Supporting Information

Mild, Selective Ru-Catalyzed Deuteration Using D₂O as a Deuterium Source

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1. General remarks

All reactions and manipulations were performed under dry nitrogen by using standard Schlenk techniques. All solvents were purified prior to use. KOD was obtained as solution in D$_2$O (40 wt. % in D$_2$O, 98 atom % D) from Sigma-Aldrich (now Merck). RuCl$_2$(PPh$_3$)$_3$ (97%) was obtained from Sigma-Aldrich (now Merck). All other chemicals were purchased from Acros Organics, Sigma-Aldrich/Merck, Alfa Aesar, TCI, abcr or ChemPUR. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz (1H NMR), 75 MHz (13C NMR), a Bruker Ascend 400 spectrometer at 400 MHz (1H NMR), 101 MHz (13C NMR), a Bruker Avance 500 spectrometer at 500 MHz (1H NMR), 126 MHz (13C NMR), or a Bruker Avance 700 spectrometer at 700 MHz (1H NMR), 176 MHz (13C NMR). Chemical shifts are reported in ppm down field using tetramethylsilane or the signal of the deuterated solvent as an internal standard. Coupling constants $J$ are given in Hz. The following abbreviations are used in the analysis of NMR spectra: s=singlet, d=doublet, t=triplet, q=quartet, hept=heptet, sept=septet. Combination of these abbreviations is applied whenever more than one coupling is observed. IR spectra were measured on a FT-IR spectrometer in an ATR mode. The intensity of the observed peaks is given in parenthesis: s=strong, m=medium, w=weak. Mass spectra were measured using electrospray ionization on a Bruker micrOTOF-Q. High performance liquid chromatography (HPLC) was performed using a Knauer K-501 pump, Knauer RI-detector K 2400 and a Macherey-Nagel VP250/21 Nucleodur 100-5 column.

$E/Z$-ratios and yields were determined by crude-NMR with internal standard. Degree of deuteration was determined by comparing the $^1$H NMR integral of non-reactive protons with the deuterated proton signals. In order to identify the signals the pure compounds were measured and displayed unless the compounds were not stable which was the case for some of the (Z)-isomers of the obtained alkenes. In that case signals were compared with literature. Signals of non-reactive protons are marked in blue whereas reactive positions are marked in red. Deuteration is given in percent next to the corresponding position. If the deuteration degree is lower than 10% the numbers were not added to the position in the molecule as we consider the measurement error in the NMR to be too significant for that value.

For volatile and very polar substrates the solvent 1,4-dioxane was replaced by THF-d$_8$ in order to measure NMRs without prior work-up.
2. Synthesis of starting materials

4-(phenylethynyl)acetophenone S1

4-Iodoacetophenone (1.72 g, 7.0 mmol, 1.00 eq.), Pd(PPh₃)₂Cl₂ (49.1 mg, 0.07 mmol, 1 mol%), CuI (53.3 mg, 0.28 mmol, 4 mol%) and phenylacetylene (0.77 ml, 7 mmol, 1 eq.) were dissolved in THF (7 ml) and triethylamine (7 ml). After stirring over night at room temperature H₂O (17.5 ml) was added and the reaction mixture was extracted with diethylether (4 x 17.5 ml). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc – 10/1).

Yield: 1.24 g (5.6 mmol, 80%).

Physical State: colourless solid.

Rf Value: 0.26 (petroleum ether/EtOAc – 10/1).

^1H NMR (Avance 300 MHz, CDCl₃) δ 7.99 – 7.90 (m, 2H), 7.65 – 7.58 (m, 2H), 7.58 – 7.50 (m, 2H), 7.43 – 7.34 (m, 3H), 2.62 (s, 3H) ppm.

^13C NMR (Avance 101 MHz, CDCl₃) δ 197.3, 136.2, 131.8, 131.7, 128.8, 128.5, 128.3, 128.2, 122.7, 92.7, 88.6, 26.6 ppm.

IR (ATR, in CDCl₃) ν 2218 (m), 1676 (s), 1601 (m), 1553 (m), 1485 (m), 1442 (m), 1433 (m), 1423 (m), 1404 (m), 1359 (m), 1262 (m), 1180 (m), 1142 (m), 1108 (m) cm⁻¹.

HRMS (EI, m/z) calcd. for C₁₆H₁₂O: 220.0888, found: 220.0890.
$^1$H- and $^{13}$C-NMR spectra of S1
2-(4-(2-phenylethynyl)phenyl)pyridine S2

\[
\begin{align*}
\text{Br} & \quad \text{pinacol [1.5 eq.]} \\
\text{B(OH)₂} & \quad \text{MgSO₄ [3.5 eq.]} \\
\text{THF [0.5 M], rt, 2 h} & \quad \text{PdCl₂(PPh₃)₂ [2 mol%]} \\
& \quad \text{Cul [6 mol%]} \\
& \quad \text{phenylacetylene [1.2 eq.]} \\
& \quad \text{NEt₃ [0.33 M], 80 °C, 14 h} \\
\text{M1} & \quad \text{91%} \\
\text{Br} & \quad \text{2-bromopyridine [1.1 eq.]} \\
\text{K₂CO₃ [3.25 eq.]} & \quad \text{Pd(OAc)₂ [2 mol%],} \\
\text{PPh₃ [20 mol%]} & \quad \text{DME/H₂O (2.7/1), reflux, 15 h} \\
\text{M2} & \quad \text{98%} \\
\text{S2} & \quad \text{51%}
\end{align*}
\]

\(p\)-bromophenylboronic acid pinacol ester M1

\[
\begin{align*}
\text{Br} & \quad \text{pinacol [1.5 eq.]} \\
\text{B(OH)₂} & \quad \text{MgSO₄ [3.5 eq.]} \\
\text{THF [0.5 M], rt, 2 h} & \quad \text{PdCl₂(PPh₃)₂ [2 mol%]} \\
& \quad \text{Cul [6 mol%]} \\
& \quad \text{phenylacetylene [1.2 eq.]} \\
& \quad \text{NEt₃ [0.33 M], 80 °C, 14 h} \\
\text{M1} & \quad \text{91%} \\
\text{Br} & \quad \text{2-bromopyridine [1.1 eq.]} \\
\text{K₂CO₃ [3.25 eq.]} & \quad \text{Pd(OAc)₂ [2 mol%],} \\
\text{PPh₃ [20 mol%]} & \quad \text{DME/H₂O (2.7/1), reflux, 15 h} \\
\text{M2} & \quad \text{98%} \\
\text{S2} & \quad \text{51%}
\end{align*}
\]

4-Bromophenyl boronic acid (2.01 g, 10 mmol, 1.0 eq.), pinacol (1.773 g, 15 mmol, 1.5 eq.) and MgSO₄ (4.213 g, 35 mmol, 3.5 eq.) were dissolved in THF (20 ml) and stirred for 2 h at room temperature. The crude mixture was filtered, purified over a pad of silica and concentrated under reduced pressure.

**Yield:** 2.58 g (9.1 mmol, 91%).

**Physical State:** Colourless solid.

**Rₚ Value:** 0.58 (petroleum ether/EtOAc – 40/1).

\(^{1}H\) NMR (Avance 400 MHz, CDCl₃) \(\delta\) 7.66 (d, \(J = 8.0\) Hz, 2H), 7.50 (d, \(J = 8.1\) Hz, 2H), 1.34 (s, 12H) ppm.

\(^{13}C\) NMR (Avance 101 MHz, CDCl₃) \(\delta\) 136.3, 131.0, 126.2, 84.0, 24.9 ppm.
IR (ATR, in CDCl₃) ν 2978 (m), 2931 (w), 1588 (s), 1558 (w), 1467 (w), 1389 (m), 1355 (s), 1324 (m), 1142 (s), 1087 (s), 1012 (s) cm⁻¹.

HRMS (EI, m/z) calcd. for C₁₂H₁₆BBrO₂: 282.0429, found: 282.0427.

4,4,5,5-tetramethyl-2-[4-(2-phenylethynyl)phenyl]-1,3,2-dioxaborolane M₂[²]

![Structure of M₂](image)

4-Bromophenylboronic acid pinacol ester M₁ (2.524 g, 8.92 mmol, 1.0 eq.), PdCl₂(PPh₃)₂ (125.2 mg, 0.18 mmol, 2 mol%) and CuI (101.9 mg, 0.54 mmol, 6 mol%) were dissolved in NEt₃ (26.8 ml). After stirring at room temperature for 5 min phenylacetylene (1.18 ml, 10.7 mmol, 1.2 eq.) was added and the mixture was stirred 22 h at 80 °C. The crude mixture was filtered through a pad of celite (eluent: EtOAc), quenched with NH₄Cl solution and extracted with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether → EtOAc).

**Yield:** 2.67 g (8.8 mmol, 98%).

**Physical State:** colourless solid.

**Rf Value:** 0.22 (petroleum ether/EtOAc – 40/1).

¹H NMR (Avance 400 MHz, CDCl₃) δ 7.78 (d, J = 8.2 Hz, 2H), 7.55 – 7.51 (m, 4H), 7.37 – 7.32 (m, 3H), 1.35 (s, 12H) ppm.

¹³C NMR (Avance 101 MHz, CDCl₃) δ 134.6, 131.7, 130.8, 128.4, 126.0, 123.2, 90.7, 89.6, 84.0, 24.9 ppm.

IR (ATR, in CDCl₃) ν 2978 (w), 1607 (m), 1488 (w), 1443 (w), 1397 (m), 1359 (s), 1323 (m), 1261 (w), 1213 (w), 1141 (m); 1087 (m), 1019 (w) cm⁻¹.

HRMS (EI, m/z) calcd. for C₂₀H₂₁BO₂: 304.1638, found: 304.1638.
2-(4-(2-phenylethynyl)phenyl)pyridine S2[^3]

The substrate M2 (0.913 g, 3 mmol, 1.0 eq.), 2-bromopyridine (0.53 g, 3.3 mmol, 1.1 eq.) and K₂CO₃ (1.35 g, 9.75 mmol, 3.25 eq.) were dissolved in dimethoxyethane (27 ml) and H₂O (10 ml). After degassing with N₂ for 30 min, Pd(OAc)₂ (33.7 mg, 0.15 mmol, 5 mol%) and PPh₃ (157.4 mg, 0.6 mmol, 20 mol%) were added and the mixture was refluxed for 15 h. DCM was added and the organic layer was dried over anhydrous Na₂SO₄ and purified by flash column chromatography on silica gel (eluent: DCM) and precipitated from hot EtOH (55 ml).

**Yield:** 0.39 g (1.5 mmol, 51%).

**Physical State:** cream-coloured solid.

**Rf Value:** 0.15 (petroleum ether/EtOAc – 40/1).

[^1]H NMR (Avance 400 MHz, CD₂Cl₂) δ 8.65 – 8.55 (m, 1H), 7.99 – 7.92 (m, 2H), 7.73 – 7.67 (m, 2H), 7.58 – 7.53 (m, 2H), 7.50 – 7.45 (m, 2H), 7.33 – 7.25 (m, 3H), 7.20 – 7.13 (m, 1H) ppm.

[^13]C NMR (Avance 101 MHz, CD₂Cl₂) δ 156.2, 149.8, 139.1, 136.8, 131.9, 131.6, 128.4, 126.7, 123.7, 123.1, 122.4, 120.3, 90.5, 89.1 ppm.

