Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Highly efficient and practical hydrogenation of olefins catalyzed by in situ generated iron complex catalysts

Na Guo, Meng-Yang Hu, Ye Feng and Shou-Fei Zhu*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China

Email: sfzhu@nankai.edu.cn

Table of Contents

1. General Information

a. Materials

All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. THF, Et_2O, DME, 1,4-dioxane, and toluene was distilled from sodium benzophenone ketyl prior to use. $FeCl_2$ (99.99%) and $LiAlH_4$ were purchased from Alfa Aesar and Admas, respectively, and used as received. Styrene, 4-methoxystyrene, 1-hexene, 1-octene, vinylcyclohexane, allylbenzene, 2-phenyl-1-propene, 1,1-diphenylethylene, 2-methyl-3-phenyl-1-propene, cyclohexene, 2-octene (*Z*/*E* = 1:4), *N*,*N*-dimethylallylamine were purchased from Acros, Alfa Aesar, TCI, or Strem. Other alkenes were prepared by Wittig olefination from corresponding ketone. All alkenes were distilled over $LiAlH_4$ or CaH_2 before use. THF-d_8 was purchased from Aldrich under an atmosphere of argon and stored in glovebox. $FeCl_2$-**L1**,[1] Fe(bipy)Cl_2,[2] Fe(phen)Cl_2,[2] $FeCl_2$-**L4**,[3] $FeCl_2$-**L7**,[4] $FeCl_2$-**L8**[5] and $FeCl_2$-phosphines[6] were prepared according to the reported procedures.

b. Analytical Methods

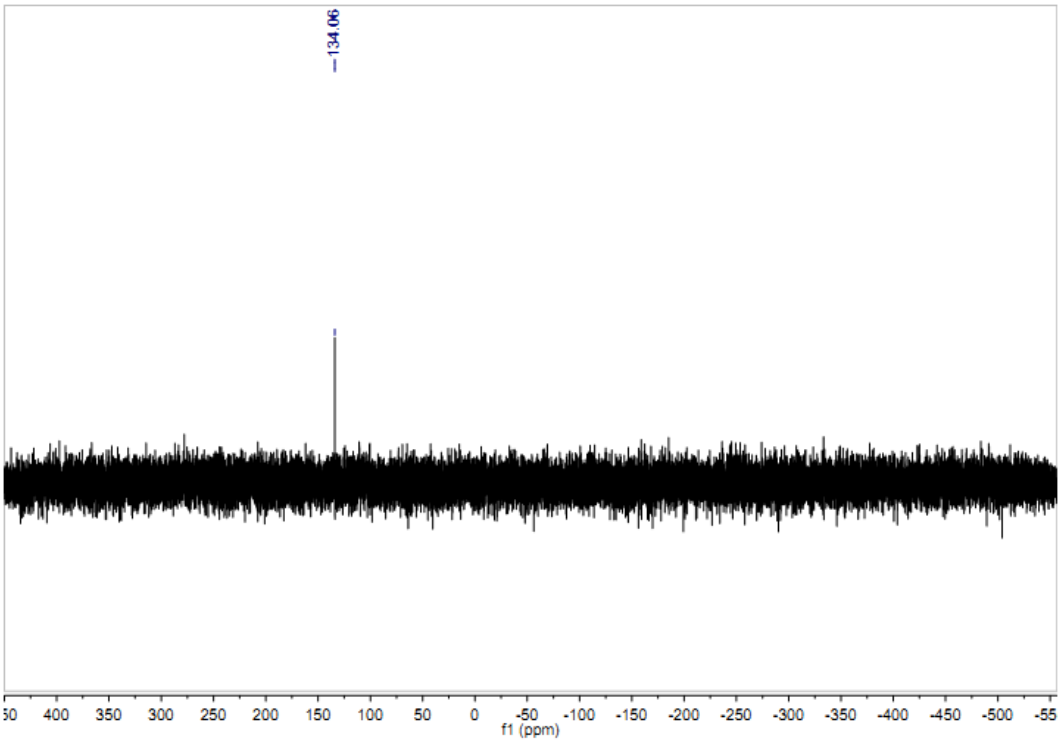
NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR) and 101 MHz (^{13}C NMR). Chemical shifts (δ values) were reported in ppm down field from internal Me_4Si (^{1}H NMR and ^{13}C NMR). ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, quint = quintuplet, m = multiplet or unresolved, br = broad, coupling constant (s) in Hz, integration). Conversions were assayed by gas-chromatography (GC) by comparison to authentic samples or by ^{1}H NMR analyses. The GC analyses were performed on an Agilent 7890A instrument equipped with an interCap-1 capillary column (30 × 0.25 × 0.25 cm).

2. Preparation and Analyses of Fe-L8 Complexes

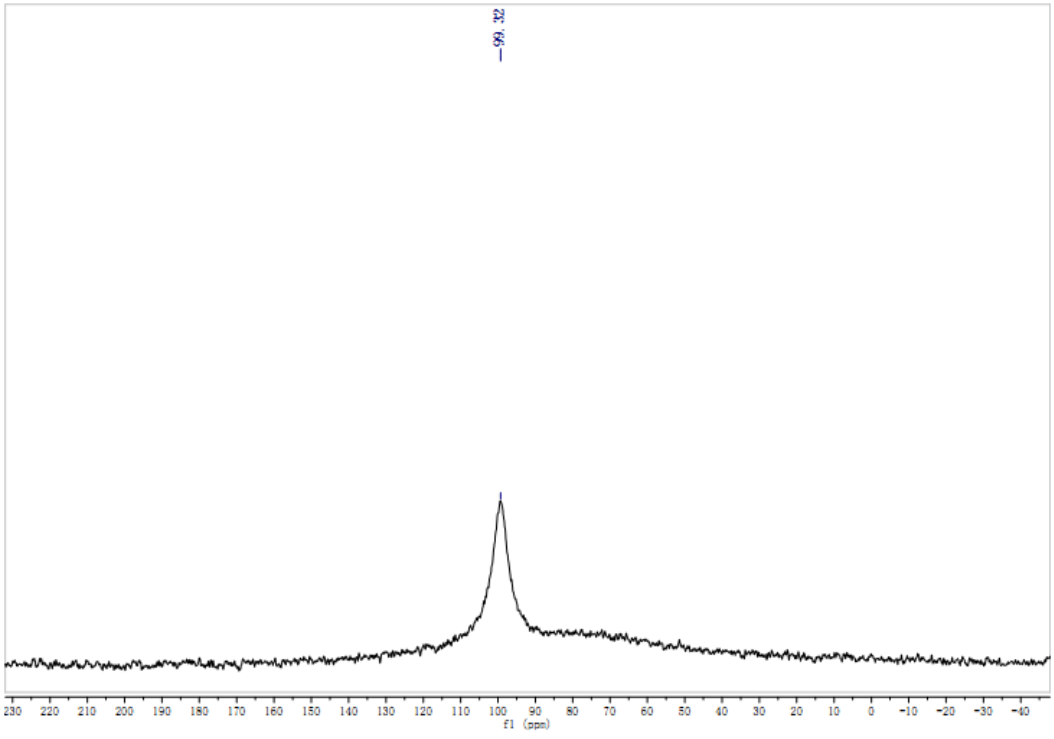
$FeCl_2$-L8:[5] $FeCl_2$ (63 mg, 0.5 mmol, 1 equiv), 6-di-*tert*-butylphosphinomethyl-2, 2'-bipyridine (L8) (157 mg, 0.55 mmol, 1.1 equiv) and THF (5 mL) were added to a 10 mL Schlenk tube filled with N_2. The reaction mixture was stirred for 24 h and then the solvent was removed under vacuum. The residue was redissolved in CH_2Cl_2 (2 mL), then Et_2O (10 mL) was added to the solution and solids precipitated. After filtered, the residue was washed with Et_2O and dried under vacuum to afford the red solids (175 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ -14.82 (s, 1H), 0.87 (s, 1H), 9.29 (s, 1H), 14.05 (s, 18H), 24.51 (s, 2H), 52.65 (s, 1H), 53.01 (s, 1H), 77.25 (s, 1H), 80.75 (s, 1H).

Fe-L8-$(H)_2$: In an argon filled glovebox, to the mixture of $FeCl_2$-L8 (0.005 mmol) and $LiAlH_4$ (0.025 mmol), 1 mL THF-d_8 was introduced and the resulting mixture was stirred for 1 min. Then the resulting dark red solution was detected through NMR. ^{1}H NMR (400 MHz, THF-d_8) δ -18.92 (d, J_{PH} = 20 Hz, 2H), 1.08 (d, J_{PH} = 8.0 Hz, 18H), 3.29 (br, 2H), 6.0 (br, 1H), 6.23 (br, 1H), 6.41 (br, 1H), 6.72 (br, 1H), 6.88 (m, 2H), 9.73 (br, 1H). ^{31}P NMR (162 MHz, THF-d_8) δ 134.06. ^{27}Al NMR(104 MHz, THF-d_8) δ 99.32 (br).

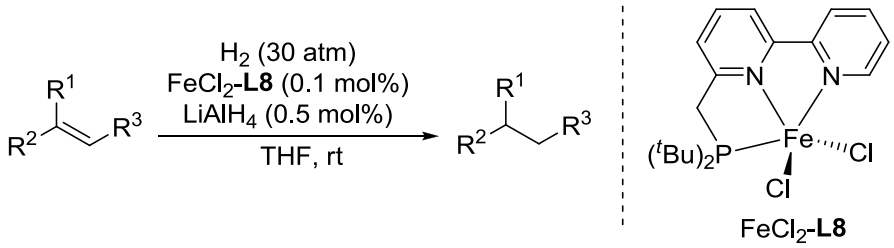
^{31}P NMR of Fe-L8-$(H)_2$



^{27}Al NMR of Fe-L8-$(H)_2$



3. Typical Procedure of Olefins Hydrogenation



$FeCl_2$-**L8**

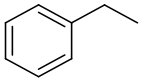
To a high-pressure autoclave charged with $FeCl_2$-**L8** (0.005 mmol), $LiAlH_4$ (0.025 mmol) and a stir bar, 1 mL of the THF was introduced. The mixture was stirred under an argon atmosphere at ambient temperature for 1 min to generate a black-red solution. Alkene (5 mmol) was then added into the resulted solution. The autoclave was purged four times with hydrogen and finally pressurized to 30 atm. The reaction mixture was stirred at room temperature until the consumption of hydrogen stopped (judged by the pressure reduction). The autoclave was depressurized. The residue was dissolved in Et_2O and filtered through a short plug of celite. All hydrogenation products are known, identified by GC-MS and ^1H NMR, and the conversions were determined by ^1H NMR and GC analysis. For the hydrogenation of styrene, the quantitative yield was observed by GC method with dodecane as an internal standard. For other substrates, the reactions are very clean, and only desired products are determined through GC and ^1H NMR analyses of crude reaction mixtures.

Table S1 The TOFs of the hydrogenation of styrene at various conversion states

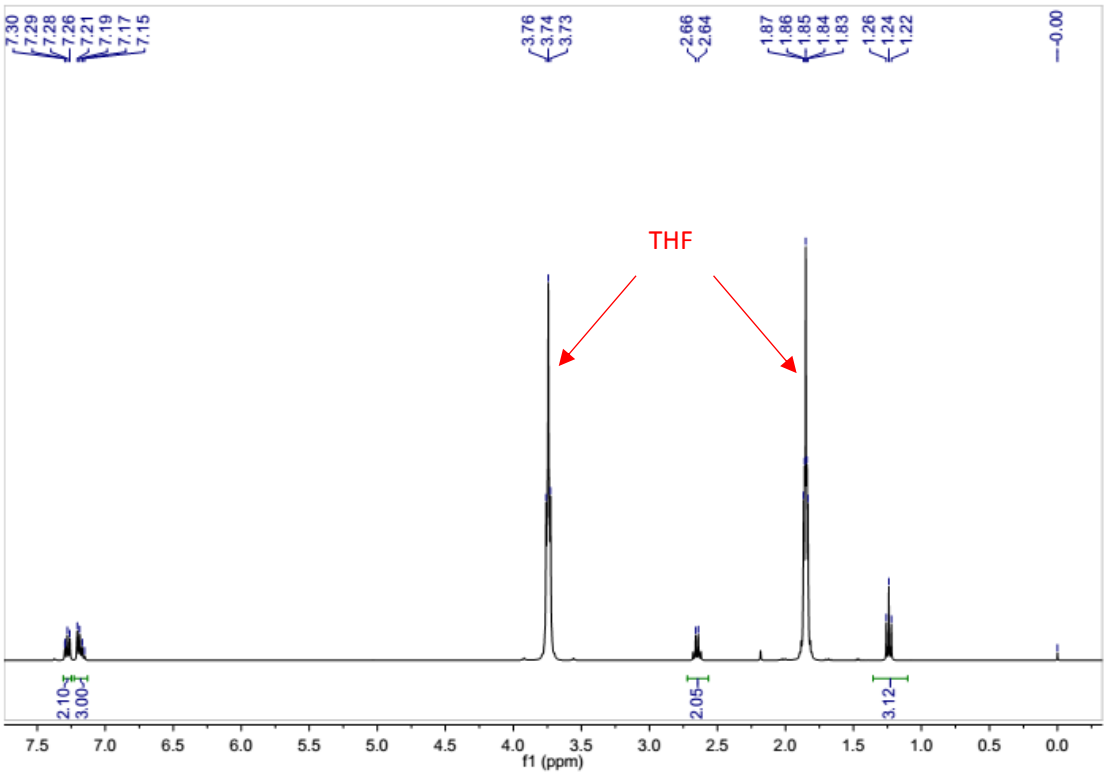
entry	Time (min)	Conv. (%)	TOF (h^{-1})
1	1	62.9	37,740
2	2	86.6	25,980
3	3	99.96	19,992

4. ^{1}H NMR Spectra and GC Charts of Hydrogenation Products

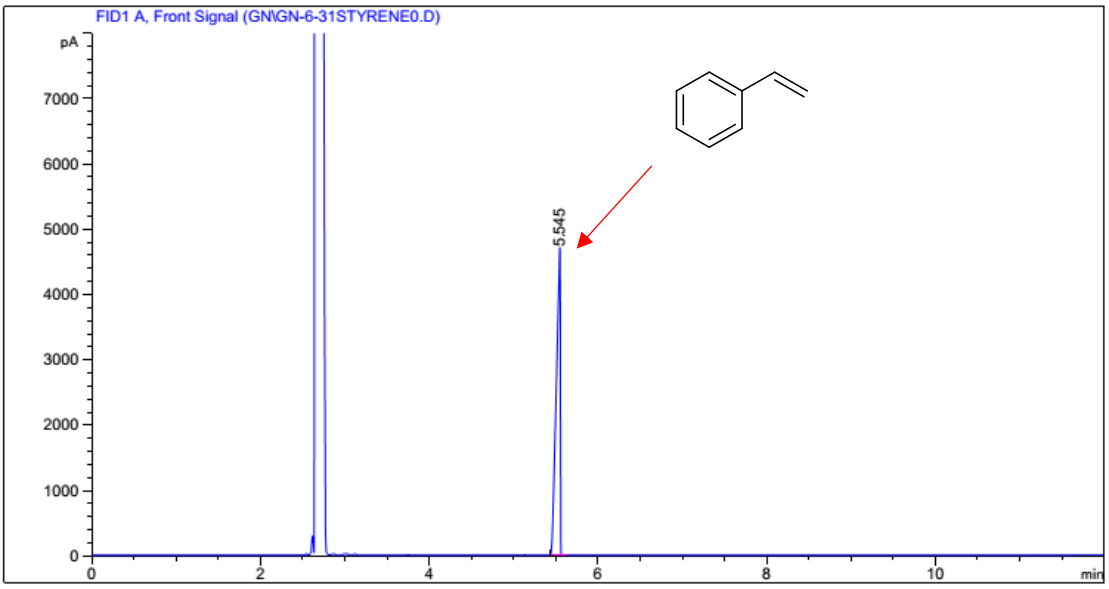
Ethylbenzene (from styrene)

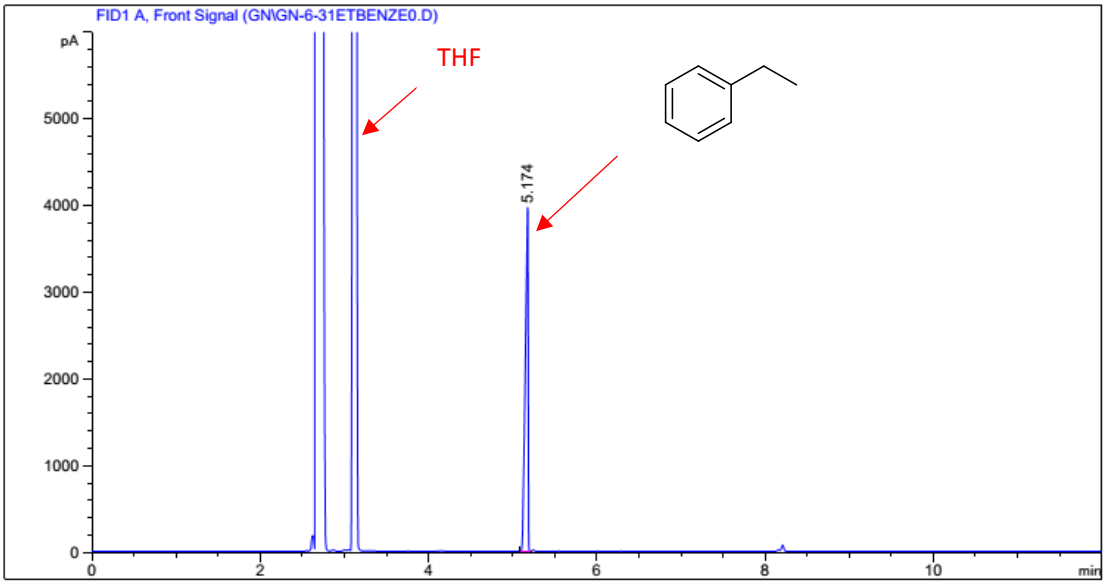


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), styrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 5 min, 100% conversion to ethylbenzene. The quantitative yield was observed by GC method with dodecane as an internal standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 8.0 Hz, 3H, CH_3), 2.65 (q, *J* = 8.0 Hz, 2H, CH_2), 7.14-7.23 (m, 3H, Ar-H), 7.25-7.30 (m, 2H, Ar-H).



