Manganese(I)-Catalyzed β-Methylation of Alcohols using Methanol as C₁ Source
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1. General Experimental

All catalytic and stoichiometric reactions were performed under argon atmosphere using a combination of Schlenk and glove box techniques. Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, TCI chemicals and used without further purification. Dry solvents were prepared according to standard procedures. Glasswares were dried under vacuum at high temperatures, evacuated, and refilled with argon at least three times. \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR spectra were recorded with spectrometers Bruker AV300 or AV400 at room temperature. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\(_3\): \(\delta_H = 7.26\) ppm, \(\delta_C = 77.3\) ppm; C\(_6\)D\(_6\): \(\delta_H = 7.16\) ppm, \(\delta_C = 127.6\) ppm; THF-d\(_8\): \(\delta_H = 1.72\) ppm, \(\delta_C = 24.2\) ppm; Toluene-d\(_8\): \(\delta_H = 2.1\) ppm, \(\delta_C = 21.4\) ppm). Chemical shifts for \(^{31}\)P are reference against H\(_3\)PO\(_4\) as external standard. Multiplicity is abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; sext, sextet; m, multiplet; br, broad.

Catalytic reactions involving high pressure gases were carried out in home built stainless steel reactors equipped with pressure transducer and external electrical heating.

**Safety advice:** High-pressure experiments represent a significant risk and must be conducted with appropriate safety procedures and in conjunction with the use of suitable equipment.
2. Synthesis of Manganese pincer complexes

Manganese pincer complexes 1, 2, 3 and 4 were prepared according to the reported literature: A. Kaithal, M. Hölscher, W. Leitner. Catalytic Hydrogenation of Cyclic Carbonates using Manganese Complexes. *Angew. Chem. Int. Ed.* 2018, 57(41): 13449-13453.[1]

Manganese pincer complex 5 was prepared according to the reported literature: A. Kaithal, S. Sen, C. Erken, T. Weyhermüller, M. Hölscher, C. Werlé, W. Leitner. Manganese-catalyzed hydroboration of carbon dioxide and other challenging carbonyl groups. *Nat. Commun.*, DOI: 10.1038/s41467-018-06831-9.[2]
3. General procedure for screening of Mn-catalysts

Mn-precursor and NaOMe (108.04 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. 2-phenyl ethanol 6a (122.2 mg, 1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to a certain temperature. After 24 h, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy.

Table S1: Mn (I) catalyzed β-methylation of 6a with methanol: Influence of catalyst precursors and reaction conditions.[a, b]

| #   | Catalyst | Conv. (%) | Yield (%) |
|-----|----------|-----------|-----------|
| 1   | 1 (0.5 mol%) | 97        | 92        |
| 2   | 2 (0.5 mol%) | 42        | 21        |
| 3   | 3 (0.5 mol%) | 51        | 24        |
| 4   | 4 (0.5 mol%) | 23        | 6         |
| 5   | 5 (0.5 mol%) | 10        | 0         |
| 6   | 1 (0.2 mol%) | 66        | 52        |
| 7[c] | 1 (0.5 mol%) | 76        | 70        |
| 8[d] | 1 (0.5 mol%) | 77        | 70        |

[a] 6a (1 mmol), MeOH (1 mL as a reagent and solvent), Mn precatalyst (0.5 mol%), and NaOMe (2 mmol) at 150 °C for 24 h. [b] Conversion and yield were measured by 1H NMR and mesitylene was used as an internal standard. [c] Reaction was carried out at 125 °C. [d] 1 mmol of NaOMe was used.
4. General procedure for the catalytic selective $\beta$-methylation of 2-aryl ethanols

Mn-MACHO $1$ (2.48 mg, 0.5 mol%) and NaOMe (108.04 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. 2-aryl ethanol (1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature for 24 h. After completion of the reaction, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. The isolation of pure product was carried out using column chromatography over silica gel (100-200 mesh) using ethyl acetate/petroleum ether (12 : 88) mixture as eluent.

2-phenylpropan-1-ol (7a): Prepared by following the general experimental procedure with: $1$ (2.48 mg, 0.5 mol%), 2-phenylethan-1-ol $6a$ (122.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.72$ (s, 3H), $\delta_{\text{product}} = 3.63$ (d, 2H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta = 7.24$-$7.28$ (m, 2H, ArCH), $7.14$-$7.18$ (m, 3H, ArCH), 3.63 (d, 2H, $J = 6.78$ Hz, CH$_2$), 2.83-$2.90$ (sext, 1H, $J = 6.94$ Hz, CH), 1.40 (br. s, 1H, OH), 1.21 (d, 3H, $J = 6.97$ Hz, CH$_3$).

$^{13}$C($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta = 143.77$ (quat-C), 128.77 (ArCH), 127.61 (ArCH), 126.81 (ArCH), 68.85 (CH$_2$), 42.57 (CH), 17.71 (CH$_3$). Isolated yield: 85%. The obtained analytical data is consistent with those previously reported in the literature.$^3$

2-(p-tolyl)propan-1-ol (7b): Prepared by following the general experimental procedure with: $1$ (2.48 mg, 0.5 mol%), 2-(p-tolyl)ethan-1-ol $6b$ (136.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 3.69$ (d, 2H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 7.15$ (s, 4H, ArCH), 3.69 (d, 2H, $J = 9$ Hz, CH$_2$), 2.90-$2.97$ (m, 1H, CH), 2.35 (s, 3H, CH$_3$), 1.27 (d, 3H, $J = 9$ Hz, CH$_3$) ppm. The obtained analytical data is consistent with those previously reported in the literature.$^3$
2-(4-iso-butyphenyl)propan-1-ol (7c): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 2-(4-isobutyphenyl)ethan-1-ol 6c (178.3 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.73$ (s, 3H), $\delta_{\text{product}} = 3.60$ (d, 2H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.10-7.16 (m, 4H, ArCH), 3.69 (d, 2H, $J = 6.84$ Hz, CH$_2$), 2.93 (sext, 1H, $J = 6.94$ Hz, CH), 2.45 (d, 2H, $J = 7.13$ Hz, CH$_2$), 1.80-1.90 (m, 1H, CH), 1.43 (br. s, 1H, OH), 1.27 (d, 3H, $J = 7.03$ Hz, CH$_3$), 0.91 (d, 6H, $J = 6.61$ Hz, CH$_3$). $^{13}$C($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta$ = 140.83 (quat-C), 140.20 (quat-C), 129.51 (ArCH), 127.29 (ArCH), 68.93 (CH$_2$), 45.17 (CH$_2$), 42.17 (CH), 30.35 (CH), 22.55 (CH$_3$), 17.75 (CH$_3$). Isolated yield: 83%. The obtained analytical data is consistent with those previously reported in the literature.$^{[4]}$

