

Supporting Information

Diastereoselective Flexible Synthesis of Carbocyclic C-nucleosides

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[§]International Center for Clinical Research, St. Anne's University Hospital Brno, Pekařská 53, 656 91 Brno, Czech Republic

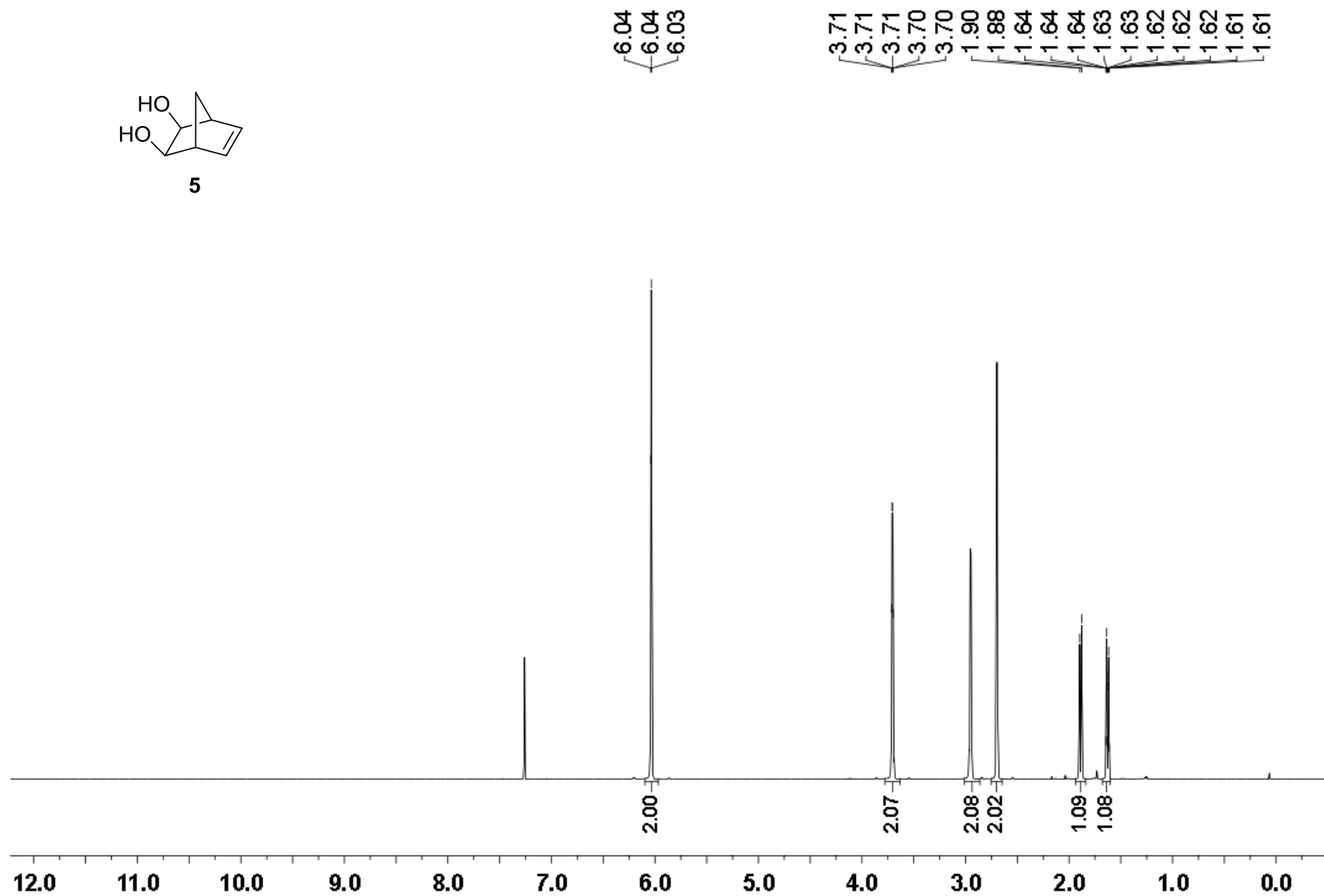
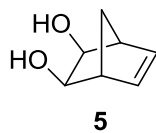
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these authors contributed equally to this work

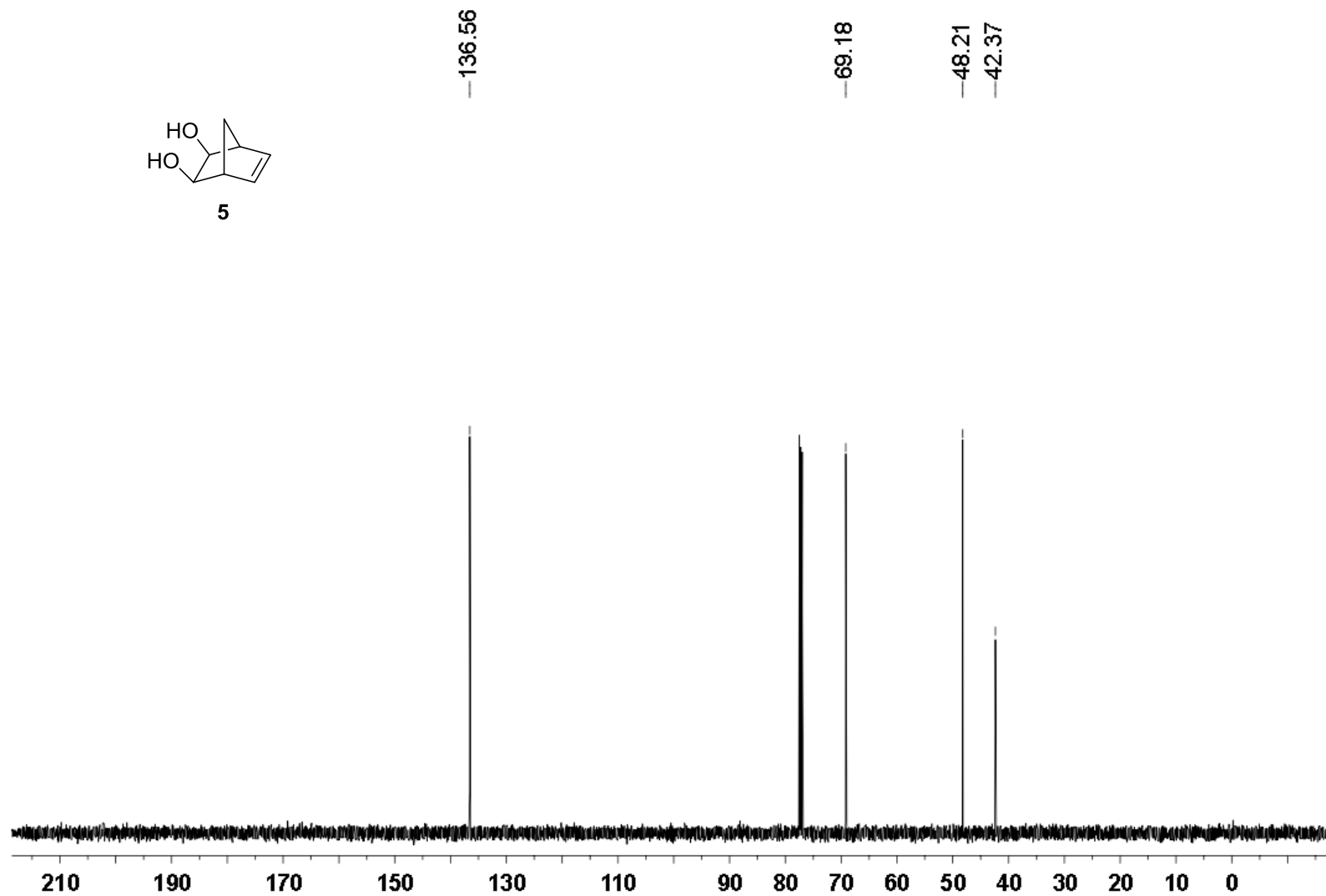