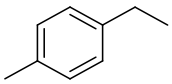
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 5.545 min for styrene and *t* = 5.174 min for ethylbenzene.



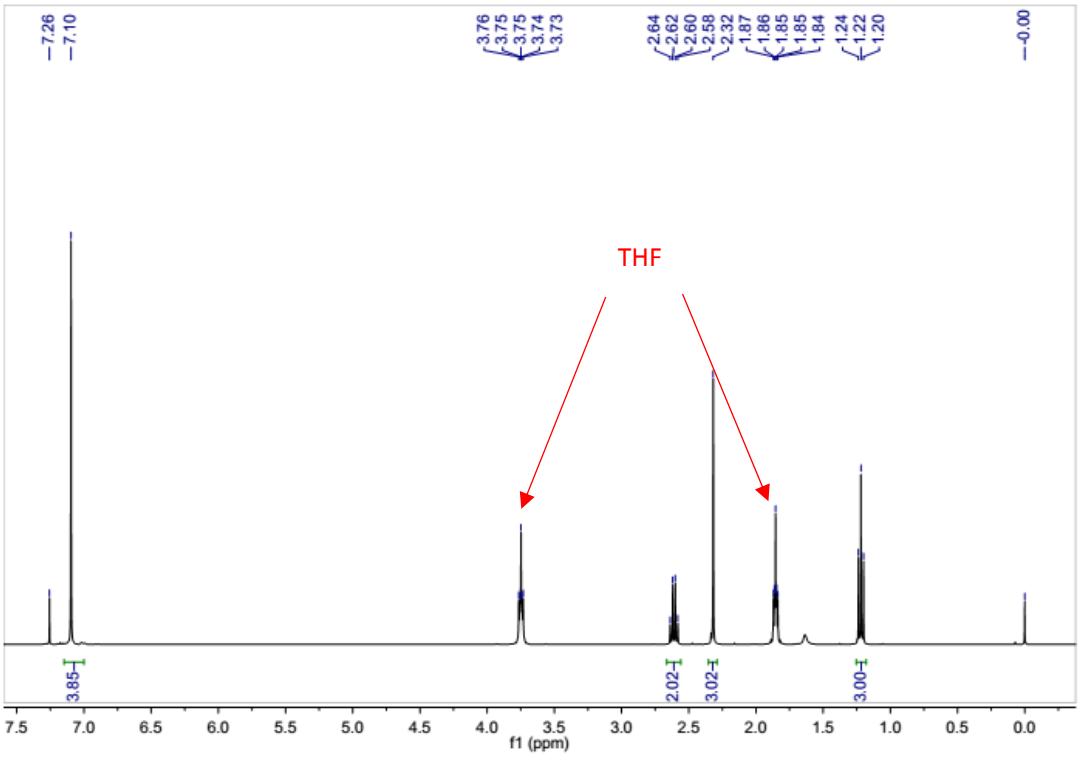


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.174	BV	0.0341	9192.59473	3961.34009	1.000e2

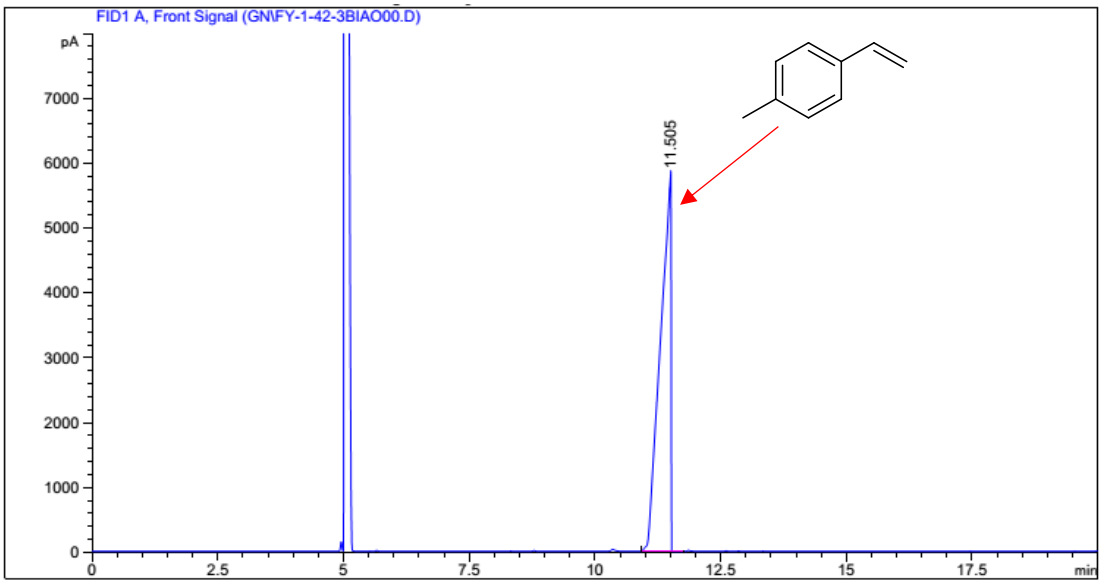
1-Ethyl-4-methylbenzene (from 4-methylstyrene)

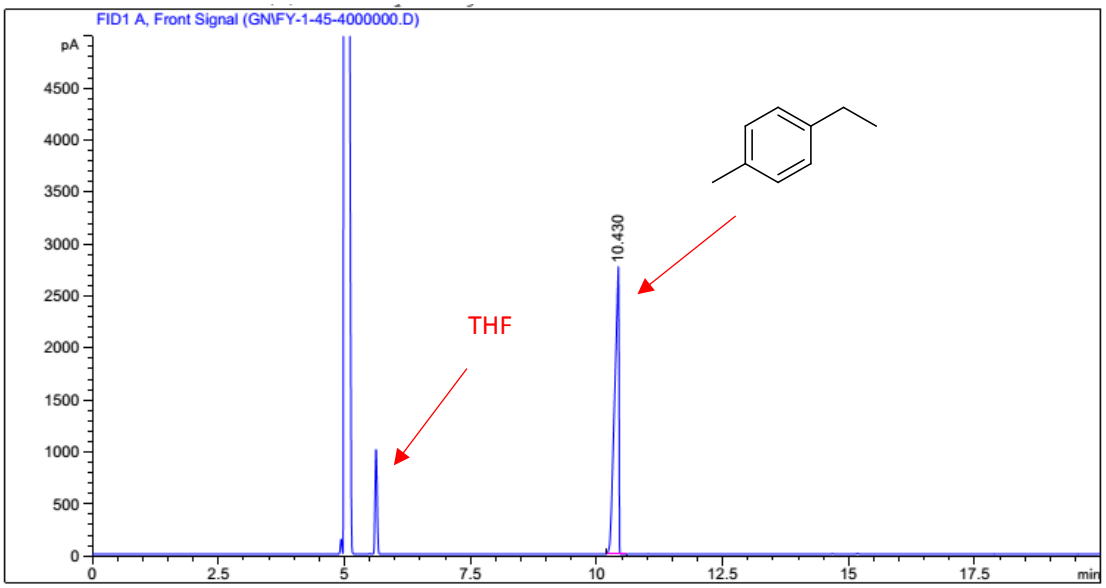


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 4-methylstyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 10 min, 100% conversion to 1-ethyl-4-methylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J = 8.0 Hz, 3H; CH_3), 2.32 (s, 3H; CH_3), 2.62 (q, J = 8.0 Hz, 2H; CH_2), 7.07-7.11 (m, 4H; Ar-H).



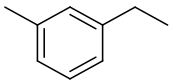
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. t = 11.505 min for 4-methylstyrene and t = 10.430 min for 1-ethyl-4-methylbenzene.



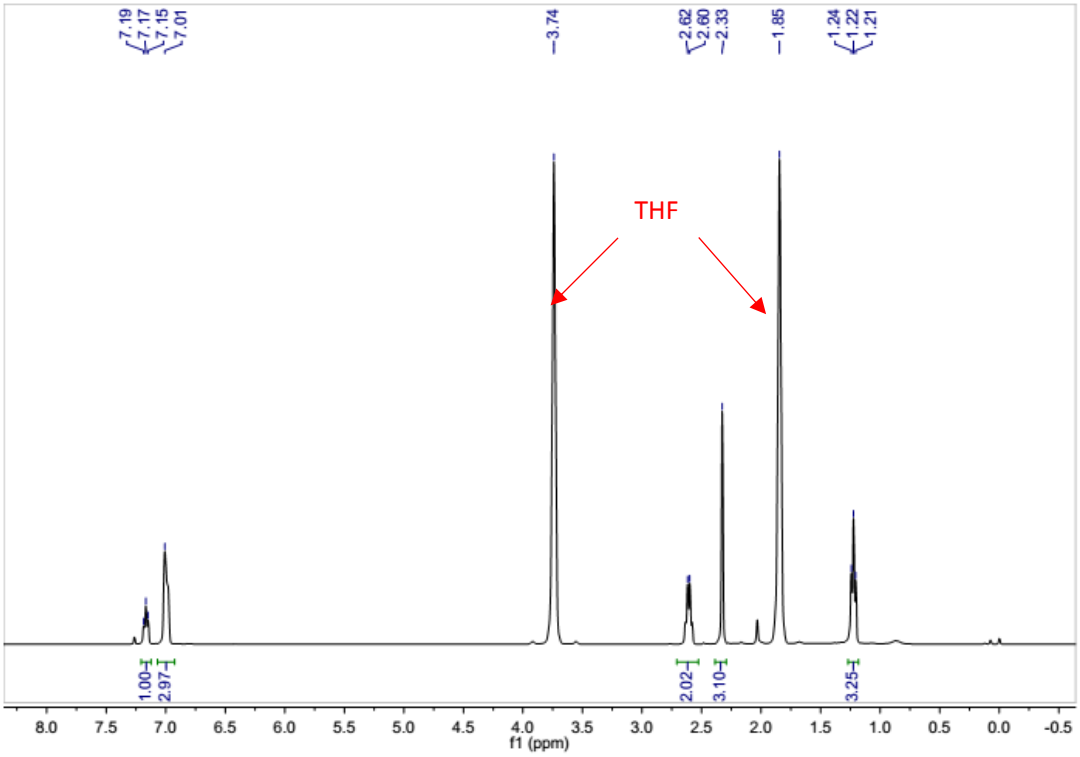


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.430	BB	0.0787	1.65077e4	2764.31689	1.000e2

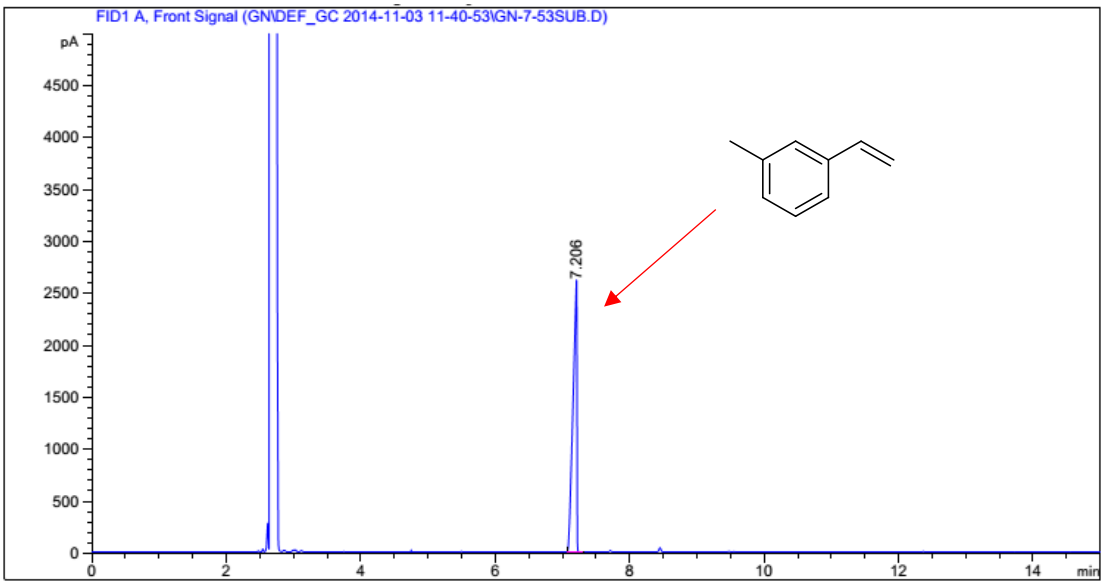
1-Ethyl-3-methylbenzene (**from 3-methylstyrene**)

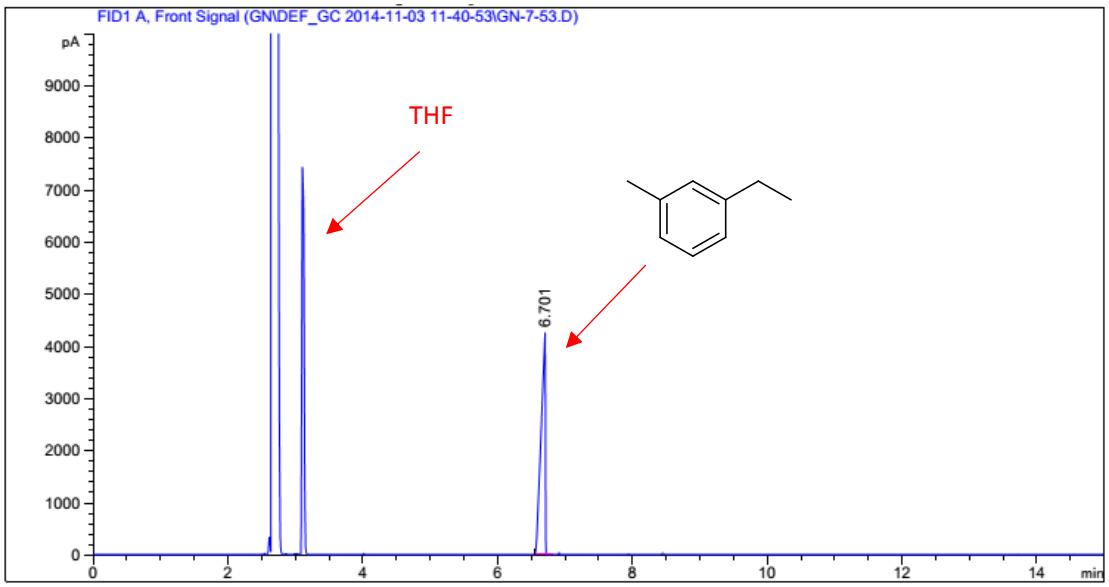


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 3-methylstyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 15 min, 100% conversion to 1-ethyl-3-methylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 8.0 Hz, 3H; CH_3), 2.33 (s, 3H; CH_3), 2.62 (q, *J* = 8.0 Hz, 2H; CH_2), 7.01-7.15 (m, 3H; Ar-H), 7.18 (t, *J* = 8.0 Hz, 1H; Ar-H).



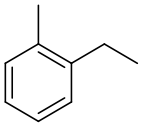
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 7.206 min for 3-methylstyrene and *t* = 6.701 min for 1-ethyl-3-methylbenzene.



