Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Solid acetylene reagent with enhanced reactivity: Fluoride-mediated functionalization of alcohols and phenols

Georg Werner[1], Konstantin S. Rodygin[1], Anton A. Kostin[1], Evgeniy G. Gordeev[2], Alexey S. Kashin[2] and Valentine P. Ananikov*[1,2]

[1]Saint Petersburg State University, Universitetsky pr. 26, Stary Petergof 198504, Russia

[2]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119991, Russia

* e-mail: val@ioc.ac.ru

Contents

S1. Materials and methods

Calcium carbide was purchased from Acros (97+% purity) and was freshly powdered before the reaction. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer. The data were processed using MestReNova (version 6.0.2) desktop NMR data processing software. Microanalyses (C, H, N) were carried out on a Euro EA3028-HT analyzer. The FE-SEM observations were performed using a Hitachi SU8000 field-emission scanning electron microscope. Most of the studied vinyl ethers were not efficiently ionizable in the ESI-MS, in some cases, the addition of Ag^{+} improved the ionization process.

Most of the products can be distilled in a vacuum if further purification is required. Purification via column chromatography on silica should be avoided due to the sensitivity of most of the vinyl ethers towards undergoing rapid polymerization or degradation. If purification via column chromatography is required for some reason, the silica should be neutralized with triethylamine. The products may be sensitive to light and should be stored in a dark place. Contact with acid or traces of metals may initiate polymerization and should be avoided.

Caution: The experimental procedures described in the present study involve the evolution of gaseous acetylene upon the reaction of water with calcium carbide – the necessary safety requirements for experiments with gases, acetylene and CaC_2 should be implemented (see corresponding regulations).

S2. General procedures

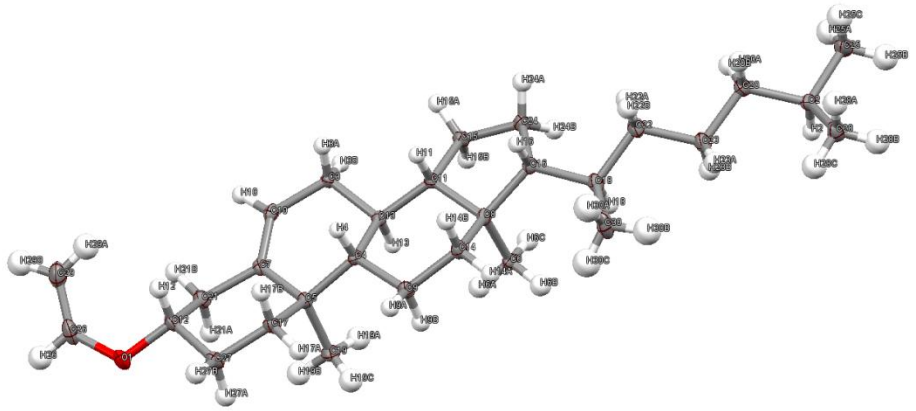
Large scale procedure. KOH (29 mmol, 1.63 g), benzyl alcohol (29 mmol, 3.20 g, 3 mL), KF (116 mmol, 6.70 g) and calcium carbide (58 mmol, 3.70 g, small stones with a diameter of ca. 5 mm) were added to a Schlenk flask (25 mL) followed by addition of 10 mL of dry DMSO. The flask was sealed with a septum. After stirring at room temperature for 5 min water (120 mmol, 2.2 mL) was added through the valve, and the mixture was heated to 130 °C with vigorous stirring for 3 h. After cooling to 25 °C the mixture was extracted with hexane (3 x 50 mL), and the collected hexane layers were concentrated under vacuum. Benzyl vinyl ether (**2p**) was obtained as a colorless oil (2.72 g, 70 %).

Sequential vinylation. K_2CO_3 (0.5 mmol, 69 mg), a phenol (1.0 mmol), KF (4.0 mmol, 232 mg) and freshly powdered calcium carbide (2.0 mmol, 128 mg) were added to a reaction tube (7 mL) with 1.5 mL of dry DMSO. After stirring at room temperature for 5 min, water (4.0 mmol, 72 µL) was added, the tube was sealed, and the mixture was heated at 130 °C for 3 h with vigorous stirring. After cooling to 25 °C, the mixture was extracted with hexane (3 x 4 mL). New portion of calcium carbide and water were added to DMSO layer, the tube was sealed and the mixture was heated at 130 °C for 3 h with vigorous stirring. After cooling to 25 °C, the mixture was extracted with hexane (3 x 4 mL). This action was repeated again and three collected hexane layers were combined and concentrated under a reduced pressure.

S3. Crystal structures

3.1 X-ray crystallography data for cholesteryl vinyl ether (2t)

Figure S1. X-ray crystal structure of cholesteryl vinyl ether (CCDC 1444527).



Crystal structure determination of Cholesteryl vinyl ether (**2t**)

Crystal Data for $C_{29}H_{48}O$ (*M* =412.67 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 12.6051(8) Å, *b* = 8.5936(3) Å, *c* = 13.0034(8) Å, *β* = 117.576(8)°, *V* = 1248.56(14) Å^3, *Z* = 2, *T* = 100(2) K, μ(MoKα) = 0.063 mm^{-1}, *Dcalc* = 1.098 g/cm^3, 10184 reflections measured (5.914° ≤ 2Θ ≤ 54.982°), 5695 unique (R_{int} = 0.0262, R_{sigma} = 0.0568) which were used in all calculations. The final R_1 was 0.0426 (I > 2σ(I)) and wR_2 was 0.0929 (all data).

Table S1. Crystal data and structure refinement for CCDC 1444527**.**

Identification code	CCDC 1444527
Empirical formula	$C_{29}H_{48}O$
Formula weight	412.67
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.6051(8)
b/Å	8.5936(3)
c/Å	13.0034(8)
α/°	90
β/°	117.576(8)
γ/°	90
Volume/Å^3	1248.56(14)
Z	2
ρ_{calc}g/cm^3	1.098
μ/mm^{-1}	0.063
F(000)	460.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.914 to 54.982
Index ranges	-16 ≤ h ≤ 16, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	10184
Independent reflections	5695 [R_{int} = 0.0262, R_{sigma} = 0.0568]
Data/restraints/parameters	5695/1/276
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.0855

Final R indexes [all data]	R_1 = 0.0555, wR_2 = 0.0929
Largest diff. peak/hole / e Å^{-3}	0.21/-0.24
Flack parameter	0.5

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for CCDC 1444527. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	212.6(13)	3128.5(19)	5985.8(14)	24.3(4)
C1	1265.7(19)	2286(3)	3785.9(19)	16.7(5)
C2	402.6(19)	2644(3)	4283.1(19)	20.6(5)
C3	1075.1(19)	2711(3)	5592.1(19)	18.0(5)
C4	2075(2)	3918(2)	5992.4(19)	18.5(5)
C5	2906.1(19)	3650(2)	5457.8(18)	14.3(4)
C6	4087.0(19)	3623(2)	6114.2(18)	14.9(4)
C7	4981.3(18)	3468(2)	5661.4(17)	14.2(4)
C8	4419.6(18)	3713(2)	4349.4(17)	13.0(4)
C9	3217.9(18)	2848(2)	3747.2(17)	12.8(4)
C10	2303.4(18)	3470(2)	4139.3(17)	14.1(4)
C11	2714.3(19)	2820(3)	2419.0(18)	16.3(4)
C12	3620.7(19)	2334(2)	2000.4(18)	16.6(5)
C13	4750.6(18)	3353(2)	2546.9(17)	13.5(4)
C14	5258.9(18)	3172(2)	3873.6(17)	12.9(4)
C15	6500.6(19)	3914(2)	4370.1(18)	15.8(5)
C16	6937.0(19)	3499(3)	3472.8(18)	17.8(5)
C17	5844.8(18)	2812(3)	2387.4(17)	14.4(4)
C18	4448(2)	5059(2)	2155.1(18)	16.6(5)
C19	1796(2)	5072(2)	3589(2)	20.1(5)
C20	5874.8(19)	3251(3)	1255.4(18)	16.8(5)
C21	4804(2)	2610(3)	174(2)	29.2(6)
C22	7054(2)	2747(3)	1271.5(19)	20.2(5)
C23	7222(2)	3445(3)	271.6(19)	20.2(5)
C24	8495.9(19)	3280(3)	426.6(18)	19.2(5)
C25	8701(2)	4101(3)	-511.6(19)	16.4(5)
C26	7961(2)	3381(3)	-1707.3(18)	22.9(5)
C27	10021(2)	4100(3)	-207(2)	24.2(5)
C28	518(2)	2867(3)	7124(2)	26.3(6)
C29	1473(2)	2203(3)	7942(2)	30.6(6)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for CCDC 1444527. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	18.3(8)	36.5(10)	23.7(9)	1.0(7)	14.4(7)	3.2(8)
C1	12.7(11)	21.5(11)	14.6(10)	-1.0(9)	5.1(9)	-0.3(9)
C2	14.3(11)	26.7(12)	21.3(12)	0.6(10)	8.6(10)	-0.4(10)
C3	15.9(11)	20.8(11)	21.2(11)	0.0(9)	11.8(10)	0.4(10)
C4	18.0(12)	20.5(12)	19.2(11)	-1.3(9)	10.6(11)	0.3(9)
C5	16.4(11)	11.6(10)	17(1)	-0.4(8)	9.4(9)	-0.4(9)
C6	20.1(11)	12.7(10)	13.1(10)	-0.8(8)	8.7(10)	-1.4(9)
C7	14.3(10)	14(1)	15.1(10)	0.8(9)	7.6(9)	-0.9(9)
C8	14.5(11)	12.6(10)	13.3(10)	0.5(8)	7.5(9)	0.4(8)
C9	13.7(10)	12.4(10)	11.8(10)	0.3(8)	5.3(9)	1.2(9)
C10	13(1)	15.1(10)	15(1)	0.6(9)	7.1(9)	-0.1(9)
C11	13(1)	21.5(11)	13.1(10)	-2.7(9)	4.9(9)	-3.6(9)

C12	15.8(11)	20.1(11)	14.4(10)	-3.3(9)	7.4(10)	-2.9(9)
C13	15.1(10)	14(1)	12.5(10)	-1.5(9)	7.3(9)	-0.7(9)
C14	12.5(10)	12.8(10)	14.1(10)	0.5(8)	6.7(9)	-0.2(9)
C15	12.9(11)	18.2(11)	16.1(11)	0.2(9)	6.4(9)	-1.7(9)
C16	14.9(11)	22.8(11)	16.5(11)	0.8(10)	7.9(9)	-0.9(10)
C17	15.1(11)	14.6(10)	13.7(10)	-0.2(9)	6.9(9)	-0.2(9)
C18	18.1(11)	18.1(11)	12.9(10)	1.8(9)	6.4(10)	2.1(10)
C19	20.7(12)	19.4(11)	21.9(12)	5.4(9)	11.2(11)	5.1(10)
C20	18.1(11)	19.1(11)	16.2(11)	-2.0(9)	10.3(10)	-0.9(10)
C21	27.2(14)	45.9(16)	19.7(12)	-11.7(11)	15.3(11)	-11.7(13)
C22	22.6(12)	19.0(11)	23.8(12)	0.9(9)	14.8(11)	1(1)
C23	20.6(12)	24.0(12)	19.7(11)	-1.3(10)	12.5(10)	-0.7(11)
C24	19.0(11)	22.1(11)	18.0(11)	2.2(9)	9.7(10)	3.5(10)
C25	15.5(11)	18.1(11)	15.0(11)	0.3(9)	6.7(10)	1.8(9)
C26	21.7(12)	30.4(13)	17.6(11)	-3.7(11)	10(1)	-3.2(11)
C27	17.2(12)	35.1(14)	19.8(12)	1.3(10)	8.2(11)	-0.7(11)
C28	25.4(13)	35.4(14)	26.6(13)	-6.5(11)	19.2(12)	-7.5(12)
C29	33.2(15)	41.2(15)	24.2(13)	-0.2(12)	18.9(13)	-4.1(13)

Table S4. Bond Lengths for CCDC 1444527**.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.445(2)	C12	C13	1.537(3)
O1	C28	1.364(3)	C13	C14	1.545(3)
C1	C2	1.532(3)	C13	C17	1.558(3)
C1	C10	1.549(3)	C13	C18	1.542(3)
C2	C3	1.511(3)	C14	C15	1.529(3)
C3	C4	1.526(3)	C15	C16	1.545(3)
C4	C5	1.519(3)	C16	C17	1.561(3)
C5	C6	1.330(3)	C17	C20	1.537(3)
C5	C10	1.528(3)	C20	C21	1.531(3)
C6	C7	1.500(3)	C20	C22	1.539(3)
C7	C8	1.529(3)	C22	C23	1.533(3)
C8	C9	1.537(3)	C23	C24	1.530(3)
C8	C14	1.525(3)	C24	C25	1.531(3)
C9	C10	1.555(3)	C25	C26	1.525(3)
C9	C11	1.540(3)	C25	C27	1.521(3)
C10	C19	1.547(3)	C28	C29	1.312(3)
C11	C12	1.533(3)			

Table S5. Bond Angles for CCDC 1444527.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C28	O1	C3	117.53(18)	C11	C12	C13	111.34(17)
C2	C1	C10	114.19(17)	C12	C13	C14	105.99(16)
C3	C2	C1	110.20(17)	C12	C13	C17	117.17(17)
O1	C3	C2	106.66(17)	C12	C13	C18	110.75(18)
O1	C3	C4	110.42(17)	C14	C13	C17	100.58(16)
C2	C3	C4	110.76(17)	C18	C13	C14	112.09(17)
C5	C4	C3	112.14(17)	C18	C13	C17	109.81(17)
C4	C5	C10	116.03(18)	C8	C14	C13	114.55(16)
C6	C5	C4	120.86(19)	C8	C14	C15	117.92(17)
C6	C5	C10	123.08(18)	C15	C14	C13	104.11(16)

C5	C6	C7	124.82(18)	C14	C15	C16	103.74(17)
C6	C7	C8	112.45(17)	C15	C16	C17	107.27(16)
C7	C8	C9	109.88(16)	C13	C17	C16	103.39(16)
C14	C8	C7	111.16(16)	C20	C17	C13	118.05(17)
C14	C8	C9	110.55(16)	C20	C17	C16	111.75(16)
C8	C9	C10	111.84(16)	C17	C20	C22	111.70(17)
C8	C9	C11	112.11(16)	C21	C20	C17	112.87(17)
C11	C9	C10	112.94(17)	C21	C20	C22	110.30(18)
C1	C10	C9	109.22(16)	C23	C22	C20	112.96(18)
C5	C10	C1	108.20(16)	C24	C23	C22	113.61(19)
C5	C10	C9	110.10(17)	C23	C24	C25	113.96(18)
C5	C10	C19	108.26(17)	C26	C25	C24	112.10(18)
C19	C10	C1	109.60(17)	C27	C25	C24	111.07(18)
C19	C10	C9	111.39(16)	C27	C25	C26	110.13(18)
C12	C11	C9	114.47(17)	C29	C28	O1	130.1(2)

Table S6. Torsion Angles for CCDC 1444527.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C3	C4	C5	-171.95(17)	C11	C9	C10	C5	-173.21(17)
C1	C2	C3	O1	177.20(17)	C11	C9	C10	C19	-53.1(2)
C1	C2	C3	C4	57.0(2)	C11	C12	C13	C14	57.8(2)
C2	C1	C10	C5	51.4(2)	C11	C12	C13	C17	169.01(17)
C2	C1	C10	C9	171.27(17)	C11	C12	C13	C18	-64.0(2)
C2	C1	C10	C19	-66.4(2)	C12	C13	C14	C8	-61.2(2)
C2	C3	C4	C5	-54.0(2)	C12	C13	C14	C15	168.62(16)
C3	O1	C28	C29	-4.0(4)	C12	C13	C17	C16	-152.59(17)
C3	C4	C5	C6	-130.5(2)	C12	C13	C17	C20	83.5(2)
C3	C4	C5	C10	51.3(2)	C13	C14	C15	C16	-35.2(2)
C4	C5	C6	C7	-175.96(19)	C13	C17	C20	C21	-59.5(2)
C4	C5	C10	C1	-48.3(2)	C13	C17	C20	C22	175.49(19)
C4	C5	C10	C9	-167.56(17)	C14	C8	C9	C10	-175.28(16)
C4	C5	C10	C19	70.4(2)	C14	C8	C9	C11	-47.3(2)
C5	C6	C7	C8	13.1(3)	C14	C13	C17	C16	-38.3(2)
C6	C5	C10	C1	133.6(2)	C14	C13	C17	C20	-162.28(17)
C6	C5	C10	C9	14.3(3)	C14	C15	C16	C17	10.5(2)
C6	C5	C10	C19	-107.7(2)	C15	C16	C17	C13	17.6(2)
C6	C7	C8	C9	-43.6(2)	C15	C16	C17	C20	145.62(17)
C6	C7	C8	C14	-166.29(17)	C16	C17	C20	C21	-179.2(2)
C7	C8	C9	C10	61.7(2)	C16	C17	C20	C22	55.8(2)
C7	C8	C9	C11	-170.32(16)	C17	C13	C14	C8	176.36(17)
C7	C8	C14	C13	179.02(17)	C17	C13	C14	C15	46.16(19)
C7	C8	C14	C15	-57.9(2)	C17	C20	C22	C23	-168.52(17)
C8	C9	C10	C1	-164.31(17)	C18	C13	C14	C8	59.8(2)
C8	C9	C10	C5	-45.6(2)	C18	C13	C14	C15	-70.4(2)
C8	C9	C10	C19	74.5(2)	C18	C13	C17	C16	80.0(2)
C8	C9	C11	C12	48.0(2)	C18	C13	C17	C20	-44.0(2)
C8	C14	C15	C16	-163.41(17)	C20	C22	C23	C24	166.42(19)
C9	C8	C14	C13	56.7(2)	C21	C20	C22	C23	65.1(2)
C9	C8	C14	C15	179.75(17)	C22	C23	C24	C25	-174.79(18)
C9	C11	C12	C13	-54.6(2)	C23	C24	C25	C26	-65.0(3)
C10	C1	C2	C3	-57.7(2)	C23	C24	C25	C27	171.36(19)
C10	C5	C6	C7	2.1(3)	C28	O1	C3	C2	163.04(19)
C10	C9	C11	C12	175.48(18)	C28	O1	C3	C4	-76.6(2)

C11 C9 C10 C1 68.1(2)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for CCDC 1444527.

Atom	*x*	*y*	*z*	U(eq)
H1A	807	2261	2929	20
H1B	1610	1237	4048	20
H2A	2	3654	3977	25
H2B	-221	1827	4040	25
H3	1421	1665	5906	22
H4A	1719	4969	5778	22
H4B	2545	3875	6848	22
H6	4386	3708	6930	18
H7A	5346	2419	5853	17
H7B	5627	4241	6053	17
H8	4265	4850	4186	16
H9	3385	1741	4012	15
H11A	2028	2093	2089	20
H11B	2409	3871	2112	20
H12A	3247	2426	1145	20
H12B	3846	1232	2207	20
H14	5389	2033	4042	16
H15A	7041	3475	5142	19
H15B	6453	5056	4442	19
H16A	7592	2725	3802	21
H16B	7240	4440	3255	21
H17	5892	1652	2457	17
H18A	3899	5473	2430	25
H18B	4067	5112	1306	25
H18C	5184	5678	2480	25
H19A	2454	5754	3672	30
H19B	1373	5541	3982	30
H19C	1238	4935	2764	30
H20	5834	4412	1196	20
H21A	4748	1483	256	44
H21B	4910	2828	-512	44
H21C	4068	3109	88	44
H22A	7732	3069	2017	24
H22B	7069	1598	1226	24
H23A	6661	2929	-461	24
H23B	7010	4564	200	24
H24A	8679	2160	426	23
H24B	9062	3709	1193	23
H25	8443	5209	-548	20
H26A	8212	2300	-1701	34
H26B	8085	3974	-2287	34
H26C	7112	3407	-1902	34
H27A	10477	4669	521	36
H27B	10125	4606	-829	36
H27C	10311	3026	-115	36
H28	-49	3220	7360	32
H29A	2082	1819	7773	37
H29B	1556	2107	8703	37

Experimental

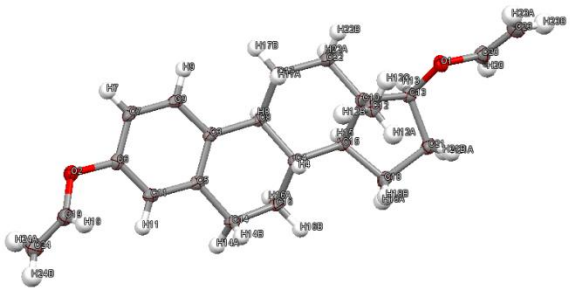
The suitable single crystal of cholesteryl vinyl ether (**2t**) was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst., 40, 786-790; Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984; Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575-580.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystallographic data for the investigated compound have been deposited with the Cambridge Crystallographic Data Center, CCDC 1444527. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk

3.2 X-ray crystallography data for estradiol divinyl ether (2s)

Figure S2. X-ray crystal structure of estradiol divinyl ether (CCDC 1444530).



Crystal structure determination of estradiol divinyl ether (**2s**)

Crystal Data for $C_{22}H_{28}O_2$ (*M* =324.44 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 7.7777(4) Å, *b* = 13.5678(7) Å, *c* = 16.7615(9) Å, *V* = 1768.78(16) Å^3, *Z* = 4, *T* = 100(2) K, μ(MoKα) = 0.076 mm^{-1}, *Dcalc* = 1.218 g/cm^3, 15531 reflections measured (5.714° ≤ 2Θ ≤ 54.998°), 4056 unique (R_{int} = 0.0357, R_{sigma} = 0.0390) which were used in all calculations. The final R_1 was 0.0393 (I > 2σ(I)) and wR_2 was 0.0950 (all data).

Table S8. Crystal data and structure refinement for CCDC 1444530.

Identification code	CCDC 1444530
Empirical formula	$C_{22}H_{28}O_2$
Formula weight	324.44
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	7.7777(4)
b/Å	13.5678(7)
c/Å	16.7615(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1768.78(16)
Z	4
ρ_{calc}g/cm^3	1.218
μ/mm^{-1}	0.076
F(000)	704.0
Crystal size/mm^3	0.15 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.714 to 54.998
Index ranges	-10 ≤ h ≤ 9, -17 ≤ k ≤ 17, -21 ≤ l ≤ 19
Reflections collected	15531
Independent reflections	4056 [R_{int} = 0.0357, R_{sigma} = 0.0390]
Data/restraints/parameters	4056/0/218
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.0911
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	0.26/-0.16
Flack parameter	0.5

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for CCDC 1444530. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	666.3(18)	3812.9(10)	3234.1(9)	24.5(3)
O2	5735.8(17)	11301.9(9)	4083.2(9)	23.2(3)
C1	1298(2)	6471.4(13)	3038.3(12)	19.7(4)
C2	522(2)	5552.2(14)	3020.2(12)	20.6(4)
C3	1442(2)	4733.7(13)	3278.1(12)	19.4(4)
C4	3114(2)	4847.4(13)	3547.3(12)	18.9(4)
C5	3891(2)	5775.2(13)	3571.6(12)	17.4(4)
C6	5708(2)	5838.5(13)	3888.9(12)	19.5(4)
C7	6596(2)	6802.4(13)	3671.3(12)	19.6(4)
C8	5407(2)	7673.8(13)	3836.4(12)	16.7(4)
C9	3852(2)	7620.6(13)	3267.9(12)	17.5(4)
C10	2985(2)	6609.4(12)	3308.5(12)	16.6(4)
C11	2630(2)	8501.4(13)	3384.1(13)	21.3(4)
C12	3567(2)	9498.8(13)	3330.3(13)	22.3(4)
C13	5097(2)	9548.3(13)	3901.6(12)	17.8(4)
C14	6282(2)	8665.7(12)	3722.0(12)	16.9(4)
C15	7929(2)	8893.9(14)	4198.7(13)	23.0(4)
C16	8060(3)	10038.7(14)	4156.3(13)	22.7(4)
C17	6372(2)	10389.7(13)	3758.2(12)	18.8(4)
C18	4483(3)	9571.4(14)	4770.7(12)	23.0(4)
C19	1198(3)	3145.4(14)	3809.8(13)	25.5(4)
C20	1646(3)	2246.3(15)	3635.8(14)	30.8(5)
C21	6741(3)	12104.0(14)	3937.6(13)	25.8(5)
C22	6387(3)	12983.4(15)	4229.4(15)	32.4(5)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 103-372-3282_RKS-2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	23.8(7)	22.6(7)	27.0(8)	0.0(6)	-5.7(6)	-4.3(6)
O2	22.6(7)	19.9(7)	27.2(8)	-2.4(6)	2.4(6)	-1.4(6)
C1	16.7(9)	22.6(9)	19.8(10)	-0.5(7)	-0.8(8)	5.2(8)
C2	14.1(9)	27.6(10)	20.0(11)	-3.1(8)	-0.6(8)	-1.2(8)
C3	19.6(9)	22.9(9)	15.8(10)	-2.2(7)	1.6(8)	-2.6(7)
C4	19.2(9)	21.9(9)	15.7(10)	0.0(7)	0.2(8)	2.7(7)
C5	16.2(9)	23.4(9)	12.7(9)	-1.2(7)	1.4(7)	1.9(7)
C6	15.8(9)	20.9(9)	21.6(11)	1.5(7)	-1.7(8)	3.0(7)
C7	13.0(9)	23.5(9)	22.4(11)	1.8(8)	-1.3(8)	2.3(7)
C8	13.1(9)	19.6(9)	17.4(10)	1.7(7)	0.3(7)	1.2(7)
C9	14.4(9)	19.9(9)	18.1(10)	0.4(7)	-1.3(8)	0.4(7)
C10	14.4(8)	21.3(9)	14.2(10)	-1.5(7)	1.2(7)	-0.3(7)
C11	14.0(9)	19.8(9)	30.2(12)	-1.2(8)	-5.2(8)	1.5(7)
C12	18.7(9)	20.8(9)	27.5(12)	1.8(8)	-4.0(8)	1.8(8)
C13	15.3(8)	18.8(9)	19.2(11)	0.7(7)	0.7(7)	0.2(7)
C14	14.4(8)	20.6(9)	15.6(10)	0.9(7)	0.4(7)	0.8(7)
C15	14.7(9)	25.5(9)	28.7(12)	1.8(8)	-3.0(8)	-2.7(8)
C16	18.5(10)	24.6(10)	25.0(12)	1.7(8)	-1.2(8)	-4.3(8)
C17	17.7(9)	20.2(9)	18.5(10)	-0.6(7)	0.9(8)	-0.7(8)
C18	22.1(10)	25(1)	21.9(11)	-1.6(8)	5.8(8)	-2.6(8)
C19	24.5(10)	27.1(10)	24.7(11)	1.2(8)	-2.5(9)	-6.2(9)
C20	33.0(13)	31.5(11)	28.0(13)	-2.9(9)	-3.8(10)	1.0(9)
C21	26.2(11)	26.4(10)	24.7(12)	2.8(8)	-2.1(9)	-4.4(8)
C22	34.8(12)	24.9(10)	37.6(14)	3.8(9)	-6.7(11)	-0.9(9)

Table S11. Bond Lengths for CCDC 1444530.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.389(2)	C8	C14	1.520(2)
O1	C19	1.387(2)	C9	C10	1.530(2)
O2	C17	1.440(2)	C9	C11	1.539(2)
O2	C21	1.362(2)	C11	C12	1.540(2)
C1	C2	1.386(2)	C12	C13	1.529(3)
C1	C10	1.400(3)	C13	C14	1.541(2)
C2	C3	1.390(3)	C13	C17	1.531(2)
C3	C4	1.385(3)	C13	C18	1.533(3)
C4	C5	1.397(2)	C14	C15	1.541(3)
C5	C6	1.512(3)	C15	C16	1.558(3)
C5	C10	1.404(2)	C16	C17	1.548(3)
C6	C7	1.523(2)	C19	C20	1.302(3)
C7	C8	1.526(2)	C21	C22	1.318(3)
C8	C9	1.541(2)			

Table S12. Bond Angles for CCDC 1444530.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C19	O1	C3	114.88(15)	C1	C10	C9	121.22(16)
C21	O2	C17	114.94(15)	C5	C10	C9	121.02(16)
C2	C1	C10	122.37(17)	C9	C11	C12	112.50(15)
C1	C2	C3	119.21(17)	C13	C12	C11	111.74(15)

O1	C3	C2	118.57(16)	C12	C13	C14	107.99(15)
C4	C3	O1	121.69(17)	C12	C13	C17	116.01(15)
C4	C3	C2	119.71(17)	C12	C13	C18	110.68(16)
C3	C4	C5	121.05(17)	C17	C13	C14	99.29(14)
C4	C5	C6	117.74(15)	C17	C13	C18	109.63(15)
C4	C5	C10	120.02(16)	C18	C13	C14	112.83(15)
C10	C5	C6	122.24(16)	C8	C14	C13	113.30(14)
C5	C6	C7	112.85(15)	C8	C14	C15	118.99(15)
C6	C7	C8	110.30(14)	C13	C14	C15	103.86(14)
C7	C8	C9	109.10(15)	C14	C15	C16	103.37(15)
C14	C8	C7	113.05(14)	C17	C16	C15	105.70(15)
C14	C8	C9	108.35(14)	O2	C17	C13	111.03(15)
C10	C9	C8	111.12(15)	O2	C17	C16	113.13(16)
C10	C9	C11	114.73(15)	C13	C17	C16	104.61(14)
C11	C9	C8	111.71(15)	C20	C19	O1	122.4(2)
C1	C10	C5	117.64(16)	C22	C21	O2	122.5(2)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for CCDC 1444530.

Atom	***x***	***y***	***z***	**U(eq)**
H1	663	7028	2861	24
H2	-625	5482	2834	25
H4	3743	4285	3718	23
H6A	6386	5282	3673	23
H6B	5682	5772	4477	23
H7A	6913	6794	3099	24
H7B	7663	6874	3988	24
H8	4984	7628	4399	20
H9	4326	7683	2716	21
H11A	2069	8447	3912	26
H11B	1720	8477	2972	26
H12A	3977	9601	2777	27
H12B	2751	10035	3459	27
H14	6596	8712	3145	20
H15A	8945	8578	3951	28
H15B	7824	8666	4758	28
H16A	8174	10323	4698	27
H16B	9068	10240	3834	27
H17	6563	10469	3172	23
H18A	5480	9568	5128	35
H18B	3768	8991	4877	35
H18C	3806	10170	4862	35
H19	1237	3352	4351	31
H20A	1615	2027	3098	37
H20B	2003	1810	4047	37
H21	7734	12027	3614	31
H22A	5400	13075	4555	39
H22B	7120	13525	4114	39

Experimental

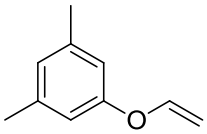
The suitable single crystal of estradiol divinyl ether (**2s**) was kept at 100(2) K during data collection. Using Olex2 [4], the structure was solved with the Superflip [5] structure solution program using Charge Flipping and refined with the ShelXL [6] refinement package using Least Squares minimisation.

4. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
5. Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst., 40, 786-790; Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984; Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575-580.
6. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystallographic data for the investigated compound have been deposited with the Cambridge Crystallographic Data Center, CCDC 1444530. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk

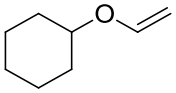
S4. Characterization and spectral data

1,3-dimethyl-5-(vinyloxy)benzene (2a)



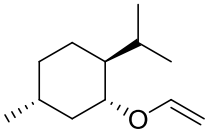
1,3-dimethyl-5-(vinyloxy)benzene was obtained as yellow oil (104 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 1H), 6.64 (s,2H), 6.63 (dd, 1H), 4.74 (dd, J = 13.7 Hz, 1.5 Hz, 1H), 4.40 (dd, J = 6.1 Hz, 1.5 Hz, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 148.6, 139.6, 125.0, 114.9, 94.7, 21.4; analysis (calcd., found for $C_{10}H_{12}O$): C (81.04, 81.09), H (8.16, 8.18).

Cyclohexyl vinyl ether (2b)



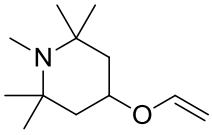
Cyclohexyl vinyl ether was obtained as colorless oil (115 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (dd, J = 14.1 Hz, 6.6 Hz, 1H), 4.28 (dd, J = 14.1 Hz, 1.4 Hz, 1H), 3.97 (dd, J = 6.6 Hz, 1.4 Hz, 1H), 3.73 (tt, J = 9.1 Hz, 3.8 Hz, 1H), 1.92 – 1.88 (m, 2H), 1.77 – 1.72 (m, 2H), 1.44 – 1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 88.2, 77.7, 32.1, 25.7, 23.9; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_8H_{14}AgO$, 233.0096; found, 233.0091.

1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane (2c)



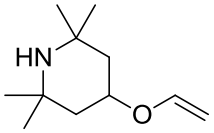
1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane was obtained as colorless oil (166 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (dd, J = 14.1 Hz, 6.5 Hz, 1H), 4.28 (dd, J = 14.1 Hz, 1.4 Hz, 1H), 3.94 (dd, J = 6.5 Hz, 1.4 Hz, 1H), 3.52 (td, J = 10.7 Hz, 4.3 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.69 – 1.62 (m, 2H), 1.44 – 1.30 (m, 2H), 1.06 – 0.96 (m, 2H), 0.96-0.84 (m, 7H), 0.77 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 87.7, 80.0, 47.9, 41.0, 34.5, 31.6, 26.0, 23.7, 22.3, 20.9, 16.5; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{12}H_{22}AgO$, 289.0722; found, 289.0721.

1,2,2,6,6-pentamethyl-4-(vinyloxy)piperidine (2d)



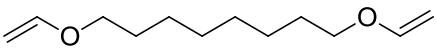
1,2,2,6,6-pentamethyl-4-(vinyloxy)piperidine was obtained as colorless oil (191 mg, 97 %). ^{1}H NMR (400 MHz, C_6D_6): δ 6.31 (dd, J = 14.2 Hz, 6.7 Hz, 1H), 4.46 (dd, J = 14.2 Hz, 1.3 Hz, 1H), 4.05 (dd, J = 6.7 Hz, 1.3 Hz, 1H), 3.98 (tt, J = 11.3 Hz, 4.0 Hz, 1H), 2.08 (s, 3H), 1.88 – 1.84 (m, 2H), 1.57 (t, J = 11.6 Hz, 2H), 1.05 (s, 6H), 0.84 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 151.0, 87.9, 71.6, 55.0, 46.7, 33.1, 28.1, 20.1; HRMS (m/z): $[M]^+$ calcd. for $C_{12}H_{24}NO$, 198.1858; found, 198.1851.

2,2,6,6-tetramethyl-4-(vinyloxy)piperidine (2e)



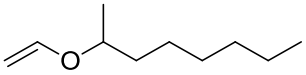
2,2,6,6-tetramethyl-4-(vinyloxy)piperidine was obtained as colorless oil (124 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, J = 14.2 Hz, 6.6 Hz, 1H), 4.29 (dd, J = 14.2 Hz, 1.6 Hz, 1H), 4.18 (tt, J = 11.3 Hz, 4.1 Hz, 1H), 4.01 (dd, J = 6.6 Hz, 1.6 Hz, 1H), 1.98 (dd, J = 1.9 Hz, 0.7 Hz, 2H), 1.20 (s, 6H), 1.15 (s, 6H), 1.13 – 1.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 88.3, 72.9, 51.5, 44.4, 34.8, 29.1; HRMS (m/z): $[M]^+$ calcd. for $C_{11}H_{22}NO$, 184.1701; found, 184.1706.

1,8-bis(vinyloxy)octane (2f)



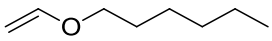
1,8-Bis(vinyloxy)octane was obtained as colorless oil (166 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (dd, J = 14.3 Hz, 6.8 Hz, 2H), 4.17 (dd, J = 14.3 Hz, 1.8 Hz, 2H), 3.97 (dd, J = 6.8 Hz, 1.8 Hz, 2H), 3.67 (t, J = 6.6 Hz, 4H), 1.65 (quint, J=7Hz, 4H), 1.41 – 1.31 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 86.4, 68.2, 29.4, 29.2, 26.1; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{12}H_{22}AgO_2$, 305.0671; found, 305.0670.

2-(vinyloxy)octane (2g)



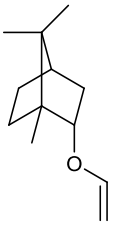
2-(vinyloxy)octane was obtained as yellow oil (131 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dd, J = 14.2 Hz, 6.6 Hz, 1H), 4.25 (dd, J = 14.2 Hz, 1.4 Hz, 1H), 3.96 (dd, J = 6.6 Hz, 1.4 Hz, 1H), 3.86 (m, 1H), 1.48 – 1.24 (m, 10H), 1.20 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 87.9, 76.2, 36.6, 31.9, 29.4, 25.5, 22.7, 19.9, 14.2; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{10}H_{20}AgO$, 263.0565; found, 263.0566.

1-Hexyl vinyl ether (2h)



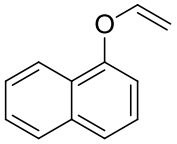
1-Hexyl vinyl ether was obtained as yellow oil (105 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (dd, J = 14.3 Hz, 6.8 Hz, 1H), 4.17 (dd, J = 14.3 Hz, 1.9 Hz, 1H), 3.97 (dd, J = 6.8 Hz, 1.9 Hz, 1H), 3.67 (t, J = 6.6 Hz, 2H), 1.63 (quint, 2H), 1.41 – 1.28 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 86.3, 68.3, 31.7, 29.2, 25.8, 22.7, 14.2; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_8H_{16}AgO$, 235.0252; found, 235.0247.

Bornyl vinyl ether (2i)



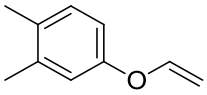
Bornyl vinyl ether was obtained as a light oil (166 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 14.3, 6.7 Hz, 1H), 4.14 (dd, *J* = 14.3, 1.5 Hz, 1H), 4.04 (ddd, *J* = 9.5, 3.2, 2.1 Hz, 1H), 3.96 (dd, *J* = 6.7, 1.6 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.03 (ddd, *J* = 14.1, 10.0, 4.4 Hz, 1H), 1.74 (dd, *J* = 7.7, 4.3 Hz, 1H), 1.70 (dd, *J* = 8.0, 3.5 Hz, 1H), 1.33 – 1.21 (m, 2H), 1.09 (dd, *J* = 13.4, 3.4 Hz, 1H), 0.92 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.87, 86.92, 83.86, 49.18, 47.75, 44.98, 36.37, 27.95, 26.71, 19.71, 18.85, 13.69. HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{12}H_{20}AgO$, 287.0560; found, 287.0567.

1-(vinyloxy)naphthalene (2j)



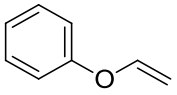
1-(vinyloxy)naphthalene was obtained as yellow oil (34 mg, 36 %). ^{1}H NMR (400 MHz, C_6D_6): δ 8.38 – 8.35 (m, 1H), 7.61 – 7.58 (m, 1H), 7.36 (dd, J = 8.3 Hz, 0.9 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.10 (dd, J = 8.2 Hz, 7.6 Hz, 1H), 6.75 (dd, J = 7.6 Hz, 1.0 Hz, 1H), 6.48 (dd, J = 13.7 Hz, 6.0 Hz, 1H), 4.83 (dd, J = 13.7 Hz, 1.5 Hz, 1H), 4.27 (dd, J = 6.0 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 153.3, 148.9, 135.3, 127.9, 126.9, 126.5, 126.1, 125.9, 123.3, 122.4, 110.7, 95.7; analysis (calcd., found for $C_{12}H_{10}O$): C (84.68, 86.16), H (5.92, 4.47).

1,2-dimethyl-4-(vinyloxy)benzene (2k)



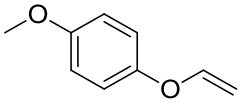
1,2-dimethyl-4-(vinyloxy)benzene was obtained as yellow oil (76 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 2.5 Hz, 1H), 6.75 (dd, J = 8.2 Hz, 2.6 Hz, 1H), 6.62 (dd, J = 13.8 Hz, 6.1 Hz, 1H), 4.71 (dd, J = 13.7 Hz, 1.6 Hz, 1H), 4.37 (dd, J = 6.1 Hz, 1.6 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 149.0, 138.2, 131.5, 130.6, 118.7, 114.5, 94.2, 20.1, 19.1; analysis (calcd., found for $C_{10}H_{12}O$): C (81.04, 81.21), H (8.16, 8.47).

Phenyl vinyl ether (2l)



Phenyl vinyl ether was obtained as yellow oil (52 mg, 54 %). ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 – 6.99 (m, 2H), 6.89 – 6.80 (m, 3H), 6.39 (dd, J = 13.7 Hz, 6.1 Hz, 1H), 4.74 (dd, J = 13.7 Hz, 1.5 Hz, 1H), 4.20 (dd, J = 6.1 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 157.4, 148.6, 129.9, 123.3, 117.4, 95.0.

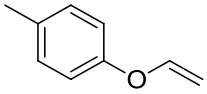
1-methoxy-4-(vinyloxy)benzene (2m)



1-methoxy-4-(vinyloxy)benzene was obtained as yellow oil (62 mg, 41 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 – 6.91 (m, 2H), 6.89 – 6.81 (m, 2H), 6.59 (dd, J = 13.8 Hz, 6.18= Hz, 1H), 4.64 (dd, J = 13.8 Hz, 1.6

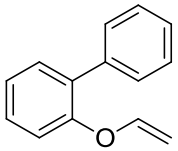
Hz, 1H), 4.33 (dd, J = 6.1 Hz, 1.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 150.7, 149.7, 118.8, 114.8, 93.7, 55.8; analysis (calcd., found for $C_9H_{10}O_2$): C (71.98, 80.01), H (6.71, 6.75).

1-methyl-4-(vinyloxy)benzene (2n)



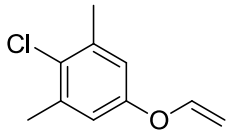
1-methyl-4-(vinyloxy)benzene was obtained as yellow oil (66 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.09 (m, 2H), 6.93 – 6.88 (m, 2H), 6.63 (dd, J = 13.7 Hz, 6.1 Hz, 1H), 4.72 (dd, J = 13.7 Hz, 1.6 Hz, 1H), 4.38 (dd, J = 6.1 Hz, 1.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 148.9, 132.8, 130.2, 117.3, 94.4, 20.8; analysis (calcd., found for $C_9H_{10}O$): C (80.56, 80.53), H (7.51, 7.48).

2-(vinyloxy)-1,1'-biphenyl (2o)



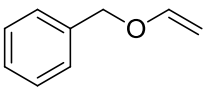
2-(vinyloxy)-1,1'-biphenyl was obtained as yellow oil (41 mg, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.52 (m, 2H), 7.45 – 7.40 (m, 3H), 7.37 – 7.32 (m, 2H), 7.19 (td, J = 7.5 Hz, 1.2 Hz, 1H), 7.11 (dd, J = 8.1 Hz, 1.1 Hz, 1H), 6.58 (dd, J = 13.8 Hz, 6.2 Hz, 1H), 4.61 (dd, J = 13.8 Hz, 1.7 Hz, 1H), 4.35 (dd, J = 6.2 Hz, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 149.3, 137.9, 132.8, 131.3, 129.5, 128.8, 128.2, 127.3, 124.0, 118.4, 94.5; HRMS (m/z): $[M]^+$ calcd. for $C_{14}H_{12}AgO$, 302.9939; found, 302.9944.

2-chloro-1,3-dimethyl-5-(vinyloxy)benzene (2p)



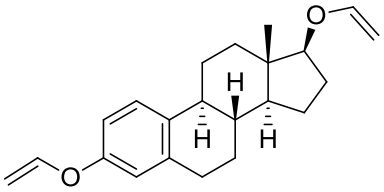
2-chloro-1,3-dimethyl-5-(vinyloxy)benzene was obtained as yellow oil (44 mg, 38 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (s, 2H), 6.58 (dd, J = 13.7 Hz, 6.1 Hz, 1H), 4.74 (dd, J = 13.7 Hz, 1.7 Hz, 1H), 4.42 (dd, J = 6.1 Hz, 1.7 Hz, 1H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 148.4, 137.7, 117.2, 95.3, 21.0; analysis (calcd., found for $C_{10}H_{11}ClO$): C (65.76, 65.81), H (6.07, 6.06).

Benzyl vinyl ether (2q)



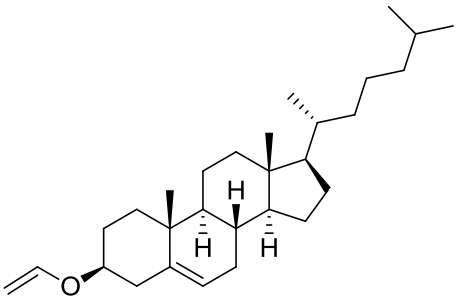
Benzyl vinyl ether was obtained as colorless oil (123 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.36 (m, 5H), 6.65 (dd, J = 14.3 Hz, 6.8 Hz, 1H), 4.83 (s, 2H), 4.40 (dd, J = 14.3 Hz, 2.1 Hz, 1H), 4.17 (dd, J = 6.8 Hz, 2.1 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 137.0, 128.7, 128.0, 127.6, 87.4, 70.1; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_9H_{10}AgO$, 240.9783; found, 240.9788.

Estradiol divinyl ether (2s)



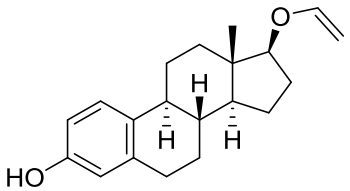
Estradiol divinyl ether was obtained as white crystals (26 mg, 52 %). ^{1}H NMR (400 MHz, C_6D_6): δ 7.06 (d, J = 8.55 Hz, 1H), 6.85 (dd, J = 8.55 Hz, 2.59 Hz, 1H), 6.76 (d, J = 2.44 Hz, 1H), 6.54 (dd, J = 13.73 Hz, 6.10 Hz, 1H), 6.36 (dd, J = 14.11 Hz, 6.64 Hz, 1H), 4.82 (dd, J = 13.73 Hz, 1.37 Hz, 1H), 4.42 (dd, J = 14.11 Hz, 1.30 Hz, 1H), 4.24 (dd, J = 6.10 Hz, 1.37 Hz, 1H), 4.03 (dd, J = 6.64 Hz, 1.30 Hz, 1H), 3.60 – 3.56 (m, 1H), 2.62 – 2.59 (m, 2H), 2.04 – 1.87 (m, 4H), 1.62 – 1.53 (m, 2H), 1.41 – 1.03 (m, 7H), 0.81 (s, 3H), 0.81 – 0.74 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 155.5, 152.2, 149.2, 138.4, 135.4, 127.0, 117.7, 115.1, 94.3, 88.2, 87.9, 49.9, 44.2, 43.7, 38.6, 37.7, 29.9, 28.1, 27.4, 26.5, 23.4, 12.0; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{22}H_{28}AgO_2$, 431.1140; found, 431.1142.

Cholesteryl vinyl ether (2t)



Cholesteryl vinyl ether was obtained as white crystals (45.6 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (dd, J = 14.1 Hz, 6.6 Hz, 1H), 5.37 (dt, J = 5.3 Hz, 1.8 H,z 1H), 4.29 (dd, J = 14.1 Hz, 1.4 Hz, 1H), 3.99 (dd, J = 6.6 Hz, 1.4 Hz, 1H), 3.63 (tt, J = 11.2 Hz, 4.6 Hz, 1H), 2.39 (ddd, J = 13.2 Hz, 4.9 Hz, 2.1 Hz, 1H), 2.34 - 2.24 (m, 1H), 2.13 – 1.76 (m, 6H), 1.67 – 1.04 (m, 20H), 1.01 (s, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.87 (dd, J = 6.6 Hz, 1.7 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 140.4, 122.4, 88.4, 79.2, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 38.9, 37.2, 36.9, 36.4, 35.9, 32.1, 32.0, 28.4, 28.3, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{29}H_{48}AgO$, 519.2756; found, 519.2758.

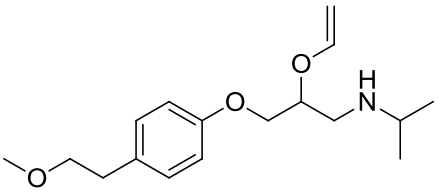
Estradiol vinyl ether (2u)



Estradiol vinyl ether was obtained as white crystals (45 mg, 74 %). ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 (d, J = 8.4 Hz, 1H), 6.48 (dd, J = 8.4 Hz, 2.7 Hz, 1H), 6.37 (dd, J = 14.1 Hz, 6.6 Hz, 1H), 6.36 (s, 1H), 4.43 (dd, J = 14.1 Hz, 1.3 Hz, 1H), 4.03 (dd, J = 6.6 Hz, 1.3 Hz, 1H), 3.96 (br. s, 1H), 3.58 (dd, J = 8.9 Hz, 7.7 Hz, 1H), 2.64 (dd, J = 6.9 Hz, 3.3 Hz, 2H), 2.12 – 1.86 (m, 4H), 1.71 – 1.51 (m, 2H), 1.45 – 1.02 (m, 7H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 154.3, 152.3, 138.0, 132.4, 126.8, 115.6, 113.1, 88.3, 87.9, 49.9,

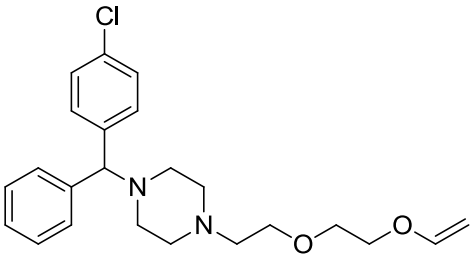
44.2, 43.7, 38.8, 37.8, 29.9, 28.1, 27.6, 26.6, 23.4, 12.0; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{20}H_{26}AgO_2$, 405.0984; found, 405.0995.

N-isopropyl-3-(4-(2-methoxyethyl)phenoxy)-2-(vinyloxy)propan-1-amine (2v)



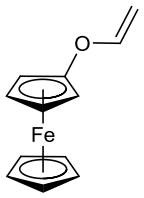
N-isopropyl-3-(4-(2-methoxyethyl)phenoxy)-2-(vinyloxy)propan-1-amine was obtained as colorless oil (43.5 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.42 (dd, J = 14.1 Hz, 6.5 Hz, 1H), 4.39 (dd, J = 14.1 Hz, 1.7 Hz, 1H), 4.26 – 4.20 (m, 1H), 4.09 – 4.02 (m, 3H), 3.55 (t, J = 7.1 Hz, 2H), 3.34 (s, 3H) 2.96 – 2.79 (m, 6H), 1.06 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 151.4, 131.6, 129.9, 114.8, 89.4, 78.1, 74.0, 68.4, 58.8, 48.8, 48.4, 35.4, 23.1, 23.0; HRMS (m/z): $[M]^+$ calcd. for $C_{17}H_{28}NO_3$, 294.2069; found, 294.2065.

1-((4-chlorophenyl)(phenyl)methyl)-4-(2-(2-(vinyloxy)ethoxy)ethyl)piperazine (2w)



1-((4-chlorophenyl)(phenyl)methyl)-4-(2-(2-(vinyloxy)ethoxy)ethyl)piperazine was obtained as colorless oil (42.5 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 4H), 7.28 – 7.16 (m, 5H), 6.48 (dd, J = 14.3 Hz, 6.8 Hz, 1H), 4.20 (s, 1H), 4.17 (dd, J = 14.3 Hz, 2.1 Hz, 1H), 4.00 (dd, J = 6.8 Hz, 2.1 Hz, 1H), 3.81 (dd, J = 5.7 Hz, 3.8 Hz, 2H), 3.68 (dd, J = 5.7 Hz, 3.8 Hz, 2H), 3.64 (t, J = 5.9 Hz, 2H), 2.62 (t, J = 5.8 Hz, 2H), 2.55 (br. s, 4H) 2.42 (br. s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 142.3, 141.5, 132.7, 129.3, 128.8, 128.7, 128.0, 127.3, 86.8, 75.6, 69.5, 69.2, 67.4, 57.8, 54.0, 51.8; HRMS (m/z): $[M]^+$ calcd. for $C_{23}H_{30}ClN_2O_2$, 401.1996; found, 401.1991.

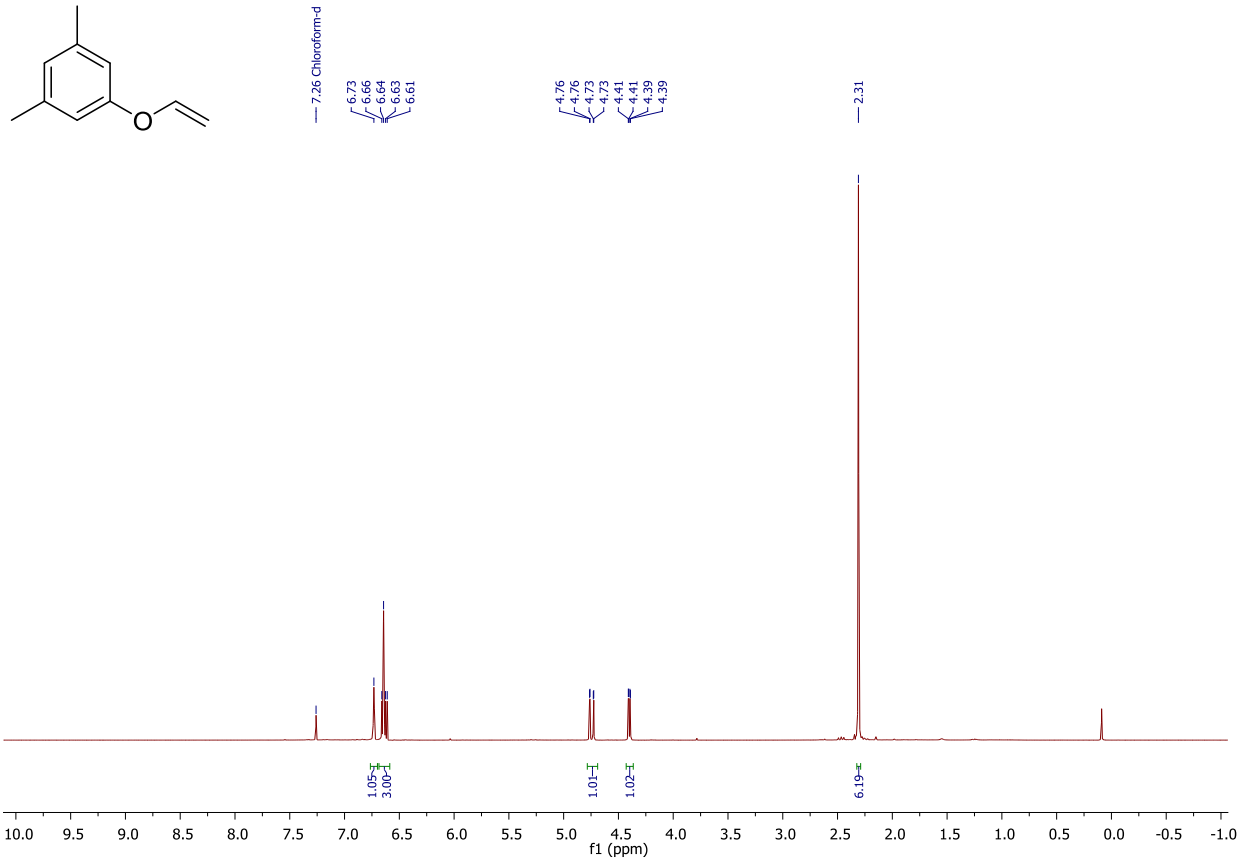
Vinyloxyferrocene (2z)

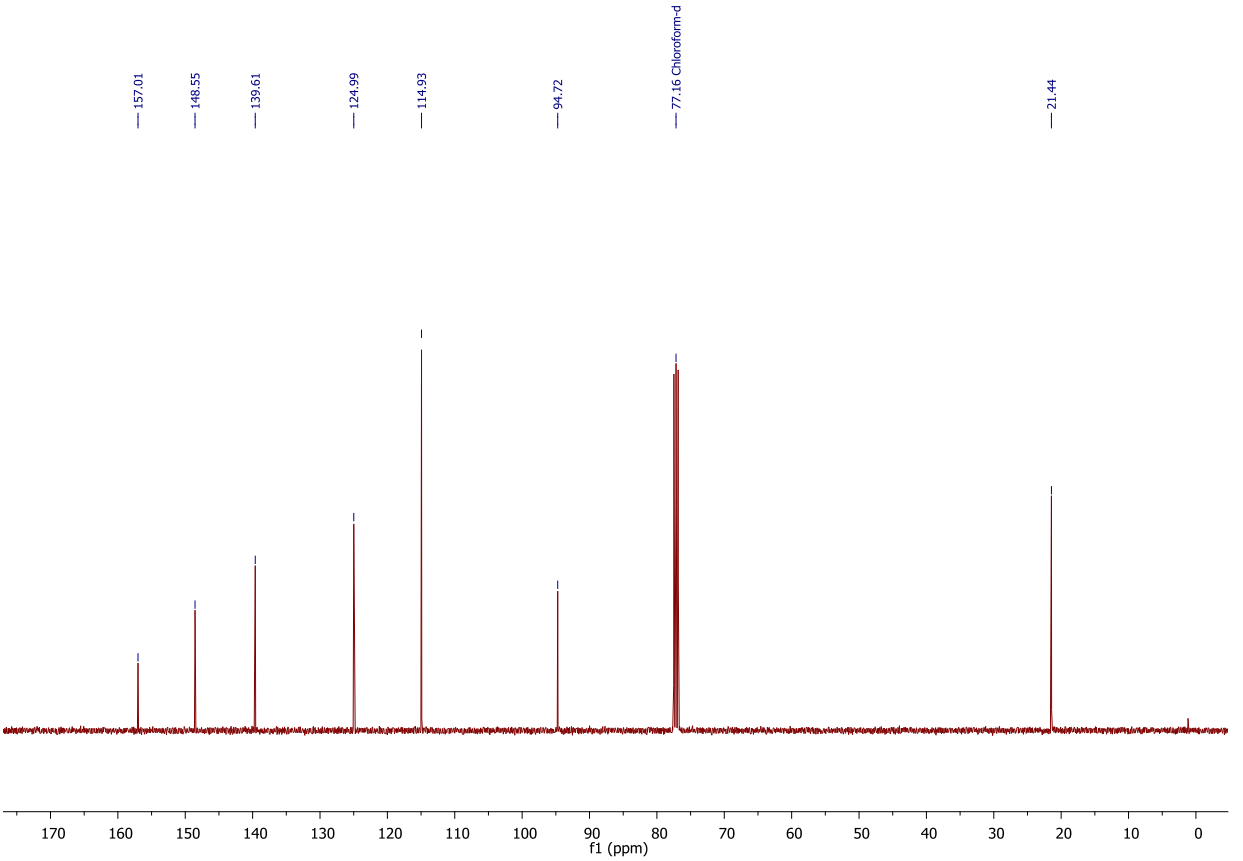


Vinyloxyferrocene was obtained as orange oil (173 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (dd, *J* = 13.8 Hz, 6.1 Hz, 1H), 4.65 (dd, *J* = 13.8 Hz, 1.7 Hz, 1H), 4.30 (dd, *J* = 6.1 Hz, 1.7 Hz, 1H), 4.24 (s, 5H), 4.17 (t, *J* = 2.0 Hz, 2H), 3.89 (t, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 123.6, 93.3, 69.0, 62.7, 57.5; HRMS (m/z): $[M+Ag]^+$ calcd. for $C_{12}H_{12}AgFeO$, 334.9289; found, 334.9286.

