SUPPORTING INFORMATION

Half-Sandwich Ruthenium Carbene Complexes Link *trans*-Hydrogenation and *gem*-Hydrogenation of Internal Alkynes

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SINGLE CRYSTAL X-RAY STRUCTURE ANALYSES

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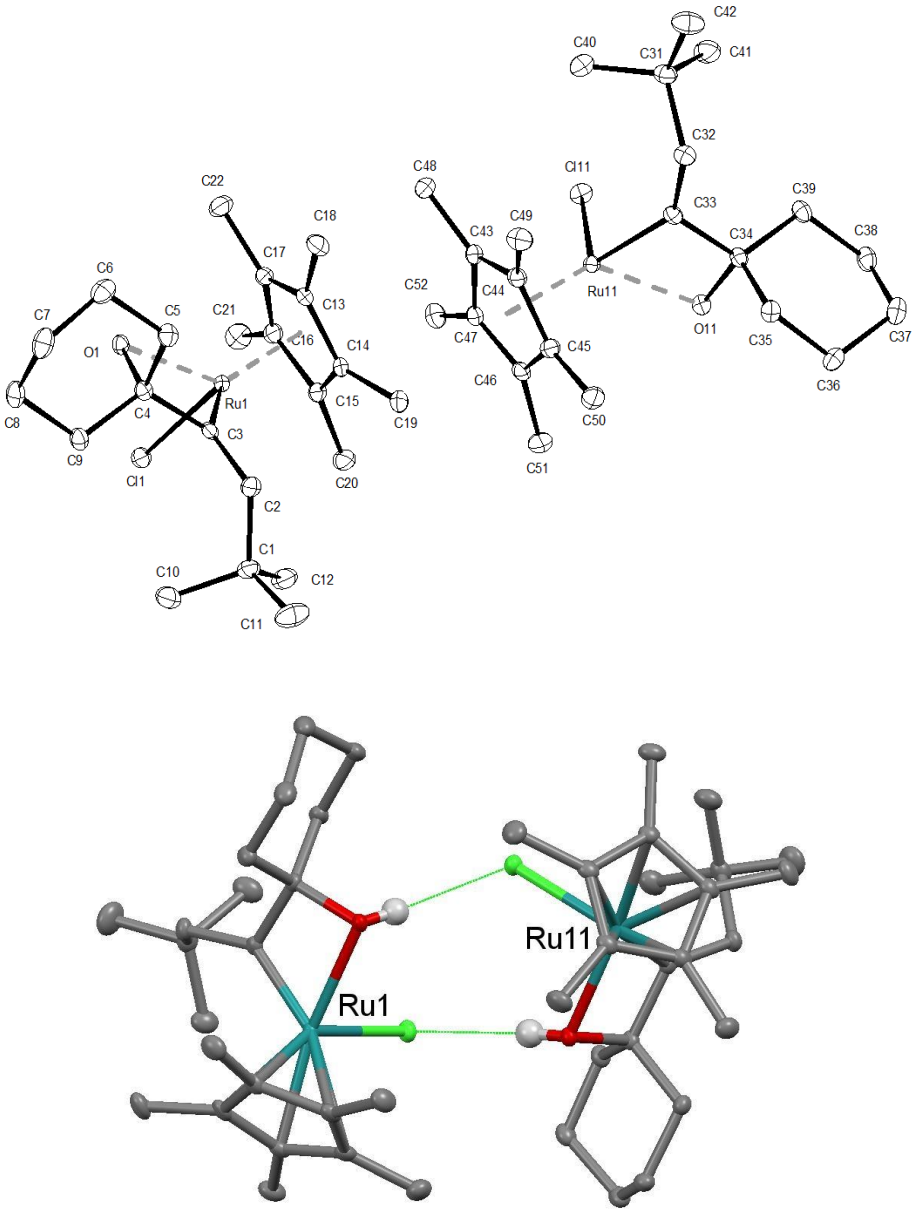


Figure S1. The molecular structure of **6e** (top) and the O-H···Cl hydrogen bond interactions in the crystal (bottom); superfluous H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of 6e: $C_{22}H_{37}ClORu$, M_r = 454.03 g · mol^{-1}, red needle, crystal size 0.024 x 0.031 x 0.141 mm^3, orthorhombic, space group *P*bcn [60], *a* = 25.256(7) Å, *b* = 16.832(5) Å, *c* = 20.826(6)

Å, V = 8853(4) Å^3, T = 100(2) K, Z = 16, D_{calc} = 1.363 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.836 mm^{-1}, analytical absorption correction (T_{min} = 0.91469, T_{max} = 0.98375), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 2.420 < θ < 33.396°, 292384 measured reflections, 17148 independent reflections, 13218 reflections with $I > 2\sigma(I)$, R_{int} = 0.0883. The structure was solved by a dual-space algorithm method (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0321 [$I > 2\sigma(I)$], wR_2 = 0.0793, 475 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.80	278	279	99.6	19.01	40.53	48.79	0.0251	0.0125
2.80 - 1.82	653	653	100.0	22.29	26.39	51.49	0.0312	0.0116
1.82 - 1.43	910	910	100.0	22.96	19.07	44.74	0.0386	0.0129
1.43 - 1.24	937	937	100.0	22.97	12.70	35.46	0.0522	0.0159
1.24 - 1.12	937	937	100.0	21.60	10.51	31.66	0.0641	0.0192
1.12 - 1.04	895	895	100.0	20.22	10.70	29.29	0.0692	0.0210
1.04 - 0.97	1027	1027	100.0	19.10	8.62	23.76	0.0819	0.0254
0.97 - 0.92	927	927	100.0	18.19	6.77	19.60	0.1020	0.0318
0.92 - 0.88	921	921	100.0	17.42	6.88	18.50	0.1059	0.0336
0.88 - 0.85	803	803	100.0	16.69	5.15	15.18	0.1307	0.0428
0.85 - 0.81	1227	1227	100.0	16.04	4.96	13.81	0.1443	0.0474
0.81 - 0.79	736	736	100.0	15.32	5.49	13.63	0.1356	0.0466
0.79 - 0.77	782	782	100.0	15.02	4.32	11.72	0.1649	0.0578
0.77 - 0.74	1363	1363	100.0	14.39	4.39	10.87	0.1705	0.0607
0.74 - 0.73	504	504	100.0	14.04	4.07	10.06	0.1781	0.0664
0.73 - 0.71	1098	1098	100.0	13.63	3.63	9.26	0.2030	0.0762
0.71 - 0.69	1208	1208	100.0	13.10	3.59	8.68	0.2169	0.0821
0.69 - 0.68	665	665	100.0	12.78	3.35	8.05	0.2275	0.0895
0.68 - 0.67	692	692	100.0	12.50	2.60	6.56	0.2775	0.1141
0.67 - 0.65	1830	1908	95.9	10.79	2.70	6.07	0.2751	0.1287
0.75 - 0.65	6474	6552	98.8	12.57	3.29	7.97	0.2248	0.0922
Inf - 0.65	18393	18472	99.6	16.48	7.70	18.84	0.0841	0.0341

Most Disagreeable Reflections (* if suppressed or used for Rfree).
Error/esd is calculated as sqrt(wD^2/<wD^2>) where w is given by the weight formula, D = Fo^2-Fc^2 and <> refers to the average over all reflections.

h	k	l	Fo^2	Fc^2	Error/esd	Fc/Fc(max)	Resolution(A)
14	0	6	6998.87	237.59	13.30	0.018	1.60
3	5	13	1102.82	152.88	10.68	0.014	1.43
12	0	6	14384.19	7692.92	9.37	0.101	1.80
7	5	13	772.52	3.95	9.22	0.002	1.34
0	8	19	1140.45	0.07	7.17	0.000	0.97

Two reflections have significantly higher Fo than Fc. We have no explanation for this other than the diffraction data were collected with high redundancy which reduces the standard uncertainties of the averaged intensites. There is a local 2-fold axis in the structure along the *a* axis at y = 0.25, z = 0.46. The hydroxyl H atoms were refined with isotropic atomic displacement parameters otherwise H atoms were refined using a riding model, S = 1.032, residual electron density 0.79 / -0.88 e Å^{-3}. **CCDC-1814786**.

Single Crystal Structure Analysis of η^5-Pentamethylcyclopentadienyl-chloro-1-(phenyl)-2-(1-methoxycyclohexyl)-ethylidene-ruthenium(II) (7d)

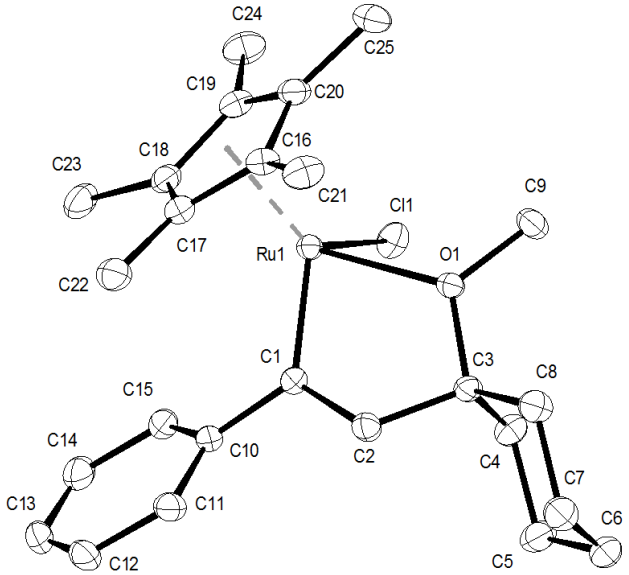


Figure S2. The molecular structure of **7d**. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of 7d: $C_{25}H_{35}ClORu$, M_r = 488.05 g · mol^{-1}, orange plate, crystal size 0.05 x 0.08 x 0.11 mm^3, monoclinic, space group $P2_1/c$ [14], a = 11.4056(9) Å, b = 10.2403(5) Å, c = 19.3428(12) Å, β = 96.648(6)º, V = 2244.0(3) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.445 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.831 mm^{-1}, analytical absorption correction (T_{min} = 0. 90782, T_{max} = 0. 96511), Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, 2.681 < θ < 33.164°, 45176 measured reflections, 8579 independent reflections, 6989 reflections with $I > 2\sigma(I)$, R_{int} = 0.0489. The structure was solved by a dual-space algorithm method (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0310 [$I > 2\sigma(I)$], wR_2 = 0.0725, 259 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles.

H atoms were refined using a riding model, S = 1.067, residual electron density 0.65 / -1.05 e Å^{-3} [0.69 Å from Ru1]. **CCDC-1814787**.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.72	135	142	95.1	10.07	101.86	65.32	0.0352	0.0124
2.72 - 1.80	323	323	100.0	7.74	61.91	50.01	0.0330	0.0143
1.80 - 1.41	467	467	100.0	7.07	40.63	42.06	0.0337	0.0167
1.41 - 1.23	454	454	100.0	6.80	26.00	34.65	0.0376	0.0200
1.23 - 1.12	424	424	100.0	6.42	21.98	30.65	0.0361	0.0227
1.12 - 1.03	494	494	100.0	6.16	20.97	27.75	0.0396	0.0252
1.03 - 0.97	458	458	100.0	5.93	17.39	23.83	0.0432	0.0287
0.97 - 0.92	468	468	100.0	5.61	15.14	21.67	0.0500	0.0330
0.92 - 0.88	443	443	100.0	5.48	11.68	18.33	0.0569	0.0394
0.88 - 0.85	393	393	100.0	5.07	10.90	16.18	0.0639	0.0439
0.85 - 0.82	460	460	100.0	5.05	9.42	14.96	0.0703	0.0496
0.82 - 0.79	522	522	100.0	4.67	8.59	13.19	0.0779	0.0570
0.79 - 0.77	402	403	99.8	4.60	8.27	12.24	0.0812	0.0599
0.77 - 0.75	443	444	99.8	4.35	7.48	10.60	0.0909	0.0691
0.75 - 0.73	459	459	100.0	4.17	7.19	10.15	0.0958	0.0743
0.73 - 0.71	547	547	100.0	4.13	6.34	9.14	0.1053	0.0839
0.71 - 0.70	317	317	100.0	3.83	6.09	8.10	0.1220	0.0934
0.70 - 0.68	640	642	99.7	3.78	5.14	7.17	0.1298	0.1079
0.68 - 0.67	337	337	100.0	3.70	4.25	6.12	0.1589	0.1330
0.67 - 0.66	383	385	99.5	3.62	4.63	6.16	0.1613	0.1298
0.66 - 0.65	419	420	99.8	3.46	4.16	5.43	0.1786	0.1478
0.75 - 0.65	3102	3107	99.8	3.83	5.46	7.58	0.1256	0.1033
Inf - 0.65	8988	9002	99.8	5.14	15.70	18.86	0.0480	0.0353

Single Crystal Structure Analysis of η^5-Pentamethylcyclopentadienyl-chloro-1-(*tert*-butylcarbonyl)-2-(1-hydroxycyclohexyl)-ethylidene-ruthenium(II) (12a)

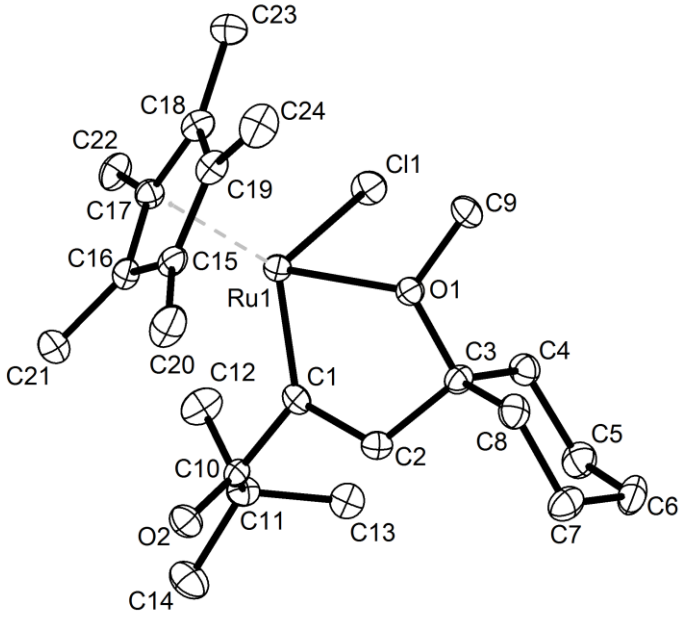


Figure S3. The molecular structure of **12a;** H-atoms have been removed for clarity.

X-ray Crystal Structure Analysis of 12a: $C_{24}H_{39}ClO_2Ru$, M_r = 496.07 g · mol^{-1}, red plate, crystal size 0.01 x 0.06 x 0.08 mm^3, monoclinic, space group $P2_1/c$ [14], a = 18.943(19) Å, b = 8.709(3) Å, c = 14.100(7) Å, β = 98.58(8)º, V = 2300(3) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.433 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.814 mm^{-1}, multiscan absorption correction (T_{min} = 0.4586, T_{max} = 0.7462), Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, 2.758 < θ < 31.079°, 46385 measured reflections, 7392 independent reflections, 4945 reflections with $I > 2\sigma(I)$, R_{int} = 0.1296. The structure was solved by a dual-space algorithm method (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0572 [$I > 2\sigma(I)$], wR_2 = 0.1276, 262 parameters. The crystal at 80 x 60 x 10 microns^3 was very small. Consequently, the standard uncertainties on all determined parameters are large. Diffraction data were collected with an average redundancy of over 6 in order to improve the signal-to-noise ratio and hence $I/\sigma(I)$.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.85	119	127	93.7	11.70	102.32	34.59	0.0547	0.0210
2.85 - 1.92	273	274	99.6	11.24	60.84	27.48	0.0632	0.0258
1.92 - 1.51	392	392	100.0	8.80	46.55	21.36	0.0671	0.0329
1.51 - 1.31	405	405	100.0	8.27	30.03	16.77	0.0898	0.0422
1.31 - 1.19	389	389	100.0	7.74	23.16	13.99	0.1051	0.0519
1.19 - 1.10	385	385	100.0	7.22	21.10	11.68	0.1164	0.0609
1.10 - 1.03	433	433	100.0	6.84	19.58	10.81	0.1224	0.0689
1.03 - 0.98	368	368	100.0	6.57	17.43	9.40	0.1401	0.0810
0.98 - 0.94	366	366	100.0	6.39	14.62	8.39	0.1638	0.0947
0.94 - 0.90	425	425	100.0	6.07	12.90	7.08	0.1777	0.1105
0.90 - 0.86	509	509	100.0	5.79	10.83	5.82	0.2072	0.1372
0.86 - 0.84	290	290	100.0	5.52	9.18	5.14	0.2473	0.1630
0.84 - 0.81	485	485	100.0	5.39	8.73	4.79	0.2603	0.1777
0.81 - 0.79	364	364	100.0	5.15	8.57	4.27	0.2770	0.1949
0.79 - 0.77	425	425	100.0	4.78	7.48	3.66	0.3063	0.2302
0.77 - 0.75	448	448	100.0	4.70	7.36	3.51	0.3263	0.2440
0.75 - 0.74	239	239	100.0	4.51	8.10	3.48	0.3037	0.2335
0.74 - 0.72	522	522	100.0	4.42	6.72	3.06	0.3413	0.2840
0.72 - 0.71	311	311	100.0	4.29	5.32	2.47	0.4315	0.3618
0.71 - 0.70	291	291	100.0	4.13	5.87	2.55	0.3949	0.3492
0.70 - 0.69	389	396	98.2	4.02	5.32	2.31	0.4326	0.3964
0.79 - 0.69	2625	2632	99.7	4.43	6.61	3.04	0.3517	0.2881
Inf - 0.69	7828	7844	99.8	6.14	17.24	8.59	0.1213	0.0928

H atoms were refined using a riding model, S = 1.048, residual electron density 1.53 [0.94 Å from Ru1] / −0.89 e Å^{-3} [0.77 Å from Ru1]. **CCDC-1814788**.

Single Crystal Structure Analysis of η^5- Pentamethylcyclopentadienyl-chloro-(*E*)-1-(*tert*-butyl-carbonyl)-2-(1-hydroxycyclohexyl)-ethylene-ruthenium(II) (13)

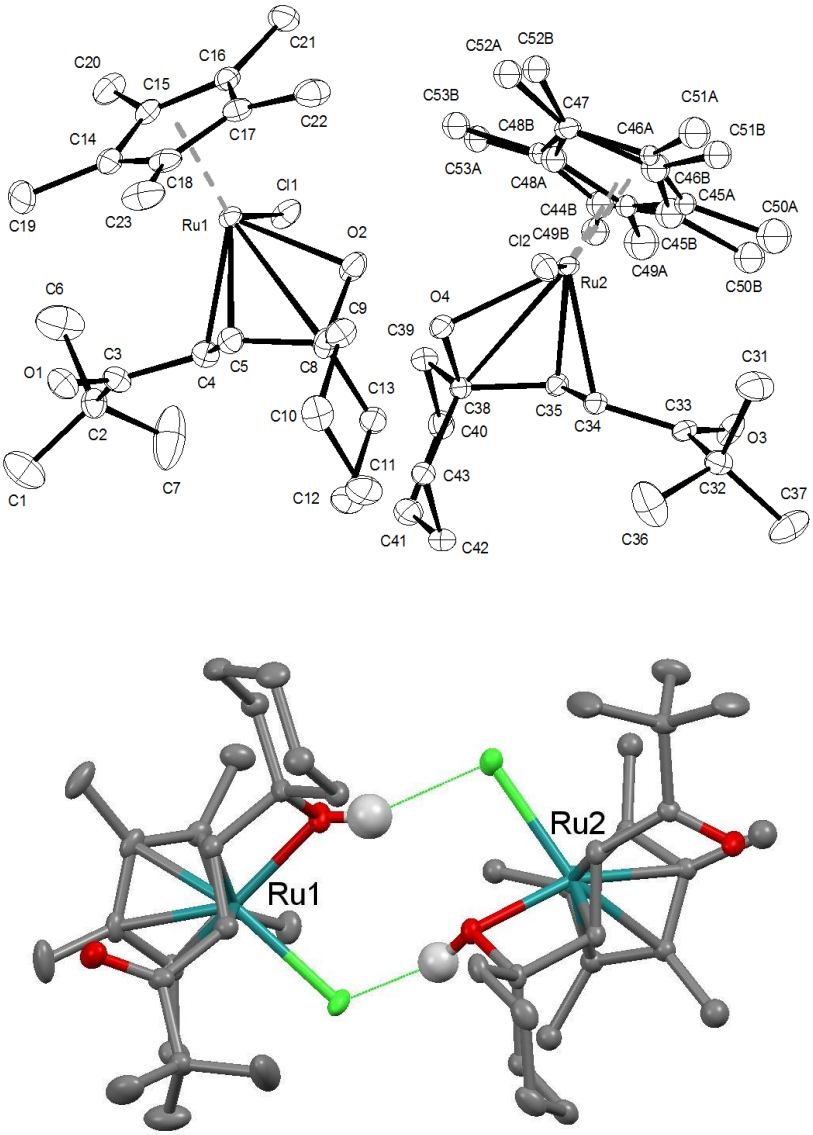


Figure S4. The molecular structure of **13** (top) and the O-H···Cl hydrogen bond interactions in the crystal (bottom); superfluous H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of 13: $C_{23}H_{37}ClO_2Ru$, M_r = 482.04 g · mol^{-1}, red prism, crystal size 0.038 x 0.087 x 0.124 mm^3, triclinic, space group $P\bar{1}$ [2], a = 10.0834(12) Å, b = 11.0235(14) Å, c = 22.691(3) Å, α = 91.135(2)°, β = 98.291(2)°, γ = 116.363(2)°, V = 2226.2(5) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.438 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.839 mm^{-1}, analytical absorption correction (T_{min} = 0. 92257, T_{max} = 0. 97346), Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, 0.911 < θ < 37.059°, 88233 measured reflections,

21953 independent reflections, 17763 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0345$. The structure was solved by a dual-space algorithm method (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0371$ [$I > 2\sigma(I)$], $wR_2 = 0.0953$, 508 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles. The H atoms on O2 and O4 were located on a difference Fourier map and their atomic coordinates were refined with istropic atomic displacement parameters.

The pentamethylcyclopentadienyl group in one of the independent molecules in the asymmetric unit is partially disordered over two positions about a pivotal C47. Disorderd C atoms were refined with isotropic atomic displacement parameters.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.41	330	337	97.9	6.05	67.19	92.26	0.0167	0.0081
2.41 - 1.61	778	779	99.9	6.29	46.21	80.73	0.0166	0.0091
1.61 - 1.28	1111	1111	100.0	6.21	25.62	61.19	0.0204	0.0115
1.28 - 1.11	1167	1167	100.0	5.79	17.56	46.96	0.0252	0.0148
1.11 - 1.01	1108	1108	100.0	5.27	16.25	39.42	0.0272	0.0174
1.01 - 0.94	1103	1103	100.0	4.92	13.85	33.72	0.0320	0.0206
0.94 - 0.89	1028	1028	100.0	4.62	10.44	27.01	0.0390	0.0262
0.89 - 0.84	1227	1227	100.0	4.39	8.18	22.36	0.0481	0.0328
0.84 - 0.81	926	926	100.0	4.12	7.47	20.15	0.0524	0.0375
0.81 - 0.77	1430	1430	100.0	3.98	6.77	17.71	0.0580	0.0422
0.77 - 0.75	841	841	100.0	3.74	6.37	15.42	0.0640	0.0482
0.75 - 0.72	1435	1435	100.0	3.64	5.44	13.51	0.0693	0.0553
0.72 - 0.70	1094	1094	100.0	3.43	5.53	12.90	0.0706	0.0598
0.70 - 0.68	1232	1233	99.9	3.36	4.70	10.93	0.0803	0.0707
0.68 - 0.67	674	676	99.7	3.20	4.33	9.83	0.0860	0.0789
0.67 - 0.65	1463	1475	99.2	3.12	3.75	8.65	0.0982	0.0906
0.65 - 0.64	820	827	99.2	3.03	3.48	7.83	0.1096	0.1022
0.64 - 0.62	1713	1751	97.8	2.86	3.15	7.07	0.1158	0.1135
0.62 - 0.61	967	987	98.0	2.79	2.64	6.01	0.1404	0.1375
0.61 - 0.60	995	1062	93.7	2.45	2.51	5.34	0.1442	0.1625
0.60 - 0.59	513	1145	44.8	0.72	2.26	3.62	0.1602	0.2389
0.69 - 0.59	7772	8550	90.9	2.63	3.30	7.37	0.1093	0.1123
Inf - 0.59	21955	22742	96.5	3.88	10.28	23.08	0.0340	0.0318

H atoms were refined using a riding model, $S = 0.988$, residual electron density 1.90 [0.49 Å from C50A] / -1.11 e Å^{-3} [0.53 Å from Ru1]. **CCDC-1814789**.

NMR INVESTIGATIONS

General. The CD_2Cl_2 used in these experiments was dried by distillation over $CaCO_3$ and stored in a Schlenk-flask in a glovebox. Unless stated otherwise, all commercially available compounds were used as received and stored under argon. $[Cp^*Ru(CH_3CN)_3]PF_6$ was prepared according to a literature procedure.[1] [Cp*Ru(cod)Cl] was purchased from Strem.

Sample Preparation. All samples were prepared in a glovebox. The substrate (0.1 mmol) and the catalyst (5.5 mol%) were dissolved in 0.4 mL CD_2Cl_2 in a 2 mL GC vial. After transferring the material into the pressure NMR-tube (5 mm medium wall precision pressure/vacuum valve NMR sample tube, Wilmad) via syringe, the tube was connected to the *p*-H_2-storage container or directly to the *p*-H_2-generator. The tubing was flushed with *p*-H_2 to ensure that no other gases were present. Then the Swagelok® connection to the NMR tube was tightened and the pressure valve opened to fill the tube with hydrogen. After closing the valve, the tube was shaken and directly transferred into the NMR magnet.

NMR Measurements. Spectra were acquired using Topspin 3.2 and a Bruker Ascend AVIII 500 MHz NMR spectrometer (11.7 Tesla) equipped with an Bruker 5mm BBFO^{plus} 500 MHz SmartProbe^{TM} (PA BBO 500S1 BBF-H-D-05 Z Plus) or Bruker 5 mm TBI Probe (PH TBI 500S1 H/C-BB-D-05 Z) at 298 K unless otherwise mentioned.

Acquired ^{1}H NMR spectra were referenced to the residual solvent signal (δ_{CHDCl2} = 5.32 ppm)[2]. The ^{13}C spectra were referenced with the Ξ-scale.[3,4]

OPSY[5] spectra were generally acquired with the following parameters: number of scans: 16, spectral width: 20 kHz (40 ppm), fid size: 32768 data points, relaxation delay: 0 s.

For OPSY-EXSY[6] typical spectral parameters were: fid size: 8192 data points, time increments: 512, number of scans per increment: 2, spectral width: 5 kHz in both dimensions, relaxation delay: 10 ms, mixing time = 300 ms. To clarify the OPSY-EXSY spectra t_1-noise with removed by the t_1-noise reduction macro of MNova 11.0.2.

The PHIP-NMR data was processed with MNova 11.0.2.

After all the dissolved hydrogen had been fully converted, samples were usually reshaken and reinserted into the magnet and the acquisition restarted. Depended on the substrate samples can be reshaken until all the hydrogen in the gas phase or all the starting material is fully consumed. Generally hyperpolarized species were observed until the reactants were fully converted.

***para*-Hydrogen Generation**.[6] The *p*-H_2 enrichment above the thermal equilibrium of 25% was achieved in two different ways:

(1) An enrichment of approx. 92 % was achieved with the commercially available *Parahydrogen pH2 Generator* from *Bruker BioSpin GmbH.*

(2) Alternatively, the *p*-H_2 can be enriched to 50% using the "U-shaped tube" method as previously described (Figure S5).[6,7] The tube was filled with a mixture (3:1) of activated charcoal (Norit PK1-3, Sigma Aldrich) and iron(III) oxide (99%, meshed powder, Alfa Aesar). The filled tube was evacuated and heated with a heat gun (150 °C) to remove any residual water and oxygen from the catalyst. This tube was used several times before the catalyst had to be reactivated. To enrich the *p*-H_2, the tube was loaded with 20 bar of hydrogen gas (99.995%, dry) and placed in a Dewar flask filled with liquid nitrogen (77 K). After an equilibration time of 1 h, the enriched hydrogen gas was transferred to an evacuated storage bottle or directly transferred to the NMR tube.

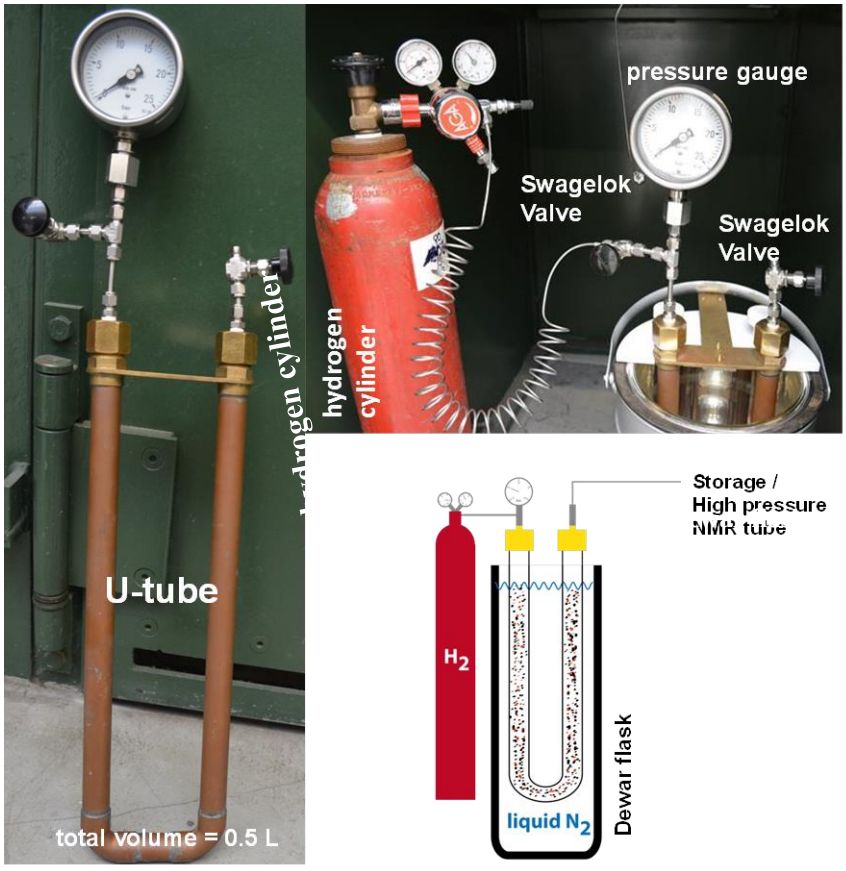


Figure S5.[6] Apparatus for the *p*-H_2 enrichment to 50%.

2D-EXSY with OPSY Filter.[6] A 2D-EXSY (EXchange SpectrosocopY) experiment was adapted to *p*–H_2 induced polarization with an OPSY-d-filter (Figure S6) to follow chemical exchanges involving the hydrogenated species during the reaction. Typically, experiments were recorded with 512 increments and 2 scans (8k points) per increments. Mixing times of $\tau_{mix} = 2\tau = 300$ ms were used. Short repetition times of 1.1 s (τ_{mix} + aq) allowed for an overall experimental time of 20 min (relaxation delays were unnecessary).

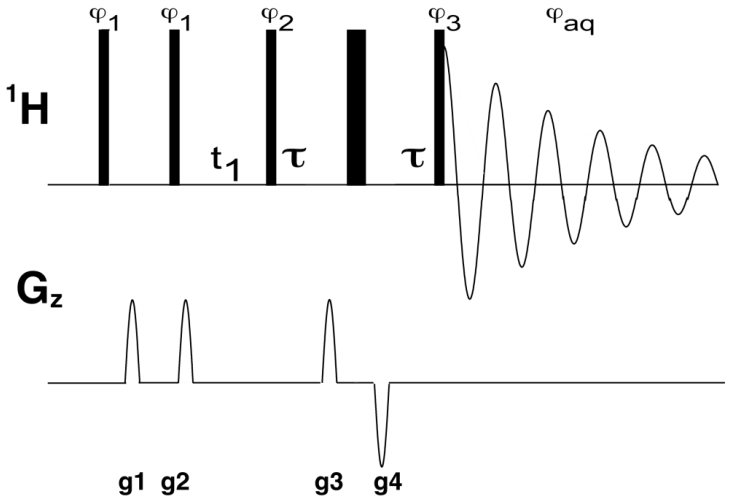


Figure S6.[6] NOESY/EXSY with OPSY-*d*-Filter (OPSY-*d*-EXSY): *Black thin bars* represent 90° *pulses* and thick *bars* represent 180° *pulses; pulses are applied with x-phase unless the phase is indicated above the bar.* Phase cycle: φ_1 = [x,-x], φ_2 = [$(x)_8$ $(-x)_8$], φ_3 = [x,x,-x,-x,y,y,-y,-y], φ_{aq} =[x,-x,-x,x,y,-y,-y,y, -x,x,x,-x,-y,y,y,-y]. Half-sine 1ms gradients were used with gradient ratio g1:g2:g3:g4 = 10:20:4:-4, and were each followed by a 0.2 ms recovery delay. The chemical exchange mixing time is represented by 2 τ.

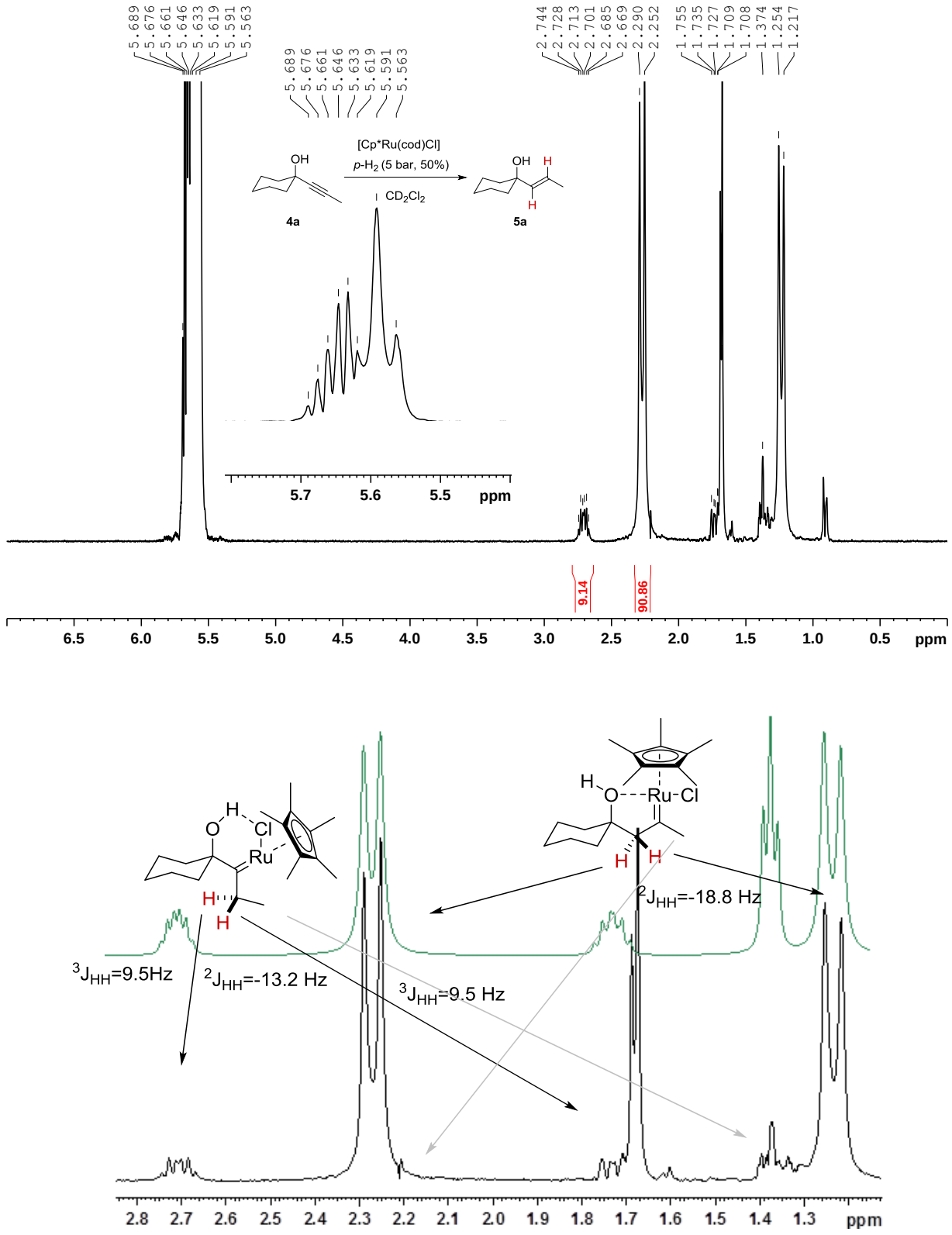


Figure S7.[6] Top: OPSY-*d*-spectrum during the reaction of alkyne **4a** in the presence of *p*-H_2 and [Cp*Ru(cod)Cl] to give carbenes **6a**/**7a**; **b**ottom: comparison of the acquired OPSY-Spectrum (black) and the simulated spectrum (green).

The ^{1}H-OPSY-COSY spectrum contains various structure informations about the carbene intermediates **6a** and **7b**. On the one hand it shows cross peaks between the geminal protons (**H2α↔H2β**, **H1α↔H1β**). On the other hand asymmetrical cross peaks to the CH_3-groups (H3) can be seen. The asymmetrical cross peaks are explained by the different polarization of the methyl and the methylene protons. The hyperpolarized geminal protons generate this cross peak (H1/2→H3), whereas the non-hyperpolarized methyl group may generate a cross peak (H3→H2/1), but the intensity is lower than the noise level and are therefore not visible.

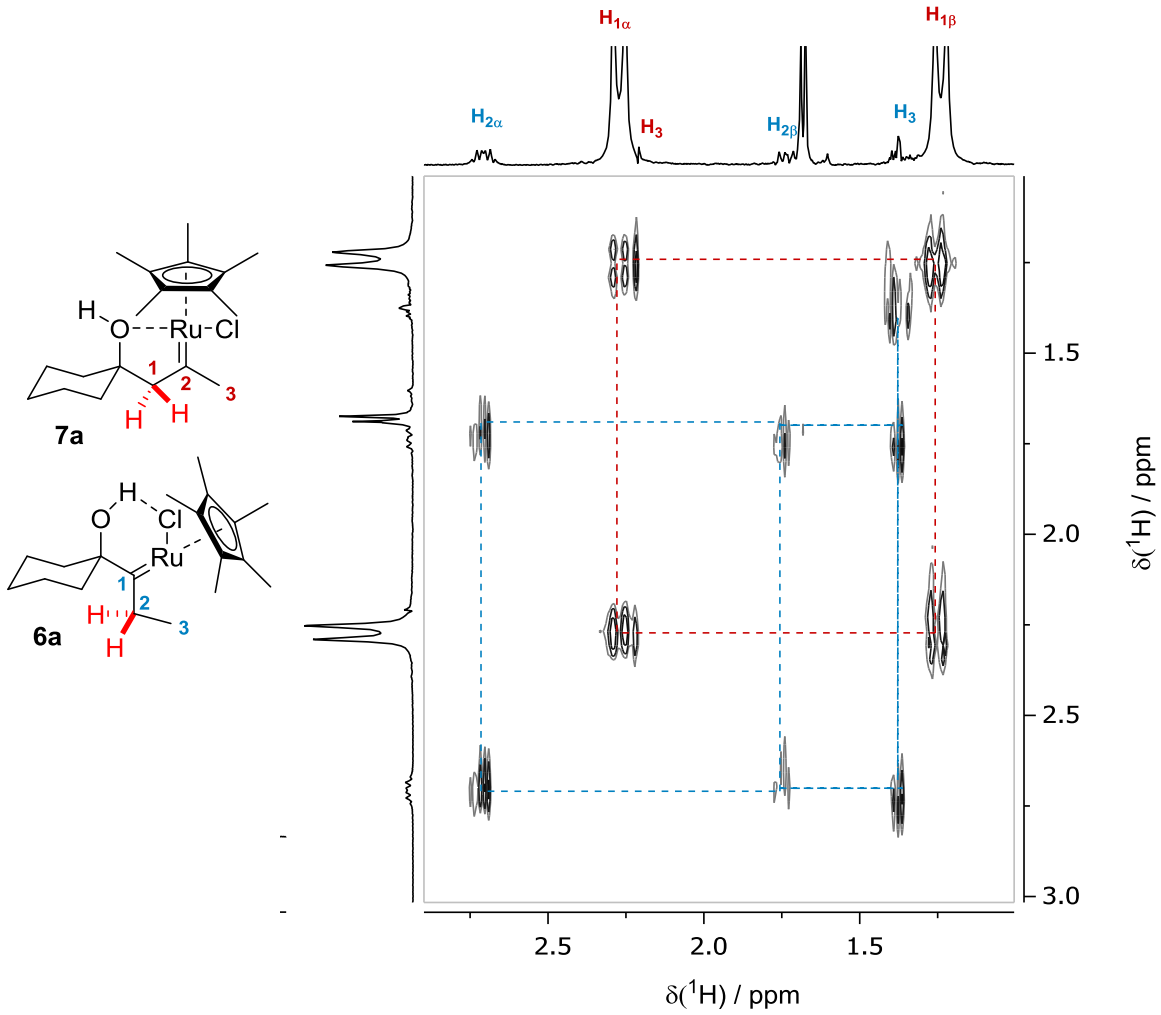


Figure S8.[6] Aliphatic region of the ^{1}H-OPSY-COSY spectrum confirming the coupling between the observed signals and the coupling to neighbored CH_3-groups in complexes **6a** and **7a**.

Exchange Spectroscopy. The analysis of the OPSY-EXSY spectrum of the reaction **4b** to **5b** (Figure S9) finds exchange correlations from the hyperpolarized hydrogens of the carbene **7b** to a number of products and by-products, namely **5b**, **16**, **17** and free H_2, as shown in Figure 6 of the main text of the publication and Figure S10. These results are in excellent accord with results of the computational study.

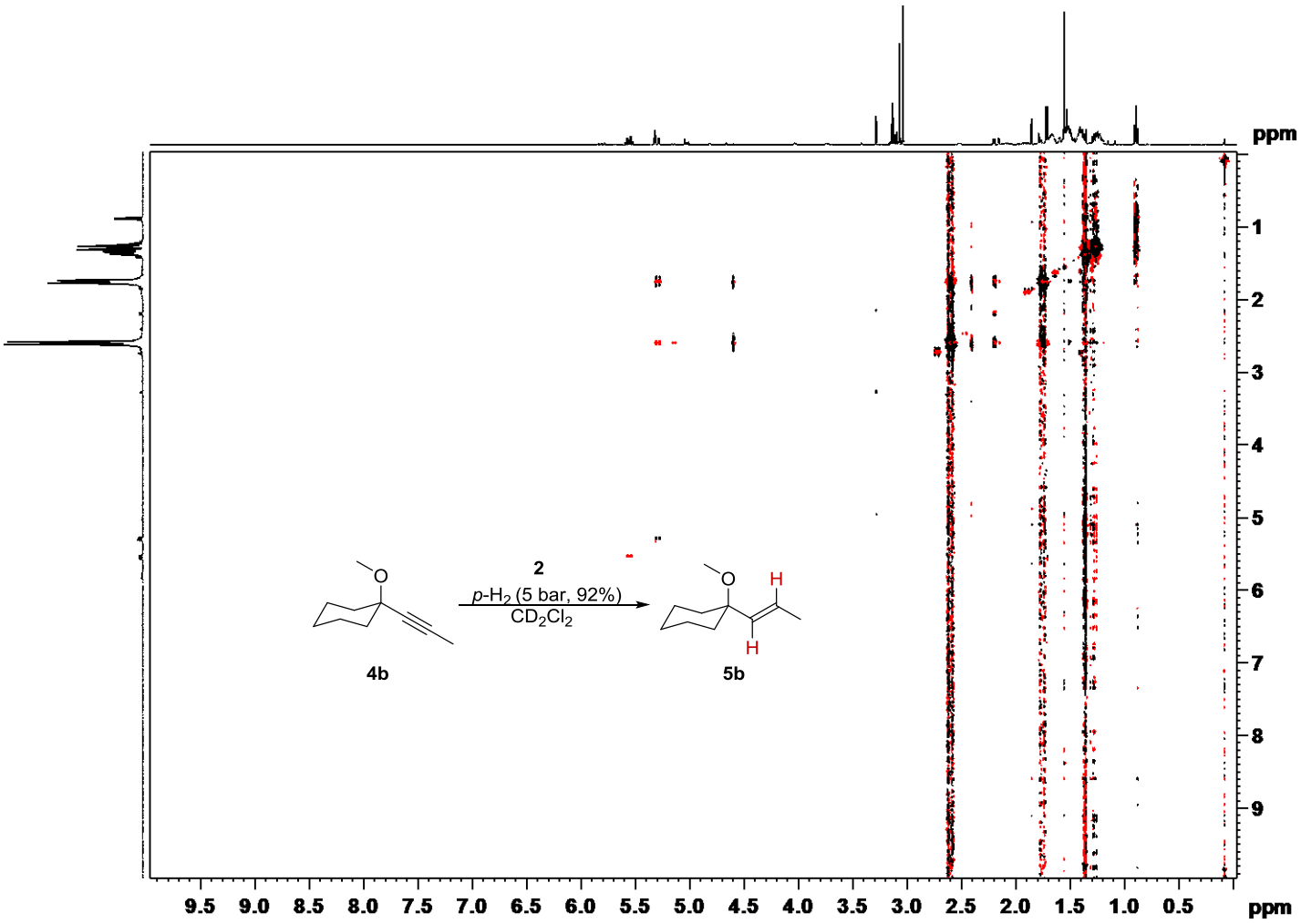


Figure S9.[6] OPSY-EXSY spectrum of **4b** during the hydrogenation with [Cp*Ru(cod)Cl].