2-(4-methoxyphenyl)propan-1-ol (7d): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 2-(4-methoxyphenyl)ethan-1-ol 6d (152.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 2.31$ (s, 9H), $\delta_{\text{product}} = 1.25$ (d, 3H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.16 (d, 2H, $J = 8.65$ Hz, ArCH), 6.88 (d, 2H, $J = 8.68$ Hz, ArCH), 3.80 (s, 3H, OCH$_3$), 3.66 (dd, 2H, $J = 6.86$ Hz, 3.58 Hz, CH$_2$), 2.90 (sext, 1H, $J = 6.90$ Hz, CH), 1.87 (br. s, 1H, OH), 1.25 (d, 3H, $J = 7$ Hz, CH$_3$). $^{13}$C($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta$ = 158.48 (quat-C), 135.70 (quat-C), 128.52 (ArCH), 114.19 (ArCH), 68.95 (CH$_2$), 55.41 (OCH$_3$), 41.71 (CH), 17.87 (CH$_3$). Isolated yield: 82%. The obtained analytical data is consistent with those previously reported in the literature.$^{[3]}

2-(3-methoxyphenyl)propan-1-ol (7e): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 2-(3-methoxyphenyl)ethan-1-ol 6e (152.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 2.30$ (s, 9H), $\delta_{\text{product}} = 1.29$ (d, 3H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta$ = 7.24-7.30 (m, 1H, ArCH), 6.78-6.87 (m, 3H, ArCH), 3.82 (s, 3H, CH$_3$), 3.71 (d, 2H, $J = 6$ Hz, CH$_2$), 2.86-2.95 (m, 1H, CH), 1.28 (d, 3H, $J = 9$ Hz, CH$_3$) ppm. The obtained analytical data is consistent with those previously reported in the literature.$^{[4]}$
2-(6-methoxynaphthalen-2-yl)propan-1-ol (7f): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2-(6-methoxynaphthalen-2-yl)ethan-1-ol 6f (202.3 mg, 1 mmol), NaOMe (108.04 mg, 1 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene}{\text{standard}}} = 6.72$ (s, 3H), $\delta_{\text{product}} = 1.26$ (d, 3H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 7.60$-$7.64$ (m, 2H, ArCH), 7.52 (s, 1H, ArCH), 7.24-$7.26$ (m, 1H, ArCH), 7.02-$7.07$ (m, 2H, ArCH), 3.82 (s, 3H, OCH$_3$), 3.68 (d, 2H, $J = 6$ Hz, CH$_2$), 2.96-$3.03$ (m, 1H, CH), 1.26 (d, 3H, $J = 6$ Hz, CH$_3$). The obtained analytical data is consistent with those previously reported in the literature.$^5$

2-(4-chlorophenyl)propan-1-ol (7g): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2-(4-chlorophenyl)ethan-1-ol 6g (156.6 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Reaction time: 14 h. Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene}{\text{standard}}} = 6.83$ (s, 3H), $\delta_{\text{product}} = 3.68$ (dd, 2H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta = 7.30$ (d, 2H, $J = 8.41$ Hz, ArCH), 7.17 (d, 2H, $J = 8.40$ Hz, ArCH), 3.68 (dd, 2H, $J = 6.79$ Hz, 2.14 Hz, CH$_2$), 2.93 (sext, 1H, $J = 6.95$ Hz, CH), 1.55 (br. s, 1H, OH), 1.25 (d, 3H, $J = 6.99$ Hz, CH$_3$). $^{13}$C($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta = 142.35$ (quat-C), 132.44 (quat-C), 128.96 (ArCH), 128.86 (ArCH), 68.61 (CH$_2$), 41.98 (CH), 17.67 (CH$_3$). Isolated yield: 76%. The obtained analytical data is consistent with those previously reported in the literature.$^6$

2-(4-fluorophenyl)propan-1-ol (7h): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2-(4-fluorophenyl)ethan-1-ol 6h (140.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (124 mg, 1.03 mmol) as an internal standard ($\delta_{\text{mesitylene}{\text{standard}}} = 6.83$ (s, 3H), $\delta_{\text{product}} = 3.68$ (d, 2H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 7.19$-$7.26$ (m, 2H, ArCH), 6.83-$7.06$ (m, 2H, ArCH), 3.68 (d, 2H, $J = 9$ Hz, CH$_2$), 2.91-$2.98$ (m, 1H, CH), 1.28 (d, 3H, $J = 6$ Hz, CH$_3$) ppm. The obtained analytical data is consistent with those previously reported in the literature.$^7$

2-(thiophen-2-yl)propan-1-ol (7i): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2-(thiophen-2-yl)ethan-1-ol 6i (128.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using
mesitylene (122 mg, 1.02 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 1.37$ (d, 3H)).

$^1\text{H NMR}$ (300 MHz, CDCl$_3$, 298 K) $\delta = \delta = 7.20$ (dd, 1H, $J = 5.02$, 1.20, ArCH), 6.97-6.99 (m, 1H, ArCH), 6.90-6.91 (m, 1H, ArCH), 3.70 (dd, 2H, $J = 6.39$, 2.46, CH$_2$), 3.21-3.28 (m, 1H, CH), 1.37 (d, 3H, $J = 6.96$ Hz, CH$_3$), 1.36.[8]

2-(1H-indol-3-yl)propan-1-ol (7j): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2-(1H-indol-3-yl)ethan-1-ol 6j (161.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL). Yield was determined by $^1\text{H NMR}$ spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.83$ (s, 3H), $\delta_{\text{product}} = 3.32$ (sext, 1H)).