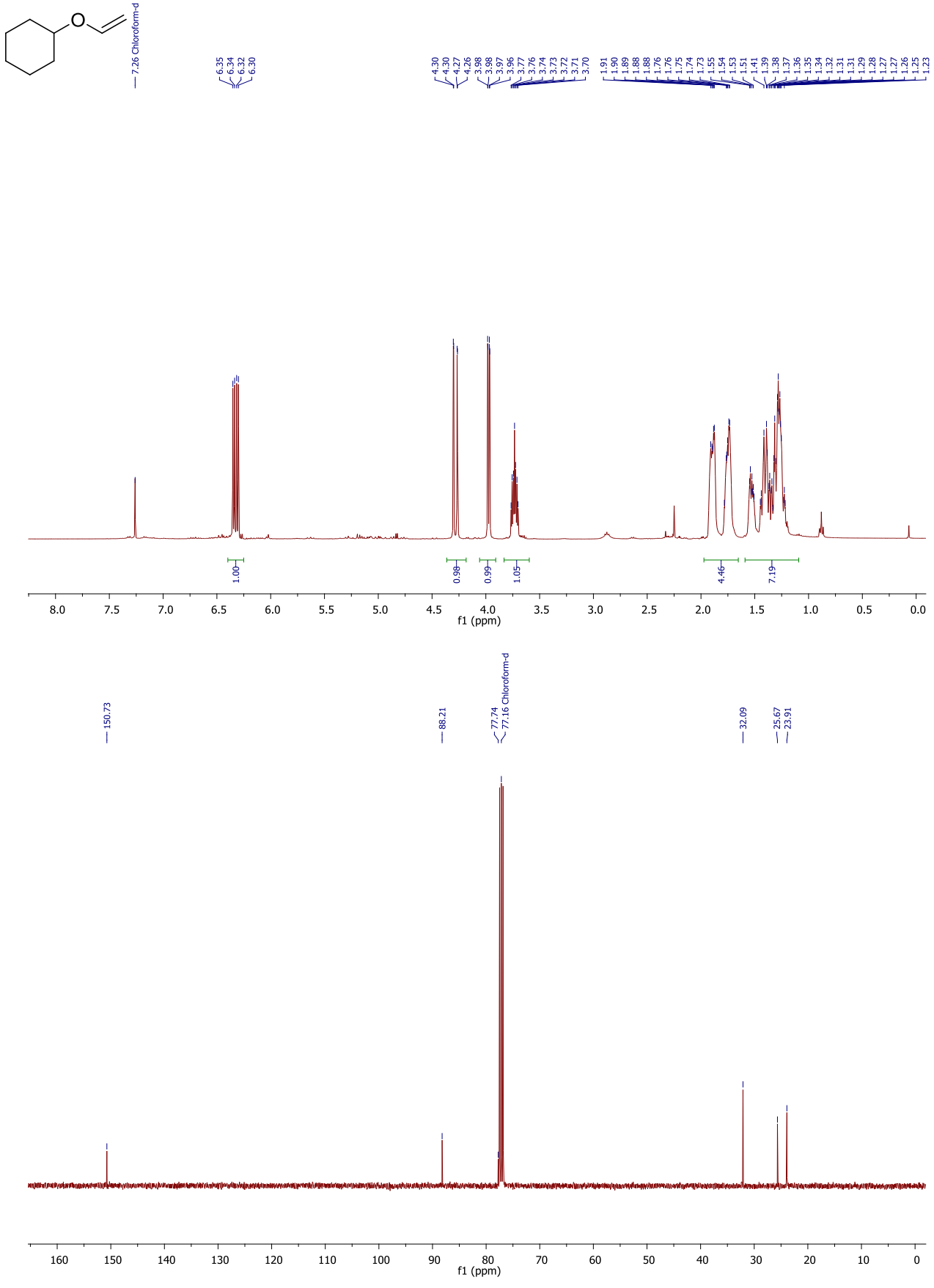
S5. NMR spectra

1,3-dimethyl-5-(vinyloxy)benzene (2a)

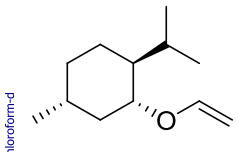


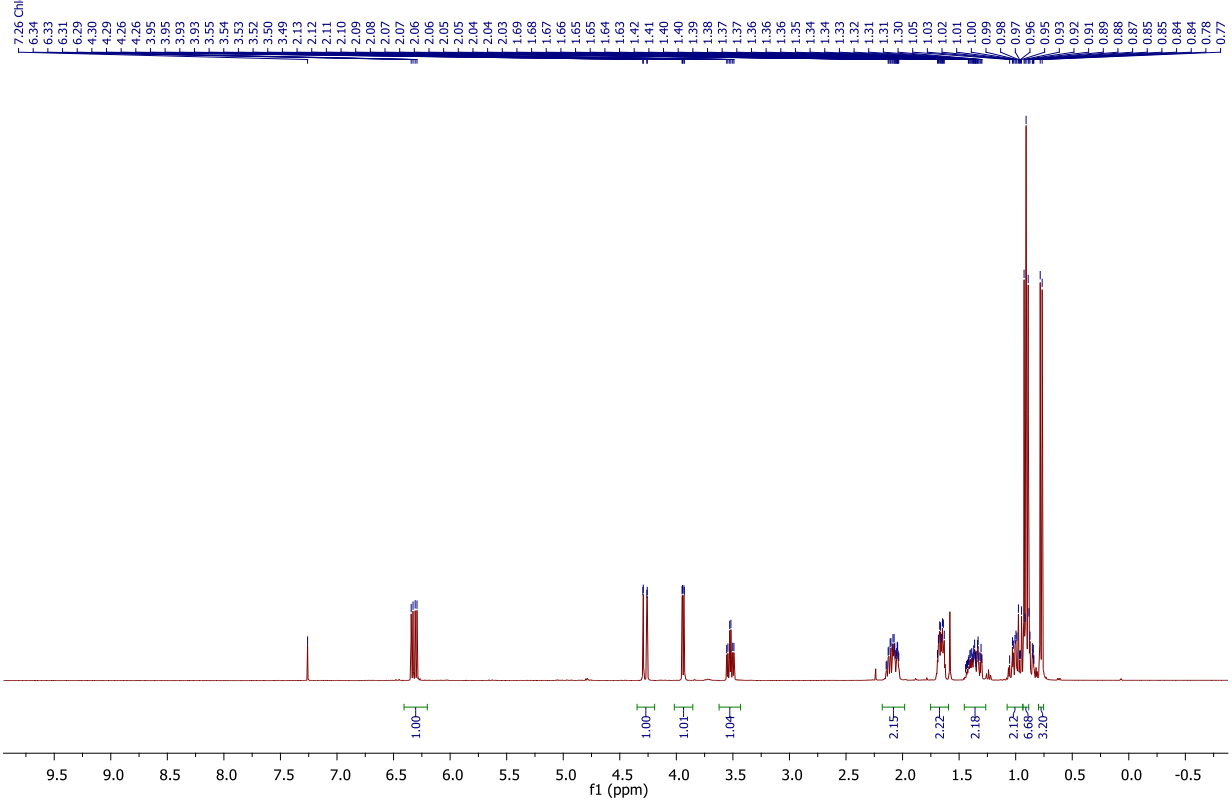


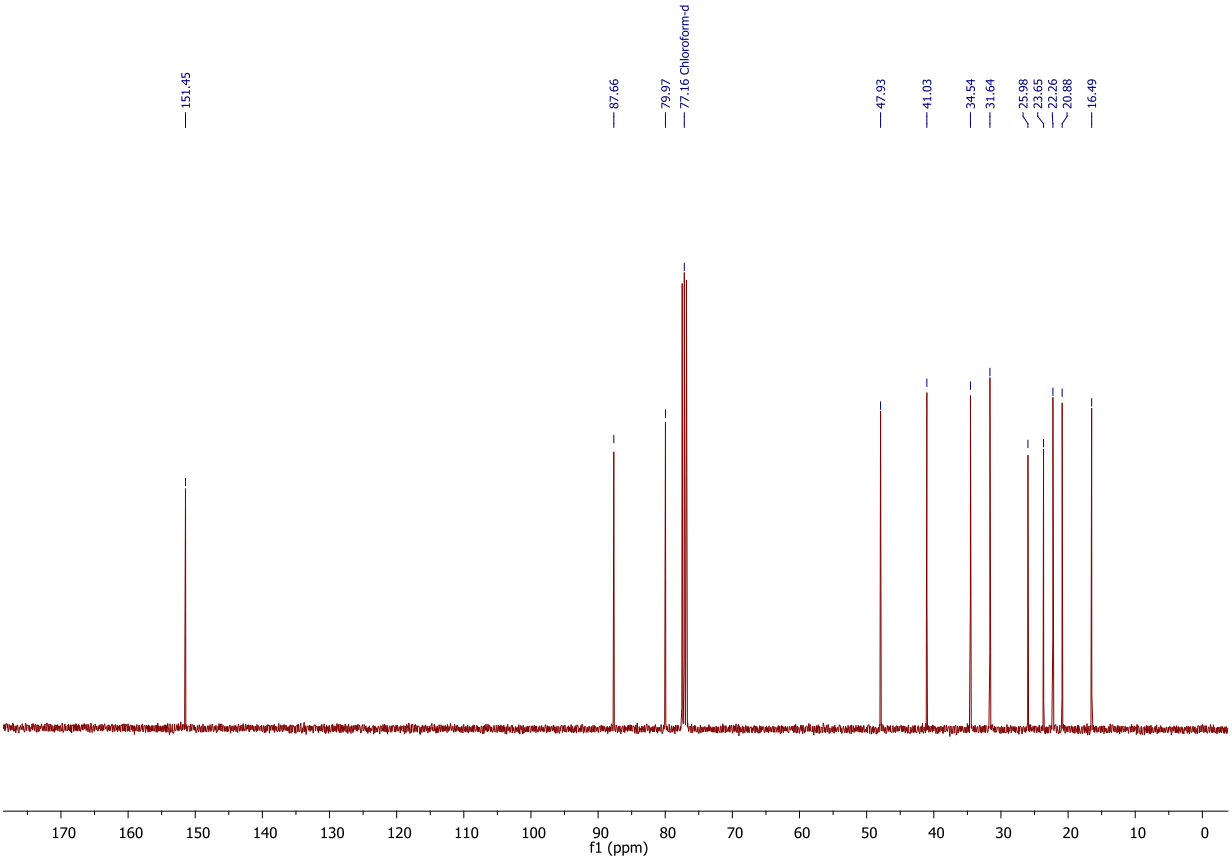
Cyclohexyl vinyl ether (2b)



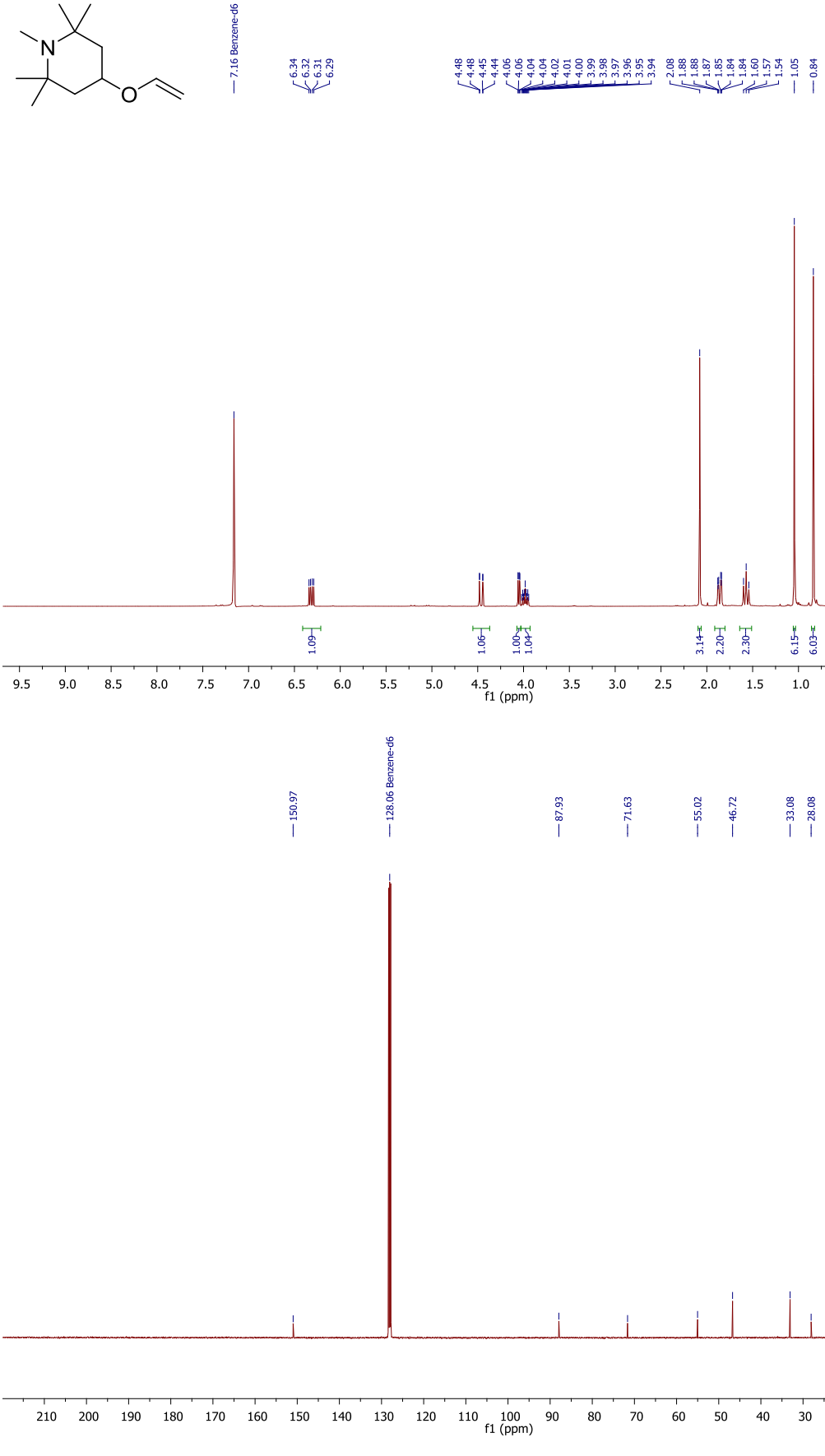
1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane (2c)



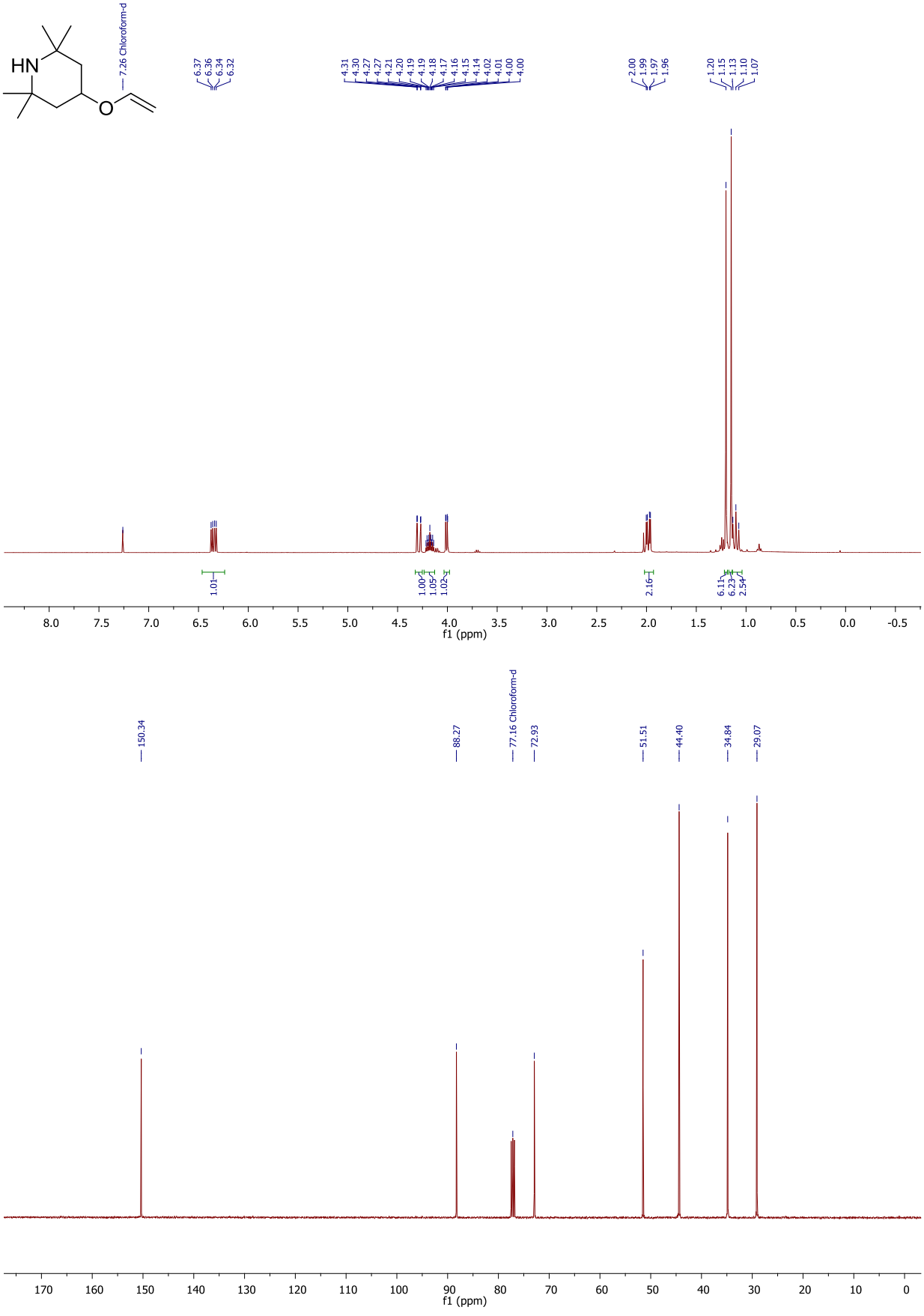




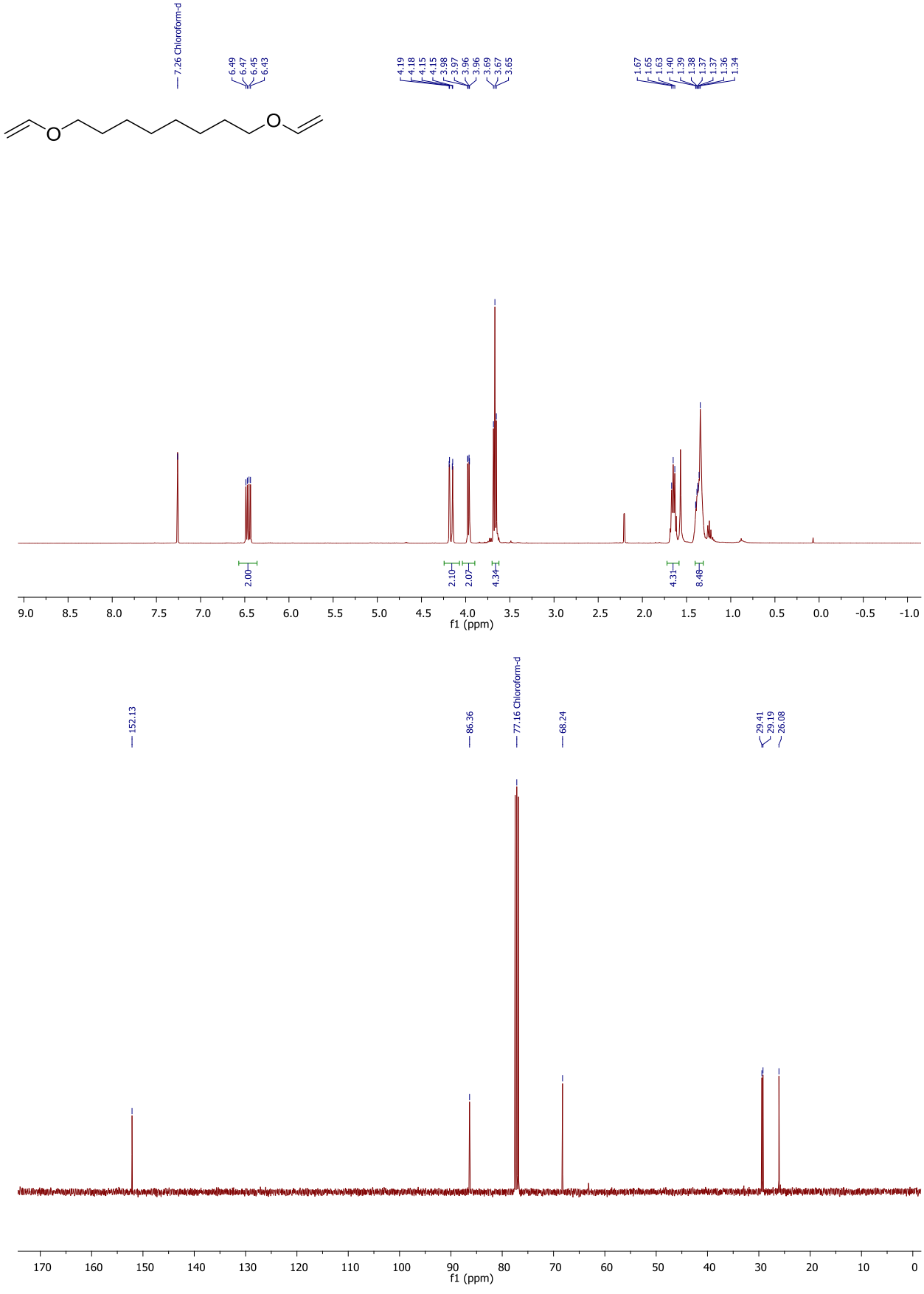
1,2,2,6,6-pentamethyl-4-(vinyloxy)piperidine (2d)



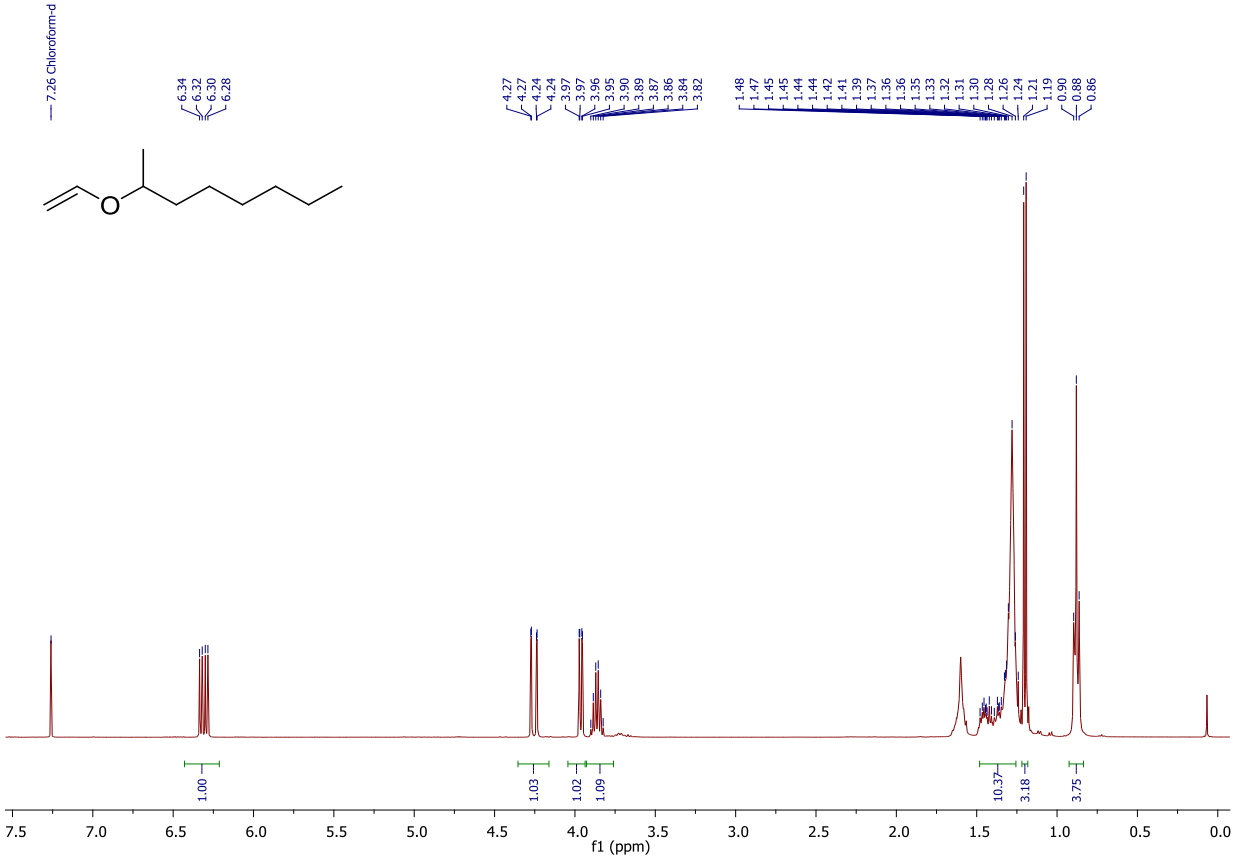
2,2,6,6-tetramethyl-4-(vinyloxy)piperidine (2e)

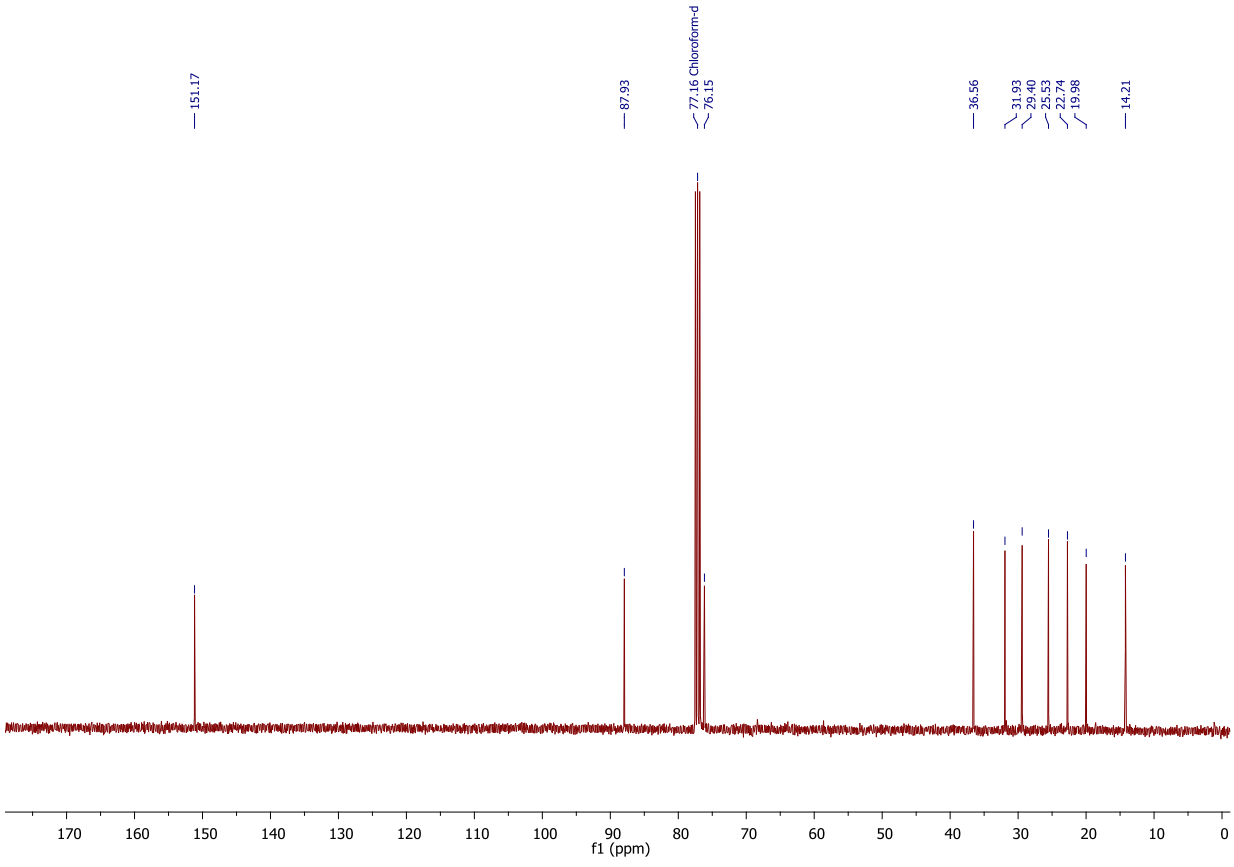


1,8-bis(vinyloxy)octane (2f)

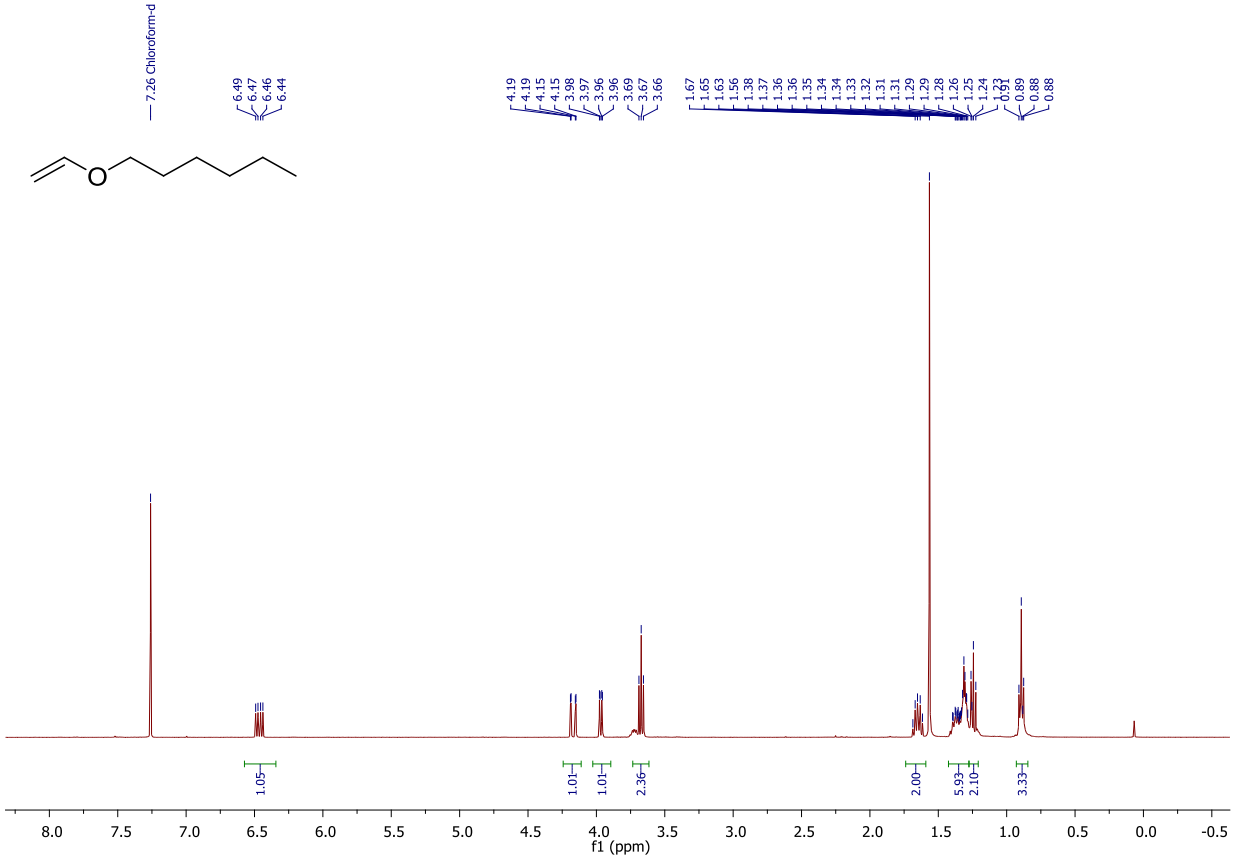


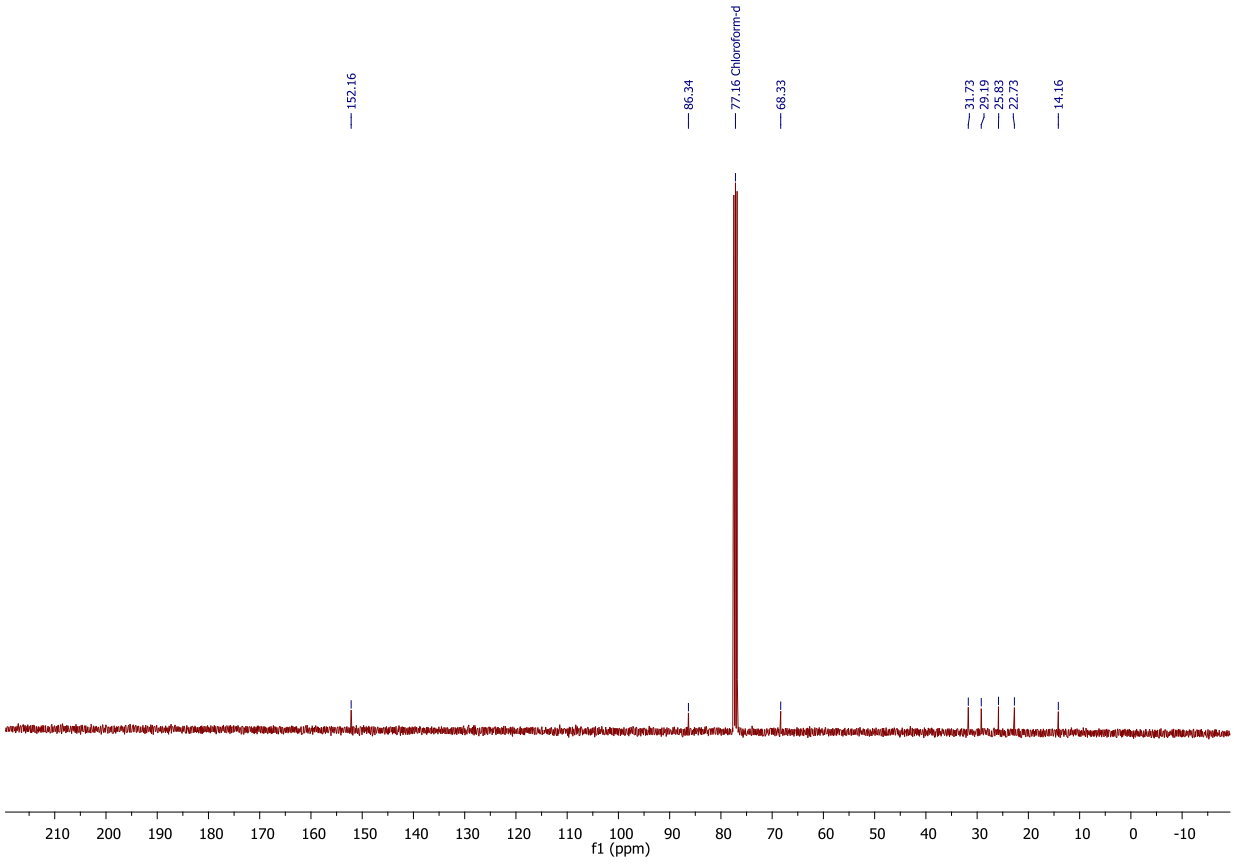
2-(vinyloxy)octane (2g)



