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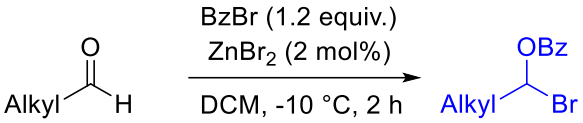
## I. General Information

All chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, or TCI and were distilled before use. Zn and LiCl were dried under vacuum at 170 °C for 30 min. $CH_2Cl_2$ and THF were dried and degassed with $N_2$ using an Innovative Technology solvent drying system. Flash column chromatography was performed with Silicycle F60 (230-400 mesh) silica gel either manually or automated by CombiFlash chromatograph. Thin layer chromatography (TLC) analyses were performed using Merck silica gel 60 F254 plates and visualized by UV (254 nm), $KMnO_4$, or $I_2$ stain. $^1H$, $^{19}F$, $^{31}P$, $^{13}C$ NMR spectra were recorded using a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer. $^1H$ NMR and $^{13}C$ NMR chemical shifts are reported in parts per million and referenced with respect to $CDCl_3$ ($^1H$: residual $CHCl_3$ at δ 7.26; $^{13}C$: $CDCl_3$ triplet at δ 77.16). $^1H$ NMR data are reported as chemical shifts (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, app = apparent), coupling constant (Hz), relative integral. $^{19}F$ NMR data are reported as chemical shifts (δ ppm). High resolution mass spectra were obtained using Bruker MicrOTOF (ESI).

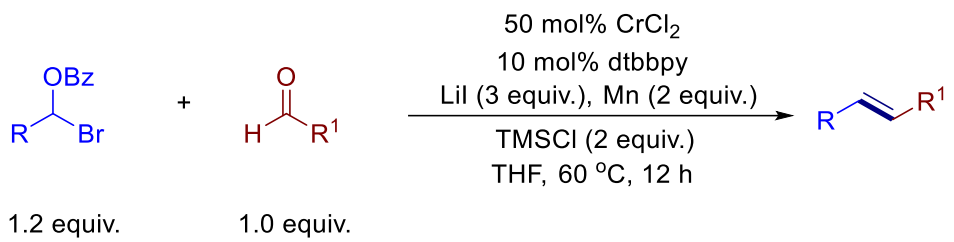
## II. General Procedures

**Alkyl Carbene Precursor**: General Procedure 1 (**GP1**)



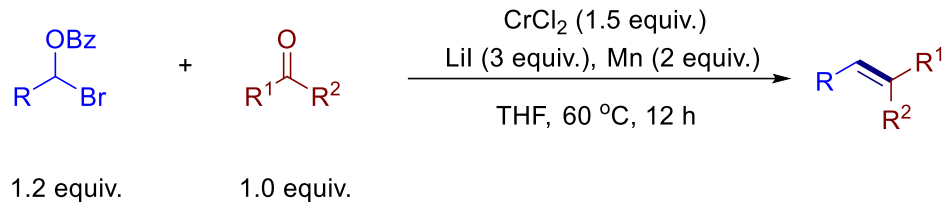

$ZnBr_2$ (2 mol%) was added to an oven-dried vial in a glovebox. Next, the sealed vial was removed from the glovebox, then dry $CH_2Cl_2$ (3.2 M) was added to the vial under $N_2$, then benzoyl bromide (1.2 equiv.). After stirring at -10 °C (ice and sodium chloride bath), aldehyde (1 equiv.) (dissolved in minimal dry DCM, if it is a solid) was added dropwise, and the reaction was stirred at -10 °C for 2 h. The mixture was filtered through neutral alumina with dry $CH_2Cl_2$. Washed with saturated sodium bicarbonate solution (repeatedly, if needed, until TLC shows no benzoic acid remaining) and brine, then dried with anhydrous sodium sulfate. After solvent removal in vacuo, the crude mixture was purified by column chromatography on silica gel to afford the product (silica is deactivated by washing with 5% $Et_3N$ in hexanes (100 mL) before loading the sample).

**Cross-metathesis for aldehydes**: General Procedure 2 (**GP2**)



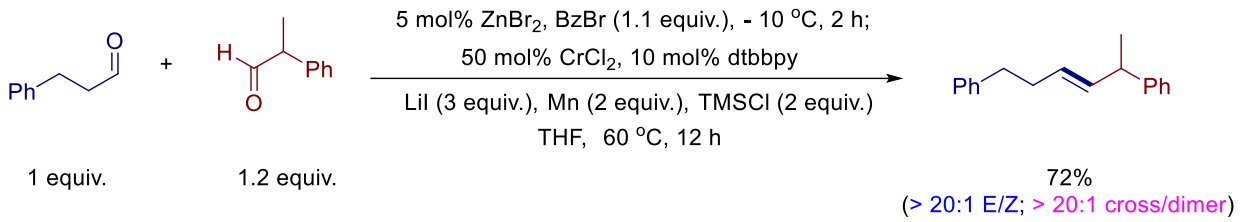

In two oven-dried vials, an activated aldehyde (1.2 equiv.) was added to **vial A**, and Mn (24 mg, 2 equiv.) and dtbbpy (5.4 mg, 10 mol%) were added to **vial B** with a stir bar, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and $CrCl_2$ (12.4 mg, 50 mol%) was added, followed by 1 mL dry THF and TMSCl (50 µL, 2 equiv.). Both vials were sealed with a cap, then removed from the glovebox. The aldehyde (1 equiv.) was added to **vial B**, then the solution of activated aldehydes in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through septa caps). After the addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C for 12 h. Upon completion, the mixture is diluted with hexanes, filtered through a short pad of silica gel, and washed with hexanes and ethers. The solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel to afford the alkene product.

**Cross-metathesis for ketones**: General Procedure 3 (**GP3**)




In two oven-dried vials, an activated aldehyde (1.2 equiv.) was added to **vial A**, and Mn (24 mg, 2 equiv.) was added to **vial B** with a stir bar, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and $CrCl_2$ (37.2 mg, 1.5 equiv.) were added, followed by 1 mL dry THF. Both vials are sealed with a cap, then removed from the glovebox. Ketone (1 equiv.) was added to **vial B**, then the solution of activated aldehyde in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through septa caps). After the addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C for 12 h. Upon completion, the mixture is diluted with hexanes, filtered through a short pad of silica gel, and washed with hexanes and ethers. The solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel to afford the alkene product.

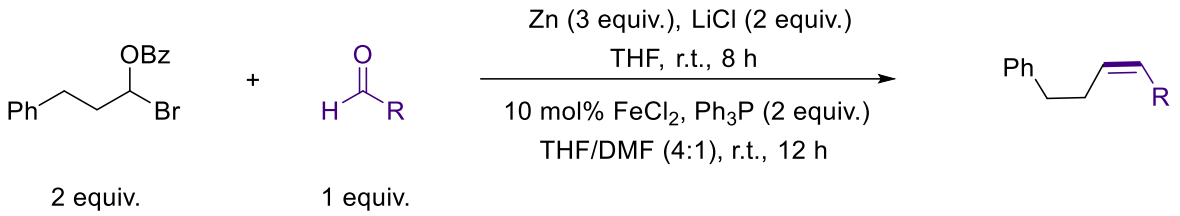
**Telescoped cross-metathesis from two aldehydes**: General Procedure 4 (**GP4**)




$ZnBr_2$ (2.2 mg, 5 mol%) was added to an oven-dried **vial A** in a glovebox. Next, the sealed vial was removed from the glovebox, then dry $CH_2Cl_2$ (0.2 mL) was added to the vial under $N_2$, then benzoyl bromide (26 $\mu$L, 1.2 equiv.) was added. After stirring at -10 °C (ice and sodium chloride bath), hydrocinnamaldehyde (27 $\mu$L, 1 equiv.) was added dropwise, and the reaction was stirred at -10 °C for 2 h.

In another oven-dried **vial B**, Mn (24 mg, 2 equiv.), dtbbpy (5.4 mg, 10 mmol%), and a stir bar were added, then introduced into a glovebox, followed by adding LiI (81 mg, 3 equiv.), $CrCl_2$ (12.4 mg, 50 mol%), dry THF (1 mL), and then TMSCl (50 µL, 2 equiv.). The vial was then sealed with a septa cap and removed from the glovebox. The aldehyde (1 equiv.) was added to **vial B**, then the solution of in situ formed activated aldehyde in **vial A** was transferred with dry THF to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through septa caps). After addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C overnight. Upon completion, the mixture is diluted with hexanes, filtered through a short pad of silica gel, and washed with hexanes and ethers. The solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel to afford the alkene product.

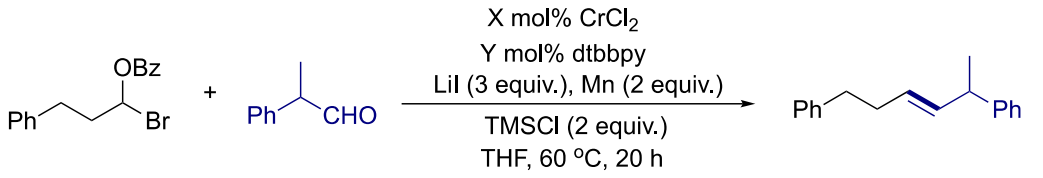
**Iron (II) catalyzed cross-metathesis**: General Procedure 5 (**GP5**)




To an oven-dried 8 mL vial was added LiCl (17 mg, 2 equiv.), Zn dust (26 mg, 3 equiv.), and a stir bar. The reaction vessel was heated under vacuum to 170 °C for 20 min with vigorous stirring. After cooling to room temperature, a solution of α-acyloxy bromide (127 mg, 2 equiv.) in dry THF (1 mL) was added dropwise. The vessel was sealed with parafilm and electrical tape and allowed to stir at room temperature for 8 h. After allowing Zn particles to settle, the resulting alkyl zinc carbenoid solution was transferred to an oven-dried vial containing $FeCl_2$ (2.6 mg, 10 mol%), a stir bar, $Ph_3P$ (105 mg, 2 equiv.), and THF (2 mL) via syringe. The mixture was stirred at room temperature for 4 h. Then aldehyde (0.2 mmol, 1 equiv.) and DMF (0.5 mL) were added and continued to stir 8 h. When the reaction is finished, diluted with $Et_2O$, and filtered through a short pad of silica gel. The solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel to afford the product.

## III. Reaction Optimization

### a. Chromium (II) catalyzed cross-metathesis



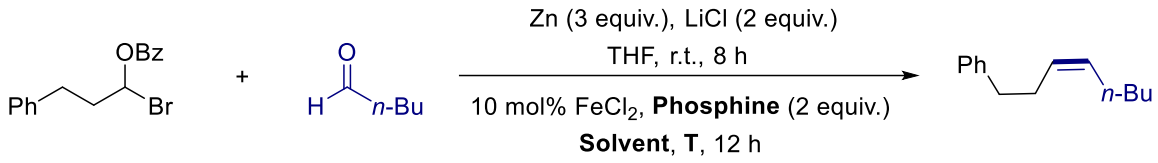

1.1 equiv. 1 equiv. Yields (E/Z); cross/dimer

| Entries | X | Y | Yields (E/Z) | cross/dimer |
|---|---|---|---|---|
| 1 | 0 | 10 | 0% | 0 |
| 2 | 25 | 10 | 79% (10:1) | 8:1 |
| 3 | 50 | 10 | 95% (> 20:1) | > 10:1 |
| 4 | 100 | 10 | 91% (> 20:1) | > 10:1 |
| 5 | 0 | 25 | 0% | 0 |
| 6 | 25 | 25 | 52% (5:1) | 3:1 |
| 7 | 50 | 25 | 90% (> 20:1) | > 10:1 |
| 8 | 100 | 25 | 90% (> 20:1) | > 10:1 |

In two oven-dried vials, activated aldehyde (1.2 equiv.) was added to **vial A**, and Mn (24 mg, 2 equiv.) and **dtbbpy** (**X** mol%) were added to **vial B** with a stir bar, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and **$CrCl_2$** (**Y** mol%) were added, followed by 1 mL dry THF and TMSCl (50 µL, 2 equiv.). Both vials are sealed with a cap, then removed from the glovebox. The aldehyde (1 equiv.) was added to **vial B**, then the solution of activated aldehydes in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through septa caps). After the addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C overnight. Upon completion, the mixture was diluted with hexanes, filtered through a short pad of silica gel, and washed with hexanes and ethers. After the solvent was removed in vacuo, the yields, *E*/*Z* ratio, and cross/dimer selectivity were calculated by $^1$H-NMR by adding 1,2,4,5-tetramethylbenzene (0.1 mmol, 0.5 eq) as internal standard.

**Results**: The best *E*/*Z* (>20:1) and cross (>10:1) selectivity is observed with 50% $CrCl_2$ and 10% ligand.

**b. Iron (II) catalyzed cross-metathesis**



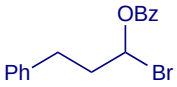

2 equiv. 1 equiv.

| Entries | **Phosphine** | **Solvent** | **T** | Yields (***Z*/*E***; **Cross/dimer**) |
|---|---|---|---|---|
| 1 | $Ph_3P$ | THF | r.t. | 100% (**4:1**; **> 20:1**) |
| 2 | $^{i}Pr_3P$ | THF | r.t. | 13% (**1:4**; **4:1**) |
| 3 | $^{i}Pr_3P$ | THF | 70 °C | 65% (**1:1**; **5:1**) |
| 4 | $(MeO)_3P$ | THF | 70 °C | trace |
| 5 | $Ph_3P$ | THF/DMF | r.t. | 100% (**9:1**; **> 20:1**) |

To an oven-dried 8 mL vial was added LiCl (17 mg, 2 equiv.), Zn dust (26 mg, 3 equiv.), and a stir bar. The reaction vessel was heated under vacuum to 170 °C for 20 min with vigorous stirring. After cooling to room temperature, a solution of α-acyloxy bromide (127 mg, 2 equiv.) in dry THF (1 mL) were added dropwise. The vessel was sealed with parafilm and electrical tape and allowed to stir at room temperature for 8 h. After allowing Zn particles to settle, the resulting alkyl zinc carbenoid solution was transferred to an oven-dried vial containing $FeCl_2$ (2.6 mg, 10 mol%), a stir bar, aldehyde (0.2 mmol, 1 equiv.), **phosphine** (2 equiv.), and **solvent** (2 mL) via syringe. The mixture was stirred at **T** for 12 h (or in the case of entry 5, following **GP5**). Upon completion, the reaction is diluted with $Et_2O$ and filtered through a short pad of silica gel. After the solvent was removed in vacuo, the yields, Z/E ratio, and cross/dimer selectivity were calculated by $^{1}$H-NMR by adding 1,2,4,5-tetramethylbenzene (0.1 mmol, 0.5 eq) as internal standard.

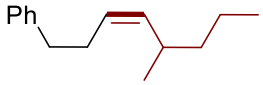
**Results**: The phosphine substituents control yield and *Z*/*E* selectivity. $Ph_3P$ is best for both. Additionally, DMF further improves *Z*/*E* selectivity.

## IV. Compound Characterization

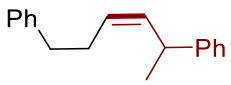



**1-bromo-3-phenylpropyl benzoate (S1):** Compound was synthesized following **GP1.** **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.65-7.59 (m, 1H), 7.51-7.44 (m, 2H), 7.34-7.28 (m, 2H), 7.25-7.18 (m, 3H), 6.87 (t, *J* = 5.9 Hz, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.70-2.56 (m, 2H); **$^{13}$C NMR:** (100 MHz, $CDCl_3$) δ: 164.1, 140.0, 134.1, 130.2, 128.9, 128.8, 128.7, 128.6, 126.6, 76.3, 41.1, 32.3; **IR** (film) $cm^{-1}$: 3027, 1738, 1602, 1453, 1245, 1065, 919, 711. **HRMS** (ESI-MS) m/z: calc'd for $[M+NH_4]^+$ 336.0594, found 336.0604.

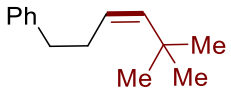

**(*Z*)-oct-3-en-1-ylbenzene (1)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 99% yield as colorless oil by following **GP5**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.24-7.16 (m, 3H), 5.49-5.35 (m, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.45-2.27 (m, 2H), 2.07-1.93 (m, 2H), 1.40-1.22 (m, 4H), 0.97-0.83 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 130.9, 128.8, 128.6, 128.4, 125.9, 36.2, 32.0, 29.3, 27.1, 22.5, 14.1; **IR** (film) $cm^{-1}$: 2957, 2925, 1495, 1454, 1378, 1075, 906, 730, 697, 649; **HRMS** (ESI-MS) m/z: calc'd for $[M+H_3O]^+$ 207.1749, found 207.1744.



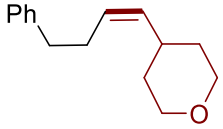

**(*Z*)-(5-methyloct-3-en-1-yl)benzene (2)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 98% yield as colorless oil by following **GP5**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.24-7.15 (m, 3H), 5.46-5.23 (m, 1H), 5.22-5.09 (m, 1H), 2.67 (t, *J* = 7.9 Hz, 2H), 2.48-2.26 (m, 3H), 1.35-1.08 (m, 4H), 0.87 (td, *J* = 6.7, 2.1 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 137.3, 128.6, 128.4, 127.2, 125.9, 39.9, 36.4, 31.7, 29.7, 21.4, 20.7, 14.4; **IR** (film) $cm^{-1}$: 3061, 3025, 2963, 2925, 1601, 1494, 1452, 907, 729, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+H_3O]^+$ 221.1905, found 221.1905.



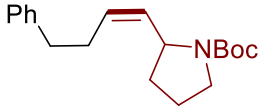

**(*Z*)-hex-3-ene-1,5-diyldibenzene (3)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 98% yield as colorless oil by following **GP5**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 4H), 7.26-7.13 (m, 6H), 5.63-5.52 (m, 1H), 5.51-5.40 (m, 1H), 3.83-3.67 (m, 1H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.58-2.37 (m, 2H), 1.35-1.22 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.6, 142.1, 135.8, 128.6, 128.5, 128.4, 127.8, 127.0, 126.0, 126.0, 37.4, 36.0, 29.6, 22.3; **IR** (film) $cm^{-1}$: 3051, 3025, 2963, 2925, 1601, 1494, 1452, 1025, 907, 729, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+NH_4]^+$ 254.1909, found 254.1918.



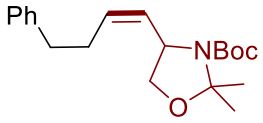

**(*Z*)-(5,5-dimethylhex-3-en-1-yl)benzene (4)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 99% yield as colorless oil by following **GP5**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.25-7.11 (m, 3H), 5.41-5.32 (m, 1H), 5.29-5.18 (m, 1H), 2.69 (t, *J* = 7.9 Hz, 2H), 2.58-2.45 (m, 2H), 1.11 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.2, 140.5, 128.6, 128.4, 127.9, 126.0, 36.7, 33.3, 31.7, 30.5; **IR** (film) $cm^{-1}$: 2956, 1604, 1495, 1453, 1361, 1203, 1078, 908, 724, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+NH_4]^+$ 206.1909, found 206.1904.




**(*Z*)-4-(4-phenylbut-1-en-1-yl)tetrahydro-2H-pyran (5)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5:95) afforded the title product in 98% yield as colorless oil by following **GP5**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.23-7.12 (m, 3H), 5.42-5.31 (m, 1H), 5.28-5.14 (m, 1H), 4.00-3.81 (m, 2H), 3.44-3.27 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.48-2.26 (m, 3H), 1.50-1.26 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.0, 135.0, 128.7, 128.4, 128.0, 126.0, 67.8, 36.2, 33.7, 32.9, 29.6; **IR** (film) $cm^{-1}$: 2928, 2840, 1495, 1454, 1385, 1236, 1128, 1085, 733, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$: 217.1592, found 217.1593.

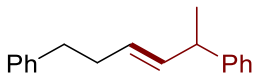



***tert*-butyl (*Z*)-2-(4-phenylbut-1-en-1-yl)pyrrolidine-1-carboxylate (6)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10:90) afforded the title product in 95% yield as colorless oil by following **GP5**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 2H), 7.23-7.09 (m, 3H), 5.48-5.24 (m, 2H), 4.42 (s, 1H), 3.49-3.25 (m, 2H), 2.82-2.69 (m, 1H), 2.69-2.57 (m, 1H), 2.55-2.28 (m, 2H), 1.98-1.67 (m, 3H), 1.50-1.34 (m, 10H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.7, 142.0, 133.1, 128.6, 128.4, 127.7, 126.0, 79.1, 54.4, 46.5, 36.0, 33.6, 29.5, 28.7, 23.7; **IR** (film) $cm^{-1}$: 2973, 1670, 1495, 1453, 1388, 1364, 1254, 1165, 1102, 916, 770, 732, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 302.2120, found 302.2129.

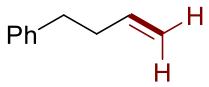



***tert*-butyl (*Z*)-2,2-dimethyl-4-(4-phenylbut-1-en-1-yl)oxazolidine-3-carboxylate (7)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10:90) afforded the title product in 93% yield as colorless oil by following **GP5**. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.33-7.23 (m, 2H), 7.22-7.06 (m, 3H), 5.60-5.31 (m, 2H), 4.63-4.31 (m, 1H), 3.80-3.62 (m, 1H), 3.38-3.14 (m, 1H),

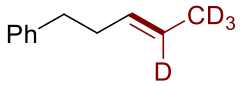
2.85-2.73 (m, 1H), 2.64-2.28 (m, 3H), 1.59-1.37 (m, 15H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 152.1, 141.7, 131.2, 130.7, 130.2, 129.3, 128.8, 128.4, 126.1, 94.1, 79.7, 68.7, 54.5, 35.9, 29.5, 28.6, 27.5, 26.5, 25.3, 24.2; **IR** (film) $cm^{-1}$: 2979, 1691, 1453, 1384, 1364, 1250, 1172, 1085, 1056, 908, 849, 729, 698; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$: 354.2045, found 354.2050.




**(*E*)-hex-3-ene-1,5-diyldibenzene (8)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 84% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.26-7.17 (m, 6H), 5.70-5.61 (m, 1H), 5.59-5.49 (m, 1H), 3.52-3.39 (m, 1H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.45-2.31 (m, 2H), 1.42-1.33 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.4, 142.2, 135.9, 128.7, 128.5, 128.4, 127.3, 126.1, 125.9, 42.3, 36.1, 34.5, 21.6; **IR** (film) $cm^{-1}$ : 2970, 2901, 1602, 1493, 1451, 1394, 1250, 1066, 966, 904, 743, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 237.1643, found 237.1632.



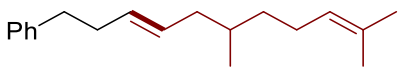

**but-3-en-1-ylbenzene (9)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 53% yield as a colorless oil by following a modified **GP2** (*1 equiv. activated aldehyde react with 3 equiv. of formaldehyde*). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.23-7.15 (m, 3H), 5.86 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09-4.94 (m, 2H), 2.77-2.66 (m, 2H), 2.38 (dt, *J* = 14.3, 7.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.0, 138.3, 128.6, 128.4, 126.0, 115.1, 35.7, 35.5; **IR** (film) $cm^{-1}$: 2958, 2922, 1454, 1406, 1380, 1249, 1065, 907, 737; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 133.1017, found 133.1014.



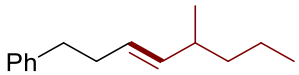

**(*E*)-(pent-3-en-1-yl-4,5,5,5-d4)benzene (10)** Column chromatography on silica gel (hexanes) afforded the title product in 83% yield (*E*/*Z* = 7/1) as a colorless oil by following **GP2**. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.17 (m, 3H), 5.52-5.42 (m, 1H), 2.68 (dd, *J* = 10.4, 5.4 Hz, 2H), 2.35-2.28 (m, 2H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 142.4, 133.8, 131.2, 130.7, 125.8, 36.3, 34.6, 19.2; **IR** (film) $cm^{-1}$: 2956, 2923, 1454, 1379, 1253, 1066, 907, 732, 698; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 173.1244, found 173.1244.


**(*E*)-oct-3-en-1-ylbenzene (11)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 95% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.23-7.16 (m, 3H), 5.52-5.37 (m, 2H), 2.74-2.62 (m, 2H), 2.42-2.25 (m, 2H), 2.07-1.91 (m, 2H), 1.41-1.20 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.4, 131.3, 129.4, 128.6, 128.4, 125.8, 36.3, 34.6, 32.4, 31.9, 22.3, 14.1; **IR** (film) $cm^{-1}$: 2970,

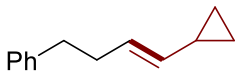
2900, 1604, 1496, 1394, 1250, 1066, 867, 891, 743, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 189.1643, found 189.1643.



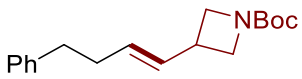

**(*E*)-(6,10-dimethylundeca-3,9-dien-1-yl)benzene (12)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 98% yield as a colorless oil by following **GP3**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.21-7.15 (m, 3H), 5.49-5.34 (m, 2H), 5.09 (dddt, *J* = 7.1, 4.2, 2.8, 1.4 Hz, 1H), 2.72-2.62 (m, 2H), 2.39-2.28 (m, 2H), 2.05-1.76 (m, 4H), 1.69 (s, 3H), 1.60 (s, 3H), 1.50-1.38 (m, 1H), 1.36-1.24 (m, 1H), 1.17-1.03 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 131.2, 130.8, 129.7, 128.6, 128.4, 125.8, 125.1, 40.1, 36.7, 36.3, 34.7, 32.9, 25.9, 25.7, 19.5, 17.8; **IR** (film) $cm^{-1}$: 2971, 2901, 1452, 1405, 1393, 1250, 1066, 1057, 892; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 279.2089, found 279.2099.




**(*E*)-(5-methyloct-3-en-1-yl)benzene (13)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 75% yield as a colorless oil by following **GP2**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24-7.16 (m, 3H), 5.42 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.34-5.25 (m, 1H), 2.74-2.65 (m, 2H), 2.37-2.28 (m, 2H), 2.15-2.01 (m, 1H), 1.34-1.18 (m, 4H), 0.99-0.93 (m, 3H), 0.92-0.84 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.4, 137.4, 128.7, 128.4, 127.5, 125.8, 39.6, 36.6, 36.4, 34.6, 21.0, 20.5, 14.3; **IR** (film) $cm^{-1}$: 2970, 2901, 0604, 1496, 1453, 1406, 1394, 1250, 1075, 1065, 967, 891, 744, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 225.1619, found 225.1617.

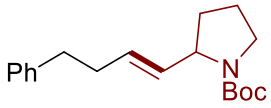



**(*E*)-(4-cyclopropylbut-3-en-1-yl)benzene (14)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 74% yield (*E*/*Z* = 5/1)as a colorless oil by following **GP2**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2H), 7.25-7.16 (m, 3H), 5.63-5.30 (m, 1H), 5.08-4.73 (m, 1H), 2.79-2.62 (m, 2H), 2.56-2.26 (m, 2H), 1.51-1.29 (m, 1H), 0.74-0.61 (m, 2H), 0.37-0.25 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 142.3, 134.7, 134.6, 128.6, 128.4, 127.4, 125.9, 36.4, 36.2, 34.6, 29.7, 13.7, 9.8, 7.0, 6.5; **IR** (film) $cm^{-1}$: 2958, 2922, 1454, 1406, 1394, 1380, 1250, 1066, 1057, 907, 735, 697; **HRMS** (ESI-TOF) m/z: calc'd for $[M+Na]^+$ 195.1150, found 195.1144.

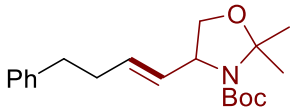



***tert*-butyl (*E*)-3-(4-phenylbut-1-en-1-yl)azetidine-1-carboxylate (15)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded the title product in 62% yield (*E*/*Z* = 6/1) as a colorless oil by following **GP2**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.13 (m, 3H), 5.67-5.42 (m, 2H), 4.10-3.92 (m, 2H), 3.71-3.51 (m, 2H), 3.35-3.05 (m, 1H), 2.73-

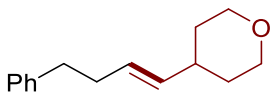
2.59 (m, 2H), 2.39-2.24 (m, 2H), 1.44 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.5, 156.4, 141.8, 141.6, 131.8, 131.5, 131.2, 130.6, 128.6, 128.6, 128.4, 126.1, 126.0, 79.4, 55.0, 35.8, 34.3, 31.5, 28.6; **IR** (film) $cm^{-1}$: 2972, 2901, 1701, 1394, 1250, 1066, 892, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 288.1964, found 288.1956.



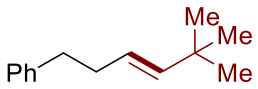

***tert*-butyl (*E*)-2-(4-phenylbut-1-en-1-yl)pyrrolidine-1-carboxylate (16)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded the title product in 66% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.22-7.13 (m, 3H), 5.61-5.45 (m, 1H), 5.44-5.30 (m, 1H), 4.56-4.01 (m, 1H), 3.51-3.19 (m, 2H), 2.81-2.56 (m, 2H), 2.53-2.24 (m, 2H), 2.06-1.88 (m, 1H), 1.84-1.74 (m, 2H), 1.68-1.57 (m, 1H), 1.44 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.2, 142.0, 131.5, 129.3, 128.5, 128.4, 125.4, 79.0, 57.9, 45.7, 36.0, 34.1, 32.2, 3, 23.0; **IR** (film) $cm^{-1}$: 2972, 2900, 1691, 1393, 1250, 1169, 1066, 880, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 302.2120, found 302.2110.



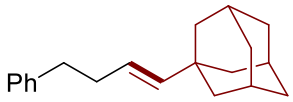

***tert*-butyl (*E*)-2,2-dimethyl-4-(4-phenylbut-1-en-1-yl)oxazolidine-3-carboxylate (17)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded the title product in 69% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.22-7.12 (m, 3H), 5.79-5.53 (m, 1H), 5.44 (ddt, *J* = 15.3, 7.7, 1.3 Hz, 1H), 4.46-4.12 (m, 1H), 4.00 (dd, *J* = 8.7, 6.1 Hz, 1H), 3.68 (dd, *J* = 8.8, 2.1 Hz, 1H), 2.76-2.62 (m, 2H), 2.41-2.25 (m, 2H), 1.70-1.29 (m, 15H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.1, 141.8, 131.6, 129.9, 129.4, 128.6, 128.4, 126.0, 93.9, 93.5, 80.1, 79.5, 68.6, 59.2, 35.8, 34.0, 28.6, 27.5, 26.7, 24.9, 23.8; **IR** (film) $cm^{-1}$: 2979, 2901, 1694, 1363, 1251, 1174, 1065, 699; **HRMS** (ESI-TOF) m/z: calc'd for $[M+Na]^+$ 354.2045, found 354.2042.



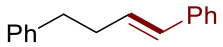

**(*E*)-4-(4-phenylbut-1-en-1-yl)tetrahydro-2H-pyran (18)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 85% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.14 (m, 3H), 5.52-5.32 (m, 2H), 3.95 (ddd, *J* = 11.1, 4.0, 1.9 Hz, 2H), 3.40 (td, *J* = 11.7, 2.2 Hz, 2H), 2.73-2.61 (m, 2H), 2.31 (dt, *J* = 7.5, 6.4 Hz, 2H), 2.21-2.05 (m, 1H), 1.61-1.51 (m, 2H), 1.50-1.32 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.1, 135.4, 128.6, 128.4, 128.0, 125.8, 67.9, 38.0, 36.2, 34.6, 32.9; **IR** (film) $cm^{-1}$: 2971, 2901, 1452, 1405, 1250, 1066, 892, 698; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 217.1592, found 217.1586.



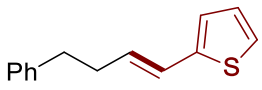

**(*E*)-(5,5-dimethylhex-3-en-1-yl)benzene (19)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 76% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.24-7.16 (m, 3H), 5.51-5.43 (m, 1H), 5.37 (dt, *J* = 13.2, 6.4 Hz, 1H), 2.73-2.63 (m, 2H), 2.36-2.26 (m, 2H), 1.00 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.4, 142.4, 128.7, 128.3, 125.8, 124.0, 36.5, 34.7, 32.9, 29.9; **IR** (film) $cm^{-1}$: 2959, 2922, 1454, 1406, 1393, 1380, 1249, 1229, 1066, 1057, 892, 737, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 211.1463, found 211.1459.



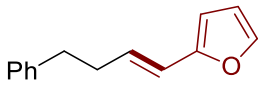

**(*3r,5r,7r*)-1-((*E*)-4-phenylbut-1-en-1-yl)adamantane (20)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 57% yield as a colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.25-7.16 (m, 3H), 5.40-5.25 (m, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.39-2.26 (m, 2H), 2.04-1.94 (m, 3H), 1.80-1.63 (m, 6H), 1.60-1.54 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.8, 142.4, 128.7, 128.3, 125.8, 124.1, 42.6, 37.1, 36.5, 34.9, 34.7, 28.7; **IR** (film) $cm^{-1}$: 2971, 2901, 1453, 1405, 1250, 1066, 1057, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 267.2113, found 267.2112.



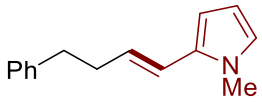

**(*E*)-but-1-ene-1,4-diyldibenzene (21)** Column chromatography on silica gel (eluent: hexanes) afforded a mixture of the title product in 75% yield (*E*/*Z* = 2/1) as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.14 (m, 10H), 6.54-6.40 (m, 1H), 6.38-5.66 (m, 1H), 2.88-2.87 (m, 2H), 2.76-2.52 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.9, 141.8, 137.9, 137.7, 132.0, 130.5, 130.1, 129.6, 128.9, 128.6, 128.5, 128.3, 127.1, 126.7, 126.1, 126.1, 126.0, 36.2, 36.0, 34.4, 30.6; **IR** (film): 2957, 2923, 1453, 1406, 1380, 1250, 1066, 907, 733, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+Li]^+$ 215.1412, found 215.1420.



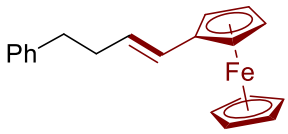

**(*E*)-2-(4-phenylbut-1-en-1-yl)thiophene (22)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded a mixture of the title product in 70% yield (*E*/*Z* = 2/1) as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.07 (m, 6H), 7.07-6.85 (m, 2H), 6.64-6.50 (m, 1H), 6.22-5.58 (m, 1H), 2.92-2.44 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.1, 141.8, 140.7, 130.1, 129.9, 128.6, 128.6, 128.5, 127.4, 127.4, 126.9, 126.1, 126.1, 125.3, 124.6, 123.8, 123.4, 122.5, 35.9, 35.6, 34.9, 31.1; **IR** (film) $cm^{-1}$: 2987, 2900, 1495, 1405, 1250, 1075, 1065, 746, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+K]^+$ 253.0453, found 253.0460.



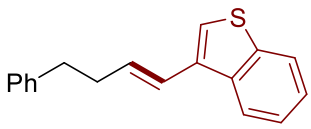

**(*E*)-2-(4-phenylbut-1-en-1-yl)furan (23)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded a mixture of the title product in 78% yield (*E*/*Z* = 2/1) as colorless oil by following **GP2**.**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.15 (m, 6H), 6.44-6.34 (m, 1H), 6.31-5.56 (m, 3H), 2.87-2.75 (m, 3H), 2.56-2.49 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.4, 153.3, 142.0, 141.8, 141.5, 141.5, 130.0, 129.1, 128.6, 128.6, 128.5, 126.0, 119.2, 117.9, 111.2, 111.2, 109.2, 106.4, 35.8, 35.8, 34.8, 31.1; **IR** (film) $cm^{-1}$: 2971, 2900, 1602, 1453, 1393, 1251, 1066, 1075, 959, 730, 697, 593; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 199.1123, found 199.1123.




**(*E*)-N-methyl-2-(4-phenylbut-1-en-1-yl)-1H-pyrrole (24)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded a mixture of the title product in 94% yield (*E*/*Z* = 1/1) as colorless oil by following **GP5**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.16 (m, 6H), 6.70-6.52 (m, 1H), 6.37-6.23 (m, 2H), 6.22-5.56 (m, 2H), 3.62-3.55 (m, 3H), 2.90-2.78 (m, 2H), 2.77-2.50 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.0, 141.9, 132.7, 132.1, 130.2, 129.7, 129.3, 128.7, 128.6, 128.5, 128.2, 126.0, 122.4, 122.3, 119.4, 117.2, 109.5, 107.8, 107.6, 105.5, 36.2, 35.8, 35.3, 34.1, 31.0; **IR** (film) $cm^{-1}$: 2971, 2901, 1452, 1406, 1394, 1250, 1066, 892, 747, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 212.1439, found 212.1437.

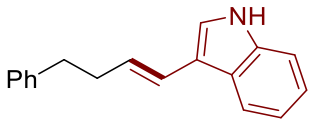



**(*E*)-(4-phenylbut-1-en-1-yl)Ferrocene (25)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded a mixture of the title product in 98% yield (*E*/*Z* = 3/1) as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.03 (m, 5H), 6.27-6.02 (m, 1H), 6.00-5.40 (m, 1H), 4.46-3.89 (m, 9H), 2.88-2.70 (m, 2H), 2.69-2.34 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.1, 142.0, 128.7, 128.6, 128.5, 128.4, 127.5, 127.4, 126.6, 126.0, 126.0, 84.1, 82.2, 69.2, 68.5, 68.3, 66.4, 36.1, 34.9, 31.0; **IR** (film) $cm^{-1}$: 2972, 2901, 1406, 1394, 1250, 1066, 879; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 339.0812, found 339.0816.

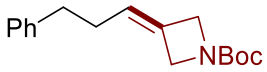



**(*E*)-3-(4-phenylbut-1-en-1-yl)benzo[b]thiophene (26)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded a mixture of the title product in 70% yield (*E*/*Z* = 1/1) as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.73 (m, 2H), 7.49-7.14 (m, 8H), 6.77-6.58 (m, 1H), 6.42-5.89 (m, 1H), 2.92-2.78 (m, 2H), 2.75-2.55 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.8, 141.7, 140.6, 139.7, 139.1, 138.0, 134.5, 133.9, 132.7, 132.1,

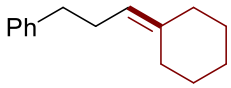
128.7, 128.6, 128.5, 126.1, 126.1, 124.5, 124.5, 124.2, 124.2, 123.3, 123.0, 122.9, 122.8, 122.2, 122.1, 121.6, 120.9, 36.0, 35.3, 31.3; **IR** (film) $cm^{-1}$: 2956, 2922, 1602, 1453, 1251, 1076, 906, 758, 729, 697; **HRMS** (ESI-TOF) m/z: calc'd for $[M+K]^+$: 303.0610, found 303.0618.



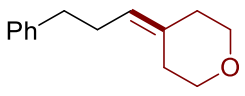

**(*E*)-3-(4-phenylbut-1-en-1-yl)-1H-indole (27)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 33% yield as colorless oil by following **GP5**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.43-7.06 (m, 9H), 6.69-6.54 (m, 1H), 6.25 (dt, *J* = 16.0, 6.8 Hz, 1H), 2.87-2.78 (m, 2H), 2.62-2.52 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 136.8, 128.7, 128.5, 127.3, 125.9, 122.8, 122.5, 122.4, 120.2, 115.7, 111.4, 36.6, 35.7; **IR** (film) $cm^{-1}$: 3674, 2956, 2923, 2873, 1455, 1405, 1379, 1250, 1066, 907, 737; **HRMS** (ESI-TOF) m/z: calc'd for $[M+Li]^+$: 254.1521, found 254.1517.




***tert*-butyl 3-(3-phenylpropylidene)azetidine-1-carboxylate (28)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded the title product in 73% yield as colorless oil by following **GP3**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.23-7.14 (m, 3H), 5.38-5.26 (m, 1H), 4.45-4.38 (m, 2H), 4.37-4.30 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.21 (dd, *J* = 14.6, 8.0 Hz, 2H), 1.45 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.5, 141.6, 128.6, 128.5, 128.5, 126.1, 121.6, 79.6, 57.8, 35.5, 30.6, 28.5; IR (film) $cm^{-1}$: 2973, 2928, 1701, 1392, 1366, 1119, 1066, 771, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 296.1626, found 296.1632.

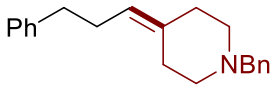



**(3-cyclohexylidenepropyl)benzene (29)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 79% yield as colorless oil by following **GP3**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.24-7.16 (m, 3H), 5.14 (t, *J* = 7.2 Hz, 1H), 2.69-2.61 (m, 2H), 2.37-2.27 (m, 2H), 2.12-2.03 (m, 4H), 1.58-1.47 (m, 4H), 1.46-1.37 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.5, 140.5, 128.7, 128.3, 125.8, 120.4, 37.3, 36.7, 29.2, 28.8, 28.8, 27.8, 27.1; **IR** (film) $cm^{-1}$: 2955, 2923, 2856, 1604, 1452, 1066, 734, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+K]^+$: 239.1202, found 239.1200.

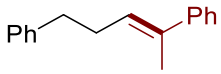



**4-(3-phenylpropylidene)tetrahydro-2H-pyran (30)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 81% yield as colorless oil by following **GP5**. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.22-7.15 (m, 3H), 5.24 (t, *J* = 7.3 Hz, 1H), 3.63 (t, *J* = 5.5 Hz, 2H), 3.48 (t, *J* = 5.5 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.34 (q, *J*

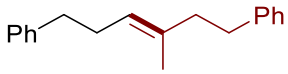
= 7.5 Hz, 2H), 2.18 (dt, *J* = 10.5, 5.4 Hz, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.1, 135.1, 128.7, 128.4, 125.9, 122.3, 69.7, 68.7, 37.1, 36.3, 29.8, 29.0; **IR** (film) $cm^{-1}$: 2956, 2923, 2873, 1455, 1393, 1378, 1085, 738; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 203.1436, found 203.1425.



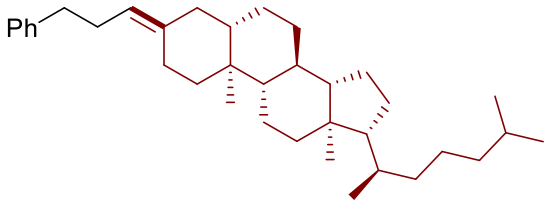

**1-benzyl-4-(3-phenylpropylidene)piperidine (31)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 10/90) afforded the title product in 48% yield as colorless oil by following **GP3**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.30-7.24 (m, 3H), 7.21-7.14 (m, 3H), 5.18 (t, *J* = 7.3 Hz, 1H), 3.49 (s, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.45-2.38 (m, 2H), 2.35-2.26 (m, 4H), 2.23-2.14 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.3, 138.6, 137.0, 129.3, 128.7, 128.3, 128.3, 127.1, 125.8, 121.6, 63.2, 55.4, 54.5, 36.5, 36.1, 29.2, 28.3; **IR** (film) $cm^{-1}$: 2955, 2923, 1453, 1066, 1057, 734, 696; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 292.2065, found 292.2057.




**(*E*)-pent-3-ene-1,4-diyldibenzene (32)** Column chromatography on silica gel (eluent: hexanes) afforded a mixture of the title product in 31% yield as colorless oil by following **GP3**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.34-7.27 (m, 4H), 7.26-7.18 (m, 4H), 5.88-5.76 (m, 1H), 2.84-2.71 (m, 2H), 2.53 (dd, *J* = 15.3, 7.4 Hz, 2H), 1.98 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.0, 142.2, 135.6, 128.7, 128.5, 128.3, 127.6, 126.7, 126.0, 125.8, 36.0, 30.9, 15.9; IR (film) $cm^{-1}$: 2956, 2922, 2872, 1457, 1378, 1250, 1066, 908, 761, 698; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$: 245.1306, found 245.1298.

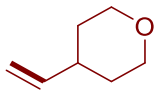



**(*E*)-(3-methylhex-3-ene-1,6-diyl)dibenzene (33)** Column chromatography on silica gel (eluent: hexanes) afforded a mixture of the title product in 51% yield (*E*/*Z* = 1/1) as colorless oil by following **GP5**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 4H), 7.24-7.13 (m, 6H), 5.23 (t, *J* = 7.1 Hz, 1H), 2.78-2.50 (m, 4H), 2.40-2.17 (m, 4H), 1.80-1.58 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.6, 142.5, 142.5, 135.4, 135.1, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 125.9, 125.8, 125.8, 125.3, 124.3, 41.7, 36.3, 36.2, 34.9, 34.4, 34.1, 30.1, 30.0, 23.6, 16.2; **IR** (film) $cm^{-1}$: 2956, 2922, 2872, 1495, 1454, 1406, 1250, 1066, 808, 735, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+Na]^+$ 273.1619, found 273.1619.

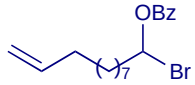



**(*5S,8R,9S,10S,13R,14S,17R,E*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(3-phenylpropylidene)hexadecahydro-1H-cyclopenta[*α*]phenanthrene (34)** Column chromatography on silica gel (eluent: hexanes) afforded a mixture of the title product in 78% yield (*E*/*Z* = 1/1) as colorless oil by following **GP3**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.23-7.16 (m, 3H), 5.12 (t, *J* = 6.1 Hz, 1H), 2.77-2.54 (m, 2H), 2.45-2.13 (m, 3H), 2.11-1.93 (m, 2H), 1.91-1.44 (m, 7H), 1.44-0.97 (m, 17H), 0.97-0.72 (m, 15H), 0.71-0.53 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.5, 142.5, 140.4, 128.7, 128.7, 128.3, 128.3, 125.8, 125.8, 120.1, 119.8, 56.7, 56.4, 54.6, 48.5, 47.3, 42.8, 40.3, 40.2, 39.7, 39.7, 39.4, 36.7, 36.6, 36.6, 36.3, 36.0, 35.6, 35.6, 32.8, 32.2, 32.1, 31.4, 29.3, 29.2, 29.0, 28.4, 28.2, 24.4, 24.4, 24.0, 23.0, 22.7, 21.3, 21.2, 18.8, 12.2, 11.9; **IR** (film) $cm^{-1}$: 2922, 2856, 2849, 1604, 1453, 1382, 1076, 744, 697; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 489.4460, found 489.4466.


**iodomethyl benzoate (S35):** commercially available reagent (CAS: 13943-33-4). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.65-7.57 (m, 1H), 7.51-7.43 (m, 2H), 6.16 (s, 2H); **$^{13}$C NMR:** (100 MHz, $CDCl_3$) δ: 164.8, 134.0, 130.1, 129.0, 128.7, 31.2; **IR** (film) $cm^{-1}$: 3062, 1734, 1600, 1451, 1421, 1280, 1228, 1078, 1060, 707; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 262.9569, found 262.9567.

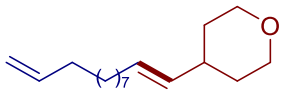



**4-vinyltetrahydro-2H-pyran (35)** Column chromatography on silica gel (eluent: ethyl acetate/ hexanes = 5/95) afforded the title product in 60% yield as colorless oil by following **GP2**. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 5.86-5.72 (m, 1H), 4.98 (ddt, *J* = 24.2, 10.4, 1.5 Hz, 2H), 3.97 (ddd, *J* = 11.1, 4.1, 1.8 Hz, 2H), 3.42 (td, *J* = 11.8, 2.2 Hz, 2H), 2.26-2.15 (m, 1H), 1.68-1.60 (m, 2H), 1.52-1.41 (m, 2H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 143.0, 112.9, 67.9, 38.9, 32.4; **IR** (film) $cm^{-1}$: 2971, 2900, 1406, 1250, 1066, 904, 726, 649; **HRMS** (ESI-MS) m/z: calc'd for $[M+NH_4]^+$: 130.1232, found 130.1239.

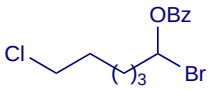



**1-bromoundec-10-en-1-yl benzoate (S36)** Compound was synthesized following **GP1. $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.05 (m, 2H), 7.65-7.57 (m, 1H), 7.52-7.43 (m, 2H), 6.88 (t, *J* = 6.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04-4.88 (m, 2H), 2.38-2.19 (m, 2H), 2.10-1.99 (m, 2H), 1.61-4.51 (m, 2H), 1.38-1.27 (m, 10H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.3, 139.3, 134.0,

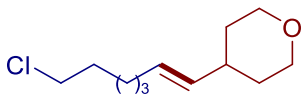
130.2, 129.0, 128.7, 114.3, 77.1, 39.7, 33.9, 29.5, 29.4, 29.2, 29.0, 28.9, 26.0; **IR** (film) $cm^{-1}$: 2923, 2851, 1469, 1445, 1226, 1130, 1085, 1016, 977, 910, 871, 822, 720. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 353.1116, found 353.1119.



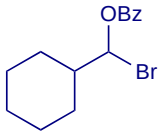

**(*E*)-4-(dodeca-1,11-dien-1-yl)tetrahydro-2H-pyran (36)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 91% yield as colorless oil by following **GP2**. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.86-5.75 (m, 1H), 5.47-5.28 (m, 2H), 5.04-4.86 (m, 2H), 3.99-3.88 (m, 2H), 3.46-3.34 (m, 2H), 2.19-2.08 (m, 1H), 2.07-2.00 (m, 2H), 2.00-1.93 (m, 2H), 1.61-1.55 (m, 2H), 1.52-1.19 (m, 14H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 139.4, 134.6, 129.1, 114.2, 68.0, 38.0, 34.0, 33.1, 32.7, 29.7, 29.6, 29.6, 29.3, 29.3, 29.1; **IR** (film) $cm^{-1}$: 2923, 2851, 1464, 1440, 1385, 1236, 1129, 1085, 1012, 966, 908, 870, 820, 721; **HRMS** (ESI-MS) m/z: calc'd for $[M+K]^+$: 289.1934, found 289.1934.



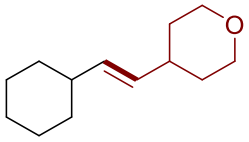

**1-bromo-6-chlorohexyl benzoate (S37)** Compound was synthesized following **GP1.** **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.04 (m, 2H), 7.65-7.59 (m, 1H), 7.51-7.44 (m, 2H), 6.89 (t, *J* = 5.9 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.41-2.22 (m, 2H), 1.87-1.77 (m, 2H), 1.63-1.50 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.2, 134.1, 130.2, 128.9, 128.8, 76.7, 44.9, 39.4, 32.4, 26.2, 25.3; **IR** (film) $cm^{-1}$: 2956, 2930, 2860, 1460, 1375, 1230, 1120, 1090, 1011, 969, 910, 878, 731, 650. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 319.0100, found 319.0108.



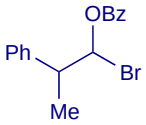

**(*E*)-4-(7-chlorohept-1-en-1-yl)tetrahydro-2H-pyran (37)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 62% yield as colorless oil by following **GP2**. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.44-5.31 (m, 2H), 3.99-3.91 (m, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 3.39 (td, *J* = 11.7, 2.2 Hz, 2H), 2.19-2.10 (m, 1H), 2.03-1.95 (m, 2H), 1.80-1.73 (m, 2H), 1.64-1.53 (m, 2H), 1.49-1.33 (m, 6H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 135.1, 128.5, 67.9, 45.2, 38.0, 33.1, 32.6, 32.5, 28.9, 26.5; **IR** (film) $cm^{-1}$: 2955, 2928, 2855, 1463, 1385, 1236, 1128, 1085, 1013, 968, 907, 870, 731, 648; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 217.1359, found 217.1356.



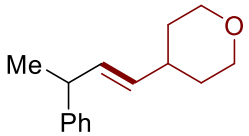

**bromo(cyclohexyl)methyl benzoate (S38)** Compound was synthesized following **GP1.** **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.03 (m, 2H), 7.65-7.57 (m, 1H), 7.51-7.44 (m, 2H), 6.78 (d, *J* = 4.7 Hz, 1H), 2.05-2.00 (m, 2H), 1.89-1.79 (m, 2H), 1.75-1.67 (m, 1H), 1.39-1.15 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.3, 134.0, 130.2, 129.2, 128.7, 82.3, 45.7, 29.4, 28.7, 26.2, 25.8, 25.7; **IR** (film) $cm^{-1}$: 3027, 2956, 2927, 2855, 1463, 910, 730. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 297.0490, found 297.0493.




**(*E*)-4-(2-cyclohexylvinyl)tetrahydro-2H-pyran (38)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 62% yield as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 5.41-5.23 (m, 2H), 3.99-3.89 (m, 2H), 3.39 (td, *J* = 11.7, 2.3 Hz, 2H), 2.18-2.03 (m, 1H), 1.96-1.80 (m, 1H), 1.75-1.53 (m, 7H), 1.51-1.34 (m, 2H), 1.32-0.96 (m, 5H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.1, 132.0, 68.0, 40.8, 38.0, 33.4, 33.2, 26.4, 26.2; **IR** (film) $cm^{-1}$: 2956, 2924, 2851, 1449, 907, 731; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$: 195.1749, found 195.1743.

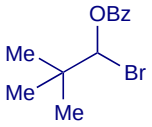



**1-bromo-2-phenylpropyl benzoate (S39)** Compound was synthesized following **GP1.** **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.11-7.94 (m, 2H), 7.68-7.56 (m, 1H), 7.54-7.41 (m, 2H), 7.41-7.27 (m, 5H), 7.03 (t, *J* = 5.5 Hz, 1H), 3.63-3.49 (m, 1H), 1.62 (dd, *J* = 15.2, 7.0 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.0, 164.0, 141.0, 140.6, 134.0, 133.9, 130.1, 130.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.2, 128.2, 127.6, 127.5, 81.7, 80.5, 48.0, 47.5, 17.8, 16.6; **IR** (film) $cm^{-1}$: 3027, 2963, 2927, 2841, 1605, 1492, 1388, 1240, 1130, 1080, 1010, 761, 683. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 319.0334, found 319.0335.

