Direct Coupling Reaction between Alcohols and Silyl Compounds: Enhancement of Lewis Acidity of Me_3SiBr Using $InCl_3$

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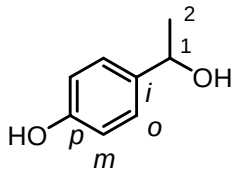
General. IR spectra were recorded as thin films or as solids in KBr pellets. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with TMS as internal standard. ^{29}Si NMR (79 MHz) spectra were obtained with TMS as external standard. ^{1}H and ^{13}C NMR signals of compounds were assigned by using HMQC, HMBC, COSY, and ^{13}C off-resonance techniques. Column chromatography was performed on silica gel 60 (70-230 mesh). Bulb-to-bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by ^{1}H NMR using internal standards.

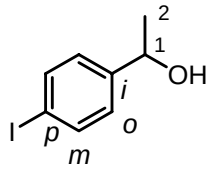
Materials. Hexane, toluene, Et_2O, and THF were distilled from sodium and benzophenone. 1,2-Dichloroethane was distilled from P_2O_5. Dehydrated MeCN and Dichloromethane (stabilized with 2-methyl-2-butene) were used as obtained. The starting alcohols **1d**, **1h-j**, **4f**, and **4j** were prepared and the experimental details are described below (These preparation methods were not optimized.). The starting alcohol **9**[1] acetate **11**[2] and the silyl nucleophiles **6b**,[3] **6c**,[4] **6e**,[5] and **6f**[6] were prepared by known methods. All other starting alcohols and silyl nucleophiles are commercially available. All catalysts were commercially available. Gallium trichloride (0.5 M in pentane) was purchased and used as obtained.

1-(4-Hydroxyphenyl)ethanol (1d)



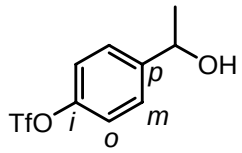
To a suspended solution of lithium aluminum hydride (100 mmol) in THF (120 mL) was slowly added a solution of *p*-hydroxyacetophenone (50 mmol) in THF (30 mL) for 1 h at 0 °C. The reaction mixture was heated and stirred under reflux for 2 h. The resulting mixture was quenched by slow addition of water with stirring at 0 °C and then adjusted to pH 4 with 1 N HCl aq. The mixture was extracted with AcOEt (150 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent evaporated and the residue was purified by recrystallization (Et_2O) to give the product (4.984 g, 72%): mp: 135-136 °C; IR: (KBr)3397 (OH), 1234 (Ar-OH), 1079 (CH-OH) cm^{-1}; ^{1}H NMR: (400 MHz, DMSO-d_6) 9.18 (s, 1H, OH, D_2O-exchangeable), 7.12 (d, J = 8.5 Hz, 2H, *o*-H), 6.68 (d, J = 8.5 Hz, 2H, *m*-H), 4.92 (d, J = 4.3 Hz, OH, D_2O-exchangeable), 4.60 (dq, J = 4.3, 6.3 Hz, 1H, 1-H), 1.26 (d, J = 6.3 Hz, 3H, 2-H_3); ^{13}C NMR: (100 MHz, DMSO-d_6) 156.0 (s, *p*), 137.7 (s, *i*), 126.4 (d, *o*), 114.6 (d, *m*), 67.8 (d, C-1), 26.0 (q, C-2); MS: (EI, 70 eV) m/z 138 (M^+, 32), 123 (M^+ - CH_3, 100), 95 (44), 77 (25) 43 (12); HRMS: (EI, 70 eV) calcd for $C_8H_{10}O_2$ 138.0681 (M^+) found m/z 138.0667. Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.47; H, 7.08.

1-(4-Iodophenyl)ethanol (1h)[7]



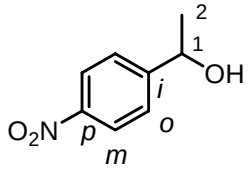
In a 100 mL round bottom flask equipped with a Widmer column was placed (*i*-PrO)$_3$Al (20 mmol), 2-propanol (20 mL), and *p*-iodoacetophenone (20 mmol). Acetone and 2-propanol were slowly distilled off from the mixture with stirring for 5 h at 100 °C. The resulting solution was quenched by addition of 1 N HCl at 0 °C until the pH dropped to 6. The salts were filtered off and then the solution was extracted with AcOEt (50 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent evaporated and the residue was purified by recrystallization (hexane) to give the product (3.746 g, 76%): mp: 49-50 °C; IR: (KBr) 3394, 3305, 1079 (CH-OH) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.67 (dt, *J* = 8.7, 1.9 Hz, 2H, *m*-H), 7.12 (dt *J* = 8.7, 1.9 Hz, 2H, *o*-H), 4.85 (dq, *J* = 2.4, 6.5 Hz, 1H, 1-H), 1.88 (d, *J* = 2.4 Hz, OH, D_2O-exchangeable), 1.46 (d, *J* = 6.5 Hz, 3H, 2-H$_3$); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.4 (s, *i*), 137.5 (d, *m*), 127.4 (d, *o*), 92.7 (s, *p*), 69.8 (d, C-1), 25.2 (q, C-2); MS: (EI, 70 eV) m/z 248 (M^+, 48), 233 (M^+ - CH_3, 100), 121 (M^+ - I, 19), 78 (67) 43 (21); HRMS: (EI, 70 eV) calcud for C_8H_9IO 247.9698 (M^+) found: m/z 247.9694. Anal. Calcd for C_8H_9IO: C, 38.73; H, 3.66; I, 51.16. Found: C, 38.64; H, 3.41; I, 50.88.

4-(1-Hydroxyethyl)phenyl trifluoromethanesulfonate (1i)



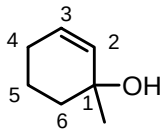
In a 50 mL round bottom flask equipped with a Widmer column was placed (*i*-PrO)$_3$Al (18.6 mmol), 2-propanol (18.6 mL), and 4-acetylphenyl trifluoromethanesulfonate (18.6 mmol). Acetone and 2-propanol were slowly distilled off from the mixture with stirring for 5 h at 100 °C. The resulting solution was quenched by addition of 1 N HCl at 0 °C until the pH dropped to 6. The salts were filtered off and then the solution was extracted with AcOEt (50 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent evaporated and the residue was purified by distillation to give the product (4.166 g, 83%): bp: 92 °C/0.4 mmHg; IR: (neat) 3367 (OH), 1087 (CH-OH) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.45 (dt, *J* = 8.7, 2.2 Hz, 2H, *m*-H), 7.25 (dt *J* = 8.7, 2.2 Hz, 2H, *o*-H), 4.93 (dq, *J* = 3.8, 6.5 Hz, 1H, C*H*OH), 2.07 (d, *J* = 3.8 Hz, OH, D_2O-exchangeable), 1.49 (d, *J* = 6.5 Hz, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 148.6 (s, *i*), 146.2 (s, *p*), 127.2 (d, *m*), 121.3 (s, *o*), 118.7 (q, $^1J_{CF}$ = 321.8 Hz, CF_3) 69.4 (d, *C*HOH), 25.3 (q, Me); MS: (EI, 70 eV) m/z 270 (M^+, 8), 255 (M^+ - CH_3, 100), 226 (8), 122 (11) 43 (24); HRMS: (EI, 70 eV) calcd for $C_9H_9F_3O_4S$ 270.0174 (M^+) found: m/z 270.0169. Anal. Calcd for $C_9H_9F_3O_4S$: C, 40.00; H, 3.36; S, 11.87; F, 21.09. Found: C, 39.74; H, 3.22; S, 11.90; F, 21.19.

1-(4-Nitrophenyl)ethanol (1j)



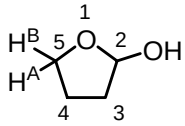
To a solution of *p*-nitroacetophenone (30 mmol) in 2-propanol (60 mL) was added sodium borohydride (30 mmol) in three equal portions. The reaction mixture was stirred under reflux for 2 h and then quenched by addition of 1 N HCl aq with stirring until the pH dropped to 6.5. The salts were filtered off then the solvent was evaporated. The residue was extracted with AcOEt (100 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent evaporated and the residue was purified by column chromatography (AcOEt) on silica gel and distillation to give the product (3.525 g, 70%): bp: 129 °C/0.7 mmHg; IR: (neat) 3397 (OH), 1523 (NO_2), 1346 (NO_2), 1087 (CH-OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 8.20 (dt, *J* = 8.7, 1.9 Hz, 2H, *m*-H), 7.55 (dt *J* = 8.7, 1.9 Hz, 2H, *o*-H), 5.03 (dq, *J* = 2.9, 6.5 Hz, 1H, 1-H), 2.09 (d, *J* = 2.9 Hz, OH, D_2O-exchangeable), 1.52 (d, *J* = 6.5 Hz, 3H, 2-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.1 (s, *i*), 147.0 (s, *p*), 126.1 (d, *o*), 123.6 (d, *m*), 69.4 (d, C-1), 25.4 (q, C-2); MS: (EI, 70 eV) m/z 167 (M^+, 1), 152 (M^+ - CH_3, 100), 122 (8), 107 (34), 77 (30) 43 (16); HRMS: (EI, 70 eV) calcd for $C_8H_9NO_3$ 167.0582 (M^+) found: m/z 167.0586. Anal. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.46; H, 5.30; N, 8.51

1-Methy-2-cyclohexene-1-ol (4f)



To a stirred solution of 2-cyclohexene-1-one (50 mmol) and Et_2O (500 mL) was added methylmagnesium iodide (60 mmol in 20 mL of Et_2O) at 0 ^oC. The mixture was stirred for 10 h at room temperature and then quenched by sat. aq. $NaHCO_3$ (200 mL) at 0 °C. The mixture was extracted with AcOEt (100 mL x 3). The collected organic layer was washed with water (50 x 3 mL) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by chromatography (hexane/ethyl acetate) on silica gel to give the product (0.99 g, 18%). Further purification was performed by distillation under reduced pressure: bp: 89 °C /32 mmHg; IR: (neat) 3371 (OH), 1654 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.75 (dt, *J* = 10.2, 3.7 Hz, 1H, 3-H), 5.63 (d, *J* = 10.2 Hz, 1H, 2-H), 2.03 (m, 1H, 4-H^A), 1.93 (m, 1H, 4-H^B), 1.80-1.60 (m, 4H, 5-H_2 and 6-H_2), 1.61 (s, 1H, OH, D_2O-exchangeable), 1.29 (s, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 133.7 (d, C-2), 129.0 (d, C-3), 67.9 (s, C-1), 37.8 (t, C-6), 29.3 (q, Me), 25.0 (t, C-4), 19.5 (t, C-5); MS: (EI, 70 eV) m/z 112 (M^+, 16), 97 (M^+ – CH_3, 100), 84 (31), 69 (42), 43 (20); HRMS: (EI, 70 eV) calcd for $C_7H_{12}O$ 112.0888 (M^+) found: m/z 112.0890.

2-Hydroxytetrahydrofuran (4j)[8]



To a solution of HCl (5 ml) and water (100 mL) was added 2,3-dihydrofuran (330 mmol) dropwise over a 20 min period at 0 °C. The mixture was stirred for 30 min at 0 °C and then adjusted to pH 8 with 20% aqueous NaOH solution. NaCl was added to the mixture to saturate the solution. The mixture was extracted with CH_2Cl_2 (200 mL x 3). The collected organic layer was dried ($MgSO_4$). The solvent evaporated and the residue was purified by distillation to give the product (11.690 g, 40%): bp: 62 °C/17 mmHg; IR: (neat) 3397 (OH), 1274 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.55-5.54 (m, 1H, 2-H), 4.05 (ddd, *J* = 8.0, 8.0, 5.6 Hz, 1H, 5-H^A), 3.85 (dt, *J* = 8.0, 6.5 Hz, 1H, 5-H^B), 3.32 (brs, 1H, OH, D_2O-exchangeable), 2.11-1.82 (m, 4H, 3-H_2 and 4-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 98.2 (d, C-2), 67.2 (t, C-5), 33.0 (t, C-3), 23.4 (t, C-4); MS: (EI, 70 eV) m/z 88 (M^+, 5), 87 (9), 71 (M^+ - OH, 8), 58 (19), 57 (39), 47 (15), 44 (21), 42 (100), 41 (43), 39 (15); HRMS: (EI, 70 eV) calcd for $C_4H_8O_2$ 88.0524 (M^+) found: m/z 88.0526. Anal. Calcd for $C_4H_8O_2$: C, 54.53; H, 9.15. Found: C, 54.73; H, 8.98.

Typical Procedure for Allylation of 1a (Table 1, Entry 3). To a mixture of $InCl_3$ (0.05 mmol) and 1-phenylethanol (**1a**, 1.0 mmol) in hexane (1 mL) was added allyltrimethylsilane (**2**, 2.0 mmol) and Me_3SiBr (0.1 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The resulting mixture was poured into Et_2O (50 mL) and aqueous $NaHCO_3$ (30 mL). The solution was extracted with Et_2O and the organic layer was dried over $MgSO_4$. The evaporation of the ether solution gave the crude product which was analyzed by NMR. The details of further purification performed for the new compounds are described in Product Data.

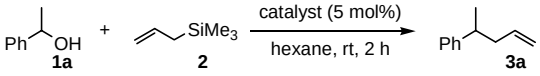
Allylation by Slow Addition of 1a (Table 2, Entry 2). To a mixture of $InCl_3$ (0.05 mmol), Me_3SiBr (0.1 mmol) and allyltrimethylsilane (**2**, 3.0 mmol) in hexane (1 mL) was slowly added a solution of 1-phenylethanol (**1a**, 1.0 mmol) in hexane (1 mL) for 10 min under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The work-up employed is the same as described in the typical reaction procedure.

Allylation of (S)-(-)-1-phenylethanol. To a mixture of $InCl_3$ (0.05 mmol), Me_3SiBr (0.1 mmol) and allyltrimethylsilane (**2**, 3 mmol) in hexane (1 mL) was slowly added a solution of (*S*)-(-)-1-phenylethanol (1 mmol) in hexane (1 mL) for 10 min under nitrogen at 50 ºC. After stirring for 110 min, the resulting mixture was poured into Et_2O (50 mL) and aqueous $NaHCO_3$ (30 mL). The mixture was extracted with Et_2O and the organic layer was dried over $MgSO_4$. The evaporation of the ether solution followed by the column chromatography (hexane) gave **3a** which was analyzed by HPLC (0% ee).

Allylation of 1-Phenylethanol (1a) by Using Various Lewis Acids

The combination of $InCl_3$ and Me_3SiBr is the most effective in the allylation of 1-phenylethanol. Other Lewis acids hardly exhibited catalytic activity in hexane even when combined with Me_3SiBr (Tables S1 and S2).

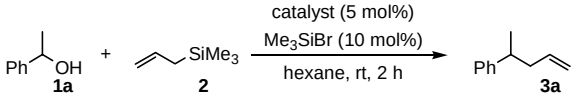
Table S1. Allylation Using Various Lewis Acids[a]



entry	catalyst (mol%)	yield/ %
1	$InCl_3$ (5)	0
2	BF_3•OEt_2 (5)	0
3	$AlCl_3$ (5)	0
4	$GaCl_3$ (5)	18
5	$Yb(OTf)_3$ (5)	0
6	$Sc(OTf)_3$ (5)	0
7	$ZnCl_2$ (5)	0
8	$BiCl_3$ (5)	0
9	$B(C_6F_5)_3$ (5)	0

[a] Reactions were carried out in a solvent (1 mL) with allylsilane **2** (2.0 mmol), alcohol **1a** (1.0 mmol), and catalyst (0.05 mmol).

Table S2. Allylation Using Various Lewis Acids with Me_3SiBr[a]



entry	catalyst (mol%)	yield/ %
1	$InCl_3$ (5)	77
2	BF_3•OEt_2 (5)	0
3	$AlCl_3$ (5)	0
4	$GaCl_3$ (5)	24
5	$Yb(OTf)_3$ (5)	0
6	$Sc(OTf)_3$ (5)	19
7	$ZnCl_2$ (5)	0
8	$BiCl_3$ (5)	0
9	$B(C_6F_5)_3$ (5)	0

[a] Reactions were carried out in a solvent (1 mL) with allylsilane **2** (2.0 mmol), alcohol **1a** (1.0 mmol), Me_3SiBr (0.1 mmol), and catalyst (0.05 mmol).

NMR Study at Low Temperature

The sharper spectrum of Me_3SiBr in the presence of $InBr_3$ on ^{29}Si NMR was observed at lower temperature (Figure S1).

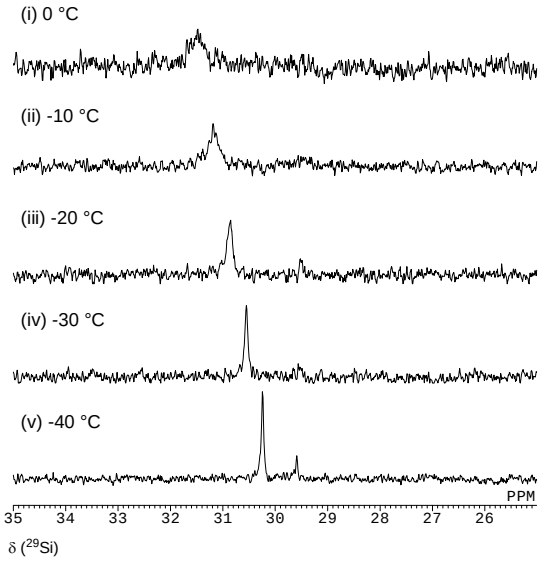


Figure S1. Effect of $InBr_3$ (equimolar amount to Me_3SiBr) on ^{29}Si NMR spectra of Me_3SiBr in MeCN at the various temperature (79 MHz, TMS external standard).

^{29}Si NMR Study on Interaction between Me_3SiOMe and Lewis Acids

No interaction was observed in the mixture of indium halide and Me_3SiOMe, while the reaction with $AlCl_3$ or $BF_3{\cdot}OEt_2$ rapidly took place to give Me_3SiCl or Me_3SiF, respectively (Figure S2).

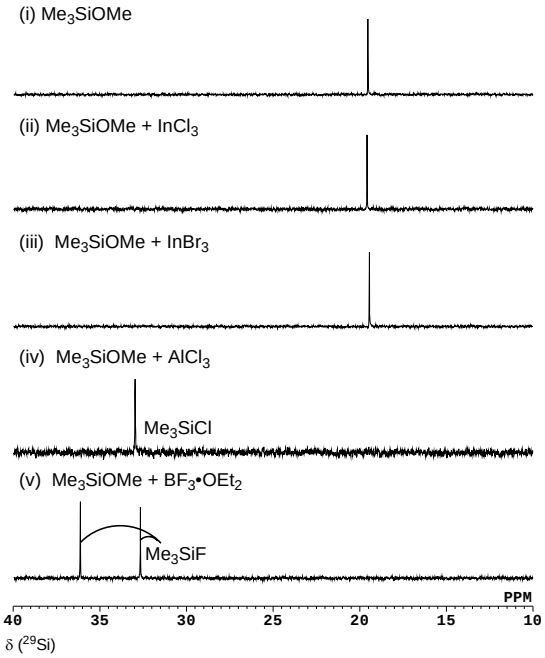
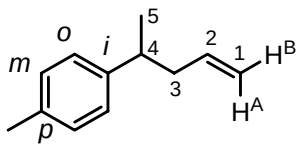


Figure S2. ^{29}Si NMR investigation on interaction between Me_3SiOMe and Lewis Acids in MeCN at room temperature (79 MHz, TMS external standard).

Product Data. The spectral data of **3a**,[9] **5a-c**,[9] **5d-e**,[10] **5g**,[9] **7a**,[11] **7c-e**,[9] **8a**,[12] **8b-e,**[9] and **14**[13] were in an excellent agreement with the reported data. The spectral data for the products **3b-j**, **5f**, **5h**, **5j**, **7b**, **7f**, **8f**, **10**, and **13** are shown below. The stereochemistry of **10** was determined based on the acetylated product of **10** which was in an excellent agreement with the reported data.[14] Other compounds were identified as shown below and the yields of them are described in the text.

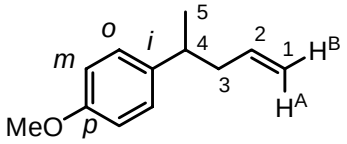
4-(4-Methyphenyl)-1-pentene (3b)



According to the typical procedure, this compound was prepared from **1b**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 140 °C /33 mmHg; IR: (neat) 1639 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.11 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 5.71 (ddt, J = 16.3, 9.1, 7.0 Hz, 1H, 2-H), 4.99 (ddt, J = 16.3, 3.5, 1.5 Hz, 1H, 1-H^A), 4.95 (ddt, J = 9.1, 3.5, 1.1 Hz, 1H, 1-H^B), 2.75 (sext, J = 7.0 Hz, 1H, 4-H), 2.32 (s, 3H, ArMe), 2.37 (ddddd, J = 14.0, 7.0, 7.0, 1.5, 1.1 Hz, 1H, 3-H^A), 2.37 (ddddd, J = 14.0, 7.0, 7.0, 1.5, 1.1 Hz, 1H, 3-H^B), 1.23 (d, J = 7.0 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 144.0 (s, *i*), 137.3 (d, C-2), 135.3 (s, *p*), 129.0 (d, *m*), 126.8 (t, *o*), 115.8 (t, C-1),

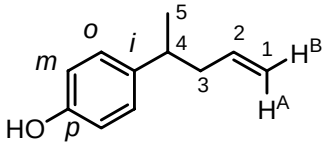
42.7 (t, C-3), 39.3 (d, C-4), 21.6 (q, C-5), 21.0 (q, ArMe); MS: (EI, 70 eV) m/z 160 (M^+, 4), 119 (M^+ – $CH_2CH=CH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{12}H_{16}$ 160.1252 (M^+) found: m/z 160.1251.