$^1\text{H NMR}$ (300 MHz, CDCl$_3$, 298 K) $\delta = 8.06$ (br. s, 1H, NH), 7.67 (dt, 1H, $J = 7.82$, 0.95 Hz, ArCH), 7.38 (dt, 1H, $J = 8.13$, 0.99 Hz, ArCH), 7.21 (ddd, 1H, $J = 8.15$, 6.99, 1.28 Hz, ArCH), 7.13 (ddd, 1H, $J = 7.99$, 7.01, 1.11 Hz, ArCH), 7.06 (br s, 1H, ArCH), 3.77-3.88 (m, 2H, CH$_2$), 3.32 (sext, 1H, $J = 6.78$ Hz, CH), 1.52 (br. s, 1H, OH), 1.41 (d, 3H, $J = 7.06$ Hz, CH$_3$). $^{13}\text{C}$$^1\text{H}$-NMR (75 MHz, CDCl$_3$, 298 K) $\delta = 136.71$ (quat-C), 126.88 (quat-C), 122.37 (ArCH), 121.37 (quat-C), 119.56 (ArCH), 119.39 (ArCH), 118.15 (ArCH), 111.42 (ArCH), 68.05 (CH$_2$), 34.07 (CH), 17.42 (CH$_3$). Isolated yield: 47%. The obtained analytical data is consistent with those previously reported in the literature.[8]
5. General procedure for the catalytic selective $\beta$-methylation of secondary alcohols

Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaOMe (216.08 mg, 4 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. Secondary alcohol (1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature. After 36 h, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard (δ\text{Ar} = 6.77 Hz, C\text{(methyl)}), 0.81 (d, 3H, C\text{(phenylpropan-ol)}), 4.54 (d, 3H, C\text{(phenylethan-1-ol)}), 1.90 (br. s, 1H, O\text{C(\text{CH}_{2}-)}), 1.01 (d, 3H, J = 6.74 Hz, CH\text{_3}), 0.81 (d, 3H, J = 6.74 Hz, CH\text{_3}) ppm. $^{13}\text{C}[^{1}\text{H}]$-NMR (101 MHz, CDCl$_3$, 298 K) δ = 143.76 (quat-C), 128.31 (ArCH), 127.53 (ArCH), 126.69 (ArCH), 80.17 (CH), 35.38 (CH), 19.12 (CH$_3$), 18.37 (CH$_3$). Isolated yield: 71%. The obtained analytical data is consistent with those previously reported in the literature.[3]

2-methyl-1-phenylpropan-1-ol (9a): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-phenylethan-1-ol 8a (122.2 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^{1}\text{H}$ NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 0.81$ (d, 3H)).

$^{1}\text{H}$ NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.27-7.38 (m, 5H, ArCH), 4.37 (d, 1H, J = 6.90 Hz, CH), 1.93-2.01 (s, 1H, J = 6.77 Hz, CH), 1.90 (br. s, 1H, OH), 1.01 (d, 3H, J = 6.74 Hz, CH$_3$), 0.81 (d, 3H, J = 6.74 Hz, CH$_3$) ppm. $^{13}\text{C}[^{1}\text{H}]$-NMR (101 MHz, CDCl$_3$, 298 K) δ = 143.76 (quat-C), 128.31 (ArCH), 127.53 (ArCH), 126.69 (ArCH), 80.17 (CH), 35.38 (CH), 19.12 (CH$_3$), 18.37 (CH$_3$). Isolated yield: 71%. The obtained analytical data is consistent with those previously reported in the literature.[3]

2-methyl-1-(naphthalen-2-y1)propan-1-ol (9b): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(naphthalen-2-y1)ethan-1-ol 8b (172.2 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^{1}\text{H}$ NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.84$ (s, 3H), $\delta_{\text{product}} = 4.54$ (d, 1H)).

$^{1}\text{H}$ NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.81-7.85 (m, 3H, ArCH), 7.75-7.76 (m, 1H, ArCH), 7.45-7.50 (m, 3H, ArCH), 4.54 (d, 1H, J = 6.84 Hz, CH), 2.02-2.16 (m, 1H, CH), 1.90 (br. s, 1H, OH), 1.05 (d, 3H, J = 6.69 Hz, CH$_3$), 0.84 (d, 3H, J = 6.80 Hz. CH$_3$) ppm. $^{13}\text{C}[^{1}\text{H}]$-NMR (101 MHz, CDCl$_3$, 298 K) δ = 141.24 (ArCH), 133.29 (quat-C), 133.08 (ArCH), 128.09 (ArCH), 128.06 (ArCH), 127.79 (ArCH), 126.19 (ArCH), 125.87 (ArCH), 3.07 (s, 3H), 1.00 (d, 3H, J = 6.69 Hz, CH$_3$) ppm. $^{13}\text{C}[^{1}\text{H}]$-NMR (101 MHz, CDCl$_3$, 298 K) δ = 141.24 (ArCH), 133.29 (quat-C), 133.08 (ArCH), 128.09 (ArCH), 128.06 (ArCH), 127.79 (ArCH), 126.19 (ArCH), 125.87 (ArCH),
125.54 (ArCH), 124.76 (quat-C), 80.30 (CH), 35.34 (CH), 19.29 (CH₃), 18.38 (CH₃). Isolated yield: 74%. The obtained analytical data is consistent with those previously reported in the literature.³

2-methyl-1-(p-toly)propan-1-ol (9c): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(p-toly)ethan-1-ol 8c (136.1 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by ¹H NMR spectrum using mesitylene (125 mg, 1.04 mmol) as an internal standard (δ<sub>Mesitylene(standard) = 6.81 (s, 3H), δ<sub>product = 1.01 (d, 3H)).

¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.20 (d, 2H, J = 8.09 Hz, ArCH), 7.15 (d, 2H, J = 7.92 Hz, ArCH), 4.32 (d, 1H, J = 6.98 Hz, CH₃), 2.35 (s, 3H, CH₃), 1.95 (sext, 1H, J = 6.74 Hz, CH₃), 1.76 (br. s, 1H, OH), 1.01 (d, 3H, J = 6.64 Hz, CH₃), 0.79 (d, 3H, J = 6.79 Hz, CH₃). ¹³C{¹H}-NMR (75 MHz, CDCl₃, 298 K) δ = 130.82 (quat-C), 137.17 (quat-C), 129.01 (ArCH), 126.63 (ArCH), 80.10 (CH), 35.35 (CH), 21.26 (CH₃), 19.15 (CH₃), 18.51 (CH₃). Isolated yield: 73%. The obtained analytical data is consistent with those previously reported in the literature.²

2-methyl-1-(o-toly)propan-1-ol (9d): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(o-toly)ethan-1-ol 8d (136.1 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by ¹H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard (δ<sub>Mesitylene(standard) = 6.82 (s, 3H), δ<sub>product = 1.05 (d, 3H)).

¹H NMR (300 MHz, CDCl₃, 298 K) δ = 7.53–7.12 (m, 4H, ArCH), 4.63 (d, 1H, J = 6 Hz, CH₃), 2.35 (s, 3H, CH₃), 2.04–1.93 (m, 1H, CH), 1.05 (d, 3H, J = 6 Hz, CH₃), 0.87 (d, 3H, J = 6 Hz, CH₃) ppm. The obtained analytical data is consistent with those previously reported in the literature.⁴

1-(4-methoxyphenyl)-2-methylpropan-1-ol (9e): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(4-methoxyphenyl)ethan-1-ol 8e (152.2 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by ¹H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard (δ<sub>Mesitylene(standard) = 6.81 (s, 3H), δ<sub>product = 4.30 (d, 1H)).

¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.23 (d, 2H, J = 8.62 Hz, ArCH), 6.87 (d, 2H, J = 8.66 Hz, ArCH), 4.30 (d, 1H, J = 7.13 Hz, CH), 3.81 (s, 3H, OCH₃), 1.89–1.97 (m, 1H, CH), 1.79 (br. s, 1H, OH), 1.01 (d, 3H, J = 6.64 Hz, CH₃), 0.77 (d, 3H, J = 6.79 Hz, CH₃). ¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K) δ = 159.06 (quat-C), 135.98 (quat-C), 127.84 (ArCH), 113.70 (ArCH), 79.90 (CH), 55.40 (OCH₃), 35.42 (CH), 19.10 (CH₃), 18.65 (CH₃). Isolated yield: 51%. The obtained analytical data is consistent with those previously reported in the literature.⁵
1-(4-fluorophenyl)-2-methylpropan-1-ol (9f): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(4-fluorophenyl)ethan-1-ol 8f (140.2 mg, 1 mmol), NaOMe (216.1 mg, 4 mmol), MeOH (1 mL). Reaction time: 42 h. Yield was determined by $^1$H NMR spectrum using mesitylene (117 mg, 0.97 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 4.31$ (d, 1H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta = 7.24$ (d, 2H, $J = 8.64$ Hz, ArCH), 6.88 (d, 2H, $J = 8.60$ Hz, ArCH), 4.29 (d, 1H, $J = 7.15$ Hz, CH), 1.86-1.99 (m, 1H, CH), 1.02 (d, 3H, $J = 6.61$ Hz, CH$_3$), 0.78 (d, 3H, $J = 6.76$ Hz, CH$_3$). The obtained analytical data is consistent with those previously reported in the literature.$^{[12]}$

1-(furan-2-y1)-2-methylpropan-1-ol (9g): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-(furan-2-y1)ethan-1-ol 8g (112.10 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR spectrum using mesitylene (116 mg, 0.96 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.81$ (s, 3H), $\delta_{\text{product}} = 0.86$ (d, 3H)).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta = 7.37$ (br. s, 1H, ArCH), 6.33 (dd, 1H, $J = 3.22$ Hz, 1.83 Hz, ArCH), 6.22 (d, 1H, $J = 3.23$ hz), 4.37 (d, 1H, $J = 7.06$ hz, CH), 2.06-2.15 (m, 1H, CH), 1.84 (br. s, 1H, OH), 1.02 (d, 3H, $J = 6.75$ Hz, CH$_3$), 0.86 (d, 3H, $J = 6.75$ Hz, CH$_3$). $^{13}C$($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta = 156.28$ (quat-C), 141.82 (ArCH), 110.17 (ArCH), 106.60 (ArCH), 73.67 (CH), 33.49 (CH), 18.85 (CH$_3$), 18.36 (CH$_3$). Isolated yield: 55%. The obtained analytical data is consistent with those previously reported in the literature.$^{[13]}$

1-cyclohexyl-2-methylpropan-1-ol (9h): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-cyclohexylethan-1-ol 8h (128.21 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 3.05$ (t, 1H). The obtained analytical data is consistent with those previously reported in the literature.$^{[14]}$

2-methyl-2,3-dihydro-1H-inden-1-ol (9i): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 2,3-dihydro-1H-inden-1-ol 8i (134.2 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.72$ (s, 3H), $\delta_{\text{product}} = 4.63$ (d, 1H), $\delta_{\text{product}} = 4.91$ (d, 1H)). The obtained analytical data is consistent with those previously reported in the literature.$^{[15]}$
2-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (9j): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1,2,3,4-tetrahydronaphthalen-1-ol 8j (148.2 mg, 1 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 mL). Yield was determined by $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 4.33$ (d, 1H), $\delta_{\text{product}} = 4.56$ (d, 1H)). The obtained analytical data is consistent with those previously reported in the literature.$^{[16]}$

6-methyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (9k): Prepared by following the general experimental procedure with: 1 (1.24 mg, 0.5 mol%), 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol 8k (81.1 mg, 0.5 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (0.5 mL). Yield was determined by $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 4.60$ (d, 1H), $\delta_{\text{product}} = 4.95$ (d, 1H)). The obtained analytical data is consistent with those previously reported in the literature.$^{[9, 15b]}$
6. General procedure for catalytic selective \(\beta\)-methylation of aliphatic alcohols

Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaOMe (108.04 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. Aliphatic alcohol (1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature. After the desired reaction time, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. The isolation of pure product was carried out using column chromatography over silica gel (100-200 mesh) using ethyl acetate/petroleum ether (12 : 88) mixture as eluent.