**IR** (ATR, in CD₂Cl₂) v 3077 (w), 3051 (w), 3005 (w), 1605 (w), 1585 (s), 1571 (m), 1552 (w), 1513 (w), 1486 (m), 1462 (s), 1434 (s), 1403 (w), 1391 (w), 1311 (w), 1293 (w), 1262 (w), 1237 (w), 1187 (w), 1177 (w), 1154 (m), 1107 (w), 1096 (w), 1070 (w), 1059 (w), 1028 (w), 1014 (w) cm⁻¹.

**HRMS** (ESI, m/z) calcd. for C₁₉H₁₃N: 255.1048, found: 255.1053.
$^1$H- and $^{13}$C-NMR spectra of S2

![NMR spectra image]
2-(3-(phenylethynyl)phenyl)pyridine S3

\[
\begin{align*}
\text{Br} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} [2 mol%]  
Cul [6 mol%]  
phenylacetylene [1.2 eq.]  
NE\textsubscript{3} [0.33 M], reflux, o.n.

2-(3-(phenylethynyl)phenyl)pyridine (1.17 g, 5 mmol, 1 eq.), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (70.2 mg, 0.1 mmol, 2 mol%) and Cul (57.1 mg, 0.3 mmol, 6 mol%) were dissolved in triethylamine (15 ml) and stirred for 5 min. Afterwards phenylacetylene (0.66 ml, 6 mmol, 1 eq) was added and the mixture was refluxed over night. A saturated NH\textsubscript{4}Cl solution was added and the mixture was extracted with Et\textsubscript{2}O, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc – 40/1→10/1→5/1).
**Yield:** 1.25 g (4.9 mmol, 98%).

**Physical State:** red-brown oil.

**R**<sub>f</sub> **Value:** 0.31 (petroleum ether/EtOAc – 10/1).

**<sup>1</sup>H NMR** (Avance 400 MHz, CDCl<sub>3</sub>) \( \delta \) 8.71 (d, \( J = 4.76 \) Hz, 1H), 8.19 (t, \( J = 1.54 \) Hz, 1H), 7.98 (dt, \( J = 7.82, 2.86 \) Hz, 1H), 7.81–7.72 (m, 2H), 7.62–7.50 (m, 3H), 7.46 (t, \( J = 7.74 \) Hz, 1H), 7.40–7.30 (m, 3H), 7.29–7.22 (m, 1H) ppm.

**<sup>13</sup>C NMR** (Avance 101 MHz, CDCl<sub>3</sub>) \( \delta \) 156.6, 149.8, 139.6, 136.9, 132.0, 131.7, 130.2, 128.8, 128.4, 128.3, 126.8, 123.9, 123.3, 122.5, 120.6, 89.6, 89.3 ppm.

**IR** (ATR, in CDCl<sub>3</sub>) \( \nu \) 3056 (w), 1601 (w), 1585 (m), 1565 (w), 1493 (w), 1470 (w), 1461 (m), 1443 (w), 1433 (w), 1405 (w), 1324 (w), 1295 (w), 1271 (w), 1153 (w), 1069 (w), 1026 (w) cm<sup>−1</sup>.

**HRMS** (ESI, m/z) calcd. for C<sub>19</sub>H<sub>13</sub>N+H⁺: 256.1121, found: 256.1122.

**<sup>1</sup>H- and <sup>13</sup>C-NMR spectra of S3**
1-(3-(pyridin-2-yl)phenyl)ethan-1-one S4

\[ \text{Br}\text{-py} + \text{Acetylphenylboronic acid} \xrightarrow{\text{K}_2\text{CO}_3 [2.9 eq.]} \xrightarrow{\text{Pd(OAc)}_2 [2 \text{ mol\%}]} \xrightarrow{\text{PPh}_3 [20 \text{ mol\%}]} \xrightarrow{\text{DME/H}_2\text{O, reflux, 15 h}} \text{S4} \]

Yield: 0.89 g (4.5 mmol, 100%).

3-Acetylphenylboronic acid (0.98 g, 6 mmol, 1.35 eq.), 2-bromopyridine (0.44 ml, 4.5 mmol, 1 eq.) and K\(_2\)CO\(_3\) (1.80 g, 13 mmol, 2.9 eq.) were dissolved in dimethoxyethane (36 ml) and H\(_2\)O (13 ml). After degassing with N\(_2\) for 30 min, Pd(OAc)\(_2\) (44.9 mg, 0.2 mmol, 5 mol\%) and PPh\(_3\) (209.8 mg, 0.8 mmol, 20 mol\%) were added and the mixture was refluxed for 15 h. DCM was added and the organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and purified by column chromatography on silica gel (petroleum ether/EtOAc – 3/1→2/1).

Yield: 0.89 g (4.5 mmol, 100%).
Physical State: red-brown oil.

R<sub>f</sub> Value: 0.24 (petroleum ether/EtOAc – 2/1).

<sup>1</sup>H NMR (Avance 400 MHz, CDCl<sub>3</sub>) δ 8.77 – 8.68 (m, 1H), 8.64 – 8.55 (m, 1H), 8.27 – 8.17 (m, 1H), 8.06 – 7.97 (m, 1H), 7.84 – 7.74 (m, 2H), 7.63 – 7.53 (m, 1H), 7.33 – 7.24 (m, 1H), 2.68 (s, 3H) ppm.

<sup>13</sup>C NMR (Avance 101 MHz, CDCl<sub>3</sub>) δ 198.0, 156.4, 149.8, 139.9, 137.7, 136.9, 131.5, 129.1, 128.7, 126.8, 122.6, 120.7, 26.8 ppm.

IR (ATR, in CDCl<sub>3</sub>) ν 3064 (w), 3005 (w), 1680 (s), 1584 (m), 1566 (m), 1488 (w), 1462 (m), 1433 (m), 1414 (m), 1356 (m), 1297 (m), 1270 (w), 1231 (s), 1175 (w), 1154 (w), 1083 (w), 1066 (w), 1041 (w), 1020 (w) cm<sup>-1</sup>.

HRMS (ESI, m/z) calcd. for C<sub>13</sub>H<sub>11</sub>NO+H<sup>+</sup>: 198.0913, found: 198.0913.
4-(phenylethynyl)toluene S5

\[
\text{Pd(PPh}_3\text{)}_2\text{Cl}_2 \ [1 \text{ mol%}] \\
\text{Cul} \ [4 \text{ mol%}] \\
\text{phenylacetylene} \ [1 \text{ eq.}]
\]

\[
\text{THF/NE}_3 \ (1/1), 60 \degree \text{C, o.n.}
\]

4-(phenylethynyl)toluene S5\(^{[1]}\)

4-Tolyl iodide (2.18 g, 10 mmol, 1 eq.), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (70.2 mg, 0.1 mmol, 1 mol%), Cul (76.2 mg, 0.4 mmol, 4 mol%) and phenylacetylene (1.1 ml, 10 mmol, 1 eq.) were dissolved in THF (10 ml) and triethylamine (10 ml). After stirring over night at 60 °C demin. H\(_2\)O (25 ml) was added and the reaction mixture was extracted with diethylether (4 x 25 ml). The combined organic layers were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc – PE→40/1).

**Yield:** 1.66 g (8.6 mmol, 86%).
**Physical State:** colourless solid.

**Rf Value:** 0.50 (petroleum ether).

**$^1$H NMR** (Avance 400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.49 (m, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.30 (m, 3H), 7.18 – 7.12 (m, 2H), 2.37 (s, 3H) ppm.

**$^{13}$C NMR** (Avance 101 MHz, CDCl$_3$) $\delta$ 138.4, 131.6, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5 ppm.

**IR** (ATR, in CDCl$_3$) $\nu$ 3080 (w), 3051 (w), 3030 (w), 2919 (w), 2861 (w), 2735 (w), 2216 (w), 1594 (m), 1571 (w), 1509 (s), 1485 (m), 1440 (m), 1310 (w), 1211 (w), 1181 (w), 1106 (w), 1070 (w), 1018 (w) cm$^{-1}$.

**HRMS** (EI, m/z) calcd. for C$_{15}$H$_{12}$: 192.0939, found: 192.0937.

---

$^1$H- and $^{13}$C-NMR spectra of S5
3-(phenylethynyl)acetophenone S6

3-Bromoacetophenone (1.990 g, 10 mmol, 1 eq.), Pd(PPh₃)₂Cl₂ (140.4 mg, 0.2 mmol, 0.02 eq.) and copper iodide (114.3 mg, 0.6 mmol, 0.06 eq.) were mixed with triethylamine (30 ml) and stirred for 5 min. Phenylacetylene (1.32 ml, 12 mmol, 1.2 eq.) was added and the mixture was refluxed for 15 h. NH₄Cl solution (10 ml) was added and the mixture was extracted with Et₂O (3 x 20 ml). The combined organic layers were dried over anhydrous Na₂SO₄ and
concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc – 10/1).

**Yield:** 1.344 g (8.82 mmol, 88%).

**Physical State:** pale brown crystals.

**Rf Value:** 0.41 (petroleum ether/EtOAc – 10/1).

**$^1$H NMR** (Avance 300 MHz, CDCl$_3$) $\delta$ 8.11 (t, $J = 1.7$ Hz, 1H), 7.92 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.72 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.40 – 7.34 (m, 3H), 2.63 (s, 3H) ppm.

**$^{13}$C NMR** (Avance 125 MHz, CDCl$_3$) $\delta$ 197.5, 137.4, 136.0, 131.8, 131.7, 128.9, 128.8, 128.6, 128.0, 124.1, 122.9, 90.6, 88.4, 26.8 ppm.

**IR** (ATR, in CDCl$_3$) $\nu$ 3062 (w), 1686 (s), 1600 (w), 1573 (w), 1492 (w), 1422 (w), 1357 (m), 1315 (w), 1280 (w), 1244 (s) cm$^{-1}$.

**MS (ESI, m/z):** calcd for [C$_{16}$H$_{12}$O$^{+}$Na]$^{+}$: 243.0780, found: 243.0795.

$^1$H- and $^{13}$C-NMR spectra of S6

![NMR spectra image]
4-(phenylethynyl)anisole S7

1-iodo-4-methoxybenzene [1 eq.]
PdCl$_2$(PPh$_3$)$_2$ [1 mol%]
CuI [4 mol%]
THF/NEt$_3$, rt, 18 h

4-(phenylethynyl)anisole S7$^{[1]}$

Pd(PPh$_3$)$_2$Cl$_2$ (70.2 mg, 0.1 mmol, 0.01 eq.) and copper iodide (76.2 mg, 0.4 mmol, 0.04 eq.) are mixed with THF (10 ml). Phenylacetylene (1.1 ml, 10 mmol, 1 eq.) and 1-iodo-4-methoxybenzene (2.340 g, 10 mmol, 1 eq.) are added. After addition of NEt$_3$ the reaction mixture was stirred at room temperature for 16 h. After addition of water (25 ml) the aqueous phase was extracted with Et$_2$O (4 x 25 ml). The combined organic layers were washed with
brine (25 ml), dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc – 90/1 → 40/1).

