SUPPORTING INFORMATION

Iron-Catalyzed Borrowing Hydrogen $\beta$-$C(sp^3)$-Methylation of Alcohols

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1. General information

Unless stated otherwise, all reactions were performed using oven-dried 10 mL microwave vials sealed with an aluminium crimp caps, and were stirred with Teflon-coated magnetic stirrer bars. Dry tetrahydrofuran (THF), toluene, hexanes and diethyl ether were obtained after passing these previously degassed solvents through activated alumina columns (Mbraun, SPS-800). All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise. Methanol was supplied as synthesis grade from Fisher Scientific (>99.9%) and was not degassed before use.

Room temperature (rt) refers to 20-25 °C. Ice/water and CO$_2$(s)/acetone baths were used to obtain temperatures of 0 °C and -78 °C respectively. All reactions involving heating were carried out using DrySyn blocks and a contact thermometer. In vacuo refers to reduced pressure through the use of a rotary evaporator. [Fe] precatalysts 2, 4, 5, 6, 7, and 8 were prepared according to the corresponding literature procedures.

Analytical thin layer chromatography was carried out using aluminium plates coated with silica (Kieselgel 60 F$_{254}$ silica) and visualization was achieved using ultraviolet light (254 nm), followed by staining with a 1% aqueous KMnO$_4$ solution. Flash chromatography used Kieselgel 60 silica in the solvent system stated.

Melting points were recorded on a Gallenkamp melting point apparatus, and corrected by linear interpolation of melting point standards benzophenone (47-49 °C), and benzoic acid (121-123 °C).

IR spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform ATIR spectrometer as thin films using a Pike MIRacle ATR accessory. Characteristic peaks are quoted ($\nu_{\text{max}}$ / cm$^{-1}$).

$^1$H, $^{13}$C, $^{19}$F NMR spectra were obtained on either a Bruker Avance 400 (400 MHz $^1$H, 101 MHz $^{13}$C, 376 MHz $^{19}$F) or a Bruker Avance 500 (500 MHz $^1$H, 126 MHz $^{13}$C, 471 MHz $^{19}$F) spectrometer at rt in the solvent stated. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. All coupling constants, $J$, are quoted in Hz. Multiplicities are reported with the following symbols: $s =$ singlet, $d =$ doublet, $t =$ triplet, $q =$ quartet, $m =$ multiplet and multiples thereof. The abbreviation Ph to denote phenyl, br to denote broad.

High resolution mass spectrometry (HRMS, m/z) data was acquired either at Cardiff University on a Micromass LCT spectrometer or at the EPSRC UK National Mass Spectrometry Facility at Swansea University.
2. Experimental and characterization data

2.1. Synthesis of substrates

2.1.1. General procedure 1

\[
\begin{array}{c}
\text{R} \quad \text{O} \\
\text{LiAlH}_4 (3 \text{ equiv.}) \\
\text{R'} \\
\text{OH} \\
\text{rt, THF, 24h}
\end{array}
\]

Under nitrogen, a 100 mL round-bottomed equipped a magnetic stirrer bar was charged with LiAlH\(_4\) (342 mg, 9.0 mmol) and dry THF (10 mL). The suspension was cooled to 0 °C and was then charged with a solution of carboxylic acid or ethyl ester (3.0 mmol) in dry THF (5 mL). The mixture was left to stir at 0 °C for 10 minutes and at rt for 24 h. The mixture was quenched with H\(_2\)O (1 mL), 2 M NaOH (2 mL) and H\(_2\)O (3 mL). MgSO\(_4\) was added and the suspension was filtered. The filtrate was then concentrated in vacuo.

2-(naphthalen-2-yl)ethan-1-ol

The title compound was prepared according to general procedure 1 using 2-naphthaleneacetic acid (559 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 20% EtOAc in hexanes, 30 x 150 mm silica) gave the title compound as a white solid (438 mg, 86%); mp 68-70 °C (Lit. 65-66 °C);\(^6\) \(R_f = 0.53\) (eluent = 50% EtOAc in hexanes); \(v_{\text{max}} / \text{ cm}^{-1}\) (film) 3285, 3053, 3013, 2940, 2868, 1597, 1504, 1368, 1043, 1020, 827, 743, 731, 484; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta_H\): 1.46 (1H, br s), 3.04 (2H, t, \(J = 6.5\)), 3.95 (2H, t, \(J = 6.5\)), 7.37 (1H, dd, \(J = 8.0, 2.0\)), 7.41-7.51 (2H, m), 7.69 (1H, s), 7.76-7.86 (3H, m); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta_C\): 39.5, 63.7, 125.6, 126.2, 127.5, 127.6, 127.6, 127.8, 128.4, 132.4, 133.7, 136.1; HRMS (EI\(^+\)) calculated for [C\(_{12}\)H\(_{12}\)O]\(^+\) (M\(^+\)) m/z : 172.0888, found 172.0892 (+2.3 ppm).
The title compound was prepared according to general procedure 1 using 4-biphenylacetic acid (637 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 10-20% EtOAc in hexanes, 30 x 170 mm silica) gave the title compound as a white solid (330 mg, 56%); mp 96-98 °C (Lit. 96-97.5 °C); Rf = 0.53 (eluent = 50% EtOAc in hexanes); \( \nu_{\text{max}}/\text{cm}^{-1} \) (film) 3240, 3063, 3032, 2941, 2874, 1520, 1487, 1404, 1368, 1121, 1059, 1045, 1013, 822, 758, 745, 685, 581; \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta_H \): 1.43 (1H, br s), 2.93 (2H, t, \( J_6.5 \)), 3.92 (2H, t, \( J_6.5 \)), 7.28-7.38 (3H, m), 7.44 (2H, t, \( J_7.0 \)), 7.56 (2H, d, \( J_7.0 \)), 7.59 (2H, d, \( J_7.5 \)); \(^13\)C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta_C \): 39.0, 63.8, 127.2, 127.3, 127.5, 128.9, 129.6, 137.7, 139.6, 141.1; HRMS (EI\textsuperscript{+}) calculated for [C\textsubscript{14}H\textsubscript{14}O]\textsuperscript{+} (M)\textsuperscript{+} m/z: 198.1045, found 198.1045 (+0.0 ppm).
The title compound was prepared according to general procedure 1 using 4-phenoxyphenylacetic acid (685 mg, 3.0 mmol) in dry THF (5 mL). Purification by flash silica chromatography (eluent = 20% EtOAc in hexanes, 35 x 130 mm silica) gave the title compound as a colourless oil (300 mg, 47%); Rf = 0.16 (20% EtOAc in hexanes); v\text{max} / cm\(^{-1}\) (film) 3327, 3059, 3030, 2936, 2870, 1587, 1504, 1487, 1229, 1161, 1045, 1015, 868, 829, 750, 692, 507; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)H: 1.41 (1H, br s), 2.86 (2H, t, \(J\) 6.5), 3.87 (2H, t, \(J\) 6.5), 6.94-6.99 (2H, m), 6.98-7.03 (2H, m), 7.06-7.13 (1H, m), 7.16-7.22 (2H, m), 7.29-7.38 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\)C: 38.6, 63.9, 118.9, 119.2, 123.3, 129.9, 130.4, 133.4, 156.0, 157.5; HRMS (ES\(^+\)) calculated for [C\(_{14}\)H\(_{13}\)O]\(^+\) ((M-H\(_2\)O)+H\(^+\)) m/z: 197.0966, found 197.0971 (+2.5 ppm).
2-(benzo[d][1,3]dioxol-5-yl)ethan-1-ol

The title compound was prepared according to general procedure 1 using 3,4-(methylenedioxy)phenylacetic acid (541 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 10-15% EtOAc in n-pentane, 30 x 180 mm silica) gave the title compound as a pale yellow oil (294 mg, 59%); R<sub>f</sub> = 0.50 (eluent = 50% EtOAc in hexanes); ν<sub>max</sub> / cm<sup>-1</sup> (film) 3341, 2941, 2882, 2779, 1501, 1483, 1441, 1242, 1184, 1034, 924, 810; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 1.39 (1H, br s), 2.79 (2H, t, J 6.5), 3.82 (2H, t, J 6.5), 5.93 (2H, s), 6.68 (1H, d, J 8.0), 6.72 (1H, s), 6.76 (1H, d, J 8.0); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 39.0, 63.9, 101.0, 108.5, 109.5, 122.1, 132.3, 146.3, 147.9; HRMS (EI) calculated for [C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>]<sup>+</sup> (M)<sup>+</sup> m/z : 166.0630, found 166.0638 (+4.8 ppm).
The title compound was prepared according to general procedure 1 using 4-(trifluoromethyl)phenylacetic acid (613 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 30 x 150 mm silica) gave the title compound as a colourless oil (428 mg, 75%); \( R_f = 0.33 \) (eluent = 30% EtOAc in hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta_H \): 1.41 (1H, br s), 2.93 (2H, t, \( J = 6.5 \)), 3.90 (2H, t, \( J = 6.5 \), CH\(_2\)OH), 7.36 (2H, d, \( J = 8.0 \)), 7.57 (2H, d, \( J = 8.0 \)); \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \( \delta_F \): -62.4; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C \): 39.1, 63.4, 124.4 (q, \( J = 272 \)), 125.6 (q, \( J = 3.8 \), 129.0 (q, \( J = 32.5 \)), 129.5, 143.0. Spectroscopic data in accordance with the literature.

