Supporting Information

Heterogeneous Copper-Catalyzed Grignard Reactions with Allylic Substrates

Shobhan Mondal,[a] Luca Deiana,[b] Armando Córdova,*[b] Haibo Wu,*[a] and Jan-E. Bäckvall*[ab]

[a]Department of Organic Chemistry
Arrhenius Laboratory, Stockholm University
106 91 Stockholm (Sweden)
Email: haibo.wu@su.se; jan.e.backvall@su.se

[b]Department of Natural Sciences
Mid Sweden University, Holmgatan 10
85179 Sundsvall (Sweden)
Email: armando.cordova@miun.se

Table of Contents

1 General information

Unless otherwise stated, all air- and moisture-sensitive reactions were carried out under a nitrogen (N_2) atmosphere in oven-dried Schlenk tubes. Solvents were obtained as p. a. grade, dried using a VAC solvent purification system, and stored over molecular sieves (4 Å) when necessary. Diethyl ether dichloromethane and tetrahydrofuran (THF) were collected from a solvent purification system and stored over molecular sieves.

All reagents were prepared following literature procedures, and commercially available chemicals were purchased from Aldrich Chemical Co., Alfa Aesar, Fluorochem, TCI Europe, and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Merck). TLC plates were visualized by exposure to short-wave ultraviolet light (254 nm). Flash chromatography was performed on VWR silica gel using standard techniques. All NMR spectra were recorded on 400 or 500 MHz Bruker AVANCE II with a BBO probe at 298 K using $CDCl_3$ as solvent. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26; ^{13}C NMR: $CDCl_3$ δ 77.16). Chemical shifts are reported in ppm, and coupling constants (*J*) are given in Hertz (Hz), with signal multiplicities described as follows: s (singlet), br (broad signal), d (doublet), t (triplet), q (quartet), pent (pentet), and m (multiplet). High-resolution mass spectra (HRMS) were measured on a Bruker microTOF with electron spray ionization (ESI). Mass calibration was performed immediately before measuring the sample using sodium formate clusters. Optical rotations were recorded on a thermostated polarimeter using a sodium lamp (589 nm) and a 1.0 dm cell. Enantiomeric excesses were determined by gas chromatography (GC) using 30 m columns with helium as the carrier gas (1 mL/min, constant pressure), and detection by either MS or FID detector.

2 Preparation of nano-copper catalyst - MCC-AmP-Cu(I/II):

The primary catalyst was prepared following the literature procedure.[1]

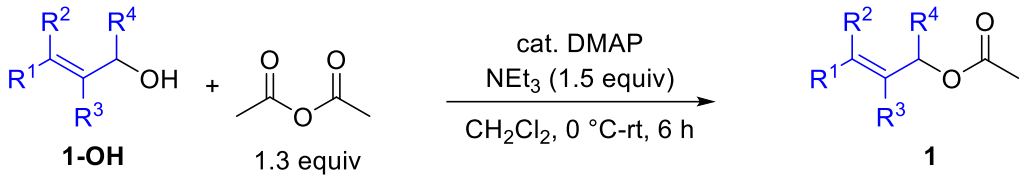
Preparation of amino-functionalized microcrystalline cellulose (AmP-MCC): In an 100 mL flask, MCC (1.0 g), tartaric acid (97.6 mg, 5 mol% to silane) was dispersed in dry toluene (20 mL). Next, 3-aminopropyltrimethoxysilane (2.27 mL, 13.0 mmol) was added and the mixture was stirred at 90 ℃ for 48 h. The suspension was then centrifuged and the crude AmP-MCC was washed using soxholated extraction with acetone. After 16 h, the resulting AmP-MCC was dried under vacuum for 24 h to afford off-white AmP-MCC (1.2 g).

Preparation of the mixed valence Cu(I/II) nanocatalyst Cu-AmP-MCC: To a suspension of AmP-MCC (1.0 g) in pH-adjusted H_2O solution (25 ml, pH 9) by the use of 0.1 N LiOH, was added a suspension of copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$, 0.3 g) in deionized water (20 mL, pH 9) at room temperature. After stirring for 24 h, the formed Cu(II)-AmP-MCC with pale-blue color was recovered by centrifugation and was washed with deionized H2O (3 × 30 mL) and acetone (3 × 30 mL) by using centrifuge. The washed Cu(II)-AmP-MCC was collected by decantation and dried overnight under vacuum.

In the next step, the dry Cu(II)-AmP-MCC was suspended in deionized water (35 mL), and $NaBH_4$ (190.0 mg, 5.0 mmol, 3.7 equiv to copper) in deionized water (15 mL) was added slowly at room temperature. After vigorous stirring for 1 h, the resulting mixed valence Cu(I/II) nanocatalyst Cu-AmP-MCC was recovered by centrifugation and was washed with deionized H2O (3×30 mL) and acetone (3×30 mL) by the use of a centrifuge. The washed Cu-AmP-MCC was collected by decantation, dried for 48 h under vacuum and obtained as dark blue amorphous powder (0.95 g). We assumed the copper content catalyst loading same as previously reported procedure.

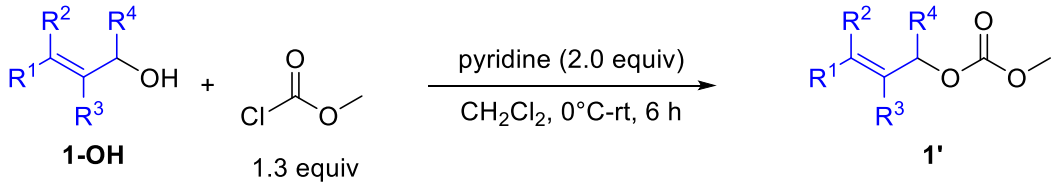
3 Synthesis of starting materials

All the allylic alcohol derivatives were made according to the literature procedure as listed below.



Scheme S1: Synthesis of allylic acetate derivatives

A. Synthesis of allylic acetate derivatives: To a solution of allyl alcohol (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 M) was added 4-dimethylaminopyridine (DMAP) (10 mol%, 0.1 equiv) and triethylamine (NEt_3) (7.5 mmol, 1.5 equiv) (Scheme S1). Then acetic anhydride (Ac_2O) (6.8 mmol, 1.3 equiv) was added dropwise at 0 C. The progress was monitored using TLC and after completion the reaction mixture was quenched with NH_4Cl solution, organic layer was collected, dried over Na_2SO_4, purified via column chromatography using (5-10)% Et_2O in petroleum ether).

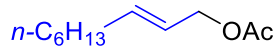
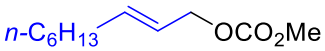
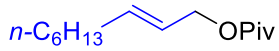
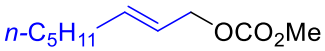
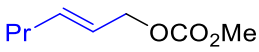
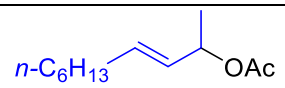
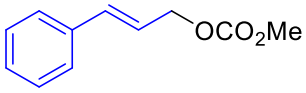
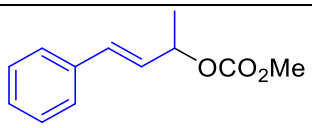
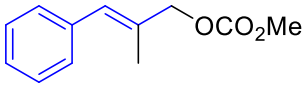
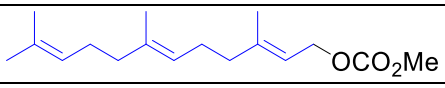
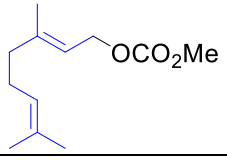
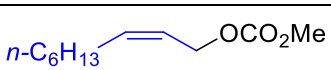
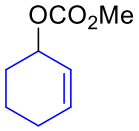
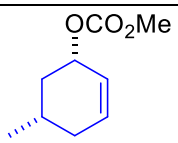
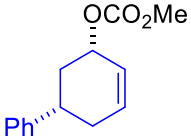


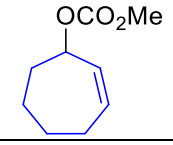
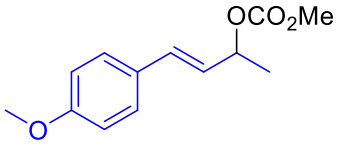
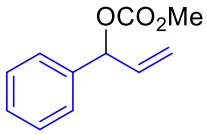
Scheme S2: Synthesis of allylic carbonate derivatives

B. Synthesis of allylic carbonate derivatives: To a solution of allyl alcohol (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 M) was added pyridine (10 mmol, 2.0 equiv) (Scheme S2). Then methyl chloroformate ($ClCO_2Me$) (6.8 mmol, 1.3 equiv) was added dropwise at 0 C. The progress was monitored using TLC and after completion the reaction mixture was quenched with NH_4Cl solution, organic layer was collected, dried over Na_2SO_4, purified via column chromatography using (5-10)% Et_2O in petroleum ether) as eluent. For compounds **1p** and **1q**, additionally 3% NEt_3 was added to the eluent system

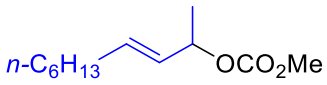
The spectral data of allylic substrates were matched with the previously reported literature as tabulated below.

Table S1: Literature data of allylic substrates 1

Allylic alcohol substrates	Number	Literature background
	**1a**	reference[2]
	**1a'**	reference[3]
	**1a''**	reference[4]
	**1b**	reference[5]
	**1c**	reference[6]
	**1d'**	reference[7]
	**1e**	reference[6]
	**1f**	reference[8]
	**1g**	reference[8]
	**1h**	reference[6]
	**1j**	reference[6]
	**1k**	reference[9]
	**1l**	reference[10]
	**1m**	reference[11]
	**1n**	reference[12]

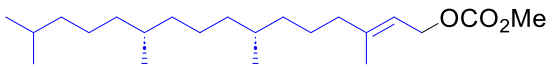
	**1o**	reference[13]
	**1p**	reference[14]
	**1a***	reference[6]

(*E*)-Dec-3-en-2-yl methyl carbonate (1d'):



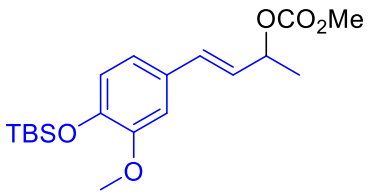
This compound was prepared using procedure 3B. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.80 – 5.69 (m, 1H), 5.46 (ddt, *J* = 15.4, 7.1, 1.5 Hz, 1H), 5.15 (p, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 2.01 (td, *J* = 7.3, 5.8 Hz, 2H), 1.41 – 1.32 (m, 5H), 1.31 – 1.23 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 155.3, 134.6, 128.9, 75.5, 54.6, 32.2, 31.5, 28.7, 22.6, 20.6, 14.2.

Methyl ((7R,11R,*E*)-3,7,11,15-tetramethylhexadec-2-en-1-yl) carbonate (1i):



This compound was prepared using procedure 3B. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.39 (tp, *J* = 7.1, 1.4 Hz, 1H), 4.68 (d, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.06 – 2.00 (m, 2H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.57 – 1.50 (m, 1H), 1.49 – 1.02 (m, 19H), 0.92 – 0.84 (m, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.0, 143.9, 117.6, 64.9, 54.8, 40.0, 39.5, 37.6, 37.5, 37.4, 36.8, 32.9, 32.8, 28.1, 25.1, 24.9, 24.6, 22.9, 22.8, 19.9, 19.8, 16.6.

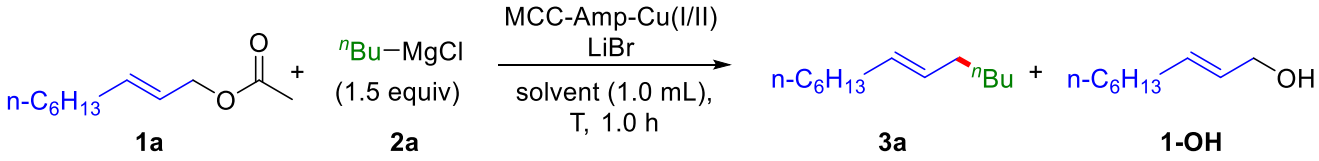
(*E*)-4-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)but-3-en-2-yl methyl carbonate (1q):



This compound was prepared using procedure 3B. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.90 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.58 (dd, *J* = 15.9, 1.0 Hz, 1H), 6.05 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.40 – 5.30 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 1.46 (d, *J* = 6.5 Hz, 3H), 0.99 (s, 9H), 0.15 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3, 151.2, 145.5, 132.6, 130.2, 126.2, 121.1, 120.1, 110.1, 75.7, 55.6, 54.7, 25.9, 20.7, 18.6, -4.5.

4 Optimization studies

The reaction conditions were optimized using €-2-nonenyl acetate **1a** and *n*-butyl magnesium chloride **2a** (Scheme S3). The reactions were conducted in oven-dried schlenk tubes under a N_2 atmosphere. After completion, the reaction mixture was quenched with drops of water and volatilities were removed under reduced pressure. Crude ^{1}H-NMR was measured using 1,3,5-trimethoxybenzene (TMB) as an internal standard.



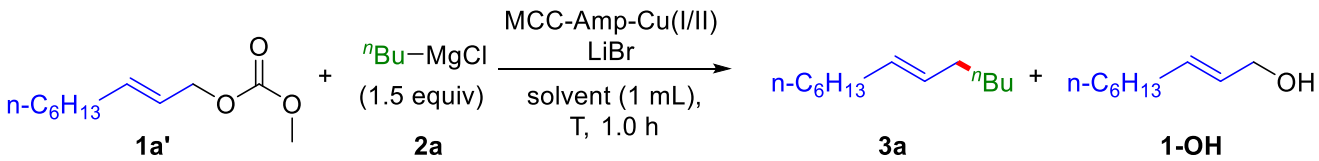
Scheme S3: Optimization of reaction conditions with nonenyl acetate 1a.

Table S2: Initial screening with nonenyl acetate 1a [a]:

entry	catalyst	additive (equiv)	solvent	T	yield of 3a (%)[b]	unreacted 1a (%)[b]	yield of 1-OH (%)[b]
1	**5 mol%**	**LiBr (2.0)**	**THF**	**rt**	**86**	-	**10**
2	5 mol%	-	THF	rt	16	42	40
3	-	LiBr (2.0)	THF	rt	-	22	74
4	5 mol%	LiBr (2.0)	THF	0 °C	81	-	16
5	5 mol%	LiCl (2.0)	THF	rt	70	-	21
6	5 mol%	LiBr (2.0)	Et_2O	rt	85		8

[a] Reaction conditions: **1a** (0.2 mmol, **2a** (0.3 mmol), THF (1.0 mL) were used under N_2 atmosphere. [b] Yields were determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene (TMB) as internal standard.

The next reactions were performed using €-2-nonenyl carbonate (**1a'**) and n-butylmagnesium chloride (**2a**).



Scheme S4: Optimization of reaction conditions with nonenyl carbonate 1a'.

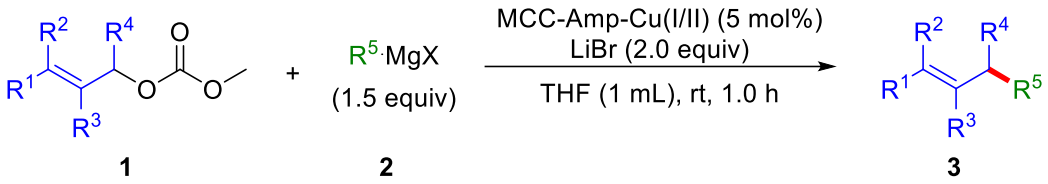
Table S3: Initial screening with nonenyl carbonate 1a' [a]:

Entry	catalyst	additive (equiv)	solvent	T	yield of 3a (%)[b]	unreacted 1a' (%)[b]	yield of 1-OH (%)[b]
1	**5 mol%**	**LiBr (2.0)**	**THF**	**rt**	**98**	**-**	**2**
2	5 mol%	-	THF	rt	54	35	8
3	-	LiBr (2.0)	THF	rt	-	65	35
4	5 mol%	LiBr (2.0)	THF	0 °C	95	-	3
5	5 mol%	LiCl (2.0)	THF	rt	89	7	3
6	5 mol%	LiBr (2.0)	Et_2O	rt	95		2
7	1 mol%	LiBr (2.0)	THF	rt	39	34	13
8	2.5 mol%	LiBr (2.0)	THF	rt	75	15	10
9[c]	5 mol%	LiBr (2.0)	THF	rt	95	-	-

[a] Reaction conditions: **1a'** (0.2 mmol), **2a** (0.3 mmol), THF (1.0 mL) were used under N_2 atmosphere. [b] Yields were determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene (TMB) as internal standard, c) OPiv (**1a''**) was used as leaving group instead of OCO_2Me.

5 General procedure for heterogeneous copper-catalyzed allylic-substitution

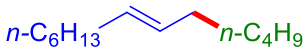
An oven-dried Schlenk tube was charged with LiBr (2.0 equiv) under a N_2 atmosphere and it was then dried under vacuum using a heat blower, followed by the addition of heterogeneous Cu-catalyst (8.0 mg, 0.01 mmol, 0.05 equiv Cu) under N_2 atmosphere. After that, the catalyst and additive mixture were dried again under vacuum at room temperature, followed by the addition of 1.0 mL of THF under N_2 atmosphere. Next, the allylic alcohol derivative **1** (1.0 equiv) was added, and finally, the Grignard reagent (1.5-2.0 equiv) was added dropwise at room temperature under N_2 atmosphere. Then the reaction mixture was stirred for 1 h or left overnight. Afterward, the reaction mixture was quenched with a few drops of water, volatiles were removed under reduced pressure, and the desired compound was isolated via flash chromatography (*n*-pentane and *n*-pentane/ diethyl ether gradient).



Scheme S5: General procedure for the synthesis of allylic substituted derivatives.

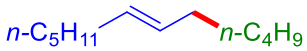
3.1 Synthetic details and characterization data

(*E*)-Tridec-6-ene (3a):[15]



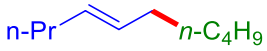
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3a** was isolated via column chromatography (pentane) as colorless oil (32.2 mg, 0.176 mmol, 88%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.39 (ddd, *J* = 5.3, 3.7, 1.6 Hz, 2H), 2.01 – 1.93 (m, 4H), 1.39 – 1.22 (m, 14H), 0.88 (td, *J* = 7.0, 0.9 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.5, 32.8, 32.7, 31.9, 31.6, 29.8, 29.5, 29.0, 22.8, 22.7, 14.3, 14.2. (olefinic carbon signals are overlapped).

(*E*)-Dodec-6-ene (3b):[16]



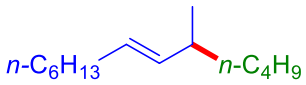
Following the general procedure, (*E*)-methyl oct-2-en-1-yl carbonate **1b** (37.3 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3b** was isolated via column chromatography (pentane) as colorless oil (30.2 mg, 0.182 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.45 – 5.33 (m, 2H), 1.97 (tdd, *J* = 7.4, 3.6, 1.4 Hz, 4H), 1.40 – 1.23 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 6H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.5, 32.7, 31.6, 29.5, 22.7, 14.2;

(*E*)-Dec-4-ene (3c):



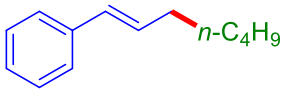
Following the general procedure, (*E*)-hex-2-en-1-yl methyl carbonate **1c** (31.7 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3c** was isolated via column chromatography (pentane) as colorless oil (26.7 mg, 0.19 mmol, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.45 – 5.33 (m, 2H), 2.00 – 1.92 (m, 4H), 1.37 – 1.23 (m, 8H), 0.91 – 0.86 (m, 6H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.8, 130.2, 34.9, 32.7, 31.6, 29.5, 22.9, 22.7, 14.2, 13.8.

(*E*)-5-Methyltridec-6-ene (3d):



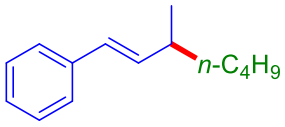
Following the general procedure, (*E*)-dec-3-en-2-yl methyl carbonate **1d'** (42.7 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3d** was isolated via column chromatography (pentane) as colorless oil (31.8 mg, 0.16 mmol, 81%) 10:1 (α:γ) selectivity; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.38 – 5.29 (m, 1H), 5.24 (ddt, *J* = 15.3, 7.5, 1.1 Hz, 1H), 2.03 (t, *J* = 6.6 Hz, 1H), 2.00 – 1.93 (m, 2H), 1.38 – 1.21 (m, 14H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.88 (td, *J* = 7.0, 2.2 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.6, 128.6, 37.1, 36.8, 32.7, 31.5, 29.8, 29.5, 23.0, 22.7, 21.1, 14.3, 14.2 (two carbon signals are overlapped).

(*E*)-Hept-1-en-1-ylbenzene (3e):[17]



Following the general procedure, cinnamyl methyl carbonate **1e** (38.5 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3e** was isolated via column chromatography (pentane) as colorless oil (33.1 mg, 0.19 mmol, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 1H), 6.38 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.25 – 2.17 (m, 2H), 1.52 – 1.43 (m, 2H), 1.39 – 1.28 (m, 4H), 0.95 – 0.88 (m, 3H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.1, 131.4, 129.8, 128.6, 126.9, 126.0, 33.2, 31.6, 29.2, 22.7, 14.2.

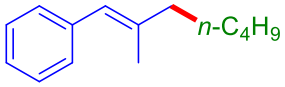
(*E*)-(3-Methylhept-1-en-1-yl)benzene (3f):[18]



Following the general procedure, (*E*)-methyl (4-phenylbut-3-en-2-yl) carbonate **1f** (41.2 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in

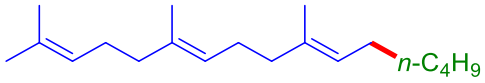
THF) were reacted in THF (1.0 mL) for 1 h. Product **3f** was isolated via column chromatography (pentane) as colorless oil (35.7 mg, 0.19 mmol, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.21 – 7.16 (m, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.9, 8.0 Hz, 1H), 2.34 – 2.22 (m, 1H), 1.42 – 1.24 (m, 6H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.92 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.1, 137.3, 128.6, 128.0, 126.9, 126.1, 37.4, 37.0, 29.8, 23.0, 20.8, 14.3.

(*E*)-(2-methylhept-1-en-1-yl)benzene (3g):[19]



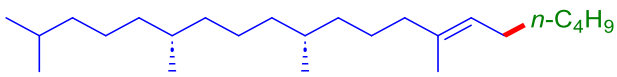
Following the general procedure, (*E*)-methyl (2-methyl-3-phenylallyl) carbonate **1g** (41.2 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 15 h. Product **3g** was isolated via column chromatography (pentane) as colorless oil (35.5 mg, 0.188 mmol, 94%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.18 (td, *J* = 6.9, 3.1 Hz, 1H), 6.27 (s, 1H), 2.17 (t, *J* = 7.6 Hz, 2H), 1.86 (s, 3H), 1.57 – 1.48 (m, 2H), 1.40 – 1.29 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.6, 138.9, 129.0, 128.1, 125.9, 124.8, 40.9, 31.7, 27.8, 22.8, 17.9, 14.3;

(6*E*,10*E*)-2,6,10-Trimethylhexadeca-2,6,10-triene (3h):[20]



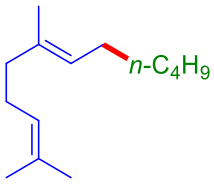
Following the general procedure, methyl ((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl) carbonate **1h** (56.1 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 15 h. Product **3h** was isolated via column chromatography (pentane) as colorless oil (48.6 mg, 0.18 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.16 – 5.06 (m, 3H), 2.12 – 2.02 (m, 4H), 2.02 – 1.93 (m, 6H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.60 (q, *J* = 1.2 Hz, 9H), 1.37 – 1.22 (m, 6H), 0.92 – 0.86 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.0, 134.9, 131.4, 125.0, 124.6, 124.4, 39.9, 39.9, 31.7, 29.7, 28.1, 26.9, 26.8, 25.8, 22.8, 17.8, 16.2, 16.1, 14.3.

(11*R*,15*R*,*E*)-7,11,15,19-tetramethylicos-6-ene (3i):



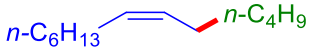
Following the general procedure, methyl ((7*R*,11*R*,*E*)-3,7,11,15-tetramethylhexadec-2-en-1-yl) carbonate **1i** (70.9 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 15 h. Product **3i** was isolated via column chromatography (pentane) as colorless oil (54.5 mg, 0.16 mmol, 81%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.15 (t, *J* = 7.2 Hz, 1H), 1.99 (p, *J* = 7.4 Hz, 4H), 1.61 (s, 3H), 1.59 – 1.50 (m, 2H), 1.46 – 1.24 (m, 17H), 1.22 – 1.05 (m, 6H), 0.96 – 0.85 (m, 15H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.3, 124.8, 40.2, 39.6, 37.6, 37.6, 37.5, 36.8, 33.0, 32.9, 31.8, 29.8, 28.2, 28.1, 25.6, 25.0, 24.7, 22.9, 22.8, 22.8, 19.9, 19.9, 16.0, 14.3; **GC MS (EI)**: 336.5 [M+], (6), 140.2 (6), 127.3 (11), 125.3 (18), 111.2 (85), 98.1 (26), 97.1 (34), 85.1 (28), 70.1 (61), 69.1 (100).

(*E*)-2,6-dimethyldodeca-2,6-diene (3j):[21]



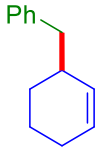
Following the general procedure, (*E*)-3,7-dimethylocta-2,6-dien-1-yl methyl carbonate **1j** (42.5 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 15 h. Product **3j** was isolated via column chromatography (pentane) as colorless oil (35.7 mg, 0.18 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.18 – 5.05 (m, 2H), 2.12 – 2.03 (m, 2H), 2.02 – 1.93 (m, 4H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.60 (dd, *J* = 4.5, 1.3 Hz, 6H), 1.38 – 1.22 (m, 6H), 0.92 – 0.86 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 131.4, 125.0, 124.6, 39.9, 31.7, 29.7, 28.0, 26.9, 25.8, 22.8, 17.8, 16.1, 14.3.

(*Z*)-Tridec-6-ene (3g) (3k):[15]



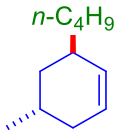
Following the general procedure, (*Z*)-methyl non-2-en-1-yl carbonate **1k** (41.2 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 15 h. Product **3k** was isolated via column chromatography (pentane) as colorless oil (25.1 mg, 0.138 mmol, 69%, 8:1 mixture of α:γ isomer); **^{1}H NMR (400 MHz, $CDCl_3$, for α -isomer)** δ 5.35 (ddd, *J* = 5.6, 4.4, 1.2 Hz, 2H), 2.07 – 1.97 (m, 4H), 1.40 – 1.20 (m, 14H), 0.88 (tt, *J* = 6.9, 2.3 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$, for α -isomer)** δ 130.1, 31.9, 31.7, 29.9, 29.6, 29.1, 27.4, 27.3, 22.8, 22.7, 14.3, 14.2 (olefinic carbon signals are overlapped).

(Cyclohex-2-en-1-ylmethyl)benzene (3l):[22]



Following the general procedure, cyclohex-2-en-1-yl methyl carbonate **1l** (31.3 mg, 0.20 mmol, 1.0 equiv) and benzylmagnesium chloride (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3l** was isolated via column chromatography (pentane) as colorless oil (31.4 mg, 0.182 mmol, 91%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.75 – 5.68 (m, 1H), 5.63 – 5.56 (m, 1H), 2.66 (dd, *J* = 13.3, 7.2 Hz, 1H), 2.56 (dd, *J* = 13.3, 8.1 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.05 – 1.97 (m, 2H), 1.80 – 1.68 (m, 2H), 1.59 – 1.47 (m, 1H), 1.35 – 1.23 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)**) δ 141.0, 131.5, 129.3, 128.3, 127.5, 125.9, 42.9, 37.3, 29.0, 25.5, 21.4.

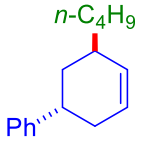
3-Butyl-5-methylcyclohex-1-ene (3m):[23, 24]



Following the general procedure, methyl (5-methylcyclohex-2-en-1-yl) carbonate **1m** (34.1 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3m** was isolated via column chromatography (pentane) as colorless oil (22.4 mg, 0.147 mmol, 74%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.67 – 5.58 (m, 2H), 2.13 – 2.02 (m, 2H), 1.85 – 1.71 (m, 1H), 1.65 – 1.54 (m, 1H), 1.50 – 1.22 (m, 8H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.92 – 0.88 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 131.7, 125.8, 36.0, 36.0,

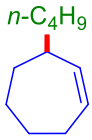
33.8, 33.8, 29.9, 24.8, 23.1, 21.6, 14.3, (trans:cis 13:1); **GC MS (EI)**: 152.2 [M+] (6), 110.1 (11), 96.1 (18), 95.2 (100), 93.1 (6), 82.1 (25), 81.1 (30), 67.1 (41).

3-Butyl-1,2,3,6-tetrahydro-1,1'-biphenyl (3n):



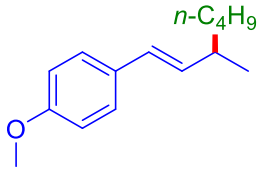
Following the general procedure, methyl (1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl) carbonate **1n** (46.5 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3n** was isolated via column chromatography (pentane) as colorless oil (39.4 mg, 0.183 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.32 (m, 2H), 7.32 – 7.21 (m, 3H), 5.86 – 5.76 (m, 2H), 3.00 – 2.90 (m, 1H), 2.40 – 2.30 (m, 1H), 2.25 – 2.13 (m, 2H), 1.93 (ddd, *J* = 13.0, 11.1, 5.7 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.46 – 1.29 (m, 6H), 1.00 – 0.89 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**) δ 147.4, 132.0, 128.4, 127.2, 126.1, 126.0, 36.1, 35.7, 34.9, 34.5, 33.3, 29.9, 23.1, 14.3.

3-Butylcyclohept-1-ene (3o):



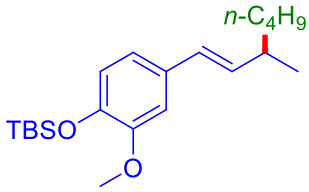
Following the general procedure, cyclohept-2-en-1-yl methyl carbonate **1o** (34.1 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3o** was isolated via column chromatography (pentane) as colorless oil (28.4 mg, 0.186 mmol, 93%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.80 – 5.70 (m, 1H), 5.56 (ddd, *J* = 11.1, 4.3, 1.9 Hz, 1H), 2.23 – 2.03 (m, 3H), 1.99 – 1.89 (m, 1H), 1.71 – 1.49 (m, 3H), 1.43 – 1.17 (m, 8H), 0.94 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.6, 131.1, 39.8, 36.9, 33.7, 30.9, 29.7, 28.9, 27.2, 23.1, 14.3; **GC MS (EI)**: 152.2 [M+] (3), 110.1 (7), 96.1 (77), 95.2 (100), 93.1 (10), 82.1 (42), 81.1 (75), 96.2 (77), 67.1 (95).

(*E*)-1-Methoxy-4-(3-methylhept-1-en-1-yl)benzene (3p):[25]



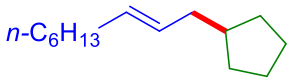
Following the general procedure, (*E*)-4-(4-methoxyphenyl)but-3-en-2-yl methyl carbonate **1p** (47.3 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3p** was isolated via column chromatography (2% Et_2O in pentane) as colorless oil (41.3 mg, 0.19 mmol, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (dd, *J* = 7.8, 1.3 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.28 (dd, *J* = 15.9, 1.0 Hz, 1H), 5.95 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.80 (s, 3H), 2.30 – 2.19 (m, 1H), 1.40 – 1.24 (m, 6H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.92 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 135.2, 131.0, 127.3, 127.1, 114.0, 55.5, 37.4, 37.1, 29.8, 23.0, 20.9, 14.3.

(*E*)-Tert-butyl(2-methoxy-4-(3-methylhept-1-en-1-yl)phenoxy)dimethylsilane (3q):



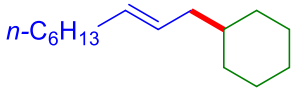
Following the general procedure, (*E*)-4-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)but-3-en-2-yl methyl carbonate **1q** (73.3 mg, 0.20 mmol, 1.0 equiv) and n-butyl magnesium chloride (0.20 mL, 0.40 mmol, 2.0 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3q** was isolated via column chromatography (2% Et_2O in pentane) as colorless oil (55.8 mg, 0.16 mmol, 80%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.88 (d, *J* = 1.9 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.27 (dd, *J* = 15.9, 1.0 Hz, 1H), 5.97 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.83 (s, 3H), 2.32 – 2.20 (m, 1H), 1.42 – 1.25 (m, 6H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.01 (s, 9H), 0.94 – 0.87 (m, 3H), 0.16 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.1, 144.4, 135.3, 132.1, 127.9, 121.0, 119.0, 109.7, 55.6, 37.4, 37.1, 29.8, 25.9, 23.0, 20.9, 18.6, 14.3, -4.5. **HRMS** $[M+Na]^+$ calcd. for $C_{21}H_{36}NaO_2Si^+$ 371.2377, found 371.2374.

(*E*)-Non-2-en-1-ylcyclopentane (3r):[26]



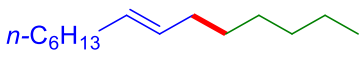
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and cyclopentylmagnesium chloride **2b** (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3r** was isolated via column chromatography (pentane) as colorless oil (35.2 mg, 0.18 mmol, 91%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.45 – 5.32 (m, 2H), 2.06 – 1.92 (m, 4H), 1.88 – 1.77 (m, 1H), 1.76 – 1.66 (m, 2H), 1.64 – 1.54 (m, 2H), 1.52 – 1.43 (m, 2H), 1.39 – 1.22 (m, 8H), 1.18 – 1.06 (m, 2H), 0.92 – 0.84 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 131.0, 129.8, 40.3, 39.2, 32.8, 32.4 (2C), 31.9, 29.8, 29.0, 25.3 (2C), 22.8, 14.3.

(*E*)-Non-2-en-1-ylcyclohexane (3s):[27]



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and cyclohexylmagnesium chloride **2c** (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3s** was isolated via column chromatography (pentane) as colorless oil (37.4 mg, 0.18 mmol, 61% yield, 67% purity, mixed with 33% inseparable 1,1'-bi(cyclohexane))[28]; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.43 – 5.30 (m, 2H), 2.00 – 1.94 (m, 2H), 1.89 – 1.82 (m, 2H), 1.75 – 1.59 (m, 9H), 1.38 – 1.14 (m, 10H), 0.90 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 131.6, 128.9, 40.8, 38.3, 33.3, 32.8, 31.9, 29.8, 29.0, 26.8, 26.5, 22.8, 14.2.

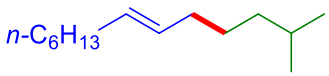
(*E*)-Tetradec-7-ene (3t):[29]



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and pentylmagnesium bromide (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3t** was isolated via column chromatography (pentane) as colorless oil (33.4 mg, 0.17 mmol, 85%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.39 (ddd, *J* = 5.3, 3.7,

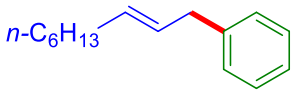
1.6 Hz, 2H), 2.01 – 1.92 (m, 4H), 1.37 – 1.22 (m, 16H), 0.91 – 0.85 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.5, 32.8, 31.9, 29.8, 29.0, 22.8, 14.3.

(*E*)-2-Methyltridec-6-ene (3u):



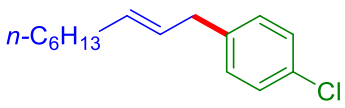
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and isopentylmagnesium bromide (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3u** was isolated via column chromatography (pentane) as colorless oil (36.2 mg, 0.184 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.41 (td, *J* = 3.7, 1.8 Hz, 2H), 2.03 – 1.94 (m, 4H), 1.61 – 1.49 (m, 1H), 1.42 – 1.26 (m, 10H), 1.22 – 1.15 (m, 2H), 0.93 – 0.87 (m, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.5, 38.7, 33.0, 32.8, 31.9, 29.8, 29.0, 28.1, 27.6, 22.8, 22.8, 14.3 (olefinic signals are overlapped); **GC MS (EI)**: 196.3 [M+] (10), 111.2 (14), , 97.1 (25), 84.1 (20), 83.1 (40), 70.1 (42), 69.1 (100).

(*E*)-Non-2-en-1-ylbenzene (3v):[30]



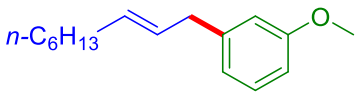
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and phenylmagnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3v** was isolated via column chromatography (pentane) as colorless oil (37.3 mg, 0.184 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.26 (m, 2H), 7.19 (dt, *J* = 6.3, 1.7 Hz, 3H), 5.62 – 5.47 (m, 2H), 3.34 (d, *J* = 5.8 Hz, 2H), 2.03 (td, *J* = 7.2, 5.6 Hz, 2H), 1.42 – 1.23 (m, 8H), 0.93 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 132.3, 128.8, 128.6, 128.5, 126.0, 39.2, 32.7, 31.9, 29.6, 29.0, 22.8, 14.2.

(*E*)-1-Chloro-4-(non-2-en-1-yl)benzene (3w):[31]



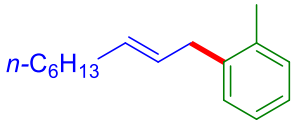
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and (4-chlorophenyl)magnesium bromide (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3w** was isolated via column chromatography (pentane) as colorless oil (45.4 mg, 0.19 mmol, 96%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.22 (m, 2H), 7.13 – 7.08 (m, 2H), 5.56 – 5.45 (m, 2H), 3.29 (d, *J* = 4.7 Hz, 2H), 2.06 – 1.97 (m, 2H), 1.41 – 1.22 (m, 8H), 0.92 – 0.84 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.7, 132.8, 131.7, 130.0, 128.5, 128.3, 38.5, 32.6, 31.9, 29.5, 29.0, 22.8, 14.2.

