Supporting Information for

Hydroindation of allenes and its application to radical cyclization

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Analysis. IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JMTC-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane as internal standard. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using MERCK Silica gel 60. Purification of products by recycle GPC system was performed by JAPAN ANALYTICAL INDUSTRY CO., LTD. LC-908. Yields were determined by ^{1}H NMR using internal standard. Stereochemistry of products was determined by NOE-difference spectrum or coupling constant of ^{1}H NMR.

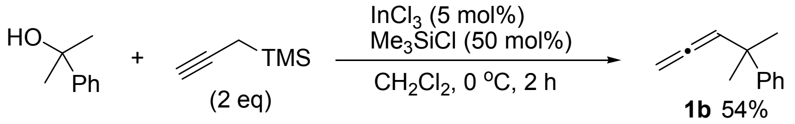
Materials:

Di-*n*-butyltin dihydride (n-Bu_2SnH_2) was prepared by the reduction of di-*n*-butyltin dichloride (n-Bu_2SnCl_2) with $LiAlH_4$.[1] Di-*n*-butyliodotin hydride (n-Bu_2SnIH) was synthesized *in situ* by the redistribution reaction between Bu_2SnI_2 and Bu_2SnH_2.[2]

THF was purchased in dehydrated form.

Undeca-1,2-diene (Octylallene) (1a) was prepared according to the known procedures.[3]

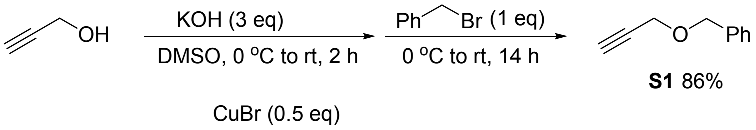
4-Methyl-4-Phenyl-penta-1,2-diene (1d) was prepared according to our reported method.[4] To the mixture of $InCl_3$ (0.275 g, 1.25 mmol) and propargyl trimethylsilane (68% purity 8.40g, 50.8 mmol) and chlorotrimethylsilane (1.39 g, 12.8 mmol) in dry dichloromethane (45 mL) was added dropwise 2-phenyl-propan-2-ol (2.98 g, 22 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 2 h, the reaction mixture was warmed up to rt and then diluted with saturated $NaHCO_3$(aq) and extracted by Hexane/AcOEt= 9/1. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with hexane and then distilled under reduced pressure (100 °C/ 8 mmHg, 1.87 g, 54% yield).

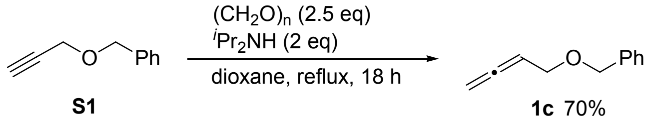


4-Benzyloxy-buta-1,2-diene (Benzyloxymethylallene) (1e) was prepared by following procedures.

To a solution of KOH (33.7 g, 600 mmol) in DMSO (200 mL) was added dropwise propargyl alcohol (11.2 g, 200 mmol) at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 4 h. The solution was cooled to 0 °C and benzyl bromide (34.21 g, 200 mmol) was added. After stirring at rt for 14 h, water was added, and extracted by Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by distillation under reduced pressure to give alkyne **S1** as colorless oil (47 °C/ 0.07 mmHg, 24.3 g, 86% yield).

Under nitrogen atmosphere to a mixture of CuBr (7.16 g, 50 mmol), paraformaldehyde (7.51 g, 250 mmol) and diisopropylamine (20.2 g, 200 mmol) in dioxane (380 mL) was added alkyne **S1** (14.6 g, 100 mmol). The resulting solution was refluxed for 18 h. After the reaction, the solution was filtrated by celite and concentrated under reduced pressure. The resulting mixture was diluted by water (30 mL), AcOEt (70 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated. The residue was purified by distillation under reduced pressure to give **1e** as colorless oil (82 °C/ 1.6 mmHg, 11.1 g, 70% yield).





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[1] W. P. Newman and J. Pedain, *Tetrahedron Lett.*, 1964, **5**, 2461-2465.

[2] T. Kawakami, I. Shibata and A. Baba, *J. Org. Chem.*, 1996, **61**, 82-87.

[3] T. Endo, K. Takagi and I. Tomita, *Tetrahedron*, 1997, **53**, 15187-15196.

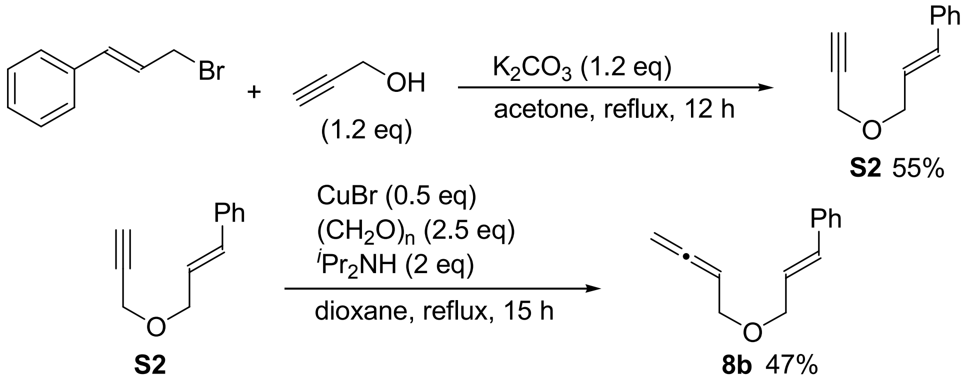
[4] M. Yasuda, T. Saito, M. Ueba and A. Baba, *Angew. Chem. Int. Ed.*, 2004, **43**, 1414-1416.

Vinylidene-cyclohexane (1f) was prepared according to the known procedures.[5] **Cyclonona-1,2-diene (1g)** was prepared according to the known procedures.[6]

Allenene **5b** was prepared from cinnamyl bromide and propargyl alcohol by following procedures.

To a mixture of propargyl alcohol (10.1 g, 180 mmol) and K_2CO_3 (24.9 g, 180 mmol) in acetone (75 mL) was added cinnamyl bromide (29.6 g, 150 mmol) at room temperature. The mixture was refluxed for 12 h. After the resulting mixture was cooled to room temperature, water was added and extracted by AcOEt. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled to give enyne **S2** as colorless oil (14.1 g, 55% yield).

Under nitrogen atmosphere to a solution of CuBr (5.88 g, 41 mmol), paraformaldehyde (6.16 g, 205 mmol) and diisopropylamine (16.6 g, 164 mmol) in dioxane (300 mL) was added enyne **S2** (14.1 g, 82 mmol). The resulting solution was refluxed for 15 h. After the reaction, the solution was filtrated by cerite and concentrated under reduced pressure. The resulting mixture was diluted by water (30 mL), AcOEt (70 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated. The residue was purified by distillation under reduced pressure to give **8b** as colorless oil (76 ^{o}C/ 0.05 mmHg, 7.17 g, 47% yield).



Allenene **8c** was prepared by following procedures.

Under nitrogen atmosphere to a solution of phosphorous ylide **S4** (52.3 g, 150 mmol) in CH_2Cl_2 (80 mL) was added dropwise aldehyde **S3** (21.1 g, 150 mmol) at 10 ^{o}C over a period of 45 min. The resulting solution was stirred at 10 ^{o}C for 1 h. After the reaction, the solution was concentrated under reduced pressure. The precipitated white solid was filtered using hexane and the solution was concentrated under reduced pressure to give ester **S5** including small amount of aldehyde (31.3 g, ca. >99% yield).

Under nitrogen atmosphere to a solution of crude ester **S5** (29.5 g, 140 mmol) in toluene (200 mL) was added dropwise aldehyde diisobutylaluminium hydride (207 mL, 1.5 M in toluene, 310 mmol) at -78 ^{o}C. The resulting solution was warmed up to room temperature over a period of 1 h. After the reaction, the solution was cooled by iced-bath and 2M HCl in water (400 mL) was added

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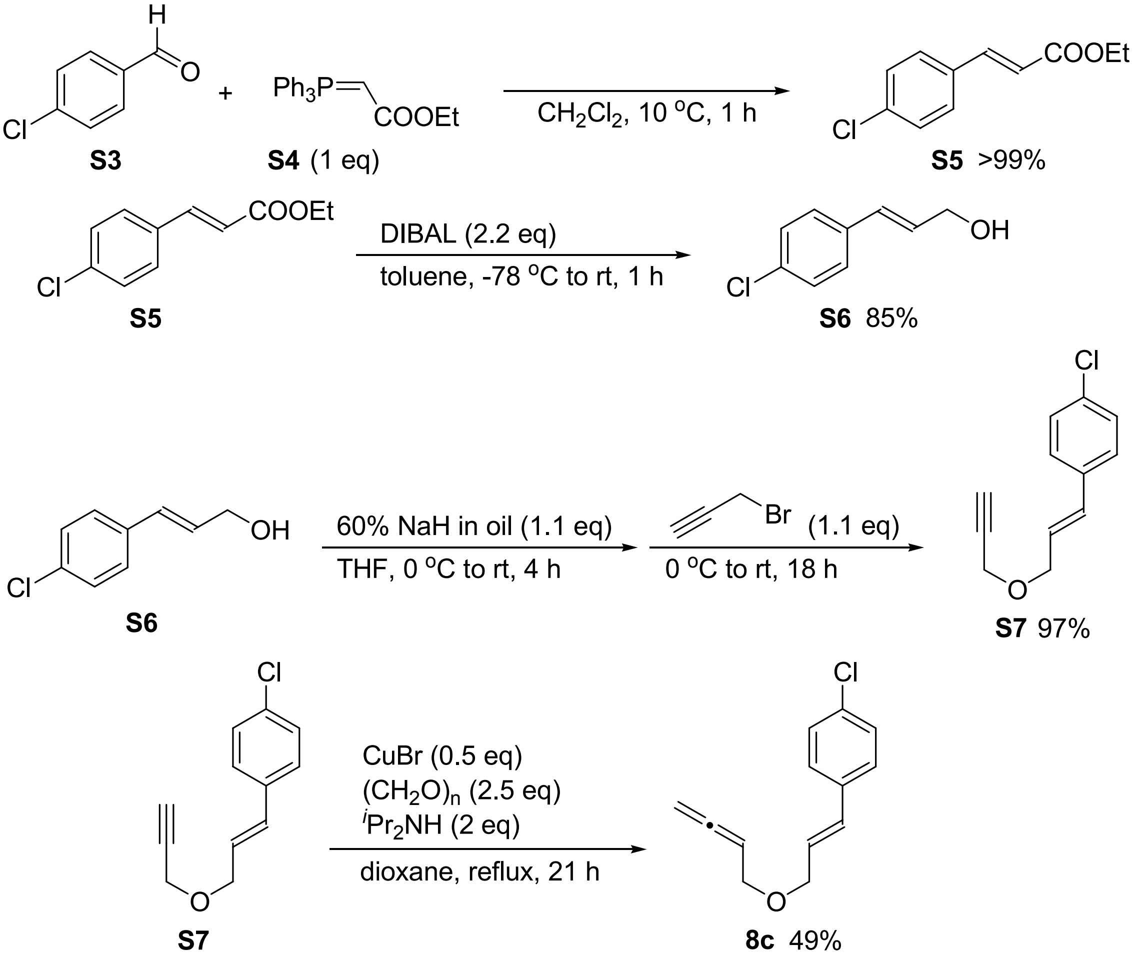
[5] J. Tsuji, T. Sugiura and I. Minami, *Synthesis*, 1987, 603-606.

[6] (a) M. S. Baird, A. V. Nizovtsev, I. G. Bolesov, *Tetrahedron*, 2002, **58**, 1581-1593; (b) K. A. Campbell, H. O. House, B. W. Surber and W. S. Trahanovsky, *J. Org. Chem.*, 1987, **52**, 2474-2481; (c) J. A. Murphy, K. A. Scott, R. S. Sinclair and N. Lewis, *Tetrahedron Lett.*, 1997, **38**, 7295-7298.

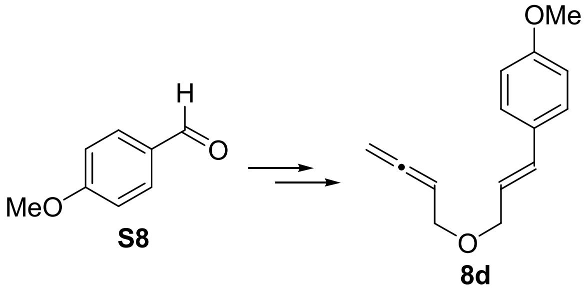
dropwise slowly. The resulting mixture was extracted by CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The precipitated solid was recrystallized by hexane to give alcohol **S6** as white solid (19.4 g, 85% yield).

To a suspension of 60% NaH in oil (4.8 g, 120 mmol) in THF (150 mL) was added dropwise a solution of alcohol **S6** (18.6 g, 110 mmol) in THF (50 mL) at 0 ^oC. The resulting solution was stirred at 0 ^oC to room temperature for 4 h. The solution was cooled by iced-bath and propargyl bromide (14.3 g, 120 mmol) was added. After stirring at 0 ^oC to room temperature for 18 h, water was added, and extracted by Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated to give enyne **S7** with small amount of impurities (22.0 g, ca. 97% yield).

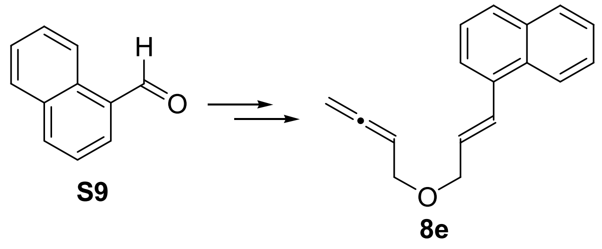
Under nitrogen atmosphere to a mixture of CuBr (5.74 g, 40 mmol), paraformaldehyde (6.01 g, 200 mmol) and diisopropylamine (16.2 g, 160 mmol) in dioxane (300 mL) was added crude enyne **S7** (16.3 g, 79 mmol). The resulting solution was refluxed for 21 h. After the reaction, the solution was filtrated by celite and concentrated under reduced pressure. The resulting mixture was diluted by AcOEt (100 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled under reduced pressure to give **8c** as colorless oil (102 ^oC/ 0.10 mmHg, 8.56 g, 49% yield).



Alleneness **8d** and **8e** were prepared by similar procedures with **8c** from aldehydes **S8** and **S9** instead of **S3**.



S8 **8d**



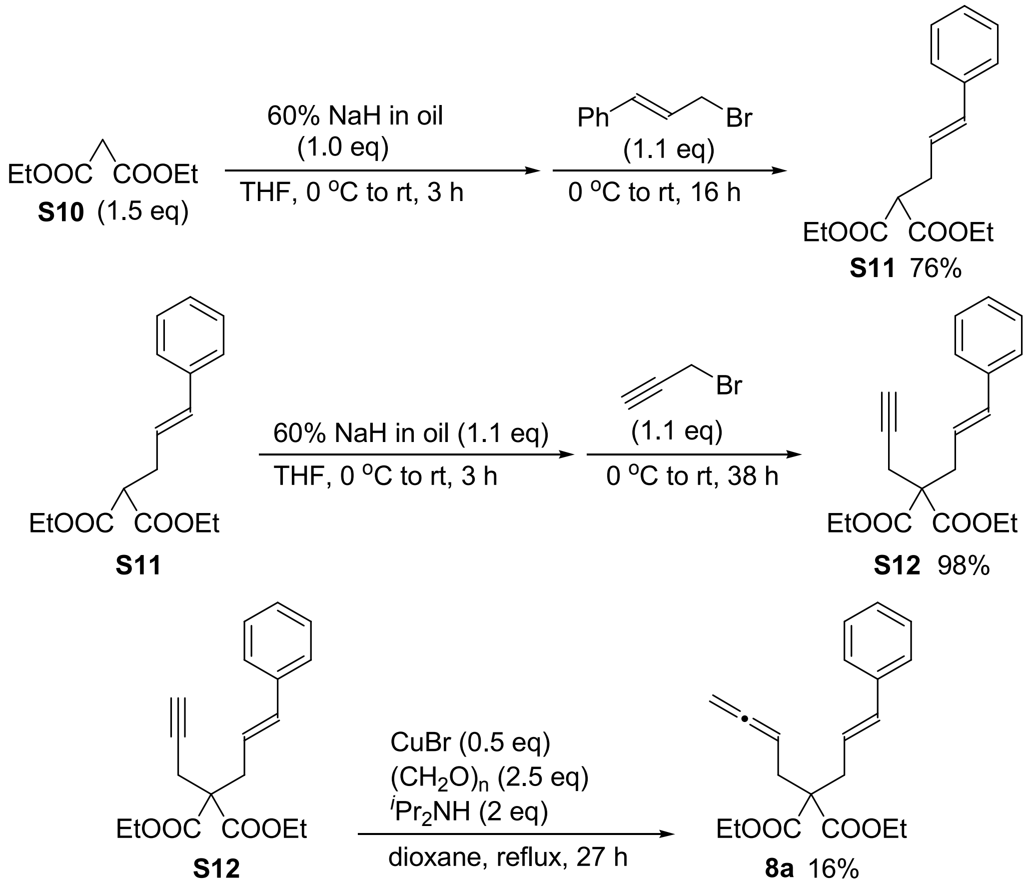
S9 **8e**

Allenene **8a** was prepared by following procedures.

To a suspension of 60% NaH in oil (4.6 g, 115 mmol) in THF (230 mL) was added dropwise diethyl malonate (**S10**) (27.7 g, 174 mmol) at 0 ^{o}C. The resulting solution was stirred at 0 ^{o}C to room temperature for 3 h. The solution was cooled by iced-bath and cinnamyl bromide (25.0 g, 127 mmol) was added. After stirring at 0 ^{o}C to room temperature for 16 h, 1M HCl aq was added, and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated. Excess **S10** was removed from residue by distillation under reduced pressure (62 ^{o}C/ 3 mmHg). The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 to give diester **S11** including small amount of impurities (26.7 g, ca. 84% yield).

To a suspension of 60% NaH in oil (4.24 g, 106 mmol) in THF (200 mL) was added dropwise diester **S11** (26.5 g, 96 mmol) at 0 ^{o}C. The resulting solution was stirred at 0 ^{o}C to room temperature for 3 h. The solution was cooled by iced-bath and propargyl bromide (12.6 g, 106 mmol) was added. After stirring at 0 ^{o}C to room temperature for 38 h, 1M HCl aq was added, and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated to give crude enyne **S12** including small amount of impurities (29.7 g, ca. 98% yield).

Under nitrogen atmosphere to a mixture of CuBr (6.89 g, 48 mmol), paraformaldehyde (7.15 g, 238 mmol) and diisopropylamine (19.2 g, 190 mmol) in dioxane (360 mL) was added crude enyne **S12** (29.9 g, 95 mmol). The resulting solution was refluxed for 27 h. After the reaction, the solution was filtrated by celite and concentrated under reduced pressure. To the resulting mixture was diluted by water (30 mL), AcOEt (70 mL), and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled under reduced pressure to give **8a** including small amount of impurities as colorless oil (150 ^{o}C/ 0.07 mmHg, 4.9 g, 16% yield).



Unless otherwise noted, materials obtained from commercial supplier were used without further purification.

