Stereoretentive Pd-Catalyzed Kumada-Corriu Couplings of Alkenyl Halides at Room Temperature

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Supporting Information

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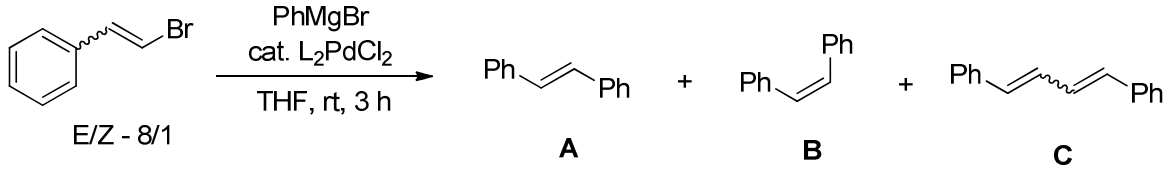
General

All experiments were carried out under an argon atmosphere. THF was distilled over potassium prior to use. Nuclear Magnetic Resonance spectra were obtained on a Varian Unity Inova AS600 system, in $CDCl_3$, with proton and carbon resonances at 600 MHz and 150 MHz, respectively, and are referenced to the residual solvent signal at 7.27 ppm. All spectral data are reported as follows; chemical shifts in the ^{1}H NMR are reported as parts per million (ppm) on the δ scale from an internal standard of chloroform (7.27 ppm). Data is presented as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz and integration. For ^{13}C NMR all peaks are reported in ppm referenced to the central peak of chloroform (77.23 ppm). Preparation[1] and titration[2] of Grignard reagents followed existing literature procedures.

General procedure for Kumada couplings.

A microwave vial containing a stir bar was flame dried under vacuum and cooled under argon prior to addition of Grignard reagent in THF (1.3-1.75 mmol), followed by *N,N,N',N'*-tetramethyl ethylenediamine (1.5-1.85 mmol) which had previously been distilled over sodium. To the solution was added palladium catalyst. Finally, alkenyl halide (1 mmol) was added dropwise over 3 min. The reaction was allowed to stir at rt shielded from light for 3-12 h. The reaction was then poured into water (20 mL) and extracted with EtOAc (3 x 12 mL). The organics were combined and dried over sodium sulfate and concentrated under vacuum. The residue was purified by silica gel column chromatography.

Screening of Representative Catalyst Systems



entry	ligand (L)	A	B	C[b]
1	TMEDA (1.1 equiv.)	51	7	42
2	TEEDA (1.1 equiv.)	55	8	37
3	EDA (1.0 equiv.)	54	7	39
4	DPEPhos	78	10	12
5	DPEPhos/TEEDA + $Pd(OAc)_2$	86	13	1
6	**DPEPhos/TMEDA + $Pd(OAc)_2$**	**86**	**14**	**<1**
7	**DPEPhos/TMEDA + $PdCl_2$**	**87**	**13**	**<1**

[a] Conditions: 0.3 mmol *beta*-bromo styrene (0.5 M in THF). Palladium catalyst (2 mol %), Grignard reagent (1.3 equiv), TMEDA (1.5 equiv); [b] GC ratio.

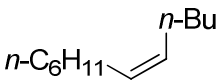
A microwave vial containing a stir bar was flame dried under vacuum and cooled under argon prior to addition of PhMgBr (1M in THF, 1.3 equiv., 0.39 mmol, 0.77 mL), followed by *N,N,N',N'*-tetramethyl ethylenediamine (1.5

equiv., 0.45 mmol, 0.06 mL) which had previously been distilled over sodium. To the solution was added palladium catalyst (2 mol %, see table). Finally, beta-bromostyrene (0.5 M in THF, 0.3 mmol, 0.6 mL) was added dropwise over 3 min. The reaction was allowed to stir at rt shielded from light for 3 h. The reaction was then poured into water (20 mL) and extracted with EtOAc (3 x 12 mL). The organics were combined and dried over sodium sulfate and analyzed by GC.

Characterization data (Table 2)

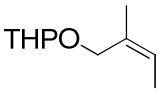
Note: For the examples from **Table 2** - **1.75 equiv.** of Grignard reagent and **1.85 equiv.** of TMEDA were used

(*Z*)-Dodec-5-ene (2)



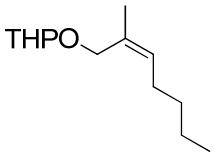
A microwave vial containing a stir bar was flame dried under vacuum and cooled under argon prior to addition of *n*-BuMgCl in THF (1M in THF, 0.525 mmol, 0.53 mL), followed by *N,N,N',N'*-tetramethyl ethylenediamine (0.555 mmol) which had previously been distilled over sodium. To the solution was added neat (dtbpf)$PdCl_2$ (2 mol%, 0.006 mmol). Finally, (*Z*)-1-iodooct-1-ene (0.25M in THF, 0.3 mmol, 1.2 mL) was added dropwise over 3 min. The reaction was allowed to stir at rt shielded from light for 3 h. The reaction was then poured into water (10 mL) and extracted with EtOAc (3 x 10 mL). The organics were combined and dried over sodium sulfate and concentrated under vacuum. The residue was purified by silica gel column chromatography. The sample was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (47 mg, 94 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90 (q, *J* = 7.5 Hz, 6H), 1.34-1.26 (m, 12H), 2.02 (dd, *J* = 4.5, 7.0 Hz, 4H), 5.36 (t, *J* = 4.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.26, 13.34, 21.61, 21.90, 26.16, 26.45, 28.24, 28.94, 31.00, 31.21, 129.06, 129.13; HRMS(FI) calcd. for $C_{12}H_{24}$ (M+): 168.1878; found: 168.1872.

(*Z*)-2-((2-Methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (12)



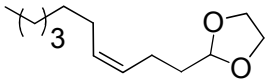
The representative procedure was followed using MeMgCl (3M in THF, 0.28 mL, 0.85 mmol), (dtbpf)$PdCl_2$ (2 mol %, 0.0097 mmol), *N,N,N',N'*-tetramethyl ethylenediamine (0.9 mmol) and (*Z*)-2-((3-iodo-2-methylallyl)oxy)tetrahydro-2H-pyran (0.25 M in THF, 0.485 mmol, 1.94 mL). The residue was purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as eluent to afford clear oil (77 mg, 93 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (m, 2H), 1.60 (m, 2H), 1.66 (d, *J* = 6.9 Hz, 3H), 1.72 (m, 1H), 1.77 (s, 3H), 1.85 (m, 1H), 3.53 (m, 1H), 3.91 (m, 1H), 4.12 (dd, *J* = 11.3, 6.8 Hz, 2H), 4.60 (t, *J* = 3.5 Hz), 5.46 (q, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.15, 17.08, 19.81, 22.01, 25.74, 30.93, 62.51, 65.55, 97.68, 124.07, 132.61. HRMS(FI) calcd. for $C_{10}H_{18}O_2$ (M+): 170.1307; found: 170.1305.

(*E*)-2-((2-Methylhept-2-en-1-yl)oxy)tetrahydro-2H-pyran (14)



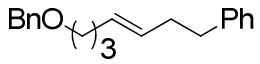
The representative procedure was followed using *n*-BuMgCl (1M in THF, 0.6 mmol, 0.6 mL), (dtbpf)$PdCl_2$ (2 mol %, 0.00684 mmol), *N,N,N′,N′*-tetramethyl ethylenediamine (0.63 mmol) and (*Z*)-2-((3-iodo-2-methylallyl)oxy)tetrahydro-2H-pyran (0.25 M in THF, 0.342 mmol, 1.368 mL). The residue was purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as the eluent to afford clear oil (69 mg, 95 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.29-1.36 (m, 4H), 1.50-1.62 (m, 5H), 1.77 (s, 3H), 1.79-1.86 (m, 1H), 2.07 (dt, *J* = 6.8, 6.3 Hz, 2H), 3.53 (m, 1H), 3.90 (m, 1H), 4.09 (s, 2H), 4.59 (t, J = 3.5 Hz, 1H), 5.37 (t, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.19, 19.80, 21.94, 22.54, 25.74, 27.60, 30.98, 32.42, 62.49, 65.61, 97.81, 130.12, 131.79; HRMS(FI) calcd. for $C_{12}H_{24}$ (M+): 212.1776; found: 235.1664 $(M+Na)^+$.

(*Z*)-2-(Dec-3-en-1-yl)-1,3-dioxolane (16)



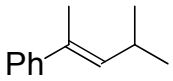
The representative procedure was followed using (dtbpf)$PdCl_2$ (2 mol %, 0.0078 mmol), *N,N,N′,N′*-tetramethyl ethylenediamine (0.72 mmol), (*Z*)-1-iodooct-1-ene (0.25 M in THF, 0.39 mmol, 1.56 mL) and (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide (0.1 M in THF, 6.82 mL, 0.6825 mmol). The residue was then purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as the eluent to afford clear oil (80 mg, 96% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.35-1.26 (m, 8H), 1.71 (dt, *J* = 4.8, 3.0 Hz, 2H), 2.17 (q *J* = 7.5 Hz, 4H), 3.92 (m, 4H), 4.87 (t, *J* = 4.8 Hz, 1H), 5.39 (dt, *J* = 6.5, 4.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.35, 22.18, 22.90, 27.42, 29.22, 29.89, 32.04, 34.14, 65.14, 104.23, 128.73, 131.12. HRMS(FI) calcd. for $C_{13}H_{24}O_2$ (M+): 212.1776; found: 212.1766.

(*E*)-(7-(Benzyloxy)hept-3-en-1-yl)benzene (19)



The representative procedure was followed using (dtbpf)$PdCl_2$ (2 mol %, 0.006 mmol), (*E*)-(((5-bromopent-4-en-1-yl)oxy)methyl)benzene (0.25 M in THF, 0.303 mmol, 1.21 mL), *N,N,N′,N′*-tetramethyl ethylenediamine (0.56 mmol), and phenethylmagnesium bromide (0.3 M in THF, 0.53 mmol, 1.77 mL). The residue was purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as eluent to afford clear oil (72 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.66 (m, 2H), 2.12 (dt, *J* = 6.3, 7.5 Hz, 2H), 2.32 (dt, *J* = 6.3, 7.5, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 3.47 (t, *J* = 6.3 Hz, 2H), 4.51 (s, 2H), 5.46 (m, 2H), 7.19-7.37 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.33, 29.73, 34.60, 36.81, 69.97, 73.07, 125.90, 127.69, 127.84, 128.42, 128.54, 128.66, 130.13, 130.45, 138.86, 142.31; HRMS(FI) calcd. for $C_{20}H_{24}O$ (M+): 280.1827; found: 280.1806.

(*E*)-(4-Methylpent-2-en-2-yl)benzene (22)



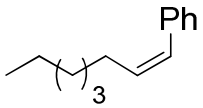
The representative procedure was followed using (dtbpf)$PdCl_2$ (2 mol %, 0.007 mmol), *N,N,N′,N′*-tetramethyl ethylenediamine (0.65 mmol), (*E*)-(1-bromoprop-1-en-2-yl)benzene (0.25 M in THF, 0.349 mmol, 1.4 mL) and *i*-PrMgCl (1 M in THF, 0.61 mL, 0.61 mmol). The residue was purified by silica gel column chromatography using pure hexanes as eluent to afford clear oil (50 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.6 Hz, 6H), 2.06 (s, 3H), 2.72 (m, *J* = 10.0, 1H), 5.60 (d, *J* =

9.1 Hz, 1H), 7.22-7.41 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.92, 23.18, 28.12, 125.84, 126.63, 128.32, 132.55, 136.35, 144.21; HRMS(FI) calcd. for $C_{12}H_{16}$ (M+): 160.1252; found: 160.1262.

Characterization data (Table 3)

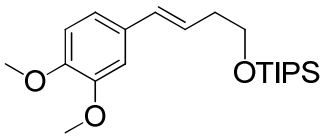
Note: For the examples from **Table 3** only **1.3 equiv.** of Grignard reagent and **1.5 equiv.** of TMEDA were used

(*Z*)-Oct-1-en-1-ylbenzene (24)



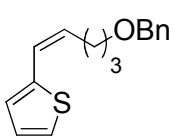
The representative procedure was followed using (dtbpf)$PdCl_2$ (2 mol %, 0.005 mmol), (*Z*)-1-iodooct-1-ene (0.25 M in THF, 0.250 mmol, 1 mL), *N,N,N',N'*-tetramethyl ethylenediamine (0.375 mmol), and phenylmagnesium bromide (1 M in THF, 0.33 mL, 0.325 mmol). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (45 mg, 96% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3H), 1.38-1.25 (m, 8H), 2.35 (dt, *J* = 7.5, 2.0 Hz, 2H), 5.69 (dt, *J* = 7.3, 11.5 Hz, 1H), 6.42 (d, *J* = 11.5 Hz, 1H), 7.36-7.22 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.28, 22.79, 28.86, 29.34, 30.09, 126.52, 128.05, 129.15, 133.30, 138.06; HRMS(FI) calcd. for $C_{14}H_{20}$ (M+): 188.16; found: 188.1552.

(*E*)-((4-(3,4-Dimethoxyphenyl)but-3-en-1-yl)oxy)triisopropylsilane (27)



The representative procedure was followed using Pd(dtbpf)Cl_2 (2 mol %, 0.006 mmol), (3,4-dimethoxyphenyl)magnesium bromide (1M in THF, 0.39 mmol, 0.39 mL), *N,N,N',N*-tetramethylethylenediamine (0.45 mmol) which had previously been distilled over sodium. This was followed by the addition of the corresponding vinyl bromide (0.25 M in THF, 0.3 mmol, 1.2 mL) in a drop-wise fashion. The reaction was allowed to stir at rt shielded from light overnight. The reaction was then poured into a saturated ammonium chloride solution (20 mL) and extracted with DCM (3 x 12 mL). The organics were combined and rinsed with brine (20 mL) before being dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by silica gel column chromatography using 9:1 mixture of hexanes/EtOAc as the eluent to afford clear oil (101 mg, 92 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.08 (m, 21H), 2.46 (d, *J* = 6.7 Hz, 2H), 3.88 (t, *J* = 6.7 Hz, 2H), 3.88 (s, 3H), 3.90 (s, 3H), 6.14 (dt, *J* = 15.8,6.7 Hz, 1H), 6.39 (d, *J* = 15.8 Hz), 6.81 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.92 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.23, 18.24, 36.94, 55.93, 56.11, 63.60, 108.63, 111.31, 119.15, 125.65, 131.16, 131.27, 148.50, 149.16; HRMS(FI) calcd. for $C_{21}H_{36}O_3Si$ (M+): 364.2434; found: 364.2454.

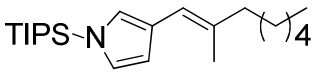
(*Z*)-2-(6-(Benzyloxy)hex-1-en-1-yl)thiophene (30)



The representative procedure was followed using Pd(dtbpf)Cl_2 (2 mol %, 0.006 mmol), thiophen-2-ylmagnesium bromide (0.4 M in THF, 0.975 mL,), *N,N,N',N*-tetramethylethylenediamine (0.45 mmol), and (*Z*)-((6-bromohex-5-en-1-yl)oxy)methyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL). The reaction was allowed to stir at rt shielded from light for 16 hours. The reaction was then

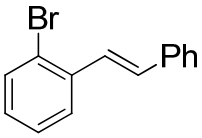
poured into a saturated ammonium chloride solution (20 mL) and extracted with DCM (3 x 12 mL). The organics were combined and rinsed with brine (20 mL) before being dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by silica gel column chromatography using 9:1 mixture of hexanes/EtOAc as the eluent to afford clear oil (45 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.29 (m, 1H), 7.25 (d, *J* = 5.0 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.98 (d, *J* = 3.4 Hz, 1H), 6.55 (d, *J* = 11.5 Hz, 1H), 5.58 (dt, *J* = 11.5, 7.2 Hz, 1H), 4.51 (s, 2H), 3.56 – 3.49 (m, 2H), 2.50 – 2.40 (m, 2H), 1.78 – 1.67 (m, 2H), 1.68 – 1.58 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.92, 138.84, 131.04, 128.56, 127.83, 127.69, 127.31, 126.90, 125.13, 122.14, 73.11, 70.39, 29.67, 29.23, 26.31; HRMS(EI) calcd. for $C_{17}H_{20}OS$ (M+): 272.1235; found: 272.1248.

(*E*)-3-(2-Methyloct-1-en-1-yl)-1-(triisopropylsilyl)-1*H*-pyrrole (33)



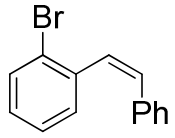
The representative procedure was followed using Pd(dtbpf)Cl_2 (2 mol %, 0.006 mmol), (1-(triisopropylsilyl)-1*H*-pyrrol-3-yl)magnesium bromide (0.82 M in THF, 0.39 mmol, 0.48 mL), *N,N,N',N*-tetramethylethylenediamine (0.45 mmol), and (*E*)-1-iodo-2-methyloct-1-ene (0.25 M in THF, 0.3 mmol, 1.2 mL). The residue was purified by silica gel column chromatography using 40:1 mixture of hexanes/DCM as eluent to afford an orange oil (88 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 – 6.72 (m, 2H), 6.41 – 6.36 (t, *J* = 1.94 Hz, 1H), 6.15 (s, 1H), 2.14 (m, 1H), 1.91 (s, 3H), 1.52 – 1.39 (m, 5H), 1.37 – 1.26 (m, 6H), 1.11 (d, *J* = 8.5 Hz, 18H), 0.94 – 0.87 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.41, 124.45, 124.34, 123.34, 118.21, 111.08, 41.29, 32.09, 29.36, 28.53, 22.88, 18.46, 18.05, 17.92, 14.35, 11.90; HRMS(FI) calcd. for $C_{22}H_{41}NSi$ (M+): 347.3008; found: 347.3010.

