Room temperature iron catalyzed transfer hydrogenation using n-butanol and poly(methylhydrosiloxane)

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1. General Considerations

Reagents were purchased from Sigma Aldrich or Alfa Aesar and dried/distilled prior to use. Laboratory grade dichloromethane (DCM) and pentane were purchased from Fisher Scientific and used without further purification. Deuterated benzene was dried over Na/benzophenone and distilled prior to use. Pre-catalyst 1 was synthesised following literature procedure. NMR data was collected at 300, 400 or 500 MHz on Bruker or Agilent instruments in benzene-d₆, toluene-d₈ or chloroform-d at 298K and referenced to residual protic solvent. Reactions were undertaken using standard glovebox (0.1 ppm H₂O and 0.1 ppm O₂) and Schlenk line techniques, unless otherwise stated. All reactions were undertaken in sealed vessels; Teflon-sealed J-Young NMR tubes, ampoules or 4 dram vials. Gas evolution experiments were undertaken using the Man on the Moon Series X103 apparatus.

2. Optimisation

Equivalents of PMHS reported correspond to the number of repeat units per equivalent of substrate, determined by the MW of a repeat unit (60.1 gmol⁻¹). For reactions undertaken in deuterated solvent, conversion and spectroscopic yield were determined by in situ ¹H NMR analysis versus starting material allyl benzene and internal standard dichloroethane (0.1 mmol) respectively (table 1, entries 1-6 and 11-15). For reactions in protic solvents, volatiles were removed under a stream of nitrogen (table 1, entry 7) or under reduced pressure (table 1, entry 8). Reactions with sugar derivatives required agitation because of poor solubility in C₆D₆ and the remaining solids were removed by filtration prior to NMR analysis (table 1, entries 11-15). When using n-butanol as proton donor, peaks in the ¹H NMR spectra are broad. Therefore, the hydrogenated product was separated from the reaction mixture by dissolving in CDCl₃ and purifying by vacuum distillation before NMR analysis (table 1, entries 16-22).

When the n-butanol:PMHS ratio was raised (table 1, entries 20 and 21), gas evolution was observed along with complete recovery of allyl benzene. With no side products present in the distillate, we suggest a dehydrocoupling reaction between n-butanol and PMHS becomes favourable in excess n-butanol.

3. General Method for Hydrogenation of Alkenes

Pre-catalyst 1 (7.0 mg, 5 mol%) was weighed out into a 4 dram vial equipped with a stirrer bar within the glovebox. n-Butanol (22.9 µL, 0.25 mmol, 1 equiv.) was added, followed by the corresponding alkene substrate (0.25 mmol, 1 equiv.). PMHS (0.5 mL) was added where the vessel was sealed and stirred for 24 hours. The vial was removed from the glovebox and exposed to air. For non-volatile products, the mixture was dissolved in DCM (1 mL) and passed through a silica plug to remove the iron complex, before DCM was removed under a stream of nitrogen. As an alternative, ethyl acetate was also shown to be a suitable work-up solvent. For volatile products, the reaction mixture was dissolved in CDCl₃ and separated by vacuum transfer. Internal standard (0.25 mmol dichloroethane (DCE) and/or mesitylene) was added and spectroscopic yield determined by ¹H NMR.

Substrates amenable to isomerization to the corresponding internal alkene (2a, 2b, 2c, 2d, 2e, 2f, 2g, 2r) show trace remaining starting material at the end of reaction. ¹H NMR spectra reveal a mixture of the hydrogenated and isomerized products, as seen in table S1.
Table S1: Spectroscopic yields of hydrogenated and isomerized products.

| Substrate | Hydrogenation\(^a\) / % | Isomerization\(^a\) / % |
|-----------|--------------------------|------------------------|
| 2a        | 85                       | 2                      |
| 2b        | 79                       | -                      |
| 2c        | 46                       | 26                     |
| 2d        | 62                       | 25                     |
| 2e        | 91                       | -                      |
| 2f        | 36                       | 34                     |
| 2g        | 50                       | 30                     |
| 2r        | 71                       | 9                      |

\(^a\)Determined by \(^1\)H NMR spectroscopy against internal standard.