2-methyl-3-phenylpropan-1-ol (11a): Prepared by following the general experimental procedure with:

\[
\begin{align*}
\text{1} & \quad (2.48 \text{ mg, 0.5 mol\%}), \\
3\text{-phenylpropan-1-ol 10a} & \quad (136.2 \text{ mg, 1 mmol}), \\
\text{NaOMe} & \quad (108.04 \text{ mg, 2 mmol}), \\
\text{MeOH} & \quad (1 \text{ mL}), \\
\text{reaction time: 24 h}
\end{align*}
\]

Yield was determined by \(^1\text{H}\) NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard \((\delta_{\text{Mesitylene(standard)}} = 6.82 \text{ (s, 3H)} \), \(\delta_{\text{product}} = 0.93 \text{ (d, 3H)})\).

\(^1\text{H}\) NMR (300 MHz, CDCl\textsubscript{3}, 298 K) \(\delta = 7.16-7.32 \text{ (m, 5H, ArCH)}, 3.51 \text{ (dq, 2H, } J = 10.57 \text{ Hz, 5.95 Hz, CH\textsubscript{2}}), 2.77 \text{ (dd, 1H, } J = 13.42 \text{ Hz, 6.33 Hz, CH}), 2.43 \text{ (dd, 1H, } J = 13.41 \text{ Hz, 8.04 Hz, CH}), 1.90-2.01 \text{ (m, 1H, CH)}, 1.59 \text{ (s, 1H, OH)}, 0.93 \text{ (d, 3H, } J = 6.75 \text{ Hz, CH\textsubscript{3}})\).

\(^{13}\text{C}^{(1}\text{H})\)-NMR (101 MHz, CDCl\textsubscript{3}, 298 K) \(\delta = 140.75 \text{ (quat-C), 129.27 (ArCH), 128.39 (ArCH), 126.00 (ArCH), 67.79 (CH\textsubscript{2}), 39.84 (CH\textsubscript{2}), 37.92 (CH), 16.60 (CH\textsubscript{3})}\). Isolated yield: 66%. The obtained analytical data is consistent with those previously reported in the literature.\(^{[17]}\)

3-(4-chlorophenyl)-2-methylpropan-1-ol (11b): Prepared by following the general experimental procedure with:

\[
\begin{align*}
\text{1} & \quad (2.48 \text{ mg, 0.5 mol\%}), \\
3\text{-}(4\text{-chlorophenyl})\text{propan-1-ol 10b} & \quad (170.6 \text{ mg, 1 mmol}), \\
\text{NaOMe} & \quad (108.04 \text{ mg, 2 mmol}), \\
\text{MeOH} & \quad (1 \text{ mL}), \\
\text{reaction time: 14 h}
\end{align*}
\]

Yield was determined by \(^1\text{H}\) NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard \((\delta_{\text{Mesitylene(standard)}} = 6.72 \text{ (s, 3H)}, \delta_{\text{product}} = 0.83 \text{ (d, 3H)})\).

\(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}, 298 K) \(\delta = 7.12-7.24 \text{ (m, 3H, ArCH)}, 7.01-7.05 \text{ (m, 1H, ArCH)}, 3.88-3.46 \text{ (m, 2H, CH\textsubscript{2}}), 2.68 \text{ (dd, 1H, } J = 13.50 \text{ Hz, 6.17 Hz, CH}), 2.32 \text{ (dd, 1H, } J = 13.49 \text{ Hz, 8.13 Hz, CH}), 1.83-1.87 \text{ (m, 1H, CH\textsubscript{3}}).}
CH), 1.42 (br. s, 1H, OH), 0.83 (d, 3H, J = 6.74 Hz, CH₃). \[^{12}\text{C}⁺\text{H}⁻\text{NMR}\] (75 MHz, CDCl₃, 298 K) δ = 139.19 (quat-C), 130.61 (ArCH), 130.27 (quat-C), 128.49 (ArCH), 67.55 (CH₂), 39.05 (CH₂), 37.82 (CH), 16.43 (CH₃). Isolated yield: 60%. The obtained analytical data is consistent with those previously reported in the literature.[18]

2-methyl-4-phenylbutan-1-ol (11c): Prepared by following the general experimental procedure with:

\[
\text{Product 1 (2.48 mg, 0.5 mol%), 4-phenylbutan-1-ol 10c (150.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 ml), reaction time: 24 h. Yield was determined by } ^{1}\text{H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard (δ}_{\text{Mesitylene (standard)}} = 6.82 (s, 3H), δ_{\text{product}} = 1.0 (d, 3H)).
\]

\[^{1}\text{H NMR}\] (300 MHz, CDCl₃, 298 K) δ = 7.17-7.32 (m, 5H, ArCH), 3.54-3.46 (m, 2H, CH₂), 2.77-2.58 (m, 2H, CH₂), 1.65-1.82 (m, 2H, CH₂), 1.49-1.41 (m, 1H, CH), 1.00 (d, J = 6.7 Hz, 3H, CH₃) ppm. The obtained analytical data is consistent with those previously reported in the literature.[19]

2-methyl-5-phenylpentan-1-ol (11d): Prepared by following the general experimental procedure with:

\[
\text{Product 1 (2.48 mg, 0.5 mol%), 5-phenylpentan-1-ol 10d (164.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 ml), reaction time: 24 h. Yield was determined by } ^{1}\text{H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard (δ}_{\text{Mesitylene (standard)}} = 6.72 (s, 3H), δ_{\text{product}} = 0.83 (d, 3H)).
\]

\[^{1}\text{H NMR}\] (400 MHz, CDCl₃, 298 K) δ = 6.72-7.21 (m, 5H, ArCH), 3.30-3.43 (m, 2H, CH₂), 2.50-2.56 (m, 2H, CH₂), 1.48-1.62 (m, 3H, CH₂ & CH), 1.28-1.42 (m, 2H, CH₂), 0.83 (d, 3H, J = 6 Hz, CH₃) ppm. The obtained analytical data is consistent with those previously reported in the literature.[20]