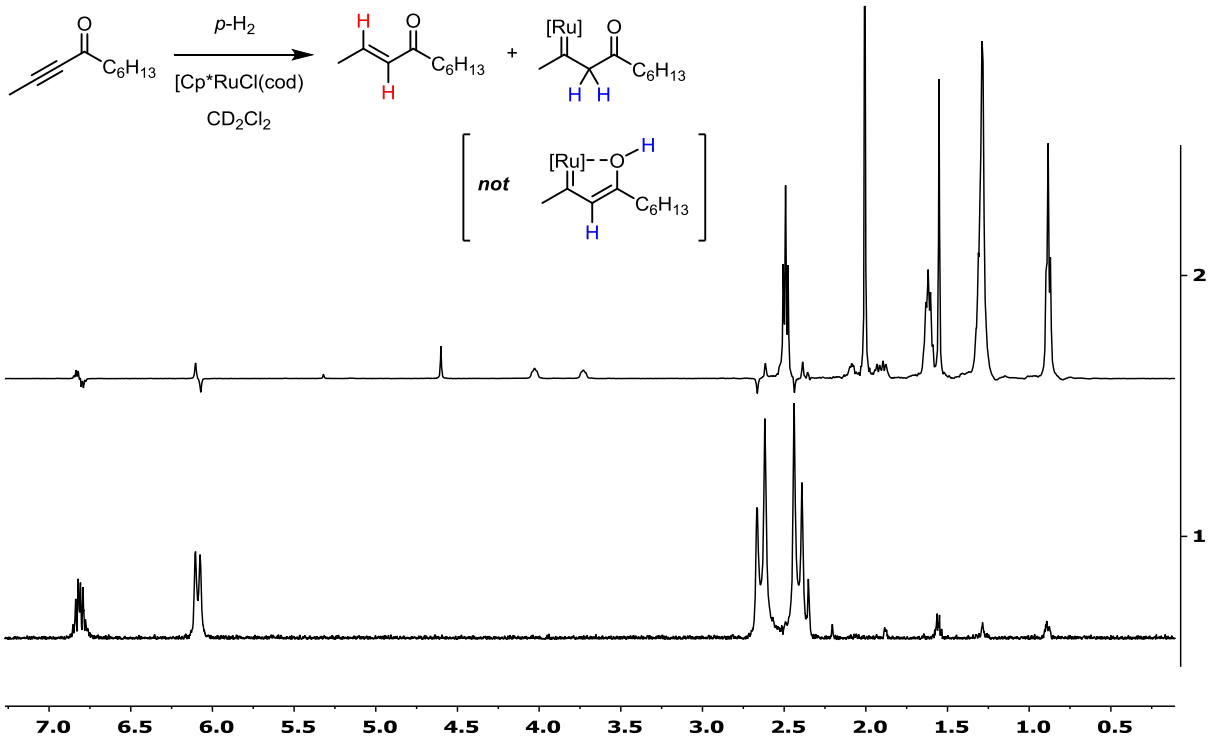


Figure S10. Hydrogenation of 2-decyne-4-one with *p*-H_2 and [Cp*RuCl(cod] affords the corresponding enone and a transient carbene chelate complex of type **10A**; top: standard ^{1}H NMR (30° excitation pulse) which allows the true intensity of the hyperpolarized signals to be assessed; bottom: OPSY spectrum; no "enolic" signals are detected

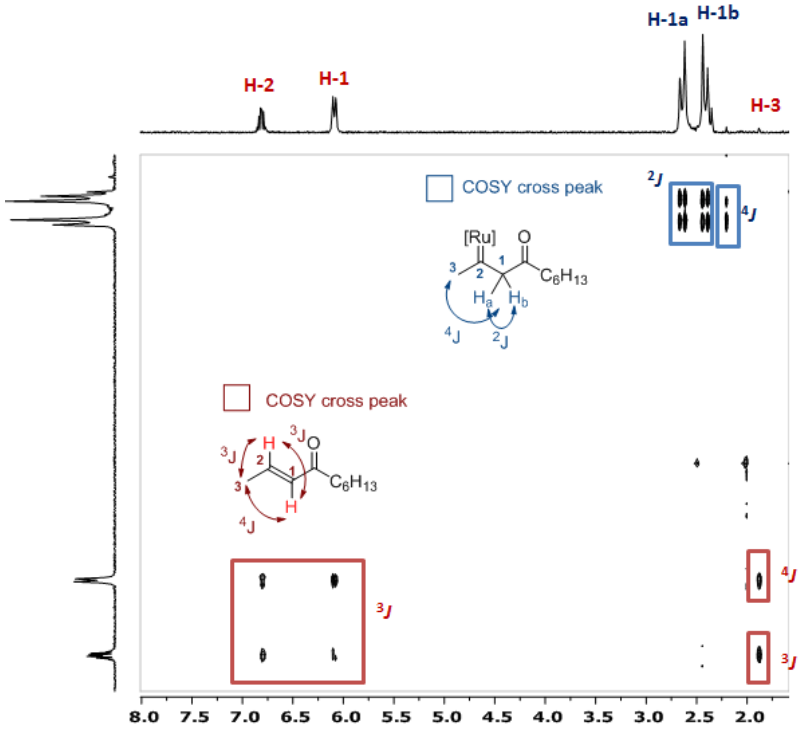


Figure S11. OPSY-COSY spectrum of the crude reaction mixture formed upon hydrogenation of 2-decyne-4-one with *p*-H_2 and [Cp*RuCl(cod]

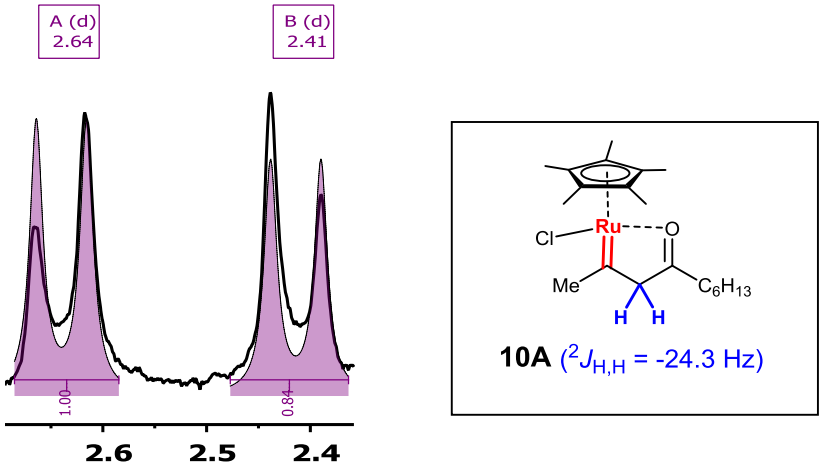


Figure S12. Hydrogenation of 2-decyne-4-one with *p*-H_2 and [Cp*RuCl(cod] affords a carbene chelate complex of type **10A** (R^1 = Me, R^2 = C_6H_{13}): determination of the coupling constant (^2J = –24.3 Hz) by line fitting

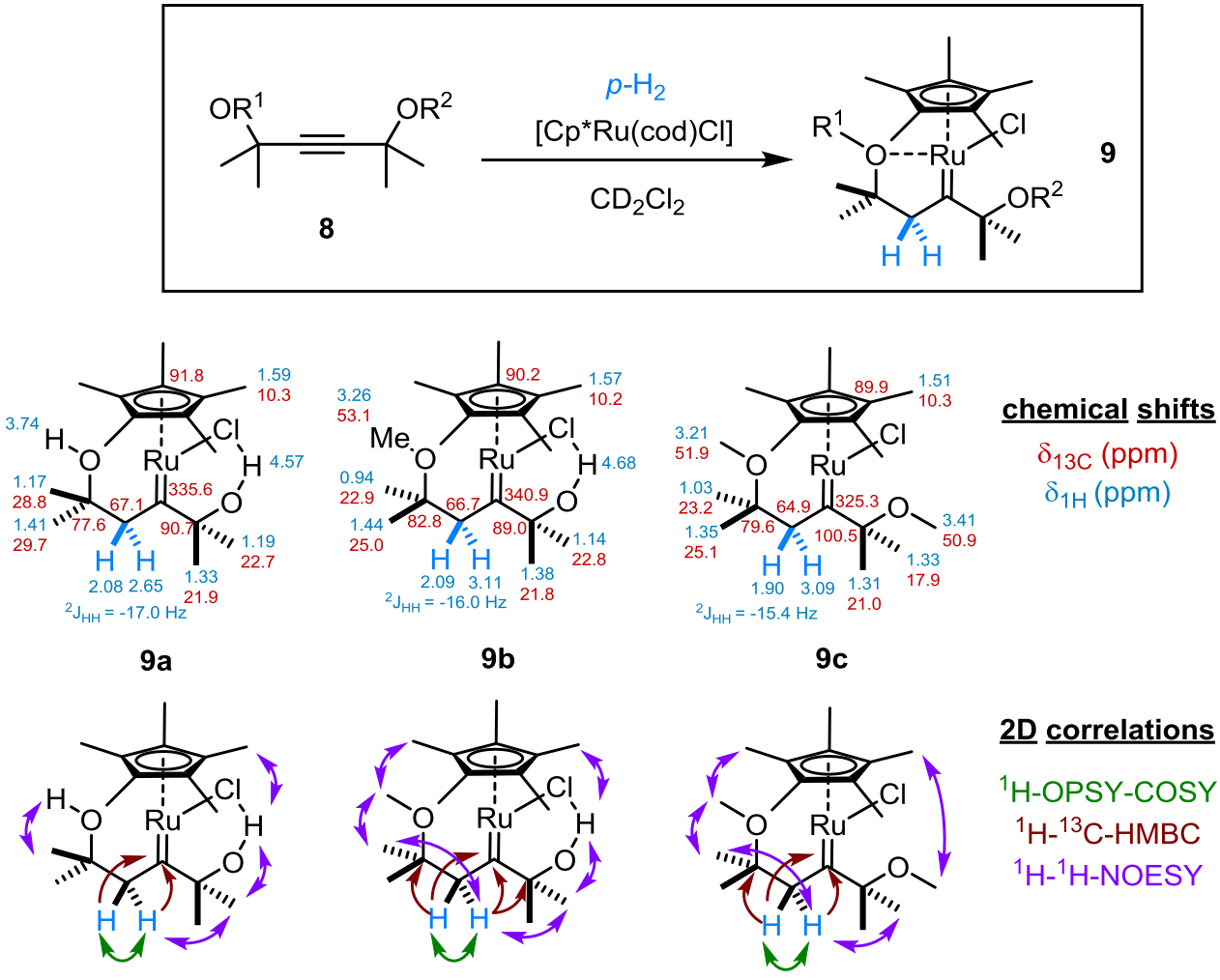


Figure S13. Summary of relevant spectral features of the ruthenium carbene complexes **9** formed by hydrogenation of alkynes **8** with *p*-H_2 and [Cp*Ru(cod)Cl], as extracted from spectra of the crude reaction mixtures

Comparison of OPSY-EXSY NMR spectra during the hydrogenation of **4b** versus [D_3]-**4b**

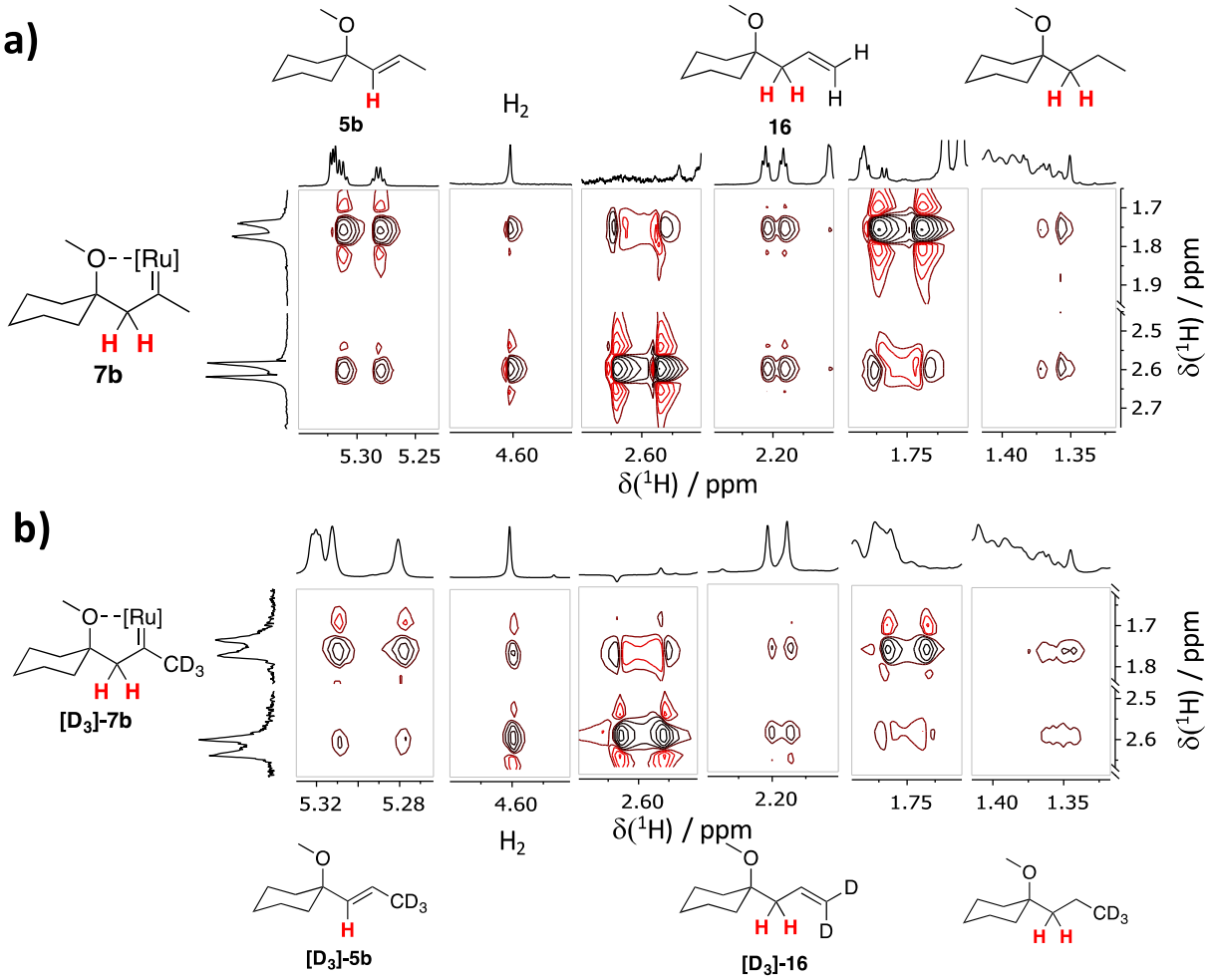
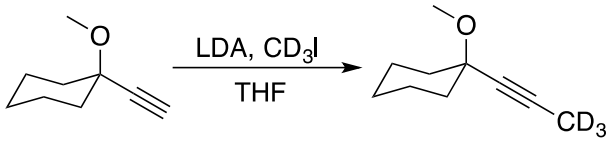


Figure S14. Slices of OPSY-EXSY spectrum during the hydrogenation of a) **4b** and b) [D_3]-**4b** showing different exchange peaks to **5b**, **16** and an over-reduced species. The vertical traces show the OPSY spectrum of the intermediate, the horizontal traces were acquired at high conversion. The third and sixth strip (from the left) represent diagonal and cross-peaks resulting from intramolecular cross-relaxation and coupling between the geminal protons.

The initial OPSY-EXSY spectrum that was acquired during the hydrogenation of **4b** by [Cp*Ru(cod)Cl] in CD_2Cl_2 is presented in Fig. S14a. The observed cross-peaks unmistakably connect carbene **7b** with the desired *E*-olefin **5b**, formation of H_2, the undesired isomerized olefin **16** and the over-reduced species (alkane). The signals originating from the carbene protons in compound **5b** and **16** clearly have an additional splitting due to an allyl coupling to the CH_3 or methylene-group. The OPSY-EXSY spectrum acquired during the hydrogenation of [D_3]-**4b** (Figure S14b) shows identical cross peaks as the non-

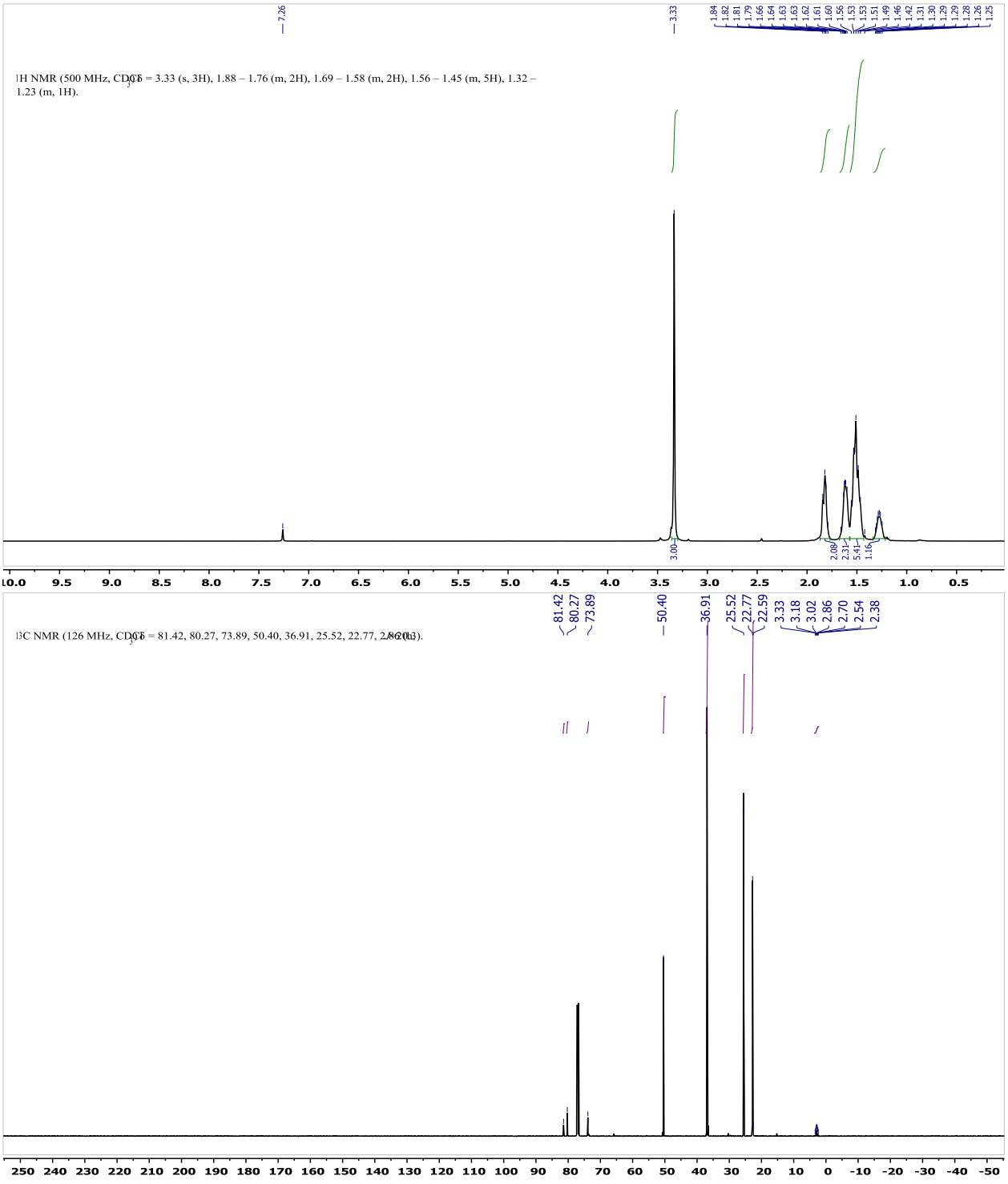
deuterated variant. The signals of carbene intermediates **7b** and [D_3]-**7b** acquired OPSY spectra show no significant differences between the 2 substrates.

In contrast to the protonated analogues, the previously described allyl-coupling to the methyl and methylene group is missing is missing in [D_3]-**5b** and [D_3]-**16** and their signals are sharper. In both reactions a cross-peak to the other olefin signal of **5b** could not be observed. This is in agreement with the computational results suggesting that the second olefin proton of **5b** is transferred from a second hydrogen molecule (associative mechanism).



[D_3]-4b

Preparation of [D_3]-4b. *n*-BuLi (2.5 M in hexanes, 7.78 mmol) was added to a solution of (*i*Pr)$_2$NH (1.14 mL, 8.1 mmol) in THF (16 mL) and the resulting mixture was stirred for 40 min at 0 °C. After adding 1-ethynyl-1-methoxycyclohexane (860 mg, 6.2 mmol) the solution was stirred for 2 h at 0 °C before CD_3I (435 μL, 6.8 mmol) was added. The mixture was warmed to ambient temperature and stirred for 4 h. The reaction was quenched with water (20 mL) and the aqueous layer was extracted with EtO_2 (3 x 20 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. After evaporation of the solvent and purification of the residue by flash chromatography (5% to 10% EtO_2/pentanes) the product was obtained as a colorless, volatile powder (240 mg, 25%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.33 (s, 3H), 1.88 – 1.76 (m, 2H), 1.69 – 1.58 (m, 2H), 1.56 – 1.45 (m, 5H), 1.32 – 1.23 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 81.4, 80.3, 73.9, 50.4, 36.9, 25.5, 22.8, 2.9 (h, *J* = 20.3 Hz). MS (EI) *m/z*: 155 (3.5%, M^+), 112 (100), 140 (28, M-CH_3), 137 (18, M-CD_3), 82 (26), 79 (20). HRMS (APPI-pos) *m/z* (M^+): calcd: 155.13895 found: 155.13840.


1H NMR (500 MHz, CDCl3) δ = 3.33 (s, 3H), 1.88 – 1.76 (m, 2H), 1.69 – 1.58 (m, 2H), 1.56 – 1.45 (m, 5H), 1.32 – 1.23 (m, 1H).
13C NMR (126 MHz, CDCl3) δ = 81.42, 80.27, 73.89, 50.40, 36.91, 25.52, 22.77, 22.59.

PREPARATIVE DATA

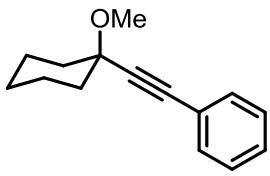
General. All reactions were carried out under Ar atmosphere in flame-dried glassware unless stated otherwise. Solvents were purified by distillation over the indicated drying agents and were transferred under Ar: toluene (Na/K, stored over molecular sieves), 1,2-dichloroethane (CaH_2), CH_2Cl_2 (CaH_2), CD_2Cl_2 (dried and stored over molecular sieves, degassed three times by the freeze-pump-thaw method), methanol (Mg), pentane (Na/K, degassed three times by the freeze-pump-thaw method); pyridine and DMF were dried by an absorption solvent purification system based on molecular sieves. Flash chromatography: Merck Geduran® Si 60 (40–63 µm). NMR: Spectra were recorded at room temperature unless stated otherwise, on Bruker AV 400s and AV 500as spectrometers in the indicated solvents; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); ^1H and ^{13}C assignments were established using NOESY, HSQC and HMBC experiments; numbering schemes as shown in the Inserts. IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS**:** EI: Finnigan MAT 8400 (70 eV), ESI: Thermo Scientific LTQ-FT or Thermo Scientific Exactive; accurate mass determinations: Finnigan MAT 95, Thermo Scientific LTQ FT, or Thermo Scientific Exactive.

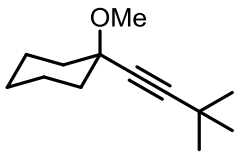
The ruthenium complexes $[Cp^*RuCl]_4$,[8] $[Cp^*Ru(cod)Cl]$,[8] $[Cp^*Ru(MeCN)_3]PF_6$,[1] **62**,[9] were prepared according to the cited literature procedures. Commercially available compounds (ABCR, Acros, Sigma-Aldrich, TCI) were used as received.

Substrates

All known alkyne substrates[10-12] were prepared according to the cited literature procedures.

((1-Methoxycyclohexyl)ethynyl)benzene (4d). A suspension of NaH (43 mg, 1.8 mmol) in THF (1 mL) was added at 0°C to a solution of 2-methyl-4-phenylbut-3-yn-2-ol (300 mg, 1.5 mmol) in THF (5 mL) and DMF (1.2 mL). After stirring for 1 h at 0°C, Me_2SO_4 (0.21 mL, 2.2 mmol) was introduced and stirring continued at room temperature for another 4 h. The reaction was quenched with NH_4Cl (sat. aq. 5 mL). The aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 2% EtOAc in hexane) to give the title compound as a colorless oil (297 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.43 (m, 2H), 7.34 – 7.28 (m, 3H), 3.45 (s, 3H), 2.08 – 1.95 (m, 2H), 1.78 – 1.50 (m, 7H), 1.39 – 1.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.8, 128.3, 128.2, 123.2, 90.4, 86.3, 74.5, 50.9, 37.0, 25.7, 23.0. IR (film): 2932, 2856, 1489, 1443, 1301, 1091, 1063, 925,730, 689 cm^{-1}; ESI-MS calcd for $C_{15}H_{18}O$ ($M+H^+$): 214.13521; found: 214.13527.

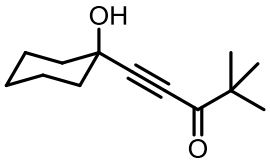




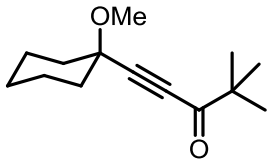
1-(3,3-Dimethylbut-1-yn-1-yl)-1-methoxycyclohexane (4f). 1-(3,3-Dimethylbut-1-yn-1-yl)cyclohexan-1-ol (15.7 mg, 0.074 mmol) was carefully added in portions to a stirred suspension of NaH (40 mg, 1.67 mmol) in DMF (4 mL) at 0°C. The mixture was stirred for 1 h at 0°C before MeI (0.11 mL, 1.82 mmol) was introduced at this

temperature. The coling bath was removed and the reaction quenched with sat. aq. NH_4Cl (5 mL) when the mixture had reached ambient temperature. The aqueous phase was extracted with Et_2O (3 x 5mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 4% EtOAc in hexane) to give the desired product (228 mg, 77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.34 (s, 3H), 1.89 – 1.80 (m, 2H), 1.69 – 1.41 (m, 7H), 1.30 – 1.24 (m, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 95.5, 79.2, 74.2, 50.5, 37.3, 31.4, 27.5, 25.8, 23.2. IR (film): 2968, 2932, 2859, 1447, 1362, 1297, 1093, 1081, 929 cm^{-1}; ESI-MS calcd for $C_{13}H_{22}ONa$ ($M+Na^+$): 217.15628; found 217.15643.

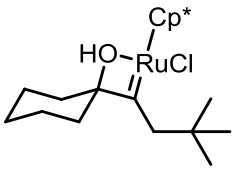
1-(1-Hydroxycyclohexyl)-4,4-dimethylpent-1-yn-3-one (11b). *n*-BuLi (5 mL, 8 mmol, 1.6 M solution in hexanes) was added at 0°C to a solution of 1-ethynyl-1-cyclohexanol (500 mg, 4 mmol) in THF (50 mL). After stirring for 1 h at 0°C the reaction was cooled to −78°C before pivaloyl chloride (0.12 mL, 1 mmol) was added dropwise. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with NH_4Cl (sat. aq. 50 mL). The aqueous phase was extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 15% EtOAc in hexane) to give the desired product (261 mg, 31%) as a white solid. mp: 46-47°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.24 (bs, 1H), 2.06 – 1.92 (m, 2H), 1.83 – 1.73 (m, 2H), 1.73 – 1.53 (m, 6H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 194.3, 96.9, 81.6, 69.2, 45.2, 39.9, 26.3, 25.5, 23.7. IR (film): 3245, 2935, 2858, 2200, 1650, 1447, 1287, 1172, 1106, 965, 946, 745 cm^{-1}. ESI-MS calcd for $C_{13}H_{20}O_2Na$ ($M+Na^+$): 231.13555; found: 231.13557.



1-(1-Methoxycyclohexyl)-4,4-dimethylpent-1-yn-3-one (11a). *n*-BuLi (0.69 mL, 1.1 mmol, 1.6 M solution in hexanes) was added dropwise to a solution of 1-ethynyl-1-methoxycyclohexane (152 mg, 2.2 mmol) in THF (2 mL) at −78 °C. The mixture was warmed to ambient temperature and stirred for 1 h. It was then cooled to −78°C before solid CuI (250 mg, 1.3 mmol) was introduced. The mixture was warmed to 0°C and stirred for 1 h before pivaloyl chloride (0.12 mL, 1 mmol) was added dropwise at 0°C. Stirring was continued for 2 h at ambient temperature. The reaction was quenched with NH_4Cl (sat. aq. 5 mL). The aqueous phase was extracted with E_2O (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 5% EtOAc in hexane) to give the desired product as a colorless oil (263.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (s, 3H), 2.01 – 1.91 (m, 2H), 1.76 – 1.60 (m, 4H), 1.59 – 1.47 (m, 3H), 1.38 – 1.28 (m, 1H). 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.0, 94.5, 83.2, 74.1, 51.4, 44.9, 36.3, 26.2, 25.4, 22.7. IR (film): 2935, 2861, 2200, 1658, 1447, 1289, 1157, 1078, 927, 732 cm^{-1}. ESI-MS calcd for $C_{14}H_{22}O_2Na$ ($M+Na^+$): 245.15120; found: 245.15110.



Complexes



Ruthenium Carbene 6e. 1-(3,3-Dimethylbut-1-yn-1-yl)cyclohexan-1-ol (33.8 mg, 0.19 mmol)[13] was added to a stirred solution of [[Cp*RuCl}$_4$] (50.9 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) under Ar. H_2 gas was bubbled through the solution for 3 min and the resulting mixture was stirred under hydrogen atmosphere for 2 h at ambient temperature. All volatile components were evaporated in vacuum and the residue was dissolved in pentane. Traces of insoluble materials were filtered off and the filtrate was evaporated. For the spectroscopic data, see Figures S15 and S16. MS (EI) calcd for $C_{22}H_{37}OClRu$ (M^+): 454.15764; found 454.15752. The solid material was dissolved in the minimum amount of pentanes and the resulting solution was cooled over the course of 13 h from 10°C to −30°C to give the title complex in the form of single crystals suitable for X-ray analysis.

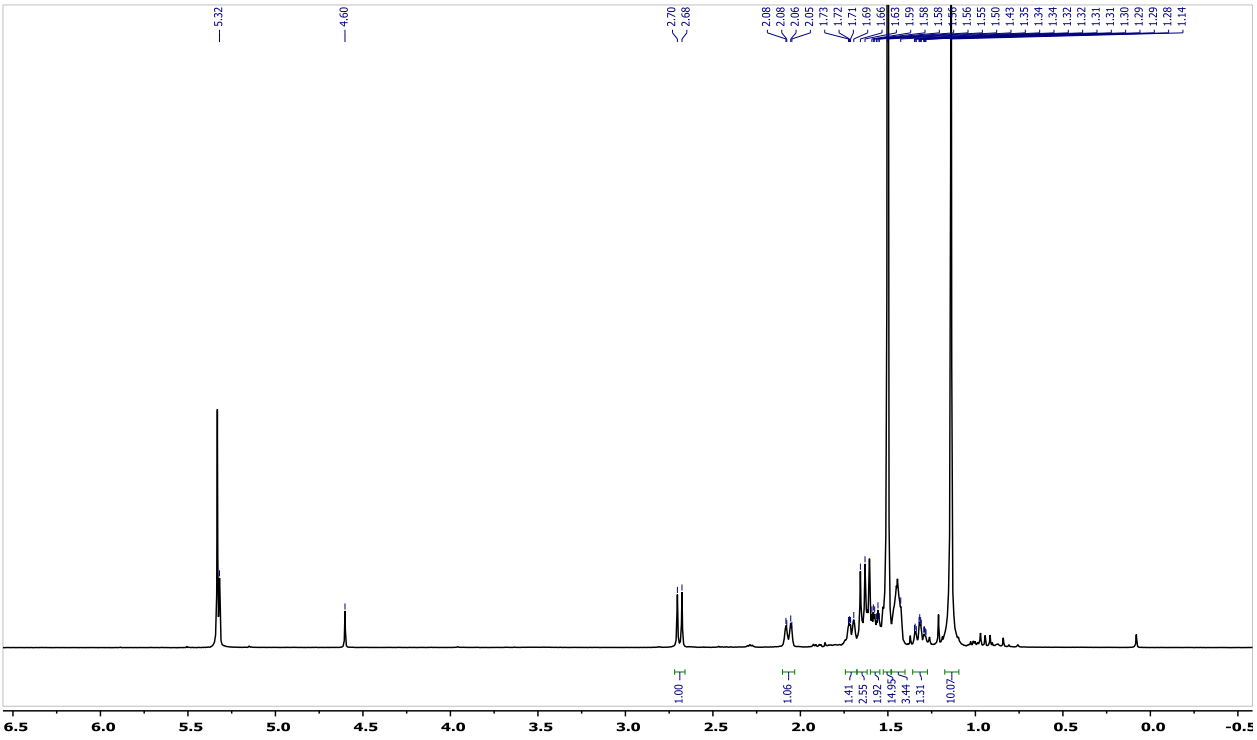


Figure S15. ^{1}H NMR spectrum of the carbene complex **6e** (500 MHz, CD_2Cl_2)

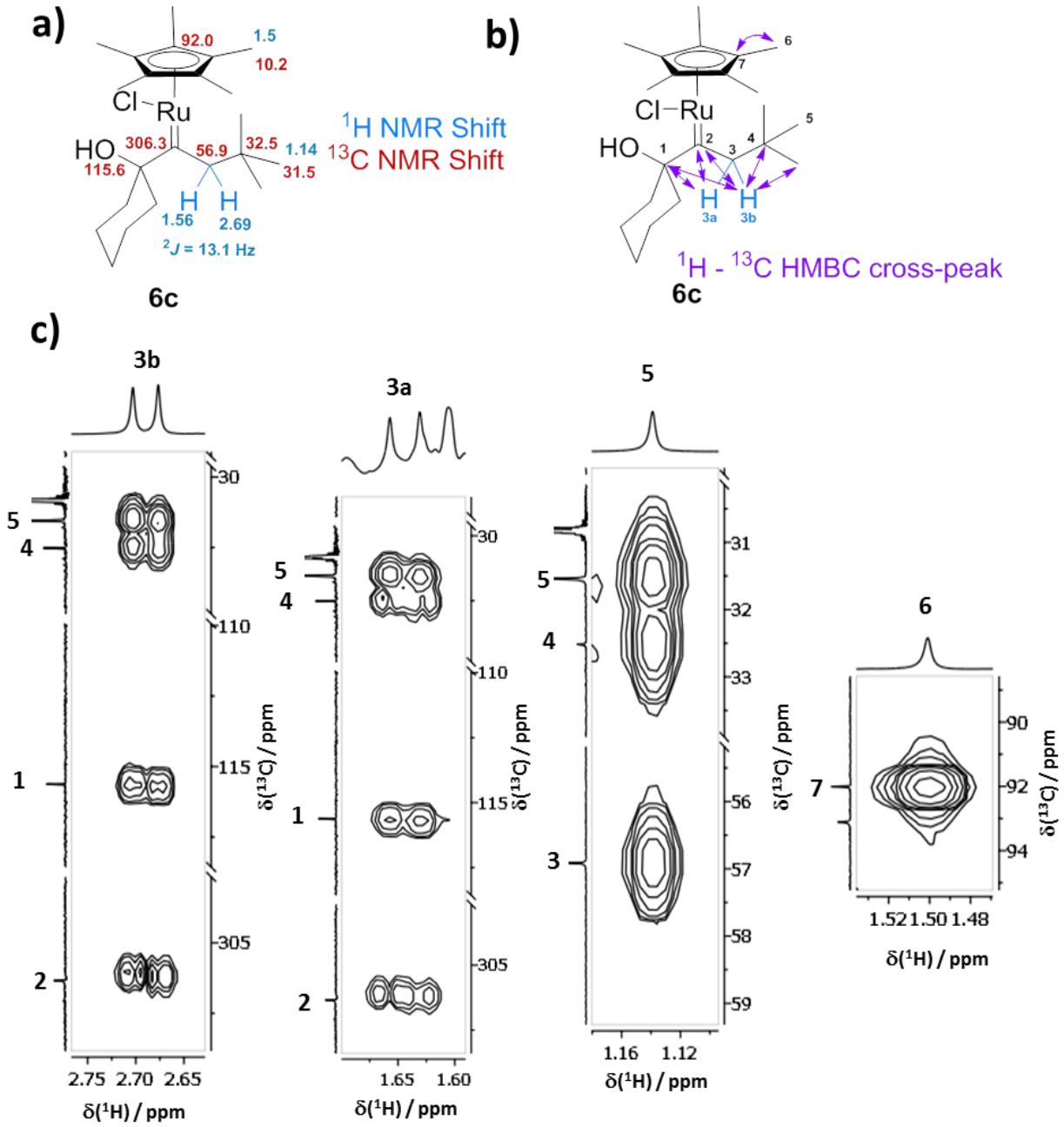
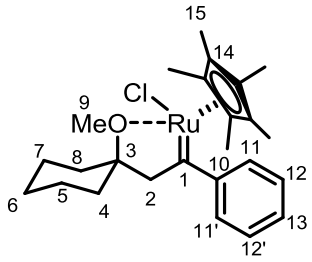


Figure S16. a) Spectral data (500 MHz, CD_2Cl_2, δ) of the carbene complex **6e**; b) observed cross-peaks in ^{1}H-^{13}C HMBC; c) selected slices of ^{1}H-^{13}C - HMBC showing relevant cross peaks

Ruthenium Carbene 7d. $[Cp^*RuCl]_4$ (20 mg, 0.018 mmol) was added under argon to a stirred solution of



alkyne **4b** (15.7 mg, 0.074 mmol) in CH_2Cl_2 (1 mL). H_2 gas was bubbled through the reaction mixture for 2 min with a charged balloon and an outlet needle through a septum. The reaction mixture was stirred for 30 min under H_2 atmosphere at ambient temperature. H_2 was removed by bubbling argon through the mixture for 5 min before the solvent was removed under vacuum. The solid was dissolved in degassed Et_2O and undissolved residues were filtered off via cannula. The filtrate was evaporated and the residue dissolved in CD_2Cl_2 for NMR inspection, which showed the presence of two isomeric carbene species in solution (**7d**:**6d** ≈ 3:1); characteristic NMR signals: ^{13}C NMR (101 MHz, CD_2Cl_2): δ 304.6 (major), 289.5 ppm (minor). Single crystal of the major isomer (**7d**) suitable for X-ray diffraction were obtained when a solution of the crude material in the minimum amount of Et_2O was cooled from ambient temperature to −40°C over the course of 12h and kept at this temperature for 2 d. The pure isomer **7d** thus obtained analyzed as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.68 (m, 2H, H-11, H-11'), 7.54 – 7.43 (m, 1H, H-13), 7.36 – 7.23 (m, 2H, H-12, H-12'), 3.50 (d, *J* = 16.7 Hz, 1H, H-2a), 3.38 (s, 3H, −OMe), 2.00 – 1.85 (m, 2H, H-4a, H-6a), 1.69 – 1.52 (m, 3H, H-4b, H-5a, H-7a), 1.59 (d, *J* = 16.9 Hz, 1H, H-2b), 1.52 – 1.40 (m, 3H, H-6b, H-8a,b), 1.27 (s, 15H, H-15), 1.24 – 1.00 (m, 2H, H-5b, H-7b). ^{13}C NMR (101 MHz, $CDCl_3$): δ 304.6 (C-1), 159.1 (C-10), 127.9 (C-12, C-12'), 127.0 (C-13), 124.7 (C-11, C-11'), 90.4 (C-14), 85.7 (C-3), 62.2 (C-2), 52.7 (C-9), 34.1 (C-4), 29.5 (C-8), 25.5 (C-6), 25.5 (C-5), 24.1 (C-7), 9.3 (C-15). MS (EI) calcd for $C_{25}H_{35}OClRu$ (M^+): 488.14136; found 488.14156.

Ruthenium carbene 12b. $[Cp^*RuCl]_4$ (20 mg, 0.018 mmol) was added under argon to a stirred solution of alkyne **11b** (15.3 mg, 0.073 mmol) in CD_2Cl_2 (1 mL) in a flame dried Schlenk tube. H_2 gas was bubbled through the mixture for 2 min and stirring was continued under an H_2 atmosphere for 30 min. H_2 was removed by bubbling argon through the mixture for 5 min before the solution was transferred to an NMR tube for measurement, which showed a mixture of **12b**, the π-complex **13** and product **14**; the NMR data of **12b** extracted from this mixture are compiled in Figure S17. MS (EI) calcd for $C_{23}H_{37}O_2ClRu$ (M^+): 482.15192; found 482.15171.

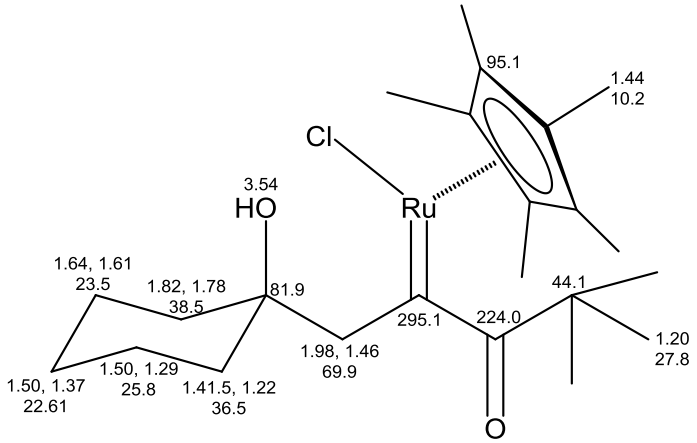


Figure S17. Spectral data (500 MHz, CD_2Cl_2, δ) of the carbene complex **12b**

Ruthenium carbene 12a. $[Cp^*RuCl]_4$ (22 mg, 0.020 mmol) was added under argon to a stirred solution of alkyne **11a** (18 mg, 0.081 mmol) in CH_2Cl_2 (1 mL) in a flame dried Schlenk tube. H_2 gas was bubbled through the mixture for 2 min and stirring was continued for 30 min under H_2 atmosphere. H_2 was removed by bubbling argon through the solution for 5 min before the solvent was removed under vacuum. The solid was triturated with degassed pentane, and insoluble material was filtrated off. The filtrate was slowly cooled to −35°C over the course of 12 h and kept at this temperature for 2 d to afford single crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.42 (s, 3H), 3.14 (d, *J* = 19.7 Hz, 1H), 1.88 – 1.73 (m, 3H), 1.72 – 1.50 (m, 4H), 1.42 (s, 15H), 1.37 – 1.27 (m, 2H), 1.25 (s, 9H), 1.17 – 1.06 (m, 1H), 0.94 (dd, *J* = 19.8, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 295.5, 223.6, 92.4, 85.7, 62.5, 53.9, 44.8, 34.8, 30.9, 27.6, 25.9, 25.7, 24.8, 9.8. MS (EI) calcd for $C_{24}H_{39}O_2ClRu$ (M^+): 496.16757; found 496.16763.

Ruthenium Enone π-Complex 13. $[Cp^*RuCl]_4$ (20 mg, 0.018 mmol) was added under argon to a stirred solution of alkyne **11b** (15.3 mg, 0.073 mmol) in CH_2Cl_2 (1 mL) in a flame dried Schlenk tube. H_2 gas was bubbled through the mixture for 2 min and stirring was continued for 30 min under H_2 atmosphere. H_2 was removed by bubbling argon through the mixture for 5 min before the solvent was removed under vacuum. The solid was dispersed in degassed Et_2O and the suspension was filtered via cannula. The filtrate was cooled to −40°C over the course of 12 h and kept at this temperature for 2 d to afford single crystals suitable for X-ray diffraction. MS (EI) calcd for $C_{23}H_{37}O_2ClRu$ (M^+): 482.15192; found 482.15180.

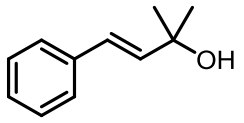
Organic Products

***(E)*-1-(1-Hydroxycyclohexyl)-4,4-dimethylpent-1-en-3-one (14).** $[Cp^*RuCl]_4$ (21.5 mg, 0.020 mmol) was added under argon to a stirred solution of alkyne **11b** (16.5 mg, 0.079 mmol) in CH_2Cl_2 (1 mL) in a flame dried Schlenk tube. H_2 gas was bubbled through the mixture for 2 min and stirring was continued for 48 h under H_2 atmosphere. The mixture was filtrated through a pad of Florisil, which was washed with Et_2O. The combined filtrates were concentrated under vacuum and the residue was purified by flash chromatography (SiO_2, 20% EtOAc in hexane) to give the title compound (4.5 mg, 27%) as a pale-brown solid. mp: 54-55°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 15.3 Hz, 1H), 1.55 – 1.49 (m, 8H), 1.34 – 1.27 (m, 2H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 205.0, 153.0, 120.6, 72.3, 43.4, 37.8, 37.4, 26.3, 25.3, 22.4, 21.7. IR (film): 3448, 2929, 2856, 1681, 1619, 1447, 1095, 1071, 990, 572 cm^{-1}. ESI-MS calcd for $C_{13}H_{21}O_2$ ($M\text{-}H^-$): 209.15470; found 209.15481.

1-(1-Methoxycyclohexyl)-4,4-dimethylpentan-3-one (15). $[Cp^*RuCl]_4$ (20 mg, 0.048 mmol) was added under argon to solution of alkyne **11a** (16.3 mg, 0.074 mmol) in CH_2Cl_2 (1 mL). H_2 gas was bubbled through the mixture for 2 min and stirring was continued for 30 min under H_2 atmosphere. Argon was then bubbled for 10 min through the solution and residual solvent was removed under high vacuum. The residue was dissolved in 1,2-dichloroethane, H_2 gas was bubbled through the mixture for 2 min and stirring continued for 18 h under H_2 atmosphere at 70°C. After cooling to ambient temperature the solvent was

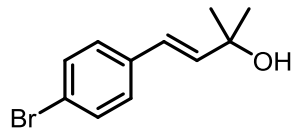
removed under vacuum. The crude product was purified by flash chromatography (SiO_2, 5% EtOAc in hexane) to give the title compound (10 mg, 60%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (s, 3H), 2.53 – 2.45 (m, 2H), 1.73 – 1.65 (m, 4H), 1.58 – 1.38 (m, 5H), 1.30 – 1.21 (m, 3H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 216.6, 74.5, 48.2, 44.5, 34.3, 29.9, 29.8, 26.7, 26.1, 21.7. IR (film): 2931, 2858, 1705, 1462, 1366, 1070, cm^{-1}. ESI-MS calcd for $C_{14}H_{26}O_2Na$ (M+Na$^+$): 249.18250; found: 249.18246.

