Supporting Information

Iron-Catalysed, Hydrogen-Mediated, Alkene Hydrogenation and Reductive Cross-Coupling

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General

All air and moisture sensitive manipulations were carried out using standard vacuum line and Schlenk techniques or a glovebox under argon atmosphere. Solvents were obtained from an Anhydrous Engineering Solvent Purification System. All glassware was cleaned using base (KOH, *i*PrOH) then acid (HCl, H_2O) baths.

^{1}H NMR spectra were recorded on Joel Lambda 300 MHz, Jeol Eclipse 400 MHz or Varian VNMR 400MHz spectrometers. All spectra were obtained at ambient temperature unless stated otherwise. ^{13}C NMR spectra were recorded on the same spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are reported in $CDCl_3$ unless otherwise stated. The chemical shifts δ are given in parts per million (ppm) and the coupling constants J in Hertz (Hz).

Gas chromatography was performed on an Agilent HP6890 gas chromatograph equipped with an Agilent J&W DB-5ms capillary column (15 m × 0.25 mm × 0.25 μm) and an Agilent 5973 mass selective detector.

[70-1]: Injector temp. 250 °C, 70 °C for 3 min, ramps 25 °C/min to 200 °C, ramps 45 °C/min to 250 °C, holds for 3 min, ramps 45 °C/min to 300 °C, holds for 3 min.

[50-1]: Injector temp. 200 °C, 50 °C for 3 min, ramps 5 °C/min to 150 °C, ramps 45 °C/min to 250 °C, holds for 3 min, ramps 45 °C/min to 300 °C, holds for 3 min.

[35-AJP]: Injector temp. 250 °C, 35 °C for 3 min, 45 °C/min to 250 °C, hold for 3 min, 45 °C/min to 300 °C, hold for 3 min.

[60-1]: Injector temp. 250 °C, 60 °C for 1.5 min, 60 °C/min to 300 °C, hold for 3 min.

Hydrogenation

General Procedure Hydrogenation

An autoclave, fitted with a stirrer bar, was charged with iron(II) chloride (3.0 mol%), (±)-[*N*,*N*'-Bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine], (±)-**3**, (3.2 mol%), anhydrous THF (5 mL/ mmol) and alkene (1.0 eq.) under a flow of nitrogen. The autoclave was cooled in an acetone/dry ice bath at –20 °C for 10 min and *i*PrMgCl (15 mol%) was added slowly. The autoclave was then pressurised to 50 bar H_2 and allowed to stir for 1-16 h while warming to rt. The pressure was released slowly and the reaction mixture was quenched with aq. HCl (1 M, 7 mL/ 2 mmol). The aqueous phase was extracted with Et_2O (3 × 20 mL), the combined organic phases were washed with brine (15 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the reaction products which were analysed by ^{1}H NMR and GC-MS or ^{13}C NMR where possible.

Table 2, entry 1: Ethylbenzene (from Styrene)

According to general hydrogenation procedure styrene (0.23 mL, 2.0 mmol) was reduced to give ethylbenzene as colourless volalile liquid in quantitative conversion.

GC-MS [35-AJP] (M^+, relative abundance): 3.24 min (106, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.27-7.32 (m, 2H), 7.23-7.20 (m, 2H), 7.19 (s, 1H), 2.66 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 144.2, 128.3, 127.8, 125.6, 28.9, 15.6 ppm.
Spectroscopic data were consistent with those reported in the literature[1]

Table 2, entry 2: 1-Ethyl-2-methylbenzene (from 2-Methylstyrene)

According to general hydrogenation procedure 2-methylstyrene (0.26 mL, 2.0 mmol) was reduced to give 1-ethyl-2-methylbenzene as an oil (219 mg, 91%).

GC-MS [35-AJP] (M^+, relative abundance): 5.16 min (120, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.21-7.07 (m, 4H), 2.64 (q, J = 7.6 Hz, 2H), 2.32 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.4, 135.7, 130.0, 127.8, 126.0, 125.7, 26.1, 19.1, 14.3 ppm.
Spectroscopic data were consistent with those reported in the literature[2]

Table 2, entry 3: 1-Ethyl-3-methylbenzene (from 1-Methyl-3-vinylbenzene)

According to general hydrogenation procedure 1-methyl-3-vinylbenzene (0.24 mL, 2.0 mmol) was reduced to give 1-ethyl-3-methylbenzene as colourless liquid (220 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, J = 7.5 Hz, 1H), 7.05-7.00 (m, 3H), 2.64 (q, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 144.3, 138.0, 128.8, 128.4, 126.5, 125.0, 29.0, 21.6, 15.8 ppm.
Spectroscopic data were consistent with those reported in the literature[2]

Table 2, entry 4: 1-(*tert*-Butyl)-4-ethylbenzene (from 1-(*tert*-Butyl)-4-vinylbenzene)

According to general hydrogenation procedure 1-(*tert*-butyl)-4-vinylbenzene (0.73 mL, 4.0 mmol) was reduced to give 1-(*tert*-butyl)-4-ethylbenzene as colourless liquid (630 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 2H), 7.19-7.14 (m, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.33 (s, 9H), 1.26 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.3, 141.1, 127.5, 125.2, 34.3, 31.4, 28.3, 15.5 ppm.
Spectroscopic data were consistent with those reported in the literature[3]

Table 2, entry 5: 2-Ethyl-1,3,5-trimethylbenzene (from 1,3,5-Trimethyl-2-vinylbenzene)
According to general hydrogenation procedure 1,3,5-trimethyl-2-vinylbenzene (0.32 mL, 2.0 mmol) was reduced to give 2-ethyl-1,3,5-trimethylbenzene as colourless liquid (293 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (s, 2H), 2.66 (q, 2H, J = 7.6 Hz), 2.33 (s, 6H), 2.29 (s, 3H), 1.15-1.13 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 138.0, 135.8, 134.9, 129.0, 22.4, 20.9, 19.6, 13.6 ppm.
Spectroscopic data were consistent with those reported in the literature[4]

Table 2, entry 6: Butylbenzene (from 4-Phenyl-1-butene)
According to general hydrogenation procedure 4-phenyl-1-butene (0.30 mL, 2.0 mmol) was reduced to give butylbenzene as colourless liquid in quantitative conversion.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.17 (m, 5H), 2.66-2.58 (m, 2H), 1.65-1.58 (m, 2H), 1.41-1.35 (m, 2H), 0.97-0.91 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.9, 128.4, 128.2, 125.5, 35.7, 33.7, 22.4, 13.9 ppm.
Spectroscopic data were consistent with those reported in the literature[5]

Table 2, entry 7: Ethylcyclohexane (from Vinylcyclohexane)
According to general hydrogenation procedure vinylcyclohexane (0.27 mL, 2.0 mmol) was reduced to give ethylcyclohexane as volatile liquid in 90% conversion.

GC-MS [35-AJP] (M^+, relative abundance): 4.70 min (112, 95%), 4.96 min (110, 5%). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 39.5, 33.0, 30.7, 26.4, 25.6, 11.4 ppm.
Spectroscopic data were consistent with those reported in the literature[6]

Table 2, entry 8: Propylbenzene (from *β*-Methylstyrene)
According to general hydrogenation procedure *β*-methylstyrene (0.26 mL, 2.0 mmol) was reduced to give propylbenzene as colourless liquid (177 mg, 75%).

GC-MS [50-1] (M^+, relative abundance): 4.20 min (120, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.29-7.17 (m, 5H), 2.64-2.59 (m, 2H), 1.73-1.62 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.8, 128.7, 128.3, 125.7, 38.2, 24.7, 14.0 ppm.
Spectroscopic data were consistent with those reported in the literature[7]

Table 2, entry 9: Bibenzyl (from *trans*-Stilbene)
According to general hydrogenation procedure *trans*-stilbene (360 mg, 2.0 mmol) was reduced to give bibenzyl as colourless solid (349 mg, 96%).

GC-MS [70-1] (M^+, relative abundance): 6.92 min (182, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.29-7.17 (m, 10H), 2.94 (s, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.3, 125.9, 37.9 ppm.
Spectroscopic data were consistent with those reported in the literature[8]

Table 2, entry 10: Bibenzyl (from *cis*-Stilbene)
According to general hydrogenation procedure *cis*-stilbene (360 mg, 2.0 mmol) was reduced to give bibenzyl as colourless solid (351 mg, 96%).

GC-MS [70-1] (M^+, relative abundance): 6.93 min (182, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.25-7.13 (m, 10H), 2.85 (s, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.3, 125.9, 37.9 ppm.
Spectroscopic data were consistent with those reported in the literature[8]

Table 2, entry 11: *iso*-Propylbenzene (from *α*-Methylstyrene)
According to general hydrogenation procedure *α*-methylstyrene (0.26 mL, 2.0 mmol) was reduced to give *iso*-propylbenzene as colourless volatile liquid in quantitative conversion.

GC-MS [35-AJP] (M^+, relative abundance): 3.90 min (120, 100%). **^{1}H NMR** (400MHz, $CDCl_3$) δ = 7.33-7.21 (m, 5H), 2.94 (sept, J = 6.9 Hz, 1H), 1.28 (d, J = 7.0 Hz, 6H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.8, 128.3, 128.4, 125.8, 34.1, 24.0 ppm.
Spectroscopic data were consistent with those reported in the literature[9]

Table 2, entry 12: 1-Chloro-2-ethylbenzene (from 2-Chlorostyrene)
According to general hydrogenation procedure 2-chlorostyrene (0.25 mL, 2.0 mmol) was reduced to give 1-chloro-2-ethylbenzene as oil (137 mg, 50%).

GC-MS [35-AJP] (M^+, relative abundance): 4.71 min (140, 84%), 11.91 min (275, 16%). **^{1}H NMR** (400 MHz $CDCl_3$): δ = 7.35 (dd, J = 7.7 Hz, J = 1.4 Hz, 1H), 7.18-7.13 (m, 1H), 7.35 (td, J = 7.4 Hz, J = 1.4 Hz, 1H), 7.08-7.03 (m, 1H), 2.76 (q, J = 7.5 Hz, 2H), 0.08 (t, J = 7.5 Hz, 3H) ppm.
Spectroscopic data were consistent with those reported in the literature[10]

Table 2, entry 13: 1-Chloro-4-ethylbenzene (from 1-Chloro-4-ethylbenzene)
According to general hydrogenation procedure 4-chlorostyrene (0.24 mL, 2.0 mmol) was reduced to give 1-chloro-4-ethylbenzene (233 mg, 83%).

GC-MS [35-AJP] (M^+, relative abundance): 5.99 min (140, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.25 (m, 2H), 7.17-7.13 (m, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 142.8, 131.4, 129.3, 128.5, 28.4, 15.7 ppm.

Spectroscopic data were consistent with those reported in the literature[10]

Table 2, entry 14: 1-Fluoro-4-ethylbenzene (from 1-Fluoro-4-ethylbenzene)
According to general hydrogenation procedure 4-fluorostyrene (0.24 mL, 2.0 mmol) was reduced to give 1-fluoro-4-ethylbenzene (214 mg, 87%).

GC-MS [35-AJP] (M^+, relative abundance): 3.52 min (124, 100%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.18-7.12 (m, 2H), 7.01-6.93 (m, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.26-1.20 (m, 3H) ppm.
Spectroscopic data were consistent with those reported in the literature[11]

Table 2, entry 15: 4-Ethylanisole (from 4-Methoxystyrene)
According to general hydrogenation procedure 4-methoxystyrene (0.26 mL, 2.0 mmol) was reduced to give 4-ethylanisole as colourless oil (199 mg, 74%).

GC-MS [70-1] (M^+, relative abundance): 4.05 min (136, 100%). **^{1}H NMR** (400 MHz $CDCl_3$): δ = 7.07-7.03 (m, 2H), 6.78-6.74 (m, 2H), 3.79 (s, 3H), 2.61 (d, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 157.6, 136.4, 128.7, 113.7, 55.3, 27.9, 15.9 ppm.
Spectroscopic data were consistent with those reported in the literature[12]

Table 2, entry 17: *tert*-Butyl(hexyloxy)dimethylsilane (from *tert*-Butyl(hex-5-en-1-yloxy)dimethylsilane)
According to general hydrogenation procedure *tert*-butyl(hex-5-en-1-yloxy)dimethylsilane (214 mg, 1.0 mmol) was reduced to give *tert*-butyl(hexyloxy)dimethylsilane as colourless oil (201 mg, 93%; 2% isomerisation).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (t, J = 6.6 Hz, 2H), 1.54-1.35 (m, 2H), 1.26-1.23 (m, 5H), 0.90-0.88 (m, 13H), 0.05 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 63.5, 33.0, 31.8, 26.1, 25.6, 22.8, 18.5, 14.2, –5.1 ppm.
Spectroscopic data were consistent with those reported in the literature[13]

Table 2, entry 18: 1-(Benzyloxy)-3-methylbenzene (from 1-(Benzyloxy)-3-vinylbenzene)
According to general hydrogenation procedure 1-(benzyloxy)-3-vinylbenzene (210 mg, 1.0 mmol) was reduced to give 1-(benzyloxy)-3-methylbenzene as colourless oil (212 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.43 (m, 2H), 7.42-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.88-6.80 (m, 3H), 5.07 (s, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 159.1, 146.1, 137.3, 129.4, 128.7, 128.0, 127.7, 120.7, 114.8, 111.8, 70.0, 29.1, 15.6 ppm.
Spectroscopic data were consistent with those reported in the literature[14]

Table 2, entry 19: Methyl 4-ethylbenzoate (from Methyl 4-vinylbenzoate)

According to general hydrogenation procedure methyl 4-vinylbenzoate (162 mg, 1.0 mmol) was reduced using 6 mol% iron ligand to give methyl 4-ethylbenzoate as yellowish oil (162 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 3.92 (s, 3H), 2.72 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.3, 149.9, 129.8, 128.0, 127.8, 52.1, 29.1, 15.3 ppm.
Spectroscopic data were consistent with those reported in the literature[16]

Reductive Cross-Coupling

General Procedure A: Reductive Cross-Coupling
An autoclave was charged with [Cl_2Fe(±)-**3**] (3.5 mol%), anhydrous THF (9 mL/ mmol) and vinyl bromide (1.0 eq.) under a flow of hydrogen or nitrogen. The autoclave was cooled to –20 ºC for 5 min and the Grignard reagent (1.5 eq.) was added slowly. The autoclave was pressurised to 50 bar. Unless otherwise stated the mixture was stirred for 18 h allowing it to warm to room temperature. The pressure was slowly released from the autoclave and the reaction mixture was quenched with aq. HCl (1 M, 7 mL/ mmol). The aqueous phase was extracted with Et_2O (3 × 20 mL), the combined organic phases were washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude reaction product.

