHCl$_3$/CDCl$_3$): δ 4.88 (s).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 140.2, 128.4, 127.9, 126.2, 72.2 (t, $J = 22.2$ Hz), 59.0.

GC-MS (EI): m/z 153, 135, 108, 105, 92, 80, 78, 51.

IR (ATR): ν 3418, 3060, 3027, 2982, 2885, 2825, 2132, 1603, 1491, 1450, 1342, 1260, 1197, 1141, 1103, 1018, 951, 861, 790, 753, 701.
4. Optimization of the Reaction Conditions

4.1. Initial Remarks
Optimization of the reaction conditions started from a catalyst system comprising Pd(acac)$_2$ (0.75 mol%, acac = acetylacetonate) and L1 in a ratio of 1:4 in 1,2-dichloroethane (1,2-DCE) at a substrate concentration of 0.5 M, which was kept throughout the whole optimization process. As cocatalyst, methanesulfonic acid (20 mol%) was added. For optimization purposes, reactions were carried out on a 500 µmol scale.

The catalytic reactions were conducted following general procedure GP1a in the way that a glass pressure tube reactor was charged with Pd(acac)$_2$ and L1 in a glove box. Outside the glove box, model substrate 1ab and solvent were added. Under stirring, the resulting solution was then treated with methanesulfonic and formic acid. Subsequently, the pressure tube was sealed and placed in a heating block already heated to the respective temperature. Afterwards, the reaction mixture was examined by means of quantitative gas chromatography (GC) analysis. Please note that 1ab is given as residual amount as we assume that it is formed back from 1ah in the course of the reaction.

4.2. Amount of Formic Acid
In a first series of experiments, the amount of formic acid was varied between three and ten equivalents (Table S1). In all of the subsequent reactions, only small amounts of alcohol S4 were detected, mostly <1 % but never surpassing 3 %.

Table S1: Variation of the amount of formic acid used in the catalytic reaction of 1aa.

| Entry | Formic acid / equiv | 2a / % | S4 / % |
|-------|---------------------|--------|--------|
| 1     | 3                   | 54     | 4      |
| 2     | 6                   | 80     | 20     |
| 3     | 10                  | 98     | 2      |
| 4c    | 10                  | 95     | 3      |

a General reaction conditions: Pd(acac)$_2$ (1.14 mg, 375 µmol, 0.75 mol%), L1 (5.92 mg, 15.0 µmol, 3 mol%), 1ab (76.1 mg, 500 µmol, 1 equiv), 1,2-DCE (1 ml), MSA (6.5 µl, 100 µmol, 20 mol%), formic acid (respective amount), 100 °C, 4 h. b Yield determined by quantitative GC analysis. c After 66 h.
4.3. Temperature

Since decomposition of more sensitive substrates must be expected at 130 °C, choice of a more appreciable lower temperature was targeted (Table S2).

Table S2: Effect of the temperature on the catalytic reaction of 1ab.

| Entry | T / °C | 1ab[^b] / % | 2a[^b] / % | 1ah[^b] / % |
|-------|--------|-------------|-------------|-------------|
| 1     | 60     | 7           | 20          | 74          |
| 2     | 70     | 6           | 44          | 47          |
| 3     | 80     | 4           | 71          | 23          |
| 4     | 90     | 1           | 93          | 6           |
| 5     | 100    | <1          | 97          | 0           |
| 6     | 110    | 0           | 98          | 0           |
| 7     | 100    | 0           | 91          | <1          |
| 8     | 100    | 0           | 17          | <1          |
| 9     | 100    | 0           | 34          | 0           |
| 10    | 100    | 0           | 29          | <1          |
| 11[^c] | 100   | 0           | 36          | <1          |

[^a] General reaction conditions: Pd(acac)$_2$ (0.75 mol%), L$_1$ (3 mol%), MeSO$_3$H (20 mol%), HCOOH (10 equiv) 1,2-DCE (1 ml), MSA (6.5 µl, 100 µmol, 20 mol%), formic acid (189 µl, 5.00 mmol, 10 equiv), T, 4 h.  
[^b] Yield determined by quantitative GC analysis.  
[^c] Non-degassed solvent was used.

When the catalytic reaction provided 2a in low yields (Table S2, entries 8–11), aldehyde 5 (2–5 %) and its aldol condensation product S5 (10–33 %, Scheme S13) were found in the reaction mixture. Apparently, reduction was inhibited in these cases. Formation of oligomers, which are not detected by GC analysis, seems plausible.

Scheme S13: Acid catalyzed dimerization of aldehyde 5 to aldol condensation product S5 as side-reaction in the case of an impeded catalytic reduction step.
4.4. Solvent

As it was found that the catalytic reaction in 1,2-DCE does not provide reproducible results at 100 °C, solvents with different polarities and boiling points were tested at 100 °C. Of the tested solvents, only chloroform provided reproducibly high yields of 2a (Table S3, entries 6–11). Toluene provided a mixture of 2a, 5 and S5 hinting towards an inhibited reduction (Table S3, entry 1). In dioxane almost no rearrangement was observed (Table S3, entry 2). Acetonitrile yielded an unknown product, presumably by reaction with the solvent (Table S3, entry 3). In methanol, 1ab was recovered in 95% (Table S3, entry 4). A mixture of 1,2-DCE and water provided only low yield of 2a (Table S3, entry 5).

Table S3: Survey of solvent effects on the catalytic reaction of 1ab.

| Entry | Solvent       | 1ab% | 2a% | 1ah%  |
|-------|---------------|------|-----|-------|
| 1     | toluene       | 0    | 27  | <1    |
| 2     | 1,4-dioxane   | 29   | 5   | 65    |
| 3     | acetonitrile  | 0    | 0   | <1    |
| 4     | methanol      | 95   | 0   | <1    |
| 5     | 1,2-DCE/water | 31   | 2   | 43    |
| 6     | chloroform    | 0    | 93  | <1    |
| 7     | chloroform    | 0    | 91  | <1    |
| 8     | chloroform    | 0    | 94  | <1    |
| 9     | chloroform    | 0    | 88  | 1     |
| 10    | chloroform    | 0    | 86  | <1    |
| 11    | chloroform    | 0    | 91  | <1    |

*General reaction conditions:* Pd(acac)$_2$ (0.75 mol%), L1 (3 mol%), MeSO$_3$H (20 mol%), HCOOH (10 equiv), solvent (100 °C, 4 h).

Further optimization was carried on at 100 °C with 4 h as reaction time. The following reactions were conducted twice in order to examine reproducibility. For evaluating the effect of the Brønsted acid, the amount of methanesulfonic acid was varied. Interestingly, both decreasing and increasing the amount led to reduced yields (Table S4, entries 4–11). When the yield was reduced, more of 5 and S5 was formed.

Replacing methanesulfonic acid by its silver salt yielded 2a in only small amounts (Table S4, entry 12). Main products were S5 (32%) and 5 (7%) showing that a Brønsted (and not a Lewis) acid is required for a successful reduction.
Table S4: Variation of the amount of methanesulfonic acid used in the catalytic reaction of 1ab.

| Entry | MeSO₃H / mol% | 1abᵇ / % | 2aᵇ / % | 1ahᵇ / % |
|-------|---------------|-----------|----------|-----------|
| 1c    | 20            | 2         | 24       | 23        |
| 2d    | 20            | 0         | 90       | 0         |
| 3e    | 20            | 0         | 92       | 0         |
| 4     | 10            | 0         | 88       | 5         |
| 5     | 10            | <1        | 81       | 7         |
| 6     | 15            | <1        | 77       | 6         |
| 7     | 15            | 0         | 80       | 4         |
| 8     | 25            | 0         | 63       | 0         |
| 9     | 25            | 0         | 47       | 0         |
| 10    | 30            | 0         | 62       | 0         |
| 11    | 30            | 0         | 59       | 0         |
| 12f   | 20            | <1        | 5        | 5         |

ᵃ General reaction conditions: Pd(acac)₂ (1.14 mg, 375 μmol, 0.75 mol%), L₁ (5.92 mg, 15.0 μmol, 3 mol%), 1ab (76.1 mg, 500 μmol, 1 equiv), CHCl₃ (1 ml), MSA (respective amount), formic acid (189 μl, 5.00 mmol, 10 equiv), 100 °C, 4 h.ᵇ Yield determined by quantitative GC analysis.ᶜ After 6 h at 80 °C.ᵈ After 6 h.ᵉ After 4 h at 110 °C.ᶠ MeSO₃Ag instead of MSA.
4.5. Order of Component Addition

As best results were obtained at 100 °C in chloroform with 20 mol% of methanesulfonic acid and a reaction time of 4 h, it was decided to proceed with the optimization under these conditions with dry and degassed chloroform as solvent.

Parallel to the optimization, NMR studies were conducted. In these, it was found that depending on the order, in which Pd(acac)₂, L₁, methanesulfonic acid and formic acid are mixed, different palladium species form. Mimicking the NMR tube experiments, three catalytic reactions were carried out. In the first experiment, L₁ was dissolved with substrate 1ab in chloroform (Table S5, entry 1). Methanesulfonic acid was added, and the resulting colorless solution was stirred at room temperature. After 10 min, Pd(acac)₂ and formic acid were added, and the yellow solution was heated to 100 °C for 4 h. Quantitative GC analysis of the reaction mixture revealed that 1ab and 1ah were consumed completely, but only 8% of the starting material had been transformed into the desired product 2a. In a repetition of the experiment, 18% of 2a were obtained (Table S5, entry 2). Apparently, reduction did not take place at a sufficient rate under these reaction conditions.