General Procedure for *trans*-Hydrogenation: *(E)*-2-Methyl-4-phenylbut-3-en-2-ol (19). $[Cp^*RuCl]_4$ (13 mg, 12 μmol) was added under argon to a stirred solution of 2-methyl-4-phenylbut-3-yn-2-ol (100 mg, 0.62 mmol) in CH_2Cl_2 (6 mL) in a flame dried Schlenk tube. H_2 gas was bubbled through the mixture for 2 min and stirring was continued for 2 h under H_2 atmosphere. The mixture was filtrated through a pad of Florisil which was carefully rinsed with Et_2O. The combined filtrates were concentrated under vacuum and the residue purified by flash chromatography (SiO_2, 15% EtOAc in hexane) to give the title compound as a colorless oil (98.5 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.20 (m, 1H), 6.60 (d, *J* = 16.1 Hz, 2H), 6.36 (d, *J* = 16.1, 1H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 137.6, 137.0, 131.7, 128.7, 128.3, 127.5, 126.5, 126.5, 71.2, 30.00. IR (film): 3369, 2973, 1361, 1147, 965, 908, 710, 675 cm^{-1}. ESI-MS calcd for $C_{11}H_{14}ONa$ (M+Na$^+$): 185.09368; found: 185.09364.

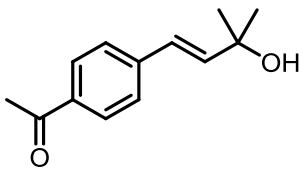


The following compounds were prepared analogously:

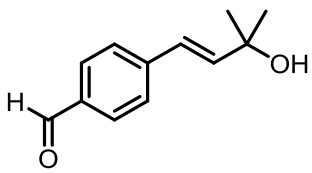
***(E)*-4-(4-Bromophenyl)-2-methylbut-3-en-2-ol (20).** White solid (26.1 mg, 86%), mp: 83-84°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 3H), 7.27 – 7.22 (m, 2H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.4, 136.0, 131.8, 128.1, 125.4, 121.3, 71.2, 30.0. IR (film): 3230, 2981, 1488, 1376, 1250, 1145, 1071, 977, 901, 818 cm^{-1}. ESI-MS calcd for $C_{11}H_{13}O_{Br}$ (M+H$^+$): 240.01499; found: 240.01472.



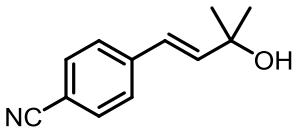
***(E)*-1-(4-(3-Hydroxy-3-methylbut-1-en-1-yl)phenyl)ethan-1-one (21).** Colorless oil (33.1 mg, 92%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 16.1 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 2.58 (s, 3H), 1.77 (bs, 1H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7, 141.9, 140.6, 136.0, 128.9, 126.6, 125.6, 71.2, 30.0, 26.7. IR (film): 3432, 2973, 1671, 1601, 1358, 1256, 1181, 958, 909, 814, 716 cm^{-1}. ESI-MS calcd for $C_{13}H_{16}O_2Na$ (M+Na$^+$): 227.10425; found: 227.10400.



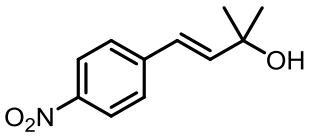
***(E)*-4-(3-Hydroxy-3-methylbut-1-en-1-yl)benzaldehyde (22).** Colorless oil (21 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.87 – 7.71 (m, 2H), 7.55 – 7.44 (m, 2H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 1.79 (bs, 1H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.9, 143.3, 141.4, 135.4, 130.3, 127.0, 125.6, 71.2, 30.0. IR (film): 3401, 2973, 1712, 1594, 1210, 1158, 969, 809, 770 cm^{-1}. ESI-MS calcd for $C_{12}H_{14}O_2Na$ (M+Na$^+$): 213.08860; found: 213.08850.



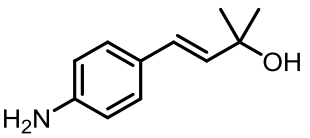
***(E)*-4-(3-Hydroxy-3-methylbut-1-en-1-yl)benzonitrile (23).** White solid (25.7 mg, 85%), mp: 39-40°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 1.65 (bs, 1H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7, 141.5, 132.5, 127.0, 125.1, 119.1, 110.7, 71.2, 30.0..IR (film): 3466, 3358, 2973, 2224, 1603, 1359, 1138, 968, 813, 556 cm^{-1}. ESI-MS calcd for $C_{12}H_{13}NONa$ (M+Na$^+$): 210.08893; found: 210.08887.



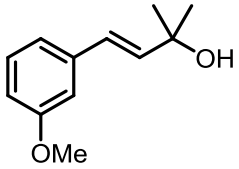
***(E)*-2-Methyl-4-(4-nitrophenyl)but-3-en-2-ol (24).** Orange solid (25.1 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.12 (m, 2H), 7.55 – 7.47 (m, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.0, 143.7, 142.4, 127.1, 124.8, 124.1, 71.3, 30.0. IR (film): 3365, 2973, 1594, 1510, 1309, 1108, 970, 827, 746, 691 cm^{-1}. ESI-MS calcd for $C_{11}H_{13}NO_3$ (M+H$^+$): 207.08899; found: 207.08902.



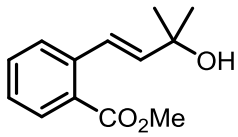
***(E)*-4-(4-Aminophenyl)-2-methylbut-3-en-2-ol (25).** Orange solid (20.6 mg, 69%), mp: 115-116°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 16.1 Hz, 1H), 1.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.0, 134.1, 127.8, 127.7, 127.6, 127.2, 126.3, 115.3, 115.3, 115.3, 71.2, 30.1. IR (film): 2911, 1606, 1512, 1241, 1177, 809 cm^{-1}. ESI-MS calcd for $C_{11}H_{15}NONa$ (M+Na$^+$): 200.10458; found 200.10469.



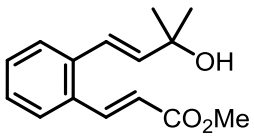
***(E)*-4-(3-Methoxyphenyl)-2-methylbut-3-en-2-ol (26).** Colorless oil (29.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.93 – 6.91 (m, 1H), 6.83 – 6.75 (m, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 3.79 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 138.5, 138.0, 129.7, 126.4, 119.2, 113.3, 111.8, 71.2, 55.4, 30.0. IR (film): 3398, 2970, 1598, 1579, 1248, 1144, 1041, 968, 788, 693cm^{-1}. ESI-MS calcd for $C_{12}H_{16}O_2$ (M+Na$^+$): 192.11448; found: 192.11442.



Methyl (*E*)-2-(3-hydroxy-3-methylbut-1-en-1-yl)benzoate (27). Colorless oil (25.8 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.42 – 7.35 (m, 1H), 7.26 (d, *J* = 16.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 1.95 (bs, 1H), 1.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 140.4, 139.2, 132.2, 130.5, 128.6, 127.6, 127.1, 125.7, 71.2, 52.2, 29.8. IR (film): 3434, 2951, 1463, 1434, 1277, 1128, 966, 752 cm^{-1}. ESI-MS calcd for $C_{13}H_{16}O_3Na$ (M+Na$^+$): 243.09916; found: 243.09895.

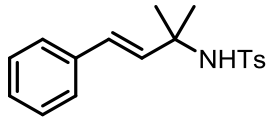


Methyl *(E)*-3-(2-(*(E)*-3-hydroxy-3-methylbut-1-en-1-yl)phenyl)acrylate (28). Prepared analogously except that 1,2-dichloroethane was used as a solvent and the reaction was performed at 70°C. Colorless oil (21.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 15.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.41 (m, 1H), 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 – 7.23 (m, 1H), 6.91 (d, *J* = 15.8 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.20 (d, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 1.73 (bs, 1H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 142.9, 142.5, 137.6, 132.7, 130.1, 127.7, 127.5, 127.2, 123.5, 119.7, 71.4, 51.9, 30.0. IR (film): 3446,



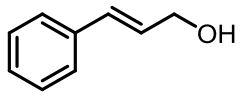
2971, 1715, 1698, 1629, 1435, 1318, 1271, 1194, 1167, 969, 761, 743. cm^{-1}. ESI-MS calcd for $C_{15}H_{18}O_3Na$ ($M+Na^+$): 269.11481; found: 269.11489.

***(E)*-4-Methyl-N-(2-methyl-4-phenylbut-3-en-2-yl)benzenesulfonamide (29).** White solid (14.9 mg, 74%).



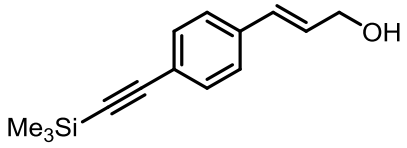
mp: 130-131°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.67 (m, 2H), 7.29 – 7.20 (m, 3H), 7.17 – 7.11 (m, 4H), 6.35 (d, *J* = 16.2 Hz, 1H), 5.93 (d, *J* = 16.1 Hz, 1H), 4.58 (bs, 1H), 2.33 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.0, 139.9, 136.5, 134.5, 129.5, 128.5, 128.3, 127.8, 127.5, 126.6, 57.0, 28.5, 21.6. IR (film): 3282, 2923, 1322, 1139, 1091, 962, 818, 754, 699, 660, 515 cm^{-1}. ESI-MS calcd for $C_{18}H_{21}NO_2SNa$ ($M+Na^+$): 338.11852; found: 338.11843.

***(E)*-3-Phenylprop-2-en-1-ol (30)** Colorless oil (33.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.18 (m,



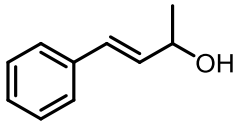
2H), 7.20 – 7.11 (m, 2H), 7.12 – 7.05 (m, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.15 (dd, *J* = 5.7, 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8, 131.2, 128.7, 128.6, 127.8, 126.6, 63.8. IR (film): 3360, 1668, 1449, 1009, 695, 744, 733, 676 cm^{-1}. ESI-MS calcd for $C_9H_{10}O$ ($M+H^+$): 134.07261; found: 134.07284.

***(E)*-3-(4-((Trimethylsilyl)ethynyl)phenyl)prop-2-en-1-ol (31).** Red solid (19.8 mg, 65%). mp: 72-74°C. ^{1}H



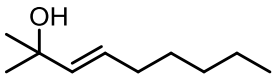
NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 6.59 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.38 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.33 (t, *J* = 4.9 Hz, 2H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): 136.9, 132.4, 130.5, 129.7, 126.4, 122.4, 105.2, 95.1, 63.7, 0.1. δ. IR (film): 3245, 2957, 2154, 1507, 1249, 971, 815, 758, 552cm^{-1}. ESI-MS calcd for $C_{14}H_{18}O_{1S}Si$ ($M+H^+$): 230.11214; found: 230.11198.

***(E)*-4-Phenylbut-3-en-2-ol (32).** Colorless oil (32.6 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m,



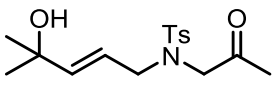
2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.20 (m, 1H), 6.57 (dd, *J* = 16.0, 1.1 Hz, 1H), 6.27 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.50 (app. quint, *J* = 6.4 Hz, 1H), 1.38 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8, 133.7, 129.5, 128.7, 127.8, 126.6, 69.1, 23.6. IR (film): 3365, 1491, 1448, 1058, 966, 747, 706 cm^{-1}. ESI-MS calcd for $C_{10}H_{12}ONa$ ($M+Na^+$): 171.07803; found: 171.07792.

(*E*)-2-Methylnon-3-en-2-ol (33). Prepared analogously except that 1,2-dichloroethane was used as a



solvent and the reaction was performed at 70°C. Colorless oil (54.4 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 – 5.55 (m, 2H), 2.08 – 1.95 (m, 2H), 1.45 – 1.22 (m, 7H), 1.31 (s, 6H), 0.93 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.0, 127.5, 70.8, 32.3, 31.5, 30.0, 29.2, 22.7, 14.2; IR (film): $\tilde{\nu}$ = 3364, 2960, 2925, 2856, 1461, 1376, 1148, 970, 906 cm^{-1}. ESI-MS calcd for $C_{10}H_{20}O$: 156.15142 (M^+); found: 156.15136.

Compound 34. Prepared analogously except that 1,2-dichloroethane was used as a solvent and the



reaction was performed at 70°C. Pale yellow oil (32.8 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.65 (m, 2H), 7.35 – 7.27 (m, 2H), 5.67 (dt, *J* = 15.6, 1.2 Hz, 1H), 5.49 (dt, *J* = 15.5, 6.8 Hz, 1H), 3.88 (s, 2H), 3.78 (dd, *J* = 6.8, 1.2 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 3H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.5, 144.1, 143.9, 136.3, 129.9,

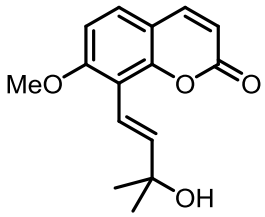
127.5, 120.7, 70.5, 56.1, 50.7, 29.7, 27.2, 21.7. IR (film): $\tilde{\nu}$ = 3516, 2972, 2927, 1733, 1335, 1155, 1099 cm^{-1}. ESI-MS calcd for $C_{16}H_{23}NO_4SNa$ ($M+Na^+$) 348.12400; found: 348.12366.

Compound 35. Prepared analogously except that 1,2-dichloroethane was used as a solvent and the reaction was performed at 70°C. Pale yellow oil (54.7 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.68 (m, 2H), 7.32 – 7.27 (m, 2H), 5.67 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.40 (dt, *J* = 15.6, 6.5 Hz, 1H), 4.51 (t, *J* = 5.4 Hz, 1H), 3.90 (dd, *J* = 6.6, 1.3 Hz, 2H), 3.39 (s, 6H), 3.20 (d, *J* = 5.4 Hz, 2H), 2.42 (s, 3H), 1.22 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 142.7, 137.5, 129.8, 127.4, 121.4, 104.9, 70.5, 55.2, 50.8, 48.6, 29.7, 21.6; IR (film): $\tilde{\nu}$ = 3512, 2969, 2928, 2837, 1448, 1336, 1154, 1122, 1087, 1068, 971 cm^{-1}. ESI-MS calcd for $C_{17}H_{27}NO_5SNa$ ($M+Na^+$) 380.15021; found: 380.15026.

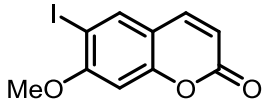
8-Iodo-7-methoxy-2H-chromen-2-one. Umbelliferone (4.00 g, 24.6 mmol) was dissolved in 20% ammonium hydroxide solution (100 mL). A solution of potassium iodide (10 g, 60 mmol) and iodine (6.5 g, 25.6 mmol) in water (200 mL) was added over 75 min. The mixture was stirred for 24 h at room temperature before sulfuric acid (100 mL, 4 M) was carefully added. A precipitate was formed which was filtered off. The solid material was suspended in acetone (100 mL) and the mixture was stirred at reflux temperature for 20 min before it was filtered; this extraction was repeated once. The filtrates were combined and the solvent was removed in vacuo. 8-Iodoumbelliferone was admixed with umbelliferone as a brown solid. The crude material was dissolved in acetone (30 mL). Potassium carbonate (3.88 g, 28 mmol) and MeI (1.73 mL, 27.8 mmol) were added, the resulting mixture was stirred at 40 °C for 24 h, diluted with ethyl acetate (50 mL) and filtered. The filtrate was evaporated under vacuum and the crude product was purified by flash chromatography (SiO_2, 30 to 40% EtOAc in hexane) to give the title product (1.78 g, 24%) and a second fraction containing *O*-methylate umbelliferone (1.21 g, 28%). The analytical and spectral data of the product were fully consistent with those described in the literature.[14]

8-(3-Hydroxy-3-methylbut-1-yn-1-yl)-7-methoxy-2H-chromen-2-one (40). $Pd(PPh_3)_2Cl_2$ (8.3 mg, 0.012 mmol), CuI (2 mg, 0.012 mmol) and PPh_3 (6.2 mg, 0.024 mmol) were added to a solution of 8-iodo-7-methoxy-2H-chromen-2-one (179 mg, 0.59 mmol) and 2-methyl-3-butin-2-ol (69 µL, 0.71 mmol) in Et_3N (4 mL) and DMF (1 mL). Ar was bubbled through the mixture for 15 min before it was stirred at 80°C for 12 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and the aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 30 to 50% EtOAc in hexane) to give the desired product (135.3 mg, 88%) as a pale yellow solid. mp: 151-152°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 9.4 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.25 (d, *J* = 9.5 Hz, 1H), 3.95 (s, 3H), 2.67 (bs, 1H), 1.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ163.0, 160.6, 155.6, 143.2, 128.4, 113.9, 112.9, 107.3, 105.2, 101.3, 71.8, 66.0, 56.7, 31.5. IR (film): 3416, 2977, 1723, 1699, 1612, 1296, 1269, 1120, 1093, 1045, 951, 828, 483 cm^{-1}. ESI-MS calcd for $C_{15}H_{14}O_4Na$ ($M+Na^+$): 281.07843; found: 281.07847.

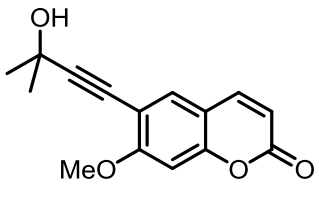
Murraol (41). Prepared according to the general procedure for *trans*-hydrogenation. Pale yellow solid (21.5 mg, 81%, 89:11 mixture of *E*-alkene and alkane). For analytical purposes, the mixture was separated by preparative HPLC to give a pure sample of murraol. mp: 129-130°C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 9.5 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 16.5 Hz, 1H), 6.94 (d, *J* = 16.5 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.25 (d, *J* = 9.4 Hz, 1H), 3.95 (s, 3H), 1.77 (s, 1H), 1.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0, 160.4, 152.8, 144.6, 144.0, 127.2, 114.5, 113.8, 113.3, 113.1, 107.7, 71.9, 56.3, 30.1. IR (film): 2959, 1719, 1712, 1598, 1555, 1273, 1248, 1020, 812 cm^{-1}. ESI-MS calcd for $C_{15}H_{16}O_2Na$ (M+Na$^+$): 283.09408; found: 283.09412.



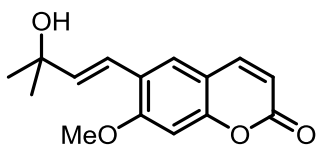
6-Iodo-7-methoxy-2H-chromen-2-one. A solution of freshly prepared MeONa [freshly prepared from Na (1.0 g) and dry methanol (25 mL)] was added to a suspension of *O*-methyl umbelliferone (1.0 g, 5.7 mmol) in dry methanol (10 mL). The mixture was stirred at reflux temperature for 4.5 h. After cooling and neutralization with HCl (2 M), the mixture was filtered and the filtrate was dried over Na_2SO_4 to give methyl (*Z*)-3-(2-hydroxy-4-methoxyphenyl)acrylate (1.1 g, 93%) as a white solid. NH_4OH (12.5 mL, 25%) was added to a solution of this ester (0.6 g, 2.9 mmol) in 1,4-dioxane (5 mL). A solution of iodine (0.79 g, 3.1 mmol) in aqueous KI (25 mL, 5% w/w) was added dropwise at 0°C. After 1 h the mixture was slightly acidified with H_2SO_4 (2.5 M) and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was dissolved in diphenyl ether (8 mL) and the resulting solution was stirred at 195°C for 4 h. After cooling, the mixture was purified by flash chromatography (SiO_2, 0, 10, 20% EtOAc in hexane) to give the title compound (230 mg 26%) as a light yellow solid, the analytical and spectral data of which were consistent with those described in the literature.[15]



6-(3-Hydroxy-3-methylbut-1-yn-1-yl)-7-methoxy-2H-chromen-2-one (42). $Pd(PPh_3)_2Cl_2$ (4.6 mg, 0.006 mmol), CuI (1.2 mg, 0.007 mmol) and PPh_3 (3.4 mg, 0.013 mmol) were added to a solution of 6-iodo-7-methoxy-2H-chromen-2-one (100 mg, 0.33 mmol) and 2-methyl-3-butin-2-ol (38 µL, 0.4 mmol) in Et_3N (2.5 mL) and DMF (0.5 mL). Ar was bubbled through the mixture for 15 min before it was stirred at 60°C for 24 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and the aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 50% EtOAc in hexane) to give the title compound as a yellow solid (68.9 mg, 81%). mp: 151-152°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 9.7, 1H), 7.50 (s, 1H), 6.78 (s, 1H), 6.28 (d, *J* = 9.5 Hz, 1H), 3.93 (s, 3H), 1.64 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 160.8, 155.7, 142.9, 132.6, 114.0, 112.3, 109.7, 99.3, 98.6, 76.7, 65.9, 56.5, 31.6. IR (film): 3415, 2977, 1697, 1615, 1601, 1558, 1316, 1292, 1151, 1011, 937, 830 cm^{-1}. ESI-MS calcd for $C_{15}H_{14}O_4Na$ (M+Na$^+$): 281.07843; found: 281.07832.



***E*-Suberenol (43).** Prepared according to the general procedure for *trans*-hydrogenation. Pale yellow solid (18 mg, 83%), mp: 163-164°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 9.5 Hz, 1H), 7.49 (s, 1H), 6.86 (d, *J* = 16.2 Hz,



1H), 6.79 (s, 1H), 6.37 (d, *J* = 16.2 Hz, 1H), 6.26 (d, *J* = 9.4 Hz, 1H), 3.91 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.2, 160.1, 155.3, 143.6, 139.3, 125.5, 123.9, 119.9, 113.6, 112.4, 99.1, 71.4, 56.1, 30.1. IR (film): 3411, 2970, 1556, 1692, 1618, 1608, 1370, 1281, 1281, 1152, 1019, 989, 912, 838, 618 cm^{-1}. ESI-MS calcd for $C_{15}H_{16}O_4Na$ ($M+Na^+$): 283.09408; found: 283.09398.

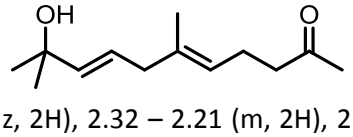
***(E)*-2-(5-Bromo-4-methylpent-3-en-1-yl)-2-methyl-1,3-dioxolane (45).** PPh_3 (1.55 g, 5.9 mmol) was added to a solution of (*E*)-2-methyl-5-(2-methyl-1,3-dioxolan-2-yl)pent-2-en-1-ol (1g, 5.37 mmol)[16] in CH_2Cl_2 (50 mL) at −30°C. Once dissolved, NBS (1.05g, 5.9 mmol) was added in one portion. The mixture was stirred for 1 h before water (50 mL) was added. The solution was allowed to reach ambient temperature, the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 7% EtOAc in hexane) to give the title compound as a colorless oil (987.7 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.59 (t, *J* = 6.8 Hz, 1H), 3.99 – 3.86 (m, 6H), 2.17 – 2.07 (m, 2H), 1.75 (s, 3H), 1.72 – 1.63 (m, 2H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.1, 131.1, 109.7, 64.8, 41.9, 38.3, 24.0, 23.1, 14.7. IR (film): 2981, 2878, 1446, 1376, 1208, 1128, 1052, 947, 864, 605 cm^{-1}. ESI-MS calcd for $C_{10}H_{18}O_2Br$ ($M+H^+$): 249.04848; found: 249.04838.

***(E)*-2,6-Dimethyl-9-(2-methyl-1,3-dioxolan-2-yl)non-6-en-3-yn-2-ol.** *n*-BuLi (5 mL, 8.1 mmol, 1.6 M in hexane) was added at 0°C to a solution of 2-methyl-3-butin-2-ol (0.414 mL, 4.28 mmol) in THF (15 mL). After 30 min, CuI (194 mg, 1 mmol) was introduced and the mixture was cooled to −30°C and stirred for 30 min at this temperature. A solution of compound **45** (508 mg, 2 mmol) in THF (5 mL) was slowly added and stirring was continued for 28 h at −30°C. The reaction was quenched with sat. aq. NH_4Cl (20 mL), the mixture was warmed to ambient temperature, the aqueous phase was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 25% EtOAc in hexane) to give the title compound (395 mg, 77%) as a 9.2/1 mixture of regioisomers. Analytically pure samples of the desired product were obtained by preparative HPLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 (tq, *J* = 7.2, 1.5 Hz, 1H), 3.99 – 3.88 (m, 4H), 2.86 (s, 2H), 2.16 – 2.07 (m, 2H) 1.92 (bs, 1H), 1.71 – 1.65 (m, 5H), 1.51 (s, 6H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.2, 125.4, 110.0, 87.5, 80.1, 65.4, 64.8, 38.9, 31.8, 28.7, 23.0, 22.8, 16.1. IR (film): 3399, 2982, 1709, 1364, 1235, 1165, 1038, 951, 860 cm^{-1}. ESI-MS calcd for $C_{15}H_{24}O_3Na$ ($M+Na^+$): 275.16184; found: 275.16179.

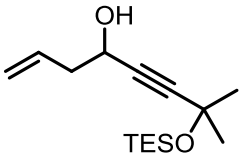
(*E*)-10-Hydroxy-6,10-dimethylundec-5-en-8-yn-2-one (46). Water (0.3 mL) and PTSA (6.5 mg, 0.03 mmol) were added to a solution of *(E)*-2,6-dimethyl-9-(2-methyl-1,3-dioxolan-2-yl)non-6-en-3-yn-2-ol (43.2 mg, 017 mmol) in acetone (1.5 mL). The solution was stirred at ambient temperature for 12 h before the reaction was quenched with Et_3N (1 drop). The mixture was concentrated under vacuum and diluted with water. The aqueous layer was extracted with E_2O (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (SiO_2, 30% EtOAc in hexane) to give the title compound as a colorless oil (22.3 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (tq, *J* = 7.2, 1.5 Hz, 1H), 2.86 (d, *J* = 1.6

Hz, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.33 – 2.24 (m, 2H), 2.14 (s, 3H), 1.67 (s, 3H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 208.7, 131.4, 124.1, 87.6, 79.9, 65.5, 43.5, 31.8, 30.1, 28.7, 22.5, 16.2. IR (film): 3392, 2982, 1710, 1364, 1234, 1163, 1036, 951, 862 cm^{-1}. ESI-MS calcd for $C_{13}H_{20}O_2Na$ ($M+Na^+$): 231.13555; found: 231.13560.

(3*E*,6*E*)-2,6-Dimethyl-10-oxo-3,6-undecadien-2-ol (47). Prepared according to the general procedure for *trans*-hydrogenation in 1,2-dichloroethane as the solvent at 70°C. Colorless oil (9.2 mg, 60%). ^{1}H NMR (400 MHz, CDCl3): δ 5.65 – 5.51 (m, 2H), 5.10 (tq, *J* = 7.2, 1.4 Hz, 1H), 2.65 (d, *J* = 5.8 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.32 – 2.21 (m, 2H), 2.13 (s, 3H), 1.59 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (101 MHz, CDCl3): δ 208.9, 139.6, 135.2, 125.2, 123.6, 70.8, 43.8, 42.4, 30.1, 30.0, 22.6, 16.2. IR (film): 3402, 2976, 2936, 1694, 1367, 1237, 1163, 1043, 982 cm^{-1}. ESI-MS calcd for $C_{13}H_{22}O_2Na$ ($M+Na^+$): 233.15120; found 233.15139.

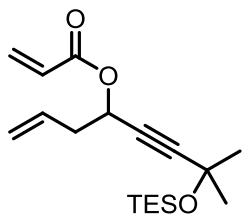


7-Methyl-7-((triethylsilyl)oxy)oct-1-en-5-yn-4-ol. $NaIO_4$ (2.4g, 11.3 mmol) was added to a solution of diol **48** (1.6g, 11.3 mmol) in CH_2Cl_2 (15 mL) and water (15 mL) at 0°C. The mixture was stirred at 0°C for 2h before it was diluted with H_2O (5 mL) and warmed to ambient temperature. The aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4. The solution of the crude aldehyde **49** was directly used in the next step.



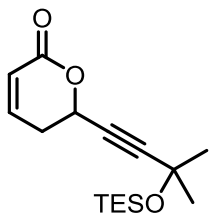
To a solution of compound **50** (1.5 g, 7.56 mmol) in THF (43 mL) was added *n*-BuLi (4.7 mL, 7.56 mmol, 1.6 M in hexane) at −78°C. The mixture was stirred for 1 h at this temperature before the solution of aldehyde **49** was added. The mixture was allowed to reach ambient temperature overnight and the reaction was quenched with NH_4Cl (sat. aq. 40 mL). The aqueous phase was extracted with E_2O (3 x 30 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 5% EtOAc in hexane) to give the title compound as a colorless oil (1.11 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 – 5.80 (m, 1H), 5.23 – 5.19 (m, 1H), 5.17 (t, *J* = 1.3 Hz, 1H), 4.43 (q, *J* = 6.0 Hz, 1H), 2.55 – 2.41 (m, 2H), 1.81 (d, *J* = 6.0 Hz, 1H), 1.47 (s, 6H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 133.2, 119.1, 90.7, 82.5, 66.3, 61.8, 42.2, 33.2, 33.2, 7.1, 6.2. IR (film): 3346, 2955, 2876, 1714, 1238, 1164, 1003, 832, 741 cm^{-1}. ESI-MS calcd for $C_{15}H_{28}O_2SiNa$ ($M+Na^+$): 291.17508; found 291.17503.

7-Methyl-7-((triethylsilyl)oxy)oct-1-en-5-yn-4-yl acrylate (51). Hünig's base (0.66 mL, 3.7 mmol) and acryloyl chloride (0.23 mL, 2.8 mmol) were added at 0°C to a solution of 7-methyl-7-((triethylsilyl)oxy)oct-1-en-5-yn-4-ol (505 mg, 1.88 mmol) in CH_2Cl_2 (19 mL). The mixture was stirred at ambient temperature for 4 h before the reaction was quenched with NH_4Cl (sat. aq. 20 mL). The aqueous phase was extracted with Et_2O (3 x 15 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 2% EtOAc in hexane) to give the title compound as a colorless oil (552.9 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.12 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.86 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.84 – 5.75 (m, 1H), 5.53 (t, *J* = 6.5 Hz, 1H), 55.20 – 5.11 (m, 2H), 2.55 (tt, *J* = 6.6, 1.3 Hz, 2H), 1.46 (d, *J* = 1.4 Hz, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 132.4, 131.4, 128.3, 118.8, 91.3, 79.2, 66.2, 63.5, 39.4, 33.1, 33.1, 7.1, 6.1. IR (film): 2954, 2876,

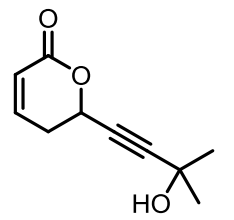


1732, 1405, 1241, 1212, 1208, 1082, 1004, 967, 742 cm^{-1}. ESI-MS calcd for $C_{18}H_{30}O_3SiNa$ ($M+Na^+$): 345.18564; found: 345.18580.

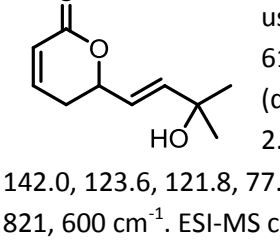
6-(3-Methyl-3-((triethylsilyl)oxy)but-1-yn-1-yl)-5,6-dihydro-2*H*-pyran-2-one. The HG^{II} catalyst (16 mg, 0.025 mmol) was added to a solution of compound **51** (410 mg, 1.27 mmol) in degassed 1,2-dichloroethane (25 mL). The mixture was stirred at 70°C for 3 h before a second batch of HG^{II} (16 mg, 0.025 mmol) was added. After stirring for another 3 h at 70°C, a third batch of HG^{II} (16 mg, 0.025 mmol) was introduced and stirring continued at this temperature for 18 h. The mixture was cooled to ambient temperature and concentrated under vacuum The residue was purified by flash chromatography (SiO_2, 10 to 15% EtOAc in hexane) to give the title compound as a brown oil (178.9 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 – 6.82 (m, 1H), 6.07 (dt, *J* = 9.8, 1.8 Hz, 1H), 5.21 (dd, *J* = 7.8, 5.3 Hz, 1H), 2.68 – 2.58 (m, 2H), 1.47 (s, 6H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 144.0, 121.8, 92.2, 77.9, 67.3, 66.2, 32.9, 30.2, 7.1, 6.2. IR (film): 2954, 2876, 1727, 1380, 1237, 1161, 1035, 1014, 813, 724 cm^{-1}. ESI-MS calcd for $C_{16}H_{26}O_3SiNa$ ($M+Na^+$): 317.15434; found: 317.15442.



6-(3-Hydroxy-3-methylbut-1-yn-1-yl)-5,6-dihydro-2H-pyran-2-one (52). AcOH (60 µL) and TBAF (1 M in THF, 0.35 mL, 0.35 mmol) were added at 0°C to a solution of 6-(3-methyl-3-((triethylsilyl)oxy)but-1-yn-1-yl)-5,6-dihydro-2*H*-pyran-2-one (104.3 mg, 0.35 mmol) in THF (5.7 mL). The reaction was stirred for 18 h at ambient temperature before it was quenched with $NaHCO_3$ (sat. aq. 5 mL). The aqueous phase was extracted with Et_2O (3 x 4 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 40% EtOAc in hexane) to give the title compound as a colorless oil (39.5 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (dt, *J* = 9.9, 4.2 Hz, 1H), 6.07 (dt, *J* = 9.8, 1.8 Hz, 1H), 5.20 (dd, *J* = 7.4, 6.0 Hz, 1H), 2.68 – 2.62 (m, 2H), 1.52 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 144.2, 121.6, 91.5, 77.8, 67.2, 65.2, 31.3, 31.2, 30.4. IR (film): 3408, 3982, 1718, 1380, 1239, 1150, 1047, 1015, 955, 813, 733 cm^{-1}. ESI-MS calcd for $C_{10}H_{12}O_3Na$ ($M+Na^+$): 203.06786; found: 203.06793.



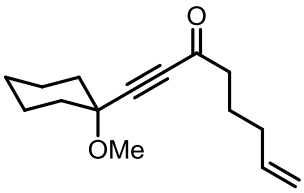
***(E)*-6-(3-hydroxy-3-methylbut-1-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (53)** Prepared according to the general procedure for *trans*-hydrogenation, except that 1,2-dichloroethane was used as a solvent and the reaction was performed at 40°C. Colorless oil (22.4 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 – 6.83 (m, 1H), 6.10 – 6.03 (m, 1H), 6.00 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.80 (dd, *J* = 15.7, 6.1 Hz, 1H), 4.97 – 4.89 (m, 1H), 2.48 – 2.41 (m, 2H), 1.34 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 144.7, 142.0, 123.6, 121.8, 77.6, 70.7, 30.0, 29.9. IR (film): 3408, 2972, 1702, 1369, 1199, 1154, 1086, 1018, 956, 821, 600 cm^{-1}. ESI-MS calcd for $C_{10}H_{14}O_3Na$ ($M+Na^+$): 205.08351; found 205.08371.



1-(Hept-6-en-1-yn-1-yl)-1-methoxycyclohexane (55). *n*-BuLi (2.26 mL, 3.6 mmol, 1.6 M in hexane) was added at 0°C to a solution of (1-ethynyl-1-methoxycyclohexane) (500 mg, 3.6 mmol) in THF (16 mL) and HMPA (7 mL). After stirring for 1 h at 0°C, the mixture was cooled to −78°C and 5-bromo-1-pentene (0.24 mL, 1.8 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight.

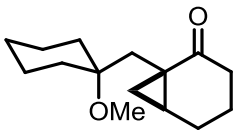
The reaction was quenched with NH_4Cl (sat. aq. 20 mL), the aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 2% EtOAc in hexane) to give the title compound as a colorless oil (370 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.10 – 4.92 (m, 2H), 3.34 (s, 3H), 2.25 (t, *J* = 7.1 Hz, 2H), 2.23 – 2.11 (m, 2H), 1.91 – 1.80 (m, 2H), 1.70 – 1.41 (m, 9H), 1.34 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 115.3, 86.1, 81.5, 74.2, 50.6, 37.2, 32.9, 28.3, 25.7, 23.1, 18.2. IR (film): 2935, 2857, 1446, 1292, 1092, 1080, 921, 910 cm^{-1}. ESI-MS calcd for $C_{14}H_{22}ONa$ (M+Na$^+$): 229.15628; found: 229.15649.

1-((1-Methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane (56). Prepared according to the general procedure for *trans*-hydrogenation; colorless oil (29.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (s, 3H), 1.92 – 1.72 (m, 4H), 1.71 – 1.47 (m, 7H), 1.47 – 1.35 (m, 2H), 1.36 – 1.24 (m, 3H), 1.24 – 1.06 (m, 2H), 0.86 (dt, *J* = 8.1, 4.1 Hz, 1H), 0.40 (t, *J* = 4.2 Hz, 1H), 0.31 (dd, *J* = 8.0, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 77.4, 48.2, 42.6, 35.1, 34.5, 32.5, 27,1, 26.1, 25.0, 23.9, 22.1, 22.1, 13.5. IR (film): 2930, 2853, 1456, 1288, 1080 1026, 806 cm^{-1}. ESI-MS calcd for $C_{14}H_{25}O$ (M+H$^+$): 209.18999; found: 209.19007.



1-(1-Methoxycyclohexyl)oct-7-en-1-yn-3-one (57). *n*-BuLi (0.77 mL, 1.2 mmol, 1.6 M in hexane) was added at 0°C to a solution of 1-ethynyl-1-methoxycyclohexane (171 mg, 1.2 mmol) in THF (5 mL). After stirring for 1 h at 0°C, the mixture was cooled to −78 °C and a solution of N-methoxy-N-methylhex-5-enamide (147 mg, 0.9 mL) in THF (3 mL) was added dropwise. The mixture was warmed to ambient temperature and stirred for another 5 h. The reaction was quenched with NH_4Cl (sat. aq. 5 mL), the aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 4% EtOAc in hexane) to give the title compound as a colorless oil (150.7 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.07 – 4.97 (m, 2H), 3.37 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.16 – 2.04 (m, 2H), 1.97 – 1.88 (m, 2H), 1.83 – 1.75 (m, 2H), 1.71 – 1.59 (m, 4H), 1.57 – 1.47 (m, 3H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 187.7, 137.6, 115.7, 93.2, 85.1, 74.0, 51.3, 45.0, 36.1, 32.9, 25.3, 23.3, 22.6. IR (film): 2935, 2559, 2203, 1675, 1146, 1288, 1222, 1093, 1079, 926, 907 cm^{-1}. ESI-MS calcd for $C_{15}H_{22}O_2Na$ (M+Na$^+$): 257.15120; found: 257.15114.

(1S,6S)-1-((1-Methoxycyclohexyl)methyl)bicyclo[4.1.0]heptan-2-one (58) Prepared according to the general procedure for *trans*-hydrogenation as a colorless oil (17.1 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (s, 3H), 2.84 (d, *J* = 15.1, 1H), 2.25 (dt, *J* = 17.0, 4.4 Hz, 1H), 2.17 – 1.92 (m, 3H), 1.82 – 1.67 (m, 3H), 1.63 – 1.36 (m, 7H), 1.27 – 1.07 (m, 3H), 0.99 (t, *J* = 5.7 Hz, 1H), 0.83 (d, *J* = 15.1 Hz, 1H), 0.74 (dd, *J* = 8.1, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.9, 76.4, 48.2, 39.5, 37.9, 34.8, 34.7, 29.9, 25.9, 22.0, 21.9, 21.9, 21.8, 18.2, 16.2.. IR (film): 2928, 2855, 1687, 1455, 1359, 1146, 1072, 910, 845 cm^{-1}. ESI-MS calcd for $C_{15}H_{24}O_2Na$ (M+Na$^+$): 259.16685; found: 259.16710.

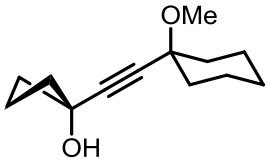


5-(1,3-Dioxan-2-yl)-1-(1-methoxycyclohexyl)pent-1-yn-3-one (67). *n*-BuLi (0.80 mL, 1.3 mmol, 1.6 M in hexane) was added at 0°C to a solution of 1-ethynyl-1-methoxy cyclohexane (176.8 mg, 1.3 mmol) in THF (5 mL). After stirring for 1 h at 0°C, the mixture was cooled to −78 °C before a solution of 3-(1,3-dioxan-2-yl)-N-methoxy-N-methylpropanamide (190 mg, 0.93 mmol) in THF (3 mL) was added dropwise. The mixture was allowed to warm to ambient temperature and stirring was continued for 5 h. The reaction was quenched with sat. aq. NH_4Cl (5 mL), the aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (SiO_2, 4% EtOAc in hexane) to give the title compound as a colorless oil (253.6 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (t, *J* = 4.9 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.80 – 3.68 (m, 2H), 3.37 (s, 3H), 2.72 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.83 (m, 4H), 1.72 – 1.59 (m, 4H), 1.57 – 1.44 (m, 4H), 1.38 – 1.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): 187.0, 100.6, 93.1, 85.0, 74.0, 67.0, 51.4, 40.0, 36.2, 29.2, 25.8, 25.3, 22.6.δ. IR (film): 2935, 2856, 2206, 1676, 1288, 1145, 1132, 1091, 1079 cm^{-1}. ESI-MS calcd for $C_{16}H_{24}O_4Na$ (M+Na$^+$): 303.15668; found: 303.15672.

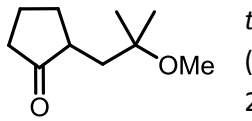
1-(1,3-Dioxan-2-yl)-5-(1-methoxycyclohexyl)pentan-3-one (68). Prepared according to the general procedure for *trans*-hydrogenation. Colorless oil (20.1 mg, 63%) as a mixture of alkane and *E*-olefin (89:11) Spectral data of the major product: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.56 (t, *J* = 4.9 Hz, 1H), 4.14 – 4.01 (m, 2H), 3.78 – 3.67 (m, 2H), 3.08 (s, 3H), 2.54 (t, *J* = 7.3 Hz, 2H), 2.47 – 2.38 (m, 2H), 2.17 – 1.97 (m, 1H), 1.87 (td, *J* = 7.3, 4.9 Hz, 2H), 1.74 – 1.62 (m, 4H), 1.54 – 1.18 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.8, 101.1, 74.4, 67.0, 48.1, 37.0, 36.3, 34.2, 29.4, 29.2, 26.0, 25.9, 21.9. IR (film): 2931, 2853, 1712, 1374, 1241, 1144, 1072, 1009, 895 cm^{-1}. ESI-MS calcd for $C_{16}H_{28}O_4Na$ (M+Na$^+$): 307.18798; found: 307.18796.

1-(3-Methoxy-3-methylbut-1-yn-1-yl)cyclobutan-1-ol (70). *n*-BuLi (0.4 mL, 0.4 mmol, 1.6 M in hexane) was added at −78°C to a solution of 3-methoxy-3-methylbut-1-yne (43 mg, 0.44 mmol) and TMEDA (0.06 mL, 0.4 mmol) in THF (1.5 mL). The mixture was stirred for 1 h at −78°C before cyclobutanone (0.015 mL, 0.2 mmol) was slowly added at this temperature. The mixture was warmed to −25°C over the course of 4 h. The reaction was quenched with sat. aq. NH_4Cl (5 mL). After reaching ambient temperature, the aqueous phase was extracted with Et_2O (3 x 3 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 7.5% EtOAc in hexane) to give the desired product as a colorless oil (25.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.36 (s, 3H), 2.47 – 2.35 (m, 2H), 2.32 – 2.19 (m, 2H), 2.03 (bs, 1H), 1.86 – 1.75 (m, 2H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 87.9, 85.2, 70.6, 67.9, 51.7, 38.8, 28.4, 13.0. IR (film): 3359, 2985, 2939, 1465, 1361, 1272, 1247, 1170, 1148, 1114, 1075, 747 cm^{-1}. ESI-MS calcd for $C_{10}H_{16}O_2Na$ (M+Na$^+$): 191.10425; found: 191.10429.

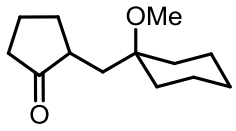
1-((1-Methoxycyclohexyl)ethynyl)cyclobutan-1-ol (73). Prepared analogously from 1-ethynyl-1-methoxycyclohexane) as a colorless oil (196.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.36 (s, 3H), 2.46 – 2.37 (m, 2H), 2.33 – 2.21 (m, 2H), 1.95 – 1.86 (m, 2H), 1.85 – 1.75 (m, 2H), 1.69 – 1.62 (m, 2H), 1.60 – 1.47 (m, 5H), 1.37 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 89.9, 84.4, 74.0, 68.0, 50.8, 34.0, 36.9, 25.6, 23.0, 13.0. IR (film): 3382, 2934, 2857, 1446, 1296, 1246, 1118, 1092, 1079, 1069, 992, 907, 740 cm^{-1}. ESI-MS calcd for $C_{13}H_{20}O_2Na$ (M+Na$^+$): 231.13555; found: 231.13568.



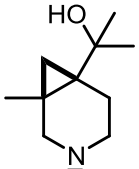
2-(2-Methoxy-2-methylpropyl)cyclopentan-1-one (72). Prepared according to the general procedure for *trans*-hydrogenation; colorless oil (12.1 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.17 (s, 3H), 2.47 – 2.38 (m, 1H), 2.36 – 2.26 (m, 1H), 2.17 – 2.10 (m, 2H), 2.09 – 1.95 (m, 2H), 1.83 – 1.65 (m, 1H), 1.57 – 1.45 (m, 1H), 1.34 – 1.23 (m, 1H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 221.4, 77.3, 77.0, 77.7, 74.2, 49.2, 45.9, 39.3, 37.3, 32.2, 26.2, 25.2, 20.8. IR (film): 2971, 2939, 1731, 1709, 1382, 1367, 1184, 1153, 1073 cm^{-1}. ESI-MS calcd for $C_{10}H_{18}O_2Na$ (M+Na$^+$): 193.11990; found: 193.11995.



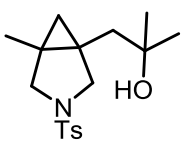
2-((1-Methoxycyclohexyl)methyl)cyclopentan-1-one (74). Prepared according to the general procedure for *trans*-hydrogenation; colorless oil (33.5 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13 (s, 3H), 2.46 – 2.38 (m, 1H), 2.36 – 2.24 (m, 1H), 2.18 – 1.94 (m, 4H), 1.77 – 1.67 (m, 3H), 1.58 – 1.40 (m, 6H), 1.31 – 1.17 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 221.6, 77.3, 77.0, 76.7, 74.6, 48.1, 44.9, 37.3, 36.1, 35.2, 33.9, 32.5, 25.8, 21.8, 20.8. IR (film): 2931, 2857, 1735, 1456, 1154, 1072, 933 cm^{-1}. ESI-MS calcd for $C_{13}H_{22}O_2Na$ (M+Na$^+$): 211.16925; found: 211.16943.