(E)-1-Bromo-2-styrylbenzene (36)



The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), (*E*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and *ortho*-bromophenylmagnesium chloride (0.5 M in THF, 0.39 mmol, 0.78 mL). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (66 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.58 (ddd, *J* = 8.0, 1.3, 0.4 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.47 (dt, *J* = 16.2, 0.6 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.11 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 7.04 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 137.13, 136.99, 133.05, 131.43, 128.76, 128.71, 128.05, 127.52, 127.45, 126.81, 126.69, 124.12; HRMS(FI) calcd. for $C_{14}H_{11}Br$ (M+): 258.0044; found: 258.0052.

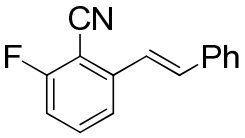
(Z)-1-Bromo-2-styrylbenzene (38)



The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), (*Z*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and *ortho*-bromophenylmagnesium chloride (0.5 M in THF, 0.39 mmol, 0.78 mL). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (63.0 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m,

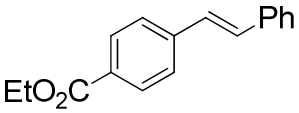
1H), 7.21 – 7.10 (m, 6H), 7.10 – 7.05 (m, 2H), 6.68 (d, *J* = 12.1 Hz, 1H), 6.61 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.93, 136.29, 132.64, 131.35, 130.82, 129.44, 128.96, 128.63, 128.12, 127.28, 126.97, 123.86; HRMS(FI) calcd. for $C_{14}H_{11}Br$ (M+): 258.0044; found: 258.0060.

(E)-2-Fluoro-6-styrylbenzonitrile (40)



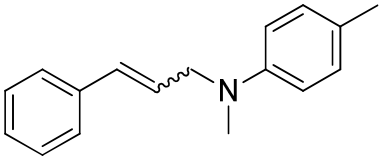
The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), (*E*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and 2-cyano-3-fluorophenylmagnesium chloride (0.78 mL, 0.39 mmol, 0.5 M). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (58 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.29 (m, 4H), 7.04 (d, *J* = 16.2 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 141.24, 136.31, 131.49, 128.71, 128.60, 128.31, 128.16, 126.29, 126.28, 123.39, 108.11, 91.71, 88.86; HRMS(FI) calcd. for $C_{15}H_{10}FN$ (M+): 223.0797; found: 223.0818.

(E)-Ethyl 4-styrylbenzoate (42)



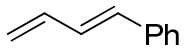
The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), (*E*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and (4-(ethoxycarbonyl)phenyl) magnesium chloride (0.78 mL, 0.39 mmol, 0.5 M). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (64 mg, 85% yield). ^{1}H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.57 – 7.50 (m, 4H), 7.40 – 7.33 (m, 2H), 7.31 – 7.25 (m, 1H), 7.20 (d, *J* = 16.3 Hz, 1H), 7.11 (d, *J* = 16.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 166.37, 141.67, 136.74, 131.10, 129.95, 129.25, 128.74, 128.17, 127.59, 126.74, 126.24, 60.89, 14.34; HRMS(FI) calcd. for $C_{17}H_{16}O_2$ (M+): 252.1150; found: 252.1183.

N,4-dimethyl-N-(3-phenylallyl)aniline (45) mixture of *E/Z* isomers 1/1



The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), N-(3-chloroallyl)-N,4-dimethylaniline (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and phenyl magnesium bromide (1M in THF, 0.39 mmol, 0.39 mL). The residue was purified by silica gel column chromatography using hexanes as eluent to afford yellow oil (76 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.18 (m, 5H), 7.08 – 6.96 (m, 2H), 6.78 – 6.46 (m, 3H), 6.24 (dt, *J* = 15.9, 5.6 Hz, 0.5H), 5.70 (dt, *J* = 11.9, 6.1 Hz, 0.5H), 4.18 (dd, *J* = 6.1, 2.0 Hz, 1H), 4.03 (dd, *J* = 5.7, 1.6 Hz, 1H), 2.93 (s, 1.5H), 2.87 (s, 1.5H), 2.24 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 147.43, 147.17, 136.90, 131.21, 129.69, 129.65, 128.90, 128.49, 128.26, 127.36, 127.01, 126.30, 126.01, 113.59, 113.09, 55.29, 51.33, 38.68, 38.22, 20.24. HRMS(FI) calcd. for $C_{17}H_{19}N$ (M+): 237.1517; found: 237.1633.

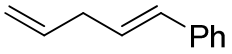
(E)-Buta-1,3-dien-1-ylbenzene (47)



The representative procedure was followed using DPEPhosPdCl_2 (5 mol %), (*E*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and vinyl magnesium chloride (0.2 mL, 0.39 mmol, 1.6 M in THF from Aldrich). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (31, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.34 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 6.78 (ddt, *J* = 15.5, 10.5,

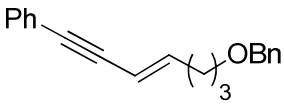
0.8 Hz, 1H), 6.60 – 6.42 (m, 2H), 5.32 (ddt, *J* = 16.9, 1.6, 0.8 Hz, 1H), 5.16 (ddt, *J* = 10.0, 1.5, 0.7 Hz, 1H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 137.13, 137.08, 132.80, 129.58, 128.56, 127.58, 126.39, 117.57; HRMS(FI) calcd. for $C_{10}H_{10}$ (M+): 130.0783; found: 130.0807.

(E)-Penta-1,4-dien-1-ylbenzene (49)



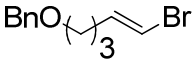
The representative procedure was followed using DPEPhosPdCl$_2$ (5 mol %), (*E*)-(2-bromovinyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and allyl magnesium chloride (0.25 mL, 0.39 mmol, 1.0 M in Et$_2$O from Aldrich). The residue was purified by silica gel column chromatography using hexanes as eluent to afford clear oil (41 mg, 95% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 6.41 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.91 (ddt, *J* = 17.2, 10.1, 6.4 Hz, 1H), 5.18 – 4.95 (m, 2H), 2.96 (tq, *J* = 6.5, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 137.58, 136.44, 130.82, 128.46, 128.15, 126.99, 125.96, 115.64, 36.99; HRMS(FI) calcd. for $C_{11}H_{12}$ (M+): 144.0939; found: 144.0955.

(*E*)-(7-(Benzyloxy)hept-3-en-1-yn-1-yl)benzene (51)



The representative procedure was followed using (dtbpf)PdCl$_2$ (2 mol %, 0.006 mmol), (*E*)-(((5-bromopent-4-en-1-yl)oxy) methyl)benzene (0.25 M in THF, 0.3 mmol, 1.2 mL), *N,N,N',N*-tetramethylethylen-ediamine (0.45 mmol) and (phenethynyl)magnesium bromide (1 M in THF, 0.39 mmol. 0.39 mL). The residue was purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as the eluent to afford clear oil (79 mg, 95% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.74 (m, 2H), 2.29 (dd, *J* = 7.5, 6.0 Hz, 2H), 3.52 (t, *J* = 6.0 Hz, 2H), 4.52 (s, 2H), 5.71 (d, *J* = 16 Hz, 1H), 6.25 (dt, 16.0 Hz, 7.0 Hz, 1H), 7.44-7.29 (m, 10H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 29.10, 30.16, 69.64, 73.23, 110.36, 123.96, 127.79, 127.89, 128.13, 128.46, 128.61, 131.64, 138.70, 144.48; HRMS(FI) calcd. for $C_{20}H_{20}O$(M+): 276.1514; found: 276.1521.

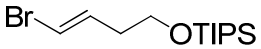
(*E*)-(((5-Bromopent-4-en-1-yl)oxy)methyl)benzene (18)



A 250 mL round bottomed flask was flame dried under vacuum to which was added zirconocene dichloride (3.53 g, 12.1 mmol) after which it was purged under argon once again. To the flask was then added THF (80 mL) that had been distilled over sodium immediately prior to use. The flask was shielded from light and cooled to 0° C before addition of lithium triethylborohydride (9.2 mL, 9.2 mmol). The flask was allowed to warm to rt and stir for 1 h before introduction of ((pent-4-yn-1-yloxy)methyl)benzene (1.069 g, 6.13 mmol) drop-wise over 5 min. The flask was shaken to rinse the sides and the reaction was allowed to stir for 30 min before the addition of NBS (1.37 g, 11.62 mmol) and cooling back to 0° C to stir overnight. The reaction was poured into a saturated solution of sodium bicarbonate in water (100 mL) and extracted with a solution of 9:1 hexanes/EtOAc (2 x 70 mL). The organics were combined, rinsed with brine (100 mL) and dried over Na$_2$SO$_4$ prior to concentration under vacuum. The remaining residue was purified by silica gel column chromatography using a polarity gradient from pure hexanes to a 9:1 mixture of hexanes/EtOAc as the eluent to afford (*E*)-(((5-bromopent-4-en-1-yl)oxy)methyl)benzene (1.36 g, 5.34 mmol, 87%) as a slightly yellow clear oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.73 (m, 2H), 2.18 (m, 3H), 3.49 (t, *J* = 6.25 Hz, 2H), 4.51 (s, 2H), 6.04 (dt, *J* = 13.5, 1.3 Hz, 1H), 6.19 (dt, *J* = 13.5, 7.3 Hz, 1H), 7.39-7.29 (m, 5H); ^{13}C NMR (150 MHz,

$CDCl_3$) δ 29.93, 29.95, 69.34, 73.22, 104.94, 127.81, 128.32, 137.56, 138.46; HRMS(FI) calcd. for $C_{12}H_{15}BrO$ (M+): 254.0306; found: 254.0312.

(*E*)-((4-Bromobut-3-en-1-yl)oxy)triisopropylsilane (26)



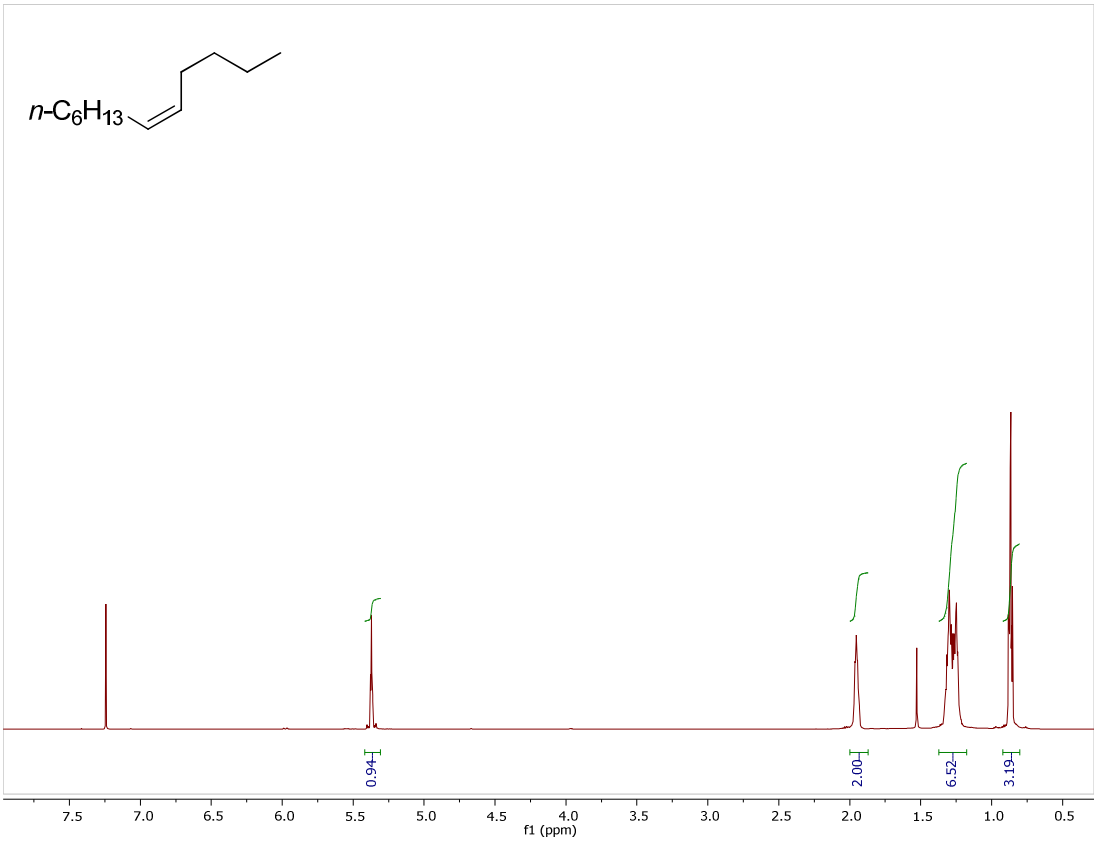
Synthesized following the procedure found in Lipshutz, B. H.; Kell, R.; Ellsworth, E. L. *Tetrahedron Lett.* **1990,** *31,*7257.

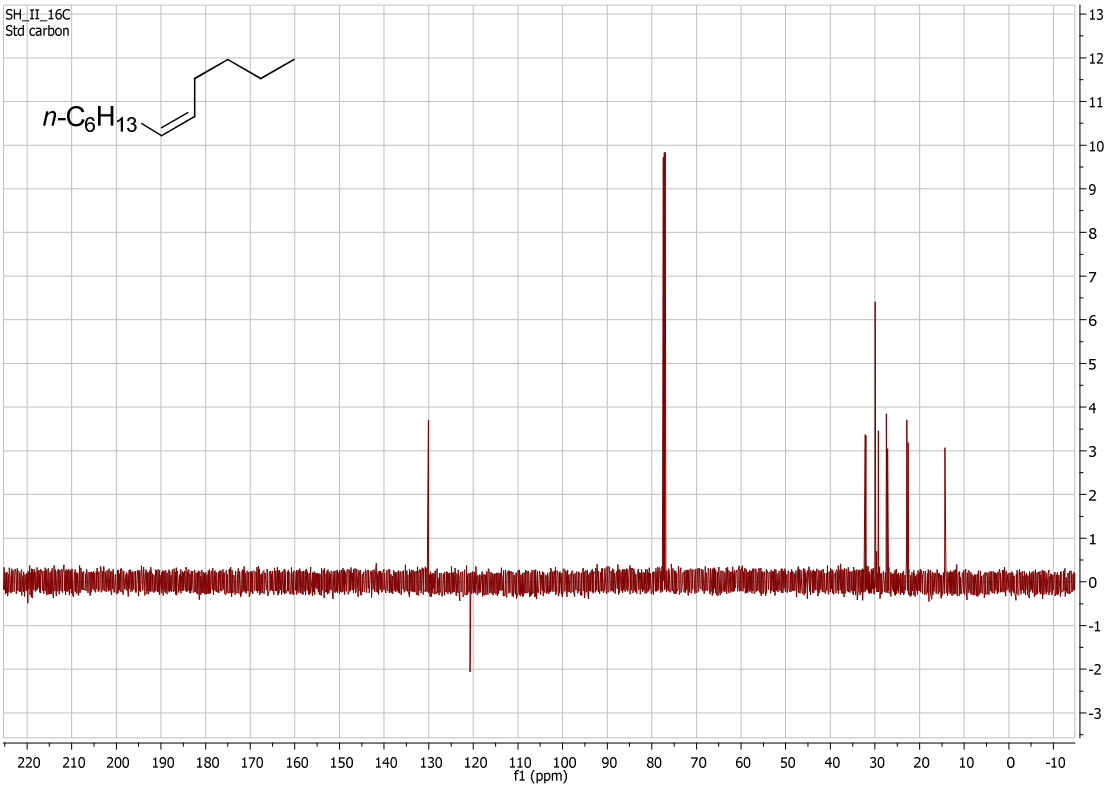
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.24 (m, 1H), 6.14 – 6.09 (m, 1dH), 3.74 (t, *J* = 6.4 Hz, 2H), 2.35 – 2.23 (m, 2H), 1.23 – 0.92 (m, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.23, 106.08, 62.46, 36.81, 18.28, 12.24; HRMS(EI) calcd. for $C_{13}H_{27}BrOSi$ $(M-C_3H_7)^+$: 263.0467; found: 263.0467.

1. Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3333.
2. Krasovskiy, A.; Knochel. P. S*ynthesis*, **2006**, *5*, 890.