2-(4-(trifluoromethyl)phenyl)ethan-1-ol

![Chemical structure of 2-(4-(trifluoromethyl)phenyl)ethan-1-ol](image)
The title compound was prepared according to general procedure 1 using 2-(3,5-bis(trifluoromethyl)phenyl)acetic acid (817 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 5-15% EtOAc in n-pentane, 30 x 180 mm silica) gave the title compound as a white solid (459 mg, 59%); mp 54-56 °C (Lit. 54-56 °C); Rf = 0.63 (eluent = 50% EtOAc in hexanes); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3343, 2965, 2920, 1624, 1379, 1271, 1157, 1111, 1030, 899, 837, 704, 683; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta_H \): 1.47 (1H, br s), 3.00 (2H, t, \( J = 6.0 \)), 3.94 (2H, t, \( J = 6.0 \)), 7.71 (2H, s), 7.76 (1H, s); \(^19\)F NMR (471 MHz, CDCl\(_3\)) \( \delta_F \): -62.8; \(^13\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C \): 38.7, 62.9, 120.7, 123.5 (q, \( J = 273.2 \)), 129.4 (m), 131.8 (q, \( J = 33.1 \)), 141.6; HRMS (EI\(^+\)) calculated for [C\(_{10}\)H\(_8\)OF\(_6\)]\(^+\) (M)\(^+\) m/z: 258.0479, found 258.0477 (-0.8 ppm).
The title compound was prepared according to general procedure 1 using ethyl-3-pyridylacetate (456 µL, 495.6 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 5% MeOH in CH₂Cl₂, 30 x 150 mm silica) gave the title compound as a pale yellow oil (247 mg, 66%); Rf = 0.17 (eluent = 50% EtOAc in hexanes); **¹H NMR (500 MHz, CDCl₃)** δ_H: 2.07 (1H, br s), 2.87 (2H, t, J 6.5), 3.88 (2H, t, J 6.5), 7.23 (1H, ddd, J 7.5, 4.5, 1.0), 7.57 (1H, ddd, J 8.0, 2.5, 1.5), 8.44 (1H, dd, J 5.0, 1.5), 8.50 (1H, d, J 2.5); **¹³C NMR (126 MHz, CDCl₃)** δ_C: 36.4, 63.3, 123.6, 134.4, 136.7, 148.0, 150.4. Spectroscopic data in accordance with that stated in the literature.⁷

2-(pyridin-3-yl)ethan-1-ol

![NMR Spectrogram](image-url)
2-(furan-2-yl)ethan-1-ol

Under nitrogen, a flame dried 100 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with furan (1.45 mL, 1.36 g, 20 mmol), THF (20 mL) and n-BuLi (11 mL, 20 mmol, 1.8 M in hexanes). The solution was cooled to -15 °C and charged with dropwise addition of ethylene oxide (8 mL, 24 mmol, 3.0 M in THF). The mixture was left to react for 1 h at -15 °C, and 16 h at rt. It was then quenched with sat. aq. NH₄Cl (10 mL) and water (50 mL). The mixture was washed with EtOAc (10 mL) and transferred to a separatory funnel filled with EtOAc (50 mL). The organic layer was collected, the aqueous layer was washed with EtOAc (2 x 50 mL). The organics were combined, washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 40 x 100 mm silica) gave the title compound as a yellow oil (859 mg, 38%); Rf = 0.41 (eluent = 25% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δH: 1.59 (1H, m), 2.91 (2H, t, J 6.5), 3.84-3.92 (2H, m), 6.10-6.13 (1H, m), 6.31 (1H, dd, J 9.0, 1.5), 7.34 (1H, dd, J 2.0, 1.0); ¹³C NMR (126 MHz, CDCl₃) δC: 31.7, 61.3, 106.7, 110.4, 141.7, 153.0. Spectroscopic data in accordance with that stated in the literature.
A 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 4’-(trifluoromethyl)acetophenone (753 mg, 4.0 mmol) and MeOH (10 mL). The solution was cooled to 0 °C and was charged with NaBH₄ (228 mg, 6.0 mmol). The mixture was left stirring for 3 h at rt. The mixture was quenched with sat. aq. NH₄Cl (2 mL) and H₂O (5 mL). EtOAc (25 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was collected. The aqueous phase was washed EtOAc (2 x 25 mL). The organics were combined, dried over MgSO₄ filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 x 110 mm silica) gave the title compound as a colourless oil (569 mg, 75%); Rf = 0.28 (eluent = 10% EtOAc in n-pentane); ¹H NMR (500 MHz, CDCl₃) δH: 1.51 (3H, d, J 6.5), 1.87 (2H, d, J 3.0), 4.97 (1H, dq, J 6.5, 3.0), 7.46-7.52 (2H, m), 7.58-7.64 (2H, m); ¹⁹F NMR (471 MHz, CDCl₃) δF: -62.5; ¹³C NMR (126 MHz, CDCl₃) δC: 25.6, 70.0, 124.3 (q, J 272), 125.6 (q, J 3.8), 125.8, 129.8 (q, J 32.4), 149.8 (m). Spectroscopic data in accordance with that stated in the literature.⁹
1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol

A flame dried round-bottomed flask equipped with a magnetic stirrer bar was charged with 3',5'-bis(trifluoromethyl)benzaldehyde (660 µL, 968.5 mg, 4.0 mmol) and THF (6 mL). The solution was cooled to 0 °C and was then charged with MeMgBr (1.6 mL, 4.8 mmol, 3M in Et₂O). The mixture was then left to reach rt and was left to stir for 16h. The mixture was quenched with sat aq. NH₄Cl (2 mL) and H₂O (5 mL). EtOAc (25 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was collected. The aqueous layer was washed with EtOAc (2 x 25 mL). The organics were combined, washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification by flash silica chromatography (eluent = 5% EtOAc in n-pentane, 30 x 150 mm silica) gave the title compound as a white solid (420 mg, 41%); mp 72-75 °C (Lit. 74 °C); Rᵣ = 0.41 (eluent = 10% EtOAc in n-pentane); \(^1\)H NMR (500 MHz, CDCl₃) δH: 1.55 (3H, d, J 6.5), 1.99 (1H, br s), 5.05 (1H, q, J 6.5), 7.79 (1H, s), 7.82-7.87 (2H, s); \(^{19}\)F NMR (471 MHz, CDCl₃) δF: -62.5; \(^{13}\)C NMR (126 MHz, CDCl₃) δC: 25.8, 69.4, 121.5 (m), 123.5 (q, J 271), 125.8 (m), 131.9 (q, J 33.3), 148.3. Spectroscopic data in accordance with that stated in the literature.\(^{11}\)
A flame dried round-bottomed flask equipped with a magnetic stirrer bar was charged with 4'-
(trifluoromethyl)benzaldehyde (410 µL, 522 mg, 3.0 mmol) and THF (6 mL). The solution was cooled
to 0 °C and was then charged with EtMgBr (1.2 mL, 3.6 mmol, 3M in Et₂O). The mixture was then left
to reach rt and was left to stir for 16h. The mixture was quenched with sat aq. NH₄Cl (2 mL) and H₂O
(5 mL). EtOAc (25 mL) was added and the mixture was transferred to a separatory funnel. The organic
layer was collected. The aqueous layer was washed with EtOAc (2 x 25 mL). The organics were
combined, washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification by flash
silica chromatography (eluent = 10% EtOAc in hexanes, 30 x 150 mm silica) gave the title compound
as a colourless oil (344 mg, 56%); \( R_f = 0.38 \) (eluent = 10% EtOAc in n-pentane); \(^1\)H NMR (500 MHz,
CDCl₃) \( \delta_H: 0.93 \) (3H, t, \( J = 7.5 \)), 1.70-1.87 (2H, m), 1.89-1.94 (1H, m), 4.69 (1H, dt,
\( J = 6.5, 3.5 \)), 7.46 (2H, d, \( J = 8.0 \)), 7.61 (2H, d, \( J = 8.0 \)); \(^1\)F NMR (471 MHz, CDCl₃) \( \delta_F: -62.5 \); \(^13\)C NMR (126 MHz, CDCl₃) \( \delta_C: 10.0, 32.2, 75.4, 124.3 \) (q, \( J = 272 \)), 125.5 (q, \( J = 3.8 \)), 126.4, 129.8 (q, \( J = 32.4 \)), 148.7 (m). Spectroscopic data in
accordance with that stated in the literature.\(^\dagger\)
A flame dried round-bottomed flask equipped with a magnetic stirrer bar was charged with 3',5'-((bistrifluoromethyl)benzaldehyde (494 µL, 726 mg, 3.0 mmol) and THF (6 mL). The solution was cooled to 0 °C and was then charged with EtMgBr (1.2 mL, 3.6 mmol, 3 M in Et₂O). The mixture was then left to reach rt and was left to stir for 16h. The mixture was quenched with sat aq. NH₄Cl (2 mL) and H₂O (5 mL). EtOAc (25 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was collected. The aqueous layer was washed with EtOAc (2 x 25 mL). The organics were combined, washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 30 x 150 mm silica) gave the title compound as a white solid (349 mg, 43%); mp 94-96 °C; Rf = 0.55 (eluent = 10% EtOAc in n-pentane); ν∕cm⁻¹ (film) 3277, 3192, 1646, 1382, 1350, 1275, 1159, 1113, 1049, 982, 937, 901, 862, 843, 739, 704, 683, 671; ^1H NMR (500 MHz, CDCl₃) δ_H: 0.97 (3H, t, J 7.5), 1.75-1.87 (2H, m), 2.03 (1H, d, J 3,5), 4.78 (1H, dt, J 6.5, 3.5), 7.79 (1H, s), 7.82 (2H, s); ^19F NMR (471 MHz, CDCl₃) δ_F: -62.8; ^13C NMR (126 MHz, CDCl₃) δ_C: 9.9, 32.4, 74.8, 121.5, 123.5 (q, J 273), 126.3 (m), 131.8 (q, J 33.4), 147.2. HRMS (EI⁺) calculated for [C₁₁H₁₀OF₆]⁺ (M) m/z : 272.0636, found 272.0627 (-3.3 ppm).
A 100 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 2-phenoxy-1-phenylethan-1-one (1.27 g, 6.0 mmol) and MeOH (15 mL). The solution was cooled to 0 °C and was then charged with NaBH$_4$ (340 mg, 9.0 mmol) portion wise. The mixture was left stirring for 16 h at rt. The mixture was quenched with sat. aq. NH$_4$Cl (5 mL) and H$_2$O (10 mL). EtOAc (50 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was collected. The aqueous phase was washed EtOAc (2 x 50 mL). The organics were combined, dried over MgSO$_4$ filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 40 x 120 mm silica) gave the title compound as a white solid (1.17 g, 91%); mp 61-63 °C (Lit. 62-64 °C).$^{14}$ Rf = 0.36 (20% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.81 (1H, s), 4.02 (1H, dd, $J$ 9.5, 9.0), 4.12 (1H, dd, $J$ 9.0, 3.0), 5.14 (1H, dd, $J$ 9.0, 3.0), 6.90-6.96 (2H, m), 6.96-7.02 (1H, m), 7.27-7.33 (2H, m), 7.32-7.38 (1H, m), 7.38-7.44 (2H, m), 7.44-7.40 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 72.7, 73.4, 114.8, 121.4, 126.4, 128.3, 128.7, 129.7, 139.8, 158.5; Spectroscopic data in accordance with the literature.$^{14}$
**2,3-dihydro-1H-inden-2-ol**