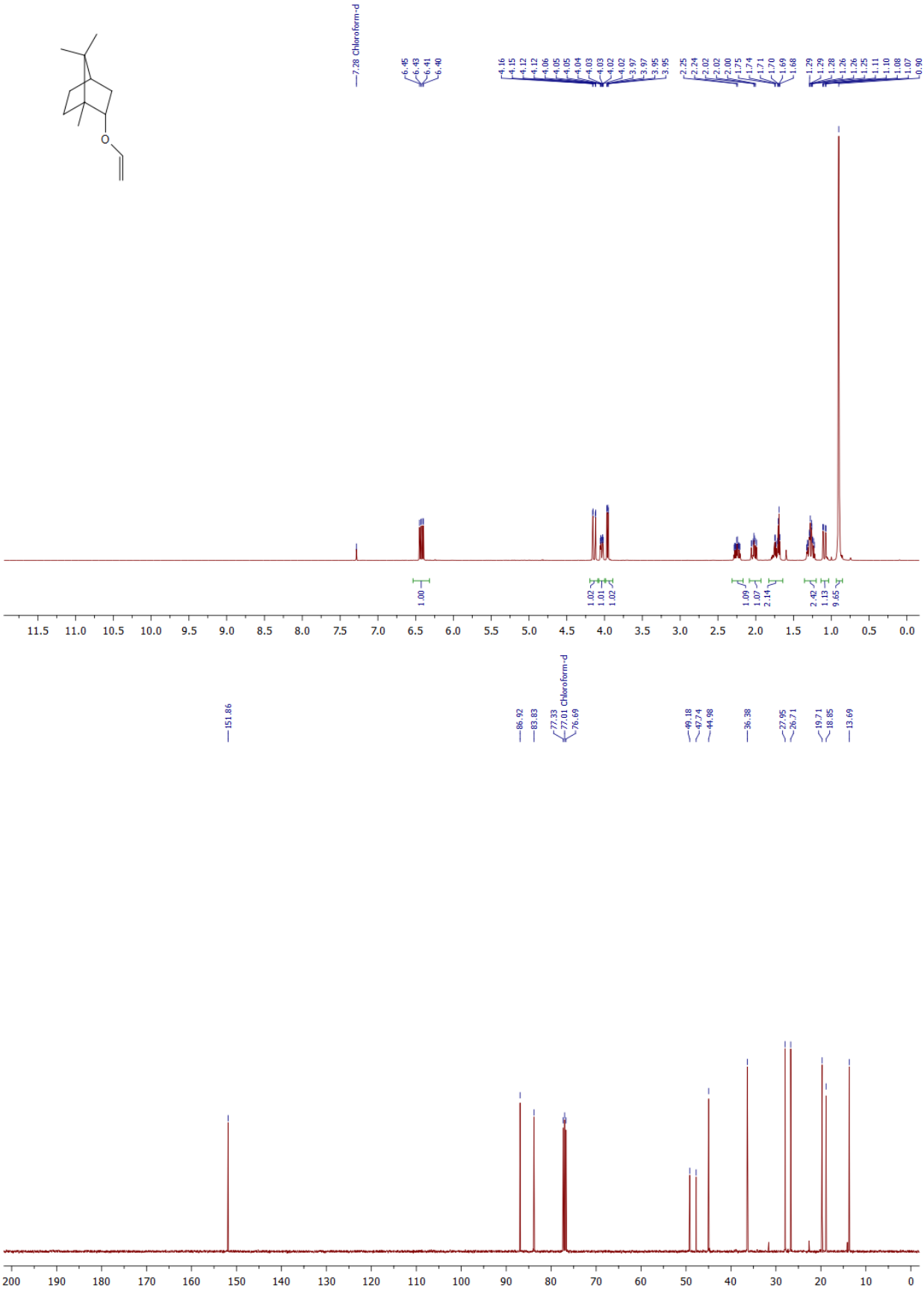


1-Hexyl vinyl ether (2h)

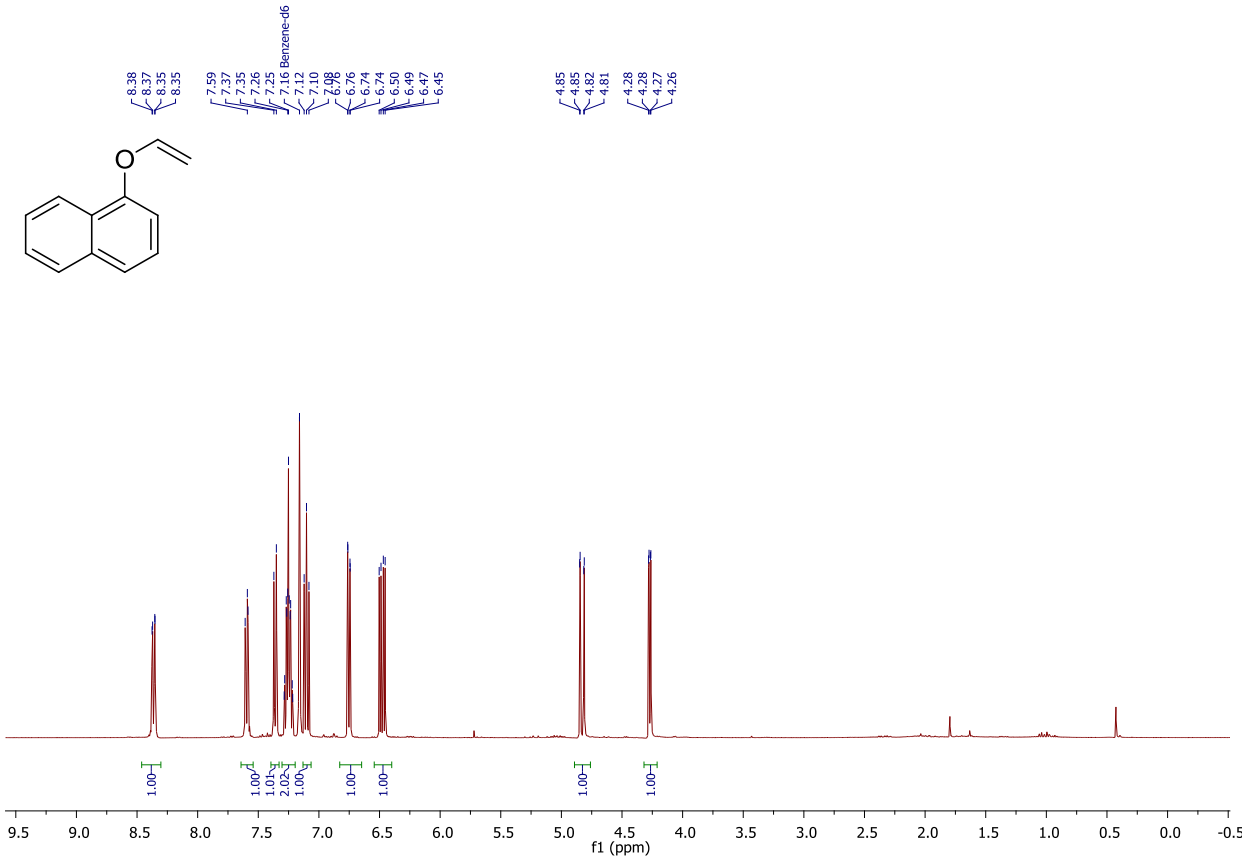


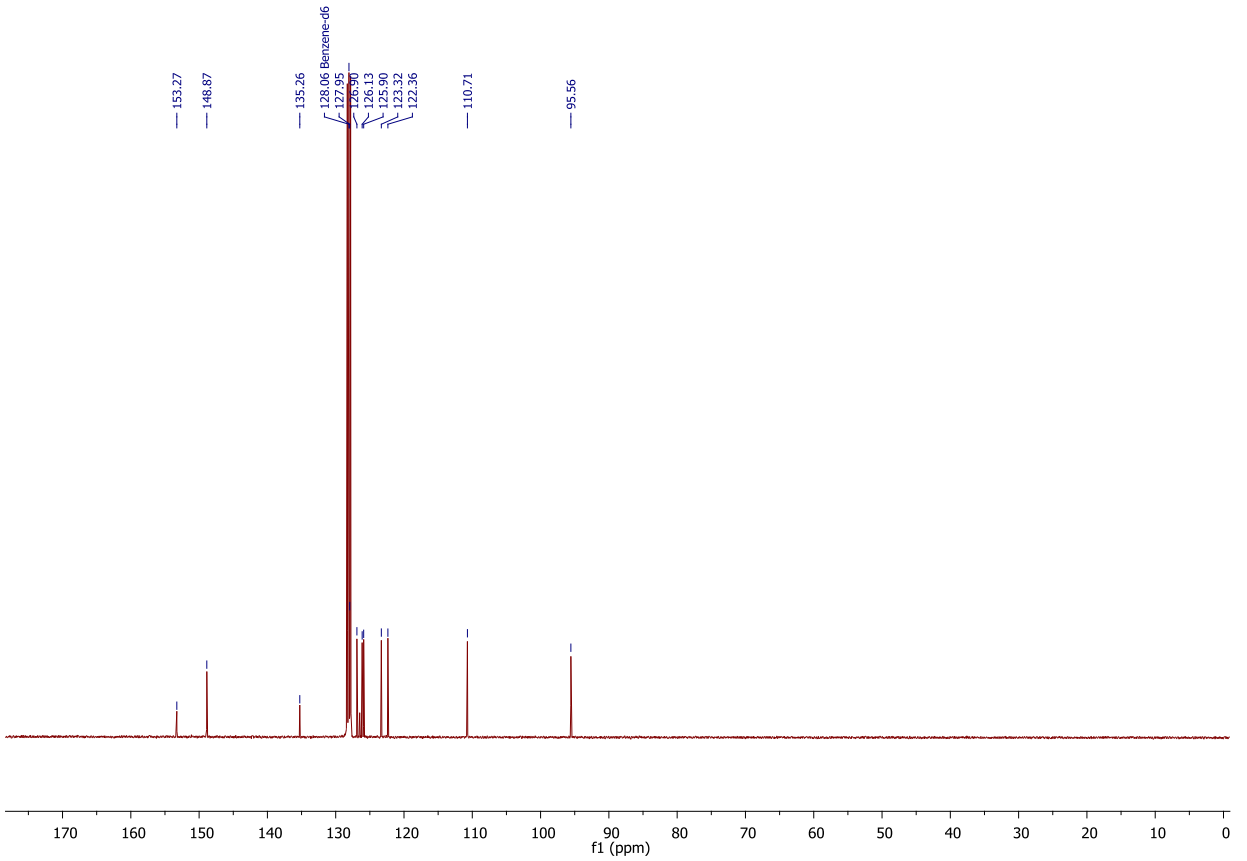


Bornyl vinyl ether (2i)

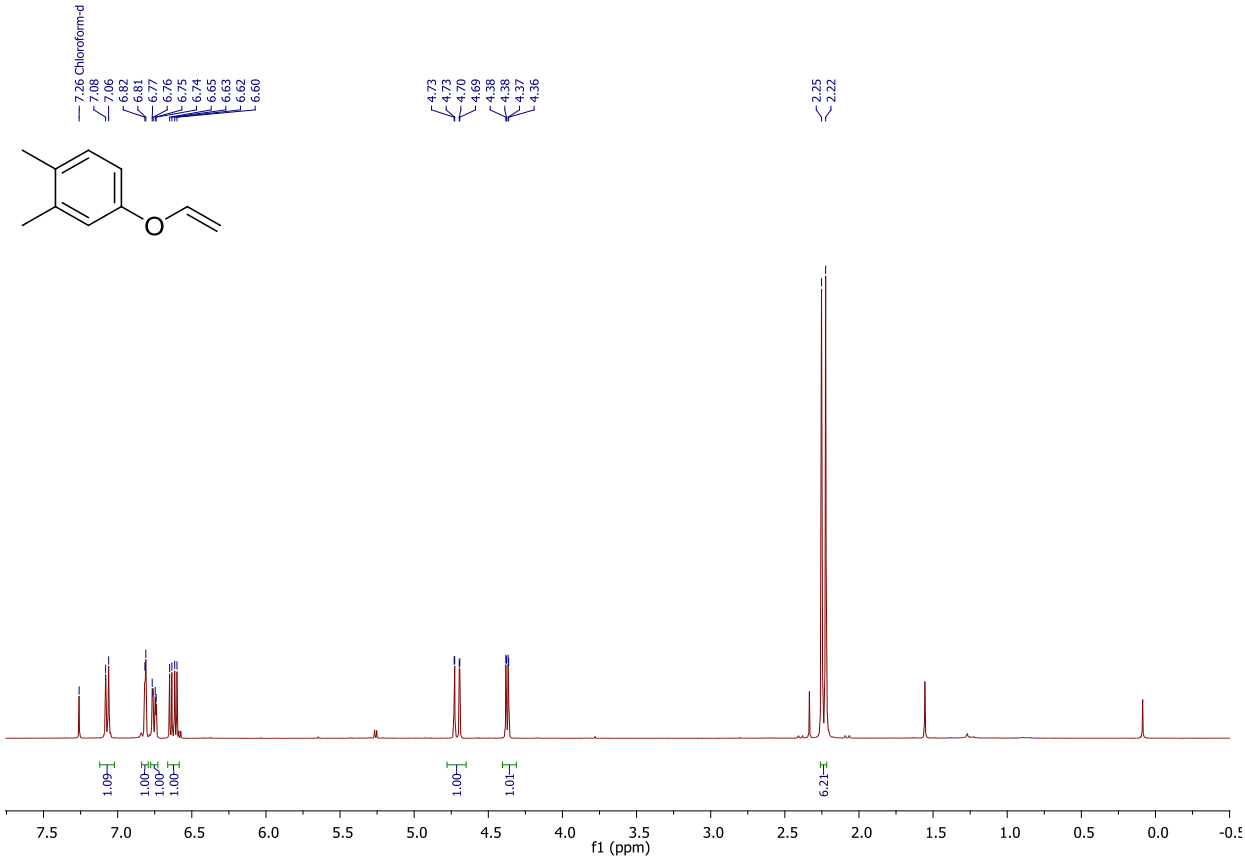


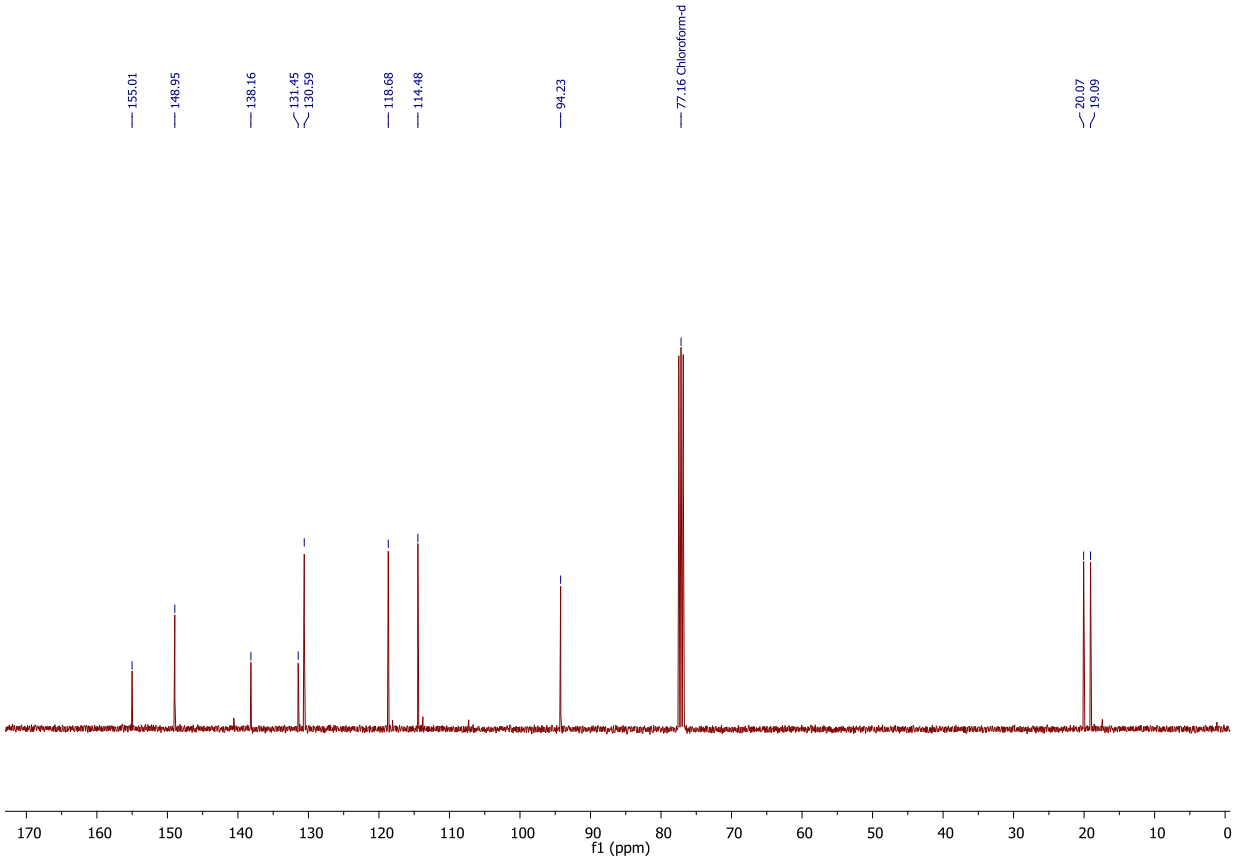
1-(vinyloxy)naphthalene (2j)





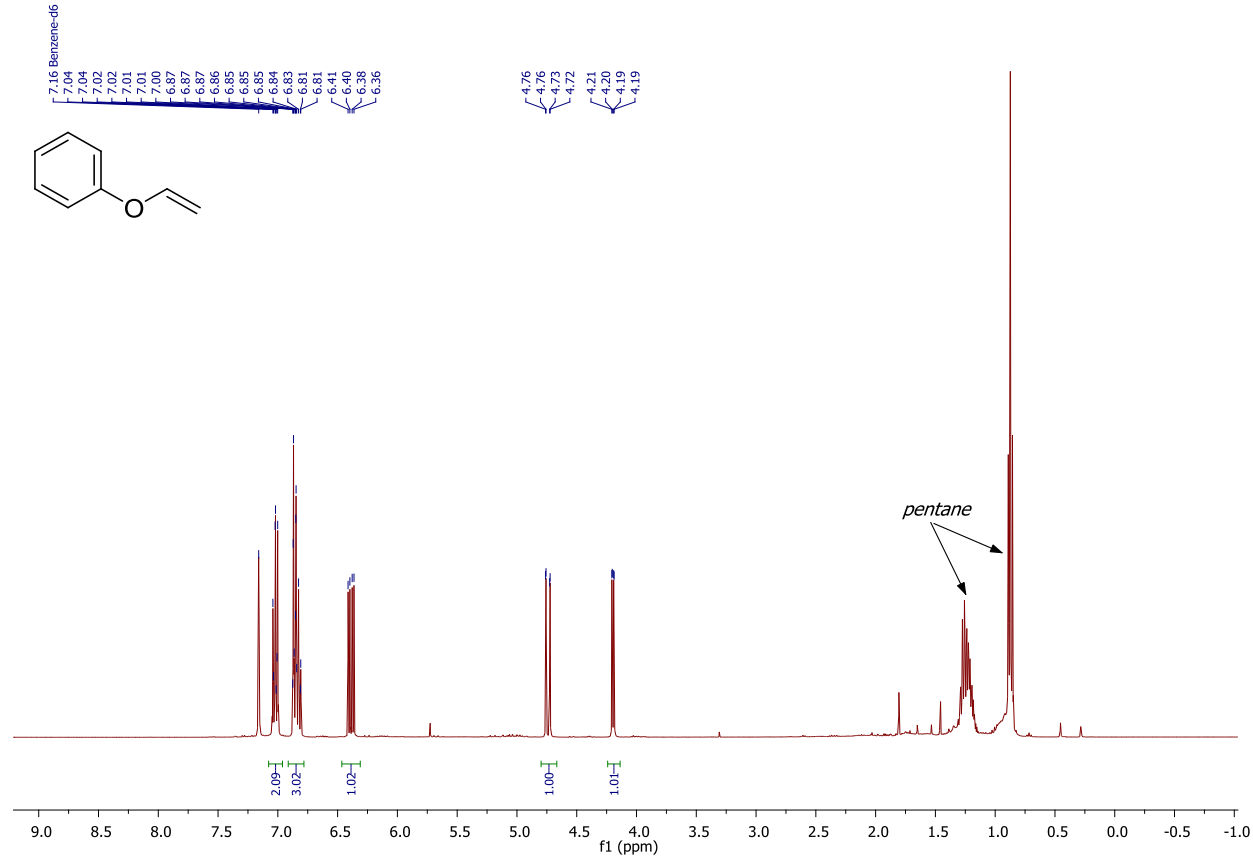
1,2-dimethyl-4-(vinyloxy)benzene (2k)

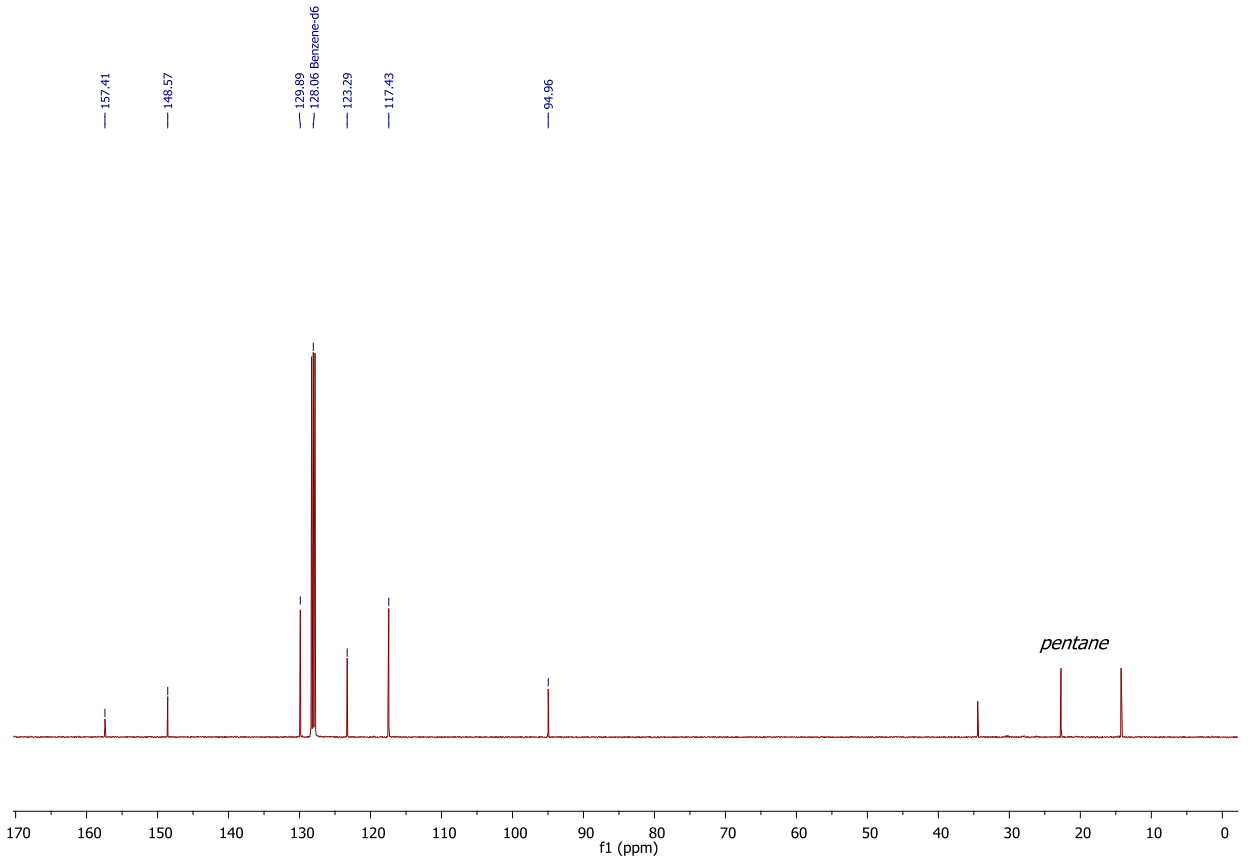




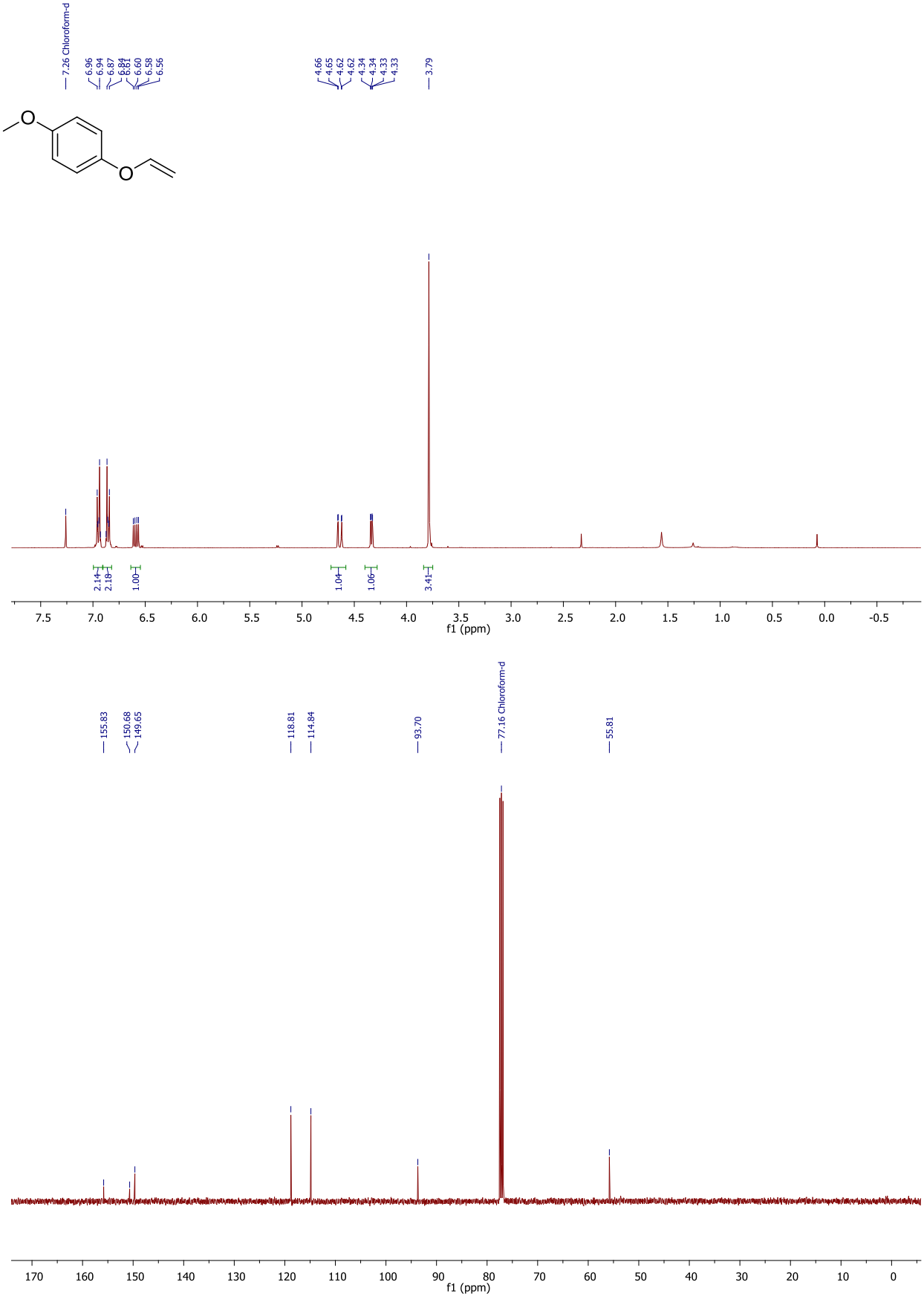
Phenyl vinyl ether (2l)

Dilution with pentane was utilized for product stabilization.