**Yield:** 1.640 g (7.87 mmol, 79%).

**Physical State:** yellow solid.

**R$_f$ Value:** 0.6 (petroleum ether/EtOAc – 10/1).

**$^1$H NMR** (Avance 400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.44 (m, 4H), 7.36 – 7.29 (m, 3H), 6.87 (d, $J = 8.9$ Hz, 2H), 3.82 (s, 3H) ppm.

**$^{13}$C NMR** (Avance 101 MHz, CDCl$_3$) $\delta$ 159.8, 133.2, 131.6, 128.4, 128.1, 123.8, 115.6, 114.2, 89.5, 88.2, 55.5 ppm.

**IR** (ATR, in CDCl$_3$) $\nu$ 3011 (w), 2214 (w), 1605 (m), 1593 (m), 1509 (s), 1440 (m), 1288 (m), 1249 (s), 1176 (m), 1027 (s) cm$^{-1}$.

**MS** (EI, 70 eV): $m/z$ (%): 208 (100), 193 (46), 165 (35), 139 (8).

$^1$H- and $^{13}$C-NMR spectra of S7
2-(4-methylphenyl)-4,5-dihydro-1,3-oxazole S8

1. thionyl chloride [3 eq.]  
   24 h, rt
2. ethanolamine [2 eq.]  
   CH₂Cl₂, 2.5 h, rt

S8  
88%

2-(4-methylphenyl)-4,5-dihydro-1,3-oxazole S8[^4]

4-Methylbenzoic acid (2.723 g, 20 mmol, 1 eq.) and thionyl chloride (4.37 ml, 60 mmol, 3 eq.) were stirred for 24 h at room temperature. The excess thionyl chloride was removed by water jet pump. The crude product was dissolved in DCM (8.3 ml) and added dropwise at 0 °C to a mixture of ethanolamine (2.4 ml, 40 mmol, 2 eq.) in DCM (5 ml) and stirred for 2.5 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated. The residue was stirred while thionyl chloride (3 ml, 40 mmol, 2 eq.) was added carefully. Afterwards diethylether (20 ml) was added to precipitate the oxazoline hydrochloride. The
product was isolated, neutralized by slow addition of a 20 % NaOH solution and extracted with diethylether, dried over anhydrous MgSO₄ and concentrated under reduced pressure.

**Yield:** 2.85 g (17.7 mmol, 88%).

**Physical State:** colourless solid.

**¹H NMR** (Avance 400 MHz, CDCl₃) δ 7.83 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 7.9, 2H), 4.41 (t, J = 9.4, 2H), 4.04 (t, J = 9.5, 2H), 2.39 (s, 3H) ppm.

**¹³C NMR** (Avance 101 MHz, CDCl₃) δ 164.7, 141.6, 129.0, 128.1, 125.0, 67.5, 54.9, 21.5 ppm.

**IR** (ATR, in CDCl₃) ν 3035 (w), 2973 (w), 2935 (w), 2904 (w), 2878 (w), 1647 (s), 1611 (m), 1517 (w), 1543 (w), 1514 (m), 1479 (w), 1448 (w), 1409 (w), 1357 (m), 1327 (w), 1311 (w), 1256 (m), 1195 (w), 1183 (w), 116 (w), 1066 (s), 1020 (m) cm⁻¹.

**HRMS** (ESI, m/z) calcd. for C₁₀H₁₁NO⁺H⁺: 162.0913, found: 162.0927.

**¹H- and ¹³C-NMR spectra of S8**

![NMR Spectra](image)
4-Chlorobenzoic acid (3.131 g, 20 mmol, 1 eq.) was dissolved in DCM (60 ml) and 5 drops of DMF were added. The reaction mixture was cooled to 0 °C and stirred for 5 min. Oxalyl chloride (2.23 ml, 26 mmol, 1.3 eq.) was slowly added and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The crude product was dissolved in DCM (8 ml) and slowly added to a solution of ethanolamine (2.40 ml, 40 mmol, 2 eq.) in DCM (5 ml) at 0 °C. The reaction mixture was stirred for 2.5 h at room temperature. The precipitation was filtered off and the filtrate was concentrated under reduced pressure. The crude product was treated with thionyl chloride (2.91 ml, 40 mmol, 2 eq.) and
Et₂O was added to precipitate the crude product. The filter cake was treated with 20% NaOH solution and extracted with Et₂O (3 x 20 ml). The combined organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure to obtain the product as yellow crystals without further purification.

**Yield:** 1.074 g (5.91 mmol, 30% over 2 steps).

**Physical State:** yellow crystals.

**Rf Value:** 0.34 (petroleum ether/EtOAc – 1/1).

**¹H NMR** (Avance 300 MHz, CDCl₃) δ 7.88 (dt, J = 8.8, 2.0 Hz, 2H), 7.39 (dt, J = 9.1, 2.1 Hz, 2H), 4.44 (td, J = 9.5, 0.7 Hz, 2H), 4.06 (td, J = 9.5, 0.8 Hz, 2H) ppm.

**¹³C NMR** (Avance 101 MHz, CDCl₃) δ 163.9, 137.5, 129.6, 128.7, 126.4, 67.9, 55.1 ppm.

**IR** (ATR, in CDCl₃) ν 2978 (w), 2937 (w), 2882 (w), 1650 (s), 1598 (m), 1490 (m), 1405 (m), 1361 (m), 1260 (m), 1177 (w), 1090 (m), 1066 (s), 1014 (m) cm⁻¹.

**HRMS** (ESI, m/z) calcd. for C₉H₈ClNO+H⁺: 182.0367, found: 182.0377.

**¹H- and ¹³C-NMR spectra of S9**

---

S23
2-(3-chlorophenyl)-4,5-dihydro-1,3-oxazole S10

3-Chlorobenzoic acid (1.047 g, 10 mmol, 1 eq.) and thionyl chloride (2.18 ml, 30 mmol, 3 eq.) were stirred for 24 h at room temperature. The excess thionyl chloride was removed by water jet pump. The crude product was dissolved in DCM (4.15 ml) and added dropwise at 0 °C to a mixture of ethanolamine (1.2 ml, 20 mmol, 1 eq.) in DCM (2.5 ml) and stirred for 2.5 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated. The residue was stirred while thionyl chloride (1.5 ml, 20 mmol, 2 eq.) was added carefully. Afterwards diethylether (20 ml) was added to precipitate the oxazolin hydrochloride. The
product was isolated, neutralized by slow addition of a 20 % NaOH solution and extracted with diethylether, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc – 3/1→1/1).

**Yield:** 0.61 g (3.4 mmol, 34%).

**Physical State:** colourless solid.

**Rᵣ Value:** 0.22 (petroleum ether/EtOAc – 3/1).

**¹H NMR** (Avance 400 MHz, CDCl₃) δ 7.99 – 7.90 (m, 1H), 7.87 – 7.79 (m, 1H), 7.48 – 7.40 (m, 1H), 7.38 – 7.30 (m, 1H), 4.44 (t, J = 9.5 Hz, 2H), 4.07 (t, J = 9.6 Hz, 2H) ppm.

**¹³C NMR** (Avance 101 MHz, CDCl₃) δ 163.5, 134.4, 131.3, 129.6, 129.5, 128.3, 126.3, 67.8, 55.0 ppm.

**IR** (ATR, in CDCl₃) ν 3069 (w), 2975 (w), 2935 (w), 2904 (w), 2878 (w), 1649 (s), 1599 (w), 1573 (m), 1480 (m), 1432 (m), 1356 (m), 1328 (w), 1297 (w), 1272 (w), 1253 (s), 1195 (w), 1162 (w), 1103 (w), 1078 (m), 1062 (s) cm⁻¹.

**HRMS** (ESI, m/z) calcd. for C₉H₈ClNO+H⁺: 182.0367, found: 182.0366.

**¹H- and ¹³C-NMR spectra of S10**
2-(4-methylphenyl)-1,3-dioxolane S11

4-Methylbenzaldehyde (0.83 ml, 7 mmol, 1 eq.) and p-toluenesulfonic acid monohydrate (66.6 mg, 0.35 mmol, 0.05 eq.) were dissolved in toluene (15 ml). Ethylene glycol (1.57 ml) was added and the mixture was refluxed over night in a Dean–Stark apparatus. The reaction mixture was cooled to room temperature and a sat. NaHCO₃-solution (10 ml) was added. The aqueous phase was extracted with Et₂O (3 x 10 ml) and the combined organic phase was washed with brine (10 ml), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc – 10/1→5/1).
**Yield:** 671 mg (4.08 mmol, 58%).

**Physical State:** colourless oil.

**R<sub>t</sub> Value:** 0.21 (petroleum ether/EtOAc – 10/1).

**<sup>1</sup>H NMR** (Avance 400 MHz, CDCl<sub>3</sub>) δ 7.36 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 5.78 (s, 1H), 4.12 (t, J = 7.0 Hz, 2H), 4.02 (t, J = 7.0 Hz, 2H), 2.35 (s, 3H) ppm.

**<sup>13</sup>C NMR** (Avance 101 MHz, CDCl<sub>3</sub>) δ 139.1, 135.1, 129.2, 126.5, 103.9, 65.4, 21.4 ppm.

**IR** (ATR, in CDCl<sub>3</sub>) ν 3371 (b), 2883 (w), 1702 (m), 1687 (m), 1604 (w), 1386 (m), 1208 (m), 1168 (w), 1077 (s), 1021 (m) cm<sup>-1</sup>.

**HRMS** (ESI, m/z) calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>-H<sup>+</sup>: 163.0759, found: 163.0757.

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**<sup>1</sup>H- and <sup>13</sup>C-NMR spectra of S11**

![NMR spectra of S11](image-url)
2-(4-methylphenyl)-1,3-dioxolane S12

\[
\begin{align*}
\text{Phenyl} & \quad \text{2-(4-methylphenyl)-1,3-dioxolane S12} \\
& \quad \text{[6]}
\end{align*}
\]

2-Phenyl-2-imidazoline (731 mg, 5 mmol, 1 eq.) was dissolved in THF (17 ml) and cooled to -78 °C. \( n \)-Butyllithium (3.16 ml, 1.6 M in Hexane, 5.05 mmol, 1.01 eq.) was added dropwise and the mixture was stirred for 45 min. Methyl iodide (0.32 ml, 5.05 mmol, 1.01 eq.) was added and the reaction was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure. The residue was dissolved in DCM (10 ml) and washed with water (3 x 10 ml). The organic phase was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (DCM/MeOH/NEt₃ - 60/5/1).
Yield: 611 mg (3.81 mmol, 76%).

Physical State: colourless oil.

Rf Value: 0.14 (DCM/MeOH/NEt₃ - 60/5/1).

^1H NMR (Avance 400 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 7.43 – 7.37 (m, 3H), 3.88 (t, J = 9.9 Hz, 2H), 4.46 (t, J = 9.9 Hz, 2H), 2.81 (s, 3H) ppm.

^13C NMR (Avance 101 MHz, CDCl₃) δ 168.3, 131.1, 130.0, 128.5, 128.3, 54.2, 53.0, 36.6 ppm.

IR (ATR, in CDCl₃) ν 2828 (w), 2861 (w), 1611 (m), 1594 (s), 1447 (w), 1330 (w), 1276 (s), 1184 (w), 1060 (s), 1025 (m) cm⁻¹.