A 50 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 2-indanone (661 mg, 5.0 mmol) and MeOH (25 mL). The solution was cooled to 0 °C and was charged with NaBH₄ (228 mg, 6.0 mmol). The mixture was left stirring for 3 h at rt. The mixture was quenched with sat. aq. NH₄Cl (2 mL) and H₂O (5 mL). EtOAc (25 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was collected. The aqueous phase was washed EtOAc (2 x 25 mL). The organics were combined, dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 50% EtOAc in hexanes, 30 x 110 mm silica) gave the title compound as a white solid (592 mg, 88%); mp 67-69 °C (Lit. 67-68 °C); Rf = 0.07 (eluent = 10% EtOAc in hexanes); νmax / cm⁻¹ (film) 3260, 2932, 1479, 1458, 1423, 1341, 1308, 1269, 1198, 1032, 1020, 051, 926, 735, 542, 417; ¹H NMR (500 MHz, CDCl₃) δH: 1.63 (1H, d, J 5.0), 2.92 (2H, dd, J 16.5, 3.0), 3.22 (2H, dd, J 16.5, 6.0), 4.66-4.76 (1H, m), 7.14-7.21 (2H, m), 7.21-7.29 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 42.8, 73.3, 125.1, 126.8, 140.9; HRMS (EI⁺) calculated for [C₉H₁₀O]⁺ (M)⁺ m/z: 134.0732, found 134.0732 (+0.0 ppm).
2.2. Optimization of iron-catalyzed β-C(sp³)-methylation

A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with base (x mmol), additive (x mol %), precatalyst (x mol %), MeOH (x mL) and 2-phenylethanol (60 μL, 61.1 mg, 0.5 mmol). The vial was sealed with a cap and was left to react at the specified temperature (°C) and time (h). It was then cooled, mesitylene (70 μL, 60.1 mg, 0.5 mmol) added, EtOAc (1 mL), sat. aq. NH₄Cl (0.5 mL) and H₂O (0.5 mL). In some cases brine (0.5 mL) was added to aid layer separation. The mixture was stirred for 5 minutes and left to settle for a further 5 minutes. The top layer was sampled and analysed using ¹H NMR.

| Entry | Cat. loading (mol %) | Additive (mol %) | Base (equiv) | Solvent | T (°C) | Time (h) | 3 (%)[^b] |
|-------|----------------------|------------------|-------------|---------|--------|----------|----------|
| 1     | -                    | -                | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 2     | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | 85 (75)  |
| 3     | [Fe] 4 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 4     | [Fe] 5 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 5     | [Fe] 6 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 6     | [Fe] 7 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 7     | [Fe] 8 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | < 2      |
| 8     | [Fe] 2 (5)           | -                | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | 81       |
| 9     | [Fe] 2 (5)           | PPh₃ (10)        | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | 76       |
| 10    | [Fe] 2 (5)           | Me₃NO (10)       | -           | MeOH (0.5 M) | 130    | 24       | < 2      |
| 11    | [Fe] 2 (5)           | Me₃NO (10)       | K₂CO₃ (2)   | MeOH (0.5 M) | 130    | 24       | 75       |
| 12    | [Fe] 2 (5)           | Me₃NO (10)       | KOt-Bu (2)  | MeOH (0.5 M) | 130    | 24       | 80       |
| 13    | [Fe] 2 (5)           | Me₃NO (10)       | Cs₂CO₃ (2)  | MeOH (0.5 M) | 130    | 24       | 54       |
| 14    | [Fe] 2 (5)           | Me₃NO (10)       | KOH (2)     | MeOH (0.5 M) | 130    | 24       | 75       |
| 15    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (0.2)  | MeOH (0.5 M) | 130    | 24       | 75       |
| 16    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (4)    | MeOH (0.5 M) | 130    | 24       | 66       |
| 17    | [Fe] 2 (10)          | Me₃NO (20)       | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | 73       |
| 18    | [Fe] 2 (2)           | Me₃NO (4)        | NaOH (2)    | MeOH (0.5 M) | 130    | 24       | 62       |
| 19    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 140    | 24       | 79       |
| 20    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 120    | 24       | 64       |
| 21    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (1 M)  | 130    | 24       | 69       |
| 22    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.25 M) | 130    | 24       | 57       |
| 23    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH/PhMe (0.5 M) | 130 | 24 | 72 |
| 24    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 6        | 70       |
| 25    | [Fe] 2 (5)           | Me₃NO (10)       | NaOH (2)    | MeOH (0.5 M) | 130    | 48       | 81       |

[^a]: Reactions performed using 1 (0.5 mmol) and reagent grade MeOH. [¹] = 0.5 M. [^b]: Yield after 24 h as determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. Isolated yield given in parentheses.
2.3. Substrate scope

2.3.1. General procedure 2

A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40 mg, 1 mmol), Me$_3$NO.2H$_2$O (5.6 mg, 0.1 mmol, 10 mol %), [Fe] precatalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), MeOH (1 mL) and alcohol (0.5 mmol). The vial was sealed with a cap and was left to stir at 130 °C for 24 hours. It was then cooled, treated with sat. aq. NH$_4$Cl (0.5 mL) and H$_2$O (0.5 mL), washed with EtOAc (15 mL) and transferred to a separatory funnel filled with brine (15 mL). The organic layer was collected and the aqueous phase washed with EtOAc (2 x 15 mL). The organics were combined, dried over MgSO$_4$, filtered and concentrated in vacuo.