General Procedure B: Reductive Cross-Coupling
A multi-cell autoclave was charged with [Cl_2Fe(±)-**3**] (3.5 mol%), anhydrous THF (8 mL/ mmol) and vinyl bromide (1.0 eq.) under a flow of hydrogen. The autoclave was cooled to –20 ºC for 5 min and the Grignard reagent (1.5 eq.) was added slowly. The autoclave was pressurised to 47 bar and recharged with H_2 every 30 min. The reaction was run for 7 h with repressurising the autoclave every 30 min. The pressure was slowly released from the autoclave and the reaction mixture quenched with aq. HCl (1 M, 7 mL/ mmol). The aqueous phase was extracted with Et_2O (3 × 10 mL), the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude reaction product.

Table 3, entry 1: Butylbenzene (from *β*-Bromostyrene)
According to general procedure A, a solution of EtMgCl in THF (2 M, 1.60 mL, 3.2 mmol, 1.5 eq.) was added to a solution of *β*-bromostyrene (400 mg, 2.18 mmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (32.0 mg, 76 µmol, 3.5 mol%) in THF (20 mL) at –20 °C to give butylbenzene as a slightly yellow (290 mg, 99%).
Spectroscopical data for butylbenzene is given in the hydrogenation section[5]

Table 3, entry 2: Isopentylbenzene
According to general procedure A, a solution of *i*PrMgCl in THF (2M, 1.60 mL, 3.2 mmol, 1.5 eq.) was added to a solution of *β*-bromostyrene (400 mg, 2.2 mmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (32.0 mg, 76 µmol, 3.5 mol%) in THF (20 mL) at –20 °C to give the crude product (350 mg) as a mixture of *iso*-pentylbenzene (84%), 1,4-diphenylbuta-1,3-diene (5%) and 1,4-diphenylbutane (11%).

Data for *iso*-pentylbenzene
LRMS: 148 (M^+) Calcld. 148.13. **^{1}H NMR** (301 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2H), 7.23-7.15 (m, 3H), 2.65-2.60 (m, 2H), 1.64-1.48 (m, 3H), 0.95 (d, J = 6.4 Hz, 6H) ppm. **^{13}C NMR** (76 MHz, $CDCl_3$): δ = 143.1, 128.3, 128.2, 125.5, 40.9, 33.8, 27.7, 22.5 ppm.
Spectroscopic data were consistent with those reported in the literature[16]

Table 3, entry 3: 1,4-Diphenylbutane
According to general procedure B, a solution of PhEtMgCl in THF (1 M, 1.10 mL, 1.1 mmol, 1.4 eq.) was added to a solution of β-bromostyrene (143 mg, 779 µmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (11.4 mg, 27 µmol, 3.5 mol%) in THF (6 mL) at –20 °C to give the crude product as a mixture of 1,4-diphenylbutane (79%) and 1,4-diphenylbutene (21%).

Data for 1,4-diphenylbutane
LRMS: 210 (M^+) Calcd. 210.14. **^{1}H NMR** (301 MHz, $CDCl_3$): δ = 7.37-7.14 (m, 10H), 2.65 (t, J = 7.1 Hz, 4H), 1.68 (dt, J = 7.2, 3.8 Hz, 4H) ppm. **^{13}C NMR** (76 MHz, $CDCl_3$): δ = 142.5, 128.4, 128.2, 125.6, 35.8, 31.1 ppm.
Spectroscopic data were consistent with those reported in the literature[17]

Table 3, entry 4: 1,2-Diphenylethane
According to general procedure A, a solution of PhMgCl in THF (2 M, 1.60 mL, 3.2 mmol, 1.5 eq.) was added to a solution of β-bromostyrene (400 mg, 2.2 mmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (32.0 mg, 76 µmol, 3.5 mol%) in THF (20 mL) at –20 °C to give the crude product (390 mg) as a slightly yellow solid which consisted of 1,2-diphenylethane (78%), stilbene (7%) and biphenyl (15%).
Spectroscopical data for 1,2-diphenylethane is given in the hydrogenation section[8]

Table 3, entry 5: (3,3-Dimethyl)butylbenzene
According to general procedure A, a solution of *t*BuMgCl in THF (1 M, 3.20 mL, 3.2 mmol, 1.5 eq.) was added to a solution of β-bromostyrene (400 mg, 2.2 mmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (32.0 mg, 76 µmol, 3.5 mol%) in THF (20 mL) at –20 °C to give the crude product (260 mg) as a slightly yellow oil as a mixture of (3,3-dimethyl)butylbenzene (18%), (3,3-dimethylbut-1-en-1-yl)benzene (32%) and 1,4-diphenylbutane (50%).

Data for (3,3-dimethyl)butylbenzene
LRMS: 162 (M^+) Calcd. 162.14. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.37 (m, 5H), 2.62-2.56 (m, 2H), 1.55-1.49 (m, 2H), 0.98 (s, 9H) ppm.
Spectroscopic data were consistent with those reported in the literature[18]

Table 3, entry 6: Pentylbenzene
According to general procedure A, a solution of AllylMgCl in THF (2 M, 1.60 mL, 3.2 mmol, 1.5 eq.) was added to a solution of β-bromostyrene (400 mg, 2.2 mmol, 1.0 eq.) and

[Cl_2Fe(±)-**3**] (32.0 mg, 76 μmol, 3.5 mol%) in THF (20 mL) at –20 °C to give the crude product (260 mg) as a slightly yellow solid as a mixture of pentylbenzene (43%), pent-1-en-1-ylbenzene (19%) and small amounts of several side products.

LRMS: 148 (M^+) Calcd. 148.13. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.33-7.20 (m, 5H), 2.68-2.60 (m, 2H), 2.72-2.58 (m, 2H), 1.40-1.33 (m, 4H), 0.95-0.91 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.1, 128.5, 128.3, 125.7, 36.1, 31.7, 31.4, 22.7, 14.2 ppm.
Spectroscopic data were consistent with those reported in the literature[19]

Table 3, entry 7: Propylbenzene
According to general procedure B, a solution of MeMgCl in THF (3 M, 370 μL, 1.1 mmol, 1.4 eq.) was added to a solution of *β*-bromostyrene (143 mg, 779 μmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (11.4 mg, 27 μmol, 3.5 mol%) in THF (6 mL) at –20 °C to give the crude product (66 mg) as a colorless liquid as a mixture of propylbenzene (40%) and *β*-methylstyrene (60%).
Spectroscopical data for propylbenzene is given in the hydrogenation section[7]

Table 3, entry 8: Butylbenzene (from *β*-Chlorostyrene)
According to general procedure A, a solution of EtMgCl in THF (2 M, 1.60 mL, 3.2 mmol, 1.5 eq.) was added to a solution of *β*-chlorostyrene (151 mg, 1.1 mmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (16.0 mg, 38 μmol, 3.5 mol%) in THF (10 mL) at –20 °C to give the crude product as a (134 mg) slightly yellow liquid which consisted of butylbenzene (94%) and 1,4-diphenylbutene (6%).
Spectroscopical data for butylbenzene is given in the hydrogenation section.[5]

Table 3, entry 9: (*E*)-But-1-en-1-ylbenzene (from *β*-Iodorostyrene)
According to general procedure A, a solution of EtMgCl in THF (2 M, 410 μL, 820 μmol, 1.5 eq.) was added to a solution of *β*-iodostyrene (125 mg, 548 μmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (8.0 mg, 19 μmol, 3.5 mol%) in THF (5 mL) at –20 °C to give the crude product (156 mg) as a slightly yellow liquid of but-1-en-1-ylbenzene.

^{1}H NMR (301 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.19 (m, 1H), 6.44-6.38 (m, 1H), 6.34-6.26 (m, 1H), 2.31-2.22 (m, 2H), 1.13 (t, J = 7.6, 3H) ppm.
Spectroscopic data were consistent with those reported in the literature[20]

Table 3, entry 10: (*E*)-But-1-en-1-ylbenzene (from (*E*)-Styryl trifluoromethanesulfonate)
According to general procedure A, a solution of EtMgCl in THF (2 M, 820 μL, 1.6 mmol, 3.0 eq.) was added to a solution of (*E*)-styryl trifluoromethanesulfonate (138 mg, 545 μmol, 1.0 eq.) and [Cl_2Fe(±)-**3**] (8.0 mg, 19 μmol, 3.5 mol%) in THF (5 mL) at –20 °C to give the crude product as a slightly yellow liquid as a mixture of (*E*)-and (*Z*)-but-1-en-1-ylbenzene ((4:1), 98%) and 1,4-diphenylbutene (2%).

Data for major (*E*)-but-1-en-1-ylbenzene

^{1}H NMR (301 MHz, $CDCl_3$): δ = 7.41-7.37 (m, 2H), 7.36-7.31 (m, 2H), 7.25-7.21 (m, 1H), 6.46-6.39 (m, 1H), 6.36-6.27 (m, 1H), 2.31-2.22 (m, 2H), 1.14 (t, J = 7.6, 3H) ppm. Spectroscopic data were consistent with those reported in the literature[20]

Table 3, entry 11: 1-Ethyl 4-methylbenzene (from vinylbromide and 4-tolylmagnesium bromide)

An autoclave was charged with $FeCl_2$ (4.4 mg, 35 μmol), ligand (±)-**3** (10.2 mg, 35 μmol) and anhydrous THF (5 mL). Toluylmagnesium bromide (1 M, 1.5 mL, 1.5 mmol) was added under a flow of nitrogen. The autoclave was cooled to –20 ºC for 5 min and vinyl bromide (1 M, 1.0 mL) was added under a flow of nitrogen. The autoclave was pressurised to 50 bar and the mixture was stirred for 18 h allowing it to warm to room temperature. The pressure was slowly released from the autoclave and the reaction mixture was quenched with aq. HCl (1 M, 7 mL). The aqueous phase was extracted with Et_2O (2 × 20 mL), the combined organic phases, dried over $MgSO_4$ and concentrated under reduced pressure to give 1-ethyl 4-methylbenzene (82 mg, 68%) as a colourless solid.

GC-MS [60-1] (M^+, relative abundance): 6.15 min (120, 100%).

ICP Analysis

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) of the reaction mixture: A standard reaction mixture ($FeCl_2$ (Strem Chemicals Inc. (UK); anhydrous iron chloride, 98% (product number 93-2631. Lot 19226800, 44.00000% Fe), tetradentate ligand **1**, *iso*-propylmagnesium bromide (2 M in Et_2O, Sigma Aldrich), THF) was evaporated to dryness, redissolved in 6 mL of HNO_3 and diluted by a factor of 50 with Milli-Q water. Analysis was conducted on a Thermo-Finnigan Neptune multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Bristol Neptune 1, Serial No. 1002), using an SLSRS5 standard for calibration. The abundance of each metal in the sample was recorded relative to the abundance of iron.

