Supplementary Information

Platinum on Carbon-Catalysed Site-Selective H-D Exchange Reaction of Allylic Alcohols Using Alkyl Amines as a Hydrogen Source

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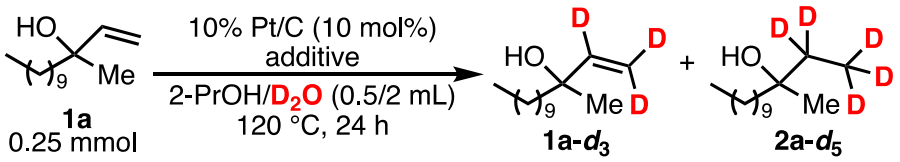
Contents

1. General

10% Pt/C catalyst was obtained from N.E. Chemcat Corporation, Japan. Unless otherwise noted, the substrates and solvents were purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 and 40–50 μm spherical, neutral). ^{1}H, ^{13}C, and ^{2}H NMR spectra were recorded on a JEOL ECZ 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or ECA 500 spectrometer (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{2}H: 77 MHz) at room temperature in $CDCl_3$ as a solvent and an internal standard (^{1}H NMR: δ = 0.00 for tetramethylsilane; ^{13}C NMR: δ = 77.0 for $CDCl_3$; ^{2}H NMR: δ = 7.26 for $CDCl_3$). The deuterium incorporation was assigned by ^{2}H NMR. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high-resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Melting points were measured by a SANSYO SMP-300 melting point apparatus. Optical rotations were measured by AP-300 automatic polarimeter (ATAGO Co. LTD.)

2. Detailed optimizations for H–D exchange reaction of 1a



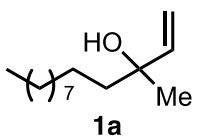
entry	additive	ave. D contents	yield

			1a-d_3	2a-d_5
1	^{n}Bu$_3$N	91	5	55
2	Et$_3$N	96	50	37
3	(^{i}Pr)$_2$EtN	95	26	39
4	*N*-ethylpiperidine	63	80	18
5	*N*-ethyltetramethylpiperidine	15	95	0
6	^{i}Pr$_2$NH	97	42	33
7	Et$_2$NH	44	87	4
8	amylamine	71	84	3
9	cyclopentylamine	54	93	7
10	cyclohexylamine	43	85	5
11	3-amino-1-propanol	12	84	0
12	glycine	10	70	0
13	alanine	4	71	0
14	benzylamine	73	83	2
15	*N*-benzylmethanesulfonamide	17	62	0
16	*N*-methylbenzylamine	31	99	0
17	4-methoxybenzylamine	58	86	6
18	NH$_4$OAc	9	72	0
19	NH$_4$HCO$_2$	21	69	7
20	amylamine[a)]	94	67	10
21	amylamine[a,b)]	95	65	10
22	amylamine[a,b,c)]	91	78	3
23	amylamine[a,c,d)]	95	79	5
24	amylamine[a,d,e)]	97	83	3

a) Amylamine (3.0 eq.) was added. b) Without 2-PrOH. c) Sodium acrylate (2.0 eq.) was added. d) Methylcyclohexane was added instead of 2-PrOH. e) Methyl acylate (2.0 eq.) was added.

3. Preparation of substrate

3-Methyltridec-1-en-3-ol (1a)

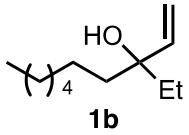


1a

To a solution of 2-dodecanone (3.7 g, 20 mmol) in THF (40 mL) was added vinylmagnesium bromide (1.0 M in THF, 22 mL, 22 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 25/1) to give 3-methyltridec-1-en-3-ol (**1a**, 2.7 g, 12.8 mmol) in 64% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.20 (dd, *J* = 17.3, 1.0 Hz, 1H), 5.04 (dd, *J* = 10.7, 1.0 Hz, 1H), 1.57–1.50 (m, 3H), 1.31–1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 111.4, 73.3, 42.4, 31.9, 30.0, 29.6(3C), 29.3, 27.6, 23.9, 22.7, 14.1; IR (ATR) cm^{-1}: 3547, 2956, 2925, 1641, 1461, 1410, 1378, 1268, 1198, 1144, 1055; ESI-HRMS m/z: 235.2024 ([M+Na]$^+$); Calcd. for $C_{14}H_{28}ONa$: 235.2032.

3-Ethyldec-1-en-3-ol (1b)

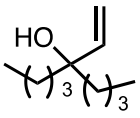


1b

To a solution of 3-decanone (737.3 mg, 4.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (1.0 M in THF, 4.8 mL, 4.8 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give 3-ethyldec-1-en-3-ol (**1b**, 575.1 mg, 3.1 mmol) in 78% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.19 (dd, *J* = 17.4, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.6, 1.6 Hz, 1H), 1.61–1.44 (m, 5H), 1.27 (br, 10H), 0.89–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 112.3, 75.6, 40.3, 33.1, 31.8, 30.0, 29.3, 23.4, 22.6, 14.1, 7.7; IR (ATR) cm^{-1}: 3459, 2958, 2925, 2854, 1641, 1461, 1412, 1378, 1268, 1198, 1144, 1059; ESI-HRMS m/z: 207.1670 ([M+Na]$^+$); Calcd. for $C_{12}H_{24}ONa$: 207.1719.

5-Vinylnonan-5-ol (1c)

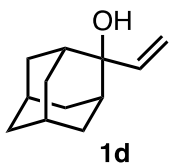


1c

To a solution of 5-nonanone (1.2 g, 7.0 mmol) in THF (15 mL) was added vinylmagnesium bromide (1.0 M in THF, 10.5 mL, 10.5 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give 5-vinylnonan-5-ol (**1c**, 918.5 mg, 5.4 mmol) in 77% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.19 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.4 Hz, 1H), 1.57–1.44 (m, 5H), 1.34–1.22 (m, 8H), 0.91–0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 112.0, 75.4, 40.5, 25.6, 23.1, 14.0; IR (ATR) cm^{-1}: 3463, 3085, 2956, 2933, 2862, 1640, 1466, 1412, 1378, 1340, 1284, 1255, 1237, 1145, 1079, 1044; ESI-HRMS m/z: 209.1300 ([M+K]$^+$); Calcd. for $C_{11}H_{22}OK$: 209.1302.

(1*r*,3*r*,5*r*,7*r*)-2-Vinyladamantan-2-ol (1d)



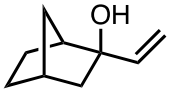
1d

To a solution of 2-adamantanone (450.7 mg, 3.0 mmol) in THF (5 mL) was added vinylmagnesium bromide (1.0 M in THF, 4.5 mL, 4.5 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture

was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give (1*r*,3*r*,5*r*,7*r*)-2-vinyladamantan-2-ol (**1d**, 480.8 mg, 2.7 mmol) in 90% yield as a colorless solid.

MP: 48–49 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.36 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.7, 1.2 Hz, 1H), 2.26 (d, *J* = 12.4 Hz, 2H), 1.90–1.82 (m, 6H), 1.74–1.69 (m, 4H), 1.62–1.56 (m, 2H), 1.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 113.5, 74.7, 37.9, 37.8, 34.6, 32.7, 27.3, 27.1; IR (ATR) cm^{-1}: 3337, 2894, 2854, 1636, 1451, 1406, 1351, 1333, 1297, 1281, 1205, 1186, 1156, 1099, 1086, 1070, 1054, 1041, 1011; ESI-HRMS m/z: 179.1436 ([M+H]$^+$); Calcd. for $C_{12}H_{19}O$: 179.1430.

(1*S*,2*R*,4*R*)-2-Vinylbucyclo[2.2.1]heptan-2-ol (1e)

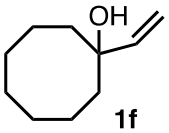


1e

To a solution of norcamphor (330.5 mg, 3.0 mmol) in THF (5 mL) was added vinylmagnesium bromide (1.0 M in THF, 4.5 mL, 4.5 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give (1*S*,2*R*,4*R*)-2-vinylbucyclo[2.2.1]heptan-2-ol (**1e**, 265.9 mg, 1.9 mmol) in 64% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.17 (dd, *J* = 17.4, 0.9 Hz, 1H), 4.99 (dd, *J* = 11.1, 0.9 Hz, 1H), 2.24 (s, 1H), 2.11 (s, 1H), 2.06–1.99 (m, 1H), 1.88–1.82 (m, 1H), 1.64–1.53 (m, 3H), 1.42–1.33 (m, 2H), 1.31–1.26 (m, 1H), 1.18 (dd, *J* = 13.0, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 110.2, 79.2, 47.3, 44.9, 38.2, 37.2, 28.8, 21.8; IR (ATR) cm^{-1}: 3356, 3085, 2949, 2870, 1729, 1638, 1476, 1453, 1413, 1373, 1308, 1291, 1256, 1234, 1194, 1162, 1124, 1071, 1048, 1016; ESI-HRMS m/z: 161.0915 ([M+Na]$^+$); Calcd. for $C_9H_{14}ONa$: 161.0937.

1-Vinylcyclooctan-1-ol (1f)

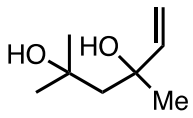


1f

To a solution of cyclooctanone (504.8 mg, 4.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (1.0 M in THF, 6.0 mL, 6.0 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give 1-vinylcyclooctan-1-ol (**1f**, 382.4 mg, 2.5 mmol) in 83% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.22 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.02 (dd, *J* = 10.8, 1.3 Hz, 1H), 1.81–1.74 (m, 2H), 1.71–1.63 (m, 7H), 1.55–1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 111.2, 75.2, 36.1, 28.1, 24.6, 21.9; IR (ATR) cm^{-1}: 3383, 3084, 3006, 2919, 2852, 1639, 1473, 1446, 1413, 1360, 1291, 1262, 1239, 1159, 1141, 1091, 1077, 1041; ESI-HRMS m/z: 177.1250 ([M+Na]$^+$); Calcd. for $C_{10}H_{18}ONa$: 177.1250.

2,4-Dimethylhex-5-ene-2,4-diol (1g)

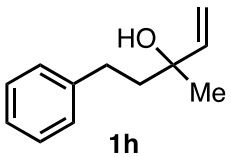


1g

To a solution of 4-hydroxy-4-methyl-2-pentanone (464.6 mg, 4.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (1.0 M in THF, 6.0 mL, 6.0 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1) to give 2,4-dimethylhex-5-ene-2,4-diol (**1g**, 236.5 mg, 1.64 mmol) in 41% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06–5.97 (m, 1H), 5.35–5.29 (m, 1H), 5.06–5.01 (m, 1H), 4.15–4.09 (m, 1H), 3.72–3.53 (m, 1H), 1.91–1.86 (m, 1H), 1.79–1.73 (m, 1H), 1.31–1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 111.0, 74.2, 72.6, 51.4, 32.8, 31.6, 30.2; IR (ATR) cm^{-1}: 3329, 3091, 2971, 2930, 1643, 1456, 1407, 1382, 1367, 1336, 1293, 1205, 1176, 1073, 1017; ESI-HRMS m/z: 167.1080 ([M+Na]$^+$); Calcd. for $C_8H_{16}O_2Na$: 167.1043.

3-Methyl-5-phenylpent-1-en-3-ol (1h)

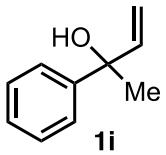


1h

To a solution of 1-phenyl-3-butanone (741.0 mg, 5.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (1.0 M in THF, 7.5 mL, 7.5 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 3-methyl-5-phenylpent-1-en-3-ol (**1h**, 759.9 mg, 4.3 mmol) in 86% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 2H), 7.19–7.15 (m, 3H), 5.96 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.26 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.11 (dd, *J* = 10.9, 1.2 Hz, 1H), 2.71–2.59 (m, 2H), 1.91–1.77 (m, 2H), 1.61 (br, 1H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 142.3, 128.4, 128.3, 125.7, 112.0, 73.2, 44.0, 30.3, 27.9; IR (ATR) cm^{-1}: 3399, 3085, 3062, 3026, 2973, 2932, 2864, 1642, 1603, 1496, 1454, 1410, 1370, 1267, 1216, 1155, 1104, 1069, 1030; ESI-HRMS m/z: 177.1263 ([M+H]$^+$); Calcd. for $C_{12}H_{17}O$: 177.1274.

2-Phenylbut-3-en-2-ol (1i)



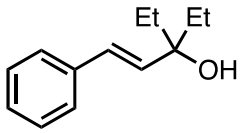
1i

To a solution of acetophenone (520.6 mg, 4.0 mmol) in THF (10 mL) was added vinylmagnesium bromide (1.0 M in THF, 8.0 mL, 8.0 mmol) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 2-phenylbut-3-en-2-ol (**1i**, 425.6 mg, 2.9 mmol) in 72% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.25–7.21 (m, 1H), 6.14 (dd, *J* = 17.3,

10.5, Hz, 1H), 5.27 (d, J = 17.3 Hz, 1H), 5.12 (d, J = 10.5 Hz, 1H), 2.24–2.22 (m, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.7, 128.1, 126.9, 125.1, 112.2, 74.7, 29.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference 1.

1,1- Diethyl-3-phenyl-2-propenol (1l)

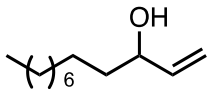


1l

To a solution of ethyl cinnamate (356.4 mg, 2.0 mmol) in THF (10 mL) was added ethylmagnesium bromide (1.0 M in THF, 8.0 mL, 8.0 mmol) at 0 ºC under argon. The reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 1,1,-diethyl-3-phenyl-2-prppenol (**1l**, 76.1 mg, 0.40 mmol) in 27% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.39 (m, 2H), 7.33–7.29 (m, 2H), 7.25–7.20 (m, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.18 (d, J = 16.0 Hz, 1H), 1.69–1.60 (m, 4H), 1.52 (br, 1H), 0.91 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.2, 128.5, 128.1, 127.2, 126.3, 75.8, 33.3, 7.9. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference 2.

1-Dodecden-3-ol (1n)

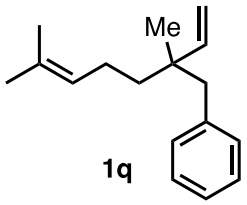


1n

To a solution of decanal (624.8 mg, 4.0 mmol) in THF (20 mL) was added vinylmagnesium bromide (1.0 M in THF, 8.0 mL, 8.0 mmol) at 0 ºC under argon. The reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 1-dodecden-3-ol (**1n**, 663.6 mg, 3.6 mmol) in 90% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.90–5.83 (m, 1H), 5.24–5.20 (m, 1H), 5.11–5.09 (m, 1H), 4.09 (d, J = 5.5 Hz, 1H), 1.60–1.47 (m, 3H), 1.40–1.26 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 114.5, 73.3, 37.0, 31.9, 29.6, 29.5(2C), 29.3, 25.3, 22.7, 14.1. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference 3.

(2-Ethenyl-2,6-dimethyl-5-hepten-1-yl)benzene (1q)



1q

To a suspension of zinc chloride (1.0 g, 8.0 mmol), lithium chloride (339.0 mg, 8.0 mmol), and copper(II) trifluoromethanesulfonate (144.0 mg, 0.4 mmol) in THF (20 mL) was added benzylmagnesium chloride (1.0 M in THF, 8.0 mL, 8.0 mmol) at -78 ºC under argon. The reaction mixture was stirred at 0 °C for 30 min. A solution of geranyl chloride (340.0 mg, 2.0 mmol) in THF (5 mL) was added to the reaction mixture at -30 °C. The reaction mixture was stirred at 0 °C

for 3 h. The reaction mixture was quenched by H_2O and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane) and PTLC to give (2-ethenyl-2,6-dimethyl-5-hepten-1-yl)benzene (**1q**, 78.2 mg, 0.34 mmol) in 17% yield as a colorless oil.

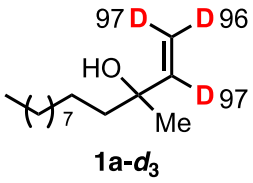
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.17 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 5.77 (dd, J = 17.6, 11.0 Hz, 1H), 5.07 (t, J = 6.6 Hz, 1H), 5.00 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 17.6 Hz, 1H), 2.64–2.56 (m, 2H), 1.98–1.89 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.39–1.29 (m, 2H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 138.5, 131.1, 130.7, 127.5, 125.8, 124.9, 112.1, 48.1, 40.8, 40.4, 25.7, 23.0, 21.9, 17.6. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference 4.

4. General procedure

A reaction mixture of an allylic alcohol derivative (0.25 mmol), 10% Pt/C (48.8 mg, 250 μmol), amylamine (87.0 μL, 0.75 mmol), and methyl acrylate (45.0 μL, 0.50 mmol) in methylcyclohexane (0.5 mL) and D_2O (2 mL) was heated to 120 °C and stirred for 24 h in a test tube. The reaction mixture was cooled to room temperature and filtered through a membrane filter (Millipore, Millex®-LH, 0.2 μm) together with ethyl acetate (10 mL) and H_2O (10 mL) to remove the catalyst, and the combined filtrates were extracted with ethyl acetate (10 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified using silica-gel column chromatography to yield the deuterated product.

5. Spectroscopic data of deuterated products

3-Methyltridec-1-en-3-ol-*d*$_3$ (1a-*d*$_3$)

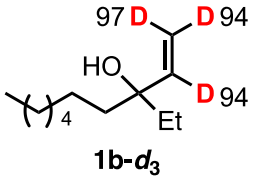


1a-*d*$_3$

According to General procedure, 3-methyltridec-1-en-3-ol (**1a**, 53.1 mg, 0.25 mmol) was used. 3-Methyltridec-1-en-3-ol-d_3 (**1a-*d*$_3$**, 44.6 mg, 0.21 mmol) was obtained in 84% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93–5.90 (m, 0.03H), 5.18–5.16 (m, 0.04H), 5.04–5.01 (m, 0.03H), 1.56–1.49 (m, 2H), 1.31–1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.93 (br), 5.20 (br), 5.05 (br).

3-Ethyldec-1-en-3-ol-*d*$_3$ (1b-*d*$_3$)

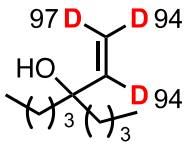


1b-*d*$_3$

According to General procedure, 3-ethyldec-1-en-3-ol (**1b**, 46.1 mg, 0.25 mmol) was used. 3-Ethyldec-1-en-3-ol-d_3 (**1b-*d*$_3$**, 34.6 mg, 0.19 mmol) was obtained in 75% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83–5.80 (m, 0.06H), 5.18–5.16 (m, 0.06H), 5.11–5.08 (m, 0.03H), 1.61–1.43 (m, 4H), 1.40 (br, H), 1.31–1.27 (m, 10H), 0.91–0.82 (m, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.83 (br), 5.20 (br), 5.12 (br).

5-Vinylnonan-5-ol-*d*$_3$ (1c-*d*$_3$)

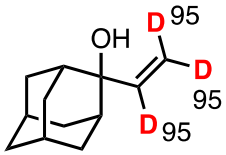


1c-*d*$_3$

According to General procedure, 5-vinylnonan-5-ol (**1c**, 42.6 mg, 0.25 mmol) was used. 5-Vinylnonan-5-ol-d_3 (**1c-*d*$_3$**, 31.9 mg, 0.19 mmol) was obtained in 75% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86–5.79 (m, 0.06H), 5.21–5.15 (m, 0.06H), 5.11–5.06 (m, 0.03H), 1.59–1.43 (m, 4H), 1.40 (br, 1H), 1.35–1.22 (m, 8H), 0.90 (t, J = 6.8 Hz, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.85 (br), 5.20 (br), 5.11 (br).

(1*r*,3*r*,5*r*,7*r*)-2-Vinyladamantan-2-ol-*d*$_3$ (1d-*d*$_3$)

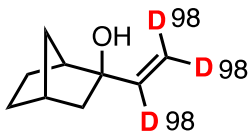


1d-*d*$_3$

According to General procedure, (1*r*,3*r*,5*r*,7*r*)-2-vinyladamantan-2-ol (**1d**, 44.6 mg, 0.25 mmol) was used. (1*r*,3*r*,5*r*,7*r*)-2-Vinyladamantan-2-ol-d_3 (**1d-*d*$_3$**, 42.3 mg, 0.24 mmol) was obtained in 95% yield as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (br, 0.05H), 5.35–5.33 (m, 0.05H), 5.16–5.15 (m, 0.05H), 2.26 (d, J = 12.4 Hz, 2H), 1.90–1.82 (m, 6H), 1.75–1.70 (m, 4H), 1.59–1.56 (m, 2H), 1.41 (s, 1H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 6.30 (br), 5.36 (br), 5.17 (br).

(1*S*,2*R*,4*R*)-2-Vinylbucyclo[2.2.1]heptan-2-ol-*d*$_3$ (1e-*d*$_3$)

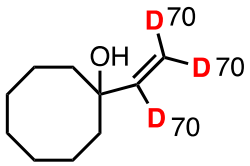


1e-*d*$_3$

According to General procedure, (1*S*,2*R*,4*R*)-2-vinylbucyclo[2.2.1]heptan-2-ol (**1e**, 34.6 mg, 0.25 mmol) was used. (1*S*,2*R*,4*R*)-2-Vinylbucyclo[2.2.1]heptan-2-ol-d_3 (**1d-*d*$_3$**, 26.6 mg, 0.19 mmol) was obtained in 77% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (br, 0.02H), 5.16–5.15 (m, 0.02H), 4.99–4.98 (m, 0.02H), 2.25–2.23 (m, 1H), 2.12–2.11 (m, 1H), 2.08–2.00 (m, 1H), 1.88–1.83 (m, 1H), 1.64–1.53 (m, 2H), 1.43–1.35 (m, 3H), 1.31–1.25 (m, 1H), 1.18 (dd, J = 13.0, 3.4 Hz, 1H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 6.08 (br), 5.18 (br), 5.01 (br).

1-Vinylcyclooctan-1-ol-*d*$_3$ (1f-*d*$_3$)

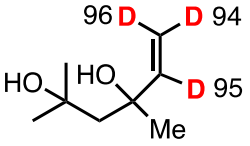


1f-*d*$_3$

According to General procedure, 1-vinylcyclooctan-1-ol (**1f**, 38.6 mg, 0.25 mmol) was used. 1-Vinylcyclooctan-1-ol-*d*$_3$ (**1f-*d*$_3$**, 30.5 mg, 0.20 mmol) was obtained in 79% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04–5.98 (m, 0.30H), 5.25–5.19 (m, 0.30H), 5.04–5.00 (m, 0.30H), 1.81–1.74 (m, 2H), 1.72–1.63 (m, 6H), 1.56–1.47 (m, 6H), 1.32 (br, 1H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 6.03 (br), 5.23 (br), 5.05 (br).

2,4-Dimethylhex-5-ene-2,4-diol-*d*$_3$ (1g-*d*$_3$)

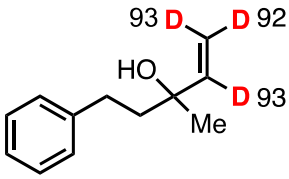


1g-*d*$_3$

According to General procedure, 2,4-dimethylhex-5-ene-2,4-diol (**1g**, 36.1 mg, 0.25 mmol) was used. 2,4-Dimethylhex-5-ene-2,4-diol-*d*$_3$ (**1g-*d*$_3$**, 35.3 mg, 0.25 mmol) was obtained in 98% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06–6.01 (m, 0.05H), 5.35–5.29 (m, 0.06H), 5.07–5.03 (m, 0.04H), 3.80 (br, 1H), 2.99 (br, 1H), 1.90 (d, *J* = 14.8 Hz, 1H), 1.77 (d, *J* = 14.8 Hz, 1H), 1.31–1.28 (m, 9H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 6.03 (br), 5.32 (br), 5.05 (br).

3-Methyl-5-phenylpent-1-en-3-ol-*d*$_3$ (1h-*d*$_3$)

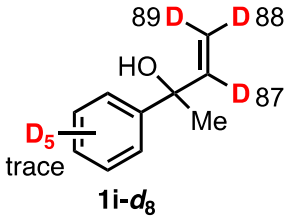


1h-*d*$_3$

According to General procedure, 3-methyl-5-phenylpent-1-en-3-ol (**1h**, 44.1 mg, 0.25 mmol) was used. 3-Methyl-5-phenylpent-1-en-3-ol-*d*$_3$ (**1h-*d*$_3$**, 42.3 mg, 0.24 mmol) was obtained in 96% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H), 7.20–7.16 (m, 3H), 5.98–5.96 (m, 0.07H), 5.25–5.24 (m, 0.08H), 5.12–5.09 (m, 0.07H), 2.72–2.59 (m, 2H), 1.92–1.78 (m, 2H), 1.50 (br, 1H), 1.35 (s, 3H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 6.01 (br), 5.29 (br), 5.14 (br).

2-Phenylbut-3-en-2-ol-*d*$_8$ (1i-*d*$_8$)

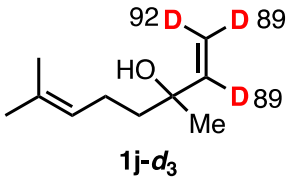


1i-*d*8

According to General procedure, 2-phenylbut-3-en-2-ol (**1i**, 37.1 mg, 0.25 mmol) was used. 2-Phenylbut-3-en-2-ol-d_8 (**1i-*d*8**, 36.3 mg, 0.25 mmol) was obtained in 98% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.46 (m, 2H), 7.36–7.32 (m, 2H), 7.27–7.23 (m, 1H), 6.21–6.14 (m, 0.13H), 5.32–5.26 (m, 0.12H), 5.16–5.12 (m, 0.11H), 1.95 (br, 1H), 1.65 (s, 3H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 7.51 (br), 6.21 (br), 5.32 (br), 5.17 (br).

Linalool-*d*3 (1j-*d*3)



1j-*d*3

According to General procedure, linalool (**1i**, 38.6 mg, 0.25 mmol) was used. Linalool-d_3 (**1j-*d*3**, 35.5 mg, 0.23 mmol) was obtained in 92% yield as a colorless oil.

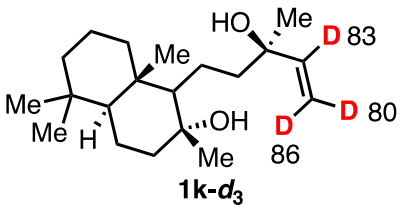
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93–5.88 (m, 0.11H), 5.21–5.18 (m, 0.11H), 5.15–5.10 (m, 1H), 5.06–5.04 (m, 0.08H), 2.10–1.95 (m, 2H), 1.68 (s, 3H), 1.63–1.52 (m, 5H), 1.28 (s, 3H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.93 (br), 5.22 (br), 5.08 (br).

Unlabeled linalool (**1j**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dd, J = 17.2, 10.8 Hz, 1H), 5.21 (dd, J = 17.2, 1.2 Hz, 1H), 5.14–5.10 (m, 1H), 5.06 (dd, J = 10.8, 1.2 Hz, 1H), 2.10–1.95 (m, 2H), 1.73 (br, 1H), 1.68 (s, 3H), 1.63–1.50 (m, 5H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 131.9, 124.3, 111.6, 73.4, 42.0, 27.8, 25.6, 22.7, 17.6.

Spectroscopic data of ^{1}H and ^{13}C NMR were measured for commercial linalool (TCI).

Sclareol-*d*3 (1k-*d*3)



1k-*d*3

According to General procedure, scraleol (**1k**, 77.1 mg, 0.25 mmol) was used. Scraleol-d_3 (**1k-*d*3**, 75.6 mg, 0.25 mmol) was obtained in 98% yield as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.96–5.90 (m, 0.17H), 5.23–5.18 (m, 0.20H), 5.03–4.99 (m, 0.16H), 1.86–1.82 (m, 1H), 1.68–1.23 (m, 14H), 1.15–1.11 (m, 5H), 0.97–0.90 (m, 2H), 0.86 (s, 3H), 0.78 (s, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.94 (br), 5.21 (br), 5.06 (br).

$[\alpha]_D^{20}$ = +27.9 ($CHCl_3$, c = 0.1)

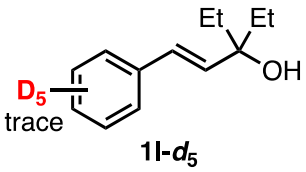
Unlabeled sclareol (**1k**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.22 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.02 (dd, *J* = 10.8, 1.4 Hz, 1H), 1.87–1.80 (m, 1H), 1.67–1.20 (m, 14H), 1.17–1.10 (m, 5H), 0.98–0.90 (m, 2H), 0.86 (s, 3H), 0.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 111.1, 74.7, 73.6, 61.6, 56.0, 44.9, 44.3, 41.9, 39.6, 39.2, 33.4, 33.2, 27.2, 24.2, 21.5, 20.5, 19.0, 18.4, 15.3.

$[\alpha]_D^{20}$ = +28.0 ($CHCl_3$, c = 0.1)

Spectroscopic data of ^{1}H and ^{13}C NMR were measured for commercial sclareol (TCI).

1,1- Diethyl-3-phenyl-2-propenol-*d*$_5$ (1l-*d*$_5$)

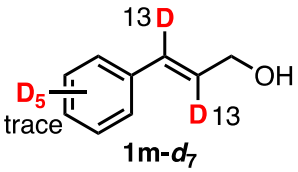


1l-*d*$_5$

According to General procedure, 1,1,-diethyl-3-phenyl-2-prppenol (**1l**, 47.6 mg, 0.25 mmol) was used. 1,1,-diethyl-3-phenyl-2-prppenol-d_5 (**1l-*d*$_5$**, 31.0 mg, 0.16 mmol) was obtained in 65% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.38 (m, 2H), 7.33–7.30 (m, 2H), 7.24–7.20 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 1.0 Hz, 1H), 1.70–1.59 (m, 4H), 1.52 (br, 1H), 0.91 (t, *J* = 7.3 Hz, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 7.36 (br).

Cinnamyl alcohol-*d*$_7$ (1m-*d*$_7$)



1m-*d*$_7$

According to General procedure, cinnamyl alcohol (**1m**, 33.5 mg, 0.25 mmol) was used. Cinnamyl alcohol-***d*$_7$** (**1m-*d*$_7$**, 15.6 mg, 0.12 mmol) was obtained in 47% yield as a colorless oil.

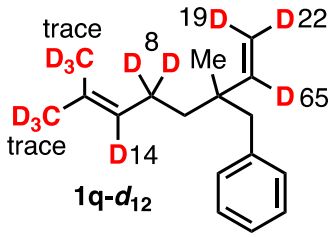
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H), 7.34–7.29 (m, 2H), 7.26–7.24 (m, 1H), 6.64–6.57 (m, 0.87H), 6.40–6.33 (m, 0.87H), 4.32 (dd, *J* = 5.4, 1.4 Hz, 2H), 1.65 (br, 1H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 7.42 (br), 6.64 (br), 6.39 (br).

Unlabeled cinnamyl alcohol (**1m**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.23 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.40–6.33 (m, 1H), 4.32 (dd, *J* = 5.8, 1.6 Hz, 2H), 1.93–1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 131.1, 128.6, 128.4, 127.7, 126.4, 63.7.

Spectroscopic data of ^{1}H and ^{13}C NMR were measured for commercial cinnamyl alcohol (TCI).

(2-Ethenyl-2,6-dimethyl-5-hepten-1-yl)benzene-*d*$_{12}$ (1q-*d*$_{12}$)

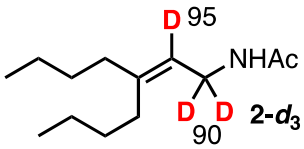


According to General procedure, (2-ethenyl-2,6-dimethyl-5-hepten-1-yl)benzene (**1q**, 57.1 mg, 0.25 mmol) was used. (2-Ethenyl-2,6-dimethyl-5-hepten-1-yl)benzene-*d*$_{12}$ (**1q-*d*$_{12}$**, 50.5 mg, 0.22 mmol) was obtained in 89% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.16 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 5.80–5.73 (m, 0.35H), 5.09–5.06 (m, 0.86H), 5.01–4.97 (m, 0.78H), 4.84–4.79 (m, 0.81H), 2.63–2.56 (m, 2H), 1.94–1.89 (m, 1.85H), 1.67 (s, 3H), 1.58 (s, 3H), 1.38–1.28 (m, 2H), 0.95 (s, 3H); ^{2}H NMR (77 MHz, $CHCl_3$): δ 5.96–5.84 (m), 5.15 (br), 5.07 (br), 4.88 (br), 2.01 (br), 1.76–1.58 (m).

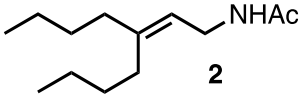
6. Procedures for applications

Synthesis of *N*-(3-butylhept-2-en-1-yl)acetamide-*d*$_3$ (2-*d*$_3$): To a solution of **1c-*d*$_3$** (42.6 mg, 0.25 mmol) and acetic anhydride (28 μL, 0.30 mmol) in acetonitrile (2 mL) was added cobalt(II) chloride (1.6 mg, 12.5 μmol) under argon at 80 °C and the reaction mixture was stirred for 12 h. The reaction mixture was extracted with ethyl acetate (20 mL × 2) and H_2O (5 mL). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 1/1) to give the deuterated *N*-(3-butylhept-2-en-1-yl)acetamide-*d*$_3$ (**2-*d*$_3$**, 41.7 mg, 0.20 mmol) in 79% yield as a colorless oil.



^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50 (br, 1H), 5.15 (br, 0.05H), 3.85–3.84 (m, 0.20H), 2.05–1.97 (m, 7H), 1.41–1.25 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): *δ* 5.16 (br), 3.80 (br).

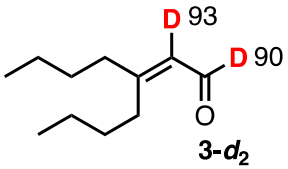
Spectroscopic data of *N*-(3-butylhept-2-en-1-yl)acetamide (**2**) without deuteration as an authentic sample.



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (br, 1H), 5.15 (t, *J* = 6.6 Hz, 1H), 3.85 (dd, *J* = 6.6, 6.6 Hz, 2H), 2.07–1.97 (m, 7H), 1.41–1.25 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 144.8, 119.4, 37.4, 36.4, 30.8,

30.1, 30.0, 23.2, 22.7, 22.5, 14.0(2C); IR (ATR) cm^{-1}: 3293, 2957, 2929, 2860, 1635, 1549, 1458, 1373, 1283, 1216, 1093, 1040, 1016; ESI-HRMS m/z: 212.2007 ($[M+H]^+$); Calcd. for $C_{13}H_{26}NO$: 212.2009.

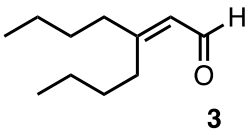
Synthesis of 3-butylhept-2-enal-*d*$_2$ (3-*d*$_2$): To a solution of **1c-*d*$_3$** (42.6 mg, 0.25 mmol) in dichloromethane (2 mL) was added pyridinium chlorochromate (107.8 mg, 0.50 mmol) under argon at room temperature and the reaction mixture was stirred for 12 h. The reaction mixture was extracted with ethyl acetate (20 mL × 2) and H_2O (5 mL). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 30/1) to give the deuterated 3-butylhept-2-enal-*d*$_2$ (**3-*d*$_2$**, 84.1 mg, 0.50 mmol) in quantitative yield as a colorless oil.