Table S5: Variation of the order in which the components of the catalytic reaction are added.

| Entry | Conditions | 1ab / % | 2a / % | 1ah / % |
|-------|------------|---------|--------|--------|
| 1     | 1ab, L₁, CHCl₃, MeSO₃H, r.t., 10 min | 0 | 8 | 0 |
|       | then Pd(acac)₂, HCOOH, 100 °C, 4 h | | | |
| 2     | as entry 1 | 0 | 18 | 0 |
| 3     | 1ab, Pd(acac)₂, L₁, CHCl₃, r.t., 2.5 h | 6 | 3 | 42 |
|       | then HCOOH, r.t., 30 min | | | |
|       | then MeSO₃H, 100 °C, 4 h | | | |
| 4     | 1ab, Pd(acac)₂, L₁, CHCl₃, r.t., 2.5 h | <1 | 94 | <1 |
|       | then MeSO₃H, r.t., 30 min | | | |
|       | then HCOOH, 100 °C, 4 h | | | |
| 5     | as entry 4 | 0 | 92 | <1 |
| 6     | 1ab, Pd(acac)₂, L₁, CHCl₃, r.t., 2.5 h | 0 | 0 | 0 |
|       | then MeSO₃H, r.t., 30 min | | | |
|       | then 100 °C, 4 h | | | |
| 7     | 1ab, Pd(acac)₂, L₁, CHCl₃, r.t., 2.5 h | 4 | 1 | 84 |
|       | then HCOOH, 100 °C, 4 h | | | |

* General reaction conditions: Pd(acac)₂ (1.14 mg, 375 µmol, 0.75 mol%), L₁ (5.92 mg, 15.0 µmol, 3 mol%), 1ab (76.1 mg, 500 µmol, 1 equiv), MSA (6.5 µl, 100 µmol, 20 mol%), formic acid (189 µl, 5.00 mmol, 10 equiv), CHCl₃ (1 ml), 100 °C, 4 h. * Yield determined by quantitative GC analysis. * In absence of formic acid. * In absence of MSA.

The second catalytic reaction started with the addition of formic acid to a yellow solution of 1ab, Pd(acac)₂ and L₁, which had previously been stirred at room temperature for 2.5 h (Table S5, entry 3). After another 30 min at room temperature, methanesulfonic acid was added and the still yellow reaction mixture was heated to 100 °C for 4 h. After that time, the reaction
mixture contained 6 % of 1ab and larger amounts of 1ah (42 %) but only 3 % of 2a. Other products were not observed in significant quantities. These results suggest that both rearrangement and reduction were inhibited.

In the third and successful experiment, substrate 1ab, Pd(acac)₂ and L₁ were stirred at room temperature for 2.5 h like in the previous experiment. Then, methanesulfonic acid was added whereupon the solution changed its color from yellow to orange (Table S5, entry 4). The reaction mixture was stirred for 30 min at room temperature before formic acid was added, and the reaction mixture was heated to 100 °C for 4 h. This way, formate 2a was obtained in 94 % yield. The reaction under these conditions appeared to be reproducible (Table S5, entry 5).

Surprised by the effect of the order of component addition on product formation, two control experiments were conducted. In absence of formic acid, aldol condensation product S₅ (9 %) was the only product observed via GC analysis. Presumably, 1ab reacts under methanesulfonic acid catalysis to aldehyde 5 and then forms higher mass oligomers. Reduction of 5 does not occur, which is in accordance with the later proven assumption of formic acid as transfer reductant.

Conducting the reaction in absence of methanesulfonic acid led to the observation of 1ah as main product (84 %). Apparently, methanesulfonic acid is required for the formation of aldehyde 5.

**Experimental Procedure for Table S5, Entries 1 and 2:**
A flame-dried glass pressure tube reactor was charged with L₁ (5.92 mg, 15.0 µmol, 3 mol%) in a glove box. Outside the glove box, model substrate 1aa (76.1 mg, 500 µmol, 1 equiv), dry and degassed chloroform (1 ml) and methanesulfonic acid (6.5 µl, 100 µmol, 20 mol%) were added. The resulting solution was stirred for 10 min at room temperature. Subsequently, Pd(acac)₂ (1.14 mg, 3.75 µmol, 0.75 mol%) and formic acid (189 µl, 5.00 mmol, 10 equiv) were added, and the pressure tube was sealed and placed in a pre-heated heating block and heated to 100 °C for 4 h. Afterwards, the reaction mixture was allowed to cool down to room temperature. QuadraSil MP and pentadecane (standard, 50 µl) were added to the reaction mixture, which was filtered through a pad of basic Al₂O₃ and Celite before subjecting it to GC analysis.

**Experimental Procedure for Table S5, Entry 3:**
A flame-dried glass pressure tube reactor was charged with Pd(acac)₂ (1.14 mg, 3.75 µmol, 0.75 mol%) and L₁ (5.92 mg, 15.0 µmol, 3 mol%) in a glove box. Outside the glove box, model substrate 1aa (76.1 mg, 500 µmol, 1 equiv) and dry and degassed chloroform (1 ml) were added. The resulting solution was treated with formic acid (189 µl, 5.00 mmol, 10 equiv) and stirred at room temperature for 30 min before methanesulfonic acid (6.5 µl, 100 µmol, 20 mol%) was added. Subsequently, the pressure tube was sealed and placed in a pre-heated heating block, and the reaction mixture was stirred at 100 °C for 4 h. Afterwards, it was allowed to cool down to room temperature. QuadraSil MP and pentadecane (standard, 50 µl) were added to the reaction mixture, which was filtered through a pad of basic Al₂O₃ and Celite before subjecting it to GC analysis.
Experimental Procedure for Table S5, Entries 4 and 5:
Following general procedure GP1b.

4.6. Further Optimization
Motivated by the insights gained in the previous series of experiments, the ratio of palladium source, ligand and acid cocatalyst was re-evaluated. In all the following experiments, the order of component addition was kept as in the successful experiment described in Table S5, entry 4 (GP1b). Since no improvement in terms of reducing the ligand or acid loading was achieved, a Pd(acac)$_2$/L$_5$/MeSO$_3$H ratio of 1:4:26.7 was kept. But still, the experiments demonstrate the central role of the acid catalyst and the ligand/acid ratio. For an effective transformation, a L$_5$/MeSO$_3$H ratio greater than 1:2 is required. High activity in the reduction step is achieved when an excess of ligand and methanesulfonic acid is used.

Table S6: Variation of the Pd(acac)$_2$/L$_5$/MeSO$_3$ ratio.

| Entry$^a$ | Pd(acac)$_2$/L$_5$/MeSO$_3$H | 1ab$^b$ / % | 2a$^b$ / % | 1ah$^b$ / % |
|----------|-----------------------------|-----------|-----------|-----------|
| 1        | 1:1:2                       | 1         | 34        | 26        |
| 2        | 1:2:2                       | 5         | 45        | 39        |
| 3        | 1:2:13.3                    | <1        | 89        | 1         |
| 4        | 1:4:2                       | 3         | 4         | 69        |
| 5        | 1:4:4                       | 5         | 20        | 62        |
| 6        | 1:4:13.3                    | <1        | 83        | 9         |

$^a$ General reaction conditions: Pd(acac)$_2$ (1.14 mg, 375 µmol, 0.75 mol%), L$_5$ (respective amount), 1ab (76.1 mg, 500 µmol, 1 equiv), CHCl$_3$ (1 ml), r.t., 2.5 h, then MSA (respective amount), r.t., 30 min, then formic acid (189 µl, 5.00 mmol, 10 equiv), 100 °C, 4 h. $^b$ Yield determined by quantitative GC analysis.

4.7. Palladium Source
Under the reaction conditions optimized for the Pd(acac)$_2$/L$_5$ system (GP1b), several palladium(0) and palladium(II) sources were tested in the catalysis, and the reaction was also carried out in the absence of palladium. With all tested palladium sources including the experiment in which a palladium source was forewent, full conversion of substrate 1ab as well as formylated substrate 1ah was observed. Both soluble palladium(II) and palladium(0) sources provided high yields around 90 % (Table S7, entries 1–3 and 5). With palladium(II) chloride a lower yield of 78 % was obtained (Table S7, entry 4). Palladium(0) EnCat nanoparticles showed only low performance (Table S7, entry 6).

In the absence of a palladium source, no 2a was observed (Table S7, entry 6). Interestingly, neither 1ab nor 1ah were found in the reaction mixture but traces of 5 and 20 % of 5. Apparently, the reaction to aldehyde 5 is catalyzed by methanesulfonic acid and not palladium, whereas palladium is solely required for a fast reduction of 5 before it undergoes oligomerization.
Table S7: Screening of palladium sources for the catalytic reaction of 1ab.

| Entry | [Pd] | Yieldb / % |
|-------|------|------------|
| 1     | Pd(acac)₂ | 92, 94    |
| 2     | Pd(OAc)₂ | 95        |
| 3     | Pd(CF₆COO)₂ | 88    |
| 4     | PdCl₂ | 78        |
| 5     | Pd(dba)₂ | 93        |
| 6     | Pd(0) EnCat 30NP | 33 |
| 7c    | –    | 0         |

a General reaction conditions: [Pd] (0.75 mol%), L₁ (3 mol%), MeSO₃H (20 mol%), HCOOH (10 equiv), CHCl₃ (100 °C, 4 h).

b Determined by quantitative GC analysis.

c MSA and formic acid were added directly to L₁ and 1ab in chloroform without previous stirring.

4.8. Acid Catalyst

As it became evident that the catalytic transformation comprises both an acid catalyzed rearrangement and a palladium catalyzed reduction, which perhaps requires the presence of a Brønsted acid co-catalyst as well, we turned our attention to the Brønsted acid catalyst. With sulfonic acids, good to very good yields were obtained (Table S8, entries 1–3). Phosphoric acid derivatives and trifluoroacetic acid yielded formate 1a as main product (Table S8, entries 4–6). Since no improvement was achieved by varying the palladium source, the ligand or the Brønsted acid catalyst, the Pd(acac)₂/L₁/MeSO₃H system with a ratio of 1:4:26.7 was kept.

