Supplementary Materials for

n-Alkanes to n-alcohols: Formal primary C—H bond hydroxymethylation via quadruple relay catalysis

Xinxin Tang, Lan Gan, Xin Zhang, Zheng Huang*

*Corresponding author. Email: huangzh@sioc.ac.cn

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Supplementary Information

1. General information
   a. Materials
      All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Tetrahydrofuran (THF), p-xylene, toluene and n-hexane were all dried with LiAlH₄ and distilled under argon prior to use. The following chemicals were purchased and used as received: cat-3a (TCI), cat-3b (Laajoo), cat-3d (TCI). Rh(acac)(CO)₂ (Alfa Aesar), biphephos ligand (Strem), (TMSO)₂MeSiH (TCI), H₂ (99.999%), and CO (99.9%). n-Pentane, n-hexane (for AD), n-heptane, n-nonane, n-dodecane, and t-butylethylene (TBE) were all purchased from TCI, dried with LiAlH₄ and distilled under argon prior to use. n-Octane was purchased from Alfa Aesar, also dried with LiAlH₄ and distilled under argon prior to use. Cat-1a (22) and cat-3c (25) were prepared according to previously reported procedures.

   b. Analytical methods
      NMR spectra were recorded on Varian Mercury 400 MHz and Agilent 400 MHz spectrometers at ambient temperature. The residual peak of deuterated solvent was used as a reference for ¹H and ¹³C chemical shifts. GC analysis was acquired on Agilent 7820A gas chromatograph equipped with a flame-ionization detector. GC-MS analysis was performed on Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert mass selective detector. High resolution mass spectrometer (HRMS) was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).
2. Procedures for Table 1

In an argon-filled glovebox, a thick-wall Kontes flask (5 mL) was charged with cat-1a (or cat-1b, cat-1c) (1.0 mol%), NaOeBu (1.2 mol%, not applicable for cat-1b or cat-1c), n-octane (2.0 mL) and TBE (0.50 mmol). The flask was sealed with a Teflon plug under an argon atmosphere, and the solution stirred in a 200 °C oil bath for 10 min. After that, the flask was cooled to room temperature. A 5-mL vial with a magnetic stirring bar was charged with Rh(acac)(CO)\(_2\) (0.8 mol%, 20 mM solution in toluene) and biphephos ligand (3.2 mol%) in the glove box. The mixture stirred at room temperature for 5 min. Then different ruthenium catalyst (2.5 mol%) and base (2.5 mol%) were subsequently added. The solution derived from alkane dehydrogenation was then added to the 5-mL vial. The vial was placed in a 50-mL autoclave, which was purged with H\(_2\), and then charged with CO and H\(_2\) at desired pressure. The autoclave was heated at 120 °C for 28 h and then cooled by an icy bath. The gases were carefully released in a well-ventilated hood. After adding mesitylene (20 µL) as an internal standard, the reaction mixture was analyzed by GC and GC-MS.

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Possible structure for high boiling by-products indicated by GC-MS:
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3. Procedures for Figure 2

3.1 Hydroxymethylation of n-alkanes

In an argon-filled glovebox, a thick-wall Kontes flask (5 mL) was charged with cat-1a (1.0 mol%), NaOeBu (1.2 mol%), n-alkane (2.0 mL) and TBE (0.50 mmol). The flask was sealed with a Teflon plug under an argon atmosphere, and the solution was stirred in a 200 °C oil bath (190 °C for 5a) for 10 min (30 min for 5a, 5b, and 5c). After that, the flask was cooled to room temperature. A 5-mL vial with a magnetic stirring bar was charged with Rh(acac)(CO)\(_2\) (20 mM in toluene) (0.8 mol%) and biphephos ligand (3.2 mol%) in the glove box. The mixture was stirred at room temperature for 5 min. Then cat-3d (1.25 mol%) was subsequently added. The solution derived from alkane dehydrogenation was then added to the 5-mL vial. The vial was placed in a 50-mL
autoclave, which was purged with H₂, and then charged with CO (5 bar) and H₂ (10 bar). The autoclave was heated at 120 °C for 28 h and then cooled by an icy bath. The gases were carefully released in a well-ventilated hood. After adding mesitylene (20 µL) as an internal standard, the reaction mixture was analyzed by GC and GC-MS. The product was isolated by flash column chromatography on silica gel (PE:EA = 10:1).

\[
\text{CH}_2\text{OH (5d)}
\]

Colorless oil (51.7 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 3.61 (t, J = 6.7 Hz, 2H), 1.73 (b, 1H), 1.54 (quint, J = 7.0 Hz, 2H), 1.34–1.26 (m, 12H), 0.86 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 63.1, 32.9, 32.0, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2. The spectroscopic data correspond to the reported data (42).

\[
\text{CH}_2\text{OH (5e)}
\]

Colorless oil (56.2 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 3.60 (t, J = 6.7 Hz, 2H), 1.82 (b, 1H), 1.54 (quint, J = 7.0 Hz, 2H), 1.34–1.25 (m, 14H), 0.86 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 63.1, 32.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2. The spectroscopic data correspond to the reported data (43).

\[
\text{CH}_2\text{OH (5f)}
\]

Colorless oil (63.1 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 3.61 (t, J = 6.6 Hz, 2H), 1.68 (b, 1H), 1.55 (quint, J = 6.3 Hz, 2H), 1.25 (b, 20H), 0.87 (t, J = 5.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 63.1, 32.9, 32.1, 29.82, 29.80, 29.79, 29.77, 29.75, 29.6, 29.5, 25.9, 22.8, 14.2. The spectroscopic data correspond to the reported data (44).