HRMS (ESI, m/z) calcd. for C₁₀H₁₂N₂+: 161.1073, found: 161.1084.

^1H- and ^13C-NMR spectra of S12
N-methyl-2-phenyl-1H-imidazole S13

\[
\begin{array}{c}
\text{HN} \\
\text{NH}
\end{array}
\xrightarrow{TBAI [7 mol-%]}
\begin{array}{c}
\text{HN} \\
\text{NH}
\end{array}
\xrightarrow{\text{MeI [1 eq.], 50 wt% NaOH eq [5 eq.]}}
\begin{array}{c}
\text{S13} \\
\text{26%}
\end{array}
\]

2-Phenylimidazole (721 mg, 5 mmol, 1 eq.) was dissolved in toluene (25 ml) and TBAI (129 mg, 0.35 mmol, 0.07 eq) was added. An aqueous NaOH solution (25 ml, 50 wt%, 5 eq.) was added and the biphasic system was stirred vigorously. MeI (0.32 ml, 5.05 mmol, 1.1 eq.) was added and the mixture was stirred for 15 min at room temperature. After the adding of additional toluene (20 ml) and water (20 ml) the mixture was extracted with DCM (3x 20 ml). The combined organic phase was dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc → EtOAc/MeOH 100:5).
Yield: 209 mg (1.32 mmol, 26%).

Physical State: orange oil.

Rf Value: 0.30 (EtOAc).

$^1$H NMR (Avance 400 MHz, CDCl$_3$) δ 7.65 – 7.61 (m, 2H), 7.48 – 7.38 (m, 3H), 7.12 (d, $J = 1.3$ Hz, 1H), 6.97 (d, $J = 1.3$ Hz, 1H), 3.74 (s, 3H) ppm.

$^{13}$C NMR (Avance 101 MHz, CDCl$_3$) δ 148.0, 130.7, 128.8, 128.8, 128.6, 128.5, 122.4, 34.6 ppm.

IR (ATR, in CDCl$_3$) ν 1499 (w), 1475 (m), 1405 (m), 1279 (m), 1139 (w), 1075 (w), 1019 (w) cm$^{-1}$.

HRMS (ESI, m/z) calcd. for C$_{10}$H$_{10}$N$_2$+H$^+$: 159.0917, found: 159.0932.

$^1$H- and $^{13}$C-NMR spectra of S13
3. Synthesis of reference compounds

2-(3-chlorophenyl)-4,5-dihydro-1,3-oxazole R1

According to GP-I: S10 (90.8 mg, 0.5 mmol, 1 eq.), RuCl\(_2\)(PPh\(_3\))\(_3\) (12.0 mg, 0.0125 mmol, 2.5 mol%), Zn (65.4 mg, 1 mmol, 2 eq.), CuI (9.5 mg, 0.05 mmol, 10 mol%) and H\(_2\)O (80 μl, 4 mmol, 8 eq.) were dissolved in dry 1,4-dioxane (1 ml) and stirred for 16 h at 80 °C. The product was crystallized in chloroform.

**Physical State:** colourless solid.
$^{1}$H NMR (Avance 400 MHz, DMSO) $\delta$ 8.55 (t, $J = 4.9$ Hz, 1H), 7.90 (t, $J = 1.8$ Hz, 1H), 7.81 (dt, $J = 7.8$, 1.2 Hz) 7.62 – 7.56 (m, 1H), 7.54 – 7.46 (m, 1H), 4.72 (t, $J = 5.4$, 1H), 3.56 – 3.47 (m, 2H), 3.36 – 3.29 (m, 2H) ppm.

$^{13}$C NMR (Avance 75 MHz, DMSO) $\delta$ 164.8, 136.5, 133.1, 130.9, 130.2, 127.0, 125.9, 59.6, 42.2 ppm.

IR (ATR, neat) ν 3376 (m), 3309 (m), 3086 (w), 3063 (w), 2940 (m), 2876 (w), 2713 (w), 1629 (s), 1599 (m), 1547 (s), 1473 (m), 1459 (m), 1433 (m), 1398 (w), 1376 (m), 1363 (m), 1322 (m), 1218 (m), 1166 (w), 1094 (m), 1063 (s), 1045 (m), 1000 (m) cm$^{-1}$.

HRMS (ESI, m/z) calcd. for C$_9$H$_{10}$ClNO$_2$+Na$: 222.0292$, found: 222.0295.

$^{1}$H- and $^{13}$C-NMR spectra of R1
1-[3-(2-pyridyl)phenyl]ethanol R2
According to GP-I: S4 (98.6 mg, 0.5 mmol, 1 eq.), RuCl$_2$(PPh$_3$)$_3$ (12.0 mg, 0.0125 mmol, 2.5 mol%), Zn (65.4 mg, 1 mmol, 2 eq.), CuI (9.5 mg, 0.05 mmol, 10 mol%) and H$_2$O (80 μl, 4 mmol, 8 eq.) were dissolved in dry 1,4-dioxane (1 ml) and stirred for 16 h at 80 °C and purified by column chromatography (petroleum ether/EtOAc – 3/1).

**Yield:** 45.1 mg (0.23 mmol, 45%).

**Physical State:** colourless liquid.

**R$_f$ Value:** 0.14 (petroleum ether/EtOAc – 3/1).

**$^1$H NMR** (Avance 400 MHz, CD$_2$Cl$_2$) δ 8.52 (d, J = 4.56 Hz, 1H), 7.90 (s, 1H), 7.78 – 7.71 (m, 1H), 7.68 – 7.57 (m, 2H), 7.35 – 7.26 (m, 2H), 7.16 – 7.06 (m, 1H), 4.53 (q, J = 6.47 Hz, 1H), 2.79 (s, 1H), 1.38 (d, J = 6.48 Hz, 3H) ppm.

**$^{13}$C NMR** (Avance 75 MHz, CD$_2$Cl$_2$) δ 157.6, 149.9, 147.3, 139.8, 137.2, 129.1, 126.4, 126.1, 124.4, 122.6, 120.9, 70.4, 25.6 ppm.

**IR** (ATR, in CD$_2$Cl$_2$) ν 3301 (broad), 3058 (w), 2969 (w), 2925 (w), 2867 (w), 1584 (m), 1565 (m), 1462 (m), 1434 (m), 1416 (m), 1367 (w), 1292 (w), 1188 (m), 1153 (w), 1108 (w), 1070 (m), 1012 (w) cm$^{-1}$.

**HRMS** (ESI, m/z) calcd. for C$_{13}$H$_{15}$NO+H$^+$: 200.1070, found: 200.1068.

$^1$H- and $^{13}$C-NMR spectra of R2
(E/Z)-2-(3-styrylphenyl)pyridine
(Z)-2-(3-styrylphenyl)pyridine R3

According to GP-I: S3 (127.7 mg, 0.5 mmol, 1 eq.), RuCl$_2$(PPh$_3$)$_3$ (12.0 mg, 0.0125 mmol, 2.5 mol%), Zn (65.4 mg, 1 mmol, 2 eq.), CuI (9.5 mg, 0.05 mmol, 10 mol%) and H$_2$O (80 μl, 4 mmol, 8 eq.) were dissolved in dry 1,4-dioxane (1 ml) and stirred for 16 h at 80 °C. The product purified by column chromatography (petroleum ether/EtOAc – 20/1).

**Physical State**: colourless liquid.

**Rf Value**: 0.22 (petroleum ether/EtOAc – 20/1).

**$^1$H NMR** (Avance 400 MHz, CD$_2$Cl$_2$) δ 8.61 – 8.47 (m, 1H), 7.83 – 7.75 (m, 2H), 7.63 – 7.56 (m, 2H), 7.47 – 7.42 (m, 1H), 7.25 – 7.16 (m, 4H), 7.16 – 7.07 (m, 4H), 6.65 – 6.53 (m, 2H) ppm.

**$^{13}$C NMR** (Avance 176 MHz, CD$_2$Cl$_2$) δ 156.9, 149.6, 139.4, 137.7, 137.3, 136.6, 130.6, 130.1, 129.3, 128.9, 128.6, 128.3, 127.4, 127.2, 125.6, 122.2, 120.2 ppm.

**IR** (ATR, in CD$_2$Cl$_2$) ν 3052 (w), 3007 (w), 1953 (w), 1888 (w), 1698 (w), 1583 (m), 1563 (m), 1491 (w), 1471 (w), 1461 (m), 1432 (m), 1390 (w), 1297 (w), 1240 (w), 1195 (w), 1179 (w), 1152 (w), 1073 (w), 1043 (w), 1028 (w) cm$^{-1}$.

**HRMS** (ESI, m/z) calcd. for C$_{19}$H$_{18}$N+H$: 258.1277, found: 258.1274.

$^1$H- and $^{13}$C-NMR spectra of R3
(E)-2-(3-styrylphenyl)pyridine R4
According to GP-I: S3 (127.7 mg, 0.5 mmol, 1 eq.), RuCl$_2$(PPh$_3$)$_3$ (12.0 mg, 0.0125 mmol, 2.5 mol%), Zn (65.4 mg, 1 mmol, 2 eq.), CuI (9.5 mg, 0.05 mmol, 10 mol%) and H$_2$O (80 μl, 4 mmol, 8 eq.) were dissolved in dry 1,4-dioxane (1 ml) and stirred for 16 h at 80 °C. The product purified by column chromatography (petroleum ether/EtOAc – 20/1).

**Physical State:** colourless solid.

**R$_f$ Value:** 0.17 (petroleum ether/EtOAc – 20/1).

**$^1$H NMR** (Avance 400 MHz, CD$_2$Cl$_2$) δ 8.73 – 8.67 (m, 1H), 8.23 (t, $J = 1.6$ Hz, 1H), 7.91 (dt, $J = 7.8$, 1.16 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.62 – 7.54 (m, 3H), 7.50 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.22 (m, 4H) ppm.

**$^{13}$C NMR** (Avance 126 MHz, CD$_2$Cl$_2$) δ 157.3, 150.0, 140.2, 138.2, 137.7, 137.1, 129.4, 129.4, 129.1, 128.8, 128.1, 127.3, 126.9, 126.5, 125.4, 122.7, 120.8 ppm.

**IR** (ATR, in CD$_2$Cl$_2$) ν 3056 (w), 3024 (w), 1949 (w), 1878 (w), 1806 (w), 1584 (m), 1565 (w), 1493 (w), 1461 (m), 1446 (w), 1433 (w), 1413 (w), 1300 (w), 1274 (w), 1247 (w), 1214 (w), 1180 (w), 1153 (w), 1073 (w), 1044 (w), 1028 (w) cm$^{-1}$.

**HRMS** (ESI, m/z) calcd. for C$_{19}$H$_{15}$N+H$: 258.1277, found: 258.1274.

$^1$H- and $^{13}$C-NMR spectra of R4
N-(n-propyl)benzamide R5
N-[(n-propyl)benzamide R5

\[ \text{O} \quad \text{PrNH}_2 \quad [1.5 \text{ eq.}] \quad \text{NEt}_3 \quad [2.0 \text{ eq.}] \quad \text{Et}_2\text{O} \quad [0.5 \text{ M}], \text{ rt}, 1 \text{ h} \]

\[ \text{O} \quad \text{N} \quad \text{R5} \]

n-Propylamine (0.62 ml, 7.5 mmol, 1.5 eq.), benzoyl chloride (0.58 ml, 5 mmol, 1.0 eq.) and NEt₃ (1.4 ml, 10 mmol, 2 eq.) were dissolved in dry Et₂O (40 ml). The reaction mixture was stirred at room temperature for 1 h. The mixture was extracted with Et₂O and purified by flash column chromatography (petroleum ether/EtOAc – 5/1 → 2/1).