Table S8: Screening of Brønsted acid catalysts in the catalytic reaction of 1ab.

| Entry | Acidb | Yieldc / % |
|-------|-------|------------|
| 1     | TFOH  | 73         |
| 2     | TsOH H₂O | 98       |
| 3     | rac-CSA | 67        |
| 4     | (PhO)₂PO₂H | 5        |
| 5     | rac-BNDHP | 12       |
| 6     | CF₃COOH | 2         |

a General reaction conditions: Pd(acac)₂ (1.14 mg, 375 µmol, 0.75 mol%), L₁ (5.92 mg, 15.0 µmol, 3 mol%), 1ab (76.1 mg, 500 µmol, 1 equiv), CHCl₃ (1 ml), r.t., 2.5 h, then acid catalyst (100 µmol, 20 mol%), r.t., 30 min, then formic acid (189 µl, 5.00 mmol, 10 equiv), 100 °C, 4 h. b CSA: camphor-10-sulfonic acid; BNDHP: 1,1''-binaphthyl-2,2''-diyl hydrogen phosphate. c Determined by quantitative GC analysis.
4.9. Ligand

In order to see if other phosphine ligands than L1 can be employed, eight more bidentate ligands were tested in the catalytic reaction of 1ab. Of all tested ligands, only dtbpx (L1) afforded 2a in high yield. No dependence on the bite angle could be observed. However, it is important to note that the bite angle has not been found to be a suitable parameter for comparing L1 to other ligands.[26]

Table S9: Ligand screening for the catalytic reaction of 1ab.

| Entry<sup>a</sup> | Ligand | Bite angle<sup>b</sup> / ° | Yield<sup>c</sup> / % |
|-------------------|--------|--------------------------|---------------------|
| 1                 | dtbpx (L1) | 102                      | 92, 94              |
| 2                 | dppdtbpf (L2) | 101                      | <1                  |
| 3                 | dppf (L3) | 96                       | <1                  |
| 4                 | Xantphos (L4) | 112                      | 2                   |
| 5                 | DPEphos (L5) | 102                      | <1                  |
| 6                 | dpdm (L6) | 72                       | 0                   |
| 7                 | dppe (L7) | 85                       | 0                   |
| 8                 | dppp (L8) | 91                       | 0                   |
| 9                 | dpbb (L9) | 98                       | 0                   |
| 10<sup>d</sup>    |        | –                        | 0                   |

<sup>a</sup> General reaction conditions: Pd(acac)<sub>2</sub> (0.75 mol%), ligand (3 mol%), CHCl<sub>3</sub> (100 °C, 4 h), MeSO<sub>3</sub>H (20 mol%), HCOOH (10 equiv).

The table shows the results of the ligand screening for the catalytic reaction of 1ab. The yield is expressed as a percentage of the product formed under the given reaction conditions.

In a control experiment, in which no ligand was added, 2a was not formed. Instead, dimer S5 (14%) was found as only product by GC analysis. It was also observed as major component in the reaction mixture when L2–9 were employed as ligands. This demonstrates that L1 specifically is required for the generation of an active Pd-catalyst.
5. Products of the Catalytic Reaction

phenethyl formate (2a)

The title compound was synthesized from 2-methoxy-1-phenylethan-1-ol (1aa, 152 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) and isolated as a yellow liquid (107 mg, 711 µmol, 71 %). Analytical data was in accordance with the literature.\[30\]

\[ R_f = 0.36 \text{(hexane/ethyl acetate 95:5)} \]

\( ^1H \text{ NMR (400 MHz, CDCl}_3\): } \delta 7.95 \text{ (s, 1H), 7.27–7.11} \text{ (m, 5H), 4.31 (t, } \text{ } J = 7.0 \text{ Hz, 2H), 2.89 (t, } \text{ } J = 7.0 \text{ Hz, 2H).} 

\( ^13C\text{('H) NMR (101 MHz, CDCl}_3\): } \delta 161.0, 137.4, 128.9, 128.6, 126.8, 64.4, 35.0. 

\( \text{GC-MS (EI): m/z 104, 91, 78, 77, 65, 51.} 

\( \text{IR (ATR): } \nu 3064, 3027, 2930, 1718, 1603, 1498, 1453, 1372, 1156, 1085, 980, 932, 820, 746, 697. 

4-(tert-butyl)phenethyl formate (2b)

The title compound was synthesized from 1-(4-(tert-butyl)phenyl)-2-methoxyethan-1-ol (1b, 208 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane→hexane/ethyl acetate 9:1) and isolated as a yellow liquid (187 mg, 905 µmol, 91 %).

\[ R_f = 0.38 \text{(hexane/ethyl acetate 95:5)} \]

\( ^1H \text{ NMR (400 MHz, CDCl}_3\): } \delta 7.97 \text{ (s, 1H), 7.29–7.24} \text{ (m, 2H), 7.12–7.06} \text{ (m, 2H), 4.31 (dt, } \text{ } J = 7.1, 0.7 \text{ Hz, 2H), 2.87 (t, } \text{ } J = 7.1 \text{ Hz, 2H), 1.24 (s, 9H).} 

\( ^13C\text{('H) NMR (101 MHz, CDCl}_3\): } \delta 161.0, 149.6, 134.3, 128.5, 125.5, 64.5, 34.4, 31.4. 

\( \text{GC-MS (EI): m/z 160, 145, 117, 91.} 

\( \text{HRMS (ESI\textsuperscript{+}): m/z calcd. for C}_{13}H_{18}O_2Na ([M+Na]\textsuperscript{+}) 229.11990, found 229.12006.} 

\( \text{IR (ATR): } \nu 2960, 1722, 1513, 1461, 1364, 1267, 1156, 1021, 980, 924, 831. 

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4-methoxyphenethyl formate (2d)

The title compound was synthesized from 2-methoxy-1-(4-methoxyphenyl)ethan-1-ol (1d, 182 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→80:20) and isolated as a colorless oil (61.6 mg, 342 µmol, 34%).

\[ R_f = 0.30 \text{ (hexane/ethyl acetate 95:5)} \]

\( ^1H \) NMR (400 MHz, CDCl_3): \( \delta \) 7.96 (s, 1H), 7.10–7.04 (m, 2H), 6.80–6.75 (m, 2H), 4.27 (dt, \( J = 7.0, 0.8 \text{ Hz}, 2H \)), 3.71 (s, 3H), 2.84 (t, \( J = 7.0 \text{ Hz}, 2H \)).

\( ^{13}C(\text{H}) \) NMR (101 MHz, CDCl_3): \( \delta \) 161.0, 158.4, 129.9, 129.4, 114.0, 64.6, 55.3, 34.1.

GC-MS (EI): m/z 180, 134, 121, 119, 91, 78, 77, 65, 51.

HRMS (ESI\(^+\)): m/z calcd. for C_{10}H_{12}O_3Na ([M+Na]\(^+\)) 203.06786, found 203.06796.

IR (ATR): \( \tilde{\nu} \) 2997, 2933, 2837, 1718, 1610, 1513, 1461, 1301, 1245, 1156, 1033, 980, 924, 831, 701.

4-(methylthio)phenethyl formate (2e)

The title compound was synthesized from 2-methoxy-1-(4-(methylthio)phenyl)ethan-1-ol (1e, 198 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 95:5) and isolated as a yellow liquid (143 mg, 731 µmol, 73%).

\[ R_f = 0.22 \text{ (hexane/ethyl acetate 95:5)} \]

\( ^1H \) NMR (400 MHz, CDCl_3): \( \delta \) 7.96 (s, 1H), 7.16–7.06 (m, 4H), 4.29 (dt, \( J = 7.0, 0.7 \text{ Hz}, 2H \)), 2.86 (t, \( J = 7.0 \text{ Hz}, 2H \)), 2.40 (s, 3H).

\( ^{13}C(\text{H}) \) NMR (101 MHz, CDCl_3): \( \delta \) 161.0, 136.7, 134.3, 129.4, 127.0, 64.3, 34.4, 16.1.

GC-MS (EI): m/z 196, 150, 137, 135, 122, 91.

HRMS (ESI\(^+\)): m/z calcd. for C_{10}H_{12}O_3SNa ([M+Na]\(^+\)) 219.04502, found 219.04539.

IR (ATR): \( \tilde{\nu} \) 3019, 2922, 1715, 1603, 1495, 1461, 1435, 1372, 1275, 1156, 1092, 1014, 969, 809.
4-fluorophenethyl formate (2f)

The title compound was synthesized from 1-(4-fluorophenyl)-2-methoxyethan-1-ol (1f, 170 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane→hexane/ethyl acetate 9:1) and isolated as a yellow liquid (79.7 mg, 474 μmol, 47 %).

$R_f = 0.29$ (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.95 (s, 1H), 7.14–7.08 (m, 2H), 6.96–6.88 (m, 2H), 4.28 (dt, J = 6.9, 0.7 Hz, 2H), 2.87 (t, J = 6.9 Hz, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 161.8 (d, J = 244.8 Hz), 160.9, 133.1 (d, J = 3.4 Hz), 130.3 (d, J = 8.0 Hz), 115.4 (d, J = 21.3 Hz), 64.3, 34.1.

$^{19}$F NMR (377 MHz, CDCl$_3$): δ −116.3 (m).

GC-MS (EI): m/z 122, 109, 96, 83.

HRMS (EI): m/z calcd. for C$_9$H$_7$O$_2$F (M$^+$) 184.08558, found 184.08275.

IR (ATR): $\tilde{\nu}$ 3030, 2930, 1718, 1595, 1491, 1372, 1156, 1088, 1014, 980, 936, 831, 716, 664.