### 3.2 Hydroxymethylation of aryl-substituted alkanes and silyl alkanes

In an argon-filled glovebox, a thick-wall Kontes flask (5 mL) was charged with cat-1a (2.0 mol%), NaOtBu (2.4 mol%), p-xylene (1.5 mL), alkane (1.5 mmol), TBE (0.50 mmol). The flask was sealed with a Teflon plug under an argon atmosphere, and the solution stirred in a 200 °C oil bath for 180 min. After that, the flask was cooled to room
temperature. A 5-mL vial with a magnetic stirring bar was charged with Rh(acac)(CO)$_2$ (0.8 mol%, 20 mM in toluene) and biphephos ligand (3.2 mol%) in a glove box. The mixture was stirred at room temperature for 5 min. Then cat-3d (1.25 mol%) was subsequently added. The solution derived from alkane dehydrogenation was then added to the 5-mL vial. The vial was placed in a 50-mL autoclave, which was purged with H$_2$, and then charged with CO (5 bar) and H$_2$ (10 bar). The autoclave was heated at 120 °C for 28 h and then cooled by an icy bath. The gases were carefully released in a well-ventilated hood. After adding mesitylene (20 µL) as an internal standard, the reaction mixture was analyzed by GC and GC-MS. The product was isolated by flash column chromatography on silica gel (PE:EA = 10:1).

![Structure of 5g](image)

Colorless oil (48.6 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38–7.31 (m, 4H), 7.22–7.18 (m, 1H), 3.57 (t, $J = 6.6$ Hz, 2H), 1.68–1.64 (m, 2H), 1.50 (quint, $J = 6.1$ Hz, 2H), 1.34 (s, 6H), 1.19–1.11 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.5, 128.2, 125.9, 125.5, 44.5, 37.8, 33.5, 29.0, 21.1. HRMS (EI), m/z calcd. for C$_{13}$H$_{20}$O (M$^+$) 192.1514, found: 192.1515.

![Structure of 5h](image)

Colorless oil (64.1 mg, 62%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35–7.29 (m, 4H), 7.20–7.16 (m, 1H), 3.56 (t, $J = 6.6$ Hz, 2H), 1.64–1.60 (m, 2H), 1.49 (quint, $J = 6.9$ Hz, 2H), 1.31–1.23 (m, 8H), 1.15–1.05 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.7, 128.1, 125.9, 125.4, 63.0, 44.7, 37.7, 32.7, 29.1, 26.5, 24.6. HRMS (EI), m/z calcd. for C$_{14}$H$_{22}$O (M$^+$) 206.1671, found: 206.1679.
Colorless oil (70.7 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35–7.28 (m, 4H), 7.20–7.15 (m, 1H), 3.59 (t, $J = 6.6$ Hz, 2H), 1.63–1.59 (m, 2H), 1.50 (quint, $J = 6.9$ Hz, 2H), 1.32–1.21 (m, 10H), 1.11–1.04 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.7, 128.1, 125.9, 125.4, 63.0, 44.6, 37.7, 32.8, 30.2, 29.1, 25.7, 24.8. HRMS (EI), m/z calcd. for C$_{15}$H$_{24}$O (M$^+$) 220.1827, found: 220.1835.

$\text{CH}_2\text{OH}$ (5j)

Colorless oil (62.7 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.61 (t, $J = 6.6$ Hz, 2H), 1.67 (br, 1H), 1.56 (quint, $J = 7.1$ Hz, 2H), 1.39–1.24 (m, 4H), 0.50–0.46 (m, 2H), 0.04 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 63.1, 32.6, 29.8, 23.8, 16.8, 1.6. HRMS (EI), m/z calcd. for C$_7$H$_{17}$OSi (M-CH$_3$)$^+$ 145.1049, found: 145.1051.

$\text{CH}_2\text{OH}$ (5k)

Colorless oil (87.9 mg, 79%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53–7.51 (m, 2H), 7.37–7.35 (m, 3H), 3.61 (t, $J = 6.6$ Hz, 2H), 1.55 (quint, $J = 7.0$ Hz, 2H), 1.45 (b, 1H), 1.40–1.34 (m, 4H), 0.79–0.75 (m, 2H), 0.27 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.7, 133.6, 128.9, 127.8, 63.0, 32.5, 29.7, 23.8, 15.8, -2.9. HRMS (DART), m/z calcd. for C$_{13}$H$_{26}$OSiN (M+NH$_4$)$^+$ 240.1778, found: 240.1777.