3-*d*$_2$

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (br, 0.10H), 5.86 (br, 0.03H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.23 (t, *J* = 7.8 Hz, 2H), 1.57–1.23 (m, 8H), 0.96–0.89 (m, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): *δ* 10.0 (br), 5.88 (br).

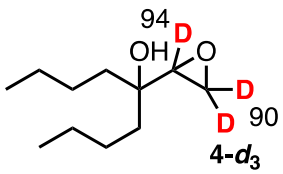
Spectroscopic data of 3-butylhept-2-enal (**3**) without deuteration as an authentic sample.



3

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 8.0 Hz, 1H), 2.56 (t, *J* = 8.1 Hz, 2H), 2.23 (t, *J* = 8.1 Hz, 2H), 1.55–1.45 (m, 4H), 1.42–1.29 (m, 4H), 0.96–0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.2, 169.2, 127.1, 37.7, 31.8, 31.1, 29.5, 22.7, 22.4, 13.8, 13.8; IR (ATR) cm^{-1}: 2958, 2931, 2862, 1731, 1672, 1628, 1465, 1379, 1342, 1293, 1215, 1169, 1135, 1098; ESI-HRMS m/z: 191.1430 ($[M+Na]^+$); Calcd. for $C_{11}H_{20}ONa$: 191.1406.

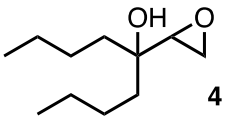
Synthesis of 5-(oxiran-2-yl)nonan-5-ol-*d*$_3$ (4-*d*$_3$): To a solution of **1c-*d*$_3$** (25.5 mg, 0.15 mmol) and vanadyl acetylacetonate (2.0 mg, 7.5 μmol) in dichloromethane (2 mL) was added *tert*-butyl hydroperoxide (70% in H_2O; 60 μL, 0.45 mmol) under argon at room temperature and the reaction mixture was stirred for 12 h. The reaction mixture was extracted with ethyl acetate (20 mL × 2) and H_2O (5 mL). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give the deuterated 5-(oxiran-2-yl)nonan-5-ol-*d*$_3$ (**4-*d*$_3$**, 24.0 mg, 0.13 mmol) in 86% yield as a colorless oil.



4-*d*$_3$

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95–2.95 (m, 0.06H), 2.82–2.80 (m, 0.10H), 2.72–2.70 (m, 0.10H), 1.65 (br), 1.63–1.48 (m, 4H), 1.43–1.25 (m, 8H), 0.94–0.88 (m, 6H); ^{2}H NMR (77 MHz, $CHCl_3$): *δ* 2.94 (br), 2.79 (br), 2.69 (br).

Spectroscopic data of 5-(oxiran-2-yl)nonan-5-ol (**4**) without deuteration as an authentic sample.



4

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (dd, J = 4.0, 3.1 Hz, 1H), 2.81 (dd, J = 5.3, 3.1 Hz, 1H), 2.71 (dd, J = 5.3, 4.0 Hz, 1H), 1.73 (br, 1H), 1.63–1.48 (m, 4H), 1.44–1.26 (m, 8H), 0.94–0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.6, 56.8, 43.5, 39.6, 36.4, 25.4, 25.3, 23.3, 23.2, 14.0(2C); IR (ATR) cm^{-1}: 3474, 2957, 2933, 2863, 1467, 1379, 1339, 1258, 1216, 1145, 1044, 1003; ESI-HRMS m/z: 209.1554 ($[M+Na]^+$); Calcd. for $C_{11}H_{22}O_2Na$: 209.1512.

7. References

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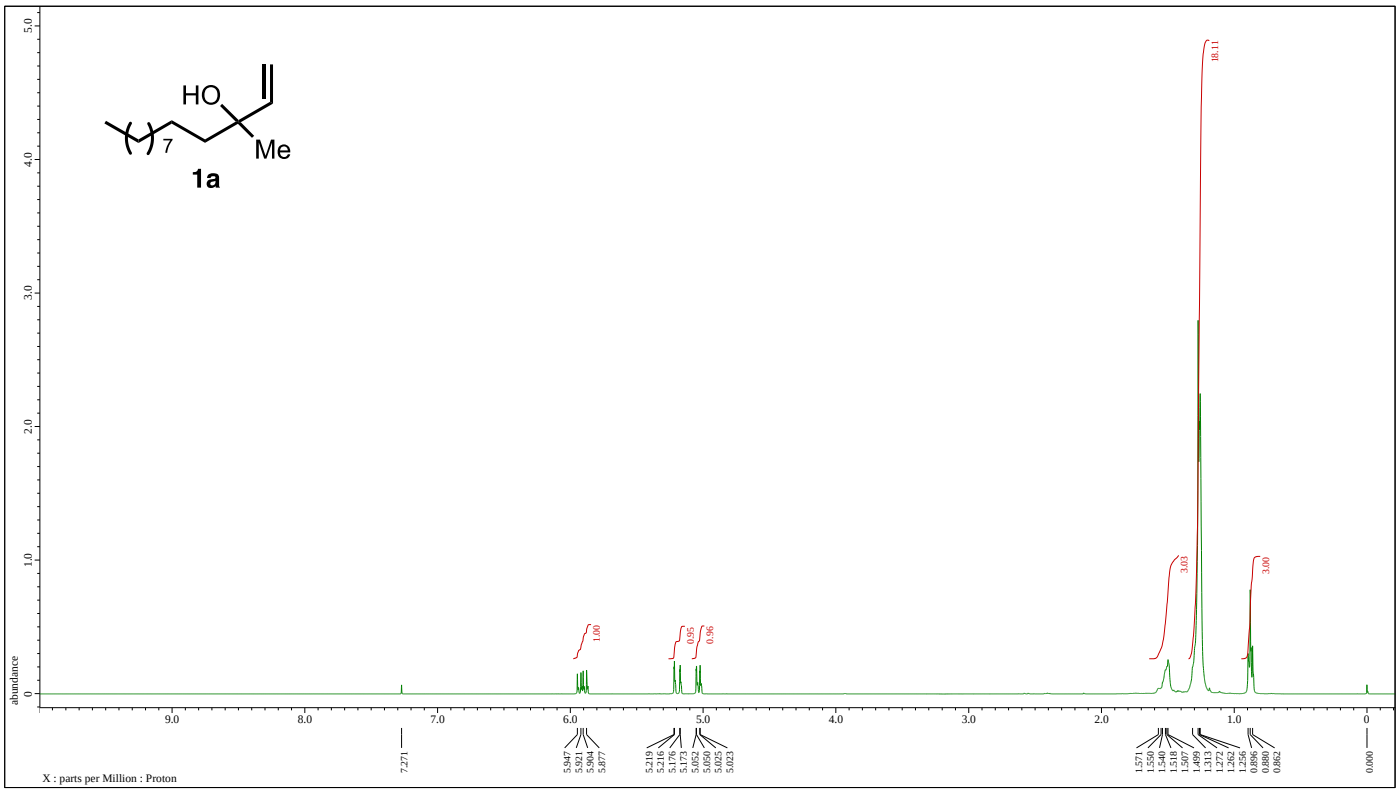
2. Kenta Morita, Reiya Ohta, Hiroshi Aoyama, Kenzo Yahata, Mitsuhiro Arisawa and Hiromichi Fujioka *Chem. Commun.* **2017**, *53*, 6605–6608.

3. Anthony N. Cuzzupe, Romina Di Florio, and Mark A. Rizzacasa *J. Org. Chem.* **2002**, *67*, 4392–4398.

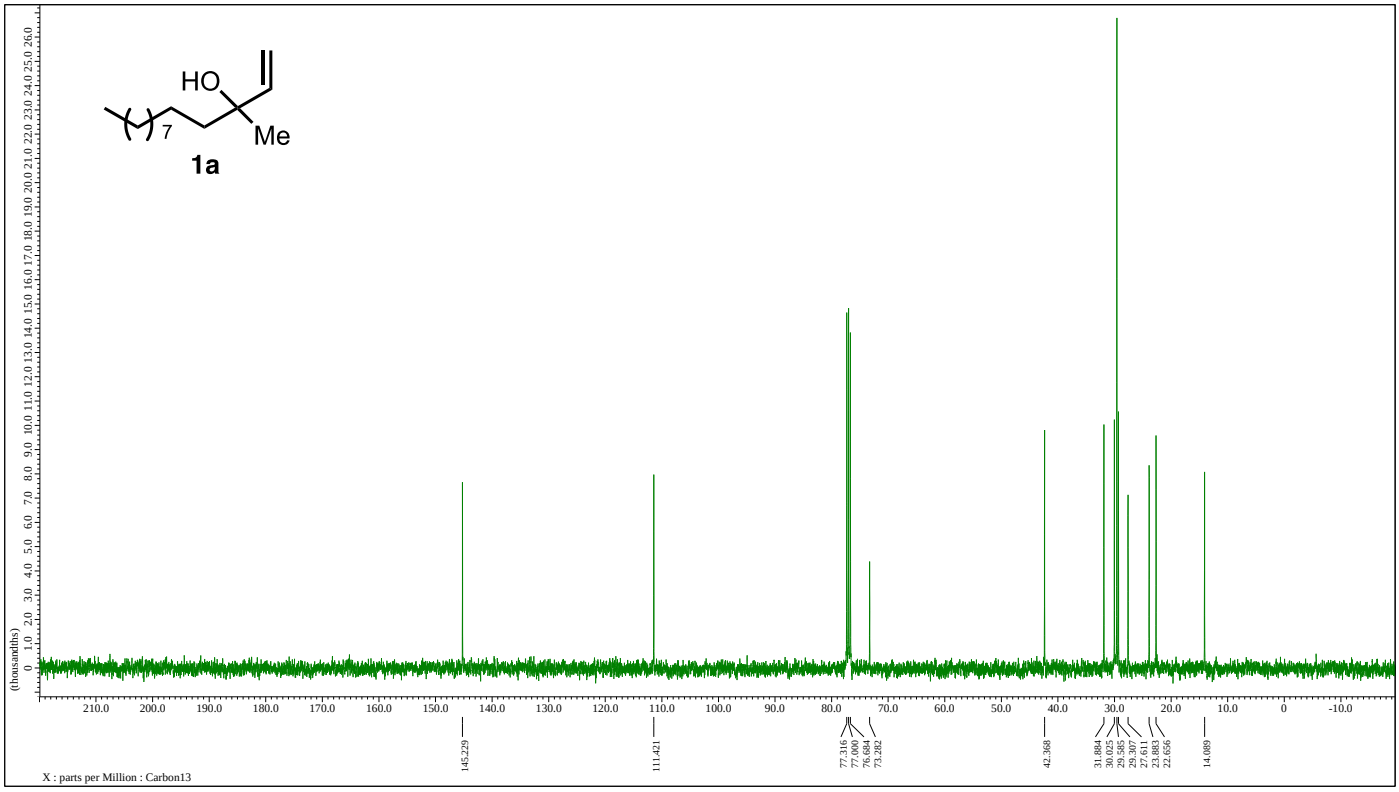
4. Nobutaka Fujii, Kazuo Nakai, Hiromu Habashita, Hidenori Yoshizawa, Toshiro Ibuka, Fabrice Garrido, André Mann, Yukiyasu Chounan, Yoshinori Yamamoto *Tetrahedron Lett.* **1993**, *34*, 4227–4230.

8. ^{1}H, ^{13}C, and ^{2}H NMR spectra

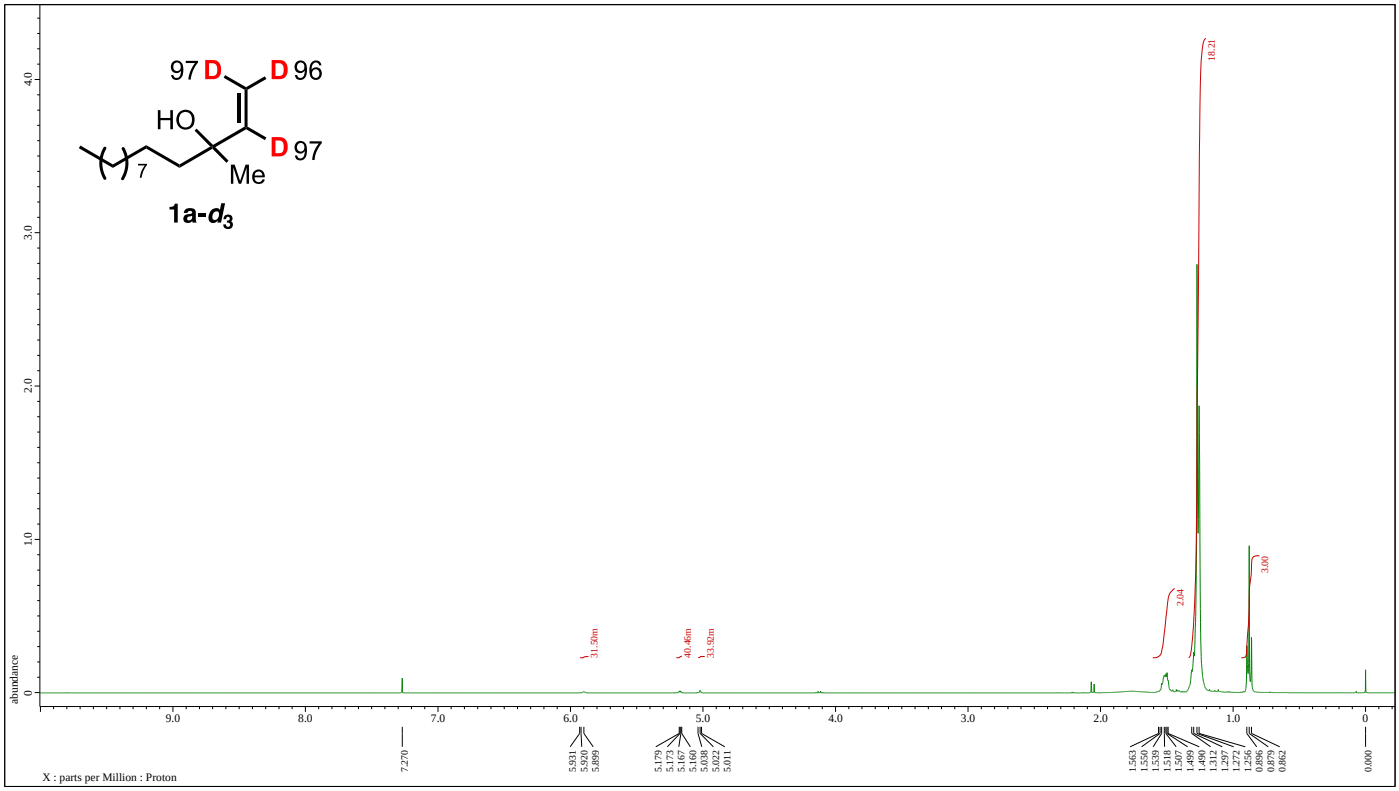
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



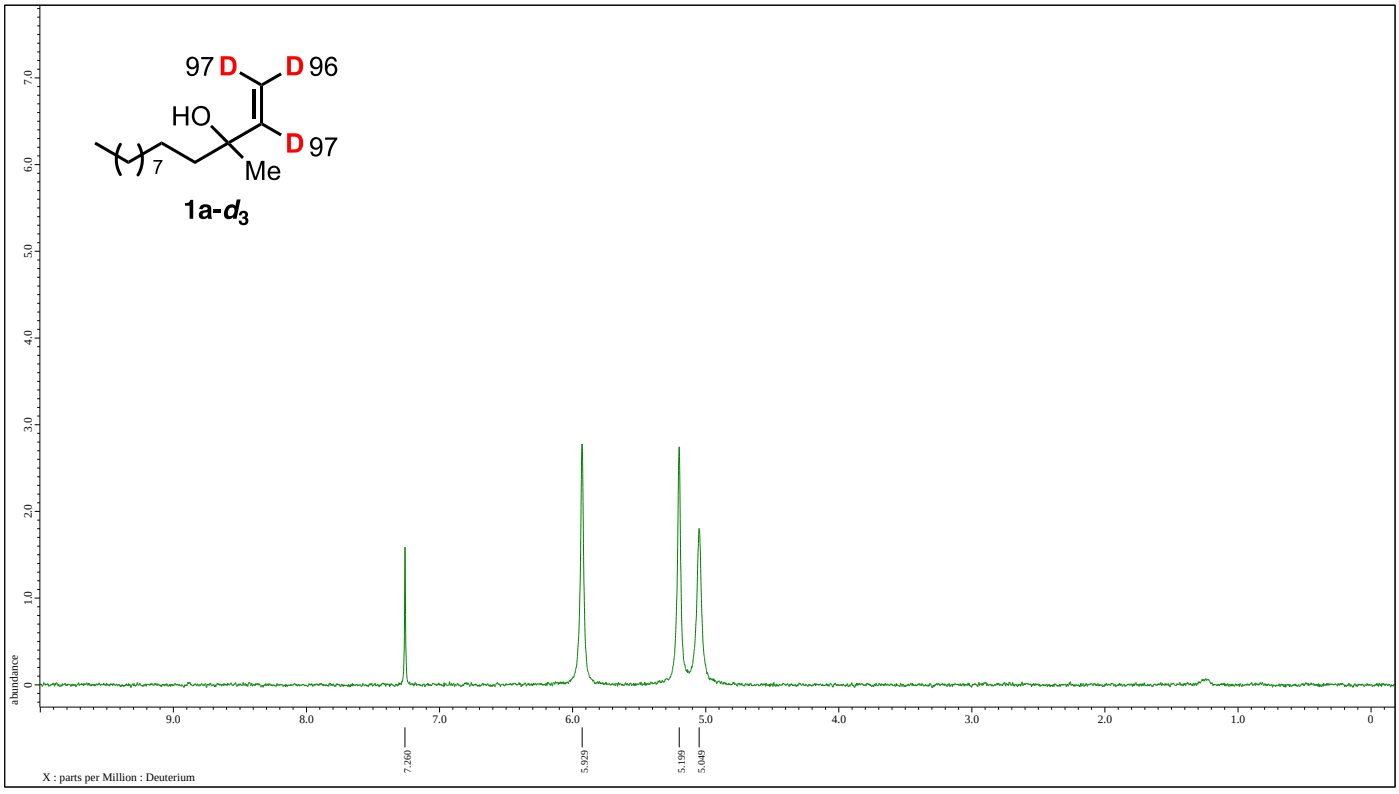
^{13}C NMR (100 MHz, $CDCl_3$) of **1a**



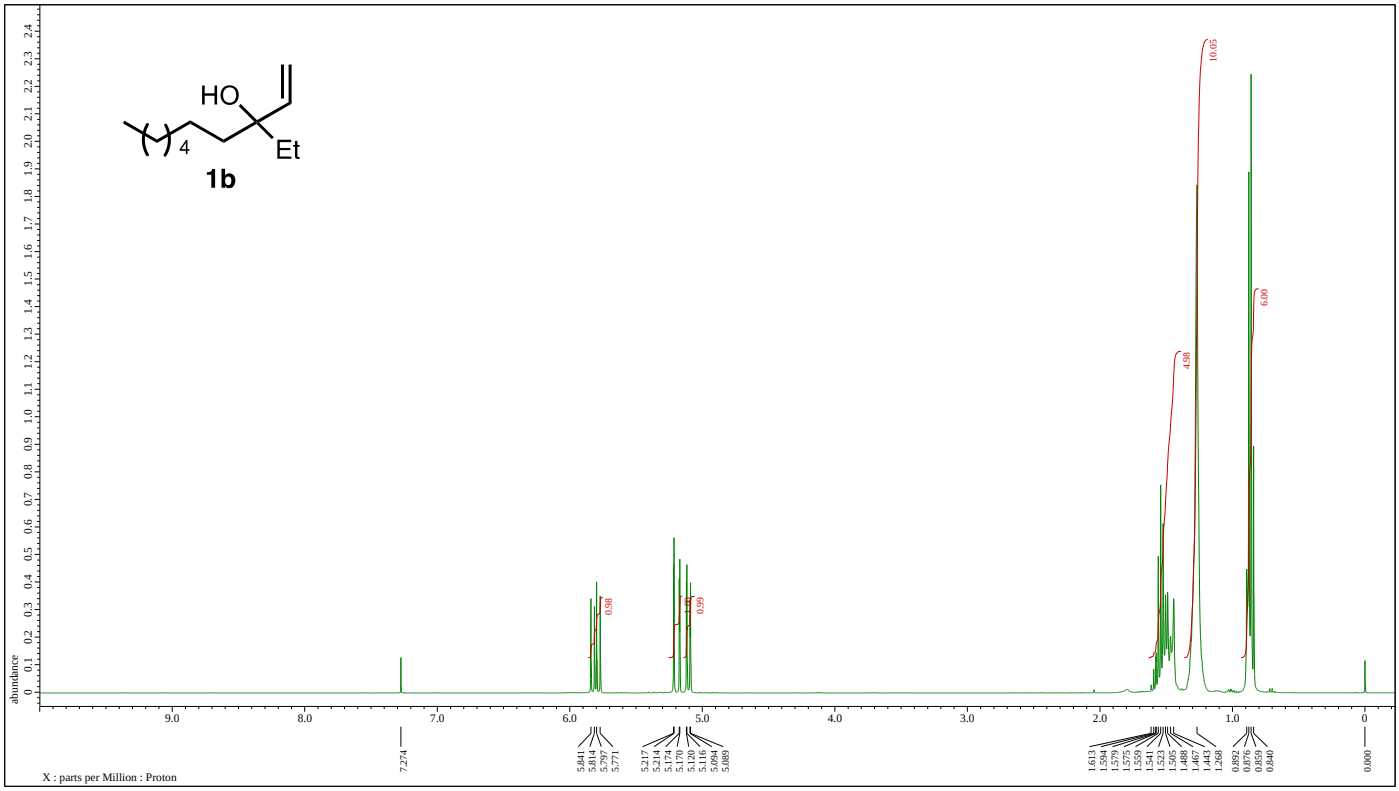
^{1}H NMR (400 MHz, $CDCl_3$) of **1a-*d*$_3$**



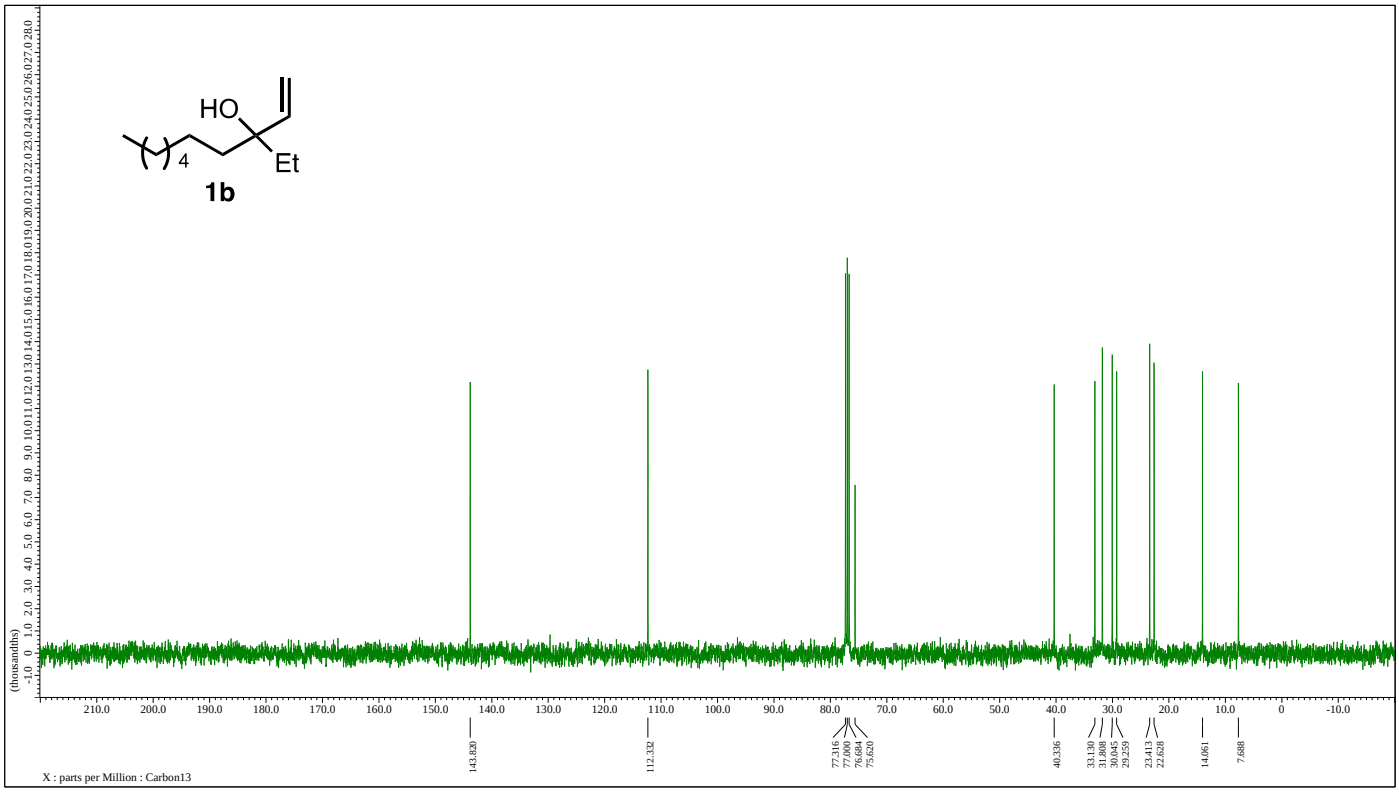
^{2}H NMR (77 MHz, $CHCl_3$) of **1a-*d*$_3$**



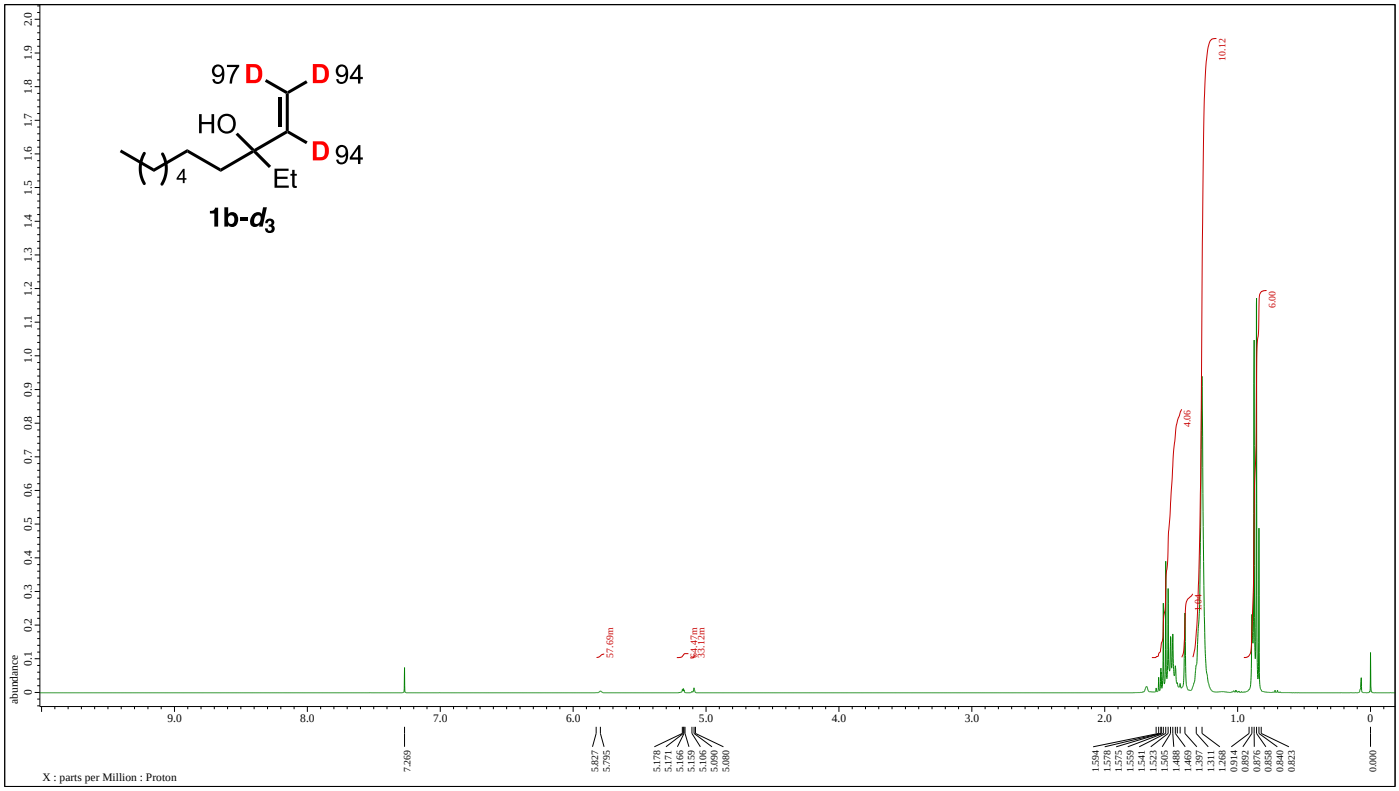
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



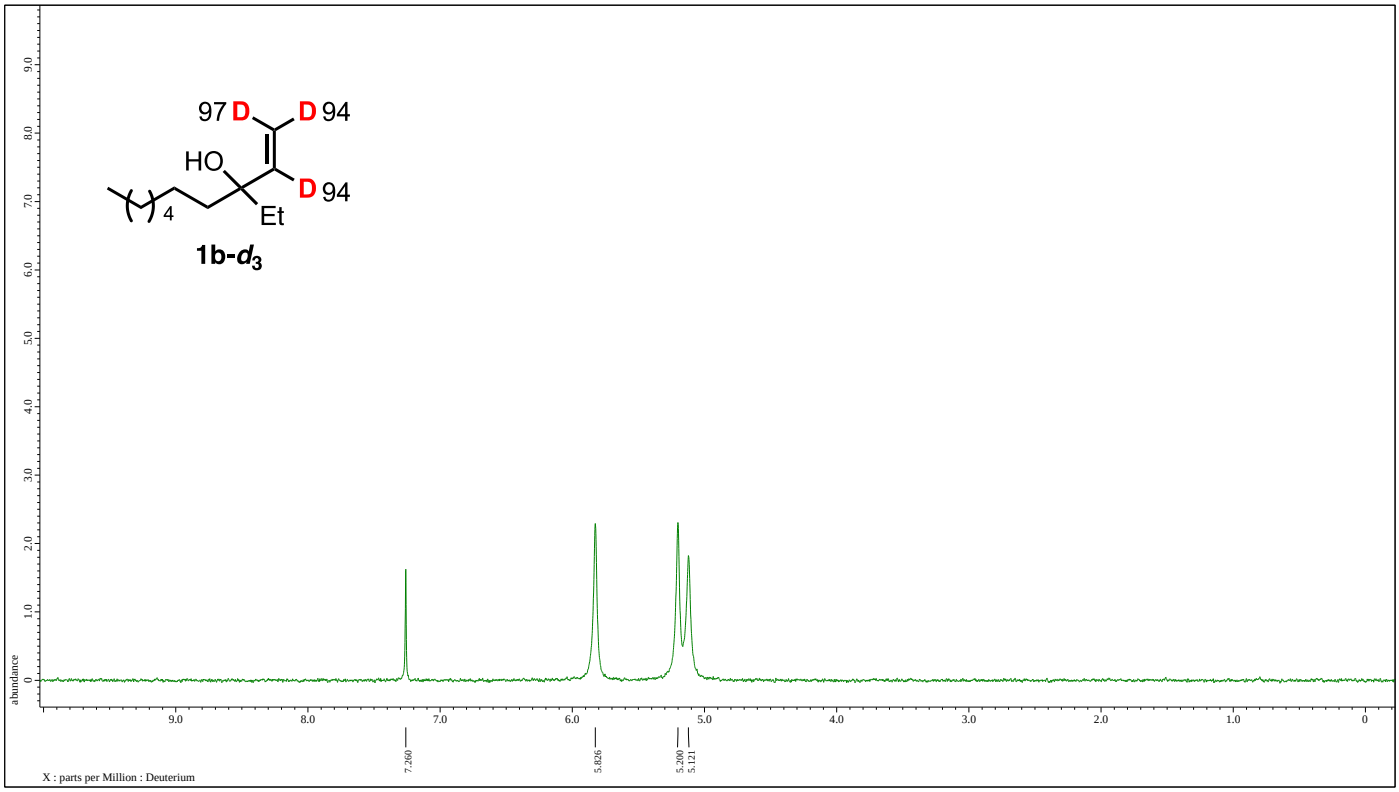
^{13}C NMR (100 MHz, $CDCl_3$) of **1b**



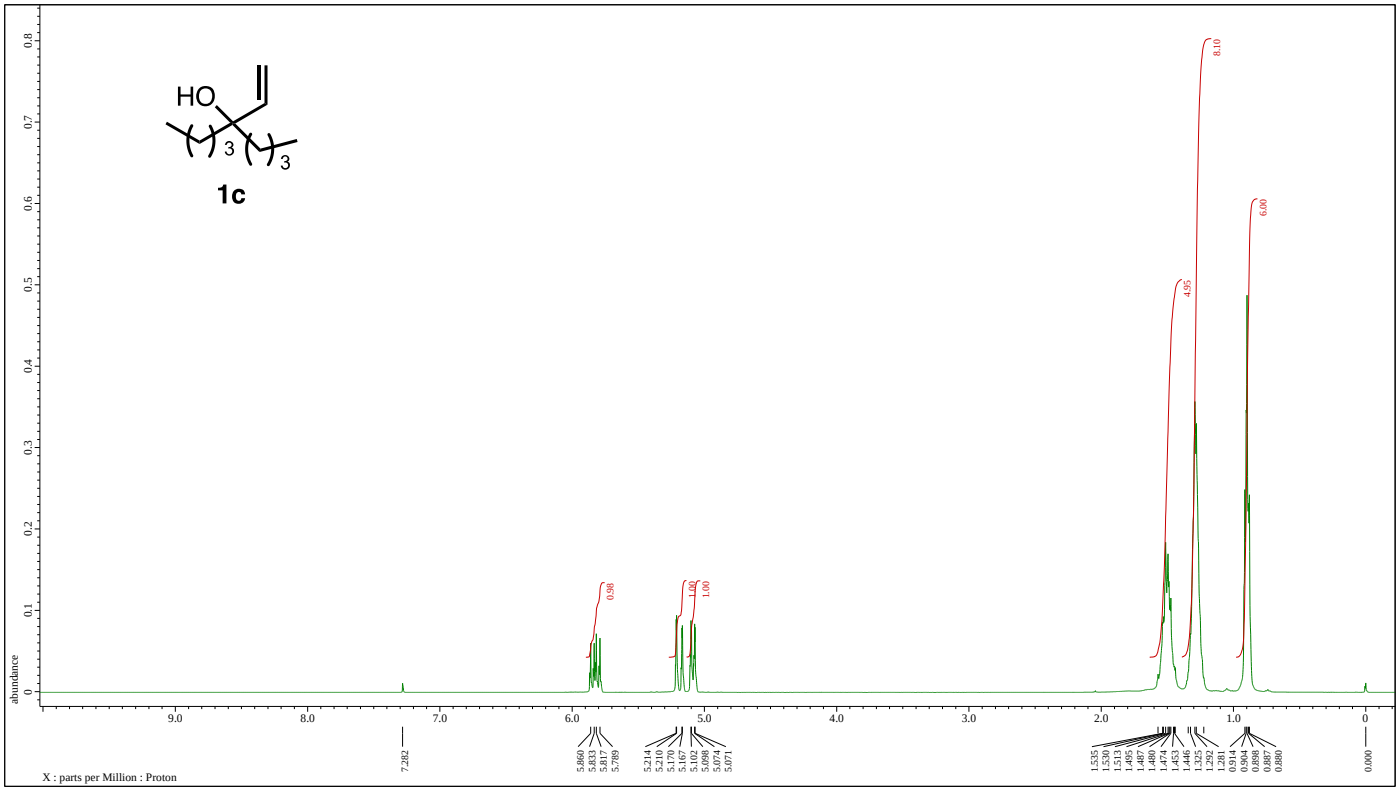
^{1}H NMR (400 MHz, $CDCl_3$) of **1b-*d*$_3$**



