

## **Supporting Information**

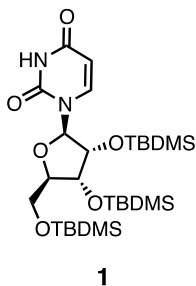
### **A GREENER TECHNIQUE FOR MICROWAVE-ASSISTED O-SILYLATION AND SILYL ETHER DEPROTECTION OF URIDINE AND OTHER SUBSTRATES**

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## 1.0 $^1\text{H}$ and $^{13}\text{C}$ NMR spectral data

### 1-((2*R*,3*R*, 4*R*,5*R*)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (1)

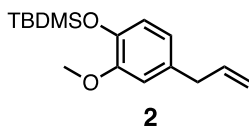


TLC Eluent: petroleum ether/ ethyl acetate 9:1. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 9:1 to afford a colorless oil (171 mg, 98.7% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.36 (s, 1H), 7.99 (d,  $J$  = 8.2 Hz, 1H), 5.85 (d,  $J$  = 3.7 Hz, 1H), 5.65 (dd,  $J$  = 8.2, 2.2 Hz, 1H), 4.13 – 4.00 (m, 3H), 3.96 (dd,  $J$  = 12.0, 1.6 Hz, 1H), 3.73 (dd,  $J$  = 11.8, 1.1 Hz, 1H), 0.97 – 0.77 (m, 27H), 0.15 – -0.03 (m, 18H).  $^{13}\text{C}$  NMR (242 MHz  $\text{CDCl}_3$ ):  $\delta$  150.00, 140.40, 101.88, 88.82, 84.69, 76.15, 70.96, 61.93, 29.71, 26.02, 25.83, 25.75, -4.23 (3C), -4.61(3C), -4.76 (3C), -4.83 (2C), -5.38 (2C), -5.57 (2C).

LCMS (ESI, negative mode):  $m/z$  = 585.3  $[\text{M}-\text{H}]^-$

### (4-allyl-2-methoxyphenoxy)(*tert*-butyl)dimethylsilane (2)

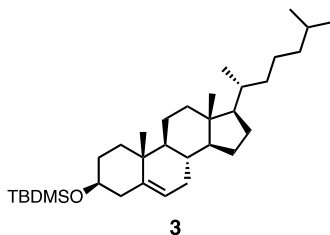


TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5 to afford a light yellow oil (29 mg, 79% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  6.75 (d,  $J$  = 7.9 Hz, 1H), 6.66 – 6.58 (m, 2H), 5.95 (ddt,  $J$  = 16.9, 10.1, 6.7 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.77 (s, 3H), 3.30 (dt,  $J$  = 6.7, 1.5 Hz, 2H), 0.98 (s, 9H), 0.13 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  150.76, 143.24, 137.80, 133.42, 120.69, 120.63, 115.46, 112.59, 55.44, 39.87, 29.70, 25.73 (3C), 18.42 (2C).

LCMS (ESI, positive mode):  $m/z$  = 279  $[\text{M}+\text{H}]^+$ ; 301  $[\text{M}+\text{Na}]^+$

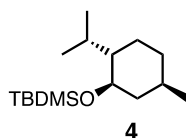
***tert*-butyl(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)dimethylsilane (3)**



TLC Eluent: petroleum ether/ ethyl acetate 99:1. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 99:1 to afford a white waxy solid (66 mg, 86% yield).

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ 5.29 (dt, *J* = 5.5, 2.0 Hz, 1H), 3.46 (tt, *J* = 11.0, 4.7 Hz, 1H), 2.31 – 2.19 (m, 1H), 2.14 (ddd, *J* = 13.4, 5.0, 2.3 Hz, 1H), 2.04 – 1.89 (m, 2H), 1.86 – 1.74 (m, 2H), 1.69 (m, 1H), 1.58–1.00 (m, 21H), 0.98 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.87 (s, 9H), 0.84 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.65 (s, 3H), 0.04 (s, 6H). <sup>13</sup>C NMR (101 MHz CDCl<sub>3</sub>): δ 141.56, 121.15, 72.63, 56.80, 56.13, 50.21, 42.81, 42.31, 39.80, 39.50, 37.38, 36.57, 36.18, 35.76, 32.08, 31.93, 28.22, 28.00, 25.92 (3C), 24.28, 23.80, 22.80, 22.54 (2C), 21.05, 19.41(2C), 18.70, 18.25, 11.83 (2C).

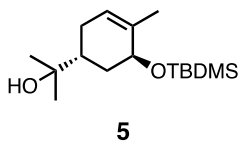
***tert*-butyl(((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)dimethylsilane (4)**



TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5 to afford a colorless oil (52 mg, 86% yield).

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ 3.36 (td, *J* = 10.3, 4.3 Hz, 1H), 2.20 (dq, *J* = 14.0, 7.0, 2.6 Hz, 1H), 1.83 (dtd, *J* = 12.3, 3.6, 1.9 Hz, 1H), 1.65 – 1.53 (m, 2H), 1.41 – 1.29 (m, 1H), 1.11 (ddt, *J* = 12.6, 9.9, 2.9 Hz, 1H), 1.01 – 0.91 (m, 2H), 0.87 (d, *J* = 6.4 Hz, 15H), 0.84 – 0.77 (m, 1H), 0.70 (d, *J* = 6.9 Hz, 3H), 0.03 (d, *J* = 5.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz CDCl<sub>3</sub>): δ 72.35, 50.24, 45.46, 34.56, 31.65, 29.68, 25.91 (3C), 24.97, 22.69, 22.34, 21.32, 15.69, 0.98 (2C).

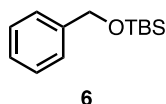
**2-((1*R*,5*S*)-5-((*tert*-butyldimethylsilyl)oxy)-4-methylcyclohex-3-en-1-yl)propan-2-ol (5)**



TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5 → 9:1 to afford a colorless oil (62 mg, 93% yield).

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ 5.50 (dt, *J* = 5.1, 1.5 Hz, 1H), 4.00 (dd, *J* = 3.9, 2.2 Hz, 1H), 2.14 – 2.05 (m, 1H), 1.90 – 1.82 (m, 1H), 1.82 – 1.75 (m, 2H), 1.73 (ddt, *J* = 4.2, 3.0, 1.6 Hz, 1H), 1.70 (q, *J* = 1.7 Hz, 3H), 1.32 (td, *J* = 12.7, 3.6 Hz, 1H), 1.17 (d, *J* = 1.1 Hz, 6H), 0.89 (s, 9H), 0.08 (s, 6H). <sup>13</sup>C NMR (101 MHz CDCl<sub>3</sub>): δ 134.90, 124.25, 72.26, 69.10, 38.74, 33.49, 27.22 (2C), 27.02, 26.94, 25.87 (3C), 21.16, 18.10 (2C).

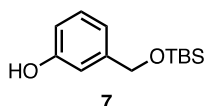
### (benzyloxy)(tert-butyl)dimethylsilane (6)



TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5 to afford a colorless oil (90 mg, 84% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.33 (d,  $J = 4.4$  Hz, 4H), 7.27 – 7.22 (m, 1H), 4.76 (s, 2H), 0.96 (s, 9H), 0.11 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  141.42, 128.19 (2C), 126.86, 126.02 (2C), 64.96, 25.96 (3C), 18.43, -5.24 (2C).

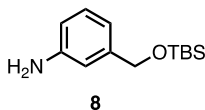
### 3-(((tert-butyl)dimethylsilyl)oxy)methyl)phenol (7)



TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5  $\rightarrow$  9:1 to afford a yellow oil (48 mg, 50% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.16 (t,  $J = 7.8$  Hz, 1H), 6.87 – 6.80 (m, 2H), 6.68 (dd,  $J = 8.1, 2.6$  Hz, 1H), 4.99 (bs, 1H,  $\text{D}_2\text{O}$  exchangeable), 4.68 (s, 2H), 0.93 (s, 9H), 0.09 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  155.61, 143.40, 129.40, 118.26, 113.75, 112.89, 64.64, 25.95 (3C), 18.42, -5.28 (2C).

### 3-(((tert-butyl)dimethylsilyl)oxy)methyl)aniline (8)

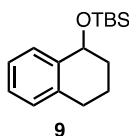


TLC Eluent: petroleum ether/ ethyl acetate 9:1. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 9:1 to afford a colorless oil (78 mg, 81% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ): 7.10 (t,  $J = 7.7$  Hz, 1H), 6.71 – 6.64 (m, 2H), 6.55 (ddd,  $J = 8.1, 2.5, 0.9$  Hz, 1H), 4.66 (s, 2H), 3.64 (bs, 2H,  $\text{D}_2\text{O}$  exchangeable), 0.94 (s, 9H), 0.10 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  146.35, 142.72, 129.10, 116.33, 113.73, 112.82, 64.93, 25.99 (3C), 18.45, -5.24 (2C).

LCMS (ESI, positive mode):  $m/z = 260.0$   $[\text{M} + \text{Na}]^+$

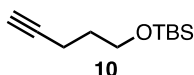
### tert-butyl)dimethyl((1,2,3,4-tetrahydronaphthalen-1-yl)oxy)silane (9)



TLC Eluent: petroleum ether/ ethyl acetate 98:2. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 98:2 to afford a colorless oil (38 mg, 43% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ )  $\delta$  7.38 (dd,  $J = 7.0, 2.1$  Hz, 1H), 7.17 (tt,  $J = 7.3, 5.4$  Hz, 2H), 7.08 – 7.05 (m, 1H), 4.80 (dd,  $J = 7.9, 3.6$  Hz, 1H), 2.88 – 2.68 (m, 2H), 2.04 – 1.95 (m, 2H), 1.85 – 1.72 (m, 2H), 0.95 (s, 9H), 0.17 (d,  $J = 3.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ )  $\delta$  139.99, 136.85, 128.62, 127.80, 126.82, 125.72, 69.35, 33.00, 29.14, 25.94 (3C), 19.68, 18.18, -4.14, -4.52.

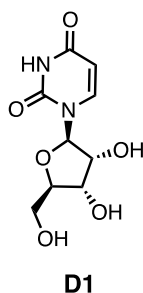
### tert-butyldimethyl(pent-4-yn-1-yloxy)silane (10)



TLC Eluent: petroleum ether/ diethyl ether 98:2. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ diethyl ether 98:2 to afford a pale yellow oil (73 mg, 62% yield).

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>) δ 3.67 (t, *J* = 6.0 Hz, 2H), 2.24 (td, *J* = 7.1, 2.7 Hz, 2H), 1.89 (t, *J* = 2.7 Hz, 1H), 1.70 (tt, *J* = 7.1, 6.1 Hz, 2H) 0.87 (s, 9H), 0.03 (s, 6H). <sup>13</sup>C NMR (101 MHz CDCl<sub>3</sub>) δ 84.18, 68.19, 61.37, 31.48, 25.87 (3C), 18.27, 14.78, -5.42 (2C).

### 1-((2*R*,3*R*,4*S*,5*R*)-3,4-dihydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (D1)

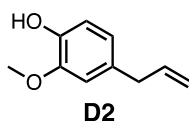


TLC Eluent: dichloromethane/ methanol 95:5. The crude product was purified by flash chromatography on silica gel and eluted with dichloromethane/methanol 95:5 → 9:1 to afford a colorless semisolid (20 mg, 83% yield).

<sup>1</sup>H NMR (400 MHz DMSO-*d*<sub>6</sub>): δ 11.26 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 5.74 (d, *J* = 5.4 Hz, 1H), 5.60 (d, *J* = 8.1 Hz, 1H), 5.33 (d, *J* = 5.7 Hz, 1H, D<sub>2</sub>O exchangeable), 5.04 (dd, *J* = 5.1, 1.7 Hz, 2H, D<sub>2</sub>O exchangeable), 4.01 – 3.89 (m, 2H), 3.80 (q, *J* = 3.4 Hz, 1H), 3.61 – 3.46 (m, 2H). <sup>13</sup>C NMR (101 MHz DMSO-*d*<sub>6</sub>): δ 163.54, 151.18, 141.15, 102.17, 88.10, 85.26, 73.96, 70.31, 61.28.

LCMS (ESI, negative mode): *m/z* = 242.9 [M-H]<sup>-</sup>; 279.0 [M+Cl]<sup>-</sup>. ESI (positive mode): *m/z* = 267.0 [M+Na]<sup>+</sup>

### 4-allyl-2-methoxyphenol (D2)

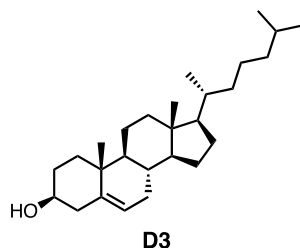


TLC Eluent: petroleum ether/ ethyl acetate 99:1. The crude product was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 99:1 → 95:5 to afford a colorless oil which turned slightly light yellow upon drying in vacuo (39 mg, 56% isolated yield).

