

Supplementary Information

Iron-Catalyzed Olefin Hydrogenation at 1 bar H₂ with a FeCl₃/LiAlH₄ Catalyst

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Germany.

General

Analytical Thin-Layer Chromatography

TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdotophosphoric acid in ethanol or a solution of potassium permanganate in water.

Column Chromatography

Flash column chromatography with silica gel 60 from *KMF* (0.040-0.063 mm). Mixtures of hexanes / ethyl acetate or *n*-pentane / ethyl acetate were used as eluents.

Chemicals and Solvents

Commercially available olefins were distilled under reduced pressure before use. Catalytic reactions were run in dry solvents. THF was distilled over sodium and benzophenone under an inert atmosphere. Lithium aluminiumhydride and iron(III)chloride (98%, anhydrous) were stored and handled in a glovebox under argon (99.996%). Lithium aluminiumhydride in Et₂O was filtrated under inert atmosphere and dried in vacuo before use. Solvents used for column chromatography were distilled under reduced pressure before use.

High Pressure Reactor

Hydrogenation reactions were carried out in 150 and 300 mL high pressure reactors (*Parr*). After the vials containing substrate and catalyst mixture in THF were placed into the reactor, it was purged with argon, then with H₂ (1 min), sealed, and the internal pressure was adjusted (1, 2, 4 or 10 bar). Hydrogen (99.9992%) was purchased from *Linde*.

¹H- und ¹³C-NMR-Spectroscopy

Nuclear magnetic resonance spectra were recorded on a *Bruker Advance 300* (300 MHz) and *Bruker Advance 400* (400 MHz). ¹H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartett. Chemical shifts δ are given in ppm relative to tetramethylsilane.

Melting Points

Melting points were recorded on an *apotec* apparatus and are uncorrected.

FT-IR

Spectra were recorded on a *Varian Scimitar 1000 FT-IR* with ATR probe at room temperature. Wavenumbers are given in cm^{-1} . Absorption band intensities are assigned with s = strong, m = medium, w = weak and b = broad.

Gas chromatography with FID (GC-FID)

HP6890 GC-system with injector 7683B and Agilent 7820A system, carrier gas: N_2 . GC-FID was used for reaction control and catalyst screening. Linear calibration curves were recorded with five data points from mixtures of the internal reference *n*-pentadecane and analytically pure samples.

Gas chromatography with mass-selective detector (GC-MS)

Agilent 6890N network GC-system, mass detector 5975 MS. Column: HP-5MS (30m x 0.25 mm x 0.25, 5% phenylmethylsiloxane, carrier gas: H_2 . Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min)

High resolution mass spectrometry (HRMS)

Mass spectra were recorded on a *Finnigan MAT SSQ 710 A* in electron ionization (EI) mode (70 eV).

Dynamic Light Scattering (DLS)

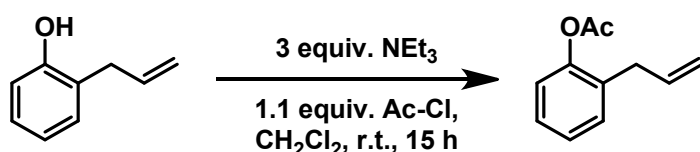
Dynamic light scattering experiments were performed at a goniometer CGS-II from ALV (Germany). The goniometer was equipped with an ALV-7004/fast multiple tau digital correlator and a vertically polarized 22 mW HeNe-laser (wavelength = 623.8 nm). All measurements were performed at a scattering angle of 90° after thermostating to 25 °C. The measurement time was 300 s. The obtained correlation functions were fitted with the software TableCurve 2d v5.01 by a monomodal equation.

Preparation of starting materials

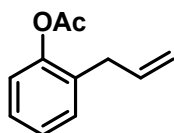
Preparation of allylbenzenes

Allylbenzenes were prepared according to: M. Mayer, W. M. Czaplik and A. Jacobi von Wangelin, *Adv. Synth. Catal.* **2010**, 352, 2147. Analytical data were in full agreement with the literature reports.

2-Allylphenyl acetate



A 50 mL flask was charged with a solution of 2-allylphenol (1.4 mL, 10.6 mmol) in 15 mL CH_2Cl_2 . Then, triethylamine (4.6 mL, 33 mmol) was added at 0 °C followed by the slow addition of the acetyl chloride (11.6 mmol). The reaction mixture was stirred at room temperature for 15 h, diluted with 20 mL of ethyl acetate and washed with saturated aqueous NH_4Cl (10 mL). The organic phases were dried (MgSO_4), concentrated, and subjected to silica gel flash chromatography (cyclohexane/ethyl acetate).



$\text{C}_{11}\text{H}_{12}\text{O}_2$, **176.21 g/mol**

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.33-7.11 (m, 1H), 7.03 (d, 8.0 Hz, 1H), 5.90 (dt, J = 16.5, 6.4 Hz, 1H), 5.21-4.93 (m, 1H), 3.30 (d, J = 6.5 Hz, 1H), 2.30 (s, 1H).

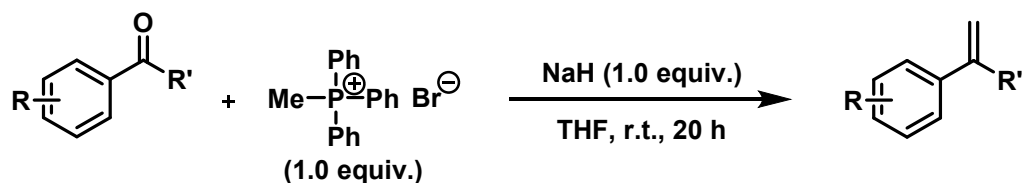
GC-MS t_R = 5.82 min, (EI, 70 eV): m/z = 176 [M^+].

For analytical data, see: M. J. Gresser, S. M. Wales, P. A. Keller, *Tetrahedron* **2010**, 66, 6965.

Preparation of styrenes

Styrenes were purchased from *SigmaAlrich*, *AlfaAesar* and *TCI* or synthesized according to the following methods:

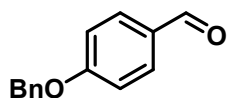
General procedure for the synthesis of styrenes from carbonyl compounds



Representative synthesis of:

A 50 mL flask was charged with a suspension of methyl triphenylphosphonium bromide (6.94 mmol, 2.48 g) in THF (10 mL). Then, a NaH suspension in paraffine (60%, 6.94 mmol, 278 mg) was added in small portions. The reaction mixture was stirred at room temperature for 20 h followed by a dropwise addition of a solution of the carbonyl compound (6.94 mmol) in THF (10 mL). The reaction was stirred for 2 d at room temperature, quenched with H₂O (15 mL) and extracted with Et₂O (3 × 15 mL). The combined organic layers were dried (NaSO₄), concentrated and subjected to silica gel flash chromatography (*n*-pentane).

Synthesis of 4-(benzyloxy)benzaldehyde according to: S. K. Das, G. Panda, *Tetrahedron* **2008**, 19, 4162-4173.

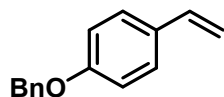


C₁₄H₁₂O₂, **212.24 g/mol**

¹H-NMR	(300 MHz, CDCl ₃) δ 9.89 (s, 1H), 7.84 (d, <i>J</i> = 8.7 Hz, 2H), 7.48 – 7.33 (m, 5H), 7.08 (d, <i>J</i> = 8.7 Hz, 2H), 5.16 (s, 2H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 190.82, 163.72, 135.93, 132.02, 130.11, 128.75, 128.36, 127.51, 115.15, 70.28.
GC-MS	<i>t</i> _R = 9.96 min, (EI, 70 eV): <i>m/z</i> = 212 [M ⁺], 152, 121, 91, 77, 65, 51.

T. Shintou, T. Mukaiyama, *J. Am. Chem. Soc.*, **2004**, 23, 7359-7367.

1-(Benzyloxy)-4-vinylbenzene



C₁₅H₁₄O, **210.27 g/mol**

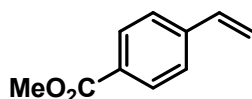
¹H-NMR (300 MHz, CDCl₃) δ 7.49 – 7.29 (m, 7H), 6.99 – 6.90 (m, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.63 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.14 (dd, *J* = 10.9, 0.9 Hz, 1H), 5.08 (s, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 158.57, 136.94, 136.21, 130.69, 128.63, 128.02, 127.50, 127.43, 114.88, 111.75, 70.03.

GC-MS *t_R* = 9.40 min, (EI, 70 eV): *m/z* = 210 [M⁺], 119, 91, 77, 65, 51.

N. Kakusawa, K. Yamaguchi, J. Kouchichiro, *J. Organomet. Chem.* **2005**, 12, 2956-2966.

Methyl 4-vinylbenzoate



C₁₀H₁₀O₂, **162.19 g/mol**

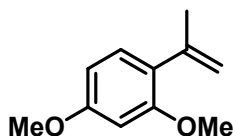
¹H-NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 3.91 (s, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 166.9, 141.9, 136.0, 129.9, 129.3, 126.1, 116.5, 52.1.

GC-MS *t_R* = 6.92 min, (EI, 70 eV): *m/z* = 162 [M⁺], 131, 117, 103, 77, 63, 51.

A. Yokoyama, T. Maruyama, K. Tagami, H. Masu, K. Katagiri, I. Azumaya, T. Yokozawa, *Org. Lett.* **2008**, *10*, 3207–3210.

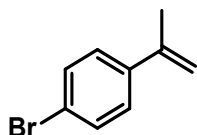
2,4-Dimethoxy- α -methylstyrene



C₁₁H₁₄O₂, **178.23 g/mol**

¹H-NMR	(300 MHz, CDCl ₃) δ 7.12 (d, J = 8.6 Hz, 1H), 6.30 – 6.15 (m, 2H), 5.10 (s, 1H), 5.05 (s, 1H), 3.81 (s, 6H), 2.10 (s, 3H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 160.07, 157.69, 143.73, 129.72, 114.55, 103.95, 98.72, 55.41, 23.42.
GC-MS	t_R = 7.23 min, (EI, 70 eV): m/z = 178 [M ⁺], 163, 148, 135, 120, 115, 105, 91, 77, 69, 63, 51.
GC-HRMS	(EI, m/z): found 178.0996 [M ⁺] (calculated 178.0994).
FT-IR	(ATR-film) in [cm ⁻¹] 2969 (w), 2955 (w), 2835 (w), 1737 (m), 1607 (s), 1578 (m), 1502 (s), 1463 (m), 1413 (w), 1371 (w), 1298 (m), 1257 (m), 1243 (m), 1206 (s), 1158 (s), 1102 (m), 1035 (s), 936 (w), 912 (w), 832 (m), 800 (m), 733 (m), 681 (w), 635 (m), 607 (w), 505 (m).

4-Bromo- α -methylstyrene



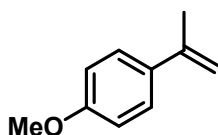
C₉H₉Br, **197.07 g/mol**

¹H-NMR	(400 MHz, CDCl ₃) δ 7.50-7.35 (m, 2H), 7.42-7.29 (m, 2H), 5.36 (s, 1H), 5.10 (s, 1H), 2.12 (s, 3H).
¹³C-NMR	(101 MHz, CDCl ₃) δ 142.2, 140.1, 131.3, 127.2, 121.4, 113.1, 21.7.

GC-MS $t_R = 6.51$ min, (EI, 70 eV): $m/z = 197$ [M^+], 183, 171, 156, 115, 102, 91, 75, 63, 51.

T. Taniguchi, A. Yajima, H. Ishibashi, *Adv. Synth. Catal.* **2011**, 353, 2643–2647.

4-Methoxy- α -methylstyrene



$C_{10}H_{12}O$, **148.20 g/mol**

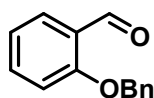
1H -NMR (300 MHz, $CDCl_3$) δ 7.42 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 5.29 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 2.13 (s, 3H).

^{13}C -NMR (75 MHz, $CDCl_3$) δ 159.05, 142.56, 133.74, 126.60, 113.54, 110.68, 55.30, 21.94.

GC-MS $t_R = 6.39$ min, (EI, 70 eV): $m/z = 148$ [M^+], 127, 133, 115, 105, 89, 77, 63, 51.

A. Fryszkowska, K. Fisher, J. M. Gardiner, G. M. Stephens, *J. Org. Chem.* **2008**, 73, 4295-4298.

Synthesis of 2-(benzyloxy)benzaldehyde according to reference: S. K. Das, G. Panda, *Tetrahedron* **2008**, 19, 4162-4173.



$C_{14}H_{12}O_2$, **212.24 g/mol**

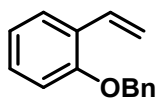
1H -NMR (300 MHz, $CDCl_3$) δ 10.57 (d, $J = 0.7$ Hz, 1H), 7.87 (dd, $J = 8.0$, 1.8 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.48 – 7.31 (m, 5H), 7.09 – 7.01 (m, 2H), 5.20 (s, 2H).

^{13}C -NMR (75 MHz, $CDCl_3$) δ 189.77, 161.05, 136.08, 135.94, 128.75, 128.46, 128.30, 127.31, 125.16, 121.02, 113.02, 70.45.

GC-MS t_R = 9.74 min, (EI, 70 eV): m/z = 212 [M^+], 183, 121, 91, 77, 65, 51.

S. K. Das, G. Panda, *Tetrahedron*, **2008**, 19, 4162-4173.

1-(Benzyloxy)-2-vinylbenzene



$C_{15}H_{14}O$, 210.27 g/mol

1H -NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.6, 1.7 Hz, 1H), 7.50 – 7.34 (m, 5H), 7.25 – 7.10 (m, 2H), 6.97 (ddd, J = 8.2, 5.9, 2.1 Hz, 2H), 5.79 (dd, J = 17.8, 1.5 Hz, 1H), 5.28 (dd, J = 11.2, 1.5 Hz, 1H), 5.12 (s, 2H).

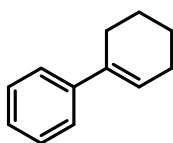
^{13}C -NMR (75 MHz, $CDCl_3$) δ 155.88, 137.16, 131.65, 128.85, 128.59, 127.91, 127.33, 127.11, 126.53, 120.99, 114.49, 112.43, 70.27.

GC-MS t_R = 9.13 min, (EI, 70 eV): m/z 210 [M^+], 193, 119, 91, 77, 65, 51.

M. Barbasiewicz, M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Wozniak, K. Grela, *Adv. Synth. Catal.* **2007**, 349, 193-203.

Synthesis of 1-phenylcyclohex-1-ene

A solution of phenylmagnesiumbromide in THF (1 M, 50.0 mmol, 50.0 mL) was added dropwise to a solution of cyclohexanone (30.0 mmol, 3.20 mL) in THF (30 mL) at 0 °C. The reaction mixture was allowed to gain room temperature while stirring for 2 Et₂O (3 × 15 mL). The combined organic layers were dried (MgSO₄), concentrated and dissolved in toluene (50 mL). After addition of a tip of a spatula *p*-toluenesulfonic acid the reaction mixture was heated under reflux for 12 h. The reaction mixture was concentrated and subjected to silica gel flash chromatography (*n*-pentane).