4. Deuterium Labelling Experiments

For PMHS experiments, pre-catalyst 1 (7.0 mg, 5 mol%) was weighed out into a 4 dram vial equipped with a stirrer bar within the glovebox. Ethanol-OD (14.6 µL, 0.25 mmol, 1 equiv.), n-butanol-d\(_{10}\) (22.9 µL, 0.25 mmol, 1 equiv.) or aniline-N,N-d\(_{2}\) (23.1 µL, 0.25 mmol, 1 equiv.) was added, followed by the corresponding alkene substrate (0.25 mmol, 1 equiv.). PMHS (0.5 mL) was added where the vessel was sealed and stirred for 24 hours at RT. The vial was removed from the glovebox and exposed to air. The mixture was dissolved in CDCl\(_3\) or CHCl\(_3\) and product was separated by vacuum transfer. For Ph\(_2\)SiH\(_2\) experiments, pre-catalyst 1 (7.0 mg, 5 mol%) was weighed into a J-young NMR tube and dissolved in C\(_6\)H\(_6\) (0.5 mL) within the glovebox. Aniline-N,N-d\(_{2}\) (23.1 µL, 0.25 mmol, 1 equiv.) or n-butanol-d\(_{10}\) (22.9 µL, 0.25 mmol, 1 equiv.) was added followed by the corresponding alkene substrate (0.25 mmol, 1 equiv.). Ph\(_2\)SiH\(_2\) (46.4 µL, 0.25 mmol, 1 equiv.) was added where the vessel was sealed for 16 hours. The product was separated by vacuum transfer into a second J-young NMR tube. Mesitylene (0.25 mmol) and DCM-d\(_2\) (0.25 mmol) were added and deuterium incorporation was determined by \(^1\)H and \(^2\)H NMR.
5. Gas Evolution Experiments

Transfer Hydrogenation Experiments

Pre-catalyst 1 (7.0 mg, 5 mol%) was weighed out into the Man on the Moon (MOTM) reaction flask within the glovebox. The corresponding quantity of n-butanol and allyl benzene (33.1 µL, 0.25 mmol, 1 equiv.) were added and the flask was sealed with a septum. The flask was removed from the glovebox and connected to the Schlenk line and pressure sensor under N₂ atmosphere. PMHS (0.5 mL) was added via syringe and hydrogen evolution was monitored until the reaction reached completion.

Dehydrocoupling Experiments

Pre-catalyst 1 (28.0 mg, 5 mol%) was weighed out into the MOTM reaction flask within the glovebox. The flask was sealed with a septum, removed from the glovebox and connected to the Schlenk line and pressure sensor under N₂ atmosphere. The corresponding alcohol (1.00 mmol, 1.0 equiv.) followed by PMHS (1.00 mmol, 59.7 C, 1.0 equiv.) were added via syringe and hydrogen evolution was monitored until the reaction reached completion.
6. H₂ Experiments

Pre-catalyst 1 was weighed into the Parr bomb reactor within the glovebox, followed by allyl benzene (33.1 µL, 0.25 mmol) and PMHS (0.5 mL) or n-butanol (22.0 µL, 0.25 mmol) and C₆D₆ (0.5 mL). The vessel was sealed, removed from the glovebox and charged with the corresponding pressure of H₂ gas. The mixture was stirred for 24 hours at RT. The vessel was depressurised and reaction progress determined by ¹H NMR. For n-butanol reactions, the mixture was filtered through a short silica plug with DCM and volatiles removed under a stream of N₂ prior to NMR analysis.

7. Substrate Scope Spectroscopic Data

1-Phenylpropane (2a)

Spectroscopic yield: 85%

¹H NMR (CDCl₃, 400 MHz): δ 7.33-7.29 (m, 2H), 7.22-7.19 (m, 3H), 2.62 (t, J = 7.6 Hz, 2H), 1.68 (h, J = 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H).

¹³C(¹H) NMR (CDCl₃, 100 MHz): δ 142.8, 128.6, 128.3, 125.7, 38.2, 24.7, 14.0.

Data comparable to literature.²

1-Methyl-4-propylbenzene (2b)

Spectroscopic yield: 79%

¹H NMR (CDCl₃, 400 MHz): δ 7.25-7.20 (m, 4H), 2.70 (t, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.78 (m, 2H), 1.09 (m, 3H).
Data comparable to literature.³

1-Methyl-3-propylbenzene (2c)

Spectroscopic yield: 46%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.23-7.15 (m, 2H), 7.04-7.00 (m, 2H), 2.59 (t, $J$ = 7.6 Hz, 2H), 2.37 (s, 3H), 1.68 (h, $J$ = 7.5 Hz, 2H), 0.99 (m, 3H).