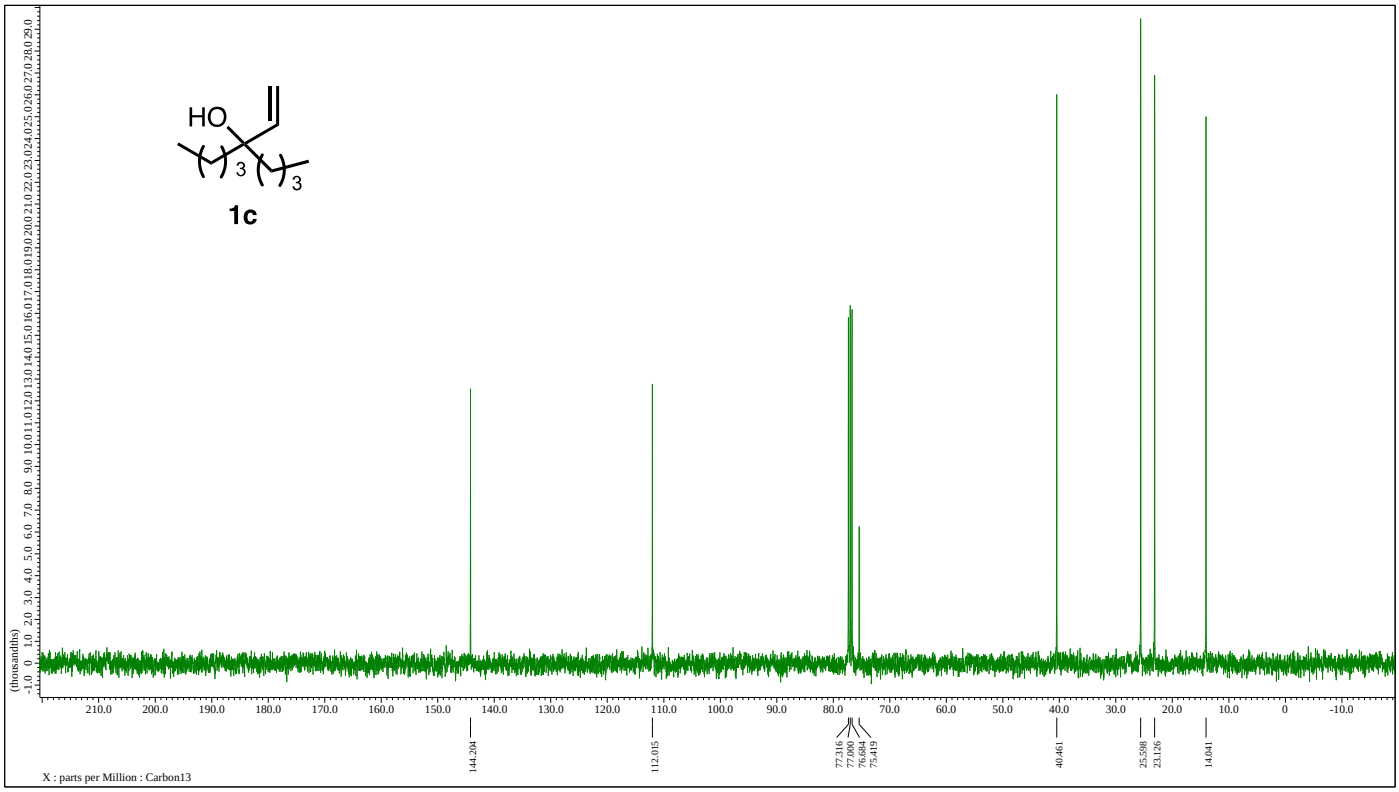
^{2}H NMR (77 MHz, $CHCl_3$) of **1b-*d*$_3$**



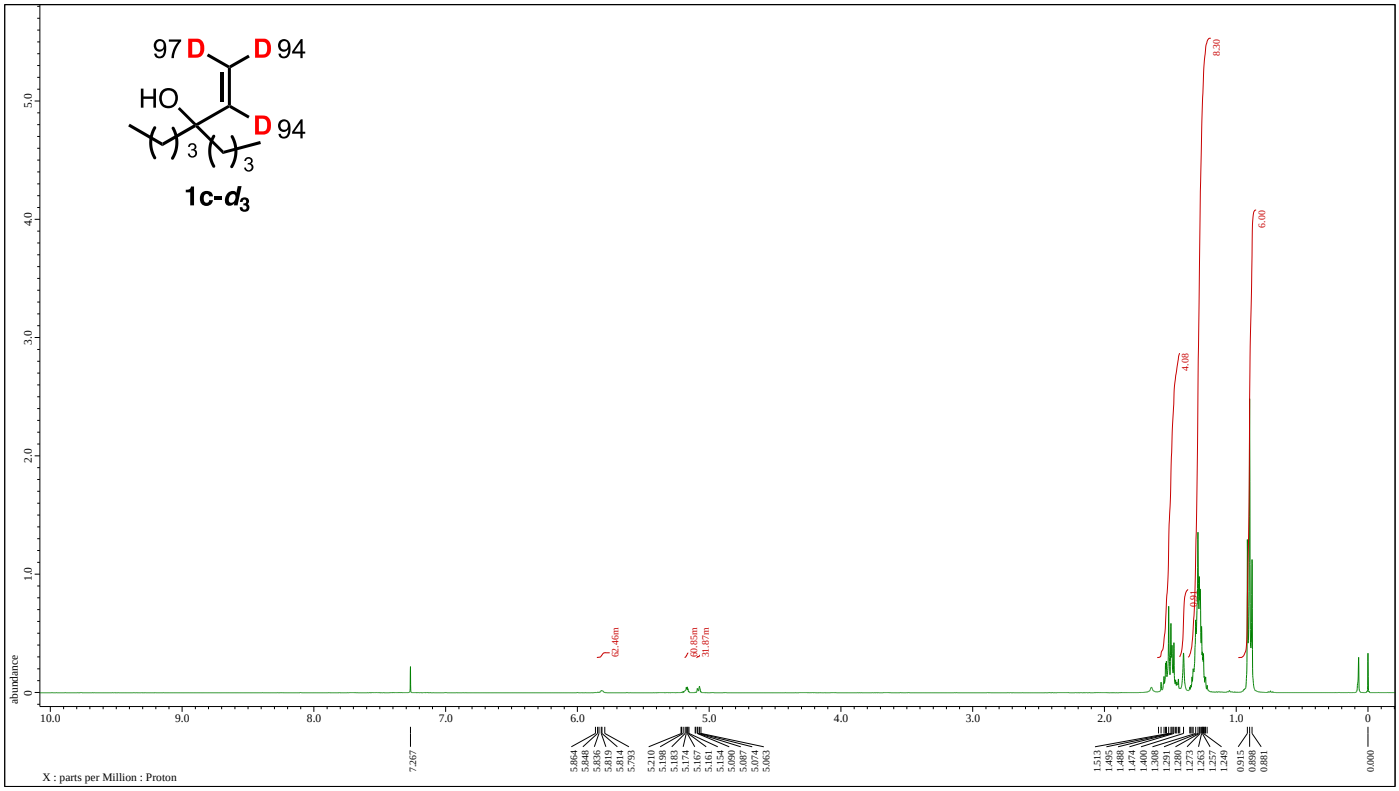
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



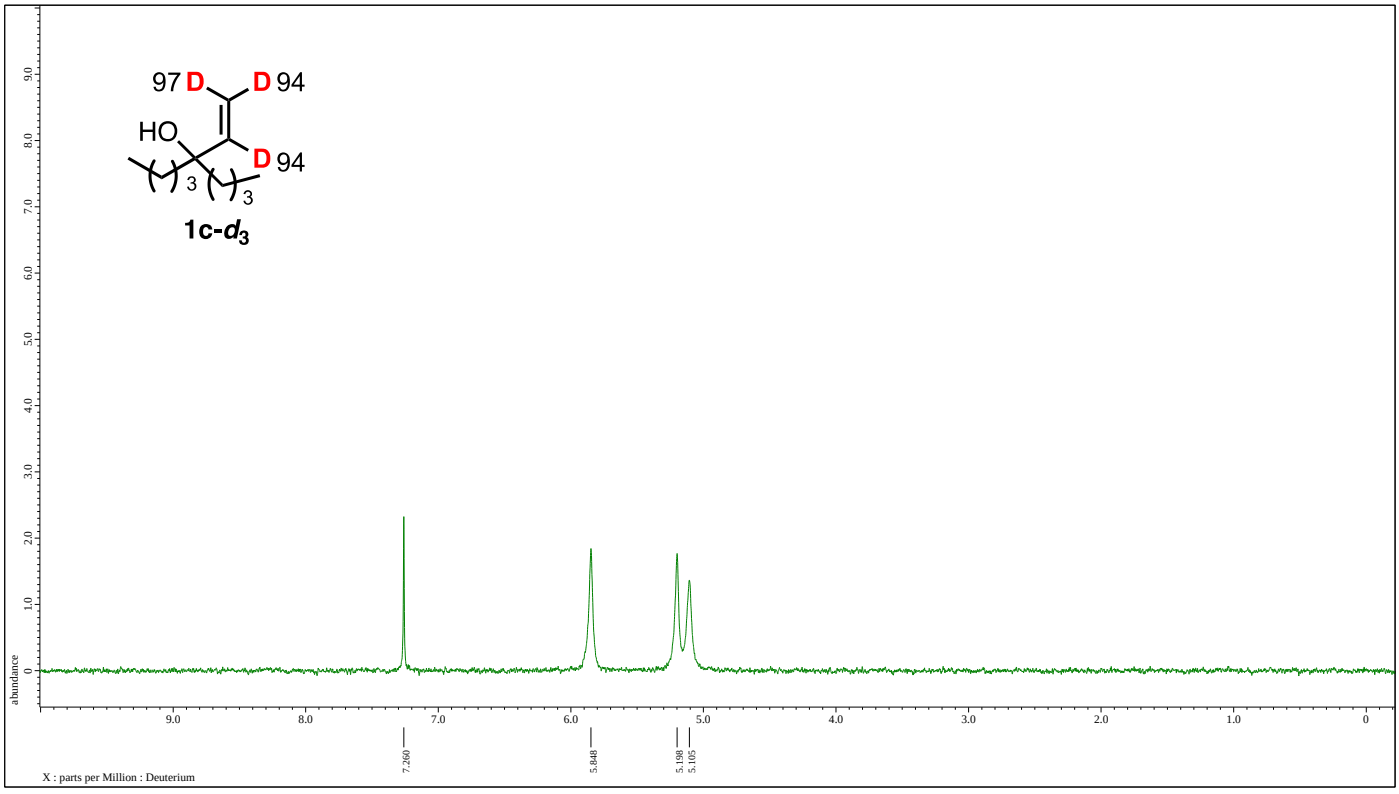
^{13}C NMR (100 MHz, $CDCl_3$) of **1c**



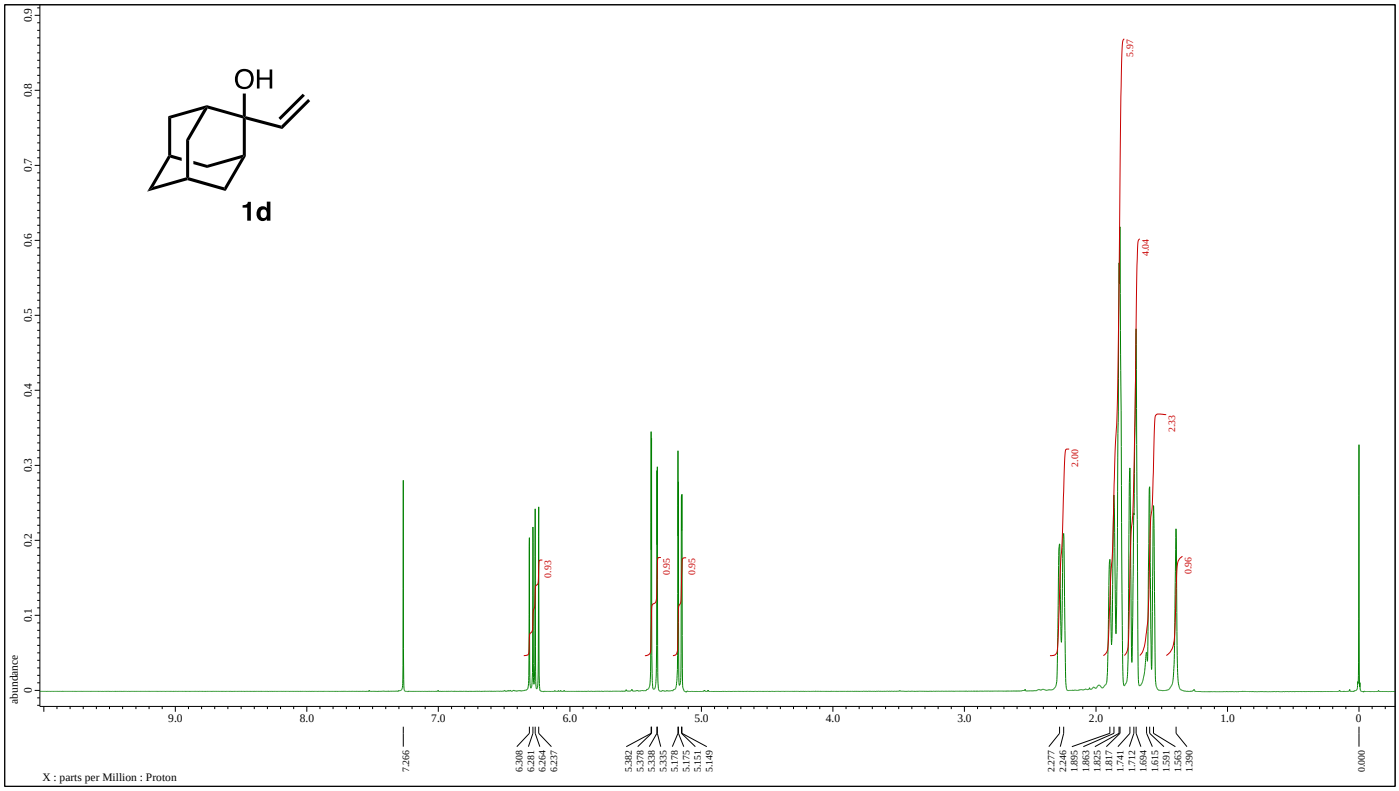
^{1}H NMR (400 MHz, $CDCl_3$) of **1c-*d*$_3$**



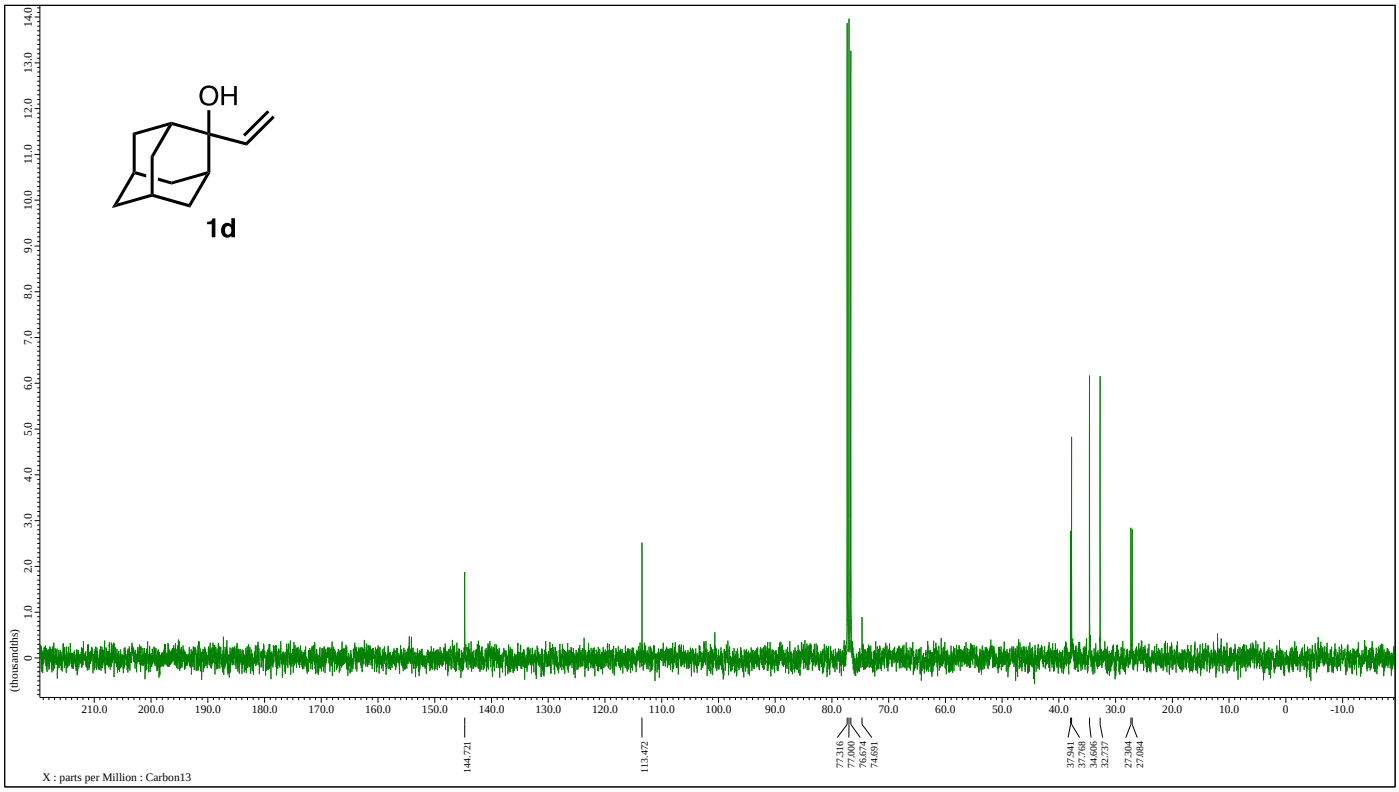
^{2}H NMR (77 MHz, $CHCl_3$) of **1c-*d*$_3$**



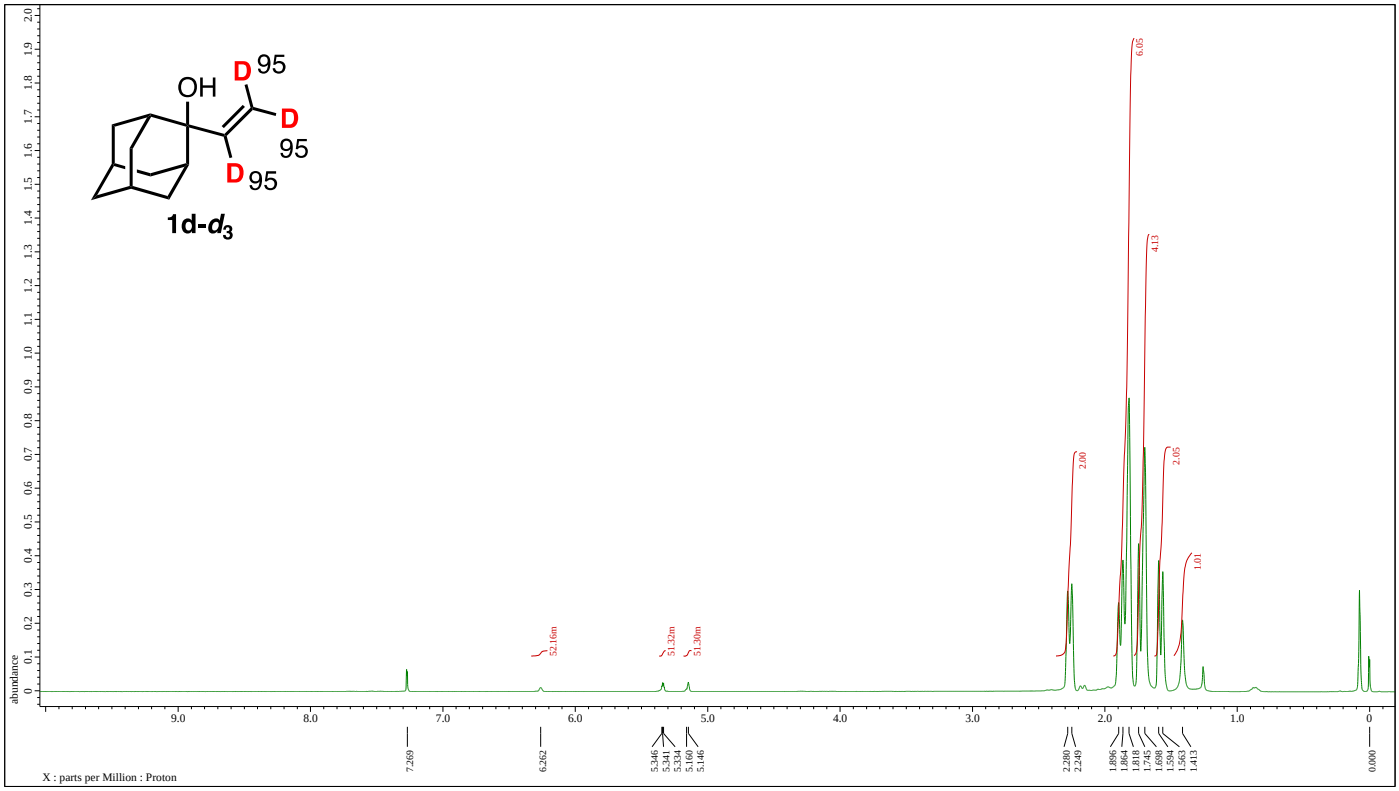
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



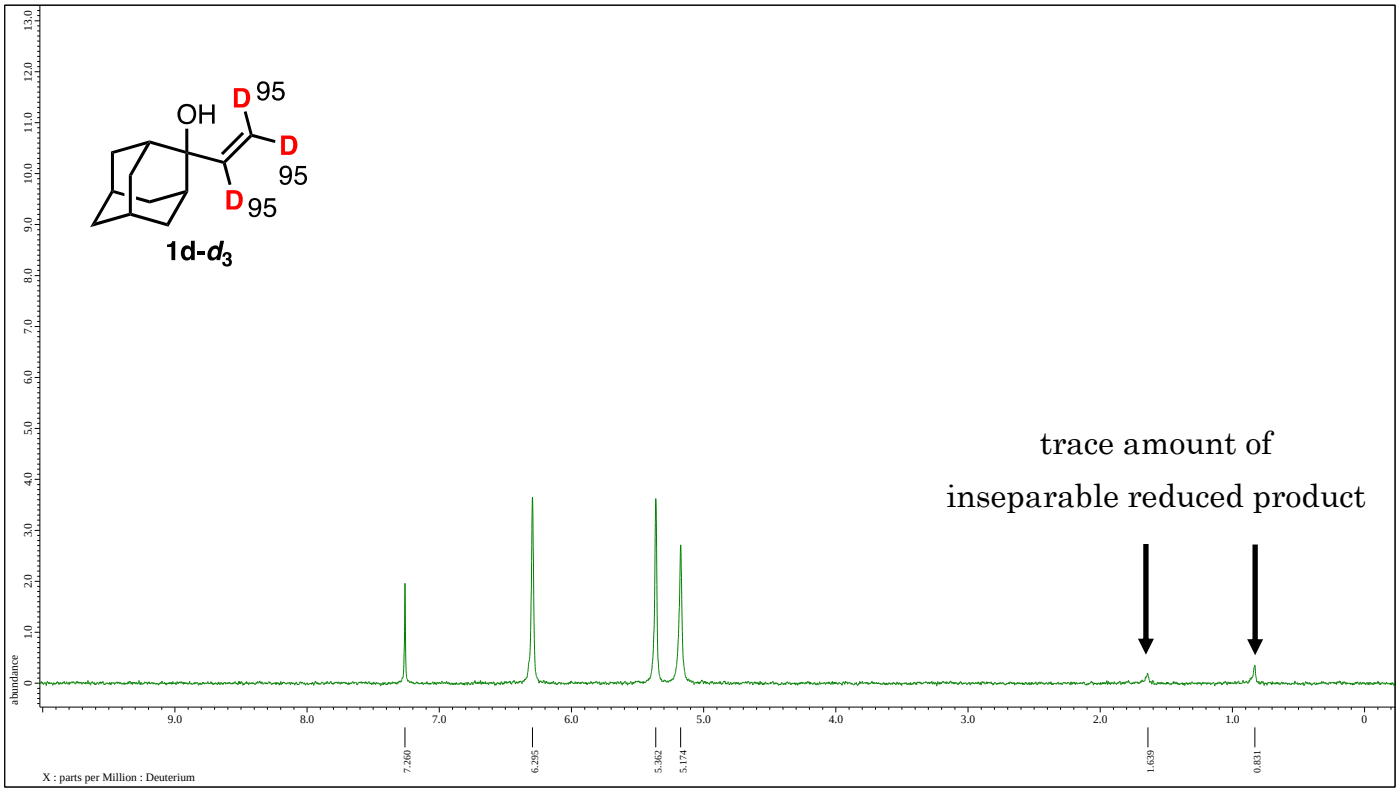
^{13}C NMR (100 MHz, $CDCl_3$) of **1d**



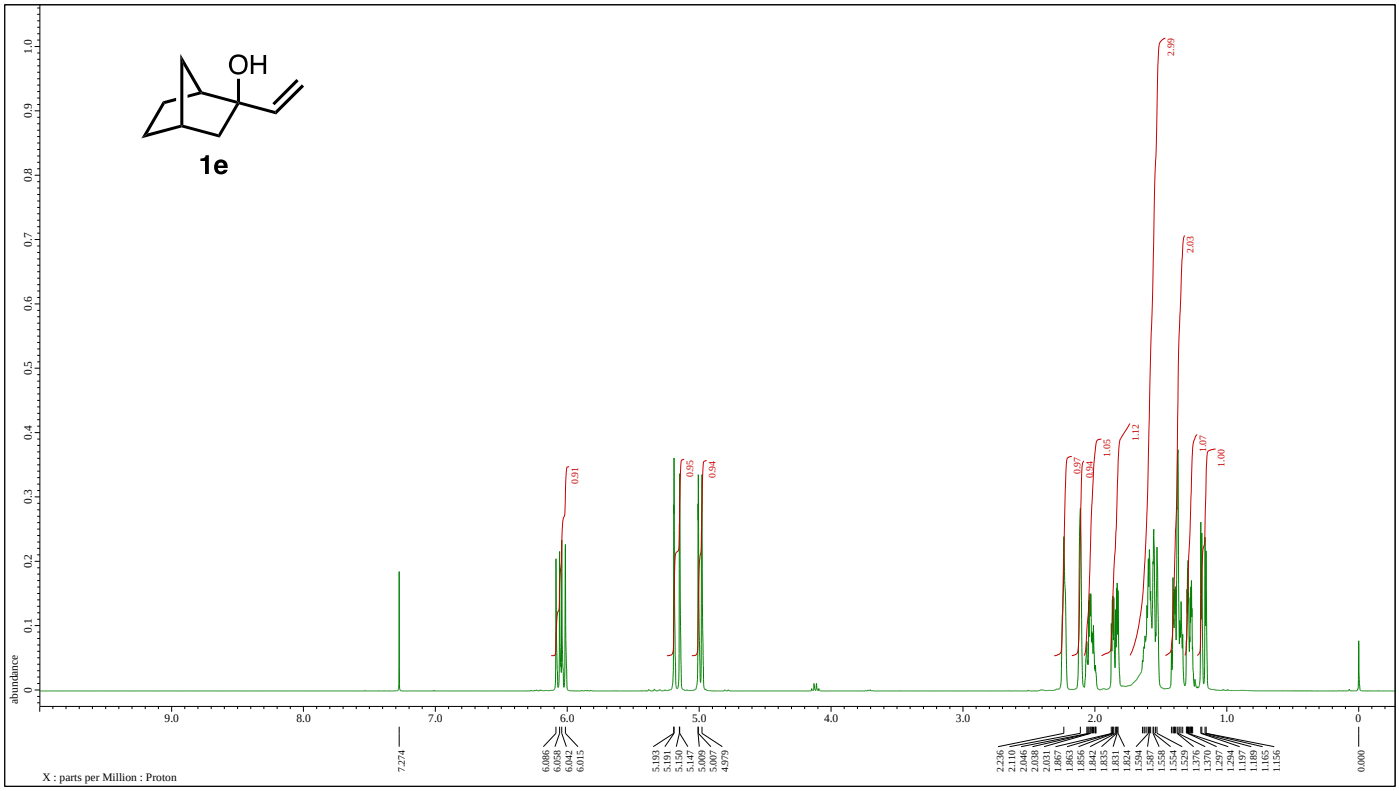
^{1}H NMR (400 MHz, $CDCl_3$) of **1d-*d*$_3$**



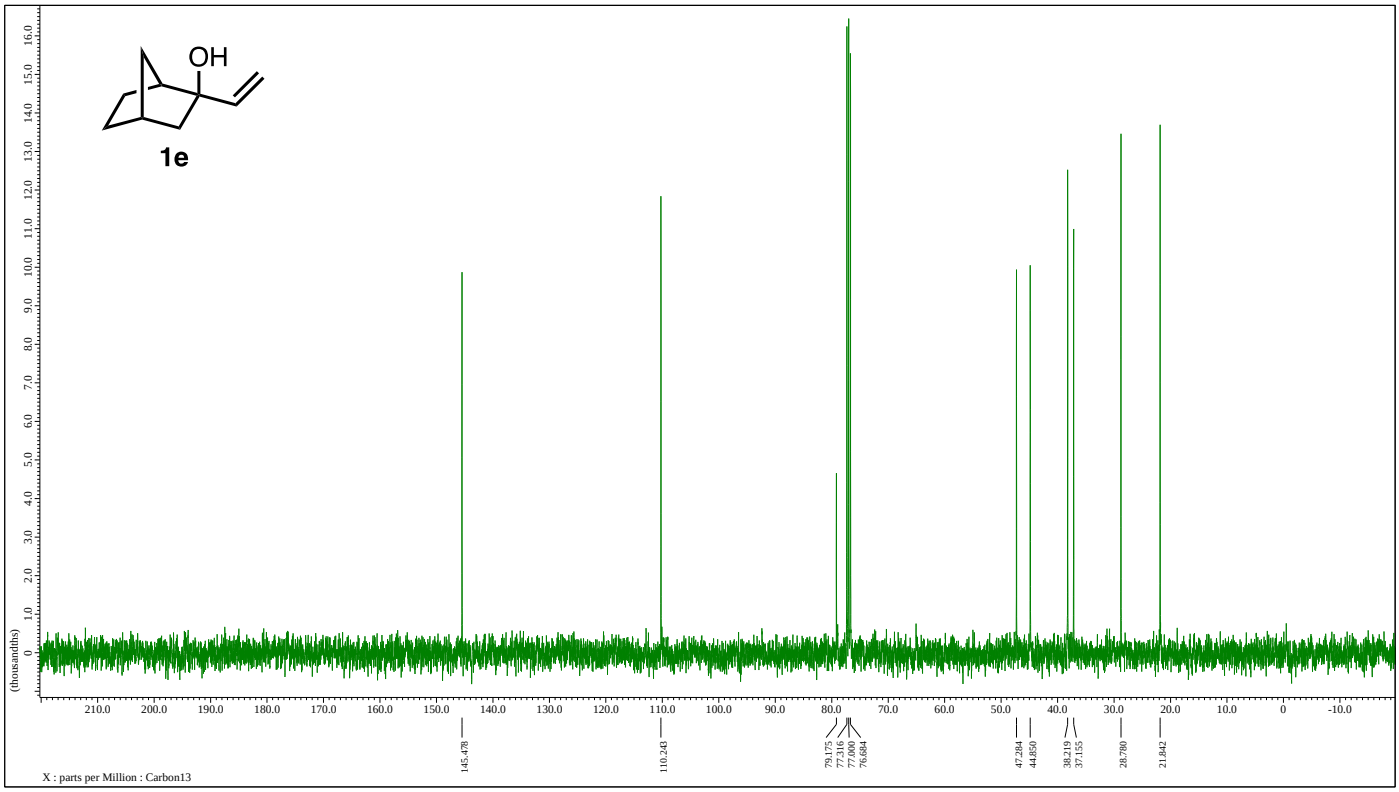
^{2}H NMR (77 MHz, $CHCl_3$) of **1d-*d*$_3$**



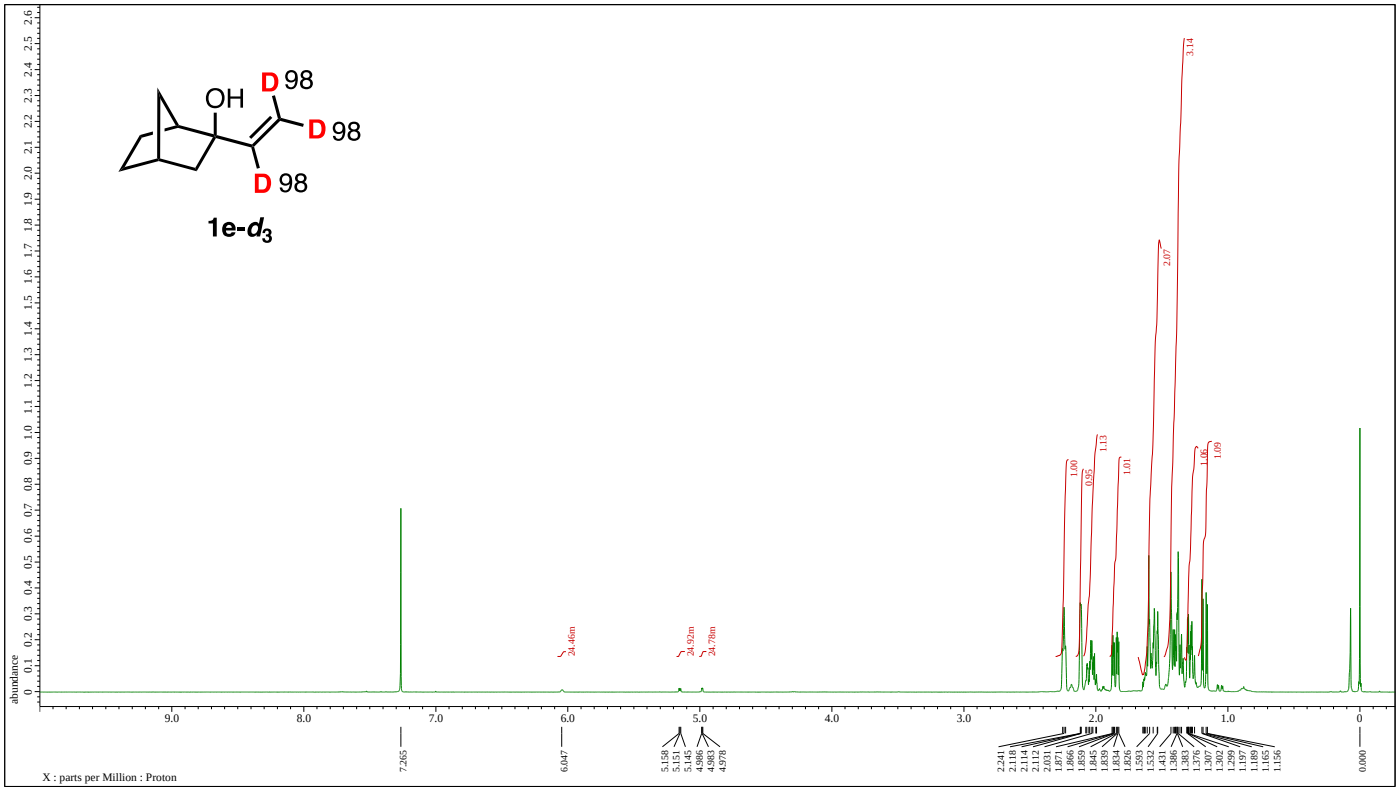
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