Typical experimental procedures:

Hydroindation of allenes using $HInCl_2$ ($InCl_3$/Et_3SiH system)

The 10 mL of round bottom flask charged with $InCl_3$ (0.442 g, 2 mmol) was heated at 110 °C in vacuo for 1 h. After nitrogen was filled, MeCN (2 mL) and Et_3SiH (0.233 g, 2.0 mmol) was added and the mixture was stirred at rt for 5 min. Then allenes (1.0 mmol) and Et_3B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively. The resulting mixture was stirred at rt for 2 h. After 1M HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated. Product was determined by ^1H NMR. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

Radical cyclization of allenenes using $HInCl_2$ ($InCl_2OMe$/$PhSiH_3$ system)

A 30 mL of round bottom flask charged with $InCl_3$ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (10 mL) was added to dissolve $InCl_3$. The resulting mixture was stirred at rt for 0.5 h. Then $PhSiH_3$ (0.260 g, 2.4 mmol), allenene (1.0 mmol) and Et_3B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After 1M HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated. Cyclized product was determined by ^1H NMR. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

Radical cyclization of allenenes and successive coupling ($InCl_2OMe$/$PhSiH_3$ system)

A 30 mL of round bottom flask charged with $InCl_3$ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (10 mL) was added to dissolve $InCl_3$. The resulting mixture was stirred at rt for 0.5 h. Then $PhSiH_3$ (0.260 g, 2.4 mmol), allenene **8b** (1.0 mmol) and Et_3B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After DMF (2 mL) was added, THF was removed under reduced pressure. Then aryl iodide (0.204 g, 1.0 mmol), $Pd(Ph_3P)_4$ (0.046 g, 4 mol%) and LiI (3.0 mmol) were added and the mixture was stirred at 100 ^oC for 5 h. After the reaction, resulting solution was filtrated by celite. After concentration of the filtrate, yield of product **12b** was determined by ^1H NMR (36% yield). Further purification was performed by silica gel column chromatography eluting with hexane/AcOEt = 9/1.

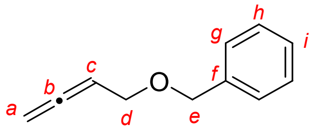
Radical cyclization of allenene 8b using Bu_2SnIH

A 30 mL of round bottom flask was dried by flame under reduced pressure. After nitrogen was filled, THF (10 mL) was added. Bu_2SnH_2 (0.234 g, 1.0 mmol) and Bu_2SnI_2 (0.486 g, 1.0 mmol) were added successively to generate Bu_2SnIH (2.0 mmol) by the redistribution reaction. To the mixture was added allenene **8b** (0.186 g, 1.0 mmol) and resulting mixture was stirred at rt for 20 h. To the resulting solution was added $CHCl_3$ (5 mL) to completely decompose the remained tin hydride and volatiles were removed under reduced pressure. Products were determined by ^1H NMR. Purification was performed by recycle GPC eluting with $CHCl_3$.

Physical and spectral data:

Starting materials

buta-2,3-dienyloxymethyl-benzene (1e)



Colorless liquid

bp 82 °C/ 1.6 mmHg

IR (neat) 1955 (C=C=C) cm^{-1}

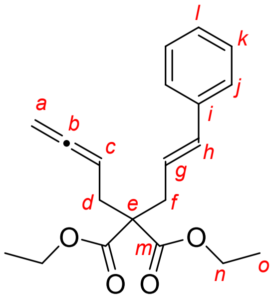
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.26 (m, 5H, *g*, *h* and *i*), 5.28 (tt, *J* = 7.0 and 6.5 Hz, 1H, *c*), 4.80 (dt, *J* = 6.5 and 2.4 Hz, 1H, *a*), 4.54 (s, 2H, *e*), 4.07 (dt, *J* = 7.0 and 2.4 Hz, 2H, *d*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.32 (*b*), 138.04 (*f*), 128.36, 127.85, 127.62 (*i*), 87.69 (*c*), 75.69 (*a*), 71.79 (*e*), 67.85 (*d*)

MS (CI) m/z 161 (M^+ + H, 23), 143 (100), 131 (42), 91 (CH_2Ph, 53)

HRMS calcd for $C_{11}H_{13}O$: 161.0966, found: m/z 161.0970 (CI, (M^+ + H), + 0.3 mmu)

(*E*)-diethyl 2-(buta-2,3-dienyl)-2-cinnamylmalonate (8a)



Colorless liquid

bp 150 °C/ 0.07 mmHg

IR (neat) 1955 (C=C=C) cm^{-1}, 1732 (C=O) cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.19 (m, 5H, *j*, *k* and *l*), 6.45 (d, *J* = 15.7 Hz, 1H, *h*), 6.04 (dt, *J* = 15.7 and 7.7 Hz, 1H, *g*), 5.00 (tt, *J* = 8.0 and 6.7 Hz, 1H, *c*), 4.69 (dt, *J* = 6.7 and 2.4 Hz, 2H, *a*), 4.20 (q, *J* = 7.2 Hz, 4H, *n*), 2.84 (dd, *J* = 7.7 and 1.2 Hz, 2H, *f*), 2.66 (dt, *J* = 8.0 and 2.4 Hz, 2H, *d*) , 1.25 (t, *J* = 7.2 Hz, 6H, *o*)

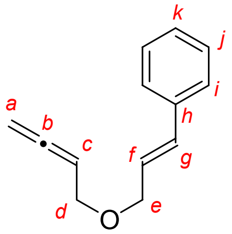
^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.12 (*b*), 170.62 (*m*), 137.09 (*i*), 134.09 (*h*), 128.47 (*k*), 127.36 (*l*), 126.17 (*j*), 123.87 (*g*), 84.28 (*c*), 74.66 (*a*), 61.34 (*n*), 57.89 (*e*), 36.08 (*f*), 32.09 (*d*), 14.12 (*o*)

MS (EI, 70 eV) m/z 328 (M^+, 0.3), 254 (39), 181 (97), 180 (53), 141 (32), 128 (23), 117 ($CH_2CH{=}CHPh$, 100), 115 (62), 91 (74)

HRMS calcd for $C_{20}H_{24}O_4$: 328.1675, found: m/z 328.1669 (EI, (M^+), - 0.6 mmu)

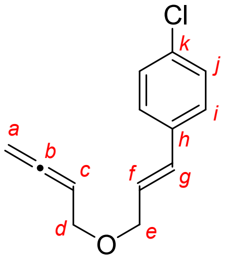
Anal. calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37, found: C, 73.11; H, 7.37.

((*E*)-3-buta-2,3-dienyloxy-propenyl)benzene (8b)



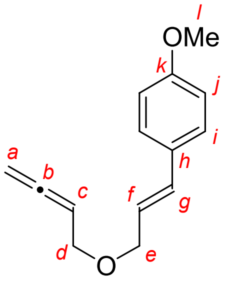
Colorless liquid
bp 87 °C/ 0.07 mmHg
IR (neat) 1955 (C=C=C) cm^{-1}, 1115 (C-O-C) cm^{-1}, 1080 (C-O-C) cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.22 (m, 5H, *i*, *j* and *k*), 6.61 (d, *J* = 15.9 Hz, 1H, *g*), 6.29 (dt, *J* = 15.9 and 6.0 Hz, 1H, *f*), 5.28 (tt, *J* = 7.0 and 6.8 Hz, 1H, *c*), 4.81 (dt, *J* = 6.8 and 2.4 Hz, 2H, *a*), 4.17 (dd, *J* = 6.0 and 1.4 Hz, 2H, *e*), 4.07 (dt, *J* = 7.0 and 2.4 Hz, 2H, *d*)
^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.21 (*b*), 136.56 (*h*), 132.51 (*g*), 128.43 (*j*), 127.57 (*k*), 126.37 (*i*), 125.71 (*f*), 87.62 (c), 75.62 (*a*), 70.29 (*e*), 67.72 (*d*)
MS (CI) m/z 187 (M^+ + H, 1), 156 (4), 133 ($PhCH=CHCH_2O$, 6), 118 (10), 117 (100)
HRMS calcd for $C_{13}H_{14}O$ + H: 187.1123, found: m/z 187.1120 (CI, (M^+ + H), - 0.3 mmu)

1-((*E*)-3-buta-2,3-dienyloxy-propenyl)-4-chloro-benzene (8c)



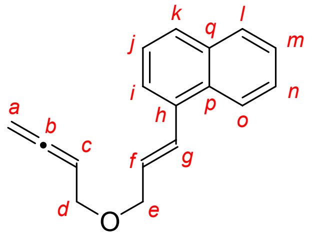
Colorless liquid
bp 102 °C/ 0.10 mmHg
IR (neat) 1955 (C=C=C) cm^{-1}, 1115 (C-O-C) cm^{-1}, 1092 (C-O-C) cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.26 (m, 4H), 6.57 (d, *J* = 15.9 Hz, 1H, *g*), 6.27 (dt, *J* = 15.9 and 6.0 Hz, 1H, *f*), 5.28 (tt, *J* = 6.8 and 6.8 Hz, 1H, *c*), 4.81 (dt, *J* = 6.8 and 2.4 Hz, 2H, *a*), 4.16 (dd, *J* = 6.0 and 1.4 Hz, 2H, *e*), 4.07 (dt, *J* = 6.8 and 2.4 Hz, 2H, *d*)
^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.32 (*b*), 135.14 (*h*), 133.25 (*k*), 131.21 (*g*), 128.68, 127.64, 126.49 (*f*), 87.58 (*c*), 75.75 (*a*), 70.19 (*e*), 67.98 (*d*)
MS (CI) m/z 221 (M^+ + H, 0.7), 153 (33), 151 ($ClC_6H_4CH=CHCH_2$, 100)
HRMS calcd for $C_{13}H_{13}ClO$ + H: 221.0733, found: m/z 221.0726 (CI, (M^+ + H), - 0.7 mmu)

1-((*E*)-3-buta-2,3-dienyloxy-propenyl)-4-methoxy-benzene (8d)

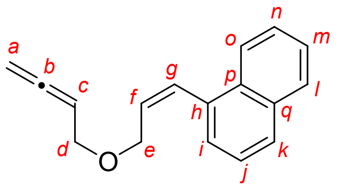


Colorless liquid
bp 121 °C/ 0.03 mmHg
IR (neat) 1955 (C=C=C) cm^{-1}, 1250 (C-O-C) cm^{-1}, 1103 (C-O-C) cm^{-1}, 1080 (C-O-C) cm^{-1}, 1038 (C-O-C) cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, *J* = 8.9 Hz , 2H, *j*), 6.85 (d, *J* = 8.9 Hz, 2H, *i*), 6.55 (d, *J* = 15.9 Hz, 1H, *g*), 6.16 (dt, *J* = 15.9 and 6.3 Hz, 1H, *f*), 5.28 (tt, *J* = 7.0 and 6.8 Hz, 1H, *c*), 4.80 (dt, *J* = 6.8 and 2.4 Hz, 2H, *a*), 4.15 (dd, *J* = 6.3 and 1.2 Hz, 2H, *e*), 4.06 (dt, *J* = 7.0 and 2.4 Hz, 2H, *d*), 3.80 (s, 3H, *l*)
^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.27 (*b*), 159.24 (*k*), 132.41 (*g*), 129.39 (*h*), 127.65 (*i*), 123.44 (*f*), 113.90 (*j*), 87.71 (*c*), 75.66 (*a*), 70.61 (*e*), 67.68 (*d*), 55.23 (*l*)
MS (EI, 70 eV) m/z 216 (M^+, 6), 186 (41), 185 (M^+ - OMe, 56), 171 (27), 163 (M^+ - $CH_2CH=C=CH_2$, 26), 147 ($MeOC_6H_4CH=CHCH_2$, 92), 135 (100), 134 (24), 131 (29), 121 (75), 115 (31), 105 (31), 103 (36), 91 (39), 77 (25)
HRMS calcd for $C_{14}H_{16}O_2$: 216.1150, found: m/z 216.1145 (EI, (M^+), - 0.5 mmu)

1-(3-buta-2,3-dienyloxy-propenyl)-naphthalene (8e)



E-isomer



Z-isomer

These compounds were obtained as mixture of stereoisomers. (***E*-isomer**:***Z*-isomer** = 94:6); See NMR spectrum. The observed data was shown below.

(*E*-isomer)

Pale yellow liquid

bp 122 °C/ 0.04 mmHg

IR (neat) 1955 (C=C=C) cm^{-1}, 1115 (C-O-C) cm^{-1}, 1076 (C-O-C) cm^{-1}

^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.12 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.61, (d, *J* = 7.0 Hz, 1H), 7.53-7.42 (m, 3H, *j*, *m* and *n*), 7.37 (d, *J* = 15.5 Hz, 1H, *g*), 6.32 (dt, *J* = 15.5 and 6.0 Hz, 1H, *f*), 5.32 (tt, *J* = 7.0 and 6.5 Hz, 1H, *c*), 4.83 (dt, *J* = 6.5 and 2.4 Hz, 2H, *a*), 4.28 (dd, *J* = 6.0 and 1.4 Hz, 2H, *e*), 4.14 (dt, *J* = 7.0 and 2.4 Hz, 2H, *d*)

^{13}C NMR (CDCl$_3$, 100 MHz) δ 209.34 (*b*), 134.45, 133.53, 131.09, 129.69 (*g*), 129.04 (*f*), 128.47, 127.97, 125.97, 125.71, 125.57, 123.92, 123.76, 87.72 (*c*), 75.74 (*a*), 70.53 (*e*), 67.89 (*d*)

MS (EI, 70 eV) m/z 236 (M$^+$, 3), 206 (48), 205 (21), 167 (NpCH=CHCH$_2$, 47), 166 (27), 165 (81), 155 (100), 154 (21), 153 (NpCH=CH, 46), 152 (58)

HRMS calcd for C$_{17}$H$_{16}$O: 236.1201, found: m/z 236.1191 (EI, (M$^+$), - 1.0 mmu)

(*Z*-isomer)

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.13 (d, *J* = 11.6 Hz, 1H, *g*), 6.11 (dt, *J* = 11.6 and 6.5 Hz, 1H, *f*), 5.17 (tt, *J* = 7.0 and 6.5 Hz, 1H, *c*), 4.63 (dt, *J* = 6.5 and 2.4 Hz, 2H, *a*), 3.95 (dt, *J* = 7.0 and 2.4 Hz, 2H, *d*)

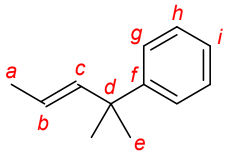
^{13}C NMR (CDCl$_3$, 100 MHz) δ 130.19, 130.08, 128.32, 127.83, 126.55, 126.04, 125.85, 125.11, 124.81, 87.57, 75.51, 70.26, 66.52

MS (EI, 70 eV) m/z 236 (M$^+$, 5), 206 (43), 168 (32), 167 (NpCH=CHCH$_2$, 59), 166 (33), 165 (95), 155 (100), 154 (24), 153 (NpCH=CH, 60), 152 (65), 128 (22)

HRMS calcd for C$_{17}$H$_{16}$O: 236.1201, found: m/z 236.1213 (EI, (M$^+$), + 1.2 mmu)

Products

((*E*)-1,1-dimethyl-but-2-enyl)-benzene (6d-*E*)



Colorless liquid

IR (neat) 1597 (C=C) cm^{-1}

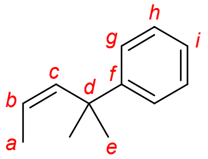
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, *J* = 8.0 Hz, 2H, *g*), 7.29 (dd, *J* = 8.0 and 7.5 Hz, 2H, *h*), 7.17 (t, *J* = 7.5 Hz, 1H, *i*), 5.64 (dq, *J* = 15.5 and 1.4 Hz, 1H, *c*), 5.45 (dq, *J* = 15.5 and 6.3 Hz, 1H, *b*), 1.71 (dd, *J* = 6.3 and 1.4 Hz, 3H, *a*), 1.38 (s, 6H, *e*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.40 (*f*), 141.08 (*c*), 127.97 (*h*), 126.11 (*g*), 125.57 (*i*), 120.95 (*b*), 40.27 (*d*), 28.86 (*e*), 18.03 (*a*)

MS (EI, 70 eV) m/z 160 (M^+, 39), 145 (M^+ -CH_3, 100), 117 (22)

HRMS calcd for $C_{12}H_{16}$: 160.1252, found: m/z 160.1257 (EI, (M^+), + 0.5 mmu)

((*Z*)-1,1-dimethyl-but-2-enyl)-benzene (6d-*Z*)



Colorless liquid

IR (neat) 1601 (C=C) cm^{-1}

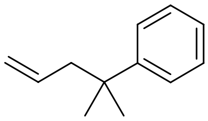
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 8.0 Hz, 2H, *g*), 7.28 (dd, *J* = 8.0 and 7.2 Hz, 2H, *h*), 7.16 (t, *J* = 7.2 Hz, 1H, *i*), 5.69 (dq, *J* = 11.4 and 1.7 Hz, 1H, *c*), 5.41 (dq, *J* = 11.4 and 7.2 Hz, 1H, *b*), 1.43 (s, 6H, *e*), 1.20 (dd, *J* = 7.2 and 1.7 Hz, 3H, *a*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.42 (*f*), 140.56 (*c*), 127.99 (*h*), 126.11 (*g*), 125.26, 124.77, 39.92 (*d*), 31.12 (*e*), 14.19 (*a*)

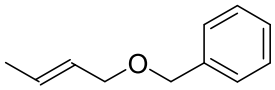
MS (EI, 70 eV) m/z 160 (M^+, 36), 145 (M^+ -CH_3, 100), 117 (23)

HRMS calcd for $C_{12}H_{16}$: 160.1252, found: m/z 160.1250 (EI, (M^+), - 0.2 mmu)

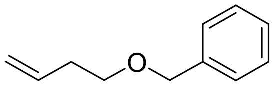
(2-methylpent-4-en-2-yl)-benzene (7d)[7]



(*E*)-((but-2-enyloxy)methyl)-benzene (6e-*E*)[8]

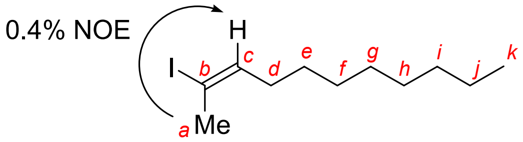


((but-3-enyloxy)methyl)-benzene (7e)[9]



(*E*)-2-iodo-undec-2-ene (2a"-*E*)

No NOE was observed at *c*-H (6.15 ppm) by irradiation at *a*-H (2.36 ppm).



Colorless liquid

IR (neat) 1635 (C=C) cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.15 (t, *J* = 7.5 Hz, 1H, *c*), 2.36 (s, 3H, *a*), 2.01 (dt, *J* = 7.5 and 7.2 Hz, 2H, *d*), 1.37-1.22 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 3H, *k*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.55 (*c*), 93.37 (*b*), 31.85, 30.65, 29.36, 29.22, 29.06, 28.88, 27.43 (*a*), 22.65 (*j*), 14.10 (*k*)

MS (EI, 70 eV) m/z 280 (M^+, 87), 181 (21), 168 (27), 97 (58), 83 (46), 69 (57), 55 (100), 41 (31)

HRMS calcd for $C_{11}H_{21}I$: 280.0688, found: m/z 280.0702 (EI, (M^+), + 1.4 mmu)

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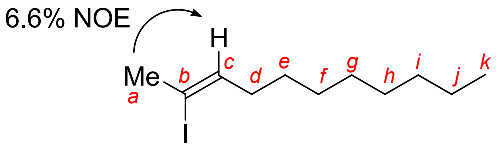
[7] De, S. K.; Gibbs, R. A. *Tetrahedron Lett*. **2005**, *46*, 8345-8350.

[8] Kim, J. D.; Han, G.; Jeong, L. S.; Park, H. –J.; Zee, O. P.; Jung, Y. H. *Tetrahedron*, **2002**, *58*, 4395-4402.

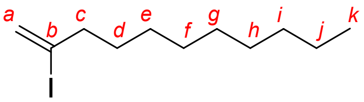
[9] Cleary, P. A.; Woerpel, K. A. *Org. Lett*. **2005**, *7*, 5531-5533.

(*Z*)-2-iodo-undec-2-ene (2a”-*Z*) and 2-iodo-undec-1-ene (3a”)

6.6% NOE was observed at *c*-H (5.40 ppm) by irradiation at *a*-H (2.49 ppm) in **2a”-*Z***.



2a"-Z



3a"

These compounds were not purely isolated and were obtained as mixture of regionisomers (**2a”-*Z***: **3a”** = 63:37). See NMR spectrum. The observed data was shown blow.