4-(4-Methoxyphenyl)-1-pentene (3c)



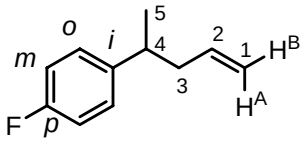
According to the typical procedure, this compound was prepared from **1c**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 95 °C /0.2 mmHg; IR: (neat) 1639 (C=C), 1250 (CO), 1038 (CO) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.11 (d, *J* = 8.7 Hz, 2H, *m*-H), 6.84 (d, *J* = 8.7 Hz, 2H, *o*-H), 5.71 (ddt, *J* = 18.4, 10.4, 6.8 Hz, 1H, 2-H), 4.98 (ddt, *J* = 18.4, 2.0, 1.4 Hz, 1H, 1-H^A), 4.95 (ddt, *J* = 10.4, 2.0, 1.0 Hz, 1H, 1-H^B), 3.79 (s, 3H, OMe), 2.75 (sext, *J* = 6.8 Hz, 1H, 4-H), 2.35 (ddddd, *J* = 13.6, 6.8, 6.8, 1.4, 1.0 Hz, 1H, 3-H^A), 2.25 (ddddd, *J* = 13.6, 6.8, 6.8, 1.4, 1.0 Hz, 1H, 3-H^B), 1.22 (d, *J* = 6.8 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 157.7 (s, *p*), 139.1 (s, *i*), 137.3 (d, C-2), 127.8 (d, *o*), 115.8 (t, C-1), 113.6 (d, *m*), 55.2 (q, OMe), 42.8 (t, C-3), 38.9 (d, C-4), 21.7 (q, C-5); MS: (EI, 70 eV) m/z 176 (M^+, 5), 135 (M^+ – $CH_2CH=CH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{12}H_{16}O$ 176.1201 (M^+) found: m/z 176.1197.

4-(4-Hydroxyphenyl)-1-pentene (3d)



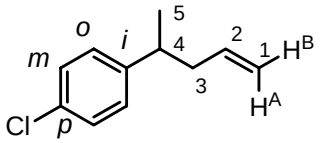
According to the typical procedure, this compound was prepared from **1d**, **2**, $InCl_3$ and Me_3SiBr to give the product as a white solid after distillation under reduced pressure: bp: 102 °C /0.2 mmHg; mp: 41~44 °C; IR: (neat) 3367 (OH), 1612 (C=C), 1234 (CO) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.06 (d, *J* = 8.8 Hz, 2H, *o*-H), 6.76 (d, *J* = 8.8 Hz, 2H, *m*-H), 5.70 (ddt, *J* = 17.6, 10.4, 7.2 Hz, 1H, 2-H), 4.98 (ddt, *J* = 17.6, 2.4, 1.6 Hz, 1H, 1-H^A), 4.95 (ddt, *J* = 10.4, 2.4, 1.2 Hz, 1H, 1-H^B), 4.61 (s,1H, OH, D_2O-exchangeable), 2.73 (tq, *J* = 7.2, 7.1 Hz, 1H, 4-H), 2.33 (ddddd, *J* = 14.4, 7.2, 7.2, 1.6, 1.2 Hz, 1H, 3-H^A), 2.25 (ddddd, *J* = 14.4, 7.2, 7.2, 1.6, 1.2 Hz, 1H, 3-H^B), 1.22 (d, *J* = 7.1 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.5 (s, *p*), 139.4 (s, *i*), 137.2 (d, C-2), 128.0 (d, *o*), 115.8 (t, C-1), 115.0 (d, *m*), 42.9 (t, C-3), 38.9 (d, C-4), 21.7 (q, C-5); MS: (EI, 70 eV) m/z 162 (M^+, 4), 121 (M^+ – $CH_2CH=CH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{11}H_{14}O$ 162.1045 (M^+) found: m/z 162.1046. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 79.71; H, 8.59.

4-(4-Fluorophenyl)-1-pentene (3e)



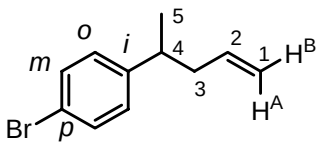
According to the typical procedure, this compound was prepared from **1e**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 91 °C /14 mmHg; IR: (neat) 1639 (C=C), 1227 (C-F) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.12 (dd, *J* = 8.8, 5.6 Hz, 2H, *o*-H), 6.97 (dd, *J* = 8.8, 8.8 Hz, 2H, *m*-H), 5.68 (ddt, *J* = 17.6, 10.0, 7.6 Hz, 1H, 2-H),4.98 (ddt, *J* = 17.6, 2.0, 1.3 Hz, 1H, 1-H^A) 4.95 (ddt, *J* = 10.0, 2.2, 1.3 Hz, 1H, 1-H^B), 2.78 (tq, *J* = 6.8, 6.8 Hz, 1H, 4-H), 2.34 (dddt, *J* = 14.0, 6.8, 6.8, 1.3 Hz, 1H, 3-H^A), 2.26 (dddt, *J* = 14.0, 6.8, 6.8, 1.3 Hz, 1H, 3-H^B), 1.23 (d, *J* = 6.8 Hz, 3H, 5-H); ^{13}C NMR: (100 MHz, $CDCl_3$) 161.2 (d, $^1J_{CF}$ = 245 Hz, *p*), 142.6 (d, $^4J_{CF}$ = 2.4 Hz, *i*), 136.9 (d, C-2), 128.3 (dd, $^1J_{CH}$ and $^3J_{CF}$ = 7.4 Hz, *o*), 116.1 (t, C-1), 115.0 (dd, $^1J_{CH}$ and $^2J_{CF}$ = 21.4 Hz, *m*), 42.8 (t, C-3), 39.1 (d, C-4), 21.6 (q, C-5); MS: (EI, 70 eV) m/z 164 (M^+, 3.7), 123 ($M^+ - CH_2CH{=}CH_2$, 100), 103 ($M^+ - CH_2CH{=}CH_2$ –HF, 21); HRMS: (EI, 70 eV) calcd for $C_{11}H_{13}F$ 164.1001 (M^+) found: m/z 164.0999.

4-(4-Chlorophenyl)-1-pentene (3f)



According to the typical procedure, this compound was prepared from **1f**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 127 °C /14 mmHg; IR: (neat) 1643 (C=C), 1095 (Ar-Cl) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.25 (d, *J* = 8.4 Hz, 2H, *m*-H), 7.11 (d, *J* = 8.4 Hz, 2H, *o*-H), 5.67 (ddt, *J* = 17.6, 10.0, 6.9 Hz, 1H, 2-H), 4.97 (ddt, *J* = 17.6, 2.7, 1.6 Hz, 1H, 1-H^A), 4.95 (ddt, *J* = 10.0, 2.7, 1.0 Hz, 1H, 1-H^B), 2.77 (tq, *J* = 7.2, 7.0 Hz, 1H, 4-H), 2.34 (ddddd, *J* = 14.4, 7.2, 7.2, 1.6, 1.0 Hz, 1H, 3-H^A), 2.26 (ddddd, *J* = 14.4, 7.2, 7.2,1.6, 1.0 Hz, 1H, 3-H^B), 1.22 (d, *J* = 7.0 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.4 (s, *i*), 136.7 (d, C-2), 131.5 (s, *p*), 128.36 (d), 128.35 (d), 116.2 (t, C-1), 42.5 (t, C-3), 39.2 (d, C-4), 21.5 (q, C-5); MS: (EI, 70 eV) m/z 182 (M^+ + 2, 1.5), 180 (M^+, 5), 141 (M^+ + 2 – $CH_2CH{=}CH_2$, 68), 139 $M^+ - CH_2CH{=}CH_2$, 100), 103 ($M^+ - CH_2CH{=}CH_2$ – HCl, 34); HRMS: (EI, 70 eV) calcd for $C_{11}H_{13}Cl$ 180.0607 (M^+) found: m/z 180.0691. Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25. Found: C, 72.88; H, 6.97

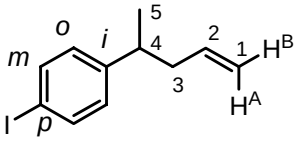
4-(4-Bromophenyl)-1-pentene (3g)



According to the typical procedure, this compound was prepared from **1g**, **2**, $InCl_3$ and Me_3SiBr to give the

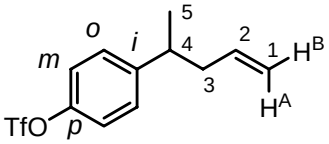
product as a colorless liquid after distillation under reduced pressure: bp: 76 °C /0.5 mmHg; IR: (neat) 1639 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40 (d, *J* = 8.6 Hz, 2H, *m*-H), 7.06 (d, *J* = 8.6 Hz, 2H, *o*-H), 5.67 (ddt, *J* = 17.6, 11.2, 7.2 Hz, 1H, 2-H), 4.98 (ddt, *J* = 17.6, 2.2, 1.4 Hz, 1H, 1-H^A), 4.95 (ddt, *J* = 11.2, 2.2, 1.2 Hz, 1H, 1-H^B), 2.76 (sext, *J* = 7.2 Hz, 1H, 4-H), 2.33 (ddddd, *J* = 14.4, 7.2, 7.2, 1.4, 1.2 Hz, 1H, 3-H^A), 2.26 (ddddd, *J* = 14.4, 7.2, 7.2, 1.4, 1.2 Hz, 1H, 3-H^B), 1.23 (d, *J* = 7.2 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 145.9 (s, *i*), 136.6 (d, C-2), 131.3 (d, *m*), 128.8 (d, *o*), 119.5 (s, *p*), 116.2 (t, C-1), 42.5 (t, C-3), 39.3 (d, C-4), 21.4 (q, C-5); MS: (EI, 70 eV) m/z 226 (M^+ + 2, 7), 224 (M^+, 7), 185 (M^+ + 2 – $CH_2CH{=}CH_2$, 100), 183 (M^+ – $CH_2CH{=}CH_2$, 99), 104 (M^+ – $CH_2CH{=}CH_2$ – Br, 81); HRMS: (EI, 70 eV) calcd for $C_{11}H_{13}Br$ 224.0201 (M^+) found: m/z 224.0207.

4-(4-Iodophenyl)-1-pentene (3h)



According to the typical procedure, this compound was prepared from **1h**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 72 °C /0.08 mmHg; IR: (neat) 1639 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.60 (d, *J* = 8.6 Hz, 2H, *m*-H), 6.95 (d, *J* = 8.6 Hz, 2H, *o*-H), 5.67 (ddt, *J* = 17.3, 10.0, 7.2 Hz, 1H, 2-H), 5.02 (ddt, *J* = 17.3, 1.9, 1.2 Hz, 1H, 1-H^A), 4.96 (ddt, *J* = 10.0, 1.9, 1.2 Hz, 1H, 1-H^B), 2.74 (sext, *J* = 7.2 Hz, 1H, 4-H), 2.33 (dddt, *J* = 14.4, 7.2, 7.2, 1.2 Hz, 1H, 3-H^A), 2.26 (dddt, *J* = 14.4, 7.2, 7.2, 1.2 Hz, 1H, 3-H^B), 1.22 (d, *J* = 7.2 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 146.6 (s, *i*), 137.3 (d, *m*), 136.6 (d, C-2), 129.2 (d, *o*), 116.3 (t, C-1), 90.9 (s, *p*), 42.4 (t, C-3), 39.4 (d, C-4), 21.4 (q, C-5); MS: (EI, 70 eV) m/z 272 (M^+, 12), 231 (M^+ – $CH_2CH{=}CH_2$, 100), 104 (M^+ – $CH_2CH{=}CH_2$ – I, 43); HRMS: (EI, 70 eV) calcd for $C_{11}H_{13}I$ 272.0062 (M^+) found: m/z 272.0072.

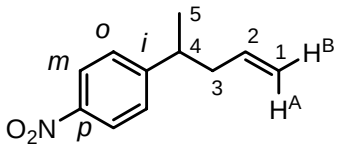
4-(4-Trifluoromethanesulfonyloxyphenyl)-1-pentene (3i)



According to the typical procedure, this compound was prepared from **1i**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 83 °C /0.09 mmHg; IR: (neat) 1504 (C=C), 1427 (S=O), 1215 (S=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.26 (d, *J* = 8.8 Hz, 2H, *o*-H), 7.19 (d, *J* = 8.8 Hz, 2H, *m*-H), 5.67 (ddt, *J* = 17.2, 9.9, 7.2 Hz, 1H, 2-H), 5.03 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H, 1-H^A), 4.97 (ddt, *J* = 9.9, 2.0, 1.0 Hz, 1H, 1-H^B), 2.84 (sext, *J* = 7.2 Hz, 1H, 4-H), 2.35 (dddt, *J* = 14.4, 7.2, 7.2, 1.7, 1.0 Hz, 1H, 3-H^A), 2.28 (dddt, *J* = 14.4, 7.2, 7.2, 1.7, 1.0 Hz, 1H, 3-H^B), 1.25 (d, *J* = 7.2 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 147.7 (s), 147.5 (s), 136.3 (d, C-2), 128.7 (d, *o*), 121.1 (d, *m*), 101.6 (q, $^1J_{CF}$ = 324 Hz, CF_3), 116.5 (t, C-1), 42.5 (t, C-3), 39.3 (d, C-4), 21.3 (q, C-5); MS: (CI, 70 eV) m/z 295 (M + H^+, 19), 253 (M + H^+ – $CH_2CH{=}CH_2$, 100); HRMS: (CI, 70 eV) calcd for $C_{12}H_{14}F_3O_3S$

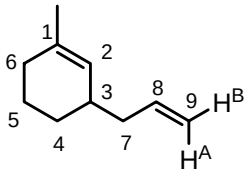
295.0616 (M^+ + 1) found: m/z 295.0620. Anal. Calcd for $C_{12}H_{13}F_3O_3S$: C, 48.97; H, 4.45; S, 10.90; F, 19.37. Found: C, 48.59; H, 4.40; S, 10.96; F, 19.11.

4-(4-Nitrophenyl)-1-pentene (3j)



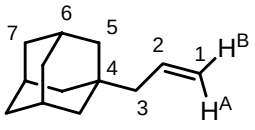
According to the typical procedure, this compound was prepared from **1j**, **2**, $InCl_3$ and Me_3SiBr to give the product as a yellow liquid after distillation under reduced pressure: bp: 98 °C /0.3 mmHg; IR: (neat) 1641 (C=C), 1520 (N=O), 1346 (N=O), 854 (C–N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 8.16 (d, *J* = 8.8 Hz, 2H, *m*-H), 7.34 (d, *J* = 8.8 Hz, 2H, *o*-H), 5.66 (ddt, *J* = 17.6, 10.0, 7.2 Hz, 1H, 2-H), 4.99 (ddt, *J* = 17.6, 1.9, 2.0 Hz, 1H, 1-H^A) 4.97 (ddt, *J* = 10.0, 1.9, 1.2 Hz, 1H, 1- H^B) 2.93 (sext, *J* = 7.2 Hz, 1H, 4-H), 2.39 (ddddd, *J* = 14.4, 7.2, 7.2, 2.0, 1.2 Hz, 1H, 3-H^A), 2.34 (ddddd, *J* = 14.4, 7.2, 7.2, 2.0, 1.2 Hz, 1H, 3-H^B), 1.29 (d, *J* = 7.2 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.7 (s, *i*), 146.4 (s, *p*), 135.8 (d, C-2), 127.8 (d, *o*), 123.6 (d, *m*), 116.8 (d, C-1), 42.2 (t, C-3), 39.8 (d, C-4), 21.1 (q, C-5); MS: (EI, 70 eV) m/z 191 (M^+, 7.2), 150 (M^+ – CH_2–CH=CH_2, 100), 104 (M^+ – CH_2–CH=CH_2 – NO_2, 18.4); HRMS: (EI, 70 eV) calcd for $C_{11}H_{13}NO_2$ 191.0946 (M^+) found: 191.0948. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.96; H, 6.64; N, 7.40.

1-Methyl-3-(2-propenyl)-1-cyclohexene (5f)



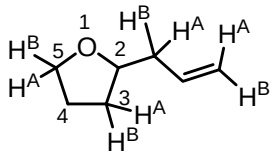
According to the typical procedure, this compound was prepared from **4f**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 120 °C /95 mmHg; IR: (neat) 1639 (C=C), 1670 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.80 (ddt, *J* = 17.6, 10.4, 7.2 Hz, 1H, 2'-H), 5.29 (m, 1H, 2-H), 5.02 (ddt, *J* = 17.6, 2.4, 0.8 Hz, 1H, 3'-H^A), 4.99 (ddt, *J* = 10.4, 2.4, 0.8 Hz, 1H, 3'-H^B), 2.08 (m, 1H, 3-H), 2.03 (m, 2H, 1'-H_2), 1.86 (m, 2H, 6-H_2), 1.72 (m, 2H, 5-C*H*H and 4-C*H*H), 1.65 (s, 3H, 1-Me), 1.51 (m, 1H, 5-CH*H*), 1.13 (m, 1H, 4-CH*H*); ^{13}C NMR: (100 MHz, $CDCl_3$) 137.5 (d, C-8), 134.3 (s, C-1), 125.5 (d, C-2), 115.5 (t, C-9), 40.9 (t, C-7), 35.3 (d, C-3), 30.2 (t, C-6), 28.7 (t, C-4), 23.9 (q, 1-Me), 21.8 (t, C-5); MS: (EI, 70 eV) m/z 136 (M^+, 4.1), 95 (M^+ – $CH_2CH=CH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{10}H_{16}$ 136.1252 (M^+) found: m/z 136.1243.

3-(1-Adamantyl)-propene (5h)



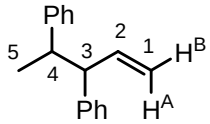
According to the typical procedure, this compound was prepared from **4h**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 119 °C /14 mmHg; IR: (neat) 1639 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.83 (ddt, *J* = 17.6, 10.4, 7.4 Hz, 1H, 2-H), 5.00 (dd, *J* = 10.4, 2.4 Hz, 1H, 1-H^B), 4.96 (dd, *J* = 17.6, 2.4 Hz, 1H, 1-H^A), 2.17 (m, 3H, 6-H_3), 1.82 (d, *J* = 7.4 Hz, 2H, 3-H_2), 1.65 (m, 6H, 7-H_6), 1.47 (m, 6H, 5-H_6); ^{13}C NMR: (100 MHz, $CDCl_3$) 134.9 (d, C-2), 116.4 (t, C-1), 49.0 (t, C-3), 42.4 (t, C-5), 37.1 (t, C-7), 32.6 (s, C-4), 28.7 (d, C-6); MS: (EI, 70 eV) m/z 176 (M^+, 0.35), 135 ($M^+ - CH_2CH{=}CH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{13}H_{20}$ 176.1565 (M^+) found: 176.1577. Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.29; H, 11.31.

2-Allyltetrahydrofuran (5j)



According to the typical procedure, this compound was prepared from **4j**, **2**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 102-105 °C/100 mmHg; IR: (neat) 1643 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.83 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H, 2-$CH_2CH{=}CH_2$), 5.11 (dd *J* = 17.1, 10.1 Hz, 1H, 2-$CH_2CH{=}CH^AH$), 5.06 (ddd, *J* = 10.1, 1.4, 1.4 Hz, 1H, 2-$CH_2CH{=}CHH^B$), 3.92-3.85 (m, 2H, 5-H^A and 2-H), 3.73 (dt, J = 6.5, 6.5 Hz, 1H, 5-H^B), 2.35 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H, 2-$CH^AHCH{=}CH_2$), 2.25 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H, 2-$CHH^BCH{=}CH_2$), 2.01-1.80 (m, 3H, 4-H_2 and 3-H^A), 1.51 (ddt, *J* = 11.8, 7.7, 7.7 Hz 1H, 3-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 135.1 (d, 2-$CH_2CH{=}CH_2$), 116.7 (t, 2-$CH_2CH{=}CH_2$), 78.5 (d, C-2), 67.9 (t, C-5), 40.0 (t, 2-$CH_2CH{=}CH_2$), 30.8 (t, C-3), 25.6 (t, C-4); MS: (CI, 70 eV) m/z 113 ($M^+ + 1$, 42), 95 (15), 71 ($M^+ - CH_2CH{=}CH_2$, 100); HRMS: (CI, 70 eV) calcd for $C_7H_{13}O$ 113.0966 ($M^+ + 1$) found: m/z 113.0967.

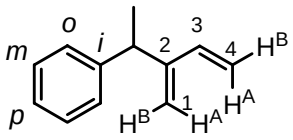
3,4-Diphenyl-1-pentene (7b)



According to the typical procedure, this compound was prepared from **1a**, **6b**, $InCl_3$ and Me_3SiBr to give the product as a diastereomixture and a colorless liquid after column chromatography (hexane) on silica gel and distillation under reduced pressure. Further separation of diastereomers was performed by TLC (hexane/AcOEt, 99/1, R_f = 0.64): bp: 108 °C/0.6 mmHg; IR: (neat) 1635 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) major: 7.14 (m, 10H, aroma), 6.08 (ddd, *J* = 16.9, 10.1, 9.4 Hz, 1H, 2-H), 5.09 (ddd, *J* = 16.9, 1.7, 0.7 Hz, 1H, 1-H^A), 5.07 (dd, *J* = 10.1, 1.7 Hz, 1H, 1-H^B), 3.39 (dd, *J* = 9.4, 9.4 Hz, 1H, 3-H), 3.06 (dq, *J* = 9.4, 7.0 Hz, 1H, 4-H), 1.33 (d, *J* = 7.0 Hz, 3H, 5-H_3), minor: 7.33-7.16 (m, 10H, aroma), 5.84 (ddd, *J* = 16.9, 10.1, 8.0 Hz, 1H, 2-H), 4.82 (ddd, *J* = 10.1, 1.7, 1.0 Hz, 1H, 1-H^B), 4.73 (ddd, *J* = 16.9, 1.7, 1.2 Hz, 1H, 1-H^A), 3.40 (dd, *J* = 9.9, 8.0 Hz, 1H, 3-H), 3.05 (dq, *J* = 9.9, 7.0 Hz, 1H, 4-H), 1.08 (d, *J* = 7.0 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) major: 145.3 (s, ipso), 143.4 (s, ipso), 140.6 (d, C-2), 128.0 (d,

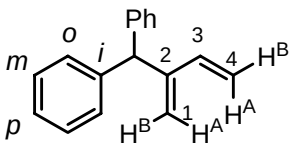
aroma-CH), 127.9 (d, aroma-CH), 127.8 (d, aroma-CH), 127.7 (d, aroma-CH), 125.8 (d, aroma-CH), 125.7 (d, aroma-CH), 115.6 (t, C-1), 58.2 (d, C-3), 45.0 (d, C-4), 20.2 (q, C-5), minor: 145.5 (s, ipso), 143.3 (s, ipso), 140.6 (d, C-2), 128.4 (d, aroma-CH), 128.2 (d, aroma-CH), 128.1 (d, aroma-CH), 127.9 (d, aroma-CH), 126.3 (d, aroma-CH), 126.1 (d, aroma-CH), 115.3 (t, C-1), 57.4 (d, C-3), 45.4 (d, C-4), 20.7 (q, C-5); MS: (EI, 70 eV) m/z major: 222 (M^+, 4), 117 (M^+ - $PhCHCH_3$, 31), 105 (M^+ - $PhCHCH=CH_2$, 100), 91 (6), 79 (5), 77 (6), minor: 222 (M^+, 4), 117 (M^+ - $PhCHCH_3$, 33), 105 (M^+ - $PhCHCH=CH_2$, 100), 91 (6), 79 (5), 77 (6); HRMS: (EI, 70 eV) major: calcd for $C_{17}H_{18}$ 222.1409 (M^+) found: m/z 222.1413, minor: calcd for $C_{17}H_{18}$ 222.1409 (M^+) found: m/z 222.1420.

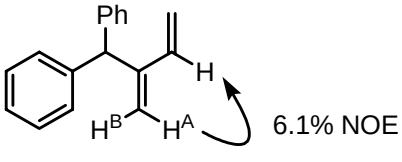
2-(1-Phenylethyl)-1,3-butadiene (7f)



According to the typical procedure, this compound was prepared from **1a**, **6f**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 132 °C /20 mmHg; IR: (neat) 1594 (C=C–C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.31 (t, *J* = 7.2 Hz, 2H, *m*-H), 7.26 (d, *J* = 7.2 Hz, 2H, *o*-H), 7.21 (t, J = 7.2 Hz, 1H, *p*-H), 6.35 (dd, *J* = 19.0, 10.8 Hz, 1H, 3-H), 5.28 (s, 1H, 1-H^A), 5.20 (d, *J* = 19.0 Hz, 1H, 4-H^A), 5.18 (s, 1H, 1-H^B), 5.00 (d, *J* = 10.8 Hz, 1H, 4-H^B), 3.82 (q, *J* = 5.2 Hz, 1H, 2-CH), 1.45 (d, *J* = 5.2 Hz, 3H, Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 149.6 (s, C-2), 145.5 (s, *i*), 138.5 (d, C-3), 128.3 (d, *m*), 127.3 (d, *o*), 126.0 (d, *p*), 115.3 (t, C-1), 114.3 (t, C-4), 40.9 (d, 2-*C*H(CH_3)Ph), 21.6 (q, Me); MS: (EI, 70 eV) m/z 158 (M^+, 68.6), 143 (M^+ – CH_3, 89.6), 129 (74.1), 128 (57.6), 105 (M^+ – CH_2=C–CH=CH_2, 100), 77 (C_6H_5, 31.7); HRMS: (EI, 70 eV) calcd for $C_{12}H_{14}$ 158.1096 (M^+) found: m/z 158.1099.

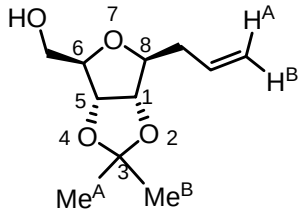
2-Diphenylmethyl-1,3-butadiene (8f)





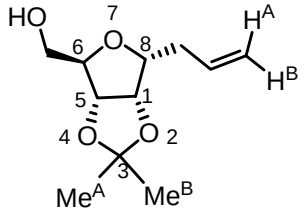
According to the typical procedure, this compound was prepared from **4c**, **6f**, $InCl_3$ and Me_3SiBr to give the product as a colorless liquid after distillation under reduced pressure: bp: 114 °C /0.2 mmHg; IR: (neat) 1597 (C=C–C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.28 (tt, *J* = 7.2, 1.6 Hz, 4H, *m*-H), 7.20 (tt, *J* = 7.2, 1.6 Hz, 2H, *p*-H), 7.14 (dt, *J* = 7.2, 1.6 Hz, 4H, *o*-H), 6.45 (dd, *J* = 16.8, 11.4 Hz, 1H, 3-H), 5.39 (s, 1H, 1-H^A), 5.17 (d, *J* = 16.8 Hz, 1H, 4-H^A), 5.14 (s, 1H, 2-CH), 5.02 (d, *J* = 11.4 Hz, 1H, 4-H^B), 4.67 (s, 1H, 1-H^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 148.4 (s, C-2), 142.5 (s, *i*), 138.5 (d, C-3), 129.2 (d, *o*), 128.2 (d, *m*), 126.3 (d, *p*), 120.1 (t, C-1), 114.9 (t, C-4), 53.0 (d, 2-*C*HPh_2); MS: (EI, 70 eV) m/z 220 (M^+, 100), 167 (M^+ – CH_2=C–CH=CH_2, 69), 165 (45), 152 (21), 129 (100), 91($PhCH_2^+$, 20); HRMS: (EI, 70 eV) calcd for $C_{17}H_{16}$ 220.1252 (M^+) found: m/z 220.1270.

(1*S*,5*R*,6*R*,8*S*)-8-Allyl-3,3-dimethyl-6-hydroxymethyl-2,4,7-trioxabicyclo[3.3.0]octane (10)



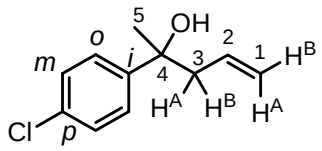
According to the typical procedure, this compound was prepared from **9**, **2**, $InCl_3$ and Me_3SiCl to give the product as a colorless liquid after distillation under reduced pressure: Further purification was performed by column chromatography (hexane/AcOEt, 50/50) on silica gel: bp: 165 °C/1 mmHg; IR: (neat) 3432 (OH), 1643 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 5.84 (ddt, *J* = 17.1, 10.4, 7.0 Hz, 1H, 8-CH_2CH=CH_2), 5.17 (ddd J = 17.1, 3.4, 1.9 Hz, 1H, 8-CH_2CH=CH^AH), 5.09 (ddt, *J* = 10.4, 2.0, 1.2 Hz, 1H, 8-CH_2CH=CHH^B), 4.60 (dd, *J* = 7.0, 4.6 Hz, 1H, 5-H), 4.36 (dd, *J* = 7.0, 5.1 Hz, 1H, 1-H), 4.01-3.96 (m, 2H, 6-H and 8-H), 3.83 (ddd, *J* = 11.8, 5.1, 3.4 Hz, 1H, 6-CH^AHOH), 3.67 (ddd, *J* = 11.8, 7.5, 4.3 Hz, 1H, 6-CHH^BOH) 2.40 (dddd, *J* = 7.0, 7.0, 3.4, 1.2 Hz, 2H, 8-CH_2CH=CH_2), 2.03 (dd, *J* = 7.5, 5.1 Hz, 1H, OH, D_2O-exchangeable), 1.54 (s, 3H, Me^A), 1.34 (s, 3H, Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 135.4 (d, 8-CH_2CH=CH_2), 118.1 (t, 8-CH_2CH=CH_2), 114.6 (s, C-3), 84.1 (d, C-6 or C-8), 84.0 (d, C-8 or C-6), 83.5 (d, C-1), 81.3 (d, C-5), 62.7 (t, 6-CH_2OH), 37.7 (t, 8-CH_2CH=CH_2), 27.4 (q, Me^A), 25.4 (q, Me^B); MS: (CI, 70 eV) m/z 215 (M^+ + 1, 100) 173 (M^+ - CH_2CH=CH_2, 45), 157 (32), 139 (7), 115 (10); HRMS: (CI, 70 eV) calcd for $C_{11}H_{19}O_4$ 215.1283 (M^+ + 1) found: m/z 215.1282.

(1S,5R,6R,8R)-8-Allyl-3,3-dimethyl-6-hydroxymethyl-2,4,7-trioxabicyclo[3.3.0]octane (10)



According to the typical procedure, this compound was prepared from **9**, **2**, $InCl_3$ and Me_3SiCl to give the product as a colorless liquid after distillation under reduced pressure: Further purification was performed by column chromatography (hexane/AcOEt, 30/70) on silica gel: ^1H NMR: (400 MHz, $CDCl_3$) 5.88 (ddt, *J* = 17.1, 10.4, 6.6 Hz, 1H, 8-CH_2CH=CH_2), 5.17 (ddd *J* = 17.1, 3.4, 2.0 Hz, 1H, 8-CH_2CH=CH^AH), 5.09 (ddt, *J* = 10.4, 2.0, 1.2 Hz, 1H, 8-CH_2CH=CHH^B), 4.67 (dd, *J* = 6.0, 3.6 Hz, 1H, 1-H), 4.63 (dd, *J* = 6.0, 1.2 Hz, 1H, 5-H), 4.14 (dt, *J* = 1.2, 6.0 Hz, 1H, 6-H), 3.96 (dt, *J* = 6.6, 3.6 Hz, 1H, 8-H), 3.60 (d, *J* = 6.0 Hz, 2H, 6-CH_2OH), 2.48 (dddd, J = 6.6, 6.6, 3.4, 1.2 Hz, 2H, 8-CH_2CH=CH_2), 2.19 (brs, 1H, OH, D_2O-exchangeable), 1.52 (s, 3H, Me^A), 1.35 (s, 3H, Me^B); ^{13}C NMR: (100 MHz, $CDCl_3$) 134.5 (d, 8-CH_2CH=CH_2), 117.1 (t, 8-CH_2CH=CH_2), 112.5 (s, C-3), 84.1 (d, C-6), 82.4 (d, C-5), 81.5 (d, C-1), 80.5 (d, C-8), 62.8 (t, 6-CH_2OH), 33.6 (t, 8-CH_2CH=CH_2), 26.3 (q, Me^A), 25.0 (q, Me^B) MS: (CI, 70 eV) m/z 215 (M^+ + 1, 100), 199 (M^+ - CH_3, 3), 173 (M^+ - CH_2CH=CH_2, 7), 157 (14), 139 (2); HRMS: (CI, 70 eV) calcd for $C_{11}H_{19}O_4$ 215.1283 (M^+ + 1) found: m/z 215.1291.

2-(4-Chlorophenyl)-4-penten-2-ol (13)



According to the competitive reaction between **1a** and **12** using Bu_4NF, this compound was gave as a colorless liquid: IR: (neat) 3432 (OH), 1639 (C=C), 1095 (Ar-Cl) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.37 (dt, *J* = 8.5, 1.9 Hz, 2H, o-H), 7.30 (dt *J* = 8.5 1.9 Hz, 2H, m-H), 5.59 (dddd, *J* = 14.5, 12.6, 8.2, 6.5 Hz, 1H, 4-H), 5.14 (d, *J* = 14.5 Hz, 1H, 5-H^A), 5.13 (d, *J* = 12.6 Hz, 1H, 5-H^B), 2.65 (dd, *J* = 13.8, 6.5 Hz, 1H, 3-H^A), 2.48 (dd, *J* = 13.8, 8.2 Hz, 1H, 3-H^B), 2.07 (s, 1H, OH, D_2O-exchangeable), 1.53 (s, 3H, 1-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 146.1 (s, *i*), 133.2 (d, C-4), 132.4 (s, *p*), 128.2 (d, *m*), 126.3 (d, *o*), 119.8 (t, C-5), 73.3 (s, C-2), 48.3 (t, C-3), 29.9 (q, C-1); MS: (CI, 70 eV) m/z 199 (M^+ + 3, 0.21), 197 (M^+ + 1, 0.86), 181 (34), 179 (100), 155 (M^+ + 1 - $CH_2CH=CH_2$, 13); HRMS: (CI, 70 eV) calcd for $C_{11}H_{14}ClO$ 197.0733 (M^+ + 1) found: m/z 197.0728.

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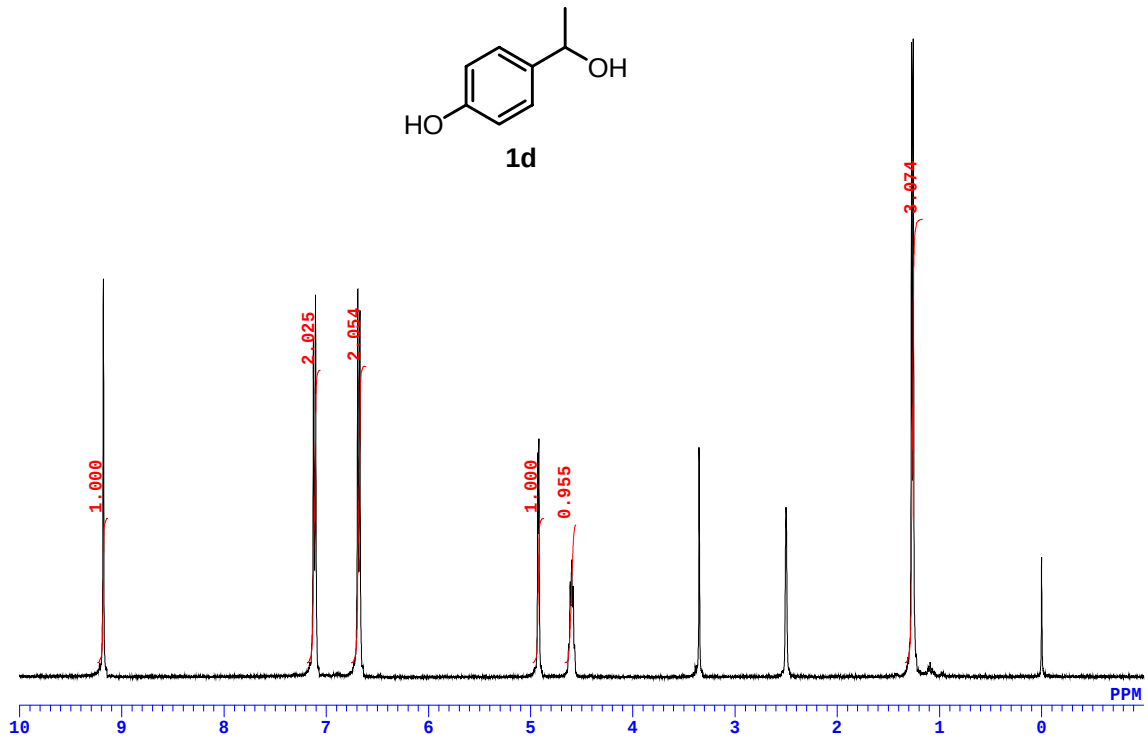
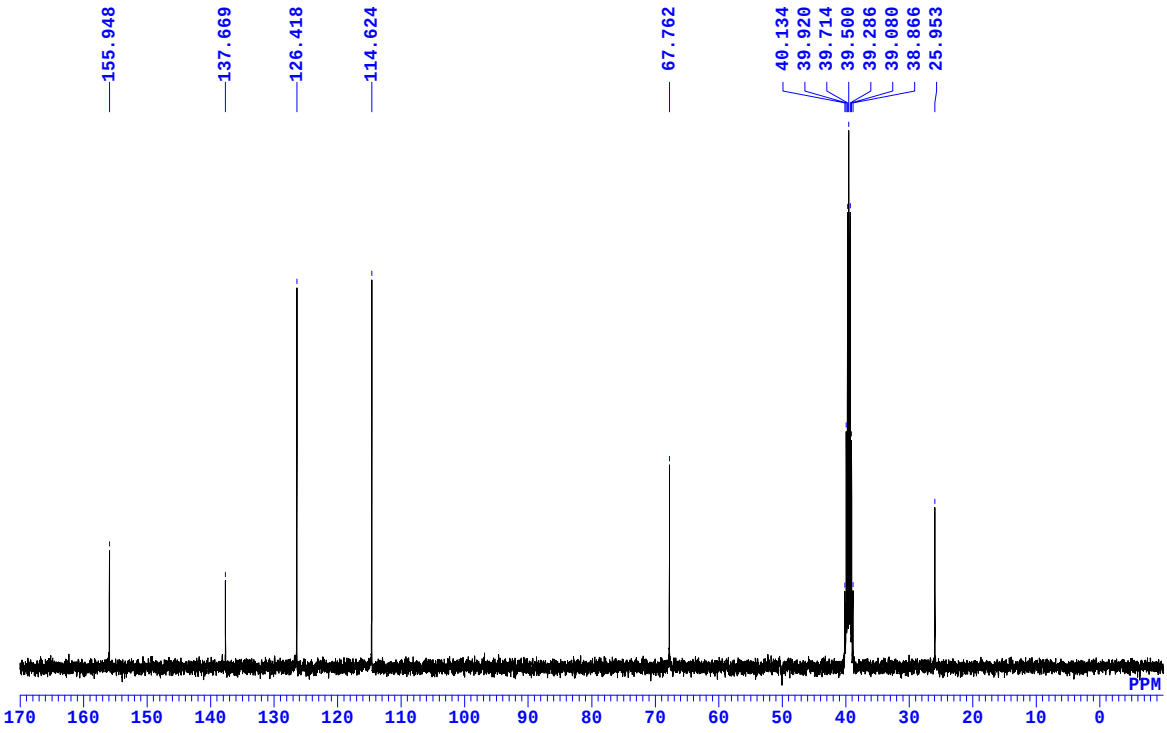
^{1}H and ^{13}C NMR spectra

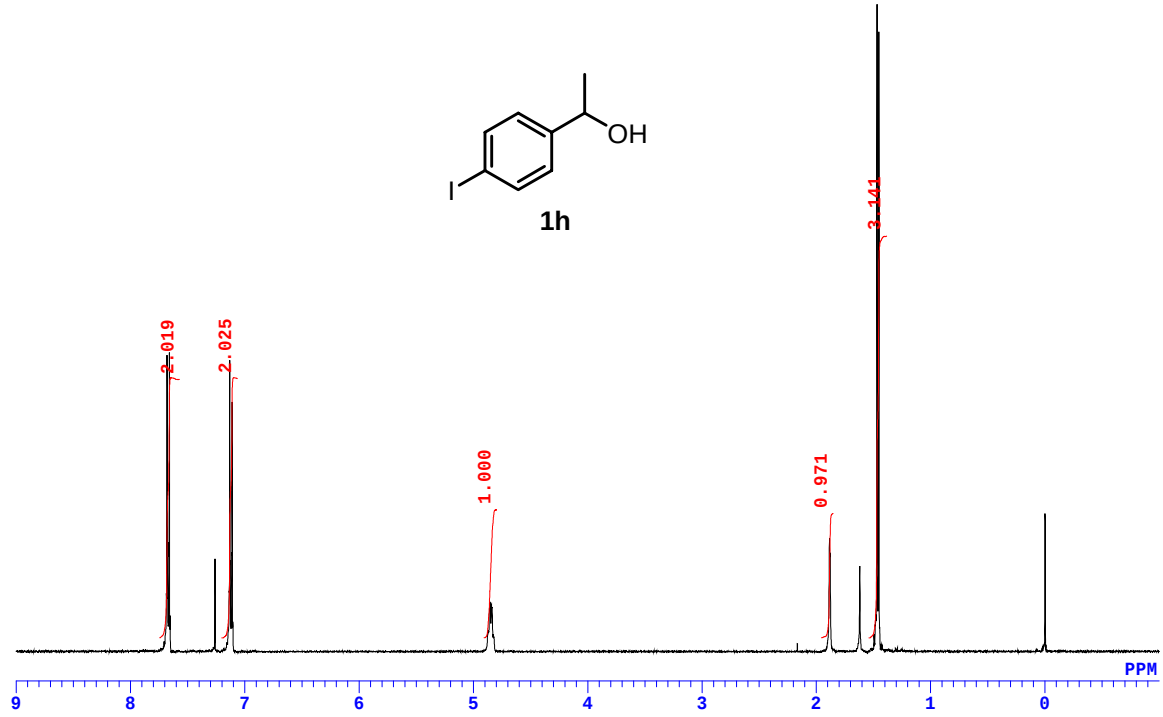
^{1}H NMR



^{13}C NMR



^{1}H NMR



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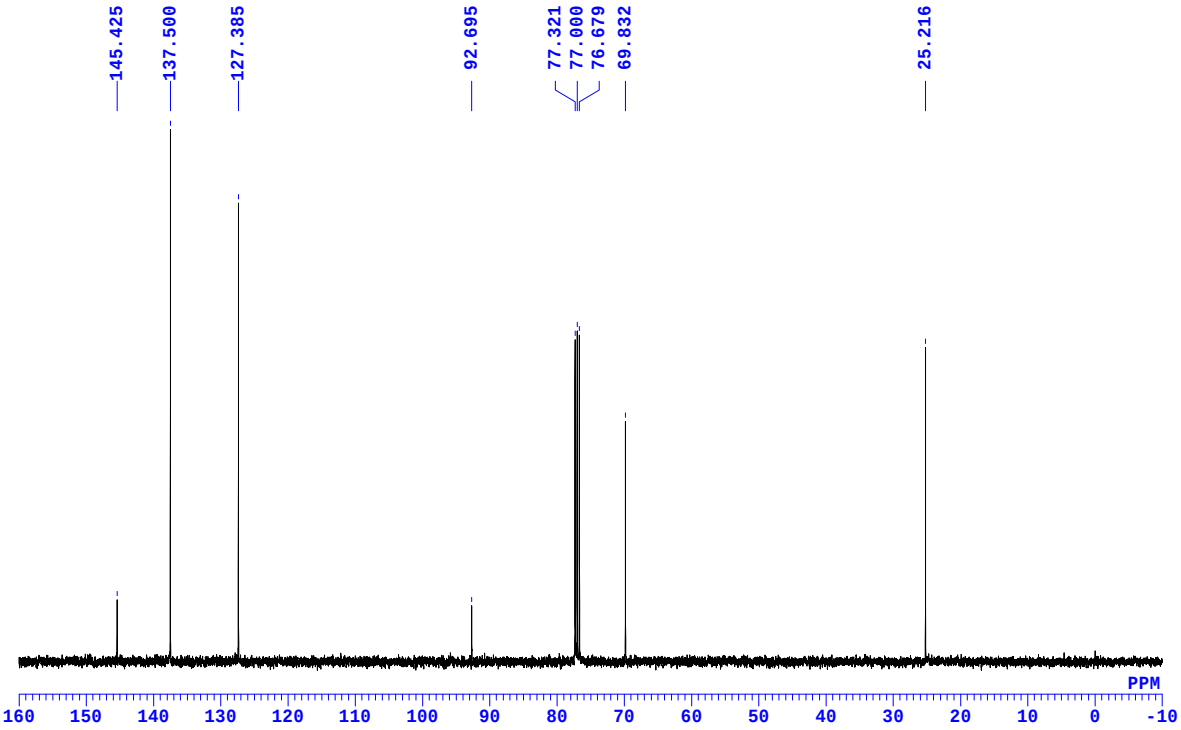