2-methylpropan-1-ol (11e): Prepared by following the general experimental procedure with:

\[
\text{Product 1 (4.95 mg, 0.5 mol%), ethanol 10e (92.1 mg, 2 mmol), NaOMe (216.08 mg, 4 mmol), MeOH (1 ml), reaction time: 36 h. Yield was determined by } ^{1}\text{H NMR spectrum using mesitylene (170 mg, 1.41 mmol) as an internal standard (δ}_{\text{Mesitylene (standard)}} = 6.82 (s, 3H), δ_{\text{product}} = 0.94 (d, 6H)).
\]

\[^{1}\text{H NMR}\] (300 MHz, CDCl₃, 298 K) δ = 3.42 (d, 2H, J = 6 Hz, CH₂), 1.85-1.71 (m, 1H, CH), 0.94 (d, 6H, J = 6 Hz, CH₃) ppm. The obtained analytical data is consistent with those previously reported in the literature.[21]

2-methylbutan-1-ol (11f): Prepared by following the general experimental procedure with:

\[
\text{Product 1 (2.48 mg, 0.5 mol%), 1-butanol 10f (74.1 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol),}
\]

14
MeOH (1 mL), reaction time: 36 h. Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 3.42-3.55$ (m, 2H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 3.48$ (m, 2H, CH$_2$), 1.61-1.51 (m, 1H, CH), 1.51-1.38 (m, 1H, CH$_2$), 0.98-0.92 (m, 6H, CH$_3$). The obtained analytical data is consistent with those previously reported in the literature.$^{[22]}$

2-methylpentan-1-ol (11g): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 1-pentanol 10g (88.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL), reaction time: 36 h. Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.82$ (s, 3H), $\delta_{\text{product}} = 3.48$ (d, 1H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 3.48$ (dd, 1H, $J = 10.46$, 5.81 Hz, CH), 3.37 (dd, 1H, $J = 10.53$, 6.57 Hz, 1H), 1.89-1.98 (m, 1H, OH), 1.53-1.68 (m, 1H, CH), 1.23-1.40 (m, 3H, CH$_2$ & CH), 1.05-1.11 (m, 1H, CH), 0.85-0.90 (m, 6H, CH$_3$). $^{13}$C($^1$H)-NMR (75 MHz, CDCl$_3$, 298 K) $\delta = 68.42$ (CH$_2$), 35.58 (CH), 35.53 (CH$_2$), 20.18 (CH$_2$), 16.64 (CH$_3$), 14.43 (CH$_3$). Isolated yield: 43%. The obtained analytical data is consistent with those previously reported in the literature.$^{[23]}

2-methylhexan-1-ol (11h): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 1-hexanol 10h (102.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL), reaction time: 24 h. Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.72$ (s, 3H), $\delta_{\text{product}} = 3.29-3.44$ (dq, 2H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 3.29-3.44$ (dq, 2H, $J = 30$, 6 Hz, CH$_2$), 1.14-1.53 (m, 7H, CH$_2$ & CH), 0.79-0.86 (m, 6H, CH$_3$). The obtained analytical data is consistent with those previously reported in the literature.$^{[24]}

2-methyloctan-1-ol (11i): Prepared by following the general experimental procedure with:

1 (2.48 mg, 0.5 mol%), 1-octanol 10i (130.2 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL), reaction time: 24 h. Yield was determined by $^1$H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard ($\delta_{\text{mesitylene(standard)}} = 6.73$ (s, 3H), $\delta_{\text{product}} = 3.31-3.46$ (dq, 2H)).

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta = 3.44$ (dd, 1H, $J = 10.43$ Hz, 6.47 Hz, CH), 3.35 (dd, 1H, $J = 10.43$ Hz, 6.47 Hz, CH), 1.48-1.56 (m, 1H, CH), 1.44 (br s, 1H, OH), 1.20-1.30 (m, 10H, CH$_2$), 0.80-0.85 (m, 6H, CH$_3$). $^{13}$C($^1$H)-NMR (101 MHz, CDCl$_3$, 298 K) $\delta = 68.59$ (CH$_2$), 35.91 (CH), 33.29 (CH$_2$), 32.00 (CH$_2$), 29.74 (CH$_2$),...
27.08 (CH₂), 22.80 (CH₂), 16.72 (CH₃), 14.23 (CH₃). Isolated yield: 62%. The obtained analytical data is consistent with those previously reported in the literature.²⁵

2-Methyldecan-1-ol (11j): Prepared by following the general experimental procedure with: 1 (2.48 mg, 0.5 mol%), 1-decanol 10j (158.3 mg, 1 mmol), NaOMe (108.04 mg, 2 mmol), MeOH (1 mL), reaction time: 24 h. Yield was determined by ¹H NMR spectrum using mesitylene (120 mg, 1 mmol) as an internal standard (δMesitylene(standard) = 6.72 (s, 3H), δ_product = 3.29-3.45 (dq, 2H)).

¹H NMR (300 MHz, CDCl₃, 298 K) δ = 3.29-3.45 (dq, 2H, J = 30, 6 Hz, CH₂), 1.43-1.51 (m, 1H, CH), 0.99-1.37 (m, 14H, CH₂), 0.78-0.84 (m, 6H, CH₃). The obtained analytical data is consistent with those previously reported in the literature.²⁶
7. General procedure for the catalytic selective $\beta$-methylation of diols

Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaOMe were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. Diol (1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature. After the desired reaction time, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture which was further analyzed by NMR spectroscopy.

2-methylpropane-1,3-diol (11k): Prepared by following the general experimental procedure with:

\[ \text{1} \quad (2.48 \text{ mg, 0.5 mol%}), \quad \text{propane-1,3-diol 10k} \quad (76.0 \text{ mg, 1 mmol}), \]

\[ \text{NaOMe (108.04 mg, 2 mmol), MeOH (1 mL), reaction time: 36 h.} \]

Yield was determined by $^1$H NMR spectrum using mesitylene (118 mg, 0.97 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.76 \text{ (s, 3H)}, \delta_{\text{product}} = 0.84 \text{ (d, 3H)}$).