2-phenylpropan-1-ol

The title compound was prepared according to general procedure 2 using 2-phenylethanol (60 µL, 61 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (51 mg, 75%); R$_f$ = 0.28 (20% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H: 1.29 (3H, d, $J$ 7.0), 2.96 (1H, sext, $J$ 7.0), 3.71 (2H, d, $J$ 7.0), 7.21 - 7.27 (3H, m), 7.30 - 7.37 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C: 17.7, 42.6, 68.9, 126.8, 127.6, 128.8, 143.8. Spectroscopic data in accordance with the literature.$^{16}$

10 mmol Scale

An ACE pressure tube rated at 150 PSI was charged with NaOH (800 mg, 20.0 mmol), Me$_3$NO.2H$_2$O (111 mg, 1.0 mmol) and [Fe] precatalyst 2 (228 mg, 0.5 mmol). The vessel was charged with MeOH (20 mL) and 2-phenylethanol (1.20 mL, 1.22 g, 10.0 mmol). It was sealed with the appropriate screw top cap, placed in an oil bath behind a blast shield, and the mixture was left to react at 130 °C for 24 hours. It was then cooled and charged with sat aq. NH$_4$Cl (10 mL), EtOAc (20 mL) and H$_2$O (10 mL). The mixture was transferred to a separatory funnel filled with brine (50 mL). The organic layer was collected and the aqueous phase washed with EtOAc (2 x 50 mL). The organics were combined, dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent
= 5-10% EtOAc in pet. ether, 40 x 220 mm silica) gave a colourless oil (1.02 g, 76%). Spectroscopic data in accordance with that reported previously.
The title compound was prepared according to general procedure 2 using 4-methylphenethyl alcohol (70 µL, 68 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (46 mg, 61%); Rf = 0.47 (eluent = 30% EtOAc in hexanes); νmax / cm⁻¹ (film) 3335, 3019, 2963, 2920, 2864, 1514, 1449, 1034, 1011, 816, 721, 556, 527; ¹H NMR (500 MHz, CDCl₃) δH: 1.26 (3H, d, J 7.0), 1.30 (1H, br s), 2.33 (3H, s), 2.92 (1H, sext, J 7.0), 3.68 (2H, d, J 7.0), 7.14 (4H, s); ¹³C NMR (126 MHz, CDCl₃) δC: 17.8, 21.1, 42.4, 68.9, 127.5, 129.5, 136.4, 140.7; HRMS (EI⁺) calculated for [C₁₀H₁₄O]⁺ (M)⁺ m/z: 150.1045, found 150.1047 (+1.3 ppm).
The title compound was prepared according to general procedure 2 using 3-methylphenethyl alcohol (68 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (49 mg, 65%); Rf = 0.47 (eluent = 30% EtOAc in hexanes); νmax / cm⁻¹ (film) 3329, 3015, 2961, 2928, 2868, 1491, 1460, 1383, 1030, 1011, 756, 723, 451; ¹H NMR (500 MHz, CDCl₃) δH: 1.27 (3H, d, J = 7.0), 1.29 (1H, t, J = 6.0), 2.35 (3H, s), 2.93 (1H, sext, J = 7.0), 3.70 (2H, t, J = 6.0), 7.01-7.09 (3H, m), 7.19-7.25 (1H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 17.8, 21.6, 42.5, 68.9, 124.6, 127.6, 128.4, 128.7, 138.4, 143.7; HRMS (EI⁺) calculated for [C₁₀H₁₄O]⁺ (M)⁺ m/z: 150.1045, found 150.1045 (+0.0 ppm).
1-(o-tolyl)propan-1-ol

The title compound was prepared according to general procedure 2 using 2-(o-tolyl)-1-ethanol (68 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (30 mg, 40%); R<sub>f</sub> = 0.43 (eluent = 30% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 1.25 (3H, d, <i>J</i> 7.0), 1.38 (1H, br s), 2.37 (3H, s), 3.27 (1H, sext, <i>J</i> 7.0), 3.70 (1H, dd, <i>J</i> 11.0, 6.5), 3.76 (1H, dd, <i>J</i> 11.0, 7.0), 7.09-7.24 (4H, m); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 17.7, 19.8, 37.3, 68.2, 125.6, 126.4, 126.5, 130.7, 136.6, 141.8. Spectroscopic data in accordance with that stated in the literature.\textsuperscript{16}
The title compound was prepared according to general procedure 2 using 2-(naphthalen-1-yl)ethan-2-ol (83 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a white solid (77 mg, 82%); mp 64-66 °C (Lit. 60 °C); \( R_f = 0.40 \) (eluent = 30% EtOAc in hexanes); \( v_{\text{max}} \) / cm\(^{-1}\) (film) 3279, 3051, 2968, 2916, 2851, 1597, 1504, 1452, 1369, 1032, 1007, 853, 816, 741, 478; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta_H \): 1.35 (1H, br s), 1.38 (3H, d, \( J = 7.0 \)), 3.14 (1H, sext, \( J = 7.0 \)), 3.80 (2H, d, \( J = 6.5 \)), 7.39 (1H, d, \( J = 8.5 \)), 7.46 (2H, quint, \( J = 7.5 \)), 7.69 (1H, s), 7.76-7.88 (3H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C \): 17.7, 42.7, 68.7, 125.7, 125.9, 126.2, 126.2, 127.8, 127.8, 128.5, 132.6, 133.7, 141.2; HRMS (EI\(^+\)) calculated for [C\(_{13}\)H\(_{14}\)O]\(^+\) (M)\(^+\) m/z: 186.1045, found 186.1045 (+0.0 ppm).
The title compound was prepared according to general procedure 2 using 2-(naphthalen-1-yl)ethan-1-ol (83 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (59 mg, 63%); $R_f = 0.40$ (eluent = 30% EtOAc in hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)) $\delta$: 1.40 (1H, br s), 1.45 (3H, d, $J = 6.5$), 3.78-4.02 (3H, m), 7.43 (1H, d, $J = 7.0$), 7.45-7.58 (3H, m), 7.76 (1H, d, $J = 8.0$), 7.88 (1H, d, $J = 8.0$), 8.16 (1H, d, $J = 8.5$); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) $\delta$: 18.0, 36.5, 68.3, 123.2, 123.2, 125.7, 125.7, 126.2, 127.2, 129.1, 132.1, 134.2, 139.7. Spectroscopic data in accordance with that stated in the literature.\(^{16}\)
The title compound was prepared according to general procedure 2 using 2-[[1,1'-biphenyl]-4-yl]ethan-1-ol (99 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 220 mm silica) gave the title compound as an off-white solid (91 mg, 86%); mp 64-66 °C; Rf = 0.63 (eluent = 50% EtOAc in hexanes); νmax / cm⁻¹ (film) 3269, 3055, 3028, 2972, 2941, 2901, 2859, 1707, 1485, 1362, 1256, 1229, 1180, 1030, 1003, 833, 816, 760, 727, 689, 673; ¹H NMR (500 MHz, CDCl₃) δH: 1.32 (3H, d, J = 7.0), 3.02 (1H, sext, J = 7.0), 3.76 (2H, d, J = 7.0), 7.30-7.37 (3H, m), 7.41-7.47 (2H, m), 7.54-7.61 (4H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 17.8, 42.3, 68.9, 127.2, 127.3, 127.5, 128.0, 128.9, 139.8, 141.1, 142.9; HRMS (AP⁺) calculated for [C₁₅H₁₅]⁺ ((M-H₂O)+H)⁺ m/z: 195.1174, found 195.1173 (-0.5 ppm).
The title compound was prepared according to general procedure 2 using 4-methoxyphenethyl alcohol (76 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (48 mg, 57%); Rf = 0.33 (eluent = 30% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H: 1.25 (3H, d, J 7.0), 1.30 (1H, br s), 2.91 (1H, sext, J 7.0), 3.60-3.72 (2H, m), 3.80 (3H, s), 6.88 (2H, d, J 8.0), 7.16 (2H, d, J 8.0); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C: 17.9, 41.7, 55.4, 69.0, 114.2, 128.5, 135.7, 158.5. Spectroscopic data in accordance with that stated in the literature.$^{16}$
The title compound was prepared according to general procedure 2 using 2-(4-phenoxyphenyl)ethan-1-ol (107 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 20% EtOAc in hexanes, 20 x 220 mm silica) gave the title compound as an colourless oil (92 mg, 81%); \( R_f = 0.20 \) (20% EtOAc in hexanes); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3327, 3036, 2961, 2920, 2870, 1587, 1504, 1489, 1234, 1198, 1167, 1036, 1009, 868, 835, 754, 691; \(^1\text{H NMR (500 MHz, CDCl}_3\text{)}\) \( \delta_H \): 1.28 (3H, d, \( J = 7.0 \)), 1.32 (1H, br s), 2.95 (1H, sext, \( J = 7.0 \)), 3.64-3.75 (2H, m), 6.96-7.00 (2H, m), 6.99-7.03 (2H, m), 7.07-7.13 (1H, m), 7.17-7.23 (2H, m), 7.30-7.37 (2H, m); \(^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}\) \( \delta_C \): 17.9, 41.9, 68.9, 118.9, 119.2, 123.3, 128.8, 129.9, 138.6, 156.1, 157.4; HRMS (ES\(^+\)) calculated for [C\(_{15}\)H\(_{15}\)O\(^+\)] \((\text{M-H}_2\text{O}+\text{H})^+\) m/z: 211.1123, found 211.1128 (+2.4 ppm).
2-(4-(benzyl oxy)phenyl)propan-1-ol