$C_{12}H_{14}$, **158.24 g/mol**

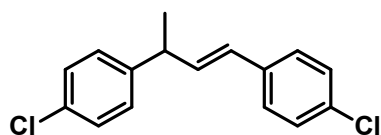
1H -NMR (300 MHz, $CDCl_3$) δ 7.49–7.38 (m, 2H), 7.34 (m, 2H), 7.27–7.19 (m, 1H), 6.15 (m, 1H), 2.44 (m, 2H), 2.30–2.14 (m, 2H), 1.90–1.75 (m, 2H), 1.75–1.61 (m, 2H).

^{13}C -NMR (101 MHz, $CDCl_3$) δ 142.8, 136.7, 128.3, 126.6, 125.0, 124.8, 27.5, 26.0, 23.2, 22.3.

GC-MS t_R = 7.35 min, (EI, 70 eV): m/z = 158 [M^+], 143, 129, 113, 91, 77, 51.

M. A. Reichle, B. Breit, *Angew. Chem. Int. Ed.* **2012**, 51, 5730–5734.

1,3-Bis-(4-chlorophenyl)-1-butene according to: J. R. Cabrero-Antonino, A. Leyva-Pérez, A. Corma, *Adv. Synth. Catal.* **2010**, 352, 1571–1576.



$C_{16}H_{14}Cl_2$, **277.19 g/mol**

1H -NMR (400 MHz, $CDCl_3$) δ 7.33–7.11 (m, 8H), 6.41–6.21 (m, 2H), 3.61 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H).

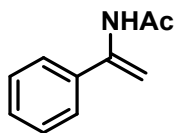
^{13}C -NMR (101 MHz, $CDCl_3$) δ 145.5, 140.6, 131.7, 131.5, 129.7, 128.6, 128.4, 128.4, 39.7, 38.9, 33.2, 22.5.

GC-MS t_R = 10.97 min, (EI, 70 eV): m/z = 276 [M^+], 241, 212, 191, 149, 125, 103, 91, 77, 65, 51.

J. R. Cabrero-Antonino, A. Leyva-Pérez, A. Corma, *Adv. Synth. Catal.* **2010**, 352, 1571–1576.

Synthesis of *N*-(1-phenylvinyl)acetamide

according to: J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu, C. H. Senanayake, *Angew. Chem. Int. Ed.* **2012**, 51, 1400-1404.



C₁₀H₁₁NO, **161.20 g/mol**

¹H-NMR (300 MHz, DMSO) δ 9.34 (s, 1H), 7.49 – 7.31 (m, 5H), 5.62 (s, 1H), 4.98 (s, 1H), 2.01 (s, 3H).

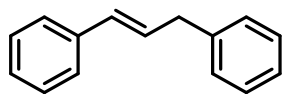
¹³C-NMR ¹³C NMR (75 MHz, DMSO) δ 169.04, 141.36, 140.94, 137.93, 128.18, 126.13, 101.78, 23.64.

GC-MS t_R = 7.87 min, (EI, 70 eV): m/z = 161 [M⁺], 146, 132, 119, 104, 77, 63, 51.

J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu, C. H. Senanayake, *Angew. Chem. Int. Ed.* **2012**, 51, 1400-1404.

Synthesis of 1,3-diphenylpropene

A round-bottom flask was charged with 1,3-diphenylpropanol (7.50 mmol, 1.59 g) and a tip of a spatula of *p*-toluenesulfonic acid in toluene (50 mL). The solution was stirred under reflux for 20 h. After cooling to room temperature the reaction mixture was extracted with Et₂O (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over Na₂SO₄ and subjected to silica gel flash chromatography (*n*-pentane).



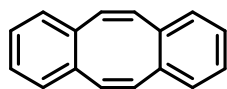
C₁₅H₁₄, **194.28 g/mol**

Appearance colorless oil

Yield	1.25 g, 6.44 mmol (86%)
TLC	R_f = 0.33 (SiO ₂ , <i>n</i> -pentane)
¹H-NMR	(300 MHz, CDCl ₃) δ 7.47 – 7.27 (m, 10H), 6.53 (d, J = 15.9 Hz, 1H), 6.43 (dt, J = 15.7, 6.4 Hz, 1H), 3.62 (d, J = 6.3 Hz, 2H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 140.25, 137.55, 131.15, 129.32, 128.78, 128.60, 127.21, 126.29, 126.22, 39.45.
GC-MS	t_R = 9.01 min, (EI, 70 eV): m/z = 194 [M ⁺], 179, 165, 152, 115, 103, 91, 78, 65, 51.

E. Alacid, C. Nájera, *Org. Lett.* **2008**, *10*, 5011–5014.

Preparation of dibenzo[*a,e*]cyclooctatetraene (dct) in a 3-step synthesis according to: G. Franck, M. Brill, G. Helmchen, *J. Org. Chem.* **2012**, *89*, 55-65.



C₁₆H₁₂, **204.27 g/mol**

¹H-NMR	(300 MHz, CDCl ₃): δ = 7.19–7.13 (m, 4H), 7.10–7.02 (m, 4H), 6.76 (s, 4H).
¹³C-NMR	(75 MHz, CDCl ₃): δ = 137.1, 133.3, 129.1, 126.8.
GC-MS	t_R = 9.35 min, (EI, 70 eV): m/z = 204 [M ⁺].

Preparation of alkenes

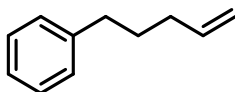
Alkenes were purchased from *SigmaAldrich*, *AcrosOrganics* and *TCI* or synthesized by the following methods:

Synthesis of allylmagnesium chloride

A 25 mL flask was equipped with magnesium (11 mmol, 267 mg) and THF (2.5 mL) under inert atmosphere. Then, allylchloride (10 mmol, 814 μ L) in THF (2.5 mL) was added dropwise. The mixture was stirred for 2 h under reflux.

Synthesis of pent-4-en-1-ylbenzene

A flask was equipped with 2-phenylethylbromide (3.40 mmol, 629 mg) and dissolved in THF (4 mL) under inert atmosphere. A freshly prepared solution of allylmagnesium chloride in THF (4 mL, 2 M) was added dropwise and the resulting reaction mixture was stirred for 1 h under reflux. After cooling to room temperature, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over Na_2SO_4 , concentrated and subjected to silica gel flash chromatography (hexanes/ethyl acetate = 98/2).



$\text{C}_{11}\text{H}_{14}$, 146.23 g/mol

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.30 – 7.13 (m, 5H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.06 – 4.93 (m, 2H), 2.65 – 2.57 (m, 2H), 2.08 (dd, J = 14.6, 6.9 Hz, 2H), 1.77 – 1.65 (m, 2H).

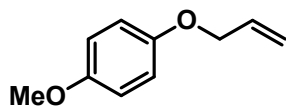
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 141.42, 137.57, 127.42, 127.23, 124.64, 113.67, 34.28, 32.26, 29.59.

GC-MS t_R = 5.77min, (EI, 70 eV): m/z = 146 $[\text{M}^+]$, 131, 117, 105, 92, 77, 65, 55, 51.

J. C. Anderson, R. H. Munday, *J. Org. Chem.* **2004**, 69, 8971–8974.

Synthesis of 1-(allyloxy)-4-methoxybenzene

according to: H. B. Mereyala, S. R. Gurralla, S. K. Mohan, *Tetrahedron*, **1999**, 55, 11331-11342.



C₁₀H₁₂O₂, 164.20 g/mol

¹H-NMR (300 MHz, CDCl₃) δ 6.91 – 6.79 (m, 4H), 6.06 (ddt, *J* = 17.3, 10.6, 5.3 Hz, 1H), 5.41 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.28 (dq, *J* = 10.6, 1.4 Hz, 1H), 4.49 (dt, *J* = 5.3, 1.5 Hz, 2H), 3.77 (s, 3H).

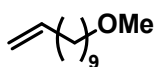
¹³C-NMR (75 MHz, CDCl₃) δ 153.89, 152.74, 133.62, 117.55, 115.71, 114.60, 69.51, 55.72.

GC-MS *t_R* = 6.88 min, (EI, 70 eV): *m/z* = 164 [M⁺], 123, 109, 95, 80, 63, 51.

A. B. Naidu, E. A. Jaseer and G.Sekar *J. Org. Chem.* **2009**, 74, 3675–3679.

Synthesis of 11-methoxyundec-1-ene

A 100 mL flask was charged with a NaH suspension in paraffine (60%, 22.5 mmol, 0.90 g) in THF (30 mL) and cooled to 0 °C. After dropwise addition of 11-undec-1-enol (15 mmol, 2.55 g) the reaction mixture was allowed to gain room temperature while stirring for 2 h. Methyl iodide (15 mmol, 2.55 g) was added and the reaction mixture was heated under reflux for 3 h. Then, the reaction mixture was quenched with an aqueous saturated solution of NH₄Cl (5 mL) and H₂O (5 mL) and extracted with Et₂O (3 × 10 mL). The combined organic layers were dried (Na₂SO₄), concentrated and subjected to silica gel flash chromatography (hexanes/ethyl acetate = 98/2).

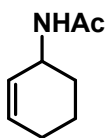


C₁₂H₂₄O 184.32 g/mol

¹H-NMR	(400 MHz, CDCl ₃) δ 5.81 (ddt, <i>J</i> = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (ddd, <i>J</i> = 17.1, 3.7, 1.6 Hz, 1H), 4.93 (ddt, <i>J</i> = 10.2, 2.3, 1.2 Hz, 1H), 3.36 (t, <i>J</i> = 6.7 Hz, 2H), 3.33 (s, 3H), 2.08 – 1.99 (m, 2H), 1.61 – 1.51 (m, 2H), 1.36 – 1.24 (m, 11H).
¹³C-NMR	(101 MHz, CDCl ₃) δ 139.25, 114.10, 72.99, 58.53, 33.81, 29.65, 29.54, 29.49, 29.43, 29.13, 28.94, 26.14.
GC-MS	<i>t</i> _R = 6.73 min, (EI, 70 eV): <i>m/z</i> = 184 [M ⁺], 169, 152, 137, 124, 109, 95, 82, 67, 55.
GC-HRMS	(CI, <i>m/z</i>): found 184.1829 [M ⁺] (calculated 184.1827).
FT-IR	(ATR-film) in [cm ⁻¹] 3077 (w), 2978 (w), 2924 (s), 2854 (s), 1641 (m), 1461 (m), 1387 (w), 1196 (w), 1119 (s), 992 (m), 908 (s), 722 (m), 635 (w).

Synthesis of *N*-(cyclohex-2-en-1-yl)acetamide

A mixture of 3-bromocyclohexene (9.3 mmol, 1.50 g) in CCl₄ (15 mL) and sodium azide (30.9 mmol, 2.00 g) in H₂O (15 mL) was stirred at room temperature for 2 days. The aqueous phase was extracted with CH₂Cl₂ (2 × 25 mL) and ethyl acetate (1 × 25 mL). The combined organic layers were dried (Na₂SO₄), concentrated and diluted in THF (6 mL). After the addition of triphenylphosphine (16.8 mmol, 4.40 g) the reaction mixture was stirred for 2 h. Then, aqueous NaOH (1 M, 40 mL) was added, the reaction mixture was stirred for 18 (1 × 50 mL) and the organic layer was extracted with aqueous HCl (1 M, 3 × 15 mL). The combined aqueous layers were concentrated and suspended in CH₂Cl₂. After the addition of Et₃N (27.9 mmol, 3.87 mL), 4-(*N,N*-dimethylamino)pyridine (0.9 mmol, 113.6 mg) and acetyl chloride (10.2 mmol, 0.73 mL) the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was washed with aqueous saturated NaCl, dried (Na₂SO₄), concentrated and subjected to silica gel flash chromatography (hexanes/ethyl acetate = 1/4).



$C_8H_{13}NO$, **139.19 g/mol**

1H -NMR (400 MHz, $CDCl_3$) δ 5.95–5.77 (m, 1H), 5.74–5.32 (m, 2H), 4.46 (m, 1H), 1.99 (m, 2H), 1.96 (s, 3H), 1.93–1.81 (m, 1H), 1.71–1.58 (m, 2H), 1.58–1.42 (m, 1H).

^{13}C -NMR (101 MHz, $CDCl_3$) δ 169.2, 130.9, 127.7, 44.7, 29.5, 24.8, 23.5, 19.7.

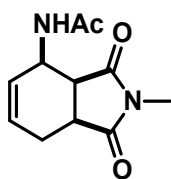
GC-MS t_R = 6.68 min, (EI, 70 eV): m/z = 139 $[M^+]$, 111, 97, 79, 69, 60, 54.

Y. Leblanc, R. Zamboni, M. A. Bernstein, *J. Org. Chem.* **1991**, 56, 1971–1972.

Synthesis of *N*-methyl-3-acetamido-1,2,3,6-tetrahydrophthalimide and *N*-methyl-3-(pyrrolidino-2-one)-1,2,3,6-tetrahydrophthalimide

according to: R. Fichtler, J.-M. Neudörfl, A. Jacobi von Wangelin, *Org. Biomol. Chem.* **2011**, 9, 7224–7236.

N-Methyl-3-acetamido-1,2,3,6-tetrahydrophthalimide



$C_{11}H_{14}N_2O_3$, **222.24 g/mol**

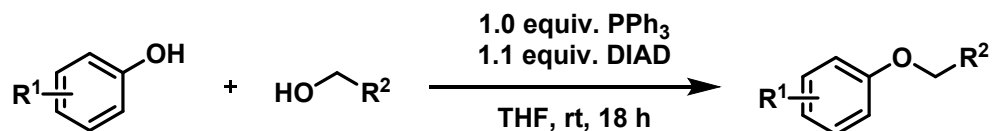
1H -NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 1H), 5.86 (m, 1H), 5.72 (m, 1H), 4.81–4.61 (m, 1H), 3.19 (m, 2H), 2.71 (m, 1H), 2.21 (m, 1H), 2.08 (s, 3H).

^{13}C -NMR (75 MHz, $CDCl_3$) δ 179.3, 179.2, 169.9, 132.9, 127.4, 45.2, 42.5, 38.8, 25.0, 24.1, 23.5.

GC-MS t_R = 9.76 min, (EI, 70 eV): m/z = 222 $[M^+]$, 204, 179, 165, 151, 136, 120, 105, 94, 79, 69, 58.

D. Strübing, H. Neumann, A. Jacobi von Wangelin, S. Klaus, S. Hübner, M. Beller, *Tetrahedron* **2006**, 62, 10962–10967.

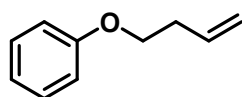
General procedure for the synthesis of aryl ω -alkenyl ethers



Representative procedure for the synthesis of (but-3-en-1-yloxy)benzene:

A flask was charged with phenol (15.0 mmol, 1.41 g) and triphenylphosphine (15.0 mmol, 3.93 g) under an inert atmosphere. After solvation in dry THF (25 mL) 3-buten-1-ol (15.0 mmol, 1.08 g) was added and the stirred solution was cooled by an external ice/water bath. Diisopropyl azodicarboxylate (16.5 mmol, 3.33 g) was added dropwise and the solution was allowed to come to room temperature and stirred for additional 18 h. After evaporation of the solvent under reduced pressure, the residue was purified by silica gel flash chromatography (hexanes).

(But-3-en-1-yloxy)benzene



C₁₀H₁₂O,
148.20 g/mol

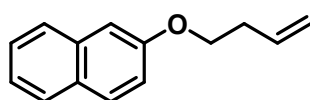
Appearance	colorless liquid
Yield	1.14 g, 7.69 mmol (51%)
TLC	R_f = 0.26 (SiO ₂ , hexanes)
¹H-NMR	(300 MHz, CDCl ₃) δ 7.37 – 7.28 (m, 2H), 7.03 – 6.90 (m, 3H), 5.96 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.27 – 5.11 (m, 2H), 4.05 (t, J = 6.7 Hz, 2H), 2.59 (qt, J = 6.7, 1.2 Hz, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 158.94, 134.56, 129.49, 120.73, 117.05, 114.61, 67.12, 33.74.