4-chlorophenethyl formate (2g)

The title compound was synthesized from 1-(4-chlorophenyl)-2-methoxyethan-1-ol (1g, 187 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) and isolated as a yellow liquid (97.6 mg, 529 μmol, 53 %).

$R_f = 0.35$ (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.95 (s, 1H), 7.22–7.18 (m, 2H), 7.11–7.06 (m, 2H), 4.29 (dt, J = 6.9, 0.7 Hz, 2H), 2.87 (t, J = 6.9 Hz, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 160.9, 135.9, 132.6, 130.2, 128.7, 64.0, 34.3.

GC-MS (EI): m/z 140, 138, 127, 125, 103, 89, 77, 63, 51.

HRMS (EI): m/z calcd. for C$_9$H$_7$O$_2$Cl (M$^+$) 184.028558, found 184.02725.

IR (ATR): $\tilde{\nu}$ 3030, 2930, 1718, 1595, 1491, 1372, 1156, 1088, 1014, 980, 936, 831, 716, 664.
3-methoxyphenethyl formate (2h)

![Chemical Structure](image)

The title compound was synthesized from 2-methoxy-1-(3-methoxyphenyl)ethan-1-ol (1h, 182 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→80:20) and isolated as a colorless liquid (66.8 mg, 371 µmol, 37 %).

Rf = 0.36 (hexane/ethyl acetate 9:1)

^1H NMR (400 MHz, CDCl₃): δ 7.96 (s, 1H), 7.19–7.12 (m, 1H), 6.77–6.68 (m, 3H), 4.31 (dt, J = 7.0, 0.7 Hz, 2H), 3.73 (s, 3H), 2.88 (t, J = 7.0 Hz, 2H).

^13C(^1H) NMR (101 MHz, CDCl₃): δ 161.0, 159.8, 139.0, 129.6, 121.2, 114.7, 112.0, 64.3, 55.2, 35.0.

GC-MS (EI): m/z 180, 134, 121, 104, 91, 78, 77, 65.

HRMS (ESI⁺): m/z calcld. for C₁₀H₁₆O₃Na ([M+Na]⁺) 203.06786, found 203.06782.

IR (ATR): v 2937, 2837, 1218, 1584, 1491, 1454, 1293, 1260, 1148, 1040, 992, 940, 880, 775, 693.

2-methylphenethyl formate (2i)

![Chemical Structure](image)

The title compound was synthesized from 2-methoxy-1-(o-tolyl)ethan-1-ol (1i, 166 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) and isolated as a colorless liquid (137 mg, 834 µmol, 83 %).

Rf = 0.36 (hexane/ethyl acetate 95:5)

^1H NMR (400 MHz, CDCl₃): δ 7.97 (s, 1H), 7.12–7.05 (m, 4H), 4.28 (dt, J = 7.3, 0.7 Hz, 2H), 2.91 (t, J = 7.3 Hz, 2H), 2.27 (s, 3H).

^13C(^1H) NMR (101 MHz, CDCl₃): δ 161.0, 136.5, 135.4, 130.5, 129.5, 126.9, 126.2, 63.5, 32.3, 19.4.

GC-MS (EI): m/z 118, 117, 105, 91, 77.

HRMS (ESI⁺): m/z calcld. for C₁₀H₁₆O₃Na ([M+Na]⁺) 187.07295, found 187.07319.

IR (ATR): v 3064, 3019, 2930, 1718, 1491, 1461, 1379, 1152, 1055, 977, 921, 742.
2-methoxyphenethyl formate (2j)

The title compound was synthesized from 1-(2-methoxyphenyl)-2-methoxyethan-1-ol (1j, 182 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→80:20) and isolated as a colorless liquid (76.9 mg, 427 µmol, 43 %).

\( R_f = 0.41 \) (hexane/ethyl acetate 9:1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.95 (s, 1H), 7.19–7.06 (m, 2H), 6.85–6.76 (m, 2H), 4.30 (dt, \( J = 7.0, 0.7 \) Hz, 2H), 3.75 (s, 3H), 2.92 (t, \( J = 7.0 \) Hz, 2H).

\(^{13}\)C\(^{\text{\scriptsize{\{1\}H}}\) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 161.2, 157.6, 130.8, 128.1, 125.6, 120.5, 110.3, 63.4, 55.3, 29.9.

GC-MS (EI): \( m/z \) 180, 134, 121, 119, 91, 77, 65, 51.

HRMS (ESI\(^+\)): \( m/z \) calcd. for C\(_{10}\)H\(_8\)O\(_3\)Na ([M+Na]\(^+\)) 203.06786, found 203.06805.

IR (ATR): \( \tilde{\nu} \) 3001, 2933, 2837, 1718, 1603, 1495, 1461, 1372, 1290, 1245, 1156, 1029, 977, 939, 835, 809, 753.

2-phenylpropyl formate (2k)

The title compound was synthesized from 1-methoxy-2-phenylpropan-2-ol (1k, 166 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 95:5) and isolated as a yellow liquid (146 mg, 889 µmol, 89 %).

\( R_f = 0.40 \) (hexane/ethyl acetate 95:5)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.94 (s, 1H), 7.29–7.12 (m, 5H), 4.25–4.13 (m, 2H), 3.05 (tt, \( J = 10.6, 7.1 \) Hz, 1H), 1.24 (d, \( J = 7.1 \) Hz, 3H).

\(^{13}\)C\(^{\text{\scriptsize{\{1\}H}}\) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 161.0, 142.8, 128.6, 127.3, 126.9, 68.8, 38.9, 18.1.

GC-MS (EI): \( m/z \) 118, 105, 103, 91, 79, 77.

HRMS (ESI\(^+\)): \( m/z \) calcd. for C\(_{10}\)H\(_{12}\)O\(_2\)Na ([M+Na]\(^+\)) 187.07295, found 187.07292.

IR (ATR): \( \tilde{\nu} \) 3064, 3030, 2967, 2933, 1718, 1603, 1495, 1454, 1383, 1159, 1021, 939, 760, 701.
2-phenylloctyl formate (2l)

![2-phenylloctyl formate](image)

The title compound was synthesized from 1-methoxy-2-phenyloctan-2-ol (1l, 236 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→95:5) and isolated as a colorless liquid (223 mg, 950 µmol, 95 %).

$R_f = 0.42$ (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (s, 1H), 7.27–7.09 (m, 5H), 4.28–4.17 (m, 2H), 2.90–2.81 (m, 1H), 1.71–1.46 (m, 2H), 1.26–1.03 (m, 8H), 0.77 (t, $J = 6.9$ Hz, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 161.0, 141.7, 128.5, 127.8, 126.8, 67.9, 44.9, 32.4, 31.7, 29.3, 27.1, 22.6, 14.1.

GC-MS (EI): m/z 188, 131, 118, 104, 91.

HRMS (ESI$^+$): m/z calc'd for C$_{15}$H$_{22}$O$_2$Na ([M+Na]$^+$) 257.15120, found 257.15125.

IR (ATR): $\tilde{\nu}$ 3064, 3027, 2926, 2855, 1722, 1603, 1495, 1454, 1375, 1252, 1159, 1077, 932, 757, 701.

2,3-diphenylpropyl formate (2m)

![2,3-diphenylpropyl formate](image)

The title compound was synthesized from 1-methoxy-2,3-diphenylpropan-2-ol (1m, 242 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane→hexane/ethyl acetate 85:15) and isolated as a yellow oil (220 mg, 915 µmol, 92 %).

$R_f = 0.28$ (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (s, 1H), 7.24–7.05 (m, 8H), 6.99–6.95 (m, 2H), 4.27 (d, $J = 6.6$ Hz, 2H), 3.18 (dt, $J = 14.2, 7.1$ Hz, 1H), 3.00–2.81 (m, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 160.9, 141.1, 139.1, 129.1, 128.5, 128.4, 127.9, 127.0, 126.3, 66.7, 46.5, 39.2.

GC-MS (EI): m/z 194, 179, 165, 149, 121, 116, 115, 104, 103, 91, 77, 65.

HRMS (ESI$^+$): m/z calc'd for C$_{16}$H$_{16}$O$_2$Na ([M+Na]$^+$) 263.10425, found 263.10404.

IR (ATR): $\tilde{\nu}$ 3060, 3027, 2926, 1718, 1603, 1495, 1454, 1375, 1156, 1029, 924, 753, 697.
2,2-diphenylethyl formate (2n)

![Structure of 2,2-diphenylethyl formate (2n)]

*From 1n:*
The title compound was synthesized from 2-methoxy-1,1-diphenylethan-1-ol (1m, 228 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 95:5) and isolated as a colorless solid (180 mg, 795 µmol, 80%).

m.p. = 64 °C

R_f = 0.33 (hexane/ethyl acetate 9:1)

^1^H NMR (400 MHz, CDCl_3): δ 7.91 (s, 1H), 7.27–7.12 (m, 10H), 4.64 (d, J = 7.7 Hz, 2H), 4.31 (t, J = 7.7 Hz, 1H).

^1^C{^1^H} NMR (101 MHz, CDCl_3): δ 160.9, 140.7, 128.7, 128.2, 127.0, 66.1, 49.8.

GC-MS (EI): m/z 180, 167, 165, 152.

HRMS (ESI^+^): m/z calcd. for C_{15}H_{20}O_2Na ([M+Na]^+) 249.08860, found 249.08875.

IR (ATR): ν 3064, 3027, 2960, 2922, 1707, 1603, 1495, 1454, 1420, 1357, 1323, 1226, 1156, 1077, 1029, 913, 790, 734, 697.

*From 3d:*
The title compound was synthesized from (±)-erythro-2-methoxy-1,2-diphenylethan-1-ol (3d, 228 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) and isolated as a colorless solid (206 mg, 910 µmol, 91 %). The analytical data was identical to the one reported above.