Colorless liquid

IR (neat) 1651 (C=C) cm^{-1}, 1616 (C=C) cm^{-1}

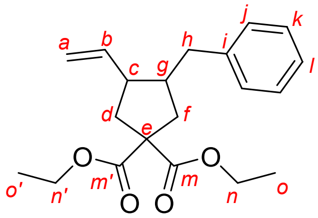
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.00 (s, 1H, a, **3a”**), 5.68 (s, 1H, a, **3a”**), 5.40 (t, *J* = 6.8 Hz, 1H, *c*, **2a”-*Z***), 2.49 (s, 3H, *a*, **2a”-*Z***), 2.37 (t, *J* = 7.0 Hz, 2H, *c*, **3a”**), 2.07 (dt, *J* = 7.0 and 6.8 Hz, 2H, *d*, **2a”-*Z***), 1.55-1.28 (m, 26H, **2a”-*Z***, **3a”**), 0.88 (t, *J* = 7.0 Hz, 6H, *k*, **2a”-*Z***, **3a”**)

^{13}C NMR (CDCl$_3$, 100 MHz) δ 135.58 (*c*, **2a”-*Z***), 125.10 (*a*, **3a”**), 112.88 (*b*, **3a”**), 100.69 (*b*, **2a”-*Z***), 45.30 (*c*, **3a”**), 36.57 (*d*, **2a”-*Z***), 33.49 (*a*, **2a”-*Z***), 31.87, 29.49, 29.46, 29.32, 29.27, 29.25, 29.17, 29.06, 28.36, 28.15, 22.67, 14.11 (*k*, **2a”-*Z***, **3a”**)

MS (EI, 70 eV) m/z 280 (M$^+$, 67), 168 (47), 97 (67), 83 (54), 69 (58), 57 (CH$_2$CH$_2$CH$_2$CH$_3$, 23), 55 (100), 43 (CH$_2$CH$_2$CH$_3$, 21), 41 (38)

HRMS calcd for C$_{11}$H$_{21}$I: 280.0688, found: m/z 280.0682 (EI, (M$^+$), - 0.6 mmu)

diethyl 3-benzyl-4-vinyl-cyclopentane-1,1-dicarboxylate (9a)



(major)

Colorless liquid

IR (neat) 1732 (C=O) cm^{-1}

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30-7.14 (m, 5H), 5.69 (ddd, *J* = 17.1, 10.2 and 8.2 Hz, 1H, *b*), 5.09 (dd, *J* = 17.1 and 1.9 Hz, 1H, *a*), 5.05 (dd, *J* = 10.2 and 1.9 Hz, 1H, *a*), 4.22-4.09 (m, 4H, *n* and *n'*), 2.92 (dd, *J* = 13.5 and 3.6 Hz, 1H, *h*), 2.50 (dd, *J* = 13.5 and 7.5 Hz, 1H, *f*), 2.36-2.21 (m, 3H), 2.05 (dd, *J* = 13.5 and 10.9 Hz, 1H), 2.00-1.87 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 3H, *o*), 1.19 (t, *J* = 7.0 Hz, 3H, *o'*)

^{13}C NMR (CDCl$_3$, 100 MHz) δ 172.63 (*m*), 172.47 (*m'*), 140.74 (*i*), 139.96 (*b*), 128.81, 128.24, 125.83 (*l*), 115.83 (*a*), 61.41 (*n*), 61.36 (*n'*), 58.21 (*e*), 50.04 (*c*), 46.71 (*g*), 40.30, 39.56, 39.17, 14.00 (*o*), 13.96 (*o'*)

MS (EI, 70 eV) m/z 330 (M$^+$, 28), 256(52), 239 (36), 211 (26), 183 (33), 182 (20), 173 (36), 165 (63), 143 (79), 91 (CH$_2$Ph, 100)

HRMS calcd for $C_{20}H_{26}O_4$: 330.1831, found: m/z 330.1813 (EI, (M$^+$), - 1.8 mmu)

(minor)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

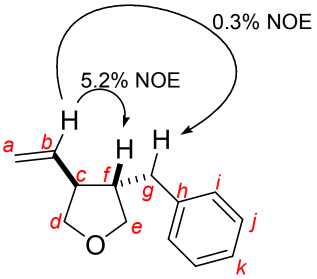
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.85 (ddd, *J* = 17.1, 10.3 and 8.5 Hz, 1H, *b*), 5.08 (dd, *J* = 10.3 and 1.9 Hz, 1H, *a*), 5.04 (dd, *J* = 17.1 and 1.9 Hz, 1H, *a*), 2.51 (dd, *J* = 14.0 and 7.2 Hz, 1H), 2.08 (dd, *J* = 13.8 and 8.2 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H, *o*), 1.21 (t, *J* = 7.0 Hz, 3H, *o'*)

^{13}C NMR (CDCl$_3$, 100 MHz) δ 172.77 (*m*), 172.69 (*m'*), 141.16 (*i*), 138.10 (*b*), 128.87, 128.22, 125.75 (*l*), 115.84 (*a*), 61.45 (*n*), 61.42 (*n'*), 58.75 (*e*), 46.57, 44.81, 38.80, 38.24, 36.30, 14.02 (*o*), 13.97 (*o'*)

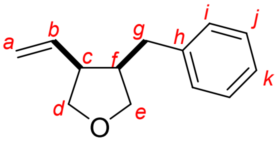
MS (EI, 70 eV) m/z 330 (M$^+$, 22), 256 (59), 239 (49), 229 (24), 184 (23), 183 (37), 182 (30), 173 (46), 165 (65), 143 (56), 91 (CH$_2$Ph, 100)

HRMS calcd for $C_{20}H_{26}O_4$: 330.1831, found: m/z 330.1820 (EI, (M$^+$), - 1.1 mmu)

3-benzyl-4-vinyl-tetrahydrofuran (9b)



9b-*trans*



9b-*cis*

(major) *trans*-3-benzyl-4-vinyl-tetrahydrofuran (9b-*trans*)

The stereochemistry of the products was determined by NOE observation.

5.2% NOE was observed at *f*-H (2.31-2.22 ppm) by irradiation at *b*-H (5.69 ppm).

0.3% NOE was observed at *g*-H (2.91 ppm) by irradiation at *b*-H (5.69 ppm).

Colorless liquid

IR (neat) 1639 (C=C) cm^{-1}, 1053 (C-O-C) cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 7.27 (dd, *J* = 7.5 and 7.4 Hz, 2H, *j*), 7.19 (t, *J* = 7.4 Hz, 1H, *k*), 7.14 (d, *J* = 7.5, 2H, *i*), 5.69 (ddd, *J* = 17.1 and 10.1 and 8.5 Hz, 1H, *b*), 5.08 (dd, *J* = 17.1 and 1.7 Hz, 1H, *a*), 5.05 (dd, *J* = 10.1 and 1.7 Hz, 1H, *a*), 4.03 (dd, *J* = 8.2 and 8.2 Hz, 1H, *d*), 3.88 (dd, *J* = 8.5 and 7.5 Hz, 1H, *e*), 3.54 (dd, *J* = 8.2 and 8.7 Hz, 1H, *d*), 3.53 (dd, *J* = 8.5 and 7.9 Hz, 1H, *e*), 2.91 (dd, *J* = 13.8 and 4.8 Hz, 1H, *g*), 2.58-2.48 (m, 2H, *c* and *g*), 2.31-2.22 (m, 1H, *f*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.28 (*h*), 137.85 (*b*), 128.62 (*i*), 128.38 (*j*), 126.09 (*k*), 116.46 (*a*), 73.35 (*e*), 72.85 (*d*), 50.32 (*c*), 47.24 (*f*), 37.75 (*g*)

MS (EI, 70 eV) m/z 188 (M^+, 1), 157 (27), 129 (30), 104 (32), 92 (51), 91 ($PhCH_2$, 100)

HRMS calcd for $C_{13}H_{16}O$: 188.1201, found: m/z 188.1210 (EI, (M^+), + 0.9 mmu)

Anal. calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57, found: C, 82.92; H, 8.31.

(minor) *cis*-3-benzyl-4-vinyl-tetrahydrofuran (9b-*cis*)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

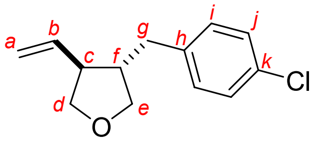
^1H NMR ($CDCl_3$, 400 MHz) δ 5.89 (ddd, *J* = 17.1 and 10.3 and 9.4 Hz, 1H, *b*), 3.96 (dd, *J* = 8.5 and 6.5 Hz, 1H), 3.81 (dd, *J* = 8.6 and 7.2 Hz, 1H), 3.74 (dd, *J* = 8.5 and 4.8 Hz, 1H), 2.78 (dd, *J* = 13.5 and 5.3 Hz, 1H, *g*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.78, 136.13, 128.75, 128.49, 125.97, 116.88, 72.67, 71.93, 46.74, 44.82, 34.25

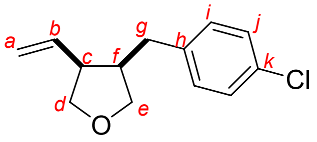
MS (EI, 70 eV) m/z 188 (M^+, 2), 157 (27), 105 (25), 104 (29), 92 (47), 91 (CH_2Ph, 100)

HRMS calcd for $C_{13}H_{16}O$: 188.1201, found: m/z 188.1198 (EI, (M^+), - 0.3 mmu)

3-(4-chlorophenylmethyl)-4-vinyl-tetrahydrofuran (9c)



6c-*trans*



6c-*cis*

The stereochemistry of the products was determined by comparison of ^{1}H NMR spectrum with **9b**. These compounds were not purely isolated and were obtained as mixture of diastereomers. (**9c-*trans***:**9c-*cis*** = 83:17); See NMR spectrum. The observed data was shown below.

Colorless liquid

IR (neat) 1639 (C=C) cm^{-1}, 1095 (C-O-C) cm^{-1}, 1053 (C-O-C) cm^{-1}

Anal. calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79; Cl, 15.92, found: C, 69.84; H, 6.58; Cl, 16.20.

(major) *trans*-3-(4-methoxyphenylmethyl)-4-vinyltetrahydrofuran (9c-*trans*)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 8.2 Hz, 2H, *j*), 7.07 (d, J = 8.2 Hz, 2H, *i*), 5.67 (ddd, J = 17.0, 10.1 and 8.5 Hz, 1H, *b*), 5.07 (dd, J = 17.0 and 1.7 Hz, 1H, *a*), 5.05 (dd, J = 10.1 and 1.7 Hz, 1H, *a*), 4.02 (dd, J = 8.5 and 8.2 Hz, 1H, *d*), 3.86 (dd, J = 8.5 and 7.5 Hz, 1H, *e*), 3.54 (dd, J = 8.5 and 8.5 Hz, 1H, *d*), 3.49 (dd, J = 8.5 and 8.2 Hz, 1H, *e*), 2.87 (dd, J = 13.8 and 5.1 Hz, 1H, *g*), 2.56-2.46 (m, 2H, *c* and *g*), 2.28-2.18 (m, 1H, *f*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.69 (*h*), 137.69 (*b*), 131.87 (*k*), 129.95 (*i*), 128.50 (*j*), 116.60 (*a*), 73.17 (*e*), 72.85 (*d*), 50.26 (*c*), 47.13 (*f*), 37.13 (*g*)

MS (EI, 70 eV) m/z 222 (M^+, 9), 138 (27), 125 ($CH_2C_6H_4Cl$, 100), 91 (22)

HRMS calcd for $C_{13}H_{15}ClO$: 222.0811, found: m/z 222.0808 (EI, (M^+), - 0.3 mmu)

(minor) *cis*-3-(4-methoxyphenylmethyl)-4-vinyltetrahydrofuran (9c-*cis*)

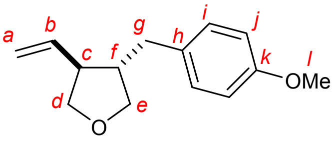
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.86 (ddd, J = 17.0, 10.1 and 9.2 Hz, 1H, *b*), 5.16 (dd, J = 10.1 and 1.7 Hz, 1H, *a*), 5.10 (dd, J = 17.0 and 1.7 Hz, 1H, *a*), 3.96 (dd, J = 8.5 and 6.5 Hz, 1H), 3.80 (dd, J = 8.5 and 7.0 Hz, 1H), 3.74 (dd, J = 8.5 and 4.8 Hz, 1H), 2.74 (dd, J = 13.5 and 5.6 Hz, 1H, *g*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.20, 135.94, 131.75, 117.10, 72.69, 71.81, 46.66, 44.71, 33.62

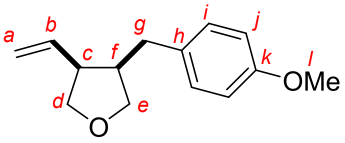
MS (EI, 70 eV) m/z 222 (M^+, 3), 167 (32), 139 (30), 138 (29), 127 (36), 125 ($CH_2C_6H_4Cl$, 100), 91 (20)

HRMS calcd for $C_{13}H_{15}ClO$: 222.0811, found: m/z 222.0818 (EI, (M^+), + 0.7 mmu)

3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d)



9d-*trans*



9d-*cis*

The stereochemistry of the products was determined by comparison of ^{1}H NMR spectrum with **9b**.

(major) *trans*-3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d-*trans*)

Colorless liquid

IR (neat) 1639 (C=C) cm^{-1}, 1250 (C-O-C) cm^{-1}, 1111 (C-O-C) cm^{-1}, 1038 (C-O-C) cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, *J* = 8.7 Hz, 2H, *i*), 6.82 (d, *J* = 8.7 Hz, 2H, *j*), 5.69 (ddd, *J* = 17.0, 10.1 and 8.5 Hz, 1H, *b*), 5.08 (dd, *J* = 17.0 and 1.4 Hz, 1H, *a*), 5.05 (dd, *J* = 10.1 and 1.4 Hz, 1H, *a*), 4.02 (dd, *J* = 8.5 and 8.2 Hz, 1H, *d*), 3.87 (dd, *J* = 8.5 and 7.5 Hz, 1H, *e*), 3.79 (s, 3H, *l*), 3.54 (dd, *J* = 8.5 and 8.5 Hz, 1H, *d*), 3.51 (dd, *J* = 8.5 and 8.2 Hz, 1H, *e*), 2.85 (dd, *J* = 13.8 and 4.8 Hz, 1H, *g*), 2.56-2.43 (m, 2H, *c* and *g*), 2.28-2.18 (m, 1H, *f*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.89 (*k*), 137.92 (*b*), 132.32 (*h*), 129.53 (*i*), 116.39 (*a*), 113.73 (*j*), 73.34 (*e*), 72.85 (*d*), 55.19 (*l*), 50.21 (*c*), 47.43 (*f*), 36.80 (*g*)

MS (EI, 70 eV) m/z 218 (M^+, 16), 121 ($CH_2C_6H_4OMe$, 100)

HRMS calcd for $C_{14}H_{18}O_2$: 218.1307, found: m/z 218.1313 (EI, (M^+), + 0.6 mmu)

(minor) *cis*-3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d-*cis*)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

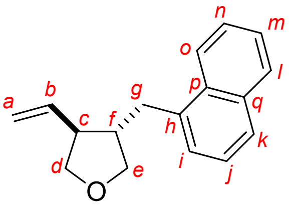
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88 (ddd, *J* = 16.9, 10.4 and 9.2 Hz, 1H, *b*), 5.15 (dd, *J* = 10.4 and 1.9 Hz, 1H, *a*), 5.11 (dd, *J* = 16.9 and 1.9 Hz, 1H, *a*), 3.96 (dd, *J* = 8.5 and 6.8 Hz, 1H), 2.72 (dd, *J* = 13.5 and 5.6 Hz, 1H, *g*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.20, 132.80, 129.52, 116.81, 72.70, 71.98, 46.73, 45.04, 33.32

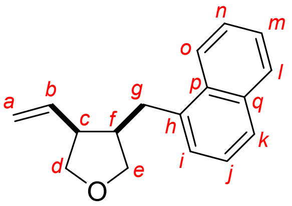
MS (EI, 70 eV) m/z 218 (M^+, 14), 163 (22), 148 (24), 121 ($CH_2C_6H_4OMe$, 100)

HRMS calcd for $C_{14}H_{18}O_2$: 218.1307, found: m/z 218.1309 (EI, (M^+), + 0.2 mmu)

3-(naphthalen-1-ylmethyl)-4-vinyl-tetrahydrofuran (9e)



9e-*trans*



9e-*cis*

The stereochemistry of the products was determined by comparison of ^{1}H NMR spectrum with **9b**.

(major) *trans*-3-(naphthalene-1-ylmethyl)-4-vinyltetrahydrofuran (9e-*trans*)

Colorless liquid

IR (neat) 1639 (C=C) cm^{-1}, 1065 (C-O-C) cm^{-1}, 1041 (C-O-C) cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.53-7.45 (m, 2H), 7.37 (dd, *J* = 8.2 and 7.0 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 5.73 (ddd, *J* = 17.0, 10.0 and 8.5 Hz, 1H, *b*), 5.14 (dd, *J* = 17.0 and 1.7 Hz, 1H, *a*), 5.10 (dd, *J* = 10.1 and 1.7 Hz, 1H, *a*), 4.07 (dd, *J* = 8.5 and 8.0 Hz, 1H, *d*), 3.80 (dd, *J* = 8.5 and 7.5 Hz, 1H, *e*), 3.60 (dd, *J* = 8.5 and 8.2 Hz, 1H, *e*), 3.54 (dd, *J* = 8.5 and 8.5 Hz, 1H, *d*), 3.45 (dd, *J* = 14.0 and 4.6 Hz, 1H, *g*), 2.85 (dd, *J* = 14.0 and 9.9 Hz, 1H, *g*), 2.65 (dddd, *J* = 8.5, 8.5, 8.2 and 8.0 Hz, 1H, *c*), 2.50-2.40 (m, 1H, *f*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.80 (*b*), 136.43, 133.84 (*q*), 131.67, 128.80, 127.02, 126.21, 125.87, 125.52, 125.39, 123.48, 116.72 (*a*), 73.58 (*e*), 72.90 (*d*), 50.85 (*c*), 46.20 (*f*), 34.98 (*g*)

MS (EI, 70 eV) m/z 238 (M^+, 32), 142 (100), 141 (CH_2Np, 96)

HRMS calcd for $C_{17}H_{18}O$: 238.1358, found: m/z 238.1362 (EI, (M^+), + 0.4 mmu)

(minor) *cis*-3-(naphthalene-1-ylmethyl)-4-vinyltetrahydrofuran (9e-*cis*)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

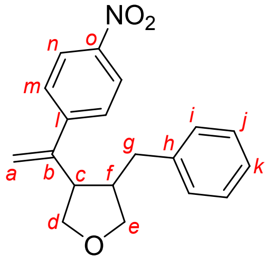
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.03 (ddd, *J* = 16.9, 10.1 and 9.2 Hz, 1H, *b*), 3.99 (dd, *J* = 8.5 and 7.0 Hz, 1H), 3.31 (dd, *J* = 13.8 and 4.3 Hz, 1H), 3.05-2.98 (m, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.78, 136.12, 133.90, 131.74, 128.84, 126.92, 126.42, 123.55, 117.26 (*a*), 72.46, 72.06, 47.08, 43.83, 31.22 (*g*)

MS (EI, 70 eV) m/z 238 (M^+, 35), 155 (28), 142 (88), 141 (CH_2Np, 100), 115 (25)

HRMS calcd for $C_{17}H_{18}O$: 238.1358, found: m/z 238.1371 (EI, (M^+), + 1.3 mmu)

3-benzyl-4-(1-(4-nitrophenyl)-vinyl)-tetrahydrofuran (12b)



(major)

Yellow liquid

IR (neat) 1597 (C=C) cm^{-1}, 1516 (NO_2) cm^{-1}, 1346 (NO_2) cm^{-1}, 1111 (C-O-C) cm^{-1}, 1061 (C-O-C) cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 8.9 Hz, 2H, *n*), 7.31-7.19 (m, 5H), 7.10 (d, *J* = 8.2 Hz, 2H, *i*), 5.45 (s, 1H, *a*), 5.38 (s, 1H, *a*), 4.15 (dd, *J* = 8.7 and 7.2 Hz, 1H, *d*), 4.01 (dd, *J* = 8.5 and 7.0 Hz, 1H, *e*), 3.77 (dd, *J* = 8.7 and 6.0 Hz, 1H, *d*), 3.65 (dd, *J* = 8.5 and 6.0 Hz, 1H, *e*), 3.03 (ddd, *J* = 7.2, 6.8 and 6.0 Hz, 1H, *c*), 2.81 (dd, *J* = 13.8 and 7.2 Hz, 1H, *g*), 2.70 (dd, *J* = 13.8 and 8.0 Hz, 1H, *g*), 2.57-2.48 (m, 1H, *f*)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.15, 147.48, 146.88, 139.63 (*h*), 128.68, 128.47, 127.06, 126.32 (*k*), 123.48 (*n*), 115.56 (*a*), 73.04, 73.00, 48.79 (*c*), 46.85 (*f*), 38.96 (*g*)

