Photoredox/Nickel Dual-Catalyzed Regio- and Stereo-selective Cross-Coupling of Allyl Trifluoroborates with Alkenyl Electrophiles: Synthesis of 1,4-Dienes

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Contents:

General Methods.

Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran and toluene were distilled from sodium and benzophenone. 1,4-Dioxane was dis tilled from sodium. Acetonitrile was purchased from J&K. *N*, *N*-Dimethylformamide was distilled from calcium hydride. 4CzIPN was purchased from J&K. $NiBr_2$•DME was purchased from Strem Chemicals Inc. Dtbbpy and 4,4'-dimethoxy-2,2'-bipyridine was purchased from J&K. DABCO was purchased from Alfa. 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine was purchased from Alfa. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources.

^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS) solutions on Varian XL-400 MHz spectrometer, Agilent XL-400 MHz spectrometer or Bruker Avance III HD 400MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethyl silane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using Agilent Technologies 7250 GCQTOF. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer.

Photoreactions were run in a vial under the irradiation from double 40W Kessil PR160L blue LEDs (456 nm) at 50 intensity settings. The distance of the reaction tube from the light source is 6-7 cm (light intensity = 60-70 mW/cm^2), and a fan was used for cooling (Figure S1). The reaction temperature is determined from the monitored temperature of the reaction solvent under illumination.

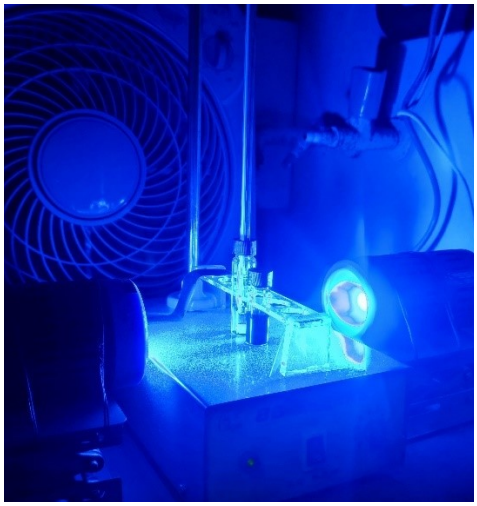
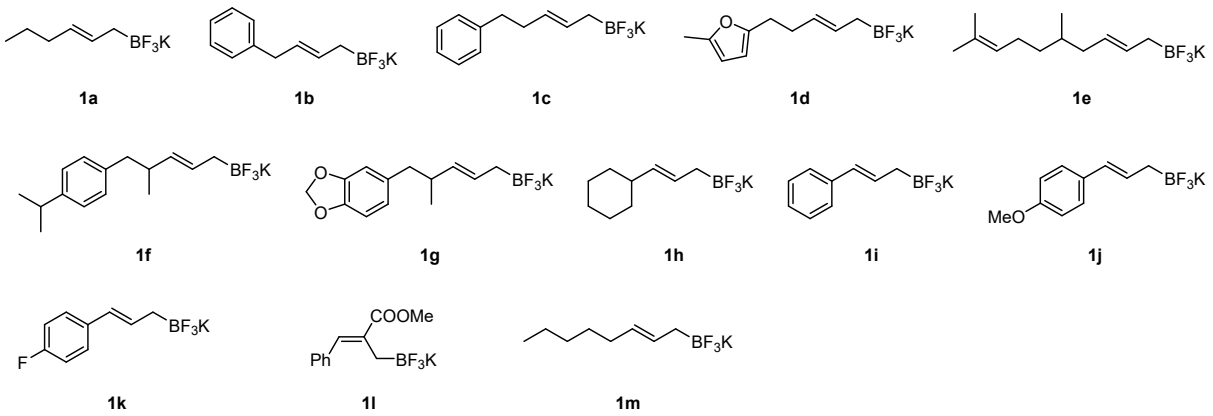
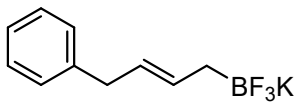


Figure S1. Photoreaction setup.

Synthesis and characterization of allyl trifluoroborates



The aryl-substituted allyl trifluoroborates **1i**, **1j** and **1k** were prepared from Ref. 1. The allyl trifluoroborate substrates **1l** were prepared from Ref. 2. The alkyl-substituted allyl trifluoroborates **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** and **1h** were prepared from the corresponding allyl boronates[3] synthesized by Ref. 3 followed by treatment with KHF_2 in $MeOH/H_2O$. The characterization of new compounds, see the following:

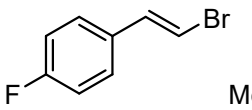


1b

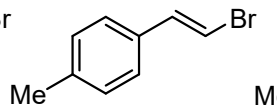
Potassium (*E*)-trifluoro(5-phenylpent-2-en-1-yl)borate (**1b**). The product **1b** was formed as a white solid (537 mg) with an overall yield of 27%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.25 (t, J = 7.2 Hz, 2H), 7.17-7.12 (m, 3H), 5.53 (dt, J = 14.4 Hz, 8.0 Hz, 1H), 5.09 (dt, J = 14.4 Hz, 6.8 Hz, 1H), 3.20 (d, J = 6.8 Hz, 2H), 0.87 (brs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.1, 135.4, 128.2, 128.1, 125.4, 123.0, 39.1. ^{19}F NMR (376 MHz, DMSO-d_6): δ -136.3. IR (neat): 3988, 2971, 2901, 1505, 1492, 1407, 1394, 1249, 1231, 1066, 1046, 964, 919, 812, 708 cm^{-1}. HRMS (ESI) m/z: $[M\text{-}Ka]^+$ Calcd for $C_{10}H_{11}BF_3$ 199.0900; Found 199.0903.

Synthesis and characterization of alkenyl bromide substrates.

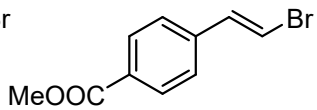
(*Z*)-(2-bromovinyl)benzene (**2e**), (*Z*)-1-bromoprop-1-ene (**2f**) and (1-bromovinyl)benzene (**2j**) are commercially available.



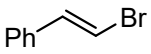
2a



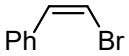
2b



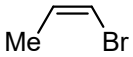
2c



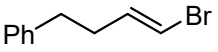
2d



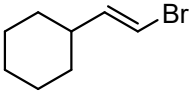
2e



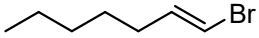
2f



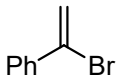
2g



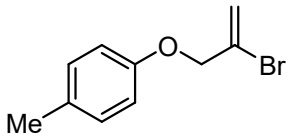
2h



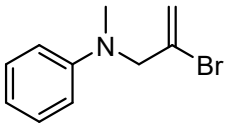
2i



2j

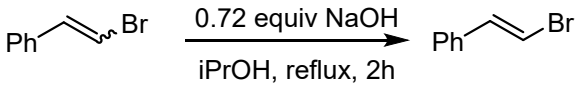


2k



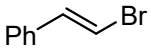
2l

For the synthesis of aryl iodides substrates 2d, see the following: [4]



S-2d **2d**

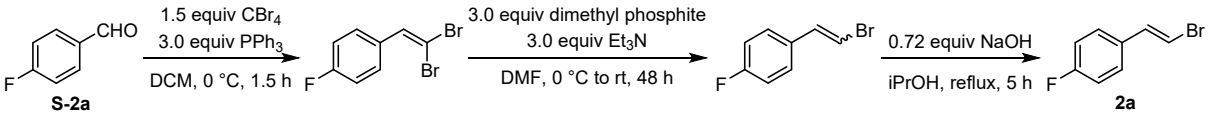
To a solution of *β*-bromostyrene (cis/trans mixtures, 10.0 mmol, 1.83 g) in ^{i}PrOH (13.3 mL) were added NaOH (7.2 mmol, 288.0 mg), the reaction was refluxed in oil bath (95 ^{o}C) for 2 h. Then the reaction mixture was cooled to room temperature and quenched by H_2O, extracted with *n*-pentane for three times, the organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to afford (*E*)-(2 bromovinyl)benzene in 81% yield (1.49 g) as a colorless liquid.



2d

(*E*)-(2-Bromovinyl)benzene (**2d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 5H), 7.08 (d, *J* = 14.0 Hz, 1H), 6.73 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.9, 128.7, 128.2, 126.1, 106.5. The spectroscopic data are in accordance with the literature.[5]

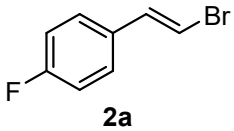
For the synthesis of aryl iodides substrates 2a and 2c, see the following: [5]



First step: To a Schlenk tube were added 4-fluorobenzaldehyde (1.07 mL, 10.0 mmol), DCM (40 mL) and CBr_4 (4.97 g, 15.0 mmol), then the reaction mixture was cooled to 0 °C and PPh_3 (30 mmol, 7.87 g, dissolved in 35 mL DCM) solution was added dropwise and stirred at 0 °C for 1 h. The resulting mixture was quenched by H_2O, extracted with *n*-pentane for three times, the organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was dissolved with *n*-pentane and filtrated through a pad of silica gel. The combined organic phase was evaporated. Then the residue was washed with *n*-pentane and filtrated through a pad of silica gel again. The combined organic phase was evaporated and purified by flash chromatography on silica gel (eluent: petroleum ether) to afford the corresponding product as a colorless oil.

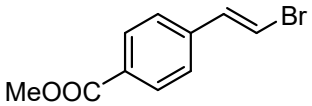
Second step: To solution of above crude product in DMF (10 mL) were added Et_3N (4.17 mL, 30.0 mmol). Then the reaction mixture was cooled to 0 °C. and dimethyl phosphite (2.75 mL, 30.0 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 48 h, then quenched with water, extracted with PE for three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4. The resulting mixture was evaporated and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford cis/trans isomers of alkenyl bromide as a colorless oil.

Third step: To a solution of above crude product in ^{i}PrOH (13.0 mL) was added NaOH (236.0 mg, 5.9 mmol) and the reaction mixture was refluxed in oil bath (110 °C) for 5 h. The resulting reaction mixture was quenched with water and extracted with *n*-pentane for three times. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford (*E*)-1-(2-bromovinyl)-4-fluorobenzene as a light yellow oil in 41% overall yield (827.0 mg).



2a

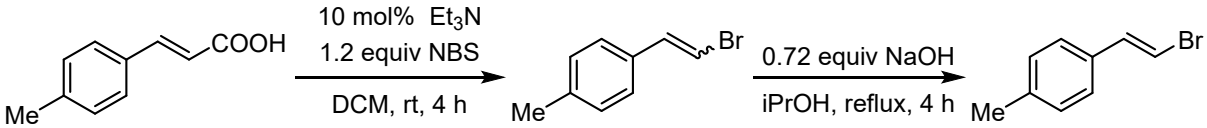
(*E*)-1-(2-Bromovinyl)-4-fluorobenzene (**2a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, J = 8.4 Hz, 5.6 Hz 2H), 7.07-6.98 (m, 3H), 6.68 (d, J = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{C\text{-}F}$ =247.4 Hz), 136.0, 132.1(d, $^4J_{C\text{-}F}$ =3.8 Hz), 127.7 (d, $^3J_{C\text{-}F}$ =7.6 Hz), 115.8 (d, $^2J_{C\text{-}F}$ =22.2 Hz), 106.1 (d, $^5J_{C\text{-}F}$ =2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.0. The spectroscopic data are in accordance with the literature.[5]



2c

Methyl (*E*)-4-(2-bromovinyl)benzoate (**2c**). 10 mmol scale, after second step, the resulting mixture was evaporated and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 300/1) to afford trans isomers of alkenyl bromide as a white solid in 51% overall yield (1.24 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 14.0 Hz, 1H), 6.92 (d, J = 14.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 140.0, 136.3, 130.1, 129.6, 125.9, 109.4, 52.1. The spectroscopic data are in accordance with the literature.[5]

For the synthesis of aryl iodides substrates 2b, see the following:[5]

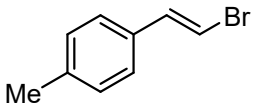


S-2b **2b**

First step: To a solution of 4-methylbenzoic acid (1.95 g, 12.0 mmol) in DCM (24 mL) was added Et_3N (167 μL, 1.2 mmol) and stirred for 5 minutes. Then NBS (2.56 g 14.4 mmol) was added. The reaction was stirred at room temperature for 4 h. The reaction mixture was evaporated and mixed solvent (PE/Et_2O = 1/1) was added. The residue was filtered through a pad of silica gel and washed with the mixed solvent (PE/Et_2O = 1/1). The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford the mixture of cis/trans isomers of alkenyl bromide.

Second step: To a solution of above crude product in ^{i}PrOH (12.0 mL) was added NaOH (345.6 mg, 8.6 mmol) and the reaction mixture was refluxed in oil bath(100 ^{o}C) for 4 h. The

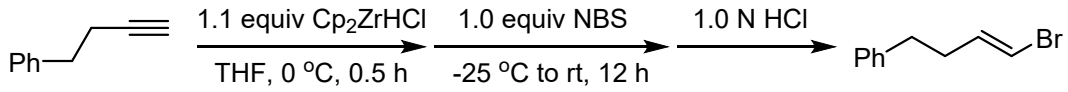
resulting reaction mixture was quenched with water and extracted with *n*-pentane for three times. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford (*E*)-1-(2-bromovinyl)-4-methylbenzene as a colorless oil in 70% overall yield (1.66 g).



2b

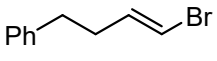
(*E*)-1-(2-Bromovinyl)-4-methylbenzene (**2b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 14.0 Hz, 1H), 6.68 (d, *J* = 14.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.0, 133.1, 129.4, 126.0, 105.4, 21.2. The spectroscopic data are in accordance with the literature.[6]

For the synthesis of aryl iodides substrates 2g, 2h and 2i, see the following:[5]



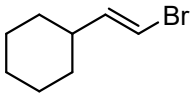
S-2g **2g**

To a solution of 4-phenyl-1-butyne (703 μL, 5.0 mmol) in THF (20 mL) at 0 °C was added Cp_2ZrHCl (1.42 g, 5.5 mmol) and stirred for 1 h. The solution was cooled to -25 °C and then NBS (889.9 mg, 5.0 mmol, dissolved in 10 mL THF) was added, the solution warmed to room temperature and stirred for 12 h. The resulting solution was quenched with 1M aqueous HCl. The organic layer was separated and the aqueous layer was extracted twice with Et_2O, the combined organic extracts were washed with saturated $NaHCO_3$ solution, saturated $Na_2S_2O_3$ solution, brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (pentane) to afford (*E*)-(4-bromobut-3-en-1-yl)benzene **2g** as a colorless oil (816 mg, 77 %,).



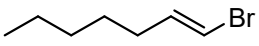
2g

(*E*)-(4-Bromobut-3-en-1-yl)benzene (2g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 -7.27 (m, 2H), 7.23-7.15 (m, 3H), 6.20 (dt, *J* = 13.6, 5.6 Hz, 1H), 6.03 (dt, *J* = 14.2, 1.2 Hz, 1H), 2.70 (t, *J* = 8.4 Hz, 2H), 2.38-2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 137.1, 128.41, 128.36, 126.1, 105.0, 35.0, 34.7. The spectroscopic data are in accordance with the literature.[7]



2h

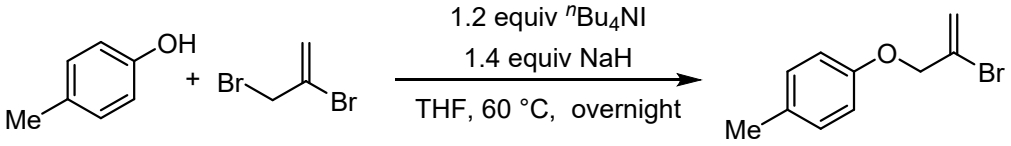
(*E*)-(2-Bromovinyl)cyclohexane (2h). 10 mmol scale, the resulting mixture was purified by flash chromatography on silica gel (eluent: pentane) to afford alkenyl bromide as a light yellow oil in 49% yield (919.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (dd, *J* = 13.6, 7.2 Hz, 1H), 5.99 (dd, *J* = 13.6, 0.8 Hz, 1H), 2.03-1.98 (m, 1H), 1.74-1.71 (m, 4H), 1.67-1.62 (m, 1H), 1.32-1.22 (m, 2H), 1.19-1.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7 ,103.1, 41.8, 32.3, 25.9, 25.7. The spectroscopic data are in accordance with the literature.[5]



2i

(*E*)-1-Bromohept-1-ene (2i). 20 mmol scale, the resulting mixture was purified by flash chromatography on silica gel (eluent: pentane) to afford alkenyl bromide as a colorless oil in 54% yield (1.93 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (dt, *J* = 13.2, 7.2 Hz, 1H), 6.01 (d, *J* = 13.2 Hz, 1H), 2.04 (q, *J* = 7.2 Hz, 2H), 1.43-1.36 (m, 2H), 1.29-1.28 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 104.0, 32.9, 31.1, 28.3, 22.4, 14.0. The spectroscopic data are in accordance with the literature.[8]

For the synthesis of aryl iodides substrates 2k, see the following:[9]

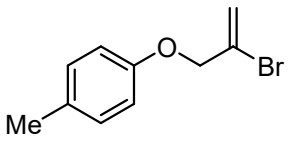


S-2k, 1.2 eq

2k

To a solution of *p*-cresol (1.30 g, 12.0 mmol) in THF (30 mL) was added ^{n}Bu$_4$NI (4.43 g,

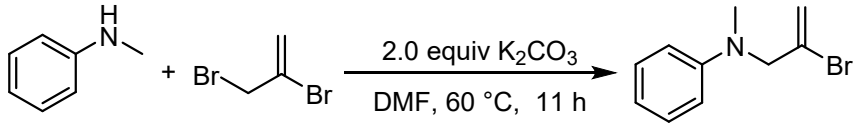
12.0 mmol), sodium hydrogen (560 mg, 14.0 mmol, 60%, dispersion in paraffin liquid) and 2,3-dibromoprop-1-ene (2.35 g, 10.0 mmol, 85+%). The mixture was stirred at 60 °C overnight. Then the reaction was cooled to room temperature and quenched by water. The mixture was filtrated with a short silica pad and washed by ethyl acetate. Then 2.0 M NaOH solution (5.0 ml) was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford the corresponding alkenyl bromide as a yellow oil in 98% yield (2.23 g).



2k

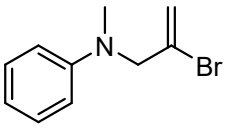
1-((2-Bromoallyl)oxy)-4-methylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.65 (d, *J* = 1.6 Hz, 1H), 4.60 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 130.8, 130.0, 127.3, 117.5, 114.8, 71.8, 20.5. The spectroscopic data are in accordance with the literature.[9]

For the synthesis of aryl iodides substrates 2l, see the following:[10]



S-2l, 3.0 eq **2l**

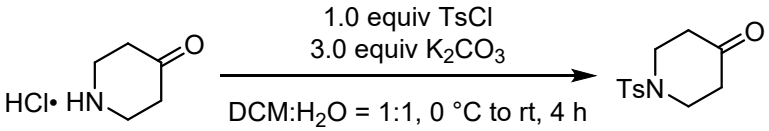
To a Schlenk tube was added K_2CO_3 (1.38 g, 10.0 mmol), DMF(10.0 mL), *N*-methylaniline (1.61 g, 15.0 mmol) and 2,3-dibromoprop-1-ene (999.4 mg, 5.0 mmol) under argon. The mixture was stirred at 80 °C for 13 h. Then the reaction was cooled to room temperature and quenched by water and extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford the corresponding alkenyl bromide as a yellow oil in 99% yield (1.13 g).



2l

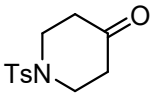
***N*-(2-Bromoallyl)-*N*-methylaniline**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 8.8 Hz, 7.2 Hz, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.64 (d, *J* = 2.0 Hz, 1H), 5.52 (d, *J* = 1.6 Hz, 2H), 4.08 (s, 2H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 129.4, 129.1, 117.1, 116.0, 111.9, 60.9, 38.3. The spectroscopic data are in accordance with the literature.[10]

Synthesis and characterization of precursor of alkenyl triflate substrates.[11]



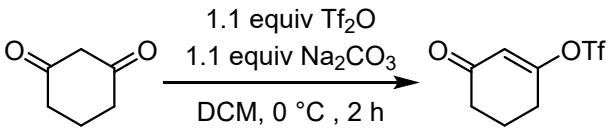
SS-4f **S-4f**

To a solution of 4-piperidone hydrochloride (2.03 g, 15.0 mmol) in DCM (4.6 mL) and H_2O (4.6 mL) was added K_2CO_3 (6.22 g, 45.0 mmol). The mixture was cooled to 0 °C and the Tosyl chloride (2.86 g, 15.0 mmol) was added dropwise. Then, the mixture was warmed to room temperature and stirred 4 h. After reaction, the mixture quenched by water. The mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 to 1/1) to afford the target product as a white solid in 89% yield (3.37 g).



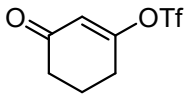
S-4f

1-Tosylpiperidin-4-one(S-4f). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 3.38 (t, *J* = 5.2 Hz, 4H), 2.53 (t, *J* = 5.2 Hz, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.4, 144.0, 133.2, 129.8, 127.4, 45.7, 40.4, 21.4. The spectroscopic data are in accordance with the literature.[12]



SS-4d **S-4d**

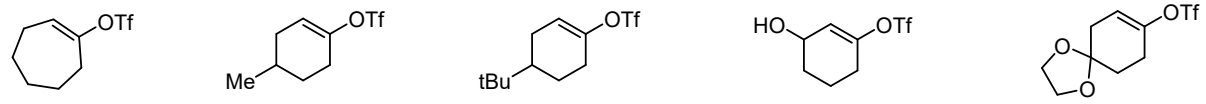
To a Schlenk tube was added cyclohexane-1,3-dione (2.24 g, 20.0 mmol), DCM (50.0 mL) and Na_2CO_3 (2.33 g, 22.0 mmol) under argon at 0 °C. The trifluoromethylsulfonic anhydride (6.21 g, 22.0 mmol) was added and the reaction was stirred for 2 h. The resulting solution was quenched with saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with DCM for three times, the combined organic extracts were washed with saturated brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 8/1) to afford the target triflate **S-4d** as colorless oil in 16% yield (793.0 mg).



S-4d

3-Oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**S-4d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06 (s, 1H), 2.70 (t, J = 6.4 Hz, 2H), 2.46 (t, J = 6.8 Hz, 2H), 2.18-2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 167.4, 119.1, 118.3(q, $^1J_{C\text{-}F}$ = 318.8 Hz), 36.2, 28.3, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.6. The spectroscopic data are in accordance with the literature.[13]

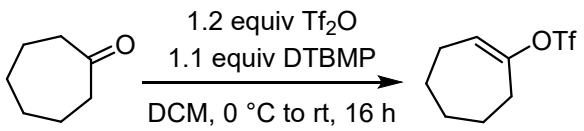
Synthesis and characterization of alkenyl triflate substrates.[11]



4a **4b** **4c** **4d** **4e**

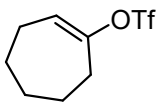
4f **4g** **4h** **4i** **4j**

For the synthesis of aryl iodides substrates **4a**, **4b**, **4c**, **4e**, **4f**, **4g**, **4h** and **4j**, see the following:[5]



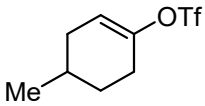
S-4a **4a**

To a Schlenk tube was added cycloheptanone (1.12 g, 10.0 mmol), DCM(30.0 mL) and 2,6-di-*tert*-butyl-4-methylpyridine (2.26 g, 11.0 mmol) under argon at 0 °C. The trifluoromethylsulfonic anhydride (3.39 g, 12.0 mmol) was added. The reaction was warmed to room temperature and stirred for 16 h. The resulting solution was added petroleum ether and filtrated with a short silica pad. The filtrate was washed with 1.0 M HCl solution and organic layer was separated. The aqueous layer was extracted with ethyl acetate for three times, the combined organic extracts were washed with saturated brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford the target triflate **4a** as colorless oil in 41% yield (1.00 g).



4a

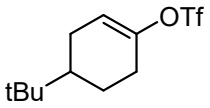
Cyclohept-1-en-1-yl trifluoromethanesulfonate (**4a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (t, *J* = 6.4 Hz, 1H), 2.53-2.51 (m, 2H), 2.16 (q, *J* = 6.0 Hz, 2H), 1.75-1.61 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 123.1, 118.5(q, $^1J_{C\text{-}F}$ = 318.0 Hz), 33.1, 29.8, 26.2, 24.71, 24.68. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.2. The spectroscopic data are in accordance with the literature.[11]



4b

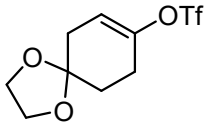
4-Methylcyclohex-1-en-1-yl trifluoromethanesulfonate (**4b**). 5 mmol scale, 2-chloropyridine (624.5 mg, 5.5 mmol) was used as base, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1) to afford the target triflate **4b** as colorless oil in 29% yield(352.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (d, *J* = 2.0 Hz, 1H), 2.38-2.22

(m, 3H), 1.84-1.74 (m, 3H), 1.48-1.39(m, 1H), 0.99 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 118.5(q, $^1J_{C\text{-}F}$ = 318.0 Hz), 117.8, 31.9, 30.5, 27.24, 27.17, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.2. The spectroscopic data are in accordance with the literature.[14]



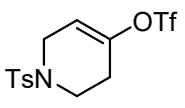
4c

4-(*tert*-Butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (**4c**). 10 mmol scale, the residue was purified by column chromatography on silica gel (petroleum ether) to afford the target triflate **4c** as colorless oil in 70% yield (2.00 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (t, J = 6.8 Hz, 1H), 2.43-2.29 (m, 2H), 2.23-2.18 (m, 1H), 1.99-1.93 (m, 2H), 1.42-1.29 (m, 2H), 0.90 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 118.5(q, $^1J_{C\text{-}F}$ = 318.9 Hz), 118.4, 42.9, 32.0, 28.5, 27.1, 25.3, 24.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.1. The spectroscopic data are in accordance with the literature.[11]



4e

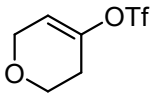
1,4-Dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (**4e**). 10 mmol scale, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1) to afford the target triflate **4e** as colorless oil in 44% yield (1.27 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67(s, 1H), 3.99 (s, 4H), 2.54 (s, 2H), 2.41 (s, 2H), 1.90 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 118.4(q, $^1J_{C\text{-}F}$ = 318.8 Hz), 115.8, 106.0, 64.6, 34.0, 30.9, 26.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.1. The spectroscopic data are in accordance with the literature.[11]



4f

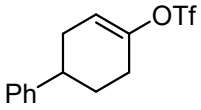
1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (**4f**). 10 mmol scale，the

reaction was stirred at 70 °C for 11.5 h, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1 to 5/1) to afford the target triflate **4b** as white solid in 87% yield (3.34 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H), 3.78 (d, *J* = 2.8 Hz, 2H), 3.35 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 1.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.2, 132.9, 129.8, 127.3, 118.2(q, $^{1}J_{C\text{-}F}$ = 318.8 Hz), 114.4, 43.3, 42.5, 27.7, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.7. The spectroscopic data are in accordance with the literature.[11]



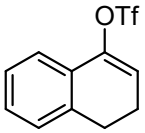
4g

3,6-Dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (**4g**). 10 mmol scale, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the target triflate **4g** as yellow oil in 33% yield (776.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83-5.82 (m, 1H), 4.26 (q, *J* = 3.2 Hz, 2H), 3.89 (t, *J* = 2.8 Hz, 2H), 2.48-2.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 118.5(q, $^{1}J_{C\text{-}F}$ = 318.8 Hz), 116.9, 64.1, 63.9, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.0. The spectroscopic data are in accordance with the literature.[11]



4h

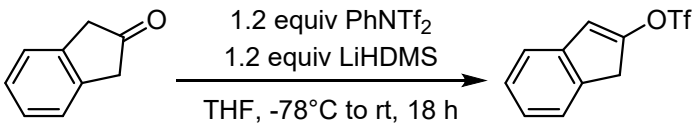
1,2,3,6-Tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (**4h**). 5 mmol scale, 2-chloropyridine (624.5 mg, 5.5 mmol) was used as base, the residue was purified by column chromatography on silica gel (petroleum ether) to afford the target triflate **4h** as yellow oil in 65% yield (1.00 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.23-7.17 (m, 3H), 5.83 (t, *J* = 2.8 Hz, 1H), 2.86-2.78 (m, 1H), 2.56-2.26 (m, 4H), 2.06-2.02 (m, 1H), 1.98-1.89(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 144.5, 128.6, 126.7, 126.6, 118.5(q, $^{1}J_{C\text{-}F}$ = 318.3 Hz), 118.1, 38.7, 31.5, 29.6, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.0. The spectroscopic data are in accordance with the literature.[5]



4j

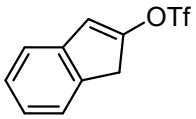
3,4-Dihydronaphthalen-1-yl trifluoromethanesulfonate (**4j**). 5 mmol scale, 2-chloropyridine (624.5 mg, 5.5 mmol) was used as base, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1 to 50/1) to afford the target triflate **4b** as yellow oil in 76% yield(1.06 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 5.2 Hz, 1H), 7.27-7.24 (m, 2H), 7.16 (t, *J* = 4.4 Hz, 1H), 6.00 (t, *J* = 5.2 Hz, 1H), 2.85 (q, *J* = 8.0 Hz, 2H), 2.51-2.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 136.2, 129.2, 128.7, 127.7, 126.9, 121.2, 118.6 (q, $^{1}J_{C\text{-}F}$ = 318.4 Hz), 117.7, 266.8, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.8. The spectroscopic data are in accordance with the literature.[5]

For the synthesis of aryl iodides substrates 4i, see the following:[11]



S-4i **4i**

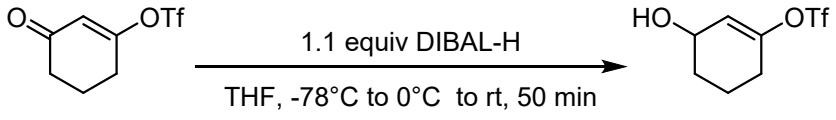
To a Schlenk tube was added 1,3-dihydro-2*H*-inden-2-one (1.32 g, 10.0 mmol) and THF(30.0 mL) under argon. The reaction was cooled to -78 ℃ and the LiHMDS (1.0 M in hexane, 12.0 mL, 12.0 mmol) was added was added dropwise. The reaction was stirred at -78 ^{o}C for 1 h and the *N*-phenyl-bis(trifluoromethanesulfonimide) (4.29 g in 10 mL THF, 12.0 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 17 h. The resulting solution was quenched with water and washed by saturated NH_4Cl solution. The aqueous layer was extracted with ethyl acetate for three times, the combined organic extracts were washed with saturated brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford the target triflate **4i** as colorless oil in 79% yield (2.10 g).



4i

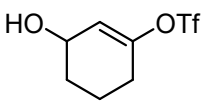
1*H*-Inden-2-yl trifluoromethanesulfonate (**4i**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 6.8 Hz, 6.0 Hz, 2H), 7.30-7.19 (m, 2H), 6.66 (s, 1H), 3.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 1401.1, 137.3, 127.2, 126.1, 123.7, 122.1, 119.5, 118.7(q, $^{1}J_{C\text{-}F}$ = 319.6 Hz), 37.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.9. The spectroscopic data are in accordance with the literature.[11]

For the synthesis of aryl iodides substrates 4d, see the following:[11]



S-4d **4d**

To a Schlenk tube was added **S-4d** (708 mg, 2.9 mmol) and THF(8.7 mL) under argon. The reaction was cooled to -78 °C and the DIBAL-H (1.0 M in hexane, 3.2 mL, 3.2 mmol) was added was added dropwise. The reaction was stirred at -78 °C for 10 min and warmed to 0 °C. After 10 min, the mixture was warmed to room temperature and stirred for 30 min. The resulting solution was quenched with saturated NH_4Cl solution at -78 °C and added potassium sodium tartrate solution. The mixture was stirred overnight. The aqueous layer was extracted with ethyl acetate for three times, the combined organic extracts were washed with saturated brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 5/1) to afford the target triflate **4d** as colorless oil in 82% yield (584.0 mg).



4d

3-Hydroxycyclohex-1-en-1-yl trifluoromethanesulfonate (**4d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (t, J = 2.0 Hz, 1H), 4.41 (d, J = 2.8 Hz, 1H), 2.90 (s, 1 H), 2.40-2.25 (m, 2H), 1.98-1.82

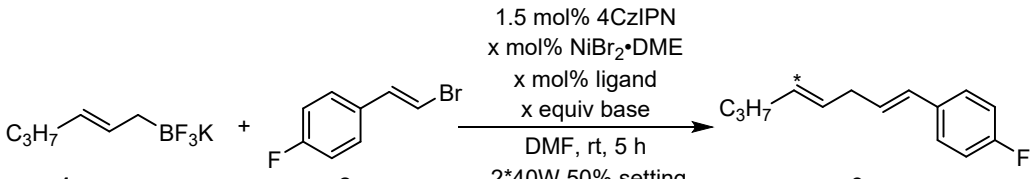
(m, 2H), 1.79-1.70 (m, 1H), 1.64-1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 120.5, 118.4 (q, $^1J_{C\text{-}F}$ = 318.0 Hz), 65.0, 30.3, 27.5, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.3. The spectroscopic data are in accordance with the literature.[11]

Optimization studies for the formation of 3a.

General procedure for optimization studies:

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (2.4 mg, 1.5 mol%, 0.003 mmol), $NiBr_2$·DME (6.2 mg, 10 mol%, 0.02 mmol), ligand (15 mol%, 0.03 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (57.0 mg, 1.5 equiv, 0.3 mmol), base (1.0 equiv, 0.2 mmol), DMF (2 mL) and (*E*)-1-(2-bromovinyl)-4-fluorobenzene (40.2 mg, 1.0 equiv, 0.2 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction was stirred at room temperature for 5 h under the irradiation of two 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2), the mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The mixture was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford the crude product as a colorless oil. The yields were determined by ^{1}H NMR using mesitylene (24.0 mg, 0.2 mmol) as the internal standard.

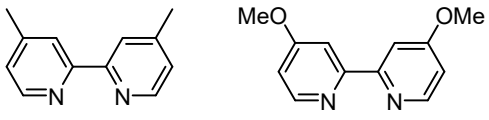
Table S1. Optimization Studies.



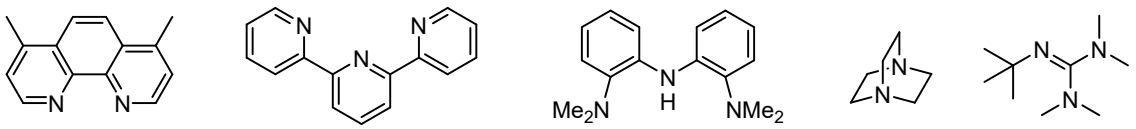
1a **2a** **3a**

entry	allyl BF_3K (equiv)	ligand (mol%)	base (equiv)	yield(%) of **3a**[a]
1	1.2	dtbbpy (10)	DABCO (1.0)	81% (*E*:*Z* = ca. 7:1)
2	1.2	dtbbpy (10)	BTMG (1.0)	66% (*E*:*Z* = ca 23:1)
3[b]	1.5	dtbbpy (10)	BTMG (1.0)	70% (*E*:*Z* = ca 42:1)
5	1.5	dtbbpy (10)	BTMG (0.5) DABCO (0.5)	74% (*E*:*Z* = ca 20:1)
7	1.5	dtbbpy (10)	BTMG (0.2) DABCO (1.0)	91% (*E*:*Z* = ca 15.4:1)
8	1.5	dtbbpy (10)	BTMG (0.5) DABCO (0.7)	84% (*E*:*Z* = ca 15.7:1)
9	1.5	dtbbpy (10)	BTMG (0.7) DABCO (0.5)	74% (*E*:*Z* = ca 20:1)
10	1.5	dtbbpy (10)	BTMG (1.0) DABCO (0.2)	69% (*E*:*Z* = ca 24:1)
11	1.5	dtbbpy (10)	BTMG (0.5) DABCO (1.0)	72% (*E*:*Z* = ca 18:1)
12	1.5	-	BTMG (0.5) DABCO (1.0)	67% (*E*+*Z*: *b* = 5.7:1)
13	1.5	**L1** (10)	BTMG (0.5) DABCO (0.5)	61% (*E*:*Z* = ca. 26:1)
14	1.5	**L2** (10)	BTMG (0.5) DABCO (0.5)	70% (*E*:*Z* = ca. 28:1)
15	1.5	**L3** (10)	BTMG (0.5) DABCO (0.5)	53% (*E*:*Z*:*b* = ca. 26 :1:2.5)
16	1.5	**L4** (10)	BTMG (0.5) DABCO (0.5)	43% (*E*:*Z*:*b* = ca. 24 :2.1:1)
17	1.5	**L5** (10)	BTMG (0.5) DABCO (0.5)	67% (*E*:*Z* = ca. 22:1)
18	1.5	**L6** (10)	BTMG (0.5) DABCO (0.5)	81% (*E*:*Z*:*b* = ca. 20 :2.3:1)
19	1.5	**L7** (10)	BTMG (0.5) DABCO (0.5)	66% (*E*:*Z*:*b* = ca. 13:1.4:1)
20	1.5	**L2** (10)	BTMG (0.2) DABCO (1.0)	81% (*E*:*Z* = ca. 16:1)
21	1.5	**L2** (10)	DABCO (1.0)	69% (*E*:*Z* = ca. 11:1)
22	**1.5**	**L2 (15)**	BTMG (0.2) DABCO (1.0)	**85% (*E*:*Z* = ca. 19:1)**
23	1.5	**L2** (20)	BTMG (0.2) DABCO (1.0)	85% (*E*:*Z* = ca. 17:1)
24[c]	1.5	**L2** (18)	BTMG (0.2) DABCO (1.0)	85% (*E*:*Z* = ca. 17:1)

[a]0.2 mmol scale. NMR yields using mesitylene as an internal standard.[b]NMR yields using 1,3,5-trifluorobenzene as an internal standard. [c]12 mol% $NiBr_2$•DME was used.

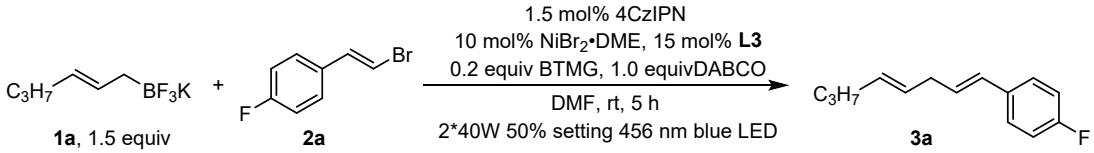


L1 **L2** **L3** **L4**



L5 **L6** **L7** DABCO BTMG

Table S2. Control experiments.

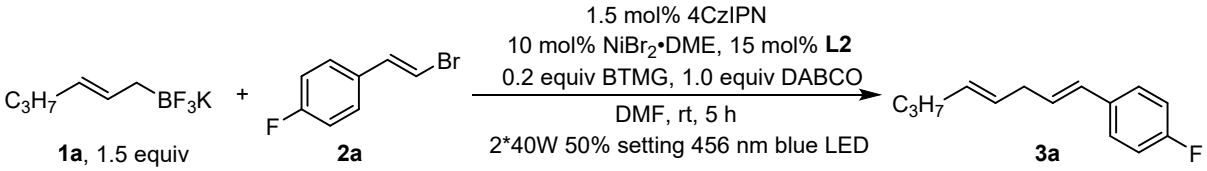


entry	photoredox-catalyst (mol%)	metal-catalyst (mol%)	ligand (mol%)	base (equiv)	yield(%) of **3a**[a]
1	4CzIPN (1.5)	$NiBr_2$•DME (10)	**L2** (15)	BTMG (0.2) DABCO (1.0)	85% (*E*:*Z* = ca. 19:1)
2	-	$NiBr_2$•DME (10)	**L2** (15)	BTMG (0.2) DABCO (1.0)	-
3	4CzIPN (1.5)	-	**L2** (15)	BTMG (0.2) DABCO (1.0)	-
4	4CzIPN (1.5)	$NiBr_2$•DME (10)	-	DABCO (1.0)	73% (*E*:*Z*:*b* = ca. 15:1.6:1)
5	4CzIPN (1.5)	$NiBr_2$•DME (10)	**L2** (15)	DABCO (1.0)	76% (*E*:*Z* = ca. 9:1)
6	4CzIPN (1.5)	$NiBr_2$•DME (10)	**L2** (15)	BTMG (0.2)	77% (*E*:*Z* = ca. 12:1)
7	4CzIPN (1.5)	$NiBr_2$•DME (10)	**L2** (15)	-	49% (*E*:*Z* = ca. 7:1)
8[b]	4CzIPN (1.5)	$NiBr_2$•DME (10)	**L2** (15)	BTMG (0.2) DABCO (1.0)	-

[a]0.2 mmol scale. NMR yields using mesitylene as an internal standard. [b]Out of blue LED.

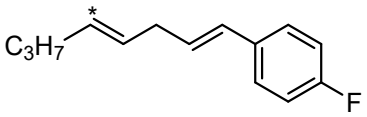
Synthesis and characterization of products 3 and 5.

Typical procedure for the synthesis of 3a (Condition A).



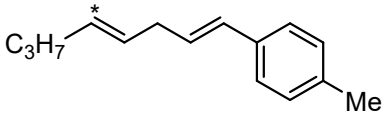
The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-1-(2-bromovinyl)-4-fluorobenzene (60.3 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction was stirred at room temperature under the irradiation of two 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2) for 5 h, the mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then

water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to afford the target product **3a** in 85% yield (52.3 mg) as a colorless oil (*E*:*Z* = ca. 19.6:1).



3a (*E*:*Z* = ca.19.6:1)

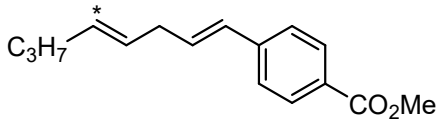
1-Fluoro-4-((1*E*,4*E*)-octa-1,4-dien-1-yl)benzene (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.00-6.94 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.12 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 5.54-5.43 (m, 2H), 2.88 (t, *J* = 5.6 Hz, 2H), 2.03-1.98 (m, 2H), 1.44-1.35 (m, 2H), 0.90(t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9 (d, $^1J_{C\text{-}F}$ = 244.2 Hz), 133.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 131.9. 129.1 (d, $^5J_{C\text{-}F}$ = 2.1 Hz), 129.0, 127.6, 127.4 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 115.3 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 35.9, 34.7, 22.6, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7. IR (neat): 3040, 2959, 2928, 2870, 1722, 1686, 1600, 1508, 1226, 1158, 969, 834 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{17}F$ 204.1309; Found 204.1309.



3b (*E*:*Z* = ca.18:1)

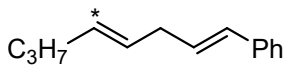
1-Methyl-4-((1*E*,4*E*)-octa-1,4-dien-1-yl)benzene (**3b**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol) , 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-1-(2-bromovinyl)-4-methylbenzene (59.1 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 84% yield (50.2 mg) as a colorless oil (*E*:*Z* = ca. 18:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* =7.6 Hz, 2H), 7.08 (d,

J = 8.0 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.15 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.50-5.47 (m, 2H), 2.87 (d, *J* = 5.6 Hz, 2H), 2.31 (s, 3H), 2.02-1.97 (m, 2H), 1.42-1.36 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 135.0, 131.6. 130.0, 129.1, 128.3, 127.9, 125.9, 35.9, 34.7, 22.6, 21.1, 13.7. IR (neat): 3027, 2959, 2929, 2870, 1726, 1704, 1686, 1605, 1514, 1456, 1287, 969, 809 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{20}$ 200.1560; Found 200.1555.



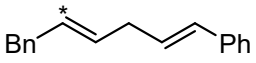
3c (*E*:*Z* = ca.16:1)

Methyl 4-((1*E*,4*E*)-octa-1,4-dien-1-yl)benzoate (**3c**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol) , $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), methyl (*E*)-4-(2-bromovinyl)benzoate (72.3 mg, 1.0 equiv, 0.3 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol) , DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the target product in 85% yield (62.2 mg) as a colorless oil (*E*:*Z* = ca. 16:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.0 Hz, 5.6 Hz, 1H), 5.51-5.47 (m, 2H), 3.89 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 2.01 (q, *J* = 6.8 Hz, 2H), 1.43-1.37 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 142.3, 132.34, 132.27, 129.8, 129.4, 128.3, 127.1, 125.8, 51.9, 36.0, 34.7, 22.5, 13.7. IR (neat): 3027, 2954, 2868, 1718, 1606, 1435, 1274, 1177, 1108, 967, 761 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{20}O_2$ 244.1458; Found 244.1461.



3d (*E*:*Z* = ca. 18:1)

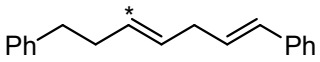
((1*E*,4*E*)-Octa-1,4-dien-1-yl)benzene (**3d**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) followed by preparative TLC on silica gel (eluent: petroleum ether) to afford the target product in 89% yield (50.0 mg) as a colorless oil (*E*:*Z* = ca. 18:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.19 (q, *J* = 7.2 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.54-5.44 (m, 2H), 2.89 (t, *J* = 5.2 Hz, 2H), 2.03-1.98 (m, 2H), 1.44-1.35 (m, 2H), 0.90 (t, *J* = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 131.8, 130.1, 129.3, 128.4, 127.7, 126.9, 126.0, 35.9, 34.7, 22.6, 13.7. The spectroscopic data are in accordance with the literature.[15]



3e (*E*:*Z* > 20:1)

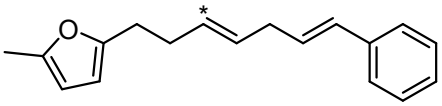
((1*E*,4*E*)-Hexa-1,4-diene-1,6-diyl)dibenzene (**3e**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(4-phenylbut-2-en-1-yl)-borate (107.1 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol), 6 h. Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 87% yield (60.9 mg) as a colorless oil (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 4H), 7.19-7.15 (m, 4H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.70-5.63 (m, 1H), 5.60-5.53 (m, 1H), 3.44 (d, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.6, 130.5. 130.4, 129.2, 128.8, 128.5, 128.44, 128.35, 126.9, 126.0, 125.9, 39.0, 35.8. IR (neat): 3063, 3027, 2912, 1699, 1601, 1494, 1453, 1072, 1029, 967, 746, 695 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{18}$ 234.1403; Found

234.1405.



3f (*E*:*Z* > 20:1)

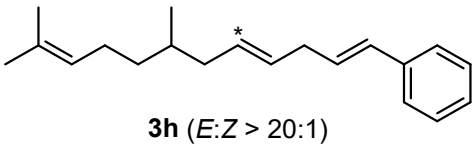
((1*E*,4*E*)-Hepta-1,4-diene-1,7-diyl)dibenzene (**3f**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(5-phenylpent-2-en-1-yl)borate (113.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: pentane) to afford the target product in 87% yield (64.6 mg) as a colorless oil (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.2 Hz, 2H), 7.29-7.24 (m, 4H), 7.19-7.16 (m, 4H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.58-5.46 (m, 2H), 2.87 (d, *J* = 5.6 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.36-2.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 137.7, 130.9, 130.2, 129.0, 128.43, 128.42, 128.3, 128.2, 126.9, 126.0, 125.7, 35.9, 35.8, 34.4. The spectroscopic data are in accordance with the literature.[16]



3g

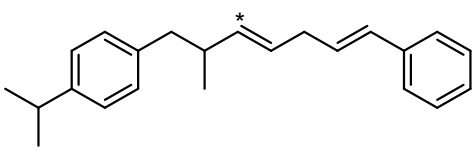
2-Methyl-5-((3*E*,6*E*)-7-phenylhepta-3,6-dien-1-yl)furan (**3g**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(5-(5-methylfuran-2-yl)pent-2-en-1-yl)borate (115.3 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford the target product in 83% yield (62.6 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H),

7.18 (t, *J* = 6.8 Hz, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.84 (d, *J* = 6.0 Hz, 2H), 5.54-5.50 (m, 2H), 2.93-2.89 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.2, 137.7, 130.6, 130.3, 129.0, 128.5, 128.4, 126.9, 126.0, 105.8, 105.4, 35.8, 31.1, 28.1, 13.5. IR (neat): 3024, 2923, 2849, 1569, 1448, 1218, 1021, 963, 933, 779, 741, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{20}O$ 252.1509; Found 252.1504.



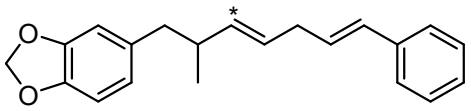
3h (*E*:*Z* > 20:1)

((1*E*,4*E*)-7,11-Dimethyldodeca-1,4,10-trien-1-yl)benzene (**3h**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-(5,9-dimethyldeca-2,8-dien-1-yl)trifluoroborate (122.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: pentane) to afford the target product in 84% yield (67.6 mg) as a colorless oil (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.21-7.16(m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.21 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.50-5.46 (m, 2H), 5.10 (t, *J* = 7.8 Hz, 1H), 2.90 (d, *J* = 4.8 Hz, 2H), 2.08-1.94 (m, 3H), 1.92-1.84 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.52-1.44 (m, 1H), 1.40-1.31 (m, 1H), 1.19-1.10 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 131.0, 130.4, 130.2, 129.3, 128.8, 128.4, 126.9, 126.0, 124.9, 40.0, 36.6, 36.0, 32.7, 25.7, 25.6, 19.4, 17.6. IR (neat): 3025, 2961, 2911, 1597, 1495, 1448, 1376, 963, 741, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{28}$ 268.2186; Found 268.2189.



3i (*E*:*Z* = ca. 13:1)

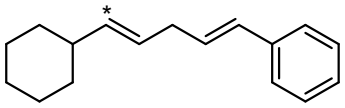
1-Isopropyl-4-((3*E*,6*E*)-2-methyl-7-phenylhepta-3,6-dien-1-yl)benzene (**3i**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol) , 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(5-(4-isopropylphenyl)-4-methylpent-2-en-1-yl)borate (138.7 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 87% yield (79.2 mg) as a colorless oil (*E*:*Z* = ca. 13:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.25 (m, 4H), 7.19-7.16(m, 1H), 7.13-7.05(m, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.16 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.51-5.34 (m, 2H), 2.87-2.82 (m, 3H), 2.67-2.62 (m, 1H), 2.50-2.38 (m, 2H), 1.22 (d, *J* = 6.8 Hz, 6H), 0.98 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 138.1, 137.7, 137.2, 130.1, 129.3, 129.2, 128.4, 126.9, 126.1, 126.03, 125.99, 43.2, 38.4, 35.9, 33.6, 24.04, 24.03, 19.9. IR (neat): 3022, 2959, 2925, 2870, 1704, 1513, 1456, 967, 838, 807, 746, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{28}$ 304.2186; Found 304.2186.



3j (*E*:*Z* = ca. 19:1)

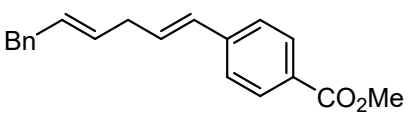
5-((3*E*,6*E*)-2-Methyl-7-phenylhepta-3,6-dien-1-yl)benzo[*d*][1,3]dioxole (**3j**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-(5-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)trifluoroborate (139.6 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol), 6 h. Purification by preparative TLC on silica gel (eluent: petroleum ether) to afford the target product in 81% yield (74.9 mg) as a colorless oil (*E*:*Z* = ca. 19:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dt, *J* = 15.2 Hz, 6.8 Hz, 4H), 7.21-7.16 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 0.8 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.15 (dt,

J = 16.0 Hz, 6.4 Hz, 1H), 5.86-5.85 (m, 2H), 5.46-5.34 (m, 2H), 2.86 (t, J = 6.0 Hz, 2H), 2.59-2.54 (m, 1H), 2.47-2.33 (m, 2H), 0.98 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 145.5, 137.7, 136.9, 134.7, 130.1, 129.2, 128.4, 126.9, 126.3, 126.0, 122.0, 109.6, 107.8, 100.6, 43.3, 38.6, 35.8, 19.9. IR (neat): 3022, 2959, 2886, 1594, 1501, 1488, 1440, 1244, 1038, 966, 804, 744, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{22}O_2$ 306.1614; Found 306.1620.



3k (*E*:*Z* = ca. 18:1)

((1*E*,4*E*)-5-Cyclohexylpenta-1,4-dien-1-yl)benzene (**3k**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-(3-cyclohexylallyl)trifluoroborate (103.6 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 84% yield (57.3 mg) as a colorless oil (*E*:*Z* = ca. 18:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 6.8 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.19 (q, J = 6.8 Hz, 1H), 6.37 (d, J = 15.6 Hz, 1H), 6.21 (dt, J = 15.6 Hz, 6.8 Hz, 1H), 5.49-5.43 (m, 2H), 2.87 (d, J = 7.2 Hz, 2H), 1.94 (brs, 1H), 1.71 (d, J = 10.8 Hz, 4H), 1.66-1.62 (m, 1H), 1.31-1.19 (m, 1H), 1.16-1.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.8, 130.1, 129.5, 128.4, 126.9. 126.0, 125.0, 40.7, 36.0, 33.1, 26.2, 26.1. The spectroscopic data are in accordance with the literature.[15]

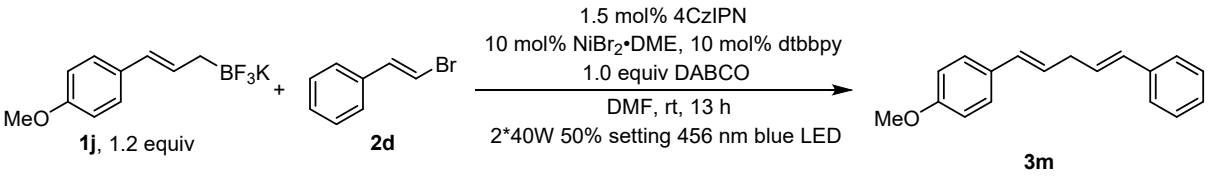


3l

Methyl 4-((1*E*,4*E*)-6-phenylhexa-1,4-dien-1-yl)benzoate (**3l**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-

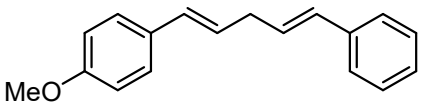
dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), methyl (*E*)-4-(2-bromovinyl)benzoate (72.3 mg, 1.0 equiv, 0.3 mmol), potassium (*E*)-trifluoro(4-phenylbut-2-en-1-yl)-borate (107.1 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford the target product in 74% yield (64.8 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.22-7.18 (m, 3H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.69 (dt, *J* = 15.2 Hz, 6.8Hz, 1H), 5.56 (dt, *J* = 15.2 Hz, 6.4 Hz, 1H), 3.88 (s, 2H), 3.37 (d, *J* = 6.4 Hz, 2H), 2.95 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 142.1, 140.5, 131.8, 130.8, 129.8, 129.7, 128.6, 128.5, 128.38, 128.36, 126.0. 125.8, 51.9, 39.0, 35.8. IR (neat): 3030, 2951, 2894, 1711, 1603, 1439, 1275, 1252, 1178, 1109, 968, 747, 738, 698 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{20}O_2$ 292.1458; Found 292.1451.

Typical procedure for the synthesis of 3m (Condition B).



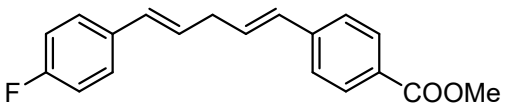
The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol) , potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and (*E*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction was stirred at room temperature under the irradiation of two 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2) for 13 h, the mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic

layers were washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 500/1 to 200/1) to afford the target product **3m** 84% yield (63.4 mg) as a white solid.



3m

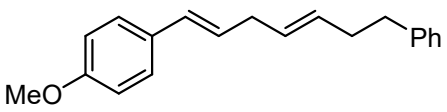
1-Methoxy-4-((1*E*,4*E*)-5-phenylpenta-1,4-dien-1-yl)benzene (**3m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30-7.26 (m, 4H), 7.21-7.17 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.46-6.38 (m, 2H), 6.27 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 6.13 (dt, *J* = 16.0 Hz, 6.8 Hz, 1H), 3.77 (s, 3H), 3.08 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 137.6, 130.8, 130.3, 128.5, 127.1, 127.0, 126.0, 125.9, 113.9, 55.2, 36.1. The spectroscopic data are in accordance with the literature.[16]



3n

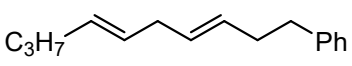
Methyl 4-((1*E*,4*E*)-5-(4-fluorophenyl)penta-1,4-dien-1-yl)benzoate (**3n**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), methyl (*E*)-4-(2-bromovinyl)benzoate (72.3 mg, 1.0 equiv, 0.3 mmol), potassium (*E*)-trifluoro(3-(4-fluorophenyl)allyl)borate (87.1 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol) and DMF (3 mL), 5 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1 to 50/1) to afford the target product in 79% yield (70.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 8.0 Hz, 4.8 Hz, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.49-6.35 (m, 1H), 6.16 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 3.88 (s, 3H), 3.11 (t, *J* =6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 162.0 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 141.9, 133.5 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 131.0, 130.21, 130.18, 129.9, 128.5, 127.5 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 127.2 (d, $^5J_{C\text{-}F}$ = 2.1 Hz), 125.9, 115.3(d, $^2J_{C\text{-}F}$ = 21.5 Hz), 51.9, 36.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.0.

IR (neat): 3014, 2962, 2865, 2808, 1718, 1604, 1507, 1435, 1273, 1231, 1178, 1113, 976, 965, 854, 741 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{17}FO_2$ 296.1207; Found 296.1204.



3o

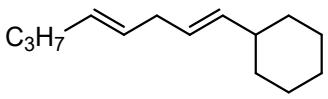
1-Methoxy-4-((1*E*,4*E*)-7-phenylhepta-1,4-dien-1-yl)benzene (**3o**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and (*E*)-(4-bromobut-3-en-1-yl)benzene (63.3 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) to afford the target product in 53% yield (44.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7. 25 (m, 4H), 7.25 (d, *J* =6.8 Hz, 3H), 6.83 (d, *J* =8.8 Hz, 2H), 6.29 (d, *J* =16.0 Hz, 1H), 6.04 (dt, *J* =16.0 Hz, 6.8 Hz, 1H), 5.54-5.50 (m, 2H), 3.78 (s, 3H), 2.86 (d, *J* =2.8 Hz, 2H), 2.69 (t, *J* =8.0 Hz, 2H), 2.34 (q, *J* =6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 142.0, 130.7, 130.5, 129.6, 128.6, 128.4, 128.2, 127.1, 126.9, 125.7, 113.9, 55.2, 35.9, 35.8, 34.4. IR (neat): 3022, 2929, 2836, 1718, 1604, 1511, 1454, 1247, 1174, 1030, 830, 747, 699 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{22}O$ 278.1665; Found 278.1663.



3p

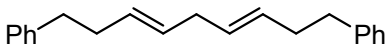
((3*E*,6*E*)-Deca-3,6-dien-1-yl)benzene (**3p**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(4-bromobut-3-en-1-yl)benzene (63.3 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 95% yield (61.0 mg) as a

colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* =7.6 Hz, 2H), 7.17 (d, *J* = 6.0 Hz, 3H), 5.45 (d, *J* = 3.2 Hz, 2H), 5.28 (s, 2H), 2.67-2.65 (m, 4H), 2.33-2.30 (m, 2H), 1.96 (s, 2H), 1.39-1.32 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 130.9, 129.9, 129.4, 128.5, 128.4, 128.2, 125.7, 36.0, 35.6, 34.7, 34.4, 22.6, 13.7. IR (neat): 3027, 2954, 2923, 1723, 1634, 1520, 1264, 1073, 966, 833, 815, 798, 750, 698 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{22}$ 214.1716; Found 214.1718.



3q

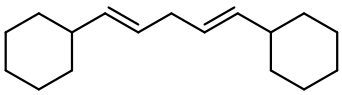
((1*E*,4*E*)-Octa-1,4-dien-1-yl)cyclohexane (**3q**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)cyclohexane (56.7 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 79% yield (45.4 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41-5.35 (m, 4H), 2.66 (s, 2H), 1.99-1.88 (m, 3H), 1.71-1.62 (m, 5H), 1.40-1.30 (m, 2H), 1.27-1.00 (m, 5H), 0.89 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 130.7, 128.9, 126.0, 40.7, 35.7, 34.7, 33.2, 26.2, 26.1, 22.7, 13.7. IR (neat): 3024, 2957, 2922, 2851, 1446, 966 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{24}$ 192.1873; Found 192.1876.



3r

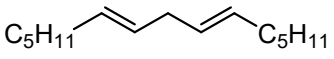
(3*E*,6*E*)-1,9-Diphenylnona-3,6-diene (**3r**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(5-phenylpent-2-en-1-yl)borate (113.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(4-

bromobut-3-en-1-yl)benzene (63.3 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether to petroleum ether/ethyl acetate = 120/1) to afford the target product in 94% yield (77.7 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* =7.6 Hz, 4H), 7.17-7.15 (m, 6H), 5.43-5.40 (m, 4H), 2.67-2.63 (m, 6H), 2.32-2.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 130.0, 129.1, 128.4, 128.2, 125.7, 35.9, 35.5, 34.4. IR (neat): 3064, 3026, 2924, 2853, 1600, 1495, 1453, 968, 744, 696 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{24}$ 276.1873; Found 276.1879.



3s

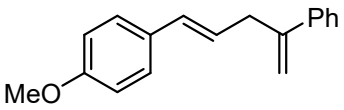
(1*E*,4*E*)-1,5-Dicyclohexylpenta-1,4-diene (**3s**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-(3-cyclohexylallyl)trifluoro-l4-borate (103.6 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-(2-bromovinyl)cyclohexane (56.7 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 86% yield (60.2 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36-5.34 (m, 4H), 2.65 (d, *J* = 4.0 Hz, 2H), 1.92-1.87 (m, 2H), 1.71-1.61 (m, 10H), 1.30-1.00 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 126.2, 40.7, 35.7, 33.2, 26.2, 26.1. IR (neat): 3016, 2920, 2849, 1448, 966, 891 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{28}$ 232.2186; Found 232.2188.



3t

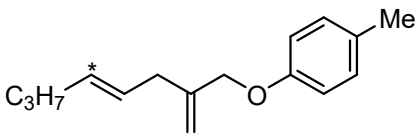
(6*E*,9*E*)-Pentadeca-6,9-diene (**3t**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(oct-2-en-1-yl)borate (98.1, 1.5 equiv, 0.45

mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*E*)-1-bromohept-1-ene (53.1 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 84% yield (52.8 mg) as a colorless oil. Containing trace stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42-5.36 (m, 4H), 2.67 (s, 2H), 1.98 (q, *J* = 5.6 Hz, 4H), 1.39-1.29 (m, 12H), 0.88 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1, 128.6, 35.7, 32.6, 31.4, 29.3, 22.6, 14.1. The spectroscopic data are in accordance with the literature.[17]



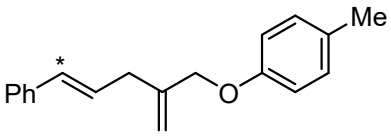
3u

(*E*)-1-Methoxy-4-(4-phenylpenta-1,4-dien-1-yl)benzene (**3u**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and (1-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1 to 50/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 20/1/1) to afford the target product in 21% yield (16.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 3H), 6.82 (dt, *J* = 8.8, 2.8 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.15 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 5.41 (s, 3H), 5.14 (, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 3.37 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 146.7, 141.0, 131.0, 130.4, 128.3, 127.5, 127.2, 126.0, 125.8, 113.9, 113.2, 55.3, 38.6. The spectroscopic data are in accordance with the literature.[18]



3v (*E*:*Z* = ca.15:1)

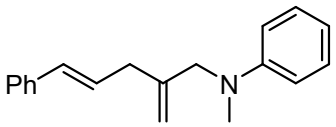
(*E*)-1-Methyl-4-((2-methyleneoct-4-en-1-yl)oxy)benzene (**3v**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), 1-((2-bromoallyl)oxy)-4-methylbenzene (68.1 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol), 8 h. Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 90% yield (62.3 mg) as a colorless oil (*E*:*Z* = ca. 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 5.54-5.40 (m, 2H), 5.13 (s, 1H), 4.99 (s, 1H), 4.41 (s, 2H), 2.82 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 3H), 1.99 (q, *J* = 6.8 Hz, 2H), 1.42-1.33 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 144.2, 132.9, 129.9, 129.8, 126.8, 114.6, 112.2, 70.5, 36.5, 34.6, 22.5, 20.4, 13.6. IR (neat): 3027, 2957, 2925, 2867, 1614, 1510, 1239, 1174. 1019, 969, 902, 817, 804 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{22}O$ 230.1665; Found 230.1665.



3w (*E*:*Z* = 17:1)

(*E*)-1-Methyl-4-((2-methylene-5-phenylpent-4-en-1-yl)oxy)benzene (**3w**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 1-((2-bromoallyl)oxy)-4-methylbenzene (68.1 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 71% yield (56.1 mg) as a colorless oil (*E*:*Z* = 17:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.21-7.17 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.24 (dt, *J* = 15.6 Hz, 7.2Hz, 1H), 5.20 (s, 1H), 5.07 (s, 1H), 4.46 (s, 2H), 3.03 (d, *J* = 6.8 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 143.6, 137.3, 132.0, 130.0, 129.8, 128.5, 127.12, 127.11, 126.1, 114.6, 113.2, 70.6, 36.7, 20.4. IR (neat): 3061, 3024,

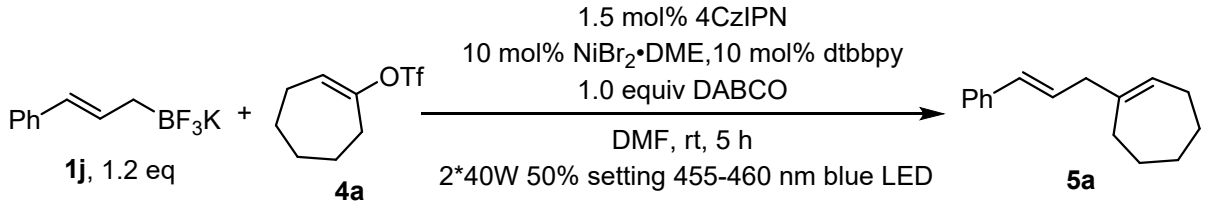
2912, 2864, 1656, 1606, 1580, 1509, 1493, 1451, 1239, 1052, 901, 824, 807, 744, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{20}O$ 264.1509; Found 264.1511.



3x

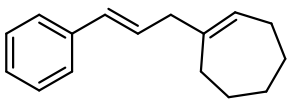
(*E*)-*N*-Methyl-*N*-(2-methylene-5-phenylpent-4-en-1-yl)aniline (**3x**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and *N*-(2-bromoallyl)-*N*-methylaniline (67.8 mg, 1.0 equiv, 0.3 mmol), 9 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) to afford the target product in 87% yield (68.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* =8.0 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.22-7.18 (m, 3H), 6.70-6.66 (m, 3H), 6.42 (d, *J* = 15.6 Hz, 2H), 6.23 (dt, *J* = 15.6 Hz, 7.2Hz, 1H), 4.93 (d, *J* = 14.8 Hz, 2H), 3.84 (s, 2H), 2.92-2.89 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 143.9, 137.4, 131.8, 129.0, 128.5, 127.5, 127.1, 126.0, 116.2, 112.0, 111.3, 57.5, 38.1, 37.3. IR (neat): 3061, 3030, 2867, 1650, 1583, 1508, 1246, 1052, 974, 901, 824, 808, 744, 692 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N$ 264.1747; Found 264.1753.

Typical procedure for the synthesis of 5a.



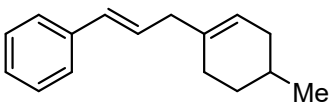
The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0

equiv, 0.3 mmol), DMF (3 mL) and cyclohept-1-en-1-yl trifluoromethanesulfonate (73.3 mg, 1.0 equiv, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction was stirred at room temperature under the irradiation of two 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2) for 5 h, the mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: *n*-pentane) followed by preparative TLC on silica gel (eluent: petroleum ether) to afford the target product **5a** in 84% yield (53.2 mg) as a colorless oil. (82% yield without DABCO)



5a

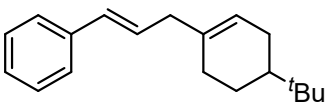
1-Cinnamylcyclohept-1-ene (**5a**), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.21-7.16 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.63 (t, *J* = 6.4 Hz, 1H), 2.86 (d, *J* = 7.2 Hz, 2H), 2.14-2.08 (m, 4H), 1.76-1.70 (m, 2H), 1.51-1.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 137.8, 130.9, 129.0, 128.4, 127.2, 126.8, 126.0, 43.7, 32.8, 32.5, 28.4, 27.3, 26.7. The spectroscopic data are in accordance with the literature.[14]



5b

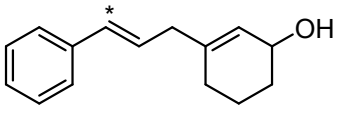
(*E*)-(3-(4-Methylcyclohex-1-en-1-yl)prop-1-en-1-yl)benzene (**5b**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 4-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (73.3 mg, 1.0 equiv, 0.3 mmol). Purification by column

chromatography on silica gel (eluent: pentane) to afford the target product in 76% yield (48.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.46 (s, 1H), 2.82 (d, *J* = 6.8 Hz, 2H), 2.09-1.96 (m, 3H), 1.72-1.61 (m, 3H), 1.27-1.19 (m, 1H), 0.94 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.1, 130.8, 128.9, 128.4, 126.9, 126.0, 121.7, 41.2, 33.9, 31.2, 28.6, 28.4, 21.8. The spectroscopic data are in accordance with the literature.[14]



5c

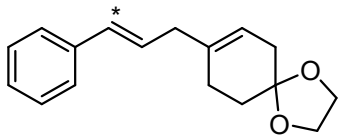
(*E*)-(3-(4-(*tert*-Butyl)cyclohex-1-en-1-yl)prop-1-en-1-yl)benzene (**5c**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 4-(*tert*-butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (85.9 mg, 1.0 equiv, 0.3 mmol), 7.5 h. Purification by column chromatography on silica gel (eluent: pentane) to afford the target product in 69% yield (52.7 mg) as a colorless oil. (54% yield without DABCO) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20-7.16 (m, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.49 (s, 1H), 2.83 (d, *J* = 6.8 Hz, 2H), 2.03-2.01 (m, 3H), 1.83-1.80 (m, 2H), 1.28-1.13 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.3, 130.8, 128.9, 128.4, 126.9, 126.0, 122.3, 44.1, 41.1, 32.2, 30.0, 27.2, 26.9, 24.2. The spectroscopic data are in accordance with the literature.[14]



5d (*E*:*Z* > 20:1)

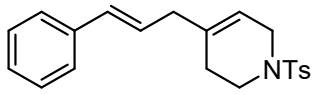
3-Cinnamylcyclohex-2-en-1-ol (**5d**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium

cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 3-hydroxycyclohex-1-en-1-yl trifluoromethanesulfonate (73.9 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 20/1/5) to afford the target product in 71% yield (45.6 mg) as a colorless oil (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.58 (s, 1H), 4.21 (s, 2H), 2.86 (d, *J* = 7.2 Hz, 2H), 2.03-1.90 (m, 2H), 1.85-1.79 (m, 1H), 1.77-1.70 (m, 2H), 1.62-1.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 137.4, 131.6, 128.5, 127.7, 127.0, 126.0, 124.9, 65.9, 41.0, 31.8, 28.6, 19.1. IR (neat): 3379, 3022, 2935, 2863, 1704, 1662, 1495, 1448, 1255, 1058, 965, 745, 692 cm^{-1}. HRMS (ESI) m/z: $[M-H]^+$ Calcd for $C_{15}H_{17}O$ 213.1274; Found 213.1277.



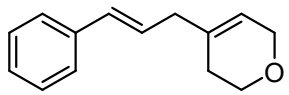
5e (*E*:*Z* > 20:1)

8-Cinnamyl-1,4-dioxaspiro[4.5]dec-7-ene (**5e**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (86.5 mg, 1.0 equiv, 0.3 mmol), 24 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the target product in 57% yield (43.8 mg) as a colorless oil (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.21 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.41 (s, 1H), 3.97 (s, 4H), 2.87 (d, *J* = 6.8 Hz, 2H), 2.28 (s, 2H), 2.22 (t, *J* = 6.0 Hz, 2H), 1.78 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 136.2, 131.3, 128.4, 128.2, 126.9, 126.0, 119.3, 108.0, 64.3, 40.5, 35.7, 31.1, 27.7. The spectroscopic data are in accordance with the literature.[14]



5f

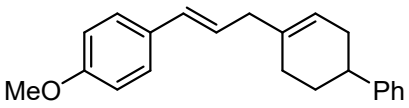
4-Cinnamyl-1-tosyl-1,2,3,6-tetrahydropyridine (**5f**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (115.6 mg, 1.0 equiv, 0.3 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol) and DMF (3 mL), 7 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 20/1/5) to afford the target product in 92% yield (97.7 mg) as a colorless oil. Containing trace impurity or isomer. (71% yield without DABCO) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.32-7.25 (m, 6H), 7.19 (t, *J* = 6.8 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.07 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.40 (s, 1H), 3.57 (s, 2H), 3.17 (t, *J* = 6.0 Hz, 2H), 2.82 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.16 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.1, 135.1, 133.2, 131.9, 129.5, 128.4, 127.6, 127.1, 126.9, 126.0, 117.4, 44.8, 42.8, 40.2, 28.3, 21.4. IR (neat): 3027, 2917, 2852, 2829, 1597, 1451, 1334, 1306, 1163, 1155, 1096, 971, 949, 816, 736, 677 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{23}NO_2S$ 353.1444; Found 353.1445.



5g

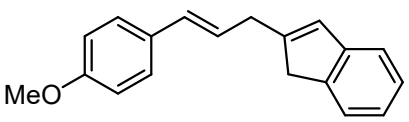
4-Cinnamyltetrahydro-2*H*-pyran (**5g**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (69.7 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1 to 50/1) f to afford the target product in 68% yield (40.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 16.0 Hz, 7.2 Hz, 1H), 5.51 (brs,

1H), 4.13 (d, *J* = 2.0 Hz, 2H), 3.79 (t, *J* = 5.6 Hz, 2H), 2.88 (d, *J* = 6.8 Hz, 2H), 2.09 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 134.3, 131.7, 128.5, 127.4, 127.1, 126.0, 120.9, 65.5, 64.3, 40.5, 28.5. The spectroscopic data are in accordance with the literature.[14]



5h

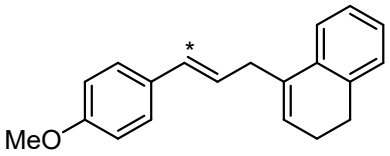
(*E*)-4-(3-(4-Methoxyphenyl)allyl)-1,2,3,6-tetrahydro-1,1'-biphenyl (**5h**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (91.9 mg, 1.0 equiv, 0.3 mmol) , 9 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford the target product in 72% yield (65.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 4H), 7.22-7.16 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.09 (dt, *J* = 16.0 Hz, 7.2 Hz, 1H), 5.57 (d, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.78-2.72 (m, 1H), 2.32-2.28 (m, 1H), 2.19-2.07 (m, 3H), 1.97-1.94 (m, 1H), 1.82-1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 147.1, 136.6, 130.5, 130.4, 128.3, 127.1, 126.8, 126.4, 125.9, 121.6, 113.9, 55.2, 41.1, 40.2, 33.6, 30.0, 29.1. IR (neat): 3022, 2936, 2909, 2831, 1606, 1509, 1249, 1174, 1029, 974, 915, 816, 759, 701 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{22}H_{24}O$ 304.1822; Found 304.1827.



5i

(*E*)-2-(3-(4-Methoxyphenyl)allyl)-1*H*-indene (**5i**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol),

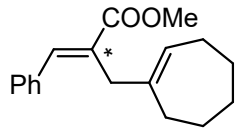
DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 1*H*-inden-2-yl trifluoromethanesulfonate (79.3 mg, 1.0 equiv, 0.3 mmol) Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 300/1/1 to 200/1/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 150/1/1) to afford the target product in 61% yield (48.4mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 3H), 7.23-7.19 (m, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.4Hz, 2H), 6.57 (s, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, 7.2 Hz, 1H), 3.78 (s, 3H), 3.35-3.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.7, 145.4, 143.2, 130.7, 130.2, 127.2, 127.1, 126.2, 125.6, 123.7, 123.4, 120.1, 113.9, 55.2, 41.0, 34.8. IR (neat): 3053, 2998, 2936, 2870, 1606, 1508, 1464, 1296, 1248, 1174, 1035, 969, 837, 754, 717 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{18}O$ 262.1352; Found 262.1356.



5j (*E*:*Z* > 20:1)

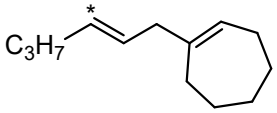
(*E*)-4-(3-(4-Methoxyphenyl)allyl)-1,2-dihydronaphthalene (**5j**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (83.5 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 150/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 160/1/20) to afford the target product in 87% yield (71.9 mg) as a white solid (*E*:*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 3H), 7.19-7.15 (m, 1H), 7.13-7.12 (m, 2H), 6.82-6.79 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.19 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 5.91 (t, *J* = 4.8 Hz, 1H), 3.30 (d, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.29-2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 136.6, 135.1, 135.0, 130.7, 130.5, 127.6, 127.2, 126.7, 126.4, 126.3, 126.1, 122.9, 113.9, 55.3, 36.2, 28.4, 23.3. IR (neat): 3014, 2956, 2923, 2881, 2831, 1605, 1508, 1439, 1243, 1172, 1028, 978, 824, 811, 768 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O$ 277.1587; Found

277.1589.



5k
(*major* : *minor* = 10:1)

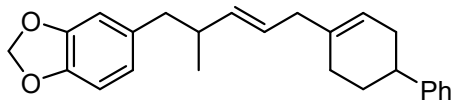
Methyl (*E*)-2-(cyclohept-1-en-1-ylmethyl)-3-phenylacrylate (**5k**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium methyl (*E*)-3-phenyl-2-((trifluoro-λ^4-boraneyl)methyl)acrylate (101.6 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and cyclohept-1-en-1-yl trifluoromethanesulfonate (73.3 mg, 1.0 equiv, 0.3 mmol) Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford the target product in 83% yield (67.5 mg) as a colorless oil (*major*:*minor* = 10:1). For the NMR data of *major* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.42-7.24 (m, 5H), 5.48 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.22 (s, 2H), 2.18-2.15 (m, 2H), 2.12-2.08 (m, 2H), 1.79-1.73 (m, 2H), 1.57-1.51 (m, 2H), 1.49-1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 141.7, 140.2, 135.6, 130.8, 129.4, 128.6, 128.34, 125.8, 52.0, 36.9, 34.0, 32.6, 28.2, 27.3, 26.4. For the partial NMR data of *minor* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.69 (s, 1H), 5.68 (t, *J* = 6.4 Hz, 1H), 3.62 (s, 3H), 3.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 133.5, 129.6, 128.4, 128.30, 128.2, 128.0, 45.9, 32.40, 32.38, 28.4, 26.7. IR (neat): 3071, 2990, 2913, 2836, 1697, 1453, 1436, 1269, 1221, 1199, 1092, 946, 771, 760, 696 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{22}O_2$ 270.1614; Found 270.1618.



5l (*E*:*Z* = 8:1)

(*E*)-1-(Hex-2-en-1-yl)cyclohept-1-ene (**5l**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (68.4 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0

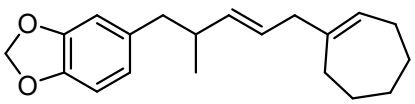
equiv, 0.3 mmol), DMF (3 mL) and cyclohept-1-en-1-yl trifluoromethanesulfonate (73.3 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: pentane) to afford the target product in 75% yield (40.2 mg) as a colorless oil (*E*:*Z* = 8:1). For the NMR data of *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (t, *J* =6.4 Hz, 1H), 5.46-5.31 (m, 2H), 2.64 (d, *J* = 6.0 Hz, 2H), 2.09-2.04 (m, 4H), 2.02-1.95 (m, 2H), 1.75-1.69 (m, 2H), 1.49-1.42 (m, 4H), 1.39-1.33 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 131.6, 128.5, 126.2, 43.4, 34.7, 32.6, 28.4, 27.4, 26.7, 22.7, 13.6. For the partial NMR data of *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 2.71 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.8, 126.0, 37.8, 32.8, 29.2, 28.3, 26.8, 22.9. IR (neat): 2957, 2918, 2848, 1446, 1375, 1274, 1216, 1093, 967, 845 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{22}$ 178.1716; Found 178.1719.



5m

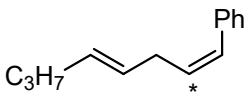
(*E*)-5-(2-Methyl-5-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)pent-3-en-1-yl)benzo[*d*][1,3]dioxole (**5m**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-(5-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)trifluoroborate (111.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (91.9 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 300/1 to 100/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford the target product in 87% yield (94.0 mg) as a colorless oil. Containing trace impurity or isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.22-7.16 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.86 (s, 2H), 5.39-5.26 (m, 3H), 2.74-2.68 (m, 1H), 2.63-2.62 (m, 2H), 2.58-2.44 (m, 2H), 2.41-2.34 (m, 1H), 2.27-2.23 (m, 1H), 2.14-2.02 (m, 2H), 1.95-1.89 (m, 2H), 1.77-1.68 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.28, 147.26, .145.5, 136.90, 136.88, 134.8, 124.8, 128.3, 126.8, 126.7, 125.9, 122.0, 120.9, 109.6, 107.8, 100.6, 43.41, 43.40, 40.8, 40.7, 40.19, 40.17, 38.7, 38.6, 33.59, 33.56, 30.0, 29.0, 28.9, 20.18, 20.16. IR (neat): 3024, 2959, 2912, 2886, 2829, 1600,

1502, 1488, 1439, 1244, 1039, 939, 927, 803, 756, 699 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{28}O_2$ 360.2084; Found 360.2082.



5n

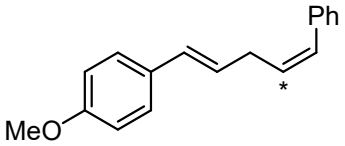
(*E*)-5-(5-(Cyclohept-1-en-1-yl)-2-methylpent-3-en-1-yl)benzo[*d*][1,3]dioxole (**5n**). 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-(5-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-2-en-1-yl)trifluoroborate (111.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and cyclohept-1-en-1-yl trifluoromethanesulfonate (73.3 mg, 1.0 equiv, 0.3 mmol) Purification by column chromatography on silica gel (eluent: petroleum ether to petroleum ether/ethyl acetate = 100/1) to afford the target product in 78% yield (70.2 mg) as a colorless oil. Containing trace impurity or isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 6.58-6.56 (m, 1H), 5.89 (s, 2H), 5.46 (t, *J* = 6.4 Hz, 1H), 5.37-5.24 (m, 2H), 2.60 (d, *J* = 6.4 Hz, 2H), 2.57-2.51 (m, 1H), 2.47-2.32 (m, 2H), 2.07-1.98 (m, 4H), 1.73-1.67 (m, 2H), 1.47-1.38 (m, 4H), 0.97-0.93 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 145.4, 143.5, 136.7, 134.8, 127.0, 126.3, 122.0, 109.6, 107.8, 100.6, 43.4, 43.3, 38.6, 32.6, 32.5, 28.3, 27.3, 26.7, 20.1. IR (neat): 3024, 2956, 2918, 2844, 1503, 1489, 1441, 1331, 1245, 1097, 1039, 971, 942, 930, 814, 737 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{26}O_2$ 298.1927; Found 298.1933.



3y (*Z*:*E* = 20:1)

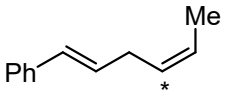
((1*Z*,4*E*)-Octa-1,4-dien-1-yl)benzene (**3y**). Condition **A** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), 4,4'-dimethoxy-2,2'-bipyridine (9.7 mg, 15 mol%, 0.045 mmol), potassium (*E*)-trifluoro(hex-2-en-1-yl)borate (85.5 mg, 1.5 equiv, 0.45 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL), (*Z*)-(2-

bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol) and 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (10.3 mg, 0.2 equiv, 0.06 mmol). Purification by column chromatography on silica gel (eluent: pentane) to afford the target product in 70% yield (39.1 mg) as a colorless oil (*Z*:*E* = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 4H), 7.23-7.19 (m, 1H), 6.46 (d, *J* = 11.6 Hz, 1H), 5.68 (dt, *J* = 11.6 Hz, 7.6 Hz, 1H), 5.55-5.44 (m, 2H), 3.02-2.99 (m, 2H), 2.02-1.97 (m, 2H), 1.43-1.34(m, 2H), 0.92-0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 131.3, 130.7, 129.3, 128.7, 128.1, 126.6, 34.7, 31.7, 22.6, 13.6. IR (neat): 3022, 2959, 2931, 2872, 1704, 1494, 1449, 969, 748, 699 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{18}$ 186.1403; Found 186.1403.



3z (*Z*:*E* = 17.5 :1)

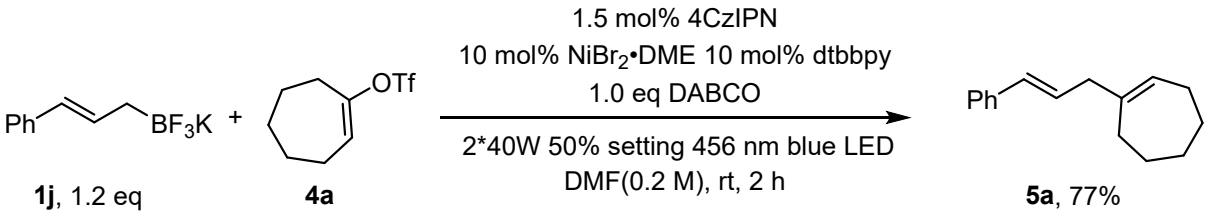
1-Methoxy-4-((1*E*,4*Z*)-5-phenylpenta-1,4-dien-1-yl)benzene (**3z**). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium (*E*)-trifluoro(3-(4-methoxyphenyl)allyl)borate (91.5 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and (*Z*)-(2-bromovinyl)benzene (54.9 mg, 1.0 equiv, 0.3 mmol), 13 h. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 500/1 to 200:1) to afford the target product in 65% yield (49.0 mg) as a white solid (*Z*:*E* = 17.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 6H), 7.24-7.20 (m, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 11.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.13 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.76 (dt, *J* = 11.2 Hz, 7.6 Hz, 1H), 3.77 (s, 3H), 3.19 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 137.2, 130.4, 130.0, 129.9, 129.7, 128.6, 128.2, 127.1, 126.7, 126.2, 113.9, 55.2, 31.9. IR (neat): 3011, 2954, 2886, 2836, 1605, 1510, 1491, 1292, 1249, 1176, 1030, 967, 840, 775, 694 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{18}O$ 250.1352; Found 250.1354.



3za (*Z*:*E* = 4.9:1)

((1*E*,4*Z*)-Hexa-1,4-dien-1-yl)benzene (3za). Condition **B** was used. 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), DMF (3 mL) and (*Z*)-1-bromoprop-1-ene (36.3 mg, 1.0 equiv, 0.3 mmol). Purification by column chromatography on silica gel (eluent: petroleum ether) to afford the target product in 54% yield (25.7 mg) as a colorless oil (*Z*:*E* = 4.9:1). For the NMR data of *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 5.60-5.54 (m, 1H), 5.52-5.45 (m, 1H), 2.96 (t, *J* = 6.8 Hz, 2H), 1.67 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 129.9, 128.8, 128.4, 127.5, 126.9, 126.0, 125.2, 30.4, 17.9, 12.8. For the partial NMR data of *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): 2.89 (t, *J* = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.2, 129.2, 126.3, 35.9, 17.9. Some peaks are overlapped with that of the major isomer. The spectroscopic data are in accordance with the literature.[19]

1.0 mmol Scale reaction:

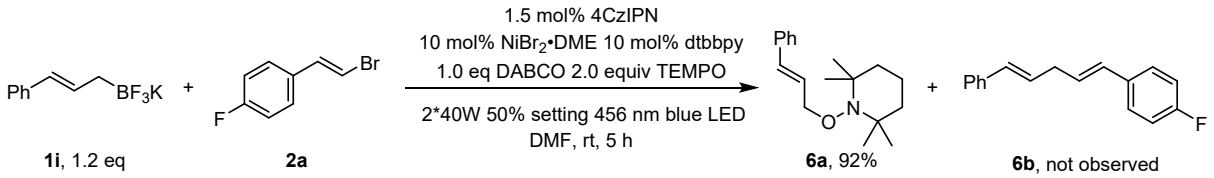


1j, 1.2 eq **4a** **5a**, 77%

The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (11.8 mg, 1.5 mol%, 0. 015 mmol), $NiBr_2$•DME (30.9 mg, 10 mol%, 0.1 mmol), dtbbpy (26.8 mg, 10 mol%, 0.1 mmol), potassium cinnamyltrifluoroborate (268.9 mg, 1.2 equiv, 1.2 mmol), DABCO (112.2 mg, 1.0 equiv, 1.0 mmol), DMF (5 mL) and cyclohept-1-en-1-yl trifluoromethanesulfonate (224.2 mg, 1.0 equiv, 1.0 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted

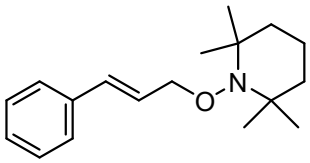
and taken outside the glove box. After the reaction mixture was stirred at room temperature under the irradiation of two 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2) for 2 h. The mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford the target product **5a** in 77% yield (162.7 mg) as a colorless oil.

Radical Scavenger Experiment.



The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, 4CzIPN (3.6 mg, 1.5 mol%, 0.0045 mmol), $NiBr_2$•DME (9.3 mg, 10 mol%, 0.03 mmol), dtbbpy (8.1 mg, 10 mol%, 0.03 mmol), potassium cinnamyltrifluoroborate (80.7 mg, 1.2 equiv, 0.36 mmol), DABCO (33.7 mg, 1.0 equiv, 0.3 mmol), TEMPO (93.8 mg, 2.0 equiv, 0.6 mmol), DMF (3 mL) and (*E*)-1-(2-bromovinyl)-4-fluorobenzene (60.3 mg, 1.0 equiv, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at room temperature under the irradiation of 40W 456 nm blue LEDs at 50 intensity settings (the distance of the reaction tube from the light source is 6-7 cm, light intensity = 60-70 mW/cm^2) for 5 h. Then the mixture was filtrated with a short silica gel pad and washed by ethyl acetate. Then water was added to the filtrate, and the mixture was extracted with ethyl acetate for three times. The combined organic layers were washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) followed by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 25/1/5) to afford

the target product **6a** in 92% yield (75.1 mg) as a colorless oil.



6a

1-(Cinnamyloxy)-2,2,6,6-tetramethylpiperidine (**6a**), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.28 (dt, *J* = 16.0 Hz, 6.0 Hz, 1H), 4.44 (d, *J* = 6.0 Hz, 2H), 1.61-1.45 (m, 5H), 1.34-1.31 (m, 1H), 1.21 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 131.3, 128.4, 127.4, 126.4, 125.5, 78.0, 59.7, 39.6, 33.0, 20.2, 17.1. The spectroscopic data are in accordance with the literature.[1]

References:

(1) Lv, P.; Wang, A.; Xie, X.; Chen, Y.; Liu, Y., Photoredox/Nickel Dual-Catalyzed Regioselective Allylic Arylations of Allyl Trifluoroborates with Aryl Halides. *Org. Lett.* **2023**, *25*, 3319–3324.

(2) Kabalka, G. W.; Venkataiah, B.; Dong, G., Pd-catalyzed cross-coupling of Baylis-Hillman acetate adducts with bis(pinacolato)diboron: an efficient route to functionalized allyl borates. *J. Org. Chem.* **2004**, *69*, 5807–5809.

(3) Shuai, B., Ph. D. thesis, Shanghai Institute of Organic Chemistry, **2020**.

(4) Muller, D.; Alexakis, A., Copper-catalyzed asymmetric 1,4-addition of alkenyl alanes to N-substituted-2-3-dehydro-4-piperidones. *Org. Lett.* **2012**, *14*, 1842–1845.

(5) Chang, D.; Gu, Y.; Shen, Q., Pd-catalyzed difluoromethylation of vinyl bromides, triflates, tosylates, and nonaflates. *Chem. Eur. J.* **2015**, *21*, 6074–6078.

(6) Dan, X.; Yang, Q.; Xing, L.; Tang, Y.; Wang, W.; Cai, Y., Heterogeneous Metallaphotocatalytic C($sp^{(2)}$)-C($sp^{(3)}$) Cross-Coupling Reactions with Integrated Bipyridyl-Ni(II)-Carbon Nitride. *Org. Lett.* **2023**, *25*, 4124–4129.

(7) Armstrong, R. J.; Garcia-Ruiz, C.; Myers, E. L.; Aggarwal, V. K., Stereodivergent Olefination of Enantioenriched Boronic Esters. *Angew. Chem. Int. Ed.* **2017**, *56*, 786 -790.

(8) Kropp, P. J.; Crawford, S. D., Surface-Mediated Reactions. 4. Hydrohalogenation of Alkynes. *J. Org. Chem.* **1994**, *59*, 3102–3112.

(9) Bakstad, E.; Olsen, A. S.; Sandberg, M.; Sydnes, L. K.; Långström, B.; Yan, S.-P.; Wang, G.-L.; Yao, X.-K.; Wang, H.-G.; Tuchagues, J. P.; Ögren, M., Neighbouring-group Influence on the Ring Opening of 2-Aryloxymethyl-1,1,2-tribromocyclopropanes under Phase-transfer Conditions. *Acta Chemica Scandinavica* **1999**, *53*, 465-472.

(10) (a) Zhang, W.; Chen, P.; Liu, G., Enantioselective Palladium(II)-Catalyzed Intramolecular Aminoarylation of Alkenes by Dual N-H and Aryl C-H Bond Cleavage. *Angew.Chem. Int.Ed.* **2017**, *56*, 5336–5340. (b) Barluenga, J.; Canteli, R. M.; FlÛrez, J.; GarcÌa-Granda, S.; Gutier-rez-Rodriguez, A.; MartÌn, E., *J. Am. Chem. Soc.* **1998**, *120*, 2514–2522.

(11) Duan, J.; Du, Y. F.; Pang, X.; Shu, X. Z., Ni-catalyzed cross-electrophile coupling between vinyl/aryl and alkyl sulfonates: synthesis of cycloalkenes and modification of peptides. *Chem. Sci.* **2019**, *10*, 8706–8712.

(12) Moustafa, M. M.; Pagenkopf, B. L., Synthesis of 5-azaindoles via a cycloaddition reaction between nitriles and donor-acceptor cyclopropanes. *Org. Lett.* **2010**, *12*, 3168–3171.

(13) Kong, C.; Jana, N.; Jones, C.; Driver, T. G., Control of the Chemoselectivity of Metal N-Aryl Nitrene Reactivity: C-H Bond Amination versus Electrocyclization. *J. Am. Chem. Soc.* **2016**, *138*, 13271–13280.

(14) Song, F.; Wang, F.; Guo, L.; Feng, X.; Zhang, Y.; Chu, L., Visible-Light-Enabled Stereodivergent Synthesis of *E*- and *Z*-Configured 1,4-Dienes by Photoredox/Nickel Dual Catalysis. *Angew.Chem. Int.Ed.* **2020**, *59*, 177–181.

(15) Lim, M.; Park, D.; Yun, J., Copper-Catalyzed Diastereoselective Borylative Allylation of Alkenyl Sulfones and Base-Controlled Synthesis of Skipped Dienes. *Org. Lett.* **2023**, *25*, 8917–8921.

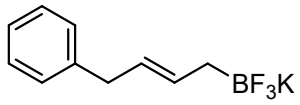
(16) Wu, X.; Yang, M.; Liu, Y., Nickel-Catalyzed Ligand-Controlled Regioselective Allylic Alkenylation of Allylic Alcohols with Easily Accessible Alkenyl Boronates: Synthesis of 1,4-Dienes. *Org. Lett.* **2023**, *25*, 8782–8786.

(17) Tallman, K. A.; Roschek, B., Jr.; Porter, N. A., Factors influencing the autoxidation of fatty acids: effect of olefin geometry of the nonconjugated diene. *J. Am. Chem. Soc.* **2004**, *126*, 30, 9240–9247.

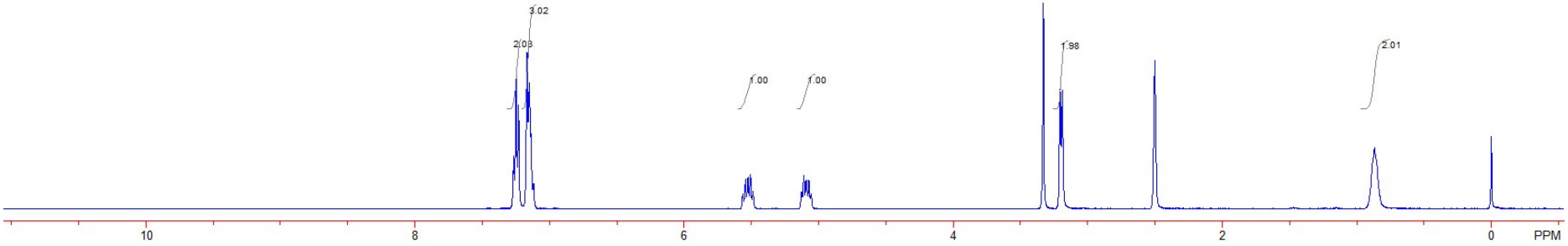
(18) Jin, Y.; Li, C.; Wu, W.; Jiang, H., Regioselective Synthesis of 1,4‐Dienes via Palladium‐Catalyzed Oxidative Allylation of N‐Tosylhydrazones. *Adv. Synth. Catal*. **2023**, *365*, 2338 – 2343.

(19) Tsukamoto, H.; Uchiyama, T.; Suzuki, T.; Kondo, Y. Palladium(0)-catalyzed direct cross-coupling reaction ofallylic alcohols with aryl- and alkenylboronic acids. *Org. Biomol. Chem.* **2008**, *6*, 3005−3013.

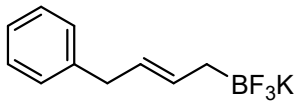
^{1}H NMR (400 MHz, in DMSO-d_6)



1b



^{13}C NMR (100 MHz, in DMSO-d_6)



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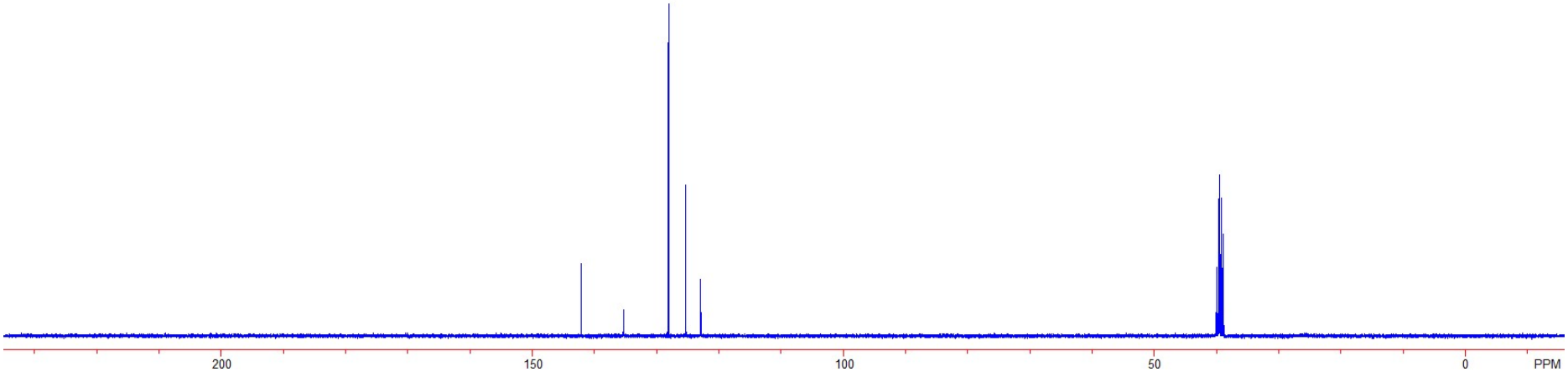
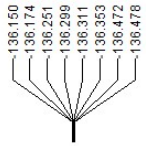
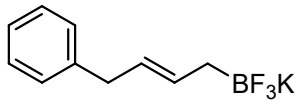


^{19}F NMR (376 MHz, in DMSO-d_6)





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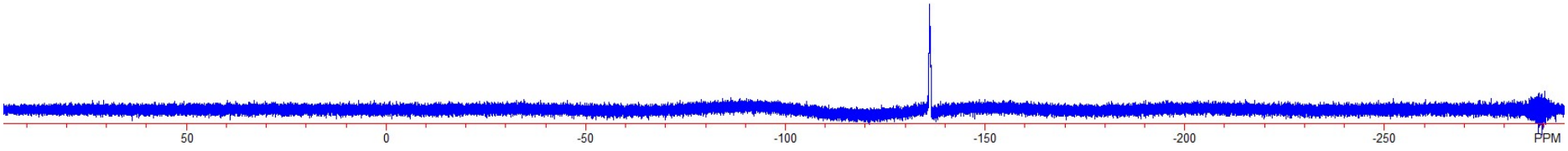

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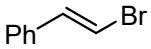
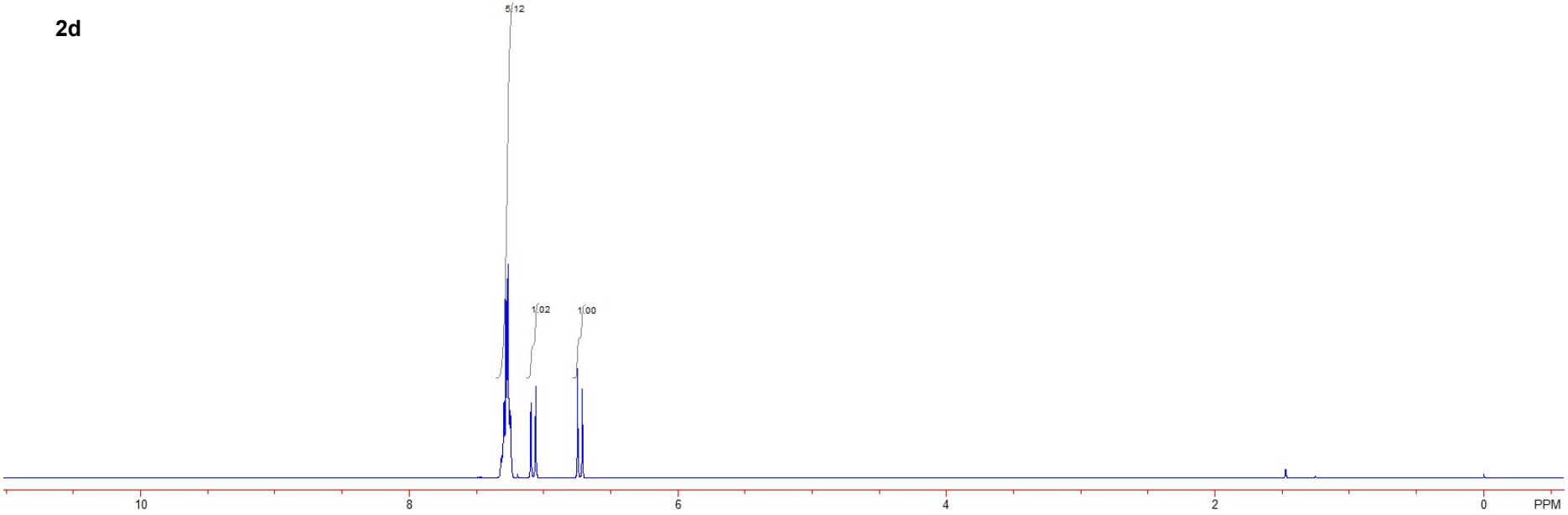
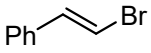


2d



^{13}C NMR (100 MHz, in $CDCl_3$)



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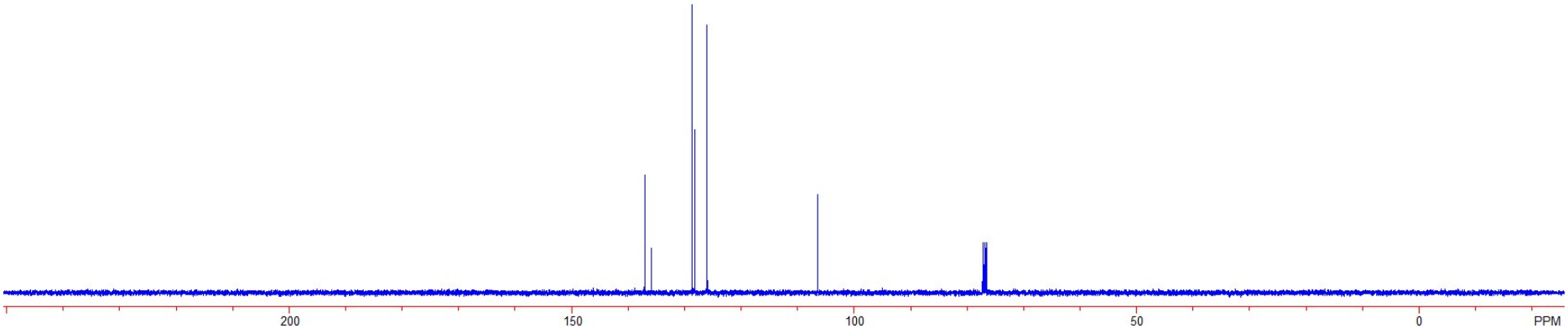
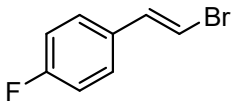


^{1}H NMR (400 MHz, in $CDCl_3$)



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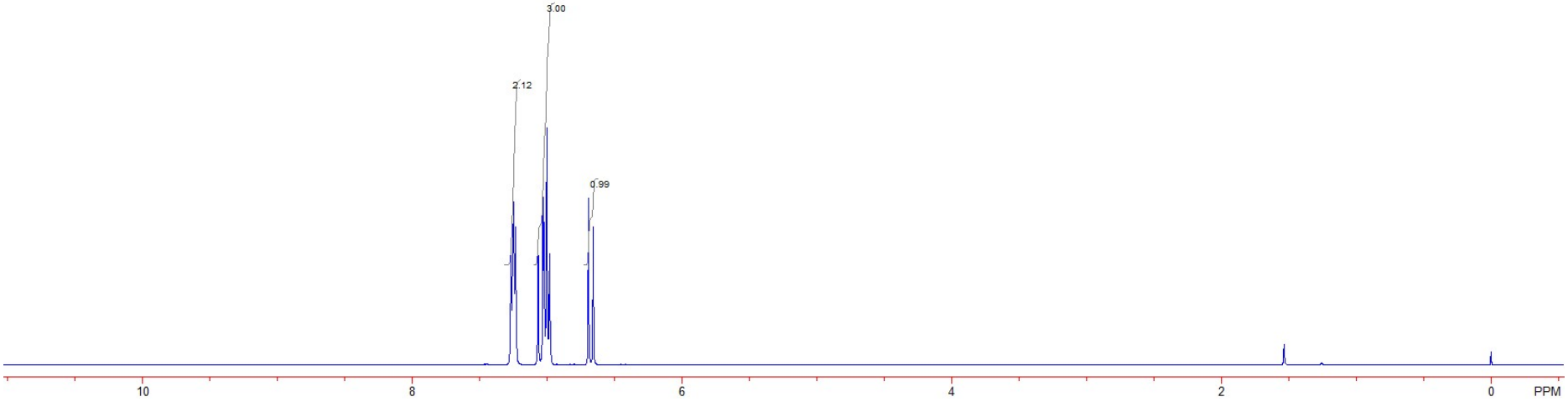
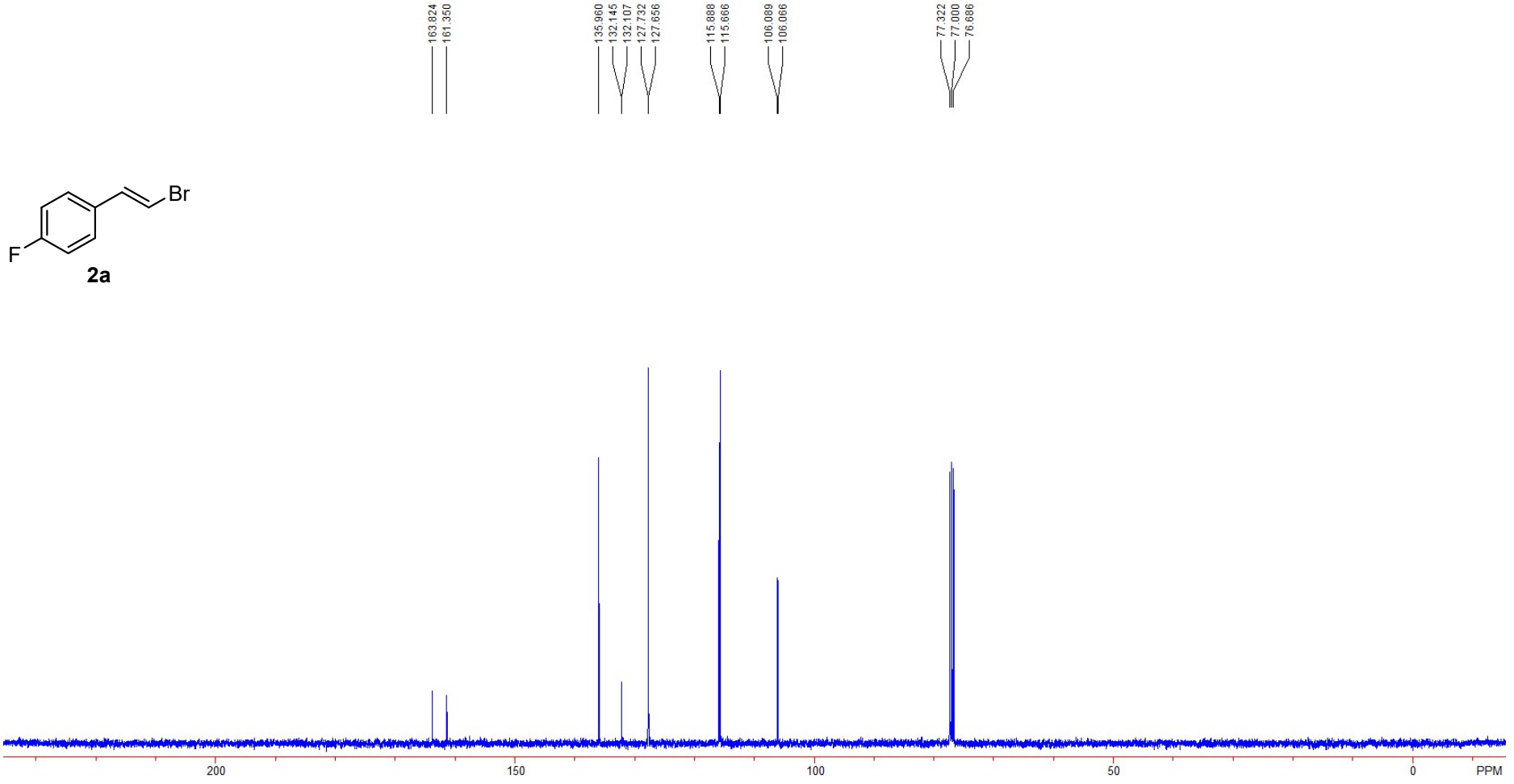
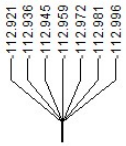
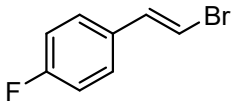


^{13}C NMR (100 MHz, in $CDCl_3$)



^{19}F NMR (376 MHz, in $CDCl_3$)





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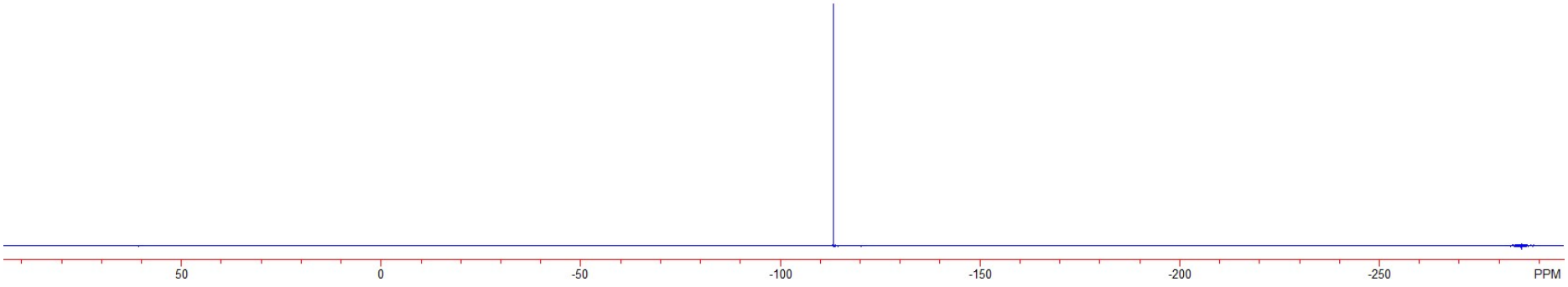
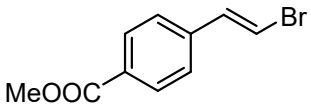


^{1}H NMR (400 MHz, in $CDCl_3$)



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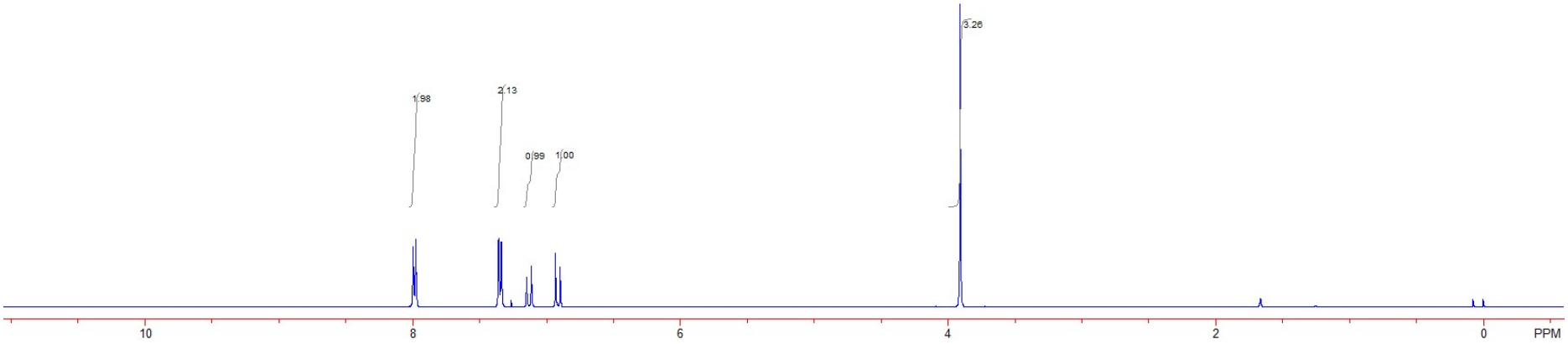
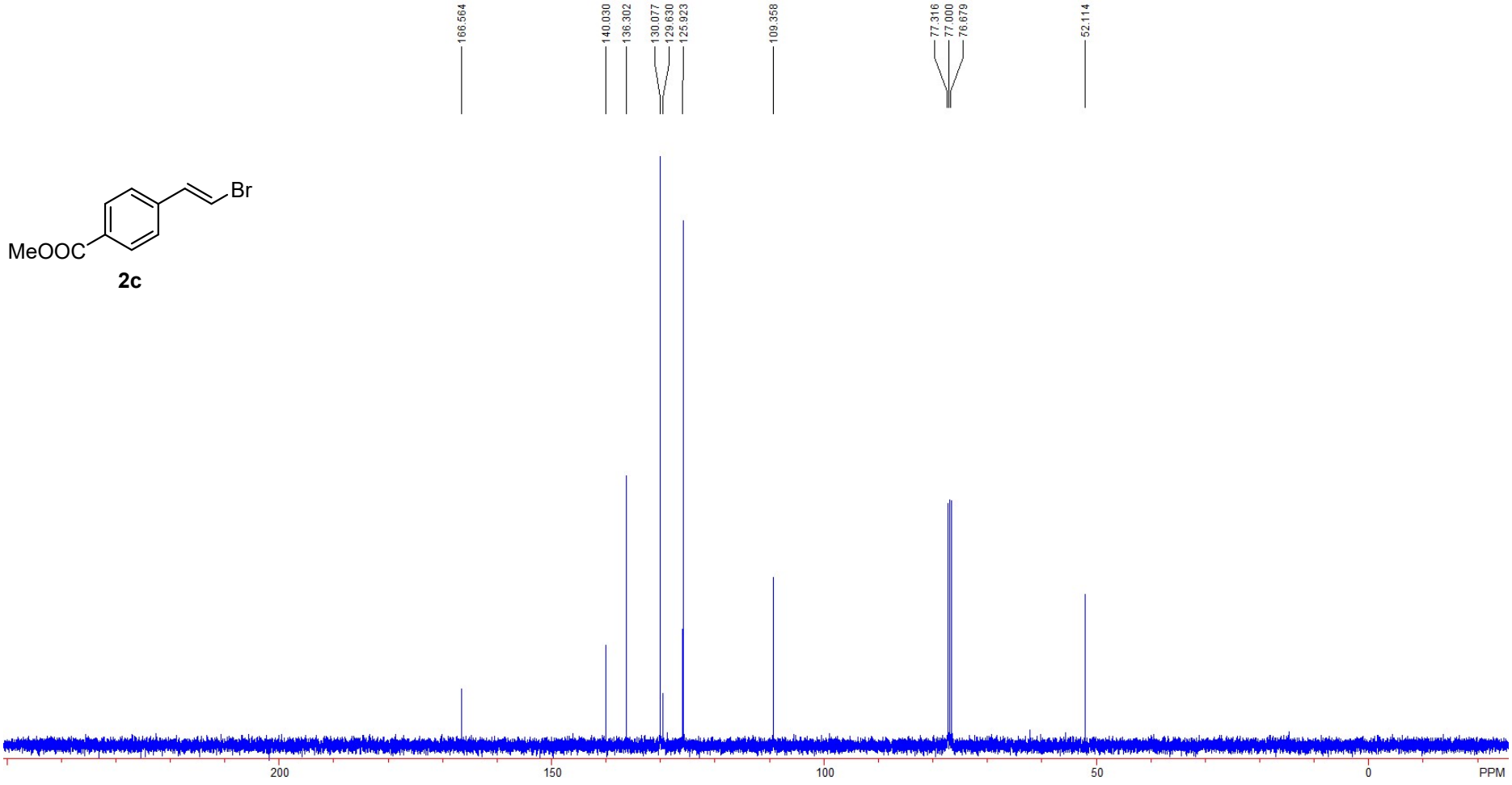
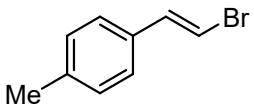


^{13}C NMR (100 MHz, in $CDCl_3$)



2c

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



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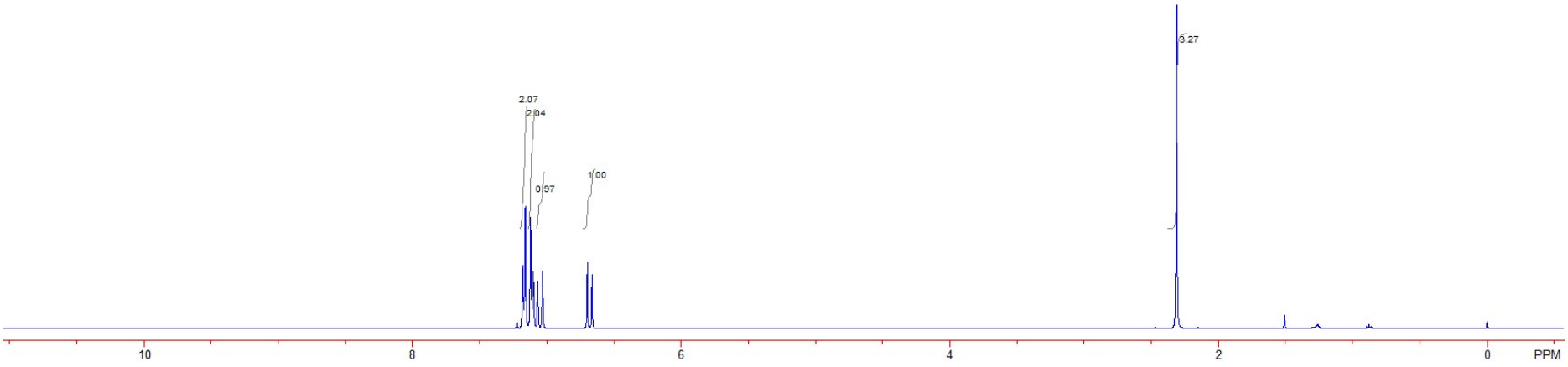
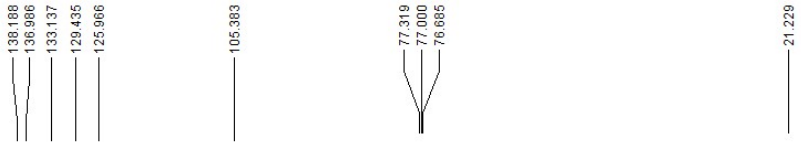
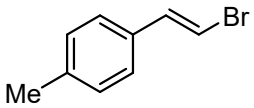


^{13}C NMR (100 MHz, in $CDCl_3$)





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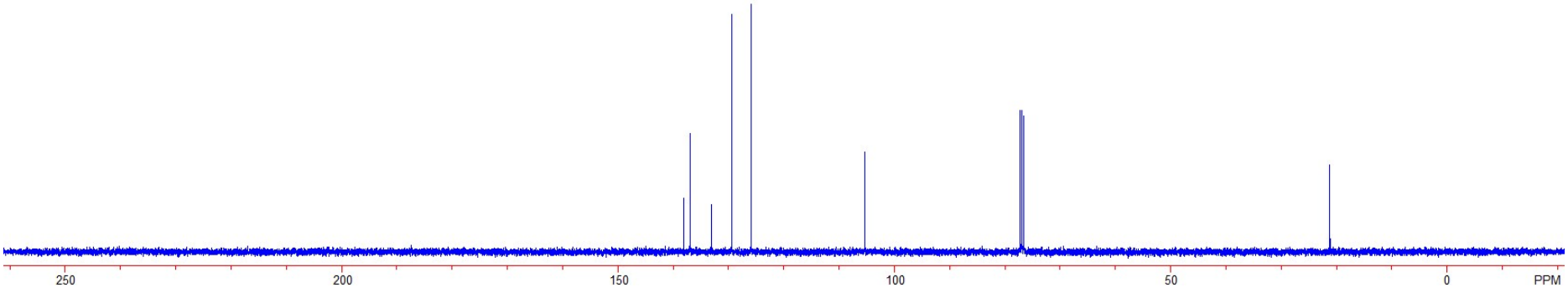
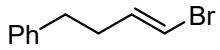


^{1}H NMR (400 MHz, in $CDCl_3$)



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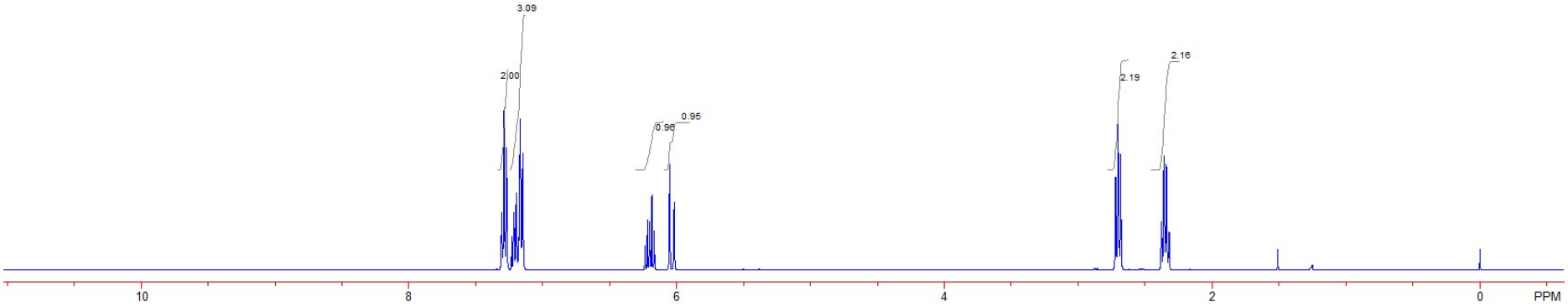
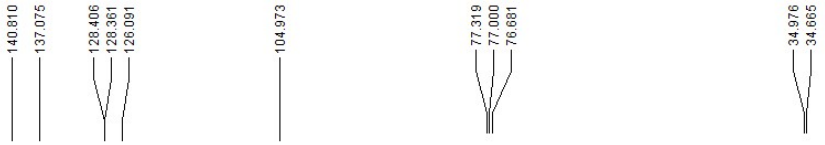
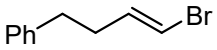


^{13}C NMR (100 MHz, in $CDCl_3$)





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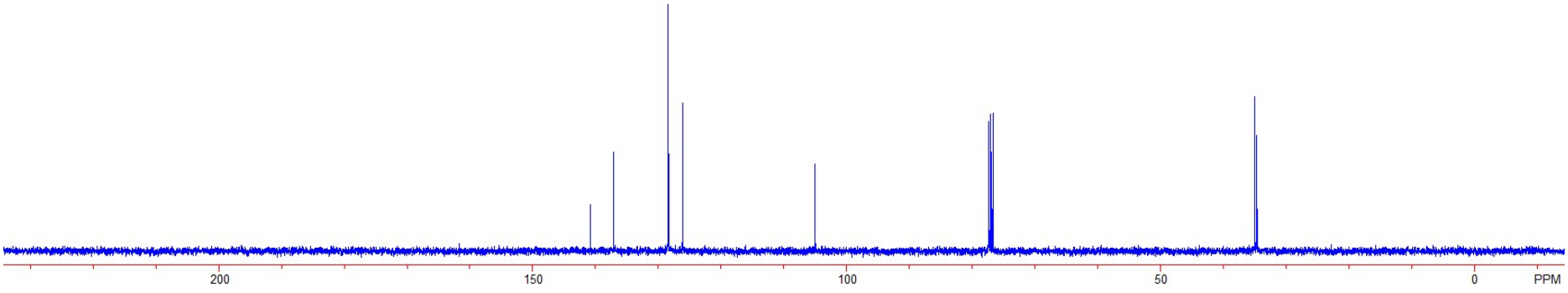
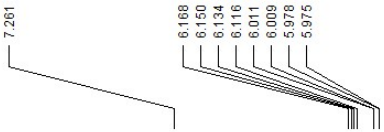
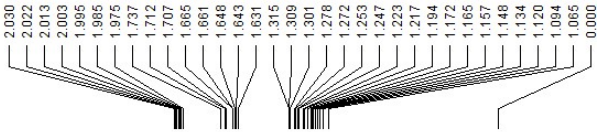
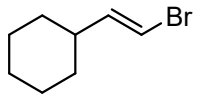


^{1}H NMR (400 MHz, in $CDCl_3$)







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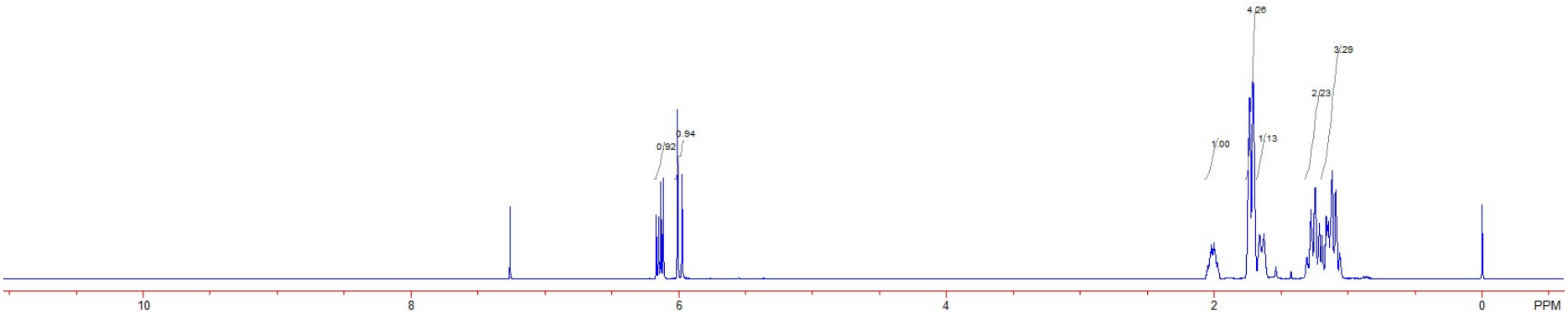
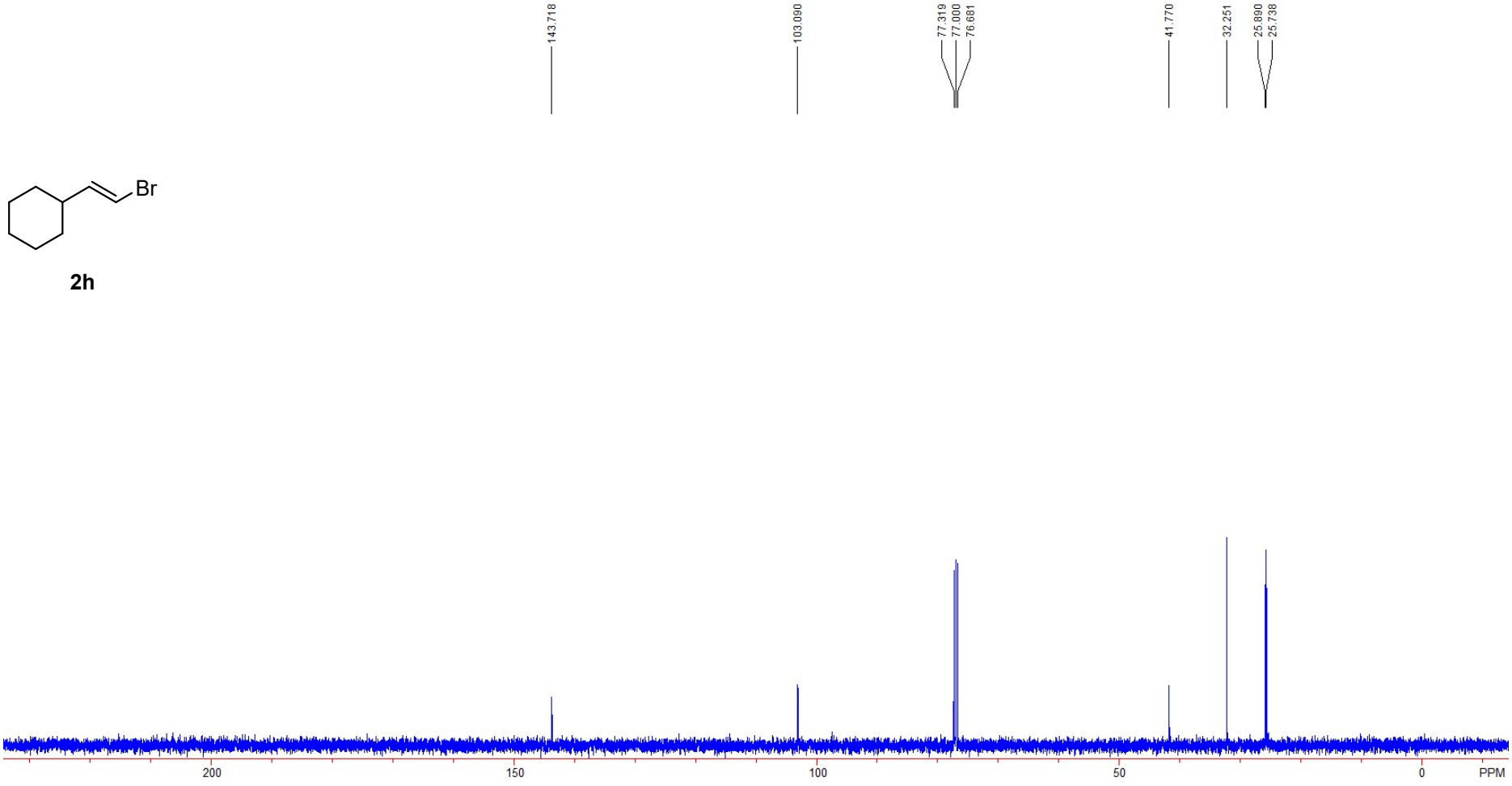
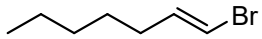


^{13}C NMR (100 MHz, in $CDCl_3$)



2h

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



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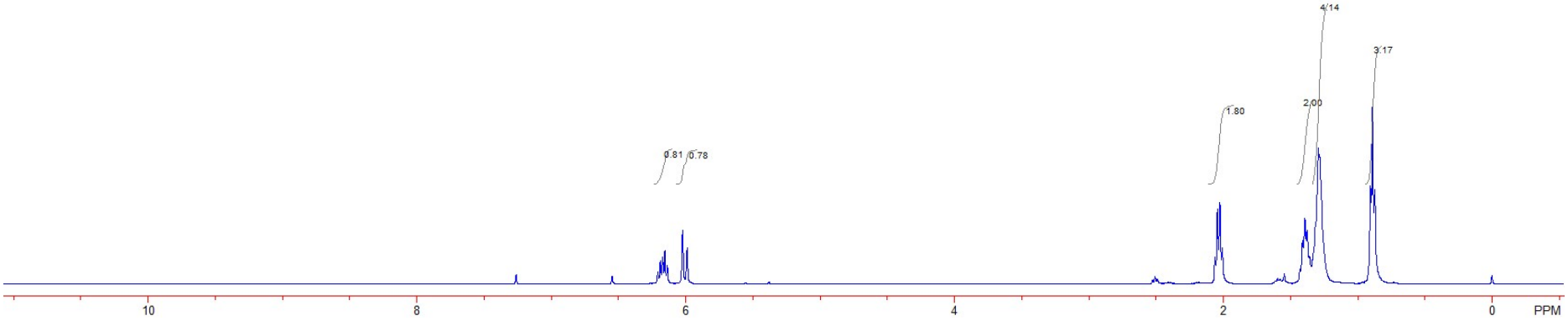
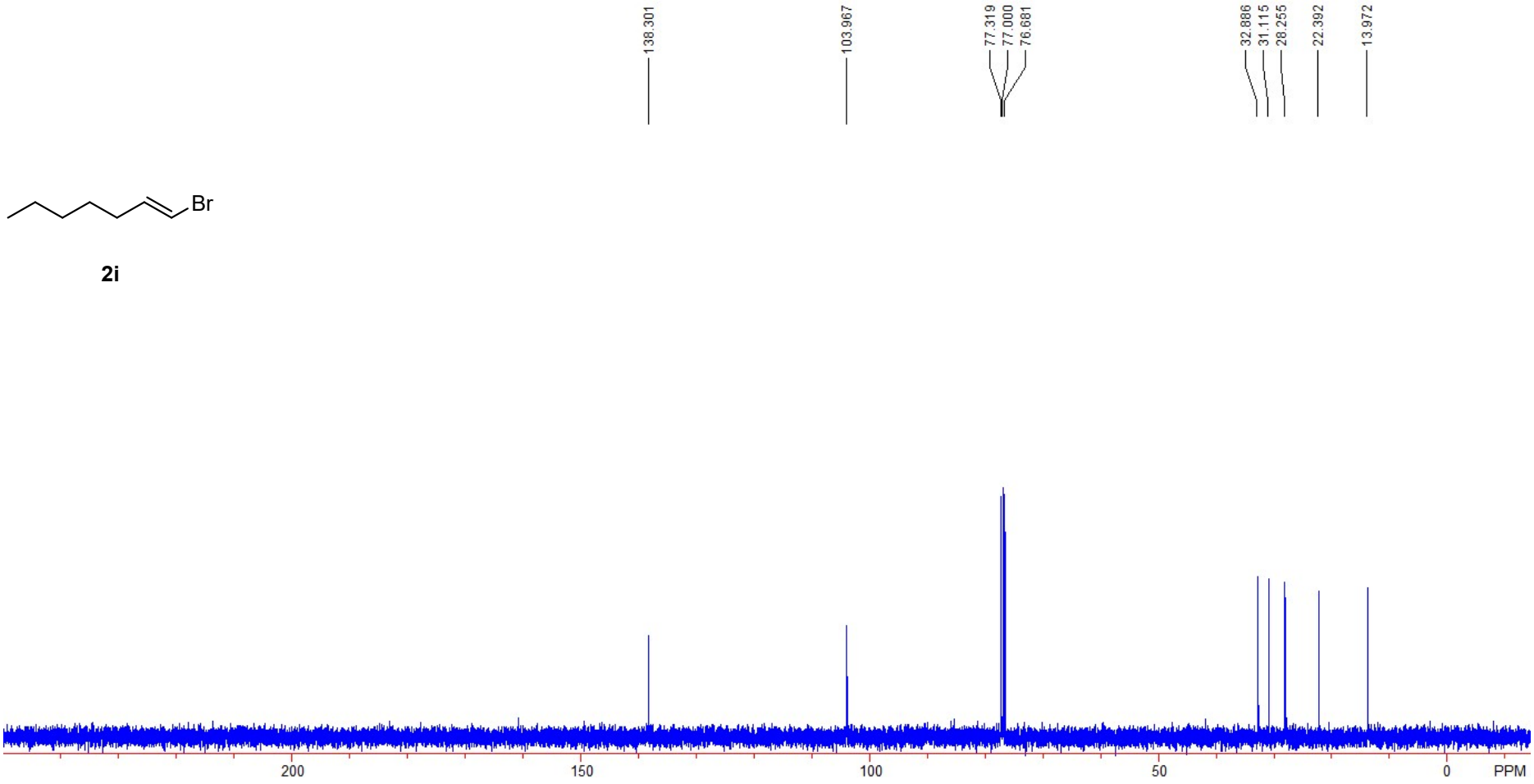
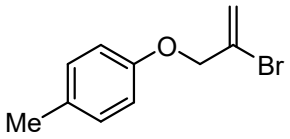


^{13}C NMR (100 MHz, in $CDCl_3$)



2i

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



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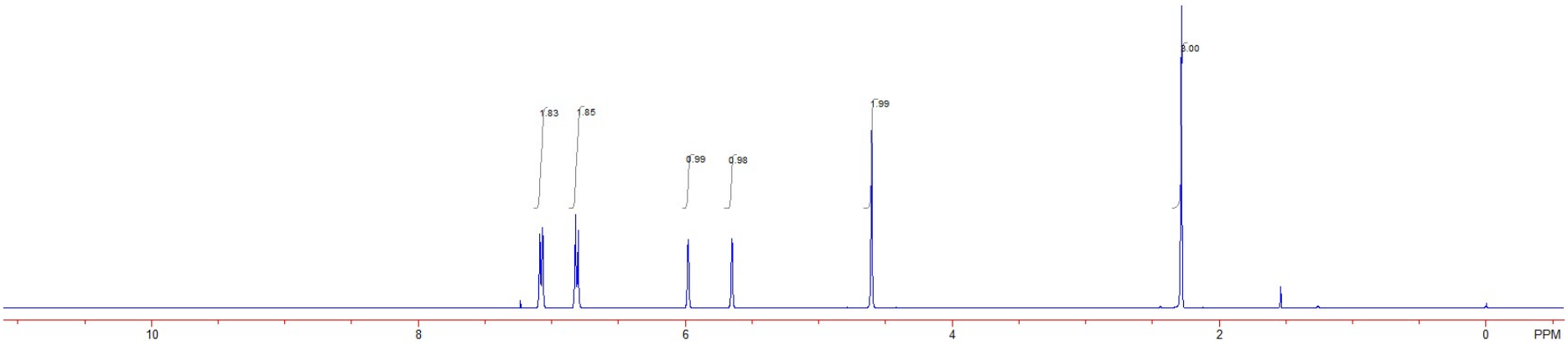
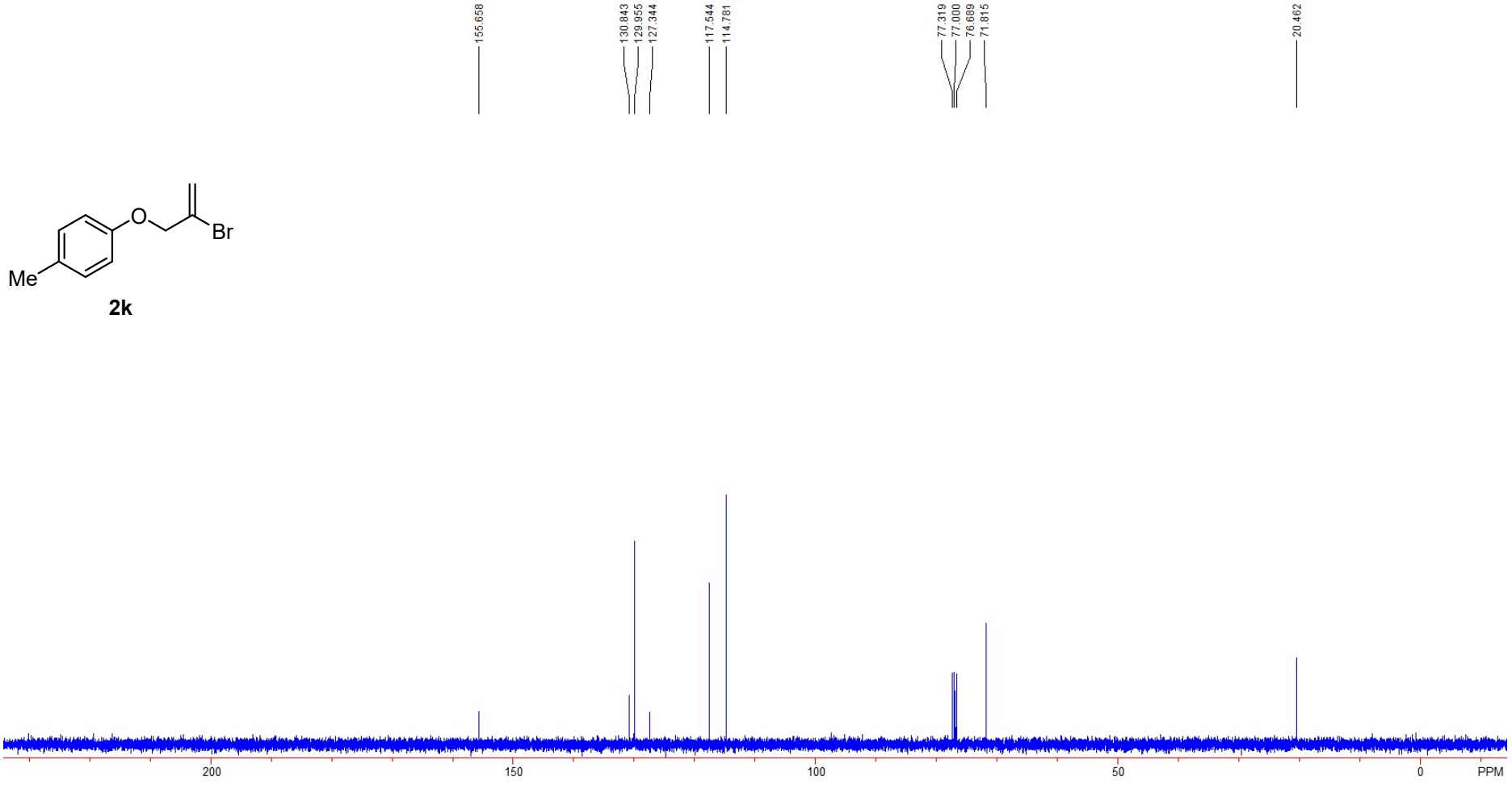
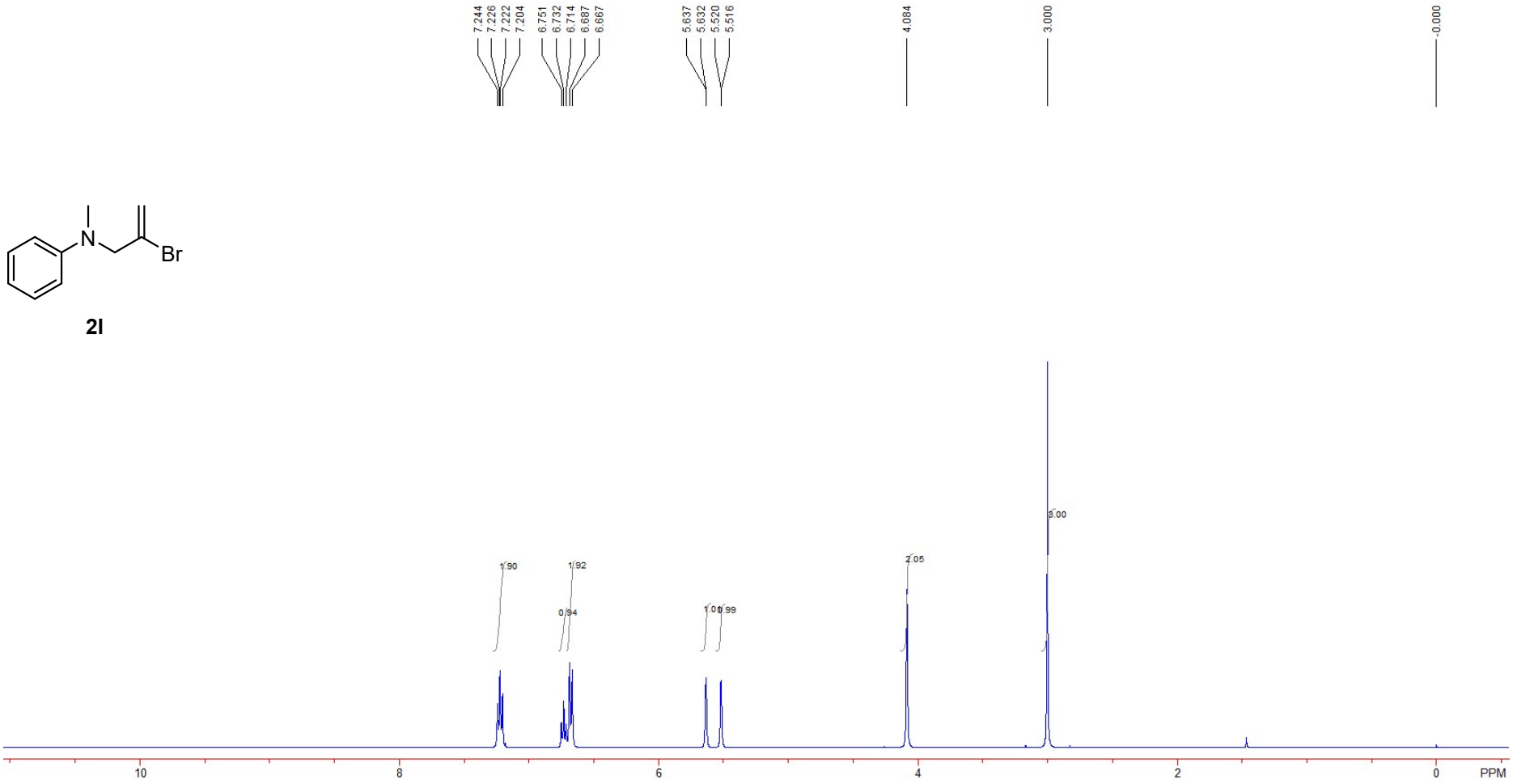


^{13}C NMR (100 MHz, in $CDCl_3$)



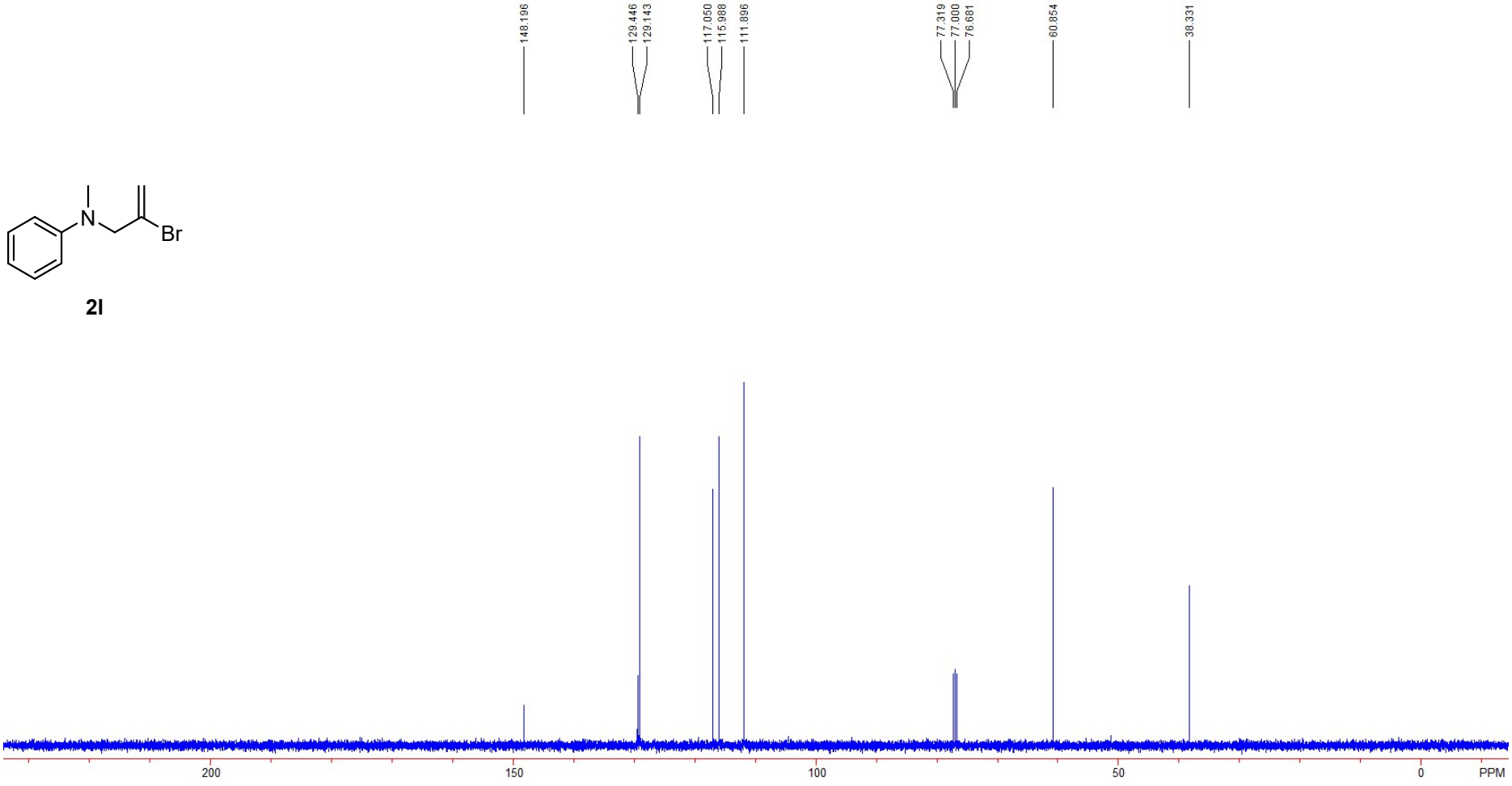
2k

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



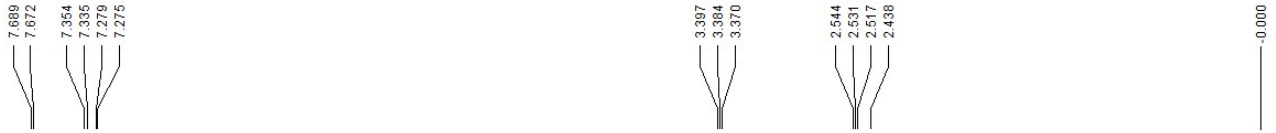
2l

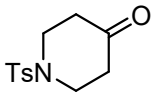
^{13}C NMR (100 MHz, in $CDCl_3$)



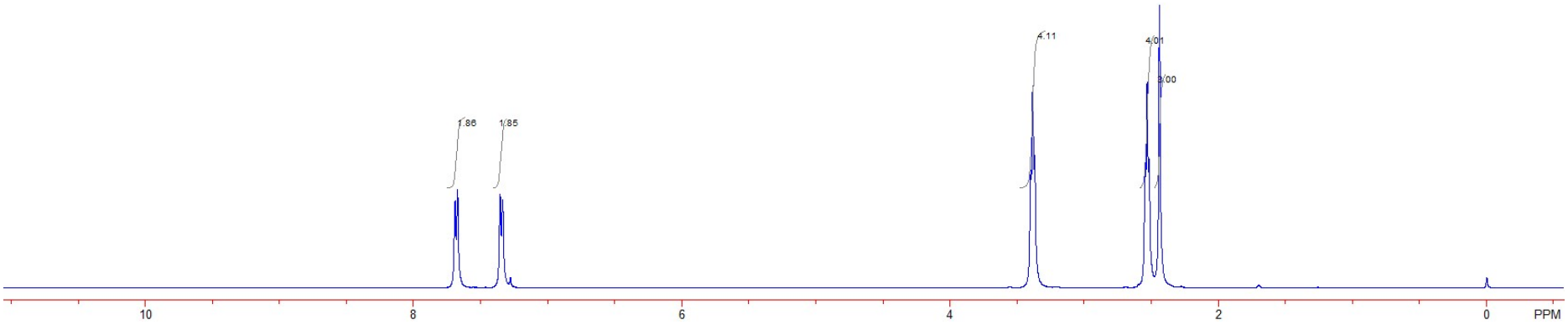
2l

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

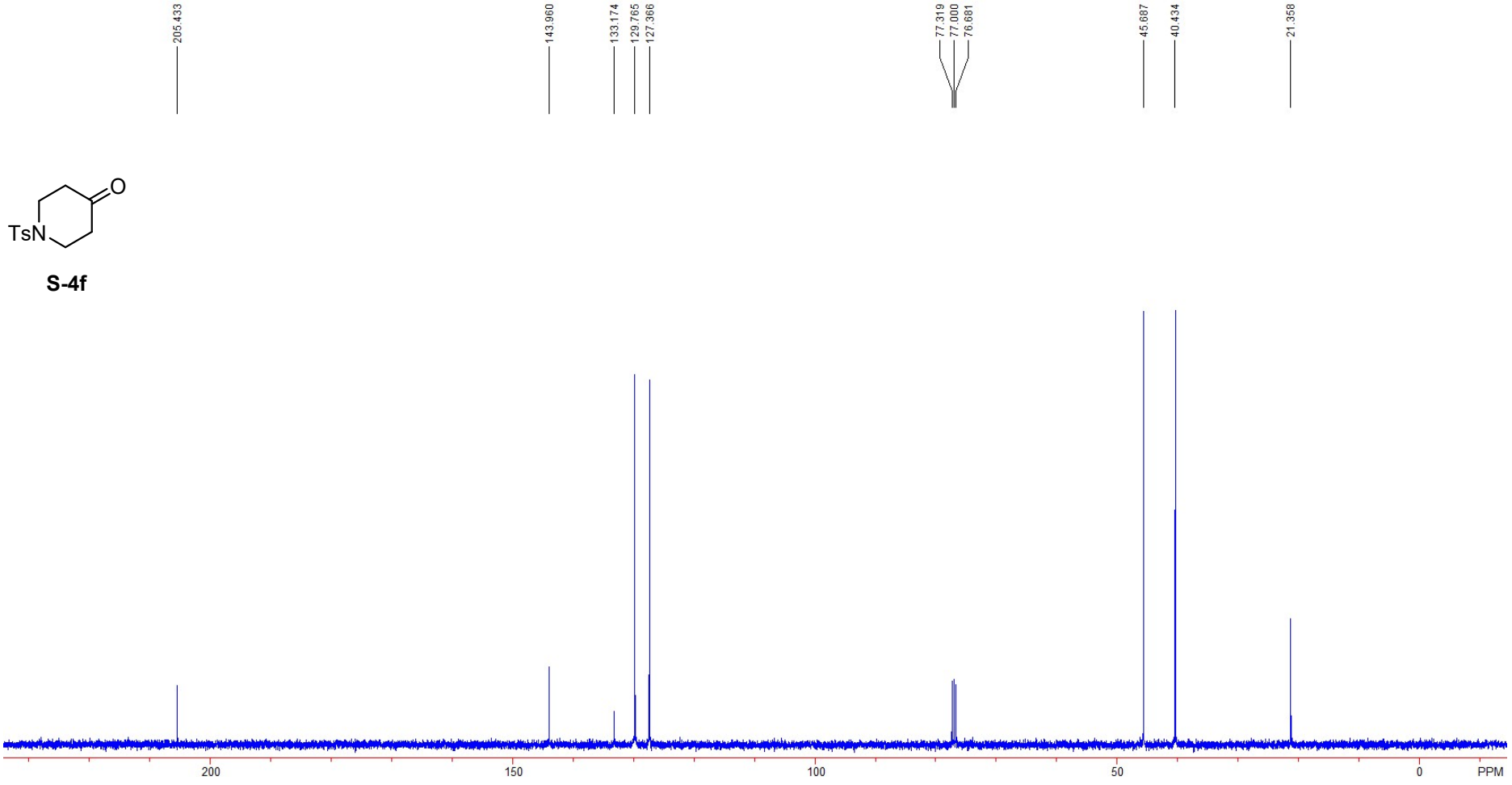




S-4f

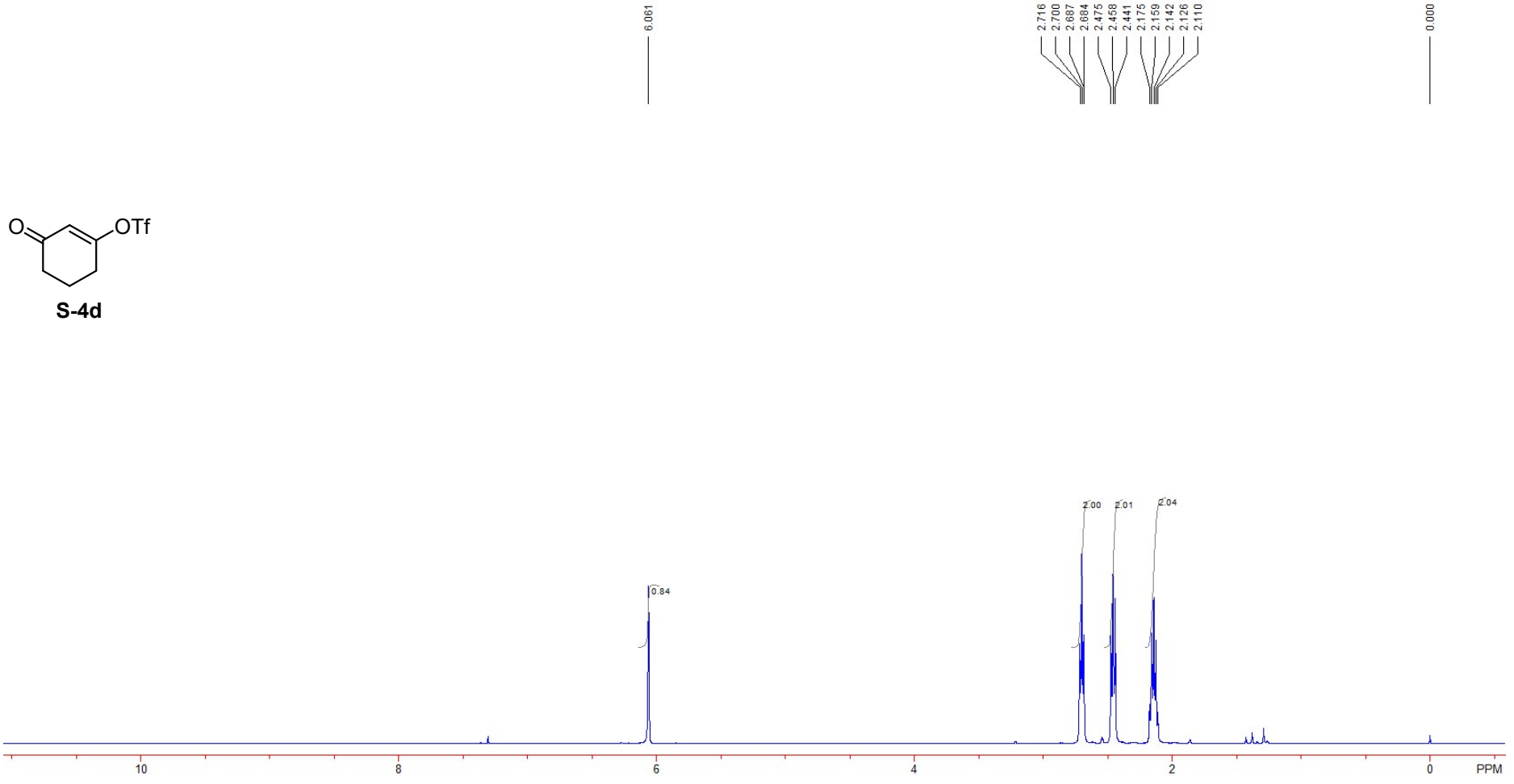


^{13}C NMR (100 MHz, in $CDCl_3$)



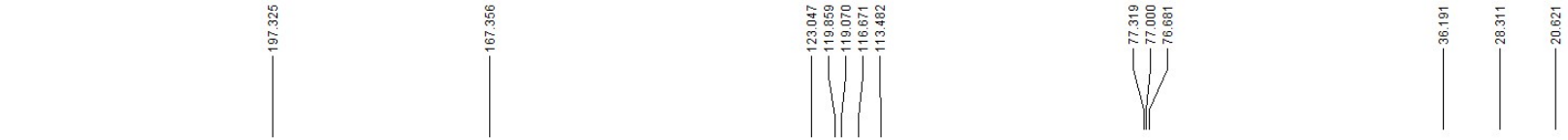
S-4f

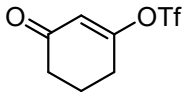
^{1}H NMR (400 MHz, in $CDCl_3$)



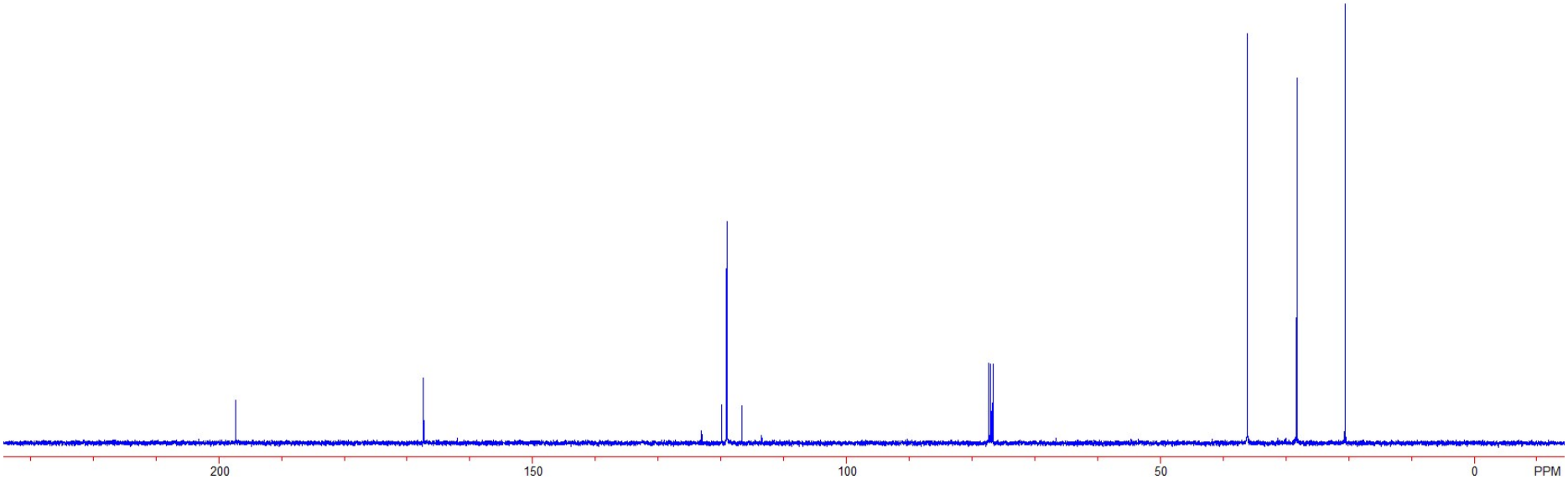
S-4d

^{13}C NMR (100 MHz, in $CDCl_3$)

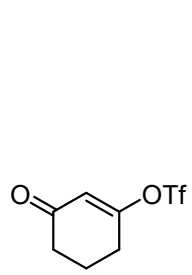




S-4d

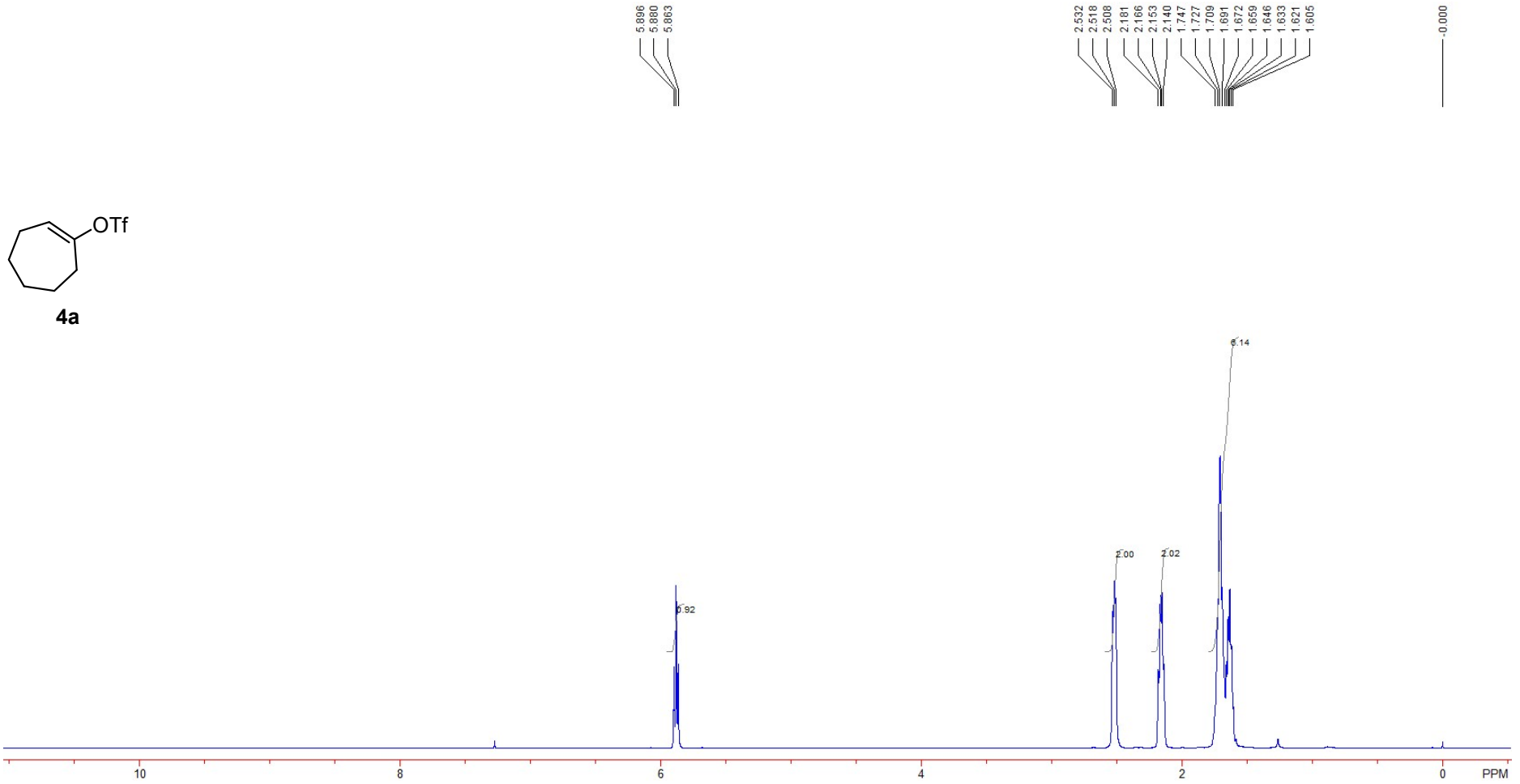


^{19}F NMR (376 MHz, in $CDCl_3$)

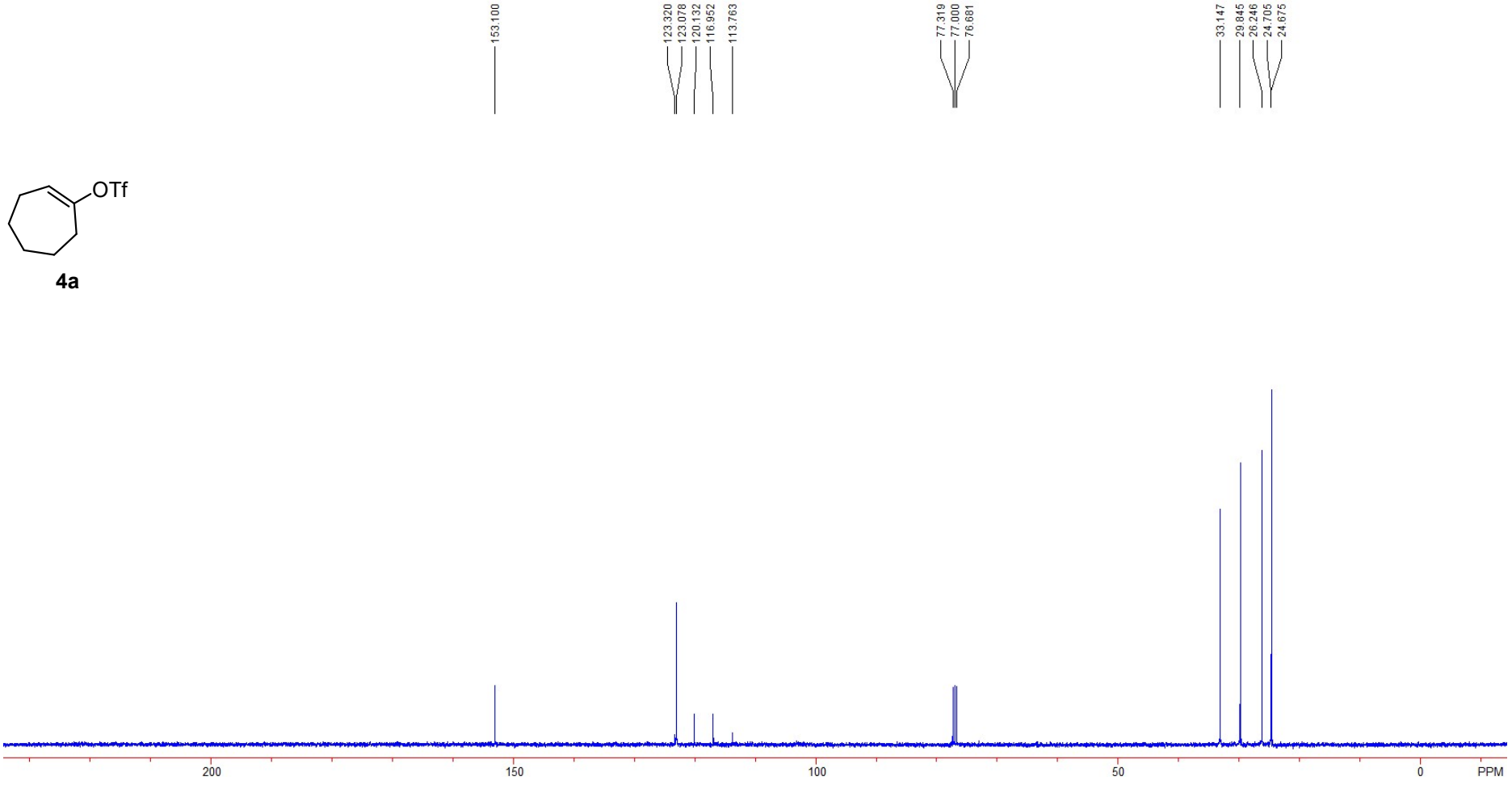


S-4d

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

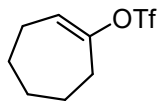


^{13}C NMR (100 MHz, in $CDCl_3$)



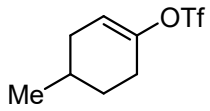
4a

^{19}F NMR (376 MHz, in $CDCl_3$)

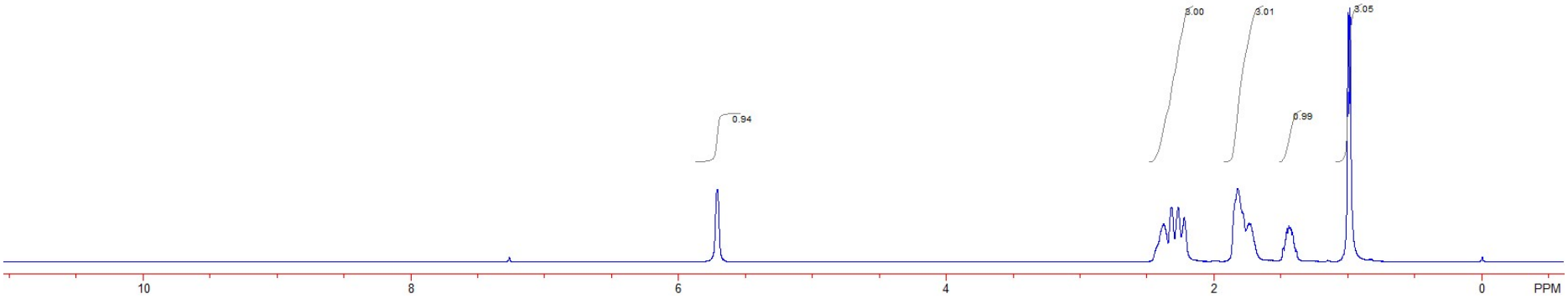


4a

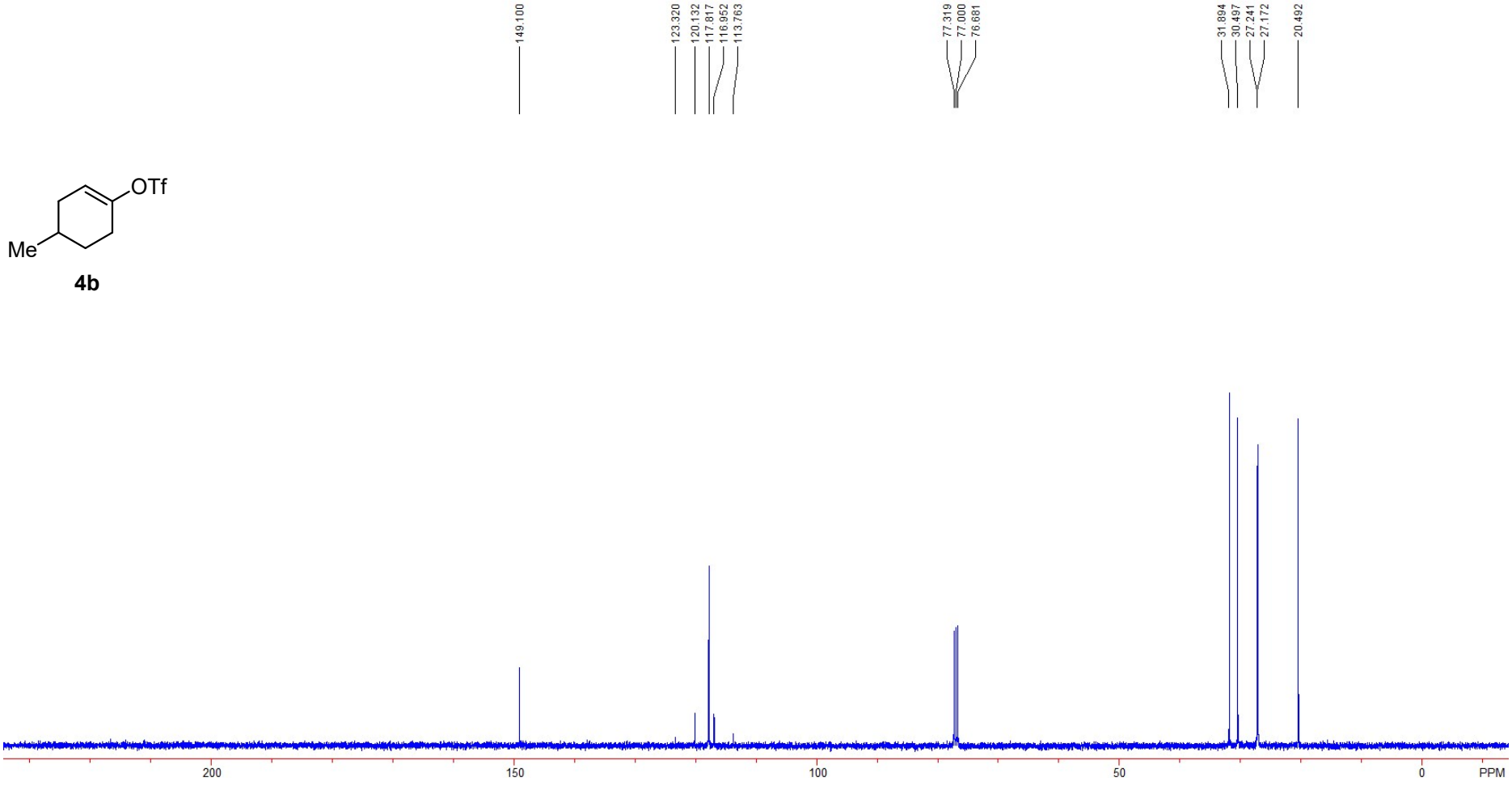
^{1}H NMR (400 MHz, in $CDCl_3$)



4b

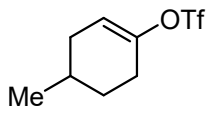


^{13}C NMR (100 MHz, in $CDCl_3$)



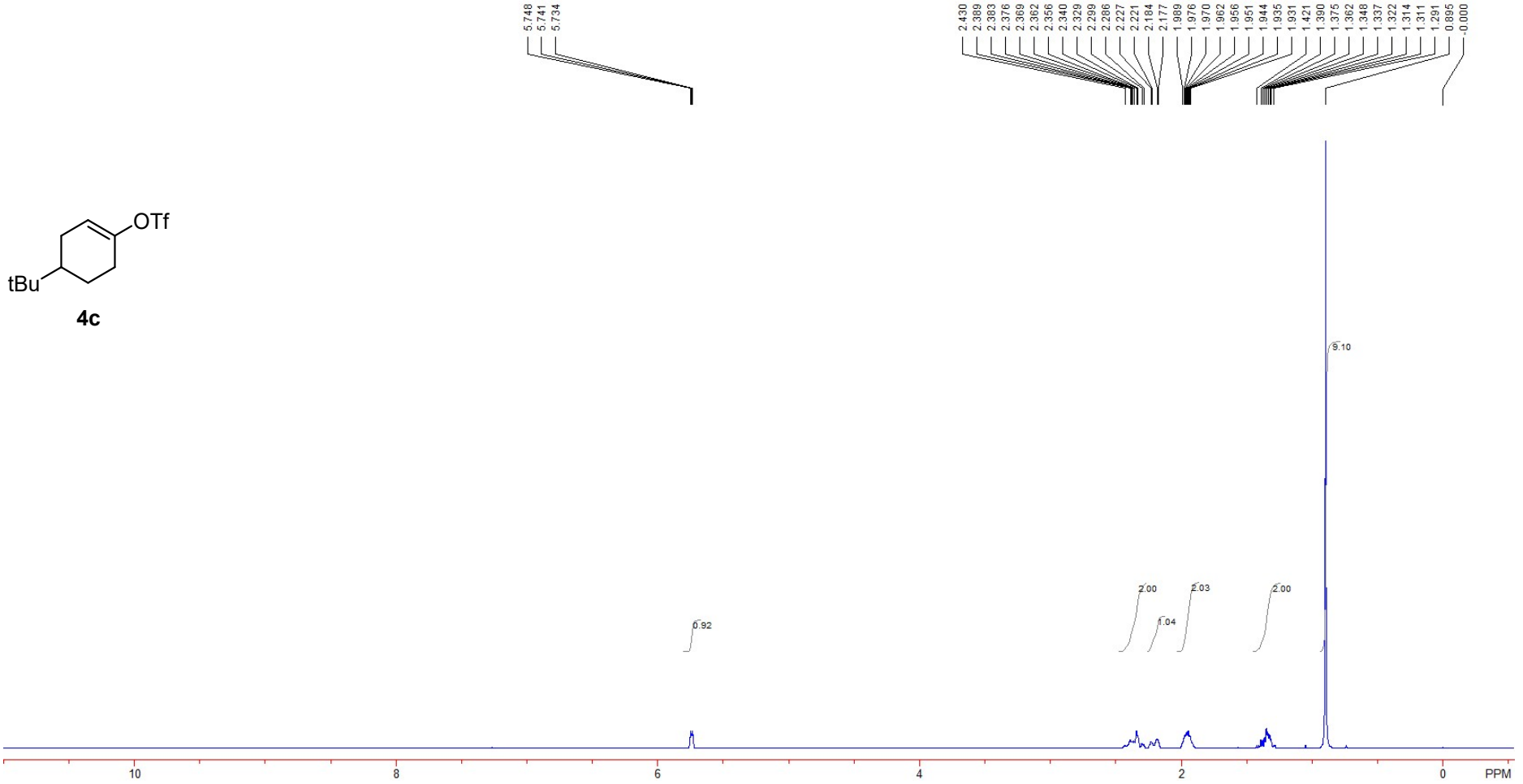
4b

^{19}F NMR (376 MHz, in $CDCl_3$)

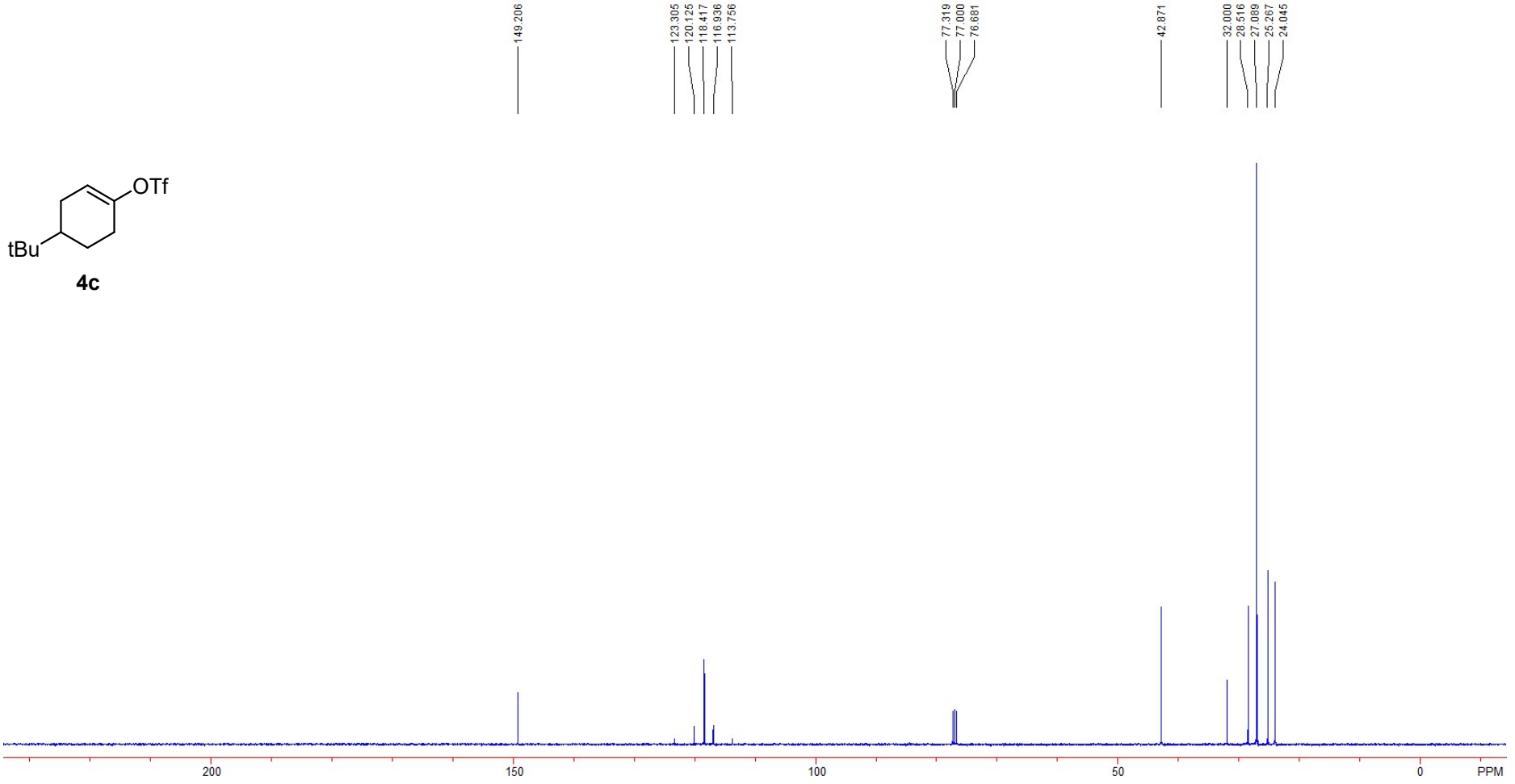


4b

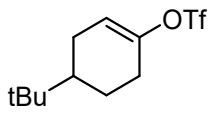
^{1}H NMR (400 MHz, in $CDCl_3$)



^{13}C NMR (100 MHz, in $CDCl_3$)

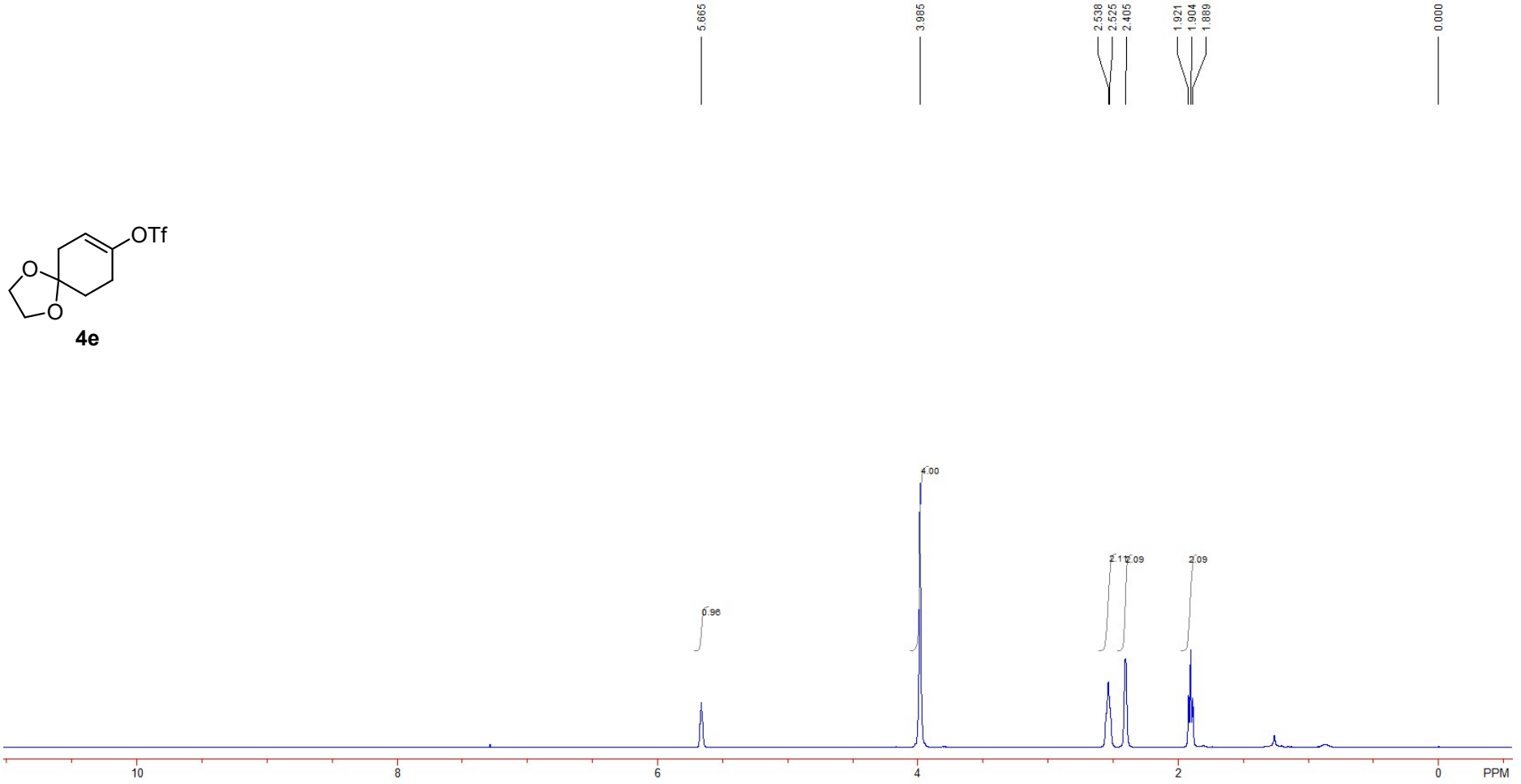


^{19}F NMR (376 MHz, in $CDCl_3$)

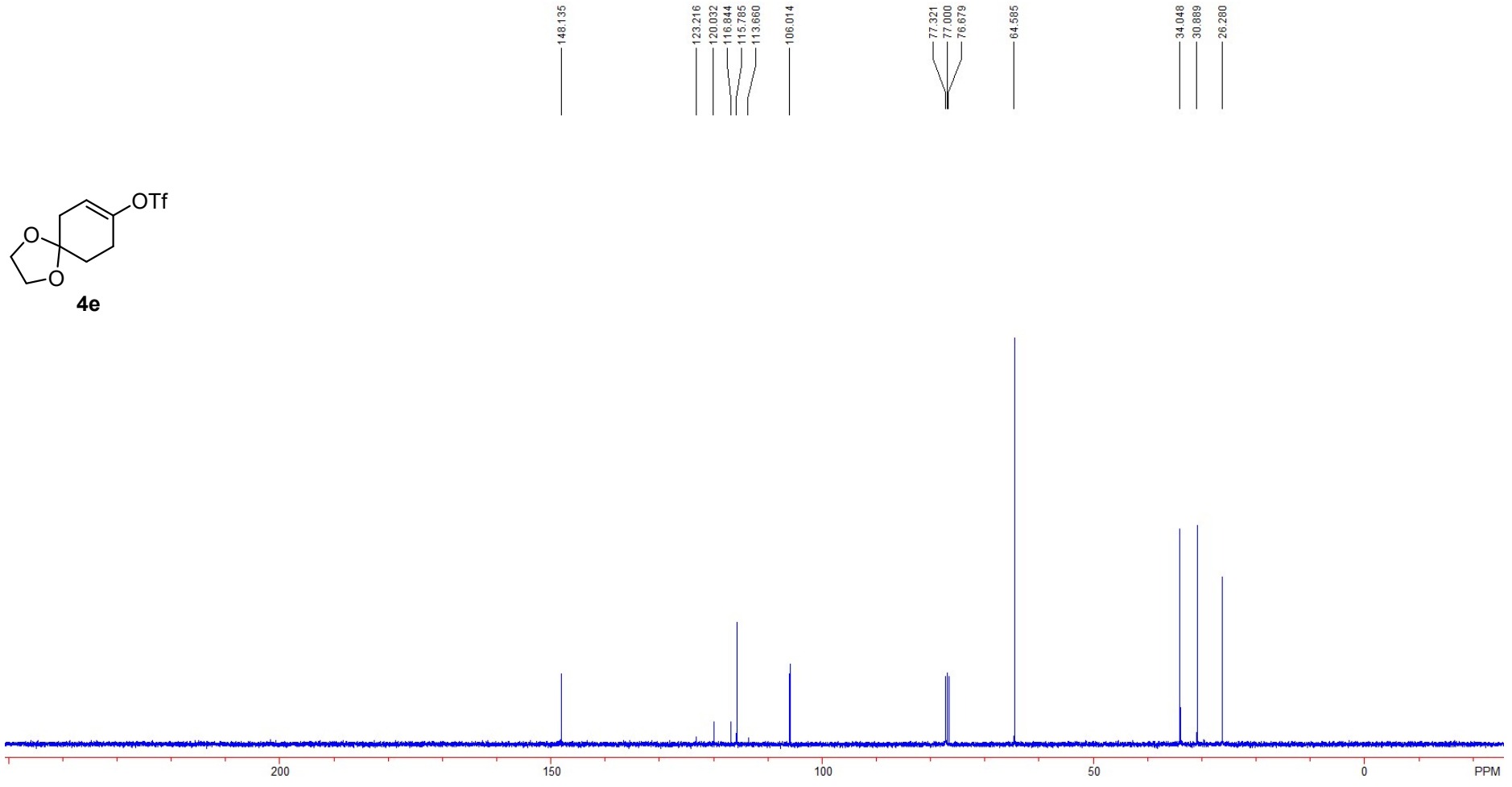


4c

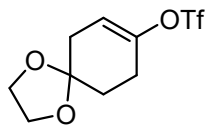
^{1}H NMR (400 MHz, in $CDCl_3$)



^{13}C NMR (100 MHz, in $CDCl_3$)

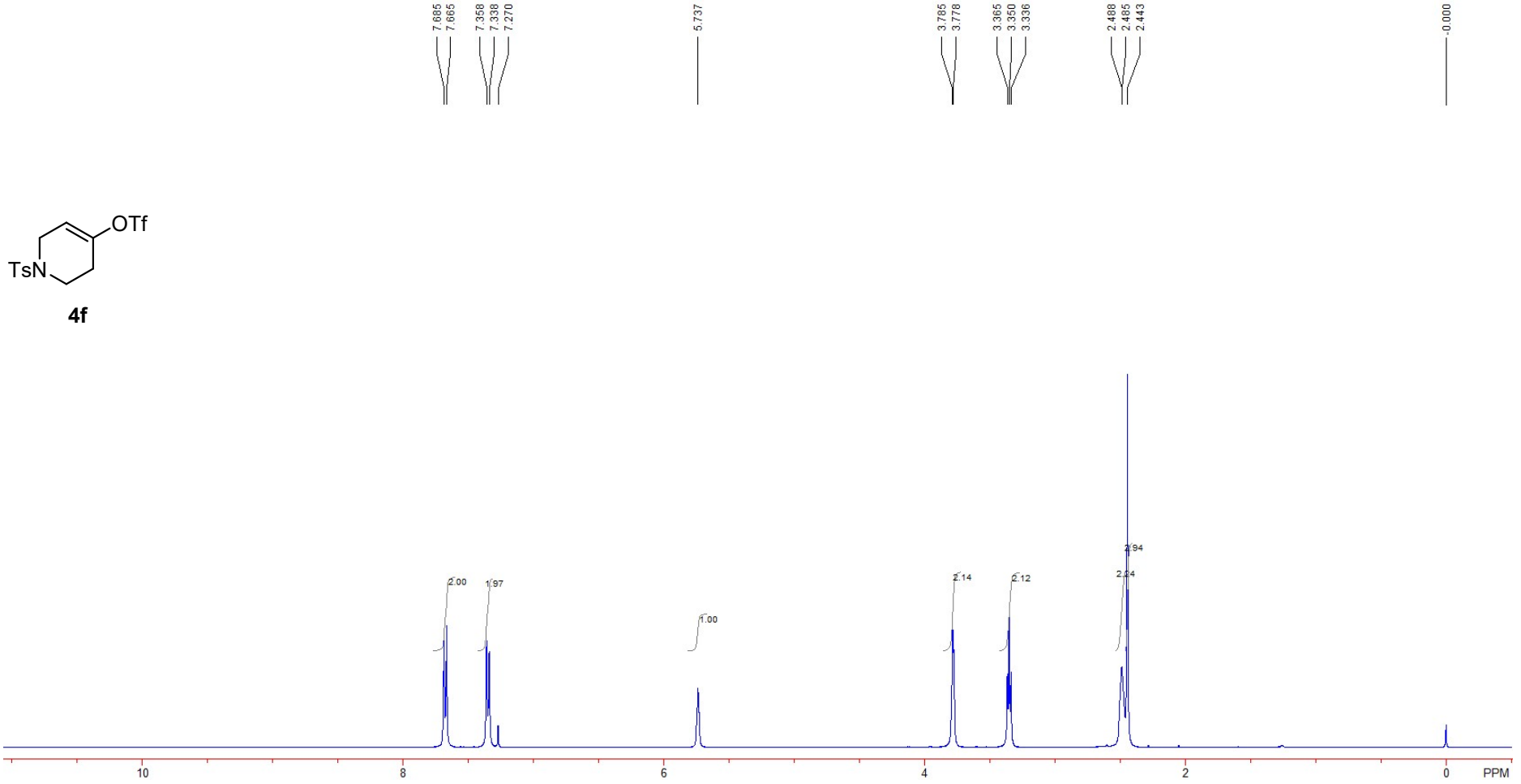


^{19}F NMR (376 MHz, in $CDCl_3$)



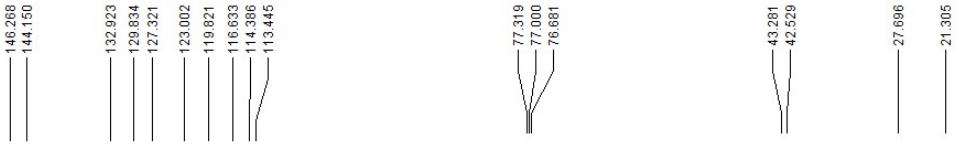
4e

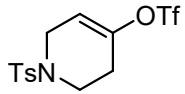
^{1}H NMR (400 MHz, in $CDCl_3$)



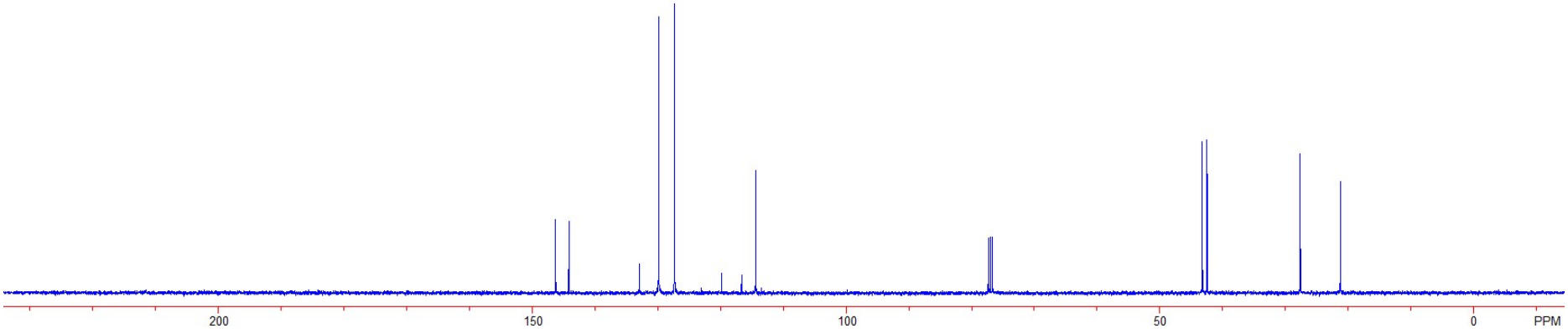
4f

^{13}C NMR (100 MHz, in $CDCl_3$)

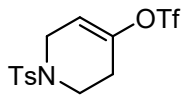




4f

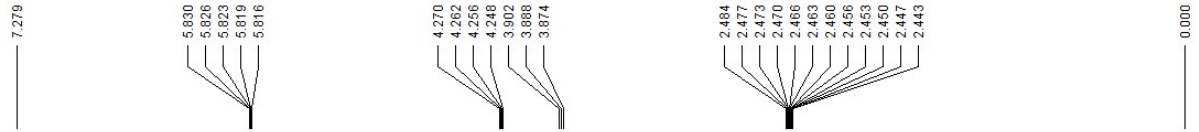


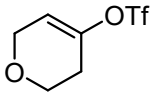
^{19}F NMR (376 MHz, in $CDCl_3$)



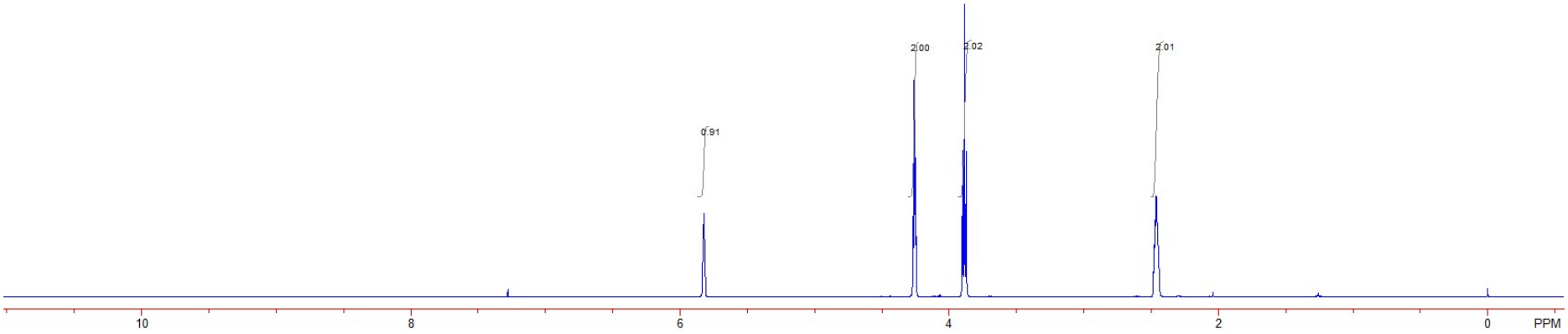
4f

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

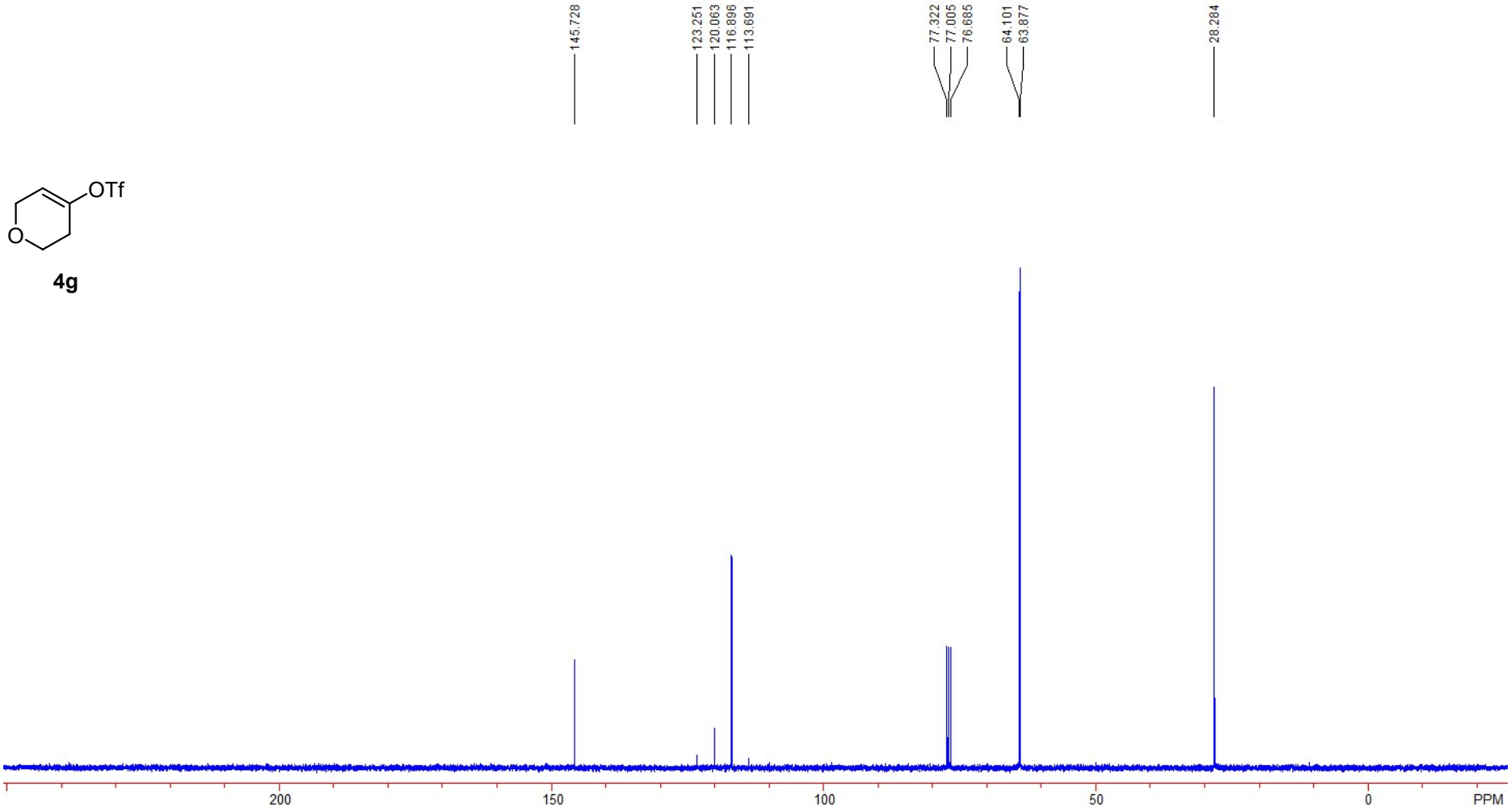




4g

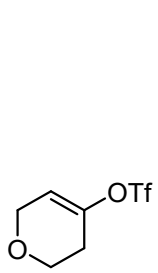


^{13}C NMR (100 MHz, in $CDCl_3$)



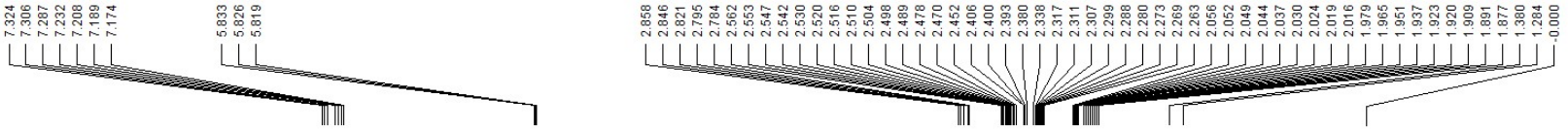
4g

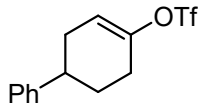
^{19}F NMR (376 MHz, in $CDCl_3$)



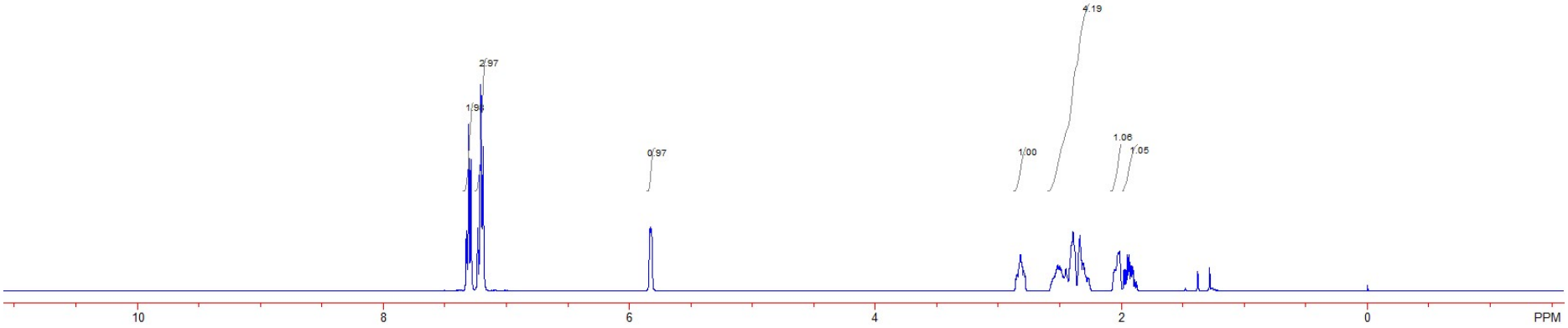
4g

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

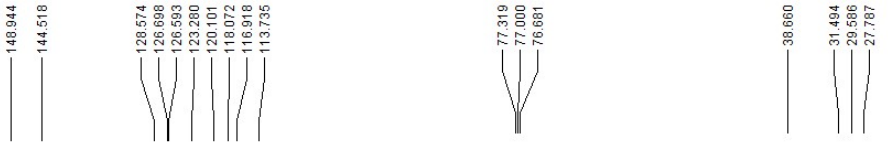


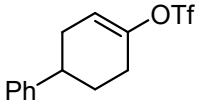


4h



^{13}C NMR (100 MHz, in $CDCl_3$)





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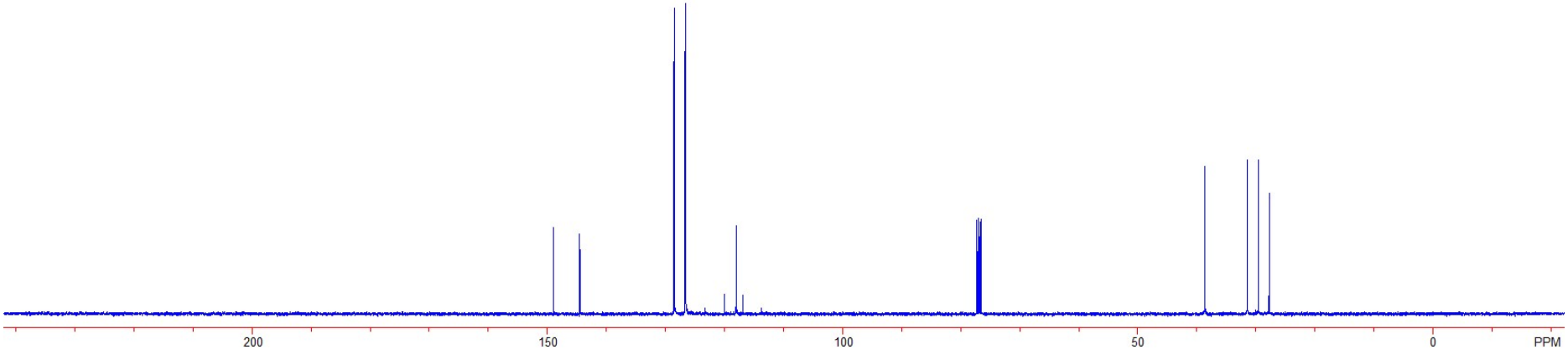
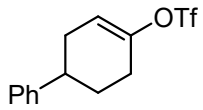
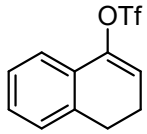


^{19}F NMR (376 MHz, in $CDCl_3$)

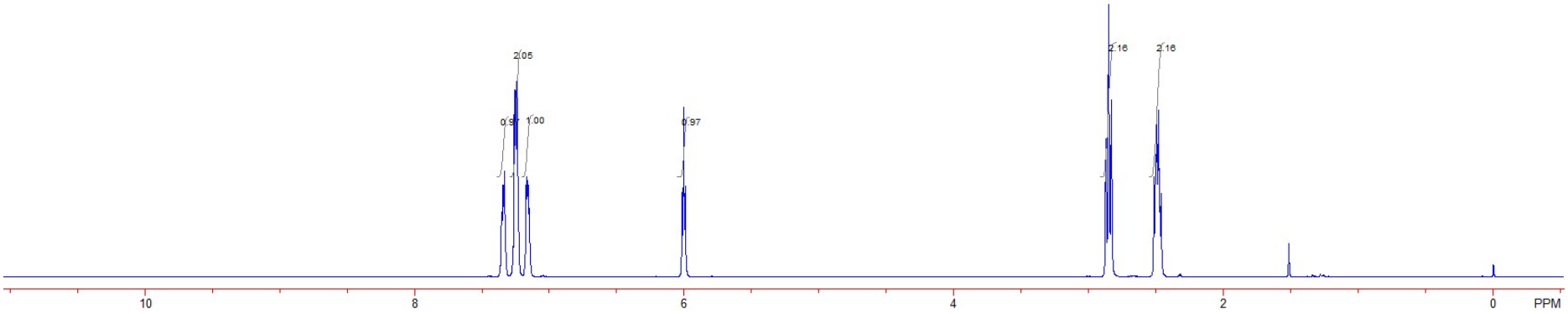


4h

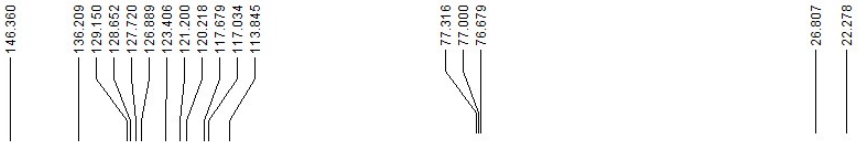
^{1}H NMR (400 MHz, in $CDCl_3$)

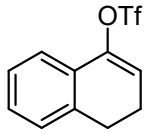


4j



^{13}C NMR (100 MHz, in $CDCl_3$)





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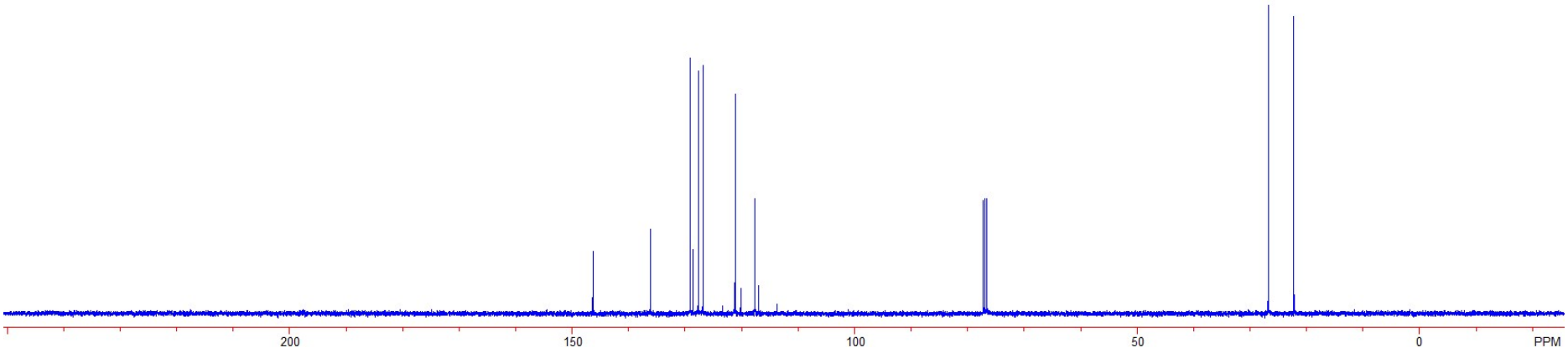
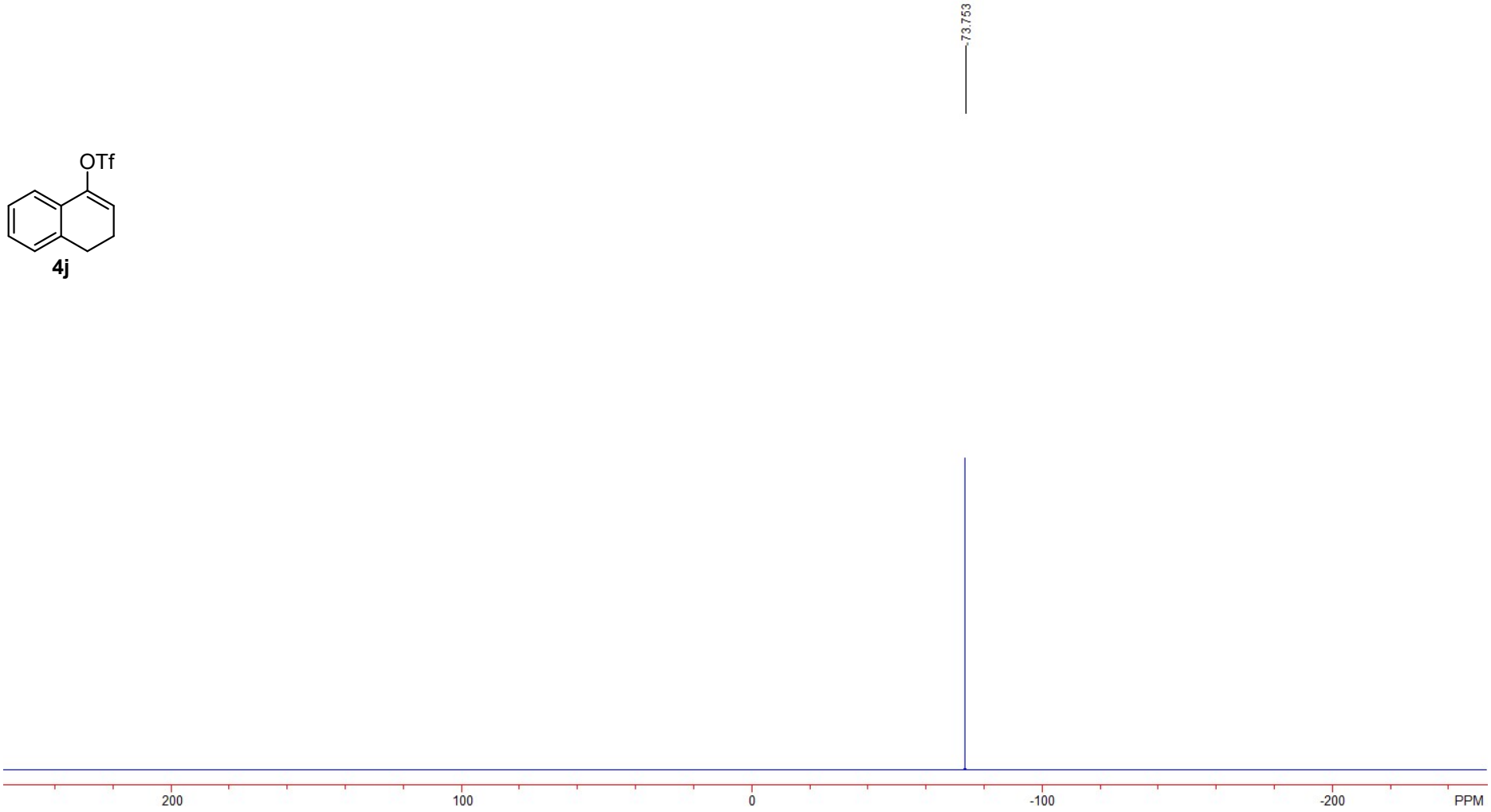
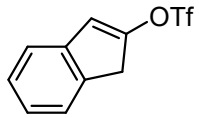


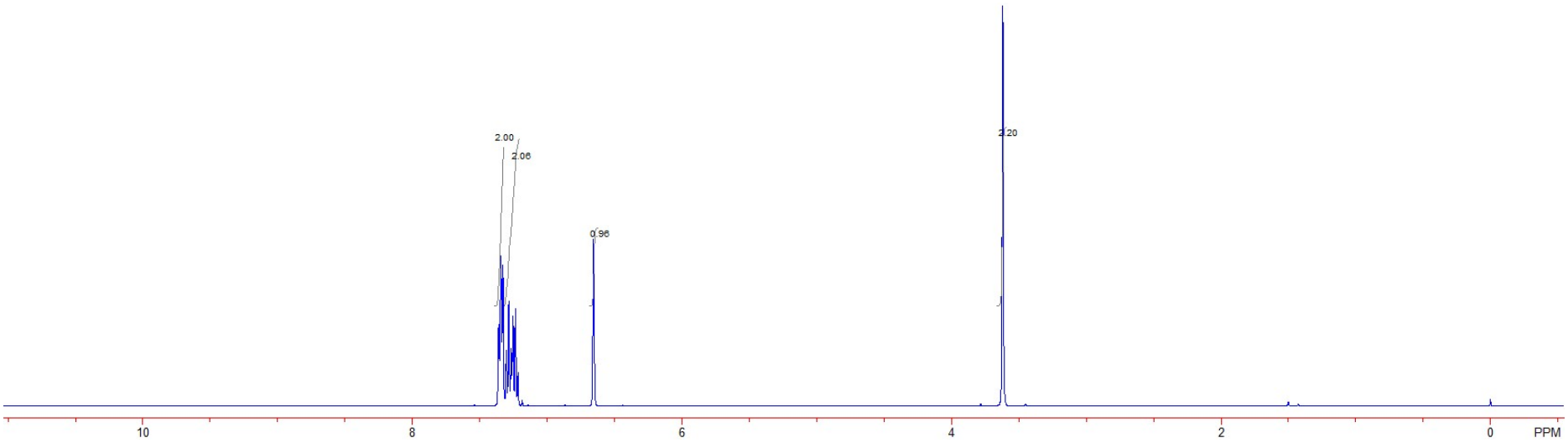
^{19}F NMR (376 MHz, in $CDCl_3$)



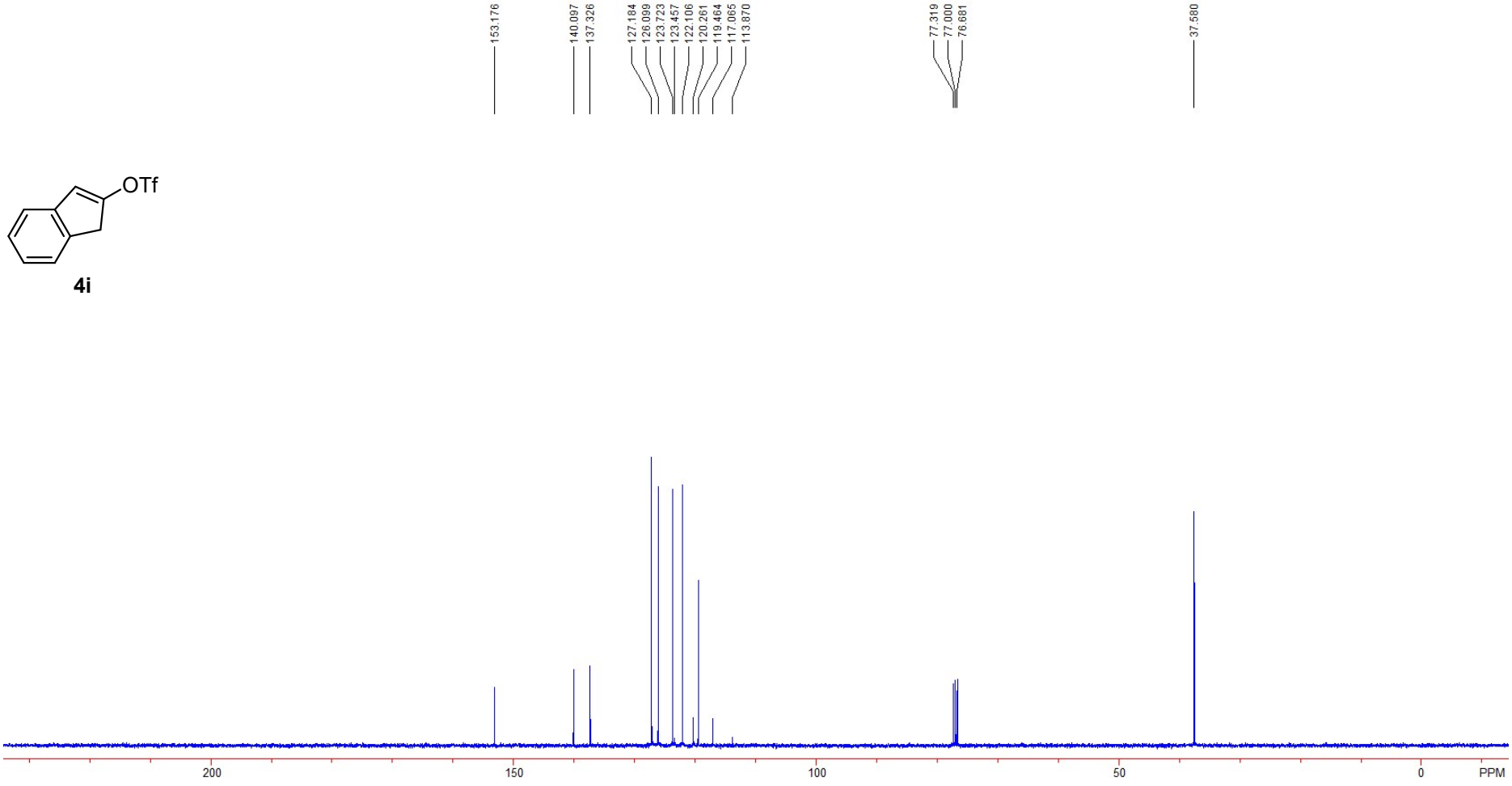
^{1}H NMR (400 MHz, in $CDCl_3$)



4i

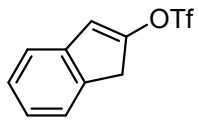


^{13}C NMR (100 MHz, in $CDCl_3$)



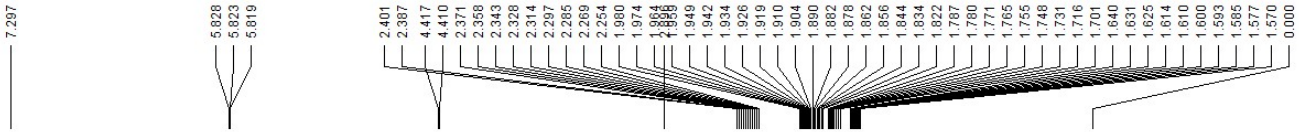
4i

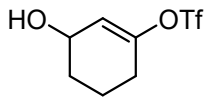
^{19}F NMR (376 MHz, in $CDCl_3$)



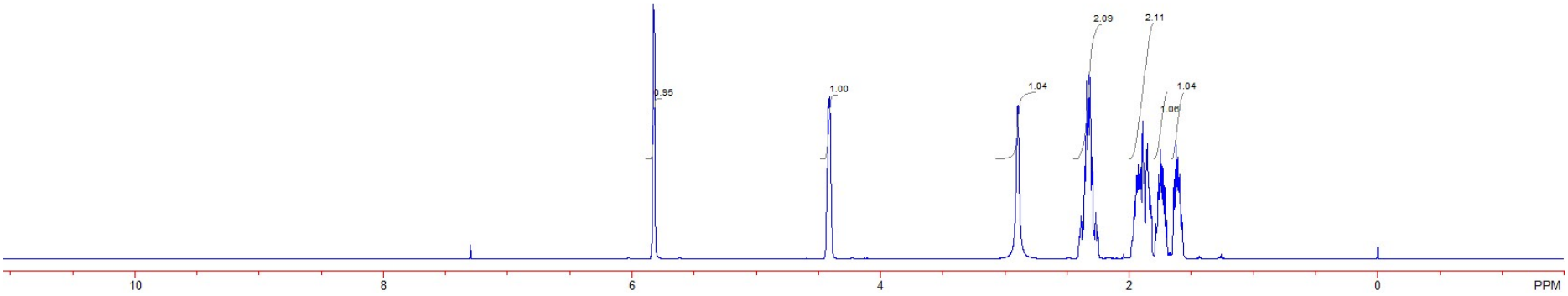
4i

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

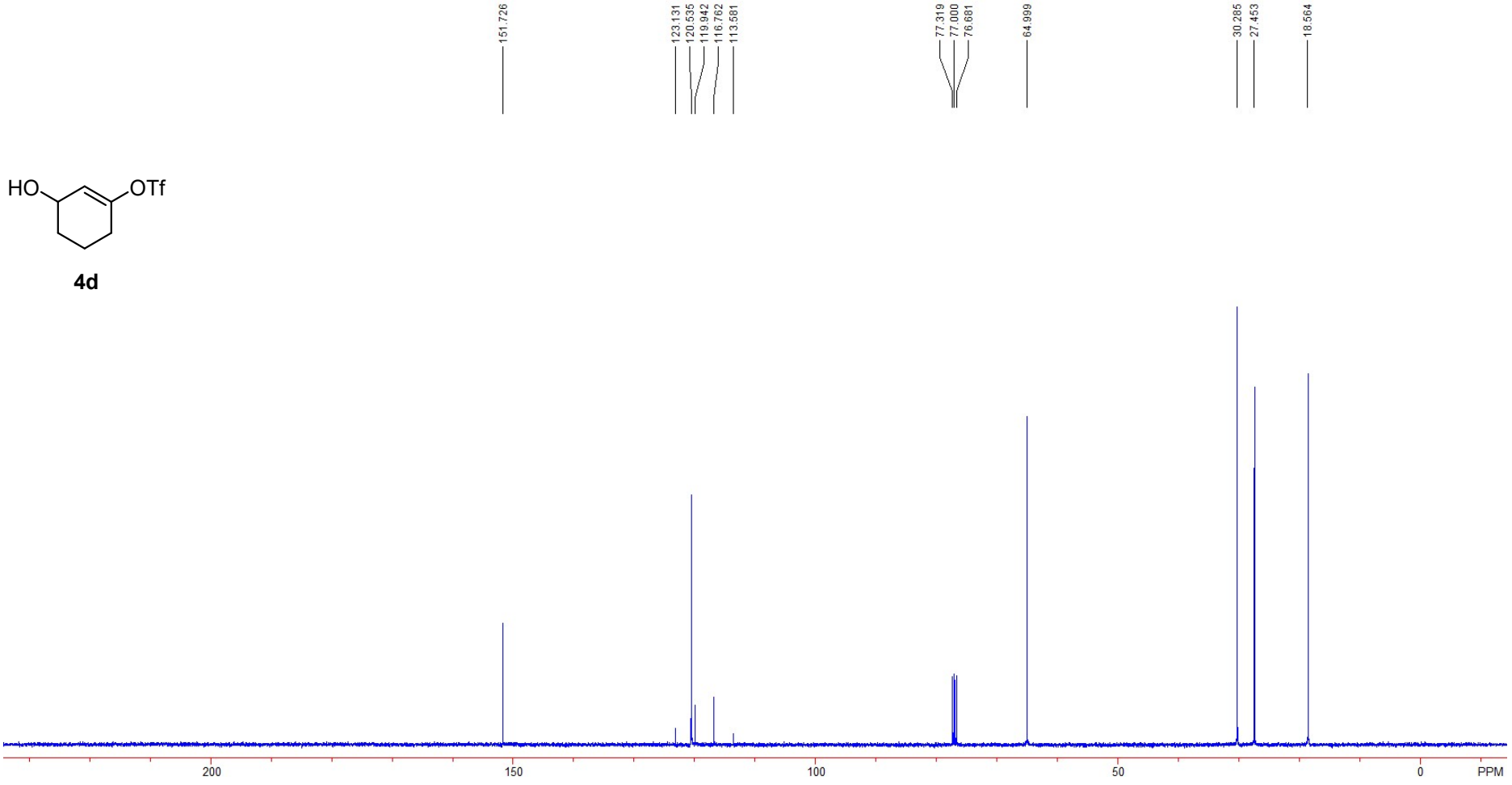




4d

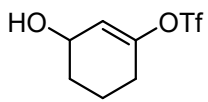


^{13}C NMR (100 MHz, in $CDCl_3$)



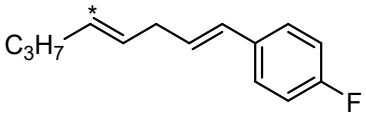
4d

^{19}F NMR (376 MHz, in $CDCl_3$)

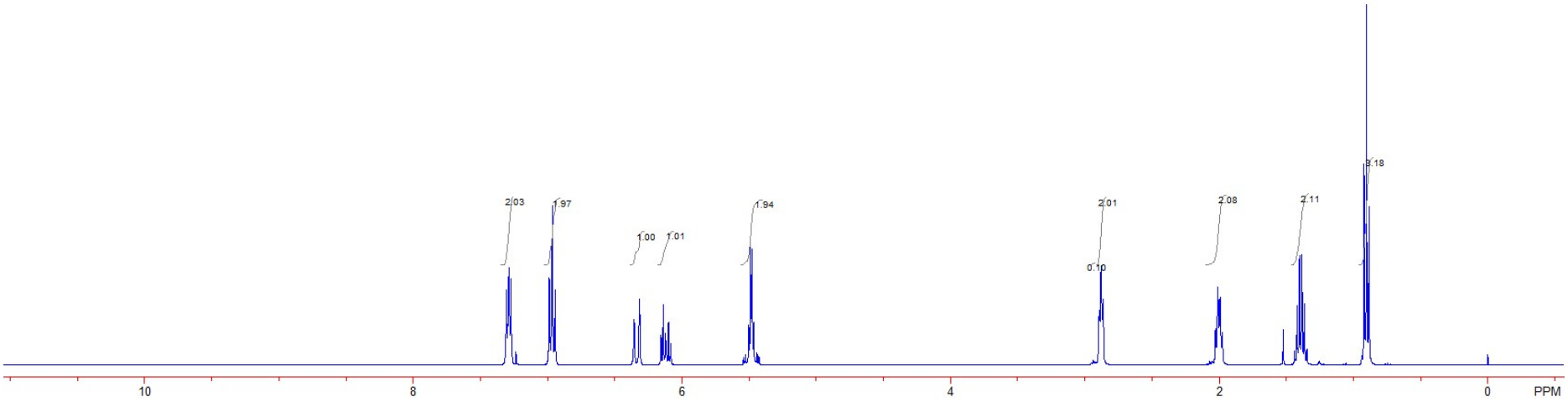


4d

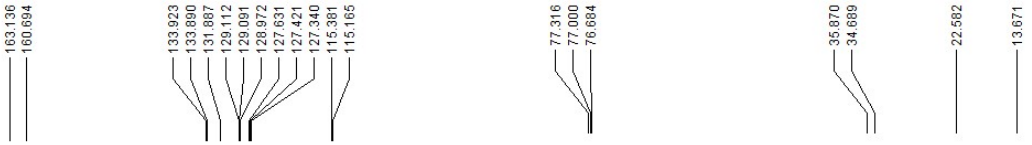
^{1}H NMR (400 MHz, in $CDCl_3$)

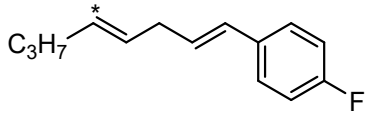


3a (*E*:*Z* = ca.19.6:1)

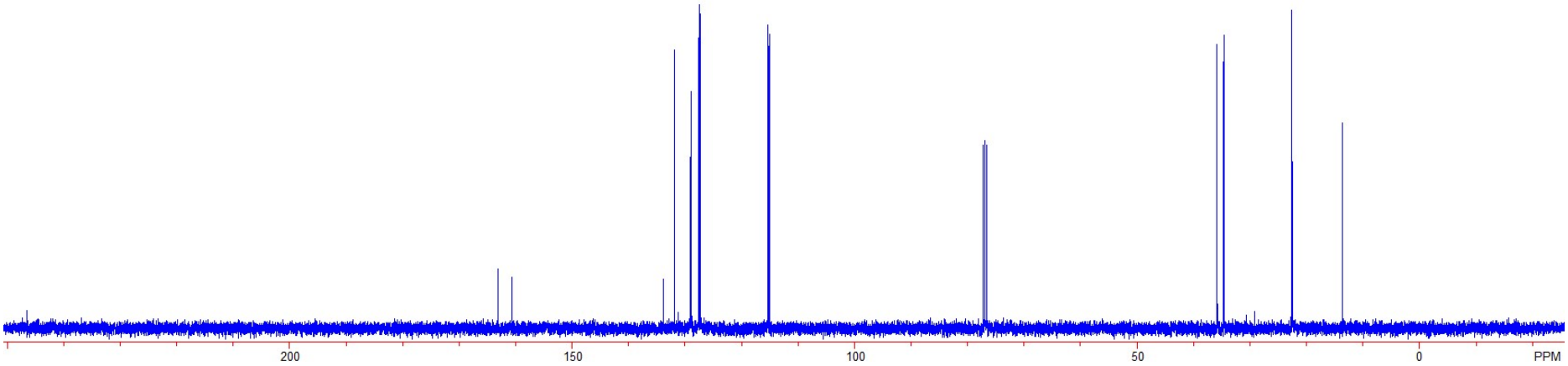


^{13}C NMR (100 MHz, in $CDCl_3$)

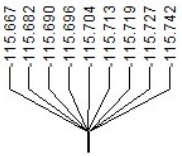


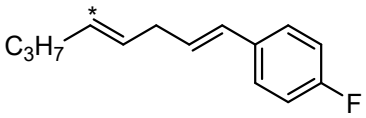


3a (*E*:*Z* = ca.19.6:1)

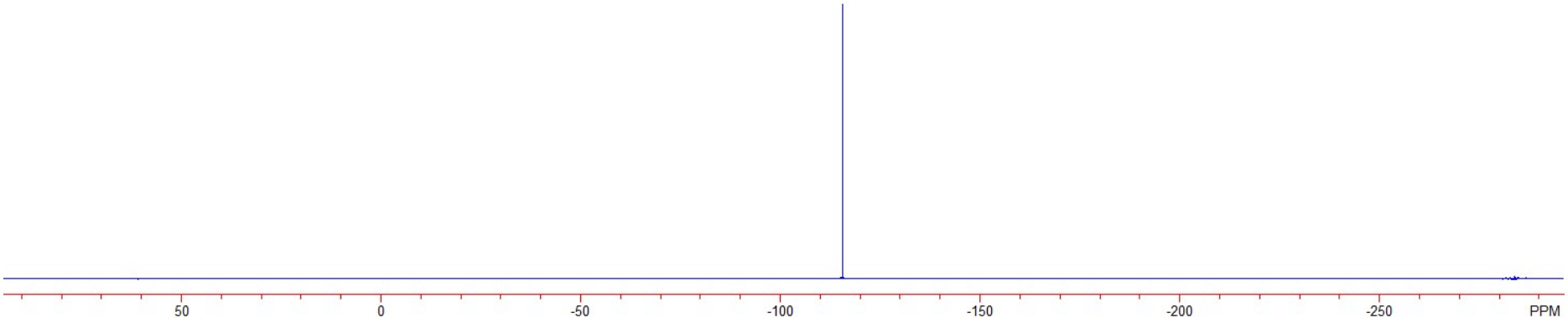


^{19}F NMR (376 MHz, in $CDCl_3$)

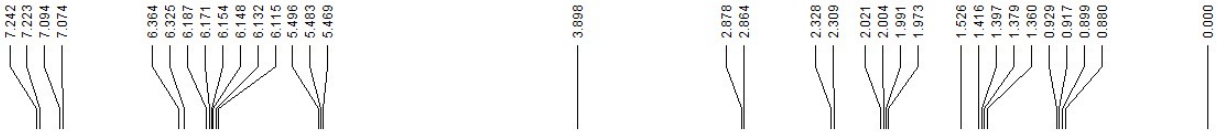


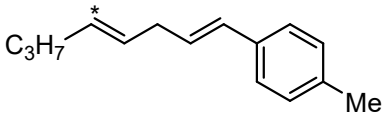


3a (*E*:*Z* = ca.19.6:1)

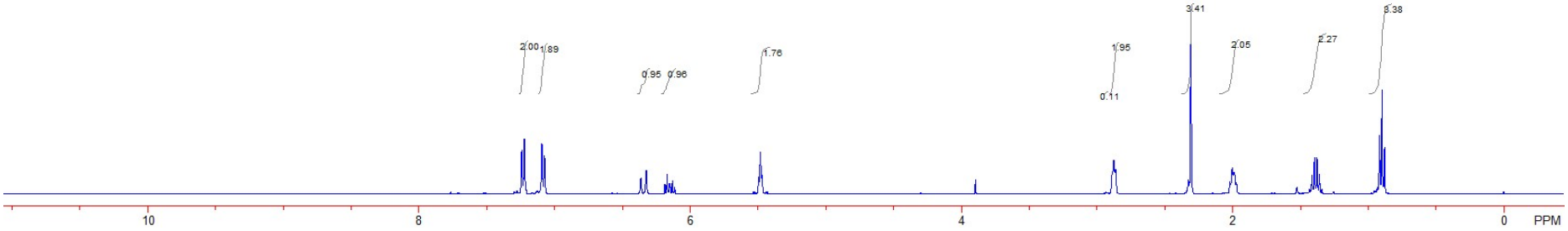


^{1}H NMR (400 MHz, in $CDCl_3$)

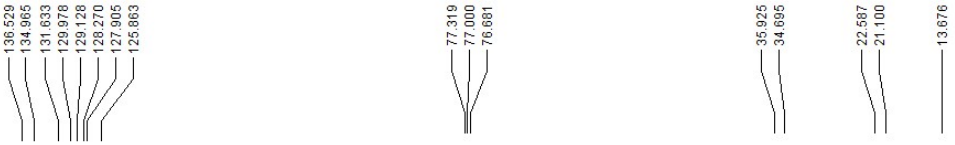


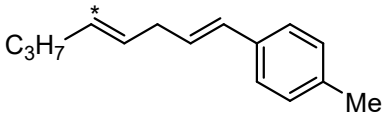


3b (*E*:*Z* = ca.18:1)

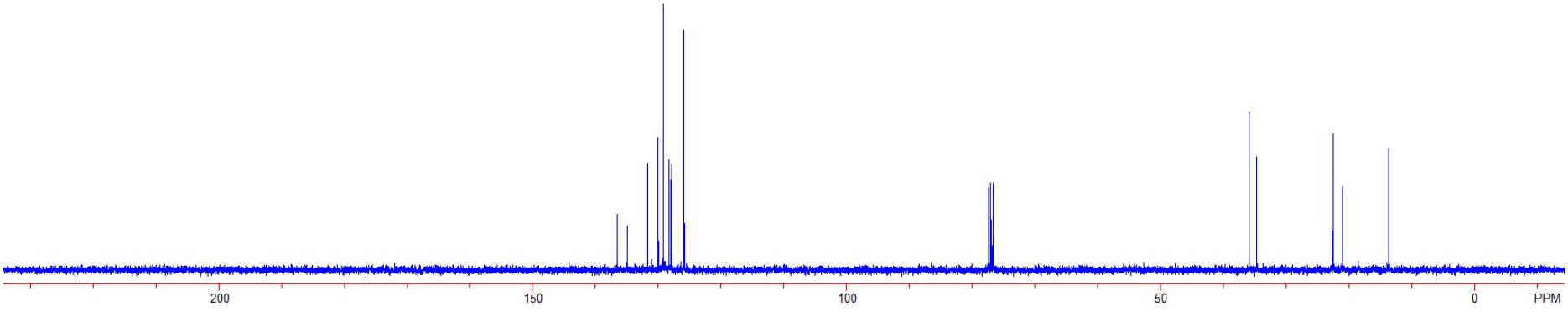


^{13}C NMR (100 MHz, in $CDCl_3$)

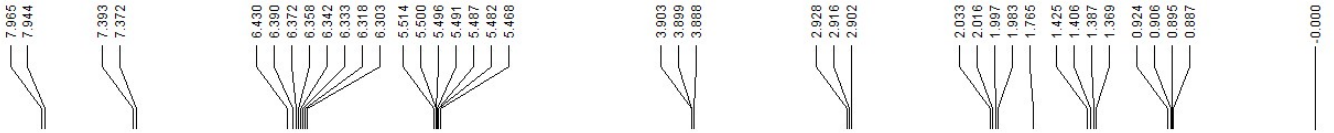


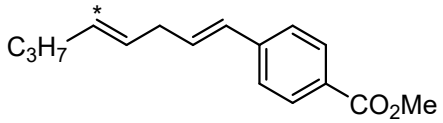


3b (*E*:*Z* = ca.18:1)

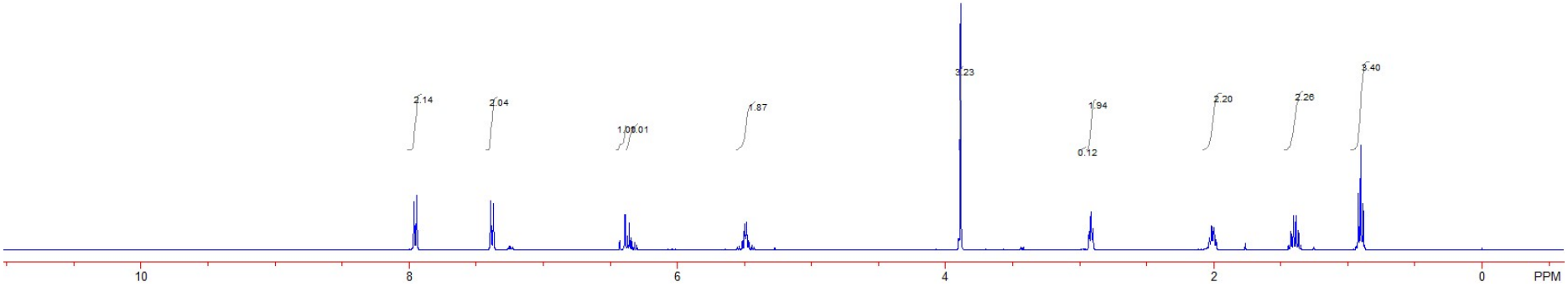


^{1}H NMR (400 MHz, in $CDCl_3$)

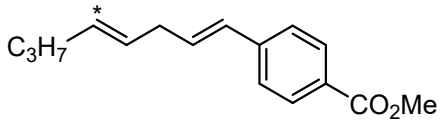




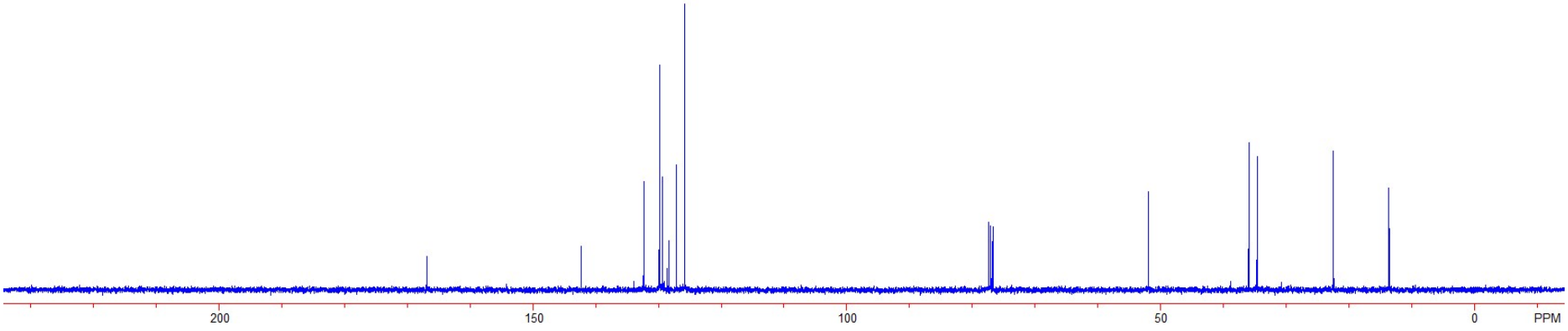
3c (*E*:*Z* = ca.16:1)



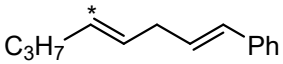
^{13}C NMR (100 MHz, in $CDCl_3$)



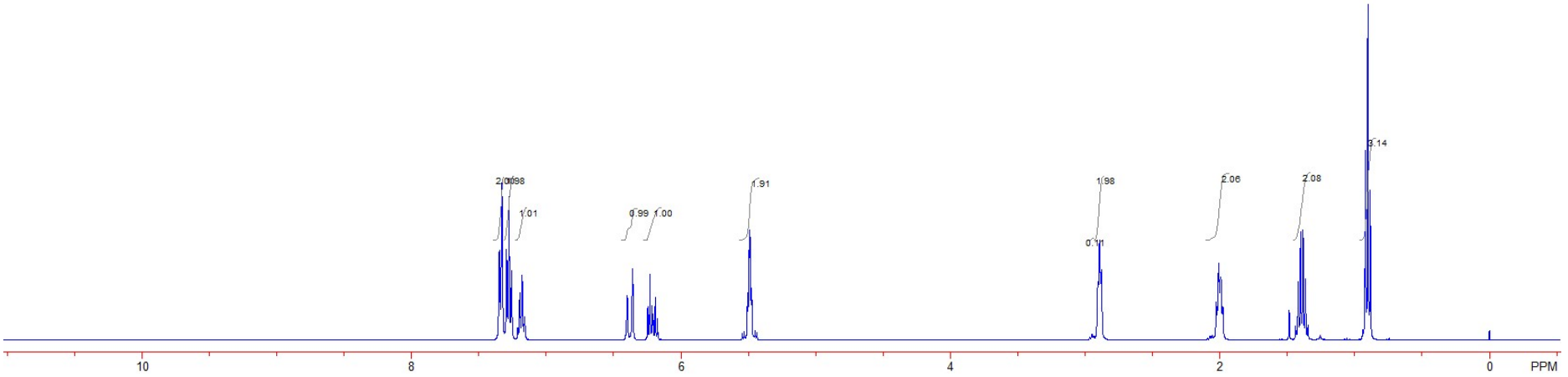
3c (*E*:*Z* = ca.16:1)



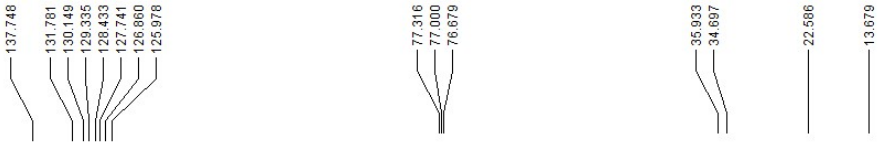
^{1}H NMR (400 MHz, in $CDCl_3$)

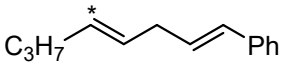


3d (*E*:*Z* = ca. 18:1)

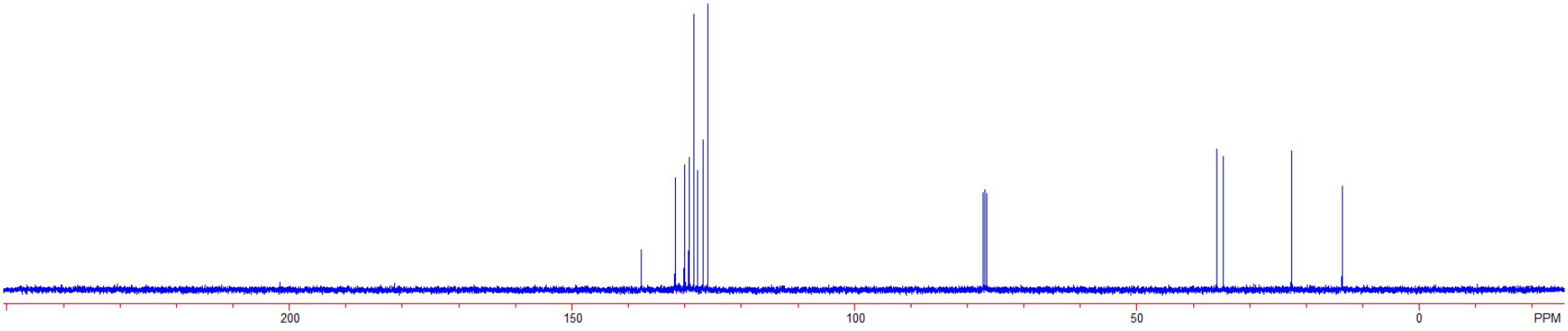


^{13}C NMR (100 MHz, in $CDCl_3$)

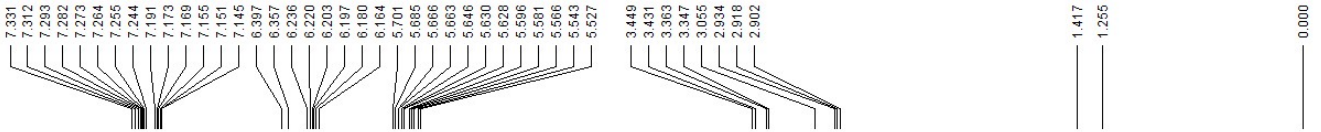


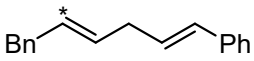


3d (*E*:*Z* = ca. 18:1)

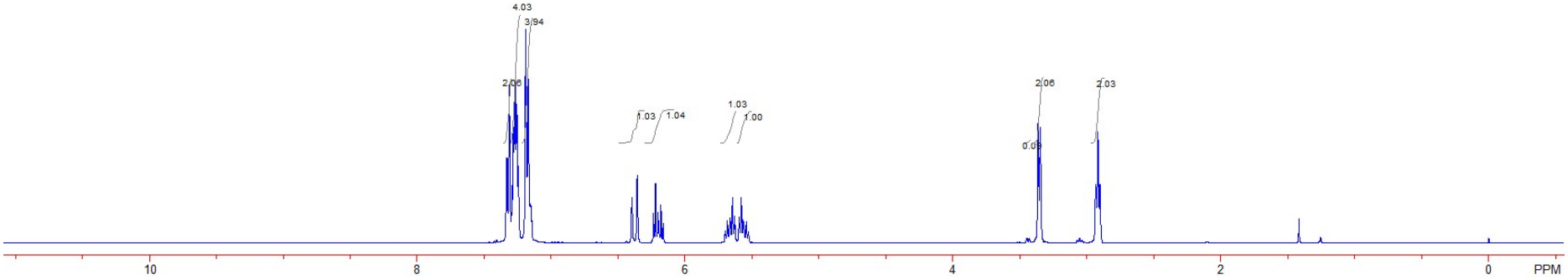


^{1}H NMR (400 MHz, in $CDCl_3$)

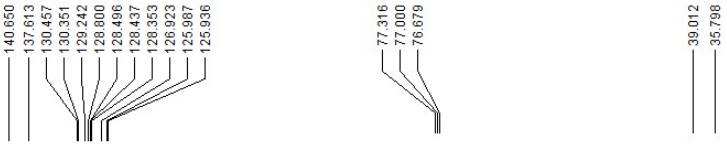


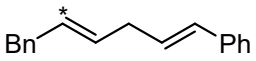


3e (*E*:*Z* > 20:1)

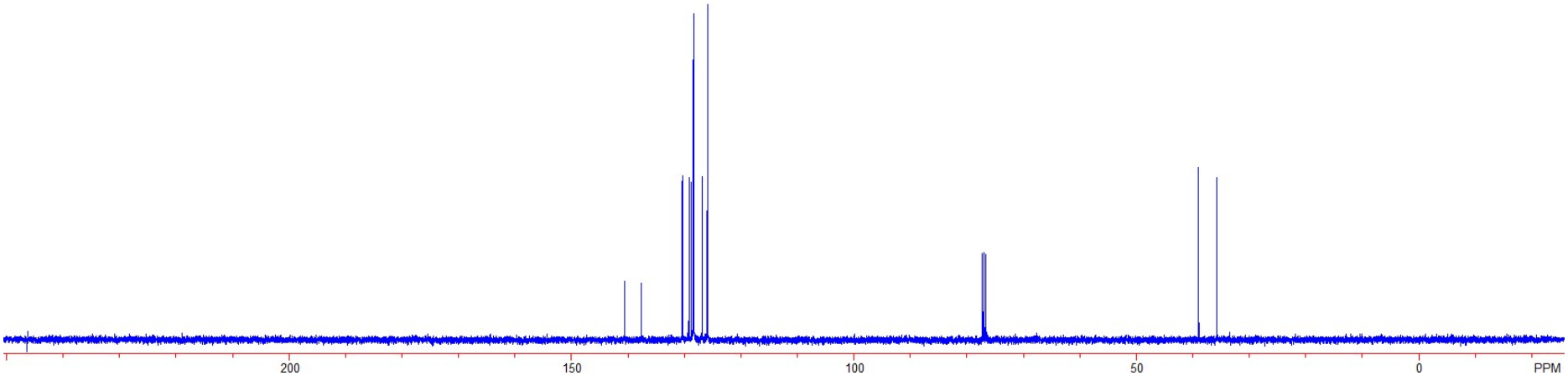


^{13}C NMR (100 MHz, in $CDCl_3$)

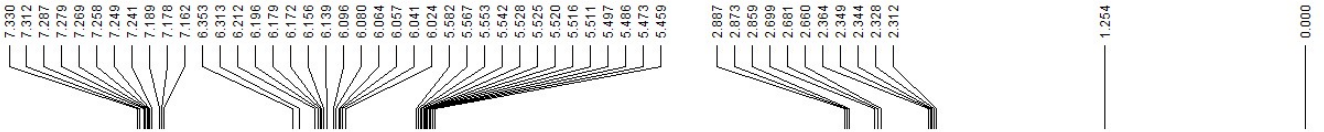


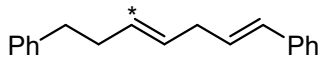


3e (*E*:*Z* > 20:1)

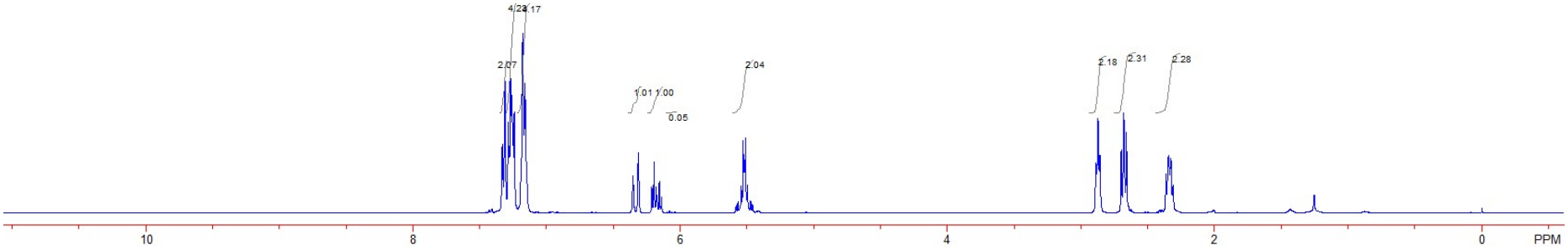


^{1}H NMR (400 MHz, in $CDCl_3$)

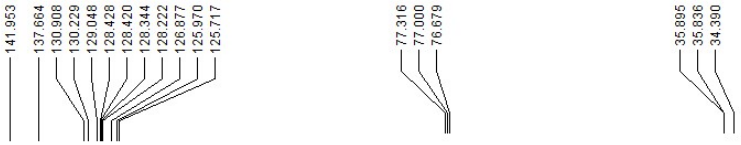


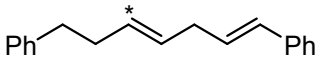


3f (*E*:*Z* > 20:1)

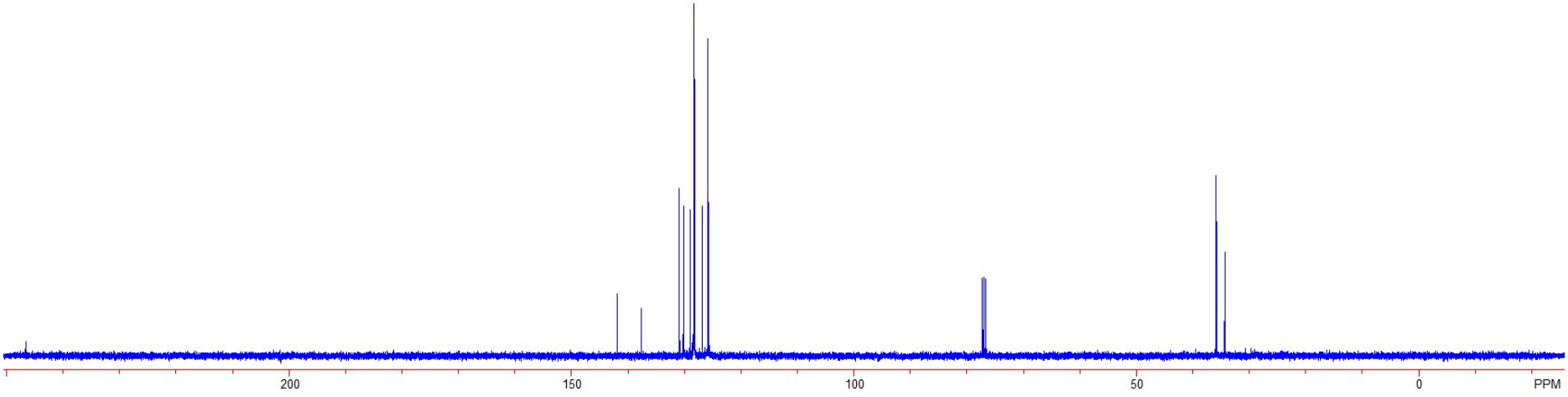


^{13}C NMR (100 MHz, in $CDCl_3$)

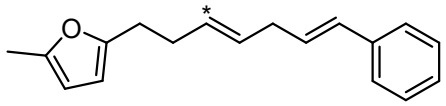




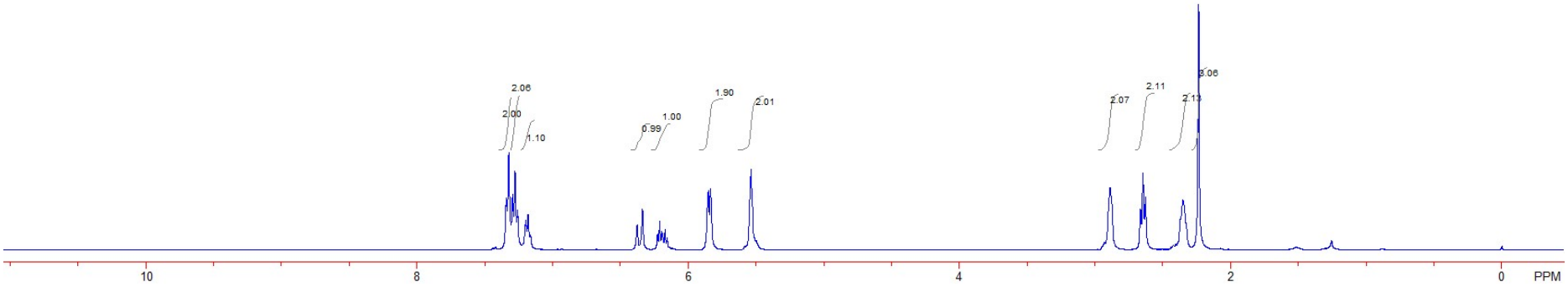
3f (*E*:*Z* > 20:1)



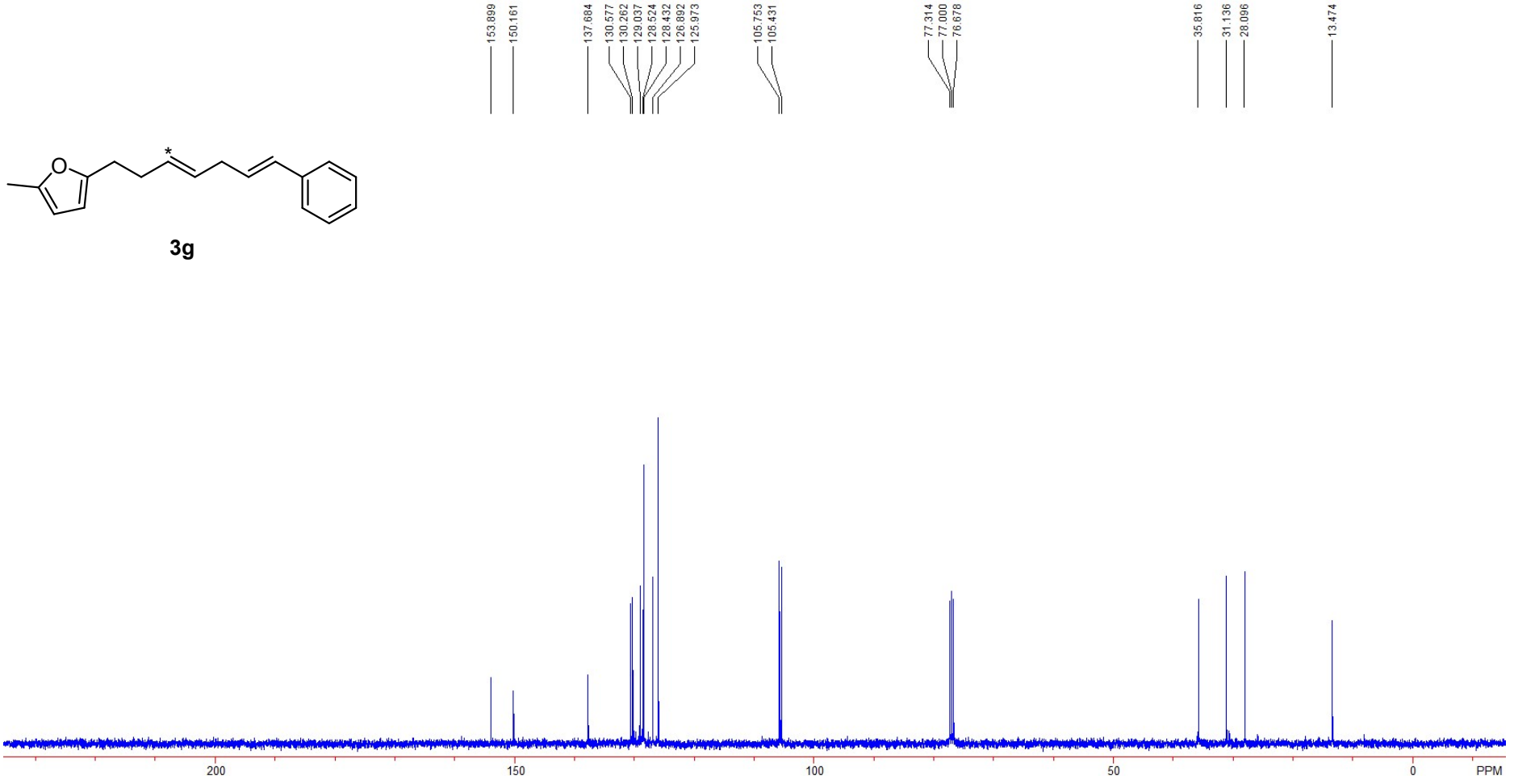
^{1}H NMR (400 MHz, in $CDCl_3$)



3g

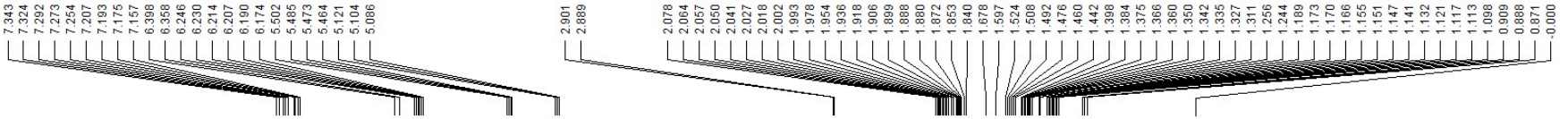


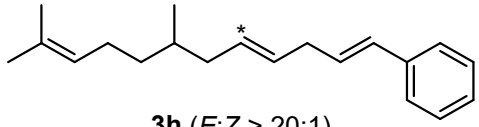
^{13}C NMR (100 MHz, in $CDCl_3$)



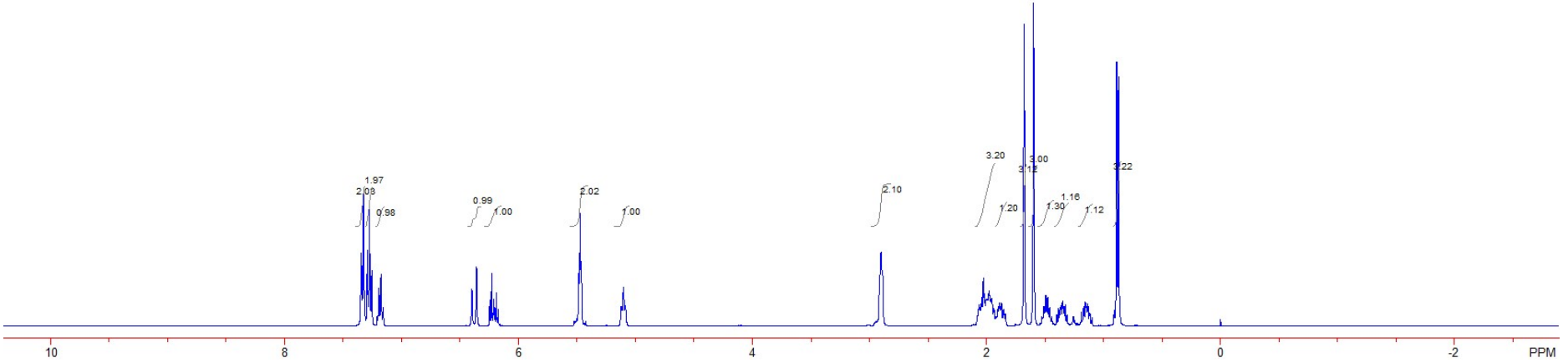
3g

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

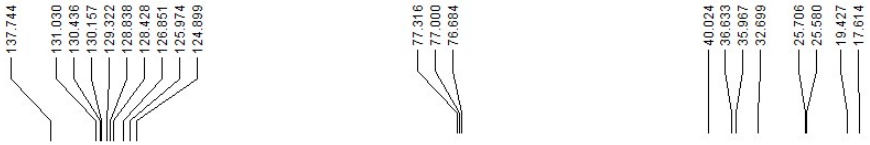


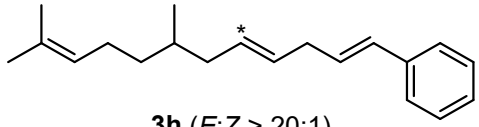


3h (*E*:*Z* > 20:1)

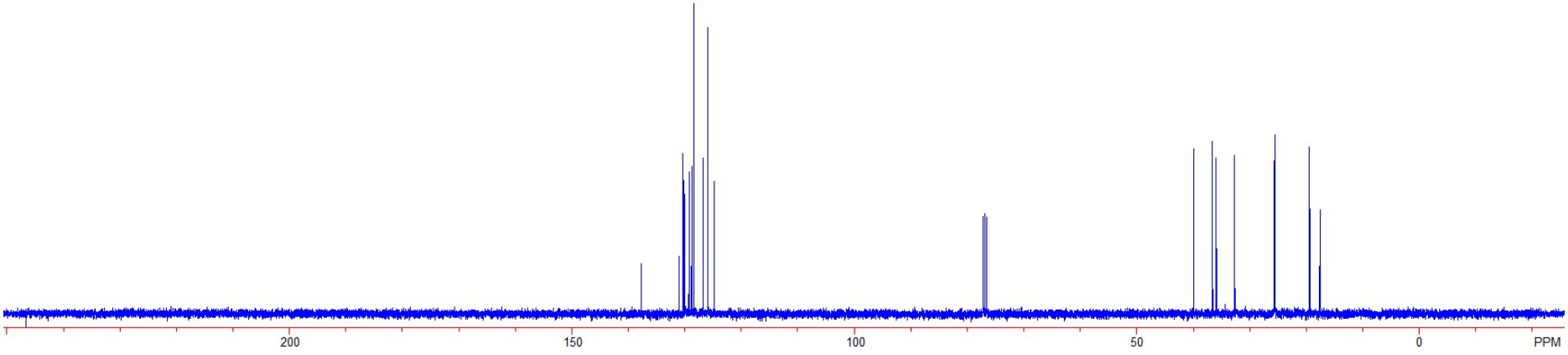


^{13}C NMR (100 MHz, in $CDCl_3$)

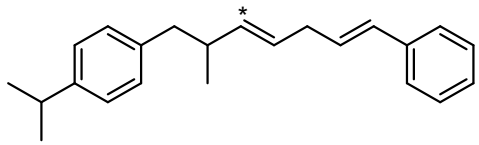




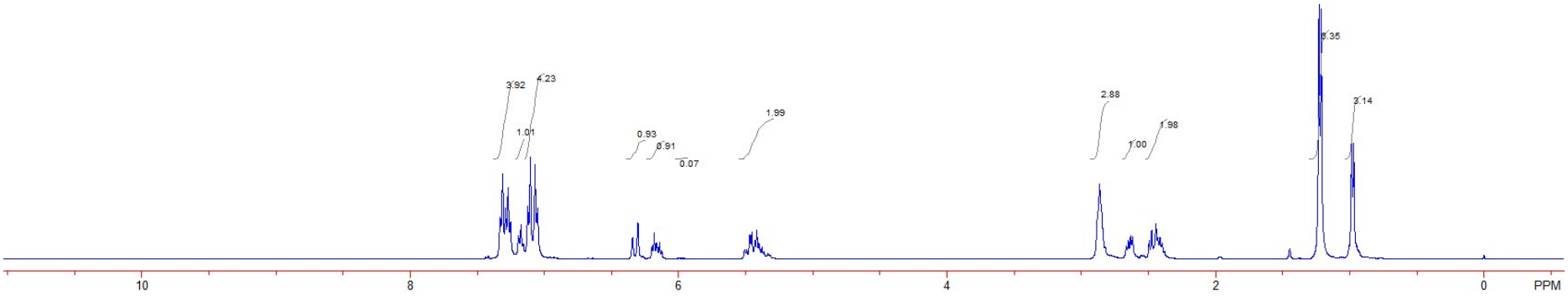
3h (*E*:*Z* > 20:1)



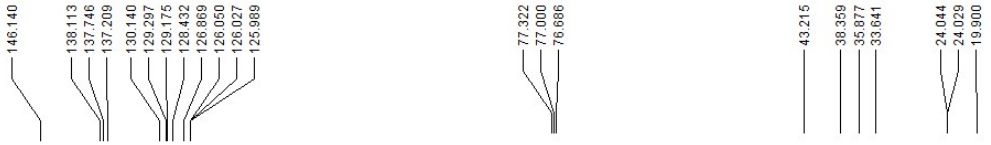
^{1}H NMR (400 MHz, in $CDCl_3$)

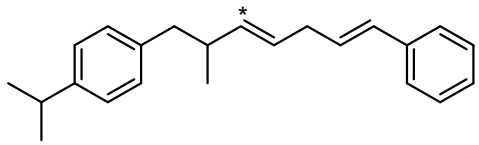


3i (*E*:*Z* = ca. 13:1)

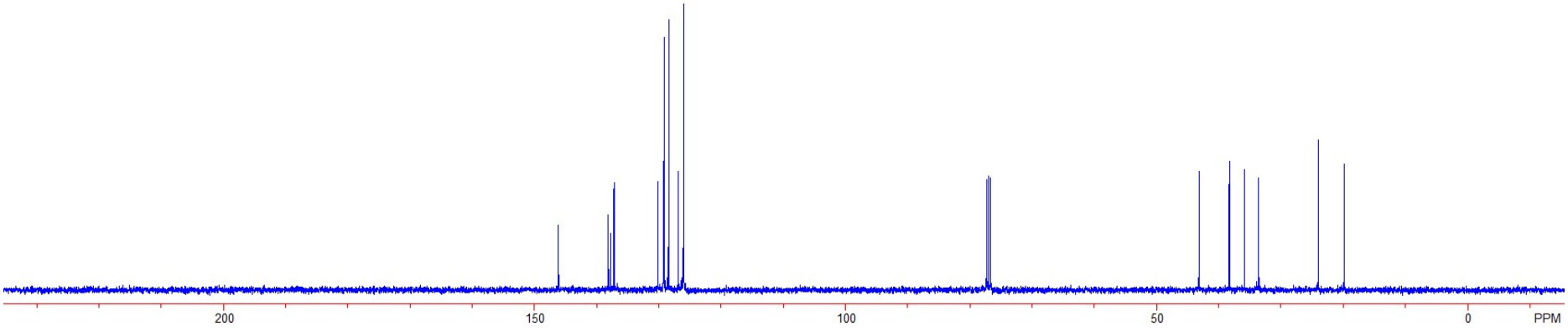


^{13}C NMR (100 MHz, in $CDCl_3$)

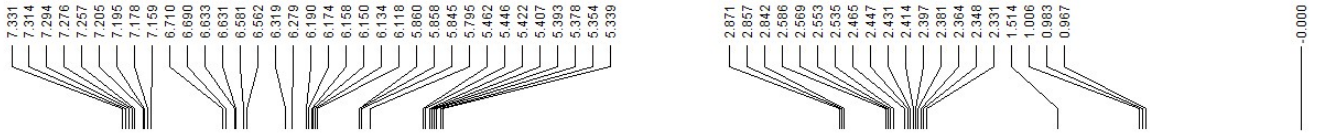


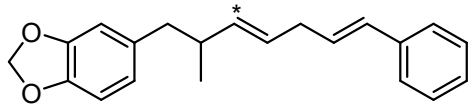


3i (*E*:*Z* = ca. 13:1)

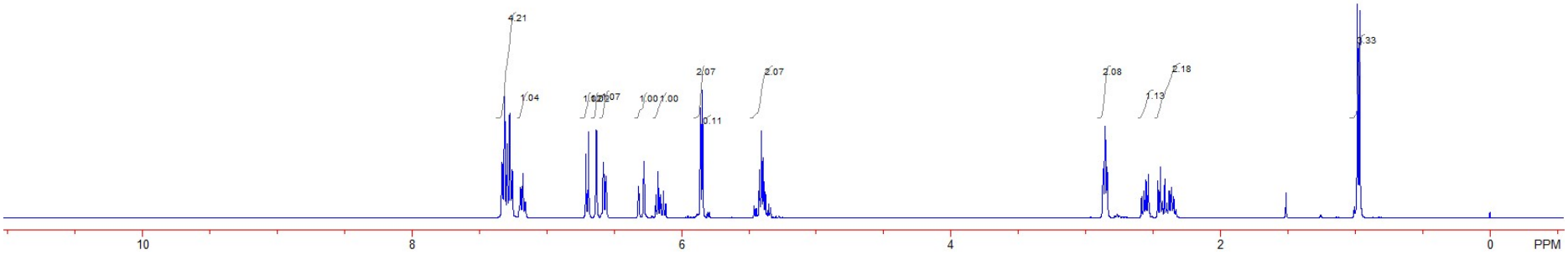


^{1}H NMR (400 MHz, in $CDCl_3$)

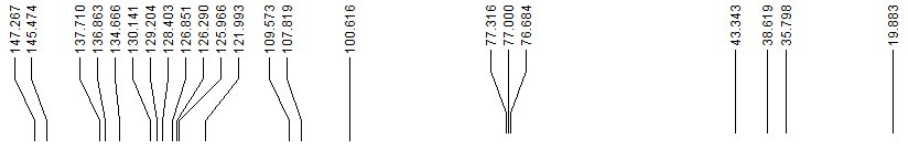


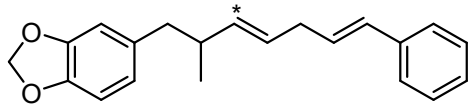


3j (*E*:*Z* = ca. 19:1)

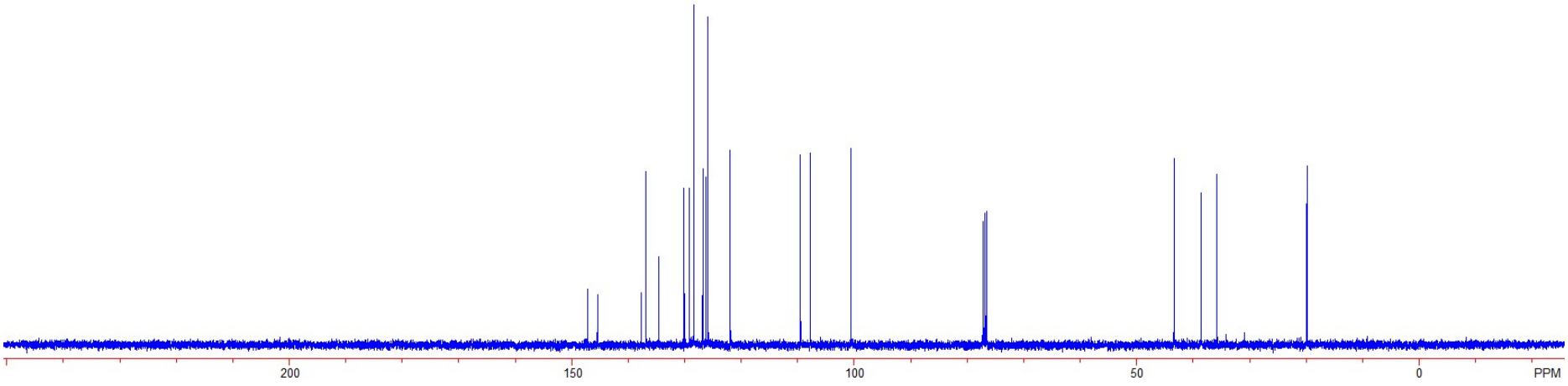


^{13}C NMR (100 MHz, in $CDCl_3$)

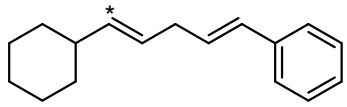




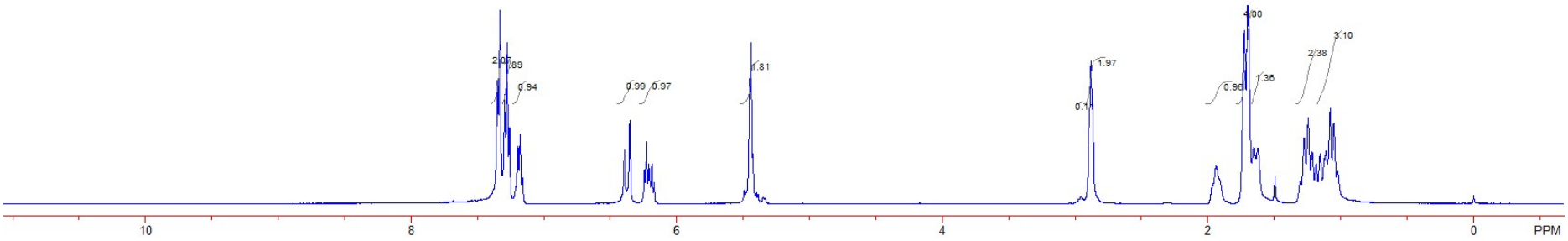
3j (*E*:*Z* = ca. 19:1)



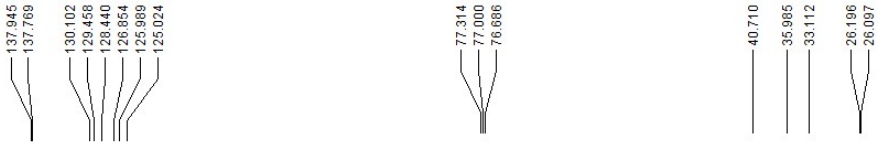
^{1}H NMR (400 MHz, in $CDCl_3$)

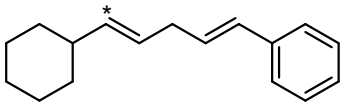


3k (*E*:*Z* = ca. 18:1)

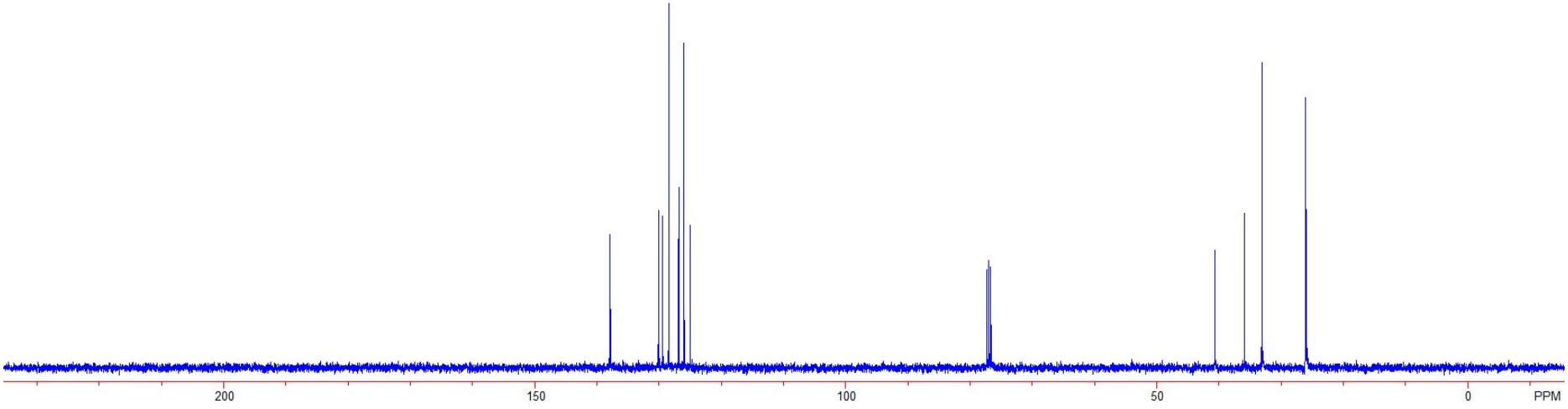


^{13}C NMR (100 MHz, in $CDCl_3$)

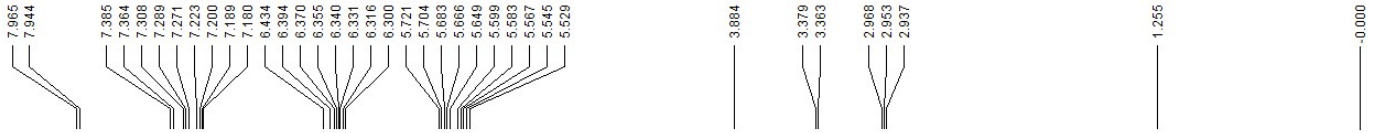


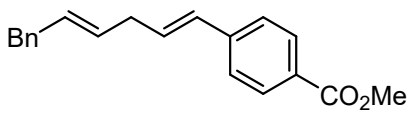


3k (*E*:*Z* = ca. 18:1)

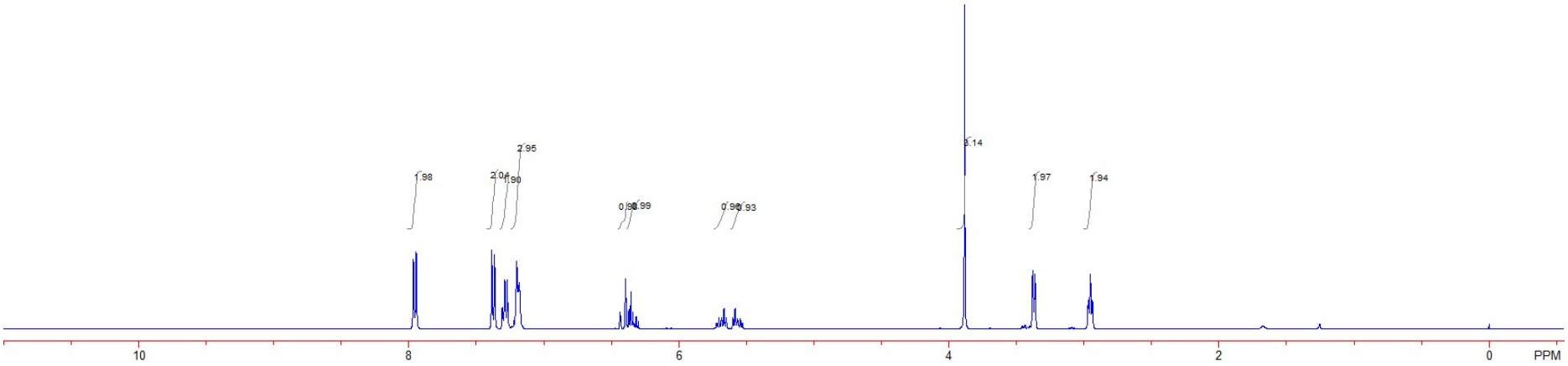


^{1}H NMR (400 MHz, in $CDCl_3$)

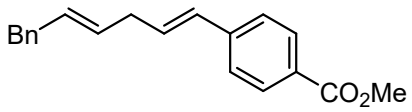




3l



^{13}C NMR (100 MHz, in $CDCl_3$)



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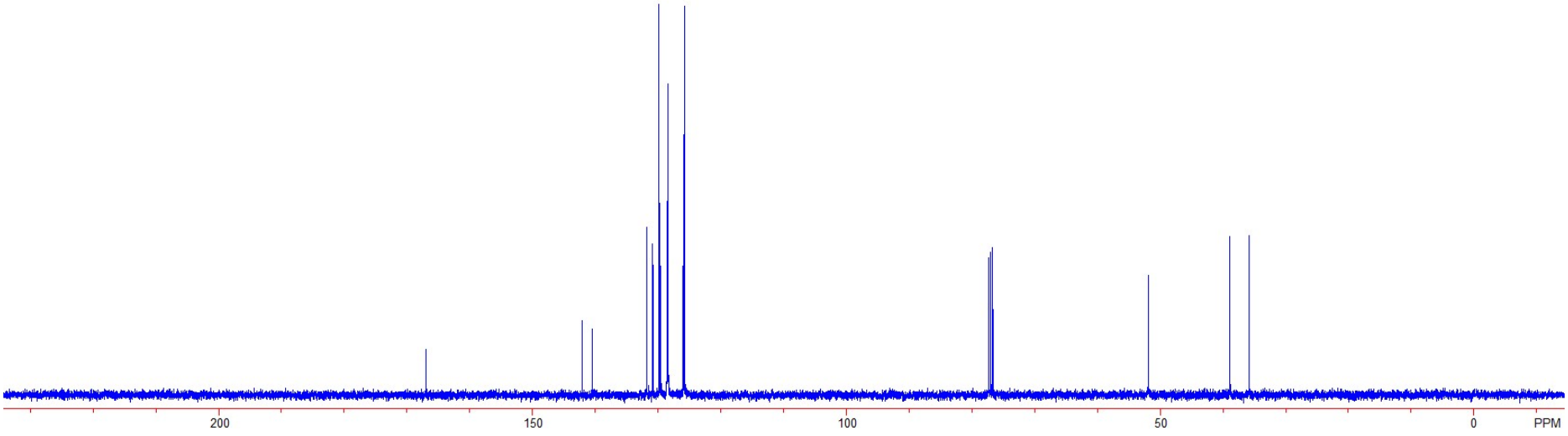
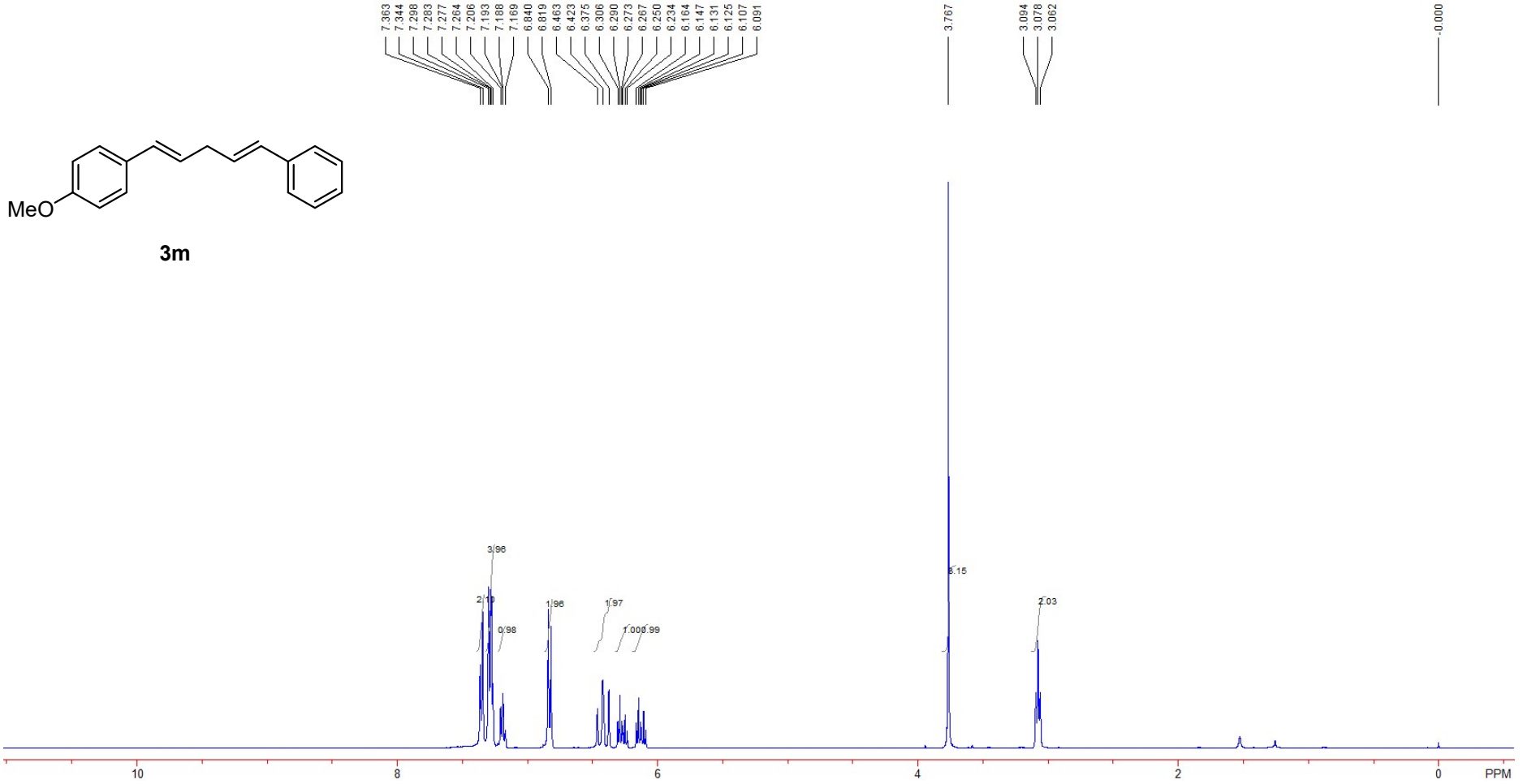
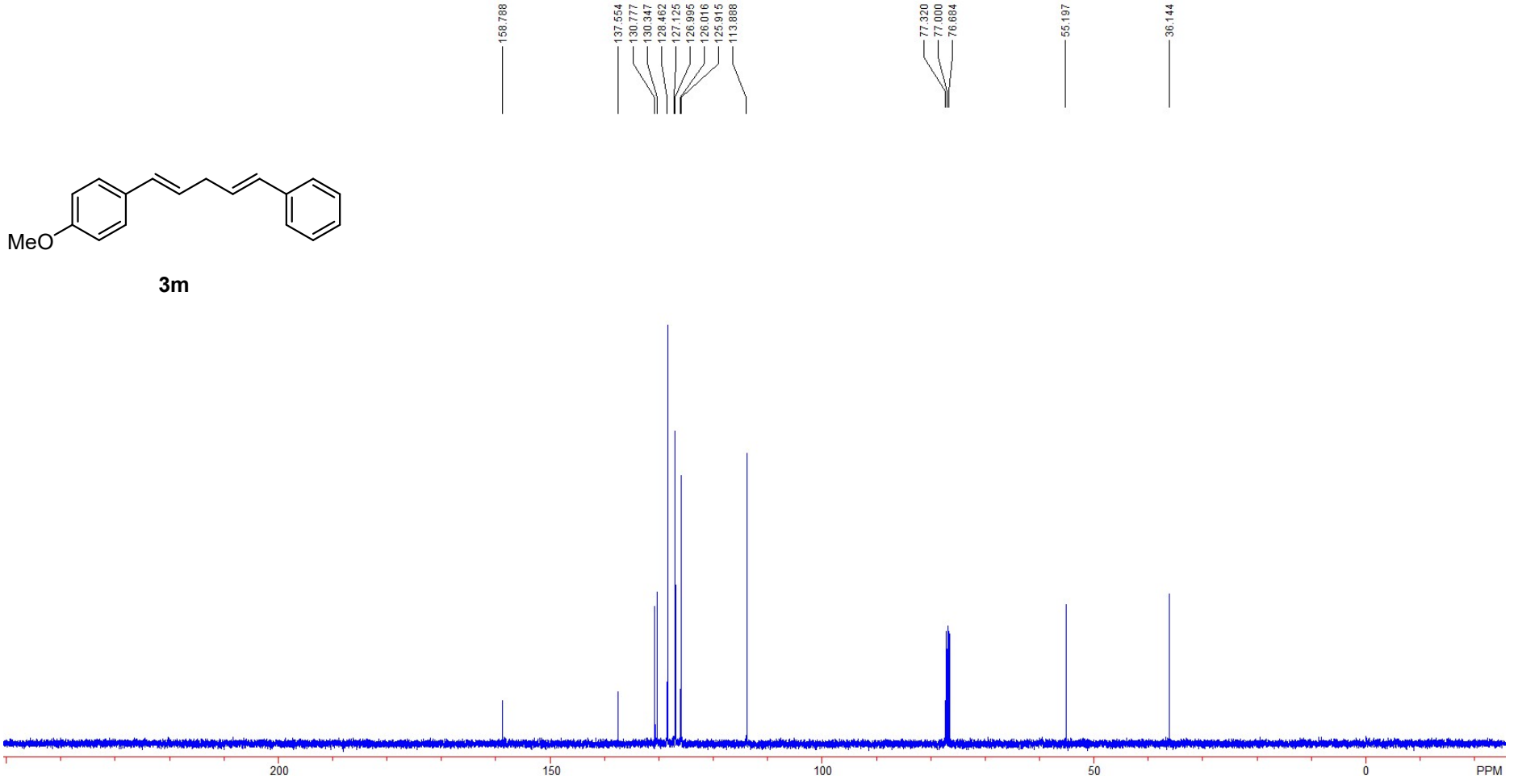


^{1}H NMR (400 MHz, in $CDCl_3$)



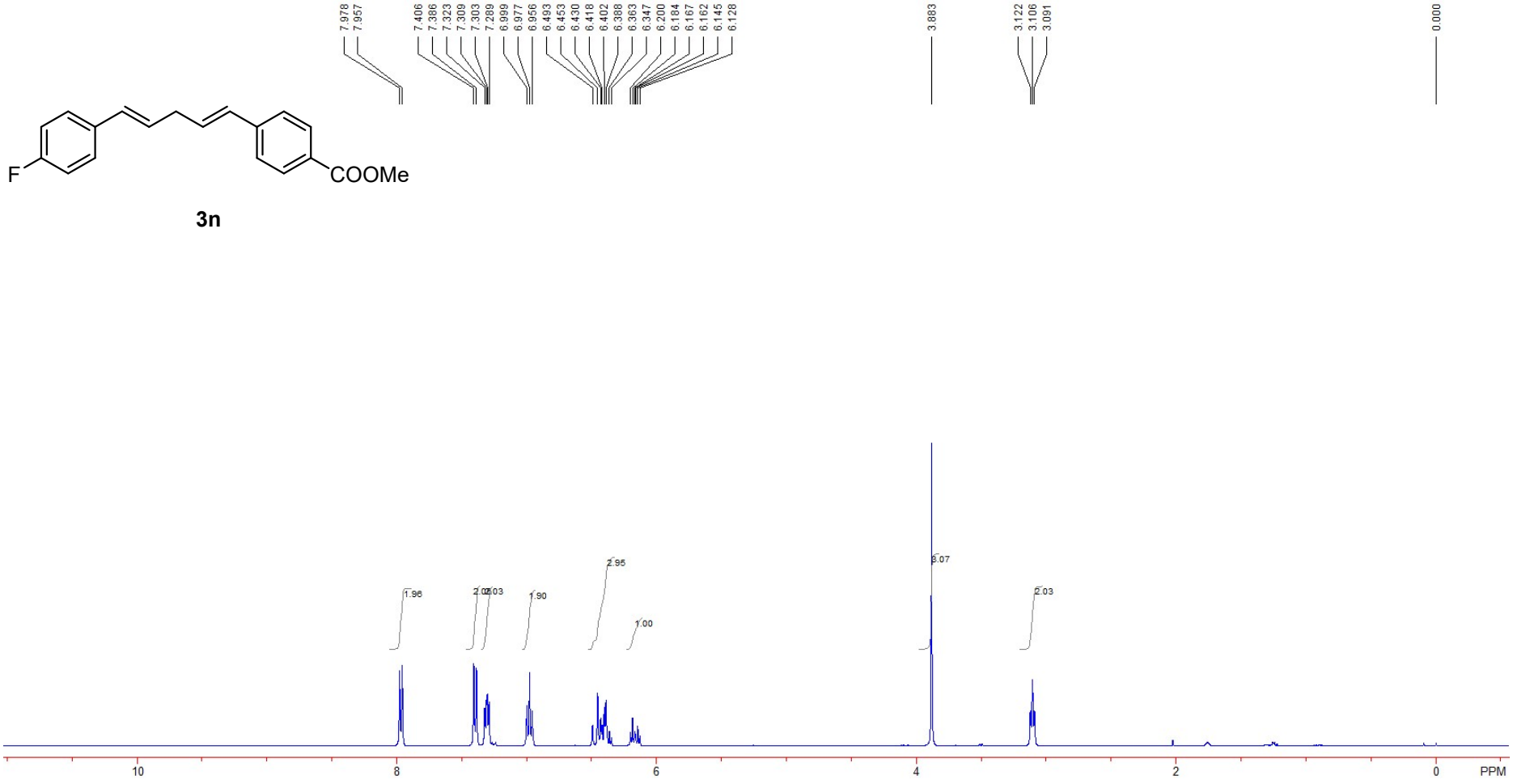
3m

^{13}C NMR (100 MHz, in $CDCl_3$)



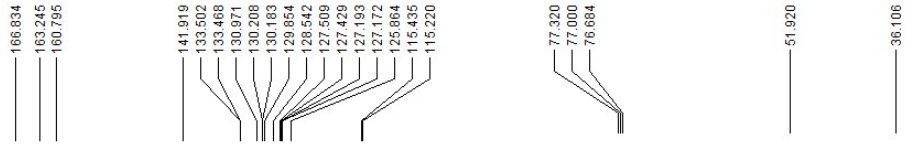
3m

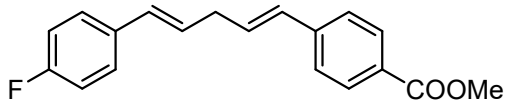
^{1}H NMR (400 MHz, in $CDCl_3$)



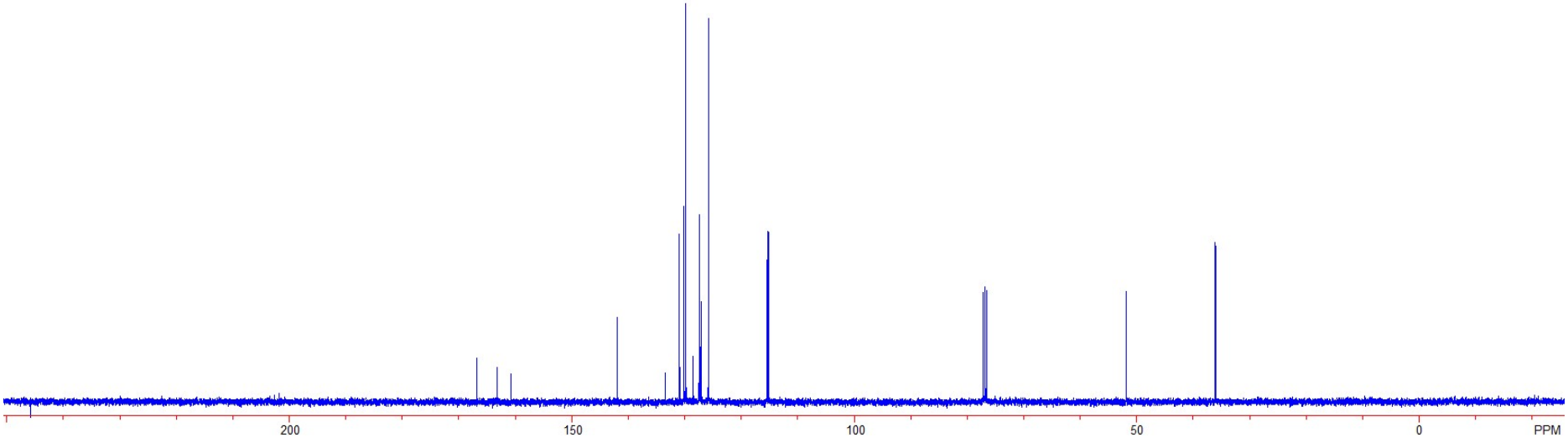
3n

^{13}C NMR (100 MHz, in $CDCl_3$)

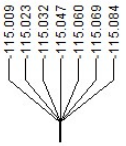


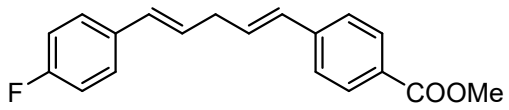


3n

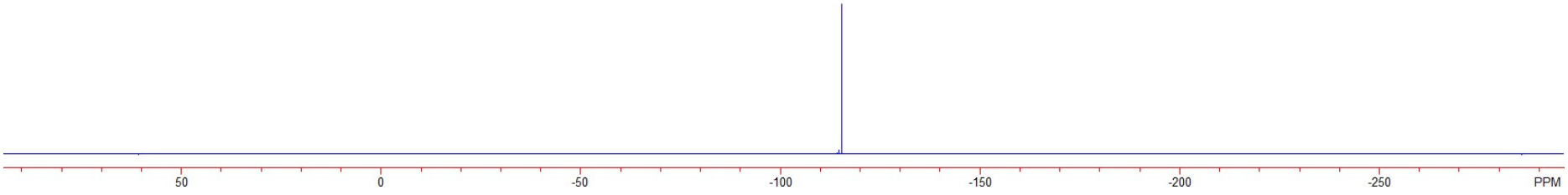


^{19}F NMR (376 MHz, in $CDCl_3$)

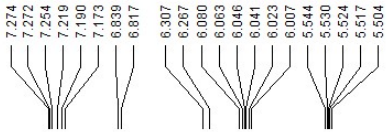


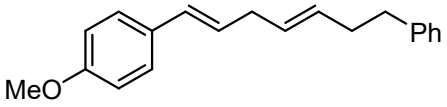


3n



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





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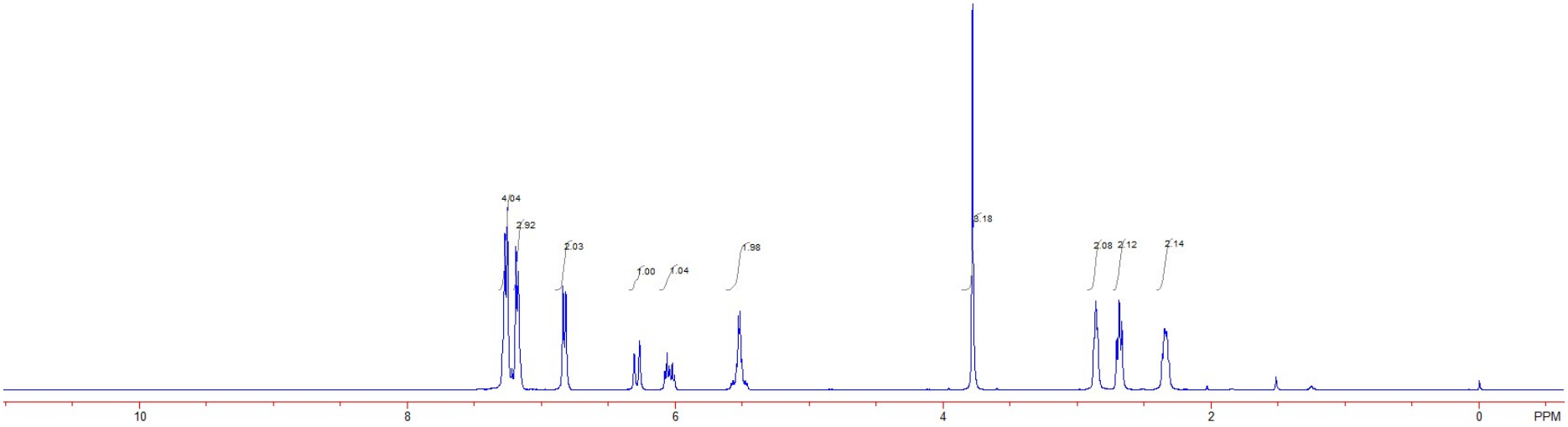
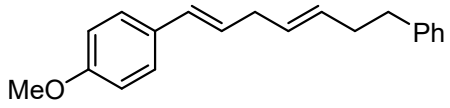


^{13}C NMR (100 MHz, in $CDCl_3$)



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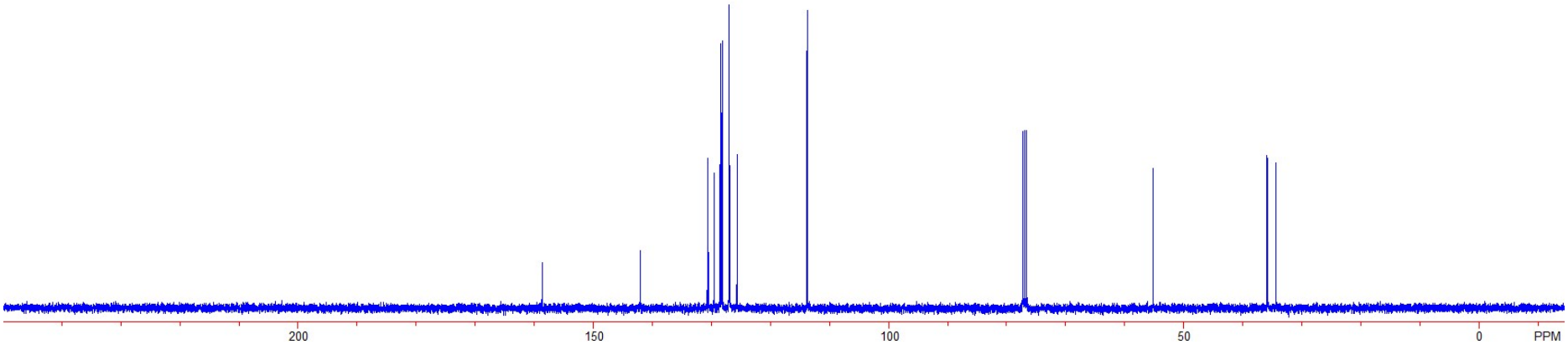
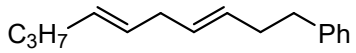
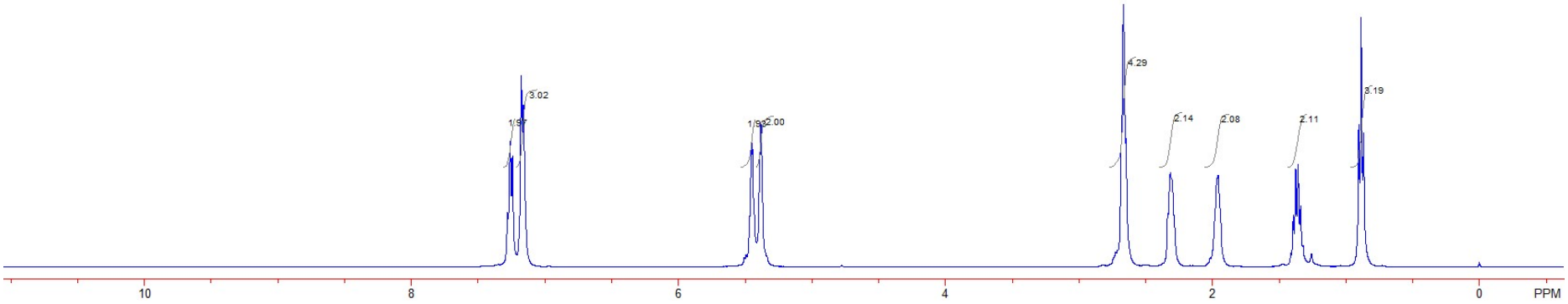


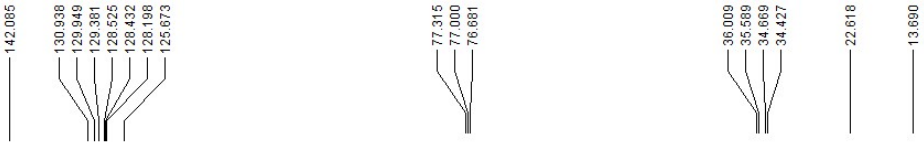
^{1}H NMR (400 MHz, in $CDCl_3$)

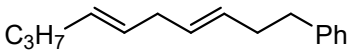


3p



^{13}C NMR (100 MHz, in $CDCl_3$)





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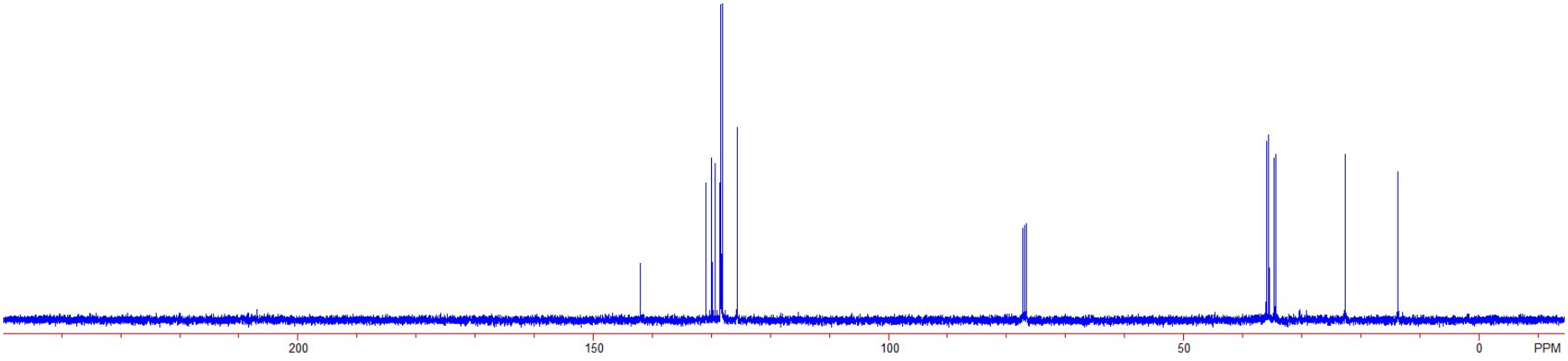
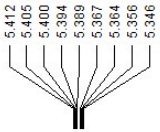
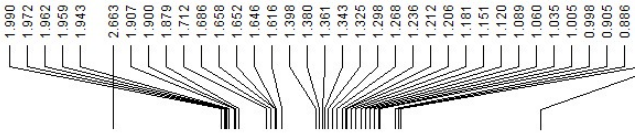
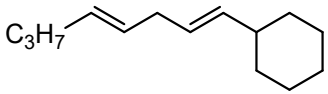


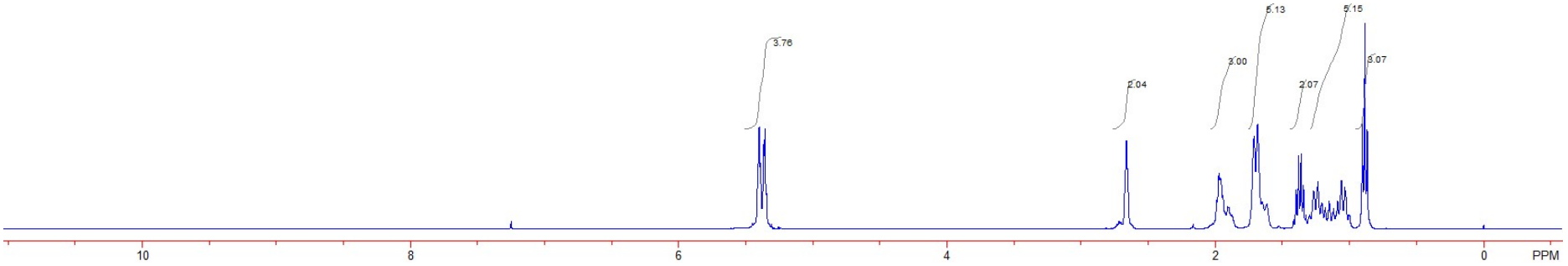
^{1}H NMR (400 MHz, in $CDCl_3$)



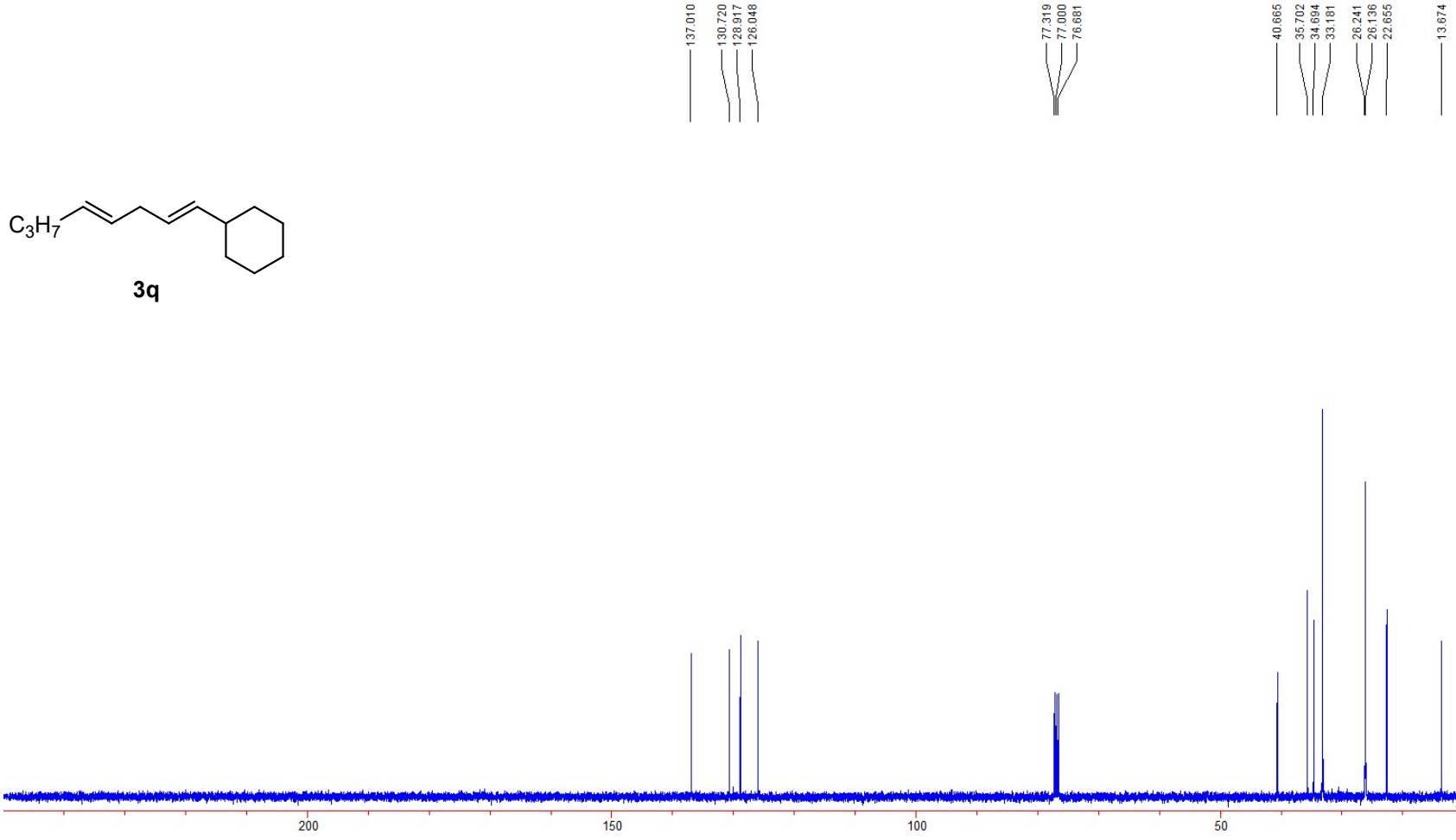




3q

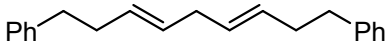


^{13}C NMR (100 MHz, in $CDCl_3$)

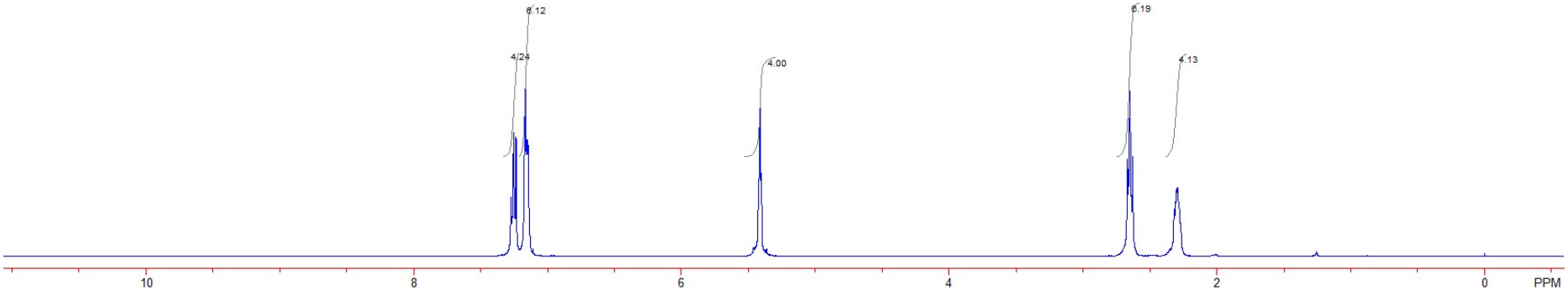


3q

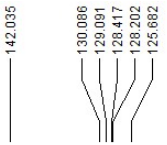
^{1}H NMR (400 MHz, in $CDCl_3$)

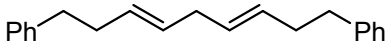


3r



^{13}C NMR (100 MHz, in $CDCl_3$)





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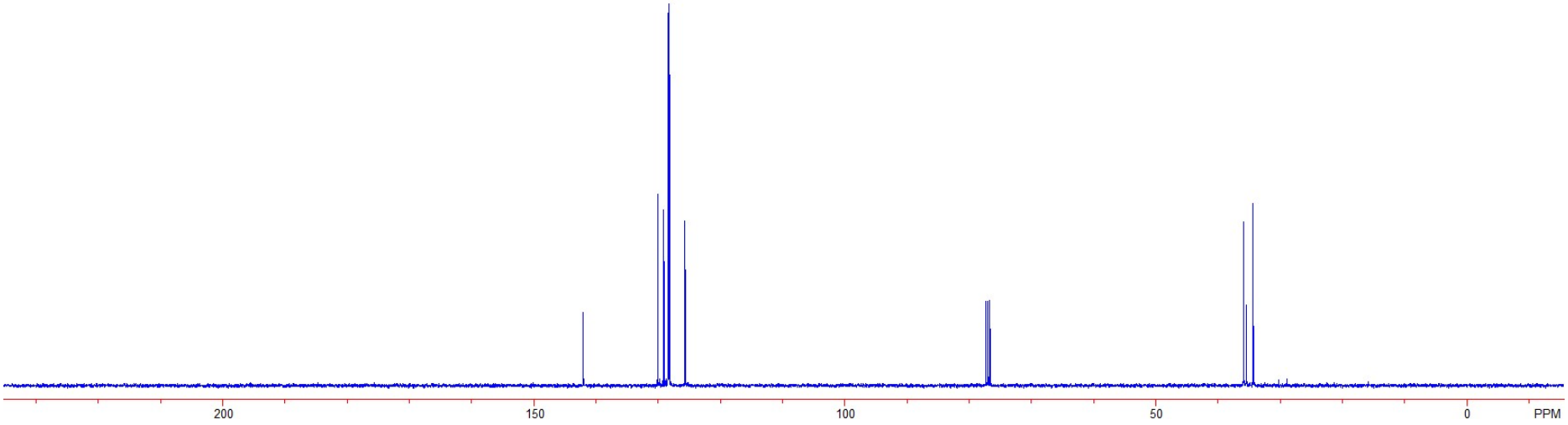
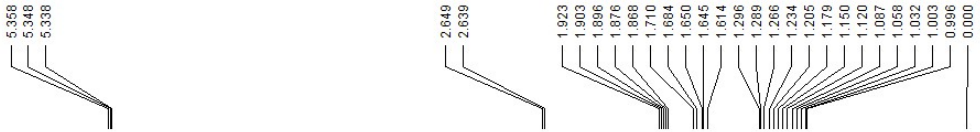
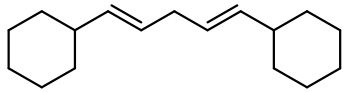
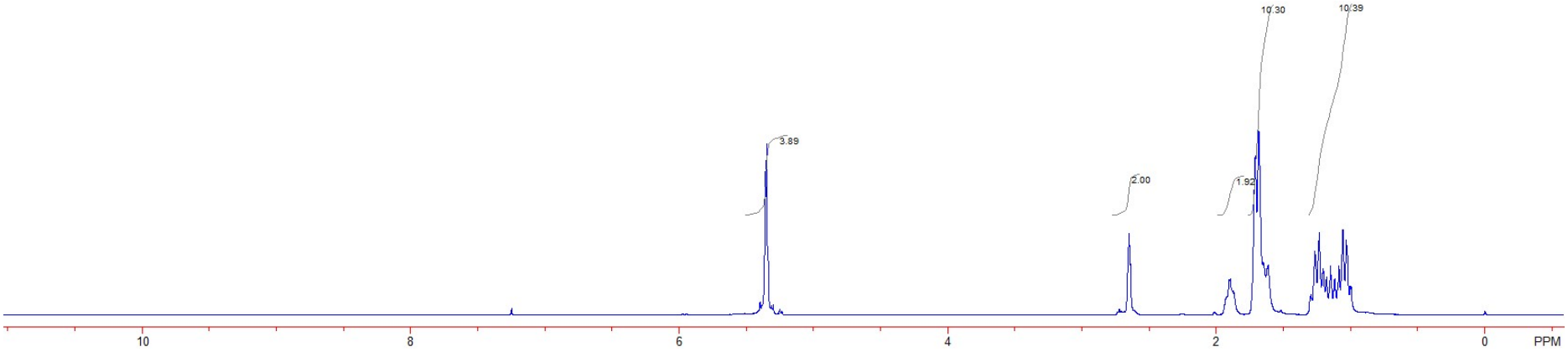


^{1}H NMR (400 MHz, in $CDCl_3$)

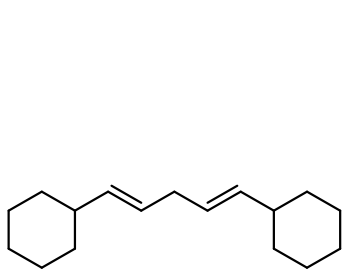




3s

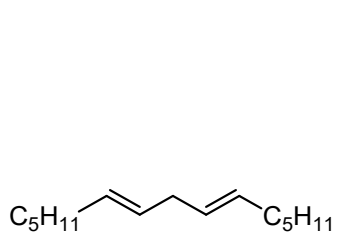


^{13}C NMR (100 MHz, in $CDCl_3$)



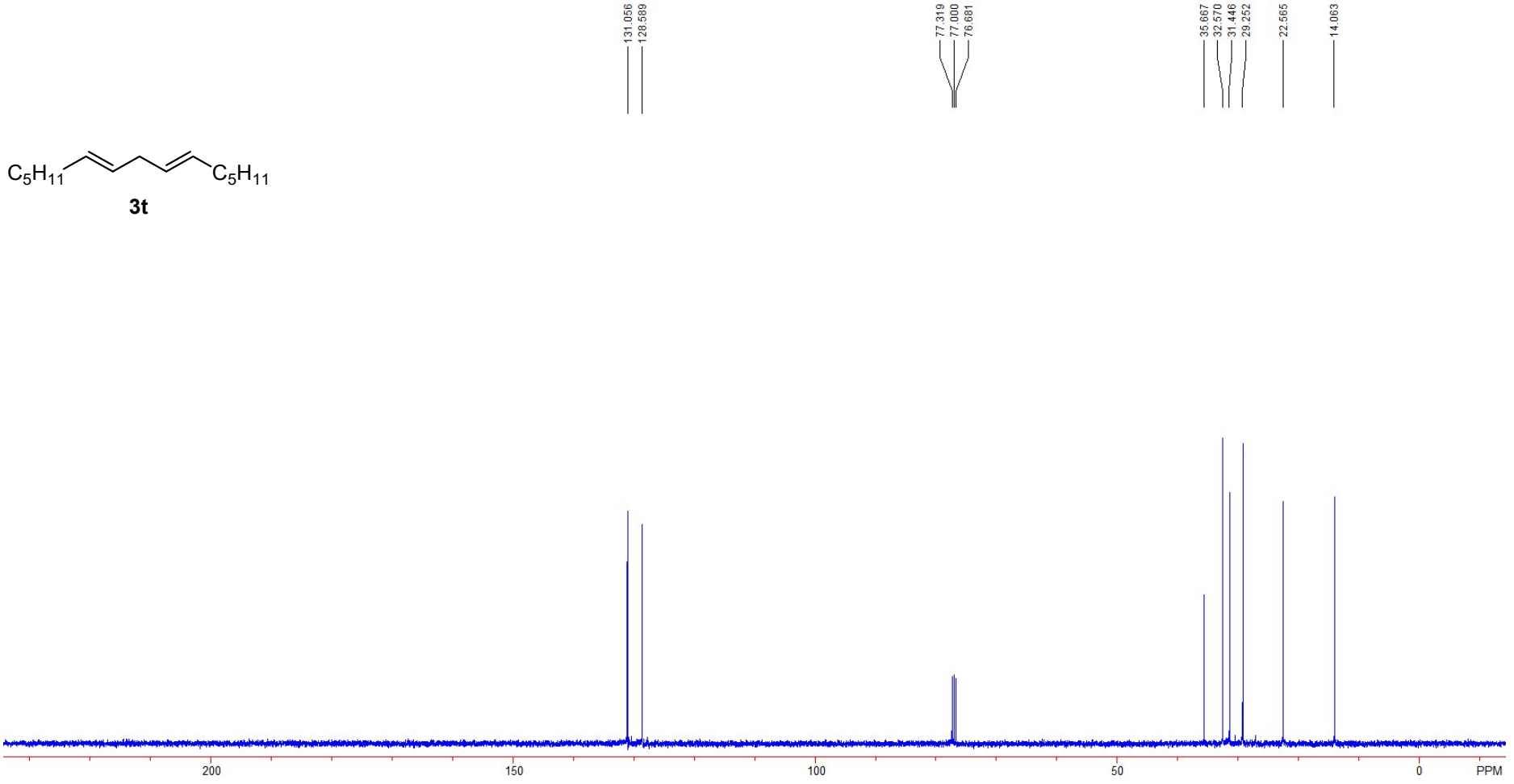
3s

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

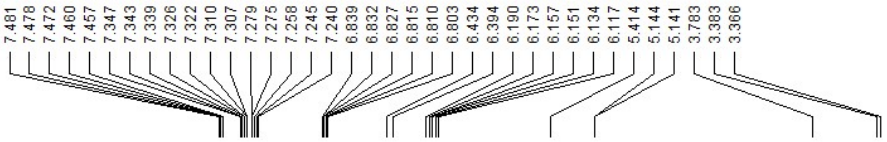


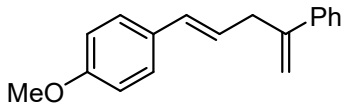
3t

^{13}C NMR (100 MHz, in $CDCl_3$)



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





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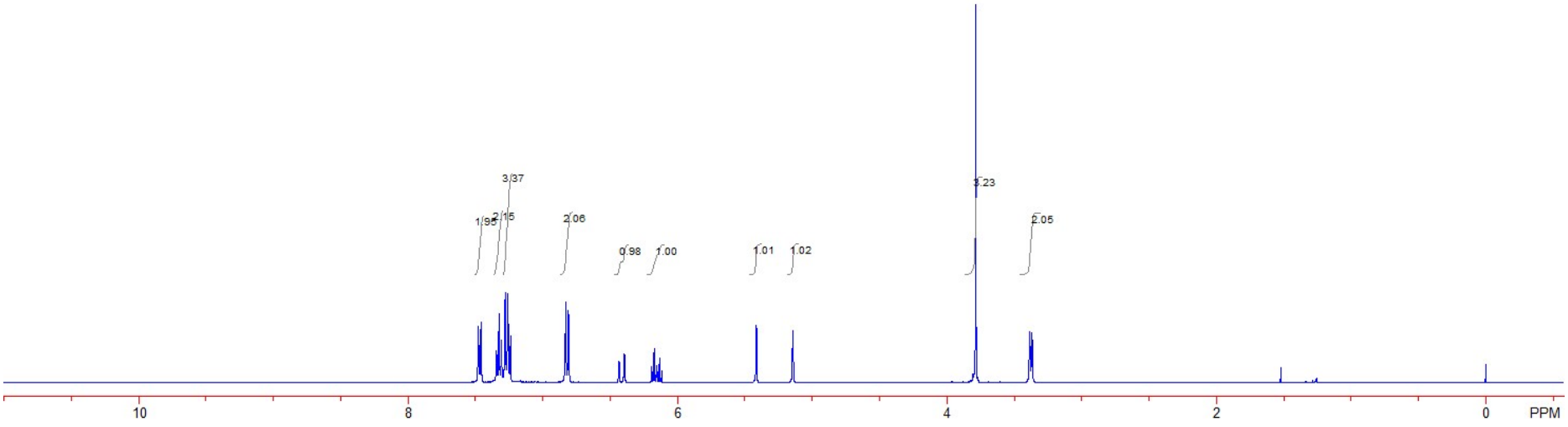
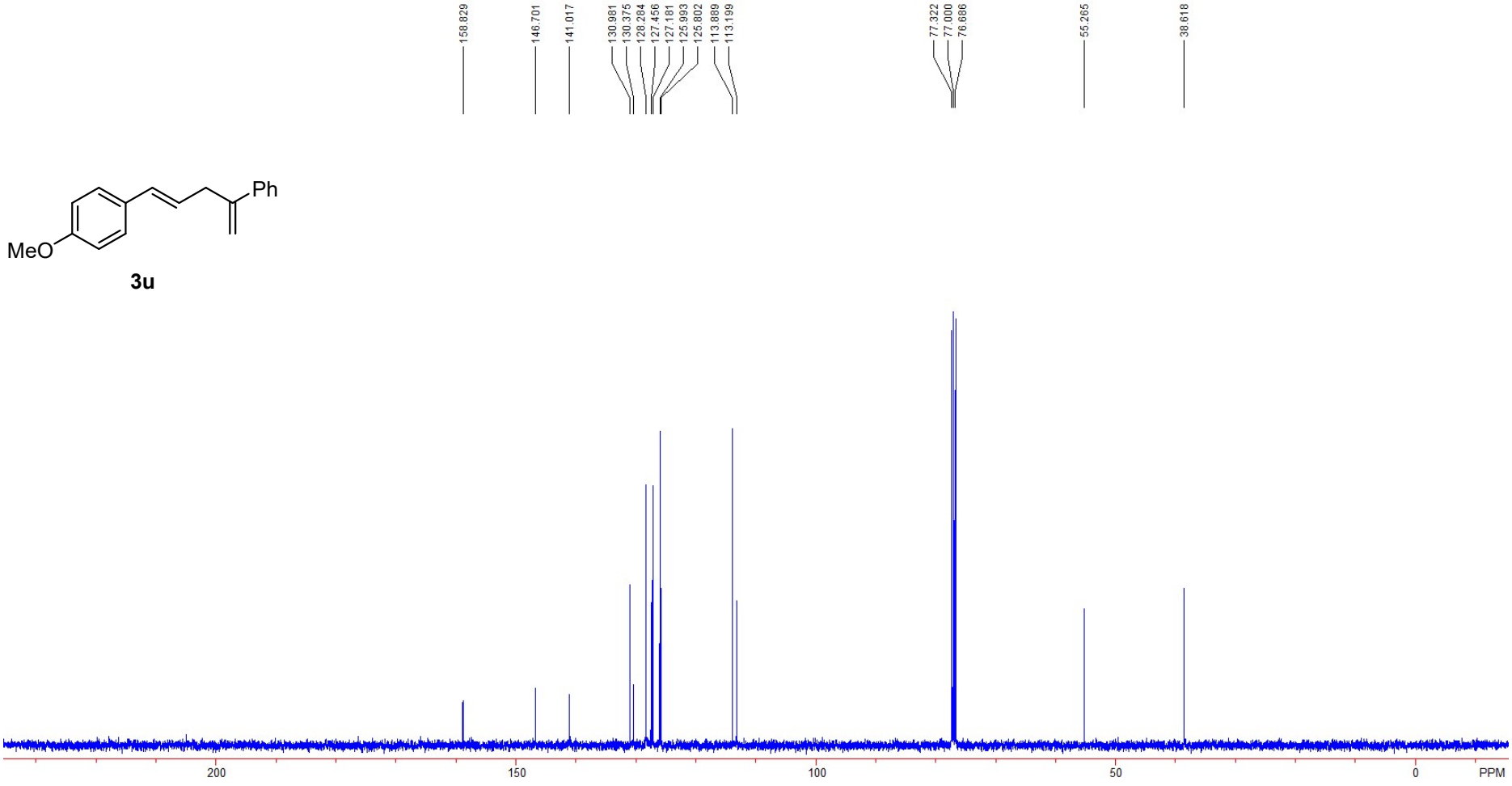
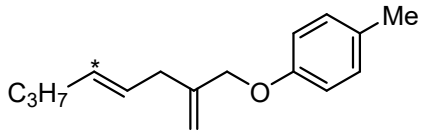


^{13}C NMR (100 MHz, in $CDCl_3$)

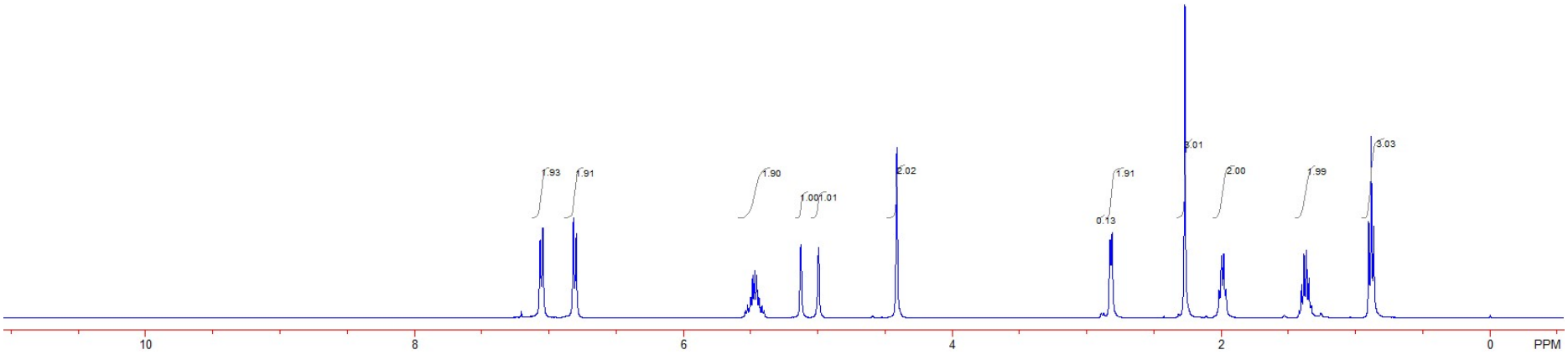


3u

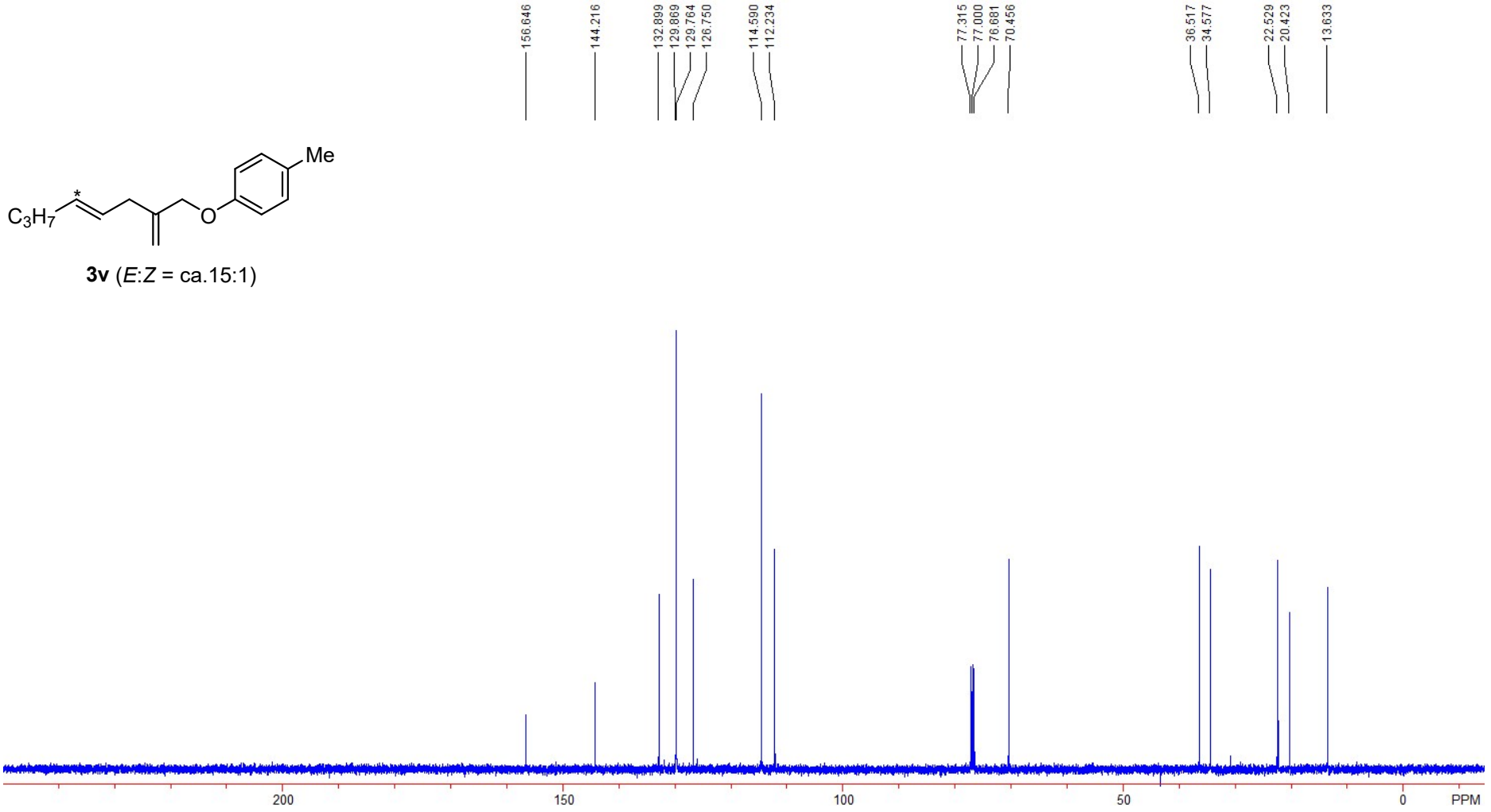
^{1}H NMR (400 MHz, in $CDCl_3$)



3v (*E*:*Z* = ca.15:1)

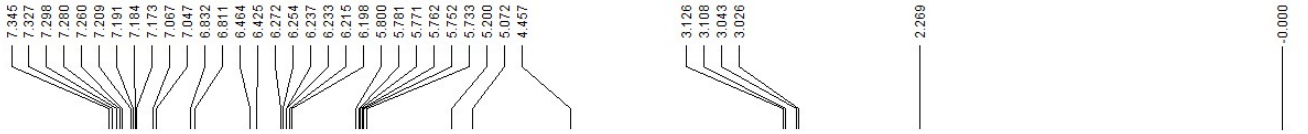


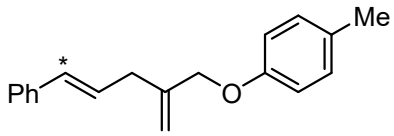
^{13}C NMR (100 MHz, in $CDCl_3$)



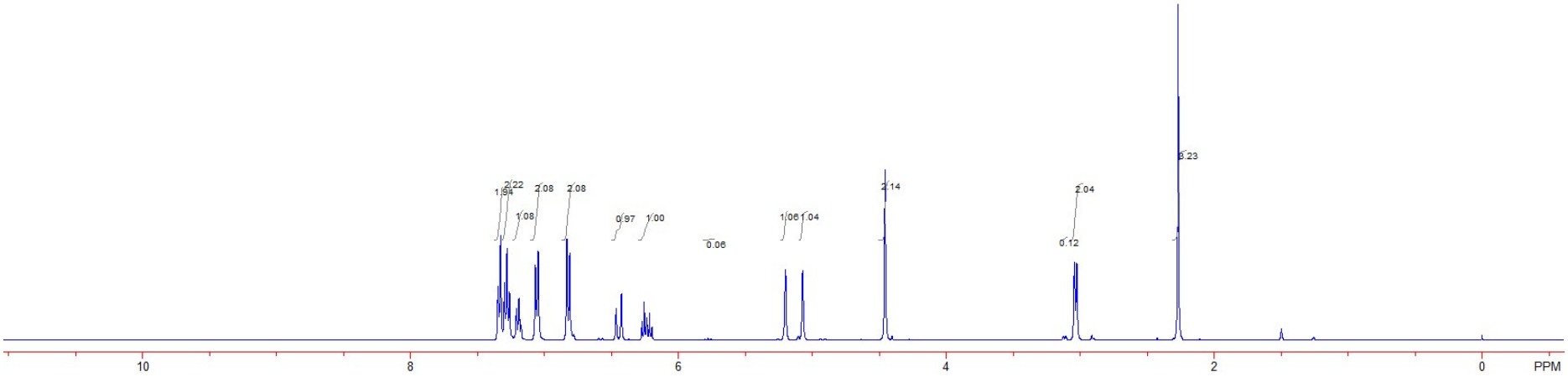
3v (*E*:*Z* = ca.15:1)

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

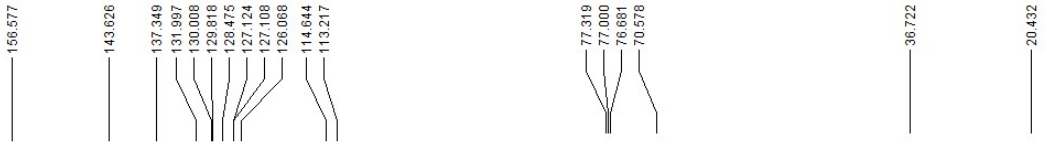


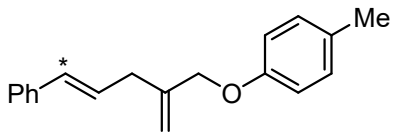


3w (*E*:*Z* = 17:1)

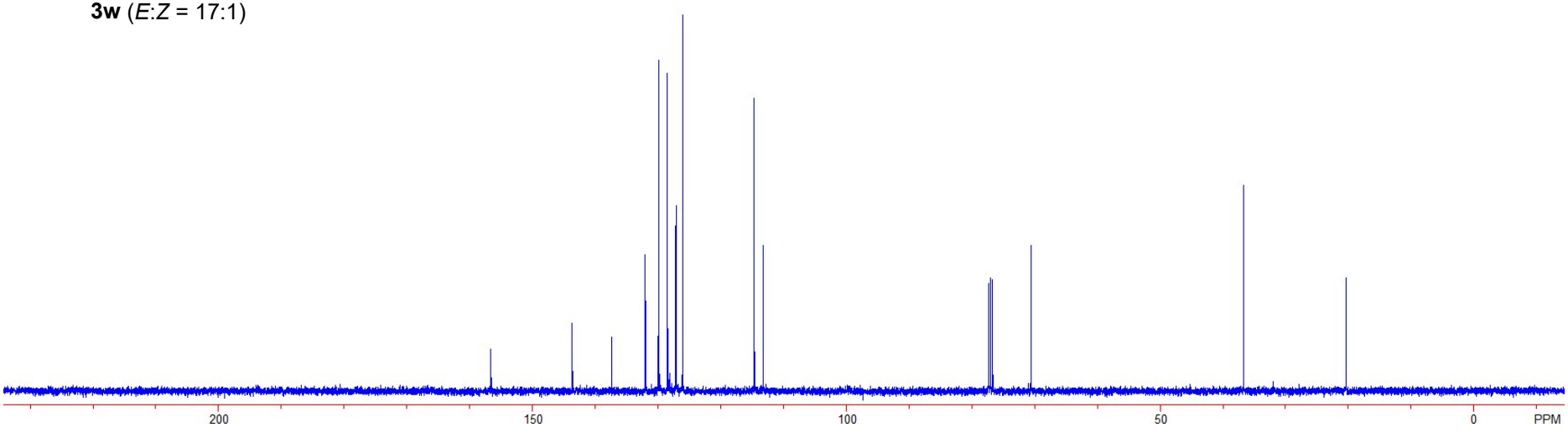


^{13}C NMR (100 MHz, in $CDCl_3$)

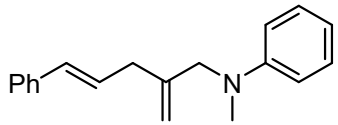




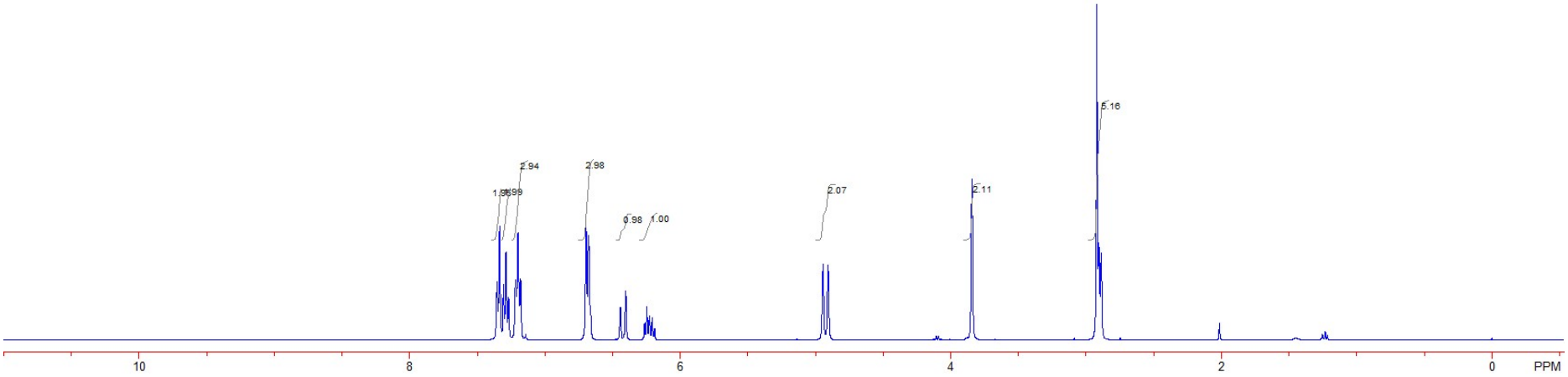
3w (*E*:*Z* = 17:1)



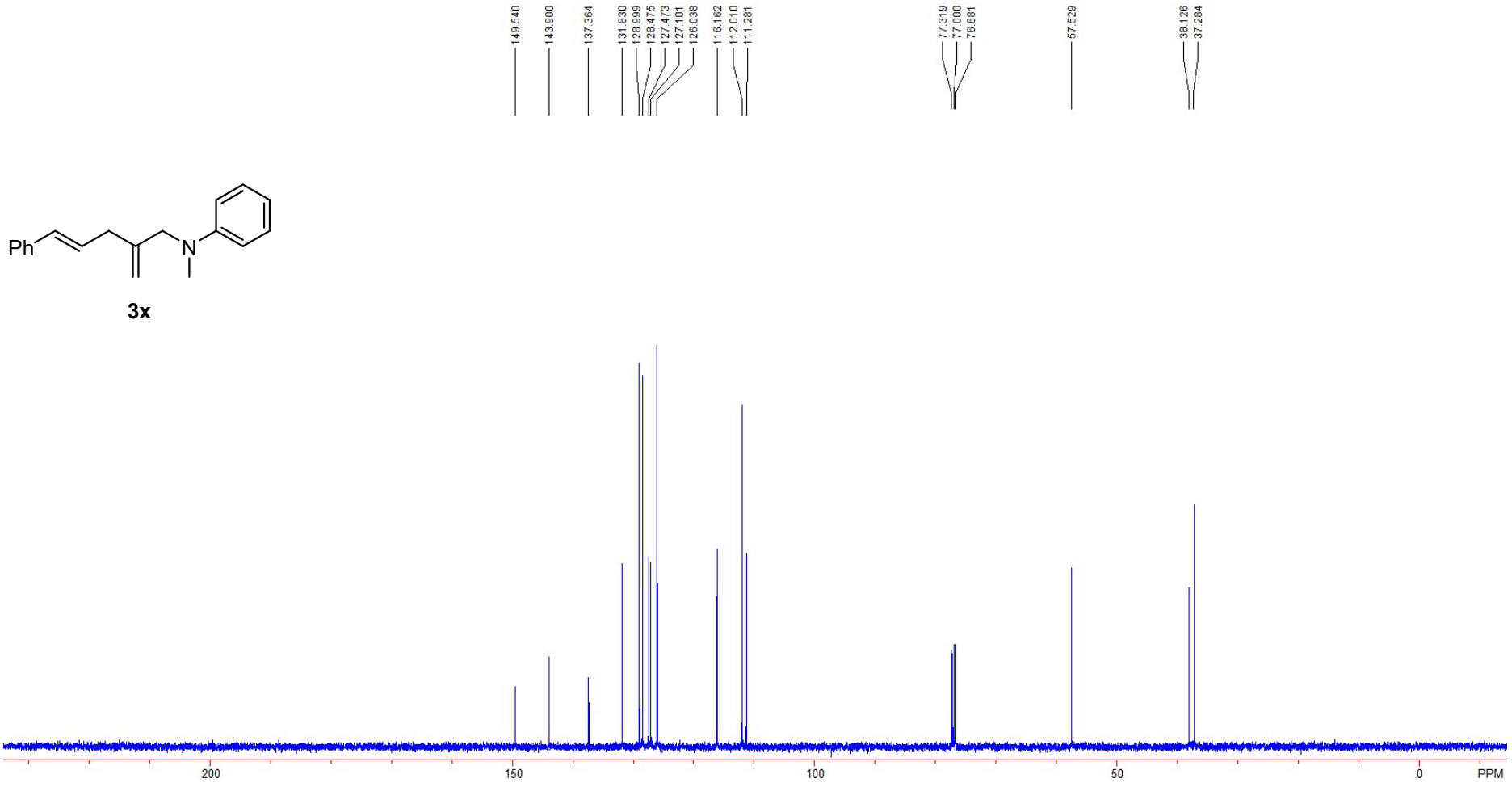
^{1}H NMR (400 MHz, in $CDCl_3$)



3x

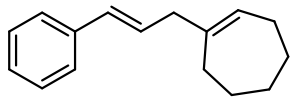


^{13}C NMR (100 MHz, in $CDCl_3$)

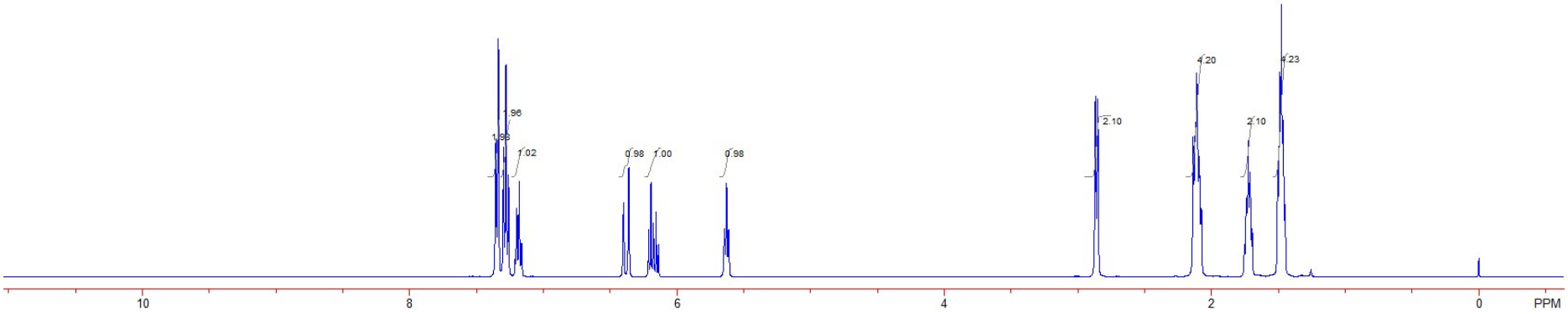


3x

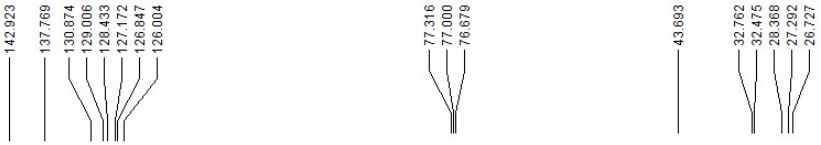
^{1}H NMR (400 MHz, in $CDCl_3$)

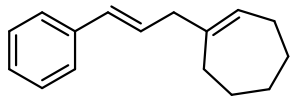


5a

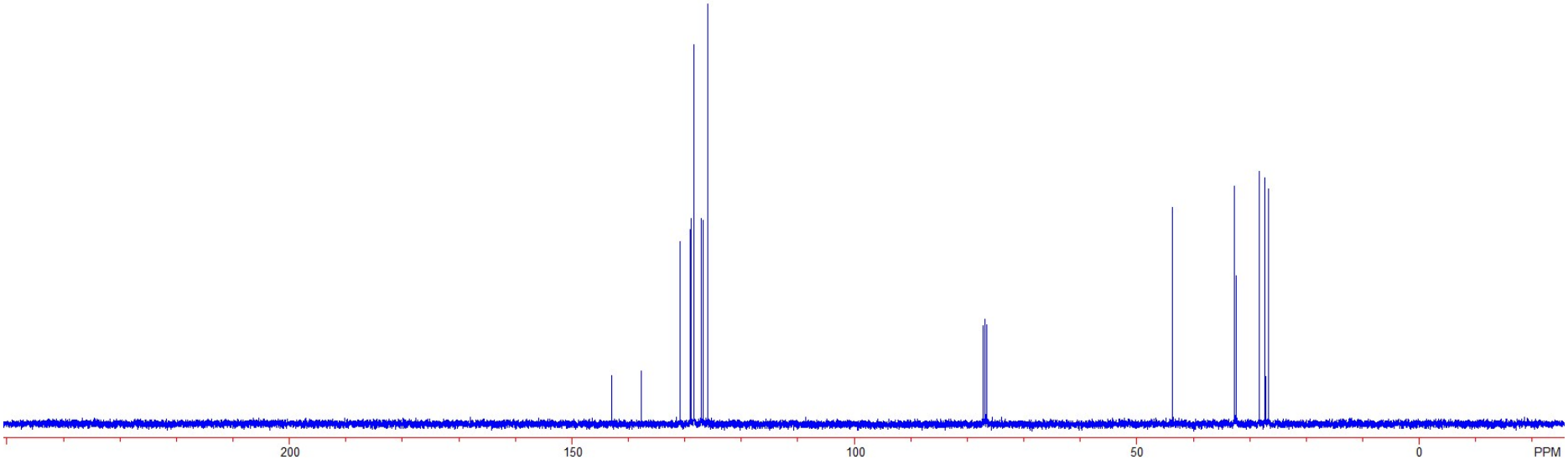


^{13}C NMR (100 MHz, in $CDCl_3$)

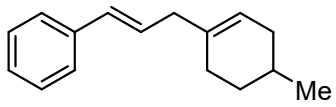




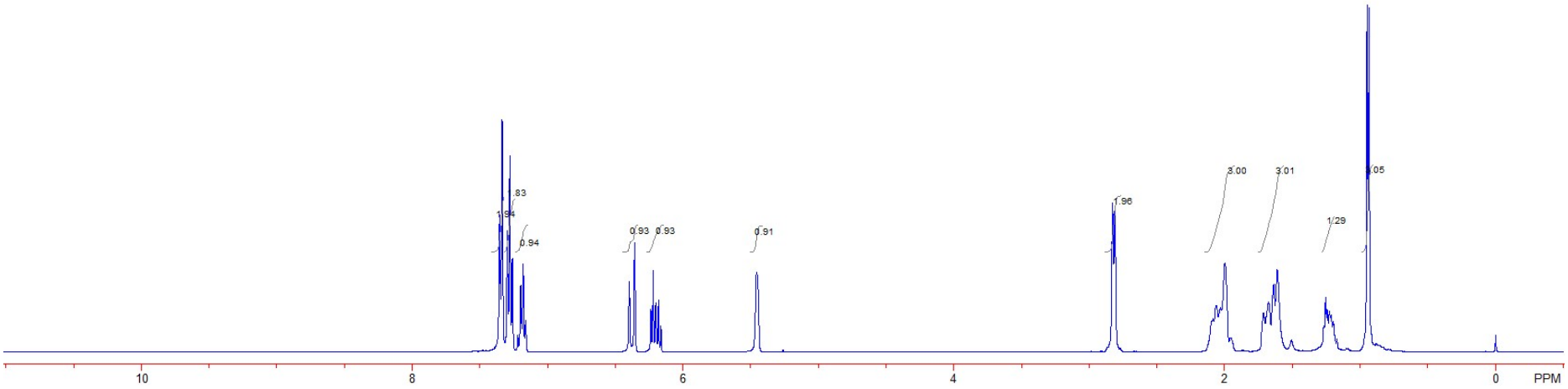
5a



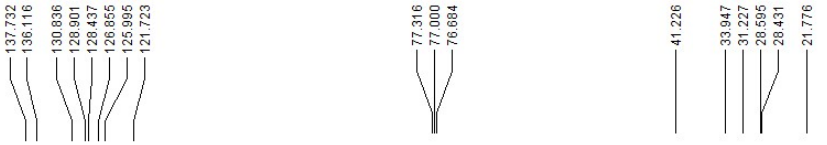
^{1}H NMR (400 MHz, in $CDCl_3$)

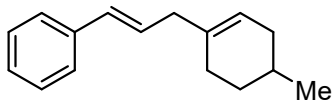


5b

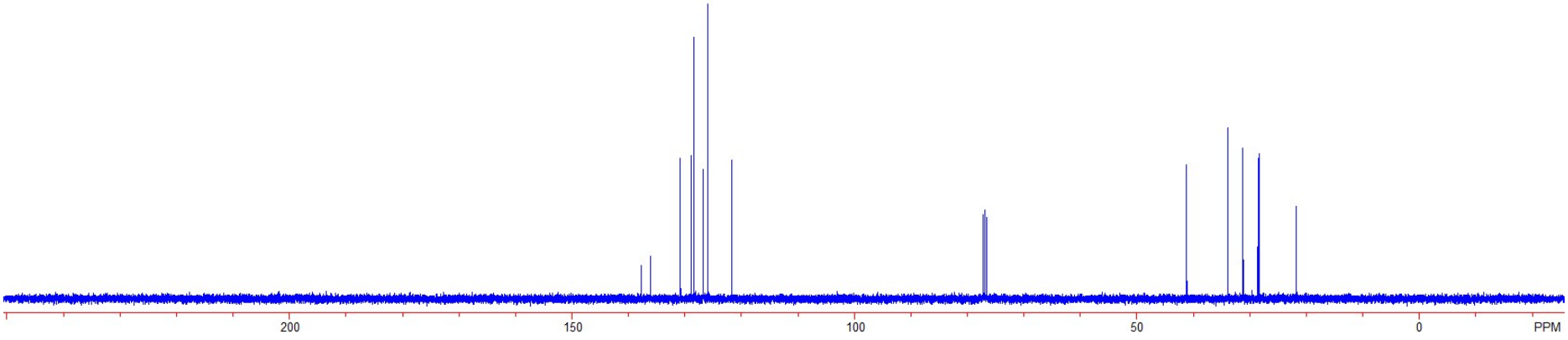


^{13}C NMR (100 MHz, in $CDCl_3$)

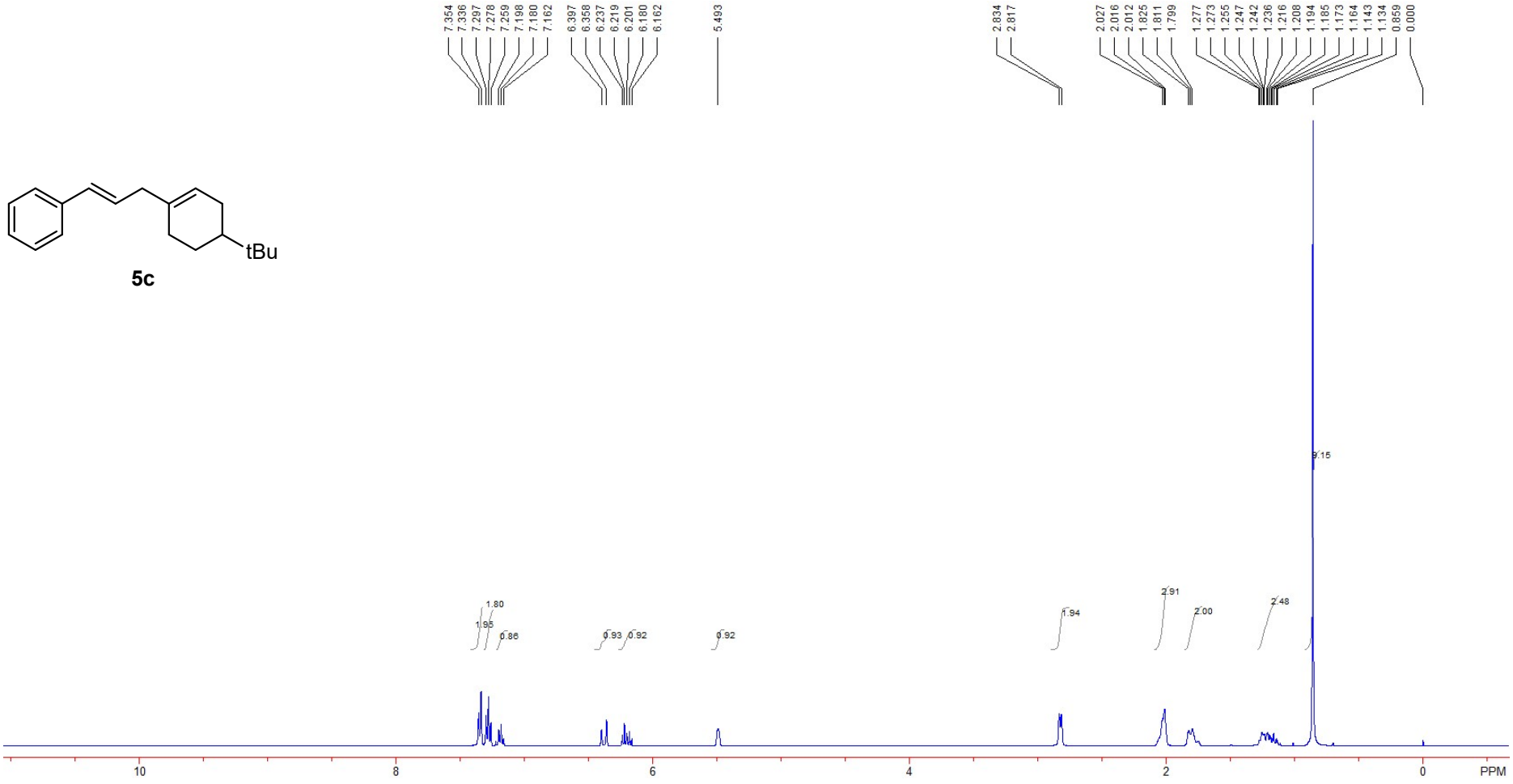




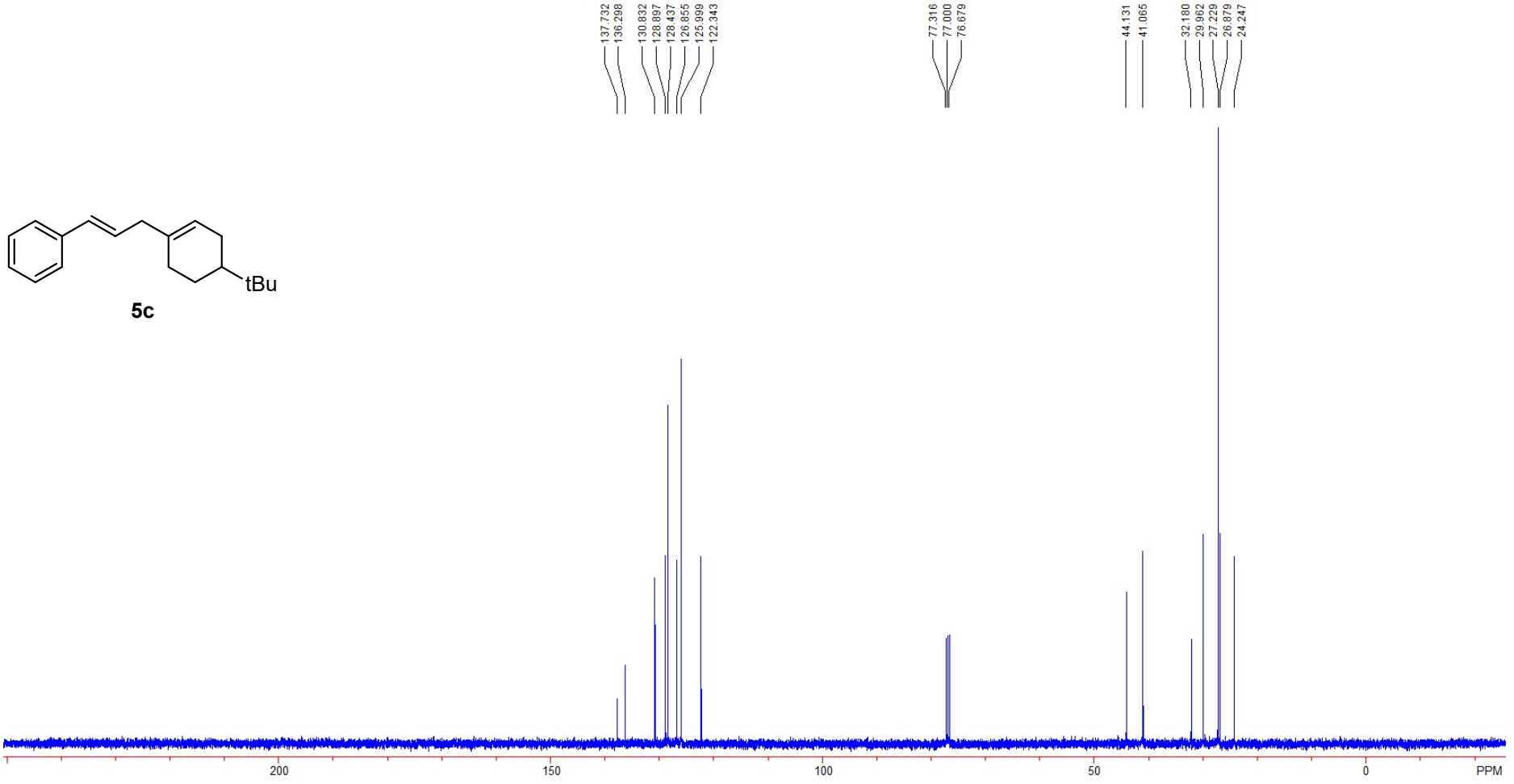
5b



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

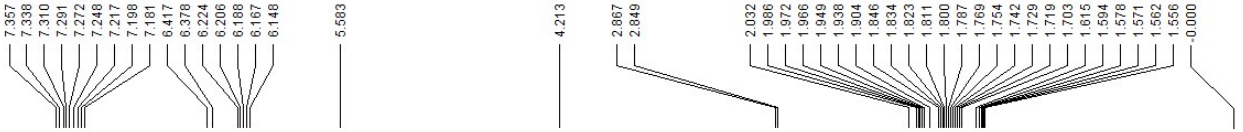


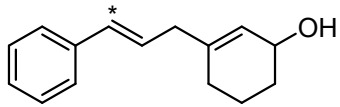
^{13}C NMR (100 MHz, in $CDCl_3$)



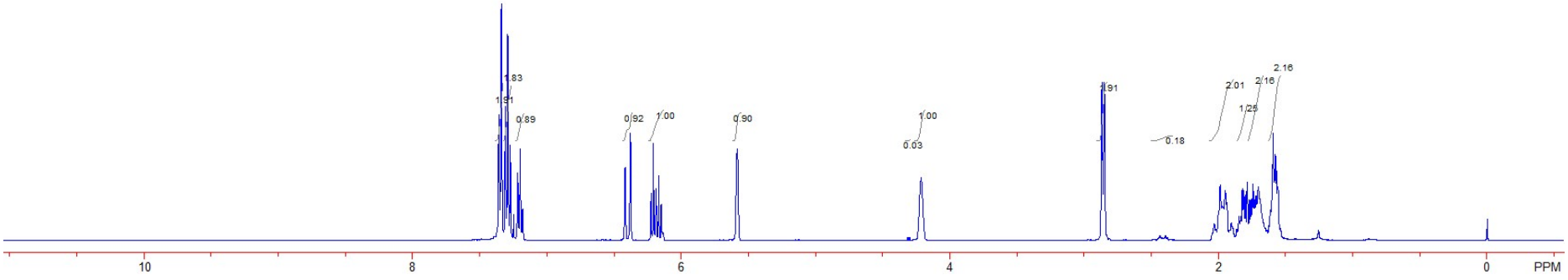
5c

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

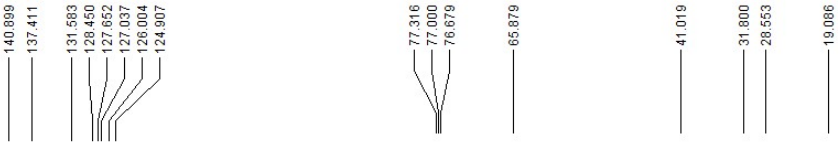


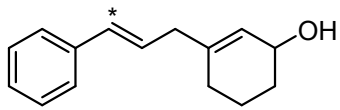


5d (*E*:*Z* > 20:1)

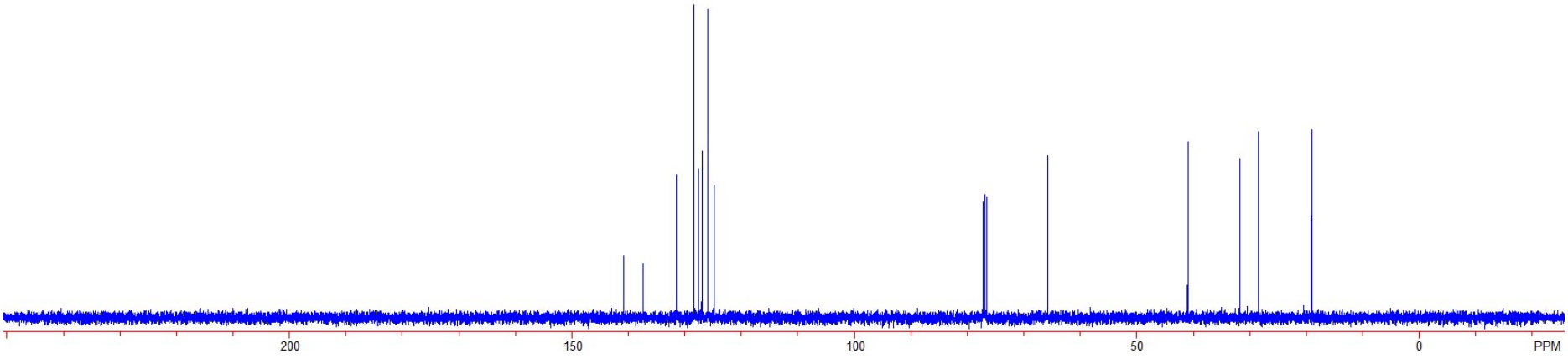


^{13}C NMR (100 MHz, in $CDCl_3$)

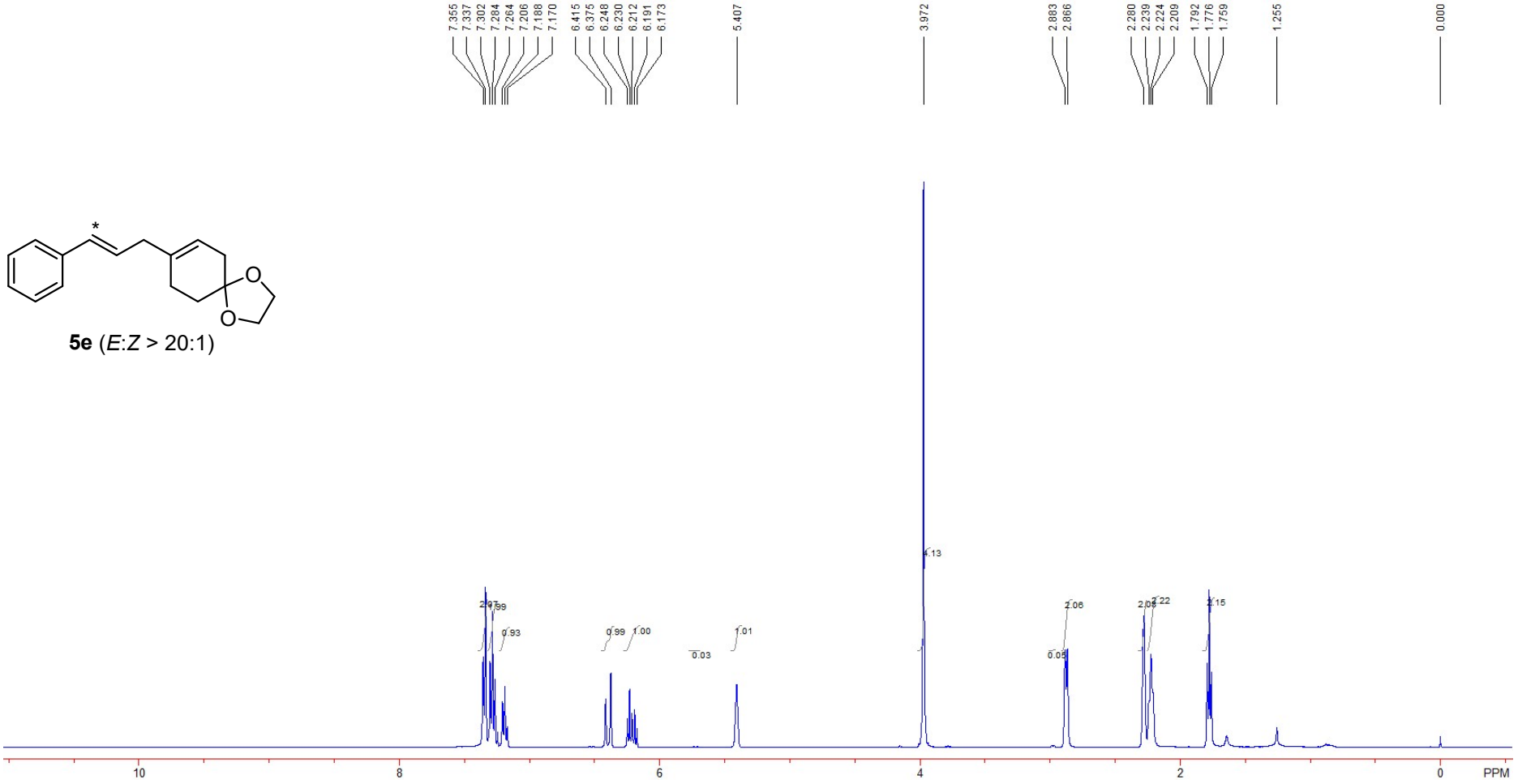




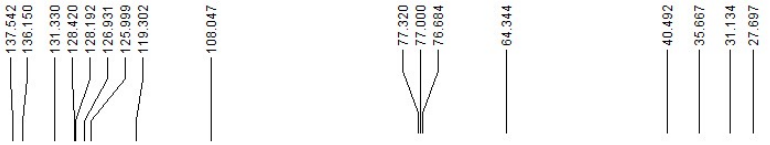
5d (*E*:*Z* > 20:1)

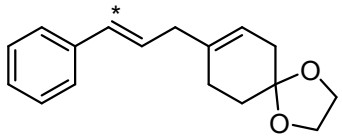


^{1}H NMR (400 MHz, in $CDCl_3$)



^{13}C NMR (100 MHz, in $CDCl_3$)





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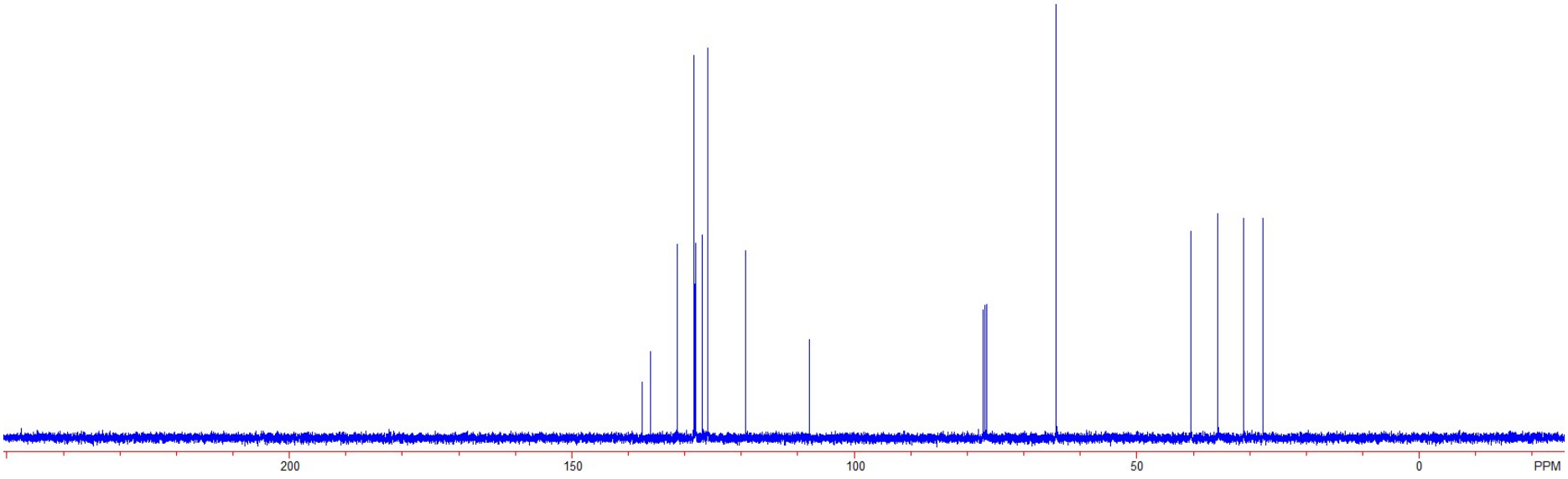
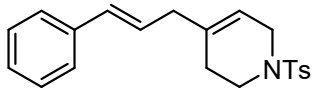


^{1}H NMR (400 MHz, in $CDCl_3$)



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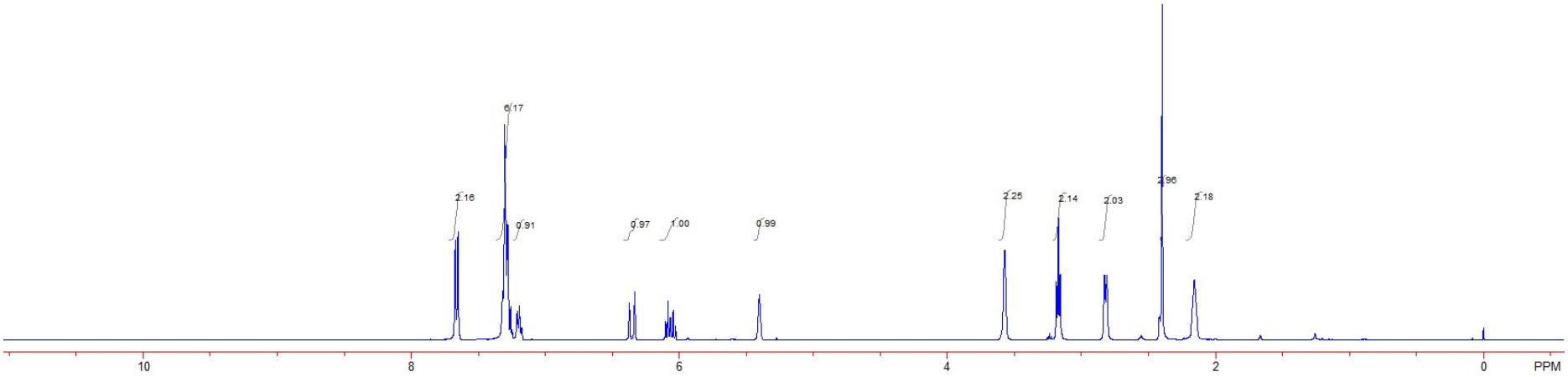
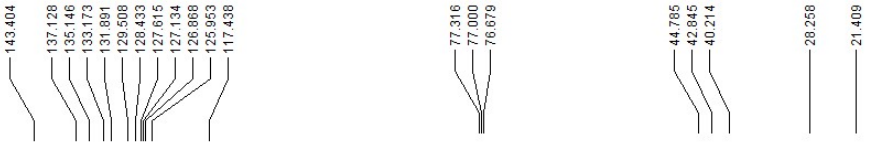
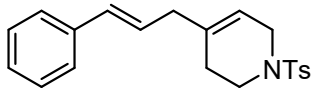


^{13}C NMR (100 MHz, in $CDCl_3$)





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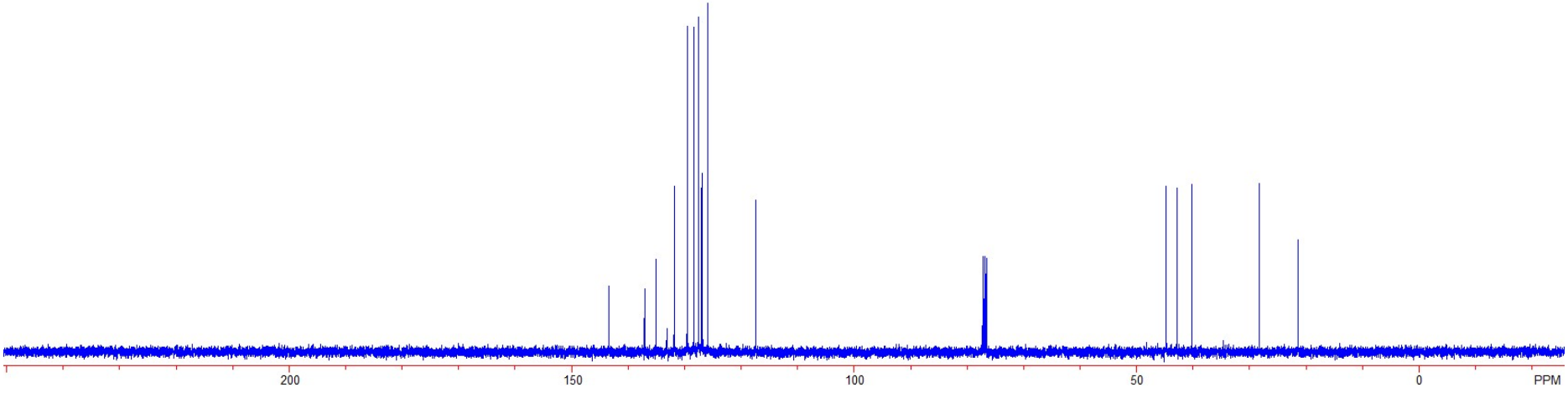
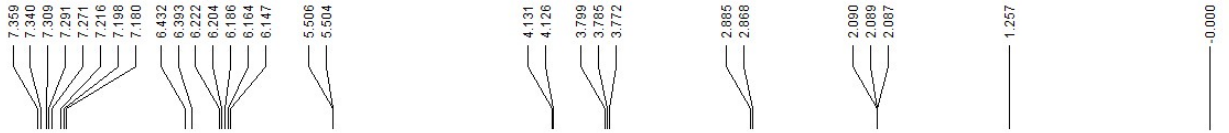
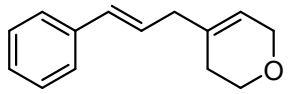


^{1}H NMR (400 MHz, in $CDCl_3$)





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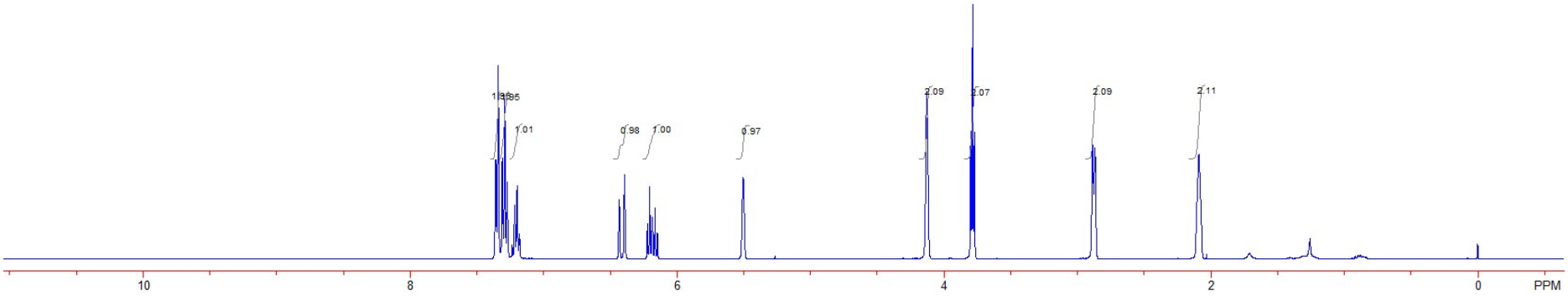
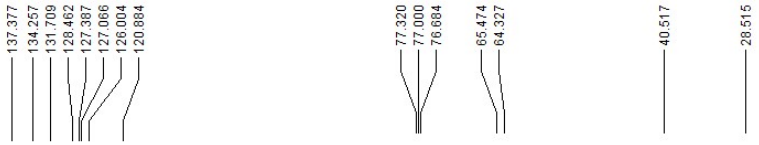
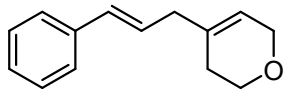


^{13}C NMR (100 MHz, in $CDCl_3$)





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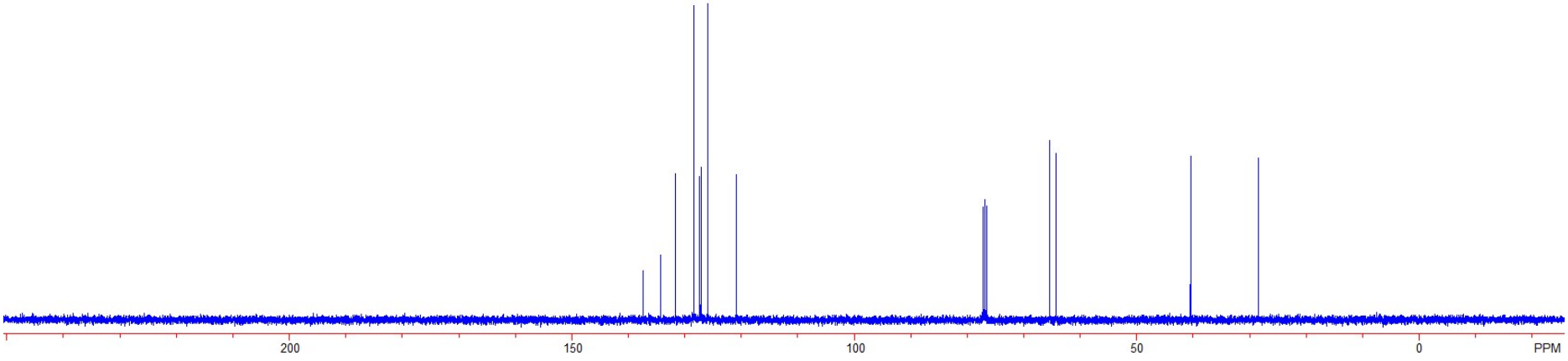
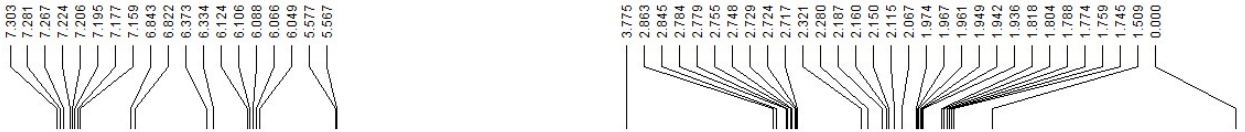
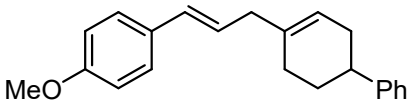


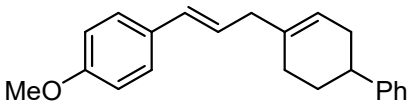
^{1}H NMR (400 MHz, in $CDCl_3$)



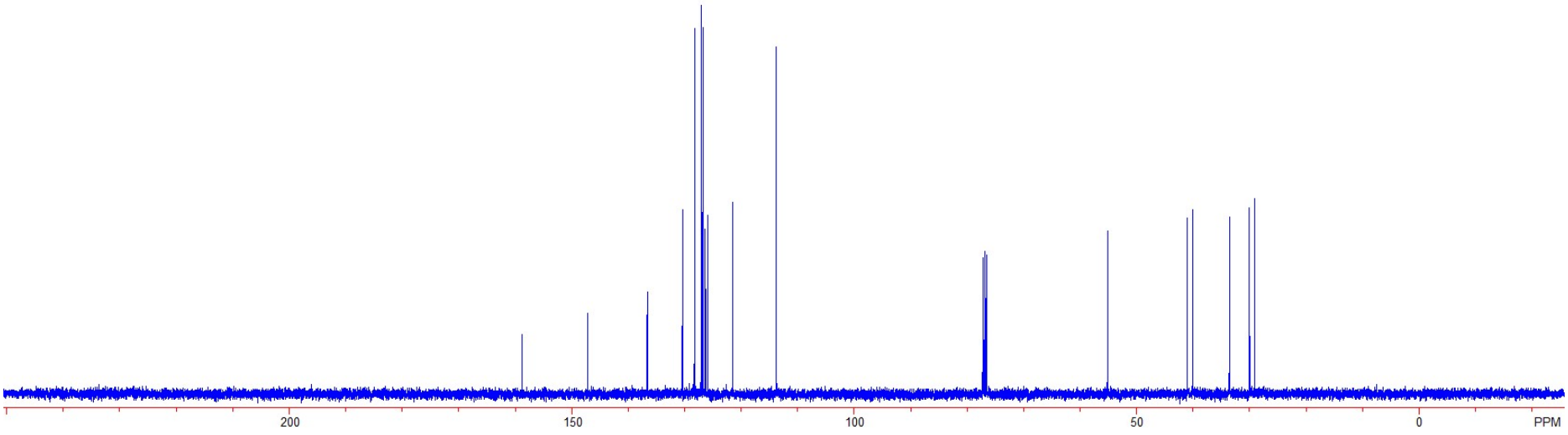


5h

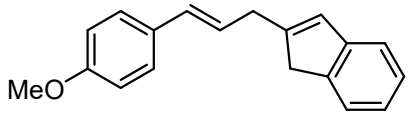
^{13}C NMR (100 MHz, in $CDCl_3$)



5h



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



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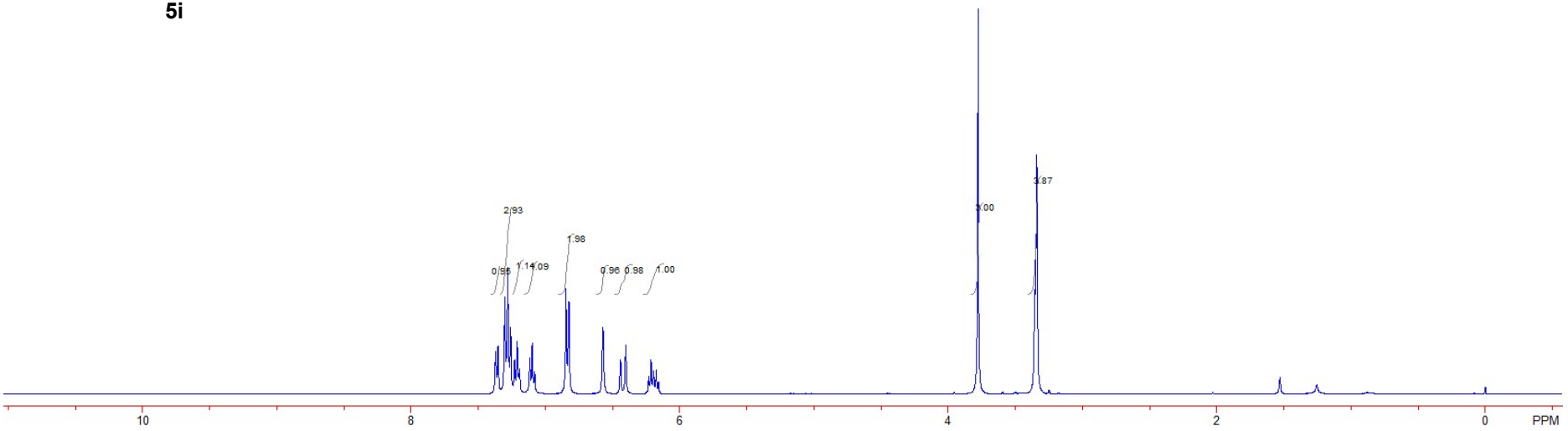
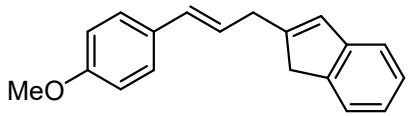


^{13}C NMR (100 MHz, in $CDCl_3$)



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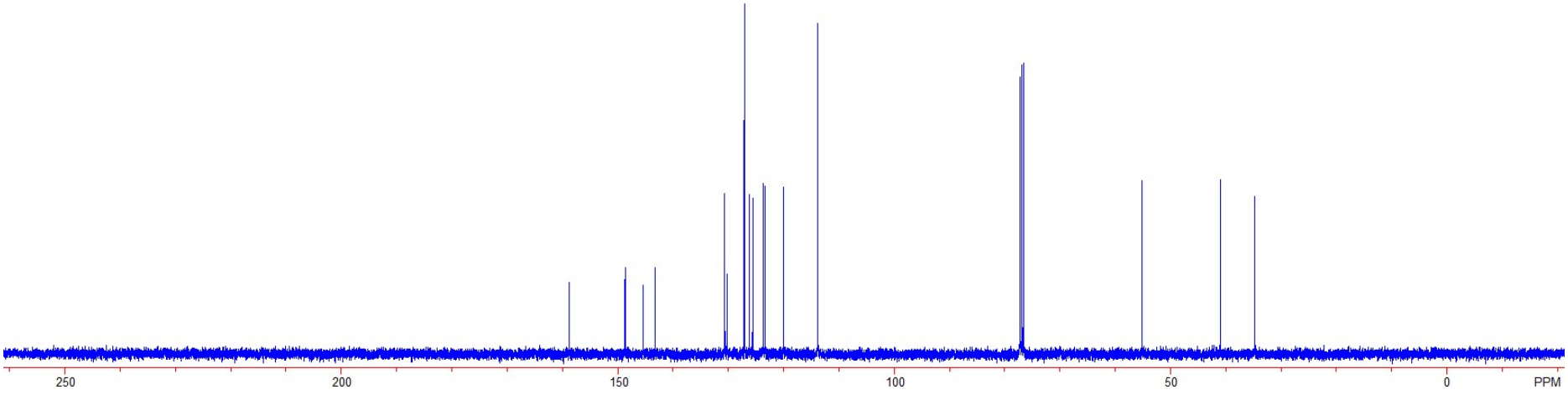
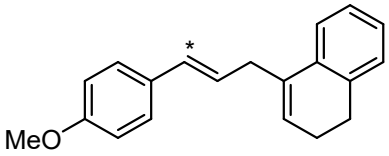
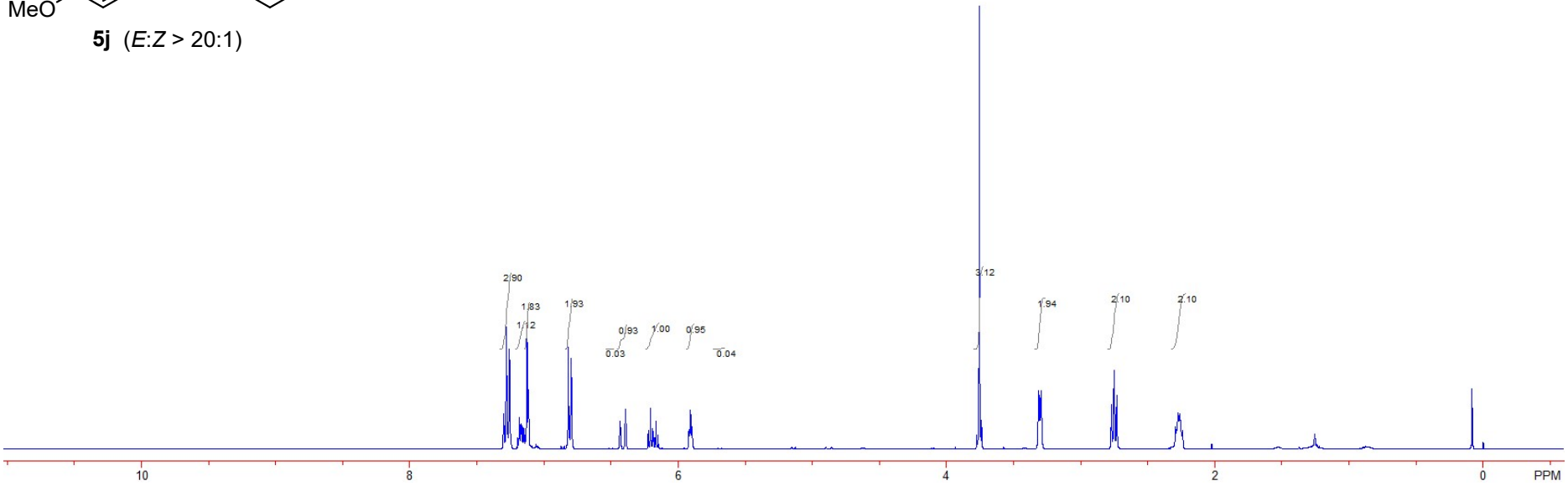


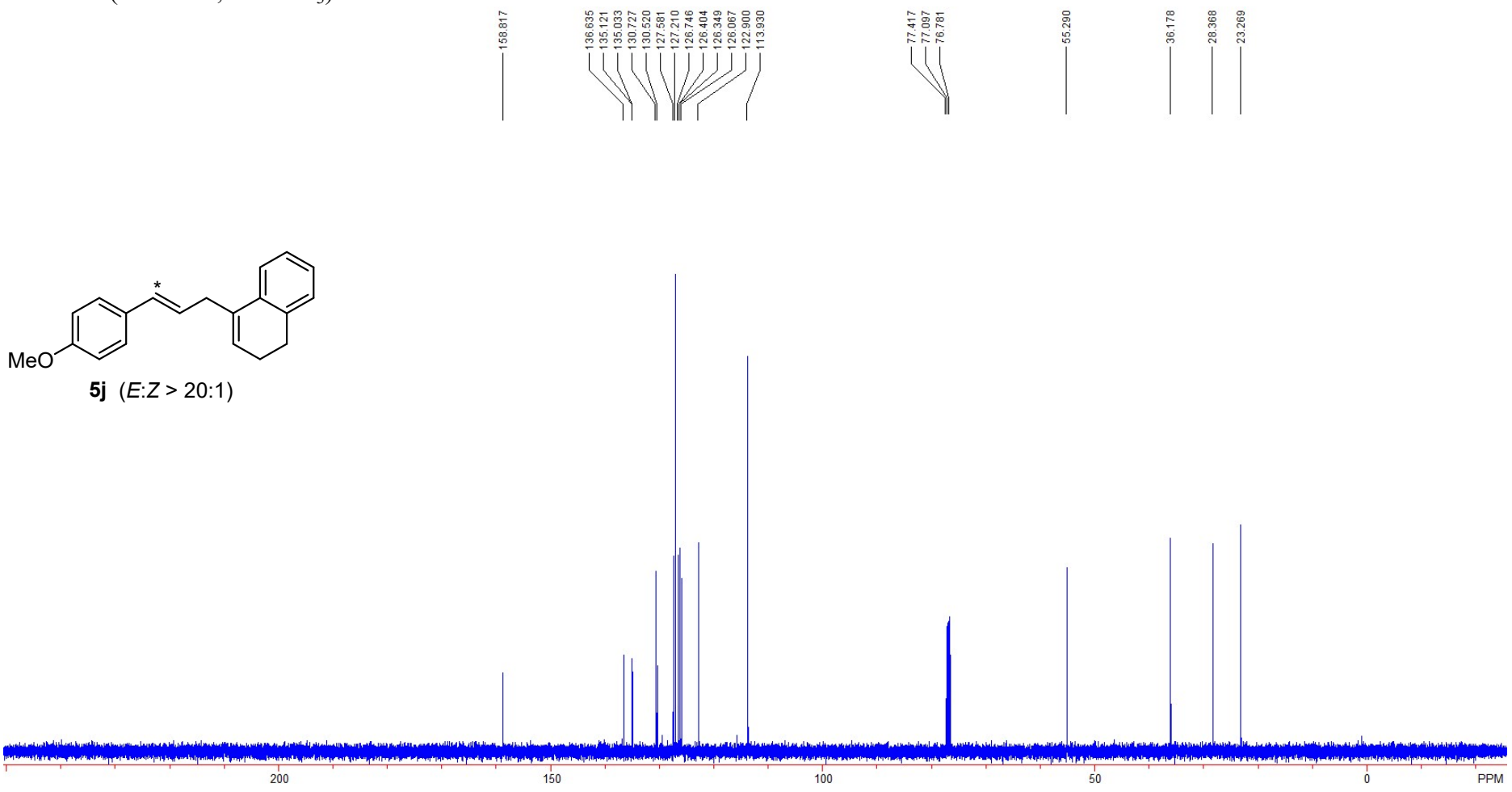
^{1}H NMR (400 MHz, in $CDCl_3$)



5j (*E*:*Z* > 20:1)

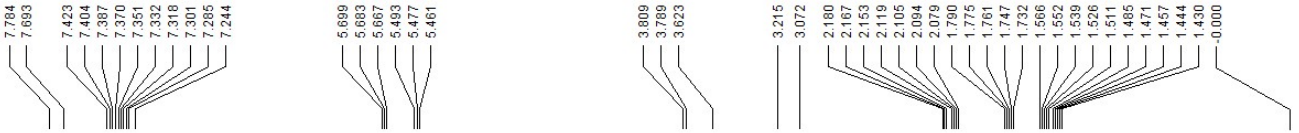


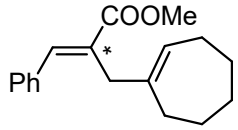
^{13}C NMR (100 MHz, in $CDCl_3$)



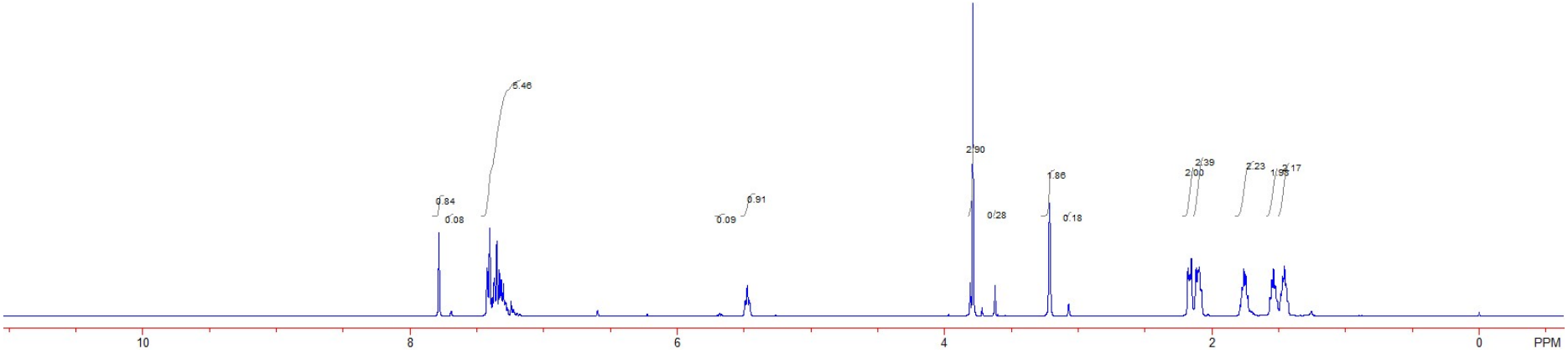
5j (*E*:*Z* > 20:1)

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

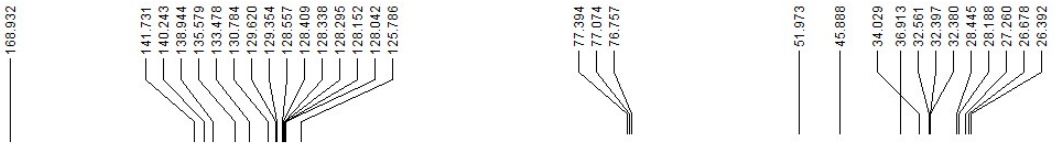


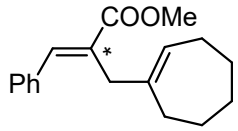


5k
(*major* : *minor* = 10:1)



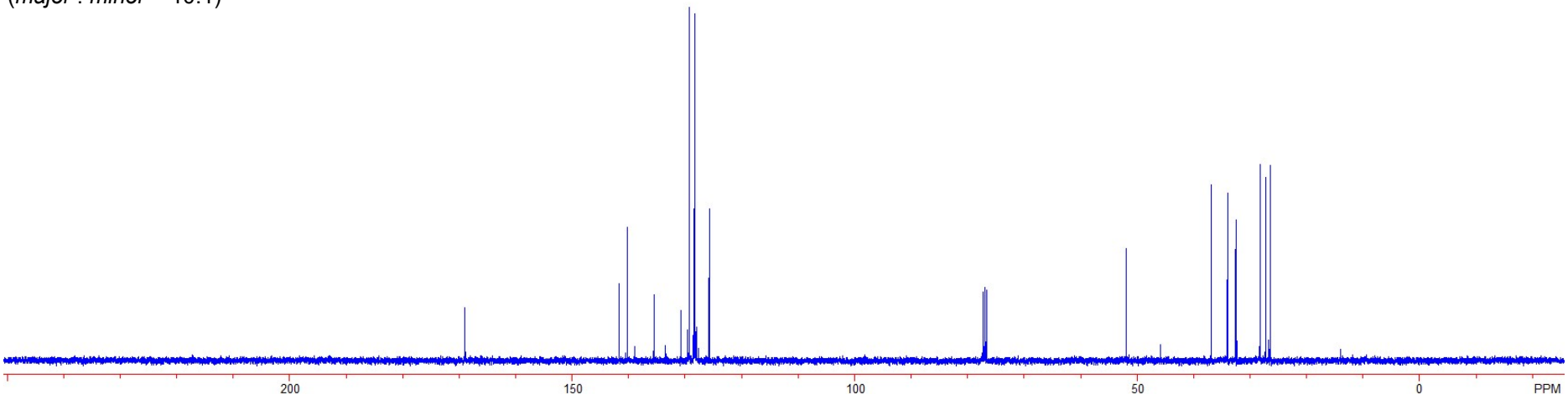
^{13}C NMR (100 MHz, in $CDCl_3$)



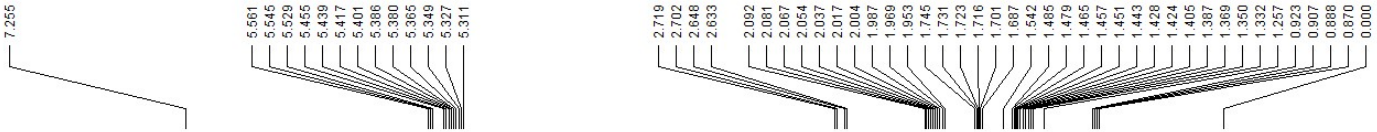


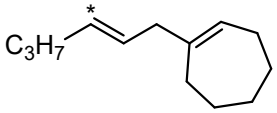
5k

(*major* : *minor* = 10:1)

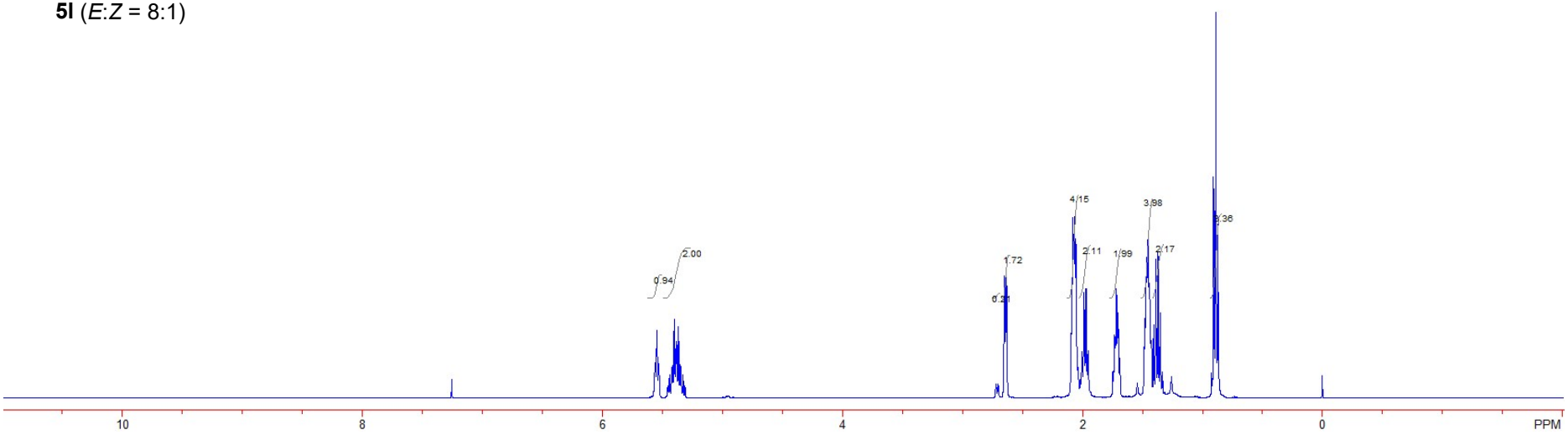


^{1}H NMR (400 MHz, in $CDCl_3$)

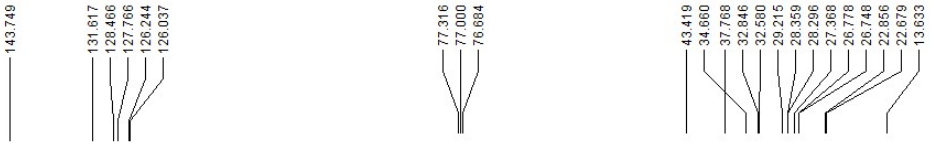


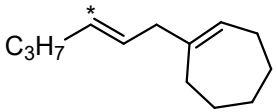


5l (*E*:*Z* = 8:1)



^{13}C NMR (100 MHz, in $CDCl_3$)





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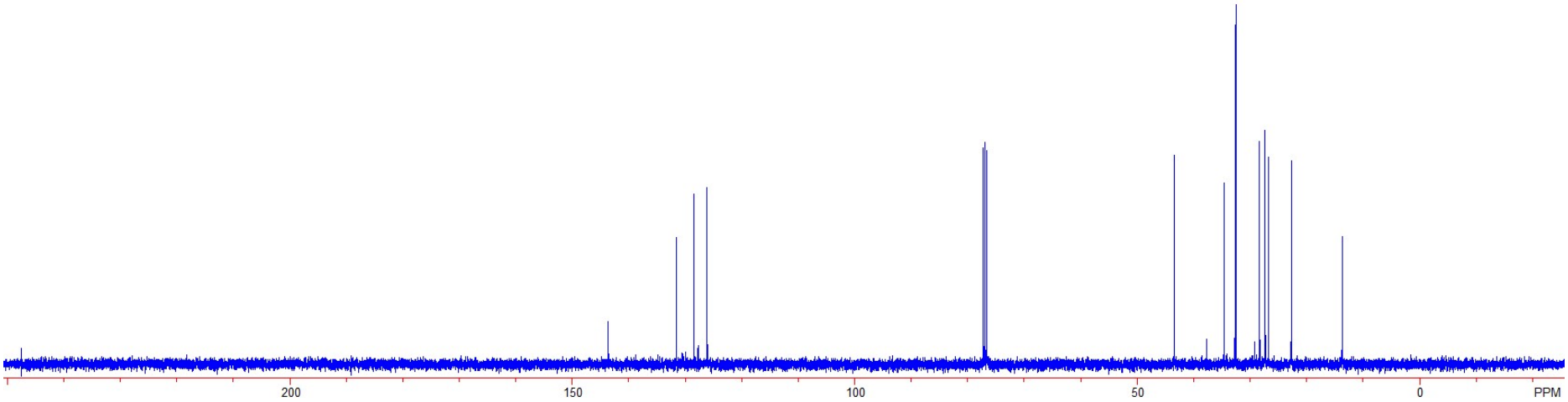
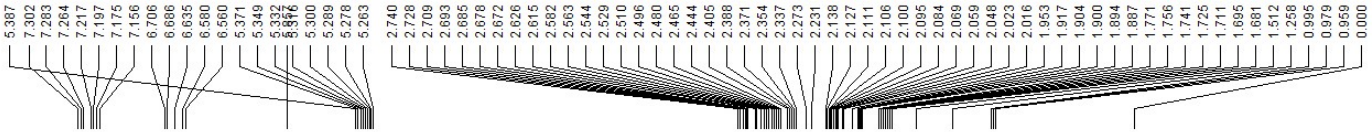
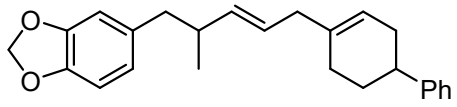
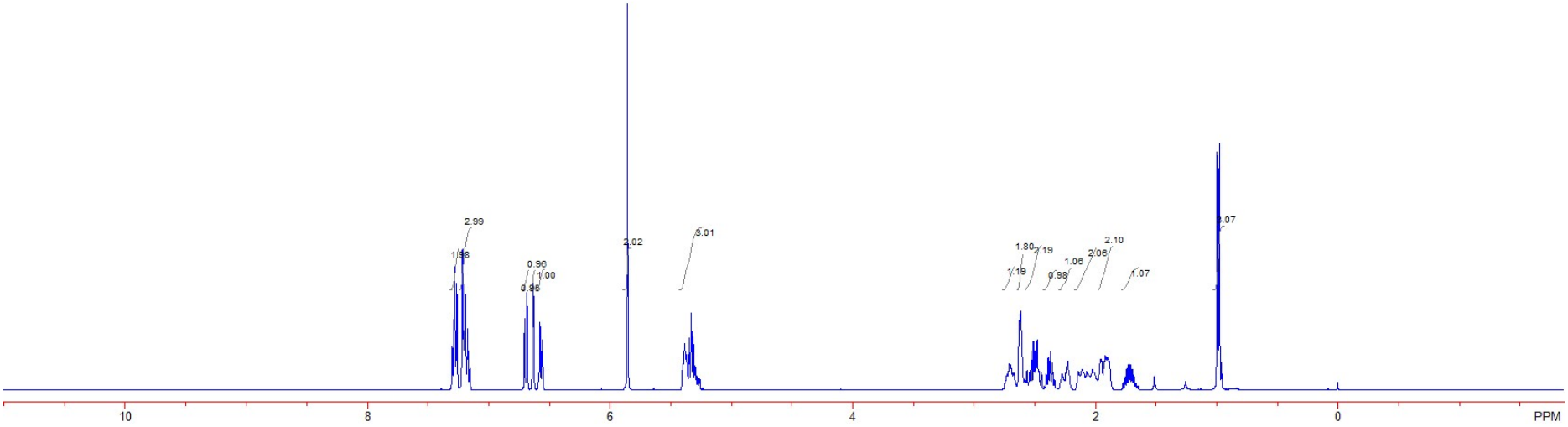


^{1}H NMR (400 MHz, in $CDCl_3$)

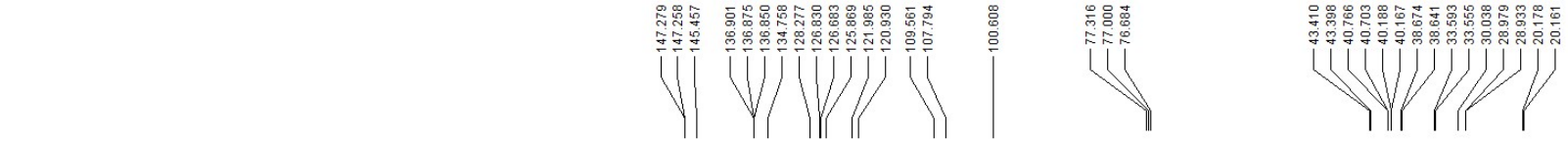


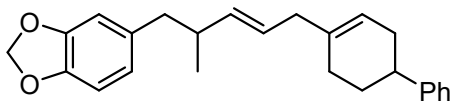


5m



^{13}C NMR (100 MHz, in $CDCl_3$)





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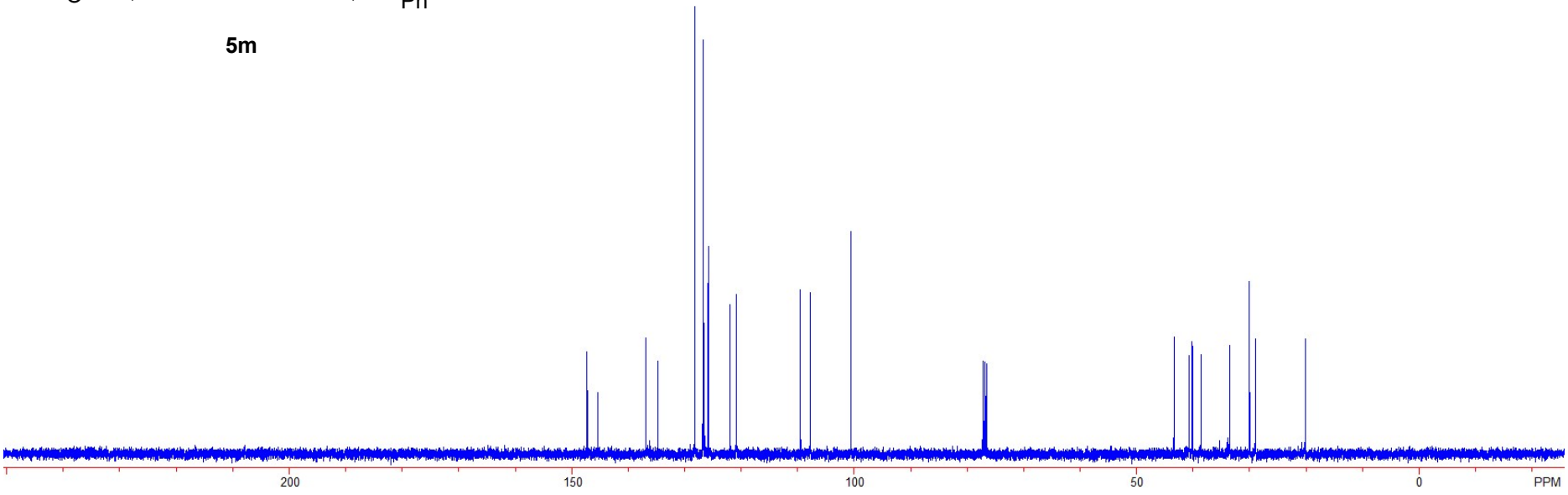
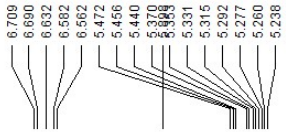
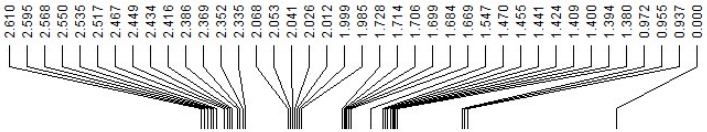
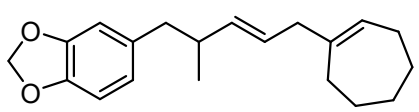


^{1}H NMR (400 MHz, in $CDCl_3$)

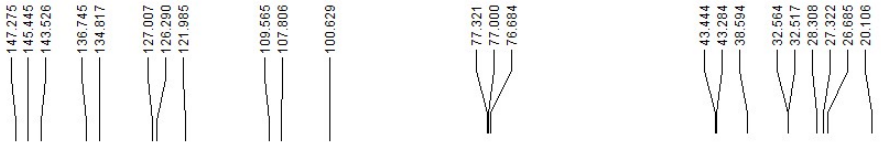


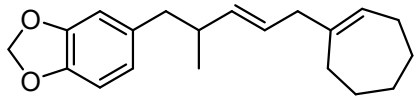




5n

^{13}C NMR (100 MHz, in $CDCl_3$)





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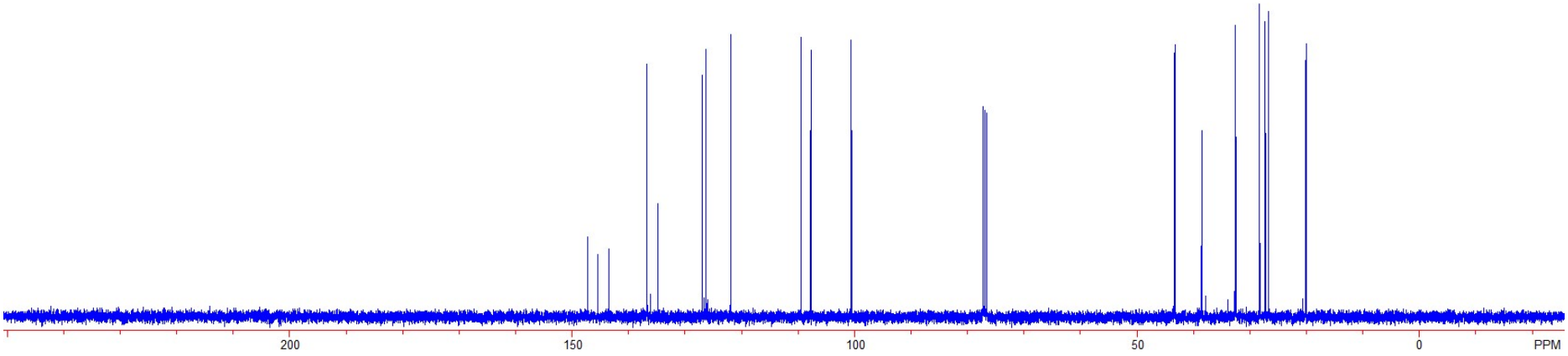
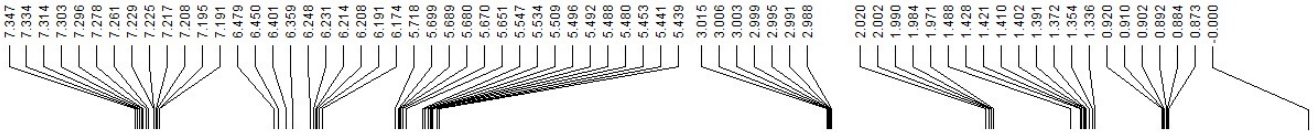
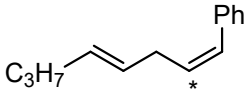
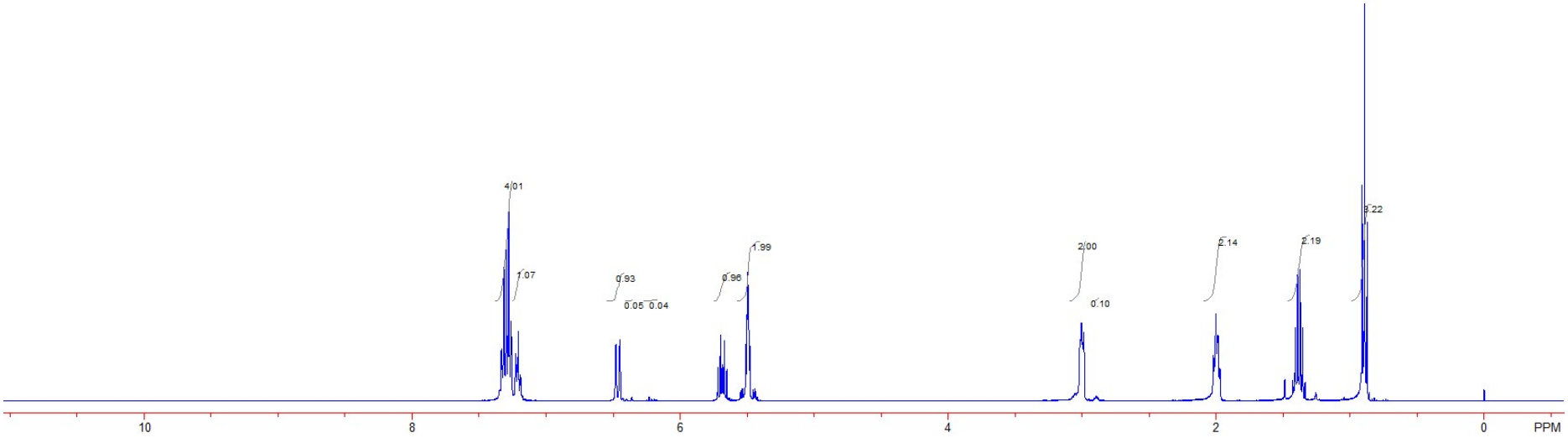


^{1}H NMR (400 MHz, in $CDCl_3$)

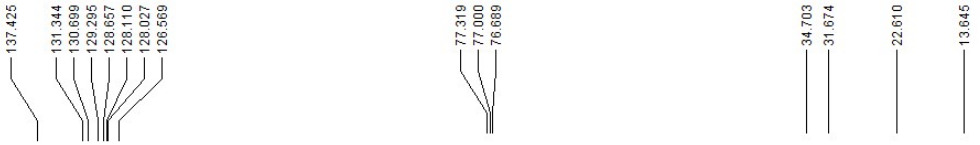


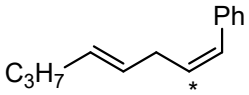


3y (*Z*:*E* = 20:1)

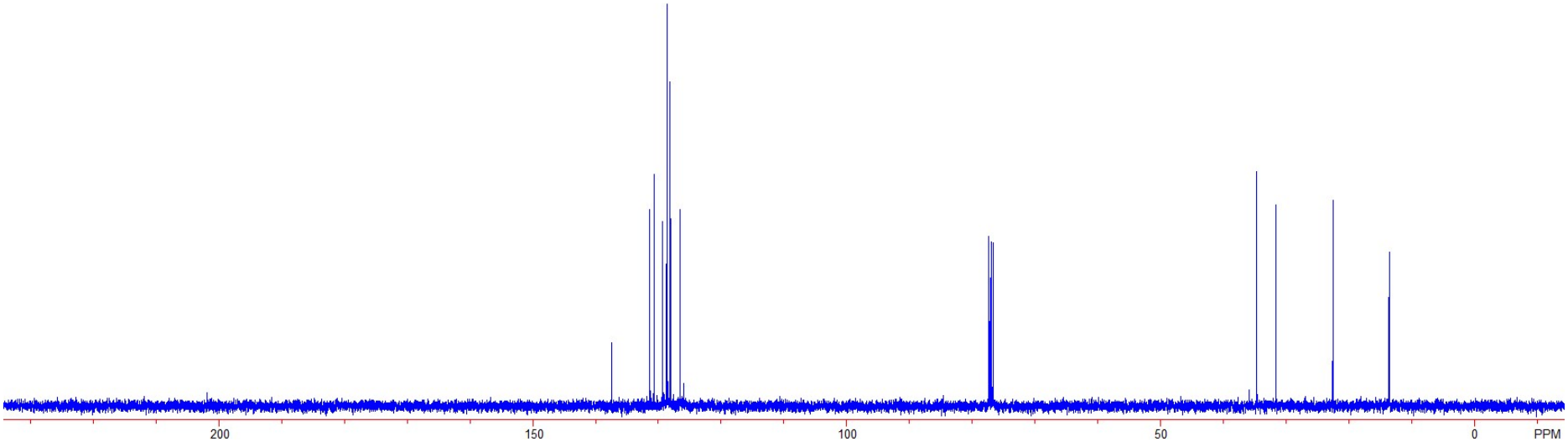


^{13}C NMR (100 MHz, in $CDCl_3$)

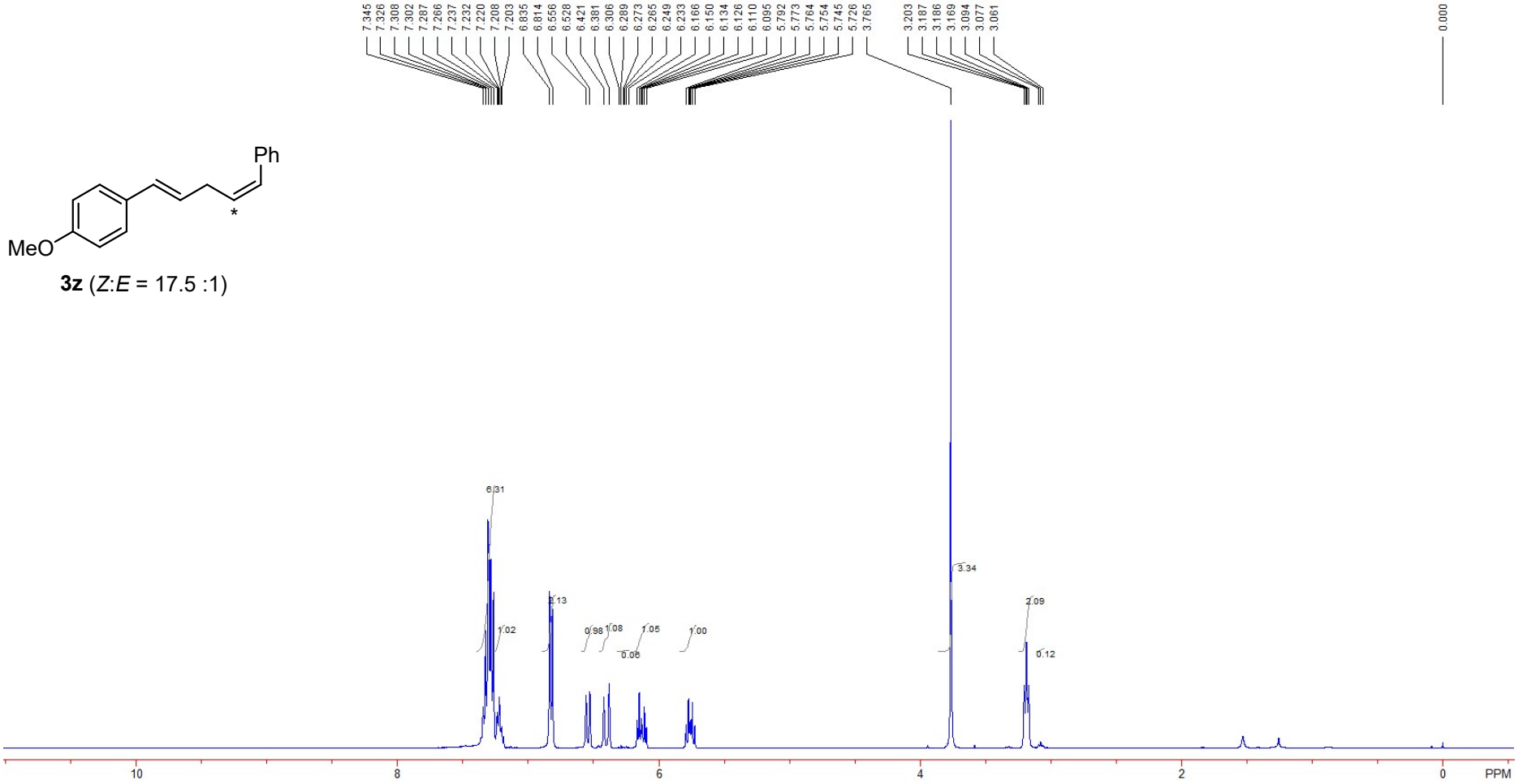




3y (*Z*:*E* = 20:1)

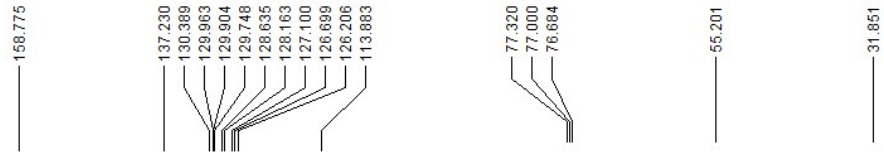


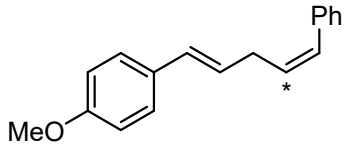
^{1}H NMR (400 MHz, in $CDCl_3$)



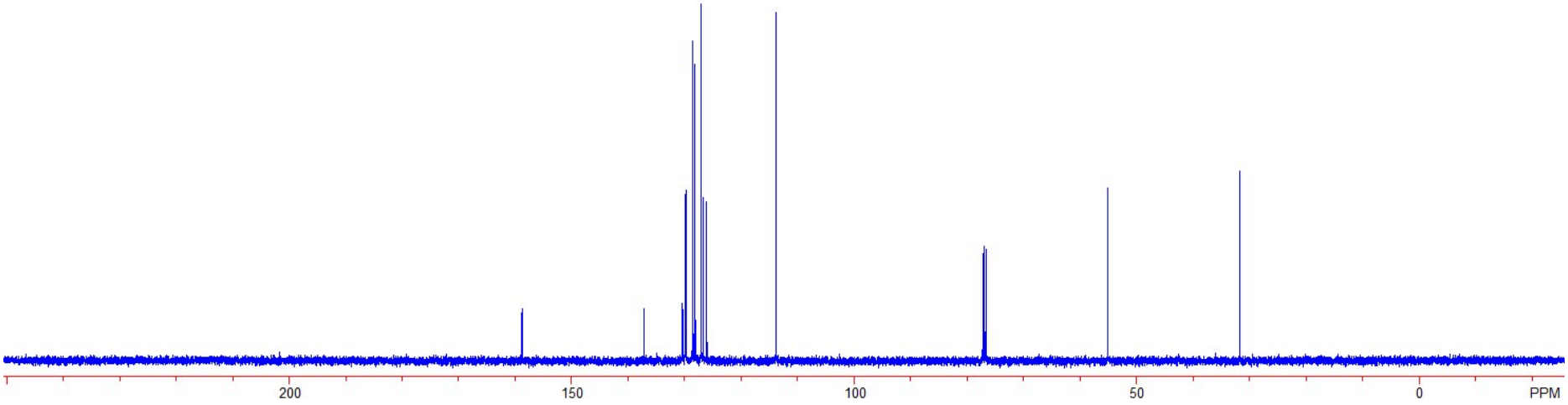
3z (*Z*:*E* = 17.5 :1)

^{13}C NMR (100 MHz, in $CDCl_3$)

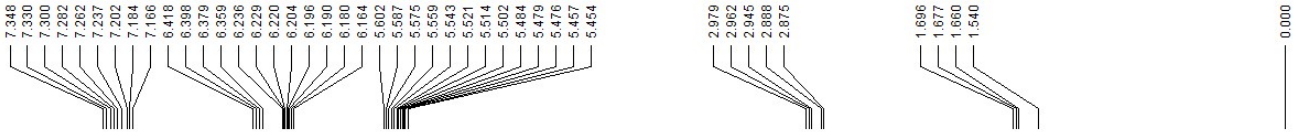


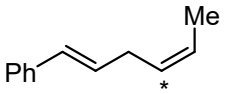


3z (*Z*:*E* = 17.5 :1)

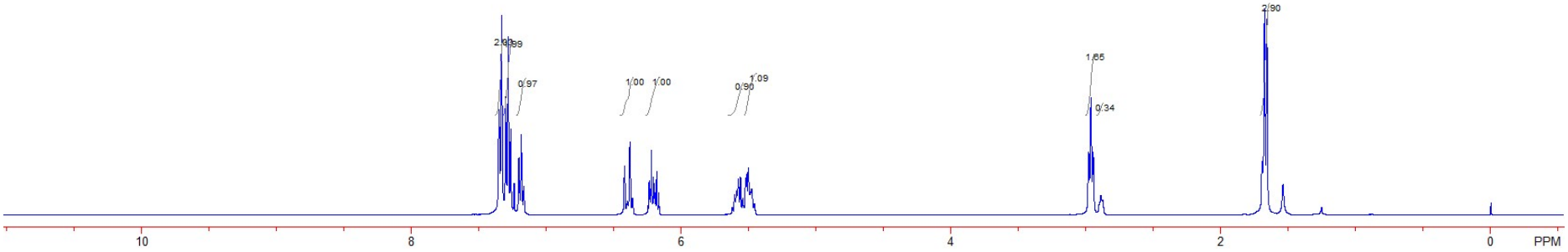


^{1}H NMR (400 MHz, in $CDCl_3$)

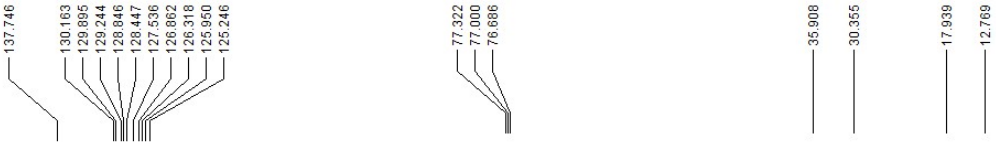


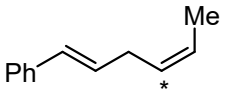


3za (*Z*:*E* = 4.9:1)

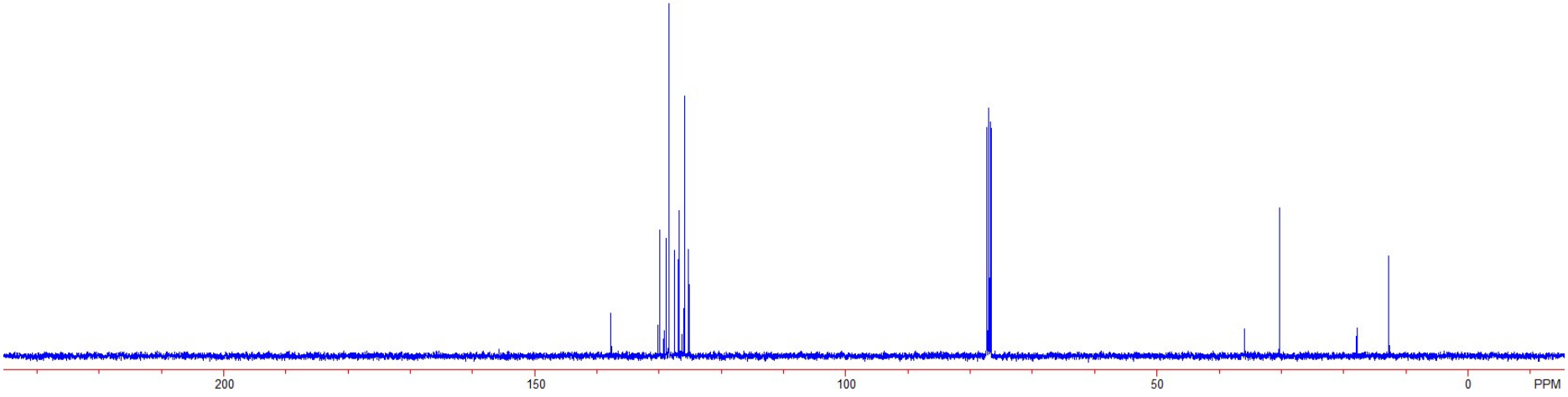


^{13}C NMR (100 MHz, in $CDCl_3$)

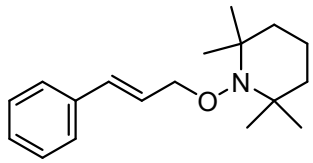




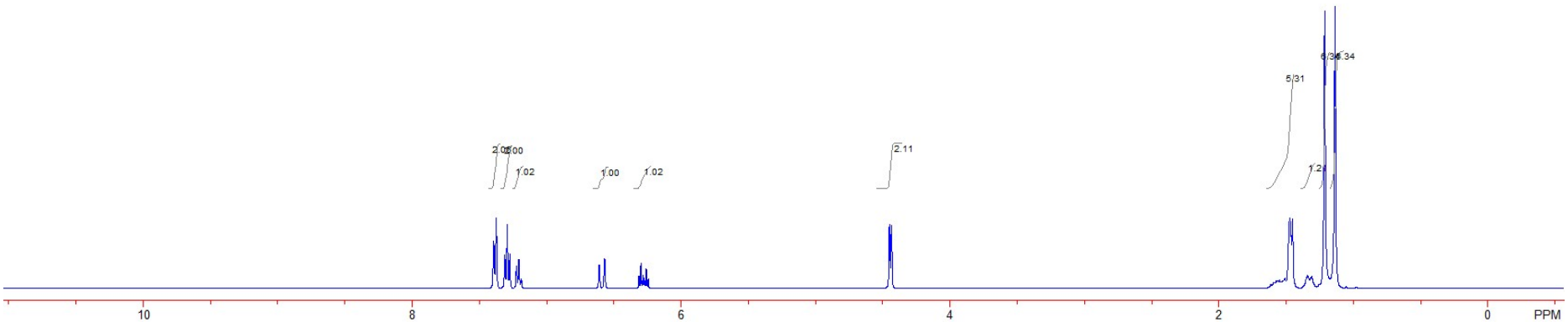
3za (*Z*:*E* = 4.9:1)



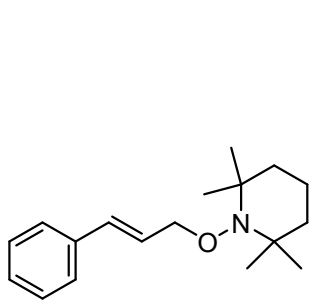
^{1}H NMR (400 MHz, in $CDCl_3$)



6a



^{13}C NMR (100 MHz, in $CDCl_3$)



6a