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ 6.89 – 6.78 (m, 1H), 6.67 (dq, *J* = 4.6, 1.9 Hz, 2H), 5.94 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.50 (s, 1H, D<sub>2</sub>O exchangeable), 5.12 – 4.96 (m, 2H), 3.86 (s, 3H), 3.31 (d, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz CDCl<sub>3</sub>): δ 146.41, 143.89, 137.81, 131.91, 121.16, 115.50, 114.24, 111.09, 55.84, 39.87

LCMS (ESI, positive mode): *m/z* = 187.1 [M+Na]<sup>+</sup>

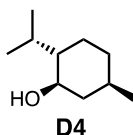
**(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (D3)**



TLC Eluent: dichloromethane/ methanol 98:2. The product was obtained pure without further purification. Aspect: white solid (9.4 mg, 64% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  5.33 (dt,  $J = 5.5, 2.0$  Hz, 1H), 3.50 (tdd,  $J = 11.1, 5.3, 4.2$  Hz, 1H), 2.31 – 2.16 (m, 2H), 2.03 – 1.91 (m, 2H), 1.82 (dtd,  $J = 11.2, 6.6, 6.0, 3.7$  Hz, 3H), 1.62 – 1.01 (m, 22H), 0.99 (s, 3H), 0.89 (d,  $J = 6.5$  Hz, 3H), 0.84 (dd,  $J = 6.7, 1.8$  Hz, 6H), 0.66 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  140.73, 121.70, 71.79, 56.74, 56.13, 50.11, 42.28, 39.76, 39.50, 37.23, 36.48, 36.17, 35.76, 31.89 (2C), 31.63, 28.21, 27.99, 24.27, 23.80, 22.79, 22.54 (2C), 21.06, 19.37, 18.70, 11.84

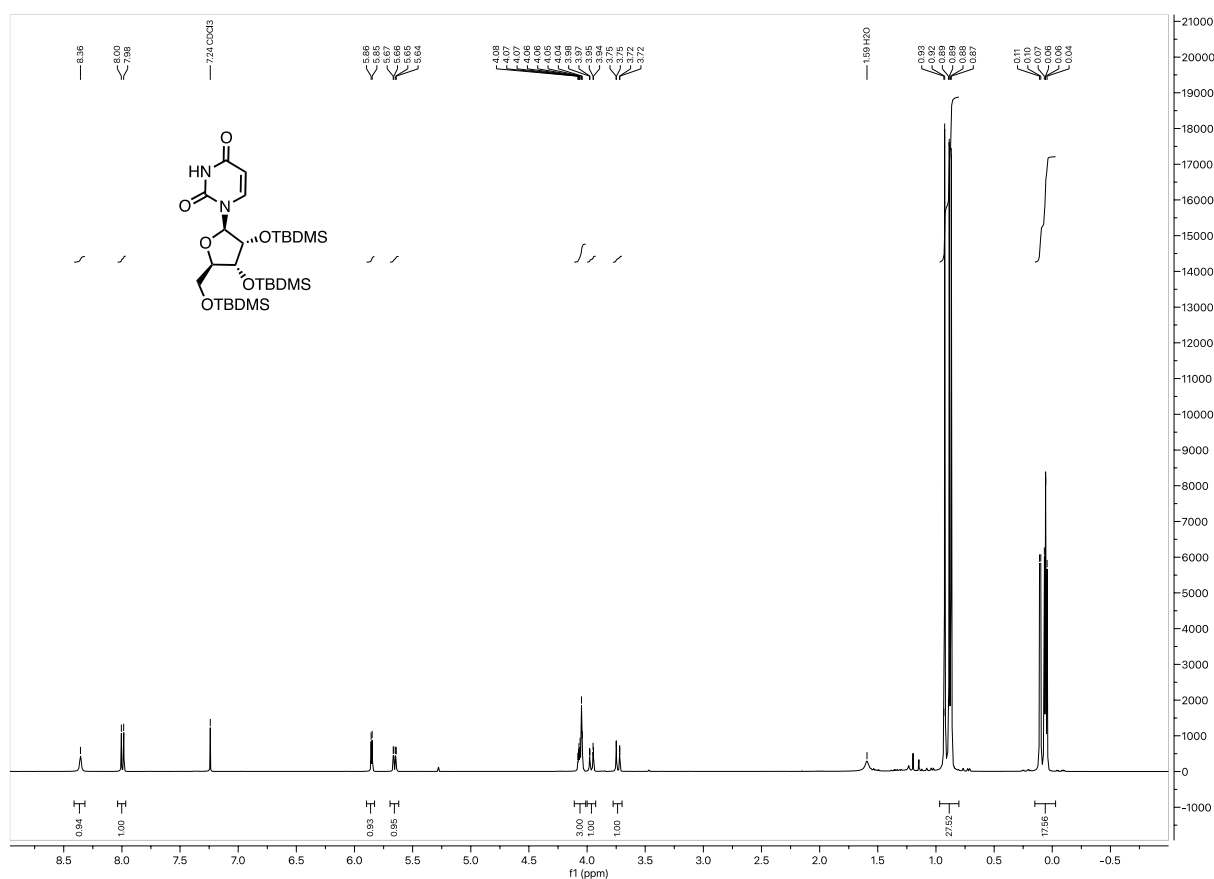
**(1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexan-1-ol (D4)**



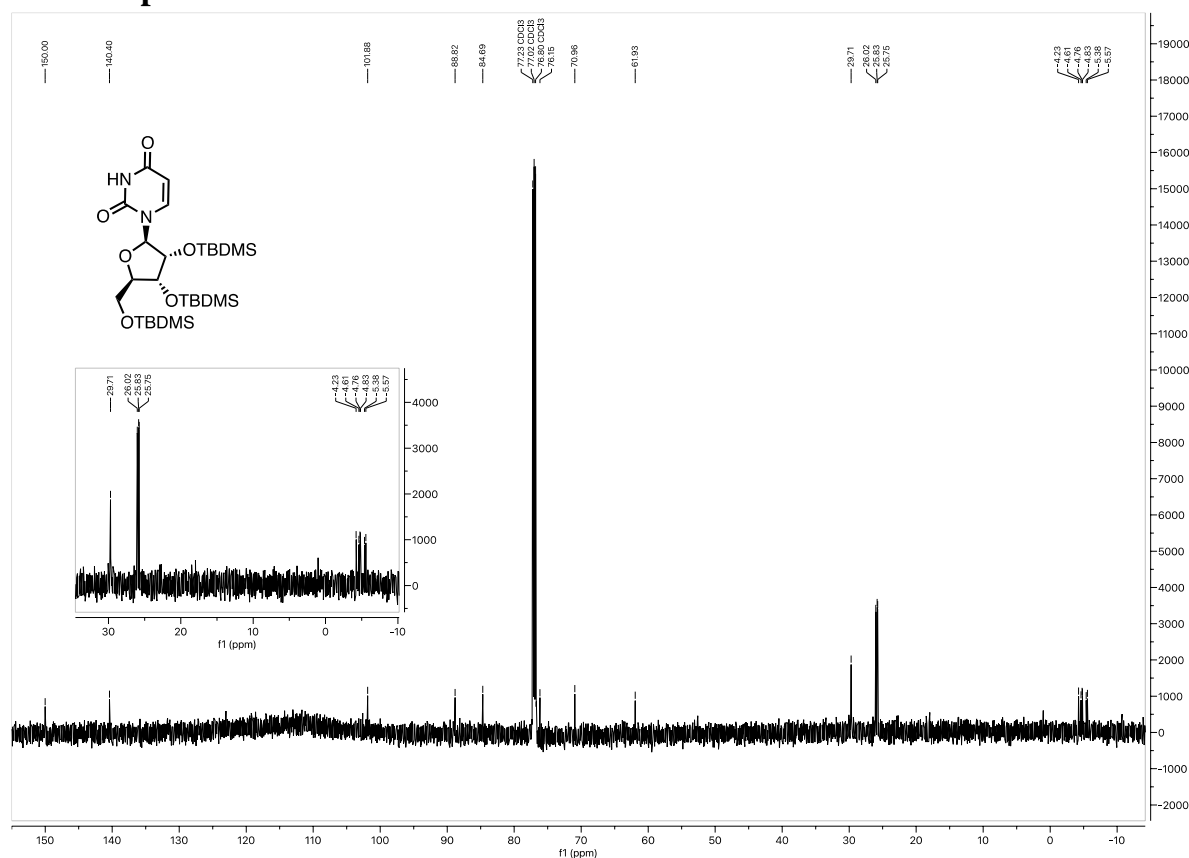
TLC Eluent: petroleum ether/ ethyl acetate 95:5. The crude was purified by flash chromatography on silica gel and eluted with petroleum ether/ ethyl acetate 95:5 to afford a colorless solid (15 mg, 45% yield).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  3.39 (td,  $J = 10.4, 4.3$  Hz, 1H), 2.15 (heptd,  $J = 7.0, 2.7$  Hz, 1H), 1.94 (dtd,  $J = 11.9, 3.9, 2.0$  Hz, 1H), 1.68 – 1.57 (m, 2H), 1.40 (tdq,  $J = 13.1, 6.6, 3.4$  Hz, 1H), 1.23 (bs, 1H,  $\text{D}_2\text{O}$  exchangeable) 1.09 (ddt,  $J = 12.9, 10.0, 3.0$  Hz, 1H), 1.01 – 0.92 (m, 1H), 0.90 (t,  $J = 6.5$  Hz, 6H), 0.88 – 0.83 (m, 2H), 0.79 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz  $\text{CDCl}_3$ ):  $\delta$  71.55, 50.14, 45.04, 34.52, 31.62, 25.84, 23.13, 22.19, 20.98, 16.09.