*From 3e:*
The title compound was synthesized from meso-1,2-diphenylethan-1,2-diol (3e, 214 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) and isolated as a colorless solid (215 mg, 951 µmol, 95 %). The analytical data was identical to the one reported above.
2-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl formate (2o)

![Structural formula of 2o]

The title compound was synthesized from 2-methoxy-1-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (1o, 296 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane→hexane/ethyl acetate 85:15) and isolated as a yellow oil (264 mg, 897 µmol, 90 %).

Rf = 0.29 (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (s, 1H), 7.50–7.46 (m, 2H), 7.30–7.11 (m, 7H), 4.65–4.62 (m, 2H), 4.36 (t, J = 7.6 Hz, 1H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 160.7, 144.8, 139.8, 129.3 (q, J = 32.5 Hz), 128.9, 128.6, 128.1, 127.4, 125.7 (q, J = 3.7 Hz), 124.1 (q, J = 272.0 Hz), 65.6, 49.6.

$^{19}$F NMR (377 MHz, CDCl$_3$): δ –62.5.

GC-MS (EI): m/z 248, 235, 215, 179, 166, 165.

HRMS (ESI⁺): m/z calcld. for C$_{26}$H$_{21}$O$_2$F$_3$Na ([M+Na]$^+$) 317.07599, found 317.07613.

IR (ATR): ν 3064, 3030, 2937, 1722, 1618, 1495, 1420, 1323, 1241, 1156, 1111, 1066, 1018, 943, 831, 731, 701.

2-(4-(methylthio)phenyl)-2-phenylethyl formate (2p)

![Structural formula of 2p]

The title compound was synthesized from 2-methoxy-1-(4-(methylthio)phenyl)-1-phenylethan-1-ol (1p, 274 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→80:20) and isolated as a yellow oil (256 mg, 940 µmol, 94 %).

Rf = 0.26 (hexane/ethyl acetate 95:5)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.89 (s, 1H), 7.25–7.19 (m, 2H), 7.18–7.05 (m, 7H), 4.60 (d, J = 7.7 Hz, 2H), 4.26 (t, J = 7.7 Hz, 1H), 2.36 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): δ 160.9, 140.6, 137.6, 137.1, 128.8, 128.7, 128.1, 127.1, 126.9, 66.0, 49.3, 15.9.

GC-MS (EI): m/z 272, 226, 213, 166, 165.

HRMS (ESI⁺): m/z calcld. for C$_{26}$H$_{21}$O$_2$SNa ([M+Na]$^+$) 295.07632, found 295.07630.

IR (ATR): ν 3060, 3027, 2922, 1718, 1599, 1490, 1454, 1405, 1320, 1238, 1152, 1096, 947, 816, 701.
2-(4-Chlorophenyl)-2-phenylethyl formate (2q)

The title compound was synthesized from 1-(4-chlorophenyl)-2-methoxy-1-phenylethan-1-ol (1q, 263 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane/ethyl acetate 99:1→80:20) and isolated as a yellow oil (254 mg, 975 µmol, 98 %).

\( R_f = 0.32 \) (hexane/ethyl acetate 95:5)

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.91 (s, 1H), 7.28–7.07 (m, 9H), 4.61 (d, \( J = 7.6 \) Hz, 2H), 4.29 (t, \( J = 7.6 \) Hz, 1H).

\(^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (101 MHz, CDCl\(_3\)): \( \delta \) 160.8, 140.2, 139.2, 132.9, 129.5, 128.9, 128.8, 128.1, 127.2, 65.8, 49.2.

\( \text{GC-MS (EI)} \): m/z 216, 214, 202, 201, 179, 178, 166, 165.

\( \text{HRMS (ESI}^+\text{): m/z calcd. for C}_{15}\text{H}_{19}\text{O}_{2}\text{ClNa ([M+Na}^+\text{]) 283.04963, found 283.04981.} \)

\( \text{IR (ATR): } \tilde{\nu} \text{ 3060, 3027, 2930, 1718, 1599, 1491, 1409, 1372, 1238, 1152, 1092, 936, 820, 746, 697.} \)

2-Hexyloctyl formate (2r)

The title compound was synthesized from 7-(methoxymethyl)tridecan-7-ol (1r, 263 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was purified by flash CC on silica gel (hexane→hexane/ethyl acetate 95:5) and isolated along with 2-hexyloctanal (ratio 91:9 by NMR) as a colorless liquid (196 mg, 743 µmol, 74 % yield of 2r).

\( R_f = 0.42 \) (hexane)

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 8.01 (s, 1H), 4.01 (dd, \( J = 5.7, 0.6 \) Hz, 2H), 1.43–1.00 (m, 21H), 0.81 (t, \( J = 6.8 \) Hz, 6H).

\(^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (101 MHz, CDCl\(_3\)): \( \delta \) 161.3, 66.6, 37.2, 31.8, 31.1, 29.6, 26.6, 22.6, 14.1.

\( \text{GC-MS (EI): m/z 126, 111, 98, 97, 85, 84, 83, 71, 70, 69, 57, 56, 55} \)

\( \text{HRMS (ESI}^+\text{): m/z calcd. for C}_{19}\text{H}_{33}\text{O}_{2}\text{Na ([M+Na}^+\text{]) 265.21380, found 265.21394.} \)

\( \text{IR (ATR): } \tilde{\nu} \text{ 2922, 2855, 1730, 1461, 1379, 1167, 932, 723.} \)
2-benzylpentyl formate (2s)

The title compound was synthesized from 2-benzyl-1-methoxypentan-2-ol (1s, 208 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. Purification of the crude product by flash CC on silica gel (hexane/ethyl acetate 98:2) gives 2s along with 2-benzylpentanal (ratio 93:7 by NMR) as a colorless oil (120 mg, 0.58 mmol, 58 % yield of 2s).

\[ R_f = 0.30 \] (hexane/ethyl acetate 95:5)

\[^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3): \delta \ 8.10–8.09 \ (m, 1H), 7.33–7.26 \ (m, 2H), 7.23–7.13 \ (m, 3H), 4.10–4.00 \ (m, 2H), 2.65 \ (d, J = 7.2 \ Hz, 2H), 2.02–1.94 \ (m, 1H), 1.46–1.29 \ (m, 4H), 0.95–0.85 \ (m, 3H). \]

\[^{13}\text{C}([\text{H}] \text{NMR} \ (101 \text{ MHz, CDCl}_3): \delta 161.2, 139.9, 129.1, 128.3, 126.0, 65.6, 39.1, 37.6, 33.0, 19.9, 14.2. \]

GC-MS (EI): m/z 206, 160, 131, 117, 104, 91.

HRMS (ESI\(^+\)): m/z calcd. for C\(_{17}\)H\(_{18}\)O\(_2\)Na ([M+Na]\(^+\)) 229.11990, found 229.12000.

IR (ATR): \(\tilde{\nu} \ 3026, 2929, 2955, 2870, 1722, 1453, 1162, 916, 730, 700. \)

2-benzyl-3-phenylpropyl formate (2t)

The title compound was synthesized from 2-benzyl-1-methoxy-3-phenylpropan-2-ol (1t, 256 mg, 1.00 mmol, 1 equiv) according to the general procedure GP2. Purification of the crude product by flash column chromatography on silica gel (hexane/ethyl acetate 95:5) afforded 2t along with 2-benzyl-3-phenylpropanal (ratio 75:25 by NMR) as a colorless oil (159 mg, 483 \(\mu\)mol, 48 % yield of 2s)

\[ R_f = 0.36 \] (hexane/ethyl acetate 95:5)

\[^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3): \delta 8.10 \ (d, J = 1.0 \ Hz, 1H), 7.26–7.21 \ (m, 5H), 7.18–7.11 \ (m, 5H), 4.00 \ (d, J = 5.0 \ Hz, 2H), 3.05–2.94 \ (m, 1H), 2.69 \ (d, J = 7.3 \ Hz, 4H). \]

\[^{13}\text{C}([\text{H}] \text{NMR} \ (75 \text{ MHz, CDCl}_3): \delta 161.0, 139.6, 138.5, 129.0, 128.4, 126.5, 126.2, 64.9, 54.8, 41.4, 37.4, 34.9. \]

GC-MS (EI): m/z 254, 208, 193, 179, 165, 117, 91.

IR (ATR): \(\tilde{\nu} \ 3063, 3026, 2926, 2855, 1722, 1494, 1453, 1166, 905, 730, 697. \)

HRMS (ESI\(^+\)): m/z calcd. for C\(_{17}\)H\(_{18}\)O\(_2\)Na ([M+Na]\(^+\)) 277.11990, found 277.12015.
2-propylpentyl formate (2u)

The title compound was synthesized from 4-(methoxymethyl)heptan-4-ol (1u, 160 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. Purification of the crude product by kugelrohr distillation (100 °C at 120 mmHg) provided it as a colorless oil (77.4 mg, 489 µmol, 49 %).

^1H NMR (300 MHz, CDCl₃): δ 8.06 (s, 1H), 4.06 (dd, J = 5.7, 0.9 Hz, 2H), 1.74–1.60 (m, 1H), 1.39–1.22 (m, 8H), 0.94–0.84 (m, 6H).

^13C(^1H) NMR (75 MHz, CDCl₃): δ 161.2, 66.5, 36.7, 33.4, 19.7, 14.3.

GC-MS (EI): m/z 159, 112, 84, 70.

IR (ATR): ν 2959, 2929, 2870, 1725, 1464, 1170, 734.

cyclohexylmethyl formate (2v)

The title compound was synthesized from 1-(methoxymethyl)cyclohexan-1-ol (1v, 144 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. Purification of the crude product by kugelrohr distillation (80 °C at 20 mmHg) afforded 2v as a colorless oil (58.2 mg, 409 µmol, 41 %).