MS (EI, 70 eV) m/z 309 (M^+, 1), 218 (M^+ - CH_2Ph, 33), 130 (35), 92 (45), 91 ($PhCH_2$, 100)

HRMS calcd for $C_{19}H_{19}NO_3$: 309.1365, found: m/z 309.1359 (EI, (M^+), - 0.6 mmu)

(minor)

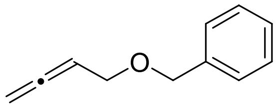
This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after silica gel column chromatography were shown below.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.61 (s, 1H, *a*), 5.28 (s, 1H, *a*)

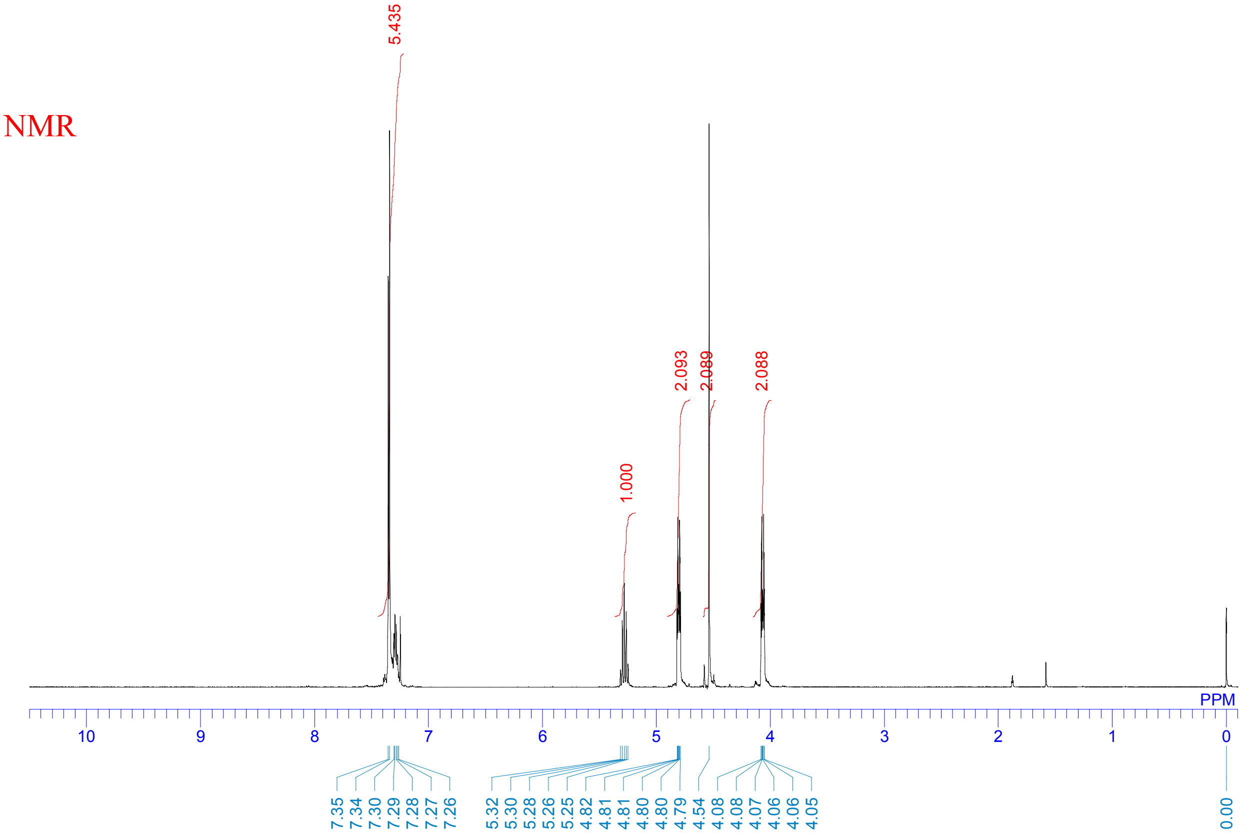
MS (EI, 70 eV) m/z 309 (M^+, 5), 278 (36), 177 (24), 160 (20), 146 (22), 133 (26), 132 (21), 131 (23), 130 (78), 129 (22), 128 (24), 117 (100), 115 (37), 105 (92), 92 (21), 91 ($PhCH_2$, 98)

HRMS calcd for $C_{19}H_{19}NO_3$: 309.1365, found: m/z 309.1364 (EI, (M^+), - 0.1 mmu)