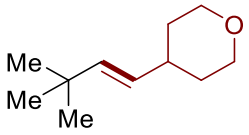



**(*E*)-4-(3-phenylbut-1-en-1-yl)tetrahydro-2H-pyran (39)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 50% yield as colorless oil by following **GP2**. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.25-7.15 (m, 3H), 5.61 (ddd, *J* = 15.5, 6.8, 1.3 Hz, 1H), 5.43 (ddd, *J* = 15.5, 6.5, 1.2 Hz, 1H), 4.02-3.90 (m, 2H), 3.46-3.37 (m, 3H), 2.26-2.15 (m, 1H), 1.65-1.56 (m, 2H), 1.54-1.40 (m, 2H), 1.35 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR**

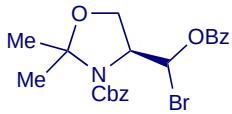
(151 MHz, $CDCl_3$) δ 146.4, 133.7, 133.4, 128.5, 127.3, 126.1, 67.9, 42.3, 38.0, 33.0, 22.0; **IR** (film) $cm^{-1}$: 2959, 2928, 2840, 1602, 1492, 1385, 1235, 1128, 1084, 1012, 979, 869, 760, 699; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 217.1592, found 217.1589.



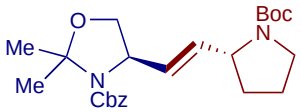

**1-bromo-2,2-dimethylpropyl benzoate (S40)** Compound was synthesized following **GP1.** **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.11-8.04 (m, 2H), 7.65-7.58 (m, 1H), 7.52-7.44 (m, 2H), 6.72 (s, 1H), 1.19 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.2, 134.0, 130.1, 129.1, 128.7, 87.0, 37.9, 26.0; **IR** (film) $cm^{-1}$: 3027, 2959, 2930, 2870, 1463, 1382, 1361, 1235, 1133, 1080, 1011, 970, 900, 731. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 271.0334, found 271.0341.



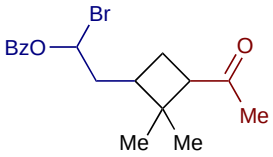

**(*E*)-4-(3,3-dimethylbut-1-en-1-yl)tetrahydro-2H-pyran (40)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 5/95) afforded the title product in 33% yield as colorless oil by following **GP2**. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.44 (dd, *J* = 15.7, 1.2 Hz, 1H), 5.24 (dd, *J* = 15.7, 6.6 Hz, 1H), 4.00-3.88 (m, 2H), 3.40 (td, *J* = 11.8, 2.2 Hz, 2H), 2.19-2.04 (m, 1H), 1.62-1.53 (m, 2H), 1.47-1.37 (m, 2H), 0.98 (s, 9H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 140.2, 129.1, 68.0, 38.1, 33.3, 32.8, 29.9; **IR** (film) $cm^{-1}$: 2956, 2927, 2872, 1456, 1384, 1361, 1235, 1130, 1082, 1012, 970, 908, 734, 648; **HRMS** (ESI-MS) m/z: calc'd for $[M+K]^+$: 207.1151, found 207.1148.



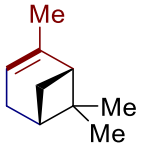

**benzyl (S)-4-((R)-(benzoyloxy)bromomethyl)-2,2-dimethyloxazolidine-3-carboxylate (S41)** Compound was synthesized following **GP1.** **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.20-7.89 (m, 2H), 7.66-7.26 (m, 8H), 7.14 (dd, *J* = 28.7, 21.3 Hz, 1H), 5.33-5.00 (m, 2H), 4.74-4.30 (m, 2H), 4.21 (ddd, *J* = 37.6, 9.7, 6.4 Hz, 1H), 1.77-1.39 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.1, 164.0, 163.8, 153.7, 153.3, 152.5, 152.1, 136.1, 135.8, 134.3, 134.2, 130.5, 130.2, 128.8, 128.8, 128.8, 128.7, 128.4, 128.4, 128.3, 128.0, 127.9, 96.4, 96.0, 95.7, 95.4, 76.5, 74.4, 74.1, 67.6, 67.4, 65.6, 65.2, 64.7, 64.3, 63.1, 62.1, 61.8, 61.0, 27.6, 26.9, 26.5, 25.9, 24.8, 24.5, 23.4, 23.2; **IR** (film) $cm^{-1}$: 3017, 1748, 1601, 1450, 1254, 1061, 920, 710; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 448.0760, found 448.0760.




**benzyl (R)-4-((E)-2-((R)-1-(tert-butoxycarbonyl)pyrrolidin-2-yl)vinyl)-2,2-dimethyloxazolidine-3-carboxylate (41)** Column chromatography on silica gel (eluent: ethyl acetate/hexanes = 30/70) afforded the title product in 52% yield as colorless oil by following **GP2**. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 5.78-5.31 (m, 2H), 5.24-4.94 (m, 2H), 4.58-4.11 (m, 2H), 4.11-3.93 (m, 1H), 3.75 (d, *J* = 8.3 Hz, 1H), 3.32 (s, 2H), 2.08-1.59 (m, 7H), 1.50-1.32 (m, 12H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.6, 152.6, 136.7, 133.4, 128.6, 128.1, 94.5, 79.2, 68.8, 66.7, 58.7, 58.6, 58.0, 46.3, 32.0, 29.8, 28.6, 26.6, 23.7; **IR** (film) $cm^{-1}$: 2977, 1696, 1477, 1458, 1389, 1364, 1258, 1170, 1089, 10567, 960, 856, 766, 721; **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$: 431.2546, found 431.2549.




**2-(3-acetyl-2,2-dimethylcyclobutyl)-1-bromoethyl benzoate (S42)** Compound was synthesized following **GP1. $^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.11-7.99 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 10.9, 4.4 Hz, 2H), 6.88-6.73 (m, 1H), 2.99-2.78 (m, 1H), 2.53-1.92 (m, 8H), 1.30 (s, 3H), 0.91 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 207.5, 207.4, 164.1, 134.1, 130.1, 128.7, 75.6, 75.4, 54.4, 54.3, 43.4, 43.4, 40.4, 40.1, 39.5, 38.8, 30.3, 30.3, 23.7, 23.4, 17.6, 17.6; **IR** (film) $cm^{-1}$: 3030, 1725, 1600, 1453, 1253, 1056, 993, 709. **HRMS** (ESI-MS) m/z: calc'd for $[M+H]^+$ 353.0752, found 353.0755.

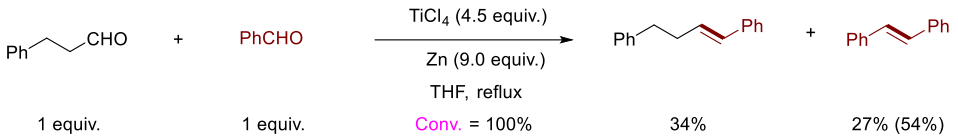



**(1*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (42)** Column chromatography on silica gel (eluent: hexanes) afforded the title product in 41% yield as colorless oil by following **GP2**. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 5.19 (dt, *J* = 4.4, 1.4 Hz, 1H), 2.34 (dt, *J* = 8.5, 5.6 Hz, 1H), 2.23 (dd, *J* = 17.3, 2.3 Hz, 1H), 2.16 (ddq, *J* = 17.3, 4.7, 2.3 Hz, 1H), 2.10-2.04 (m, 1H), 1.93 (td, *J* = 5.7, 1.3 Hz, 1H), 1.66 (dd, *J* = 3.9, 2.0 Hz, 3H), 1.27 (s, 3H), 1.15 (d, *J* = 8.5 Hz, 1H), 0.84 (s, 3H); **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 144.7, 116.2, 47.2, 40.9, 38.1, 31.6, 31.4, 26.5, 23.1, 21.0; The data is identical with an authentic sample.

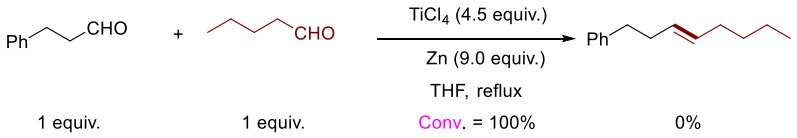
## V. Mechanistic experiments

### *a.* Comparison with McMurry reaction

**1) Aryl aldehyde**




**2) Aliphatic aldehyde**

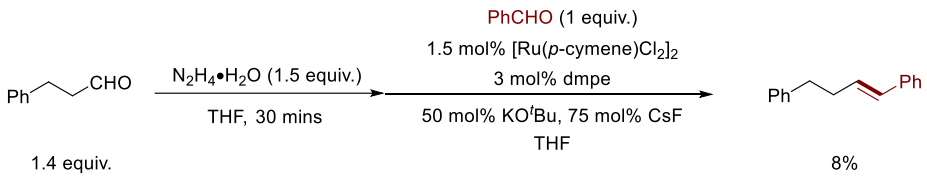



Zn dust (9 equiv.) was added to an oven-dried vial containing a stir bar, then dry THF (3 mL) was added after degassing the reaction vial. Titanium(IV) chloride (4.5 equiv.) was added dropwise via a syringe. When the addition was complete, the mixture was refluxed for 1 h. Next, to the cooled suspension of the titanium reagent, a solution of respective aldehydes (0.2 mmol each) in dry THF (1 mL) were added dropwise. The mixture was refluxed overnight, cooled, and poured into 10% aqueous potassium carbonate solution and extracted with ether. The combined ether extracts were dried (anhydrous $Na_2SO_4$) and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethylbenzene as internal standard.

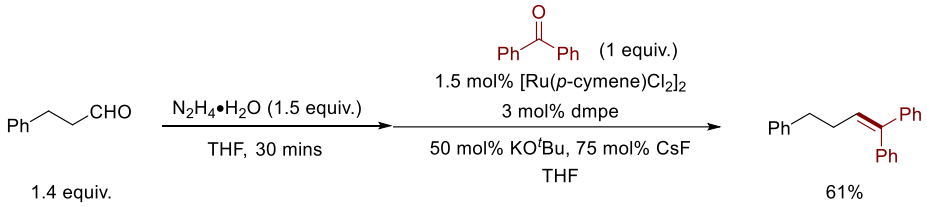
**Result:** These experiments show alkyl aldehydes are not viable acceptors in the McMurry strategy (current state of the art). Additionally, aryl aldehydes yield a statistical mixture of cross and dimer products.

## *b.* Comparison with hydrazone strategy

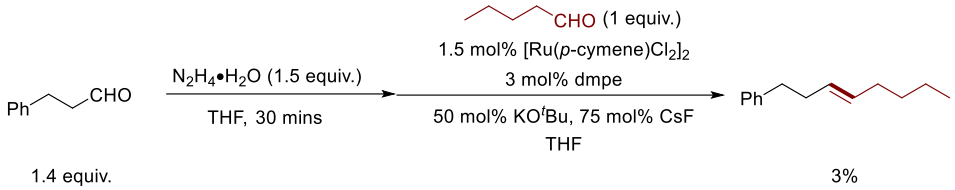
**1) Aryl aldehyde**




**2) Ketone**




**3) Aliphatic aldehyde**

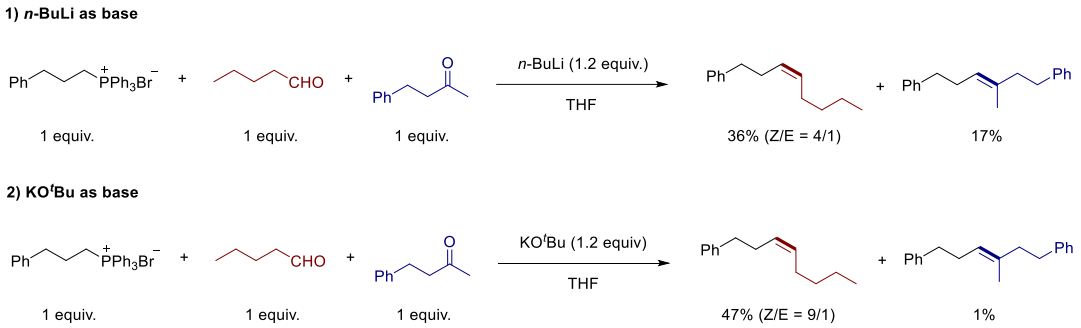



According to Ref 15, a flame-dried vial equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)$Cl_2$]$_2$ (1.8 mg, 0.003 mmol, 1.5 mol%) and KO$^t$Bu (11.2 mg, 0.1 mmol, 50 mol%). The reaction vial was then transferred into the glovebox and charged with dmpe (1.0 μL, 0.006 mmol, 3 mol%) and CsF (22.8 mg, 0.15 mmol, 75 mol%), before being sealed with a rubber septum. The reaction vial was then moved out of the glovebox and sequentially charged with ketones or aldehydes (0.2 mmol, 1.0 equiv.) and the **hydrazone solution** (0.28 mmol). The reaction mixture was then heated to 45 $^o$C in an oil bath. Upon stirring for 12 h, the reaction mixture was filtered through a plug of silica gel with $CH_2Cl_2$ (10 mL) as eluent, concentrated and the relevant yields were measured by $^1$H NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Hydrazone solution**: A mixture of carbonyls (0.28 mmol, 1.4 equiv.) and hydrazine monohydrate (17.5 μL, 0.3 mmol, 64-65 wt%, 1.5 equiv.) in THF (0.14 mL) solution was stirred at room temperature for 30 min. Prior to the injection of this hydrazone solution into reaction mixture, a small amount of anhydrous $Na_2SO_4$ was added.

**Result:** These experiments show alkyl aldehydes are not viable acceptors for the hydrazone strategy (current state of the art).

## *c.* Comparison with Wittig reaction




### Procedure for using *n*BuLi as base

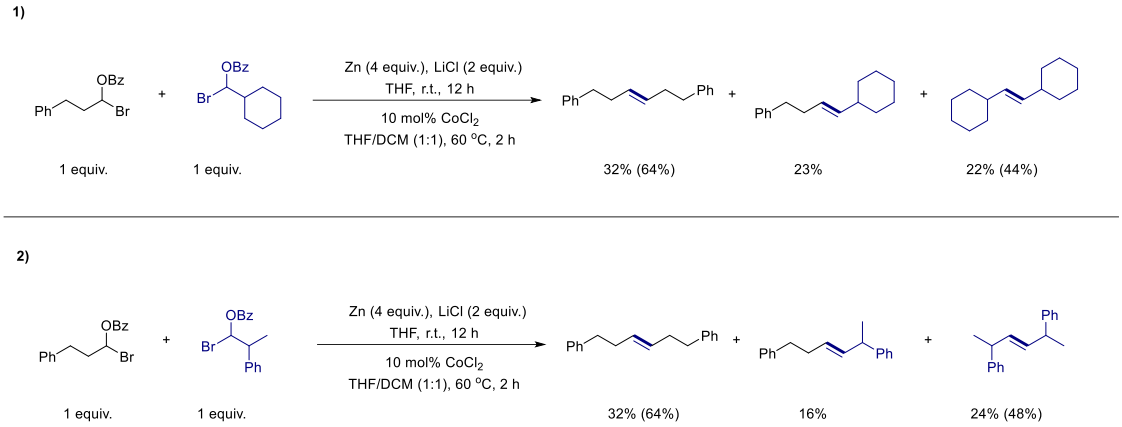
(3-Phenylpropyl)triphenylphosphonium bromide (1 equiv., 0.5 mmol) was added to an oven-dried vial containing a stir bar, then dry THF (1.5 mL) was added after degassing the reaction vial. Next, *n*BuLi (1.2 equiv., 2.5 M in hexanes) was added dropwise at -10 °C, and the reaction was stirred for 30 mins at this temperature. A solution of pentanal (0.5 mmol, 1 equiv.) and 4-phenylbutan-2-one (0.5 mmol, 1 equiv.) in dry THF (1.25 mL) was added dropwise, then warmed to room temperature and stirred overnight. The reaction mixture was filtered through a plug of silica gel with $CH_2Cl_2$ (10 mL) as eluent, concentrated, and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethyl-benzene as internal standard.

### Procedure for using KO$^t$Bu as base

(3-Phenylpropyl)triphenylphosphonium bromide (1 equiv., 0.5 mmol) was added to an oven-dried vial containing a stir bar, then dry THF (1.5 mL) was added after degassing the reaction vial. Next, *KO$^t$Bu* (1.25 equiv., 1 M in THF) was added dropwise at room temperature, and the reaction was stirred for 30 mins. A solution of pentanal (0.5 mmol, 1 equiv.) and 4-phenylbutan-2-one (0.5 mmol, 1 equiv.) in dry THF (1.25 mL) was added dropwise and stirred overnight. The reaction mixture was filtered through a plug of silica gel with $CH_2Cl_2$ (10 mL) as eluent, concentrated, and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show aldehydes are better acceptors than ketones in the Wittig reaction, and this selectivity is dependent on the choice of base.

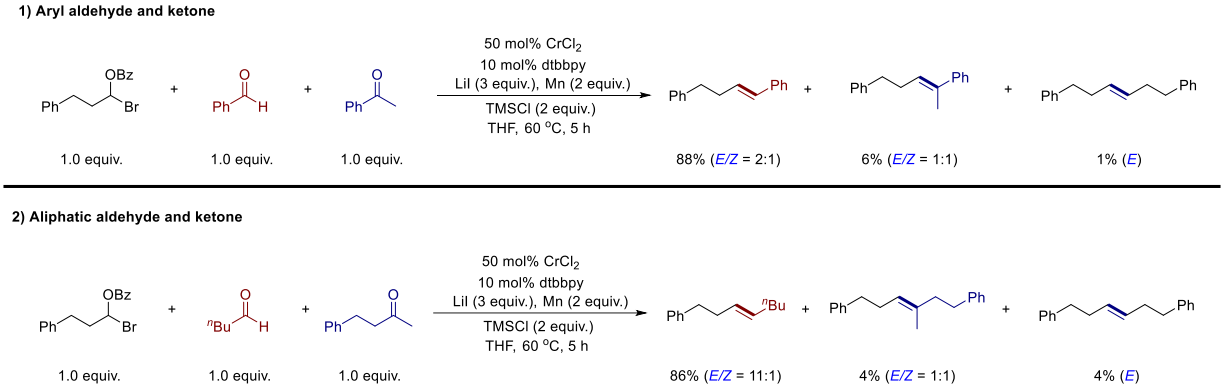
### *d.* Comparison with Co-catalyzed carbene reaction




To an oven-dried 8 mL vial was added LiCl (17 mg, 2 equiv.), Zn dust (52 mg, 4 equiv.) and a stir bar. The reaction vessel was heated under vacuum to 170 °C for 20 min with vigorous stirring. After cooling to room temperature, a solution of $\alpha$-acyloxy bromide (0.2 mmol/each, 1 equiv./each) in dry THF (2 mL) was added dropwise. The vessel was sealed with parafilm and electrical tape and allowed to stir at room temperature for 12 h. After allowing Zn particles to settle, the resulting alkyl zinc carbenoid solution was transferred to an oven-dried vial containing $CoCl_2$ (2.6 mg, 10 mol%), a stir bar and 1:1 THF/DCM (1 mL/1 mL). The mixture was then stirred at 60 $^oC$ for 2 h then diluted with $Et_2O$ and filtered through a short pad of silica gel. The solvent was removed in vacuo and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show our previous carbene method was limited to generating statistical mixtures, where the only mechanism for (minimal) differentiation between the aldehydes is sterics.

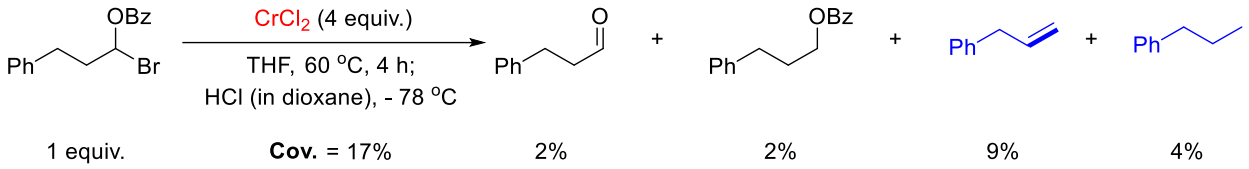
## *e.* Competition experiments




In two separate oven-dried vials, activated aldehyde (1.0 equiv.) was added in **vial A**, and Mn (24 mg, 2 equiv.) and dtbbpy (5.4 mg, 10 mol%) were added to **vial B** with a stir bar, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and $CrCl_2$ (12.4 mg, 50 mol%) was added, followed by 1 mL dry THF and TMSCl (50 µL, 2 equiv.). Both vials are sealed with a cap, then moved out of the glovebox. The mixture of aldehyde and ketone (1 equiv./each, 0.2 mmol/each) was added to **vial B**, then the solution of activated aldehydes in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through septa caps). After addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C for 5 h. When the reaction is complete, the reaction mixture is diluted with hexanes, then filtered through a short pad of silica gel and washed with hexanes and ethers. The solvent was removed in vacuo and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethylbenzene as internal standard.

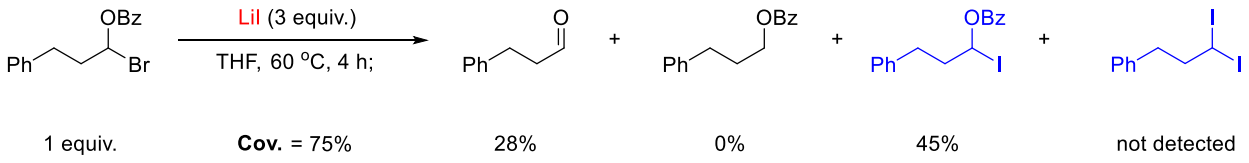
**Result:** These experiments show aldehydes are better acceptors than ketones (>20:1) for both aryl and alkyl cases. Additionally, cross-to-dimer selectivity remains high (>20:1) in these three-way competitions.

### *f.* Control experiments



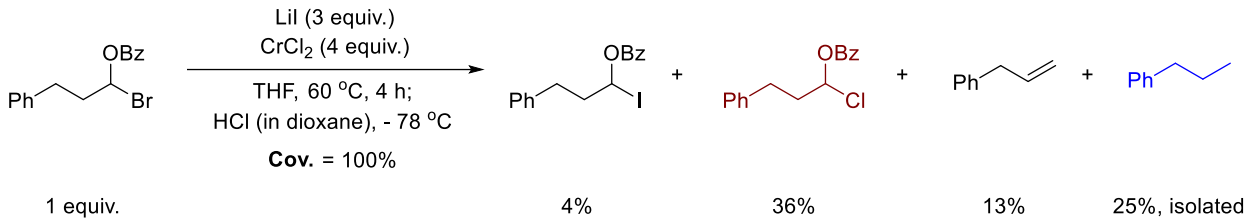

In two oven-dried vials, activated aldehyde (0.2 mmol, 1.2 equiv.) was added in **vial A**. Then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, $CrCl_2$ (4 equiv.) and 1 mL dry THF were added. Both vials were sealed with a cap, then removed from the glovebox. The solution of activated aldehyde in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through caps). After the addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C for 4 h. The reaction was cooled to -78 °C by using an acetone/dry ice bath and quenched by adding 4M HCl solution in dioxane dropwise, then warmed to room temperature gradually. The reaction was filtered through a short pad of silica gel and washed with hexanes and ethers. The solvent was removed in vacuo and the relevant yields were measured by $^1$H NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show minimal conversion in the absence of LiI (17%).



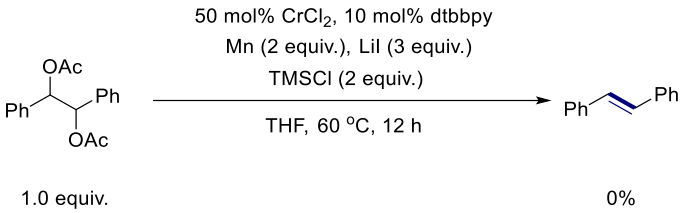

In an oven-dried vial, activated aldehyde (1 equiv.) was added and introduced into glovebox. LiI (3 equiv.) and dry THF (1 mL) were added. The vial is sealed with a cap, then moved out of the glovebox and stirred at 60 °C for 4 h. The reaction was filtering through a short pad of silica gel, washed with hexanes and ethers. The solvent was removed in vacuo and the relevant yields were measured by $^1$H NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show greater conversion with LiI (75%) via an α-iodide intermediate.




In two oven-dried vials, activated aldehyde (0.2 mmol, 1 equiv.) was added in **vial A**, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and $CrCl_2$ (4 equiv.) were added, followed by 1 mL dry THF. Both vials are sealed with a cap, then moved out of the glovebox. The solution of activated aldehydes in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through caps). After the addition, the vessel was sealed with parafilm and electrical tape and stirred at 60 °C for 4 h. The reaction was filtering through a short pad of silica gel, washed with hexanes and ethers. The solvent was removed in vacuo and the relevant yields were measured by $^1H$ NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show full conversion with LiI and $CrCl_2$. Only fully reduced product (25% isolated) from a dichromium intermediate is observed. No singly reduced product from proto-demetallation of a mono-chromium intermediate is observed.

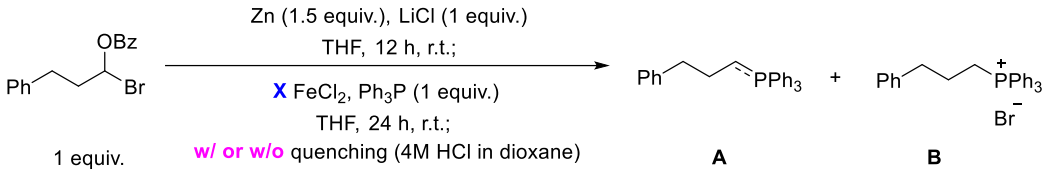



In two oven-dried vials, 1,2-diphenylethane-1,2-diyl diacetate (1 equiv.) was added in **vial A**. Mn (24 mg, 2 equiv.) and dtbbpy (5.4 mg, 10 mol%) were added to **vial B** with a stir bar, then both vials were introduced into a glovebox. In **vial A**, dry THF (1 mL) was added. In **vial B**, LiI (81 mg, 3 equiv.) and $CrCl_2$ (12.4 mg, 50 mol%) was added, followed by 1 mL dry THF and TMSCl (50 µL, 2 equiv.). Both vials are sealed with a cap, then moved out of the glovebox. The solution of 1,2-diphenylethane-1,2-diyl diacetate in THF in **vial A** was transferred to **vial B** via syringe while it stirs at room temperature under $N_2$ protection (a needle connected to $N_2$ was inserted through caps). After addition, the vessel was sealed with parafilm and electrical tape and stirred at

60 °C overnight. After completion, the mixture is diluted with hexanes, filtered through a short pad of silica gel, and washed with hexanes and ethers. The solvent was removed in vacuo and the relevant yields were measured by $^1$H NMR using 1,2,4,5-tetramethylbenzene as internal standard.

**Result:** These experiments show a pinacol intermediate is not involved.

### *g.* $^{31}$P NMR studies



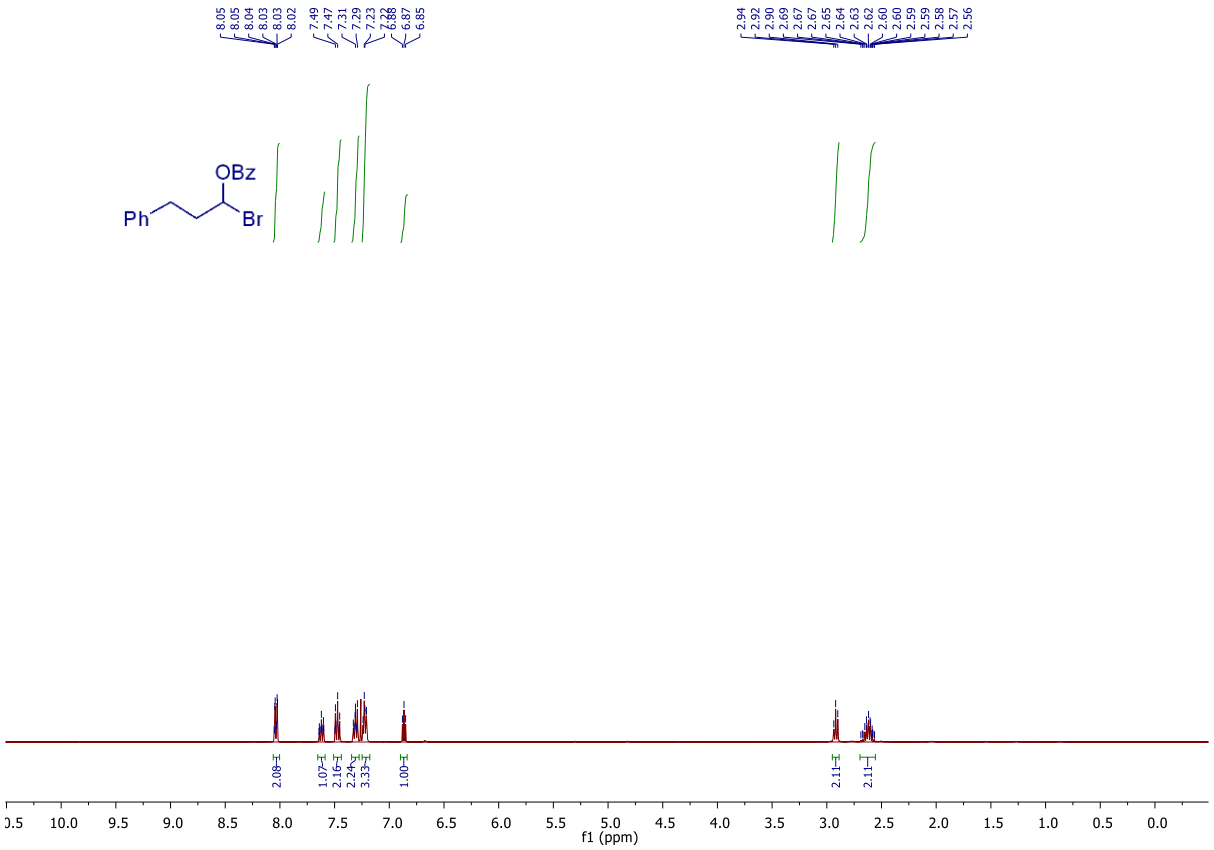

| Entries | X | *w/* or *w/o* | Yields **A** | Yields **B** |
|---|---|---|---|---|
| **1** | 20 mol% | *w/o* | 0% | 69% |
| **2** | 100 mol% | *w/o* | 0% | > 90%, only one 31P NMR peak |
| **3** | 20 mol% | *w/* | 0% | > 90%, only one 31P NMR peak |
| **4** | 100 mol% | *w/* | 0% | > 90%, only one 31P NMR peak |

**Note**: NMR were measured by dissolving the crude reaction in $d_8$-DMSO without other work-up

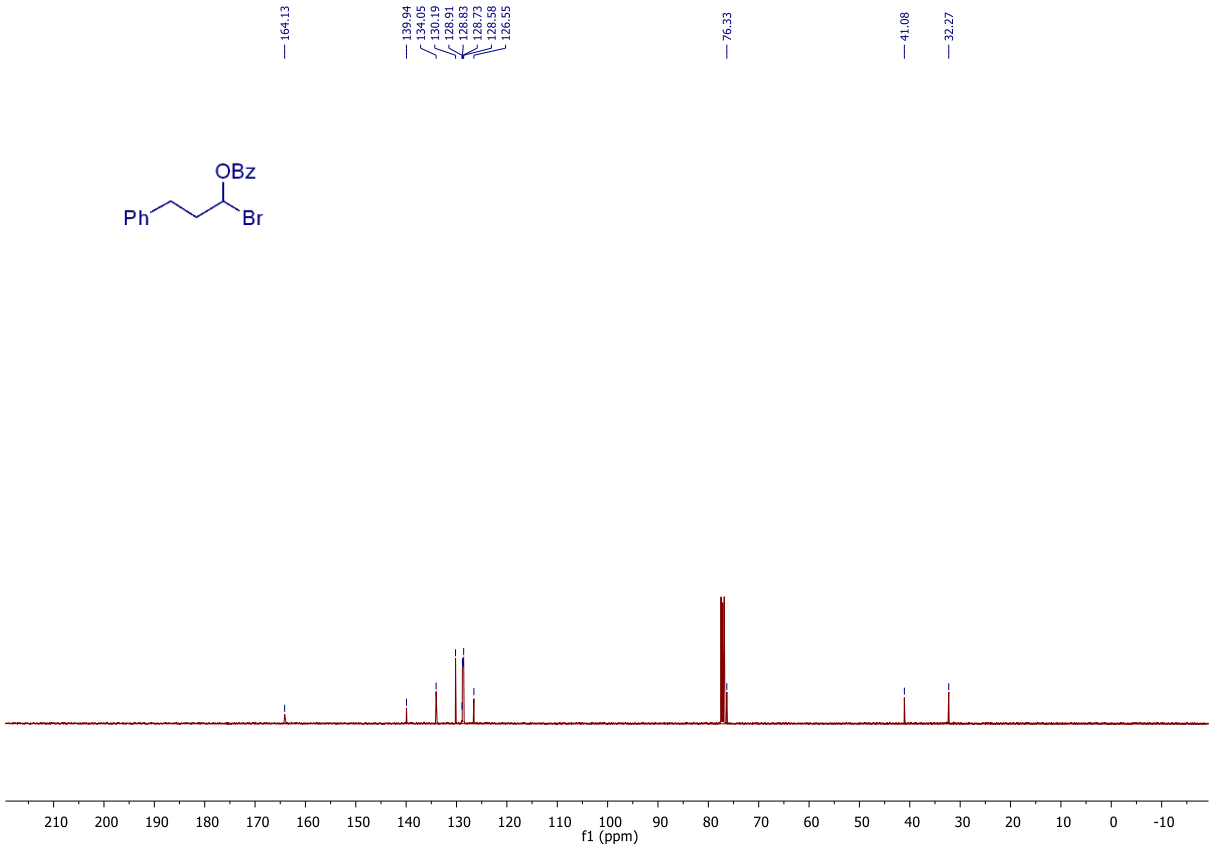
To an oven-dried 8 mL vial was added LiCl (1 equiv.), Zn dust (1.5 equiv.) and a stir bar. The reaction vessel was heated under vacuum to 170 °C for 20 min with vigorous stirring. After cooling to room temperature, a solution of α-acyloxy bromide (1 equiv.) in dry THF (1 mL) were added dropwise. The vessel was sealed with parafilm and electrical tape and allowed to stir at room temperature for 12 h. After allowing Zn particles to settle, the resulting alkyl zinc carbenoid solution was transferred to an oven-dried vial containing $FeCl_2$ (**X**), a stir bar, $Ph_3P$ (1 equiv.), and THF (1 mL) via syringe. The mixture was stirred at room temperature for 24 h. In the case of **with quenching**, the reaction was cooled to -78 °C by using acetone/dry ice bath and quenched by adding 4M HCl in dioxane (10 equiv.) dropwise, warm up to room temperature gradually and diluted with 2 mL $d_6$-DMSO. In the case of **without quenching**, the reaction was diluted with 2 mL *d*$_8$-DMSO. The relevant yields were measured by $^{31}$P NMR using $Ph_3P$ as internal standard.

**Result:** These experiments show the phosphonium ylide is generated in greater quantities than catalyst loading (>90% conversion vs 20% Fe catalyst).