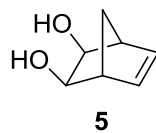
* e-mail: paruch@chemi.muni.cz

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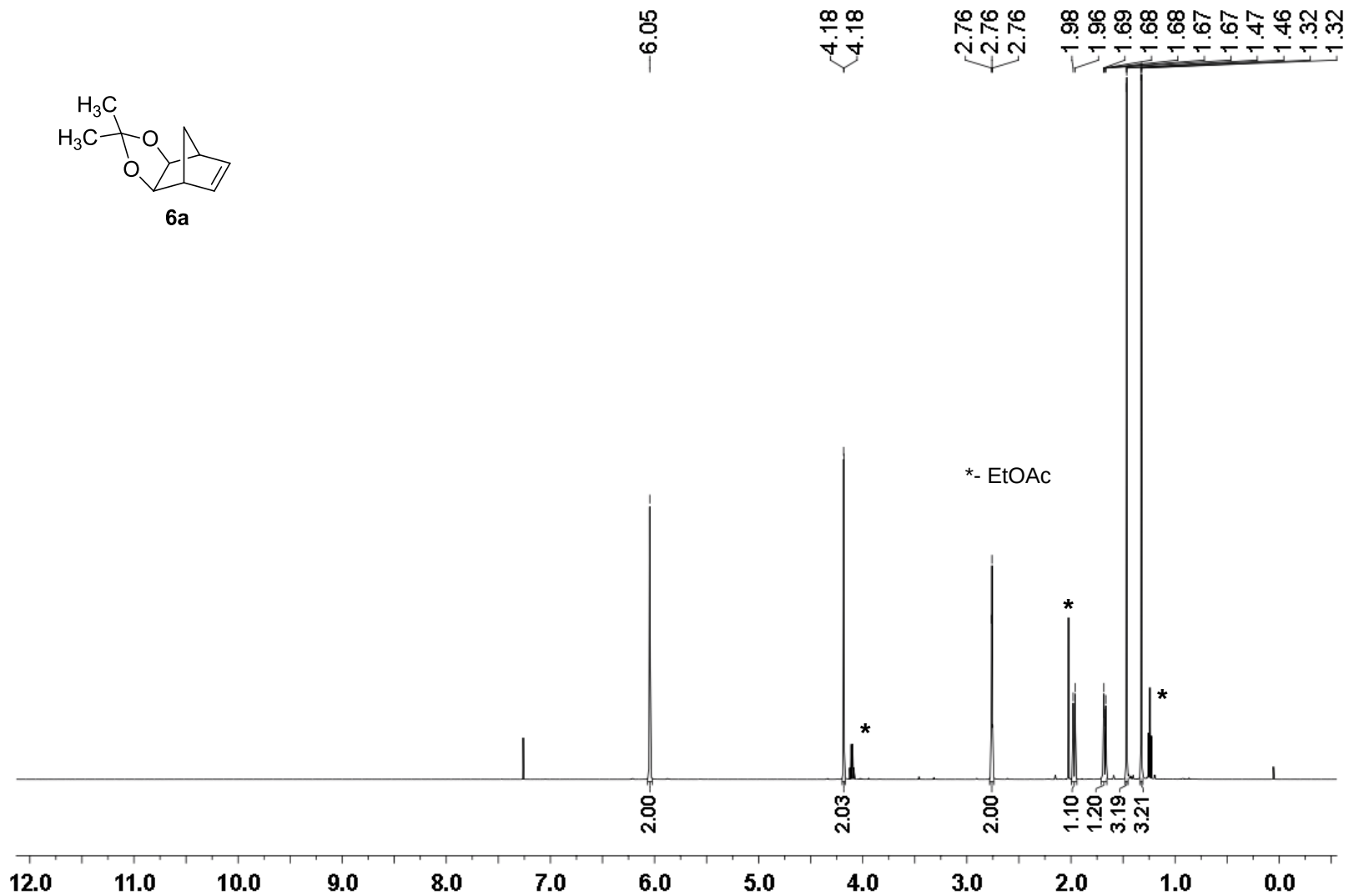
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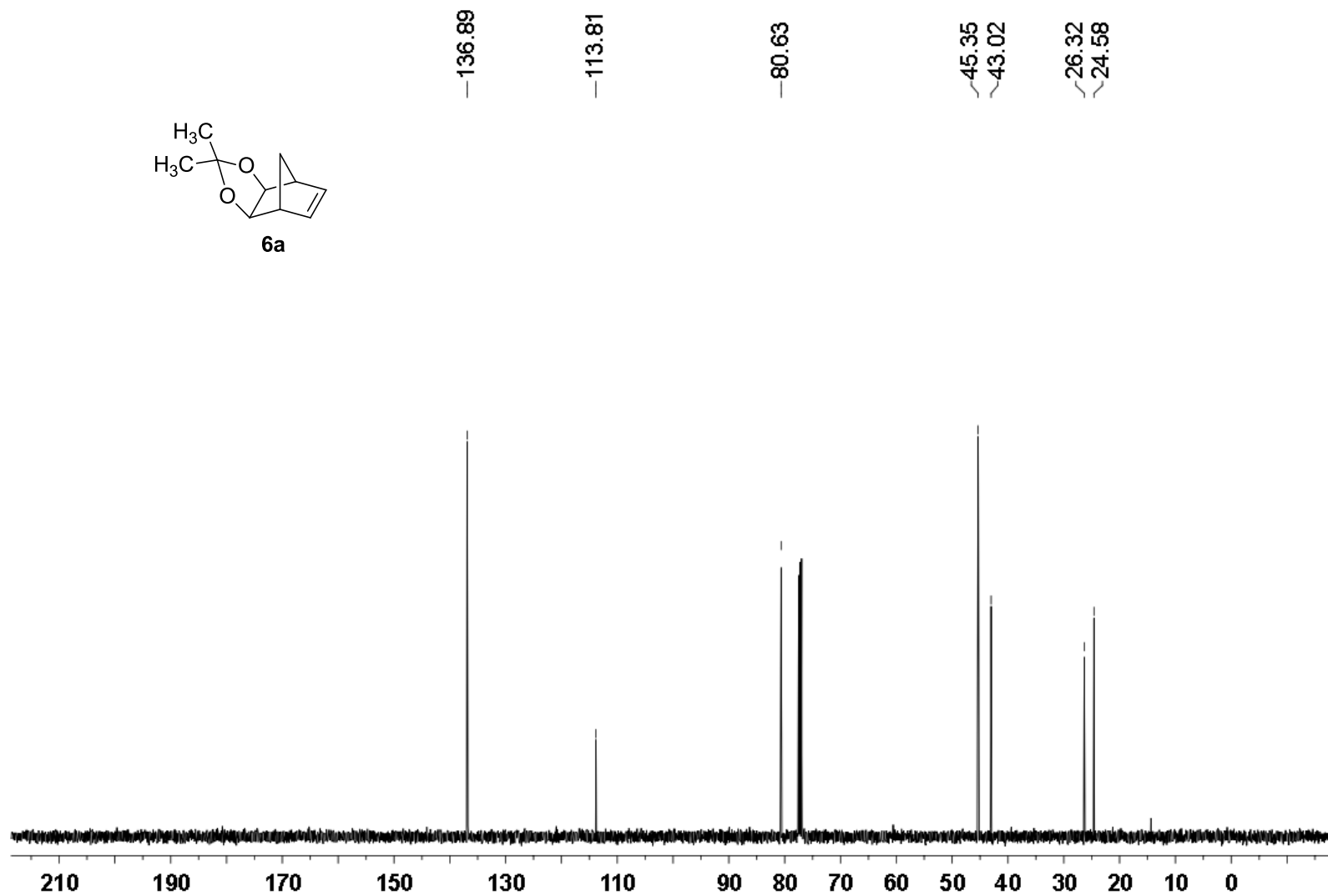
¹H NMR (500MHz) spectrum of **5** in CDCl₃



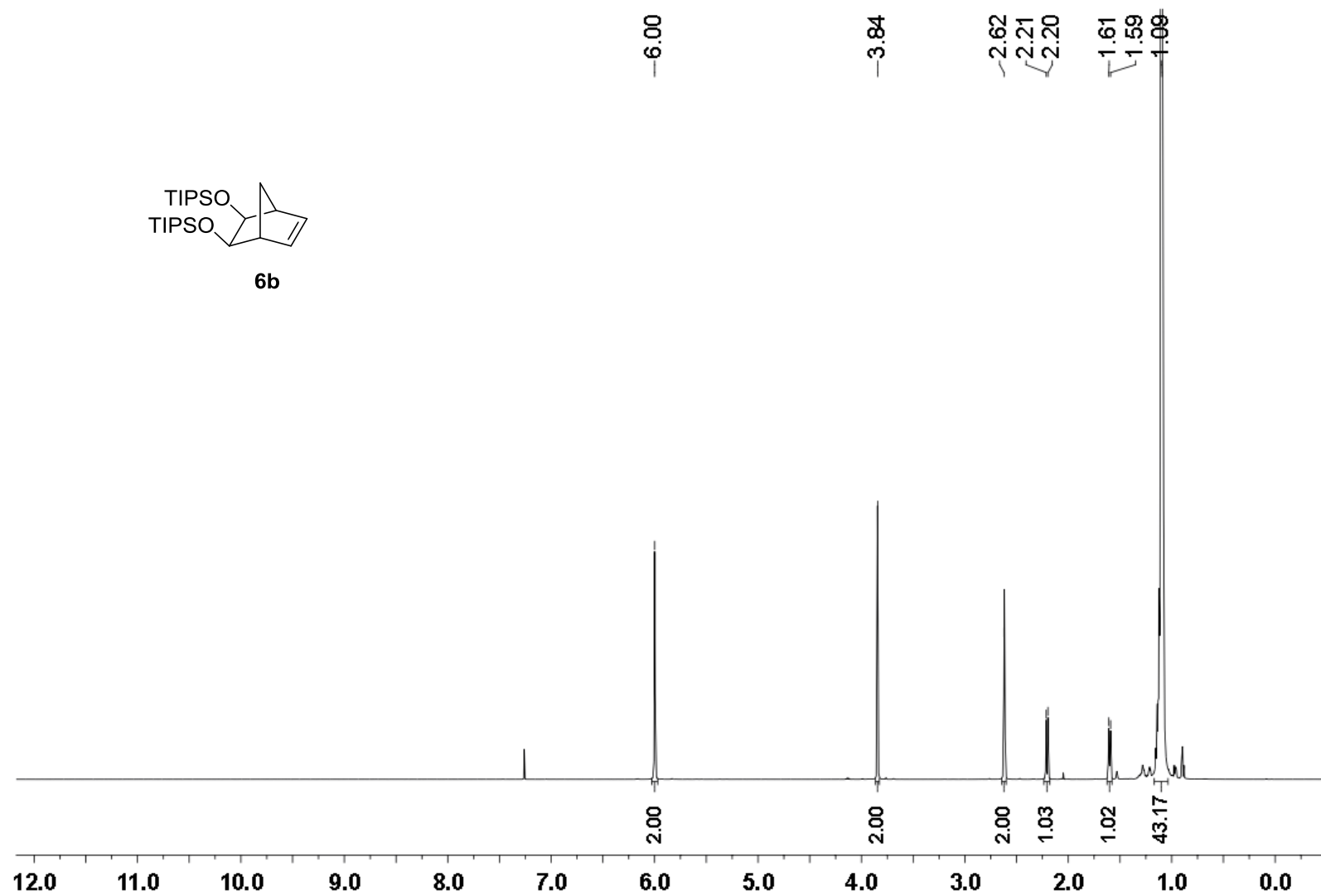
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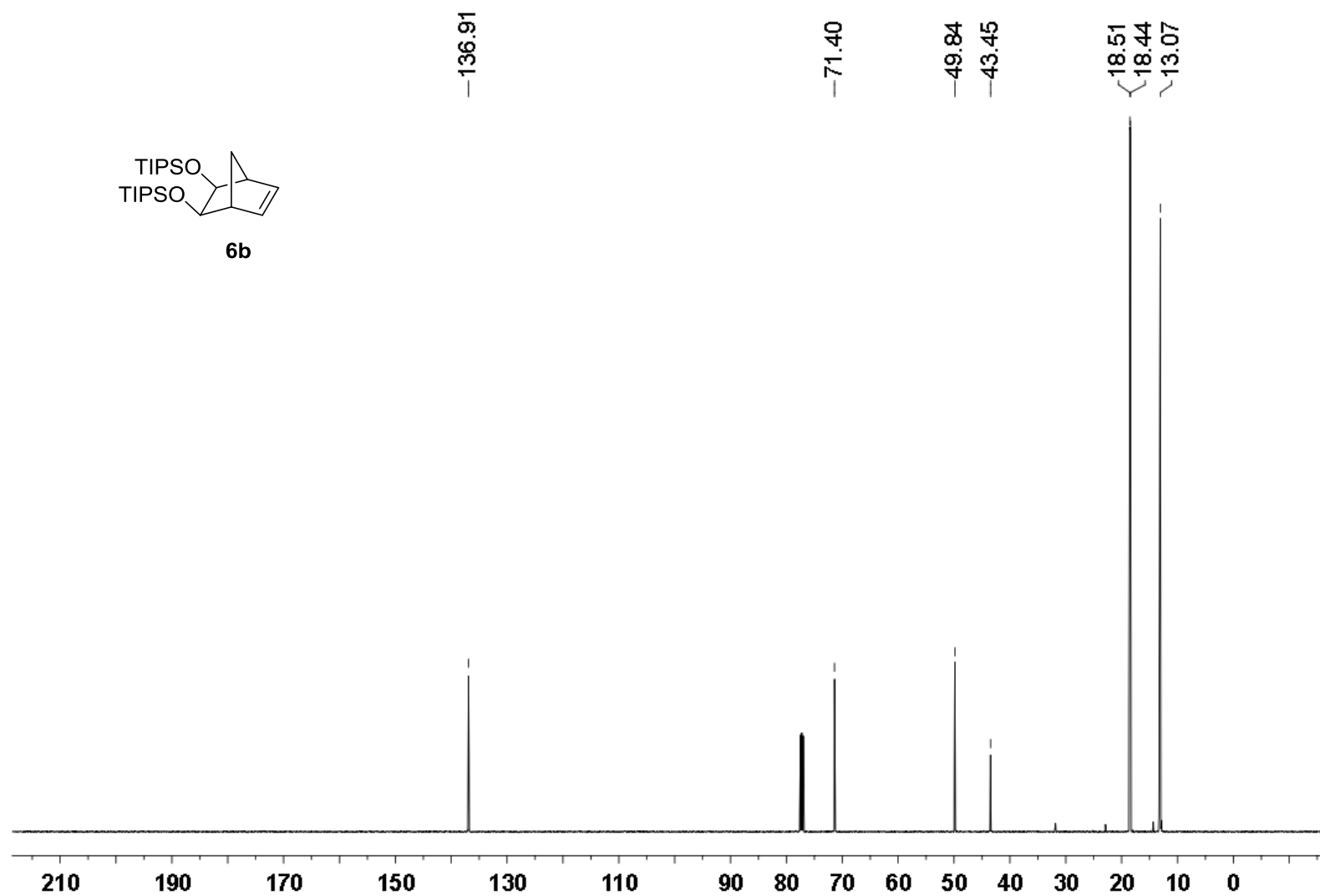