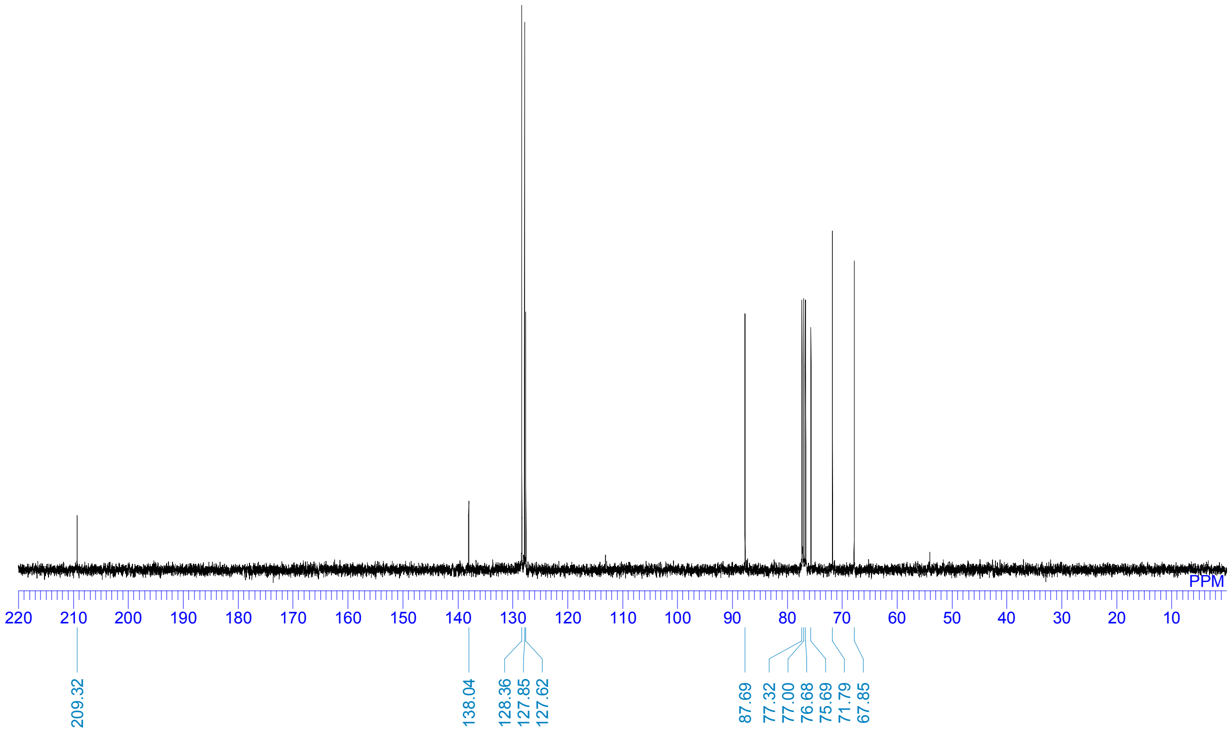
1e



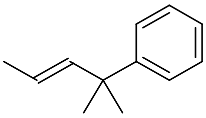
^{1}H NMR



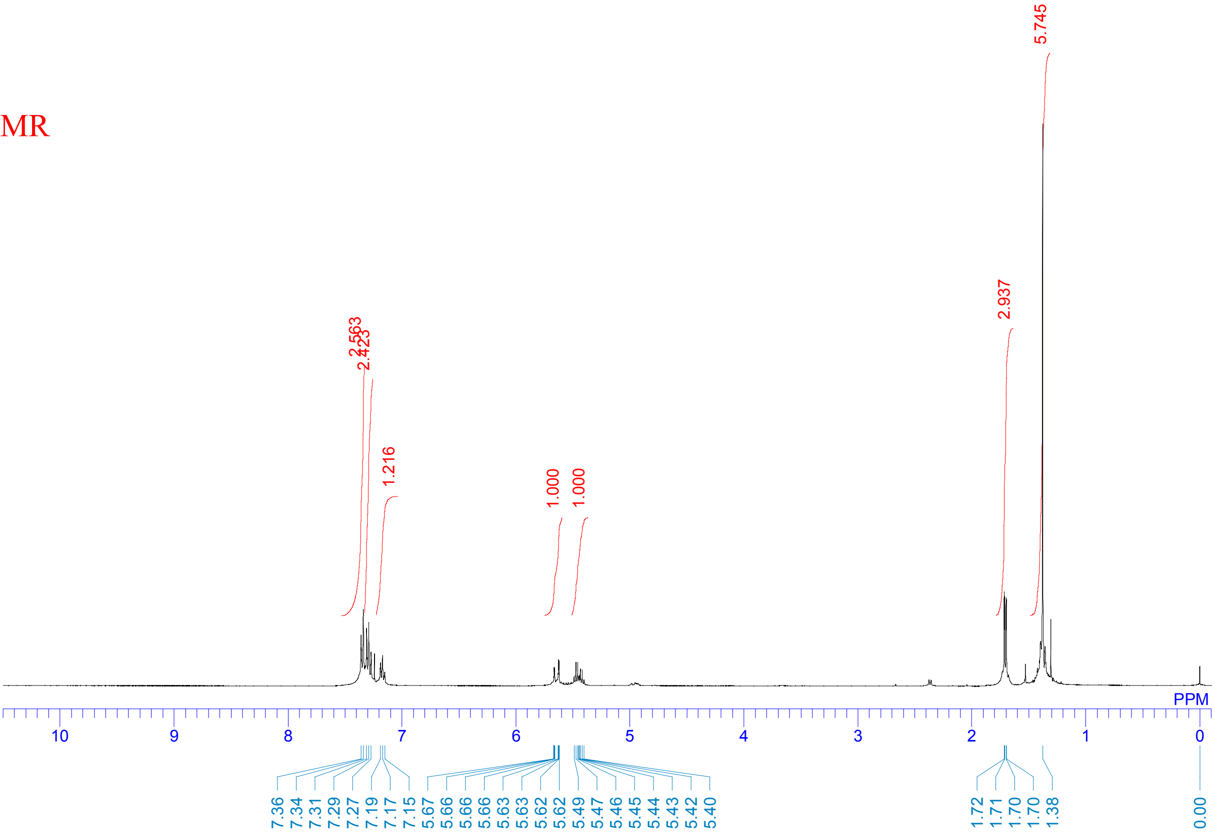
^{13}C NMR



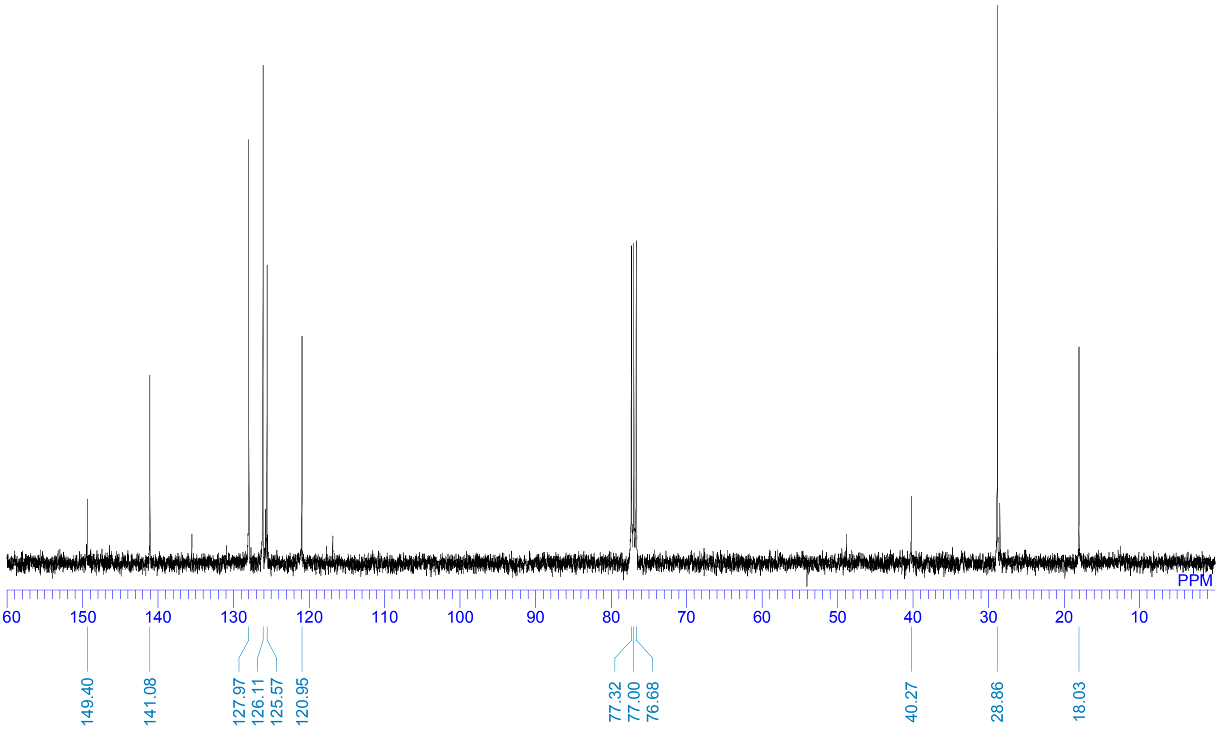
6d-*E*



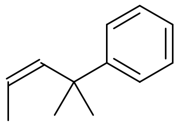
^{1}H NMR



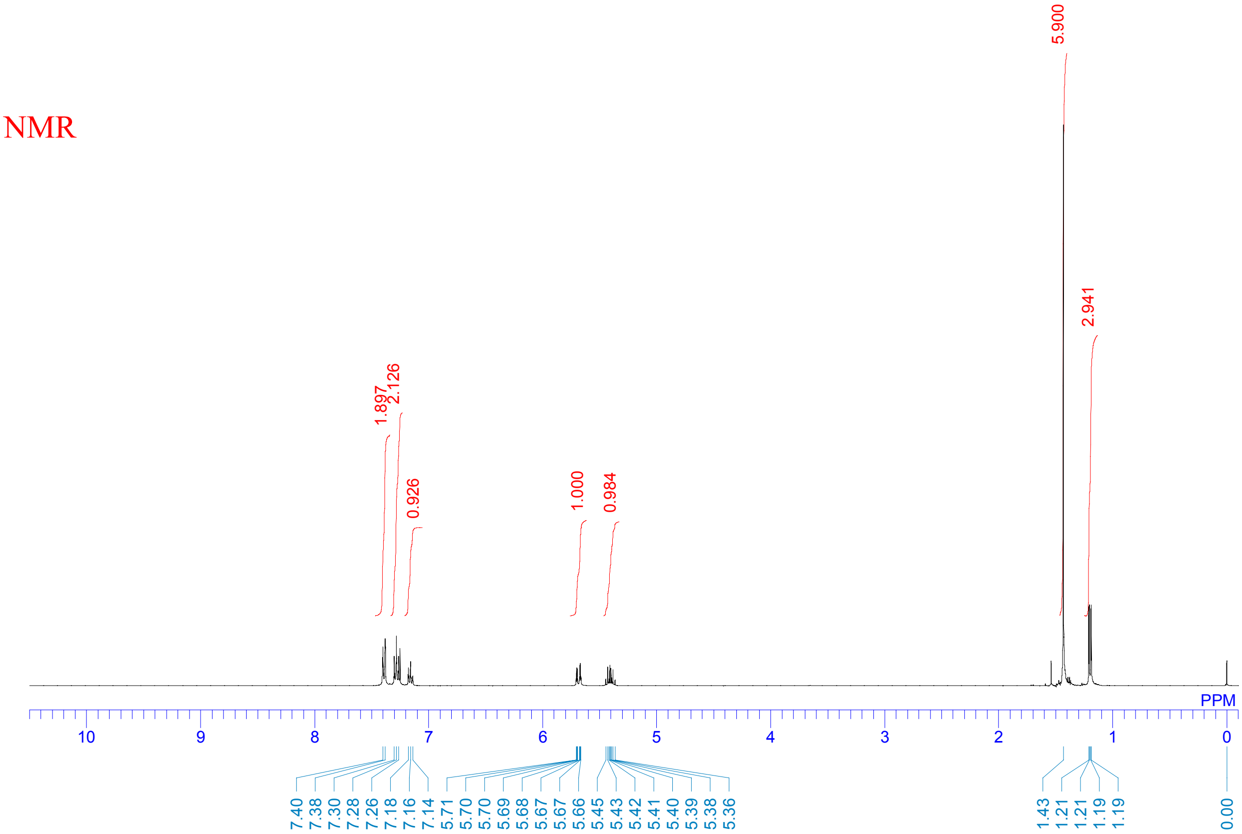
^{13}C NMR



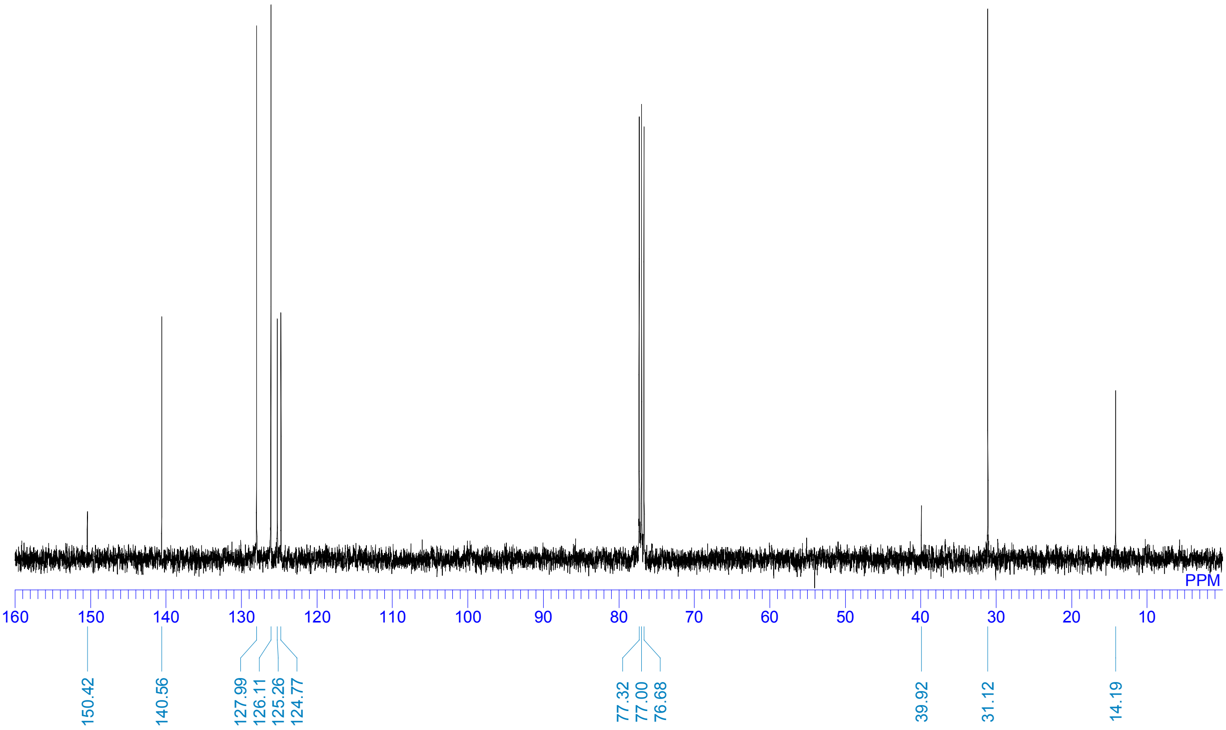
6d-*Z*



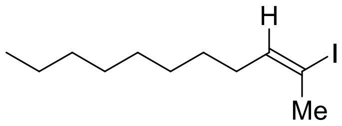
^{1}H NMR



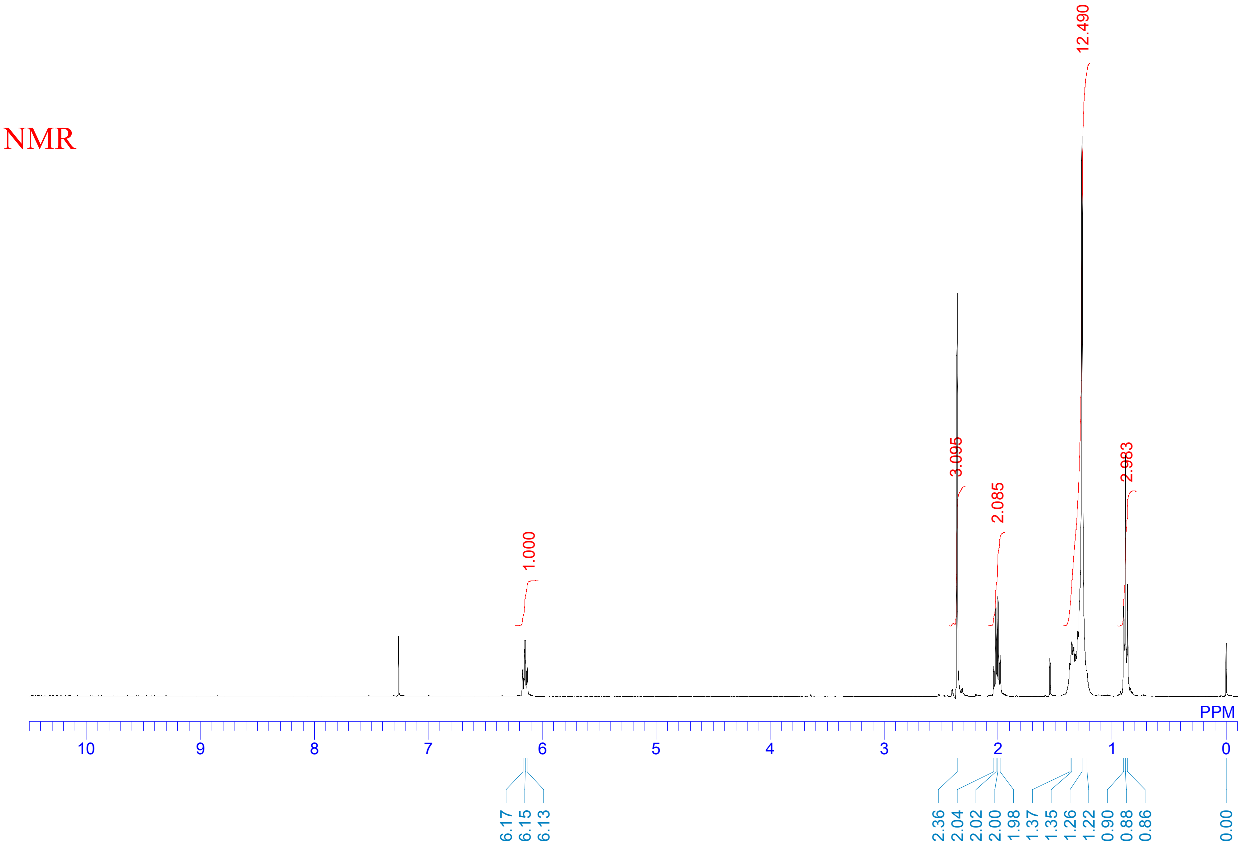
^{13}C NMR



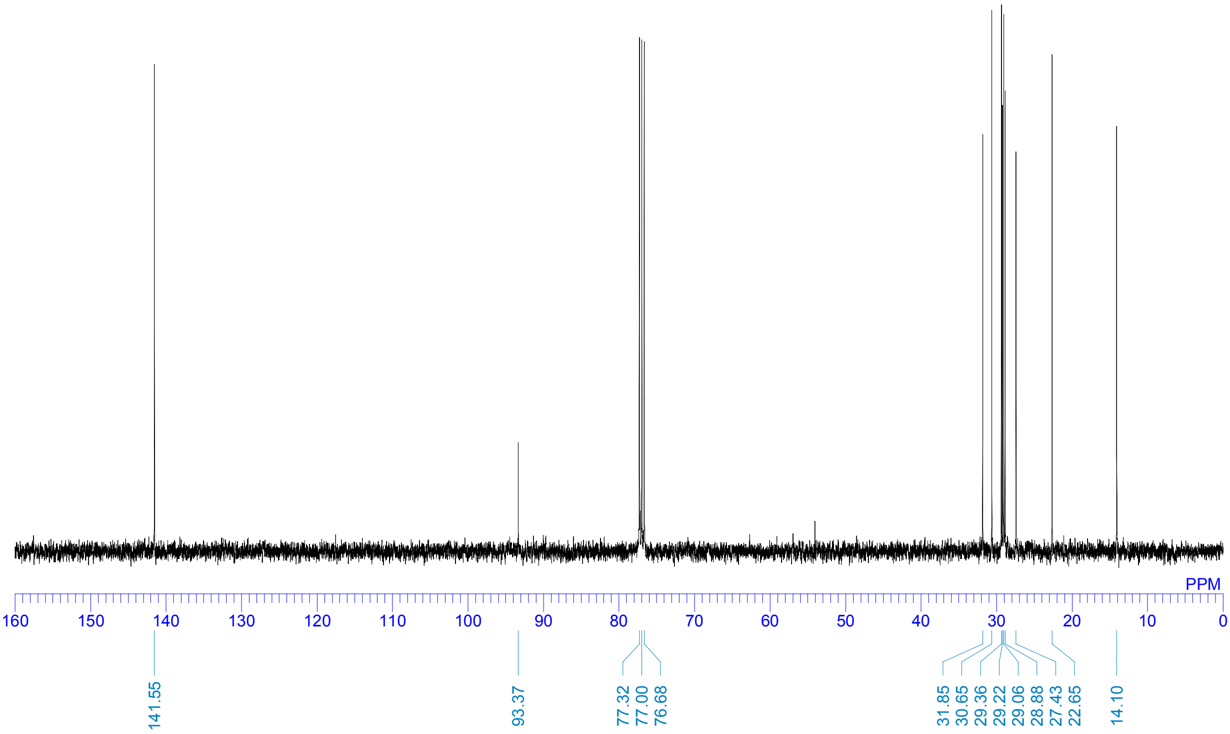
2a”-*E*



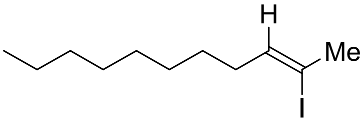
^{1}H NMR



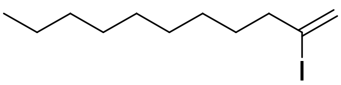
^{13}C NMR



2a”-*Z* and 3a”

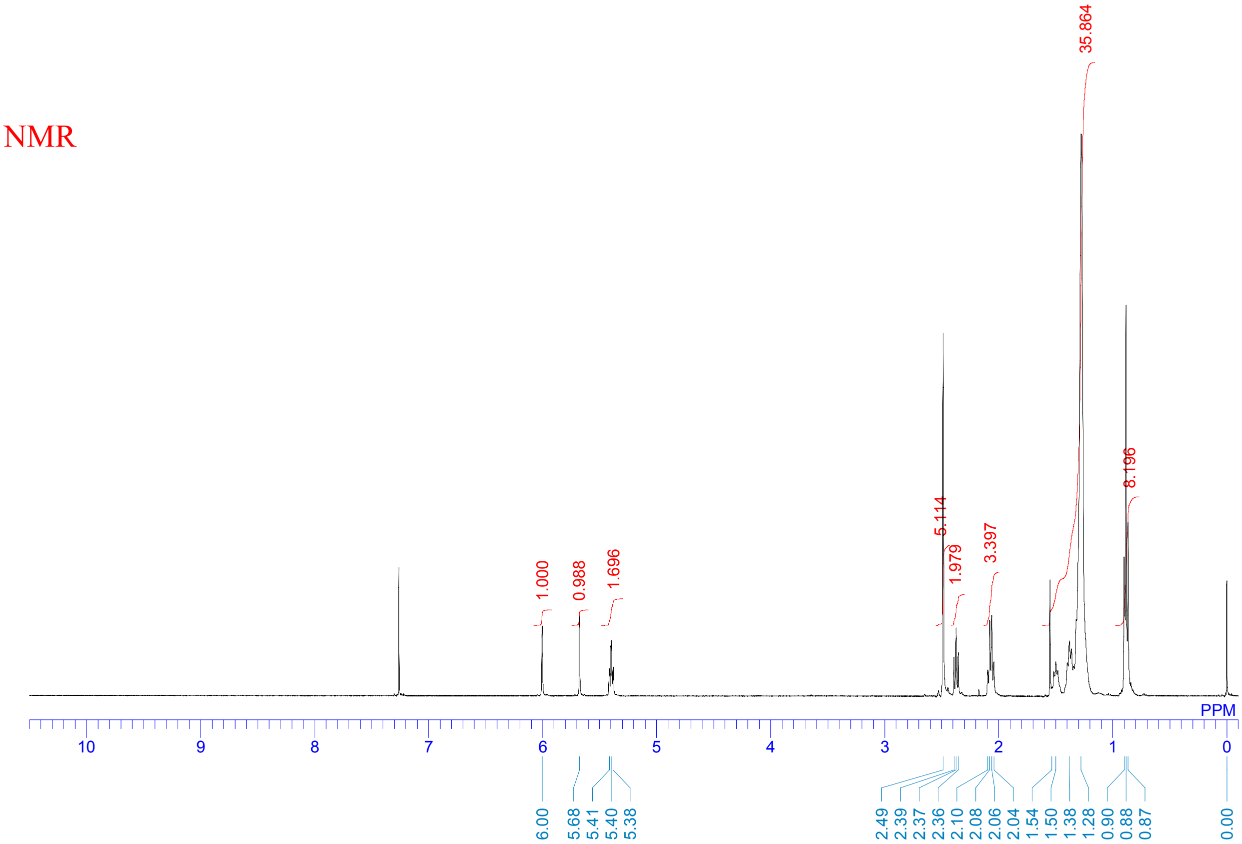


2a”-*Z*

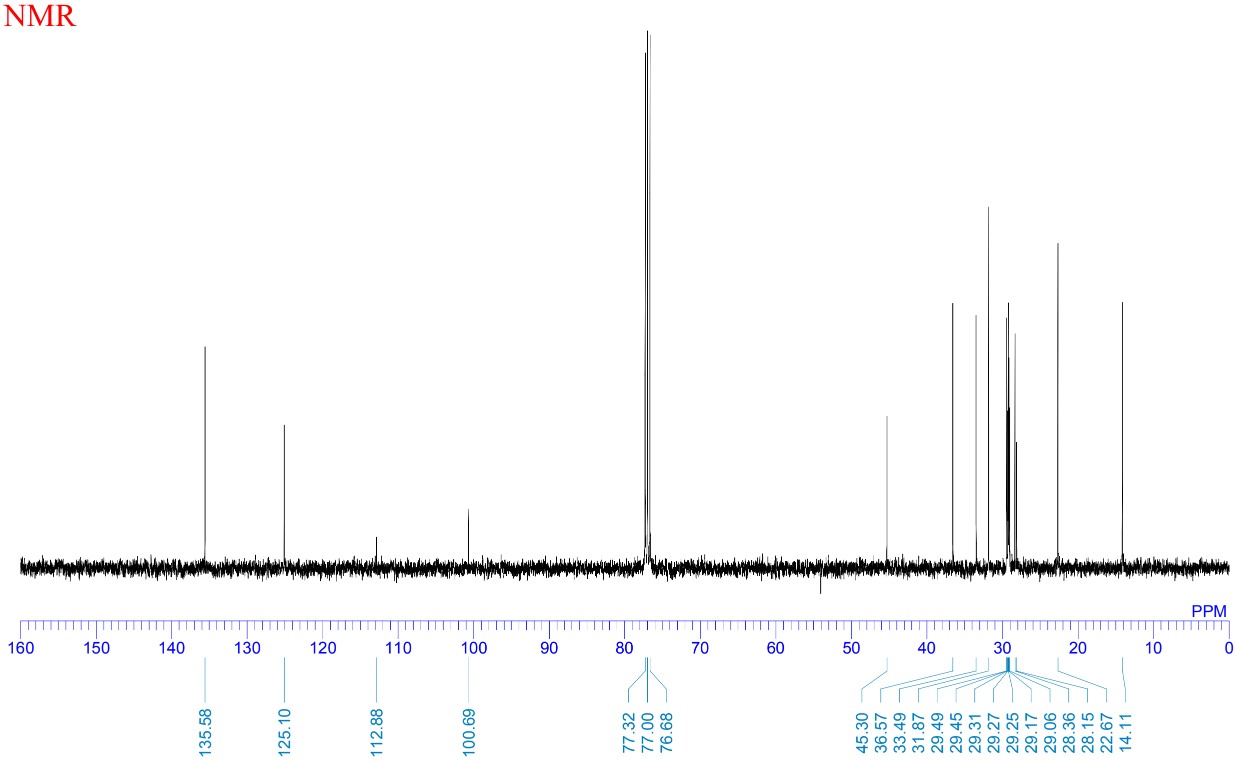


3a”

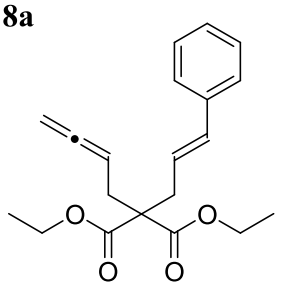
^{1}H NMR



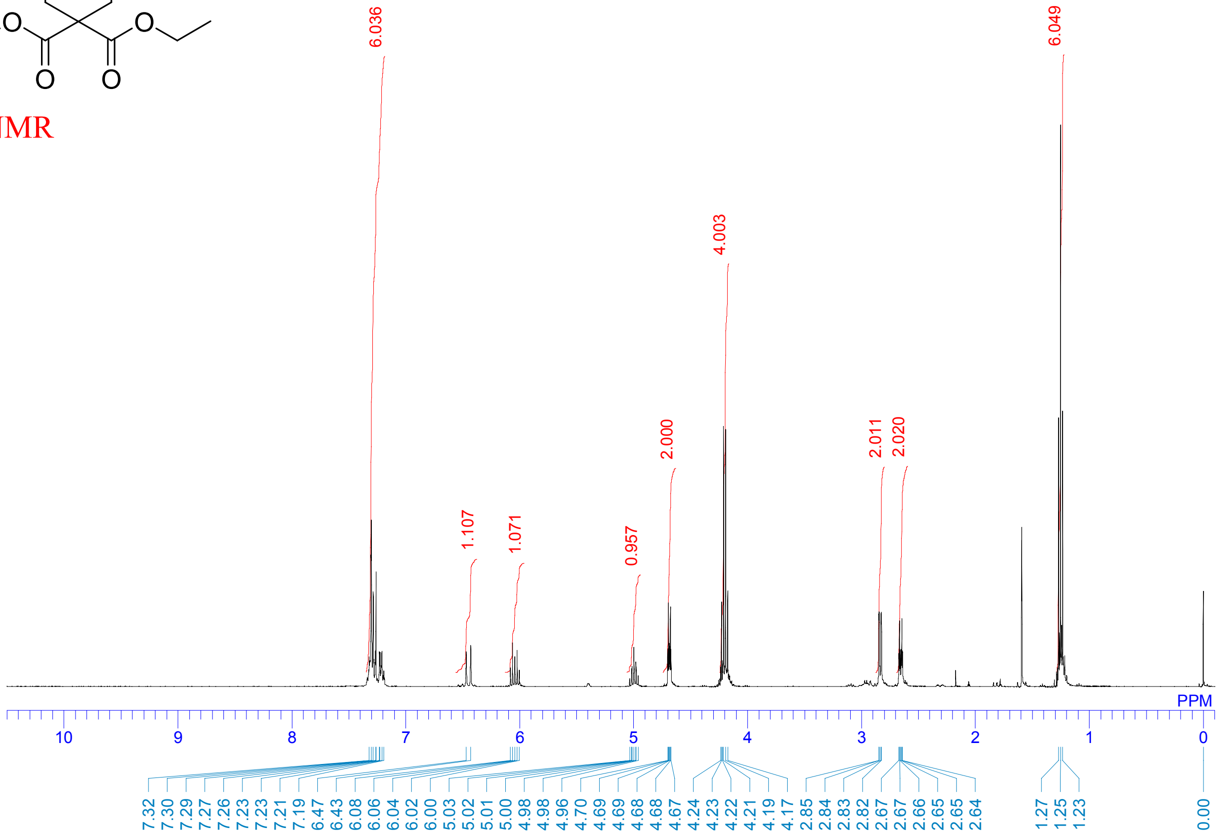
^{13}C NMR



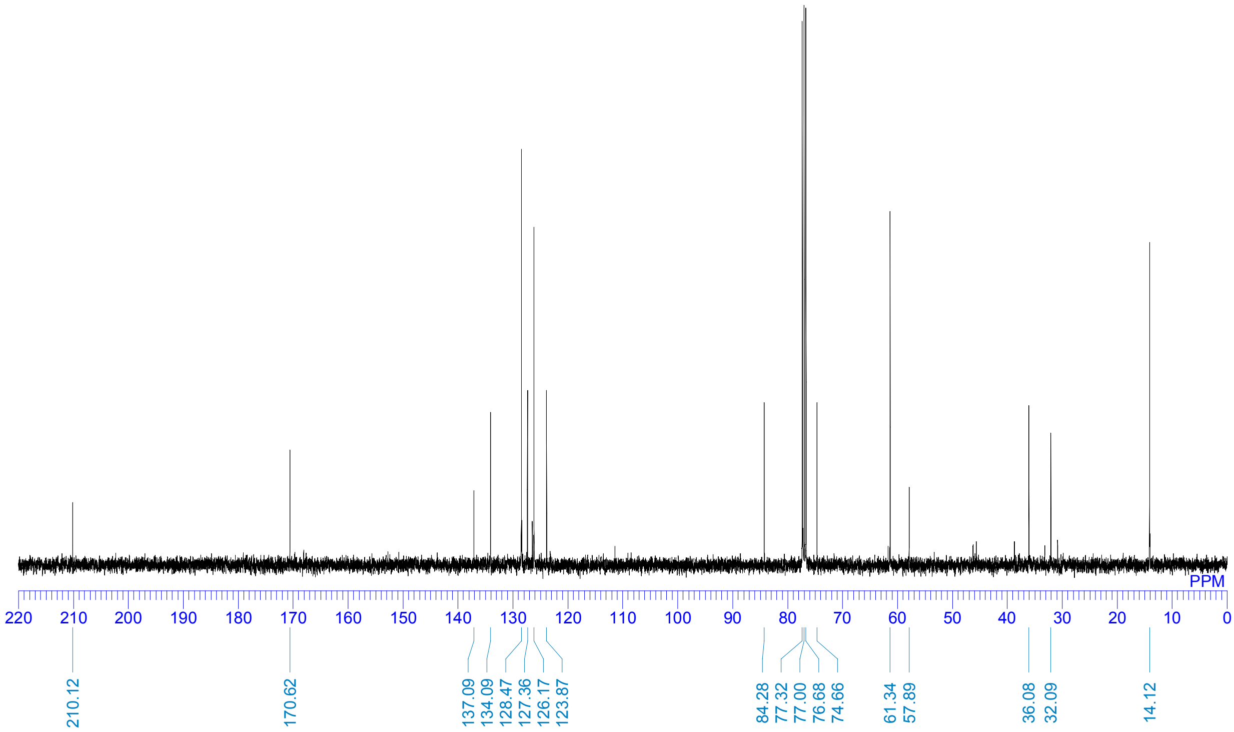
8a



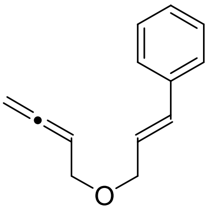
^{1}H NMR



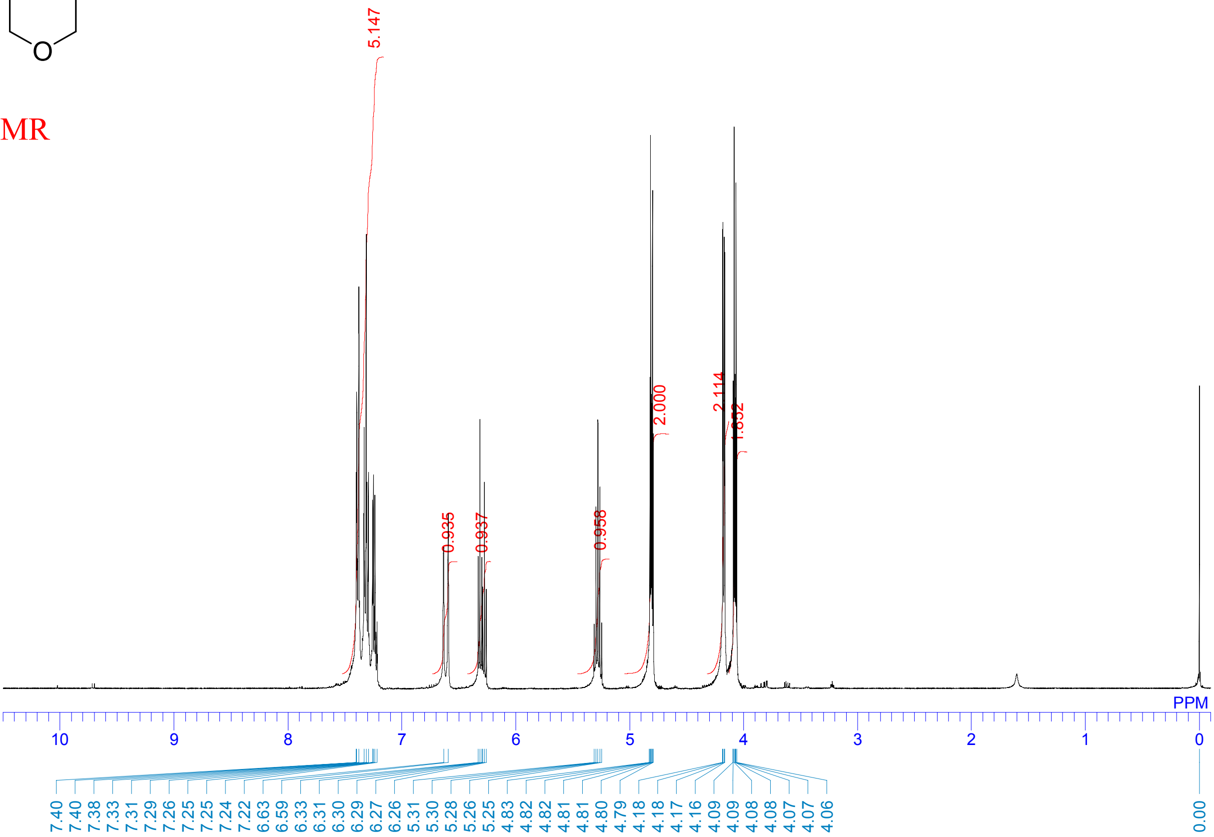
^{13}C NMR



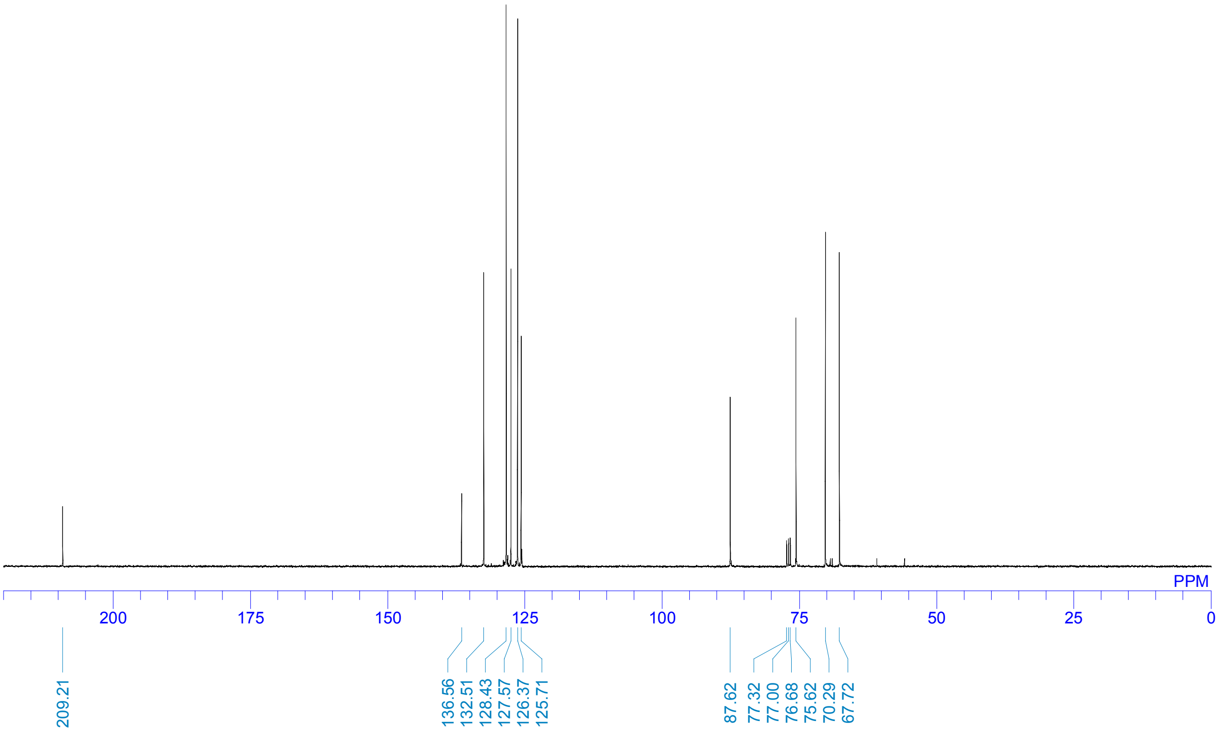
8b



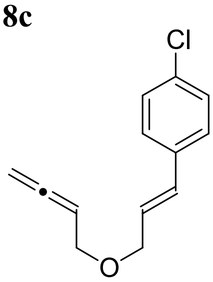
^{1}H NMR



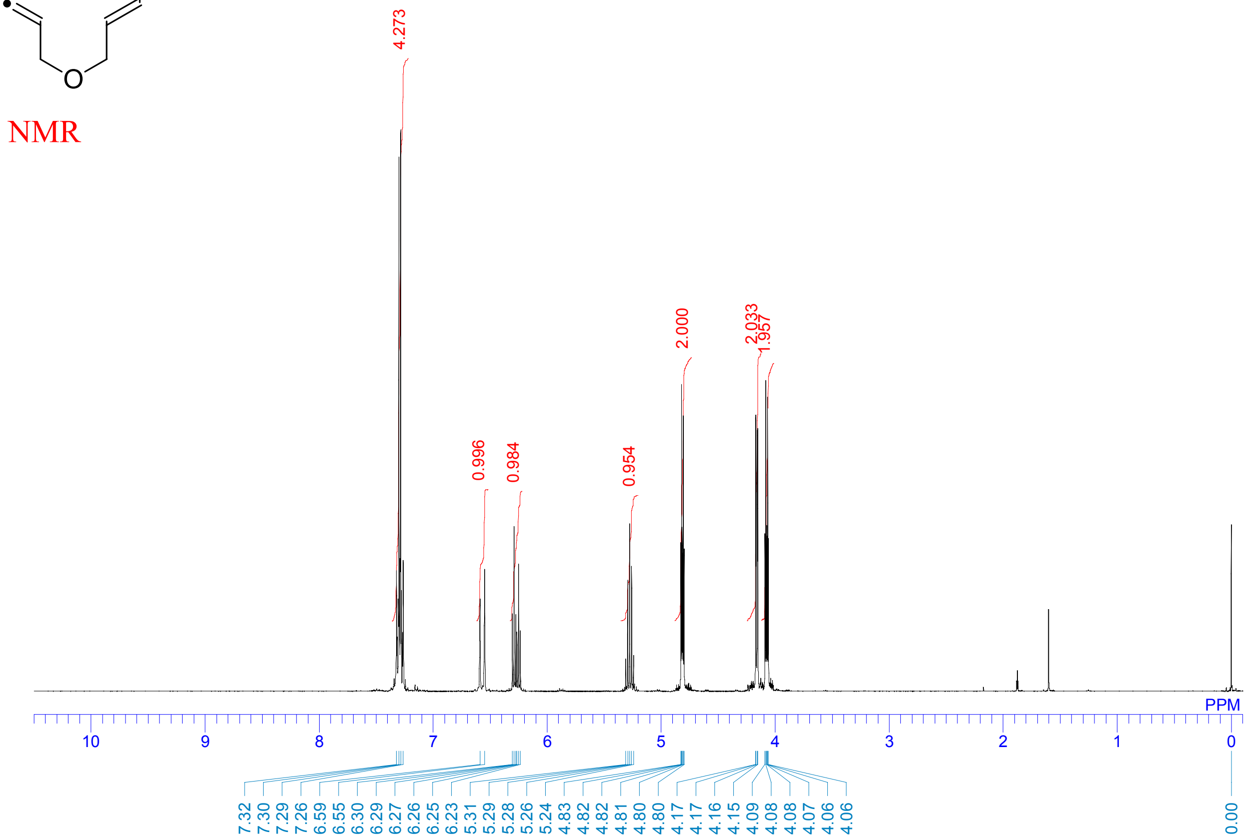
^{13}C NMR



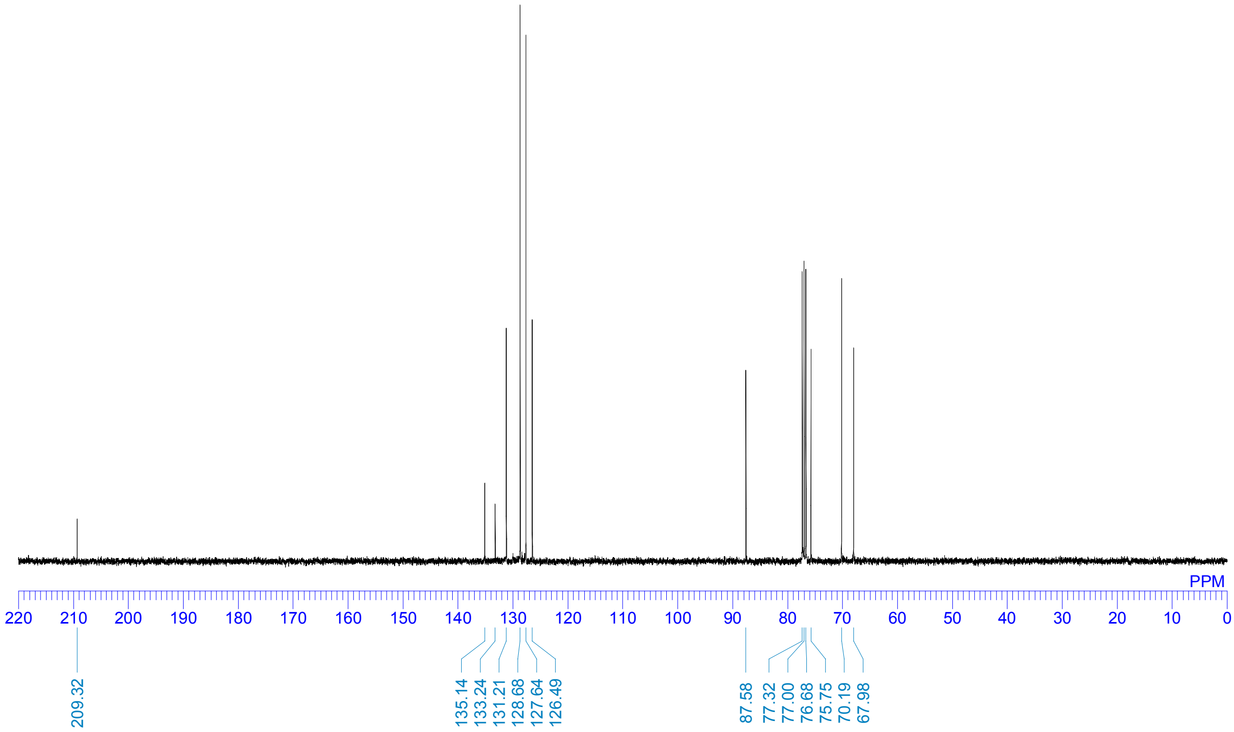
8c



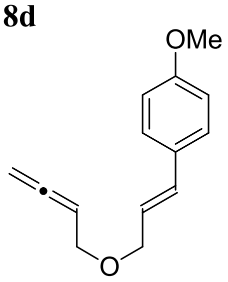
^{1}H NMR



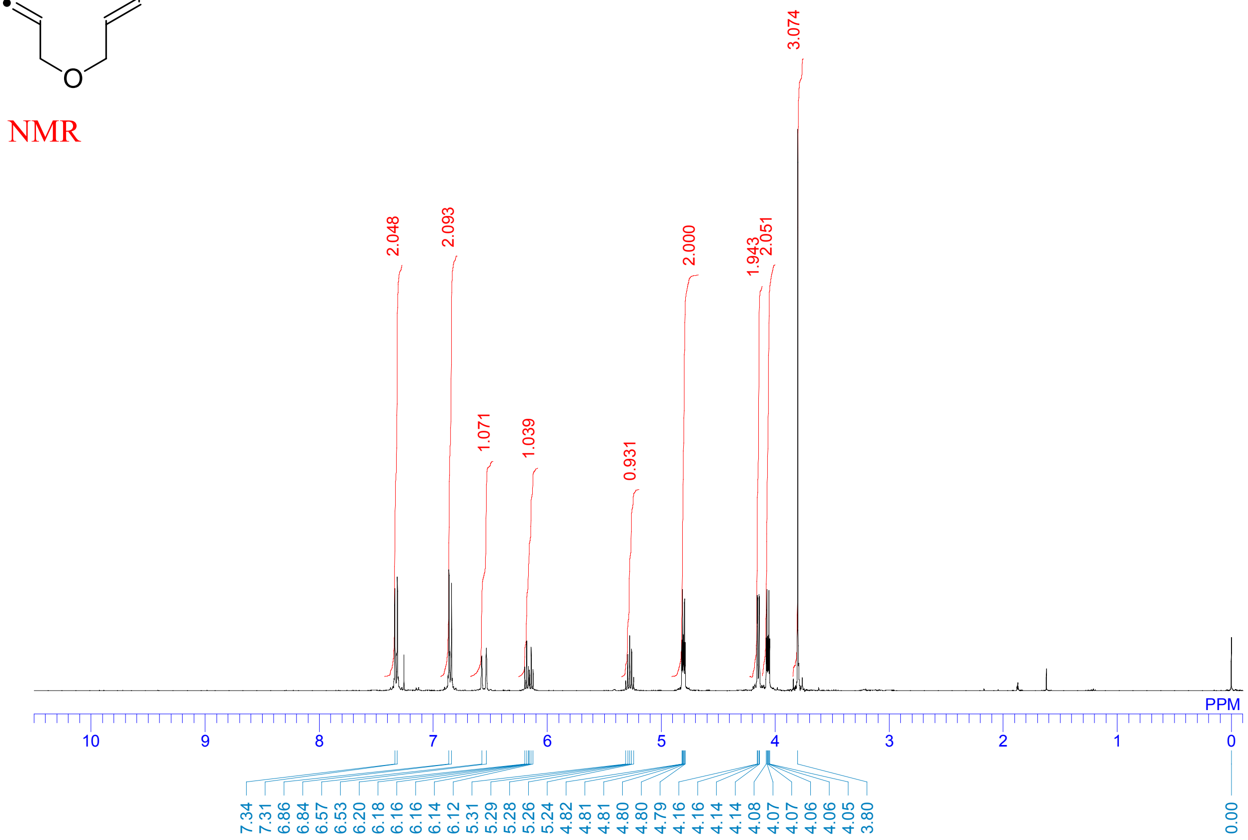
^{13}C NMR



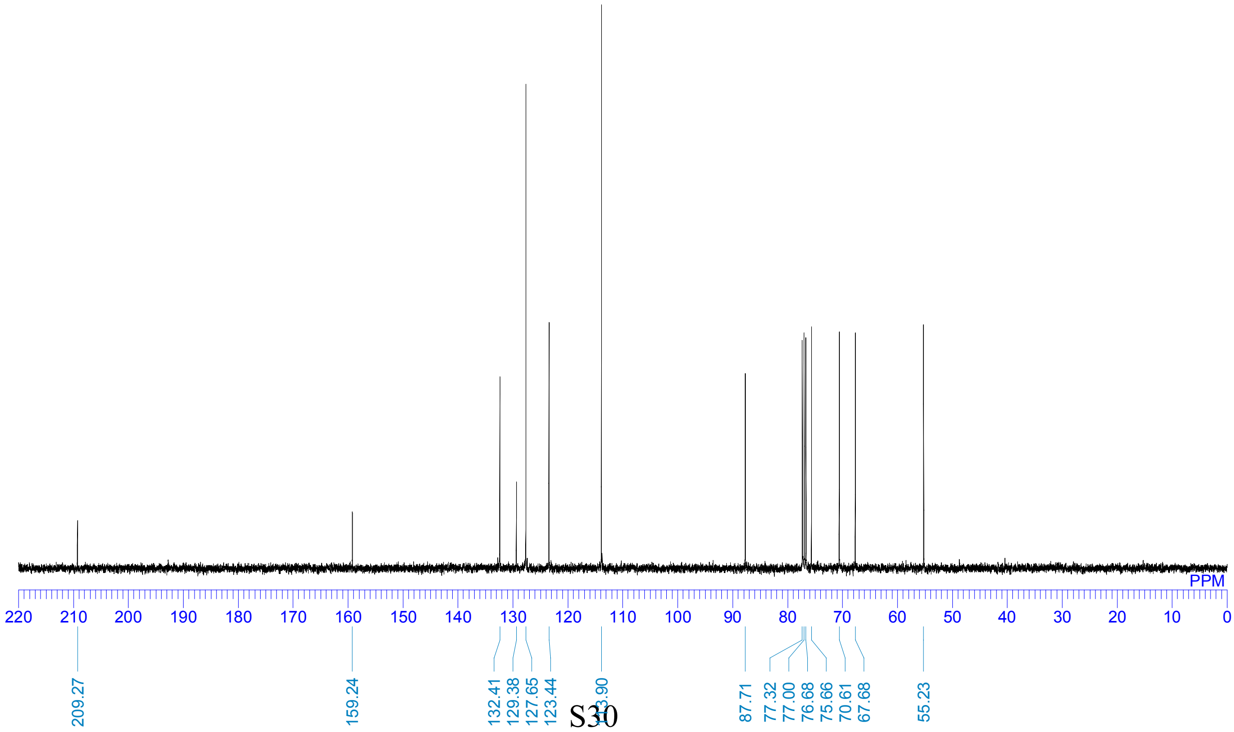
8d



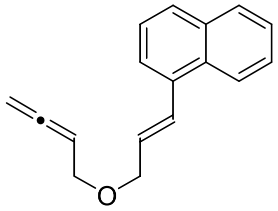
^{1}H NMR



^{13}C NMR

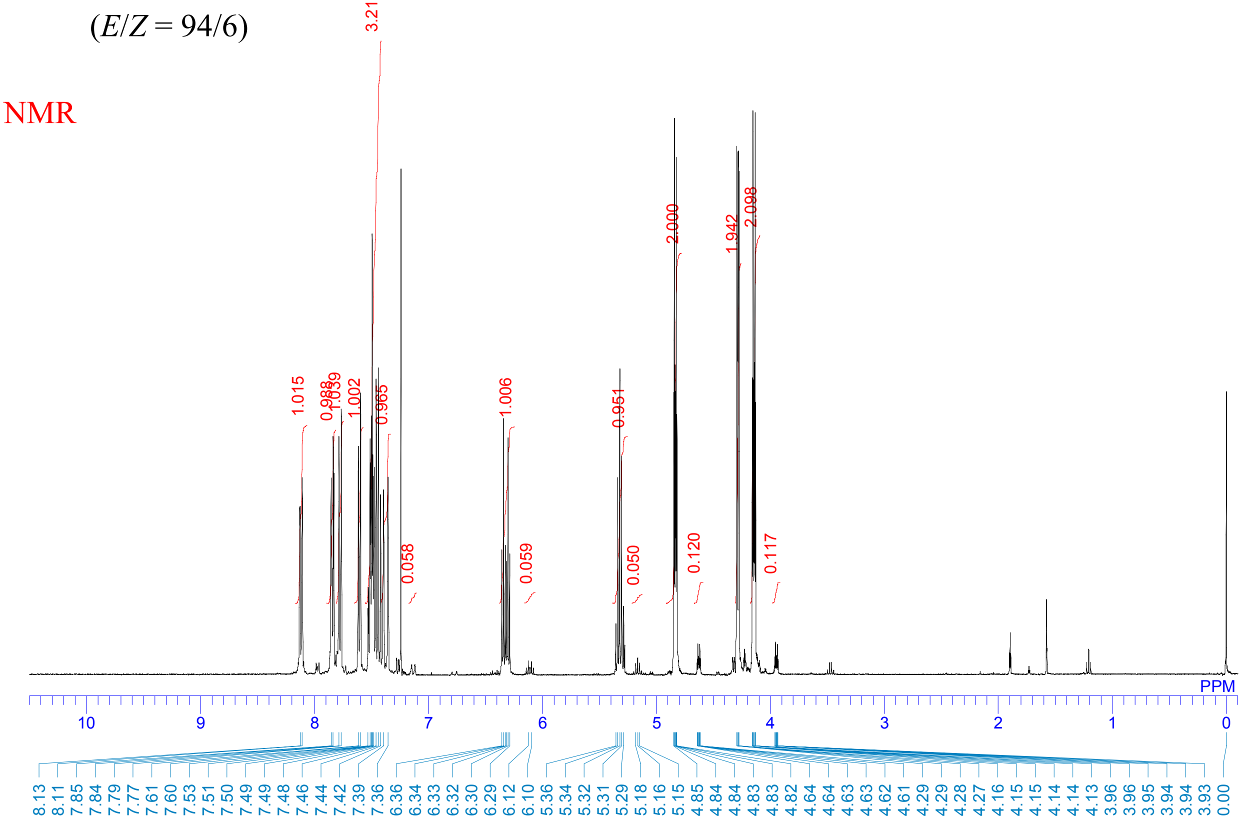


8e

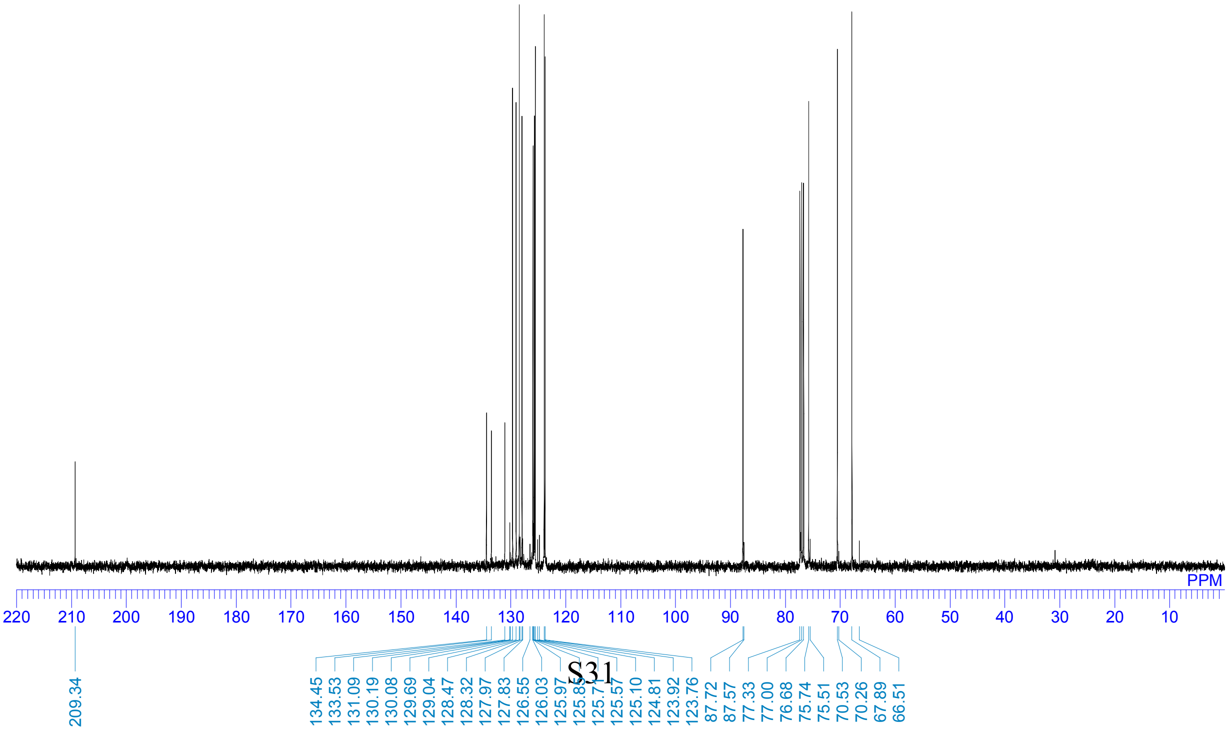


(*E*/*Z* = 94/6)