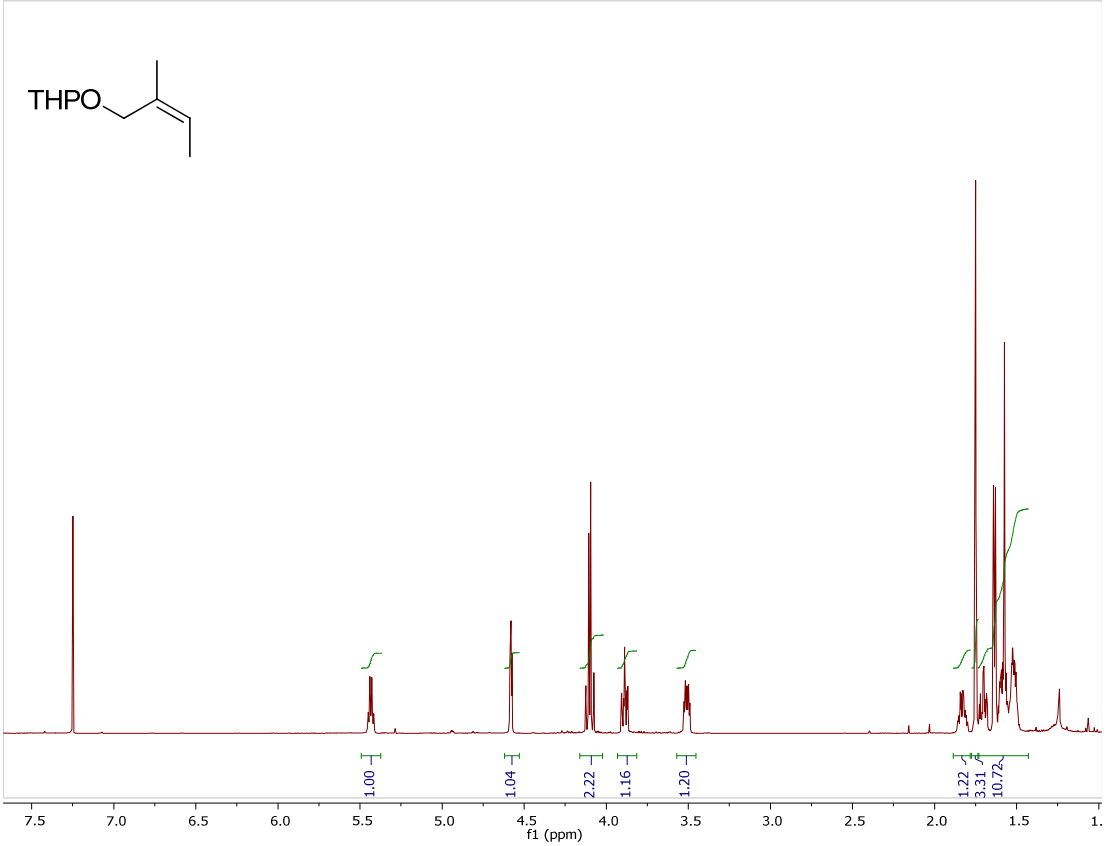
NMR's

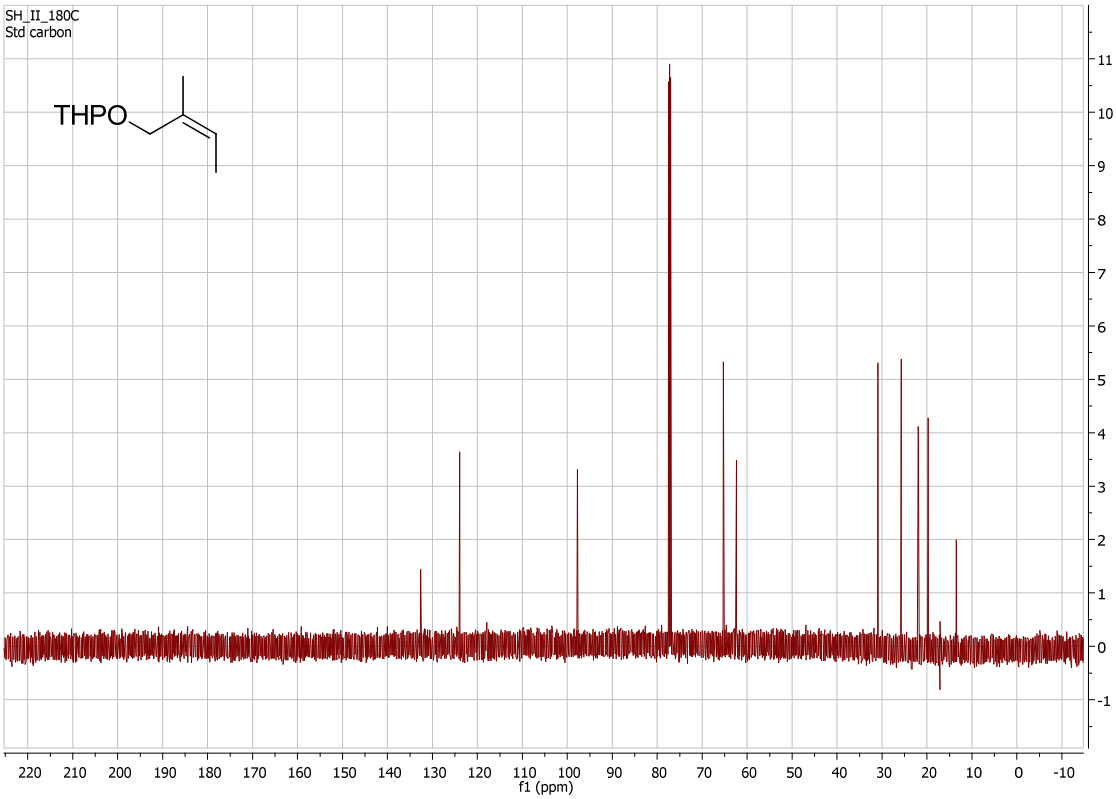
(*Z*)-Dodec-5-ene (2)



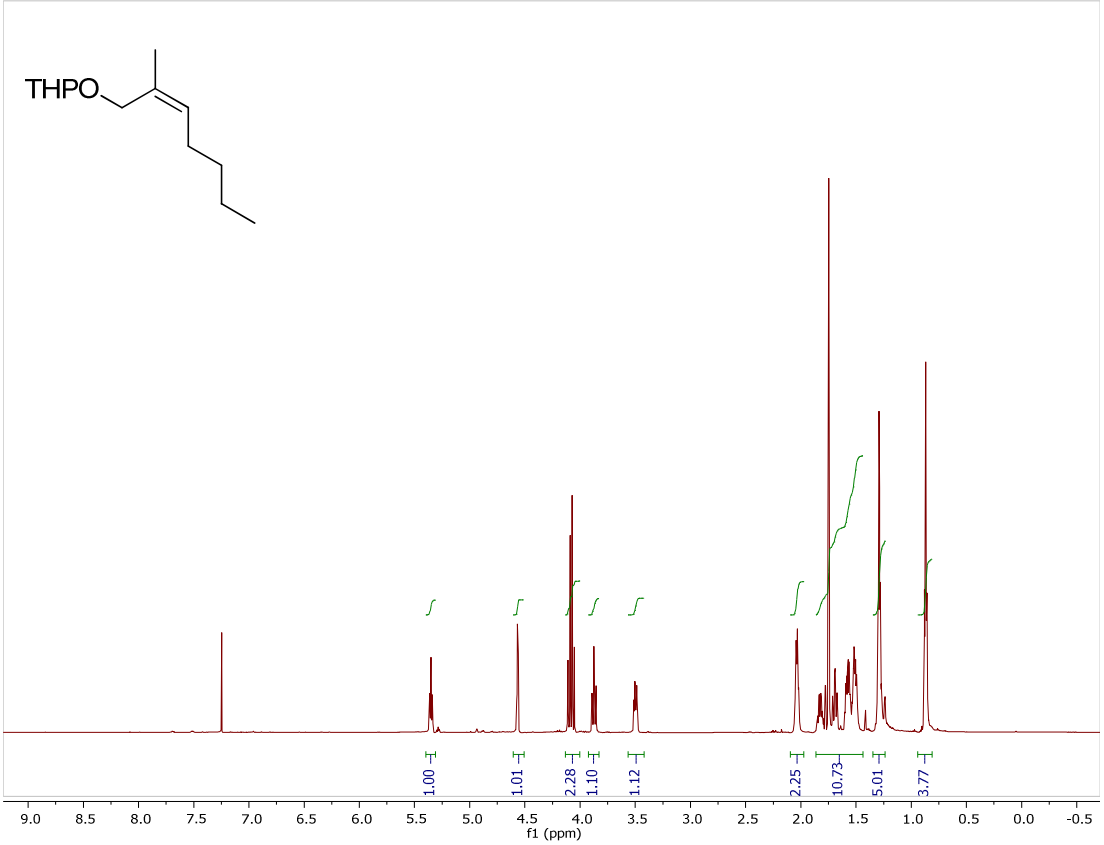


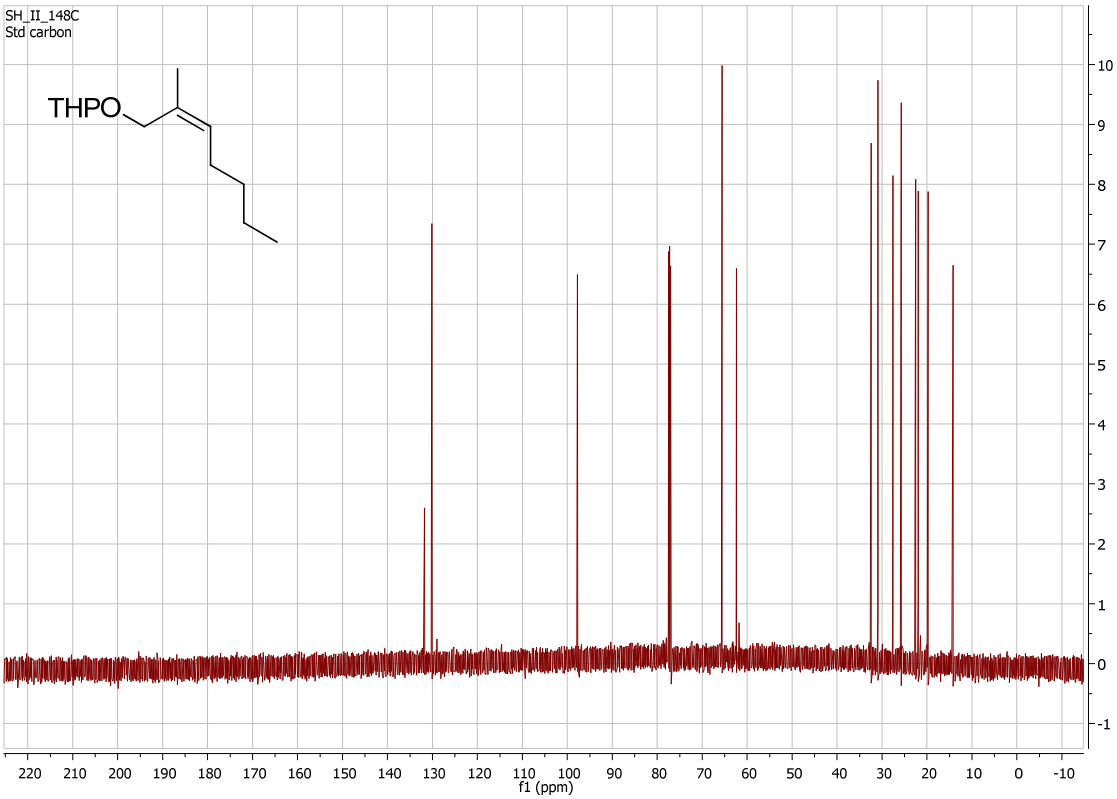
(*Z*)-2-((2-Methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (12)



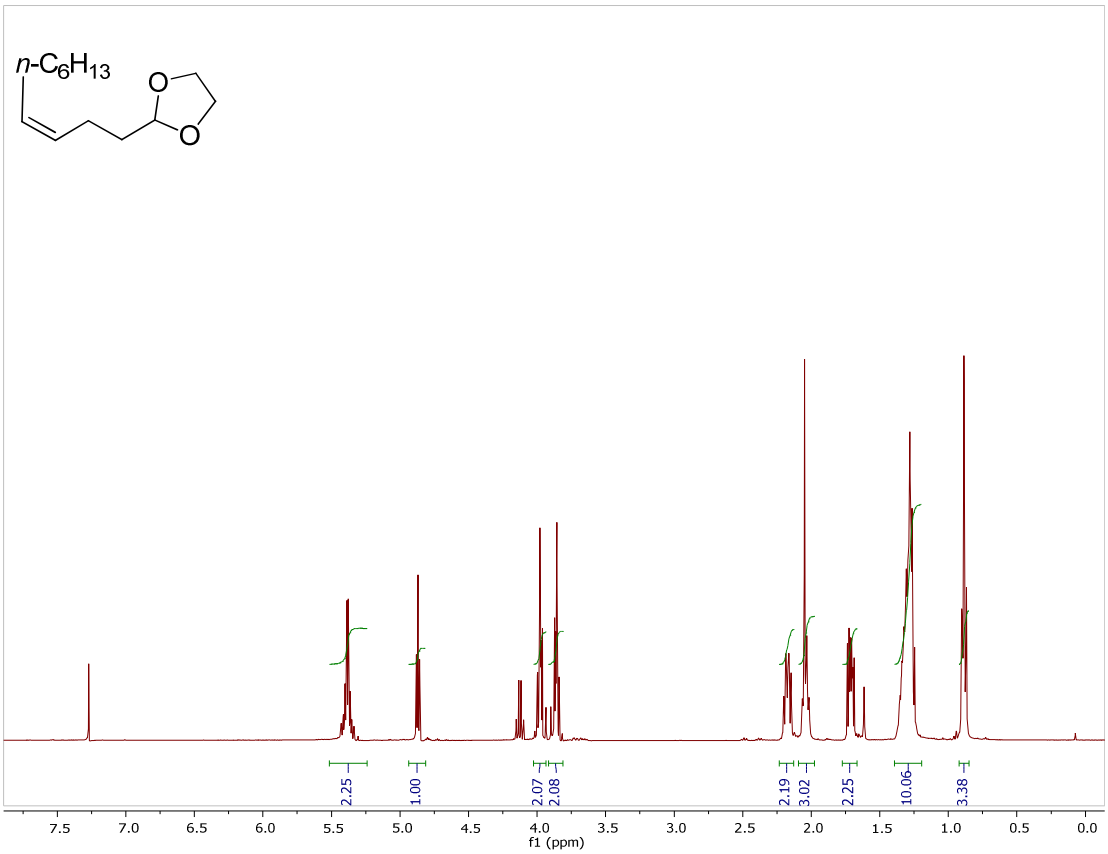


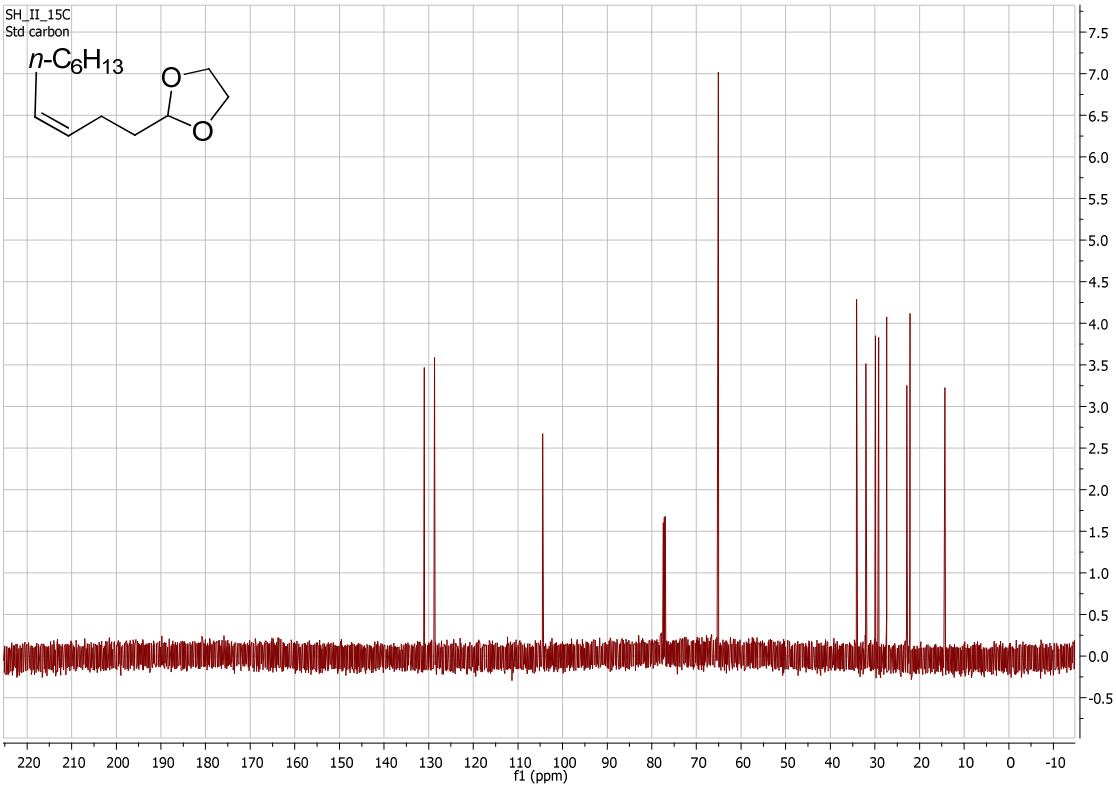
(*E*)-2-((2-Methylhept-2-en-1-yl)oxy)tetrahydro-2H-pyran (14)