^1H NMR (500 MHz) spectrum of **6a** in CDCl_3



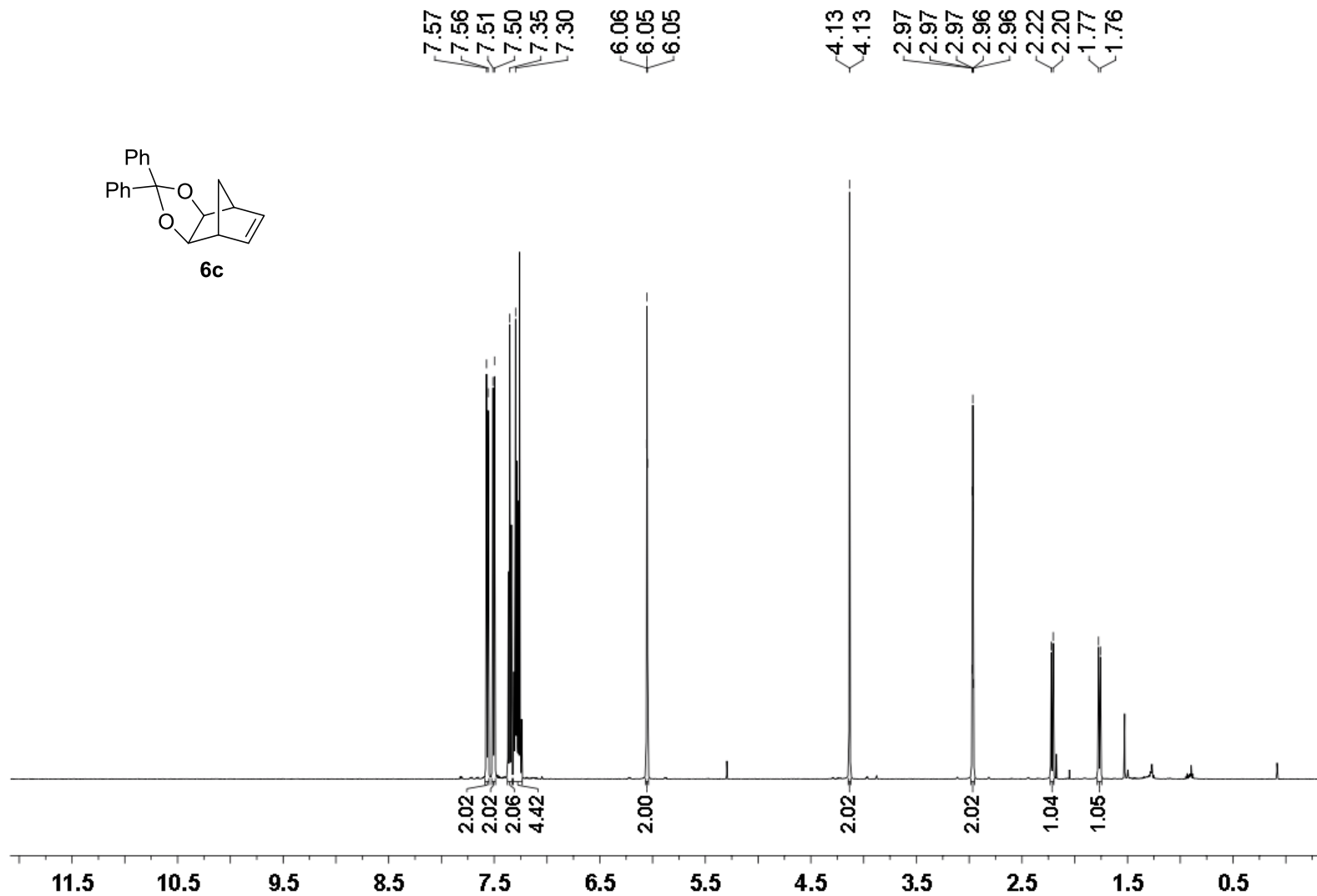
^{13}C NMR (126 MHz) spectrum of **6a** in CDCl_3



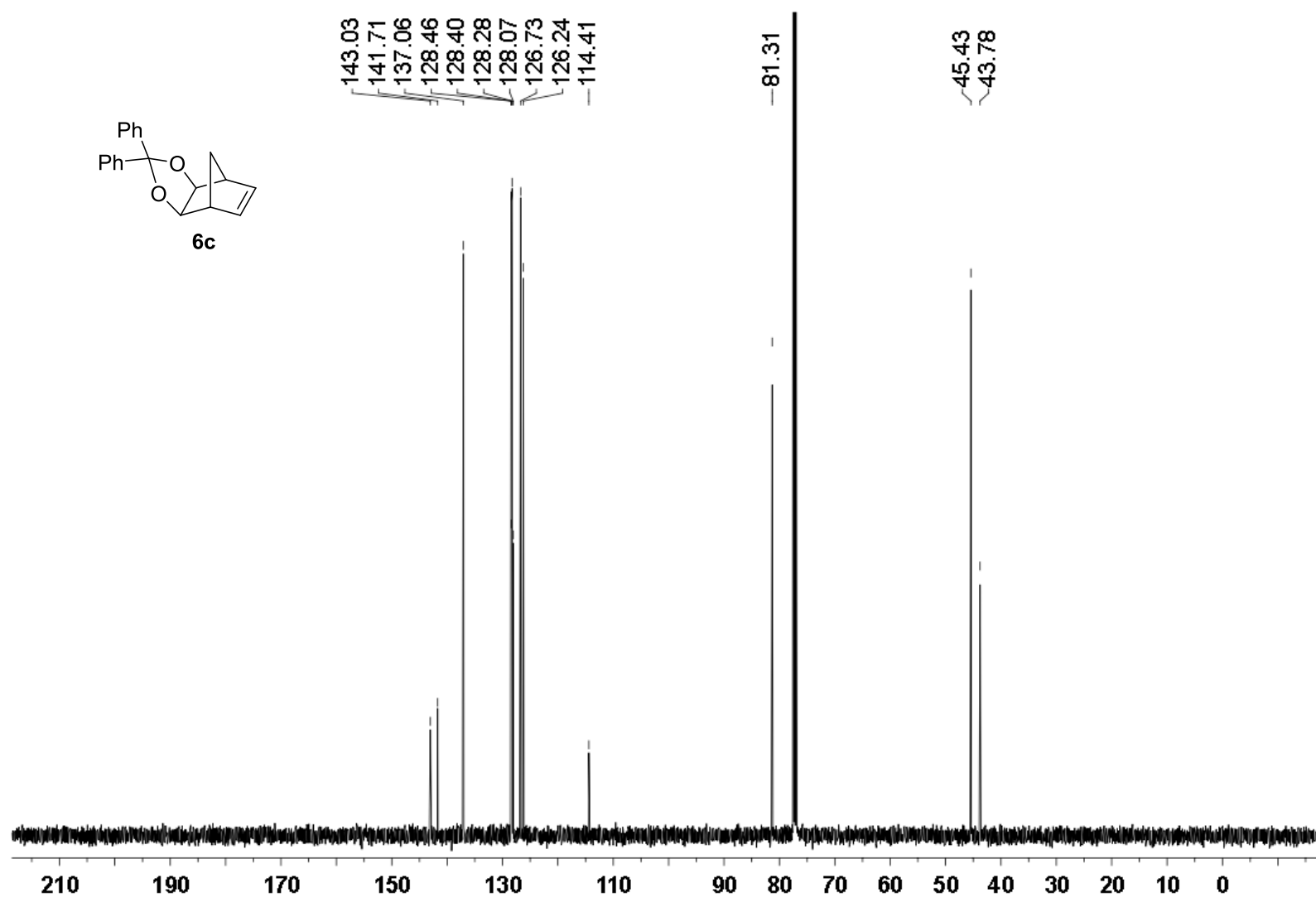
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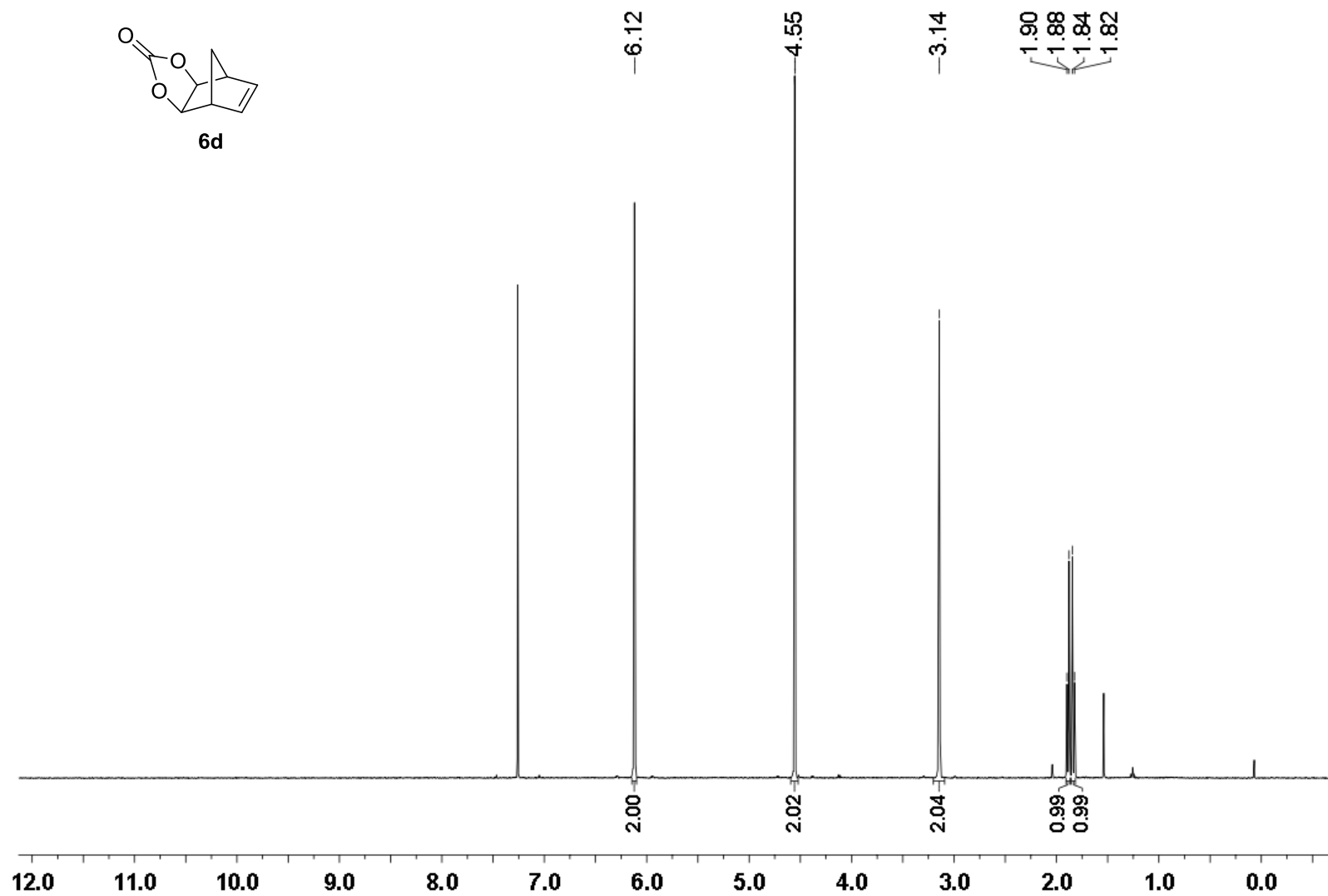
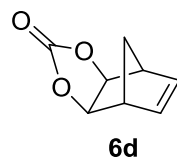
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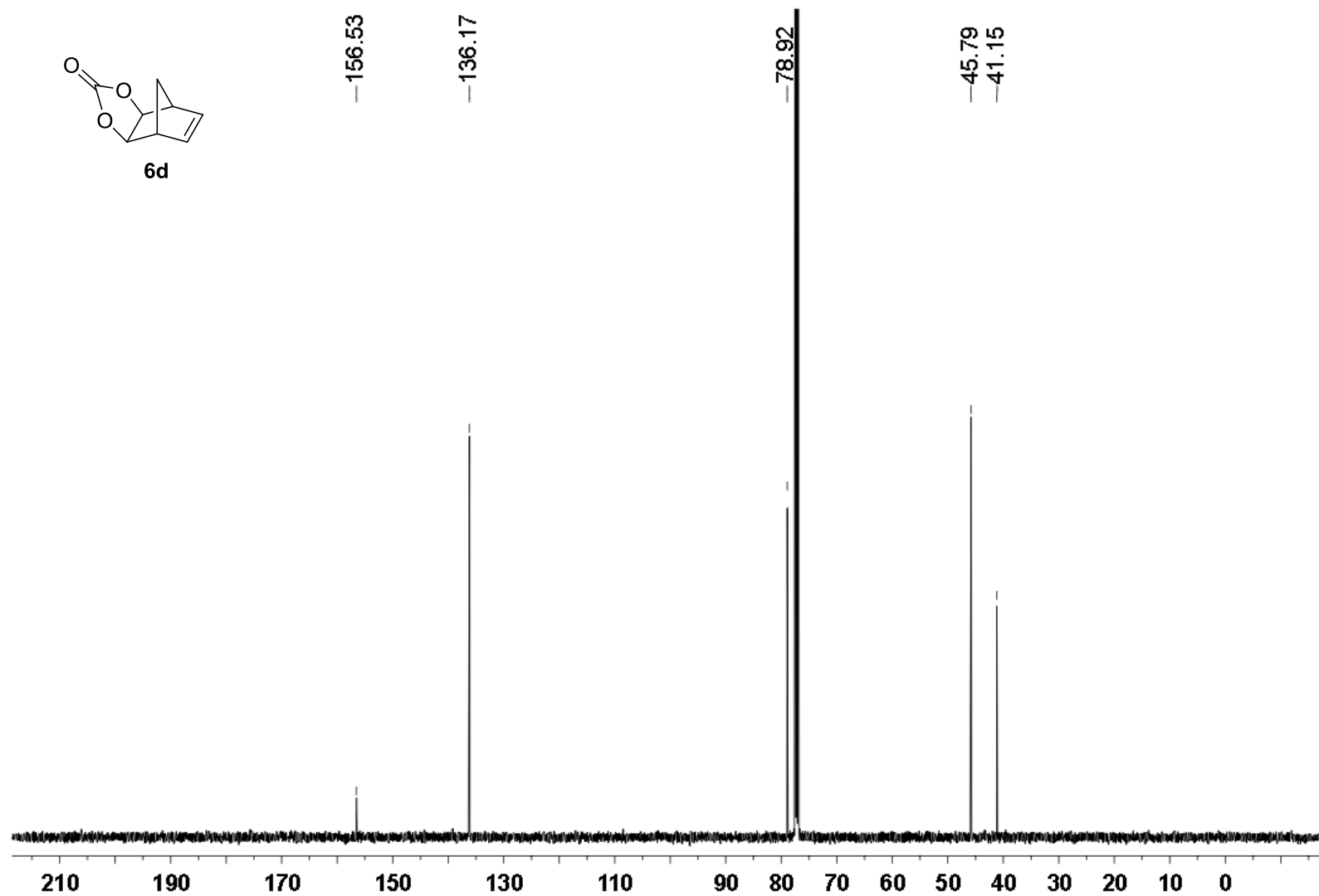
^1H NMR (500 MHz) spectrum of **6c** in CDCl_3



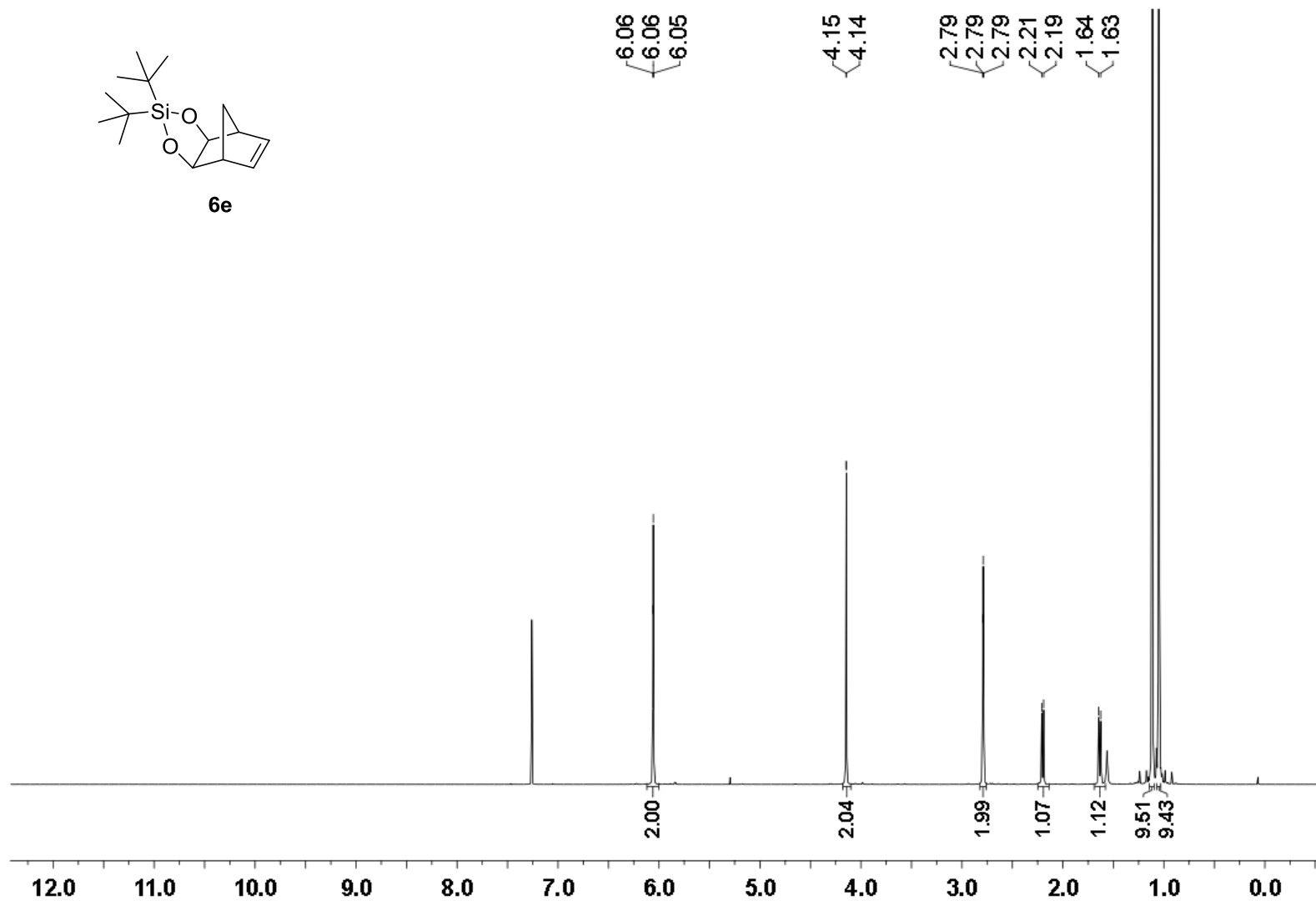