# <sup>1</sup>H NMR spectrum of 1

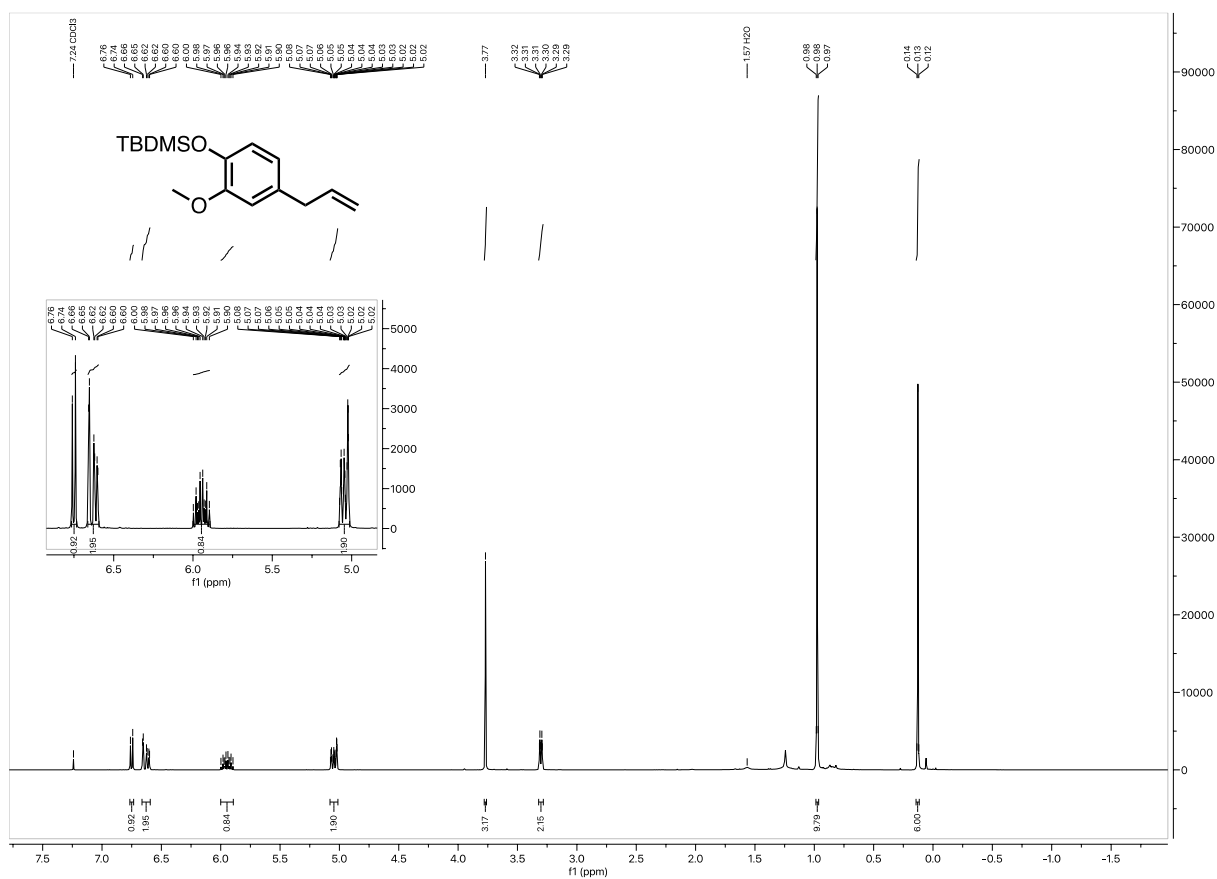


# <sup>13</sup>C NMR spectrum of 1

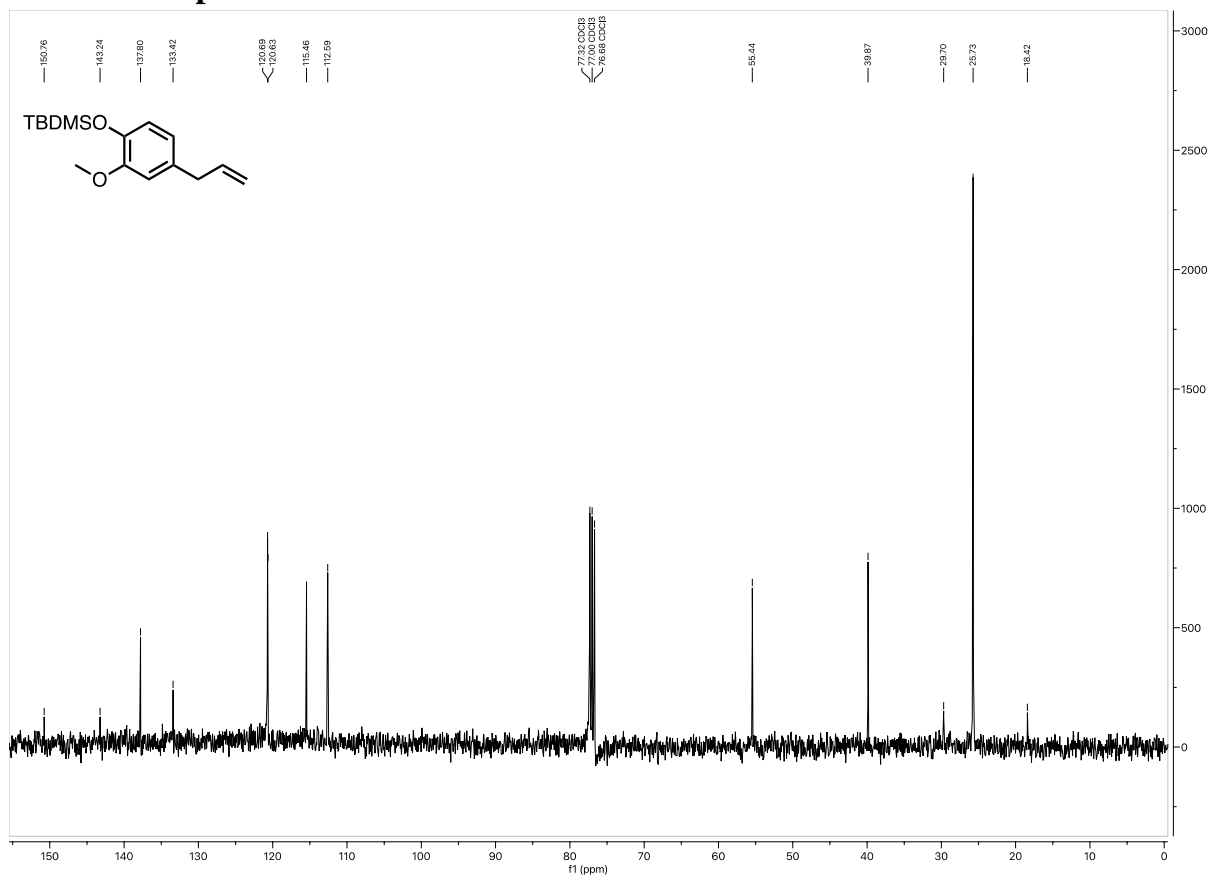




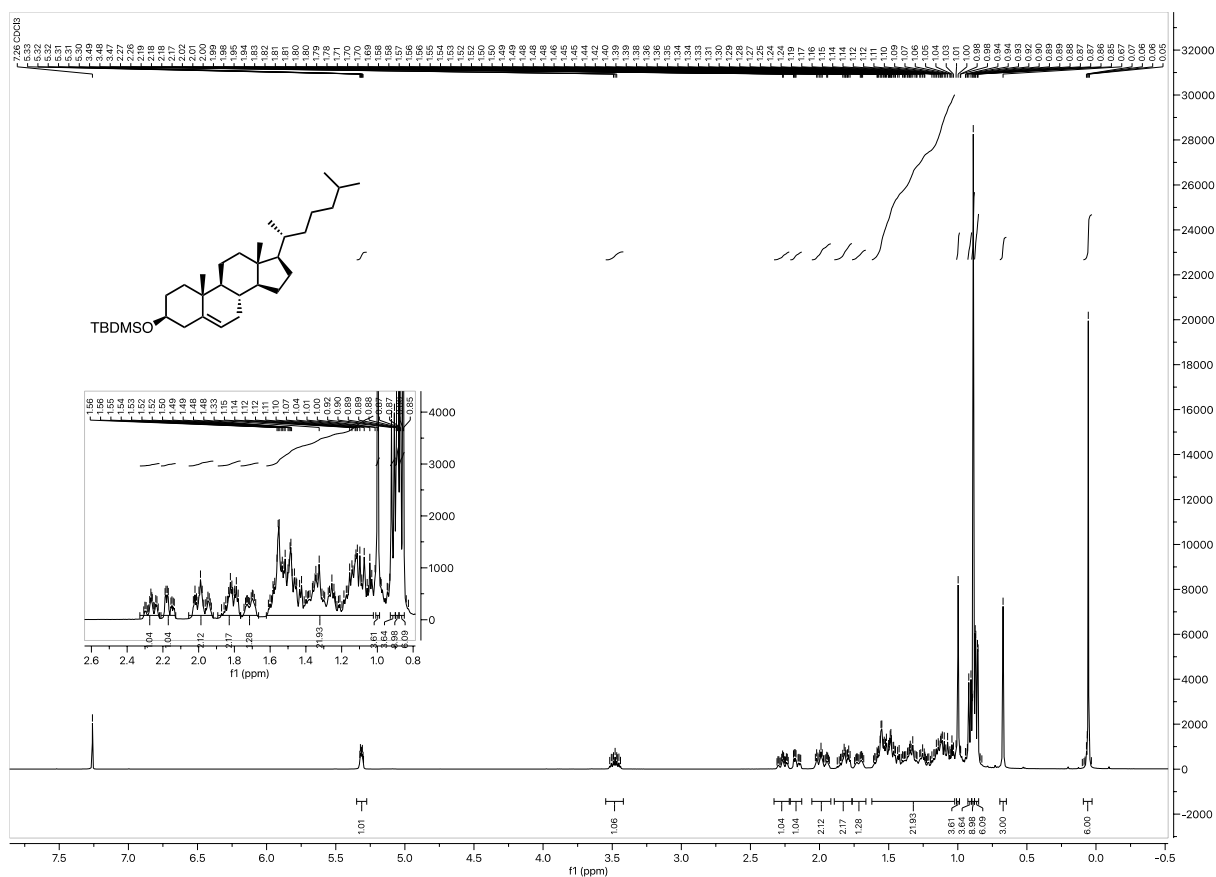
# <sup>1</sup>H NMR spectrum of 2



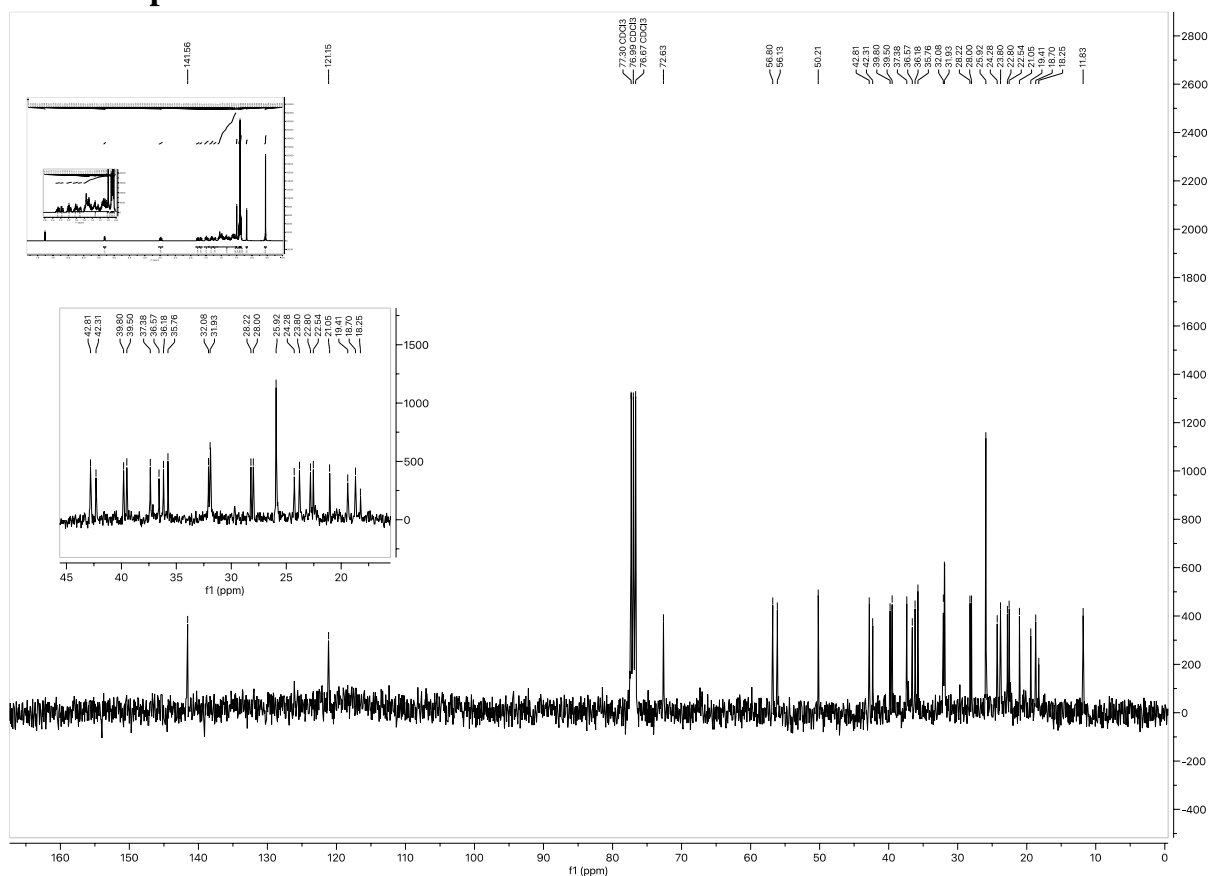
# <sup>13</sup>C NMR spectrum of 2



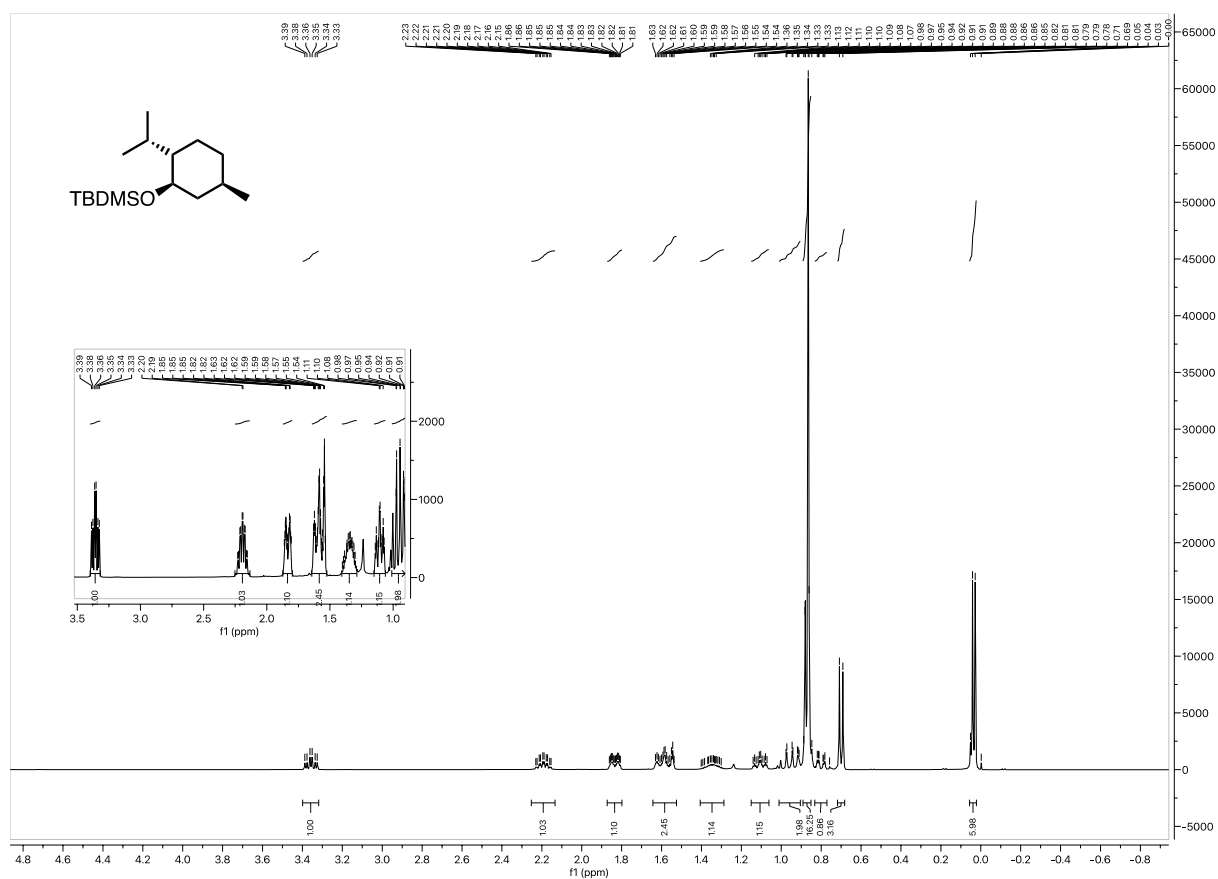
# <sup>1</sup>H NMR spectrum of 3



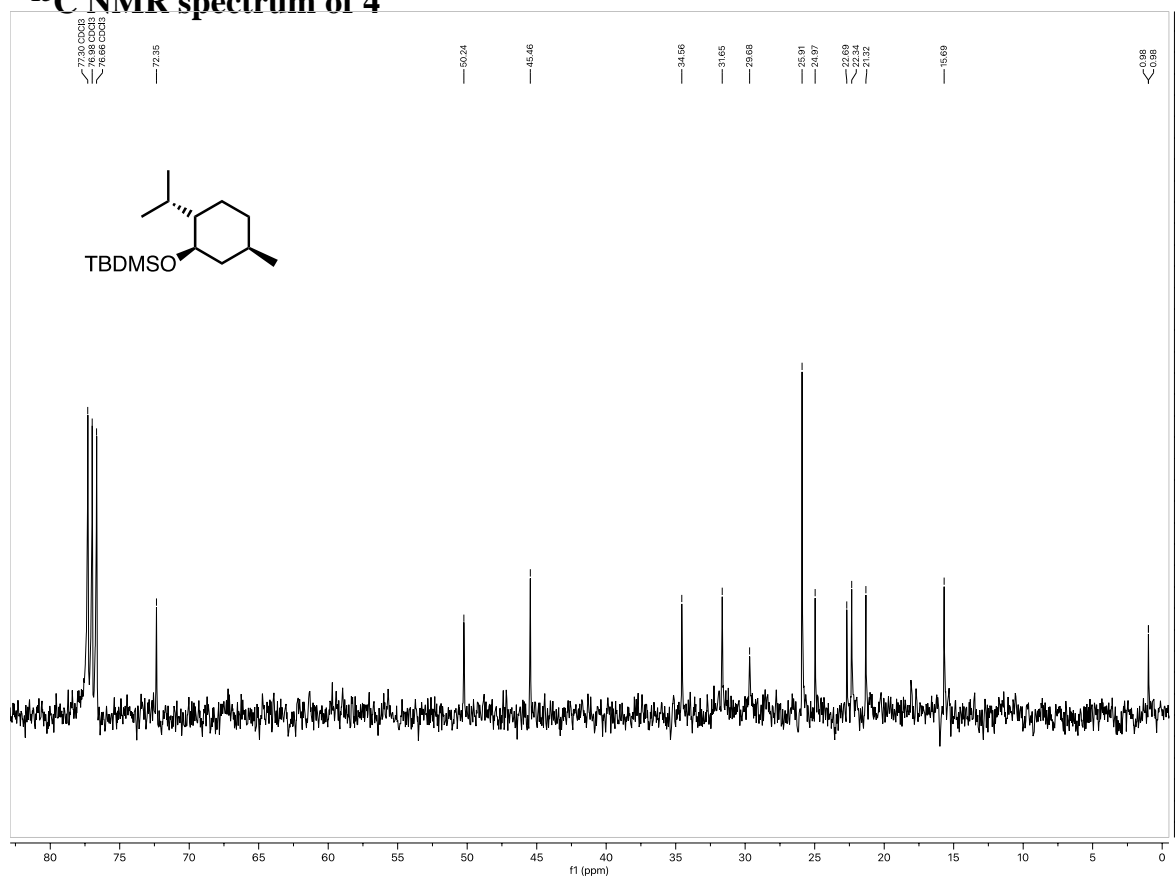
# <sup>13</sup>C NMR spectrum of 3



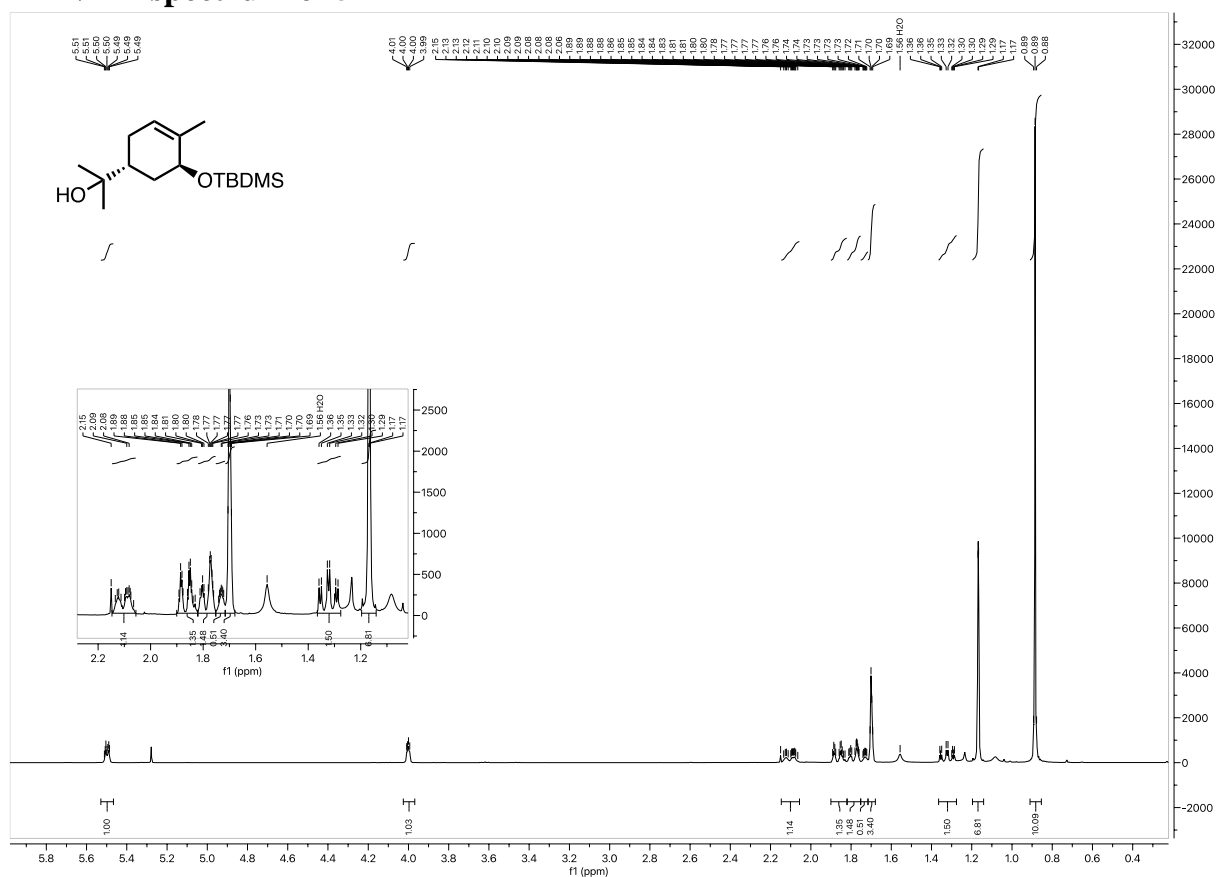
# <sup>1</sup>H NMR spectrum of 4



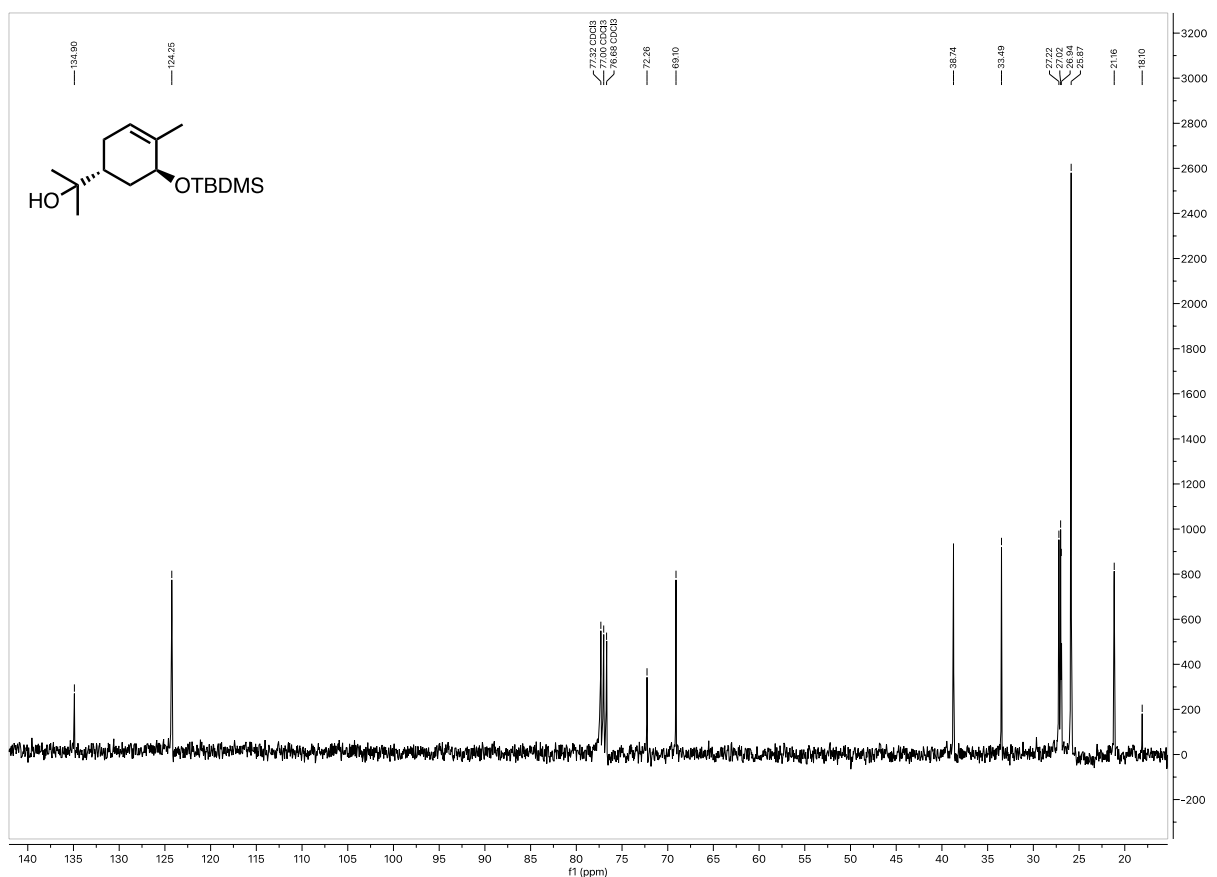
# <sup>13</sup>C NMR spectrum of 4



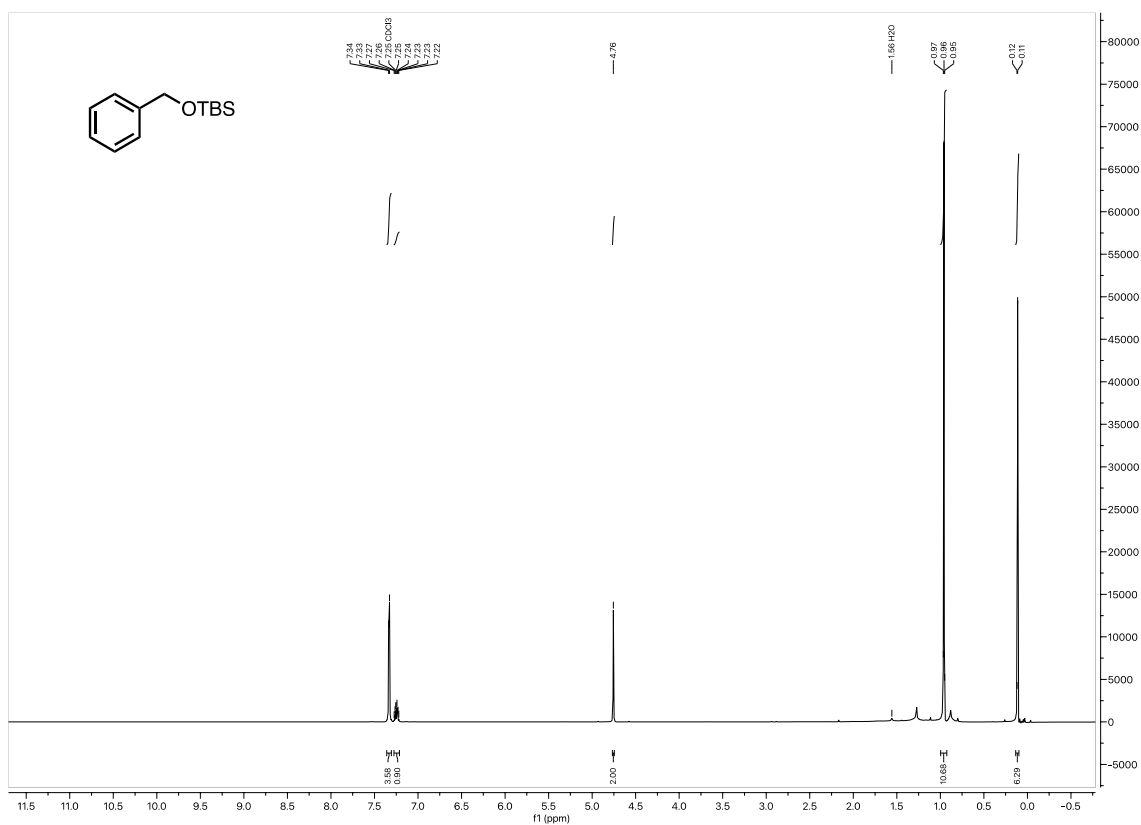
# <sup>1</sup>H NMR spectrum of 5



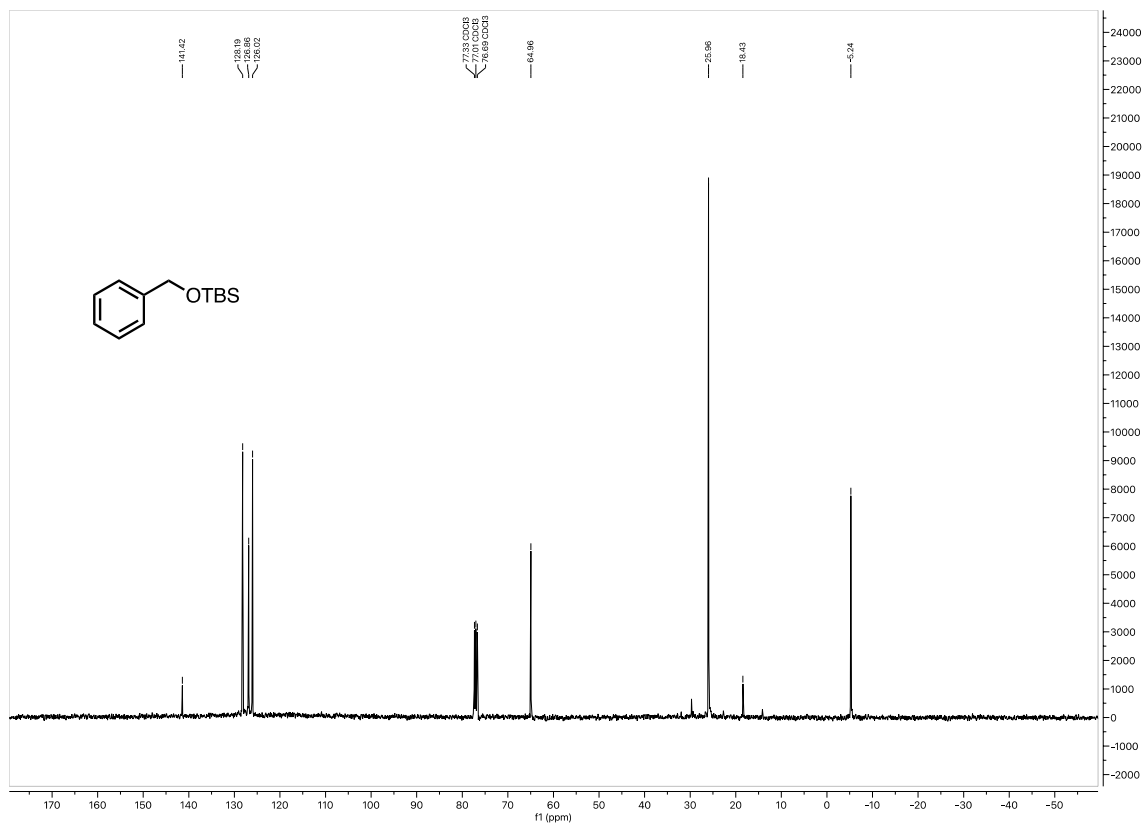
# <sup>13</sup>C NMR spectrum of 5



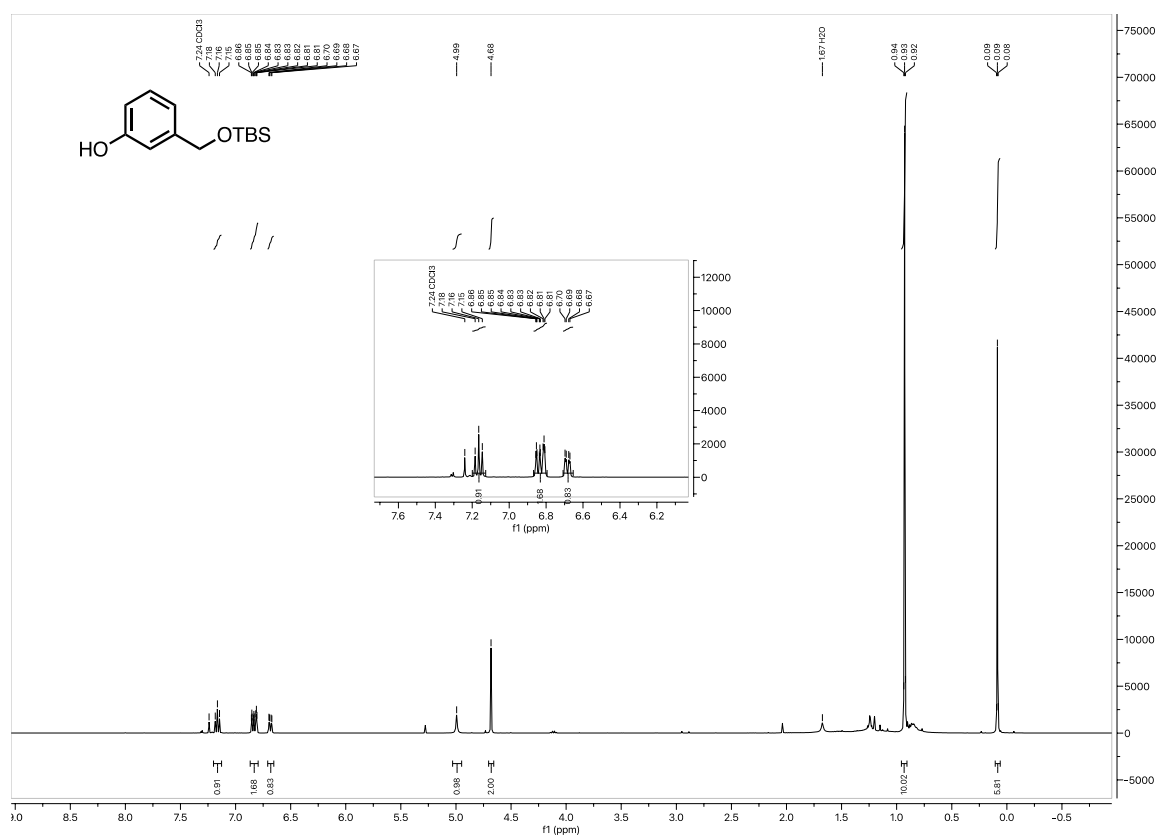
### <sup>1</sup>H NMR spectrum of 6



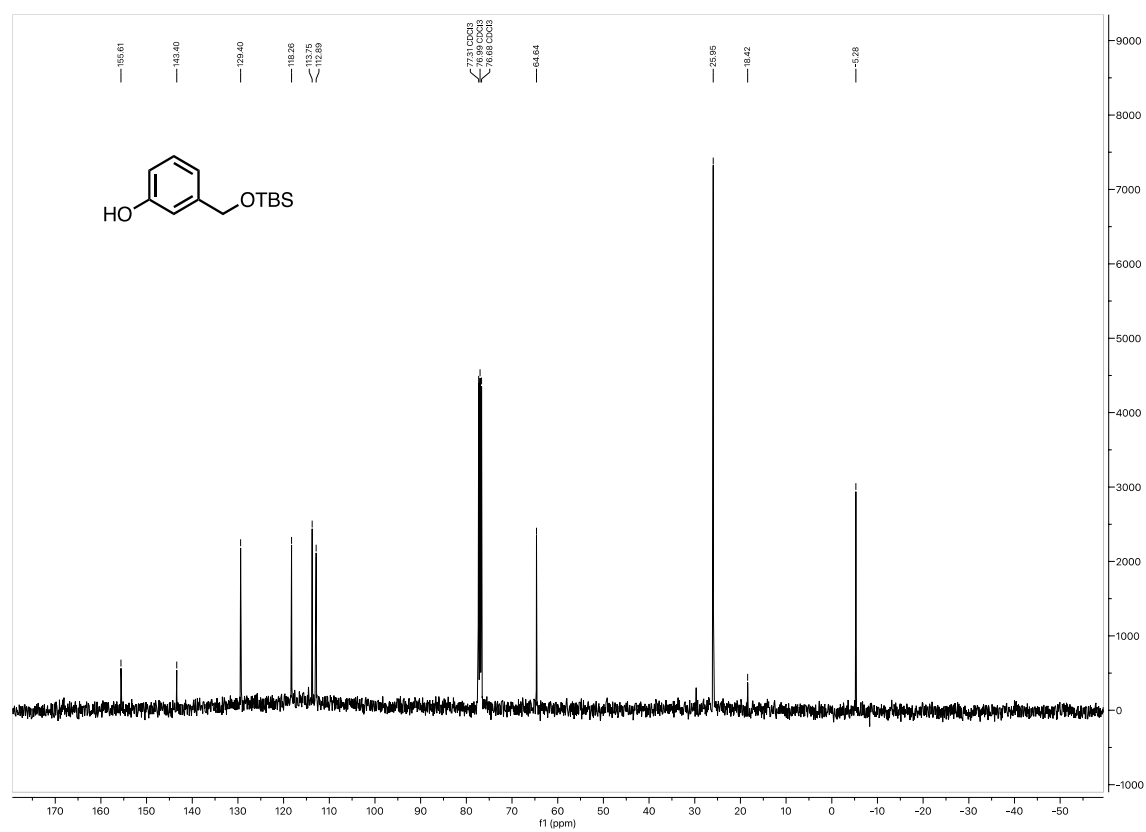
### <sup>13</sup>C NMR spectrum of 6



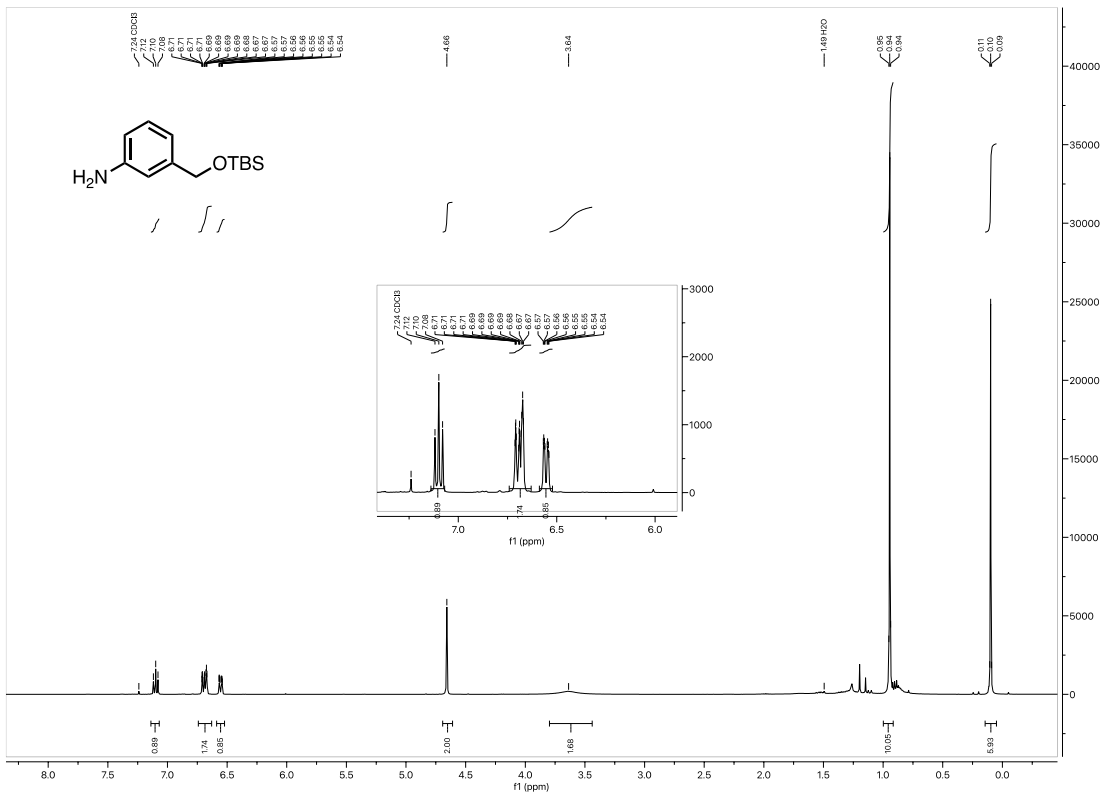
# <sup>1</sup>H NMR spectrum of 7



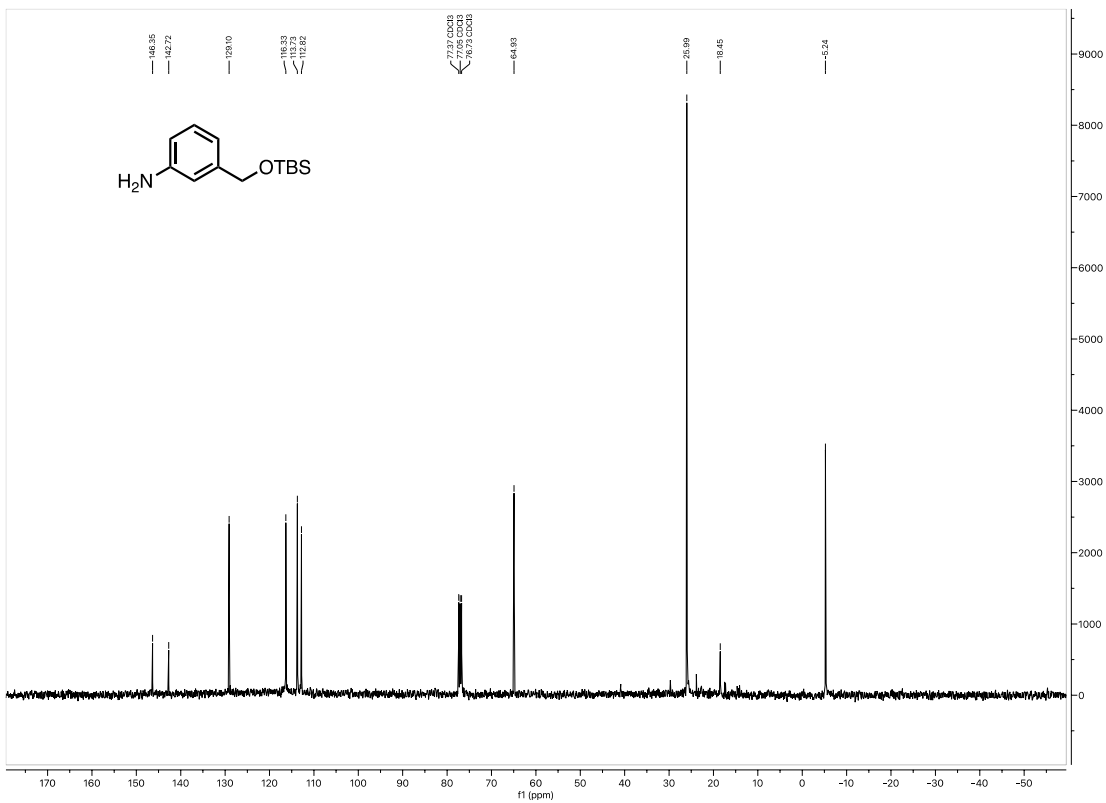
# <sup>13</sup>C NMR spectrum of 7



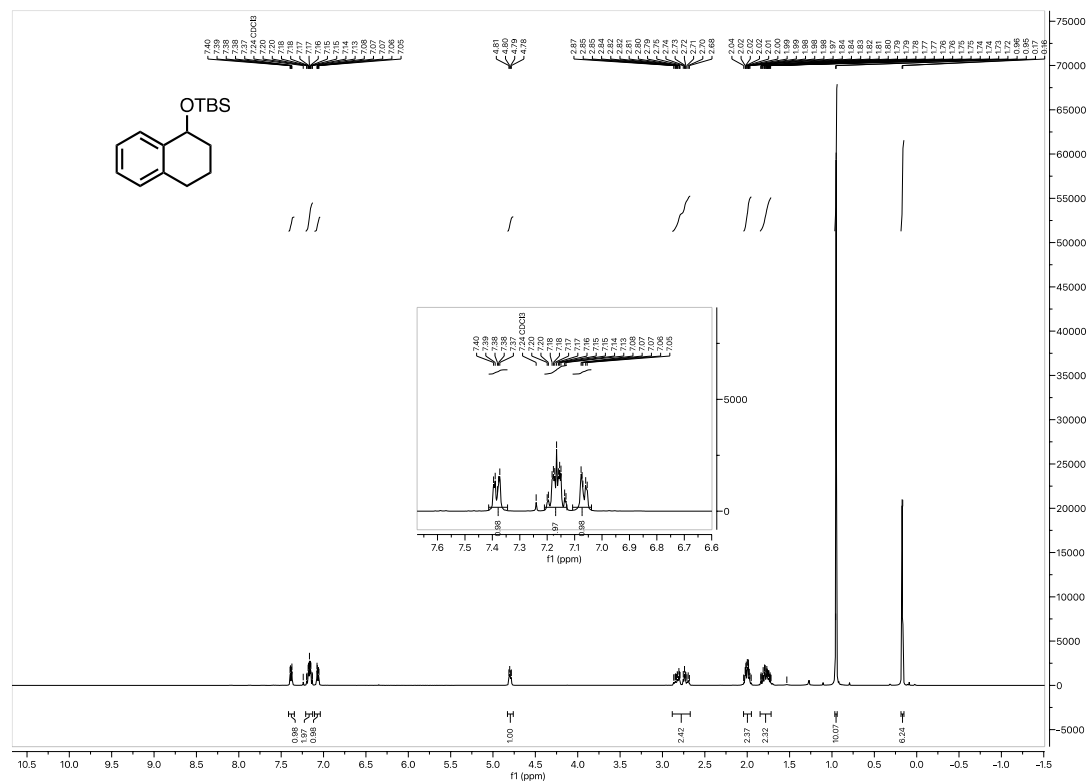
### <sup>1</sup>H NMR spectrum of 8



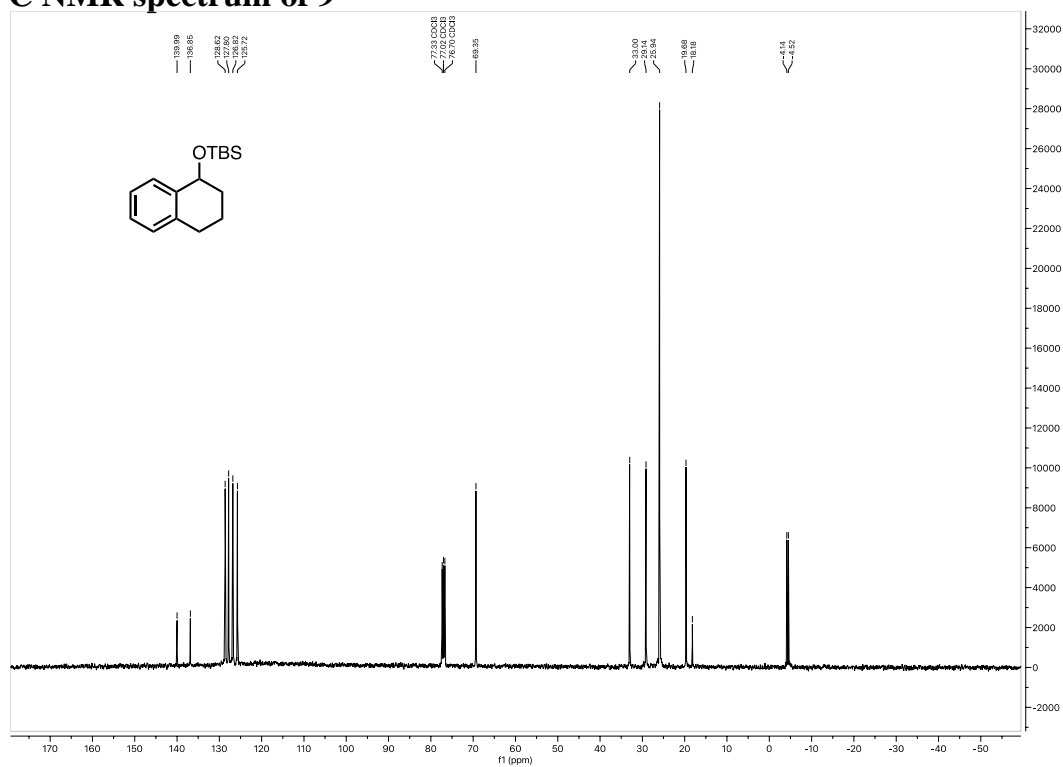
**$^{13}\text{C}$  NMR spectrum of 8**



# <sup>1</sup>H NMR spectrum of 9

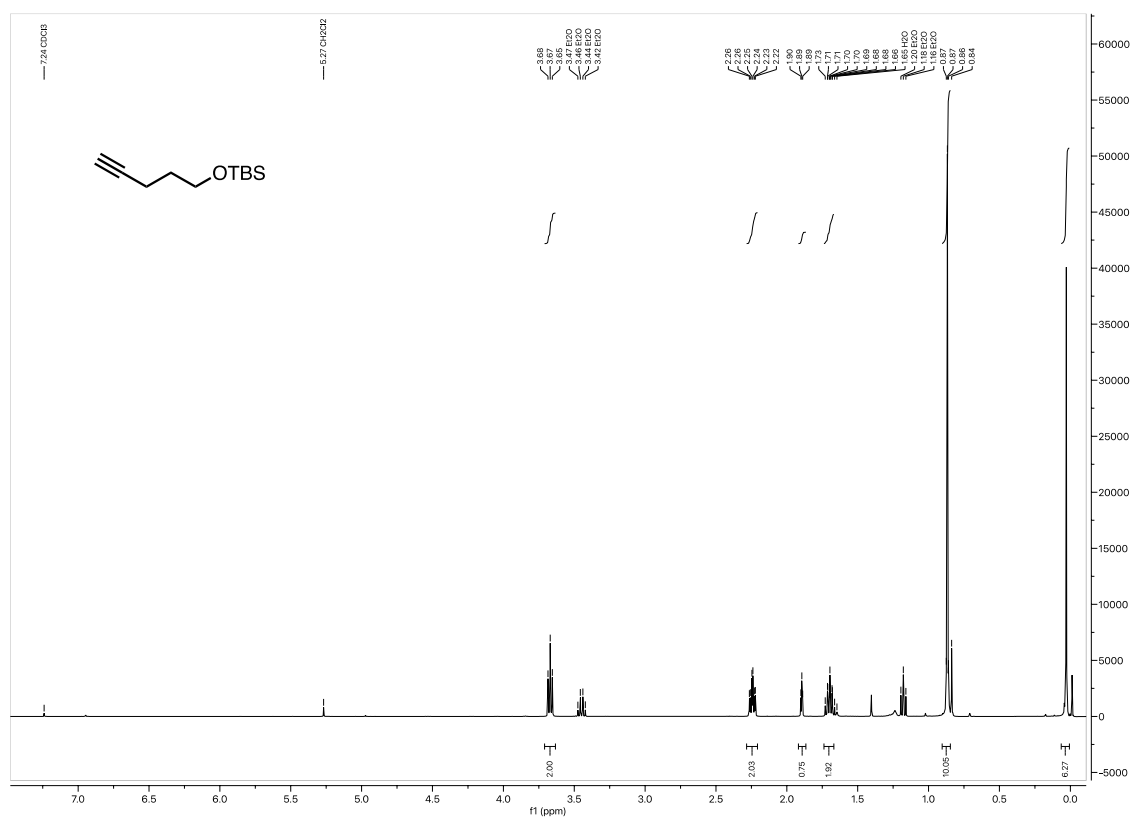


# <sup>13</sup>C NMR spectrum of 9

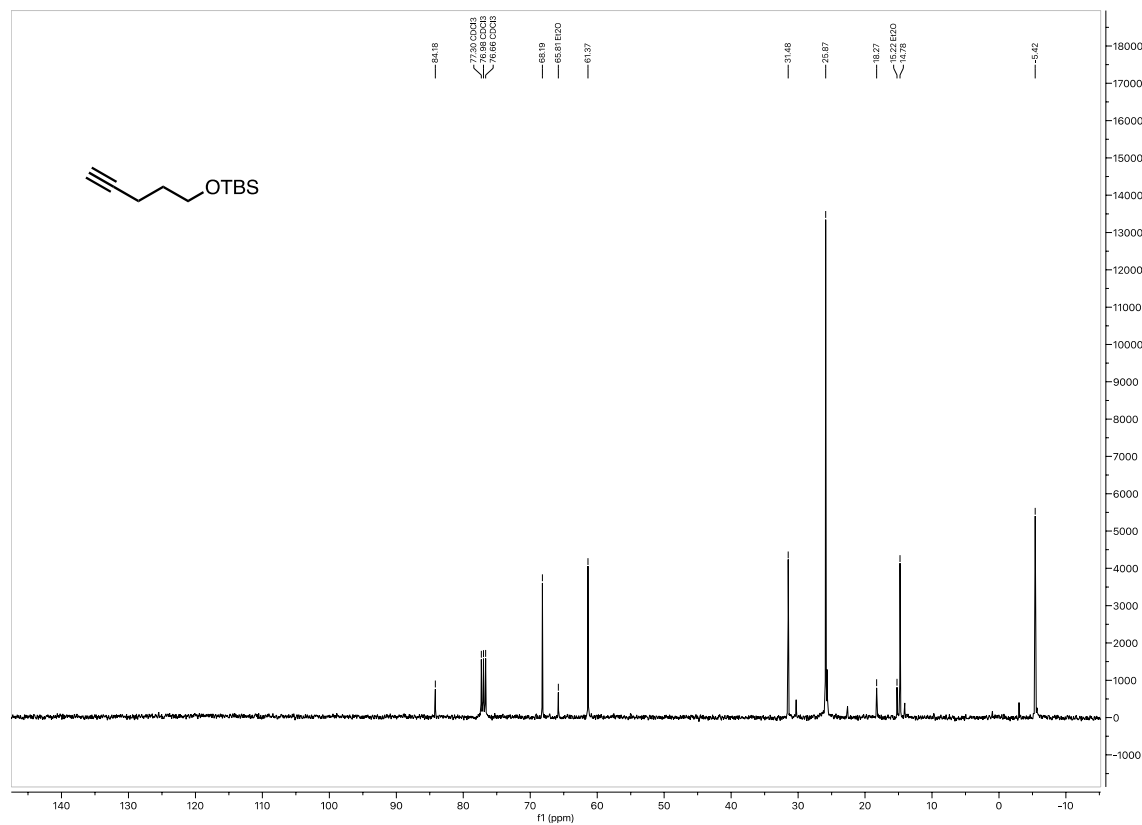