The title compound was prepared according to general procedure 2 using 4-benzyl oxyphenethyl alcohol (114 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a white solid (90 mg, 74%); mp 52-54 °C; Rf = 0.33 (eluent = 30% EtOAc in hexanes); νmax / cm⁻¹ (film) 3256, 3034, 2980, 2882, 1611, 1508, 1447, 1379, 1242, 1179, 1013, 833, 731, 694, 546. ¹H NMR (500 MHz, CDCl₃) δH: 1.25 (3H, d, J 6.5), 1.29 (1H, br s), 2.91 (1H, sext, 7.0), 3.60-3.73 (2H, m), 5.05 (2H, s), 6.95 (2H, d, J 8.0), 7.16 (2H, d, J 8.0), 7.32 (1H, t, J 7.5), 7.39 (2H, t, J 7.5), 7.43 (2H, d, J 7.5); ¹³C NMR (126 MHz, CDCl₃) δC: 17.9, 41.7, 69.0, 70.2, 115.1, 127.6, 128.1, 128.6, 128.7, 136.0, 137.2, 157.8; HRMS (EI⁺) calculated for [C₁₆H₁₈O₂]⁺ (M)+ m/z: 242.1307 found 242.1312 (+2.1 ppm).
The title compound was prepared according to general procedure 2 using 2-(benzo[d][1,3]dioxol-5-yl)ethan-1-ol (83 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 20% Et₂O in n-pentane, 20 x 220 mm silica) gave the title compound as a pale-yellow oil (66 mg, 73%); Rf = 0.20 (20% EtOAc in hexanes); νmax / cm⁻¹ (film) 3360, 2961, 2874, 1501, 1483, 1439, 1240, 1186, 1011, 935, 916, 860, 806, 637; ¹H NMR (500 MHz, CDCl₃) δH: 1.23 (3H, d, J 7.0), 1.33 (1H, br s), 2.89 (1H, sext, J 7.0), 3.56-3.74 (2H, m), 5.94 (1H, d, J 8.0), 6.07 (1H, d, J 8.0), 6.74 (1H, s), 6.77 (1H, d, J 8.0); ¹³C NMR (126 MHz, CDCl₃) δC: 17.9, 42.3, 68.9, 101.0, 107.7, 108.5, 120.7, 137.7, 146.4, 148.0; HRMS (EI⁺) calculated for [C₁₀H₁₂O₃]⁺ (M)⁺ m/z: 180.0786, found 180.0789 (+1.7 ppm).
The title compound was prepared according to general procedure 2 using 4-aminophenethyl alcohol (69 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 20-50% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a pale-yellow oil (43 mg, 52%); Rf = 0.08 (20% EtOAc in hexanes); νmax / cm⁻¹ (film) 3404, 3347, 2961, 2920, 2876, 2805, 1612, 1522, 1315, 1256, 1180, 1034, 1015, 1003, 820; ¹H NMR (500 MHz, CDCl₃) δ: 1.23 (3H, d, J 7.0), 2.79-2.90 (4H, m), 3.58-3.70 (2H, m), 6.58-6.64 (2H, m), 7.04-7.10 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ: 17.9, 31.0, 41.7, 69.0, 112.9, 128.4, 132.0, 148.3; HRMS [EI⁺] calculated for [C₁₀H₁₅NO]⁺ (M)⁺ m/z: 165.1154, found 165.1152 (-1.2 ppm).
The title compound was prepared according to general procedure 2 using 4-(trifluoromethyl)phenethyl alcohol (76 µL, 95 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (82 mg, 80%); Rf = 0.43 (eluent = 30% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H: 1.30 (3H, d, J 7.0), 1.34 (1H, br s), 3.03 (1H, sext, J 7.0), 3.75 (2H, d, J 6.5), 7.36 (2H, d, J 7.5), 7.59 (2H, d, J 8.0); $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$F: -62.4; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C: 17.6, 42.5, 68.5, 124.4 (q, J 272), 125.7 (q, J 3.8), 128.0, 129.1 (q, J 32.5), 148.2 (m). Spectroscopic data in accordance with the literature.$^{16}$

2-(4-(trifluoromethyl)phenyl)propan-1-ol
The title compound was prepared according to general procedure 2 using 2-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol (136 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 20% Et₂O in n-pentane, 20 x 140 mm silica) gave the title compound as a colourless oil (119 mg, 88%); R<sub>f</sub> = 0.28 (20% EtOAc in hexanes); ν<sub>max</sub> / cm<sup>-1</sup> (film) 3337, 2976, 2930, 2882, 1470, 1381, 1344, 1273, 1165, 1119, 1076, 1030, 978, 893, 847, 721, 704, 679; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 1.34 (3H, d, J<sub>7.5</sub>), 1.42 (1H, br s), 3.11 (1H, sext, J<sub>7.0</sub>), 3.71-3.85 (2H, m), 7.70 (2H, s), 7.76 (1H, s); <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ<sub>F</sub>: -62.8; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 17.5, 42.3, 68.0, 120.8 (sept, J<sub>3.8</sub>), 123.5 (q, J<sub>272.9</sub>), 127.9 (m), 131.8 (q, J 33.1), 146.8; HRMS (EI<sup>+</sup>) calculated for [C<sub>11</sub>H<sub>10</sub>OF<sub>6</sub>]<sup>+</sup> (M)<sup>+</sup> m/z: 272.0636, found 272.0627 (-3.3 ppm).
The title compound was prepared according to general procedure 2 using 2-(trifluoromethyl)phenethyl alcohol (79 µL, 95 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 15% Et₂O in n-pentane, 20 x 210 mm silica) gave the title compound as a colourless oil (23 mg, 23%); Rᵋ = 0.16 (eluent = 20% Et₂O in n-pentane); νₓₓₙₓ max / cm⁻¹ (film) 3021, 2953, 2880, 1605, 1456, 1312, 1157, 1109, 1059, 1038, 770, 743, 652, 515; ¹H NMR (500 MHz, CDCl₃) δₓ: 1.30 (3H, d, J 7.0), 1.37 (1H, br s), 3.42 (1H, dsext, J 7.0, 1.0), 3.69-3.77 (1H, m), 3.78-3.86 (1H, m), 7.32 (1H, t, J 7.5), 7.46 (1H, d, J 7.5), 7.54 (1H, d, J 7.5), 7.65 (1H, d, J 7.5); ¹⁹F NMR (471 MHz, CDCl₃) δₓ: -58.5; ¹³C NMR (126 MHz, CDCl₃) δₓ: 18.7, 37.6 (m), 68.2, 124.7 (q, J 274), 126.1 (q, J 5.9), 126.5, 127.8, 129.0 (q, J 29.2), 132.2 (m), 143.3 (m); HRMS (El⁺) calculated for [C₁₀H₁₁OF₃]⁺ (m)⁺ m/z : 204.0762, found 204.0763 (+0.5 ppm).
The title compound was prepared according to general procedure 2 using 2-(4-bromophenyl)ethan-1-ol (70 µL, 101 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (73 mg, 68%); R_f = 0.60 (eluent = 50% EtOAc in hexanes); ν_max / cm⁻¹ (film) 3321, 2963, 2922, 2874, 1487, 1449, 1406, 1076, 1038, 1007, 816, 714, 550, 519. ¹H NMR (500 MHz, CDCl₃) δ_H: 1.26 (3H, d, J 7.0), 2.92 (1H, sext, J 7.0), 3.64-3.73 (2H, m), 7.09-7.15 (2H, m), 7.42-7.48 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ_C: 17.6, 42.1, 68.6, 120.5, 129.4, 131.8, 142.9; HRMS (EI⁺) calculated for [C₉H₁₁OBr⁺] (M)⁺ m/z: 213.0993, found 213.0995 (+0.9 ppm).
The title compound was prepared according to general procedure 2 using 4-chlorophenethyl alcohol (68 µL, 78 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (69 mg, 81%); Rf = 0.40 (eluent = 30% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl$_3$) δ$_H$: 1.26 (3H, d, $J$ 7.0), 1.31 (1H, br s), 2.94 (1H, sext, $J$ 7.0), 3.63-3.75 (2H, m), 7.18 (2H, d, $J$ 8.0), 7.30 (2H, d, $J$ 8.0); $^{13}$C NMR (126 MHz, CDCl$_3$) δ$_C$: 17.7, 42.0, 68.7, 128.9, 129.0, 132.5, 142.4. Spectroscopic data in accordance with that stated in the literature.$^{16}$
The title compound was prepared according to general procedure 2 using 4-fluorophenethyl alcohol (63 µL, 70 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (60 mg, 77%); Rf = 0.37 (eluent = 30% EtOAc in hexanes); $v_{\text{max}}$ / cm$^{-1}$ (film) 3327, 2961, 2930, 2876, 1601, 1512, 1221, 1159, 1034, 1011, 827, 550, 527; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H: 1.26 (3H, d, $J$ 7.0), 1.30 (1H, br s), 2.94 (1H, sext, $J$ 7.0), 3.62-3.74 (2H, m), 7.02 (2H, t, $J$ 8.5) 7.20 (2H, dd, $J$ 8.0, 5.5); $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$F: -116.6; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C: 17.9, 41.8, 68.8, 115.5 (d, $J$ 21.0), 129.0 (d, $J$ 7.9), 139.5, (d, $J$ 5.4), 161.8 (d, $J$ 244); HRMS (EI$^+$) calculated for [C$_9$H$_{11}$OF]$^+$ (M)$^+$ m/z: 154.0794, found 154.0791 (-1.9 ppm).
The title compound was prepared according to general procedure 2 using tryptophol (80 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 25% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a pale-yellow oil (49 mg, 56%); R₂ = 0.13 (eluent = 30% EtOAc in hexanes). v_{\text{max}}/\text{cm}^{-1} (film) 3545, 3402, 3283, 3055, 2963, 2926, 2870, 1454, 1341, 1221, 1090, 1020, 1005, 731. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ\textsubscript{H}: 1.38 (1H, br s), 1.41 (3H, d, J = 7.0), 3.32 (1H, sext, J = 6.5), 3.76 - 3.89 (2H, m), 7.07 (1H, s), 7.13 (1H, t, J = 7.5), 7.21 (1H, t, J = 7.5), 7.38 (1H, d, J = 8.0), 7.67 (1H, d, J = 8.0), 8.05 (1H, br s); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ\textsubscript{C}: 17.4, 34.1, 68.1, 111.4, 118.2, 119.4, 119.6, 121.3, 122.4, 126.9, 136.7; HRMS (EI\textsuperscript{+}) calculated for [C\textsubscript{10}H\textsubscript{13}NO]\textsuperscript{+} (M)\textsuperscript{+} m/z: 175.0997, found 175.1001 (+2.3 ppm).