$^1$H NMR (300 MHz, DMSO-$d_6$, 298 K) $\delta = 3.44-3.51 \text{ (m, 4H, } C_2H_2), 1.58-1.68 \text{ (m, 1H, } CH), 0.83 \text{ (d, 3H, } J = 9 \text{ Hz, } CH_3)$. The obtained analytical data are consistent with those previously reported in the literature.\[27\]

2,5-dimethylhexane-1,6-diol (11l): Prepared by following the general experimental procedure with:

\[ \text{1} \quad (2.48 \text{ mg, 0.5 mol%}), \quad \text{hexane-1,6-diol 10l} \quad (118.0 \text{ mg, 1 mmol}), \]

\[ \text{NaOMe (216.08 mg, 4 mmol), MeOH (1 mL), reaction time: 48 h.} \]

Yield was determined by $^1$H NMR spectrum using mesitylene (111 mg, 0.93 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.77 \text{ (s, 3H)}, \delta_{\text{product}} = 0.82 \text{ (d, 3H)}$).

$^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) $\delta = 3.20-3.24 \text{ (m, 4H, } C_2H_2), 1.30-1.43 \text{ (m, 4H, } CH_2 \& CH), 0.93-1.05 \text{ (m, 2H, } CH_2), 0.82 \text{ (d, 3H, } J = 3 \text{ Hz, } CH_3), 0.80 \text{ (d, 3H, } J = 3 \text{ Hz, } CH_3)$. The obtained analytical data are consistent with those previously reported in the literature.\[28\]

2,9-dimethyldecane-1,10-diol (11m): Prepared by following the general experimental procedure with:

\[ \text{1} \quad (2.48 \text{ mg, 0.5 mol%}), \quad \text{decane-1,10-diol 10m} \quad (174.0 \text{ mg, 1 mmol}), \]

\[ \text{NaOMe (216.08 mg, 4 mmol), MeOH (1 mL), reaction time: 48 h.} \]

Yield was determined by $^1$H NMR spectrum using mesitylene (117 mg, 0.97 mmol) as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.76 \text{ (s, 3H)}, \delta_{\text{product}} = 0.82 \text{ (d, 6H)}$).
\textbf{H NMR} (400 MHz, DMSO-$d_6$, 298 K) \textit{\delta} = 3.14-3.28 (m, 4H, $CH_2$), 1.40-1.50 (m, 2H, $CH$), 1.13-1.28 (m, 10H, $CH_2$), 0.96-1.03 (m, 2H, $CH_2$), 0.82 (d, 6H, $J=6.64$ Hz, $CH_3$). \textbf{\textsuperscript{13}C\textit{\{H\}}-NMR} (101 MHz, DMSO-$d_6$) \textit{\delta} = 66.73 (CH$_2$), 35.82 (CH), 33.37 (CH$_3$), 29.95 (CH$_2$), 26.98 (CH$_2$), 17.19 (CH$_3$). \textbf{HRMS} (ESI-) found [M-H]$^- = 201.185960$; $C_{12}H_{25}O_2$ requires 201.186005. Isolated yield: 69%.
8. $^1$H NMR spectra of reaction mixtures for $\beta$-methylated alcohols

Figure S1: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 7a

Figure S2: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7b
Figure S3: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7c

Figure S4: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7d
Figure S5: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7e

Figure S6: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7f
Figure S7: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7g

Figure S8: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7h
Figure S9: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 7i
Figure S10: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9a

Figure S11: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9b
Figure S12: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9c

Figure S13: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 9d
Figure S14: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9e

Figure S15: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9f
Figure S16: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9g

Figure S17: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9h
Figure S18: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 9i

Figure S19: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 9j
Figure S20: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 9k
Figure S21: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11a

Figure S22: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11b
Figure S23: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11c

Figure S24: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 11d
Figure S25: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11e

Figure S26: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 11f
Figure S27: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11g

Figure S28: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11h
Figure S29: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11i

Figure S30: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11j
Figure S31: $^1$H NMR (300 MHz, DMSO-$d_6$, 298 K) spectrum for 11k.

Figure S32: $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) spectrum for 11l.
Figure S33: $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) spectrum for 11m

Figure S34: $^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$, 298 K) spectrum for 11m
Figure S35: $^{13}$C APT-NMR (101 MHz, DMSO-$d_6$, 298 K) spectrum for 11m
9. NMR spectra of isolated products

Figure S36: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 7a

Figure S37: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 7a
Figure S38: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 7c

Figure S39: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 7c
Figure S40: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 7d

Figure S41: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 7d
Figure S42: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 7g

Figure S43: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 7g
Figure S44: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of 7j

Figure S45: $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, 298 K) spectrum of 7j
Figure S46: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 9a

Figure S47: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 9a
Figure S48: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 9b

Figure S49: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 9b
Figure S50: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 9c

Figure S51: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 9c
Figure S52: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 9e

Figure S53: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 9e
Figure S54: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 9g

Figure S55: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 9g
Figure S56: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 11a

Figure S57: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 11a
Figure S58: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 11b

Figure S59: $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, 298 K) spectrum for 11b
Figure S60: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for 11g

Figure S61: $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$, 298 K) spectrum for 11g
Figure S62: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum for 11i

Figure S63: $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, 298 K) spectrum for 11i
Figure S64: $^1$H NMR (400 MHz, DMSO-d$_6$, 298 K) spectrum for 11l

Figure S65: $^{13}$C($^1$H) NMR (101 MHz, DMSO-d$_6$, 298 K) spectrum for 11l
10. Conversion/time profile from experiments for the $\beta$-methylation of 6a with MeOH at different time intervals

Nine reactions were performed for the reaction progress experiments at different time intervals. Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaOMe (108.04 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. 6a (122.1 mg, 1 mmol), and MeOH (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature. After the desired reaction time, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. Yield was determined by $^1$H NMR spectrum using mesitylene as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.72$ (s, 3H), $\delta_{\text{product}} = 3.58$ (d, 2H)). The graph is shown in the manuscript which corresponds to Figure 1.