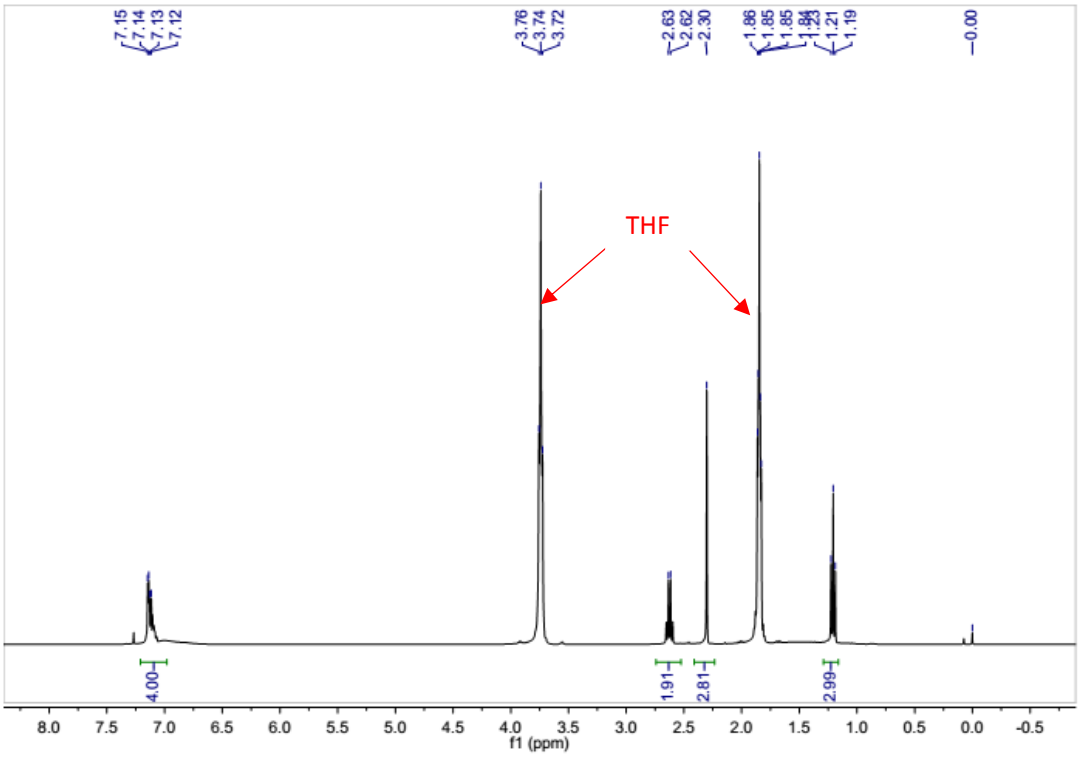


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.340	BB	0.0581	1.82501e4	4170.23828	1.000e2

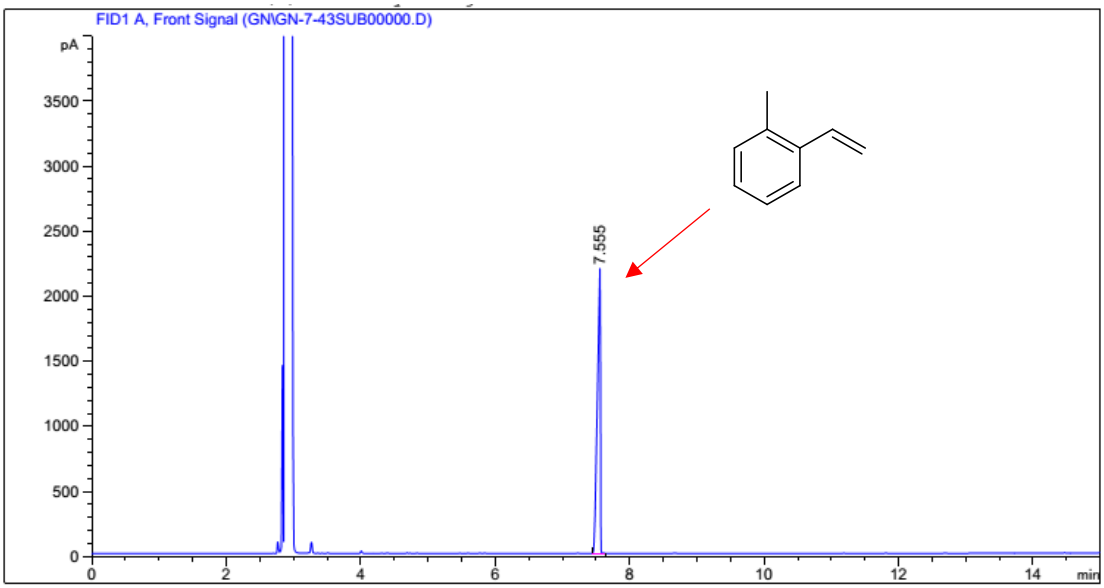
1-Ethyl-2-methylbenzene (from 2-methylstyrene)

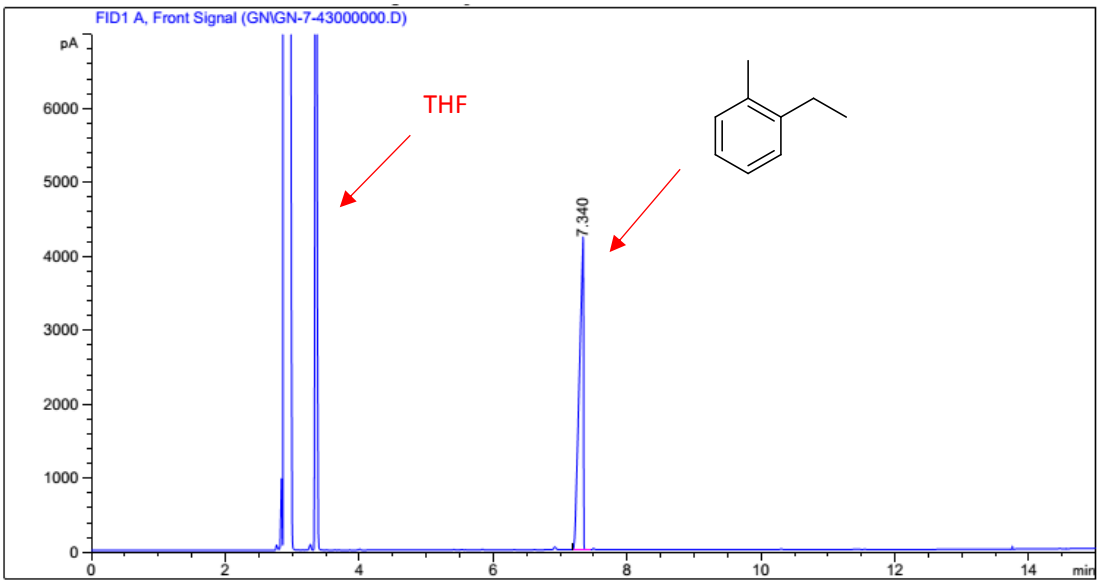


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 2-methylstyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 15 min, 100% conversion to 1-ethyl-2-methylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 8.0 Hz, 3H; CH_3), 2.30 (s, 3H; CH_3), 2.63 (q, *J* = 8.0 Hz, 2H; CH_2), 7.05-7,15 (m, 4H; Ar-H).



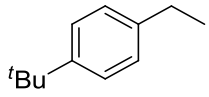
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 7.555 min for 2-methylstyrene and *t* = 7.340 min for 1-ethyl-2-methylbenzene.



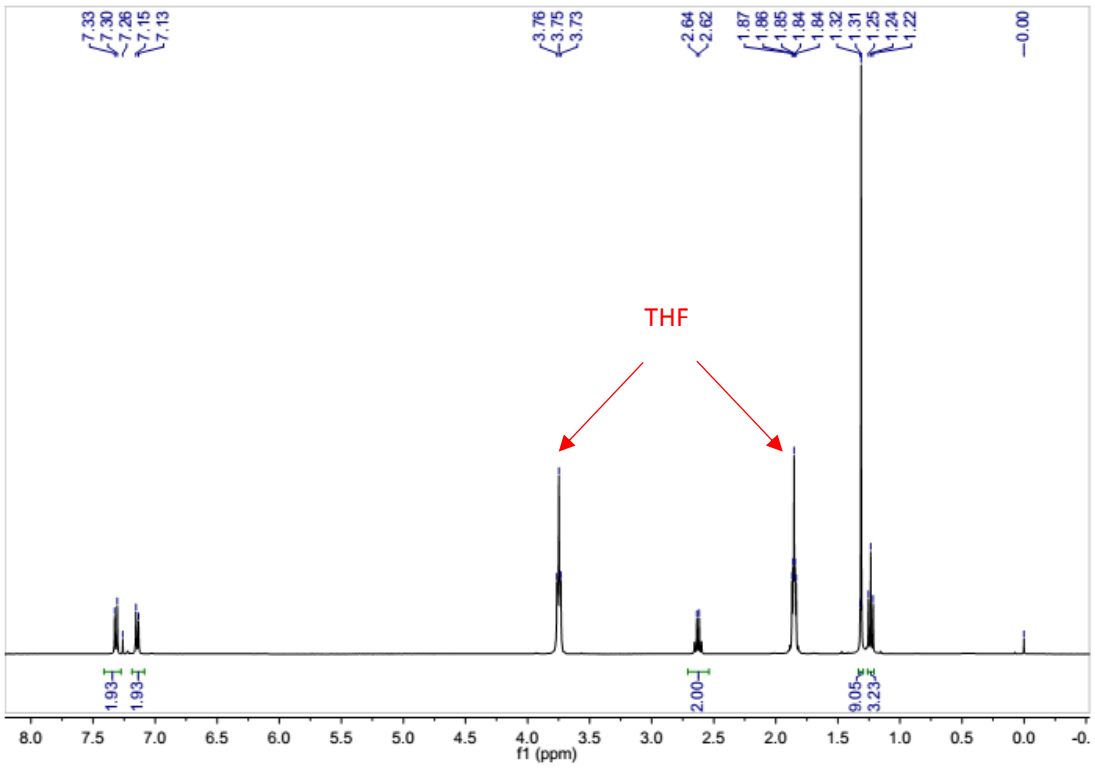


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.340	BB	0.0581	1.82501e4	4170.23828	1.000e2

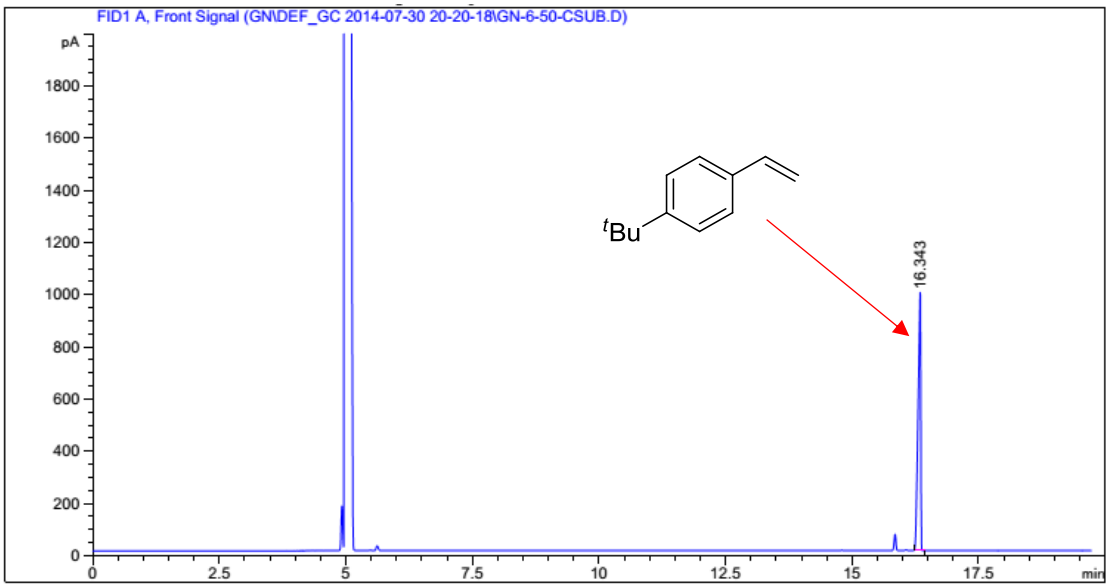
1-*tert*-Butyl-4-ethylbenzene (from 4-*tert*-butylstyrene)

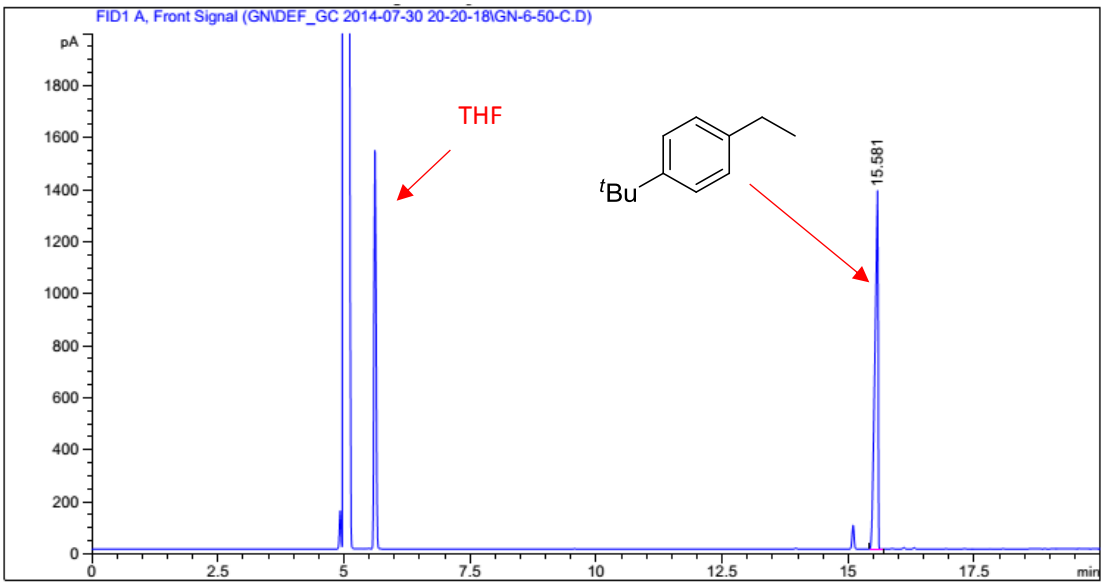


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 4-*tert*-butylstyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 5 min, 100% conversion to 1-*tert*-butyl-4-ethylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 8.0 Hz, 3H; CH_3), 1.31 (s, 9H; CH_3), 2.63 (q, *J* = 8.0 Hz, 2H; CH_2), 7.14 (d, *J* = 8.0 Hz, 2H; Ar-H), 7.32 (d, *J* = 8.0 Hz, 2H; Ar-H).



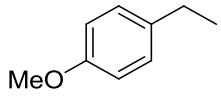
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* =16.343 min for 4-*tert*-butylstyrene and *t* = 15.581 min for 1-*tert*-butyl-4-ethylbenzene.