**Yield:** 0.764 g (4.68 mmol, 94%).

**Physical State:** colourless solid.

**Rₚ Value:** 0.20 (petroleum ether/EtOAc – 5/1).

**¹H NMR** (Avance 400 MHz, CDCl₃) δ 7.76 (d, J = 7.96 Hz, 2H), 7.55 – 7.31 (m, 3H), 6.45 - 6.04 (m, 1H), 3.52 – 3.27 (m, 2H), 1.73 – 1.54 (m, 2H), 1.04 – 0.90 (m, 3H) ppm.

**¹³C NMR** (Avance 101 MHz, CDCl₃) δ 167.6, 134.9, 131.3, 128.5, 126.8, 41.8, 22.9, 11.4 ppm.

**IR** (ATR, in CDCl₃) ν 3302 (m), 3084 (w), 2965 (w), 2933 (w), 2872 (w), 1632 (s), 1603 (w), 1577 (m), 1547 (s), 1493 (m), 1465 (w), 1449 (w), 1433 (w), 1374 (w), 1327 (m), 1315 (m), 1291 (m), 1246 (w), 1151 (w) cm⁻¹.

**MS** (ESI): m/z (%): for C₁₀H₁₃NO+Na⁺ 186.1 (87), 164.1 (100), 122.1 (9), 105.0 (14).

**¹H- and ¹³C-NMR spectra of R5**
3. Ru-catalyzed C-H-deuteration

3.1 General procedure for the deuteration following the CuI procedure (condition A) (GP-I)

To a flame-dried schlenk tube was added RuCl₂(PPh₃)₃ (2.5 mol%), CuI (10 mol%) and Zinc (2 eq.) under nitrogen stream. After the addition of 1,4-dioxane (1 ml) the substrate (0.5 mmol) was added. D₂O (8 eq.) was added and the reaction mixture was stirred for the time given at 80 °C. For work-up the mixture was filtered over silica and ethyl acetate was used as eluant. The solvent was evaporated under reduced pressure and crude NMRs were measured with mesitylene (0.5 mmol) as internal standard.

3.2 General procedure for the deuteration following the KOD/Zn procedure (condition B) (GP-II)

To a flame-dried schlenk tube was added RuCl₂(PPh₃)₃ (2.5 mol%) and Zinc (2 eq.) under nitrogen stream. After the addition of 1,4-dioxane (1 ml) the substrate (0.5 mmol) was added. KOD in D₂O (25 mol%, 40 wt% in D₂O, 98 atom % D) and D₂O (8 eq.) were added. The reaction mixture was stirred for the time given at 80 °C. For work-up the mixture was filtered over silica and ethyl acetate was used as eluant. The solvent was evaporated under reduced pressure and crude NMRs were measured with mesitylene (0.5 mmol) as internal standard.

3.3 General procedure for the deuteration following the KOD procedure (condition C) (GP-III)

To a flame-dried schlenk tube was added RuCl₂(PPh₃)₃ (2.5 mol%) under nitrogen stream. After the addition of 1,4-dioxane (1 ml) the substrate (0.5 mmol) was added. KOD in D₂O (25 mol%, 40 wt% in D₂O, 98 atom % D) and D₂O (8 eq.) were added and the reaction mixture was stirred for the time given at 80 °C. For work-up the mixture was filtered over silica and ethyl acetate was used as eluant. The solvent was evaporated under reduced pressure and crude NMRs were measured with mesitylene (0.5 mmol) as internal standard.

3.4 General remarks on overview tables

All experiments performed on each substrate are condensed into a table displayed above the spectra. The following abbreviations were used:
- for no experimental data
n.o. for not observed.
n.d. for not determinable

3.5. Spectral data and overviews

3.5.1 Tolan 5

\[
\begin{array}{c|c|c|c|c|c|c}
& & I (Z) & & II (E) & \\
\hline
& t & D_A & Yield & D_A & Yield & \\
cond. (A) & 16 h & 80\% & 80\% & 70\% & 13\% & \\
& 62 h & n.o. & n.o. & 80\% & 98\% & \\
cond. (B) & 16 h & - & - & - & - & \\
& 62 h & - & - & - & - & \\
\end{array}
\]

(Z/E)-Stilben 8 (I and II)

\(^1\)H-NMR (400 MHz, CD\(_2\)Cl\(_2\)) Spectra of pure compound:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 8 following the CuI procedure for 16 h: (Z/E: 6:1)

Enlargement of relevant area:
Yield of Z-Isomer$^8$: 80%
Yield of E-Isomer: 13%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 8 following the CuI procedure for 62 h: Yield: 98%

Enlargement of relevant area:
3.5.2 4-(phenylethynyl)toluene 6

| Condition | Time (h) | I (Z) t | D<sub>A</sub> | Yield | D<sub>A</sub> | Yield |
|-----------|---------|---------|-------------|-------|-------------|-------|
| (A)       | 16      | 85%     | 86%         | 79%   | 7%          |       |
|           | 62      | n.o.    | n.o.        | 77%   | 99%         |       |
| (B)       | 16      | -       | -           | -     | -           | -     |
|           | 62      | -       | -           | -     | -           | -     |

(Z/E)-4-Methylstilbene 8 (I and II)

<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) Spectra of pure compound 8:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of crude deuterated mixture following the CuI procedure for 16 h: (Z/E: 12:1)

Enlargement of relevant area:
Yield of Z-Isomer$^{[9]}$: 86%
Yield of E-isomer before column chromatography: 7%

H-NMR (400 MHz, CDCl₃, mesitylene) after column chromatography:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound following the CuI procedure for 62 h: Yield: 99%

Enlargement of relevant area:
3.5.3 4-(phenylethynyl)anisole 7

|       | I (Z) | II (E) |
|-------|-------|--------|
|       | $t$   | $D_A$  | Yield | $D_A$  | Yield |
| cond. (A) | 16 h | 86% | 37% | 75% | 57% |
|         | 62 h | n.o. | n.o. | 77% | >99% |
| cond. (B) | 16 h | - | - | - | - |
|         | 62 h | - | - | - | - |

4-(phenylethynyl)anisole 10 (I and II)
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 10:

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 10 following the CuI procedure for 16 h: (Z/E: 1:1.5)
Enlargement of relevant area:
Yield of Z-Isomer$^{[9]}$: 37%
Yield of $E$-Isomer: 57%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 10 following the CuI procedure for 62 h: Yield: >99%

Enlargement of relevant area:
3.5.4 Acetophenone 11

\[
\text{O} \quad \begin{array}{cccccc}
\text{(A) or (B)} & & & & & \\
\text{cond. (A)} & 16 \text{ h} & 89\% & \text{n.o.} & \text{n.o.} & 98\% \\
\text{cond. (B)} & 16 \text{ h} & 50\% & 79\% & \text{n.o.} & 25\% \\
& 62 \text{ h} & \text{n.o.} & \text{n.o.} & \text{n.o.} & 65\% \\
\end{array}
\]

|        | I |        |        |        |        |        |
|--------|---|--------|--------|--------|--------|--------|
| t      | 16 h | 89% | n.o. | n.o. | 98% |        |
| cond. (A) | 16 h | 50% | 79% | n.o. | 25% |        |
| cond. (B) | 62 h | n.o. | n.o. | n.o. | 65% | 74% |

Acetophenone 11 (I)

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) Spectra of pure compound 11:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 11:

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 11 following the KOD/Zn procedure for 16 h: Yield: 25%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 11 following the CuI procedure for 16 h: Yield: 98%
Enlargement of relevant area:
1-Phenylethanol 14

$^1$H-NMR (400 MHz, THF-$d_8$) Spectra of reduced substrate 14:

$^1$H-NMR (400 MHz, THF-$d_8$) Spectra of deuterated compound 14 following the KOD/Zn procedure for 16 h: Yield: 45%
Enlargement of relevant area:
$^1$H-NMR (400 MHz, THF-d$_8$) Spectra of deuterated compound 14 following the KOD/Zn procedure for 62 h: Yield: 78%.

Enlargement of relevant area:
3.5.5 4-Methylacetophenone 12

$\text{Me} \quad \xrightarrow{\text{(A) or (B)}} \quad \text{I} \quad \text{II}$

|       | $t$ | $D_A$ | $D_B$ | $D_C$ | Yield | $D_A$ | $D_B$ | $D_C$ | Yield |
|-------|-----|-------|-------|-------|-------|-------|-------|-------|-------|
| cond. (A) | 16 h | 63%   | n.o.  | n.o.  | 93%   | n.o.  | n.o.  | n.o.  | n.o.  |
|       | 62 h | -     | -     | -     | -     | -     | -     | -     | -     |
| cond. (B) | 16 h | 69%   | 81%   | n.o.  | 49%   | 66%   | 80%   | 71%   | 47%   |
|       | 62 h | n.o.  | n.o.  | n.o.  | n.o.  | 74%   | 78%   | 81%   | 86%   |

4-Methylacetophenone 12 (I)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 12:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 12 following the CuI procedure for 16 h: Yield: 93%
1-(4-Methylphenyl)ethanol 15 (II)

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 15:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 15 following the KOD/Zn procedure for 16 h: Yield: 47%
\(^1\)H-NMR (400 MHz, CD\(_2\)Cl\(_2\), mesitylene) Spectra of deuterated compound 15 following the KOD/Zn procedure for 62 h: Yield: 86%
3.5.6 4-Methoxyacetophenone 13

4-Methoxyacetophenone 13 (I)

\(^1\)H-NMR (400 MHz, CD\(_2\)Cl\(_2\)) Spectra of pure compound 13:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 13 following the CuI procedure for 16 h: Yield: >99%
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 13 in CD$_2$Cl$_2$ following the KOD/Zn procedure for 16 h: Yield: 49%
1-(4′-methoxyphenyl)ethanol 16 (II)

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 16:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 16 following the KOD/Zn procedure for 16 h: Yield: 41%
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 16 following the KOD/Zn procedure for 62 h: Yield: >99%
3.5.7 2-Phenylpyridine 20

![Chemical structures and NMR spectrum]

| Condition | Time (h) | Yield | DA (%) | DB (%) |
|-----------|----------|-------|--------|--------|
| (A)       | 16       | 84%   | n.o.   | >99%   |
| (A)       | 62       | -     | -      | -      |
| (C)       | 16       | 71%   | n.o.   | >99%   |
| (B)       | 16       | 67%   | 20%    | >99%   |

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 20:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 20:

Enlargement of relevant area:
\[ ^1H\text{-NMR (400 MHz, CDCl}_3, \text{ mesitylene) Spectra of deuterated compound 20 following the KOD procedure for 16 h: Yield: >99\%} \]
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, nitromethane) Spectra of deuterated compound 20 following the KOD/Zn procedure for 16 h: Yield: >99%