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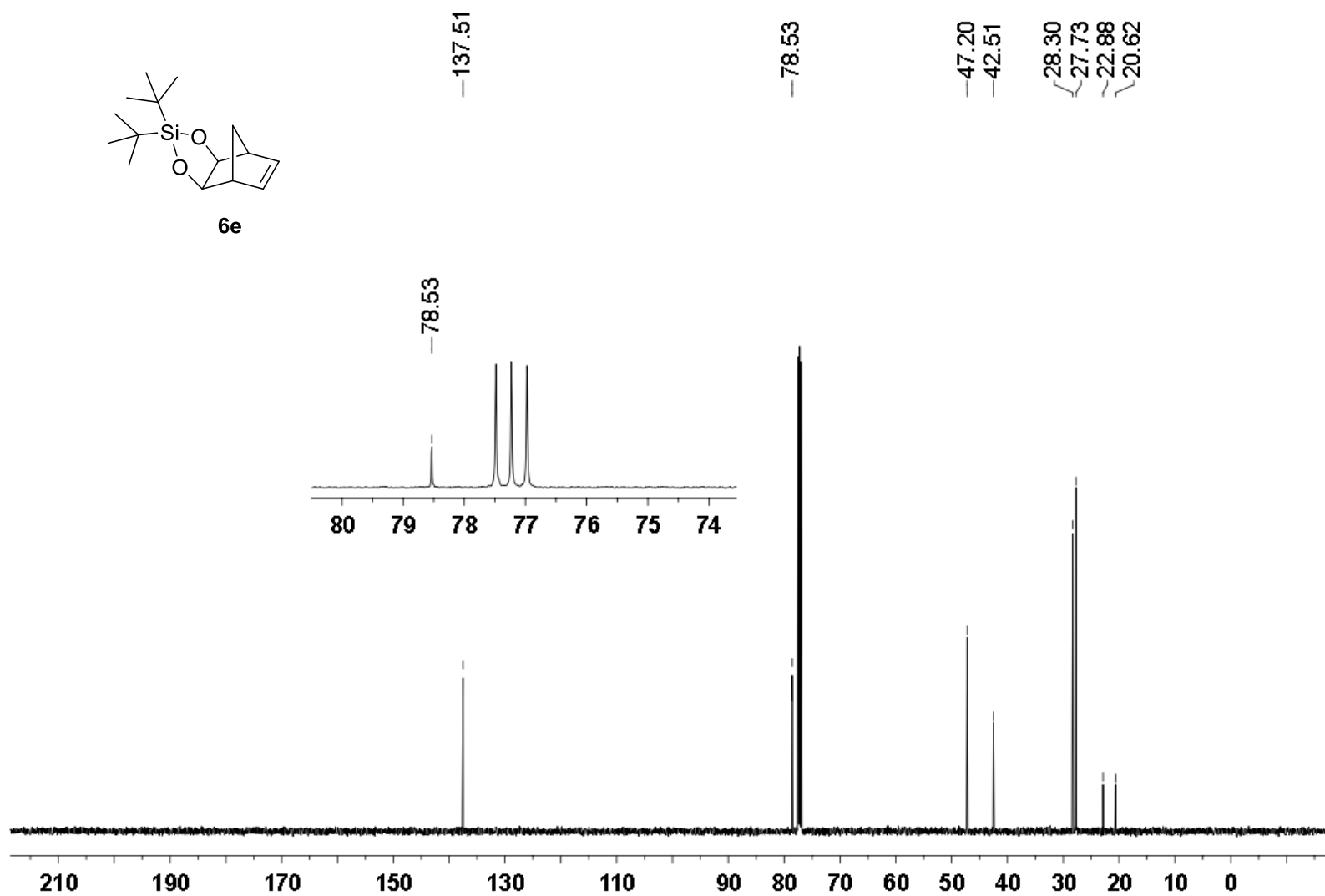
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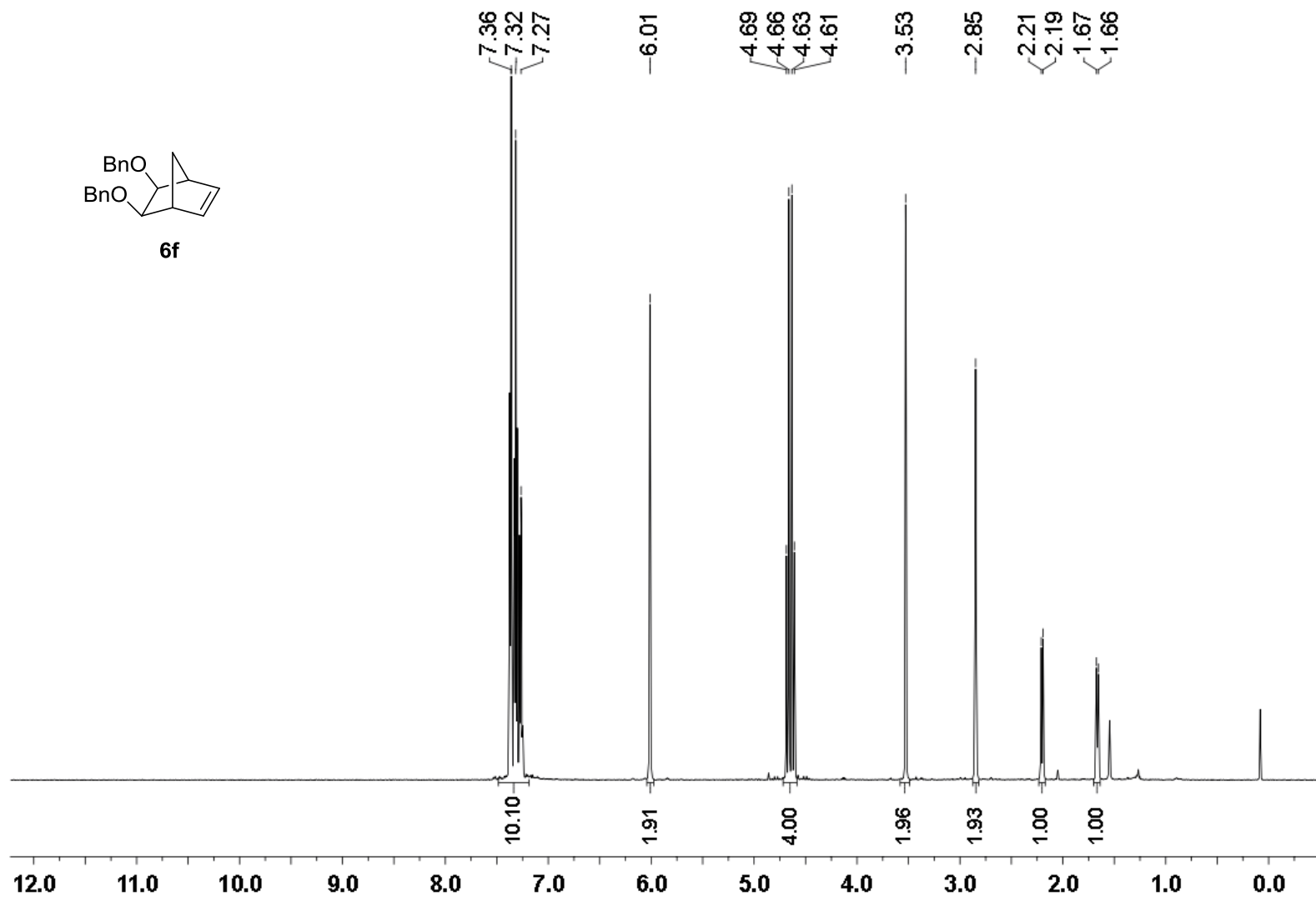
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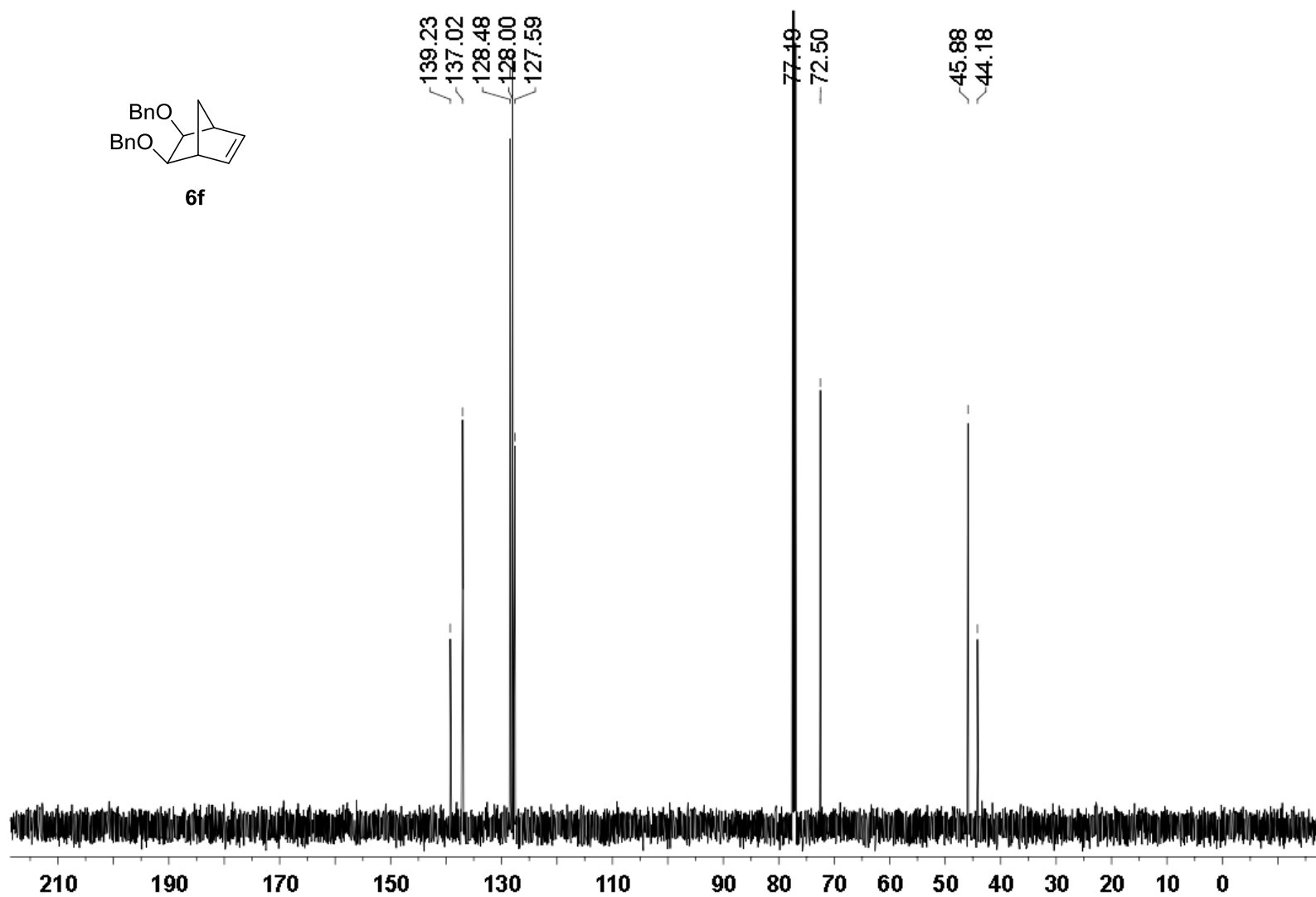
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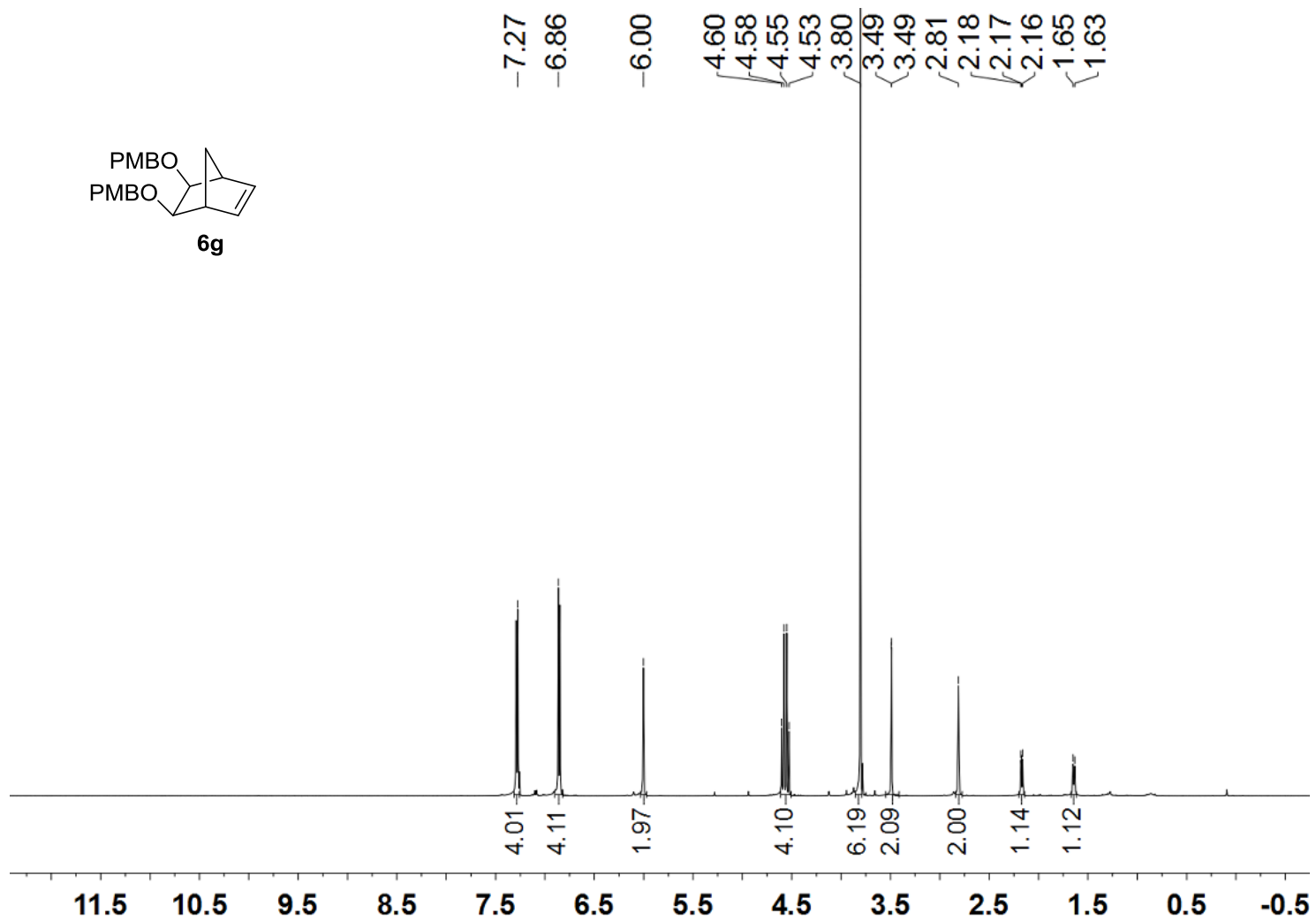
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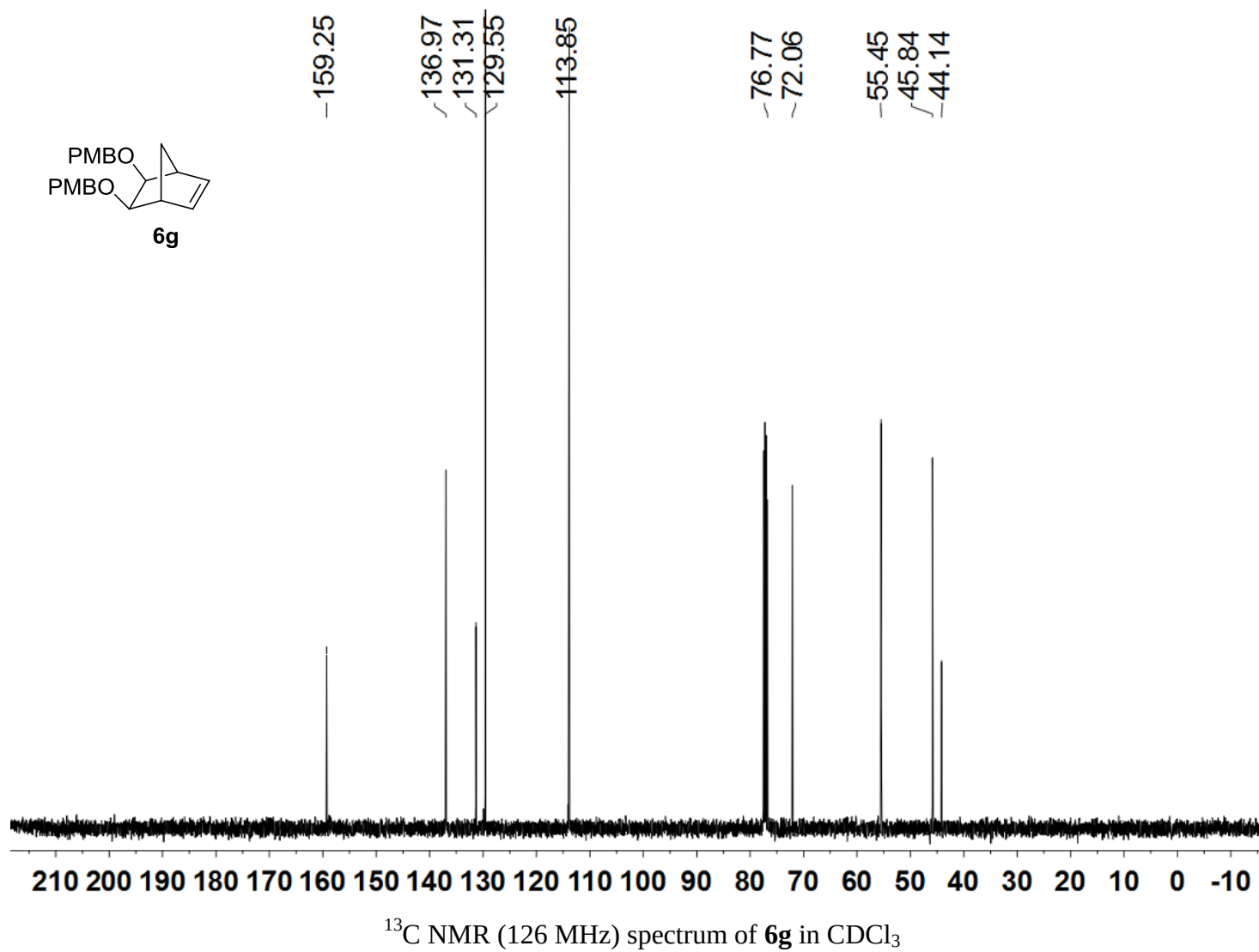