Table S1. ICP-MS Analysis on the abundance (ppm) of elements in reaction mixture, relative to Fe

Ti	Co	Ni	Cu	Zr	Ru	Rh	Pd	Ag	Ir	Pt	Au
140	390	50	420	130	10	20	380	200	30	5	>1

Table 2, entry 1: Ethylbenzene (from Styrene)

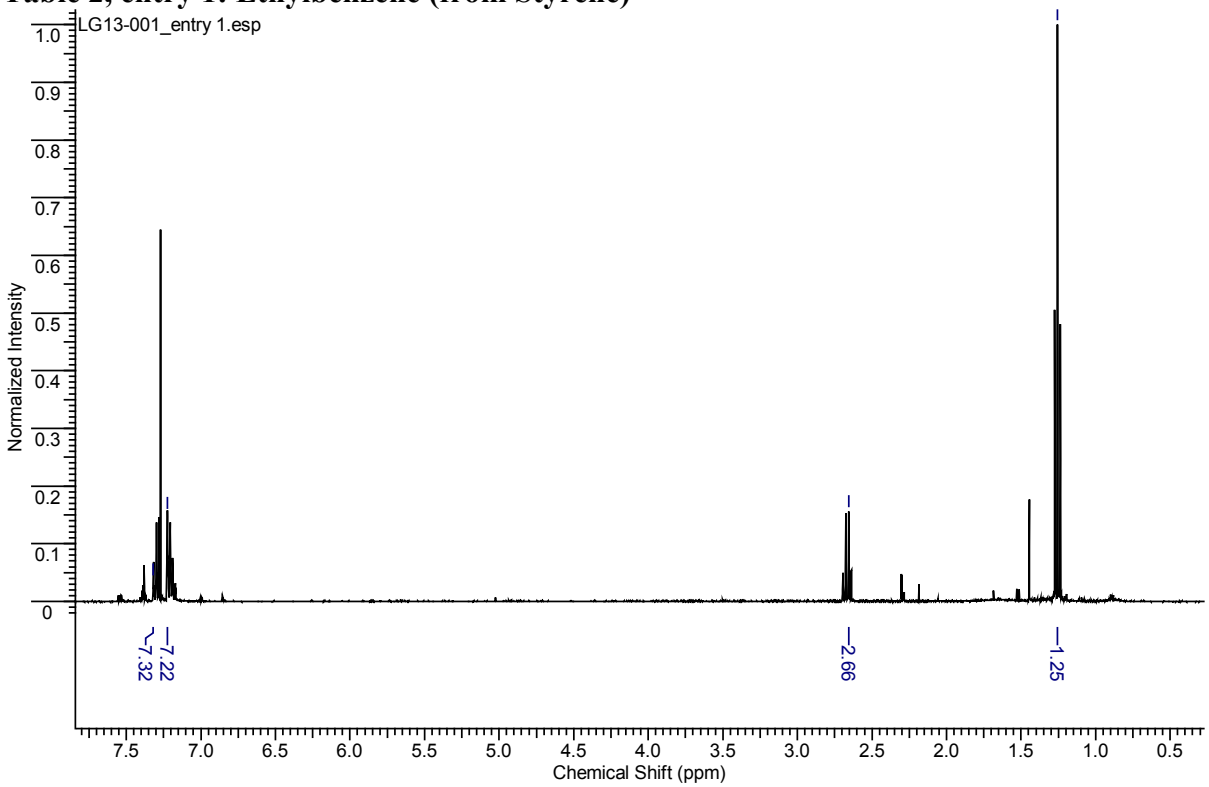


Table 2, entry 2: 1-Ethyl-2-methylbenzene (from 2-Methylstyrene)

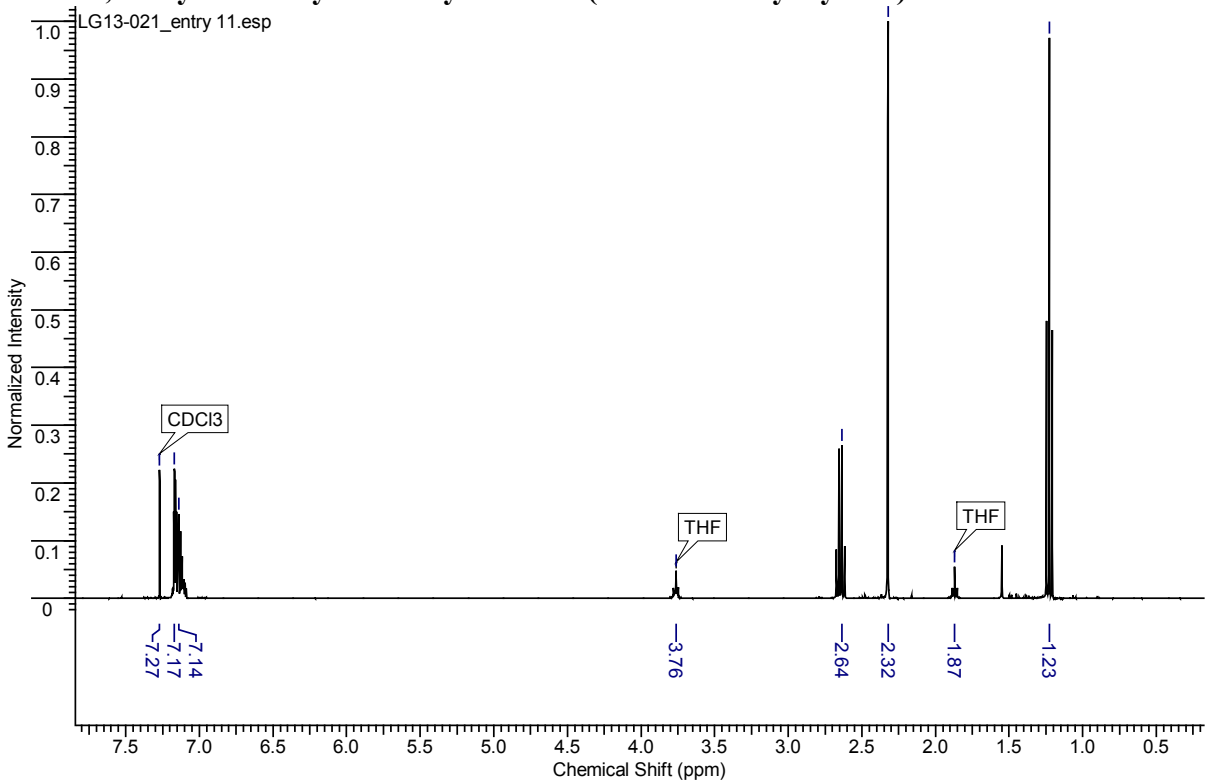


Table 2, entry 3: 1-Ethyl-3-methylbenzene (from 1-Methyl-3-vinylbenzene)

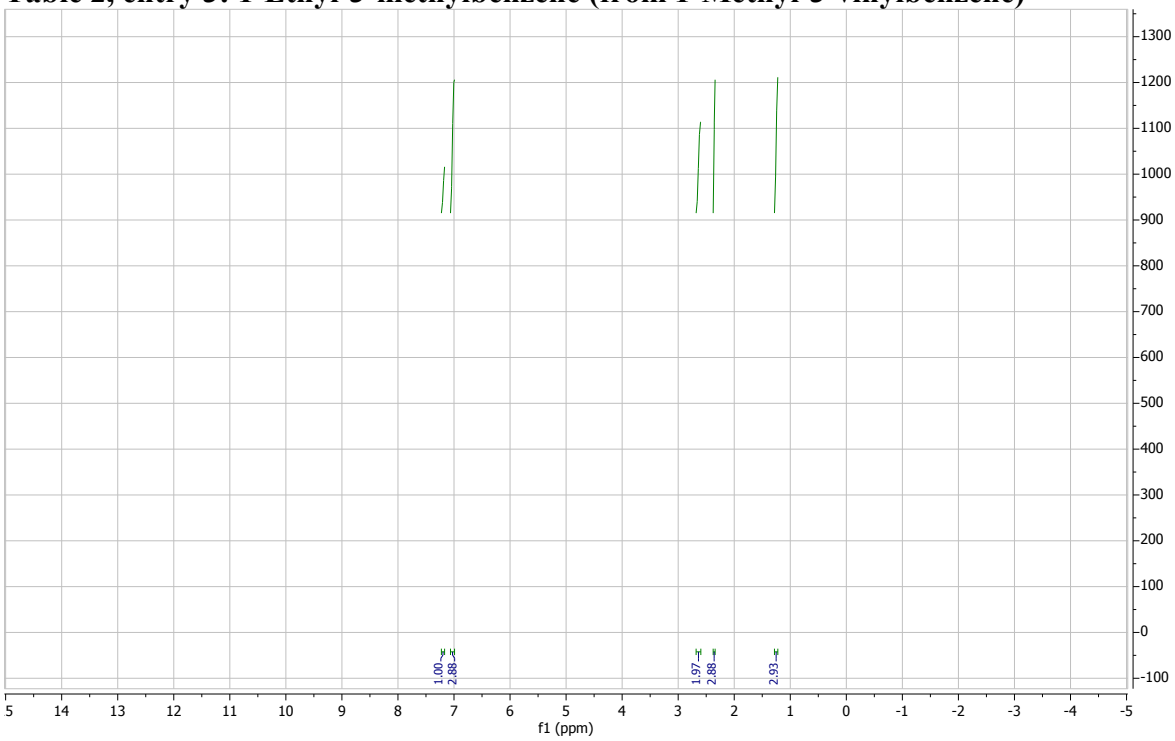


Table 2, entry 4: 1-(*tert*-Butyl)-4-ethylbenzene (from 1-(*tert*-Butyl)-4-vinylbenzene)

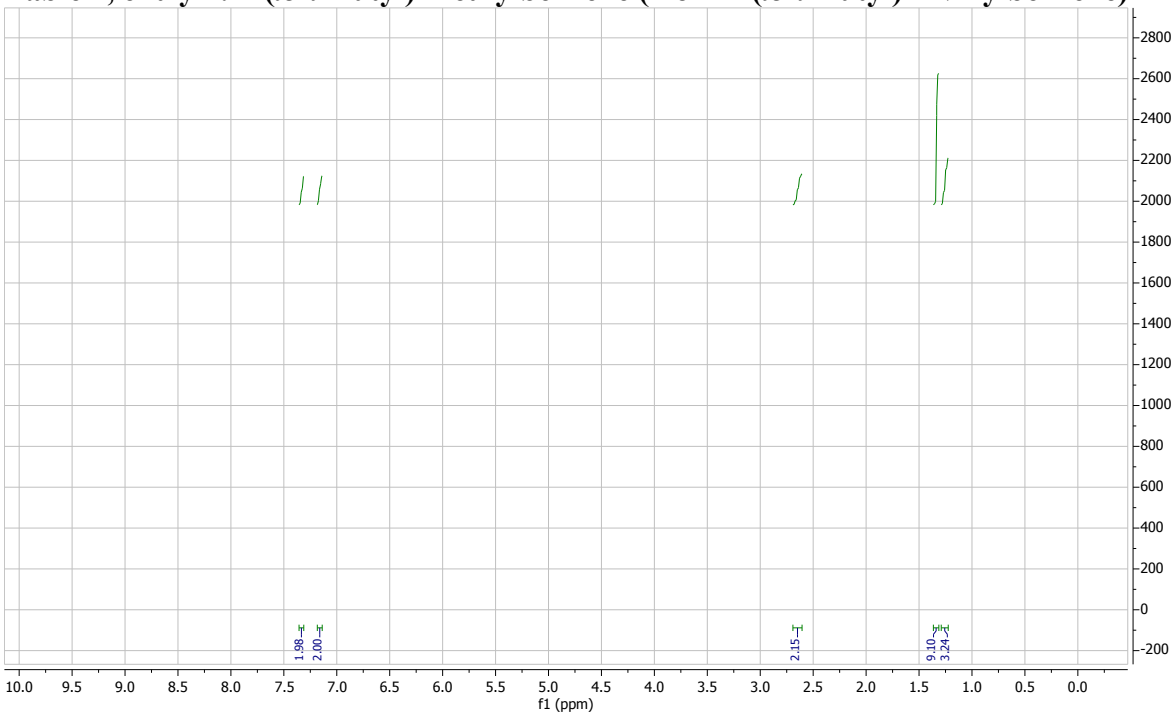


Table 2, entry 5: 2-Ethyl-1,3,5-trimethylbenzene (from 1,3,5-Trimethyl-2-vinylbenzene)

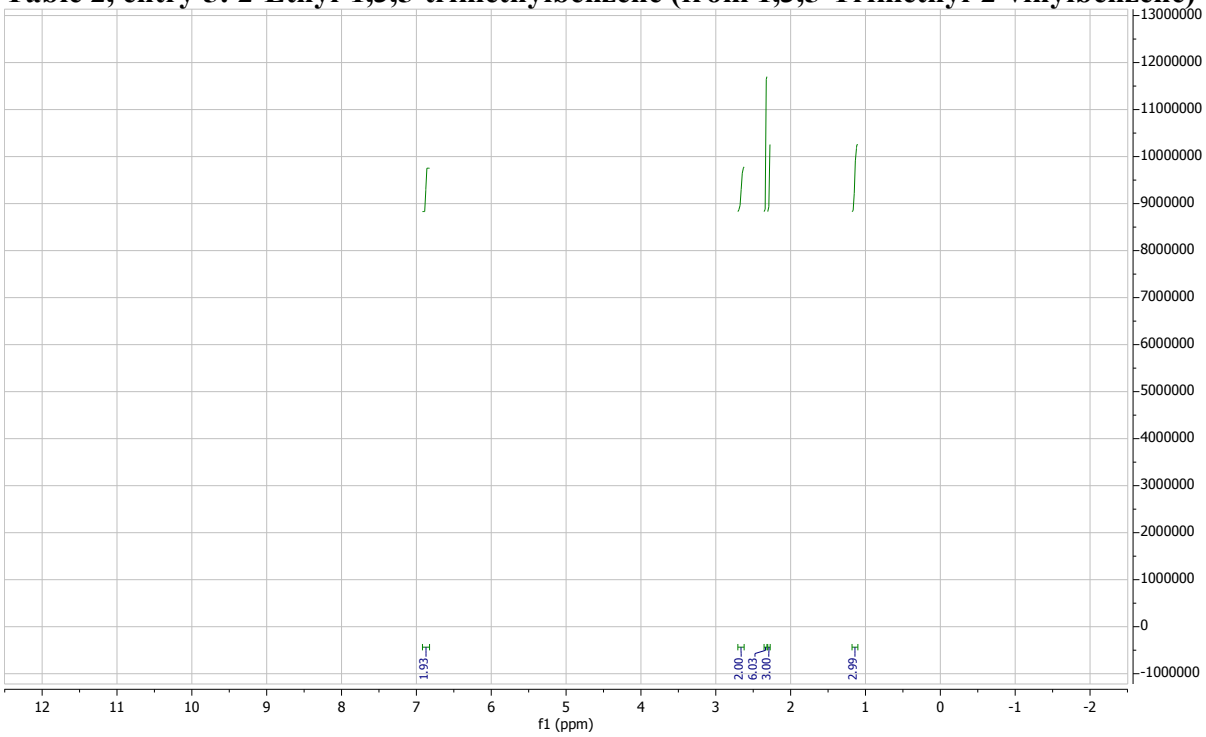


Table 2, entry 6: Butylbenzene (from 4-Phenyl-1-butene)