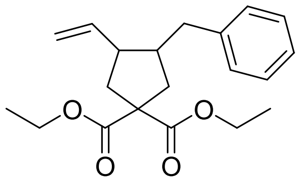
^{1}H NMR



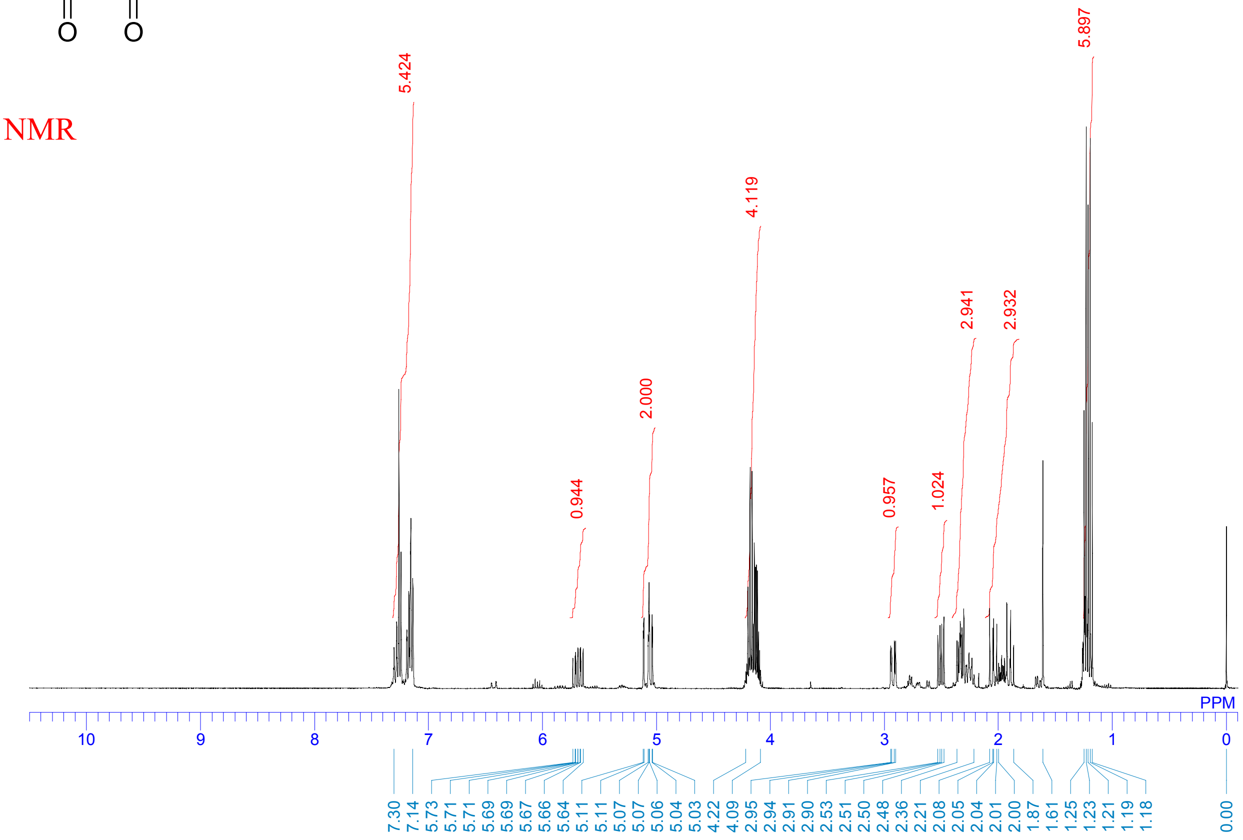
^{13}C NMR



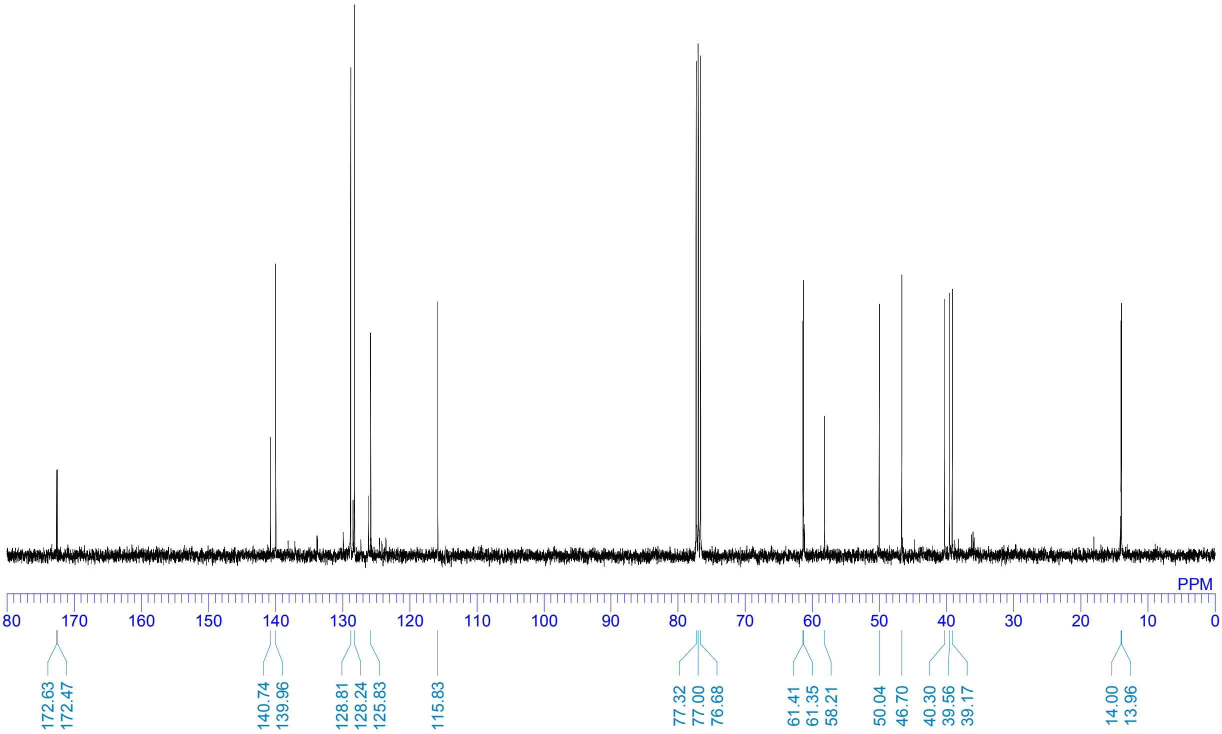
9a-major



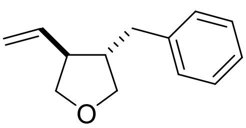
^{1}H NMR



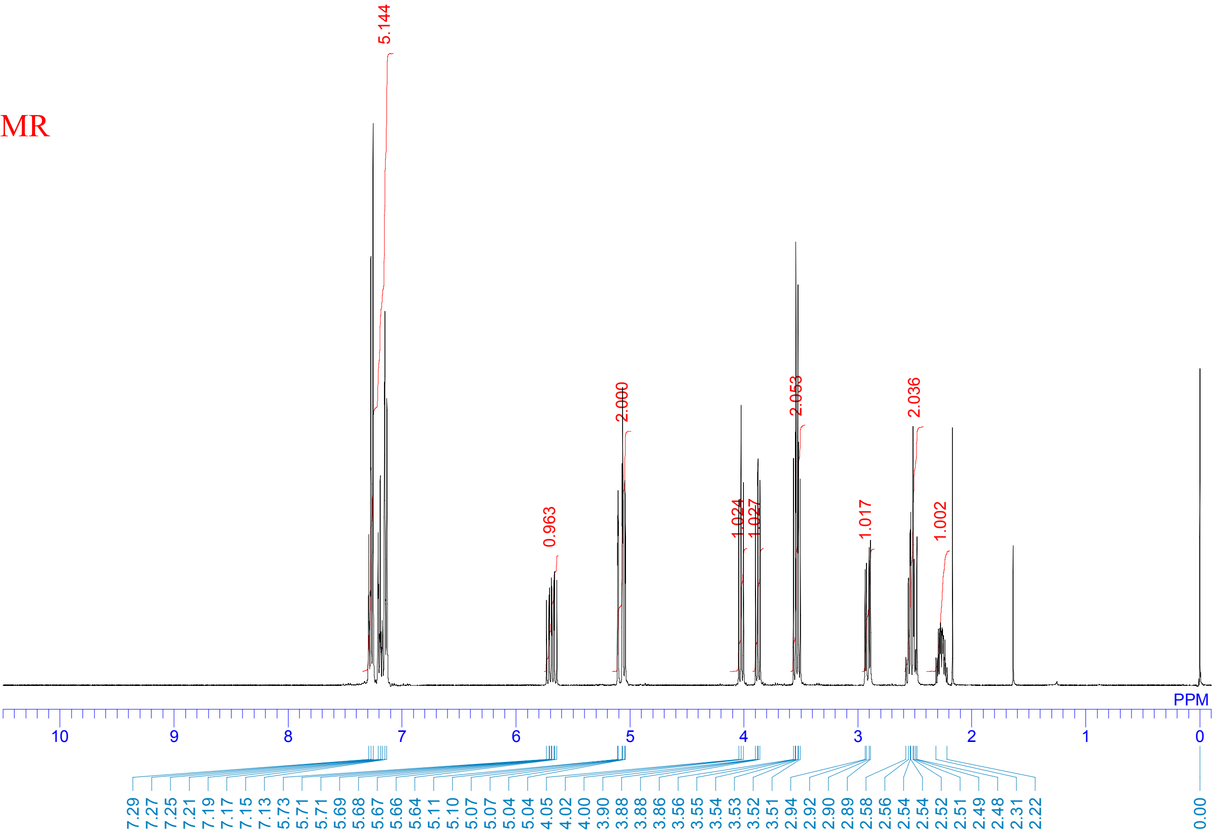
^{13}C NMR



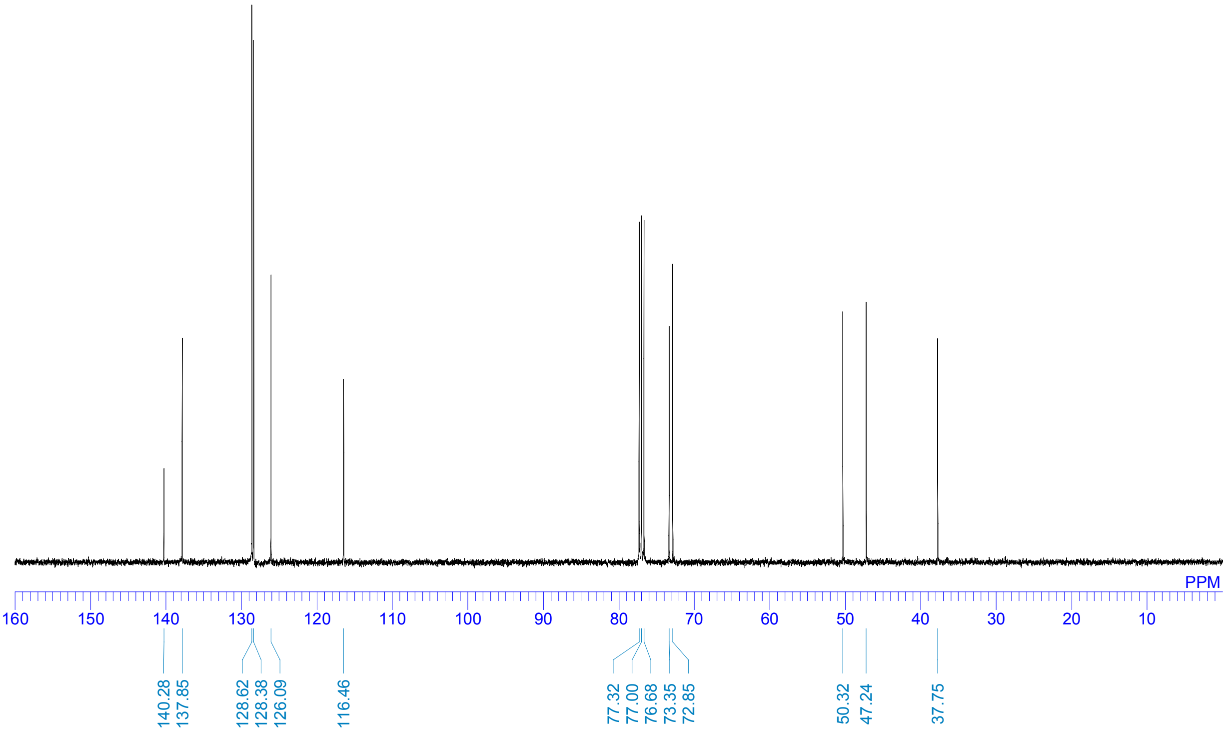
9b-*trans*



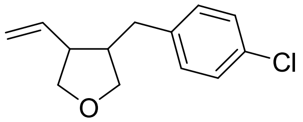
^{1}H NMR



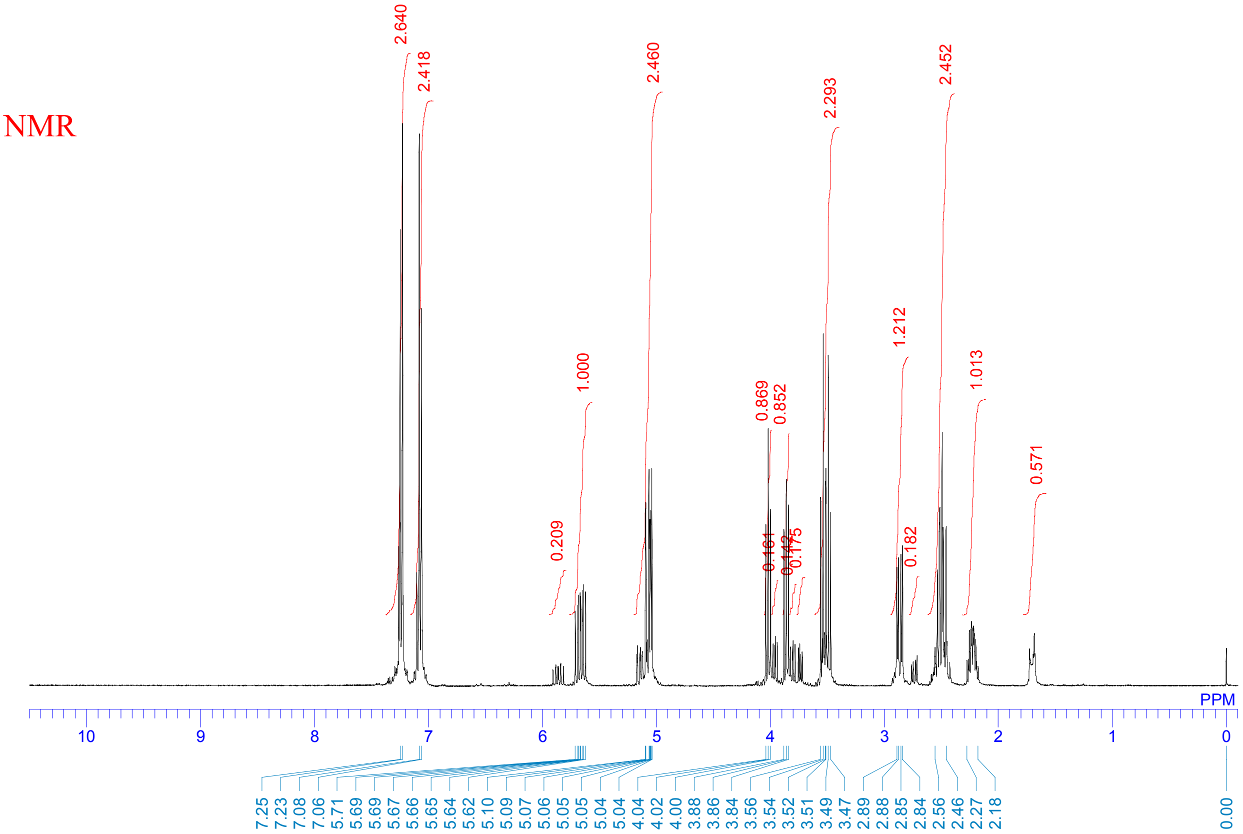
^{13}C NMR



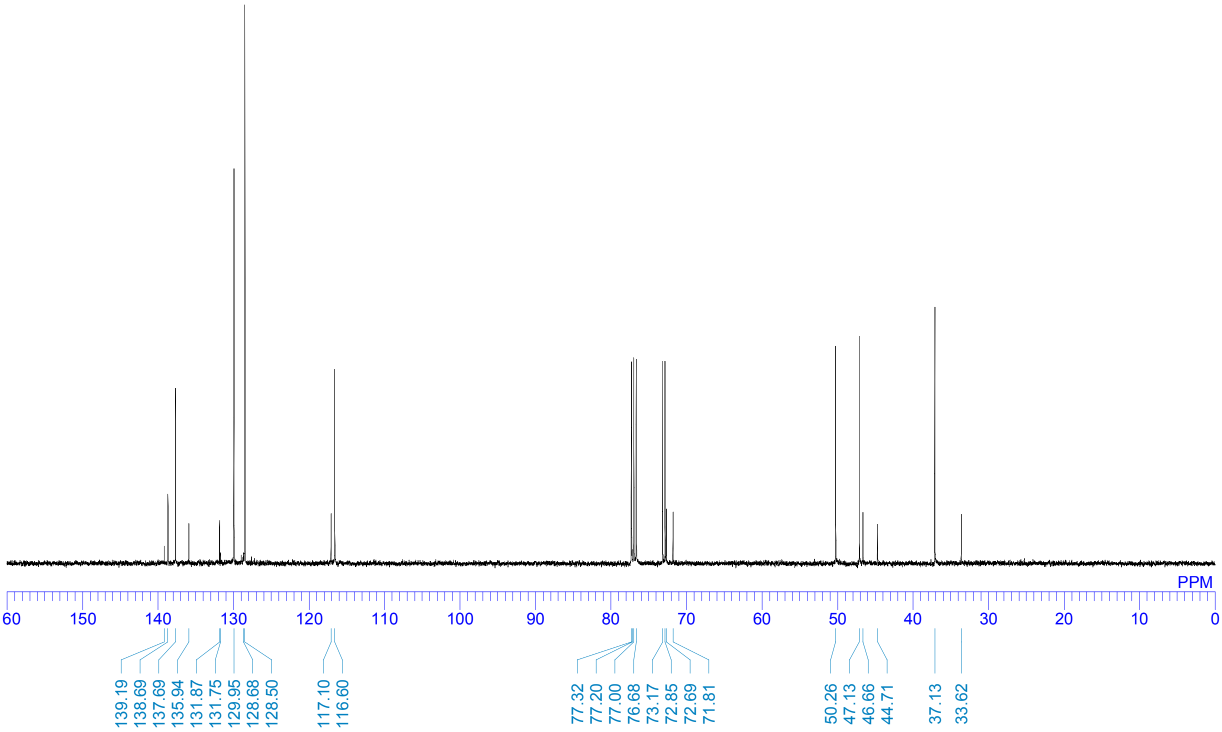