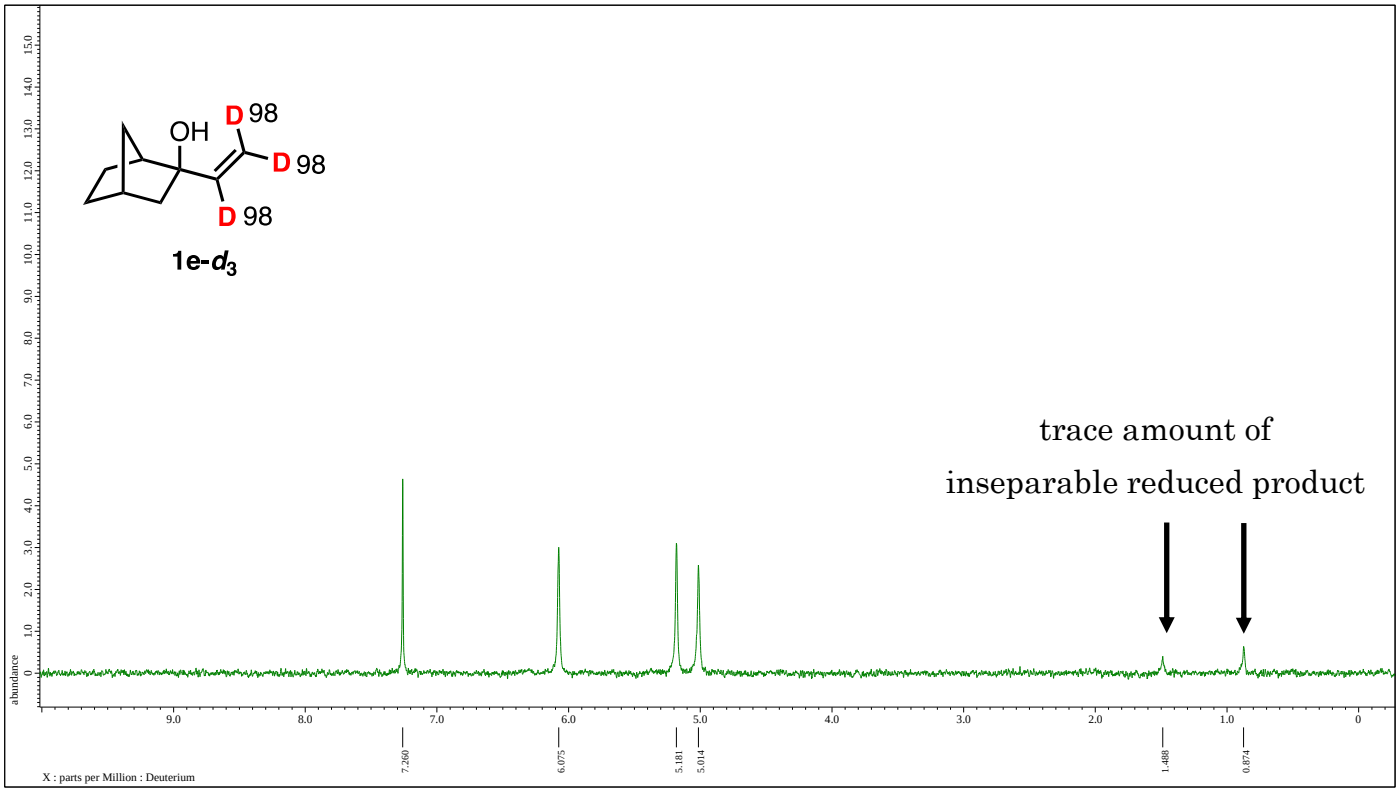
^{13}C NMR (100 MHz, $CDCl_3$) of **1e**



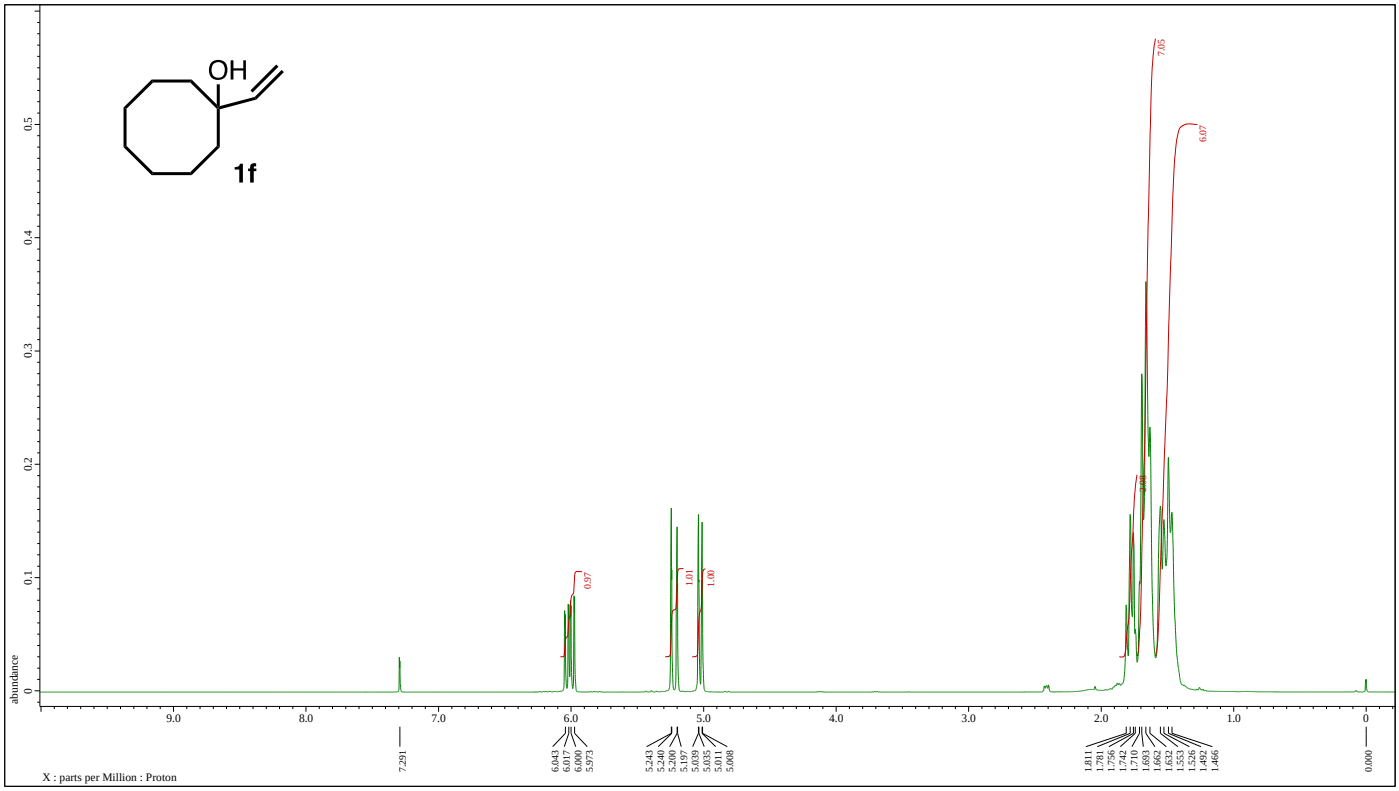
^{1}H NMR (400 MHz, $CDCl_3$) of **1e-*d*$_3$**



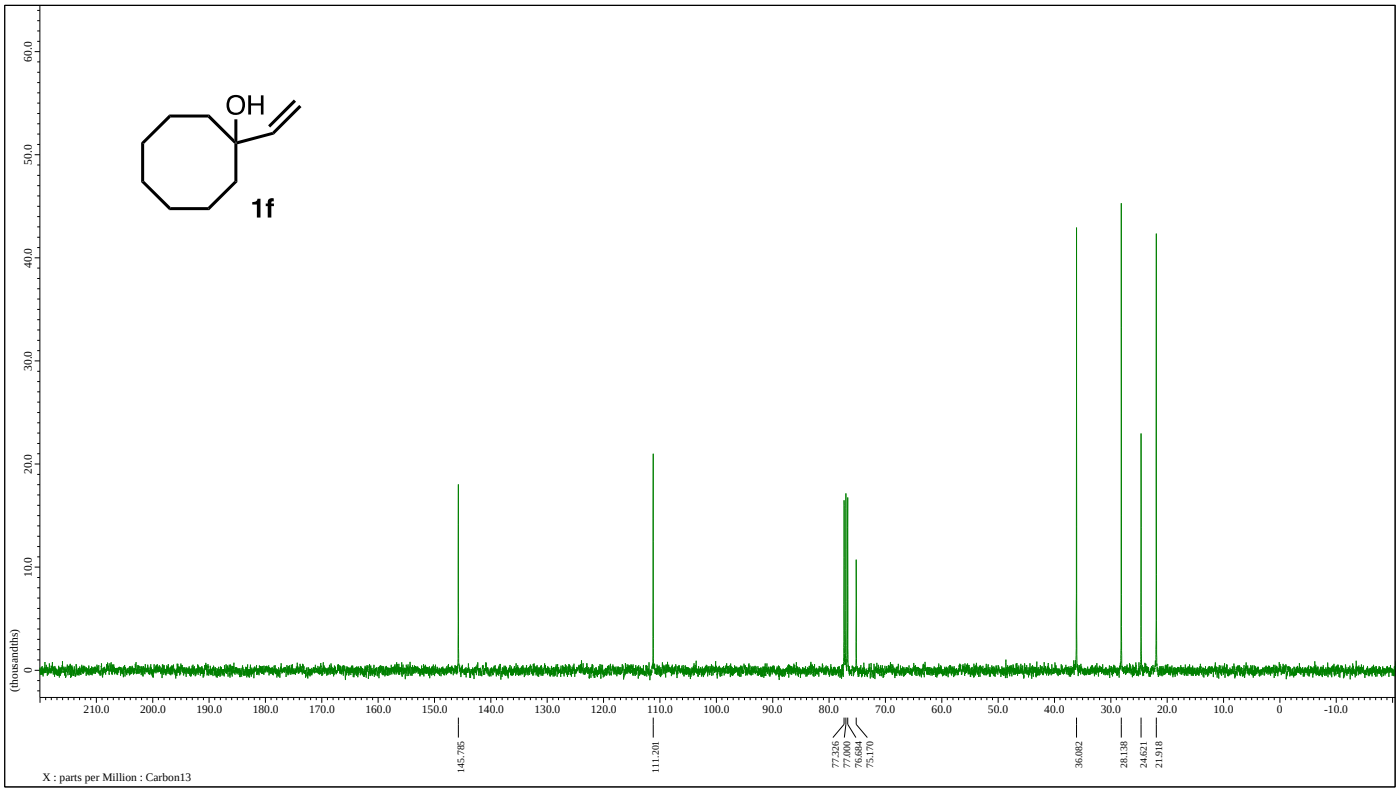
^{2}H NMR (77 MHz, $CDCl_3$) of **1e-*d*$_3$**



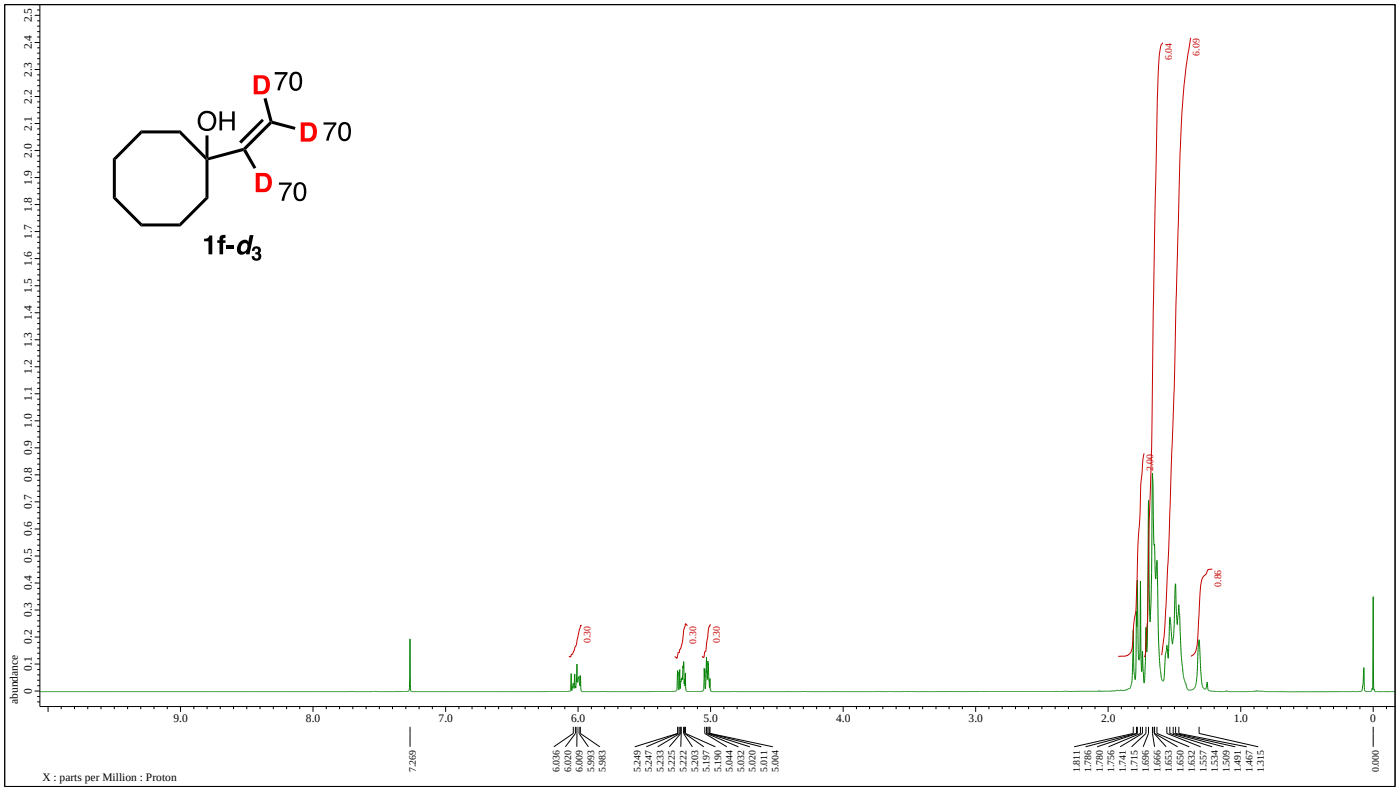
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



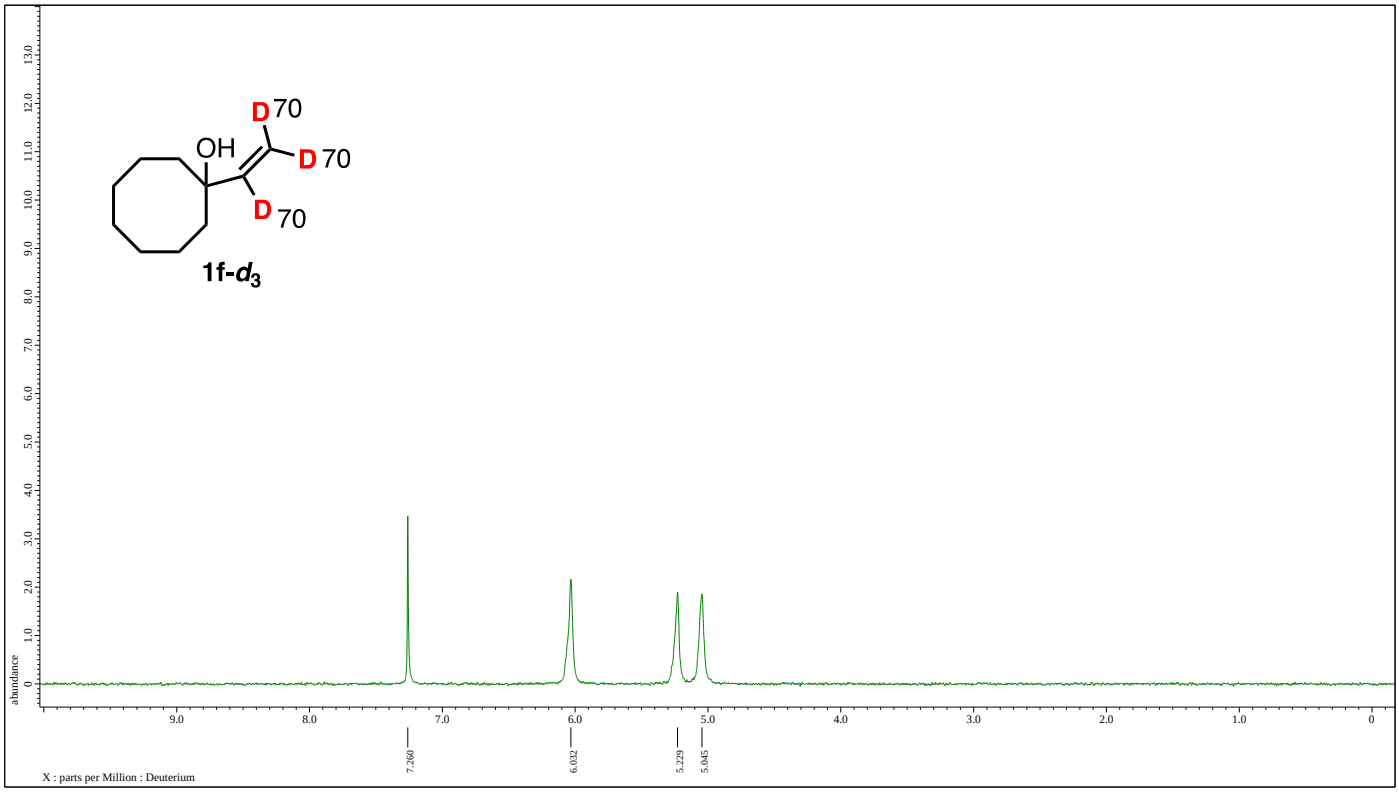
^{13}C NMR (100 MHz, $CDCl_3$) of **1f**



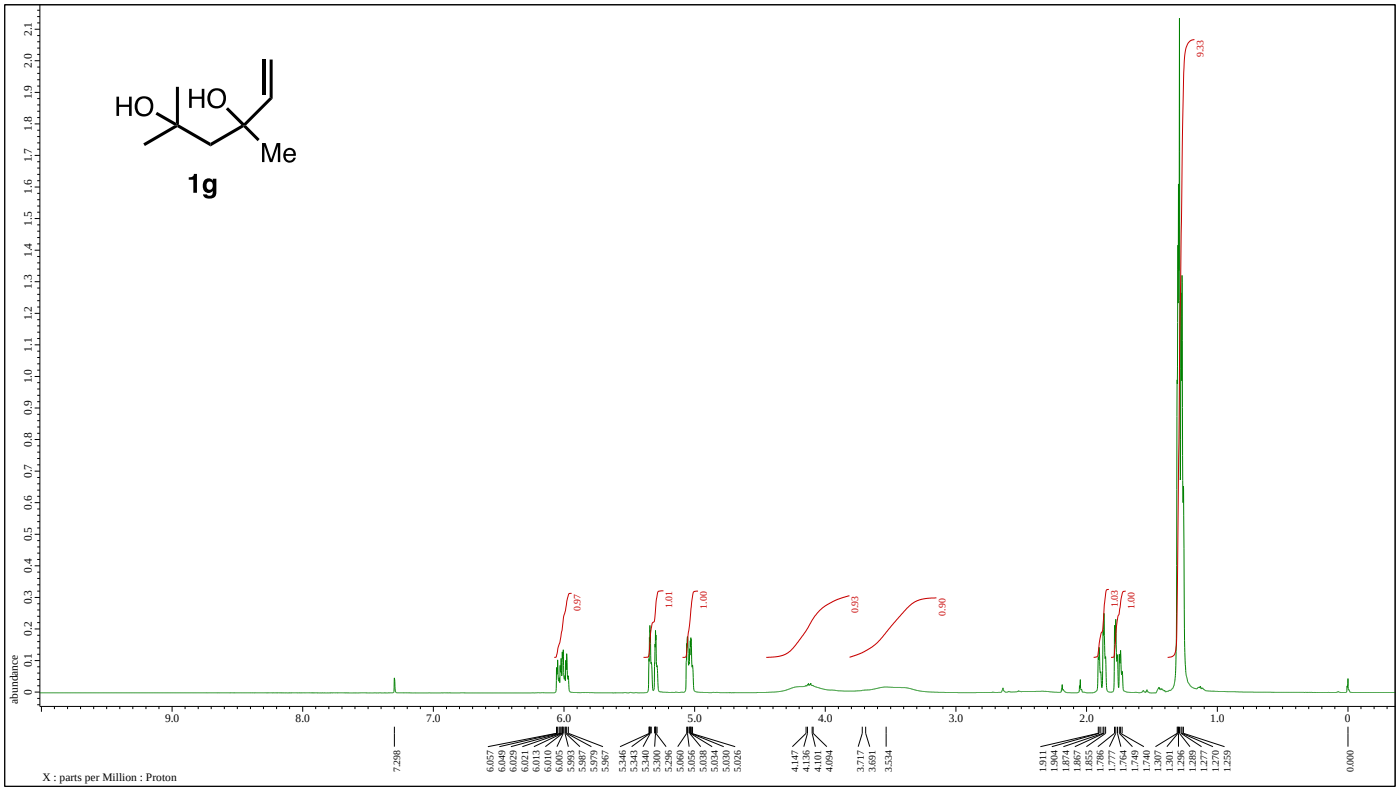
^{1}H NMR (400 MHz, $CDCl_3$) of **1f-*d*$_3$**



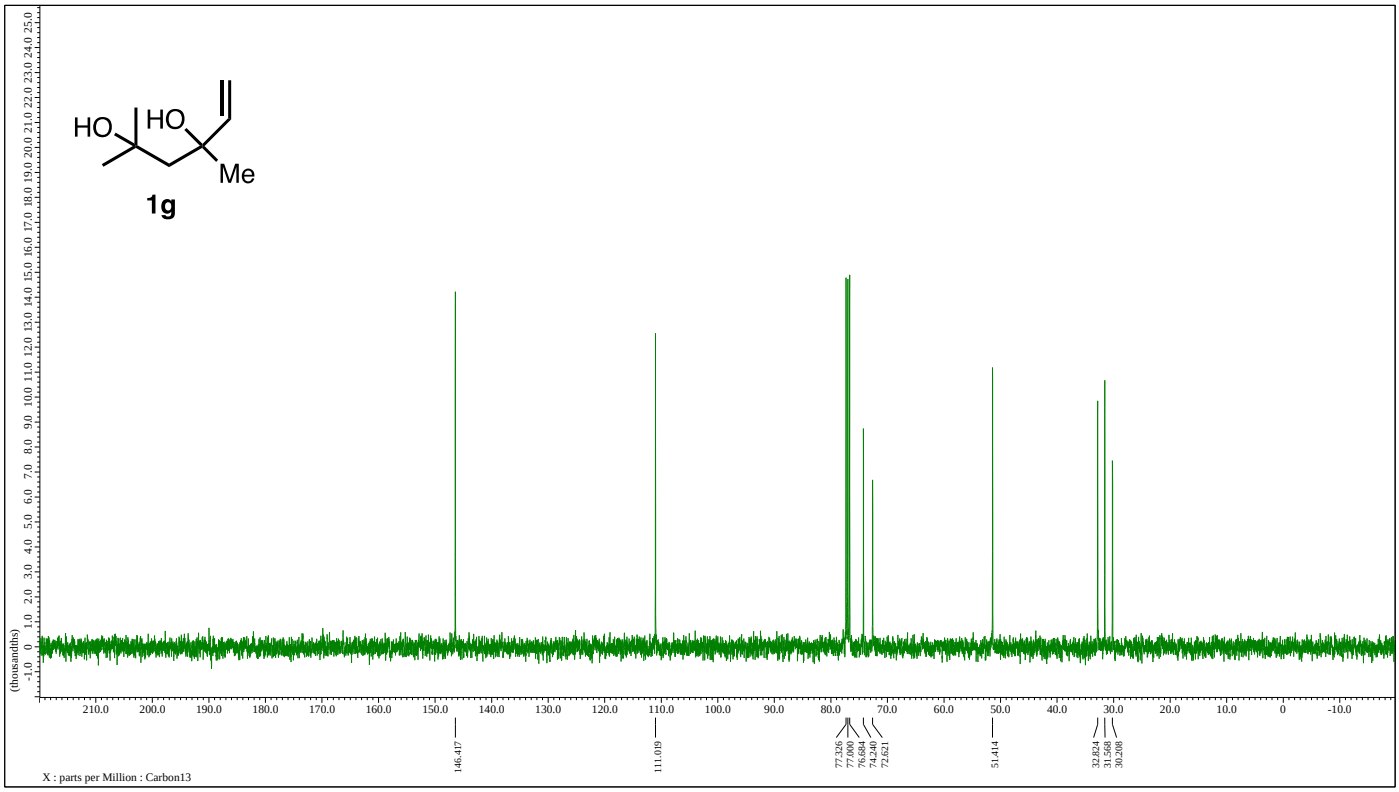
^{2}H NMR (77 MHz, $CDCl_3$) of **1f-*d*$_3$**



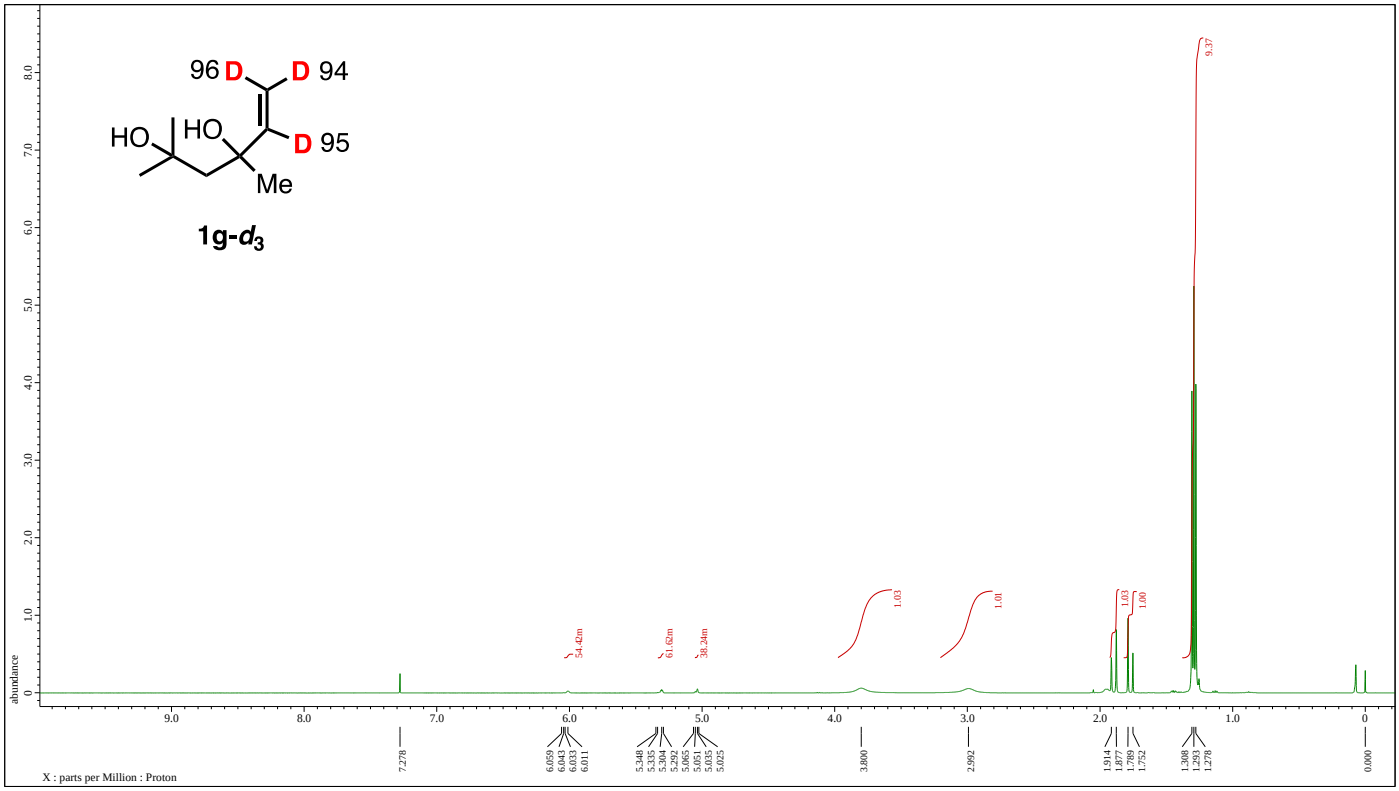
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



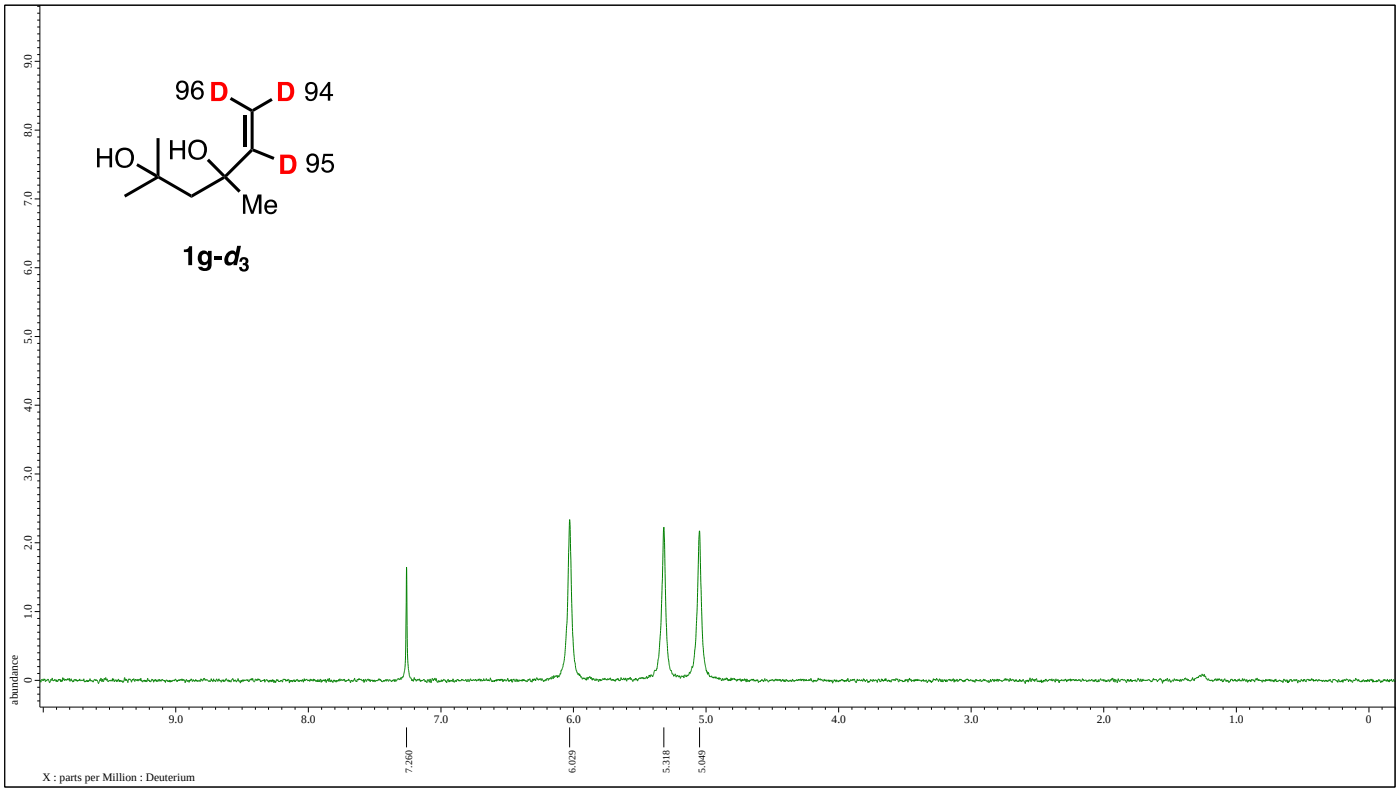
^{13}C NMR (100 MHz, $CDCl_3$) of **1g**