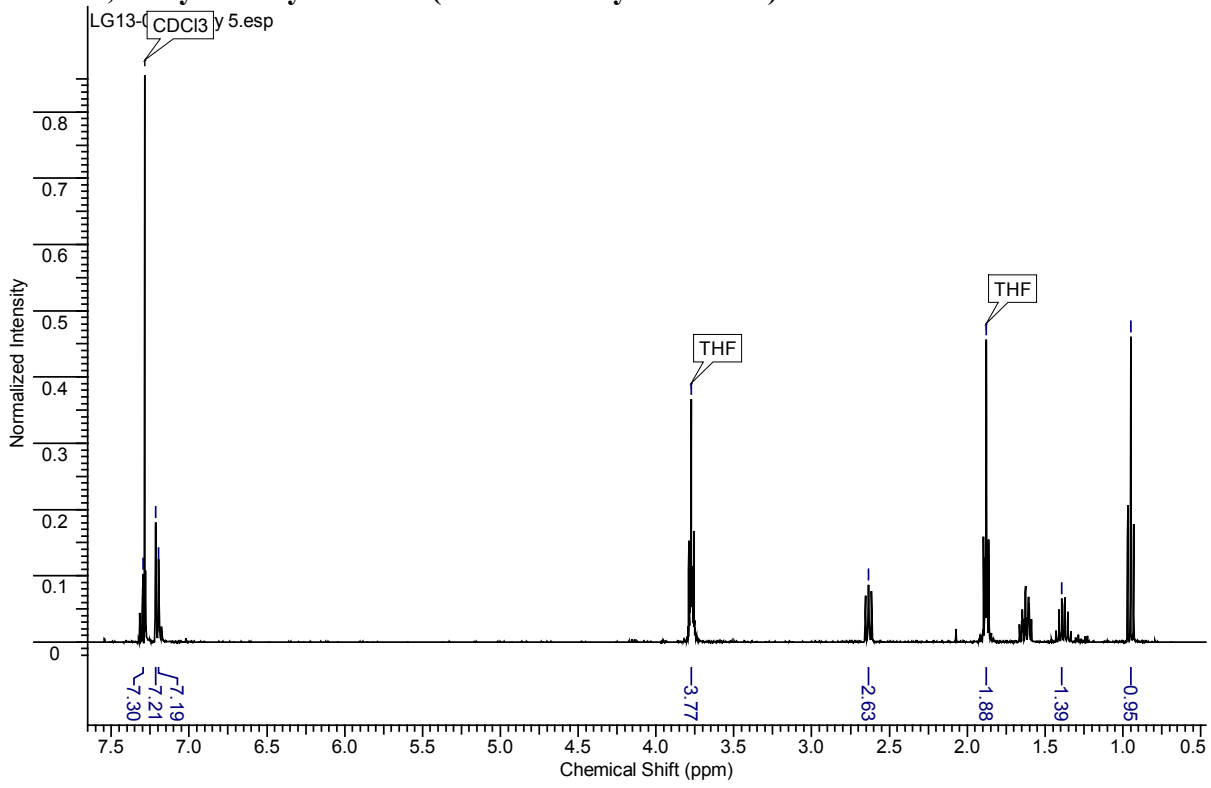


Table 2, entry 7: Ethylcyclohexane (from Vinylcyclohexane)

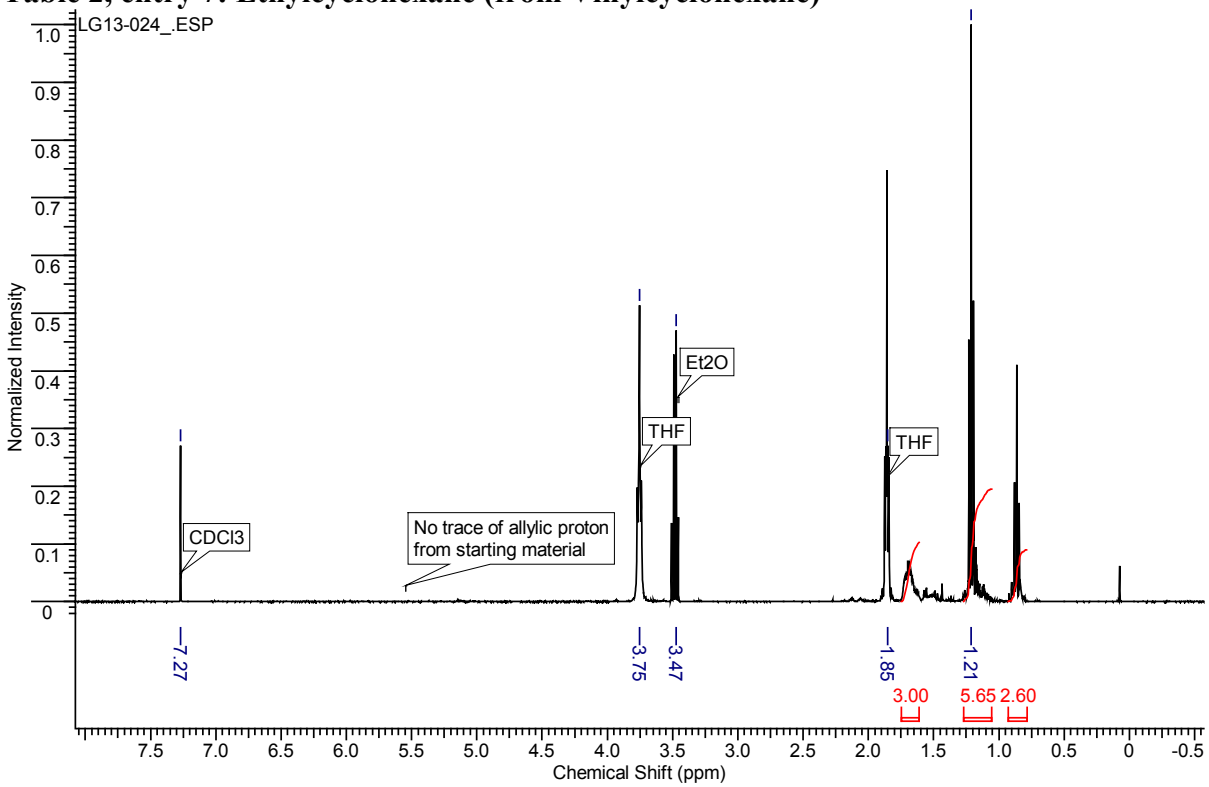


Table 2, entry 8: Propylbenzene (from *β*-Methylstyrene)

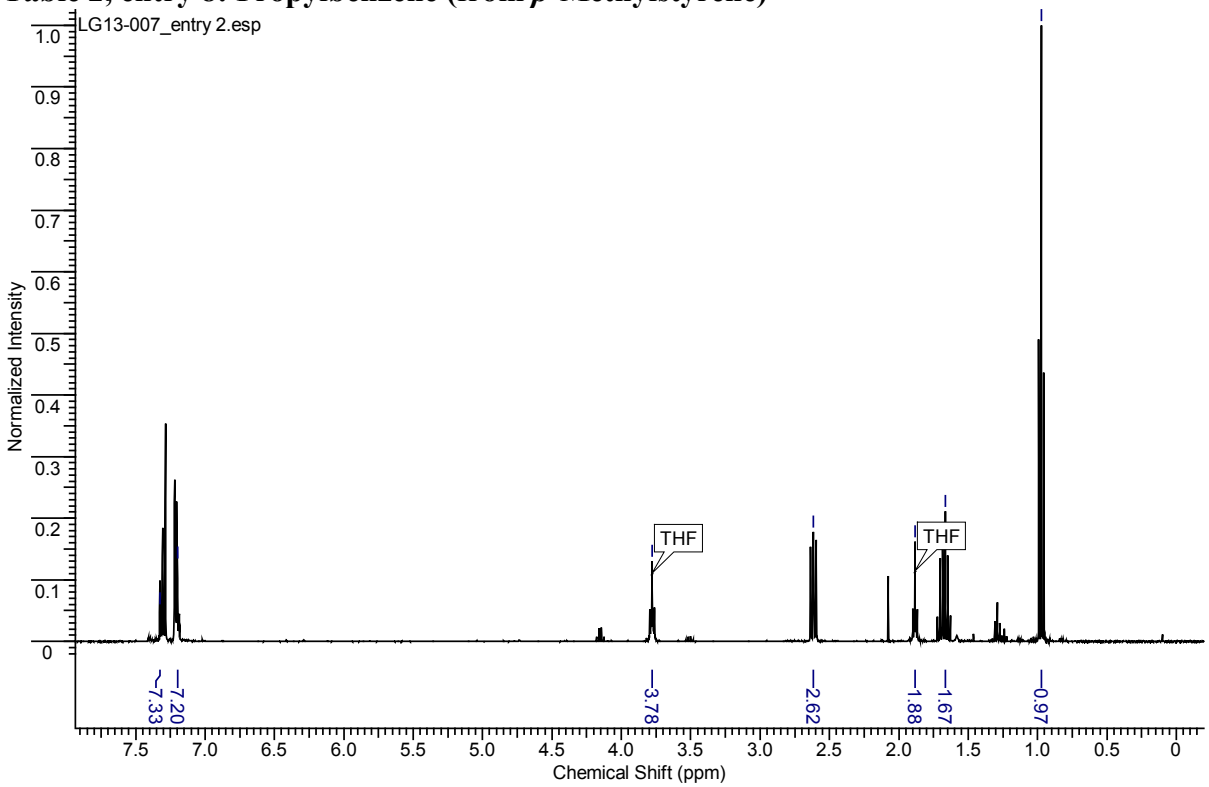


Table 2, entry 9: Bibenzyl (from *trans*-Stilbene)

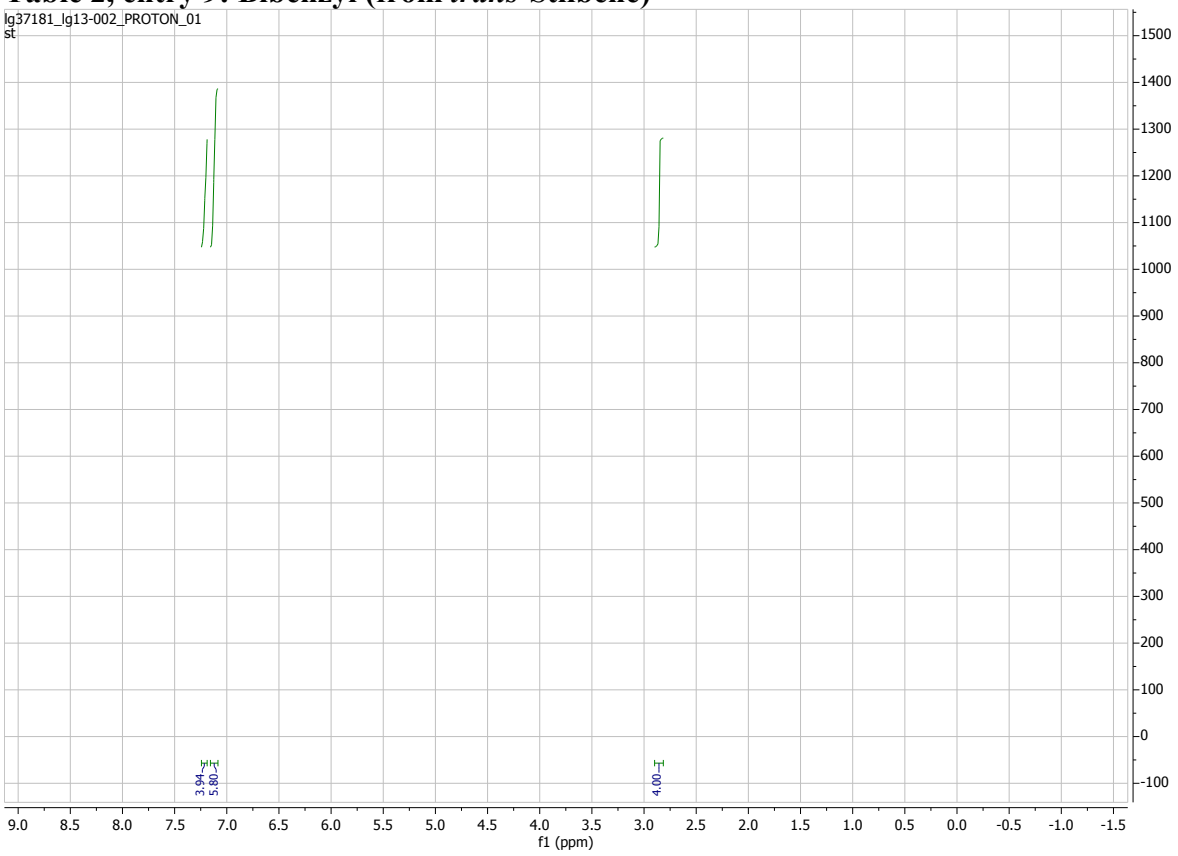


Table 2, entry 10: Bibenzyl (from *cis*-Stilbene)