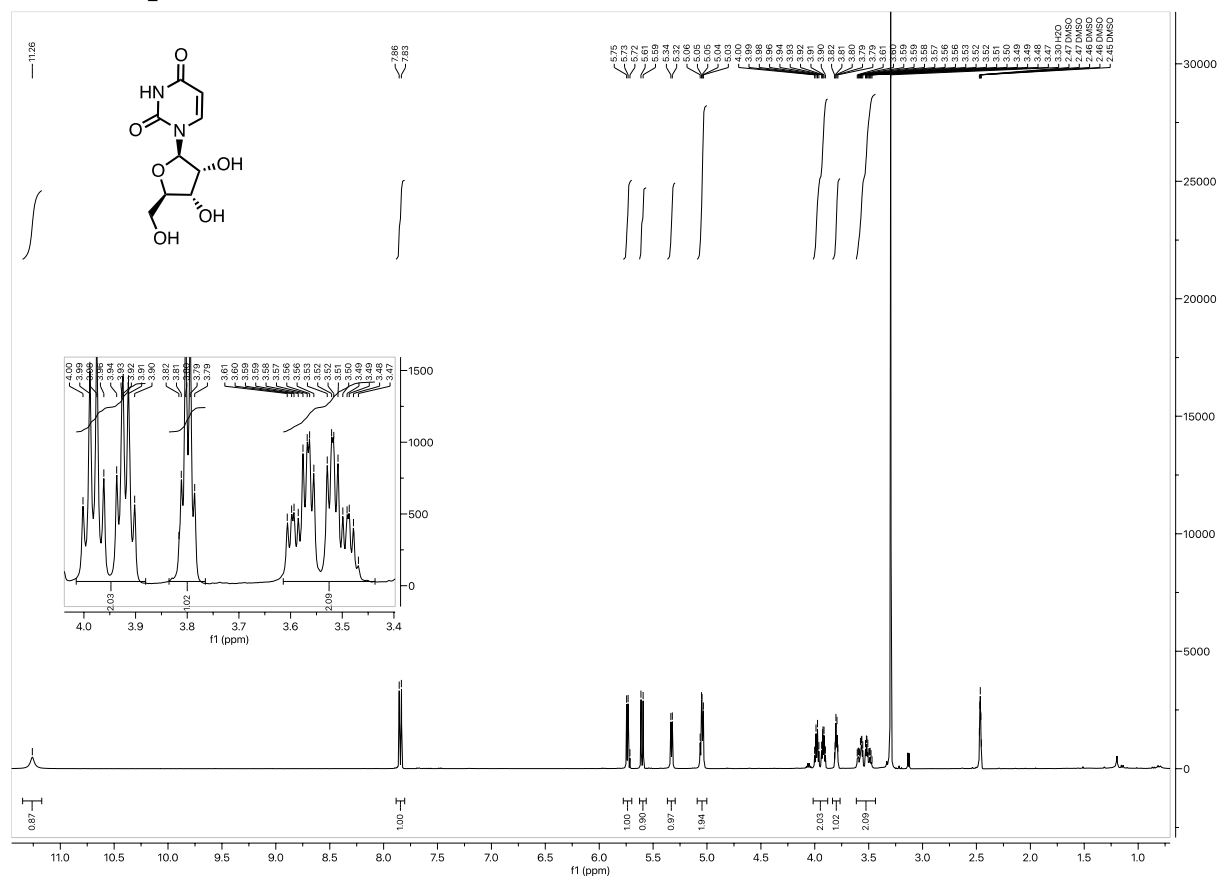
# <sup>1</sup>H NMR spectrum of 10



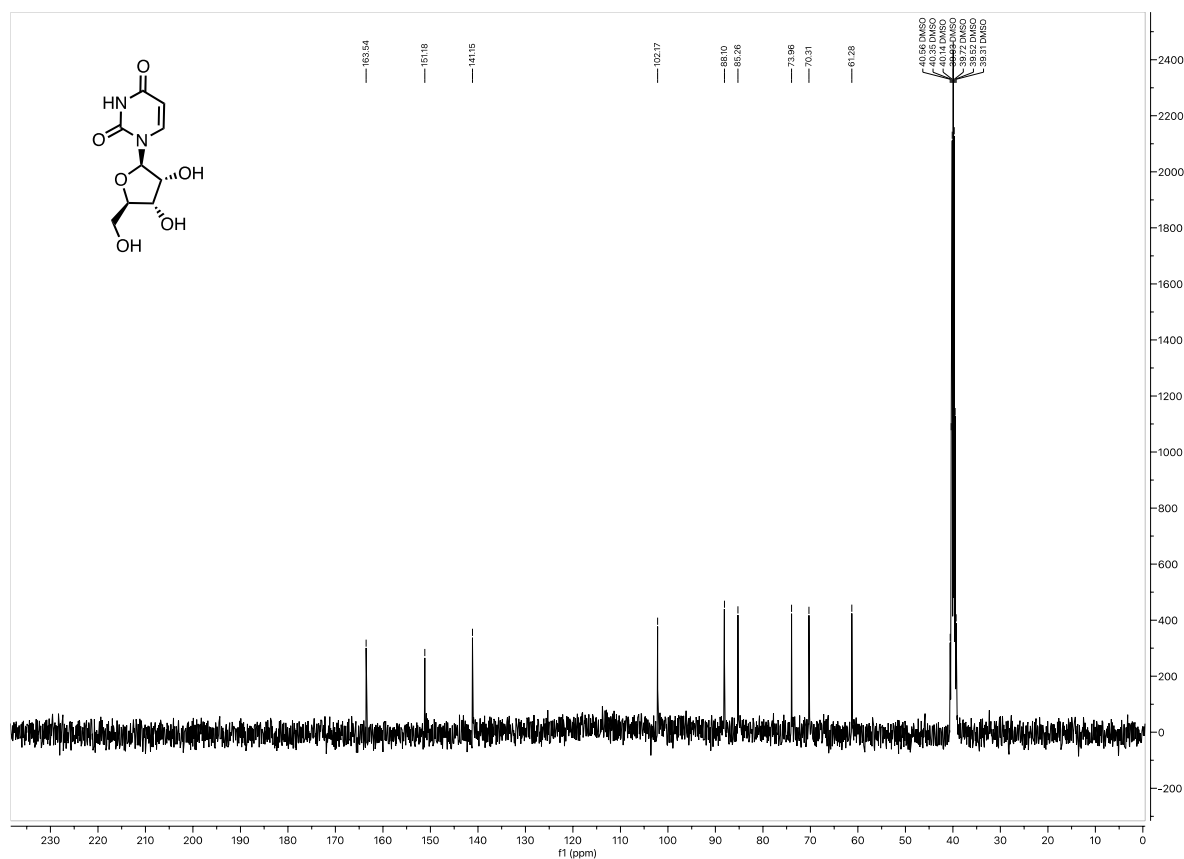
# <sup>13</sup>C NMR spectrum of 10



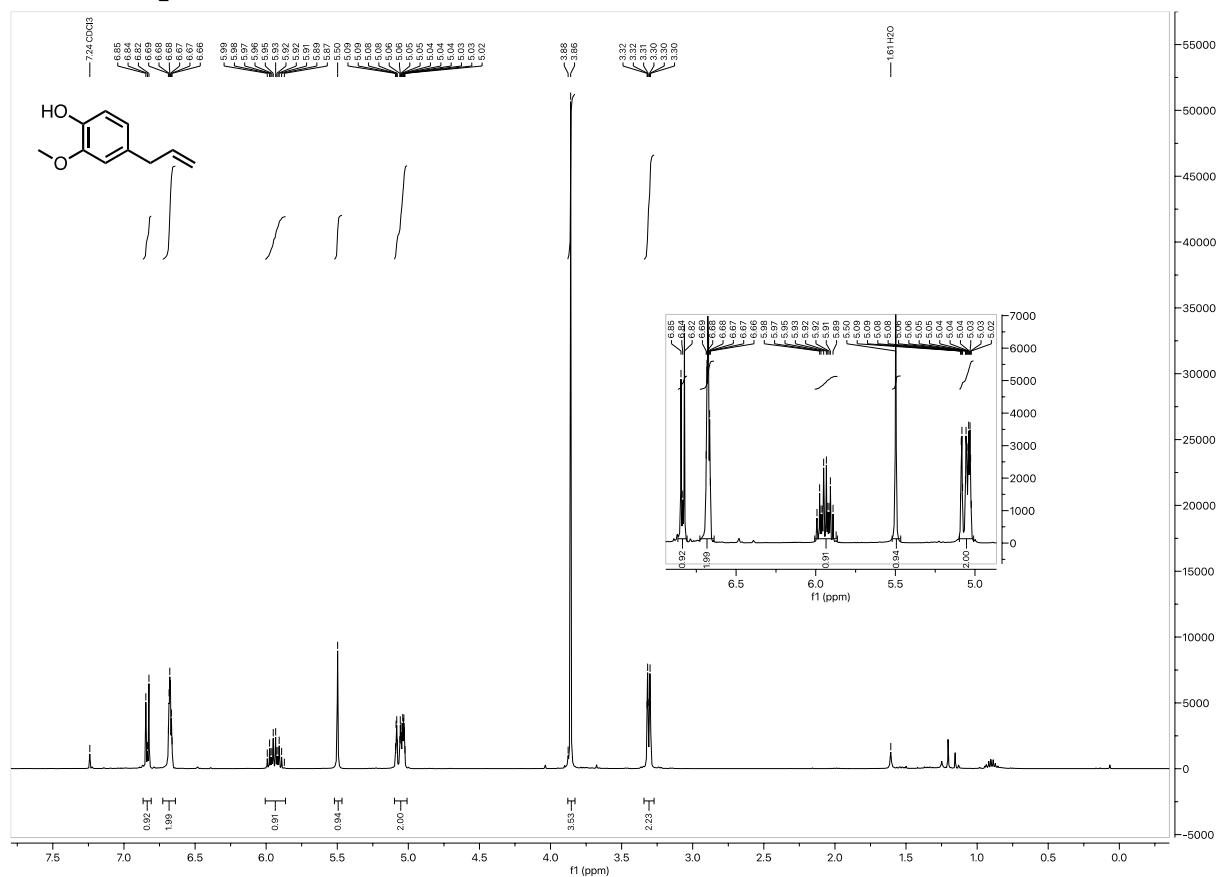
# <sup>1</sup>H NMR spectrum of D1



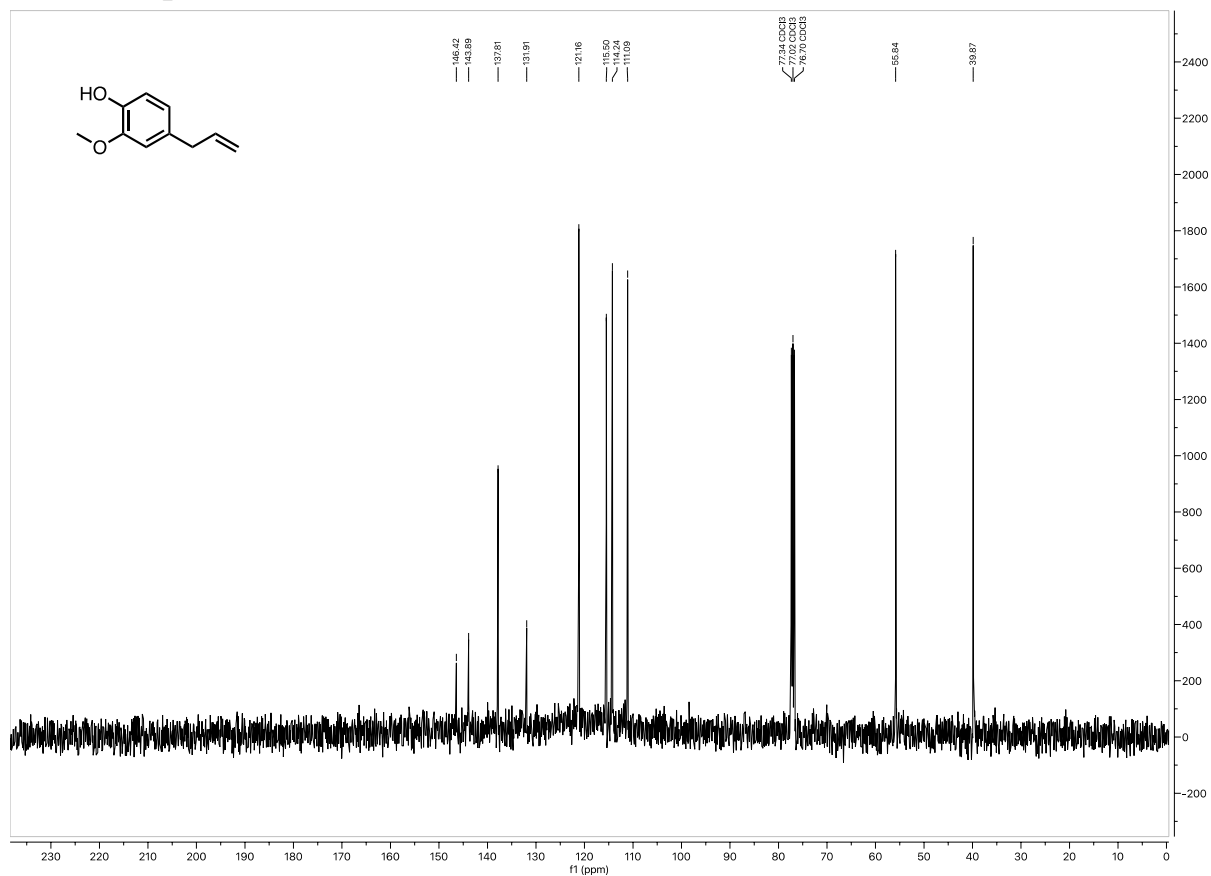
# <sup>13</sup>C NMR spectrum of D1



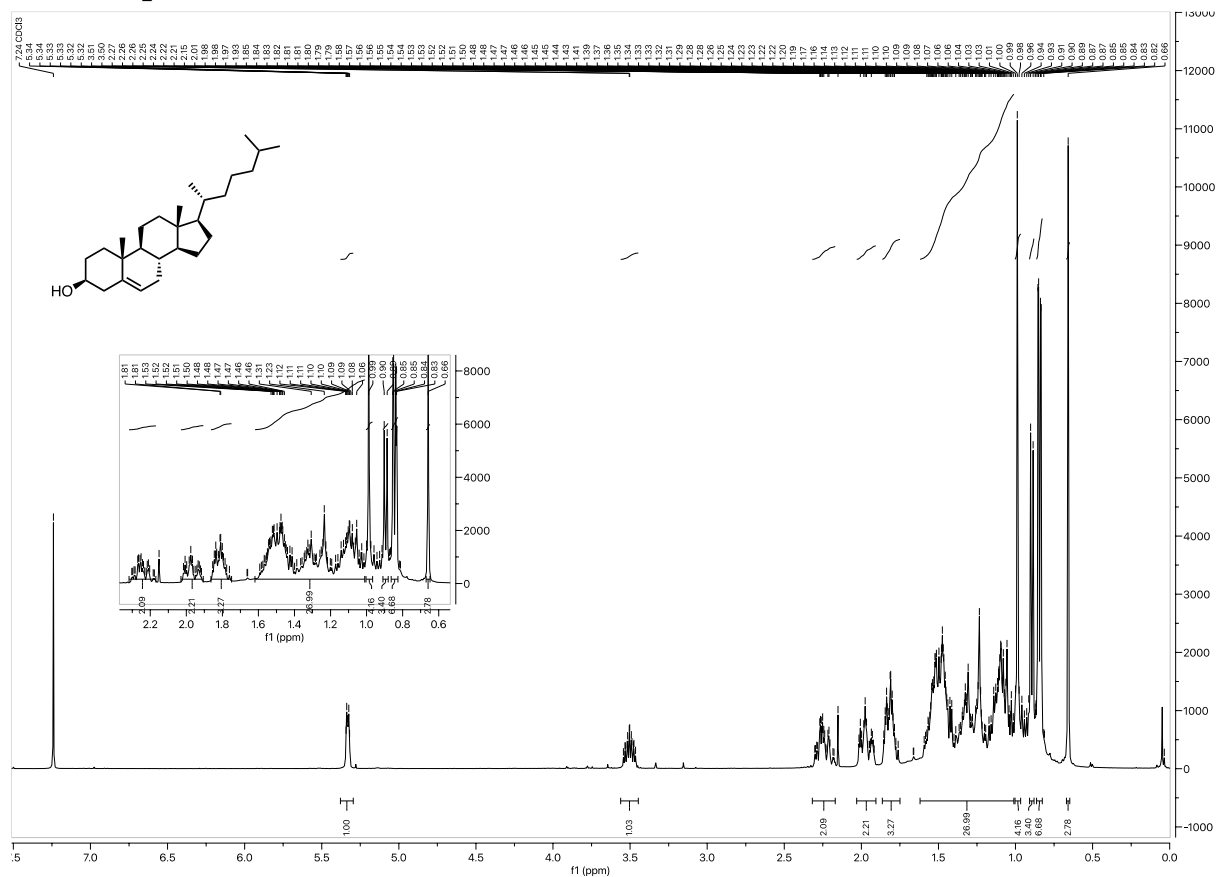