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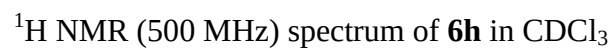


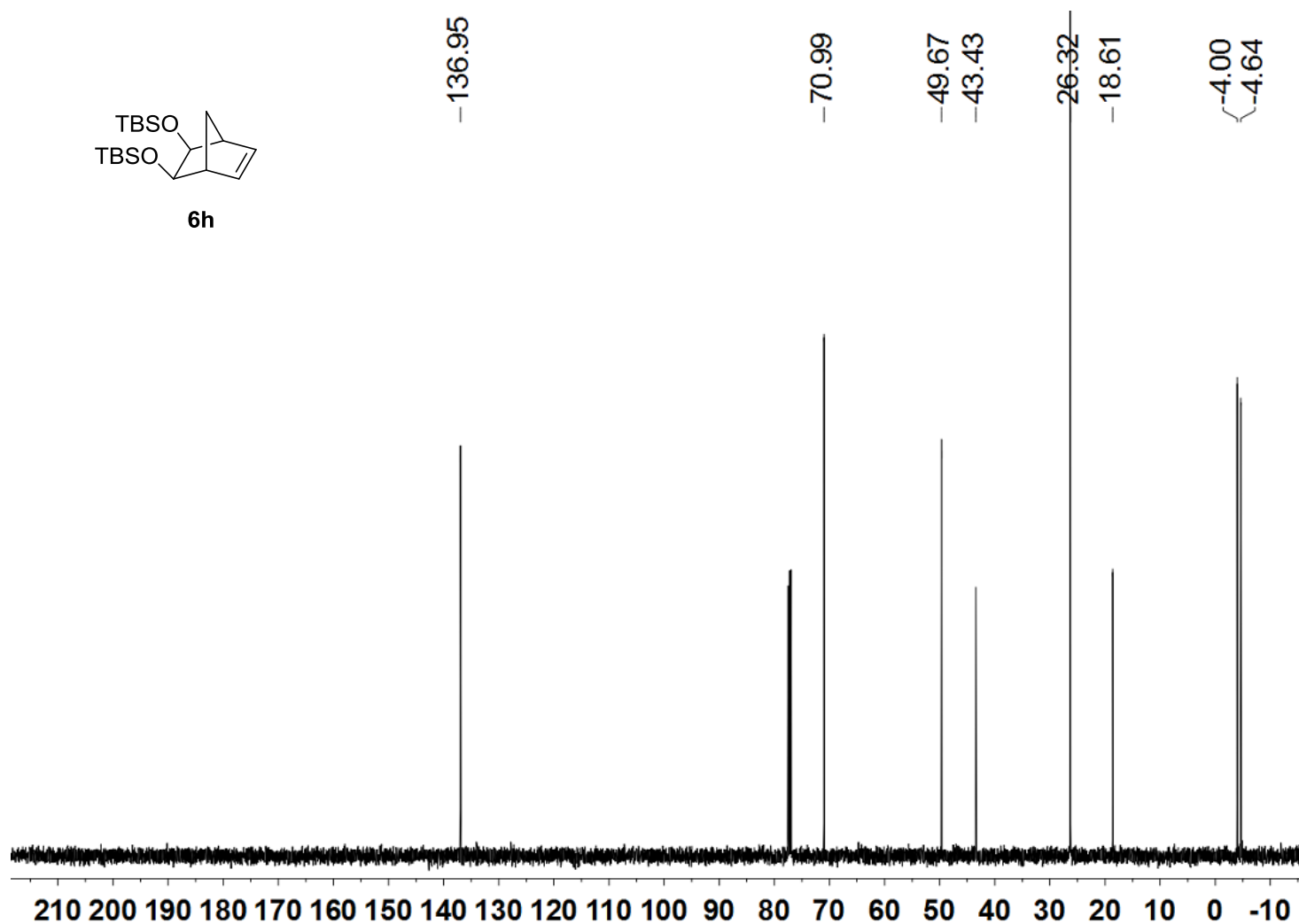
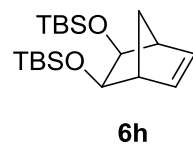
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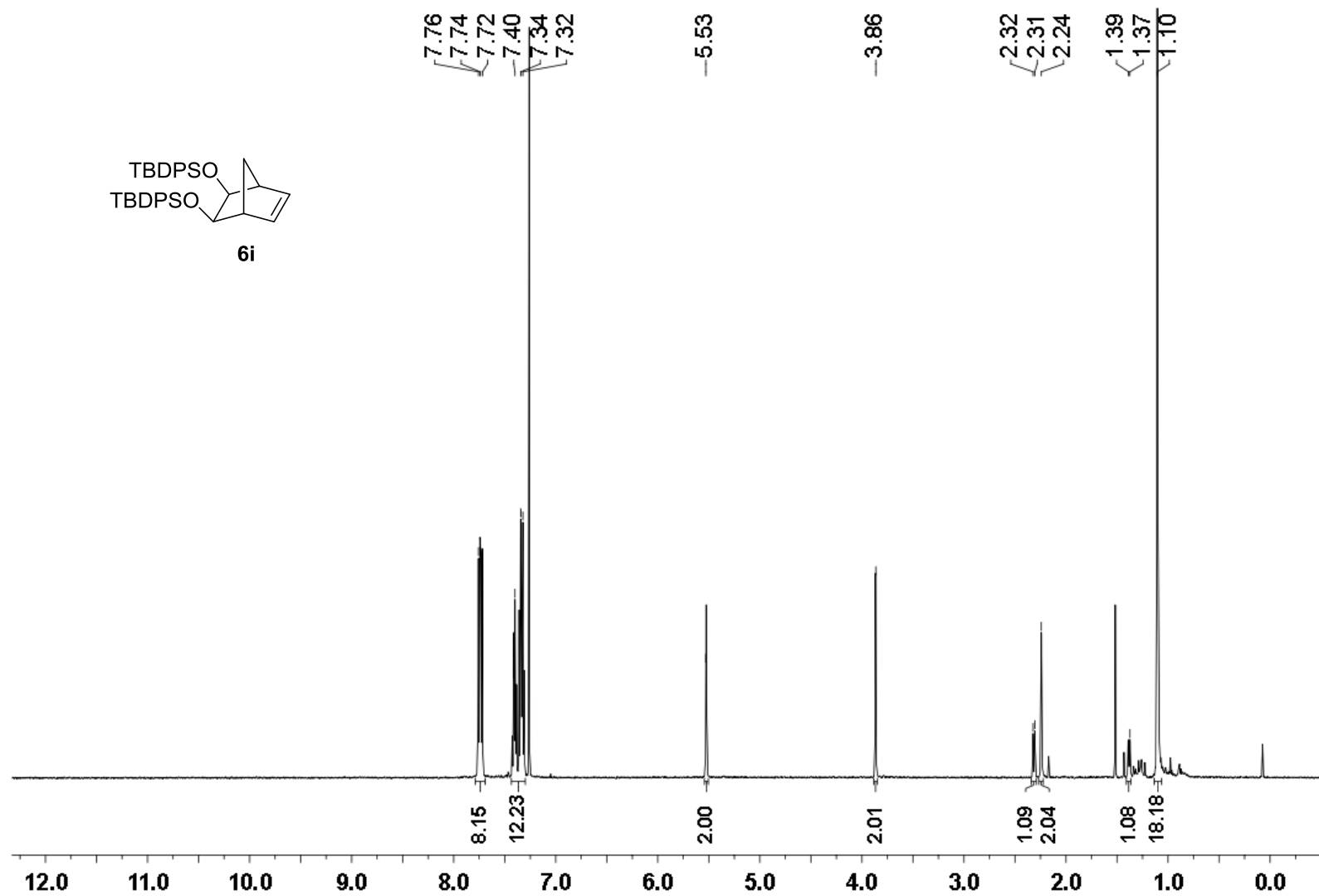
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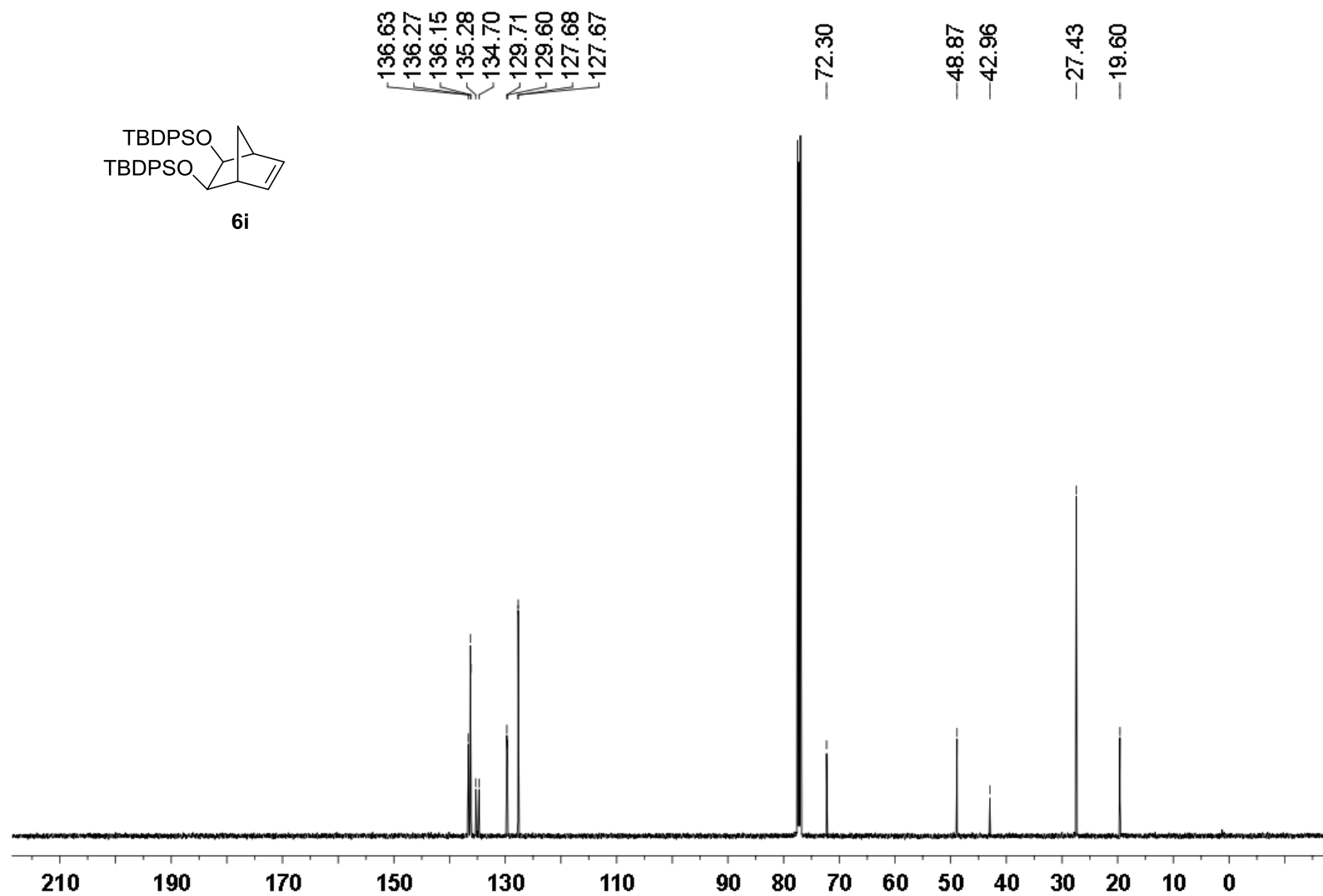




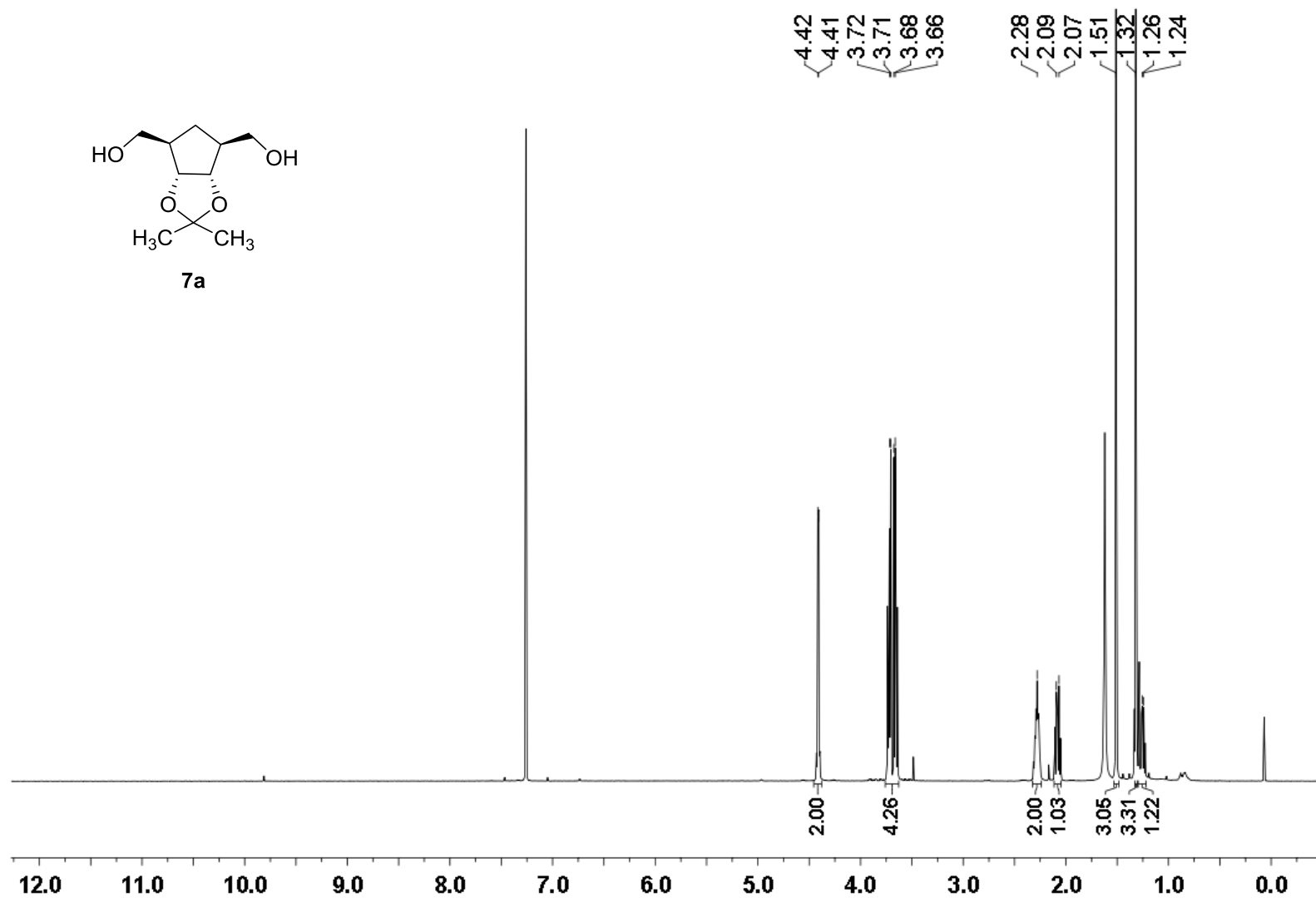
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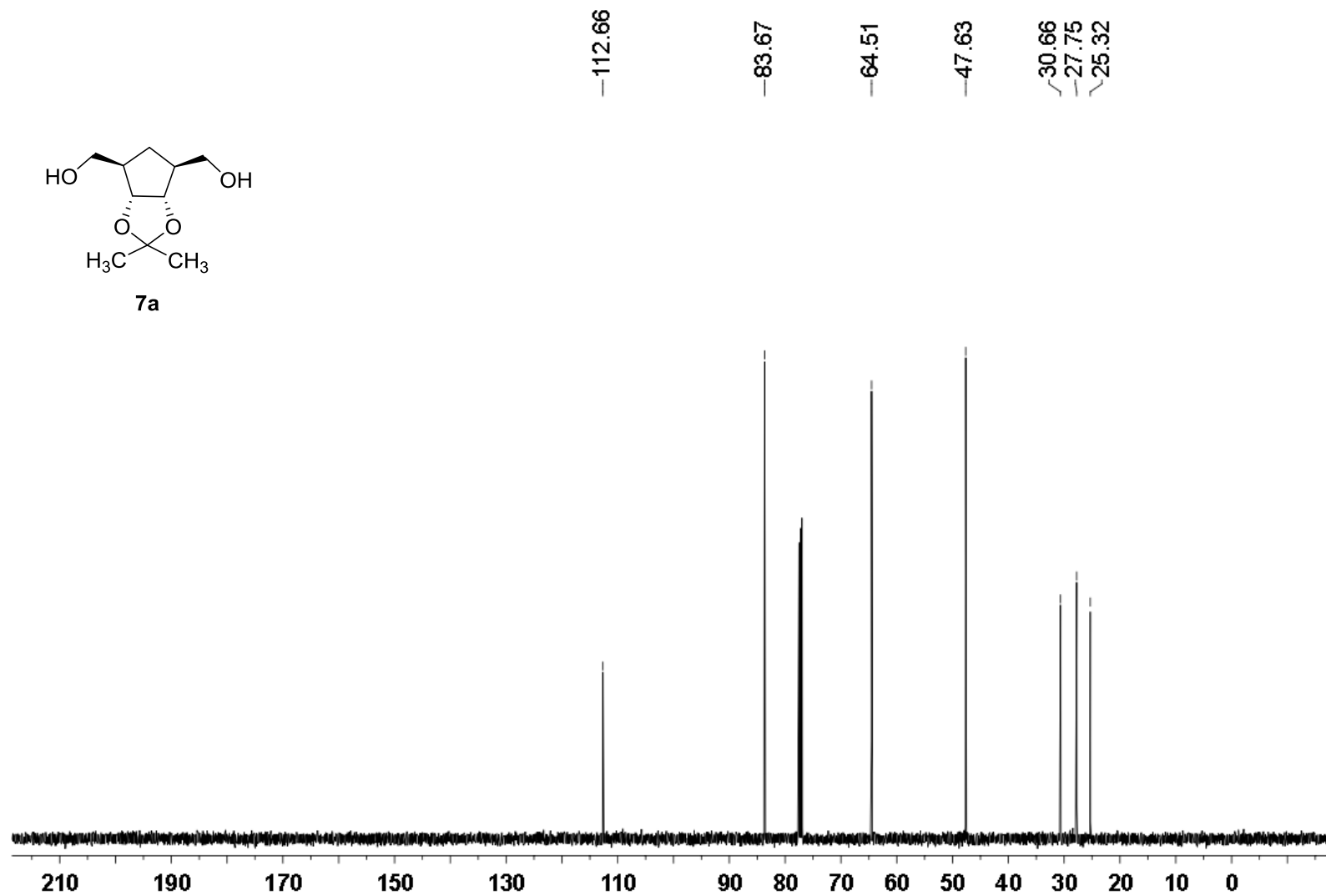