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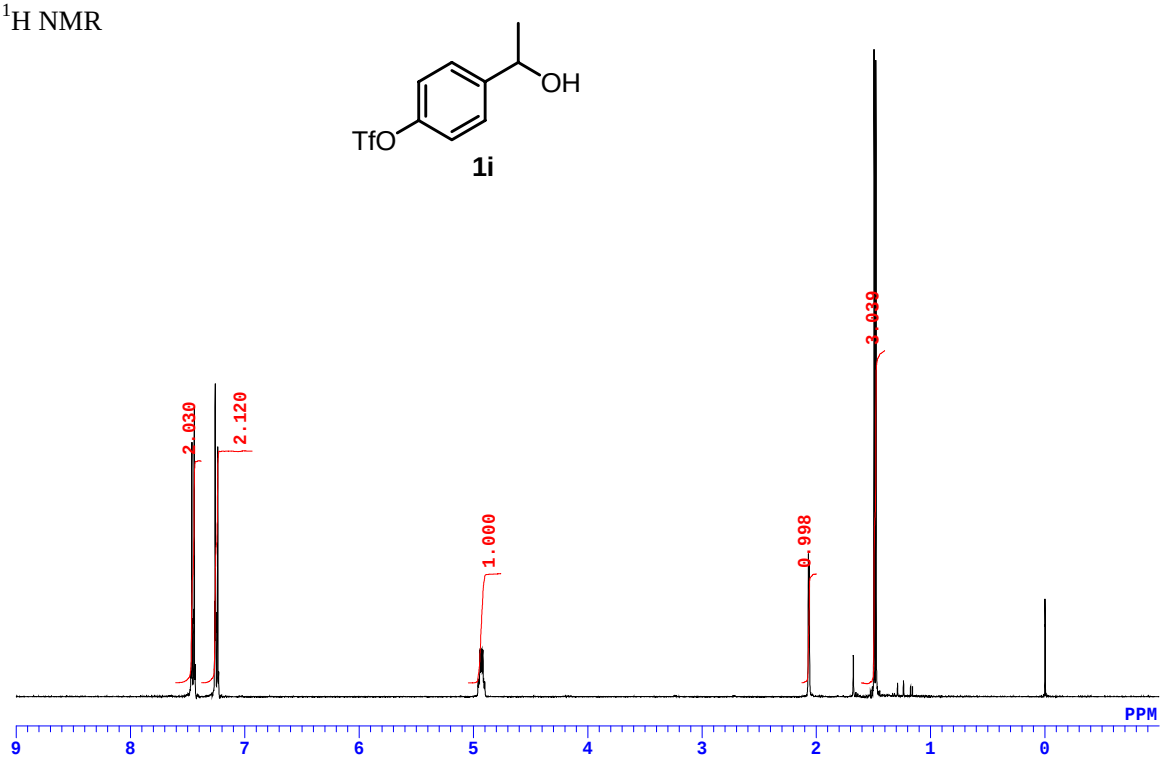

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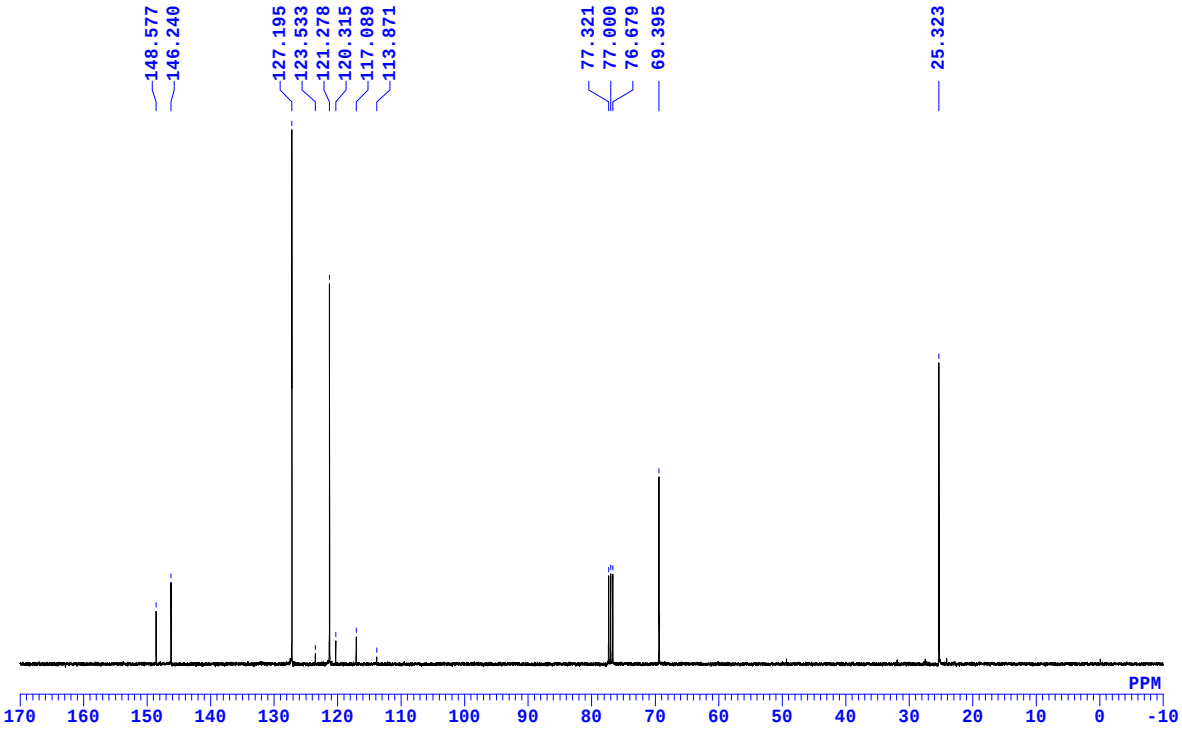

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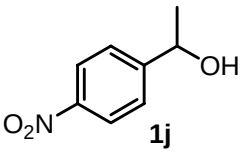
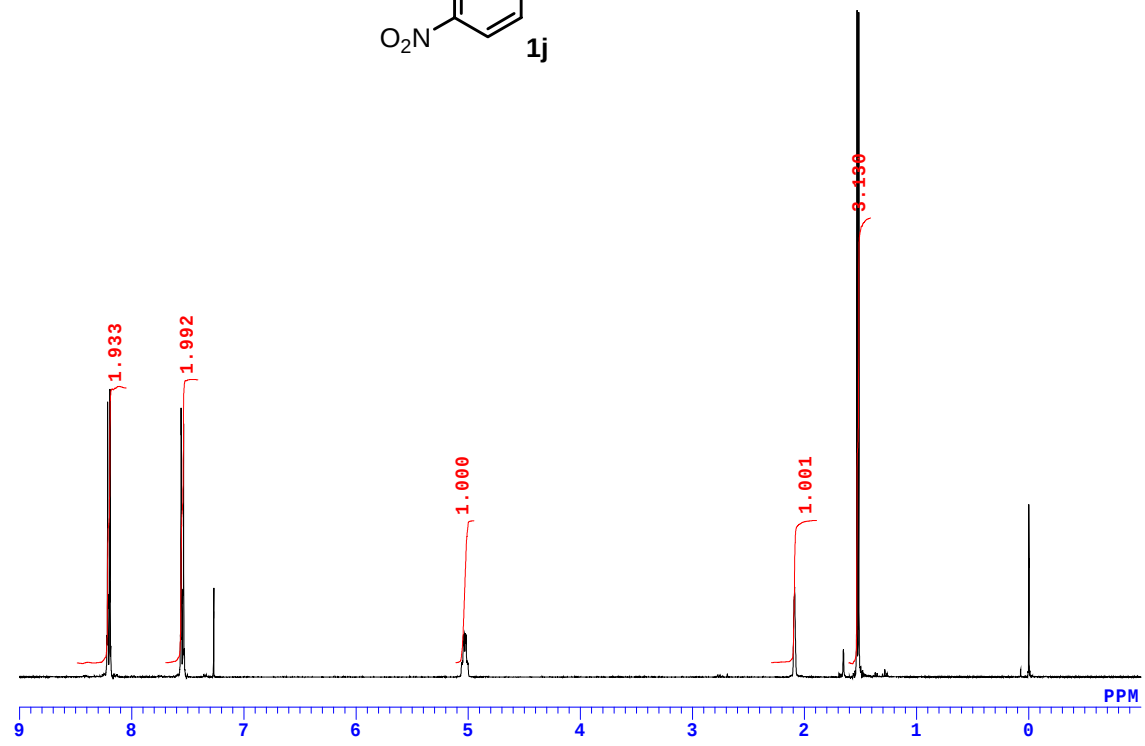
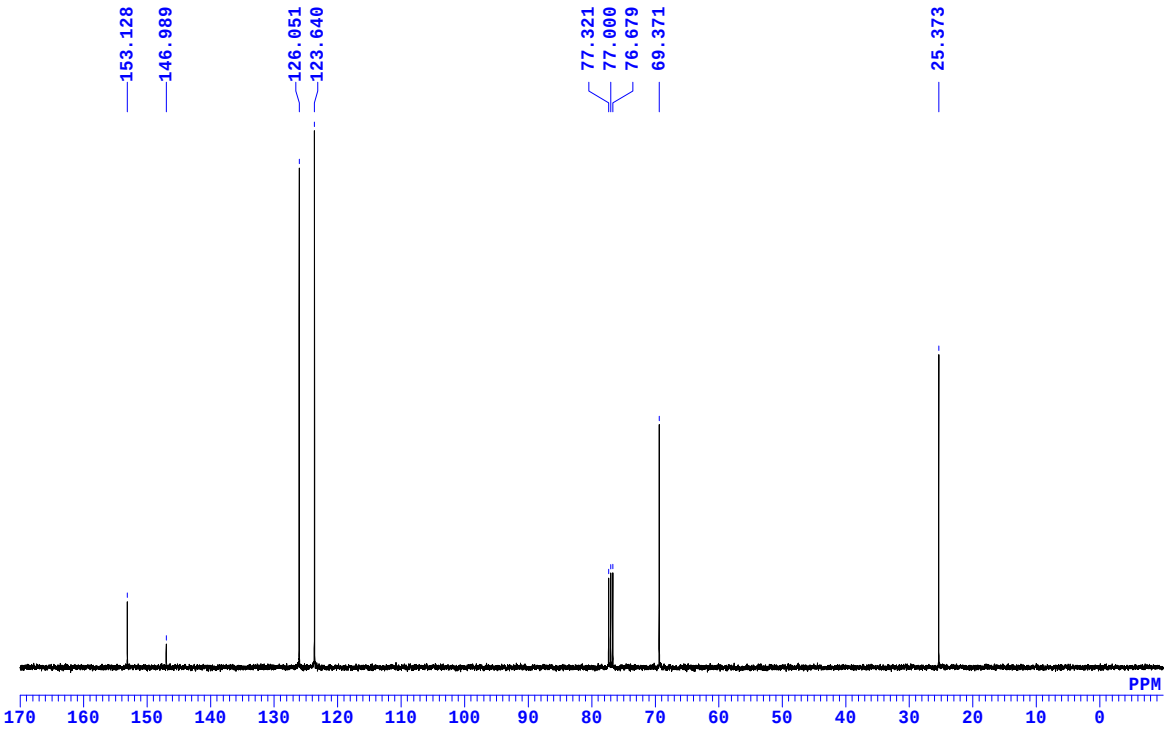