(*E*)-1-Methoxy-3-(non-2-en-1-yl)benzene (3x):[32]



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and (3-methoxyphenyl)magnesium bromide (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3x** was isolated via column chromatography (pentane) as colorless oil (44.2 mg, 0.19 mmol, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 7.17 (m, 1H), 6.80 – 6.77 (m, 1H), 6.76 – 6.72 (m, 2H), 5.60 – 5.47 (m, 2H), 3.80 (s, 3H), 3.31 (d, *J* = 5.2 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.42 – 1.22 (m, 8H), 0.92 – 0.84 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 143.0, 132.5, 129.4, 128.6, 121.0, 114.3, 111.4, 55.3, 39.2, 32.7, 31.9, 29.6, 29.0, 22.8, 14.2.

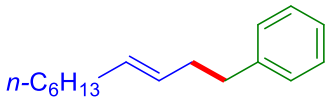
(*E*)-1-Methyl-2-(non-2-en-1-yl)benzene (3y):[31]



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and *o*-tolylmagnesium chloride (0.40 mL, 0.40 mmol, 2.0 equiv, 1.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3y** was isolated via column chromatography (pentane) as colorless oil (38.3 mg, 0.177 mmol, 89%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 – 7.08 (m, 4H), 5.57 – 5.50 (m, 1H), 5.47 – 5.39 (m, 1H), 3.31 (dq, *J* = 6.3, 1.2 Hz, 2H), 2.30 (s, 3H), 2.01 (tdd, *J* = 7.6, 6.0, 1.2 Hz, 2H), 1.43 – 1.20 (m, 8H), 0.93 – 0.84 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**

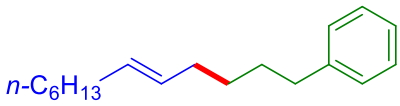
δ 139.3, 136.4, 132.1, 130.2, 129.1, 127.9, 126.2, 126.1, 36.7, 32.7, 31.9, 29.6, 29.0, 22.8, 19.5, 14.2.

(*E*)-Dec-3-en-1-ylbenzene (3z):[33]



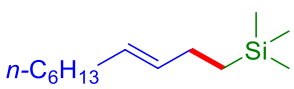
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and benzylmagnesium chloride (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3z** was isolated via column chromatography (pentane) as colorless oil (35.6 mg, 0.164 mmol, 82%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 5.52 – 5.40 (m, 2H), 2.70 (dd, *J* = 9.0, 6.7 Hz, 2H), 2.33 (ddd, *J* = 10.4, 5.8, 2.5 Hz, 2H), 2.05 – 1.95 (m, 2H), 1.41 – 1.24 (m, 8H), 0.91 (t, *J* = 6.8 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, 32.7, 31.9, 29.7, 29.0, 22.8, 14.3.

(*E*)-Dodec-5-en-1-ylbenzene (3aa):[34]



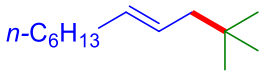
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and (3-phenylpropyl)magnesium bromide (0.80 mL, 0.40 mmol, 1.5 equiv, ~ 0.5 M in THF)[35] were reacted in THF (1.0 mL) for 1 h. Product **3aa** was isolated via column chromatography (pentane) as colorless oil (44.8 mg, 0.183 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.47 – 5.35 (m, 2H), 2.66 – 2.59 (m, 2H), 2.08 – 1.95 (m, 4H), 1.70 – 1.59 (m, 2H), 1.48 – 1.39 (m, 2H), 1.39 – 1.23 (m, 8H), 0.96 – 0.86 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.0, 130.8, 130.1, 128.6, 128.4, 125.7, 36.0, 32.8, 32.6, 31.9, 31.1, 29.8, 29.4, 29.0, 22.8, 14.3.

(*E*)-Dec-3-en-1-yltrimethylsilane (3ab):[36]



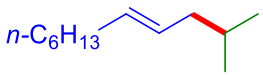
Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and ((trimethylsilyl)methyl)magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 1.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3ab** was isolated via column chromatography (pentane) as colorless oil (33.3 mg, 0.158 mmol, 78%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.50 – 5.32 (m, 2H), 2.05 – 1.91 (m, 4H), 1.39 – 1.19 (m, 8H), 0.94 – 0.84 (m, 3H), 0.64 – 0.51 (m, 2H), -0.02 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.2, 129.0, 32.7, 31.9, 29.8, 29.0, 27.0, 22.8, 16.8, 14.3, -1.4; **GC MS (EI)**: 212.2 [M+], (2), 197.2 (2), 72.1 (2), 67.1 (2), 74.1 (8), 99.1 (10), 73.1 (100).

(*E*)-2,2-dimethylundec-4-ene (3ac):



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and *tert*-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3ac** was isolated via column chromatography (pentane) as colorless oil (35.1 mg, 0.192 mmol, 78%), 4:1 (α:γ) selectivity; **^{1}H NMR (400 MHz, $CDCl_3$** for major isomer**)** δ 5.47 – 5.32 (m, 2H), 2.00 (q, *J* = 6.5 Hz, 2H), 1.85 (d, *J* = 6.2 Hz, 2H), 1.38 – 1.22 (m, 8H), 0.89 – 0.82 (m, 12H).; **^{13}C NMR (101 MHz, $CDCl_3$** (for major isomer**)** δ 132.9, 127.4, 47.3, 32.8, 31.9, 31.0, 29.8, 29.0, 27.9, 22.8. 14.3; **GC MS (EI)**: 182.3 [M+] (15), 126.2 (69), 124.2 (38), 97.2 (65), 83.1 (52), 70.1 (47), 69.1 (100), 67.1 (23).

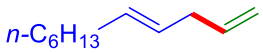
(*E*)-2-Methylundec-4-ene (3ad):[37]



Following the general procedure, (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and isopropyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3ad** was isolated via column chromatography (pentane) as colorless oil (19.2 mg, 0.114 mmol, 57%), 20:1 (α:γ) selectivity; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.45 – 5.32 (m, 2H), 2.09 – 1.82 (m, 4H), 1.57 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.37 – 1.24 (m, 8H),

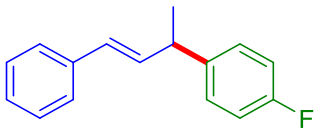
0.92 – 0.81 (m, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 131.7, 129.1, 42.2, 32.8, 31.9, 29.8, 29.0, 28.7, 22.8, 22.4, 14.2.

(*E*)-Undeca-1,4-diene (3ae):[37]



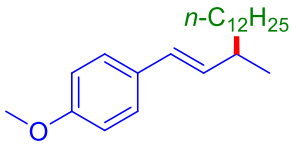
Following the general procedure **1** (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.20 mmol, 1.0 equiv) and vinyl magnesium bromide (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3ae** was isolated via column chromatography (pentane) as colorless oil (11.3 mg, 0.07 mmol, 37%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.90 – 5.80 (m, 1H), 5.53 – 5.38 (m, 2H), 5.09 – 4.97 (m, 2H), 2.77 (ddd, *J* = 6.7, 4.1, 2.6 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.41 – 1.24 (m, 8H), 0.95 – 0.86 (m, 3H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 132.0, 127.6, 114.8, 36.9, 32.7, 31.9, 29.6, 29.0, 22.8, 14.3.

(*E*)-1-Fluoro-4-(4-phenylbut-3-en-2-yl)benzene (3af):[38]



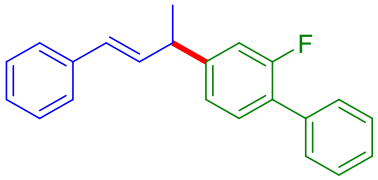
Following the general procedure, (*E*)-methyl (4-phenylbut-3-en-2-yl) carbonate **1f** (41.3 mg, 0.20 mmol, 1.0 equiv) and (4-fluorophenyl)magnesium bromide (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3af** was isolated via column chromatography (pentane) as colorless oil (41.6 mg, 0.18 mmol, 92%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (dd, *J* = 7.3, 1.5 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 7.06 – 6.98 (m, 2H), 6.46 – 6.32 (m, 2H), 3.65 (p, *J* = 6.8 Hz, 1H), 1.47 (dd, *J* = 7.1, 1.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.5 (d, *J* = 243.9 Hz), 141.4 (d, *J* = 3.2 Hz), 137.6, 135.1, 128.8 (d, *J* = 7.8 Hz), 128.8, 128.7, 127.3, 126.3, 115.3 (d, *J* = 21.0 Hz), 41.9, 21.5.

(*E*)-1-Methoxy-4-(3-methylpentadec-1-en-1-yl)benzene (3ag):



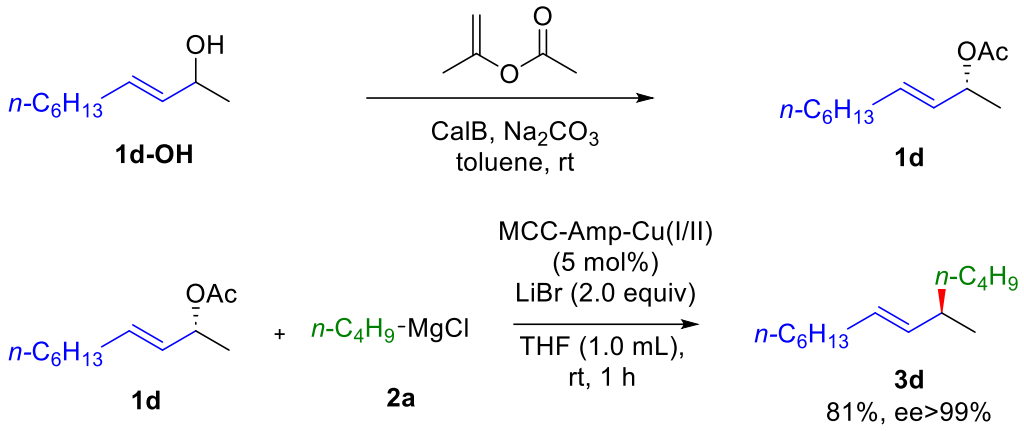
Following the general procedure, (*E*)-4-(4-methoxyphenyl)but-3-en-2-yl methyl carbonate **1n** (47.3 mg, 0.20 mmol, 1.0 equiv) and dodecylmagnesium bromide (0.30 mL, 0.30 mmol, 1.5 equiv, 1.0 M in Et_2O) were reacted in THF (1.0 mL) for 1 h. Product **3ag** was isolated via column chromatography (pentane) as colorless oil (61.8 mg, 0.19 mmol, 93%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.26 (m, 2H), 6.87 – 6.80 (m, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 5.95 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.80 (s, 3H), 2.25 (hept, *J* = 6.7 Hz, 1H), 1.26 (s, 22H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.91 – 0.85 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 135.2, 131.0, 127.3, 127.1, 114.0, 55.4, 37.4, 37.4, 32.1, 30.0, 29.8, 29.8, 29.5, 27.6, 22.8, 20.9, 14.3 (three signals are overlapping with other signals). **HRMS** $[M+Na]^+$ calcd. for $C_{23}H_{38}NaO^+$ 353.2815, found 353.2812.

(*E*)-2-Fluoro-4-(4-phenylbut-3-en-2-yl)-1,1'-biphenyl (3ah):[39]



Following the general procedure **1** (*E*)-methyl non-2-en-1-yl carbonate **1f** (40.1 mg, 0.20 mmol, 1.0 equiv) and (2-fluoro-[1,1'-biphenyl]-4-yl)magnesium bromide (0.80 mL, 0.40 mmol, 2.0 equiv, 0.5 M in THF) were reacted in THF (1.0 mL) for 1 h. Product **3ah** was isolated via column chromatography (*n*-pentane) as light yellow oil (50.8 mg, 0.17 mmol, 84%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.52 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (q, *J* = 7.3 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.9, 6.6 Hz, 1H), 3.69 (p, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9 (d, *J* = 247.8 Hz), 147.5 (d, *J* = 7.2 Hz), 137.5, 135.9, 134.4, 130.8 (d, *J* = 4.0 Hz), 129.3, 129.1 (d, *J* = 2.9 Hz), 128.7, 128.6, 127.6, 127.4, 127.0 (d, *J* = 13.5 Hz), 126.4, 123.4 (d, *J* = 3.2 Hz), 115.0 (d, *J* = 23.0 Hz), 42.3 (d, *J* = 1.6 Hz), 21.2; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -118.08 (d, *J* = 2.2 Hz).

6 Chirality transfer experiment:

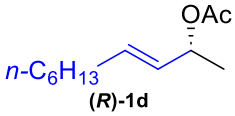


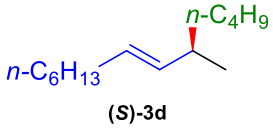
Scheme S6: Chirality transfer experiment

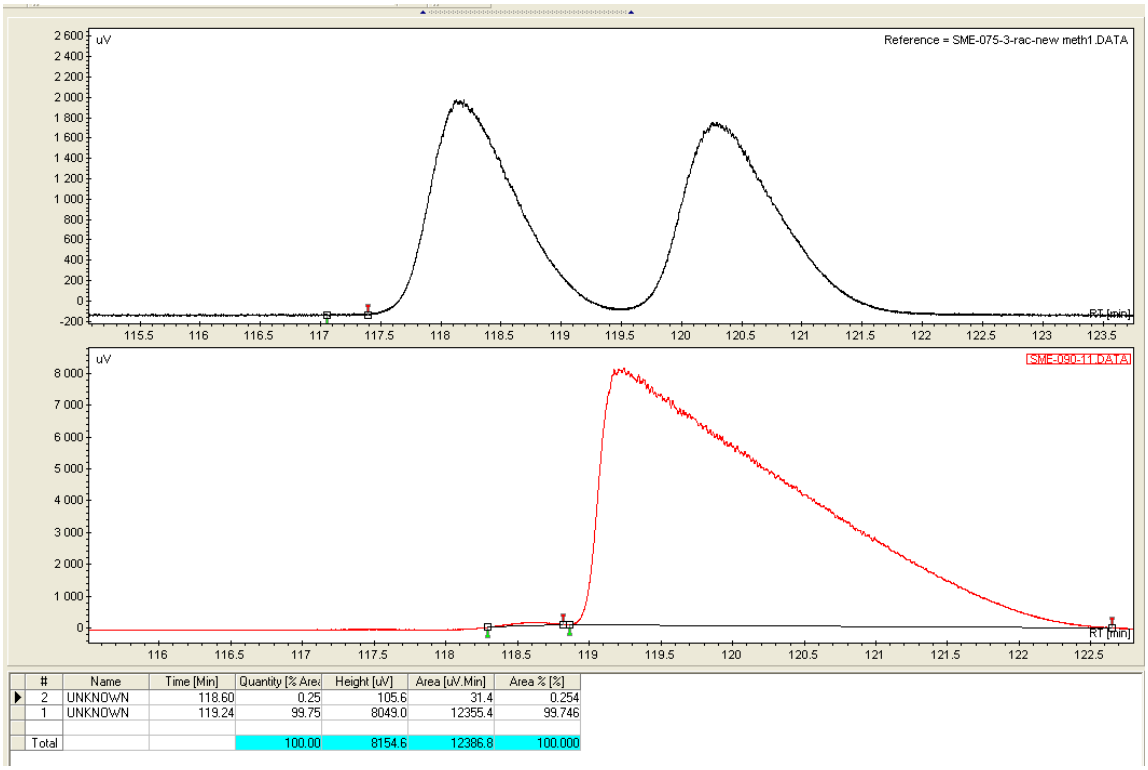
Following a modified literature procedure,[40] to a solution of **1d-OH** in toluene was added isopropenyl acetate (1.0 equiv), Na_2CO_3 (1.0 equiv), and Candida antarctica lipase B (CalB, 8.0 mg) sequentially. The mixture was stirred at room temperature overnight and then purified by column chromatography on silica gel (eluent petroleum ether/diethyl ether = 20/1) to afford enantiopure allylic alcohol acetate (*R*)-**1d** in 43% yield.

An oven-dried Schlenk tube was charged with LiBr (34.4 mg, 0.4 mmol, 2.0 equiv) and carefully dried. MCC-AmP-Cu(I/II) (8.0 mg, 0.01 mmol, 0.05 equiv Cu) was then added under N_2 atmosphere. Dry THF (1.0 mL) and (*R*)-**1d** (39.7 mg, 0.02 mmol, 1.0 equiv) were added sequentially. Next, n-butyl magnesium chloride (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) was added dropwise to the solution, and the reaction mixture was stirred for an hour. The desired compound **3d** was purified via column chromatography (pentane) with 81% yield.

Table S4: Optical rotation table

Substrate	Optical rotation
 (*R*)-1d	$[\alpha]_D^{24}$ = +62.7, (c = 1000 g/100 mL, $CHCl_3$)

 **(*S*)-3d**	$[\alpha]_D^{24}$ = -28.868, (c = 0.433 g/100 mL $CHCl_3$)

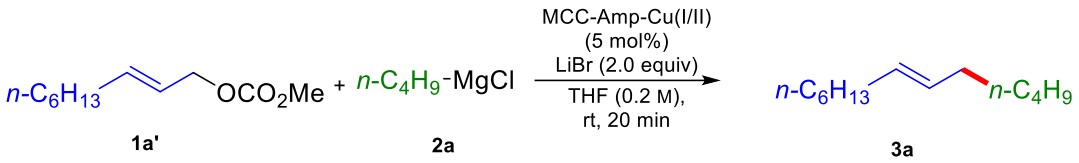


#	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
2	UNKNOWN	118.60	0.25	105.6	31.4	0.254
1	UNKNOWN	119.24	99.75	8049.0	12355.4	99.746
Total			100.00	8154.6	12386.8	100.000

Figure S1: Chromatography diagram of chirality transfer experiment; racemic (1d), bottom chiral (1d).

7 Catalyst recycle experiment:

5.1 Catalyst recycling experiment using carbonate derivative as substrate:



Scheme S7: Catalyst recycling experiment with carbonates

Step 1:

An oven-dried Schlenk tube was charged with LiBr (34.4 mg, 0.4 mmol, 2.0 equiv) and carefully dried. MCC-AmP-Cu(I/II) (8.0 mg, 0.01 mmol, 0.05 equiv Cu) was then added under N_2 atmosphere. Dry THF (1.0 mL) and (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.02 mmol, 1.0 equiv) were added sequentially. Next, n-butyl magnesium chloride **2a** (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) was added dropwise to the solution, and the reaction mixture was allowed to stir for 20 minutes. The mixture was then transferred to a 2.0 mL micro-centrifuge tube and centrifuged for 1 minute at 13000 rpm. The supernatant liquid was transferred to a vial, while the solid residue was washed twice with dry THF, followed by two additional washes with acetone. The heterogeneous catalyst was then dried for several hours. The supernatant liquid was quenched with a few drops of water and 1,3,5 trimethoxy benzene was added to determine the ^{1}H-NMR yield.

Step 2:

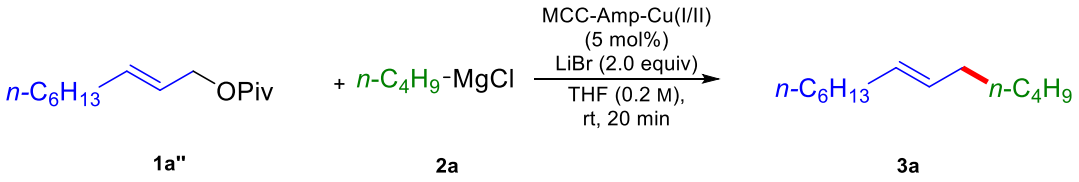
Once again, an oven-dried Schlenk tube was charged with LiBr (34.4 mg, 0.4 mmol, 2.0 equiv), and carefully dried. The heterogeneous catalyst recovered from **Step 1** was then added under N_2 atmosphere followed by (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.02 mmol, 1.0 equiv) and the procedure was carried out as described in **Step 1**.

The process was repeated for both **Step 3** and **Step 4**, and the calculated yields are summarized in the table below.

Table S5: Catalyst recycling experiment with carbonates

Reaction cycle	Yield of 3a	Unreacted 1a' observed	Detected allylic alcohol 1d-OH
1st	94	n.d.	n.d.
2nd	95	3	2
3rd	95	2	3
4th	91	n.d.	9

5.2 Catalyst recycling experiment using pivalate derivative as substrate:



1a" **2a** **3a**

Scheme S8: Catalyst recycling experiment with pivalates

An oven-dried Schlenk tube was charged with LiBr (34.2 mg, 0.2 mmol, 1.0 equiv) and carefully dried. MCC-AmP-Cu(I/II) (8.0 mg, 0.01 mmol, 0.05 equiv Cu) was then added under N_2 atmosphere. Dry THF (1.0 mL) and (*E*)-non-2-en-1-yl pivalate **1a''** (45.3 mg, 0.2 mmol, 1.0 equiv) was added sequentially. Following this, n-butylmagnesium chloride **2a** (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF) was added dropwise and the reaction mixture was stirred at room temperature. After 20 minutes, the reaction mixture was transferred to a 2.0 mL microcentrifuge tube and centrifuged at 13000 rpm for 1 minute. Then the supernatant liquid was transferred to a vial, and the heterogeneous catalyst was washed with THF and centrifuged again. This washing process was repeated twice, with all the supernatant liquid collected in the same vial. The solution was then quenched with a few drops of water, and ^{1}H-NMR yield of **3a** was measured using 1,3,5-trimethoxybenzene as internal standard.

For the next run, another oven dried Schlenk tube was charged with LiBr (34.2 mg, 0.2 mmol, 1.0 equiv) and carefully dried. THF (1.0 mL) was then added to the micro-centrifuge tube containing heterogeneous Cu catalyst, and the resulting catalyst suspension was quickly transferred to the Schlenk tube under N_2 atmosphere. The (*E*)-non-2-en-1-yl pivalate **1a''** (45.3 mg, 0.2 mmol, 1.0 equiv) was then added followed by dropwise addition of *n*-butyl magnesium chloride **2a** (0.15 mL, 0.30 mmol, 1.5 equiv, 2.0 M in THF). After 20 minutes, the reaction mixture was transferred to another microcentrifuge tube and previously described procedure was followed.

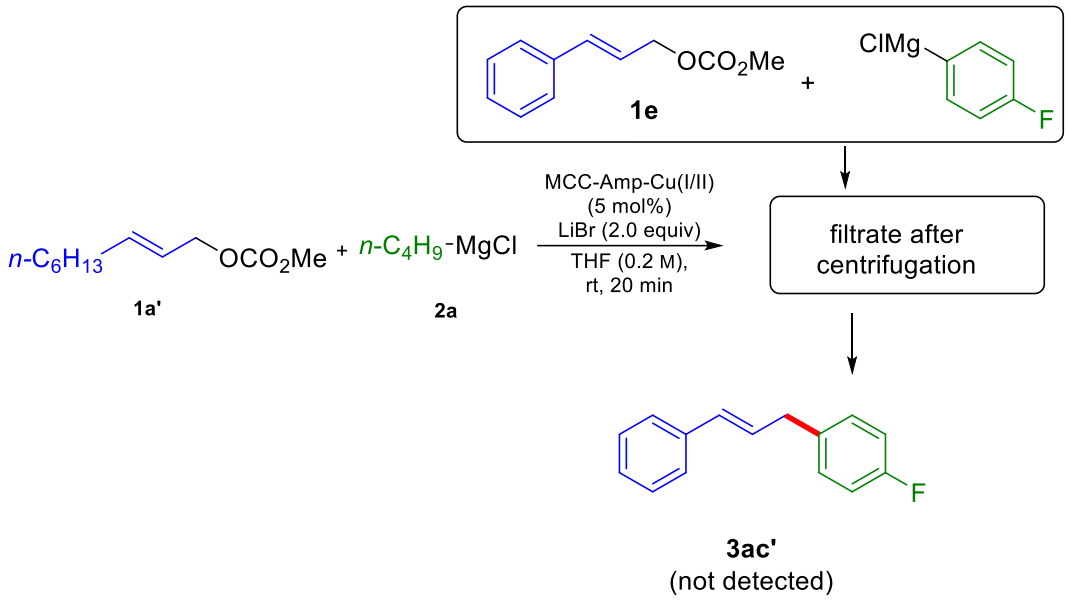
Similarly, this process was repeated twice more until four cycles using the recovered catalyst from the previous cycle.

Table S6: Catalyst recycling experiment with pivalates

Reaction cycle	**Yield of 3a**	**Unreacted 1a'' observed**	**Detected allylic alcohol 1d-OH**
1st	94	n.d.	n.d.
2nd	95	n.d.	n.d.
3rd	95	n.d.	n.d.
4th	91	n.d.	6

5.3 Control Experiments:

In our next attempt, we aimed to determine whether the reaction proceeds via leached Cu catalyst in a homogeneous medium. For this purpose, we commenced the reaction using filtrate of another reaction.



Scheme S9: Control experiment to check catalytic activity of filtrate

An oven-dried Schlenk tube was charged with LiBr (34.4 mg, 0.4 mmol, 2.0 equiv) and carefully dried. MCC-AmP-Cu(I/II) (8.0 mg, 0.01 mmol, 0.05 equiv Cu) was then added under N_2 atmosphere. Dry THF (1.0 mL) and (*E*)-methyl non-2-en-1-yl carbonate **1a'** (40.1 mg, 0.02 mmol, 1.0 equiv) were added sequentially. Next, *n*-butyl magnesium chloride **2a** (0.12 mL, 0.24 mmol, 1.2 equiv, 2.0 M in THF) was added dropwise to the solution, and the reaction mixture was allowed to stir for 20 minutes. The mixture was then transferred to a 2.0 mL micro-centrifuge tube and centrifuged for 1 minute at 13000 rpm. Then the supernatant liquid was collected in a vial after short silica filtration.

Another oven-dried vial was charged cinnamyl methyl carbonate **1e** (0.2 mmol, 1.0 equiv) and 0.5 mL THF was added. Then the supernatant liquid was transferred carefully without disturbing the lower sediment. Then (4-fluorophenyl)magnesium chloride (0.3 mmol, 1.5 equiv) was added dropwise under an N_2 atmosphere. After 20 mins of the reaction, ^{1}H-NMR yield was calculated using 1,3,5-trimethoxybenzene as an internal standard. However, 3ac' was not detected in crude ^{1}H-NMR.

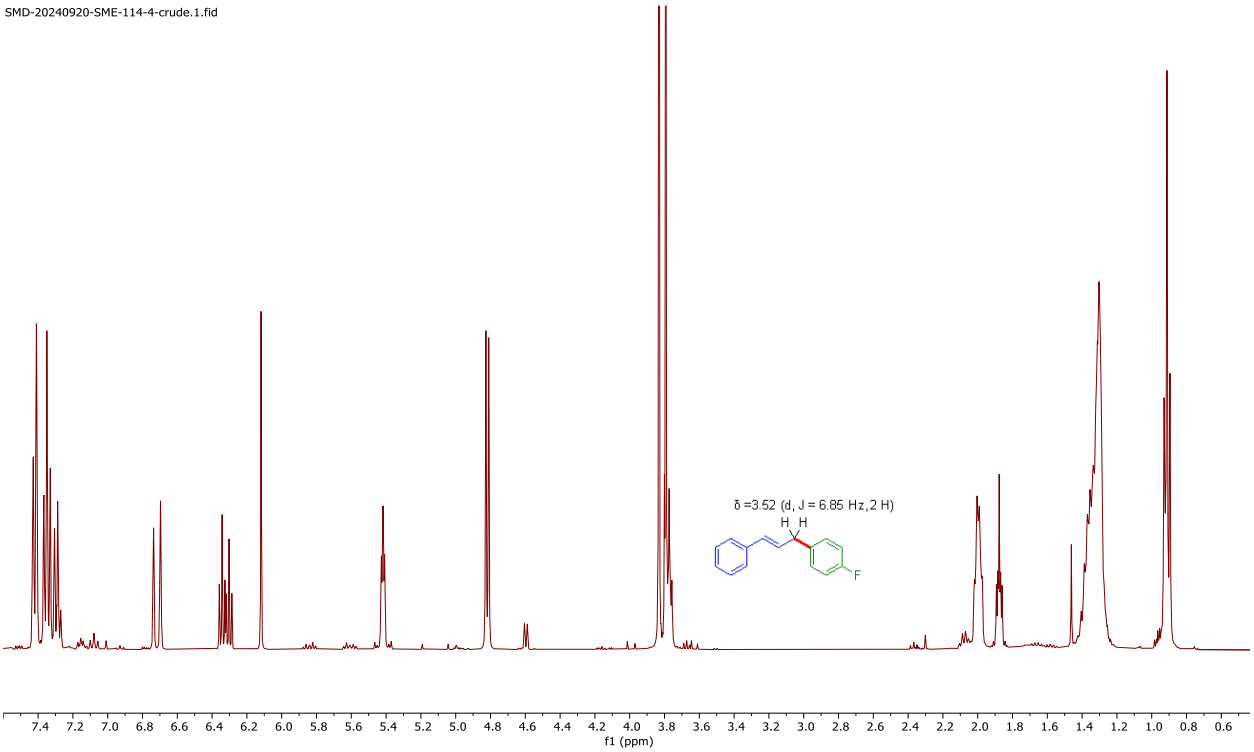
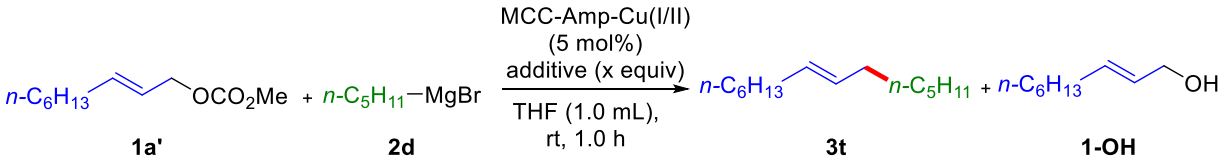


Figure S2: Filtration catalytic activity test

8 Control experiments for investigation of the role of LiBr

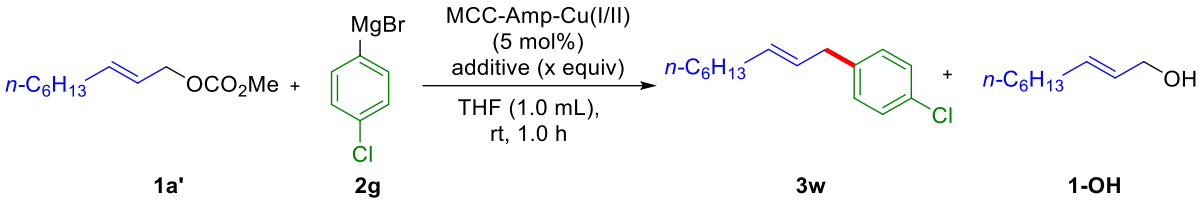
To investigate the role of LiBr in the developed reaction conditions, we performed the following control experiments:

Table S7: Control experimental with aliphatic Grignard reagent 2d



entry	Additive (equiv)	Yield (3t) (%)	Unreacted 1a' (%)	Detected 1a-OH (%)
1	-	40	46	14
2	LiBr (2.0)	**85 (isolated)**	-	-
3	LiCl (2.0)	79	5	7
4	NaBr (2.0)	52	41	7

Table S8: Control experimental with aromatic Grignard reagent 2g



entry	Additive (equiv)	Yield (3w) (%)	Unreacted 1a' (%)	Detected 1a-OH (%)
1	-	55	20	16
2	LiBr (2.0)	**96 (isolated)**	-	-
3	LiCl (2.0)	81	7	9

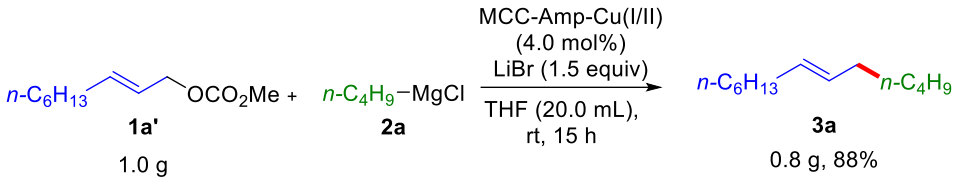
The results are summarized in Table S7 and Table S8. First, comparison of the results from experiments using RMgBr (Table S7, entries 1 and 2) instead of RMgCl (main text, Table 1, entries 1 and 7) demonstrate that LiBr is essential for achieving high reactivity and selectivity in both

cases, regardless of the anion in the Grignard reagents. Second, a control experiment using LiCl instead of LiBr (Table S7, entry 3) indicates that LiCl can also play a similar role in the reaction, albeit less efficiently than LiBr. Third, another control experiment using NaBr instead of LiBr (Table S7, entry 4) indicates that the lithium counter ion is important for enhancing the rate of the reaction. Fourth, these observations are also applicable to reactions involving aromatic Grignard reagents (Table S8). Based on these control experiments, we can exclude the possibility that the role of LiBr in facilitating the reaction is to promote a Cl/Br exchange to generate RMgBr from RMgCl.

In a relevant study by Knochel and co-workers,[41] it was found that LiCl plays a key role in increasing the reactivity of standard Grignard reagents by forming a more reactive Li complex (RMgX•LiCl). In our current study using a heterogeneous nanocopper catalyst, the high electrophilicity of Grignard reagents is crucial for achieving high selectivity toward the desired allylic substitution over competing side reactions.

Inspired by Knochel's study and based on our current experimental outcomes, we postulate that LiBr coordinates with the Grignard reagent to form a Li complex (RMgX·LiBr), which exhibits higher electrophilicity than standard Grignard reagents in the developed heterogeneous copper-catalyzed allylic substitution.

9 Gram-scale reaction:



Scheme S10: Gram-scale reaction

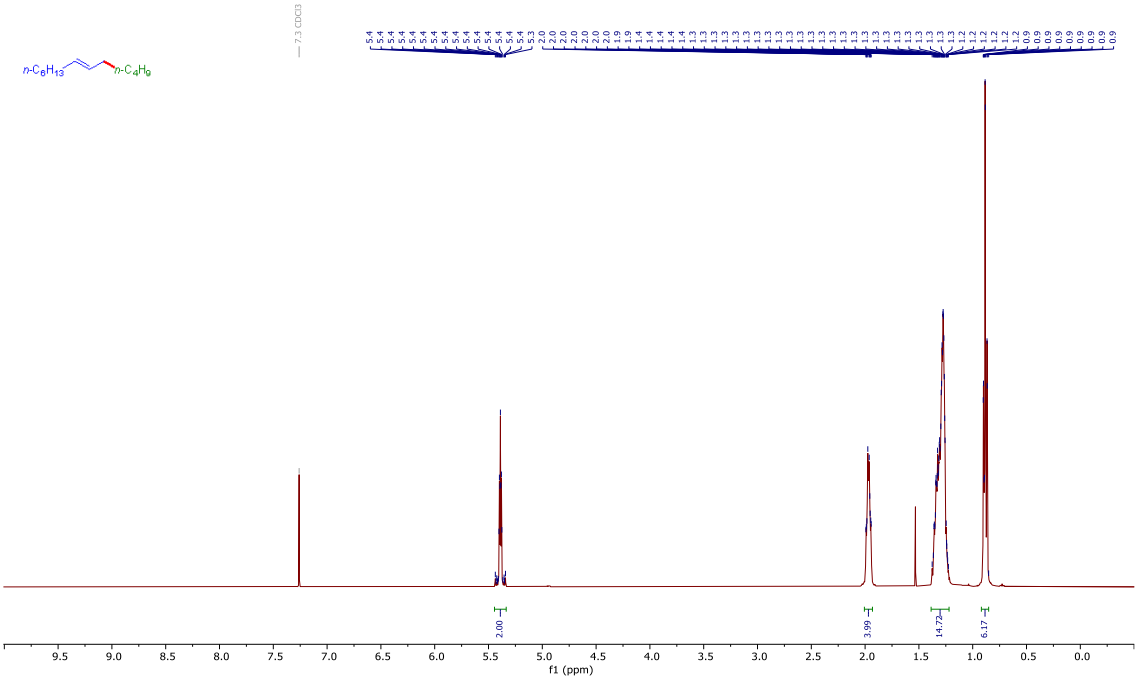
To enhance the applicability of our protocol we conducted the reaction on gram-scale. An oven-dried Schlenk flask was charged with LiBr (644.0 mg, 7.5 mmol, 1.5 equiv) under a N_2 atmosphere and it was then dried under vacuum using a heat blower, followed by the addition of heterogeneous Cu-catalyst (160.0 mg, 0.2 mmol, 0.04 equiv Cu) under N_2 atmosphere. After that, the catalyst and additive mixture were dried again under vacuum at room temperature, followed by the addition of 20.0 mL of THF under N_2 atmosphere. Next, the allylic alcohol derivative **1a'** (1.0 g, 4.99 mmol, 1.0 equiv) was added, and finally, the *n*-butyl magnesium chloride (3.8 mL, 7.5 mmol, 1.5 equiv, 2 M in THF) was added dropwise at room temperature with the reaction vessel placed in a water bath under N_2 atmosphere. Then the reaction mixture was stirred overnight. Afterward, the reaction mixture was quenched with water, extracted with diethylether. The organic layer was collected, dried over Na_2SO_4. Volatiles were removed under reduced pressure, and the desired compound was isolated via flash chromatography (*n*-pentane) with 87% yield (801.6 mg, 4.40 mmol, 87%).