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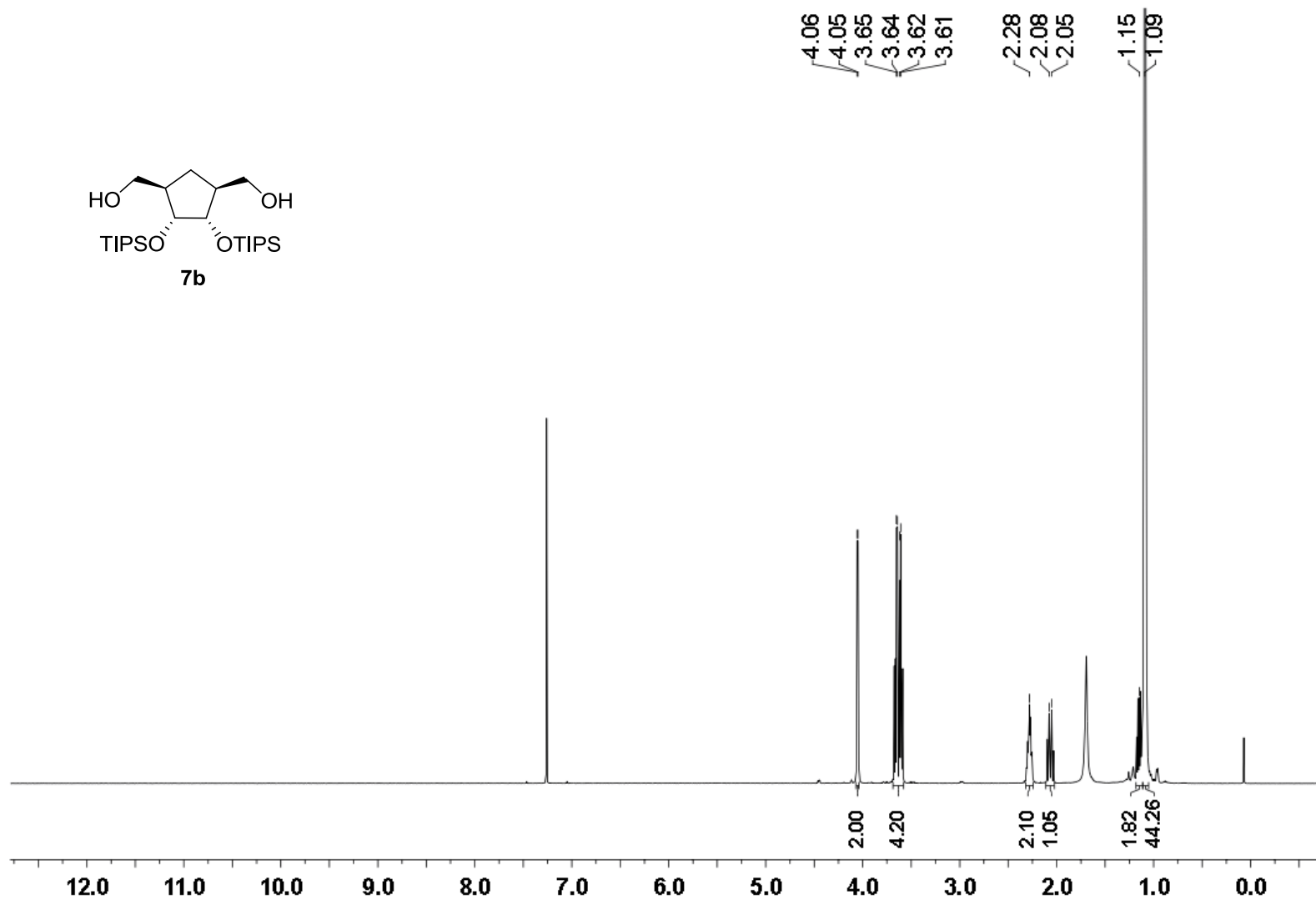
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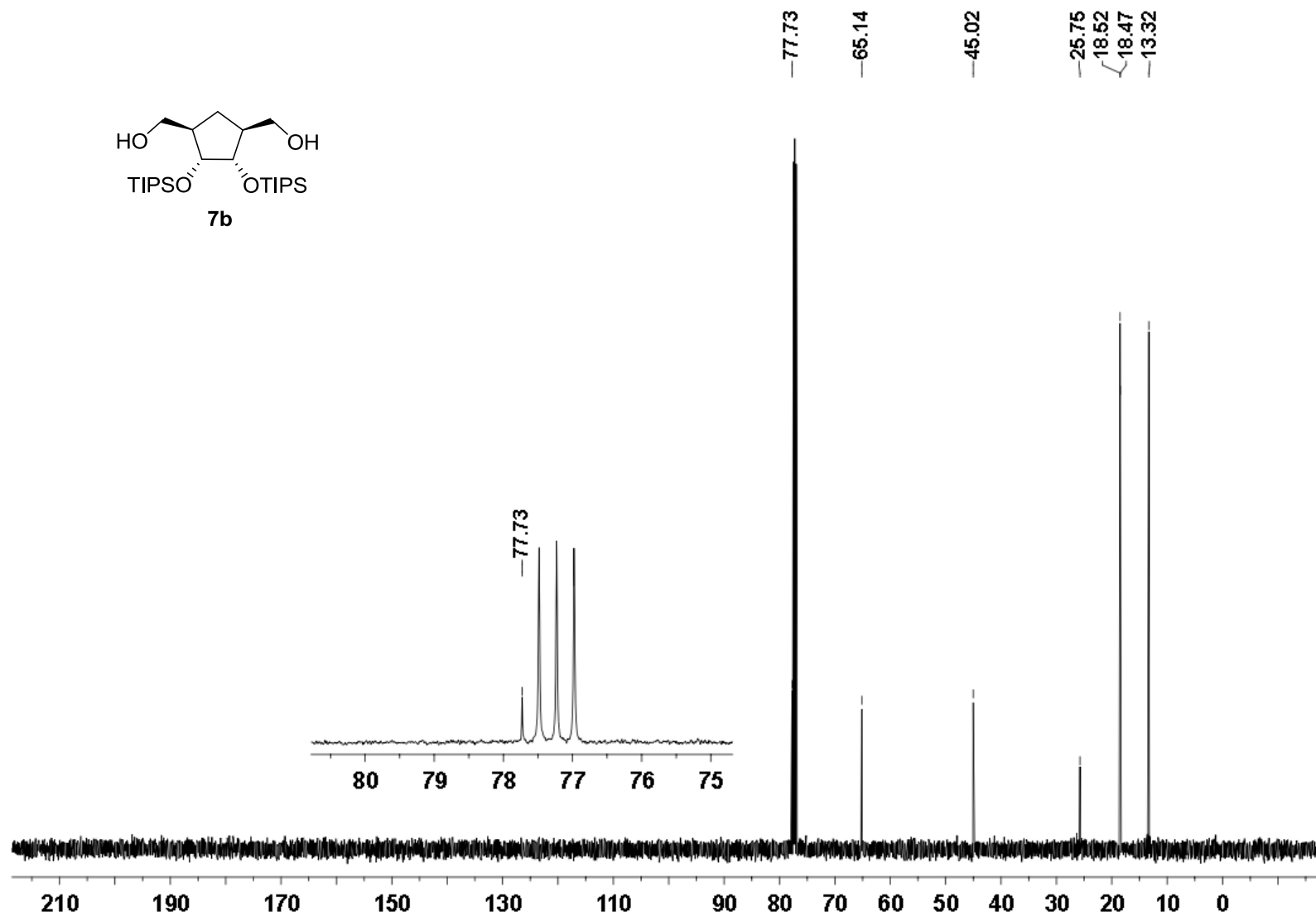
¹H NMR (500 MHz) spectrum of **7a** in CDCl₃



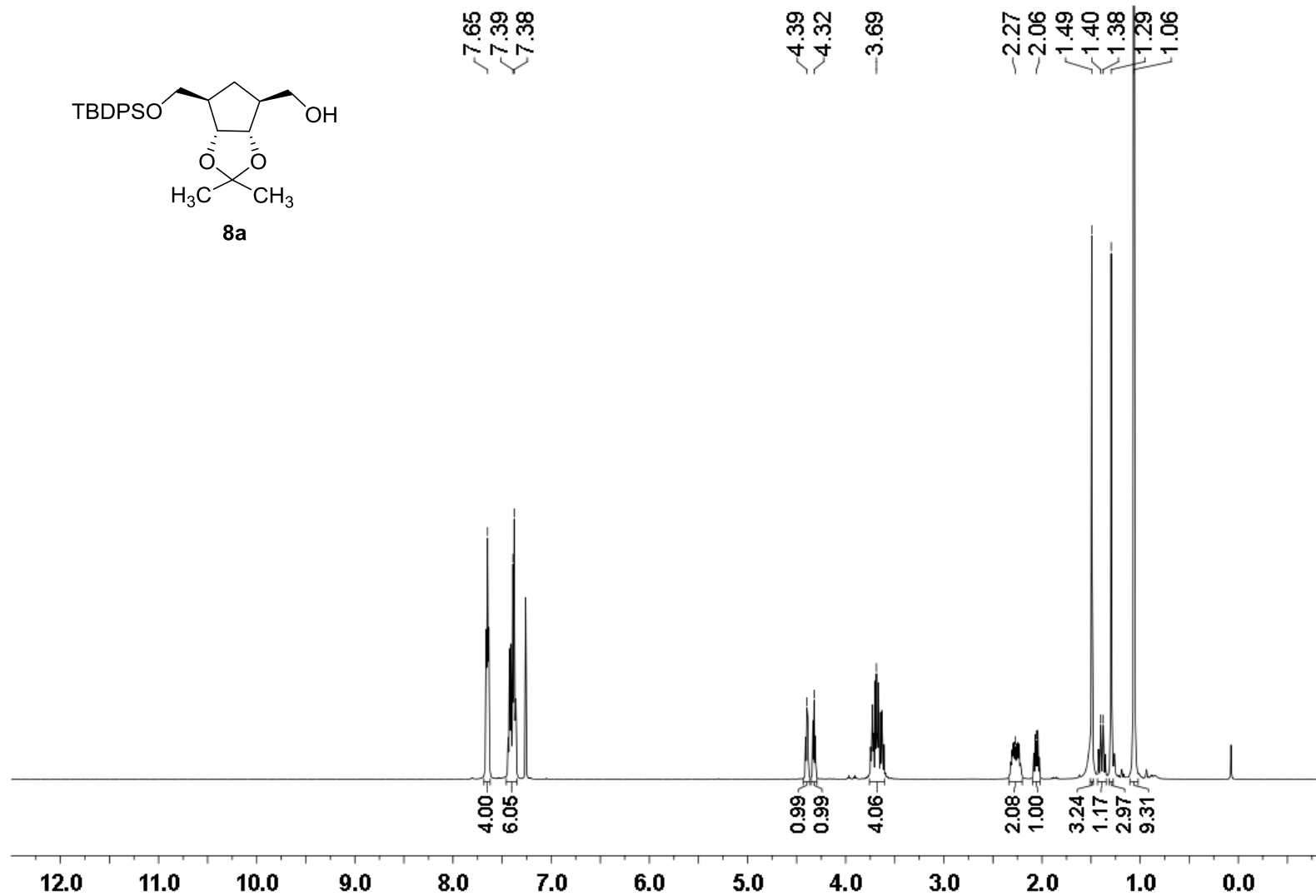
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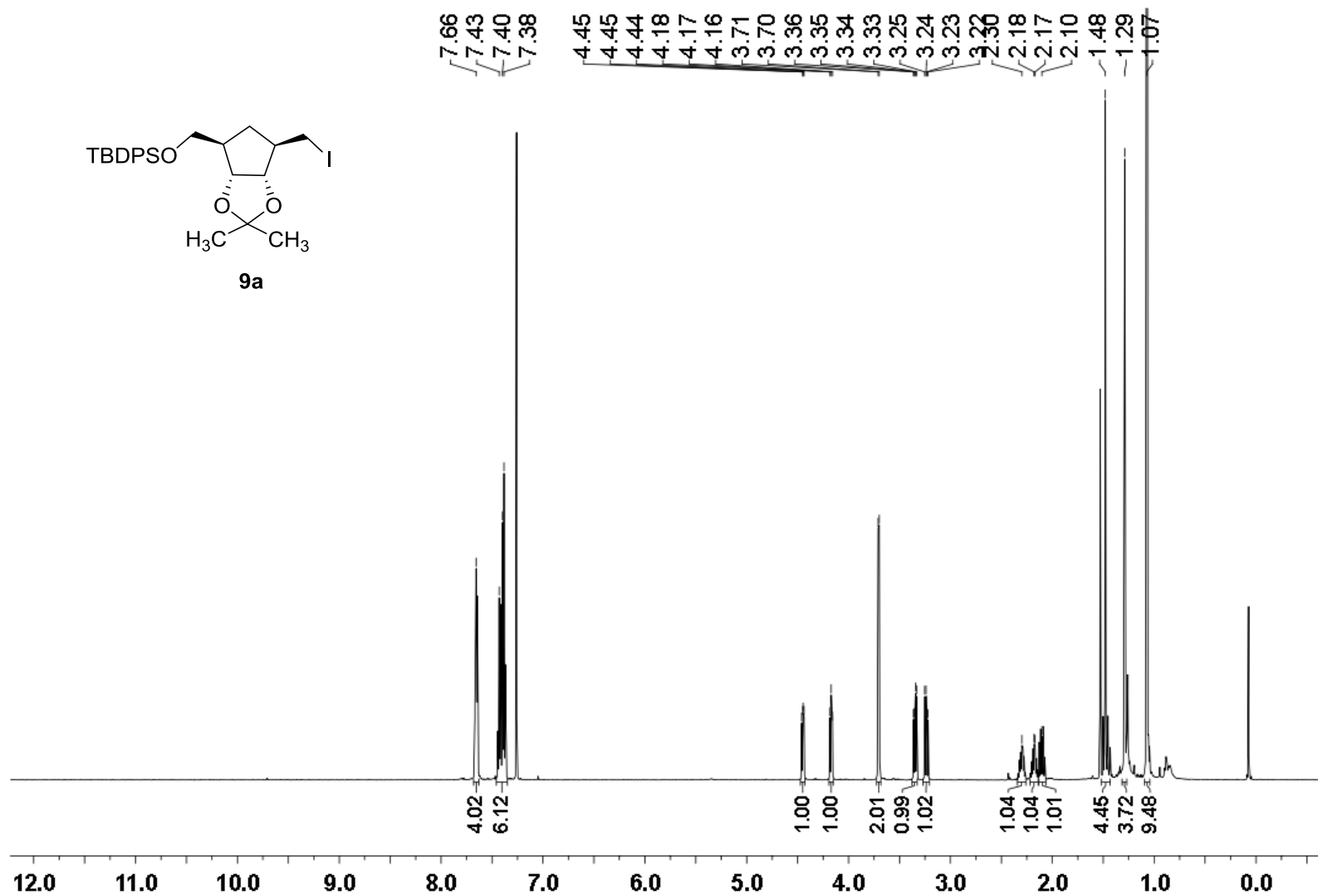
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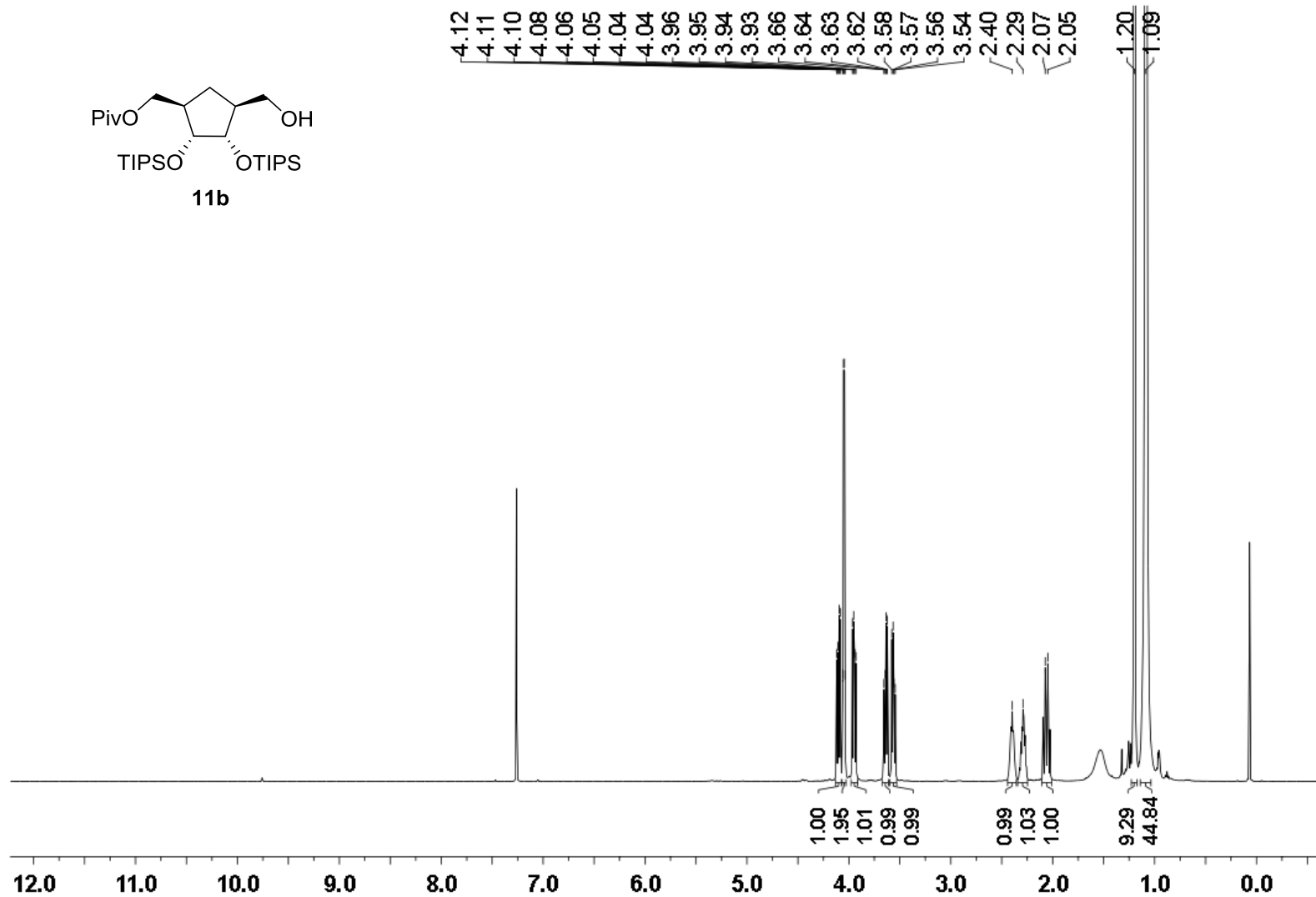