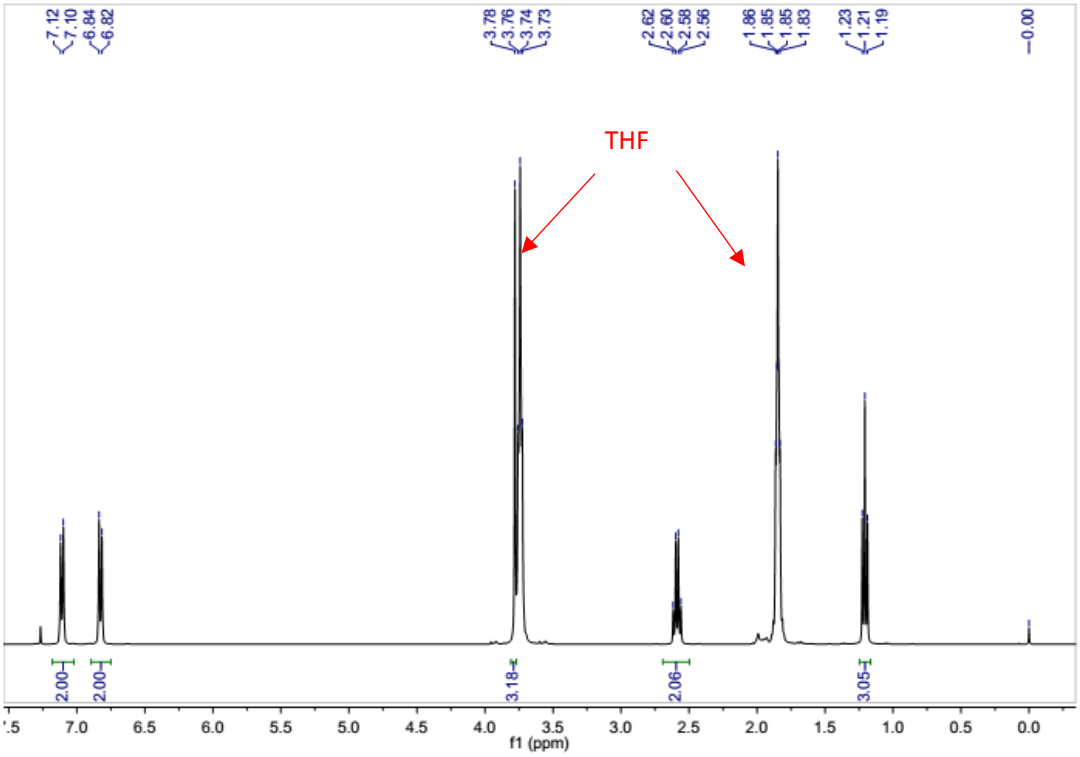


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.581	BB	0.0597	6215.60303	1376.26416	1.000e2

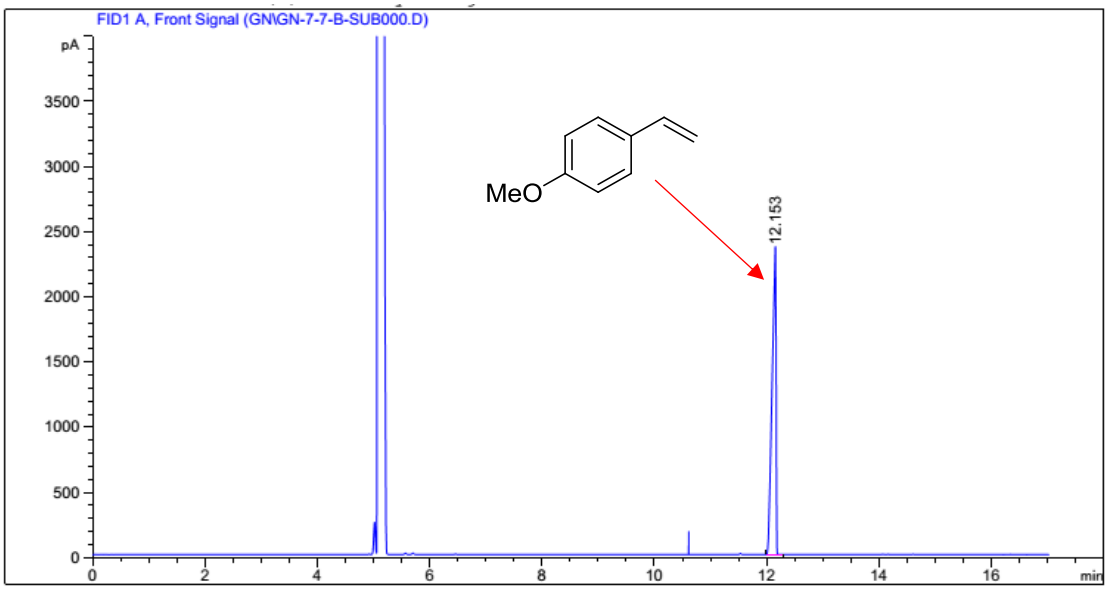
1-Ethyl-4-methoxybenzene (from 4-methoxystyrene)

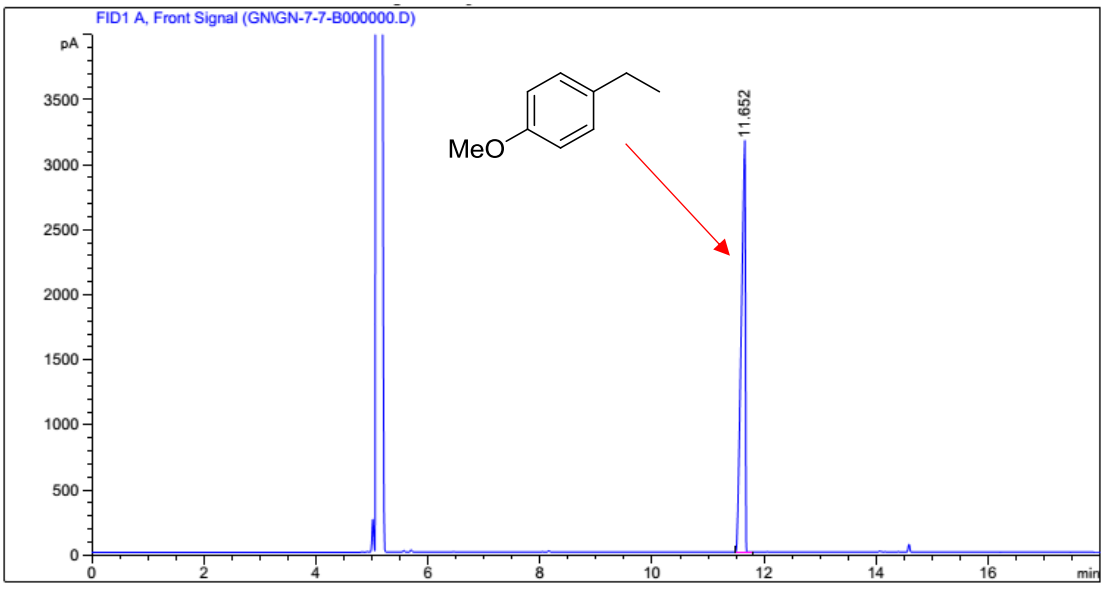


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 4-methoxystyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 3 min, 100% conversion to 1-ethyl-4-methoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 8.0 Hz, 3H; CH_3), 2.60 (q, *J* = 8.0 Hz, 2H; CH_2), 3.78 (s, 3H; CH_3), 6.83 (d, *J* = 8.0 Hz, 2H; Ar-H), 7.11 (d, *J* = 8.0 Hz, 2H; Ar-H).



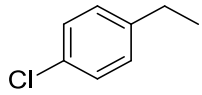
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 12.153 min for 4-methoxystyrene and *t* = 11.652 min for 1-ethyl-4-methoxybenzene.



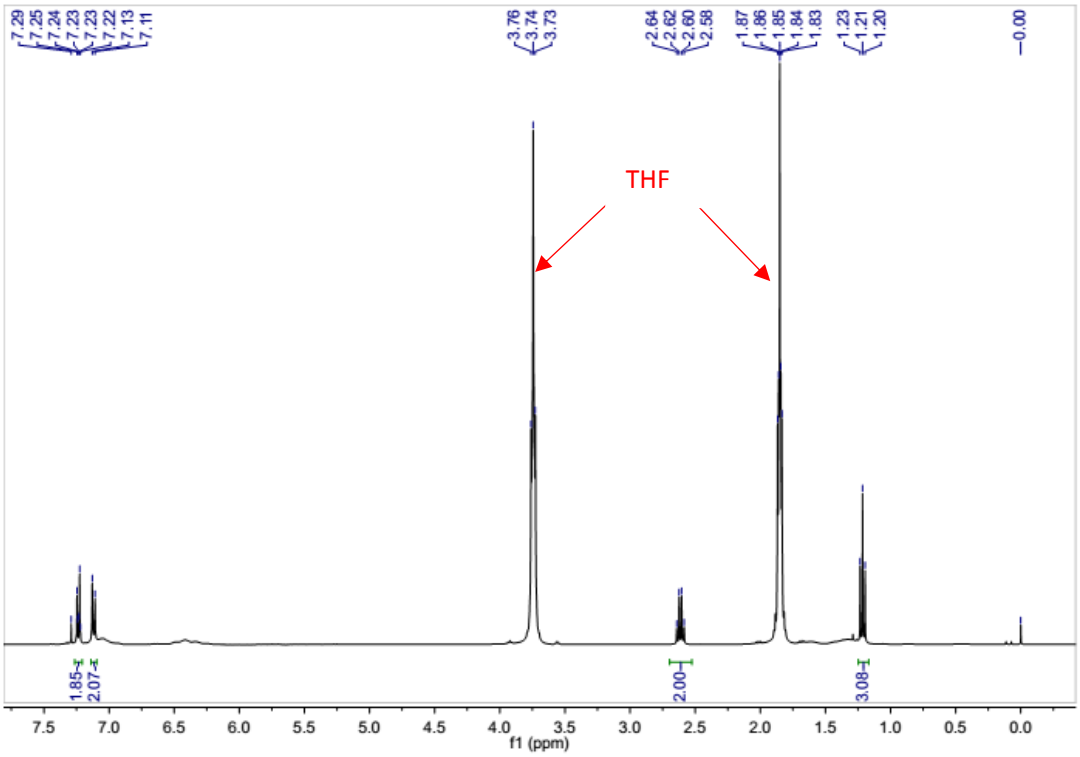


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.652	BB	0.0703	1.60234e4	3151.21411	1.000e2

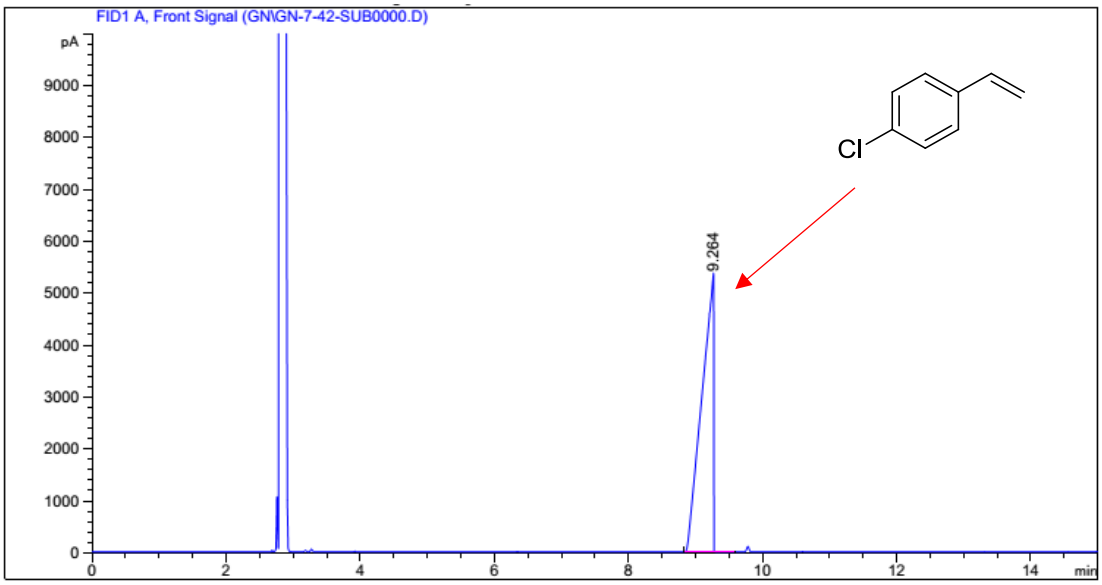
1-Chloro-4-ethylbenzene (from 4-chlorostyrene)

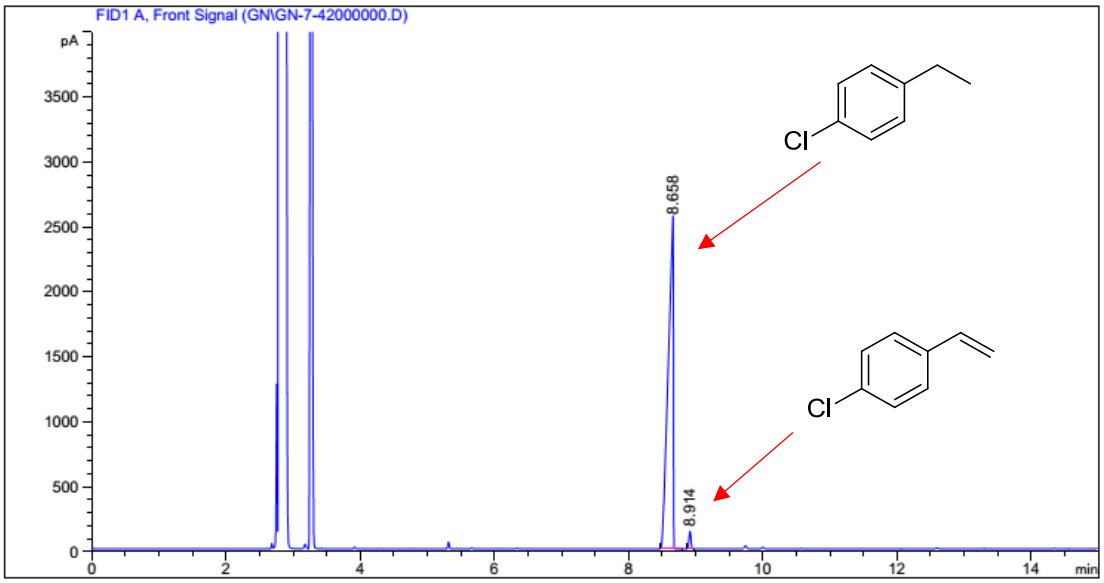


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 4-chlorostyrene (5 mmol), 1 mL THF, 30 atm H_2, rt, 6 h, 98% conversion to 1-chloro-4-ethylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 8.0 Hz, 3H; CH_3), 2.62 (q, *J* = 8.0 Hz, 2H; CH_2), 7.11-7.22 (m, 2H; Ar), 7.23-7.25 (m, 2H; Ar).



GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 9.264 min for 4-chlorostyrene and *t* = 8.658 min for 1-chloro-4-ethylbenzene.

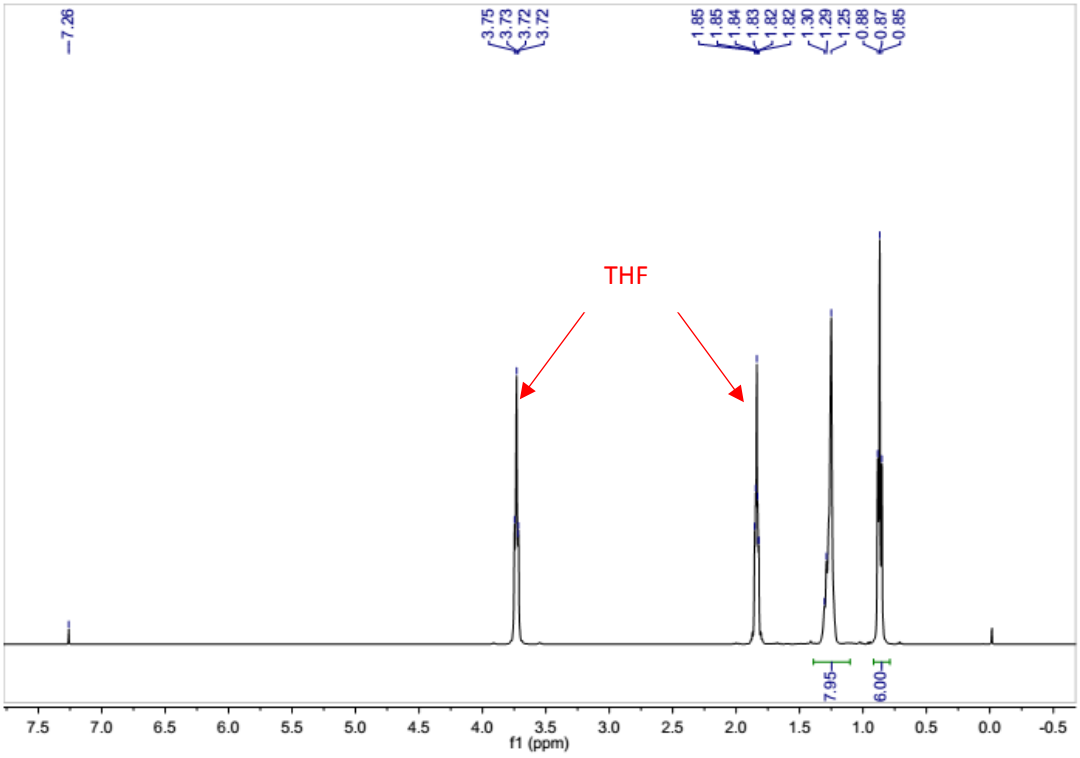




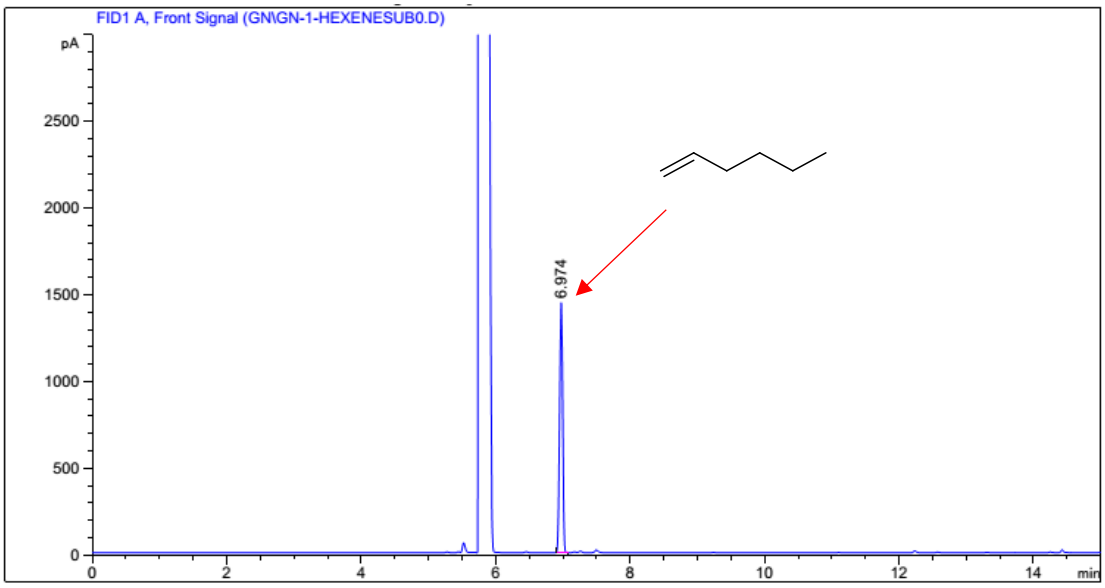
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.658	BB	0.0679	1.34554e4	2537.01123	97.99019
2	8.914	BB	0.0318	275.97473	135.55830	2.00981