^1H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 3.97 (d, J = 5.7 Hz, 2H), 1.78–1.61 (m, 6H), 1.32–1.11 (m, 3H), 1.05–0.90 (m, 2H).

^13C(^1H) NMR (101 MHz, CDCl₃): δ 161.2, 69.0, 36.9, 29.5, 26.2, 25.6.

GC-MS (EI): m/z 96, 81, 67, 55.
2-methyl-2-phenylpropyl formate (2x) and 3-phenylbutan-2-one (4b)

The catalytic reaction of 2-methoxy-2-methyl-1-phenylpropan-1-ol (3c, 180 mg, 1.00 mmol, 1 equiv) according to general procedure GP2 afforded after separation by flash CC on silica gel (hexane→hexane/ethyl acetate 94:6) formic ester 2x as a colorless oil (46.2 mg, 259.2 µmol, 26 %) and ketone 4b as a yellow liquid (26.7 mg, 180 µmol, 18 %). Analytical data for 4b was in accordance with the literature.[33]

**Analytical data for 2x:**

- \( R_f = 0.27 \) (hexane/ethyl acetate 97:3)
- \(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.94 (s, 1H), 7.32–7.23 (m, 3H), 7.18–7.13 (m, 2H), 4.16 (s, 2H), 1.31 (s, 6H).
- \(^{13}C\)\((^1H)\) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 161.1, 145.8, 128.4, 126.4, 125.9, 72.5, 38.1, 25.8.
- GC-MS (EI): m/z 178, 132, 119, 117, 103, 91, 79, 77.

**Analytical data for 4b:**

- \( R_f = 0.21 \) (hexane/ethyl acetate 97:3)
- \(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.28–7.22 (m, 2H), 7.20–7.11 (m, 3H), 3.66 (q, \( J = 7.0 \) Hz, 1H), 1.96 (s, 3H), 1.31 (d, \( J = 7.0 \) Hz, 3H).
- \(^{13}C\)\((^1H)\) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 208.9, 140.6, 129.0, 127.8, 127.2, 53.8, 28.4, 17.2.
- GC-MS (EI): m/z 148, 105, 79, 77.
- IR (ATR): \( \tilde{\nu} \) 3060, 3027, 2974, 2933, 2874, 1711, 1599, 1491, 1454, 1320, 1249, 1197, 1163, 1070, 1029, 951, 805, 764, 701.
Phenylacetone (4a)

![Phenylacetone (4a)](image)

The title compound was synthesized from 2-methoxy-1-phenylpropan-1-ol (3a, 166 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was obtained after flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) as a colorless oil (96.1 mg, 716 µmol, 72 %). Besides, formic ester 2k was found in traces in the reaction mixture. Analytical data of 4a was in accordance with the literature.\textsuperscript{[3]} \( R_f = 0.20 \) (hexane/ethyl acetate 95:5)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.28–7.11 (m, 5H), 3.61 (s, 2H), 2.07 (s, 3H).

\(^{13}\)C\(^{('}\)H\) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 206.5, 134.3, 129.4, 128.8, 127.1, 51.1, 29.3.

GC-MS (El): m/z 134, 92, 91, 65.

IR (ATR): \( \tilde{\nu} \) 3064, 3027, 2960, 2922, 1707, 1603, 1495, 1454, 1420, 1357, 1323, 1226, 1156, 1077, 1029, 980, 913, 887, 790, 734, 697.

3-phenylbutan-2-one (4b)

![3-phenylbutan-2-one (4b)](image)

\textit{From 3b:}

The title compound was synthesized from (±)-\textit{erythro}-3-methoxy-2-phenylbutan-2-ol (3b, 180 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was obtained after flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) as a yellow liquid (55.3 mg, 373 µmol, 37 %). Besides, formic ester 2x was found in traces in the reaction mixture. Analytical data of 4b was identical to the one reported above.

\textit{From 3b\':}

The title compound was synthesized from (±)-\textit{threo}-3-methoxy-2-phenylbutan-2-ol (3b\', 180 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. It was obtained after flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) as a yellow liquid (83.7 mg, 565 µmol, 57 %). Besides, formic ester 2x was found in traces in the reaction mixture. Analytical data of 4b was identical to the one reported above.
2,2,2-triphenylacetophenone (4c)

\[
\text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
\text{4c}
\]

The title compound was synthesized from 1,1,2,2-tetraphenylethan-1,2-diol (3f, 367 mg, 1.00 mmol, 1 equiv) according to general procedure GP2. Recrystallization from ethyl acetate provided it as a white solid (236 mg, 678 µmol, 68 %). Analytical data was in accordance with the literature.\(^\text{[32]}\)

\text{m.p.} = 184 \ ^\circ\text{C} \\
R_f = 0.33 \text{ (hexane/ethyl acetate 95:5)}

\text{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \delta 7.61–7.58 (m, 2H), 7.24–7.04 (m, 18H).

\text{\textsuperscript{13}C(\textsuperscript{1}H) NMR} (101 MHz, CDCl\textsubscript{3}): \delta 198.9, 143.2, 137.4, 131.7, 131.1, 130.9, 127.8, 127.6, 126.7, 71.1.

\text{GC-MS (EI)}: m/z 243, 165, 105, 77.

\text{IR (ATR)}: \tilde{\nu} 3083, 3023, 2670, 1580, 1491, 1443, 1320, 1729, 1215, 1182, 1088, 1036, 999, 943, 842, 787, 746, 697.
6. Miscellaneous Molecules

(Z)-2,4-diphenylbut-2-enal (S5)

![Chemical Structure]

Following an adapted literature procedure, a DCM (20 ml) solution of phenylacetaldehyde (2.50 g, 20.8 mmol, 1 equiv), pyrrolidine (172 µl, 2.08 mmol, 10 mol%) and benzoic acid (508 mg, 4.16 mmol, 20 mol%) was heated to 45 °C for 3 h. After cooling down to room temperature, a saturated aqueous solution of NaHCO₃ (20 ml) was added, and the aqueous phase was separated and extracted with DCM (3×20 ml). The combined organic phases were washed with brine (20 ml), dried over MgSO₄ and filtered. The solvent was evaporated in vacuo, and the residue was purified by flash CC on silica gel (hexane/ethyl acetate 9:1) yielding the title compound as a yellow oil (1.07 g, 4.79 mmol, 46 %). Analytical data was in accordance with the literature.

Rf = 0.46 (hexane/ethyl acetate 9:1)

1H NMR (400 MHz, CDCl₃): δ 9.56 (s, 1H), 7.38–7.04 (m, 10H), 6.77 (t, J = 7.6 Hz, 1H), 3.60 (d, J = 7.6 Hz, 2H).

13C{1H} NMR (101 MHz, CDCl₃): δ 193.6, 153.5, 144.2, 138.1, 132.3, 129.5, 128.9, 128.5, 128.5, 128.3, 126.9, 35.9.

GC-MS (EI): m/z 222, 120, 115, 103, 91, 78, 77, 65, 51.

IR (ATR): ν 3056, 3027, 2825, 2710, 1946, 1882, 1808, 1685, 1633, 1599, 1491, 1450, 1405, 1368, 1334, 1275, 1230, 1178, 1029, 939, 917, 753, 697.

1-decyl formate (S6)

The title compound was synthesized from 1-decanol (1.58 g, 10.0 mmol, 1 equiv) and formic acid (4.5 ml, 120 mmol, 12 equiv) in presence of acetic anhydride (8.5 ml, 90 mmol, 9 equiv) and NaHCO₃ (1.68 g, 20.0 mmol, 2 equiv) according to general procedure GP10 affording it as colorless liquid (1.73 g, 9.31 mmol, 93 %), which was used without further purification.

Rf = 0.46 (hexane)

1H NMR (400 MHz, CDCl₃): δ 7.99 (s, 1H), 4.09 (dt, J = 6.7, 0.6 Hz, 2H), 1.63–1.55 (m, 2H), 1.34–1.15 (m, 14H), 0.81 (t, J = 6.9 Hz, 3H).

13C{1H} NMR (101 MHz, CDCl₃): δ 161.2, 64.1, 31.9, 29.5, 29.5, 29.3, 29.2, 28.5, 25.8, 22.7, 14.1.

GC-MS (EI): m/z 112, 97, 84, 83, 82, 70, 69, 68, 57, 56, 55.

LRMS (Cl⁺): m/z calcd. for C₁₁H₂₃O₂ ([M+H⁺]⁺) 187.2, found 187.1.

IR (ATR): ν 2922, 2855, 1726, 1465, 1379, 1163, 969, 917, 723.
7. Reaction Progress Analysis

Inside a glove box, a Schlenk tube was charged with Pd(acac)$_2$ (3.43 mg, 11.3 µmol, 0.75 mol%) and L1 (17.8 mg, 45.0 µmol, 3 mol%) and subsequently sealed with a septum. Outside the glove box, model substrate 1ab (228.3 mg, 1.500 mmol, 1 equiv), chloroform (3 ml) and pentadecane (standard, 150 µl) were added. The resulting yellow solution was stirred at room temperature for 2.5 h. Methanesulfonic acid (19.5 µl, 300.0 µmol, 20 mol%) was added whereupon the reaction mixture attained a dark yellow color. The solution was stirred for another 30 min at room temperature before formic acid (565.9 µl, 15.00 mmol, 10 equiv) was added under vigorous stirring. Within 2 min, the reaction mixture was transferred into inert reaction tubes (ca. 0.25 ml per tube) via syringe. Immediately after, the reaction tubes were placed in a heating block heated to 100 °C. In regular time intervals, tubes were removed from the heating block and cooled down by dipping them shortly into liquid nitrogen. Quadrasil MP was added to the reaction mixture, which was filtered through a pad of basic Al$_2$O$_3$ and Celite and subsequently subjected to GC analysis.