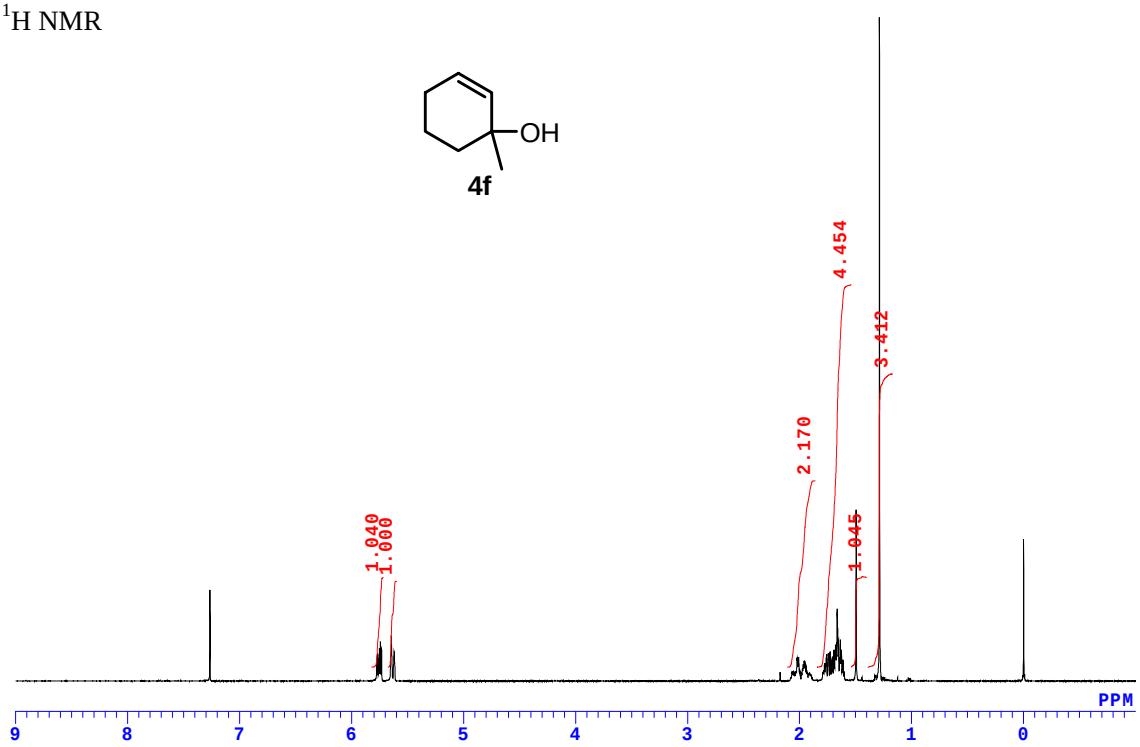
1j



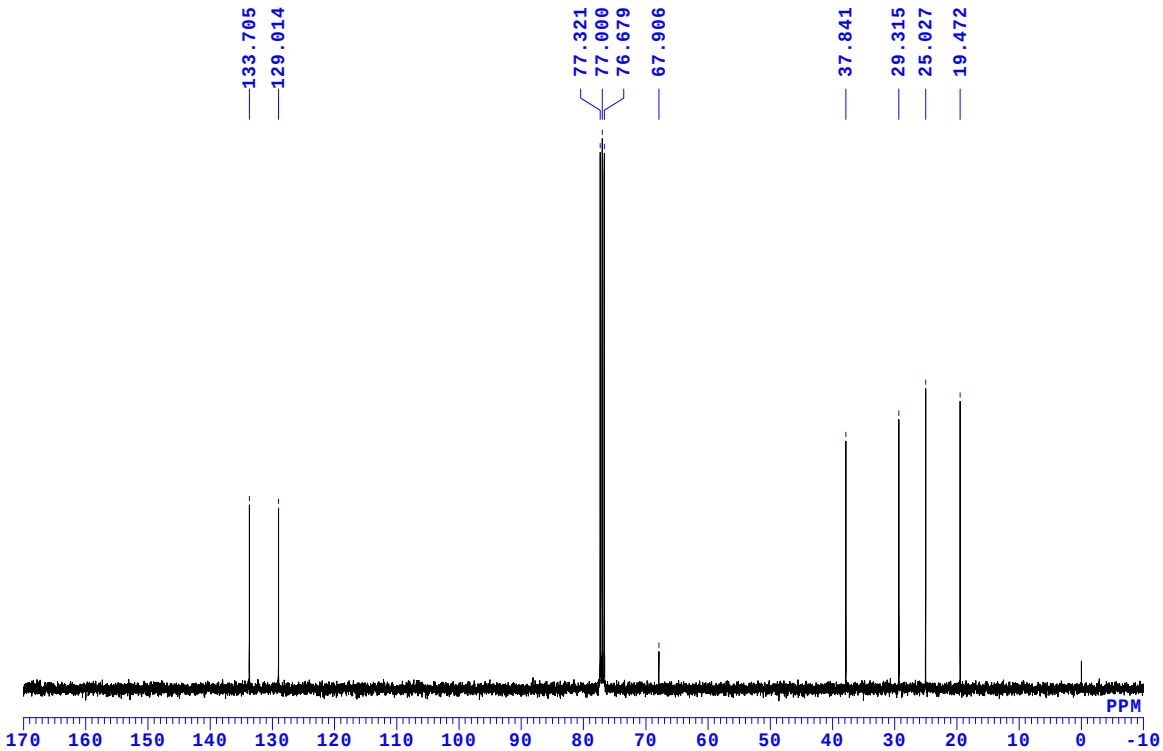
^{13}C NMR



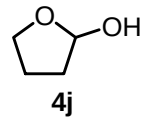
^{1}H NMR



^{13}C NMR

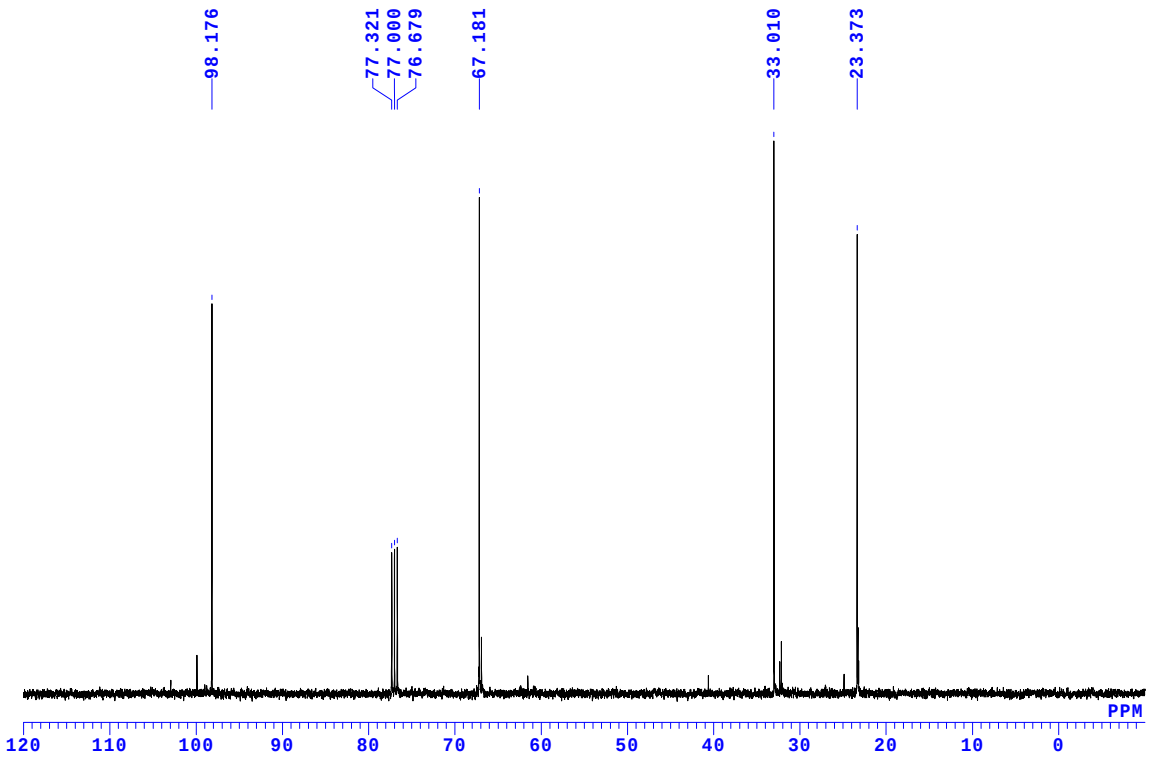


^{1}H NMR

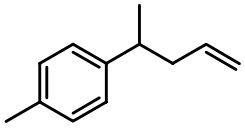


4j

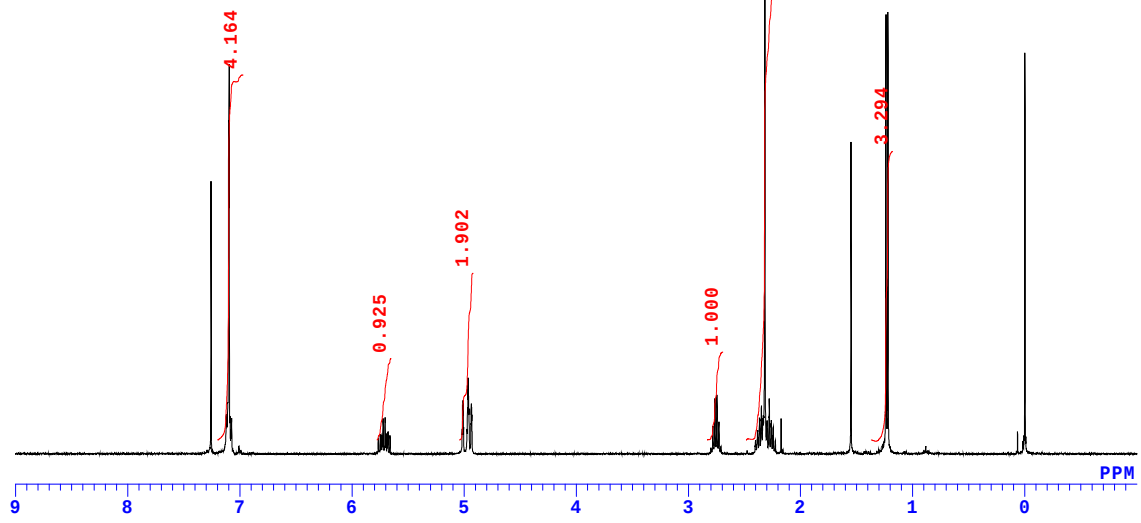
^{13}C NMR



^{1}H NMR



3b



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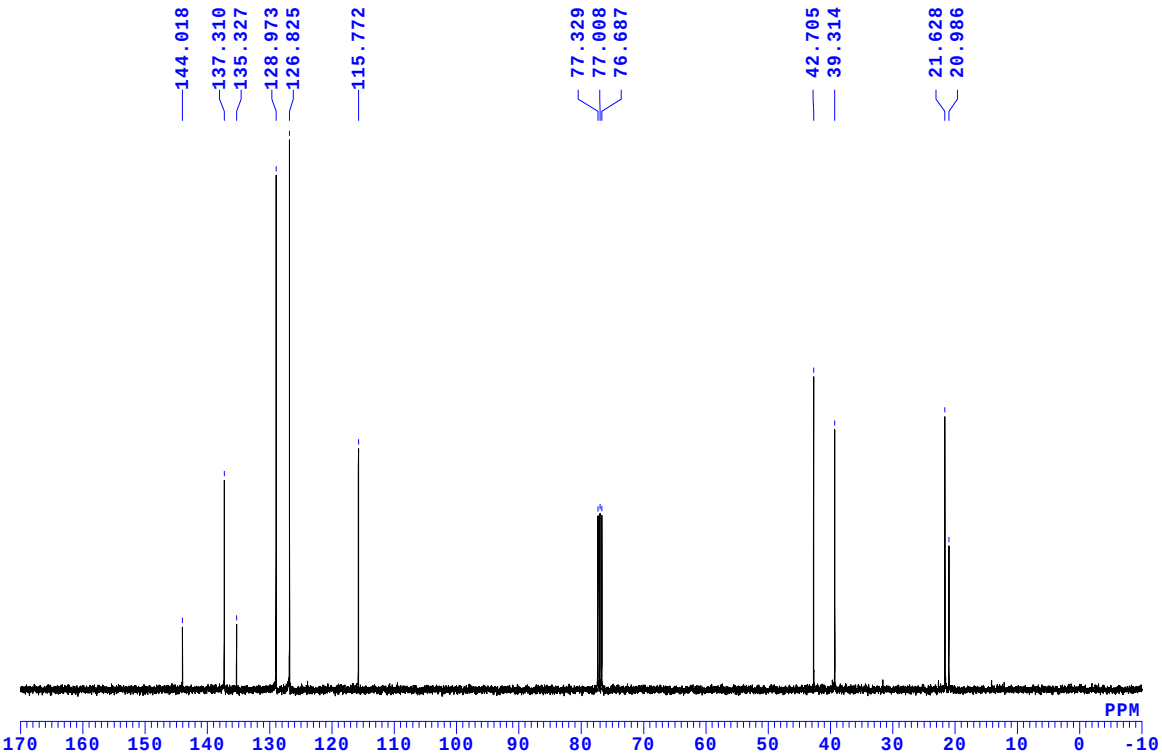

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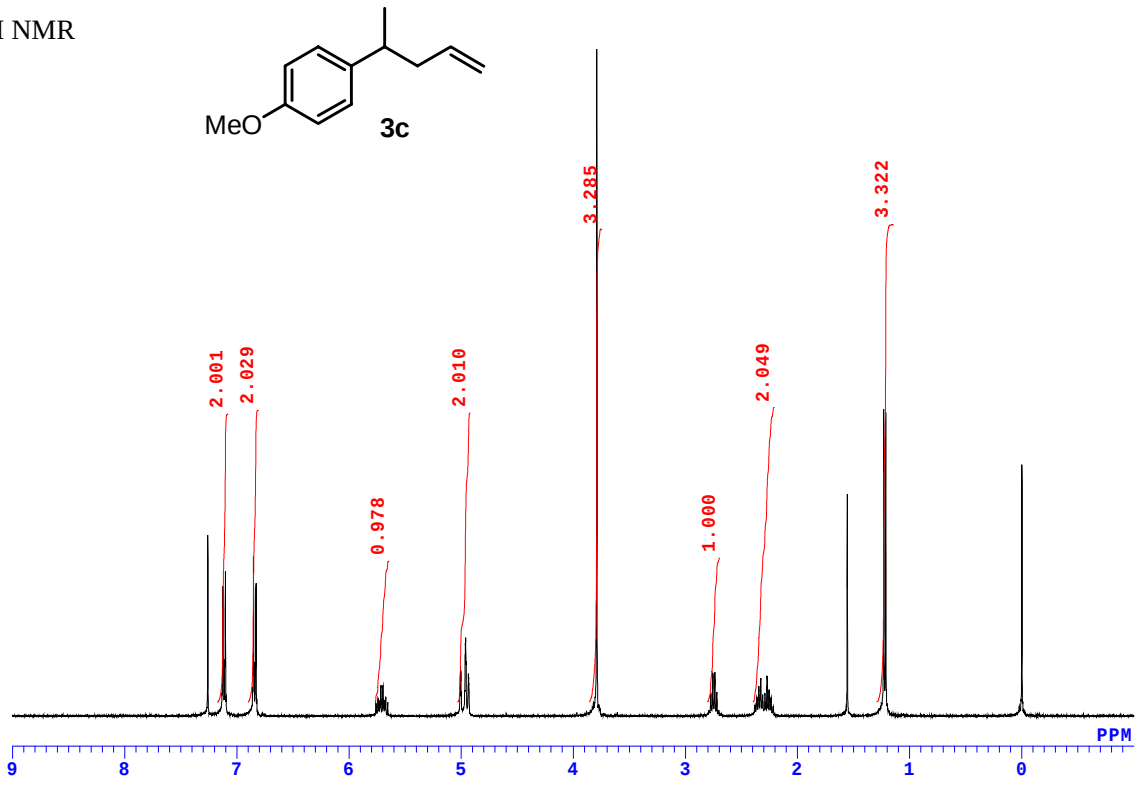

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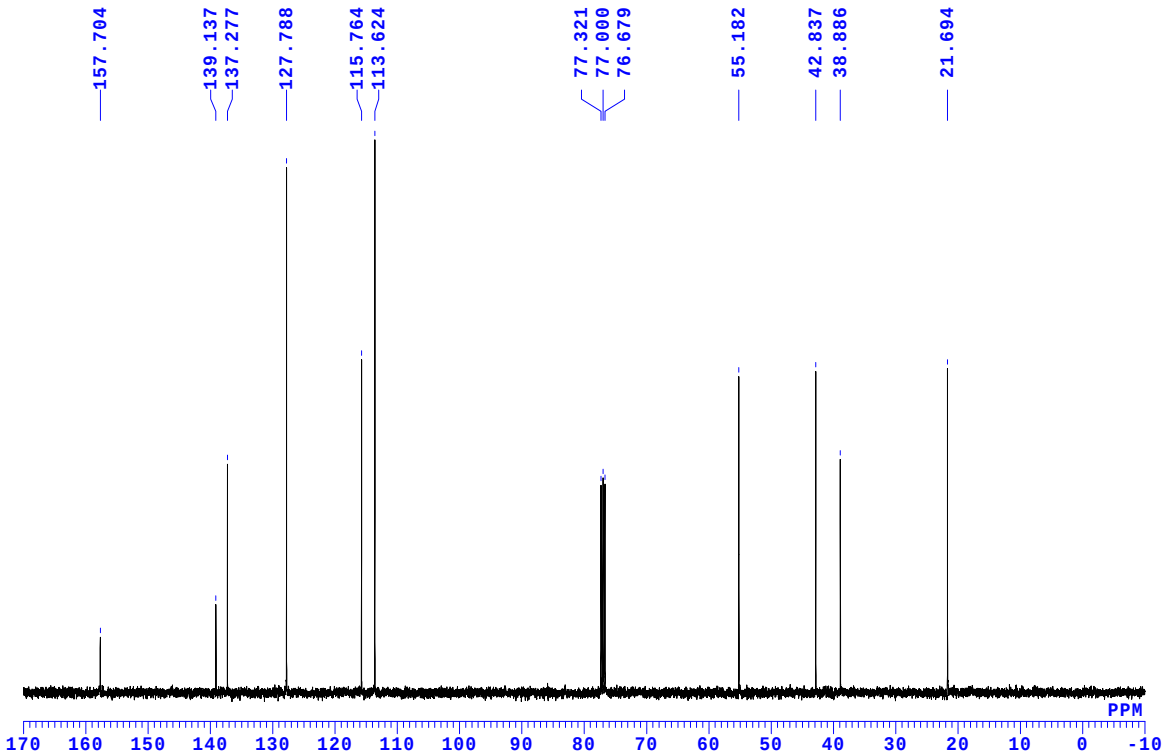

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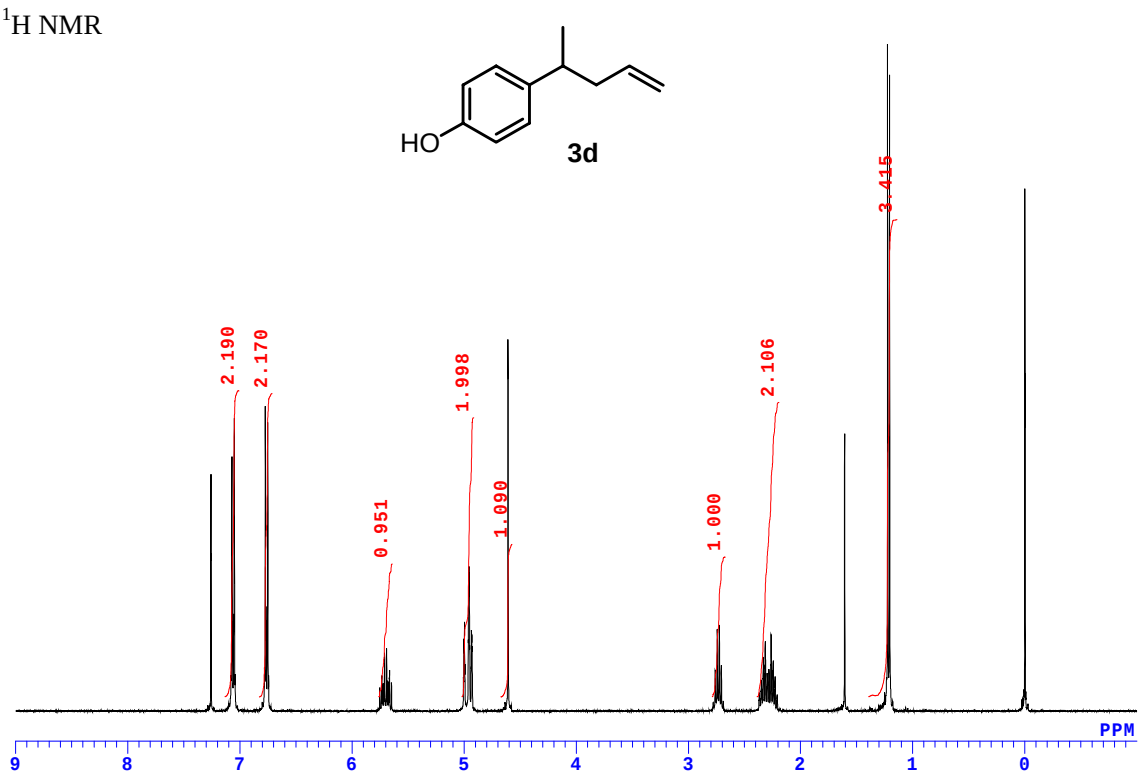

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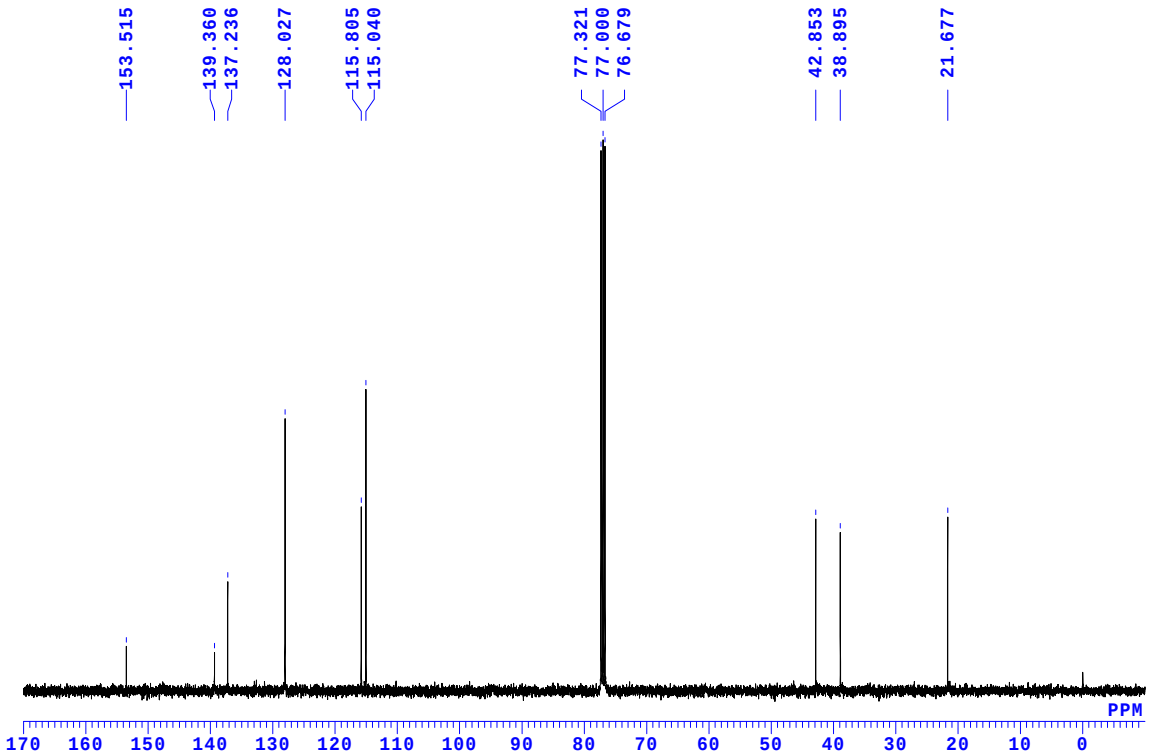

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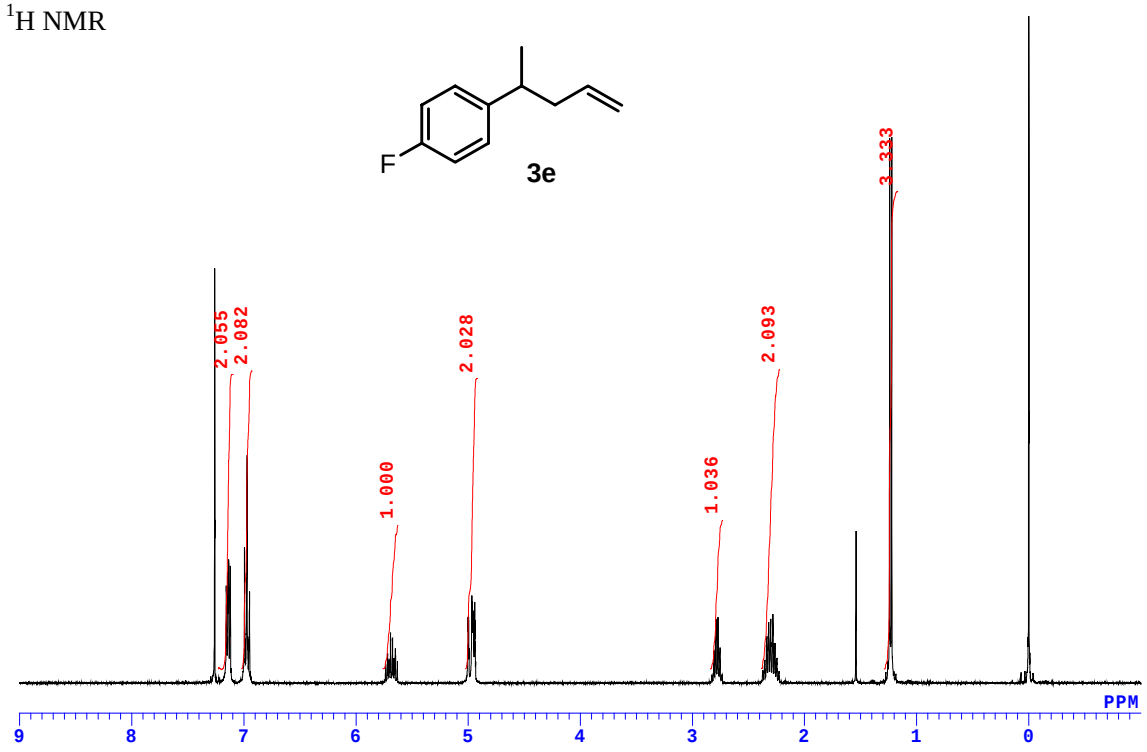

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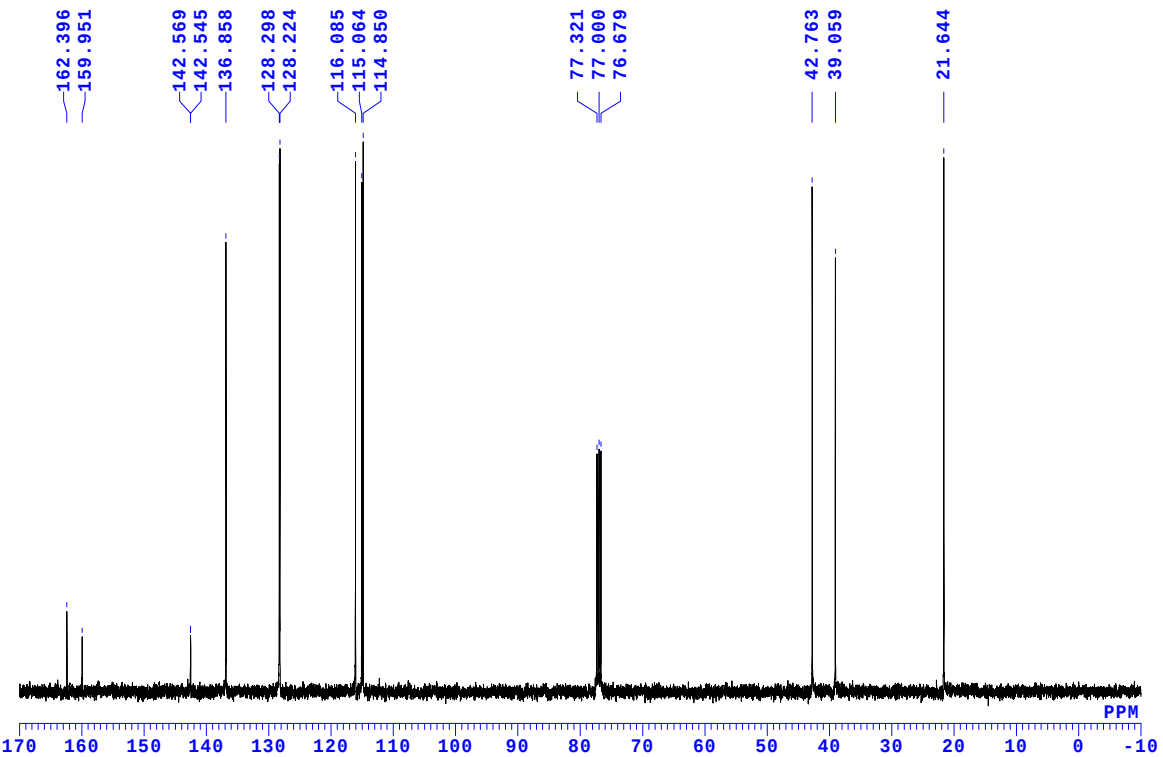