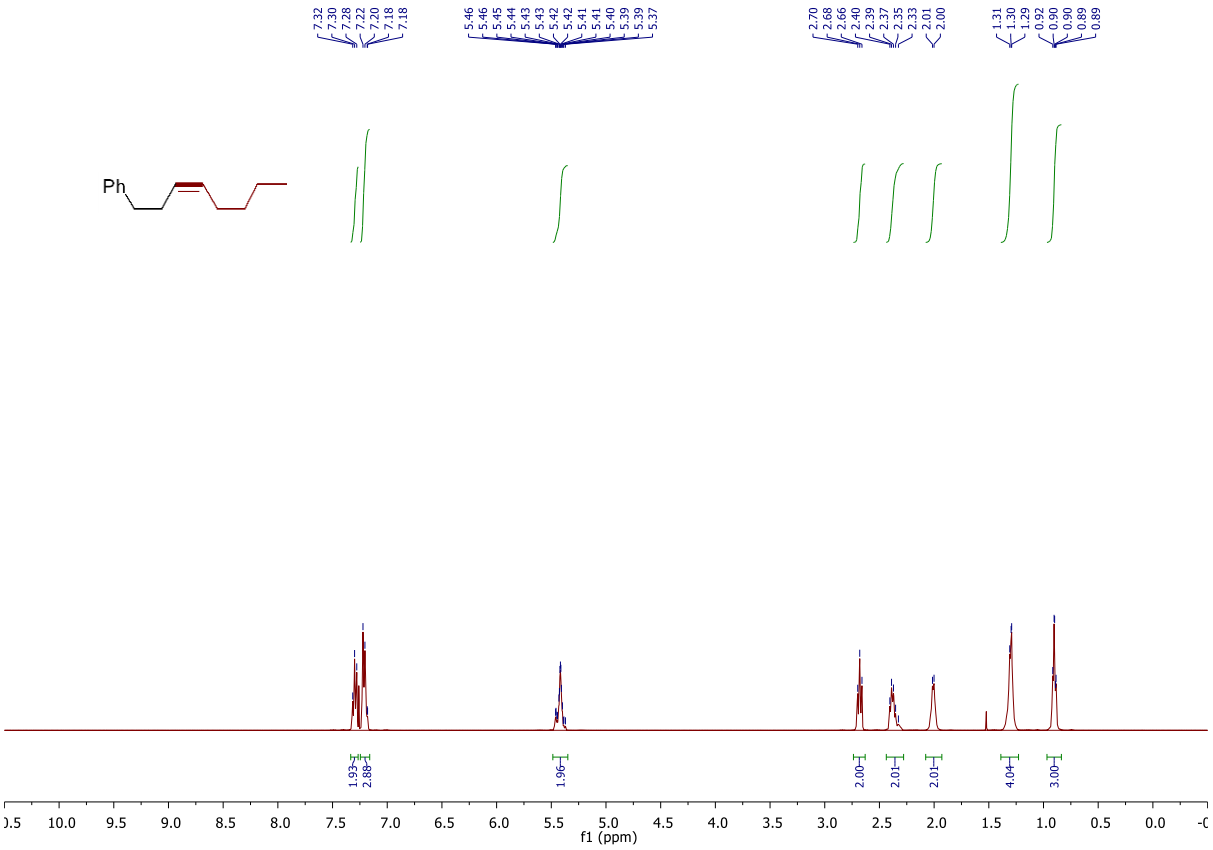
$^{1}$H-NMR spectrum of **S1**



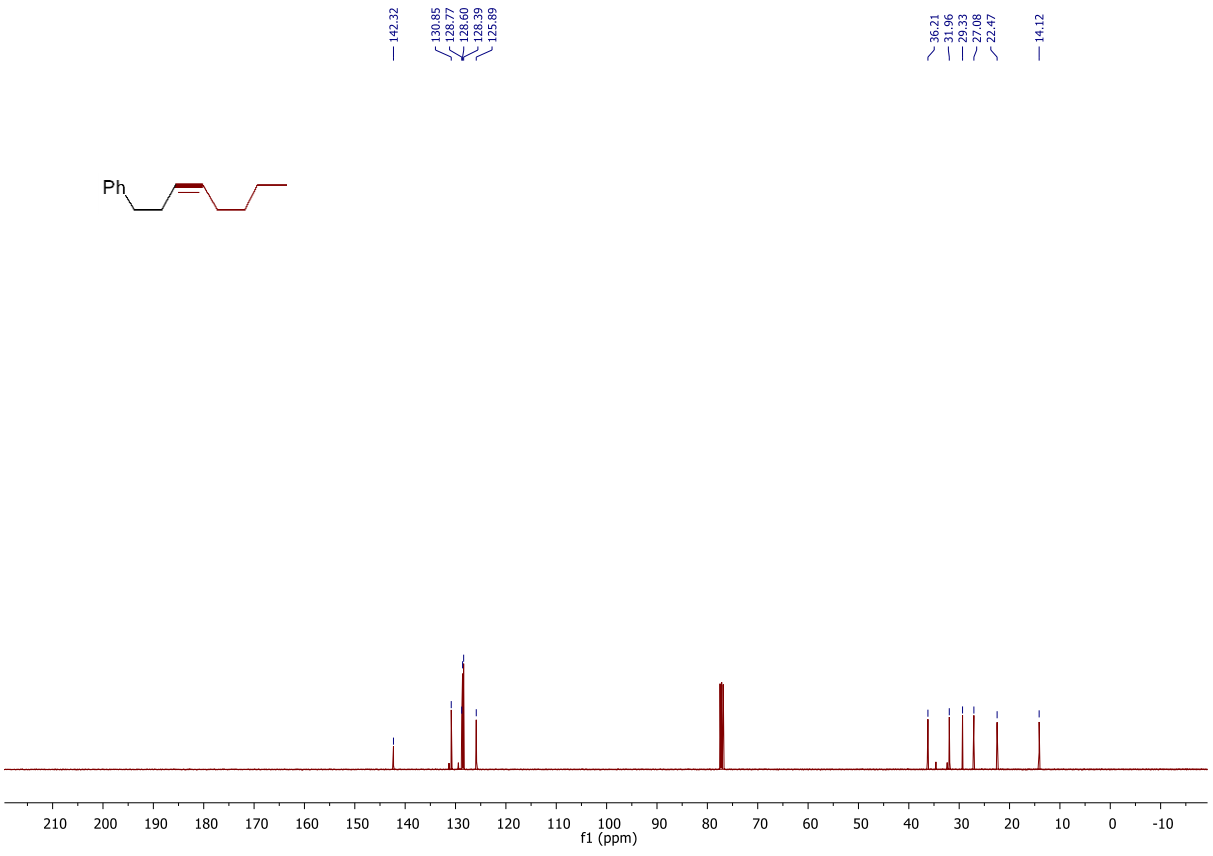

$^{13}$C-NMR spectrum of **S1**



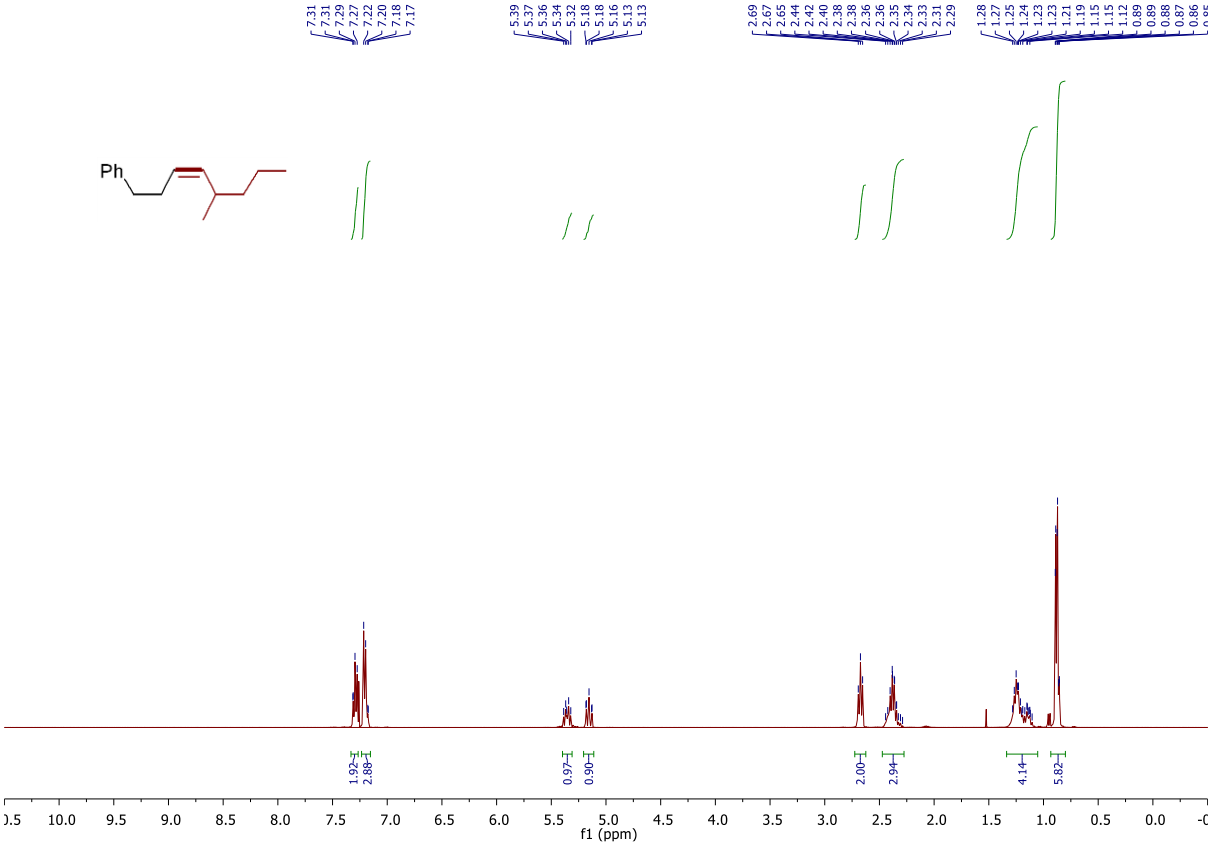
$^{1}$H-NMR spectrum of **1**



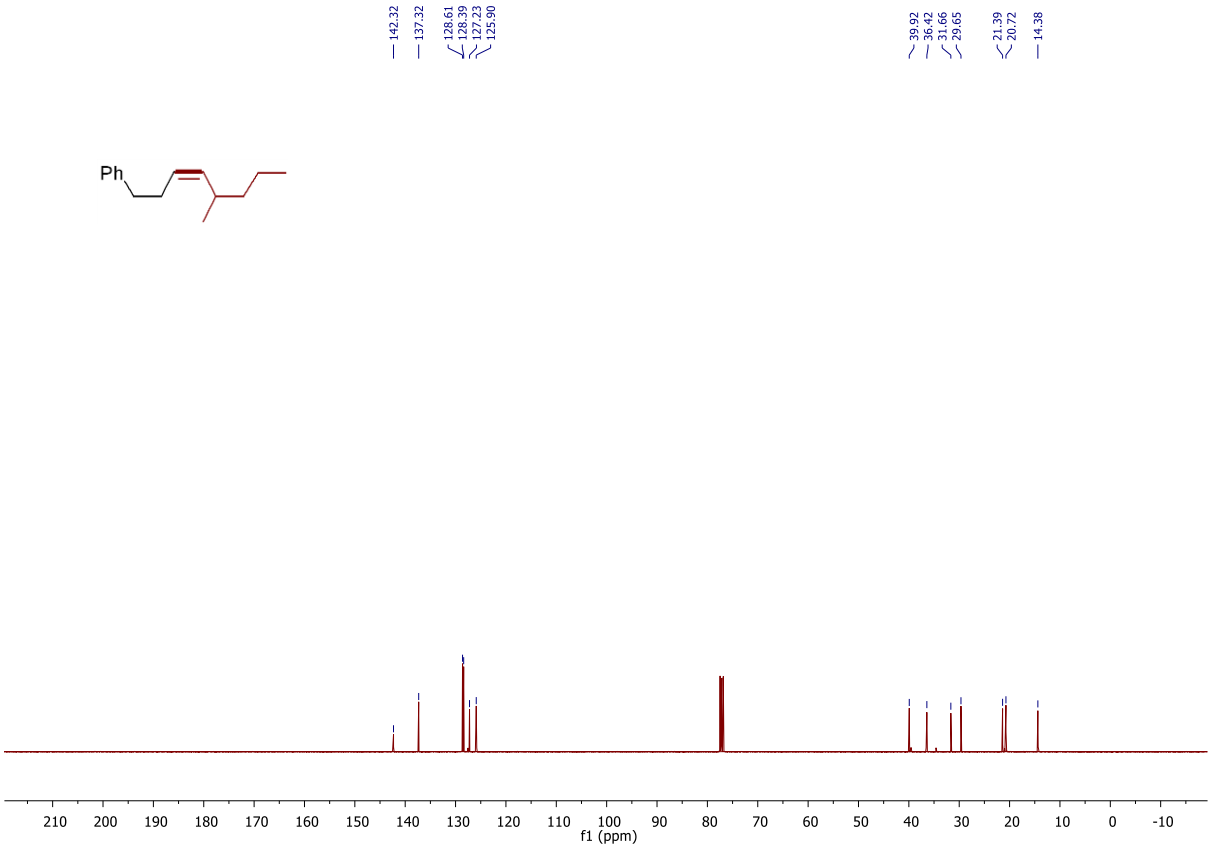

$^{13}$C-NMR spectrum of **1**



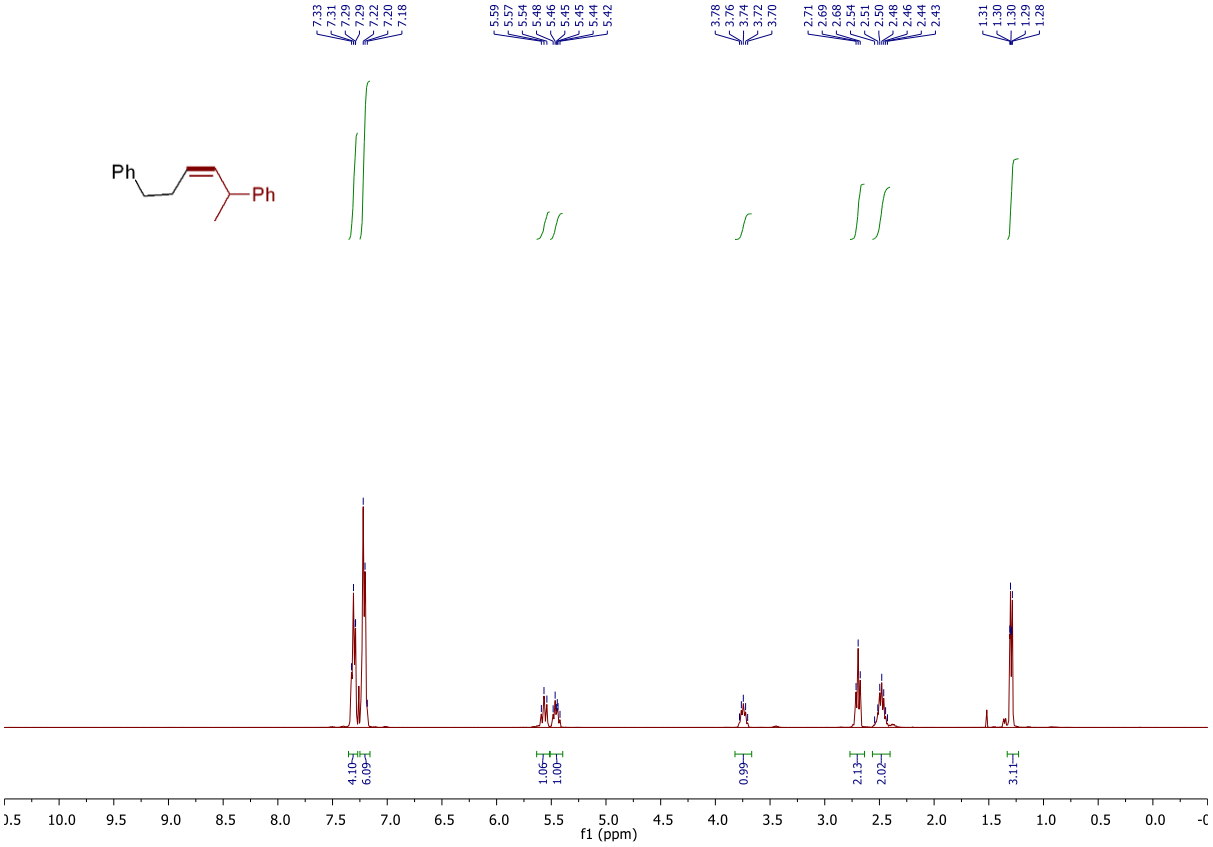
$^{1}$H-NMR spectrum of **2**



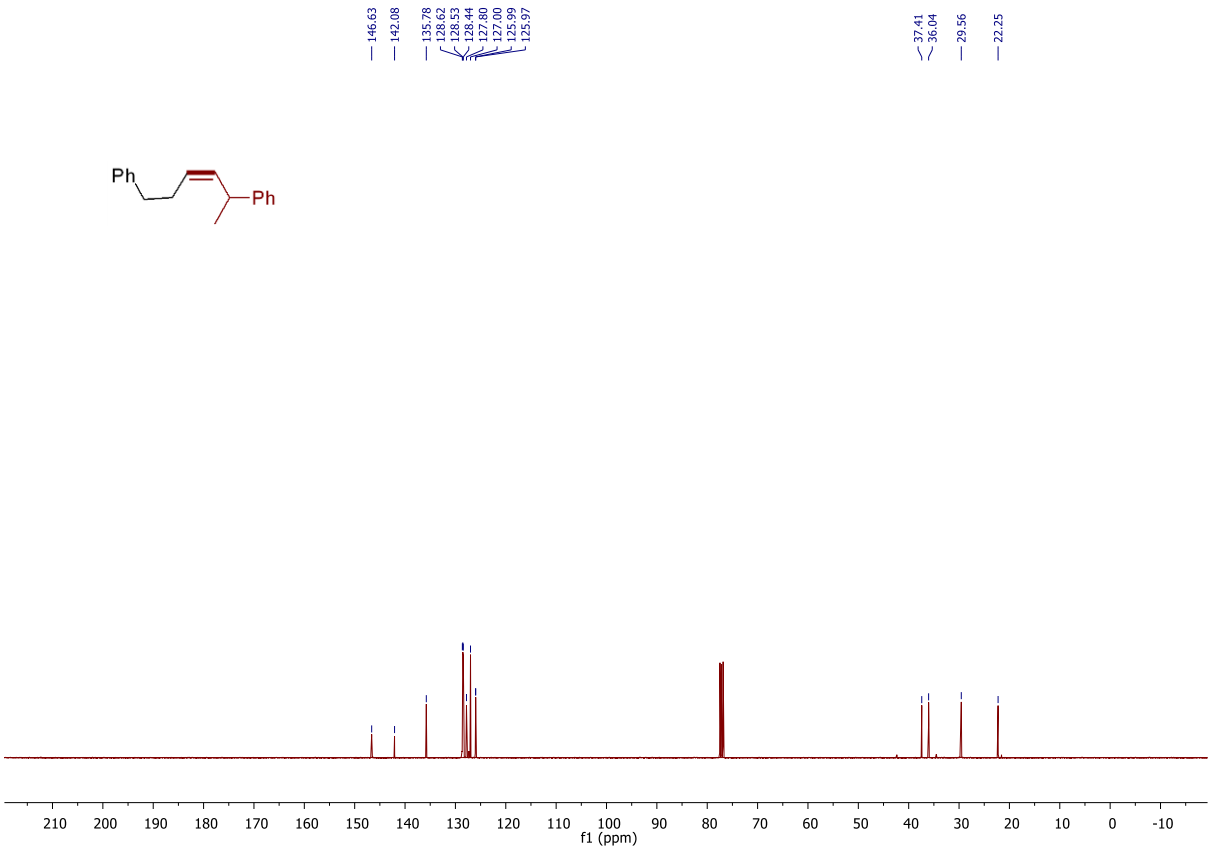

$^{13}$C-NMR spectrum of **2**



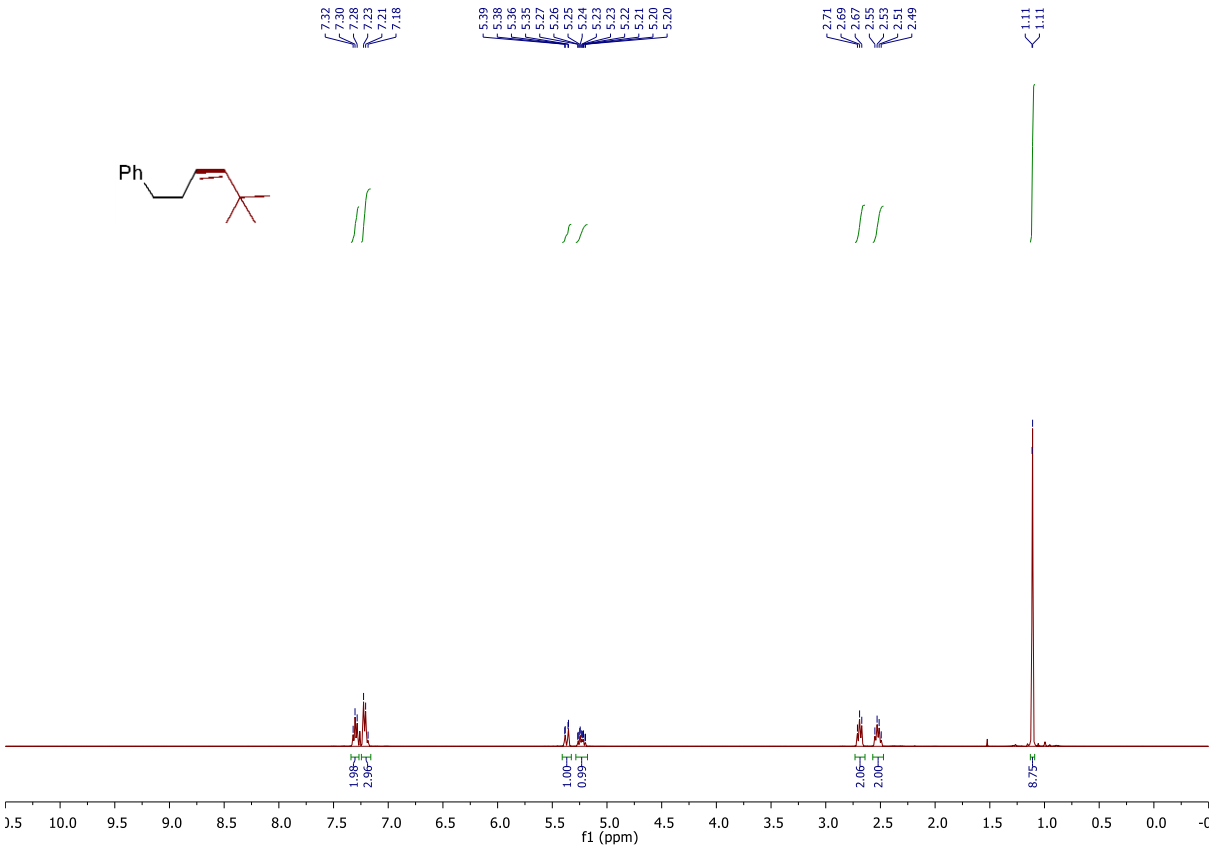
$^{1}$H-NMR spectrum of **3**



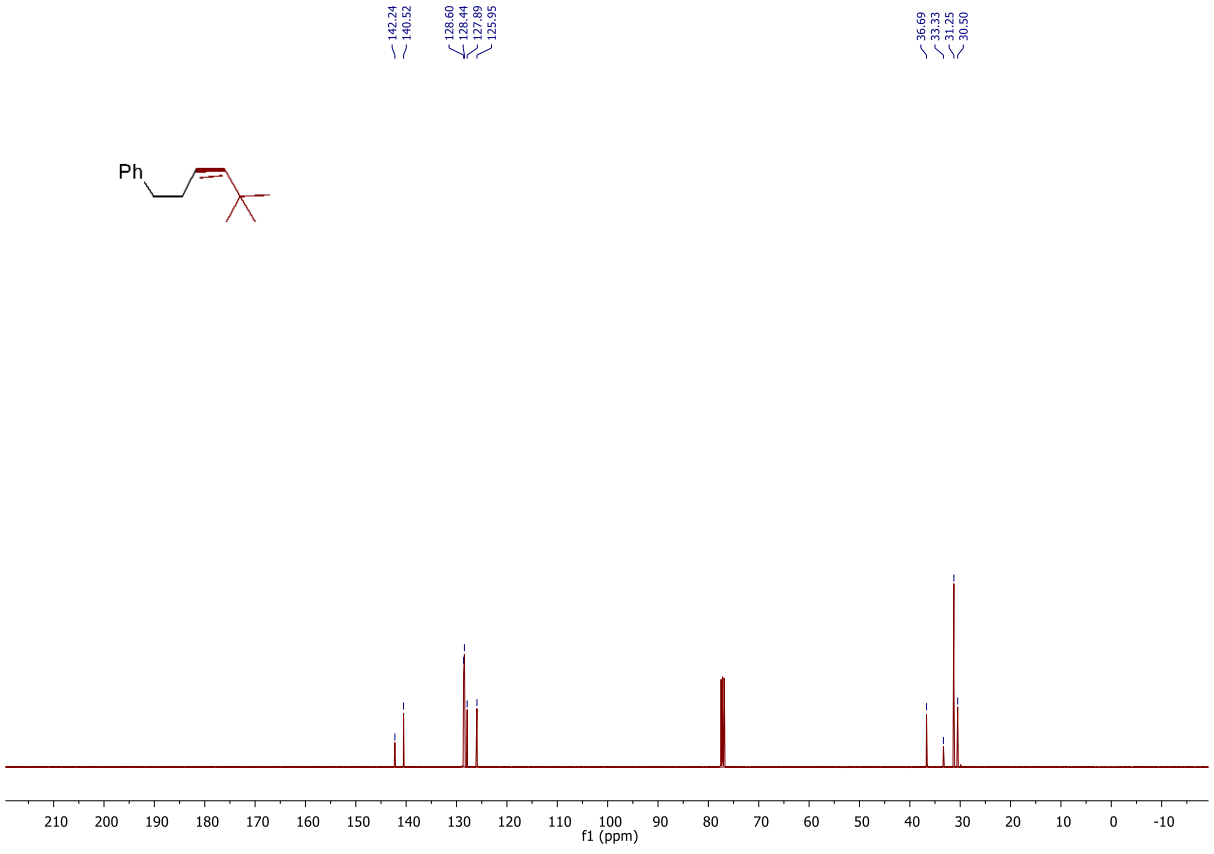

$^{13}$C-NMR spectrum of **3**



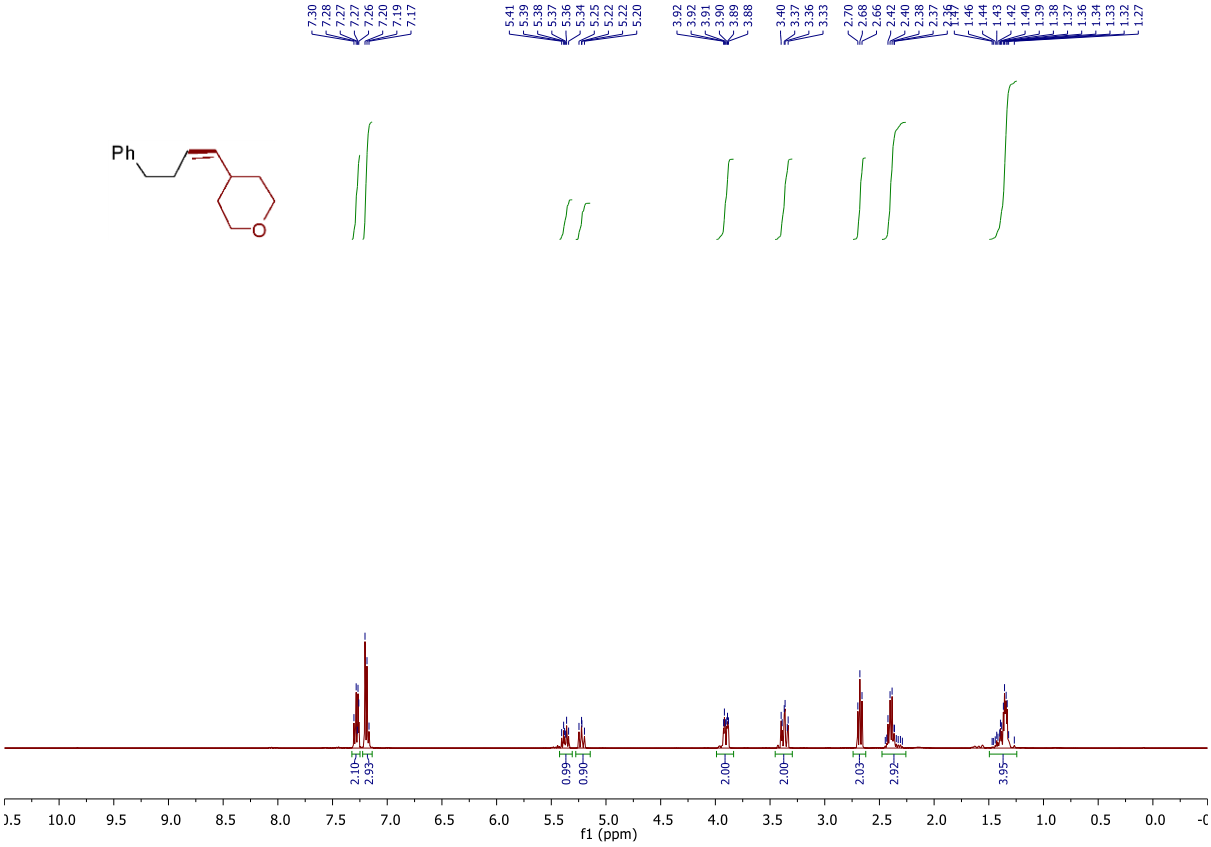
$^{1}$H-NMR spectrum of **4**



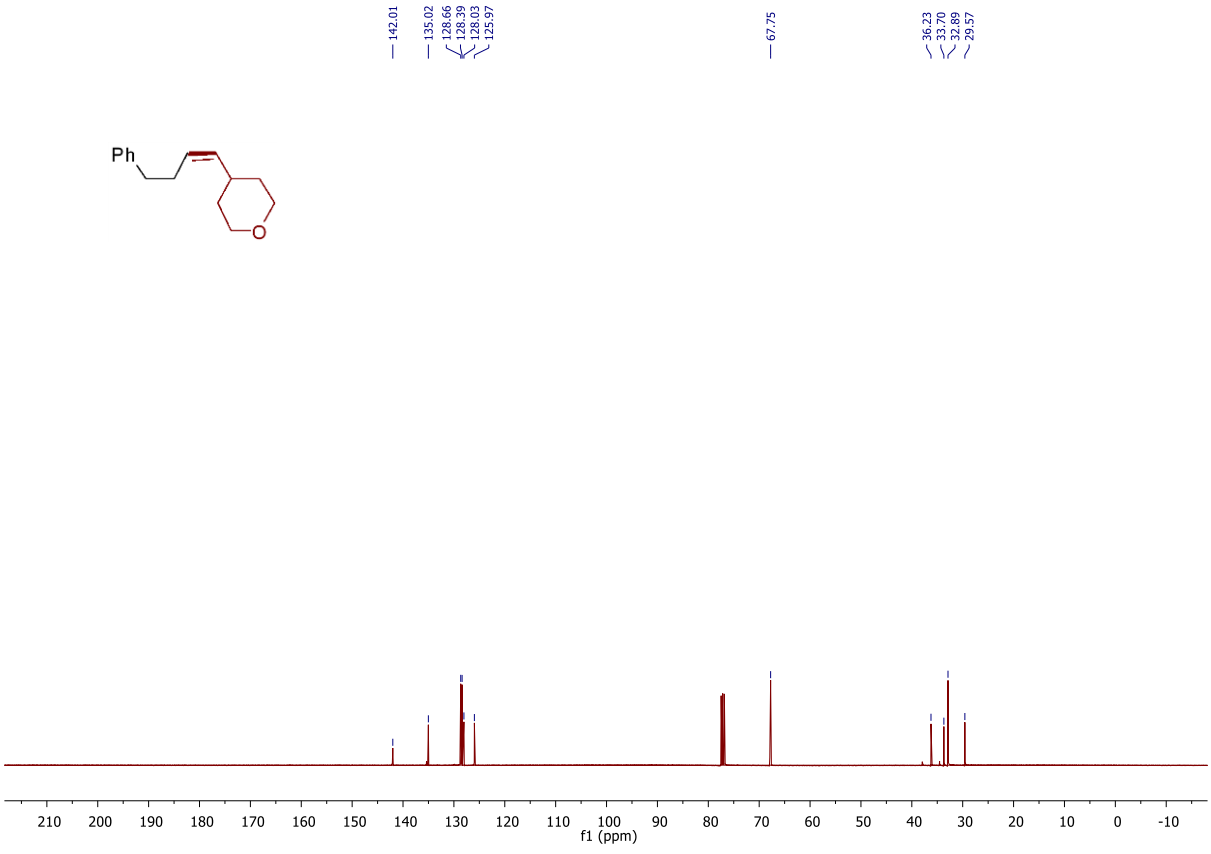

$^{13}$C-NMR spectrum of **4**



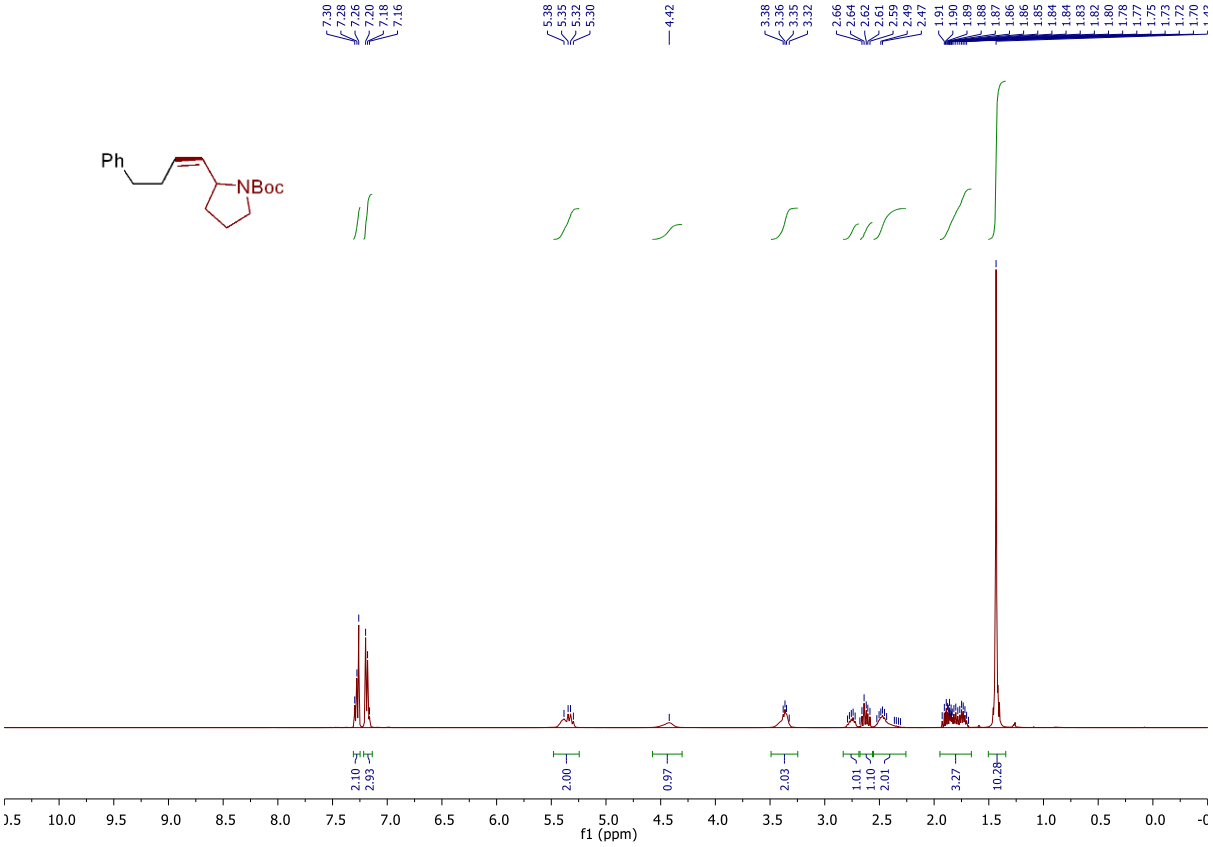
$^{1}$H-NMR spectrum of **5**



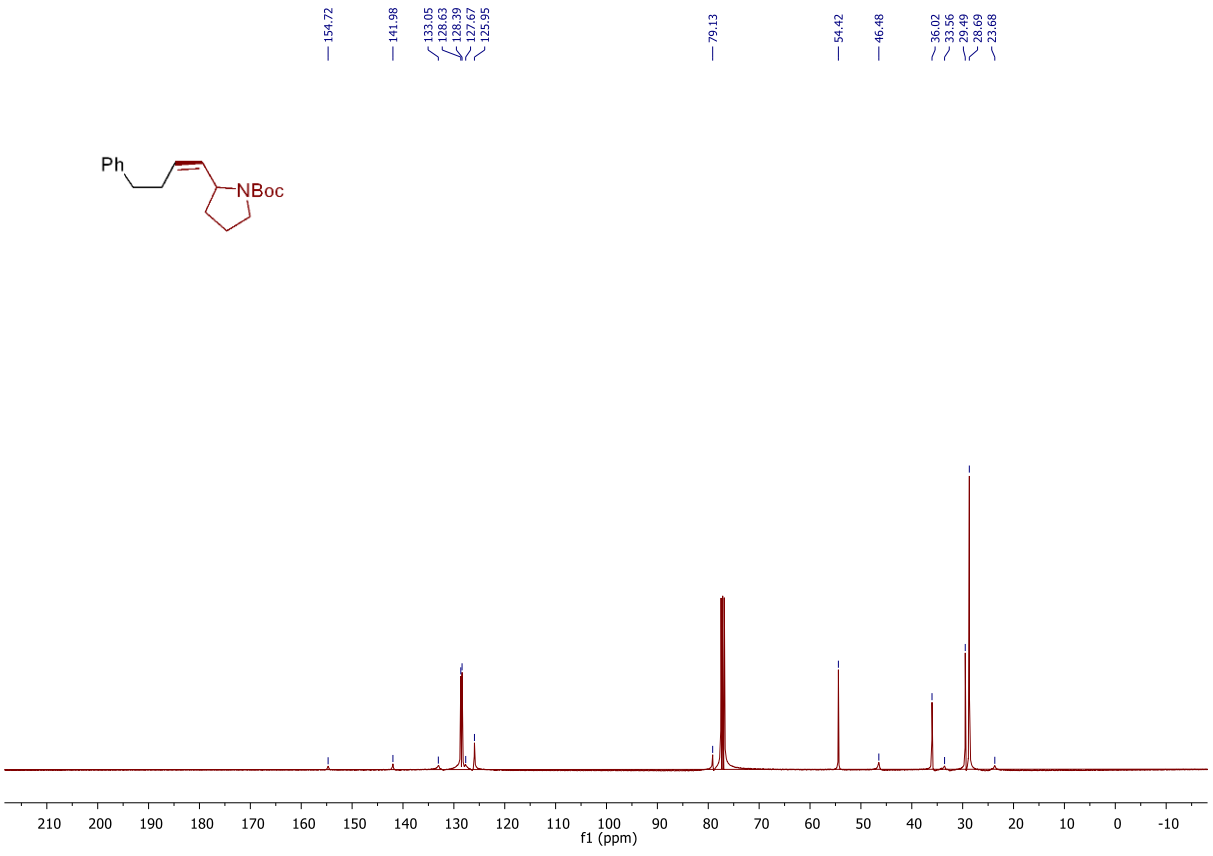

$^{13}$C-NMR spectrum of **5**



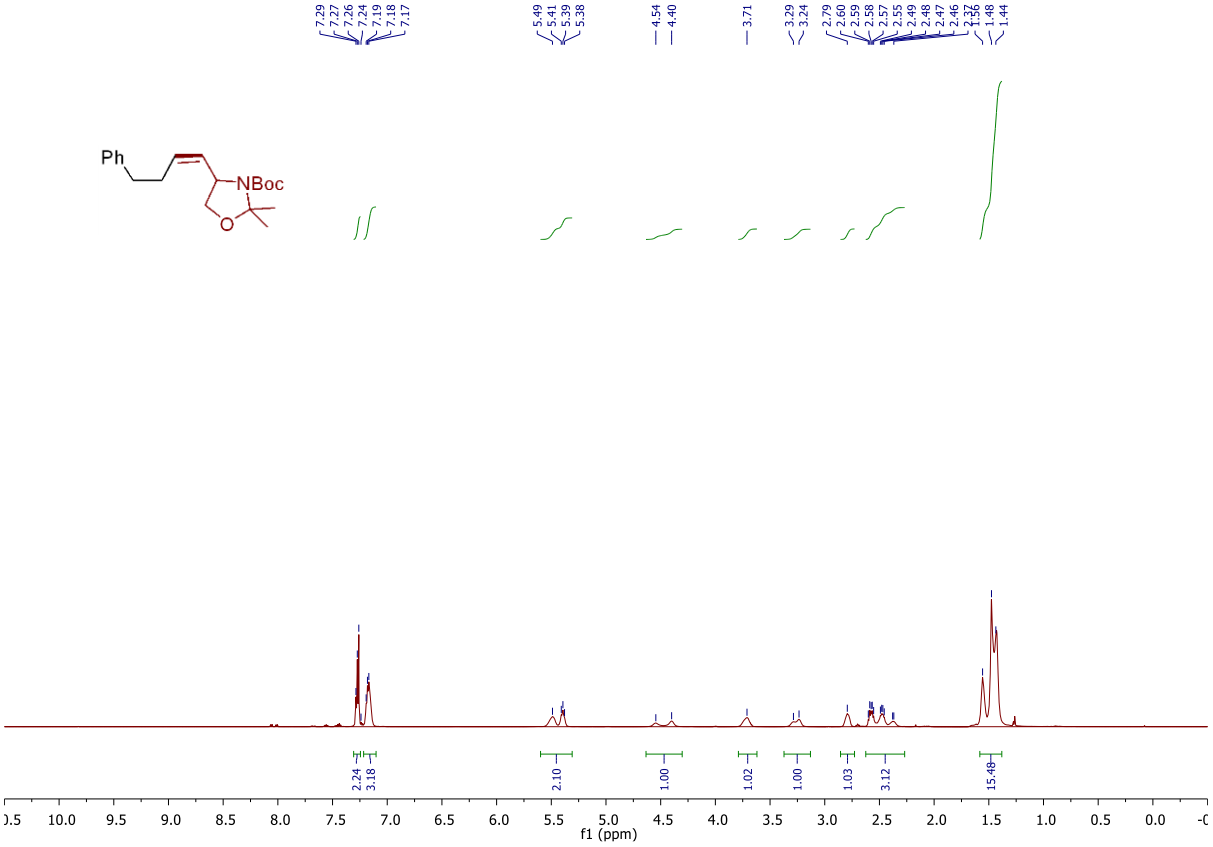
[1]H-NMR spectrum of **6**



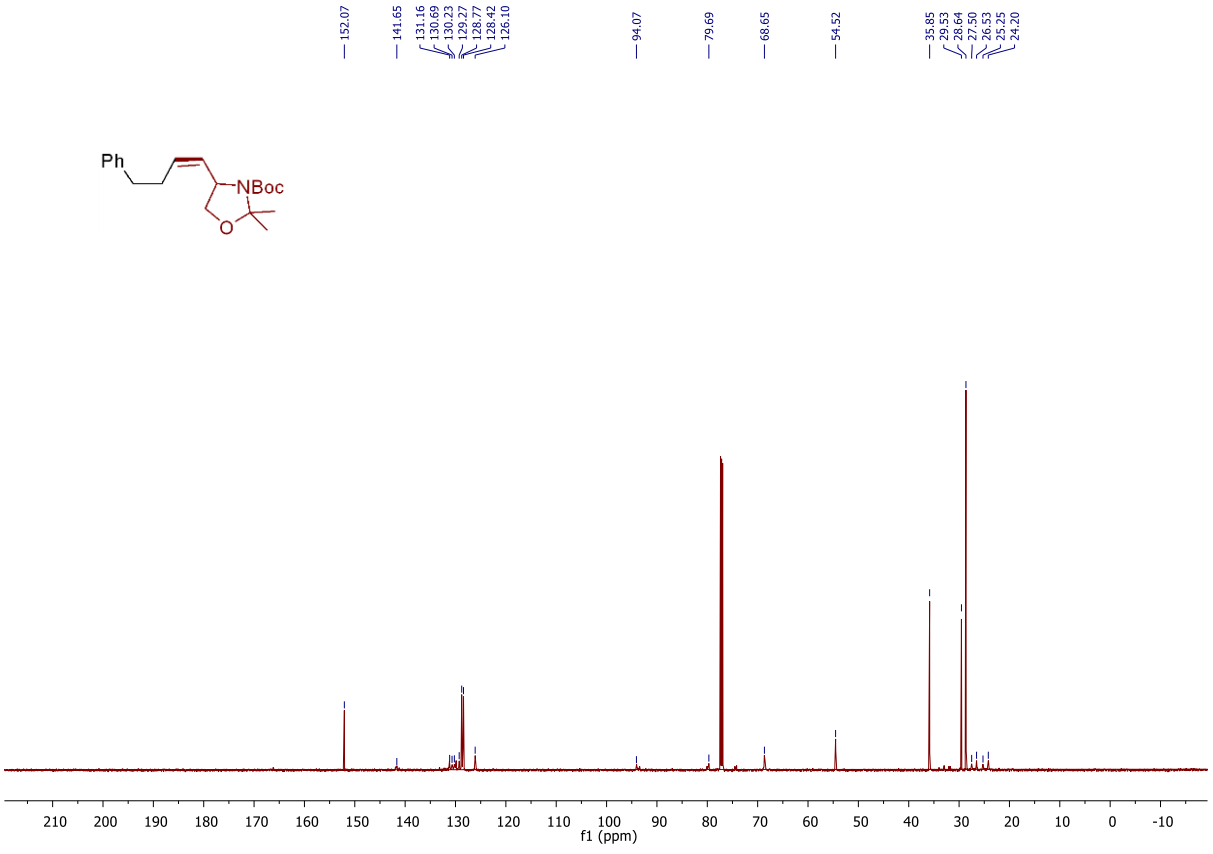

[13]C-NMR spectrum of **6**



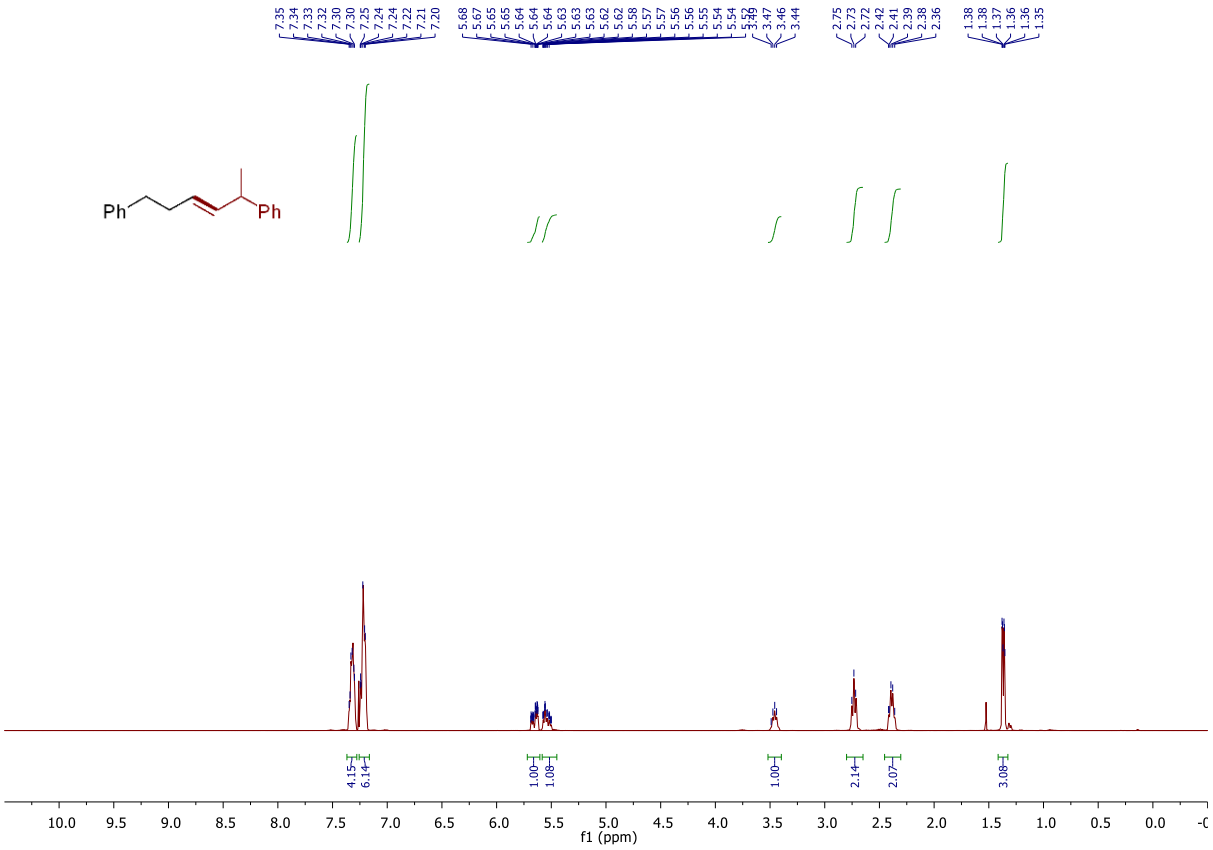
$^{1}$H-NMR spectrum of **7**



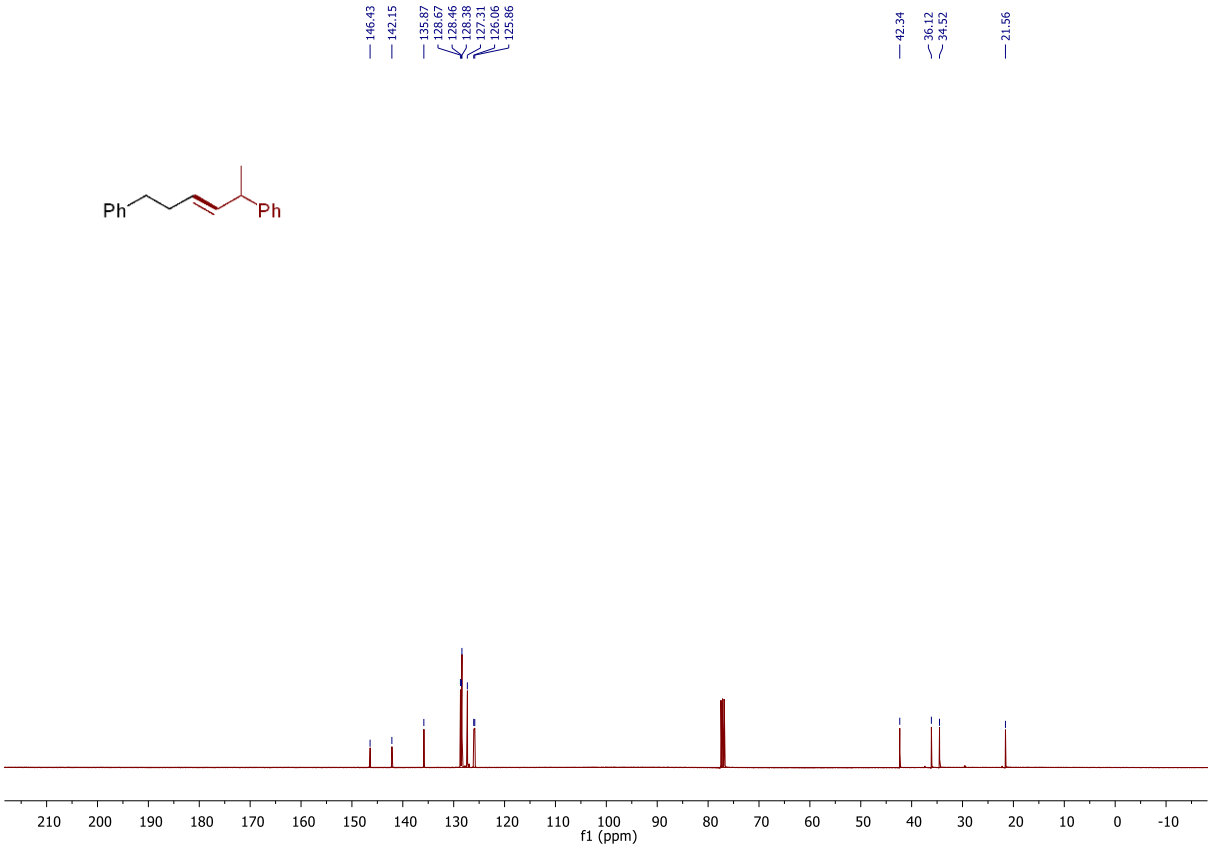

$^{13}$C-NMR spectrum of **7**



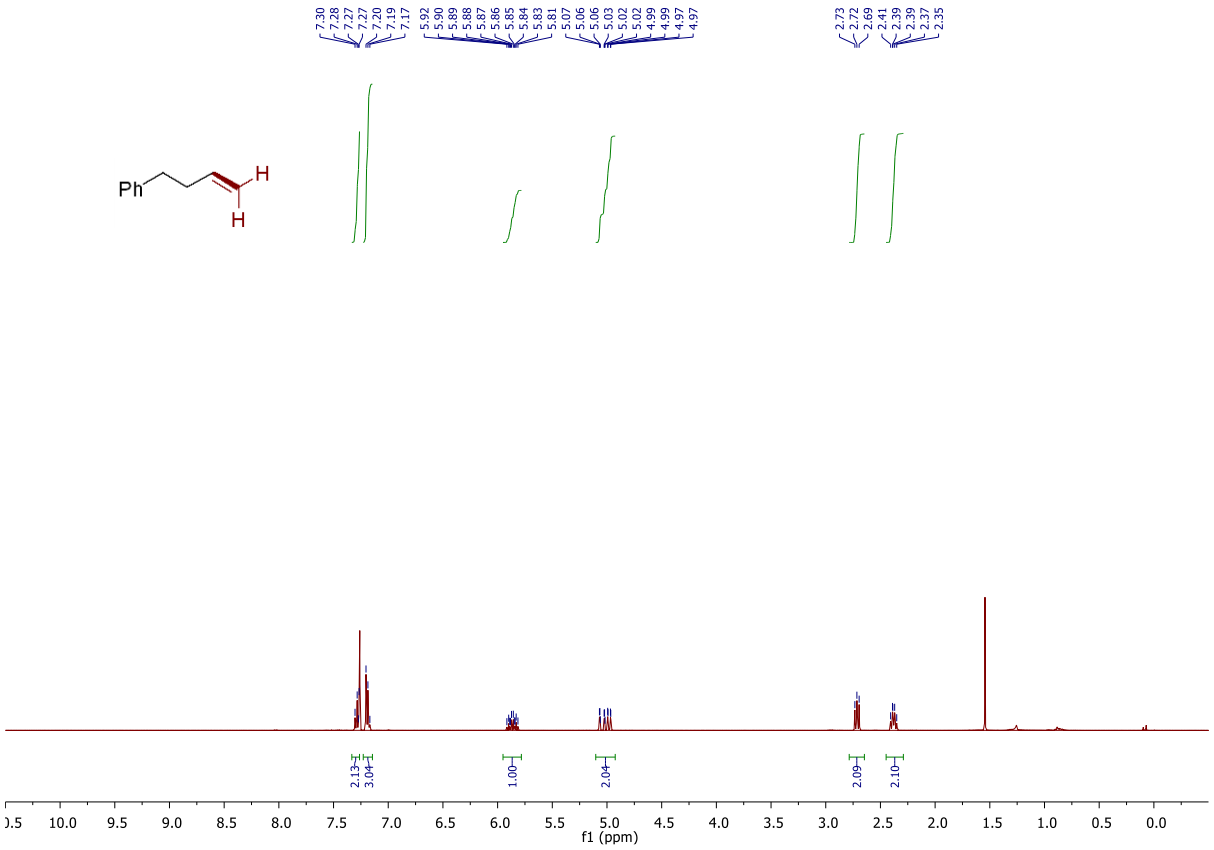
[1]H-NMR spectrum of **8**