$\text{CH}_2\text{OH}$ (5l)

Colorless oil (86.7 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43–7.41 (m, 2H), 7.20–7.18 (m, 2H), 3.61 (t, $J = 6.6$ Hz, 2H), 2.36 (s, 3H), 1.56 (quint, $J = 6.9$ Hz, 2H), 1.37 (t, $J = 3.3$ Hz, 4H), 0.78–0.74 (m, 2H), 0.26–0.25 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.7, 136.0, 133.7, 128.7, 63.1, 32.6, 29.7, 23.9, 21.6, 15.9, -2.8. HRMS (EI), m/z calcd. for C$_{13}$H$_{29}$OSi (M-CH$_3$)$^+$ 221.1362, found: 221.1368.

$\text{CH}_2\text{OH}$ (5m)
Colorless oil (72.7 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62-7.57 (m, 4H), 3.61 (t, $J$ = 6.6 Hz), 1.55 (qui, $J$ = 5.7 Hz, 2H), 1.40-1.31 (m, 4H), 0.80-0.75 (m, 2H), 0.28 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.7, 133.9, 130.9 (q, $J_{C\cdot F}$ = 32.5 Hz), 124.4 (q, $J$ = 272.3 Hz), 124.3 (q, $J$ = 3.7 Hz), 63.0, 32.5, 29.7, 23.7, 15.6, -3.1. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.9. HRMS (EI), m/z calcd. for C$_{13}$H$_{18}$OF$_3$Si (M-$\text{CH}_3$$^+$) 275.1079, found: 275.1080.

![Image](5n)

Colorless oil (52.4 mg, 52%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35–7.27 (m, 1H), 6.83–6.79 (m, 2H), 3.63 (t, $J$ = 6.5 Hz, 2H), 1.58 (quint, $J$ = 7.0 Hz, 2H), 1.40-1.38 (m, 4H), 0.87 (t, $J$ = 9.3 Hz, 2H), 0.37 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.1 (dd, $J$ = 243.7 Hz, $J$ = 16.0 Hz), 131.8 (t, $J$ = 10.4 Hz), 111.1-110.8 (m), 63.0, 32.4, 29.4, 23.6, 16.2, -1.5 (t, $J$ = 3.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -97.1. HRMS (EI), m/z calcd. for C$_{12}$H$_{17}$OF$_2$Si (M-$\text{CH}_3$$^+$) 243.1017, found: 243.1010.

![Image](5o)

Colorless oil (77.2 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53–7.50 (m, 2H), 7.36–7.35 (m, 3H), 3.60 (t, $J$ = 6.5 Hz, 2H), 1.59-1.52 (m, 2H), 1.43–1.38 (m, 4H), 1.11–1.07 (m, 2H), 0.55 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.5, 134.6, 129.2, 127.9, 63.1, 32.5, 29.7, 23.8, 14.3, -4.3. HRMS (EI), m/z calcd. for C$_{17}$H$_{21}$OSi (M-$\text{CH}_3$$^+$) 269.1362, found: 269.1360.

![Image](5p)

Colorless oil (78.0 mg, 62%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.51 (m, 2H), 7.36-7.35 (m, 3H), 3.62 (t, $J$ = 6.6 Hz, 2H), 1.55 (quint, $J$ = 6.5 Hz, 2H), 1.31 (b, 8H), 0.75 (t, $J$ = 7.0 Hz, 2H), 0.26 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.8, 133.7, 128.9, 127.8, 63.2, 33.6, 32.9, 29.2, 25.8, 23.9, 15.8, -2.9. HRMS (EI), m/z calcd. for C$_{14}$H$_{23}$OSi (M-$\text{CH}_3$$^+$) 235.1518, found: 235.1512.
3.3 Hydroxymethylation of alkanes with ethylene as hydrogen acceptor

An oven-dried autoclave (130 mL) was charged with cat-1a (2.5 mM), NaOtBu (3.0 mM), n-nonane (4.0 mL) and stirred for 2 min in a glovebox. The autoclave was then purged with ethylene and then charged with ethylene (two atmospheres) at room temperature. Then the autoclave was heated in a 180 °C oil bath for 15 h. After it was cooled to room temperature, the gas pressure was carefully released. The solution derived from the alkane dehydrogenation was then added to a 20-mL vial, which was equipped with cat-2 (1.0 mM) and cat-3d (1.6 mM). The vial was placed in a 250-mL autoclave, which was purged with H₂, and then charged with CO (5 bar) and H₂ (10 bar). The autoclave was heated at 120 °C for 28 h and then cooled by an icy bath. The gases were carefully released in a well-ventilated hood. After adding mesitylene (20 µL) as an internal standard, the reaction mixture was analyzed by GC.

3.4 General procedures for synthesis of linear alcohols (5q-5t)

In an argon-filled glovebox, a thick-wall Kontes flask (5 mL) was charged with cat-1a (2.0 mol%), NaOtBu (2.4 mol%), p-xylene (1.5 mL), alkane (1.5 mmol), TBE (0.50 mmol). The flask was sealed with a Teflon plug under an argon atmosphere, and the solution stirred in a 200 °C oil bath for 180 min. After that, the flask was cooled to room temperature. A 5-mL vial with a magnetic stirring bar was charged with Rh(acac)(CO)₂ (0.8 mol%, 20 mM in toluene) and biphephos ligand (3.2 mol%) in a glove box. The mixture stirred at room temperature for 5 min. Then cat-3d (1.25 mol%) was subsequently added. The solution derived from alkane dehydrogenation was then added to the 5-mL vial. The vial was placed in a 50-mL autoclave, which was purged with H₂, and then charged with CO (5 bar) and H₂ (10 bar). The autoclave was heated at 120 °C for 28 h and then cooled by an icy bath. The gases were carefully released in a well-ventilated hood. After adding mesitylene (20 µL) as an internal standard, the reaction mixture was
analyzed by GC and GC-MS. The product was isolated by flash column chromatography on silica gel (PE:EA = 10:1).

Colorless oil (86.7 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.62 (t, $J = 6.3$ Hz, 2H), 1.55 (quint, $J = 7.6$ Hz, 2H), 1.35–1.30 (m, 6H), 0.45 (t, $J = 6.7$ Hz, 2H), 0.07 (s, 18H), -0.02 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 63.2, 33.1, 32.9, 25.6, 23.2, 17.7, 2.0, -0.2. HRMS (DART), m/z calcd. for C$_{13}$H$_{35}$O$_3$Si$_3$ (M+H$^+$) 323.1889, found: 323.1887.

Colorless oil (85.4 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.62 (t, $J = 6.6$ Hz, 2H), 1.57-1.52 (m, 2H), 1.30 (b, 8H), 0.44 (t, $J = 7.1$ Hz, 2H), 0.08 (s, 18H), -0.02 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 63.2, 33.3, 33.0, 29.3, 25.8, 23.2, 17.7, 2.0, -0.1. HRMS (DART), m/z calcd. for C$_{14}$H$_{37}$O$_3$Si$_3$ (M+H$^+$) 337.2045, found: 337.2043.

Colorless oil (78.8 mg, 45%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.63 (t, $J = 6.6$ Hz, 2H), 1.56 (quint, $J = 7.0$ Hz, 2H), 1.29 (b, 10H), 0.44 (t, $J = 7.5$ Hz, 2H), 0.08 (s, 18H), -0.01 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 63.1, 33.2, 32.8, 29.4, 29.3, 25.8, 23.1, 17.6, 1.9, -0.3. HRMS (EI), m/z calcd. for C$_{14}$H$_{35}$O$_3$Si$_3$ (M-CH$_3$)$^+$ 335.1894, found: 335.1899.

Colourless oil (85.4 mg, 51%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.66 (t, $J = 6.7$ Hz, 2H), 1.59 (quint, $J = 7.4$ Hz, 2H), 1.30 (b, 12H), 0.44 (t, $J = 7.7$ Hz, 2H), 0.1 (s, 18H), 0.01 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 63.2, 33.4, 33.0, 29.7, 29.6, 29.4, 25.9, 23.2, 17.7, 2.0, -0.1. HRMS (EI), m/z calcd. for C$_{15}$H$_{37}$O$_3$Si$_3$ (M-CH$_3$)$^+$ 349.2051, found: 349.2059.

3.5 General procedures for Tamao oxidation

The Tamao oxidation was conducted using a modified procedure according to
literature report (45). A 50-mL flask with a magnetic stirring bar was charged with linear alcohol (1.0 equiv), KF (8.0 equiv) and DMF (0.1 M). Then peracetic acid (12.0 equiv, 40 wt% in acetic acid) was added to the above solution and stirred for 48 h. The reaction was quenched by a Na₂SO₃ aqueous solution. The organic phase was extracted with EtOAc three times, washed with saturated brine, dried and concentrated. The excess DMF was further evaporated under reduced pressure. The residue was purified by silica gel column chromatography (PE:EA 1:1) to afford the pure diol products.

\[ \text{HO-} \text{CH}_2- \text{CH}_2- \text{OH (6q)} \]
Colorless oil (23.6 mg, 74%). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 3.62 (t, \( J = 6.6 \) Hz, 4H), 2.14 (s, 2H), 1.56 (quint, \( J = 6.5 \) Hz, 4H), 1.39–1.36 (m, 4H). \(^13\)C NMR (101 MHz, CDCl₃) \( \delta \) 62.8, 32.7, 25.6. The spectroscopic data correspond to the reported data (42).