GC-MS t_R = 5.93 min, (EI, 70 eV): m/z = 148 [M⁺], 120, 107, 94, 77, 65, 55.

J. Niu, H. Zhou, Z. Li, J. Xu, S. Hu, *J. Org. Chem.* **2008**, 73, 7814–7817.

2-(But-3-en-1-yloxy)naphthalene



C₁₄H₁₄O, 198.26 g/mol

Appearance yellowish, opaque liquid

Yield 2.50 g, 12.61 mmol (84%)

TLC R_f = 0.32 (SiO₂, hexanes)

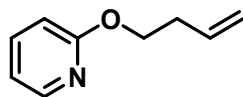
¹H-NMR (300 MHz, CDCl₃) δ 7.81 – 7.69 (m, 3H), 7.44 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.34 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.20 – 7.12 (m, 2H), 5.97 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.22 (dq, J = 17.2, 1.6 Hz, 1H), 5.15 (ddd, J = 10.2, 3.0, 1.2 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 2.63 (qt, J = 6.7, 1.3 Hz, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 156.88, 134.57, 134.50, 129.39, 128.97, 127.66, 126.74, 126.35, 123.58, 119.01, 117.12, 106.67, 67.21, 33.65.

GC-MS t_R = 8.99 min, (EI, 70 eV): m/z = 198 [M⁺], 183, 170, 157, 143, 126, 114, 101, 89, 77, 63, 53.

B. Branchi, C. Galli, P. Gentili, *Eur. J. Org. Chem.* **2002**, 2002, 2844–2854.

2-(But-3-en-1-yloxy)pyridine



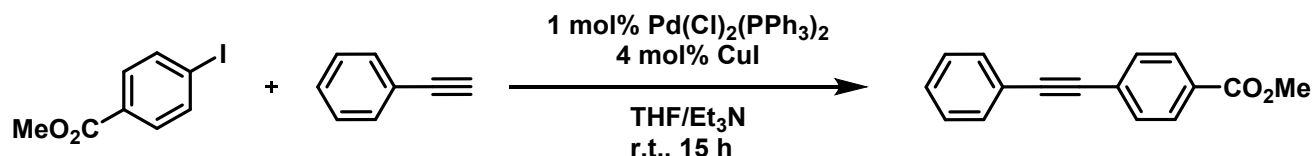
C₉H₁₁NO, 149.19 g/mol

Appearance	yellowish liquid
Yield	949 mg, 6.36 mmol (42%)
TLC	R_f = 0.26 (SiO ₂ , hexanes/Et ₂ O = 30/1)
¹H-NMR	(300 MHz, CDCl ₃) δ 8.15 (ddd, J = 5.1, 2.0, 0.7 Hz, 1H), 7.56 (ddd, J = 8.4, 7.1, 2.0 Hz, 1H), 6.85 (ddd, J = 7.1, 5.1, 0.9 Hz, 1H), 6.73 (dt, J = 8.4, 0.8 Hz, 1H), 5.91 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.16 (ddd, J = 17.2, 3.4, 1.6 Hz, 1H), 5.09 (ddd, J = 10.2, 3.1, 1.2 Hz, 1H), 4.35 (t, J = 6.8 Hz, 2H), 2.54 (qt, J = 6.8, 1.4 Hz, 2H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 163.77, 146.76, 138.64, 134.72, 116.84, 116.64, 111.19, 65.09, 33.47.
GC-MS	t_R = 5.70 min, (EI, 70 eV): m/z = 149 [M ⁺], 132, 120, 108, 95, 78, 67, 51.
GC-HRMS	(APCI, m/z): found 150.0917 [M+H ⁺] (calculated 150.0913).

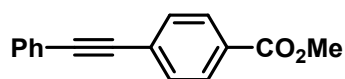
Preparation of alkynes

Alkynes were purchased from *SigmaAldrich*, *AlfaAesar* or synthesized by the following methods:

Synthesis of methyl 4-(phenyl-ethynyl) benzoate



A 50 mL *Schlenk* tube with a screw cap was equipped with a stirring bar, charged with CuI (0.14 mmol, 27.0 mg), (0.04 mmol, 25.2 mg) $\text{Pd}(\text{Cl})_2(\text{PPh}_3)_2$ and 3.59 mmol of the substituted iodobenzene, evacuated three times and purged with nitrogen. Then 4 mL THF and 4 mL Et_3N was added. Phenylacetylene (3.59 mmol, 395 μL) was added slowly *via* syringe and the reaction mixture was stirred at room temperature for 15 h. Then, CH_2Cl_2 (25 mL) and aqueous HCl (25 mL, 1 M) were added and the reaction mixture was extracted with CH_2Cl_2 (2 $\times$ 25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed by vacuum evaporation. The residue was then purified by silica gel flash chromatography (hexanes)

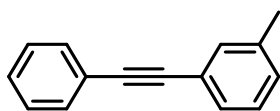


$\text{C}_{16}\text{H}_{12}\text{O}_2$, 236.27 g/mol

$^1\text{H-NMR}$	(300 MHz, CDCl_3) δ 8.02 (m, 2H), 7.60 (m, 1H), 7.59 – 7.51 (m, 3H), 7.41 – 7.32 (m, 3H), 3.92 (s, 3H).
$^{13}\text{C-NMR}$	(75 MHz, CDCl_3) δ 166.57, 131.76, 131.53, 129.55, 129.47, 128.80, 128.47, 128.02, 122.71, 92.40, 88.67, 52.26.
GC-MS	t_R = 10.59 min, (EI, 70 eV): m/z = 236 [M^+], 205, 176, 151, 126, 102, 91, 76, 63, 51.

T. Schabel, C. Belge, B. Plietker, *Org. Lett.* **2013**, 15, 2858–2861.

Synthesis of 1-methyl-3-(phenylethynyl)benzene



$C_{15}H_{12}$, **192.26 g/mol**

1H -NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.40 – 7.31 (m, 5H), 7.24 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 2.36 (s, 3H).

^{13}C -NMR (75 MHz, $CDCl_3$) δ 138.04, 132.20, 131.61, 129.19, 128.70, 128.35, 128.26, 128.19, 77.45, 77.03, 76.61, 21.27.

GC-MS t_R = 9.23 min, (EI, 70 eV): m/z = 192 [M^+], 176, 165, 152, 139, 126, 115, 95, 74, 63, 51.

H. Kim, P. H. Lee, *Adv. Synth. Catal.* **2009**, 351, 2827–2832.

General procedure of hydrogenations

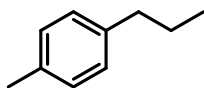
5 mol% FeCl₃ + 10 mol% LiAlH₄:

A 4 mL vial was charged with a freshly prepared solution of FeCl₃ in THF (0.50 mL, 0.05 M) and an aliquot of a vigorously stirred suspension of LiAlH₄ in THF (0.50 mL, 0.1 M) under argon atmosphere. After stirring the dark mixture for 30 min; the olefin (0.50 mmol) was added and the vial transferred to a high pressure reactor. The reactor was purged with H₂ (1 min), sealed, and the internal pressure adjusted to 1 bar H₂. After x h (see tables 1-4 in article for individual reaction times) at room temperature, the vial was retrieved. The reaction was quenched with saturated aqueous NaHCO₃ (1 mL) and extracted with ethyl acetate (2 × 2 mL). The organic phases were dried (Na₂SO₄) and subjected to flash chromatography (SiO₂, pentane/ethyl acetate) or analyzed by quantitative GC-FID analysis vs. *n*-pentadecane as internal reference.

5 mol% FeCl₃ + 5 mol% LiAlH₄:

A 25 mL flask was charged with a freshly prepared solution of FeCl₃ in THF (2 mL, 0.05 M) and an aliquot of a suspension of LiAlH₄ in THF (2 mL, 0.05 M) was added over 20 minutes at -78 °C under argon atmosphere *via* a syringe pump. After stirring the dark mixture for 10 additional minutes 1 mL of the catalyst suspension was added to a 4 mL vial with the olefin (0.50 mmol) and the vial was transferred to a high pressure reactor. The reactor was purged with H₂ (1 min), sealed, and the internal pressure adjusted to 1 bar H₂. After x h (see tables 1-4 in article for individual reaction times) at room temperature, the vial was retrieved. The reaction was quenched with saturated aqueous NaHCO₃ (1 mL) and extracted with ethyl acetate (2 × 2 mL). The organic phases were dried (Na₂SO₄) and subjected to flash chromatography (SiO₂, pentane/ethyl acetate) or analyzed by quantitative GC-FID analysis vs. *n*-pentadecane as internal reference.

1-Methyl-4-propylbenzene



C₁₀H₁₄, **134.22 g/mol**

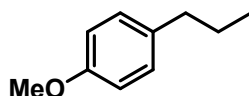
¹H-NMR (300 MHz, CDCl₃) δ 7.07 (s, 4H), 2.54 (t, 2H), 2.31 (s, 3H), 1.61 (m, 2H), 0.93 (t, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 139.55, 134.92, 128.83, 128.28, 37.51, 37.58, 24.65, 20.94, 13.80.

GC-MS *t*_R = 5.09 min, (EI, 70 eV): *m/z* = 134 [M⁺].

N. Sakai, K. Nagasawa, R. Ikeda, Y. Nakaike, T. Konakahara, *Tetrahedron Lett.* **2011**, 52, 3133-3136.

1-Methoxy-4-propylbenzene



C₁₀H₁₄O, **150.22 g/mol**

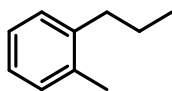
¹H-NMR (300 MHz, CDCl₃) δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 3H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.71-1.46 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H)

¹³C-NMR (75 MHz, CDCl₃) δ 157.58, 134.71, 129.24, 113.55, 55.12, 37.42, 37.09, 24.75, 13.71.

GC-MS *t*_R = 5.07 min, (EI, 70 eV): *m/z* = 150 [M⁺].

A. Dhakshinamoorthy, A. Sharmila, K. Pitchumani, *Chem. Eur. J.* **2010**, 16, 1128-1132.

1-Methyl-2-propylbenzene



C₁₀H₁₄, **134.22 g/mol**

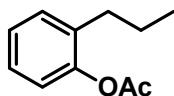
¹H-NMR (300 MHz, CDCl₃) δ 7.14-7.09 (m, 4H), 2.6-2.54 (m, 2H), 2.3 (s, 3H), 1.67-1.54 (m, 2H), 0.98 (t, 3H)

¹³C-NMR (75 MHz, CDCl₃) δ 140.86, 135.87, 130.03, 128.83, 125.76, 125.71, 35.39, 23.35, 19.28, 14.17.

GC-MS t_R = 5.18 min, (EI, 70 eV): m/z = 134 [M⁺].

X. Qian, L. N. Dawe, C. M. Kozak, *Dalton Trans.* **2011**, 40, 933-943.

2-Propylphenyl acetate



C₁₁H₁₄O₂, **178.23 g/mol**

¹H-NMR (300 MHz, CDCl₃) δ 7.18 (dd, J = 13.8, 6.0 Hz, 3H), 7.00 (d, J = 7.5 Hz, 1H), 2.53–2.40 (t, 2H), 2.29 (s, 3H), 1.59 (m, J = 15.0, 7.5 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H).

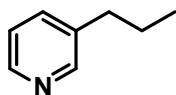
¹³C-NMR (75 MHz, CDCl₃) δ 169.64, 148.97, 134.27, 130.26, 126.89, 126.04, 122.22, 32.21, 23.10, 20.89, 14.00.

GC-MS t_R = 5.84 min, (EI, 70 eV): m/z = 178 [M⁺].

GC-HRMS (EI, 70 eV): m/z = 178.009 +/- 5 ppm

FT-IR (ATR-film) in [cm⁻¹]: 3466 (w), (w), 3026 (w), 2958 (m), 2926 (m), 2866 (m), 1759 (s), 1636 (w), 1580 (w), 1487 (s), 1453 (s), 1367 (s), 1201 (s), 1179 (s), 1115 (s), 1036 (m), 1009 (m), 940 (m), 856 (w), 830 (m), 786 (m), 751 (s), 660 (m).

3-Propylpyridine



C₈H₁₁N, **121.18 g/mol**

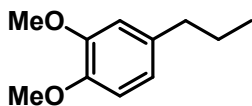
¹H-NMR (300 MHz, CDCl₃) δ 8.43 (d, *J* = 4.8 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.26-7.12 (m, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.78-1.32 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 149.87, 147.07, 137.69, 135.85, 123.34, 123.20, 34.99, 24.21, 23.98, 13.60.

GC-MS *t*_R = 4.20 min, (EI, 70 eV): *m/z* = 121 [M⁺].

A. Fischer, M. J. King, F. P. Robinson, *Can. J. Chem.* **1978**, *56*, 3072-3077.

1,2-Dimethoxy-4-propylbenzene



C₁₁H₁₆O₂, **180.24 g/mol**

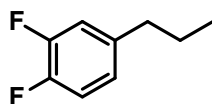
¹H-NMR (300 MHz, CDCl₃) δ 6.83-6.64 (m, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.72-1.50 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 148.72, 147.03, 135.36, 120.19, 111.79, 111.13, 55.81, 37.66, 24.77, 13.80.

GC-MS *t*_R = 6.59 min, (EI, 70 eV): *m/z* = 180 [M⁺].

A. R. Katritzky, S. C. Jurczyk, M. Szajda, I. V. Shcherbakova, J. N. Lam, *Synthesis* **1994**, *1994*, 499-504.

1,2-Difluoro-4-propylbenzene



C₉H₁₀F₂, **156.17 g/mol**

¹H-NMR (300 MHz, CDCl₃) δ 7.10-6.90 (m, 3H), 2.58 (t, 2H), 1.69-1.57 (m, 2H), 0.94 (t, 3H).

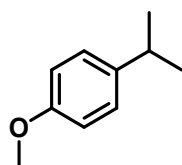
¹³C-NMR (75 MHz, CDCl₃) δ 150.97, 147.71, 139.55, 124.13, 117.01, 116.75, 37.14, 24.35, 13.57.

GC-MS *t_R* = 6.38 min, (EI, 70 eV): *m/z* = 156 [M⁺].

GC-HRMS (EI, 70 eV): *m/z* = 156.038 +/- 5 ppm

FT-IR (ATR-film) in [cm⁻¹]: 3066 (w), 2920 (s), 2851 (m), 2358 (w), 2326 (w), 1731 (w), 1604 (w), 1518 (s), 1487 (m), 1454 (m), 1376 (w), 1260 (s), 1220 (w), 1190 (w), 1116 (m), 1093 (m), 1020, 950 (w), 916 (w), 870 (m), 812 (s), 770 (m), 756(w).

1-Isopropyl-4-methoxybenzene



C₁₀H₁₄O, **150.22 g/mol**

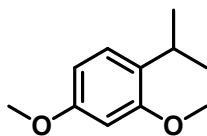
¹H-NMR (300 MHz, CDCl₃) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 – 2.78 (m, 1H), 1.24 (s, 3H), 1.21 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 156.86, 141.06, 127.26, 113.77, 55.27, 33.28, 24.24.