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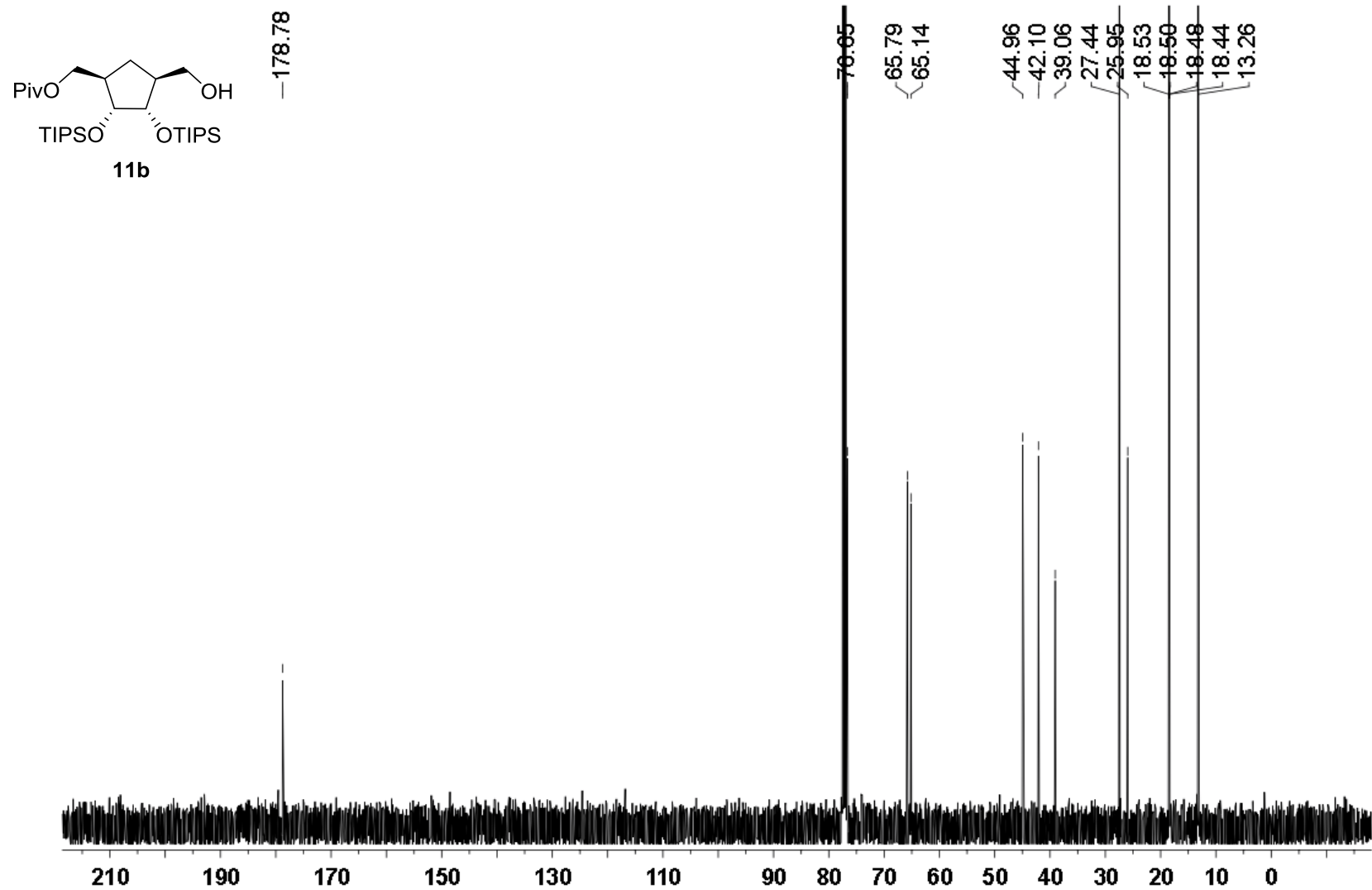
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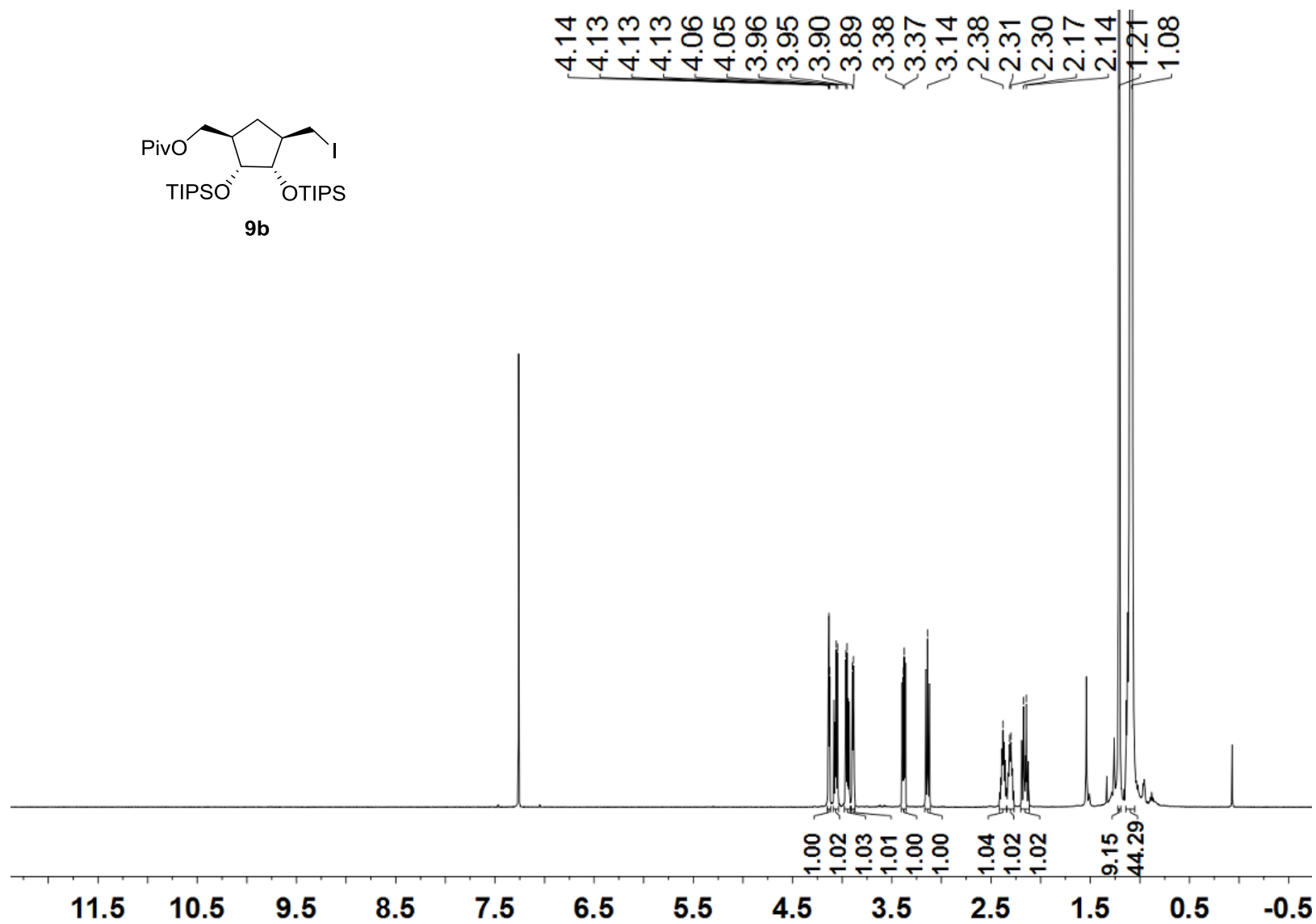
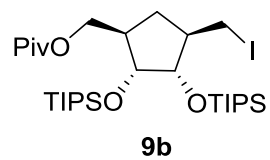
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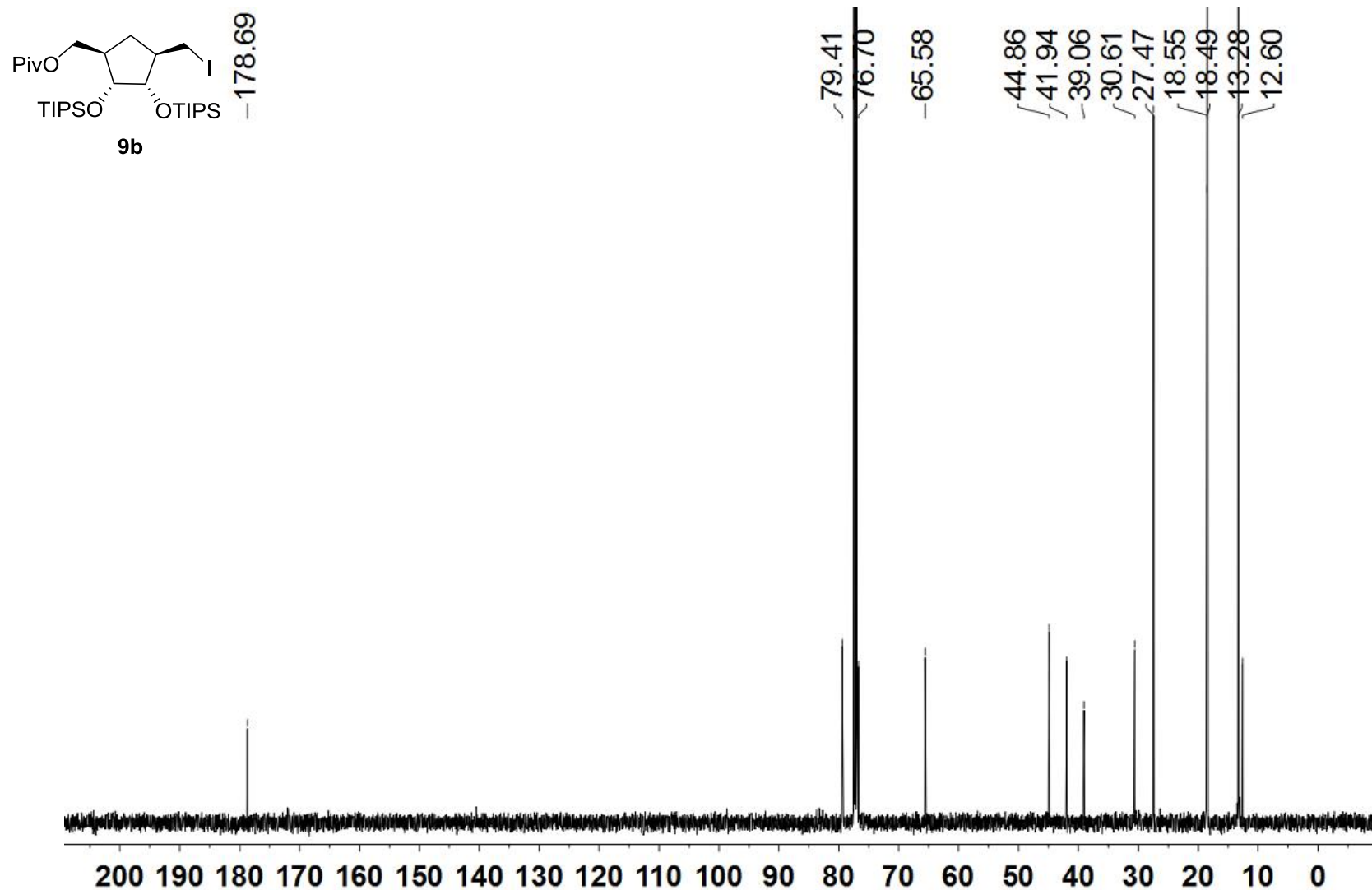
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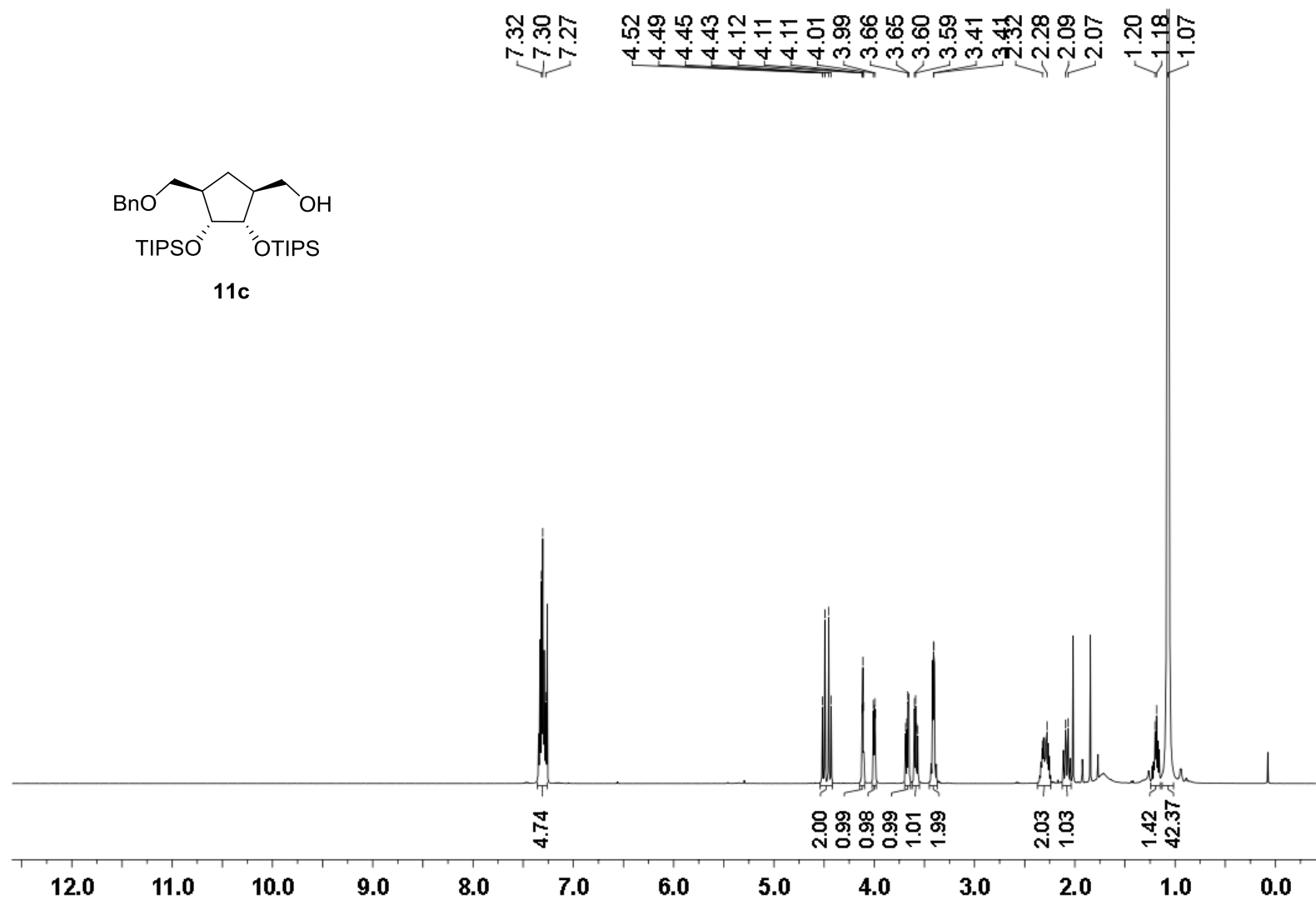
