

# **Synthesis of Cyclic Alkenyl Dimethylsiloxanes from Alkynyl Benzylidemethylsilanes, and Application in Polyene Synthesis**

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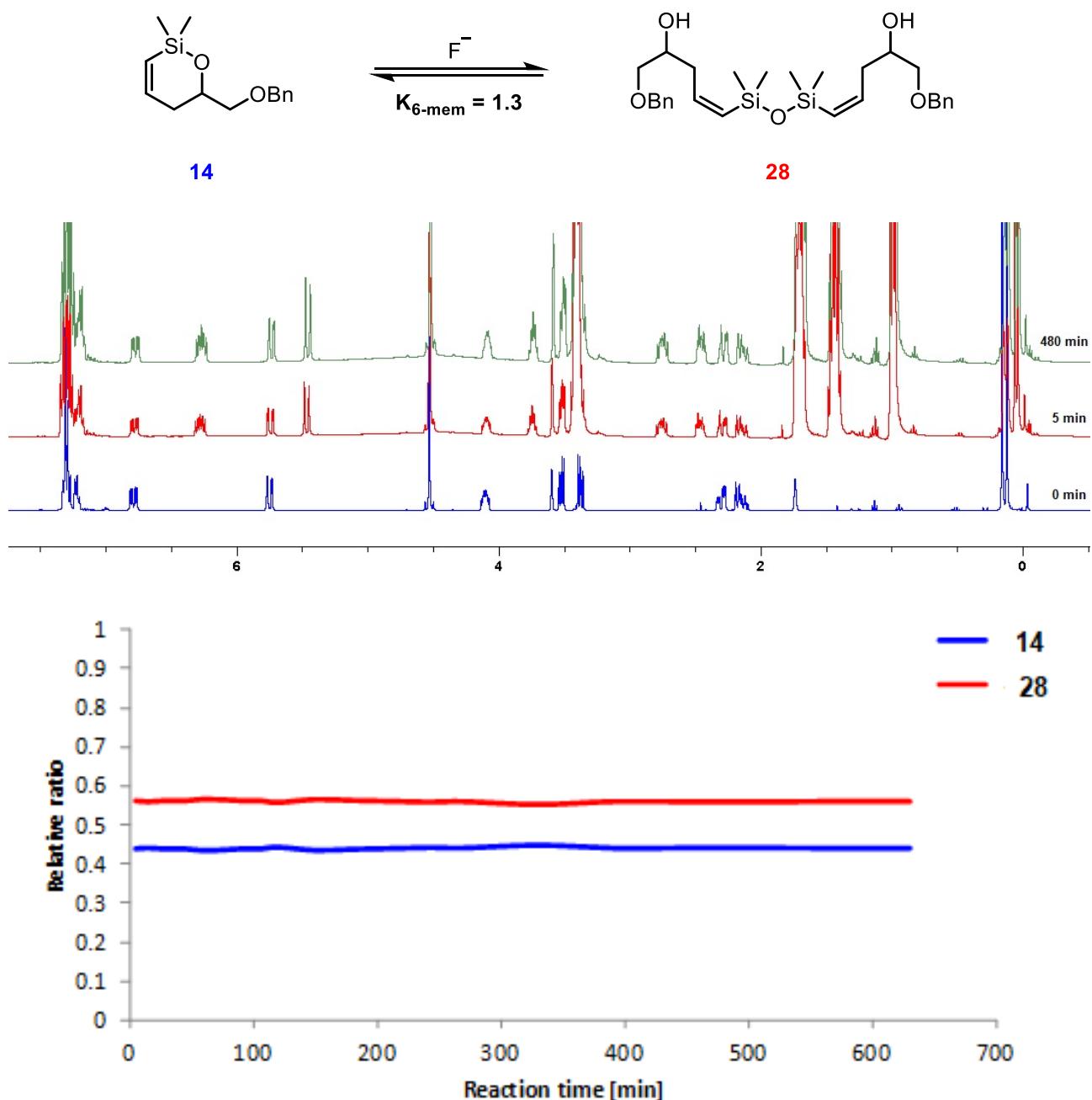
## **Supporting Information**

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## <sup>1</sup>H NMR studies – 6-Membered dimethylsiloxane **14**

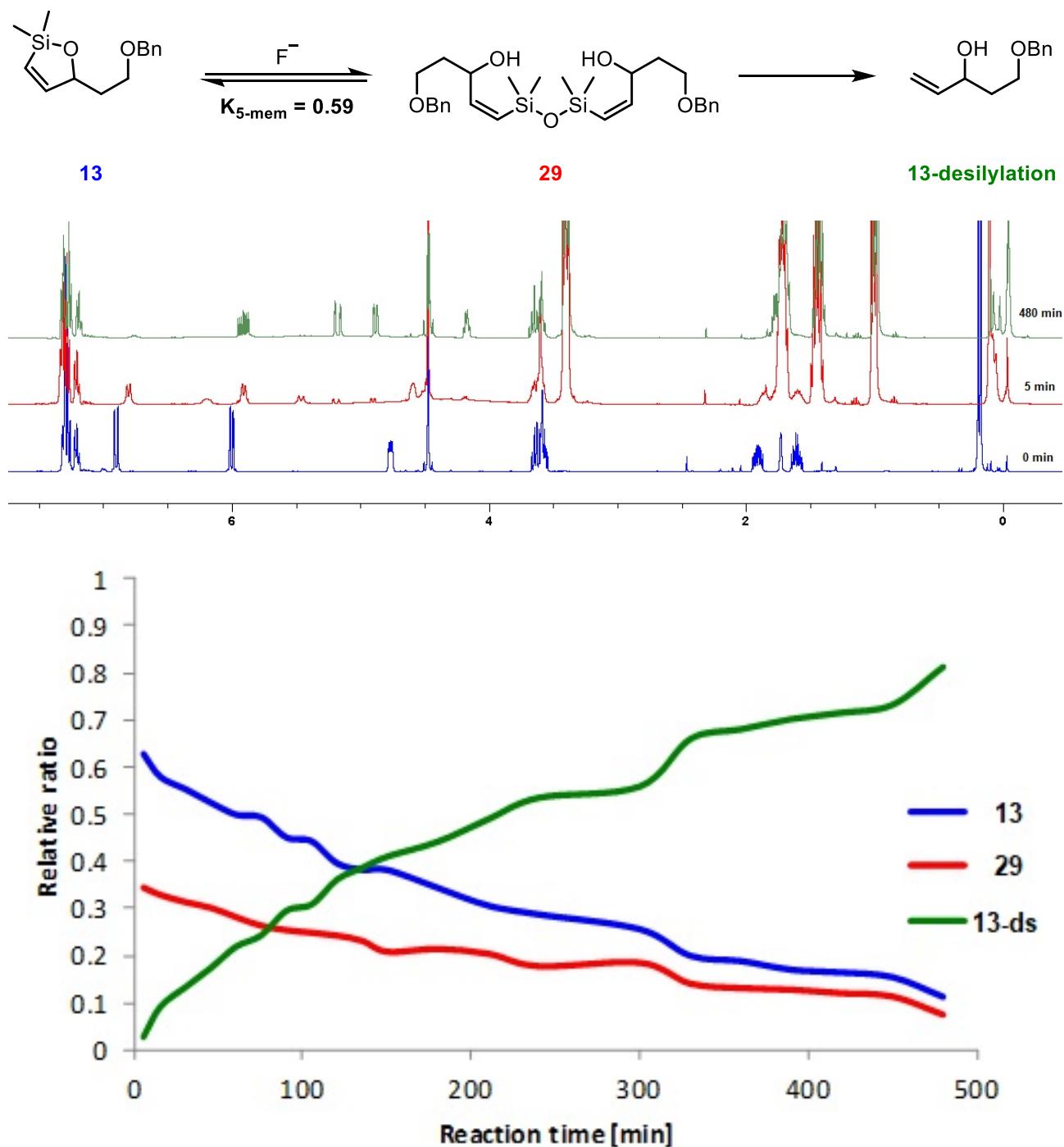
Upon treatment of 6-membered siloxane **14** (49 mg, 0.2 mmol, 1.0 equiv.) with TBAF•3H<sub>2</sub>O (189 mg, 0.6 mmol, 3 equiv.) in d<sub>8</sub>-THF (0.6 mL), a rapid equilibrium was established between siloxane **14** and acyclic disiloxane **28**, which remained at a constant ratio (**14**:**28**, 1:1.3) throughout the course of the experiment (Figure S1).



**Figure S1.** Treatment of 6-membered dimethyl siloxane **14** with TBAF•3H<sub>2</sub>O (3 equiv.) in d<sub>8</sub>-THF, monitored periodically by <sup>1</sup>H NMR spectroscopy

## <sup>1</sup>H NMR studies – 5-Membered dimethyl siloxane 13

Upon treatment of 5-membered siloxane **13** (49 mg, 0.2 mmol, 1.0 equiv.) with TBAF•3H<sub>2</sub>O (189 mg, 0.6 mmol, 3 equiv.) in d<sub>8</sub>-THF (0.6 mL), a rapid equilibrium is established between siloxane **13** and acyclic disiloxane **29** at an initial ratio of **13:29**, 1.7:1. These compounds slowly convert to protodesilylated product **13-desilylation** over the course of the experiment (Figure S2).



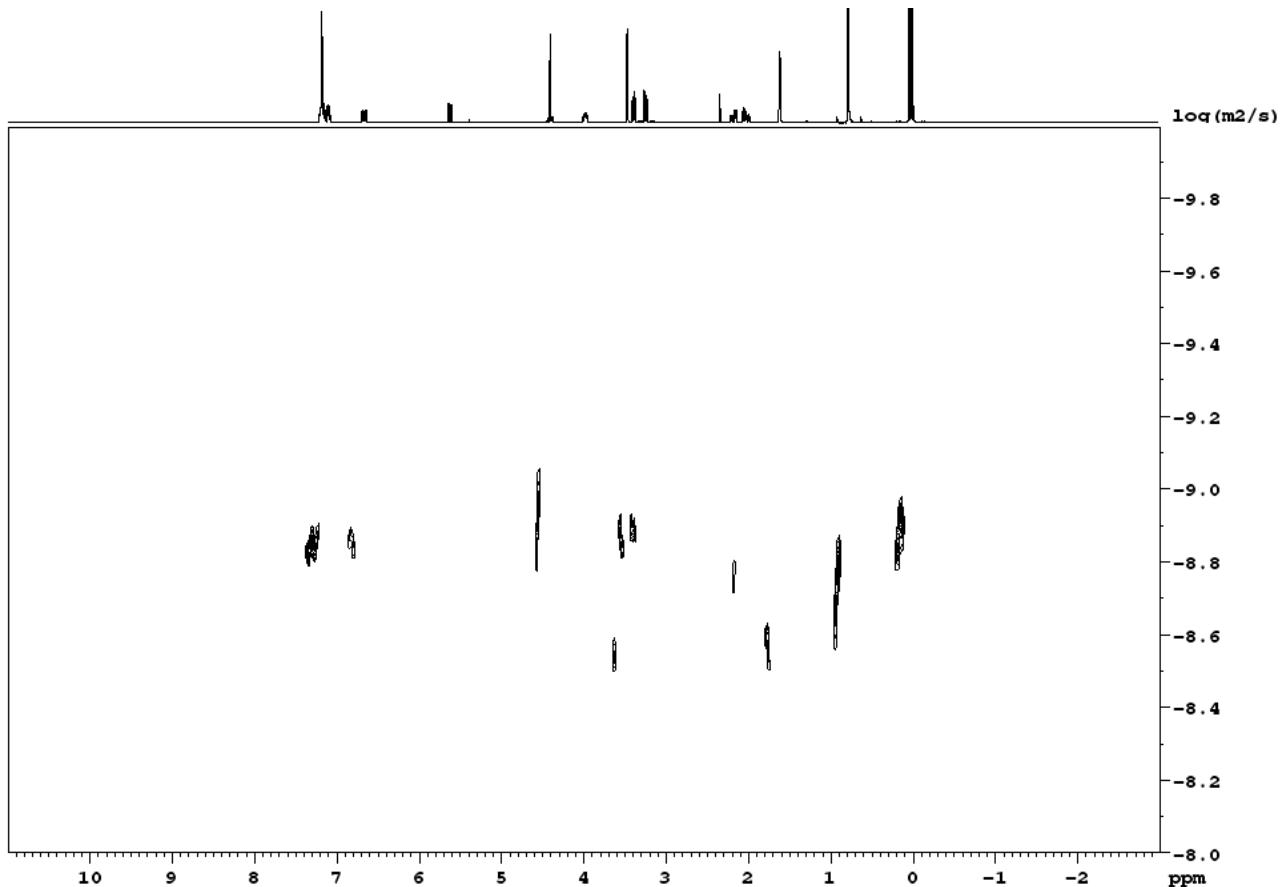
**Figure S2.** Treatment of 5-membered dimethyl siloxane **13** with TBAF•3H<sub>2</sub>O (3 equiv.) in d<sub>8</sub>-THF, monitored periodically by <sup>1</sup>H NMR spectroscopy

## <sup>1</sup>H NMR studies – ECC DOSY experiment

### ECC DOSY experiment of 6-membered siloxane **14** in THF

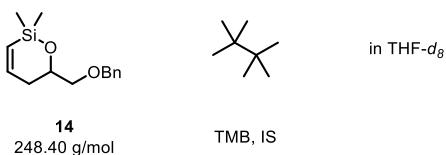
6-membered siloxane **14** (10.2 mg, 41.1 µmol) and internal standard tetramethylbutane (TMB) (3.4 mg, 29.8 mmol) were dissolved in *d*<sub>8</sub>-THF (0.6 mL). NMR spectra were recorded at 25 °C.

After processing only data points from signals with qualitatively good diffusion, decay curves are taken forward to calculate molecular weights using the methods described by Stalke *et. al.*<sup>1,2</sup>. Calculated molecular weights are shown in table S1.



*ECC DOSY experiment for disiloxane **14**.*

Table S1: Estimated molecular weights of cyclic siloxane species by ECC-DOSY NMR



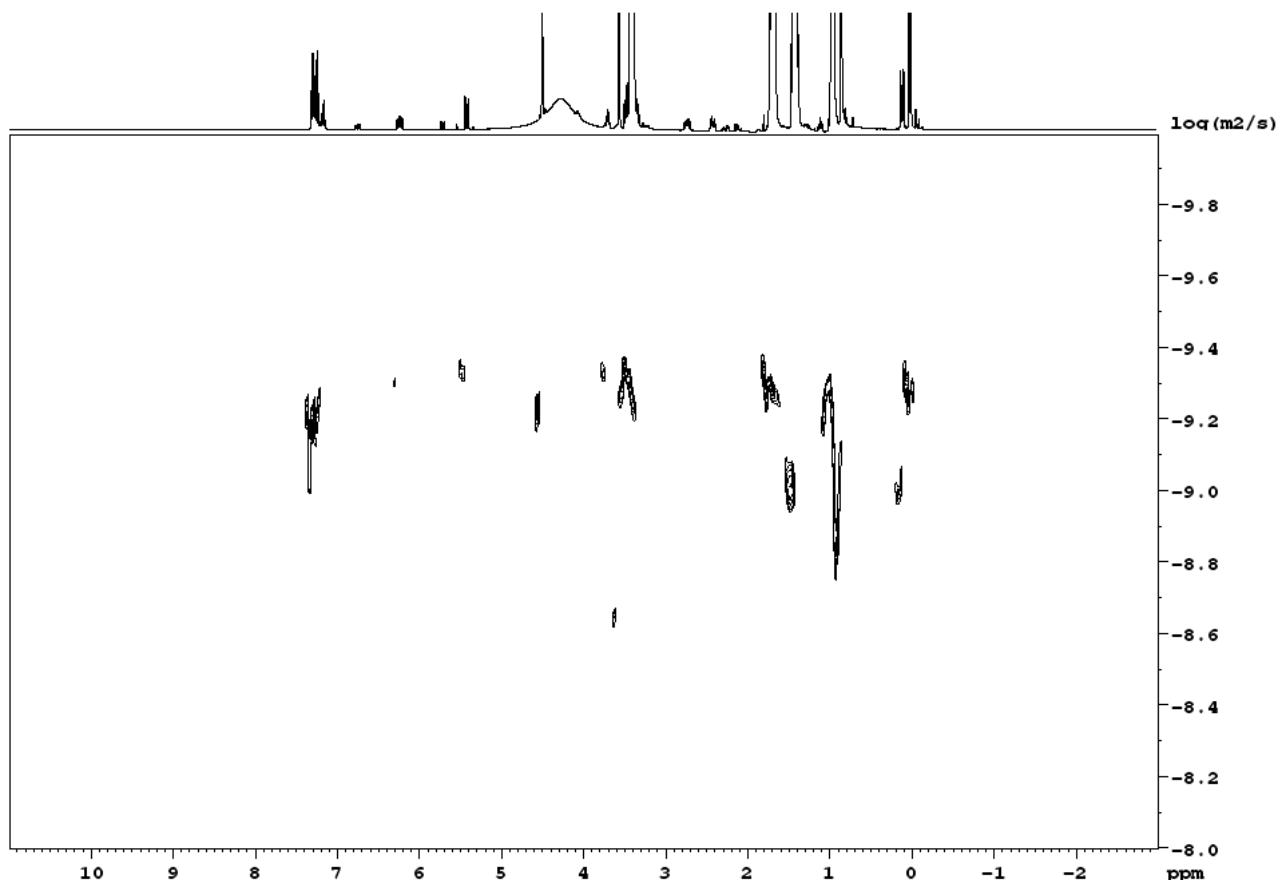
Entry	signal [ppm] <sup>a</sup>	Diff.Coeff. [m <sup>2</sup> /s] <sup>a</sup>	species <sup>a</sup>	MW [g/mol] <sup>b</sup>	shape	MW <sub>det</sub> [g/mol]	MW <sub>dif</sub>
1	7.34	$1.458 \cdot 10^{-9}$	<b>14</b>	248	CS	192	29%
					Merge	196	27%
					DSE	191	30%
					ED	211	18%
2	4.56	$1.222 \cdot 10^{-9}$	<b>14</b>	248	CS	275	-10%
					Merge	271	-8%
					DSE	260	-5%
					ED	268	-7%
3	3.62	$2.835 \cdot 10^{-9}$	<b>14</b>	248	CS	250	-1%
					Merge	248	0%
					DSE	239	4%
					ED	251	-1%
4	0.18	$1.430 \cdot 10^{-9}$	<b>14</b>	248	CS	201	23%
					Merge	204	22%
					DSE	199	25%
					ED	217	14%

<sup>a</sup> determined from DOSY NMR; <sup>b</sup> calculated molecular weight; <sup>c</sup> molecular shape: CS: compact spheres, DSE: dissipated spheres and ellipsoids, ED: expanded discs, Merge: merged calibration curves.

ECC-DOSY experiment of siloxane **14** in THF with TBAF•3H<sub>2</sub>O

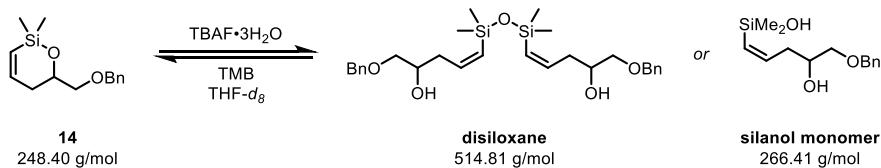
To the above mixture of 6-membered siloxane **14** (10.2 mg, 41.1 µmol, 1.0 equiv.) and internal standard tetramethylbutane (TMB) (3.4 mg, 29.8 mmol) in *d*<sub>8</sub>-THF (0.6 mL) was added TBAF•3H<sub>2</sub>O (38 mg, 120 µmol, 3.0 equiv.). NMR spectra were recorded at 25 °C.

Calculated molecular weights are shown in Table S2.