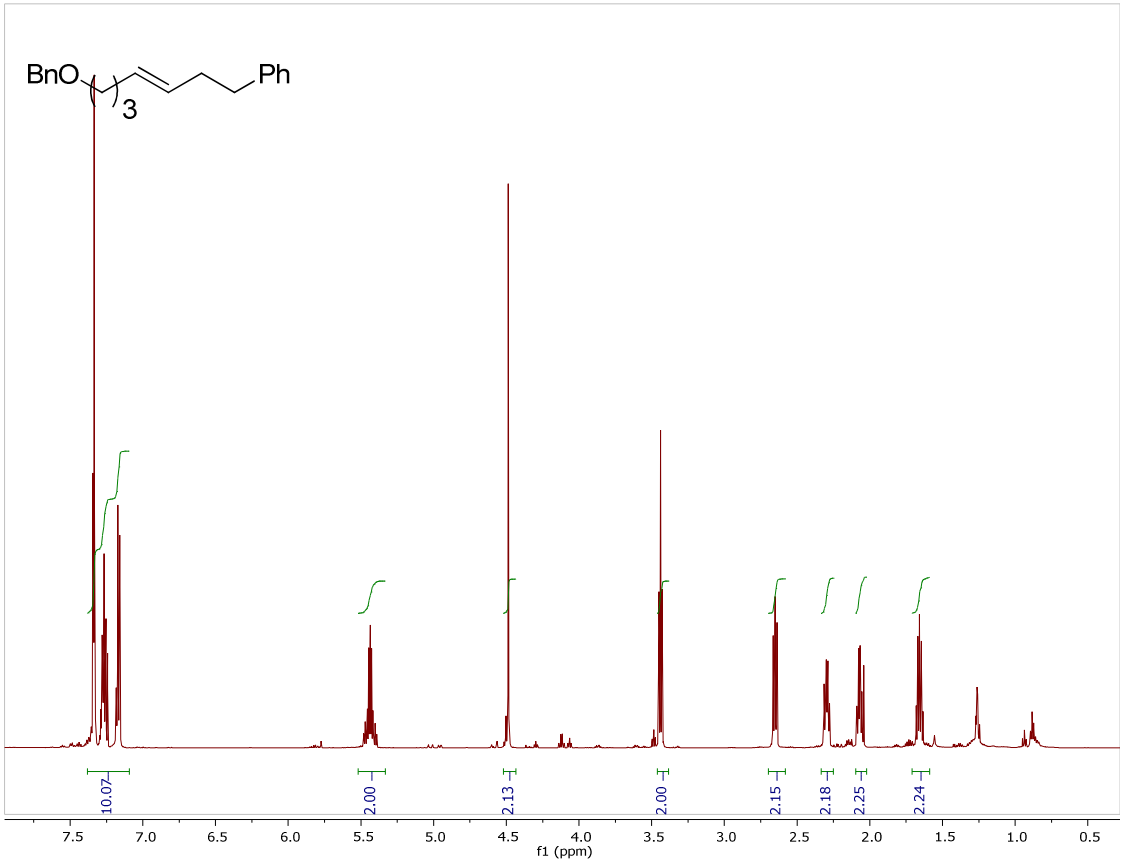


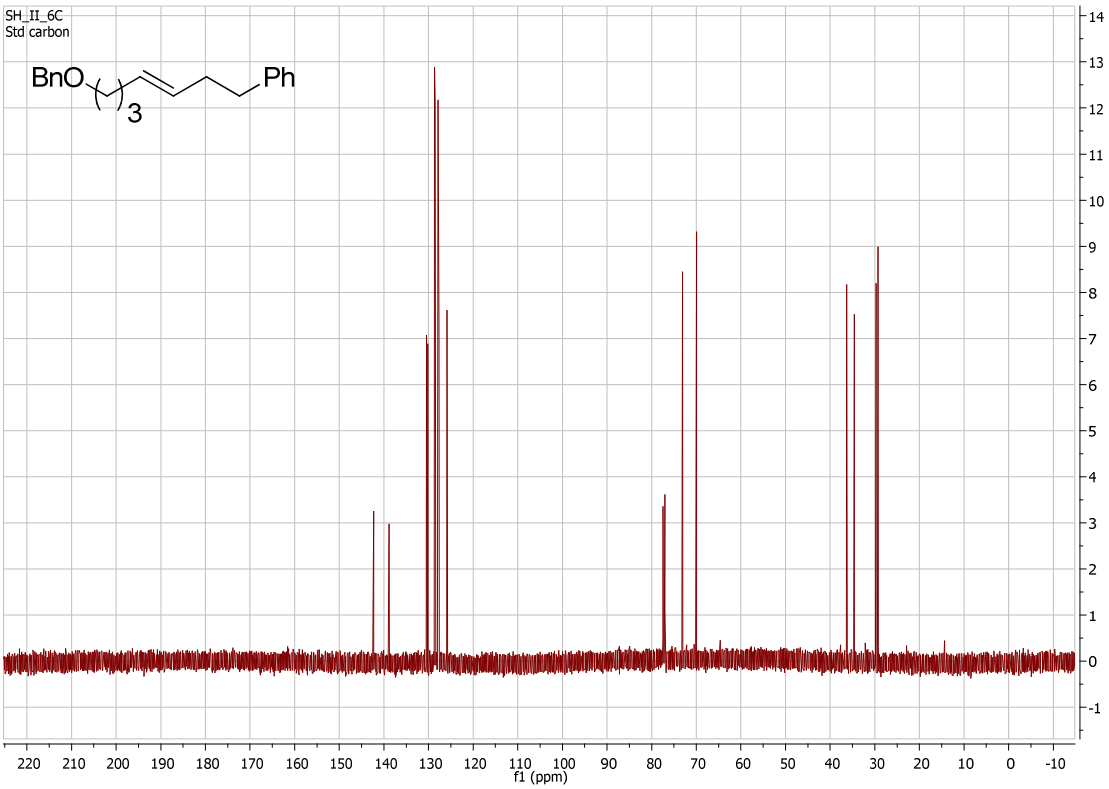
(*Z*)-2-(Dec-3-en-1-yl)-1,3-dioxolane (16)



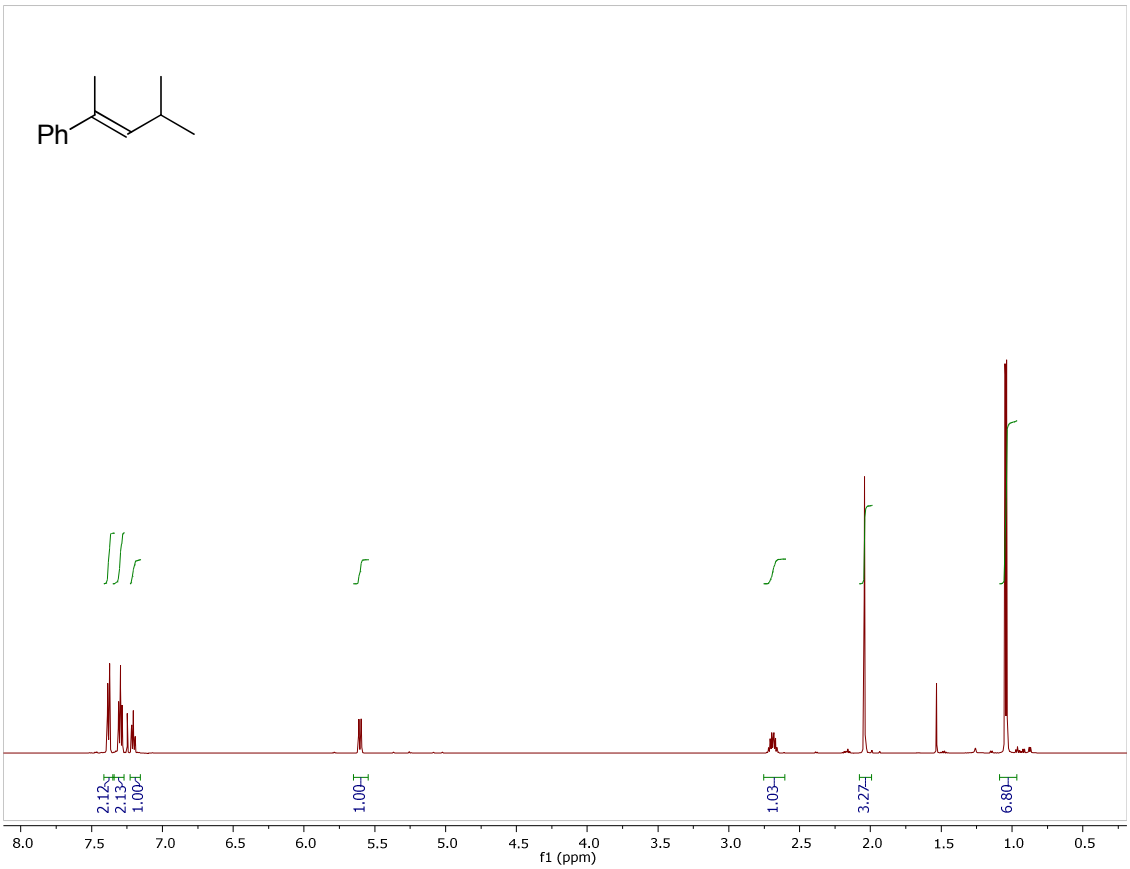


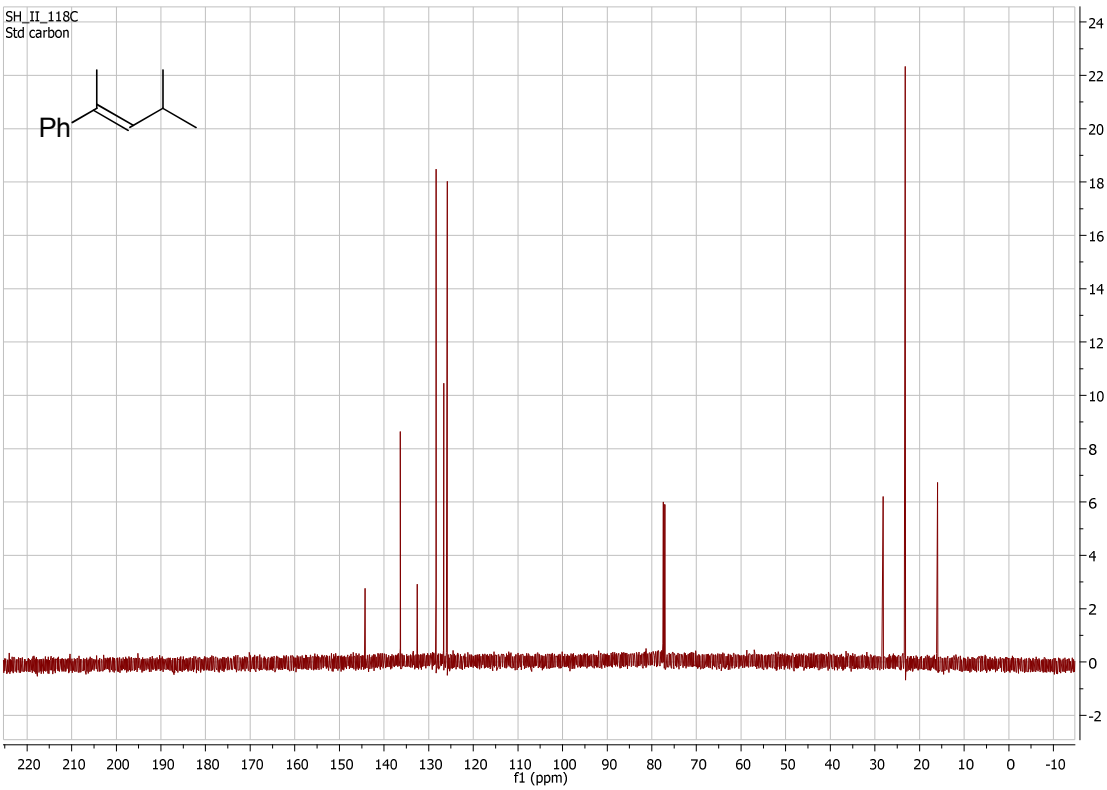
(*E*)-(7-(Benzyloxy)hept-3-en-1-yl)benzene (19)



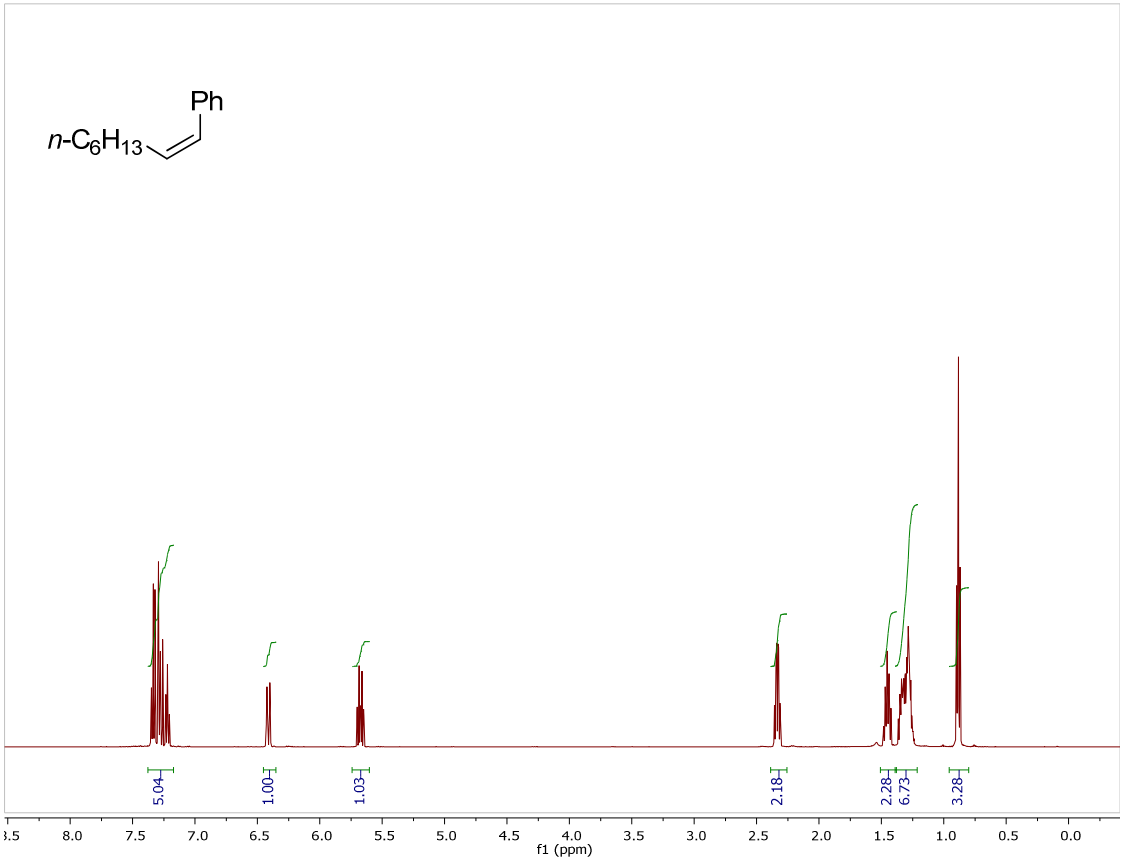


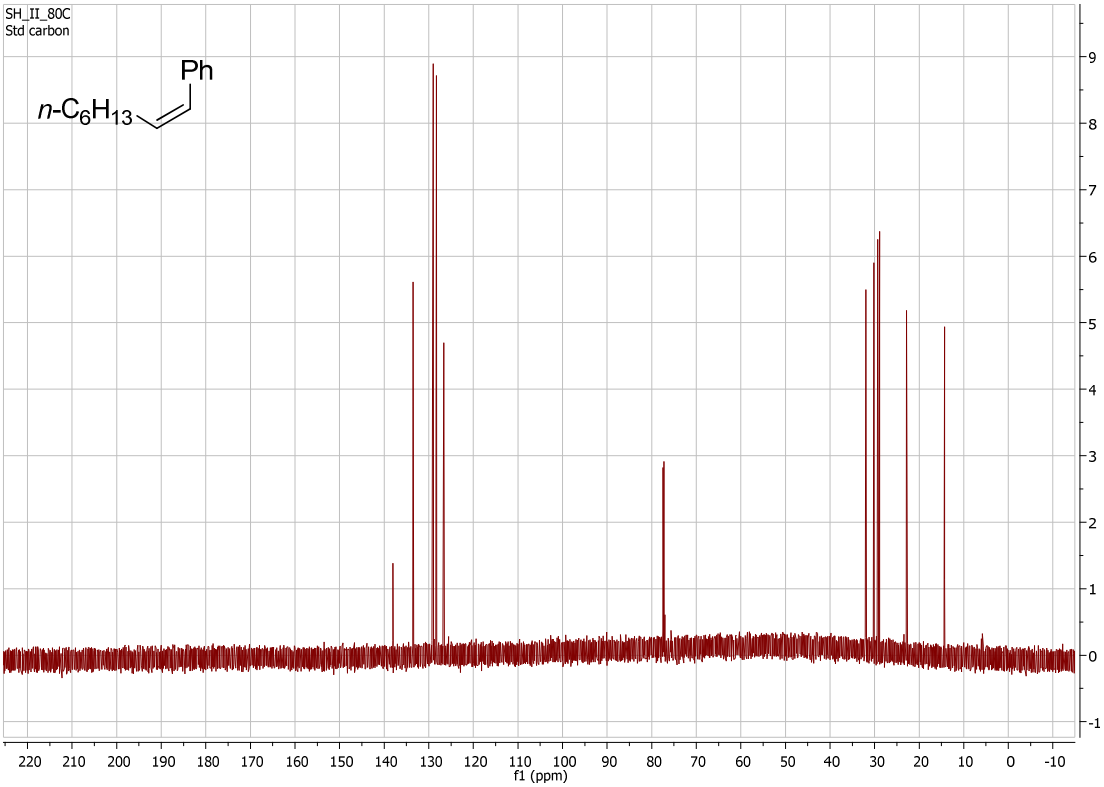
(*E*)-(4-Methylpent-2-en-2-yl)benzene (22)



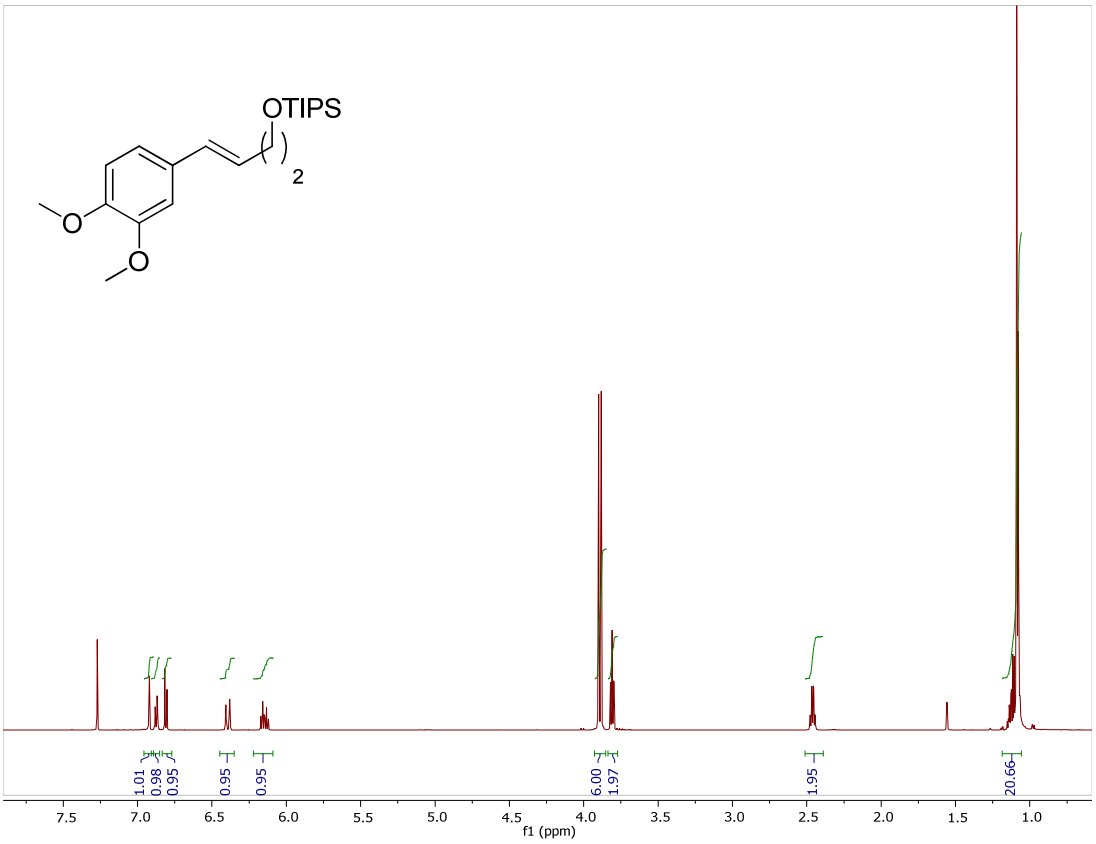


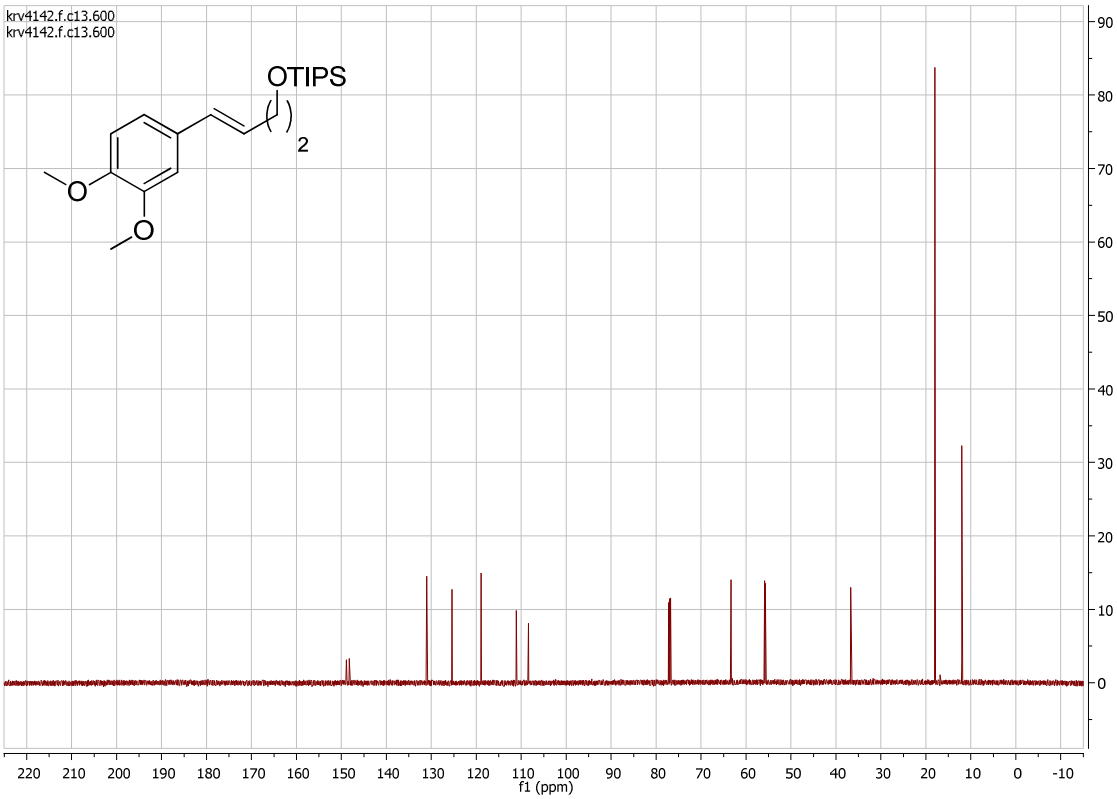
(*Z*)-Oct-1-en-1-ylbenzene (24)



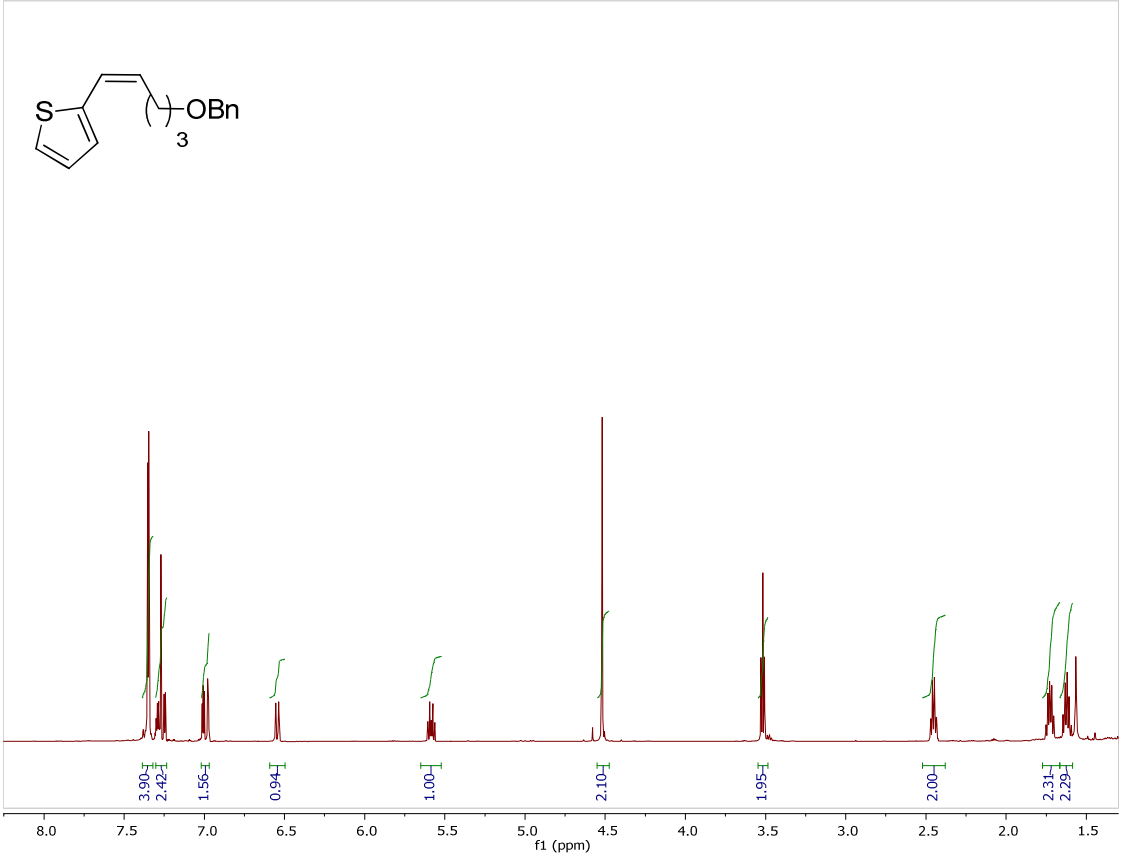


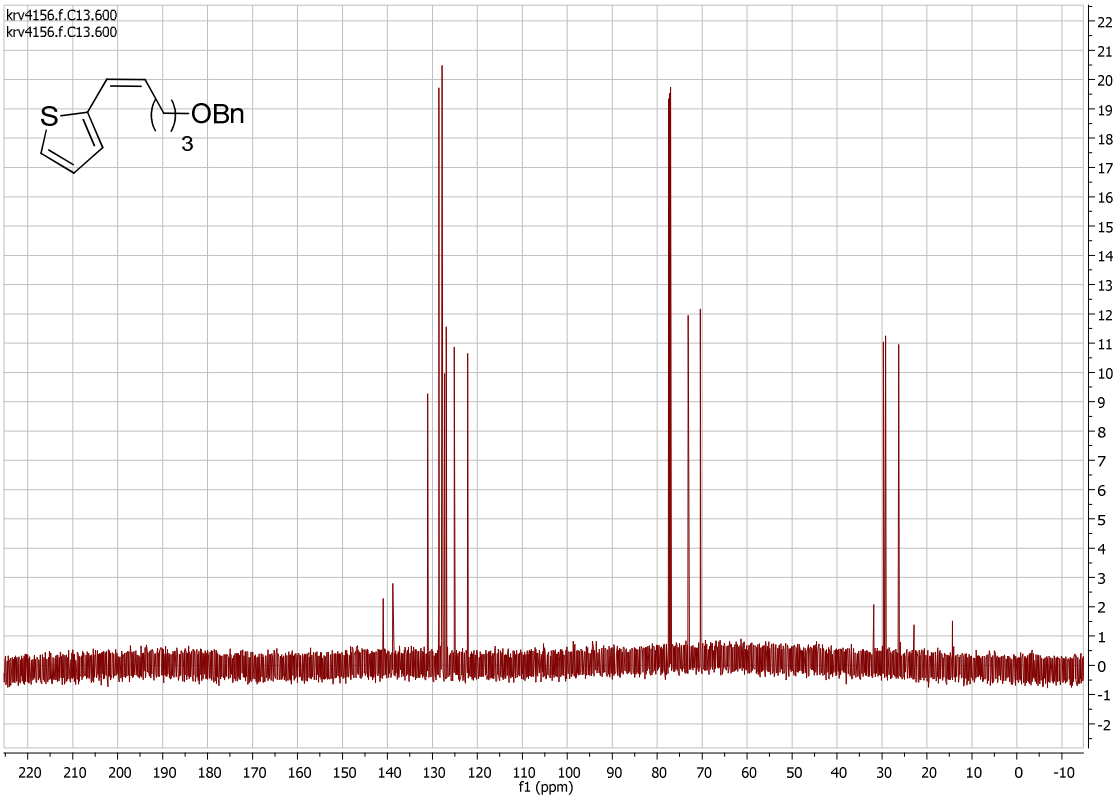
(*E*)-((4-(3,4-Dimethoxyphenyl)but-3-en-1-yl)oxy)triisopropylsilane (27)



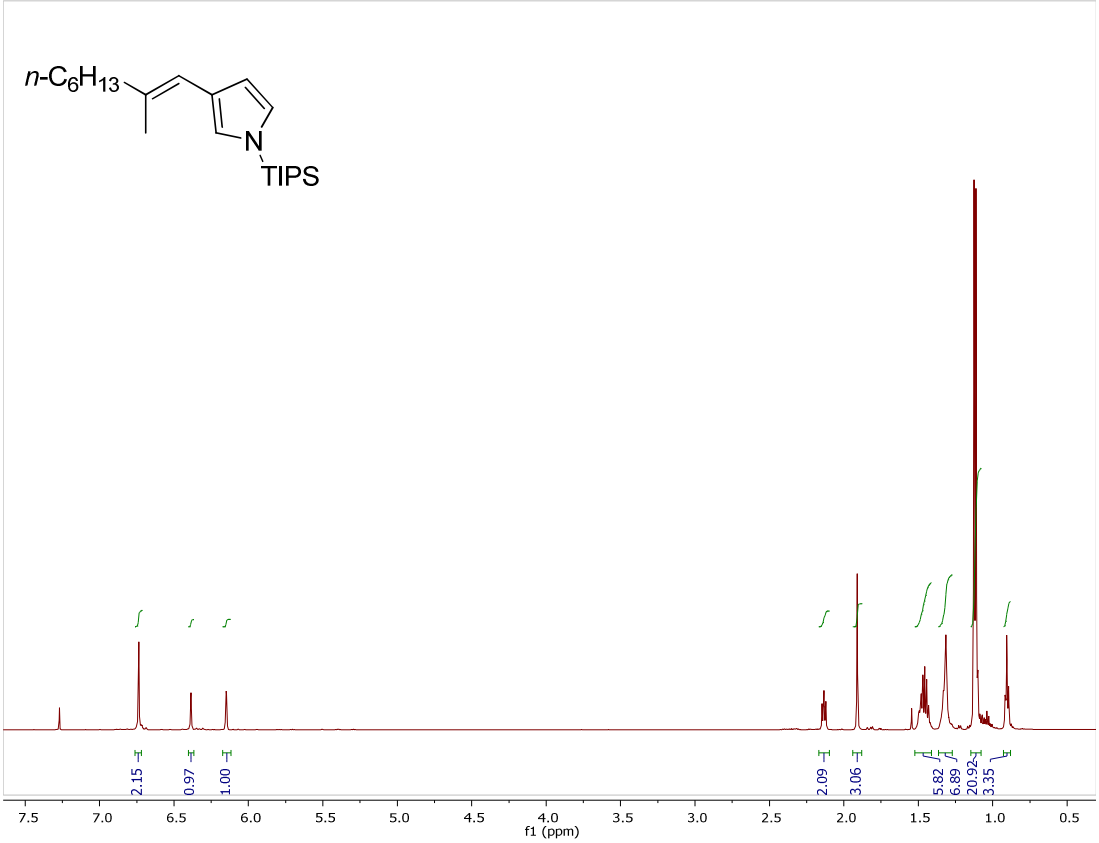


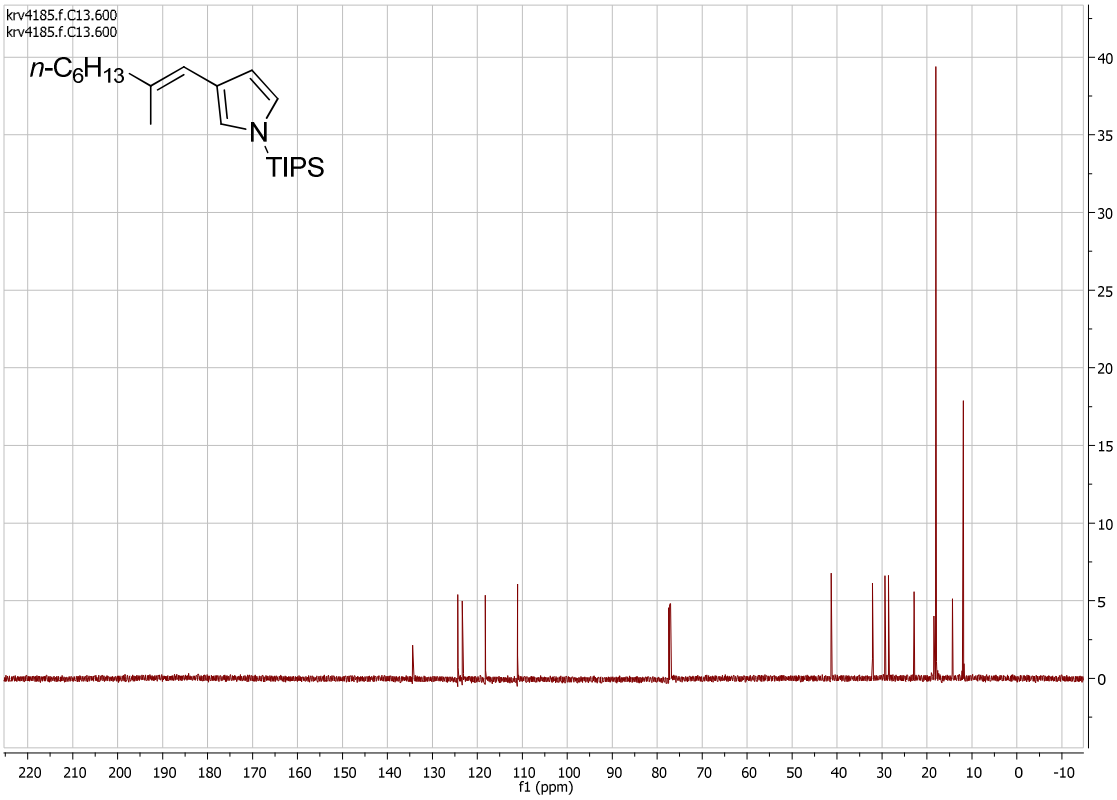
(*Z*)-2-(6-(Benzyloxy)hex-1-en-1-yl)thiophene (30)



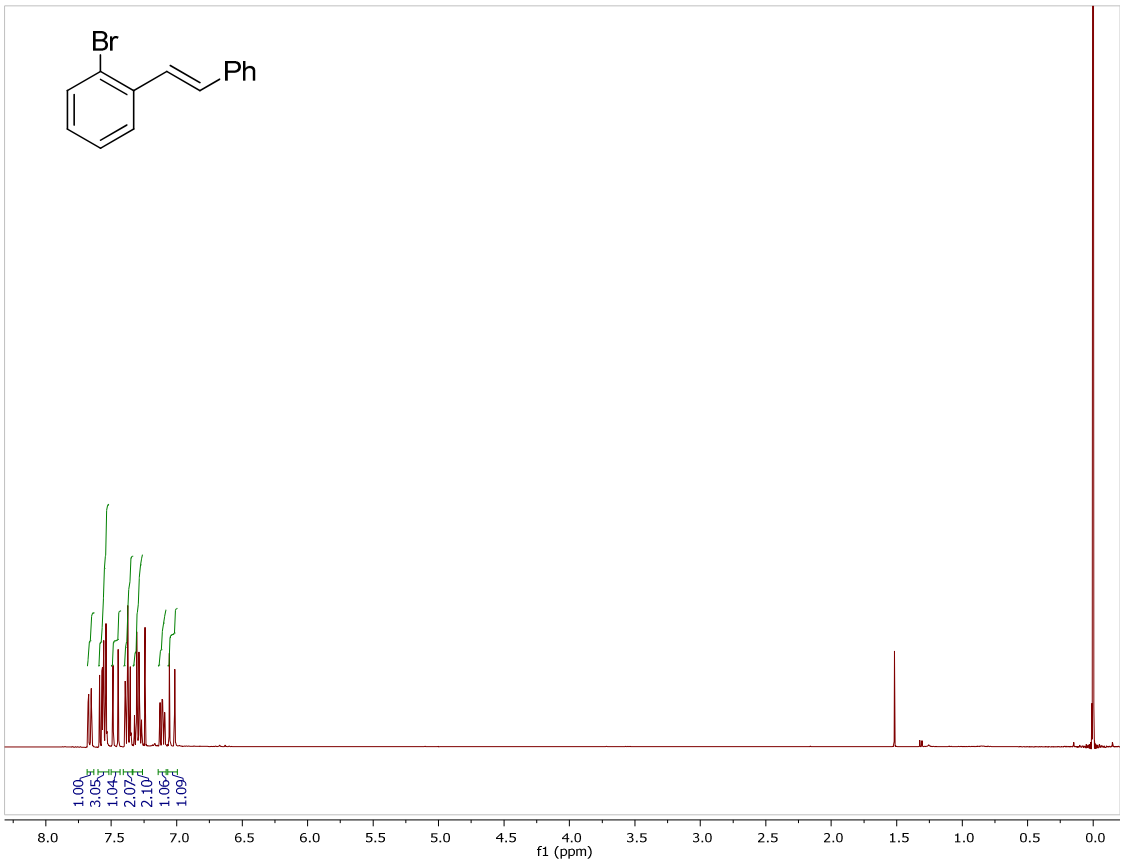


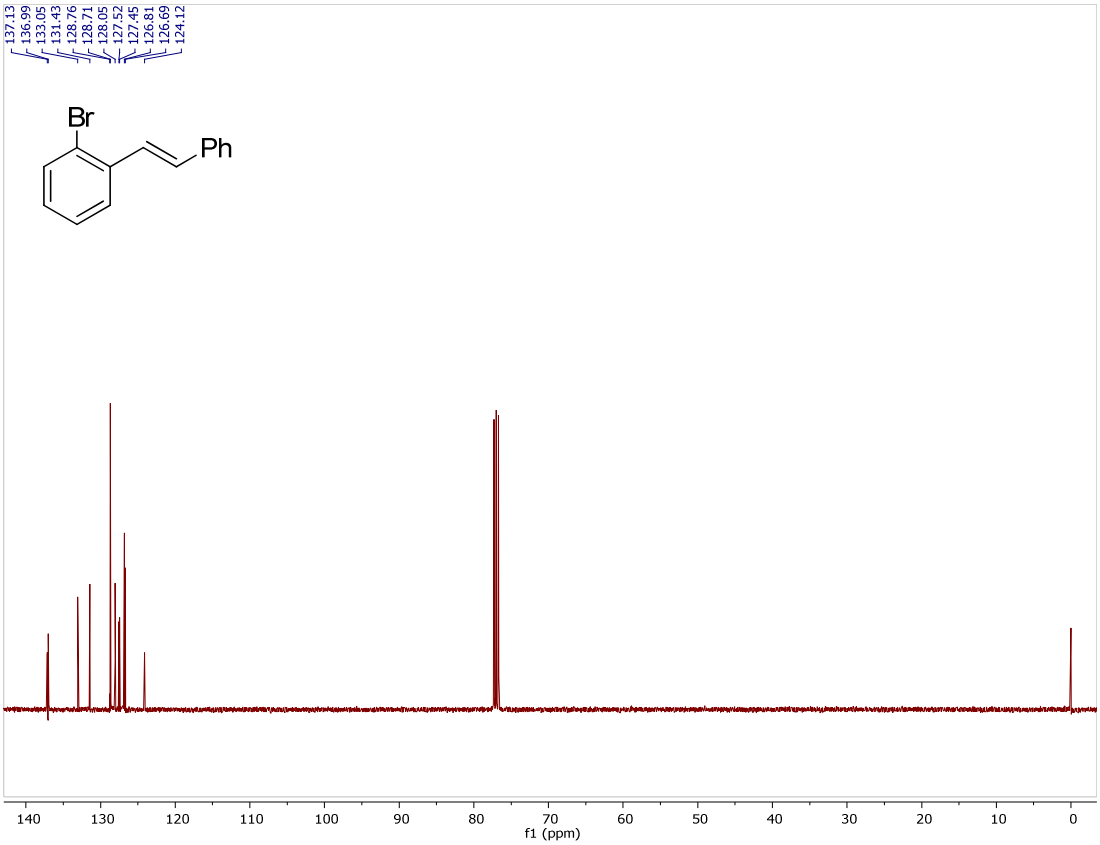
(*E*)-3-(2-Methyloct-1-en-1-yl)-1-(triisopropylsilyl)-1*H*-pyrrole (33)



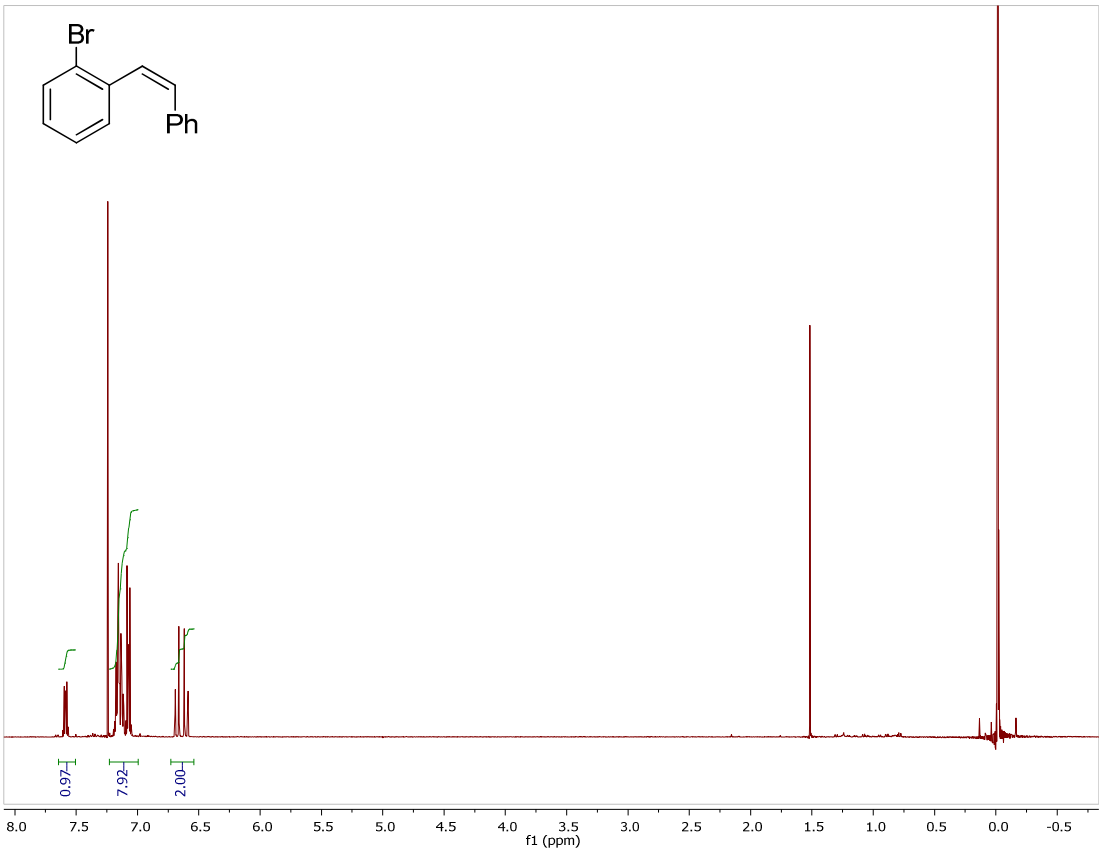


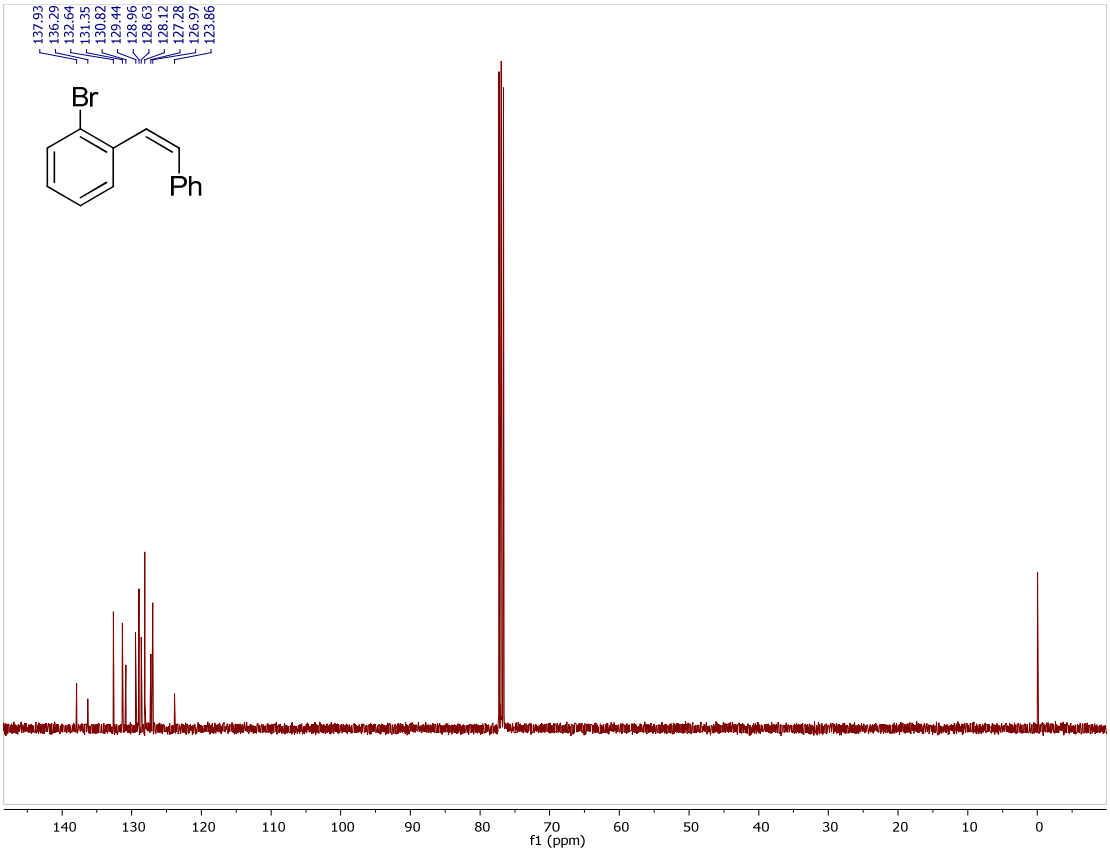
***(E)-1-bromo-2-styrylbenzene* (36)**



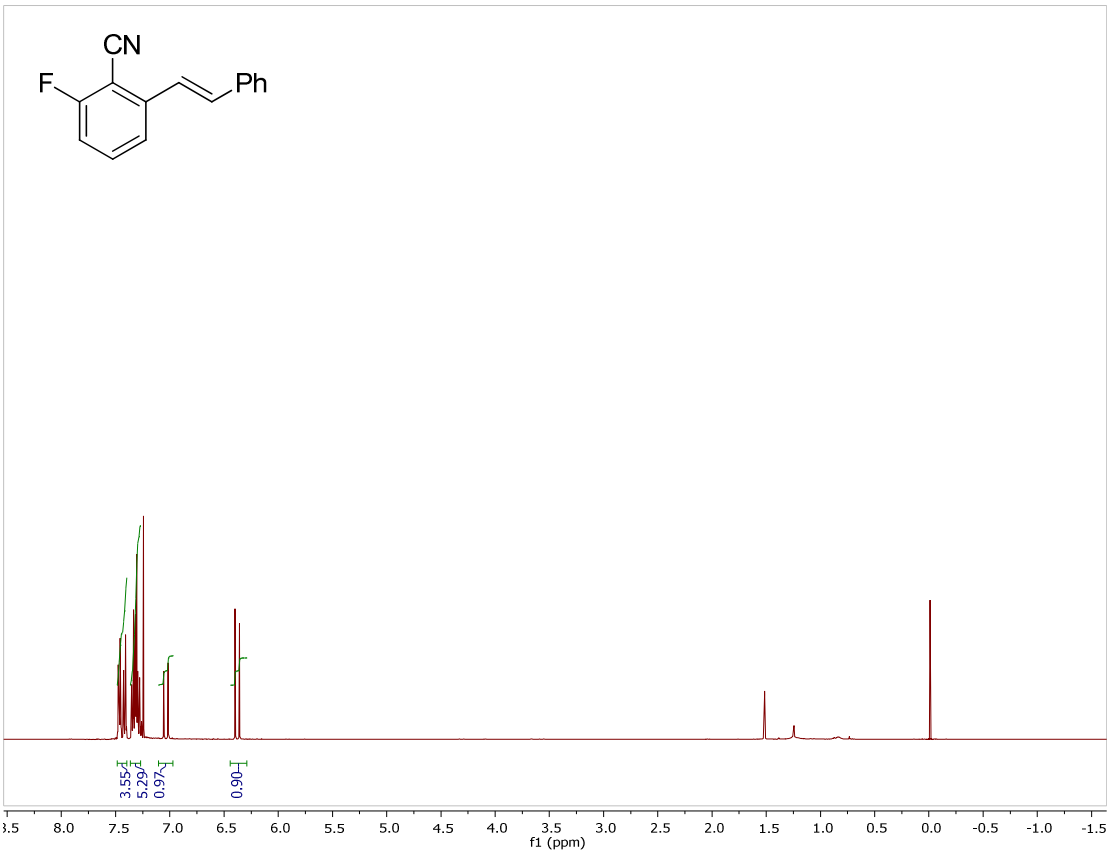


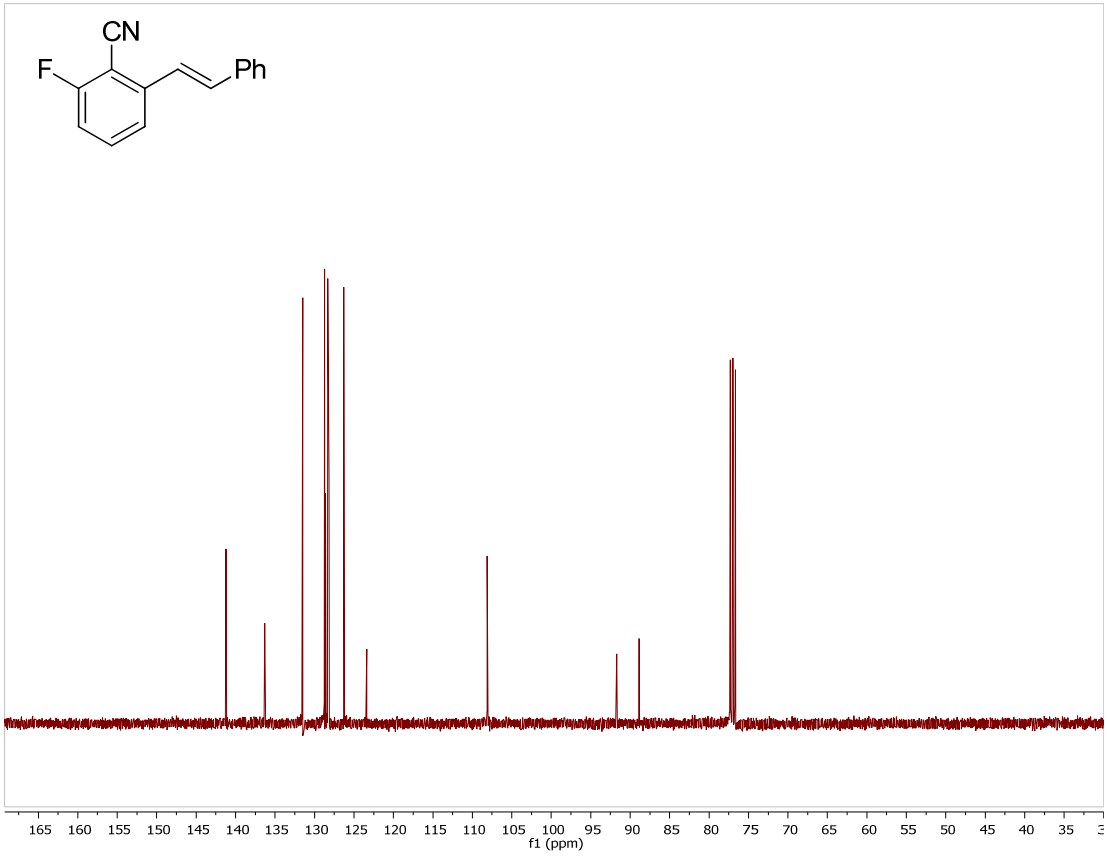
***(Z)-1-bromo-2-styrylbenzene* (38)**



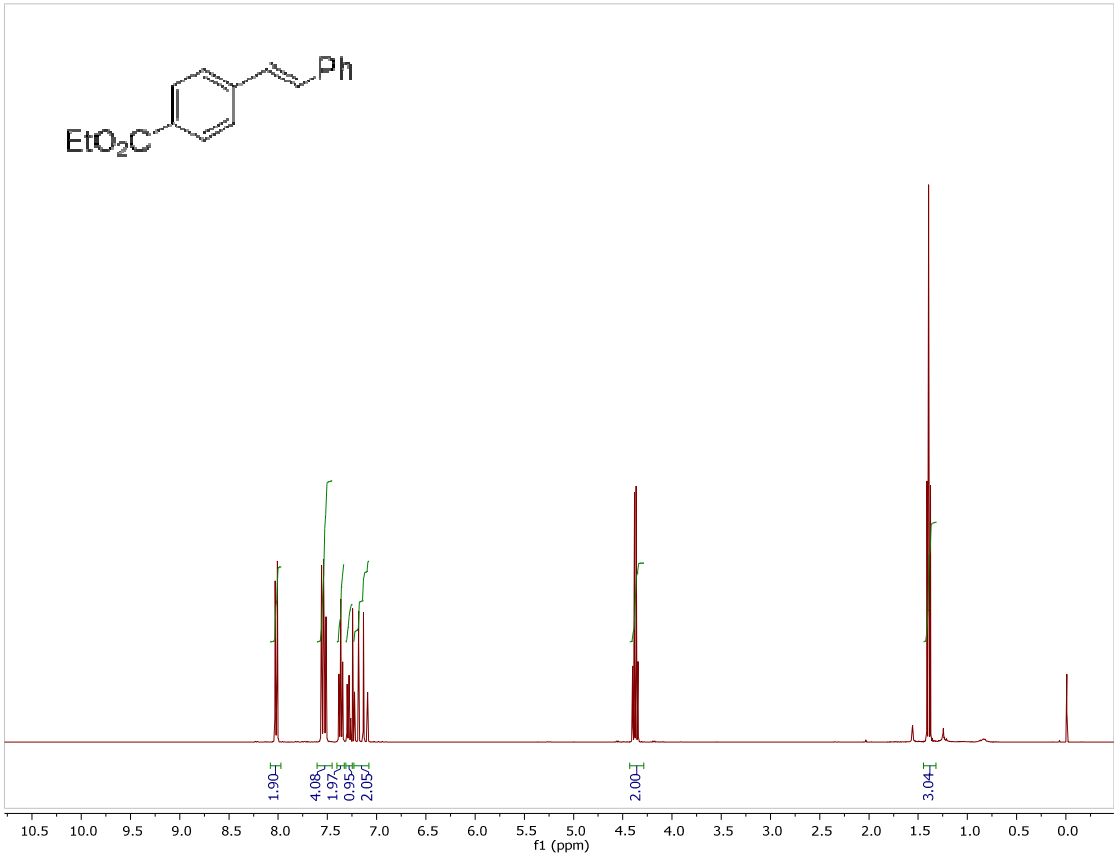


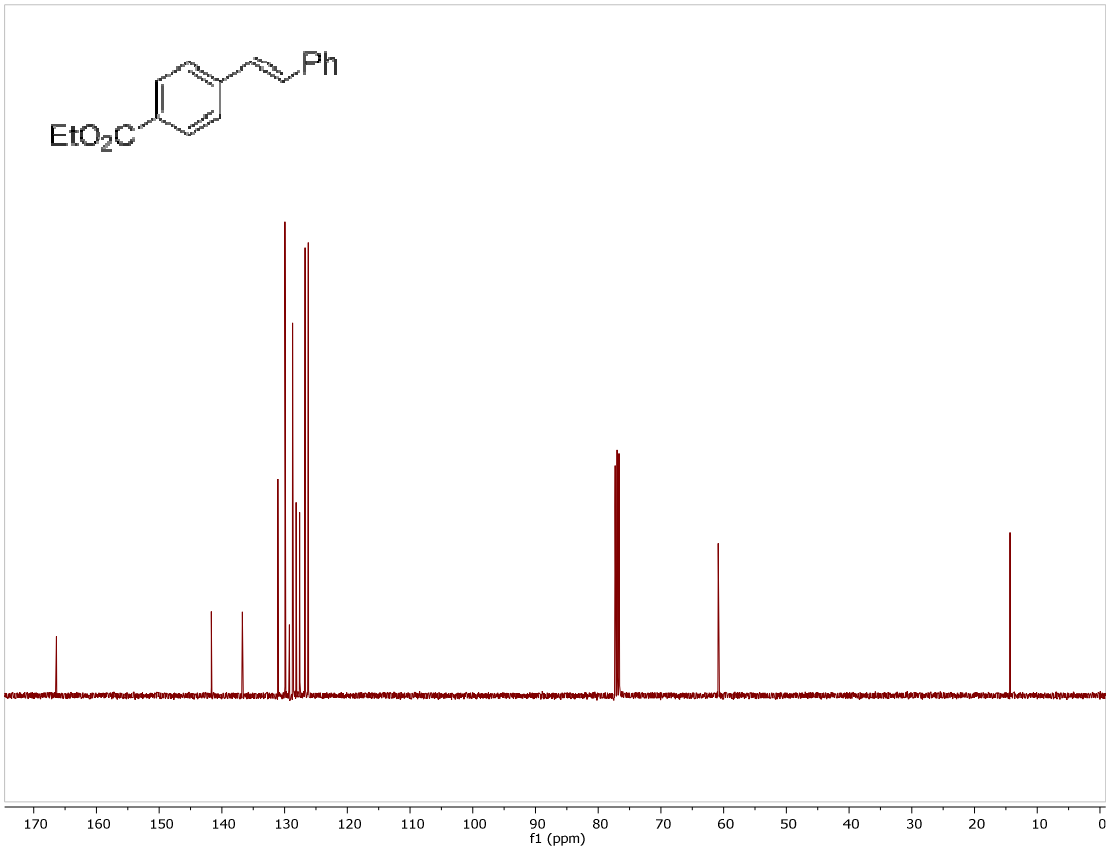
***(E)-2-fluoro-6-styrylbenzonitrile* (40)**



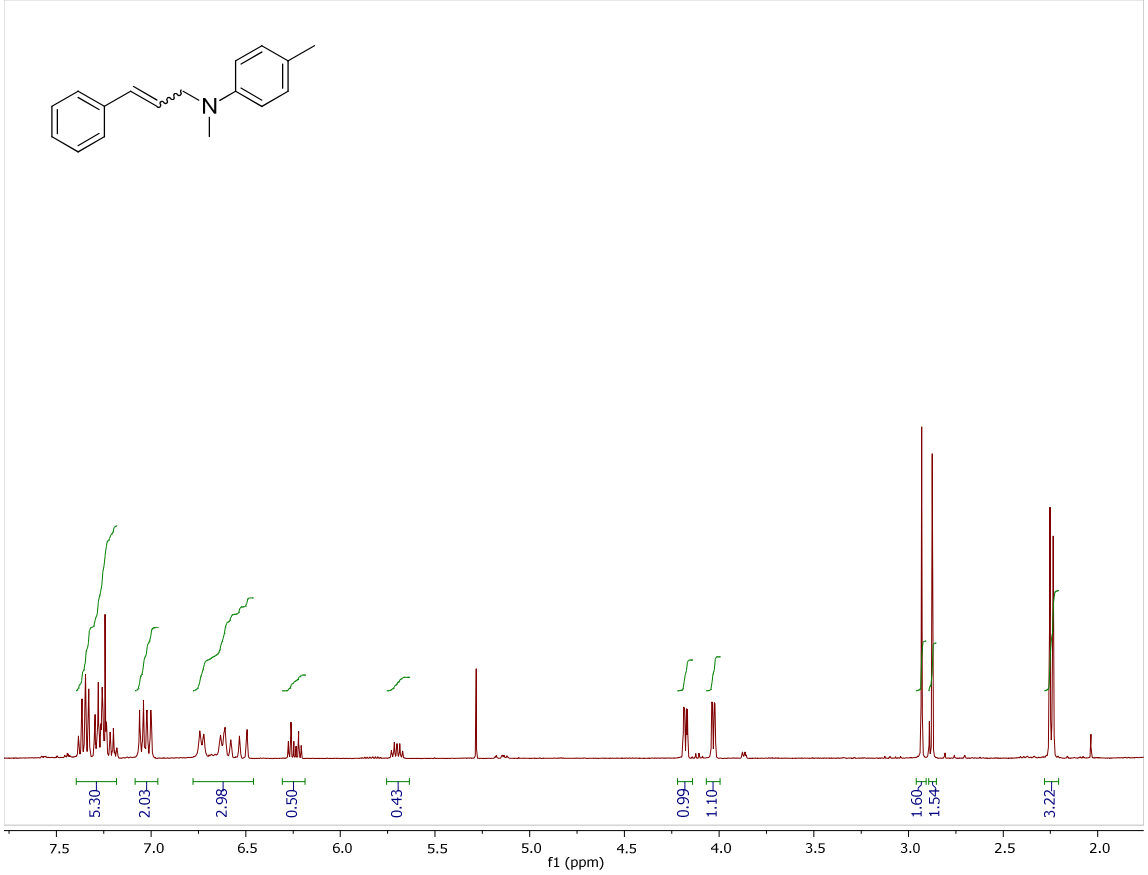


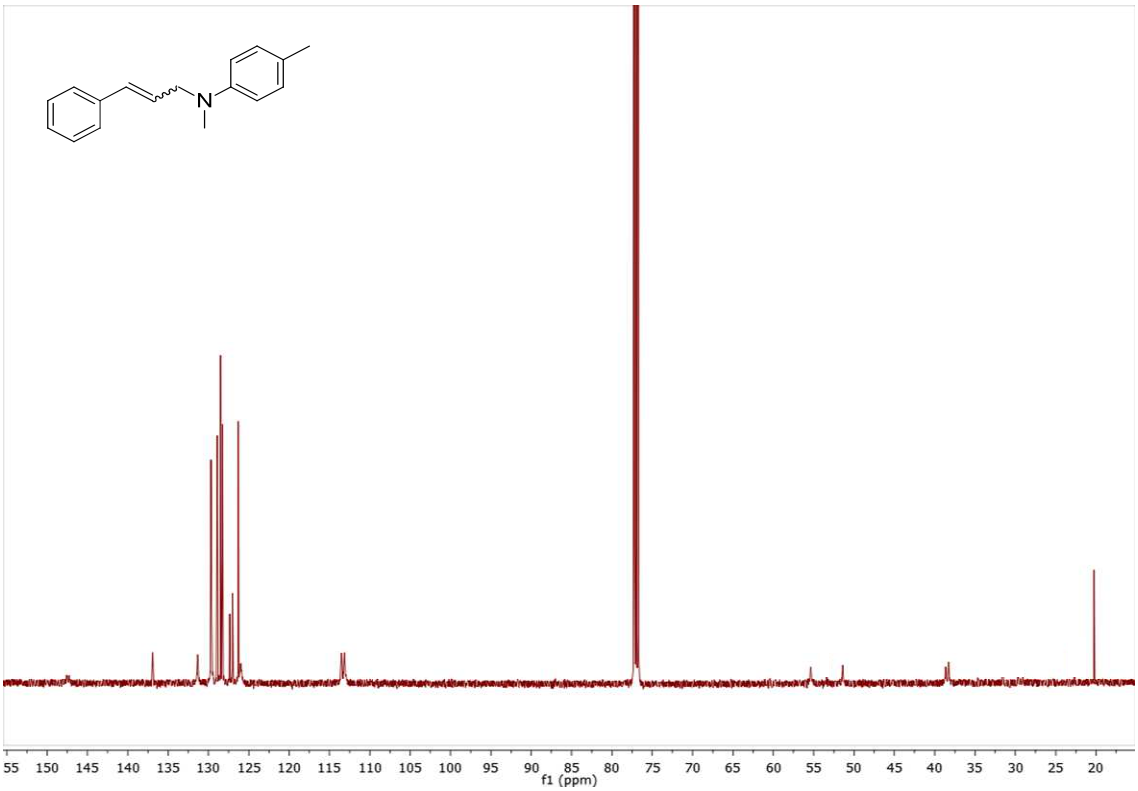
***(E)-ethyl 4-styrylbenzoate* (42)**



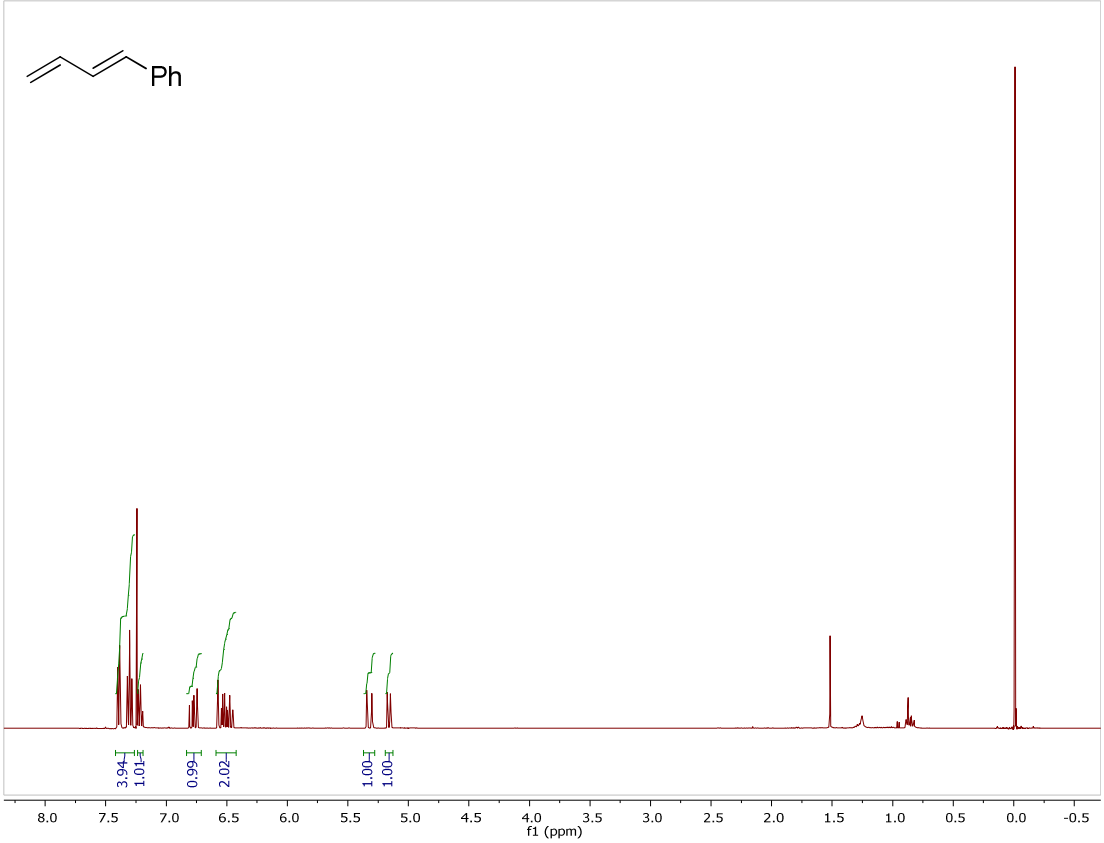


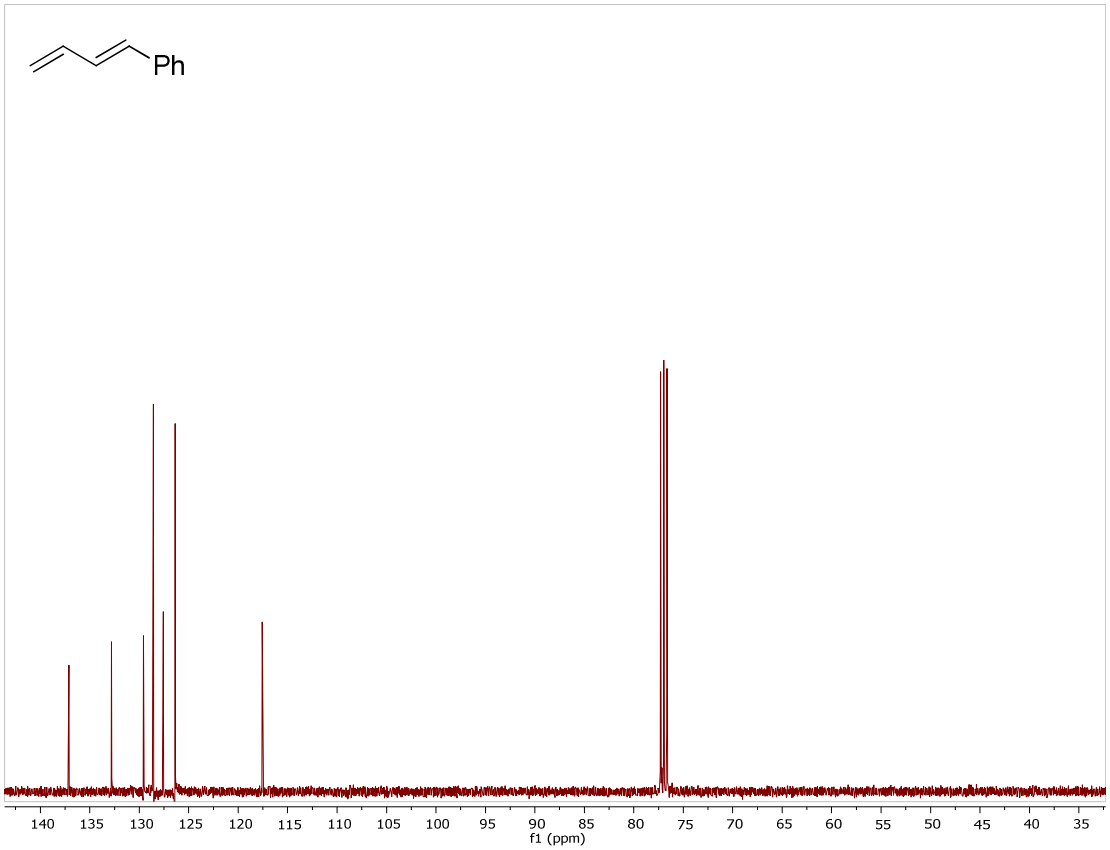
N,4-dimethyl-N-(3-phenylallyl)aniline (45) mixture of *E/Z* isomers 1/1



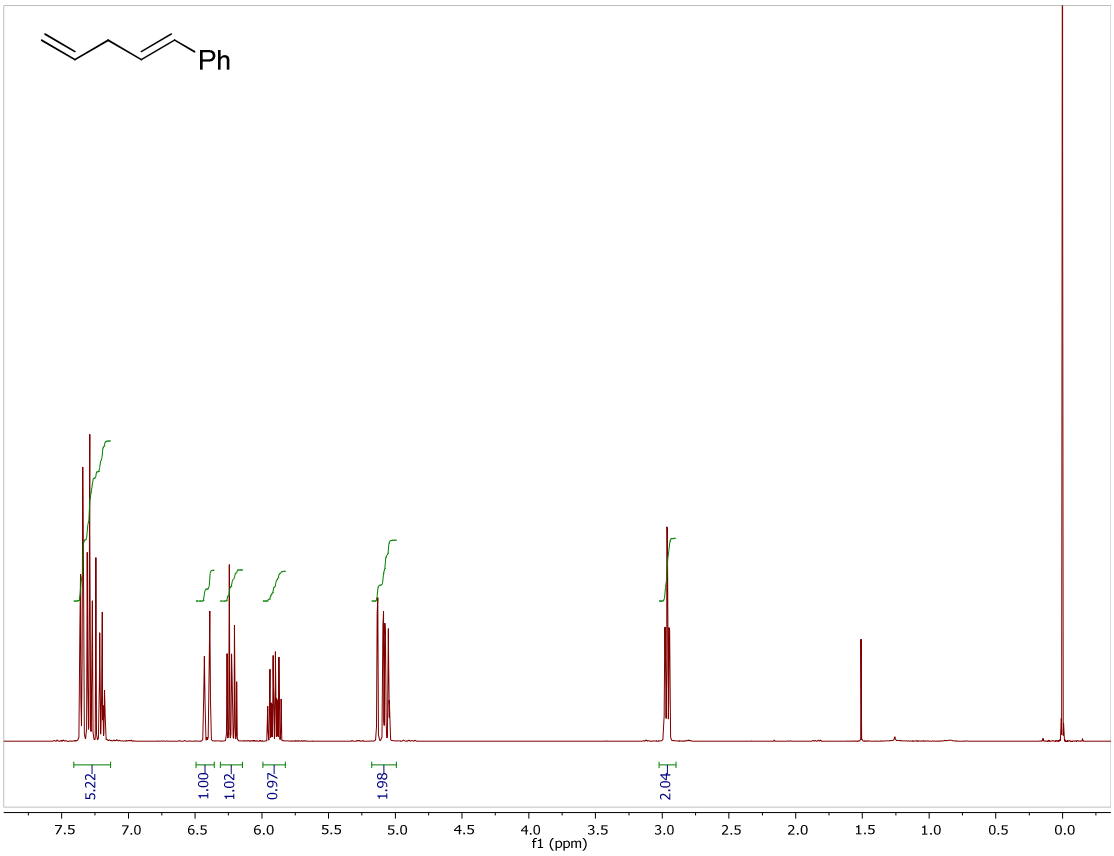


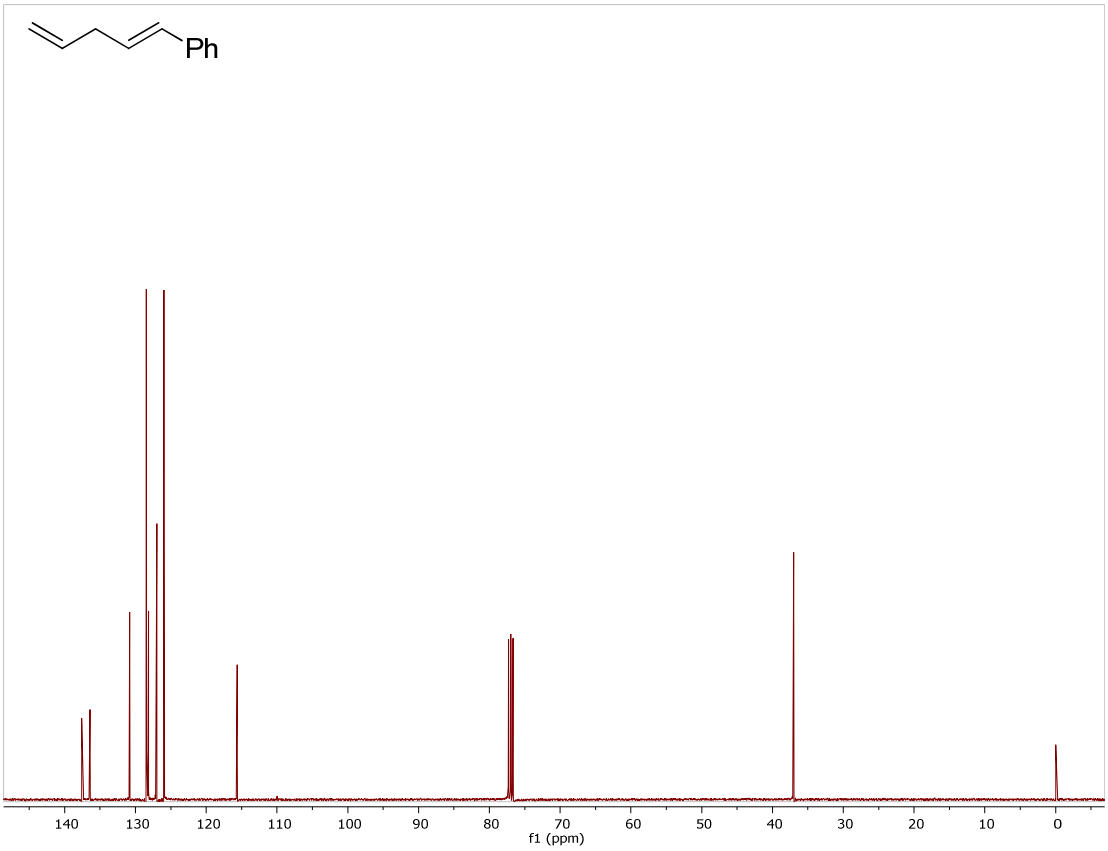
***(E)-buta-1,3-dien-1-ylbenzene* (47)**



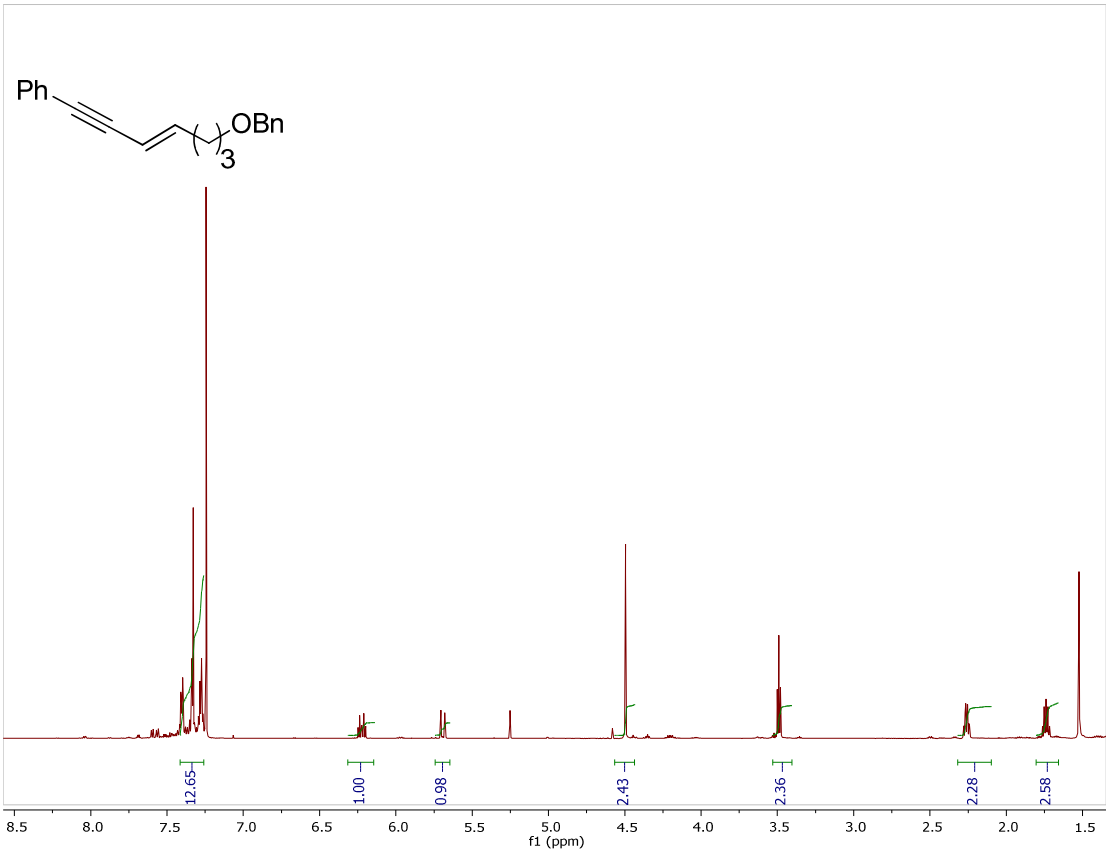


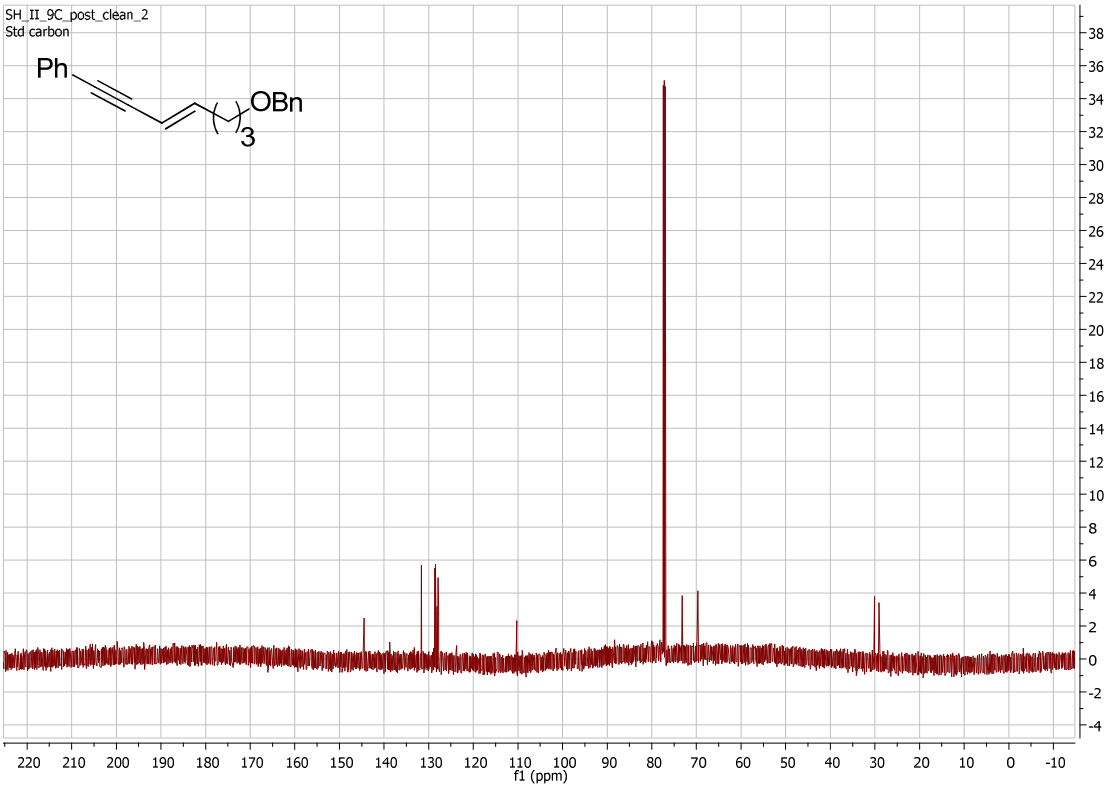
***(E)-penta-1,4-dien-1-ylbenzene* (49)**



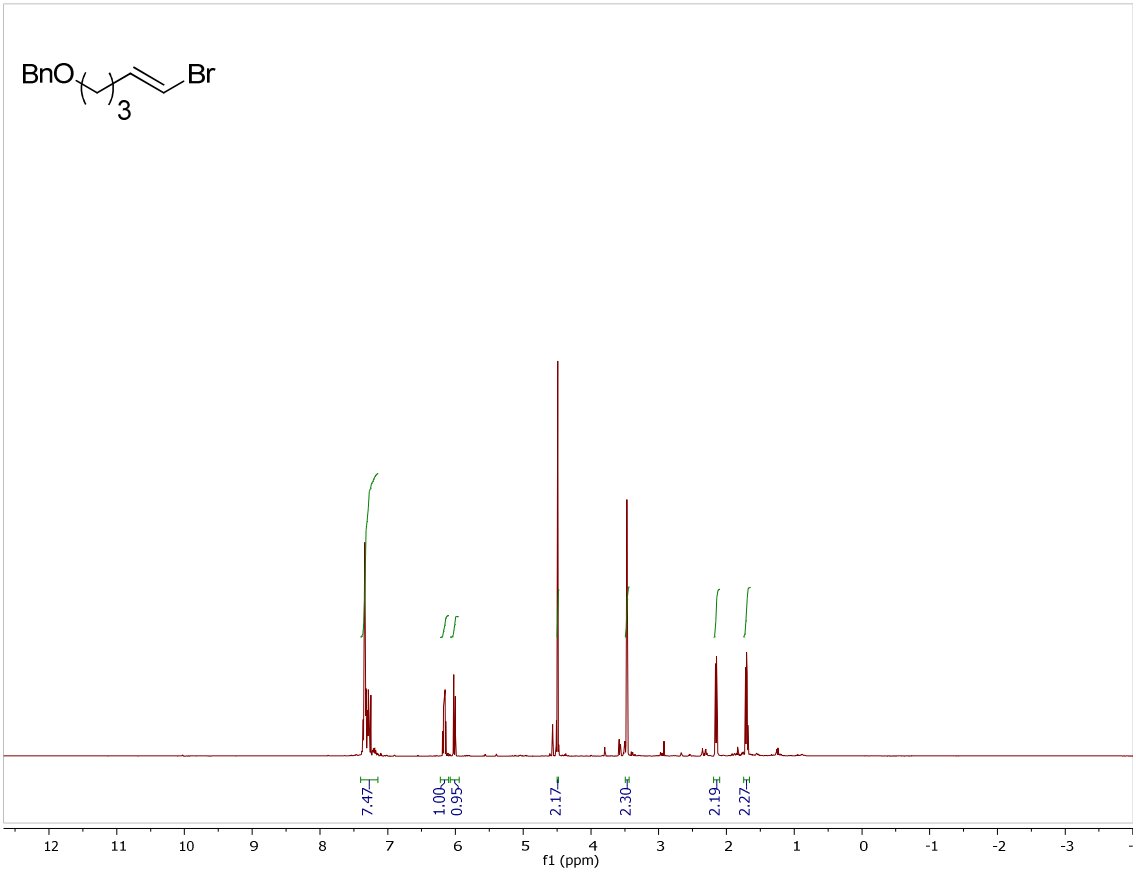


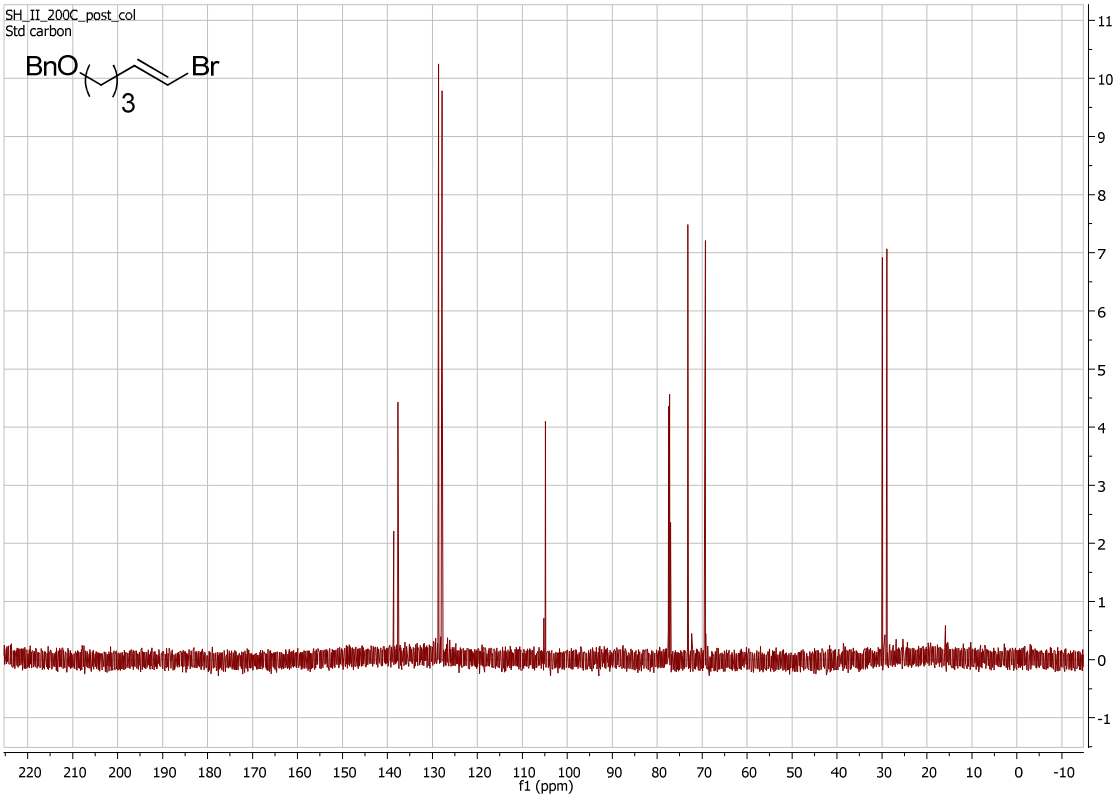
(*E*)-(7-(Benzyloxy)hept-3-en-1-yn-1-yl)benzene (51)





(*E*)-(((5-bromopent-4-en-1-yl)oxy)methyl)benzene (18)





(*E*)-((4-bromobut-3-en-1-yl)oxy)triisopropylsilane (26)