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, nitromethane) Spectra of deuterated compound 20 following the CuI procedure for 16 h: Yield: >99%
3.5.8 2-Phenylimidazole 21

| Condition | Time (h) | D_A (%) | D_B (%) | Yield |
|-----------|----------|---------|---------|-------|
| cond. (A) | 16       | 71      | n.o.    | 41%   |
|           | 62       | -       | -       | -     |
| cond. (C) | 16       | 76      | 64      | >99%  |
| cond. (B) | 16       | -       | -       | -     |

2-Phenylimidazole 21 (I and II)

$^1$H-NMR (300 MHz, CDCl$_3$) Spectra of pure compound 21:
$^1$H-NMR (400 Hz, CDCl$_3$, nitromethane) Spectra of deuterated compound 21 following the KOD procedure for 16 h: Yield: >99%
$^1$H-NMR (400 Hz, CDCl$_3$, nitromethane) Spectra of deuterated compound 21 following the CuI procedure for 16 h: Yield: 41%
3.5.9  \( N \)-methyl-2-phenyl-1H-imidazole 22

\[
\begin{array}{c}
\text{cond. (A)} \\
16 \text{ h} & 83\% & 50\%
\end{array}
\]

\[
\begin{array}{c}
\text{cond. (C)} \\
16 \text{ h} & 36\% & 84\%
\end{array}
\]

\[
\begin{array}{c}
\text{cond. (B)} \\
16 \text{ h} & - & -
\end{array}
\]

\(^1\text{H-NMR (300 MHz, CDCl}_3\text{) Spectra of pure compound 22:}\)

\[^1\text{H-NMR (400 MHz, CDCl}_3\text{, mesitylene) Spectra of deuterated compound 22 following the KOD procedure for 16 h: Yield: 84%}\]
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 22 following the CuI procedure for 16 h: Yield: 50%
Enlargement of relevant area:
3.5.10 2-phenyl-2-imidazoline 23

| Condition (A) | t   | \(D_A\) | \(D_B\) | Yield   |
|---------------|-----|---------|---------|---------|
| 16 h          | 57% | 25%     | >99%    |         |
| 62 h          | -   | -       | -       | -       |
| Condition (C) | 16 h| 72%     | n.o.    | 97%     |
| Condition (B) | 16 h| -       | -       | -       |

2-phenyl-2-imidazoline 23 (I and II)

\(^1\)H-NMR (400 MHz, THF-\(d_8\)) Spectra of pure compound 23:

\(^1\)H-NMR (400 Hz, CD₂Cl₂, mesitylene) Spectra of deuterated compound 23 following the KOD procedure for 16 h: Yield: 97%
\(^1\)H-NMR (400 Hz, CD₂Cl₂, mesitylene) Spectra of deuterated compound 23 following the CuI procedure for 16 h: Yield: >99%
3.5.11 4,5-dihydro-1-methyl-2-phenyl-1H-imidazole 24

\[
\text{cond. (A)} \quad 16 \text{ h} \quad 46\% \quad 79\% \quad 43\% \quad 83\%
\]
\[
\text{62 h} \quad - \quad - \quad - \quad -
\]
\[
\text{cond. (C)} \quad 16 \text{ h} \quad 31\% \quad \text{n.o.} \quad \text{n.o.} \quad 74\%
\]
\[
\text{cond. (B)} \quad 16 \text{ h} \quad - \quad - \quad - \quad -
\]

4,5-dihydro-1-methyl-2-phenyl-1H-imidazole 24 (I and II)

\(^1\text{H-NMR (300 MHz, CDCl}_3\text{)}\) Spectra of pure compound 24:
$^1$H-NMR (400 Hz, THF-$d_8$, nitromethane) Spectra of deuterated compound 24 following the KOD procedure for 16 h: Yield: 74\%
$^{1}$H-NMR (400 MHz, THF-d$_8$, mesitylene) Spectra of deuterated compound 24 following the CuI procedure for 16 h: Yield: 83%
3.5.12 2-phenyl-2-oxazoline 25

![Chemical structures and reactions](attachment:image)

| cond. | $t$ | $D_A$ | $D_B$ | Yield | $D_A$ | $D_B$ | Yield |
|-------|-----|-------|-------|-------|-------|-------|-------|
| (A)   | 16 h| -     | -     | -     | -     | -     | -     |
| (C)   | 16 h| 85%   | n.o.  | >99%  | n.o.  | n.o.  | n.o.  |
| (B)   | 62 h| -     | -     | -     | -     | -     | -     |

2-phenyl-2-oxazoline 25 (I)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 25:

![NMR spectrum](attachment:image)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, nitromethane) Spectra of deuterated compound 25 following the KOD procedure for 16 h: Yield: >99%
N-(2-hydroxyethyl)benzamide 26 (II)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of pure compound 26:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 26 following the CuI procedure for 62 h: Yield: 69%
3.5.13 2-(4-methylphenyl)-4,5-dihydro-1.3-oxazole 27

![Chemical structure](image)

|          | I          | II         |
|----------|------------|------------|
|          | $t$        | $D_A$ | $D_B$ | $D_C$ | Yield | $D_A$ | $D_B$ | $D_C$ | Yield |
| cond. (A) | 16 h       | n.o.  | n.o.  | n.o.  | 81%   | 74%   | 26%   | 98%   |
|          | 62 h       | -     | -     | -     | -     | -     | -     | -     |
| cond. (C) | 16 h       | 22%   | n.o.  | 90%   | n.o.  | n.o.  | n.o.  | n.o.  |
|          | 62 h       | 85%   | n.o.  | 83%   | n.o.  | n.o.  | n.o.  | n.o.  |

2-(4-methylphenyl)-4,5-dihydro-1.3-oxazole 27 (I)

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 27:
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 27 following the KOD procedure for 16 h: Yield: 90%
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 27 following the KOD procedure for 62 h: Yield: 83%
N-(2-Hydroxyethyl)-4-methylbenzamide 28\textsuperscript{[10]} (II)

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}, mesitylene) Spectra of deuterated compound 28 following the CuI procedure for 16 h: Yield: 98%
3.5.14 2-(4-chlorophenyl)-4,5-dihydro-1.3-oxazole 29

![Chemical structure]

|       | I                      | II                     |
|-------|------------------------|------------------------|
|       | \( t \) | \( D_A \) | \( D_B \) | \( D_C \) | Yield | \( D_A \) | \( D_B \) | \( D_C \) | Yield |
| cond. (A) | 16 h | n.o. | n.o. | n.o. | 80% | 69% | <10% | 68% |
|         | 62 h | -    | -    | -    | -   | -   | -   | -   |
| cond. (C) | 16 h | <10% | n.o. | n.o. | 95% | n.o. | n.o. | n.o. |
|         | 62 h | 84%  | n.o. | n.o. | 91% | n.o. | n.o. | n.o. |

2-(4-chlorophenyl)-4,5-dihydro-1.3-oxazole 29 (I)

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) Spectra of pure compound 29:
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 29 following the KOD procedure for 16 h: Yield: 95%
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 29 following the KOD procedure for 62 h: Yield: 91%
4-Chloro-N-(2-Hydroxyethyl)benzamide 30\textsuperscript{10} (II)

$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 30 following the CuI procedure for 16 h: Yield: 68%
3.5.15 2-(3-chlorophenyl)-4,5-dihydro-1.3-oxazole 31

\[
\begin{array}{ccc}
\text{Cond. (A)} & 16 \text{ h} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{Cond. (C)} & 62 \text{ h} & - & - & - & - & - \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{Cond. (A)} & 16 \text{ h} & 24\% & 25\% & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{Cond. (C)} & 62 \text{ h} & 82\% & 83\% & 30\% & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{Yield} & \text{D}_A & \text{D}_B & \text{D}_C & \text{D}_D & \text{D}_E \\
\text{74\%} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{80\%} & \text{95\%} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{66\%} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{16\%} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\text{93\%} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} & \text{n.o.} \\
\end{array}
\]

2-(3-chlorophenyl)-4,5-dihydro-1.3-oxazole 31 (I)

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 31:
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 31 following the KOD procedure for 16 h: Yield: 95%
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 31 following the KOD procedure for 62 h: Yield: 96%

Enlargement of relevant area:
3-chloro-N-(2-hydroxyethyl)benzamide 32 (II)

$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of pure compound 32:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 32 following the CuI procedure for 16 h: Yield: 93%
Enlargement of relevant area:
3.5.16  N-\(n\text{-propyl}\)benzamide 33

\[
\text{cond. (A)} \quad 16 \text{ h} \quad 65\% \quad \text{>99}\% \\
62 \text{ h} \quad 80\% \quad \text{>99}\% \\
\text{cond. (B)} \quad 16 \text{ h} \quad 36\% \quad \text{>99}\% \\
62 \text{ h} \quad 85\% \quad \text{>99}\% \\
\text{cond. (C)} \quad 62 \text{ h} \quad 10\% \quad \text{>99}\% \\
\]

N-\(n\text{-propyl}\)benzamide 33

\(^1\text{H-NMR (400 MHz, CDCl}_3\text{)}\) Spectra of pure compound 33:

\[
\begin{align*}
&7.65, 7.62, 7.35, 6.47, 5.35, 5.55, 5.24, 4.51, 4.17, 3.57, 3.17, 2.24, 1.97, 1.89, 1.77, 1.74, 1.47, 1.44, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.81, 0.80, 0.79, 0.78, 0.77, 0.76, 0.75, 0.74, 0.73, 0.72, 0.71, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.64, 0.63, 0.62, 0.61, 0.60, 0.59, 0.58, 0.57, 0.56, 0.55, 0.54, 0.53, 0.52, 0.51, 0.50, 0.49, 0.48, 0.47, 0.46, 0.45, 0.44, 0.43, 0.42, 0.41, 0.40, 0.39, 0.38, 0.37, 0.36, 0.35, 0.34, 0.33, 0.32, 0.31, 0.30, 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23, 0.22, 0.21, 0.20, 0.19, 0.18, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.10, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00, 0.00 \text{ ppm}
\end{align*}
\]
$^{1}$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 33 following the KOD procedure for 62 h: Yield: >99%

$^{1}$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 33 following the KOD/Zn procedure for 16 h: Yield: >99%
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 33 following the KOD/Zn procedure for 62 h: Yield: >99%
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 33 following the CuI procedure for 16 h: Yield: >99%
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 33 following the CuI procedure for 62 h: Yield: >99%
3.5.17 2-(4-Morpholinyl)pyridine 34

\[
\begin{align*}
\text{Yield} & \quad \text{cond. (A)} \quad \text{cond. (C)} \\
16 \text{ h} & \quad 21\% & \quad n.o. \\
62 \text{ h} & \quad - & \quad n.o.
\end{align*}
\]

2-(4-Morpholinyl)pyridine 34

\( ^1 \text{H-NMR (300 MHz, CDCl}_3 \text{)} \) Spectra of pure compound 34:
$^1$H-NMR (400 MHz, CDCl$_3$, mesitylene) Spectra of deuterated compound 34 following the CuI procedure for 16 h: Yield: 93%
3.5.18 2-Ethylpyridin 35