### <sup>1</sup>H NMR spectrum of D2



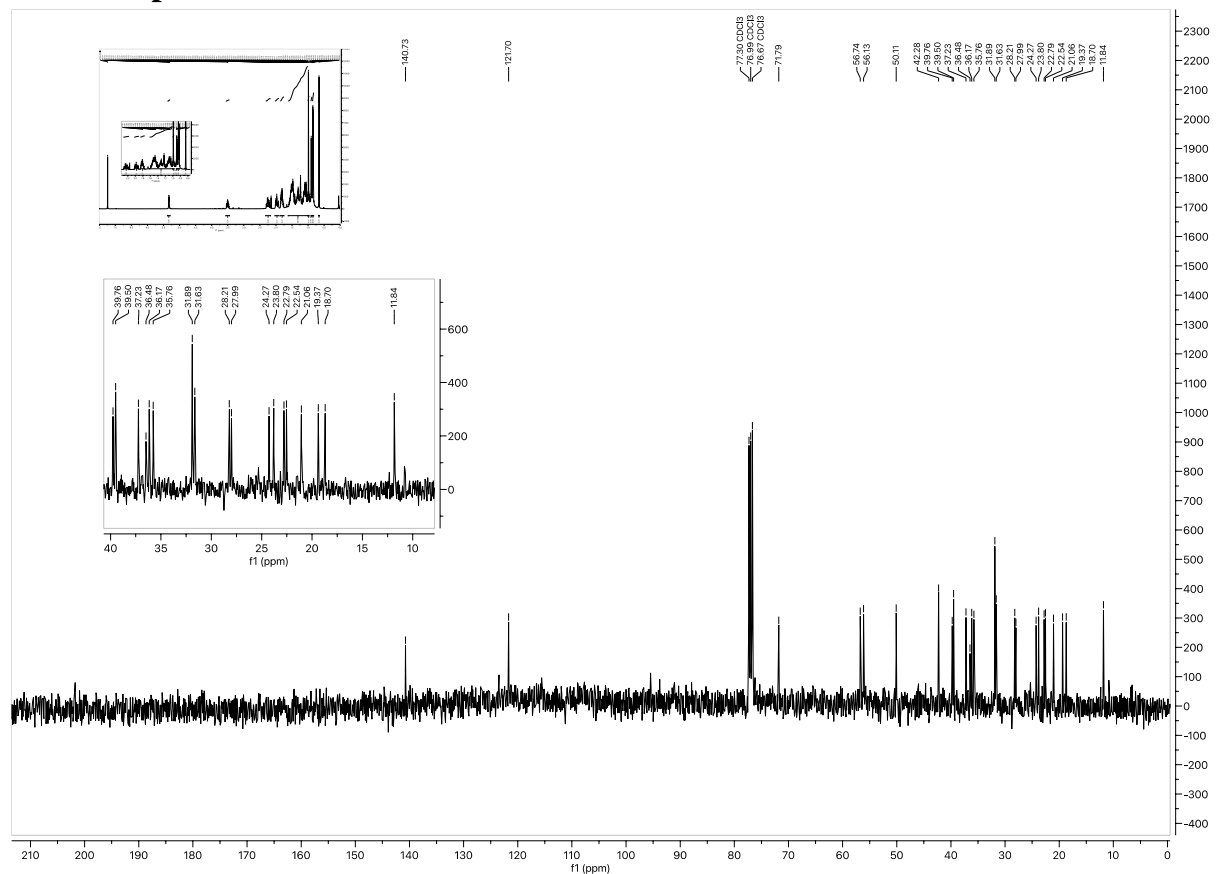
### <sup>13</sup>C NMR spectrum of D2



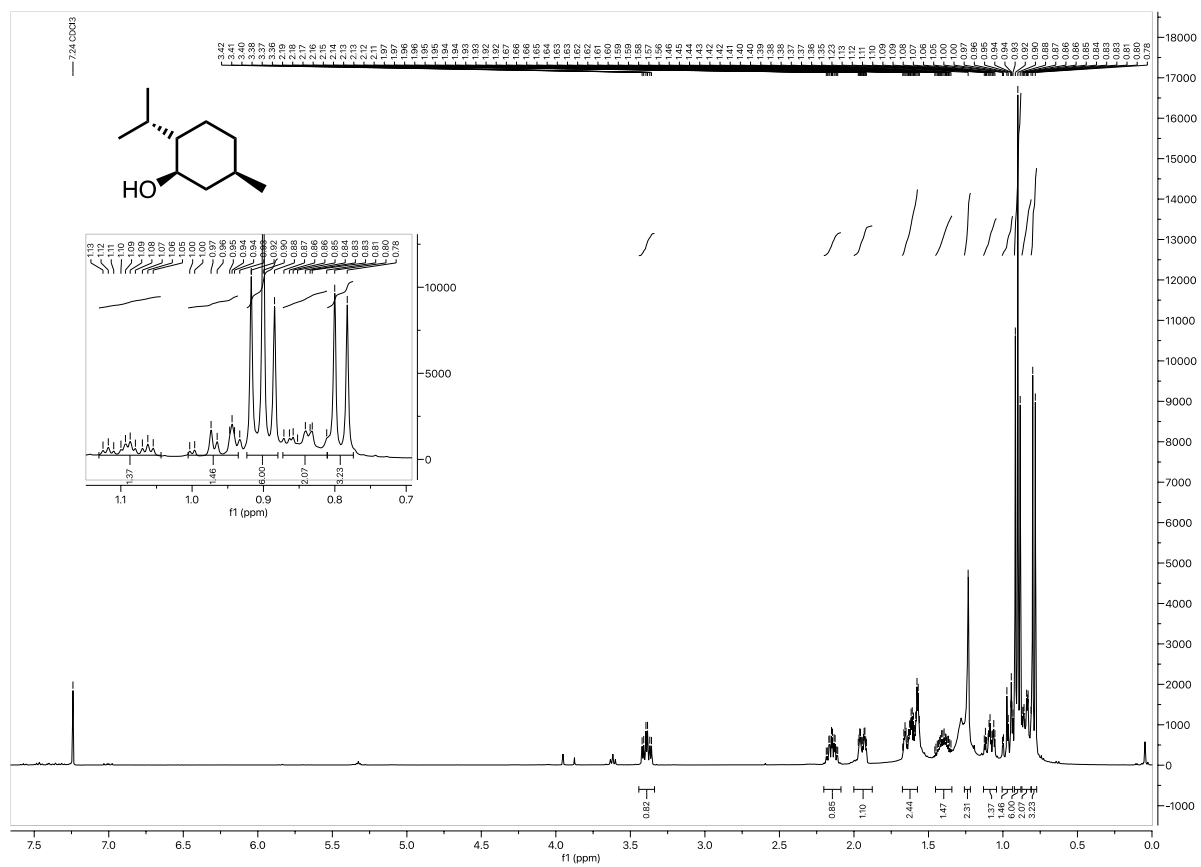
# <sup>1</sup>H NMR spectrum of D3



# <sup>13</sup>C NMR spectrum of D3



# **<sup>1</sup>H NMR spectrum of D4**



# **<sup>13</sup>C NMR spectrum of D4**