2-((1S*,6R*)-1-Methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)propan-2-ol (60). A solution of enyne **59** (32.1 mg, 0.1 mmol)[10] and $[Cp^*RuI]_4$ (3.6 mg, 2.5 mol%) in 1,2-dichloroethane (1 mL) under Ar was immersed in a preheated oil bath (70°C). H_2 gas was then bubbled through the solution for 3 min before the mixture was stirred at this temperature for 2 h under the resulting hydrogen atmosphere. The mixture was cooled to ambient temperature, all volatile materials were evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 5/1 to 3/1) to give the title compound as a pale yellow syrup (19.1 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.59 (m, 2H), 7.36 – 7.28 (m, 2H), 3.52 (dd, *J* = 11.3, 1.8 Hz, 1H), 3.41 (dddd, *J* = 11.7, 6.4, 3.4, 1.8 Hz, 1H), 2.43 (s, 3H), 2.41 (d, *J* = 11.3 Hz, 1H), 2.21 (ddd, *J* = 11.6, 10.8, 5.5 Hz, 1H), 1.84 (ddd, *J* = 14.1, 10.8, 6.4 Hz, 1H), 1.72 (dddd, *J* = 14.1, 5.5, 3.4, 1.0 Hz, 1H), 1.32 (s, 3H), 1.25 (s, 3H), 1.19 (s, 3H), 0.80 (d, *J* = 4.4 Hz, 1H), 0.58 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 133.6, 129.8, 127.8, 72.7, 52.0, 44.5, 31.0, 29.5, 28.6, 26.5, 22.5, 21.7, 18.9, 16.9. IR (film): $\tilde{\nu}$ = 3538, 2975, 2926, 2869, 1337, 1163, 1090, 969 cm^{-1}. ESI-MS calcd for $C_{17}H_{25}NO_3SNa$ (M+Na$^+$) 346.14474; found: 346.14451.

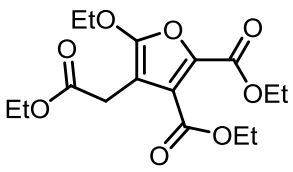


2-Methyl-1-(5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)propan-2-ol (61). H_2 gas was bubbled for 5 min through a stirred solution of enyne **59** (32.1 mg, 0.1 mmol)[10] and complex **62** (4.0 mg, 0.005 mmol, 5 mol%) in CH_2Cl_2 (1 mL). Stirring was continued for 16 h under H_2 atmosphere before all volatile matertials were removed under vacuum and the residue was purified by flash chromatography (hexane/EtOAc, 5/1 to 2/1) to yield the title



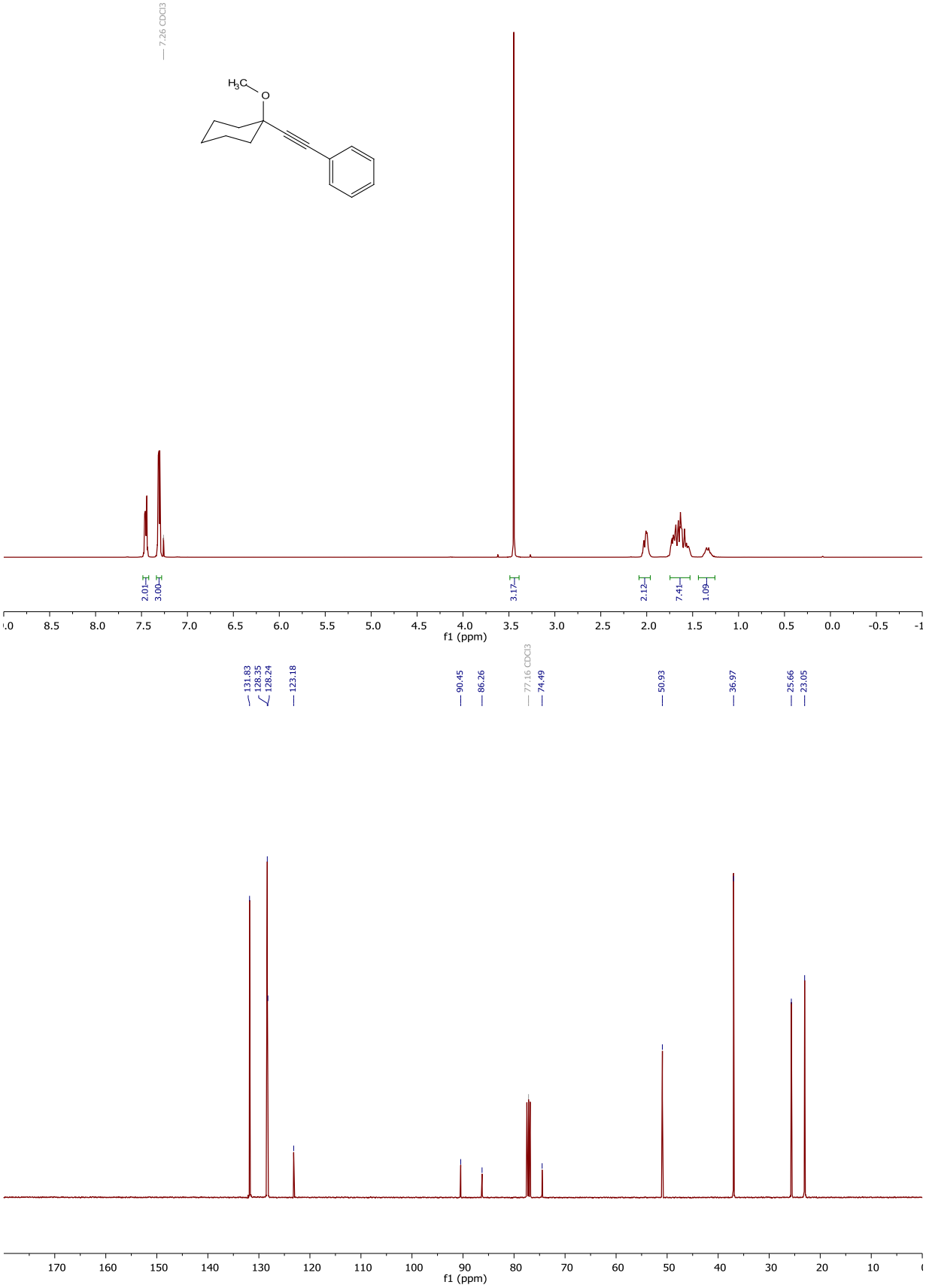
compound as pale yellow oil that solidified upon standing (22.2 mg, 71%, containing trace amounts of over-reduced alkyne as an impurity). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.65 (m, 2H), 7.35 – 7.30 (m, 2H), 3.75 (d, *J* = 9.6 Hz, 1H), 3.49 (d, *J* = 8.9 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.76 – 2.68 (m, 1H), 2.44 (s, 3H), 1.76 (d, *J* = 14.6 Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H), 1.14 (d, *J* = 14.7 Hz, 1H), 1.04 (s, 3H), 0.90 – 0.83 (m, 1H), 0.36 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 133.7, 129.7, 127.7, 72.1, 55.1, 54.5, 43.7, 31.7, 29.0, 27.4, 25.2, 21.7, 20.1, 15.0. IR (film): 3528, 2968, 2926, 2871, 1453, 1339, 1162, 1117, 1092, 1056, 1016 cm^{-1}. ESI-MS calcd for $C_{17}H_{26}NO_3S$ ($M+H^+$) 324.16279; found: 324.16247.

Diethyl 5-ethoxy-4-(2-ethoxy-2-oxoethyl)furan-2,3-dicarboxylate (76). Hydrogen gas was bubbled through a stirred solution of [{Cp*RuCl}$_4$] (2.8 mg, 0.0026 mmol, 1.25 mol%) in THF (10 mL) for 5 min.

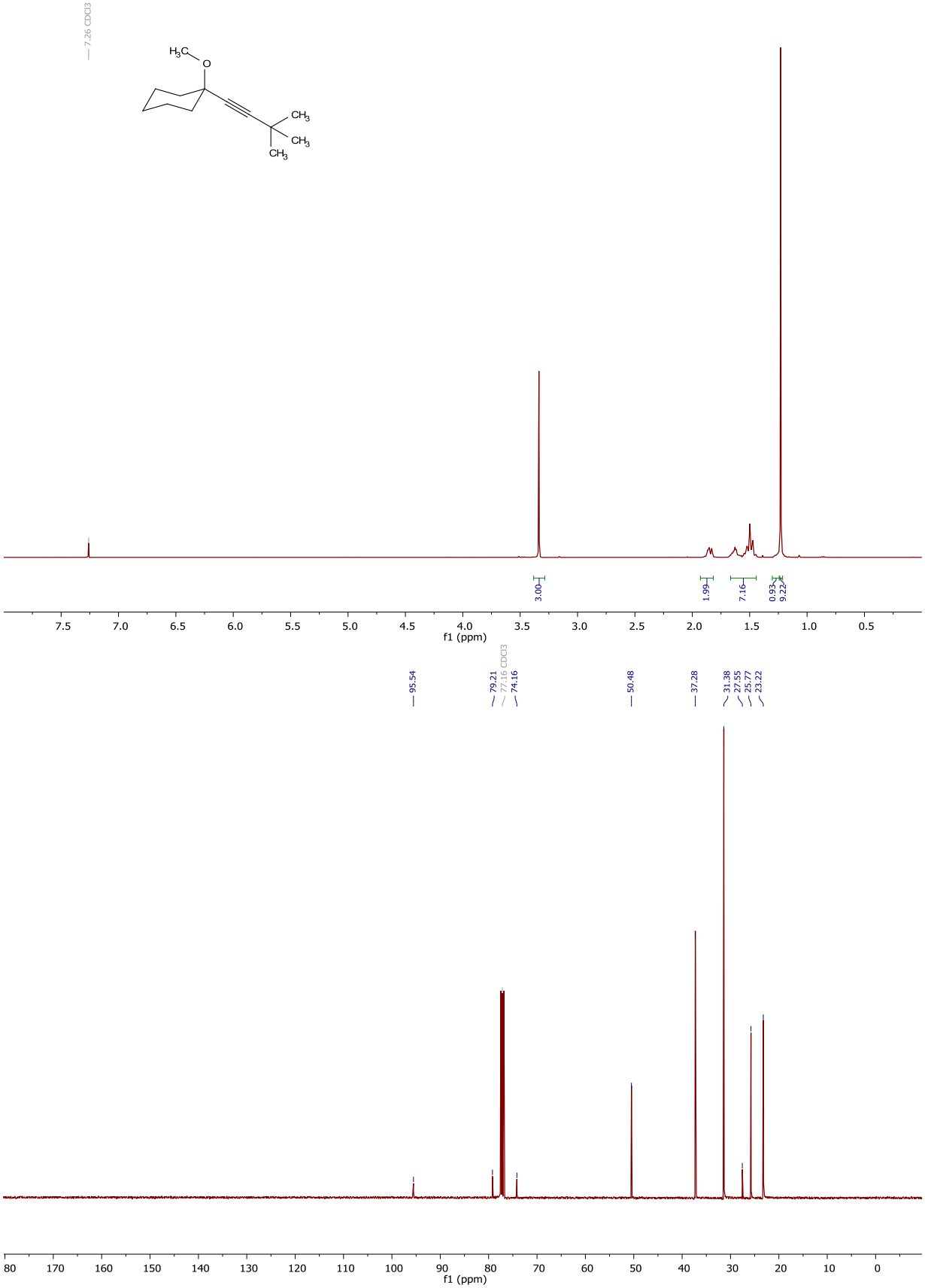


Diethyl acetylenedicarboxylate (32 µL, 0.2 mmol) was added and stirring was continued for 3 h under H_2 atmosphere. For work up, all volatile materials were removed under vacuum and the residue was purified by flash chromatography (pentane/Et_2O, 3/1) to yield the title compound as pale yellow oil (23.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (q, *J* = 7.3 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.4 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 163.1, 158.0, 157.7, 133.1, 127.3, 95.2, 68.8, 61.6, 61.2, 28.3, 15.1, 14.4, 14.3, 14.2. IR (film): 2983, 2939, 2907, 1714, 1634, 1560, 1442, 1371, 1303, 1276, 1175, 1156, 1058, 1023 cm^{-1}. ESI-MS calcd for $C_{16}H_{23}O_8$ ($M+H^+$) 343.13875; found: 343.13846.

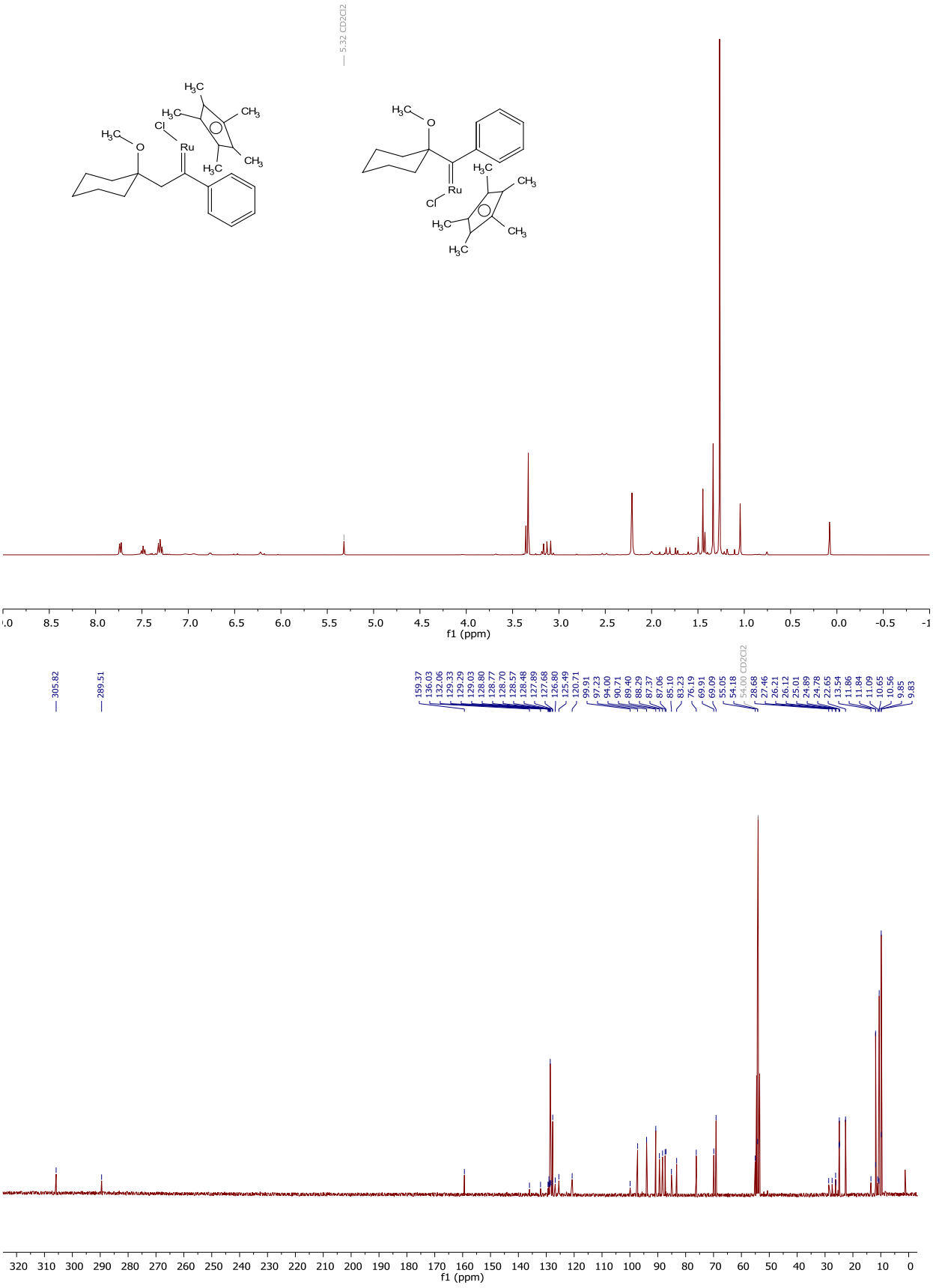
((1-methoxycyclohexyl)ethynyl)benzene (4d)



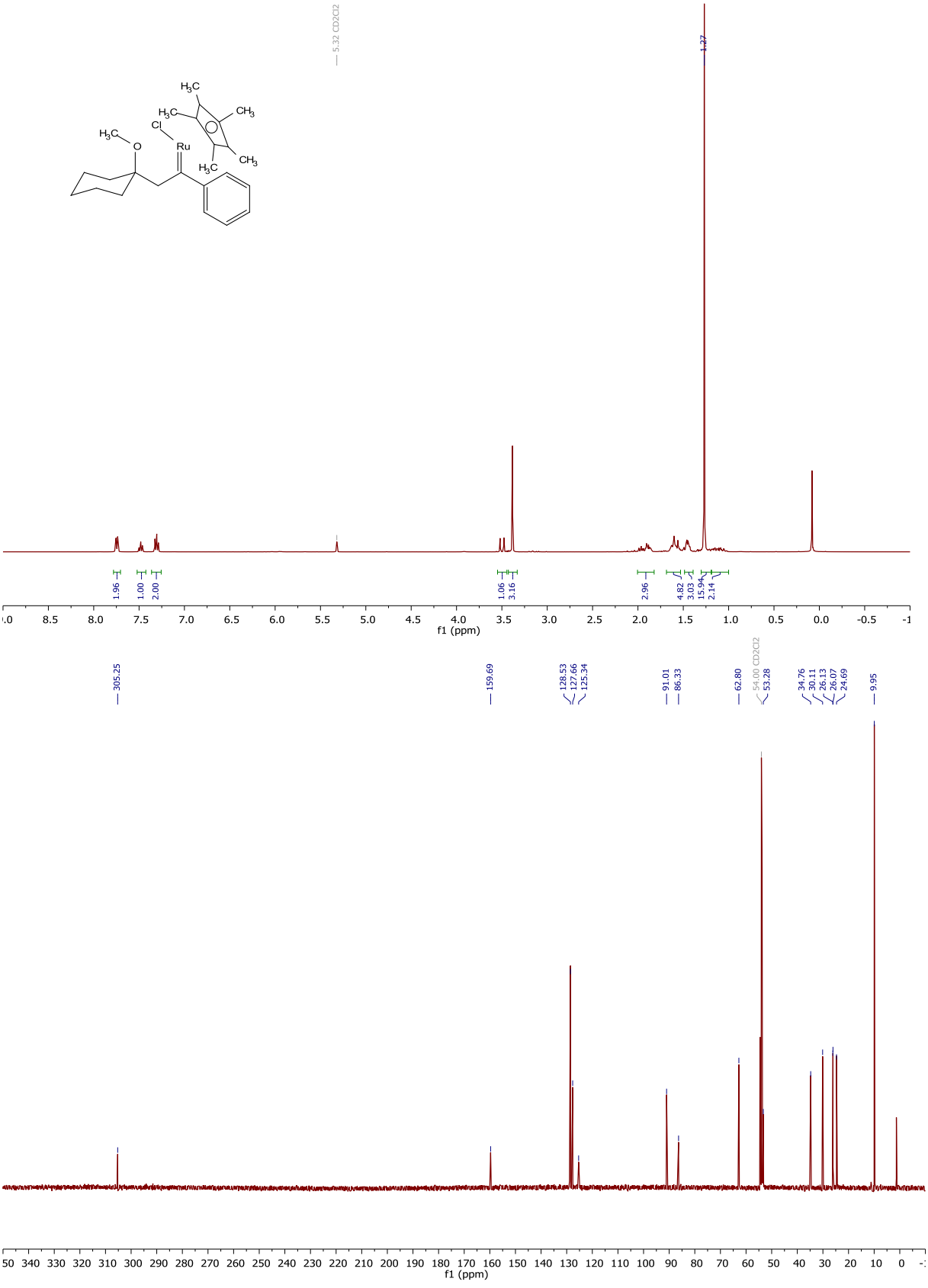
1-(3,3-dimethylbut-1-yn-1-yl)-1-methoxycyclohexane (4f)



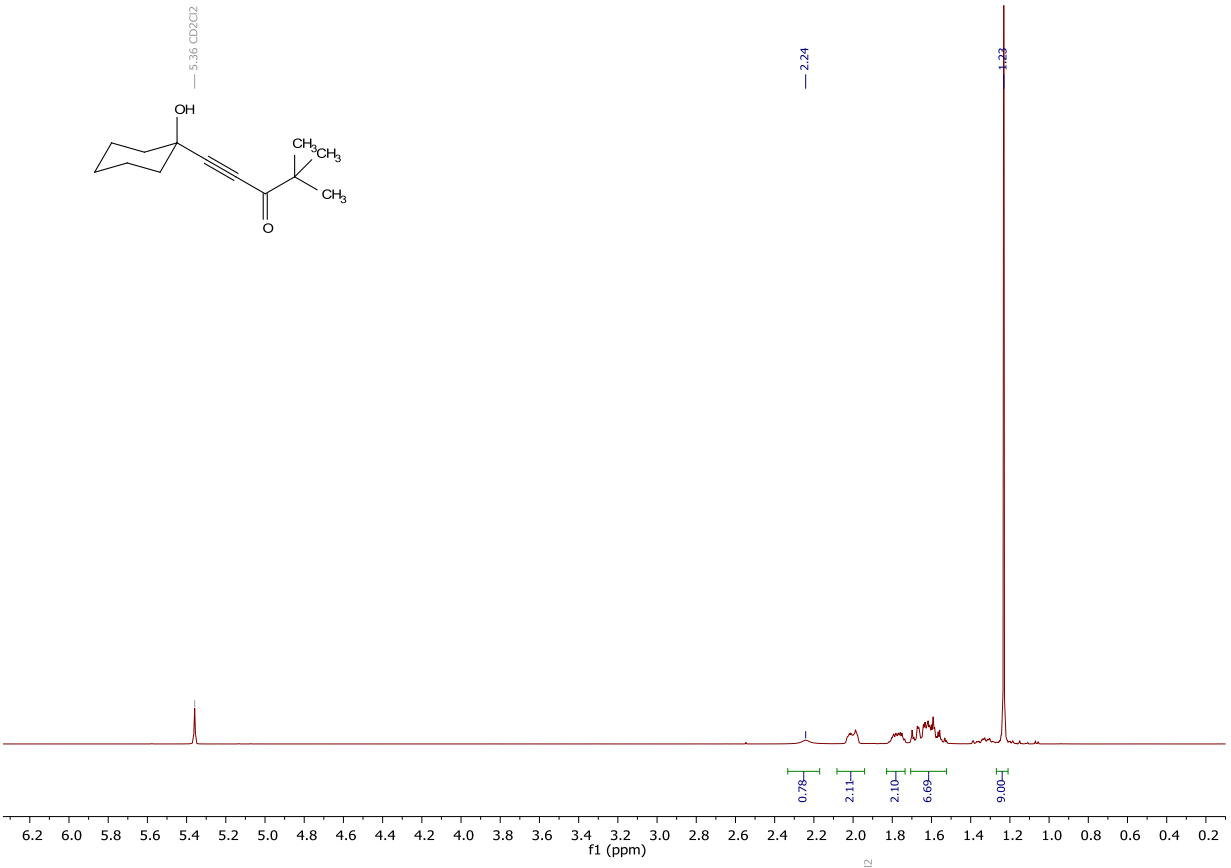
Ruthenium carbene (7d) + Isomeric Ruthenium carbene (6d): Crude reaction mixture

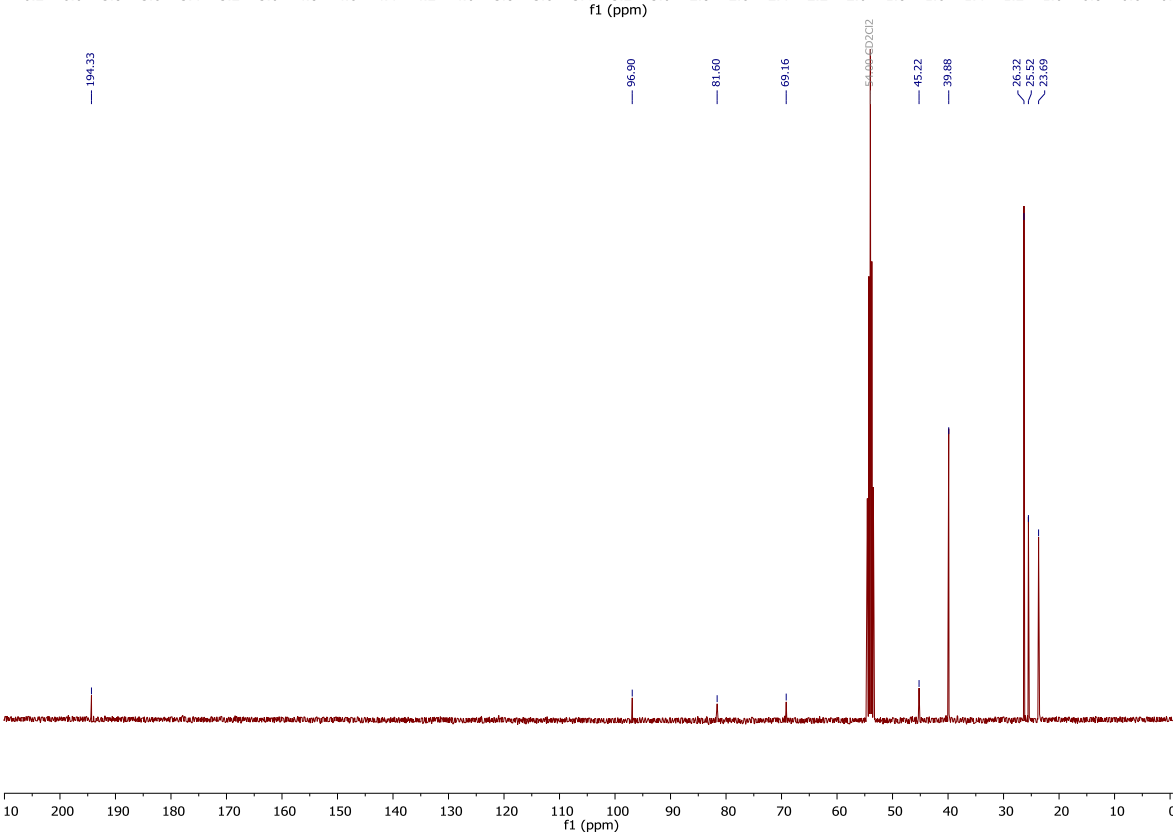


Ruthenium carbene (7d) after Crystallization

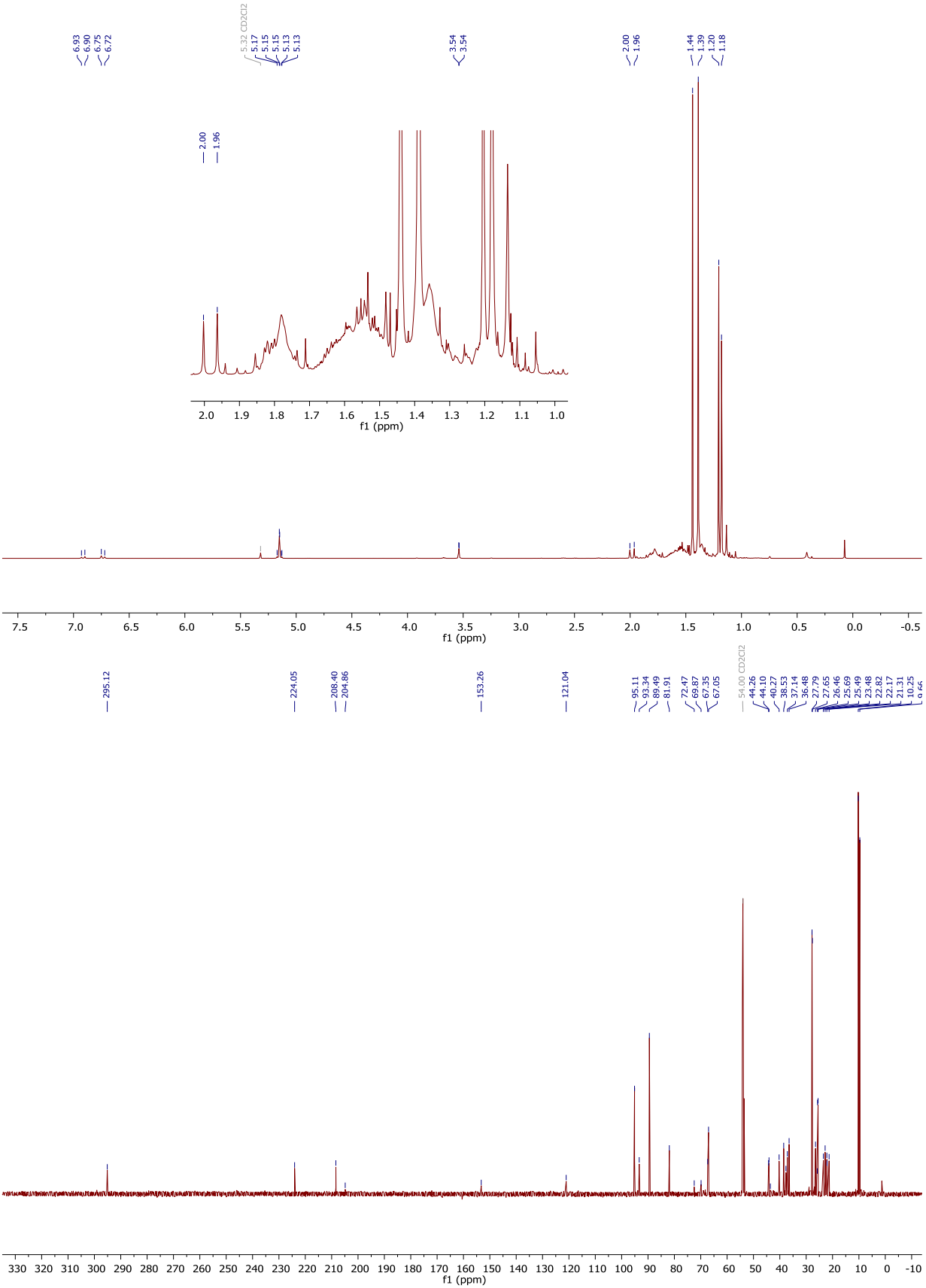


(1-Hydroxycyclohexyl)-4,4-dimethylpent-1-yn-3-one (11b)

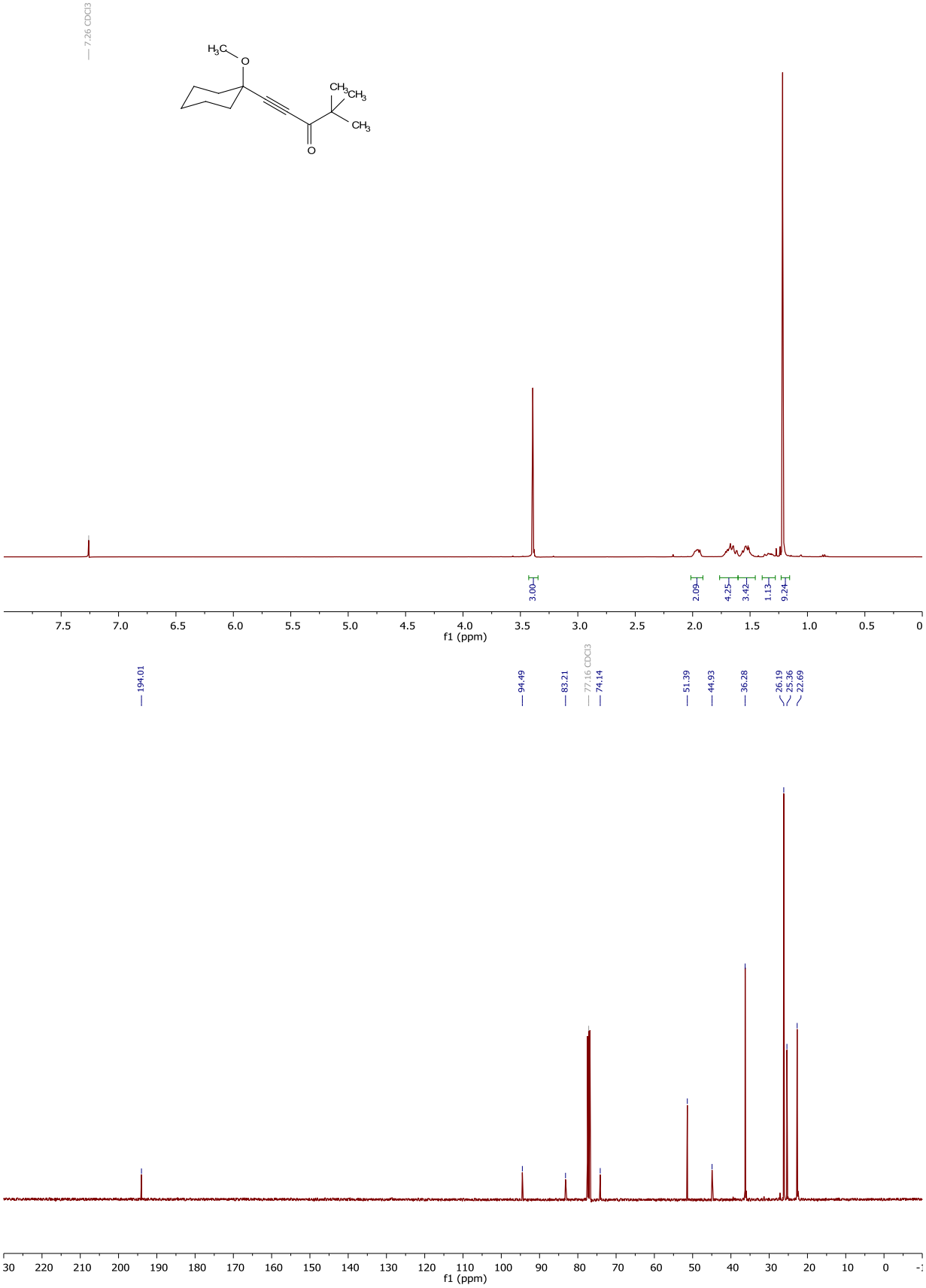




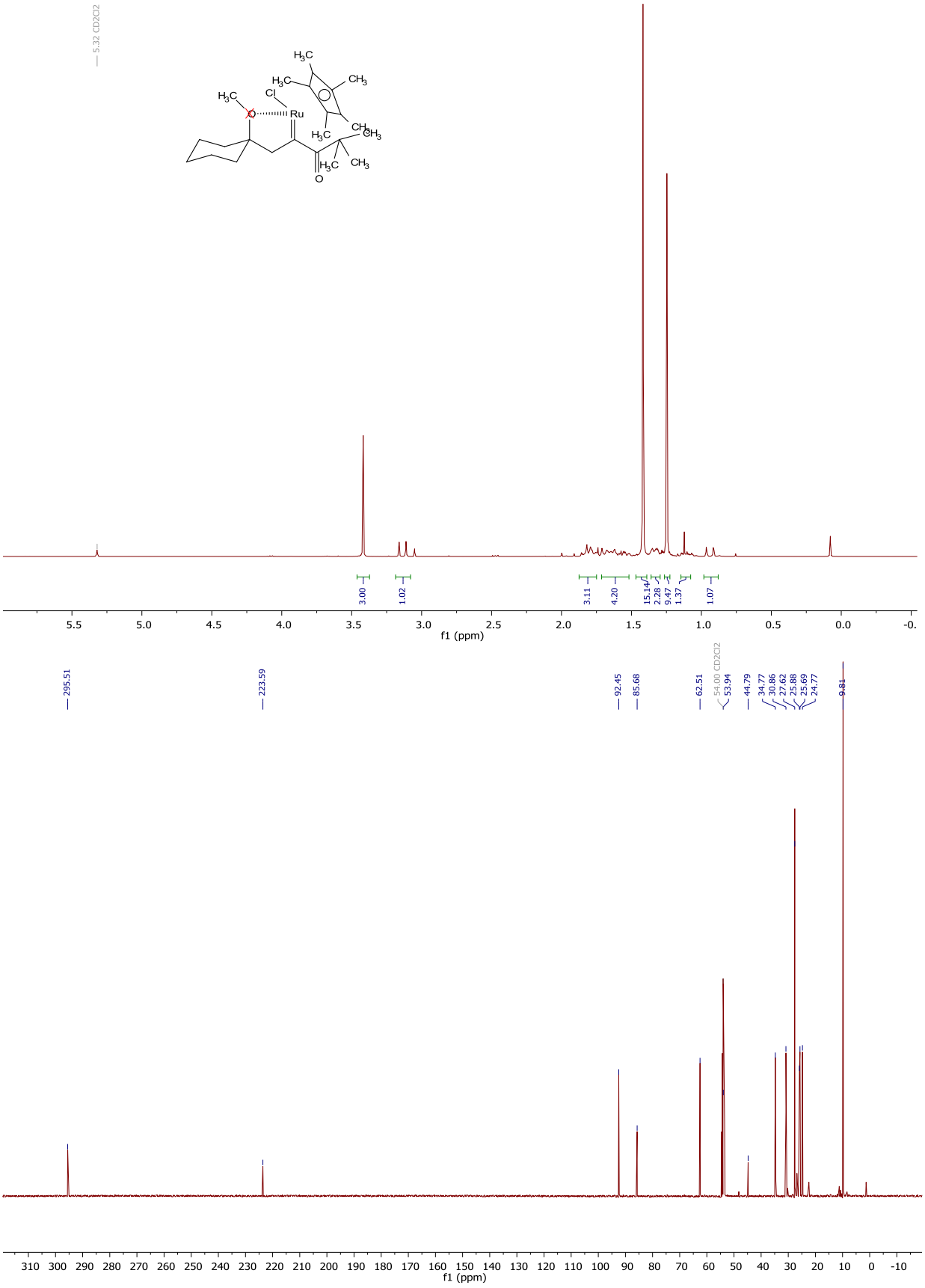
Ruthenium carbene (12b) in a mixture with the π-Complex 13 and free Ligand 14



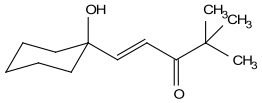
1-(1-methoxycyclohexyl)-4,4-dimethylpent-1-yn-3-one (11a)

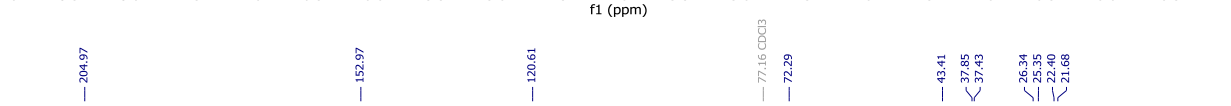


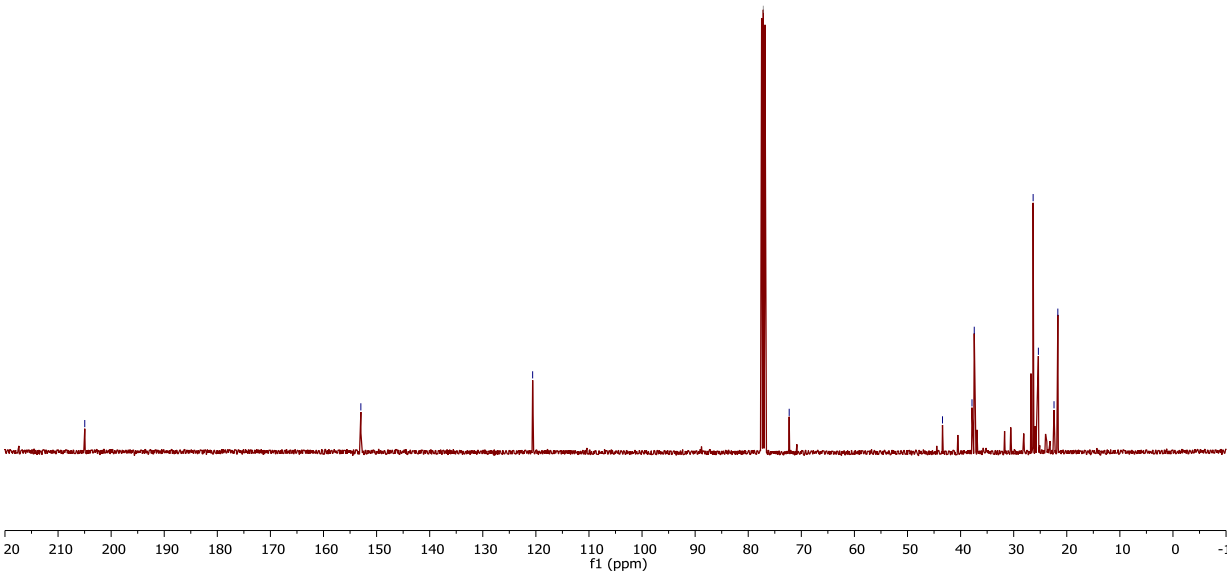
Ruthenium carbene (12a)



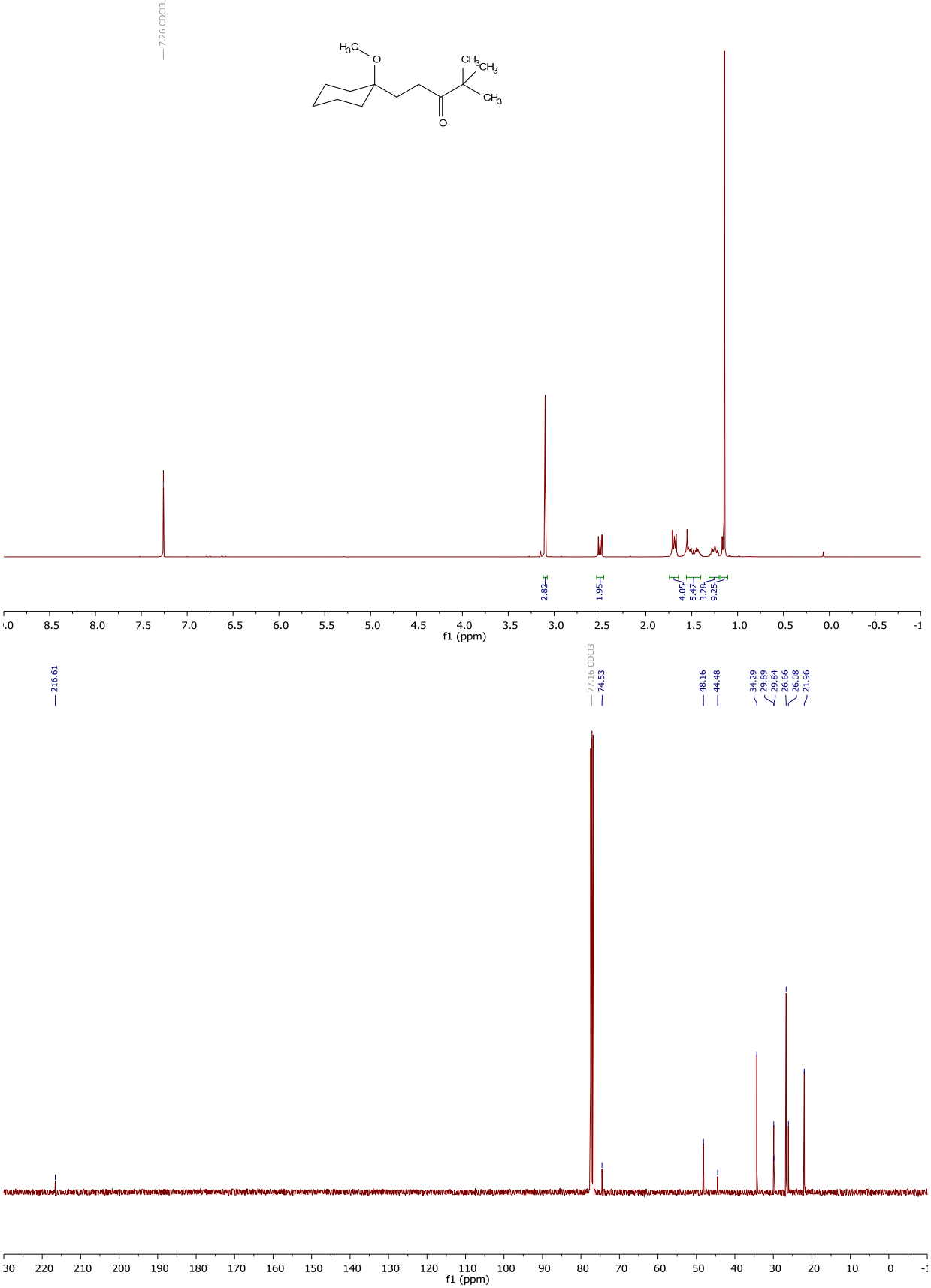
***(E)*-1-(1-Hydroxycyclohexyl)-4,4-dimethylpent-1-en-3-one (14)**



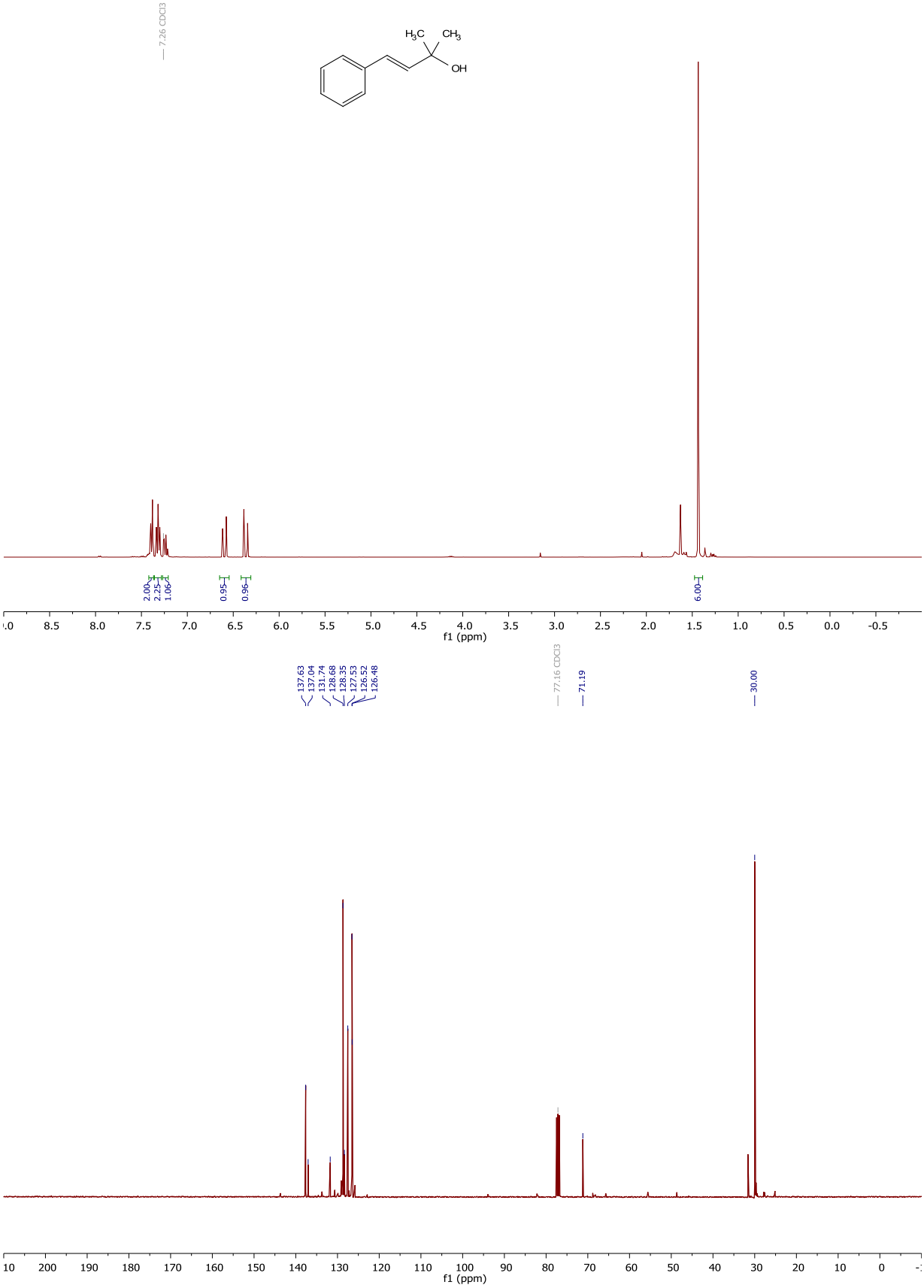




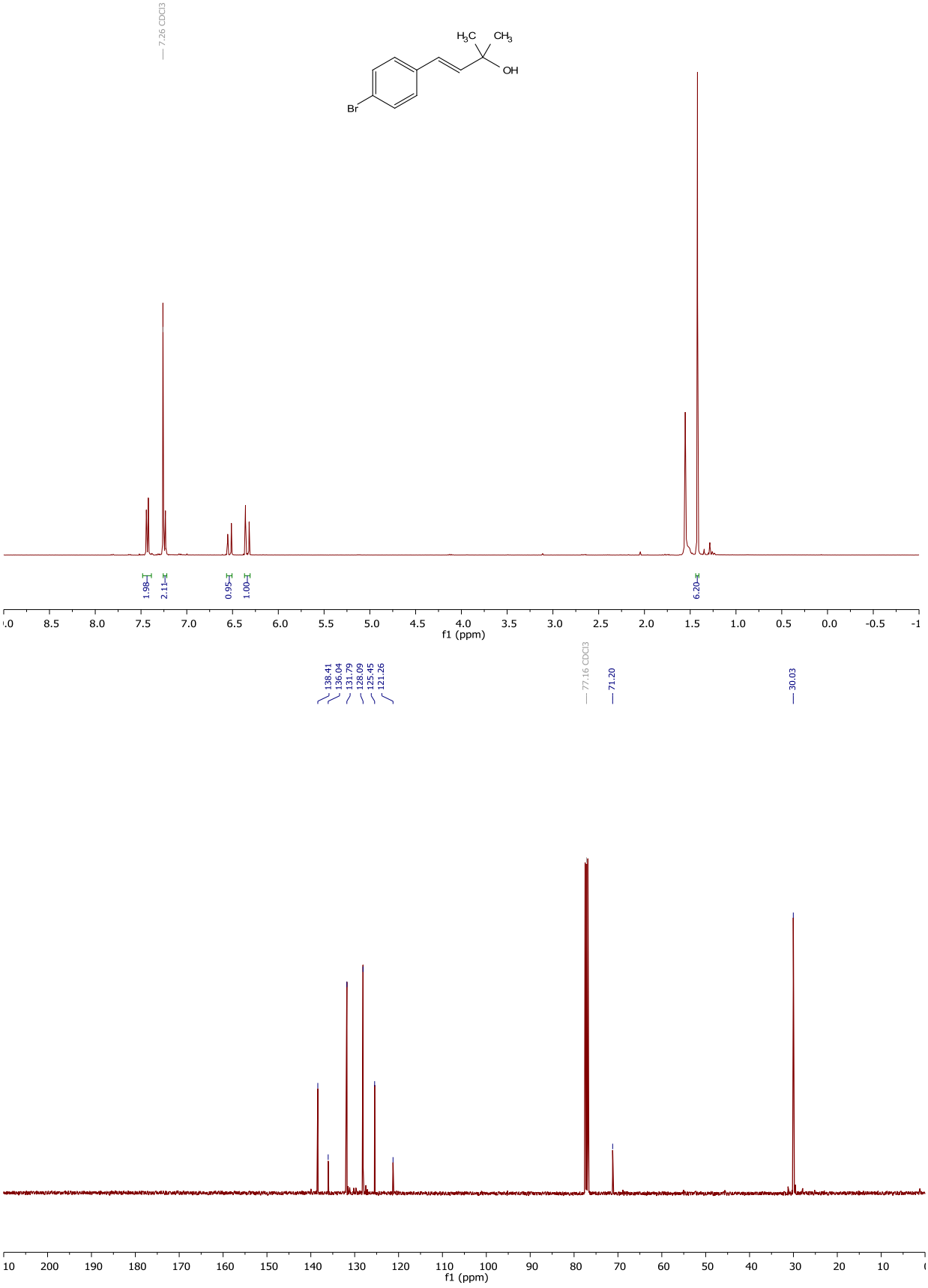
1-(1-Methoxycyclohexyl)-4,4-dimethylpentan-3-one (15)



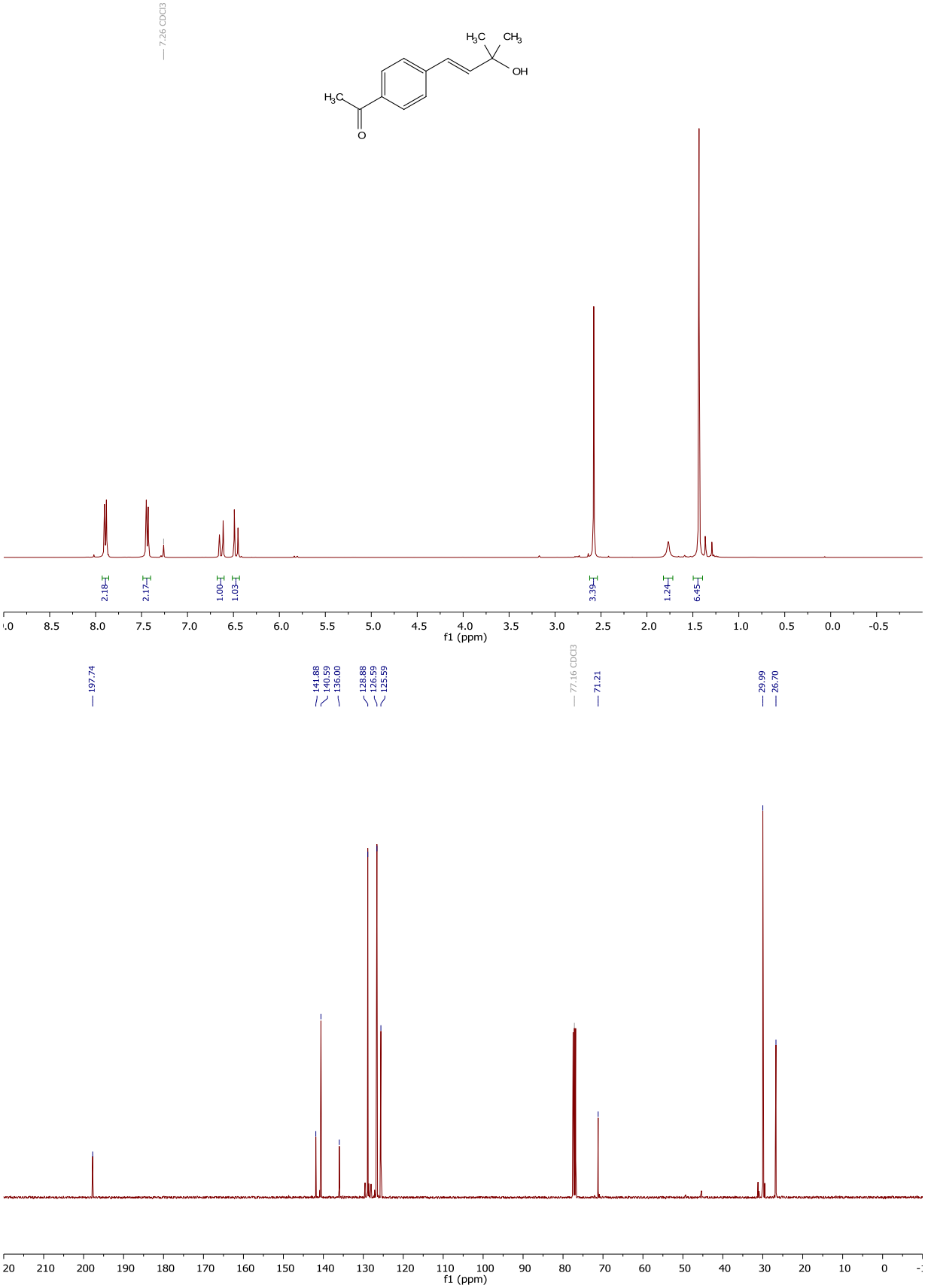
***(E)*-2-methyl-4-phenylbut-3-en-2-ol (19)**



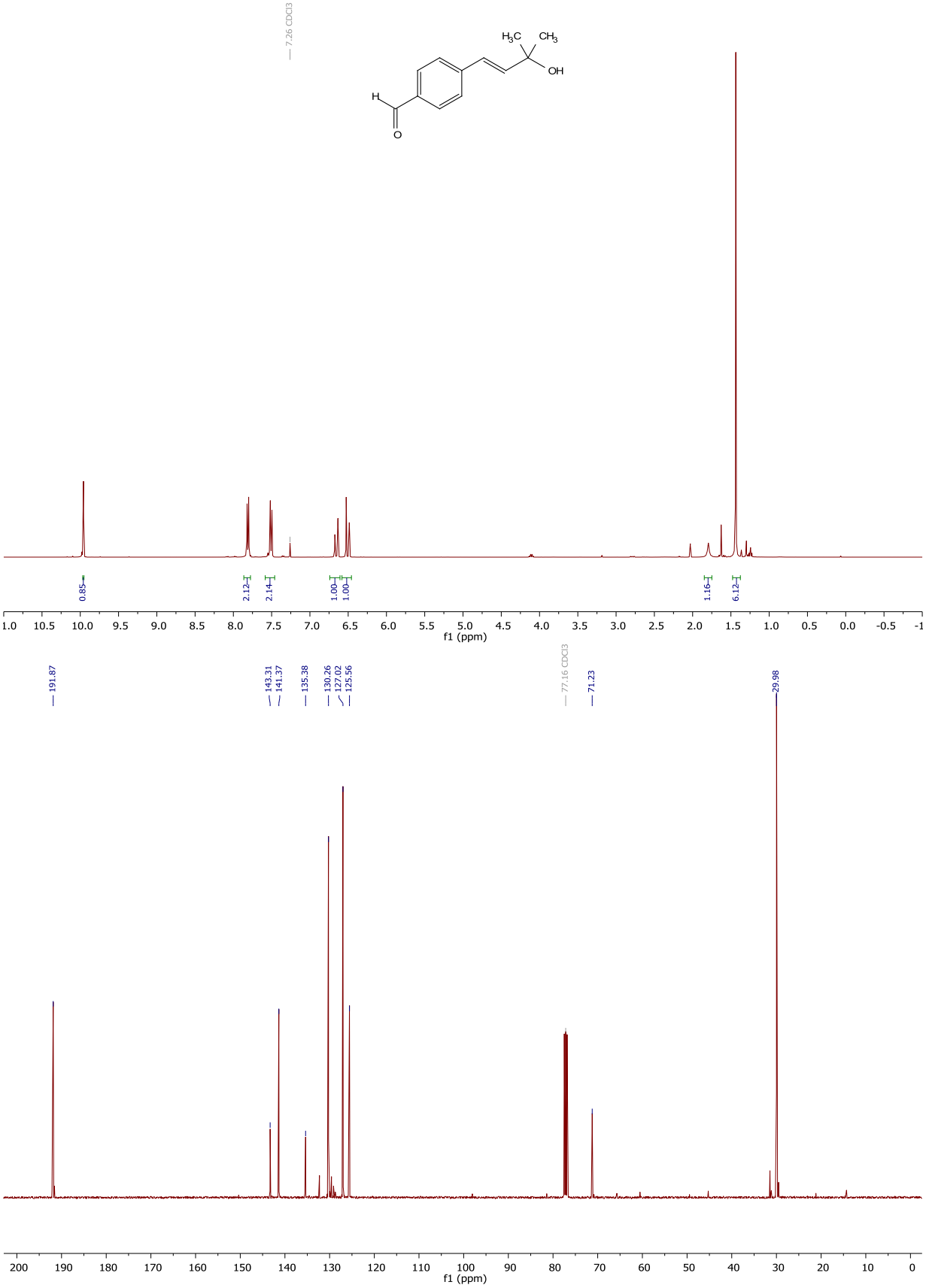
***(E)*-4-(4-bromophenyl)-2-methylbut-3-en-2-ol (20)**



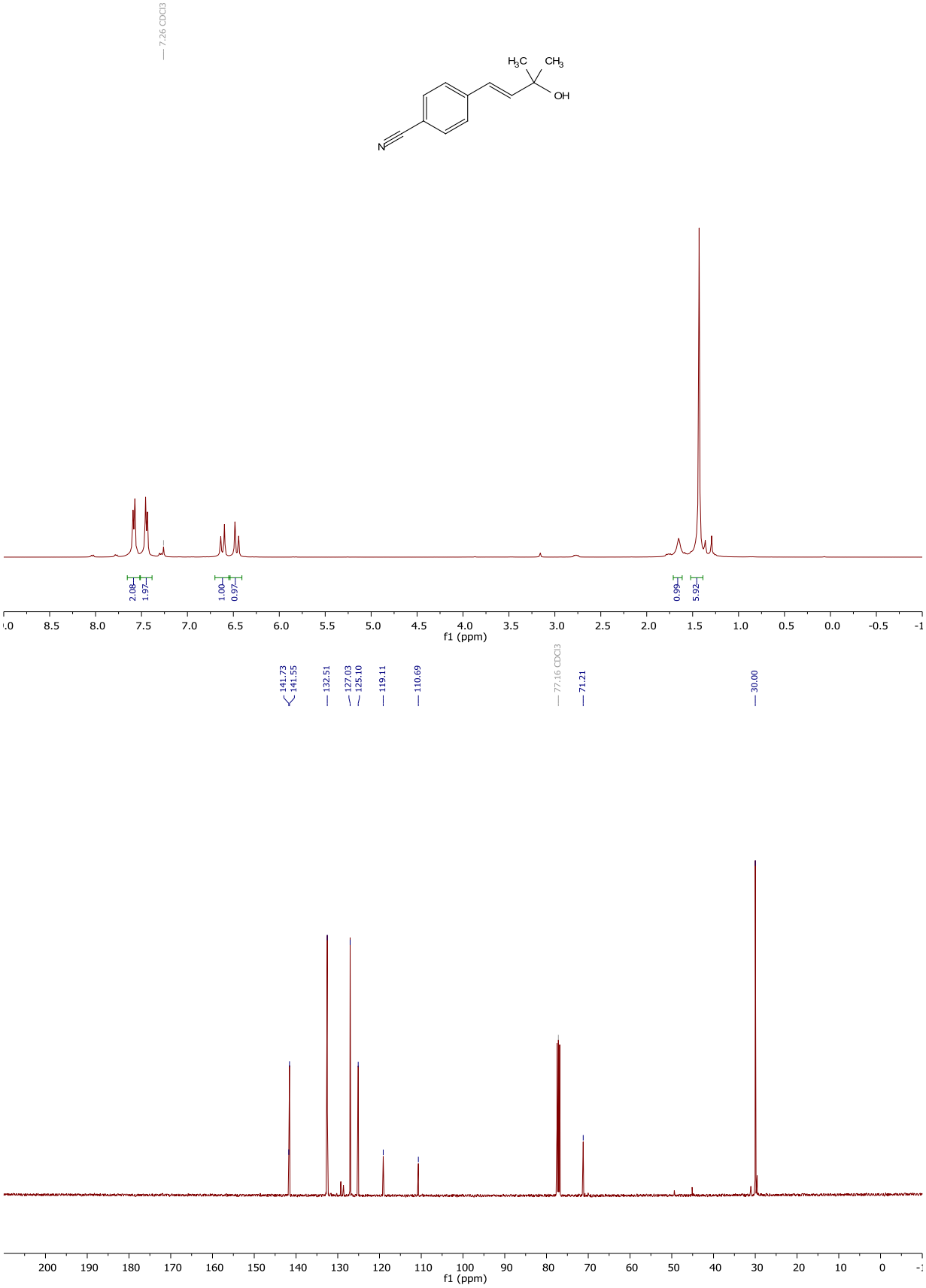
***(E)*-1-(4-(3-hydroxy-3-methylbut-1-en-1-yl)phenyl)ethan-1-one (21)**



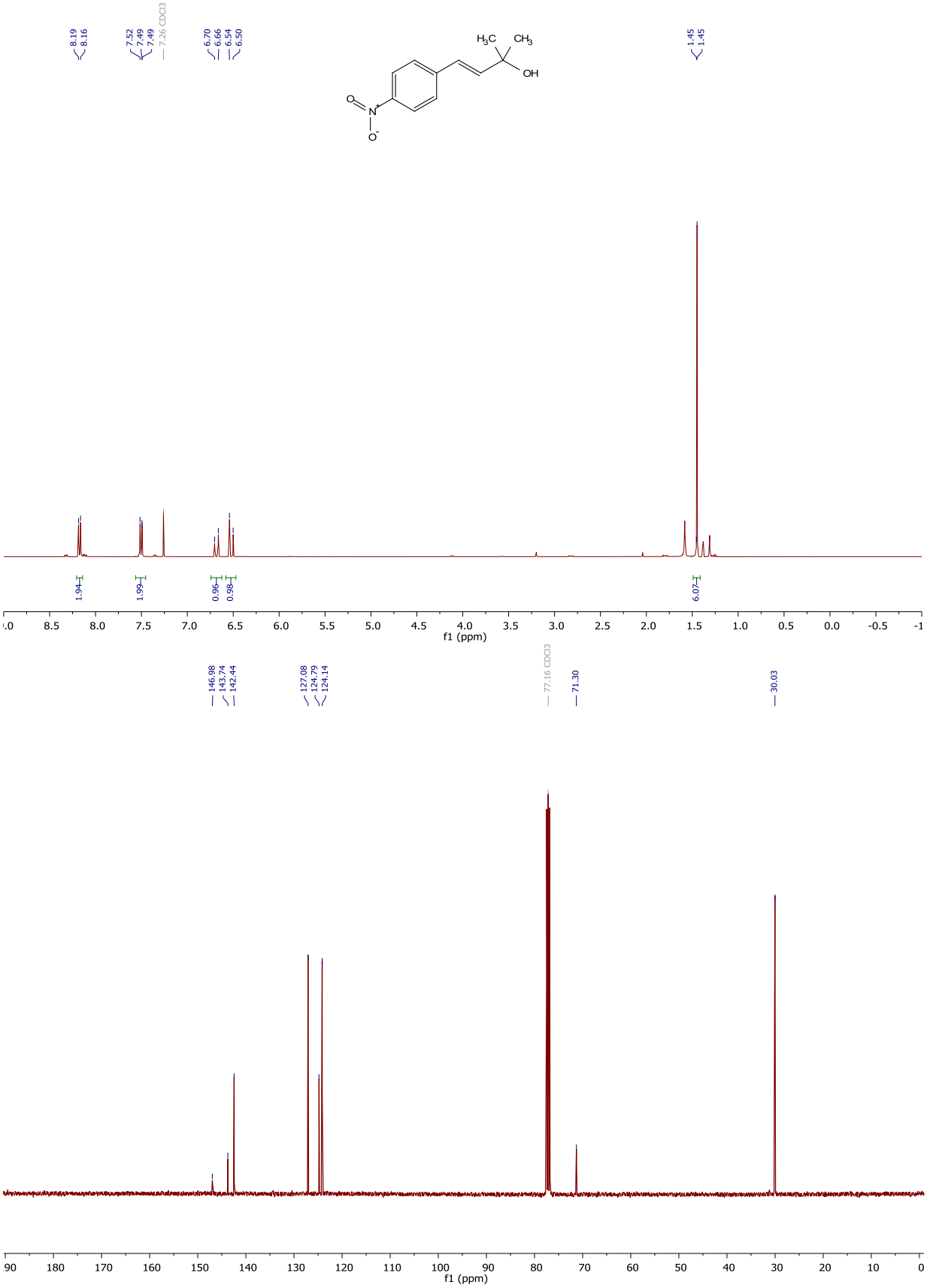
***(E)*-4-(3-hydroxy-3-methylbut-1-en-1-yl)benzaldehyde (22)**



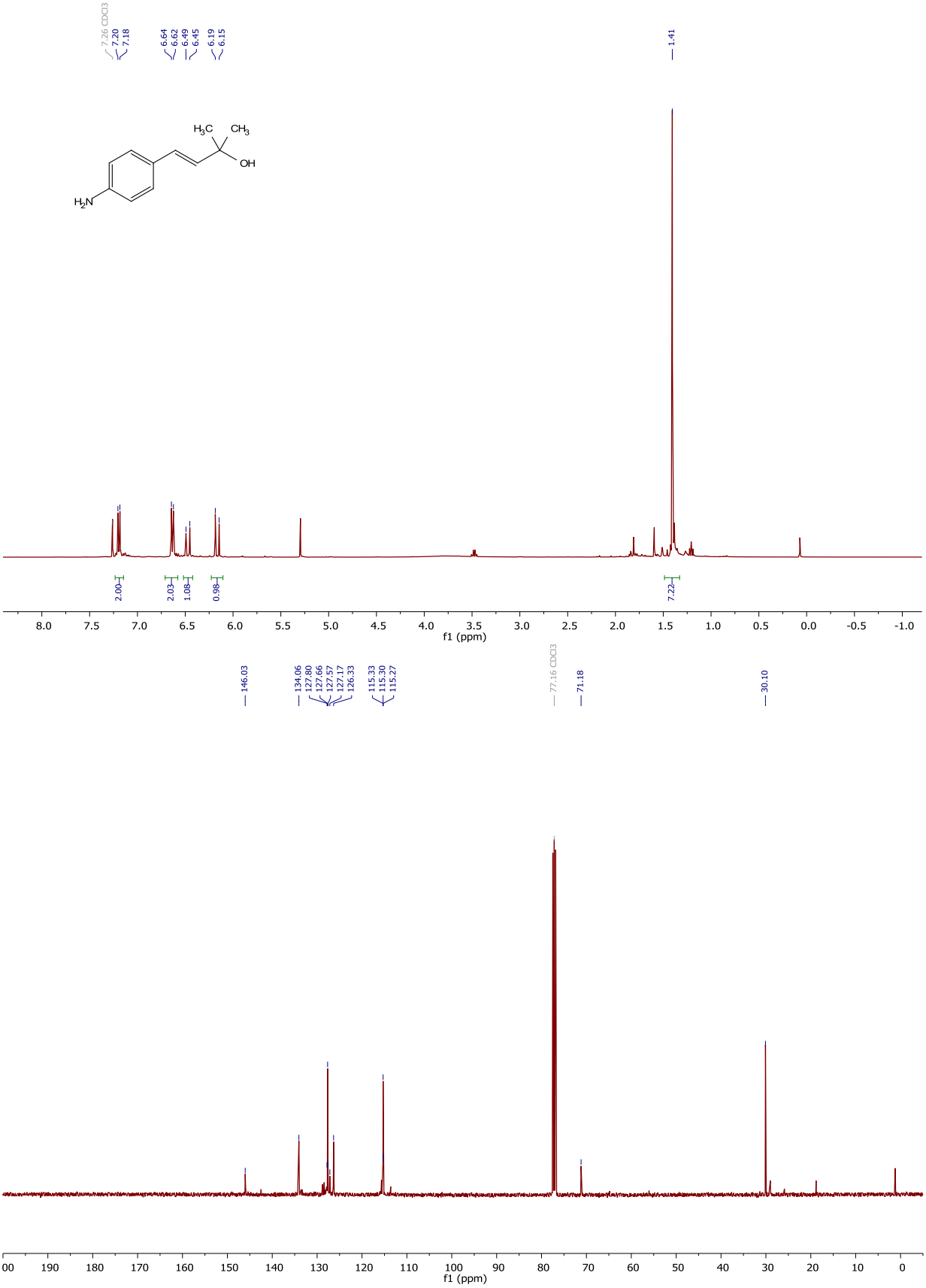
***(E)*-4-(3-hydroxy-3-methylbut-1-en-1-yl)benzonitrile (23)**



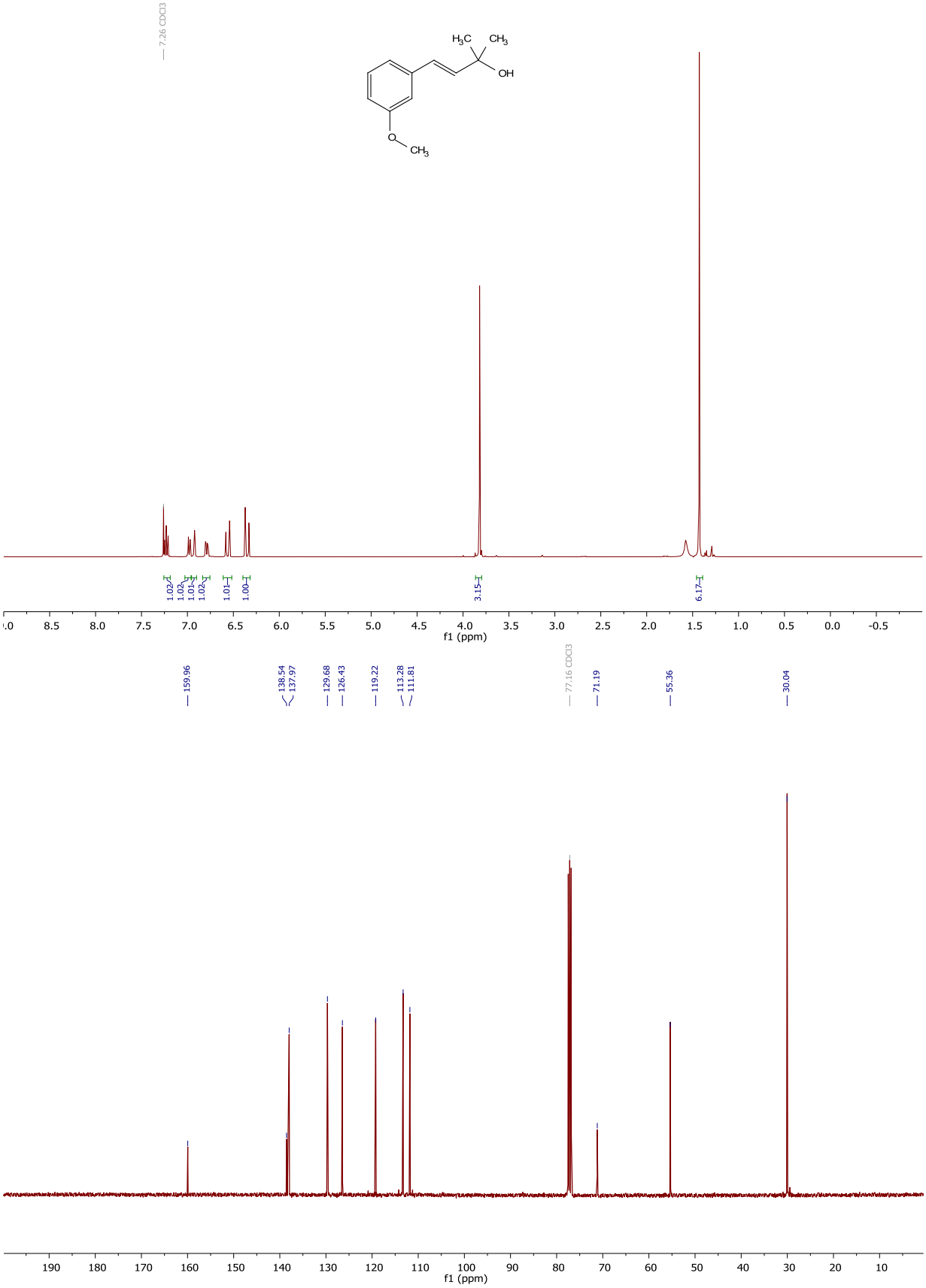
***(E)*-2-methyl-4-(4-nitrophenyl)but-3-en-2-ol (24)**



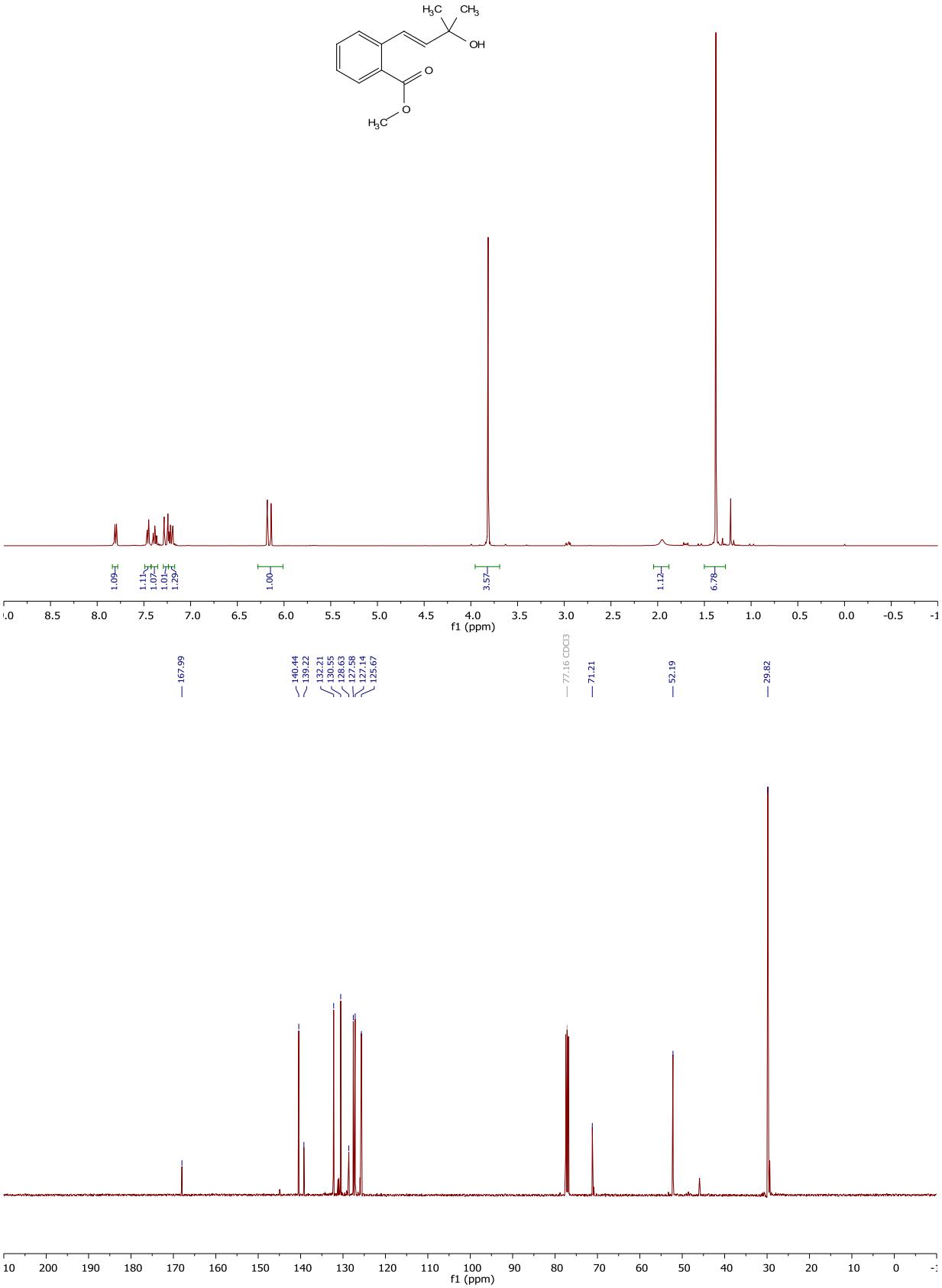
(E)-4-(4-aminophenyl)-2-methylbut-3-en-2-ol (25)



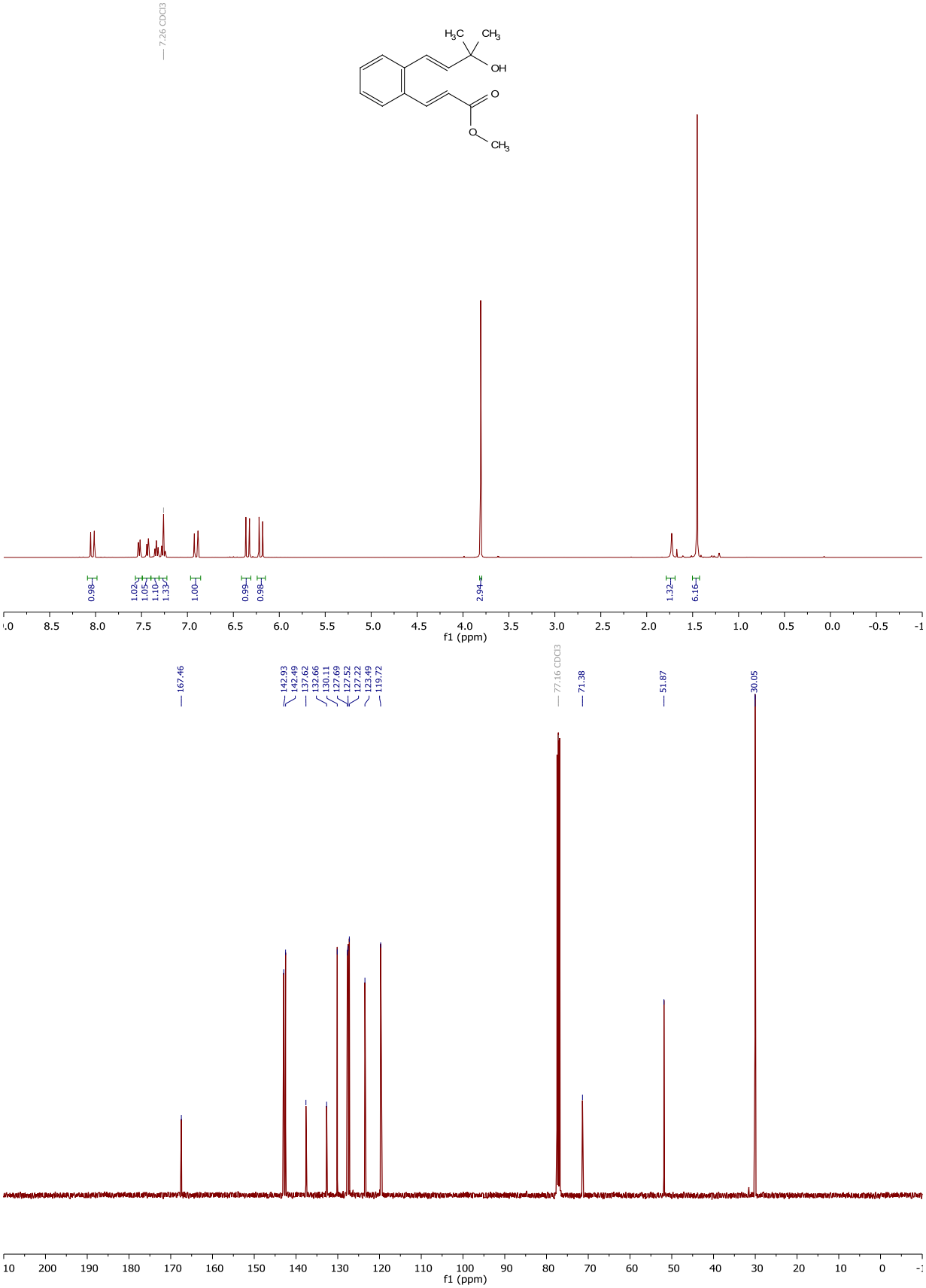
***(E)*-4-(3-methoxyphenyl)-2-methylbut-3-en-2-ol (26)**



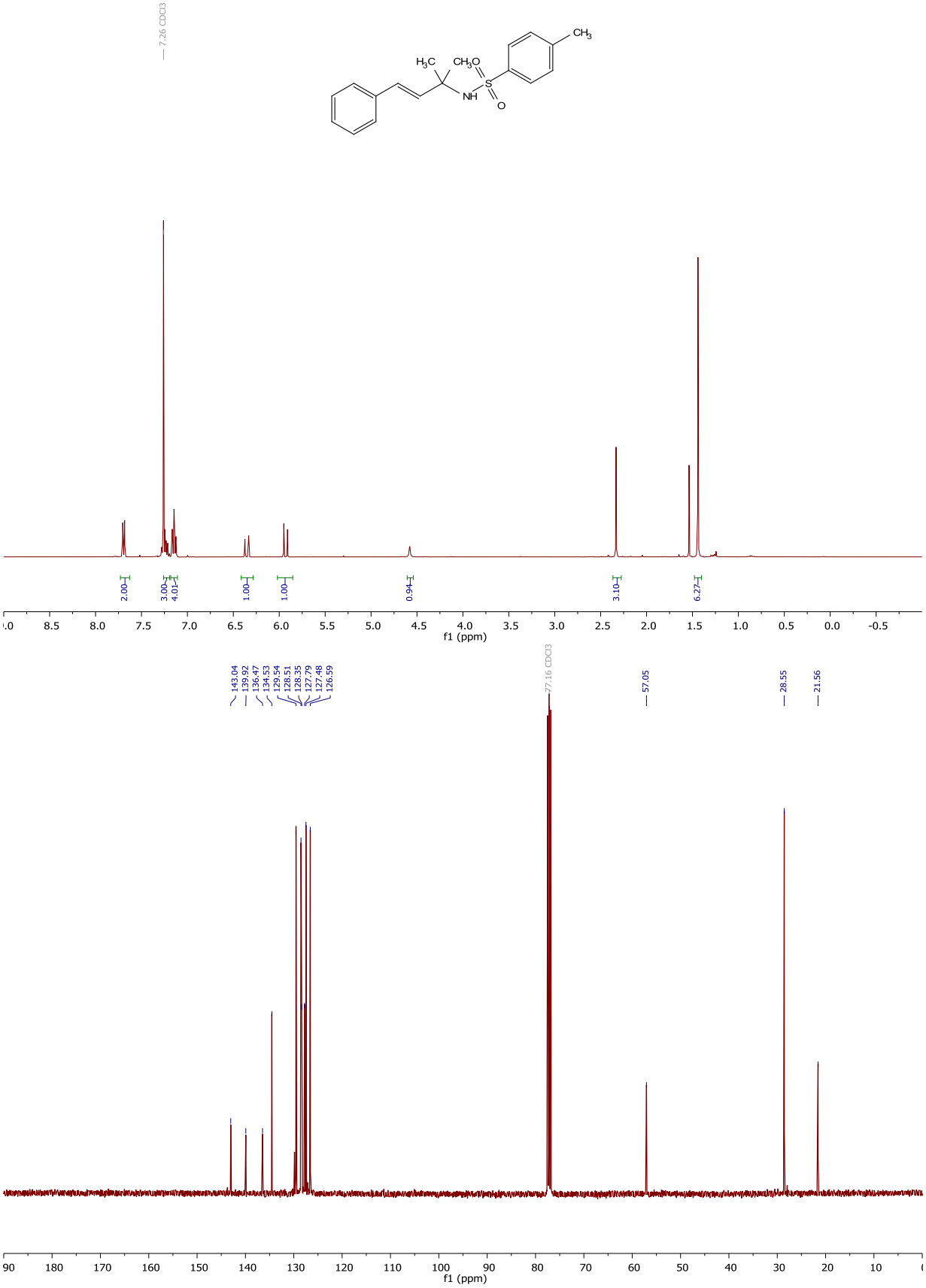
methyl (*E*)-2-(3-hydroxy-3-methylbut-1-en-1-yl)benzoate (27)



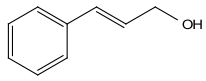
methyl *(E)*-3-(2-((*E*)-3-hydroxy-3-methylbut-1-en-1-yl)phenyl)acrylate (28)

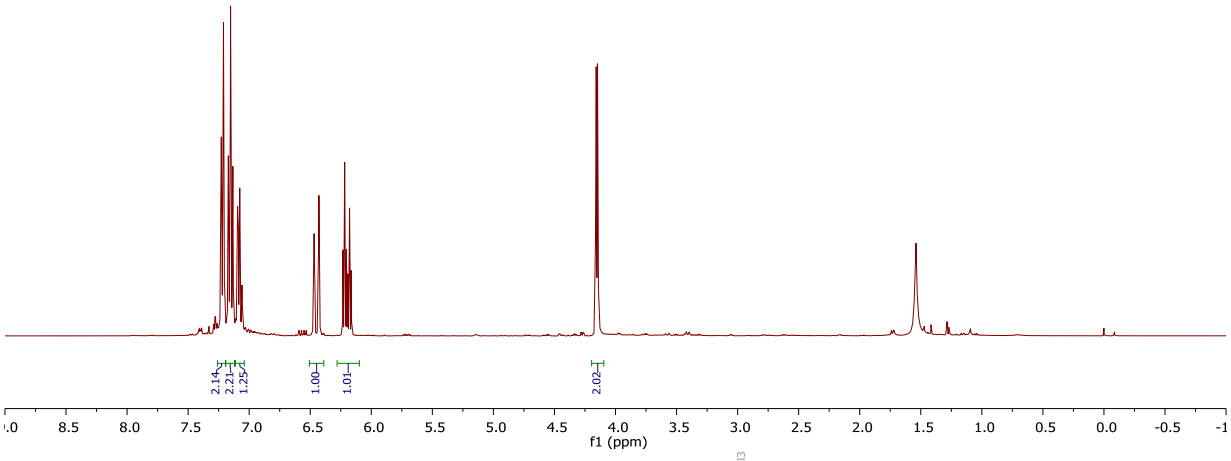


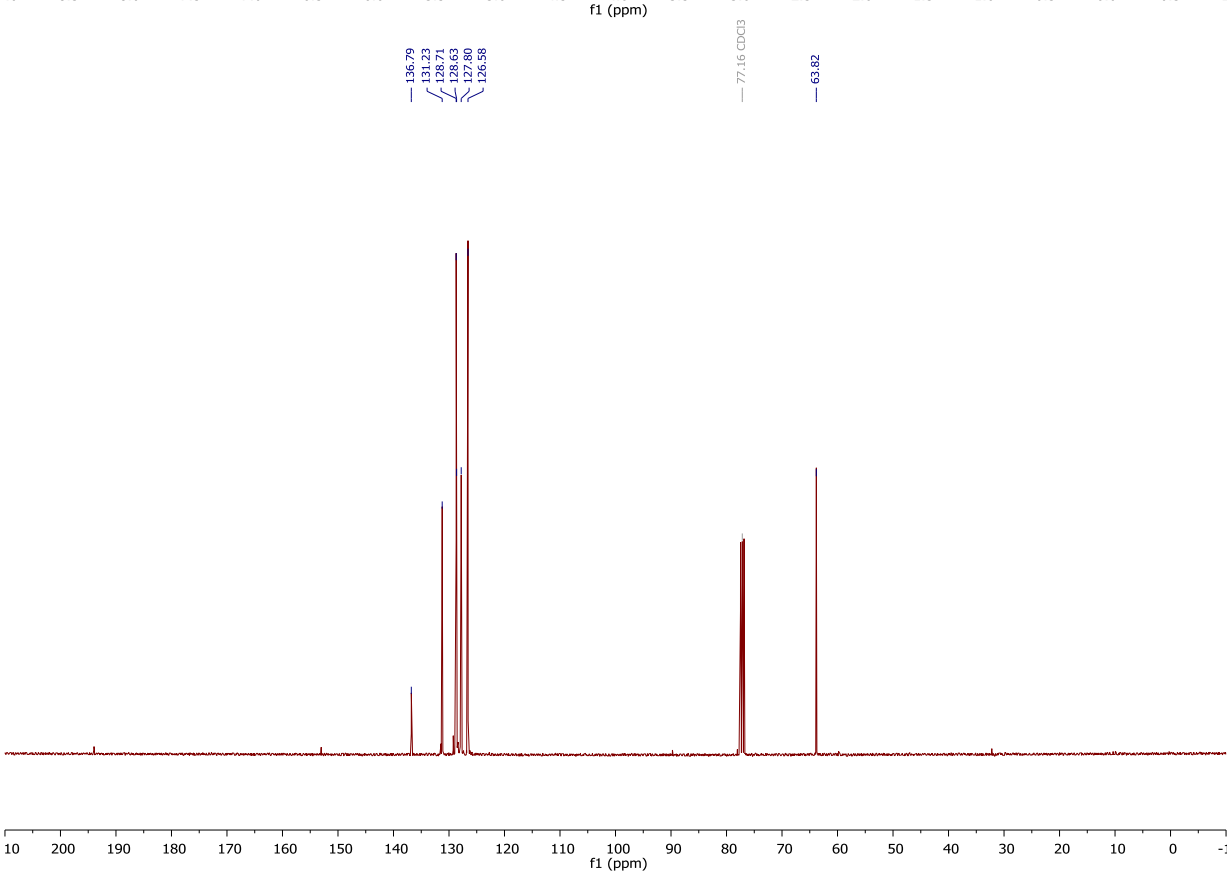
***(E)*-4-methyl-N-(2-methyl-4-phenylbut-3-en-2-yl)benzenesulfonamide (28)**