GC-MS *t_R* = 5.93 min, (EI, 70 eV): *m/z* = 150 [M⁺], 120, 105, 91, 77, 65, 51.

Cahiez, G.; Foulgoc, L.; Moyeux, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 2969–2972.

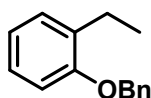
1-Isopropyl-2,4-dimethoxybenzene



C₁₁H₁₆O₂, 180.25 g/mol

¹H-NMR	(300 MHz, CDCl ₃) δ 7.15 – 7.05 (m, 1H), 6.50 – 6.40 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.23 (hept, <i>J</i> = 6.9 Hz, 1H), 1.19 (d, <i>J</i> = 6.9 Hz, 6H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 158.67, 157.67, 129.52, 126.23, 103.81, 98.50, 55.33, 26.24, 22.89.
GC-MS	<i>t</i> _R = 7.11 min, (EI, 70 eV): <i>m/z</i> = 180 [M ⁺], 166, 150, 135, 121, 105, 91, 77, 65, 51.
GC-HRMS	(EI, <i>m/z</i>): found 180.1153 [M ⁺] (calculated 180.1150).
FT-IR	(ATR-film) in [cm ⁻¹]: 2961 (m), 2870 (w), 2835 (w), 1612 (m), 1587 (m), 1504 (s), 1462 (m), 1446 (w), 1298 (m), 1257 (m), 1205 (s), 1151 (s), 1115 (w), 1096 (m), 1036 (s), 937 (w), 924 (w), 833 (m), 831 (m), 795 (m), 692 (w), 635 (w), 557 (w).

2-Benzyloxy-4-ethylbenzene

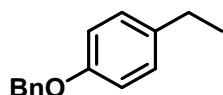


C₁₅H₁₆O, 212.29 g/mol

¹H-NMR	(300 MHz, CDCl ₃) δ 7.51 – 7.30 (m, 5H), 7.19 (m, 2H), 6.98 – 6.88 (m, 2H), 5.11 (s, 2H), 2.74 (q, <i>J</i> = 7.5 Hz, 2H), 1.26 (t, <i>J</i> = 7.5 Hz, 3H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 156.49, 137.59, 133.03, 129.09, 128.55, 127.74, 127.09, 126.79, 120.77, 111.50, 69.77, 23.44, 14.26.
GC-MS	<i>t</i> _R = 8.86 min, (EI, 70 eV): <i>m/z</i> = 212 [M ⁺], 122, 107, 91, 77, 65, 51.
GC-HRMS	(CI, <i>m/z</i>): found 212.1203 [M ⁺] (calculated 212.1201).

FT-IR (ATR-film) in $[\text{cm}^{-1}]$ 3063 (w), 3035 (w), 2965 (m), 2928 (m), 2873 (w), 1601 (m), 1587 (m), 1491 (s), 1450 (s), 1379 (m), 1290 (w), 1236 (s), 1186 (w), 1125 (m), 1042 (m), 1020 (m), 851 (w), 747 (s), 733 (s), 694 (s), 624 (m), 462 (m).

4-Benzyloxy-4-ethylbenzene



$\text{C}_{15}\text{H}_{16}\text{O}$, **212.29 g/mol**

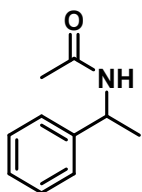
$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.51 – 7.30 (m, 5H), 7.18 – 7.11 (m, 2H), 6.97 – 6.89 (m, 2H), 5.07 (s, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 156.89, 137.30, 136.72, 128.78, 128.60, 127.92, 127.52, 114.72, 70.08, 28.03, 15.93.

GC-MS $t_R = 9.17$ min, (EI, 70 eV): $m/z = 212$ [M^+], 122, 107, 91, 77, 65, 51.

C. Zhu, N. Yukimura, M. Yamane, *Organometallics* **2010**, 29, 2098–2103.

N-(1-Phenylethyl)acetamide



$\text{C}_{10}\text{H}_{13}\text{NO}$, **163.22 g/mol**

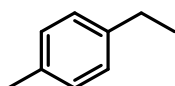
$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.38 – 7.23 (m, 5H), 5.80 (s, 1H), 5.19 – 5.07 (m, 1H), 2.00 (s, 3H), 1.50 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 143.03, 128.73, 127.47, 126.23, 48.90, 23.47, 21.69.

GC-MS $t_R = 7.58$ min, (EI, 70 eV): $m/z = 163$ [M^+], 148, 120, 106, 91, 77, 65, 51

B. V. Subba Reddy, N. Sivasankar Reddy, C. Madan, J. S. Yadav *Tetrahedron Lett.* **2010**, 51, 4827–4829.

1-Ethyl-4-methylbenzene



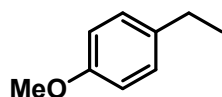
C_9H_{12} , **120.19 g/mol**

1H -NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 4H), 2.60 (q, $J = 7.6$ Hz, 2H), 2.31 (s, 3H), 1.21 (t, $J = 7.6$ Hz, 3H).

GC-MS $t_R = 4.36$ min, (EI, 70 eV): $m/z = 120$ [M^+].

M. L. Kantam, R. Kishore, J. Yadav, M. Sudhakar, A. Venugopal, *Adv. Synth. Catal.* **2012**, 354, 663-669.

1-Ethyl-4-methoxybenzene



$C_9H_{12}O$, **136.19 g/mol**

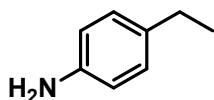
1H -NMR (300 MHz, $CDCl_3$) 7.1 (d, 2H), 6.82 (d, 2H), 3.77 (s, 3H), 2.58 (t, 2H), 1.20 (t, 3H).

^{13}C -NMR (75 MHz, $CDCl_3$) 157.5, 136.4, 128.7, 115.38, 55.3, 28, 15.9.

GC-MS $t_R = 5.75$ min, (EI, 70 eV): $m/z = 136$ [M^+].

B. Wang, H.-X. Sun, Z.-H. Sun, *Eur. J. Org. Chem.* **2009**, 22, 3688-3692.

4-Ethylaniline



C₈H₁₁N, **121,18 g/mol**

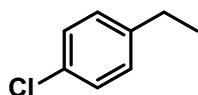
¹H-NMR (300 MHz, CDCl₃) δ 6.98 (d, 2H), 6.61 (d, 2H), 3.34 (bs, 2H), 2.53 (q, 2H), 1.19 (t, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 144.1, 134.5, 128.6, 115.4, 28, 16.

GC-MS *t_R* = 5.75 min, (EI, 70 eV): *m/z* = 121 [M⁺].

B. Wang, H.-X. Sun, G.-Q. Lin, Z.-H. Sun, *Adv. Synth. Catal.* **2009**, 351, 415-422.

1-Ethyl-4-chlorobenzene



C₈H₉Cl, **140.61 g/mol**

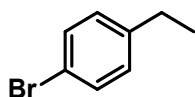
¹H-NMR (300 MHz, CDCl₃) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.23 (t, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 142.63, 131.26, 129.22, 128.37, 28.28, 15.55.

GC-MS *t_R* = 4.92 min, (EI, 70 eV): *m/z* = 140 [M⁺], 125, 105, 89, 77, 63, 51.

M. E. Sloan, A. Staubitz, K. Lee, I. Manners, *Eur. J. Org. Chem.* **2011**, 4, 672-675.

1-Ethyl-4-bromobenzene



C₈H₉Br, **185.06 g/mol**

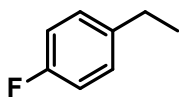
¹H-NMR (400 MHz, CDCl₃) δ 7.45–7.35 (m, 2H), 7.09–6.96 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 143.2, 131.4, 129.7, 119.3, 28.4, 15.5.

GC-MS *t*_R = 5.76 min, (EI, 70 eV): *m/z* = 184 [M⁺], 169, 105, 89, 77, 63, 51.

T. Maegawa, T. Takahashi, M. Yoshimura, H. Suzuka, Y. Monguchi, H. Sajiki, *Adv. Synth. Catal.* **2009**, 351, 2091–2095.

1-Ethyl-4-fluorobenzene



C₈H₉F, **124.16 g/mol**

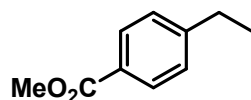
¹H-NMR (300 MHz, CDCl₃) δ 7.12–7.01 (m, 2H), 6.94–6.83 (m, 2H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 6.6 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 162.75, 139.78, 129.18, 129.08, 115.15, 114.84, 28.11, 15.80.

GC-MS *t*_R = 3.54 min, (EI, 70 eV): *m/z* = 124 [M⁺].

E. C. Taylor, E. C. Bigham, D. K. Johnson, *J. Org. Chem.* **1977**, 42, 362–363.

Methyl 4-ethylbenzoate



C₁₀H₁₂O₂, **164.20 g/mol**

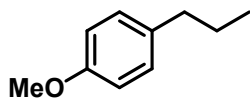
¹H-NMR (400 MHz, CDCl₃) δ 7.96 (m, 2H), 7.27 (m, 2H), 3.90 (s, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 167.2, 149.8, 129.7, 127.9, 127.7, 52.0, 29.0, 15.2.

GC-MS *t*_R = 6.81 min, (EI, 70 eV): *m/z* = 164 [M⁺], 149, 133, 121, 105, 89, 77, 63, 51.

R. J. Rahaim, R. E. Maleczka, *Org. Lett.* **2011**, *13*, 584–587.

1-Methoxy-4-propylbenzene



C₁₀H₁₄O, **150.22 g/mol**

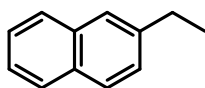
¹H-NMR (300 MHz, CDCl₃) δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 3H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.71-1.46 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H)

¹³C-NMR (75 MHz, CDCl₃) δ 157.58, 134.71, 129.24, 113.55, 55.12, 37.42, 37.09, 24.75, 13.71.

GC-MS *t*_R = 5.07 min, (EI, 70 eV): *m/z* = 150 [M⁺].

A. Dhakshinamoorthy, A. Sharmila, K. Pitchumani, *Chem. Eur. J.* **2010**, *16*, 1128-1132.

2-Ethynaphthalene



C₁₂H₁₂, **156.22 g/mol**

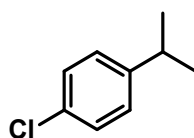
¹H-NMR (400 MHz, CDCl₃) δ 7.84–7.73 (m, 3H), 7.62 (s, 1H), 7.48–7.31 (m, 3H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 141.8, 133.7, 132.0, 127.8, 127.6, 127.4, 127.1, 125.8, 125.6, 125.0, 77.4, 77.0, 76.7, 29.1, 15.5.

GC-MS *t*_R = 7.33 min, (EI, 70 eV): *m/z* = 156 [M⁺], 141, 128, 115, 102, 89, 77, 63, 51.

M. E. Sloan, A. Staubitz, K. Lee, I. Manners, *Eur. J. Org. Chem.* **2011**, 4, 672–675.

1-Chloro-4-isopropylbenzene



C₉H₁₁Cl, **154.64 g/mol**

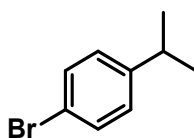
¹H-NMR (300 MHz, CDCl₃) δ 7.25 (m, 2H), 7.21–7.09 (m, 2H), 2.89 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

¹³C-NMR (75 MHz, CDCl₃) δ 142.3, 131.3, 128.4, 127.8, 33.6, 23.9.

GC-MS *t*_R = 5.37 min, (EI, 70 eV): *m/z* = 154 [M⁺], 139, 125, 119, 105, 89, 77, 63, 51.

S. S. Kim, C. S. Kim, *J. Org. Chem.* **1999**, 64, 9261–9264.

1-Bromo-4-isopropylbenzene



C₉H₁₁Br, **199.09 g/mol**

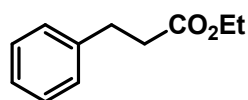
¹H-NMR (400 MHz, CDCl₃) δ 7.47–7.32 (m, 2H), 7.08 (m, 2H), 2.85 (sept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H).

¹³C-NMR (101 MHz, CDCl₃) δ 147.8, 131.3, 128.2, 119.3, 33.7, 30.9, 23.8.

GC-MS *t*_R = 6.16 min, (EI, 70 eV): *m/z* = 198 [M⁺], 185, 169, 158, 143, 119, 104, 91, 77, 63, 51.

M. A. Hall, J. Xi, C. Lor, S. Dai, R. Pearce, W. P. Dailey, R. G. Eckenhoff, *J. Med. Chem.* **2010**, 53, 5667–5675.

Ethyl 3-phenylpropanoate



C₁₁H₁₄O₂, 178.23 g/mol

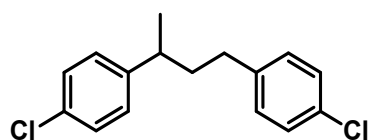
¹H-NMR (400 MHz, CDCl₃) δ 7.33–7.26 (m, 2H), 7.24–7.16 (m, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.01–2.90 (m, 2H), 2.66–2.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 172.9, 140.6, 128.5, 128.3, 126.2, 60.4, 36.0, 31.0, 14.2.

GC-MS *t*_R = 6.99 min, (EI, 70 eV): *m/z* = 178 [M⁺], 133, 104, 91, 77, 65, 51.

M. Amatore, C. Gosmini, J. Périchon, *J. Org. Chem.* **2006**, 71, 6130–6134.

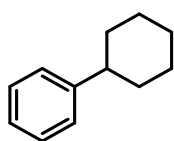
1,3-Bis-(4-chlorophenyl)-butane



$C_{16}H_{16}Cl_2$, **279.20 g/mol**

1H-NMR	(400 MHz, $CDCl_3$) δ 7.34–6.97 (m, 8H), 2.79–2.61 (m, 1H), 2.55–2.39 (m, 2H), 1.95–1.82 (m, 2H), 1.25 (d, $J = 6.9$ Hz, 3H).
^{13}C-NMR	(101 MHz, $CDCl_3$) δ 145.5, 140.6, 131.7, 131.5, 129.7, 128.6, 128.4, 128.4, 39.7, 38.9, 33.2, 22.5.
GC-MS	$t_R = 10.61$ min (EI, 70 eV): $m/z = 279$ [M^+], 191, 166, 139, 121, 103, 77, 51.
GC-HRMS	(CI, m/z): found 278.0632 [M^{++}] (calculated 278.0629).
FT-IR	(ATR-film) in $[cm^{-1}]$ 3025 (w), 2960 (m), 2926 (m), 2859(w), 1894 (w), 1597 (w), 1491 (s), 1455 (m), 1408 (m), 1091 (s), 1013 (s), 825 (s), 531 (s), 489 (m).

Cyclohexylbenzene



$C_{12}H_{16}$, **160.26 g/mol**

1H-NMR	(300 MHz, $CDCl_3$) δ 7.41–7.10 (m, 5H), 2.49 (m, 1H), 2.02–1.68 (m, 5H), 1.56–1.15 (m, 5H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 148.1, 128.3, 126.9, 125.8, 44.7, 34.52, 27.0, 26.2.
GC-MS	$t_R = 6.88$ min, (EI, 70 eV): $m/z = 160$ [M^+], 131, 117, 104, 91, 78, 65, 51.

W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2009**, *48*, 607–610.