Spectrum comparable to a sample of commercially available 1-methyl-3-propylbenzene.

1-Methyl-2-propylbenzene (2d)

Spectroscopic yield: 62%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.17-7.10 (m, 5H), 2.61 (t, $J$ = 7.8 Hz, 2H), 2.34 (s, 3H), 1.65 (h, $J$ = 7.5 Hz, 2H), 1.02 (t, $J$ = 7.3 Hz, 3H).

Data comparable to literature.⁴

1-Methoxy-4-propylbenzene (2e)

Spectroscopic yield: 91%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.12 (d, $J$ = 8.5 Hz, 2H), 6.85 (d, $J$ = 8.6 Hz, 2H), 3.80 (s, 3H), 2.56 (t, $J$ = 7.6 Hz, 2H), 1.65 (h, $J$ = 7.5 Hz, 2H), 0.97 (t, $J$ = 7.3 Hz, 3H).

Data comparable to literature.⁴

1-Propyl-4-(trifluoromethyl)benzene (2f)

Spectroscopic yield: 36%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.52 (d, $J$ = 8.1 Hz, 2H), 7.26 (d, $J$ = 8.0 Hz, 2H), 2.64 (t, $J$ = 7.6 Hz, 2H), 1.67 (h, $J$ = 7.4 Hz, 2H), 0.96 (m, 3H).

$^{19}$F NMR (CDCl$_3$, 378 MHz): δ -62.1 (s, 3F).

Data comparable to literature.⁵

1-Propyl-4-fluorobenzene (2g)

Spectroscopic yield: 50%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.13-7.09 (m, 2H), 6.98-6.92 (m, 2H), 2.56 (t, $J$ = 7.6 Hz, 2H), 1.63 (h, $J$ = 7.5 Hz, 2H), 0.94 (t, $J$ = 7.3 Hz, 3H).
$^{19}$F NMR (CDCl$_3$, 378 MHz): δ -118.02 (s, 1F).

Data comparable to literature.$^6$

**Ethylbenzene (2h)**

![structure](image)

0.25 mmol, 24 h: Spectroscopic yield: 71%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.36-7.28 (m, 2H), 7.24-7.17 (m, 3H), 2.67 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H).

2.5 mmol, 48 h: Colourless oil isolated by vacuum distillation (225 mg, 2.12 mmol, 85%).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.34-7.30 (m, 2H), 7.25-7.19 (m, 3H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.28 (t, $J = 7.6$ Hz, 3H).

$^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz): δ 144.4, 128.4, 128.0, 125.7, 29.1, 15.8.

FTIR: cm$^{-1}$ 3084, 3064, 3030, 2967, 2930, 2877, 1603, 1496, 1456.

Data comparable to literature.$^7$

**1-Ethyl-4-methylbenzene (2i)**

![structure](image)

Spectroscopic yield: 52%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.07 (s, 4H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.30 (s, 3H), 1.21 (t, $J = 7.6$ Hz, 3H).

Data comparable to literature.$^6$

**1-Ethyl-4-methoxybenzene (2j)**

![structure](image)

0.25 mmol, 24 h: Spectroscopic yield: 78%

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.18 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 3.84 (s, 3H), 2.67 (q, $J = 7.6$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H).

0.50 mmol, 24 h: Colourless oil isolated by silica gel column chromatography (hexane/EtOAc (95:5)), (47.0 mg, 0.35 mmol, 69%).

$^1$H NMR (CDCl$_3$, 300 MHz): δ 7.14 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 3.81 (s, 3H), 2.62 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H).

$^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz): δ 157.7, 136.5, 128.8, 113.8, 55.4, 28.1, 16.1.

FTIR: cm$^{-1}$ 2997, 2962, 2934, 2836, 1610, 1583, 1512, 1034.

Data comparable to literature.$^4$

**1-Ethyl-4-(trifluoromethyl)benzene (2k)**

![structure](image)
Spectroscopic yield: 44%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.57 (d, $J = 7.9$ Hz, 2H), 7.33 (d, $H = 7.9$ Hz, 2H), 2.75 (q, $J = 7.6$ Hz, 2H), 1.31 (t, $J = 7.6$ Hz, 3H).