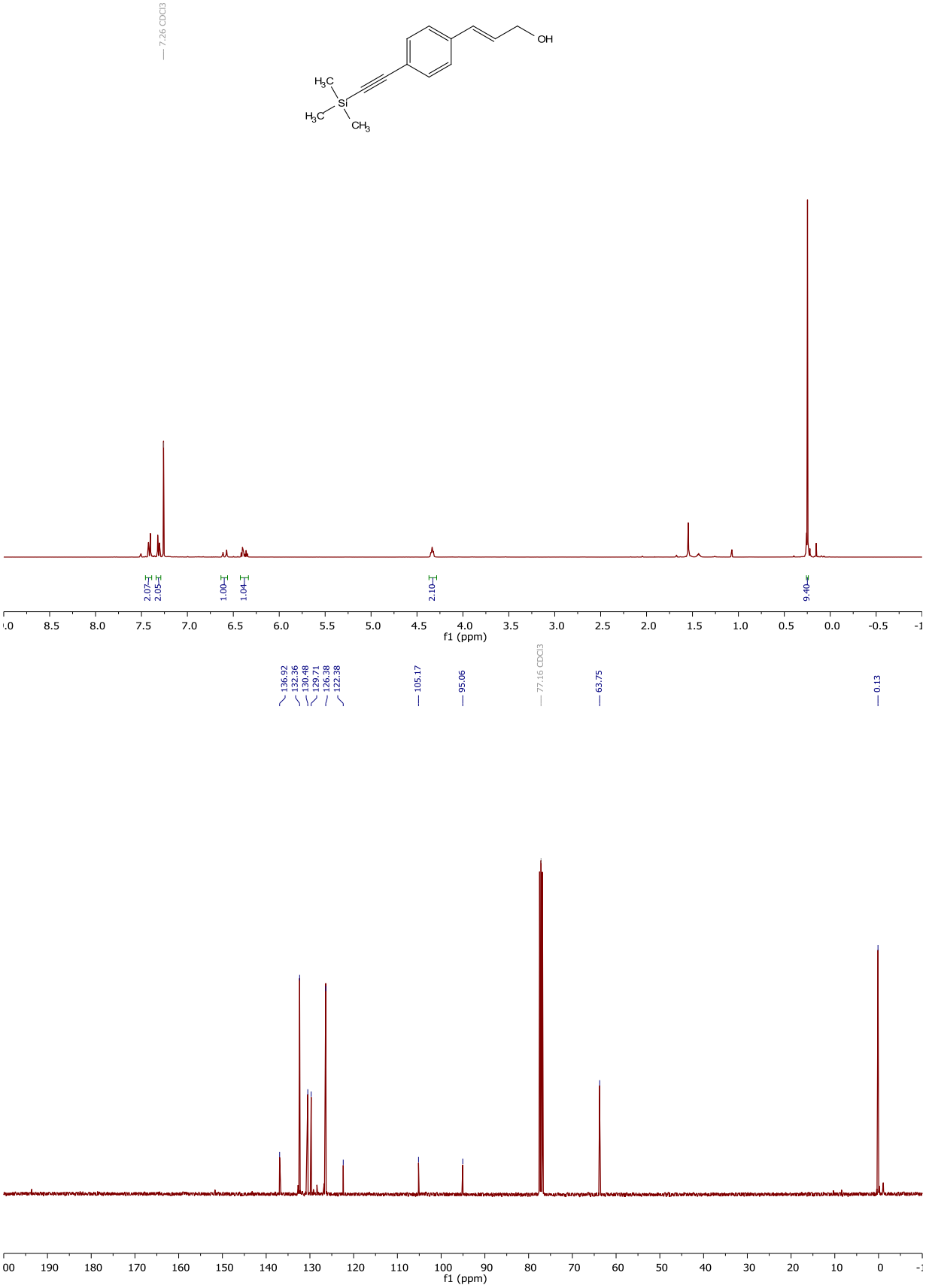
***(E)*-3-phenylprop-2-en-1-ol (29)**



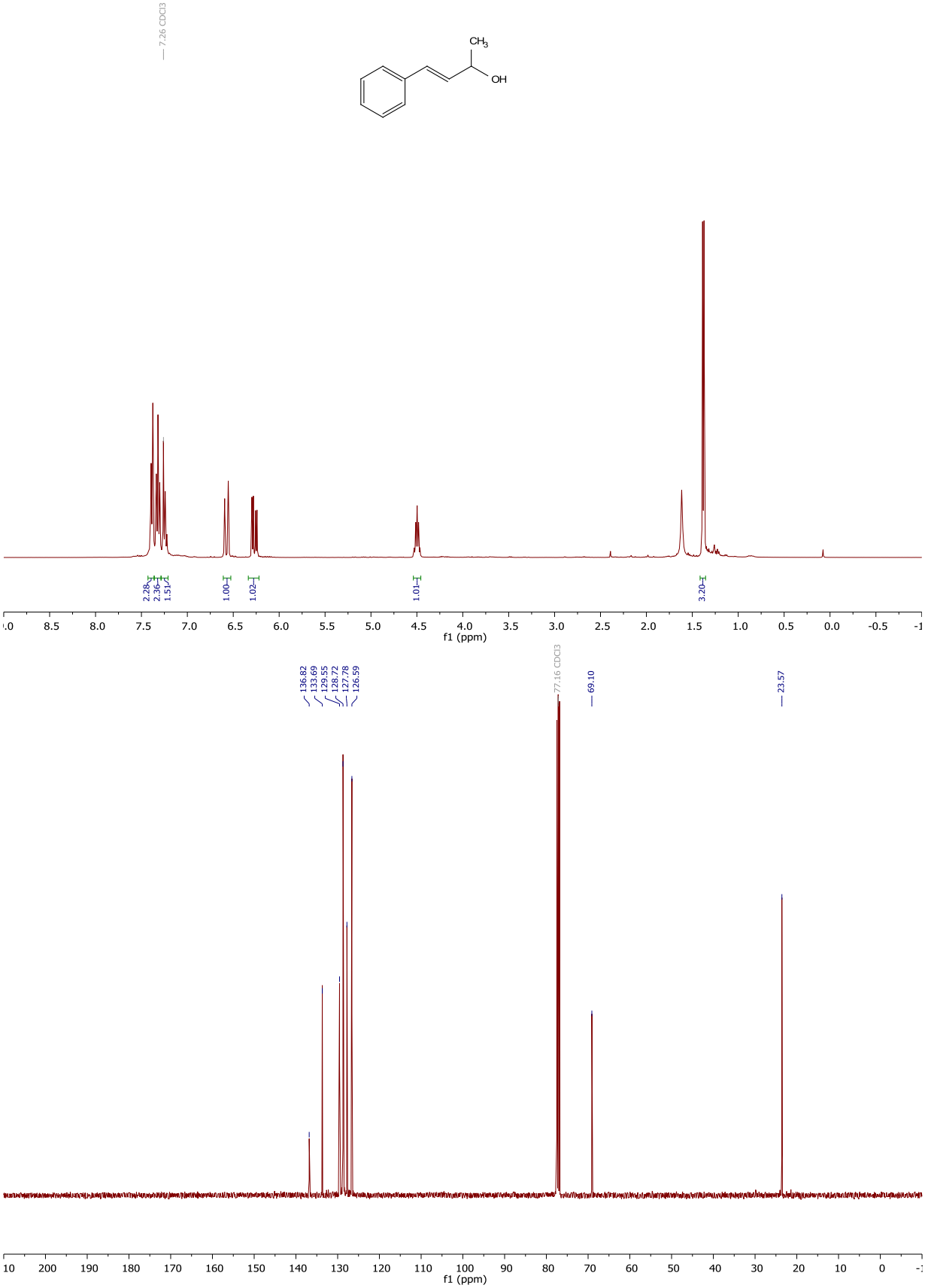


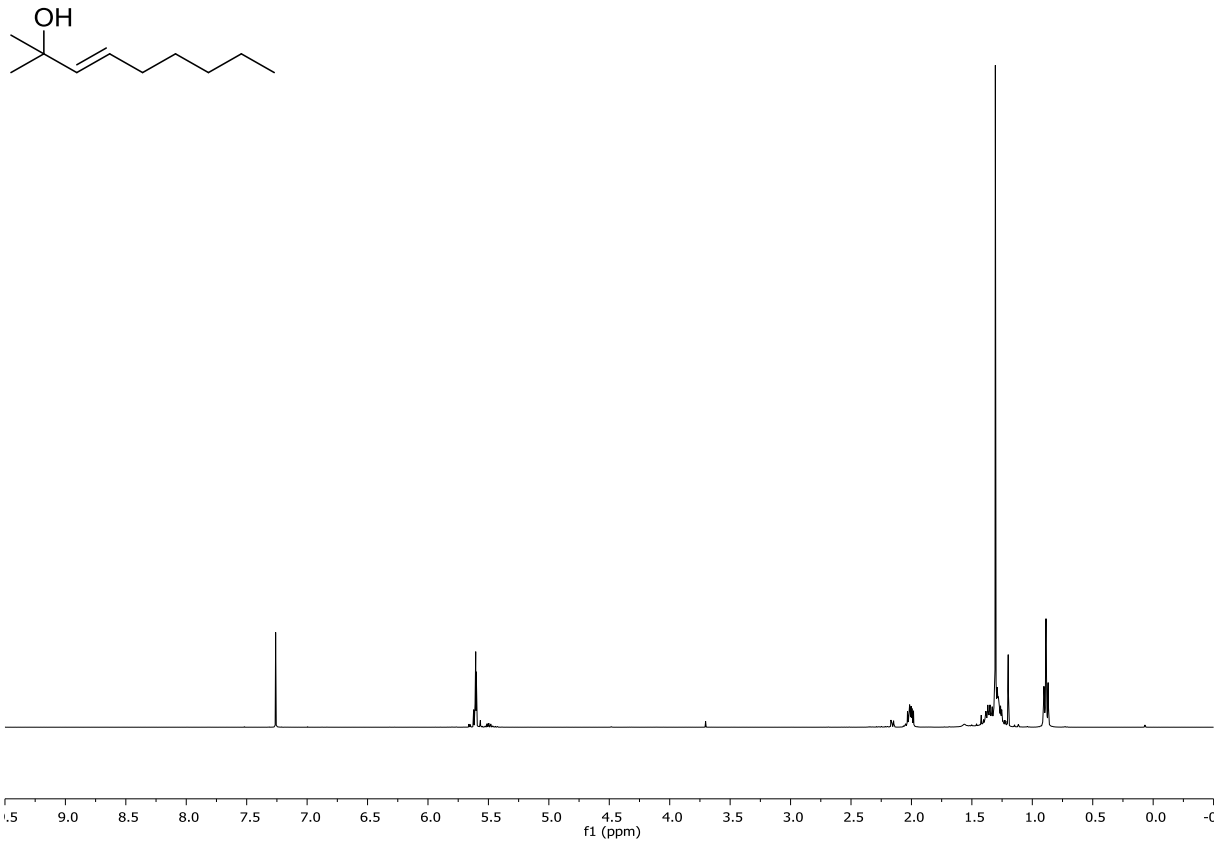


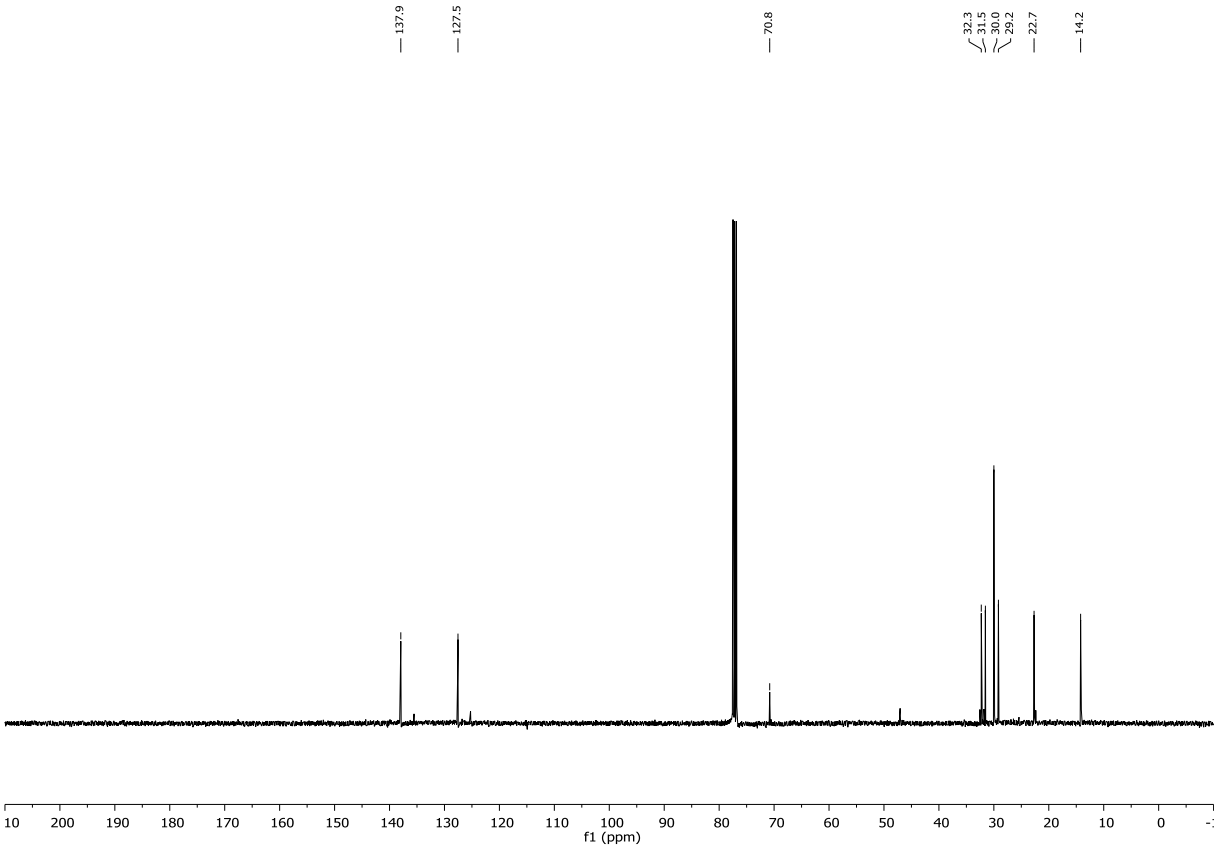
***(E)*-3-(4-((trimethylsilyl)ethynyl)phenyl)prop-2-en-1-ol (30)**

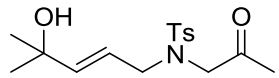


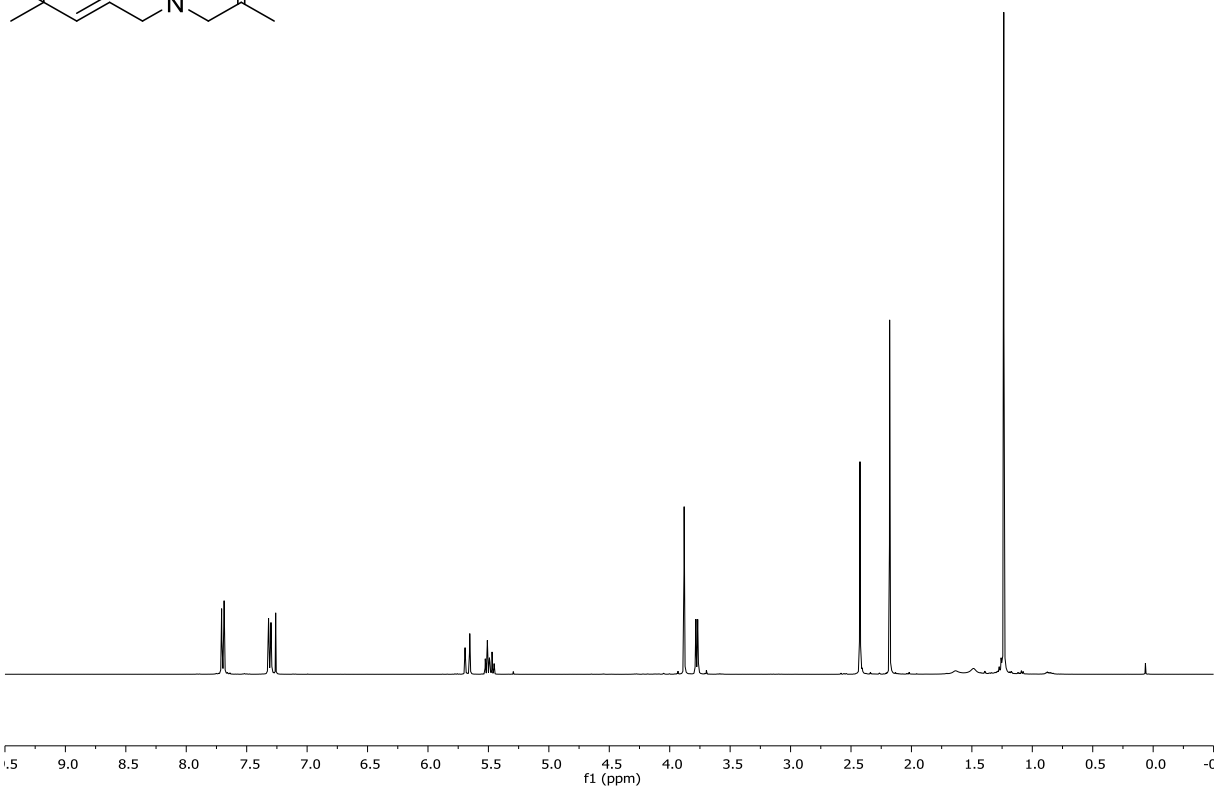
***(E)*-4-phenylbut-3-en-2-ol (31)**



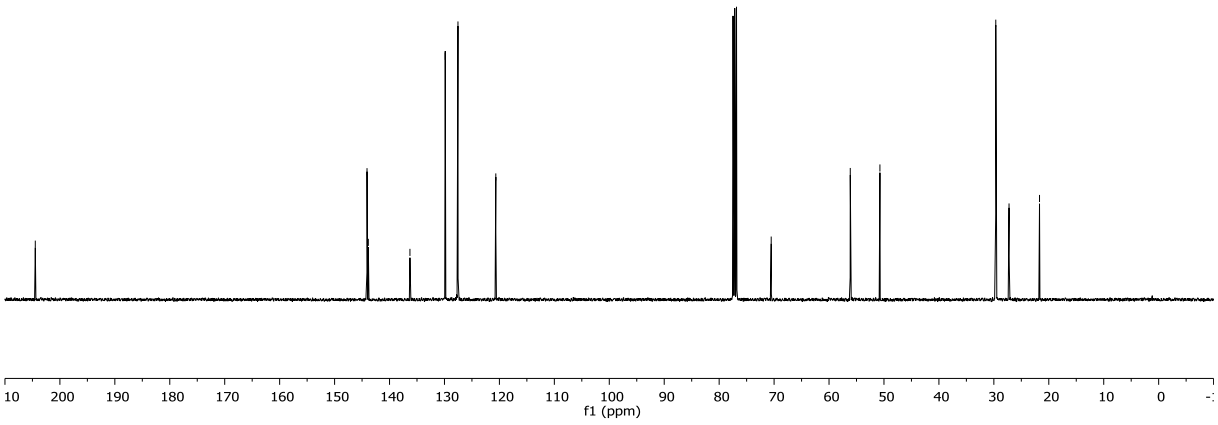

OH
f1 (ppm)

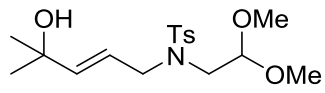

137.9
127.5
70.8
32.3
31.5
30.0
29.2
22.7
14.2
f1 (ppm)

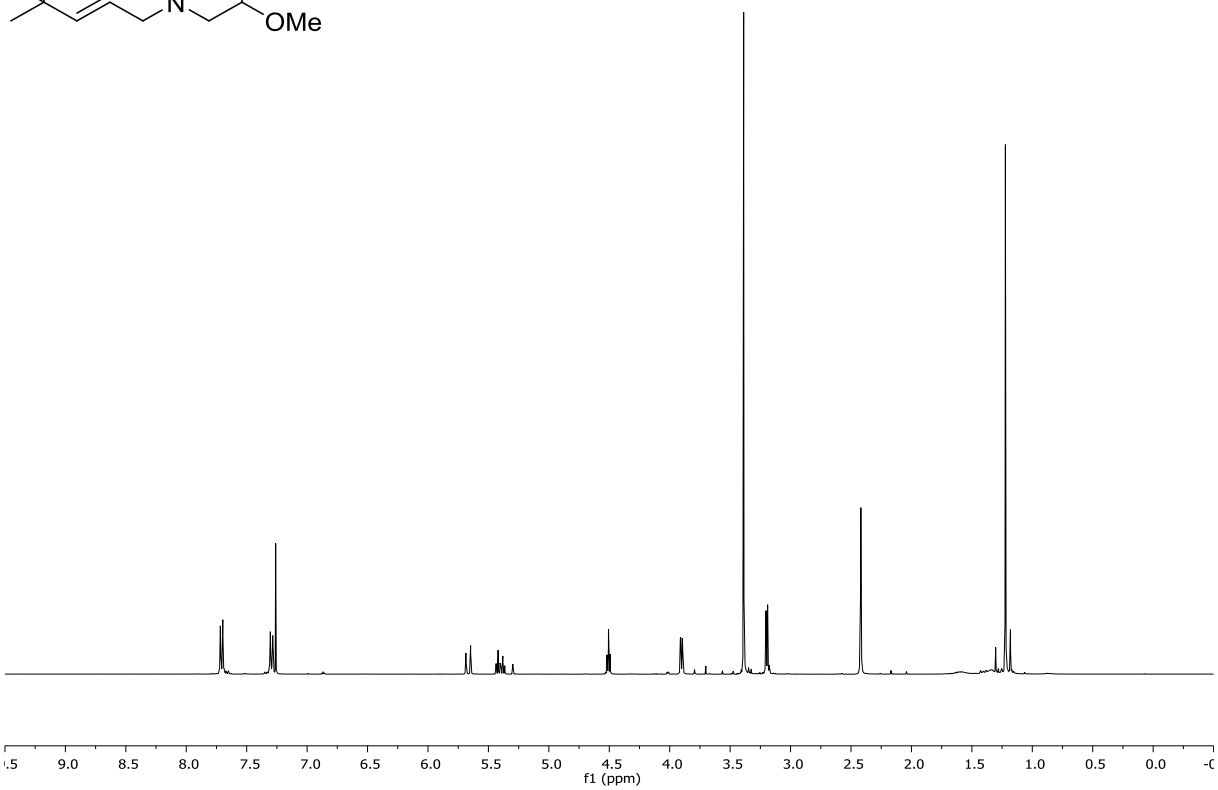

OH
Ts
N
O

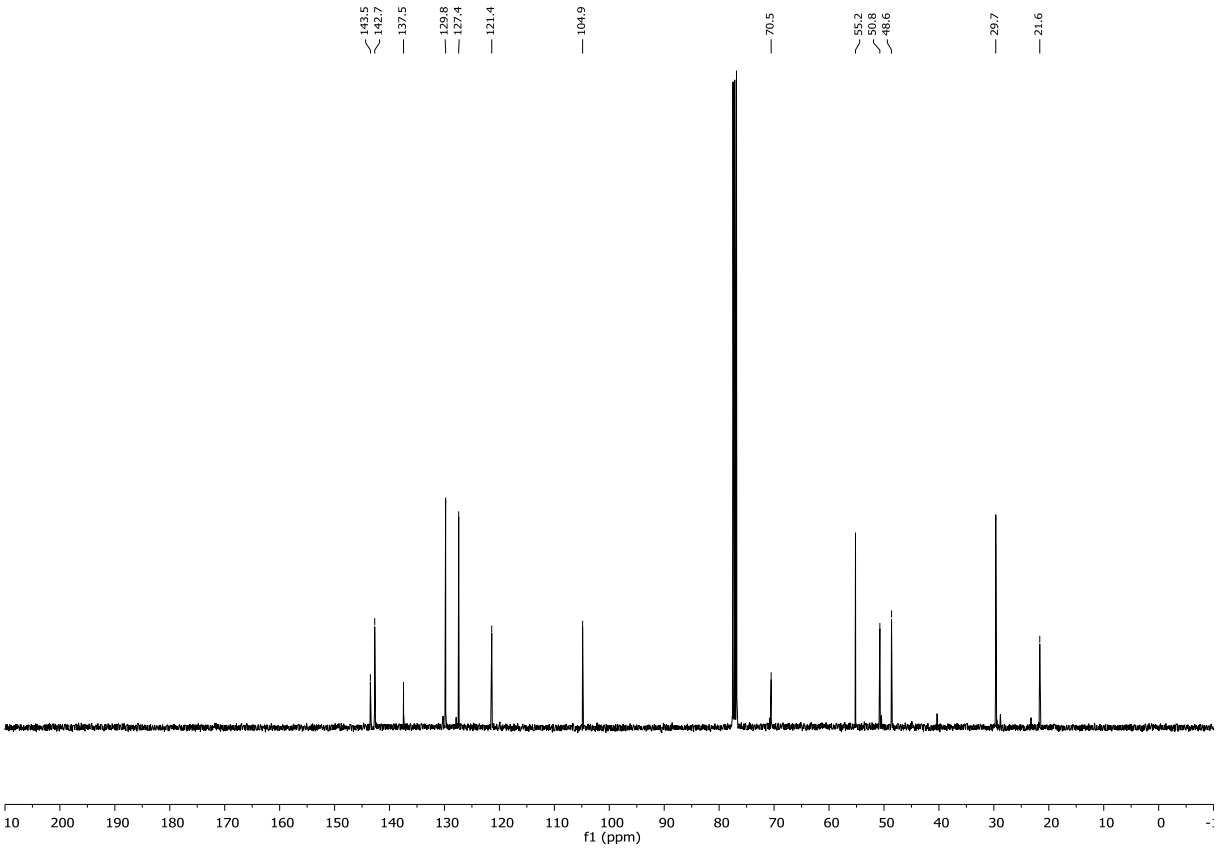

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.5
144.1
143.9
136.3
129.9
127.5
120.7
70.5
56.1
50.7
29.6
27.2
21.7

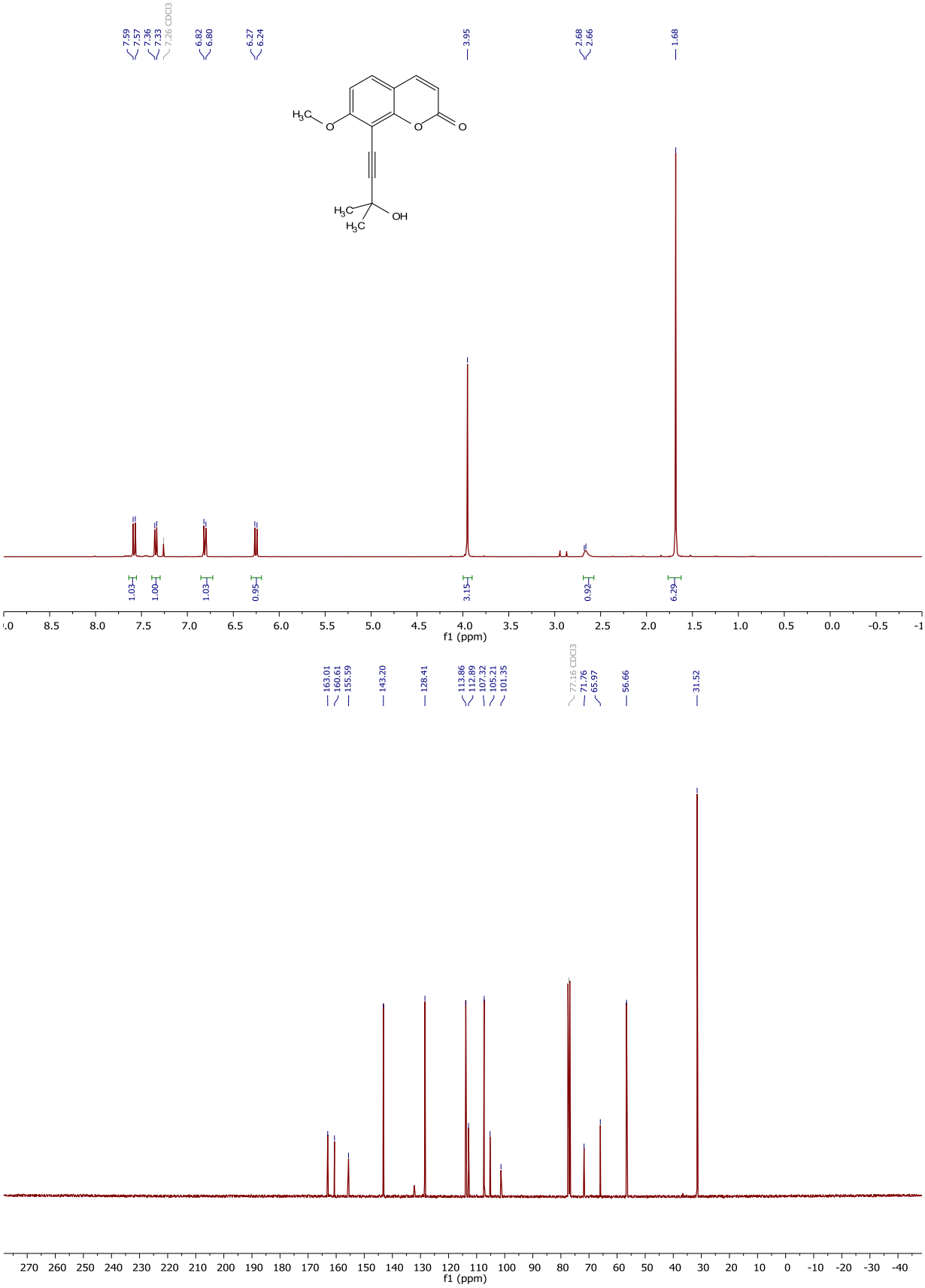

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Ts
N
OMe
OMe

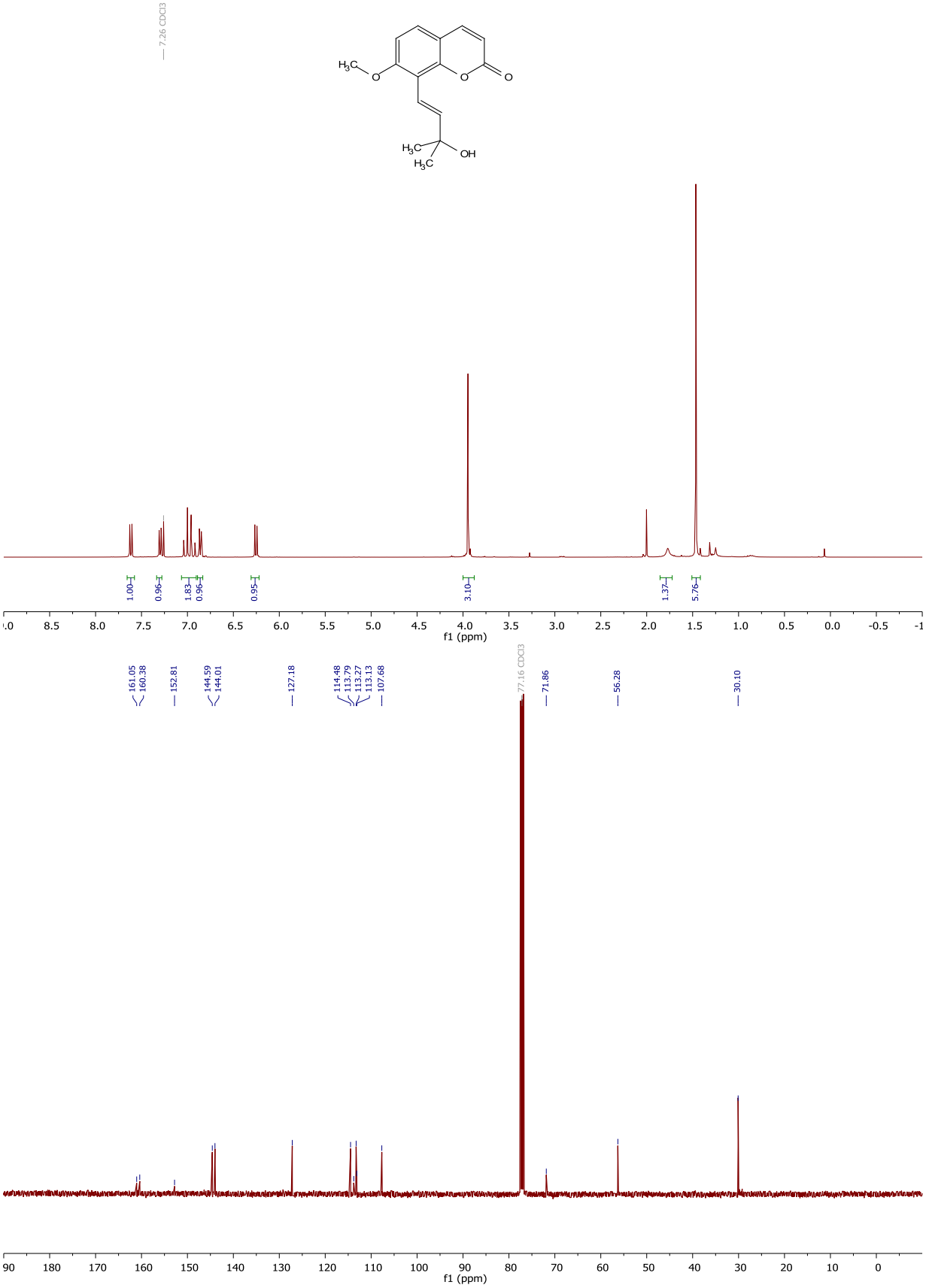

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.5
142.7
137.5
129.8
127.4
121.4
104.9
70.5
55.2
50.8
48.6
29.7
21.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

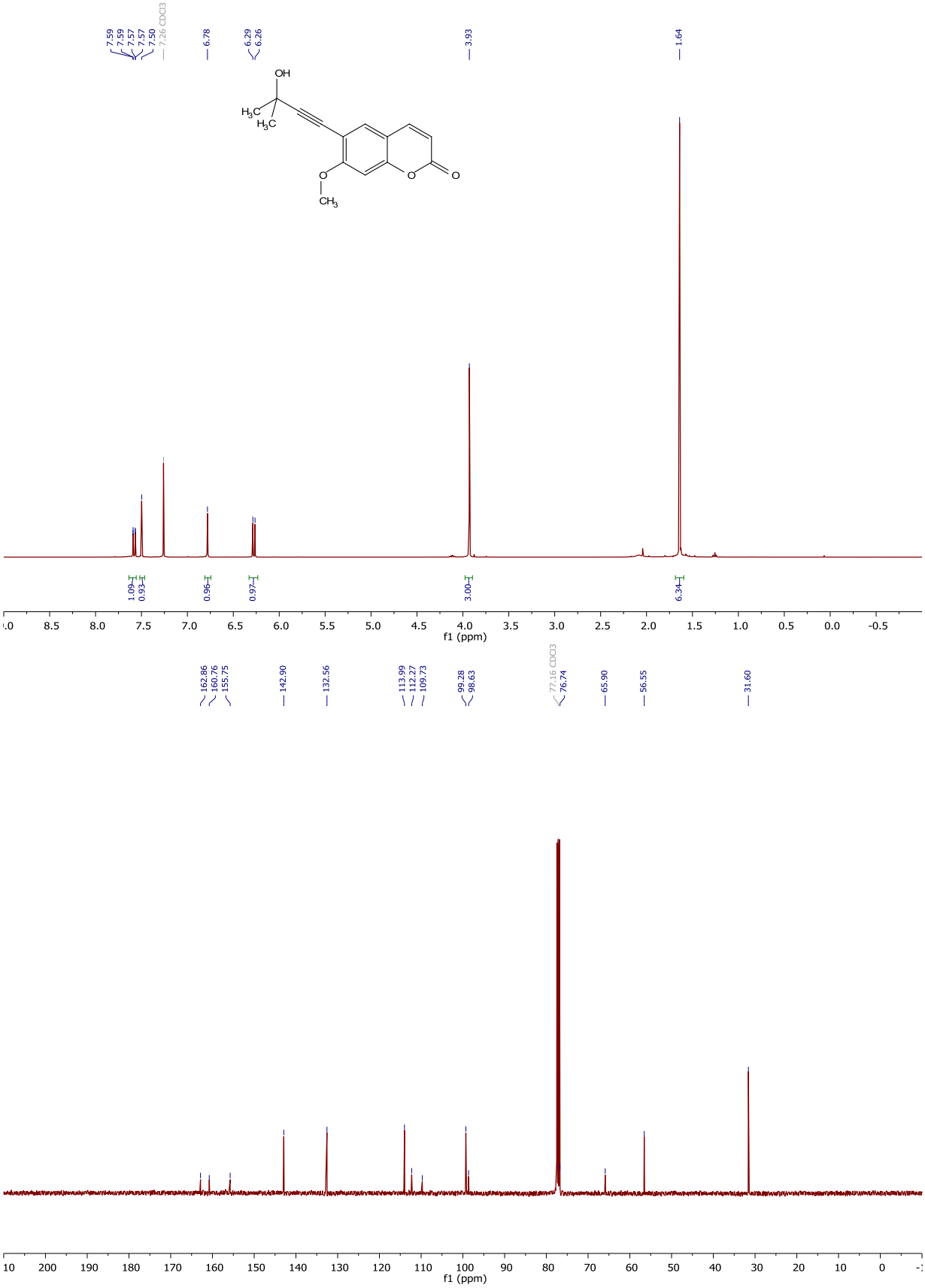
8-(3-hydroxy-3-methylbut-1-yn-1-yl)-7-methoxy-2H-chromen-2-one (40)



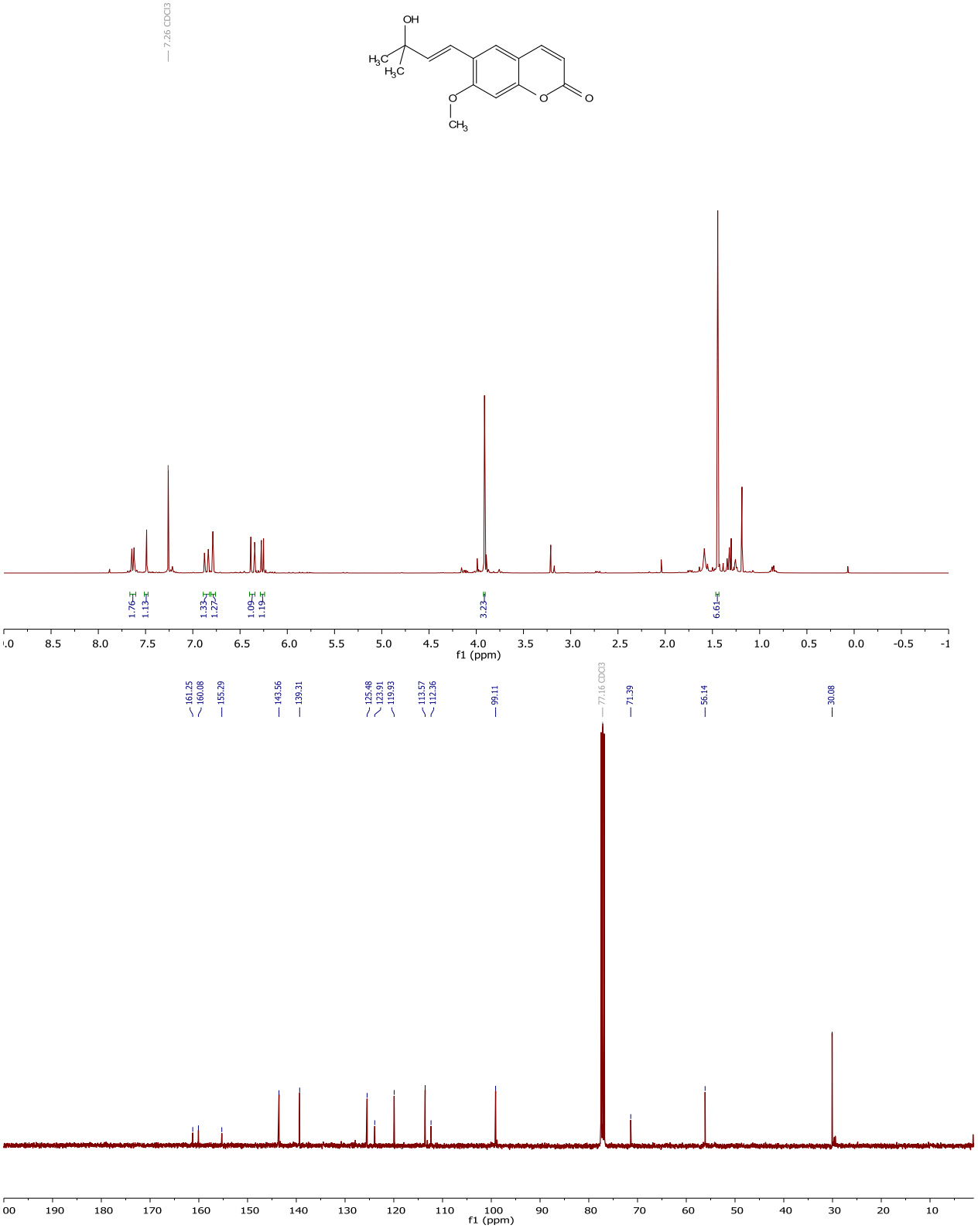
Murraol (41)


7.26 CDCl3
H3C
O
O
O
H3C
H3C
OH
1.00
0.96
1.83
0.96
0.95
3.10
1.37
5.76
f1 (ppm)
161.05
160.38
152.81
144.59
144.01
127.18
114.48
113.79
113.27
113.13
107.68
77.16 CDCl3
71.86
56.28
30.10
f1 (ppm)

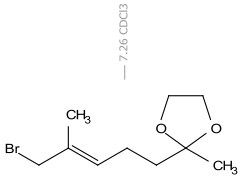
6-(3-hydroxy-3-methylbut-1-yn-1-yl)-7-methoxy-2H-chromen-2-one (42)

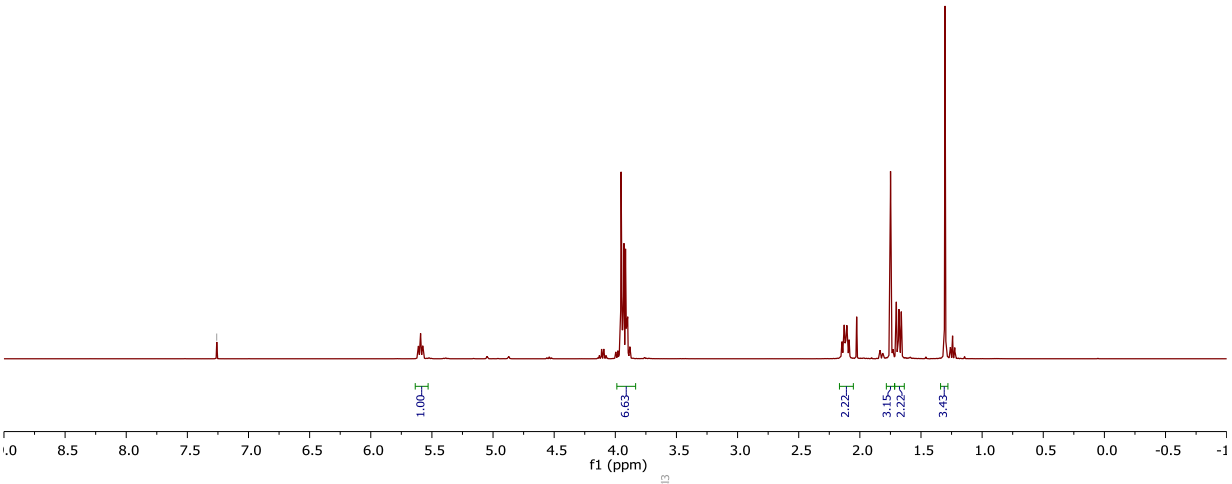


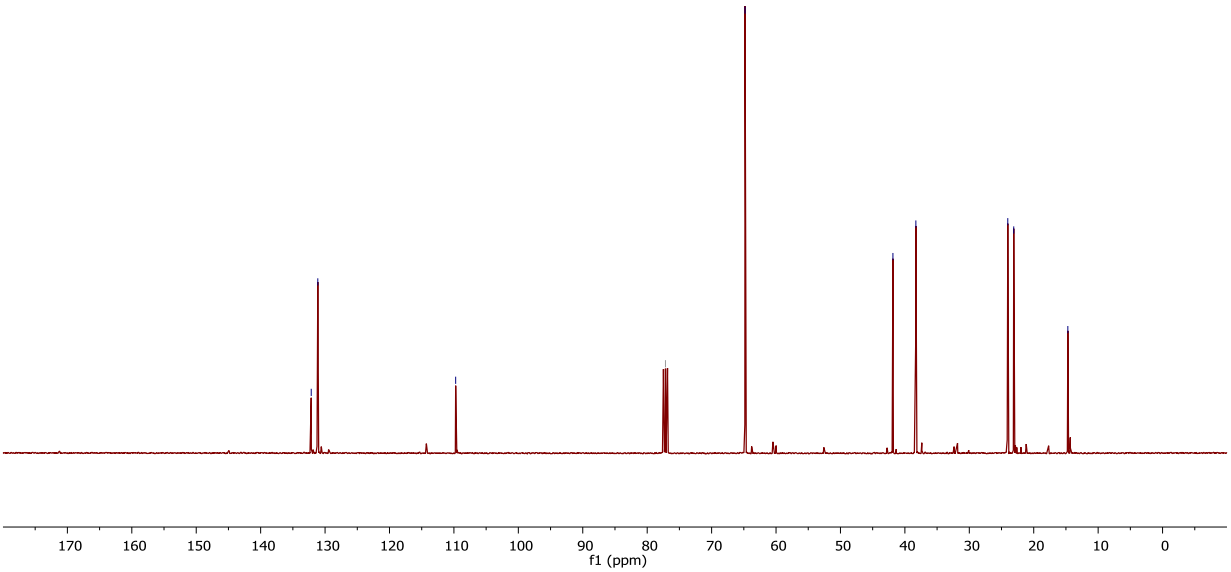
E-Suberenol (43)