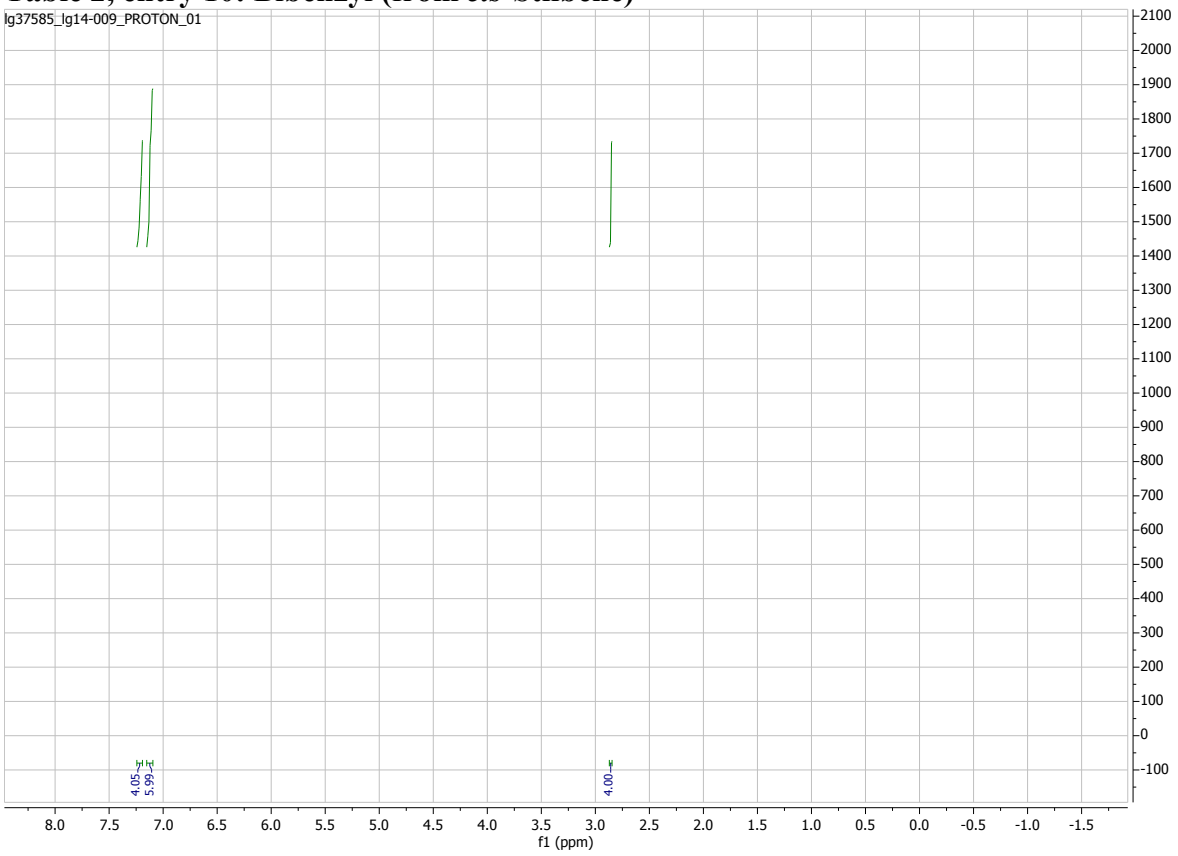


Table 2, entry 11: *iso*-Propylbenzene (from *α*-Methylstyrene)

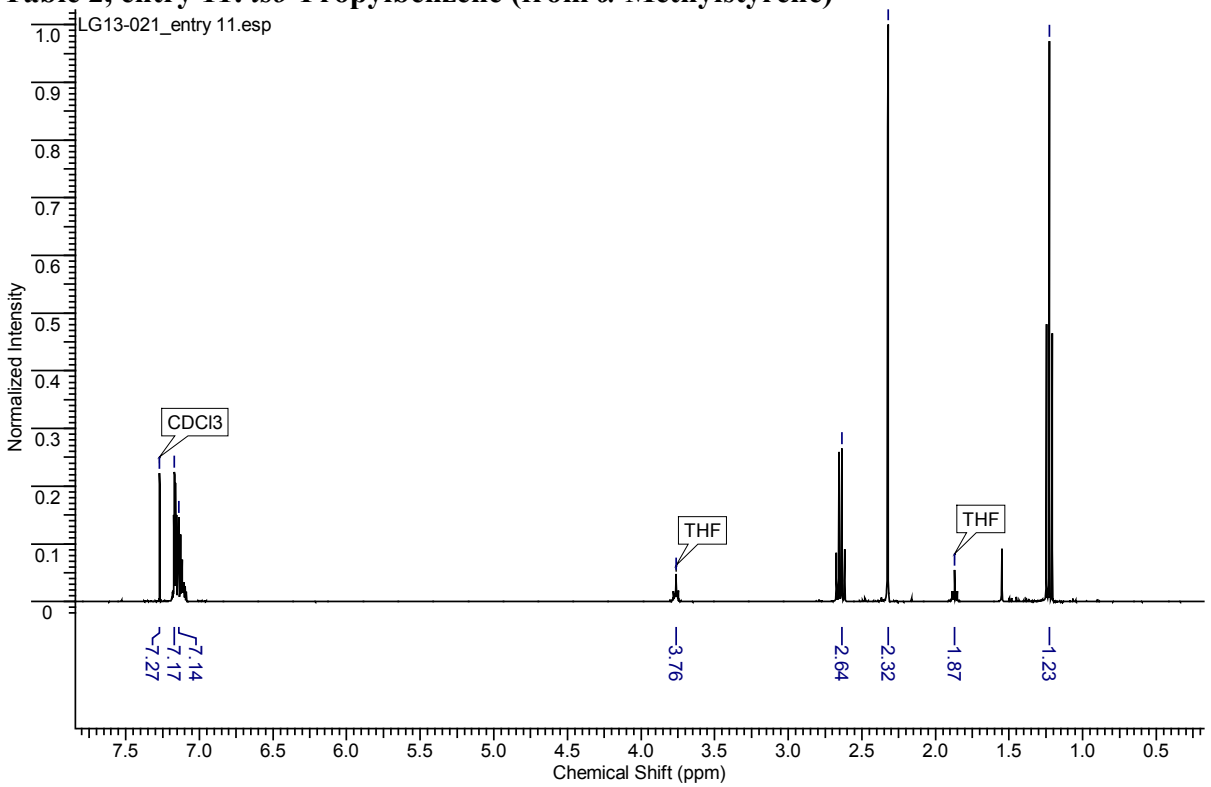


Table 2, entry 12: 1-Chloro-2-ethylbenzene (from 2-Chlorostyrene)

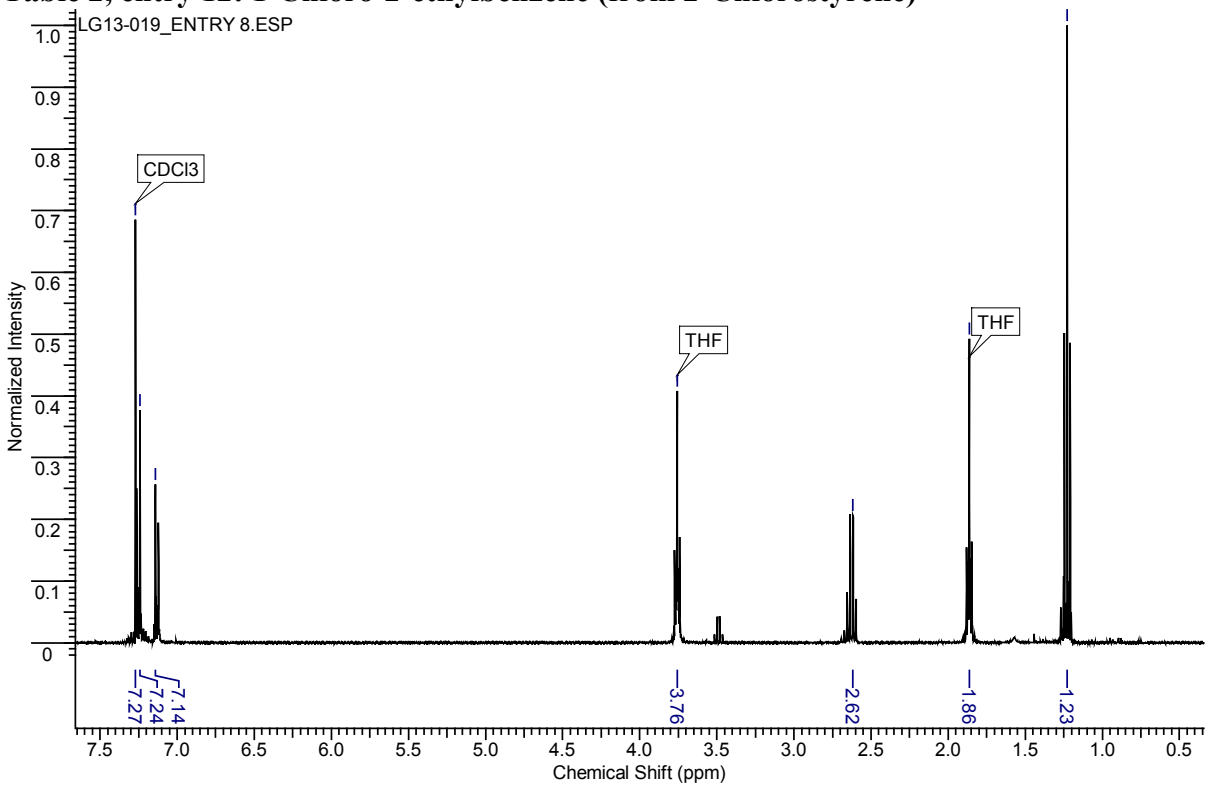


Table 2, entry 13: 1-Chloro-4-ethylbenzene (from 1-Chloro-4-ethylbenzene)

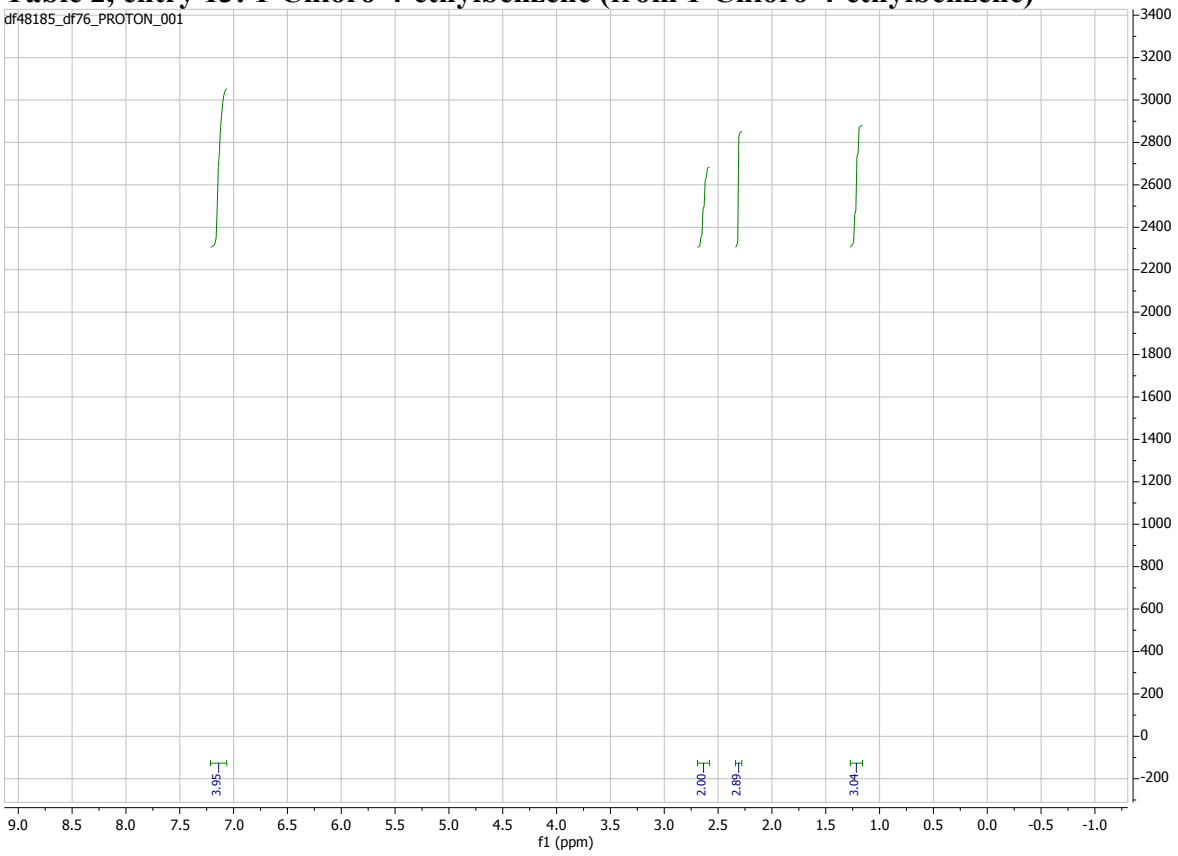


Table 2, entry 14: 1-Fluoro-4-ethylbenzene (from 1-Fluoro-4-ethylbenzene)