1,3-Diphenylpropane

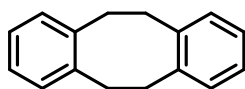


C₁₅H₁₆, **196.29 g/mol**

Appearance	colorless liquid
¹H-NMR	(300 MHz, CDCl ₃) δ 7.37 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.77 – 2.59 (m, 2H), 2.05 – 1.90 (m, 1H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 142.33, 128.49, 128.35, 125.78, 35.48, 33.02.
GC-MS	<i>t</i> _R = 8.65 min, (EI, 70 eV): <i>m/z</i> = 196 [M ⁺], 179, 165, 152, 115, 105, 92, 79, 65, 51.

C.-T. Yang, Z.-Q. Zhang, Y.-C. Liu, L. Liu, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 3904–3907.

Dibenzo-1,5-cyclooctadiene

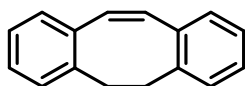


C₁₆H₁₆, **208.30 g/mol**

Appearance	colorless solid
¹H-NMR	(300 MHz, CDCl ₃) δ 7.00 (m, 8H), 3.07 (s, 8H).
¹³C-NMR	(75 MHz, CDCl ₃) δ 140.62, 129.69, 126.12, 35.16.
GC-MS	<i>t</i> _R = 9.27 min, (EI, 70 eV): <i>m/z</i> = 208 [M ⁺], 193, 178, 165, 152, 128, 115, 104, 91, 78, 63, 51.

D. Guijarro, B. Mancheno, M. Yus, *Tetrahedron.* **1992**, *48*, 4593-4600.

Dibenzo-1,3,5-cyclooctatriene



C₁₆H₁₄, 206.29 g/mol

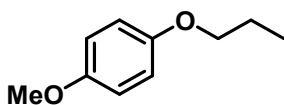
¹H-NMR (300 MHz, CDCl₃) δ 7.22 – 7.16 (m, 1H), 7.16 – 7.09 (m, 3H), 6.79 (s, 1H), 3.24 (s, 2H).

¹³C-NMR (101 MHz, CDCl₃) δ 139.85, 136.82, 131.51, 130.22, 129.97, 127.05, 125.55, 35.84.

GC-MS *t_R* = 9.50 min, (EI, 70 eV): *m/z* = 206 [M⁺], 191, 178, 165, 151, 139, 115, 106, 89, 77, 67, 51.

A. C. Cope, R. D. Smith, *J. Am. Chem. Soc.* **1955**, 77, 4596–4599.

1-Methoxy-4-propoxybenzene



C₁₀H₁₄O₂, 166.22 g/mol

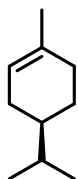
¹H-NMR (300 MHz, CDCl₃) δ 6.84 (s, 4H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 1.87 – 1.70 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 153.65, 153.29, 115.43, 114.61, 70.17, 55.75, 22.70, 10.56.

GC-MS *t_R* = 6.87 min, (EI, 70 eV): *m/z* = 166 [M⁺], 124, 109, 95, 81, 64, 53.

A. B. Naidu, E. A. Jaseer, G. Sekar, *J. Org. Chem.* **2009**, 74, 3675–3679.

(R)-4-Isopropyl-1-methylcyclohex-1-ene



C₁₀H₁₈, 138.25 g/mol

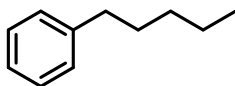
¹H-NMR (300 MHz, CDCl₃) δ 5.42 – 5.33 (m, 1H), 2.05 – 1.91 (m, *J* = 23.4, 8.0 Hz, 3H), 1.79 – 1.67 (m, *J* = 14.3, 4.6 Hz, 2H), 1.64 (s, 3H), 1.52 – 1.39 (m, *J* = 6.7 Hz, 1H), 1.25 – 1.15 (m, *J* = 13.8, 7.9 Hz, 2H), 0.89 (d, *J* = 4.3 Hz, 3H), 0.87 (d, *J* = 4.3 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 133.97, 121.03, 40.01, 32.30, 30.83, 28.97, 26.49, 23.50, 20.02, 19.70.

GC-MS *t*_R = 4.81 min, (EI, 70 eV): *m/z* = 138 [M⁺], 123, 95, 79, 67, 55.

D. F. Schneider, M. S. Viljoen, *Tetrahedron* **2002**, 58, 5307-5315.

Pentylbenzene



C₁₁H₁₆, 148.25 g/mol

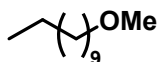
¹H-NMR (300 MHz, CDCl₃) δ 7.31 – 7.13 (m, 5H), 2.64 – 2.56 (m, 2H), 1.62 (dt, *J* = 15.2, 7.4 Hz, 2H), 1.38 – 1.26 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 141.93, 127.37, 127.18, 124.51, 34.93, 30.50, 30.20, 21.53, 13.01.

GC-MS *t*_R = 5.81 min, (EI, 70 eV): *m/z* = 148 [M⁺], 133, 105, 91, 78, 65.

L. Ackermann, A. R. Kapdi, C. Schulzke, *Org. Lett.* **2010**, 12, 2298–2301.

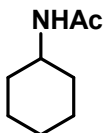
1-Methoxyundecane



C₁₂H₂₆O, **186.33 g/mol**

¹H-NMR	(400 MHz, CDCl ₃) δ 3.36 (t, <i>J</i> = 6.7 Hz, 2H), 3.32 (s, 3H), 1.61–1.50 (m, 2H), 1.39–1.18 (m, 16H), 0.87 (t, <i>J</i> = 6.9 Hz, 3H).
¹³C-NMR	(101 MHz, CDCl ₃) δ 73.0, 58.5, 31.9, 29.7, 29.6, 29.5, 29.4, 26.2, 22.7, 14.1.
GC-MS	<i>t</i> _R = 6.76 min, (EI, 70 eV): <i>m/z</i> = 186 [M ⁺], 154, 126, 111, 97, 83, 69, 56.
GC-HRMS	(CI, <i>m/z</i>): found 186.1987 [M ⁺] (calculated 186.1984).
FT-IR	(ATR-film) in [cm ⁻¹] 2923 (s), 2853 (s), 1745 (w), 1459 (m), 1379 (w), 1238 (w), 1195 (w), 1118 (s), 965 (w), 722 (w).

N-Cyclohexylacetamide

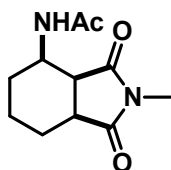


C₈H₁₅NO, **141.21 g/mol**

¹H-NMR	(400 MHz, CDCl ₃) δ 5.32 (s, 1H), 3.87–3.65 (m, 1H), 1.95 (s, 3H), 1.94–1.87 (m, 2H), 1.75–1.66 (m, 2H), 1.66–1.55 (m, 1H), 1.43–1.29 (m, 2H), 1.23–1.04 (m, 3H).
¹³C-NMR	(101 MHz, CDCl ₃) δ 169.0, 48.2, 33.3, 25.6, 24.9, 23.6.
GC-MS	<i>t</i> _R = 6.71 min, (EI, 70 eV): <i>m/z</i> = 141 [M ⁺], 112, 82. 60.

R. Pelagalli, I. Chiarotto, M. Feroci, S. Vecchio, *Green Chem.* **2012**, *14*, 2251-2255.

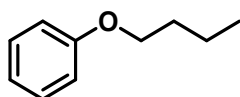
N-Methyl-3-(acetamido)-hexahydrophthalimide



C₁₁H₁₆N₂O₃, 224.26 g/mol

¹H-NMR	(400 MHz, CDCl ₃) δ 7.16 (s, 1H), 4.31 (ddt, J = 12.7, 9.0, 5.3 Hz, 1H), 3.10–2.99 (m, 2H), 2.98 (s, 3H), 2.09–2.02 (m, 1H), 2.01 (s, 3H), 2.00–1.93 (m, 1H), 1.68–1.50 (m, 2H), 1.40 (m, 1H), 1.15 (m, 1H).
¹³C-NMR	(101 MHz, CDCl ₃) δ 179.2, 179.2, 169.5, 44.9, 42.3, 41.3, 27.6, 24.7, 24.6, 23.5, 20.5.
GC-MS	<i>t</i> _R = 9.81 min, (EI, 70 eV): <i>m/z</i> = 224 [M ⁺], 207, 181, 165, 153, 138, 126, 112, 96, 80, 70, 60, 51.
GC-HRMS	(CI, <i>m/z</i>): found 225.1234 [M+H ⁺] (calculated 225.1234).
Melting Point	128 °C
FT-IR	(ATR-film) in [cm ⁻¹] 3324 (m), 2957 (w), 2924 (w), 2861 (w), 1769 (m), 1703 (s), 1647 (s), 1539 (s), 1460 (w), 1431 (s), 1378 (s), 1306 (m), 1271 (s), 1197 (w), 1162 (w), 1113 (m), 1050 (m), 982 (m), 952 (m), 910 (m), 762 (m), 682 (S), 596 (s), 543 (s), 454 (m).

n-Butoxybenzene



C₁₀H₁₄O, 150.22 g/mol

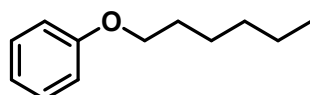
Appearance	colorless liquid
¹H-NMR	(300 MHz, CDCl ₃) δ 7.37 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.77 – 2.59 (m, 2H), 2.05 – 1.90 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃) δ 159.13, 129.43, 120.46, 114.49, 67.56, 31.38, 19.29, 13.90.

GC-MS *t_R* = 6.00 min, (EI, 70 eV): *m/z* = 150 [M⁺], 94, 77. 65. 51.

J. Niu, H. Zhou, Z. Li, J. Xu, S. Hu, *J. Org. Chem.* **2008**, 73, 7814–7817.

(Hexyloxy)benzene



C₁₂H₁₈O, **178.28 g/mol**

Appearance colorless liquid

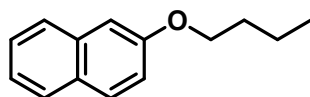
¹H-NMR (300 MHz, CDCl₃) δ 7.32 – 7.24 (m, 2H), 6.98 – 6.86 (m, 3H), 3.96 (t, *J* = 6.6 Hz, 4H), 1.84 – 1.73 (m, 2H), 1.53 – 1.40 (m, 2H), 1.40 – 1.29 (m, 4H), 0.98 – 0.85 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 159.12, 129.42, 120.45, 114.48, 77.47, 77.25, 77.04, 76.62, 67.88, 31.63, 29.29, 25.77, 22.64, 14.08.

GC-MS *t_R* 7.2 min, (EI, 70 eV): *m/z* = 178 [M⁺], 107, 95, 84, 77, 66, 57, 51

O. Vechorkin, X. Hu, *Angew. Chem. Int. Ed. Engl.* **2009**, 48, 2937–2940.

2-(Butoxy)naphthalene



C₁₄H₁₆O, **200.28 g/mol**

Appearance colorless liquid

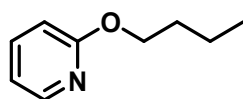
¹H-NMR (300 MHz, CDCl₃) δ 7.80 – 7.70 (m, 3H), 7.44 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.33 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.19 – 7.10 (m, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.77 (m, 2H), 1.63 – 1.47 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 157.13, 134.63, 129.32, 128.88, 127.65, 126.71, 126.30, 123.47, 119.06, 106.52, 67.71, 31.34, 19.36, 13.93.

GC-MS t_R = 9.01 min, (EI, 70 eV): m/z = 200 [M⁺], 144, 127, 115, 89, 57.

C. Cazorla, E. Pfordt, M.-C. Duclos, E. Metay, M. Lemaire, *Green Chem* **2011**, *13*, 2482–2488.

2-Butoxypyridine



C₉H₁₃NO, **151.21 g/mol**

Appearance colorless solid

¹H-NMR (300 MHz, CDCl₃) δ 8.14 (ddd, J = 5.1, 2.0, 0.7 Hz, 1H), 7.55 (ddd, J = 8.4, 7.1, 2.0 Hz, 1H), 6.83 (ddd, J = 7.1, 5.1, 0.9 Hz, 1H), 6.76 – 6.66 (m, 1H), 4.27 (t, J = 6.7 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.48 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

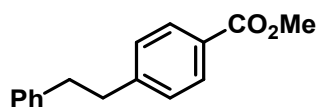
¹³C-NMR (75 MHz, CDCl₃) δ 164.08, 146.89, 138.48, 116.45, 111.08, 65.70, 31.17, 19.29, 13.91.

GC-MS t_R = 5.82 min, (EI, 70 eV): m/z = 151 [M⁺], 121, 108, 95, 78, 67, 51.

R. D. Chambers, M. Parsons, G. Sandford, C. J. Skinner, M. J. Atherton, J. S. Moilliet, *J. Chem. Soc., Perkin Trans. 1* **1999**, 803–810.

Hydrogenation of alkynes

Methyl 4-phenethylbenzoate



C₁₆H₁₆O₂, **240.30 g/mol**

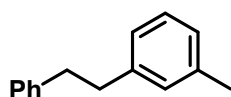
¹H-NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 7.21 – 7.15 (m, 2H), 3.92 (s, 3H), 3.07 – 2.90 (m, 4H).

¹³C-NMR (75 MHz, CDCl₃) δ 167.17, 147.22, 141.19, 129.74, 128.60, 128.50, 128.45, 127.97, 126.14, 52.03, 37.94, 37.50.

GC-MS *t*_R = 10.13 min, (EI, 70 eV): *m/z* = 240 [M⁺], 209, 178, 165, 149, 118, 105, 91, 78, 65, 50.

P. J. Rushworth, D. G. Hulcoop, D. J. Fox, *J. Org. Chem.* **2013**, 78, 9517–9521.

1-Methyl-3-phenethylbenzene



C₁₅H₁₆, **196.29 g/mol**

Appearance colorless liquid

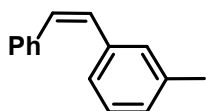
¹H-NMR (300 MHz, CDCl₃) δ 7.33 (m, 2H), 7.26 – 7.15 (m, 4H), 7.09 – 6.99 (m, 3H), 2.93 (s, 4H), 2.37 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃) δ 141.98, 141.82, 137.95, 129.31, 128.48, 128.38, 128.30, 126.70, 125.94, 125.47, 38.08, 37.99, 21.47.

GC-MS *t*_R = 8.43min, (EI, 70 eV): *m/z* = 196 [M⁺], 189, 178, 165, 152, 141, 128, 115, 106, 97, 79, 65, 51.

G. A. Olah, S. Hamanaka, J. A. Wilkinson, J. A. Olah, *Proc. Nat. Acad. Sci. USA* **1992**, 89, 915–917.

(Z)-1-Methyl-3-styrylbenzene



C₁₅H₁₄, **194.28 g/mol**

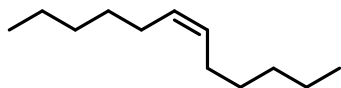
¹H-NMR (400 MHz, CDCl₃) δ 7.29 – 6.98 (m, 10H), 6.58 (s, 2H), 2.27 (s, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 137.91, 137.47, 137.33, 129.31, 129.01, 128.84, 128.47, 128.39, 127.98, 127.18, 126.00, 123.54, 21.47.

GC-MS *t*_R = 8.37 min, (EI, 70 eV): *m/z* = 194 [M⁺], 179, 165, 152, 128, 115, 105, 91, 83, 65, 50.

F. Alonso, P. Riente, M. Yus, *Eur. J. Org. Chem.* **2009**, 2009, 6034–6042.

(Z)-6-Dodecene



C₁₂H₂₄, **168.32 g/mol**

¹H-NMR (300 MHz, CDCl₃) δ 5.43 – 5.28 (m, 2H), 2.08 – 1.93 (m, 4H), 1.39 – 1.24 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 6H).