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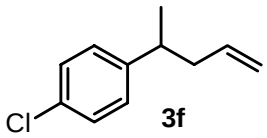

3f

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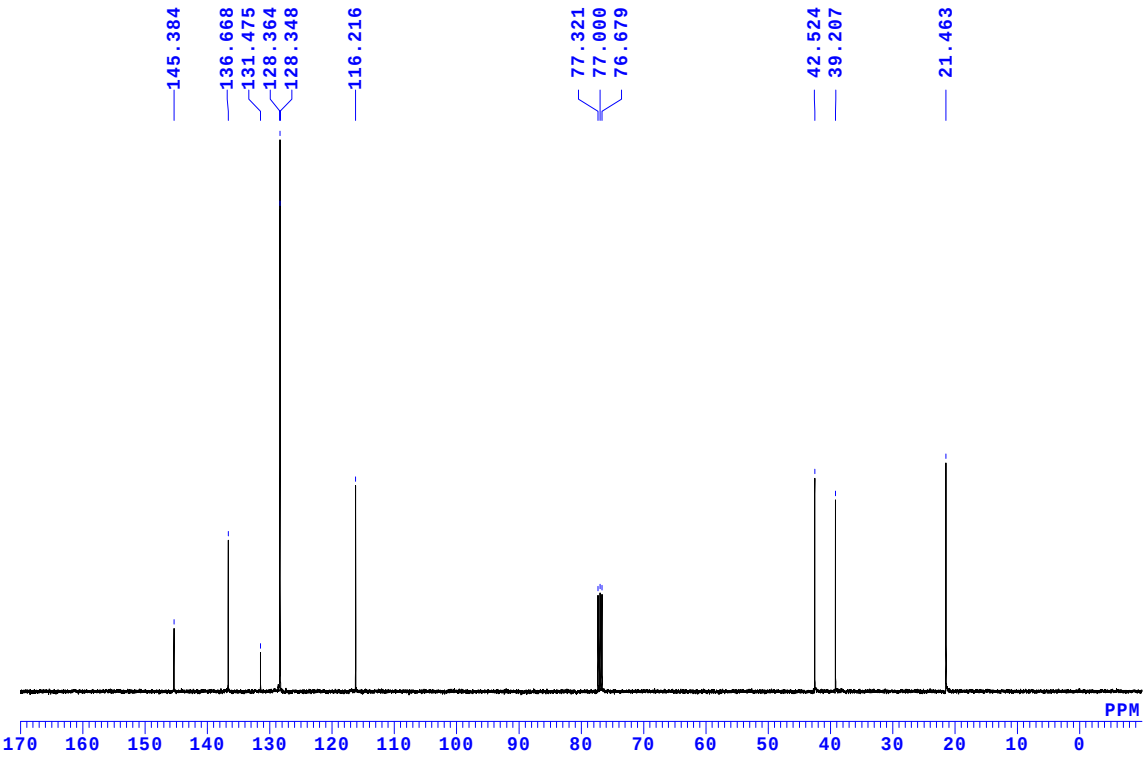

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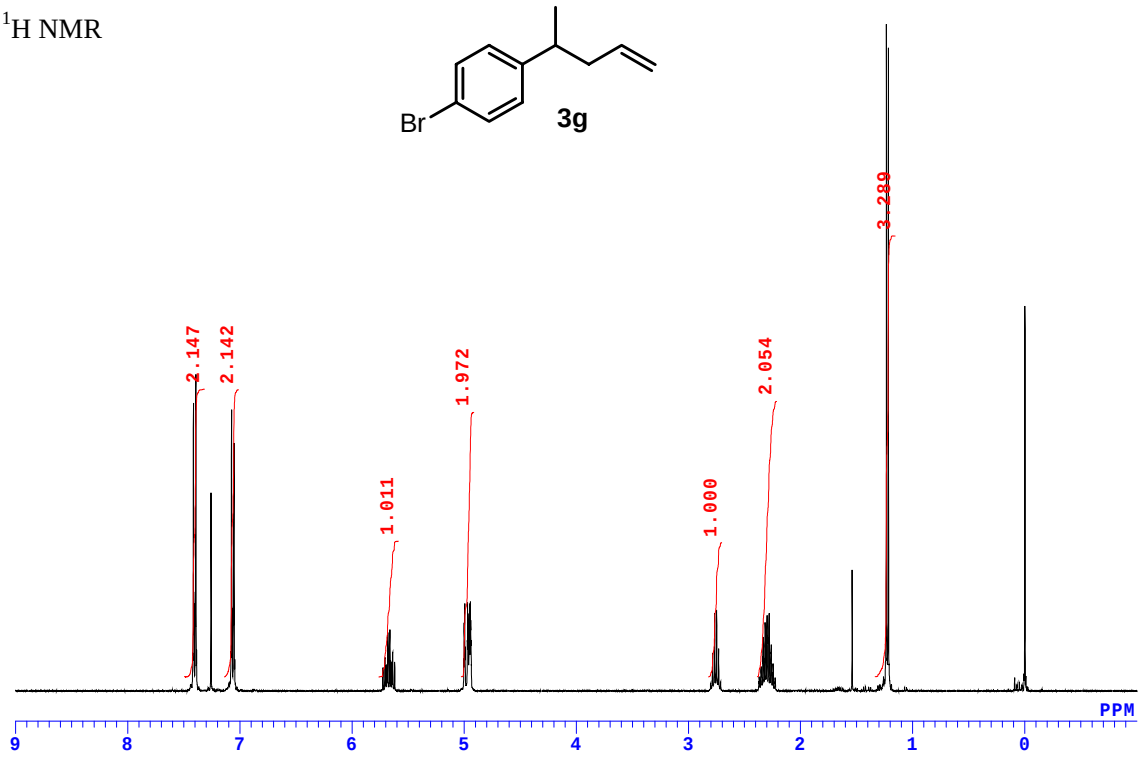

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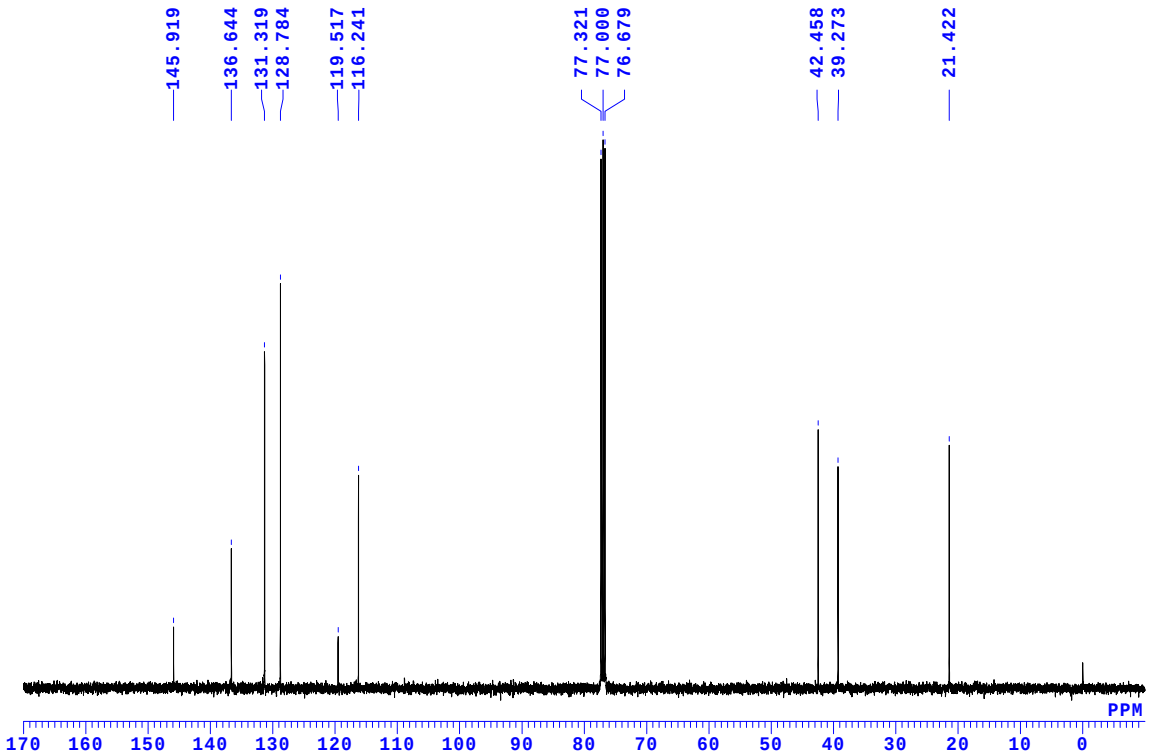

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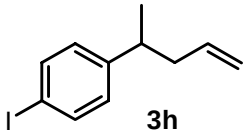

3h

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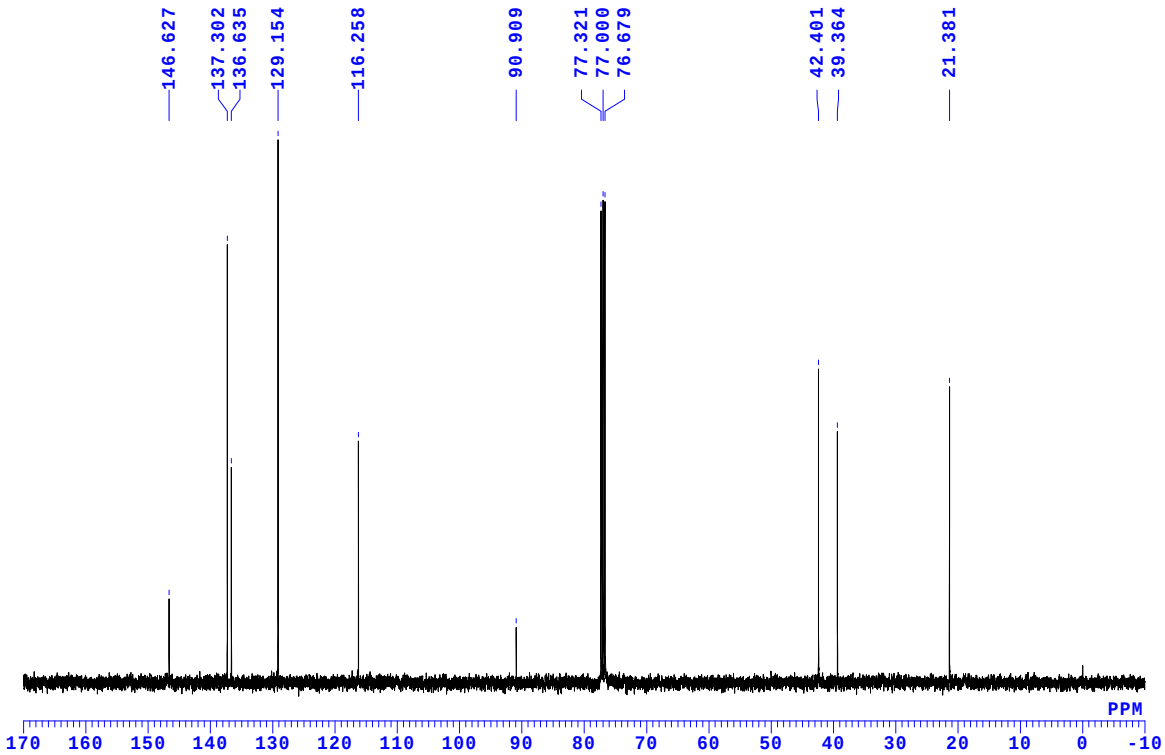

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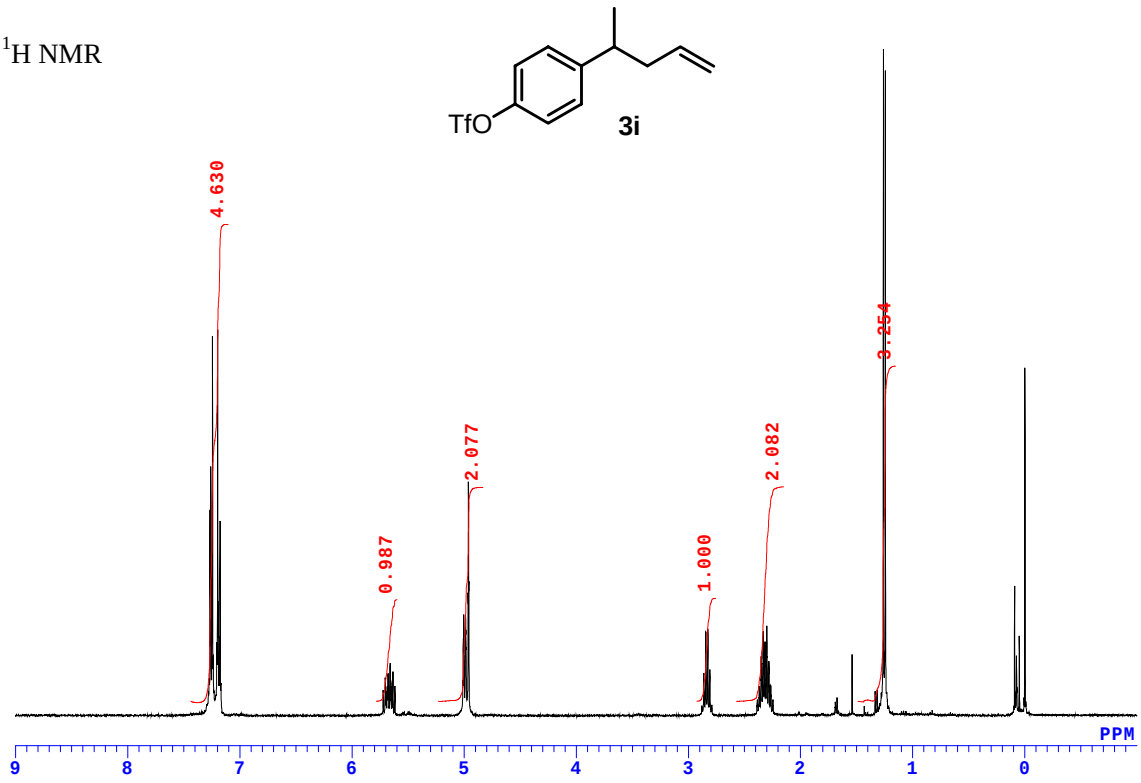

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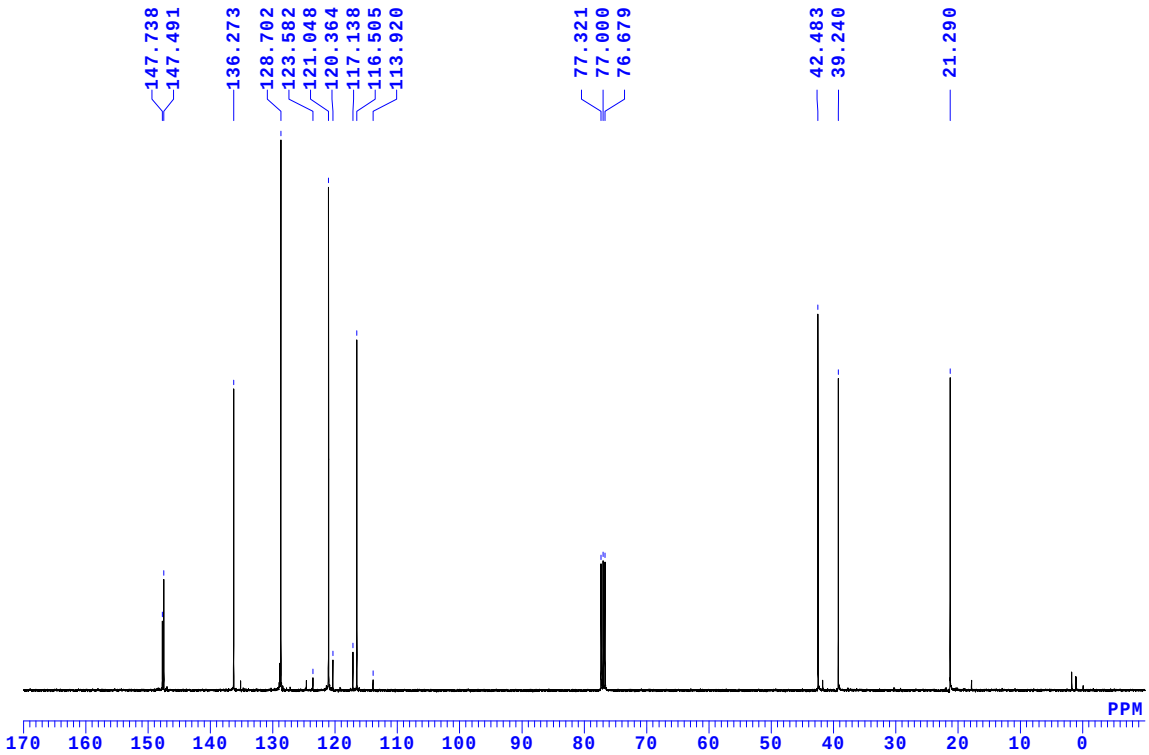

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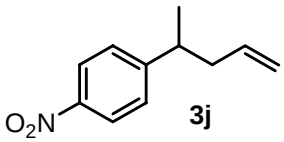

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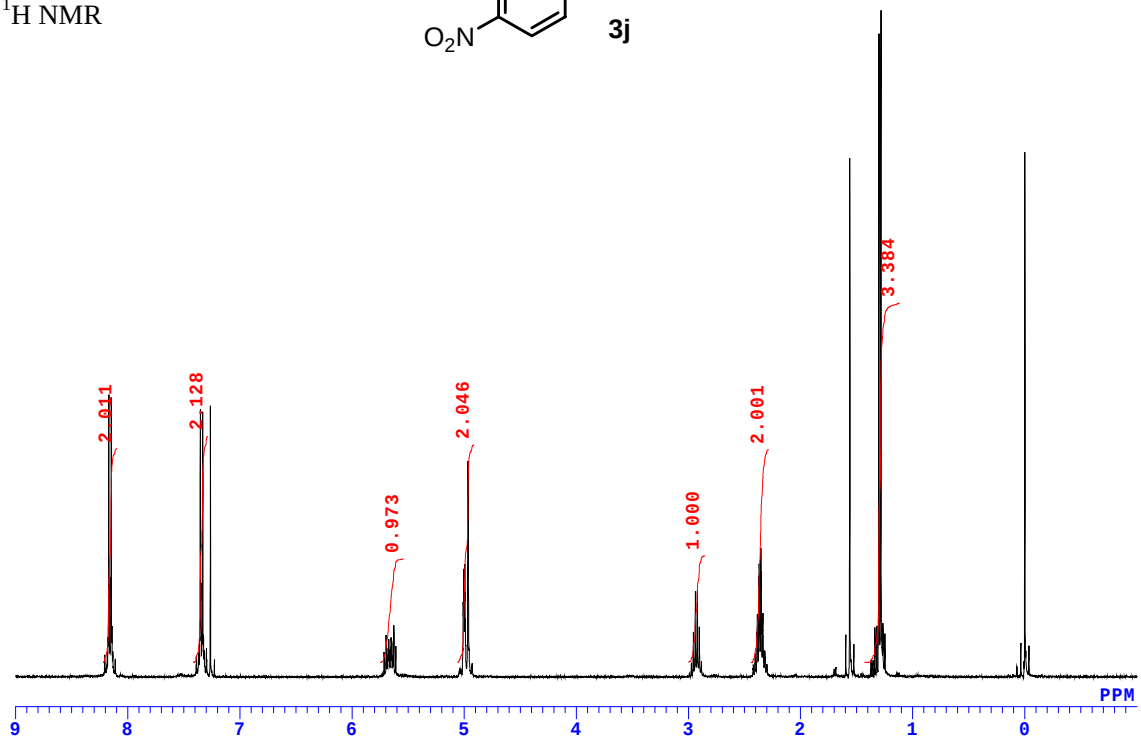