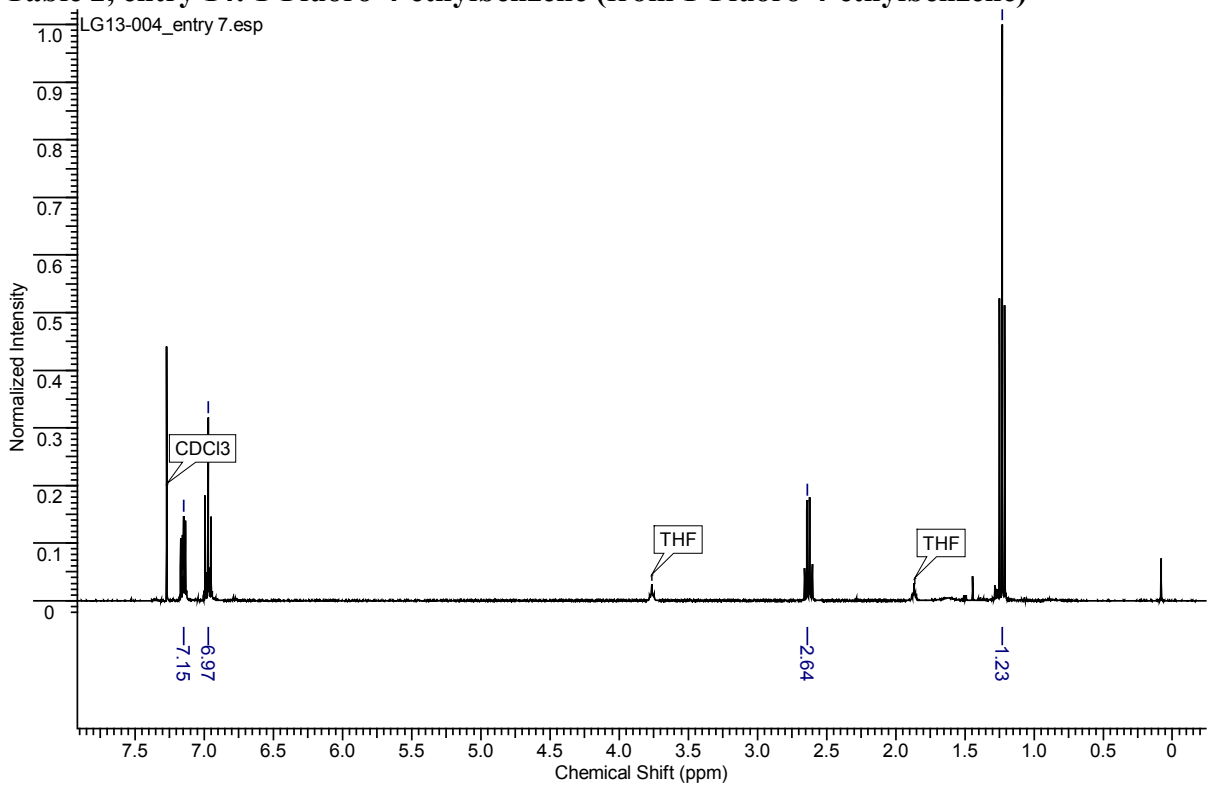


Table 2, entry 15: 4-Ethylanisole (from 4-Methoxystyrene)

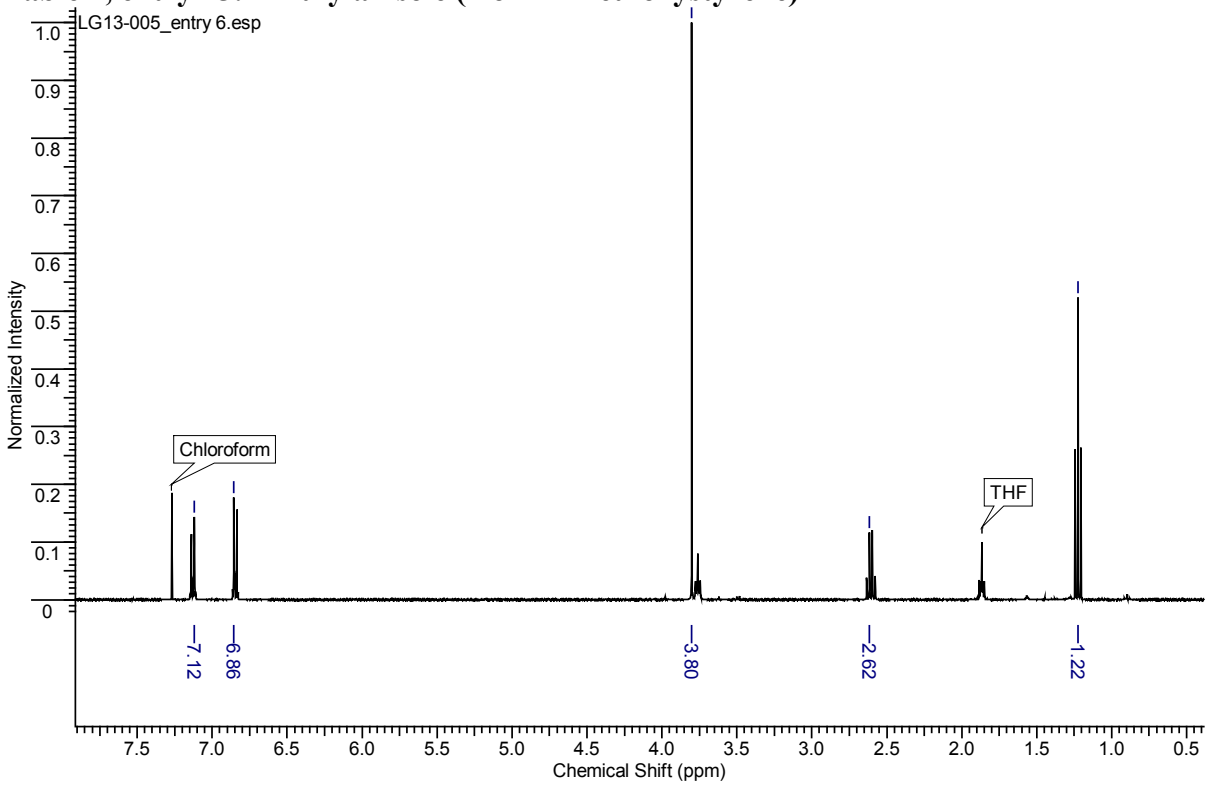


Table 2, entry 17 *tert*-Butyl(hexyloxy)dimethylsilane (from *tert*-Butyl(hex-5-en-1-yloxy)dimethylsilane)

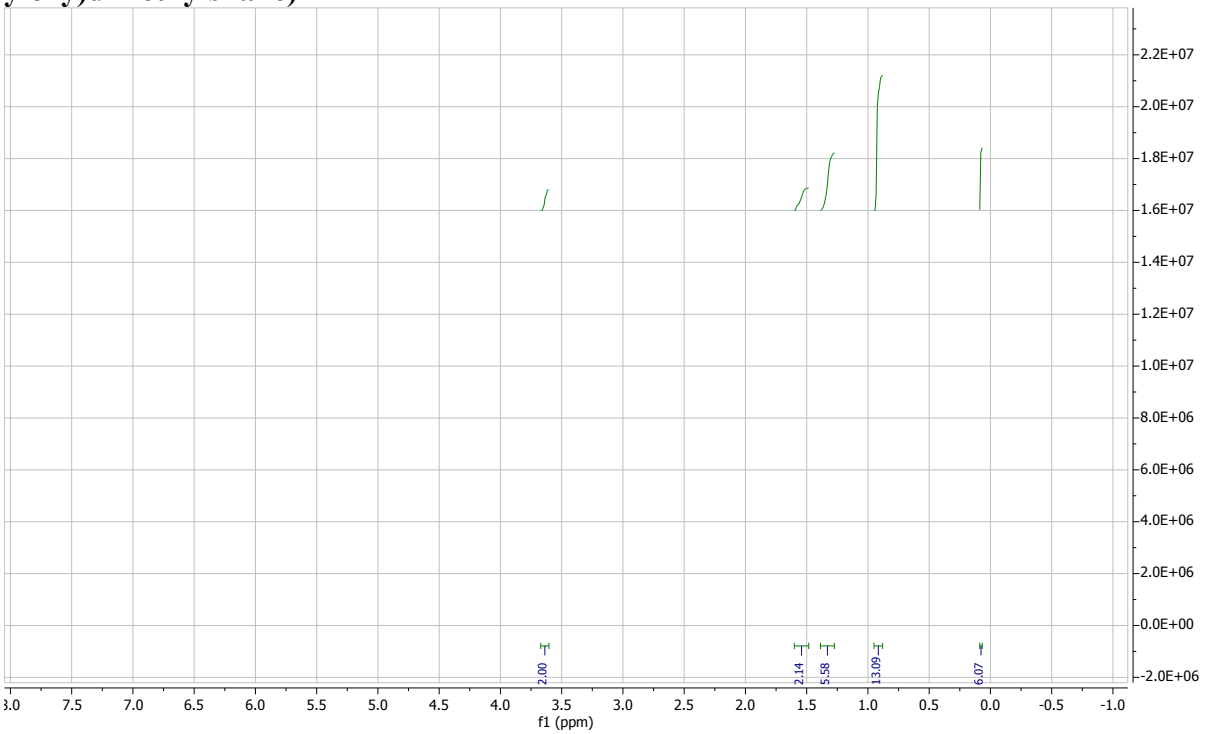


Table 2, entry 18: 1-(Benzyloxy)-3-methylbenzene (from 1-(Benzyloxy)-3-vinylbenzene)

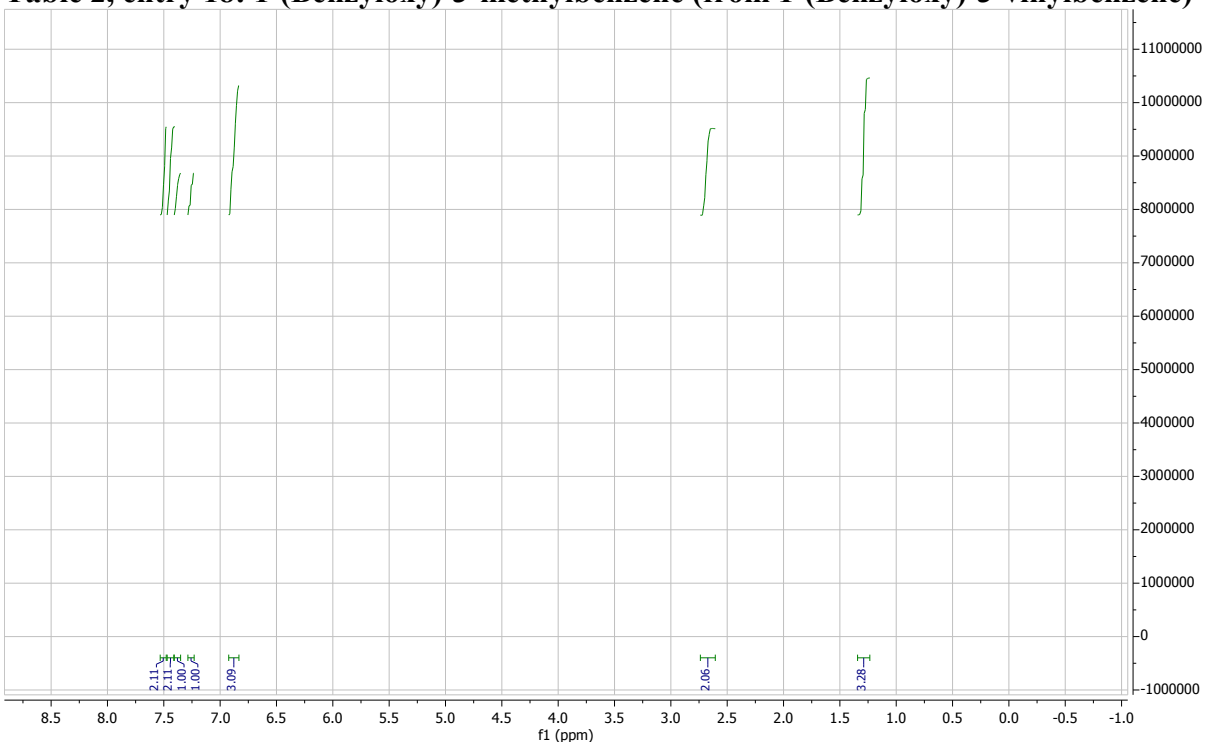


Table 2, entry 19: Methyl 4-ethylbenzoate (from Methyl 4-vinylbenzoate)