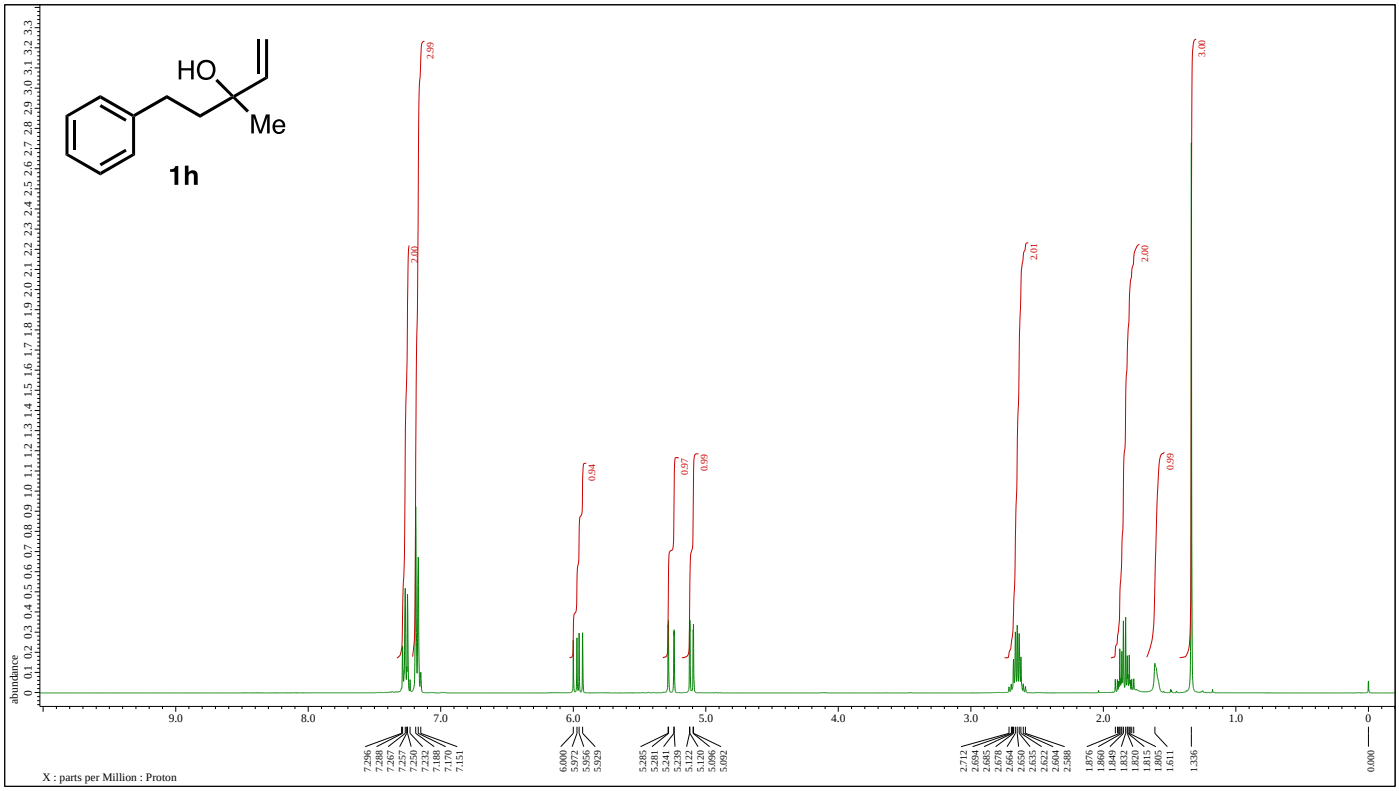
^{1}H NMR (400 MHz, $CDCl_3$) of **1g-*d*$_3$**



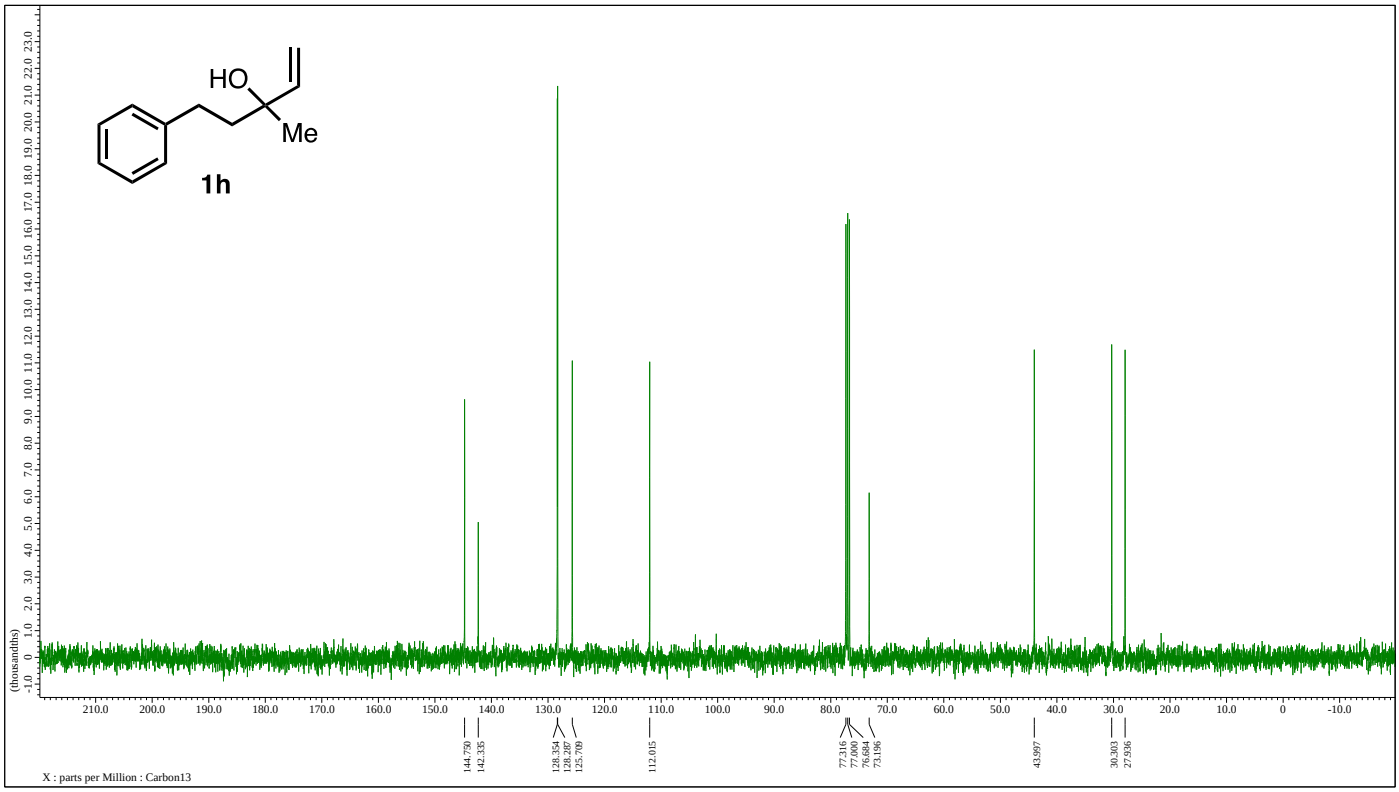
^{2}H NMR (77 MHz, $CDCl_3$) of **1g-*d*$_3$**



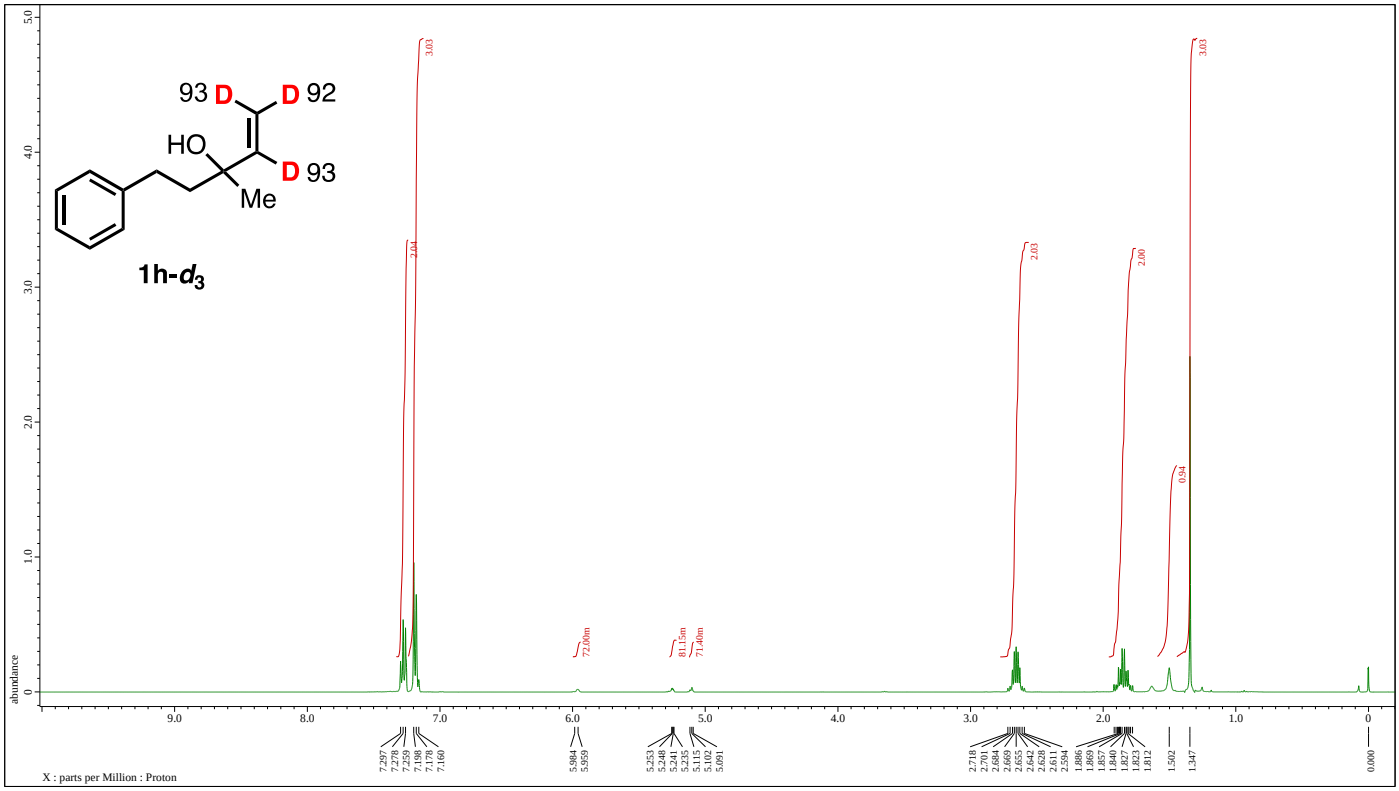
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



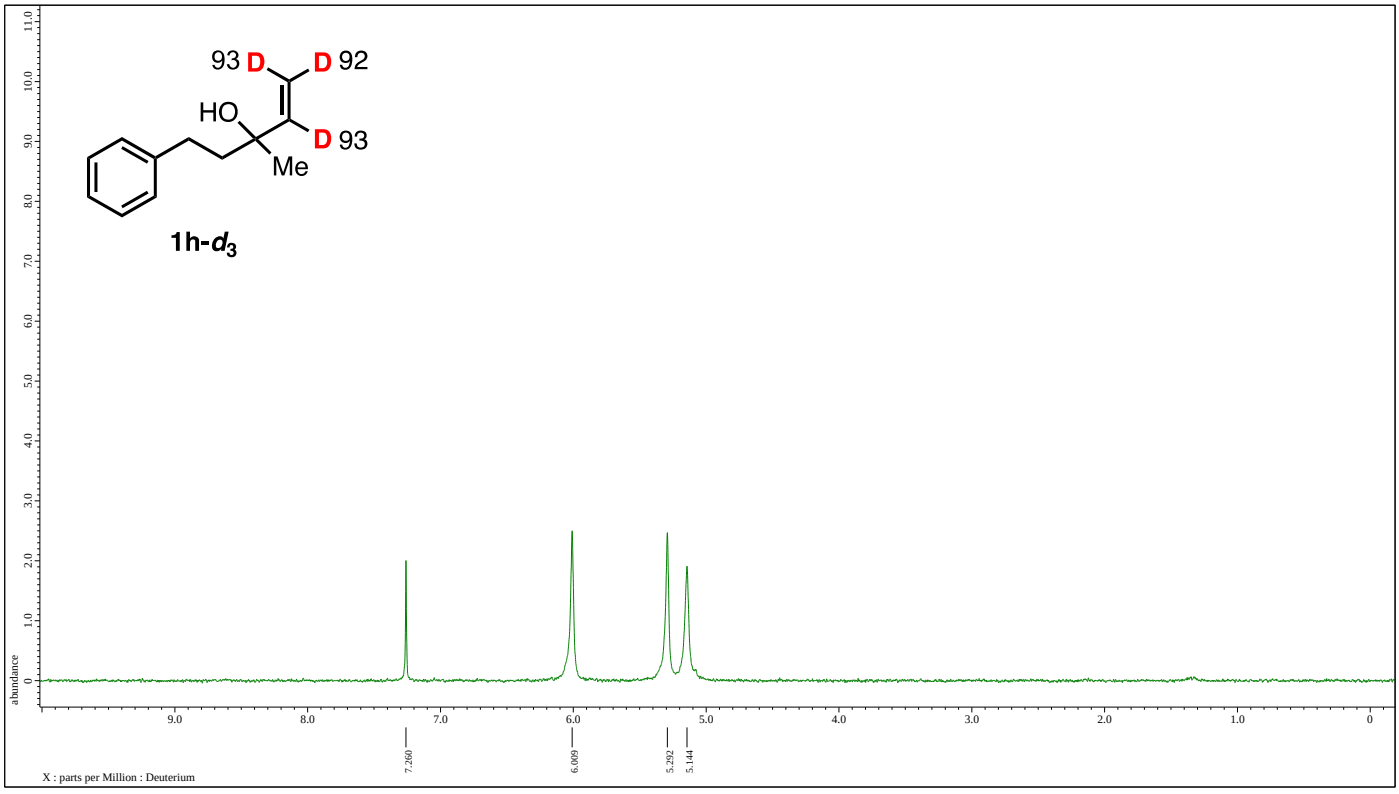
^{13}C NMR (100 MHz, $CDCl_3$) of **1h**



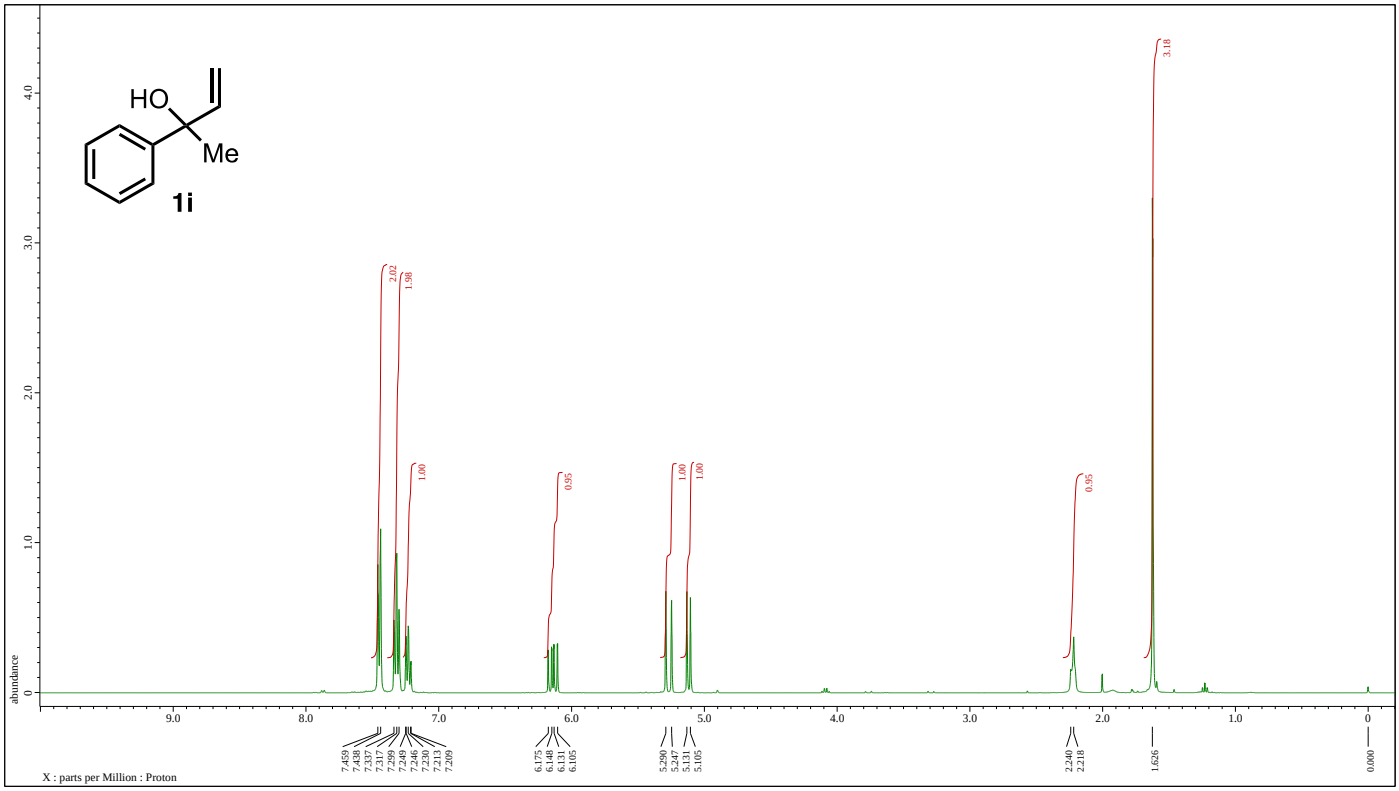
^{1}H NMR (400 MHz, $CDCl_3$) of **1h-*d*$_3$**



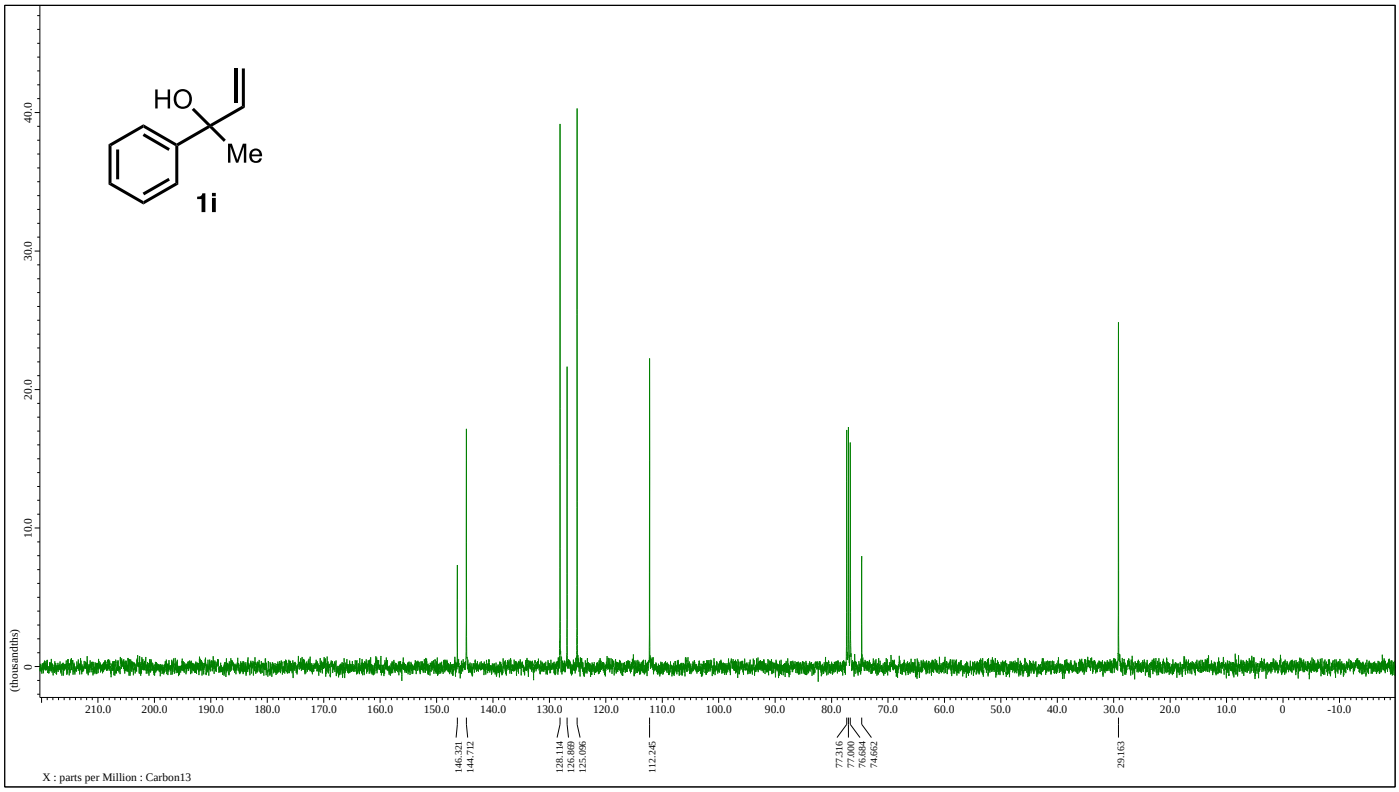
^{2}H NMR (77 MHz, $CHCl_3$) of **1h-*d*$_3$**



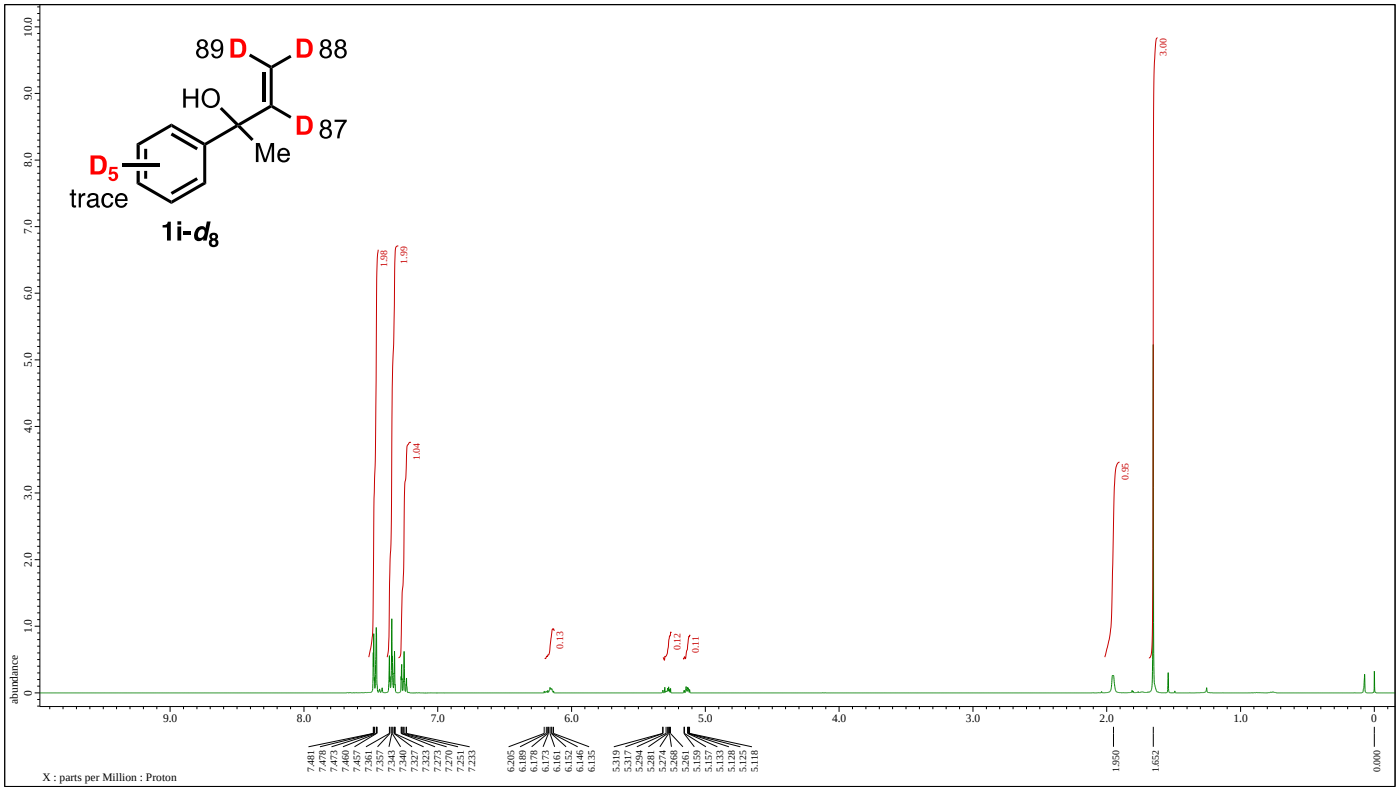
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



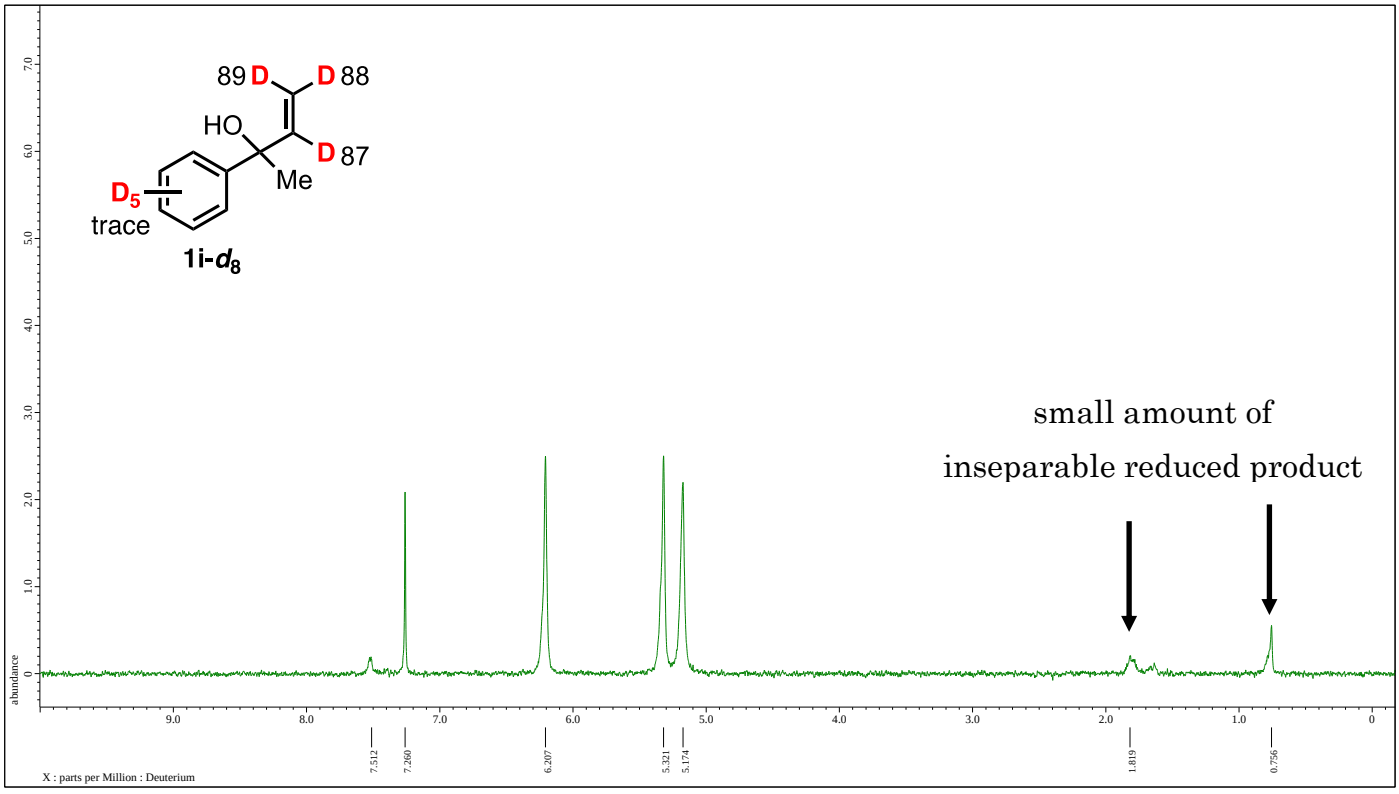
^{13}C NMR (100 MHz, $CDCl_3$) of **1i**



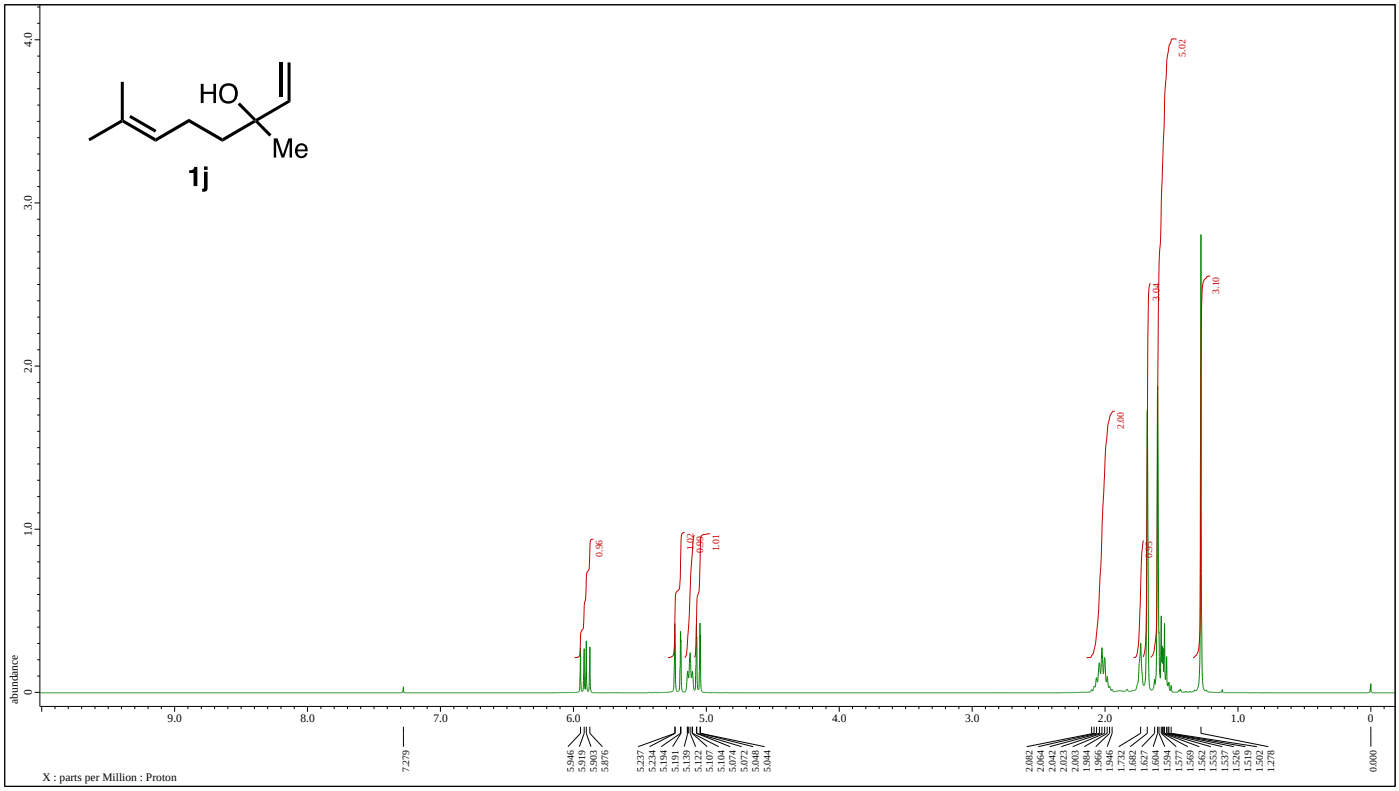
^{1}H NMR (400 MHz, $CDCl_3$) of **1i-*d*$_8$**



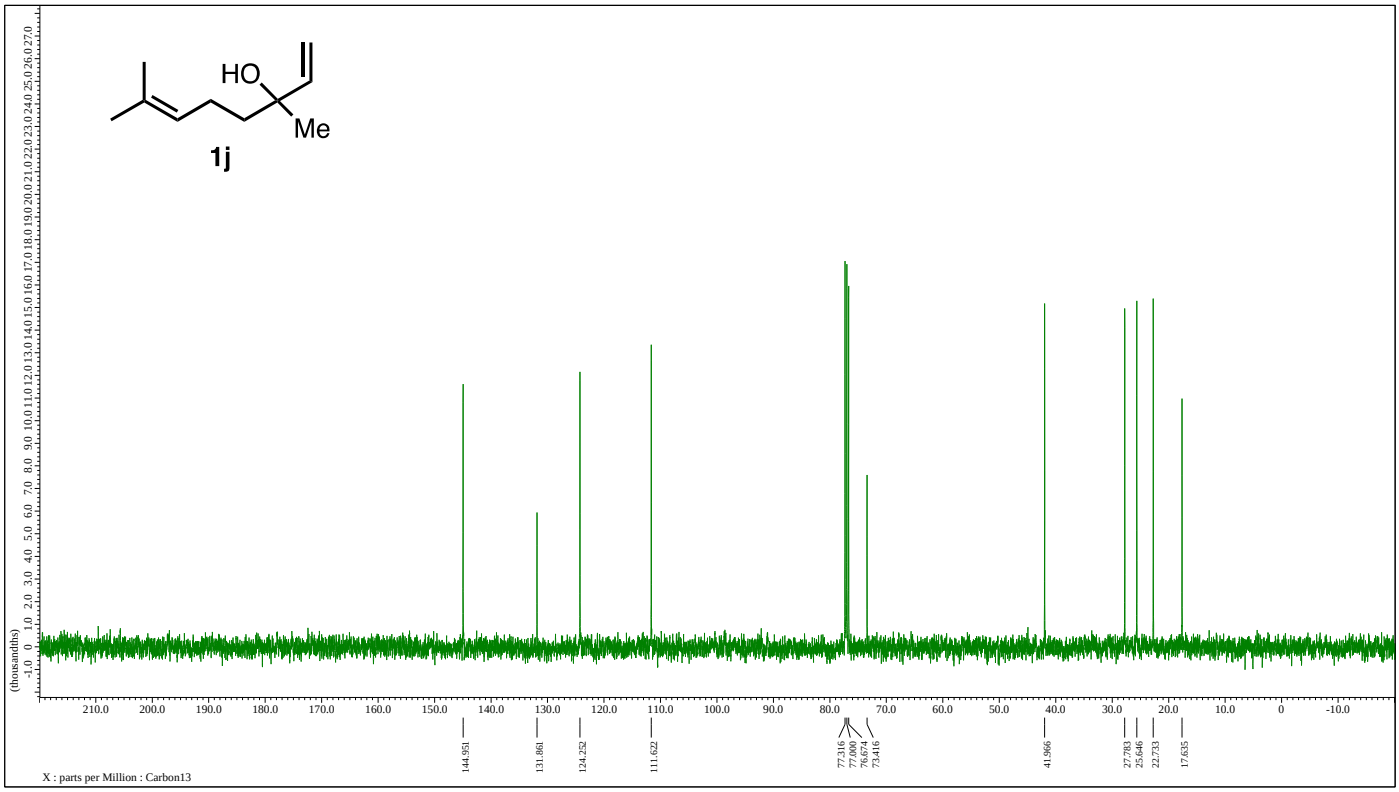
^{2}H NMR (77 MHz, $CDCl_3$) of **1i-*d*$_8$**