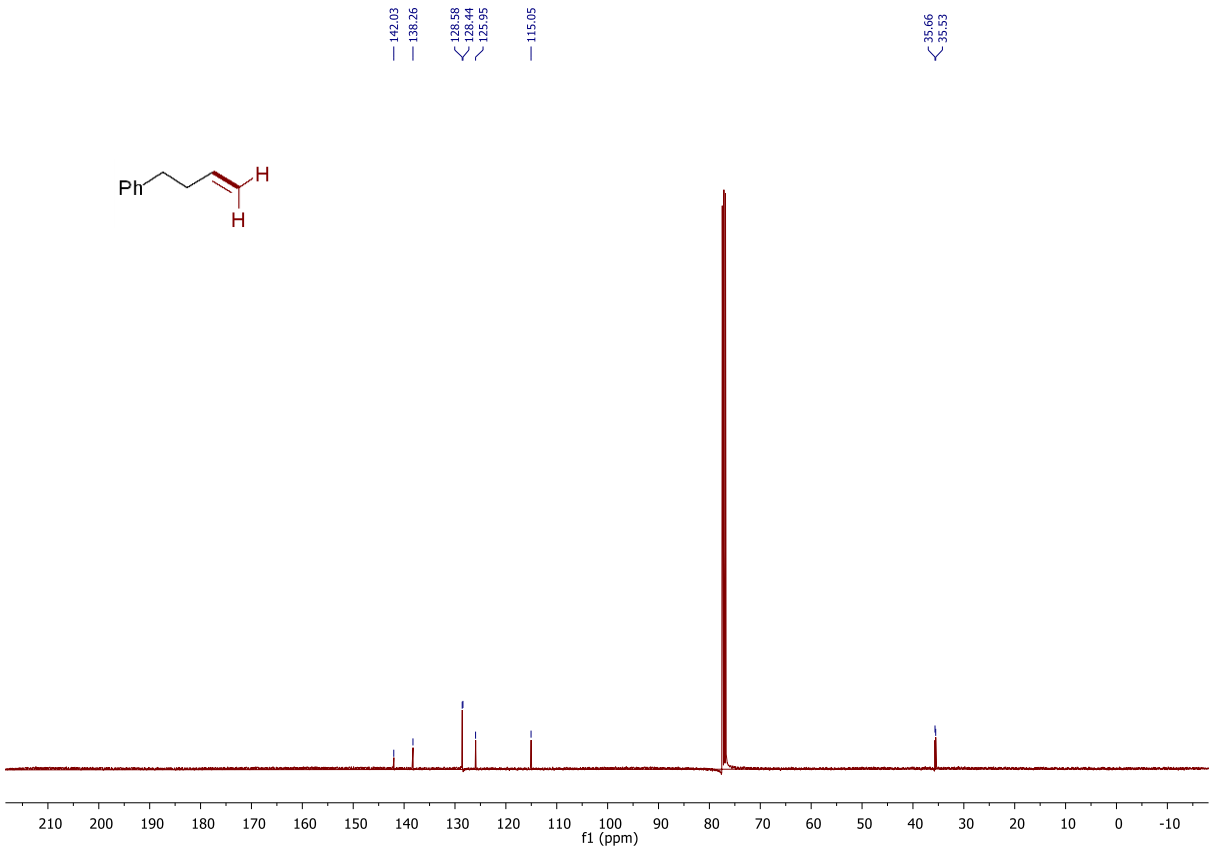

[13]C-NMR spectrum of **8**



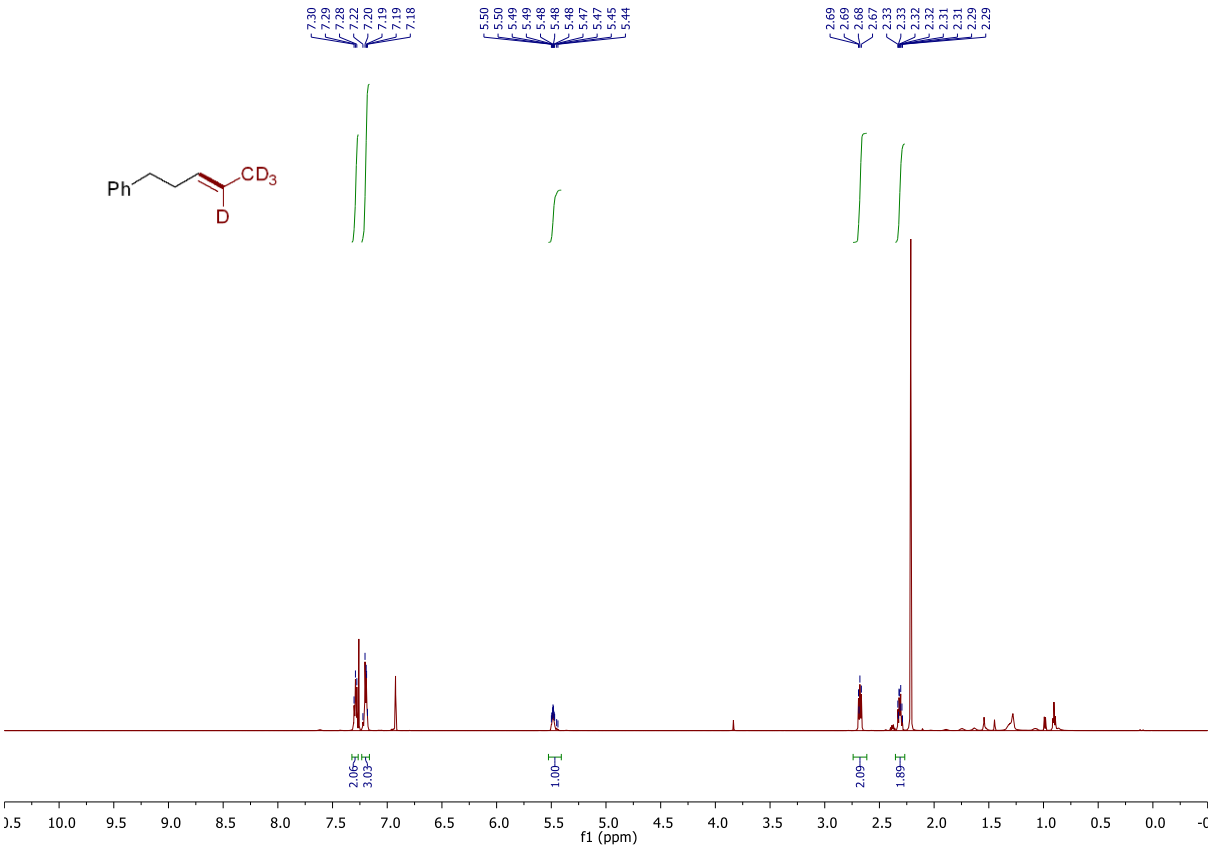
$^{1}$H-NMR spectrum of **9**



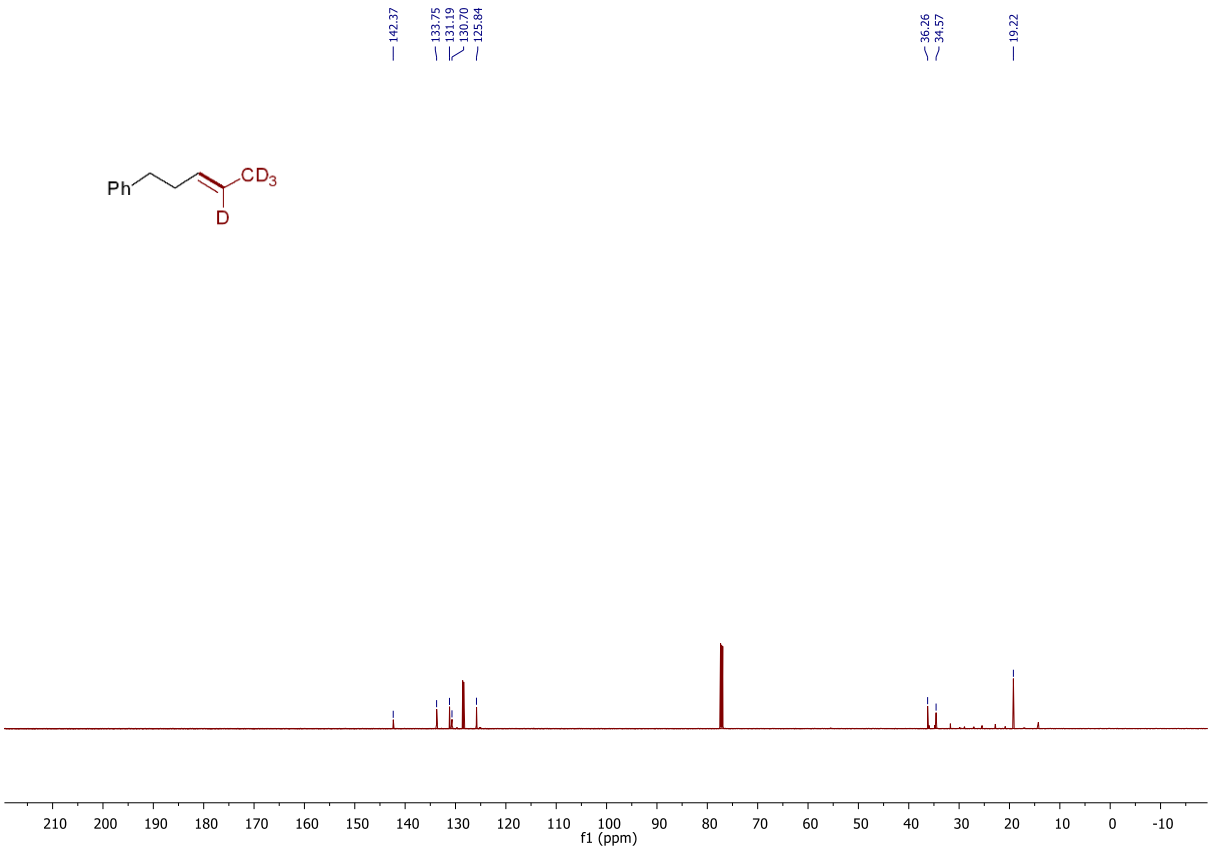

$^{13}$C-NMR spectrum of **9**



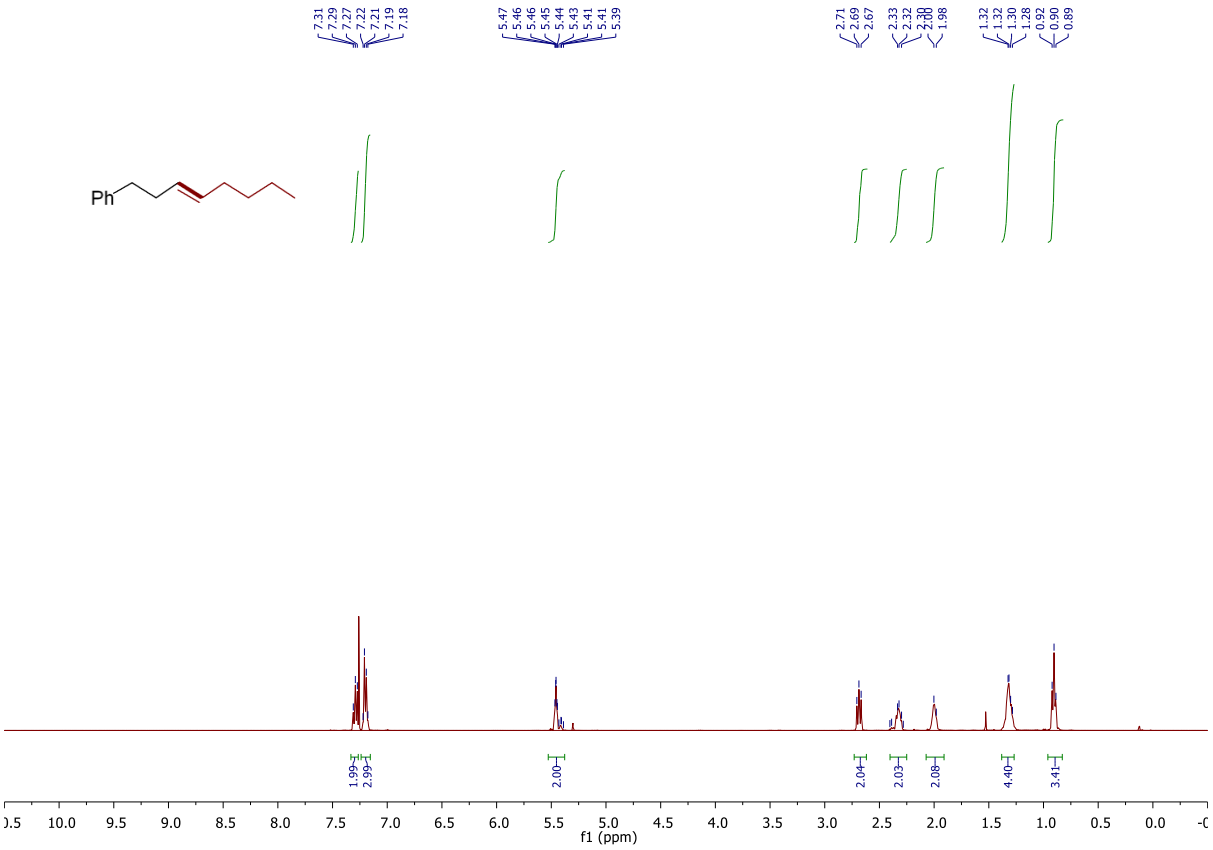
$^{1}$H-NMR spectrum of **10**



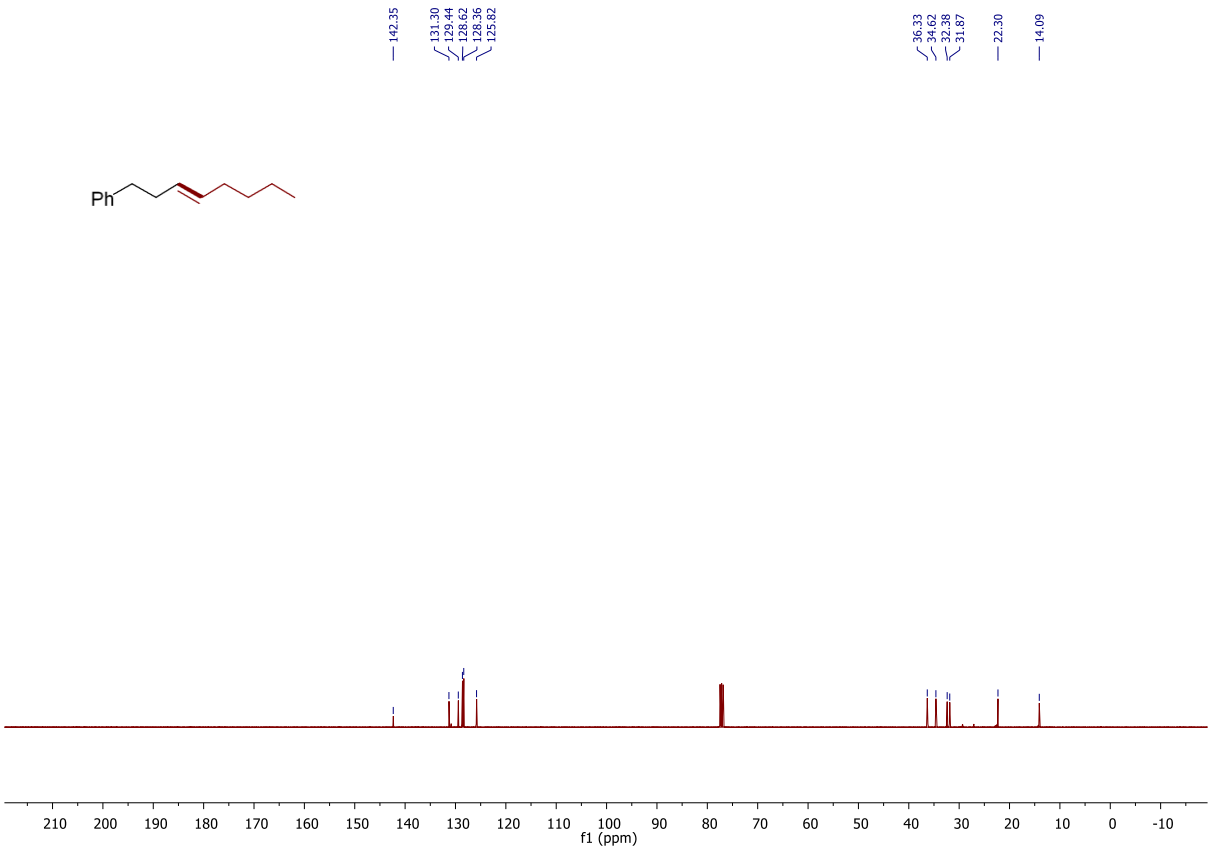

$^{13}$C-NMR spectrum of **10**



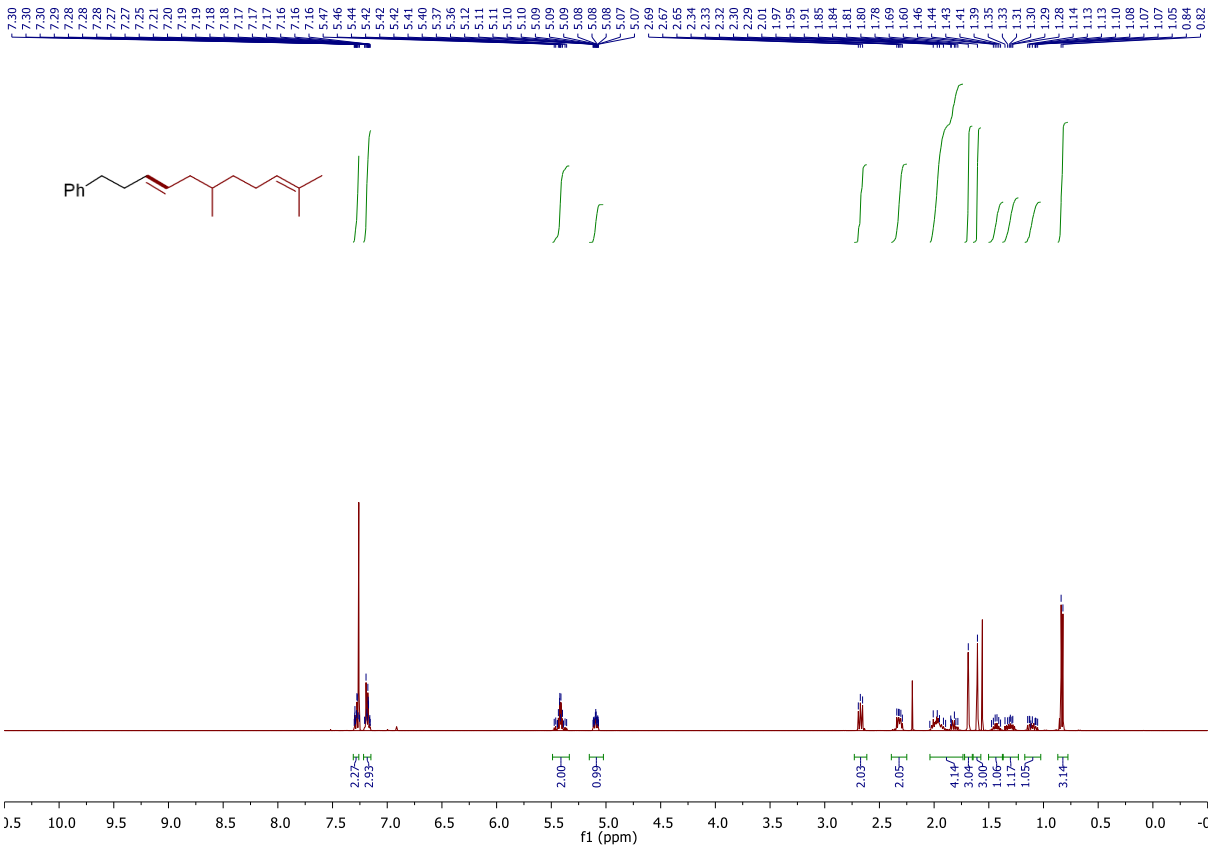
$^{1}$H-NMR spectrum of **11**



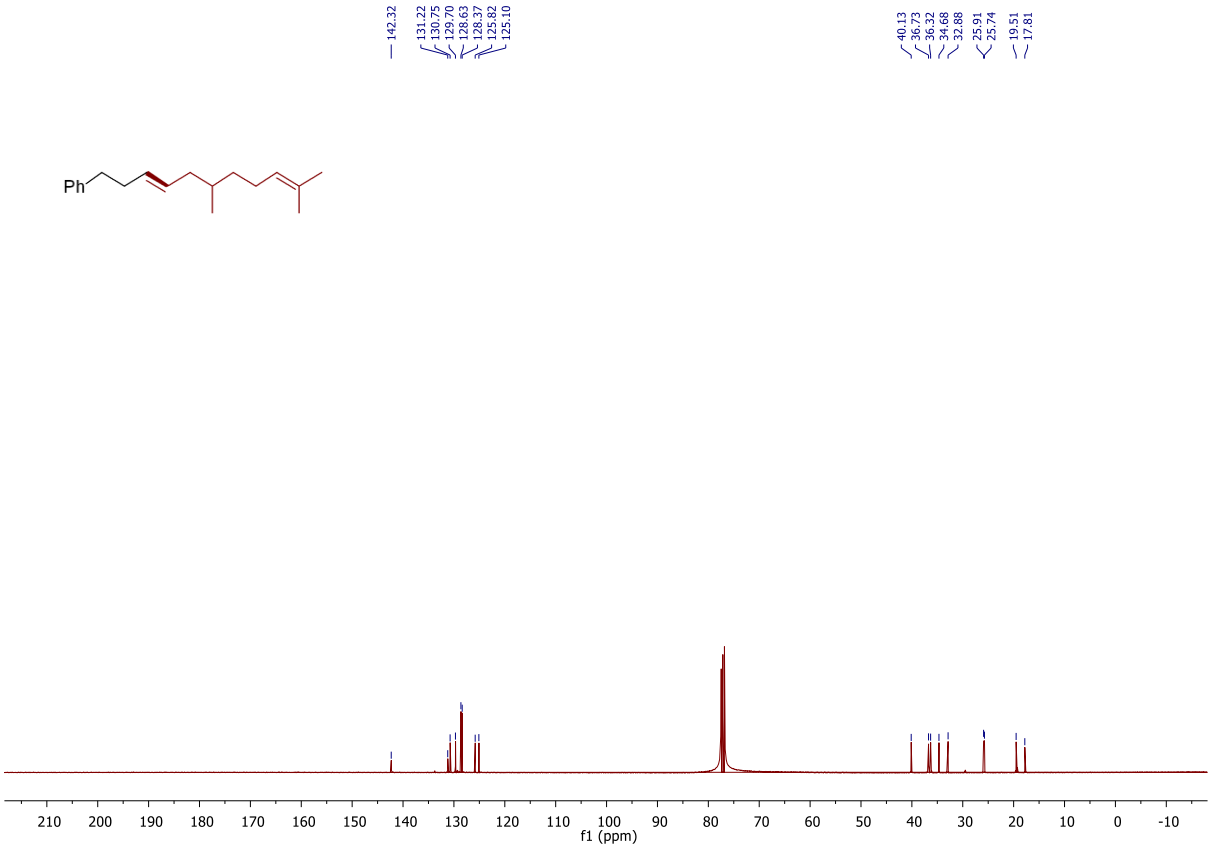

$^{13}$C-NMR spectrum of **11**



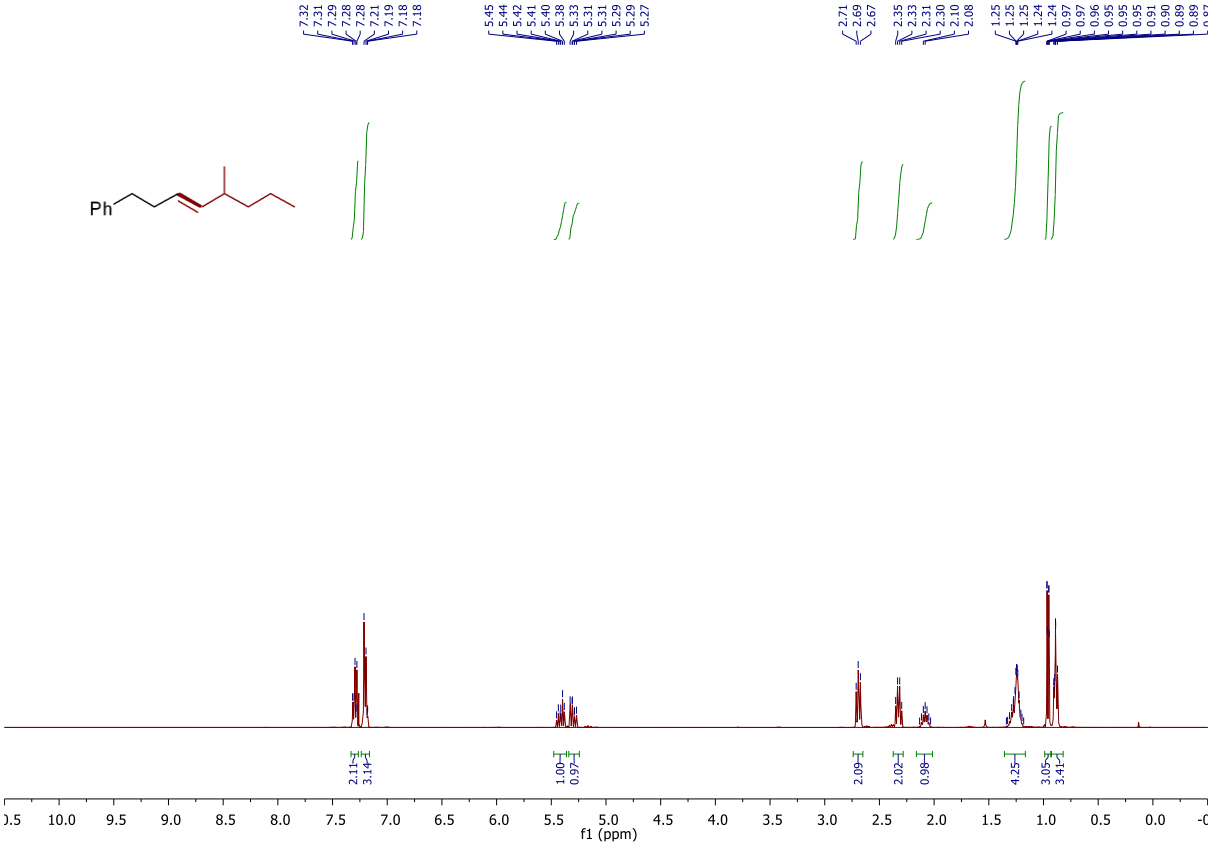
[1]H-NMR spectrum of **12**



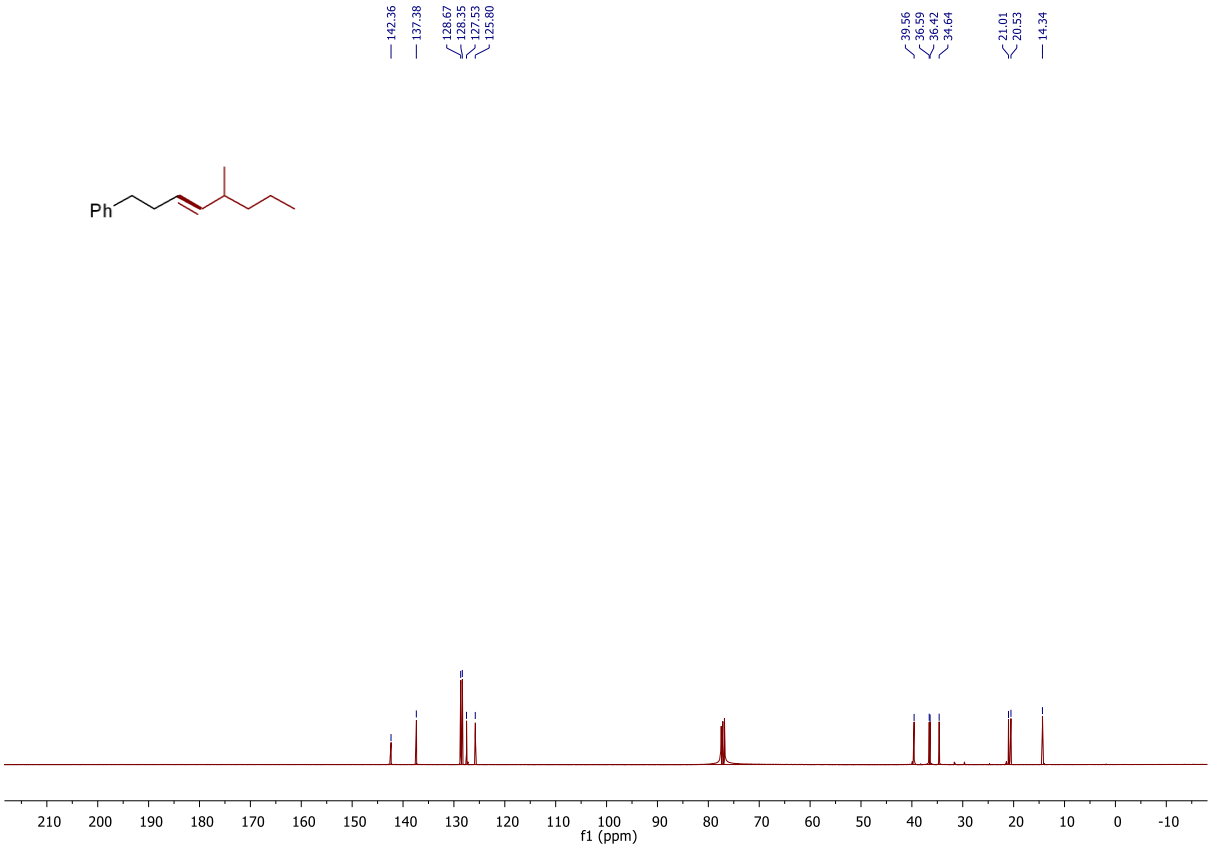

[13]C-NMR spectrum of **12**



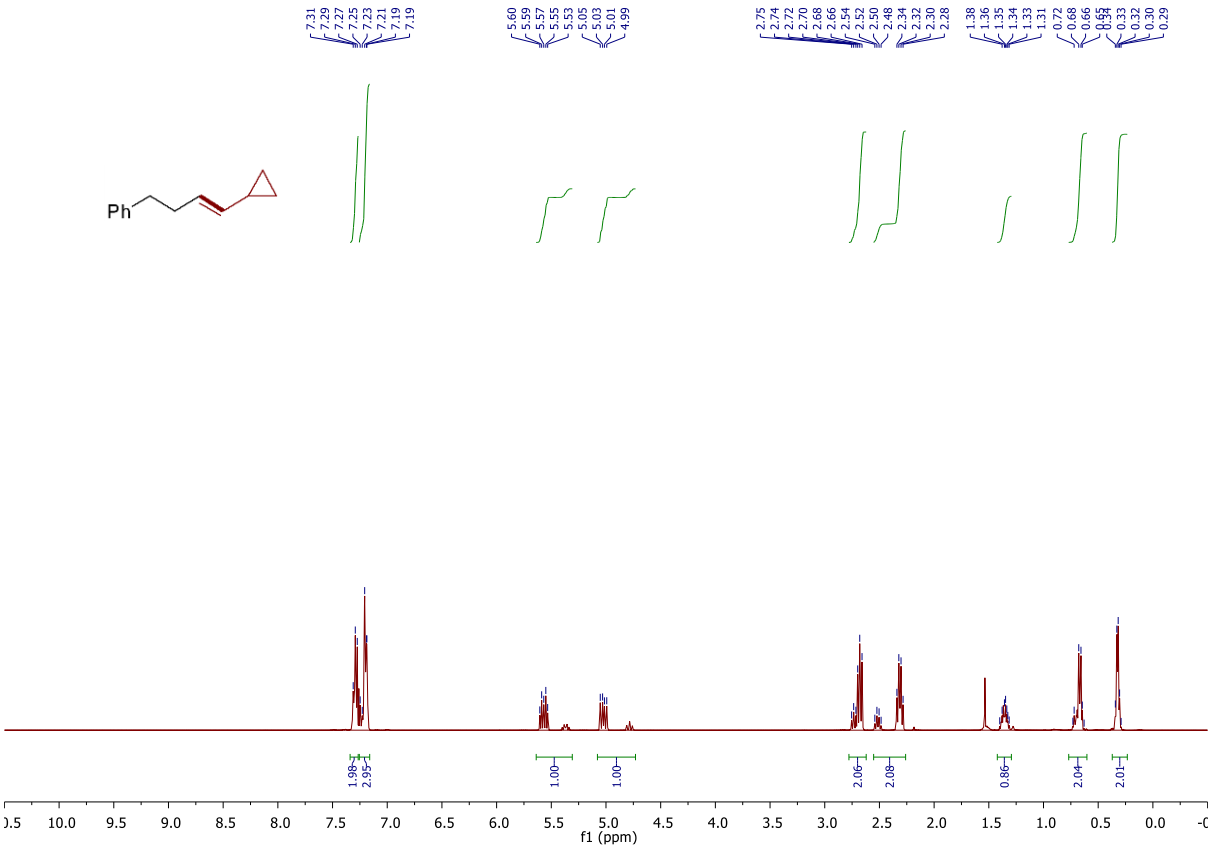
$^{1}$H-NMR spectrum of **13**



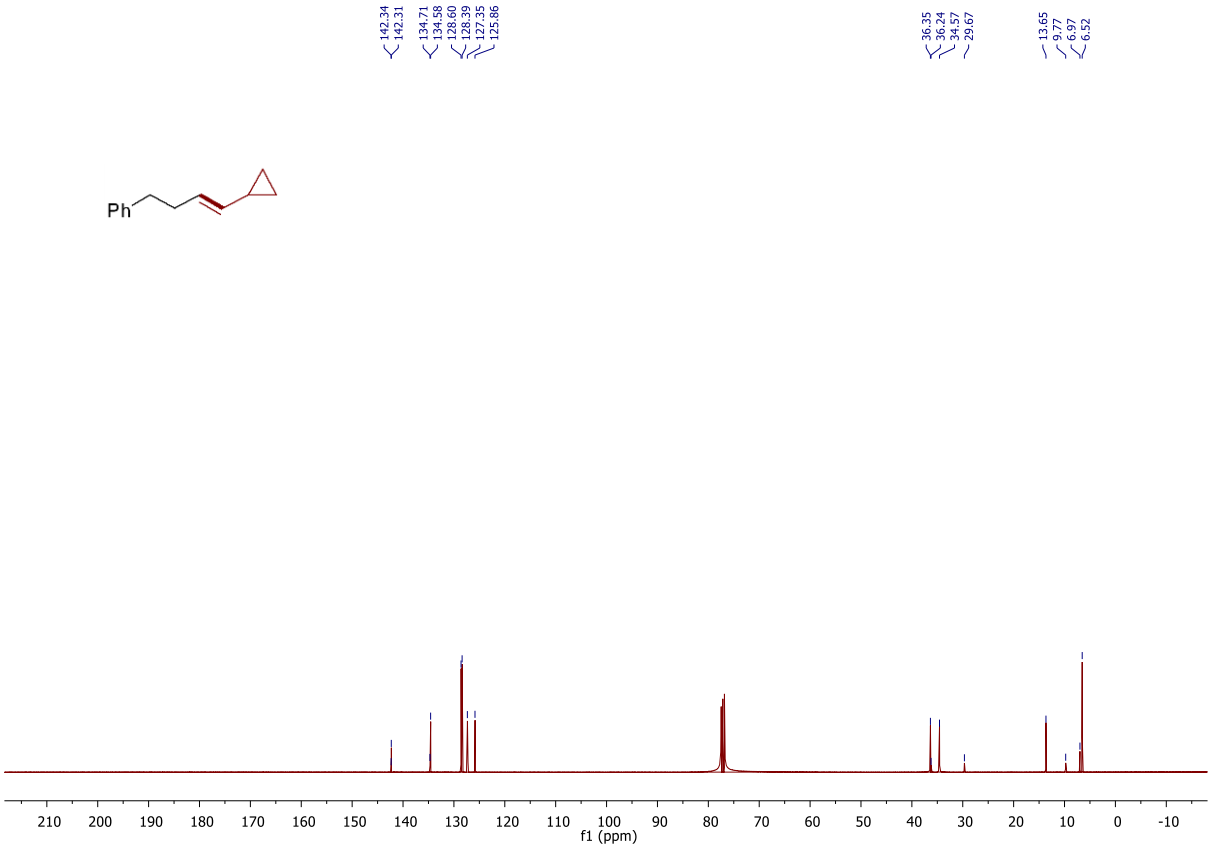

$^{13}$C-NMR spectrum of **13**



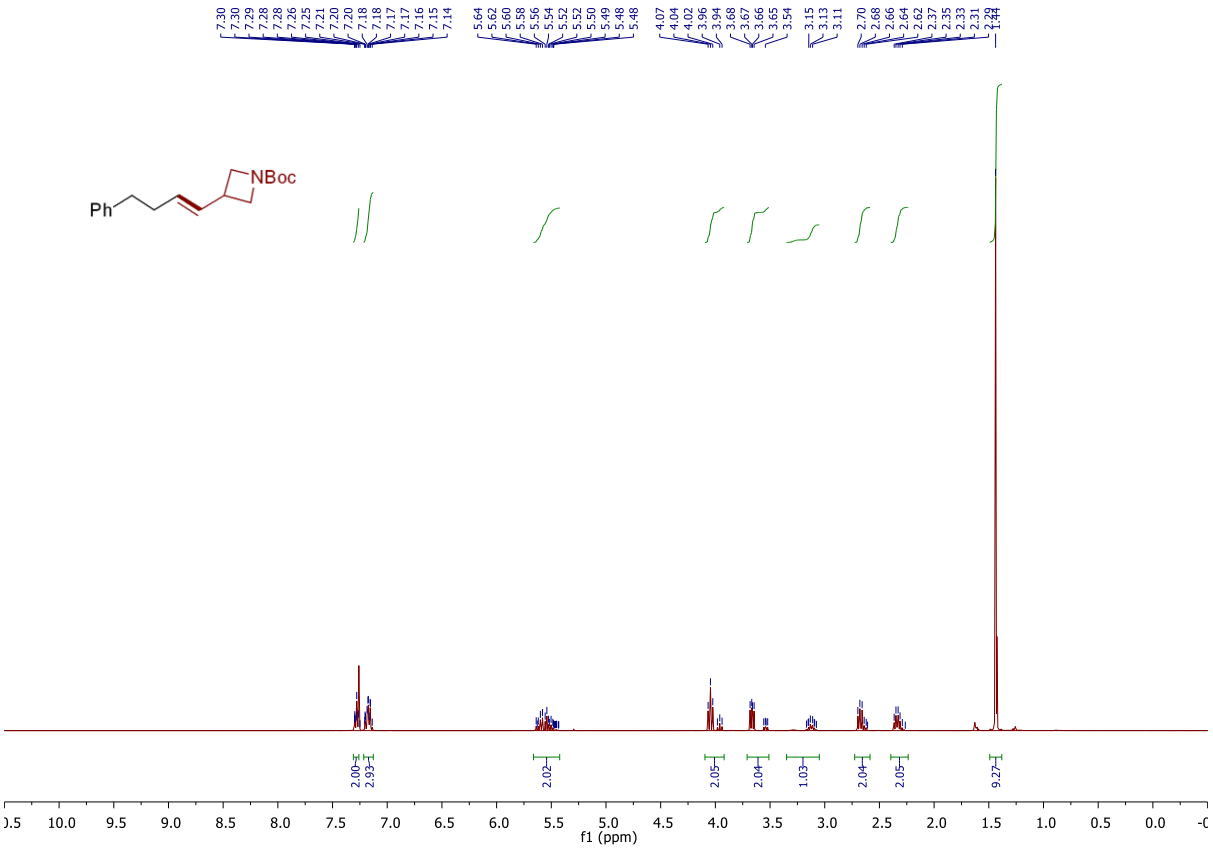
[1]H-NMR spectrum of **14**



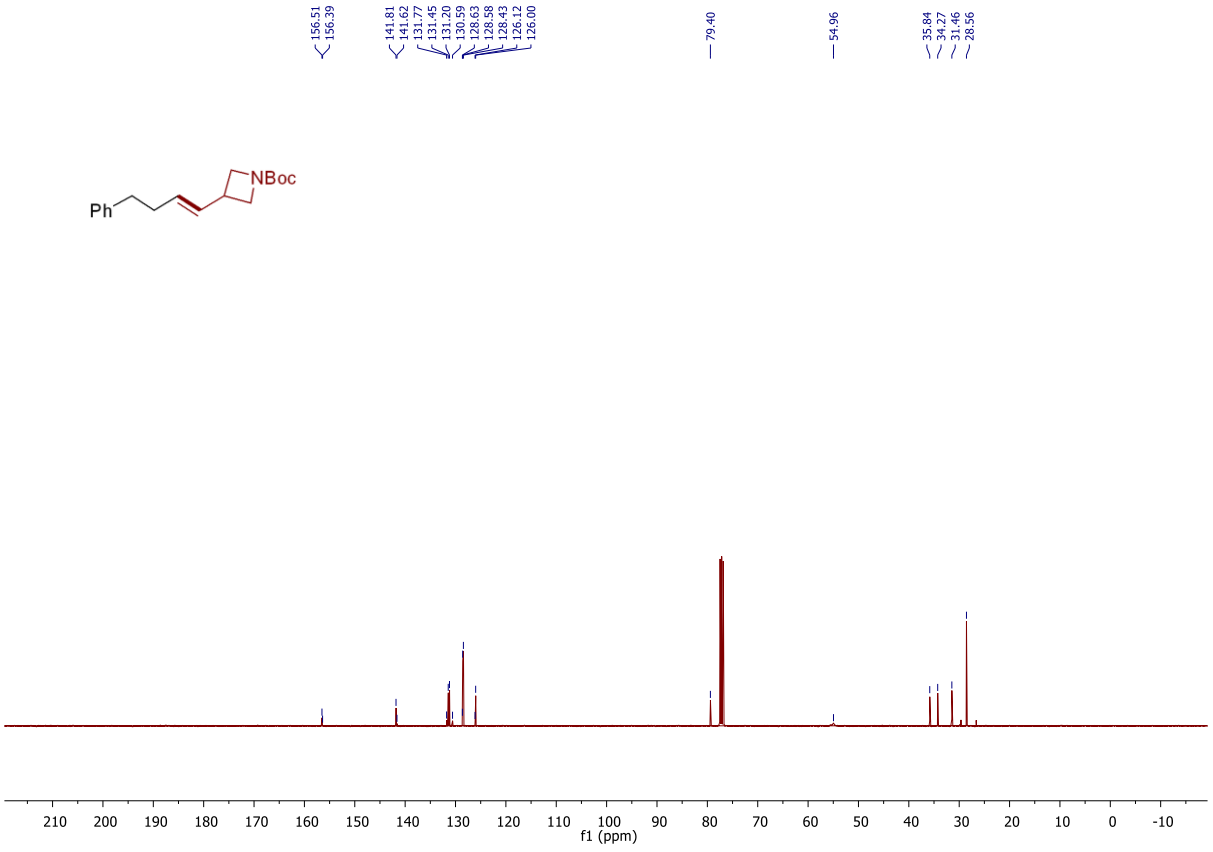

[13]C-NMR spectrum of **14**



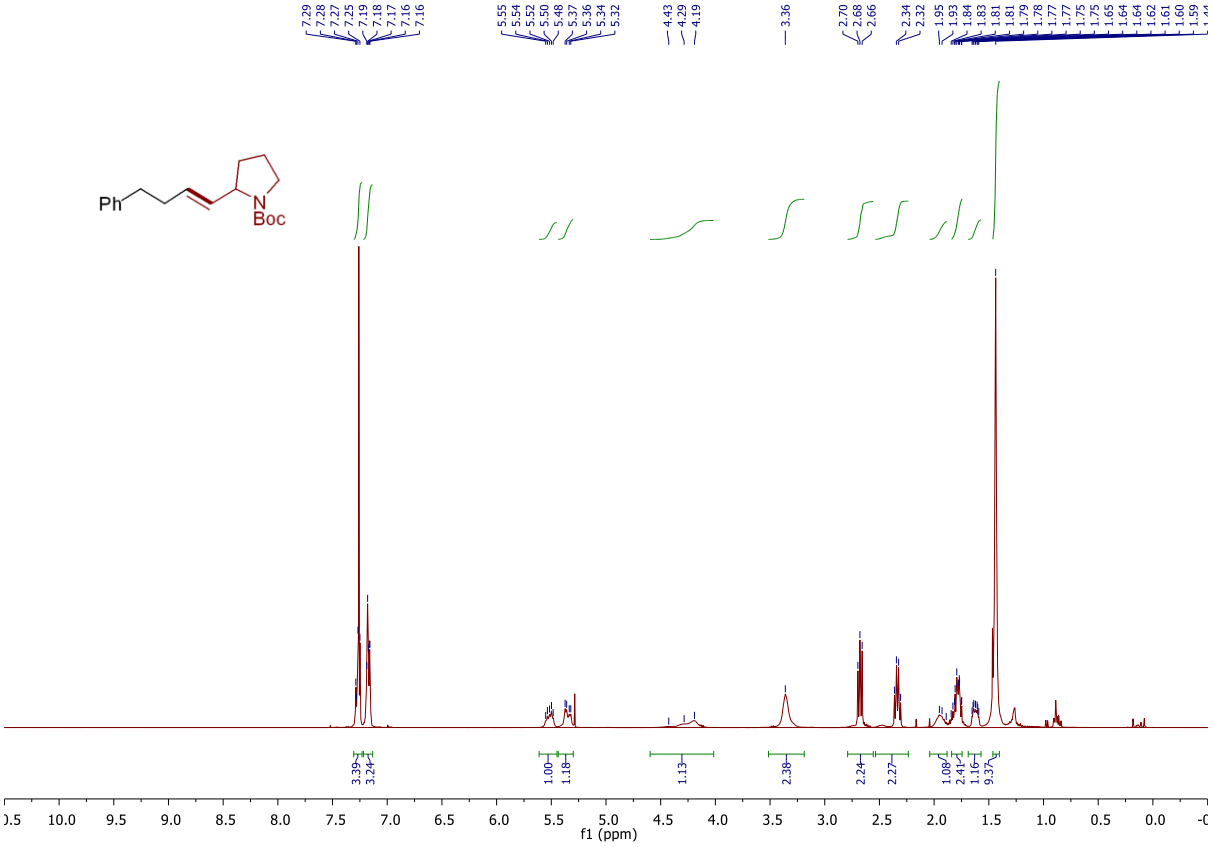
$^{1}$H-NMR spectrum of **15**



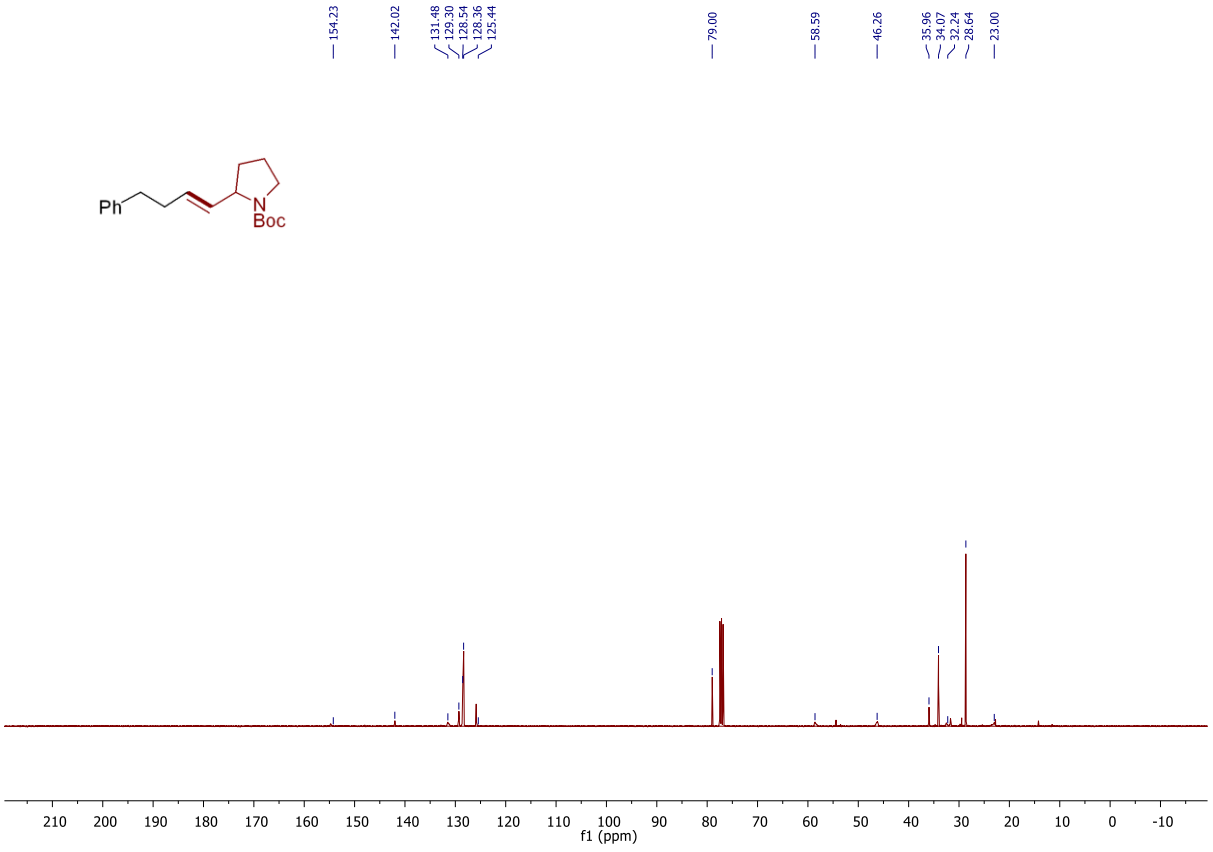

$^{13}$C-NMR spectrum of **15**



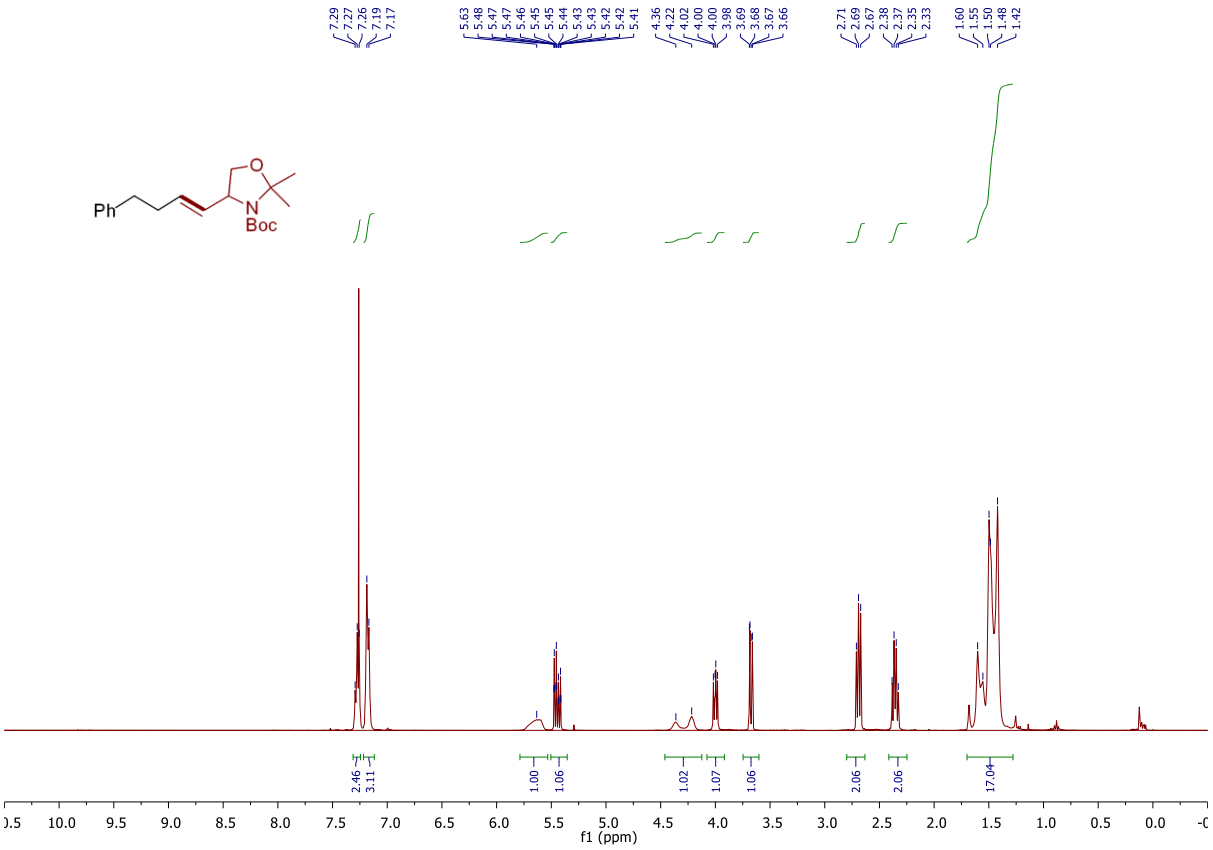
[1]H-NMR spectrum of **16**



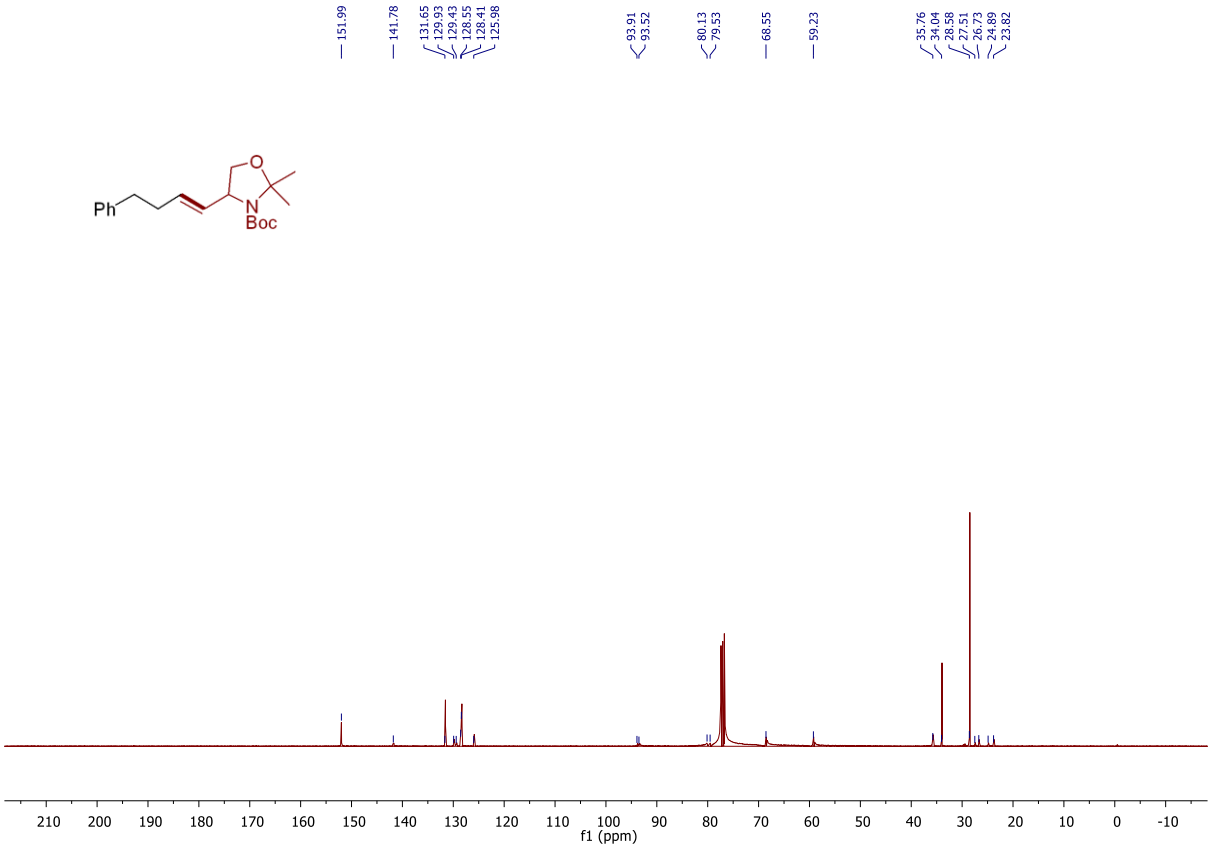

[13]C-NMR spectrum of **16**



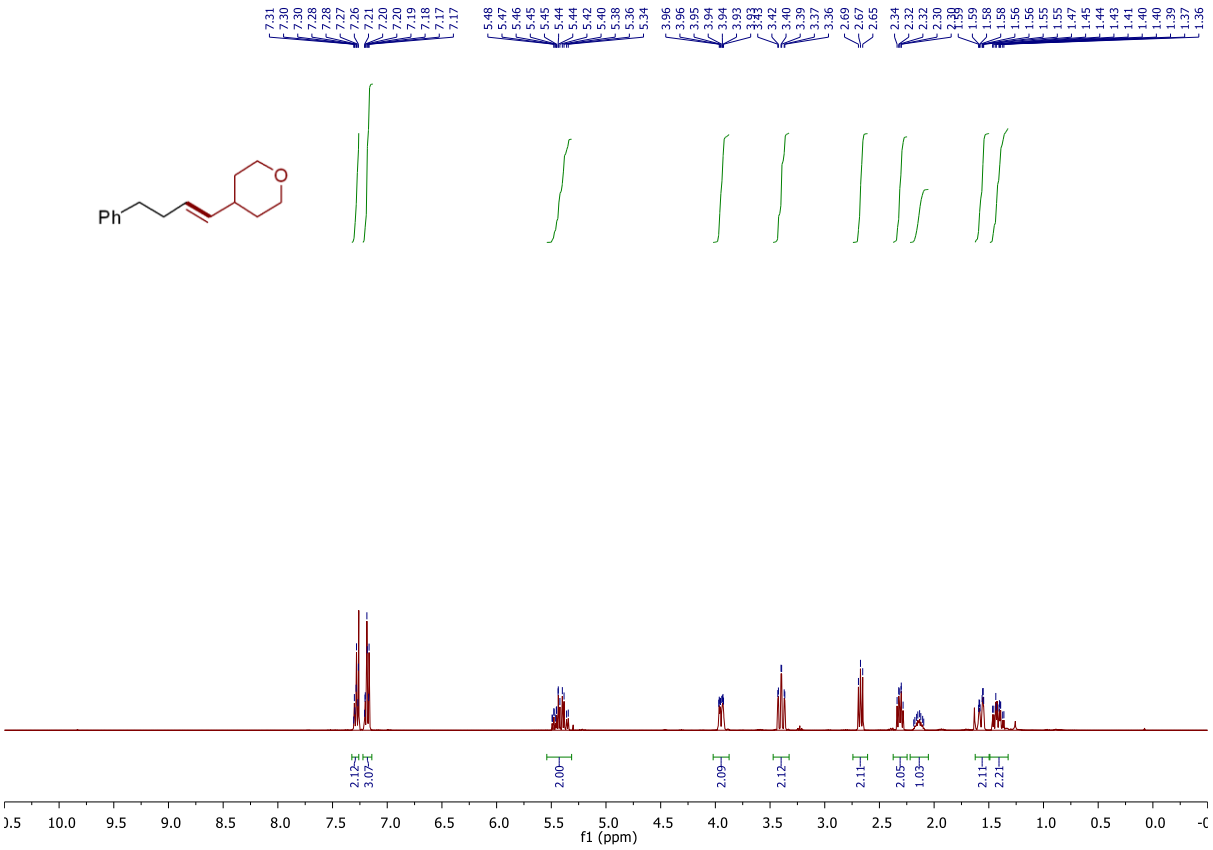
[1]H-NMR spectrum of **17**



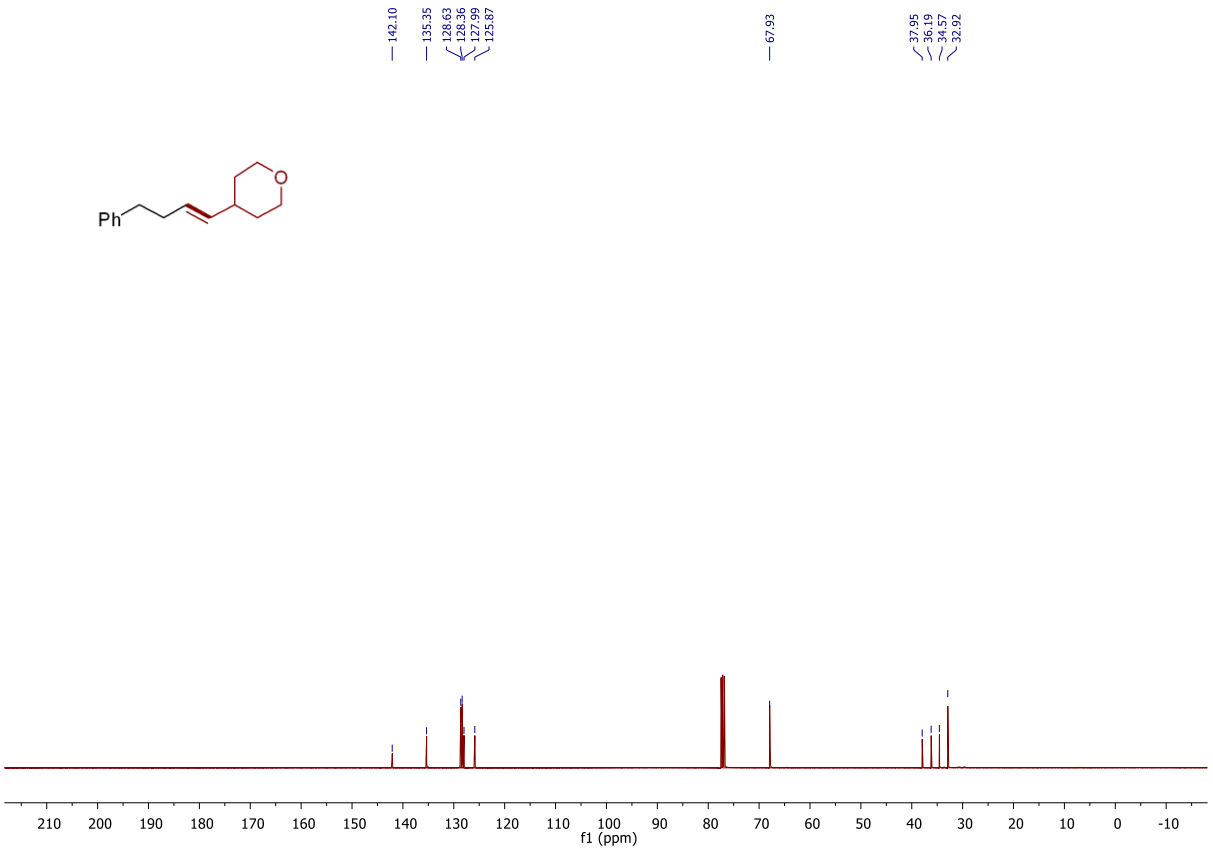

[13]C-NMR spectrum of **17**



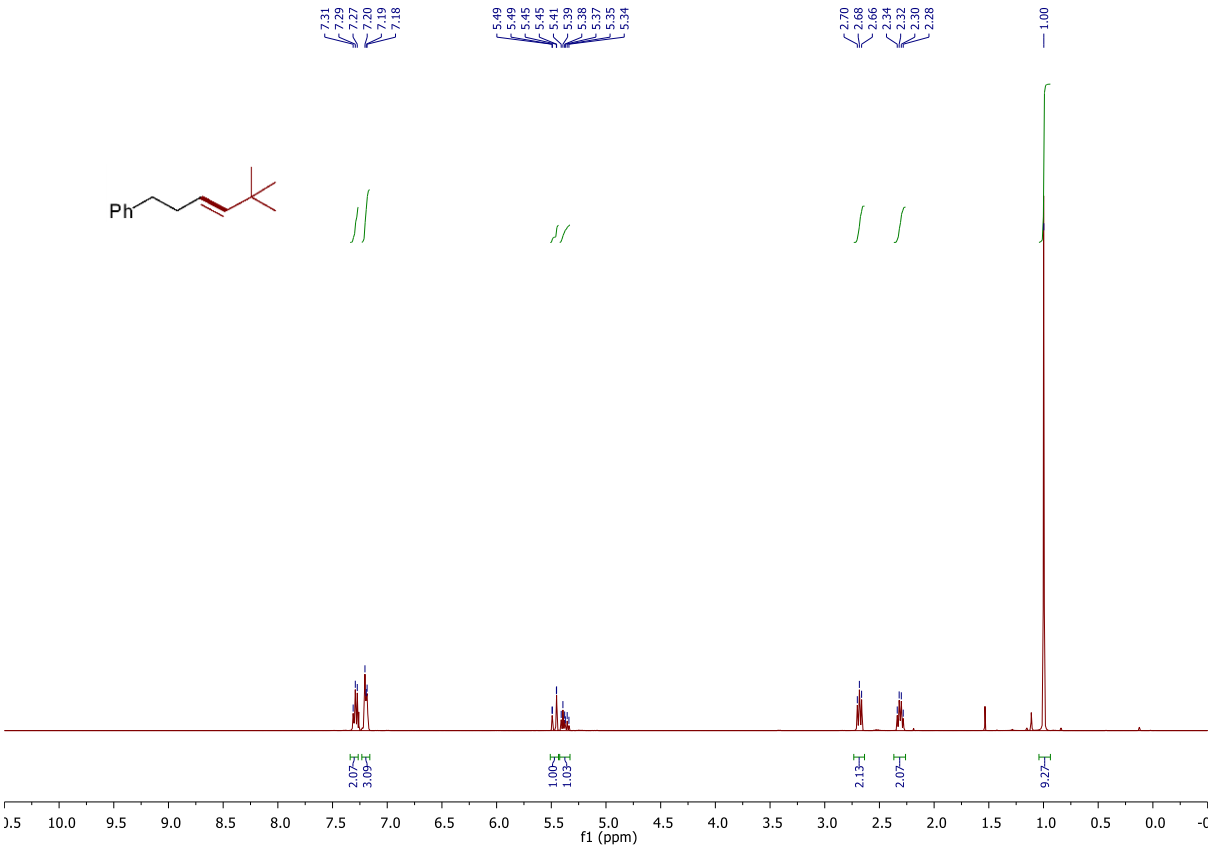
$^{1}$H-NMR spectrum of **18**



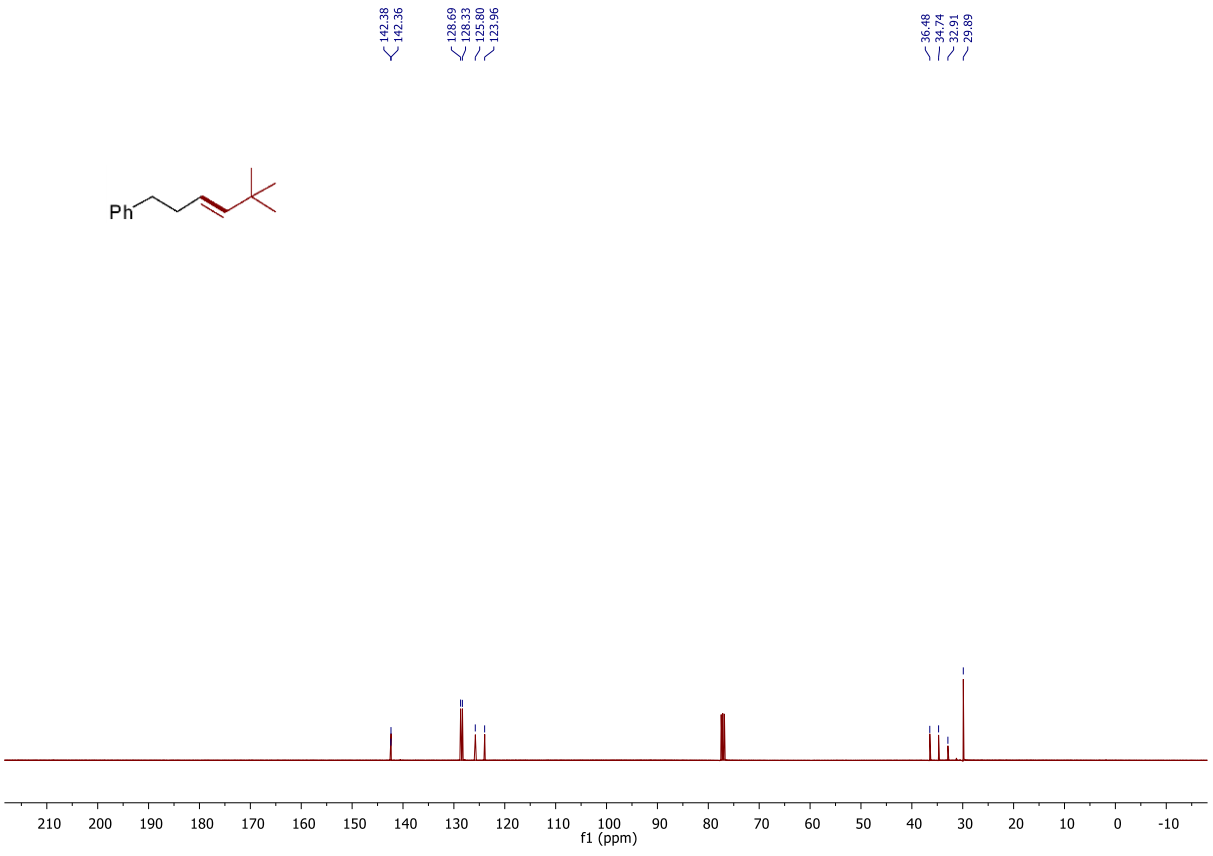

$^{13}$C-NMR spectrum of **18**



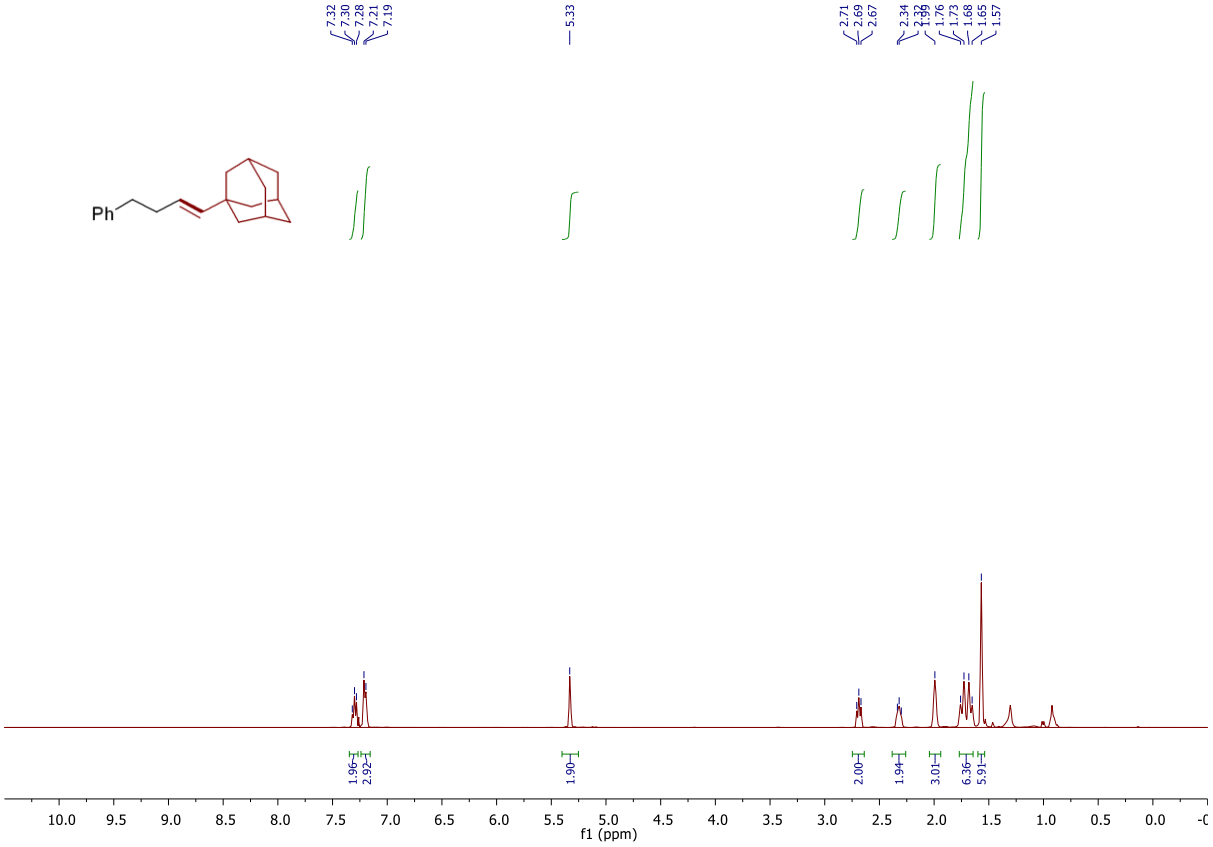
$^{1}$H-NMR spectrum of **19**



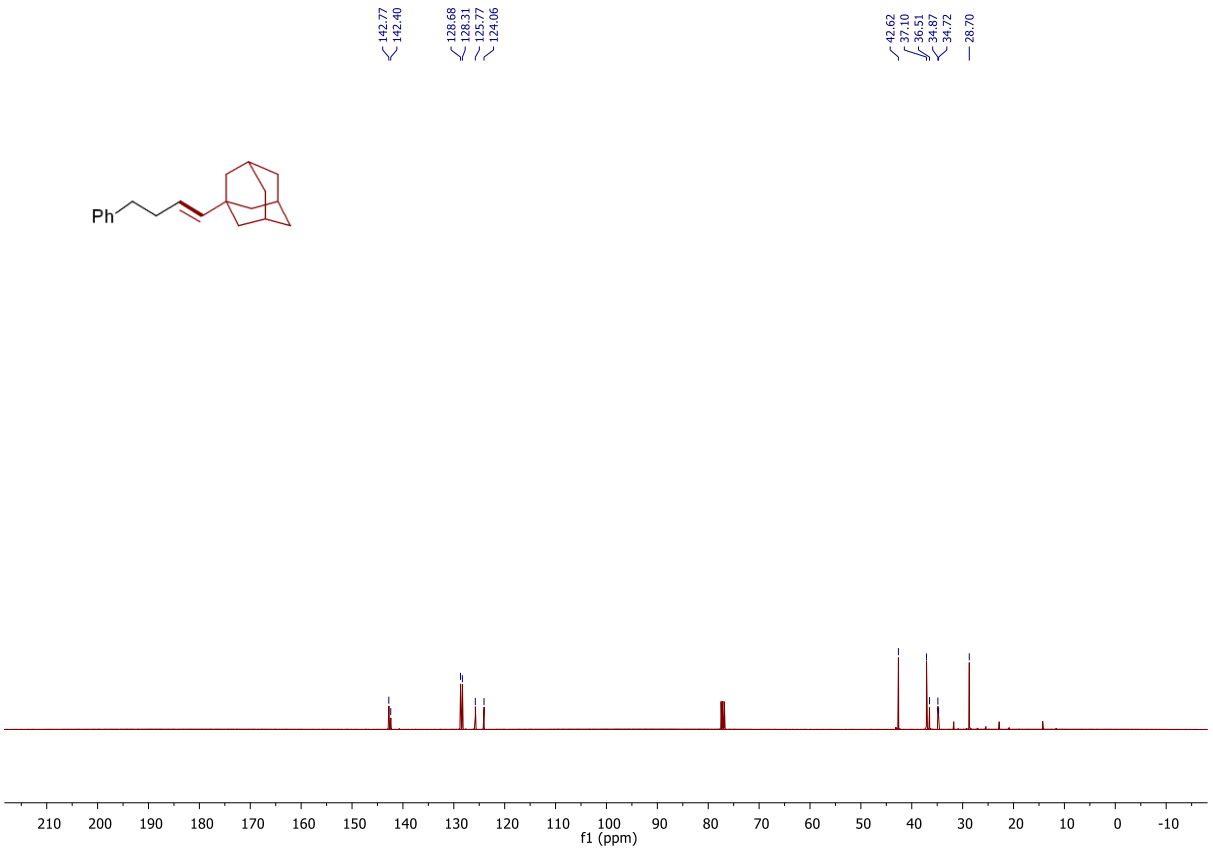

$^{13}$C-NMR spectrum of **19**



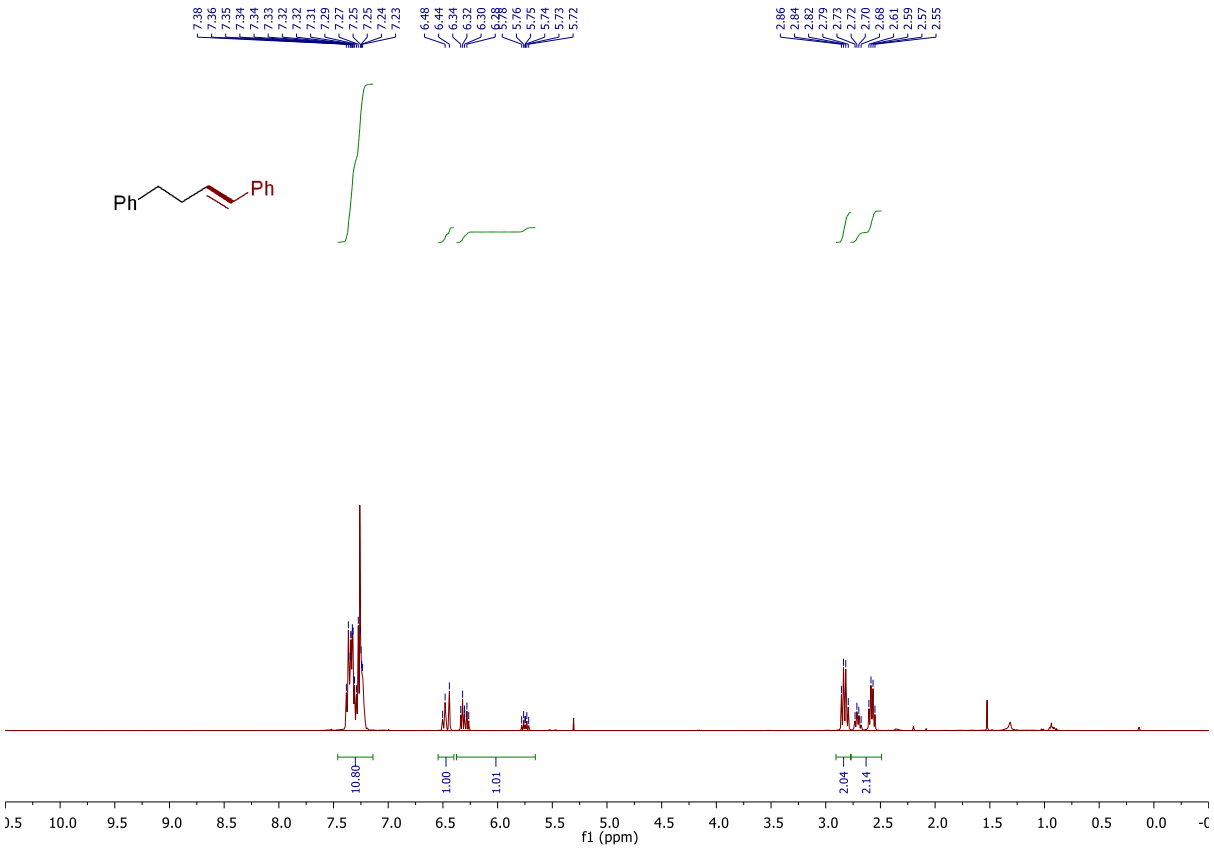
$^{1}$H-NMR spectrum of **20**



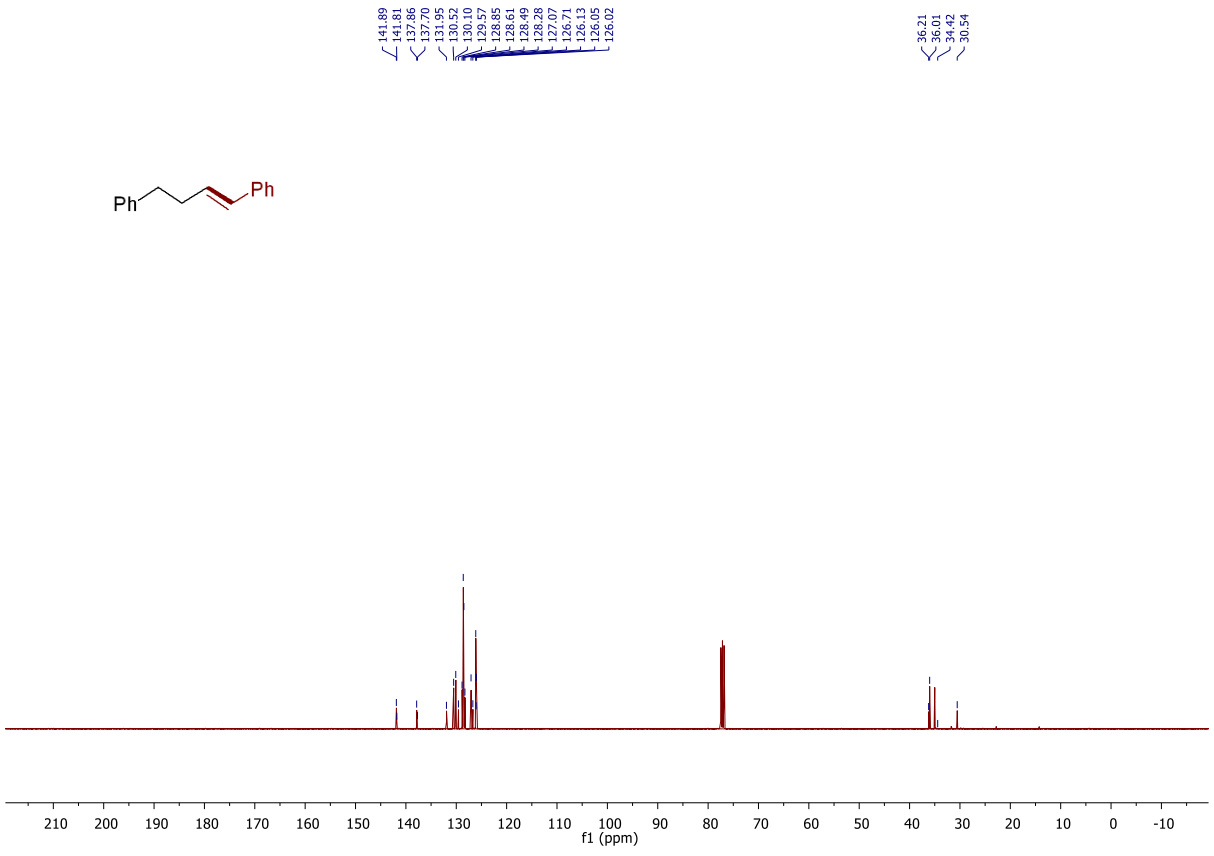

$^{13}$C-NMR spectrum of **20**



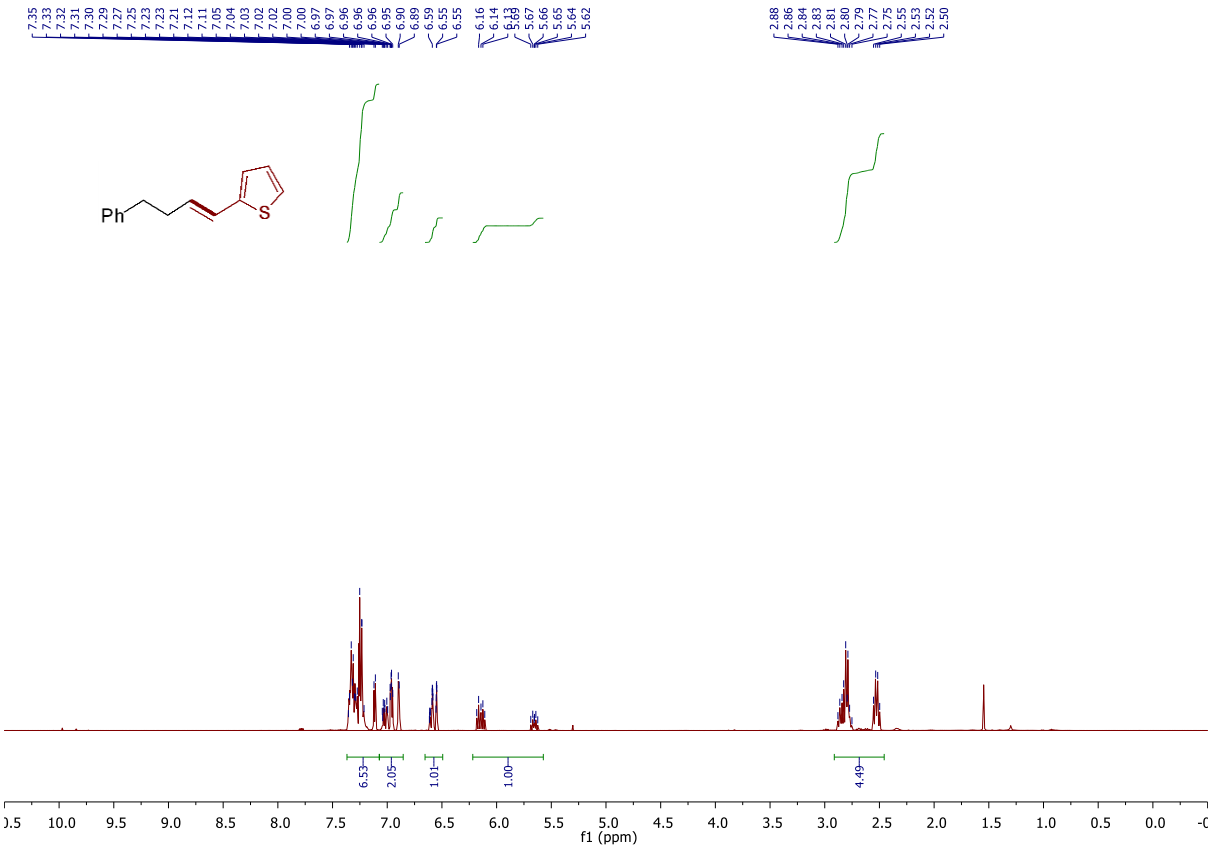
[1]H-NMR spectrum of **21**



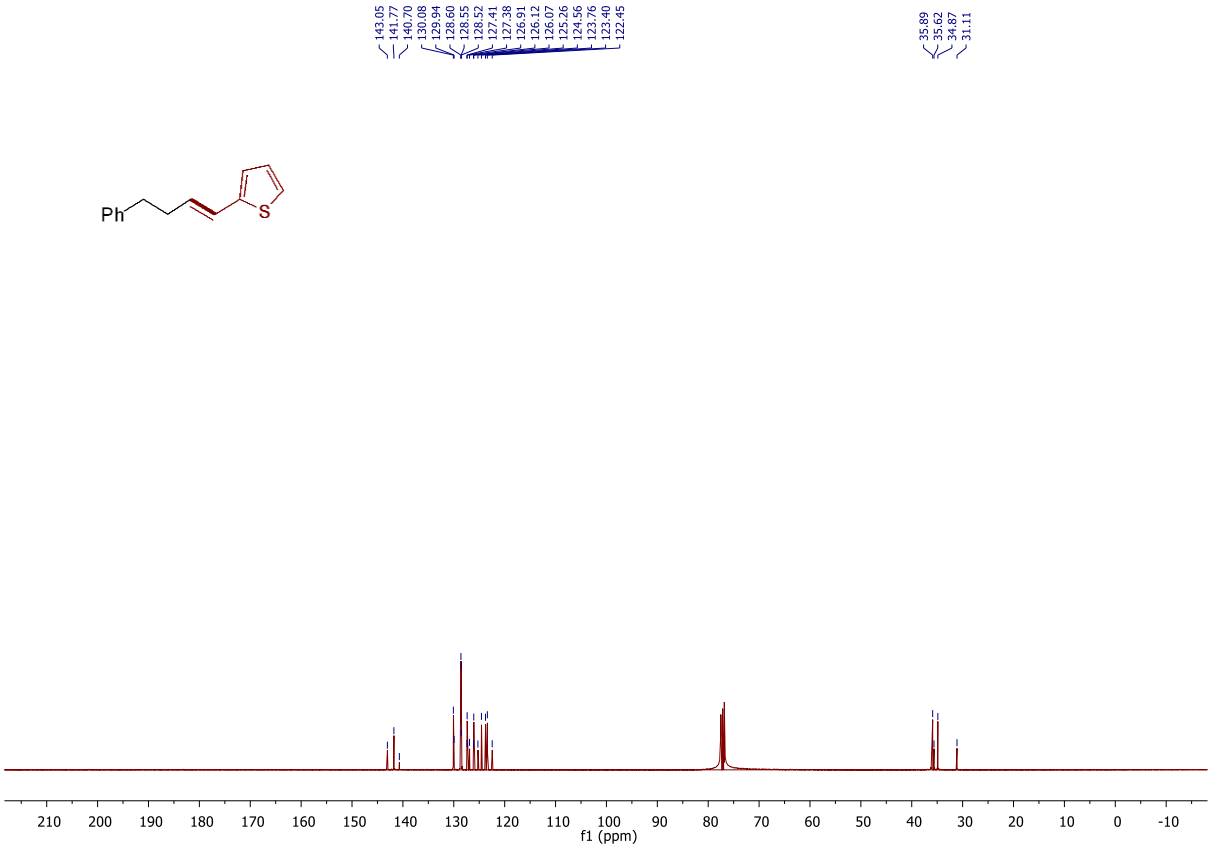

[13]C-NMR spectrum of **21**



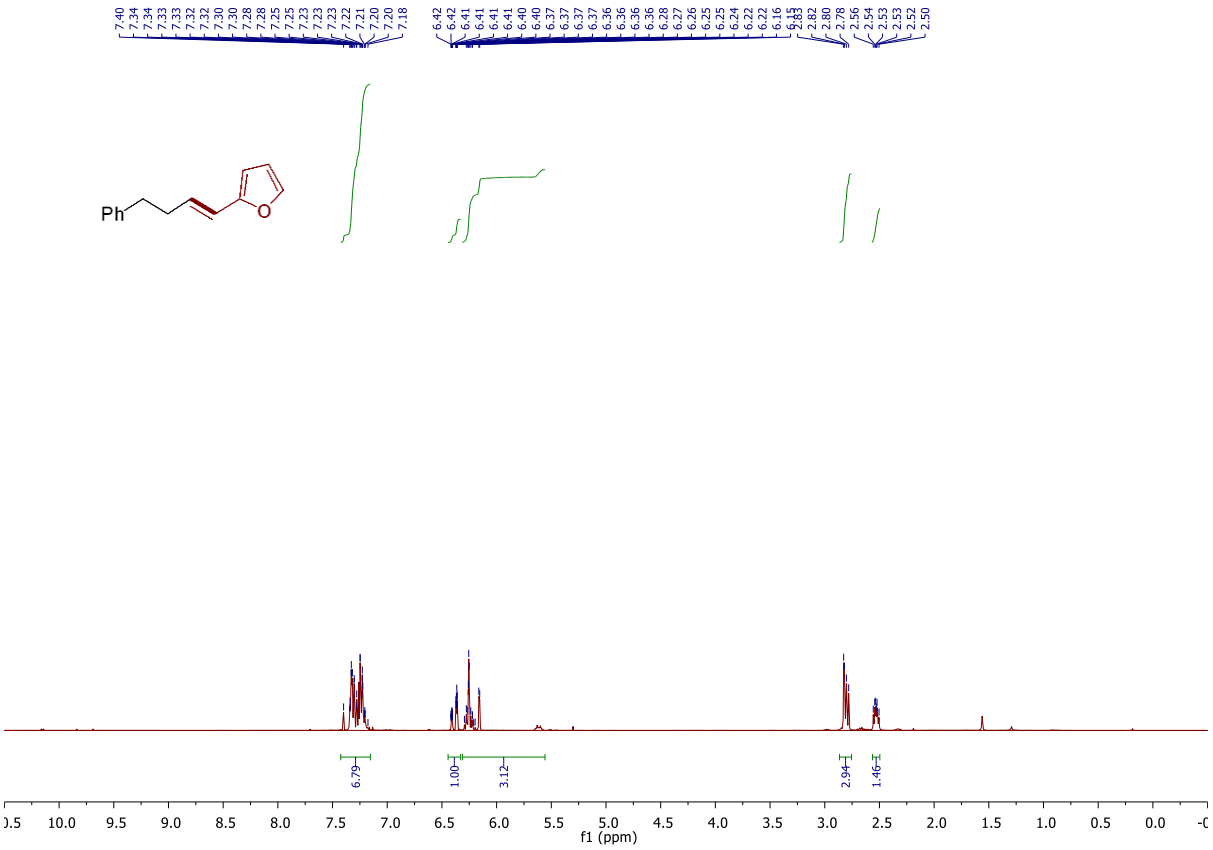
[1]H-NMR spectrum of **22**



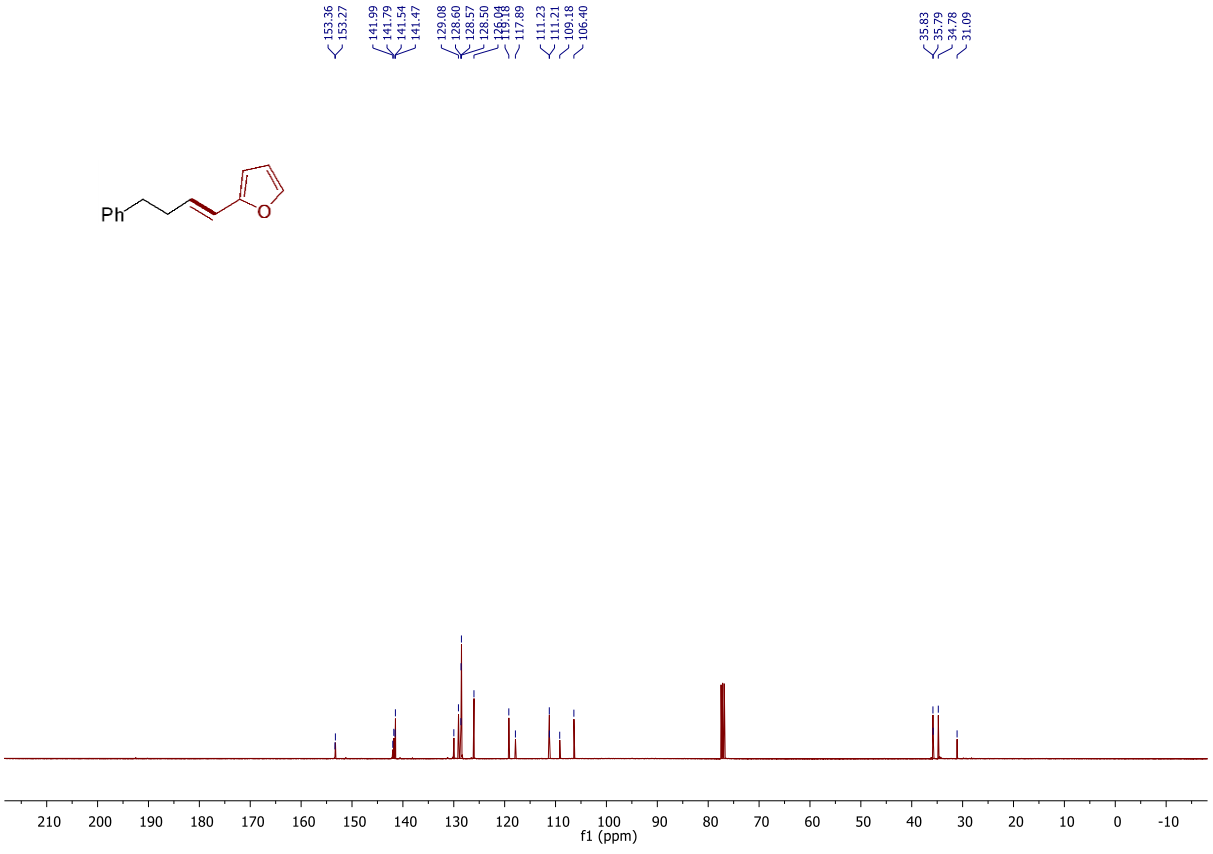

[13]C-NMR spectrum of **22**



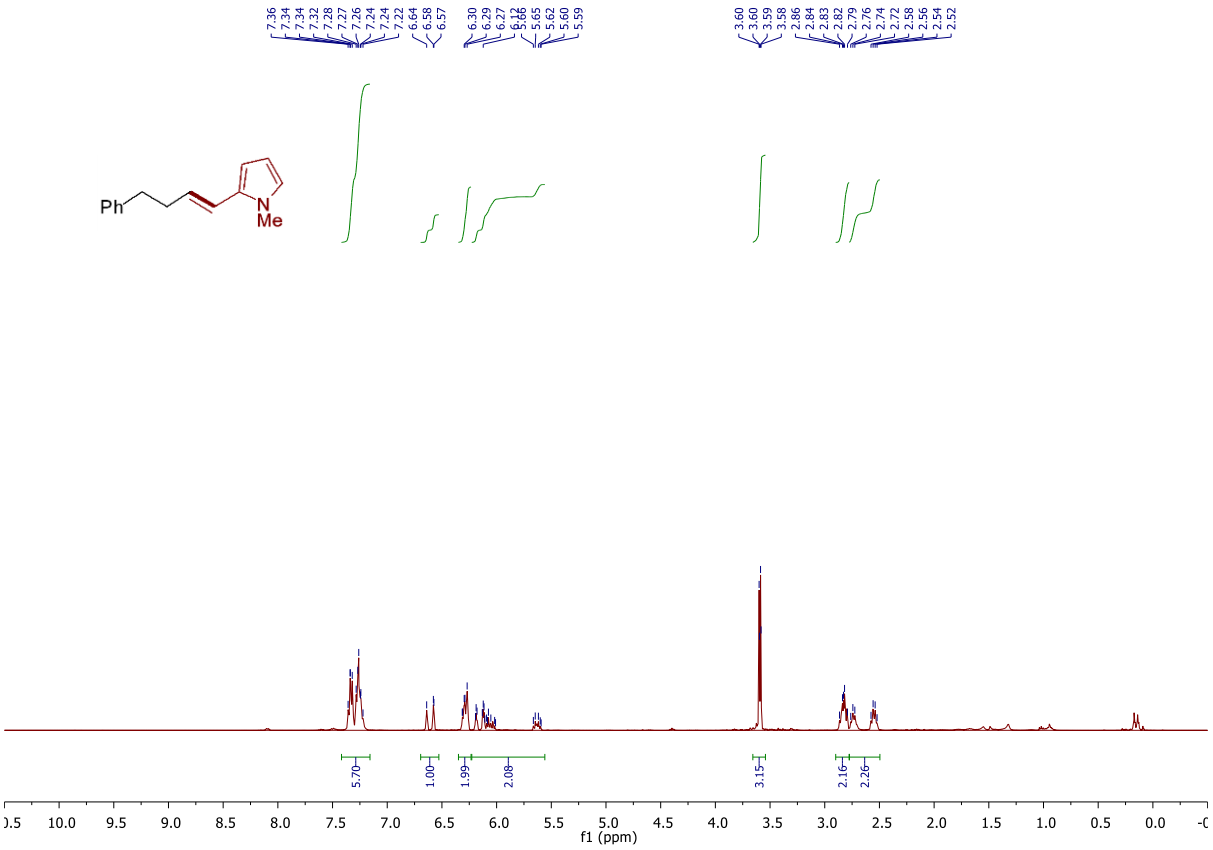
[1]H-NMR spectrum of **23**



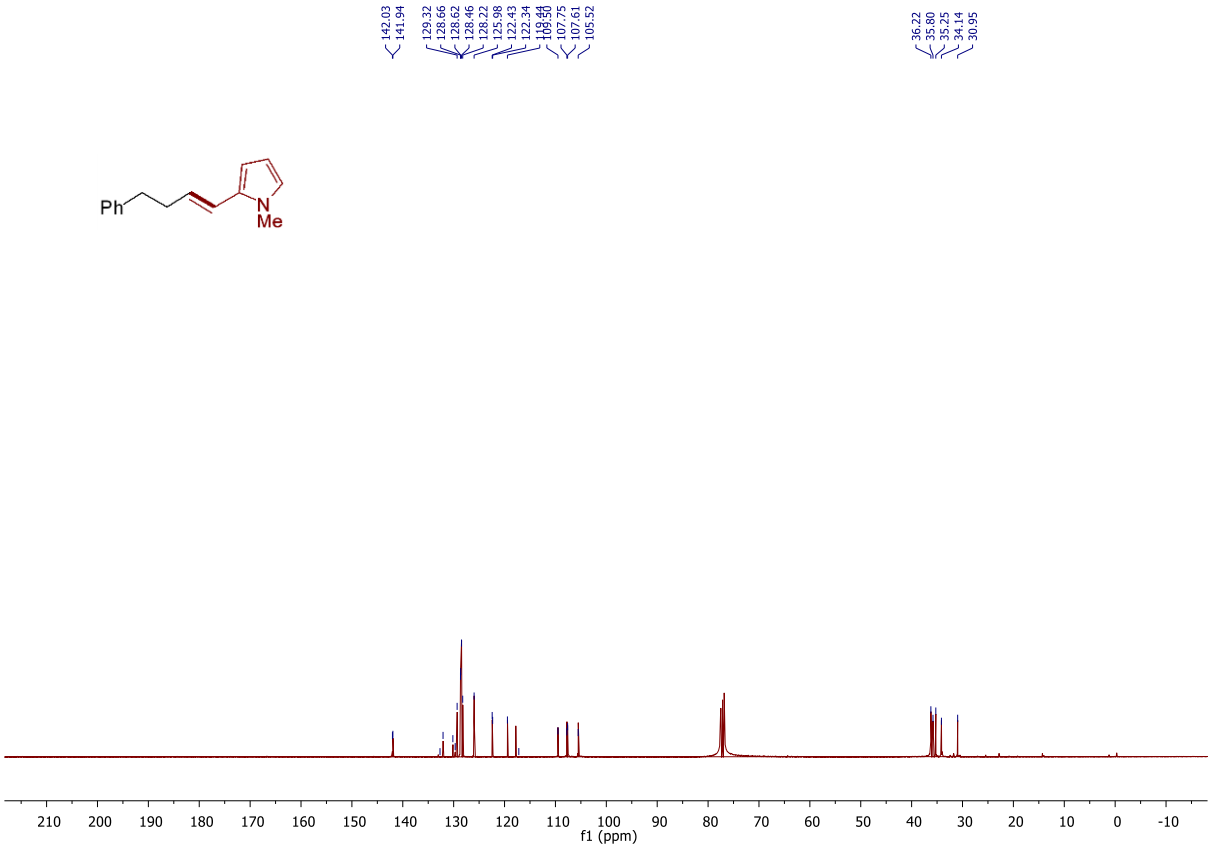

[13]C-NMR spectrum of **23**



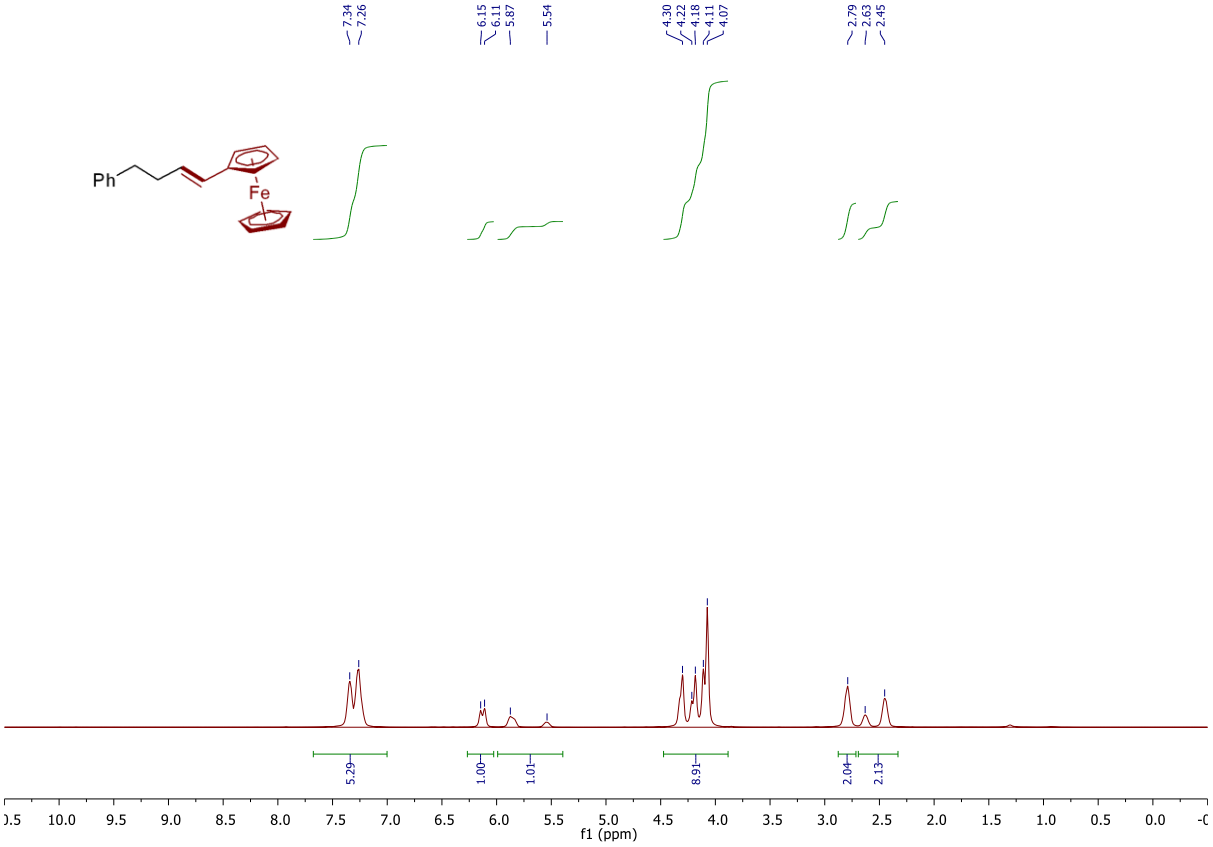
[1]H-NMR spectrum of **24**



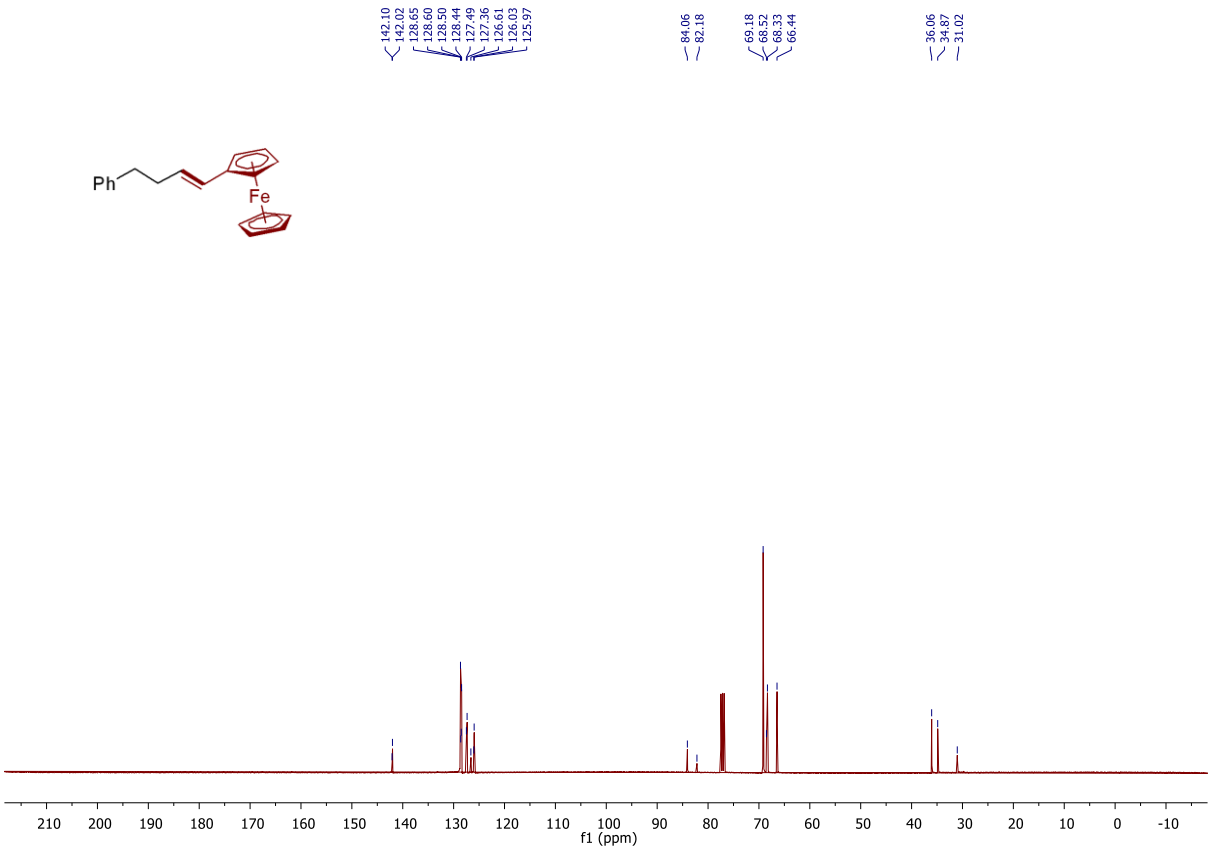

[13]C-NMR spectrum of **24**



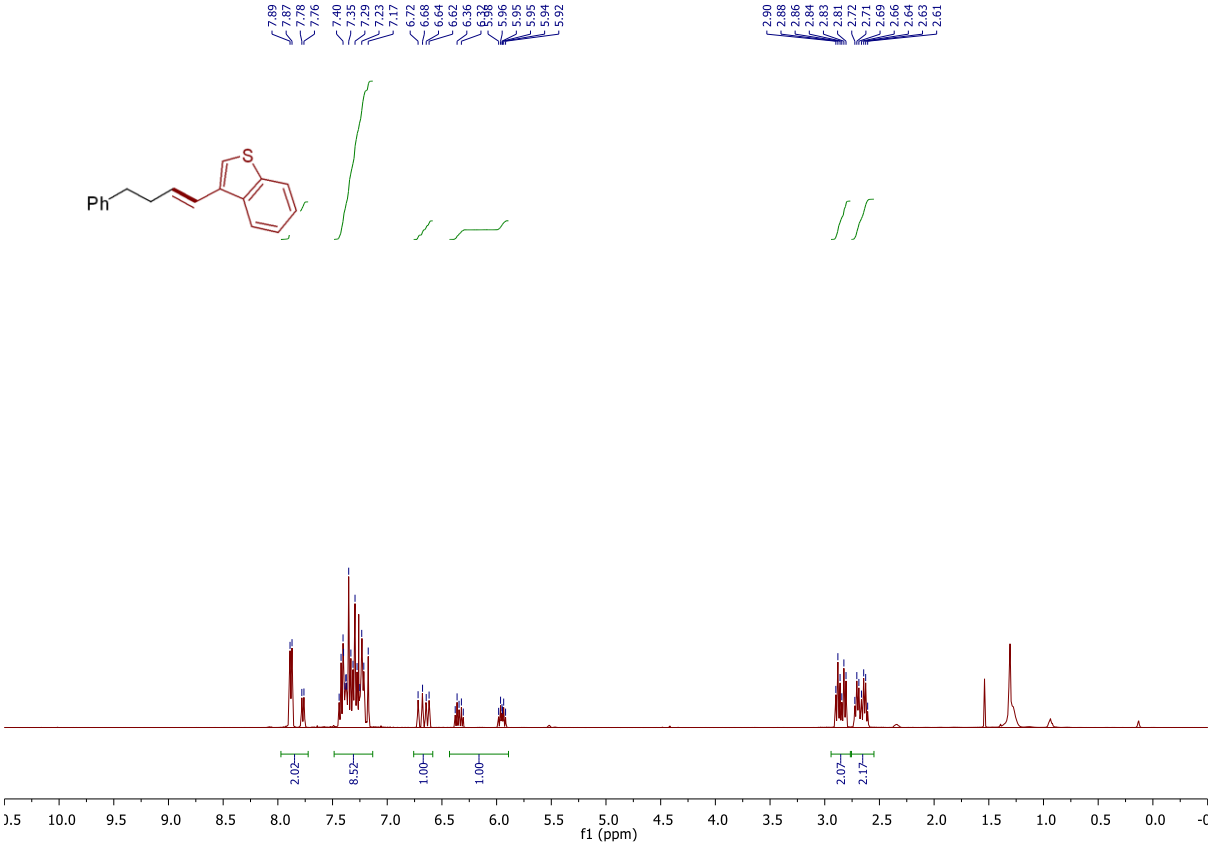
$^{1}$H-NMR spectrum of **25**



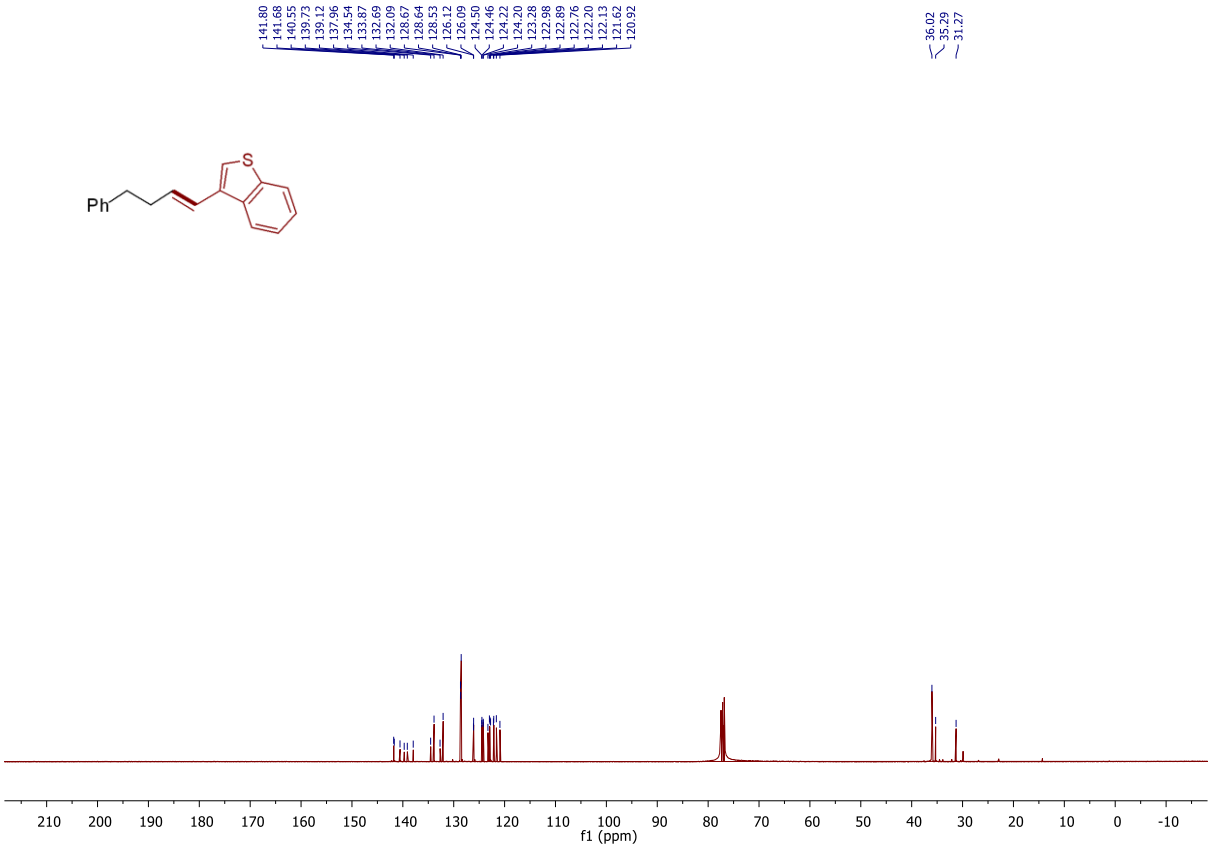

$^{13}$C-NMR spectrum of **25**



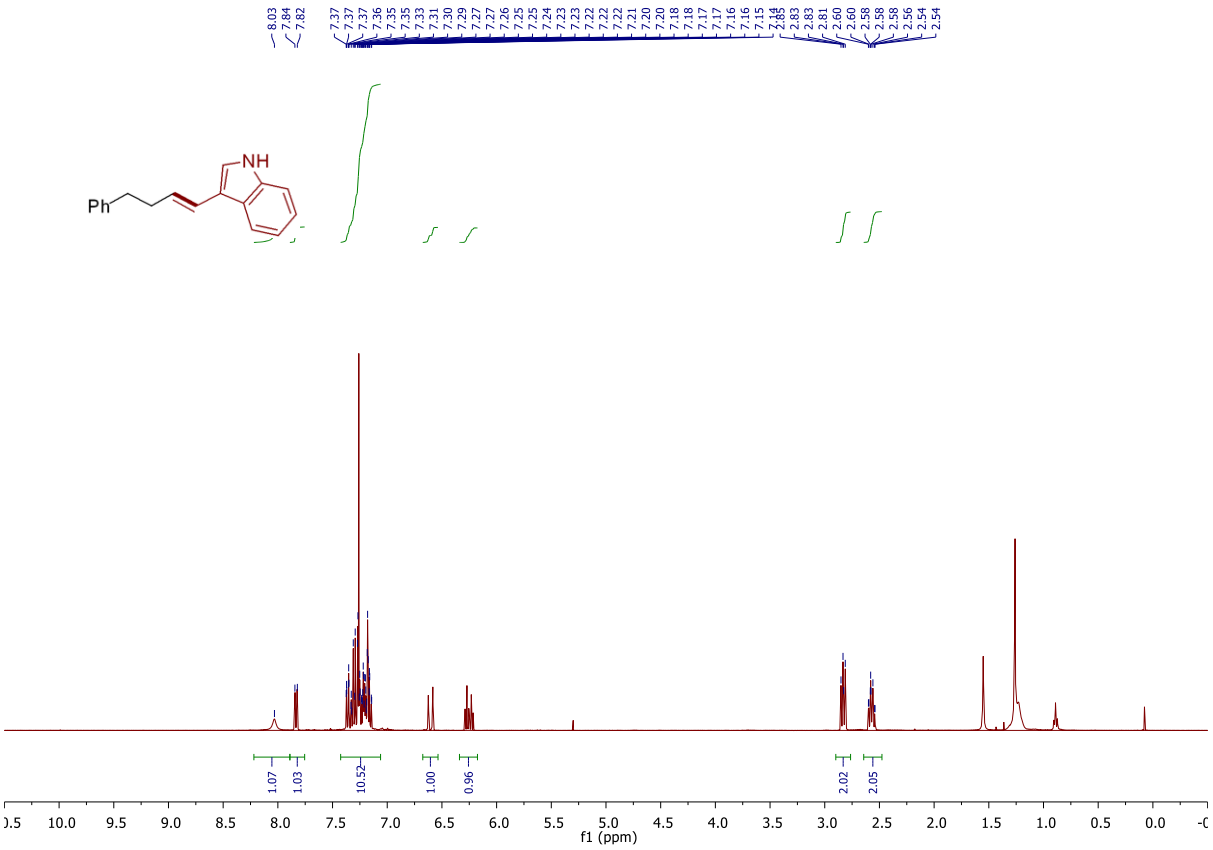
[1]H-NMR spectrum of **26**



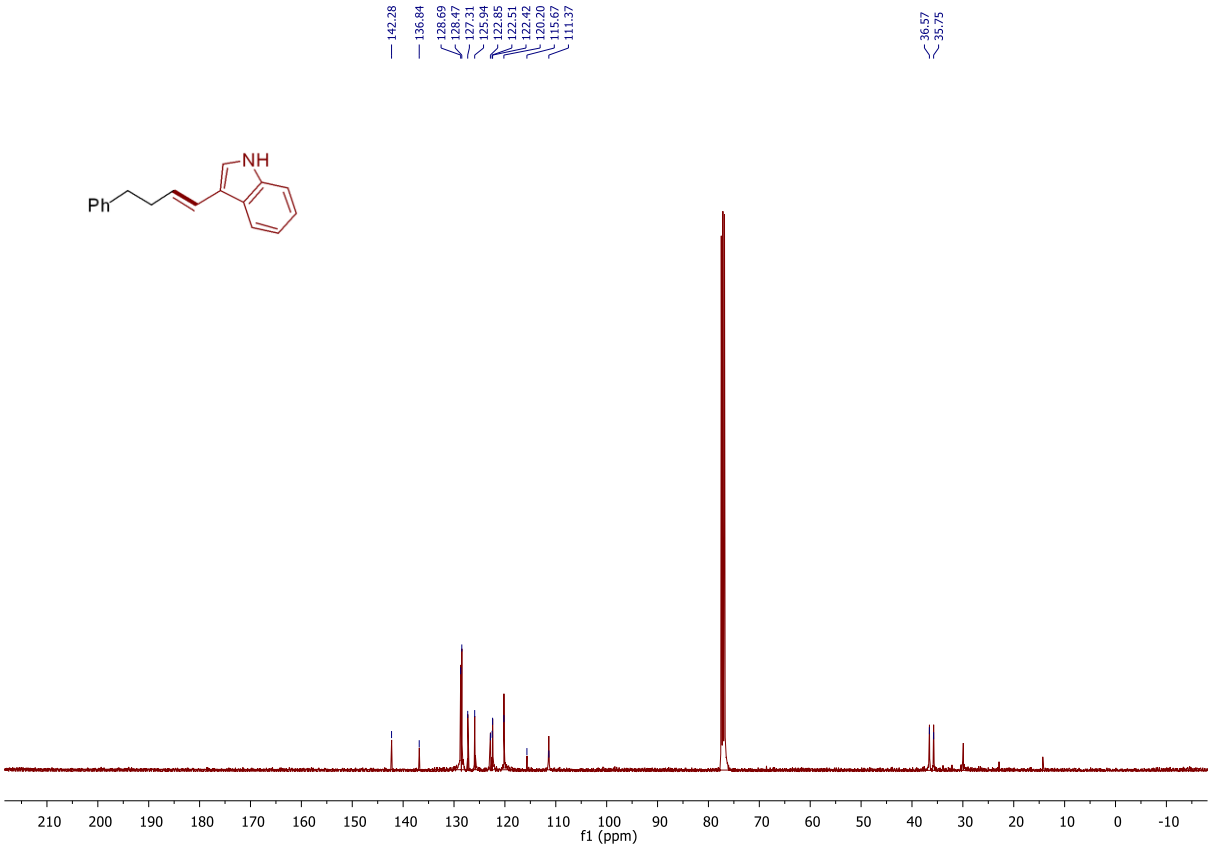

[13]C-NMR spectrum of **26**



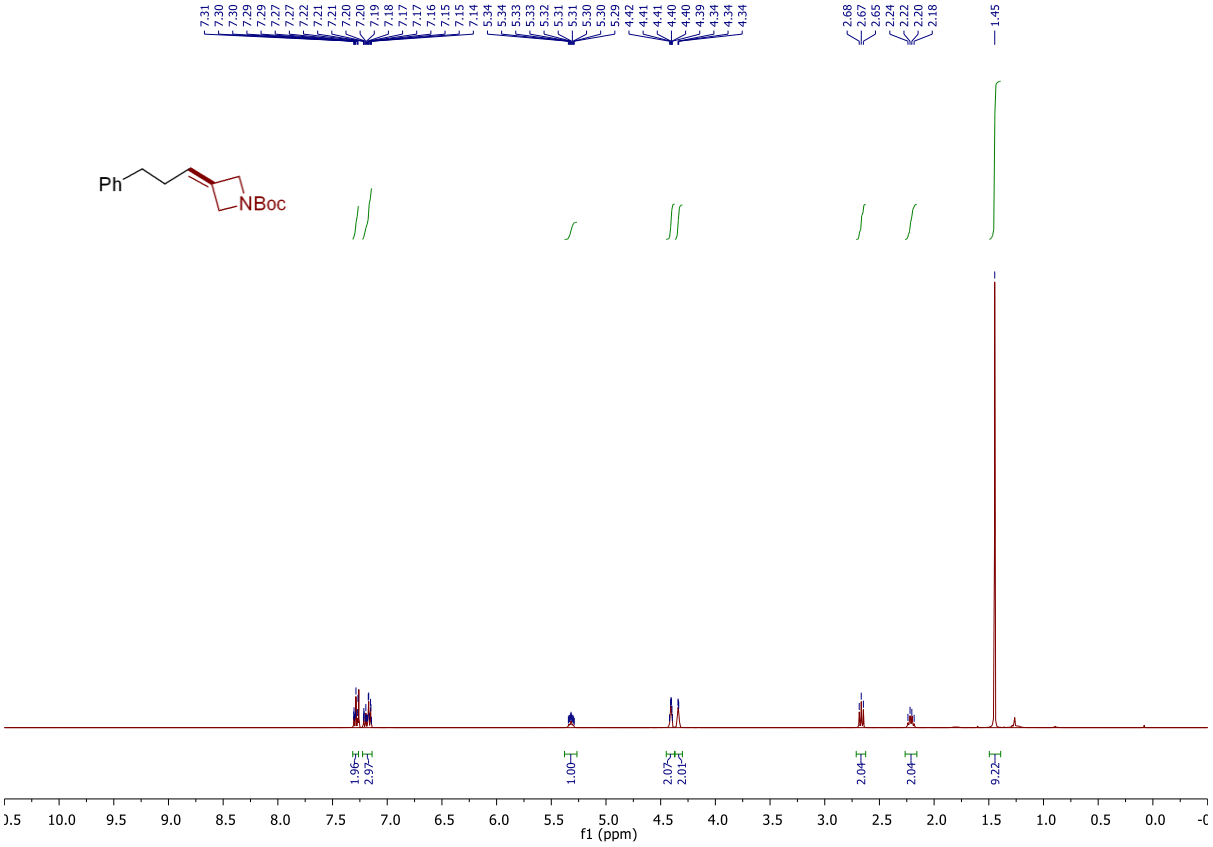
[1]H-NMR spectrum of **27**



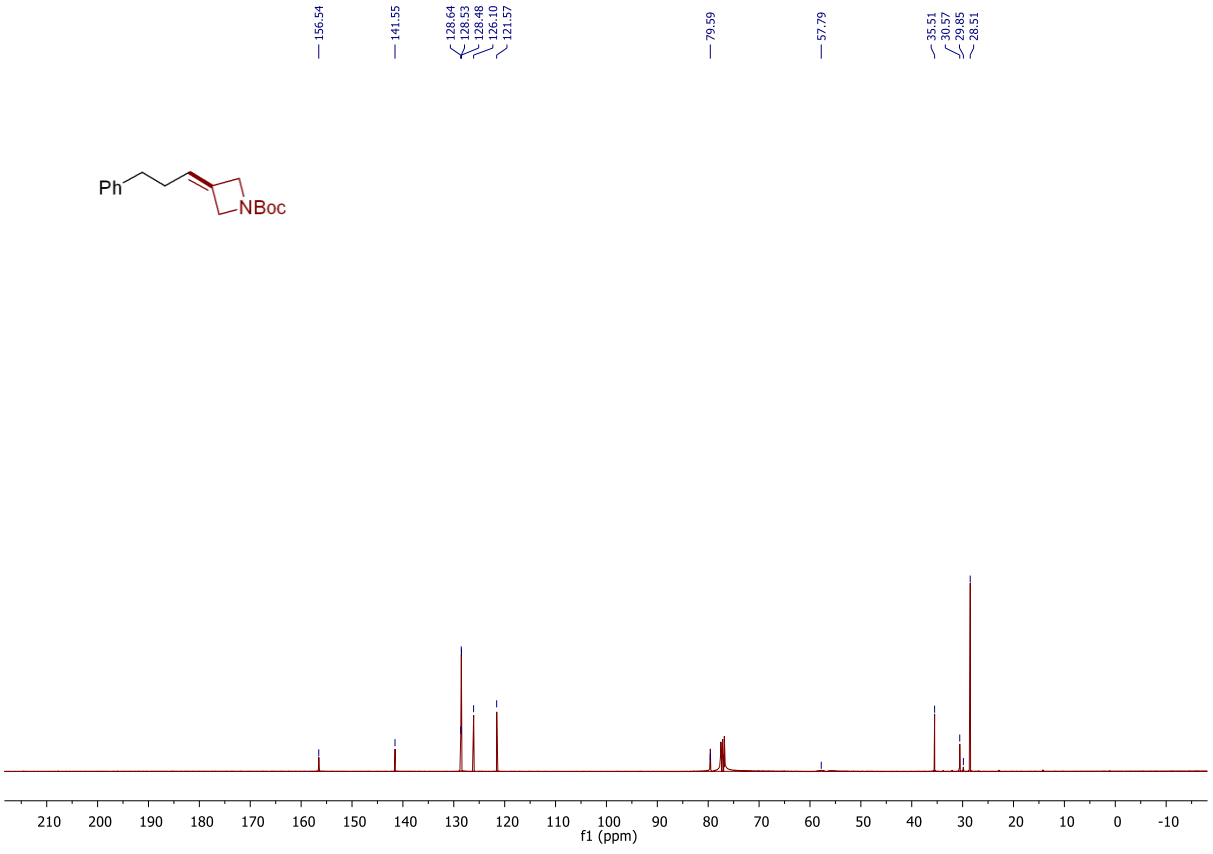

[13]C-NMR spectrum of **27**



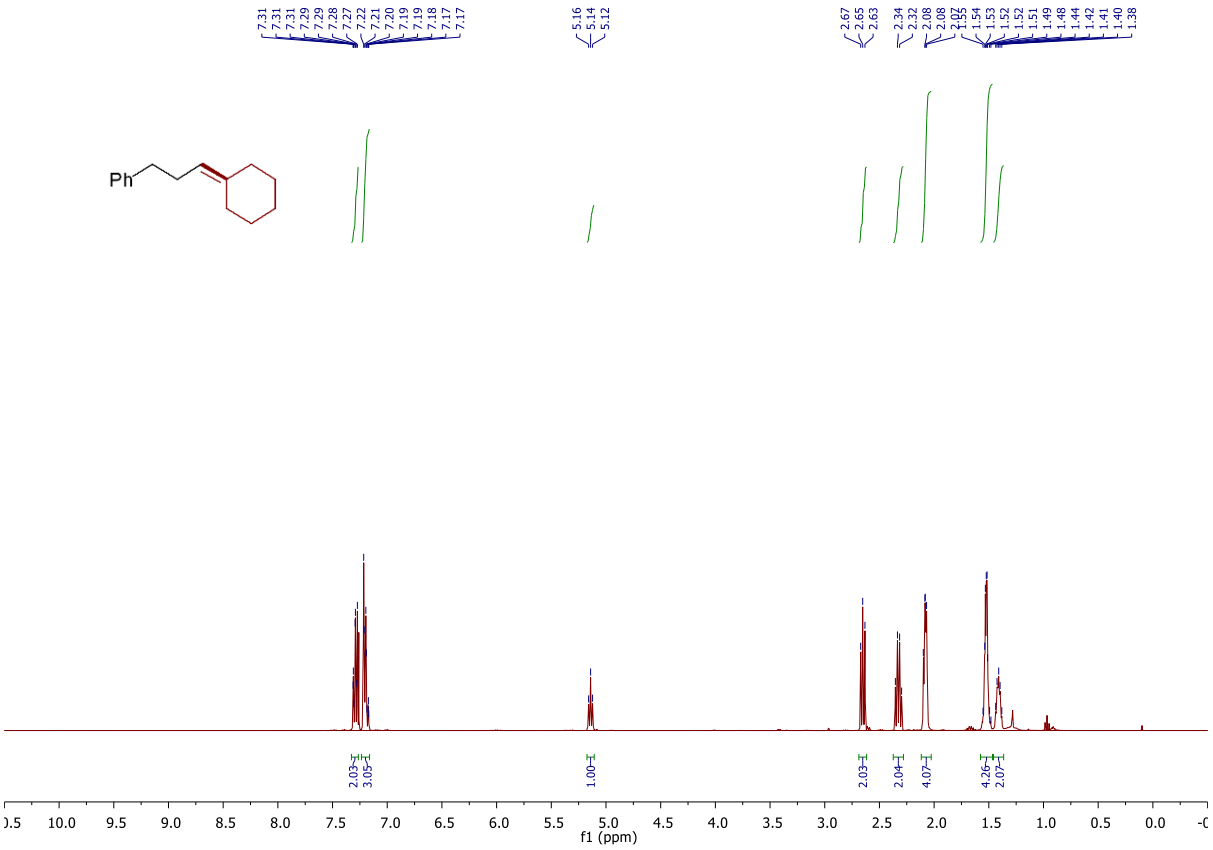
$^{1}$H-NMR spectrum of **28**



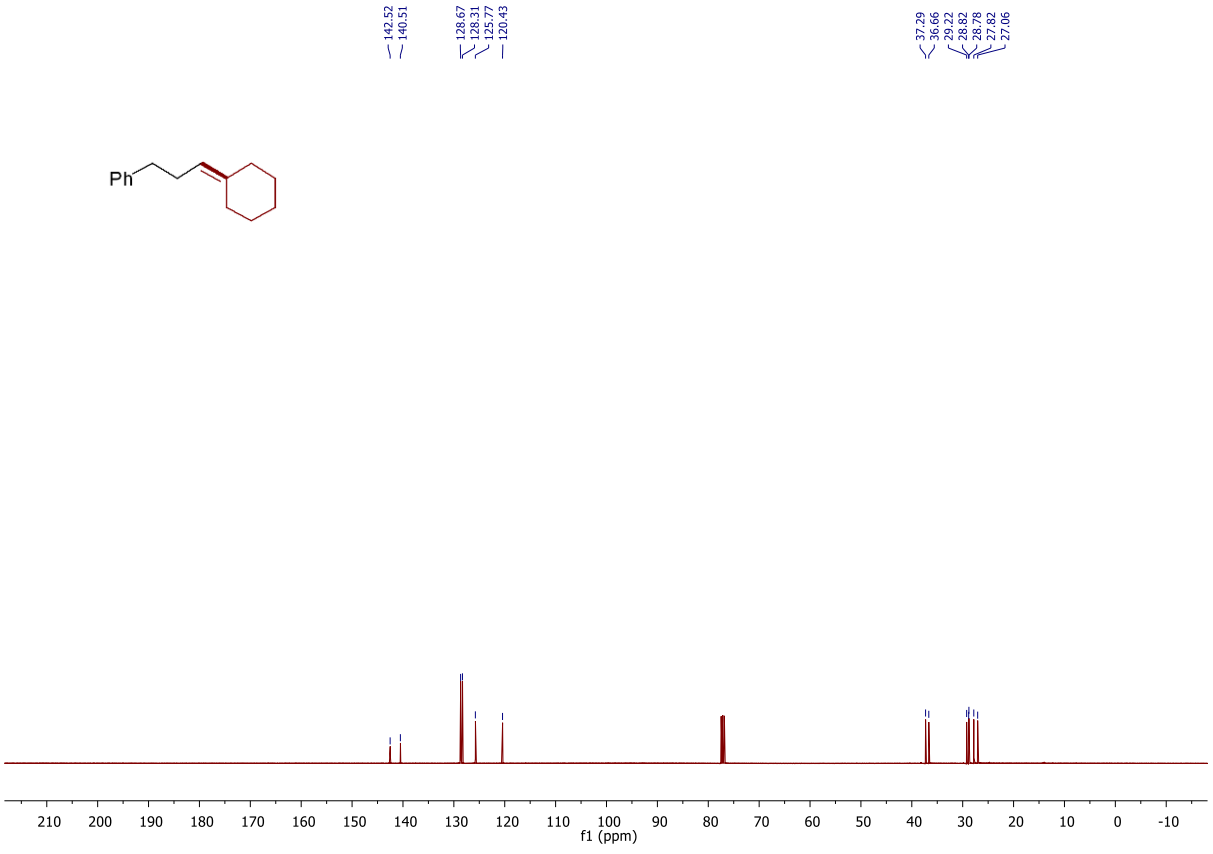

$^{13}$C-NMR spectrum of **28**



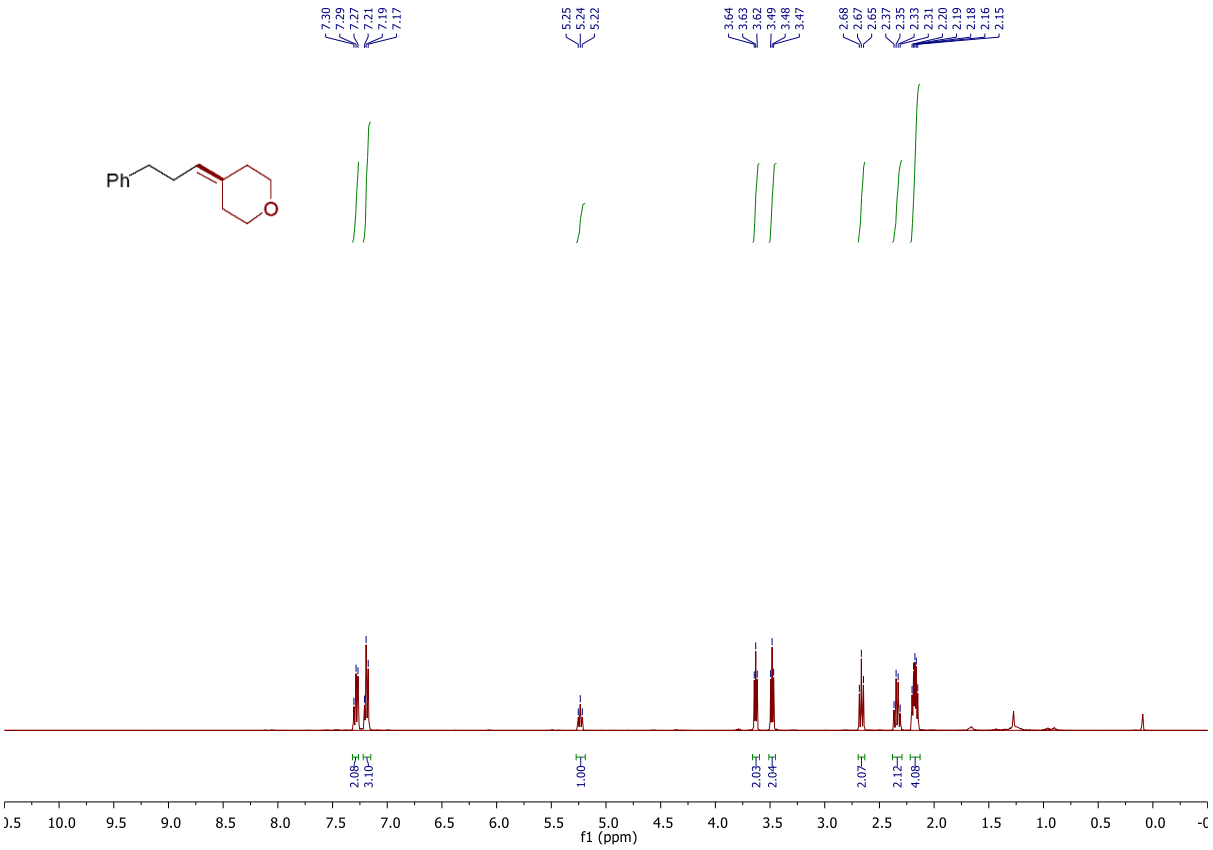
$^{1}$H-NMR spectrum of **29**



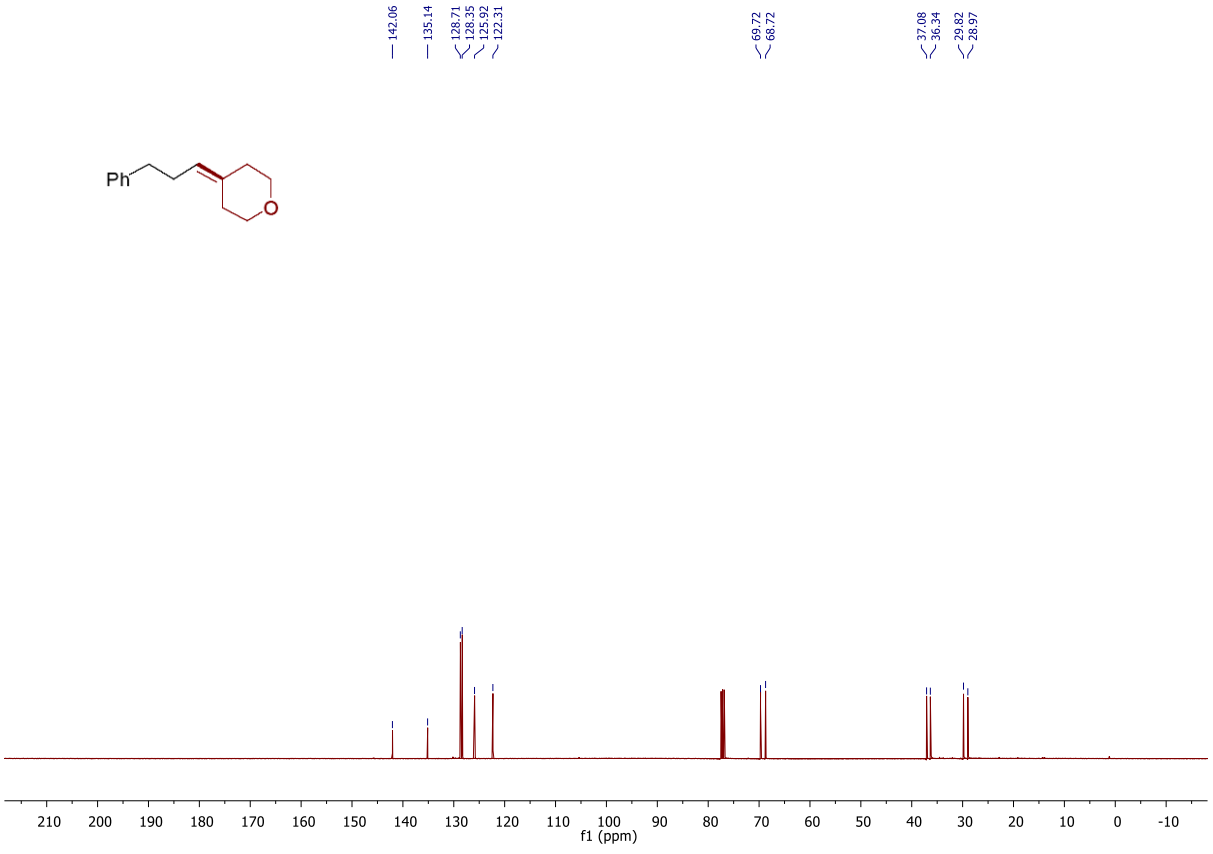

$^{13}$C-NMR spectrum of **29**



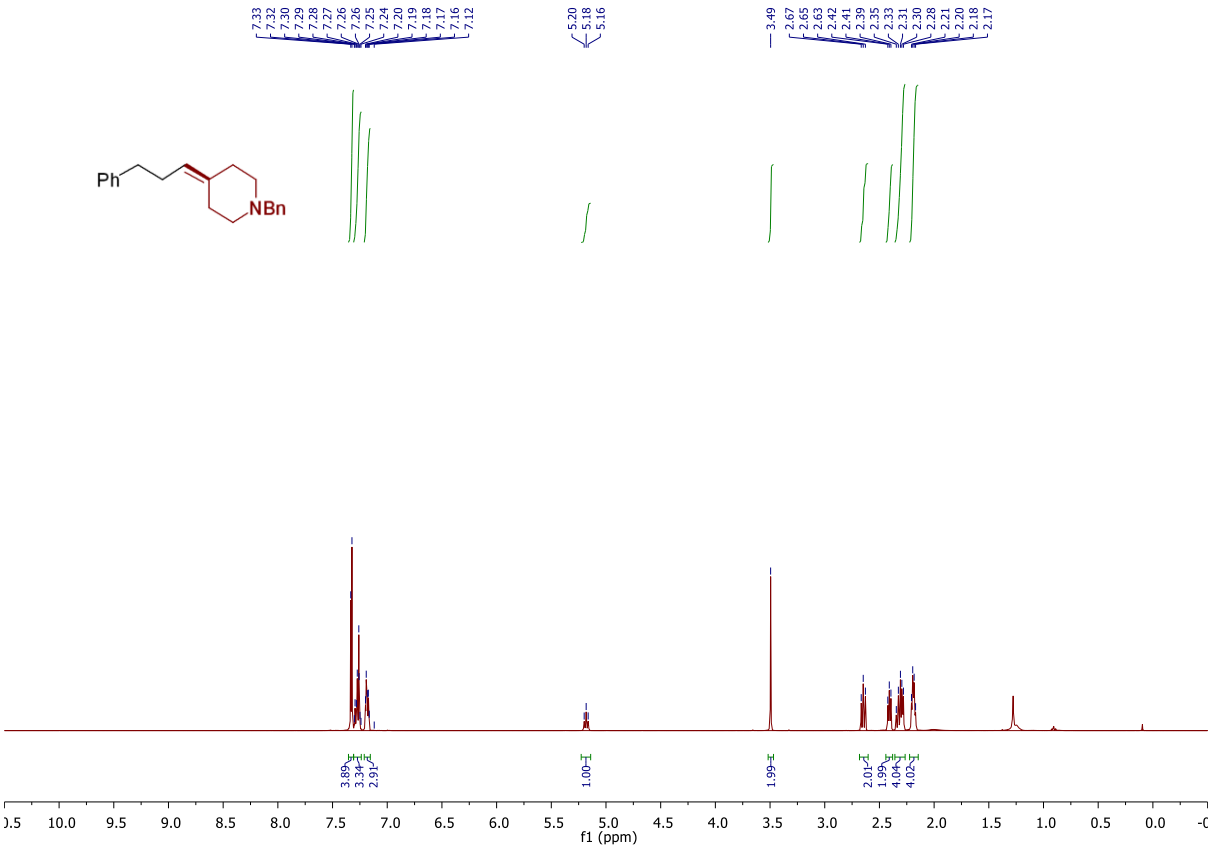
$^{1}$H-NMR spectrum of **30**



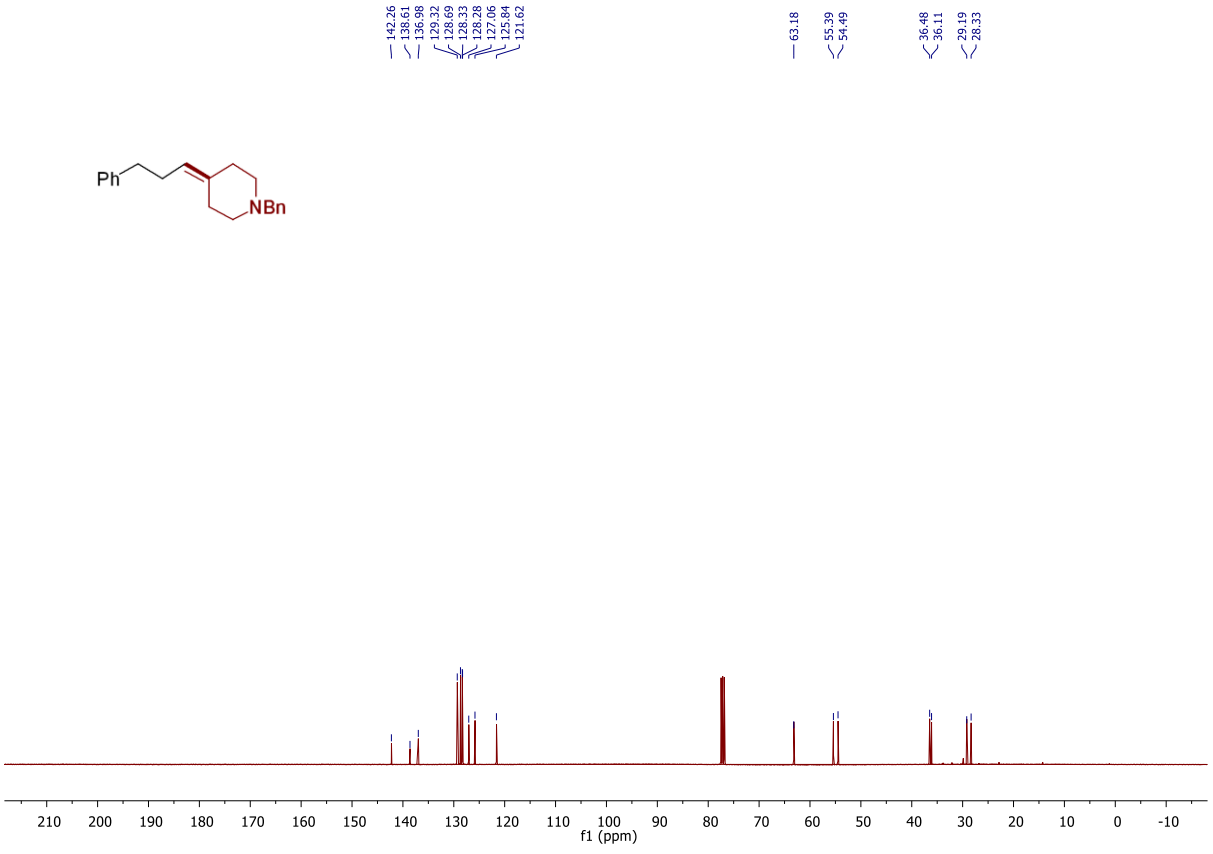

$^{13}$C-NMR spectrum of **30**



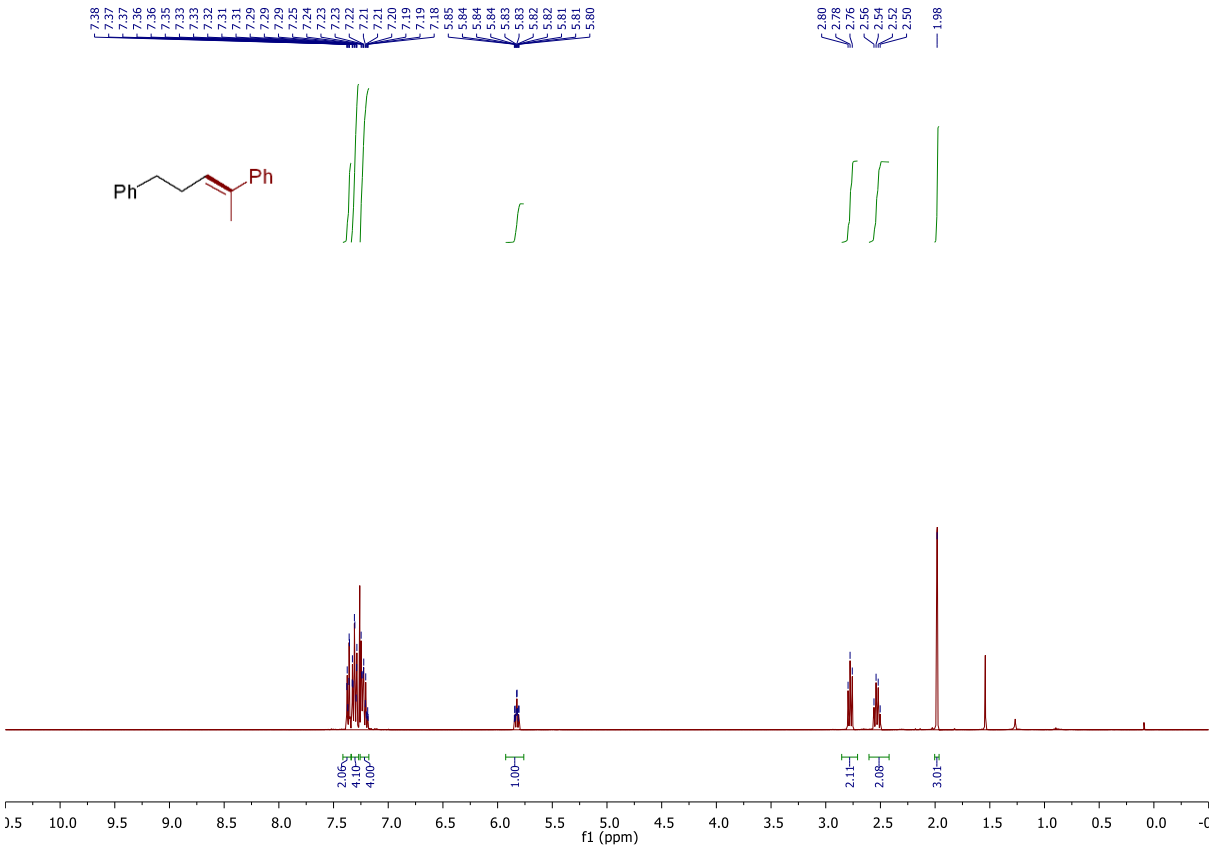
[1]H-NMR spectrum of **31**



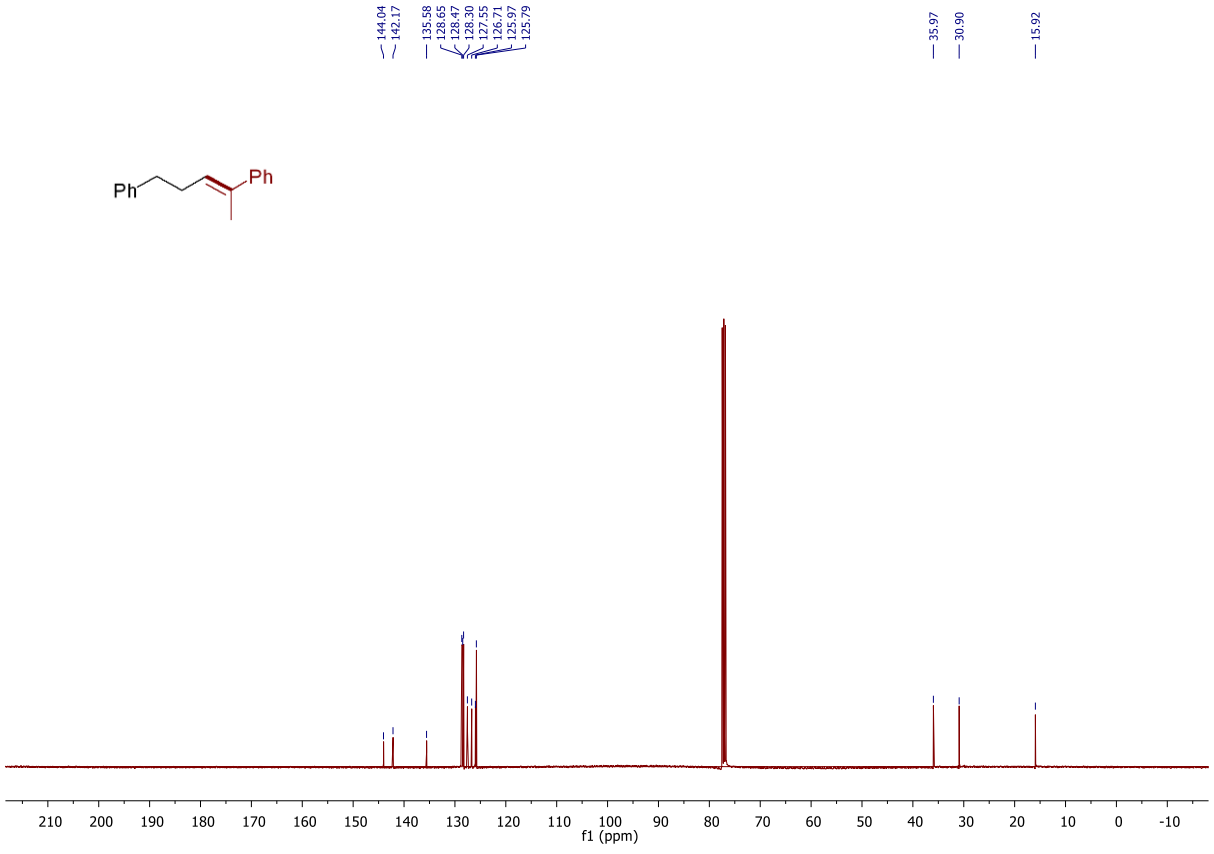

[13]C-NMR spectrum of **31**



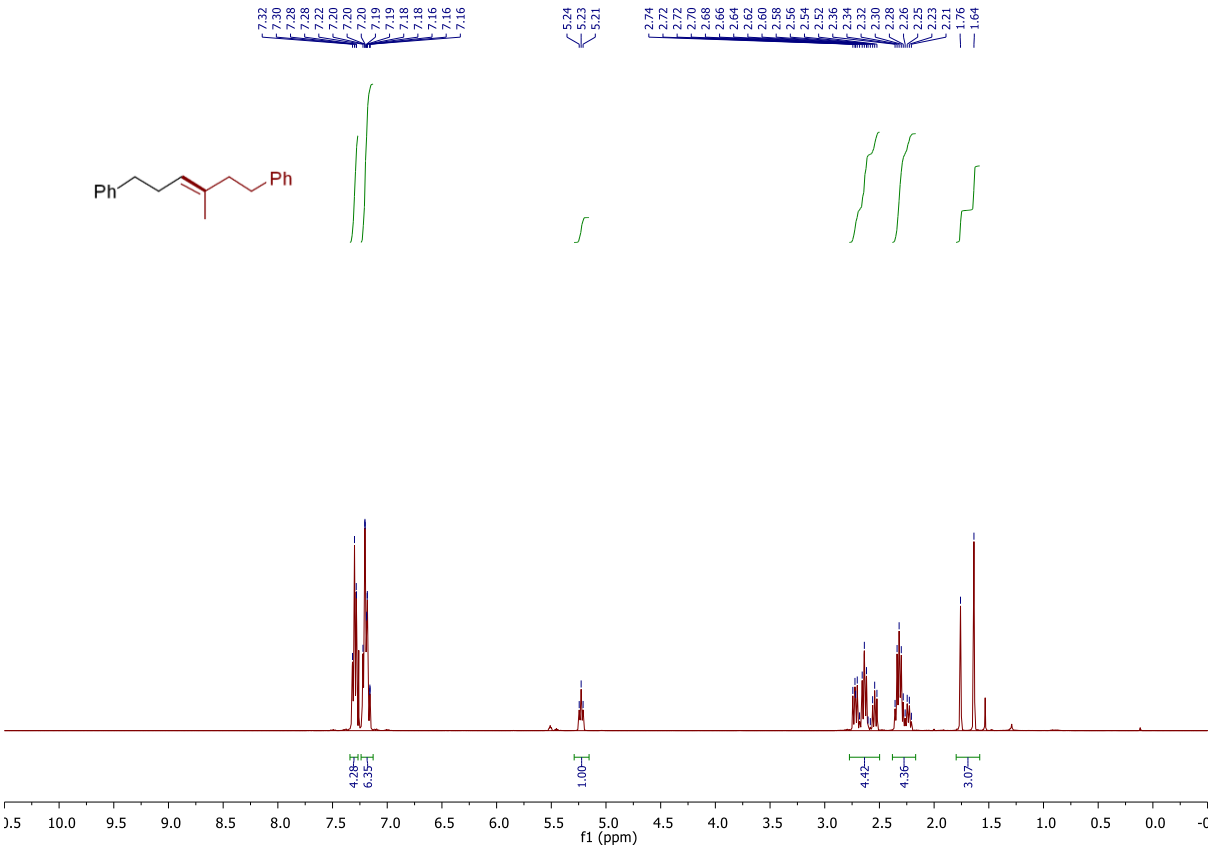
[1]H-NMR spectrum of **32**



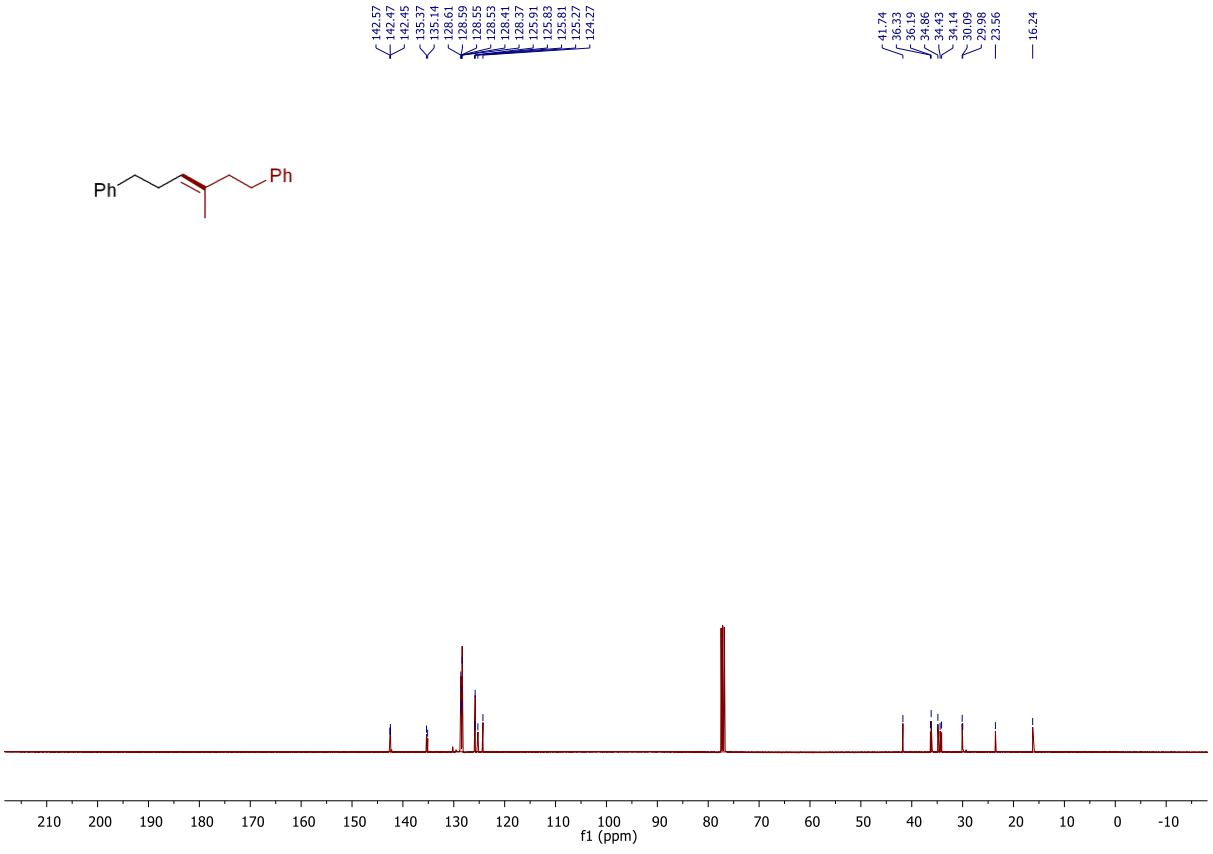

[13]C-NMR spectrum of **32**



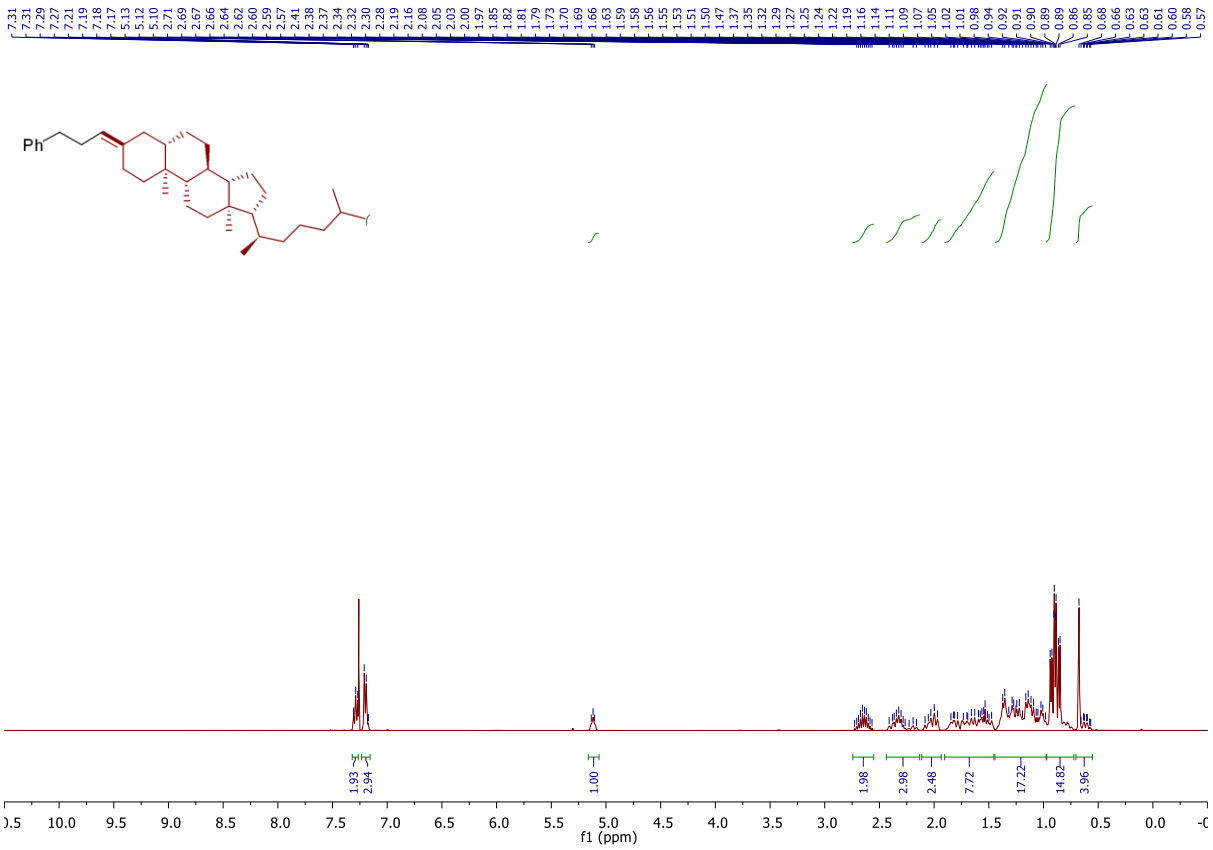
[1]H-NMR spectrum of **33**



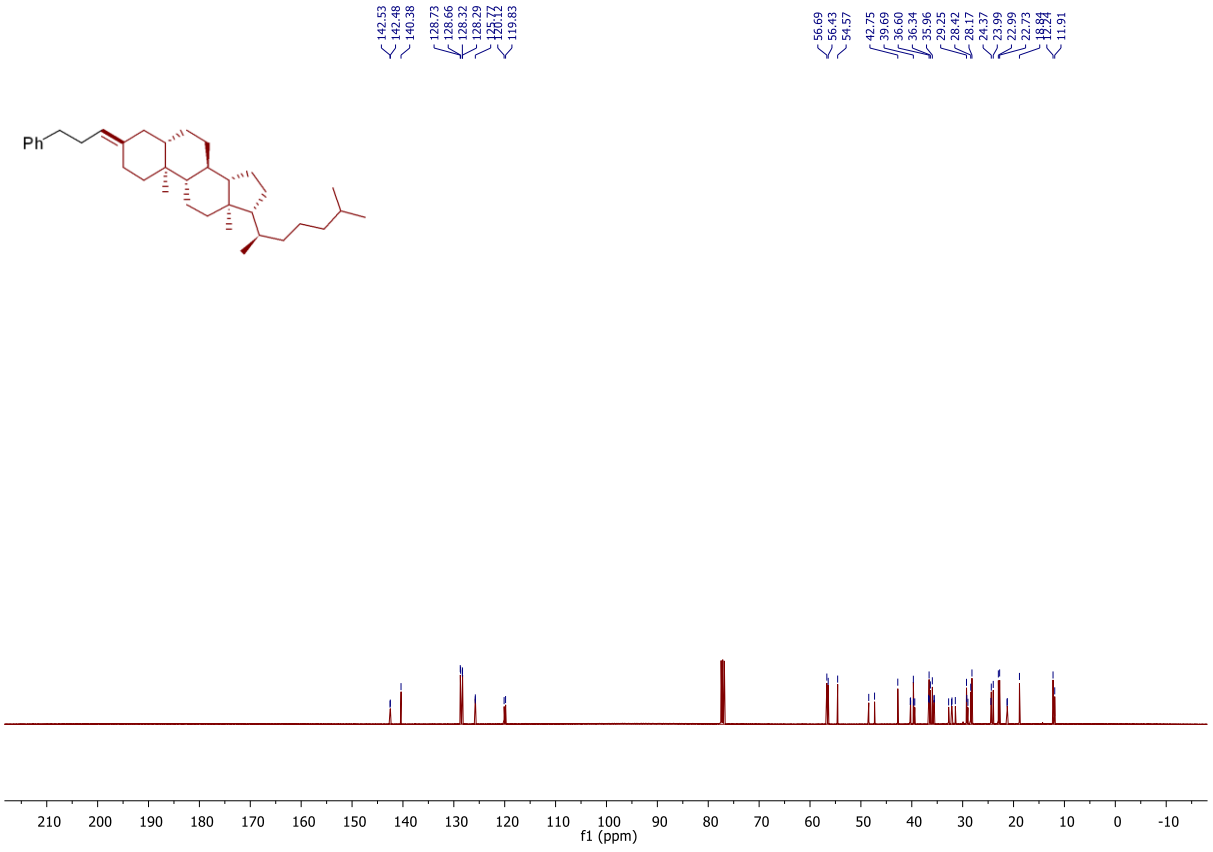

[13]C-NMR spectrum of **33**



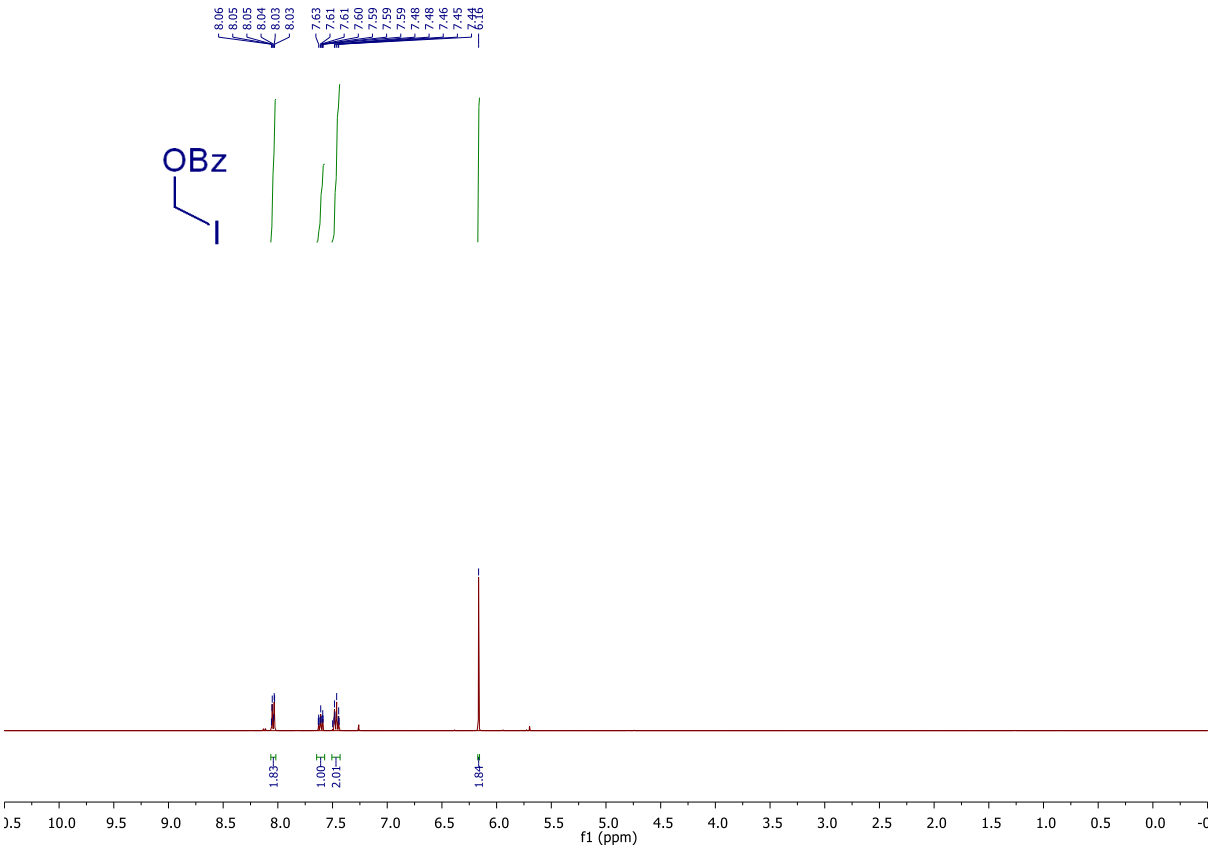
$^{1}$H-NMR spectrum of **34**



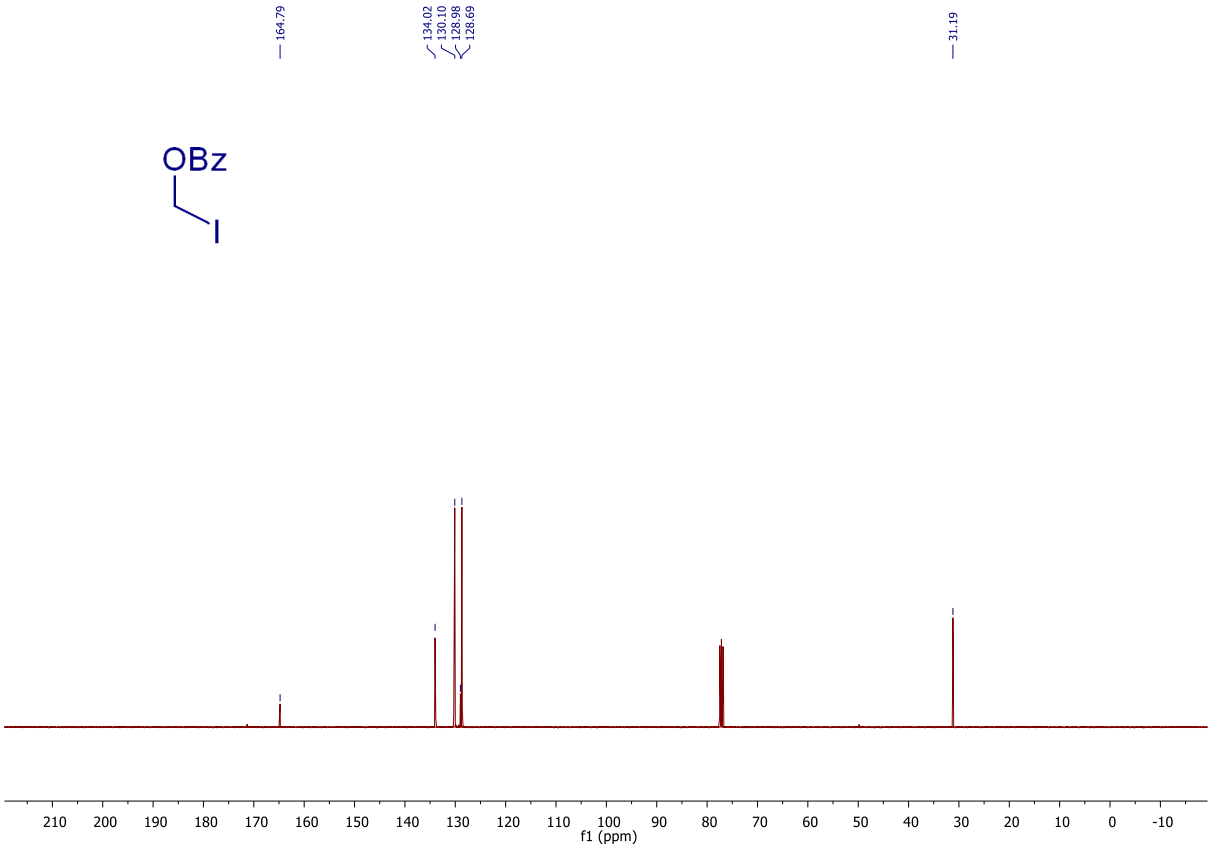

$^{13}$C-NMR spectrum of **34**



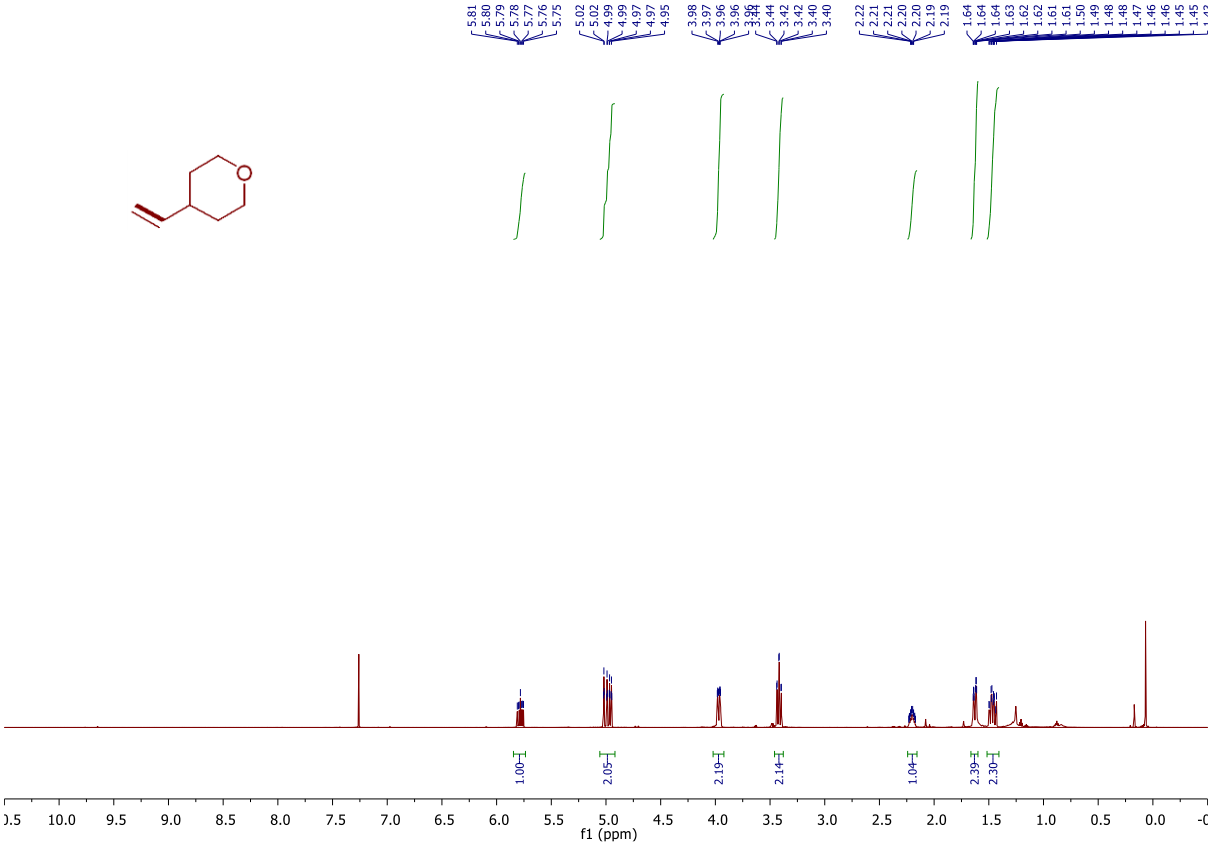
[1]H-NMR spectrum of **S35**



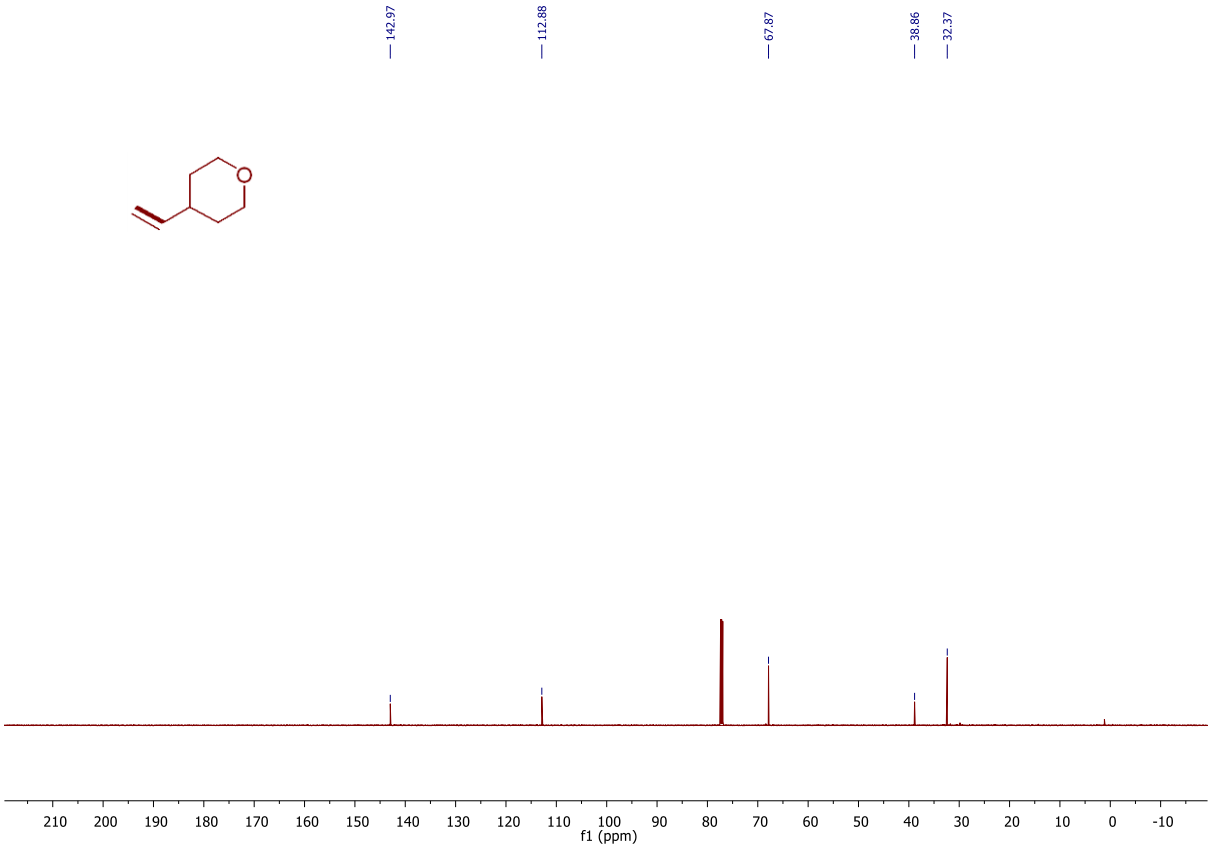

[13]C-NMR spectrum of **S35**



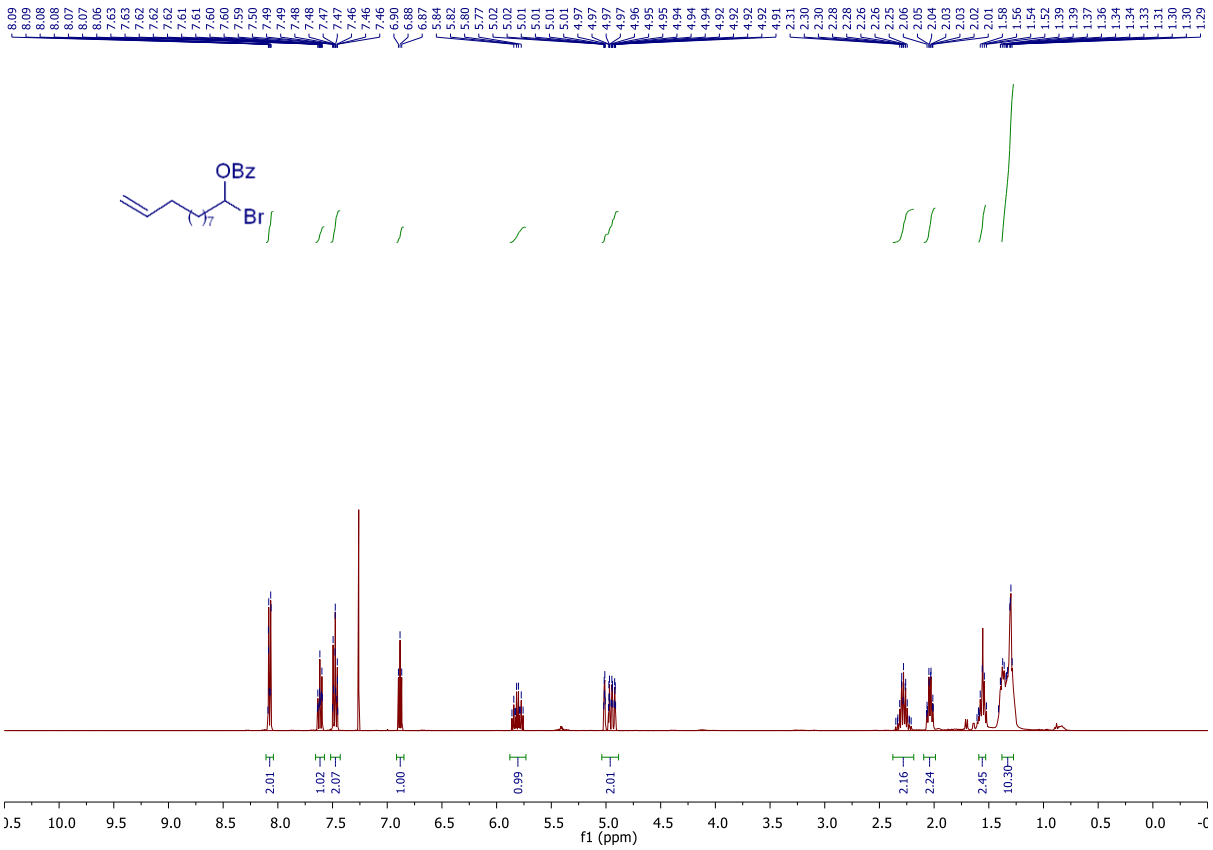
[1]H-NMR spectrum of **35**



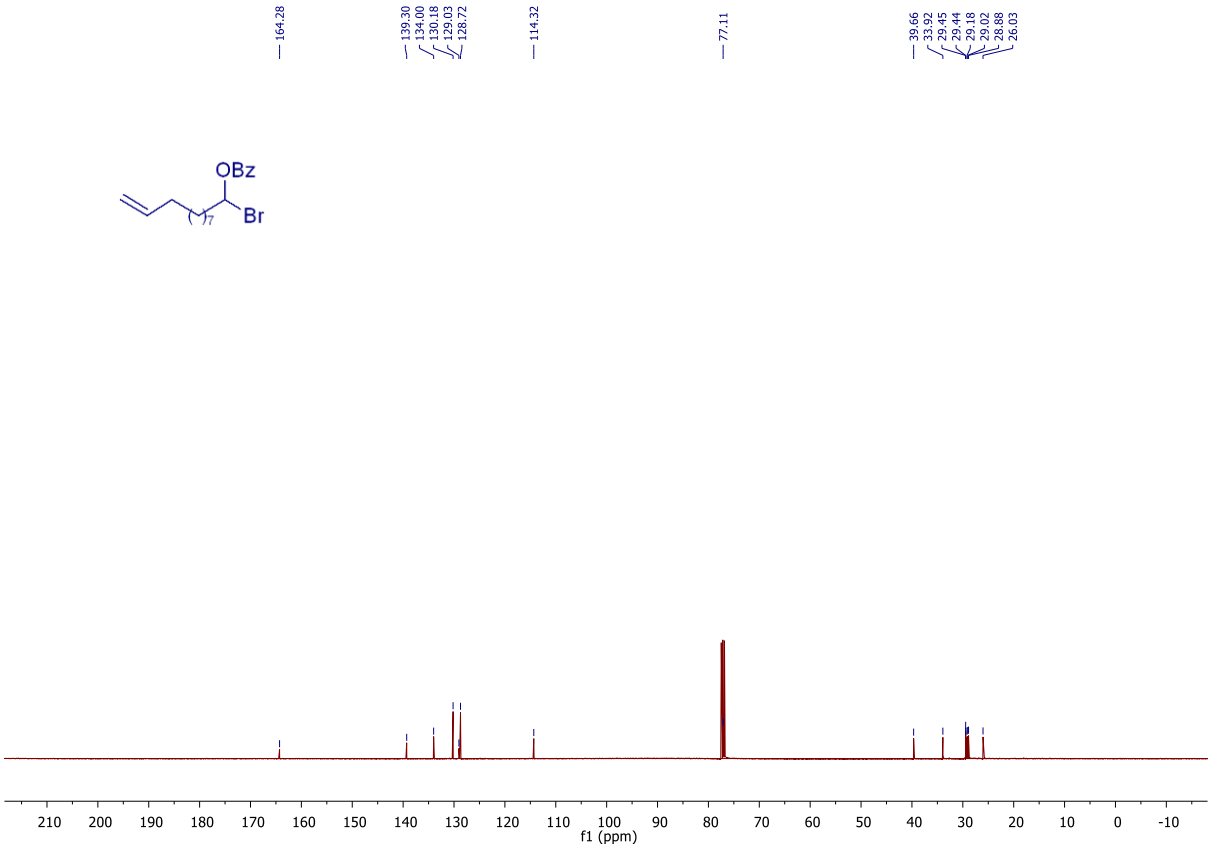

[13]C-NMR spectrum of **35**



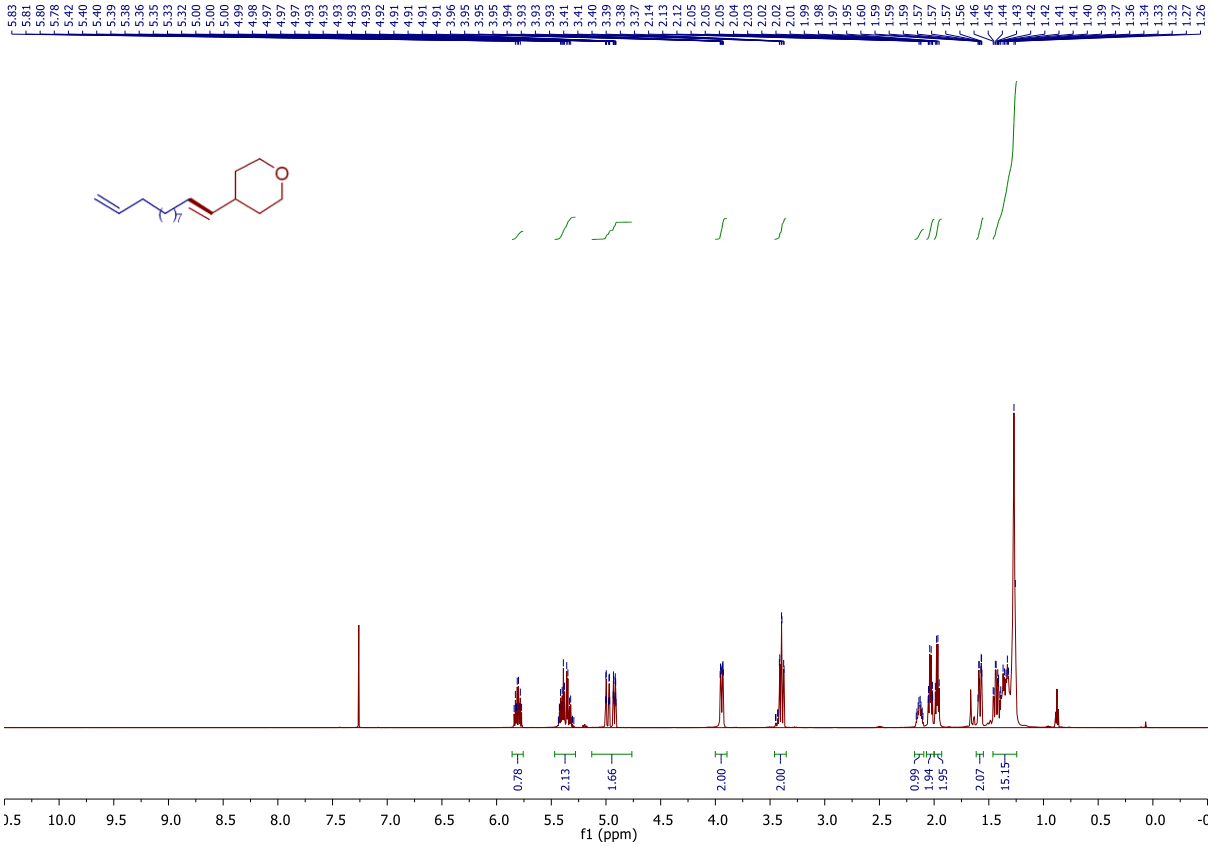
[1]H-NMR spectrum of **S36**



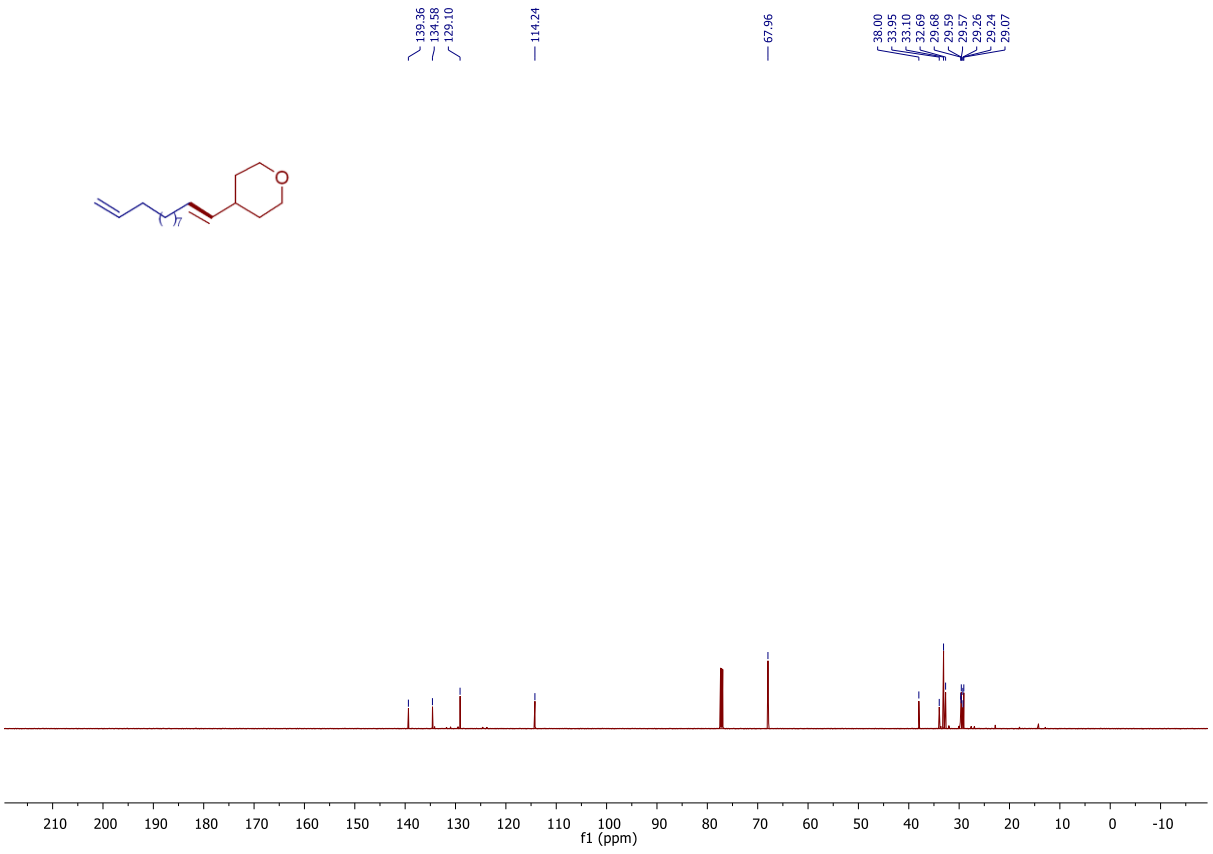

[13]C-NMR spectrum of **S36**



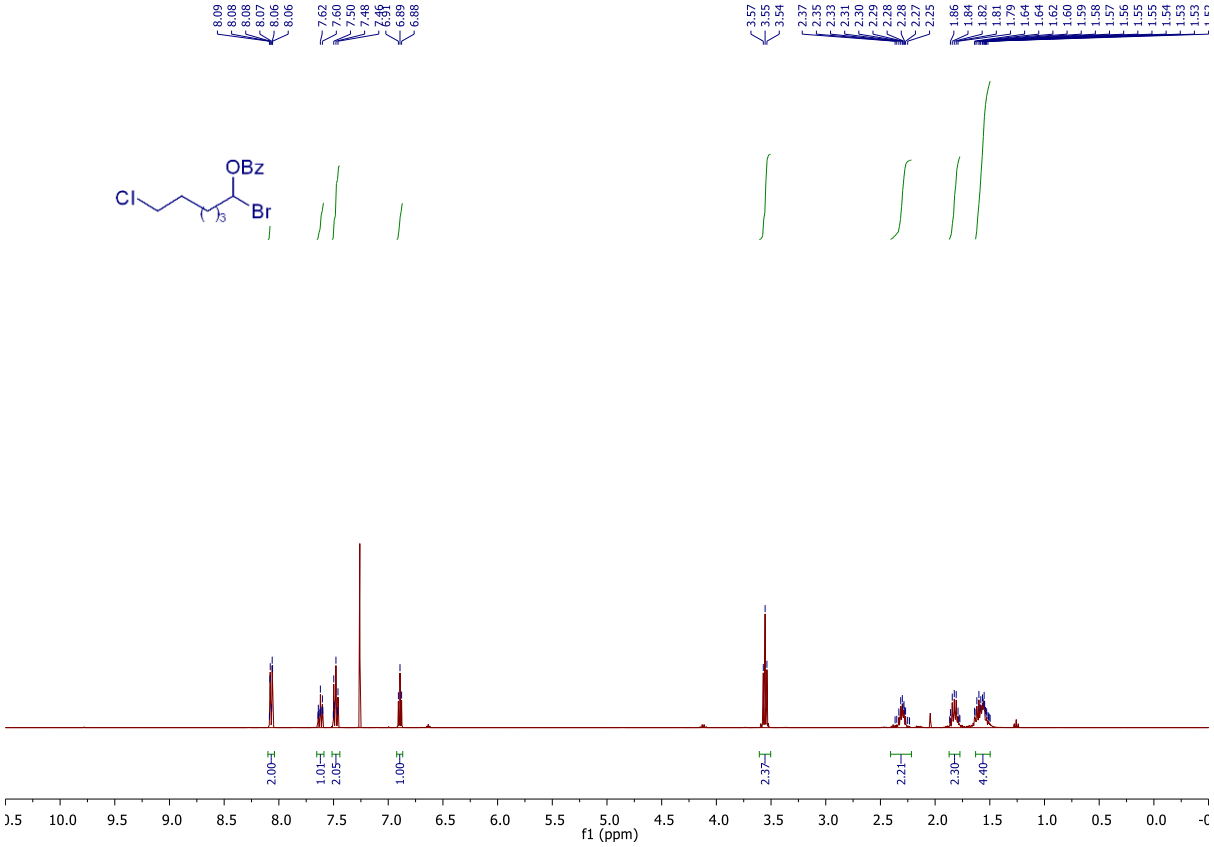
[1]H-NMR spectrum of **36**



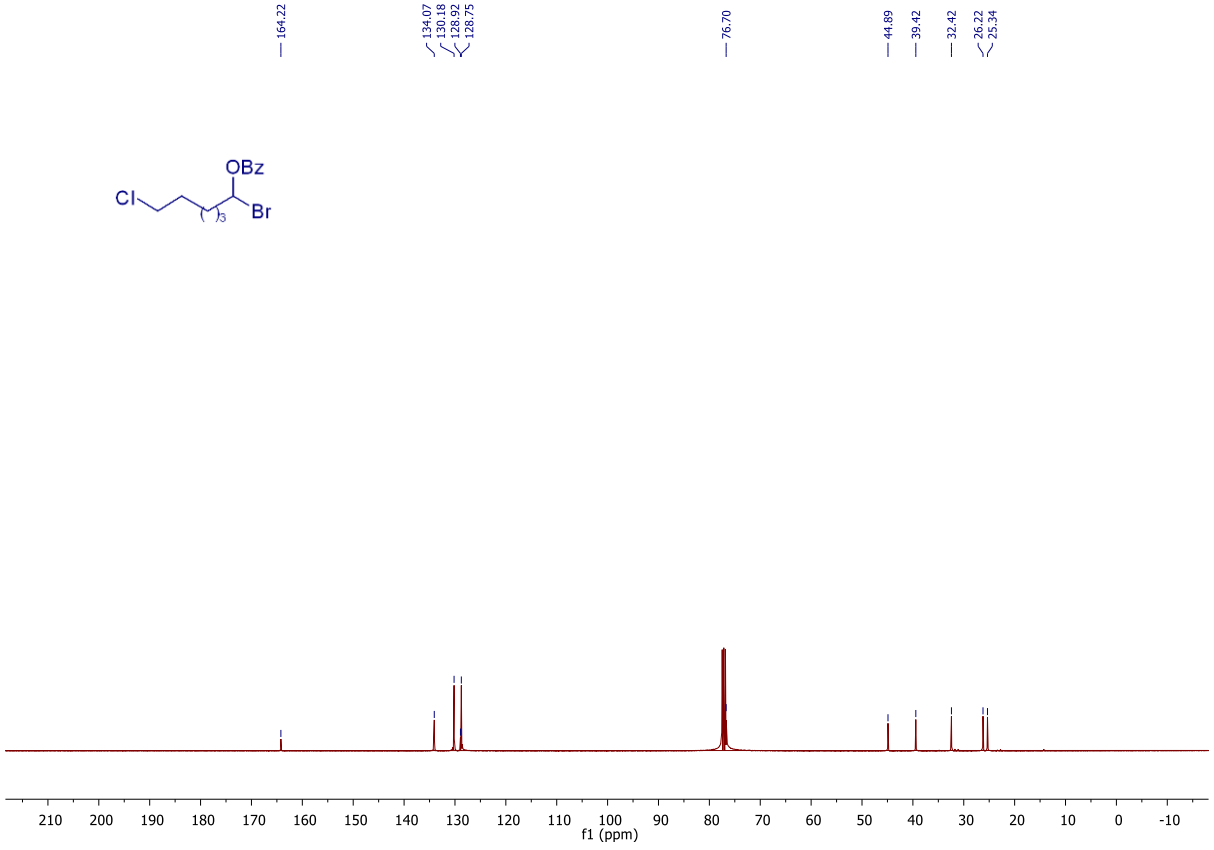

[13]C-NMR spectrum of **36**



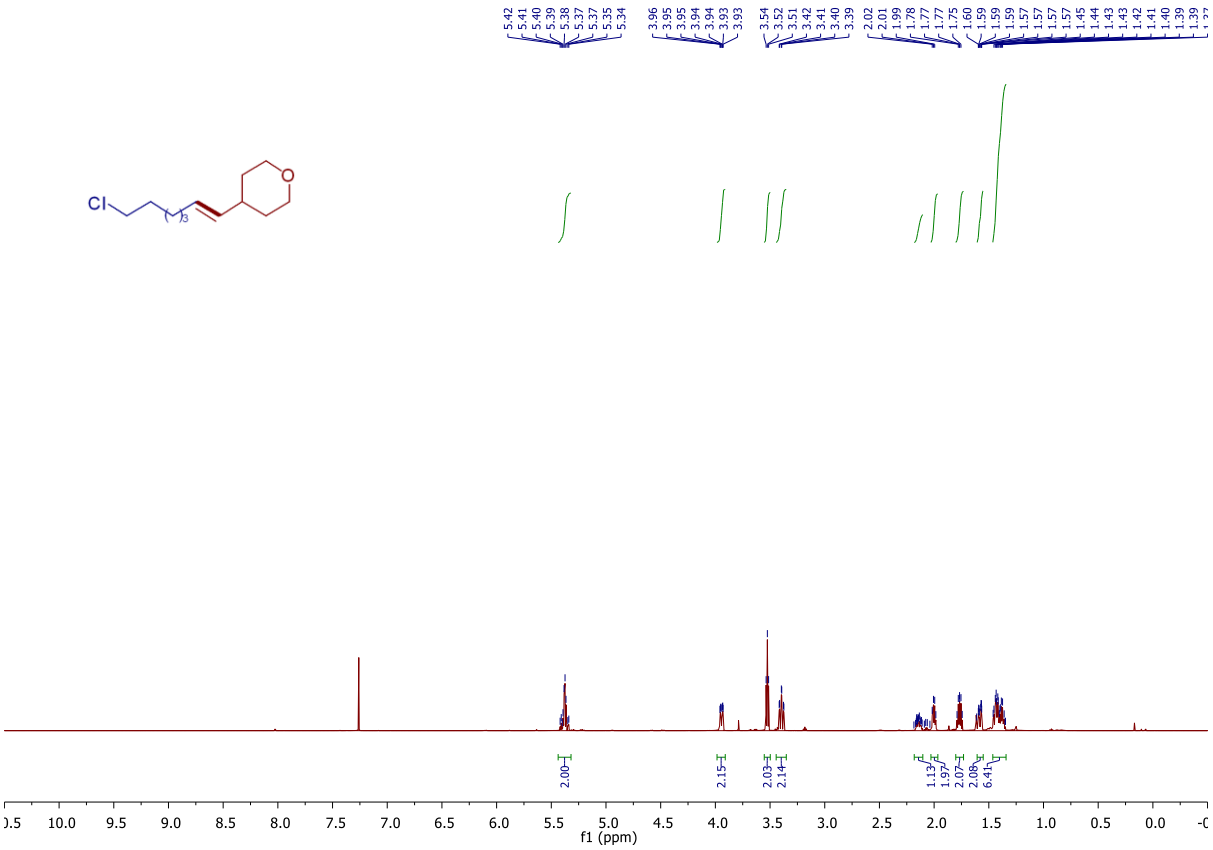
[1]H-NMR spectrum of **S37**



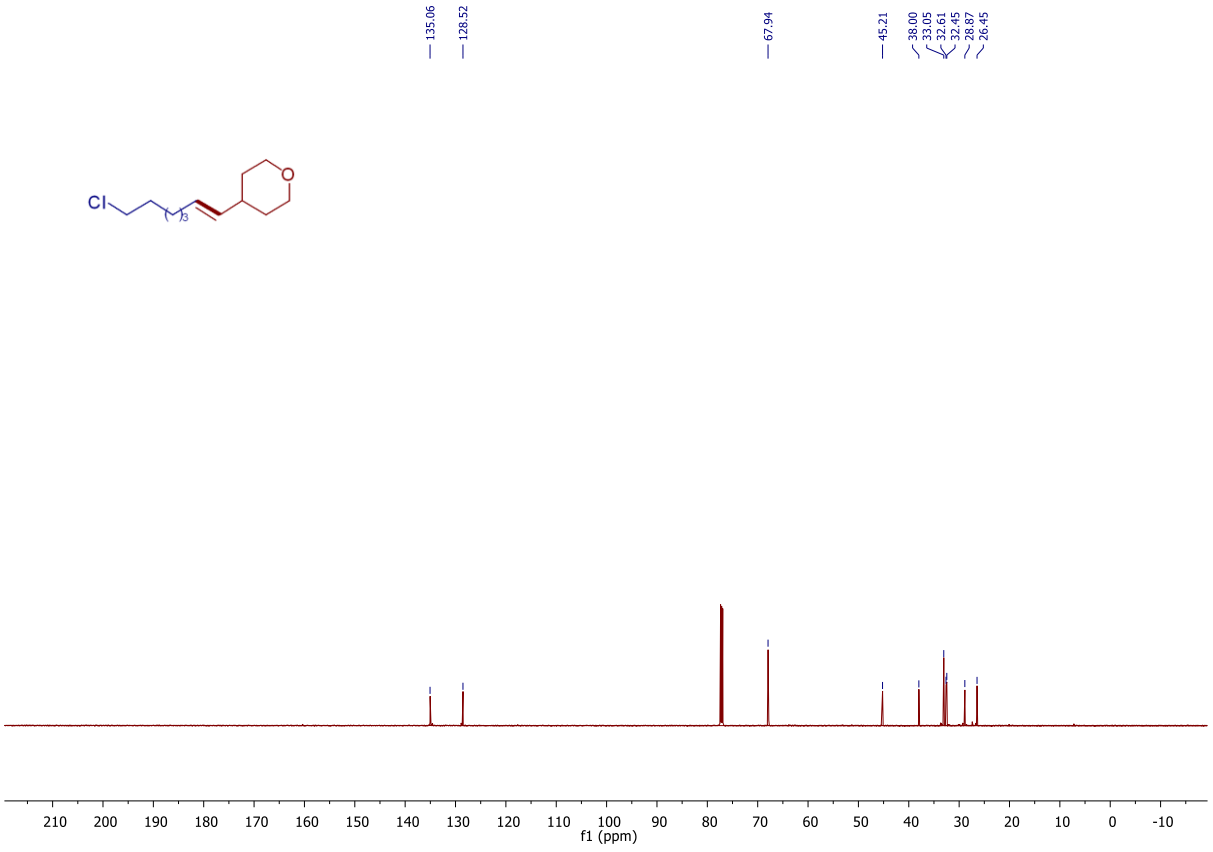

[13]C-NMR spectrum of **S37**



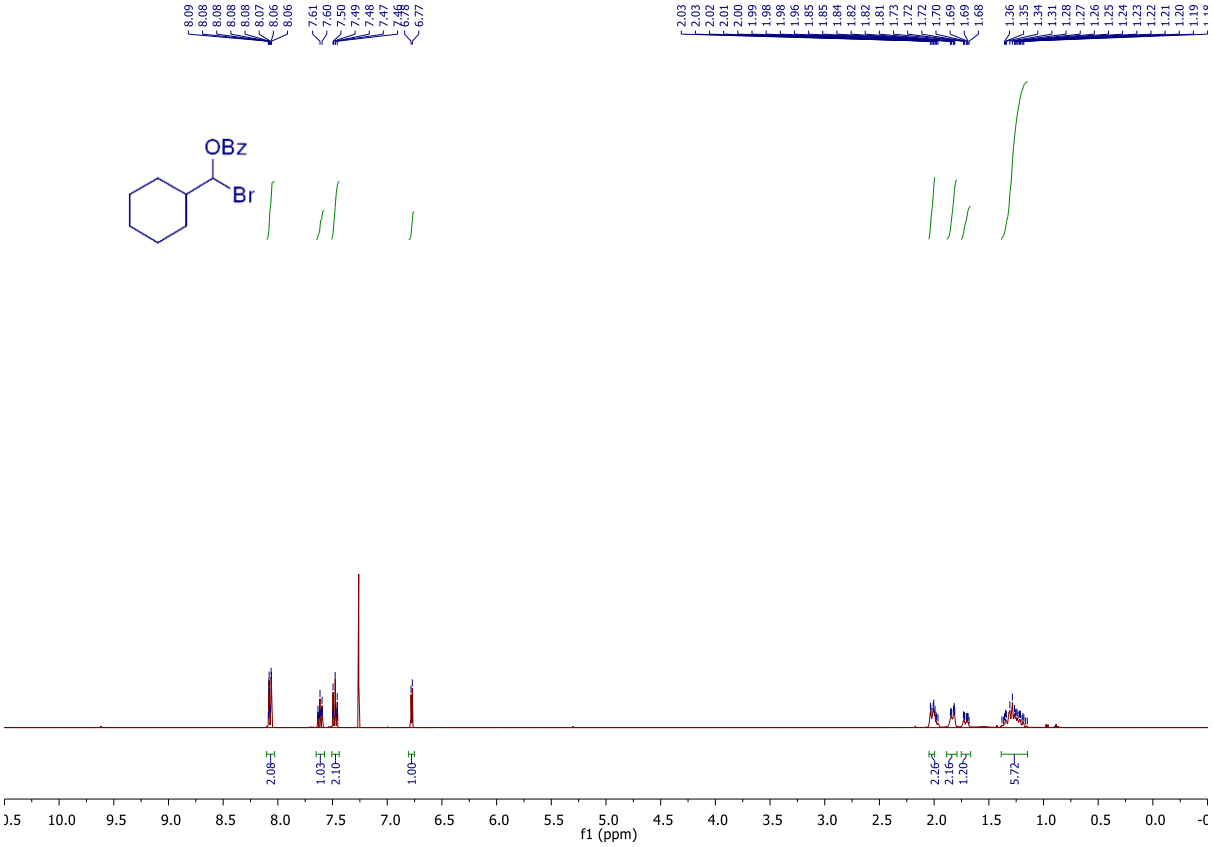
$^{1}$H-NMR spectrum of **37**



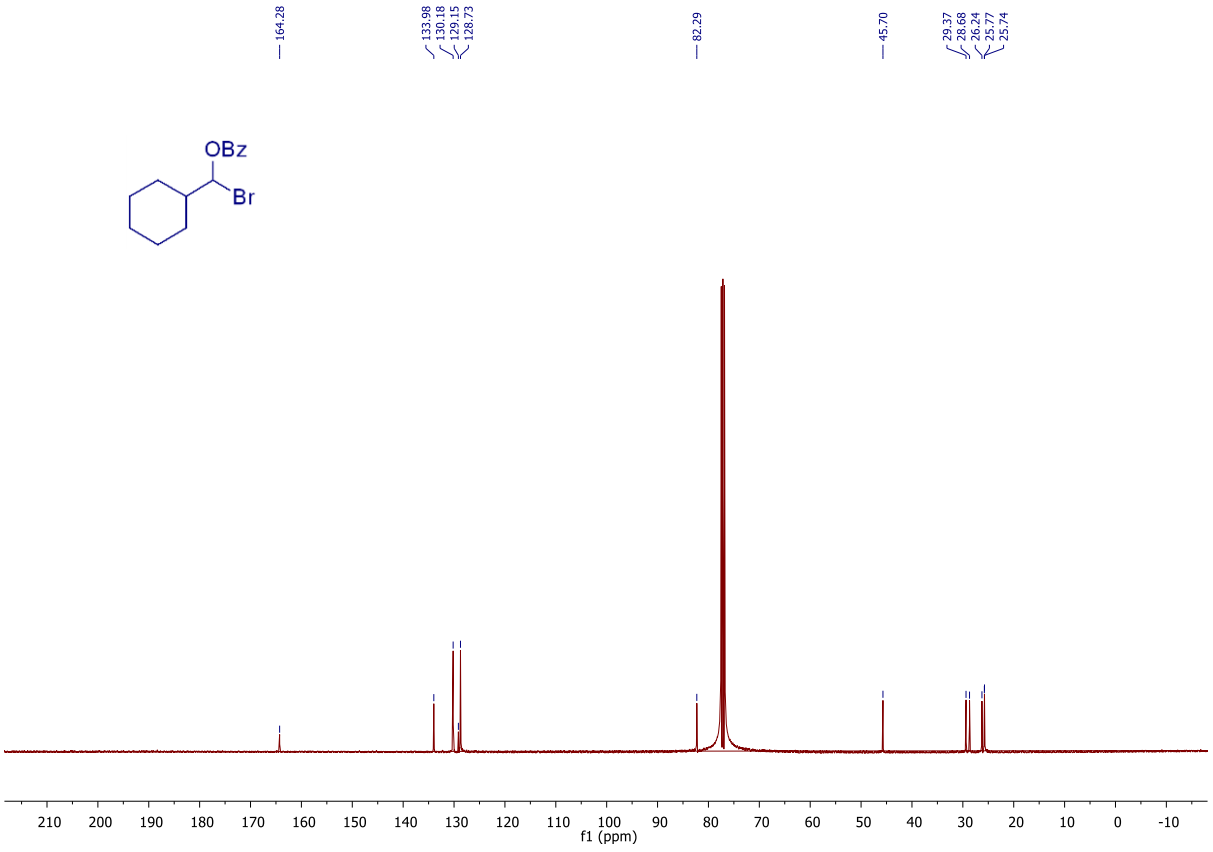

$^{13}$C-NMR spectrum of **37**



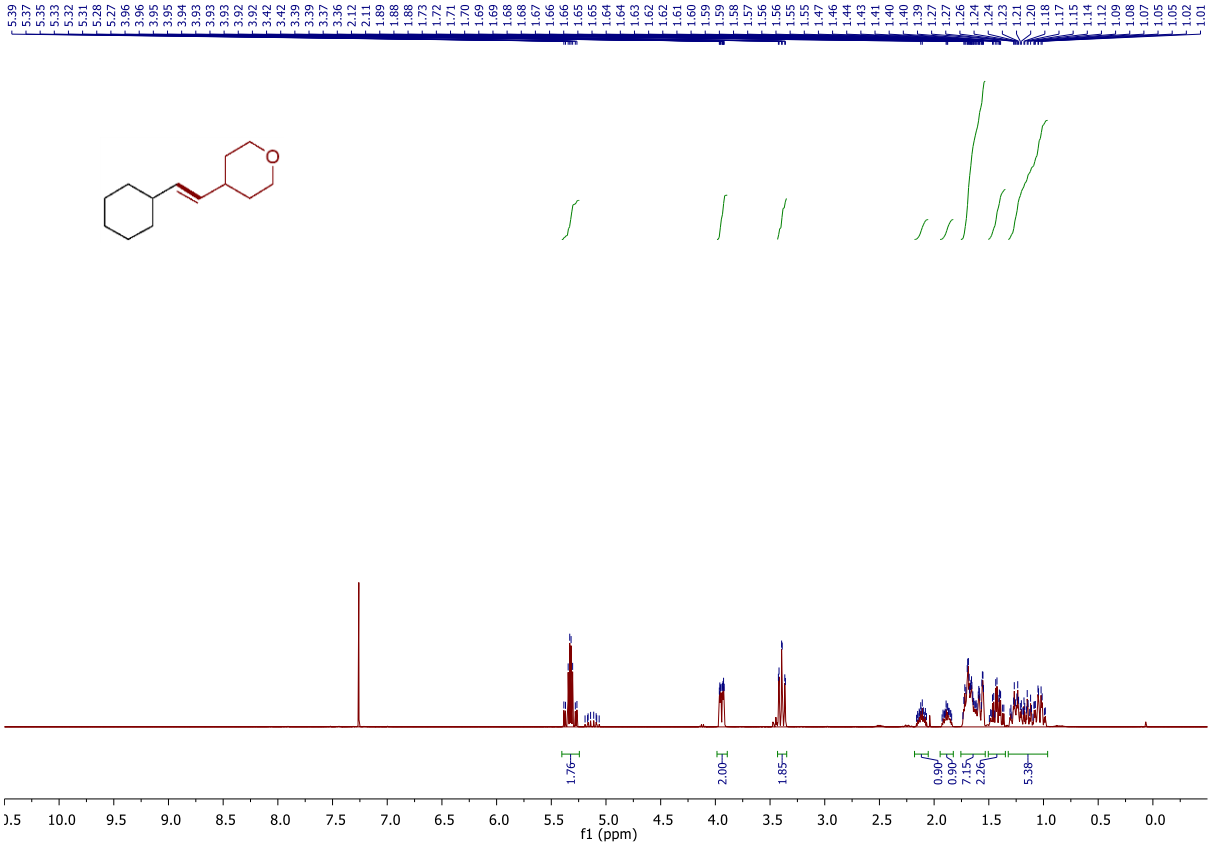
$^{1}$H-NMR spectrum of **S38**



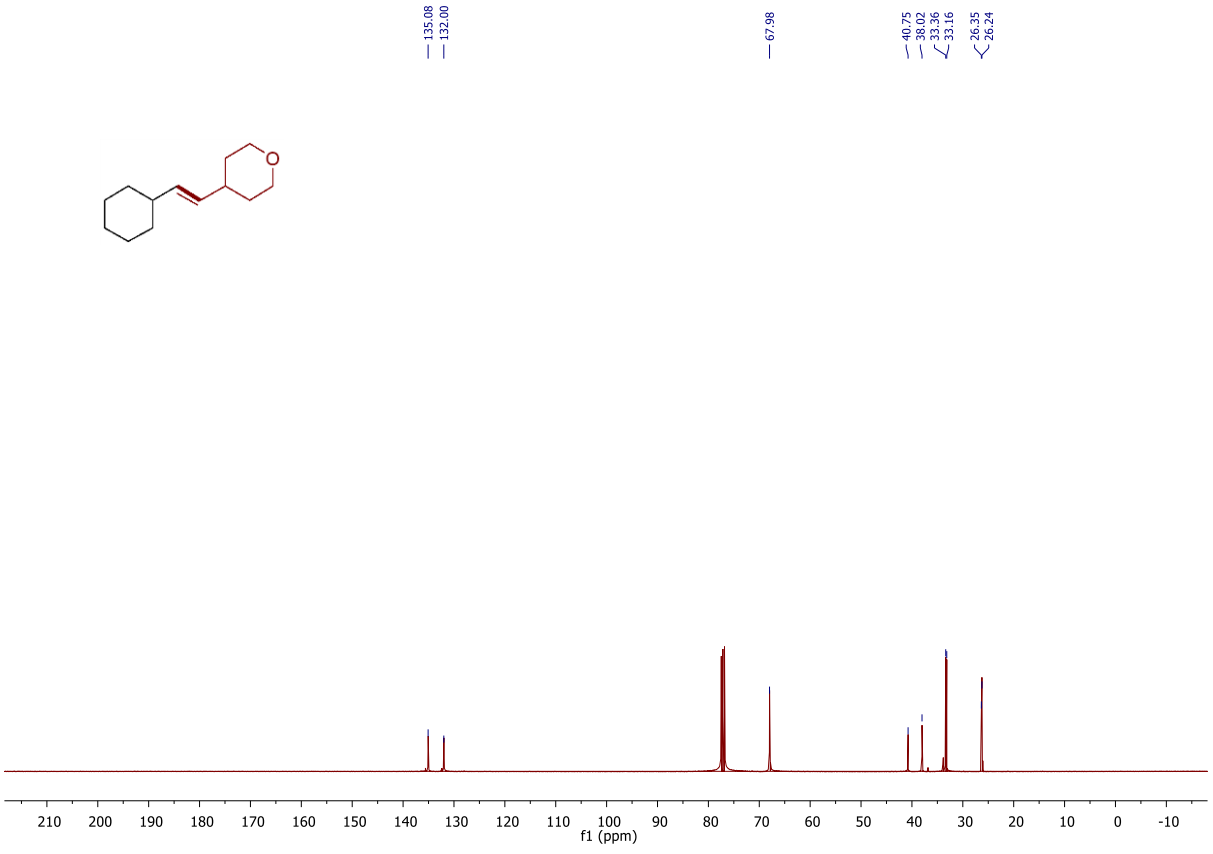

$^{13}$C-NMR spectrum of **S38**



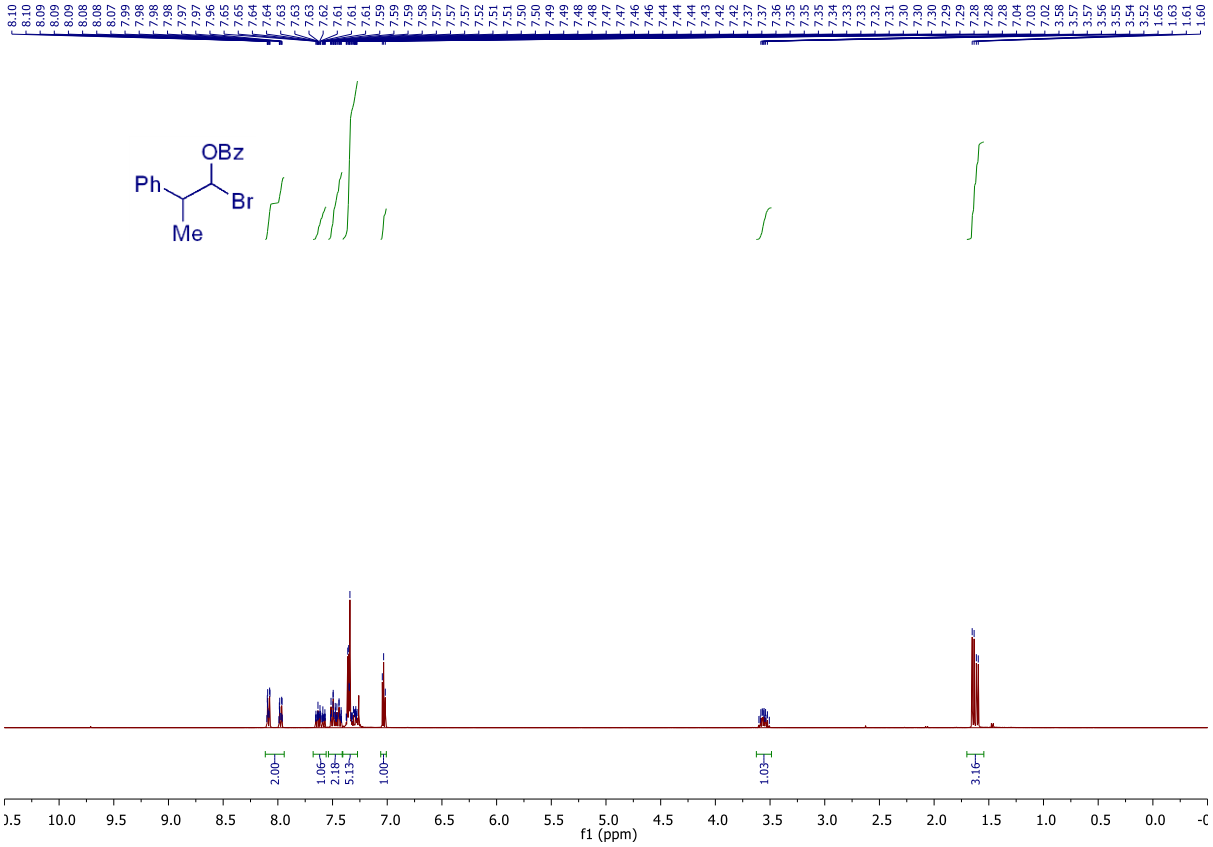
$^{1}$H-NMR spectrum of **38**



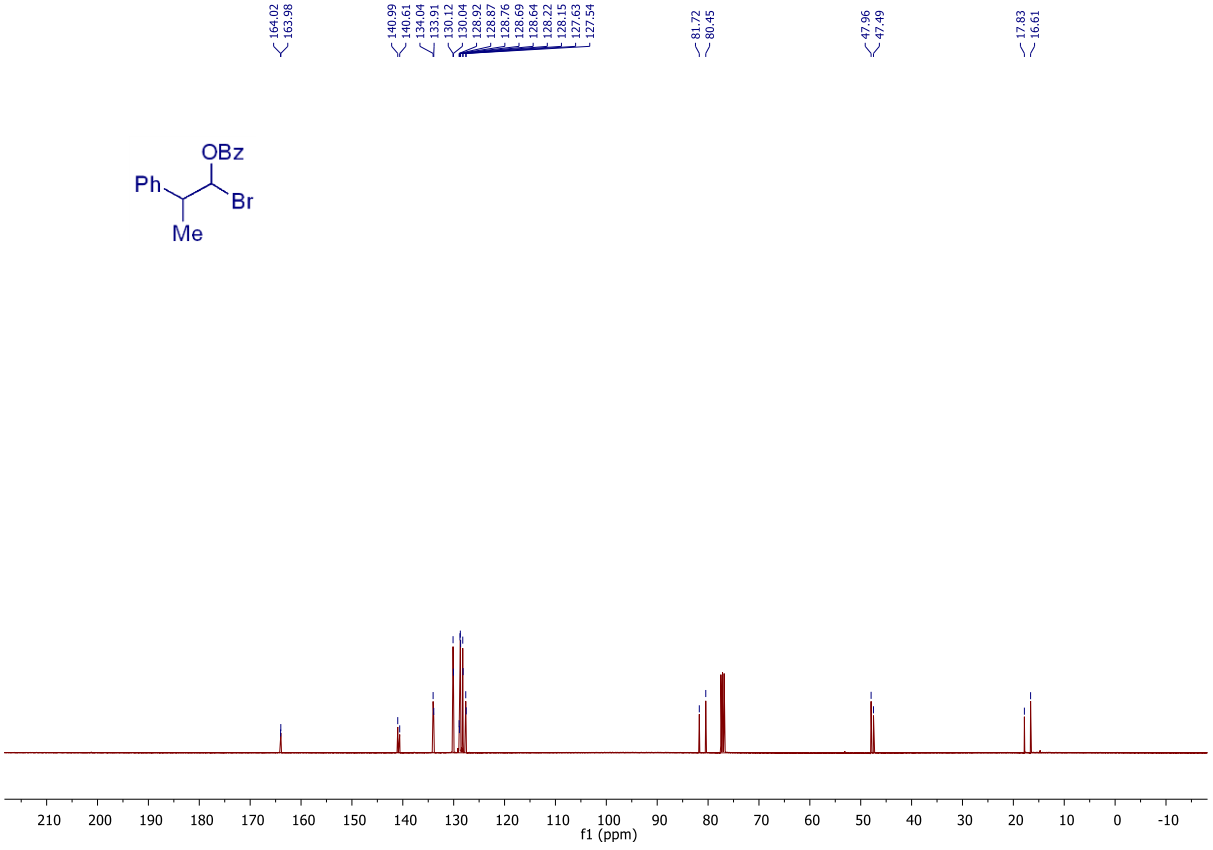

$^{13}$C-NMR spectrum of **38**