2-(1H-indol-3-yl)propan-1-ol
2-(pyridin-3-yl)propan-1-ol

The title compound was prepared according to general procedure 2 using 2-(pyridin-3-yl)ethan-1-ol (62 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 60-70% EtOAc in hexanes, 20 x 180 mm silica) gave the title compound as a colourless oil (53 mg, 77%); Rf = 0.17 (eluuent = 50% EtOAc in hexanes); $\nu_{\text{max}}$ / cm$^{-1}$ (film) 3225, 2967, 2920, 2870, 1580, 1476, 1425, 1047, 1016, 810, 714, 635; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.31 (3H, d, $J$ 7.0), 2.99 (1H, sext, $J$ 7.0), 3.70-3.79 (2H, m), 7.23-7.28 (1H, m), 7.55-7.60 (1H, m), 8.47 (1H, dd, $J$ 5.0, 2.0), 8.50 (1H, d, $J$ 2.0); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 17.4, 40.2, 68.3, 123.7, 135.1, 139.4, 148.1, 149.5; HRMS (EI$^+$) calculated for [C$_8$H$_{11}$NO]$^+$ (M)$^+$ m/z: 137.0841, found 137.0836 (-3.6 ppm).
The title compound was prepared according to general procedure 2 using 2-(2-hydroxyethyl)pyridine (62 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 30-50% EtOAc in hexanes, 20 x 180 mm silica) gave the title compound as a colourless oil (40 mg, 65%); Rf = 0.17 (eluent = 50% EtOAc in hexanes); νmax / cm⁻¹ (film) 3269, 2972, 2926, 2870, 1593, 1570, 1476, 1439, 1150, 1045, 1018, 997, 783, 750, 629, 557, 536; ¹H NMR (500 MHz, CDCl₃) δH: 1.33 (3H, d, J = 7.0), 3.08 (1H, dquint, J = 7.0, 4.0), 3.84 (1H, dd, J = 11.0, 6.5), 3.94 (1H, dd, J = 10.5, 4.0), 7.16 (1H, ddd, J = 7.5, 5.0, 1.0), 7.65 (1H, dt, J = 7.5, 2.0), 8.50 (1H, ddd, J = 5.0, 2.0, 1.0); ¹³C NMR (126 MHz, CDCl₃) δC: 17.3, 42.0, 67.3, 121.7, 122.3, 137.0, 148.7, 165.1; HRMS (AP⁺) calculated for [C₈H₁₂NO⁺] (M+H)⁺ m/z: 138.0919, found 138.0922 (+2.2 ppm).
2-(furan-2-yl)propan-1-ol

The title compound was prepared according to general procedure 2 using 2-(furan-2-yl)ethan-1-ol (56 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 210 mm silica) gave the title compound as a colourless oil (31 mg, 50%); R_f = 0.42 (eluent = 25% EtOAc in hexanes); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ\textsubscript{H}: 1.27 (3H, d, J 7.0), 1.65 (1H, br s), 3.05 (1H, sext, J 7.0), 3.68-7.78 (2H, m), 6.09 (1H, dt, J 3.5, 1.0), 6.31 (1H, dd, J 3.5, 2.0), 7.34 (1H, dd, J 2.0, 1.0); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ\textsubscript{C}: 15.3, 36.3, 66.8, 105.3, 110.2, 141.5, 157.6. Spectroscopic data in accordance with that stated in the literature.\textsuperscript{18}
2-(thiophen-2-yl)propan-1-ol

The title compound was prepared according to general procedure 2 using 2-thiopheneethanol (56 µL, 64 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 x 200 mm silica) gave the title compound as a colourless oil (51 mg, 72%); R_f = 0.47 (eluent = 30% EtOAc in hexanes); ν_max / cm⁻¹ (film) 3356, 2963, 2934, 2874, 2835, 1611, 1512, 1458, 1300, 1244, 1177, 1032, 1018, 1001, 827, 806, 559, 538; ¹H NMR (500 MHz, CDCl₃) δ_H: 1.36 (3H, d, J 7.0), 1.51 (1H, br s), 3.26 (1H, sext, J 7.0), 3.63-3.78 (2H, m), 6.87-6.93 (1H, m), 6.94-7.02 (1H, m), 7.20 (1H, d, J 5.0); ¹³C NMR (126 MHz, CDCl₃) δ_C: 18.7, 38.3, 69.1, 123.7, 124.0, 127.0, 147.5; HRMS (EI⁺) calculated for [C₇H₁₀OS⁺] (M)⁺ m/z: 142.0452, found 142.0450 (-1.4 ppm).
2-methyl-3-phenylpropan-1-ol

The title compound was prepared according to general procedure 2 using 3-phenyl-1-propanol (68 µL, 68 mg, 0.5 mmol). The crude $^1$H NMR showed 9% conversion to 31 as shown in the below spectrum. The integrated peak corresponds to that stated in the literature.$^{19}$
2-methyl-1-phenylpropan-1-ol

The title compound was prepared according to general procedure 2 using 1-phenylethanol (60 µL, 61 mg, 0.5 mmol). The crude $^1$H NMR showed 11% conversion to 32 as shown in the below spectrum. The integrated peak corresponds to that stated in the literature.$^{20}$
2-methyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol

The title compound was prepared according to general procedure 2 using 1-(4-(trifluoromethyl)phenyl)ethan-1-ol (95 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 x 190 mm silica) gave the title compound as a colourless oil (31 mg, 28%); Rf = 0.52 (eluent = 10% EtOAc in n-pentane); νmax / cm⁻¹ (film) 3389, 2972, 2930, 2874, 1616, 1470, 1418, 1319, 1161, 1119, 1067, 1013, 837, 793, 611; ¹H NMR (500 MHz, CDCl₃) δH: 0.84 (3H, d, J 6.5), 0.97 (3H, d, J 6.5), 1.88 (1H, br s), 1.97 (1H, oct, J 6.5), 4.48 (1H, d, J 6.5), 7.44 (2H, d, J 8.0), 7.60 (2H, d, J 8.0); ¹⁹F NMR (471 MHz, CDCl₃) δF: -62.4; ¹³C NMR (126 MHz, CDCl₃) δC: 17.9, 19.0, 35.5, 79.3, 124.3 (q, J 272), 125.3 (q, J 3.8), 127.0, 129.7 (q, J 32.4), 147.6 (m); HRMS (EI⁺) calculated for [C₁₁H₁₃OF₃]⁺ (M)⁺ m/z : 218.0918, found 218.0914 (-1.4 ppm).
The title compound was prepared according to general procedure 2 using 1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol (129 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 x 190 mm silica) gave the title compound as a white solid (55 mg, 38%); mp 51-53 °C; Rf = 0.14 (eluent = 5% EtOAc in cyclohexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3389, 3325, 2972, 2926, 2895, 2855, 1472, 1379, 1329, 1275, 1159, 1117, 1103, 1034, 901, 847, 827, 710, 679, 664; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta_H \): 0.89 (3H, d, \( J = 7.0 \)), 0.95 (3H, d \( J = 6.5 \)), 1.90-2.08 (2H, m), 4.59 (1H, d, \( J = 6.0 \)), 7.79 (3H, s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C \): 17.3, 19.0, 35.5, 78.5, 121.4 (m), 123.5 (q, \( J = 273 \)), 126.8, 131.5 (q, \( J = 33.3 \)), 146.2; HRMS (EI) calculated for [C\(_{12}\)H\(_{12}\)OF\(_6\)]\(^+\) (M\(^+\) m/z : 286.0792, found 286.0783 (-3.1 ppm).
2-methyl-1-phenylpropan-1-ol

The title compound was prepared according to general procedure 2 using 1-phenyl-1-propanol (68 mg, 0.5 mmol). The crude $^1$H NMR showed 12% conversion to 35 as shown in the below spectrum. The integrated peak corresponds to that stated in the literature.  