10 References

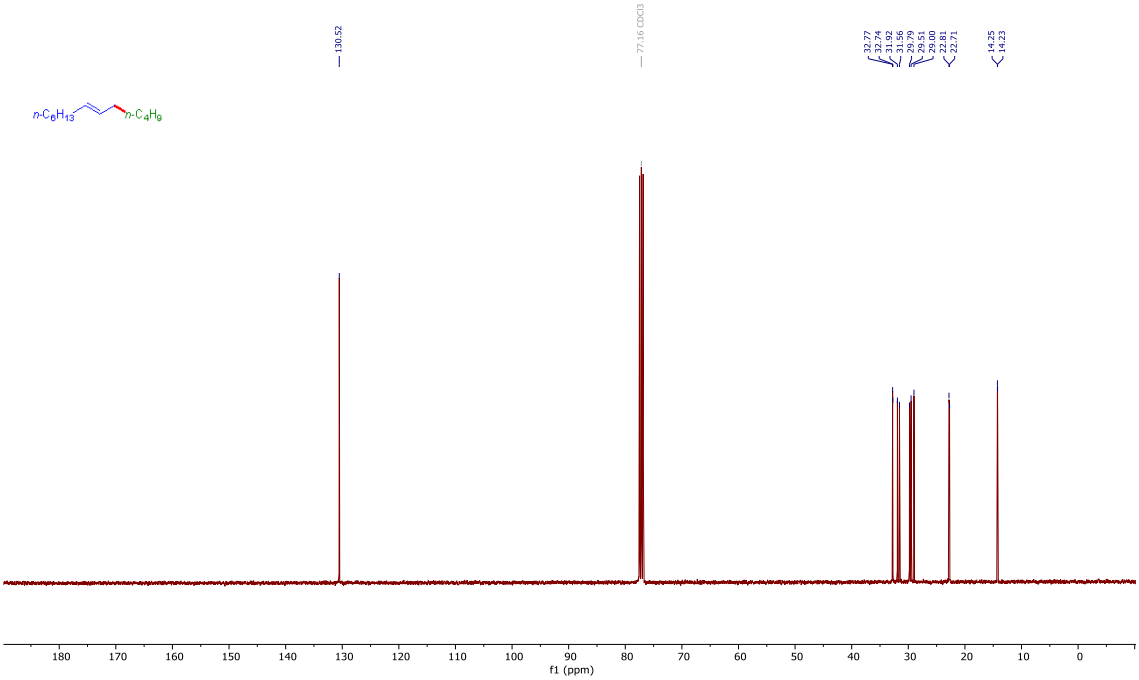
1. Z. Zheng, L. Deiana, D. Posevins, A. A. Rafi, K. Zhang, M. J. Johansson, C.-W. Tai, A. Córdova and J.-E. Bäckvall, *ACS Catal.*, 2022, **12**, 1791-1796.
2. A. Fernández-Mateos, S. E. Madrazo, P. H. Teijón and R. R. González, *Eur. J. Org. Chem.*, 2010, **2010**, 856-861.
3. M. Jäkel, J. Qu, T. Schnitzer and G. Helmchen, *Chem. Eur. J.*, 2013, **19**, 16746-16755.
4. E. Thiery, C. Aouf, J. Belloy, D. Harakat, J. Le Bras and J. Muzart, *J. Org. Chem.*, 2010, **75**, 1771-1774.
5. C.-Y. Shi, J.-Z. Xiao and L. Yin, *Chem. Commun.*, 2018, **54**, 11957-11960.
6. T. Schlatzer, H. Schröder, M. Trobe, C. Lembacher-Fadum, S. Stangl, C. Schlögl, H. Weber and R. Breinbauer, *Adv. Synth. Catal.*, 2020, **362**, 331-336.
7. V. K. Yadav and K. G. Babu, *Tetrahedron*, 2003, **59**, 9111-9116.
8. R. Matsubara and T. F. Jamison, *J. Am. Chem. Soc.*, 2010, **132**, 6880-6881.
9. D. J. Wang, K. Targos and Z. K. Wickens, *J. Am. Chem. Soc.*, 2021, **143**, 21503-21510.
10. M. Hatano, S. Kamiya and K. Ishihara, *Chem. Commun.*, 2012, **48**, 9465-9467.
11. I. D. Watson and A. K. Yudin, *J. Am. Chem. Soc.*, 2005, **127**, 17516-17529.
12. A. Misale, S. Niyomchon, M. Luparia and N. Maulide, *Angew. Chem. Int. Ed.*, 2014, **53**, 7068-7073.
13. H. Iwamoto, Y. Ozawa, Y. Takenouchi, T. Imamoto and H. Ito, *J. Am. Chem. Soc.*, 2021, **143**, 6413-6422.
14. K. Takizawa, T. Sekino, S. Sato, T. Yoshino, M. Kojima and S. Matsunaga, *Angew. Chem. Int. Ed.*, 2019, **58**, 9199-9203.
15. D.-J. Dong, Y. Li, J.-Q. Wang and S.-K. Tian, *Chem. Commun.*, 2011, **47**, 2158-2160.
16. A. Chołuj, P. Krzesiński, A. Ruszczyńska, E. Bulska, A. Kajetanowicz and K. Grela, *Organometallics*, 2019, **38**, 3397-3405.
17. A. Link, C. Fischer and C. Sparr, *Angew. Chem. Int. Ed.*, 2015, **54**, 12163-12166.
18. N. Zhang, Z. J. Quan and X. C. Wang, *Adv. Synth. Catal.*, 2016, **358**, 3179-3183.
19. T. Stüdemann, M. Ibrahim-Ouali and P. Knochel, *Tetrahedron*, 1998, **54**, 1299-1316.
20. J. F. Quilez del Moral, V. Domingo, Á. Pérez, K. A. Martínez Andrade, L. Enríquez, M. Jaraiz, J. L. López-Pérez and A. F. Barrero, *J. Org. Chem.*, 2019, **84**, 13764-13779.
21. M. F. Mechelke and D. F. Wiemer, *J. Org. Chem.*, 1999, **64**, 4821-4829.
22. F.-H. Cui, Y. Hua, Y.-M. Lin, J. Fei, L.-H. Gao, X. Zhao and H. Xia, *J. Am. Chem. Soc.*, 2022, **144**, 2301-2310.
23. Y. Yamamoto, S. Yamamoto, H. Yatagai and K. Maruyama, *J. Am. Chem. Soc.*, 1980, **102**, 2318-2325.
24. C. C. Tseng, S. D. Paisley and H. L. Goering, *J. Org. Chem.*, 1986, **51**, 2884-2891.
25. N. Zhang, Z.-J. Quan and X.-C. Wang, *Adv. Synth. Catal.*, 2016, **358**, 3179-3183.
26. S. Kawamura, R. Agata and M. Nakamura, *Org. Chem. Front.*, 2015, **2**, 1053-1058.
27. Z. D. Miller, R. Dorel and J. Montgomery, *Angew. Chem. Int. Ed.*, 2015, **54**, 9088-9091.
28. Y. Liu, S. Xiao, Y. Qi and F. Du, *Chem. Asian J.*, 2017, **12**, 673-678.
29. R. Maazaoui, R. Abderrahim, F. Chemla, F. Ferreira, A. Perez-Luna and O. Jackowski, *Org. Lett.*, 2018, **20**, 7544-7549.
30. A. Noble, S. J. McCarver and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2015, **137**, 624-627.
31. K. Nakajima, X. Guo and Y. Nishibayashi, *Chem. Asian J.*, 2018, **13**, 3653-3657.
32. A. Desaintjean, S. Belrhomari, L. Rousseau, G. Lefèvre and P. Knochel, *Org. Lett.*, 2019, **21**, 8684-8688.
33. I. E. Markó, F. Murphy, L. Kumps, A. Ates, R. Touillaux, D. Craig, S. Carballares and S. Dolan, *Tetrahedron*, 2001, **57**, 2609-2619.
34. T. Di Franco, A. Epenoy and X. Hu, *Org. Lett.*, 2015, **17**, 4910-4913.
35. A. Sahari, C. D. Do, J. K. Mannisto, E. Antico, A. Amaratunga, K. H. Hopmann and T. Repo, *Chem. Commun.*, 2022, **58**, 3027-3030.
36. R. Mizojiri, H. Urabe and F. Sato, *J. Org. Chem.*, 2000, **65**, 6217-6222.
37. N. R. Patel, C. B. Kelly, M. Jouffroy and G. A. Molander, *Org. Lett.*, 2016, **18**, 764-767.
38. C. Wang, Y. Guo, X. Wang, Z. Wang and K. Ding, *Chem. Eur. J.*, 2021, **27**, 15903-15907.
39. L. K. Thalén, A. Sumic, K. Bogár, J. Norinder, A. K. Persson and J.-E. Bäckvall, *J. Org. Chem.*, 2010, **75**, 6842-6847.
40. M.-B. Li, D. Posevins, K. P. J. Gustafson, C.-W. Tai, A. Shchukarev, Y. Qiu and J.-E. Bäckvall, *Chem. Eur. J.*, 2019, **25**, 210-215.
41. A. Krasovskiy and P. Knochel, *Angew. Chem. Int. Ed.*, 2004, **43**, 3333-3336.

11 NMR spectra

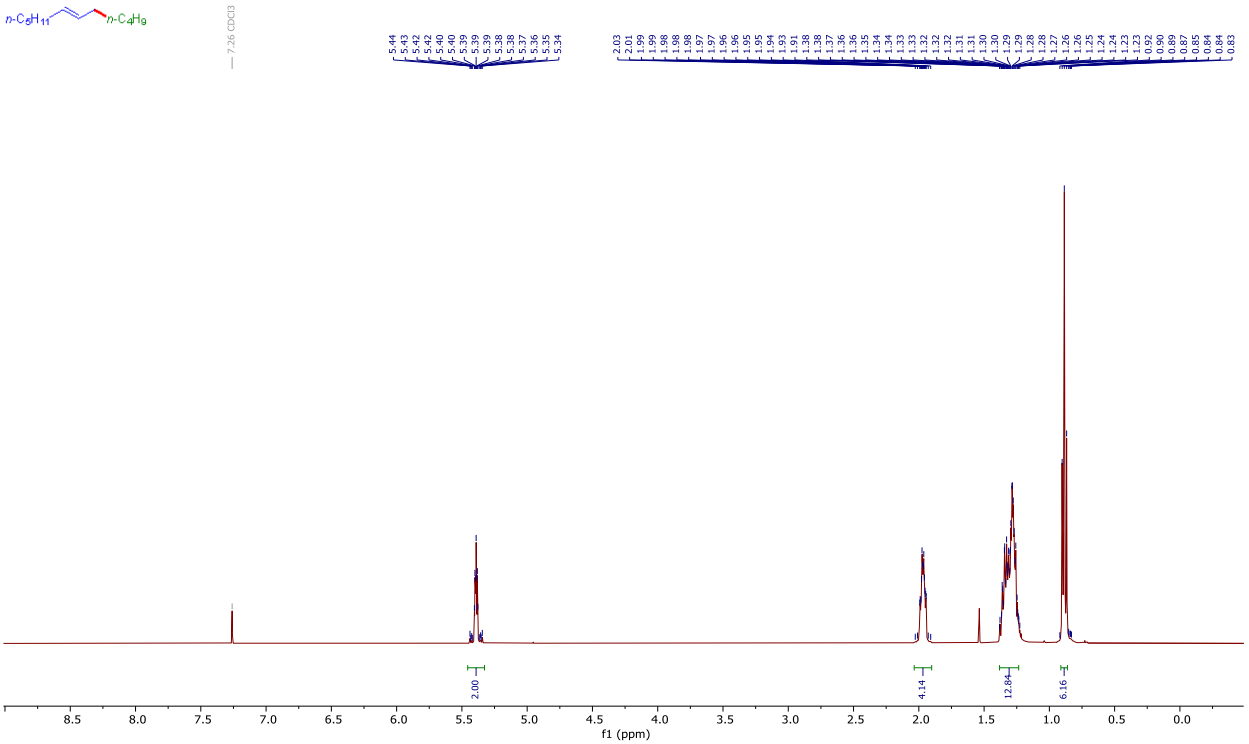
^{1}H NMR (400 MHz, $CDCl_3$), 3a:



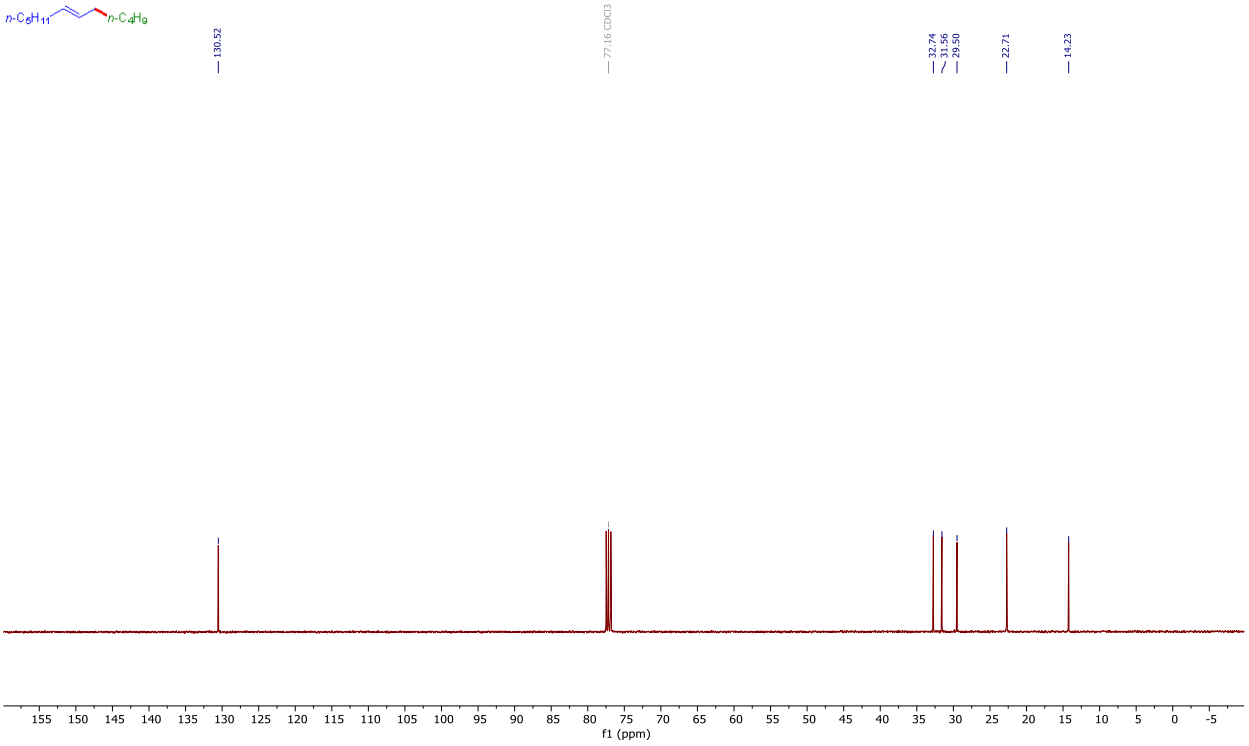
^{13}C NMR (101 MHz, $CDCl_3$), 3a:



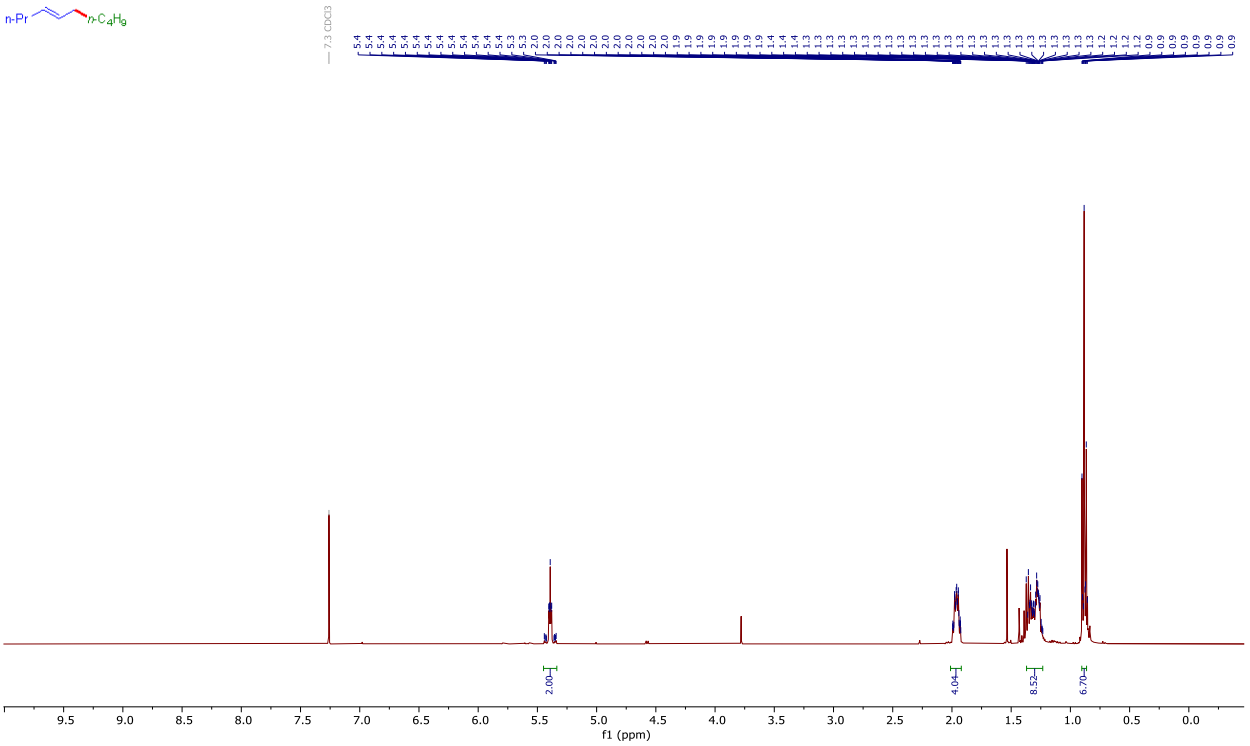
^{1}H NMR (400 MHz, $CDCl_3$), 3b:



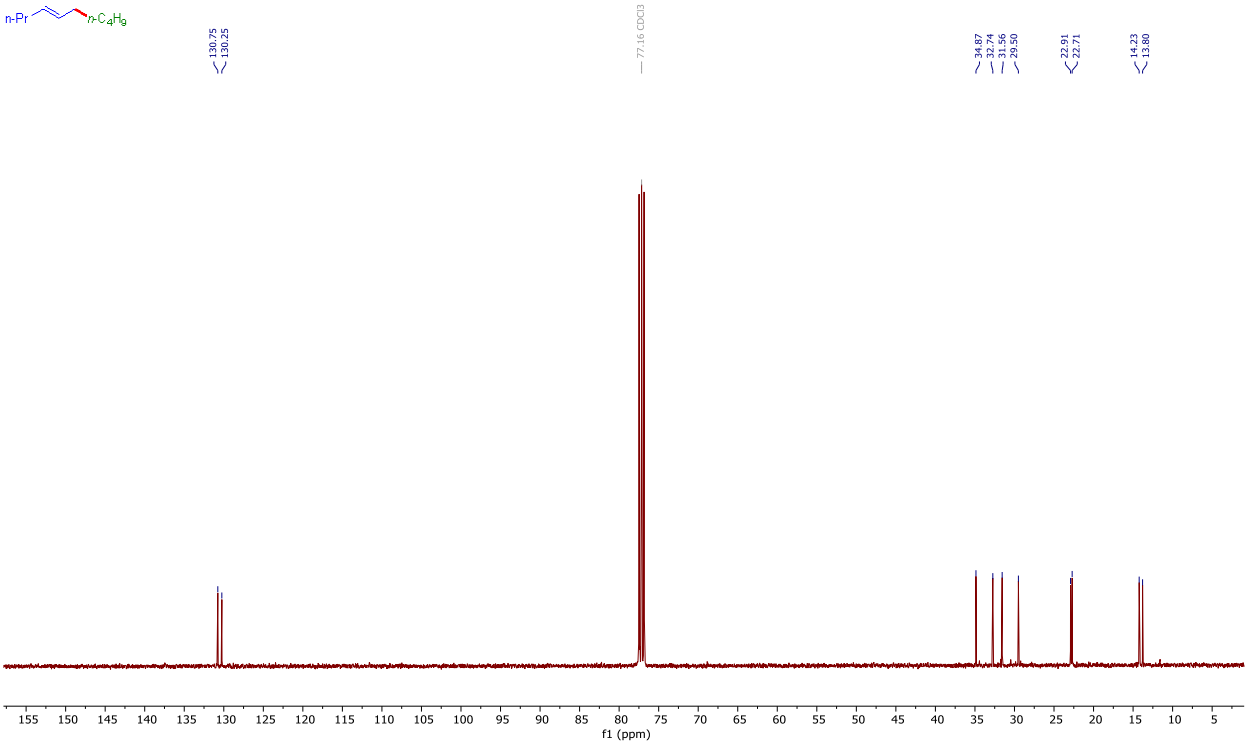
^{13}C NMR (101 MHz, $CDCl_3$), 3b:



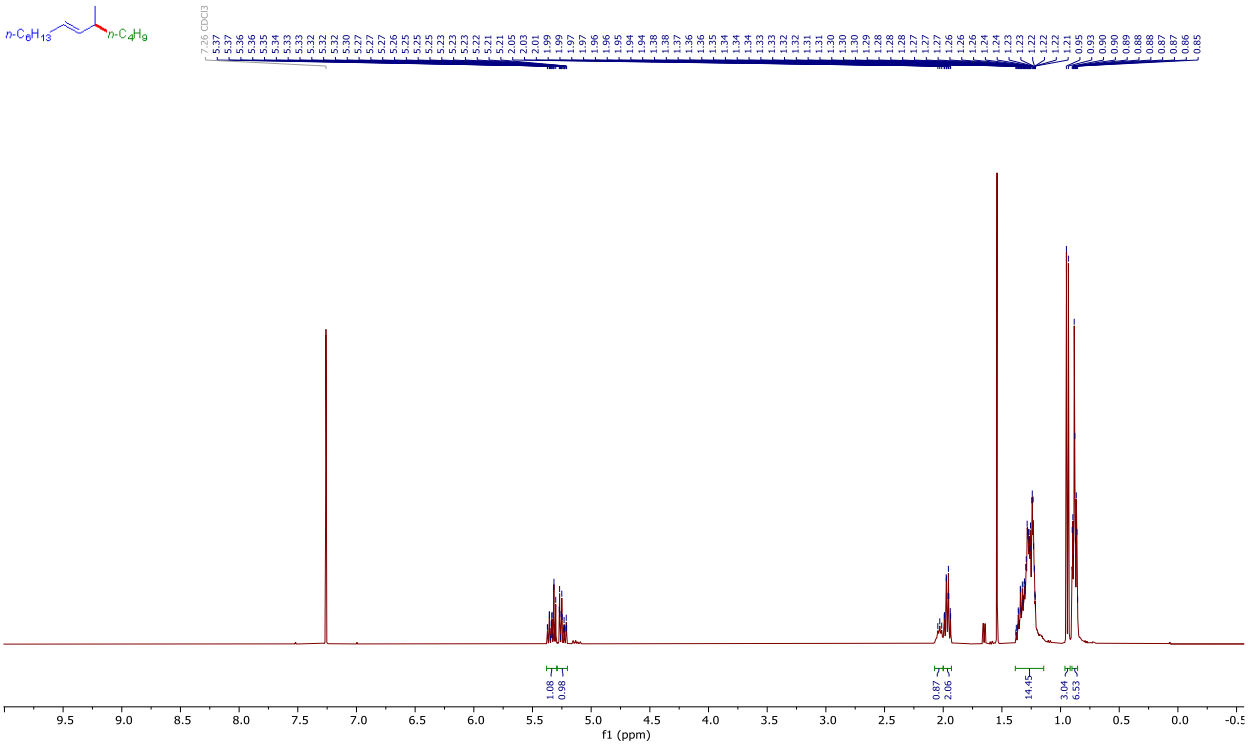
^{1}H NMR (400 MHz, $CDCl_3$), 3c:



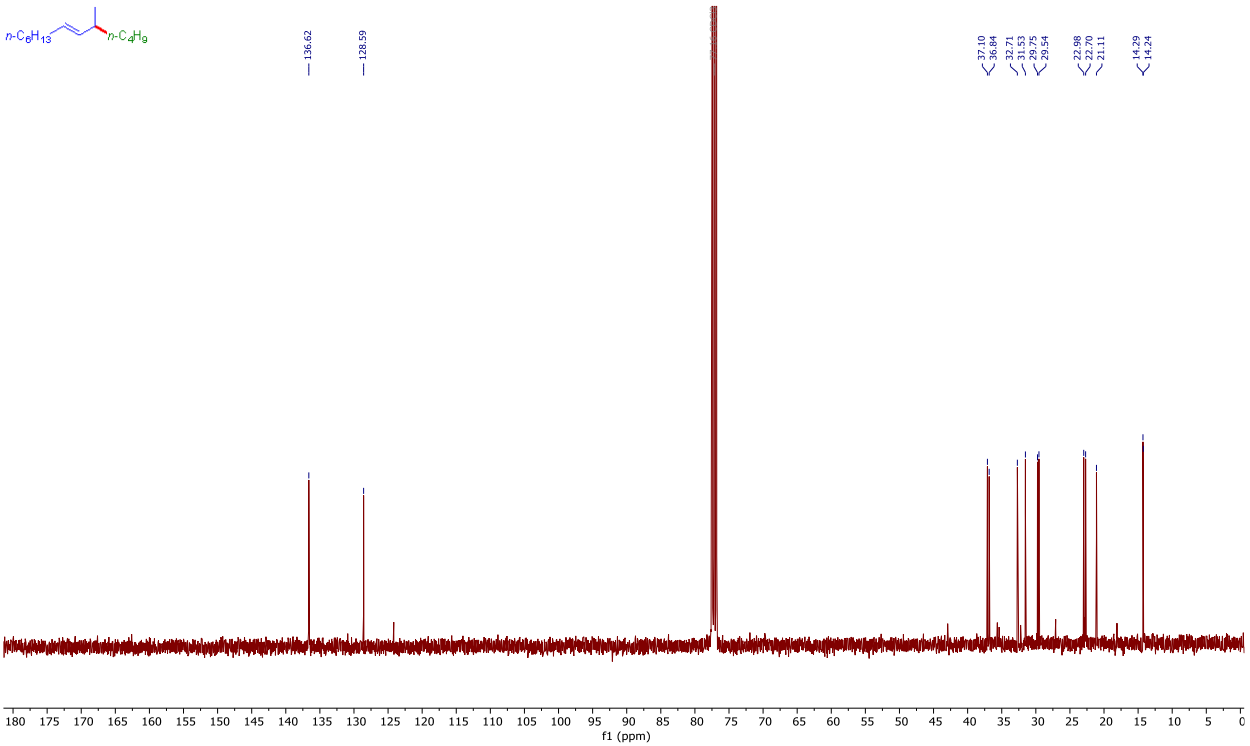
^{13}C NMR (101 MHz, $CDCl_3$), 3c:



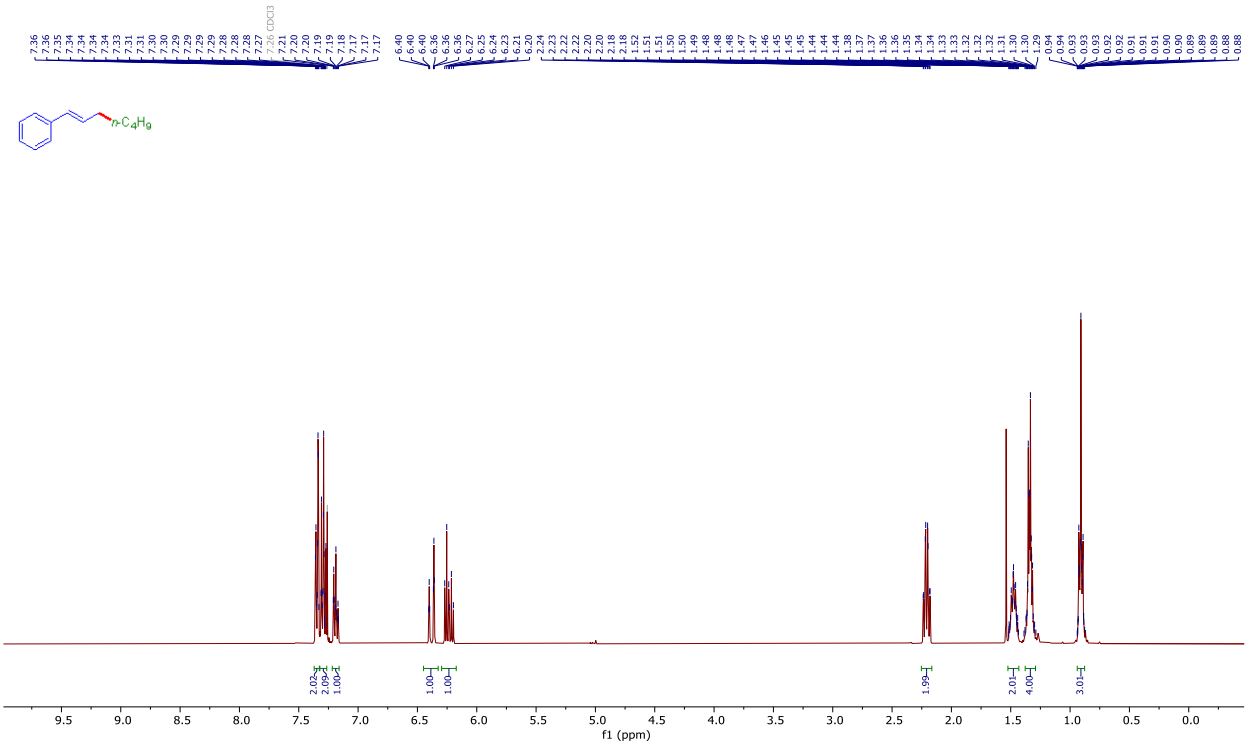
^{1}H NMR (400 MHz, $CDCl_3$), 3d:



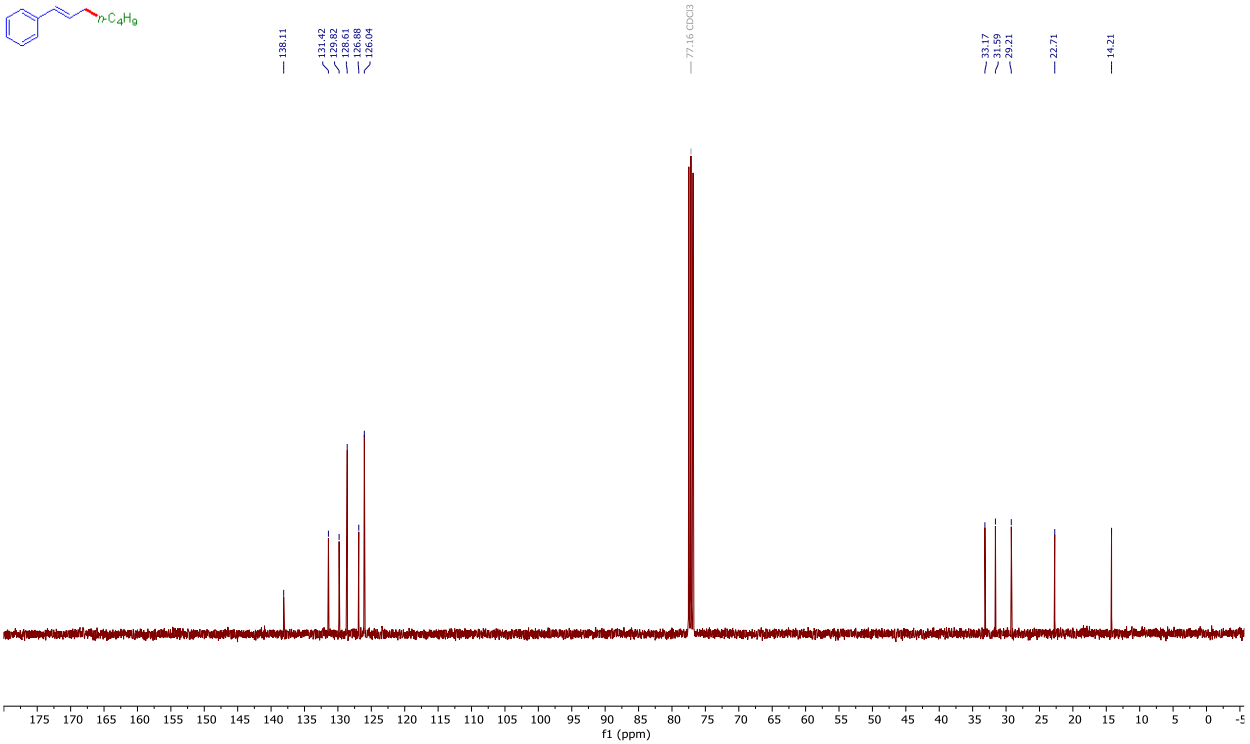
^{13}C NMR (101 MHz, $CDCl_3$), 3d:



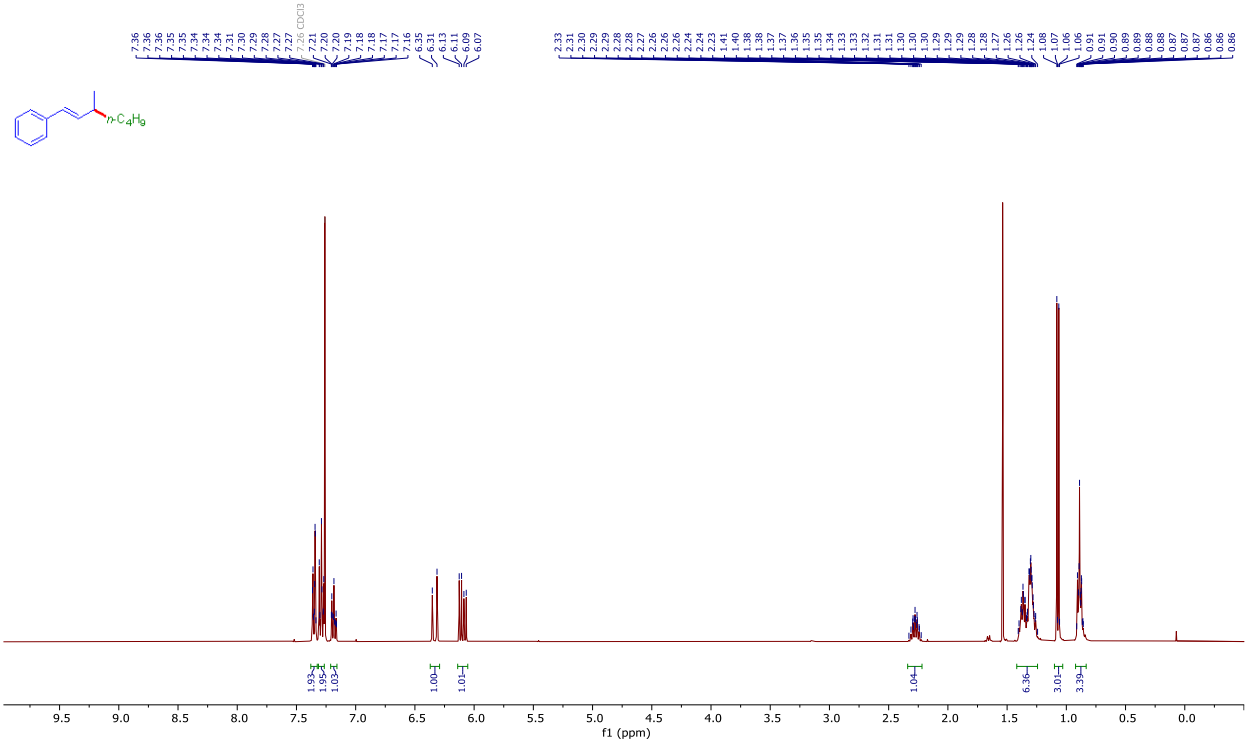
^{1}H NMR (400 MHz, $CDCl_3$), 3e:



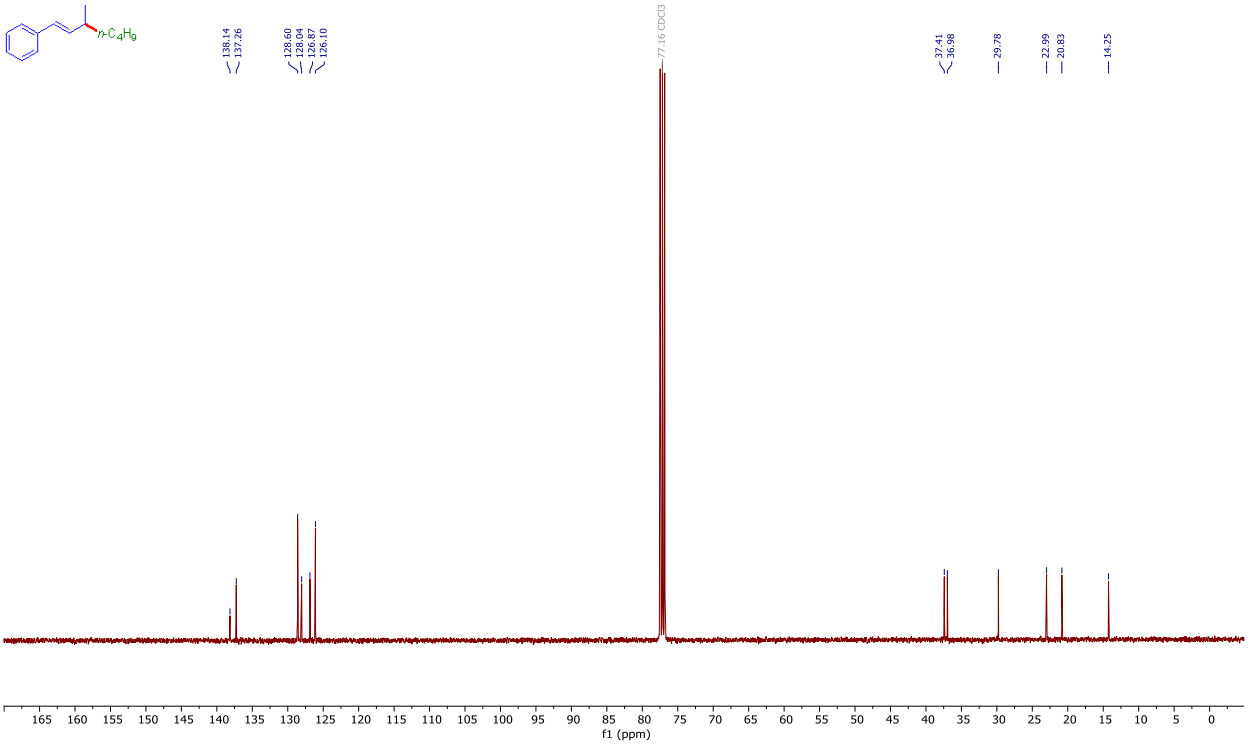
^{13}C NMR (101 MHz, $CDCl_3$), 3e:



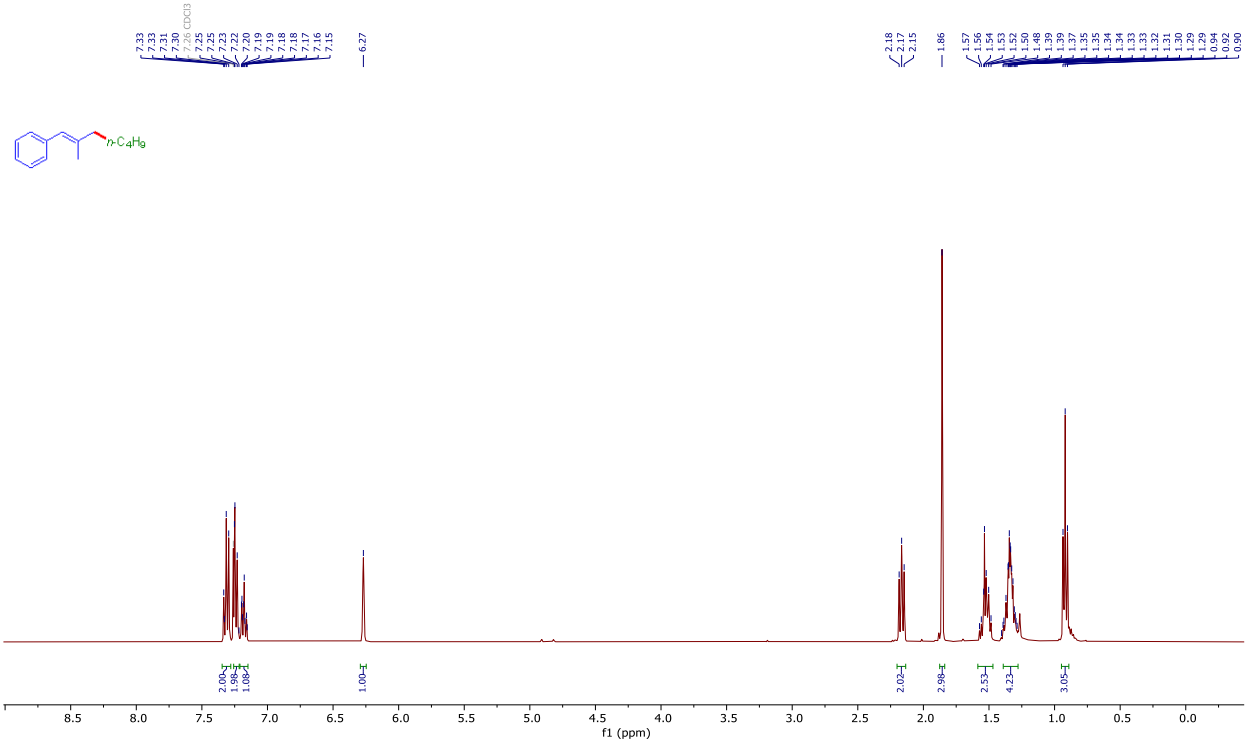
^{1}H NMR (400 MHz, $CDCl_3$), 3f:



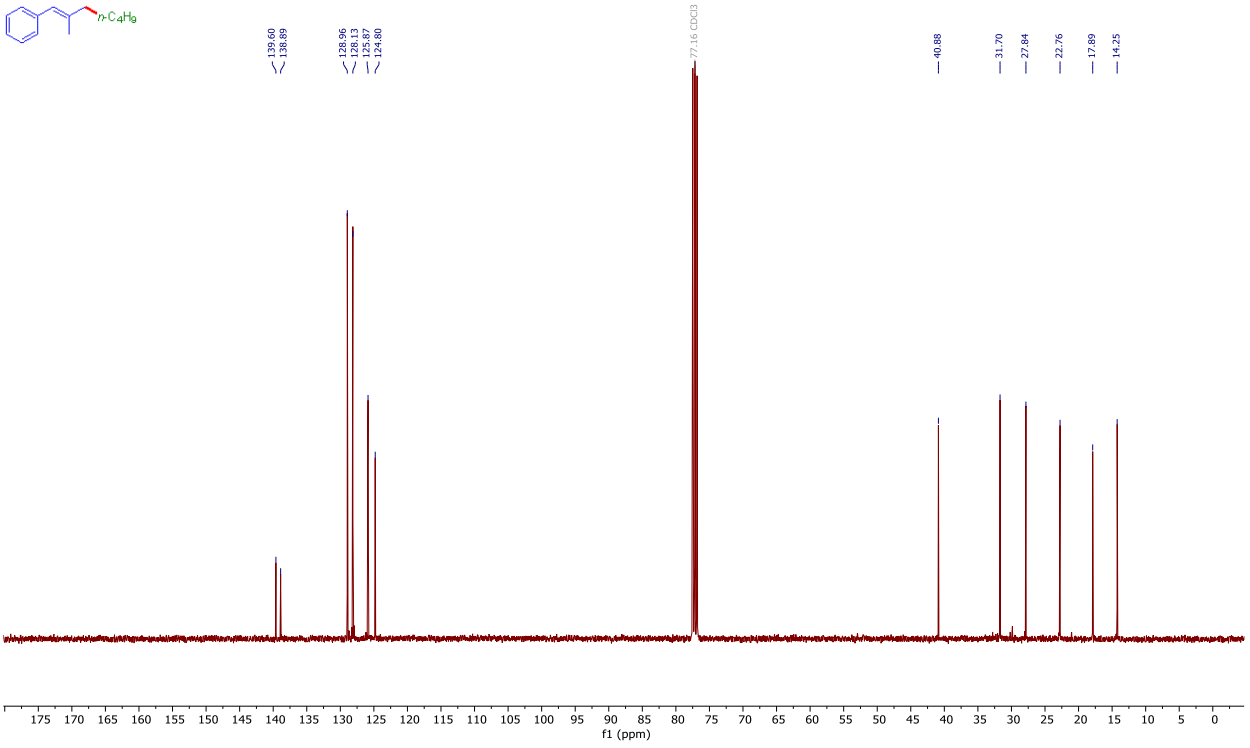
^{13}C NMR (101 MHz, $CDCl_3$), 3f:



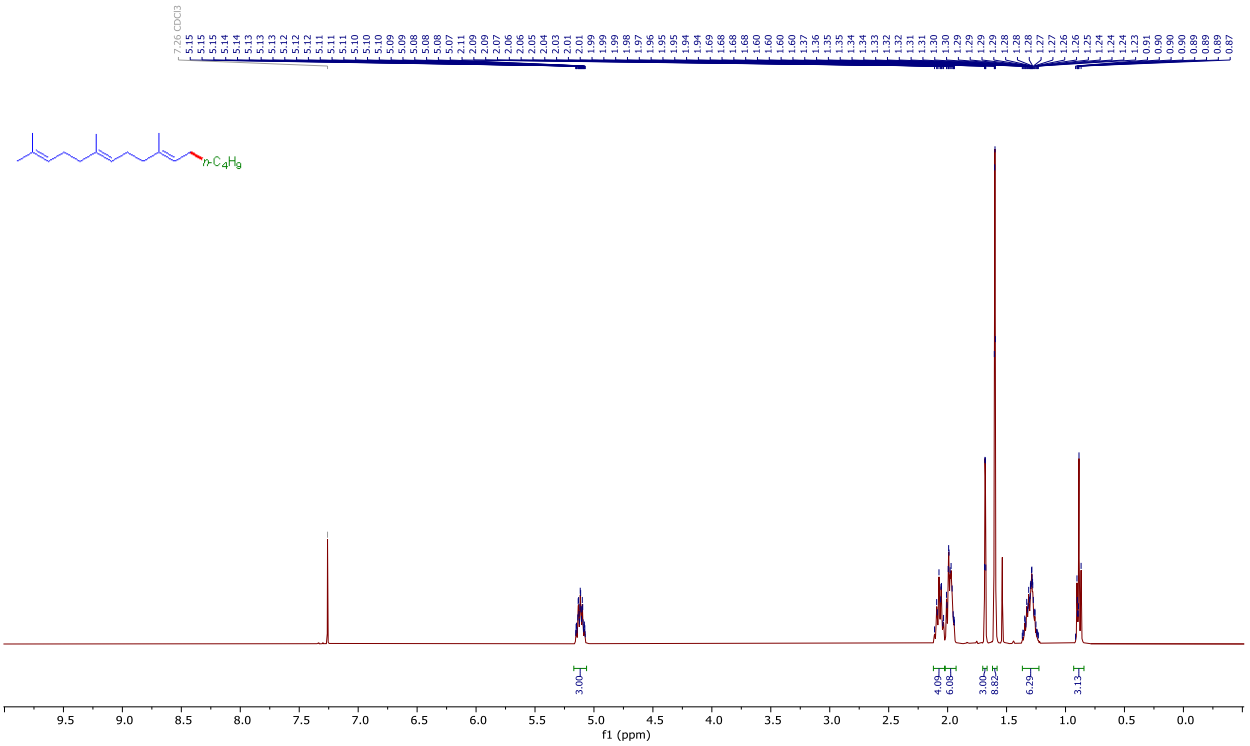
^{1}H NMR (400 MHz, $CDCl_3$), 3g:



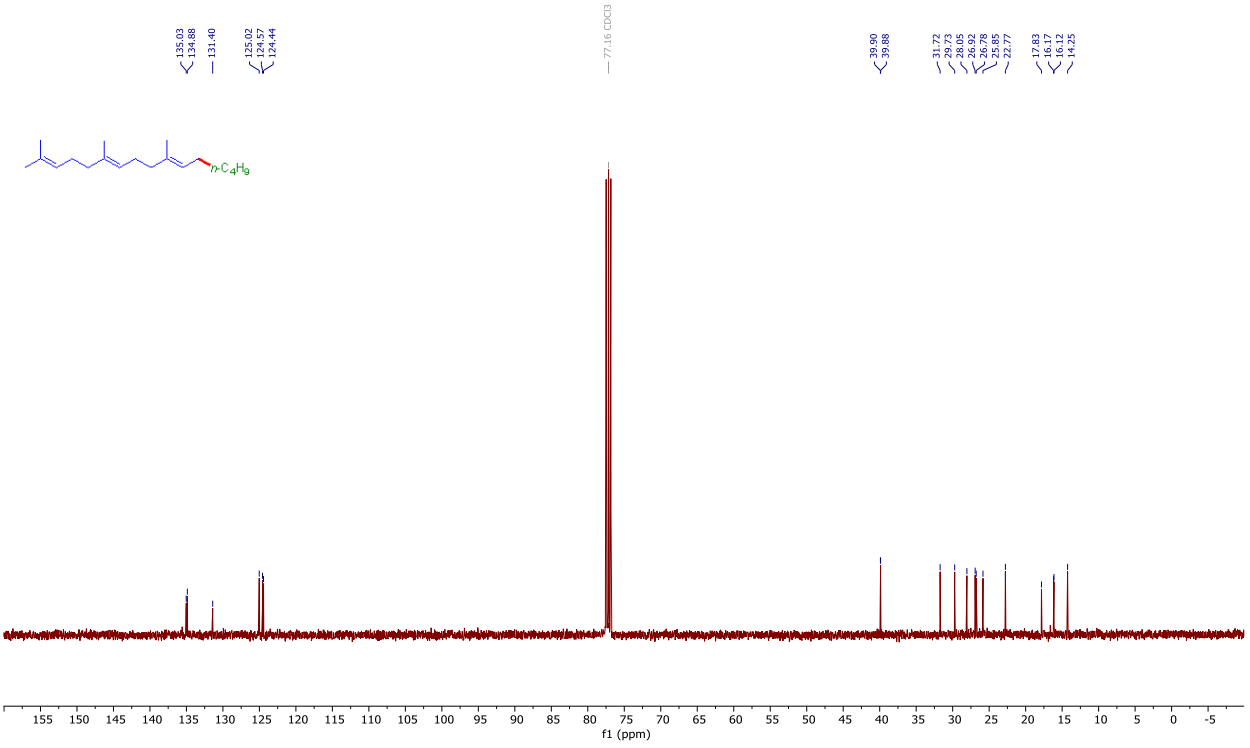
^{13}C NMR (101 MHz, $CDCl_3$), 3g:



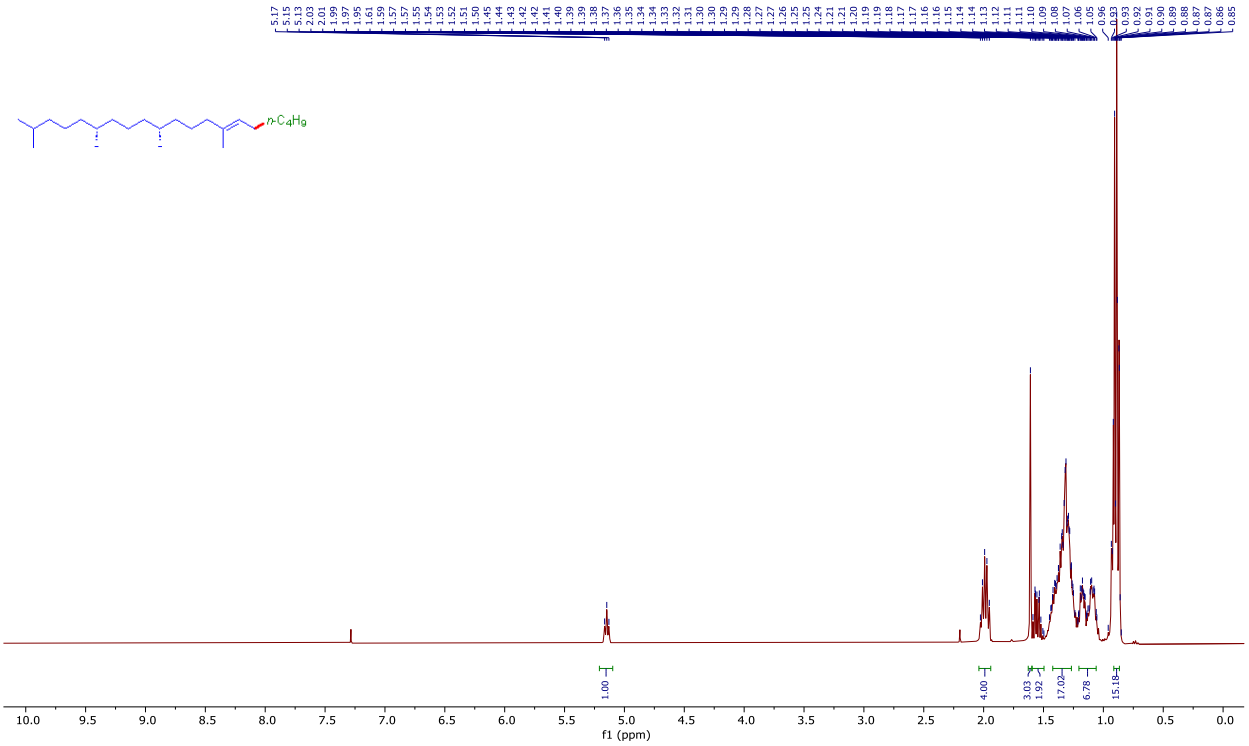
^{1}H NMR (400 MHz, $CDCl_3$), 3h:



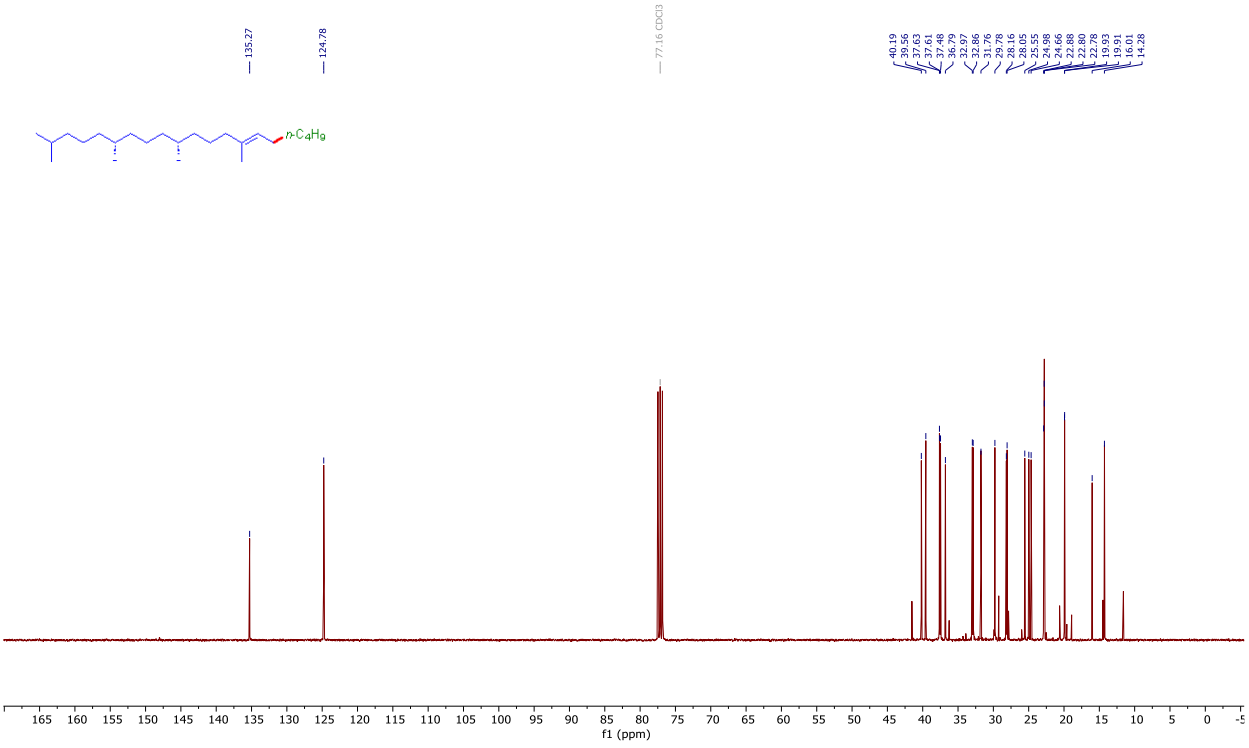
^{13}C NMR (101 MHz, $CDCl_3$), 3h:



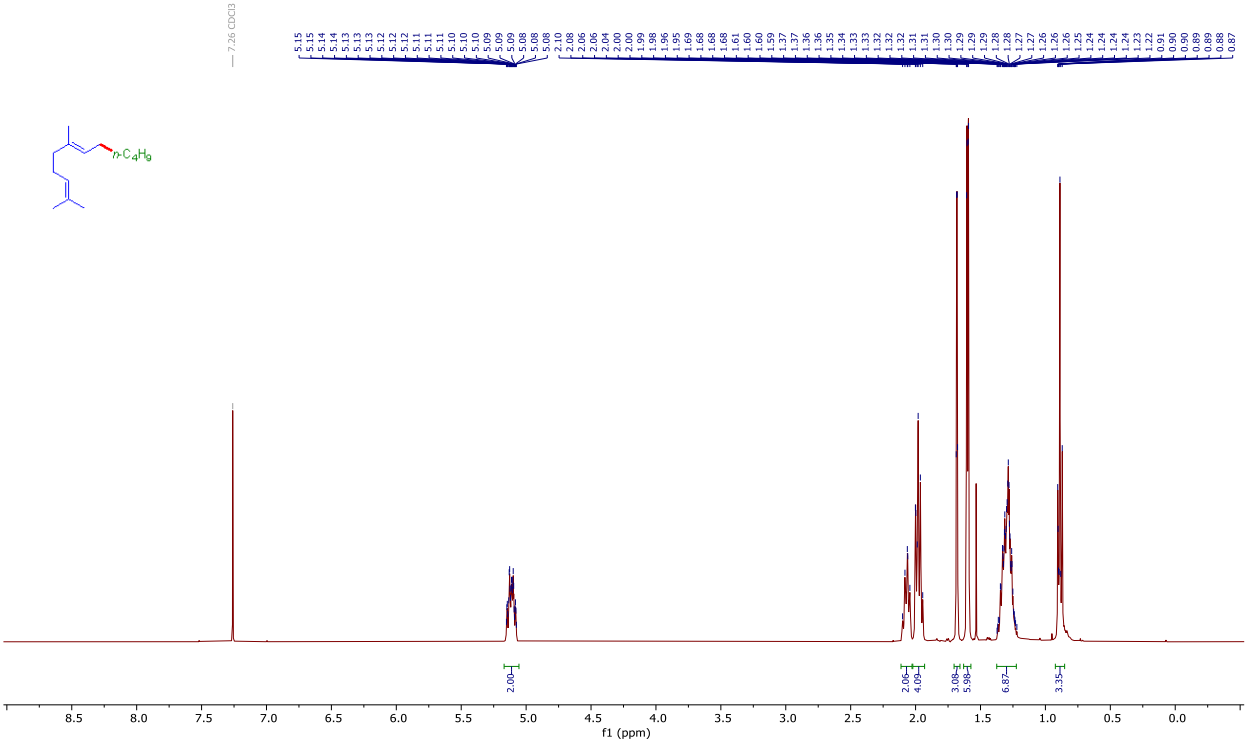
^{1}H NMR (400 MHz, $CDCl_3$), 3i:



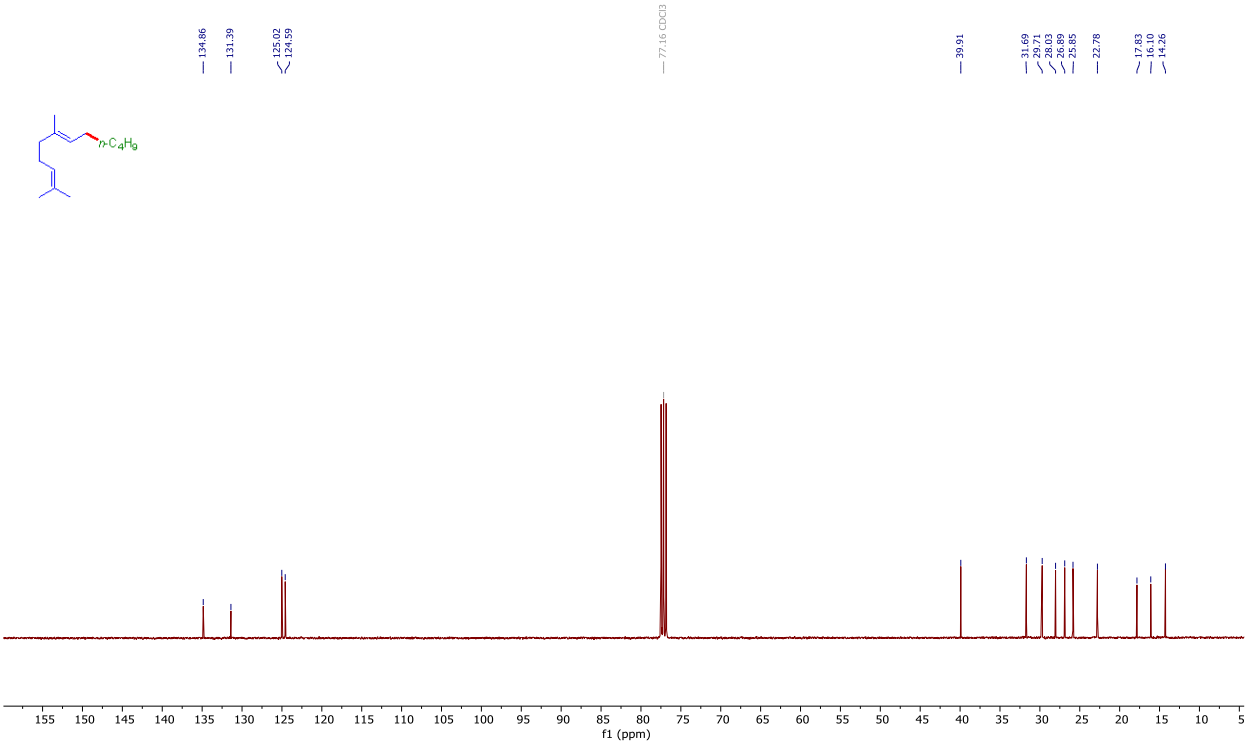
^{13}C NMR (101 MHz, $CDCl_3$), 3i:



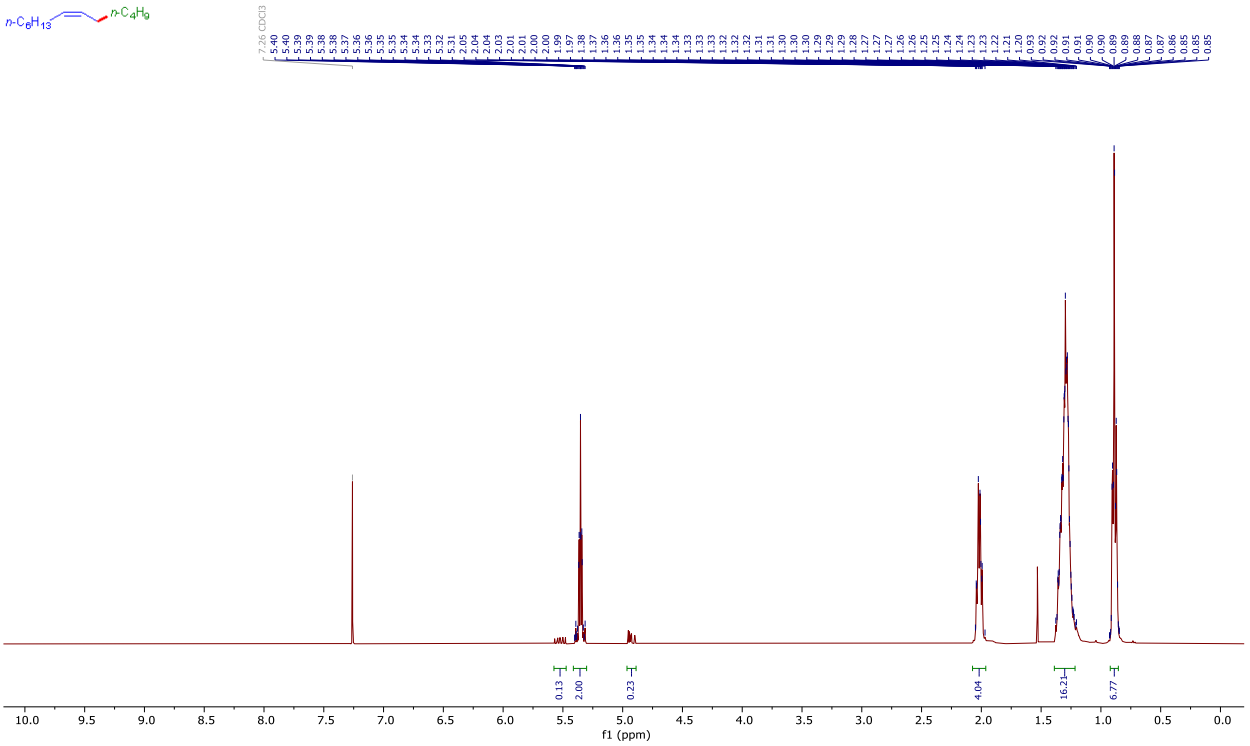
^{1}H NMR (400 MHz, $CDCl_3$), 3j:



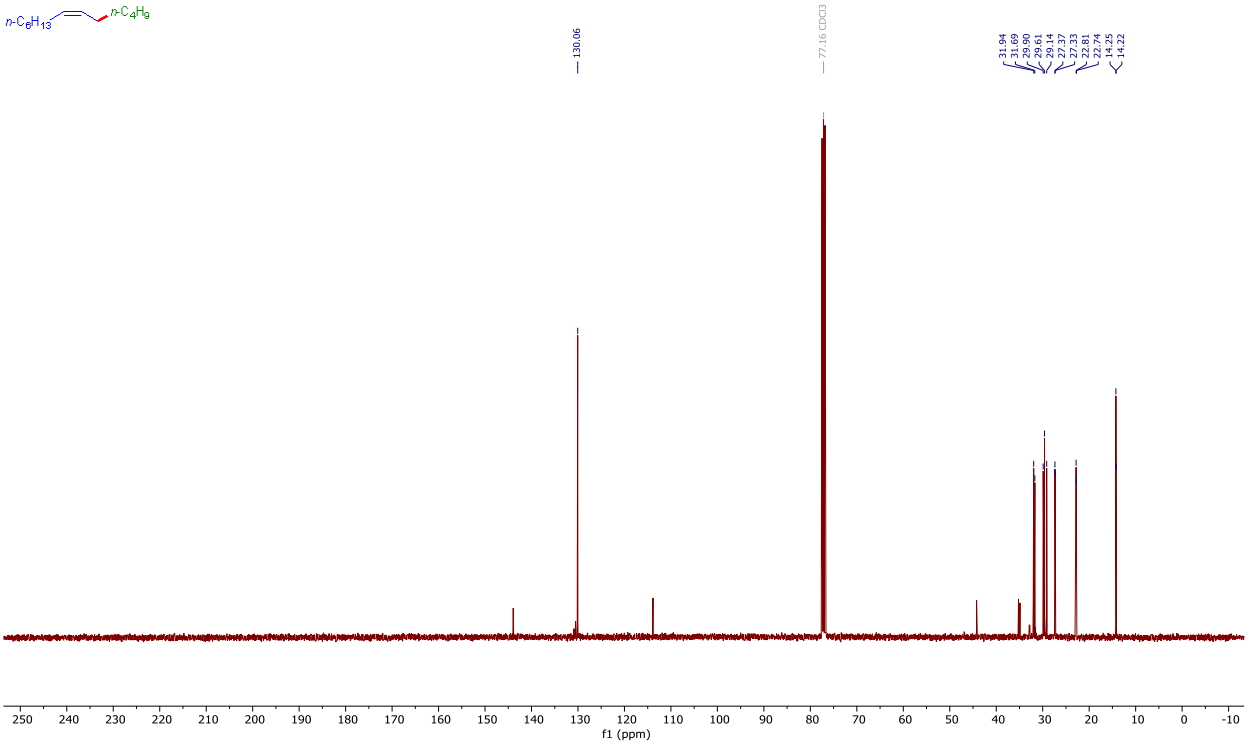
^{13}C NMR (101 MHz, $CDCl_3$), 3j:



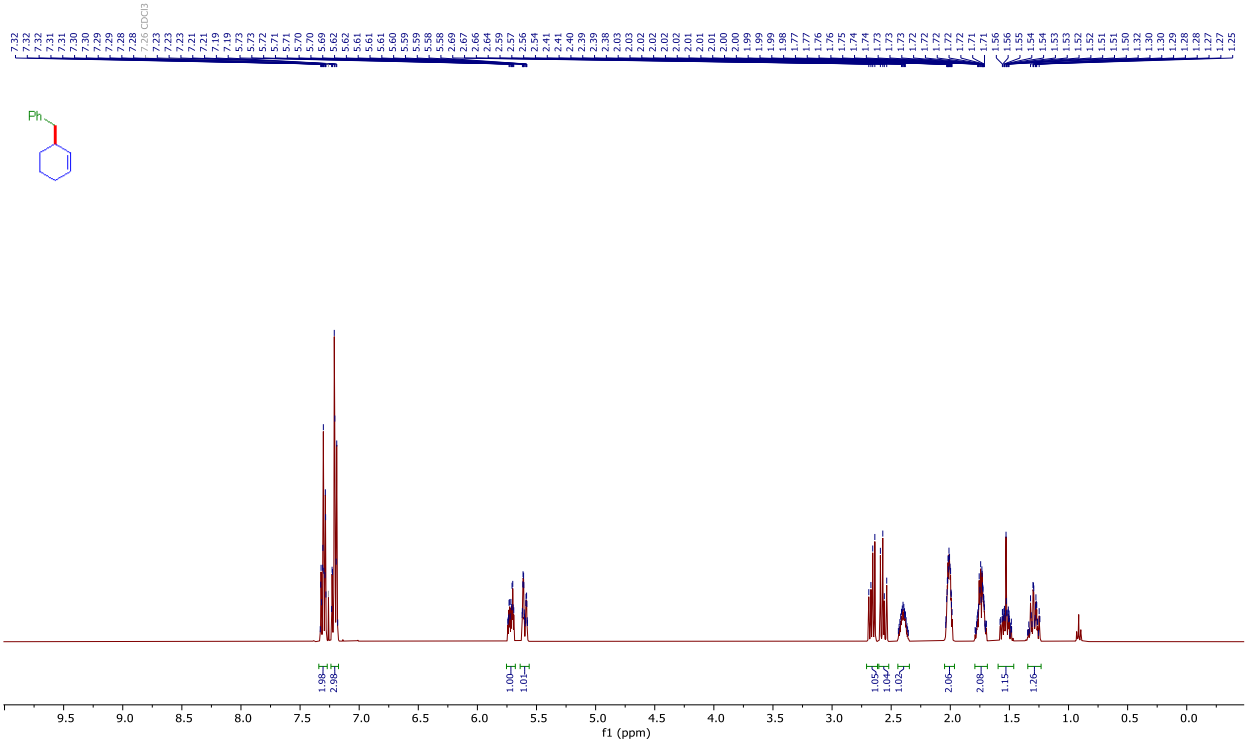
^{1}H NMR (400 MHz, $CDCl_3$), 3k:



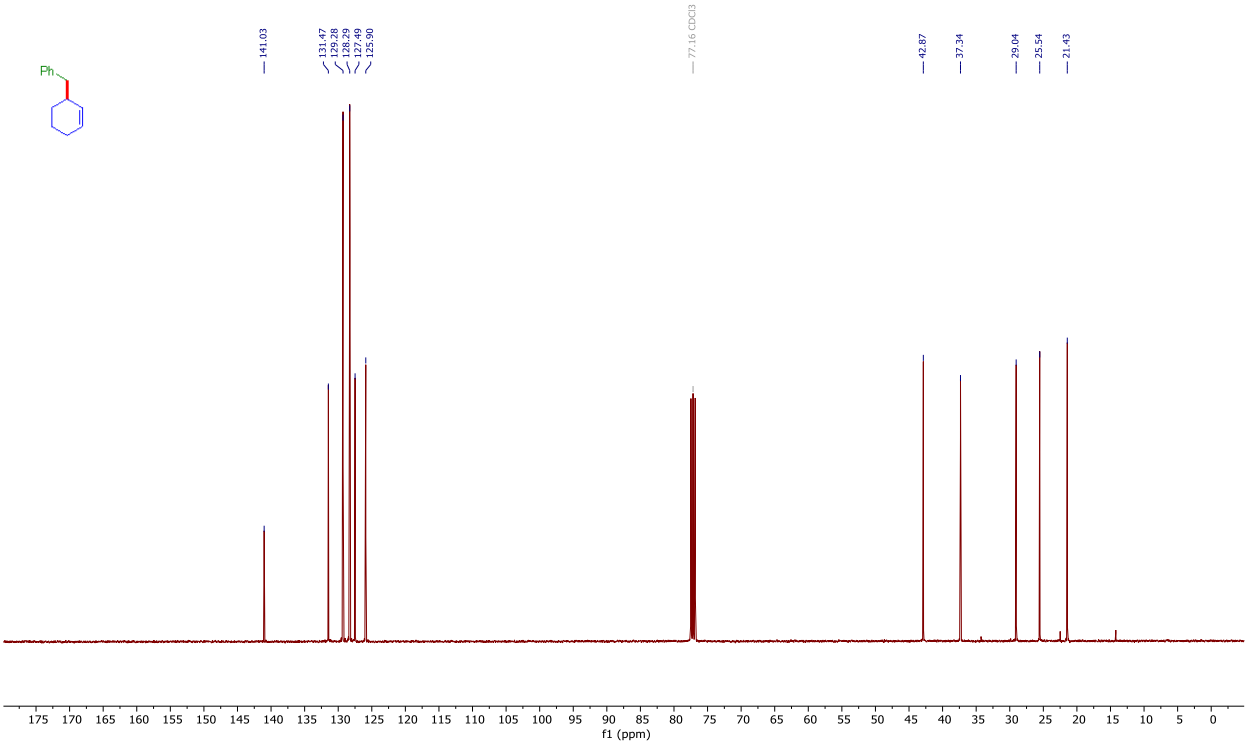
^{13}C NMR (101 MHz, $CDCl_3$), 3k:



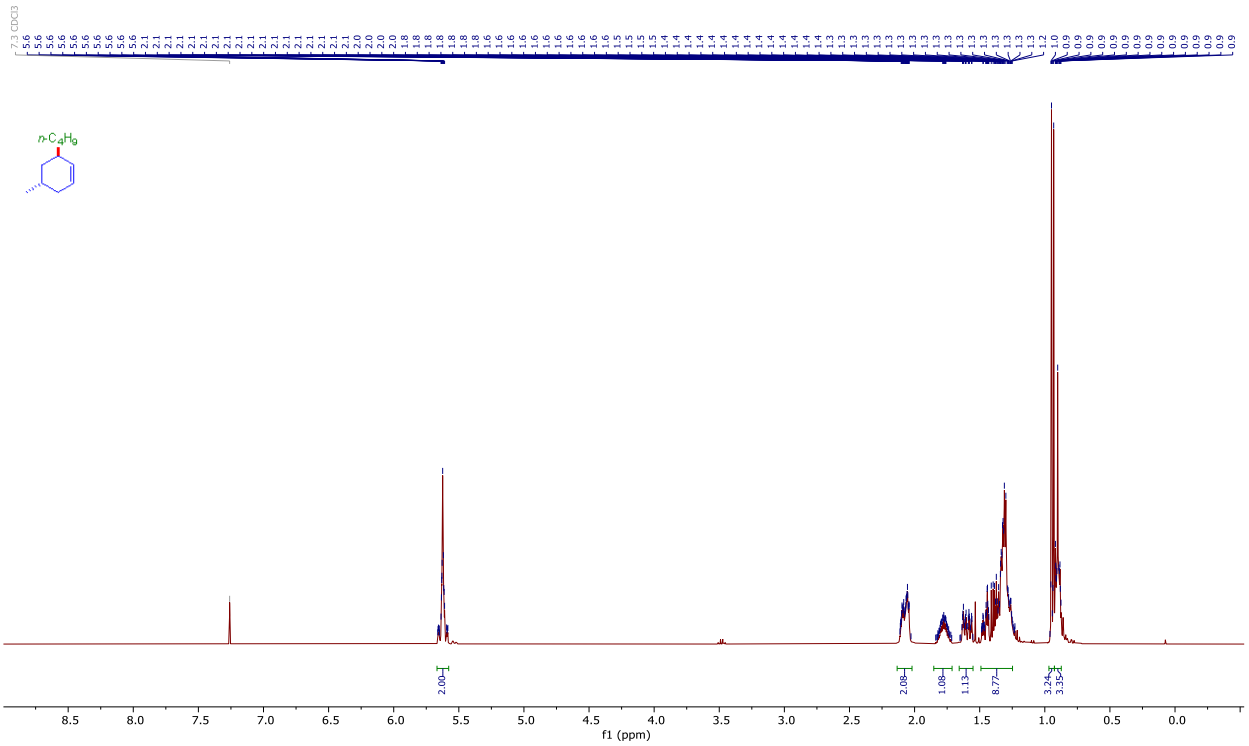
^{1}H NMR (400 MHz, $CDCl_3$), 3l:



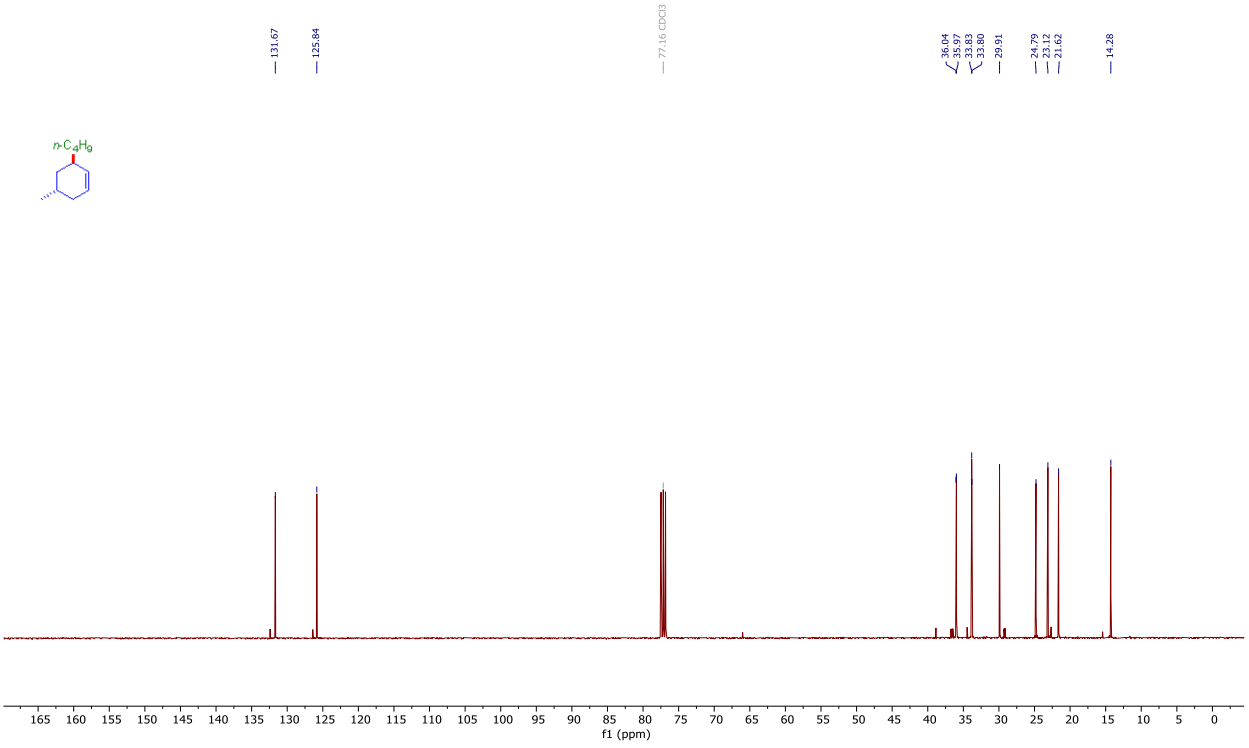
^{13}C NMR (101 MHz, $CDCl_3$), 3l:



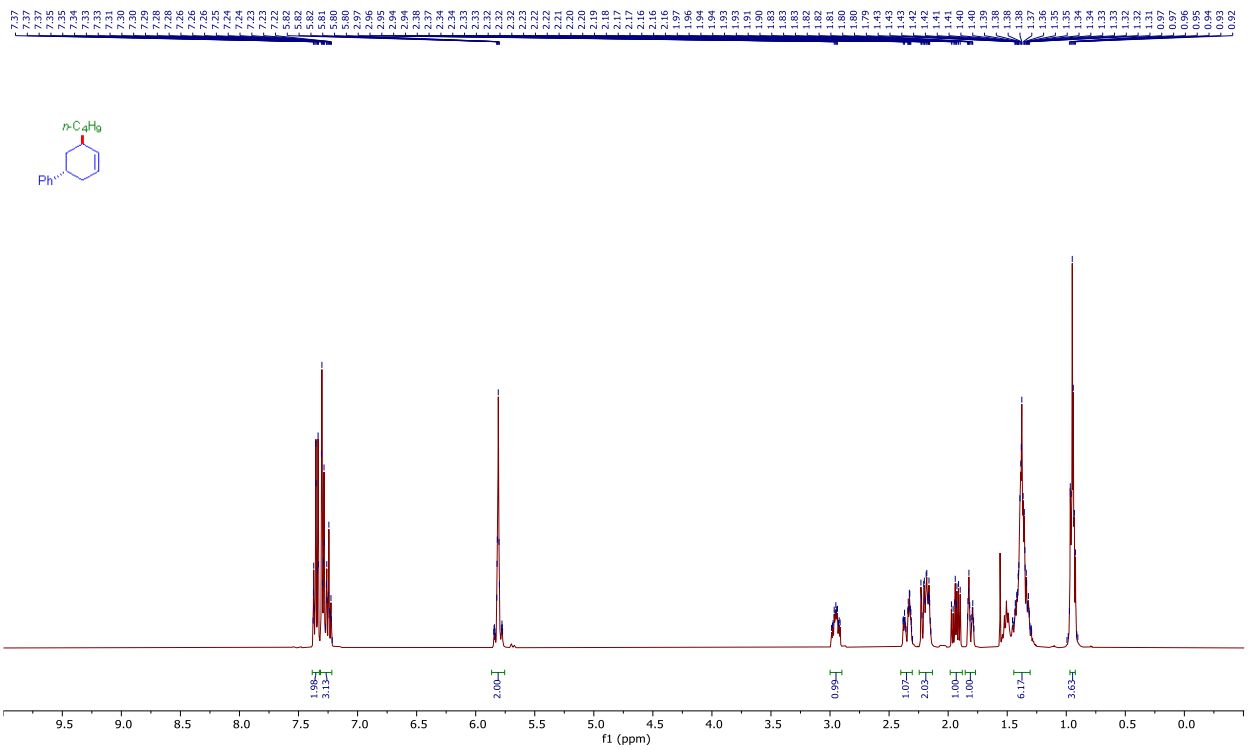
^{1}H NMR (400 MHz, $CDCl_3$), 3m:



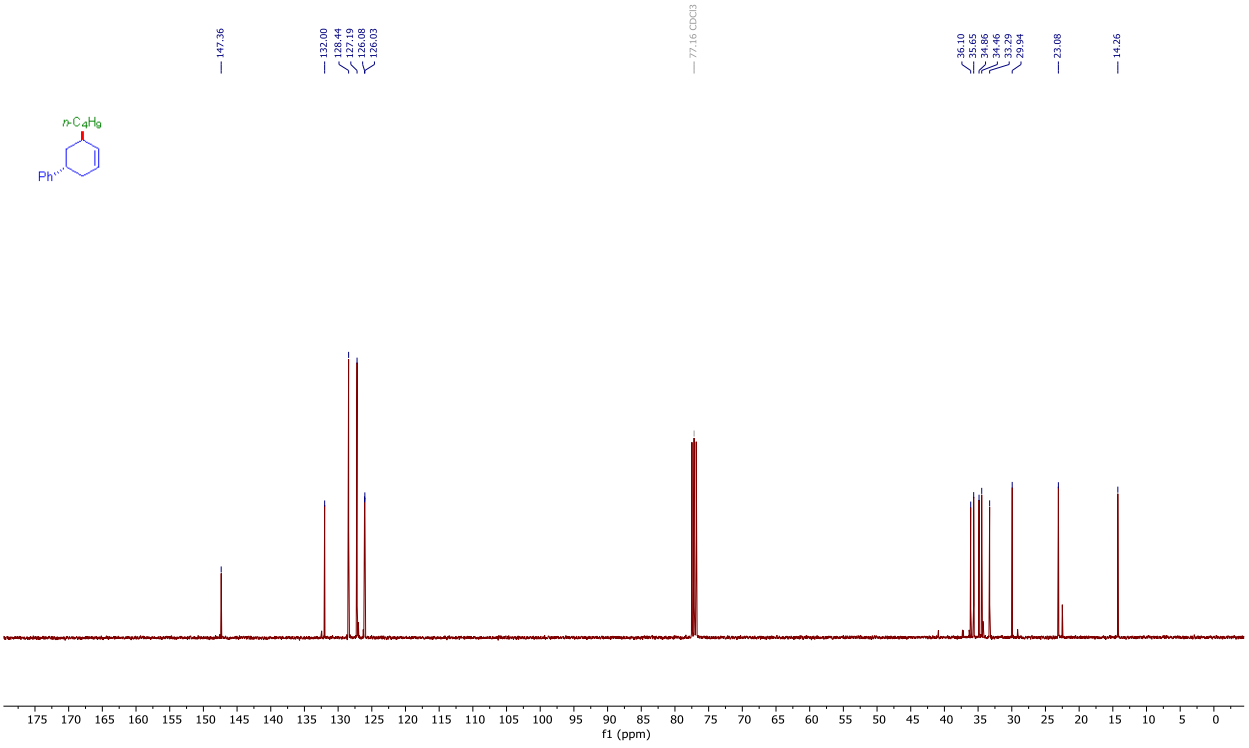
^{13}C NMR (101 MHz, $CDCl_3$), 3m:



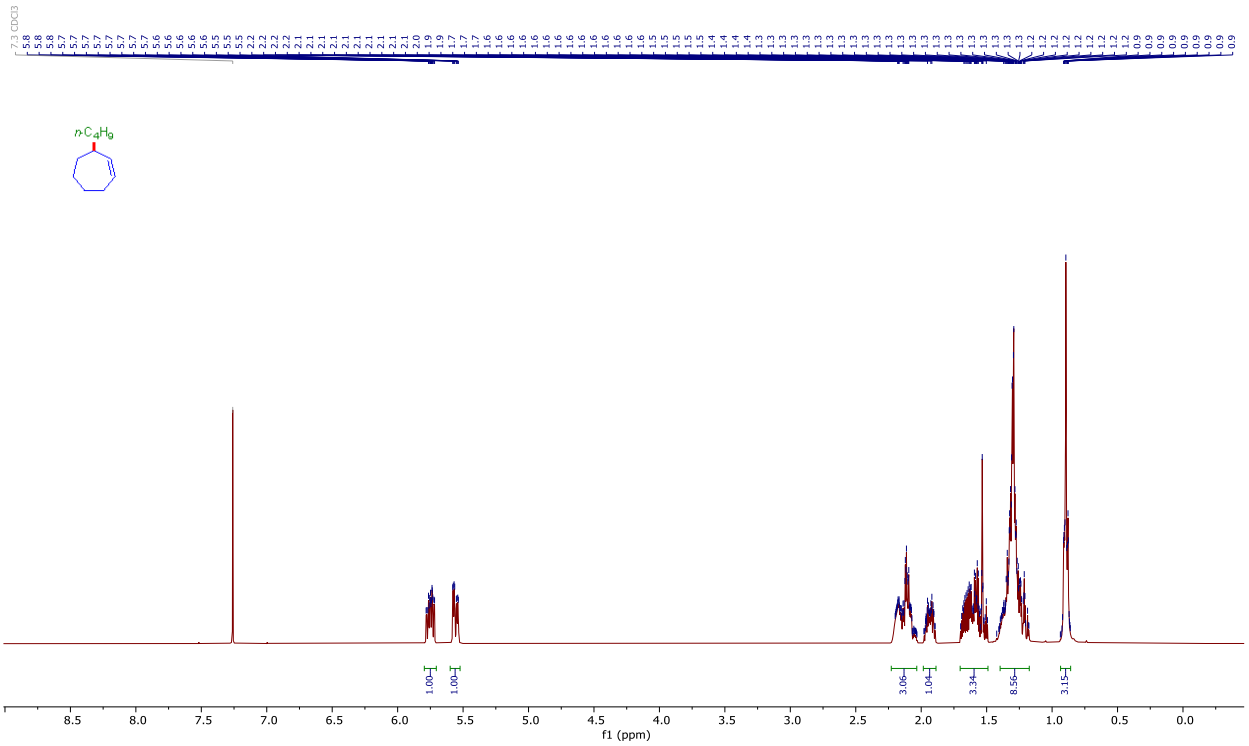
^{1}H NMR (400 MHz, $CDCl_3$), 3n:



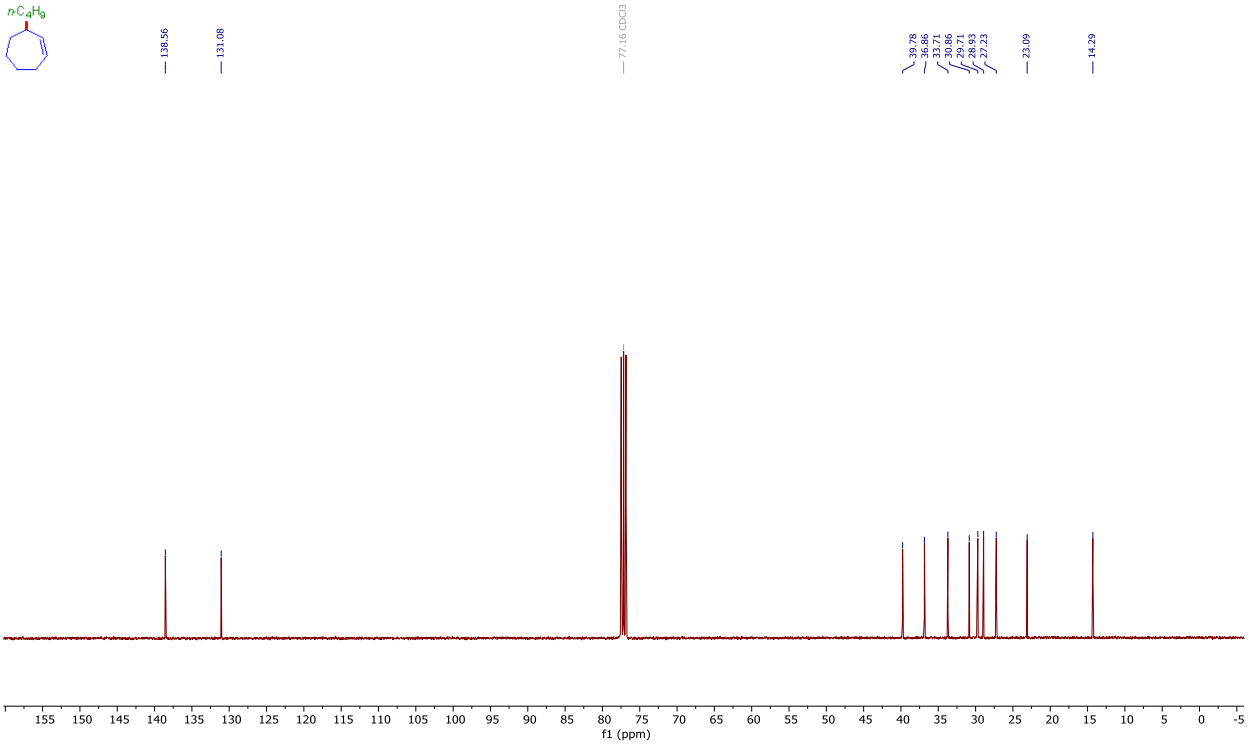
^{13}C NMR (101 MHz, $CDCl_3$), 3n:



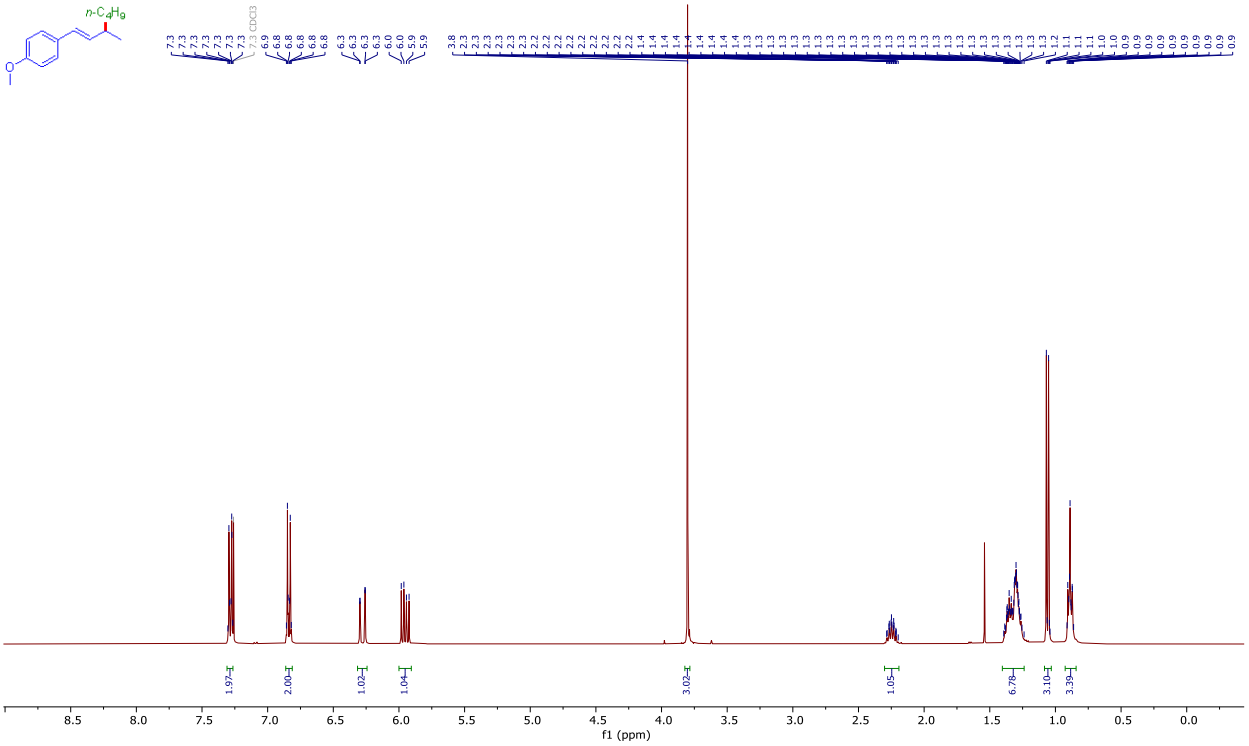
^{1}H NMR (400 MHz, $CDCl_3$), 3o:



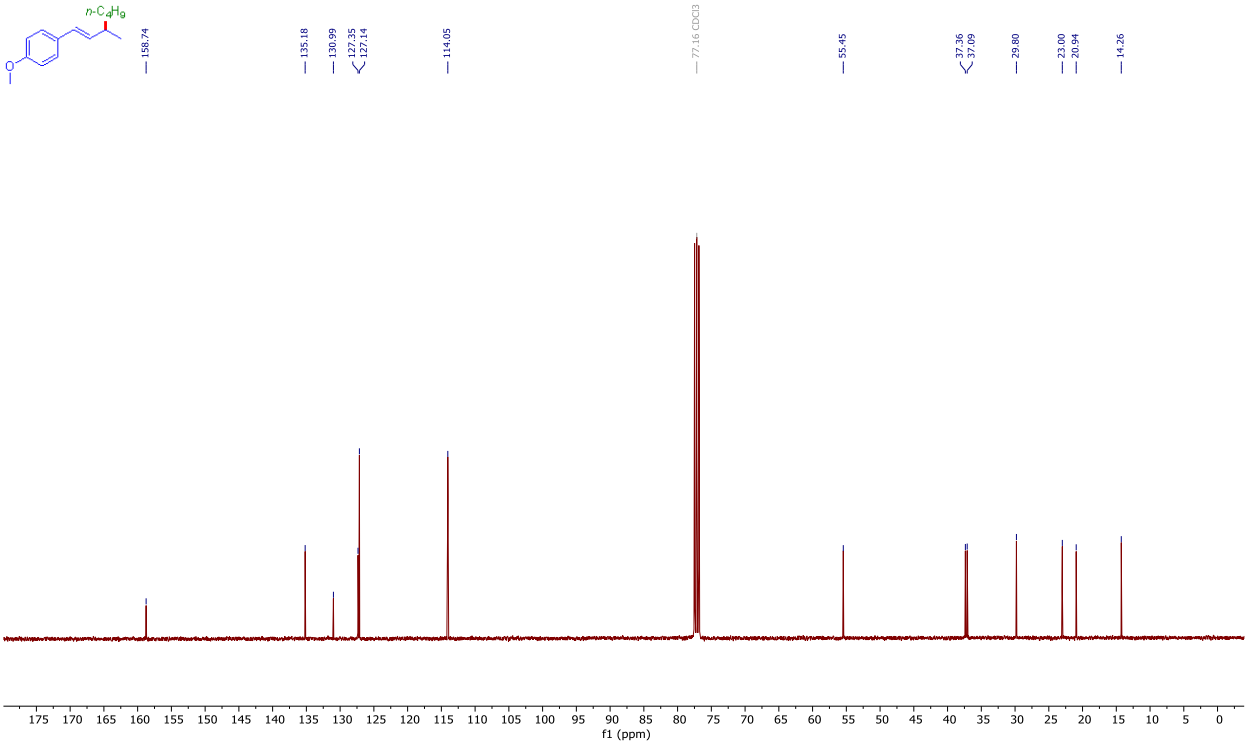
^{13}C NMR (101 MHz, $CDCl_3$), 3o:



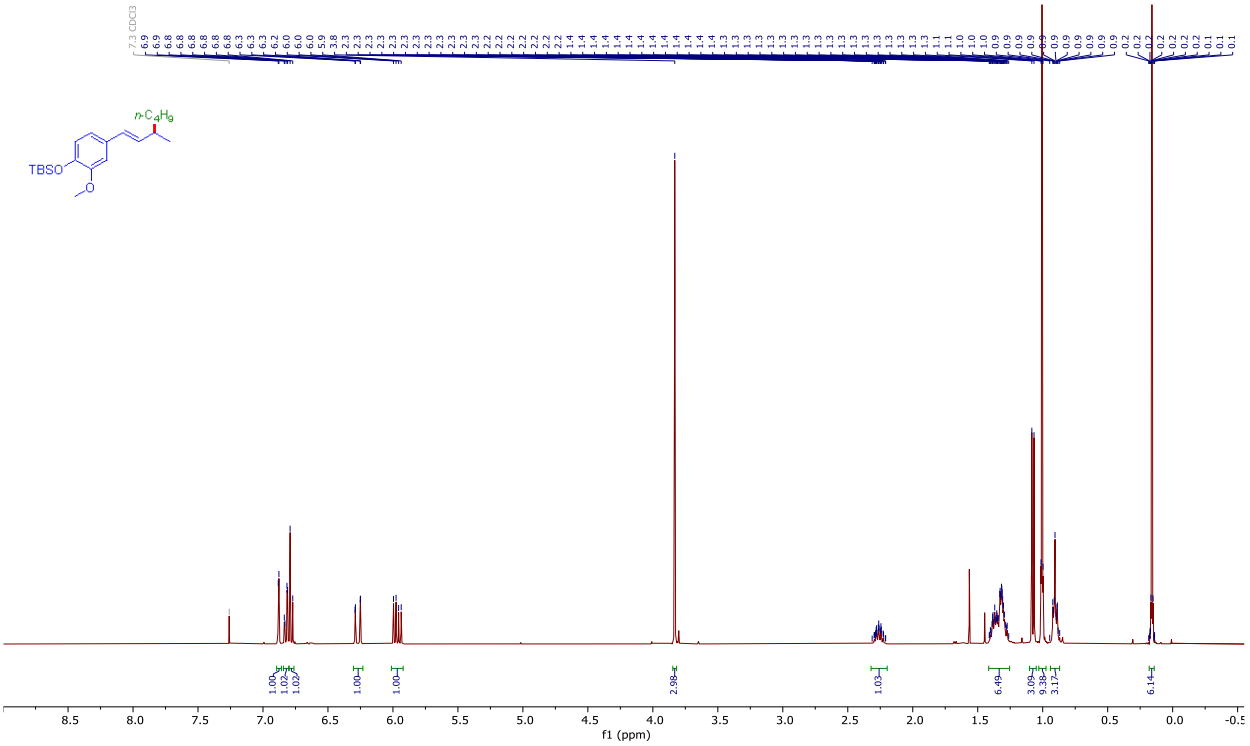
^{1}H NMR (400 MHz, $CDCl_3$), 3p:



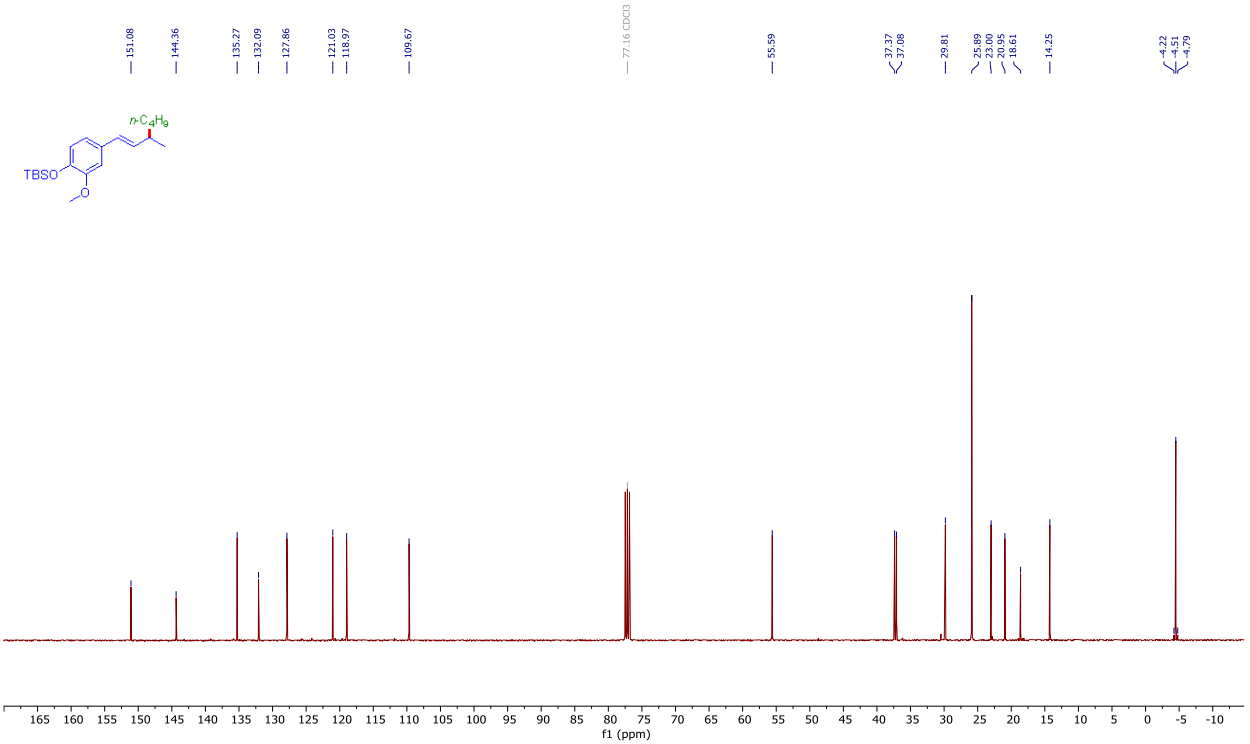
^{13}C NMR (101 MHz, $CDCl_3$), 3p:



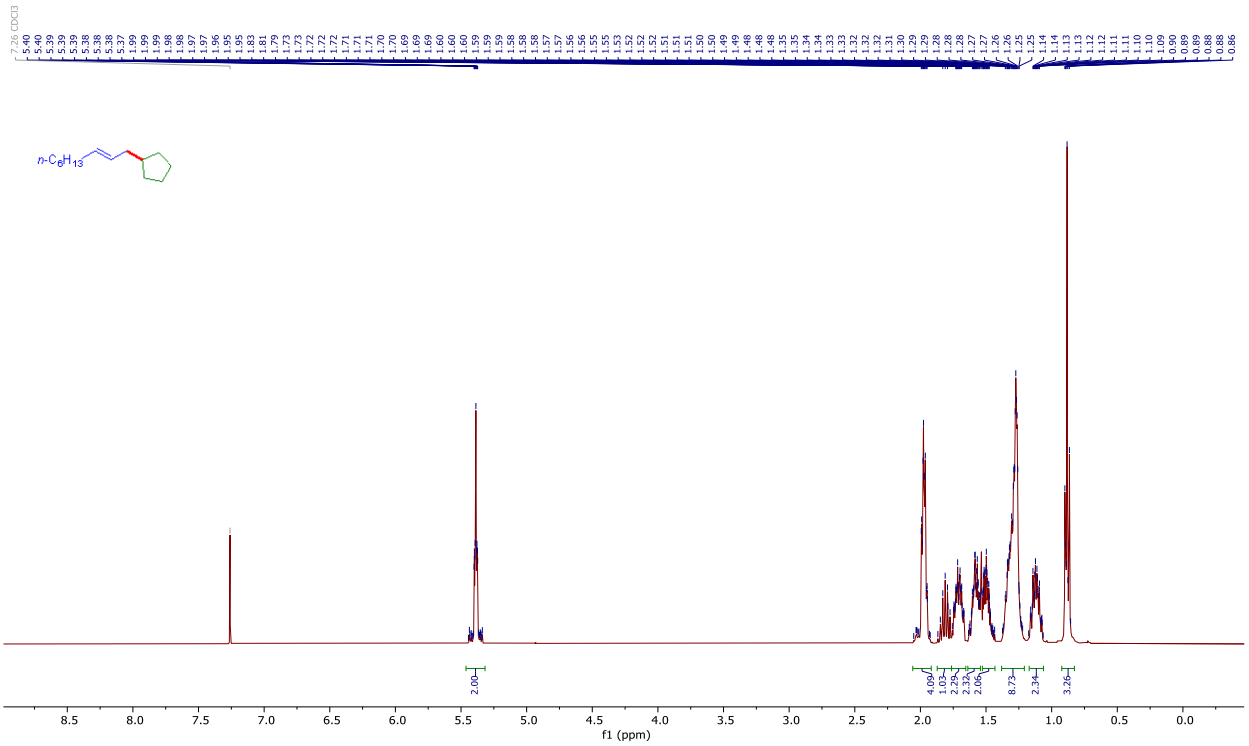
^{1}H NMR (400 MHz, $CDCl_3$), 3q:



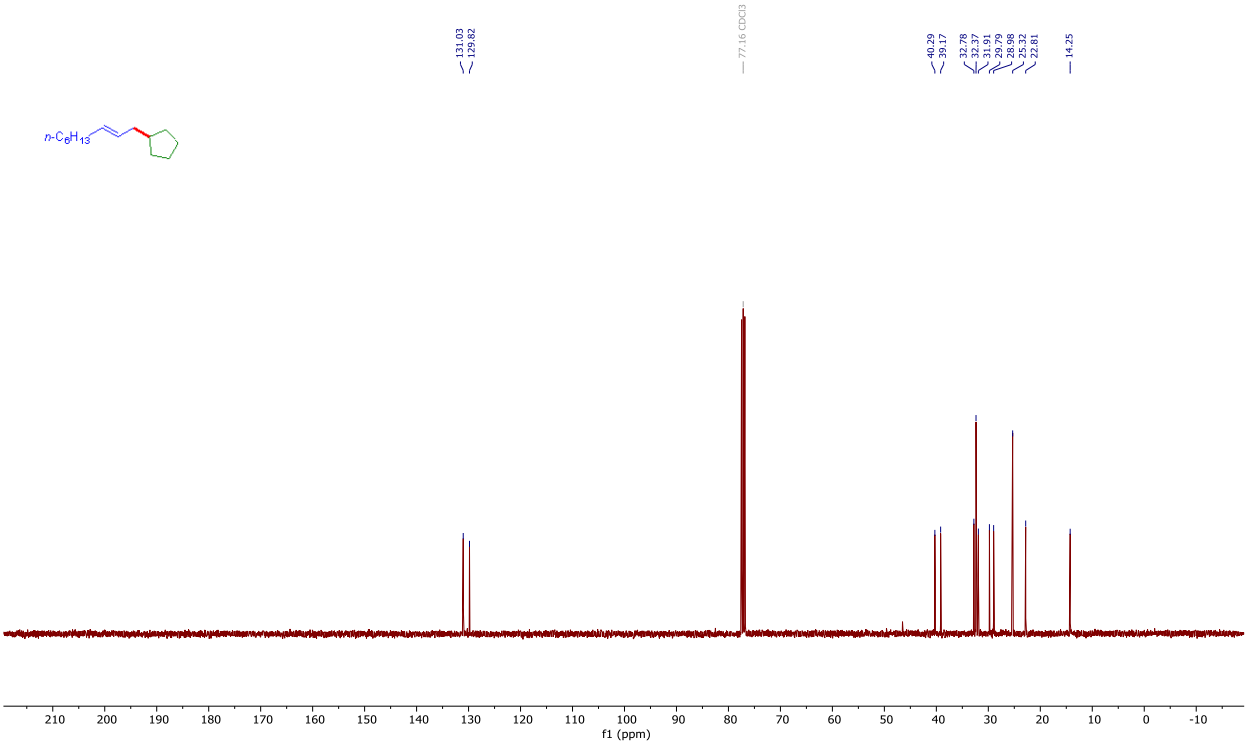
^{13}C NMR (101 MHz, $CDCl_3$), 3q:



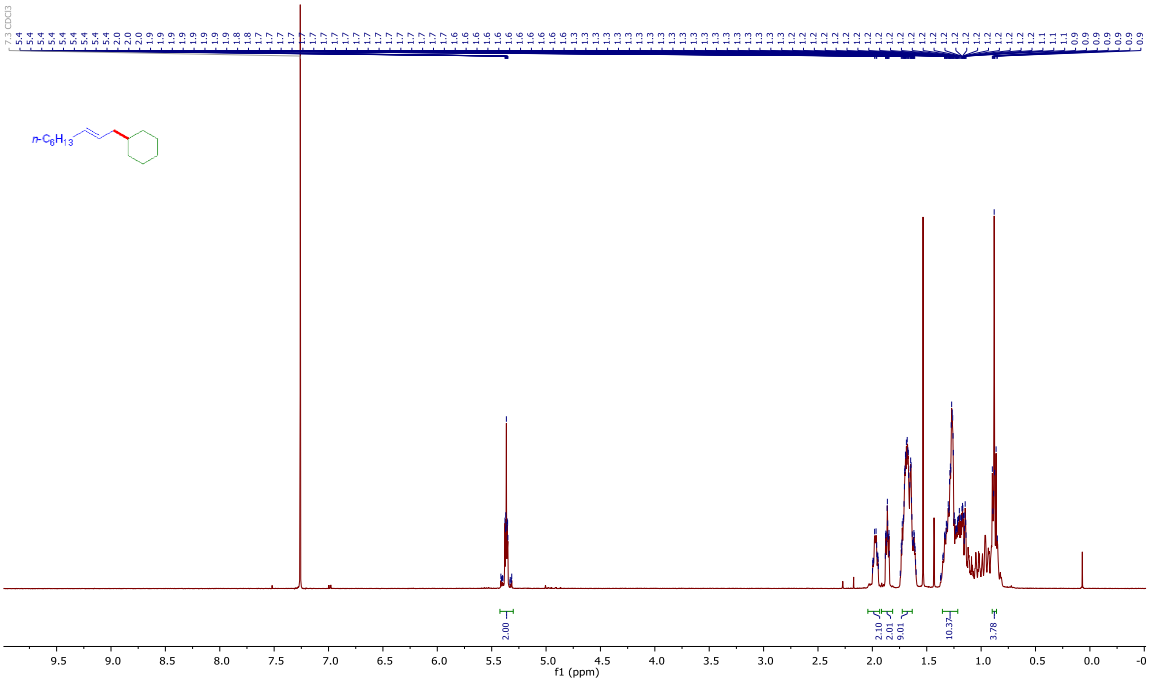
^{1}H NMR (400 MHz, $CDCl_3$), 3r:



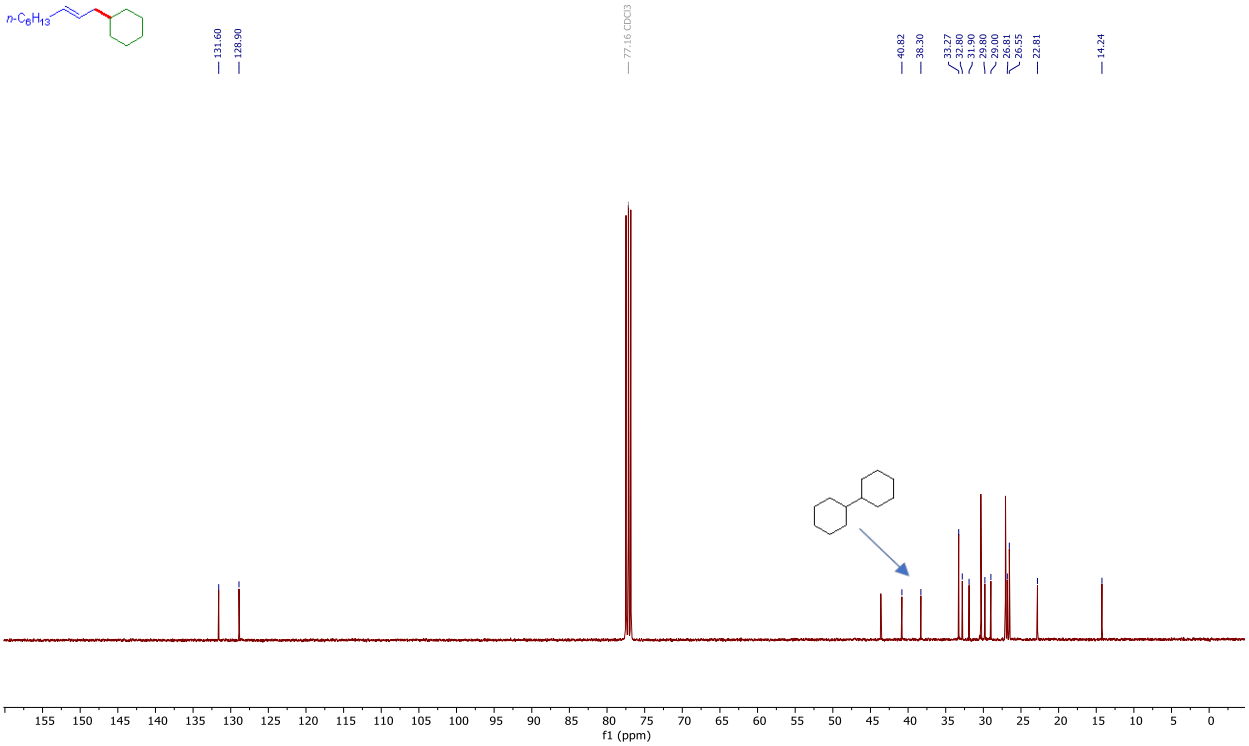
^{13}C NMR (101 MHz, $CDCl_3$), 3r:



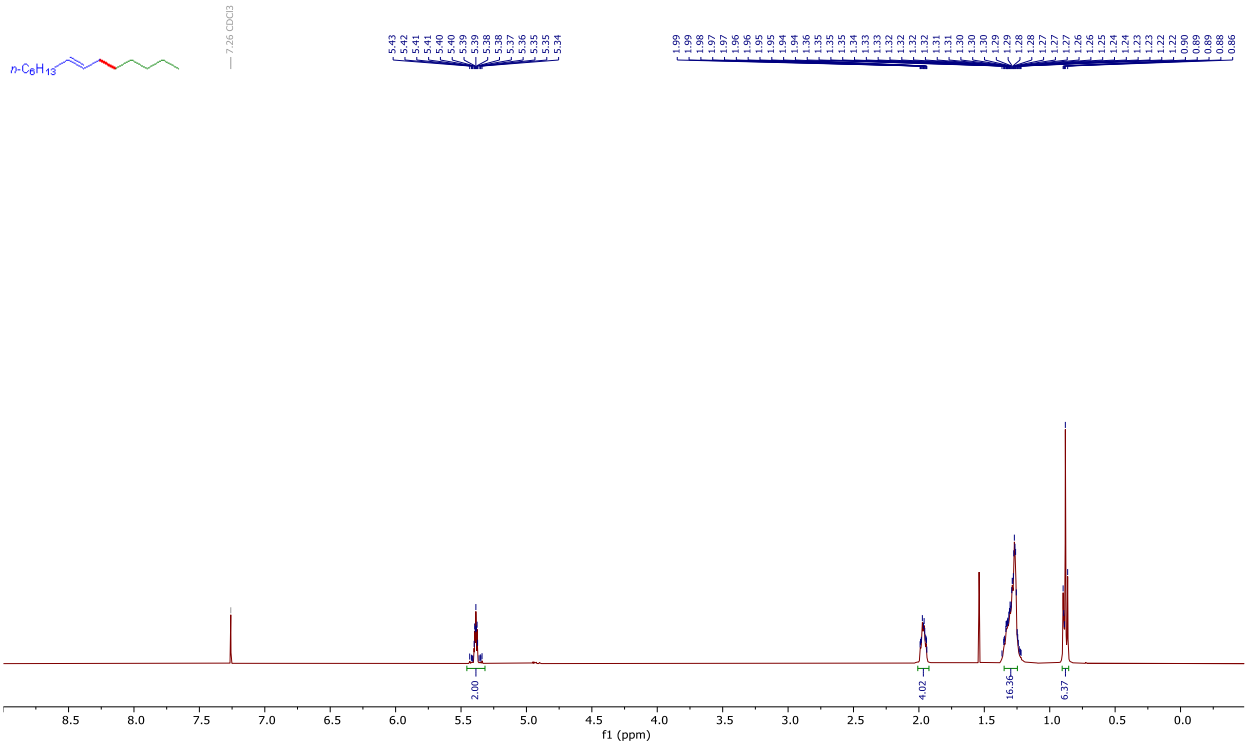
^{1}H NMR (400 MHz, $CDCl_3$), 3s:



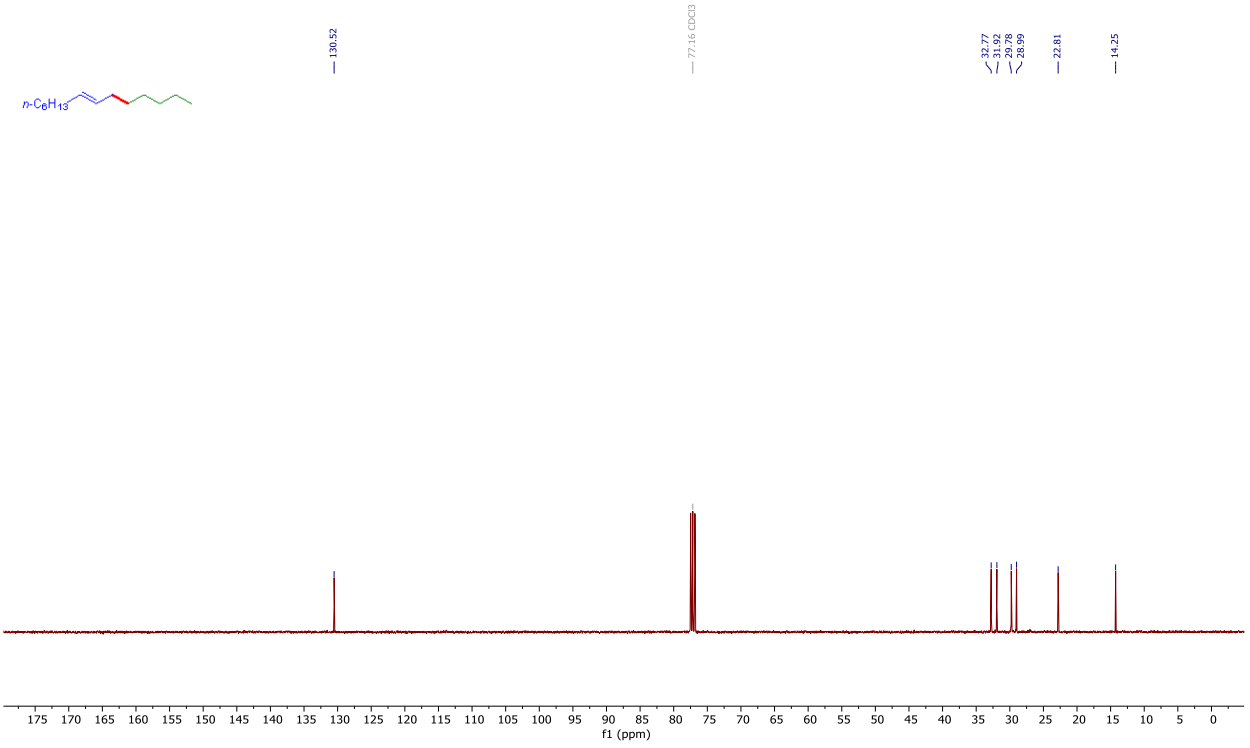
^{13}C NMR (101 MHz, $CDCl_3$), 3s:



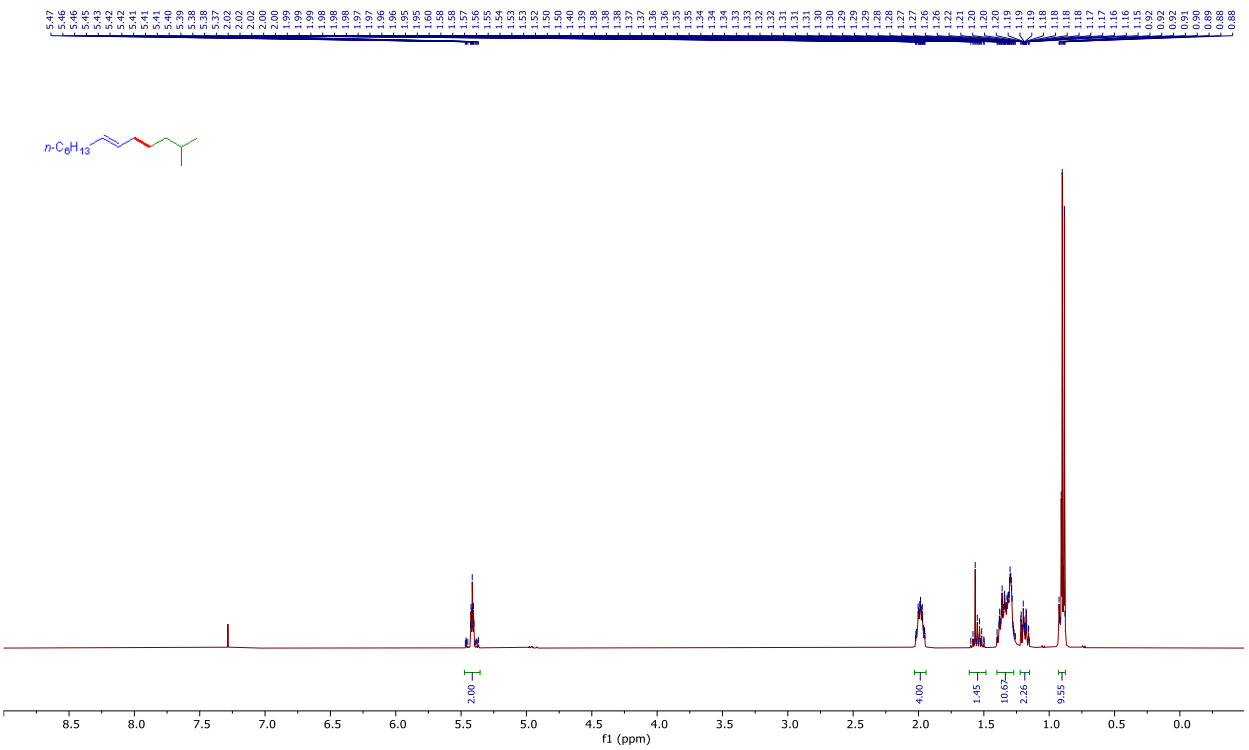
^{1}H NMR (400 MHz, $CDCl_3$), 3t:



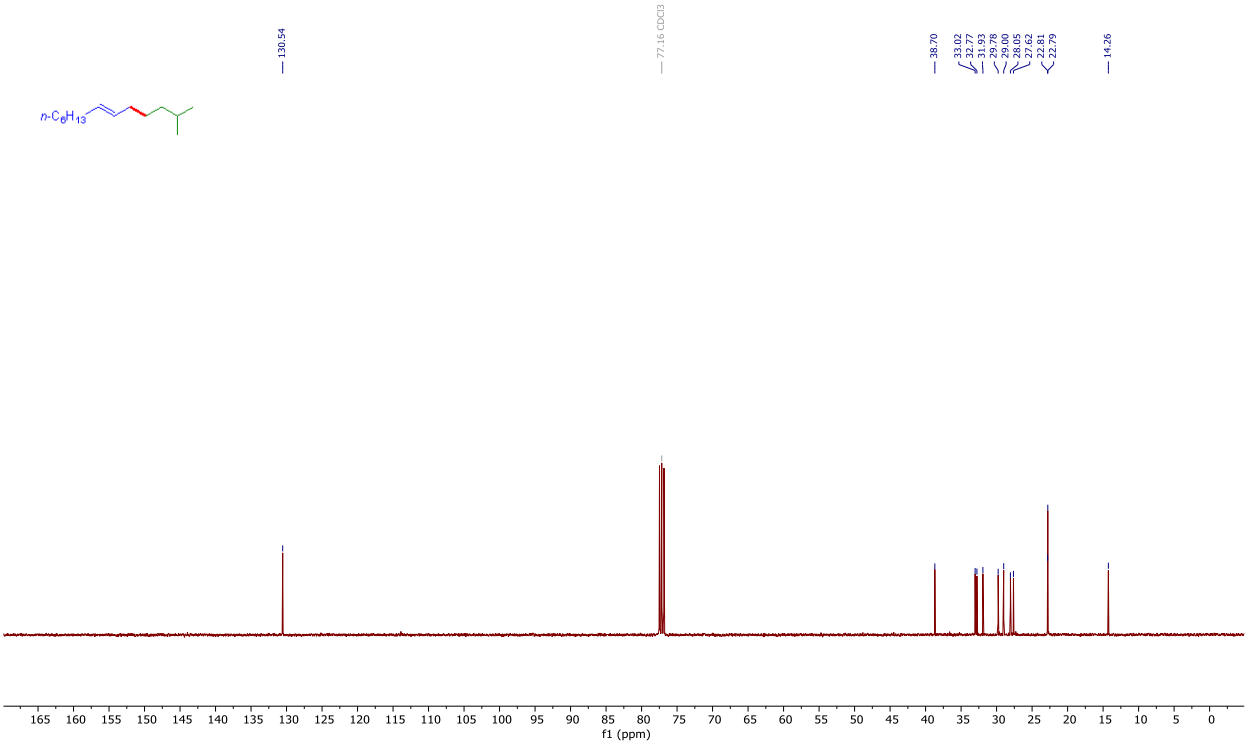
^{13}C NMR (101 MHz, $CDCl_3$), 3t:



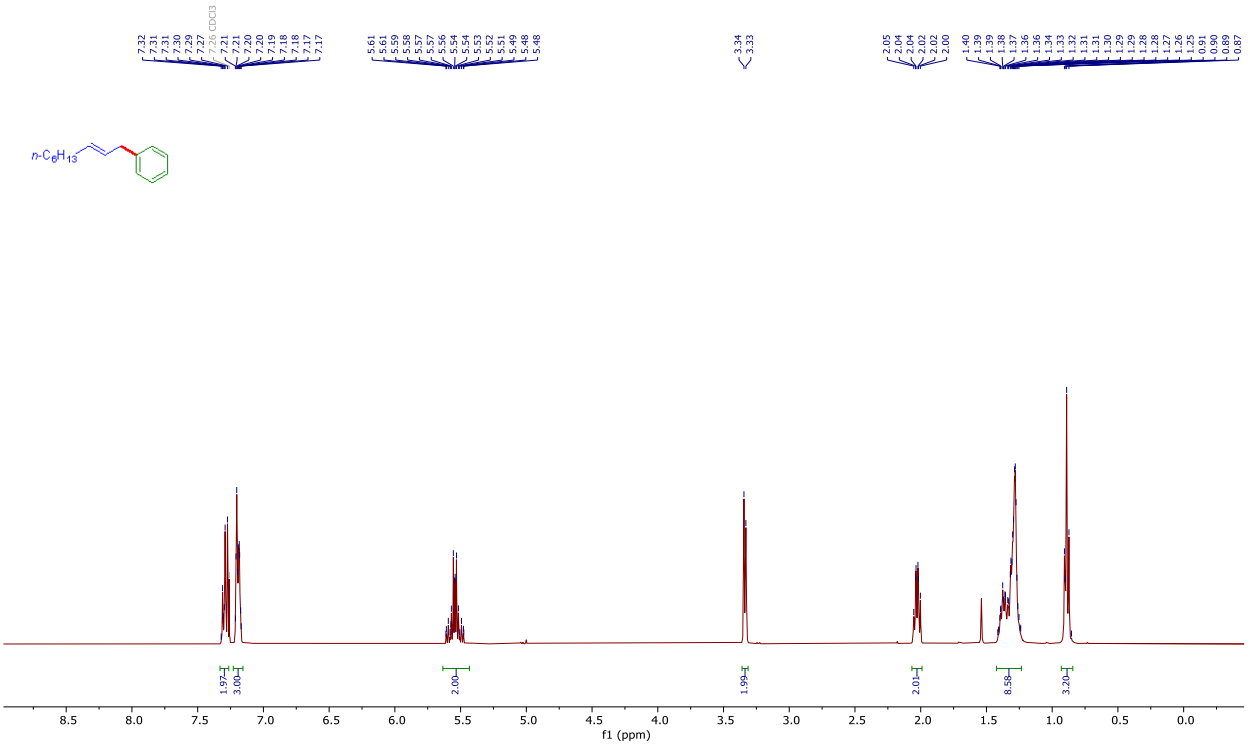
^{1}H NMR (400 MHz, $CDCl_3$), 3u:



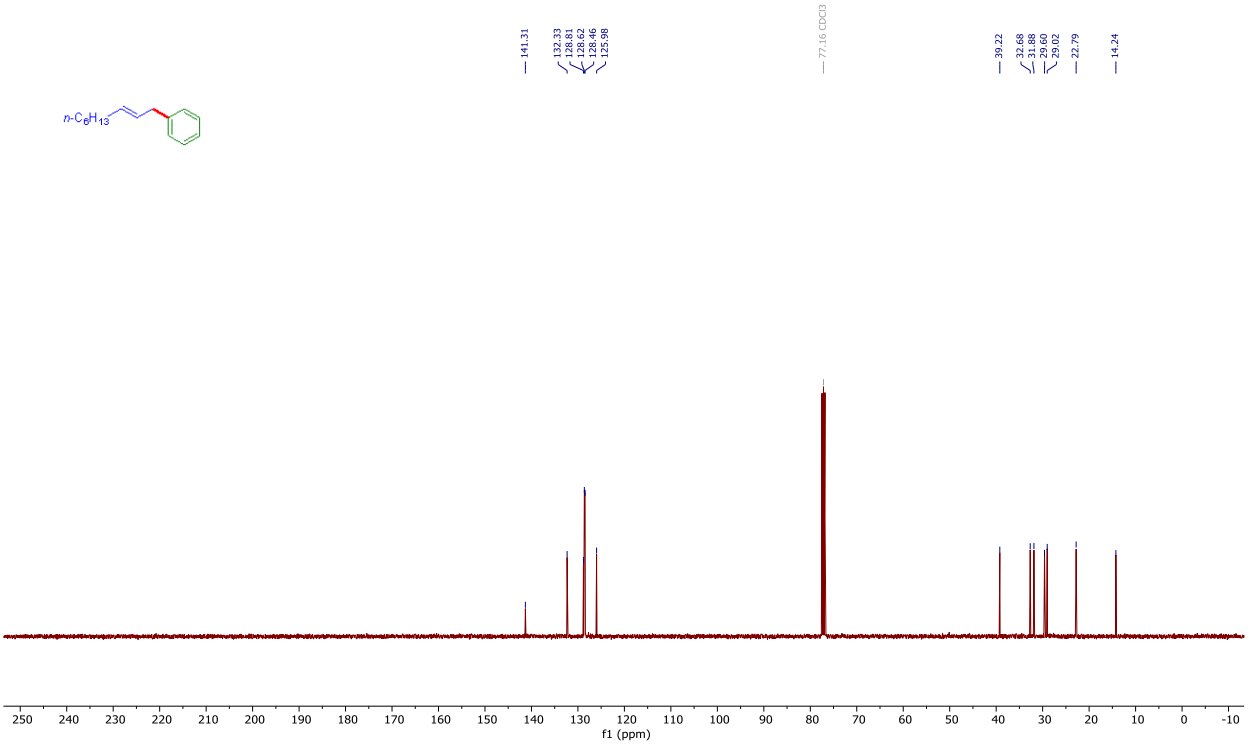
^{13}C NMR (101 MHz, $CDCl_3$), 3u:



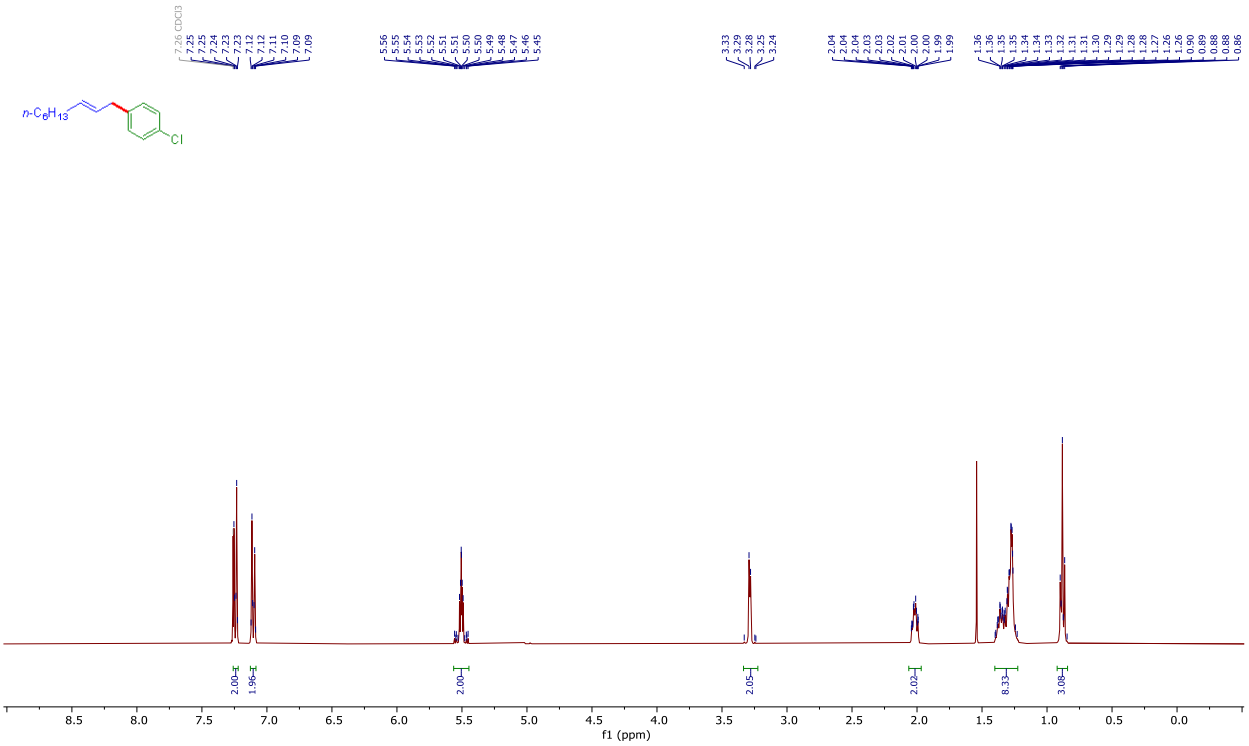
^{1}H NMR (400 MHz, $CDCl_3$), 3v:



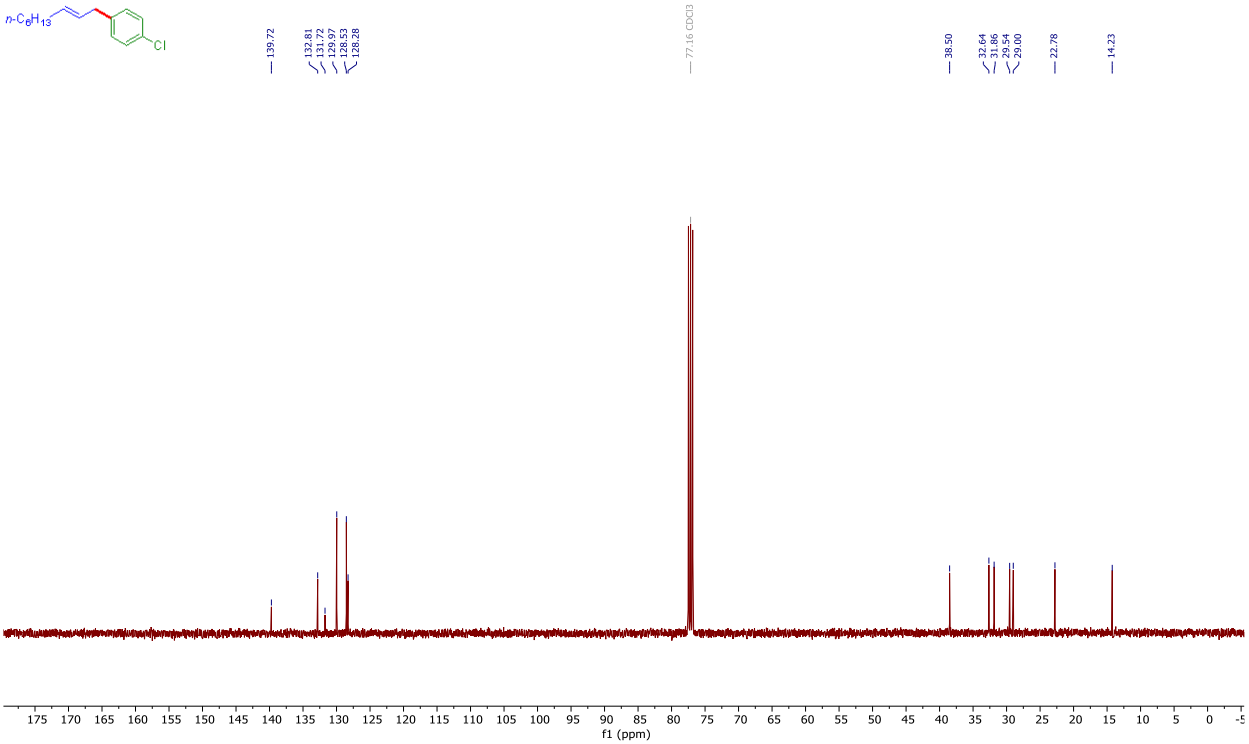
^{13}C NMR (101 MHz, $CDCl_3$), 3v:



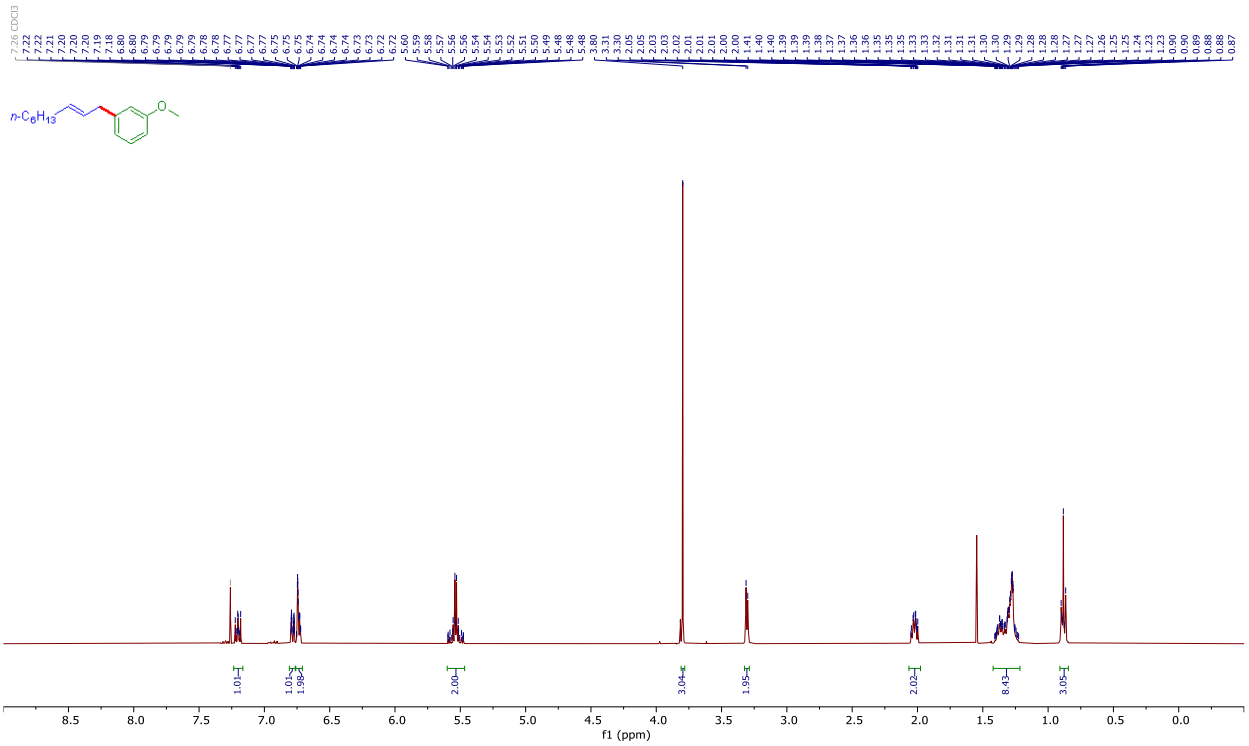
^{1}H NMR (400 MHz, $CDCl_3$), 3w:



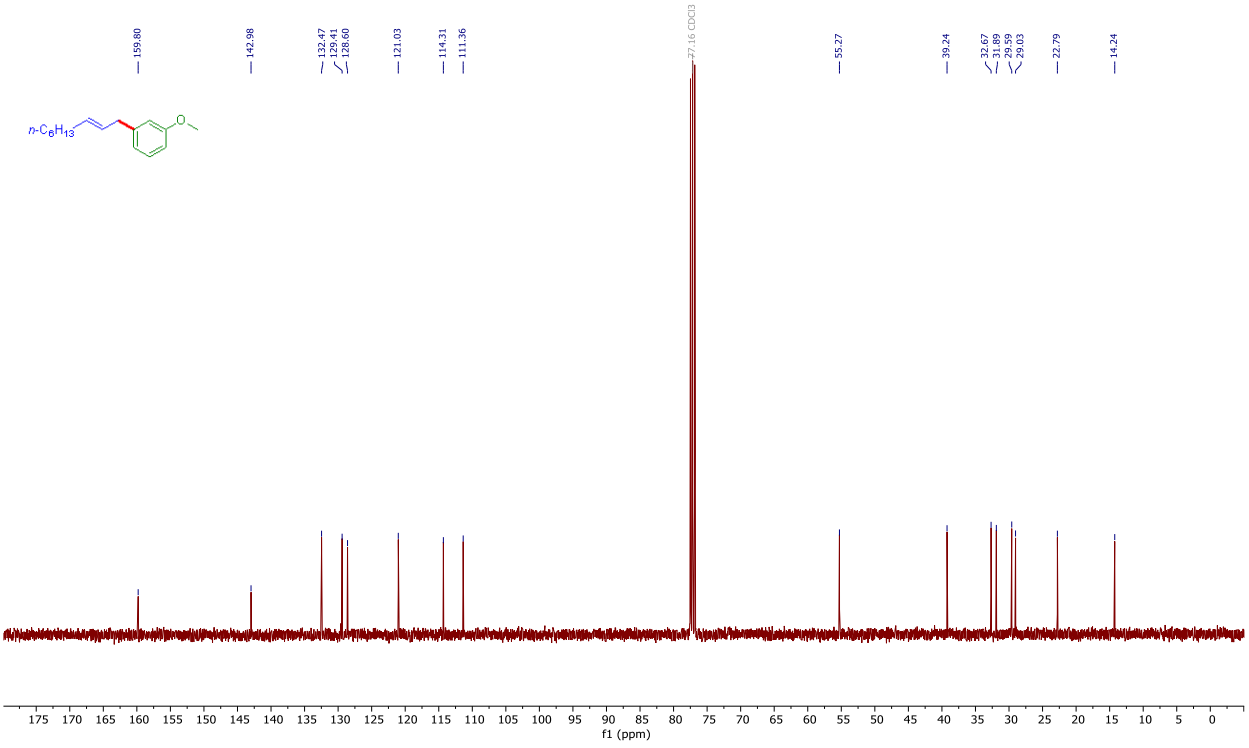
^{13}C NMR (101 MHz, $CDCl_3$), 3w:



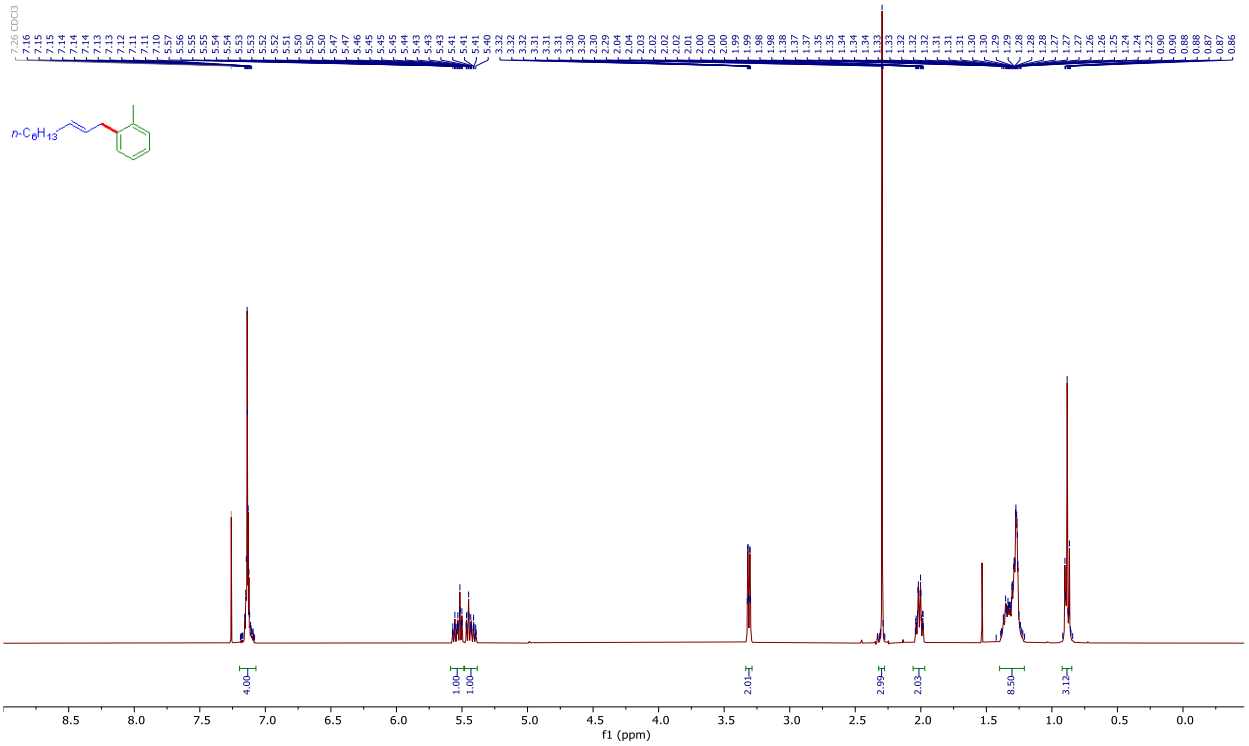
^{1}H NMR (400 MHz, $CDCl_3$), 3x:



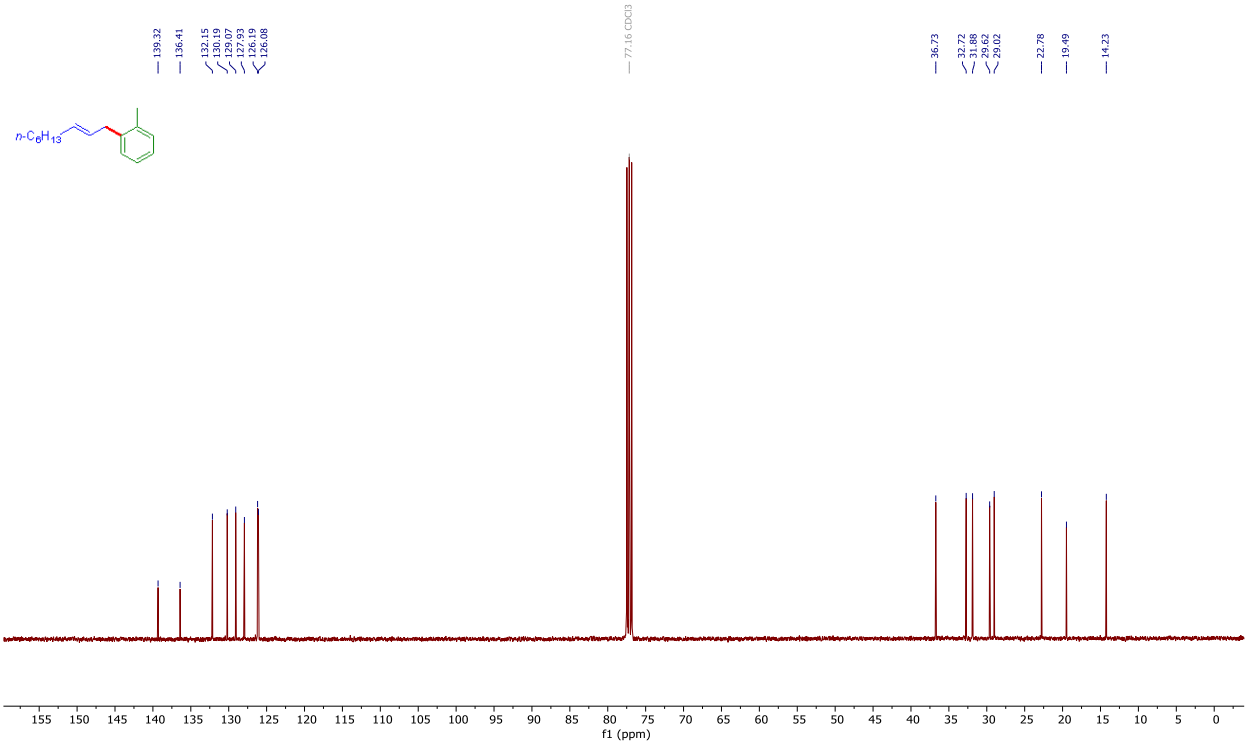
^{13}C NMR (101 MHz, $CDCl_3$), 3x:



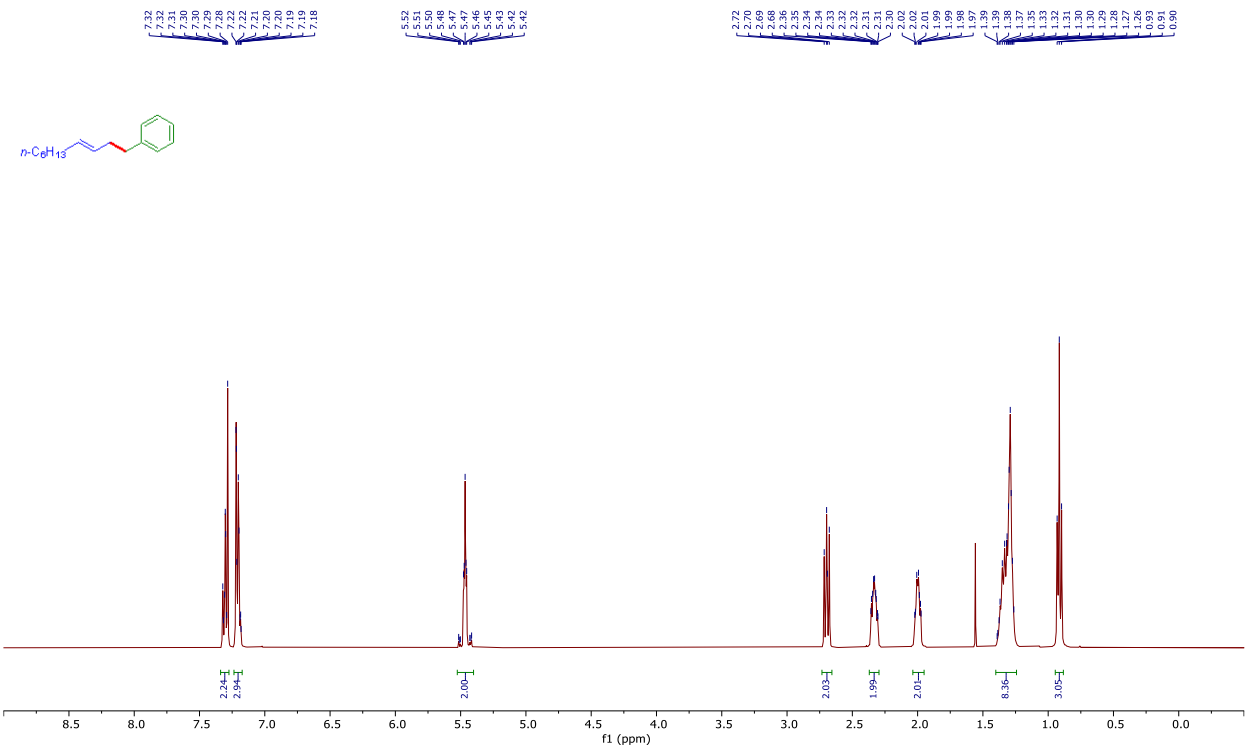
^{1}H NMR (400 MHz, $CDCl_3$), 3y:



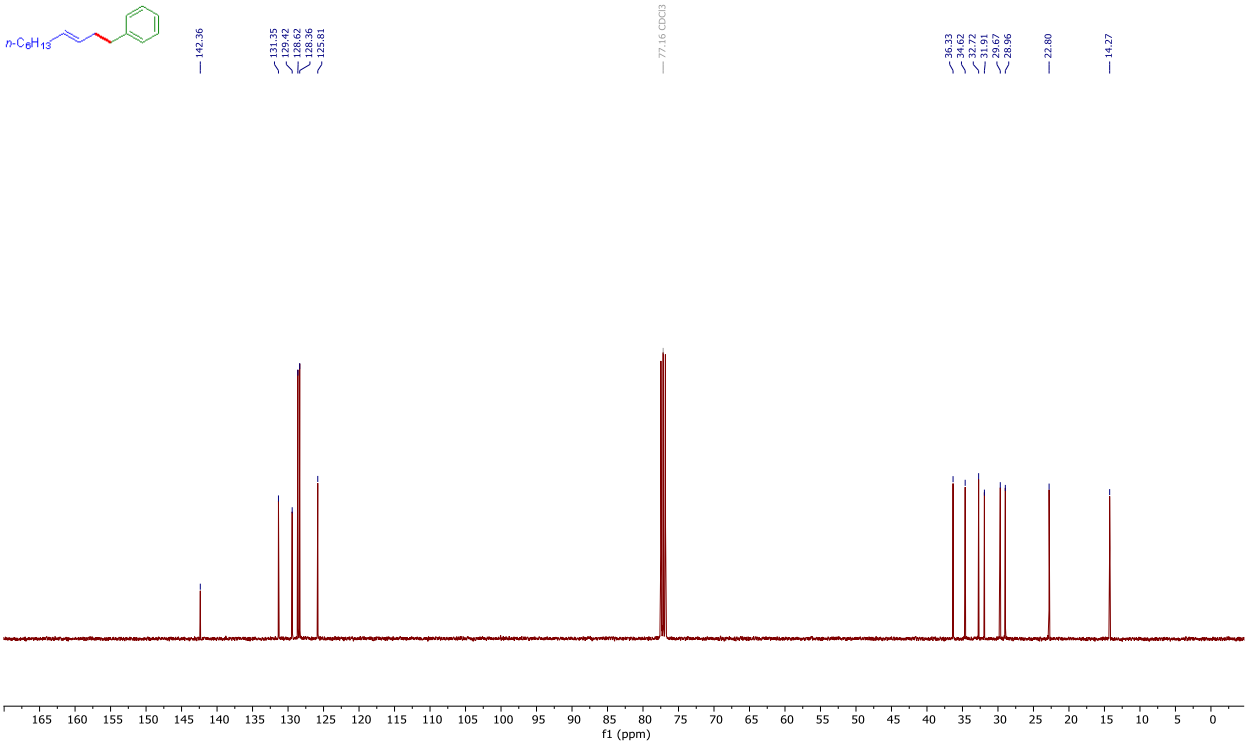
^{13}C NMR (101 MHz, $CDCl_3$), 3y:



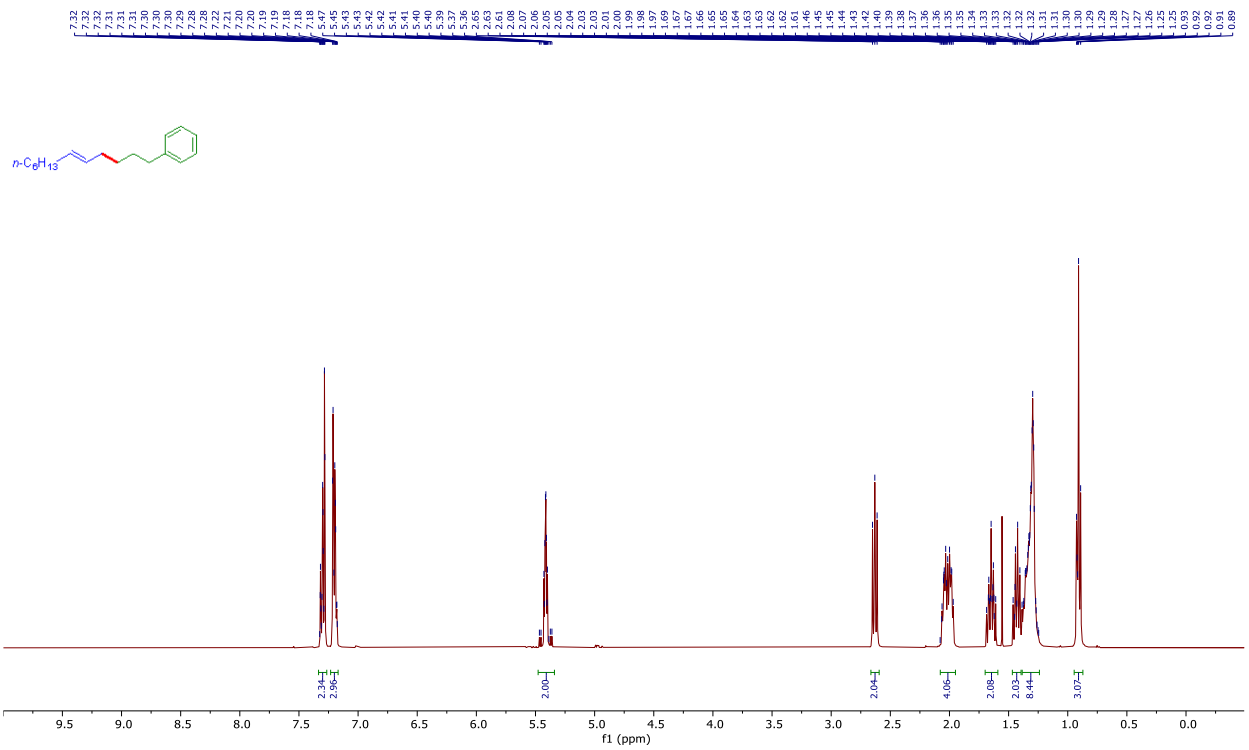
^{1}H NMR (400 MHz, $CDCl_3$), 3z:



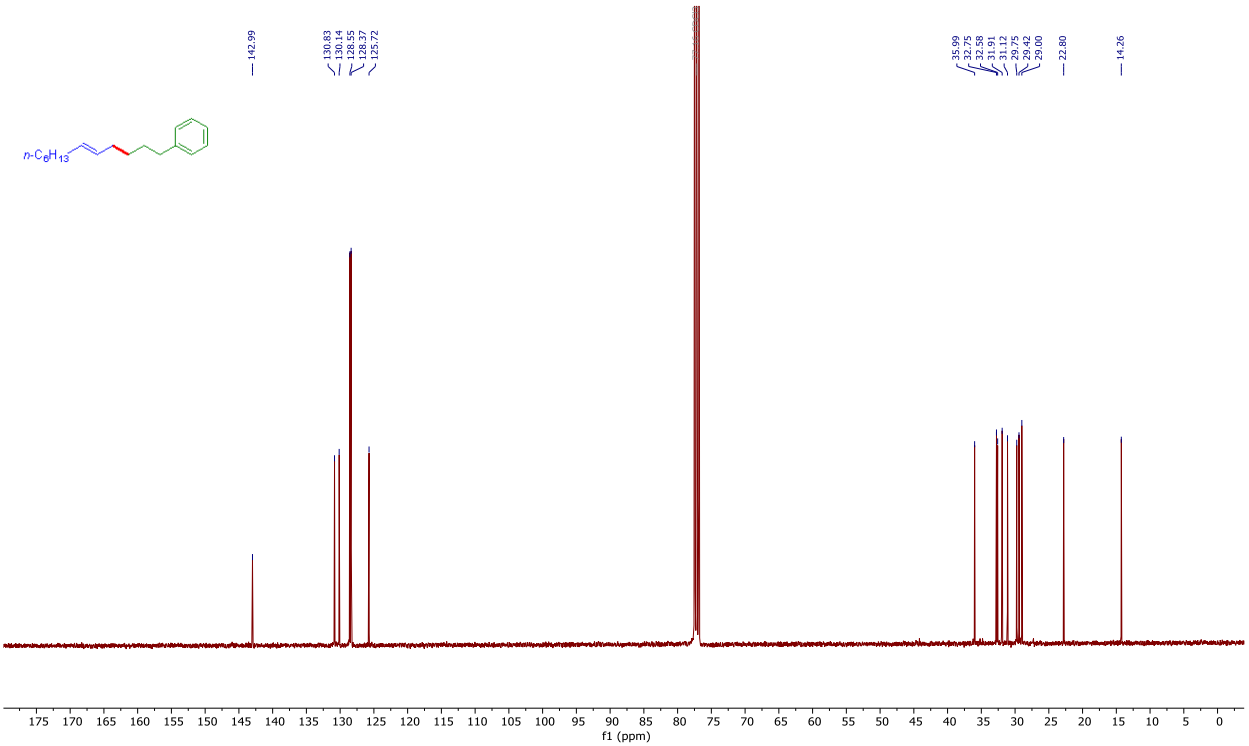
^{13}C NMR (101 MHz, $CDCl_3$), 3z:



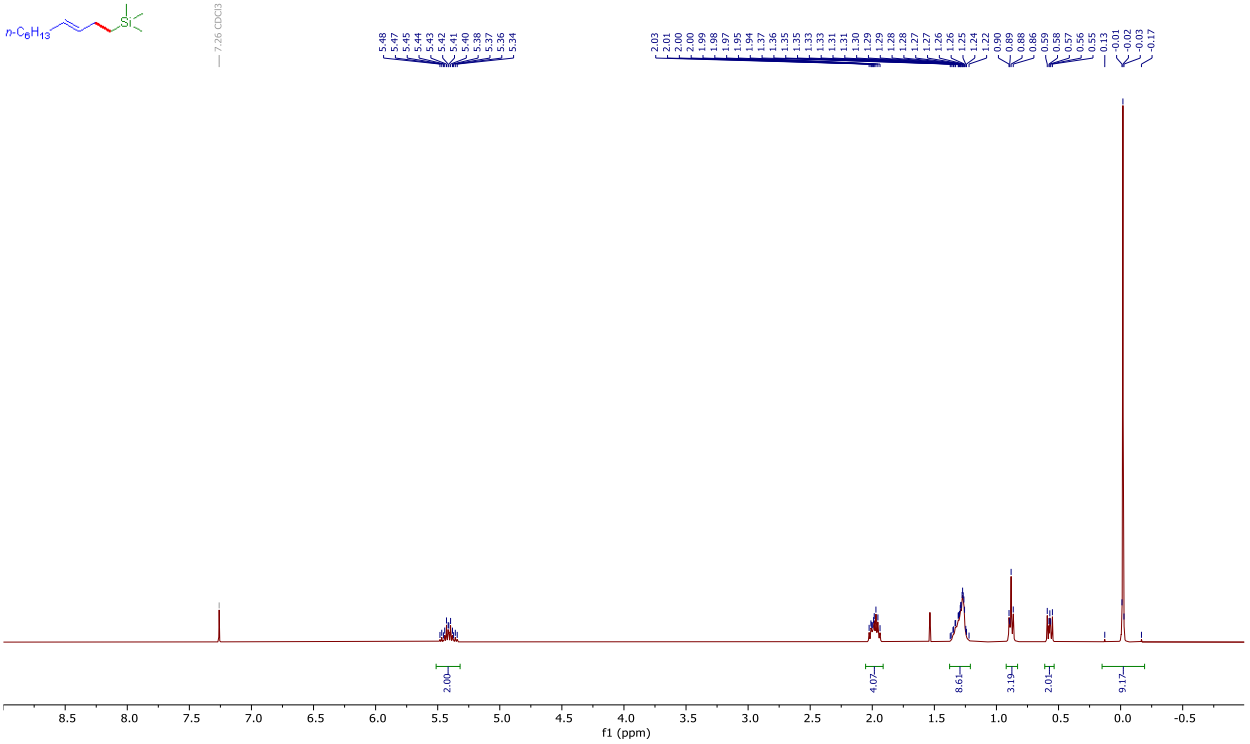
^{1}H NMR (400 MHz, $CDCl_3$), 3aa:



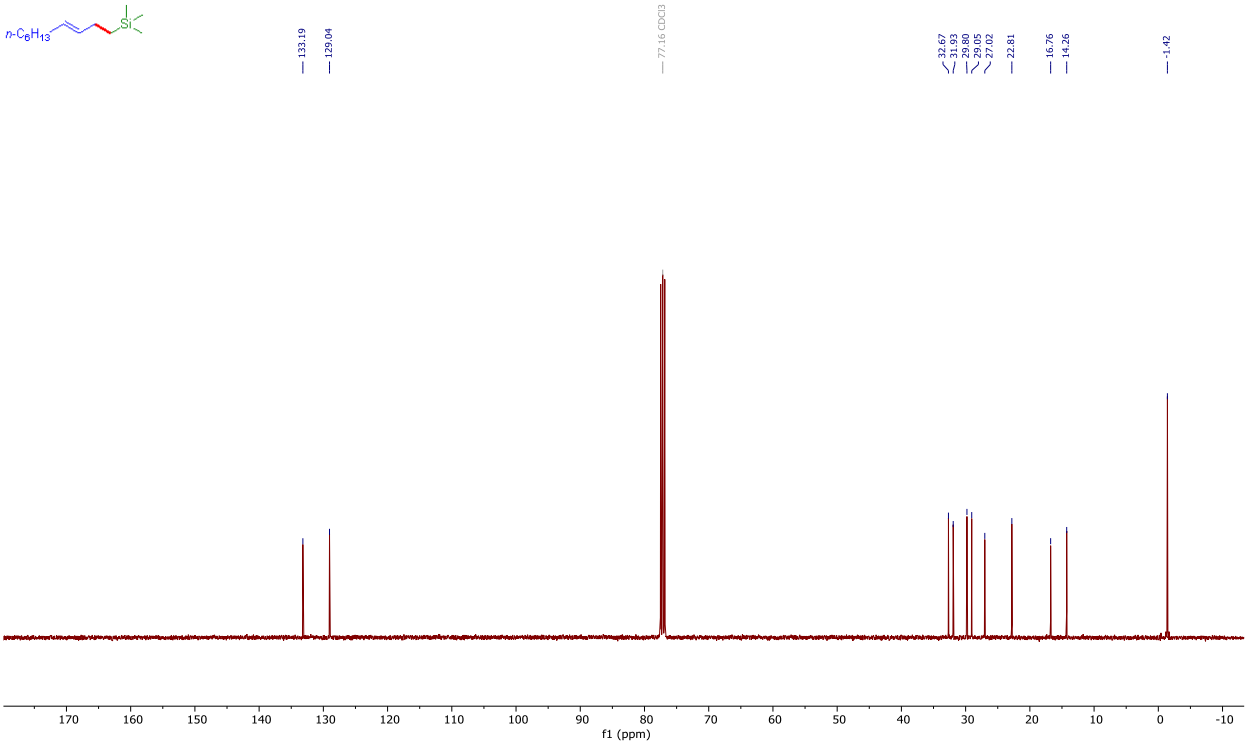
^{13}C NMR (101 MHz, $CDCl_3$), 3aa:



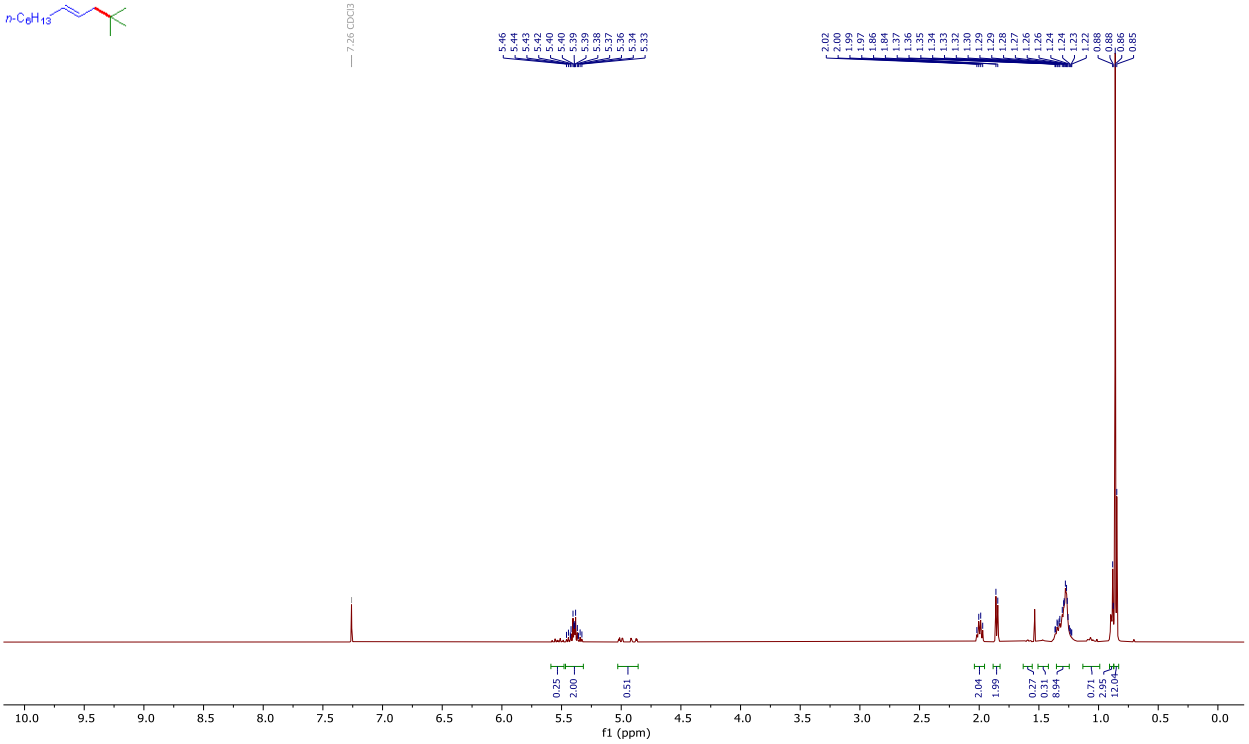
^{1}H NMR (400 MHz, $CDCl_3$), 3ab:



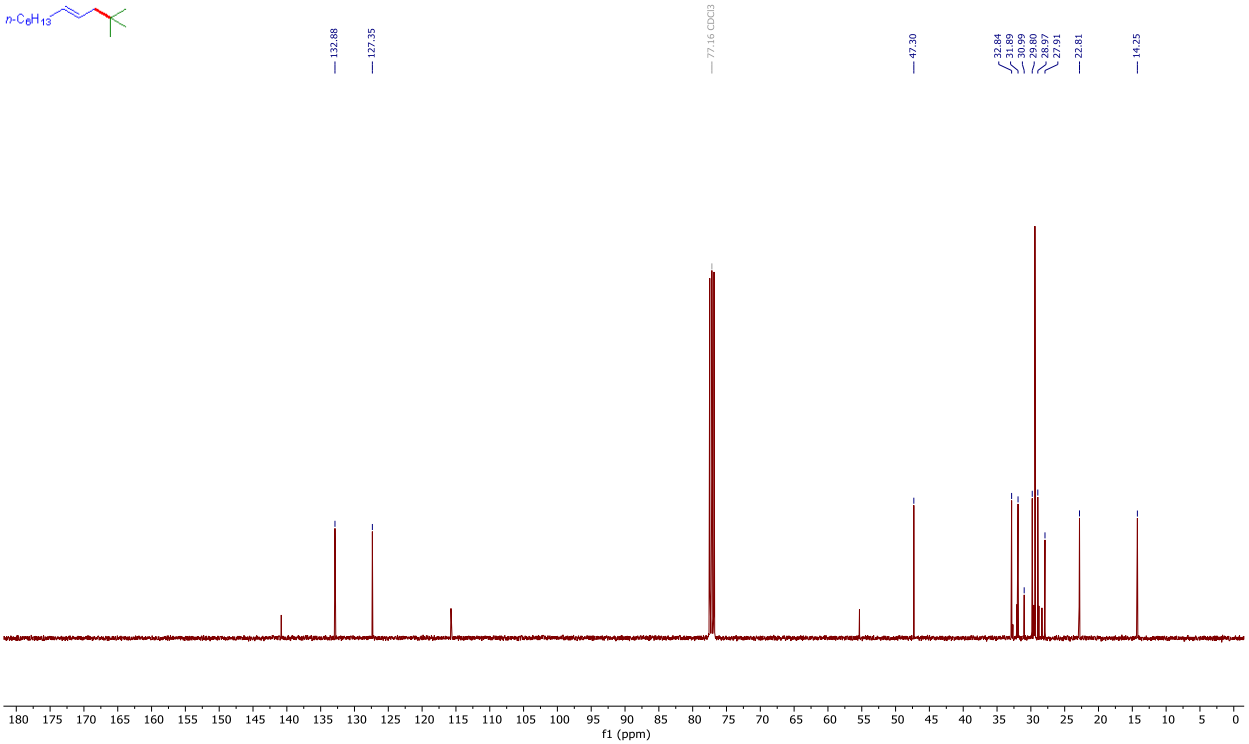
^{13}C NMR (101 MHz, $CDCl_3$), 3ab:



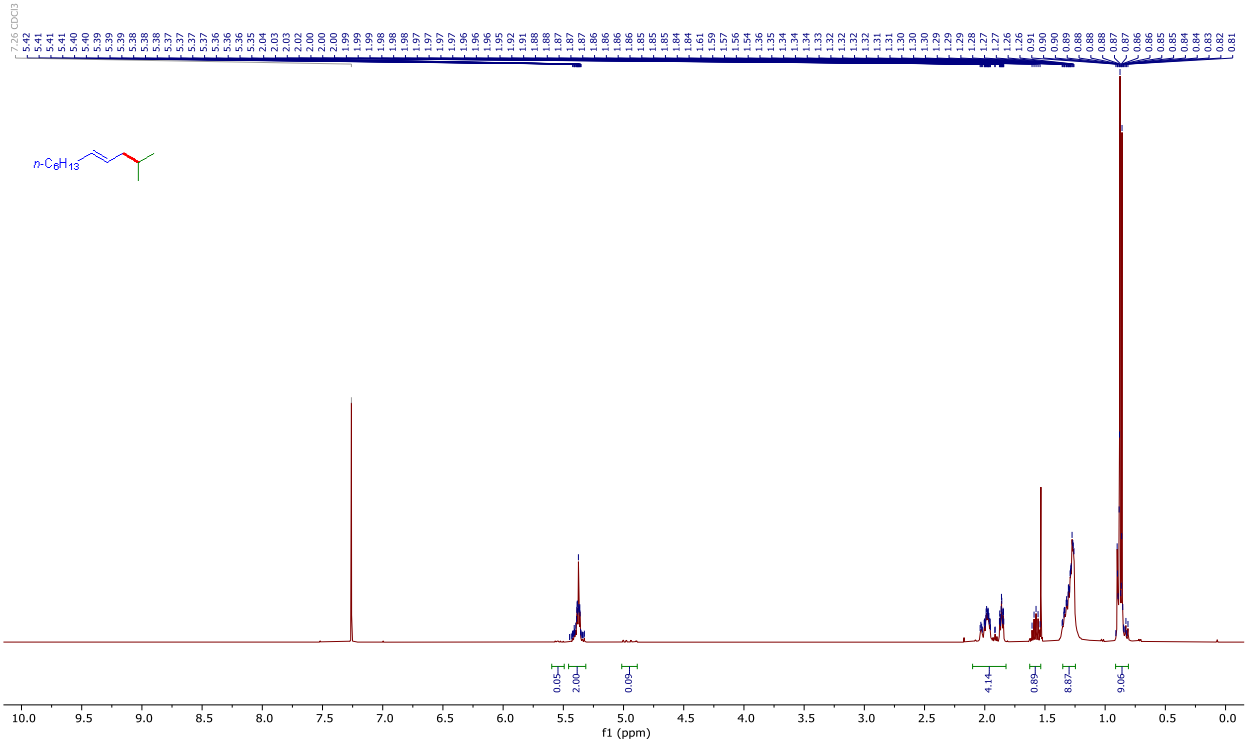
^{1}H NMR (400 MHz, $CDCl_3$), 3ac:



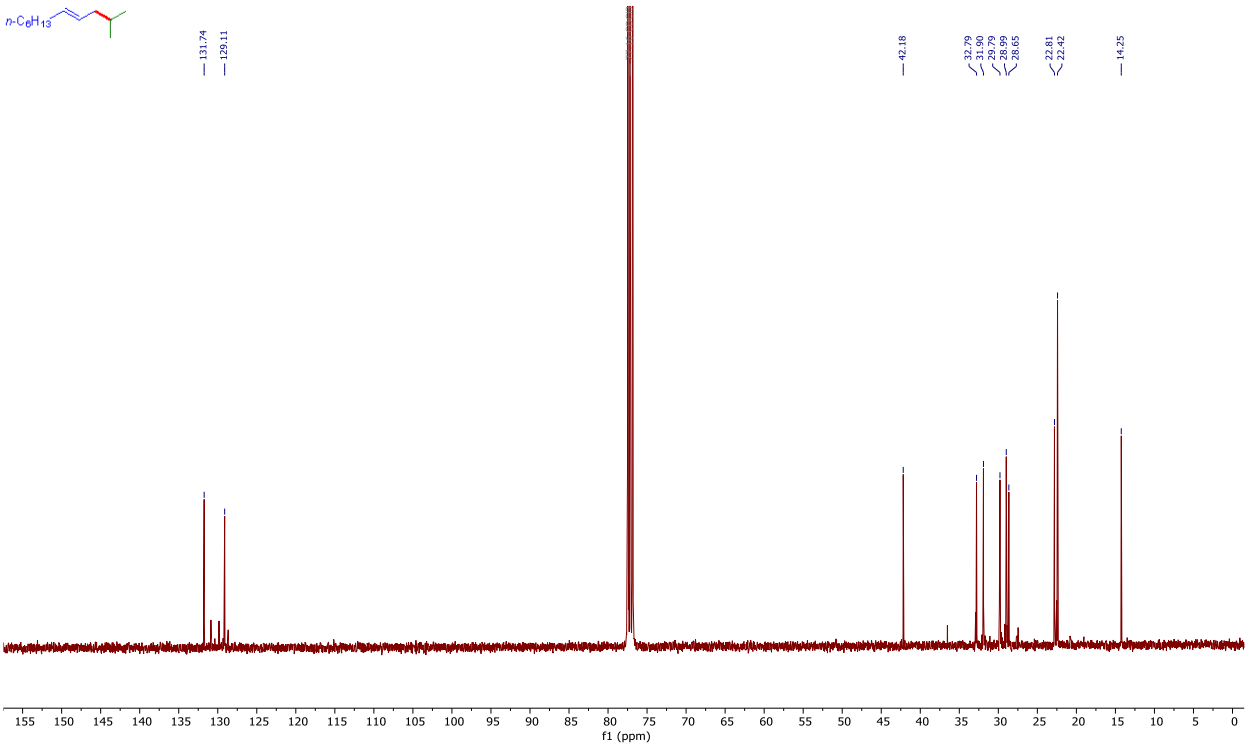
^{13}C NMR (101 MHz, $CDCl_3$), 3ac:



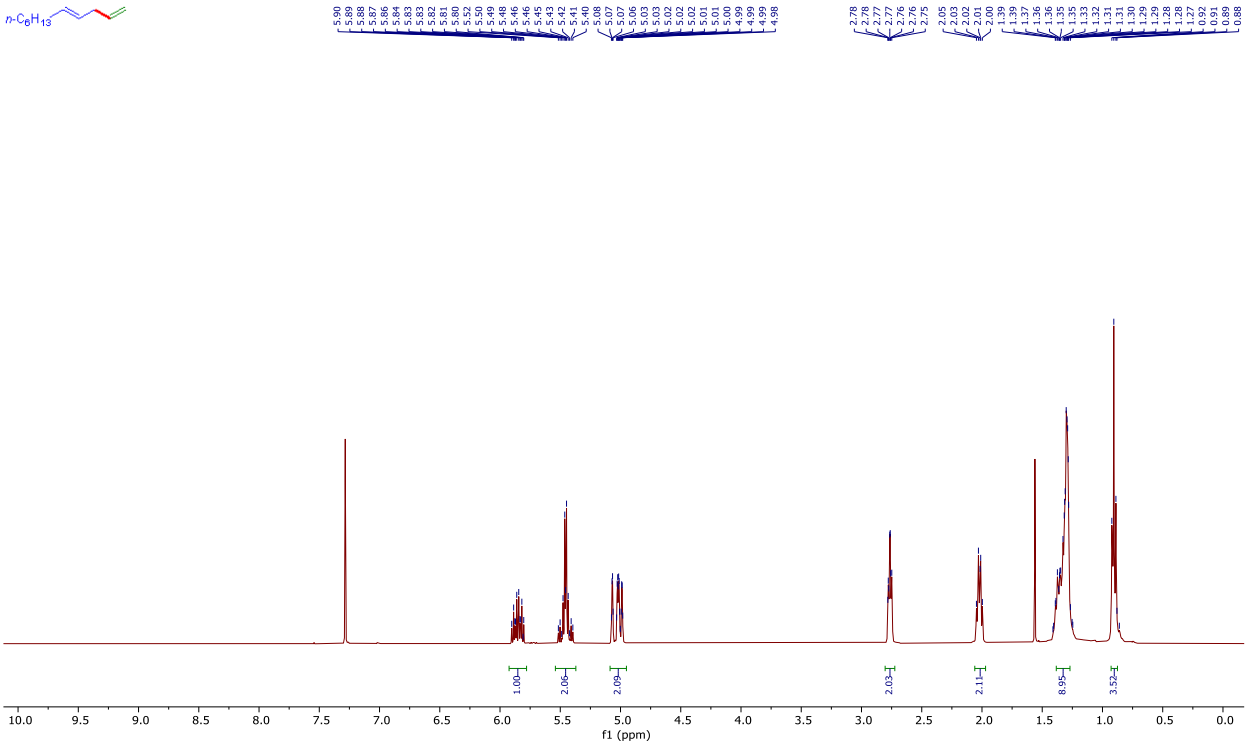
^{1}H NMR (400 MHz, $CDCl_3$), 3ad:



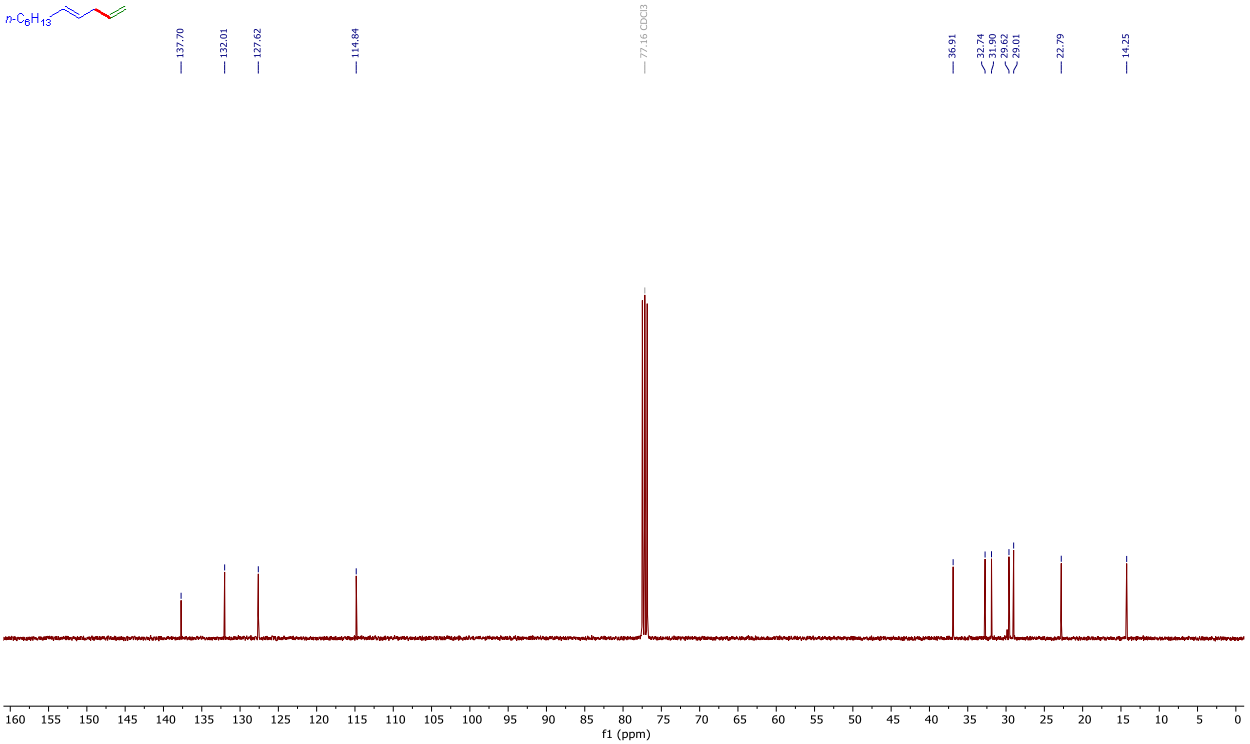
^{13}C NMR (101 MHz, $CDCl_3$), 3ad:



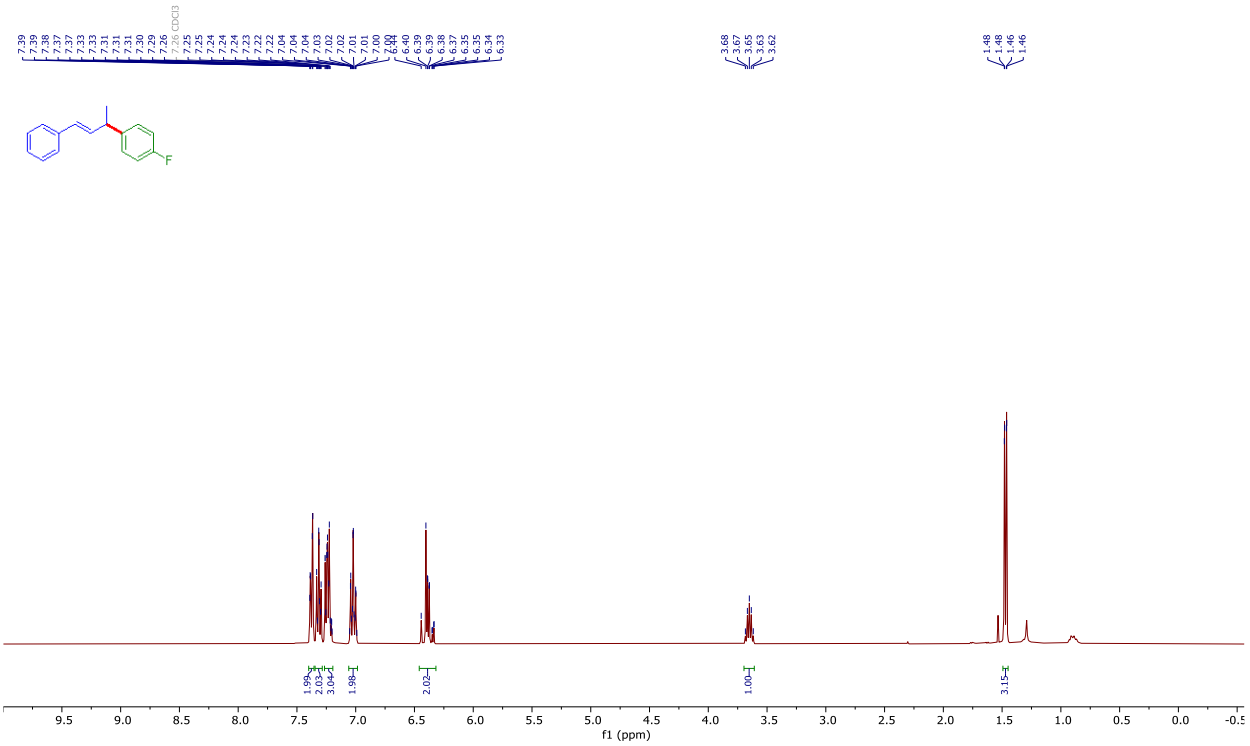
^{1}H NMR (400 MHz, $CDCl_3$), 3ae:



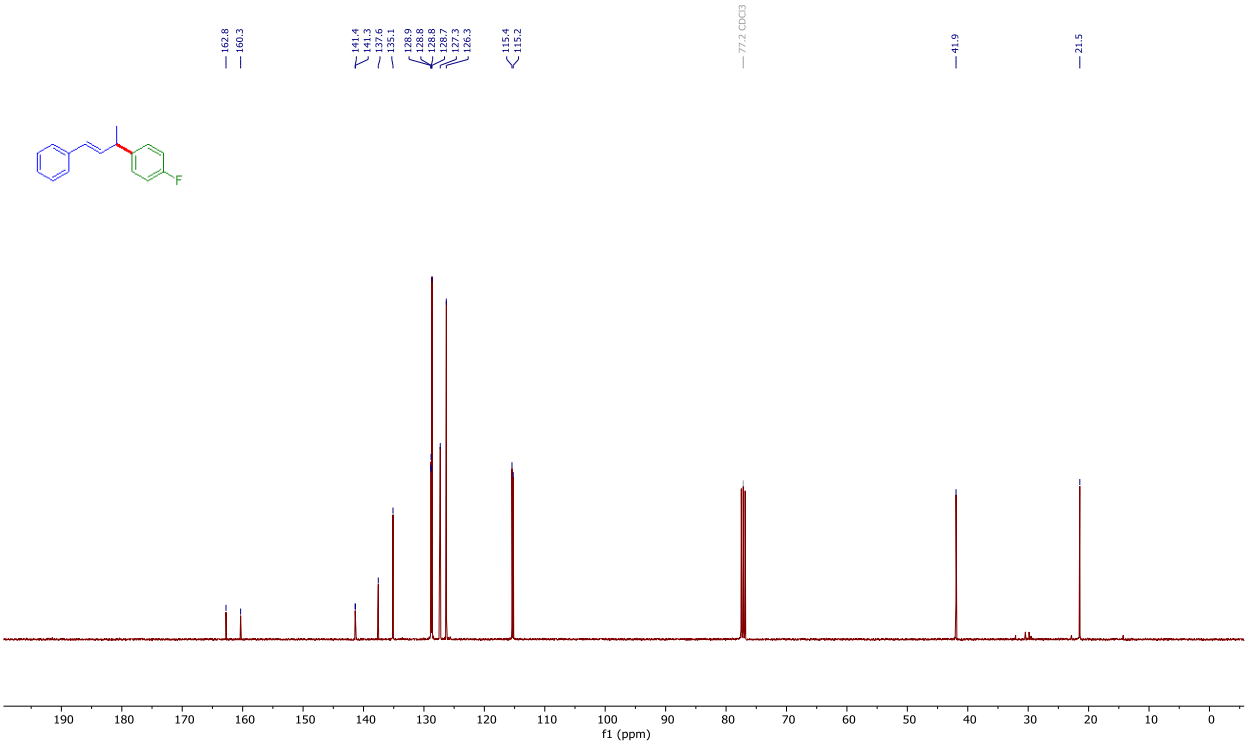
^{13}C NMR (101 MHz, $CDCl_3$), 3ae:



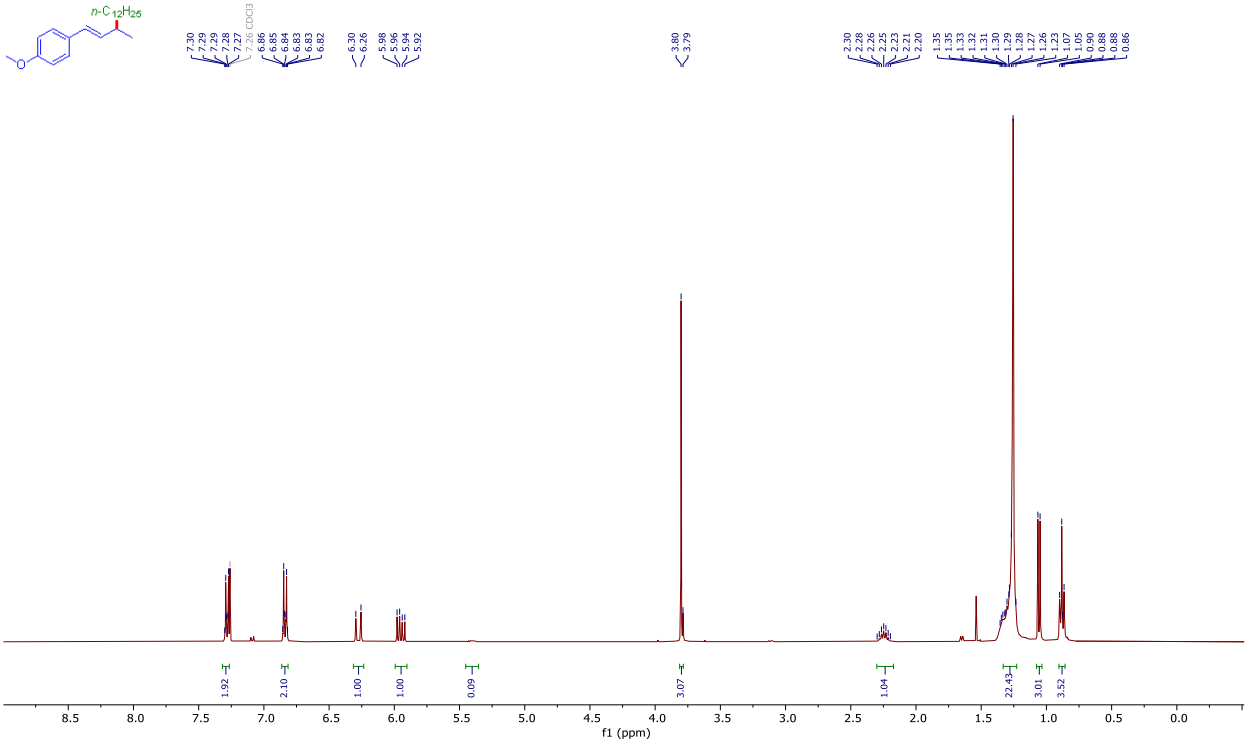
^{1}H NMR (400 MHz, $CDCl_3$), 3af:



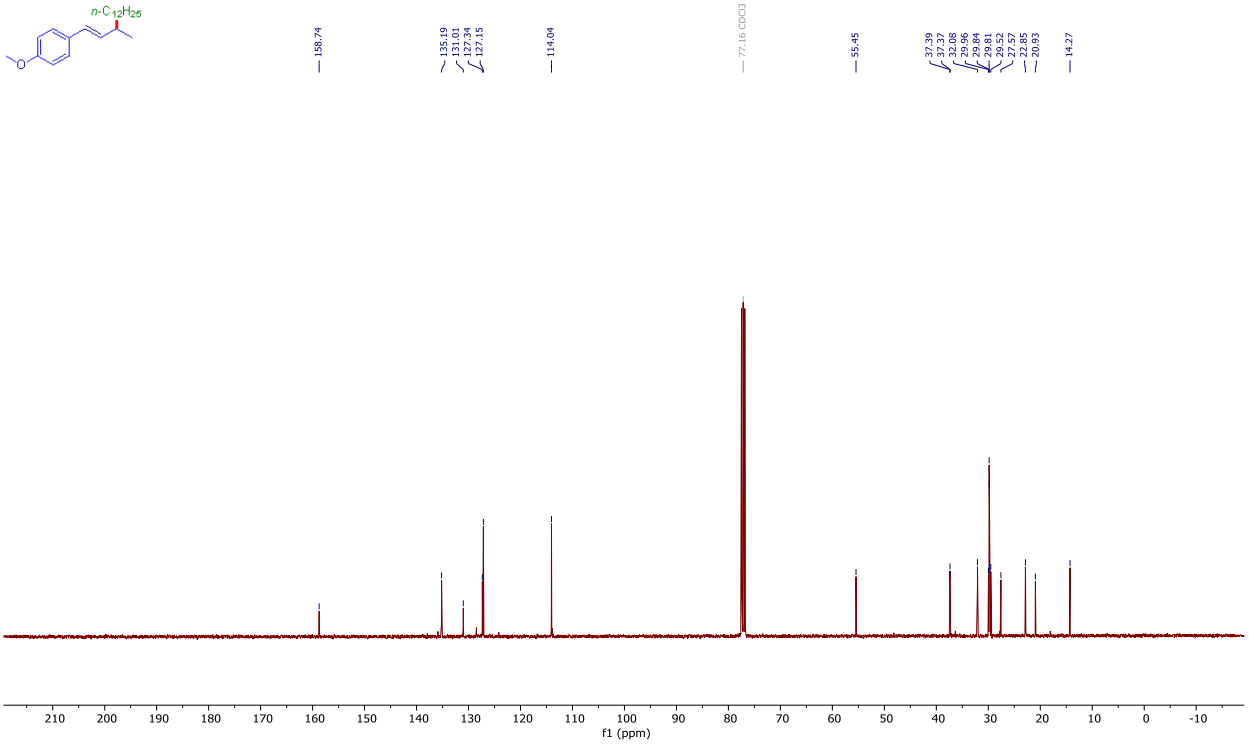
^{13}C NMR (101 MHz, $CDCl_3$), 3af:



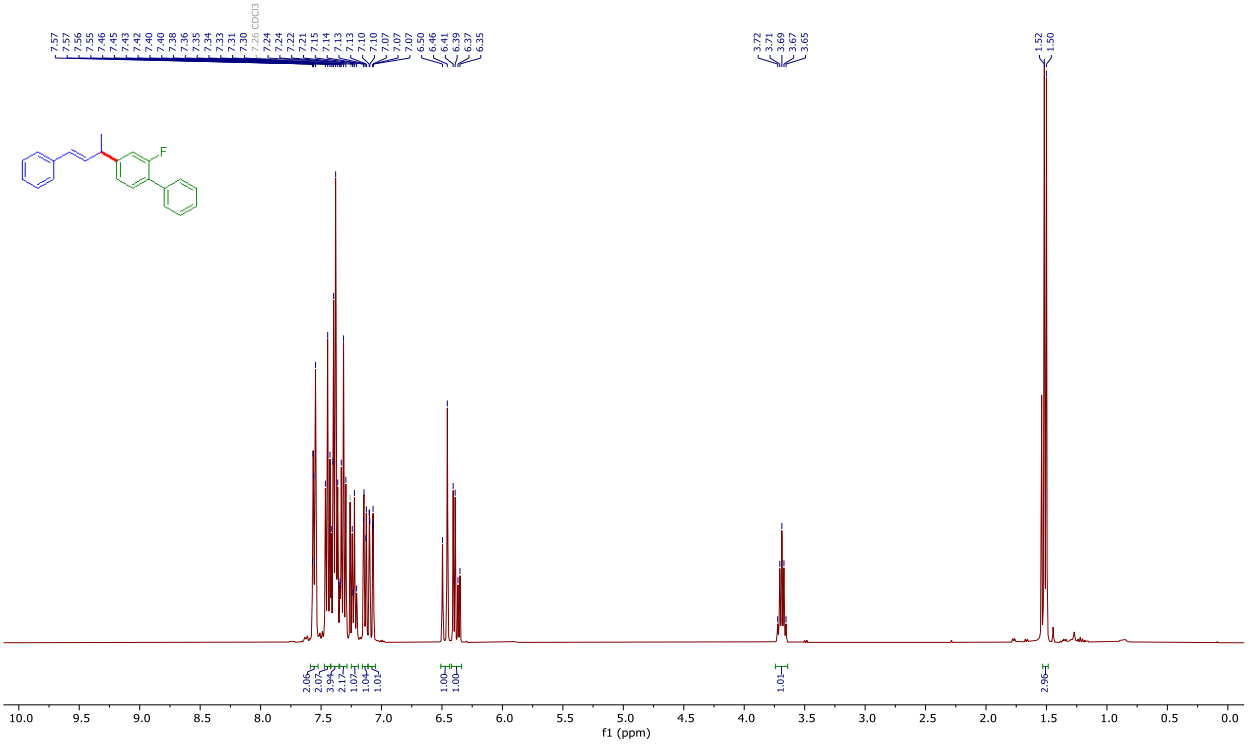
^{1}H NMR (400 MHz, $CDCl_3$), 3ag:



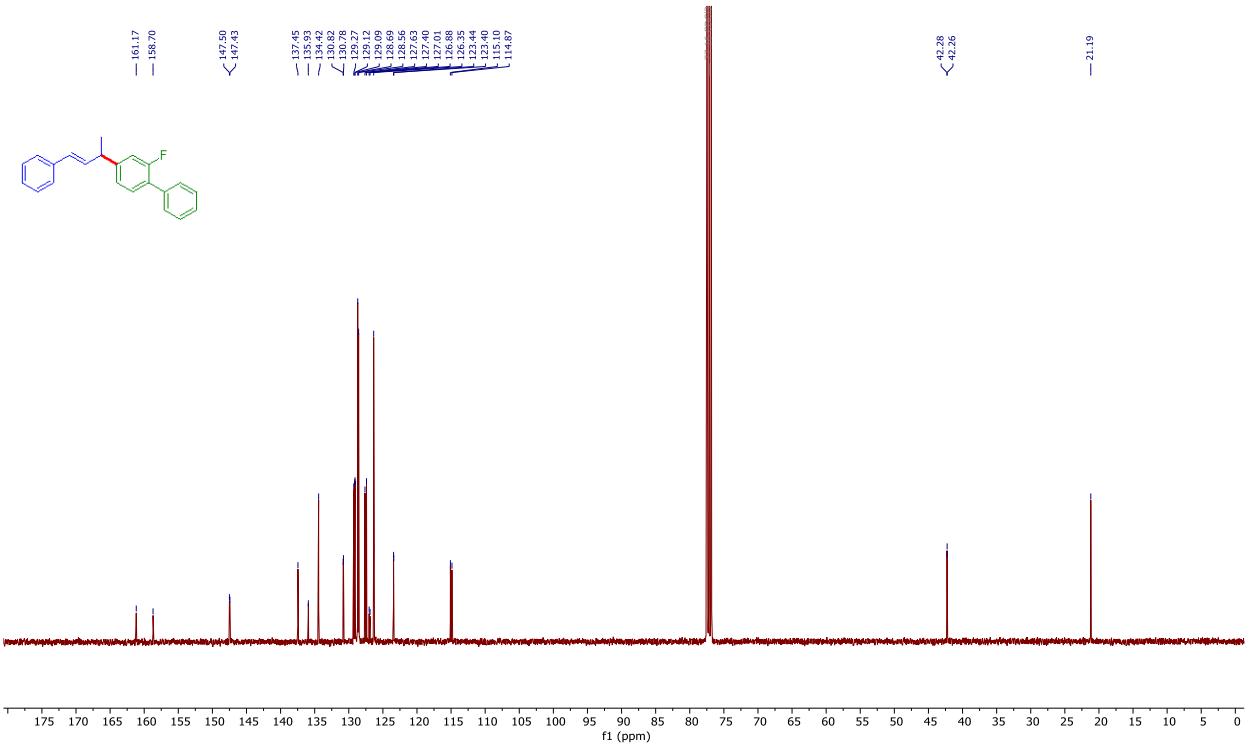
^{13}C NMR (101 MHz, $CDCl_3$), 3ag:



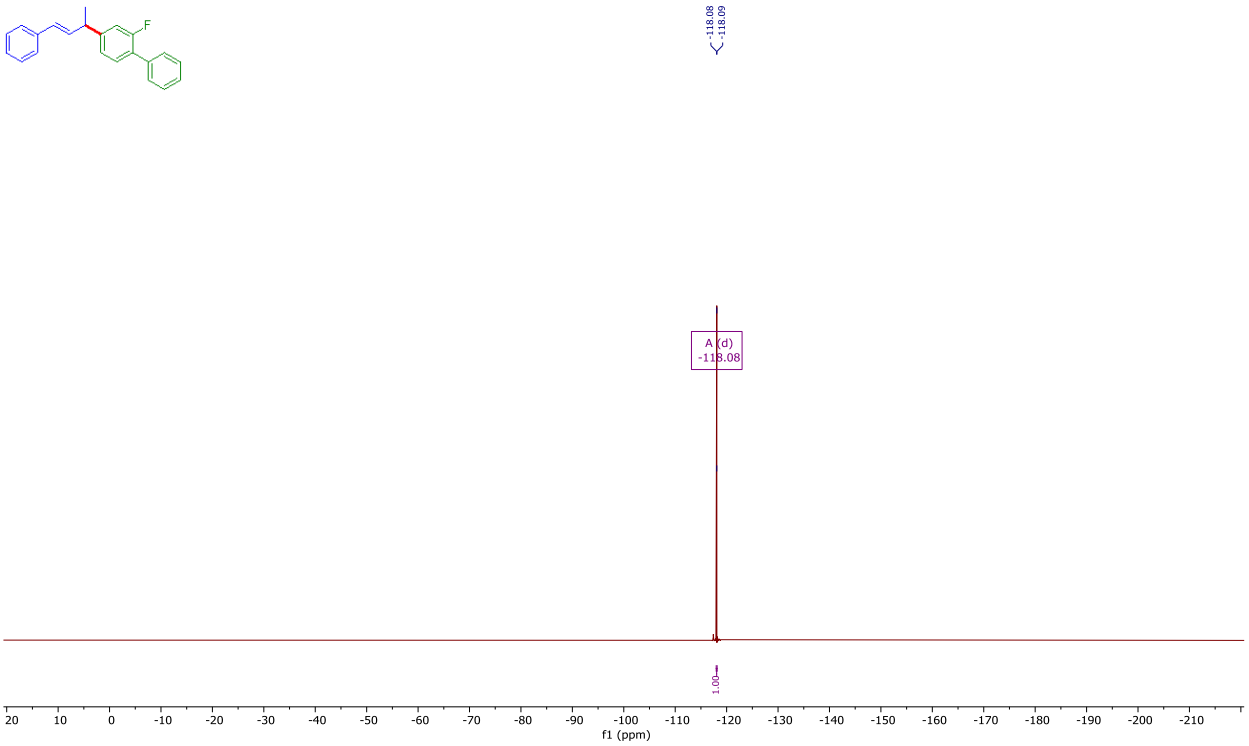
^{1}H NMR (400 MHz, $CDCl_3$), 3ah:



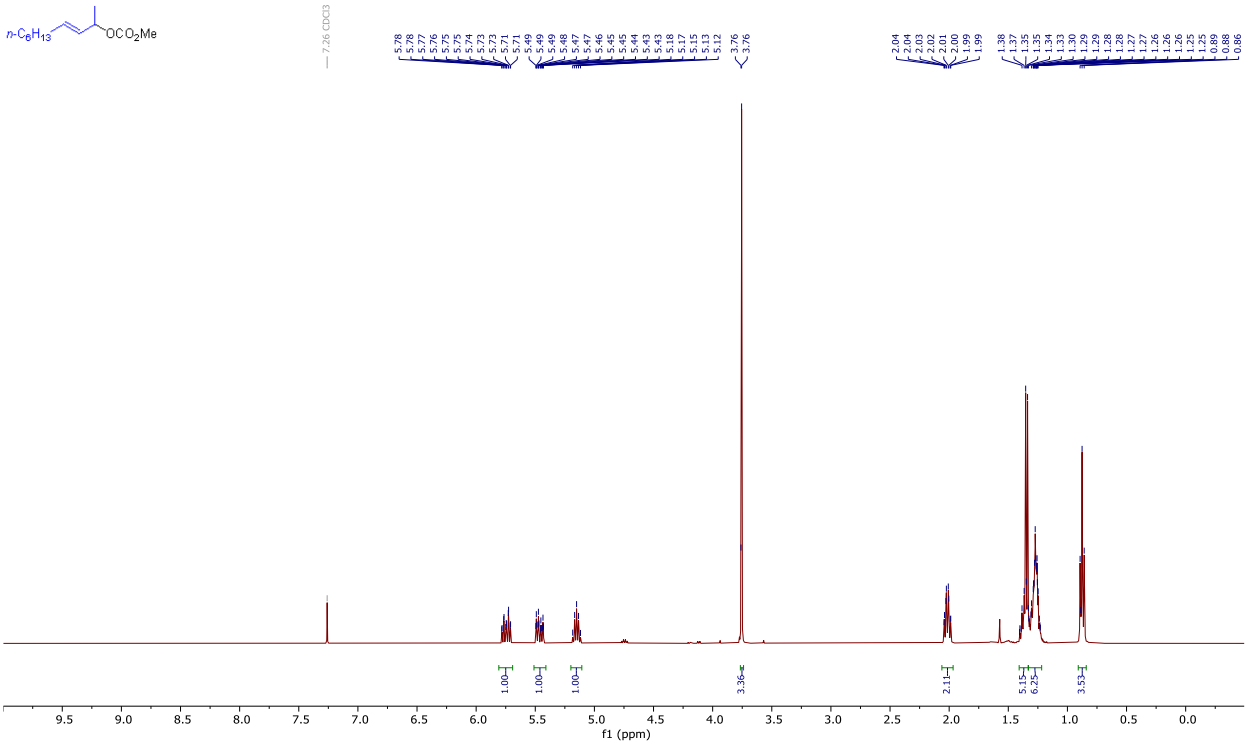
^{13}C NMR (101 MHz, $CDCl_3$), 3ah:



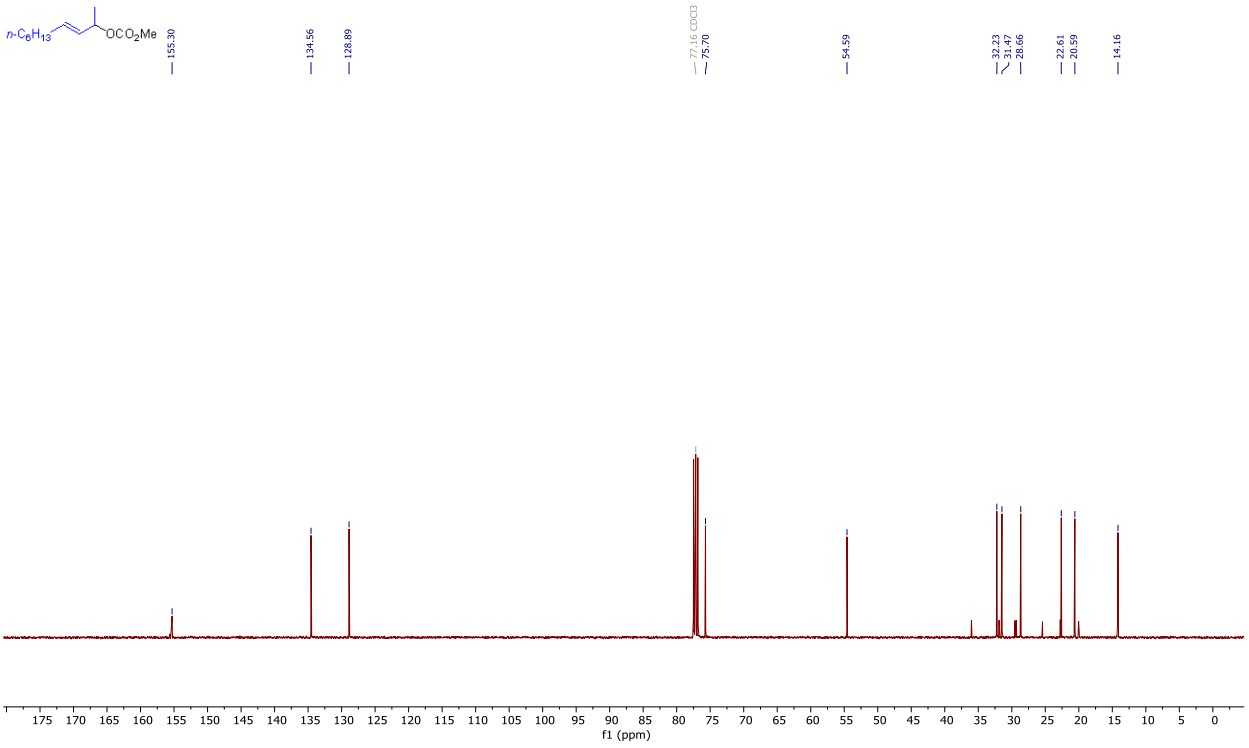
^{19}F NMR (377 MHz, $CDCl_3$), 3ah:



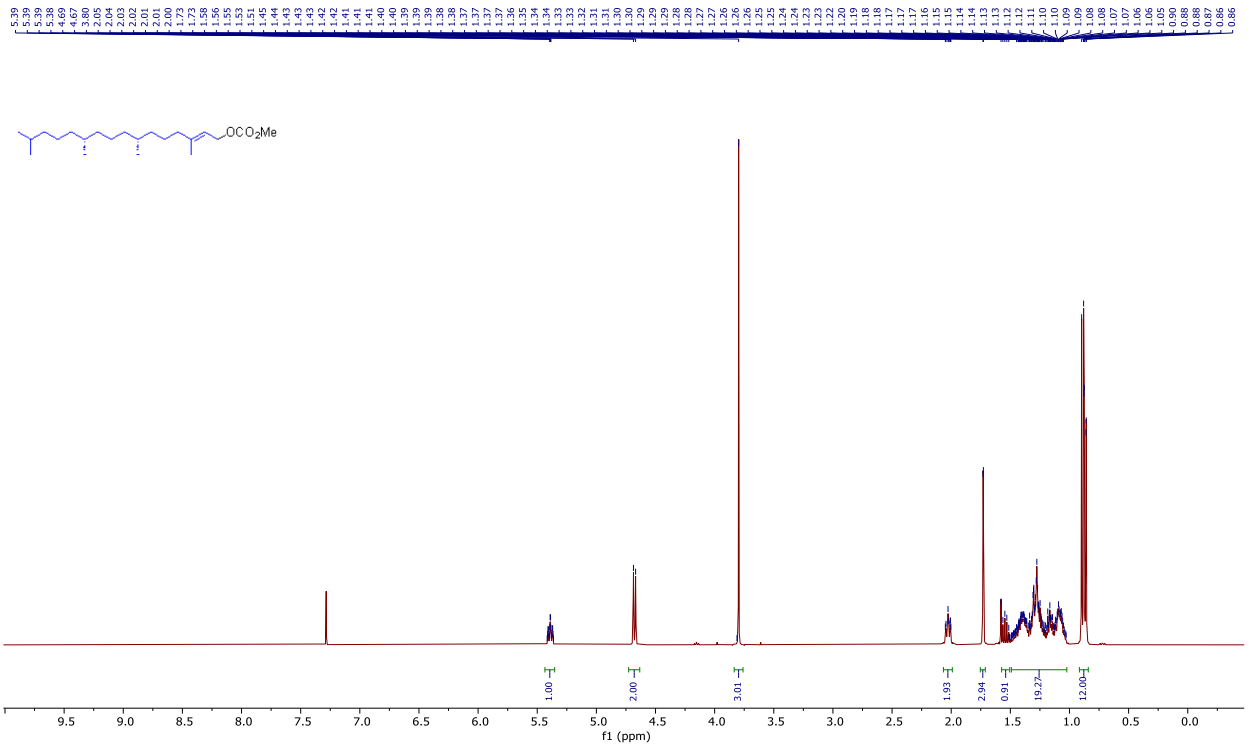
^{1}H NMR (400 MHz, $CDCl_3$), 1d':



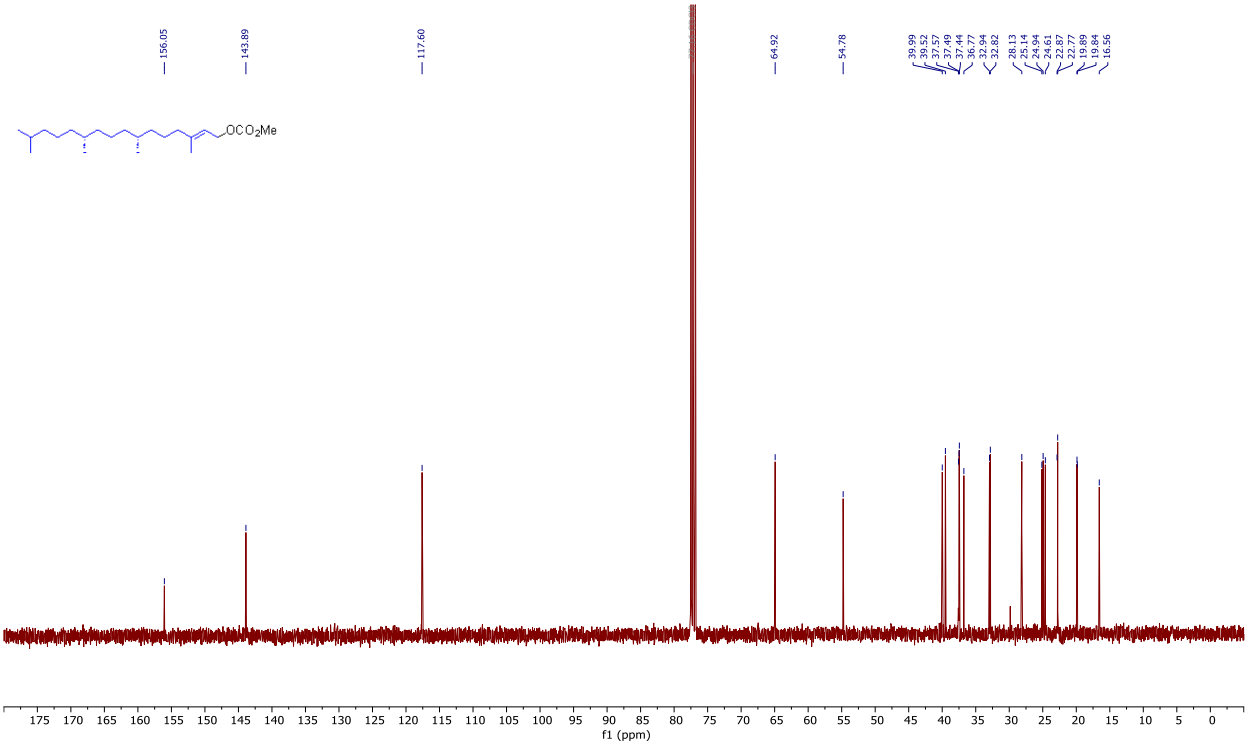
^{13}C NMR (101 MHz, $CDCl_3$), 1d':



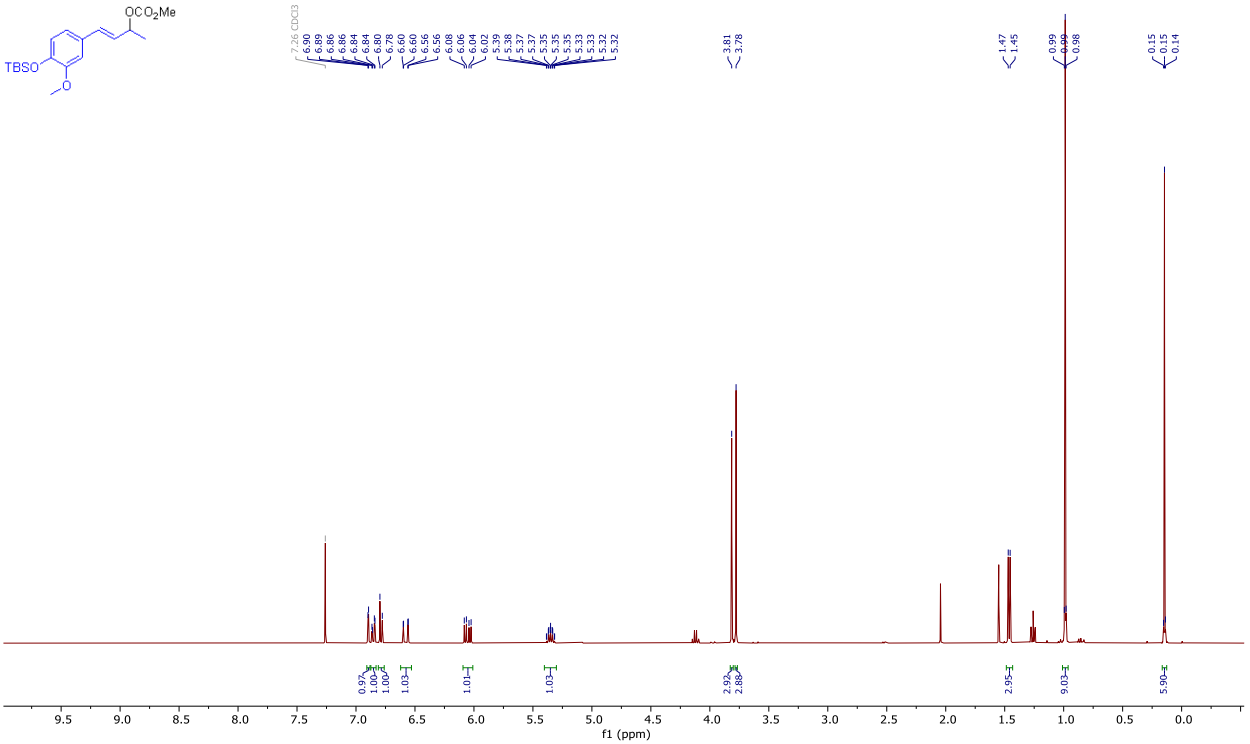
^{1}H NMR (400 MHz, $CDCl_3$), 1i:



^{13}C NMR (101 MHz, $CDCl_3$), 1i:



^{1}H NMR (400 MHz, $CDCl_3$), 1q:



^{13}C NMR (101 MHz, $CDCl_3$), 1q: