Supporting Information for:

Stereospecific Iron-catalyzed Carbon(sp^2)-Carbon(sp^3) Cross-coupling with Alkyllithium and Alkenyl Iodides

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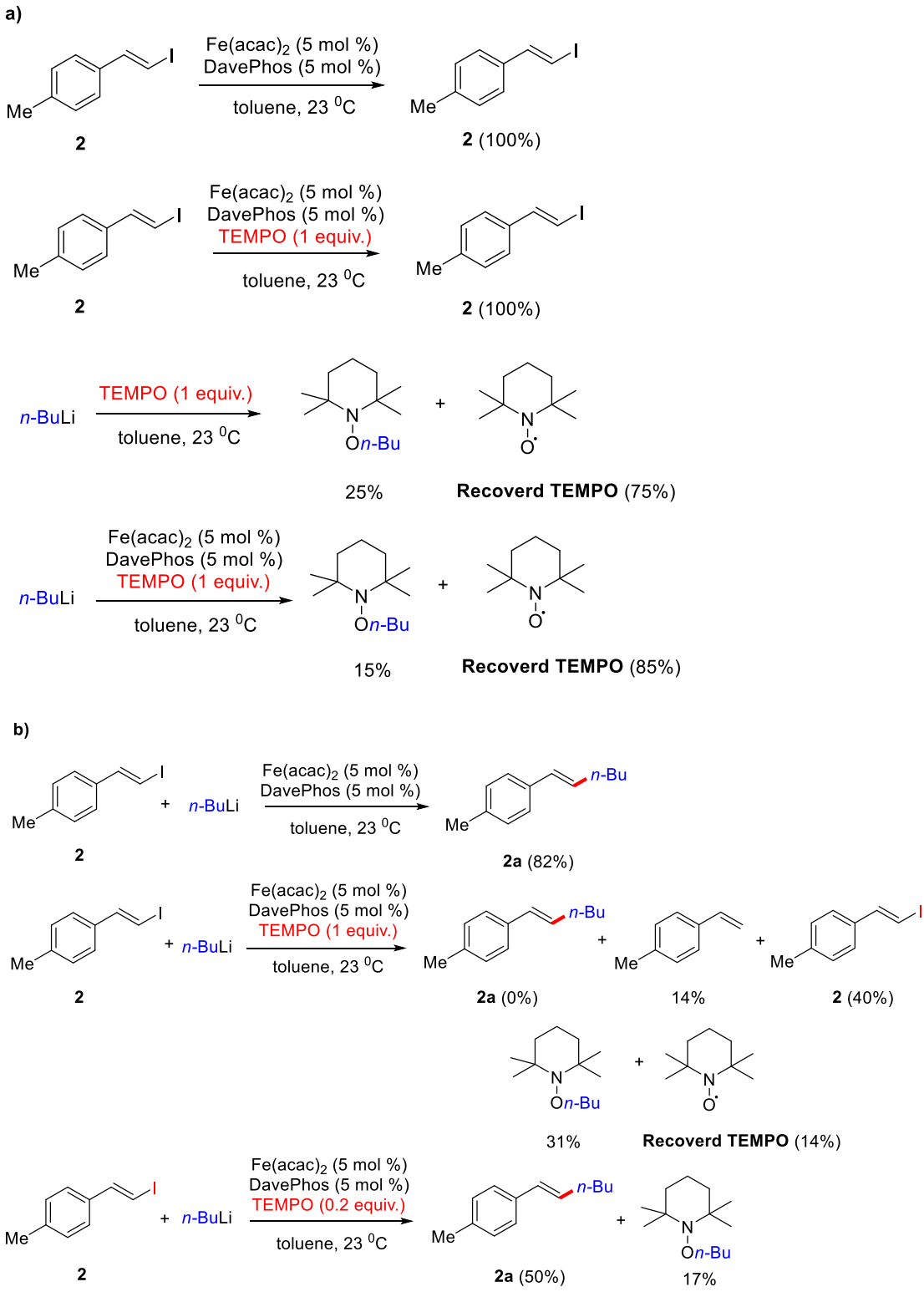
1. General information

All reactions were carried out under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox unless otherwise specified. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) on MERCK silica gel 60 F254 coated on aluminum plates. Visualization was accomplished by irradiation with UV light at 254 nm followed by staining with ceric ammonium molybdate (CAM). Organic solvents were concentrated under reduced pressure at appropriate temperature on a rotary evaporator unless otherwise stated. Column chromatography was performed on silica gel (300-400 mesh). Preparative thin-layer chromatography (PTLC) was performed on glass plates (20 × 20 cm) impregnated with silica gel 60 F254 (0.3-0.4 mm thickness). Diethyl ether, tetrahydrofuran (THF) and toluene for reactions were dried over sodium wire and distilled under an atmosphere of dry Ar. CH_2Cl_2 was dried over calcium hydride and distilled under an atmosphere of dry Ar. NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 377 MHz for ^{19}F) or Bruker Ascend 500 NMR spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C, 471 MHz for ^{19}F). Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were reported as parts per million in δ scale using residual solvent signal as internal standard (note: $CDCl_3$ referenced at δ 7.26 in ^{1}H and δ 77.0 for central line of the triplet in ^{13}C; CD_2Cl_2 referenced at δ 5.32 in ^{1}H and δ 54.0 for central line of the quintet in ^{13}C). Chemical shifts of ^{19}F NMR spectra were reported as parts per million in δ scale using CF_3CO_2H (-76.55 ppm) as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Thermo Finnigan MAT95XL Mass Spectrometer or a Thermo Scientific Q Exactive Focus Mass Spectrometer. GC-MS analyses were performed on an Agilent 7890B system with an Agilent 5977B MSD.

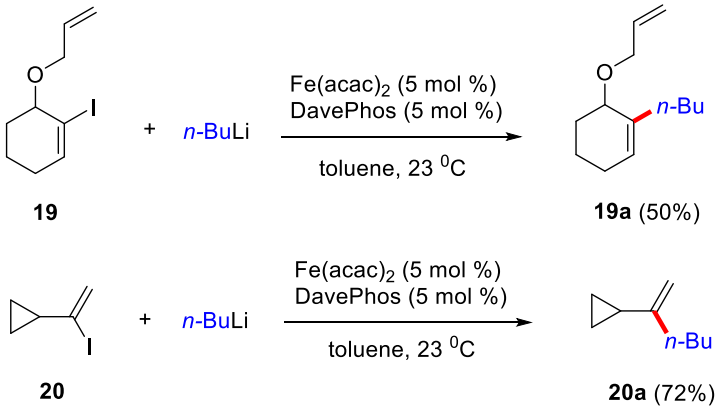
2. Mechanistic study

2.1 Primary mechanistic study

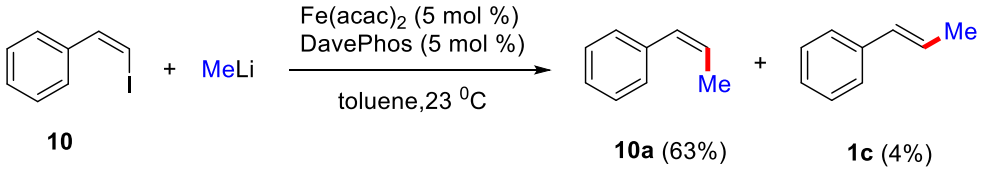


Scheme S1 Control experiments with TEMPO.

To test whether this iron-catalysed cross-coupling reaction is related to a radical pathway, some primary experiments were performed and all the data was collected by GC-MS (Scheme S1). Firstly, TEMPO, a common radical trapper was used and it made the yield decreasing dramatically (Scheme S1b). But due to the situation that *n*-butyllithium could be trapped by TEMPO directly even without any iron catalysts (Scheme S1a), it was hard to say the inherited reaction was caused by the trapped radical or insufficient lithium. Then we tried some radical clock experiments, which showed the expected ring-opening or ring closing products were not found (Scheme S2). In addition, it was observed that the *Z*-configuration substrate **10** could remain the configuration after reaction and the ration of Z/E is more than 15:1 (Scheme S3). These evidences demonstrated that radical pathways were not likely to be involved in this reaction.



Scheme S2 Radical clock experiments.



Scheme S3 Reaction of *Z*-configuration substrate **10**.

After that we monitored a typical reaction by every 30min using GC-MS. It showed lithium-halide exchange would occur at initial stage, but after 30min cross-coupling compound increased rapidly, as well as some homo-coupling product. Finally, only very little lithium-halide exchange product stayed, and the largest proportion of starting materials conversed into cross-coupling product (Figure 1).

Then we did a series of control experiments to compare different situations (Scheme S4). We found that vinyl-lithium could not be coupled with *n*-iodobutane under iron-catalysed condition. And without *n*-iodobutane, the vinyl-lithium conversed into homo-coupling product with 65% GC yield under the same condition. Noticeably, when vinyl-lithium was firstly stirred under iron-catalysed condition for a while,

followed by the addition of *n*-butyllithium, very little cross-coupling product was observed. But with the addition of the mixture of (*E*)-2-iodovinylbenzene and *n*-butyllithium, after vinyl-lithium stirring for several seconds under iron-catalysed condition, the proportion of cross-coupling product increased. Even under iron(zero) condition, small portion of cross-coupling product was found.

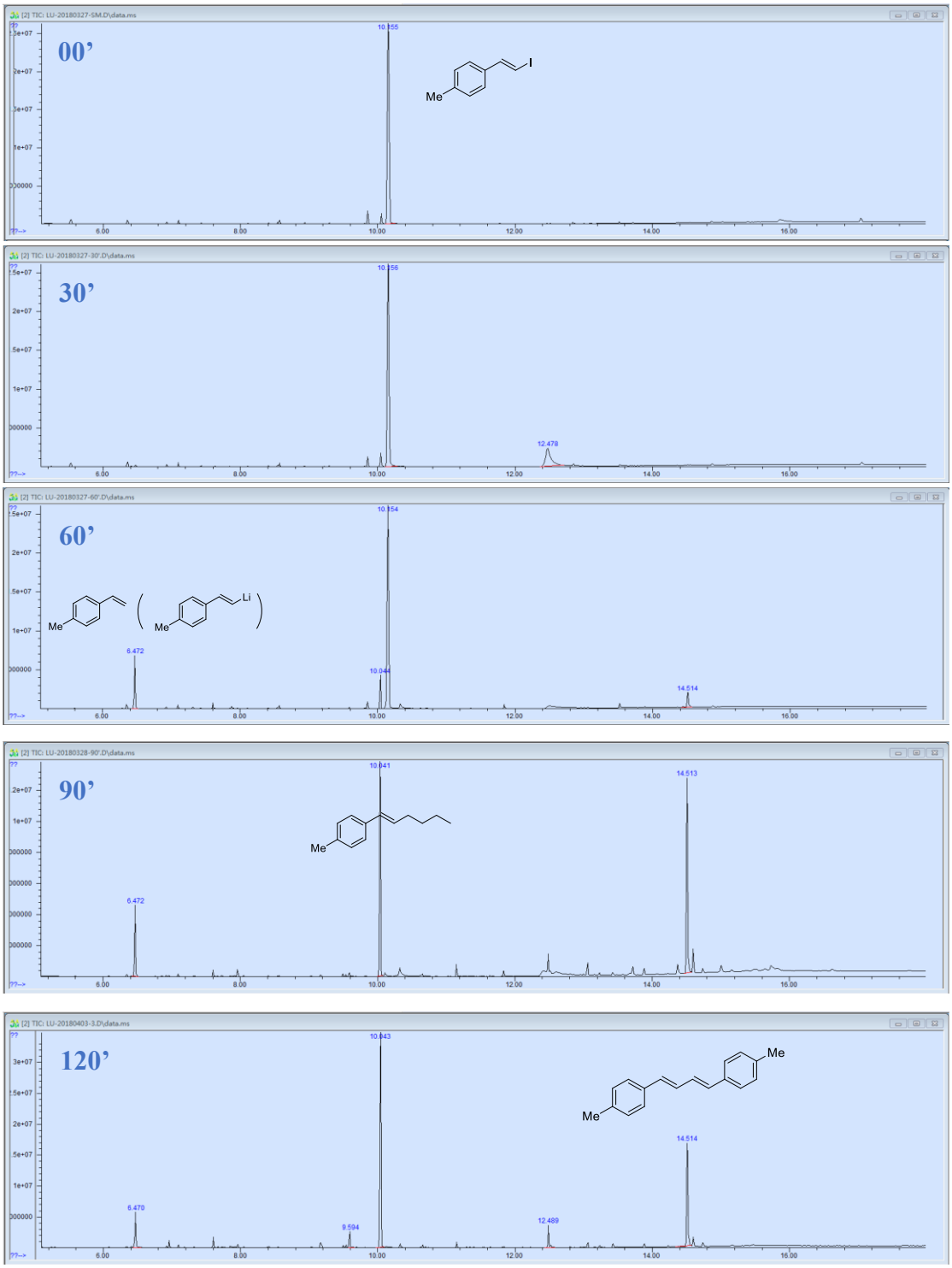
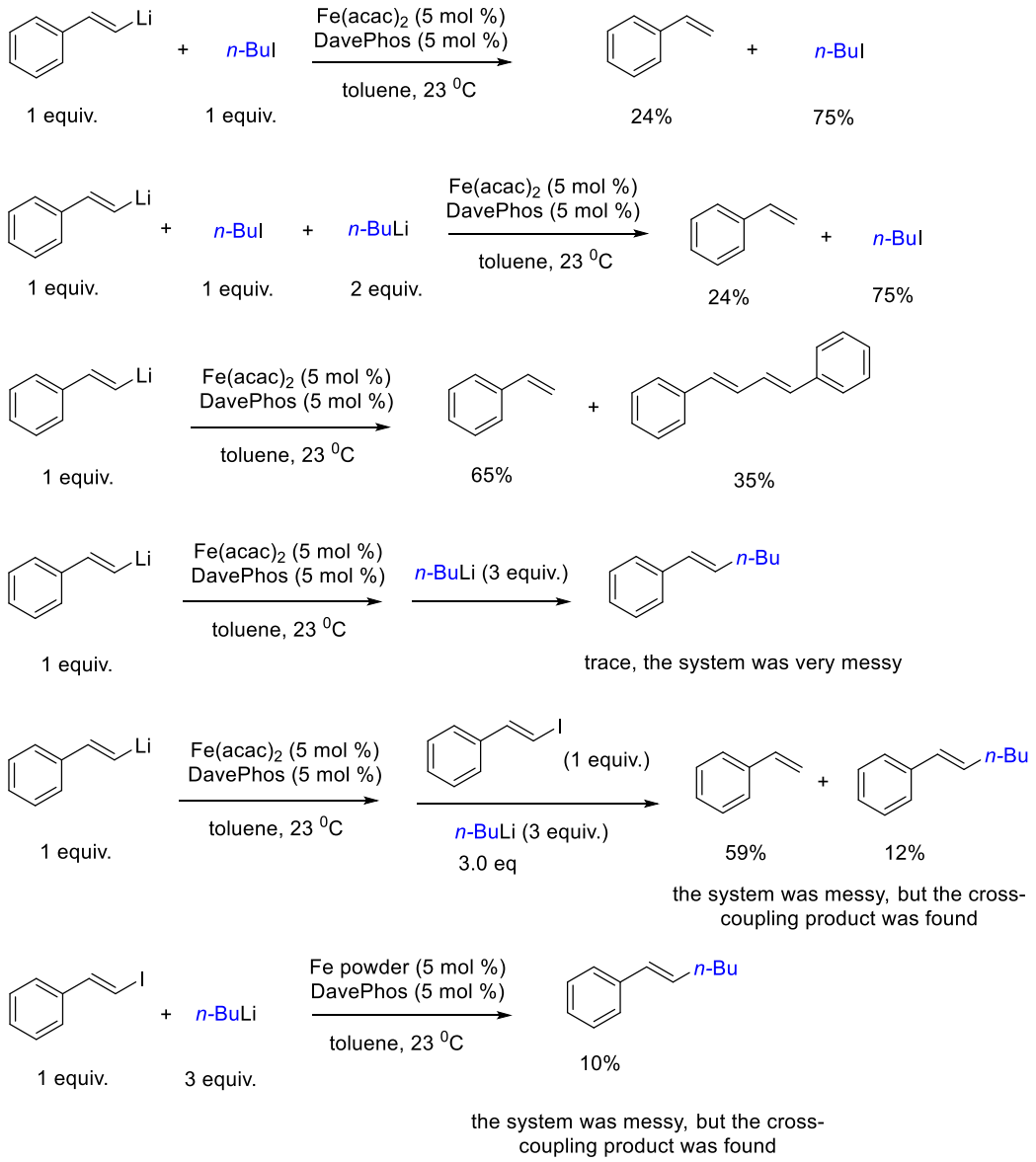
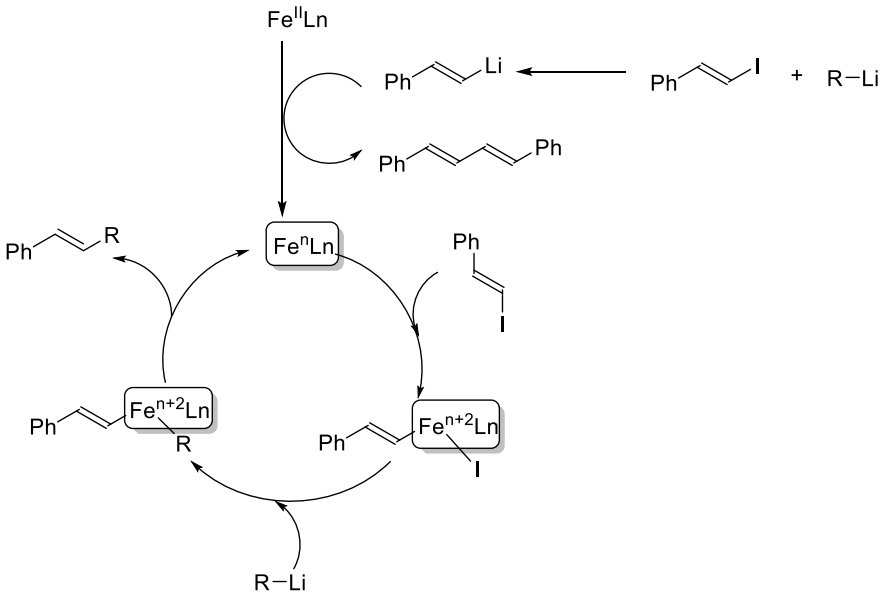


Figure 1. GC-MS results.



Scheme S4 Control experiments.

2.2 Proposed plausible mechanism

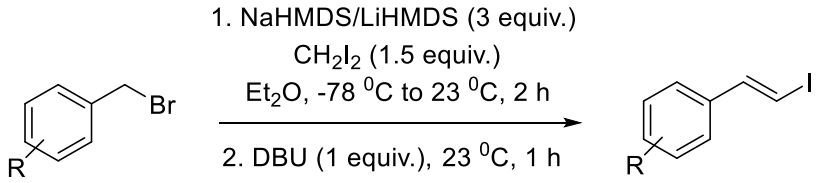


Scheme S5 Proposed plausible mechanism.

3. General procedures & experimental data

3.1 General procedures

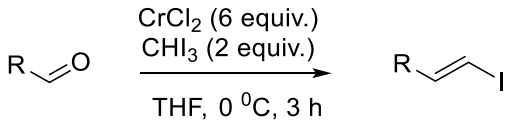
Method A[1]:



To a solution of Et_2O was added NaHMDS/LiHMDS (2.0 M solution in THF, 3.0 equiv.) dropwise at -78 ^{0}C under Ar. CH_2I_2 (1.5 equiv.) was added dropwise at the same temperature. After 20-30 min, benzyl bromide (1.0 equiv.) was added and the reaction system was allowed to stir at -78 ^{0}C for 1-1.5h and then warm up to room temperature. DBU (1.0 equiv.) was added at room temperature. and the reaction system was stirred for another 1h. When the reaction was completed (monitored by TLC), it was diluted by Et_2O and filtered through a pad of Celite. The residue was dried over Na_2SO_4 and the solvent was removed by reduced pressure. Purification on column chromatography afforded the corresponding product.

Using the compound **1** as the example: CH_2I_2 (6 mmol, 0.48 mL) was added dropwise to a solution of NaHMDS (12 mmol, 6.0 mL) in Et_2O (6 mL) at -78 ^{0}C under Ar. After 30 min, benzyl bromide (4 mmol, 0.47 mL) was added dropwise at the same temperature under Ar. Then the reaction system was stirred at -78 ^{0}C for 90 min and then warm up to room temperature for 30 min. DBU (1.0 equiv.) was added at room temperature and the reaction system was stirred for another 1h. It was diluted by Et_2O and filtered through a pad of Celite. The residue was dried over Na_2SO_4 and the solvent was removed by reduced pressure. Purification on column chromatography (eluent: 100% Hexane) afforded the corresponding product as a light-orange oil (819.0 mg, 89% in yield).

Method B[2]:

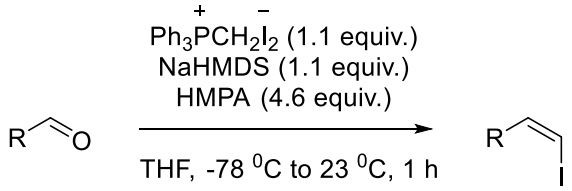


To a suspension of $CrCl_2$ (6.0 equiv.) in dry THF was added the solution of aldehyde and CHI_3 in THF at 0 ^{0}C. After 3 h, H_2O was poured into the system and it was extracted with Et_2O. The organic layer was collected, dried over Na_2SO_4, and concentrated. Purification on column chromatography afforded the corresponding product.

Using the compound **6** as the example: to a suspension of $CrCl_2$ (12 mmol, 1.47g) in

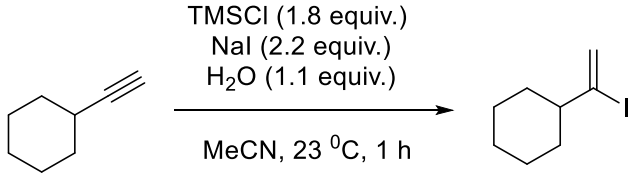
THF (4 mL) was added the solution of CHI_3 (4 mmol, 1.57g) and piperonal (2 mmol, 300.2 mg) in 2 mL of THF at room temperature. After 3 h, H_2O was poured into the system and it was extracted with Et_2O. The organic layer was collected, dried over Na_2SO_4, and concentrated. Purification on column chromatography (eluent: Hexane/Ethyl acetate = 30:1) afforded the corresponding product as a white solid (312.4 mg, 57% in yield).

Method C[3]:



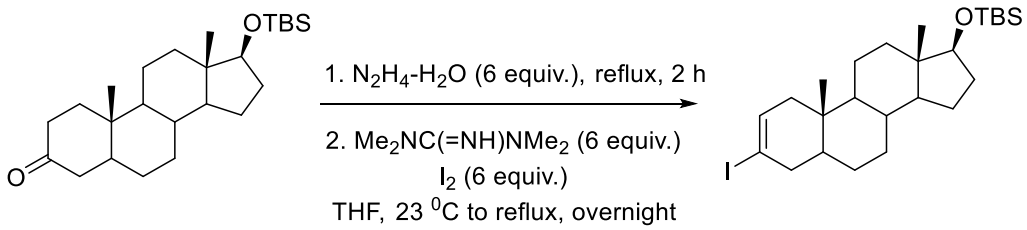
To a solution of NaHMDS (1.1 equiv.) in THF was added the Wittig reactant (1.1 equiv.) at room temperature under Ar. After it turned clearly blood red of dark orange, the reaction system was cooled down to -78 ^{0}C, followed by the addition of HMPA (4.6 equiv.). After 10min, aldehyde (1.0 equiv.) was added at -78 ^{0}C. The reaction system was allowed to warm up to room temperature in 1 h. When it was completed, it was quenched with aqueous $NaHCO_3$ and extracted with Hexane. The organic layer was collected, dried over Na_2SO_4 and concentrated. Column Chromatography gave the product.

Using the compound **11** as the example: to a suspension of $Ph_3PCH_2I_2$ (1.1 mmol, 443.5 mg) in THF (1 mL) was added NaHMDS (1.1 mmol, 0.55 mL) at room temperature. After a few minutes, HMPA (4.6 mmol, 0.80 mL) was added at -78 ^{0}C, followed by the addition of the solution of 4-bromobenzaldehyde (1 mmol, 185.0 mg). After 3 h, it was quenched with aqueous $NaHCO_3$ and extracted with Hexane. The organic layer was collected, dried over Na_2SO_4 and concentrated. Column Chromatography (eluent: 100% Hexane) gave the product as a colorless oil (141.0 mg, 45% in yield).



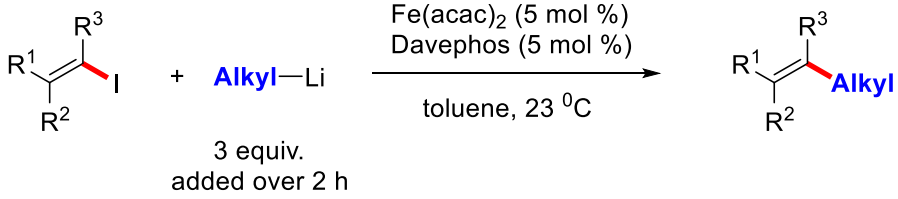
Method D[4]**:** Using the compound **17** as example. At room temperature TMSCl (3.6 mmol, 0.47 mL) was added to a solution of NaI (4.4 mmol, 0.64 g) in MeCN (4 mL), followed by water (2.2 mmol, 0.02 mL). After 10 minutes, cyclohexylacetylene (2 mmol, 0.24 mL) was added and the reaction was stirred for 1 hour at room

temperature. The reaction was then quenched with water. The aqueous layer was washed twice with diethyl ether and the combined organic layers were washed twice with aqueous saturated sodium thiosulfate. Crude material was collected as a colorless oil (379.0 mg, 80% in yield) and was used immediately without any purification.



Method E[5]**:** Using the compound **18** as the example. The cyclohexanone derivative (2 mmol, 809.4 mg) was added dropwise over 5-10 min to hydrazine monohydrate (3 mmol, 0.10 mL) with vigorous stirring. A white precipitate was formed and the reaction mixture was refluxed at 150 °C for 2 h. The mixture was cooled to room temperature and then water was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with saturated NaCl solution, dried with Na_2SO_4 and concentrated to give the crude hydrazone. Tetramethylguanidine (9.4 mmol, 1.18 mL) in THF (1 mL) was added to iodine (1.2 mmol, 303.7 mg) in 1 mL of THF at 0 ^{0}C. After 15 min, the crude hydrazone in THF was added via dropping funnel to the resulting solution over 15 min at 0 ^{0}C. The reaction mixture was then allowed to warm up to room temperature overnight, refluxed for 2 h at 85 °C and then cooled to room temperature. The organic layer was washed with aqueous HCl (1 M) and saturated NaCl solution. The aqueous layer was extracted with Et_2O, dried with Na_2SO_4, concentrated and purified via column chromatography (eluent: 100% Hexane) to give the product as a light-yellow solid (679.3 mg, 66% in yield).

Method F:



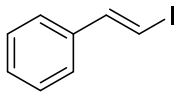
$Fe(acac)_2$ (5 mol %) and Davephos (5 mol %) were carried out in test tube in glove box and then the solution of vinyl iodine (1.0 equiv.) in 2 mL of toluene was added to the test tube at room temperature. Alkyl lithium (3 equiv.) was added by syringe pump

over 2h at room temperature. After addition, the reaction system was stirred at r.t. for another 30min. It was then filtered through a pad of Celite using EtOAc and CH_2Cl_2. The solvent was removed by reduced pressure and the residue was purified by column chromatograph to afford the product.

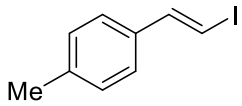
Using the compound **1a** as the example: $Fe(acac)_2$ (0.01 mmol, 2.5 mg) and Davephos (0.01 mmol, 3.9 mg) were carried out in test tube in glove box and then the solution of compoumd **1** (0.2 mmol, 46 mg) in 1 mL of toluene was added to the test tube at room temperature. *n*-Butyl lithium (0.6 mmol, 0.37 ml) was added by syringe pump over 2 h at room temperature. After addition, the reaction system was stirred at room temperature for another 30min. It was then filtered through a pad of Celite using Ethyl acetate and CH_2Cl_2. The solvent was removed by reduced pressure and the residue was purified by column chromatograph (eluent: 100% Hexane) to afford the product as a colorless oil (23.1 mg, 72%).

3.2 Experimental data

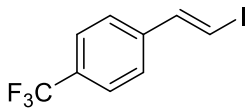
3.2.1 Data of substrates



(*E*)-2-Iodovinylbenzene 1: 4 mmol was employed with Method A and 819.0 mg was obtained as a light-orange oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 14.9Hz, 1H), 7.33-7.39 (m, 5H), 6.83 (d, *J* = 14.9 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 137.7, 132.3, 128.7, 128.4, 126.0 ppm.

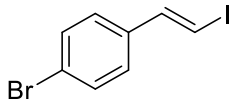


(*E*)-1-(2-Iodovinyl)-4-methylbenzene 2: 6 mmol was employed with Method A and 1.22 g was obtained as a light-yellow solid using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 14.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 14.9 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 138.4, 135.0, 129.4, 125.9, 75.4, 21.3 ppm.

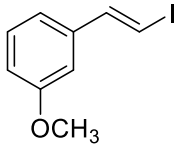


(*E*)-1-(2-Iodovinyl)-4-(trifluoromethyl)benzene 3: 1 mmol was employed with Method A and 353.7 mg was obtained as a light-orange oil using column chromatography (eluent: 100% Hexane).Method A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ =

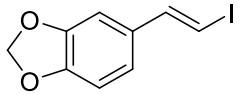
7.58 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 15.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 15.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.7, 140.8, 130.6, 130.2, 129.9, 129.6, 128.1, 126.9, 126.2, 125.8, 125.8, 125.7, 125.7, 125.4, 122.7, 120.0, 80.0 ppm.



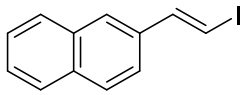
(*E*)-1-(2-Iodovinyl)-4-bromobenzene 4: 1 mmol was employed with Method A and 144.5 mg was obtained as a light-orange oil using column chromatography (eluent: 100% Hexane).Method A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 15.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 14.7 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.3, 136.1, 133.1, 131.4, 127.0, 121.9 ppm.



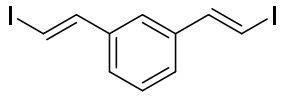
(*E*)-1-(2-Iodovinyl)-3-methoxylbenzene 5: 2 mmol was employed with Method A and 152.2 mg was obtained as a light-orange oil using column chromatography (eluent: Hexane/Ethyl acetate = 40:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 14.9 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 6.90-6.84 (m, 3H), 6.83 (d, *J* = 14.9 Hz, 1H) 3.81 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 144.9, 139.0, 129.7, 118.6, 114.0, 111.3, 55.3 ppm.



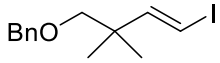
5-[(1*E*)-2-Iodoethenyl]-1,3-benzodioxole 6: 2 mmol was employed with Method B and 312.4 mg was obtained as a white solid using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 (d, J = 14.8 Hz, 1H), 6.81 (s, 1H), 6.74 (d, J = 1.4 Hz, 2H), 6.62 (d, J = 14.8 Hz, 1H), 5.96 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.7, 147.4, 143.9, 131.8, 120.5, 107.9, 104.8, 100.8, 73.7 ppm.



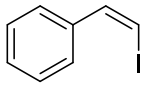
(*E*)-2-(2-Iodovinyl)naphthalene 7: 1 mmol was employed with Method A and 84.0 mg was obtained as a light-yellow oil using column chromatography (eluent: 100% Hexane).Method A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.7 Hz, 3H), 7.68(s, 1H), 7.59 (d, *J* = 15 Hz, 1H), 7.49-7.46 (m, 3H), 6.97 (d, *J* = 14.8 Hz, 1H) ppm.



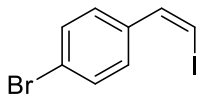
1,3-Bis[(1*E*)-2-iodoethenyl]benzene 8: 2 mmol was employed with Method A and 132.1 mg was obtained as a light-orange oil using column chromatography (eluent: 100% Hexane).. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 (d, J = 14.9 Hz, 1H), 7.30-7.27 (m, 2H), 7.23 (d, J = 1.4 Hz, 1H), 7.20 (d, J = 6.0 Hz, 1H), 6.87 (d, J = 14.9 Hz, 1H) ppm.



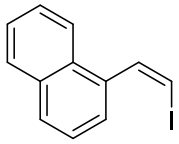
(*E*)-(((4-Iodo-2,2-dimethylbut-3-en-1-yl)oxy)methyl)benzene 9: 1.2 mmol was employed with Method B and 139.1 mg was obtained as a light-yellow oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37-7.28 (m, 5H), 6.60 (d, *J* = 14.7 Hz, 1H), 6.04 (d, *J* = 14.6 Hz, 1H), 4.51 (s, 2H), 3.19 (s, 2H), 1.04 (s, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.3, 138.5, 128.4, 127.5, 127.4, 78.2, 74.0, 73.3, 42.1, 23.8 ppm.



(*Z*)-(2-Iodovinyl)benzene 10: 1 mmol was employed with Method C and 103.0 mg was obtained as a light-yellow oil using column chromatography (eluent: 100% Hexane).Method C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.5 Hz, 2H), 7.40–7.34 (m, 3H), 7.32(d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 138.6, 136.7, 128.4, 128.4, 128.2, 79.3 ppm

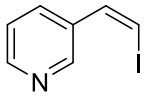


(*Z*)-1-(2-Iodovinyl)-4-bromobenzene 11: 1 mmol was employed with Method C and 141.0 mg was obtained as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52–7.48 (m, 4H), 7.25(d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.5, 136.1, 131.4, 129.9, 122.4, 80.4 ppm.

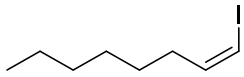


1-[(1*Z*)-2-Iodoethenyl]naphthalene 12: 1 mmol was employed with Method C and 109.4 mg was obtained as a light-orange oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.6 Hz, 3H), 7.72 (d, *J* =

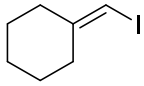
8.3 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.53-7.48 (m, 3H), 6.90 (d, *J* = 8.3 Hz, 1H) ppm.



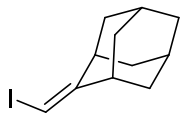
3-[(1*Z*)-2-Iodoethenyl]pyridine 13: 1 mmol was employed with Method C and 90.5 mg was obtained as a light-orange oil using column chromatography (eluent: Hexane/Et_3N = 100:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.74 (d, J = 2.5 Hz, 1H), 8.57 (dd, J = 4.5, 1.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 6.75 (d, J = 8.5 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.0, 149.3, 135.5, 134.9, 132.7, 122.9, 82.4 ppm.



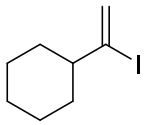
(*Z*)-1-Iodo-1-octene 14: 3 mmol was employed with Method C and 272.5 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.17 (t, *J* = 7.5 Hz, 2H), 2.13 (td, *J* = 7.0, 2.5 Hz, 2H), 1.54–1.50 (m, 2H), 1.30–1.28 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 141.5, 82.1, 34.7, 31.8, 29.1, 29.1, 28.0, 14.1 ppm.



(Iodomethylene)cyclohexane 15: 1 mmol was employed with Method B and 151.6 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).Method B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.77 (s, 1H), 2.28 (d, *J* = 6.0 Hz, 4H), 1.55-1.51(m, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.3, 71.1, 37.3, 35.9, 28.0, 27.0, 26.1 ppm.

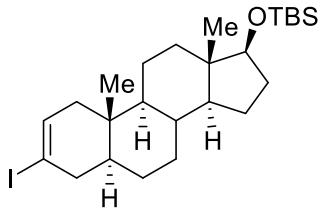


(1*r*, 3*r*, 5*R,7*S**)-2-(Iodomethylene)adamantane 16:** 1 mmol was employed with Method B and 157.3 mg was obtained as a light-yellow solid using column chromatography (eluent: 100% Hexane).Method B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.69 (s, 1H), 2.93 (s, 1H), 2.70 (s, 1H), 1.89 (d, *J* = 23.4 Hz, 3H), 1.82 (t, *J* = 6.1 Hz, 6H), 1.77 (d, *J* = 11.6 Hz, 3H) ppm.



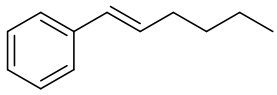
(1-Iodoethenyl)cyclohexane 17: 2 mmol was employed with Method D and 379.0 mg was obtained as a colorless oil using column chromatography (eluent: 100%

Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.05 (dd, *J* = 1.6, 1.1 Hz, 1H), 5.69 (d, *J* = 1.6 Hz, 1H), 3.09 (s, 1H), 2.18 (d, *J* = 12.7 Hz), 2.04-1.63 (m, 8H) ppm.

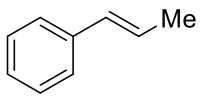


***tert*-Butyl(((5*S*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-iodo-10,13-dimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)oxy)dimethylsilane 18:** 2 mmol was employed with Method E and 679.3 mg was obtained as a light-yellow solid using column chromatography (eluent: 100% Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.11 (dd, *J* = 3.3, 1.7 Hz, 1H), 3.55 (tt, *J* = 10.9, 4.8 Hz, 1H), 2.12 (ddd, *J* = 14.9, 6.4, 3.3 Hz, 1H), 1.91 (ddd, *J* = 15.0, 11.3, 1.7 Hz, 1H), 1.73-1.61 (m, 4H), 1.61-1.56 (m, 1H), 1.49-1.41 (m, 3H), 1.38-1.31 (m, 2H), 1.31-1.25 (m, 2H), 1.17 (td, *J* = 12.6, 4.5 Hz, 1H), 1.12-1.05 (m, 1H), 0.99-0.90 (m, 2H), 0.88 (s, 9H), 0.82 (d, *J* = 0.6 Hz, 3H), 0.71 (s, 3H), 0.05 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.5, 112.9, 72.1, 54.8, 50.1, 45.2, 38.6, 37.0, 36.3, 35.7, 34.6, 33.7, 31.9, 31.6, 28.6, 26.0, 21.1, 18.3, 15.3, 12.3, -4.5 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{25}H_{44}IOSi$ [M+H]+ 515.2200; found:515.2201.

3.2.2 data of products

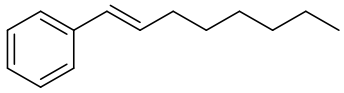


(*E*)-1-Hexenylbenzene 1a: 0.2 mmol was employed with Method F and 23.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 1.5 Hz, 1H), 7.33-7.27 (m, 2H), 7.20-7.17 (m, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* =15.7, 6.8 Hz, 1H), 2.24-2.18 (m, 2H), 1.48-1.44 (m, 2H), 1.42-1.34 (m, 2H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 138.0, 131.2, 129.7, 128.5, 126.7, 125.9, 32.7, 31.5, 22.3, 14.0 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{12}H_{16}$ [M+H]+ 161.1325; found: 161.1328.

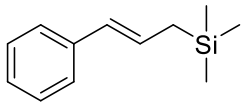


1-Propenyl-benzene 1b: 0.2 mmol was employed with Method F and 21.3 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35-7.29 (m, 4H), 7.22- 7.16 (m, 1H), 6.41 (dd, *J* = 15.8, 1.7 Hz, 1H), 6.25 (dq, *J* = 15.8, 6.6 Hz, 1H), 1.89 (dd, *J* = 6.6, 1.6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.9, 131.0, 128.5, 126.7, 125.8, 125.7, 18.5 ppm.

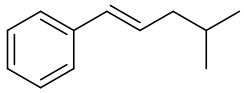
HRMS (APCI+): m/z calcd. for C_9H_{10} [M+H]+ 119.0855; found: 119.0857.



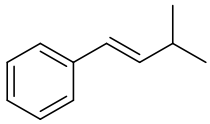
(1*E*)-1-Octen-1-ylbenzene 1c: 0.29 mmol was employed with Method F and 34.5 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.22 (q, *J* = 7.2 Hz, 2H), 1.47 (q, *J* = 7.2 Hz, 2H), 1.39- 1.29 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 31.8, 29.4, 28.9, 22.7, 14.1 ppm.



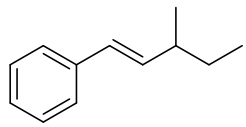
[(1*E*)-3-(Trimethylsilyl)-1-propen-1-yl]benzene 1d: 0.20 mmol was employed with Method F and 24.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33-7.28 (m, 5H), 6.27-6.23 (m, 2H), 1.73-1.64 (m, 2H), 0.06 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.6, 138.1, 128.0, 127.4, 125.7, 125.1, 23.5, -2.3 ppm.



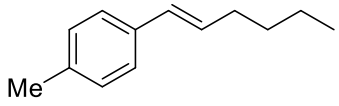
(*E*)-(4-Methyl-1-pentenyl)benzene 1e: 0.30 mmol was employed with Method F and 22.6 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 7.1 Hz, 2H), 7.33-7.27 (m, 2H), 7.23-7.16 (m, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.6, 7.2 Hz, 1H), 2.10 (t, *J* = 7.0 Hz, 2H), 1.75-1.70 (m, 1H), 0.95 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.5, 130.3, 129.5, 128.0, 126.3, 125.5, 42.0, 28.2, 22.0 ppm. **HRMS** (APCI+): m/z calcd. for $C_{12}H_{16}$ [M+H]+ 161.1325; found: 161.1328.



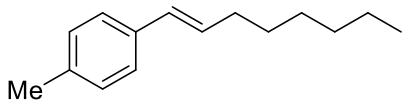
[(1*E*)-3-Methyl-1-butenyl]-benzene 1f: 0.30 mmol was employed with Method F and 18.6 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.34 (m, 2H), 7.31-7.26 (m, 2H), 7.21-7.19 (m, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.53-2.44 (m, 1H), 2.32 -2.27 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, CDCl3) δ = 137.6, 128.0, 126.4, 126.3, 125.5, 99.5, 31.1, 26.5, 22.0 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{11}H_{14}$ [M+H]+ 147.1168; found: 147.1170.



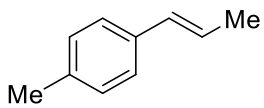
[(1*E*)-3-Methyl-1-penten-1-yl]benzene 1g: 0.30 mmol was employed with Method F and 28.8 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39-7.33 (m, 2H), 7.31-7.26 (m, 2H), 7.22-7.16 (m, 1H), 6.35 (d, *J* = 15.9, 1H), 6.10 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.24-2.17 (m, 1H), 1.45-1.40 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (1250 MHz, $CDCl_3$) δ = 138.0, 136.8, 128.5, 128.1, 126.7, 126.0, 38.9, 29.8, 20.2, 11.8 ppm.



1-(1*E*)-1-Hexen-1-yl-4-methylbenzene 2a: 0.30 mmol was employed with Method F and 42.8 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (s, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.38 (d, *J* = 15.8, 1H), 6.20 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.35 (s, 3H), 2.20 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.52- 1.45 (m, 2H), 1.43-1.37 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.0, 134.8, 129.7, 129.1, 128.7, 125.4, 32.4, 31.2, 21.9, 20.7, 13.6 ppm. **HRMS** (ESI+): m/z calcd. For $C_{13}H_{18}$ [M]+ 174.1403; found: 174.1401. **HRMS** (APCI+): m/z calcd. for $C_{13}H_{18}$ [M+H]+ 175.1481; found: 175.1481.

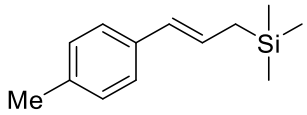


1-Methyl-4-(1*E*)-1-octen-1-ylbenzene 2b: 0.30 mmol was employed with Method F and 52.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.34 (s, 3H), 2.20 (dd, *J* = 16.0, 8.0 Hz, 2H), 1.47 (q, *J* = 7.4 Hz, 2H), 1.41-1.27 (m, 7H), 0.92 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.4, 135.2, 130.2, 129.5, 129.2, 125.8, 33.1, 31.9, 29.5, 28.9, 22.7, 21.1, 14.5 ppm. **HRMS** (APCI+): m/z calcd. for $C_{15}H_{22}$ [M+H]+ 203.1794; found: 203.1797.

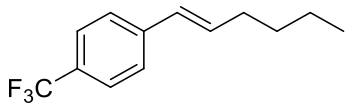


1-Methyl-4-(1*E*)-1-propen-1-ylbenzene 2c: 0.33 mmol was employed with Method F and 39.5 mg was obtained as a colorless oil using column chromatography (eluent:

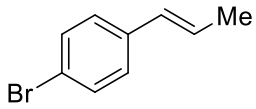
100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (s, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.7, 6.6 Hz, 1H), 2.35 (s, 3H), 1.89 (dd, *J* = 6.6, 1.6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.4, 135.2, 130.9, 129.2, 125.7, 124.6, 21.2, 18.5 ppm.



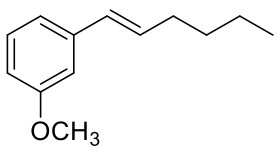
1-Methyl-4-[(1*E*)-3-(trimethylsilyl)-1-propen-1-yl]benzene 2d: 0.32 mmol was employed with Method F and 62.0 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.20 (s, 2H), 2.32 (s, 3H), 0.93-0.81 (m, 2H), 0.04 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.0, 129.3, 128.2, 126.9, 125.2, 29.0, 24.0, 21.2, -1.7 ppm. **HRMS** (APCI+): m/z calcd. for $C_{13}H_{20}Si$ [M+H]+ 205.1407; found: 205.1042.



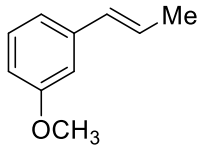
1-(1*E*)-1-Hexen-1-yl-4-(trifluoromethyl)benzene 3a: 0.28 mmol was employed with Method F and 53.5 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.38-6.29 (m, 1H), 2.24 (dd, *J* = 16.0, 8.0 Hz, 2H), 1.52-1.44 (m, 2H), 1.41-1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.4, 134.1, 128.6, 128.4, 126.0, 125.7, 125.5, 125.4, 125.4, 125.3, 123.0, 120.3, 32.7, 31.3, 22.3, 13.9 ppm. **HRMS** (APCI+): m/z calcd. for $C_{13}H_{13}F$ [M-F]+ 209.1136; found: 209.1136.



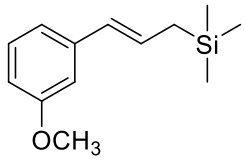
1-Bromo-4-(1-propen-1-yl)benzene 4a: 0.21 mmol was employed with Method F and 37.4 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44-7.37 (m, 2H), 7.22-7.15 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.29-6.19 (m, 1H), 2.36 (s, 1H), 1.87 (dd, *J* = 6.4, 1.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 136.9, 131.5, 129.9, 127.4, 126.6, 120.3, 18.5 ppm.



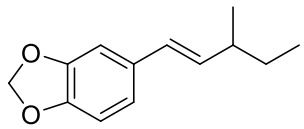
(*E*)-1-(1-Hexenyl)-3-methoxybenzene 5a: 0.18 mmol was employed with Method F and 22.0 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.89 (s, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.27-6.21 (m, 1H), 3.82 (s, 3H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.45 (q, *J* = 7.5 Hz, 2H), 1.37 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.3, 139.0, 131.5, 129.1, 129.0, 118.2, 111.9, 110.8, 54.7, 32.3, 31.1, 21.9, 13.5 ppm.



1-Methoxy-3-(1*E*)-1-propen-1-ylbenzene 5b: 0.30 mmol was employed with Method F and 36.6 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.88 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.29-6.21 (m, 1H), 3.82 (s, 3H), 1.89 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 139.4, 130.9, 129.4, 126.1, 118.5, 112.3, 111.2, 55.2, 18.5 ppm.

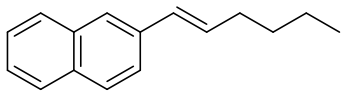


1-Methoxy-3-[(1*E*)-3-(trimethylsilyl)-1-propen-1-yl]benzene 5c: 0.30 mmol was employed with Method F and 56.6 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.23 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.31-6.21 (m, 2H), 3.83 (s, 3H), 1.70 (d, *J* = 7.0 Hz, 2H), 0.08 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 140.0, 129.4, 128.3, 128.1, 118.2, 111.7, 111.1, 55.2, 23.4, -1.8 ppm.

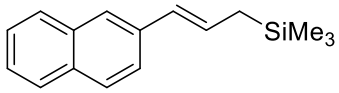


(*E*)-5-(3-Methylpent-1-en-1-yl)benzo[*d*][1,3]dioxole 6a: 0.30 mmol was employed with Method F and 30.3 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.91 (s, 1H), 6.78-6.72 (m, 2H), 6.25 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.20-2.05 (m, 1H), 1.43-1.35 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 2H), 0.89 (t, *J* = 14.8 Hz,

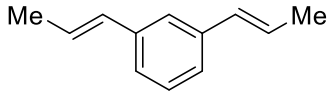
3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.9, 135.1, 132.5, 127.6, 120.2, 108.2, 105.4, 100.9, 38.8, 29.9, 20.2, 11.8 ppm. **HRMS** (ESI+): *m/z* calcd. for $C_{13}H_{16}O_2$ [M]+ 204.1145; found: 204.1144.



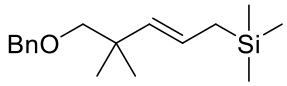
2-(1-Hexen-1-yl)naphthalene 7a: 0.30 mmol was employed with Method F and 46.4 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78 (t, *J* = 7.9 Hz, 3H), 7.68 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.47-7.39 (m, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.37 (dt, *J* = 15.6, 6.9 Hz, 1H), 2.28 (q, *J* = 7.1 Hz, 2H), 1.51 (ddd, *J* = 11.3, 7.9, 5.3 Hz, 2H), 1.41 (q, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 135.0, 133.3, 132.2, 131.3, 129.4, 127.6, 127.4, 127.2, 125.7, 125.0, 124.8, 123.1, 32.4, 31.1, 21.9, 13.6 ppm. **HRMS** (APCI+): m/z calcd. for $C_{16}H_{18}$ [M+H]+ 211.1481; found: 211.1481.



2-[(1*E*)-3-(Trimethylsilyl)-1-propen-1-yl]naphthalene 7b: 0.40 mmol was employed with Method F and 73.9 mg was obtained as a light yellow solid using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78-7.73 (m, 3H), 7.62 (s, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.45-7.37 (m, 2H), 6.43(s, 1H), 1.73 (d, J = 4.2 Hz, 2H), 0.08 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 135.9, 133.8, 132.4, 128.4, 128.4, 128.0, 127.7, 127.6, 126.1, 125.2, 124.5, 124.5, 123.5, 24.2, -1.8 ppm. **HRMS** (APCI+): m/z calcd. for $C_{16}H_{20}Si$ [M+H]+ 241.1407; found: 241.1415.

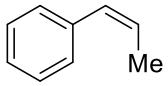


1,3-Di-(1*E*)-1-propenylbenzene 8a: 0.35 mmol was employed with Method F and 51.8 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30-7.27 (m, 1H), 7.25-7.20 (m, 1H), 7.19-7.16 (m, 2H), 6.40 (d, *J* = 15.7 Hz, 2H), 6.31-6.19 (m, 2H), 1.89 (d, *J* = 8.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 138.1, 131.0, 128.6, 125.7, 124.3, 123.5, 18.5 ppm. **HRMS** (APCI+): m/z calcd. for $C_{12}H_{14}$ [M+H]+ 159.1168; found: 159.1168.

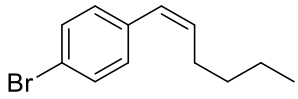


(*E*)-(5-(Benzyloxy)-4,4-dimethylpent-2-en-1-yl)trimethylsilane 9a: 0.22 mmol was employed with Method F and 61.2 mg was obtained as a colorless oil using column

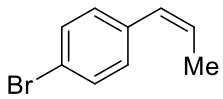
chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34-7.26 (m, 5H), 5.43-5.35 (m, 1H), 5.30 (d, *J* = 16 Hz, 1H), 4.52 (s, 2H), 3.17 (s, 2H), 1.42 (d, *J* = 7.4 Hz, 2H), 1.02 (s, 6H), -0.02 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 139.0, 136.1, 128.2, 127.3, 127.2, 123.1, 80.0, 73.2, 37.4, 25.0, 22.8, -2.0 ppm. **HRMS** (APCI+): m/z calcd. for $C_{17}H_{28}Si$ [M+H]+ 277.1982; found: 277.1988.



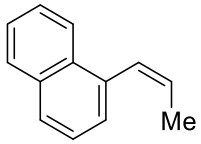
(1*Z*)-1-Propen-1-ylbenzene 10a: 0.40 mmol was employed and 29.8 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.22 (m, 5H), 6.44 (dd, *J* = 11.6, 1.5 Hz**,** 1H), 5.84-5.76 (m, 1H), 1.91 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.6, 129.8, 128.8, 128.1, 126.8, 126.4, 14.6 ppm. **HRMS** (APCI+): *m/z* calcd. for C_9H_{10} [M+H]+ 119.0855; found: 119.0858.



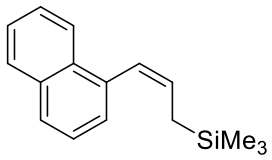
1-Bromo-4-(1*Z*)-1-hexen-1-yl-benzene 11a: 0.23 mmol was employed with Method F and 25.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ =7.50-7.41 (m, 2H), 7.18-7.07 (m, 2H), 6.32 (d, *J* = 11.7 Hz, 1H), 5.73-5.63 (m, 1H), 2.28 (d, *J* = 7.4 Hz, 2H), 1.46-1.38 (m, 2H), 1.37-1.31 (m, 2H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 133.6, 130.8, 129.9, 128.6, 127.8, 124.7, 34.2, 24.9, 20.4, 11.0 ppm. **HRMS** (ESI+): *m/z* calcd. for $C_{12}H_{15}Br$ [M]+ 238.0352; found: 238.0353.



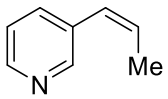
1-Bromo-4-(1*Z*)-1-propen-1-ylbenzene 11b: 0.23 mmol was employed with Method F and 26.4 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.20-7.10 (m, 2H), 6.35 (d, *J* = 11.6 Hz, 1H), 5.81 (dd, *J* = 12.7, 6.4 Hz, 1H), 1.86 (t, *J* = 8.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 137.5, 130.8, 130.0, 128.6, 127.8, 127.2, 60.0, 13.7 ppm. **HRMS** (EI+): *m/z* calcd. for C_9H_9Br [M]+ 195.9882; found: 195.9881.



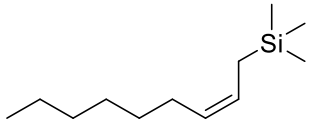
1-(1*Z*)-1-Propen-1-ylnaphthalene 12a: 0.19 mmol was employed with Method F and 30.0 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.05-7.96 (m, 1H), 7.92-7.84 (m, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.54-7.43 (m, 3H), 7.38 (d, *J* = 1.1 Hz, 1H), 6.91 (d, *J* = 11.5 Hz, 1H), 6.06 (dq, *J* = 11.4, 7.0 Hz, 1H), 1.76 (dd, *J* = 7.0, 1.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 134.1, 133.1, 128.6, 128.1, 127.9, 127.4, 126.6, 126.0, 125.3, 125.2, 124.8, 124.6, 13.8 ppm. HRMS (APCI+): m/z calcd. for $C_{11}H_{13}$ [M]+ 169.1012; found: 169.1018.



(*Z*)-Trimethyl[3-(1-naphthalenyl)-2-propenyl]silane 12b: 0.36 mmol was employed with Method F and 70.7 mg was obtained as a light-yellow solid using column chromatography (eluent: 100% Hexane).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.05 (t, J = 3.5 Hz, 1H), 7.86 (dd, *J* = 6, 2.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 3H), 7.46 (d, *J* = 8 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 11.5 Hz, 1H), 6.06 (td, *J* = 11.0, 8.5 Hz, 1H), 1.67 (dd, *J* = 9.0, 2.0 Hz, 2H), -0.02 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 135.3, 133.7, 132.0, 130.6, 128.3, 126.8, 126.3, 125.6, 125.6, 125.3, 125.3, 125.0, 19.6, -1.6 ppm.

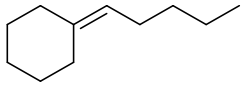


(*Z*)-3-(1-Propenyl)pyridine 13a: 0.39 mmol was employed with Method F and 23.0 mg was obtained as a colorless oil using column chromatography (eluent: Hexane/Ethyl acetate/Et_3N = 100:10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 2.3 Hz, 1H), 8.43 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.57 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.24 (ddd, *J* = 7.9, 4.8, 0.9 Hz, 1H), 6.36 (dd, *J* = 11.6, 2.0 Hz, 1H), 5.90 (dd, *J* = 11.6, 7.3 Hz, 1H), 1.88 (dd, *J* = 7.2, 1.9 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.0, 147.4, 135.7, 129.2, 126.3, 123.0, 14.6 ppm. **HRMS** (ESI+): *m/z* calcd. for C_8H_9N [M]+ 119.0730; found: 119.0730.

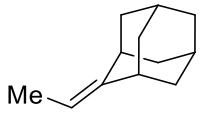


Trimethyl(2*Z*)-2-nonen-1-ylsilane 14a: 0.57 mmol was employed with Method F and 80.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.38 (d, *J* = 9.6 Hz, 1H), 5.31-5.20 (m, 1H), 1.97 (d, *J* = 7.0 Hz, 2H), 1.46 (d, *J* = 8.6 Hz, 2H), 1.43 (s, 3H), 0.88 (d, *J* =

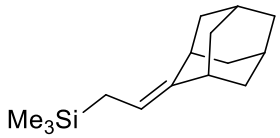
7.2 Hz, 5H), 0.00 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 127.8, 125.2, 31.9, 29.8, 29.4, 29.3, 27.1, 26.9, 22.7, 18.4, 14.1, -1.8 ppm. **HRMS** (APCI+): m/z calcd. for $C_{12}H_{26}Si$ [M+H]+ 199.1877; found: 199.1880.



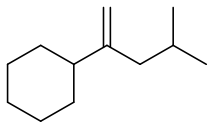
Pentylidenecyclohexane 15a: 0.20 mmol was employed with Method F and 31.8 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.99 (s, 1H), 2.30-2.28(m, 2H), 2.14 (s, 3H), 1.56-1.54 (m, 9H), 1.31-1.24 (m, 2H), 0.94-0.88 (m, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 140.9, 117.2, 37.7, 28.9, 28.6, 27.7, 26.9 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{11}H_{20}$ [M+H]+ 153.1638; found: 153.1639.



(1*r*, 3*r*, 5*R,7*S**)-2-Ethylideneadamantane 16a:** 0.64 mmol was employed with Method F and 47.8 mg was obtained as a white solid using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.08 (q, *J* = 6.7 Hz, 1H), 2.84 (s, 1H), 2.32 (s, 1H), 1.94 (q, *J* = 3.1 Hz, 2H), 1.84 (ddt, *J* = 14.6, 5.4, 3.0 Hz, 8H), 1.78-1.65 (m, 5H), 1.55 (d, *J* = 8.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.0, 109.8, 40.5, 39.8, 38.7, 37.4, 31.6, 28.7, 12.0 ppm. **HRMS** (APCI+): m/z calcd. for $C_{12}H_{18}$ [M+H]+ 163.1481; found: 163.1481.

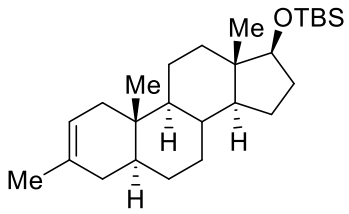


(2-((1*r*, 3*r*,5*R,7*S**)-Adamantan-2-ylidene)ethyl)trimethylsilane 16b:** 0.57 mmol was employed with Method F and 18.7 mg was obtained as a light-yellow solid using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.03 (t, *J* = 8.5 Hz, 1H), 2.75 (s, 1H), 2.31 (s, 1H), 1.94 (s, 2H), 1.84 (d, *J* = 12.5 Hz, 6H), 1.75-1.69 (m, 4H), 1.36 (d, *J* = 8.5 Hz, 2H), 0.00 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.8, 111.5, 40.8, 40.0, 38.8, 37.4, 31.6, 31.6, 22.7, 17.1, 14.1, -1.7 ppm. **HRMS** (ESI+): *m/z* calcd. for $C_{15}H_{26}Si$ [M]+ 234.1798; found: 234.1796.



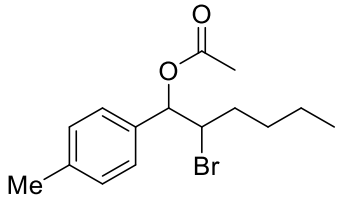
(4-Methylpent-1-en-2-yl)cyclohexane 17a: 0.40 mmol was employed with Method F and 25.7 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.77, (d, *J* = 98.4 Hz, 1H), 4.74 (d, *J* = 16.7 Hz, 1H), 1.89 (d, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 10.3 Hz, 2H), 1.71-1.66 (m, 1H),

1.30-1.24 (m, 6H), 1.21-1.10 (m, 4H), 0.86 (d, *J* = 6.5 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 108.2, 107.9, 45.2, 43.6, 40.9, 32.7, 26.9, 26.5, 22.6 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{12}H_{22}$ [M+H]+ 167.1794; found: 167.1798.

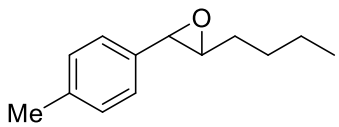


***tert*-Butyldimethyl(((5*S*,9*S*,10*S*,13*S*,14*S*,17*S*)-3,10,13-trimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)oxy)silane**

18a: 0.20 mmol was employed with Method F and 68.7 mg was obtained as a white solid using column chromatography (eluent: 100% Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.25 (s, 1H), 3.54 (dt, *J* = 10.9, 5.9 Hz, 1H), 1.98 (d, *J* = 11.7 Hz, 1H), 1.78 (t, *J* = 13.5 Hz, 1H), 1.68 (d, *J* = 11.8 Hz, 4H), 1.61 (s, 3H), 1.50-1.36 (m, 4H), 1.36-1.18 (m, 6H), 1.08 (s, 1H), 0.95 (dd, *J* = 12.4, 4.9 Hz, 2H), 0.88 (d, *J* = 1.1 Hz, 9H), 0.83 (s, 3H), 0.71 (s, 3H), 0.05 (s, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.6, 122.6, 72.2, 57.1, 55.1, 46.4, 45.3, 38.7, 37.1, 35.8, 34.4, 34.3, 32.1, 32.0, 31.1, 28.8, 26.0, 21.1, 18.3, 15.2, 12.5, 12.4, -4.5 ppm. **HRMS** (ESI+): *m/z* calcd. for $C_{26}H_{46}OSi$ [M+H]+ 403.3391; found: 403.3389.

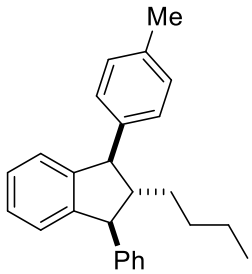


1-Bromopentyl-4-methyl-1-acetatebenzenemethanol 2aa: 0.30 mmol was employed and 68.7 mg was obtained as a colorless oil using column chromatography (eluent: Hexane/Ethyl acetate = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.94 (d, *J* = 5.5 Hz, 1H),4.26-4.23 (m, 1H), 2.35 (s, 3H), 2.13 (s, 3H), 1.84-1.83 (m, 2H), 1.74-1.70 (m, 2H), 1.61-1.54 (m, 1H), 1.52-1.50 (m, 1H), 0.85 (t, *J* = 3.5 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.7, 138.3, 134.3, 129.0, 127.2, 77.8, 57.7, 34.7, 33.1, 31.6, 29.1, 25.3, 22.7, 21.2, 13.9 ppm. **HRMS** (ESI+): *m/z* calcd. for $C_{15}H_{21}BrO_2$ [M+Na]+ 335.0617; found: 335.0615.



4-(3-Butyl-2-oxiranyl)toluene 2ab: 0.30 mmol was employed and 32.0 mg was obtained as a colorless oil using column chromatography (eluent: Hexane/Ethyl

acetate = 20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.15 (s, 4H), 3.58 (s, 1H), 2.94 (t, *J* =5.5 Hz, 1H), 2.34 (s, 3H), 1.71-1.65 (m, 2H), 1.51-1.46 (m, 2H), 1.44-1.27 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 137.7, 134.9, 129.1, 125.5, 63.1, 58.6, 32.1, 28.1, 22.5, 21.2, 14.0 ppm. **HRMS** (APCI+): *m/z* calcd. for $C_{13}H_{18}O$ [M+H]+ 191.1430; found: 191.1430.



(1*S*, 2*R*, 3*R*)-2-Pentyl-1-phenyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-indene 2ac: 0.30 mmol was employed and 36.1 mg was obtained as a colorless oil using column chromatography (eluent: 100% Hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.24 (m, 6H), 7.20-7.10 (m, 5H), 6.83-6.80 (m, 2H), 3.99 (d, *J* = 9.6 Hz, 2H), 2.59-2.51 (m, 1H), 2.36 (s, 3H), 1.61-1.55 (m, 3H), 1.88 (t, *J* = 3.6 Hz, 4H), 0.70 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.1, 147.0, 144.5, 141.3, 136.0, 129.1, 129.0, 128.8, 128.5, 128.4, 126.7, 126.7, 126.5, 124.5, 60.3, 56.6, 56.2, 31.7, 29.2, 22.9, 21.1, 13.9 ppm.

4. References

[1] Bull, J. A.; Mousseau, J. J.; Charette, A. B. *Org. Lett.* **2008**, *10*, 5485.

[2] Stor, G.; Zhao, K. *Tetrahedron Lett*. **1989**, *30*, 2173.

[3] Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.

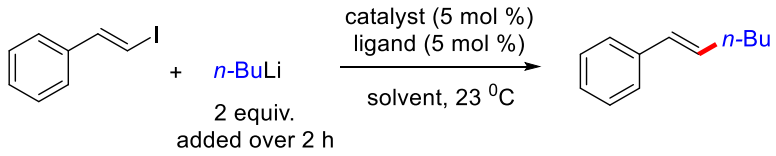
[4] Cheung, L. L. W.; Yudin, A. K. *Org. Lett.* **2009**, *11*, 1281.

[5] Mousseau, J. J.; Bull, J. A.; Ladd, C. L.; Fortier, A.; Roman, D. S.; Charette, A. B. *J. Org. Chem.* **2011**, *76*, 8243.

5. Optimization

5.1. Influence of iron catalysts

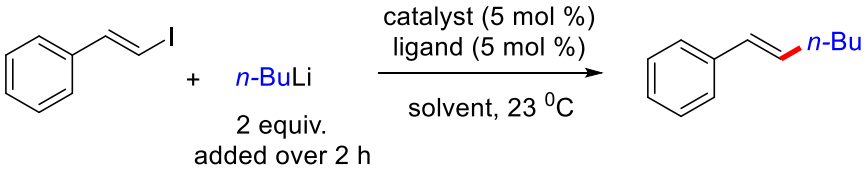
Table S1



entry	catalyst	ligand	solvent	conv. (%)	GC yield (%)
1	$FeCl_2$	TMEDA	toluene	100	16
2	$Fe(acac)_3$	TMEDA	toluene	75	12
3	$Fe(acac)_3$	--	toluene	66	22
4	$FeCl_3$	--	toluene	100	26
5	$FeCl_2$	--	toluene	93	9
6	$Fe(acac)_2$	--	toluene	100	34
7	FeF_3	--	toluene	94	7
8	FeF_2	--	toluene	100	13
9	$FeBr_2$	--	toluene	100	22
10	$FeBr_3$	--	toluene	100	20
11	$Fe(OAc)_2$	--	toluene	100	11

5.2. Influence of solvent

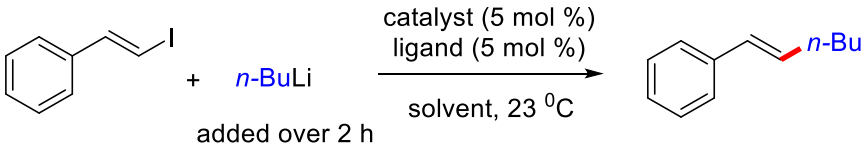
Table S2



entry	catalyst	solvent	conv. (%)	GC yield (%)
1	$Fe(acac)_2$	toluene	100	36
2		THF	100	27
3		Et_2O	100	17
4		toluene/THF (1:1)	100	18

5.3. Influence of the amount of lithium

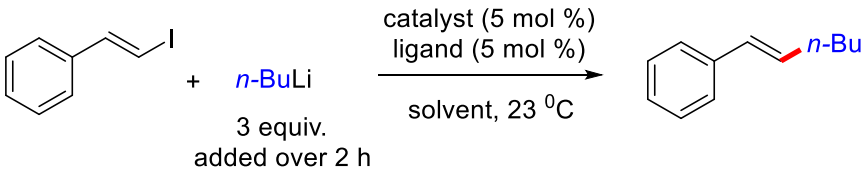
Table S3



entry	*n*-Buli (equiv.)	catalyst	ligand	solvent	conv. (%)	GC yield (%)
1	2.0	$Fe(acac)_2$	rac-BINAP	toluene	40	17
2	3.0				100	52
3	4.0				100	32

5.4. Influence of ligand

Table S4

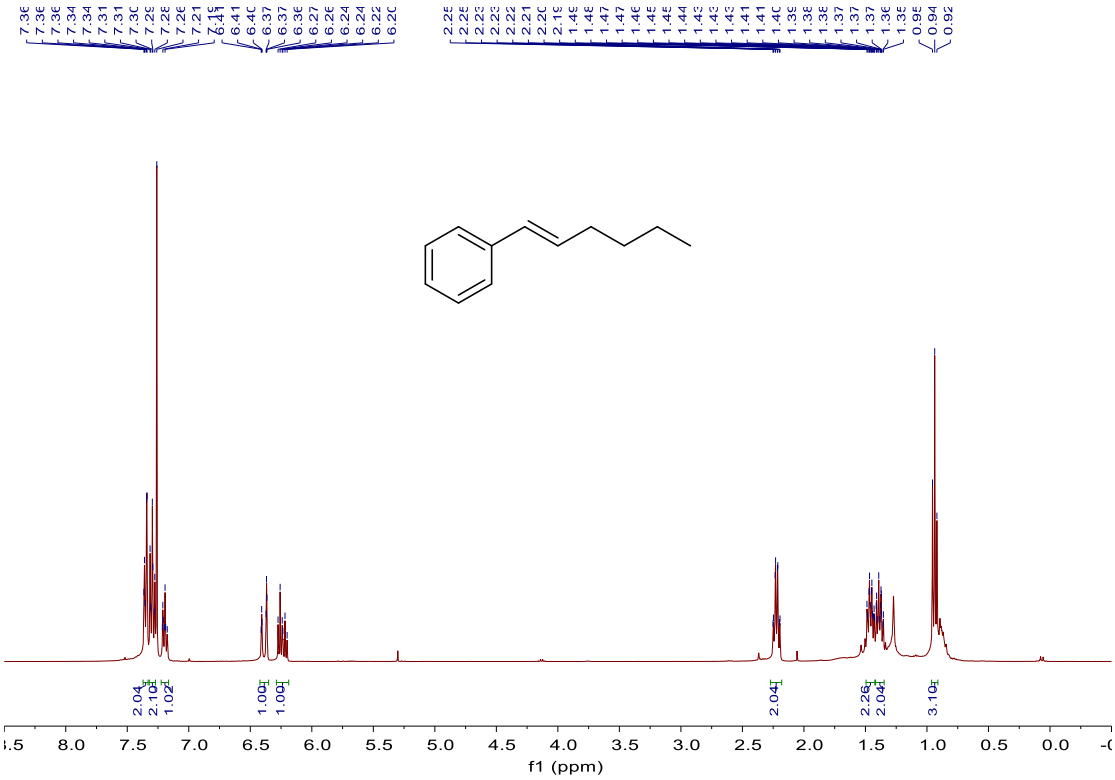


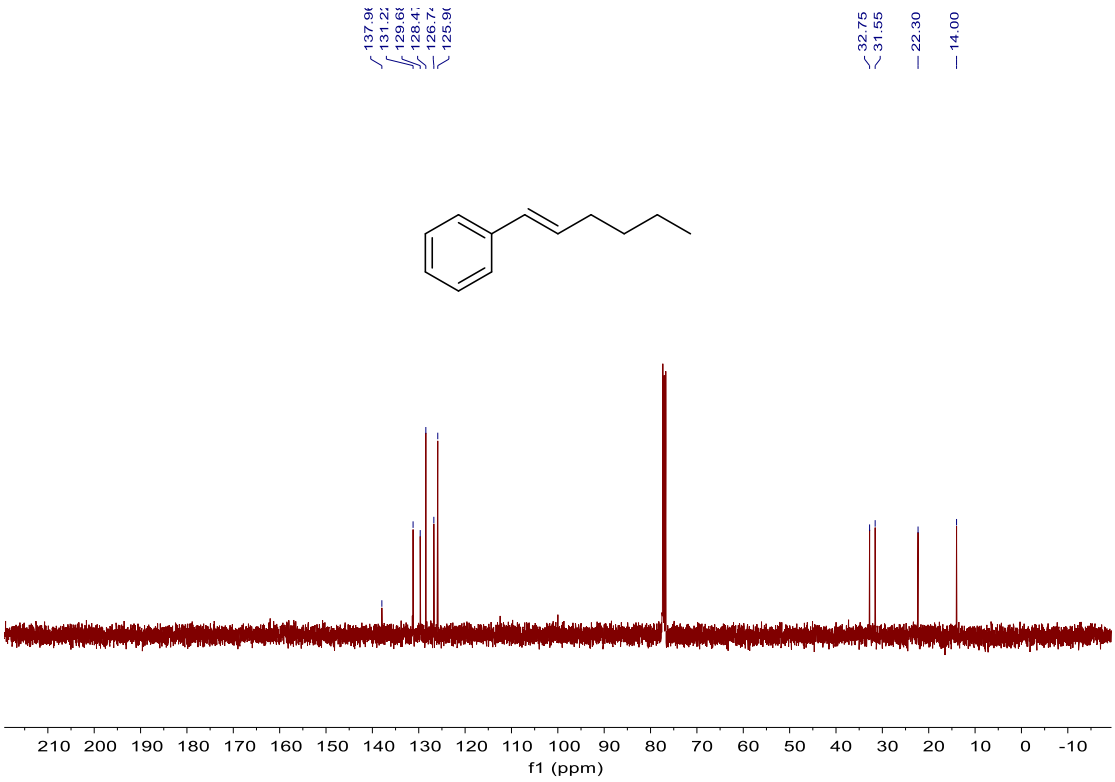
entry	catalyst	ligand	solvent	conv. (%)	GC yield (%)
1	$Fe(acac)_2$	Rac-BINAP	toluene	100	52
2		dppe		100	39
3		CPhos		100	50
4		RuPhos		100	51
5		IPr·HCl		65	20
6		SIMe·HBF_4		100	60
7		IMe·HCl		100	39
8		SIMe·HCl		100	42
9		SIPr·HCl		65	13
10		SIPr·HBF_4		100	34
11		PhDavePhos		100	53
12		BrettPhos		100	45
13		CyJohnPhos		100	53
14		*t*-BuXPhos		100	34
15		MePhos		60	42
16		*t*-BuMePhos		50	21
17		SPhos		57	25
18		**DavePhos**		**100**	**72[a]**
19		Me4 *t*-BuXPhos		100	42

a: Isolated yield

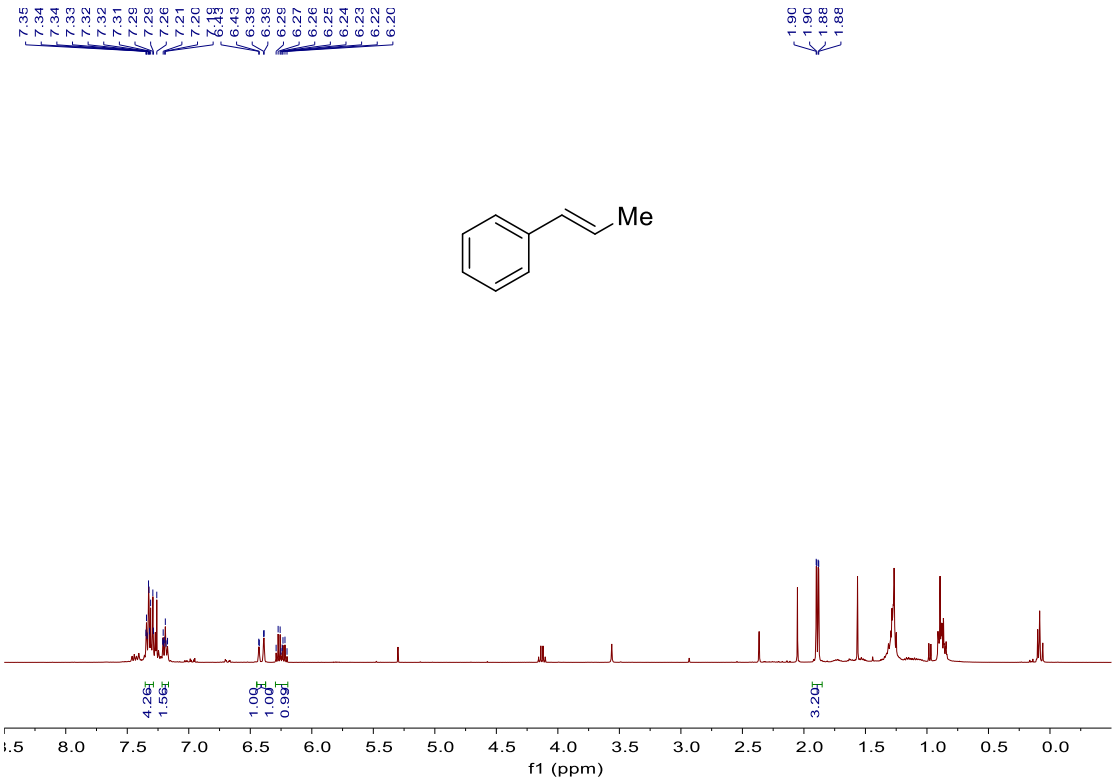
6. Copies of ^{1}H-NMR, ^{13}C-NMR Spectra

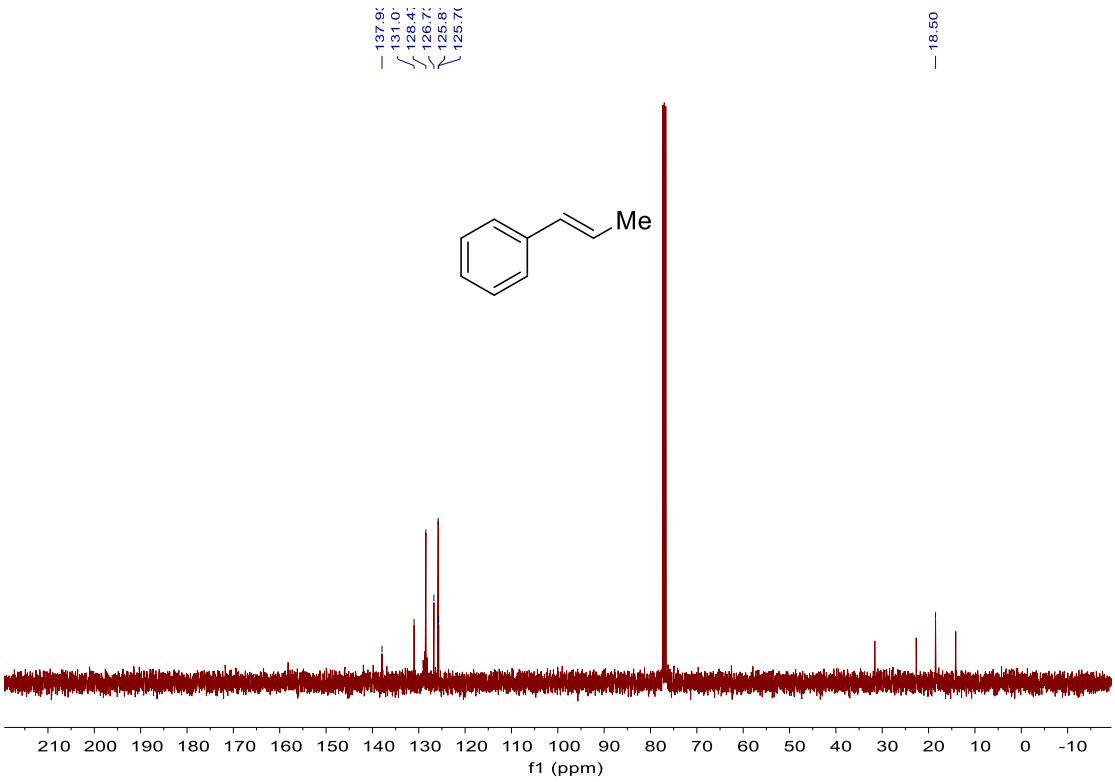
1) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1a



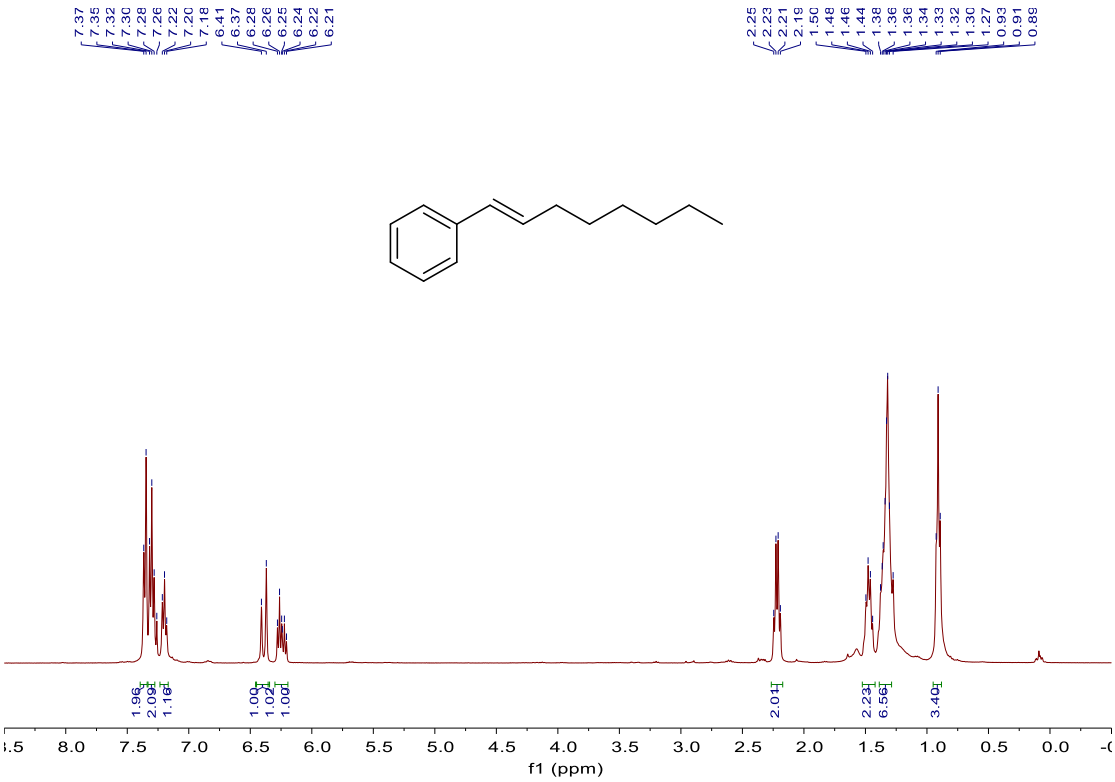


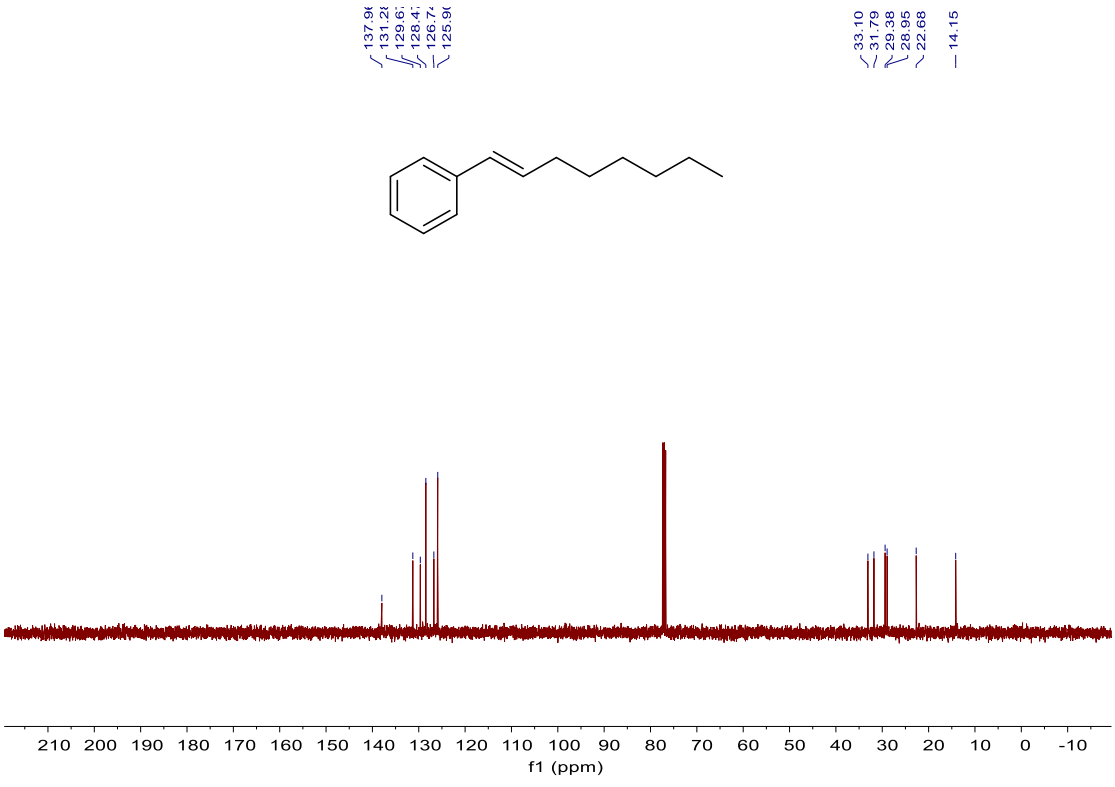
2) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1b



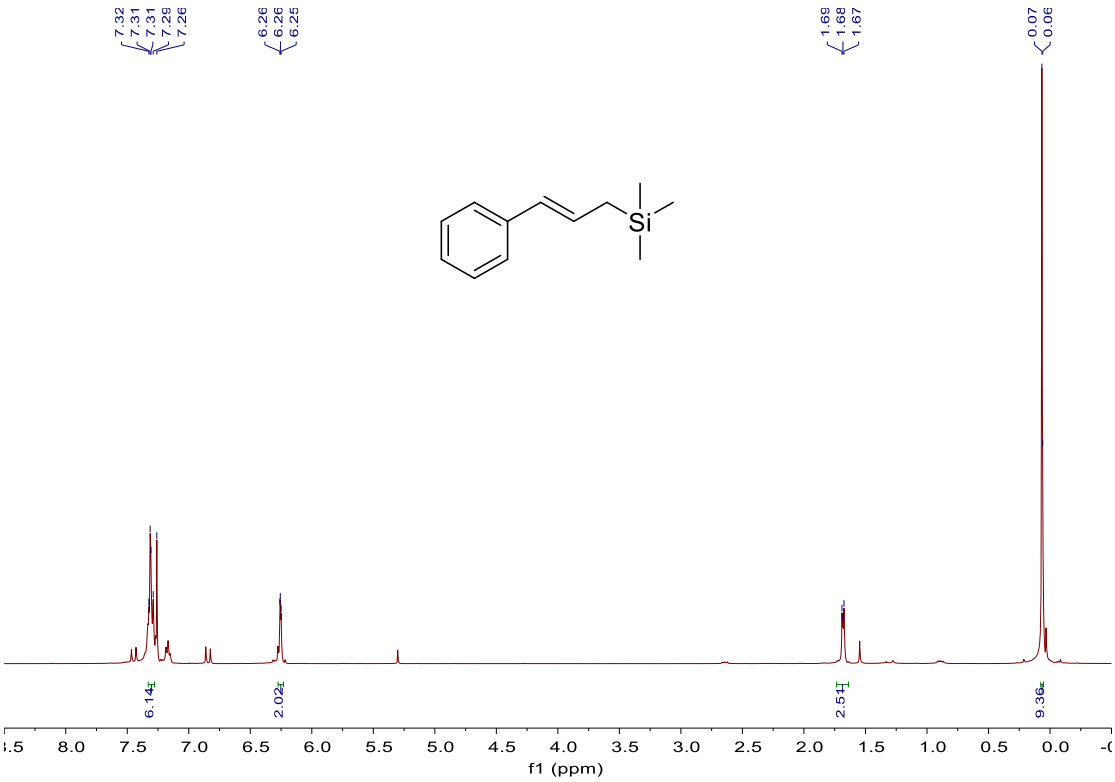


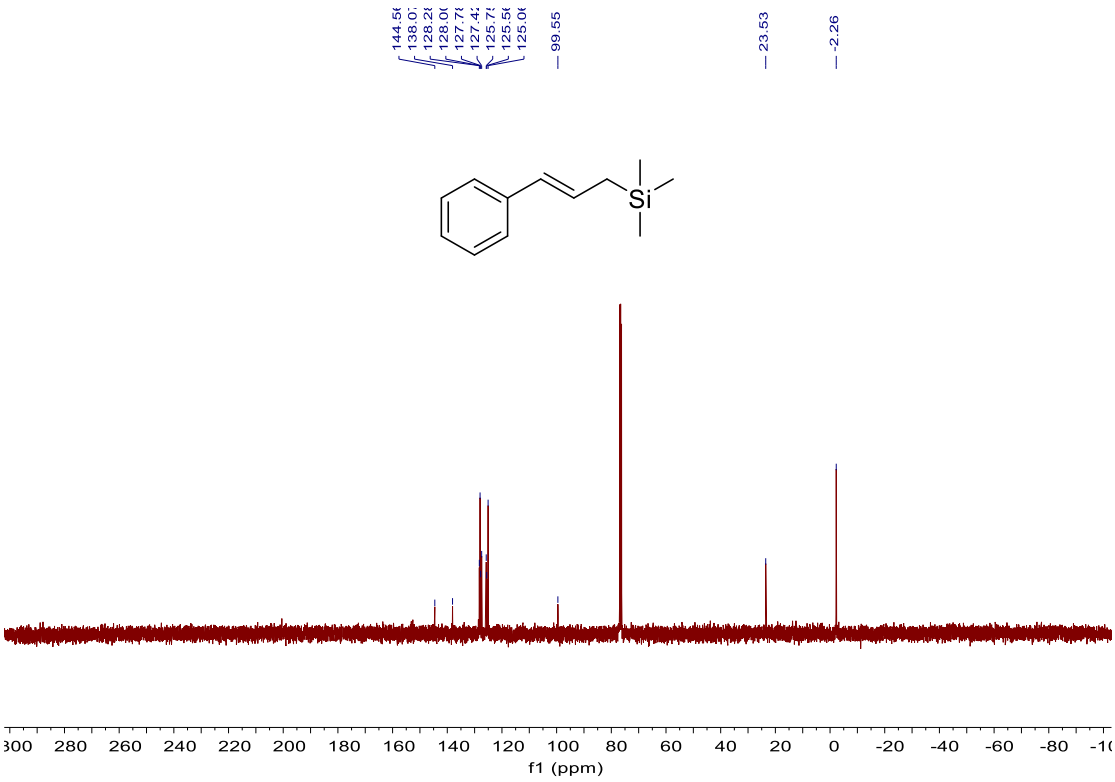
3) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1c



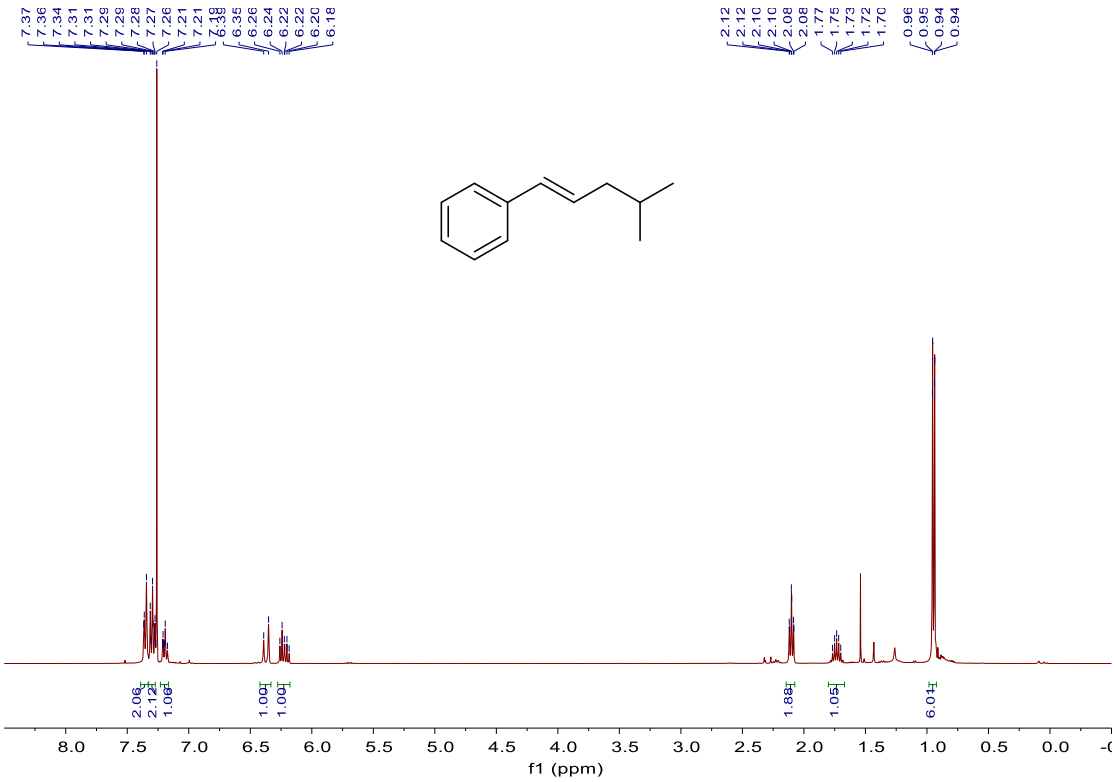


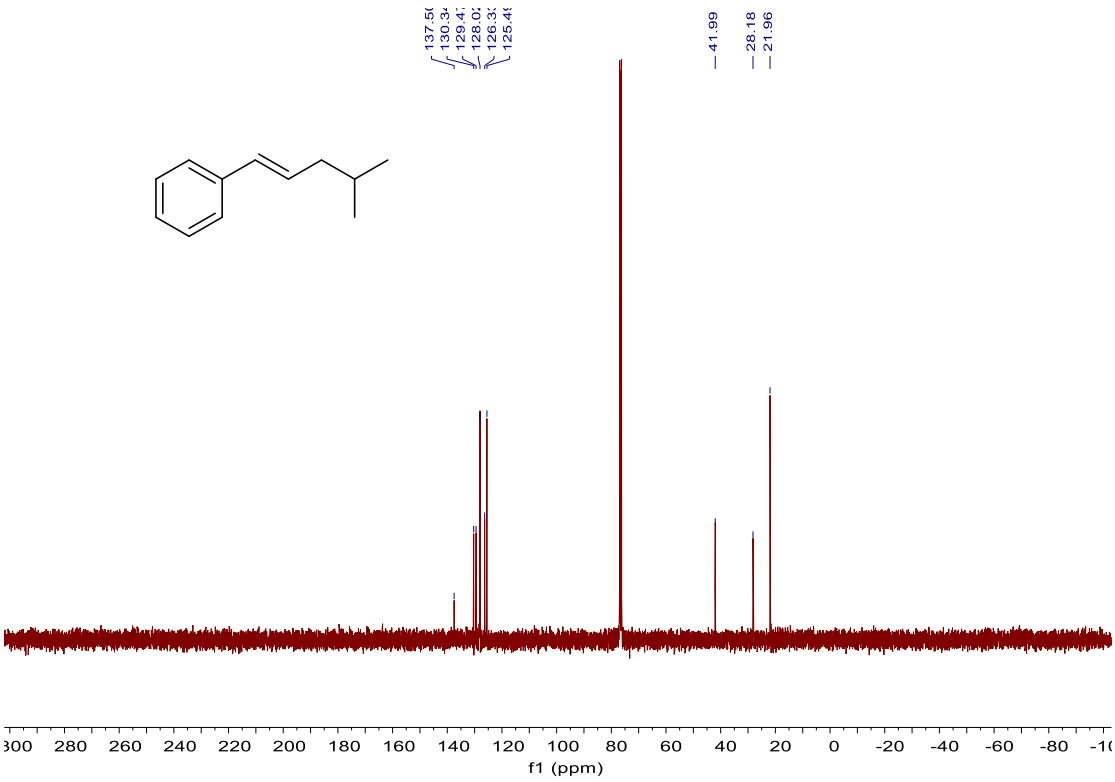
4) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1d



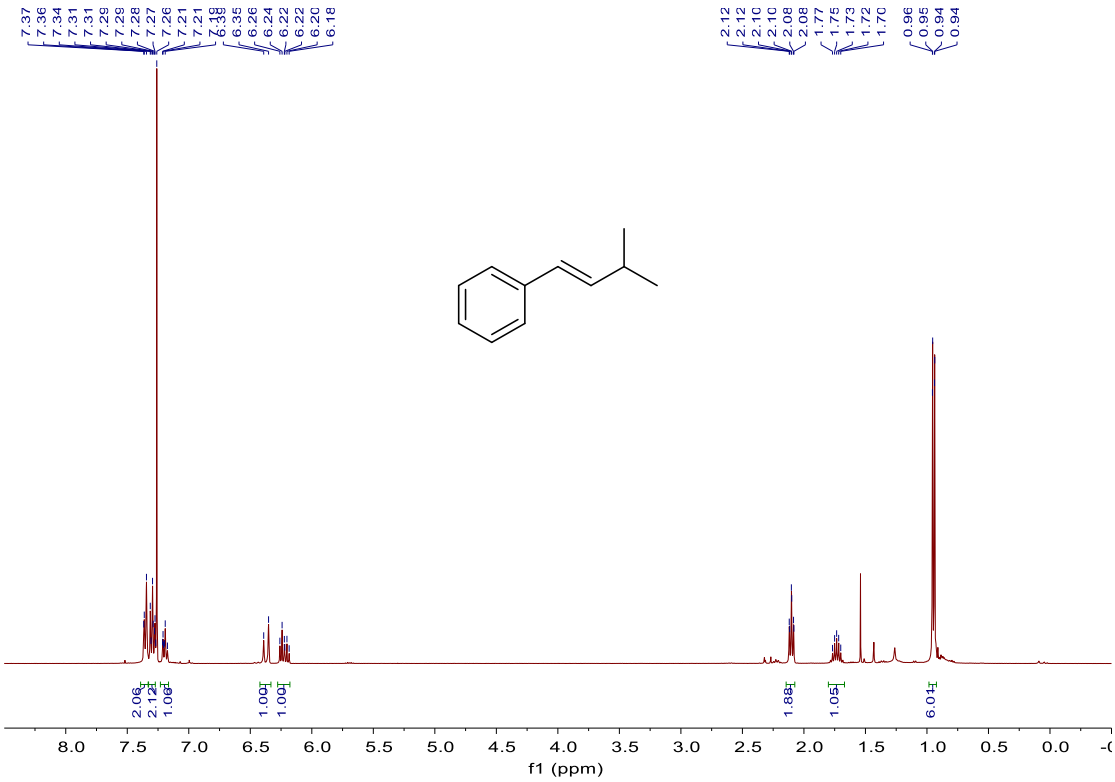


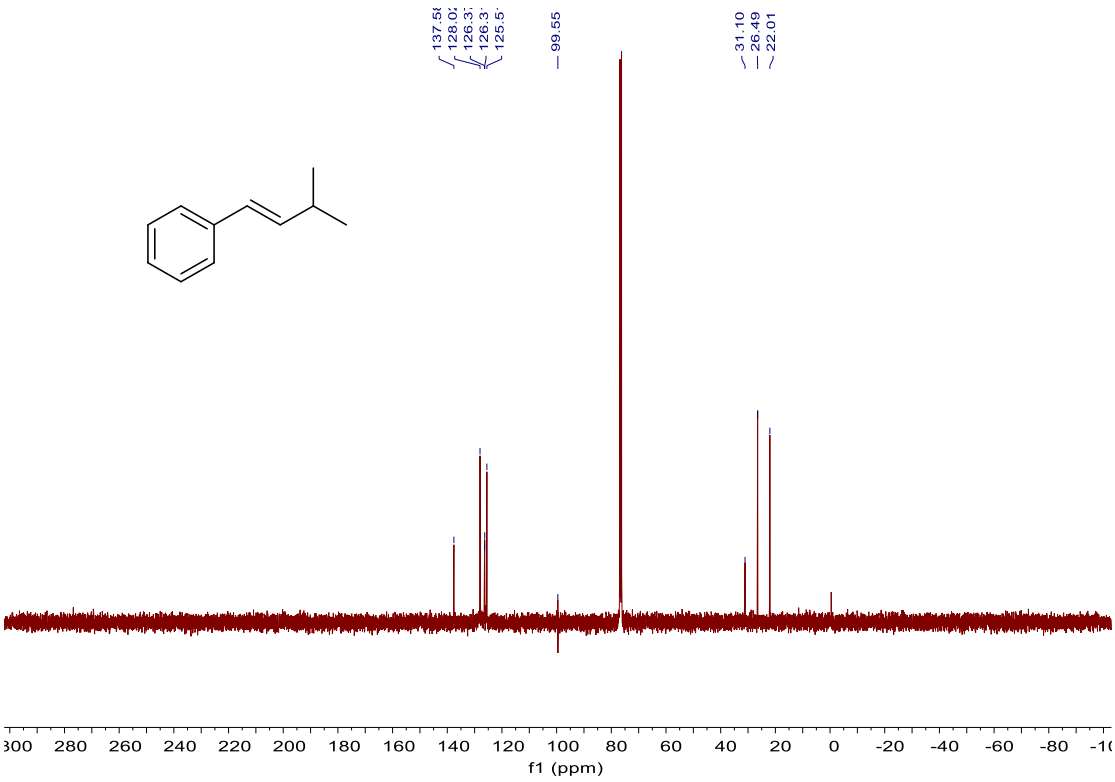
5) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1e



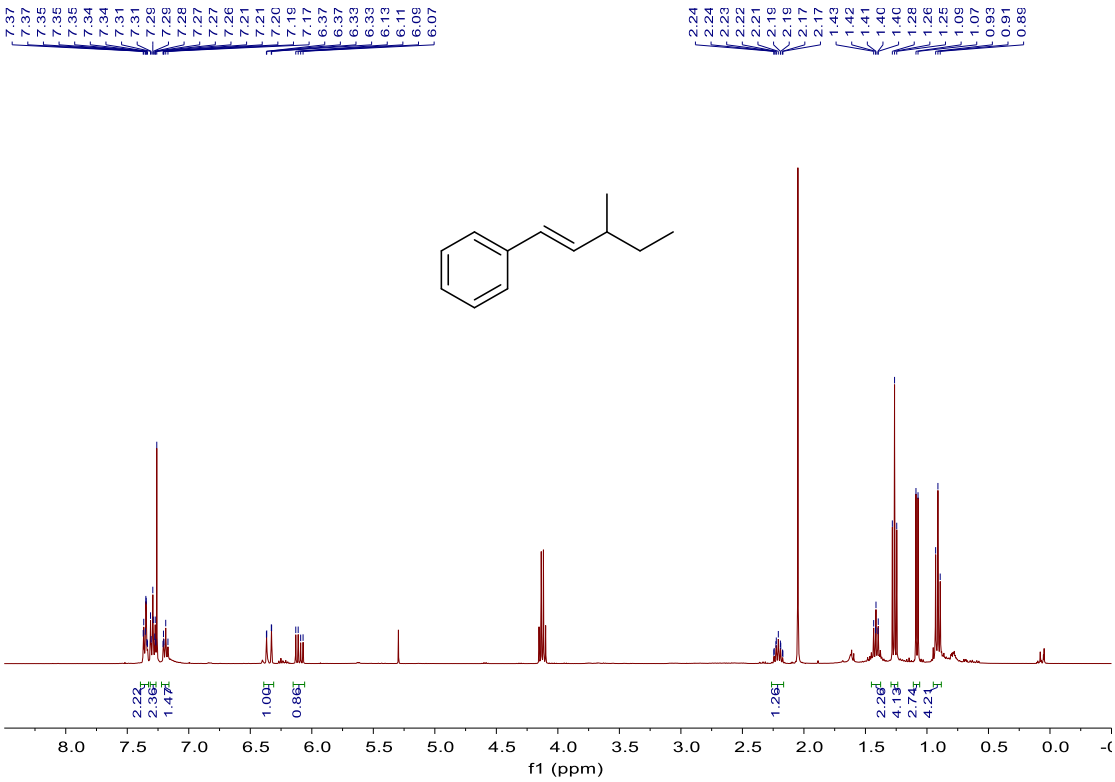


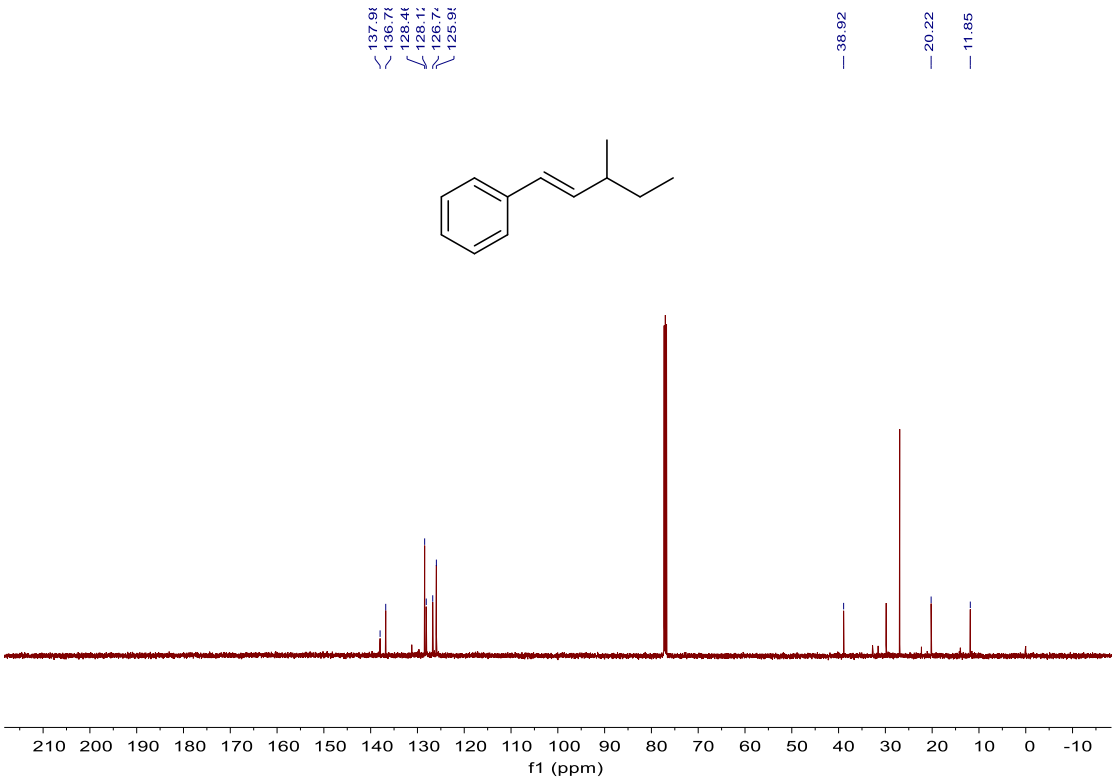
6) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1f



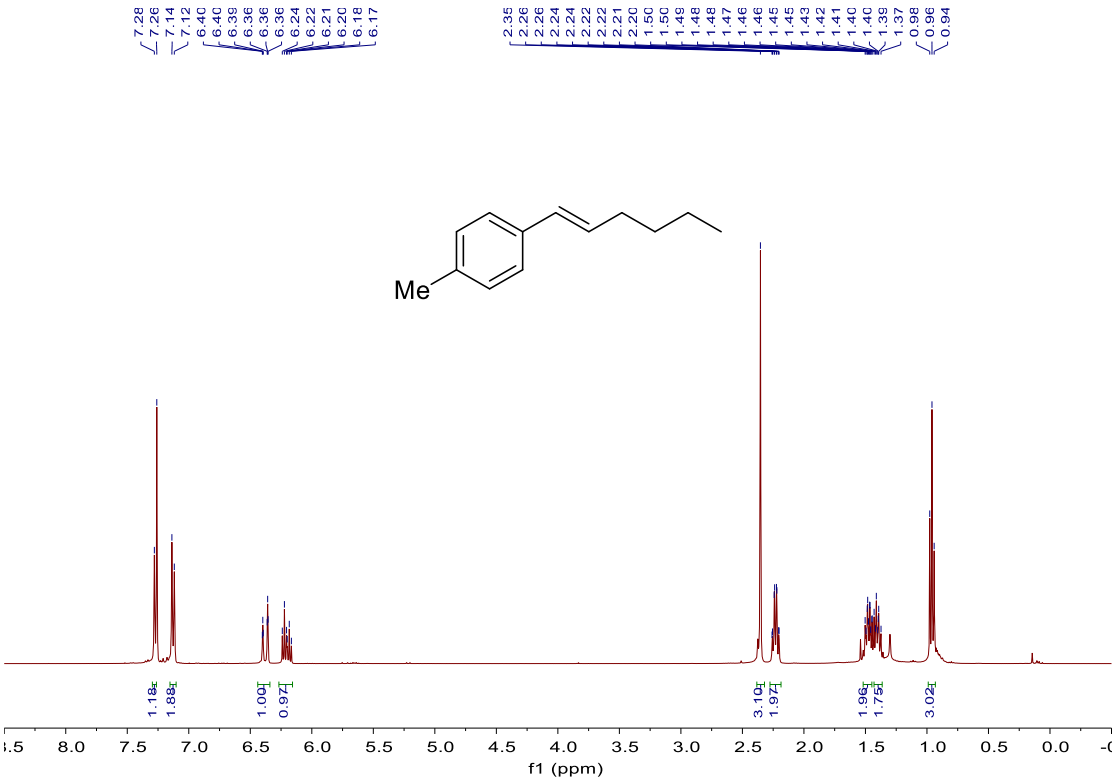


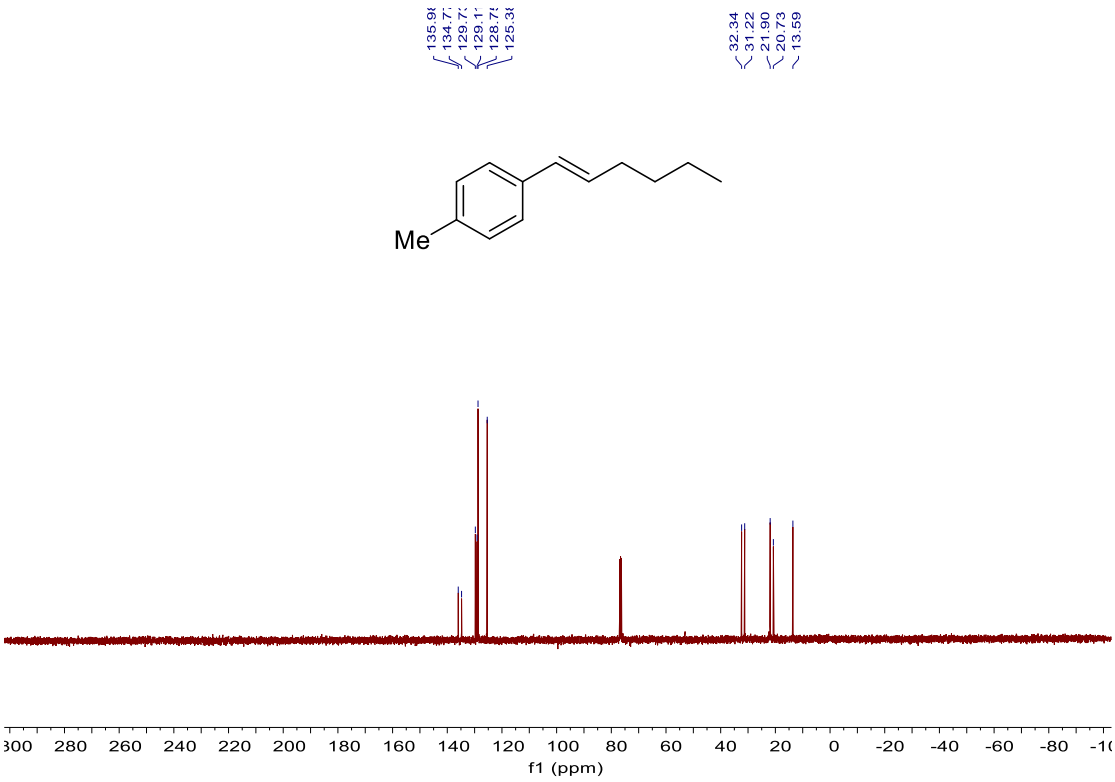
7) ^{1}H NMR and ^{13}C NMR Spectra of Compound 1g



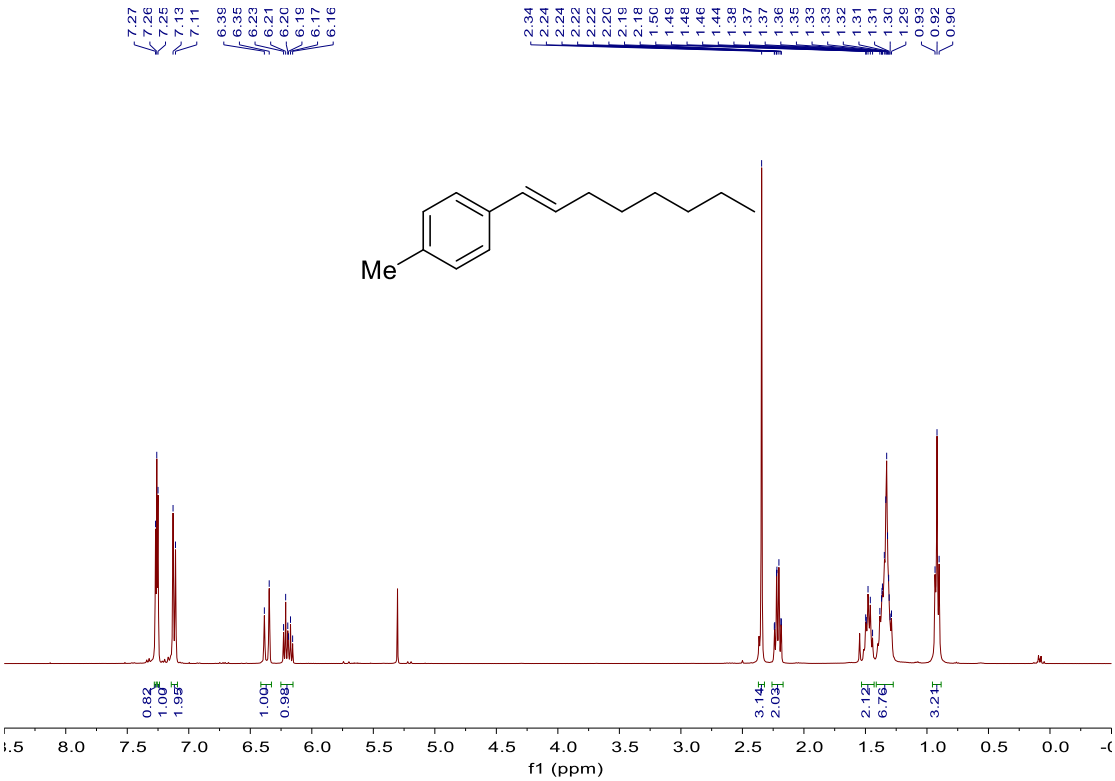


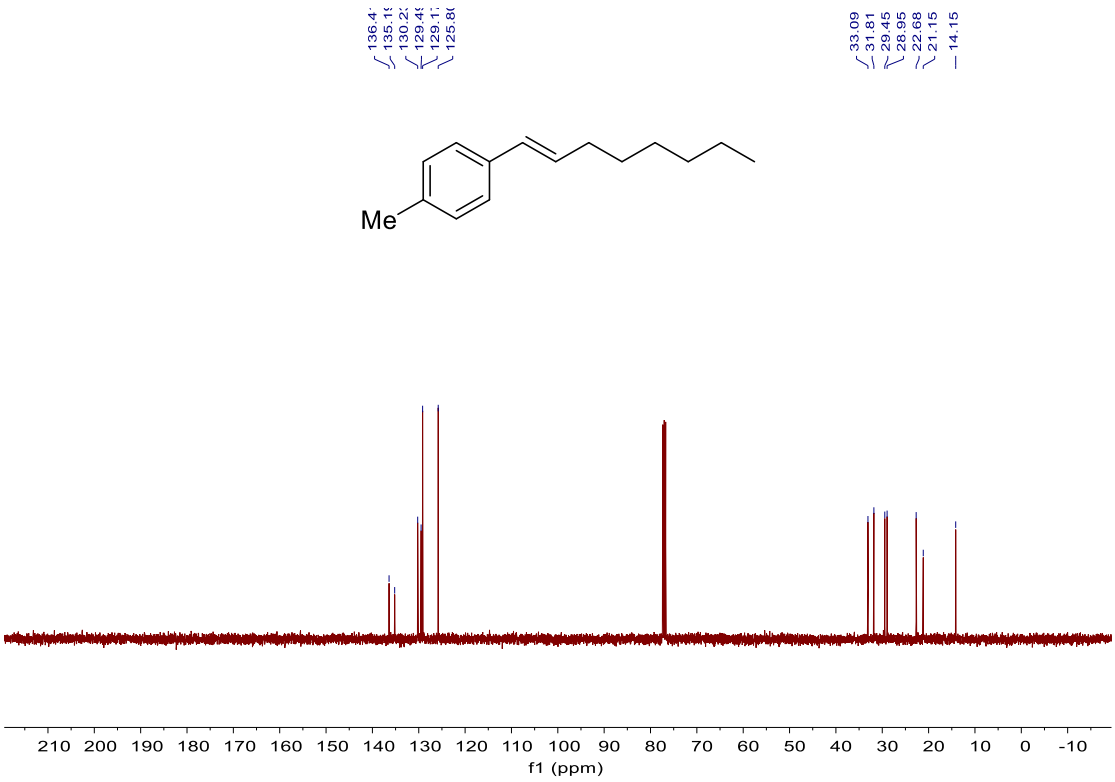
8) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2a



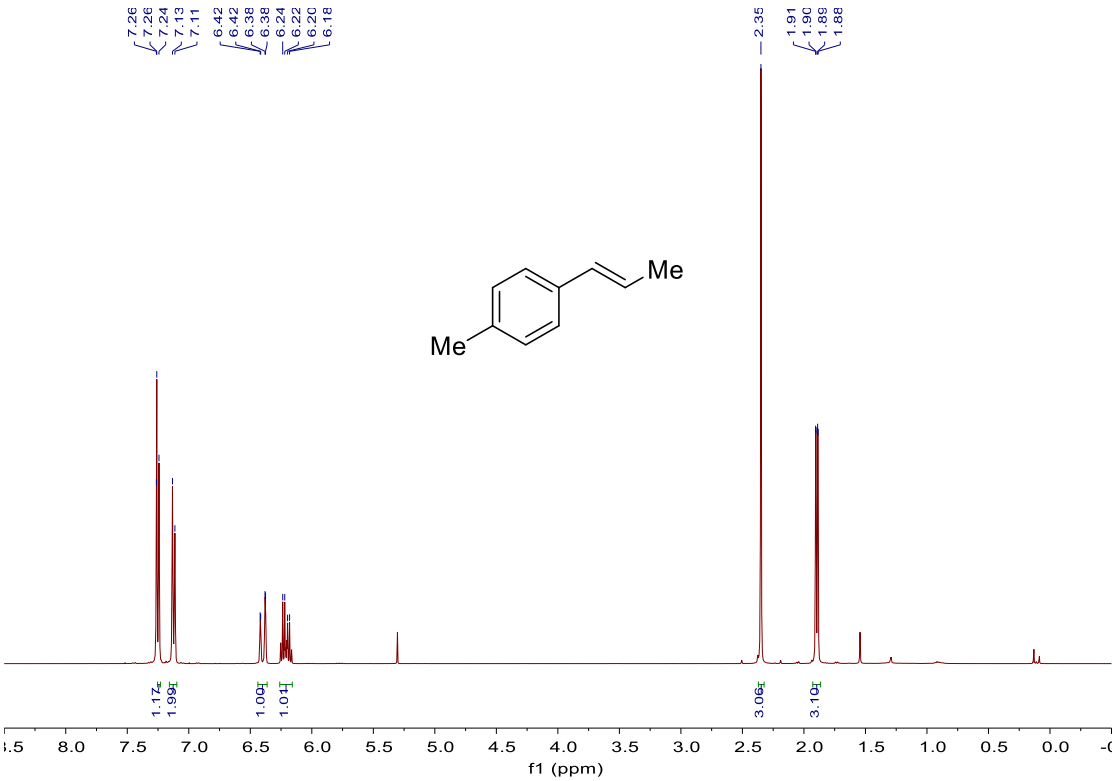


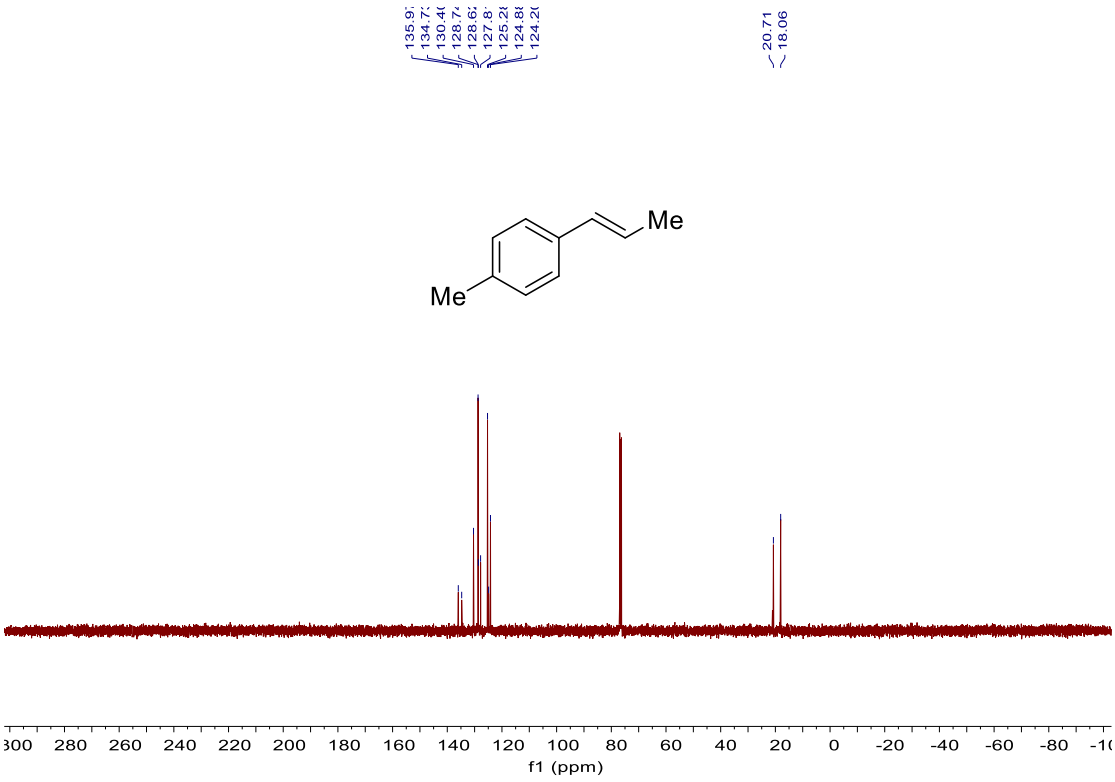
9) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2b



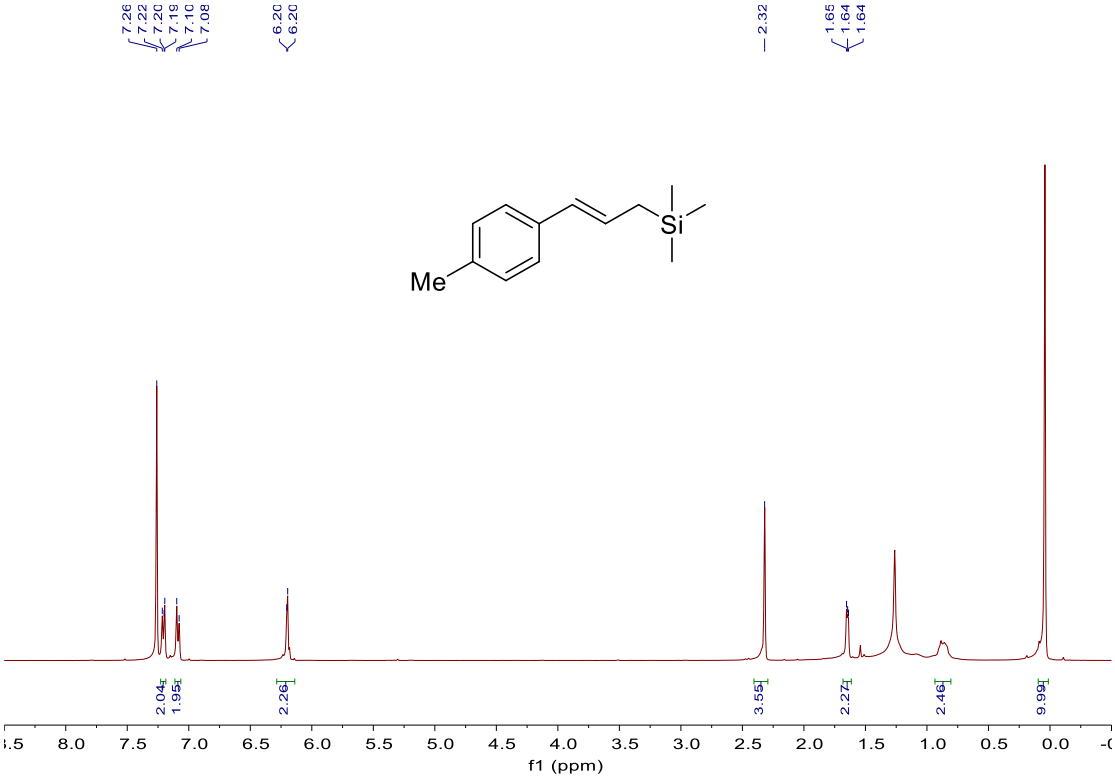


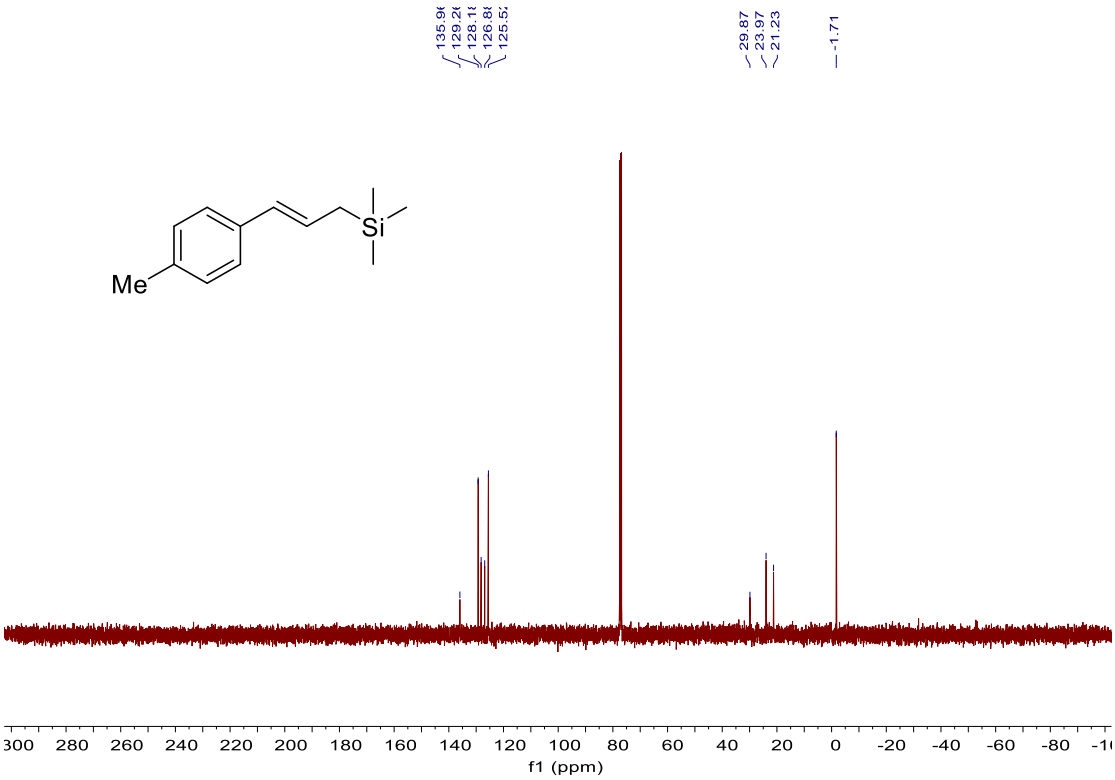
10) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2c



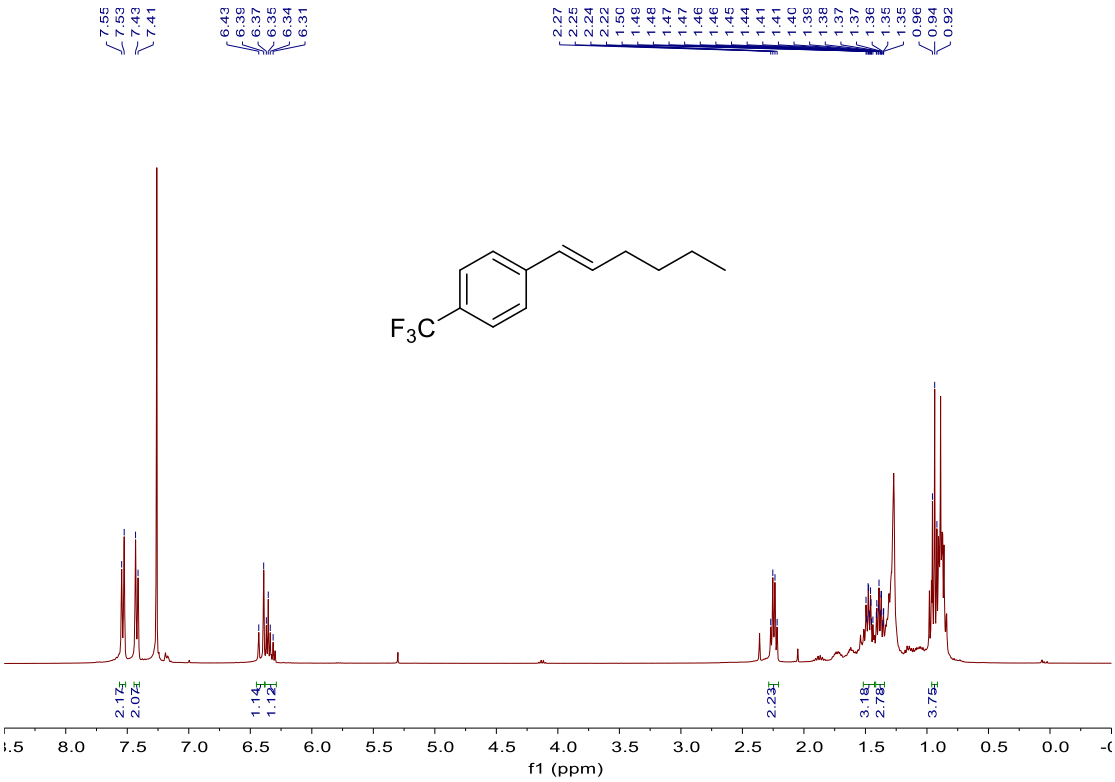


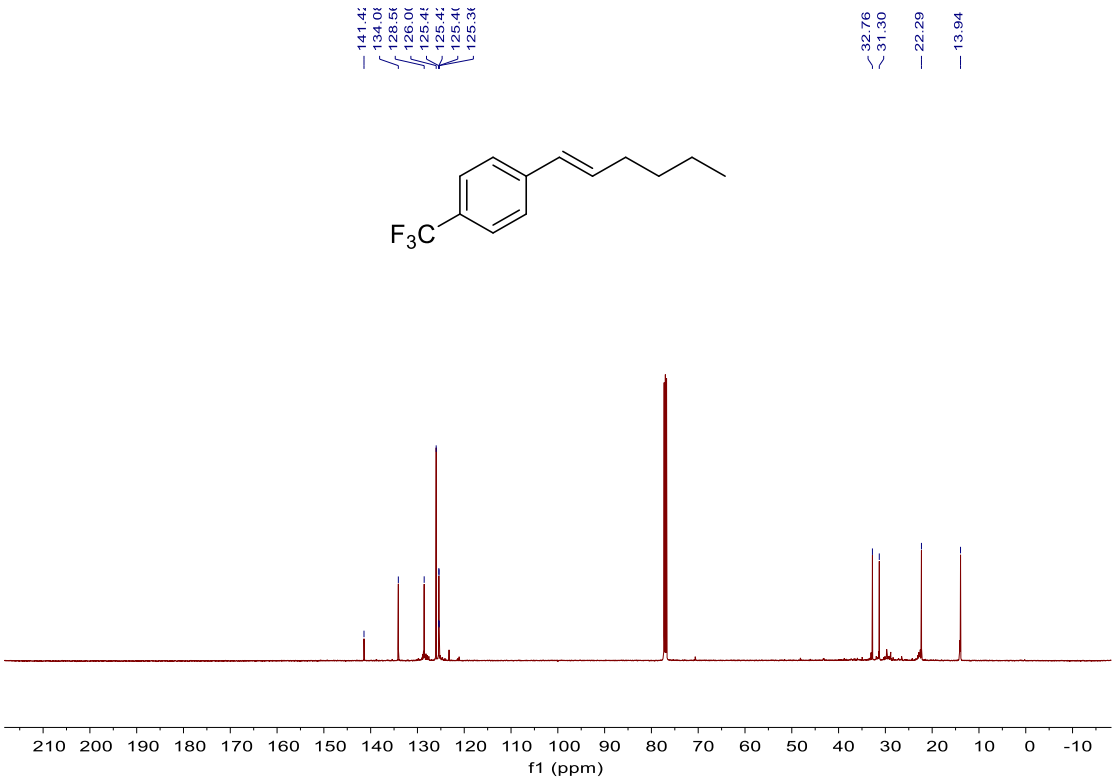
11) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2d



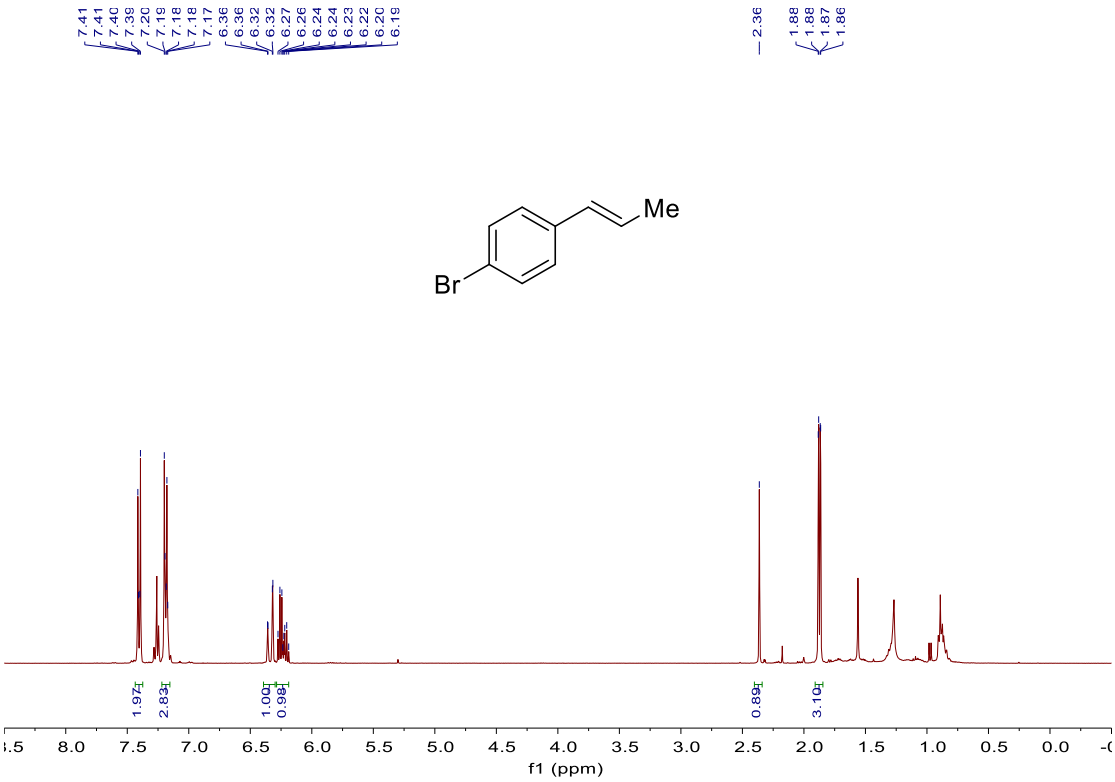


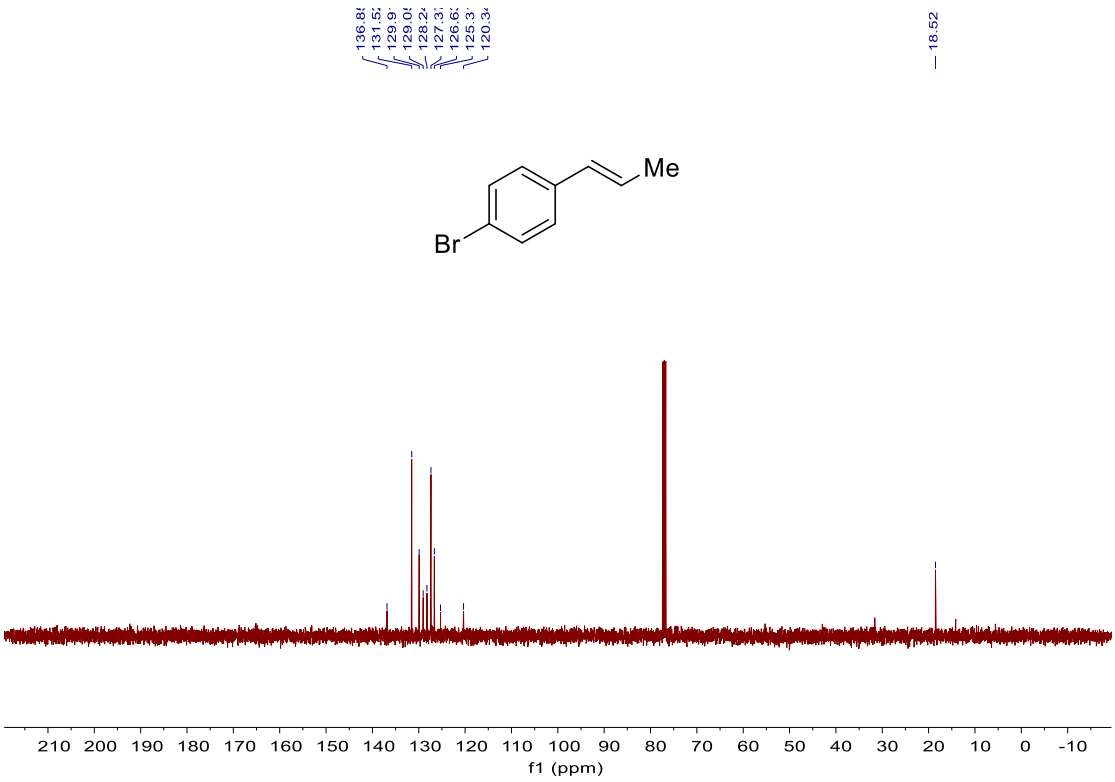
12) ^{1}H NMR and ^{13}C NMR Spectra of Compound 3a



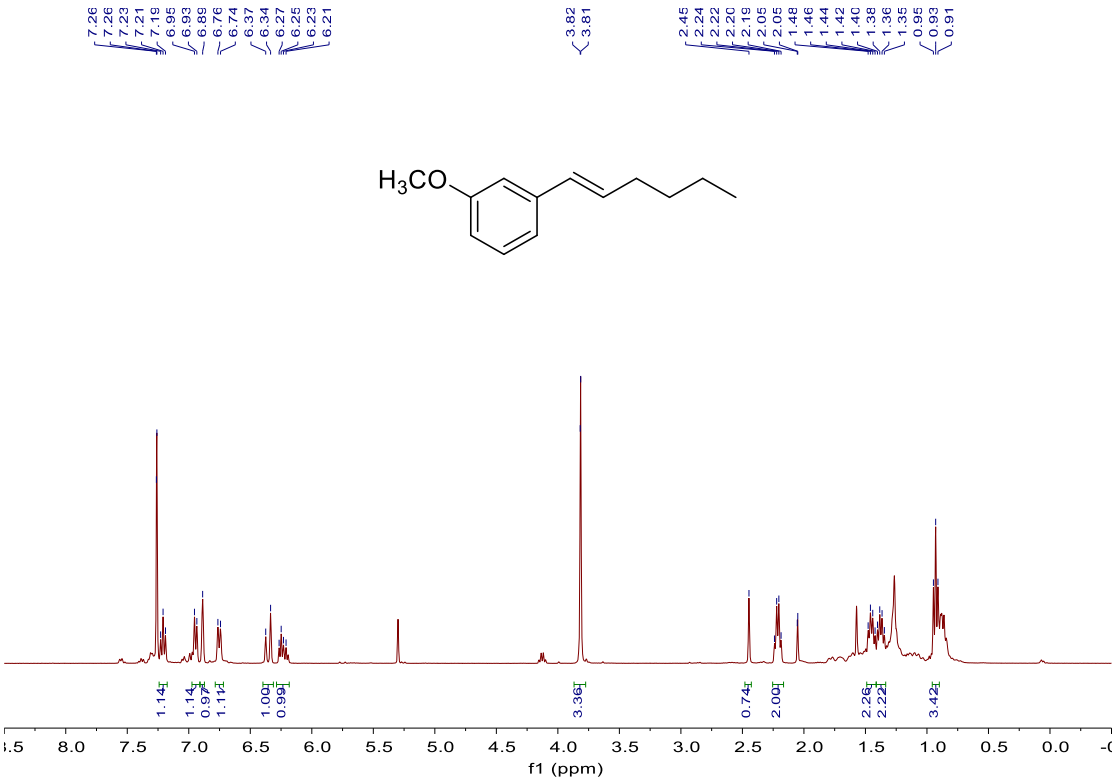


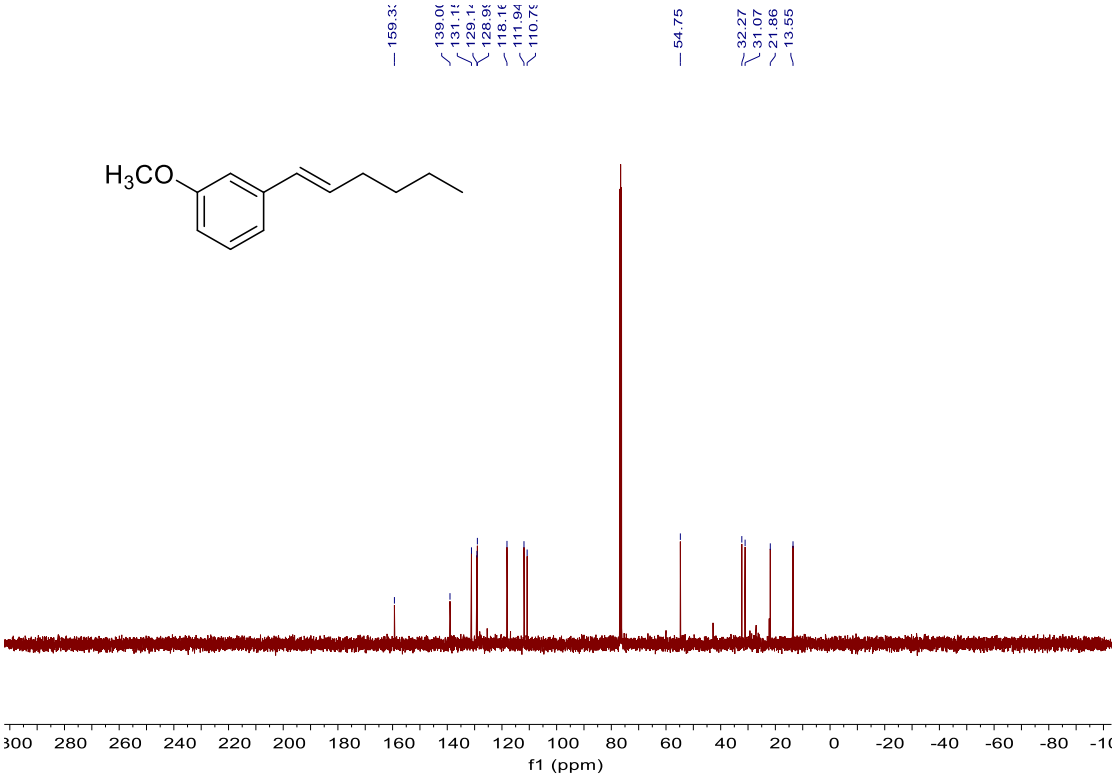
13) ^{1}H NMR and ^{13}C NMR Spectra of Compound 4a



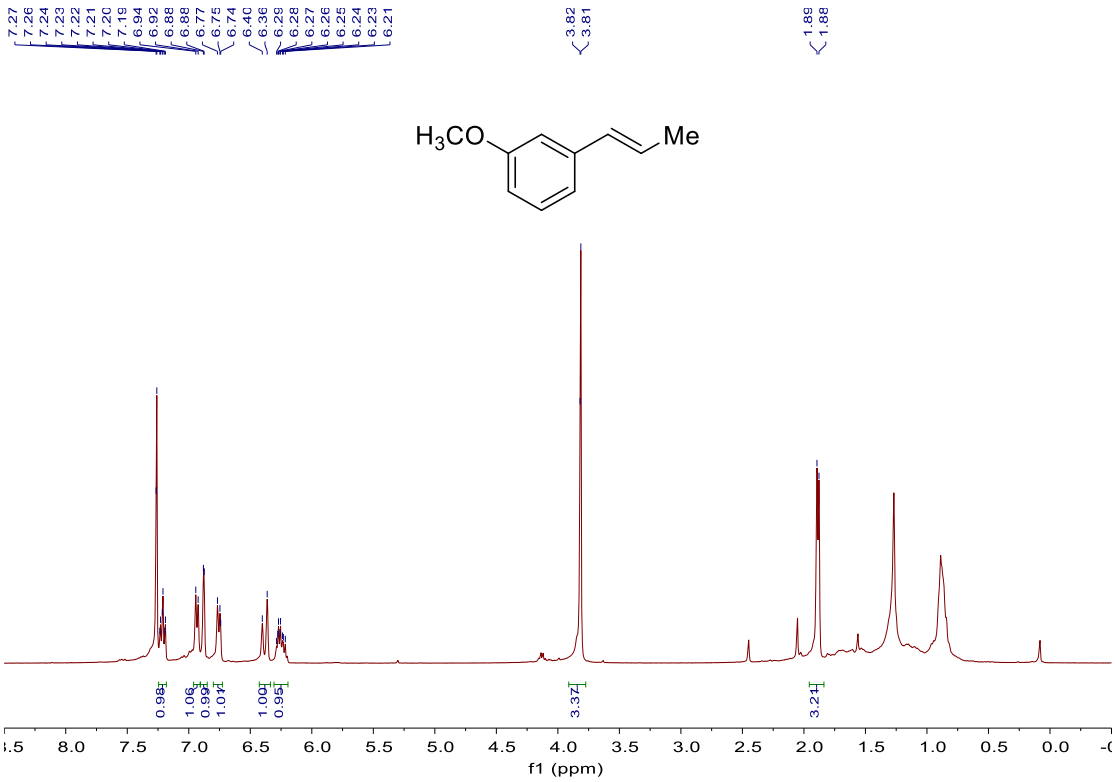


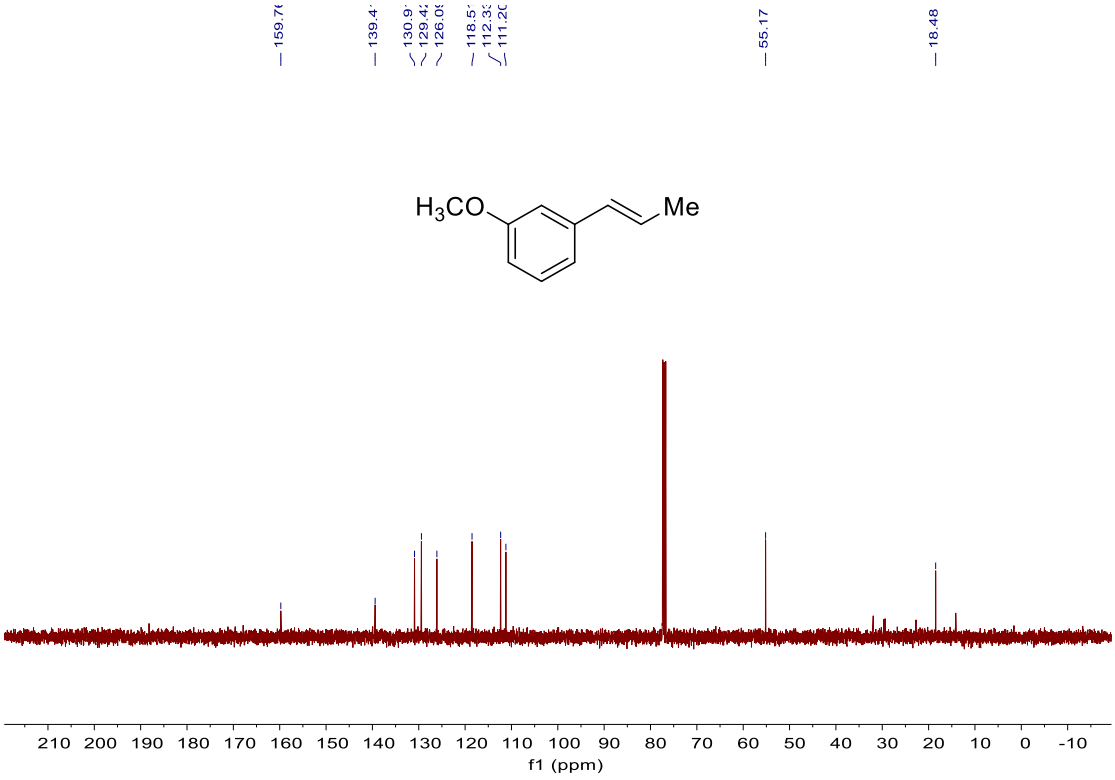
14) ^{1}H NMR and ^{13}C NMR Spectra of Compound 5a



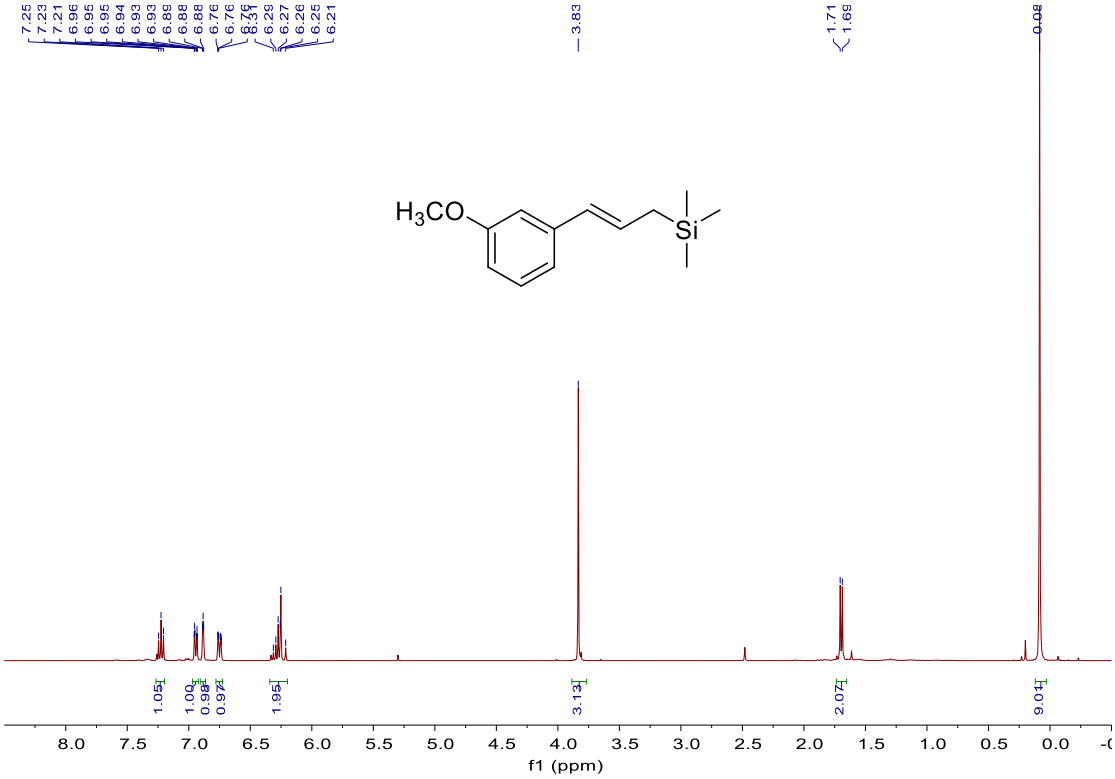


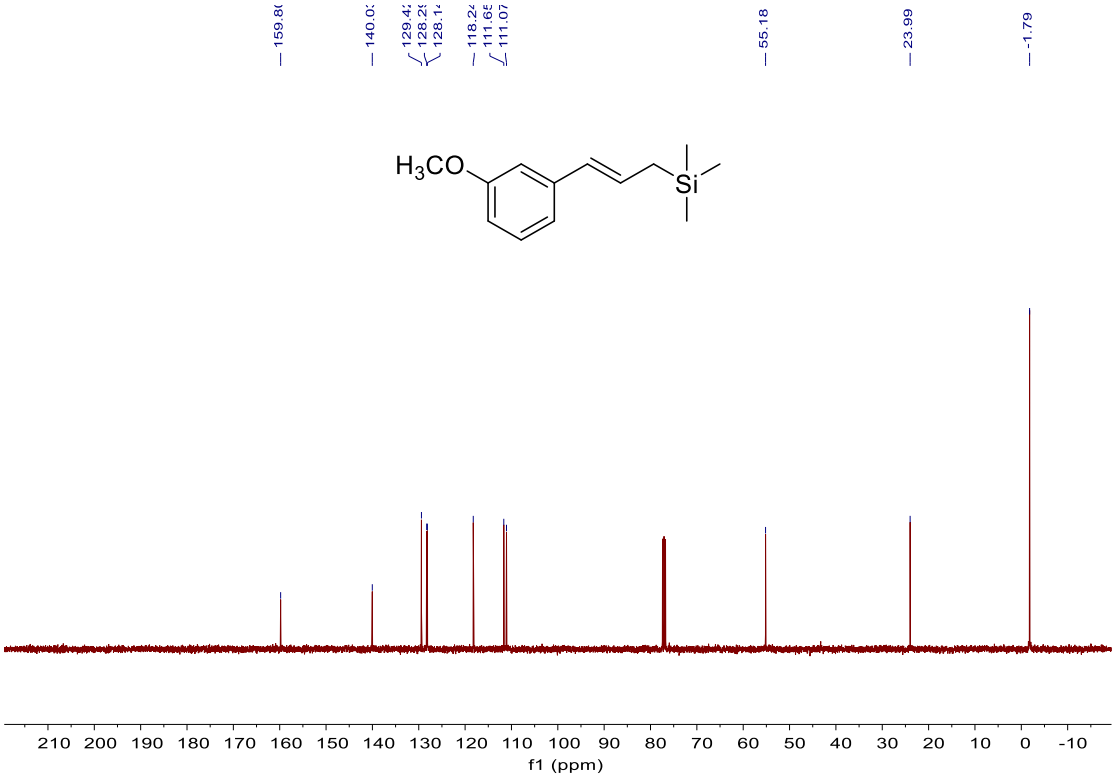
15) ^{1}H NMR and ^{13}C NMR Spectra of Compound 5b



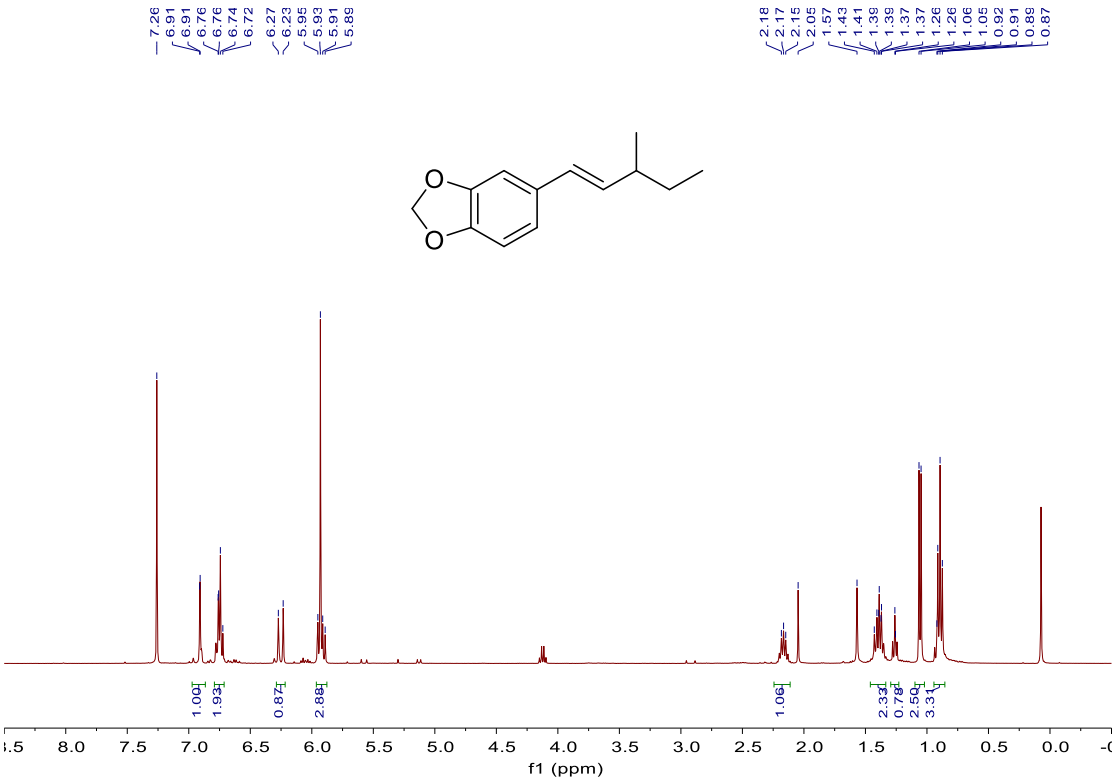


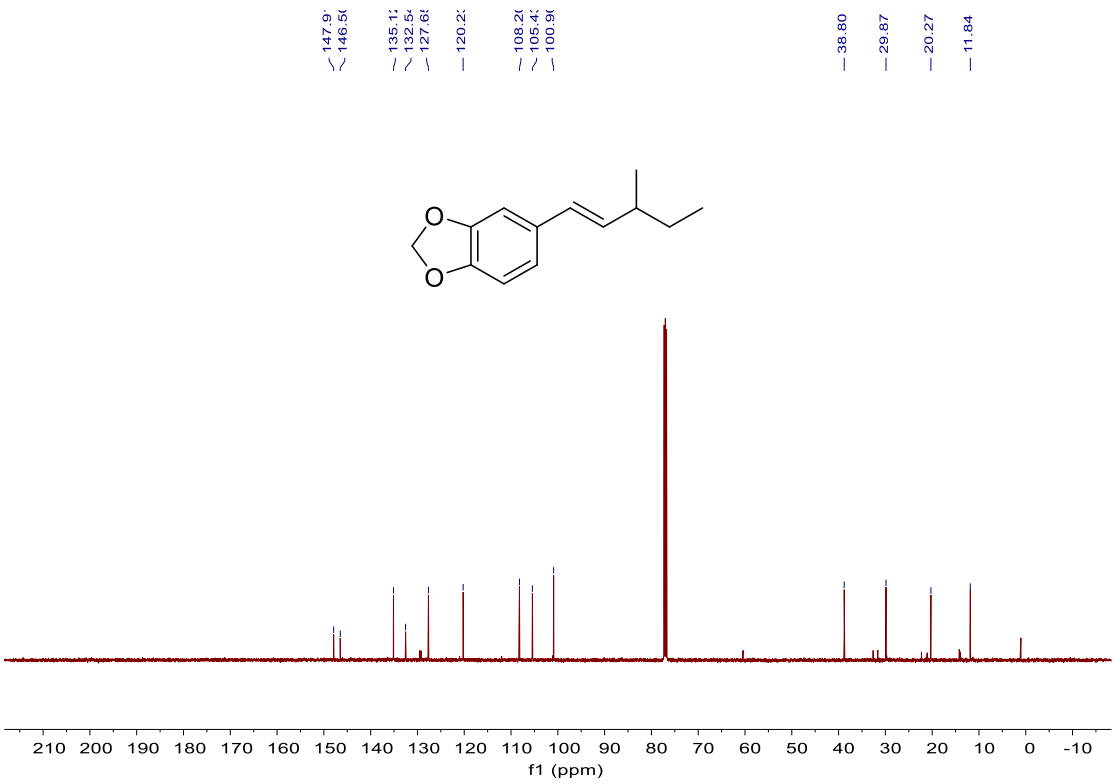
16) ^{1}H NMR and ^{13}C NMR Spectra of Compound 5c



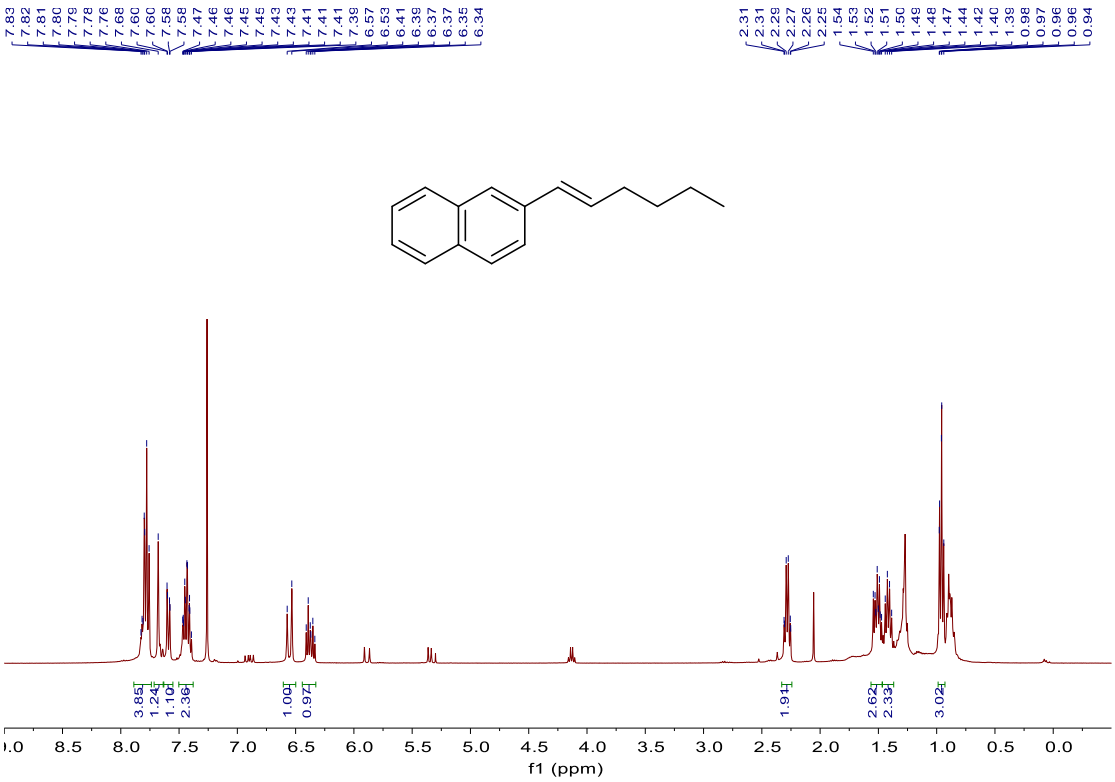


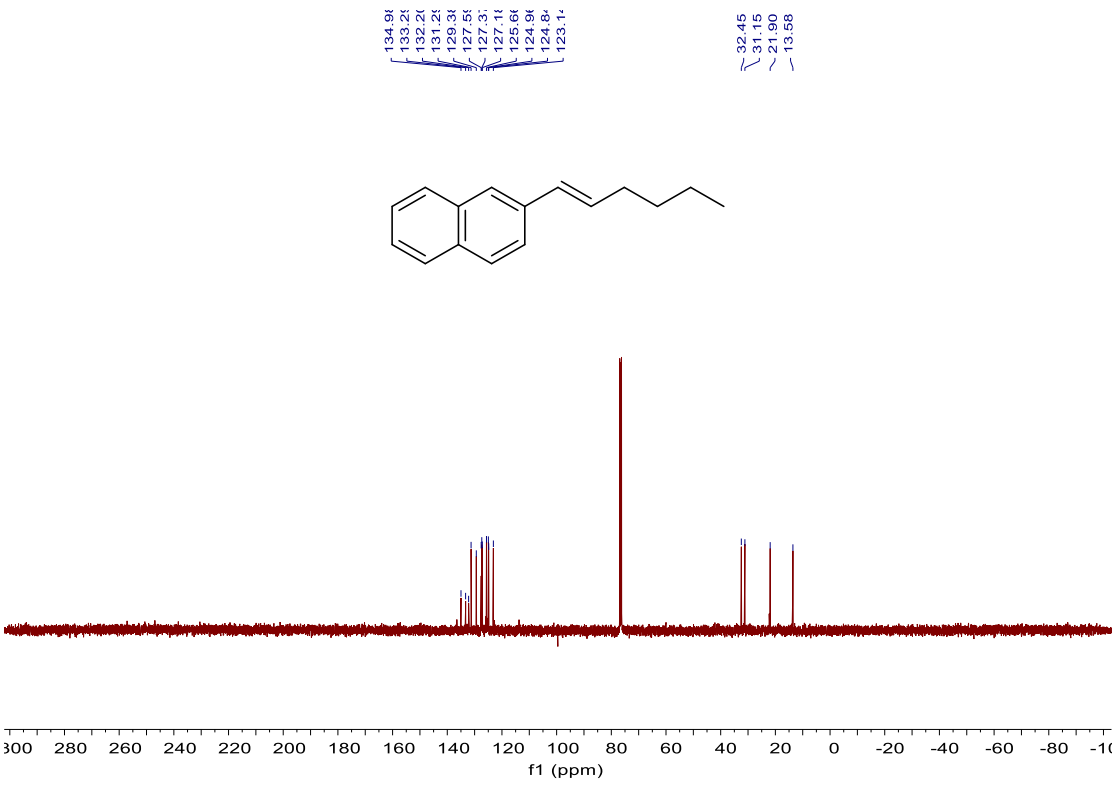
17) ^{1}H NMR and ^{13}C NMR Spectra of Compound 6a



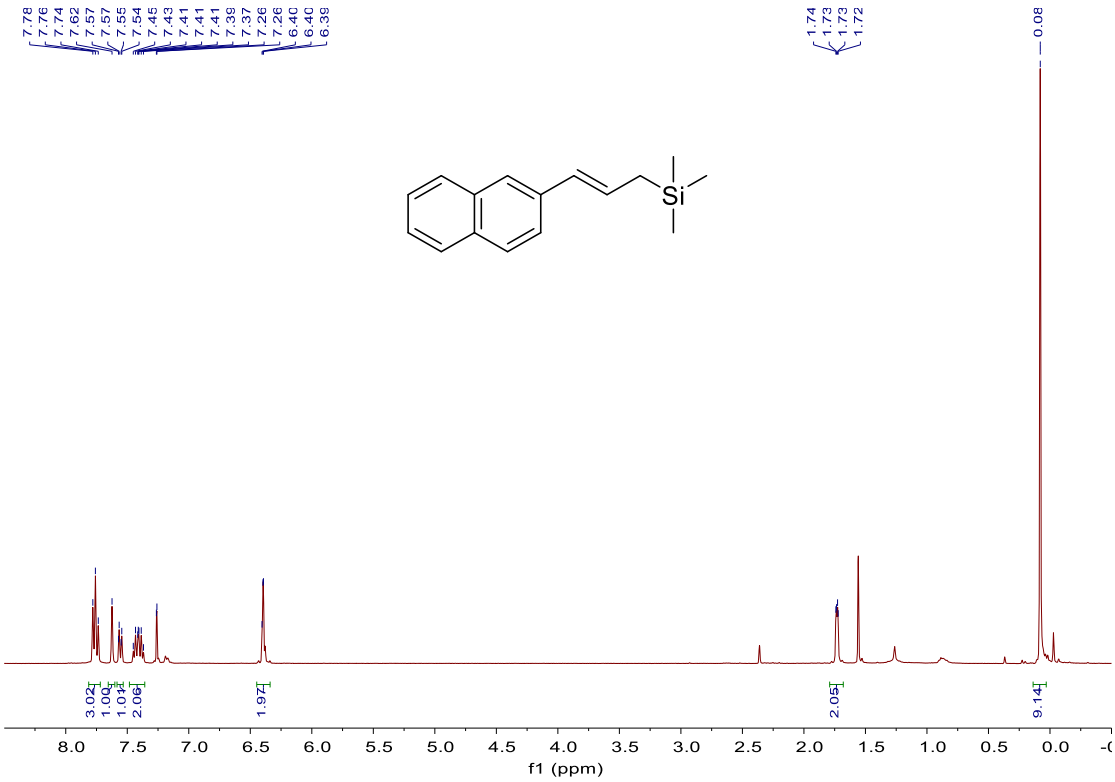


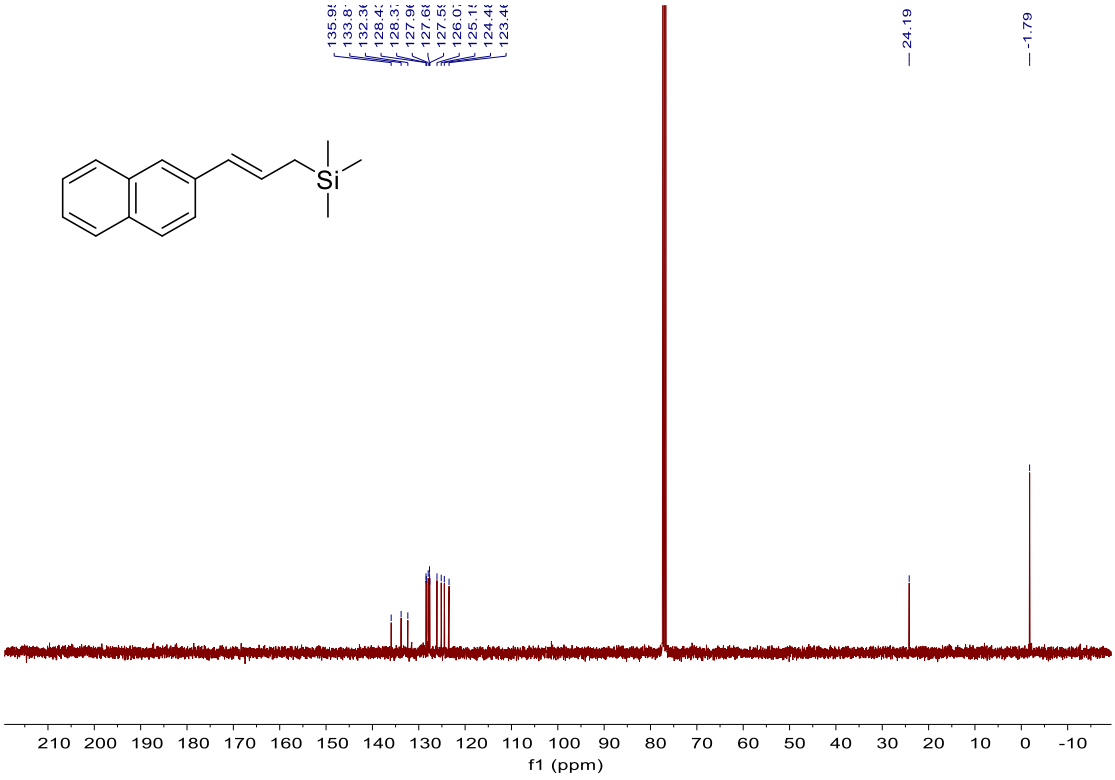
18) ^{1}H NMR and ^{13}C NMR Spectra of Compound 7a



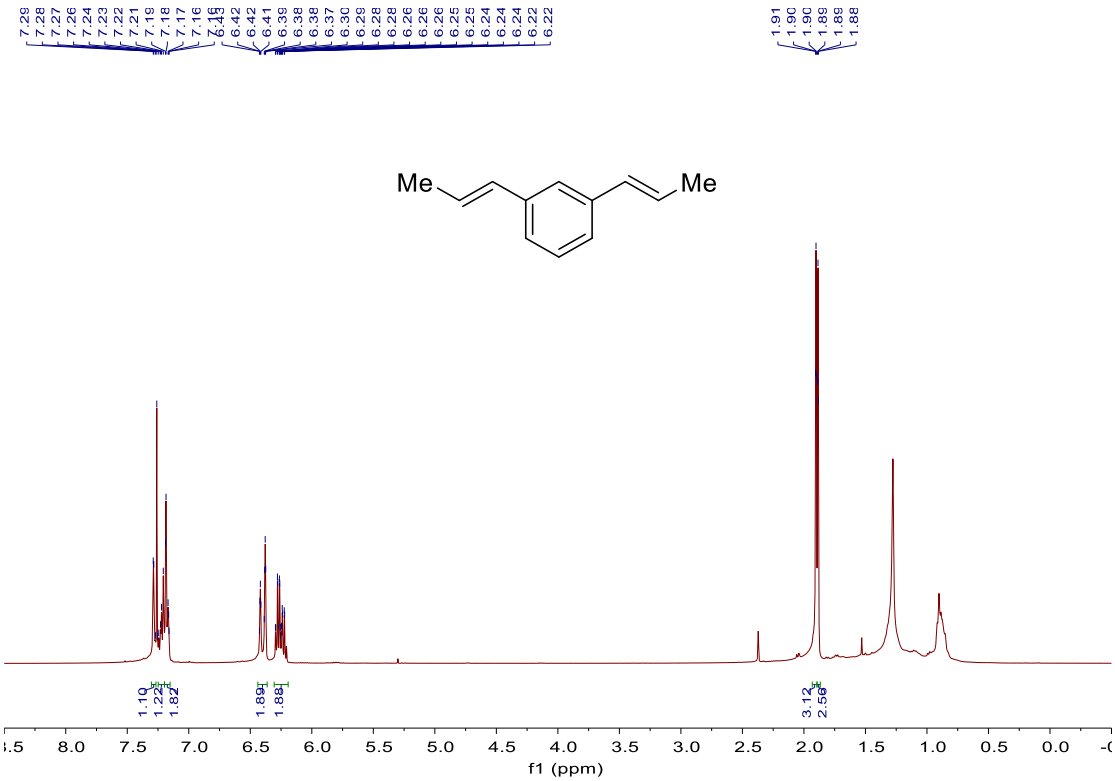


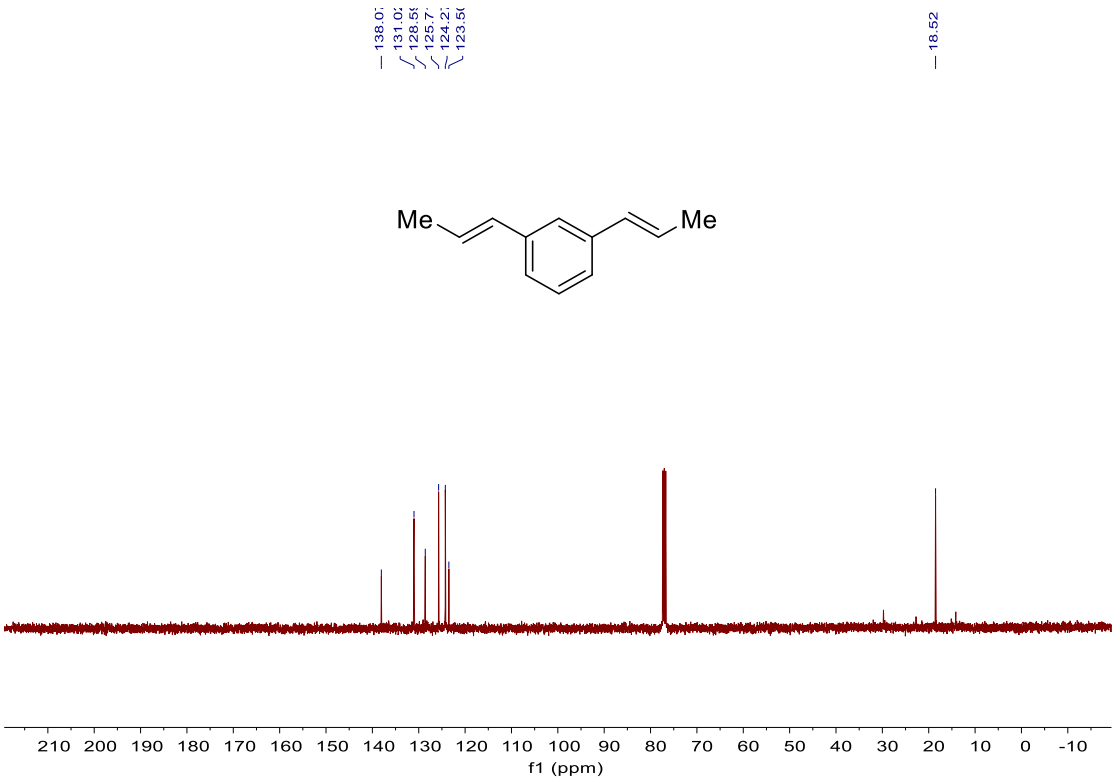
19) ^{1}H NMR and ^{13}C NMR Spectra of Compound 7b



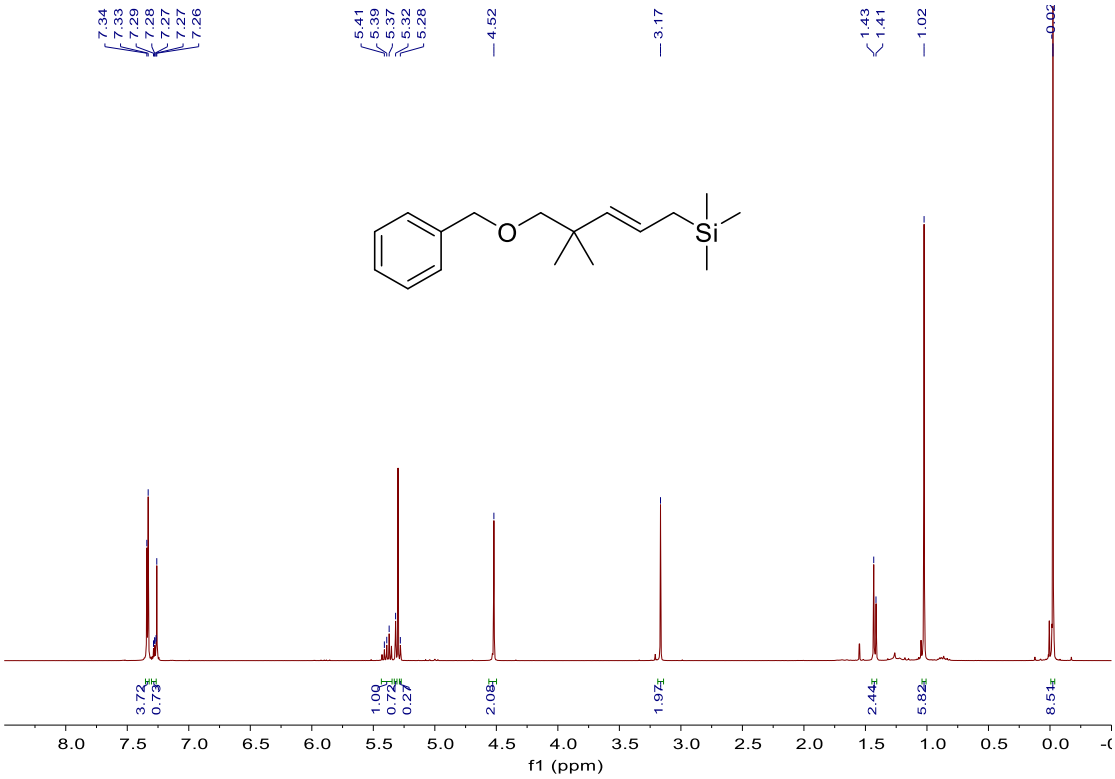


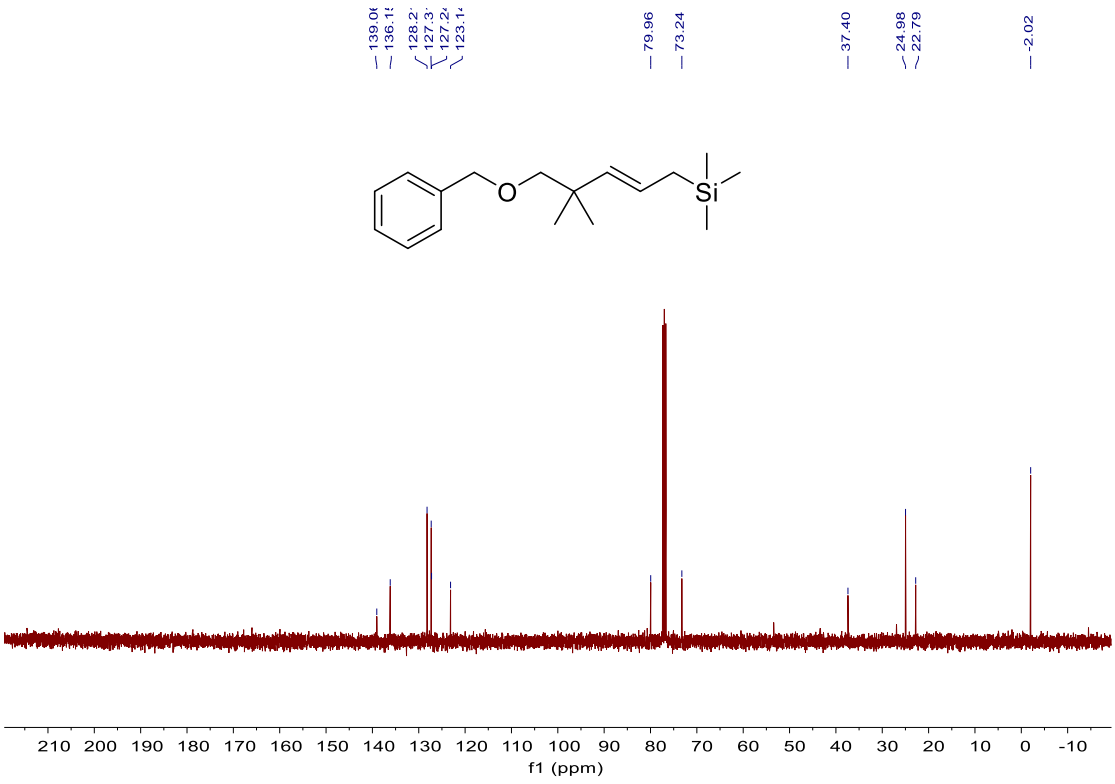
20) ^{1}H NMR and ^{13}C NMR Spectra of Compound 8a



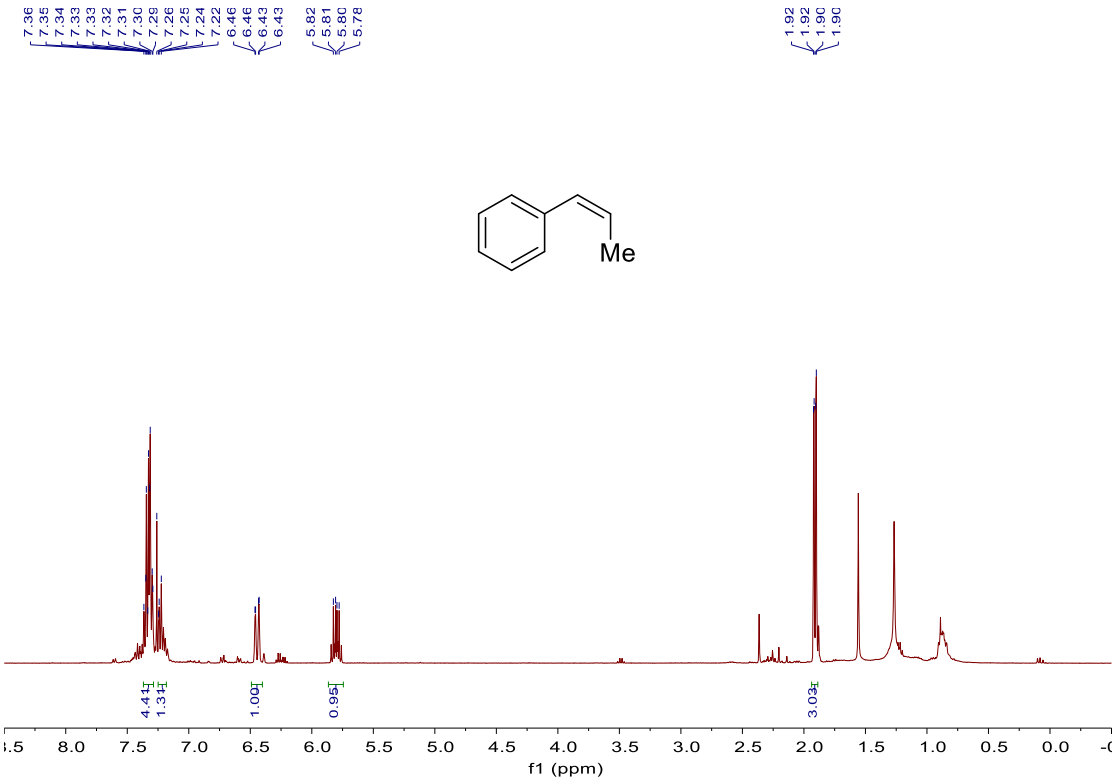


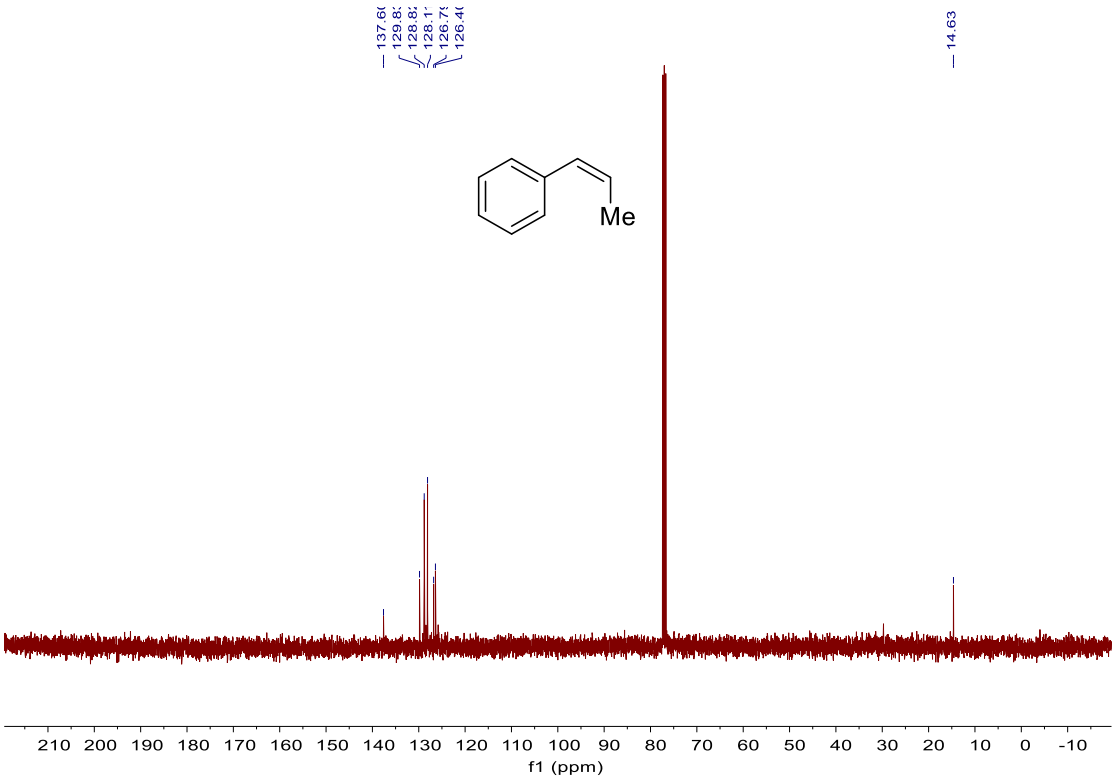
21) ^{1}H NMR and ^{13}C NMR Spectra of Compound 9a



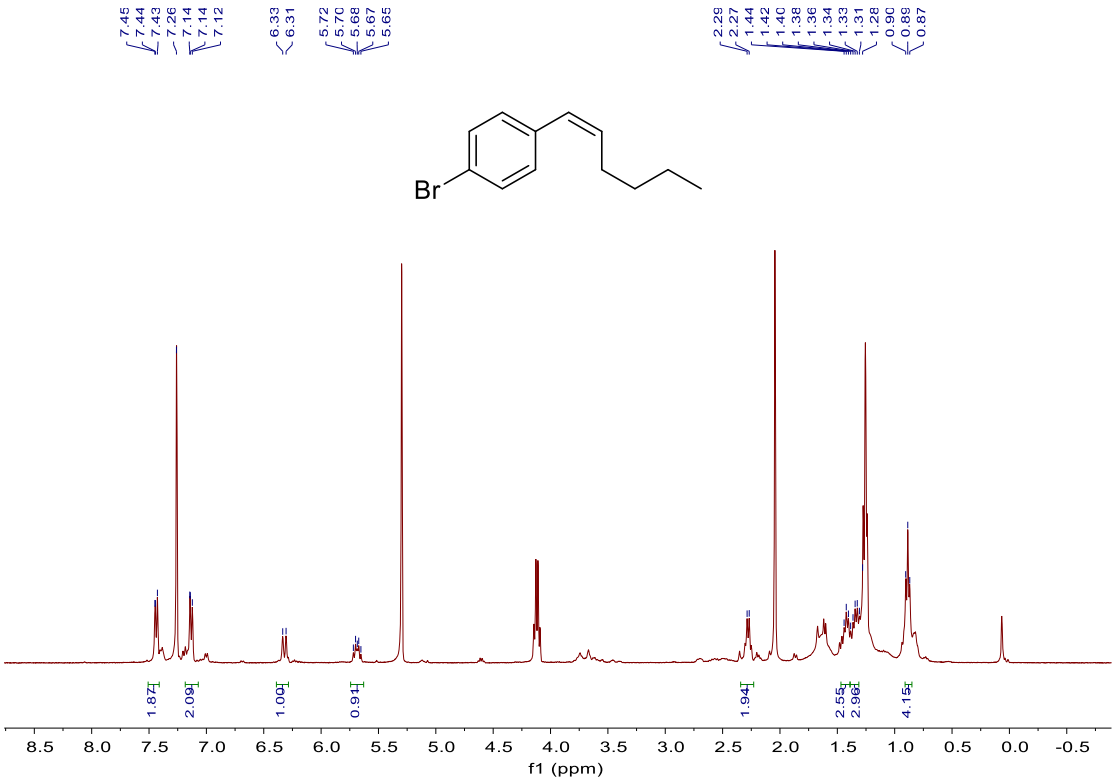


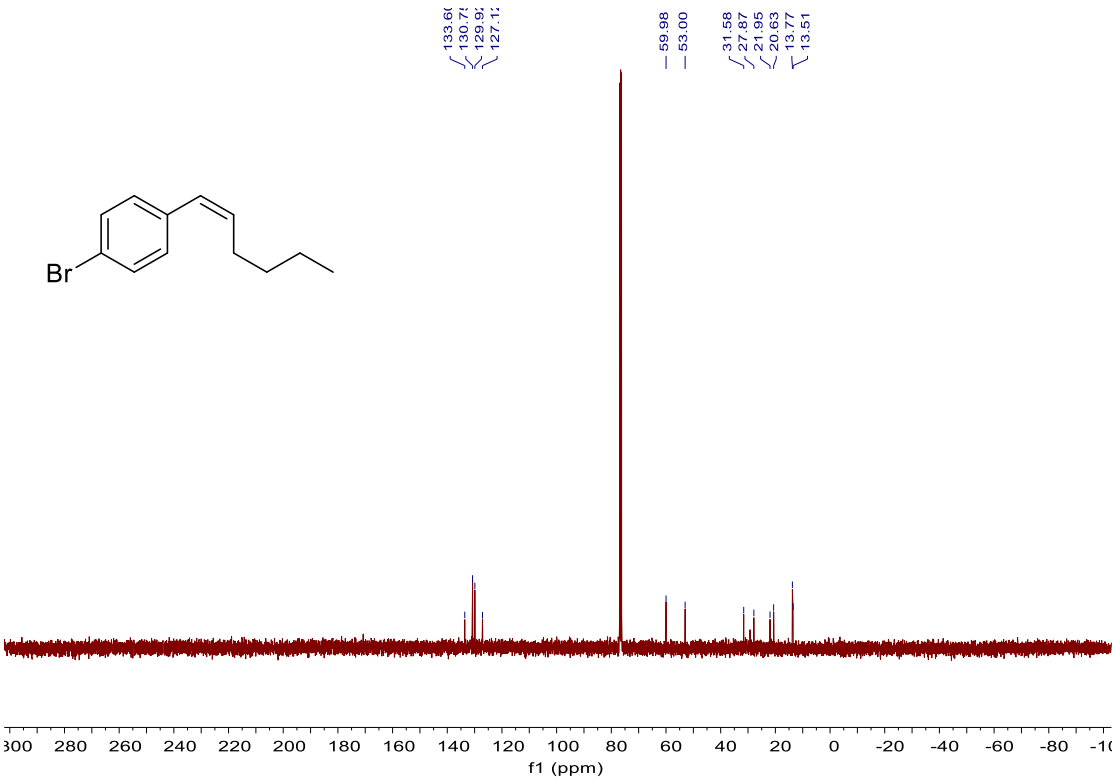
22) ^{1}H NMR and ^{13}C NMR Spectra of Compound 10a



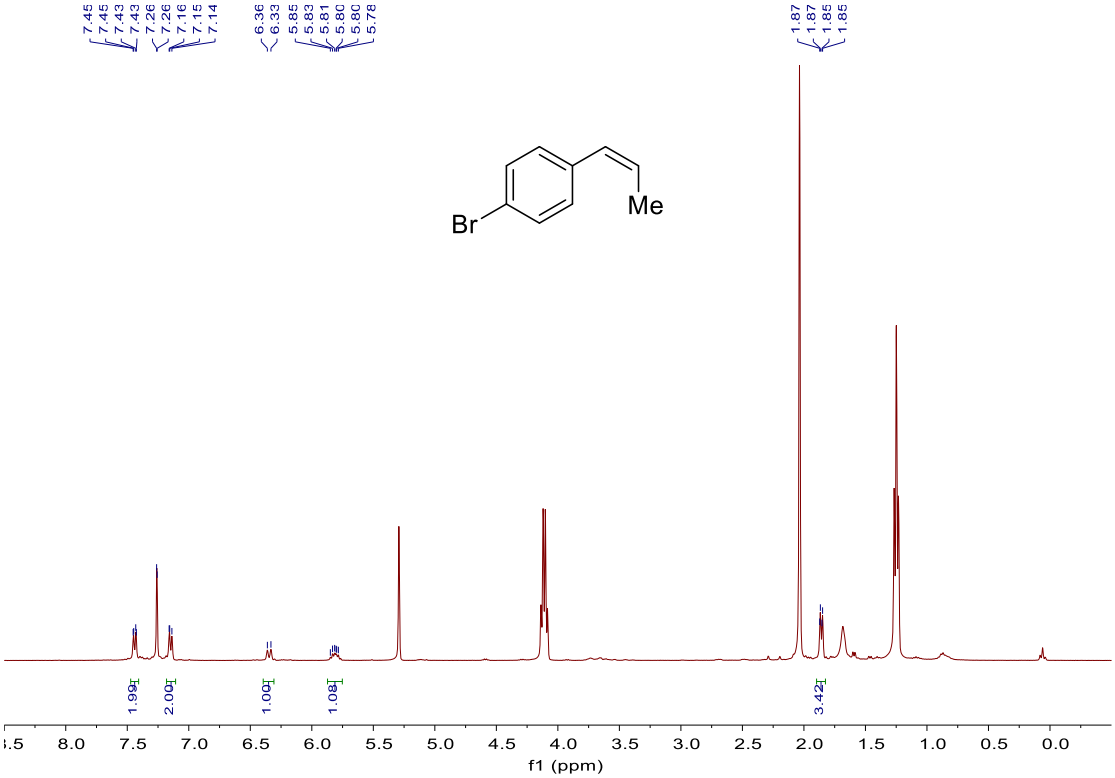


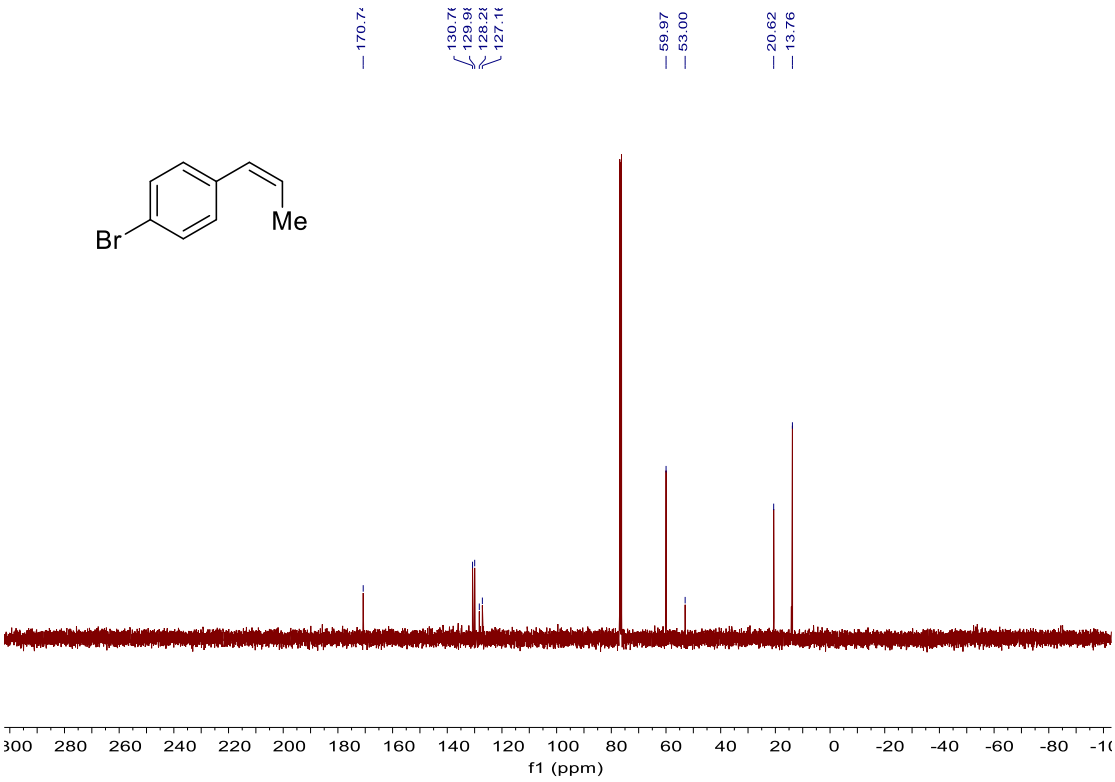
23) ^{1}H NMR and ^{13}C NMR Spectra of Compound 11a



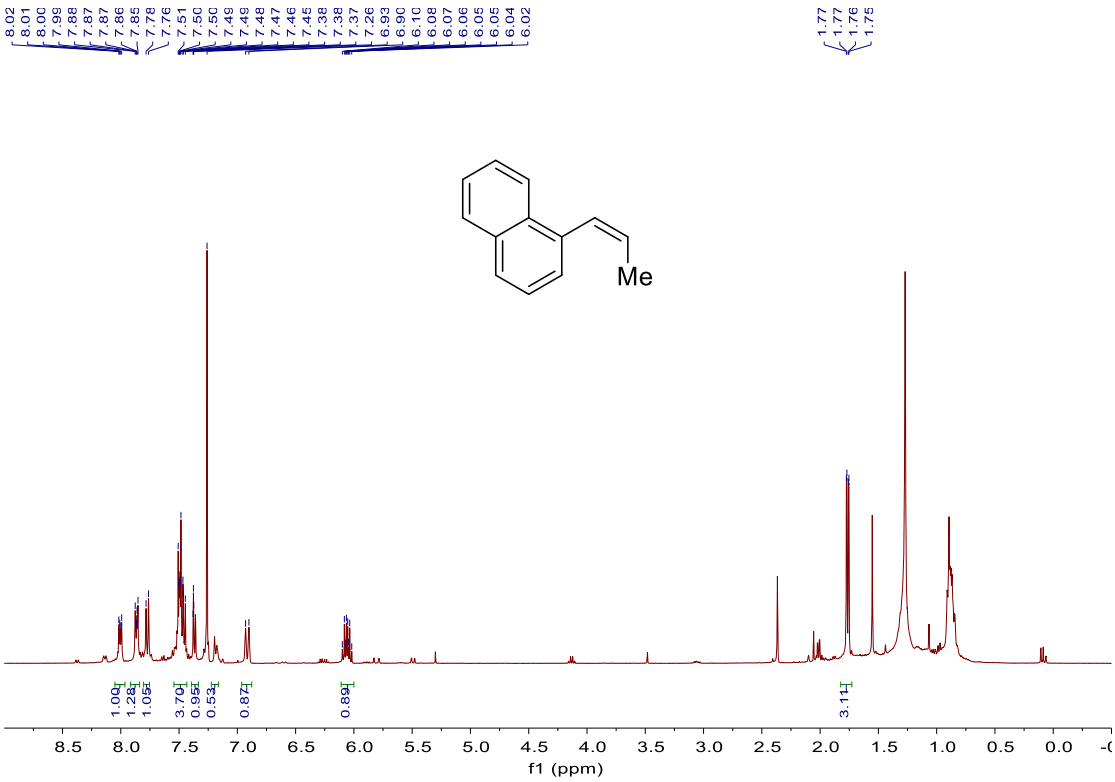


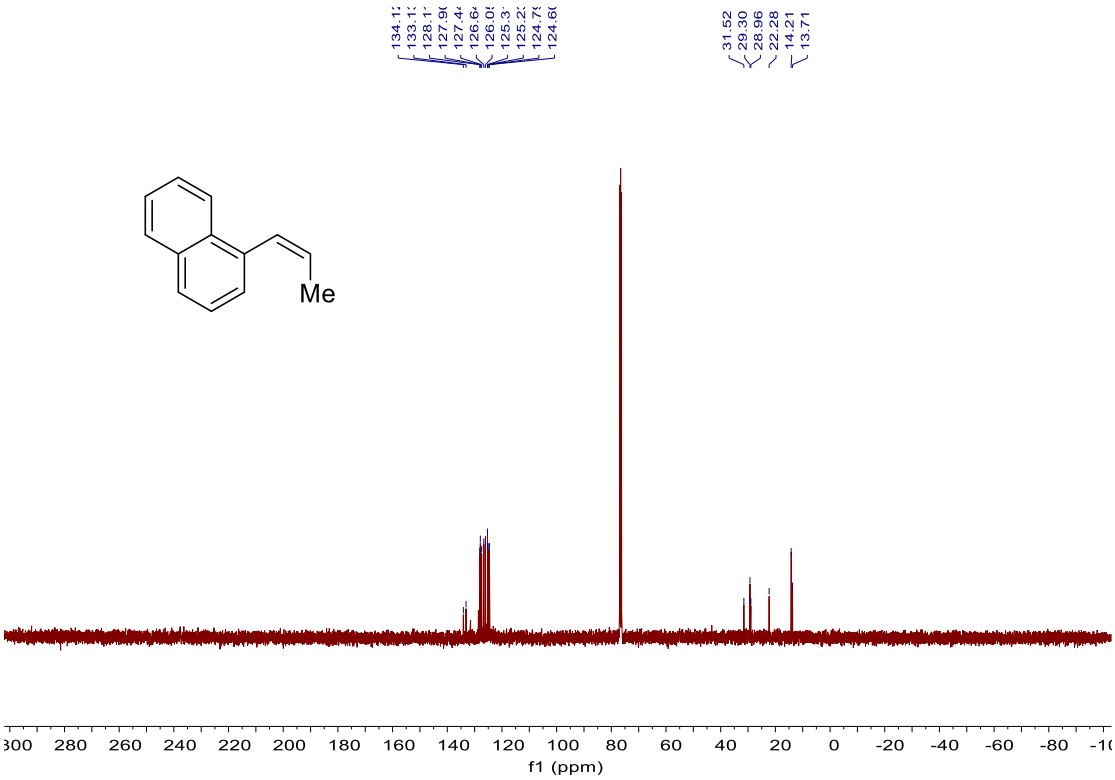
24) ^{1}H NMR and ^{13}C NMR Spectra of Compound 11b



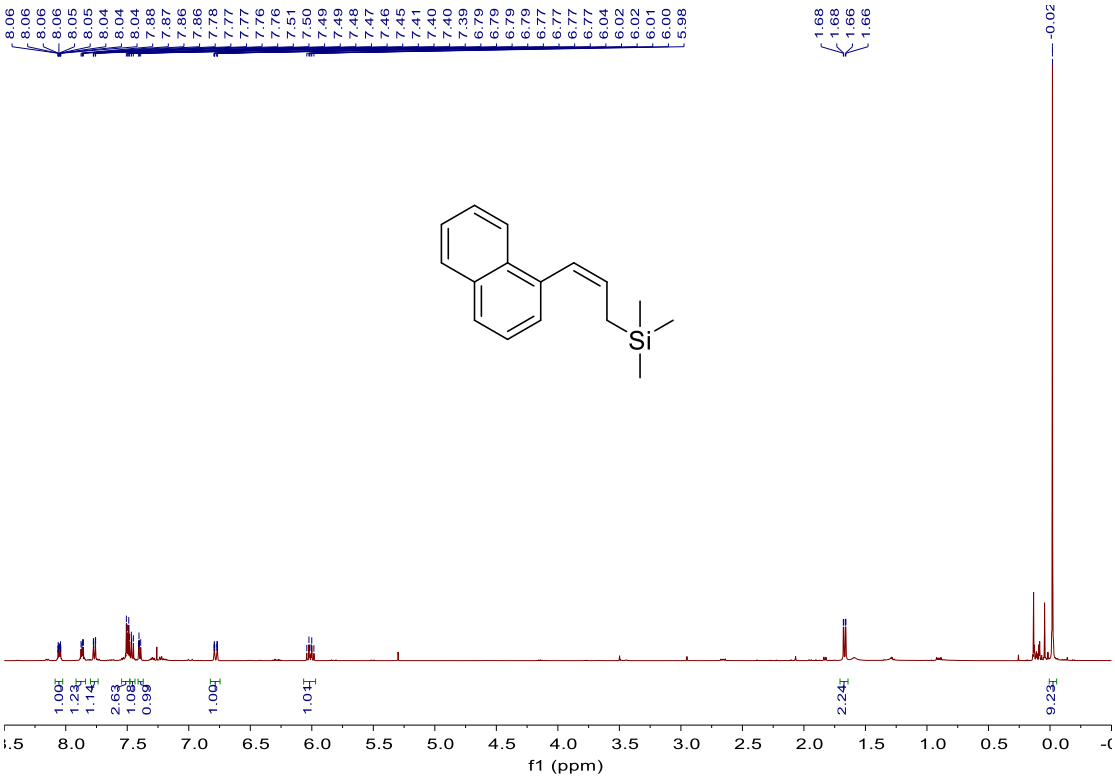


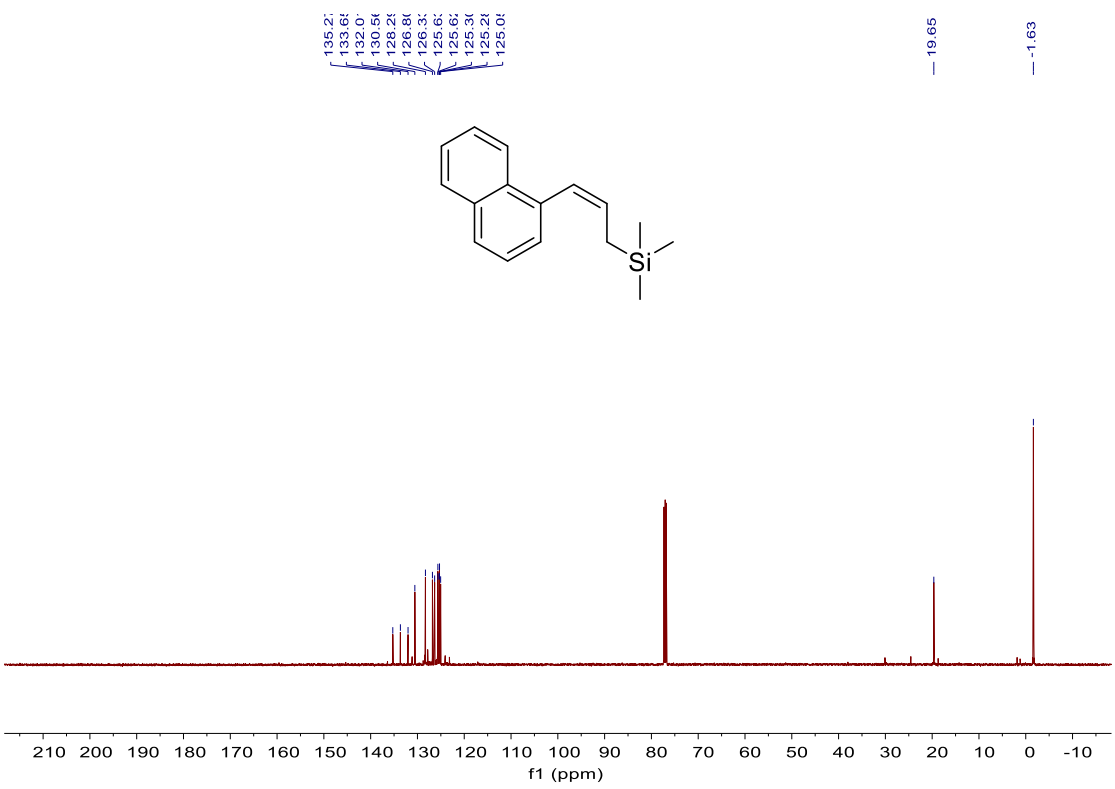
25) ^{1}H NMR and ^{13}C NMR Spectra of Compound 12a



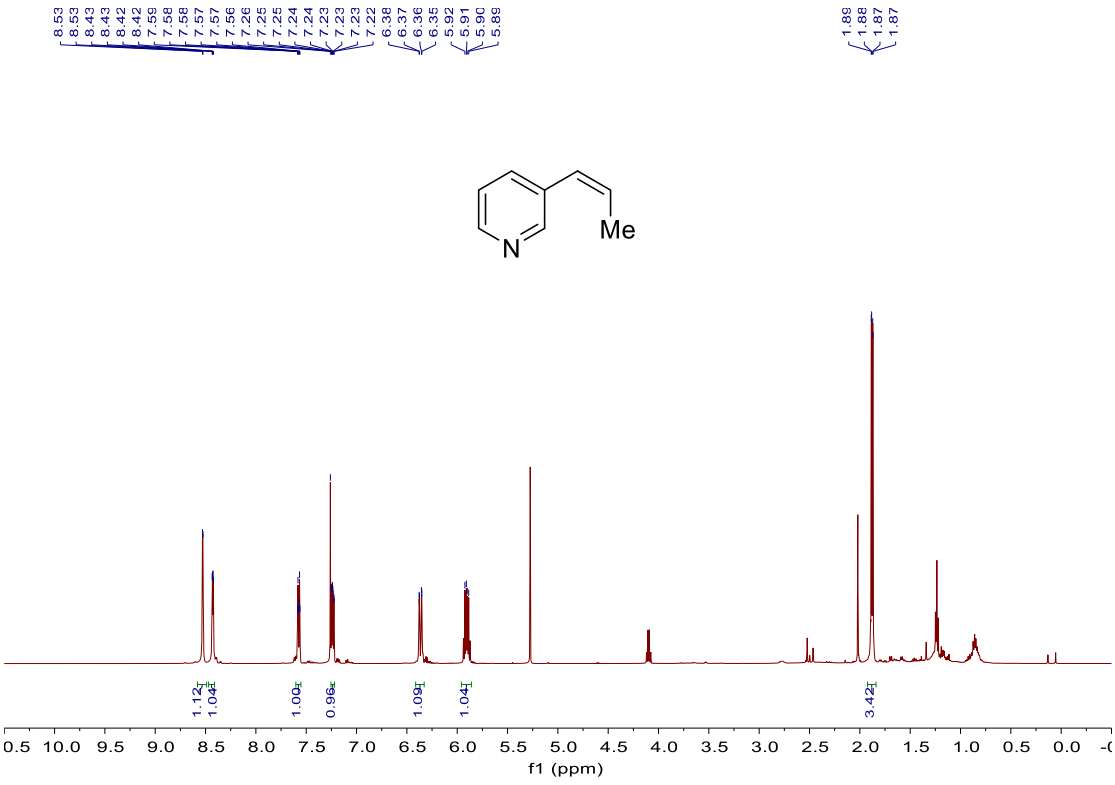


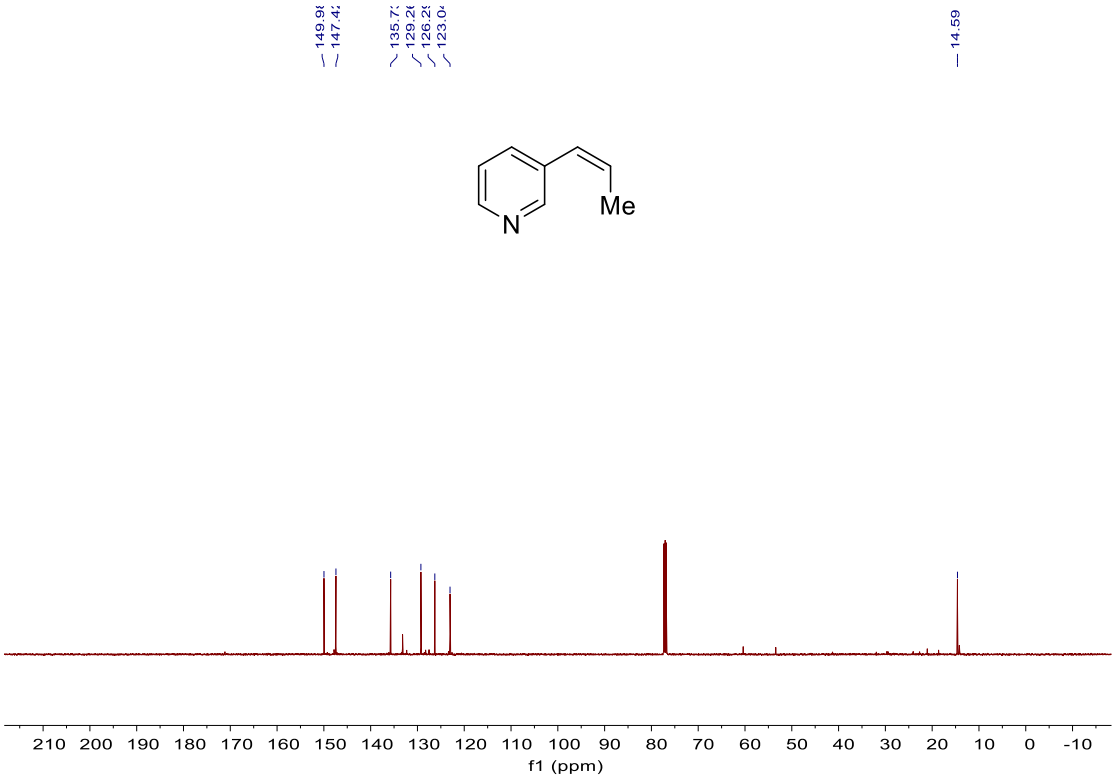
26) ^{1}H NMR and ^{13}C NMR Spectra of Compound 12b



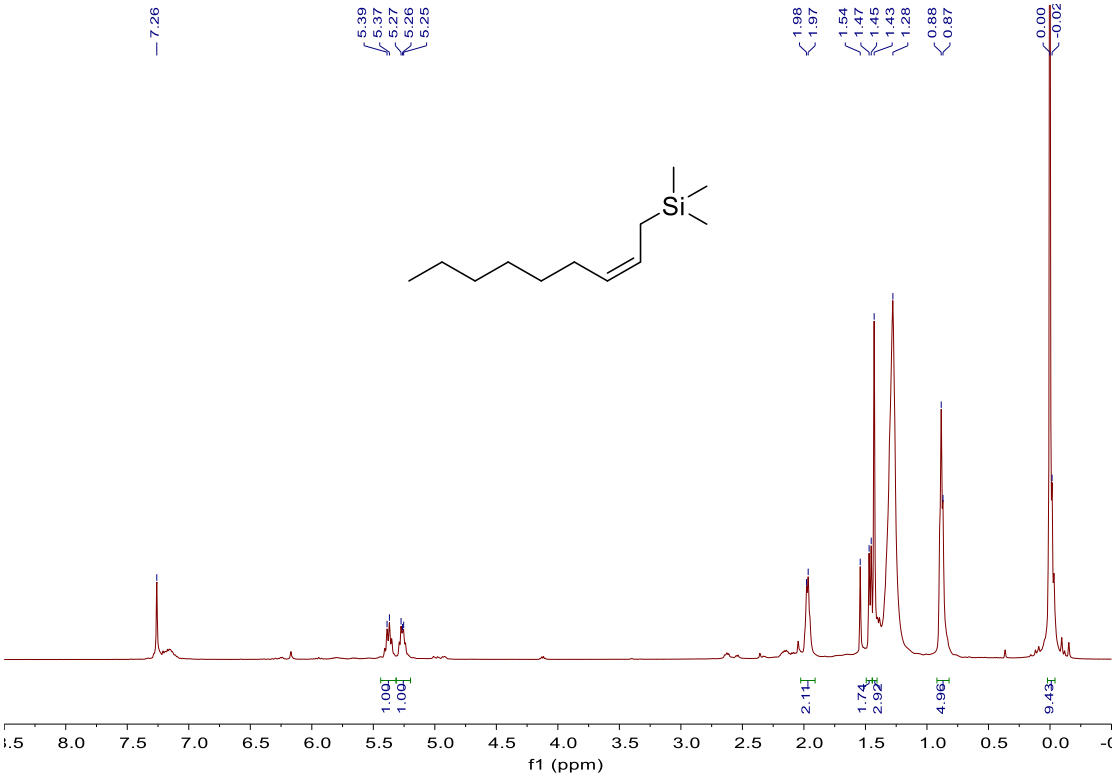


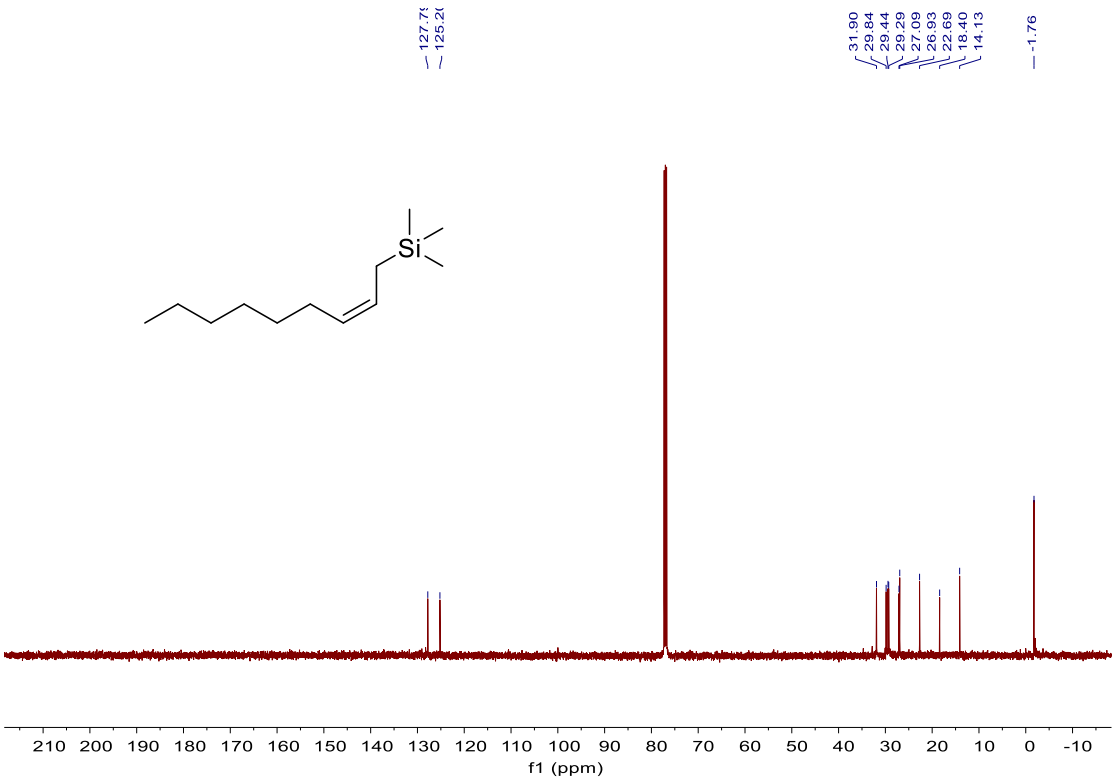
27) ^{1}H NMR and ^{13}C NMR Spectra of Compound 13a



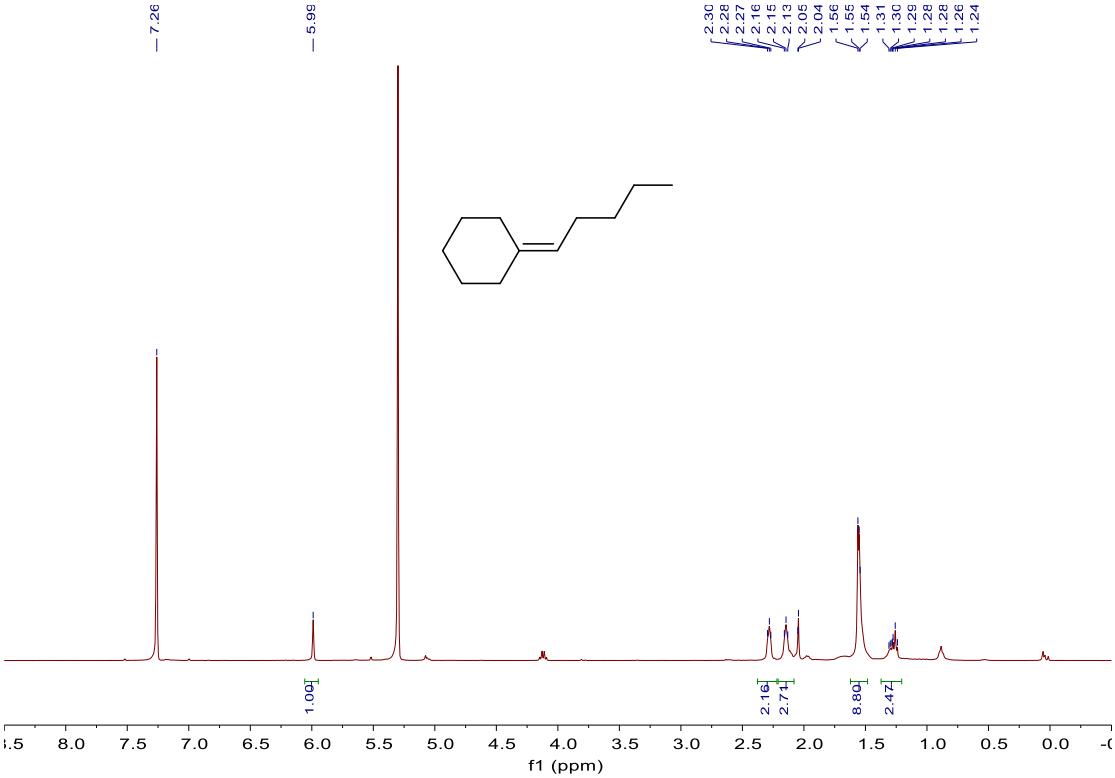


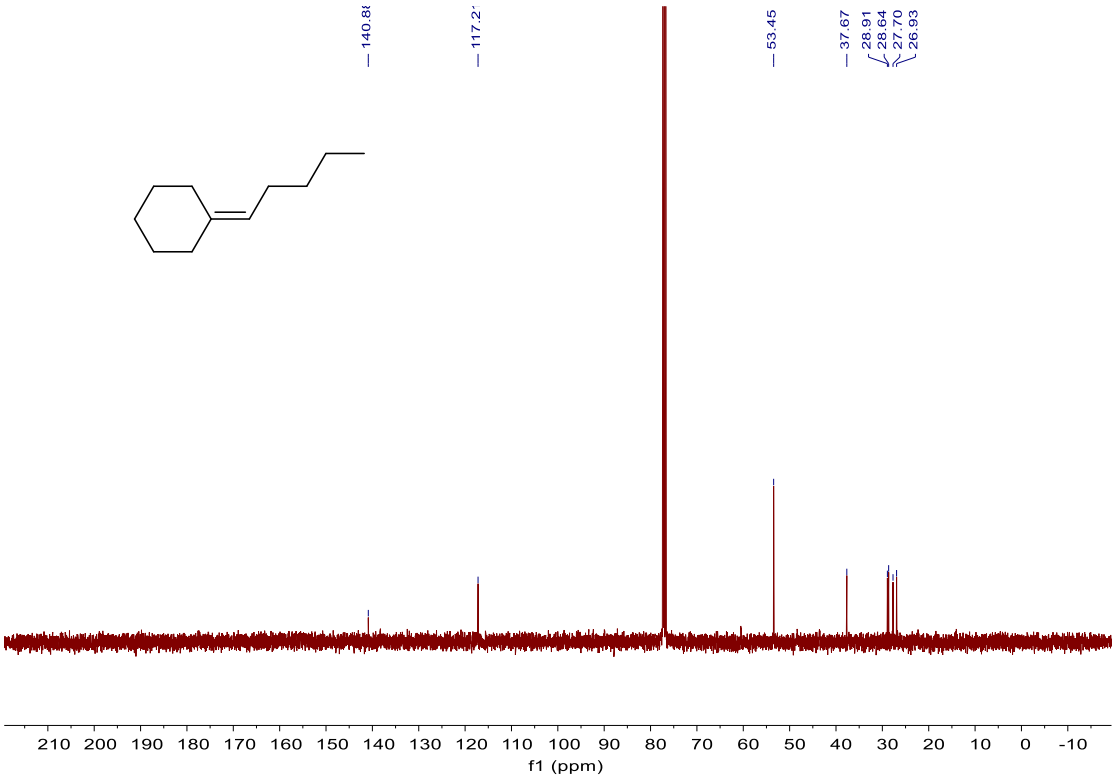
28) ^{1}H NMR and ^{13}C NMR Spectra of Compound 14a



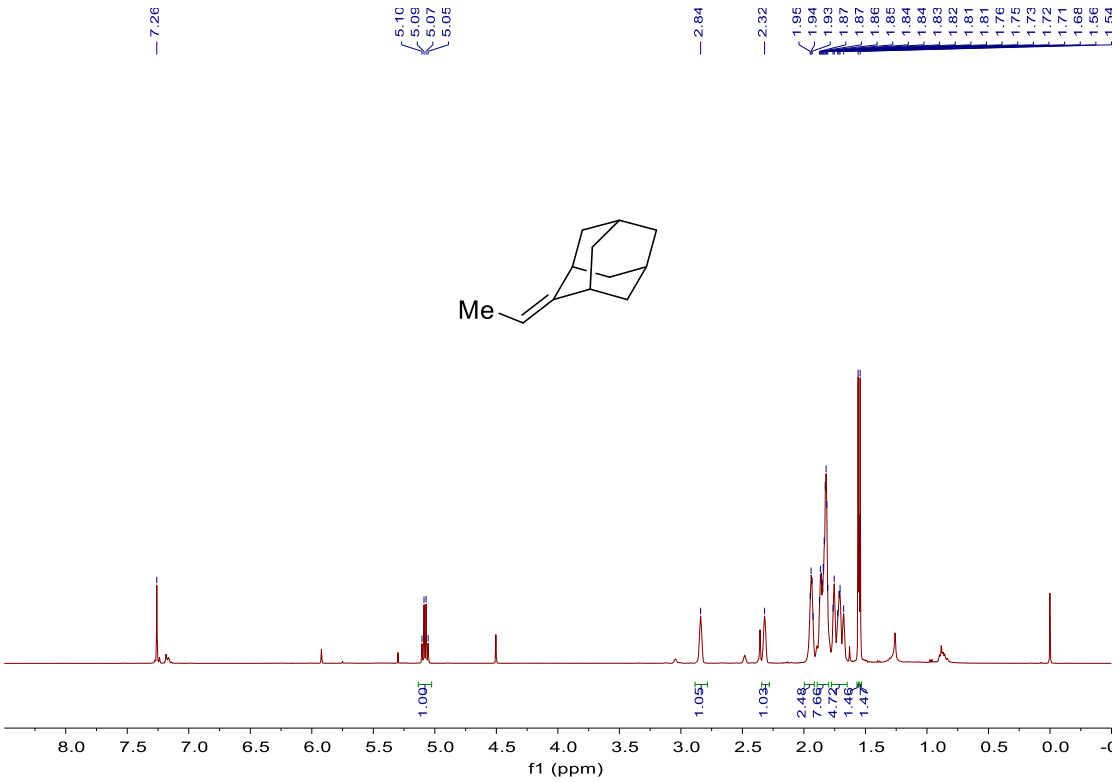


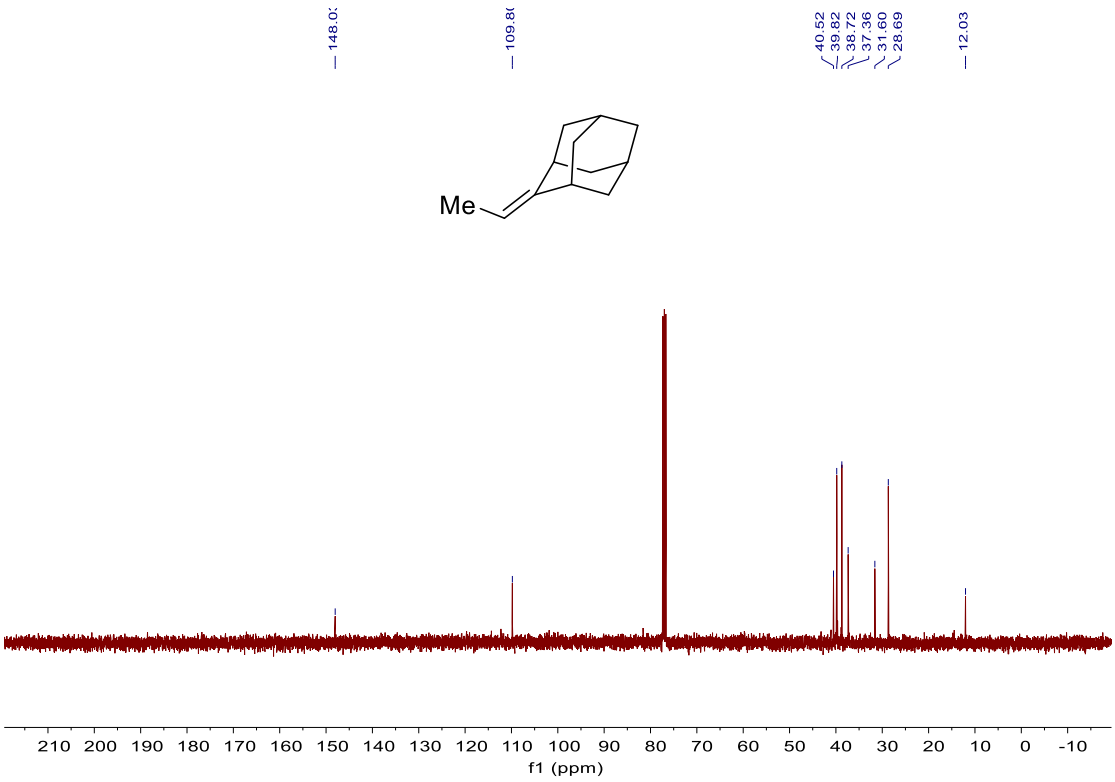
29) ^{1}H NMR and ^{13}C NMR Spectra of Compound 15a



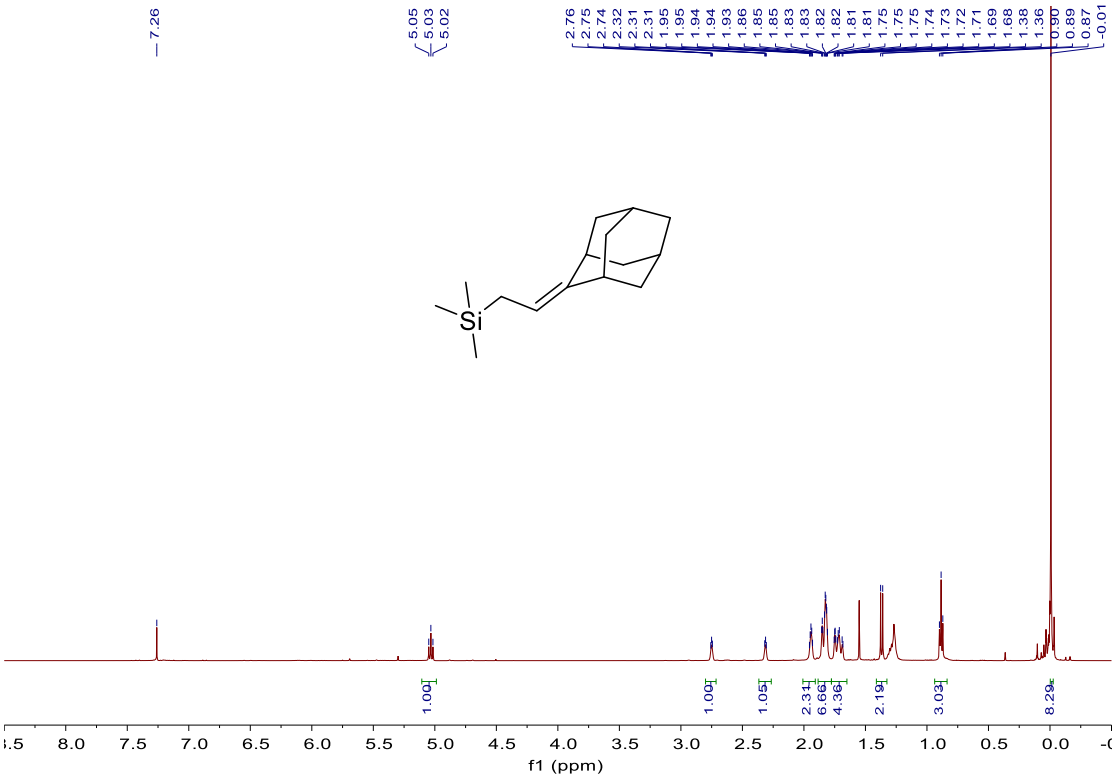


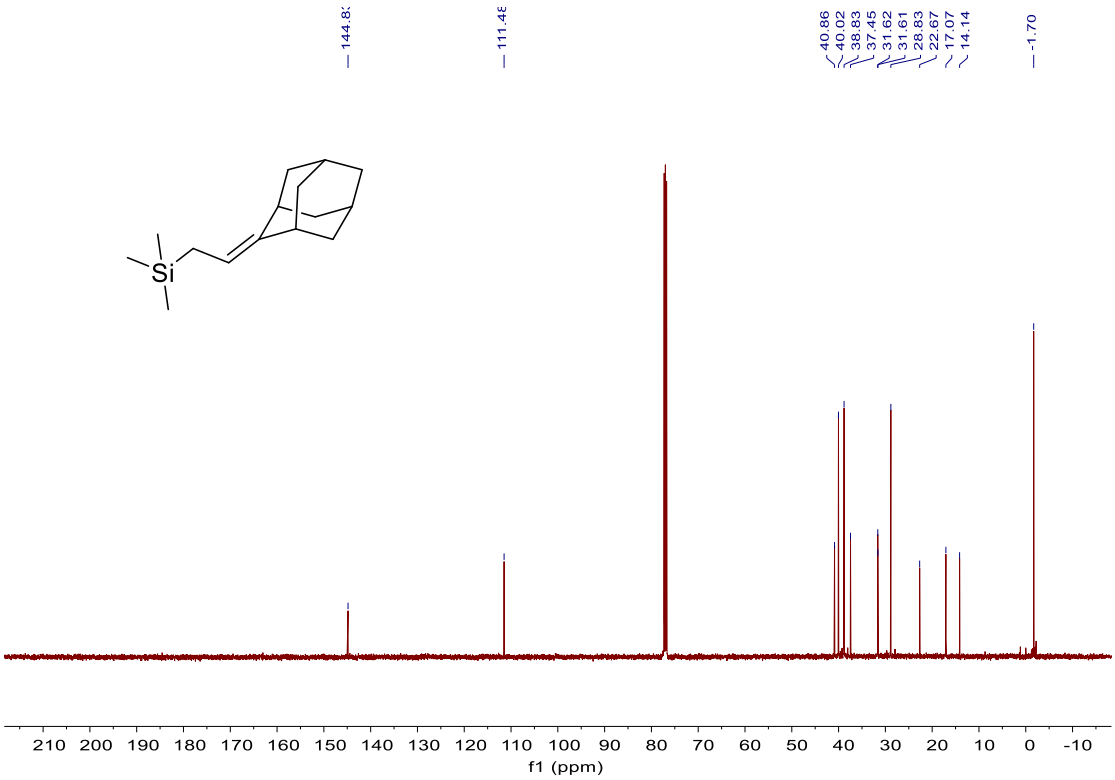
30) ^{1}H NMR and ^{13}C NMR Spectra of Compound 16a



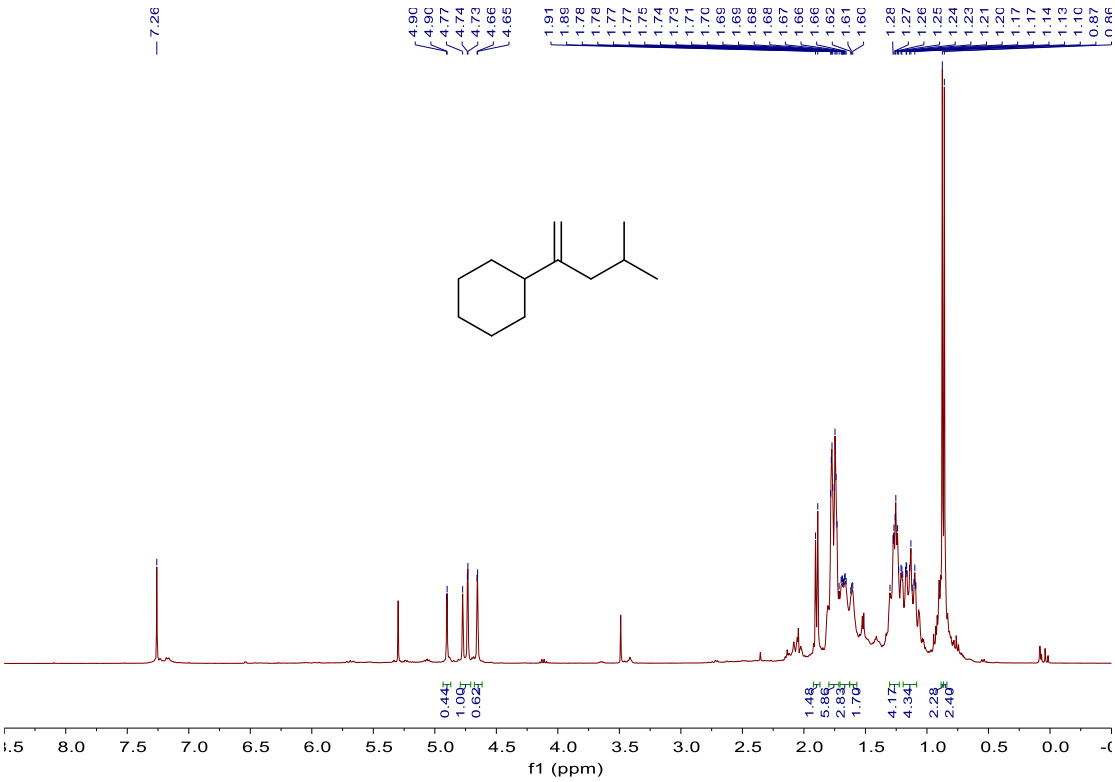


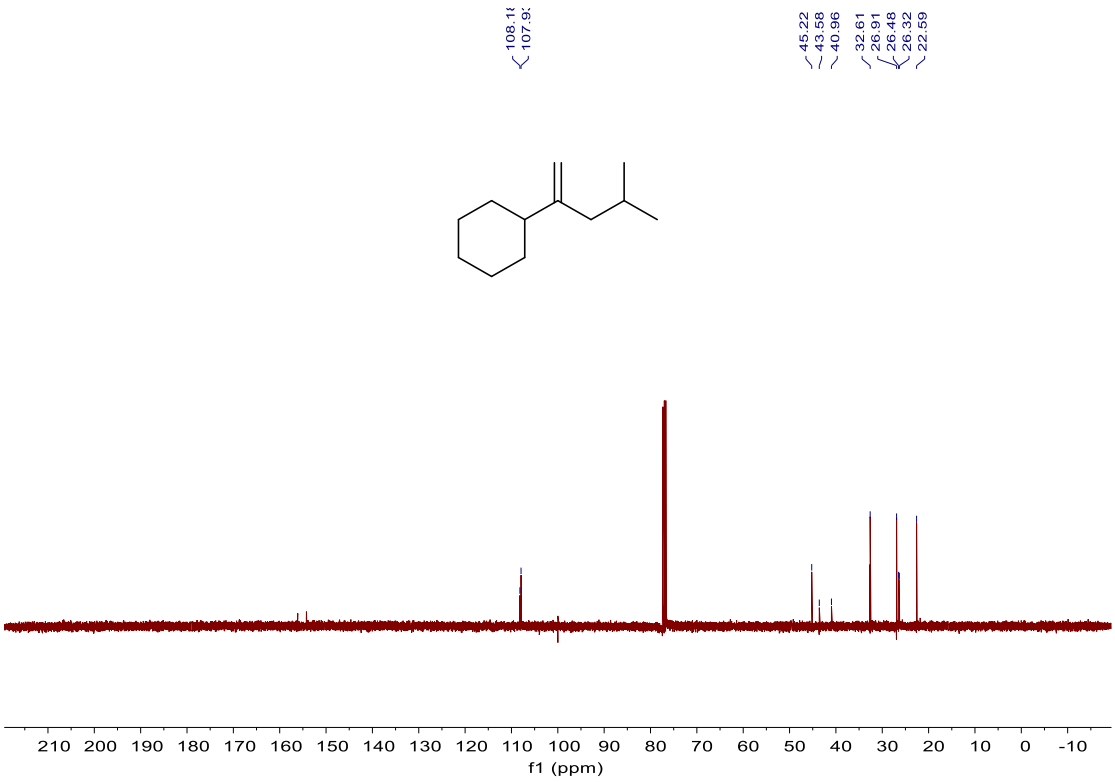
31) ^{1}H NMR and ^{13}C NMR Spectra of Compound 16b



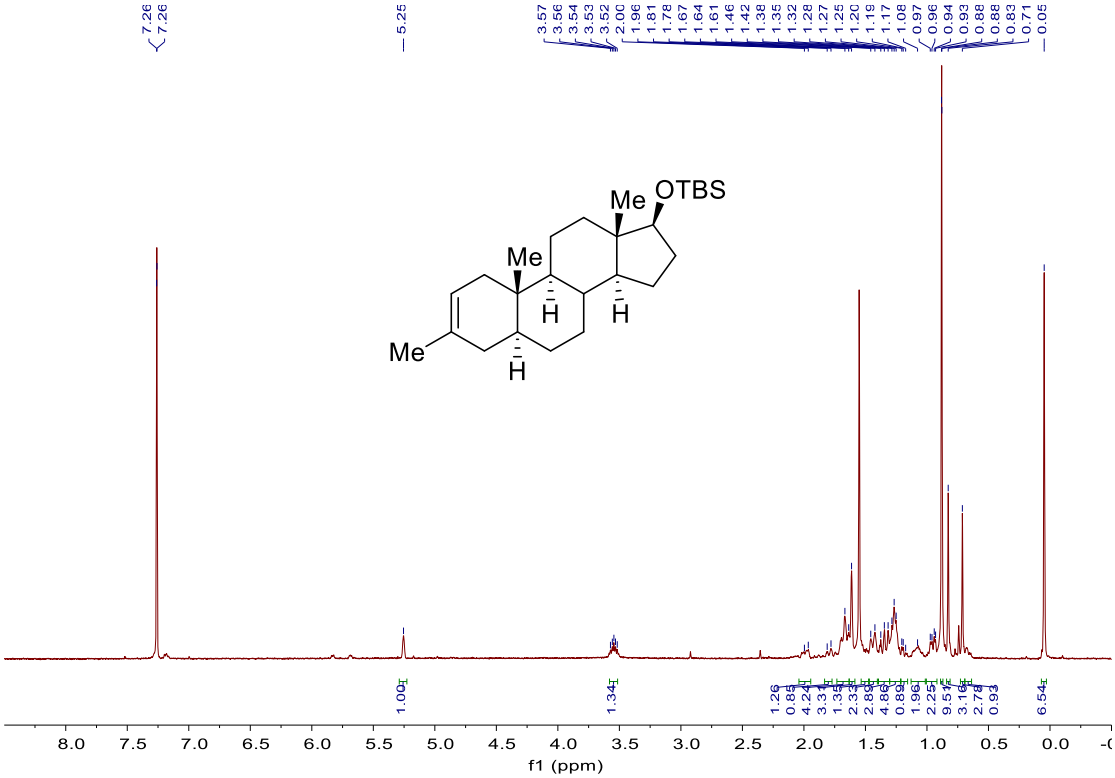


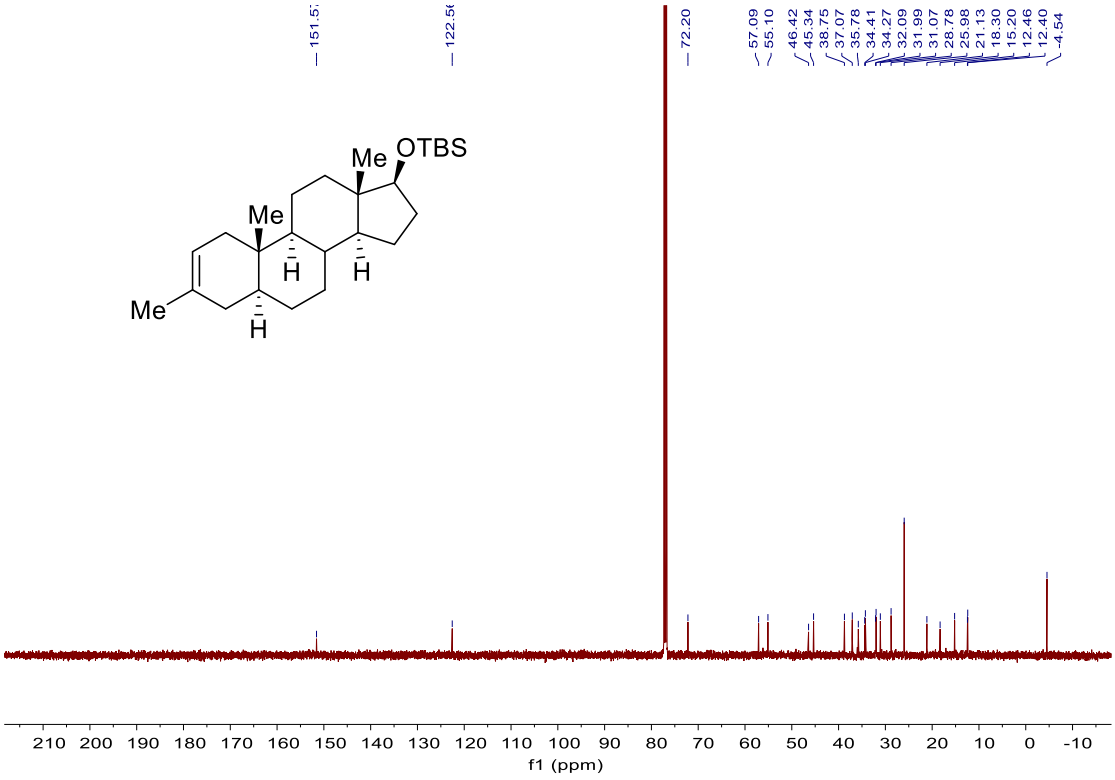
32) ^{1}H NMR and ^{13}C NMR Spectra of Compound 17a



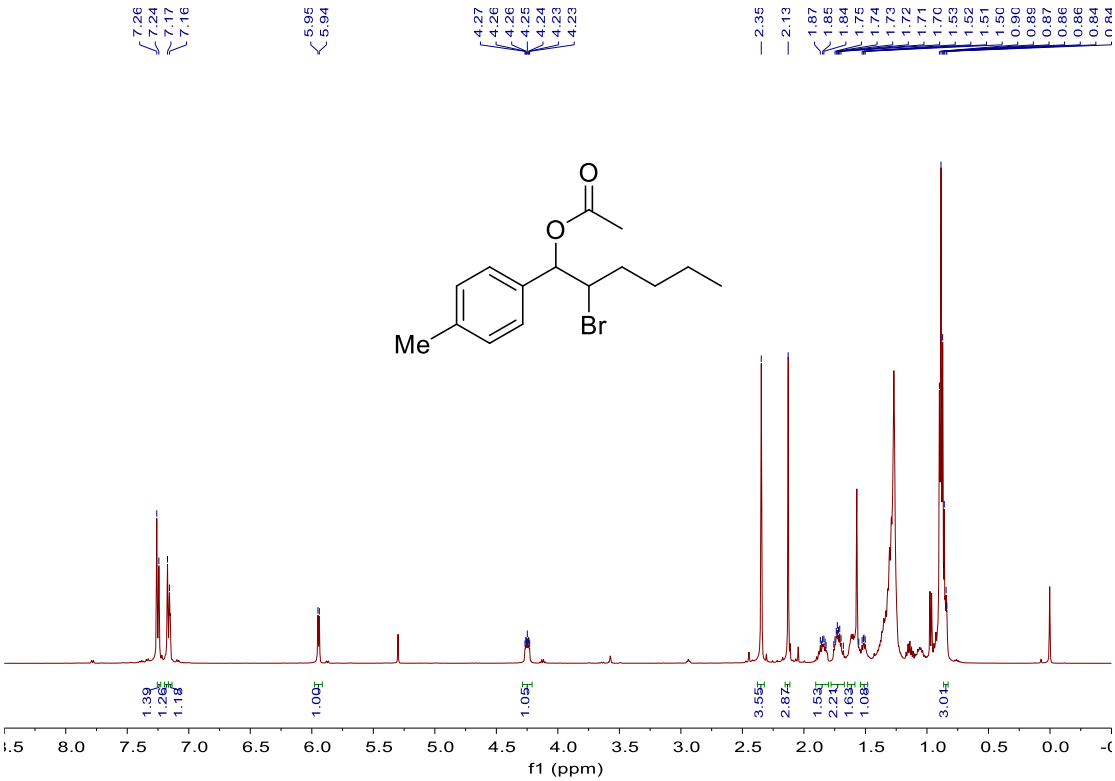


33) ^{1}H NMR and ^{13}C NMR Spectra of Compound 18a

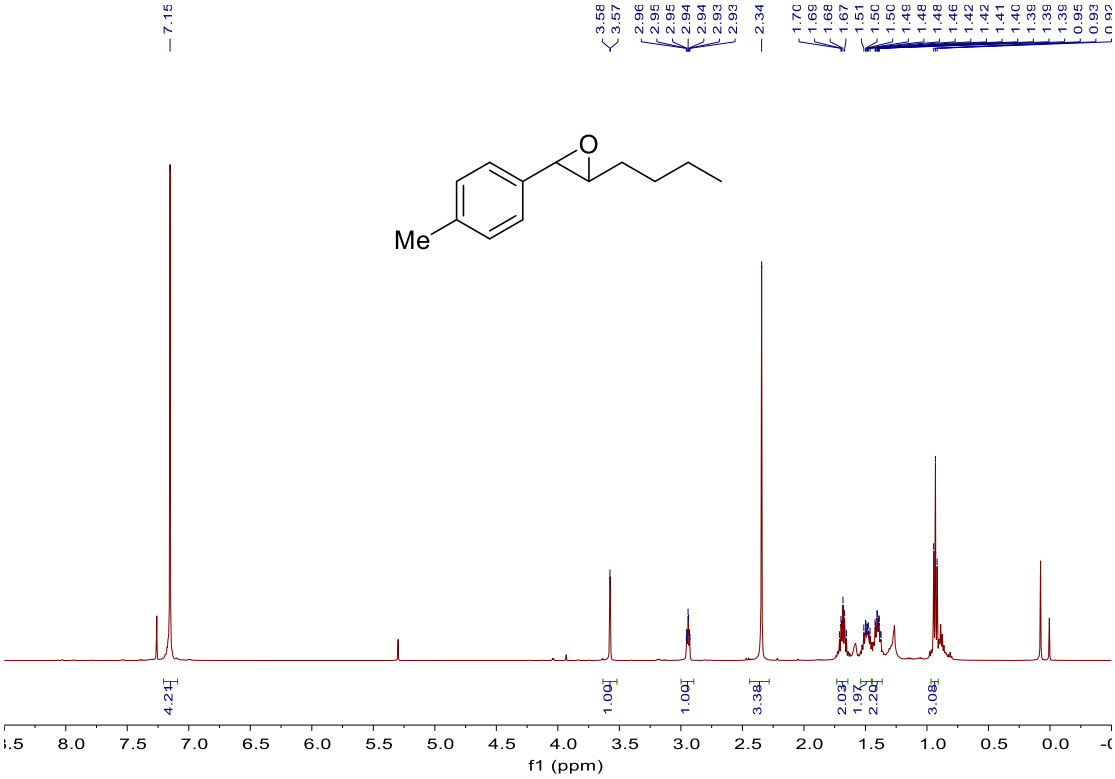


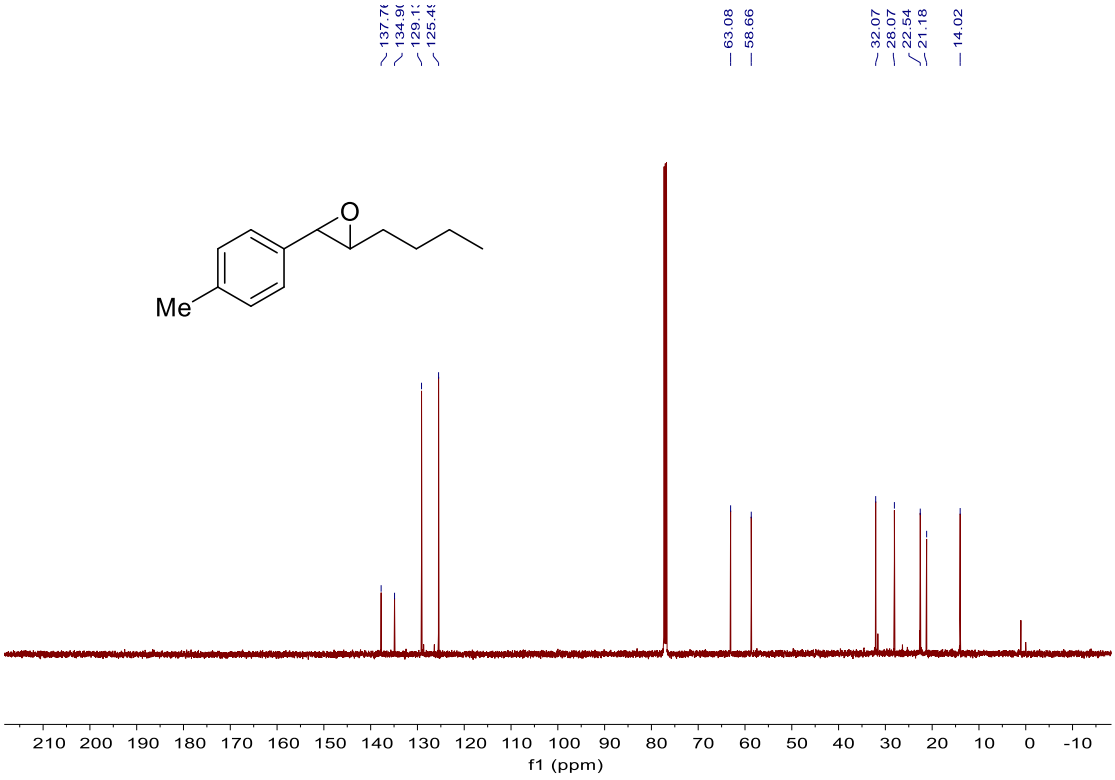


34) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2aa



35) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2ab





36) ^{1}H NMR and ^{13}C NMR Spectra of Compound 2ac