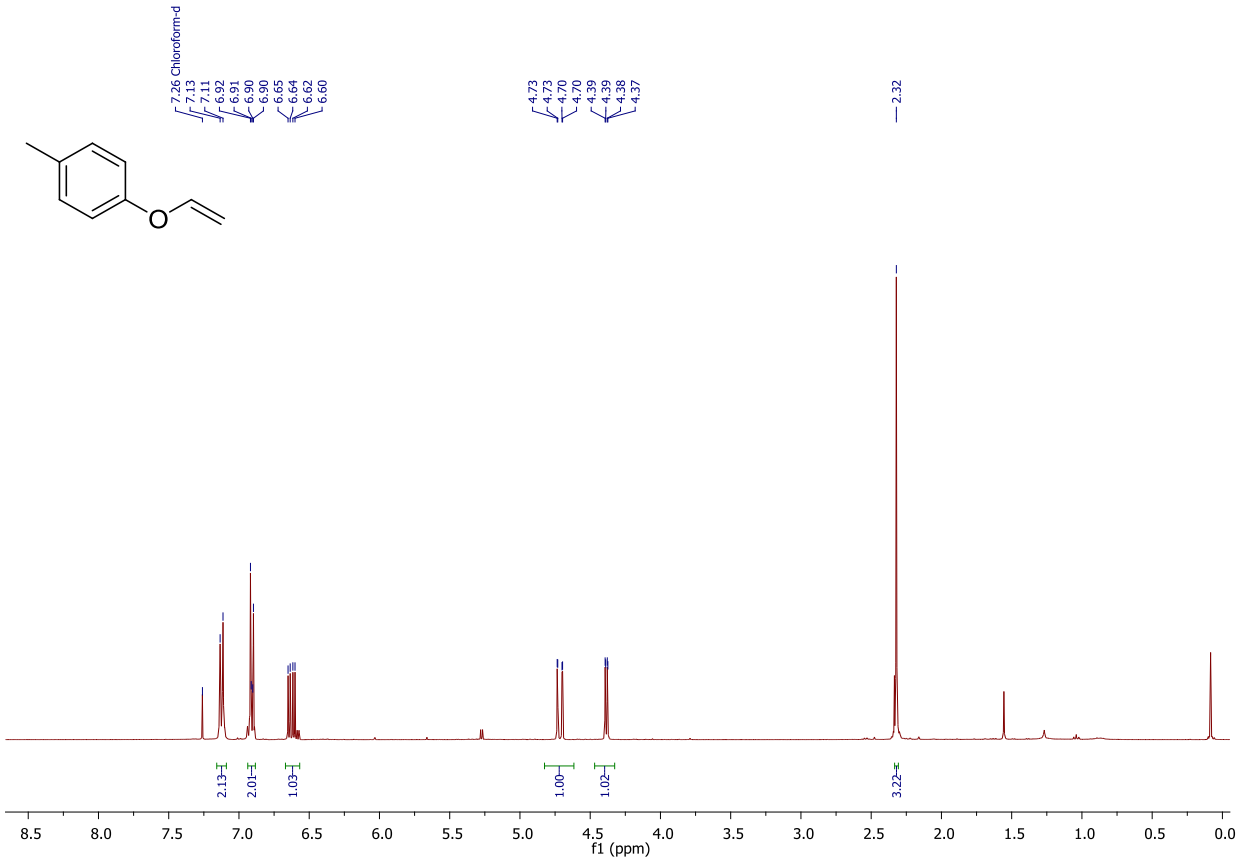


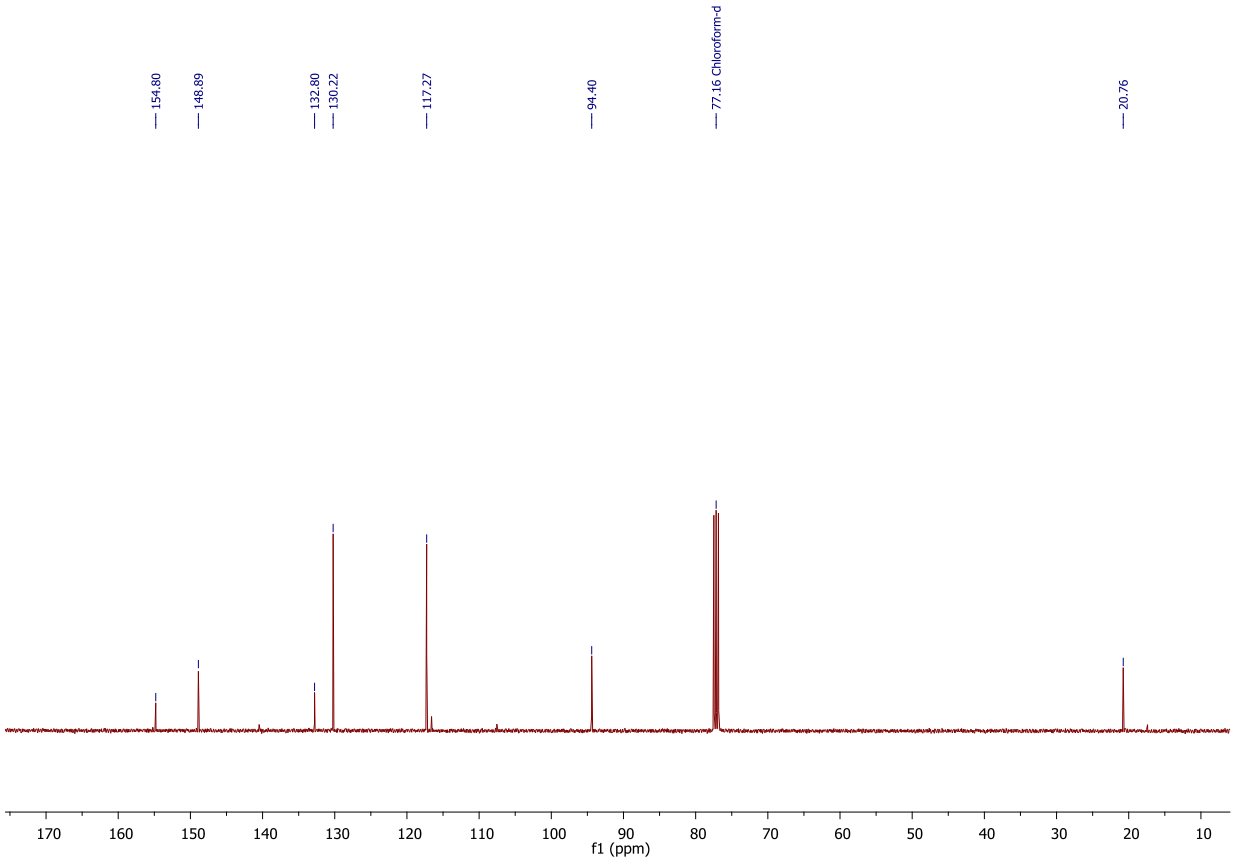


1-methoxy-4-(vinyloxy)benzene (2m)

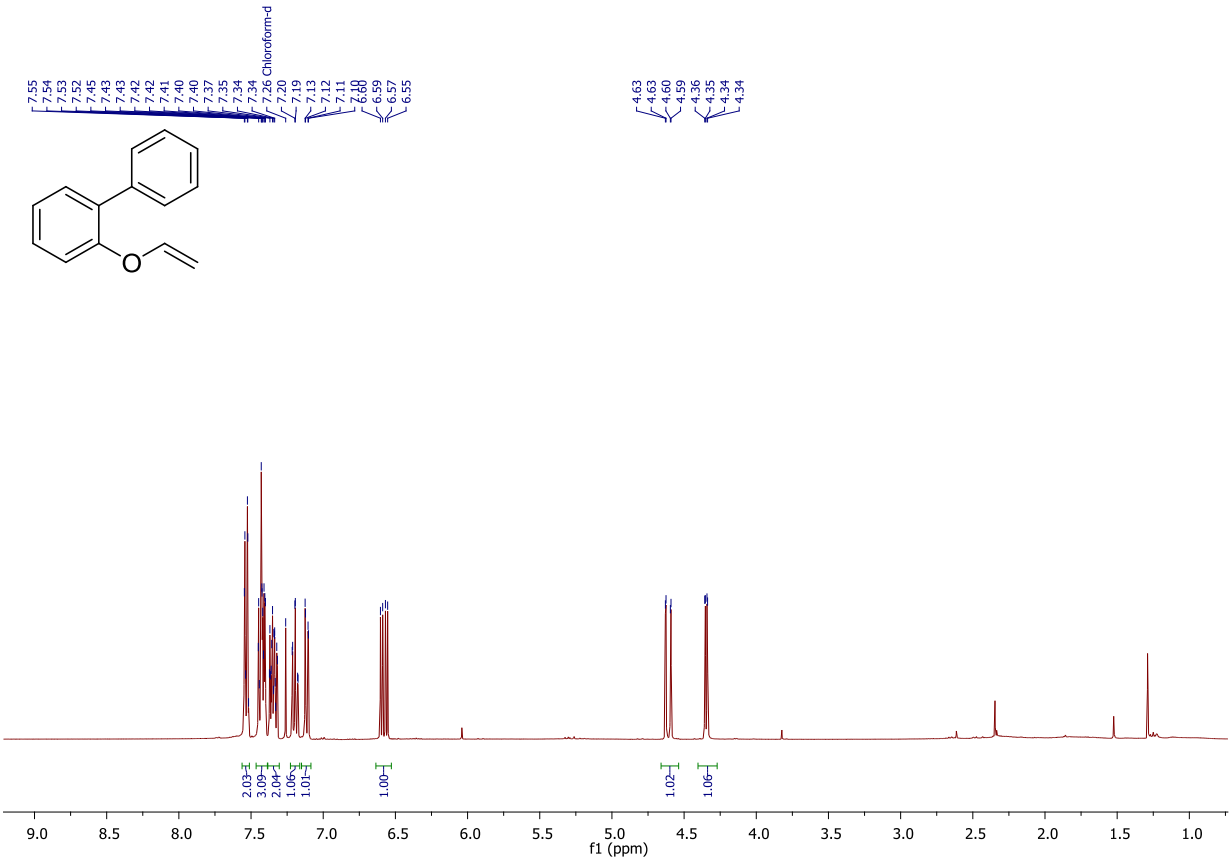


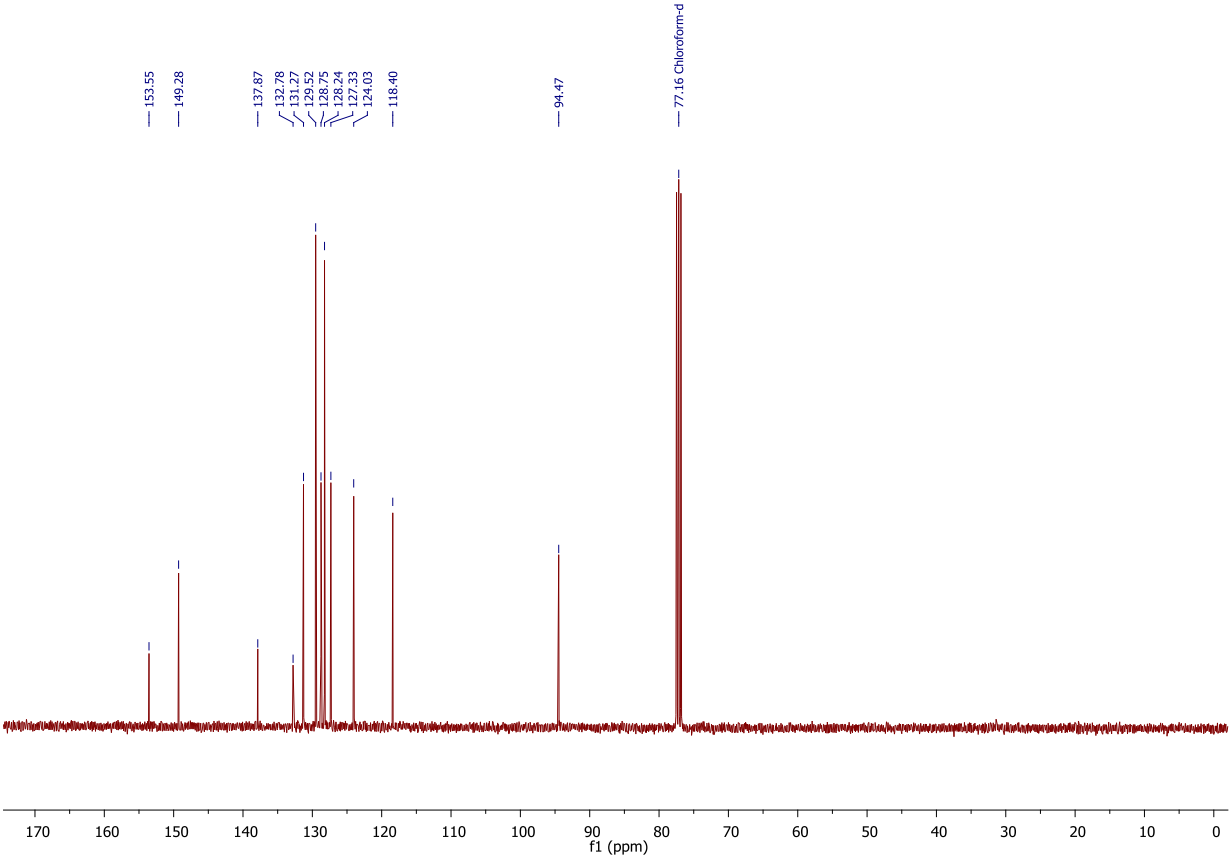
1-methyl-4-(vinyloxy)benzene (2n)



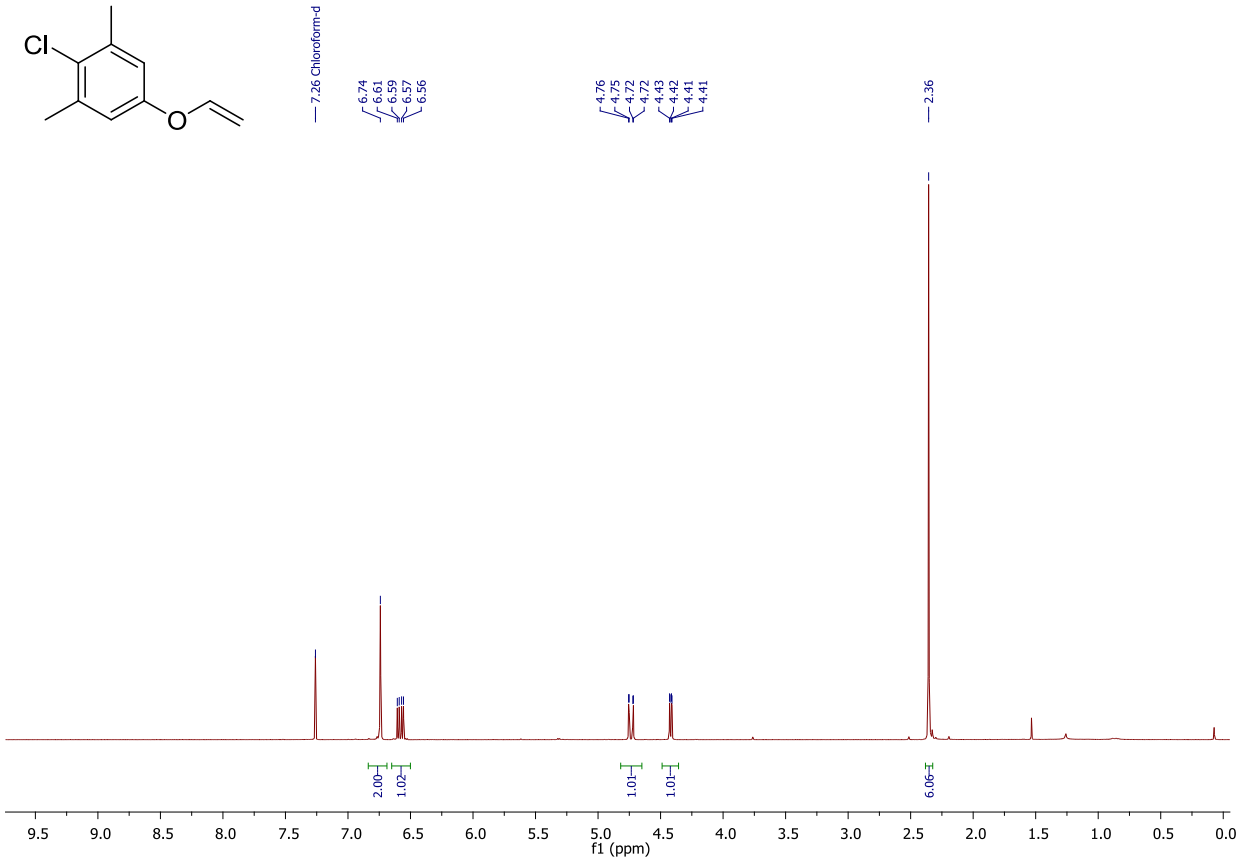


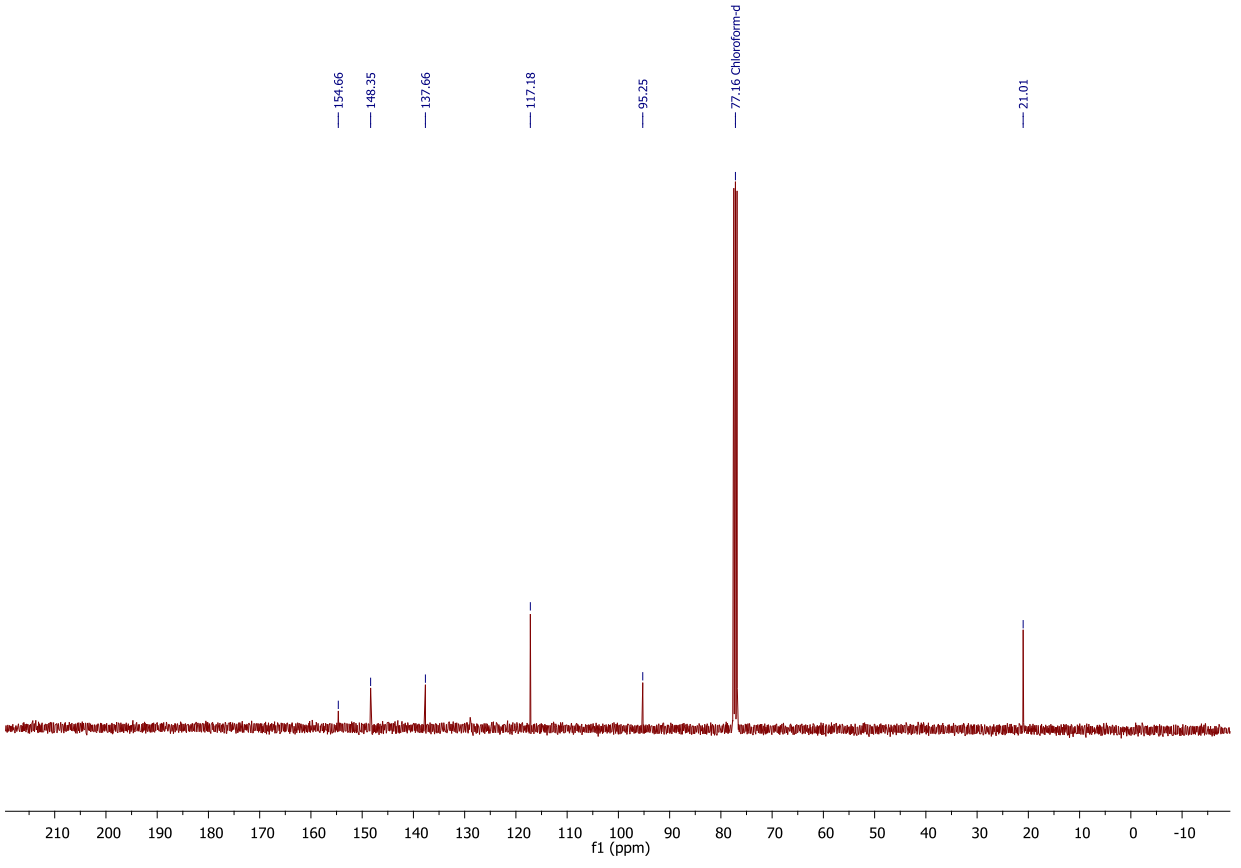
2-(vinyloxy)-1,1'-biphenyl (2o)



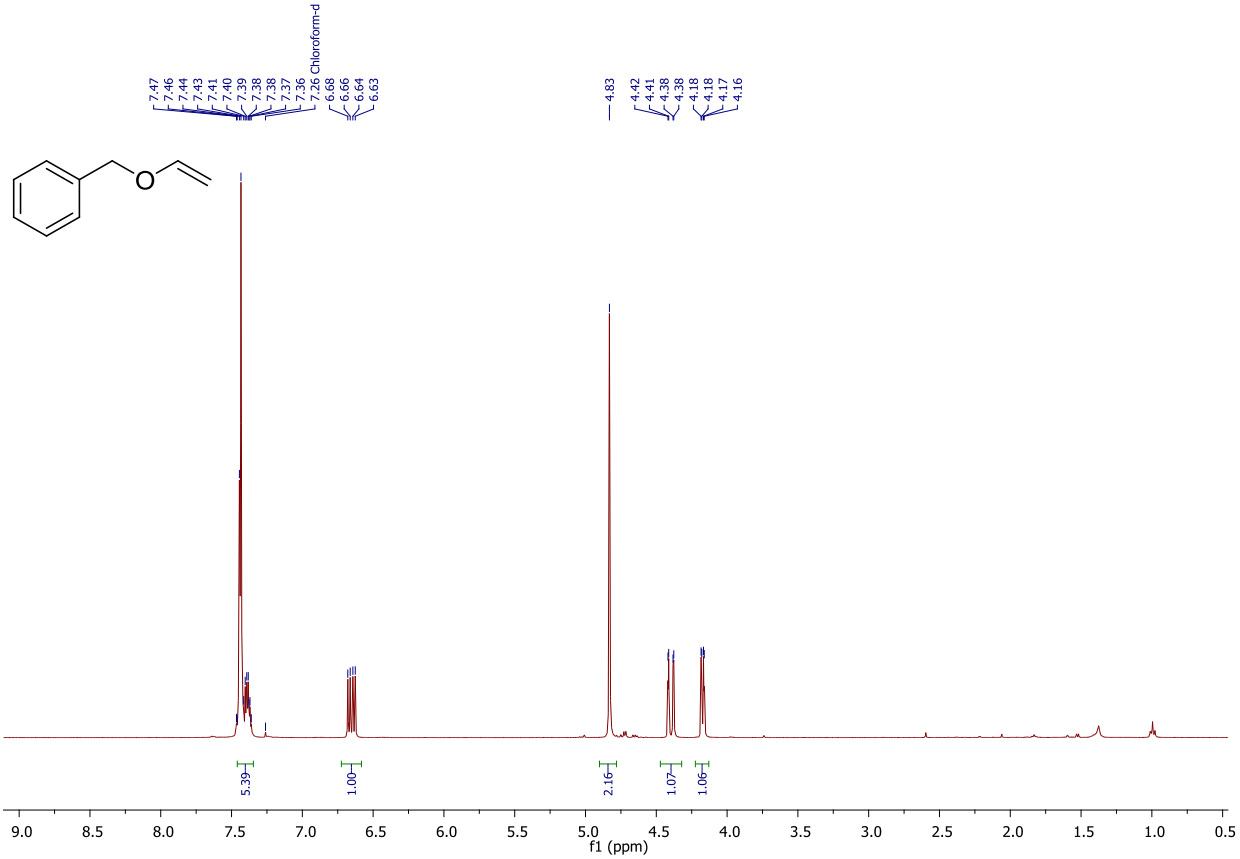


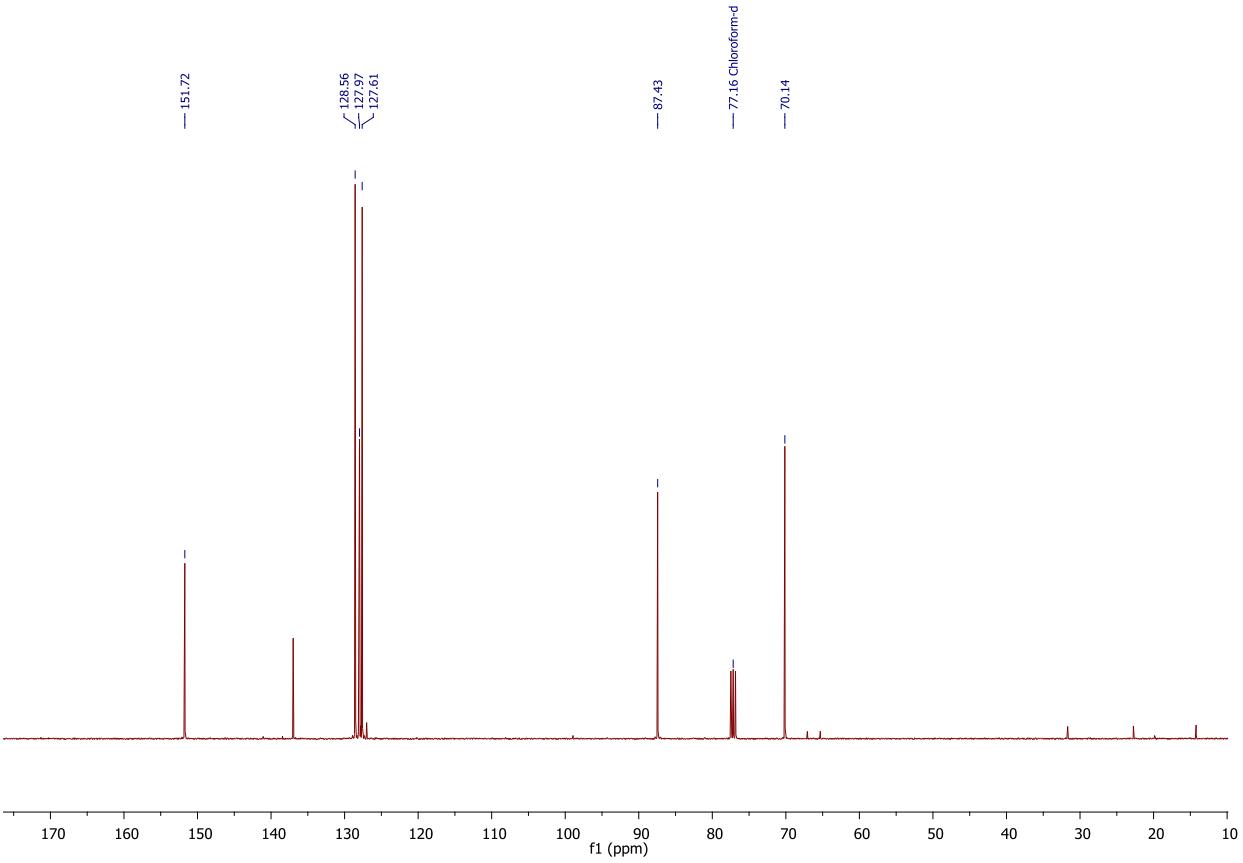
2-chloro-1,3-dimethyl-5-(vinyloxy)benzene (2p)