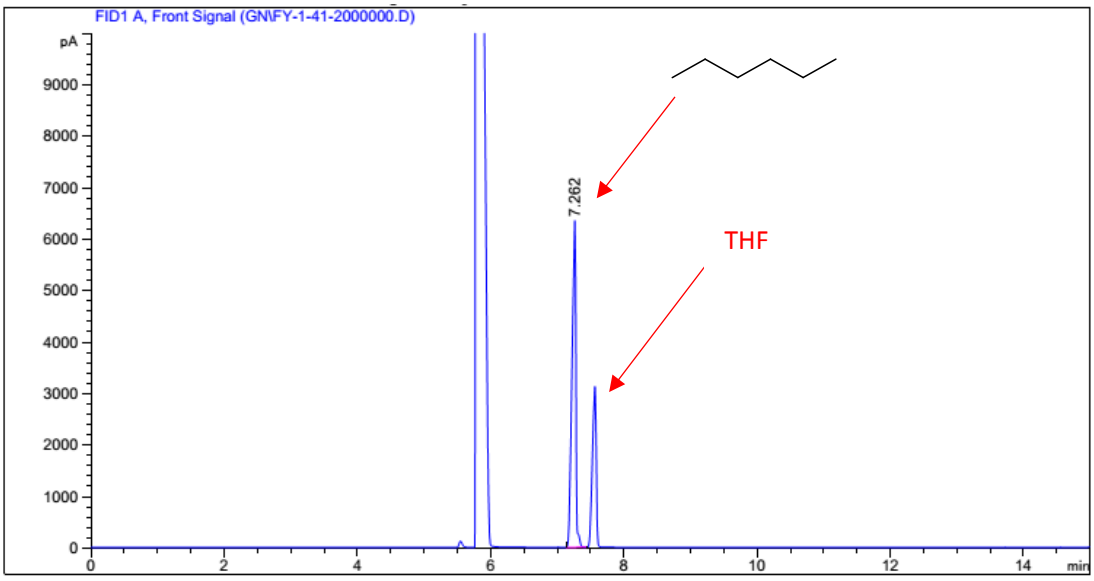
***n*-Hexane (from 1-hexene)**

Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 1-hexene (5 mmol), 1 mL THF, 30 atm H_2, rt, 20 min, 100% conversion to *n*-hexane. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 8.0 Hz, 6H; CH_3), 1.23-1.30 (m, 8H; CH_2).



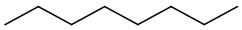
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 45 ℃ holds for 10 min, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 6.974 min for 1-hexene and *t* = 7.262 min for *n*-hexane.



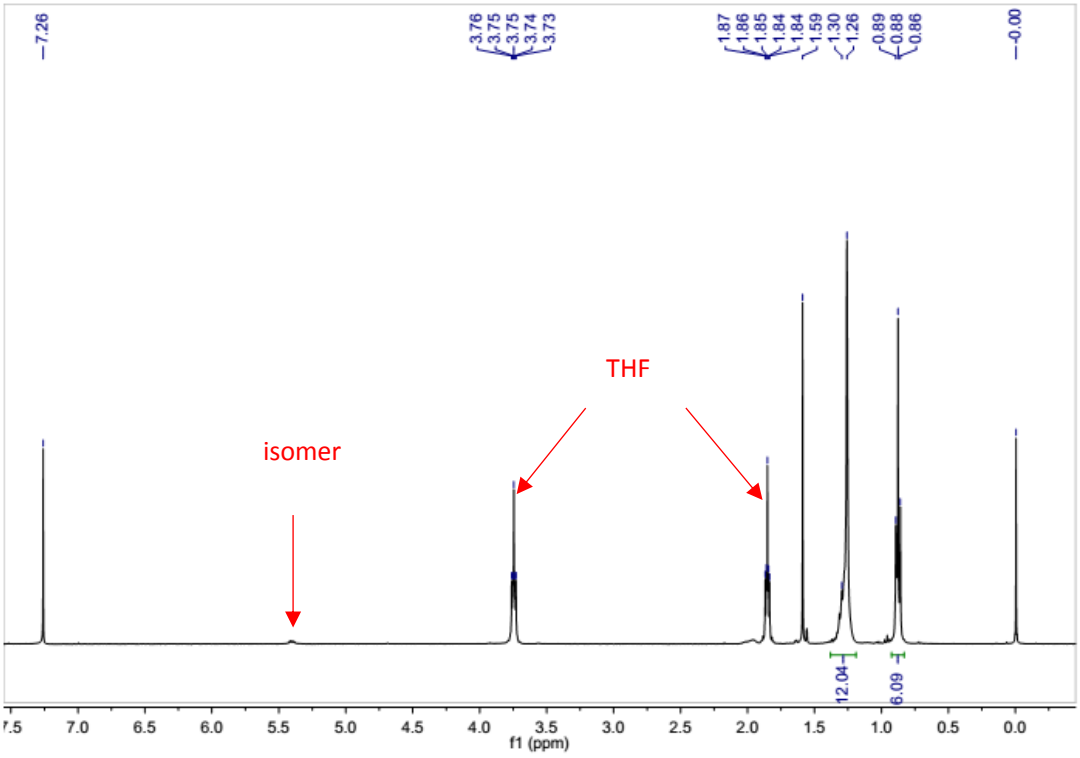


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.262	BV	0.0670	2.60615e4	6338.10889	1.000e2

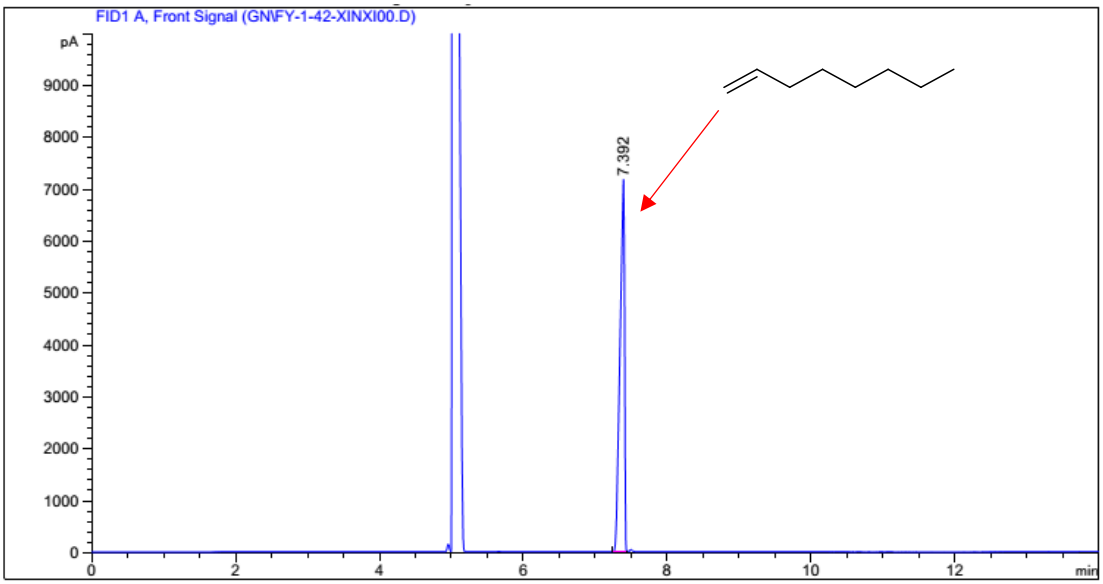
***n*-Octane (from 1-octene)**

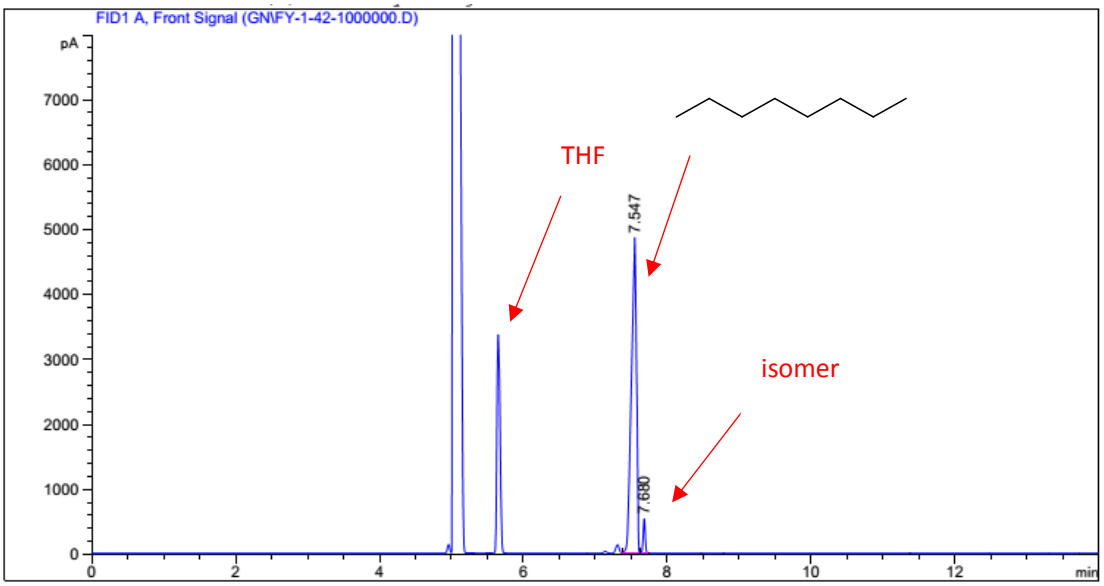


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 1-octene (5 mmol), 1 mL THF, 30 atm H_2, rt, 30 min, 96% conversion to *n*-octane. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 8.0 Hz, 6H; CH_3), 1.24-1.30 (m, 12H; CH_2).



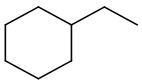
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. t =7.392 min for 1-octene, t = 7.547 min for *n*-octane and t = 7.680 min for isomer of 1-octene .



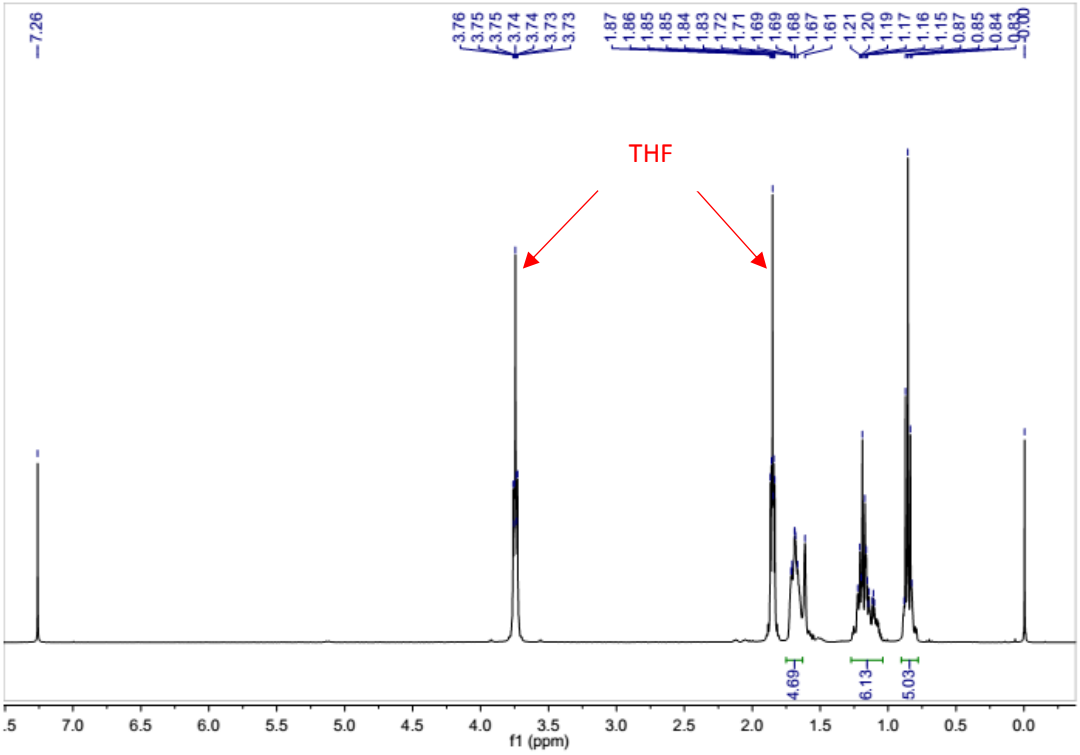


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.547	VV	0.0674	2.38796e4	4856.62402	95.78315
2	7.680	VB	0.0313	1051.29907	526.50568	4.21685

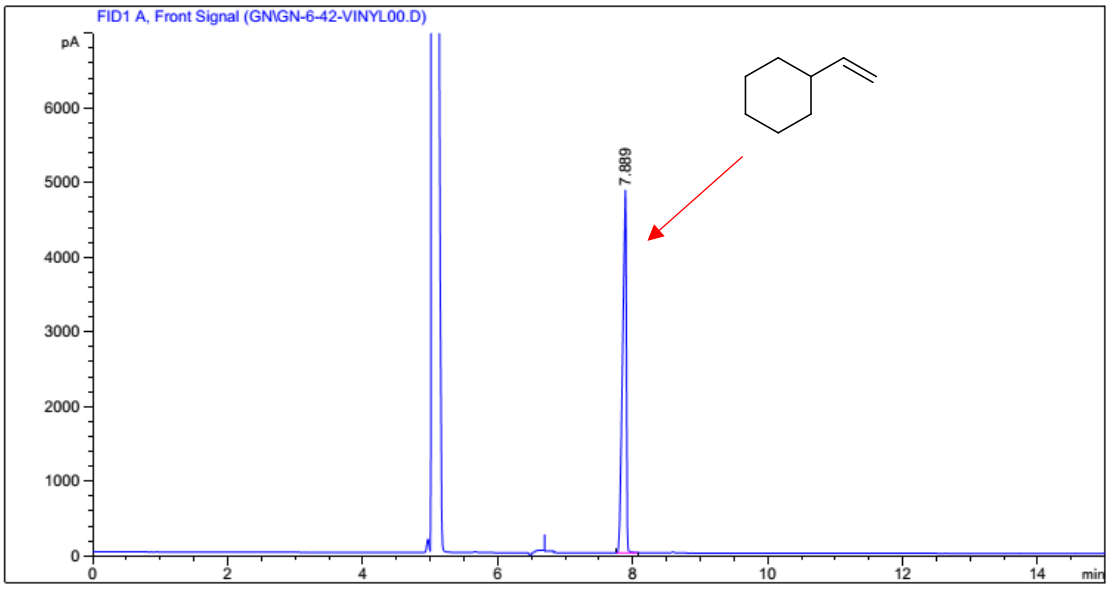
Ethylcyclohexane (from vinylcyclohexane)

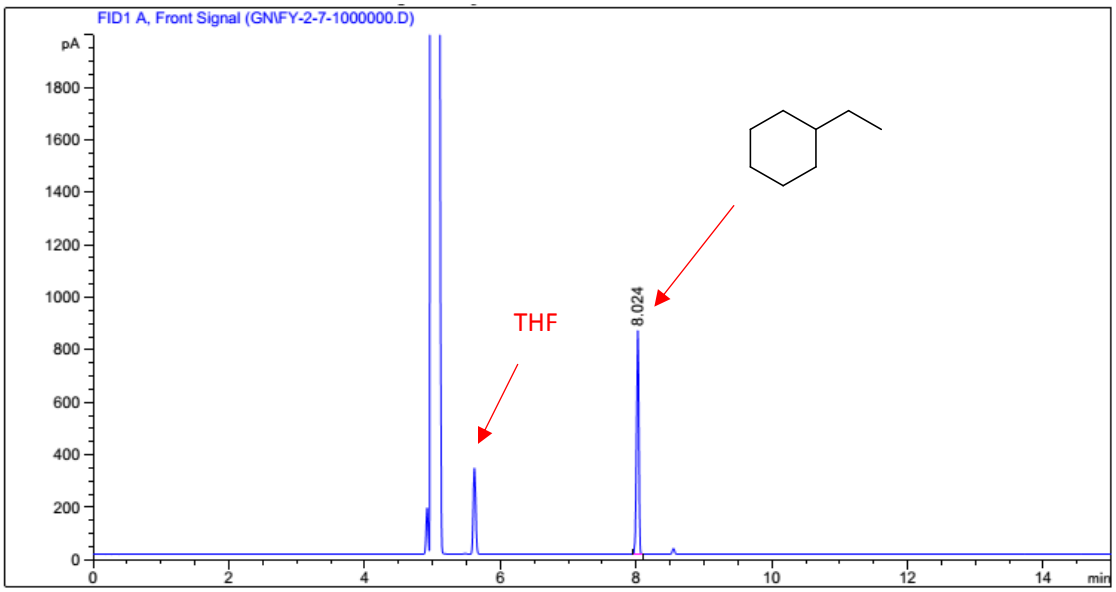


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), vinylcyclohexane (5 mmol), 1 mL THF, 30 atm H_2, rt, 20 min, 100% conversion to ethylcyclohexane. ^1H NMR (400 MHz, $CDCl_3$) δ 0.83-0.89 (m, 5H; CH_3, CH_2), 1.13-1.22 (m, 6H; CH_2), 1.65-1.73 (m, 5H; CH_2, CH).