$^{19}$H NMR (CDCl$_3$, 376 MHz): $\delta$ -62.4 (s, 3F).
Data comparable to literature.$^8$

1-Ethyl-4-fluorobenzene (2l)

\[
\text{F} \quad \text{C}_6 \text{H}_4 \text{CH}_2 \text{CH}_3 
\]

Spectroscopic yield: 31%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.19-7.16 (m, 2H), 7.02-6.97 (m, 2H), 2.66 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H).

$^{19}$H NMR (CDCl$_3$, 376 MHz): $\delta$ -118.2 (s, 1F).
Data comparable to literature.$^9$

4-Ethyl-1,1'-biphenyl (2m)

\[
\text{C}_6 \text{H}_4 \text{CH}_2 \text{CH}_3 \quad \text{C}_6 \text{H}_4 \text{CH}_2 \text{CH}_3
\]

Spectroscopic yield: 66%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.58-7.23 (m, 9H), 2.67 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H).
Data comparable to literature.$^{10}$

1-Ethyl-2-methoxybenzene (2n)

\[
\text{C}_6 \text{H}_4 \text{CH}_2 \text{OCH}_3
\]

Spectroscopic yield: 43%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.16-6.82 (m, 4H), 2.83 (s, 3H), 2.64 (q, $J = 7.5$ Hz, 2H), 1.19 (t, $J = 7.5$ Hz, 3H).
Data comparable to literature.$^{11}$

1-Phenylpropane (2o)

\[
\text{C}_6 \text{H}_4 \text{CH}_2 \text{CH}_3
\]

Spectroscopic yield: 9%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.38-7.21 (m, 5H), 2.65 (t, $J = 7.6$ Hz, 2H), 1.71 (h, $J = 7.5$ Hz, 2H), 1.01 (m, 3H).
Data comparable to literature.$^2$

1,1-Diphenylethane (2p)
Spectroscopic yield: 76%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.39-7.19 (m, 10H), 4.20 (q, $J$ = 7.2 Hz, 1H), 1.69 (d, $J$ = 7.3 Hz, 3H).

Data comparable to literature.$^{12}$

**Isopropylbenzene (2q)**

Spectroscopic yield: 63%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.37-7.16 (m, 5H), 2.94 (hept, $J$ = 6.9 Hz, 1H), 1.29 (d, $J$ = 6.9 Hz, 6H).

Spectrum comparable to a sample of commercially available cumene.

**1-Butylbenzene (2r)**

Spectroscopic yield: 71%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.27-7.22 (m, 2H), 7.16-7.10 (m, 3H), 2.59 (t, $J$ = 7.7 Hz, 2H), 1.63-1.51 (m, 2H), 1.39-1.30 (m, 2H), 0.92 (m, 3H).

Data comparable to literature.$^9$

**Cyclohexane (2s)**

0.25 mmol, 24 h: Spectroscopic yield : 68%

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.38 (s, 12H).

2.5 mmol, 24 h: Colourless oil isolated by vacuum distillation (156 mg, 1.85 mmol, 74%).

Spectrum comparable to a sample of commercially available cyclohexane.

**Hexane (2t)**

Spectroscopic yield, $2t_1$: 64%

$2t_{trans-2}$: 50%

$2t_{cis-2}$: 63%

$2t_{trans-3}$: 61%

$2t_{cis-3}$: 71%
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.37-1.29 (m, 8H), 0.94 (t, $J = 6.9$ Hz, 6H).

Spectrum comparable to a sample of commercially available hexane.
8. Substrate Scope Spectra

1-Phenylpropane (2a)
4-Methyl-1-propylbenzene (2b)

1-Methyl-3-propylbenzene (2c)
1-Methyl-2-propylbenzene (2d)

1-Methoxy-4-propylbenzene (2e)
1-Propyl-4-(trifluoromethyl)benzene (2f)
1-Propyl-4-fluorobenzene (2g)
Ethylbenzene (2h)
1-Ethyl-4-methylbenzene (2i)
1-Ethyl-4-methoxybenzene (2j)
1-Ethyl-4-(trifluoromethyl)benzene (2k)
1-Ethyl-4-fluorobenzene (2f)
4-Ethyl-1,1'-biphenyl (2m)

1-Ethyl-2-methoxybenzene (2n)
1-Phenylpropane (2o)

*Aromatic and C-3 protons indistinguishable from remaining starting material and PMS-butoxide side product respectively.