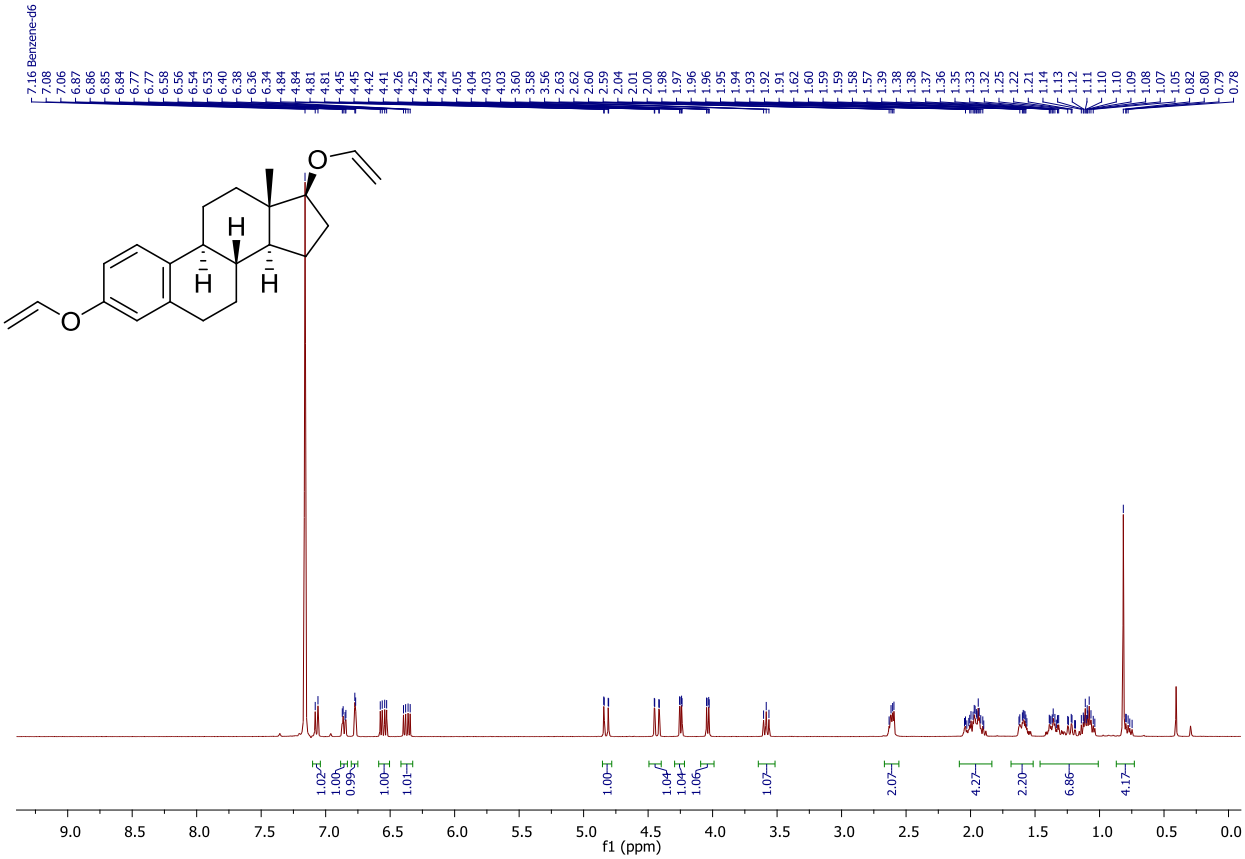


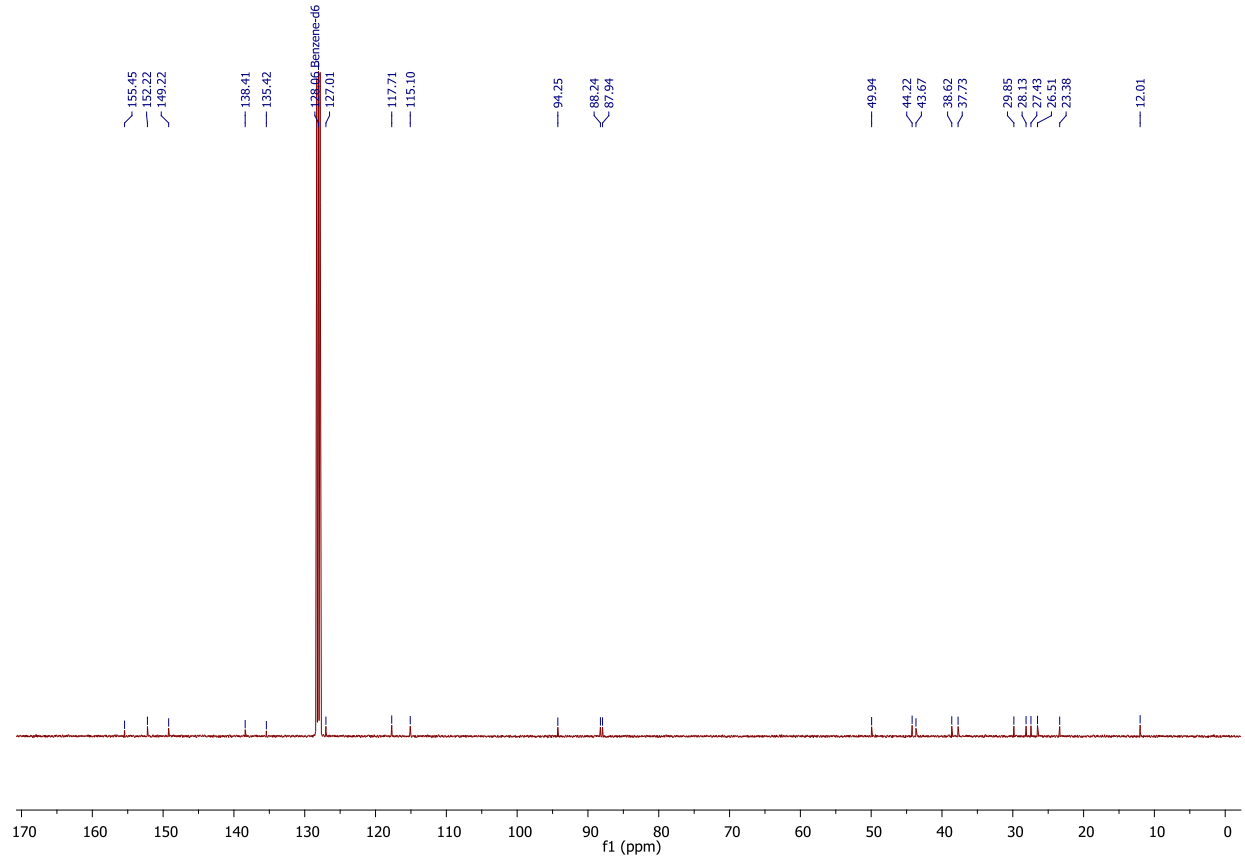
Benzyl vinyl ether (2q)



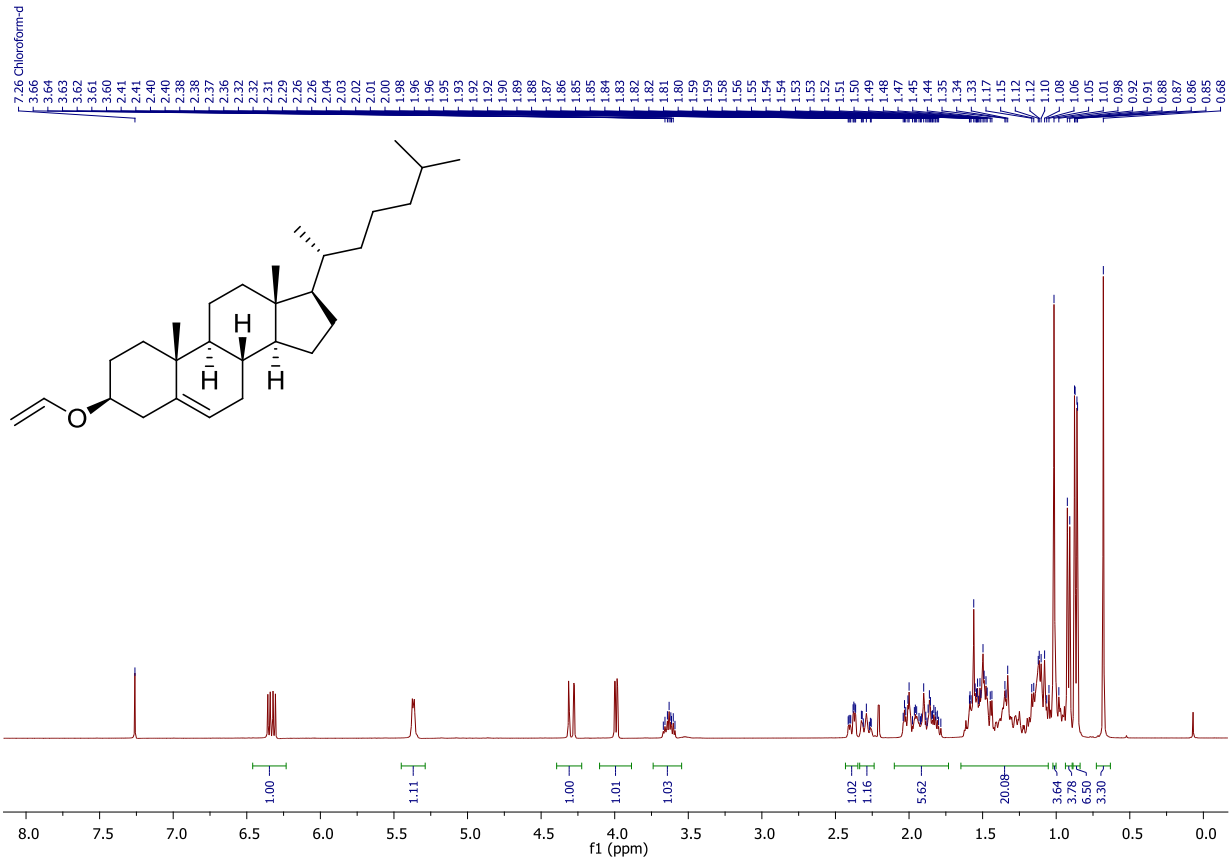


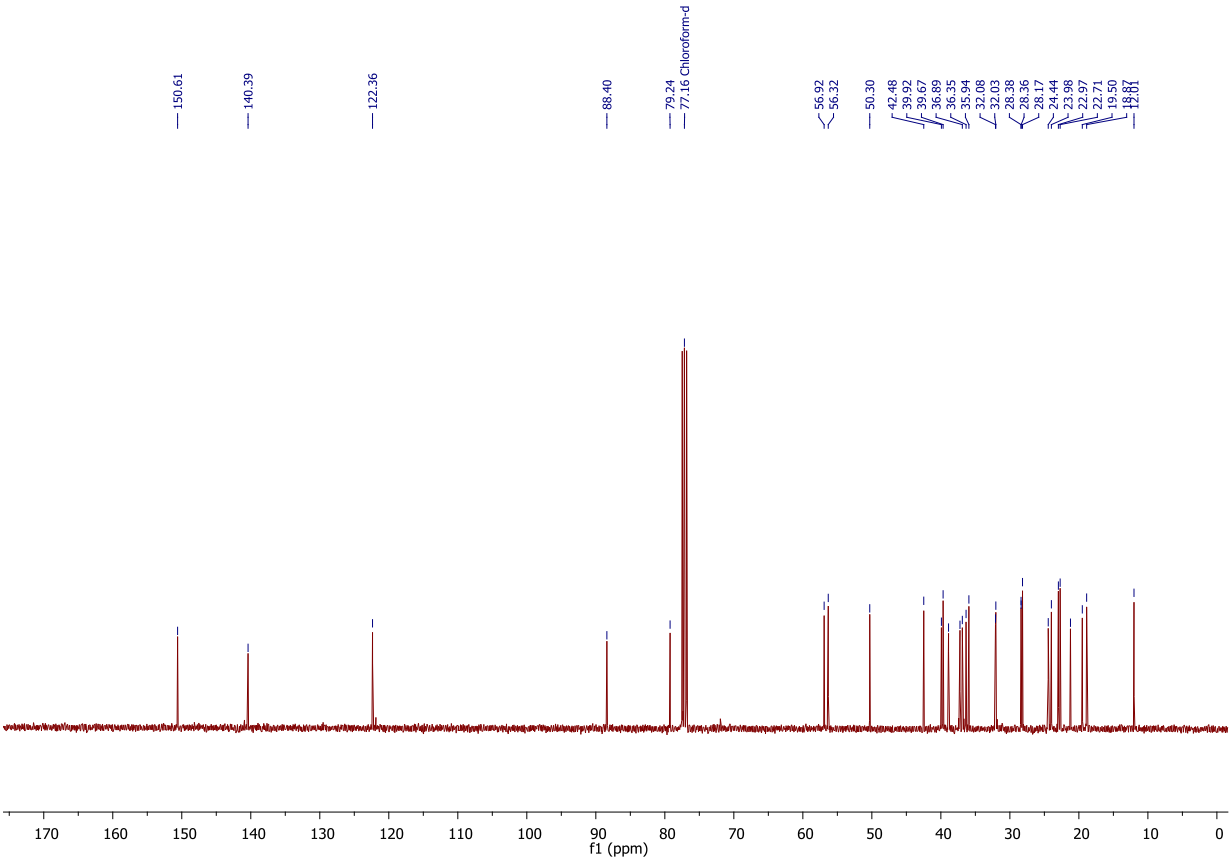
Estradiol divinyl ether (2s)



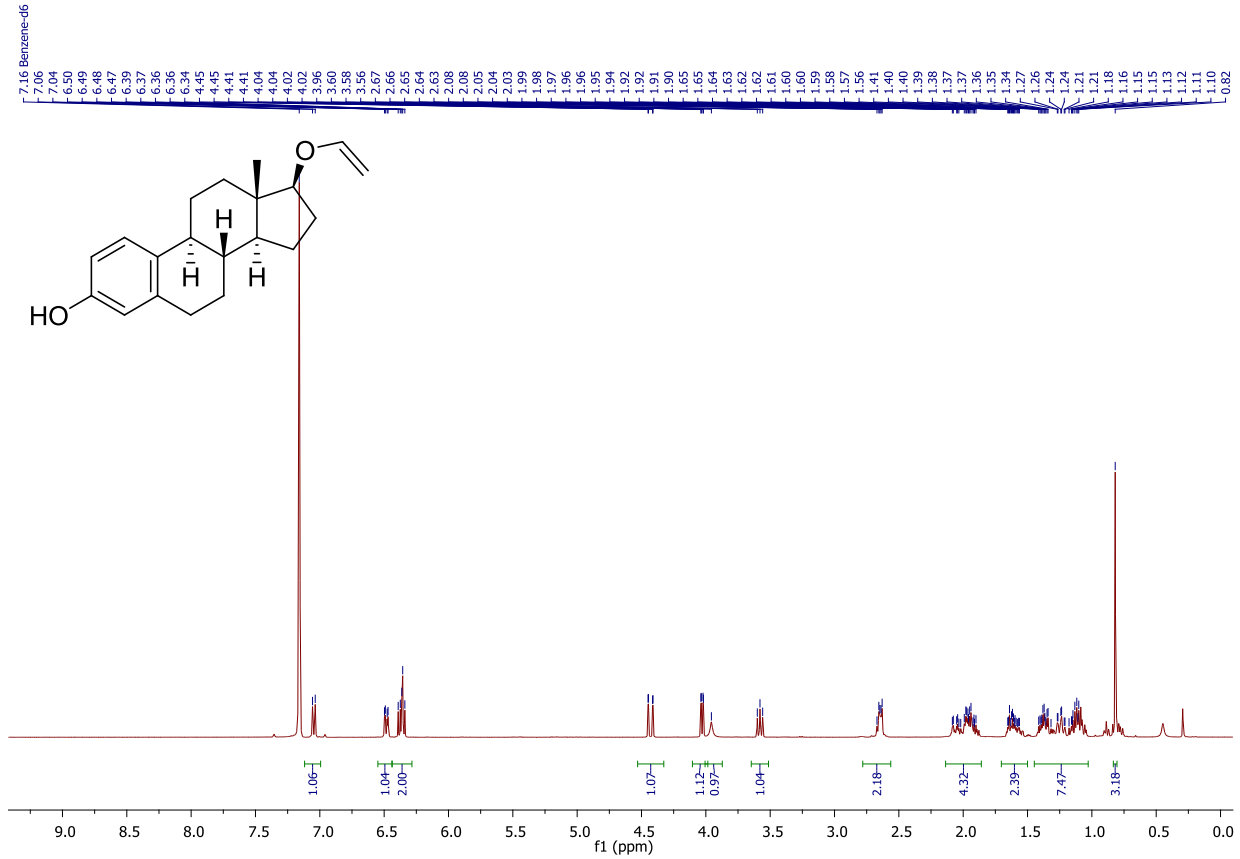


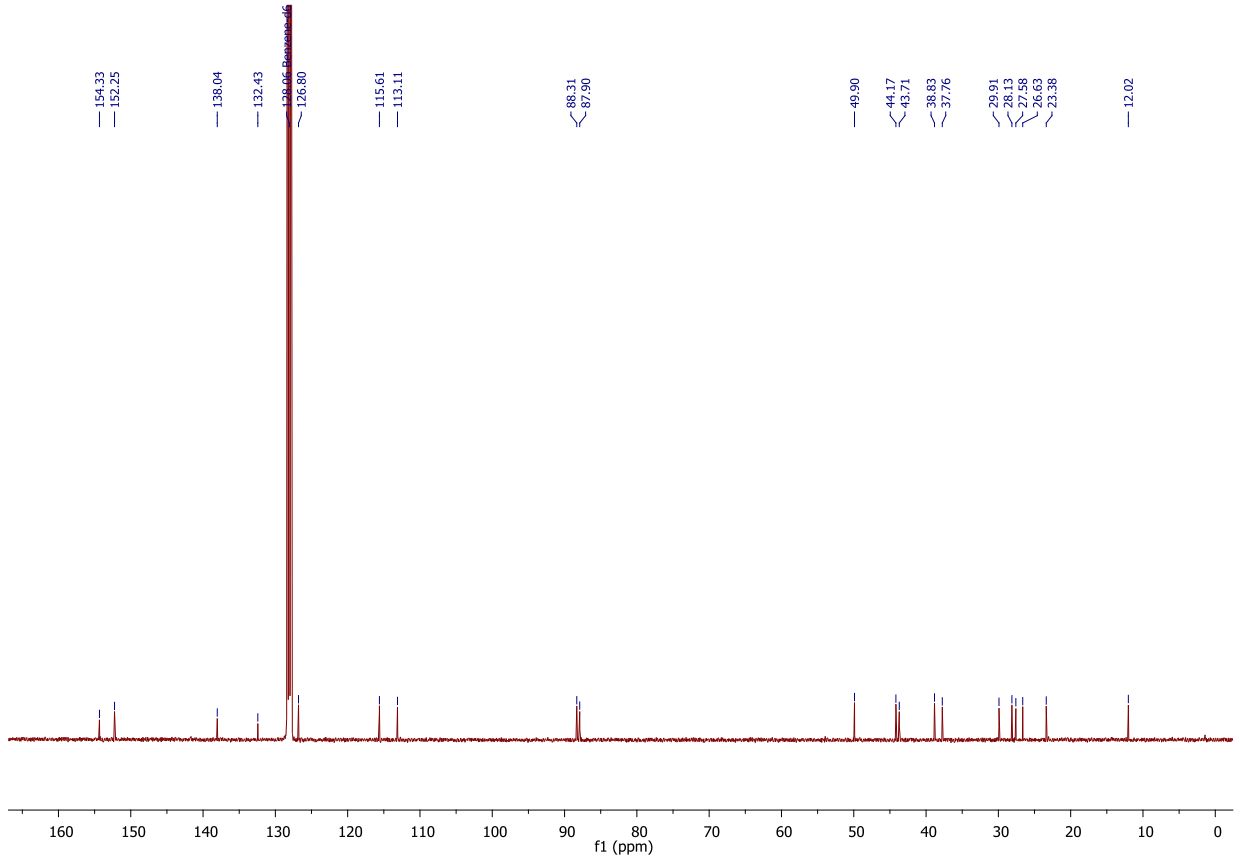
Cholesteryl vinyl ether (2t)



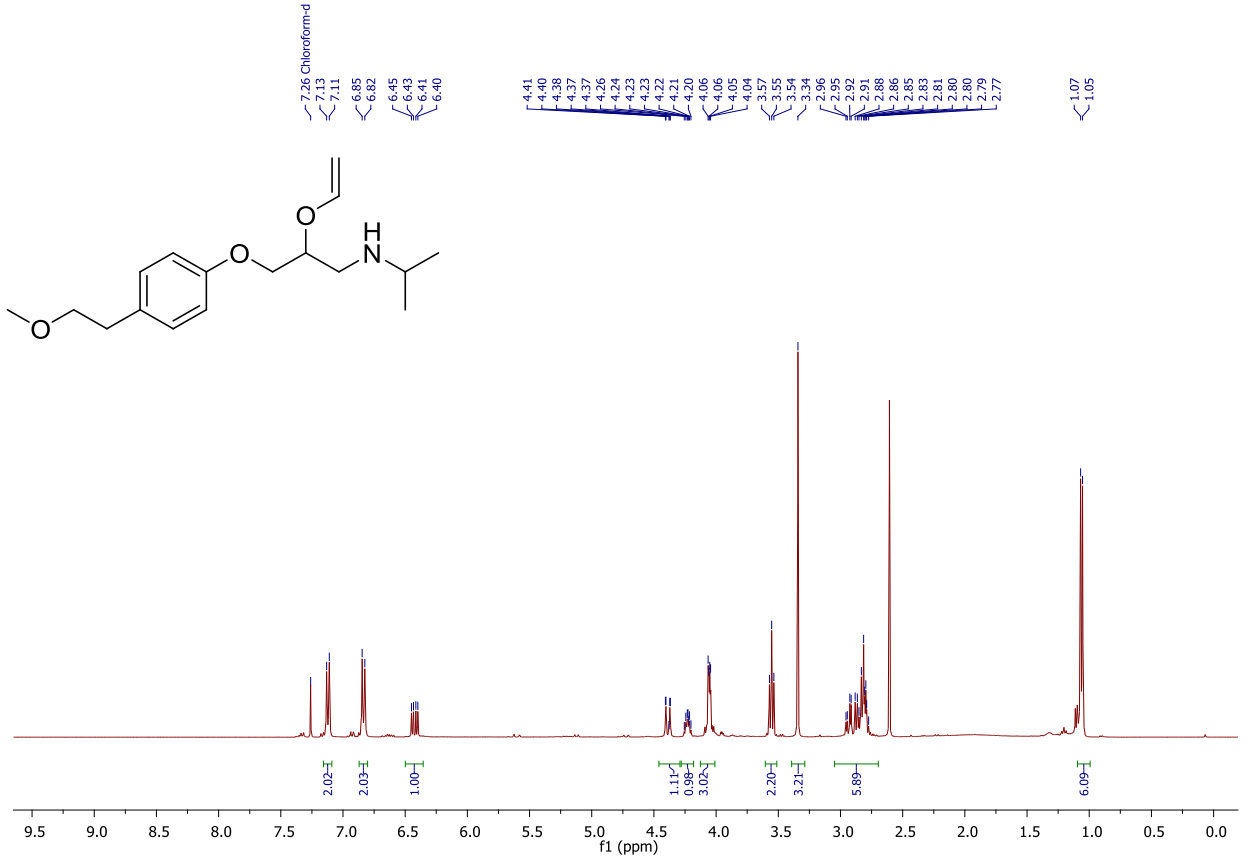


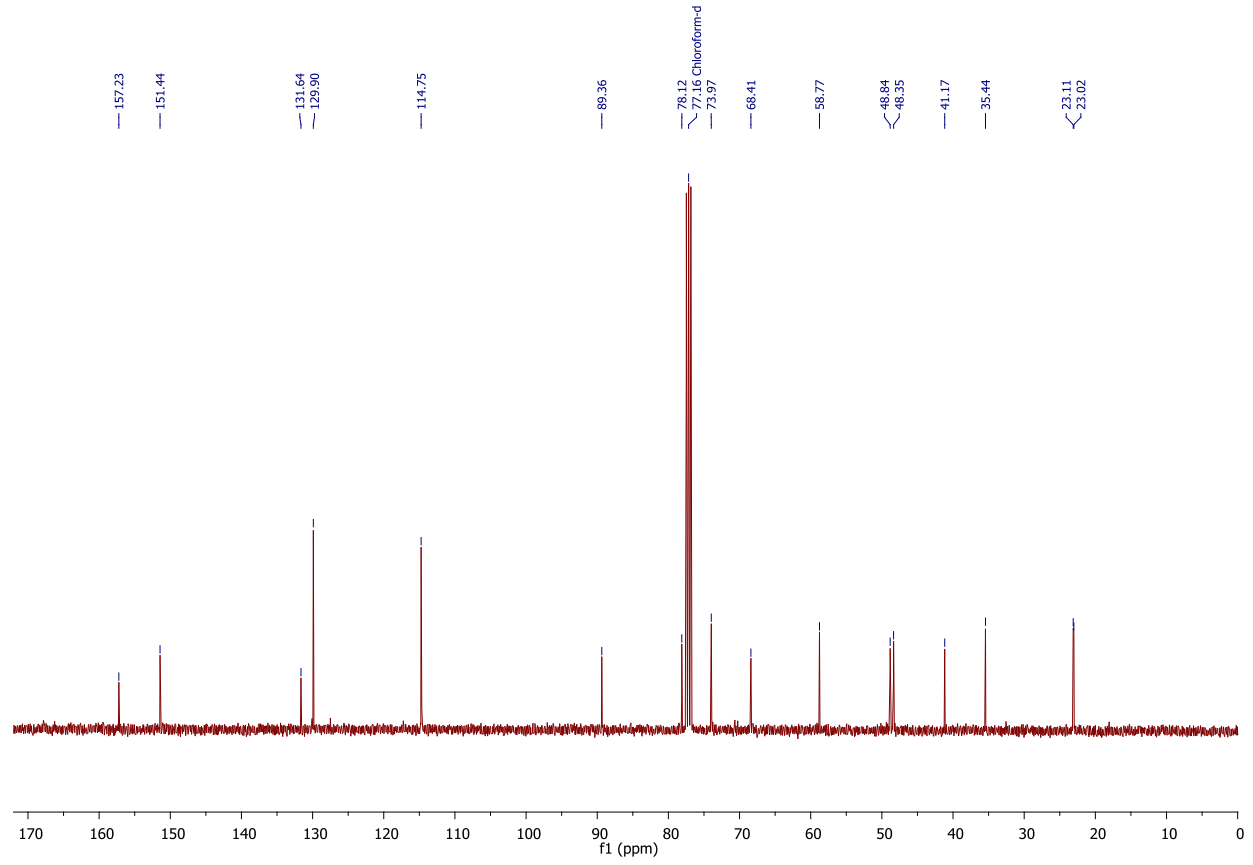
Estradiol vinyl ether (2u)



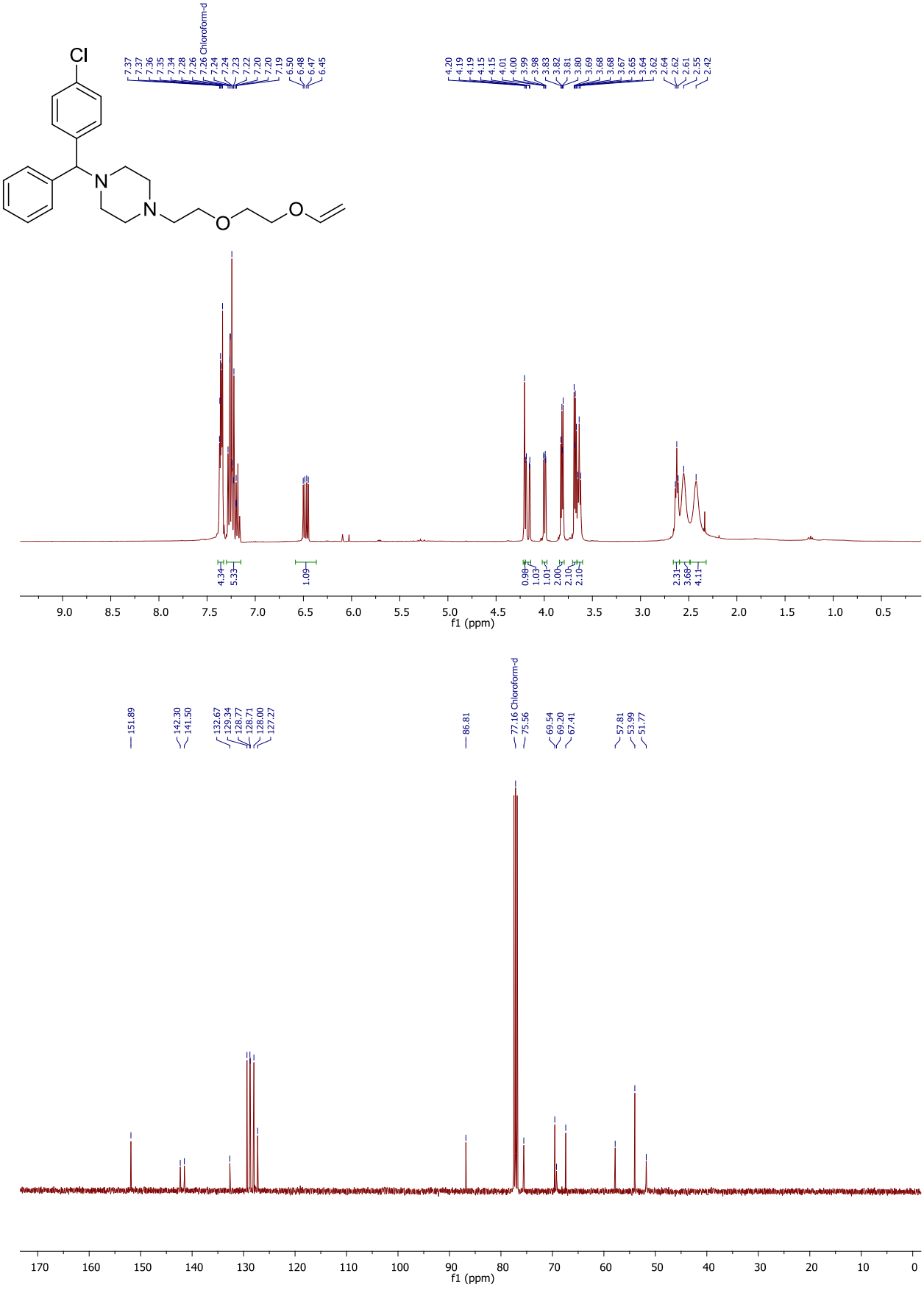


N-isopropyl-3-(4-(2-methoxyethyl)phenoxy)-2-(vinyloxy)propan-1-amine (2v)

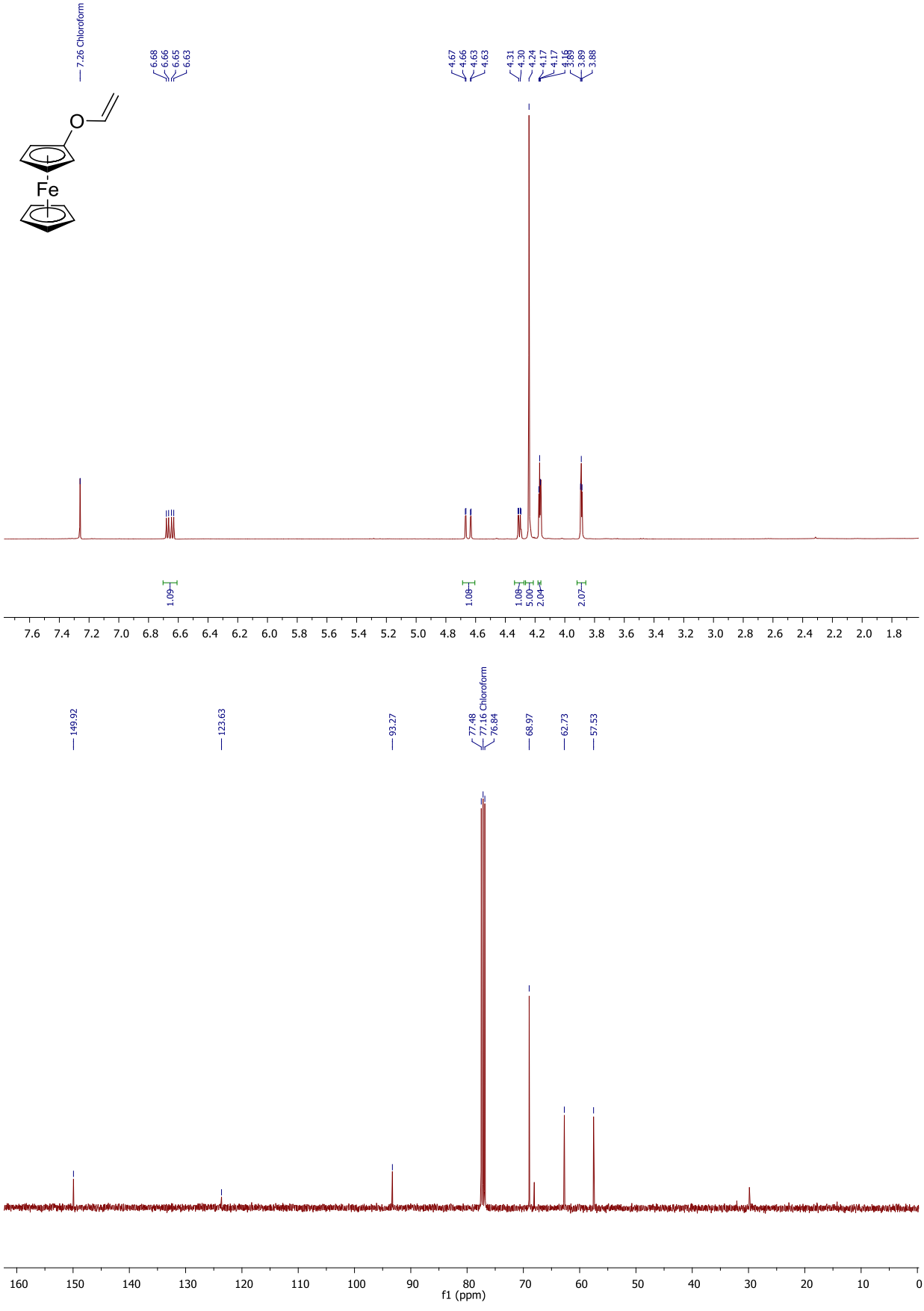




1-((4-chlorophenyl)(phenyl)methyl)-4-(2-(2-(vinyloxy)ethoxy)ethyl)piperazine (2w)