2-methyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol

The title compound was prepared according to general procedure 2 using 1-(4-(trifluoromethyl)phenyl)propan-1-ol (102 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 x 190 mm silica) gave the title compound as a colourless oil (24 mg, 22%); $R_f = 0.52$ (eluent = 10% EtOAc in n-pentane). Spectroscopic data in accordance with that reported previously.
1-(3,5-bis(trifluoromethyl)phenyl)-2-methylpropan-1-ol

The title compound was prepared according to general procedure 2 using 1-(3,5-bis(trifluoromethyl)phenyl)propan-1-ol (136 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 x 190 mm silica) gave the title compound as a white solid (40 mg, 28%); mp 51-53 °C; Rf = 0.14 (eluent = 5% EtOAc in cyclohexane). Spectroscopic data in accordance with that reported previously.

2-phenoxy-1-phenylpropan-1-ol

The title compound was prepared according to general procedure 2 using 2-phenoxy-1-phenylethan-1-ol (107 mg, 0.5 mmol) giving the crude product after work up (2:1 dr). Purification by flash silica chromatography (eluent = 5% EtOAc in hexanes, 20 x 220 mm silica) gave the title compound as a colourless oil (36 mg, 30%, 56:44 dr); Rf = 0.44 (eluent = 20% EtOAc in hexanes); νₘₐₓ / cm⁻¹ (film) 3557, 3433, 3063, 3036, 2982, 2920, 1597, 1584, 1491, 1449, 1229, 1173, 1063, 993, 937, 883, 748, 692, 505;

Selected data for major diastereomer:

¹H NMR (500 MHz, CDCl₃) δH: 1.20 (3H, d, J 6.0), 2.51 (2H, d, J 3.0), 4.59 (1H, dq, J 6.0, 3.5), 5.06 (1H, t, J 3.0), 6.92-7.02 (3H, m), 7.27-7.41 (5H, m), 7.41-7.46 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 13.0, 75.2, 77.9, 116.4, 121.5, 126.4, 128.5, 129.8, 140.1, 157.5.

Selected data for minor diastereomer:

¹H NMR (500 MHz, CDCl₃) δH: 1.13 (3H, d, J 6.0), 3.05 (2H, d, J 2.0), 4.45 (1H, dq, J 7.5, 6.0), 4.71 (1H, dd, J 7.5, 2.5), 6.92-7.02 (3H, m), 7.27-7.41 (5H, m), 7.41-7.46 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 15.6, 78.3, 79.0, 116.4, 121.6, 127.5, 128.6, 129.8, 139.9, 157.7.

HRMS (EI⁺) calculated for [C₁₅H₁₆O₂]⁺ (M)⁺ m/z : 228.1150, found 228.1156 (+2.6 ppm).
(1R,2S,3S)-1,3-dimethyl-2,3-dihydro-1\textit{H}-inden-2-ol
(1R,3R)-1,3-dimethyl-2,3-dihydro-1\textit{H}-inden-2-ol

The title compounds were prepared according to general procedure 2 using 2-indanol (67 mg, 0.5 mmol) giving the crude products after work up (71:29 dr). Purification by flash silica chromatography (eluent = 5-10% EtOAc in n-pentane, 20 x 140 mm silica) gave 36a as a white solid (7 mg, 9%); mp 105-107 °C, R\textsubscript{f} = 0.39 (eluent = 10% EtOAc in n-pentane); and 36b as a colourless oil (27 mg, 33%); R\textsubscript{f} = 0.35 (eluent = 10% EtOAc in n-pentane).

Data for 36a:
\(\nu_{\text{max}} / \text{cm}^{-1} \) (film) 3291, 3071, 3017, 2965, 2930, 2870, 2839, 1474, 1373, 1323, 1240, 1144, 1034, 1016, 962, 876, 768, 758, 712; \(^{1}\text{H} \text{NMR (}500 \text{ MHz, CDCl}_3\) \(\delta_H\): 1.39 (6H, d, \(J 7.0\)), 3.15 (2H, dq, \(J 7.0, 3.6\)), 4.32 (1H, t, \(J 3.6\)), 7.17-7.25 (4H, m); \(^{13}\text{C} \text{NMR (}126 \text{ MHz, CDCl}_3\) \(\delta_C\): 12.0, 43.7, 80.2, 123.5, 126.9, 145.3; HRMS (EI\textsuperscript{+}) calculated for [C\textsubscript{11}H\textsubscript{14}O\textsuperscript{+}] (M\textsuperscript{+}) m/z : 162.1045, found 162.1044 (-0.6 ppm).
Data for 36b:

\( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3358, 3021, 2961, 2930, 2870, 1477, 1450, 1375, 1103, 1098, 1061, 1011, 972, 752, 498, 461; ***\(^1\)H NMR (500 MHz, CDCl\(_3\))*** \( \delta \) \( H \): 1.25 (3H, d, \( J = 7.0 \)), 1.31 (3H, d, \( J = 7.0 \)), 3.05-3.13 (1H, m), 3.23-3.33 (1H, m), 4.10 (1H, t, \( J = 6.0 \)), 7.16-7.23 (4H, m); ***\(^{13}\)C NMR (126 MHz, CDCl\(_3\))*** \( \delta \) \( C \): 13.3, 17.1, 42.0, 45.8, 82.4, 124.0, 124.1, 127.1, 127.1, 144.9, 145.2; HRMS (EI\(^+\)) calculated for [C\(_{11}\)H\(_{14}\)O]\(^+\) (M)^+ m/z : 162.1045, found 162.1045 (+0.0 ppm).
The title compound was prepared according to general procedure 2 using 1-indanol (67 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% Et₂O in n-pentane, 30 x 120 mm silica) gave the title compound as a colourless oil (46 mg, 62%); Rᵢ = 0.27 (eluent = 5% EtOAc in hexanes); 

$^{1}H$ NMR (500 MHz, CDCl₃) $\delta$H: 1.32 (3H, d, J 7.0), 2.67-2.77 (2H, m), 3.35-3.45 (1H, m), 7.34-7.40 (1H, m), 7.42-7.49 (1H, m), 7.59 (1H, dt, J 1.5, 7.5), 7.76 (1H, d, J 7.5); 

$^{13}C$ NMR (126 MHz, CDCl₃) $\delta$C: 16.4, 35.1, 42.1, 124.1, 126.7, 127.5, 134.8, 136.5, 153.6, 209.6. Spectroscopic data in accordance with that stated in the literature.²¹
The title compound was prepared according to general procedure 2 using 1-tetralol 1-tetralol (74.1 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% Et₂O in n-pentane, 30 x 120 mm silica) gave the title compound as a colourless oil (43 mg, 53%); Rf = 0.34 (eluent = 5% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl₃) δH: 1.28 (3H, d, J 7.0), 1.83-1.95 (1H, m), 2.20 (1H, dq, J 13.5, 4.5), 2.54-2.65 (1H, m), 2.92-3.11 (2H, m), 7.23 (1H, d, J 7.5), 7.30 (1H, t, J 7.5), 7.45 (1H, dt, J 7.5, 1.5), 8.04 (1H, dd, J 7.5, 1.5); $^{13}$C NMR (126 MHz, CDCl₃) δC: 15.6, 29.0, 31.5, 42.8, 126.6, 127.5, 128.8, 133.2, 132.5, 144.3, 201.0; Spectroscopic data in accordance with that stated in the literature. 22

2-methyl-3,4-dihydronaphthalen-1(2H)-one

![Chemical structure](image)

The title compound was prepared according to general procedure 2 using 1-tetralol 1-tetralol (74.1 mg, 0.5 mmol). Purification by flash silica chromatography (eluent = 5% Et₂O in n-pentane, 30 x 120 mm silica) gave the title compound as a colourless oil (43 mg, 53%); Rf = 0.34 (eluent = 5% EtOAc in hexanes); $^1$H NMR (500 MHz, CDCl₃) δH: 1.28 (3H, d, J 7.0), 1.83-1.95 (1H, m), 2.20 (1H, dq, J 13.5, 4.5), 2.54-2.65 (1H, m), 2.92-3.11 (2H, m), 7.23 (1H, d, J 7.5), 7.30 (1H, t, J 7.5), 7.45 (1H, dt, J 7.5, 1.5), 8.04 (1H, dd, J 7.5, 1.5); $^{13}$C NMR (126 MHz, CDCl₃) δC: 15.6, 29.0, 31.5, 42.8, 126.6, 127.5, 128.8, 133.2, 132.5, 144.3, 201.0; Spectroscopic data in accordance with that stated in the literature. 22