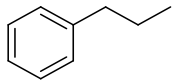
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 7.889 min for vinylcyclohexane and *t* = 8.024 min for ethylcyclohexane.



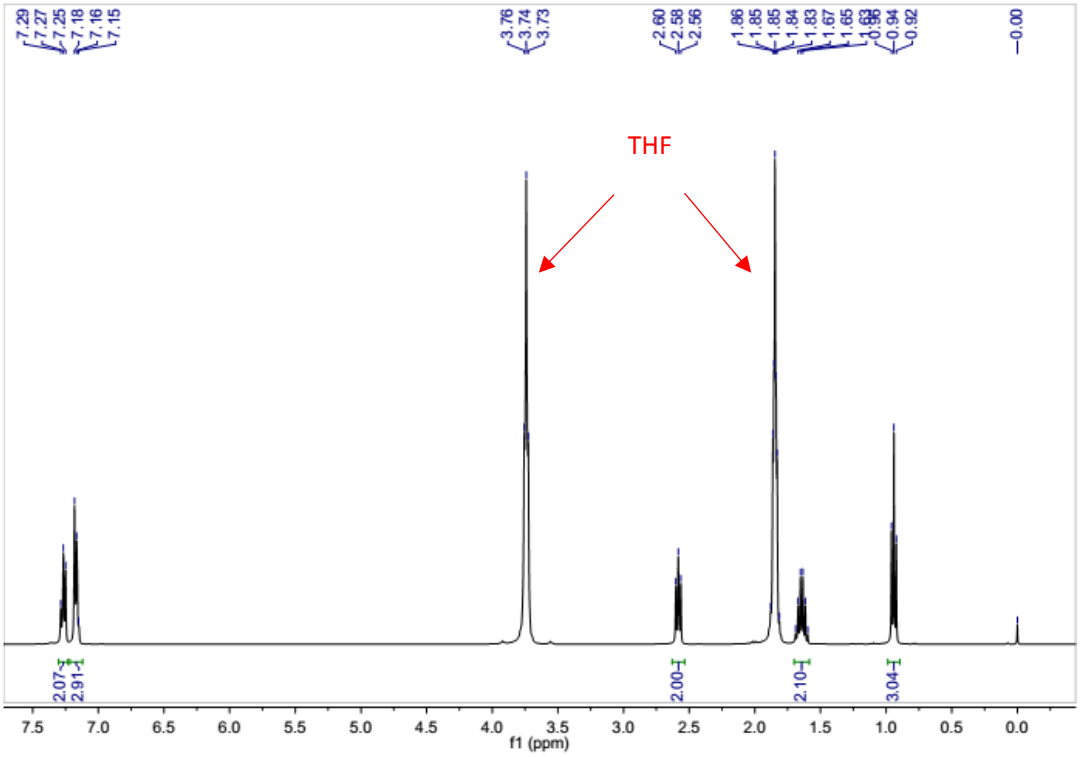


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.024	BB	0.0382	2054.60449	850.40735	1.000e2

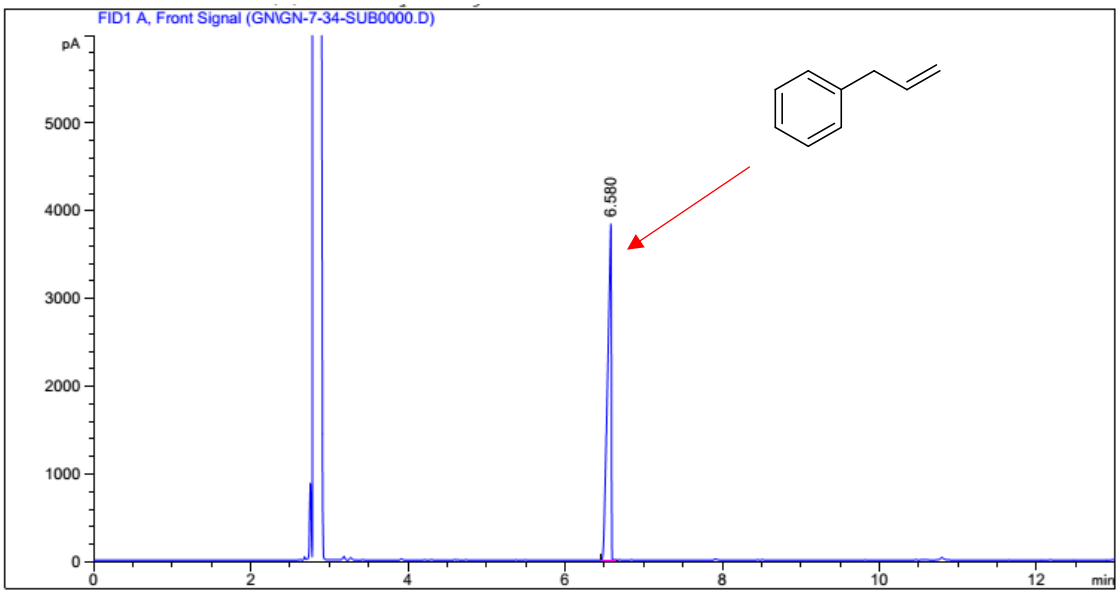
Propylbenzene (from allylbenzene)

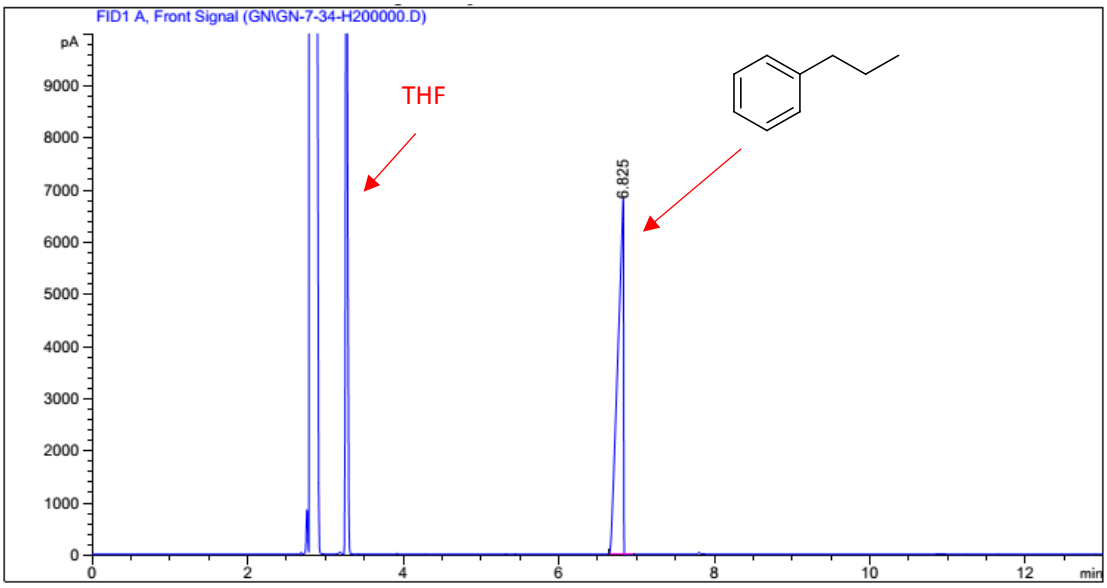


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), allylbenzene (5 mmol), 1 mL THF, 30 atm H_2, 15 min, 100% conversion to propylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 8.0 Hz, 3H; CH_3), 1.62-1.68 (m, 2H; CH_2), 2.58 (t, *J* = 8.0 Hz, 2H; CH_2), 7.15-7.18 (m, 3H; Ar-H), 7.25-7.29 (m, 2H; Ar-H).



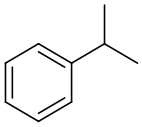
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 6.580 min for allylbenzene and *t* = 6.825 min for propylbenzene.



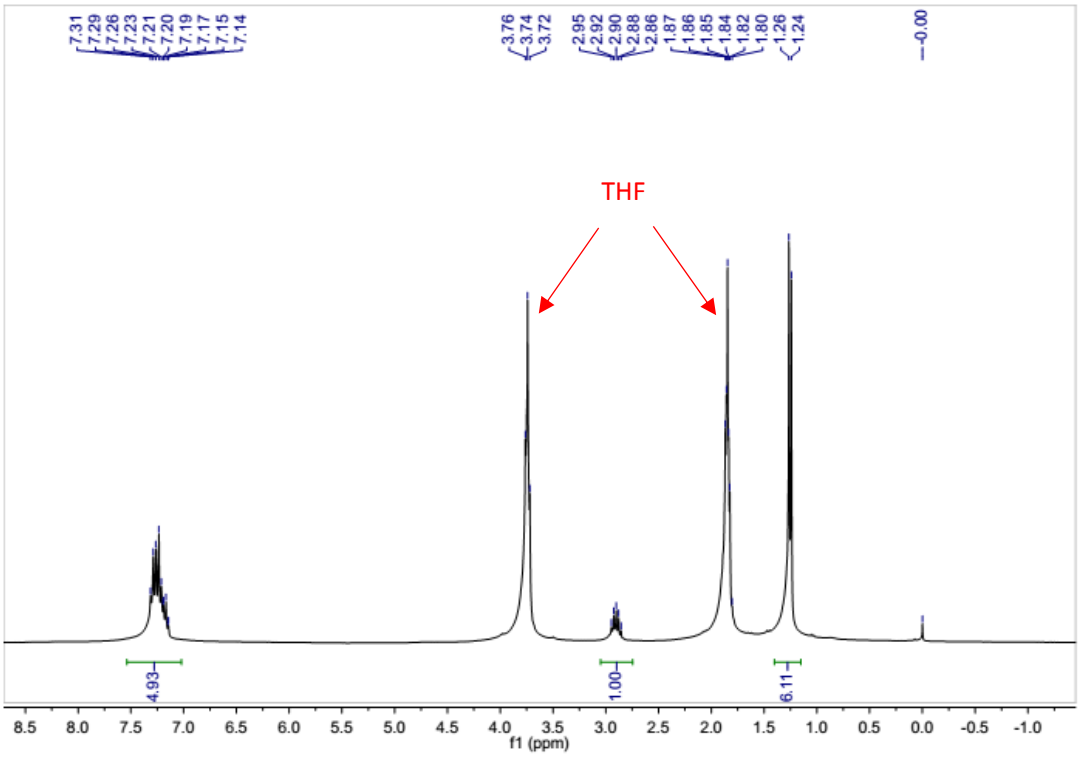


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.825	BB	0.0654	3.54163e4	6734.84131	1.000e2

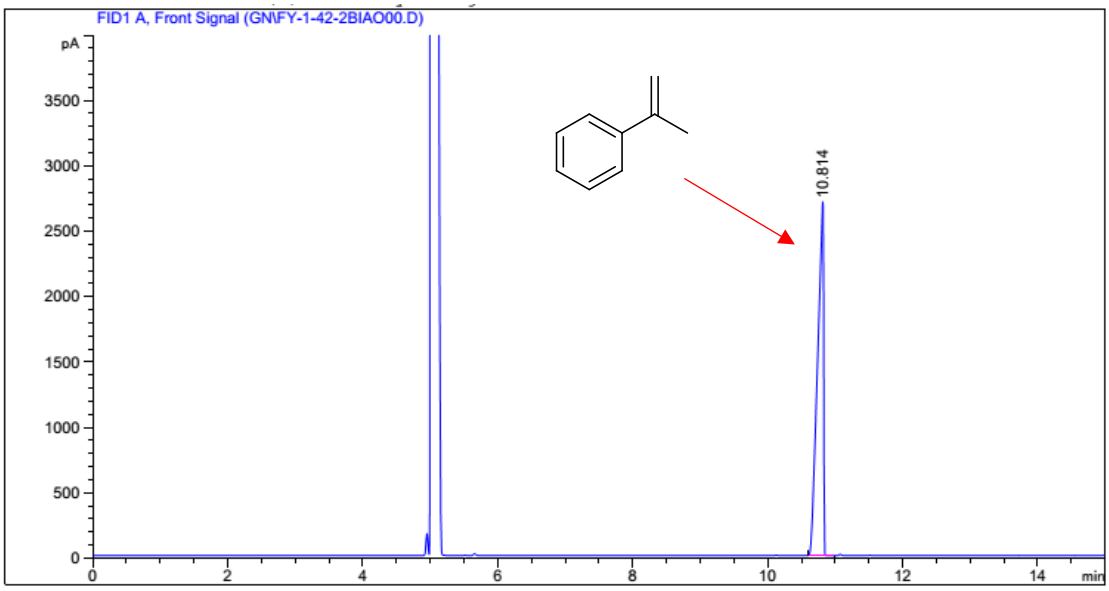
Isopropylbenzene (from 2-phenyl-1-propene)

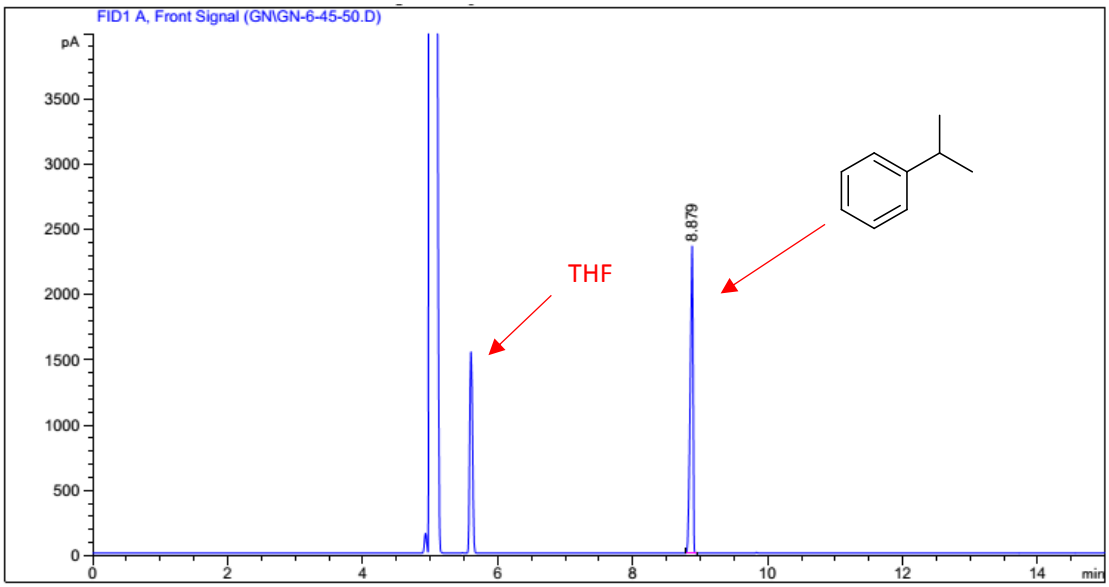


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 2-phenyl-1-propene (5 mmol), 1 mL THF, 30 atm H_2, 50 °C, 1 h, 100% conversion to isopropylbenzene. ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, J = 8.0 Hz, 6H; CH_3), 2.86-2.95 (m, 1 H; CH), 7.14-7.32 (m, 5 H; Ar-H).



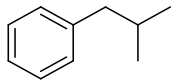
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. t = 10.814 min for 2-phenyl-1-propene and t = 8.879 min for isopropylbenzene.