Vinyloxyferrocene (2z)



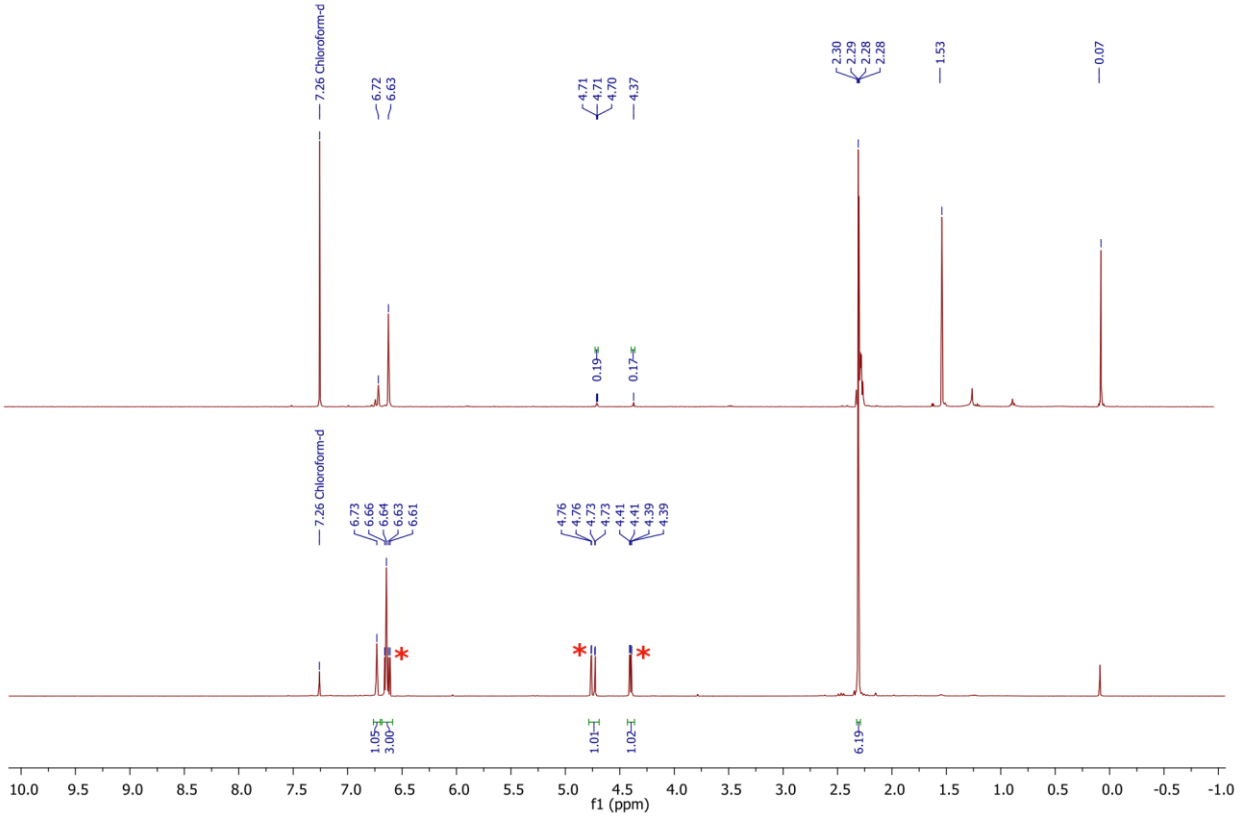


Figure S3. Bottom: ^{1}H NMR spectrum of product **2a** synthesized under regular experimental conditions using H_2O as a reagent and DMSO as a solvent (signals of the vinyl protons are marked by the asterisk); top: ^{1}H NMR spectrum of product **2a** synthesized in the deuteration study with deuterated ROD derivative of **1a** and using D_2O as a reagent and DMSO-d_6 as a solvent.

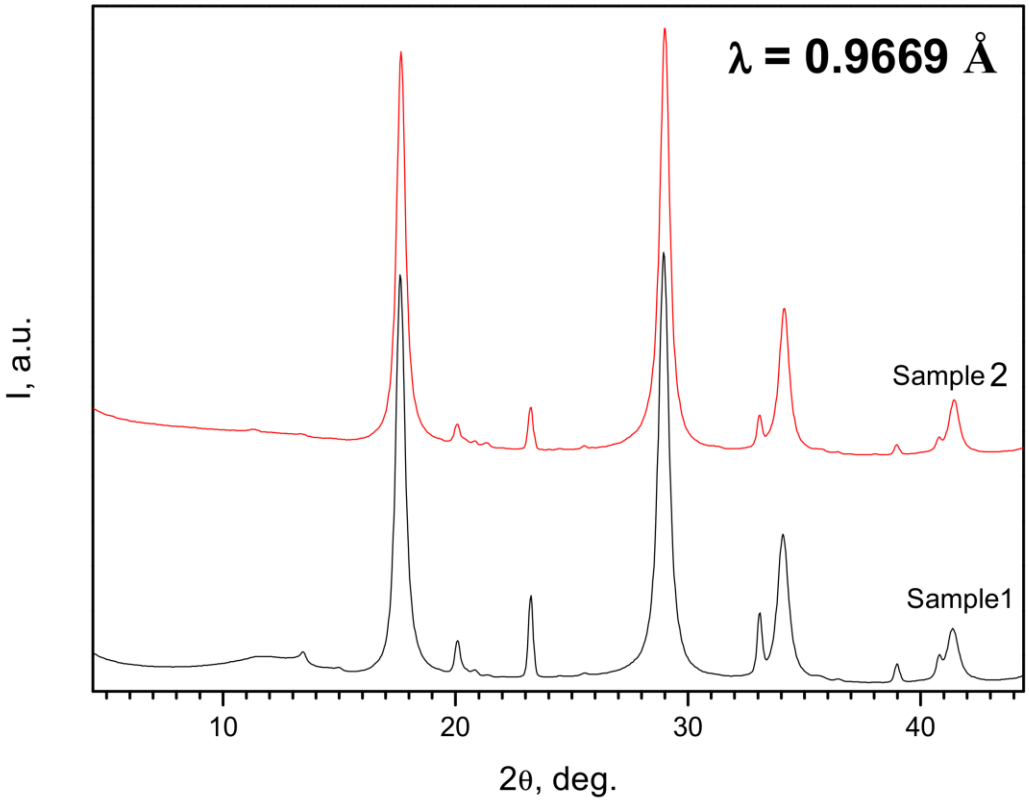
S6. XPD and SEM study of inorganic residue

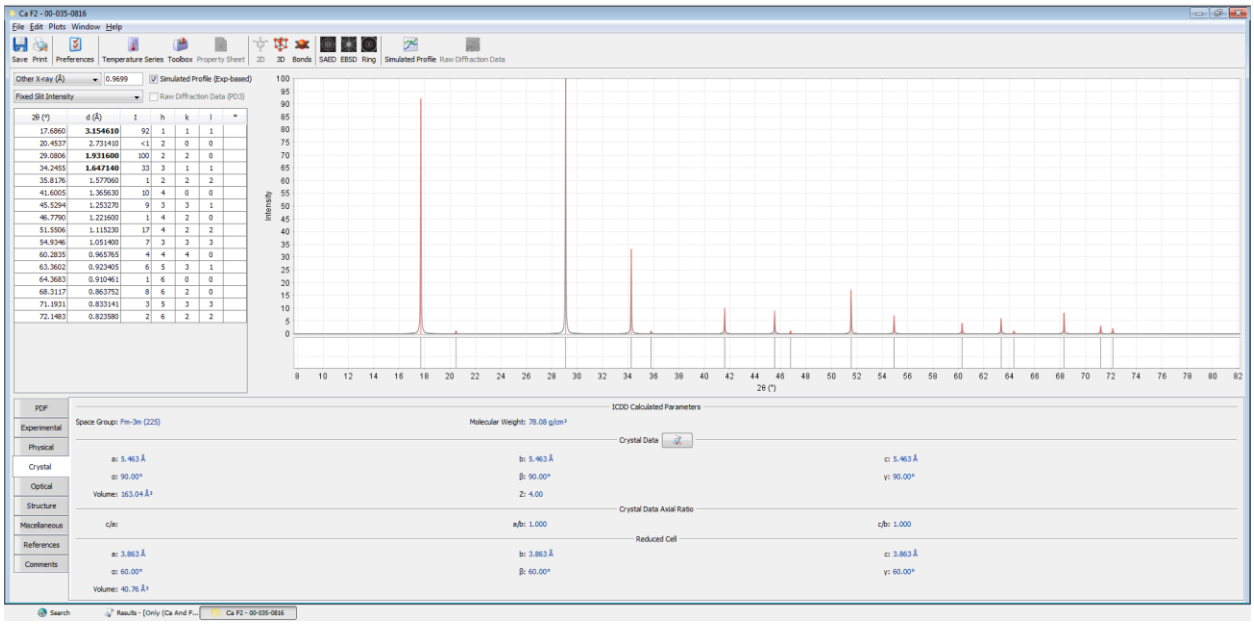
Scanning electron microscopy of the initial calcium carbide and inorganic residue isolated after the reaction were studied at low, medium and high magnifications (Figure 4 in the article). In order to estimate the composition of the inorganic solid residue isolated after the reaction of phenol **1a** with CaC_2 in the presence of KF the X-ray microanalysis technique in the combination with scanning electron microscopy (EDS-SEM) was used. Elemental composition of CaF_2 was confirmed by EDS-SEM analysis.

In addition to EDS-SEM, two samples were studied by synchrotron X-ray powder diffraction (XPD). Sample 1: Inorganic residue isolated after the reaction of phenol **1a** with calcium carbide and KF (Table 1, entry 9 in the article); Sample 2: Inorganic residue isolated after the reaction of calcium carbide with water in the presence of KF (reaction 2, Figure 5 in the article). The resulting pattern for sample 1 completely corresponds to the pattern obtained for the

sample 2 (Figure S4). Both samples predominantly contain CaF_2 phase with some CaO phase as an impurity (the later originated from $Ca(OH)_2$ after drying). The content of the studied inorganic phase is in agreement with proposed reaction mechanisms.

Figure S4. Measured XPD diagrams for samples 1 and 2 (top), and reference data (bottom).





S7. Theoretical calculations

Computational Details

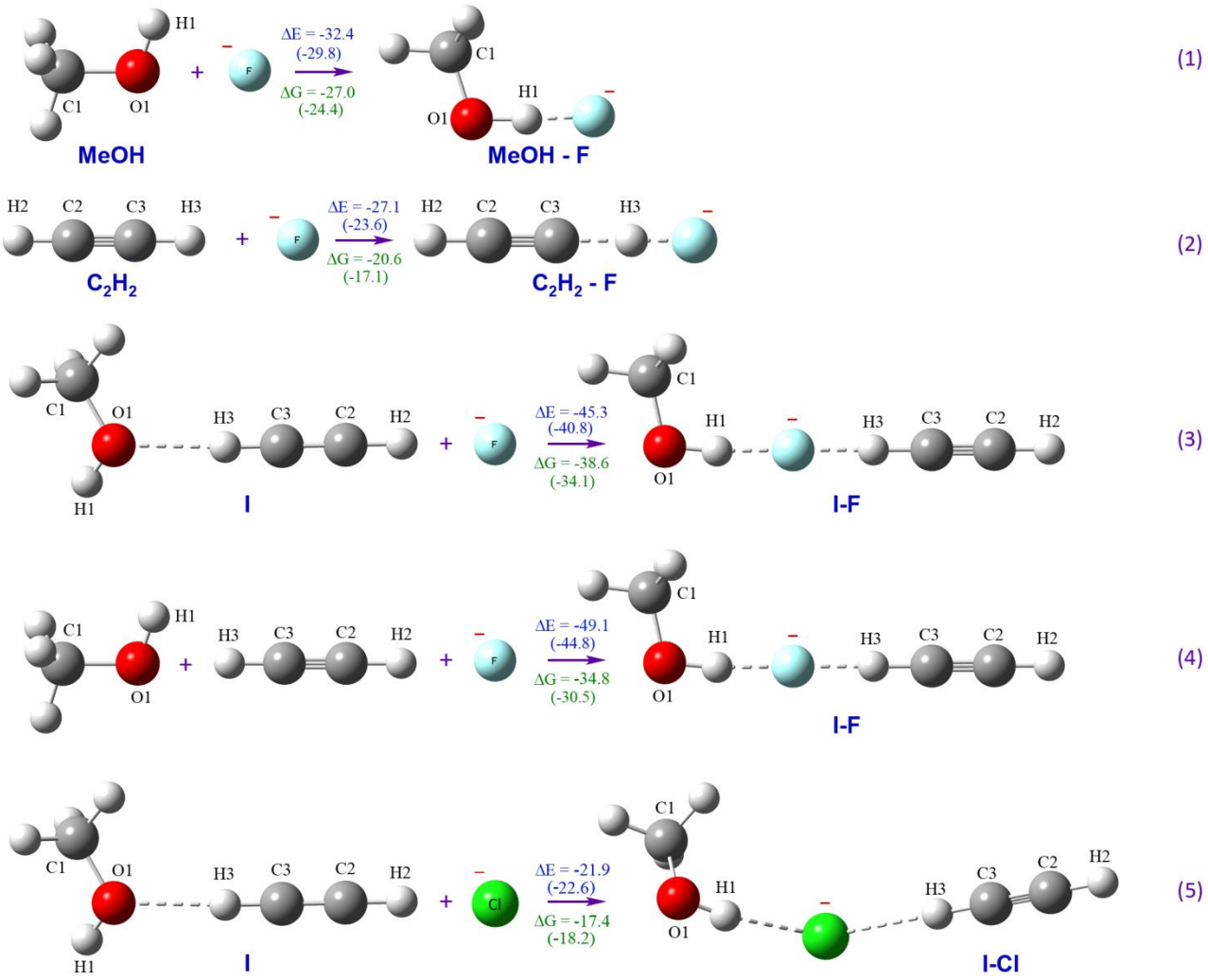
All structures were optimized by PBE1PBE[10] DFT method with 6-311++G(d,p) basis set[11] (Grid=UltraFine). Calculations in DMSO medium were performed by SMD continuum solvation model.[12] Molecular structures were optimized in DMSO medium. For all molecules the normal mode analysis was carried out at DFT level and all transition states have one imaginary frequency corresponding to hydroalkoxylation reaction. The validity of all transition states was confirmed by intrinsic reaction coordinate calculations (IRC).[13] For all optimized structures the single point CCSD(T)[14] calculations at same basis set in vacuum and DMSO (SMD) was performed. The CCSD(T) thermodynamic parameters were calculated as sum G(CCSD(T)) = E(CCSD(T)) + DFT(Thermal correction to Gibbs Free Energy) and H(CCSD(T)) = E(CCSD(T)) + DFT(Thermal correction to Enthalpy). Gaussian 09[15] program package was used for all calculations.
Detailed description of the calculations for the reaction with MeOH as a substrate (Figure 7 in the manuscript) was provided below. Similar procedure was utilized for the calculations with PhOH as a substrate (Figure 8 in the manuscript).

(10) a) Perdew, J.P.; Burke, K.; Ernzerhof M. *Phys. Rev. Lett.* **1996**, *77*, 3865. b) Adamo, C; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
(11) a) McLean, A.D.; Chandler, G.S. *J. Chem. Phys.* **1980**, *72*, 5639. b) Krishnan, R; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.* **1980**, *72*, 650. c) Clark T., Chandrasekhar J., Spitznagel G.W., Schleyer P.v.R. *J. Comp. Chem.* **1983**, *4*, 294.
(12) Marenich A.V., Cramer C. J., Truhlar D.G. *J. Phys. Chem. B*, **2009**, *113*, 6378.
(13) Hratchian H.P., Schlegel H.B. J. Chem. Theory Comput. **2005**, *1*, 61.
(14) a) Bartlett, R.J.; Purvis, G.D. *Int. J. Quantum Chem.* **1978**, *14*, 561. b) Pople, J.A.; Krishnan, R.; Schlegel, H.B.; Binkley, J.S. *Int. J. Quantum Chem.* **1978**, *14*, 545. c)Pople, J.A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. d) Bartlett, R.J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.
(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2013.

Halide ion association with substrate molecules

Isolated molecules

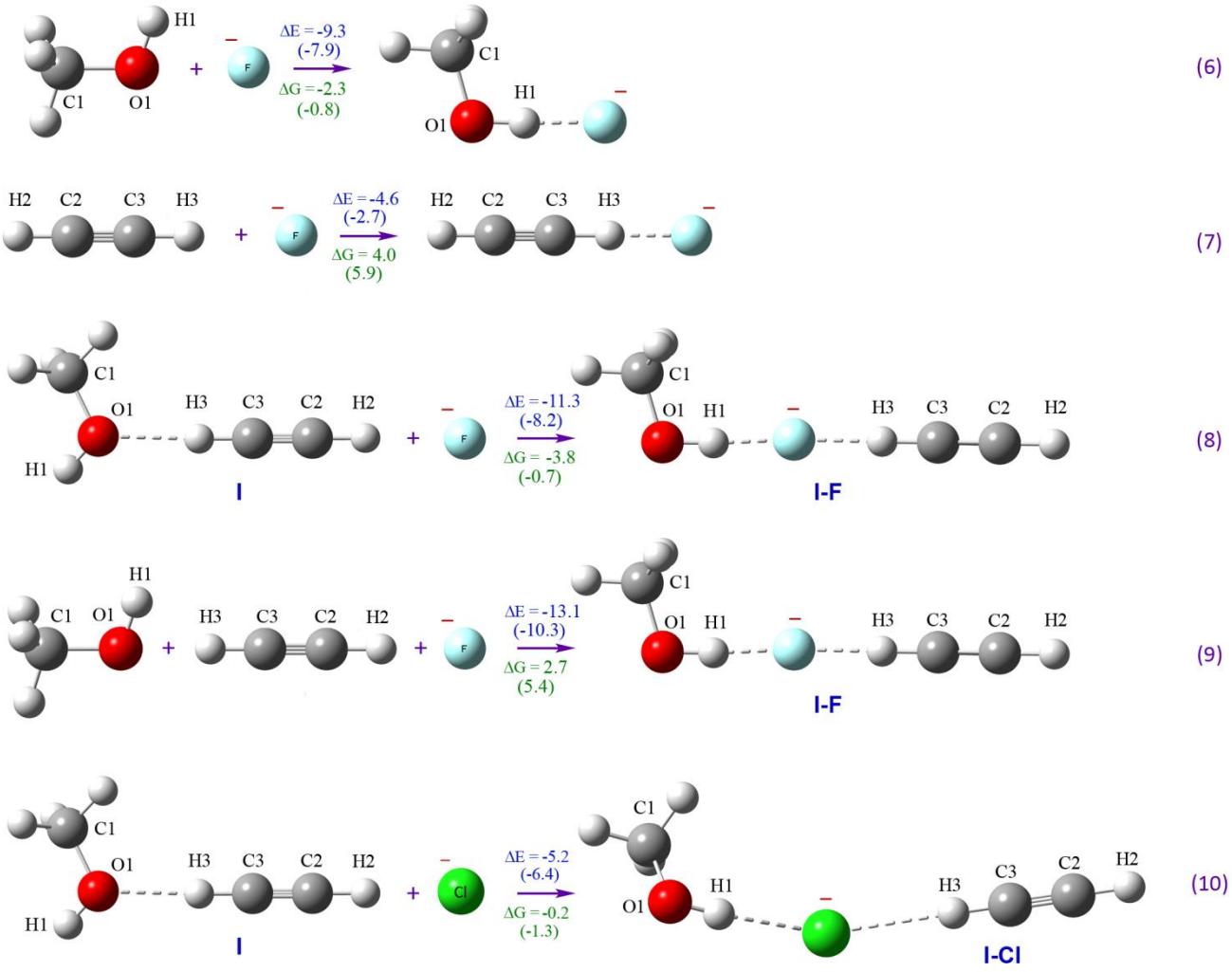
Figure S5. Optimized molecular structures of the substrate molecules and fluoride associates, PBE1PBE/6-311++G(d,p). The CCSD(T) single point energies are in parentheses.



(1) (2) (3) (4) (5)

DMSO (SMD continuum solvation model)

Figure S6. Optimized molecular structures of the substrate molecules and fluoride associates, PBE1PBE/6-311++G(d,p), DMSO (SMD model). The CCSD(T) single point energies are in parentheses.



Hydroalkoxylation reaction

Isolated molecules

Figure S7. Optimized molecular structures of the reagents, transition states and product for the acetylene hydroalkoxylation reactions promoted by fluoride ion in vacuum. The DFT imaginary frequencies for transition states are denoted by red color. The atomic movements corresponding to imaginary frequencies are denoted by red arrows. Activation energies (ΔE_a, ΔG_a) and reaction energy (ΔE, ΔG) are in kcal/mol. The CCSD(T) single point energies are in parentheses.

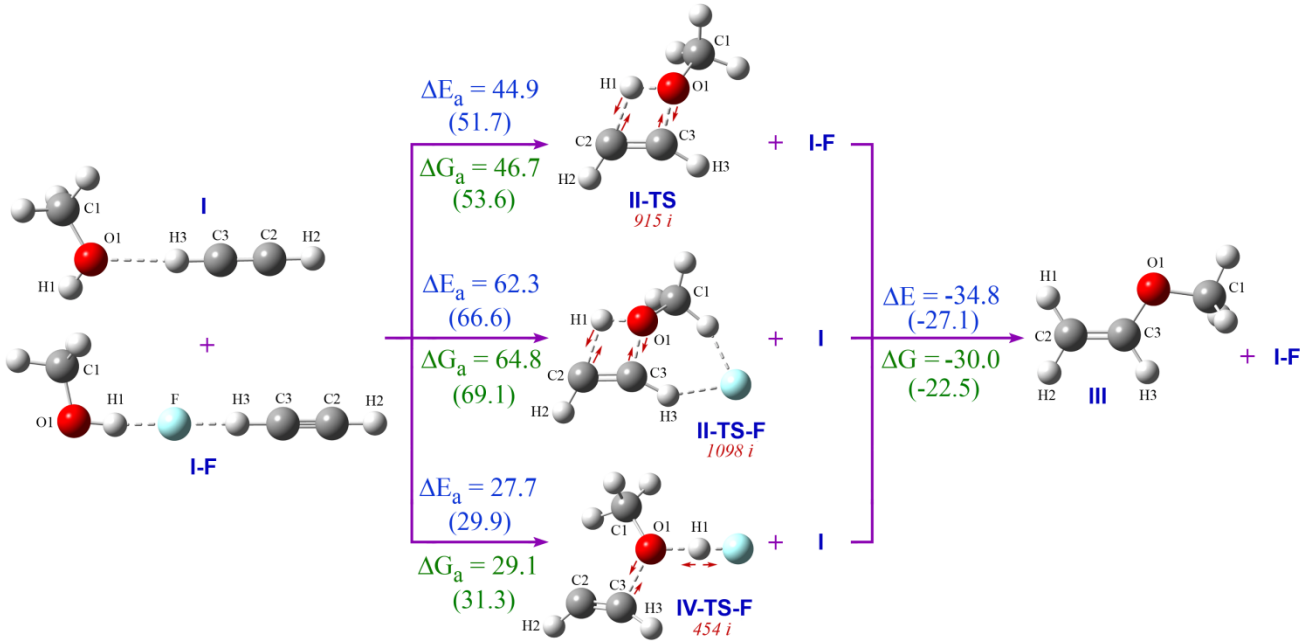


Figure S8. Optimized molecular structures of the reagent, transition state and product for the acetylene hydroalkoxylation reactions promoted by chloride ion in vacuum. The DFT imaginary frequencies for transition states are denoted by red color. The atomic movements corresponding to imaginary frequencies are denoted by red arrows. Activation energies (ΔE_a, ΔG_a) and reaction energy (ΔE, ΔG) are in kcal/mol. The CCSD(T) single point energies are in parentheses.

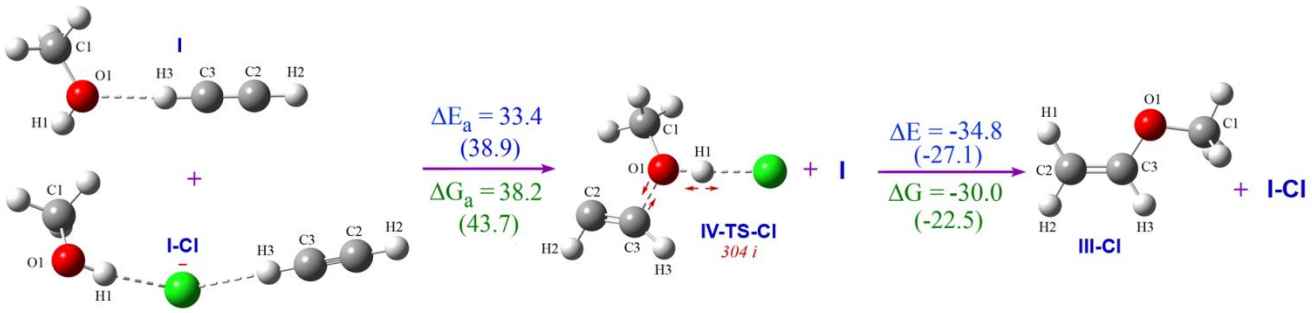


Figure S9. Intrinsic reaction coordinate (IRC) for the II-TS (only a fraction of reaction coordinate is shown near the TS region; further optimizations are carried out to reach stationary points of initial structure and product).

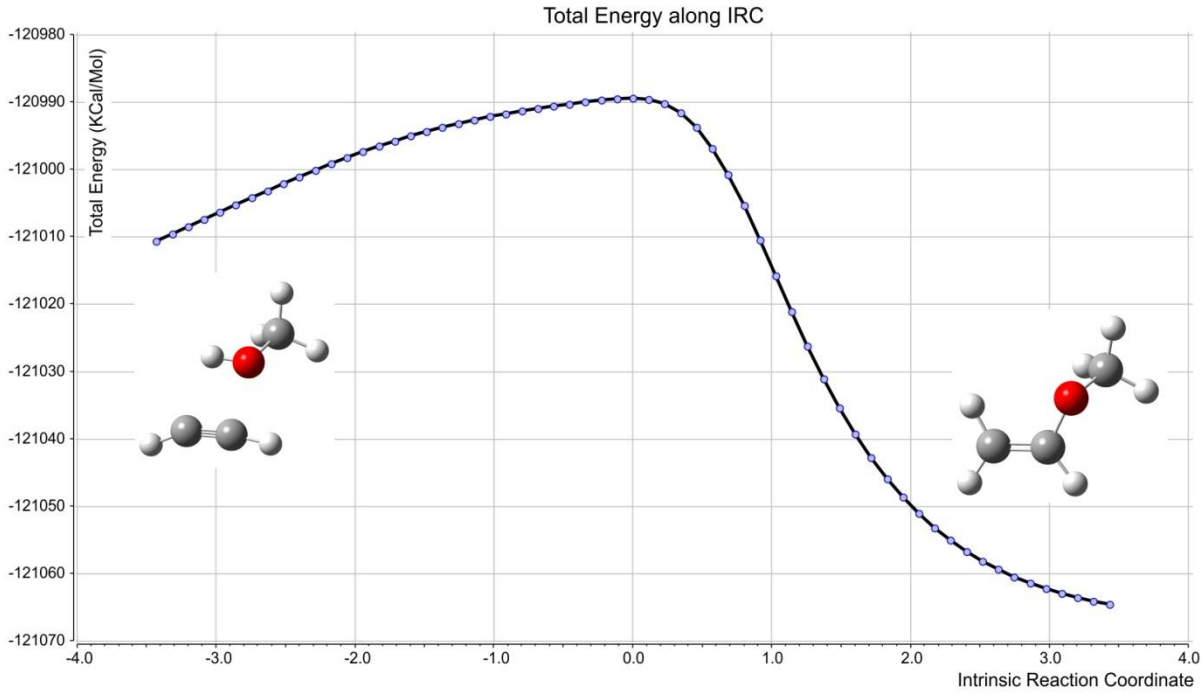


Figure S10. Intrinsic reaction coordinate (IRC) for the II-TS-F (only a fraction of reaction coordinate is shown near the TS region; further optimizations are carried out to reach stationary points of initial structure and product).