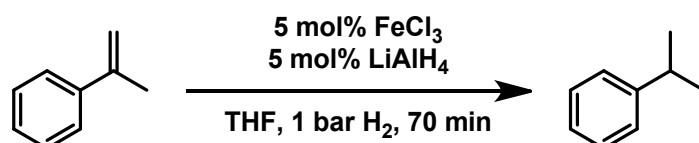
¹³C-NMR (75 MHz, CDCl₃) δ 129.92, 31.55, 29.47, 27.18, 22.60, 14.10.

GC-MS *t*_R = 5.91 min, (EI, 70 eV): *m/z* = 168 [M⁺], 140, 125, 111, 97, 83, 69, 55.

T. Hamatani, S. Matsubara, H. Matsuda, M. Schlosser, *Tetrahedron* **1988**, 44, 2875–2881.

Kinetic Studies

Kinetic studies were performed in a rubber septum sealed schlenk tube under a hydrogen atmosphere. Samples were taken via a syringe (50 μL) and quenched with an aqueous solution of sodium hydrogencarbonate. After extraction with ethyl acetate and filtration over a pad of silica, the samples were analysed by GC-FID. The catalyst poisons (dct, Hg) were added after 30 minutes via syringe (Hg in pure form, dct dissolved in 100 μL THF).



time /min	yield (determined by GC-FID)	
	addition of dct (30 mol%) at 30 min	addition of Hg (300 mol%) at 30 min
0	0	0
10	22	15
20	35	38
30	52	54
40	57	69
50	61	91
60	63	92
70	62	92

Consumption of dct under identical conditions (determined by relative peak areas of GC-FID, identification by GC-MS):

time /min			
30	100	0	0
40	68	30	2
50	47	49	5
60	38	55	7
70	29	59	7

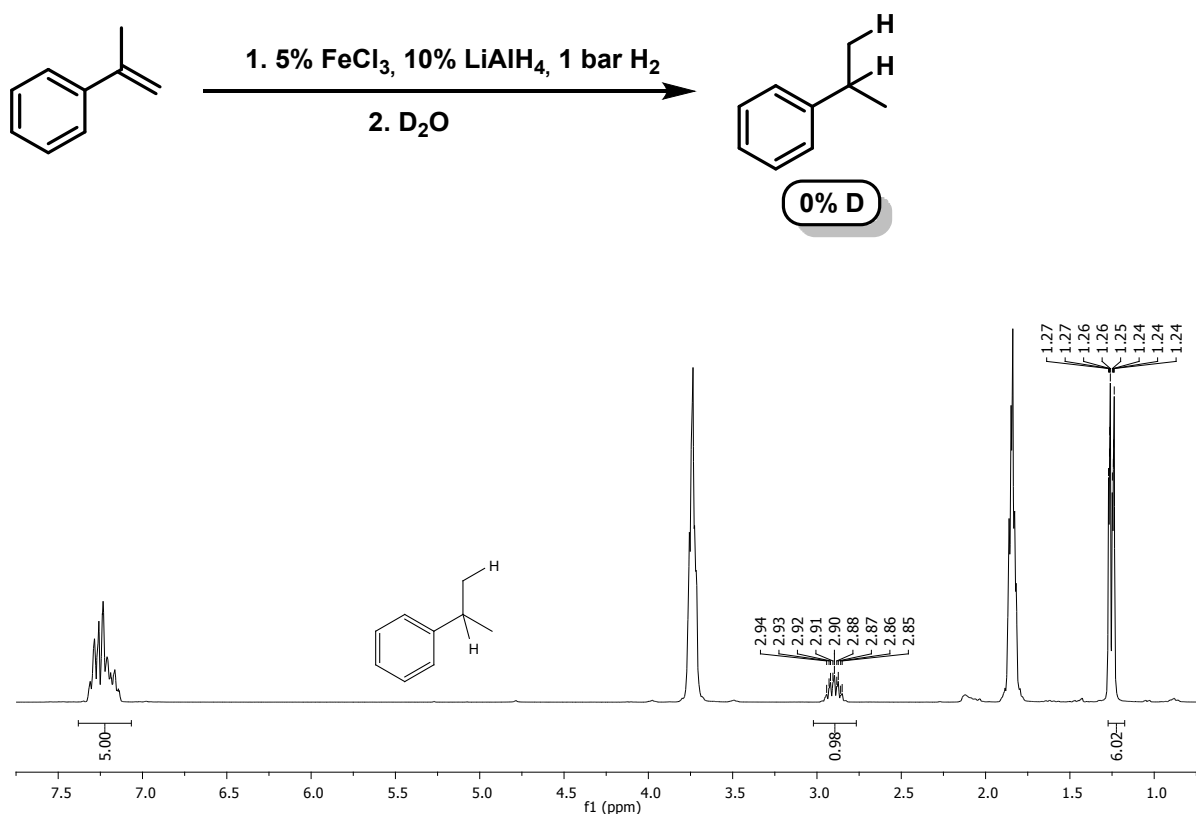
Further experiments

Deuteration experiments

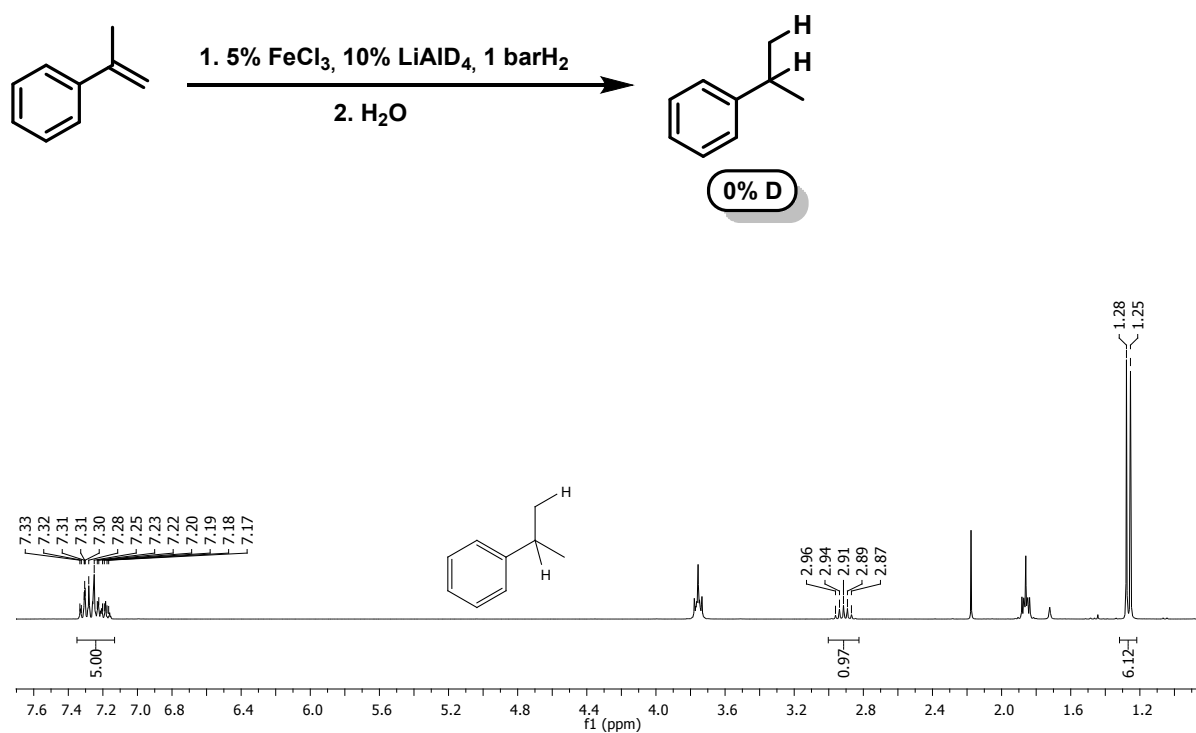
For deuterium exchange experiments, the reaction mixture after hydrogenation of α -methylstyrene in 3 was quenched with D_2O , extracted with Et_2O (2×1 mL), filtered over a pad of silica and analyzed by GC-FID, 1H and 2H -NMR to check for D-incorporation.

In a second experiment, $LiAlD_4$ was used instead of $LiAlH_4$. The reaction mixture after hydrogenation of α -methylstyrene in 3 was quenched with H_2O , extracted with Et_2O (2×1 mL), filtered over a pad of silica and analyzed by GC-FID, 1H -NMR to check for D-incorporation.

In both experiments no incorporation of D has been detected.



1H -NMR spectrum after hydrogenation of α -methylstyrene and quench with D_2O .



^1H -NMR spectrum after hydrogenation of α -methylstyrene with 5 mol% FeCl_3 and 10 mol% LiAlD_4 .

Deuterium incorporation in H₂-free reactions with high catalyst loadings:

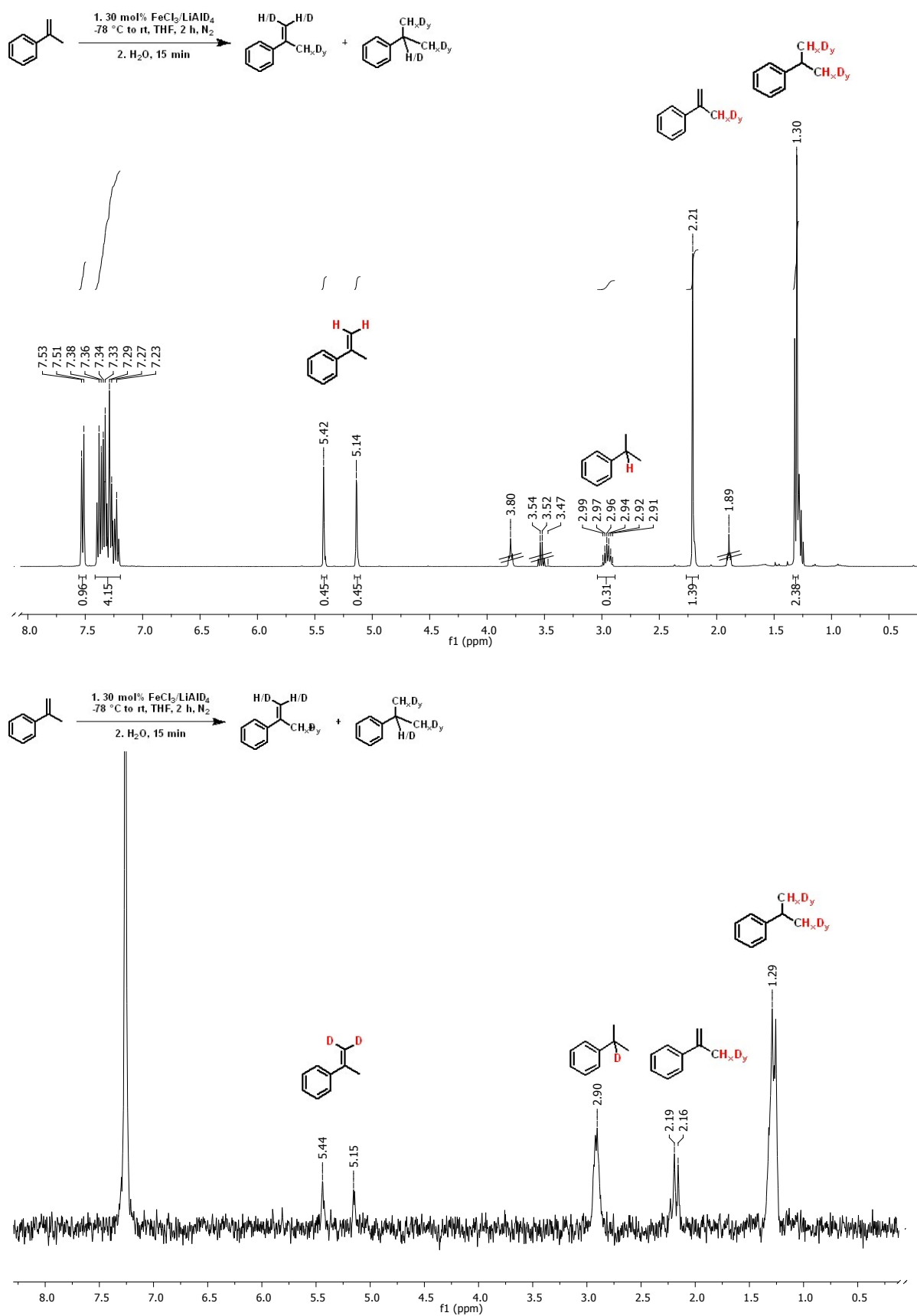


Figure: ¹H-NMR (top) and ²H-NMR (bottom) of crude reaction mixture after extraction. Substrate addition 20 min after catalyst preparation (30 mol% FeCl₃, LiAlD₄), after 2h aqueous quench. ~55% product yield.