Figure S1: Conducting the reaction progress analysis.
8. Deuterium Labelling Studies

The extent of deuterium incorporation was determined by means of NMR spectroscopy. In the case of the products obtained from the catalytic reaction of 1ab-[2,2-d₂] and 1ab-[1-d], their ¹H NMR spectra were used. The integrals of the aliphatic proton signals were internally referenced to the integral of the formyl-H signal (0 % deuteration) and compared to the integrals in the spectrum of non-deuterated 2a, which were also internally referenced to the formyl-H signal.

When 1ab was reacted with formic-d acid, deuterium incorporation into the product was determined using its ²H NMR spectrum. The integrals of the aliphatic proton signals were compared to the formyl-H signal (100 % deuteration) without referencing to perdeuterated 2a.
Catalytic Reaction of 1ab-[2,2-d₂]:

Reaction of 2-methoxy-1-phenylethan-2,2-d₂-1-ol (1ab-[2,2-d₂], 154.2 mg, 1.000 mmol, 1 equiv) according to general procedure GP2 yielded after purification by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) partially deuterated phenethyl formate (2a) as a yellow liquid (68.1 mg).
$^{2}H$ NMR (108 MHz, CHCl$_3$)

$^{13}$C{($^{1}H$) NMR (101 MHz, CDCl$_3$)
Catalytic Reaction of 1ab-[1-d]:

Reaction of 2-methoxy-1-phenylethanol-1-1-1-ol (1ab-[1-d]), 153.2 mg, 1.000 mmol, 1 equiv) according to general procedure GP2 yielded after purification by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) partially deuterated phenethyl formate (2a) as a yellow liquid (86.3 mg).
$^2$H NMR (108 MHz, CHCl$_3$)

$^{13}$C{($^1$H)} NMR (101 MHz, CDCl$_3$)
Catalytic Reaction of 1ab with Formic-d Acid:

Reaction of 2-methoxy-1-phenylethan-1-ol (1ab, 152.2 mg, 1.000 mmol, 1 equiv) with formic-d acid (95 % in water, 397.3 µl, 10.00 mmol, 10 equiv) according to general procedure GP2 yielded after purification by flash CC on silica gel (hexane/ethyl acetate 99:1→90:10) partially deuterated phenethyl formate (2a) as a yellow liquid (93.5 mg).

\[ \text{2 % D} \rightarrow \text{100 % D} \]

\[ \text{31 % D} \]

\[ \text{1H NMR (400 MHz, CDCl}_3) \]
$^2$H NMR (108 MHz, CHCl$_3$)

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$)
9. NMR Tube Experiments

In order to identify the palladium complexes involved in the transformation of 1ab to 2a, NMR tube experiments were conducted in CDCl₃. In these, Pd(acac)₂, L₁, methanesulfonic acid and formic acid were employed in stoichiometric amounts. For ensuring full protonation of acetylacetonate, two equivalents of each acid were added.

When a solution of L₁ was treated with methanesulfonic acid, the ¹H and ³¹P{¹H} NMR spectra showed the signals of protonated diphosphine L₁·2 MsOH, which were comparable to those of L₁·2 TfOH (NMR spectra are depicted below).[54] However, the P-bound protons exchanged with free protons from the solution, and two broad singlets were obtained instead of a doublet of triplets in the ¹H NMR spectrum. After adding one equivalent of Pd(acac)₂, its consumption and the release of acetylacetonate could be followed during the course of two days. In parallel, signals of three symmetric complexes of L₁ emerged. The complexes showed two broad signals around 109 ppm in the ³¹P{¹H} NMR spectrum, which can be assigned to ortho-metalated complexes of L₁,[26, 35] and a sharp singlet at 39 ppm. Exact structures are unknown. Signals attributable to [Pd(dtbpx)(H₂-MsO)](MsO) (C2), the formation of which was observed in another study, were not found. Addition of formic acid did not lead to the observation of newly formed species in the following 2.5 h.

The catalytic reaction, which was conducted in the way that Pd(acac)₂ was added to a solution of ligand L₁ and methanesulfonic acid, yielded only small amounts of 2a. Hence, it appears that no catalytically active species is formed from protonated ligand L₁·2 MsOH and Pd(acac)₂, or that its formation is very slow even at elevated temperatures.

Suspecting that complexation of palladium by L₁ should take place before methanesulfonic acid is added, synthesis of a complex from Pd(acac)₂ and L₁ was envisaged (Scheme S14). Dissolving equal amounts of Pd(acac)₂ and L₁ in CDCl₃ resulted in the formation of a symmetric complex Pd(dtbpx)(acac)₂ (C₁). In palladium(II) complexes derived from Pd(acac)₂ and phosphine ligands, the acetylacetonate ligand(s) can attain several coordination modes including monodentate or chelating as well as C- or O-coordination. In these complexes, diphosphines can adopt bridging, chelating or monodentate coordination.[38] From the ¹H and the ³¹P{¹H} NMR spectra of C₁, no determination of the coordination mode of acetylacetonate can be made. Complex C₁ shows one ³¹P resonance at 43 ppm suggesting chelating coordination of L₁. The ¹H NMR spectrum exhibits two singlets for the protons of acetylacetonate speaking for symmetric coordination of two acetylacetonate fragments or fast exchange of nuclei in different surroundings. Howsoever, broadening of the tert-butyl and methylene proton signals of L₁ indicates a certain degree of dynamics in the molecule.
Addition of two equivalents of formic acid to a solution of C5 started the slow formation of an unsymmetrical complex (major), a symmetric complex (minor) and a hydride complex C3 (traces). $^{31}$P as well as $^1$H resonances of the hydride complex were comparable to the ones of known palladium(II) hydride complexes of L5. The $^1$H NMR spectrum showed a doublet of doublets at $-10.54$ ppm with a $^2J_{HP}$ coupling constants of $199.2$ Hz (trans-coupling) and $24.0$ Hz (cis-coupling). The $^{31}$P($^1$H) signals appeared as doublets at 67 and $20$ ppm with a coupling constant of $22.9$ Hz ($^2J_{PP}$). Whether the palladium center is coordinated by a solvent molecule or an anion (e.g. formate), is unclear and cannot be deduced from chemical shift. Hydride complex formation with formic acid (Scheme S15) can be assumed to be analogous to the mechanism in $1^\circ$ and $2^\circ$ alcohols. That the presence of a weakly coordinating anion like tosylate is not required for the hydride complex generation with formic acid can be explained by the higher coordination strength of formate compared to the one of alcohols.

Scheme S15: Hypothetic mechanism of hydride complex formation with formic acid.

The formation of the hydride complex was accompanied by appearance of a 1:1:1 triplet ($J = 1.1$ Hz) at 5.22 ppm in the $^1$H NMR spectrum. By its spectral data, the corresponding molecule was identified as methylene chloride-$d$. Hydrogenation of CDC$_3$ to CHDCl$_2$ in presence of a late transition metal hydride has been reported. Formation of CHDCl$_2$ was also observed under conditions similar to the one of the optimized reaction suggesting the formation of a palladium hydride under these conditions.

The structures of both the symmetric and asymmetric complex, which were the predominant species in the reaction mixture, could not be solved. At room temperature, the asymmetric species showed a broad singlet at 58 ppm and a doublet at 29 ppm ($J = 33.5$ Hz) in the $^{31}$P($^1$H) NMR spectrum. A singlet at 37 ppm was assigned to the symmetric species. In addition to these signals, a singlet at 100 ppm was attributed to an ortho-metalated palladium species.
Under the impact of methanesulfonic acid, all so far described $^{31}$P signals vanished. Instead, the spectrum showed the signals of an asymmetric (major) and a symmetric species (minor). The asymmetric complex appeared with doublets at 81 and 36 ppm and a coupling constant of 38.4 Hz. Presumably, these signals correspond to a square-planar palladium(II) complex coordinated by an anion and a solvent molecule. The symmetric complex showed a singlet at 45 ppm which is in the range of complexes of the type $[\text{Pd(dtbp}(X)_{2}]^{2+}$ and $\text{Pd(dtbp}(X)_{2}]^{2+}$. However, these assignments are highly speculative.

Completely different observations were made when methanesulfonic acid was added to a solution of C1, which yielded reported complex $[\text{Pd(dtbp}(X)_{2}]^{2+}$. Its formation was nearly complete after 30 min. Upon addition of two equivalents of formic acid, the reaction mixture started turning brown, and a black solid, presumably elemental palladium, precipitated. After the addition of formic acid, no change of the NMR spectra was observed within 17 h at room temperature. Heating a mixture of C2 and formic acid to 100 °C for 30 min did not change the spectra either. In the catalytic reaction, a color change similar to the one observed in this NMR tube experiment was found. When 1ab, Pd(acac)$_2$ and L1 were dissolved in chloroform, a yellow solution was obtained. Adding methanesulfonic acid after 2.5 h led to a fast color change to dark yellow/orange. Upon addition of formic acid, the reaction mixture became turbid within minutes. During heating it turned into an opaque brown mixture, which changed into a colorless solution in the course of few hours. Since only this order of addition resulted in high yields, it is apparent that the active palladium species is formed from C2 after addition of formic acid. Perhaps, the weakly coordinated palladium(II) complex is reduced by formic acid to one or more palladium(0) species, from which the active catalyst is generated.

During optimization, palladium was found to be required only for reduction. Formation of aldehyde 5 is catalyzed by methanesulfonic acid. The deuterium incorporation studies support the hypothesis of a reduction of 5 with formic acid as hydrogen donor. Hence, a palladium(II) hydride complex would be an assumable active catalyst. Aldehyde 5 could insert into its Pd–H bond forming a palladium(II) alkoxide complex.