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2.4. Synthesis of plausible intermediates

2-phenylprop-2-en-1-ol

\[
\text{Cul (0.5 equiv.)} \quad \text{PhMgBr (3.0 equiv.)}
\]

\[
\text{-78 °C - rt, PhMe, 24 h}
\]

Under nitrogen, a three-necked 250 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with Cul (1.9 g, 10 mmol) and dry toluene (25 mL). The suspension was cooled to -78 °C followed by the addition of propargyl alcohol (1.16 mL, 1.12 g, 20 mmol). To this solution was then added a fresh prepared solution of phenylmagnesium bromide (60 mL, 60 mmol, 1 M in THF). The mixture was left to gradually warm up to room temperature and left stirring for 16 h. Sat. aq. NH₄Cl (10 mL), H₂O (20 mL) and EtOAc (50 mL) were then added. The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was washed with EtOAc (2 x 50 mL). The organics were combined, dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 5-25% EtOAc in hexanes, 35 x 170 mm silica) gave the title compound as a colourless oil (1.21 g, 45%); Rf = 0.28 (eluent = 20% EtOAc in hexanes); 

\[\text{^1H NMR (500 MHz, CDCl}_3\text{)}\ \delta_H: 1.56-1.66 (1H, m), 4.55 (2H, d, J 6.0), 5.36 (1H, q, J 1.5), 5.48 (1H, q, J 1.5), 7.28-7.33 (1H, m), 7.33-7.39 (2H, m), 7.43-7.48 (2H, m); \text{^13C NMR (126 MHz, CDCl}_3\text{)}\ \delta_C: 65.2, 112.8, 126.2, 128.1, 128.7, 138.6, 147.4. Spectroscopic data in accordance with that stated in the literature.\]
A 50 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 2-phenylpropane-1,3-diol (1.52 g, 10 mmol) and dry DMF (20 mL). The solution was cooled to 0 °C and was then charged with NaH (400 mg, 10 mmol, 60% suspension in mineral oil). After 30 min at this temperature, MeI (747 µL, 1.70 g, 12 mmol) was added. The flask was sealed with a cap and the mixture was left to stir at rt for 20 h. The mixture was quenched with sat aq. NH₄Cl (10 mL), H₂O (10 mL) and was then transferred to a separatory funnel filled with EtOAc (50 mL). The organic layer was collected. The aqueous phase was washed with EtOAc (2 x 50 mL). The organics were combined, washed with brine (5 x 100 mL), dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 30-70% EtOAc in hexanes, 35 x 110 mm silica) gave the title compound as a colourless oil (749 mg, 45%), Rₘ = 0.24 (eluent = 30% EtOAc in hexanes); vₘₐₓ / cm⁻¹ (film) 3408, 3032, 2930, 2874, 2826, 1495, 1450, 1194, 1117, 1090, 1028, 756, 700; ¹H NMR (500 MHz, CDCl₃) δH: 2.44 (1H, t, J 6.0), 3.12-3.24 (1H, m), 3.39 (3H, s), 3.65-3.79 (2H, m), 3.80-3.91 (1H, m), 3.94-4.03 (1H, m), 7.18-7.28 (3H, m), 7.29-7.36 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δC: 47.8, 59.3, 66.8, 76.6, 127.2, 128.1, 128.8, 139.7; HRMS (EI⁺) calculated for [C₁₀H₁₄O₂]⁺ (M)⁺ m/z : 166.0994, found 166.0992 (-1.2 ppm).
2.5. Evidence supporting possible reaction intermediates

A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40 mg, 1 mmol), Me$_3$NO (5.6 mg, 0.05 mmol, 10 mol %), [Fe] pre catalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), MeOH (1 mL) and 2-phenylpropane-1,3-diol (76 mg, 0.5 mmol). The vial was sealed with a cap and was left to react at 130 °C for 24 hours. It was then cooled, treated with mesitylene (70 µL, 60.1 mg, 0.5 mmol), EtOAc (1 mL), sat. aq. NH$_4$Cl (0.5 mL) and H$_2$O (0.5 mL). Brine (0.5 mL) was added to aid layer separation. The mixture was stirred for 5 minutes and left to settle for a further 5 minutes. The top layer was sampled and analysed using $^1$H NMR. The result gave a 78% NMR yield of 3.
A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40 mg, 1 mmol), Me$_3$NO (5.6 mg, 0.05 mmol, 10 mol %), [Fe] precatalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), MeOH (1 mL) and 2-phenylprop-2-en-1-ol (67 mg, 0.5 mmol). The vial was sealed with a cap and was left to react at 130 °C for 24 hours. It was then cooled, treated with mesitylene (70 µL, 60.1 mg, 0.5 mmol), EtOAc (1 mL), sat. aq. NH$_4$Cl (0.5 mL) and H$_2$O (0.5 mL). Brine (0.5 mL) was added to aid layer separation. The mixture was stirred for 5 minutes and left to settle for a further 5 minutes. The top layer was sampled and analysed using $^1$H NMR. The result gave a 85% NMR yield of 3.
Crude $^1$H NMR

3

44
A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40 mg, 1 mmol), Me₃NO (5.6 mg, 0.05 mmol, 10 mol %), [Fe] precatalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), MeOH (1 mL) and 3-methoxy-2-phenylpropan-1-ol (83 mg, 0.5 mmol). The vial was sealed with a cap and was left to react at 130 °C for 24 hours. It was then cooled, treated with mesitylene (70 µL, 60.1 mg, 0.5 mmol), EtOAc (1 mL), sat. aq. NH₄Cl (0.5 mL) and H₂O (0.5 mL). Brine (0.5 mL) was added to aid layer separation. The mixture was stirred for 5 minutes and left to settle for a further 5 minutes. The top layer was sampled and analysed using ¹H NMR. The result gave a 57% NMR yield of 3.
Kinetic time course experiments

A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40 mg, 1 mmol), Me$_3$NO (5.6 mg, 0.05 mmol, 10 mol %), [Fe] precatalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), MeOH (1 mL) and 2-phenylethanol (60 µL, 61 mg, 0.5 mmol). The vial was sealed with a cap and was left to react at 130 °C for a specific amount of time. It was then cooled to 20 °C, treated with mesitylene (70 µL, 60.1 mg, 0.5 mmol), EtOAc (1 mL), sat. aq. NH$_4$Cl (0.5 mL) and H$_2$O (0.5 mL). Brine (0.5 mL) was added to aid layer separation. The mixture was stirred for 5 minutes and left to settle for a further 5 minutes. The top layer was sampled and analysed using $^1$H NMR. This was repeated for 7 parallel reactions ranging from 0.25 h to 24 h, as shown in the table below.
| Time (h) | Starting Material (%) | Product (%) |
|---------|-----------------------|-------------|
| 0.25    | 70                    | 21          |
| 0.5     | 56                    | 31          |
| 1       | 43                    | 44          |
| 2       | 22                    | 72          |
| 4       | 20                    | 74          |
| 8       | 16                    | 78          |
| 16      | 16                    | 79          |
| 24      | 15                    | 80          |

2.7. Mechanistic experiments employing CD$_3$OD as solvent

A 10 mL microwave vial equipped with a magnetic stirrer bar was charged with NaOH (40.0 mg, 1 mmol), Me$_3$NO.2H$_2$O (5.6 mg, 0.1 mmol, 10 mol %), [Fe] precatalyst 2 (11.4 mg, 0.025 mmol, 5 mol %), CD$_3$OD (1 mL) and 2-phenethyl alcohol (60 µL, 61 mg, 0.5 mmol). The vial was sealed with a cap and was left to stir at 130 °C for 24 hours. It was then cooled, treated with sat. aq. NH$_4$Cl (0.5 mL) and H$_2$O (0.5 mL), washed with EtOAc (15 mL) and transferred to a separatory funnel filled with brine (15 mL). The organic layer was collected and the aqueous phase washed with EtOAc (2 x 15 mL). The organics were combined, dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by flash silica chromatography (eluent = 20% Et$_2$O in n-pentane, 20 x 220 mm silica) gave the title compound as a colourless oil (43 mg, 60%). The product was subjected to D$_2$O exchange by placing a drop of D$_2$O in the NMR tube with CDCl$_3$ as solvent.
Deuterium incorporation equation:

\[
\% \text{ D} = 100 - \left( \frac{\text{peak integral}}{\text{equivalent protons}} \right) \times 100
\]

Peak A: 100 - \left( \frac{0.53}{2} \right) \times 100 = 74\% \text{ D}
Peak B: 100 - \left( \frac{0.09}{1} \right) \times 100 = 91\% \text{ D}
Peak C: 100 - \left( \frac{0.50}{3} \right) \times 100 = 83\% \text{ D}

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