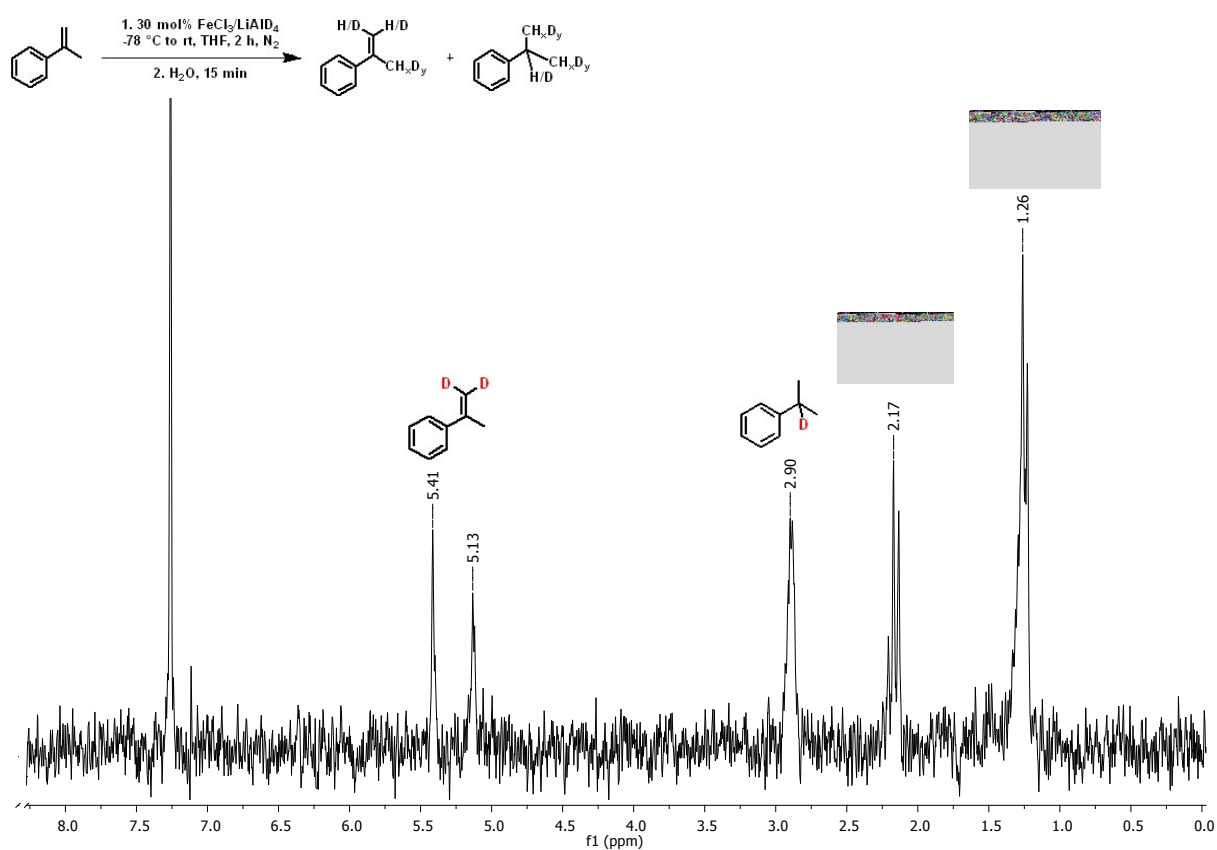
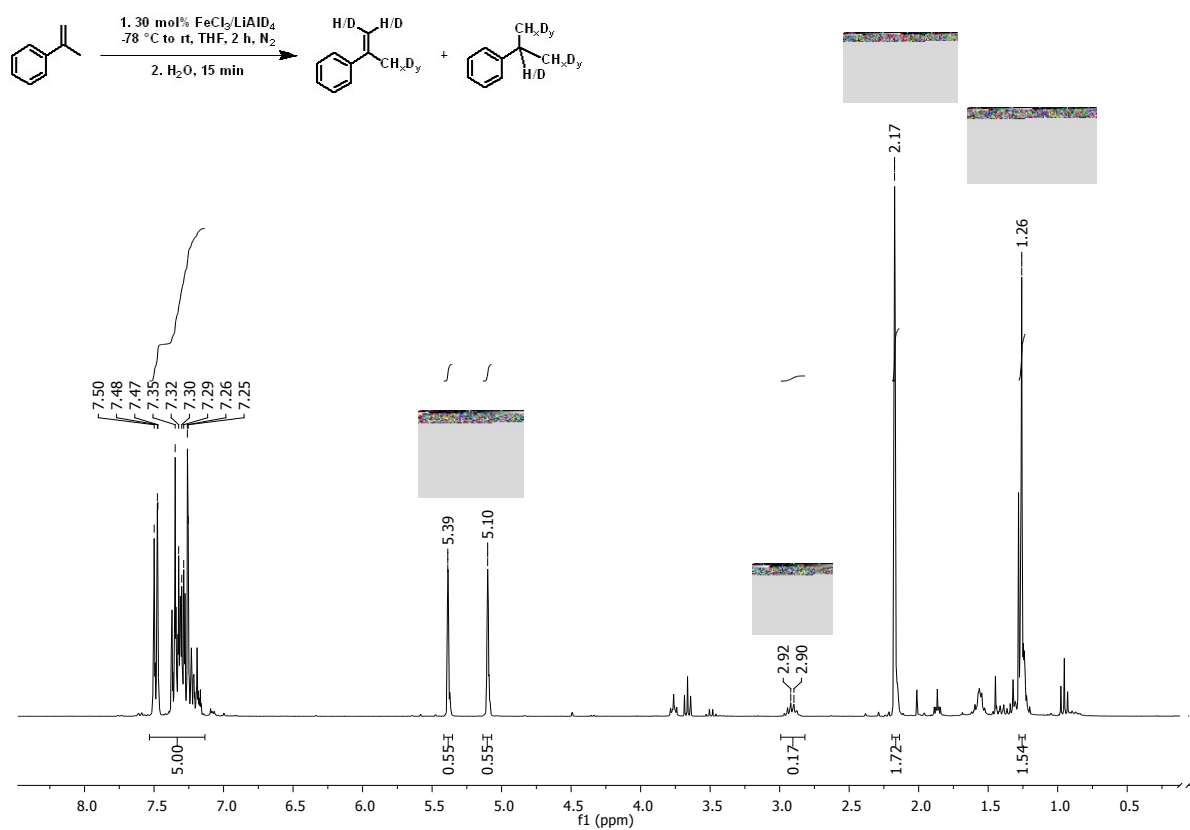


Figure: ^1H -NMR (top) and ^2H -NMR (bottom) of crude reaction mixture after extraction. Substrate addition prior to catalyst preparation (30 mol% FeCl_3 , LiAlD_4), after 2h aqueous quench. ~52% product yield.

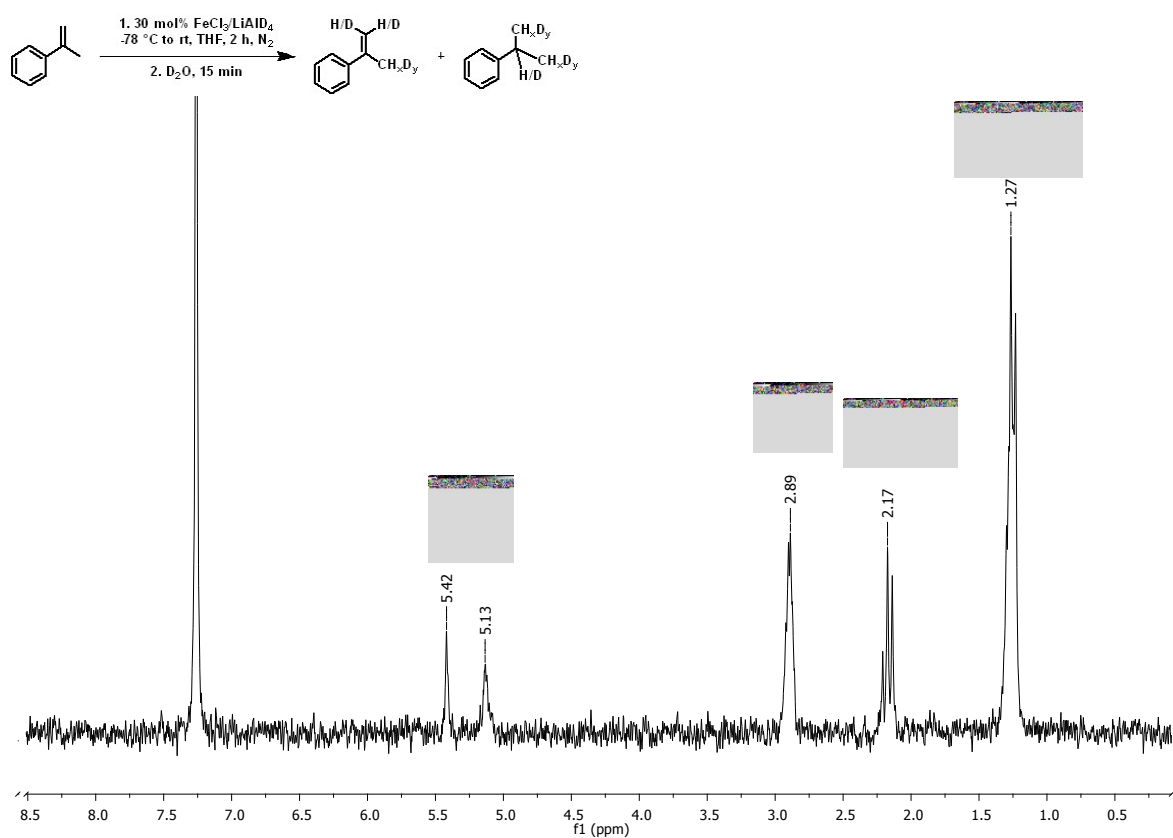
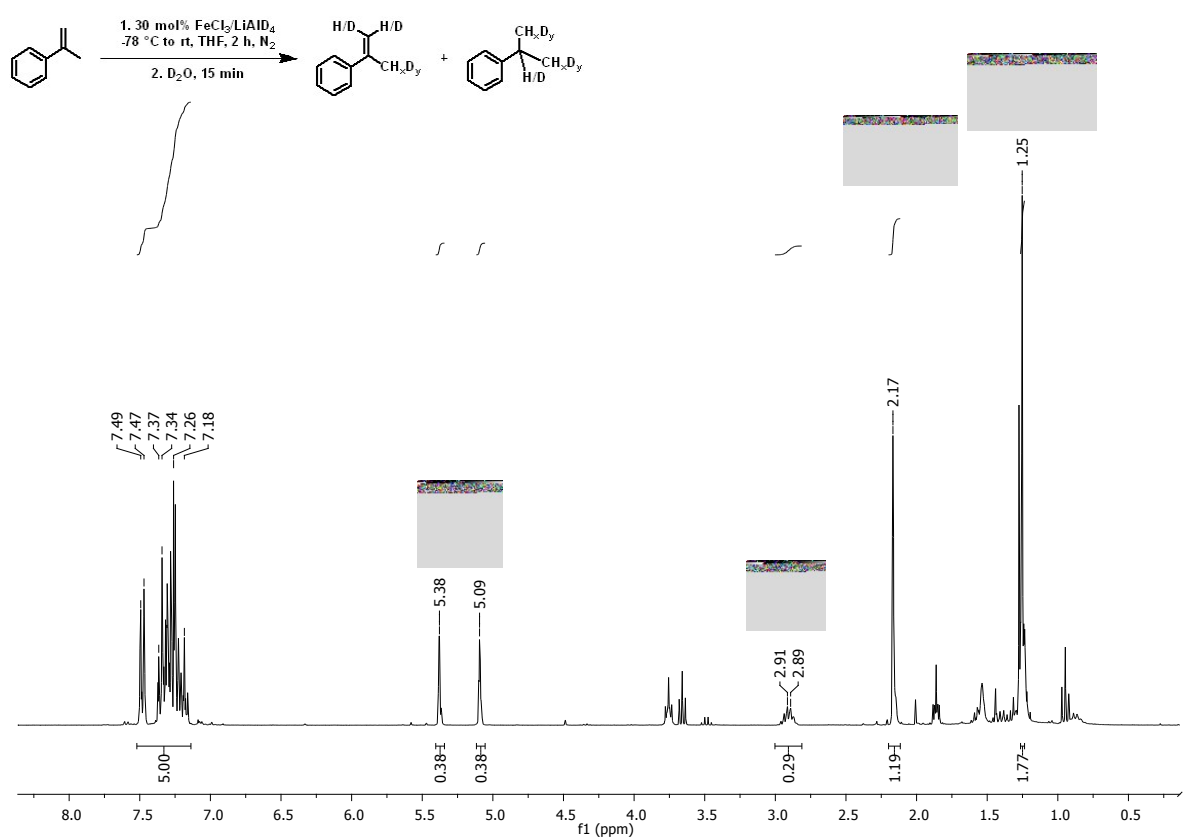


Figure: ^1H -NMR (top) and ^2H -NMR (bottom) of crude reaction mixture after extraction. Substrate addition prior to catalyst preparation (30 mol% FeCl_3 , LiAlD_4), after 2h D_2O quench. ~61% product yield.

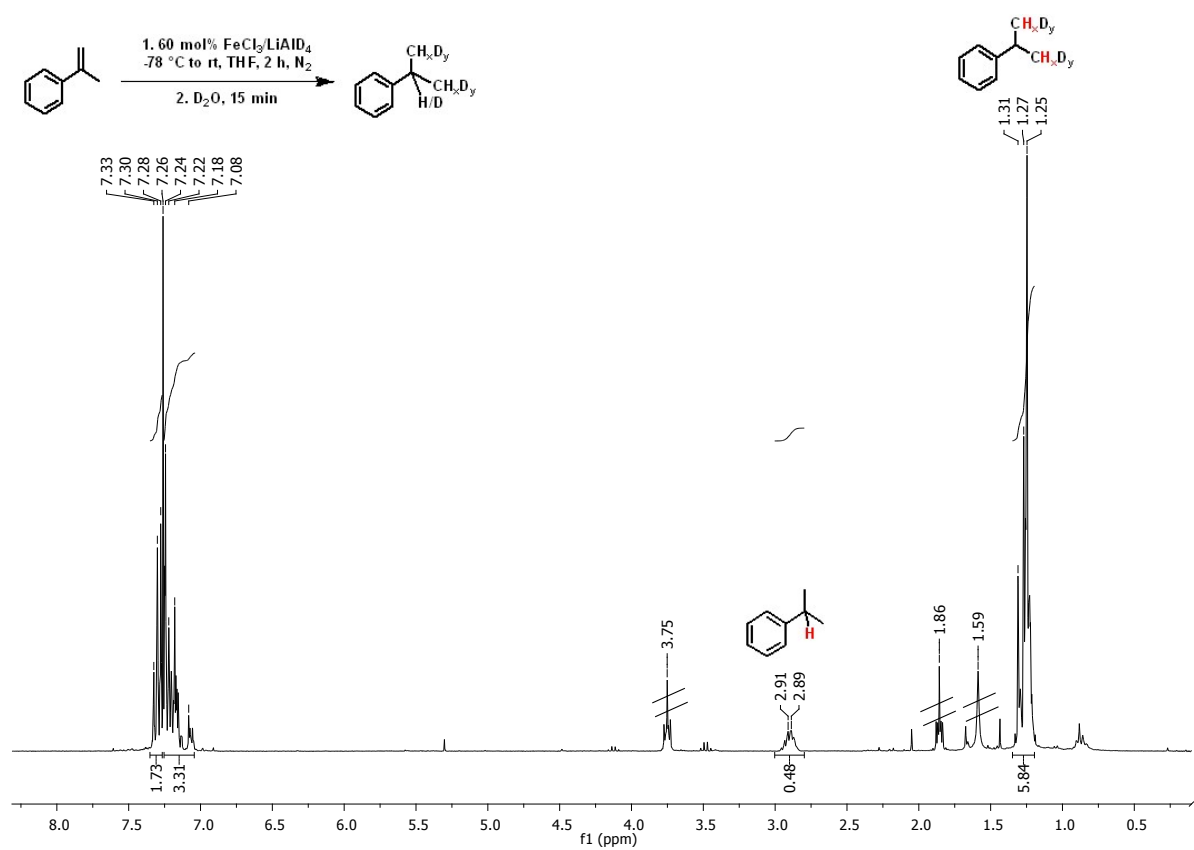
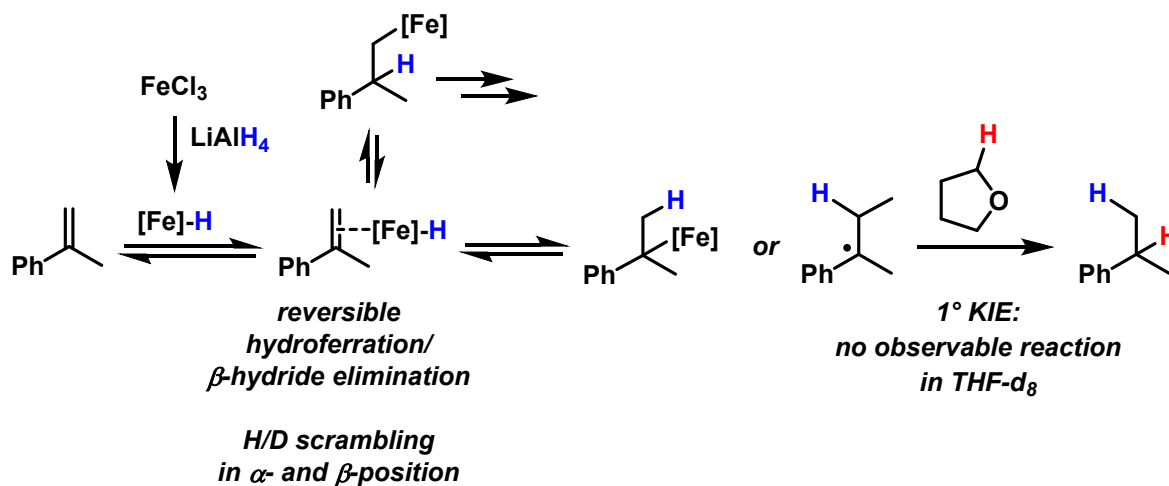


Figure: ^1H -NMR of crude reaction mixture after extraction. Substrate addition prior to catalyst preparation (60 mol% FeCl_3 , LiAlD_4), after 2h D_2O quench. 98% product yield.