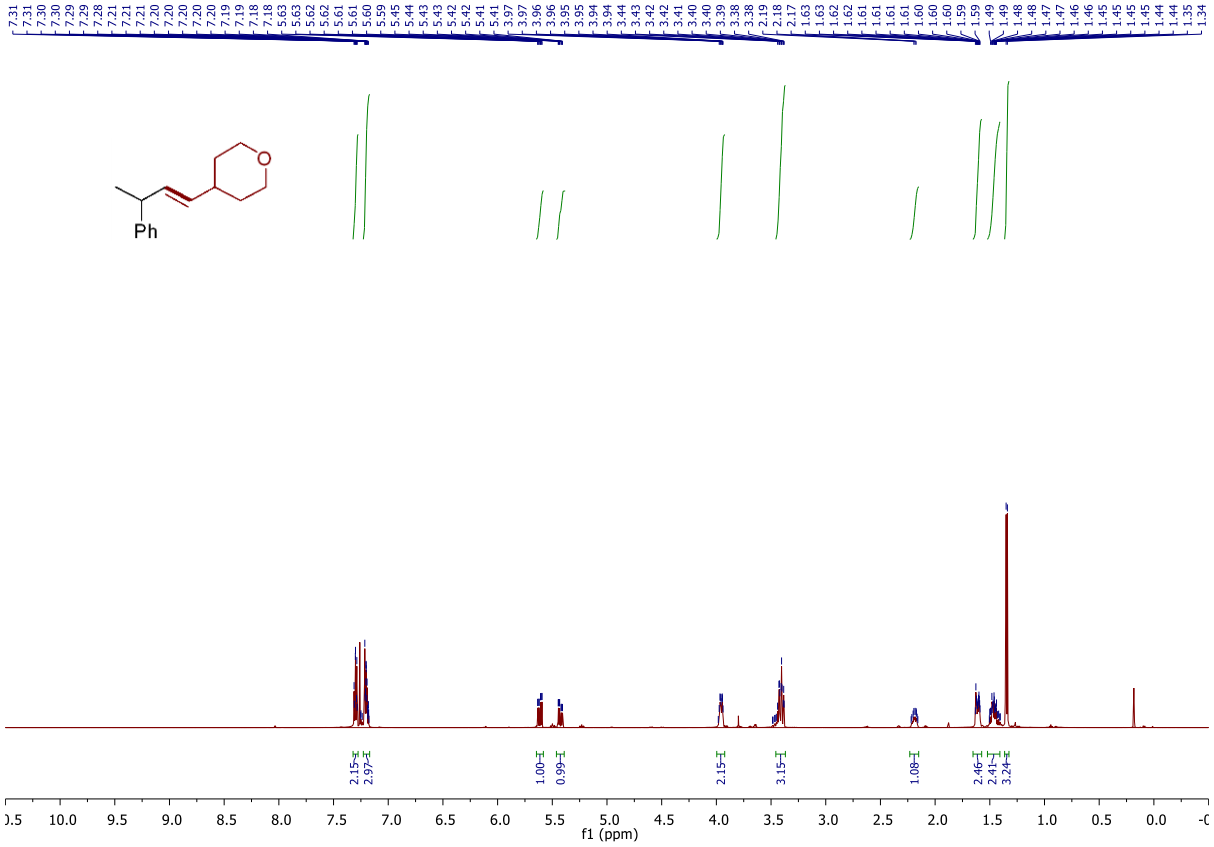
$^{1}$H-NMR spectrum of **S39**



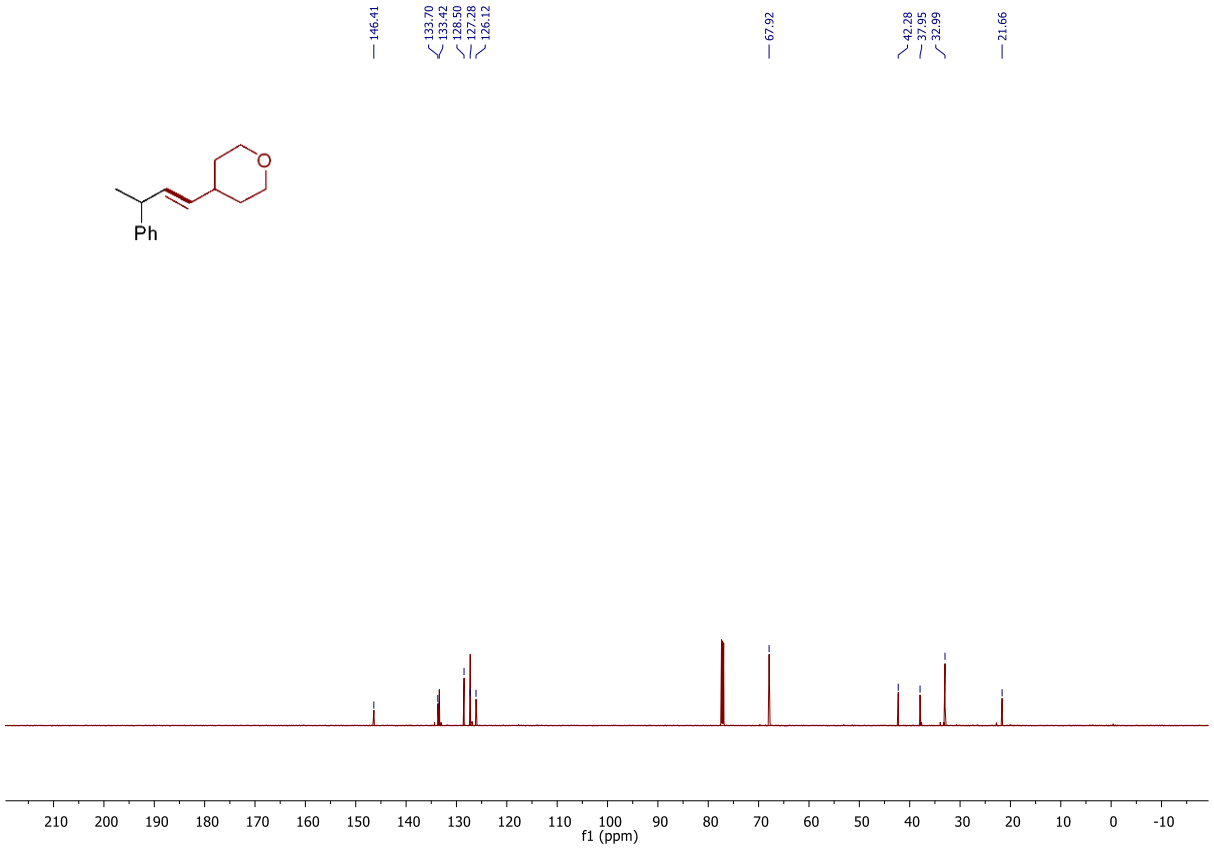

$^{13}$C-NMR spectrum of **S39**



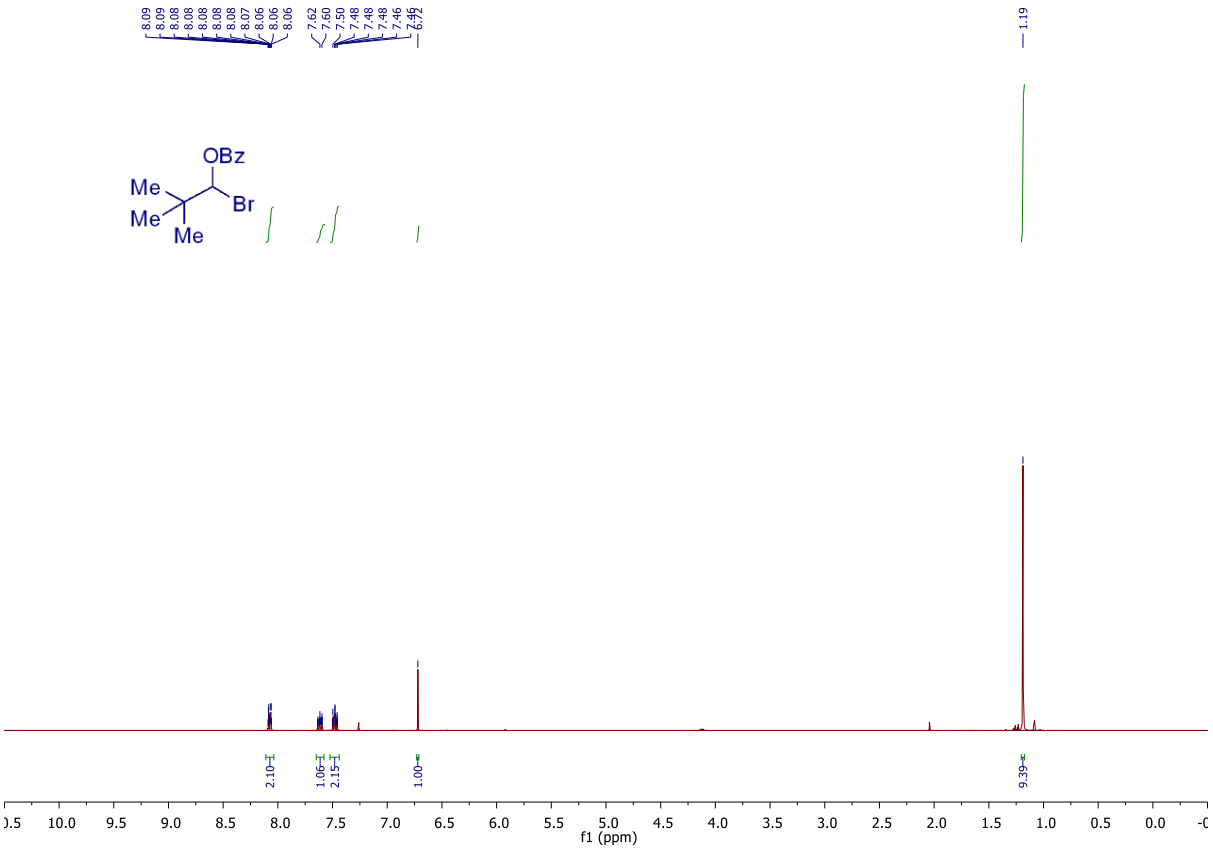
[1]H-NMR spectrum of **39**



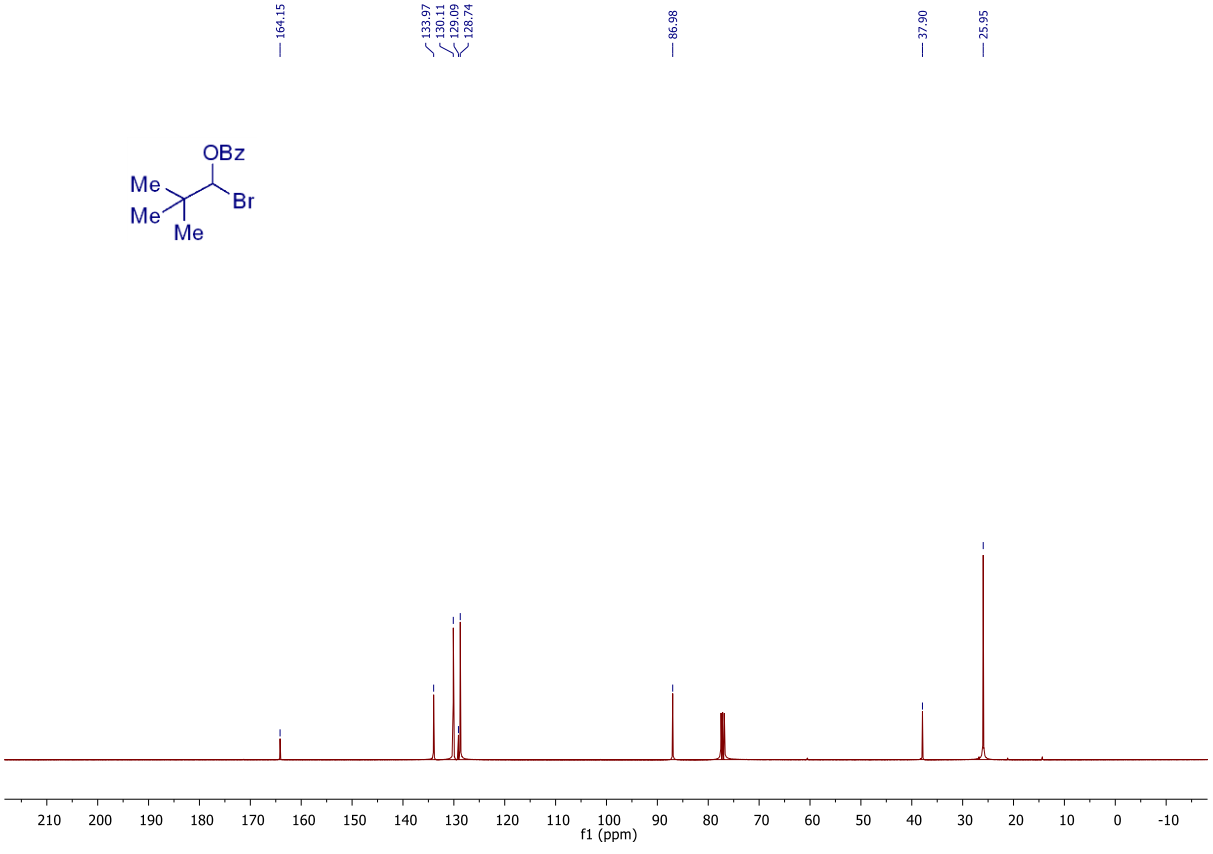

[13]C-NMR spectrum of **39**



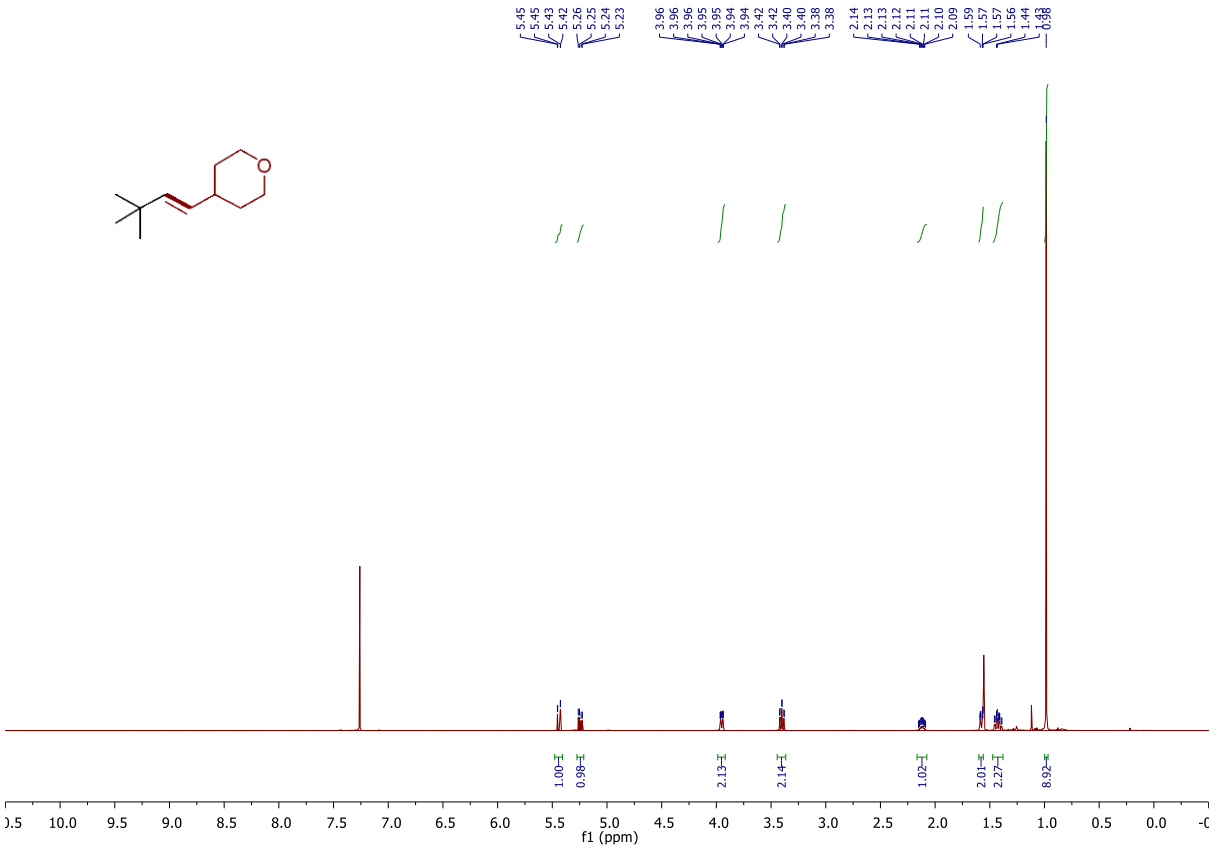
$^{1}$H-NMR spectrum of **S40**



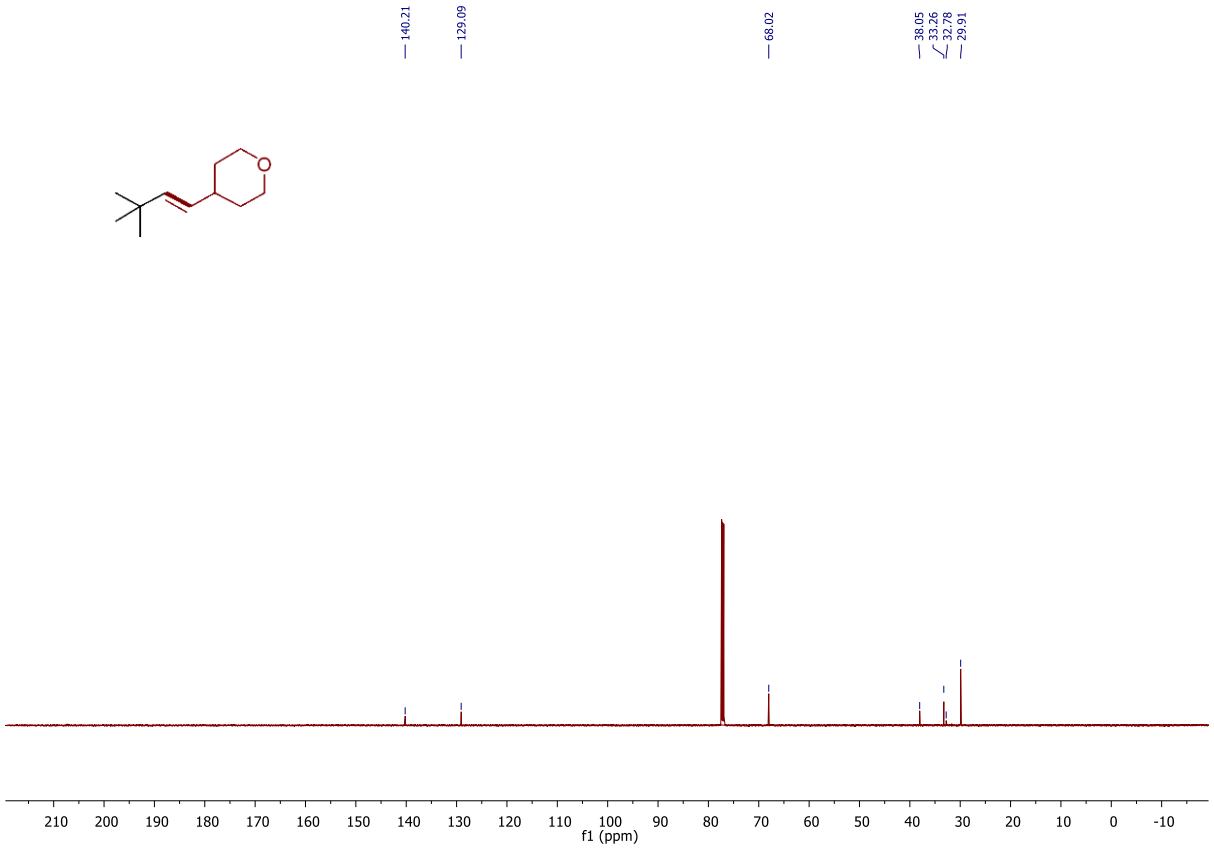

$^{13}$C-NMR spectrum of **S40**



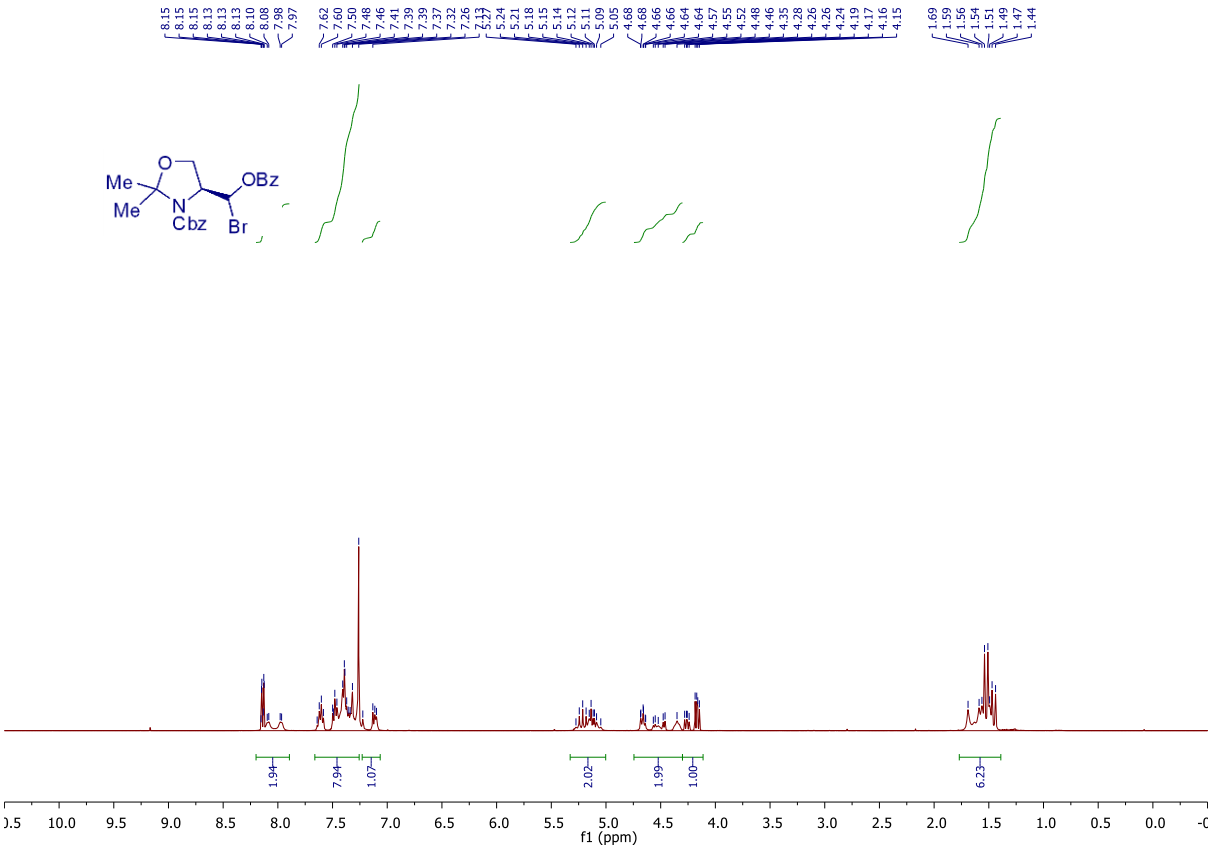
$^{1}$H-NMR spectrum of **40**



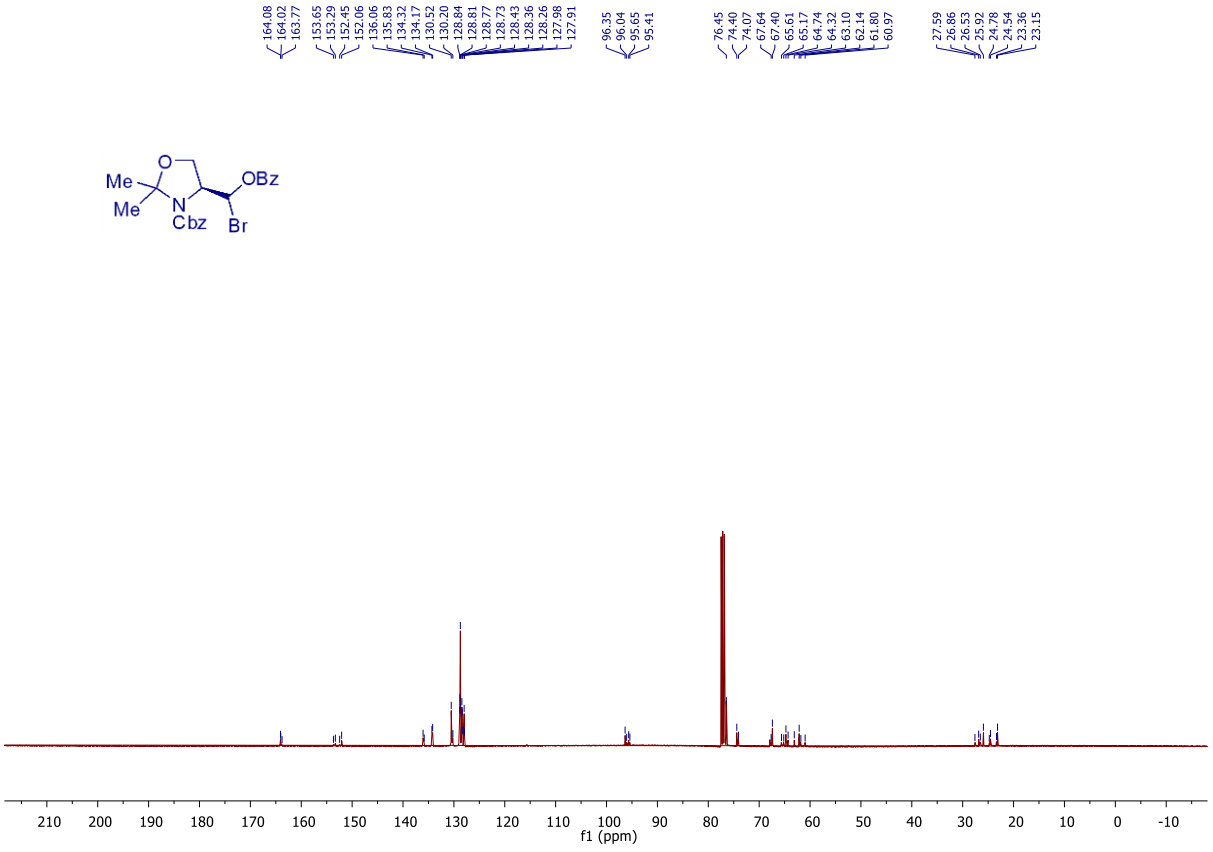

$^{13}$C-NMR spectrum of **40**



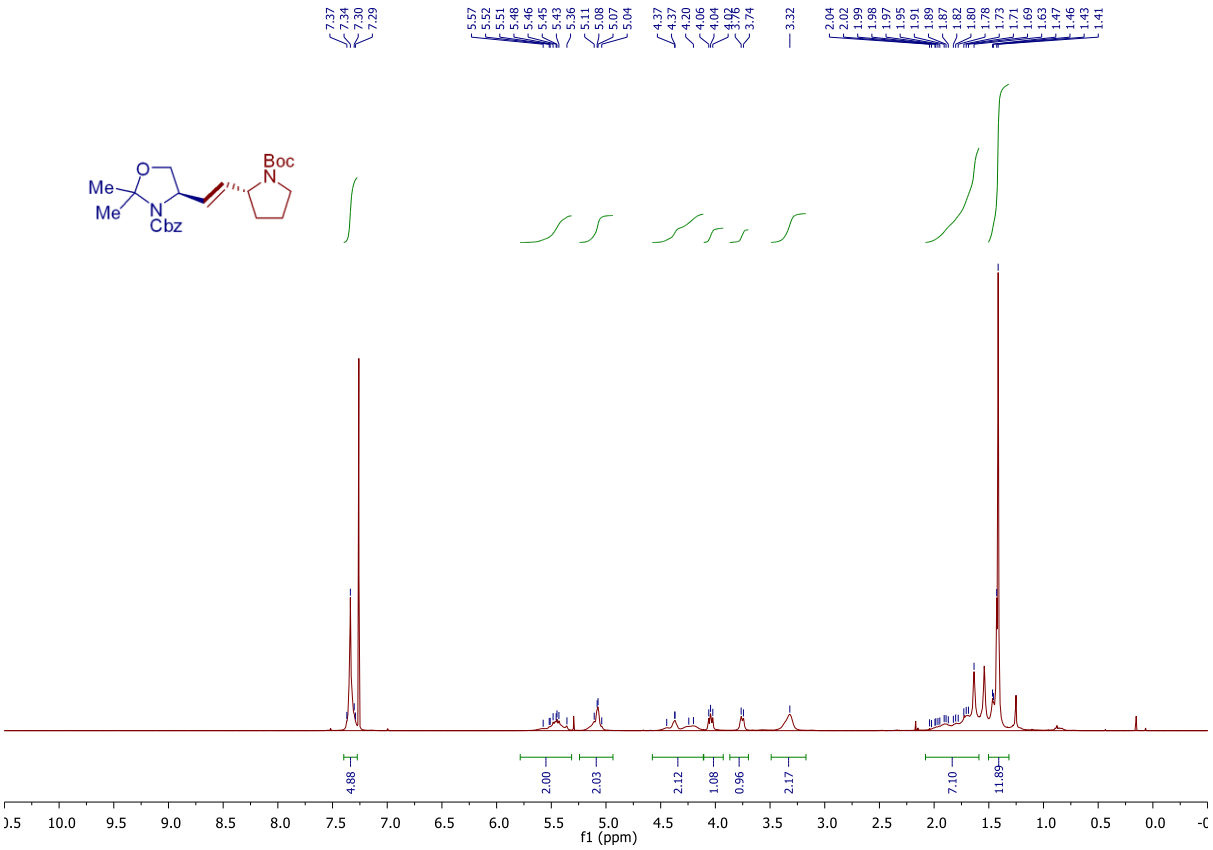
[1]H-NMR spectrum of **S41**



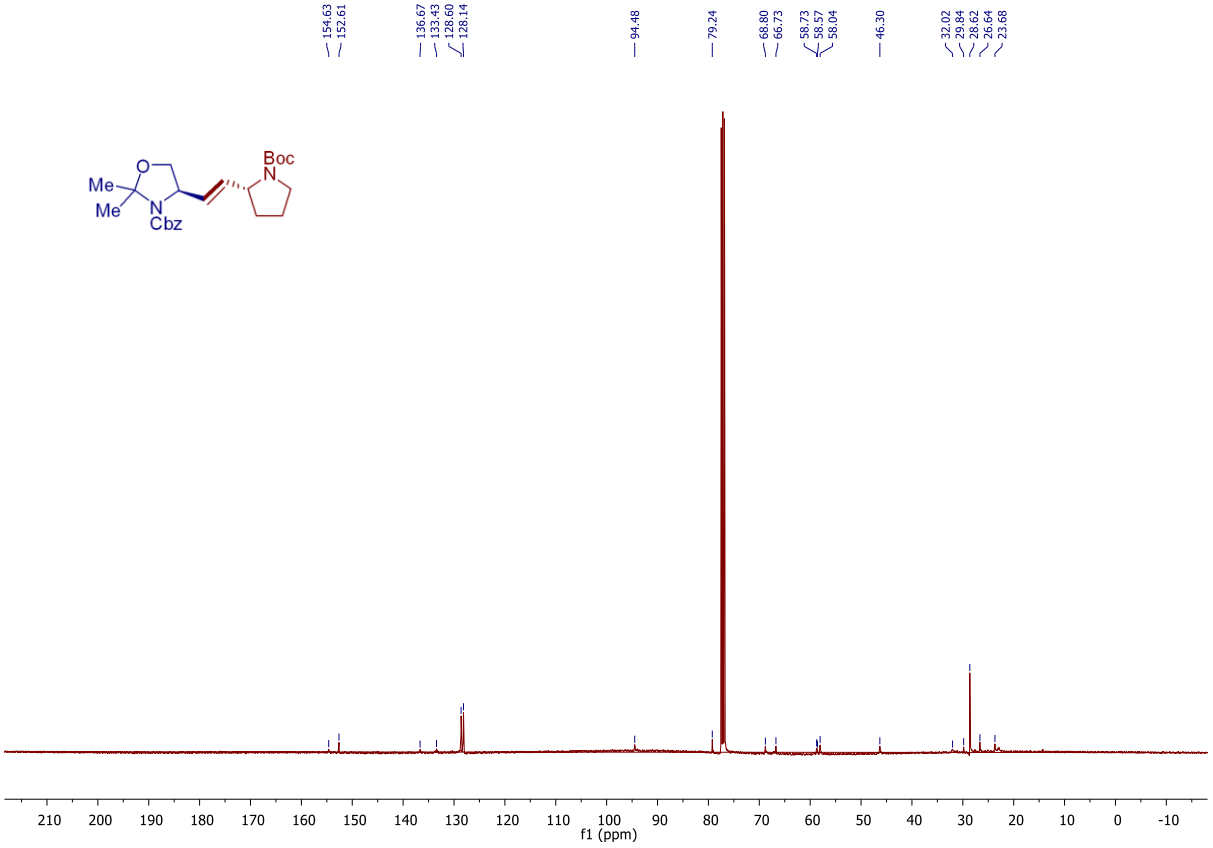

[13]C-NMR spectrum of **S41**



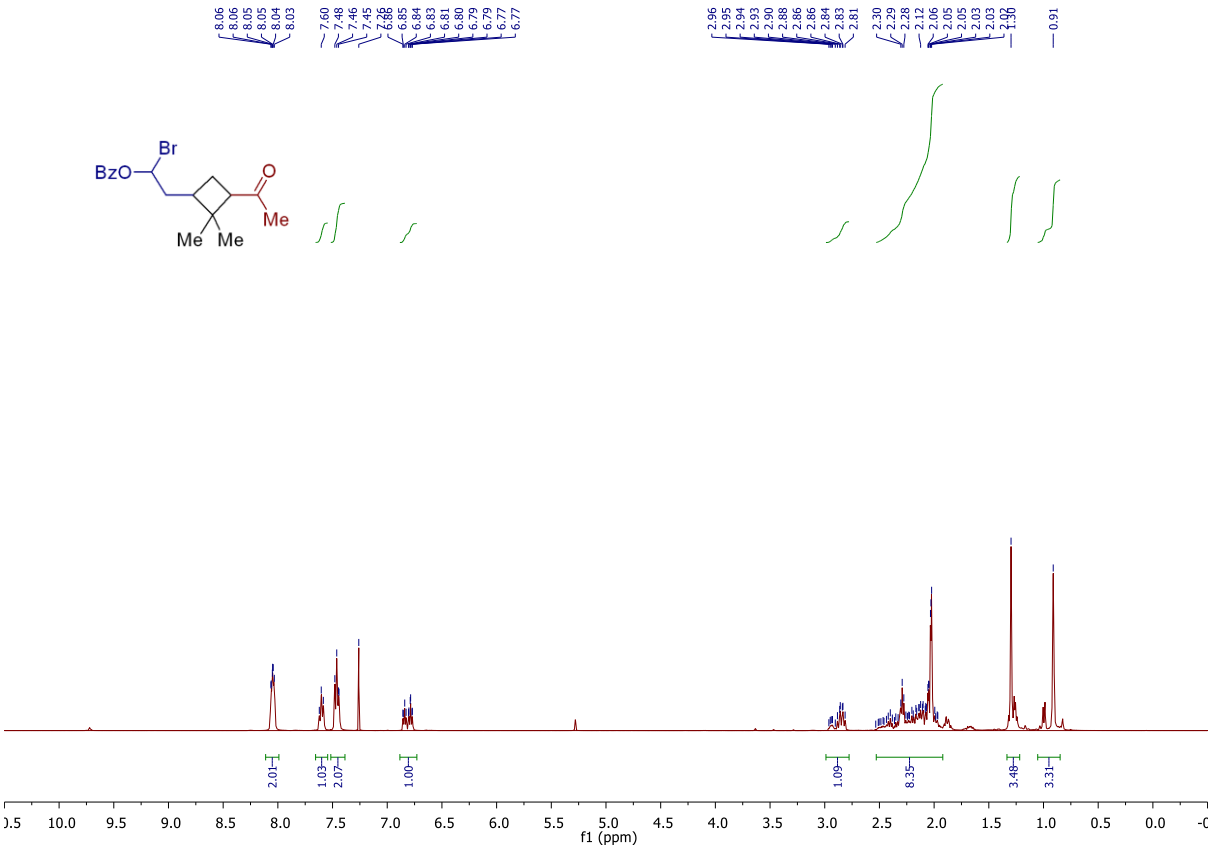
[1]H-NMR spectrum of **41**



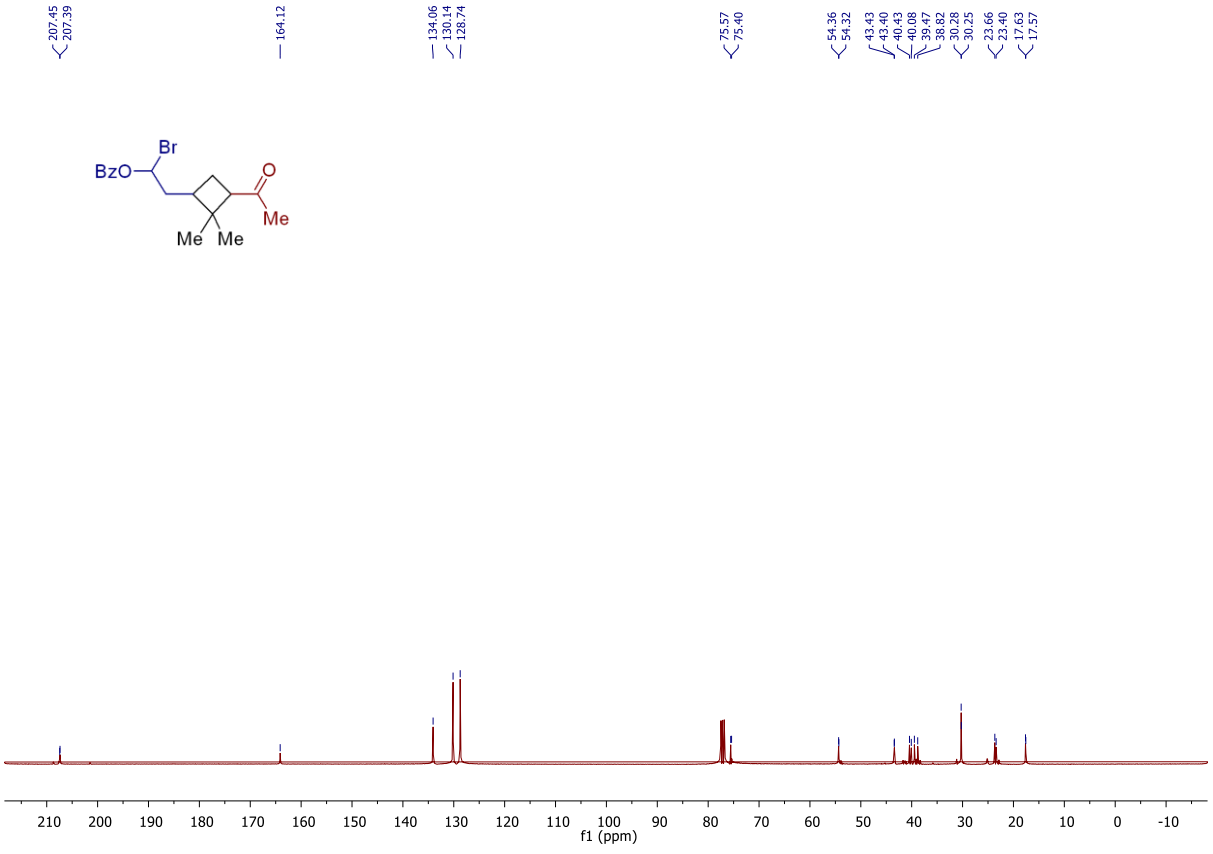

[13]C-NMR spectrum of **41**



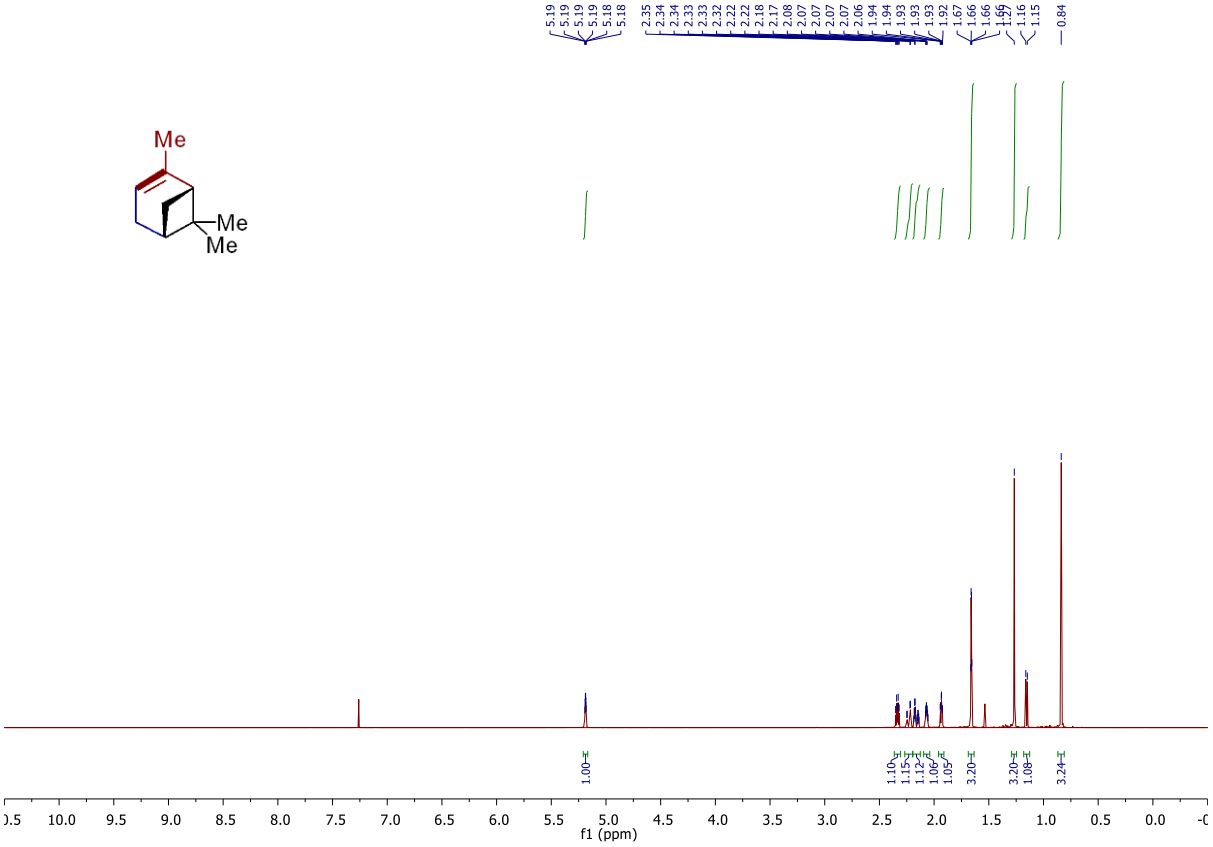
$^{1}$H-NMR spectrum of **S42**



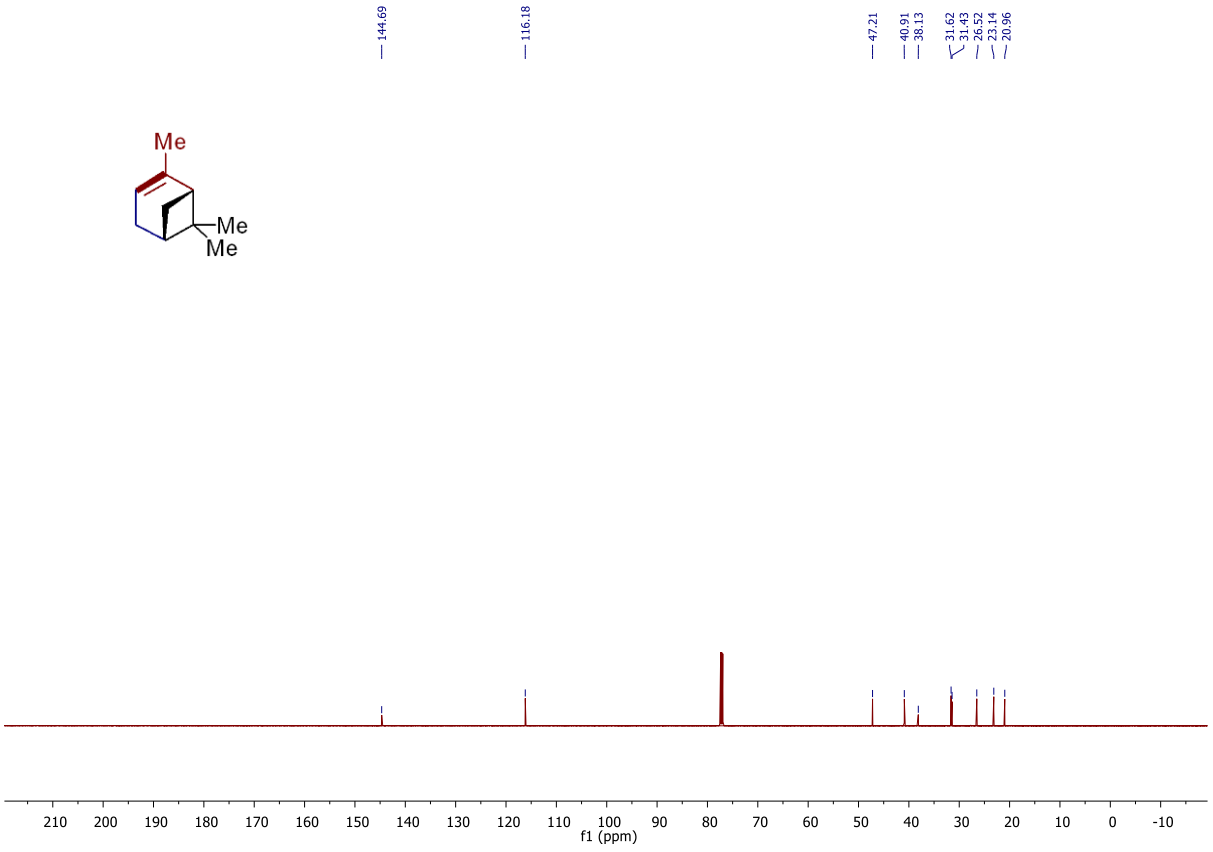

$^{13}$C-NMR spectrum of **S42**



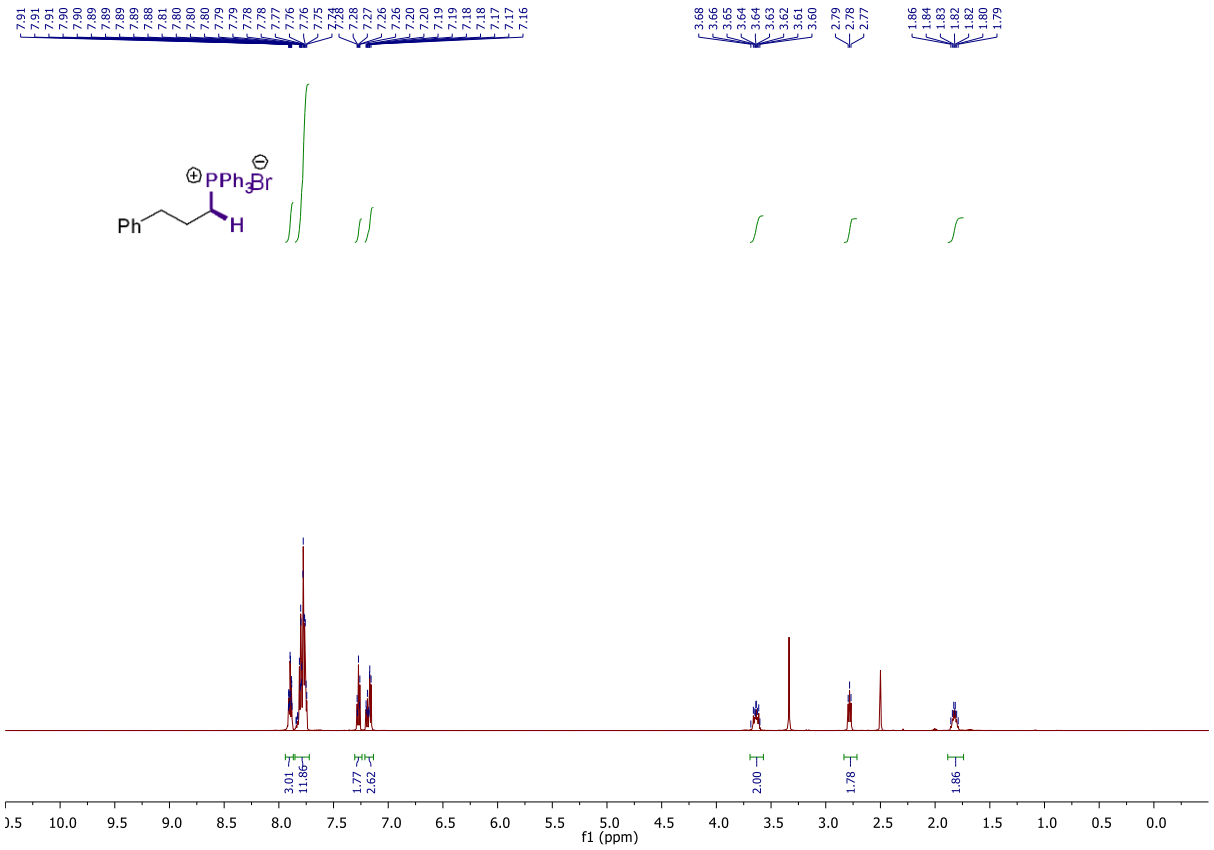
[1]H-NMR spectrum of **42**



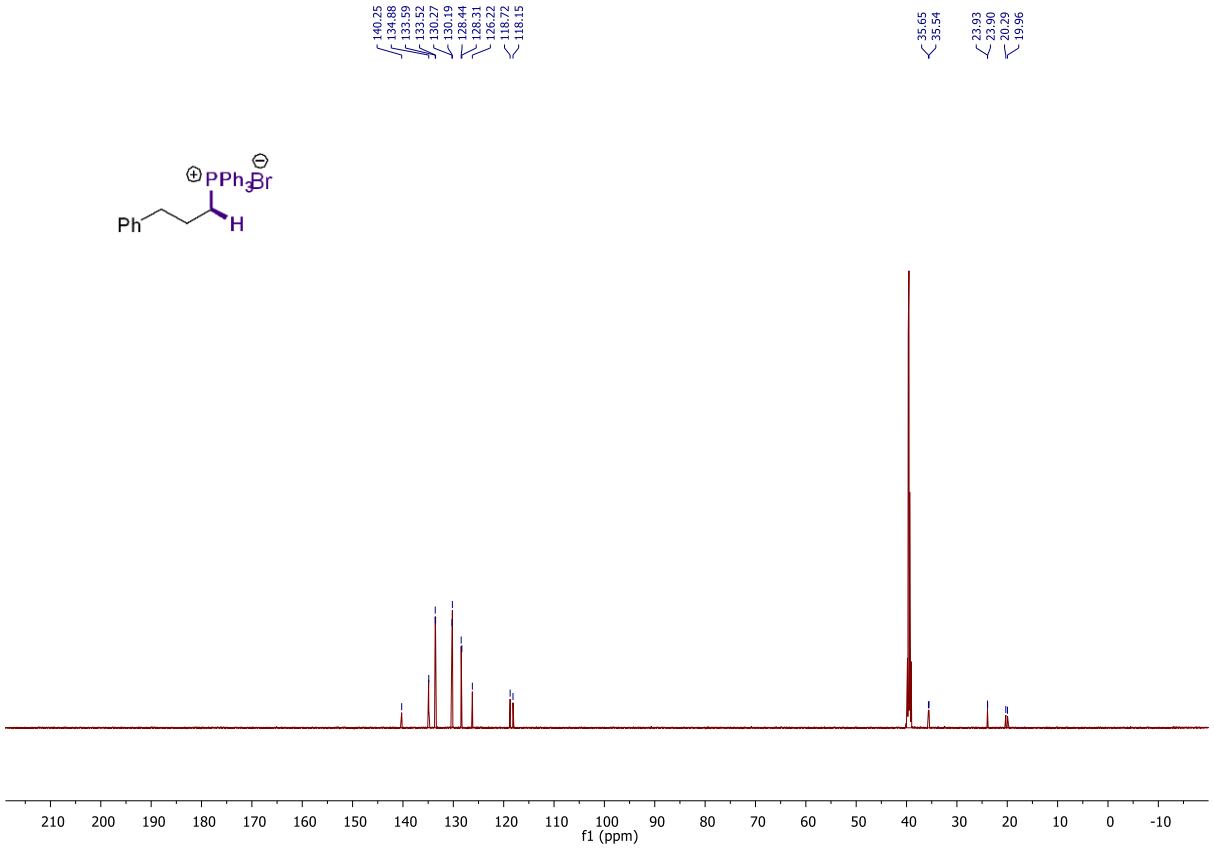

[13]C-NMR spectrum of **42**



[1]H-NMR spectrum of **46**




[13]C-NMR spectrum of **46**



$^{31}$P-NMR spectrum of **46**