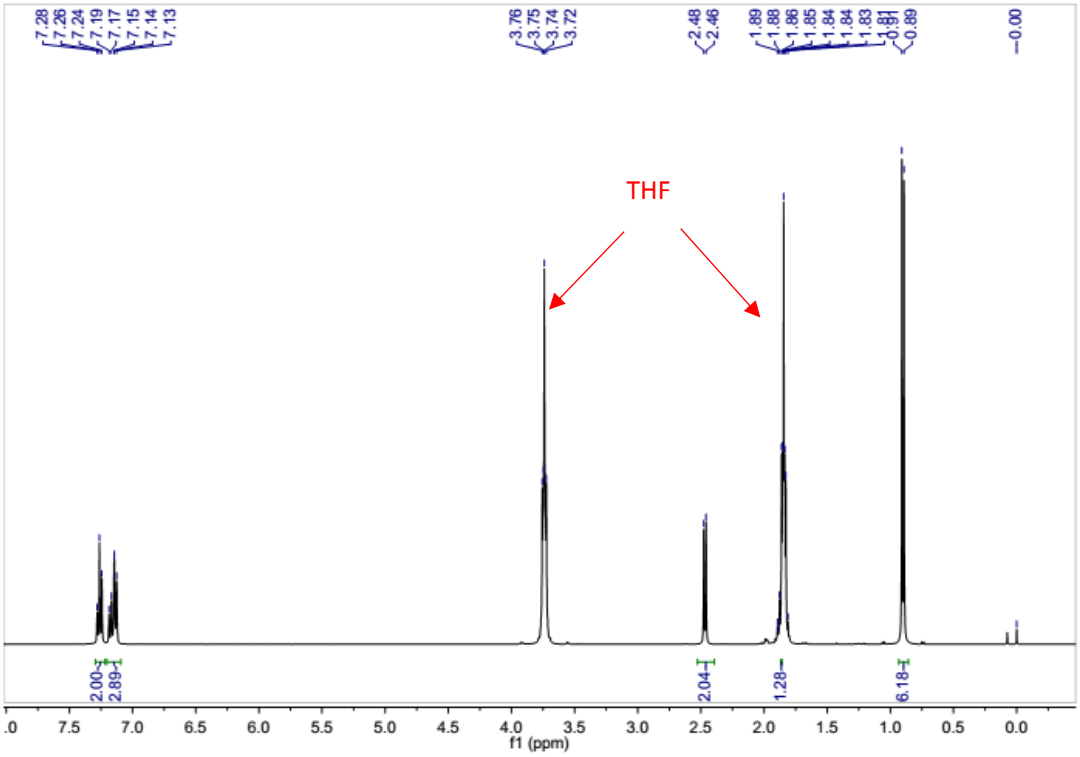


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.879	BB	0.0441	6860.85986	2348.16968	1.000e2

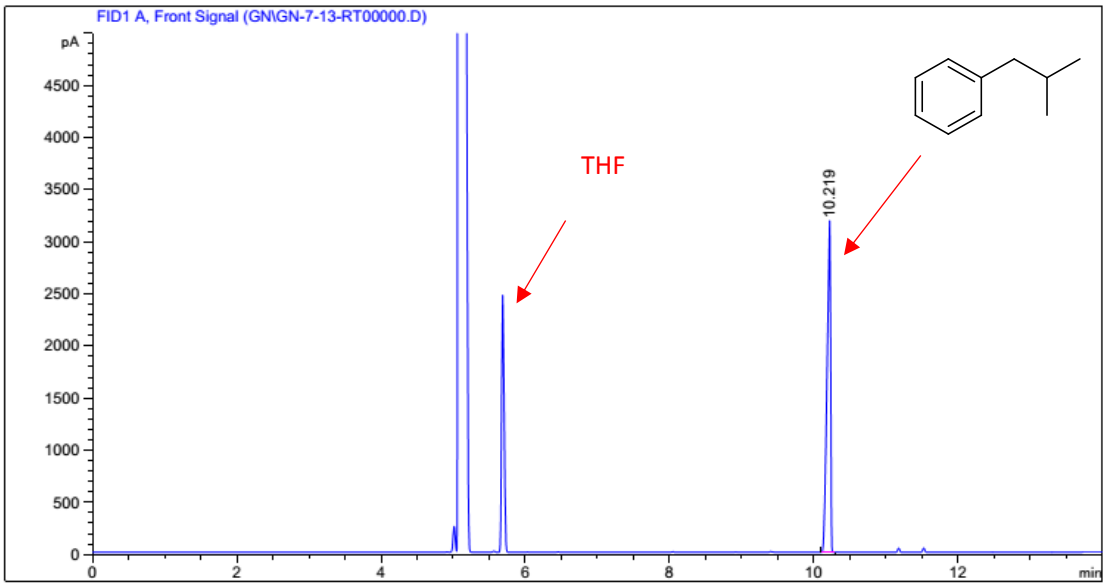
Isobutylbenzene (from 2-methyl-3-phenyl-1-propene)



Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 2-methyl-3-phenyl-1-propene (5 mmol), 1 mL THF, 30 atm H_2, rt, 1.5 h, 100% conversion to isobutylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (d, *J* = 8.0 Hz, 6H; CH_3), 1.81-1.89 (m, 1H; CH), 2.47 (d, *J* = 8.0 Hz, 2H; CH_2), 7.13-7.19 (m, 3H; Ar-H), 7.23-7.29 (m, 2H; Ar-H).

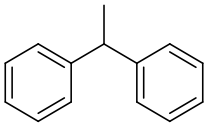


GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 10.390 min for 2-methyl-3-phenyl-1-propene and *t* = 10.219 min for isobutylbenzene.

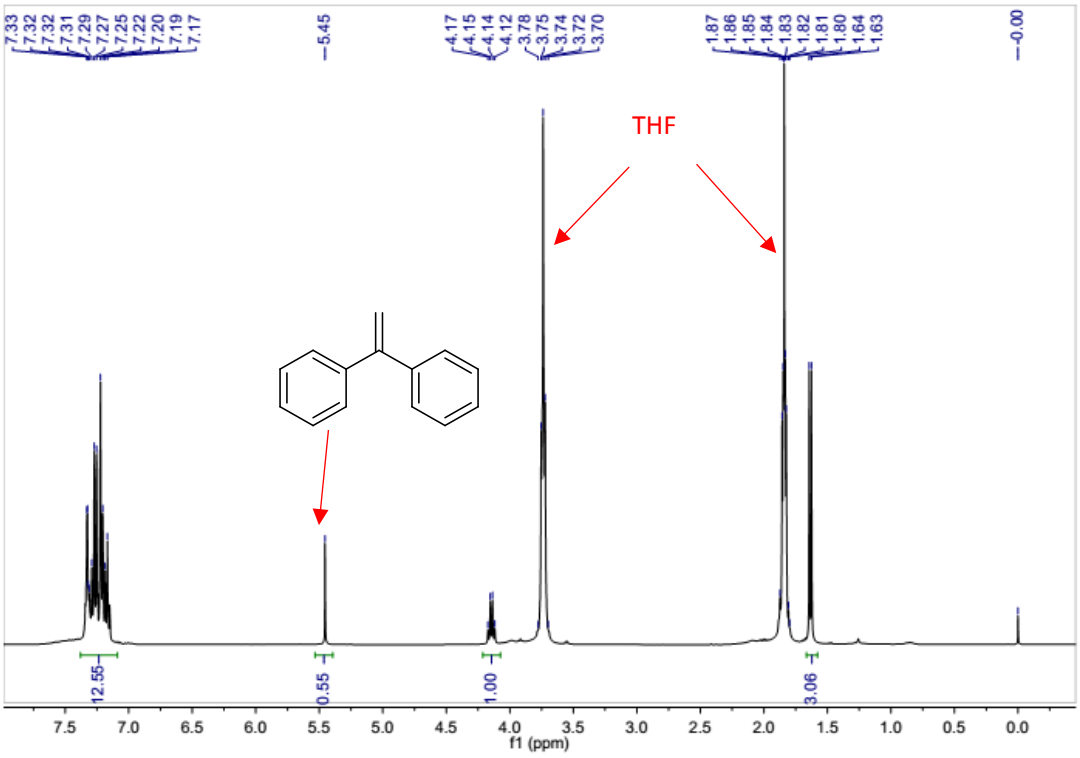


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.219	BV	0.0524	1.09908e4	3170.76489	1.000e2

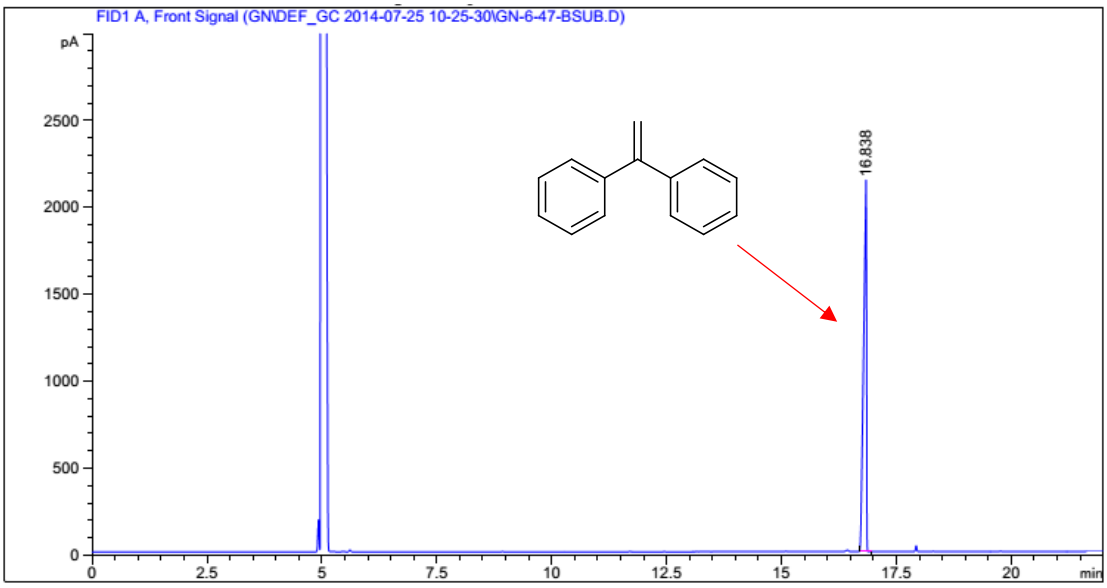
Ethane-1,1-diyldibenzene (from 1,1-diphenylethylene)

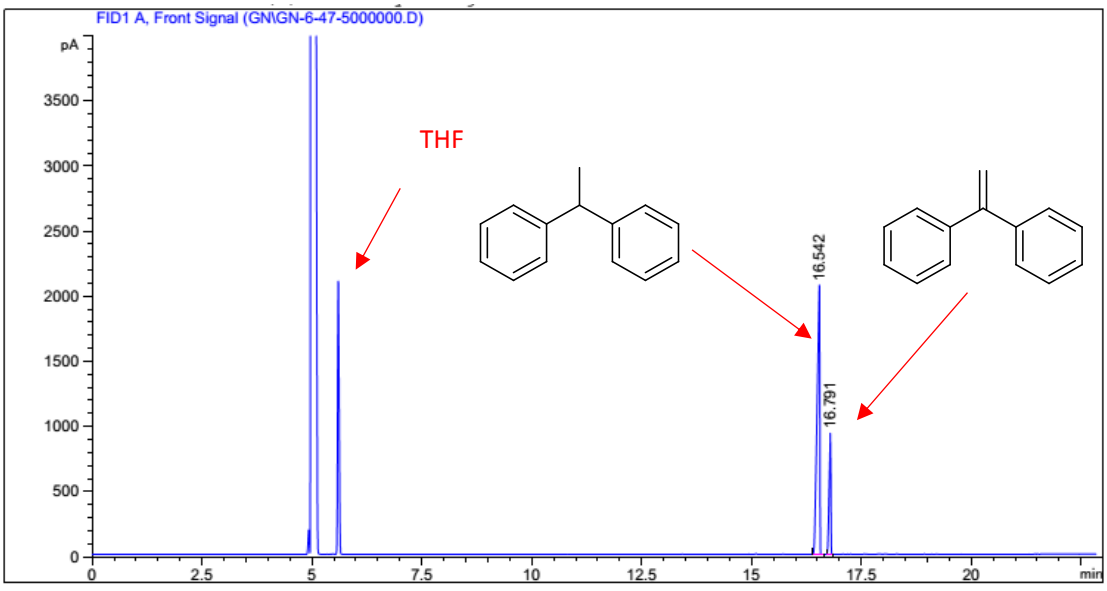


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 1,1-diphenylethylene (5 mmol), 1 mL THF, 30 atm H_2, 2 h, 50 ^oC, rt, 78% conversion to ethane-1,1-diyldibenzene. ^1H NMR (400 MHz, $CDCl_3$) δ 1.64 (d, J = 4.0 Hz, 3H; CH_3), 4.15 (q, J = 8.0 Hz, 1H; CH), 7.17-7.33 (m, 10H; Ar-H)



GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. t = 16.838 min for 1,1-diphenylethylene and t = 16.542 min for ethane-1,1-diyldibenzene.

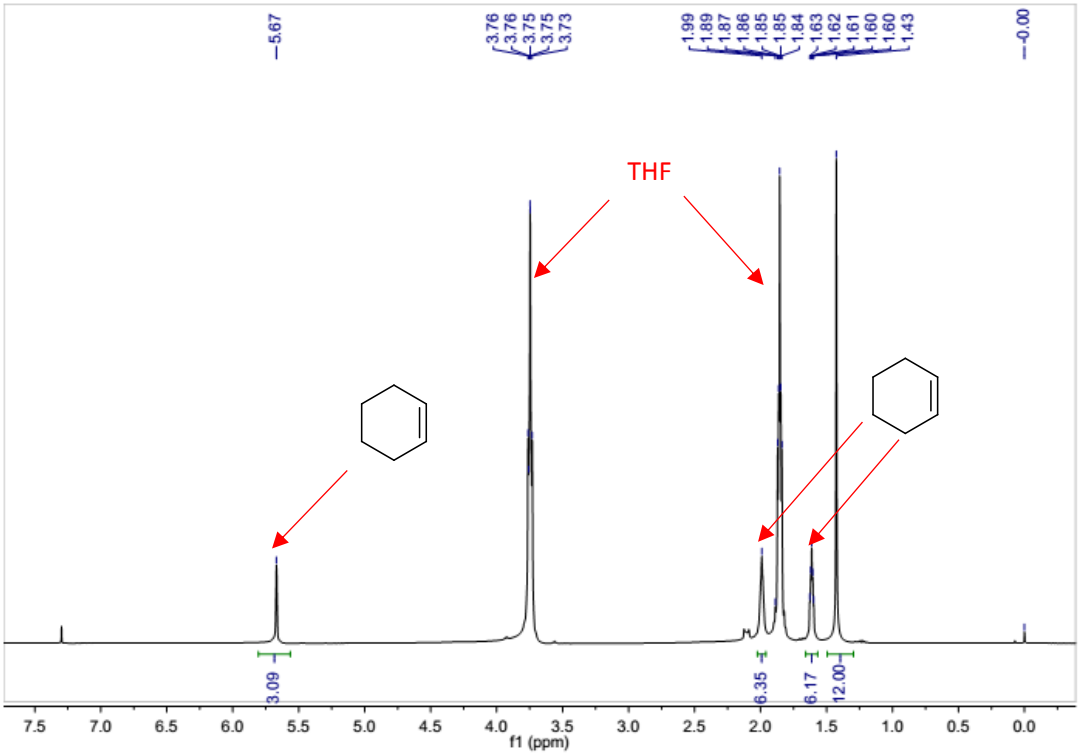




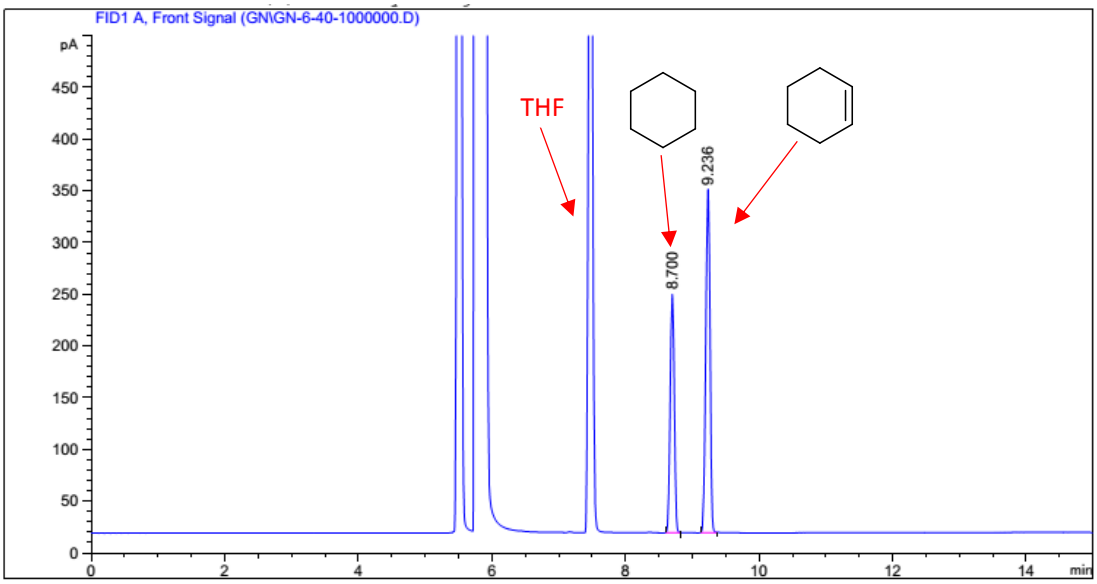
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.542	BB	0.0577	8778.71875	2059.73315	78.12795
2	16.791	BB	0.0399	2457.61743	929.24011	21.87205

Cyclohexane (from cyclohexene)

Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), cyclohexene (5 mmol), 1 mL THF, 30 atm H_2, 50 ^oC, 1 h, 40% conversion to cyclohexane. ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 12 H).