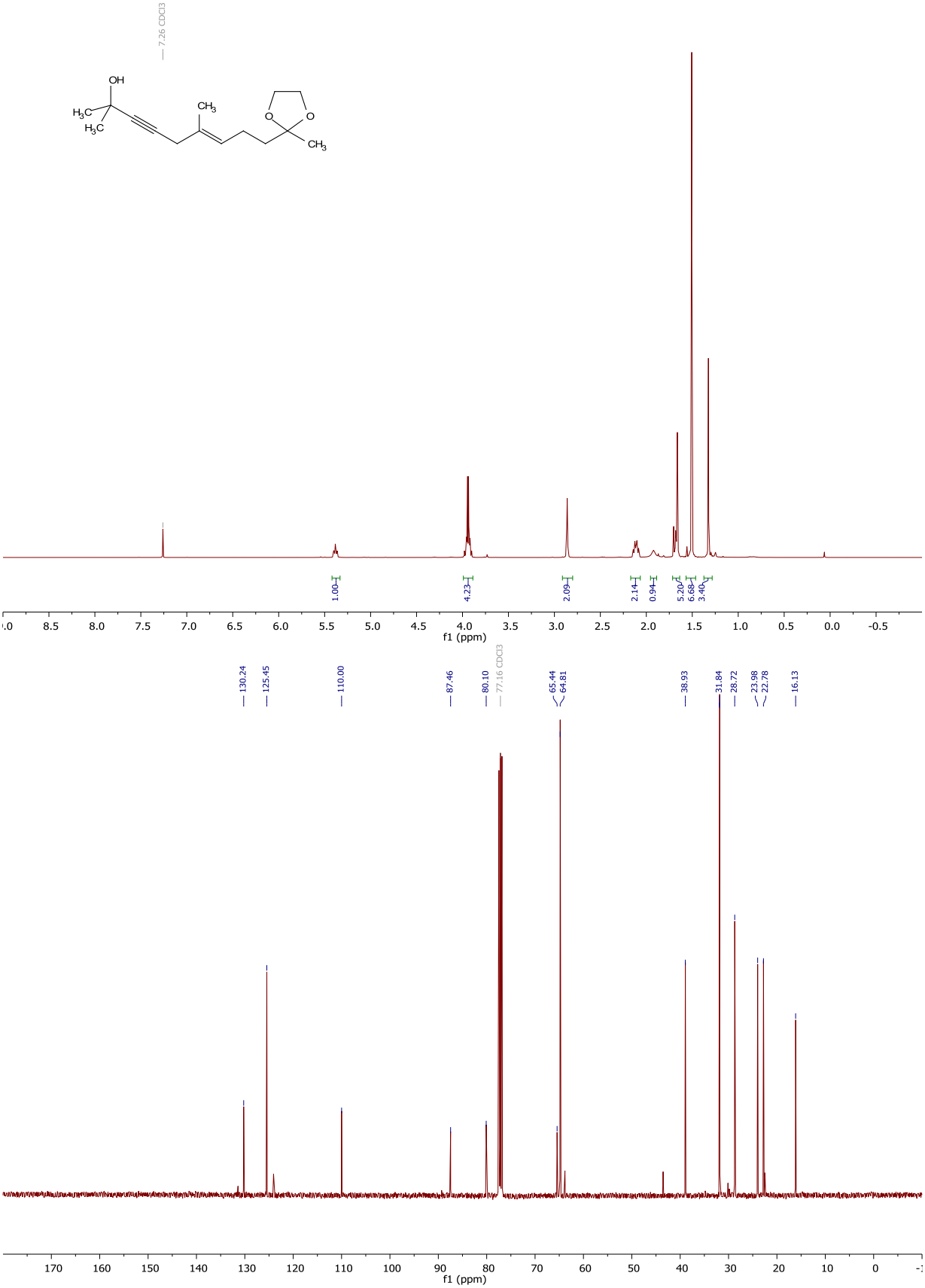
***(E)*-2-(5-bromo-4-methylpent-3-en-1-yl)-2-methyl-1,3-dioxolane (45)**



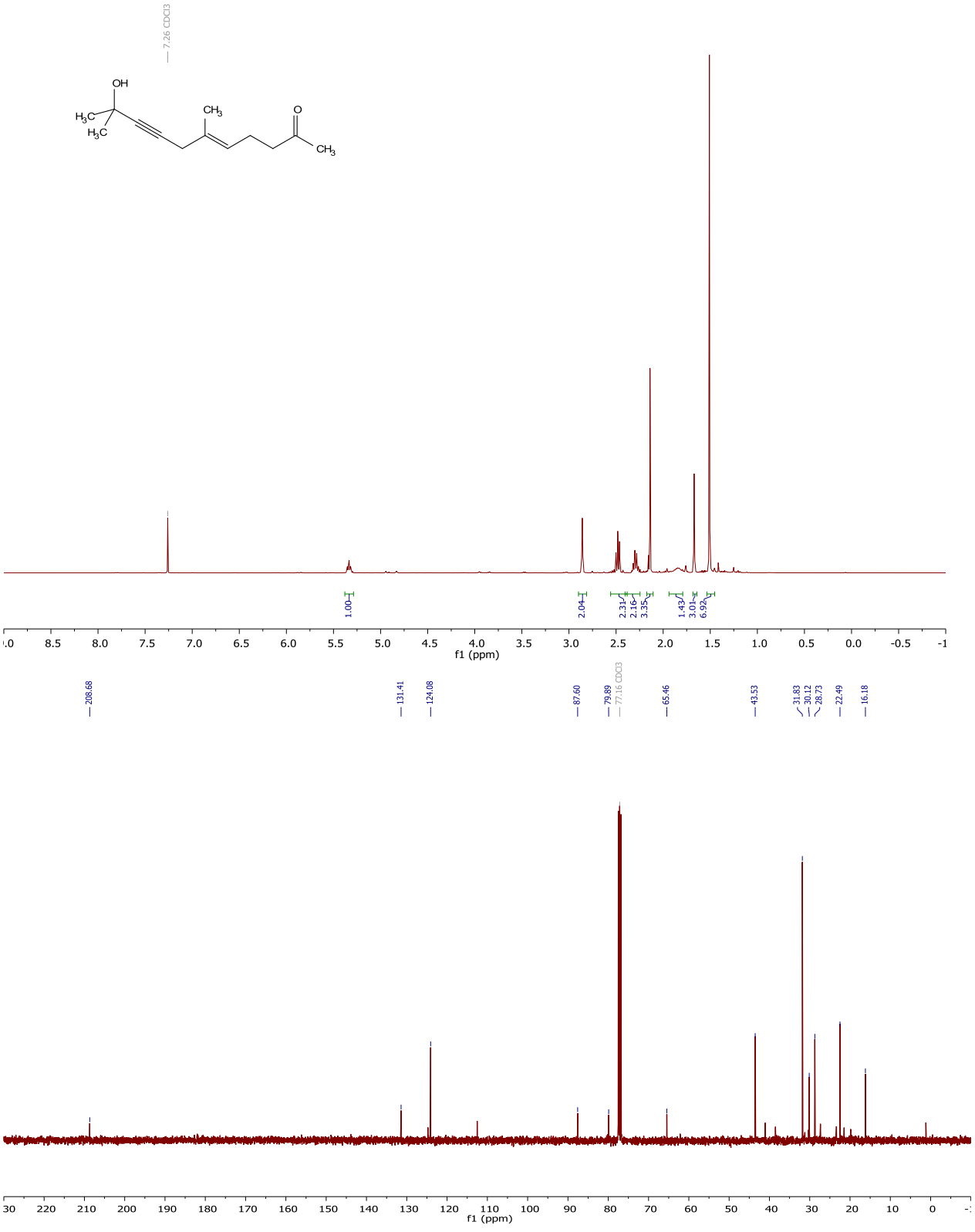




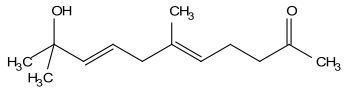
***(E)*-2,6-dimethyl-9-(2-methyl-1,3-dioxolan-2-yl)non-6-en-3-yn-2-ol**

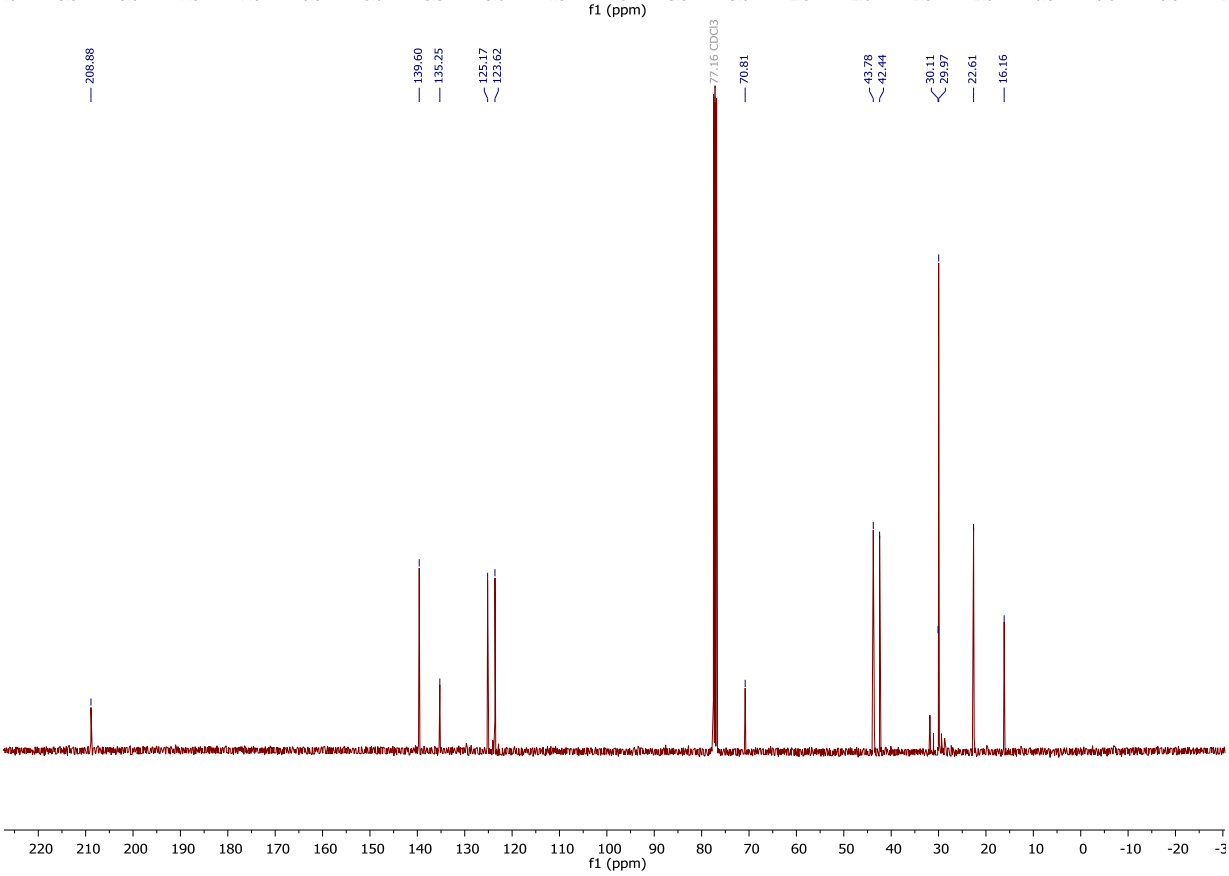


(*E*)-10-hydroxy-6,10-dimethylundec-5-en-8-yn-2-one (46)

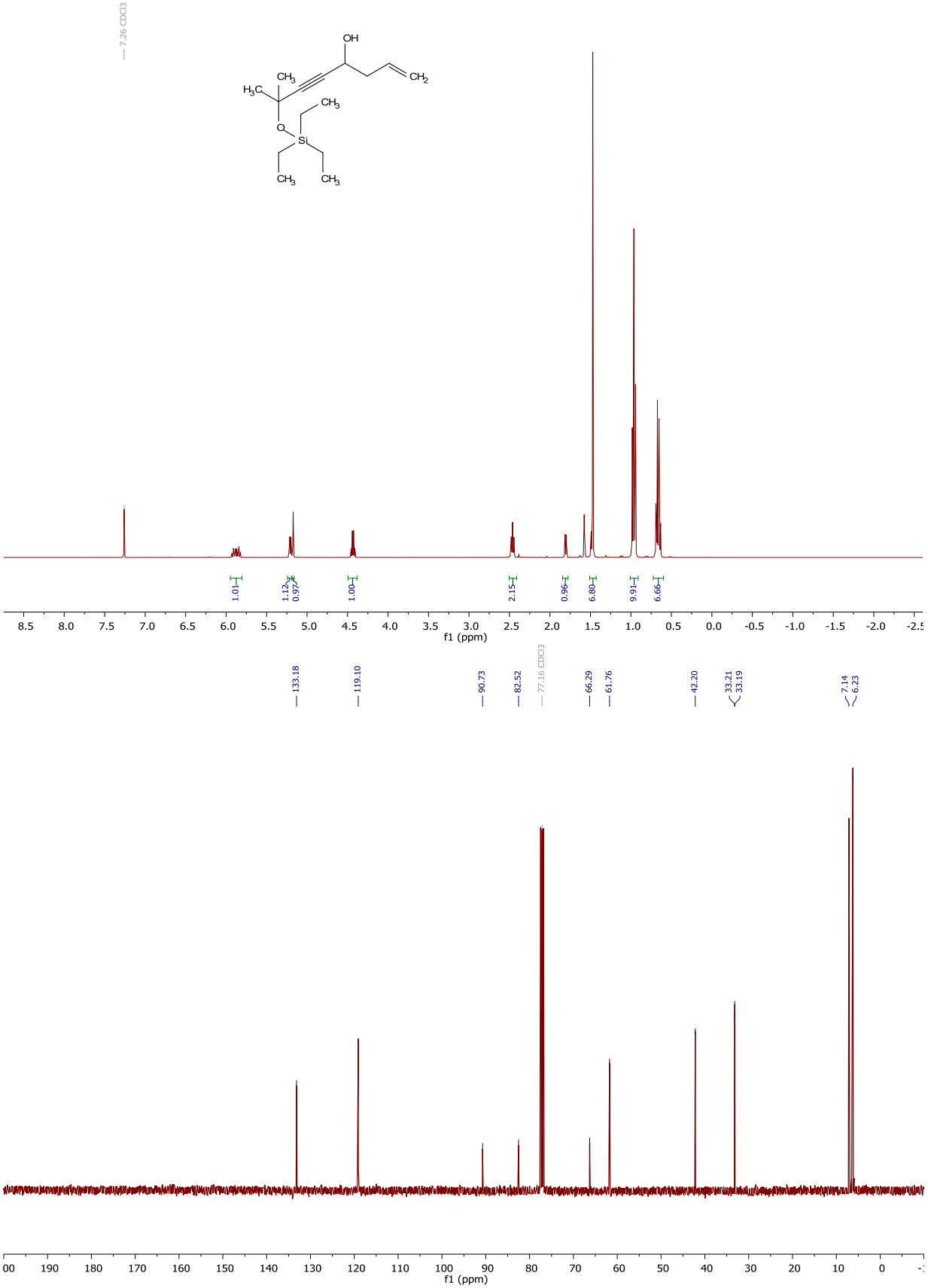


(3*E*,6*E*)-2,6-Dimethyl-10-oxo-3,6-undecadien-2-ol (47)

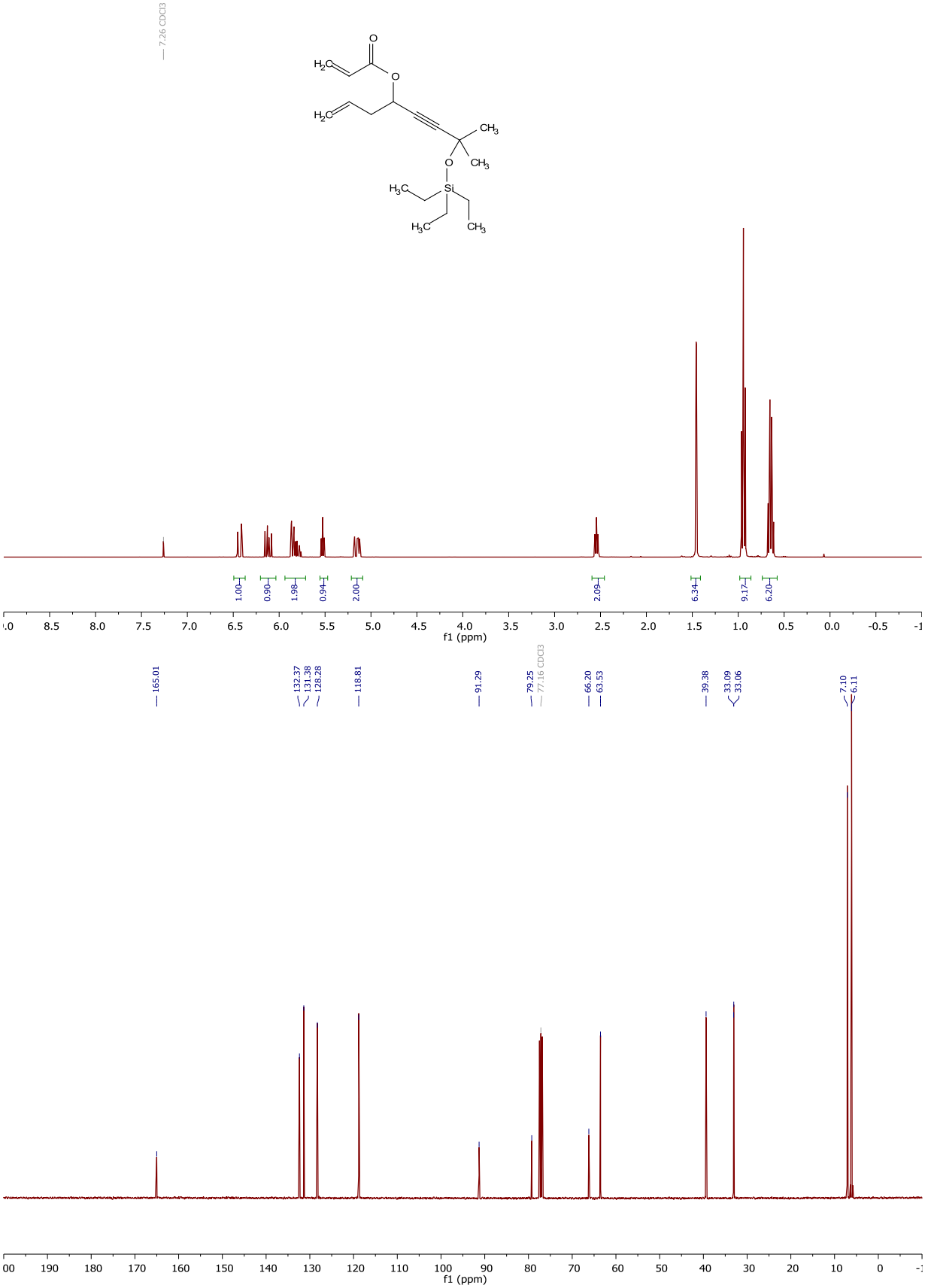




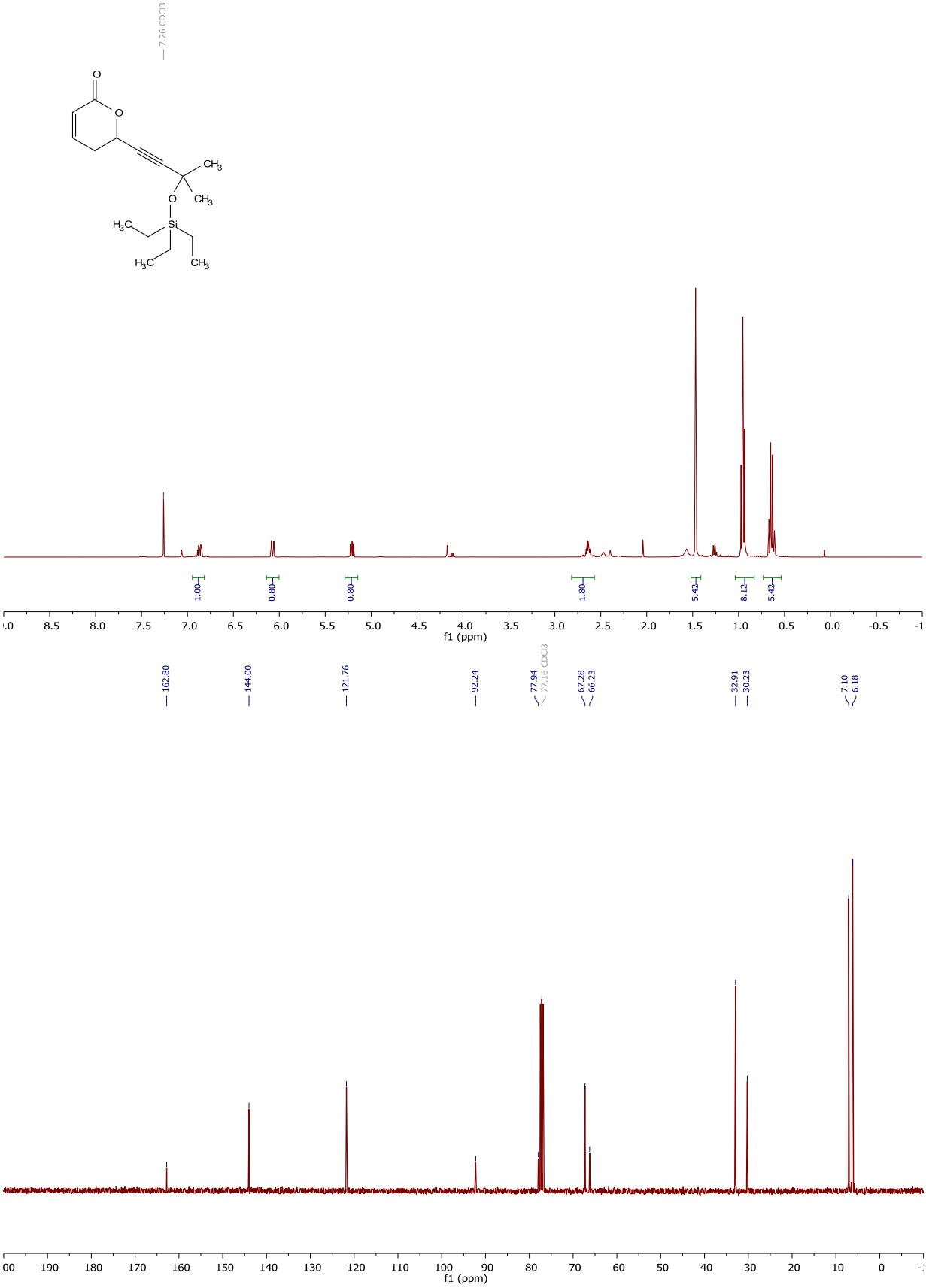
7-methyl-7-((triethylsilyl)oxy)oct-1-en-5-yn-4-ol



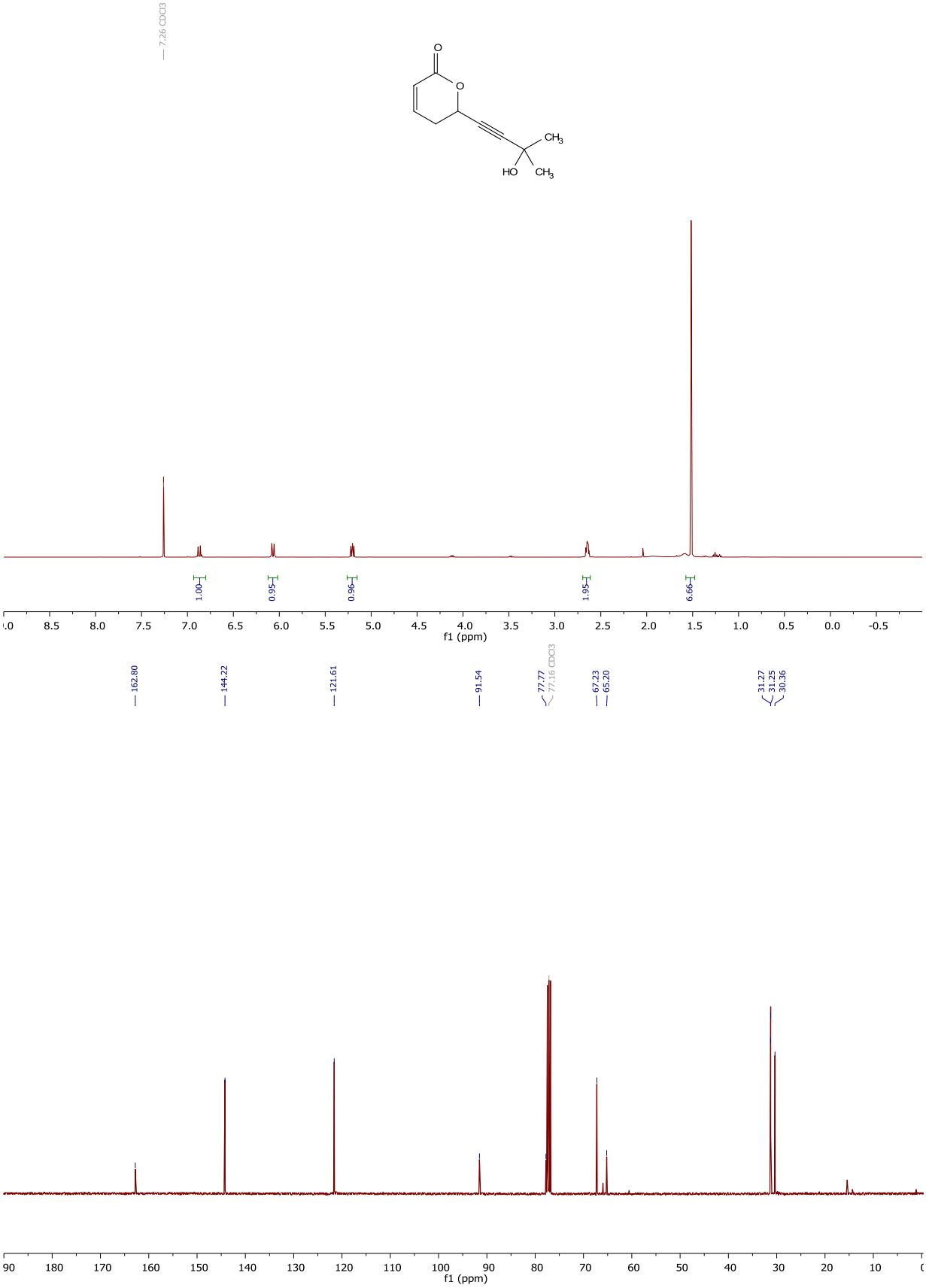
7-methyl-7-((triethylsilyl)oxy)oct-1-en-5-yn-4-yl acrylate (51)



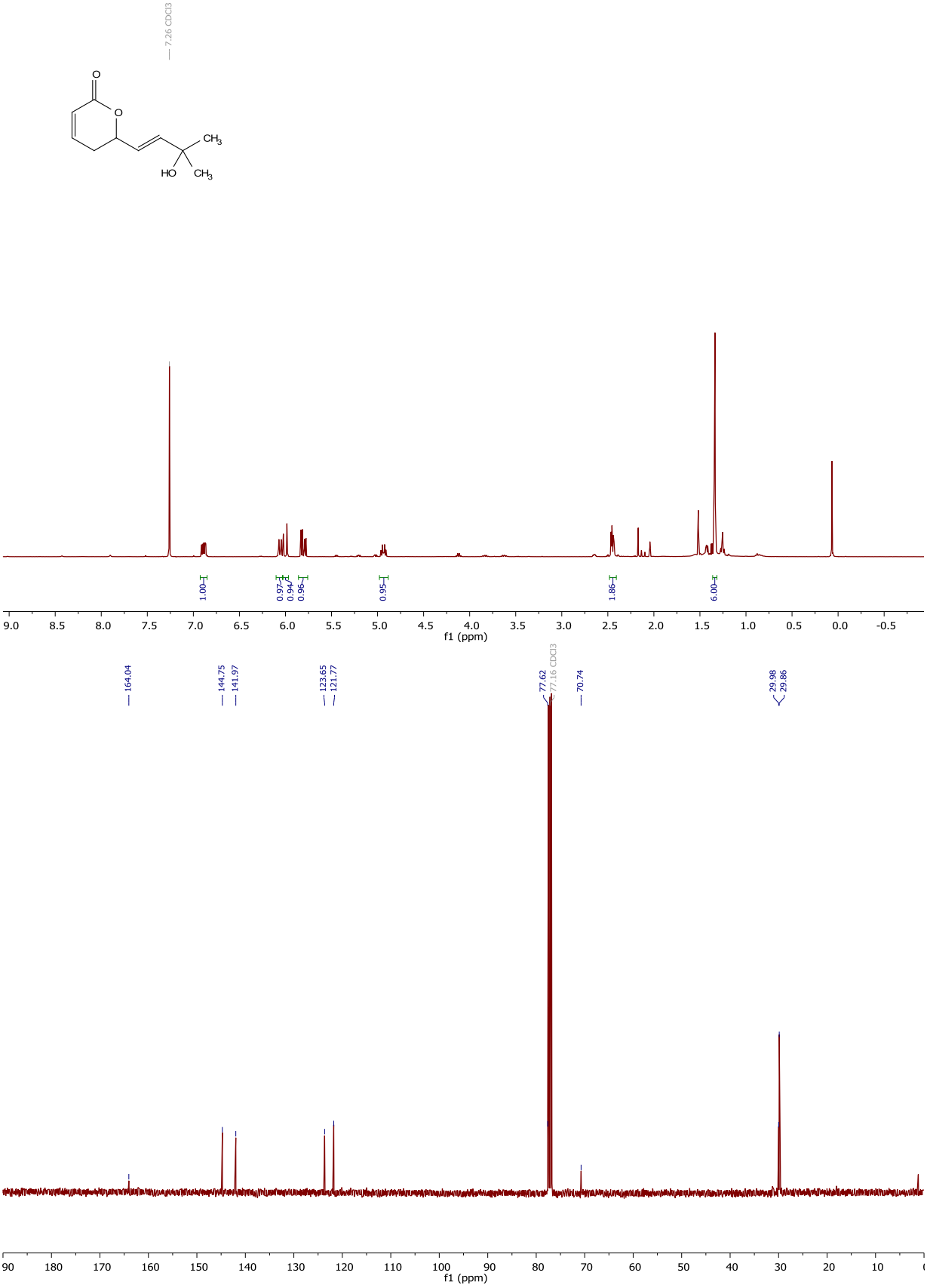
6-(3-methyl-3-((triethylsilyl)oxy)but-1-yn-1-yl)-5,6-dihydro-2H-pyran-2-one



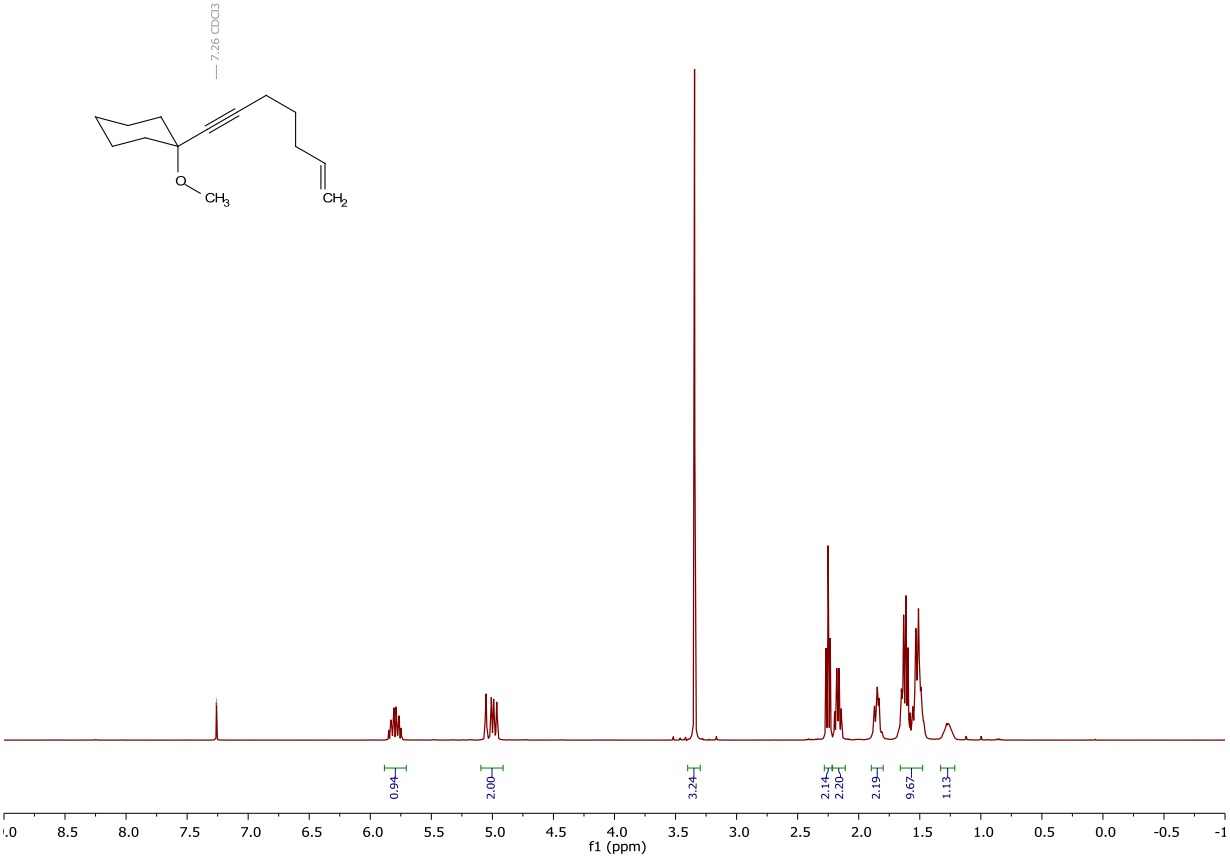
6-(3-hydroxy-3-methylbut-1-yn-1-yl)-5,6-dihydro-2H-pyran-2-one (52)

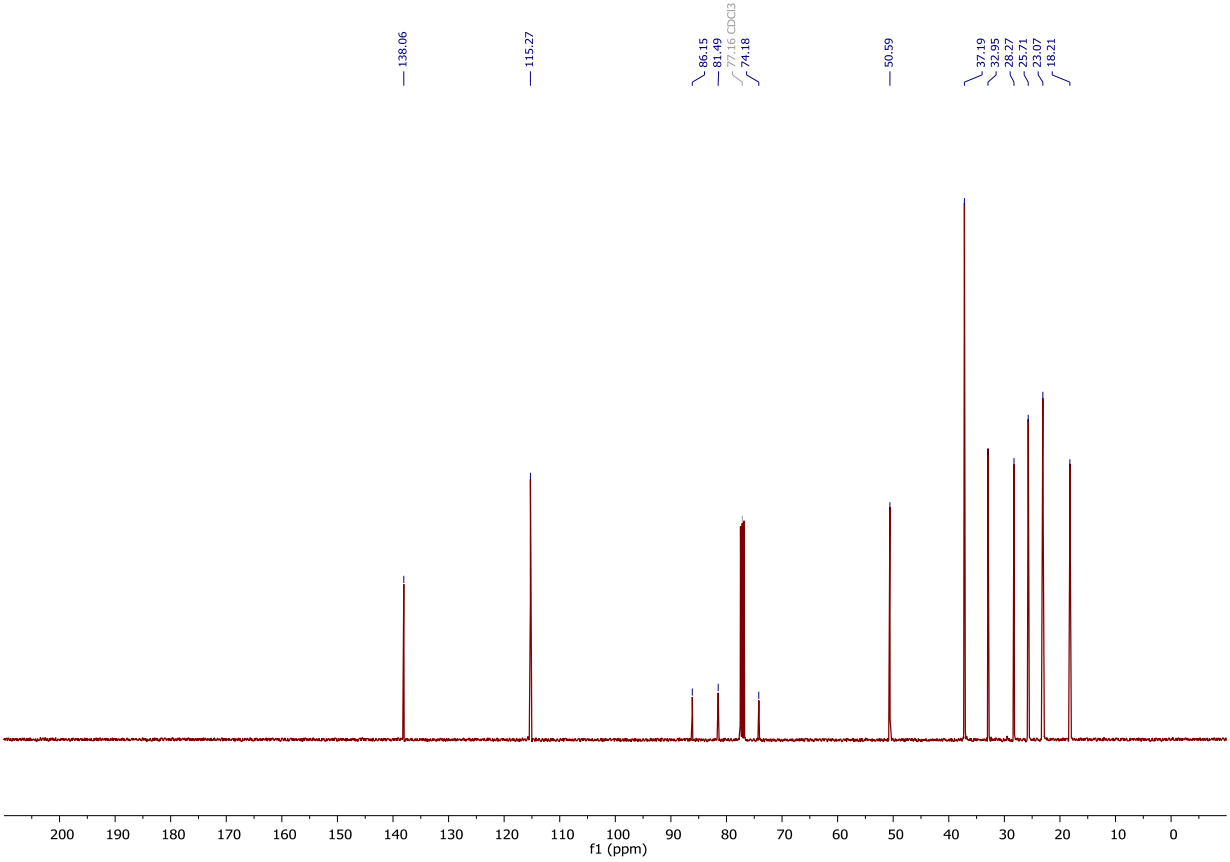


_(E)_-6-(3-hydroxy-3-methylbut-1-en-1-yl)-5,6-dihydro-2H-pyran-2-one (53)

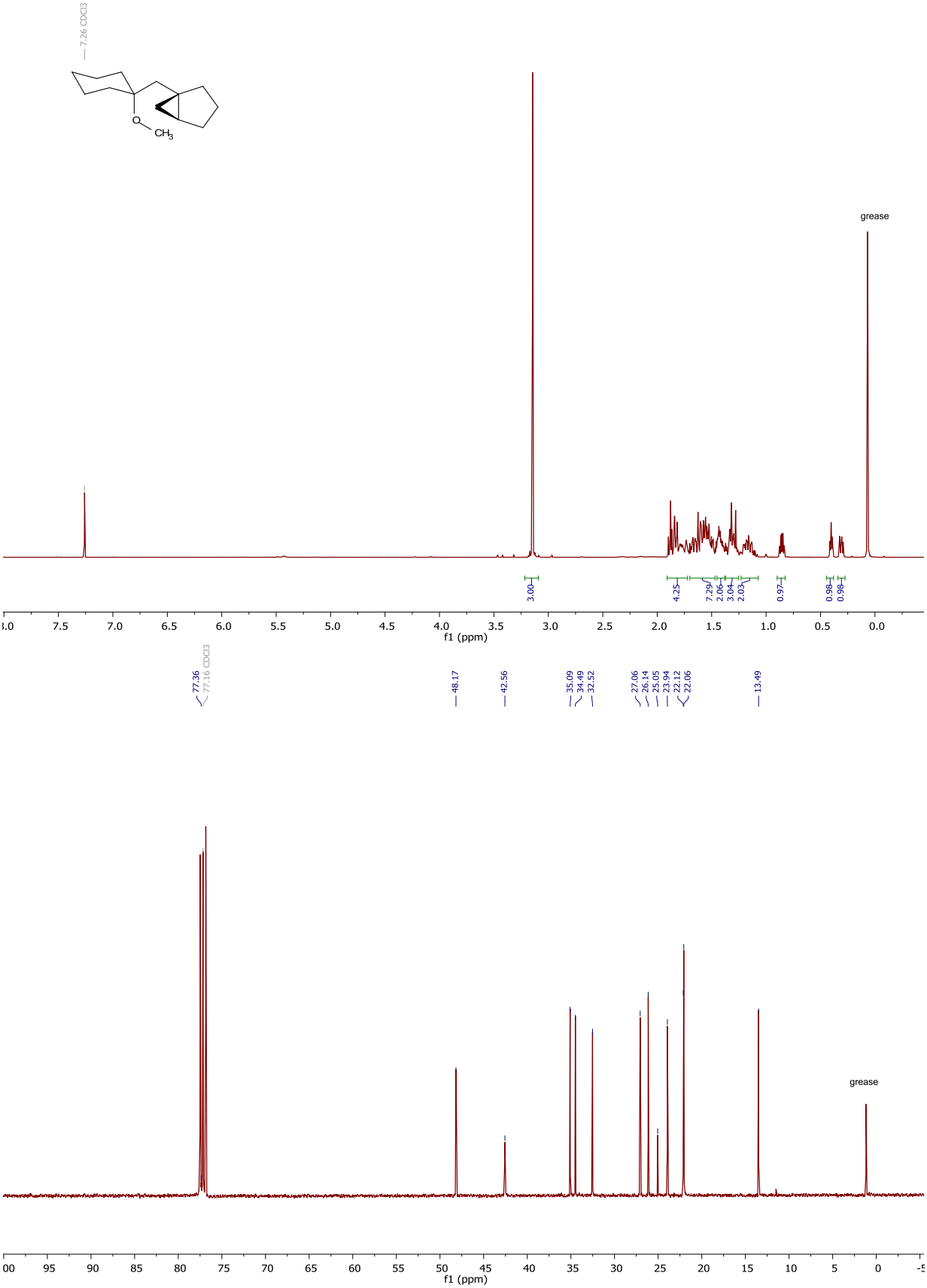


1-(hept-6-en-1-yn-1-yl)-1-methoxycyclohexane (55)

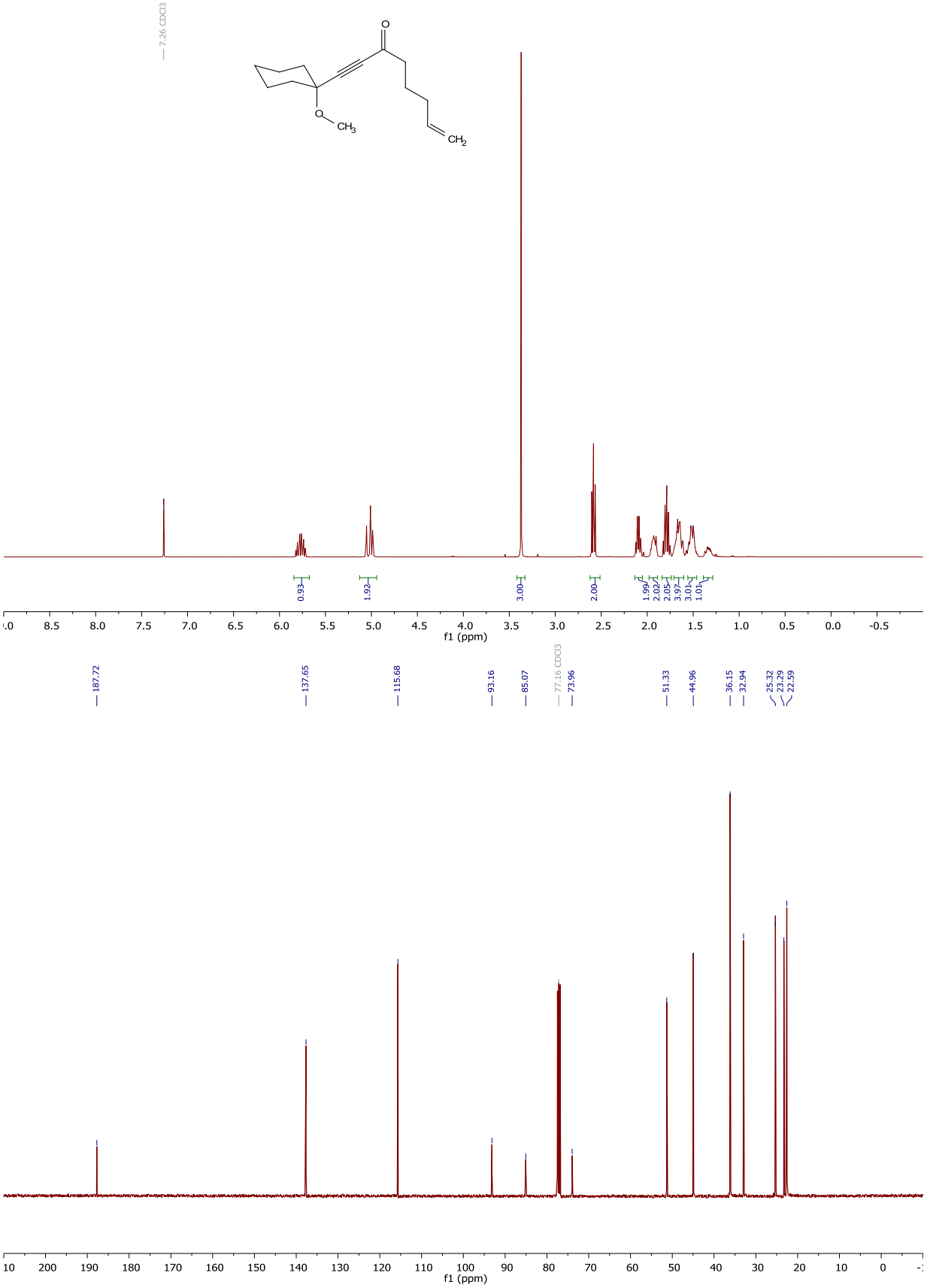




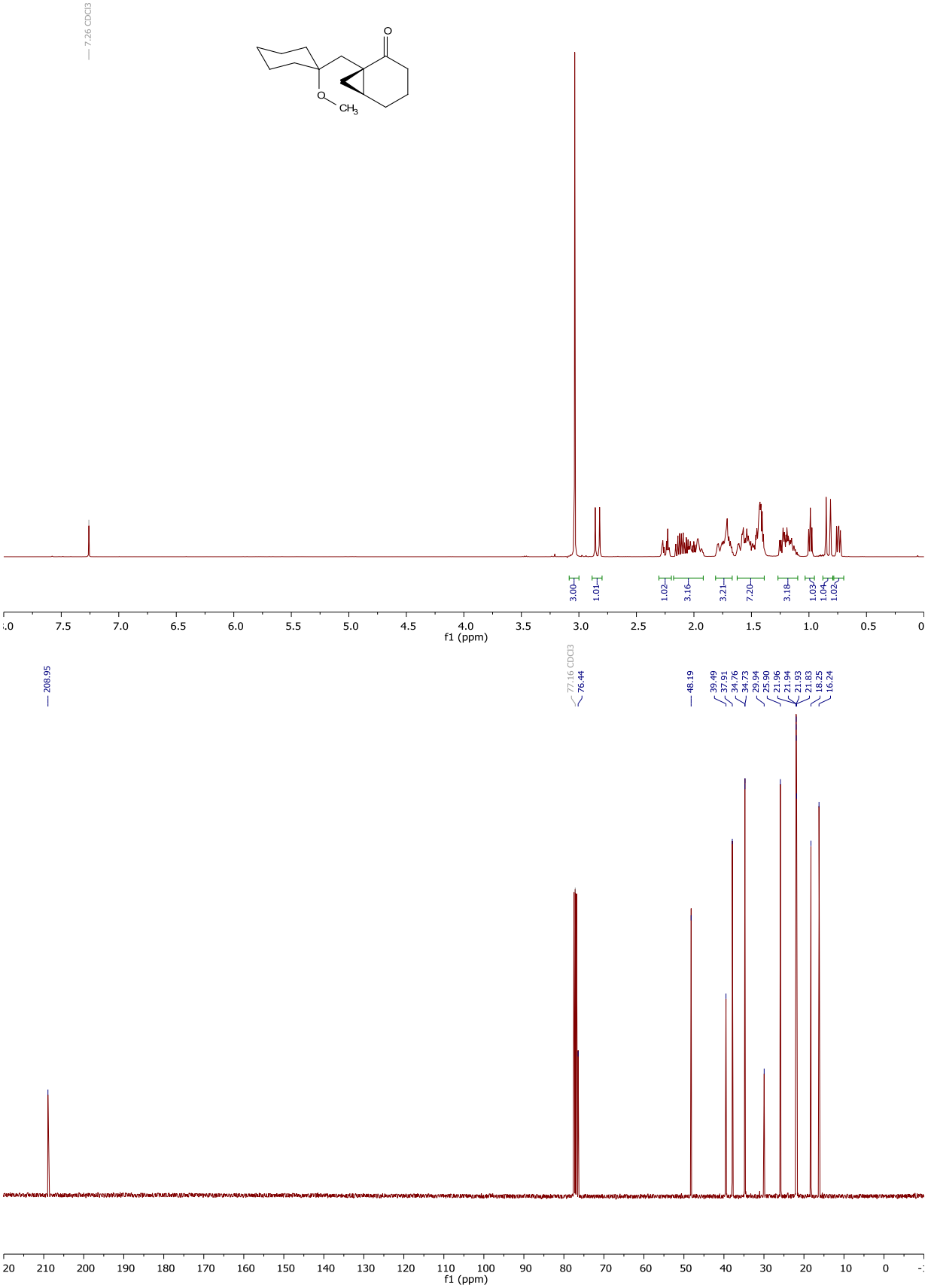
1-((1-methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane (56)