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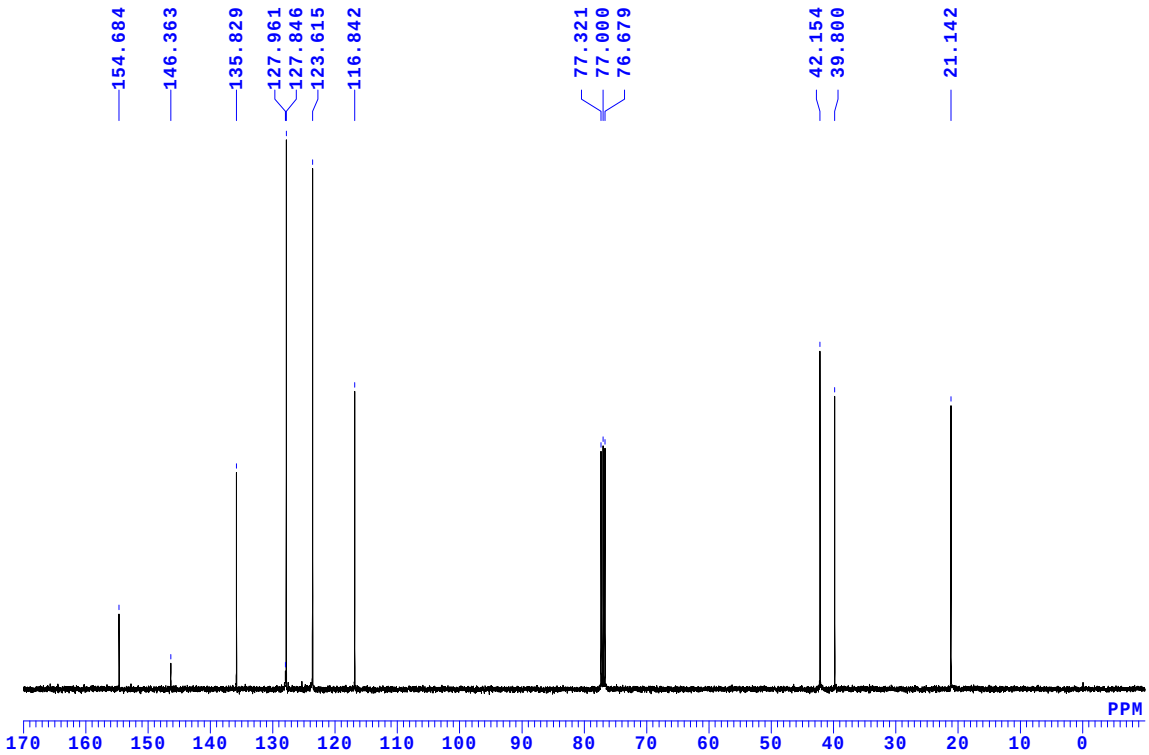

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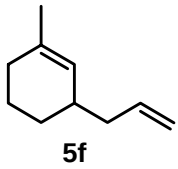

5f

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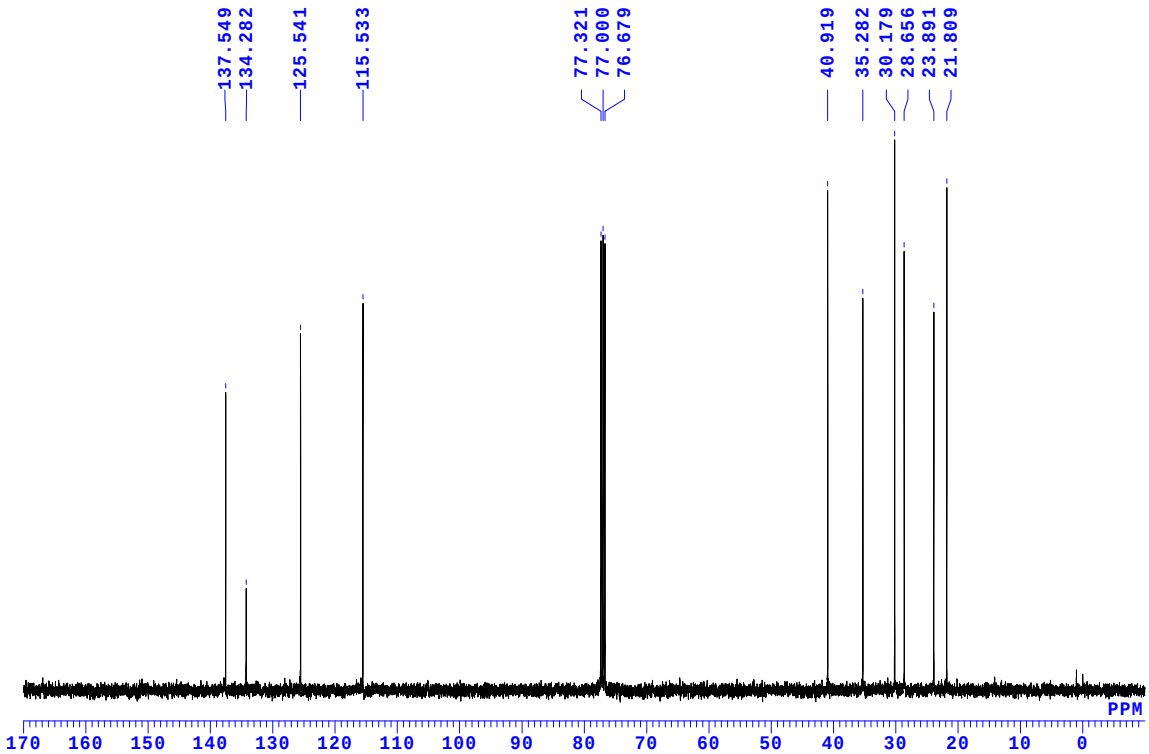

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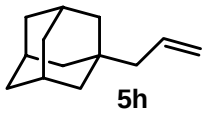

5h

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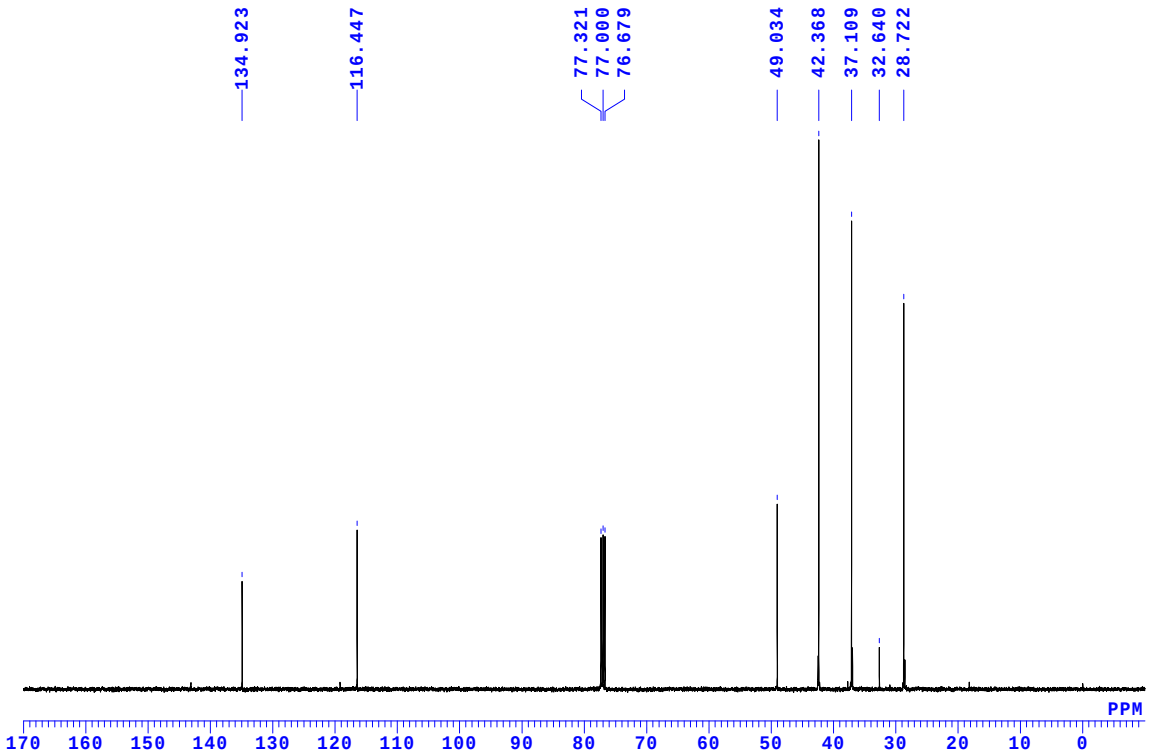

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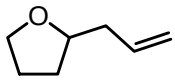

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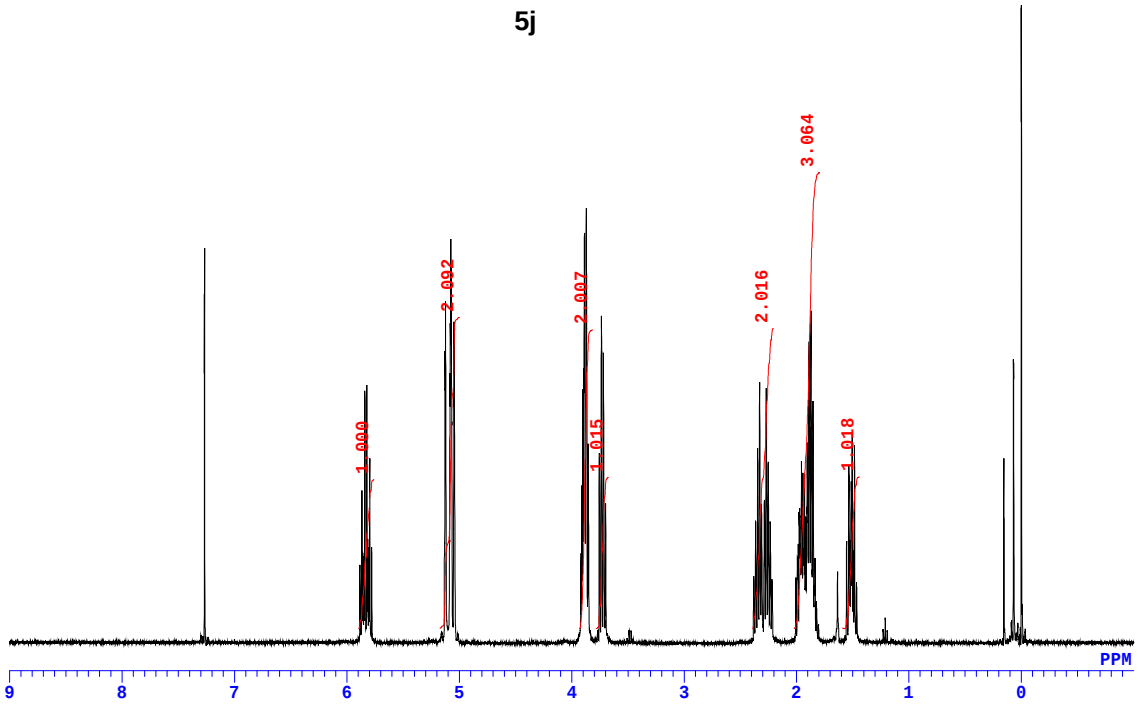

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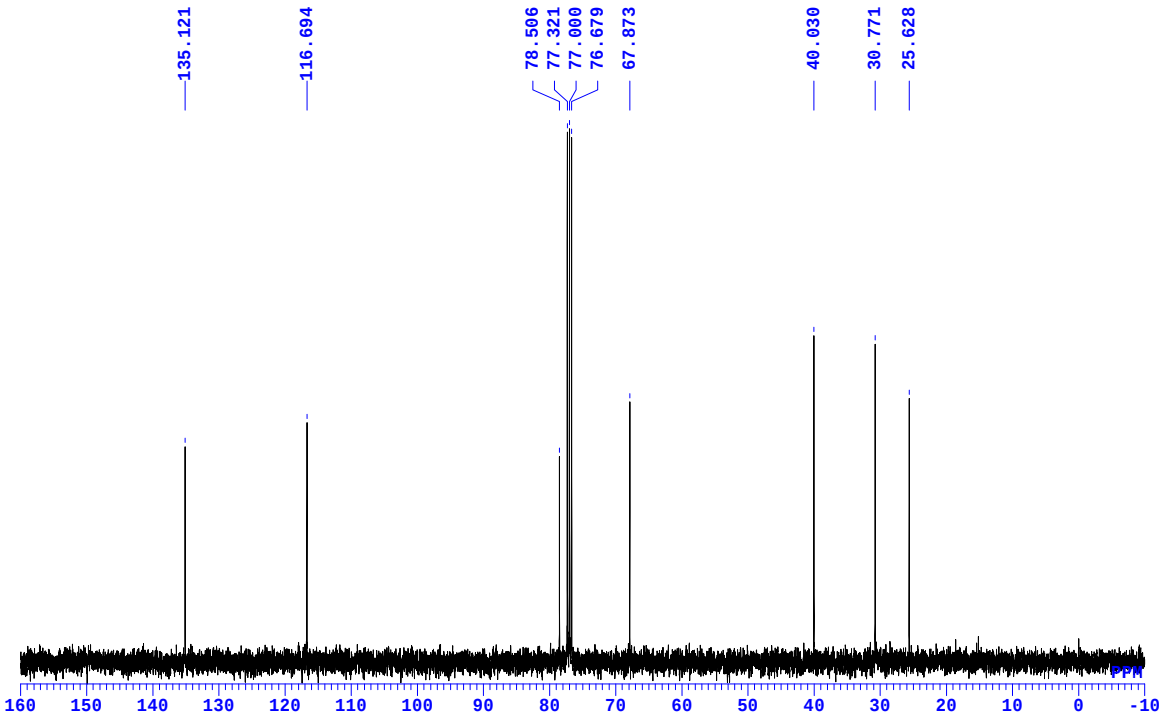

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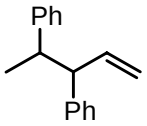
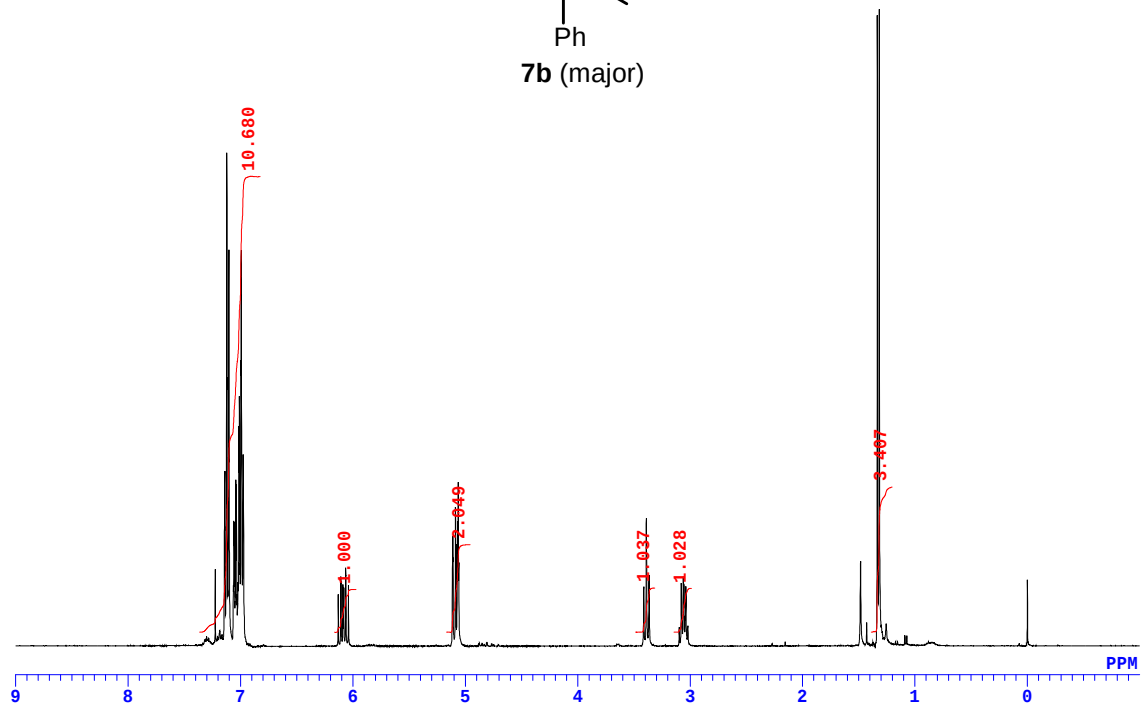


7b (major)



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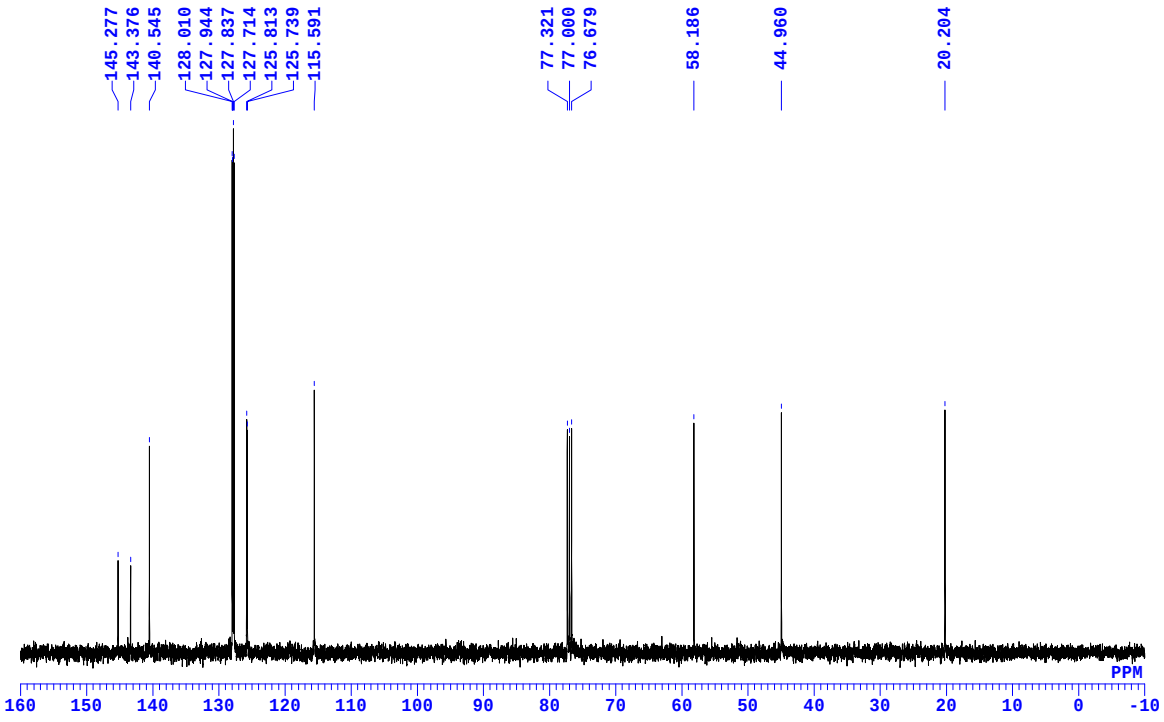

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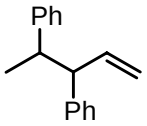
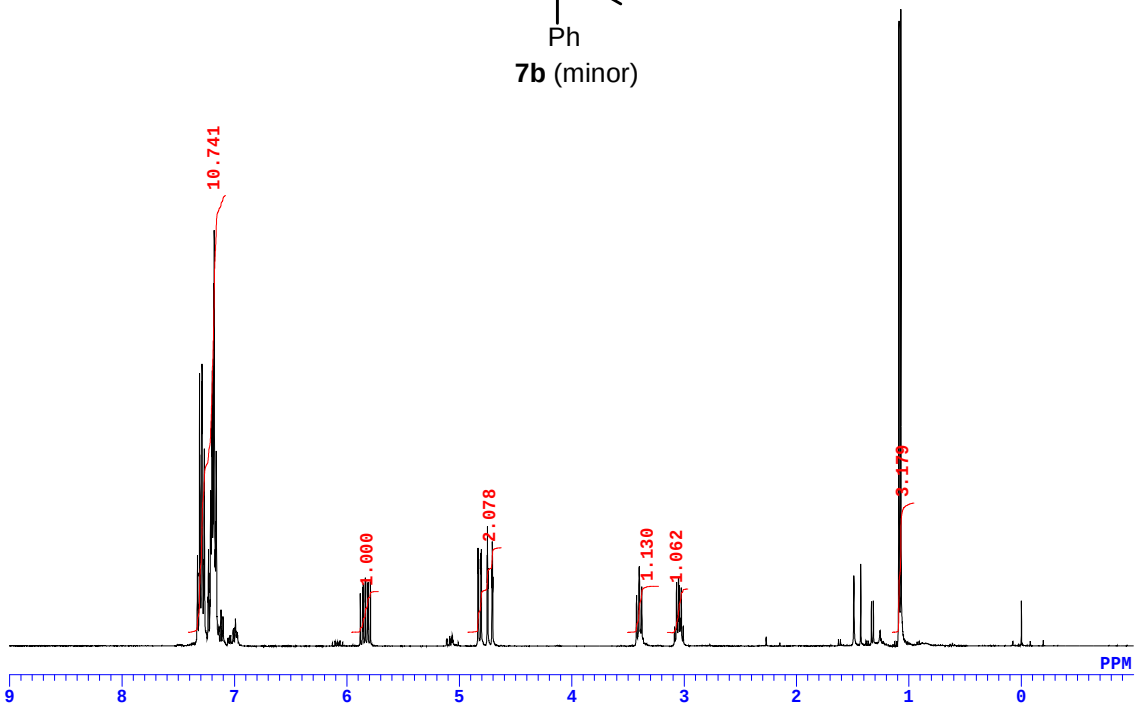


7b (minor)