Postulated mechanisms under H₂-free and hydrogenation conditions:

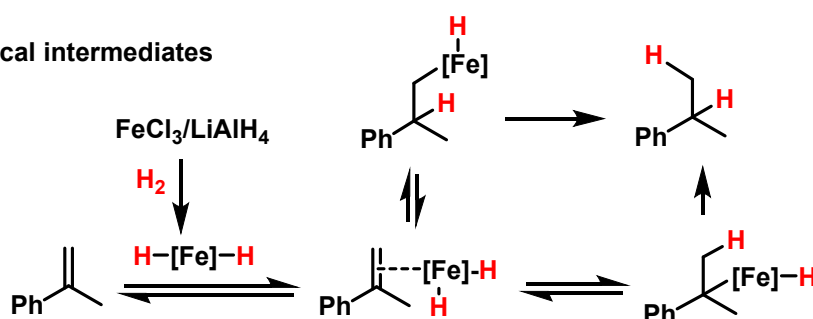
A) H₂-free reaction:

- slower
- radical intermediates ?



B) Hydrogenation reaction:

- faster
- no radical intermediates



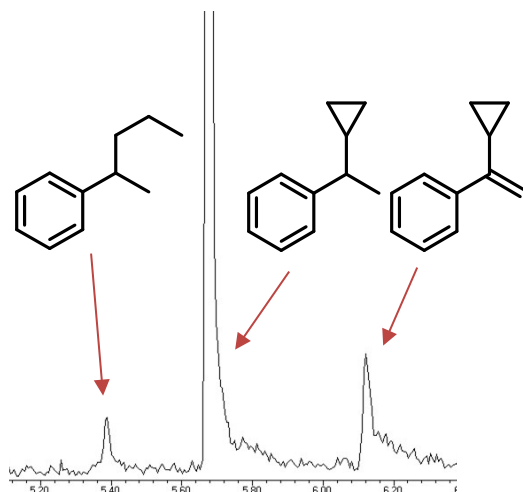
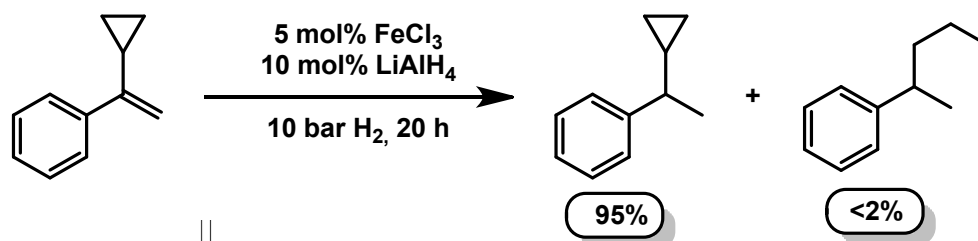
Scheme. Competing radical mechanism in the absence of H₂ and hydrogenation mechanism in the presence of H₂.

The observation of H/D scrambling in the olefin and product with D incorporation into the α- and β-positions suggests reversible hydroferration/β-hydride elimination at the Fe center.

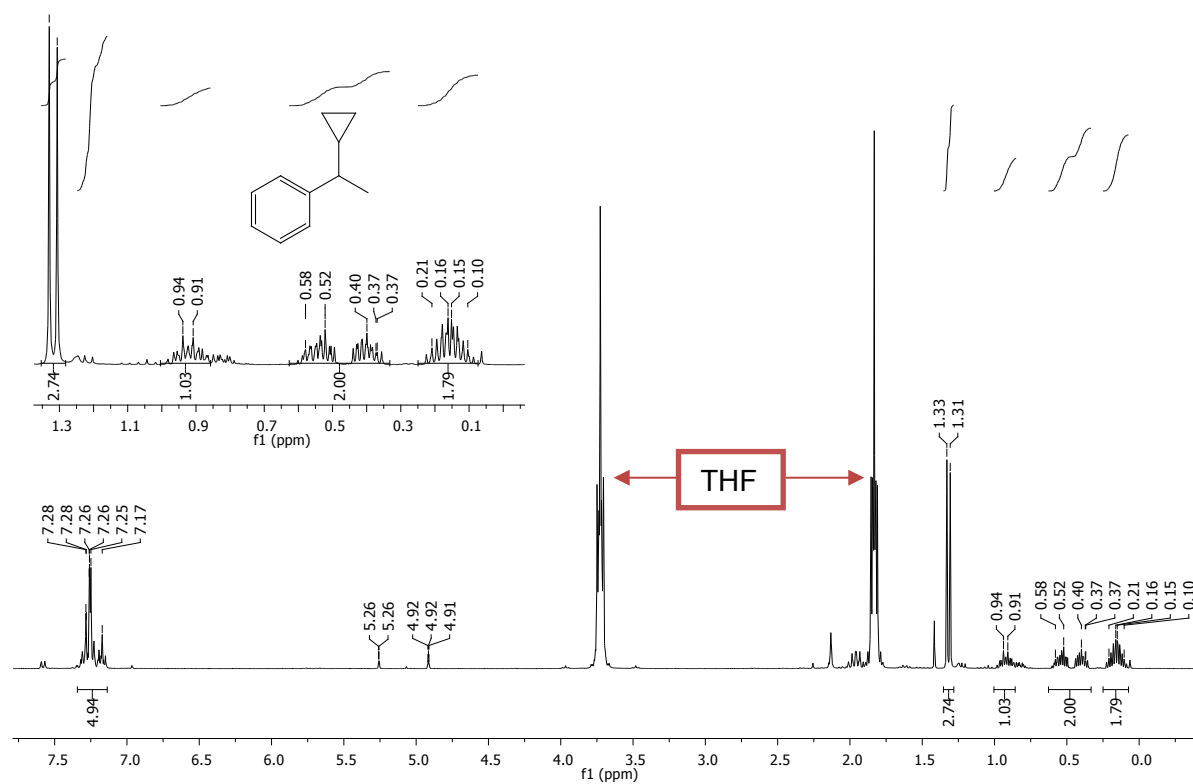
The very slow reaction in THF-d₈ under H₂-free conditions support the notion of a radical H/D-abstraction which is governed by a primary kinetic isotope effect (1° KIE).

The operation of a radical mechanism is slower than the hydrogenation mechanism, especially at high H₂ pressures. See radical clock experiment at 10 bar H₂ below.

Radical clock experiment



GC-MS chromatogram of reaction mixture
after hydrogenation



^1H -NMR spectrum after hydrogenation of α -cyclopropylstyrene

DLS measurement

The particles were synthesized as described in the general procedure of hydrogenation reactions with $\text{FeCl}_3/\text{LiAlH}_4 = 1/1$ but in the absence of any unsaturated substrate. After stirring for additional 10 minutes, the particle solution was diluted with anhydrous THF to achieve a final concentration $c[\text{Fe}] = 0.00125 \text{ M}$. The mixture was filtered through a 100 nm PTFE filter (sample B). The samples were measured after ageing at room temperature for 30 minutes.

Mean particle sizes:

Sample A:

$d = 297 \text{ nm } (\pm 30)$

Sample B (after filtration through 100 nm filter, three independent experiments):

$d = 334 \text{ nm } (\pm 30)$

$d = 1490 \text{ nm } (\pm 400)$

$d = 244 \text{ nm } (\pm 80)$ at higher dilution with $c[\text{Fe}] = 0.00025 \text{ M}$

Synthesis and characterization of $[\text{Li}(\text{thf})_2\{\text{Fe}(\text{tmeda})\}_2(\mu\text{-AlH}_5)(\mu\text{-Al}_2\text{H}_9)]$ (**4**):

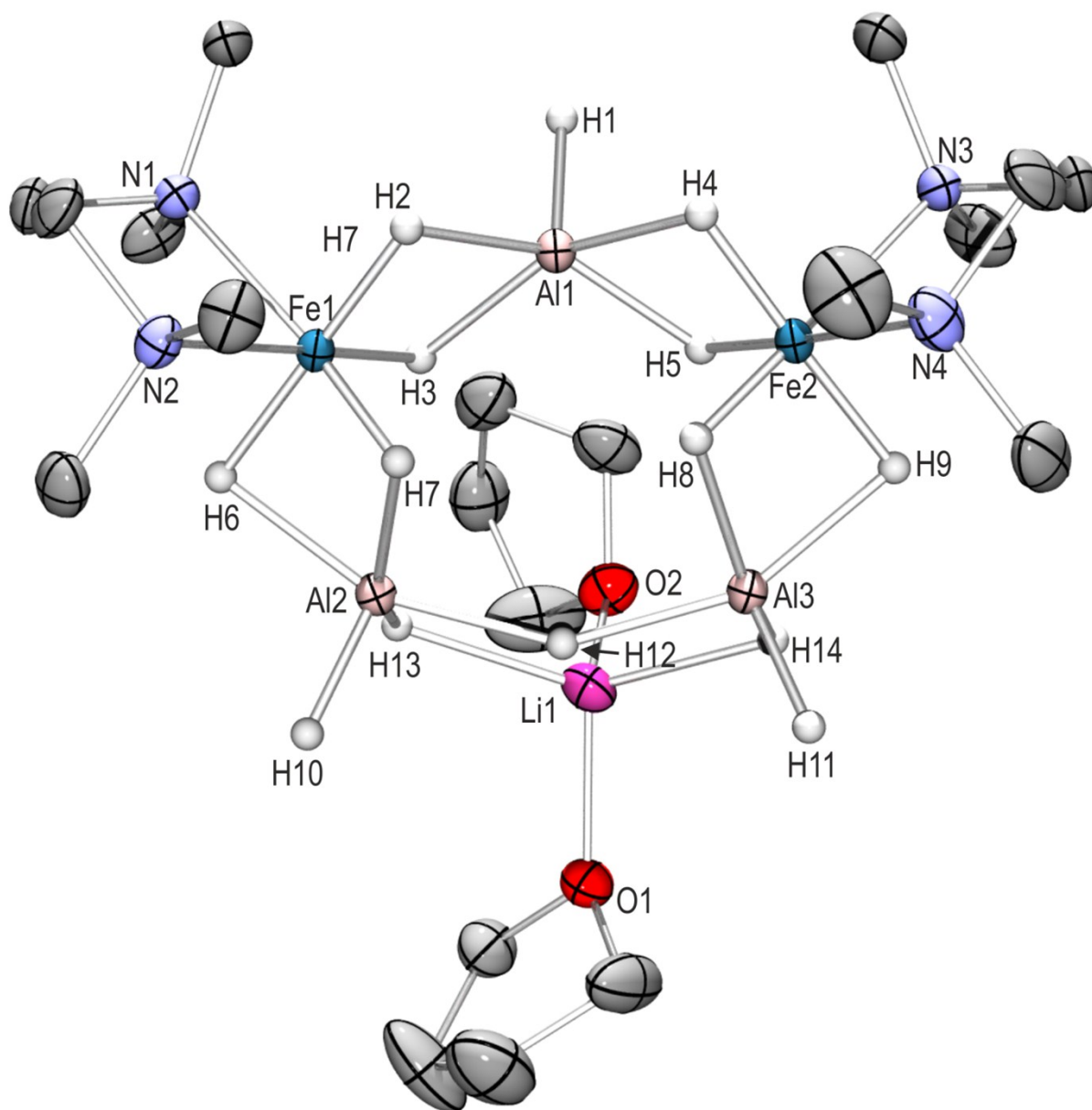
All manipulations were carried out under an inert atmosphere of purified argon, using standard Schlenk or glovebox techniques. Solvents (THF, *n*-hexane) were dried by refluxing over sodium and distilled under argon prior to use. Commercial lithium aluminium hydride was purified by extraction with diethyl ether and subsequent removal of the solvent under high vacuum. $[\text{FeCl}_2(\text{tmeda})]_2$ was prepared according to: S. C. Davies, D. L. Hughes, G. J. Leigh, J. R. Sanders, J. S. de Souza, *J. Chem. Soc., Dalton Trans.* **1997**, 1981.

Synthesis of **4**: $[\text{FeCl}_2(\text{tmeda})]_2$ (2.490 g, 5.12 mmol, 1.0 equiv.) was dissolved in THF (120 mL). The cooled (-78°C) solution was added to a suspension of LiAlH_4 (0.912 g, 23.38 mmol) in 120 ml THF, which was also cooled at -78°C with a dry ice acetone bath. A deep red suspension formed that was stirred for 30 min at -78°C . Subsequently, the cold solution was filtered through a P4 frit. The filtrate was layered with pre-cooled (-20°C) *n*-hexane. Storage at -78°C gave a deep red crystalline solid. The mother liquor was removed with a cannula. Dark red crystals of **4** were obtained by dissolving the remaining solid in cold toluene (50 mL) at -78°C and layering this solution with pre-cooled *n*-hexane. A suitable crystal was selected, transferred to paratone oil that was cooled under a stream of cooled N_2 gas, and mounted on a glass fibre in the cooled nitrogen stream of the diffractometer for the X-ray structure determination. The further spectroscopic characterization of the compound was prevented by its high thermal instability. Decomposition to a dark brown residue was observed at temperatures above -10°C in the solid state as well as in solution. The crystallographic data of **4** were collected on a Bruker APEXII diffractometer equipped with a rotating anode (Mo-K_α radiation, $\lambda = 0.71073 \text{ \AA}$). A red plate with the dimensions $0.19 \times 0.11 \times 0.05 \text{ mm}^{-3}$. The structures were solved using direct methods and refined against F^2 using the program suite SHELXTL-97.23.

a) *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison, WI, **1990**; b) Sheldrick, G. M. *SHELXL 97*, Program for the Refinement of Structures, University of Göttingen, **1997**; c) Sheldrick, G.M., *Acta Cryst.*, 2008, **A64**, 112.

The positions of the hydrogen atoms bound to aluminium and iron were located on the Fourier difference map and refined freely. All other hydrogen atoms were placed on calculated positions and refined using a riding model. Crystal Data for

$\text{C}_{20}\text{H}_{62}\text{Al}_3\text{Fe}_2\text{LiN}_4\text{O}_2$ ($M = 590.32 \text{ g mol}^{-1}$): orthorhombic, space group $Pca2_1$, $a = 15.4965(7) \text{ \AA}$, $b = 16.8579(7) \text{ \AA}$, $c = 12.6159(6) \text{ \AA}$, $V = 3295.8(3) \text{ \AA}^3$, $Z = 4$, $T = 153(1) \text{ K}$, $\mu(\text{Mo } K\alpha) = 0.981 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.190 \text{ g mm}^{-3}$, 30041 reflections measured ($6.86 \leq \Theta \leq 27.10$), 5799 unique ($R_{\text{int}} = 0.0617$, $R_{\text{sigma}} = 0.0489$) which were used in all calculations. The final R_1 was 0.0329 ($I \geq 2\sigma(I)$) and wR_2 was 0.1674 (all data). The crystallographic information file (CIF) has been deposited at the **CCDC**, 12 Union Road, Cambridge, CB21EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition number **1034372**.



Selected spectra