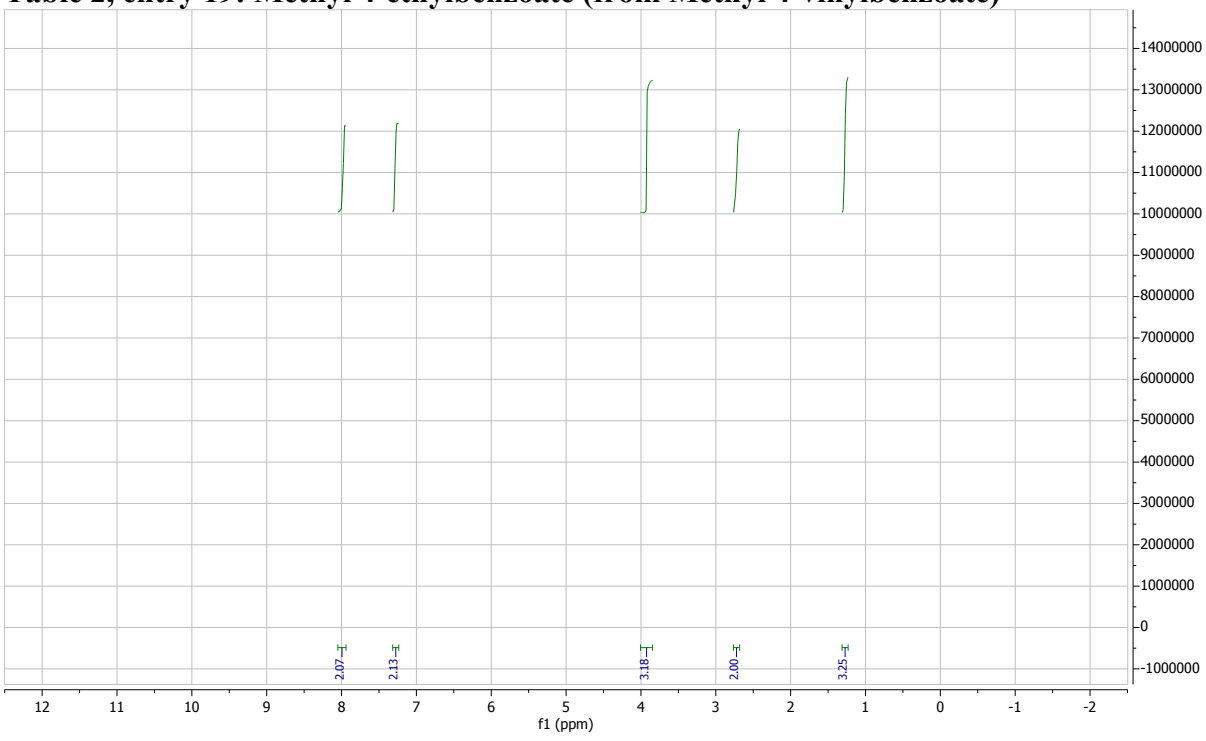


Table 3, entry 1: Butylbenzene (from *β*-Bromostyrene)