![NMR Spectrum](image)

Figure S66: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of 6a with MeOH after 2.00 h as example
Figure S67: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of 6a with MeOH after 4.00 h as example
11. Labeling experiments and observation of potential intermediates

11.1. Procedure for $\beta$-methylation of 6a with $^{13}$CH$_3$OH

Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaO$^t$Bu (192.3 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. 6a (122.1 mg, 1 mmol), $^{13}$CH$_3$OH (66.06 mg, 2 mmol) and toluene (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature for 36 h. After completion of the reaction, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene (120 mg, 1 mmol) was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. Yield was determined by $^1$H NMR spectrum using mesitylene as an internal standard ($\delta_{\text{Mesitylene(standard)}} = 6.98 \text{ (s, 3H)}, \delta_{\text{product}} = 3.80-3.84 \text{ (m, 2H)})$.

![Figure S68: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for the $\beta$-Methylation of 6a with $^{13}$CH$_3$OH](image-url)
11.2. Procedure for selective $\beta$-methylation of 6a with $\text{CD}_3\text{OD}$

Mn-MACHO 1 (2.48 mg, 0.5 mol%) and NaO'Bu (192.3 mg, 2 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. 6a (122.1 mg, 1 mmol) and $\text{CD}_3\text{OD}$ (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature for 24 h. After 24 h, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene (120 mg, 1 mmol) was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. $^{13}\text{C}^{(1}\text{H})$-NMR (101 MHz, CDCl$_3$) δ 143.72 (quat-C), 128.64 (ArCH), 127.51 (ArCH), 126.66 (quat-C), 67.80-68.48 (m, CD$_2$), 41.42-42.12 (m, CD), 16.47-16.93 (m, CD$_3$).

Figure S69: $^{13}\text{C}^{(1}\text{H})$ NMR (75 MHz, CDCl$_3$, 298 K) spectrum for the $\beta$-Methylation of 6a with $\text{CD}_3\text{OD}$
11.3. Procedure for $\beta$-methylation of 6a with paraformaldehyde and H$_2$

Mn-MACHO 1 (2.48 mg, 0.5 mol%), NaO'Bu (192.3 mg, 2 mmol) and paraformaldehyde (150.1 mg, 5 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was transferred to a 10 mL stainless autoclave that was evacuated and refilled with argon at least three times. 6a (122.1 mg, 1 mmol) and toluene (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and pressurized with 10 bar of hydrogen. The autoclave was heated to 150 $^\circ$C temperature for 24 h. After 24 h, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene (120 mg, 1 mmol) was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy. Yield was determined by $^1$H NMR spectrum using mesitylene as an internal standard ($\delta_{\text{Mesitylene[standard]}}$=6.84 (s, 3H), $\delta_{\text{product}}$= 3.71 (d, 2H)).

![Figure S70: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for the $\beta$-Methylation of 6a with paraformaldehyde and H$_2$](image-url)
11.4. Procedure for $\beta$-methylation of Acetophenone (14) with methanol

\[
\text{Mn-MACHO} \ 1 \ (2.48 \text{ mg}, 0.5 \text{ mol%}) \text{ and NaOMe (216.08 mg}, 4 \text{ mmol}) \text{ were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was purged with argon three times. Acetophenone 14 (120.2 mg, 1 mmol) and methanol (1 mL) were added at room temperature through a valve under argon. The autoclave was sealed and heated to 150 °C temperature. After 24 h, the autoclave was cooled to room temperature and slowly vented while stirring continued. Mesitylene was added as an internal standard to the reaction mixture that was then passed through a short path of acidic alumina before the composition was analyzed by NMR spectroscopy.}
\]

![Figure S71: $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum for the $\beta$-Methylation of Acetophenone 14 with methanol](image-url)
**11.5. Preparation of complex 15**

A high pressure NMR tube was charged with complex 1 (15 mg, 0.03 mmol), NaO\text{Bu} (3.36 mg, 0.035 mmol) and Tol.-d8 (0.4 mL). The resulting solution was stirred for 30 minutes at room temperature leading to a color change from yellow to orange red. $^1$H-NMR (300 MHz, Tol-d8, 298 K) and $^{31}$P($^1$H)-NMR (121 MHz, Tol-d8, 298 K) spectroscopies are consistent with the formation of complex 15. $^{[1]}$
11.6. Reaction of Mn-complex (1) with 2-phenyl ethanol (6a)

6a (1.22 mg, 0.01 mmol), Mn-complex 1 (4.95 mg, 0.01 mmol), NaO'Bu (1.2 mg, 0.012 mmol) and Tol-d8 (0.5 ml as a solvent) were charged in a Teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at 100 °C temperature. $^{31}$P{$^1$H} NMR of the reaction mixture of 1 and 6a were measured at different time intervals which confirmed the formation of Mn(I) intermediate 15 and 16.[3]

![Figure S72: Superposed $^{31}$P{$^1$H}-NMR spectrum of Mn-intermediates 15 and 16 at different time intervals](image-url)
Figure S73. $^{31}$P($^1$H)-NMR (121 MHz, Toluene-$d_8$, 298 K) spectrum of Mn-intermediates 15 and 16
11.7. Reaction of Mn-complex (15) with methanol

Mn-complex 15 (4.15 mg, 0.01 mmol), MeOH (1.6 mg, 0.05 mmol) and Tol-d8 (0.4 ml as a solvent) were charged in a teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at 100 °C temperature. \(^1\)H NMR of the reaction mixture of 15 and methanol were measured at different time intervals which confirmed the formation of formaldehyde, \(\text{H}_2\) and Mn(I) intermediates 17 and 18 respectively.\(^{[1]}\)

![Figure S74: Superposed \(^1\)H-NMR spectra of formaldehyde, \(\text{H}_2\) and intermediate 18 at different time intervals](image)

Figure S75: $^1$H-NMR (300 MHz, tol-$d_8$, 298 K) spectrum of intermediates 17 and 18 after 120 minutes at 100 °C

Figure S76: $^{31}$P($^1$H)-NMR (121 MHz, tol-$d_8$, 298 K) spectrum of the reaction between complex 15 with MeOH in presence of base
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