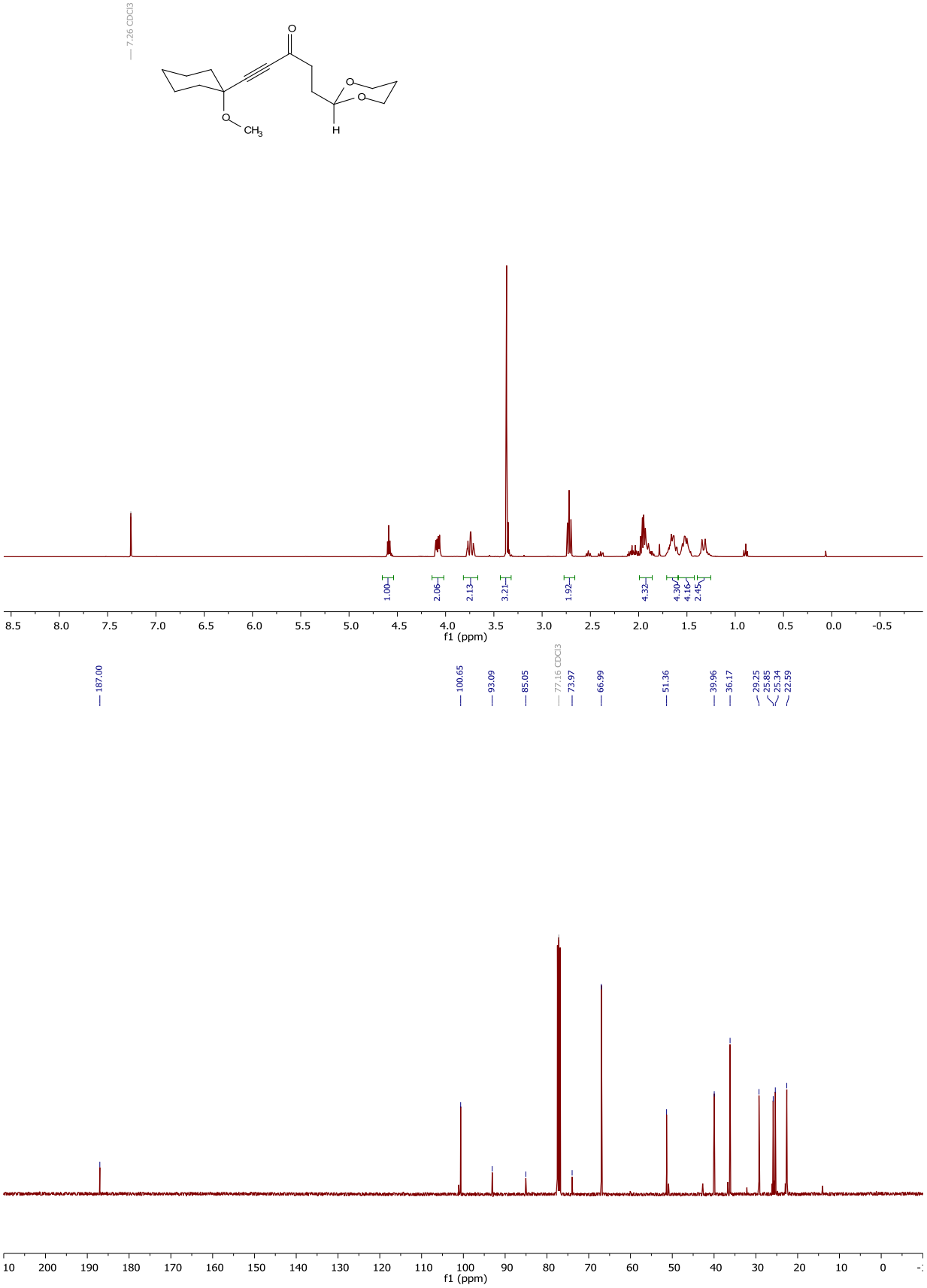
1-(1-methoxycyclohexyl)oct-7-en-1-yn-3-one (57)



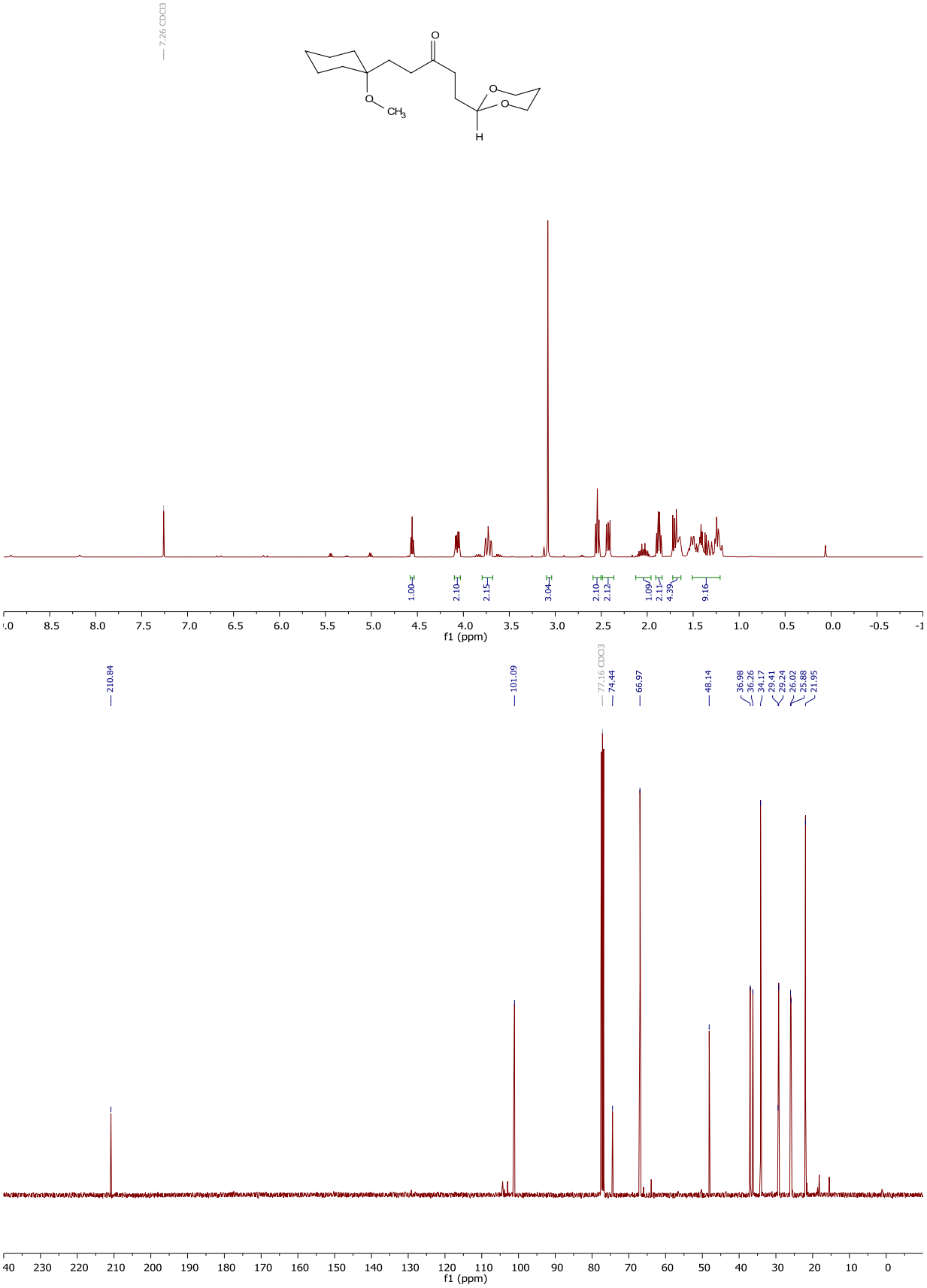
(1S,6S)-1-((1-methoxycyclohexyl)methyl)bicyclo[4.1.0]heptan-2-one (58)



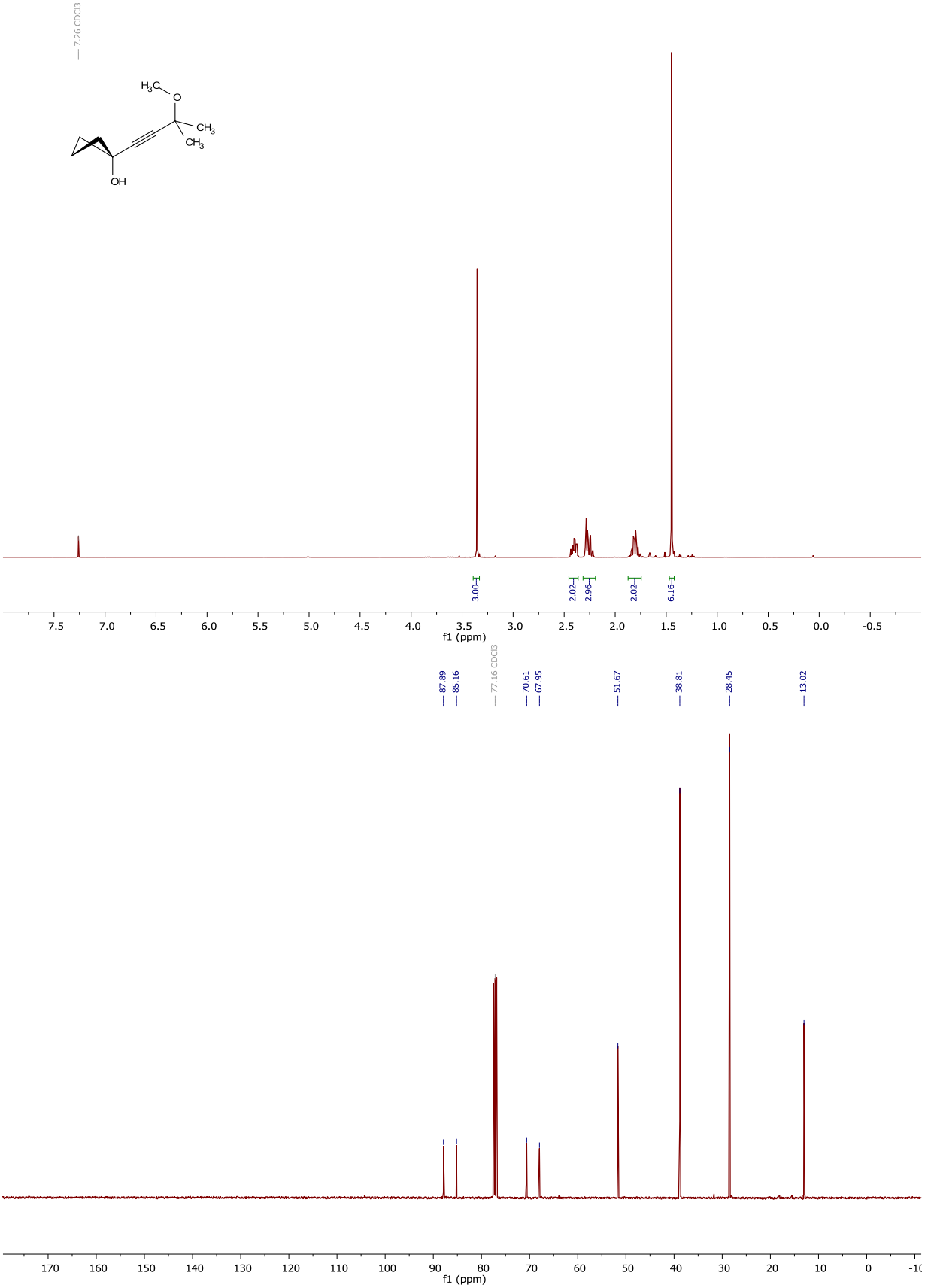
5-(1,3-dioxan-2-yl)-1-(1-methoxycyclohexyl)pent-1-yn-3-one (67)



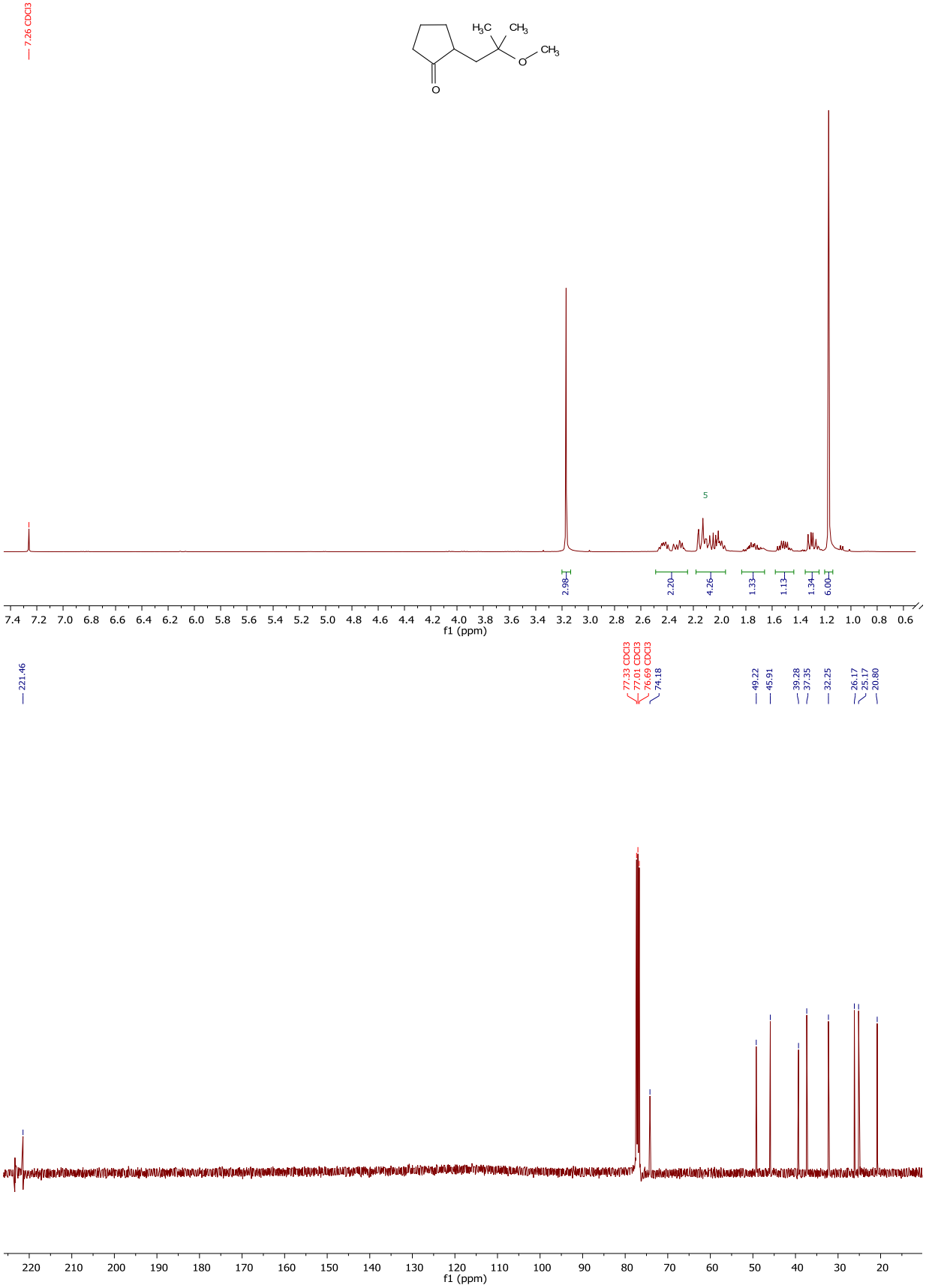
1-(1,3-dioxan-2-yl)-5-(1-methoxycyclohexyl)pentan-3-one (68)



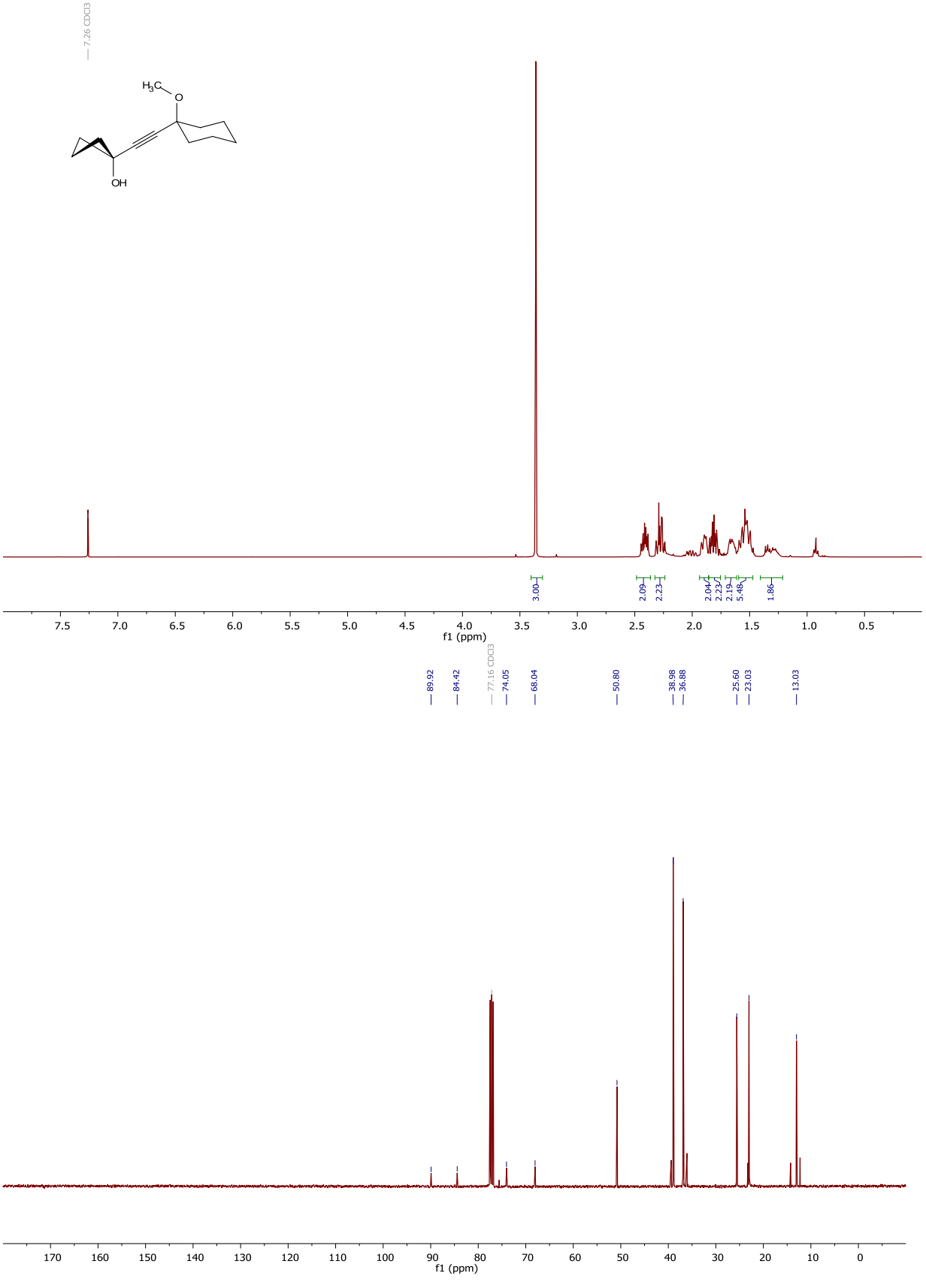
-(3-methoxy-3-methylbut-1-yn-1-yl)cyclobutan-1-ol (70)



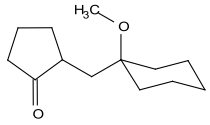
2-(2-methoxy-2-methylpropyl)cyclopentan-1-one (72)

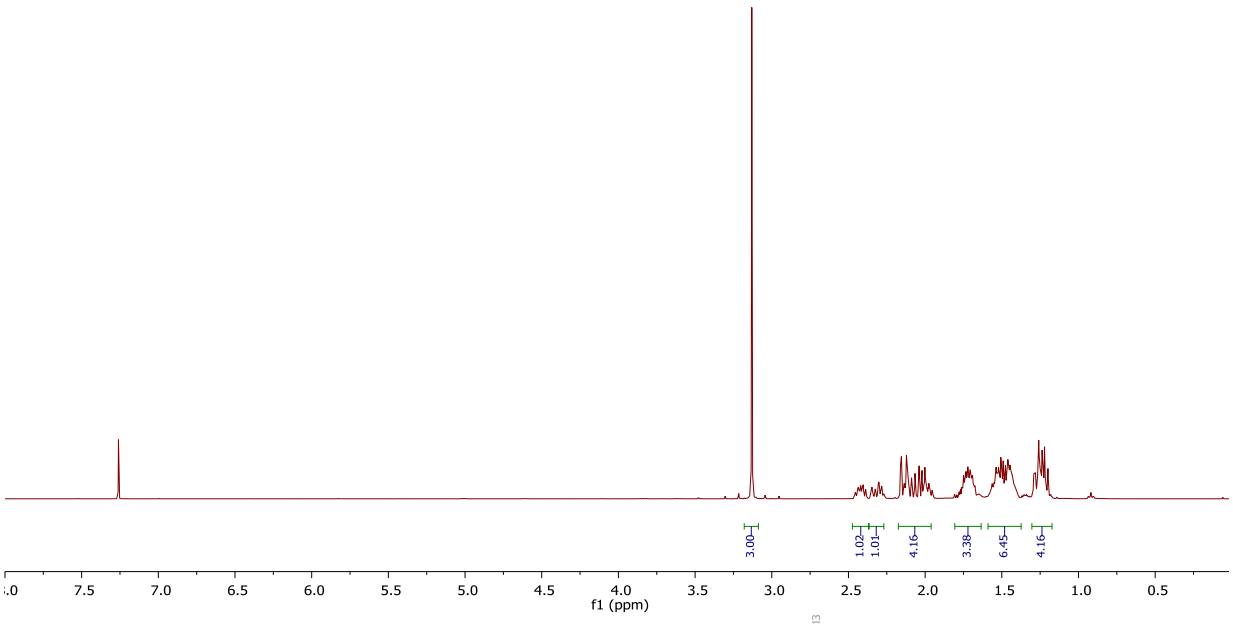


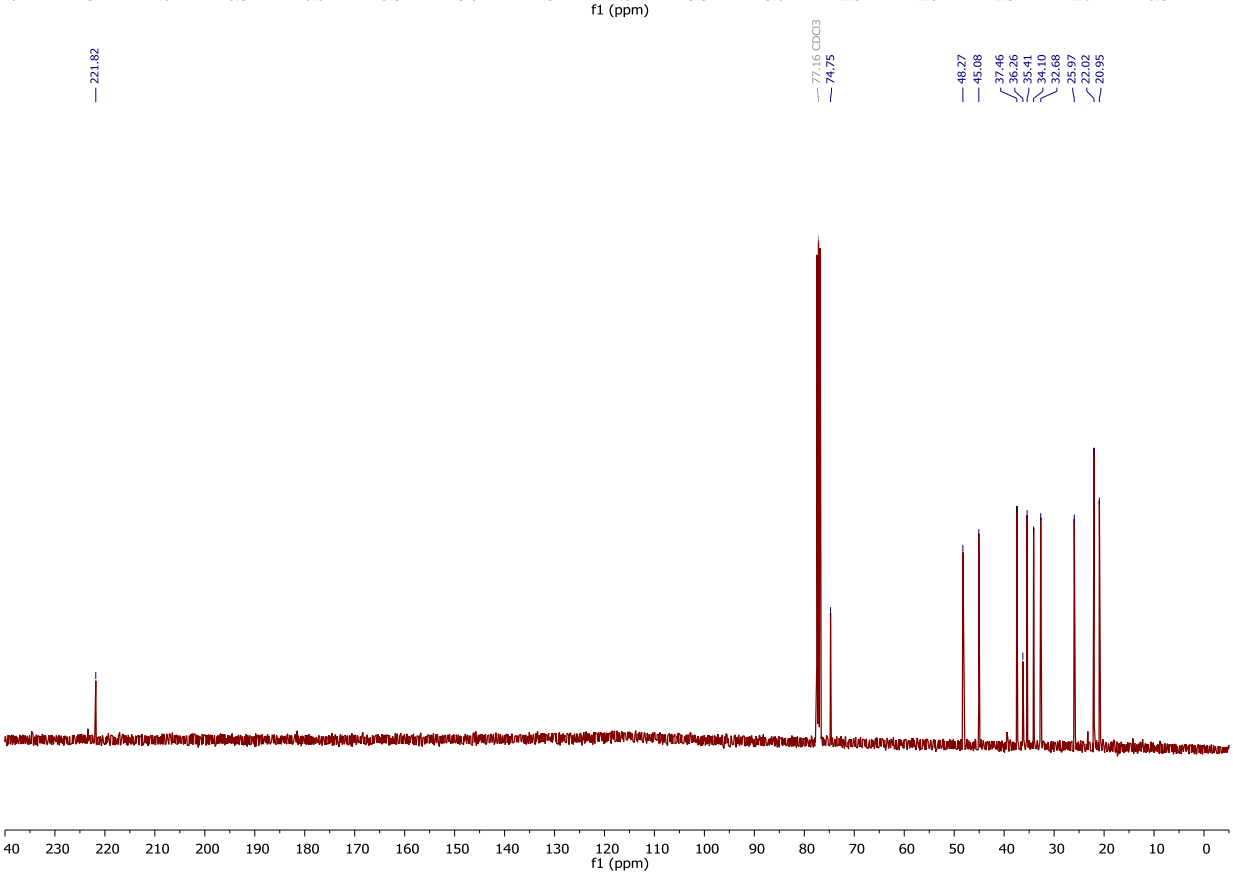
1-((1-methoxycyclohexyl)ethynyl)cyclobutan-1-ol (73)

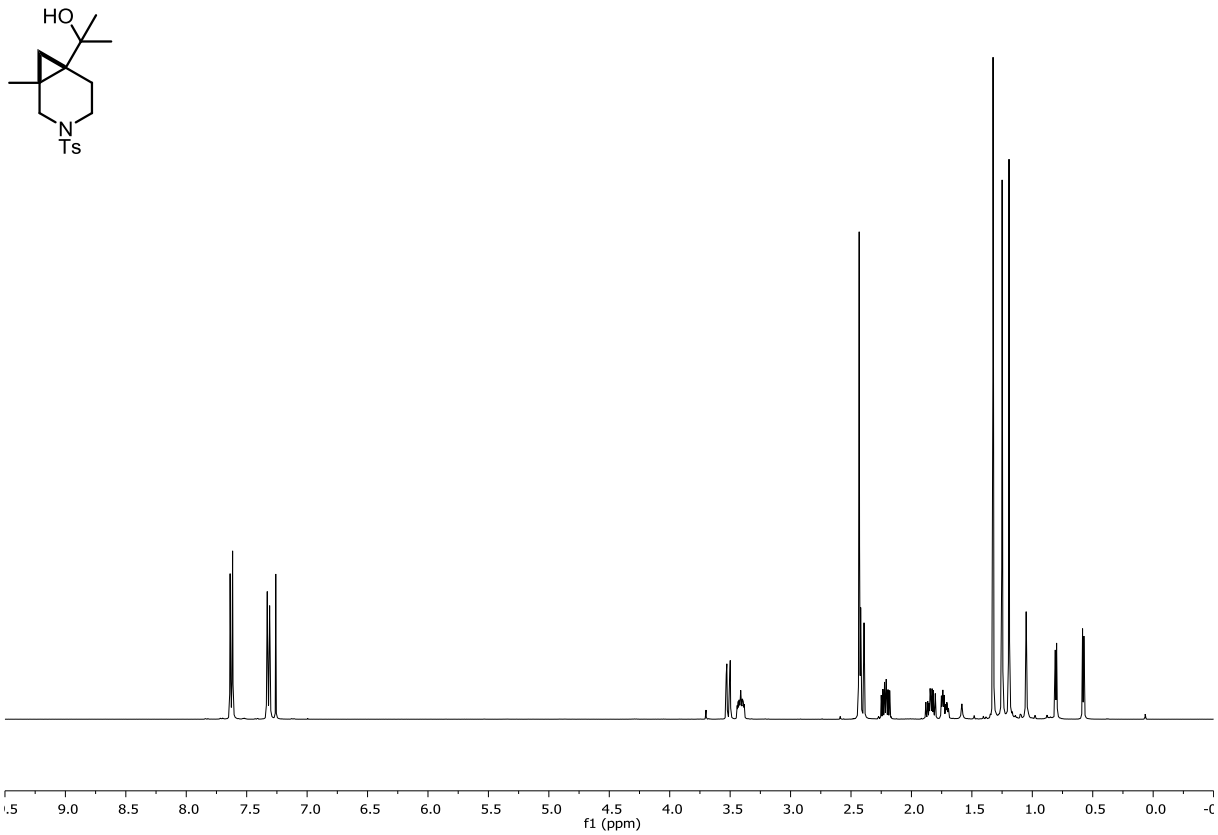


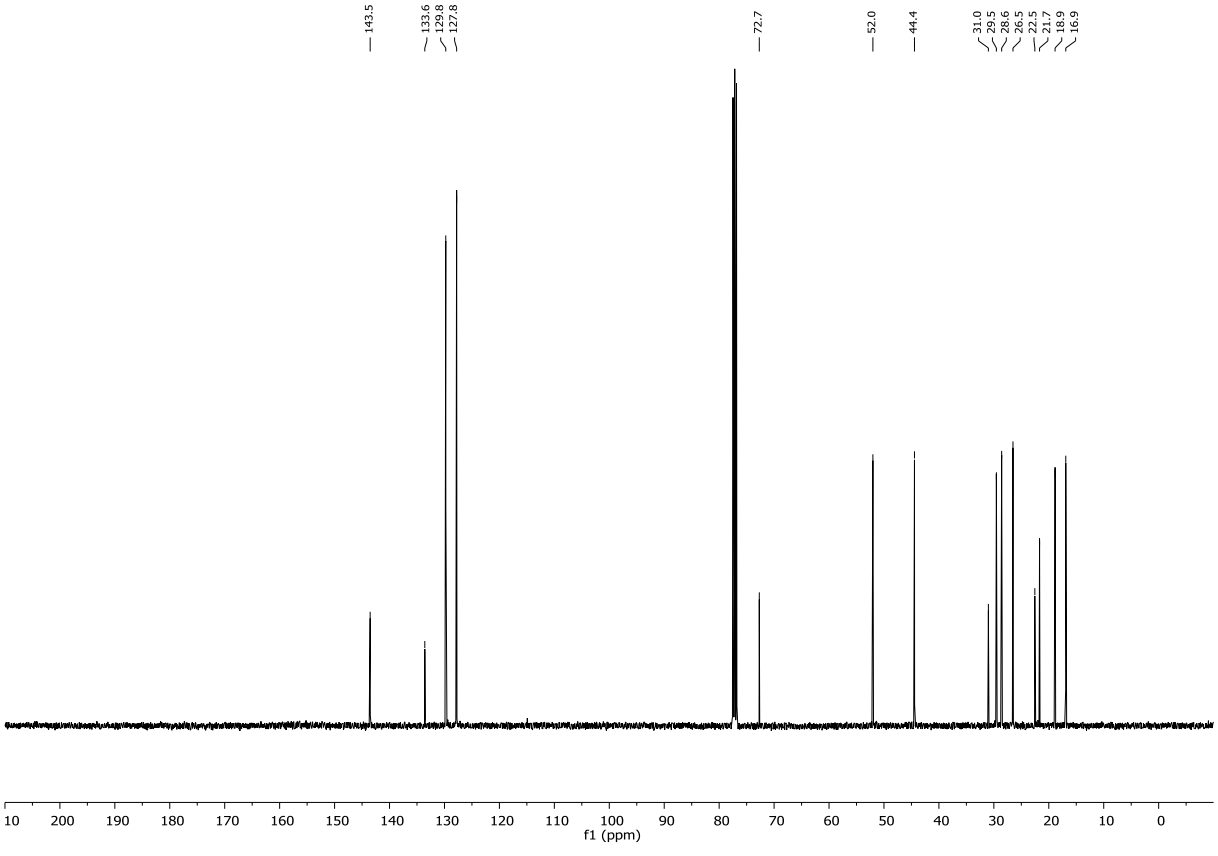
2-((1-methoxycyclohexyl)methyl)cyclopentan-1-one (74)

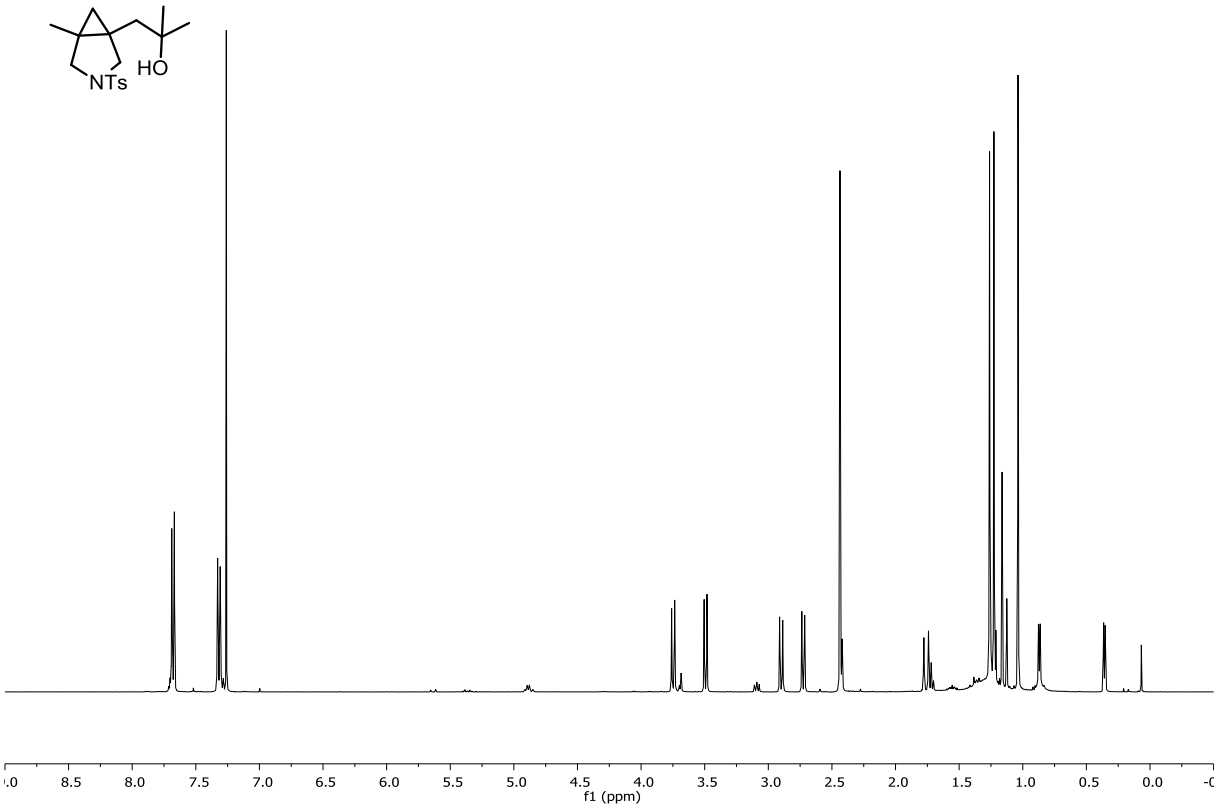


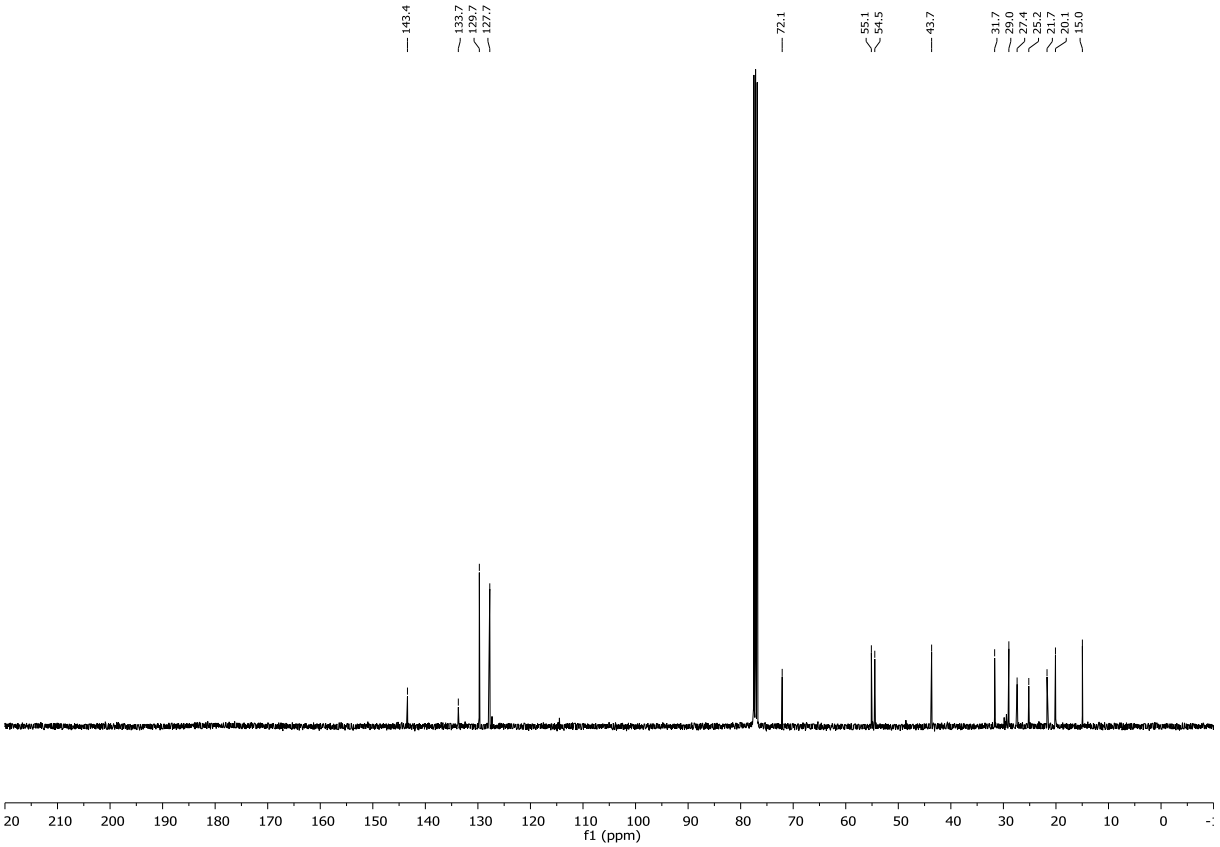


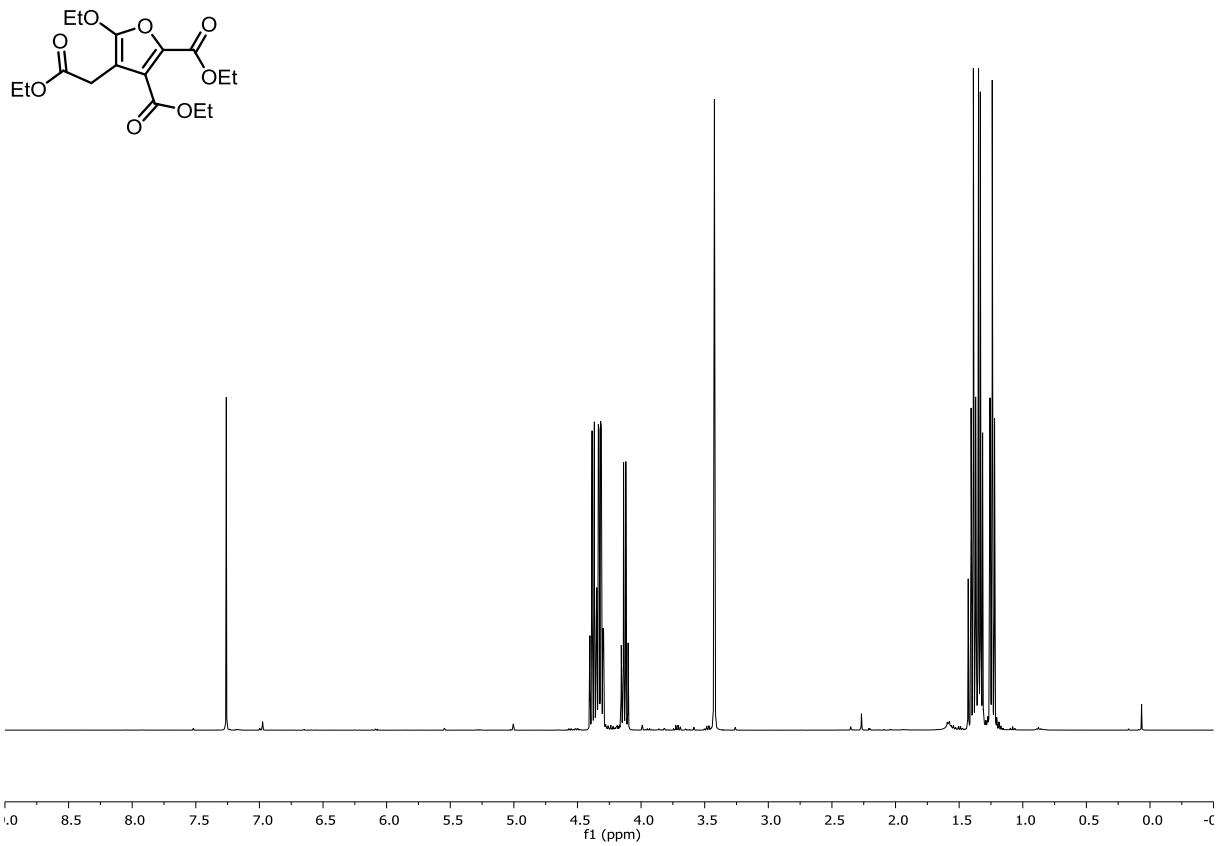


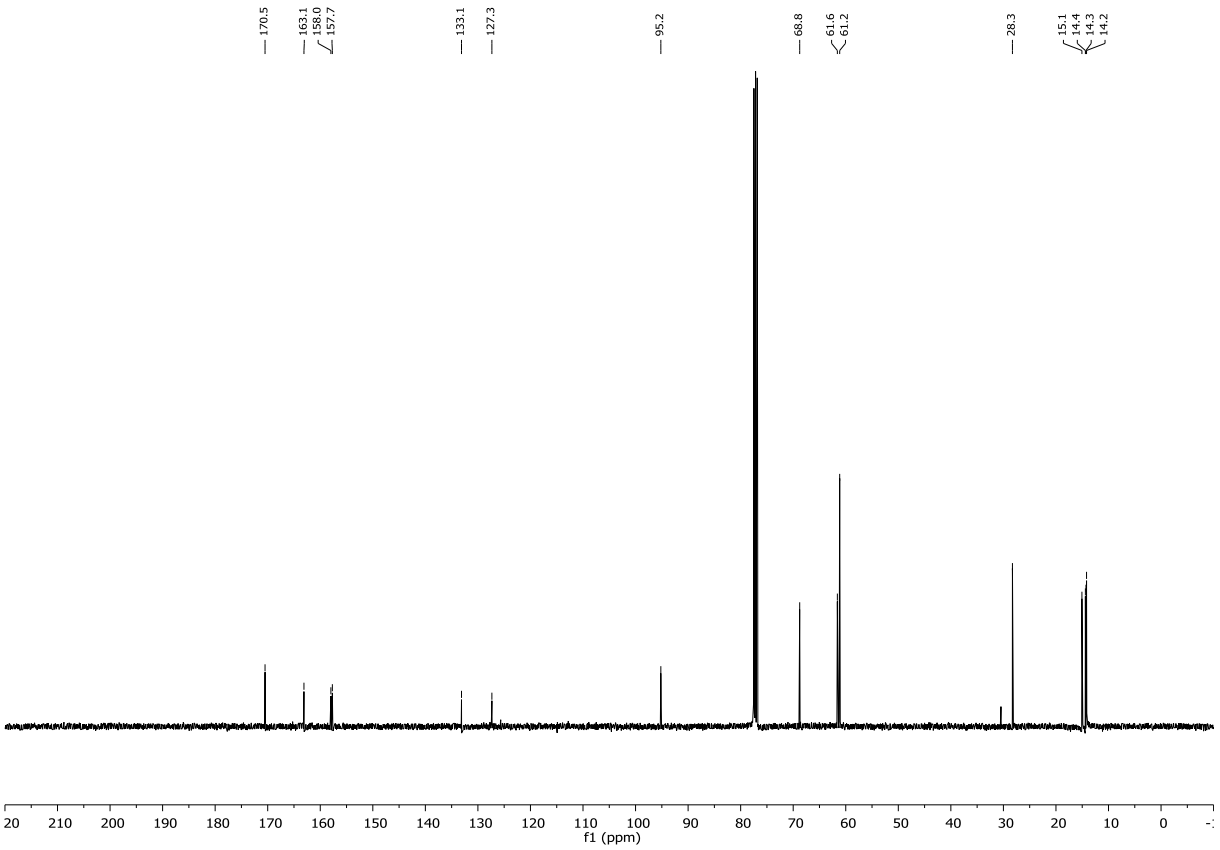

HO
N
Ts
f1 (ppm)


143.5
133.6
129.8
127.8
72.7
52.0
44.4
31.0
29.5
28.6
26.5
22.5
21.7
18.9
16.9
f1 (ppm)


NTs
HO
f1 (ppm)


143.4
133.7
129.7
127.7
72.1
55.1
54.5
43.7
31.7
29.0
27.4
25.2
21.7
20.1
15.0
f1 (ppm)


EtO
O
O
OEt
EtO
O
OEt
f1 (ppm)


170.5
163.1
158.0
157.7
133.1
127.3
95.2
68.8
61.6
61.2
28.3
15.1
14.4
14.3
14.2
f1 (ppm)

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