9c (*trans*/*cis* = 83/17)



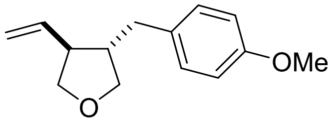
^{1}H NMR



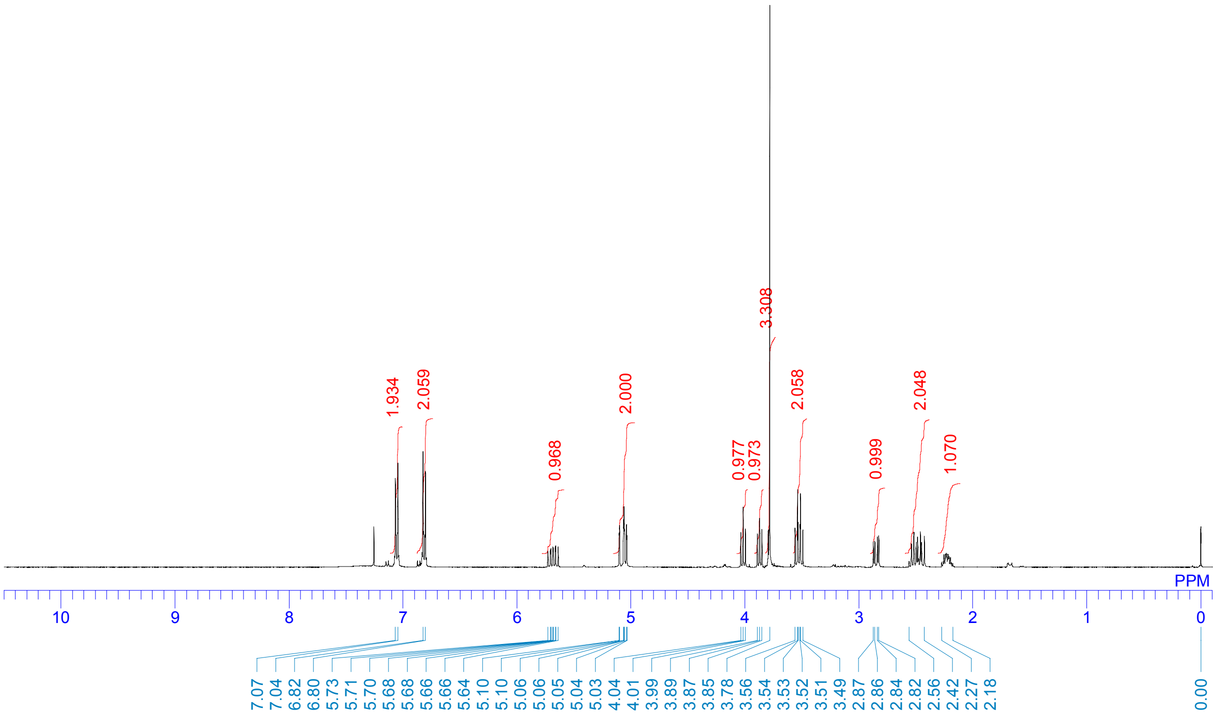
^{13}C NMR



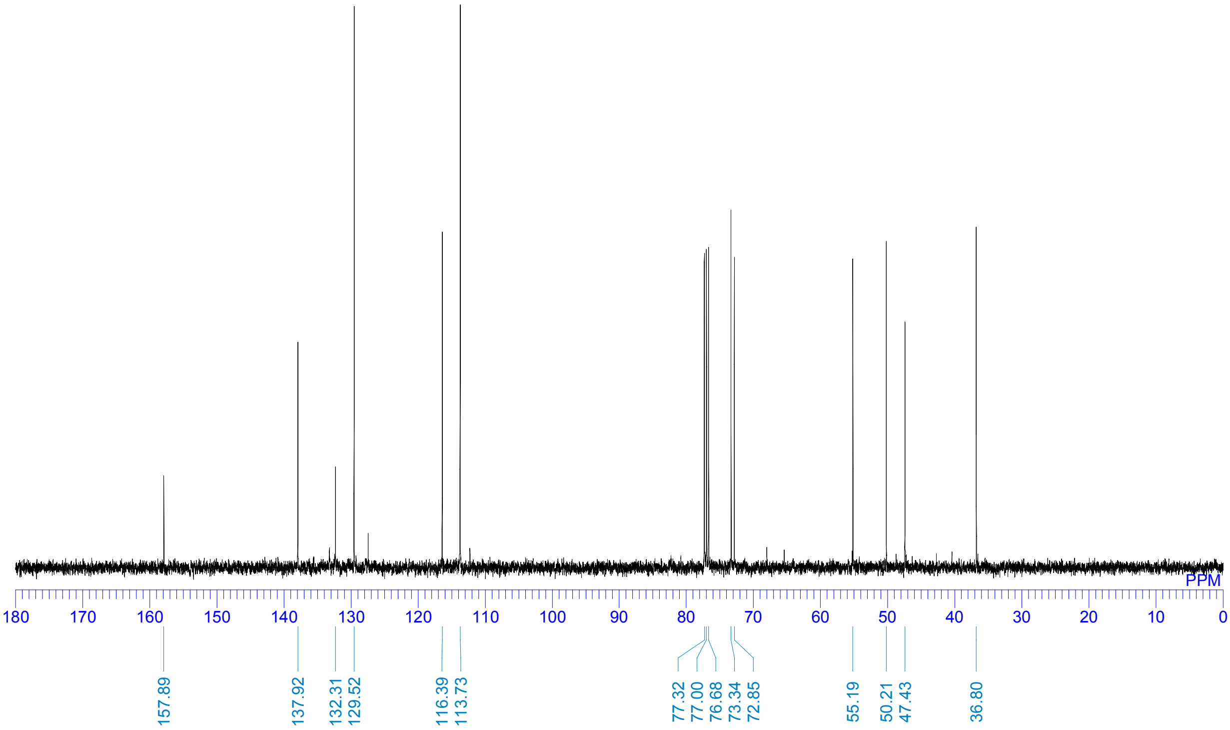
9d-*trans*



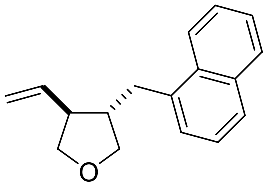
^{1}H NMR



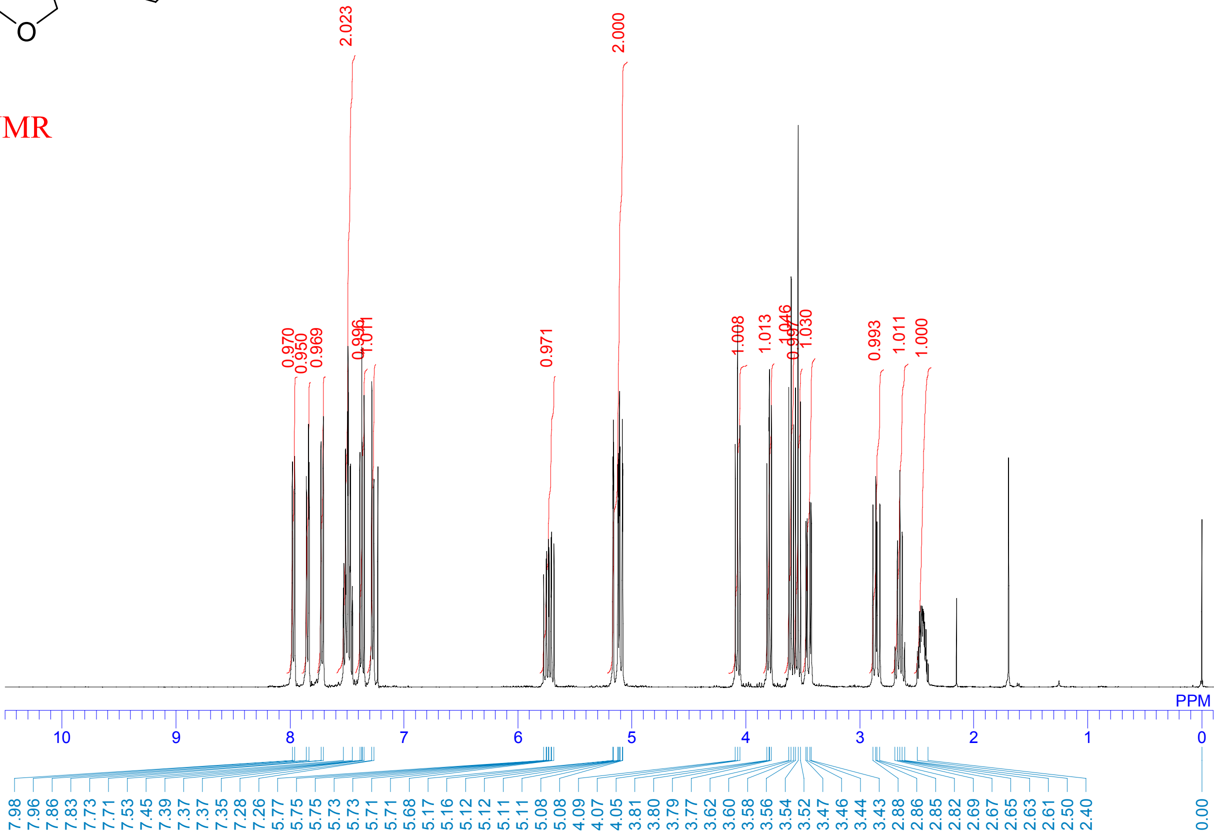
^{13}C NMR



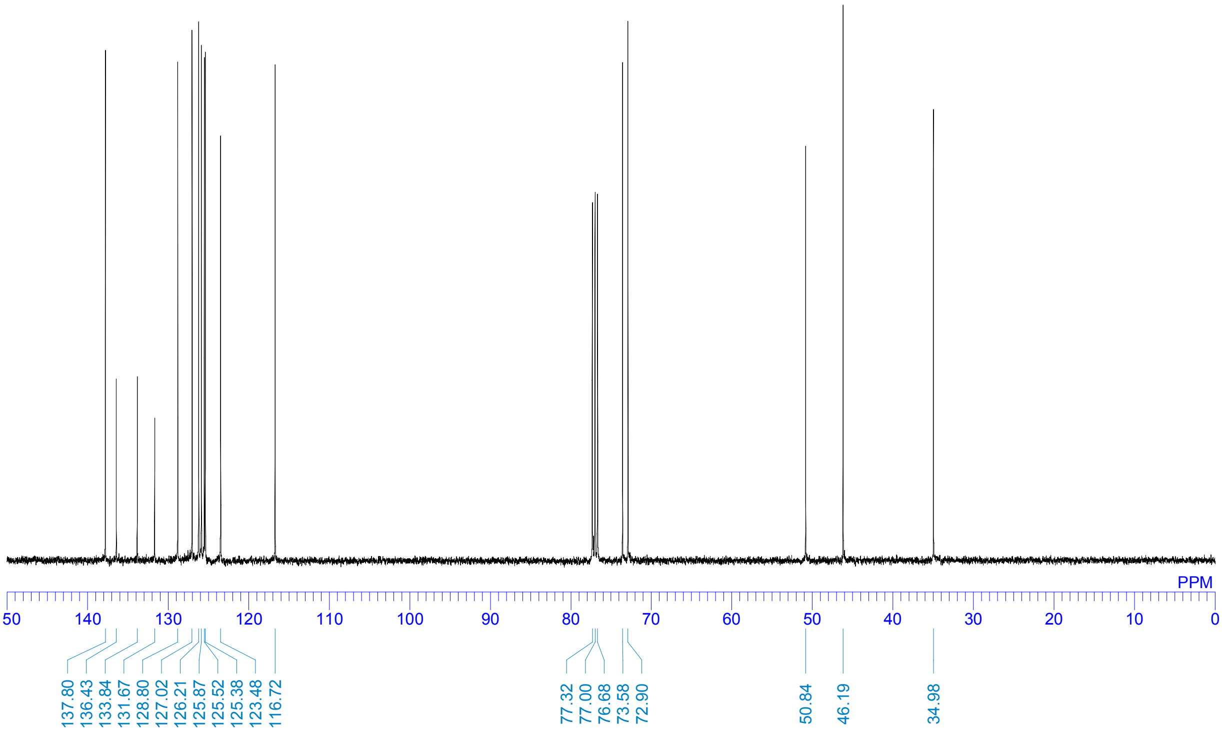
9e-*trans*



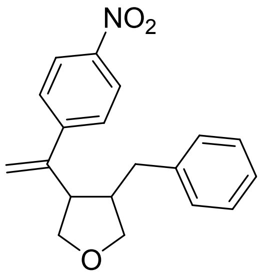
^{1}H NMR



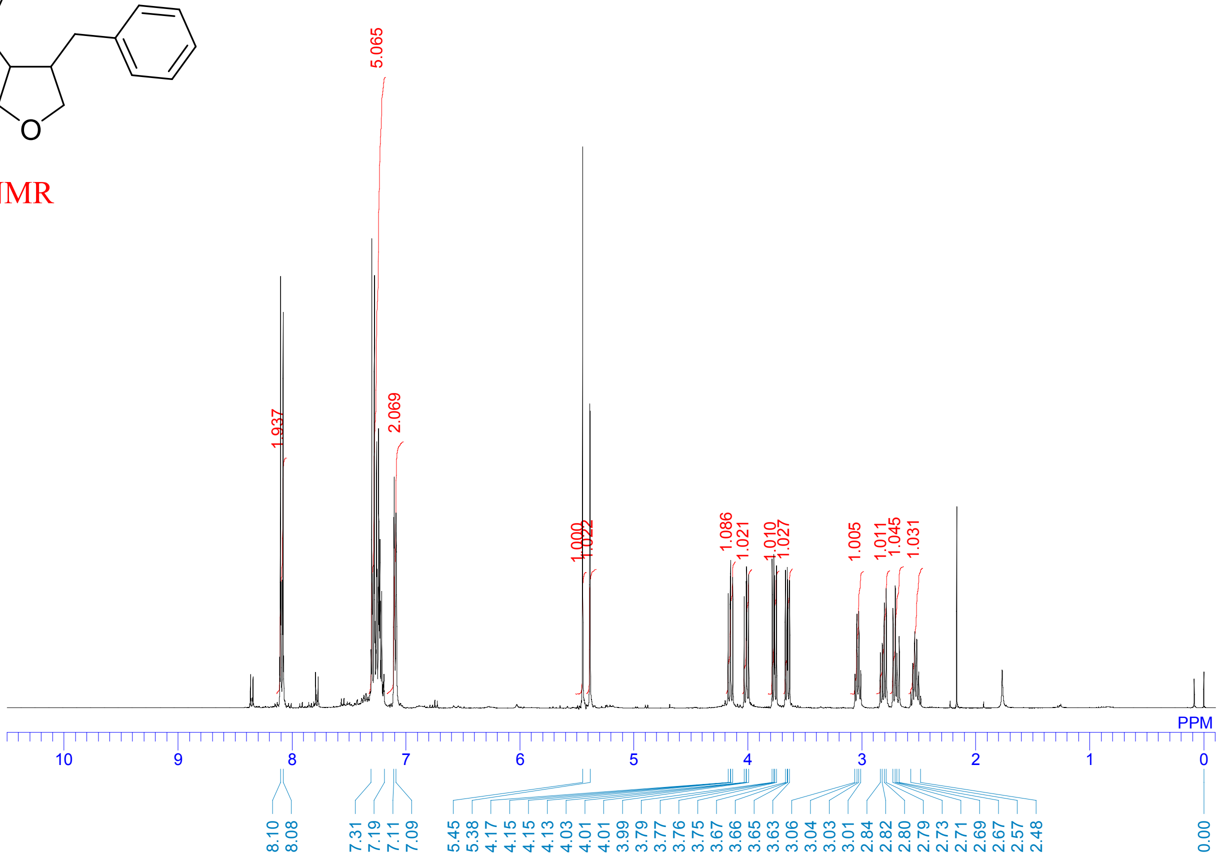
^{13}C NMR



12b-major



^{1}H NMR



^{13}C NMR