![Diagram showing the structure and spectral data of 2-Ethylpyridin 35](image)

| Cond. (A) | $t$  | $D_A$ | $D_B$ | Yield |
|-----------|------|-------|-------|-------|
| 16 h      | n.o. | n.o.  | n.o.  | n.o.  |
| 62 h      | -    | -     | -     | -     |
| Cond. (B) | 16 h | 37%   | 72%   | <99%  |
| 62 h      | 59%  | 84%   | 96%   |

2-Ethylpyridin 35

$^1$H-NMR (400 MHz, THF-d$_8$) Spectra of pure compound 35:
$^1$H-NMR (400 MHz, THF-d$_8$, mesitylene) Spectra of deuterated compound 35 following the KOD/Zn procedure for 16 h: Yield: >99%
Enlargement of relevant area:

\[
\begin{align*}
&\text{H} \\
&D \quad \text{CD}_3 [37\%] \\
&[72\%]
\end{align*}
\]
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 35 following the KOD/Zn procedure for 62 h: Yield: 96%

Enlargement of relevant area:
3.5.19 2-(4-(2-phenylethynyl)phenyl)pyridine 36

|     | I   | II (Z) | III (E) |
|-----|-----|--------|---------|
|     | t   | D_A   | Yield  | D_A | D_B | Yield | D_A | D_B | Yield |
| cond. (A) | 16 h | n.o. | n.o. | 67% | 73% | 32% | 66% | n.d. | 47% |
|       | 62 h | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |
| cond. (C) | 16 h | n.o. | 81% | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |
2-(4-(2-phenylethynyl)phenyl)pyridine 36 (I)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 36:
$^{1}$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 36 following the KOD procedure for 16 h: Yield: 81%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 36 following the KOD procedure for 62 h: 93%
Enlargement of relevant area:
(Z)-2-(4-styrylphenyl)pyridine (II)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound:

Enlargement of relevant area:
S136

$^{1}$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound following the CuI procedure for 16 h: Yield: 32% (Z/E: 1:1.5)
Enlargement of relevant area:
(E)-2-(4-styrylphenyl)pyridine 41 (III)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 41:

Enlargement of relevant area:
$^{1}$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 41 following the CuI procedure for 16 h: Yield: 47%
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 41 following the CuI procedure for 62 h: Yield: 67%

Enlargement of relevant area:
3.5.20 2-(3-(phenylethynyl)phenyl)pyridine 37

| cond. (A) | 16 h | n.o. | n.o. | 34% | 60% | 66% | 51% | 39% | 59% | 24% | 20% |
|-----------|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|
|           | 62 h | n.o. | n.o. | n.d. | n.d. | 71% | 20% | 61% | 89% | 25% | 50% |

| cond. (C) | 16 h | n.o. | 94% | n.o. | n.o. | n.o. | 91% | 39% | n.o. | n.o. | n.o. |
|-----------|------|------|-----|------|------|------|-----|-----|-----|-----|-----|
|           | 62 h | 44%  | 92% | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |

| I          | II (Z) | III (E) |
|------------|--------|---------|
| t          | D_B    | Yield   | D_A   | D_B   | D_C   | Yield   | D_A   | D_B   | D_C   | Yield   |
| 16 h       | n.o.   | n.o.    | 34%   | 60%   | 66%   | 51%     | 39%   | 59%   | 24%   | 20%     |
| 62 h       | n.o.   | n.o.    | n.d.  | n.d.  | 71%   | 20%     | 61%   | 89%   | 25%   | 50%     |
| 16 h       | n.o.   | n.o.    | n.o.  | n.o.  | n.o.  | n.o.    | n.o.  | n.o.  | n.o.  | n.o.    |
| 62 h       | 44%    | 92%     | n.o.  | n.o.  | n.o.  | n.o.    | n.o.  | n.o.  | n.o.  | n.o.    |

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S142
2-(3-(phenylethynyl)phenyl)pyridine 37 (I)

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) Spectra of pure compound 37:

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated 37 compound following the KOD procedure for 16 h: Yield: 94%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated 37 compound following the KOD procedure for 62 h: Yield: 92%
Enlargement of relevant area:
(Z)-2-(3-styrylphenyl)pyridine (II)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound:

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound following the CuI procedure for 16 h: Yield: 51% (Z/E: 2.5:1)
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound following the CuI procedure for 62 h: Yield: 20%

Enlargement of relevant area:
(E)-2-(3-styrylphenyl)pyridine 42 (III)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 42:

Signal too broad to differentiate between the 2 protons
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 42 following the CuI procedure for 16 h: Yield: 20% (Z/E: 2.5:1)

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 42 following the CuI procedure for 62 h: Yield: 50%
3.5.21 4-(phenylethynyl)acetophenone 38

\[
\begin{align*}
\text{(A) or (B)} & \\
\text{I} & \\
\text{II (Z)} & \\
\text{III (E)} & 
\end{align*}
\]

|       | I       | II (Z) | III (E) |
|-------|---------|--------|---------|
|       | \(t\)   | \(D_A\) | \(D_C\) | Yield  | \(D_A\) | \(D_B\) | \(D_C\) | Yield  |
| cond. (A) | 16 h | n.o.  | n.o.  | n.o.  | 82%   | n.o.  | 42%   | n.o.  | 63%   | n.o.  | 13%   |
|         | 62 h | n.o.  | n.o.  | n.o.  | n.d.  | n.o.  | n.o.  | 88%   | 84%   | <10%  | n.o.  | 52%   |
| cond. (C) | 16 h | n.o.  | 87%   | >99%  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  |
|         | 62 h | n.o.  | 87%   | >99%  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  | n.o.  |

4-(phenylethynyl)acetophenone 38 (I)

\(^1H\)-NMR (300 MHz, CDCl\(_3\)) Spectra of pure compound 38:
\[^1\text{H}-\text{NMR (400 MHz, CDCl}_3, \text{ nitromethan) Spectra of deuterated compound 38 following the KOD procedure for 16 h: Yield: >99\%}

\[^1\text{H}-\text{NMR (400 MHz, CDCl}_3, \text{ mesitylene) Spectra of deuterated compound 38 following the KOD procedure for 62 h: Yield: >99\%}

S158
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound following the CuI procedure for 16 h: (Z/E: 3:1)
Enlargement of relevant area:

Yield of Z-Isomer (II): 42%
Yield of E-isomer 43 (III): 13%
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 43 following the CuI procedure for 62 h: Yield: 52%

Enlargement of relevant area:
3.5.22 1-(3-(2-phenylethynyl)phenyl)ethanone 39

![Chemical structures and reaction schemes](image)

|       | I       | II (Z)   | III (E)   |
|-------|---------|----------|-----------|
| t     | $\text{DA}$ | $\text{DB}$ | $\text{DD}$ | Yield | $\text{DA}$ | $\text{DB}$ | $\text{DC}$ | $\text{DD}$ | Yield | $\text{DA}$ | $\text{DB}$ | $\text{DC}$ | $\text{DD}$ | Yield |
| cond. (A) | 16 h | n.o. | n.o. | n.o. | n.o. | n.o. | 88% | <10% | 68% | n.o. | n.o. | n.o. | n.o. | n.o. |
|        | 62 h | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |
| cond. (C) | 16 h | n.o. | n.o. | 84% | >99% | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |
|        | 62 h | n.o. | n.o. | 87% | >99% | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. | n.o. |

1-1(3-(2-phenylethynyl)phenyl)ethanone 39 (I)

$^1$H-NMR (300 MHz, CDCl$_3$) Spectra of pure compound 39:

![NMR spectra](image)

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound 39 following the KOD procedure for 16 h: Yield: >99%
$^1\text{H}-\text{NMR}$ (400 MHz, CDCl$_3$) Spectra of deuterated compound 39 following the KOD procedure for 62 h: Yield: >99%
(Z)-1-(3-styrylphenyl)ethan-1-one (I)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CDCl$_3$) Spectra of deuterated compound following the CuI procedure for 16 h: Yield: 63% (Z/E: 9:1)

Enlargement of relevant area:
(E)-1-(3-styrylphenyl)ethan-1-one 44 (III)

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 44:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 44 following the CuI procedure for 62 h: Yield: 91%

Enlargement of relevant area:
3.5.23 1-(3-(pyridin-2-yl)phenyl)ethan-1-one 40

\[
\begin{array}{c}
\text{[86%]} \\
\text{[79%]} \\
\text{[79%]}
\end{array}
\]

| $t$   | $D_A$ | $D_B$ | $D_D$ | Yield |
|-------|-------|-------|-------|-------|
| 16 h  | n.o.  | 80%   | <10%  | 82%   |
| 62 h  | -     | -     | -     | -     |
| 16 h  | 76%   | 74%   | 80%   | >99%  |
| 62 h  | -     | -     | -     | -     |

1-(3-(pyridin-2-yl)phenyl)ethan-1-one 40

$^1$H-NMR (500 MHz, CD$_2$Cl$_2$) Spectra of pure compound 40:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 40 following the KOD procedure for 16 h: Yield: $>$99%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$, mesitylene) Spectra of deuterated compound 40 following the CuI procedure for 16 h: Yield: 82%
3.5.24 Piribedil 45

2-(4-(benzo[d][1,3]dioxol-5-ylmethyl)piperazin-1-yl)pyrimidine, Piribedil 45 (I)

\(^1\)H-NMR (400 MHz, CD₂Cl₂) Spectra of pure compound 45:

| Condition | Time  | DA | DB | Yield  |
|-----------|-------|----|----|--------|
| A         |       |    |    |        |
| 16 h      | 49%   | 83%|
| 62 h      | 67%   | 87%|
| 62 + 16 h | <10%  | 83%| 49%   |
| B         |       |    |    |        |
| 16 h      | 21%   | 48%| >99% |
| 62 h      | 40%   | 73%| 90%  |
| 62 + 16 h | 52%   | 80%| 58%  |
$^1\text{H-NMR}$ (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the CuI procedure for 16 h: Yield: 83%.

$^1\text{H-NMR}$ (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the CuI procedure for 62 h: Yield: 87%. 
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the CuI procedure for 62 h and another subsequent run for 16 h: Yield: 49%.
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the KOD/Zn procedure for 16 h: Yield: >99%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the KOD/Zn procedure for 62 h: Yield: 90%
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 45 following the KOD/Zn procedure for 62 h and another subsequent run for 16 h: Yield: 58\%
3.5.25 Boscalid 46

\[ \text{cond. (B)} \quad 16 \text{ h} \quad 31\% \quad \text{n.o.} \quad 54\% \quad 55\% \quad \text{n.o.} \quad 35\% \]

1H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of pure compound 46:
Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 46 following the KOD/Zn procedure for 16 h: Yield: 54%

Enlargement of relevant area:
$^{1}$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 47 following the KOD/Zn procedure for 16 h: Yield: 35%
\[ \begin{array}{|c|c|c|c|c|c|c|c|c|} \hline \text{cond. (A)} & t & \text{DA} & \text{DB} & \text{DC} & \text{Yield} & \text{DA} & \text{DB} & \text{DC} & \text{Yield} \\ \hline 16 \text{ h} & \text{n.o.} & \text{n.o.} & 32\% & 50\% & 24\% & 68\% & 62\% & 40\% \\ \hline \end{array} \]

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 46 following the CuI procedure for 16 h: Yield: 50%.