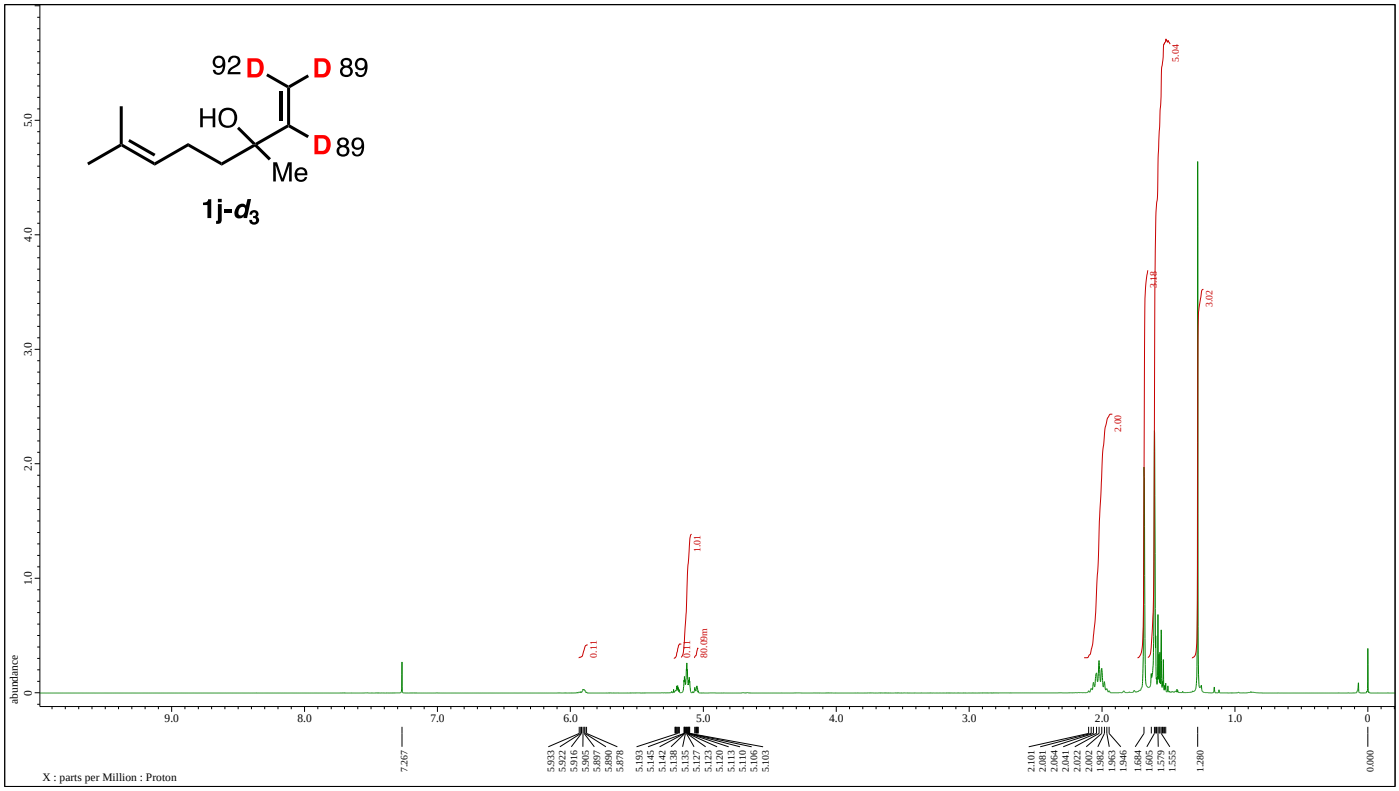
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**



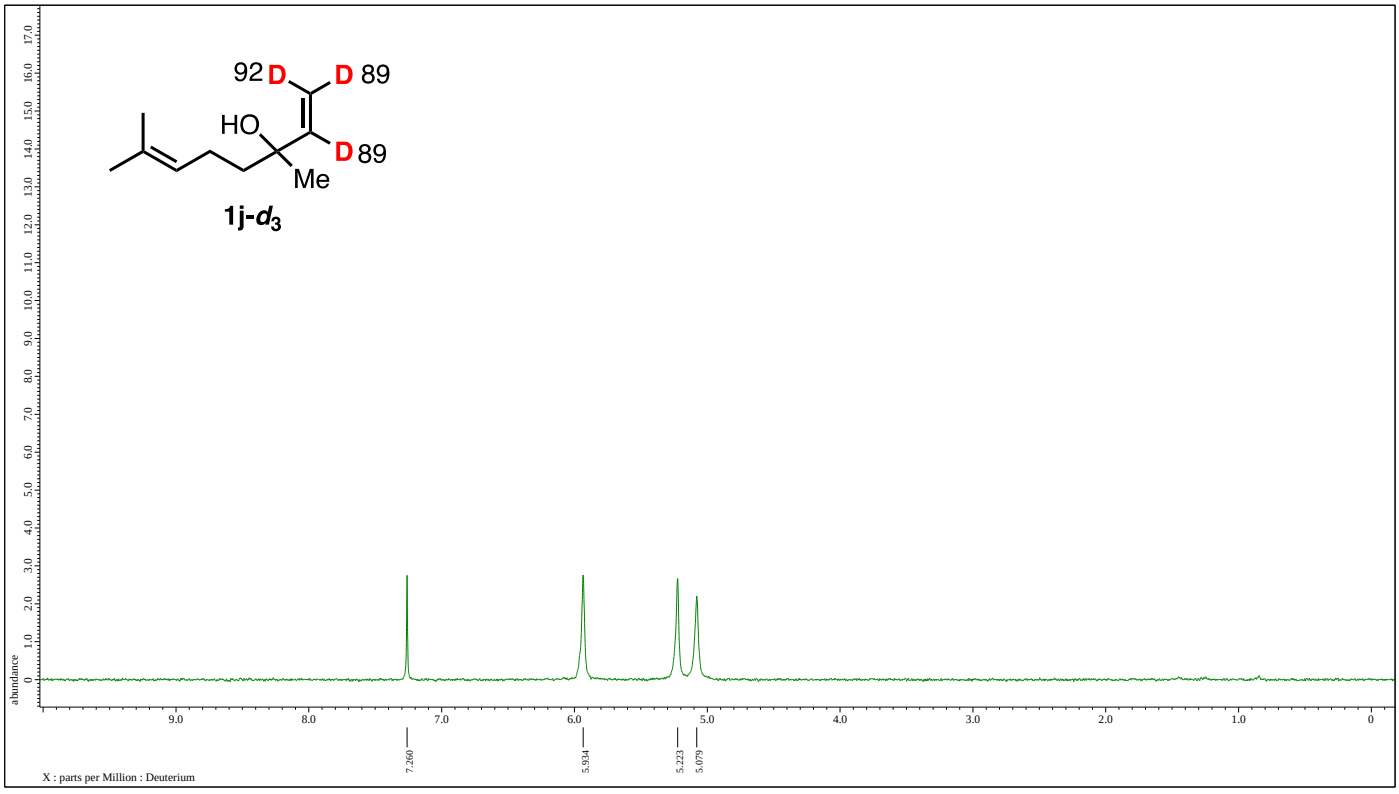
^{13}C NMR (100 MHz, $CDCl_3$) of **1j**



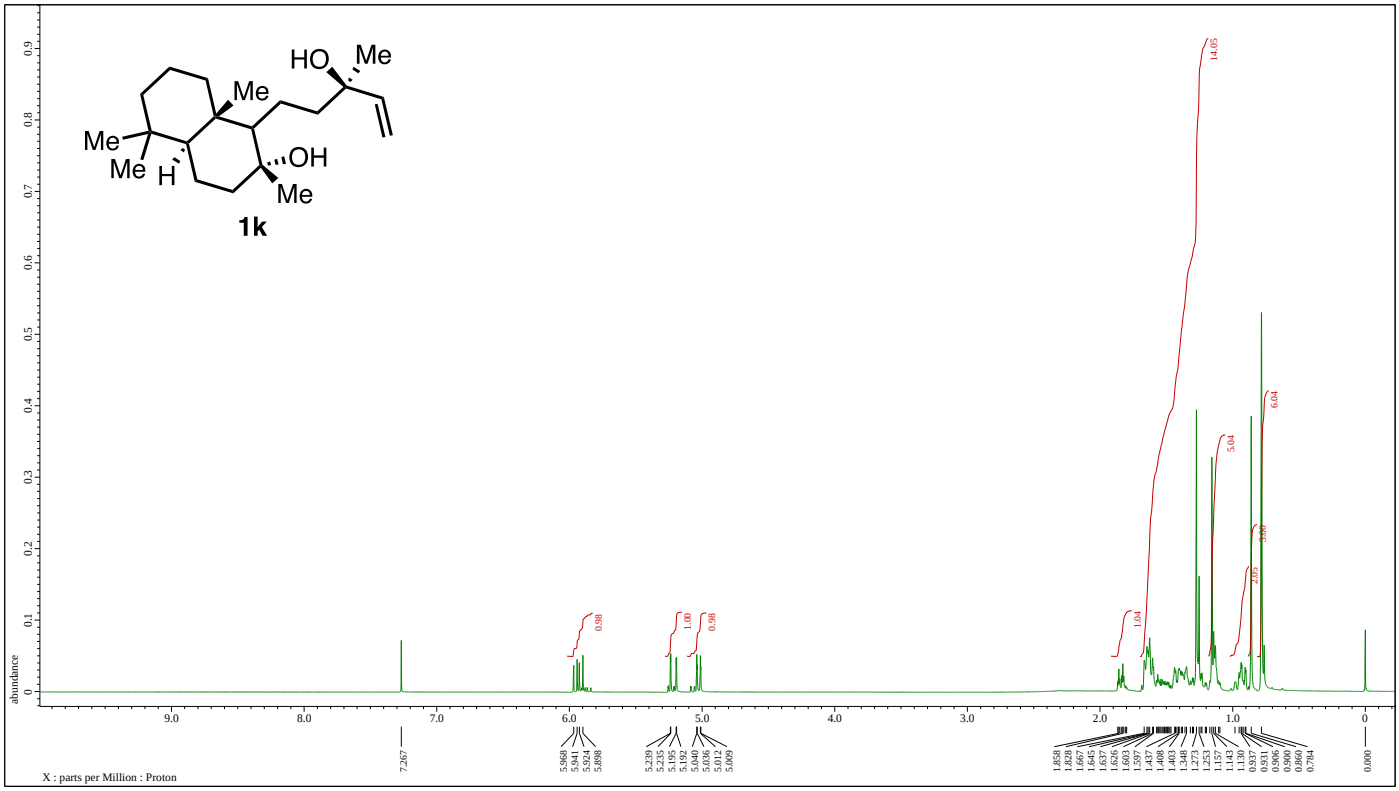
^{1}H NMR (400 MHz, $CDCl_3$) of **1j-*d*$_3$**



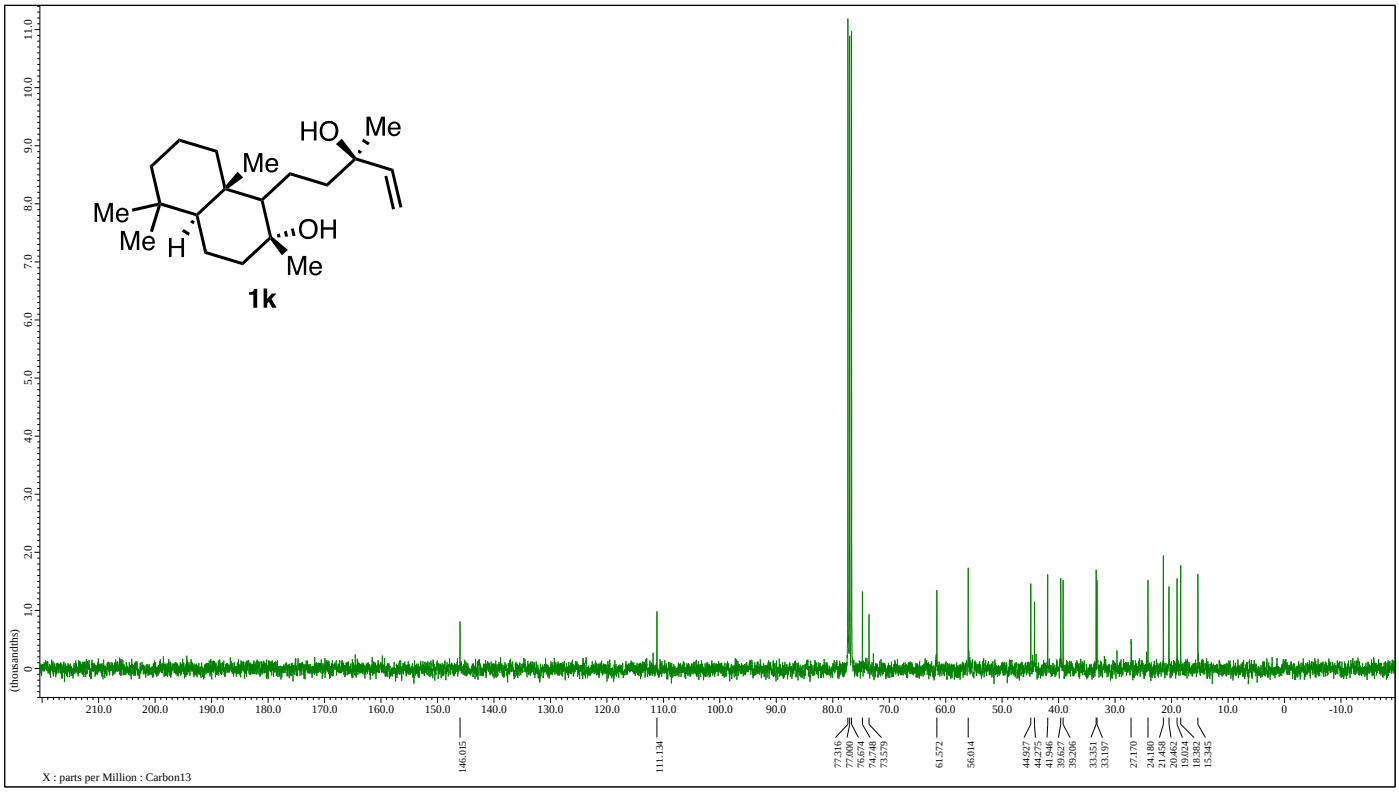
^{2}H NMR (77 MHz, $CHCl_3$) of **1j-*d*$_3$**



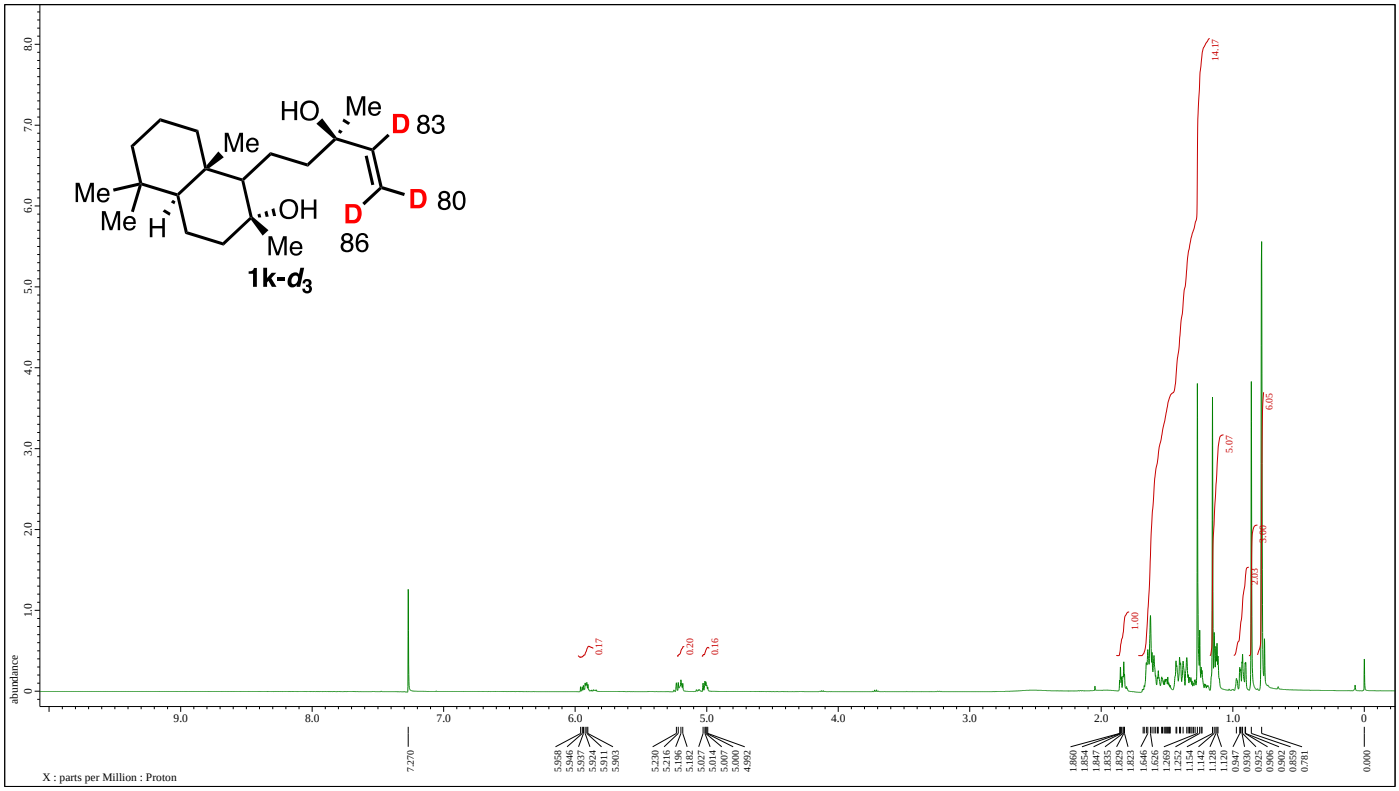
^{1}H NMR (400 MHz, $CDCl_3$) of **1k**



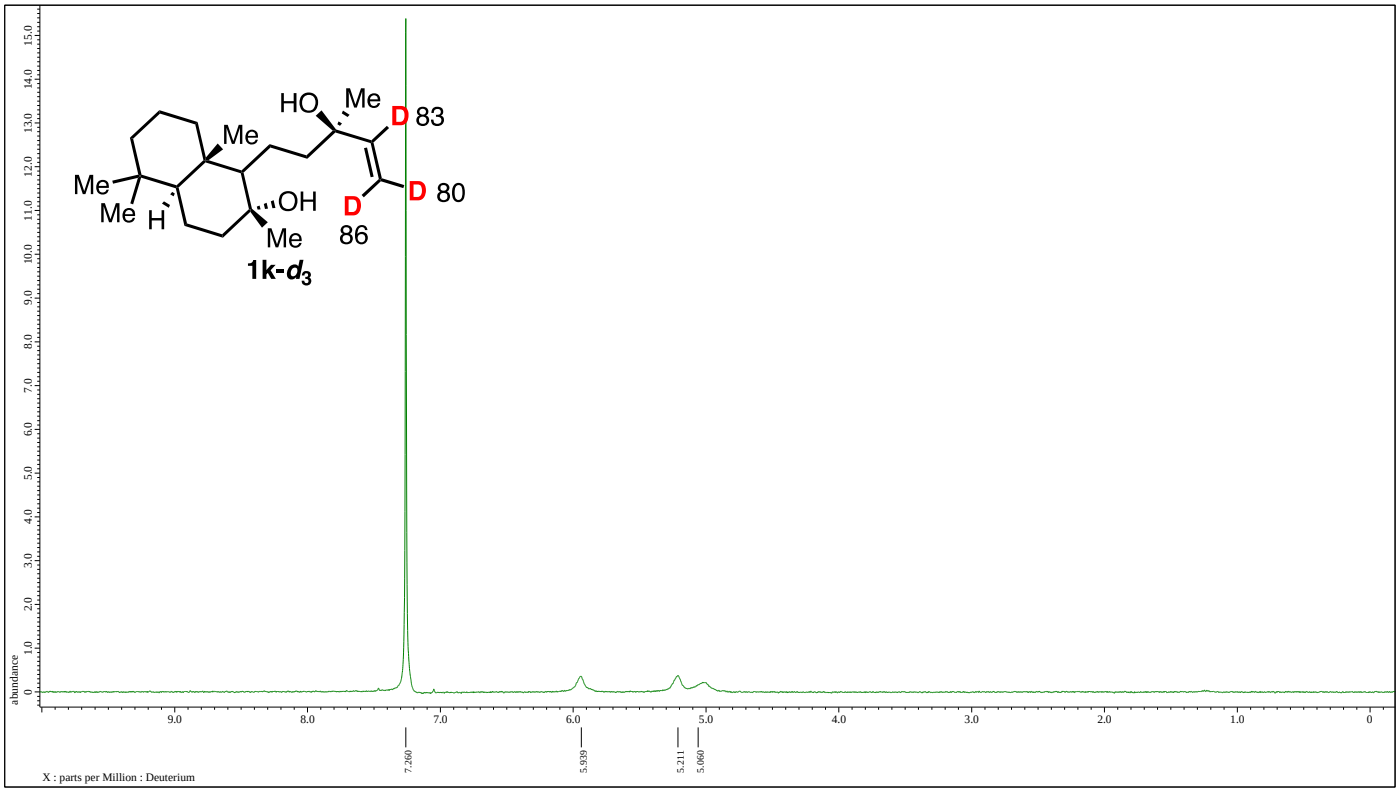
^{13}C NMR (100 MHz, $CDCl_3$) of **1k**



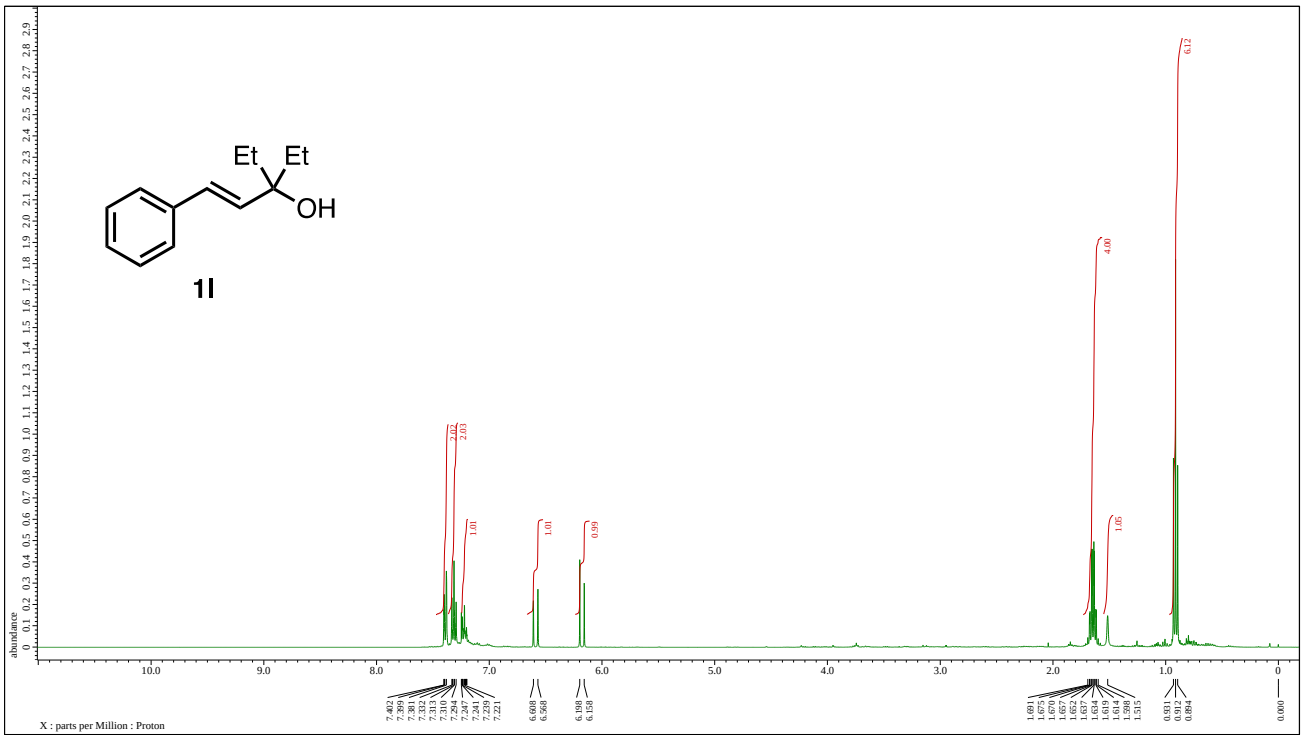
^{1}H NMR (500 MHz, $CDCl_3$) of **1k-*d*$_3$**



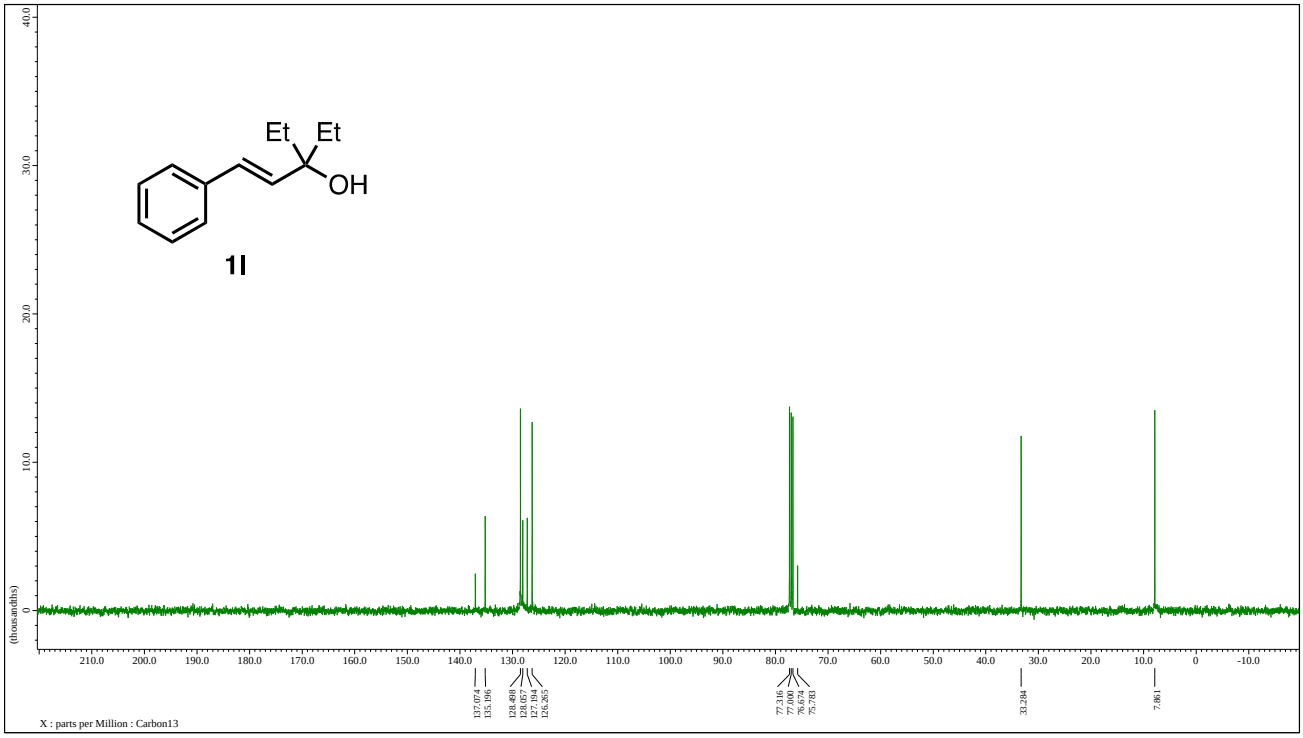
^{2}H NMR (77 MHz, $CHCl_3$) of **1k-*d*$_3$**



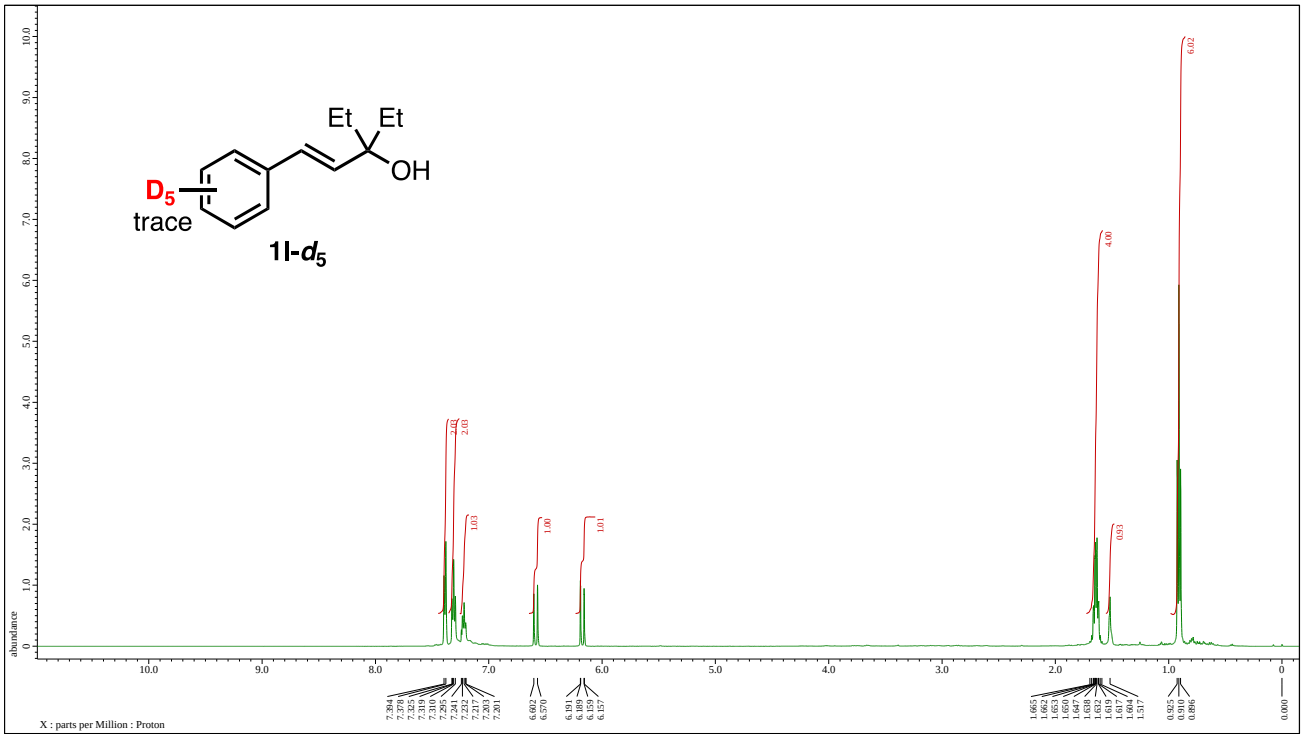
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



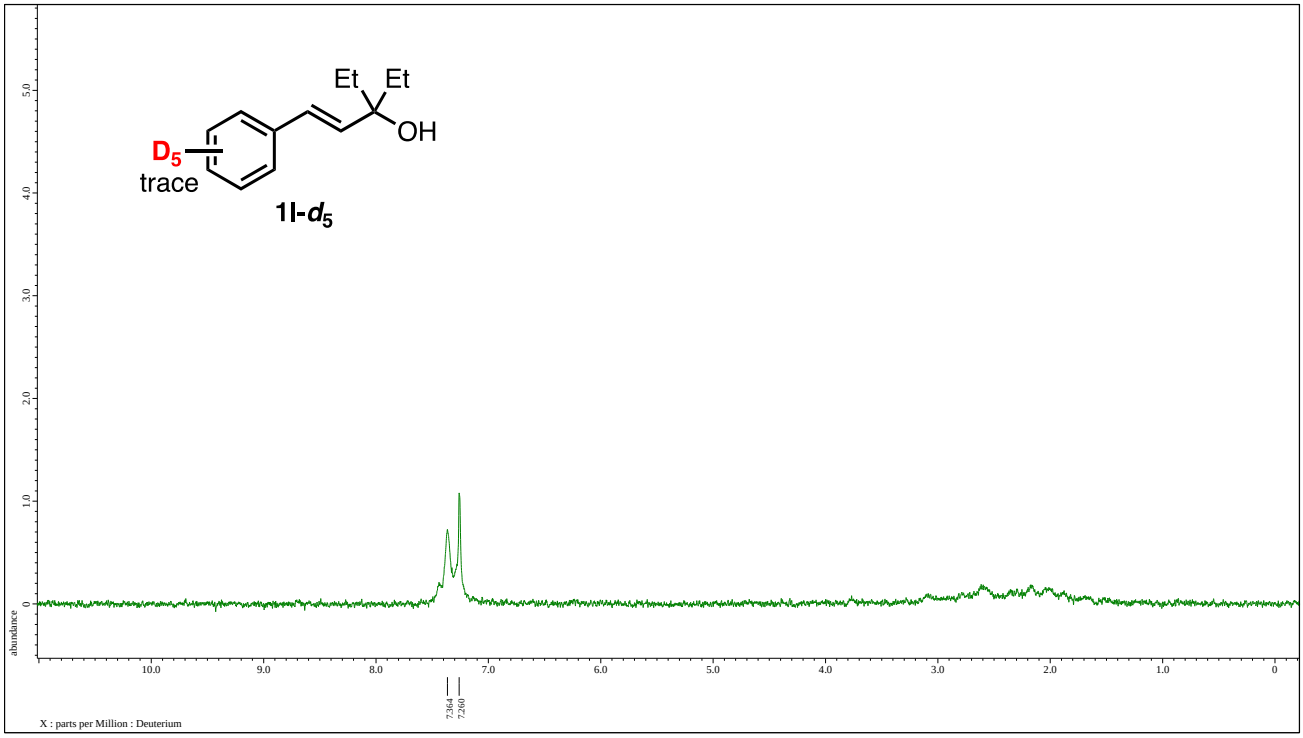
^{13}C NMR (100 MHz, $CDCl_3$) of **1l**



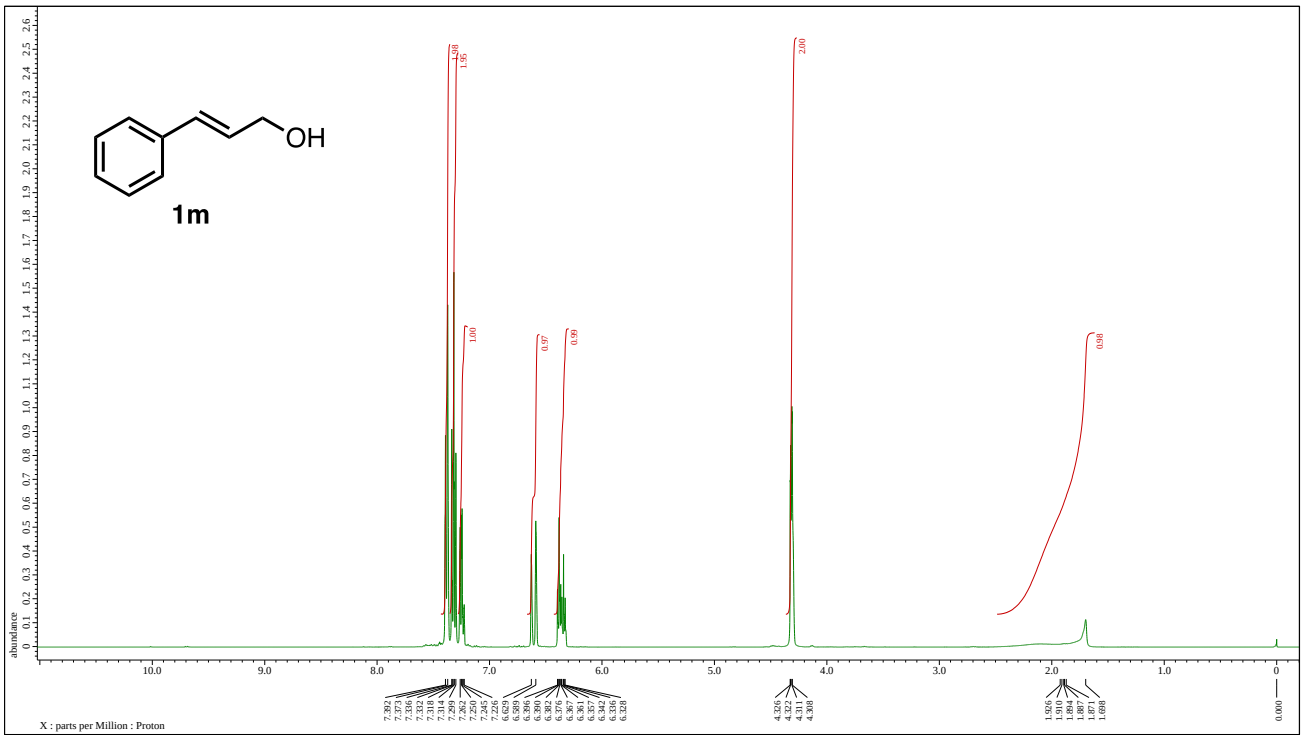
^{1}H NMR (500 MHz, $CDCl_3$) of **1l-*d*$_5$**