*ECC DOSY experiment for disiloxane **14** plus TBAF•3H<sub>2</sub>O*

Table S2: Estimated molecular weights of cyclic and acyclic siloxane species by ECC-DOSY NMR

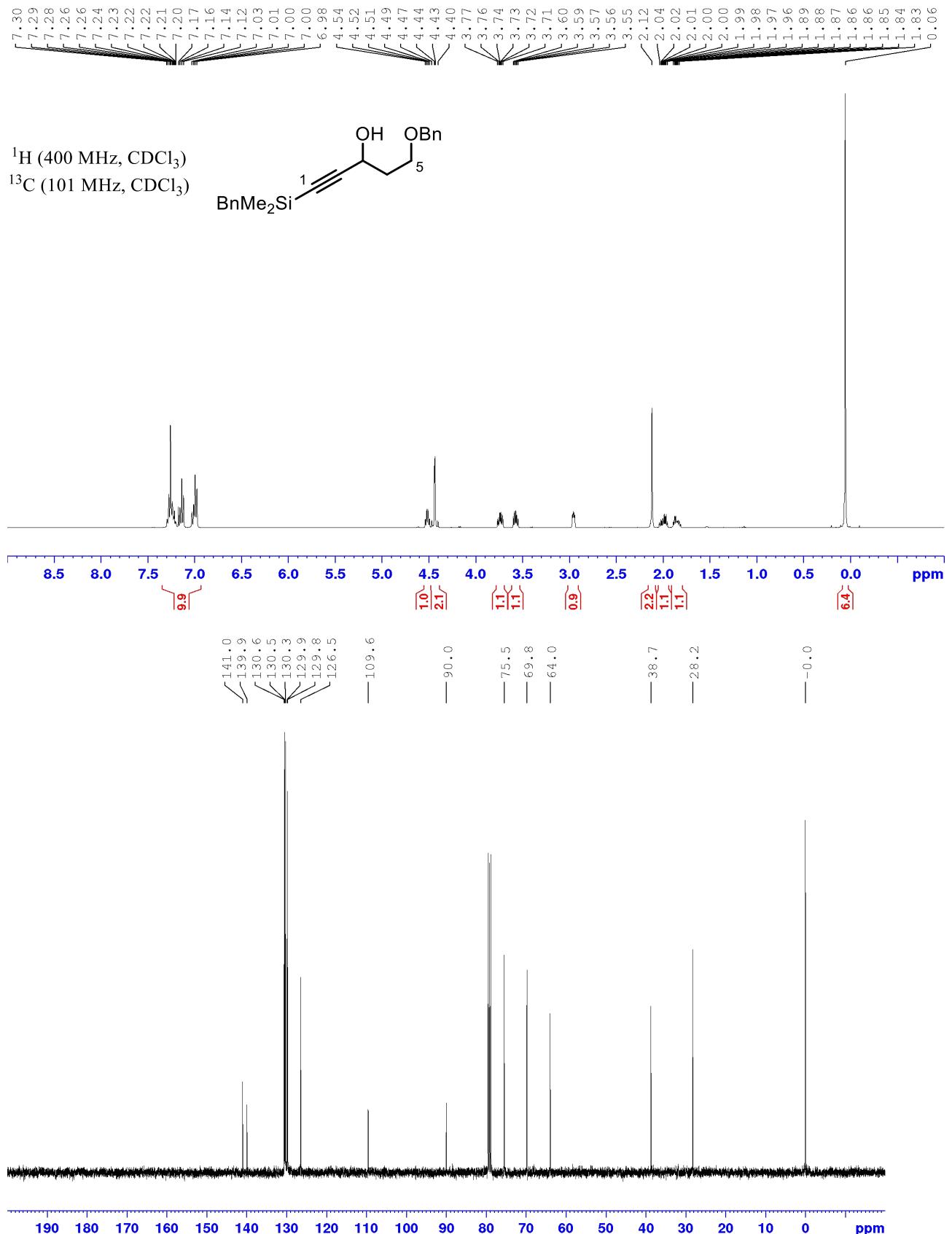


Entry	signal [ppm] <sup>a</sup>	Diff.Coeff. [m <sup>2</sup> /s] <sup>a</sup>	species <sup>a</sup>	MW [g/mol] <sup>b</sup>	shape	MW <sub>det</sub> [g/mol]	MW <sub>dif</sub>
1	7.34	$5.073 \cdot 10^{-10}$	acyclic	515	CS	1117	-54%
					Merge	946	-46%
					DSE	853	-40%
					ED	671	-23%
2	6.94	$4.795 \cdot 10^{-10}$	acyclic	515	CS	1252	-59%
					Merge	1048	-51%
					DSE	939	-45%
					ED	723	-29%
3	4.57	$5.686 \cdot 10^{-10}$	acyclic	515	CS	887	-42%
					Merge	770	-33%
					DSE	701	-27%
					ED	577	-11%
4	3.55	$4.738 \cdot 10^{-10}$	acyclic	515	CS	1283	-60%
					Merge	1071	-52%
					DSE	959	-45%
					ED	735	-30%
5	3.41	$5.284 \cdot 10^{-10}$	acyclic	515	CS	1029	-50%
					Merge	879	-41%
					DSE	795	-35%
					ED	635	-19%
6	2.50	$5.439 \cdot 10^{-10}$	acyclic	515	CS	970	-47%
					Merge	834	-38%
					DSE	757	-32%
					ED	612	-15%
7	0.06	$5.053 \cdot 10^{-10}$	acyclic	515	CS	1126	-54%
					Merge	953	-46%
					DSE	859	-40%
					ED	675	-24%
8	0.16	$1.006 \cdot 10^{-9}$	cyclic	248	CS	279	-11%
					Merge	274	-9%
					DSE	263	-6%
					ED	270	-8%

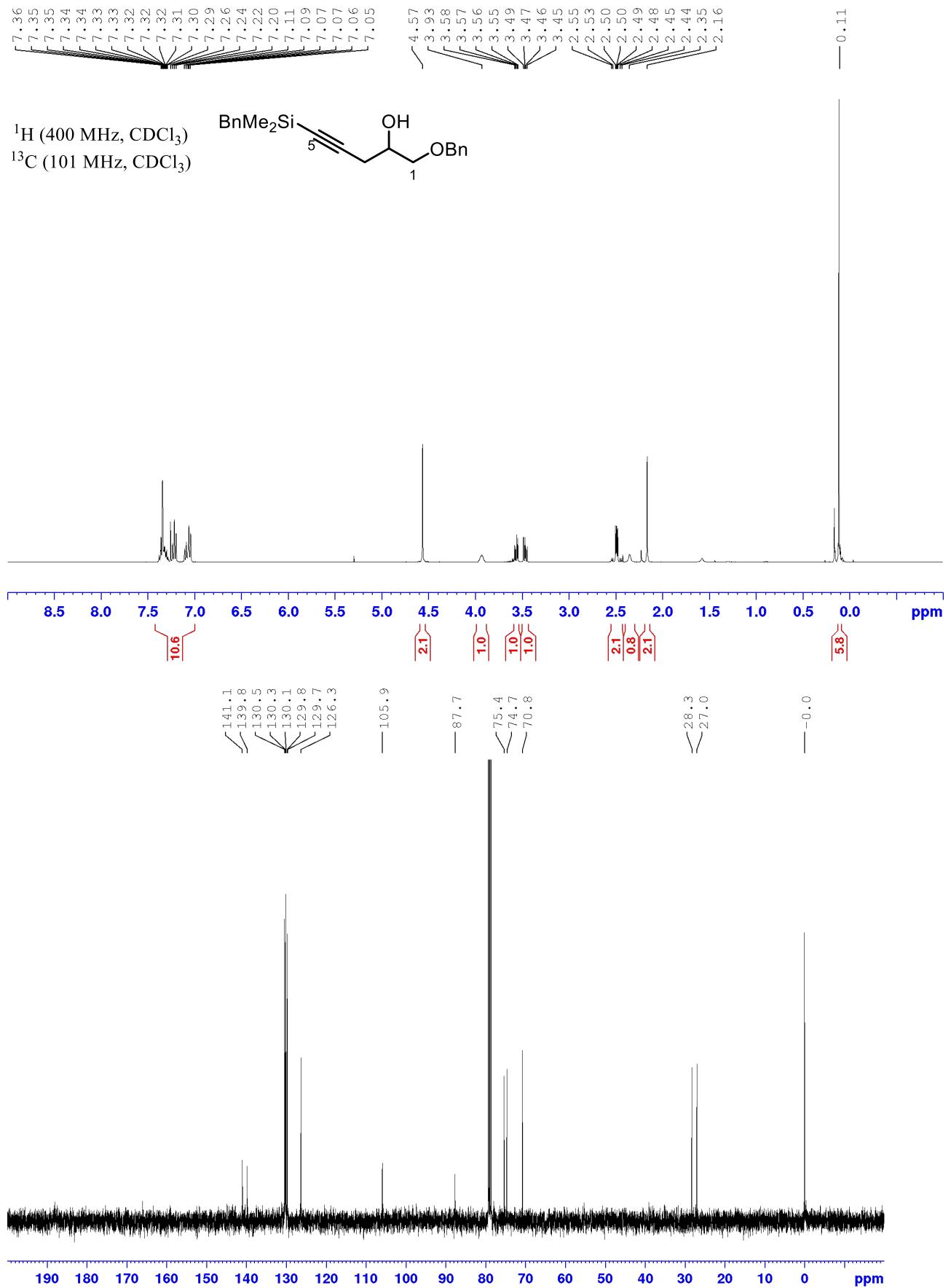
<sup>a</sup> determined from DOSY NMR; <sup>b</sup> calculated molecular weight; <sup>c</sup> molecular shape: CS: compact spheres, DSE: dissipated spheres and ellipsoids, ED: expanded discs, Merge: merged calibration curves.

## Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR data

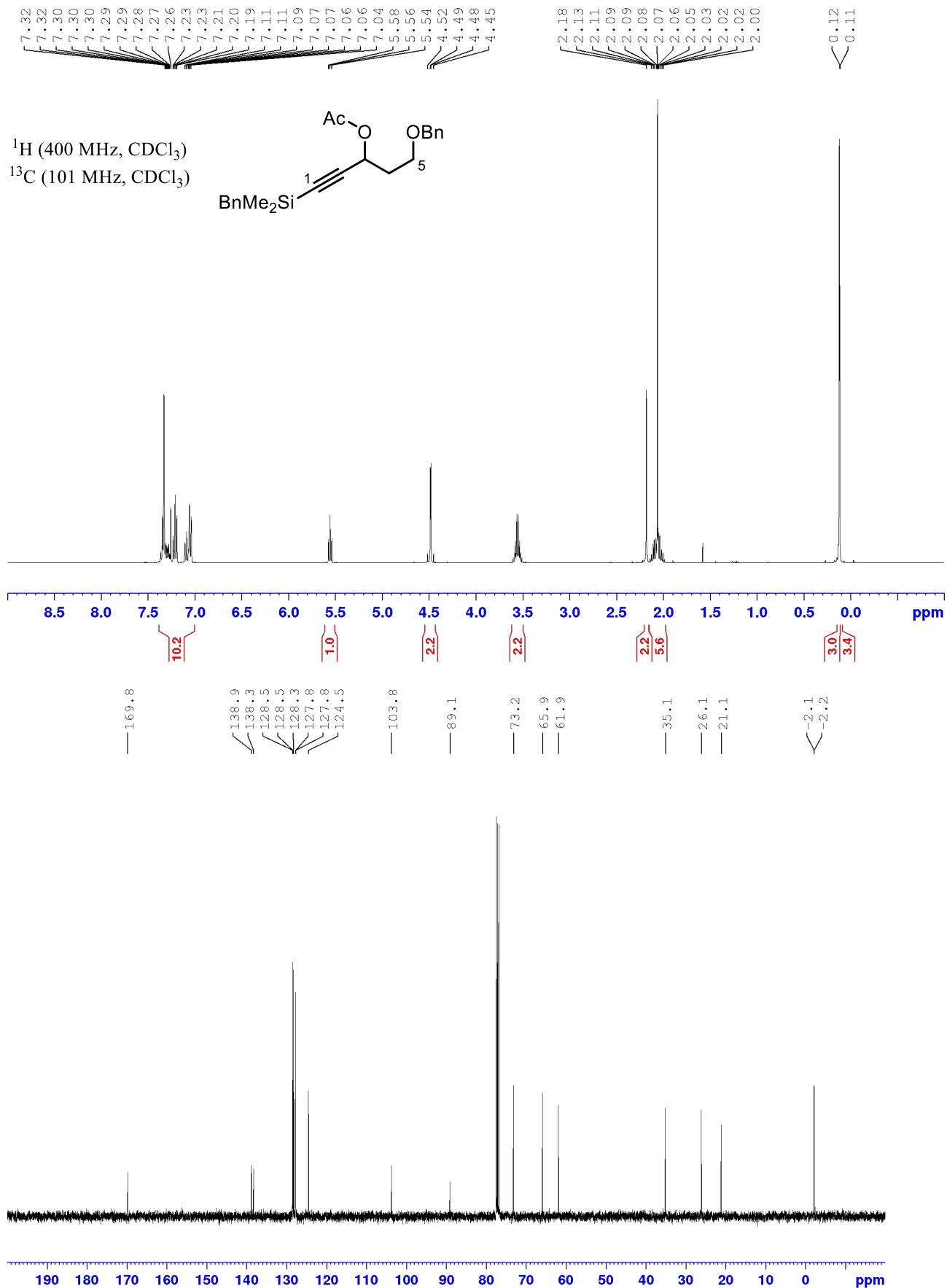
### 1-(Benzylidimethylsilyl)-5-(benzyloxy)pent-1-yn-3-ol, 7a



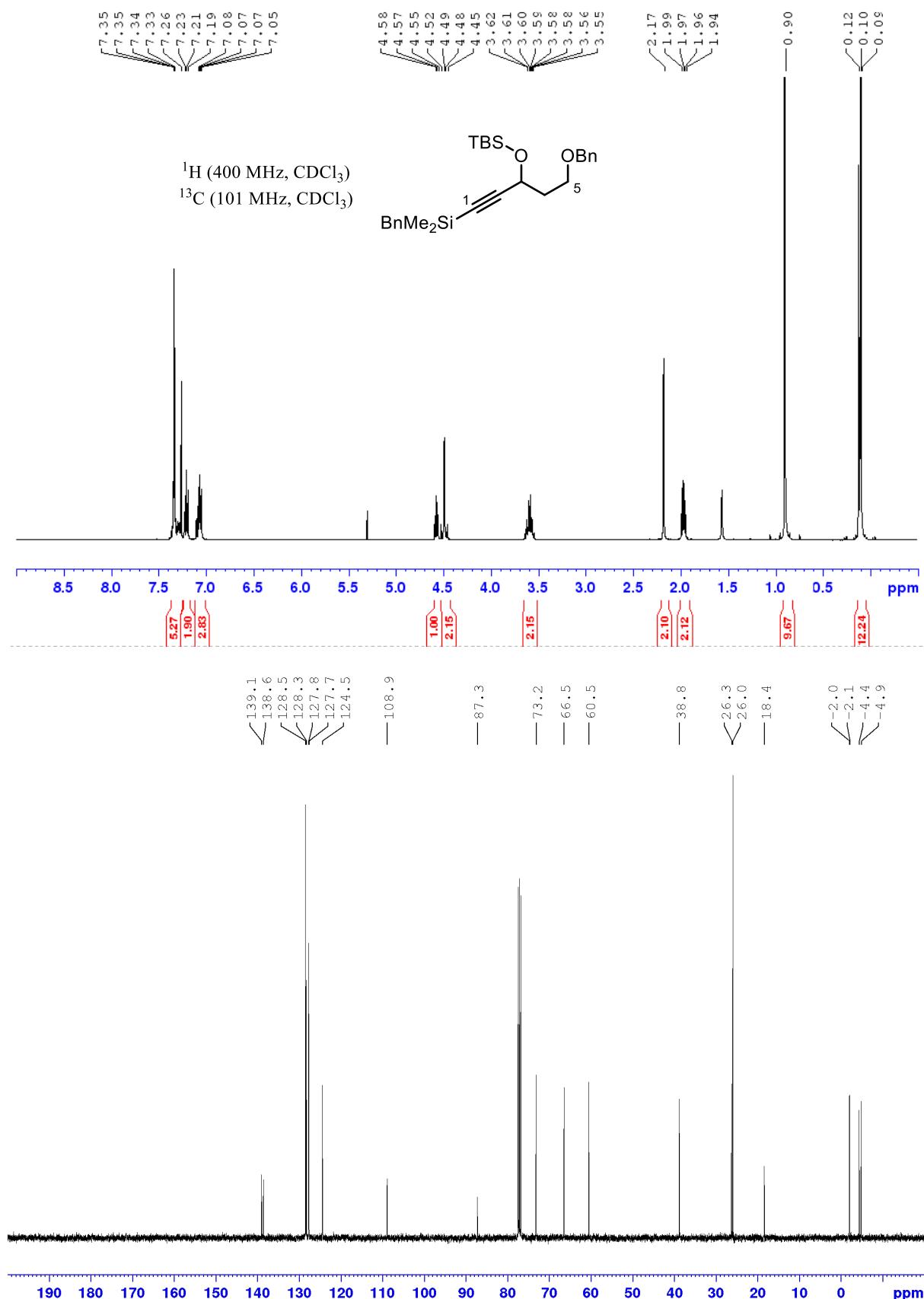
**5-(Benzylidemethylsilyl)-1-(benzyloxy)pent-4-yn-2-ol, 8a**



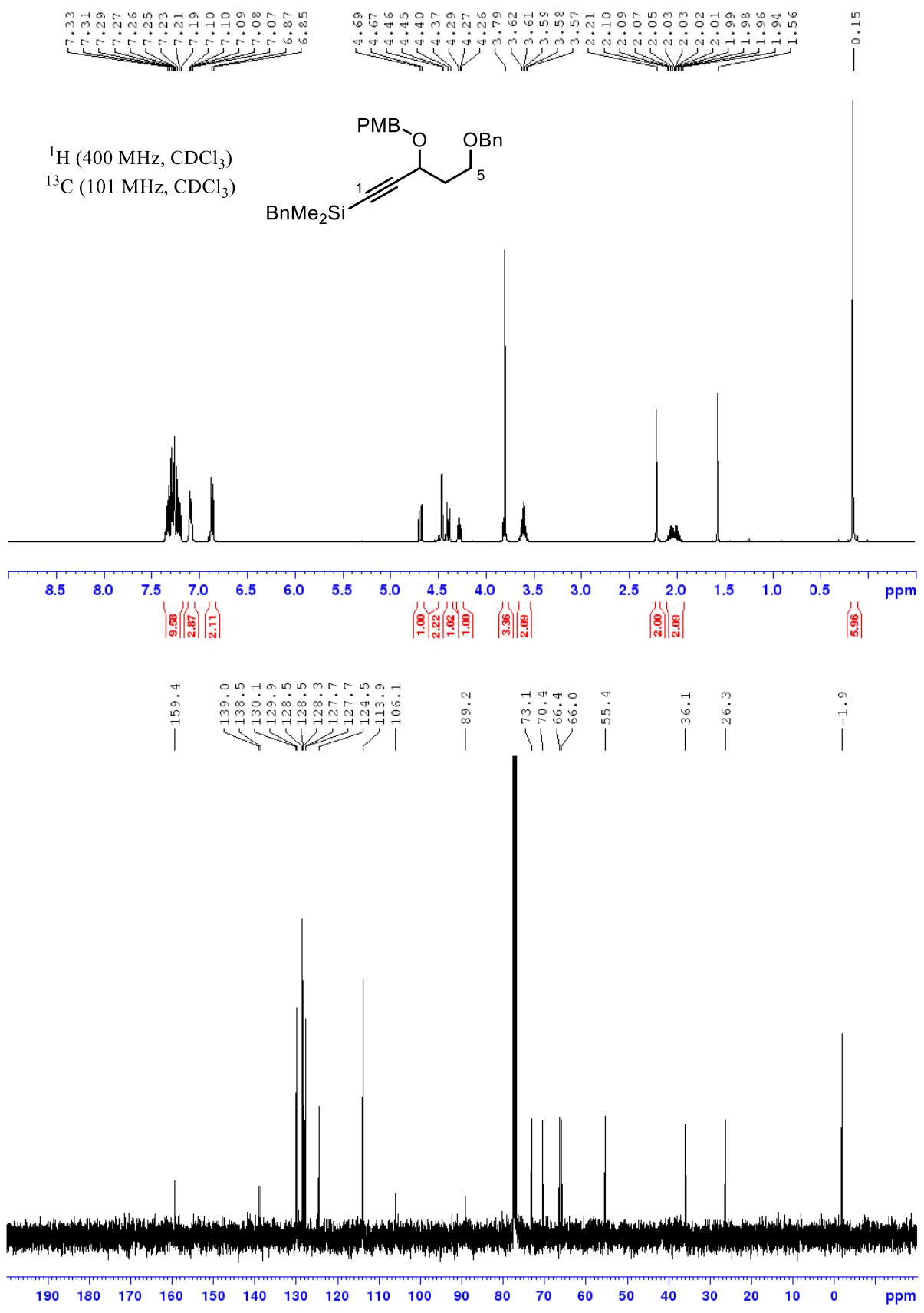
**1-(Benzylidemethylsilyl)-5-(benzyloxy)pent-1-yn-3-yl acetate, 7b**



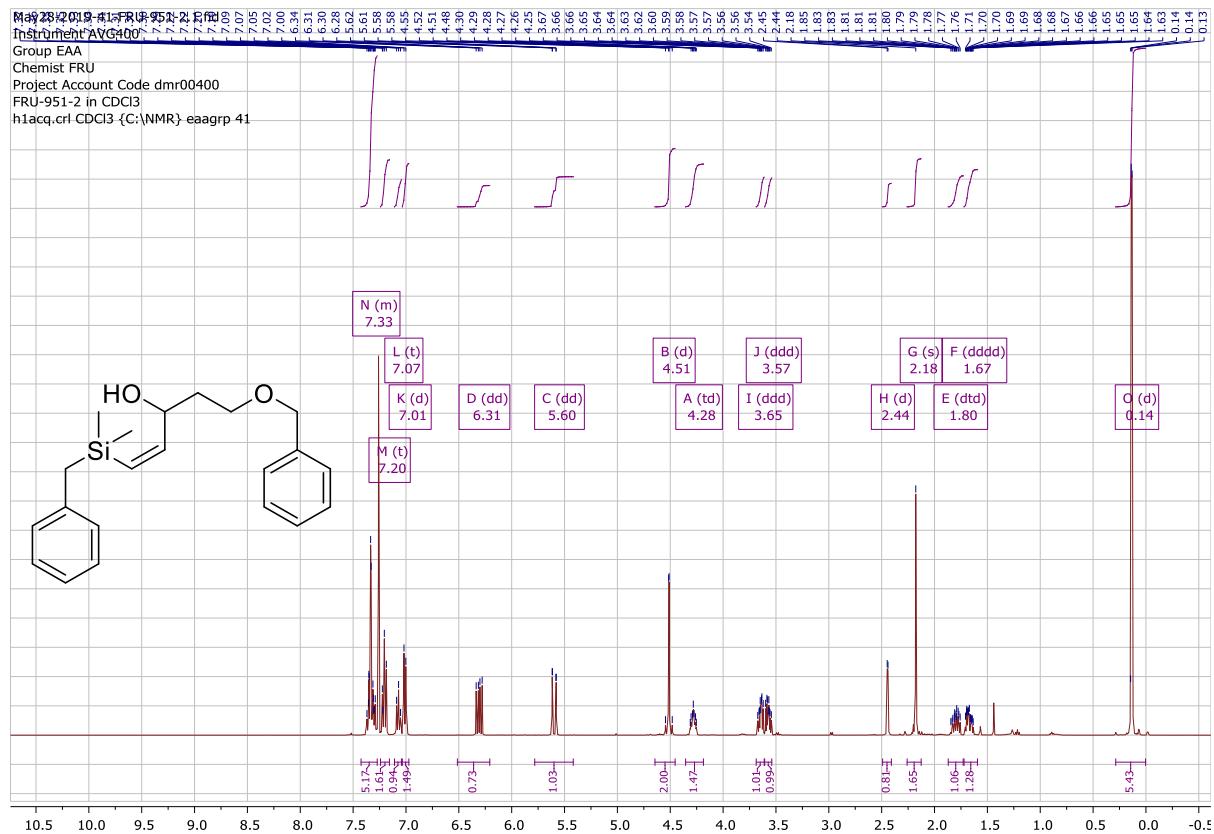
**Benzyl(5-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)dimethylsilane, 7c**



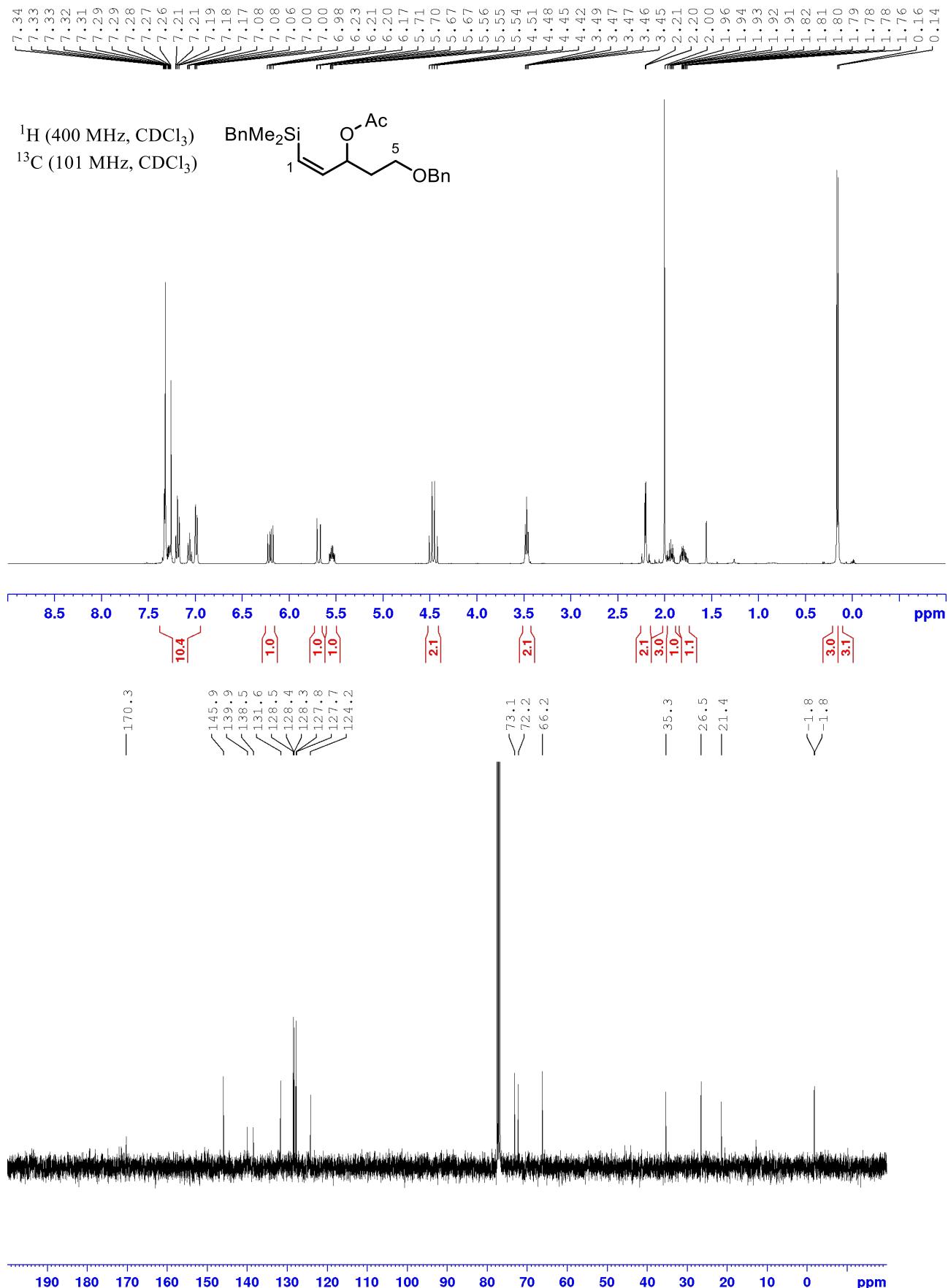
**Benzyl(5-(benzyloxy)-3-((4-methoxybenzyl)oxy)pent-1-yn-1-yl)dimethylsilane, 7d**



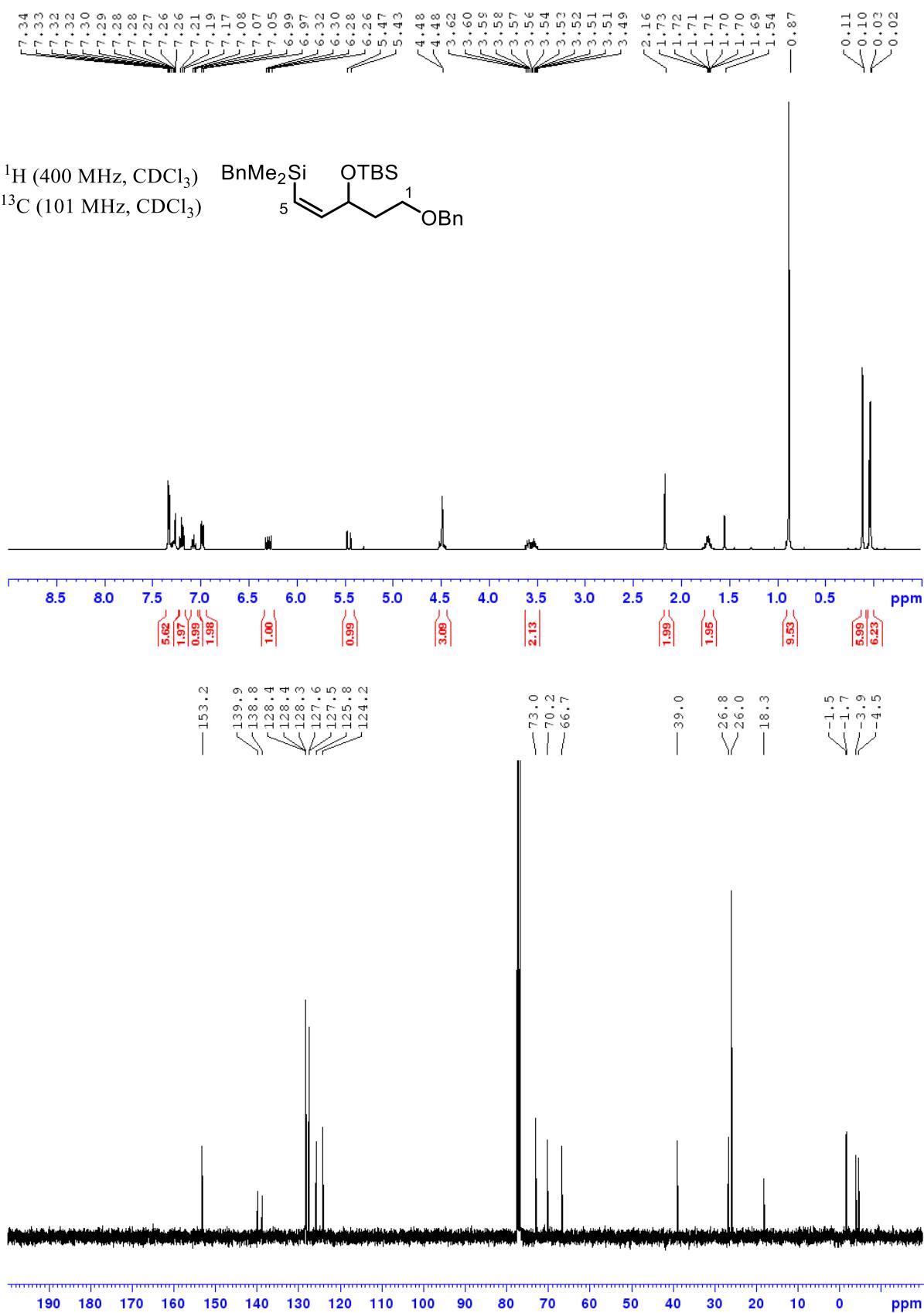
**(Z)-1-(Benzylidemethylsilyl)-5-(benzyloxy)pent-1-en-3-ol, 11a**



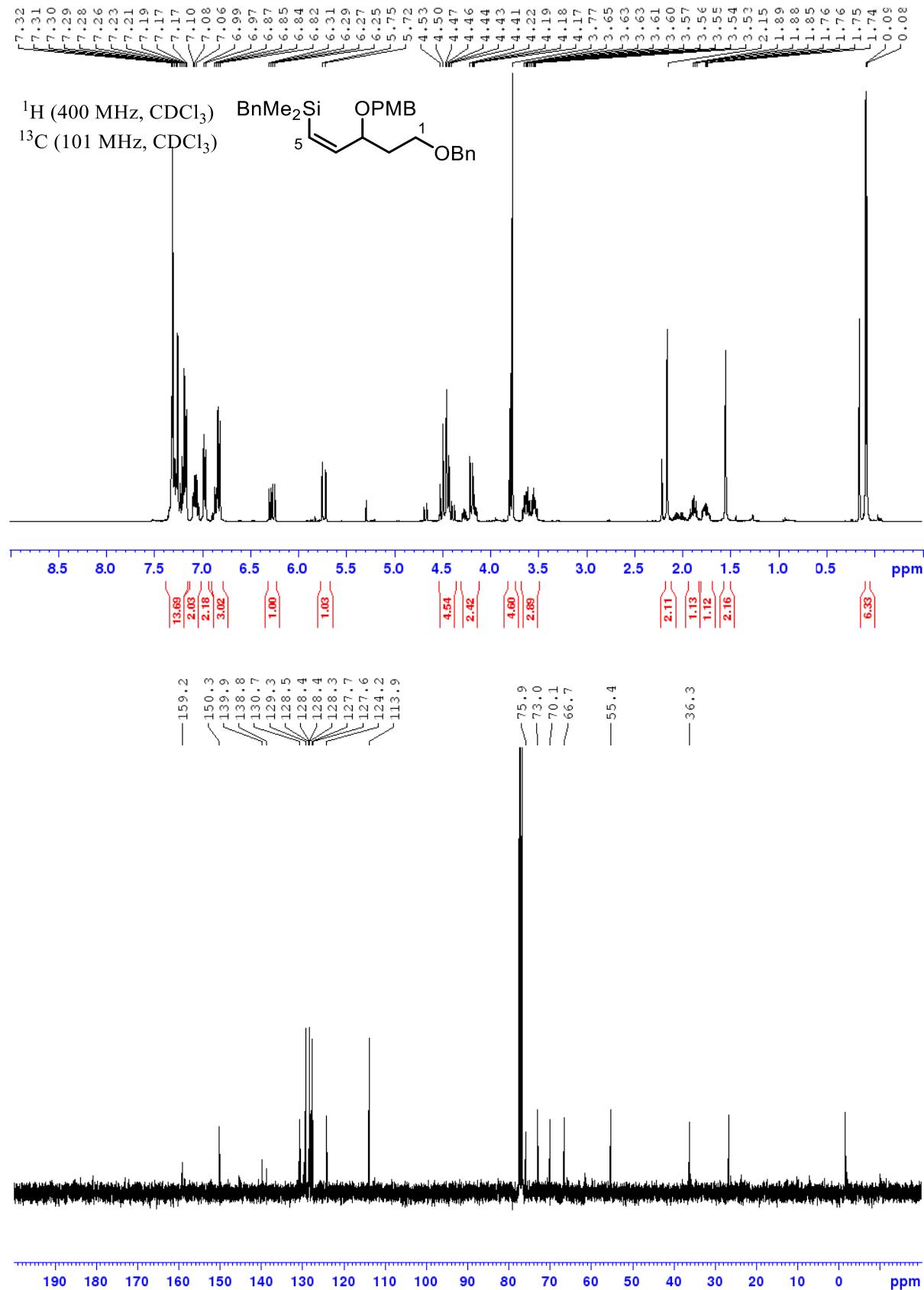
**(Z)-1-(Benzylidemethylsilyl)-5-(benzyloxy)pent-1-en-3-yl acetate, 11b**



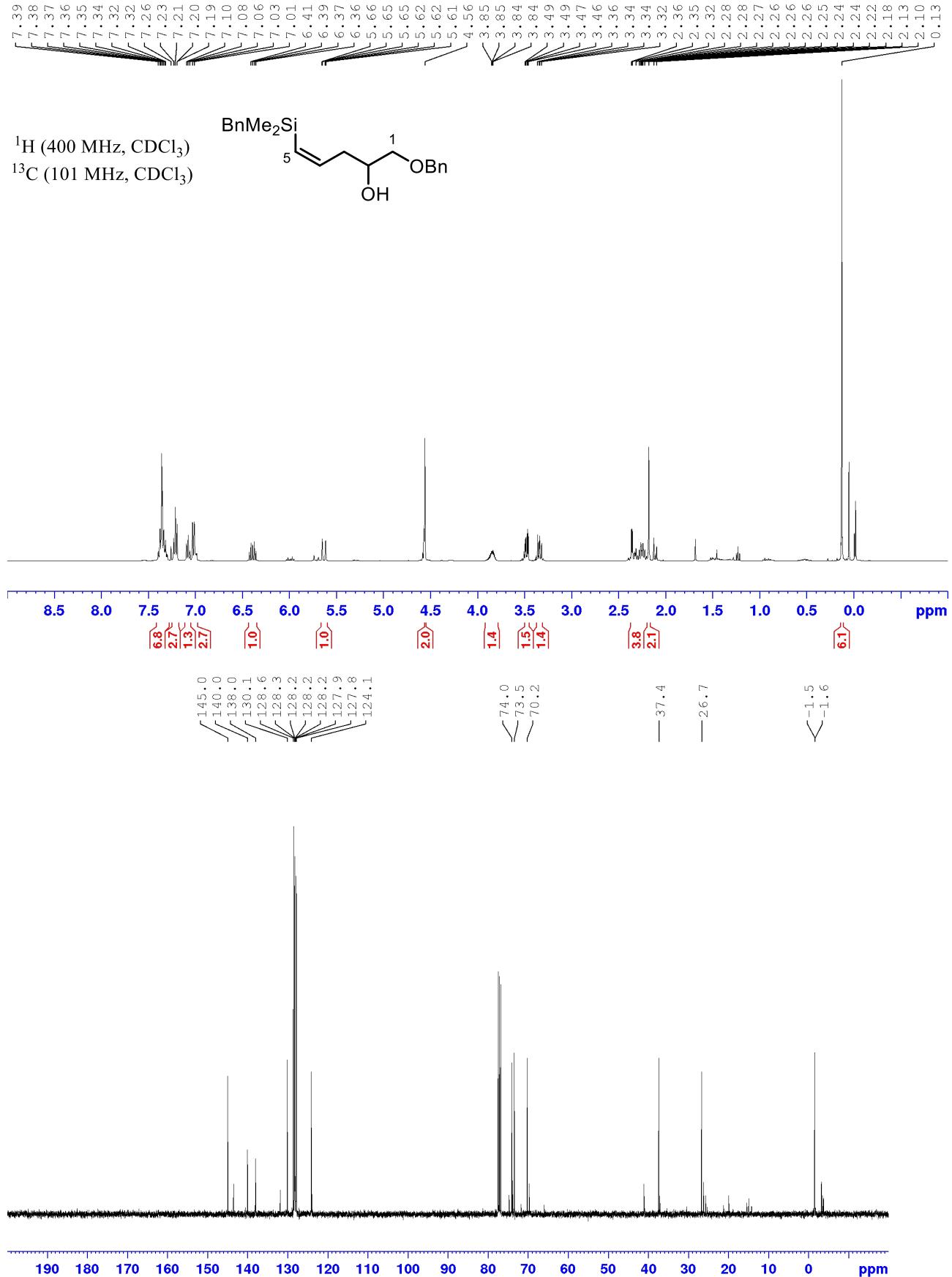
**(Z)-Benzyl(5-(benzyloxy)-3-((tert-butyldimethylsilyl)oxy)pent-1-en-1-yl)dimethylsilane, 11c**



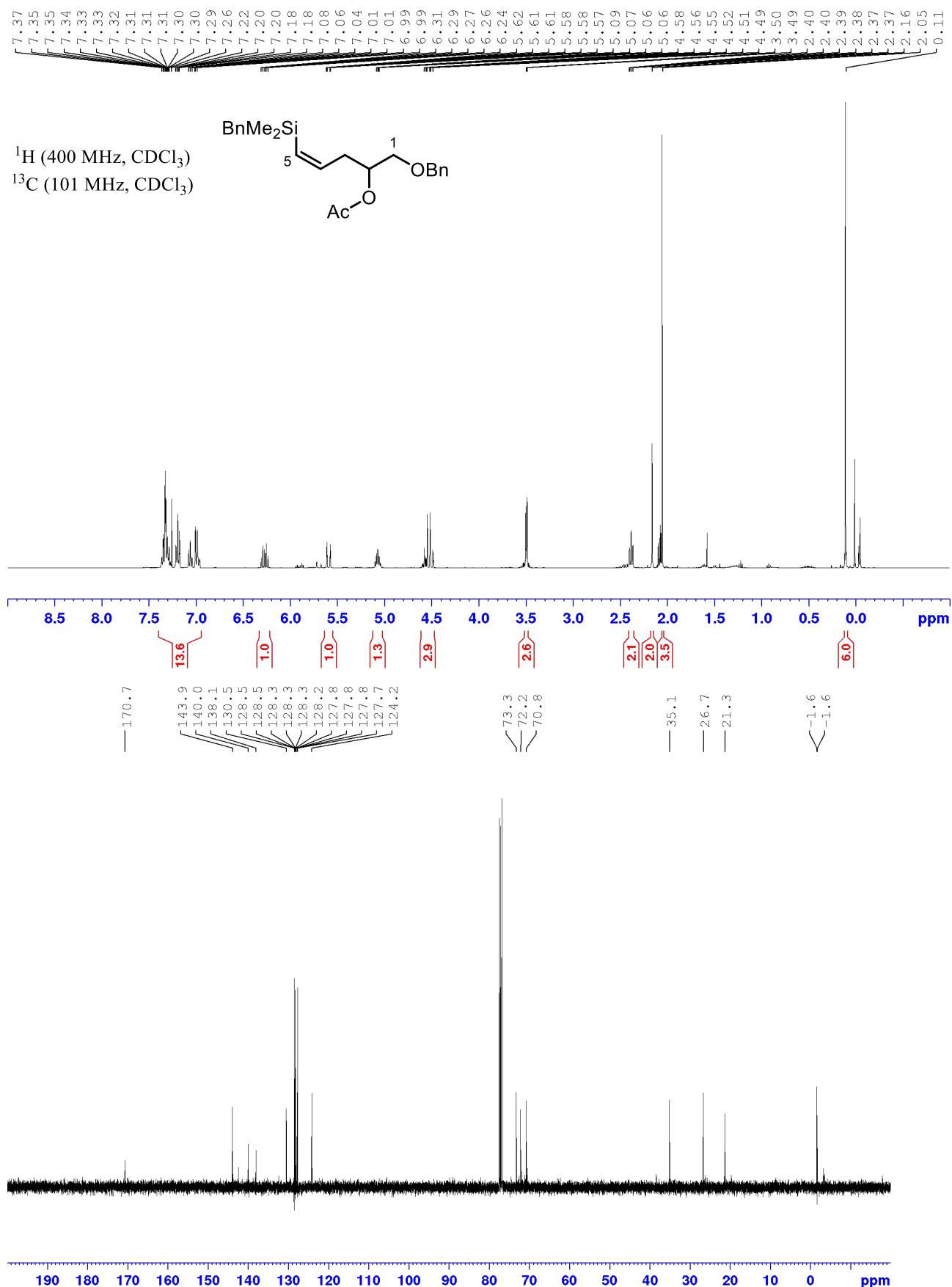
**(Z)-Benzyl(5-(benzyloxy)-3-((4-methoxybenzyl)oxy)pent-1-en-1-yl)dimethylsilane, 11d**



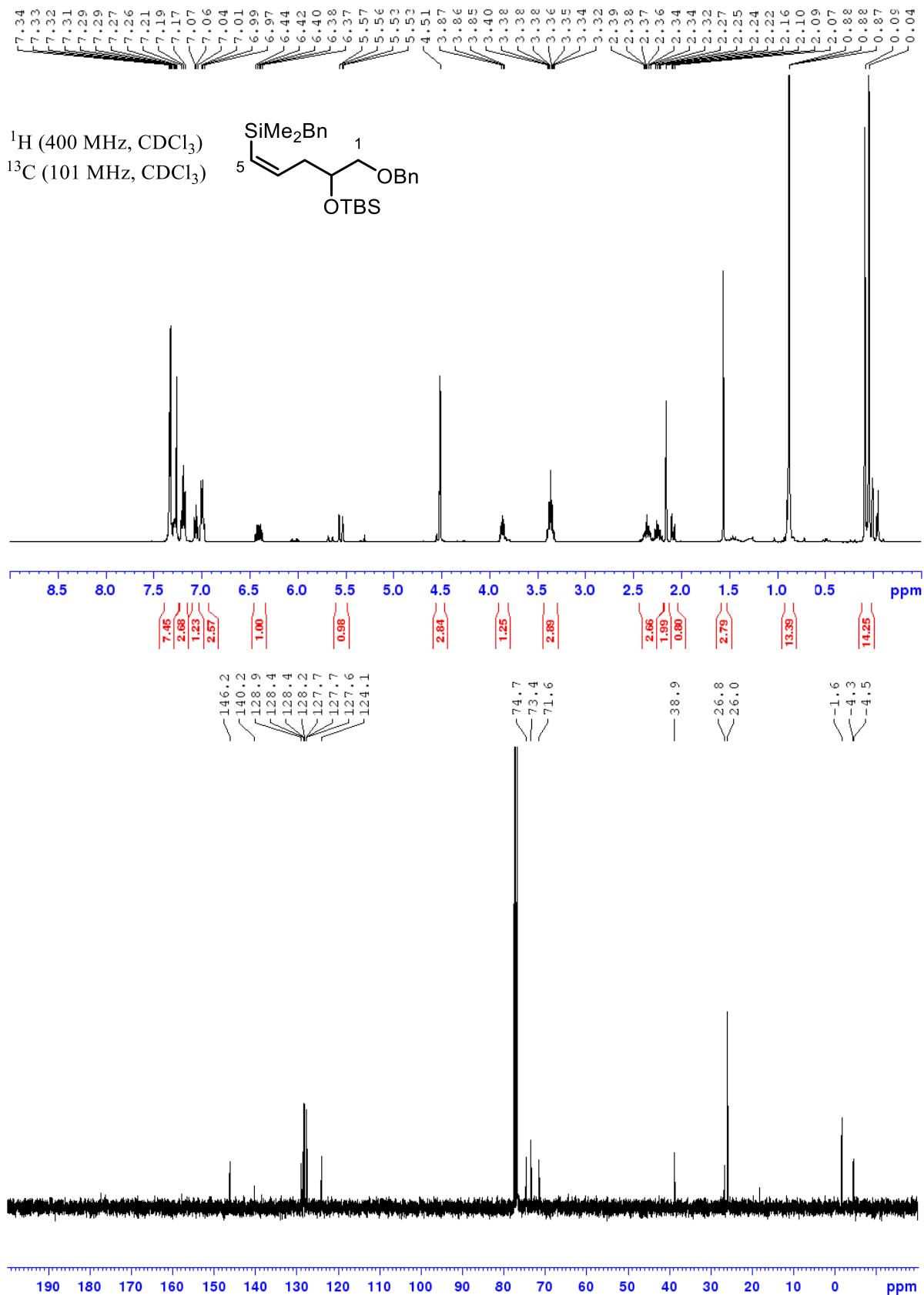
**(Z)-5-(Benzylidemethylsilyl)-1-(benzyloxy)pent-4-en-2-ol, 12a**



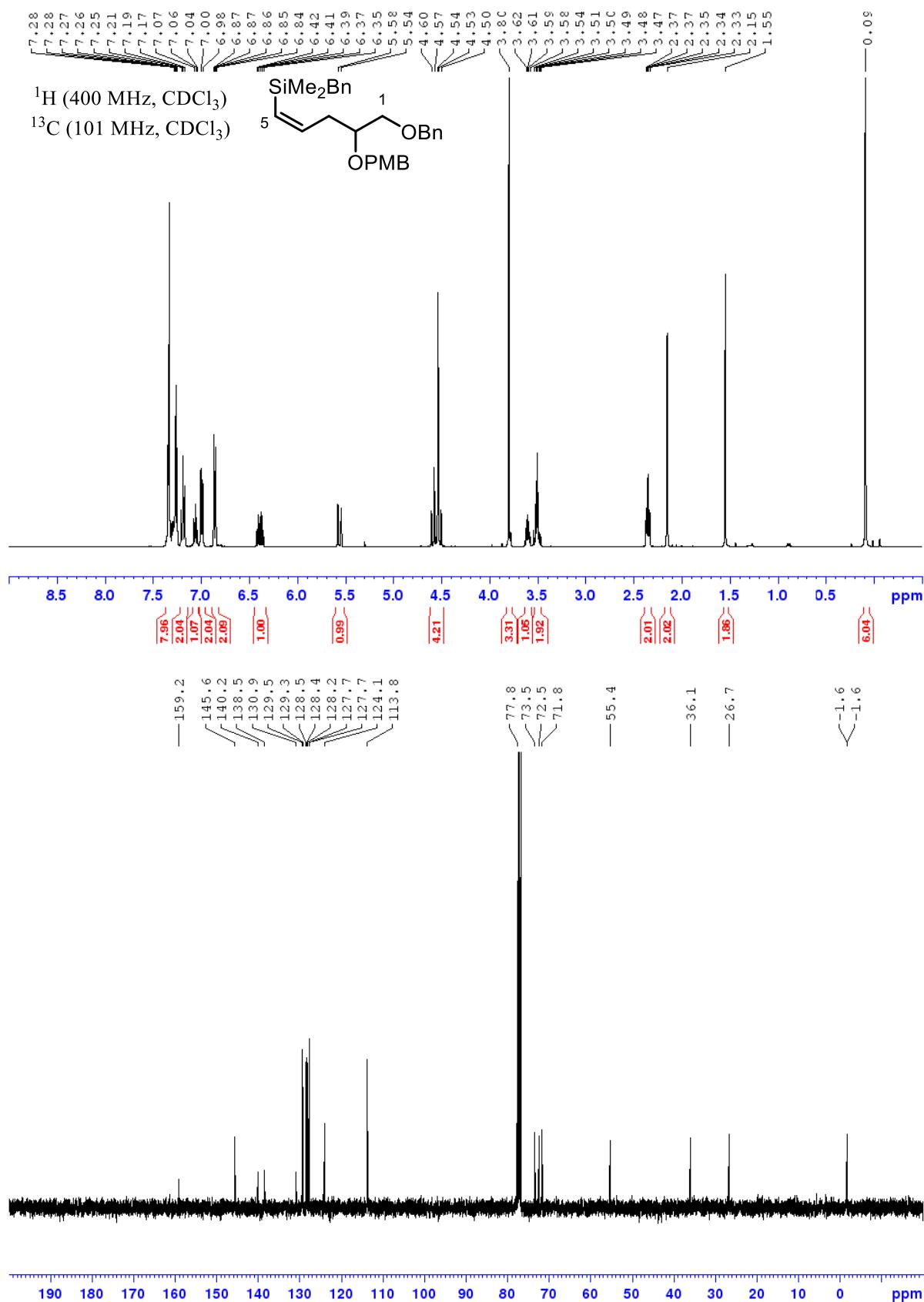
**(Z)-5-(Benzylidemethylsilyl)-1-(benzyloxy)pent-4-en-2-yl acetate, 12b**



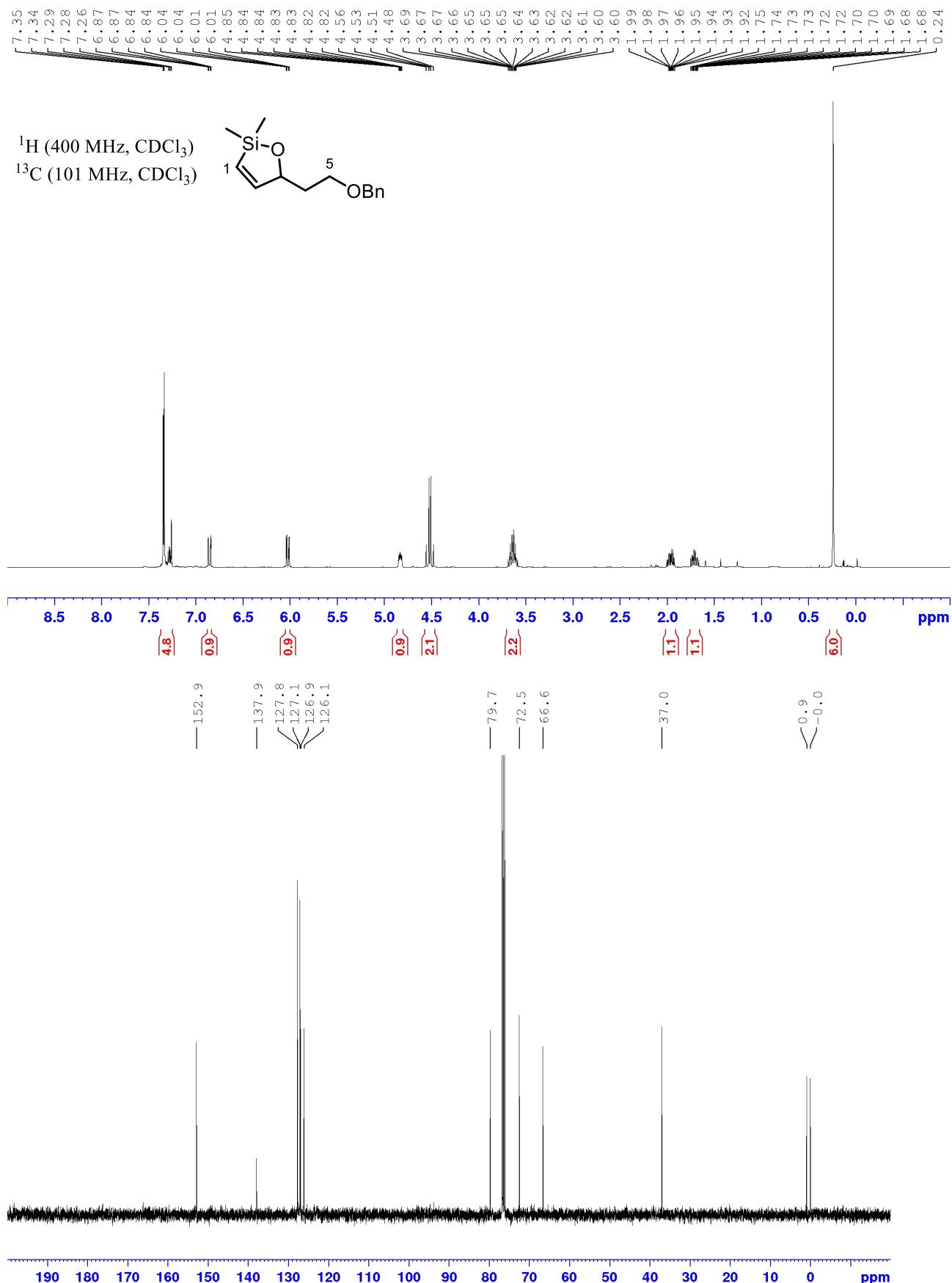
**(Z)-Benzyl(5-(benzyloxy)-4-((tert-butyldimethylsilyl)oxy)pent-1-en-1-yl)dimethylsilane, 12c**



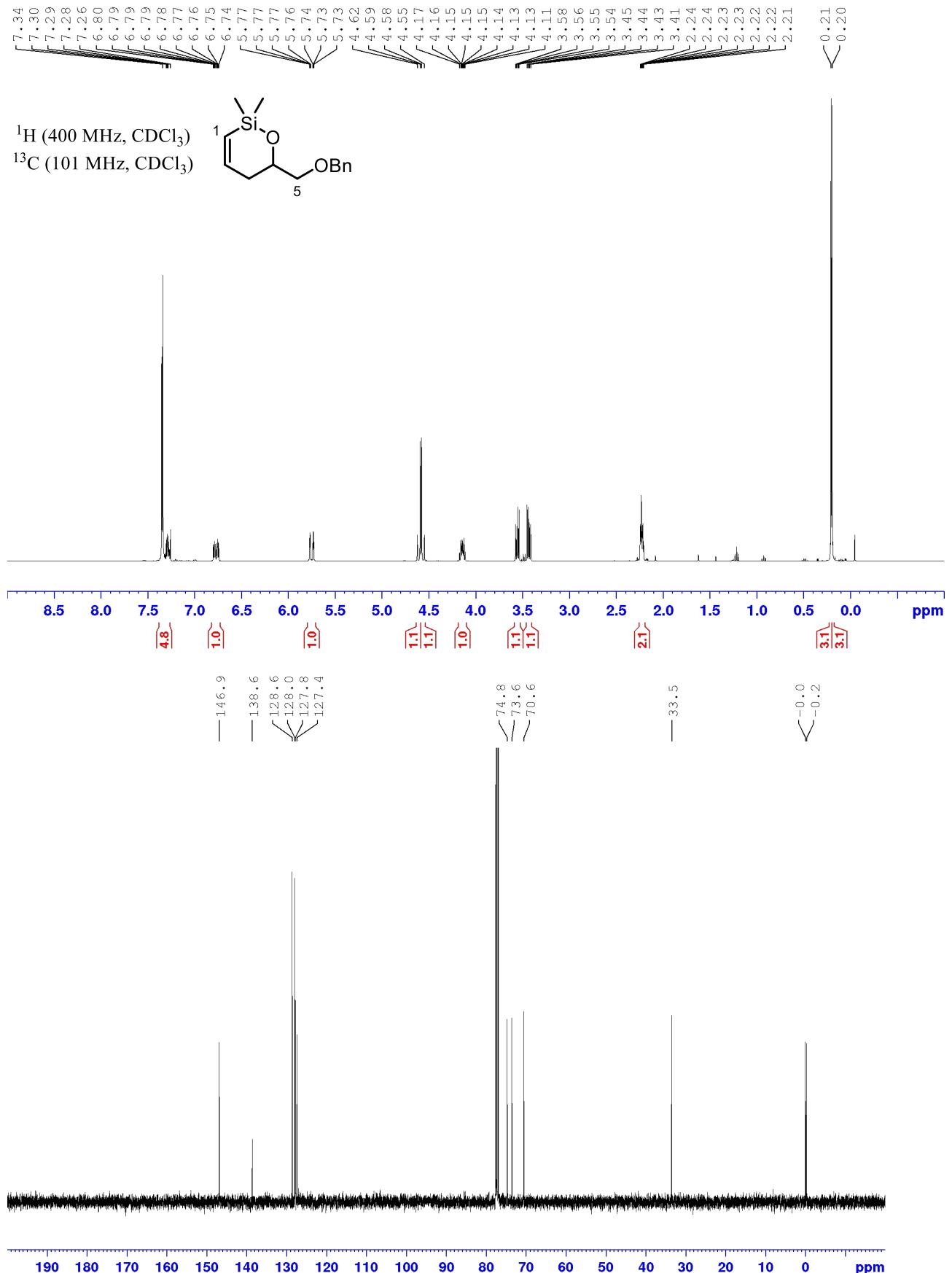
**(Z)-Benzyl(5-(benzyloxy)-4-((4-methoxybenzyl)oxy)pent-1-en-1-yl)dimethylsilane, 12d**



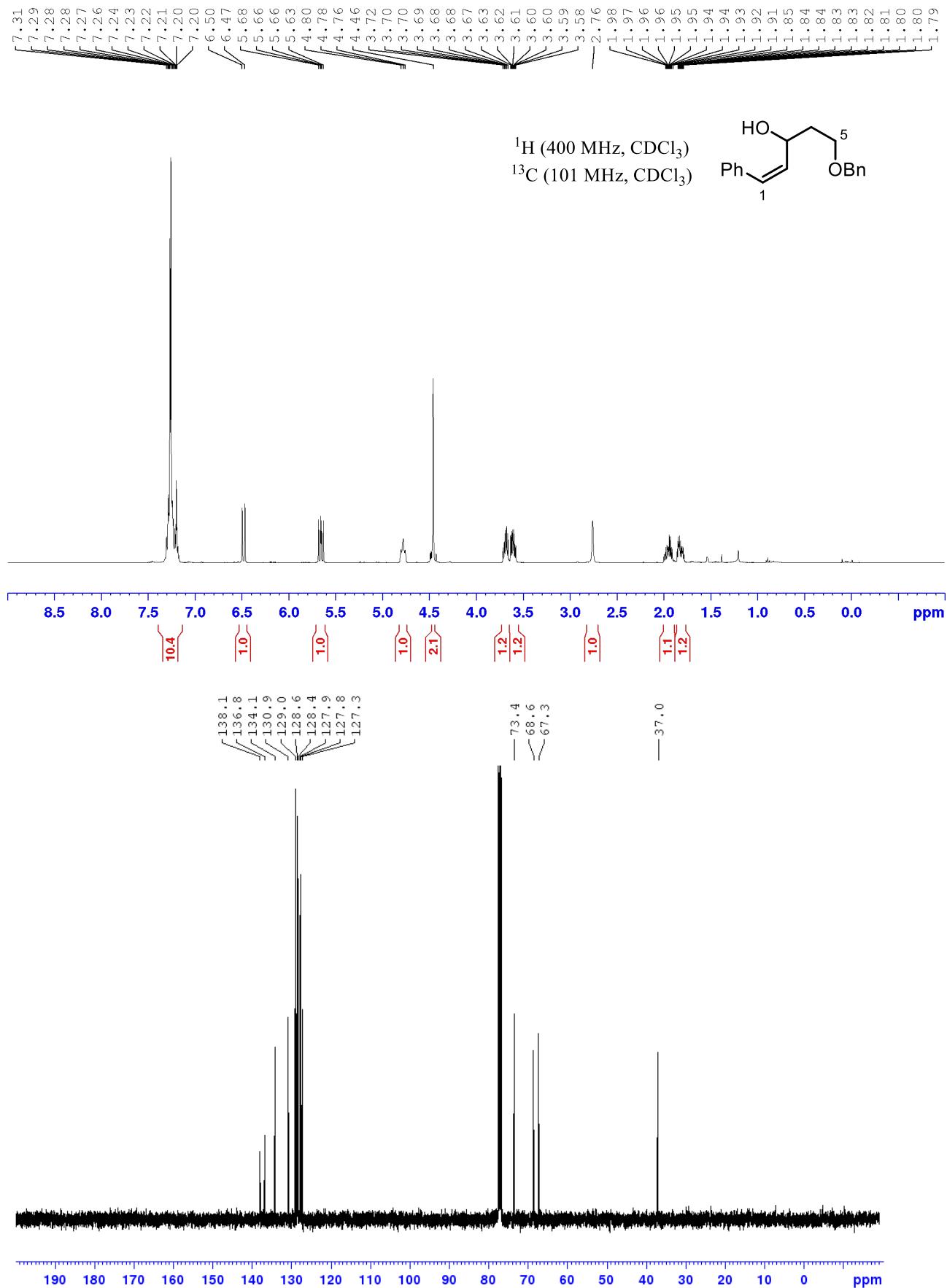
**5-(2-(BenzylOxy)ethyl)-2,2-dimethyl-2,5-dihydro-1,2-oxasilole, 13**



**6-((Benzyl)oxy)methyl-2,2-dimethyl-5,6-dihydro-2*H*-1,2-oxasiline, 14**

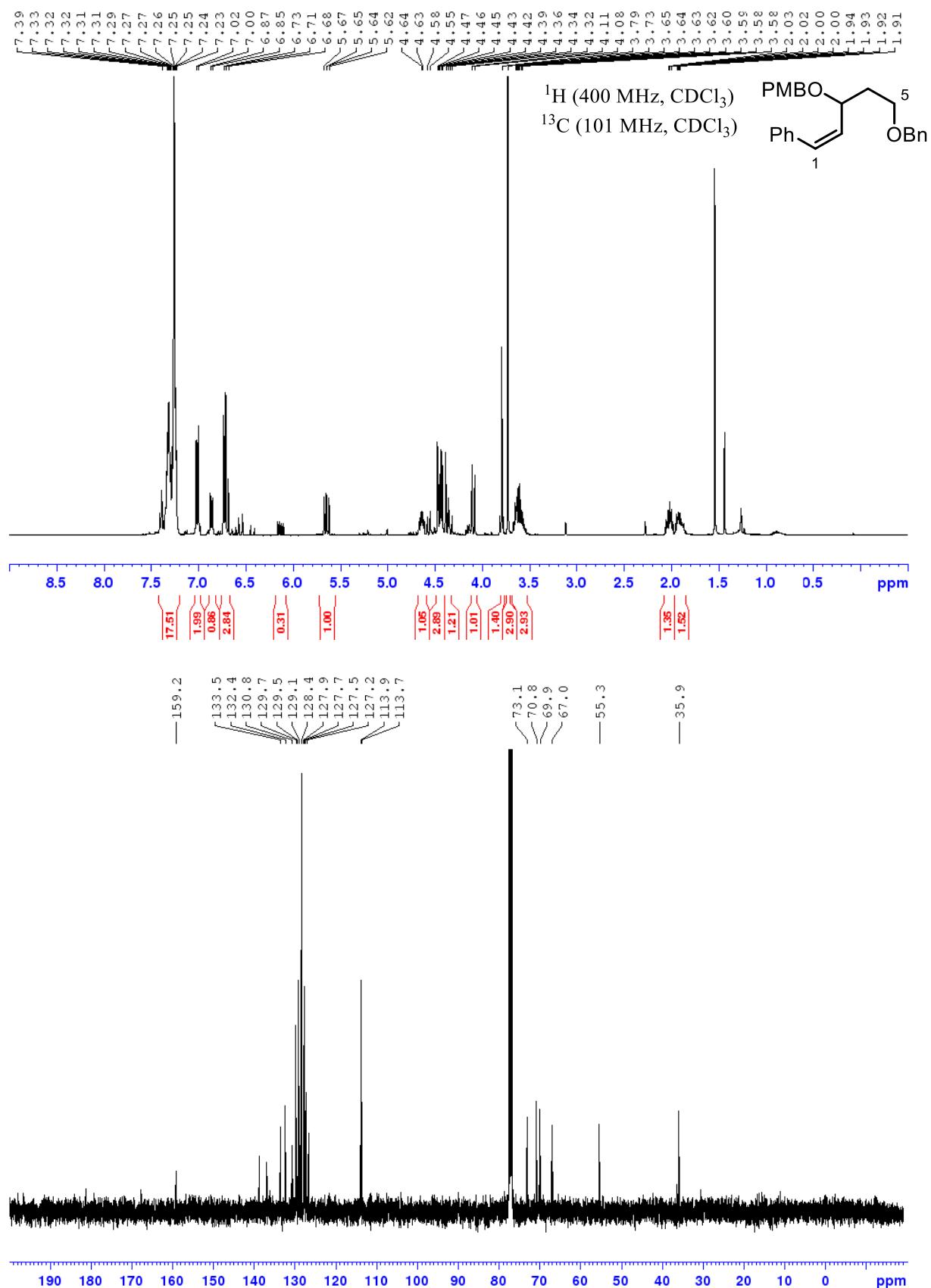


**(Z)-5-(Benzylxy)-1-phenylpent-1-en-3-ol, 26a**

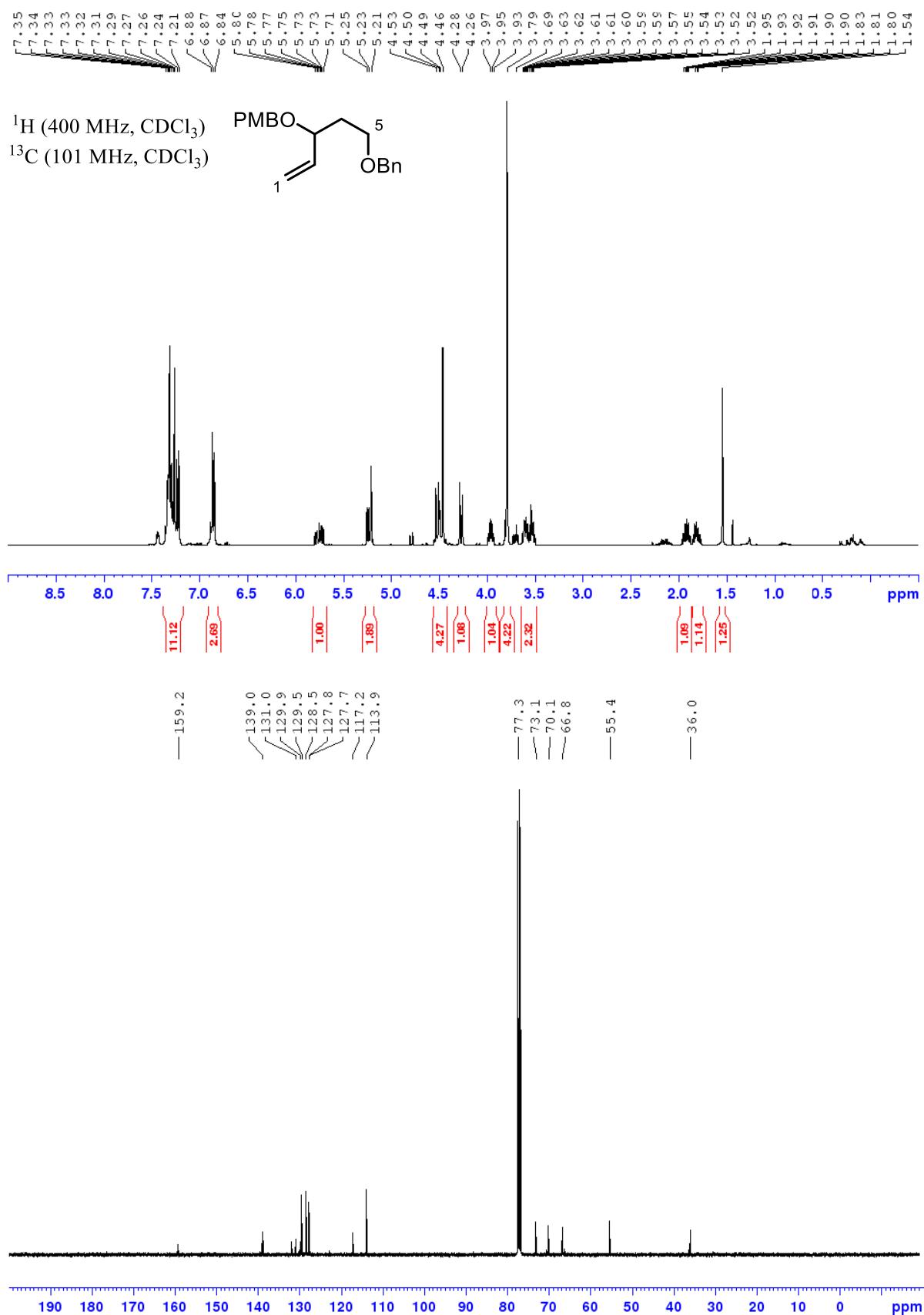


**(Z)-1-(((5-(Benzylxy)-1-phenylpent-1-en-3-yl)oxy)methyl)-4-methoxybenzene, 26b**

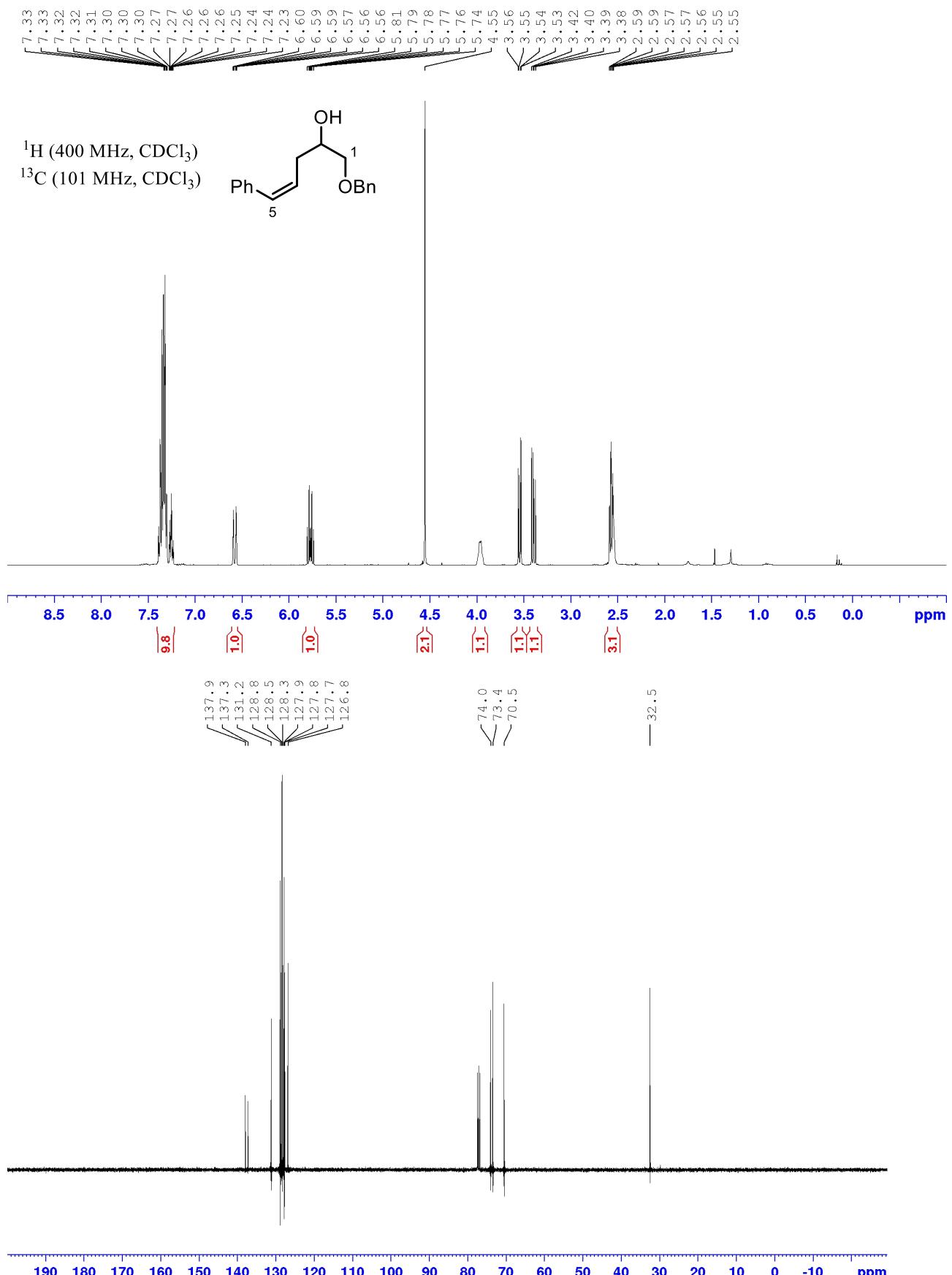
NMR spectra contain a 1:0.31 mixture of Z and E isomers.



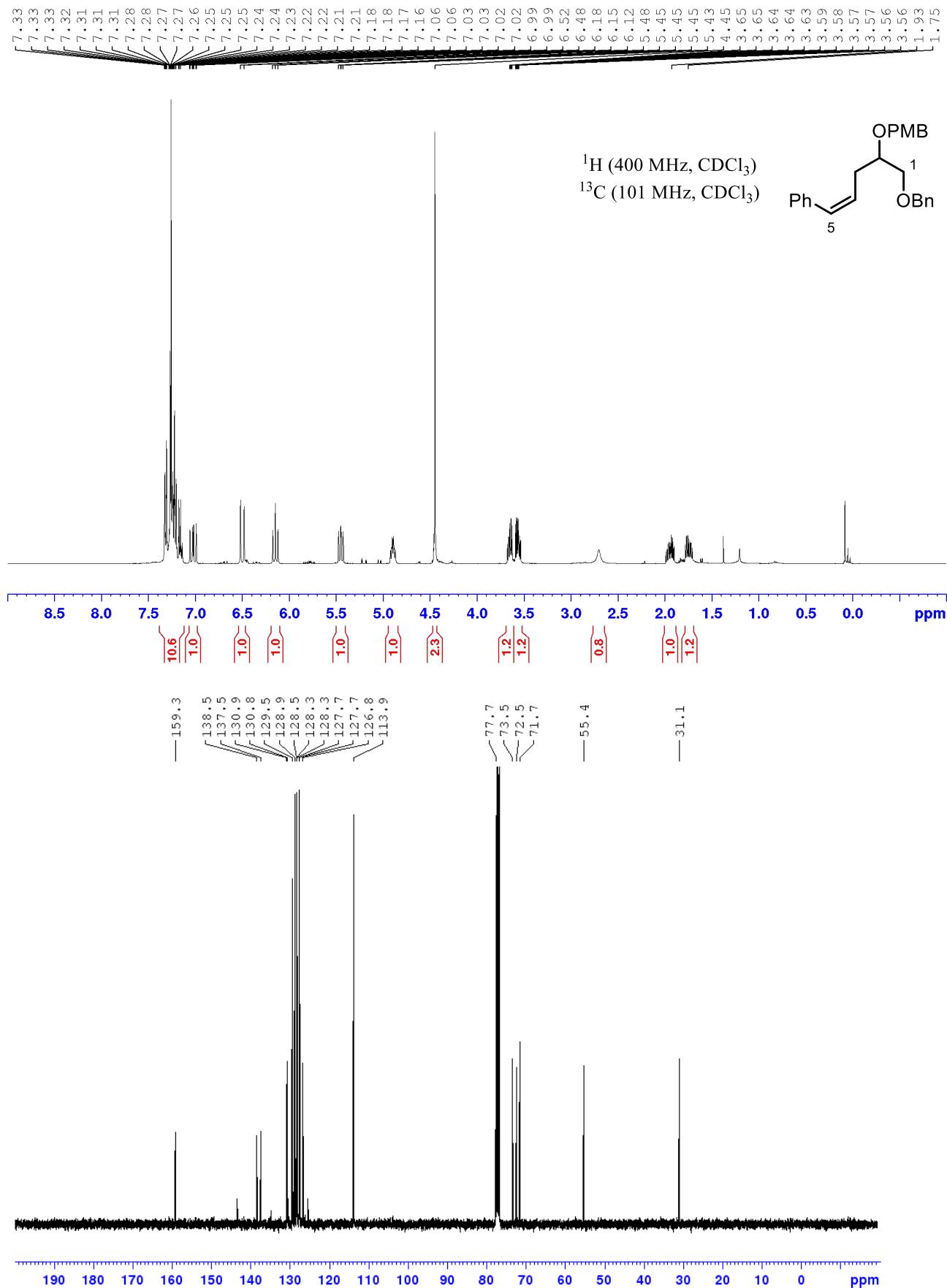
**1-(((5-(benzyloxy)pent-1-en-3-yl)oxy)methyl)-4-methoxybenzene, 26b-desilylation**



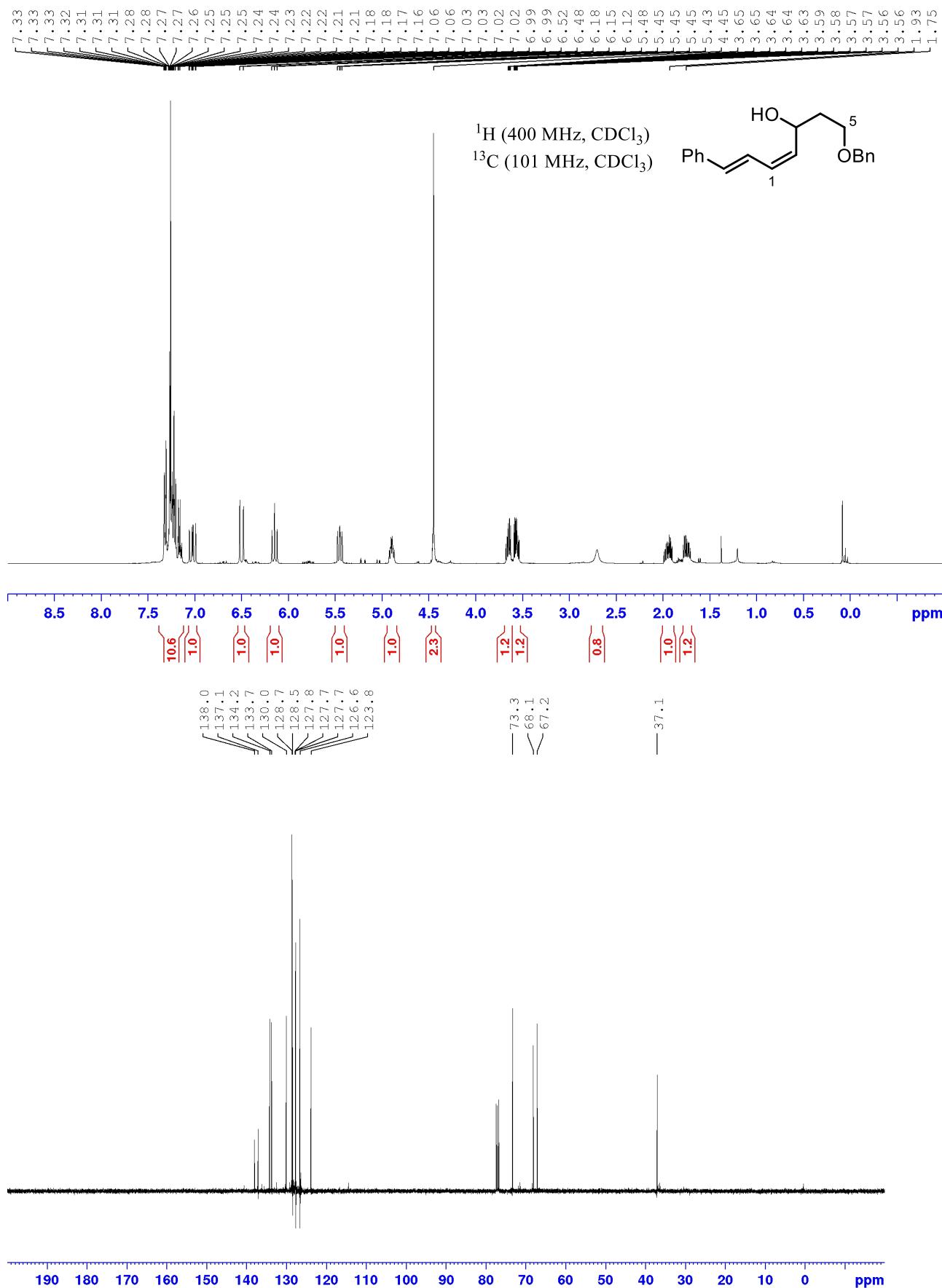
**(Z)-1-(Benzylxy)-5-phenylpent-4-en-2-ol, 27a**



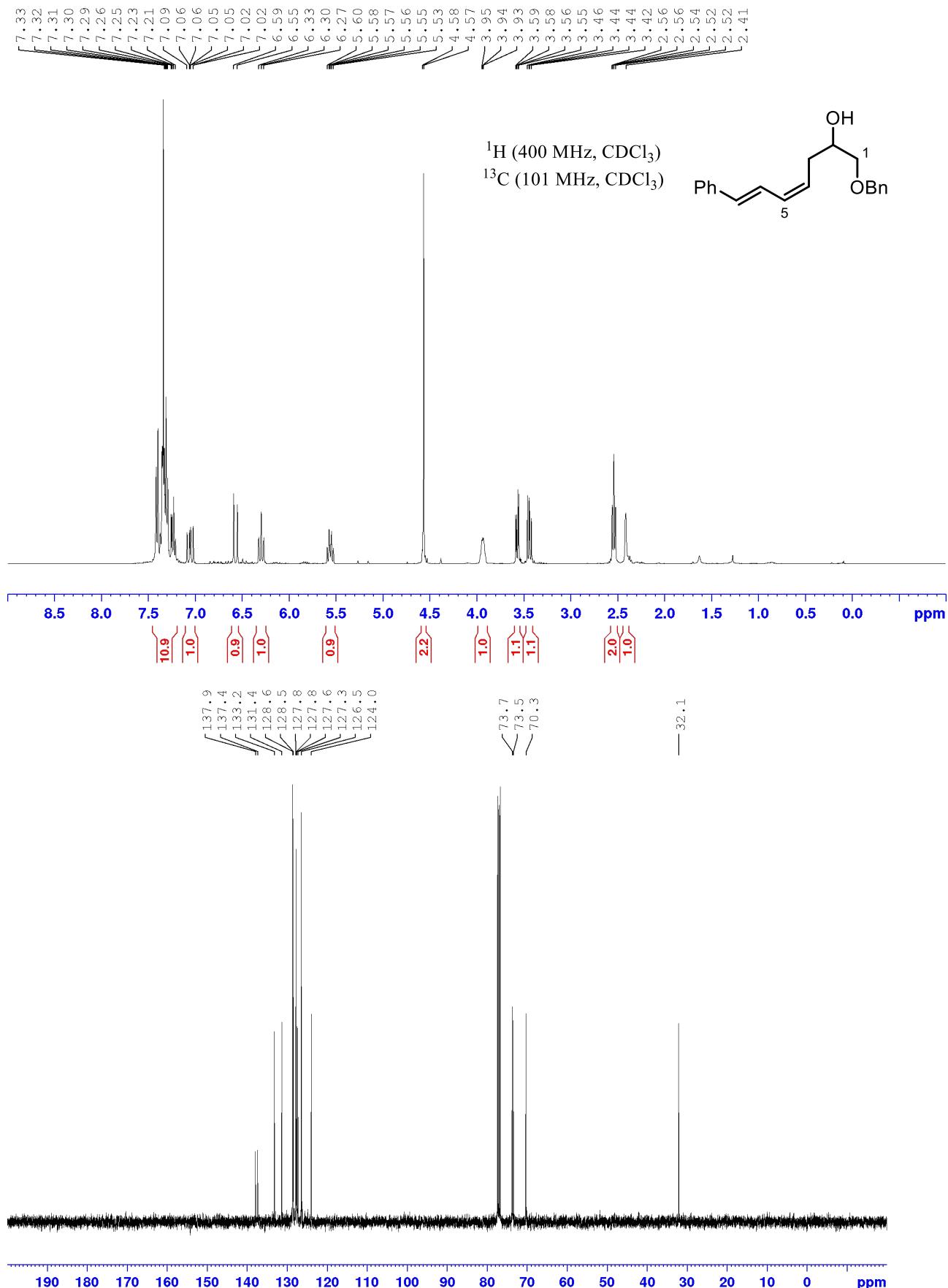
**(Z)-1-(((1-(Benzylxy)-5-phenylpent-4-en-2-yl)oxy)methyl)-4-methoxybenzene, 27b**



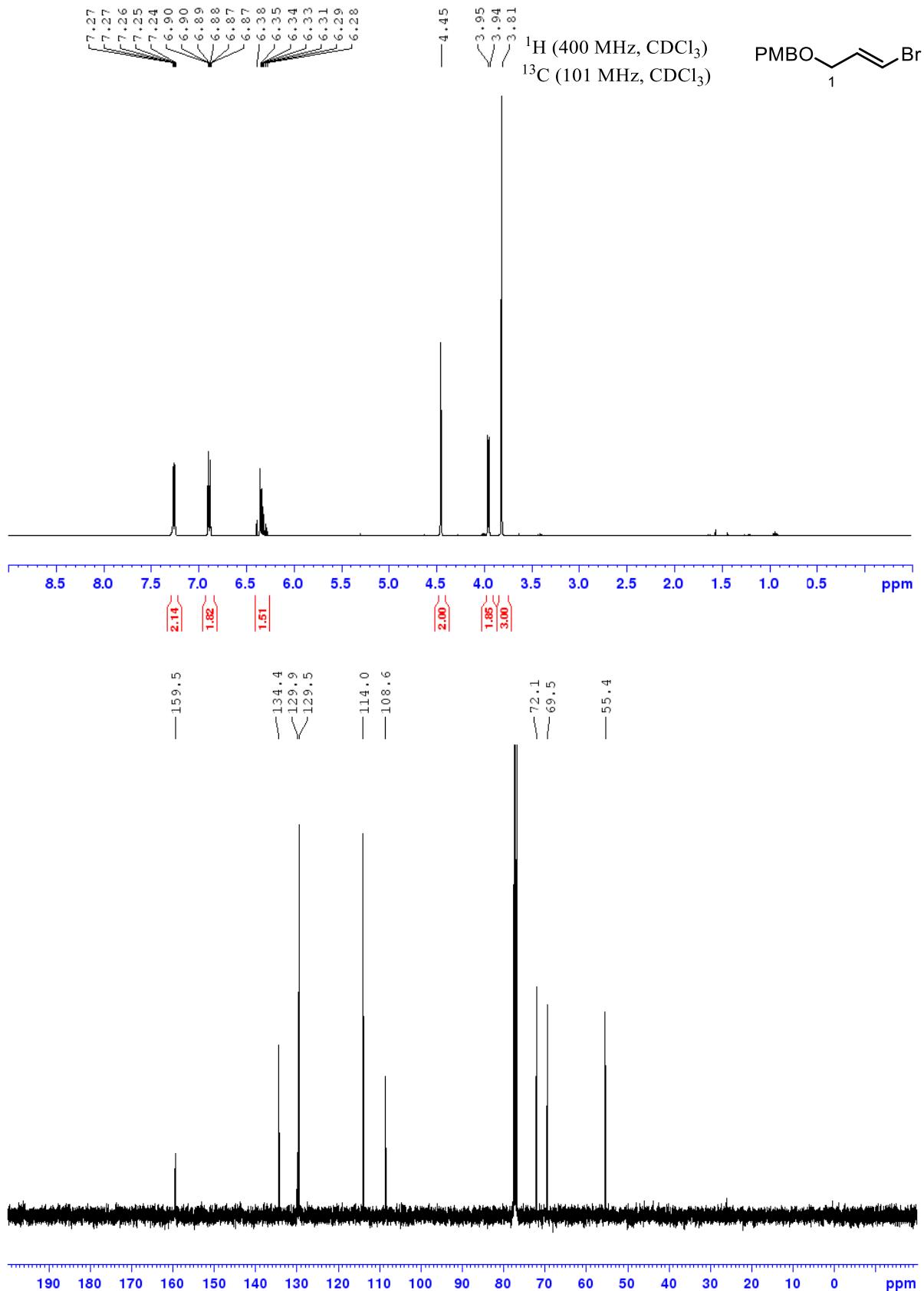
**(4Z,6E)-1-(Benzylxyloxy)-7-phenylhepta-4,6-dien-3-ol, 26C**



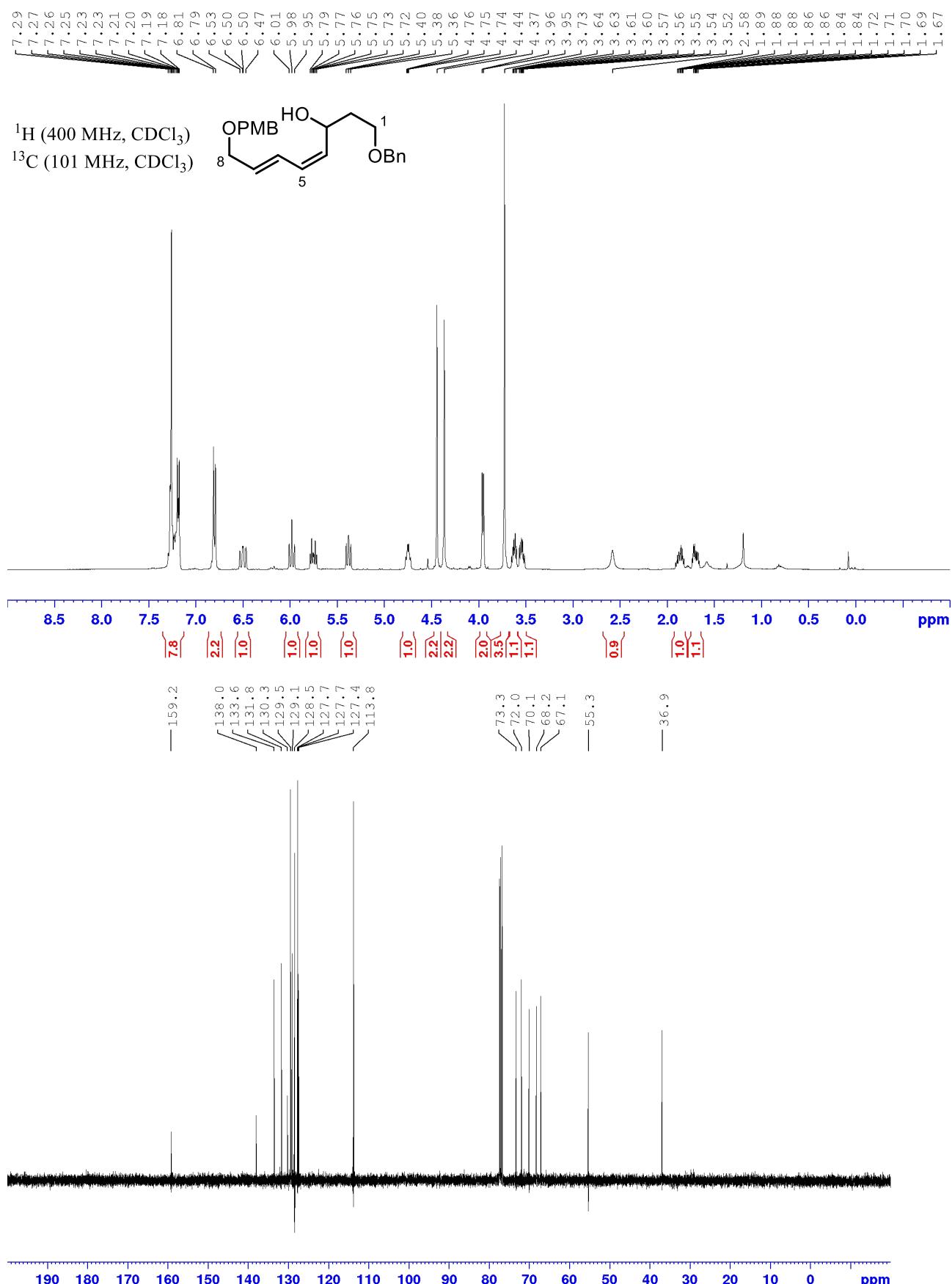
**(4Z,6E)-1-(Benzylxy)-7-phenylhepta-4,6-dien-2-ol, 27c**



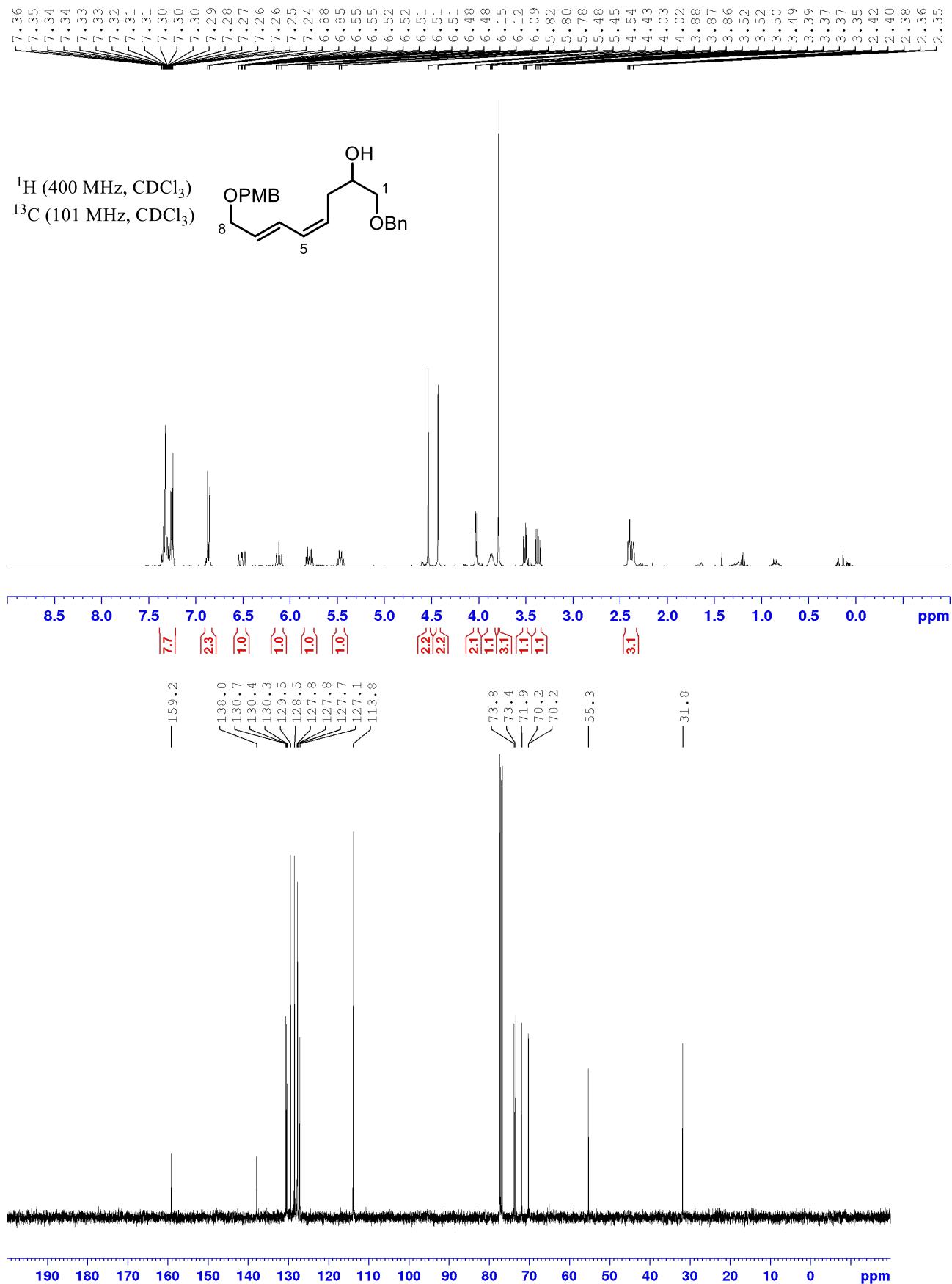
*(E)-1-(((3-Bromoallyl)oxy)methyl)-4-methoxybenzene, 25e*



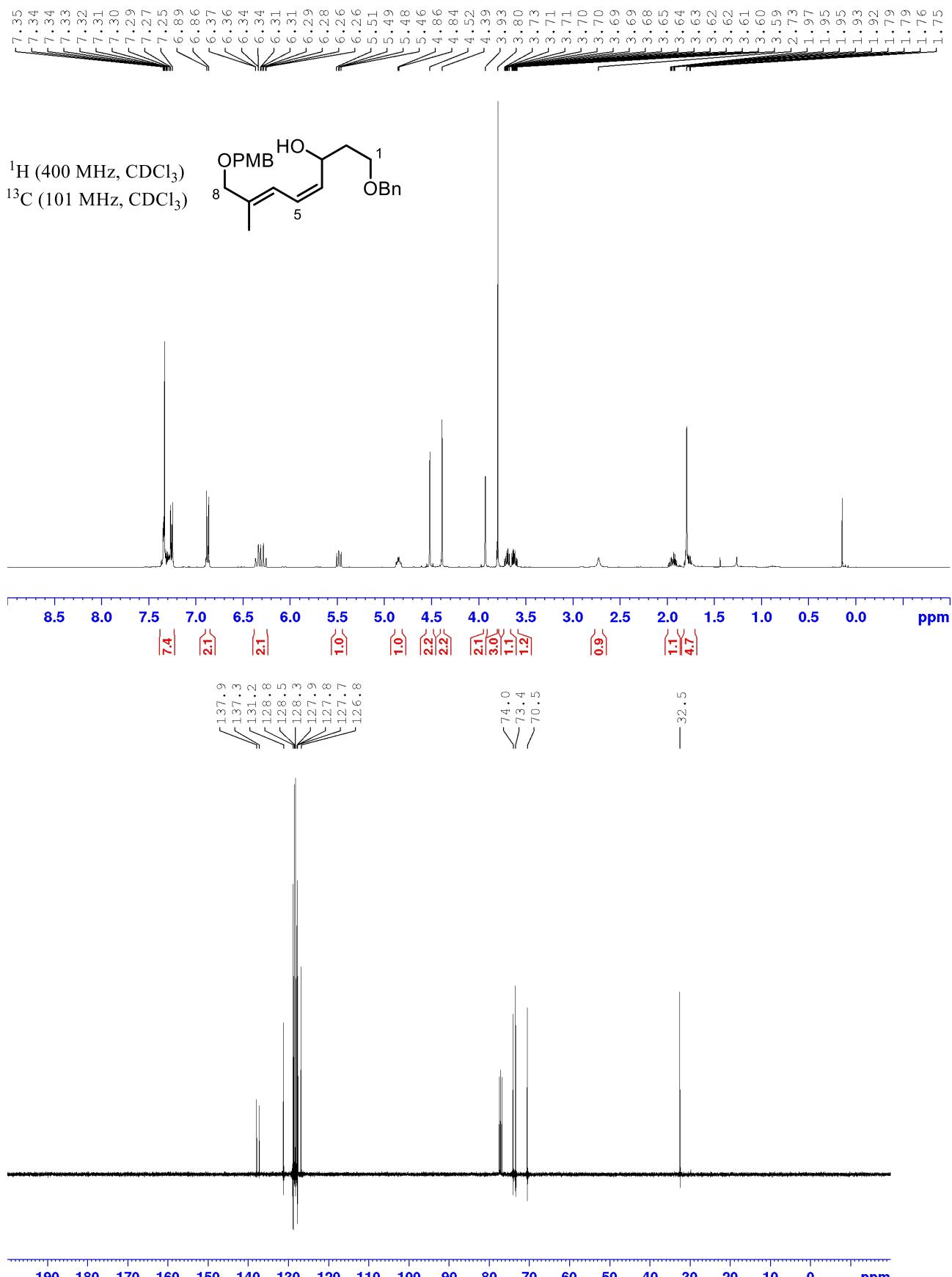
**(4Z,6E)-1-(Benzylxyloxy)-8-((4-methoxybenzyl)oxy)octa-4,6-dien-3-ol, 26d**



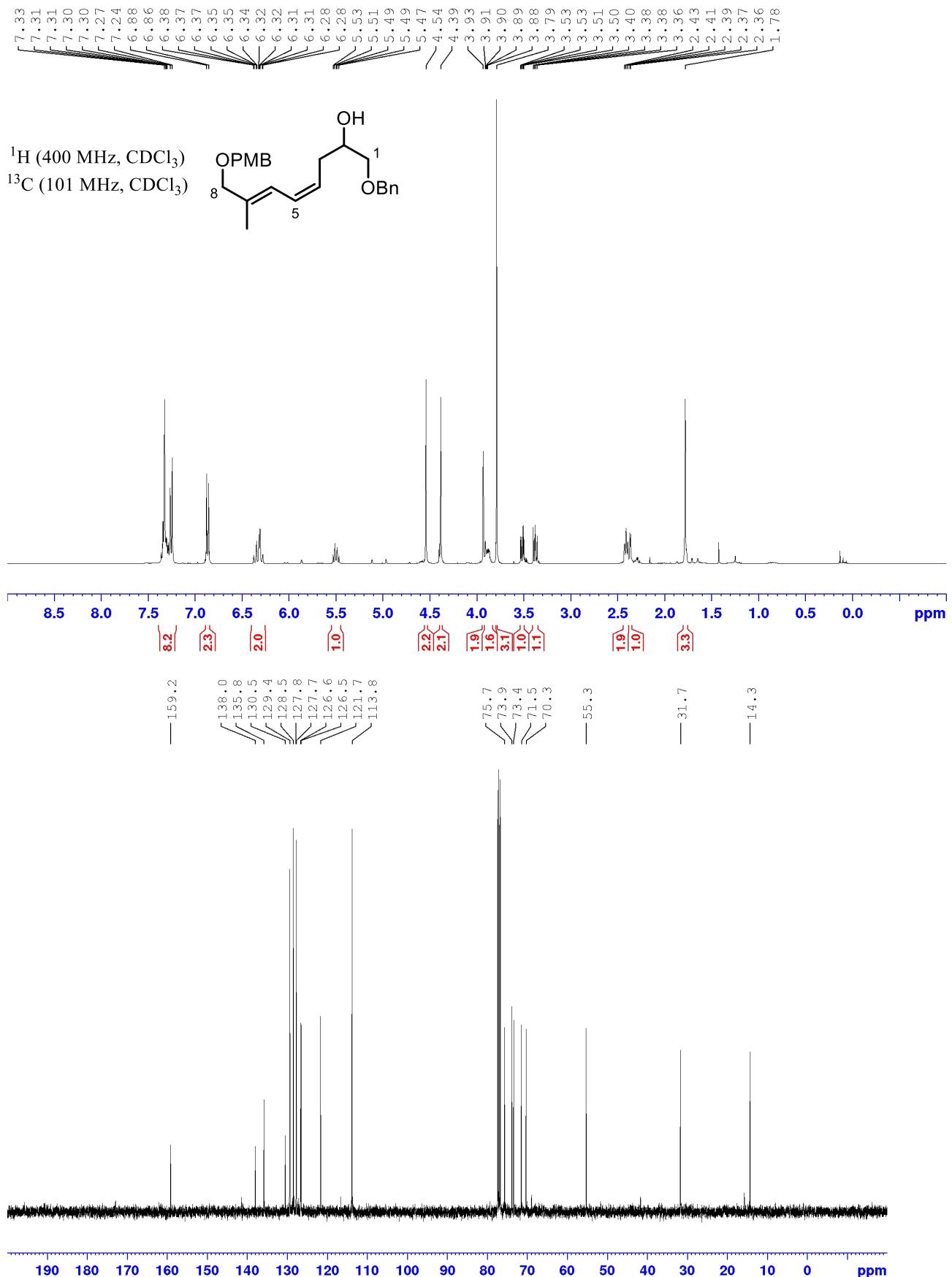
**(4Z,6E)-1-(benzyloxy)-8-((4-methoxybenzyl)oxy)octa-4,6-dien-2-ol, 27d**



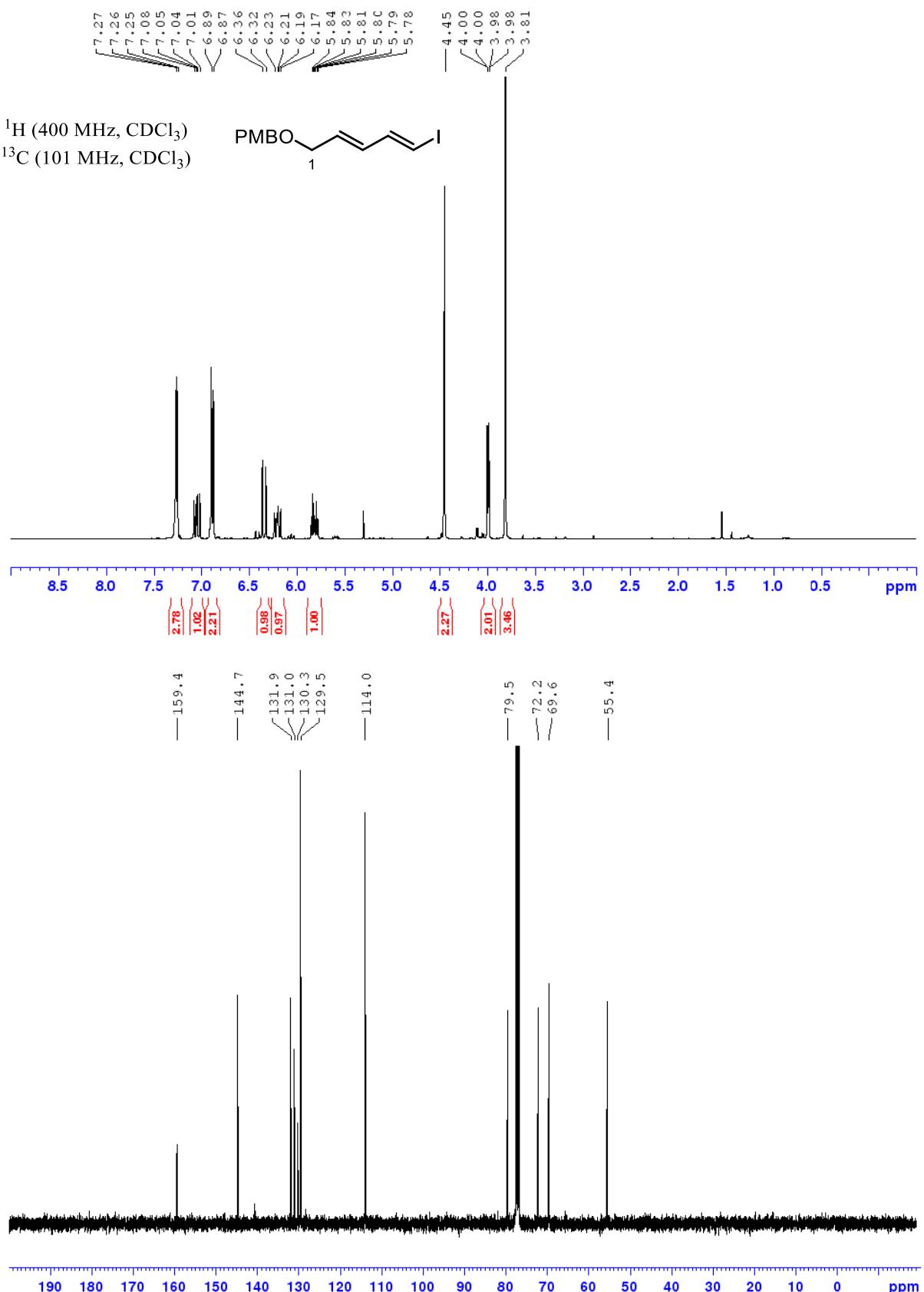
**(4Z,6E)-1-(Benzyl)-8-((4-methoxybenzyl)oxy)-7-methylocta-4,6-dien-3-ol, 26e**



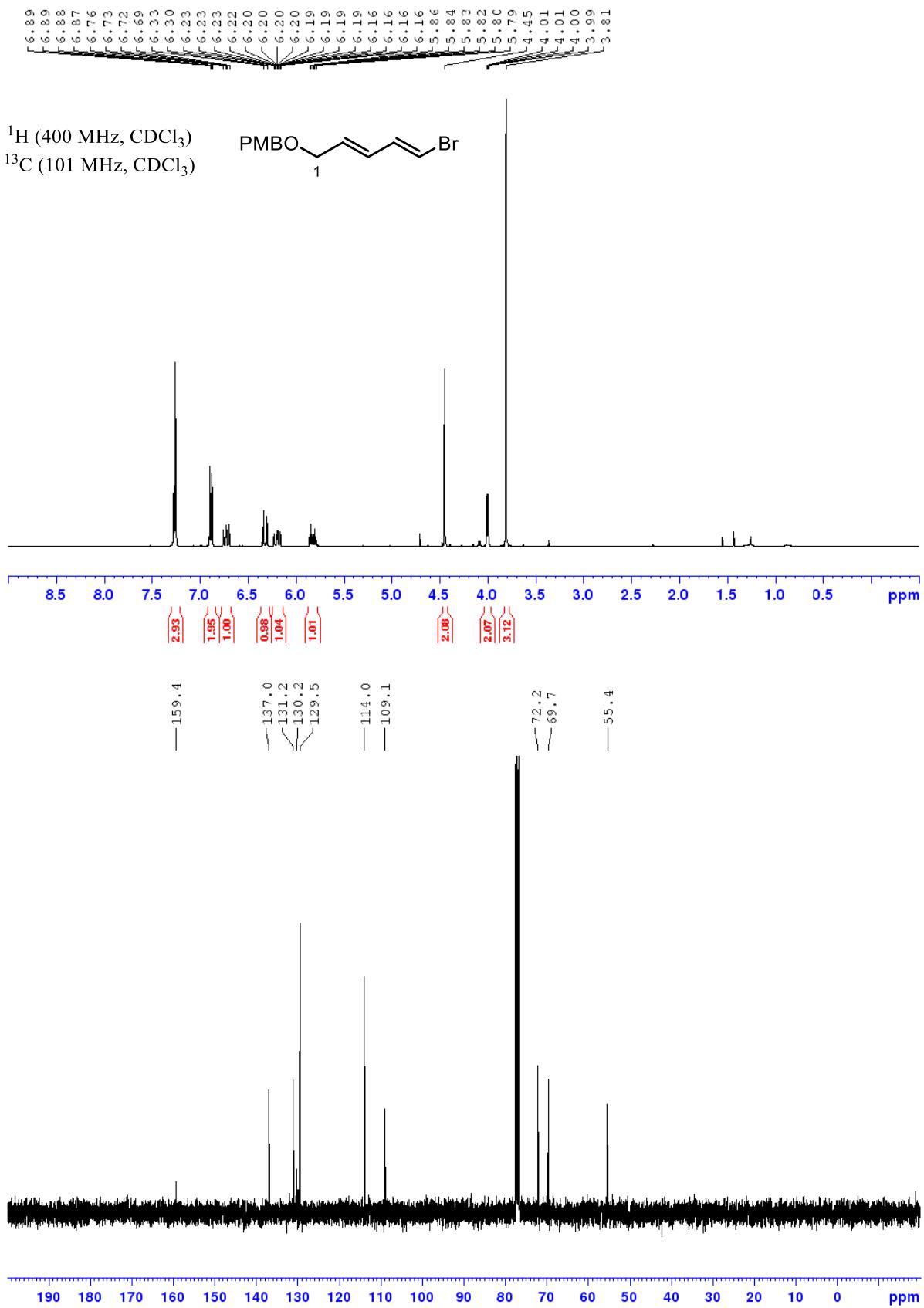
**(4Z,6E)-1-(Benzylxyloxy)-8-((4-methoxybenzyl)oxy)-7-methylocta-4,6-dien-2-ol, 27e**



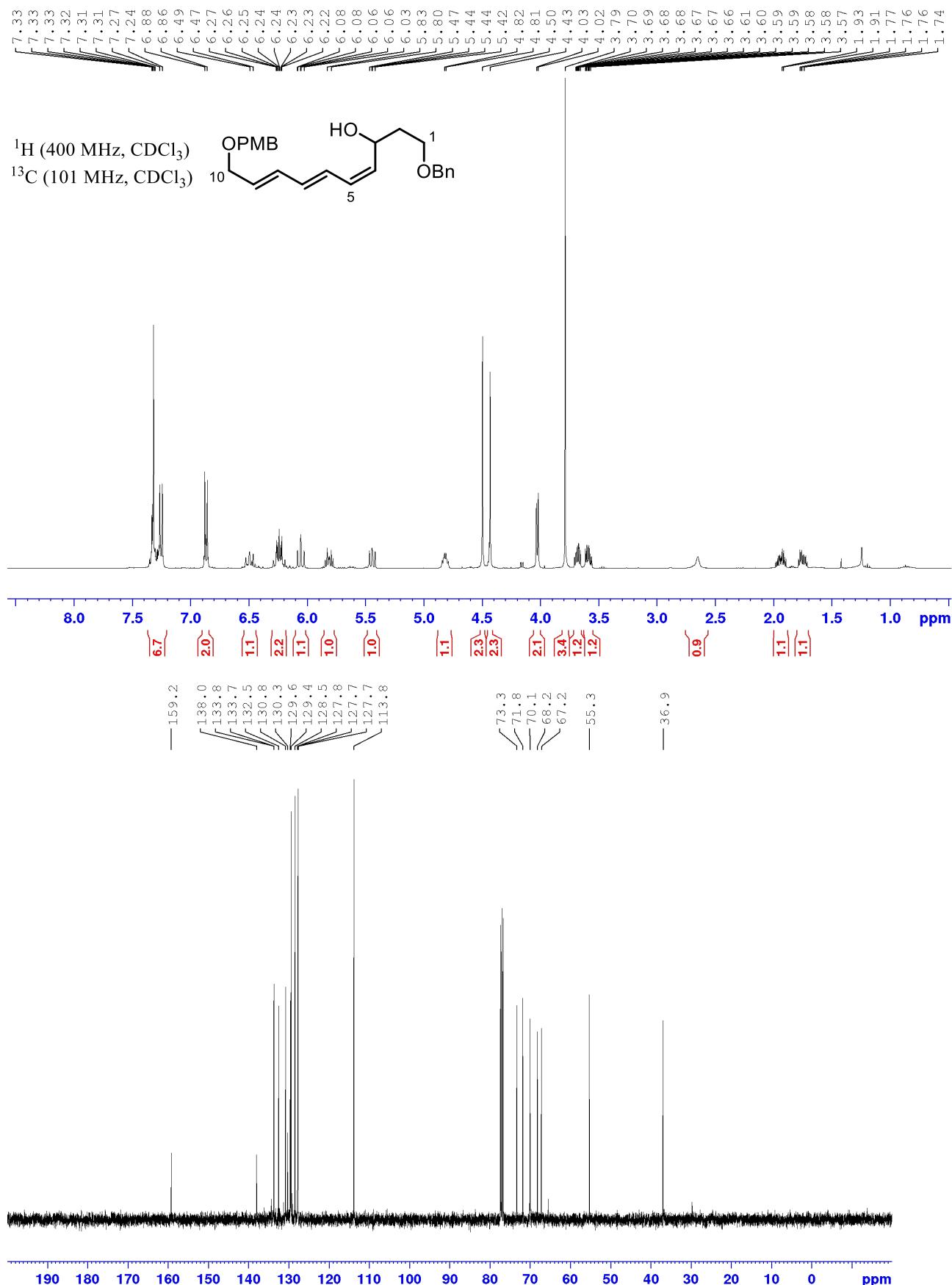
**1-(((2E,4E)-5-Iodopenta-2,4-dien-1-yl)oxy)methyl)-4-methoxybenzene, 25g**



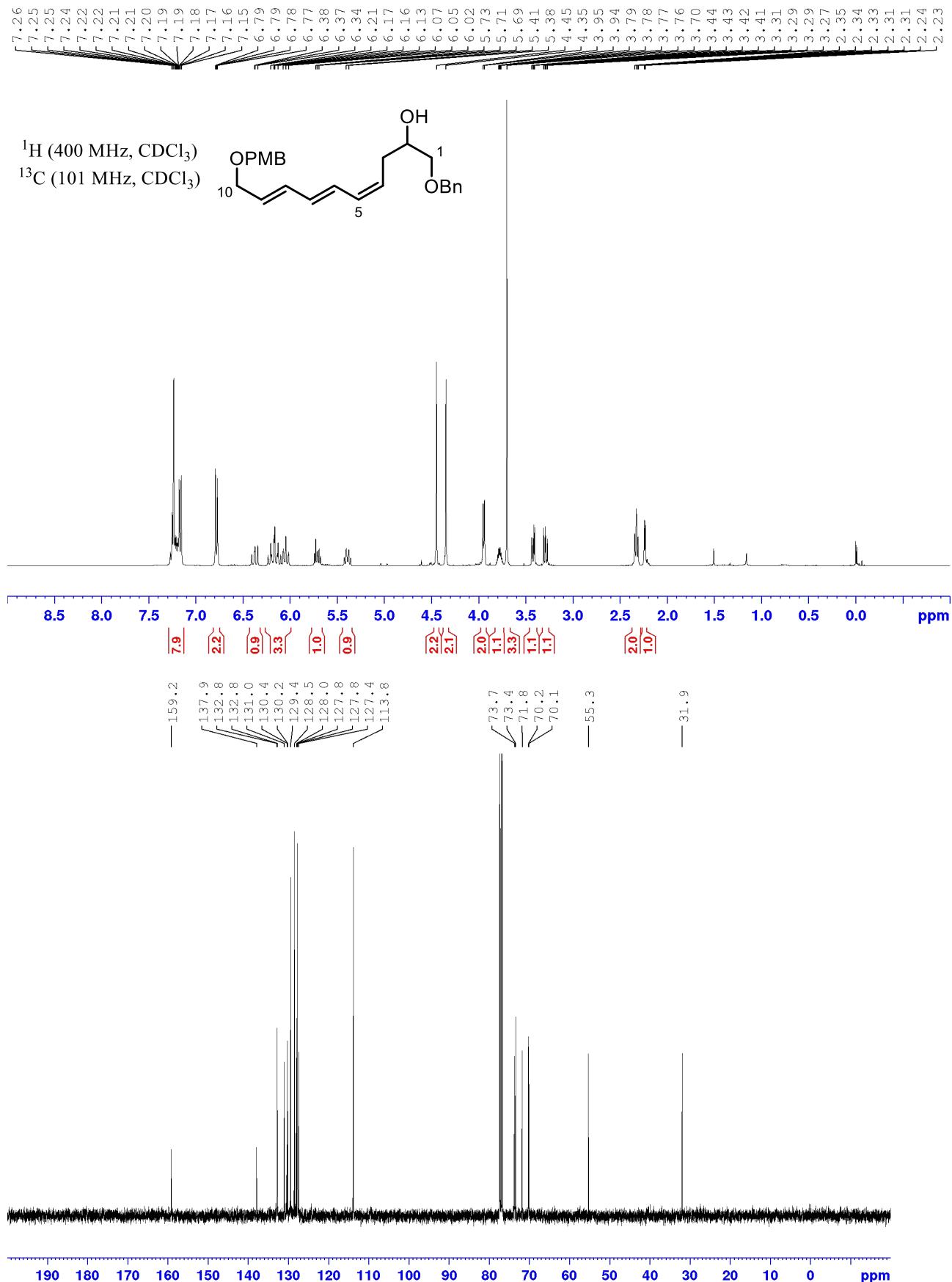
**1-(((2E,4E)-5-Bromopenta-2,4-dien-1-yl)oxy)methyl)-4-methoxybenzene, 25h**



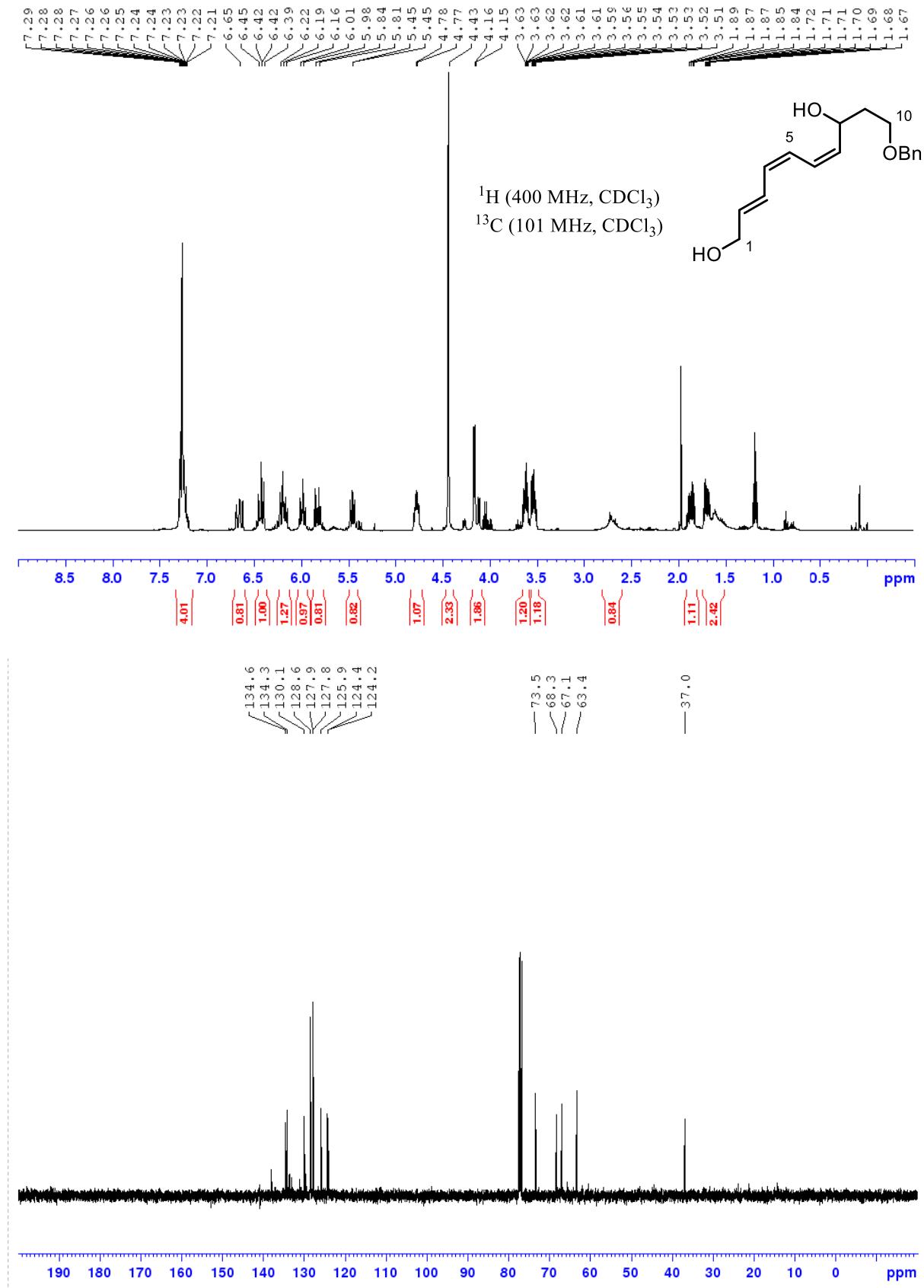
**(4Z,6E,8E)-1-(Benzylxy)-10-((4-methoxybenzyl)oxy)deca-4,6,8-trien-3-ol, 26f**



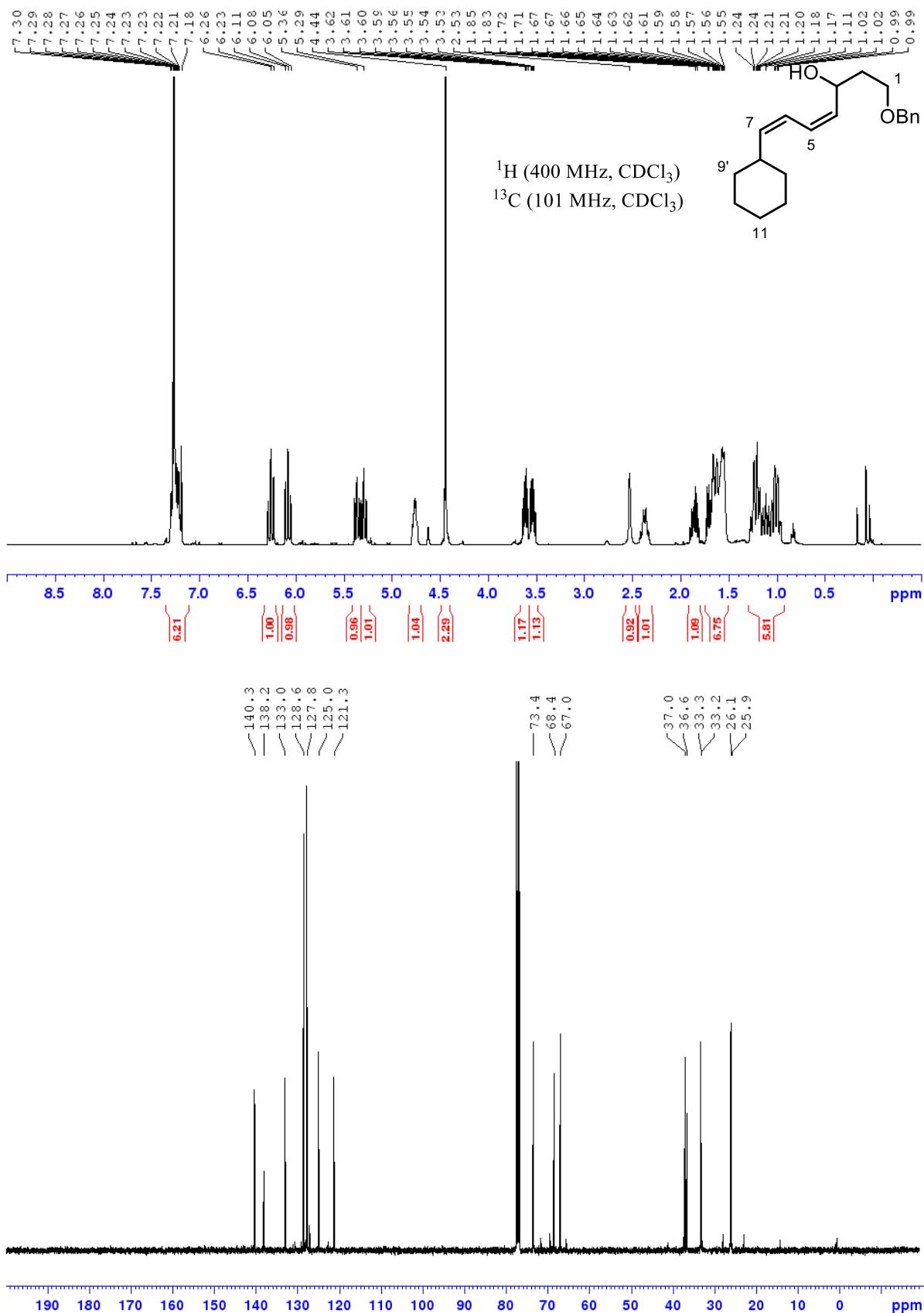
(4Z,6E)-1-(Benzyl)-10-((4-methoxybenzyl)oxy)deca-4,6,8-trien-2-ol, 27f



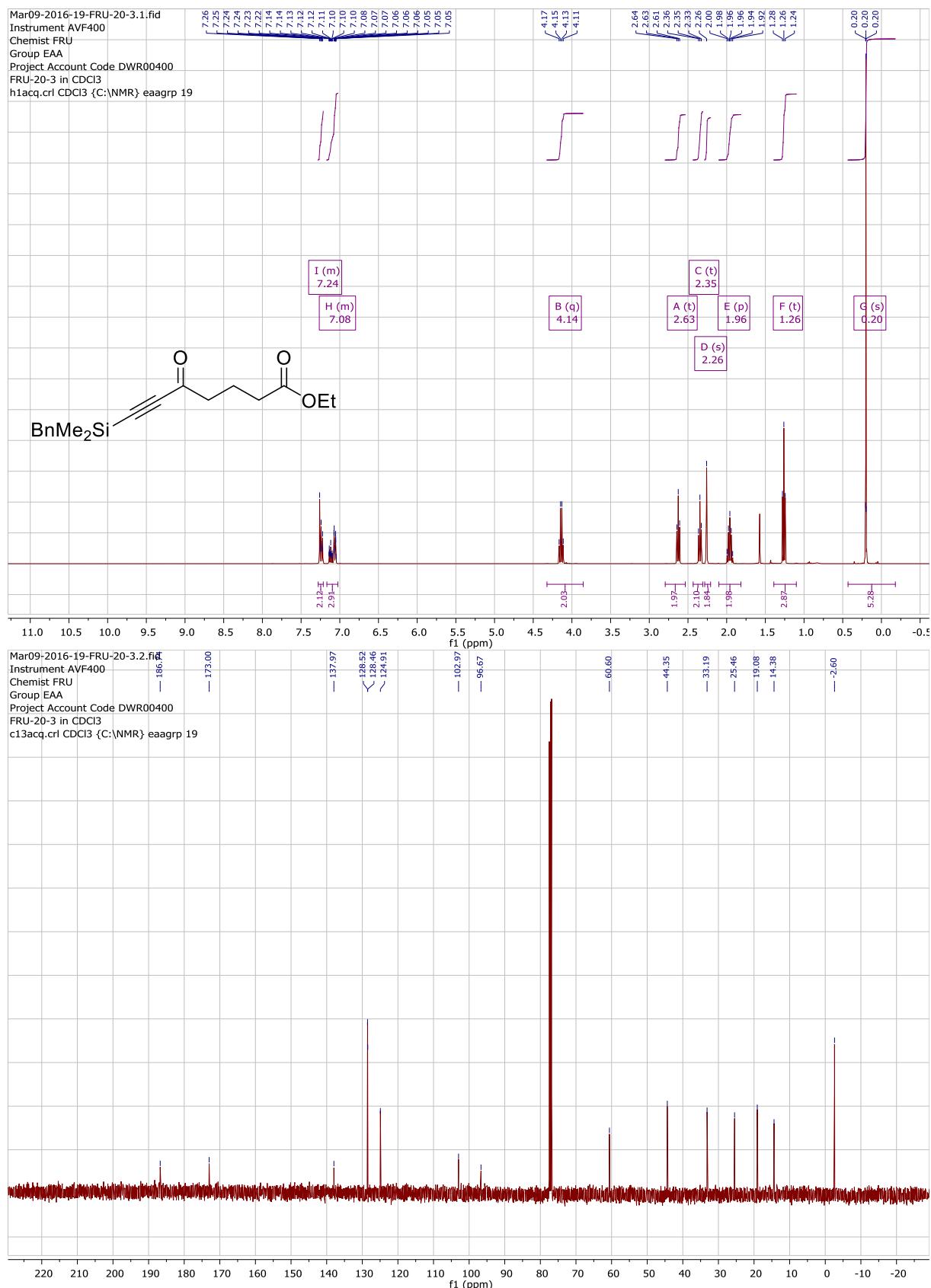
**(2E,4Z,6Z)-10-(Benzylxy)deca-2,4,6-triene-1,8-diol, 26g**



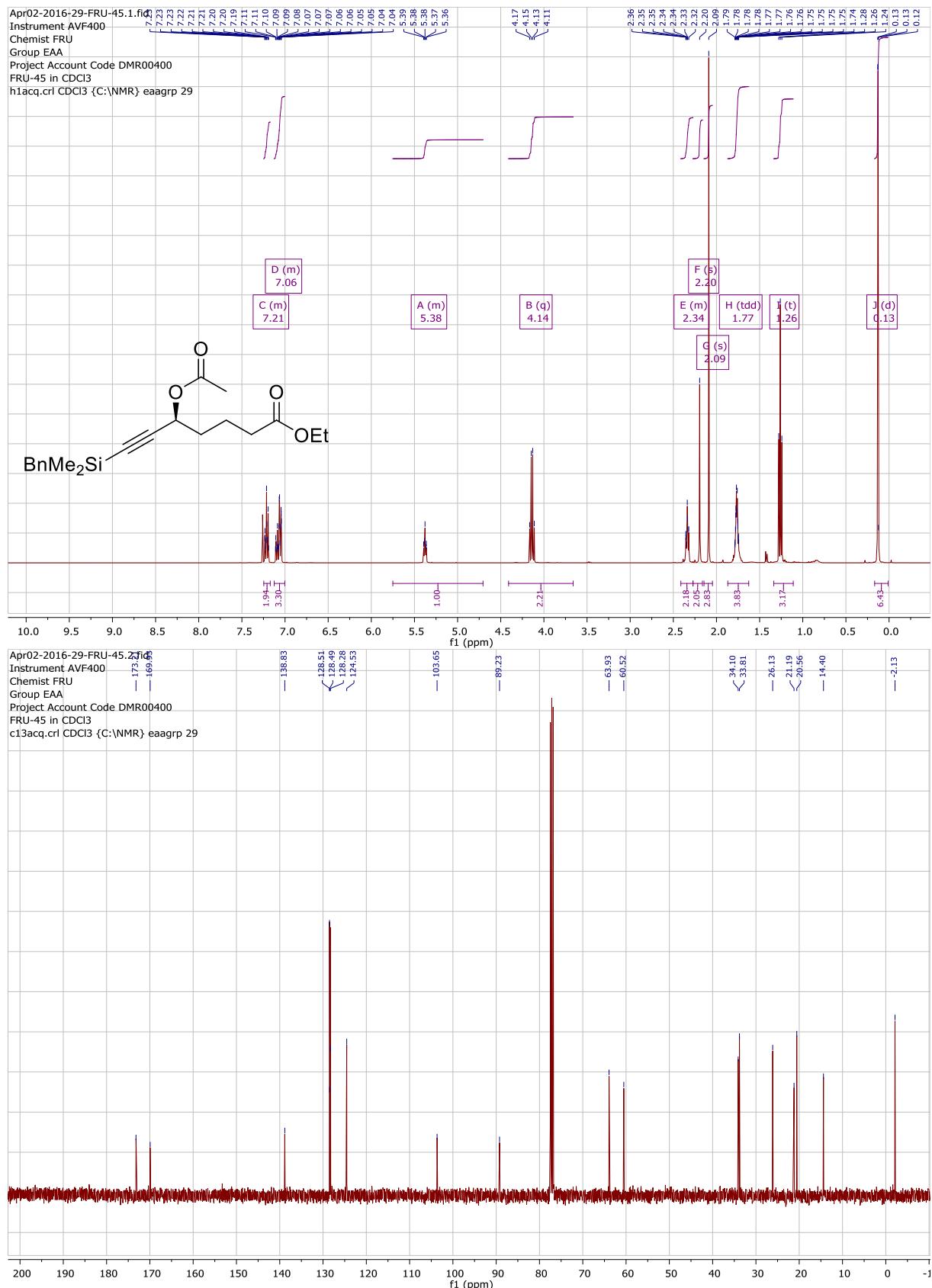
**(4Z,6Z)-1-(Benzylxy)-7-cyclohexylhepta-4,6-dien-3-ol, 26h**



## Ethyl 7-(benzyldimethylsilyl)-5-oxohept-6-yneate, 36



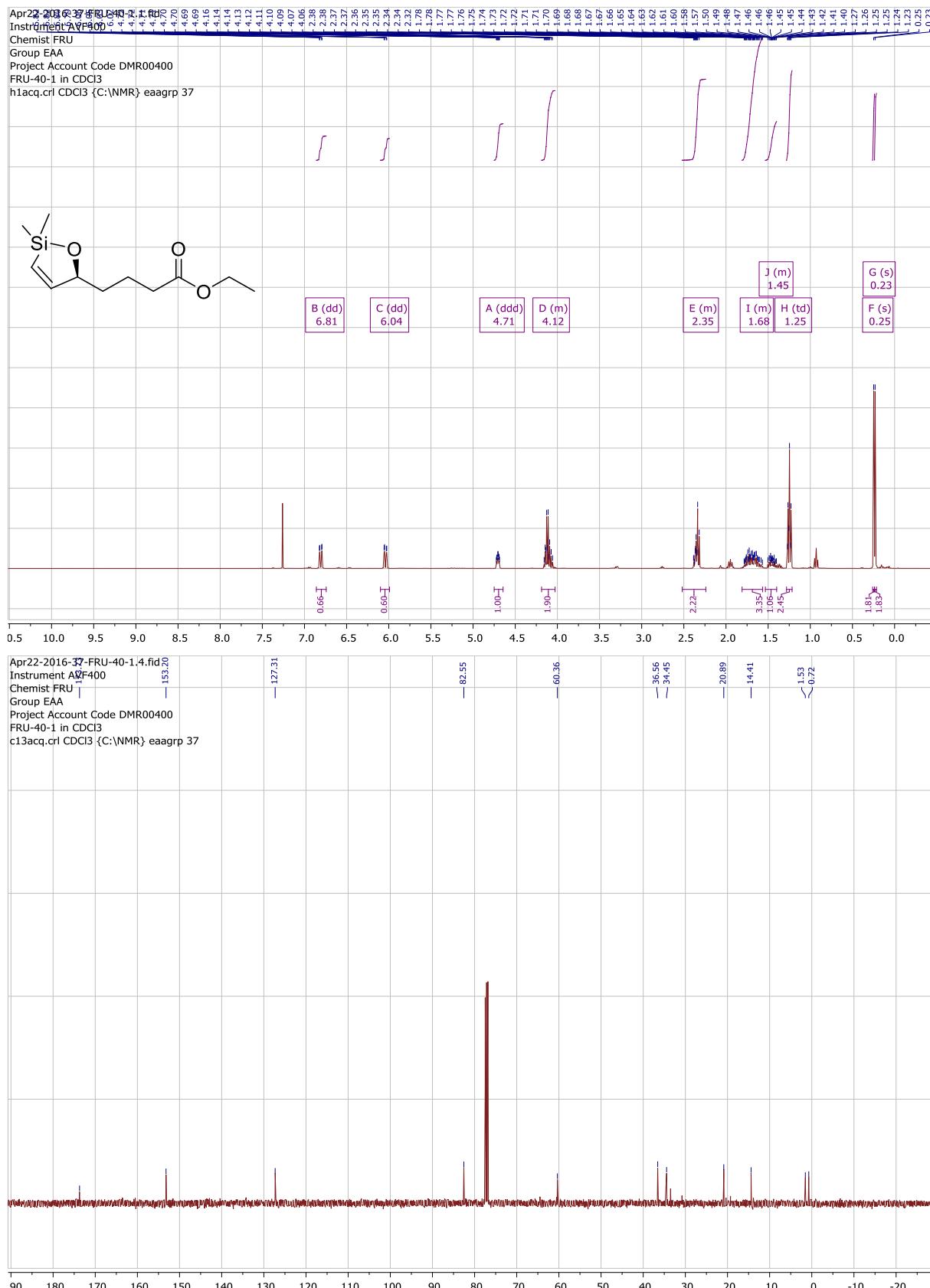
## Ethyl (S)-5-acetoxy-7-(benzyldimethylsilyl)hept-6-yneate, 37



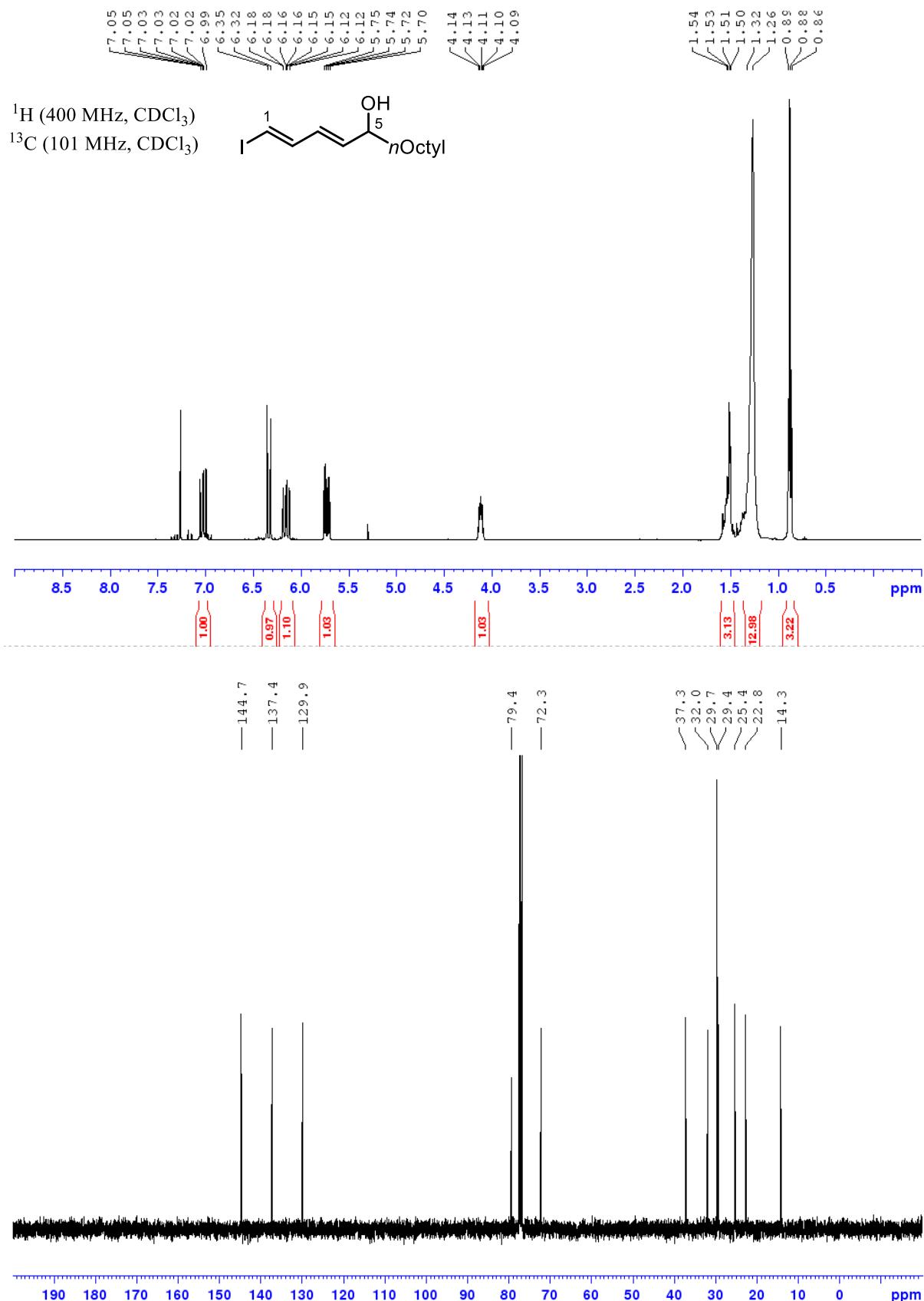
## Ethyl (S,Z)-5-acetoxy-7-(benzylidemethylsilyl)hept-6-enoate



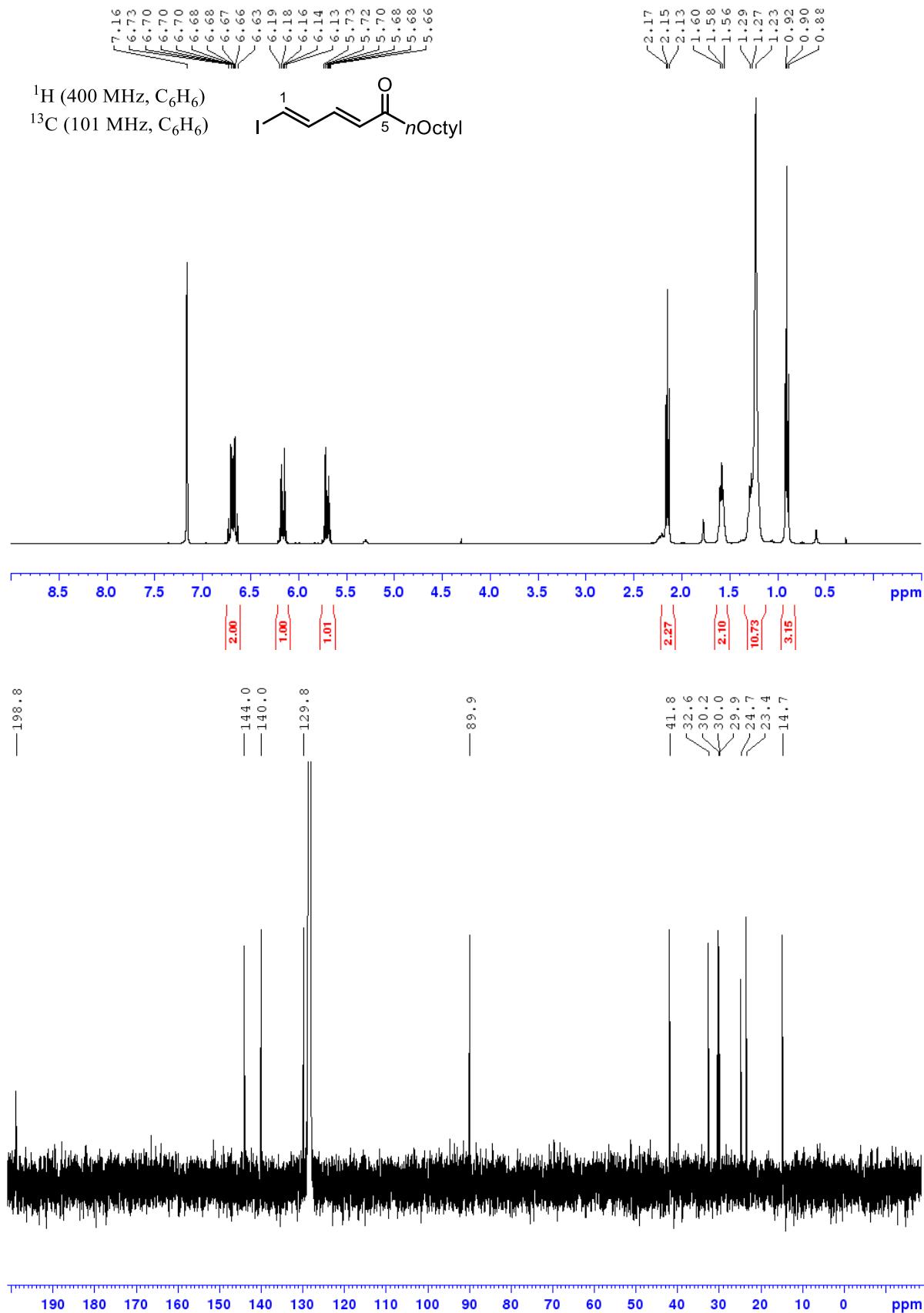
## Ethyl (S)-4-(2,2-dimethyl-2,5-dihydro-1,2-oxasilol-5-yl)butanoate, 34



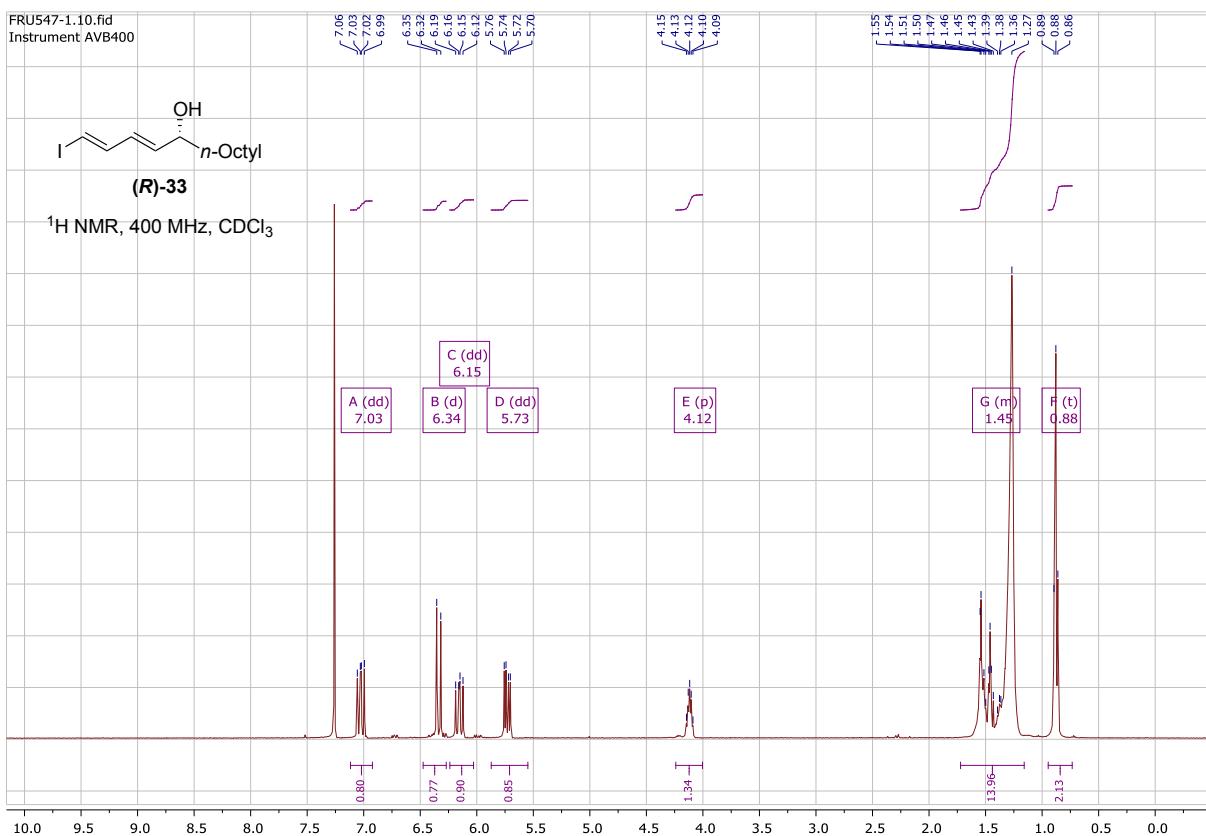
**(1*E*,3*E*)-1-Iodotrideca-1,3-dien-5-ol, ( $\pm$ )-38**



**(1E,3E)-1-Iodotrideca-1,3-dien-5-one**

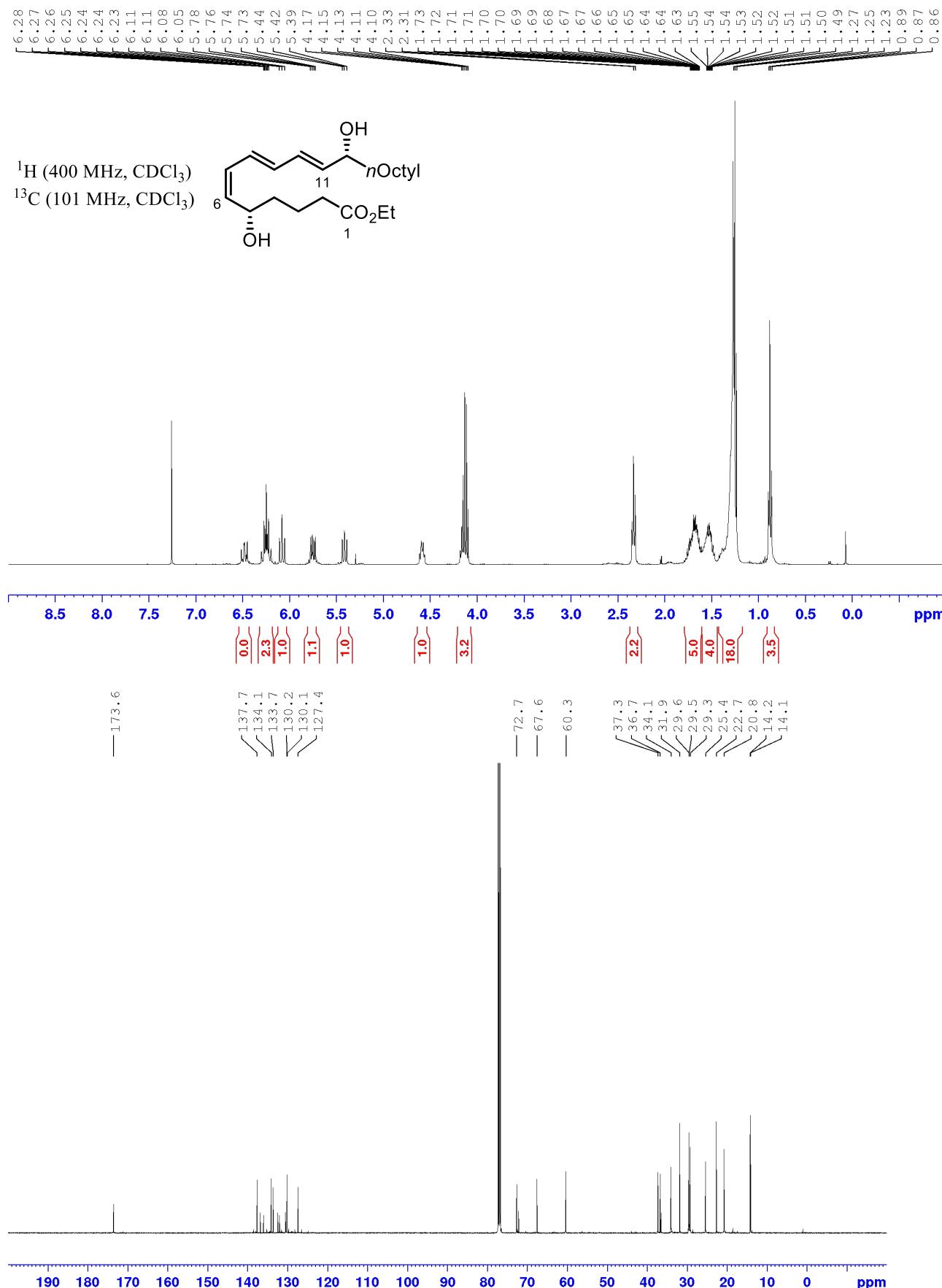


### **(5*R*,1*E*,3*E*)-1-Iodotrideca-1,3-dien-5-ol, (*R*)-38**

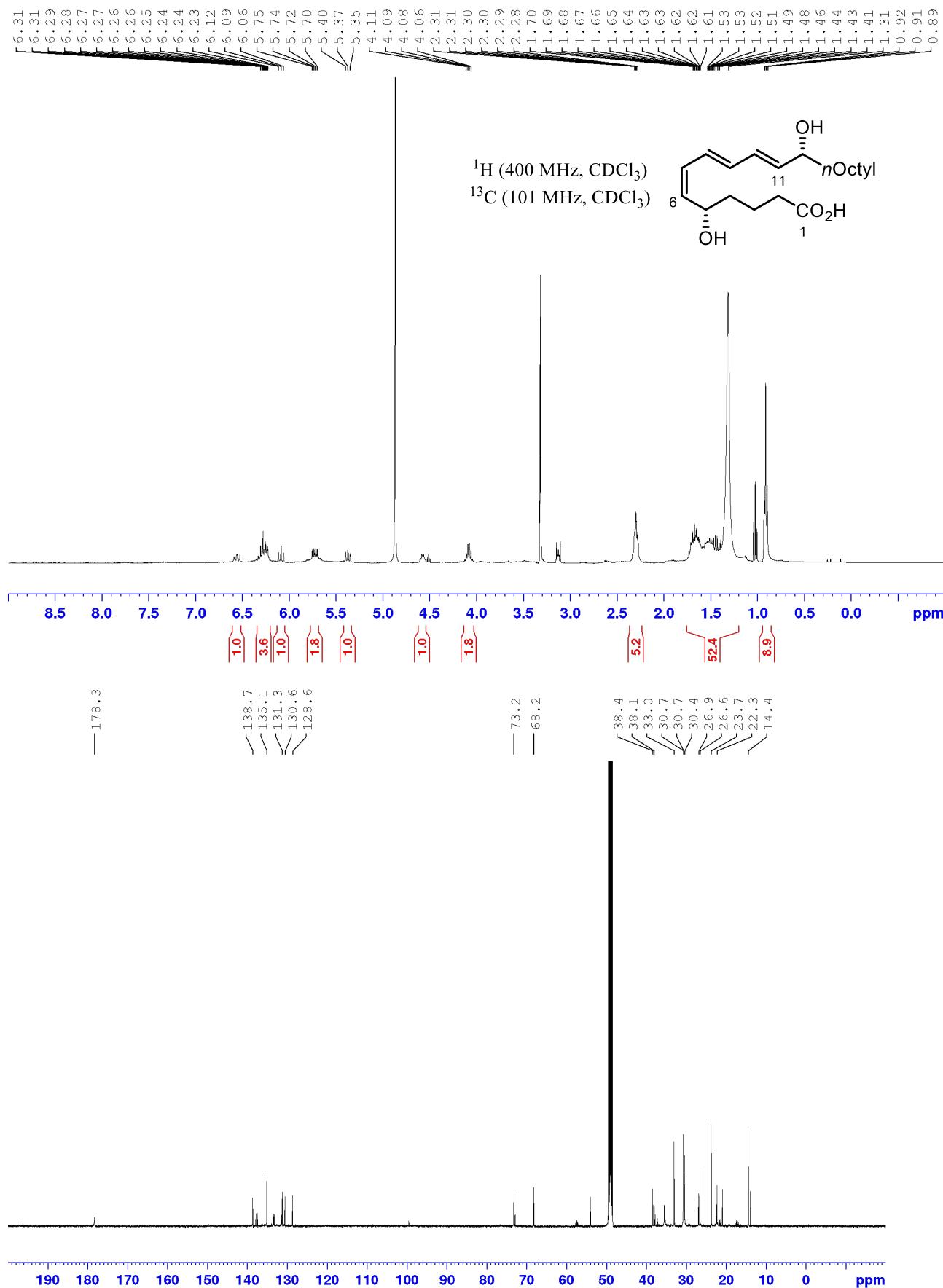


- Spectroscopic data identical to  $(\pm)$ -38

**Ethyl (5*S*,6*Z*,8*E*,10*E*,12*R*)-5,12-dihydroxyicos-a-6,8,10-trienoate, 39 (partial decomposition occurred during acquisition of the  $^{13}\text{C}$  NMR spectrum)**



**Leukotriene B<sub>3</sub>, 33**



## References

- (1) Bachmann, S.; Gernert, B.; Stalke, D. *Chemical Communications (Cambridge)* **2016**, *52*, 12861.
- (2) Bachmann, S.; Neufeld, R.; Dzemski, M.; Stalke, D. *Chem. Eur. J.* **2016**, *22*, 8462.