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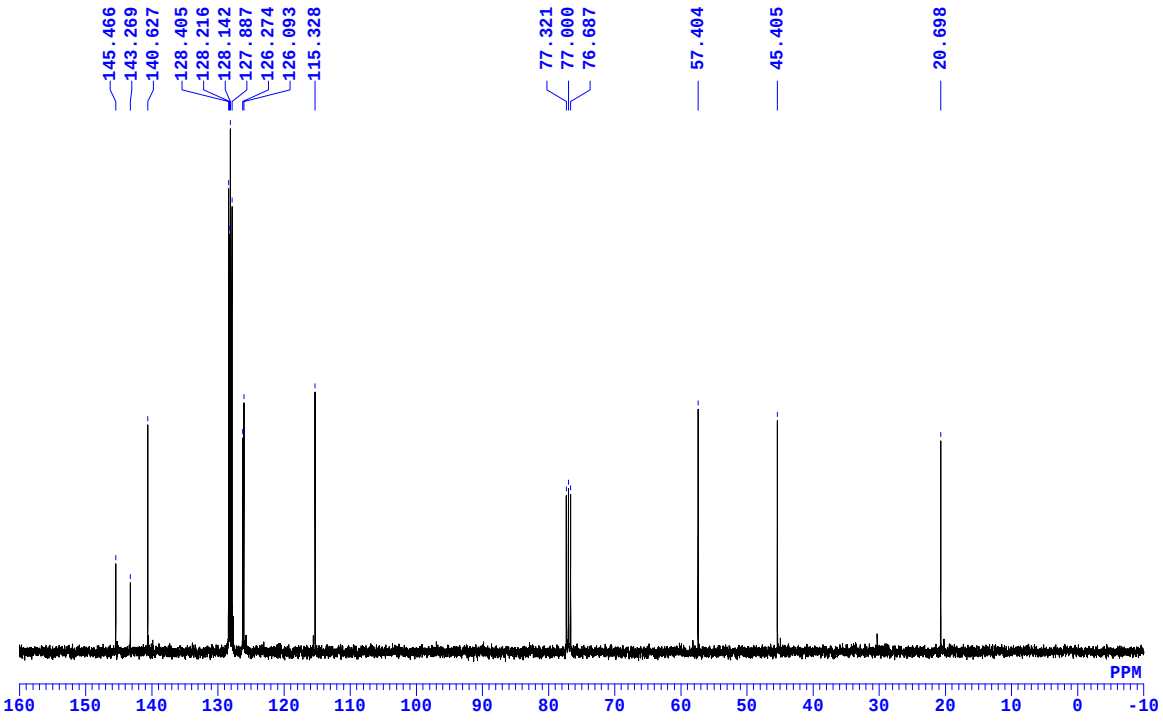

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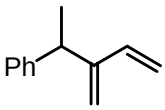

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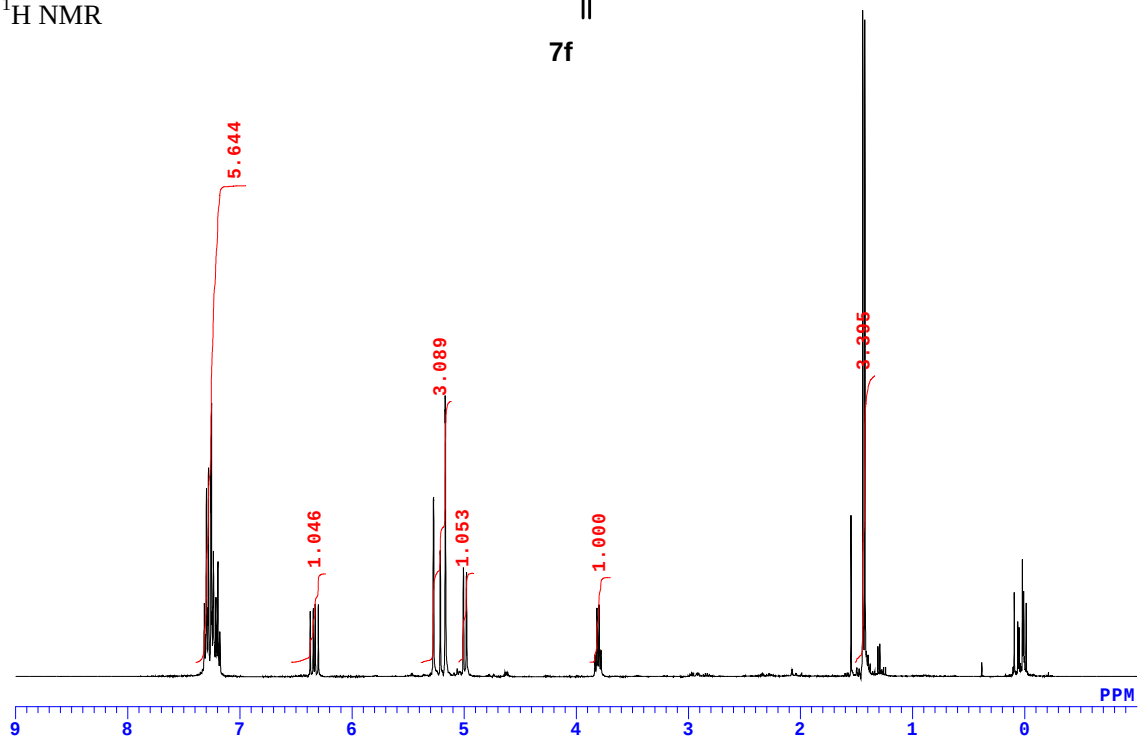

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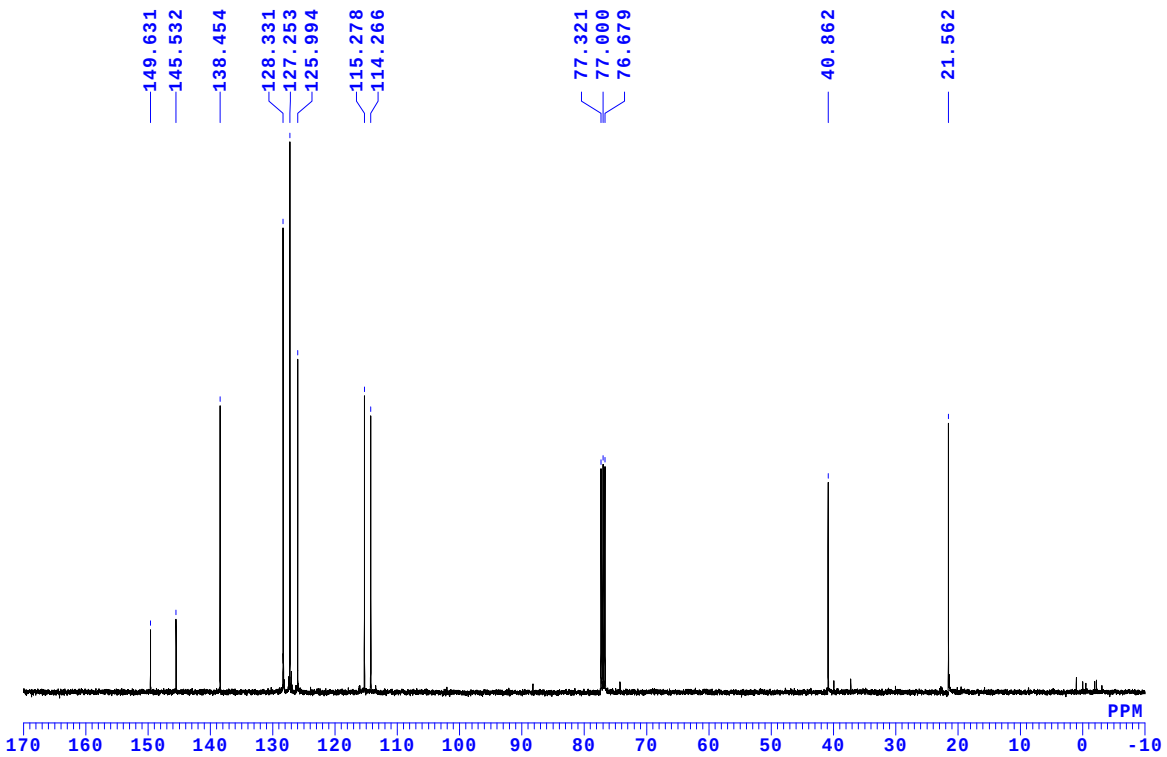

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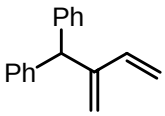

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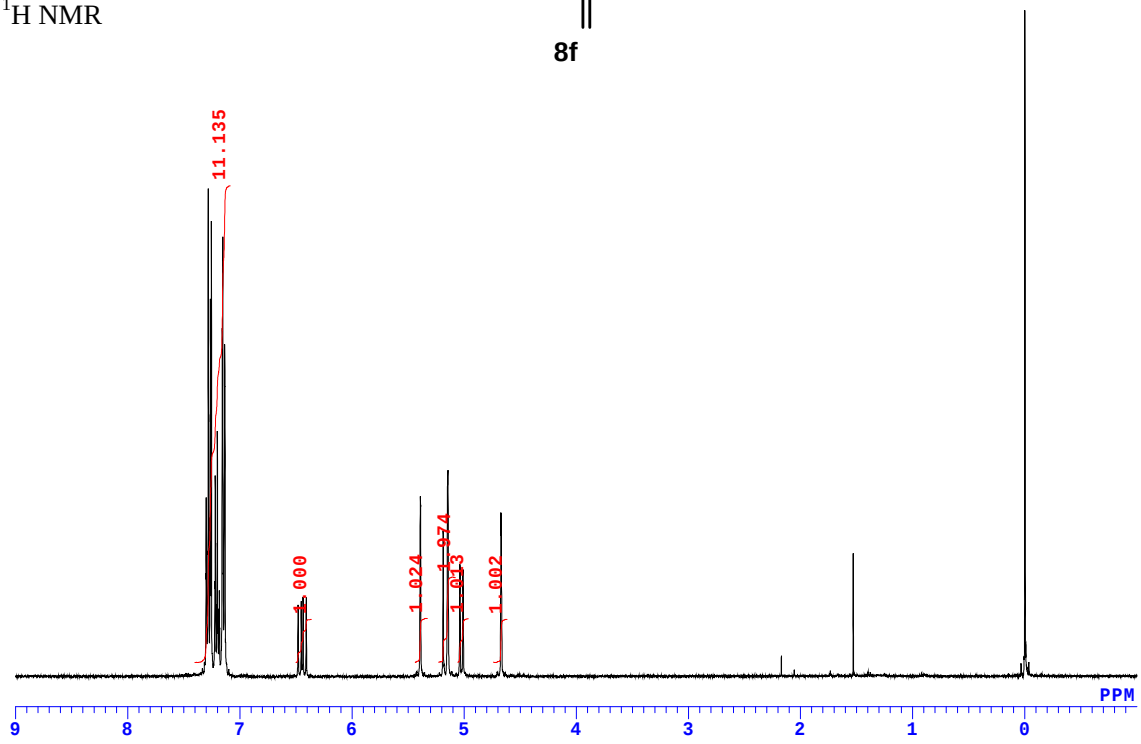

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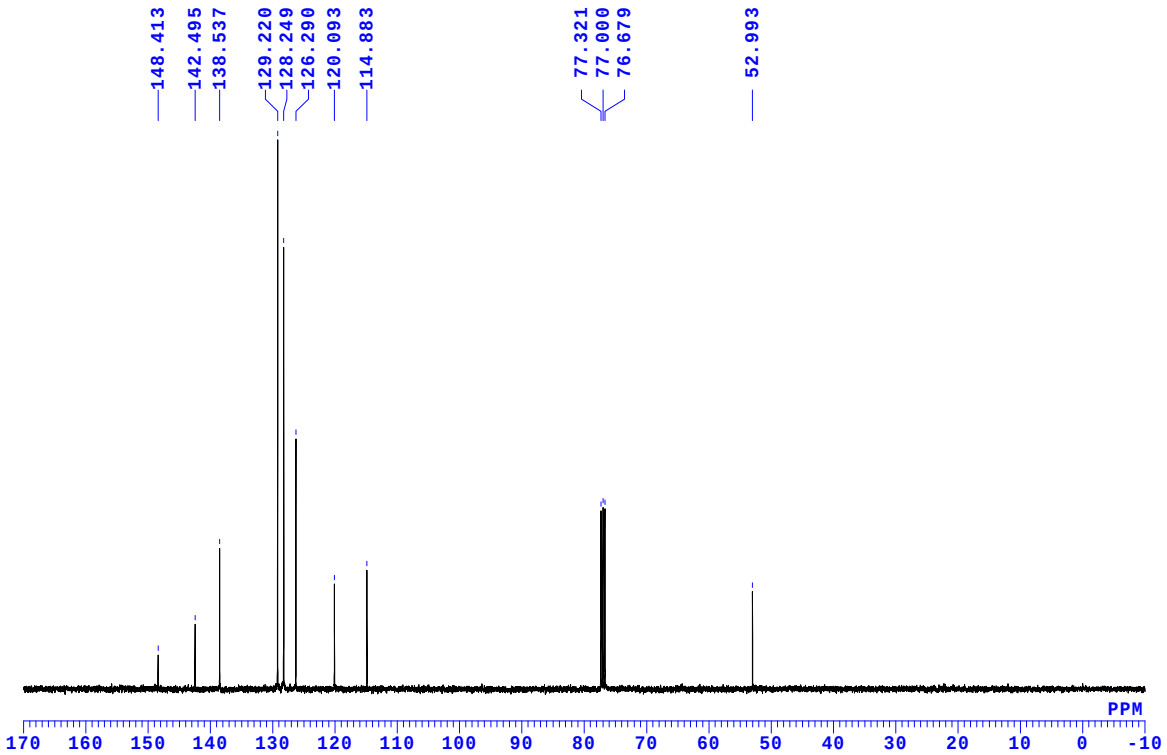

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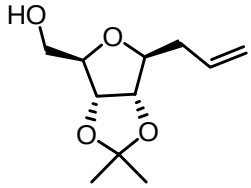
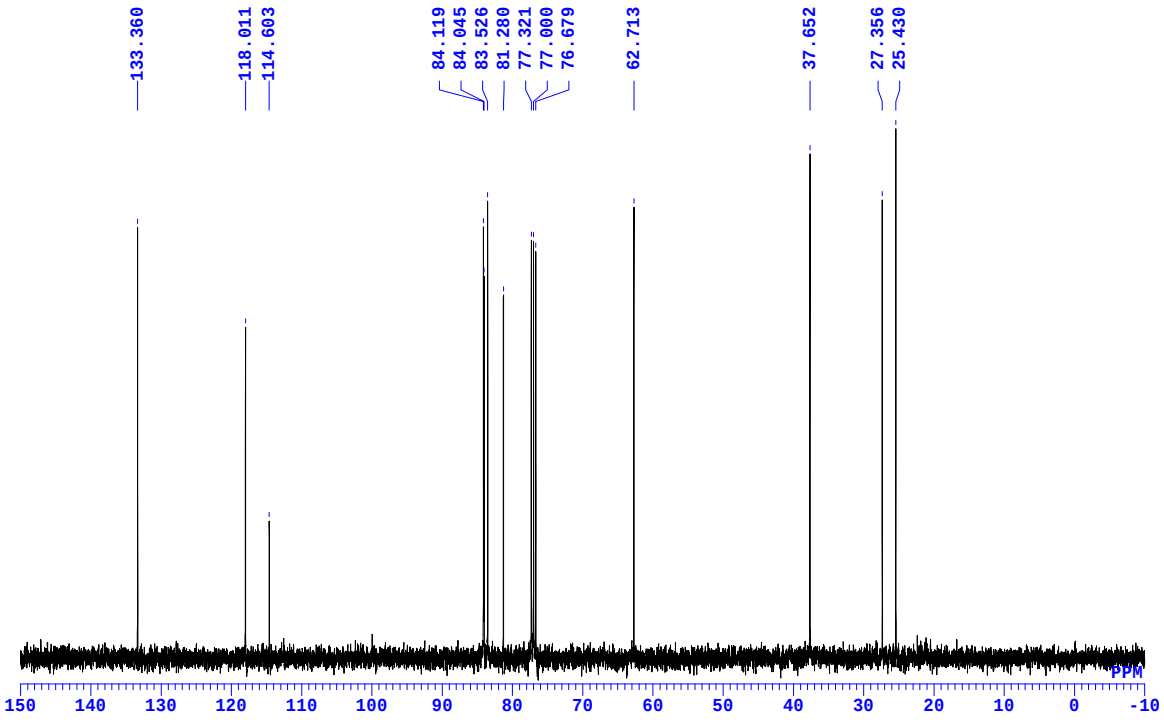
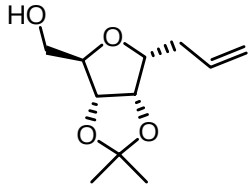


10 (major)

^{13}C NMR

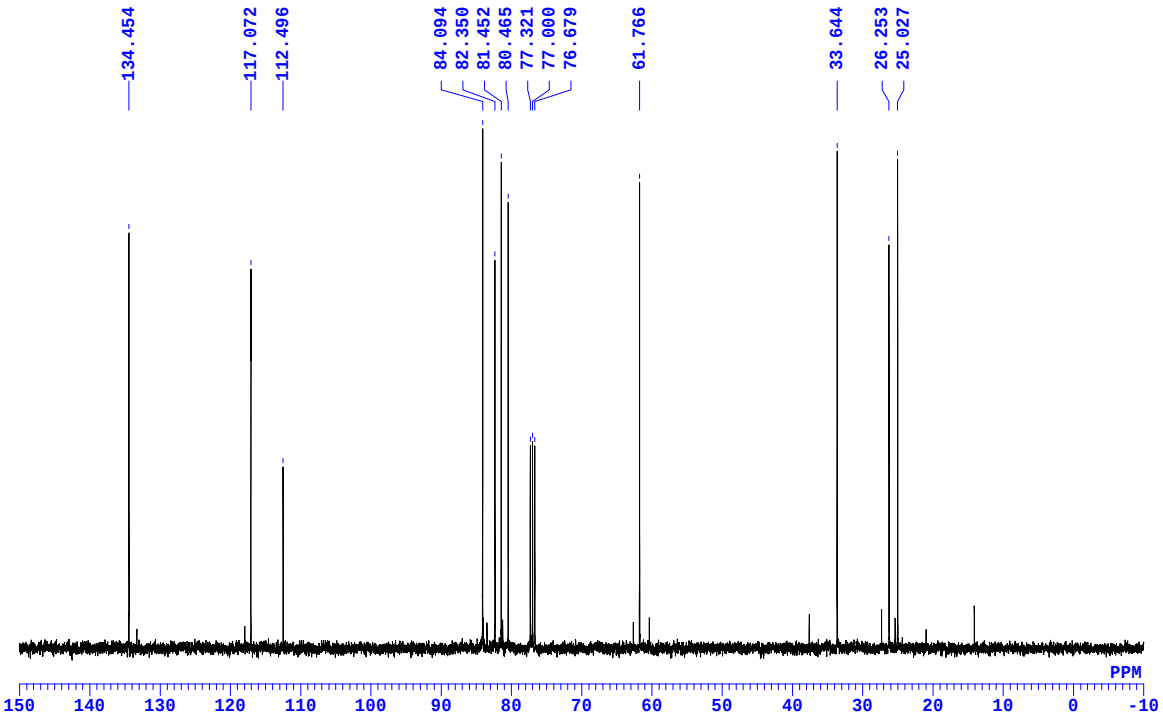


^{1}H NMR

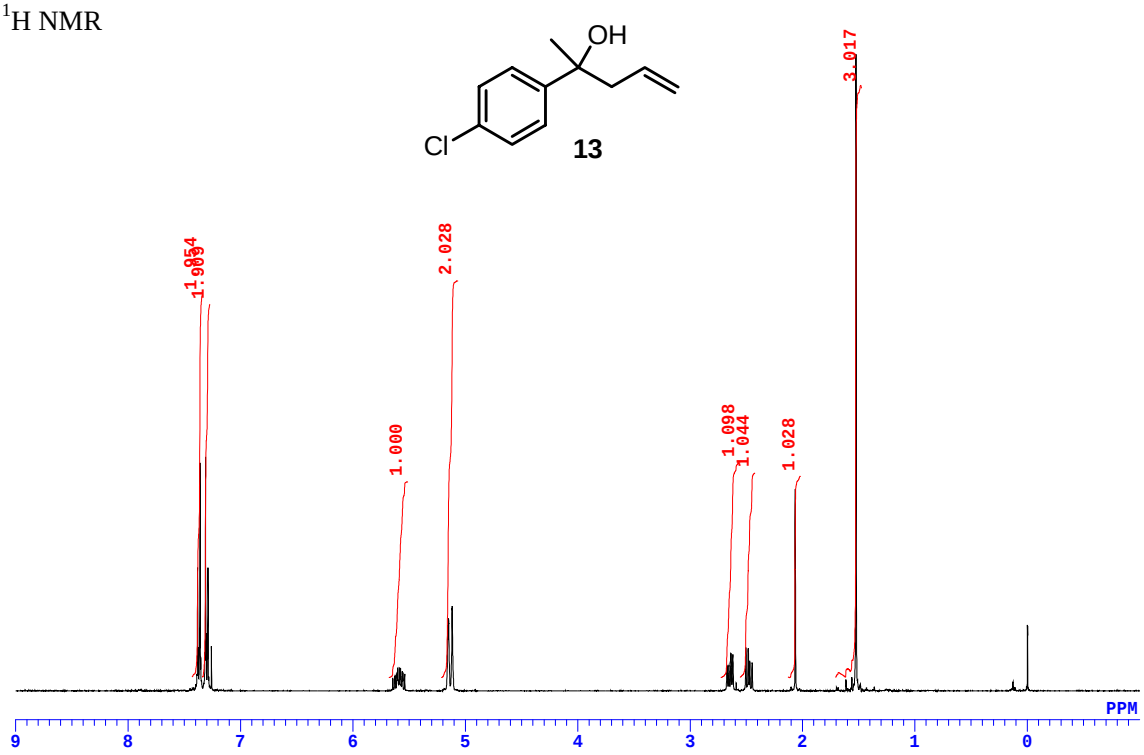


10 (minor)

^{13}C NMR



^{1}H NMR



^{13}C NMR