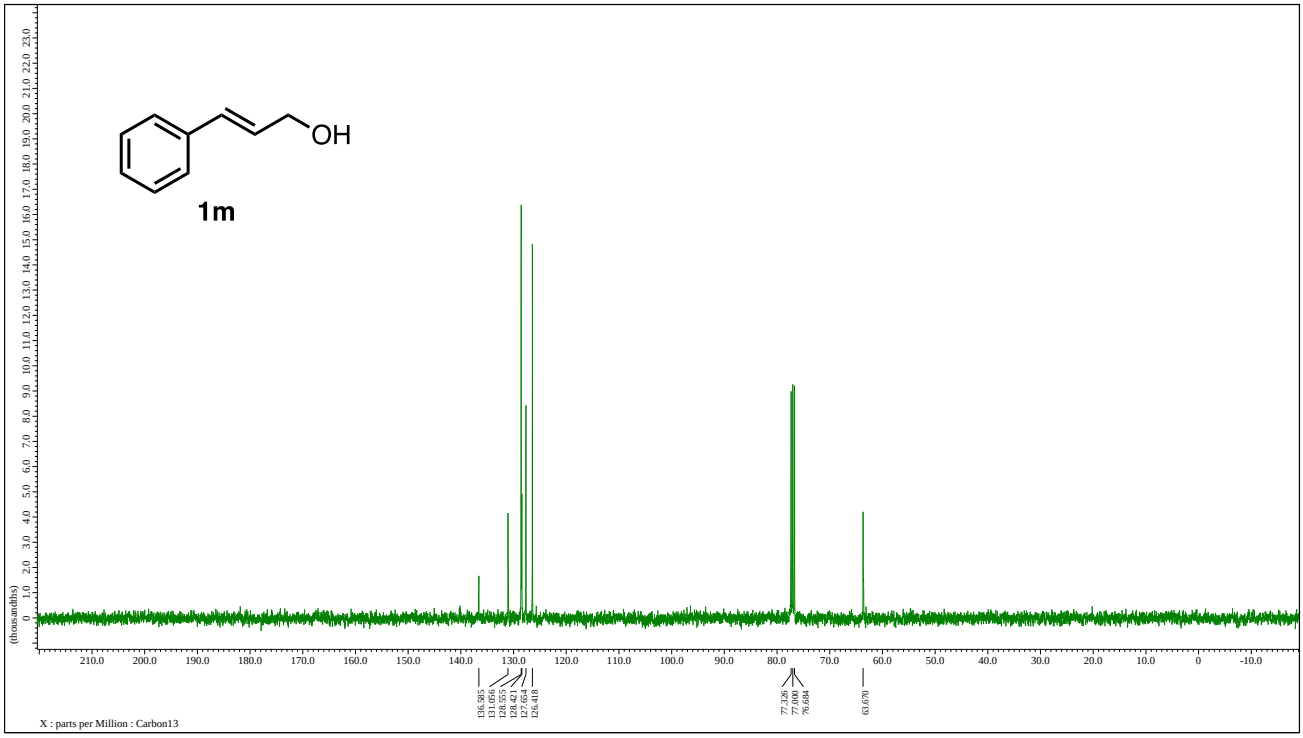
^{2}H NMR (77 MHz, $CHCl_3$) of **1l-*d*$_5$**



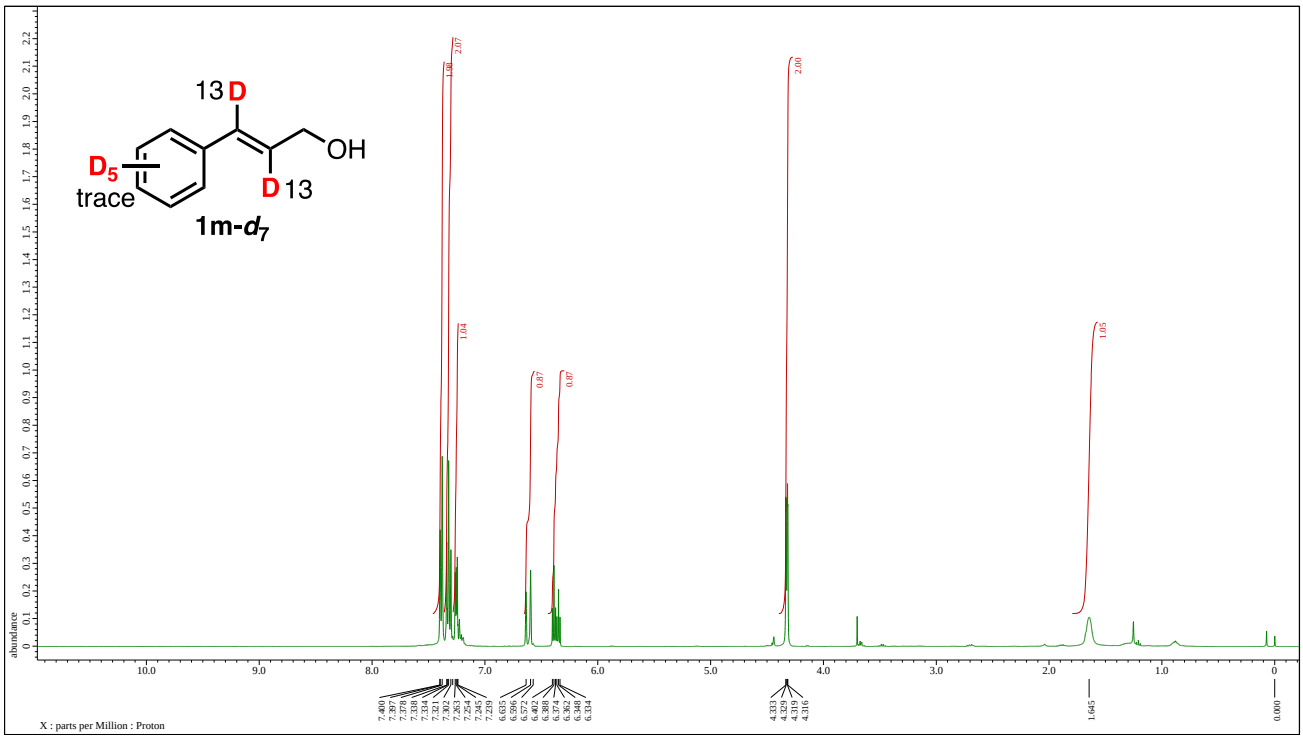
^{1}H NMR (400 MHz, $CDCl_3$) of **1m**



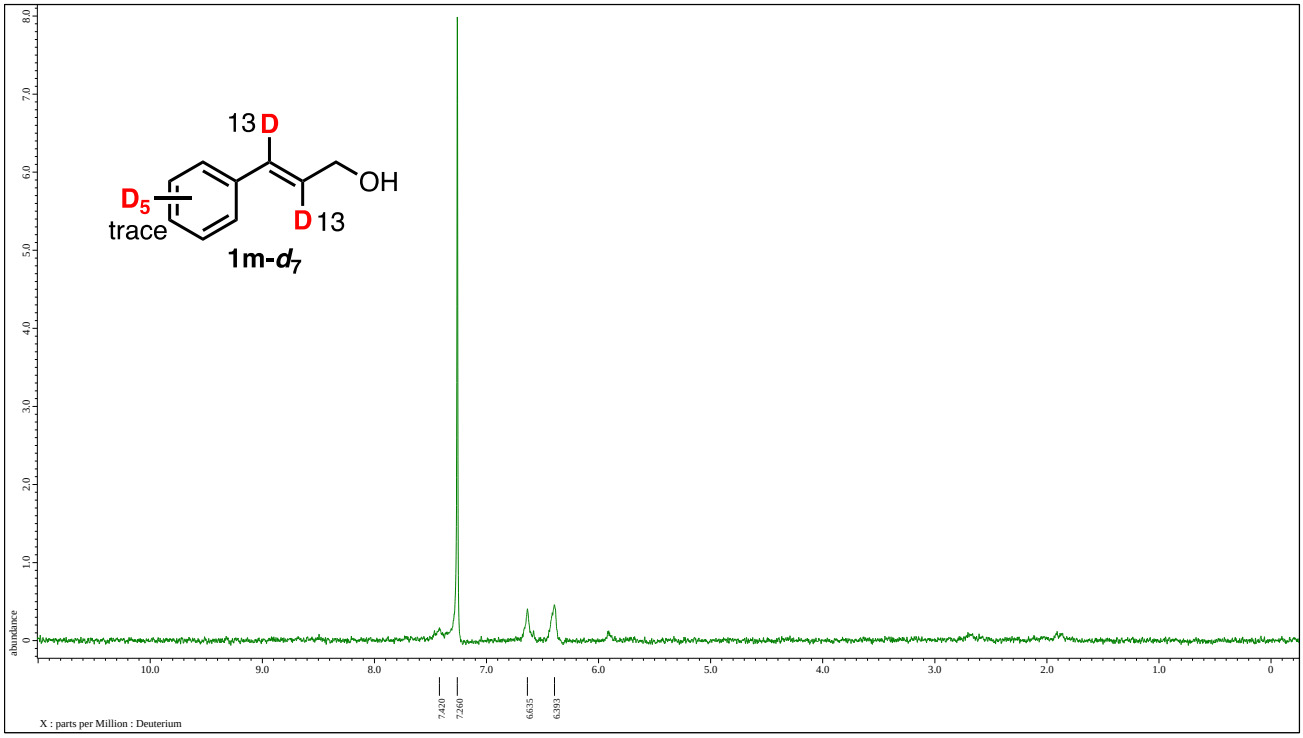
^{13}C NMR (100 MHz, $CDCl_3$) of **1m**



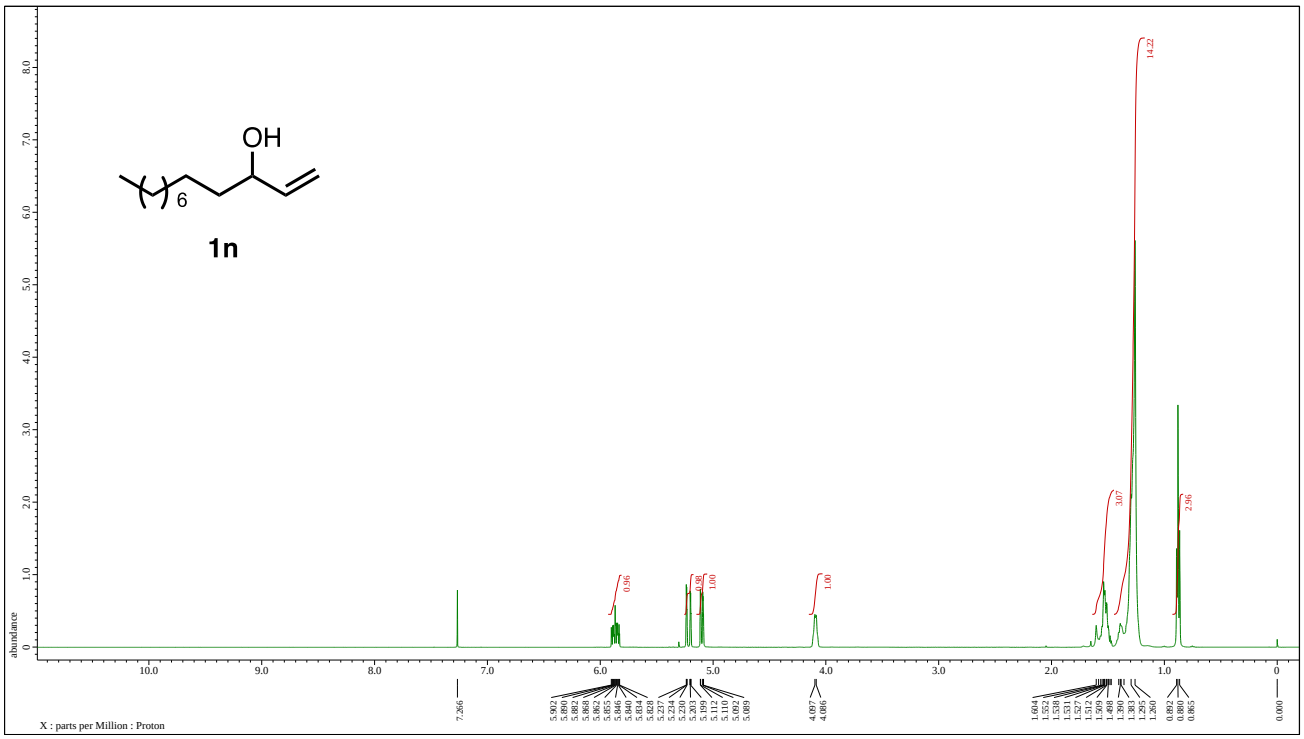
^{1}H NMR (400 MHz, $CDCl_3$) of **1m-*d*$_7$**



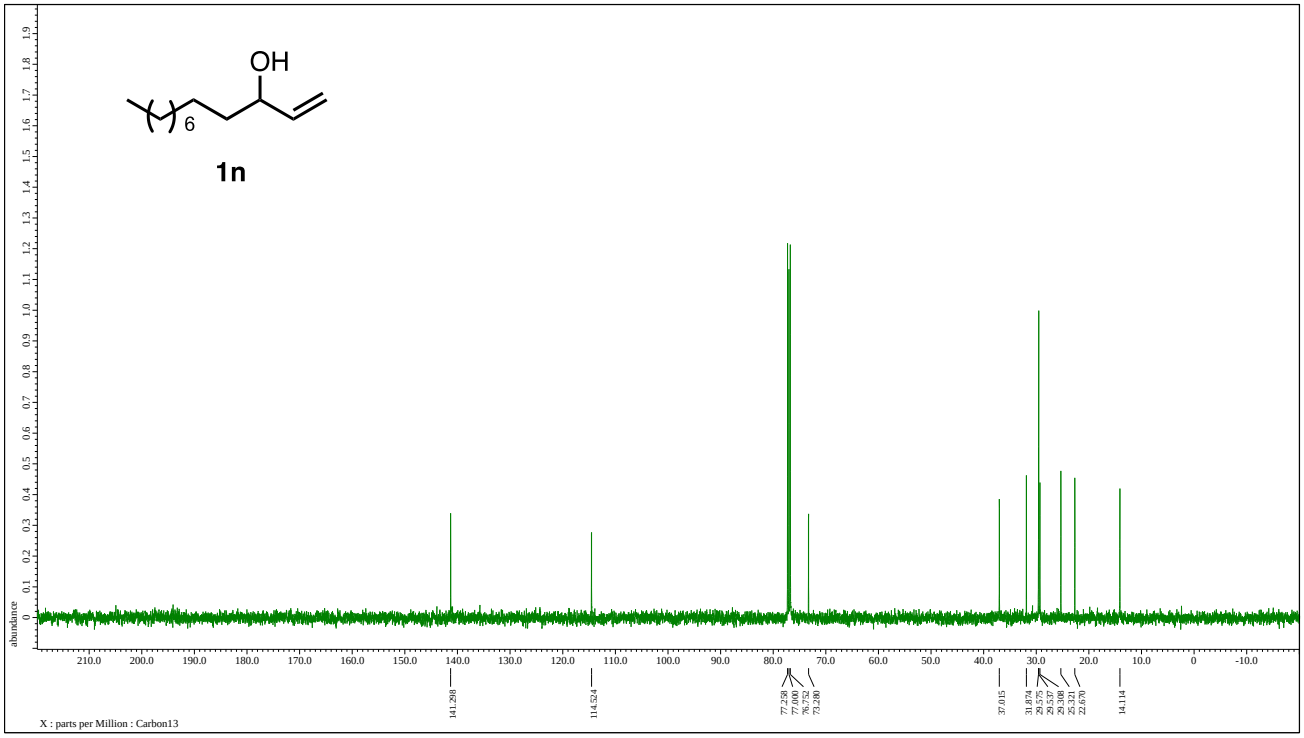
^{2}H NMR (77 MHz, $CHCl_3$) of **1m-*d*$_7$**



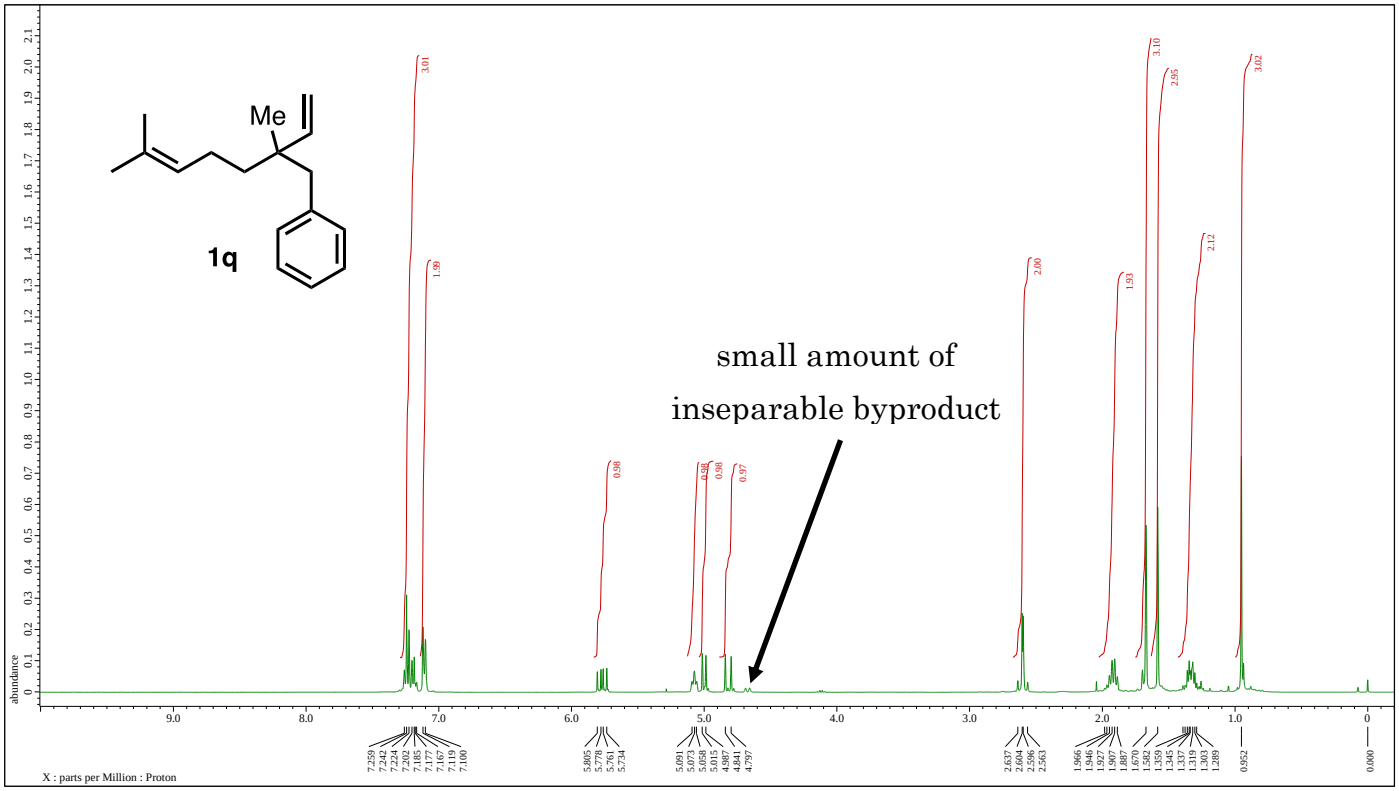
^{1}H NMR (500 MHz, $CDCl_3$) of **1n**



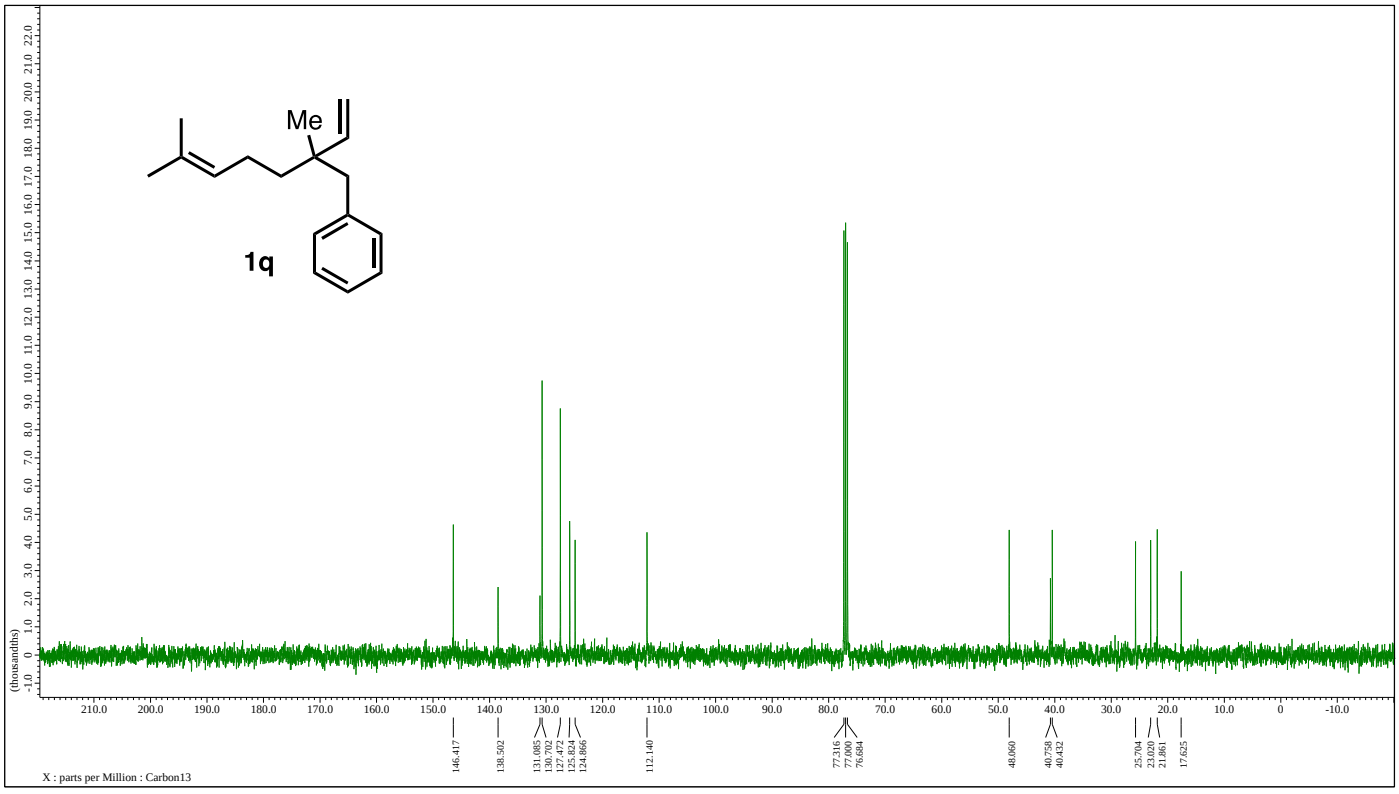
^{13}C NMR (125 MHz, $CDCl_3$) of **1n**



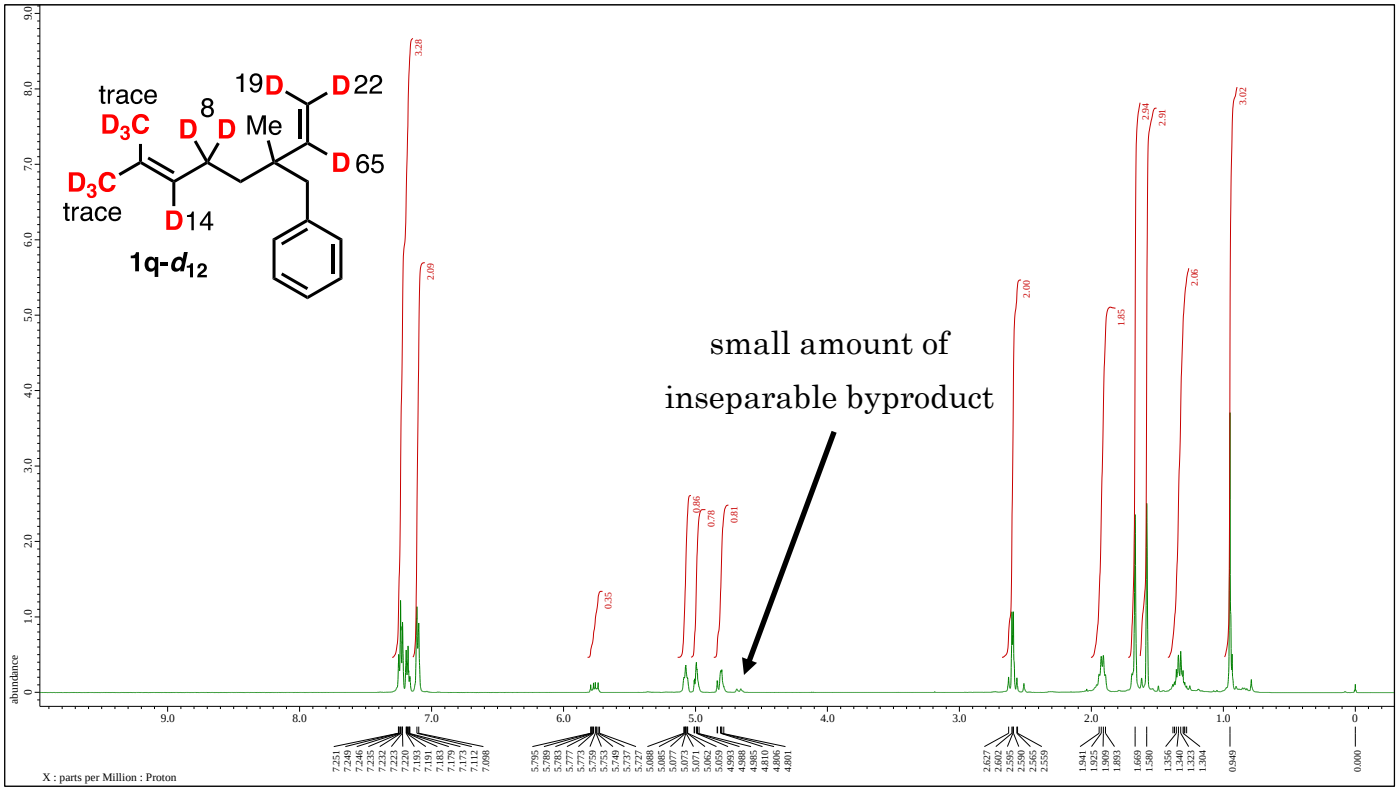
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



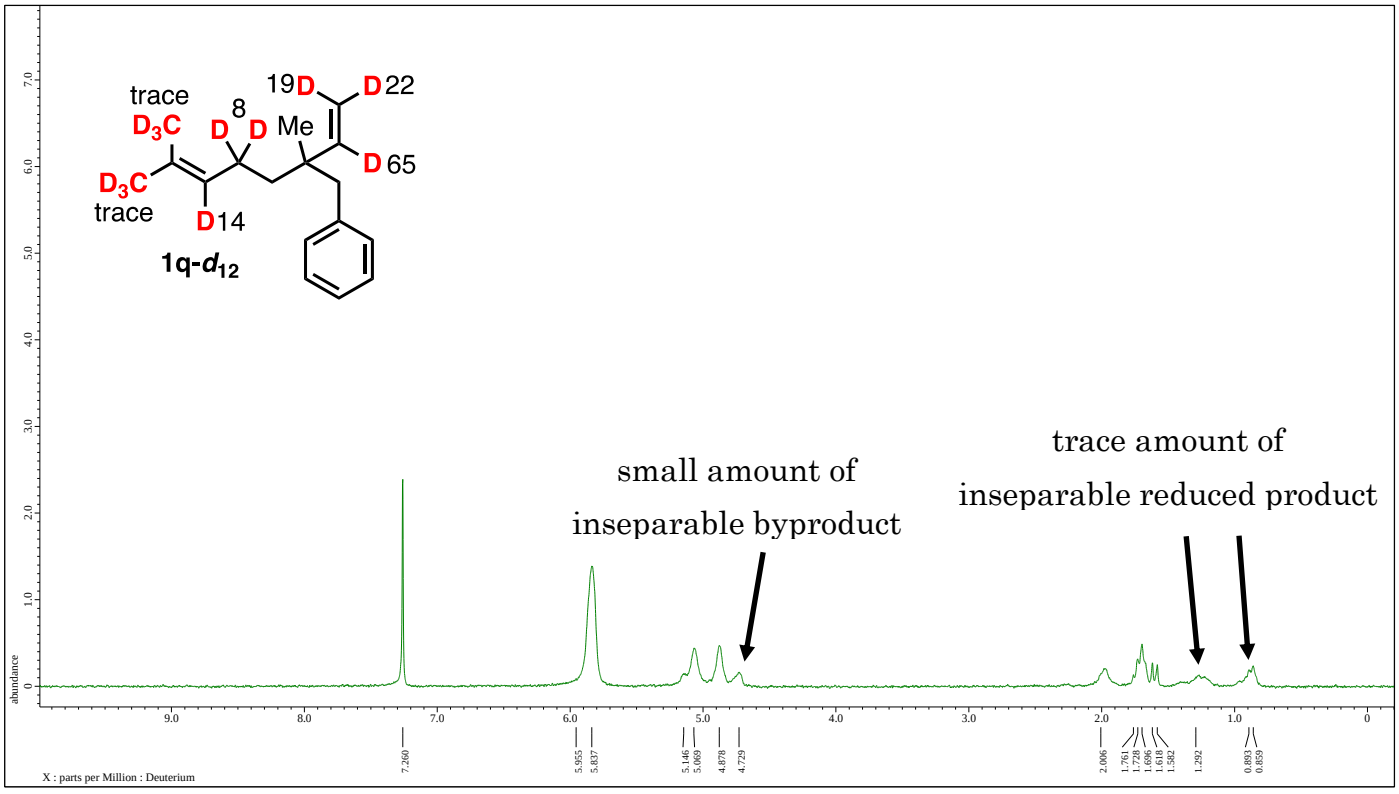
^{13}C NMR (100 MHz, $CDCl_3$) of **1q**



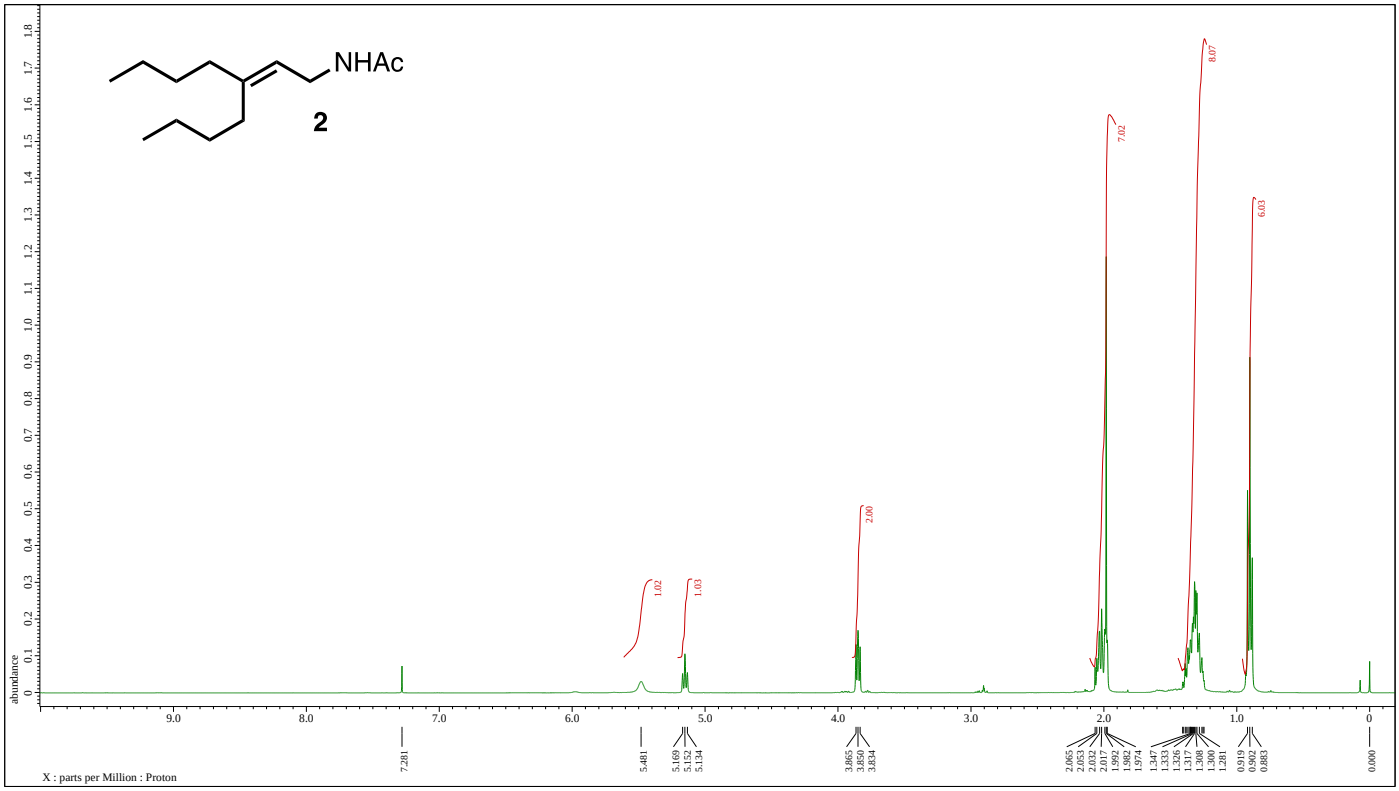
^{1}H NMR (500 MHz, $CDCl_3$) of **1q-*d*$_{12}$**