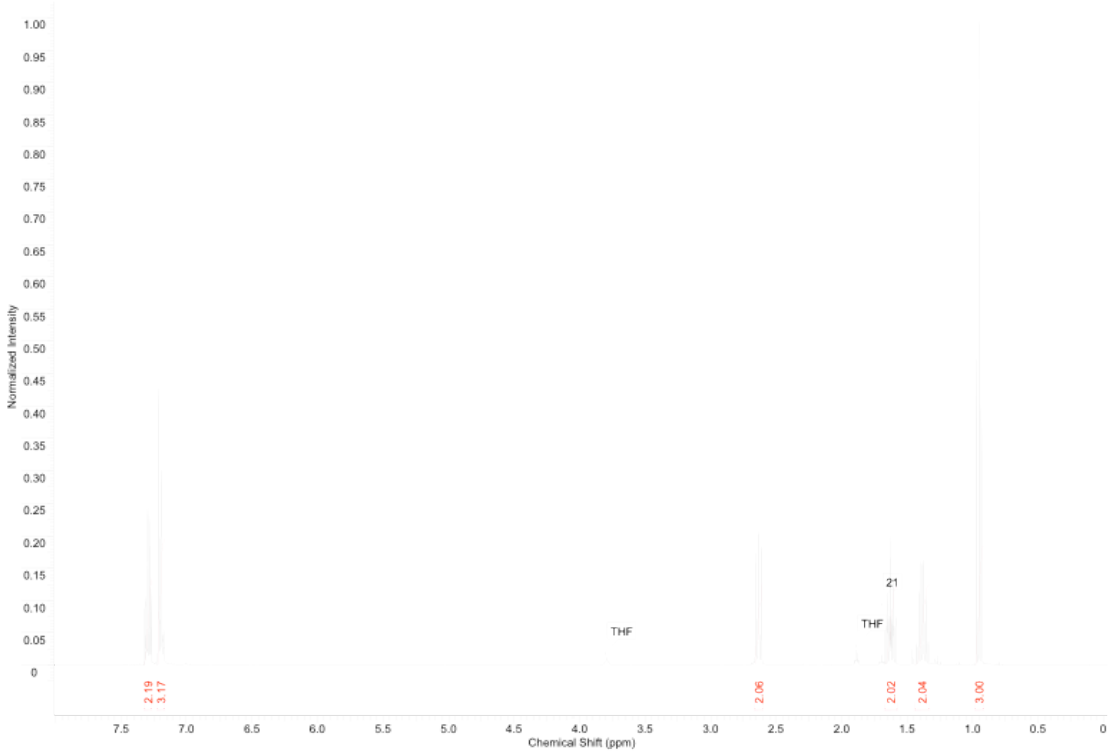


Table 3, entry 2: Isopentylbenzene

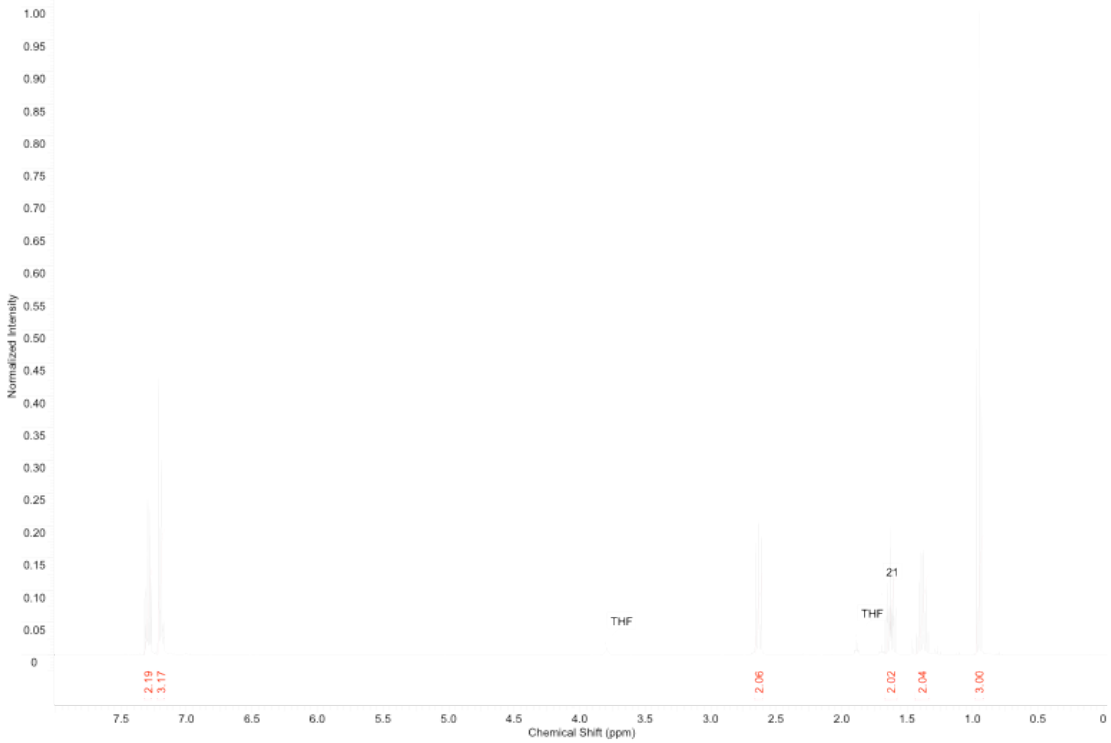


Table 3, entry 3: 1,4-Diphenylbutane

Table 3, entry 4: 1,2-Diphenylethane

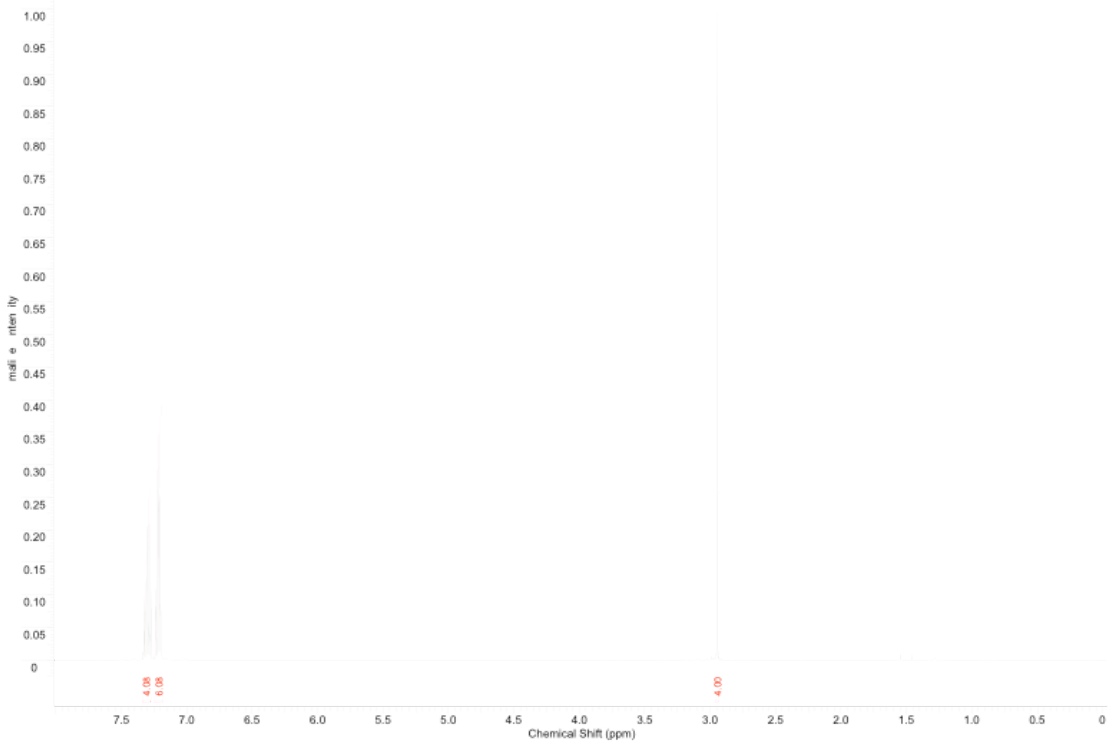


Table 3, entry 5: (3,3-Dimethyl)butylbenzene

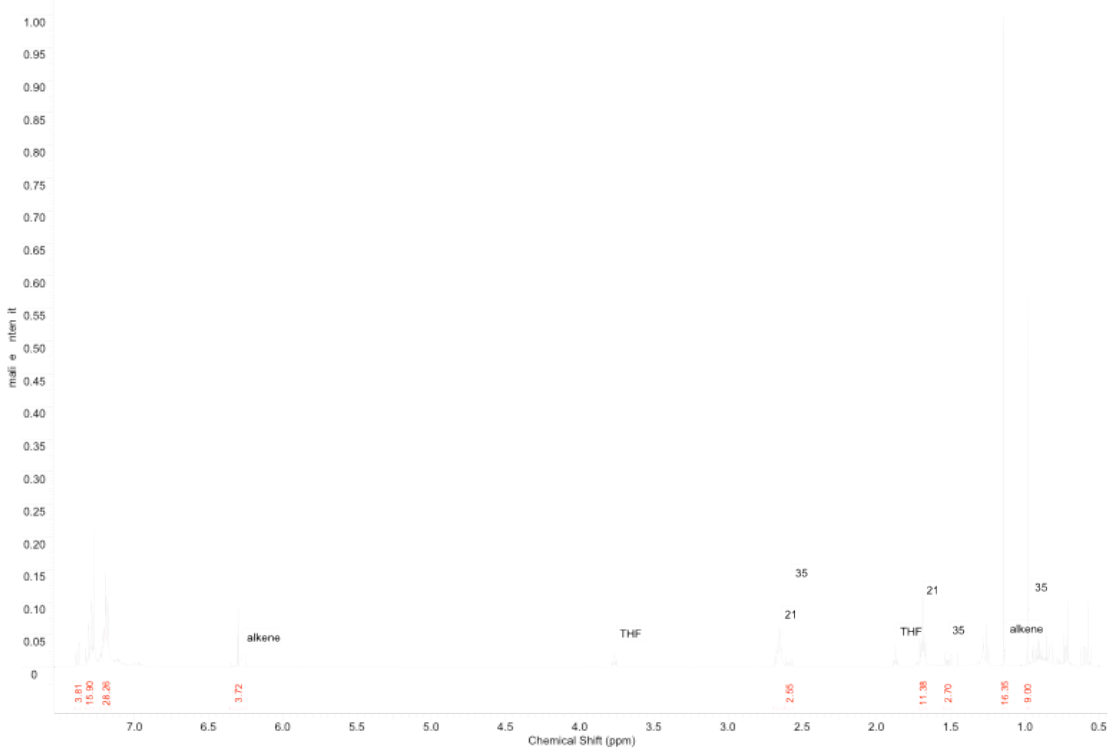


Table 3, entry 6: Pentylbenzene

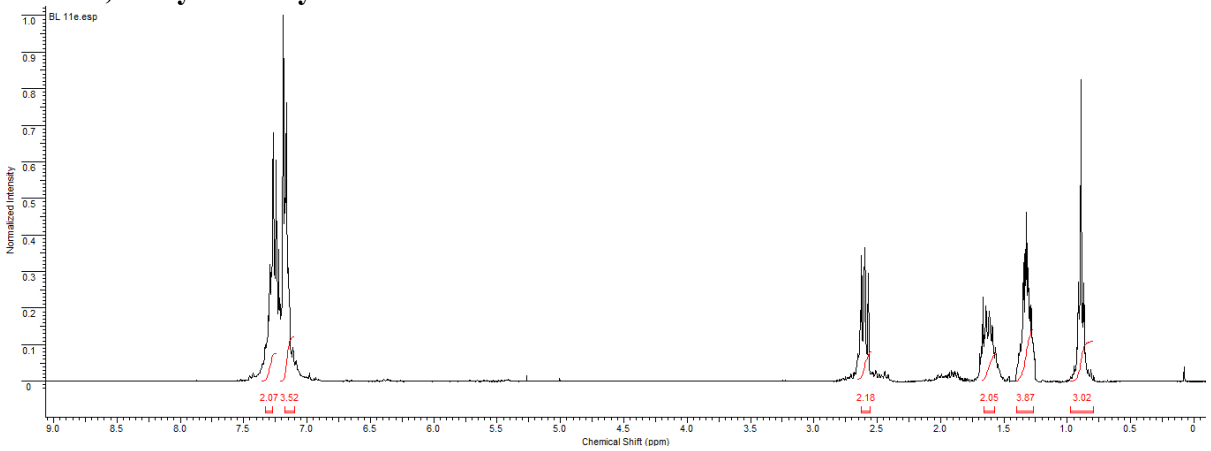


Table 3, entry 7: Propylbenzene

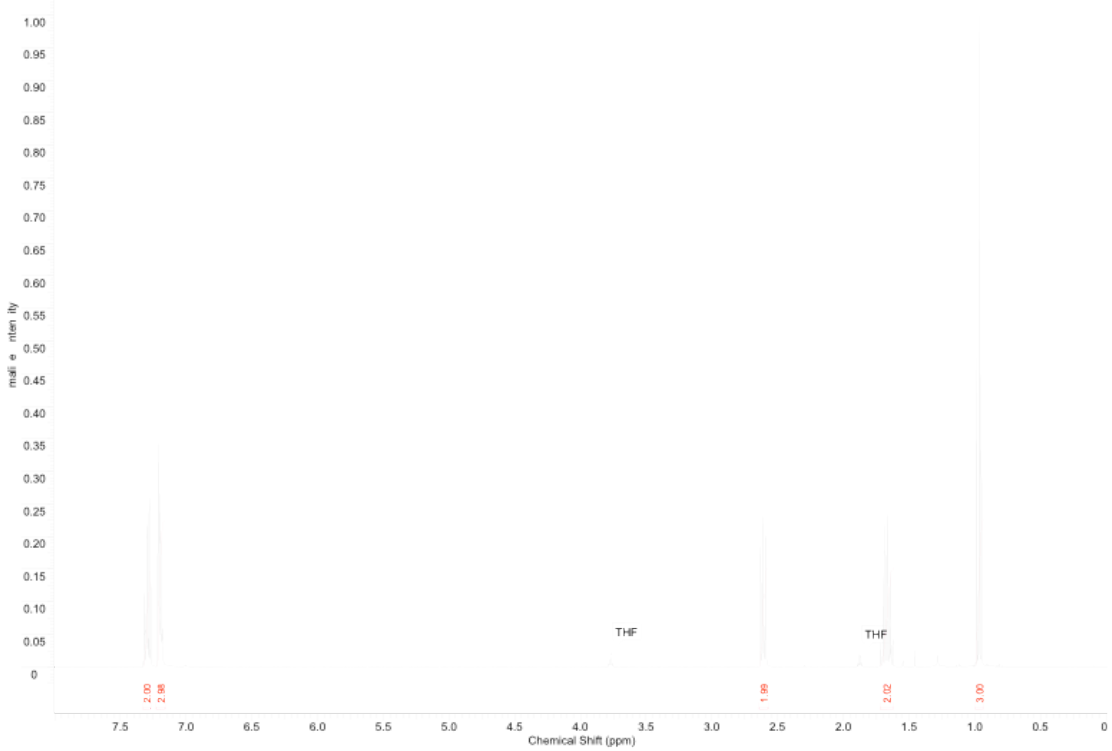


Table 3, entry 8: Butylbenzene (from β-Chlorostyrene)

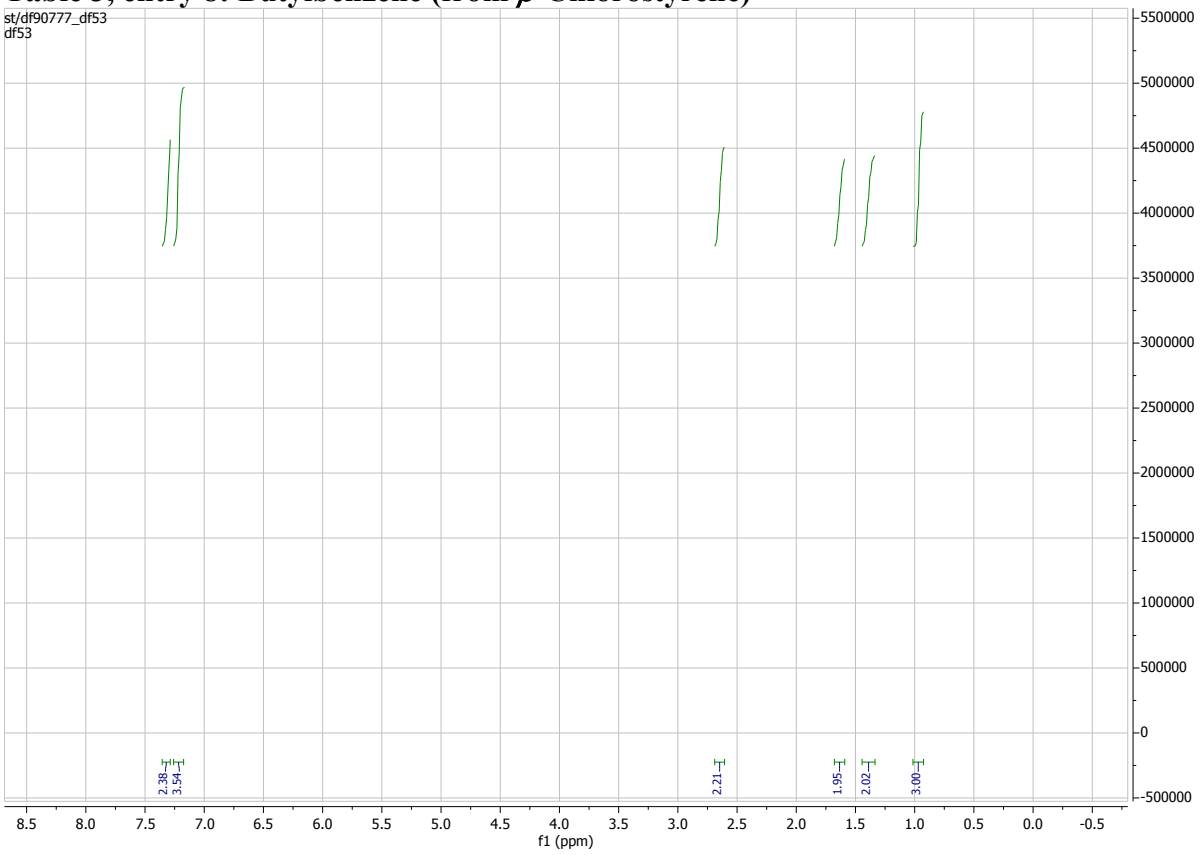


Table 3, entry 9: (*E*)-But-1-en-1-ylbenzene (from *β*-Iodorostyrene)

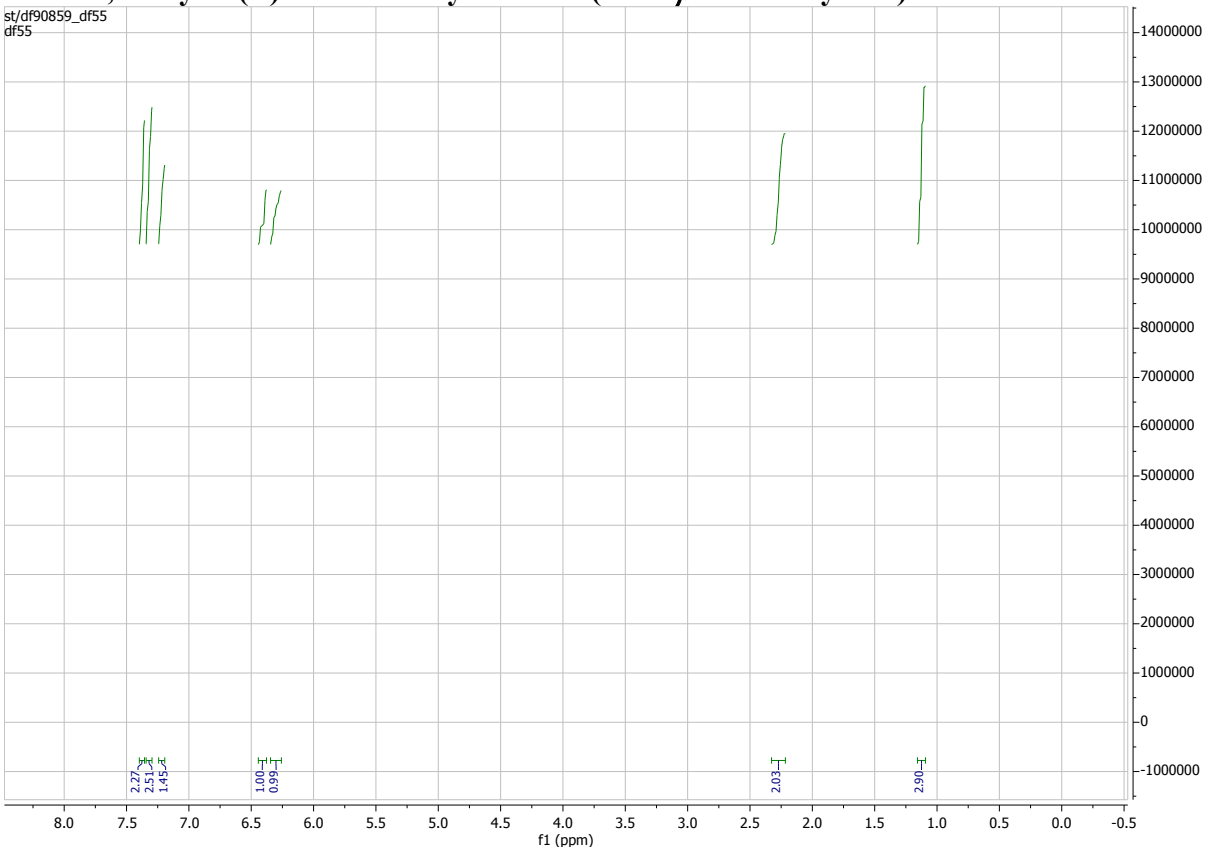
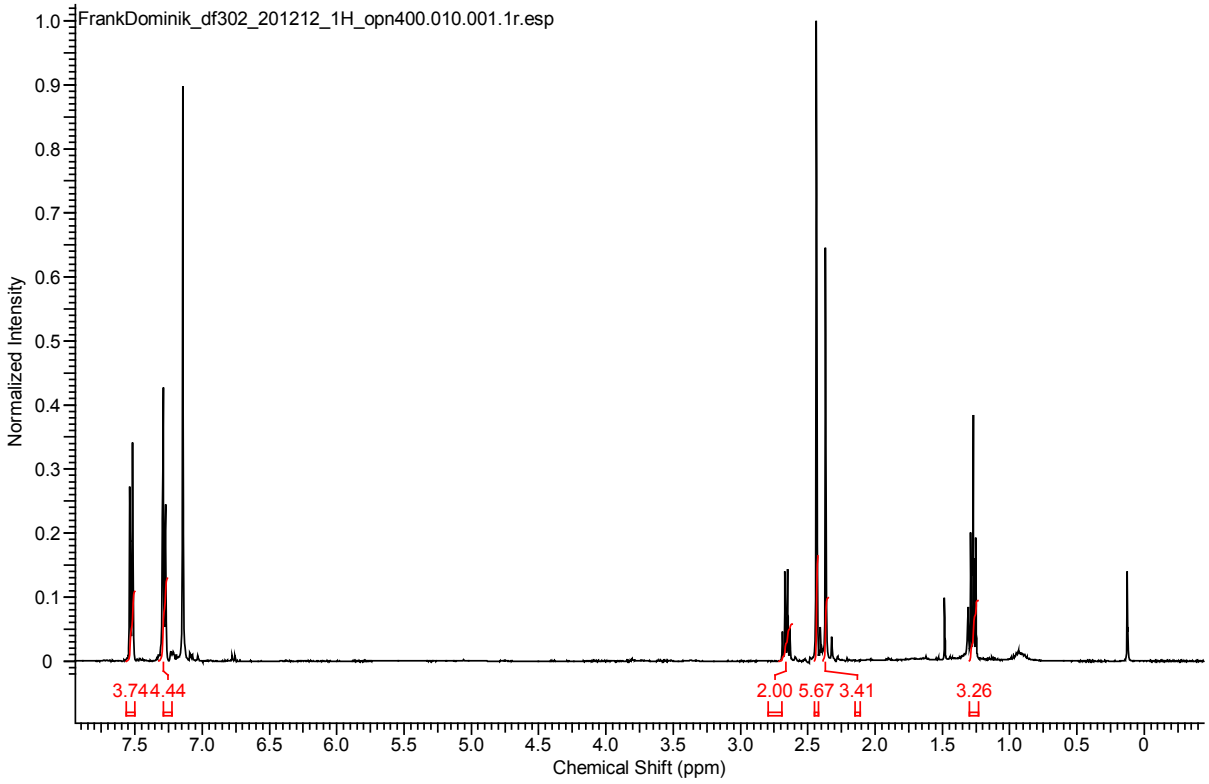


Table 3, entry 10: (*E*)-But-1-en-1-ylbenzene (from (*E*)-Styryl trifluoromethanesulfonate)

Table 3, entry 11: 1-Ethyl 4-methylbenzene (from vinylbromide and 4-tolylmagnesium bromide)

As a mixture of 1:1 with toluene.



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