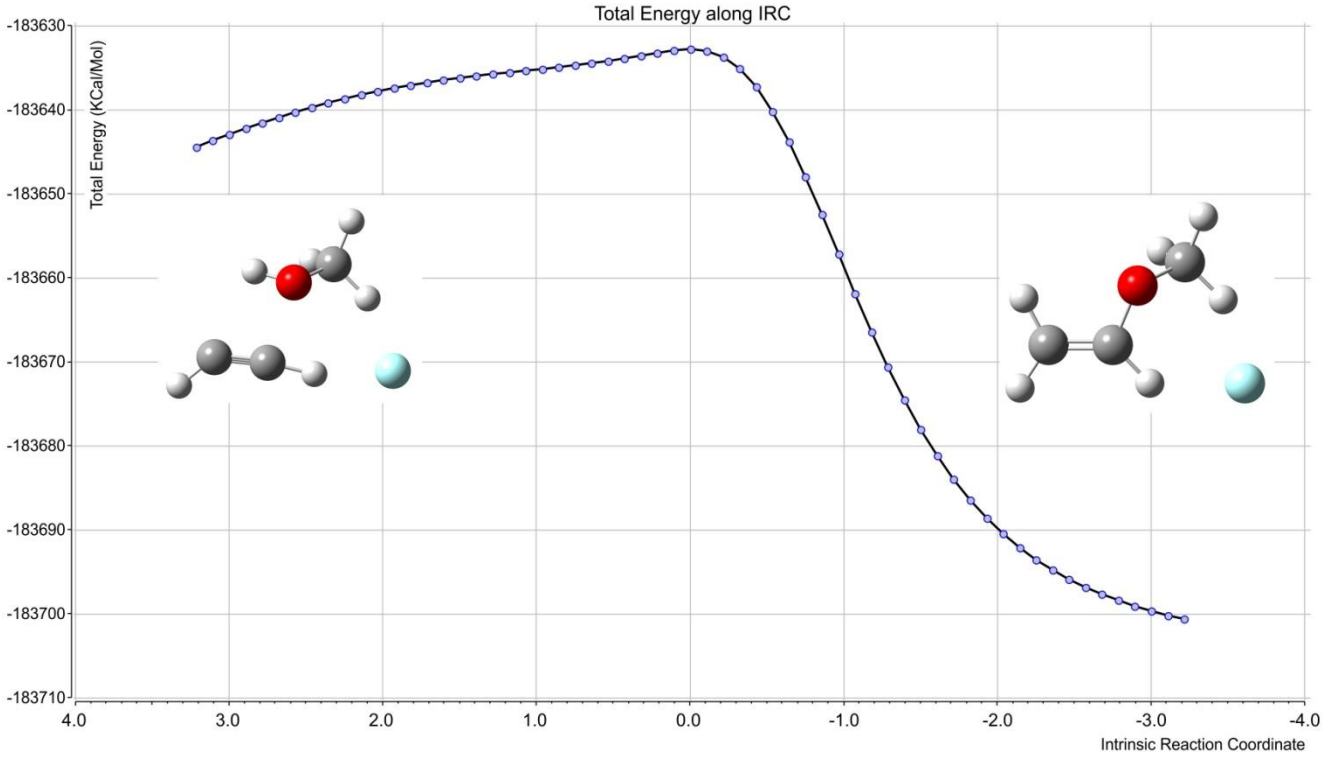
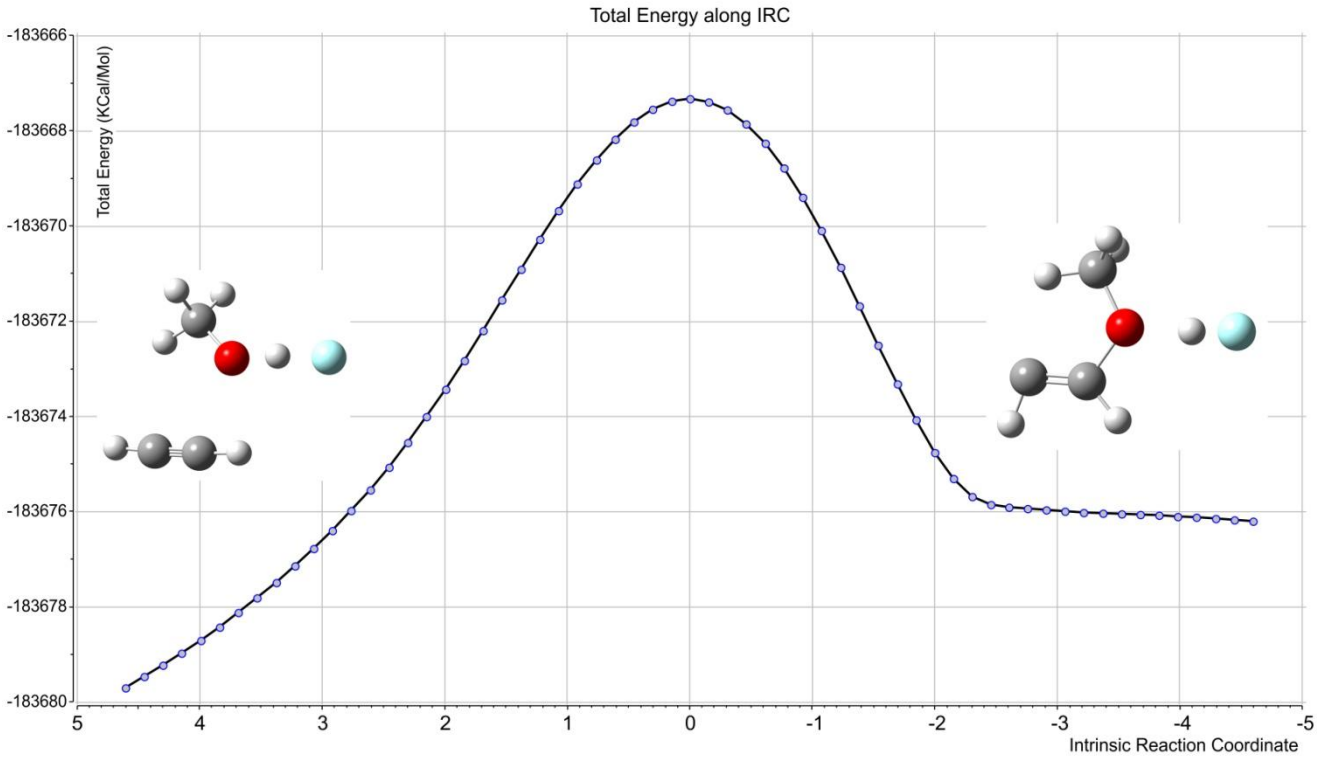


Figure S11. Intrinsic reaction coordinate (IRC) for the IV-TS-F (only a fraction of reaction coordinate is shown near the TS region; further optimizations are carried out to reach stationary points of initial structure and product).



DMSO (SMD continuum solvation model)

Figure S12. Optimized molecular structures of the reagents, transition states and product for the acetylene hydroalkoxylation reactions promoted by fluoride ion in the DMSO medium (SMD continuum model). The DFT imaginary frequencies for transition states are denoted by red color. The atomic movements corresponding to imaginary frequencies are denoted by red arrows. The CCSD(T) single point energies are in parentheses.

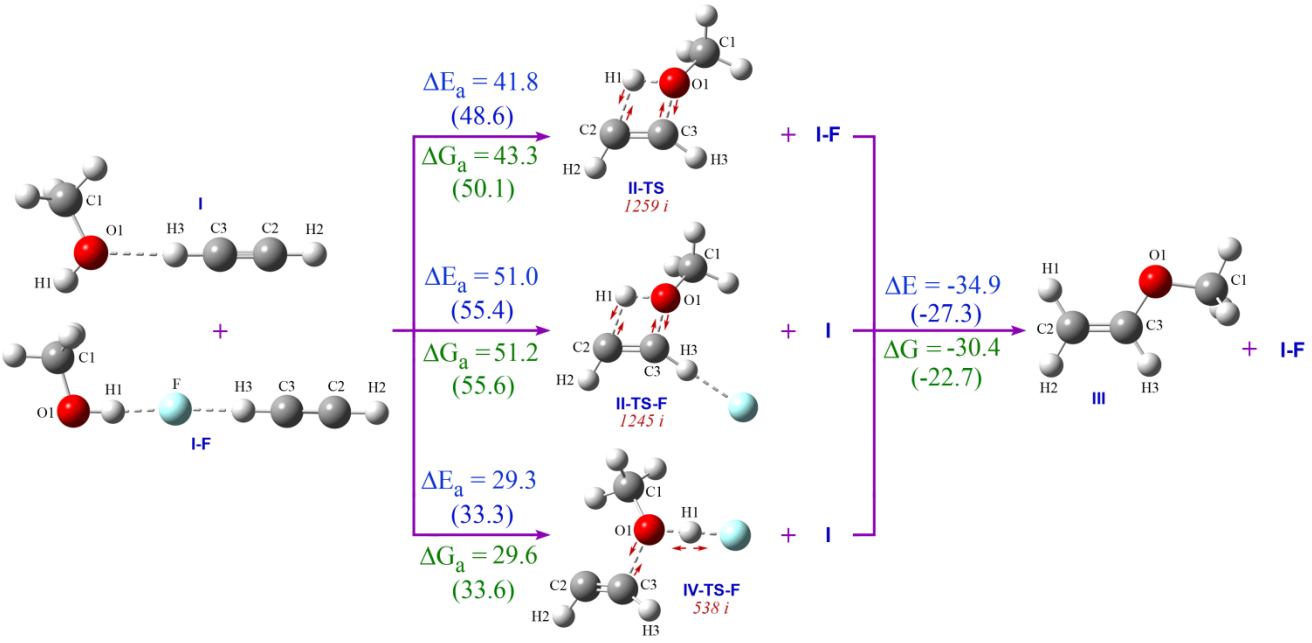


Figure S13. Optimized molecular structures of the reagents, transition states and product for the acetylene hydroalkoxylation reactions promoted by chloride ion in the DMSO medium (SMD continuum model). The DFT imaginary frequencies for transition states are denoted by red color. The atomic movements corresponding to imaginary frequencies are denoted by red arrows. The CCSD(T) single point energies are in parentheses.

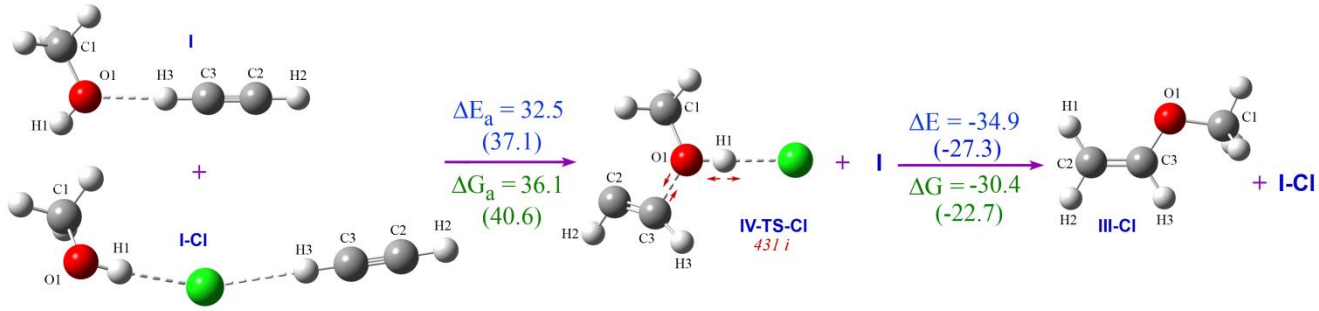


Figure S14. PES of the non-catalytic and fluoride-assisted hydroalkoxylation reaction for isolated molecules and DMSO-medium, PBE1PBE/6-311++G(d,p).

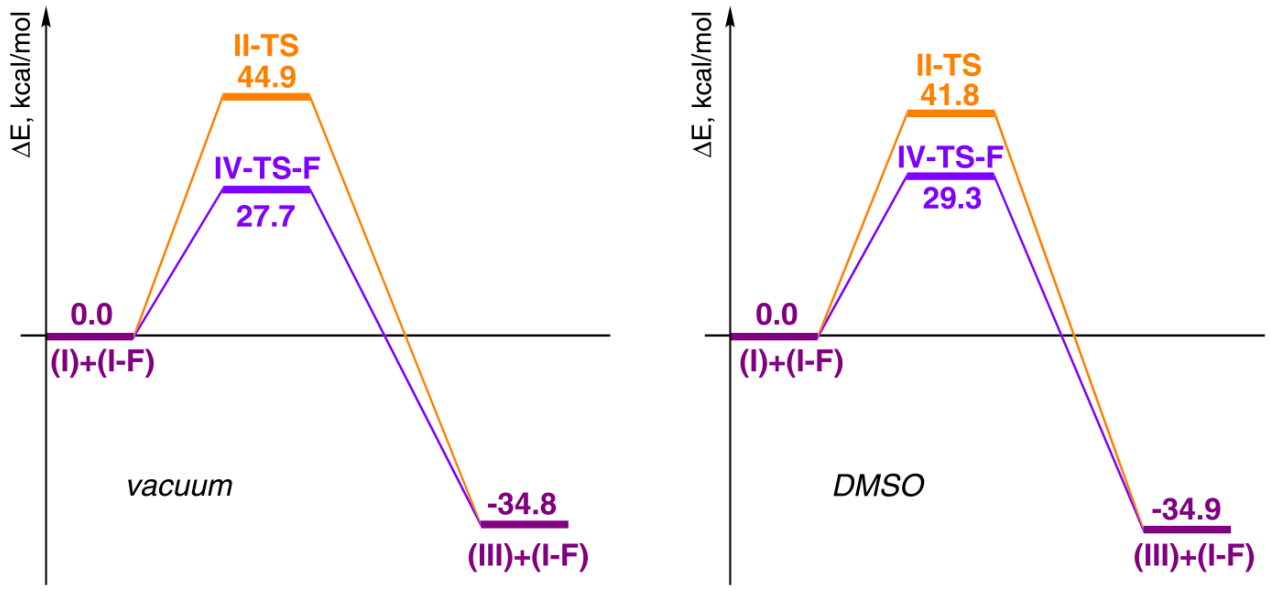


Table S20. Interatomic distances (Å) and valence angles (degrees) for optimized molecules in vacuum and DMSO (SMD), PBE1PBE/6-311++G(d,p) (X = F, Cl).

	MeOH	**MeOH-F**	**C_2H_2**	**C_2H_2-F**	**I**	**I-F**	**I-Cl**	**II-TS**	**II-TS-F**	**IV-TS-F**	**IV-TS-Cl**	**III/III-F/III-Cl**
	vacuum											
C1-O1	1.411	1.375	–	–	1.416	1.386	1.397	1.437	1.447	1.380	1.416	1.411
O1-H1	0.958	1.080	–	–	0.959	1.018	0.984	1.086	1.108	1.316	1.046	–
H1-X	–	1.308	–	–	–	1.469	2.121	–	–	1.048	1.801	–
H2-X	–	–	–	–	–	–	–	–	–	–	–	–
C2-H2	–	–	1.065	1.067	1.065	1.064	1.064	1.086	1.091	1.074	1.088	1.082
C2-C3	–	–	1.200	1.225	1.201	1.210	1.205	1.298	1.313	1.248	1.277	1.329
C3-H3	–	–	1.065	1.365	1.073	1.129	1.091	1.082	1.101	1.075	1.081	1.090
H1-C2	–	–	–	–	–	–	–	1.664	1.618	–	–	1.084
O1-C3	–	–	–	–	–	–	–	1.576	1.534	1.862	1.696	1.352
C1-O1-H1	108.6	107.8	–	–	109.1	107.1	106.5	113.1	119.4	115.0	110.3	–
O1-H1-C2	–	–	–	–	–	174.7	149.5	108.6	107.6	–	–	–
C3-O1-H1	–	–	–	–	121.1	–	–	78.3	79.3	112.3	110.6	–
O1-H1-X	–	176.8	–	–	–	174.2	167.8	–	–	179.8	176.6	–
	DMSO											
C1-O1	1.418	1.399	–	–	1.421	1.401	1.408	1.449	1.446	1.402	1.424	1.422
O1-H1	0.961	1.001	–	–	0.962	0.994	0.976	1.120	1.119	1.117	1.013	–
H1-X	–	1.537	–	–	–	1.572	2.159	–	–	1.221	1.912	–
H2-X	–	–	–	–	–	–	–	–	–	–	–	–
C2-H2	–	–	1.070	1.069	1.069	1.069	1.069	1.090	1.091	1.082	1.089	1.083
C2-C3	–	–	1.202	1.207	1.203	1.205	1.203	1.310	1.312	1.257	1.269	1.332
C3-H3	–	–	1.070	1.111	1.078	1.099	1.080	1.084	1.100	1.078	1.080	1.090
H1-C2	–	–	–	–	–	–	–	1.618	1.609	–	–	1.086
O1-C3	–	–	–	–	–	–	–	1.500	1.516	1.826	1.766	1.348
C1-O1-H1	107.8	107.3	–	–	108.2	107.2	107.1	115.3	115.4	111.3	108.6	–
O1-H1-C2	–	–	–	–	–	176.3	158.7	106.9	107.4	–	–	–
C3-O1-H1	–	–	–	–	126.1	–	–	79.1	79.0	106.2	106.2	–
O1-H1-X	–	177.3	–	–	–	176.5	174.4	–	–	179.6	178.2	–

XYZ coordinates (Å) and E, H, G values (a.u) of the optimized molecular structures

VACUUM

MeOH (vacuum)

E (DFT) = -115.626113
H (DFT) = -115.570335
G (DFT) = -115.597377
E(CCSD(T)) = -115.4771217

C	0.65990	-0.02020	0.00000
O	-0.74410	0.12180	0.00000
H	1.08110	0.98620	-0.00000
H	1.02610	-0.54420	0.89260
H	1.02610	-0.54430	-0.89250
H	-1.13990	-0.75060	0.00000

$F^{(-)}$ (vacuum)

E (DFT) = -99.784183
H (DFT) = -99.781823
G (DFT) = -99.798342
E(CCSD(T)) = -99.6799293

F	0.00000	0.00000	0.00000

MeOH-F (vacuum)

E (DFT) = -215.461896
H (DFT) = -215.406086
G (DFT) = -215.438774
E(CCSD(T)) = -215.2044813

C	-1.31180	-0.36990	0.00000
O	-0.46050	0.71090	0.00000
H	-2.36380	-0.03150	-0.00010
H	-1.19070	-1.02810	-0.88530
H	-1.19080	-1.02810	0.88530
H	0.55170	0.33390	0.00000
F	1.74980	-0.19050	-0.00000

C_2H_2 (vacuum)

E (DFT) = -77.248126
H (DFT) = -77.217207
G (DFT) = -77.240537
E(CCSD(T)) = -77.1407696

C	0.00000	0.00000	0.59980
C	0.00000	0.00000	-0.59980
H	0.00000	0.00000	1.66470
H	0.00000	0.00000	-1.66490

C_2H_2-F (vacuum)

E (DFT) = -177.075504
H (DFT) = -177.046211
G (DFT) = -177.071637
E(CCSD(T)) = -176.8583661

C	-1.84710	0.00060	-0.00000
C	-0.62210	-0.00200	0.00000
H	-2.91370	0.00360	0.00000
H	0.74280	-0.00130	0.00000
F	1.88730	0.00060	0.00000

I (vacuum)

E (DFT) = -192.880297
H (DFT) = -192.791611
G (DFT) = -192.831814
E(CCSD(T)) = -192.6243356

C	1.78940	0.06870	-0.02020
C	2.96850	-0.15770	0.01980
H	0.73590	0.27080	-0.05420
H	4.01370	-0.35770	0.05420
C	-2.23710	-0.50410	0.01940
O	-1.34540	0.59150	-0.07290
H	-1.76300	-1.34290	-0.49200
H	-2.42600	-0.79530	1.05960
H	-3.19300	-0.29430	-0.47500
H	-1.72900	1.34610	0.37680

I-F (vacuum)

E (DFT) = -292.736683
H (DFT) = -292.647326
G (DFT) = -292.691724
E(CCSD(T)) = -292.3692842

C	-2.88340	0.65970	0.00000
O	-2.40110	-0.63990	-0.00090
H	-3.98350	0.63760	-0.00150
H	-2.56680	1.23730	0.88720
H	-2.56440	1.23940	-0.88490
H	-1.38470	-0.58210	-0.00020
C	3.91830	0.21800	-0.00050
C	2.72200	0.03870	0.00000
H	4.97070	0.37500	-0.00100
H	1.60500	-0.12780	0.00050
F	0.06570	-0.35100	0.00120

$Cl^{(-)}$ (vacuum)

E (DFT) = -460.129342
H (DFT) = -460.126982
G (DFT) = -460.144365
E(CCSD(T)) = -459.718588

Cl	0.00000	0.00000	0.00000

I-Cl (vacuum)

E (DFT) = -653.0445265
H (DFT) = -652.953992
G (DFT) = -653.003961
E(CCSD(T)) = -652.379014

C	-3.16150	-0.74290	0.44120
O	-2.74980	-0.18770	-0.77310
H	-4.16640	-1.16020	0.30250
H	-2.49750	-1.55270	0.78070
H	-3.20720	0.00220	1.25010
H	-1.85360	0.18900	-0.61840
C	4.32880	-0.64270	-0.06490
C	3.18850	-0.25680	-0.01950
H	5.33490	-0.98560	-0.10620
H	2.15660	0.09470	0.02220
Cl	0.00570	0.86870	0.14190

II-TS (vacuum)

E (DFT) = -192.808791
H (DFT) = -192.724297
G (DFT) = -192.757317
E(CCSD(T)) = -192.5419192

C	-0.86460	0.57790	0.02740
C	-1.64250	-0.45270	0.15470
H	-0.73060	1.64950	0.10090
H	-2.66740	-0.37970	0.50580
C	1.57620	-0.08730	0.31380
O	0.45210	-0.03820	-0.58050
H	1.89820	0.93550	0.50800
H	1.28100	-0.57660	1.24610
H	2.37480	-0.63810	-0.18300
H	-0.18710	-0.91290	-0.50870

II-TS-F (vacuum)

E (DFT) = -292.637399
H (DFT) = -292.550930
G (DFT) = -292.588382
E(CCSD(T)) = -292.2631576

C	0.77050	-0.69280	-0.11300
C	2.03760	-0.63090	0.22680
H	-0.18440	-1.23860	-0.16690
H	2.57230	-1.53440	0.52210
C	-0.57830	1.36640	0.29300
O	0.46860	0.76010	-0.50150
H	-1.41850	0.63480	0.26070
H	-0.20840	1.50650	1.31550
H	-0.81760	2.32810	-0.16750
H	1.52290	0.84960	-0.17240
F	-2.06600	-0.98690	-0.00220

IV-TS-F (vacuum)

E (DFT) = -292.692491
H (DFT) = -292.606037
G (DFT) = -292.645291
E(CCSD(T)) = -292.3216359

C	-0.03020	-1.51930	-0.07420
O	-0.26540	-0.26100	0.44050
H	-0.15600	-2.30500	0.69130
H	-0.70060	-1.75480	-0.91820
H	1.01690	-1.56240	-0.44070
F	-2.30680	0.72730	-0.22450
H	-1.40270	0.28730	0.06980
C	2.23060	0.38720	-0.27590
C	1.18440	0.88150	0.19260
H	3.22600	0.69010	-0.54200
H	0.59200	1.69040	0.58140

IV-TS-Cl (vacuum)

E (DFT) = -652.9913142
H (DFT) = -652.903153
G (DFT) = -652.943092
E(CCSD(T)) = -652.3170579

C	-0.74190	1.56920	-0.12070
O	-0.42650	0.33590	0.49900
H	-0.66980	2.37080	0.61960
H	-0.04770	1.75320	-0.94510
H	-1.77220	1.47000	-0.48890
C	-2.63530	-0.61860	-0.30560
C	-1.49100	-0.94010	0.16080
H	-3.34500	-1.41810	-0.50930
H	-0.82330	-1.72660	0.48300
H	0.55820	0.06060	0.28030
Cl	2.27780	-0.30940	-0.10820

III (III-F, III-Cl) (vacuum)

E (DFT) = -192.935792
H (DFT) = -192.845140
G (DFT) = -192.879632
E(CCSD(T)) = -192.6674568

H	-2.11070	-1.12540	0.08590
C	1.71240	0.10920	0.04040
O	0.44380	-0.50120	-0.06020
H	2.45210	-0.68420	-0.06370
H	1.86440	0.84620	-0.75780
H	1.84420	0.59650	1.01390
C	-1.86730	-0.07070	0.03460
C	-0.60770	0.34760	-0.03230
H	-2.67090	0.65330	0.03020
H	-0.35420	1.40680	-0.08260

DMSO (SMD)

MeOH (DMSO)

E (DFT) = -115.631319
H (DFT) = -115.575762
G (DFT) = -115.602809
E(CCSD(T)) = -115.482282

C	0.66290	-0.01930	0.00000
O	-0.74760	0.12300	0.00000
H	1.09030	0.98540	-0.00000
H	1.02230	-0.54770	0.89190
H	1.02230	-0.54770	-0.89190
H	-1.13150	-0.75810	0.00000

$F^{(-)}$ (DMSO)

E (DFT) = -99.924846
H (DFT) = -99.922486
G (DFT) = -99.939005
E(CCSD(T)) = -99.8203019

F	0.00000	0.00000	0.00000

MeOH-F (DMSO)

E (DFT) = -215.571025
H (DFT) = -215.512848

C_2H_2 (DMSO)

E (DFT) = -77.250304
H (DFT) = -77.219400

G (DFT) = -215.545447 E(CCSD(T)) = -215.3151077	G (DFT) = -77.242675 E(CCSD(T)) = -77.1420218
C -1.35420 -0.39850 -0.00000 O -0.51800 0.72350 -0.00000 H -2.39790 -0.06460 -0.00010 H -1.21120 -1.03410 -0.88850 H -1.21120 -1.03410 0.88840 H 0.42680 0.39220 0.00000 F 1.85140 -0.18410 0.00000	C 0.00000 0.00000 -0.60090 C 0.00000 0.00000 0.60090 H 0.00000 0.00000 -1.67040 H 0.00000 0.00000 1.67030
C_2H_2-F (DMSO)	**I (DMSO)**
E (DFT) = -177.182484 H (DFT) = -177.149801 G (DFT) = -177.175236 E(CCSD(T)) = -176.9666512	E (DFT) = -192.884580 H (DFT) = -192.796200 G (DFT) = -192.835218 E(CCSD(T)) = -192.6277349
C 1.92120 0.00050 0.00000 C 0.71440 -0.00110 -0.00000 H 2.99070 0.00170 -0.00000 H -0.39650 -0.00140 0.00000 F -2.04530 0.00040 0.00000	C 1.73650 0.07230 0.01240 C 2.91770 -0.15500 0.00200 H 0.67840 0.27910 0.01960 H 3.96760 -0.35840 -0.00650 C -2.16780 -0.52900 0.01580 O -1.33100 0.61590 -0.07760 H -1.62120 -1.36730 -0.42070 H -2.40670 -0.77290 1.05750 H -3.10090 -0.39330 -0.54280 H -1.78770 1.35670 0.33180
I-F (DMSO)	**$Cl^{(-)}$ (DMSO)**
E (DFT) = -292.827360 H (DFT) = -292.737010 G (DFT) = -292.780222 E(CCSD(T)) = -292.4610994	E (DFT) = -460.234928 H (DFT) = -460.232568 G (DFT) = -460.249951 E(CCSD(T)) = -459.823789
C 3.03210 0.62620 -0.00500 O 2.46870 -0.65520 -0.06630 H 4.12350 0.53390 -0.00850 H 2.75060 1.25380 -0.86550 H 2.74790 1.16980 0.90950 H 1.48190 -0.54570 -0.01210 C -4.06230 0.18460 -0.04460 C -2.86630 0.04200 0.00380 H -5.12310 0.31280 -0.08670 H -1.77590 -0.08740 0.04450 F -0.06400 -0.27910 0.09150	Cl 0.00000 0.00000 0.00000
I-Cl (DMSO)	**II-TS (DMSO)**
E (DFT) = -653.1278373 H (DFT) = -653.037165 G (DFT) = -653.085462 E(CCSD(T)) = -652.4616685	E (DFT) = -192.817999 H (DFT) = -192.733454 G (DFT) = -192.766163 E(CCSD(T)) = -192.5503218
C 3.41560 -0.76550 -0.25650 O 2.93520 0.18520 0.66400 H 4.45770 -0.98540 -0.00720 H 2.85140 -1.70830 -0.21570 H 3.38650 -0.39620 -1.29170 H 2.00400 0.36500 0.43200 C -4.59530 -0.48210 0.14660 C -3.42800 -0.20670 0.05070 H -5.63270 -0.72740 0.23110 H -2.38050 0.04190 -0.03490 Cl -0.03070 0.62670 -0.23940	C -0.81550 0.56370 -0.03230 C -1.65740 -0.41510 0.19220 H -0.70020 1.64180 -0.01810 H -2.67710 -0.21010 0.51900 C 1.58910 -0.04460 0.29970 O 0.41540 -0.12270 -0.54640 H 1.91070 0.99570 0.33350 H 1.34260 -0.40610 1.30090 H 2.35730 -0.66200 -0.16370 H -0.25330 -1.00170 -0.35790
II-TS-F (DMSO)	**IV-TS-F (DMSO)**
E (DFT) = -292.746020 H (DFT) = -292.658833 G (DFT) = -292.698577 E(CCSD(T)) = -292.3728194	E (DFT) = -292.780635 H (DFT) = -292.694301 G (DFT) = -292.733064 E(CCSD(T)) = -292.4079682
C 0.00800 -0.74960 -0.03270 C 0.74920 -1.80920 0.19240 H -1.01400 -0.34360 -0.02270 H 0.29020 -2.74230 0.52260 C 1.23250 1.41480 0.30000 O 1.00960 0.26470 -0.54820	C 0.12060 1.55240 -0.10650 O 0.25770 0.29990 0.50930 H 0.30360 2.35550 0.61630 H 0.81330 1.66190 -0.94930 H -0.90850 1.64480 -0.48830 F 2.15450 -0.83070 -0.26000

H 0.31460 2.00140 0.32050	H 1.16470 -0.23710 0.14000
H 1.49970 1.08460 1.30710	C -2.15570 -0.36170 -0.33970
H 2.03960 1.99380 -0.14730	C -1.14830 -0.83540 0.24400
H 1.67630 -0.61230 -0.35170	H -3.09490 -0.84140 -0.58230
F -2.75800 0.37390 -0.00000	H -0.62980 -1.63870 0.74190
IV-TS-Cl	**III (III-F, III-Cl)**
E (DFT) = -653.0760769 H (DFT) = -652.986961 G (DFT) = -653.027993 E(CCSD(T)) = -652.4026068	E (DFT) = -192.940199 H (DFT) = -192.849542 G (DFT) = -192.883590 E(CCSD(T)) = -192.6711692
C -0.78610 1.61580 -0.17030	H -2.13750 -1.11850 -0.00000
O -0.46210 0.45540 0.58870	C 1.71880 0.11310 -0.00000
H -0.04600 2.38570 0.05780	O 0.44020 -0.50910 0.00000
H -0.78950 1.40130 -1.24260	H 2.45820 -0.68790 0.00010
H -1.77520 1.95760 0.13330	H 1.85580 0.72970 -0.89480
C -2.47520 -0.78260 -0.47850	H 1.85580 0.72980 0.89470
C -1.49290 -0.95040 0.30630	C -1.87210 -0.06580 0.00000
H -3.15260 -1.61390 -0.66780	C -0.60410 0.34340 0.00000
H -0.92610 -1.58600 0.97020	H -2.66470 0.67280 -0.00000
H 0.48040 0.16740 0.35310	H -0.34480 1.40230 0.00000
Cl 2.26060 -0.33250 -0.13290	