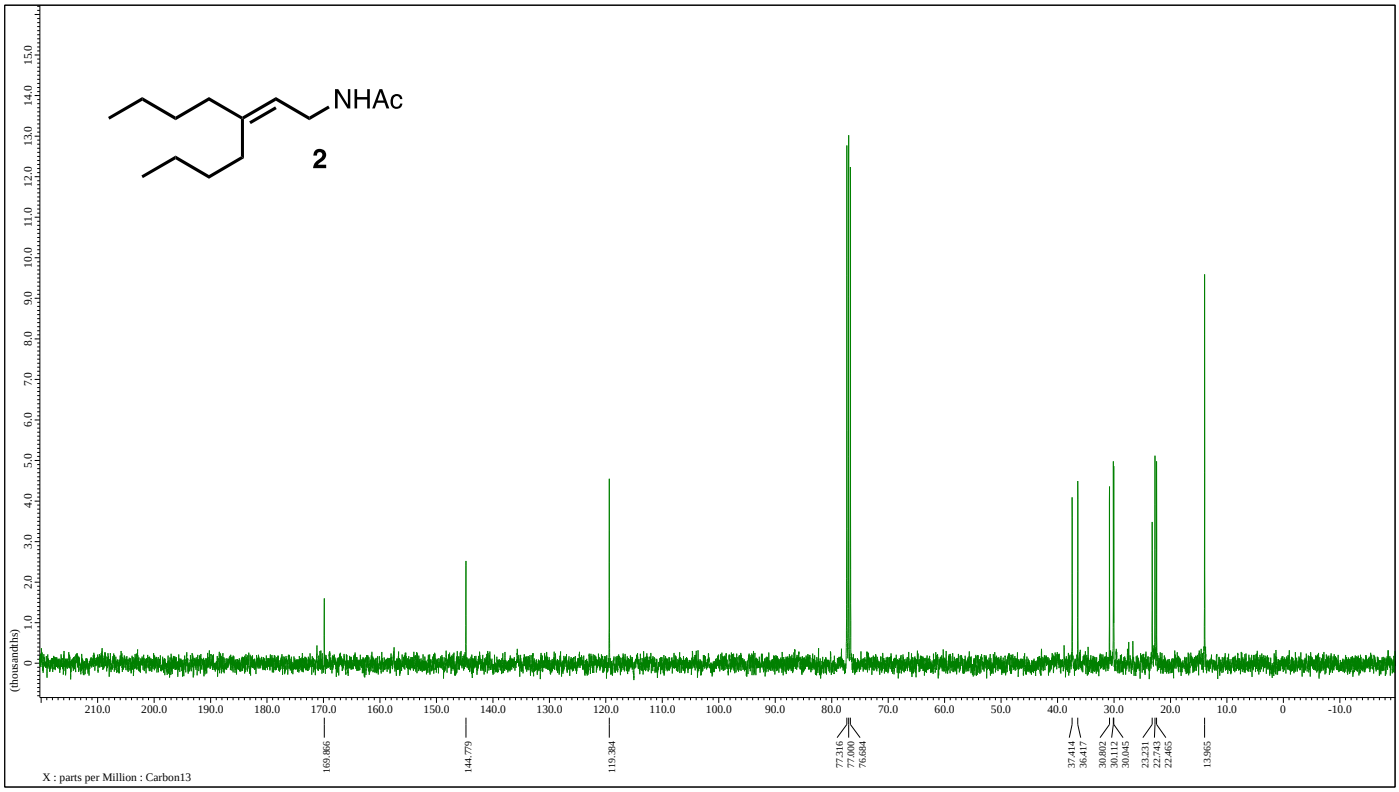
^{2}H NMR (77 MHz, $CHCl_3$) of **1q-*d*$_{12}$**



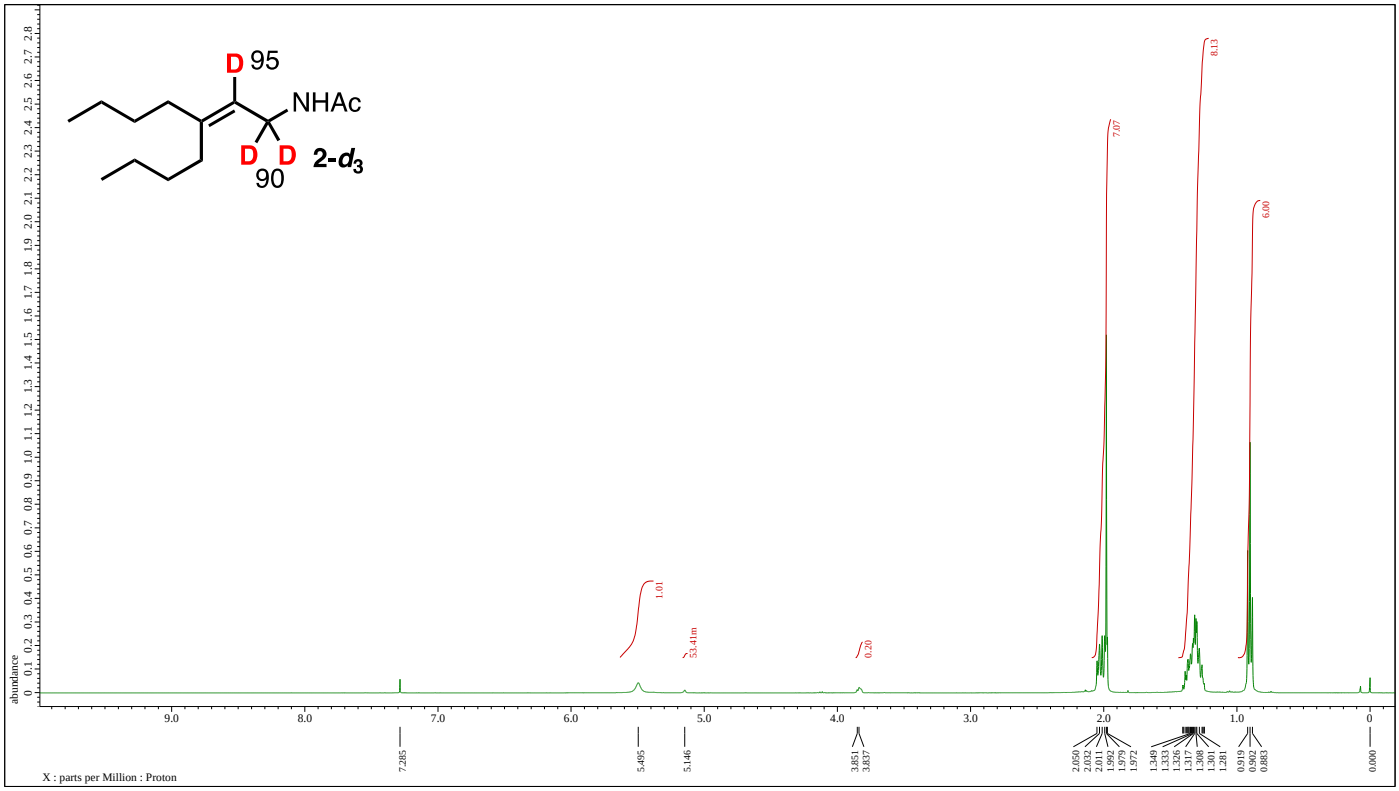
^{1}H NMR (400 MHz, $CDCl_3$) of **2**



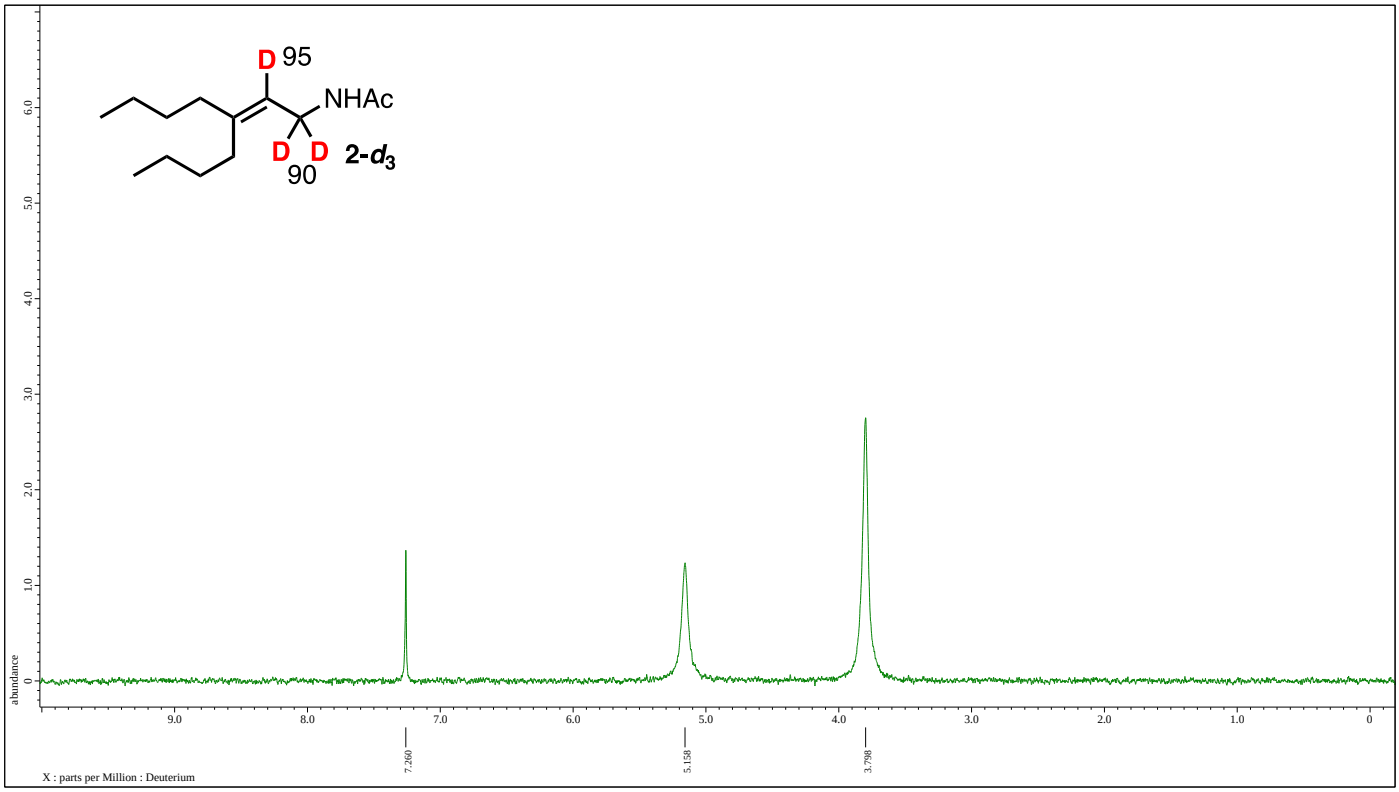
^{13}C NMR (100 MHz, $CDCl_3$) of **2**



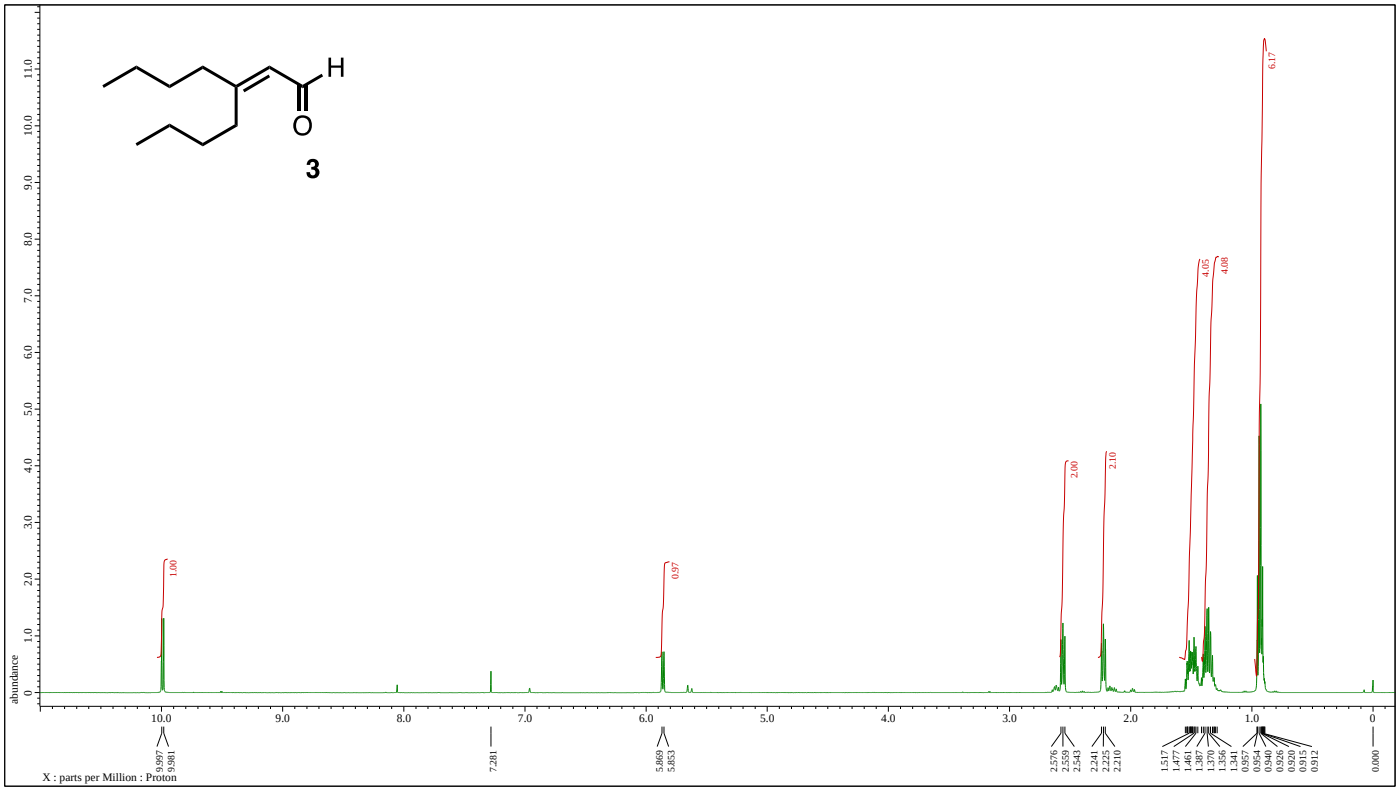
^{1}H NMR (400 MHz, $CDCl_3$) of **2-d_3**



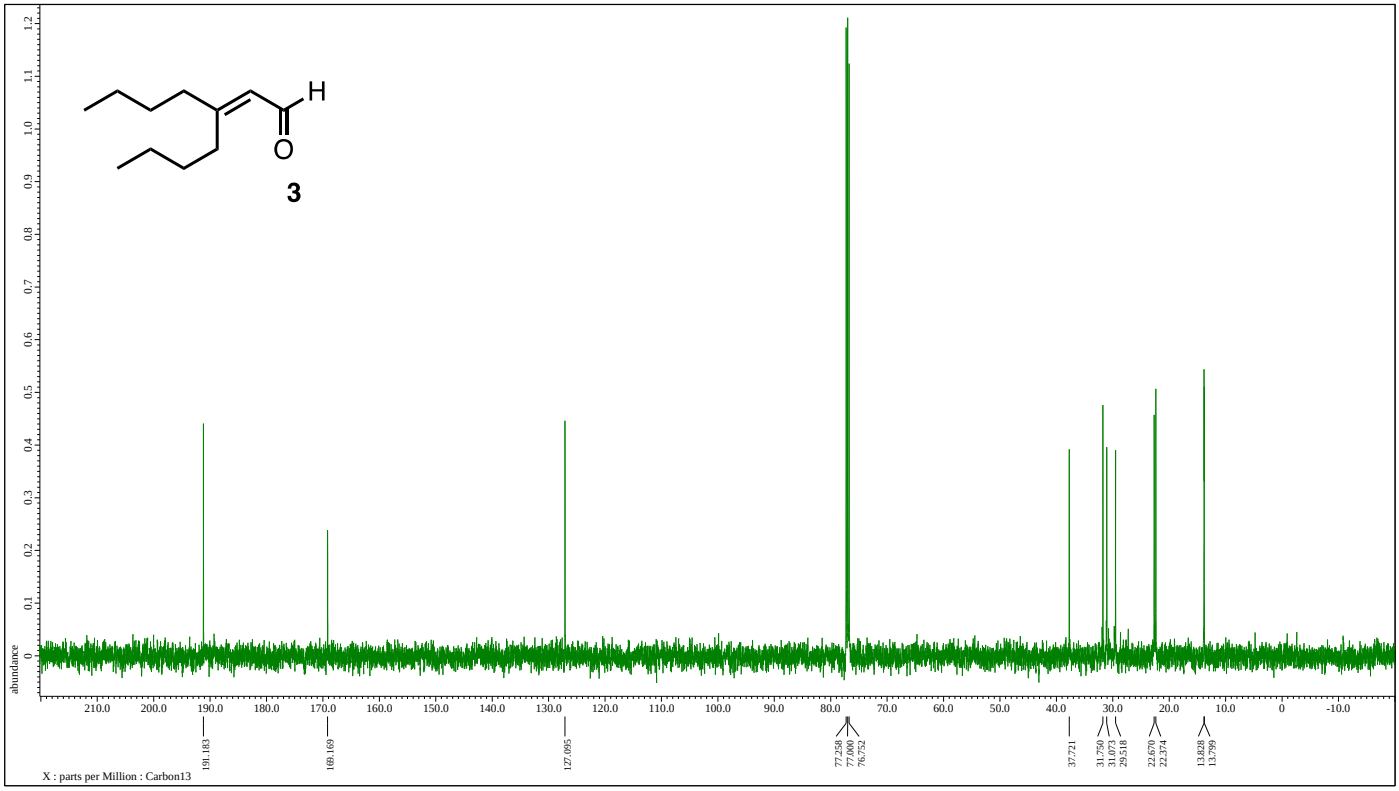
^{2}H NMR (77 MHz, $CHCl_3$) of **2-d_3**



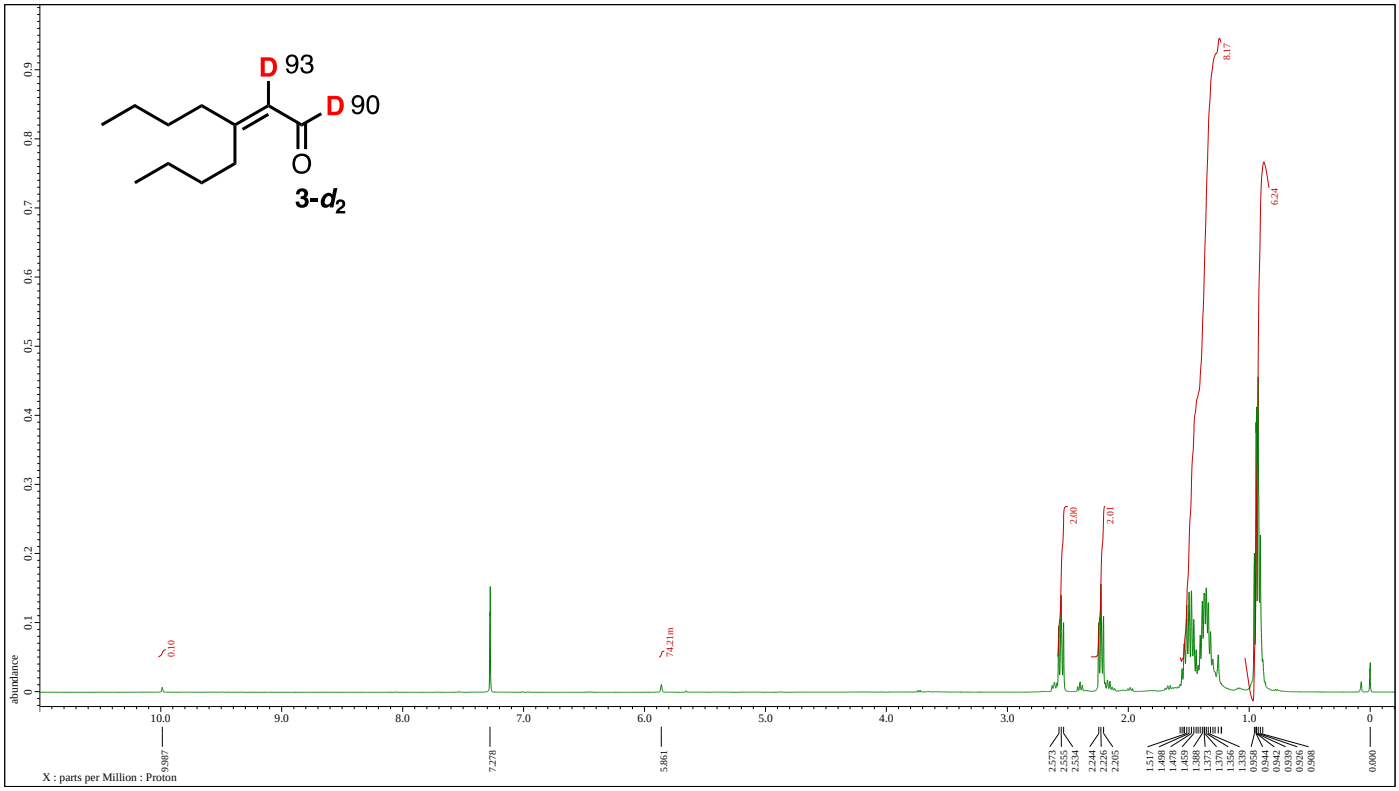
^{1}H NMR (500 MHz, $CDCl_3$) of **3**



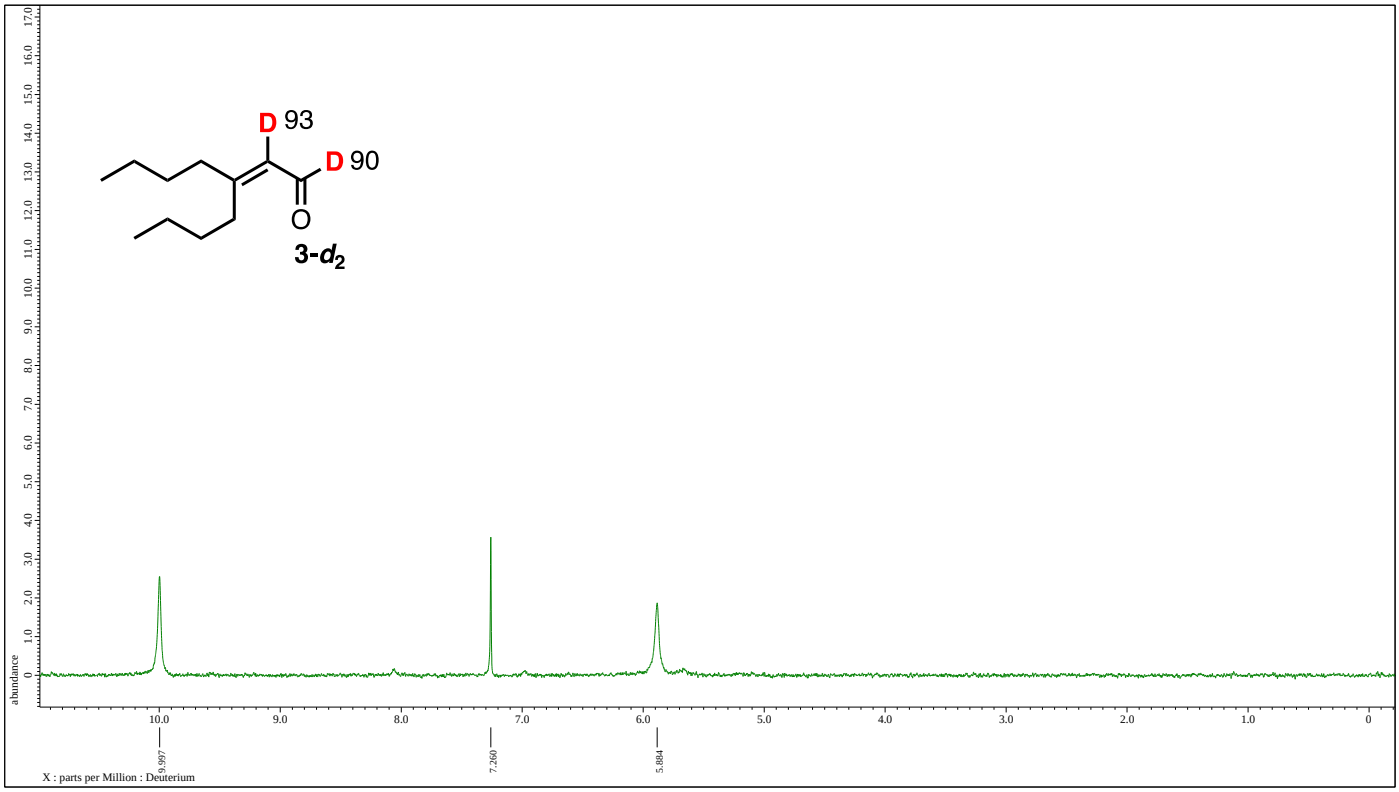
^{13}C NMR (125 MHz, $CDCl_3$) of **3**



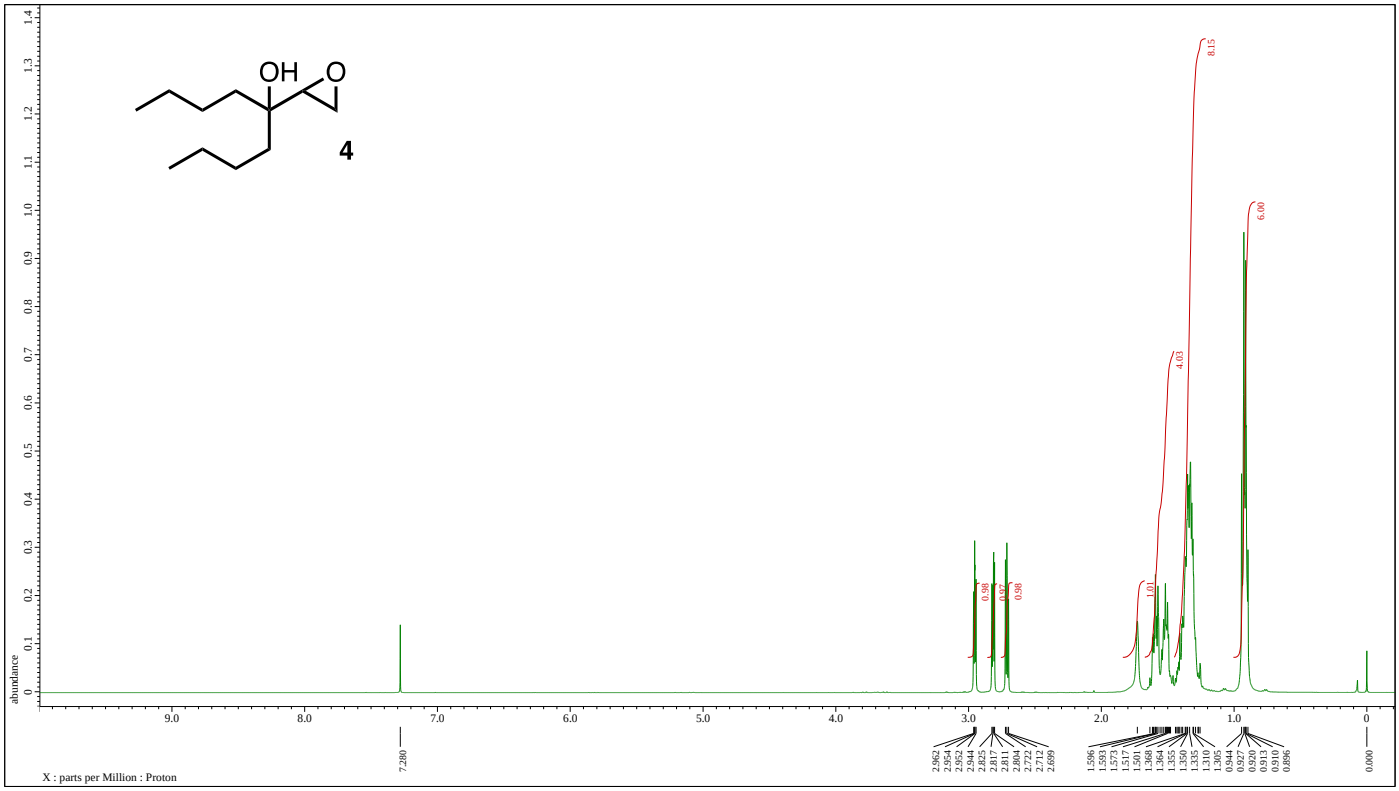
^{1}H NMR (400 MHz, $CDCl_3$) of **3-d_2**



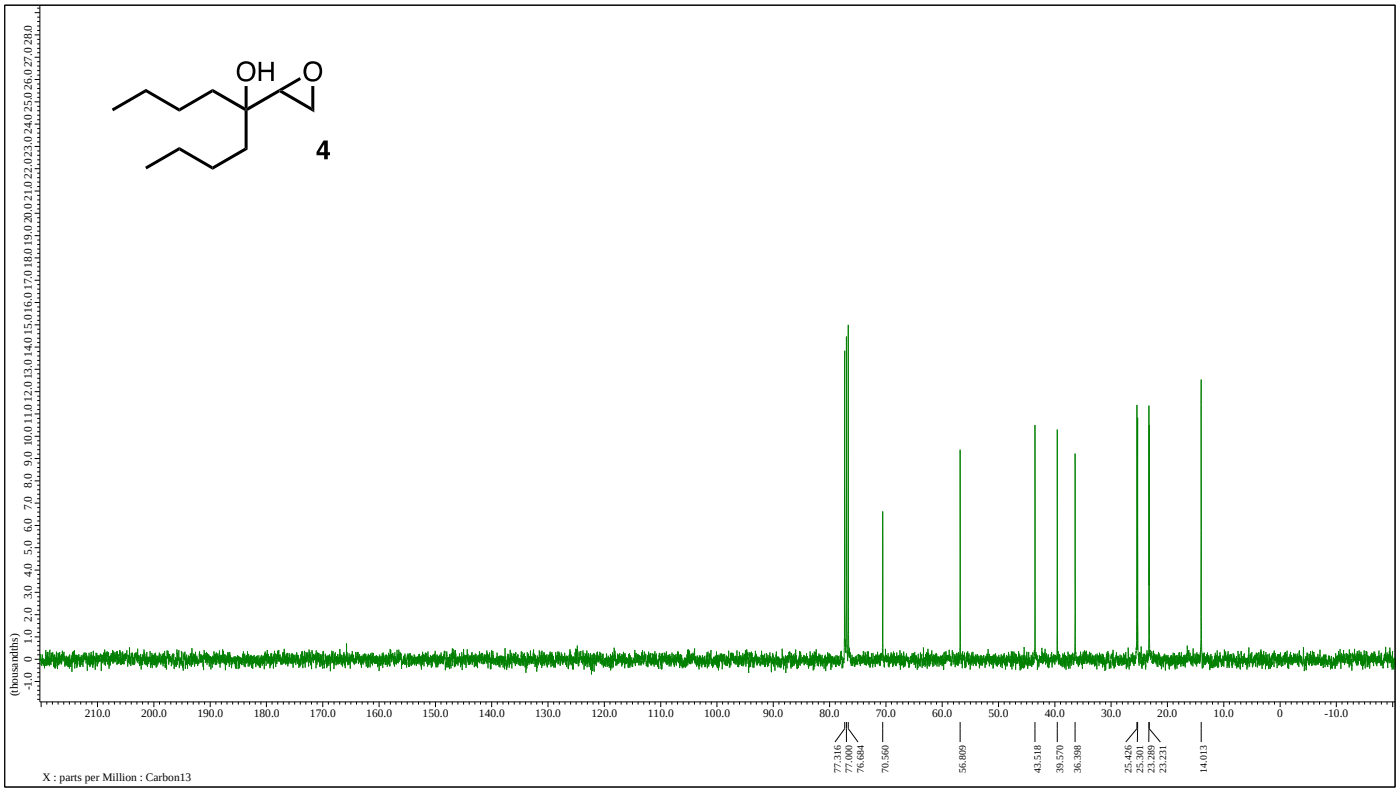
^{2}H NMR (77 MHz, $CHCl_3$) of **3-d_2**



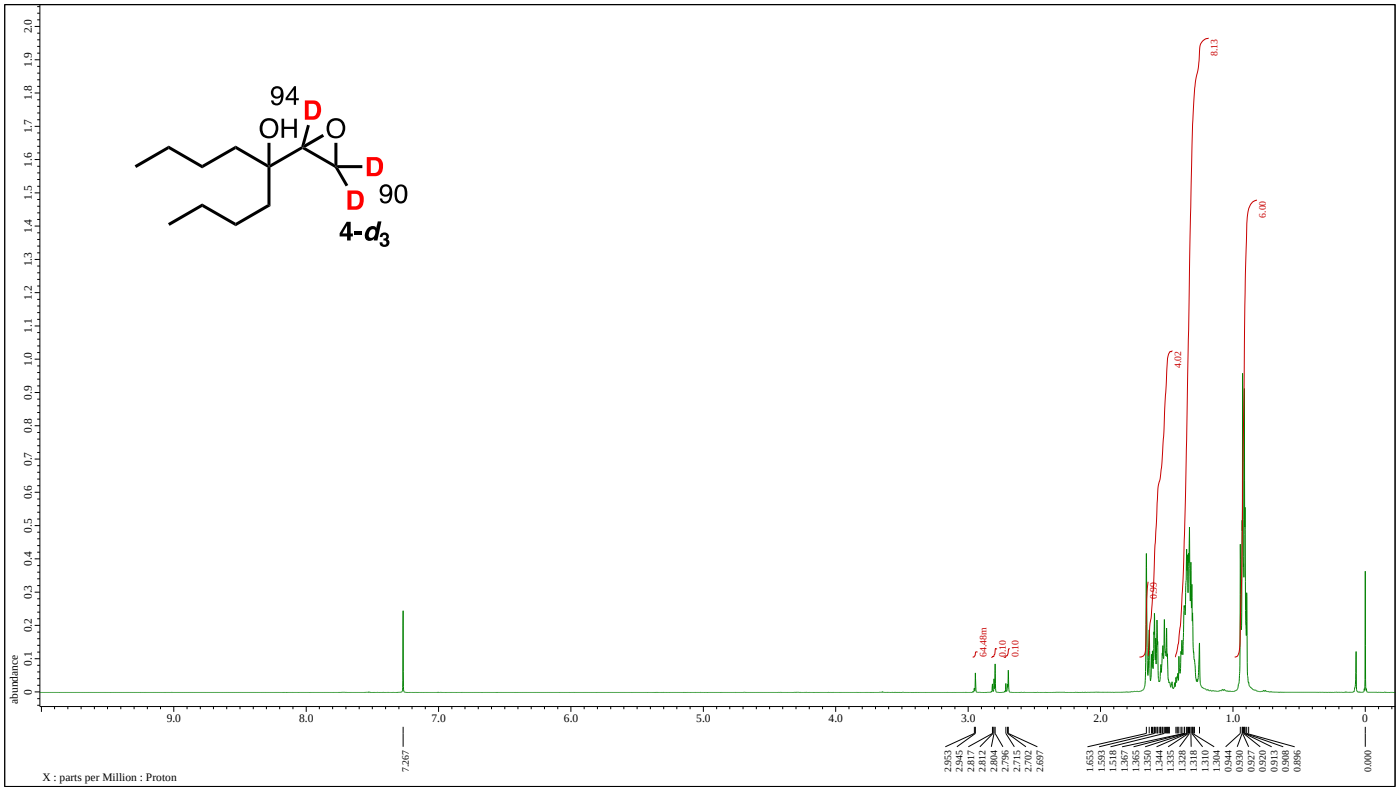
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



^{13}C NMR (100 MHz, $CDCl_3$) of **4**



^{1}H NMR (400 MHz, $CDCl_3$) of **4-*d*$_3$**



^{2}H NMR (77 MHz, $CHCl_3$) of **4-*d*$_3$**