1,1-Diphenylethane (2p)
Isopropylbenzene (2q)

Butylbenzene (2r)
9. Deuterated Products

D-1-phenylpropane

From EtOD and PMHS:

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 MHz): & \delta 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 2.61-2.58 (m, 1.8H), 1.69-1.61 (m, 1.6H), 0.96-0.91 (m, 2.6H). \\
\text{H NMR (CHCl}_3, 77 MHz): & \delta 2.59 (\text{minor}, 0.12D), 1.65 (\text{major}, 0.50D), 0.96 (\text{minor}, 0.38D).
\end{align*}
\]
From nBuOD and PMHS:

\[
\begin{align*}
\text{D} & \quad \text{D} \\
\text{15\%} & \quad \text{36\%} \\
\text{D} & \quad \text{49\%}
\end{align*}
\]

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.32-7.29 (m, 2H), 7.21-7.19 (m, 3H), 2.63-2.60 (m, 1.8H), 1.70-1.64 (m, 1.7H), 0.99-0.97 (m, 2.5H).

\(^2\)H NMR (CHCl\(_3\), 77 MHz): \(\delta\) 2.62 (minor, 0.15D), 1.67 (major, 0.49D), 0.98 (minor, 0.36D).
From D$_2$NPh and PMHS:

\[
\begin{array}{c}
\text{D} & \text{D} \\
0\% & 90\% \\
\text{D} & 10\% \\
\end{array}
\]

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.32-7.29 (m, 2H), 7.22-7.19 (m, 3H), 2.63-2.60 (m, 2H), 1.72-1.64 (m, 1.9H), 1.00-0.94 (m, 2.1H).

$^2$H NMR (CHCl$_3$, 77 MHz): $\delta$ 1.66 (minor, 0.10D), 0.97 (major, 0.90D).
From D₂NPh and Ph₂SiH₂:

\[ \text{D} \quad \text{D} \quad \text{D} \quad \text{0\%} \]

\[ \text{D} \quad \text{D} \quad \text{D} \quad \text{0\%} \]

\(^1\)H NMR (C₆D₆, 500 MHz): \( \delta \) 7.17-7.14 (m, 2H), 7.08-7.03 (m, 3H), 2.43-2.40 (m, 1.9H), 1.52-1.46 (m, 1.9H), 0.83-0.78 (m, 2.1H).

\(^2\)H NMR (C₆H₆, 77 MHz): \( \delta \) 0.79 (major, 1.00D).
From nBuOD and Ph₂SiH₂:

1H NMR (C₆D₆, 500 MHz): δ 7.16-7.12 (m, 2H), 7.06-7.01 (m, 3H), 2.41-2.38 (m, 1.9H), 1.51-1.45 (m, 1.8H), 0.81-0.76 (m, 2.3H).

2H NMR (C₆H₆, 77 MHz): δ 1.43 (minor, 0.24D), 0.80 (major, 0.76D).
From nBuOD and 1.0 equiv. PMHS:

\[
\begin{align*}
\text{H NMR (CDCl}_3\text{, 500 MHz): } & \delta 7.36-7.28 \text{ (m, 2H), 7.23-7.20 (m, 3H), 2.63-2.58 (m, 1.7H), 1.71-1.64 (m, 1.6H), 0.99-0.94 (m, 2.7H).} \\
\text{H NMR (CHCl}_3\text{, 77 MHz): } & \delta 2.62 \text{ (minor, 0.23D), 1.67 (major, 0.49D), 0.98 (minor, 0.28D).}
\end{align*}
\]
D-1-phenylethane

From EtOD and PMHS:

\[
\text{D}^{38\%} \quad \text{D}^{62\%}
\]

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.35-7.28 (m, 2H), 7.22-7.17 (m, 3H), 2.69-2.64 (m, 1.6H), 1.27-1.24 (m, 2.4H).

\(^2\)H NMR (CHCl\(_3\), 77 MHz): \(\delta\) 2.66 (minor, 0.38D), 1.26 (major, 0.62D).
From nBuOD and PMHS:

\[
\begin{array}{c}
\text{D} 37 \\
\text{D} 63 \\
\end{array}
\]

\( ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz): } \delta 7.35-7.31 (m, 2H), 7.25-7.20 (m, 3H), 2.72-2.66 (m, 1.7H), 1.31-1.25 (m, 2.3H). \)

\( ^2H \text{ NMR (CHCl}_3, 77 \text{ MHz): } \delta 2.67 \text{ (minor, 0.37D), 1.27 \text{ (major, 0.63D).} } \)
From D$_2$NPh and PMHS:

$\text{D} \quad 17\%$

$\text{D} \quad 83\%$

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.32-7.29 (m, 2H), 7.23-7.16 (m, 3H), 2.70-2.65 (m, 1.8H), 1.28-1.23 (m, 2.2H).