\[ \text{HO-} \text{CH}_2- \text{CH}_2- \text{OH (6r)} \]
White solid (25.2 mg, 75%). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 3.61 (t, \( J = 6.7 \) Hz, 4H), 2.09 (br, 2H), 1.55 (quint, \( J = 6.7 \) Hz, 4H), 1.39–1.33 (m, 6H). \(^13\)C NMR (101 MHz, CDCl₃) \( \delta \) 63.0, 32.7, 29.3, 25.8. The spectroscopic data correspond to the reported data (46).

\[ \text{HO-} \text{CH}_2- \text{CH}_2- \text{OH (6s)} \]
White solid (16.0 mg, 80%). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 3.63 (t, \( J = 6.7 \) Hz, 4H), 1.80 (br, 2H), 1.56 (quint, \( J = 7.0 \) Hz, 4H), 1.37–1.33 (m, 8H). \(^13\)C NMR (101 MHz, CDCl₃) \( \delta \) 63.1, 32.8, 29.5, 25.8. The spectroscopic data correspond to the reported data (47).

\[ \text{HO-} \text{CH}_2- \text{CH}_2- \text{OH (6t)} \]
White solid (14.7 mg, 81%). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 3.63 (t, \( J = 6.6 \) Hz, 4H), 2.08 (br, 2H), 1.55 (quint, \( J = 6.8 \) Hz, 4H), 1.36–1.27 (m, 10H). \(^13\)C NMR (101 MHz, CDCl₃) \( \delta \) 63.1, 32.8, 29.6, 29.4, 25.8. The spectroscopic data correspond to the reported data (48).

**4. Preparation of alkane substrates**

**4.1 General procedure for synthesis of alkane substrates in Fig. 2A**
In a 250-mL three-necked flask equipped with a magnetic stirring bar was charged with magnesium (1.3 g, 55 mmol) and anhydrous THF (4 mL) under an argon atmosphere. (1-Chloro-2-methylpropan-2-yl)benzene (8.4 g, 50 mol) was added to the above reaction mixture. One drop of 1,2-dibromoethane was added to trigger the reaction upon heating. The reaction further refluxed for 3 h to complete the preparation of Grignard reagent. Then the prepared Grignard reagent was added to a THF solution (50 mL) of iodoethane (6.4 mL, 80 mmol) at room temperature. The mixture was further stirred at room temperature for 8 h, then quenched with NH₄Cl. The organic phase was separated and aqueous phases were extracted with CH₂Cl₂ (20 mL × 2). The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and then concentrated. The residue was purified by silica gel column chromatography (n-hexane) to afford 1.6 g of 4g (20% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.36 (m, 4H), 7.27–7.23 (m, 1H), 1.70–1.65 (m, 2H), 1.39 (s, 6H), 1.23–1.13 (m, 2H), 0.91 (t, J = 7.2 Hz 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 128.1, 125.9, 125.4, 47.3, 37.9, 29.1, 18.1, 14.9. The spectroscopic data correspond to the reported data (33).

Procedure used for the synthesis of 4g was applied to the preparation of 4h, affording 3.5 g of 4h (40% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.37 (m, 4H), 7.28–7.24 (m, 1H), 1.72–1.68 (m, 2H), 1.39 (s, 6H), 1.32 (quint, J = 7.3 Hz 2H), 1.17–1.09 (m, 2H), 0.92 (t, J = 7.3 Hz 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 128.1, 126.0, 125.4, 44.5, 37.7, 29.1, 27.1, 23.6, 14.2. The spectroscopic data correspond to the reported data (49).
A 250-mL three-necked flask equipped with a magnetic stirring bar was charged with magnesium (1.4 g, 58.3 mmol) and anhydrous THF (20 mL) under an argon atmosphere. 1-Bromo-4-methylbenzene (6.2 mL, 50 mmol), which was diluted with 100 mL THF, was added to the above reaction mixture to trigger the reaction upon heating. The Grignard reagent generated in situ was added to a THF solution (10.0 mL) of dichlorodimethylsilane (4.8 mL, 50 mmol). The mixture stirred under room temperature for 8 h, then quenched with NH₄Cl. The organic phase was separated and aqueous phases were extracted with hexane (20 mL × 2). The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and then concentrated. The residue was distilled and the 62 °C fraction was collected under reduced pressure (15 mbar) to afford 4.4 g product (48%) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H), 0.75 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 133.2, 132.8, 129.0, 21.6, 2.3. The spectroscopic data correspond to the reported data (50).

\[
\begin{align*}
\text{PhSiCl} & + n\text{-BuLi} \rightarrow \text{PhSi(CH₃)}₂ \quad \text{hexane} \quad 0 \degree \text{C-r.t.}
\end{align*}
\]

4l

In a 250-mL three-necked flask equipped with a magnetic stirring bar was charged with chlorodimethyl(p-tolyl)silane (4.4 g, 24 mmol) and hexane (40 ml) under an argon atmosphere. The solution was cooled to 0 °C. n-BuLi (9.6 mL, 2.5 M in hexane, 117.5 mmol) was added to the above solution dropwise over a period of 10 min. The reaction mixture stirred at 0 °C for 30 min before it was warmed to room temperature and stirred further for 8 h. The reaction mixture was quenched with water at 0 °C. The organic phase was separated, and the aqueous phases were extracted with CH₂Cl₂ (50 mL × 2). The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and concentrated. The residue was purified by silica gel column chromatography (n-hexane) to afford 4.1 g of 4l (84% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.9 Hz 2H), 7.30–7.27 (m, 2H), 2.46 (s, 3H), 1.45–1.41 (m, 4H), 0.99 (t, J = 6.8 Hz 3H), 0.88–0.84 (m, 2H), 0.36 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 138.6, 136.2, 133.8,
In a 250-mL three-necked flask equipped with a magnetic stirring bar was charged with bromo(2,6-difluorophenyl)dimethylsilane (3.7 g, 20 mmol) and THF (20 ml) under an argon atmosphere. The solution was cooled to -78 °C. n-BuLi (9.9 mL, 2.5 M in hexane, 24.7 mmol) was added to the above solution dropwise and stirred for 1 h. Then the reaction mixture was further stirred at -40 °C for 1 h. Butylchlorodimethylsilane (3.0 g, 20 mmol) was added to the above solution at -78 °C and it was gradually warmed to room temperature and stirred for 18 h. The reaction mixture was quenched with water at 0 °C. The organic phase was separated, and the aqueous phases were extracted with CH$_2$Cl$_2$ (30 mL × 2). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (n-hexane) to afford 1.2 g of 4n (26% yield) as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.28 (m, 1H), 6.83 (q, $J$ = 7.0 Hz, 2H), 1.37 – 1.36 (m, 4H), 0.93–0.90 (m, 5H), 0.40 (d, $J$ = 1.7 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.3 (dd, $J$ = 243.7 Hz, $J$ = 15.9 Hz), 131.9 (t, $J$ = 10.6 Hz), 113.2 (t, $J$ = 34.5 Hz), 111.2–110.9 (m), 26.6, 26.1, 16.1, 13.9, -1.41 (t, $J$ = 3.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -97.0. HRMS (EI), m/z calcd. for C$_{12}$H$_{18}$F$_{2}$Si (M$^+$) 228.1146, found: 228.1149.

A 250-mL Schlenk flask equipped with a magnetic stirring bar was charged with AgNO$_3$ (102 mg, 0.6 mmol) (52), chloro(hexyl)dimethylsilane (2.5 mL, 12 mmol) and anhydrous THF (15 mL) under an argon atmosphere. Phenylmagnesium bromide (7.2 mL, 18 mmol, 2.5 M in THF) was added to the above solution at room temperature and stirred for 8 h. Then it was quenched with water at 0 °C. The organic phase was separated, and
the aqueous phases were extracted with hexane (15 mL × 2). The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and concentrated. The residue was purified by silica gel column chromatography (n-hexane) to afford 1.9 g of 4p (73% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.58–7.56 (m, 2H), 7.40–7.39 (m, 3H), 1.34 (d, J = 20.7 Hz, 8H), 0.93-0.91 (m, 3H), 0.80 (t, J = 6.8 Hz, 2H), 0.32–0.31 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 133.7, 128.9, 127.8, 33.5, 31.7, 24.0, 22.8, 15.9, 14.3, -2.9. HRMS (EI), m/z calcd. for C₁₃H₂₁Si (M−CH₃)⁺ 205.1413, found: 205.1417.

4.2 General procedure for synthesis of alkane substrates in Fig. 2B

In a three-necked flask equipped with a magnetic stirring bar was charged with α-olefin (1.0 equiv) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.2 equiv). The Karstedt catalyst (0.1%) was then added to the above solution. The mixture stirred at room temperature for 8 h. The unreacted 1,1,1,3,5,5,5-heptamethyltrisiloxane was removed in vacuo and the crude product was purified by silica gel column chromatography (n-hexane) to afford pure product.

Colorless oil (13.0 g, 89%). ¹H NMR (400 MHz, CDCl₃) δ 1.34–1.30 (m, 6H), 0.89 (t, J = 6.9, 3H), 0.48–0.44 (m, 2H), 0.09 (s, 18H), 0.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 35.7, 22.9, 22.6, 17.7, 14.2, 2.0, -0.1. The spectroscopic data correspond to the reported data (32).

Colorless oil (13.8 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 1.31–1.28 (m, 8H), 0.90 (t, J = 6.8, 3H), 0.46 (t, J = 7.7, 2H), 0.10 (s, 18H), 0.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 33.2, 31.8, 23.2, 22.8, 17.8, 14.3, 2.0, -0.1. The spectroscopic data correspond to the reported data (34).
Colorless oil (15.2 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.29–1.27 (m, 10H), 0.89 (t, $J = 6.8$, 3H), 0.45 (t, $J = 7.6$, 2H), 0.09 (s, 18H), 0.00 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 33.4, 32.0, 29.2, 23.2, 22.9, 17.8, 14.3, 2.0, -0.1. The spectroscopic data correspond to the reported data (53).

Colorless oil (15.4 g, 92%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.31–1.27 (m, 12H), 0.89 (t, $J = 6.6$, 3H), 0.46 (t, $J = 7.9$, 2H), 0.09 (s, 18H), 0.00 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 33.5, 32.1, 29.5, 29.5, 23.3, 22.9, 17.8, 14.3, 2.0, -0.1. The spectroscopic data correspond to the reported data (54).

5. Preparation of cat-1b and cat-1c

**Synthesis of (PCP)Ir(C$_2$H$_4$).** Ethylene was bubbled into a pentane solution (60 mL) of (PCP)IrHCl (1.0 mmol) for 10 min until the solution was colorless. LiBEt$_3$H (1.0 M in THF) was added dropwise to the above solution under ethylene atmosphere. The solution was further stirred overnight. Insoluble solid was removed through filtration and the volatile was evaporated to afford 330 mg dark red solid with 57% yield. $^1$H NMR (400 MHz, Benzene-d$_6$) $\delta$ 6.96 (s, 2H), 3.58 (s, 3H), 3.04 (t, $J = 4.0$ Hz, 4H), 2.99 (t, $J = 3.4$ Hz, 4H), 2.02 (p, $J = 7.1$ Hz, 4H), 0.99 (dq, $J = 61.6$, 7.0 Hz, 24H). $^{13}$C NMR (101 MHz, Benzene-d$_6$) $\delta$ 171.9 (d, $J = 4.0$ Hz), 158.5 (d, $J = 2.0$ Hz), 154.8(t, $J = 11.0$ Hz), 106.2 (t, $J = 8.9$ Hz), 54.3, 38.8 (t, $J = 15.2$ Hz), 34.3, 24.4 (t, $J = 12.9$ Hz), 18.4 (t, $J = 2.3$ Hz), 18.0. $^{31}$P NMR (162 MHz, Benzene-d$_6$) $\delta$ 49.12.

**Synthesis of (POCOP)Ir(C$_2$H$_4$).** Ethylene was bubbled into a solution of NaOtBu (77 mg, 0.8 mmol) and (POCOP)IrHCl (433 mg, 0.76 mmol) in 20 mL toluene for 2 h. After toluene was evaporated, the residue was dissolved in pentane. Insoluble solid was removed through filtration and the volatile was evaporated to afford 230 mg dark red solid with 54% yield. $^1$H NMR (400 MHz, Benzene-d$_6$) $\delta$ 7.07 – 6.98 (m, 1H), 6.93 (d, $J = 7.7$ Hz, 2H), 2.57 (d, $J = 2.6$ Hz, 4H), 2.28 (p, $J = 7.1$ Hz, 4H), 1.04 (dq, $J = 41.0$, 7.8,
7.3 Hz, 24H). $^{13}$C NMR (101 MHz, Benzene-d$_6$) $\delta$ 165.4 (t, $J = 10.1$ Hz), 140.3 (t, $J = 10.3$ Hz), 124.2, 104.2 (t, $J = 6.7$ Hz), 33.0, 30.7 (t, $J = 16.5$ Hz), 18.7 – 17.2 (m), 16.9.

$^{31}$P NMR (162 MHz, Benzene-d$_6$) $\delta$ 182.9.

6. Study of deactivation of (PSCOP)Ir catalyst by Syngas

In an argon-filled glove box, to a 5-mL Kontes tube, (PSCOP)IrHCl (0.04 mmol) was dissolved in a solution of decane (2.0 mL) and TBE (64.0 $\mu$L, 0.5 mmol). NaOrBu (0.08 mmol) was then added to the solution. The reaction tube was heated in a pre-heated oil-bath at 200 °C for 10 min. The solution was transferred into a 25-mL autoclave, which was further charged with 2 bar CO and 2 bar H$_2$. The mixture was stirred under room temperature for 12 h. $^{31}$P NMR analysis of the reaction mixture showed two peaks at $\delta$ 181 ppm (d, $J = 314$ Hz) and 108 ppm (d, $J = 314$ Hz), indicating the formation of (PSCOP)Ir(CO) species (40). 1-Octene (0.5 mmol) was added to the above solution, which was further charged with 2 bar CO and 2 bar H$_2$. The solution stirred at 120 °C for 5 h. GC analysis of the crude reaction mixture revealed no isomerization and hydrogenation products, indicating the deactivation of the (PSCOP)Ir catalyst.

Crude $^{31}$P NMR spectrum showing the formation of (PSCOP)Ir(CO) species.
7. GC spectra

GC spectrum for 5d (obtained from run 8 in Table 1)

GC spectrum for 5d (obtained from run 10 in Table 1)
GC spectrum for 5f

dodecane
linear alcohol
branched alcohols
mesitylene

GC spectrum for 5g

mesitylene
aldehydes
branched alcohols
linear alcohol
GC spectrum for 5l

GC spectrum for 5m
GC spectrum for 5p

- Mesitylene
- Branched alcohols
- Linear alcohol
- Aldehydes

Retention times:
- 14.60 minutes
- 17.00 minutes
- 17.89 minutes
8. NMR spectra

NMR spectra for iridium complexes:

$^1$H NMR (400 MHz, C$_6$D$_6$) for cat-1b

$^{13}$C NMR (101 MHz, C$_6$D$_6$) for cat-1b
$^{31}$P NMR (162 MHz, C$_6$D$_6$) for cat-1b

$^1$H NMR (400 MHz, C$_6$D$_6$) for cat-1c
$^{13}$C NMR (101 MHz, C$_6$D$_6$) for cat-1c

$^{31}$P NMR (162 MHz, C$_6$D$_6$) for cat-1c
$^1$H NMR (400 MHz, CDCl$_3$) for 5d

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5d
$^1$H NMR (400 MHz, CDCl$_3$) for 5e

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5e
$^1$H NMR (400 MHz, CDCl$_3$) for 5f

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5f
$^{1}H$ NMR (400 MHz, CDCl$_3$) for 5g

$^{13}C$ NMR (101 MHz, CDCl$_3$) for 5g
$^1$H NMR (400 MHz, CDCl$_3$) for 5h

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5h
1H NMR (400 MHz, CDCl₃) for 5i

13C NMR (101 MHz, CDCl₃) for 5i
$^{1}H$ NMR (400 MHz, CDCl$_3$) for 5j

$^{13}C$ NMR (101 MHz, CDCl$_3$) for 5j
$^1$H NMR (400 MHz, CDCl$_3$) for 5k

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5k
$^1$H NMR (400 MHz, CDCl$_3$) for 5l

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5l
$^1$H NMR (400 MHz, CDCl$_3$) for 5m

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5m
$^{19}$F NMR (376 MHz, CDCl$_3$) for 5m

$^1$H NMR (400 MHz, CDCl$_3$) for 5n
$^{13}$C NMR (101 MHz, CDCl$_3$) for 5n

$^{19}$F NMR (376 MHz, CDCl$_3$) for 5n
$^1$H NMR (400 MHz, CDCl$_3$) for 5o

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5o
$^1$H NMR (400 MHz, CDCl$_3$) for 5p
$^{13}$C NMR (101 MHz, CDCl$_3$) for 5p

$^1$H NMR (400 MHz, CDCl$_3$) for chlorodimethyl(p-toly)silane
$^{13}$C NMR (101 MHz, CDCl$_3$) for chlorodimethyl($\rho$-tolyl)silane

$^1$H NMR (400 MHz, CDCl$_3$) for 4g
$^{13}$C NMR (101 MHz, CDCl$_3$) for 4g

$^{1}H$ NMR (400 MHz, CDCl$_3$) for 4h
$^{13}$C NMR (101 MHz, CDCl$_3$) for 4h

$^1$H NMR (400 MHz, CDCl$_3$) for 4l
$^{13}$C NMR (101 MHz, CDCl$_3$) for 4l

$^1$H NMR (400 MHz, CDCl$_3$) for 4n
$^{13}$C NMR (101 MHz, CDCl$_3$) for 4n

$^{19}$F NMR (376 MHz, CDCl$_3$) for 4n
$^1$H NMR (400 MHz, CDCl$_3$) for 4p

$^{13}$C NMR (101 MHz, CDCl$_3$) for 4p
1H NMR (400 MHz, CDCl₃) for 5q

13C NMR (101 MHz, CDCl₃) for 5q
$^1$H NMR (400 MHz, CDCl$_3$) for 5r

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5r
$^1$H NMR (400 MHz, CDCl$_3$) for 5s

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5s
$^1$H NMR (400 MHz, CDCl$_3$) for 5t

$^{13}$C NMR (101 MHz, CDCl$_3$) for 5t
$^1$H NMR (400 MHz, CDCl$_3$) for 4q

$^{13}$C NMR (101 MHz, CDCl$_3$) for 4q
$^1$H NMR (400 MHz, CDCl$_3$) for 4r

$^{13}$C NMR (101 MHz, CDCl$_3$) for 4r
$^1$H NMR (400 MHz, CDCl$_3$) for 4s

$^{13}$C NMR (101 MHz, CDCl$_3$) for 4s
$^1$H NMR (400 MHz, CDCl$_3$) for 4t

$^{13}$C NMR (101 MHz, CDCl$_3$) for 4t
$^1$H NMR (400 MHz, CDCl$_3$) for $6q$

$^{13}$C NMR (101 MHz, CDCl$_3$) for $6q$
$^1$H NMR (400 MHz, CDCl$_3$) for 6r

$^{13}$C NMR (101 MHz, CDCl$_3$) for 6r
$^1$H NMR (400 MHz, CDCl$_3$) for 6s

$^{13}$C NMR (101 MHz, CDCl$_3$) for 6s
$^1$H NMR (400 MHz, CDCl$_3$) for 6t

$^{13}$C NMR (101 MHz, CDCl$_3$) for 6t
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