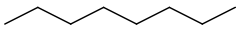


GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ holds for 10 min, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* =9.182 min for cyclohexene and *t* = 8.700 min for cyclohexane

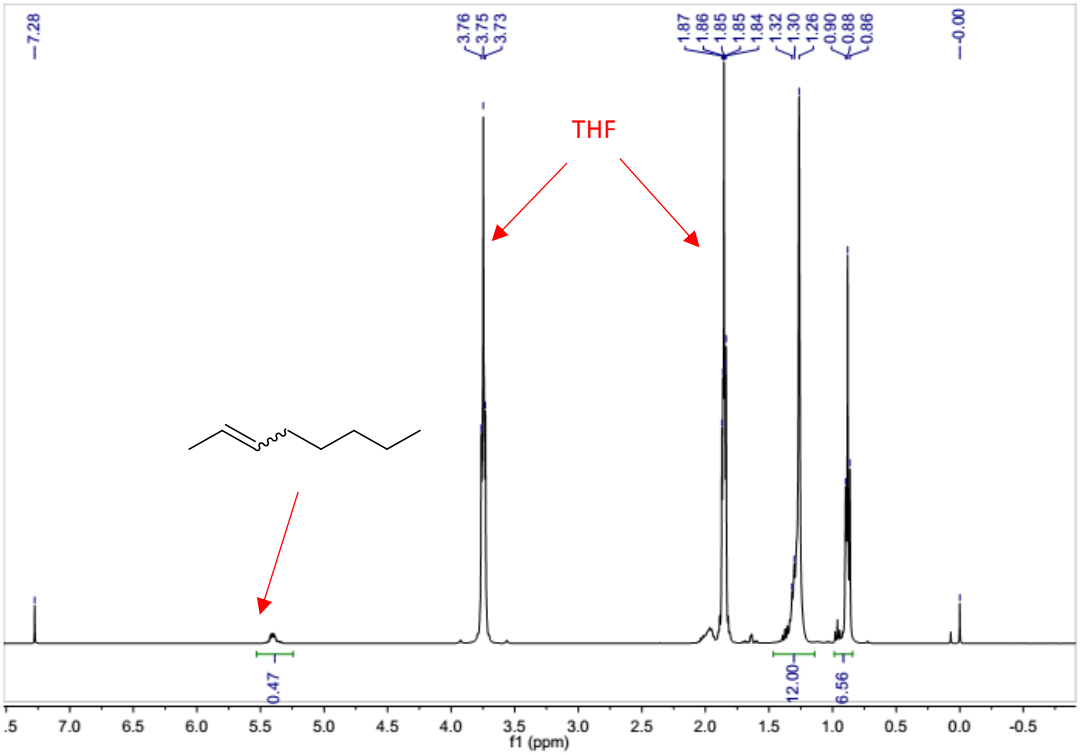


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.700	BB	0.0683	992.41956	230.28899	40.21303
2	9.236	BB	0.0699	1475.48608	331.78387	59.78697

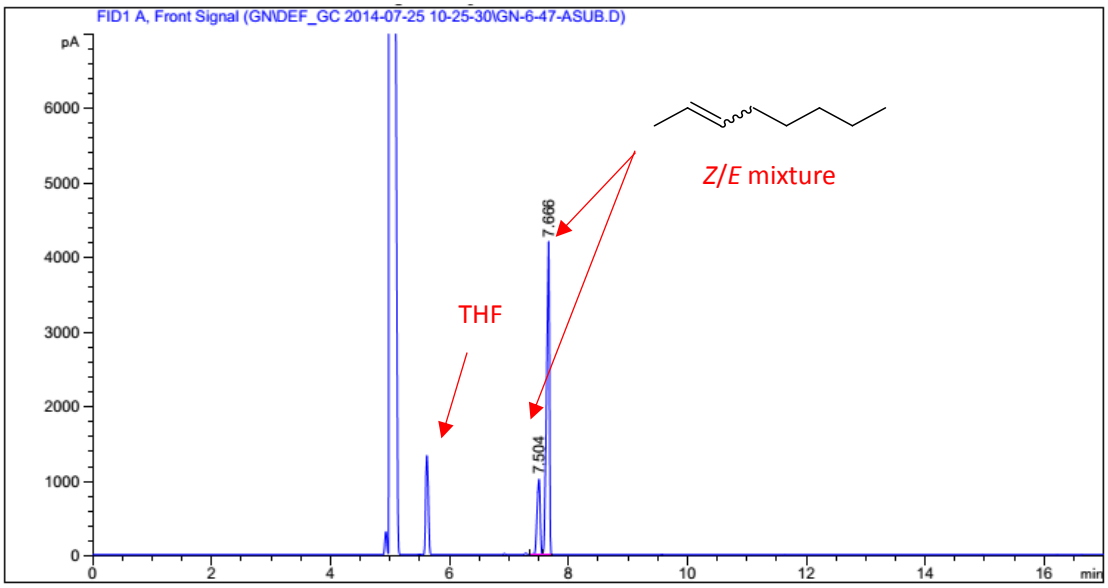
***n*-Octene (from 2-octene)**

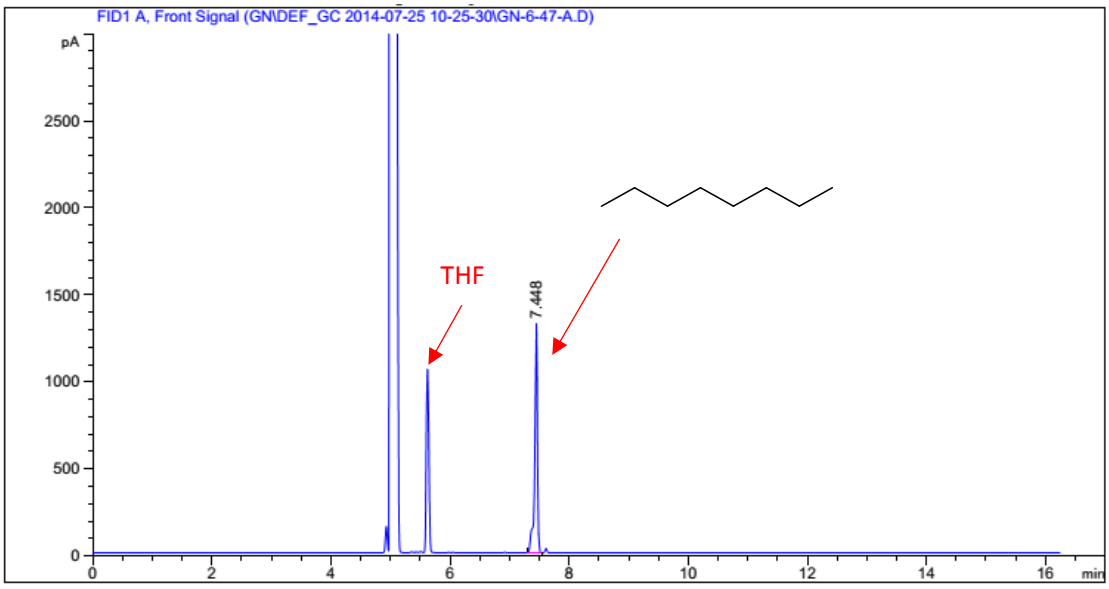


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), 2-octene (*Z*/*E* = 1:4, 5 mmol), 1 mL THF, 30 atm H_2, 50 ^oC, 5 h, 80% conversion to *n*-octane. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 8.0 Hz, 6H; CH_3), 1.24-1.32 (m, 12 H; CH_2).



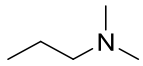
GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ ramps 10 ℃/min to 100 ℃, ramps 3 ℃/min to 120 ℃, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 7.504 min and *t* = 7.666 min for 2-octene (*Z*/*E* mixture) and *t* = 7.448 min for *n*-octane and isomers of the substrate.



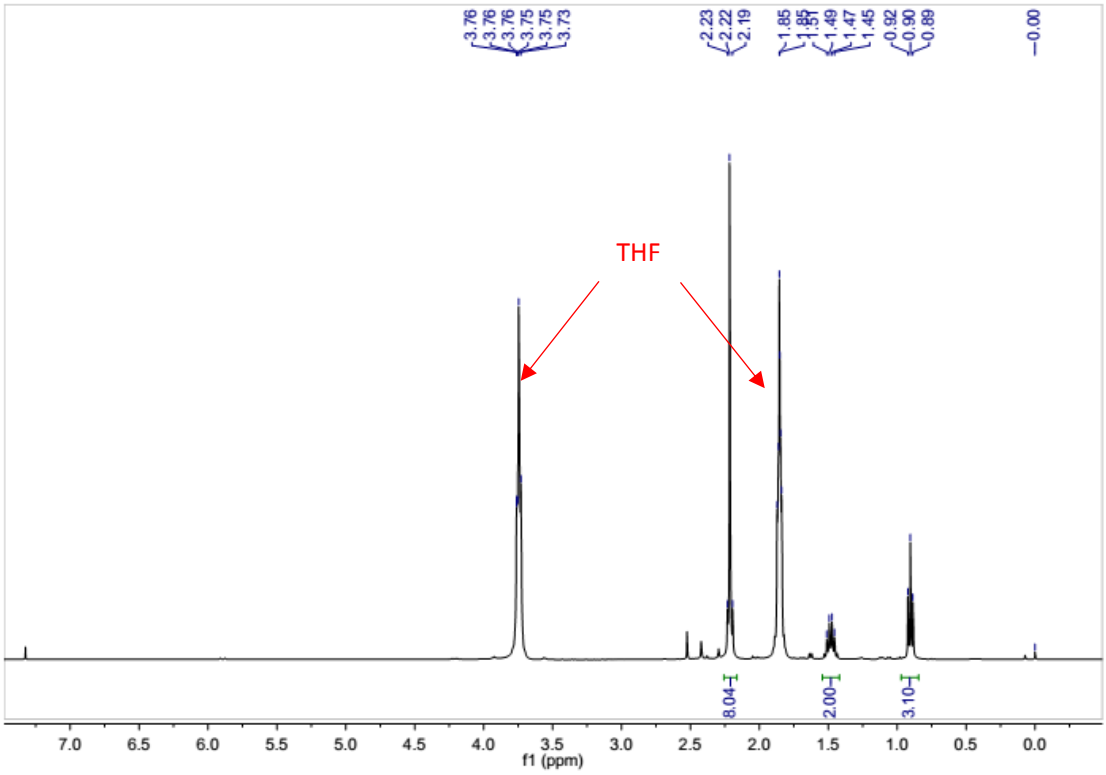


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.448	BB	0.0458	4038.39990	1316.28149	1.000e2

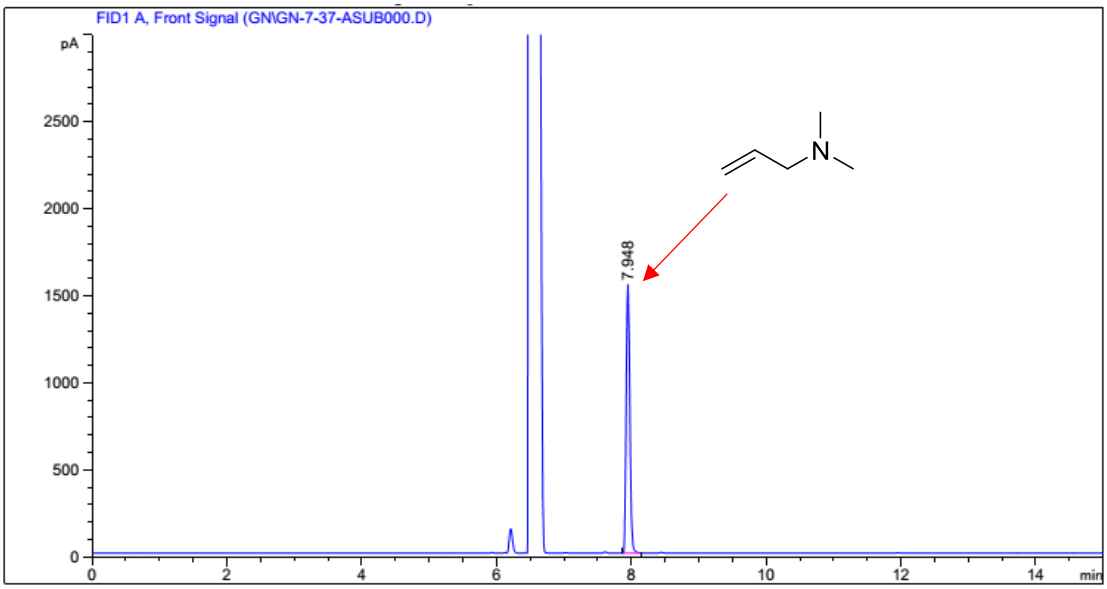
***N*,*N*-dimethyl-*n*-propylamine (from *N*,*N*-dimethylallylamine)**

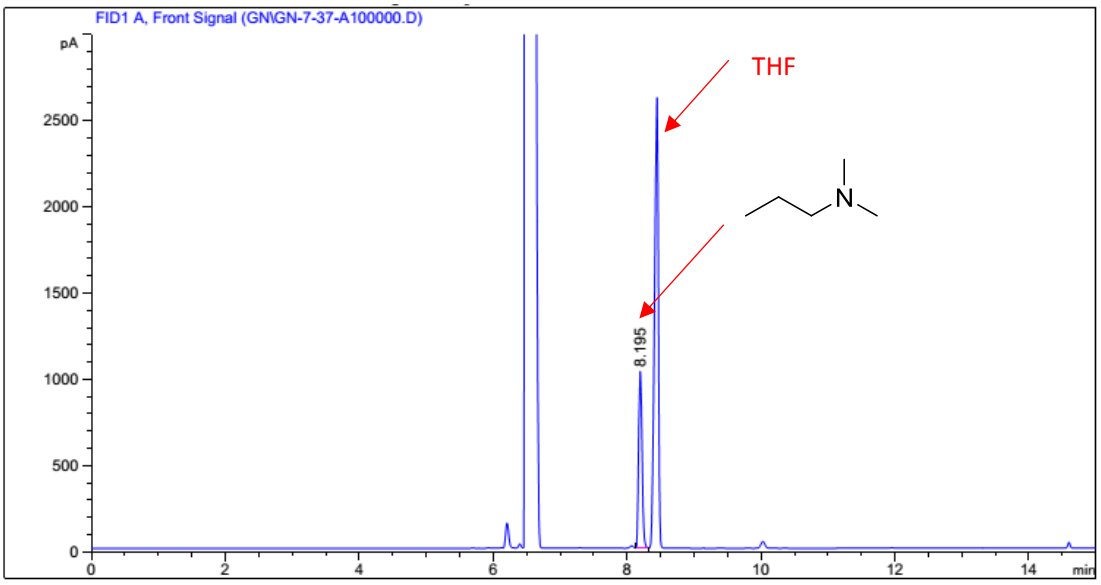


Reaction conditions: general procedure, $FeCl_2$-L8 (0.005 mmol), $LiAlH_4$ (0.025 mmol), *N*,*N*-dimethylallylamine (5 mmol), 1 mL THF, 30 atm H_2, rt, 6 h, 100% conversion to *N*,*N*-dimethyl-*n*-propylamine. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 8.0 Hz, 3H; CH_3), 1.42-1.54 (m, 2H; CH_2), 2.19-2.23 (m, 8H; CH_3 + CH_2).



GC conditions: interCap-1 column, injector temp. 230 ℃, detector temp. 250 ℃, 50 ℃ holds for 10 min, ramps 10 ℃/min to 300 ℃, N_2 fluency 1.0 mL/min. *t* = 7.948 min for *N*,*N*-dimethylallylamine and *t* = 8.195 min for *N*,*N*-dimethyl-*n*-propylamine.





Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.195	VV	0.0580	3686.62842	1025.18494	1.000e2

5. References:

1 B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.

2 G. Ricci, D. Morganti, A. Sommazzi, R. Santi and F. Masi, *J. Mol. Catal. A: Chem.*, 2003, **204–205**, 287.

3 (a) V. C. Gibson, R. K. O'Reilly, D. F. Wass, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2003, 2824; (b) J. Y. Wu, B. Moreau and T. Ritter, *J. Am. Chem. Soc.*, 2009, **131**, 12915.

4 J. Zhang, M. Gandelman, D. Herrman, G. Leitus, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Inorg. Chim. Acta*, 2006, **359**, 1955.

5 (a) L. Zhang, D. Peng, X. Leng and Z. Huang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3676; (b) T. Zell, R. Langer, M. A. Iron, L. Konstantinovski, L. J. W. Shimon, Y. Diskin-Posner, G. Leitus, E. Balaraman, Y. Ben-David and D. Milstein, *Inorg. Chem.*, 2013, **52**, 9636.

6 D. J. Evans, P. B. Hitchcock, G. J. Leigh, B. K. Nicholson, A. C. Niedwieski, F. S. Nunes and J. F. Soares, *Inorg. Chim. Acta*, 2001, **319**, 147.