However, in the NMR tube experiment no hydride complex could be prepared from C2. But still, if palladium(0) is formed after the addition of formic acid, hydride complex formation could occur via the oxidative addition of protonated ligand. Hence, excess ligand and presence of a strong acid for its protonation would be favorable for an effective hydride generation in the beginning of the reaction. Later on, hydride complex formation should mainly take place in the way depicted in Scheme S15 as suggested by the results of the deuterium labelling experiments.
Addition of Pd(acac)$_2$ and Formic Acid to Protonated Ligand $L1\cdot2\text{MsOH}$:

A solution of $L1$ (9.50 mg, 24.1 µmol, 1 equiv) in CDCl$_3$ (0.6 ml) was treated with methanesulfonic acid (3.13 µl, 48.2 µmol, 2 equiv). NMR spectra recorded 40 min later showed the signals of protonated phosphine $L1\cdot2\text{MsOH}$.

Addition of Pd(acac)$_2$ (7.33 mg, 24.1 µmol, 1 equiv) led to formation of a yellow solution. In the course of two days, consumption of Pd(acac)$_2$ by protonation and release of acetylacetone was observed. During that time, formation of three symmetric complexes of $L1$ was observed. [Pd(dtbpx)(η$^2$-MsO)](MsO) (C2) was not among these.

After the addition of formic acid (1.82 µl, 24.1 µmol, 2 equiv), no formation of new species was observed within 2.5 h.

Analytical data for $L1\cdot2\text{MsOH}$:

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.62–7.54 (m, 2H), 7.36–7.26 (m, 2H), 4.12 (d, $J_{HP} = 14.1$ Hz, 4H), 2.70 (s, 6H), 1.46 (d, $J_{HP} = 16.5$ Hz, 36 H).

$^{31}$P($^1$H) NMR (122 MHz, CDCl$_3$): δ 39.1 (s).
$^1$H NMR (300 MHz)

L1-2 MsOH + Pd(acac)$_2$ + HCOOH

L1-2 MsOH + Pd(acac)$_2$

L1-2 MsOH

$^{31}$P($^1$H) NMR (122 MHz)

L1-2 MsOH + Pd(acac)$_2$ + HCOOH

L1-2 MsOH + Pd(acac)$_2$

L1-2 MsOH
Formation of Pd(dtbpx)(acac)$_2$ (C1):

In an NMR tube, Pd(acac)$_2$ (7.72 mg, 25.3 µmol, 1 equiv) and L1 (10.0 mg, 25.3 µmol, 1 equiv) were dissolved in CDCl$_3$ (0.6 ml). In the course of 3 h, full conversion of L1 to Pd(dtbpx)(acac)$_2$ (C1) could be observed by NMR spectroscopy. After that, the $^1$H NMR spectrum still showed signals of residual Pd(acac)$_2$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30–7.25 (m, 2H), 7.20–7.14 (m, 2H), 5.53 (s, 1H), 3.69 (br, 4H), 1.96 (s, 6H), 1.48 (d, $J_{HP} = 12.4$ Hz, 36H).

$^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$): $\delta$ 42.6 (s).

$^1$H NMR (400 MHz)

$^{31}$P($^1$H) NMR (162 MHz)
Addition of Formic Acid to Pd(dtbp)(acac)$_2$ (C1) Followed by Methanesulfonic Acid:

Pd(dtbp)(acac)$_2$ (C1) was formed by stirring a solution of Pd(acac)$_2$ (7.72 mg, 25.3 µmol, 1 equiv) and L1 (10.0 mg, 25.3 µmol, 1 equiv) in CDCl$_3$ (0.8 ml) at room temperature for 2.5 h. The $^{31}$P($^1$H) NMR spectrum of the yellow solution showed the signal of C1 beside the signal of residual L1. $^1$H NMR spectroscopy showed full conversion of Pd(acac)$_2$.

Formic acid (1.91 µl, 50.7 µmol, 2 equiv) was added, and the formation of a symmetric (minor), an asymmetric (major), a hydride complex C3 (trace amounts) and CHDCl$_2$ in the still yellow solution was observed by NMR spectroscopy in the course of 4 h.

Methanesulfonic acid (3.29 µl, 50.7 µmol, 2 equiv) was added whereupon the reaction mixture turned orange. Within 30 min, the formation of a symmetric (minor) and an asymmetric complex (major) was observed.

Selected analytical data for C3:

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ –10.54 (dd, $J_{HP} = 199.2$, 24.0 Hz).

$^{31}$P($^1$H) NMR (122 MHz, CDCl$_3$): $\delta$ 66.5 (d, $J_{PP} = 22.9$ Hz), 20.2 (d, $J_{PP} = 22.9$ Hz).
$^1$H NMR (300 MHz)

C1 + HCOOH + MeSO$_3$H

C1 + HCOOH

C1

$^{31}$P($^1$H) NMR (122 MHz)

C1 + HCOOH + MeSO$_3$H

C1 + HCOOH

C1
Addition of Methanesulfonic Acid to Pd(dtbp)(acac)$_2$ (C1) Followed by Formic Acid:

Pd(dtbp)(acac)$_2$ (C1) was formed by stirring a solution of Pd(acac)$_2$ (7.72 mg, 25.3 µmol, 1 equiv) and L1 (10.0 mg, 25.3 µmol, 1 equiv) in CDCl$_3$ (0.8 ml) at room temperature for 2.5 h. The $^{31}$P{H} NMR spectrum of the yellow solution showed full conversion of L1. The $^1$H NMR spectrum showed the signals of residual Pd(acac)$_2$.

Upon addition of methanesulfonic acid (6.0 µl, 50.7 µmol, 2 equiv), the reaction mixture turned orange, and NMR spectroscopy showed formation of [Pd(dtbp)(η$_2$-MsO)](MsO) (C2) and acetylacetone and nearly complete consumption of Pd(acac)$_2$ within 60 min.

When formic acid (1.91 µl, 50.7 µmol, 2 equiv) was added, the reaction mixture started turning brown, and a black solid (presumably elemental palladium) precipitated. The NMR spectra did not change within 17 h at room temperature.
$^1$H NMR (300 MHz)

C1 + HCOOH + MeSO$_3$H

C1 + HCOOH

C1

$^{31}$P($^1$H) NMR (122 MHz)

C1 + MeSO$_3$H + HCOOH

C1 + MeSO$_3$H

C1
Similar to the Catalytic Reaction under Semi-Optimized Conditions:

In a glass pressure tube reactor, Pd(dtbpx)(acac)₂ (C1) was formed by stirring a solution of Pd(acac)₂ (7.72 mg, 25.3 µmol, 1 equiv) and L₁ (20.0 mg, 50.7 µmol, 1 equiv) in CDCl₃ (1 ml) at room temperature for 2.5 h. Methanesulfonic acid (6.58 µl, 101 µmol, 4 equiv) was added, and the reaction mixture was stirred at room temperature for 30 min before it was treated with formic acid (7.65 µl, 203 µmol, 8 equiv) and heated to 100 °C for 1.5 h. After cooling to room temperature, the reaction mixture was transferred to an NMR tube and studied by NMR spectroscopy. Both, ¹H and ³¹P{¹H} NMR spectrum showed a multitude of signals including the one of CDHCl₂.

¹H NMR (300 MHz)

³¹P{¹H} NMR (122 MHz)
10. References

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11. Abbreviations

acac  acetylacetonate
APCI  atmospheric-pressure chemical ionization
ATR  attenuated total reflectance
BNDHP 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate
Bn  benzyl-
"Bu  n-butyl-
′Bu  tert-butyl-
Cl  chemical ionization
CC  column chromatography
CSA  camphor-10-sulfonic acid
dba  dibenzylideneacetone
DCE  dichloroethane
DCM  dichloromethane
DEPT  distortionless enhancement by polarization transfer
DMF  N,N-dimethylformamide
DMSO  dimethylsulfoxide
dppb  1,4-bis(diphenylphosphino)butane
dppdtbpf 1-diphenylphosphino-′-(di-tert-butylphosphino)ferrocene
dppe  1,2-bis(diphenylphosphino)ethane
dppf  1,1′-bis(diphenylphosphino)ferrocene
dppm  1,1-bis(diphenylphosphino)methane
dppp  1,3-bis(diphenylphosphino)propane
d.r.  diastereomeric ratio
dtbp  α,α′-bis(di-tert-butylphosphino)-o-xylene
EI  electron ionization
equiv  equivalent(s)
ESI  electrospray ionization
Et  ethyl-
FID  flame ionization detector
FTIR  Fourier-transform infrared
GC  gas chromatography
Me  methyl-
m.p.  melting point
Ms  mesyl-
MS  mass spectrometry
NMR  nuclear magnetic resonance
Ph  phenyl-
′Pr  isopropyl-
Tf  triflyl-
TFA  trifluoroacetic acid
THF  tetrahydrofuran
| Abbreviation | Description                  |
|--------------|------------------------------|
| Ts           | tosyl-                       |
| TLC          | thin-layer chromatography    |
| UV           | ultraviolet                  |
| xs           | excess                       |
12. NMR Spectra
1ab-[1-d]
**1p**

- Substituents: MeS, Ph, OMe, OH

**1q**

- Substituents: Cl, Ph, OMe, OH

**Diagram**

- Two spectra are shown, one for each compound.

**NMR Peaks**

- **1p**: Various chemical shift values are indicated on the spectrum.
- **1q**: Similar chemical shift values are indicated on the spectrum.
PhO-H-O-Me

1y

Ph

Ph

Ph

2a
S1ab-[2,2-d₂]
Ph\text{O} \rightarrow \text{OMe}

S3a

Ph\text{O} \rightarrow \text{OMe}

S3a