Enlargement of relevant area:
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) Spectra of deuterated compound 47 following the CuI procedure for 16 h: Yield: 40%.
Enlargement of relevant area:
4. Synthesis of literature-known Ru-complexes

$^1$H and $^{31}$P NMR-data for known Ru-H-complexes RuH(OH)(solvent)(PPh$_3$)$_3$ 4, Ru$_2$(H)$_2$($\mu$-OH)$_2$(solvent)$_2$(PPh$_3$)$_4$ 48, RuH$_2$(H$_2$)(PPh$_3$)$_3$ 3 and RuHI(PPh$_3$)$_3$ 2 were in accordance with those given in the literature.$^{[11-14]}$ Characteristic hydride-signals, as well as $^{31}$P-signals for the given complexes in THF-$d_8$ or CD$_2$Cl$_2$ were recorded as reference and are listed in table 1.

Table 1: Hydride- and $^{31}$P-signals of ruthenium hydride-complexes in THF-$d_8$.

| Complex | Hydride (ppm) | $^{31}$P (ppm) |
|---------|---------------|----------------|
| RuH(OH)(solvent)(PPh$_3$)$_3$ 4$^{[11]}$ | -23.8 (t, $J = 33.8$ Hz) | 73.8 (s) |
| | 0.91 (s, 1H, Ru-OH) | |
| Ru$_2$(H)$_2$($\mu$-OH)$_2$(solvent)$_2$(PPh$_3$)$_4$ 48$^{[11]}$ | -18.4 (t, $J = 33.0$ Hz) | 43.5 (s) |
| RuH$_2$(H$_2$)(PPh$_3$)$_3$ 3$^{[12]}$ | -7.5 (br) | 57.4 (s) |
| RuHI(PPh$_3$)$_3$ 2 (CD$_2$Cl$_2$)$^{[13]}$ | -15.3 (q, $J = 25.1$ Hz) | 56.7 (br) |
| (PPh$_3$)$_3$Ru($\mu$-H)$_3$RuH(PPh$_3$)$_2$ 49$^{[14]}$ | -10.9 (br) | 75.0 (br) |
| | -20.7 (t, $J = 34.1$ Hz) | 55.8 (br) |
| (PPh$_3$)$_3$Ru($\mu$-H)$_3$RuH(PPh$_3$)$_2$ 49$^{[14]}$ | -9.0 (d, $J = 67.7$ Hz) | 83.7 – 82.1 (m) |
| | -10.8 (t, $J = 44.3$ Hz) | 73.3 – 71.7 (m) |
| | -11.8 (t, $J = 46.8$ Hz) | 63.3 – 60.1 (m) |
| | -19.8 (t, $J = 37.4$ Hz) | 59.0 (s) |
4.1 Ru$_2$(H)$_2$(μ-OH)$_2$(solvent)$_2$(PPh$_3$)$_4$ 48 and RuH(OH)(solvent)(PPh$_3$)$_3$ 4$_{11}$

$^1$H-NMR (300 MHz, THF-d$_8$)

$^{31}$P-NMR (121 MHz, THF-d$_8$)
4.2 RuH\(_2\)(H\(_2\))(PPh\(_3\))\(_3\) \(^{[12]}\)

\(^1\)H-NMR (300 MHz, THF-d\(_8\))

\[^{31}\)P-NMR (121 MHz, THF-d\(_8\))
4.3 RuHI(PPh₃)₃ 2

All solvents were degased with argon and the whole reaction was carried out under argon atmosphere. RuCl₂(PPh₃)₃ (1.92 g, 2 mmol, 1 eq.), Zn (10.47 g, 160 mmol, 320 eq.) and CuI (1.52 g, 8 mmol, 4 eq.) were dissolved in 1,4-dioxane (160 ml). Deionized H₂O (12.8 ml, 640 mmol, 320 eq.) was added and the crude mixture was stirred for 2 h at 80 °C. The solid was isolated using a filter frit and washed with 1,4-dioxane (50 ml) and deionized H₂O (30 ml). The residue was dried in high vacuum for 2 h, washed with n-pentane (35 ml) and dissolved with DCM (110 ml). The solvent was evaporated using an ether bridge and the resulting purple solid dried in high vacuum for 1 h.

**Yield:** 1.77 g (1.7 mmol, 87%).

**Physical State:** purple solid.

**¹H NMR** (Avance 400 MHz, CD₂Cl₂) δ 7.16 – 7.08 (m, 27H), 6.90 (t, J = 7.6 Hz, 18H), -15.38 (q, J = 25.1 Hz, 1H) ppm.

**³¹P NMR** (Avance 162 MHz, CD₂Cl₂) δ 56.8 (broad) ppm.

The analytical data were in accordance with the literature.¹³
\textsuperscript{1}H-NMR (400 MHz, DCM-d\textsubscript{2})

\textsuperscript{31}P-NMR (162 MHz, DCM-d\textsubscript{2})
5. Mechanistic studies

In order to investigate the additive-dependent chemoselectivity we focused on isolating the hypothetically catalytic active species and subsequent evaluation of their activity in deuteration reactions.

The following scheme shows the additive-dependent pathways that lead to each species.

Scheme 1: Overview of hypothetical catalytic species.

5.1 KOH-protocol

We started our studies by subjecting complex 1 to exemplary basic conditions and observed the formation of the dimeric (µ-OH) complex 48 (Figure 1).
Figure 1: Formation of dimeric ruthenium hydrido-hydroxy complex 48.

$^{1}$H-NMR (400 MHz, THF-d$_8$)
When the equivalents of water were raised to a level similar to the reaction conditions (Figure 2) we observed an increase in the monomeric ruthenium hydroxy species 4. *Wilkinson* reported the formation of both complexes depending on reaction time and equivalents of water and base.\textsuperscript{[11]} In our case we observed that the ratio of monomeric to dimeric species is highly dependent on the amount of water used.

**Figure 2:** Formation of monomeric ruthenium hydrido-hydroxy species 4.
We were not able to test the pure complexes for their respective catalytic activity due to both complexes being instable upon isolation. The aforementioned experiments give us strong
indication that a mixture of both the monomeric complex 4 as well as the dimeric complex 4 are present in our catalysis. Ultimately we assume the monomeric species to be the major component and thus the catalytic active species.

5.2 KOH/Zn-protocol

Under reductive basic conditions the formation of the tetrahydrido ruthenium complex 3 and its closely related dimeric complex 49 is observed.

**Figure 3:** Formation of ruthenium hydride complexes under reductive conditions.
We assigned the signals of the hydride complexes by previously reported literature.\cite{12,14}

By recording the $^1$H NMR at low temperature (-50 °C) we obtained a better resolution for the ($\mu$-H$_3$) signals of the dimeric complex 49 (Figure 4).

**Figure 4:** Low-temperature $^1$H NMR of dimeric hydride complex 49.

We increased the equivalents of the reagents to match the conditions in our catalytic protocol (Figure 5) but saw no significant change in complex ratio.
Figure 5: Formation of ruthenium hydride complexes 3 and 49 under catalysis reaction conditions.

We assume that the tetrahydrido ruthenium complex 3 is the active species in our catalysis as there are many reported applications in which complex 3 acts as a powerful reduction catalyst.\textsuperscript{[15]}

5.2.1 Deuteration with RuH\textsubscript{2}(H\textsubscript{2})(PPh\textsubscript{3})\textsubscript{3}

Furthermore, we synthesized the complex 3 following a slightly modified procedure from Grushin\textsuperscript{[12]} and employed the complex in an exemplary catalysis (Figure 6).

Figure 6: Deuteration of 4-methylacetophenone with RuH\textsubscript{2}(H\textsubscript{2})(PPh\textsubscript{3})\textsubscript{3} as catalyst.

To our delight, we saw the same degree of deuteration compared to our result when using RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3} as precatalyst. This is a strong indication that under these conditions the reactive species of our deuteration is indeed the tetrahydrido species 3.

\textsuperscript{1}H-NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) spectra of deuterated compound 15 following the KOD/Zn procedure for 62 h with RuH\textsubscript{2}(H\textsubscript{2})(PPh\textsubscript{3})\textsubscript{3} 3 (2.5 mol%): Yield: 72%
5.3 CuI-protocol

For the CuI protocol, we were able to observe the iodide complex 2 that was smoothly formed under the reaction conditions (Figure 7).

**Figure 7:** Formation of the iodide complex 2 under conditions A.
5.3.1 Deuteration with RuHI(PPh₃)₃ 2

When the iodide catalyst 2 was used in an exemplary deuteration reaction, we were able to surpass the degree of deuteration that we observed when we used the precatalyst 1 (Figure 8). Additionally, we observed the same selectivity and thus conclude that the iodide ruthenium complex 2 is the catalytic active species under conditions A.

![Figure 8: Deuteration of 2-phenyl-2-imidazole 23 with RuHI(PPh₃)₃ 2 under conditions A.](image)

$^1$H-NMR (400 MHz, CD₂Cl₂) spectra of deuterated compound 23 following the CuI procedure for 16 h with RuHI(PPh₃)₃ 2 (2.5 mol%): Yield: >99%

5.3.2 Reduction with RuHI(PPh₃)₃ 2

Regarding the chemoselectivity we studied the behaviour of complex 2 in the reduction of 4-(phenylethynyl)acetophenone 38. To our delight we were able to demonstrate the high
selectivity of 2 towards the reduction of alkynes while no reduction of the carbonyl was observed. This further strengthens our hypothesis that 2 is the catalytic active species.

Figure 9: Reduction of 4-(phenylethinyl)acetophenone 38 with RuHI(PPh₃)₃ 2 under conditions A.

¹H-NMR (400 MHz, (CD)₂(Cl₂)₂) Spectra of deuterated compound 43-Z following the CuI procedure for 62 h with RuHI(PPh₃)₃ 2 (2.5 mol%): Yield: 20%

Enlargement of relevant area:
$\mathrm{H-NMR\ (400\ MHz,\ \text{CD}_2\text{Cl}_2)}$ Spectra of deuterated compound $43-\text{E}$: Yield: 23%
Enlargement of relevant area:
5.4 Verification of D₂ gas formation

To verify the formation of D₂ gas from the deuterium source D₂O when using zinc as additive, we designed a control experiment where the formation of D₂ can take place separated from the deuterium labeling while still sharing the same gas atmosphere. That way, we hope to prove the formation of D₂ gas.

The reactions took place in a two chambered Schlenktube with connected gas atmosphere (Figure 9).

![Figure 9: Two-chambered Schlenktube.](image)

For convenience we named one chamber “D₂ chamber” and the other one “deuteration chamber”. We performed the control experiments with the following chamber loadings:
The result of these experiments is summarized in the following scheme (scheme 2):

**Scheme 2:** Overview of deuteration with *in situ* generated D₂ gas.

For the CuI/Zn conditions (eq. (1), scheme 2) we observed approximately the same yield and deuteration degrees as when the one-pot procedure was used. For the KOD/Zn protocol (eq. (2), scheme 2) a slight adjustment had to be made. Since KOD is obtained as a solution in D₂O we used KOH for the “deuteration chamber”. Therefore we expected a lower degree of
deuteration since the KIE might lead to a preferential implementation of hydrogen instead of deuterium. Nevertheless we observed deuteration with the same chemoselectivity as when the one-pot procedure was applied. With regard to the experimental setup we interpreted these results as a proof for the formation of D₂ gas when the additive zinc was used.
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