$^2$H NMR (CHCl$_3$, 77 MHz): $\delta$ 2.66 (minor, 0.17D), 1.26 (major, 0.83D).
From D$_2$NPh and Ph$_2$SiH$_2$:

\[ \begin{array}{c}
\text{D} \\
\text{D}
\end{array} \]

D 27%  
D 73%

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ 7.17-7.14 (m, 2H), 7.07-7.04 (m, 3H), 2.46-2.42 (m, 1.7H), 1.09-1.04 (m, 2.3H).

$^2$H NMR (C$_6$H$_6$, 77 MHz): $\delta$ 2.39 (minor, 0.27D), 1.04 (major, 0.73D).
From nBuOD and Ph₂SiH₂:

$\text{D} 33\%$

$\text{D} 67\%$

$^1$H NMR (C₆D₆, 500 MHz): δ 7.15-7.12 (m, 2H), 7.08-7.01 (m, 3H), 2.44-2.40 (m, 1.7H), 1.06-1.02 (m, 2.3H).

$^2$H NMR (C₆H₆, 77 MHz): δ 2.39 (minor, 0.33D), 1.04 (major, 0.67D).
From nBuOD and 1.0 equiv. PMHS:

\[ \text{D 37\%} \]
\[ \text{D 63\%} \]

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) 7.31-7.25 (m, 2H), 7.21-7.16 (m, 3H), 2.68-2.62 (m, 1.6H), 1.27-1.21 (m, 2.4H).

\(^2\)H NMR (CHCl\(_3\), 77 MHz): \( \delta \) 2.68 (minor, 0.37D), 1.28 (major, 0.63D).
D-hexane

From EtOD and PMHS:

\[
\text{\begin{tikzpicture}
\draw[thick,->] (0,0) -- (1,0) node[below] {D 59\%};
\draw[thick,->] (1,0) -- (2,0) node[below] {D 41\%};
\end{tikzpicture}}
\]

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 1.31-1.23 (m, 7.5H), 0.90-0.87 (m, 5.5H).

\(^2\)H NMR (CHCl\(_3\), 77 MHz): \(\delta\) 1.28 (0.59D), 0.89 (0.41D).
From nBuOD and PMHS:

\[ ^1\text{H NMR (CDCl}_3, 500 \text{ MHz): } \delta 1.37-1.33 \text{ (m, 7.4H), 0.96-0.94 \text{ (m, 5.6H).} \]

\[ ^2\text{H NMR (CHCl}_3, 77 \text{ MHz): } \delta 1.34 \text{ (0.60D), 0.95 \text{ (0.40D).} \]
From D$_2$NPh and PMHS:

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.37-1.33 (m, 8H), 0.96-0.93 (m, 5H).

$^2$H NMR (CHCl$_3$, 77 MHz): $\delta$ 0.93 (1.00D).
From nBuOD and Ph₂SiH₂:

\[ \text{D 11\%} \]
\[ \text{D 89\%} \]

\(^1\)H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz): \( \delta \) 1.25-1.18 (m), 0.87-0.84 (m, 5.1H).

\(^2\)H NMR (C\textsubscript{6}H\textsubscript{6}, 77 MHz): \( \delta \) 1.21 (0.11D), 0.85 (0.89D).
From D$_2$NPh and Ph$_3$SiH$_2$:

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ 1.28-1.23 (m, 8.0H), 0.90-0.86 (m, 5.0H).

$^2$H NMR (C$_6$H$_6$, 77 MHz): $\delta$ 0.89 (1.00D).
From nBuOD and 1.0 equiv. PMHS:

\[ \text{D 60\%} \]
\[ \text{D 40\%} \]

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.36-1.31 (m, 7.3H), 0.95-0.90 (m, 5.7H).

$^2$H NMR (CHCl$_3$, 77 MHz): $\delta$ 1.30 (0.59D), 0.91 (0.41D).
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