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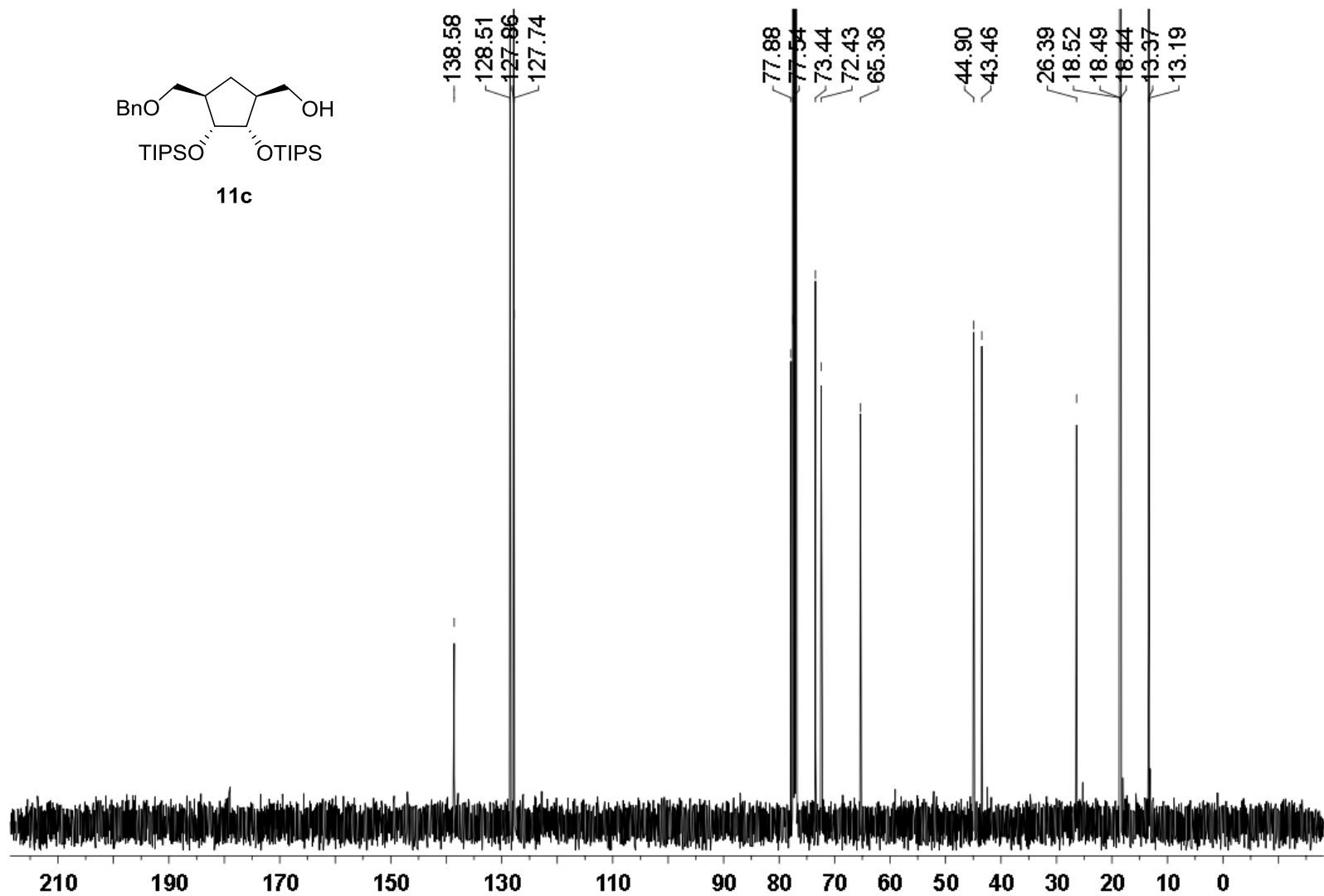
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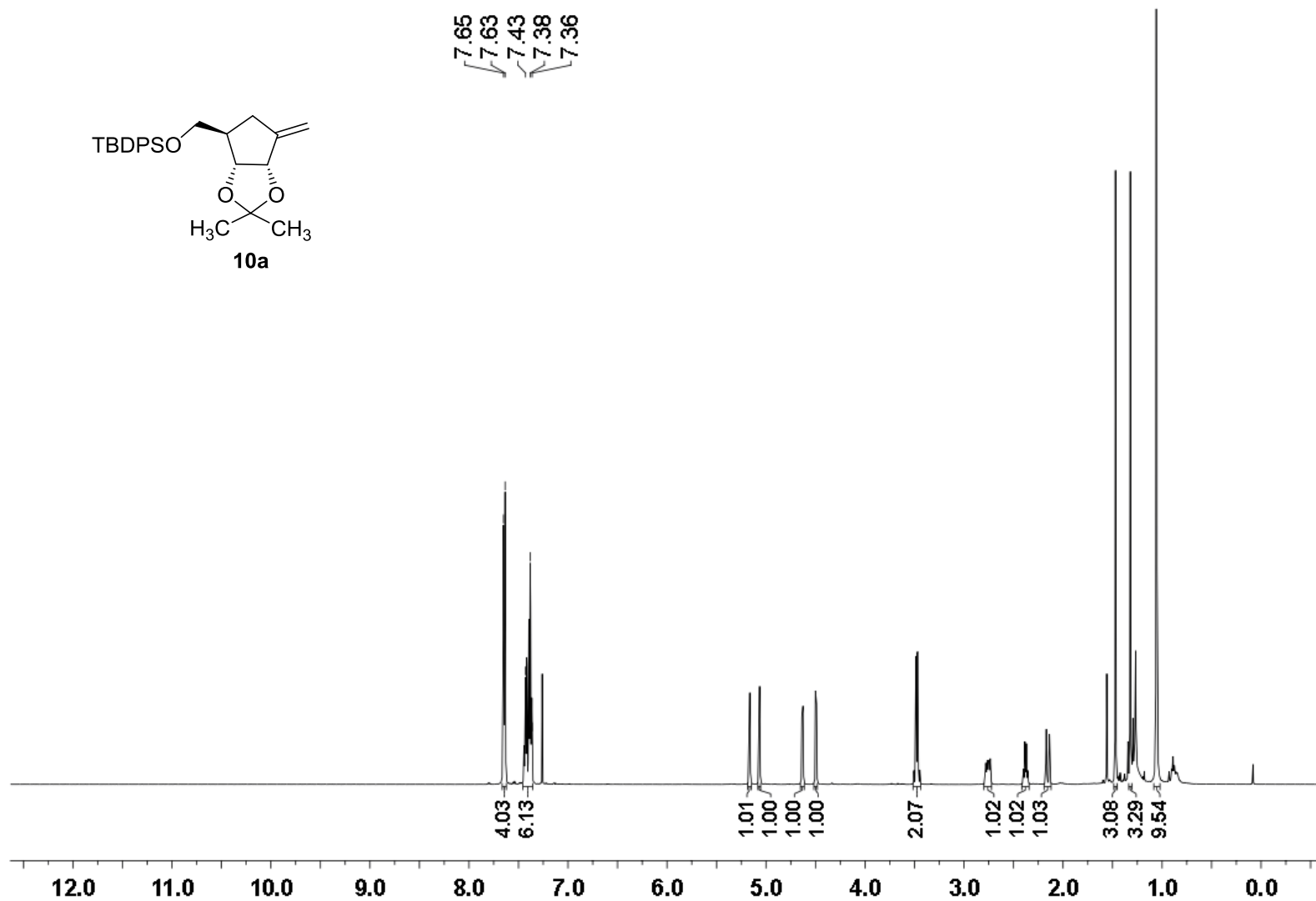
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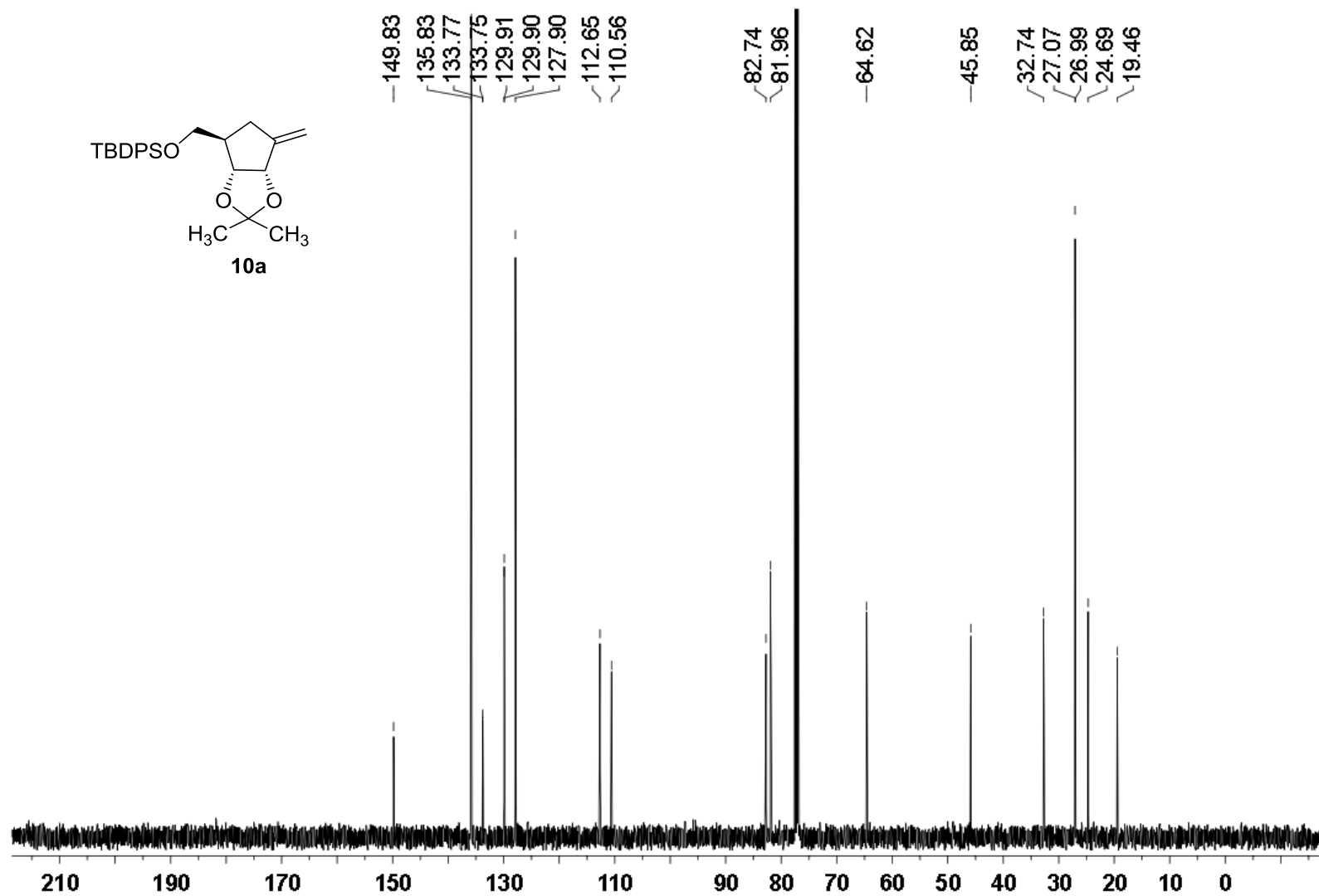
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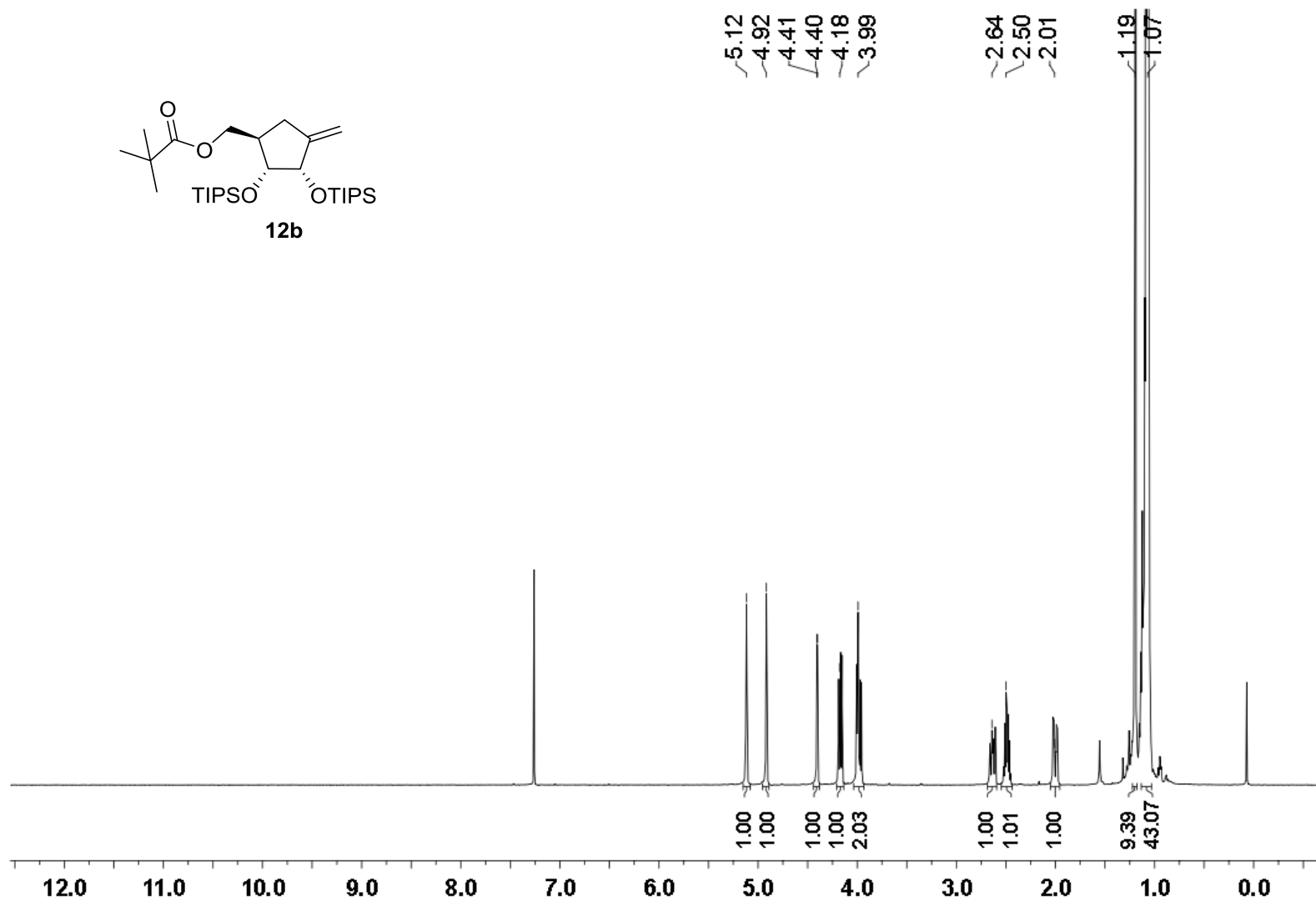
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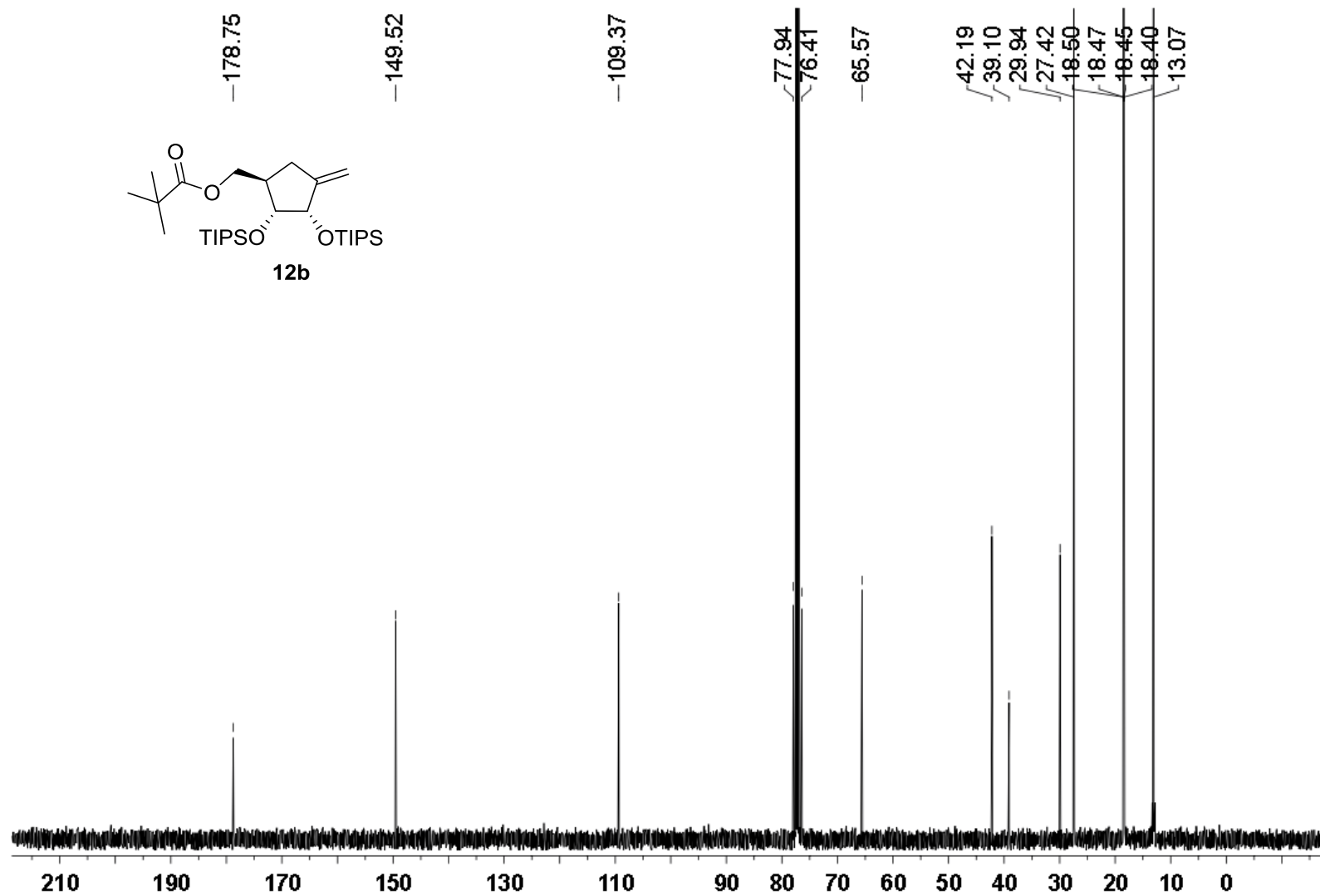
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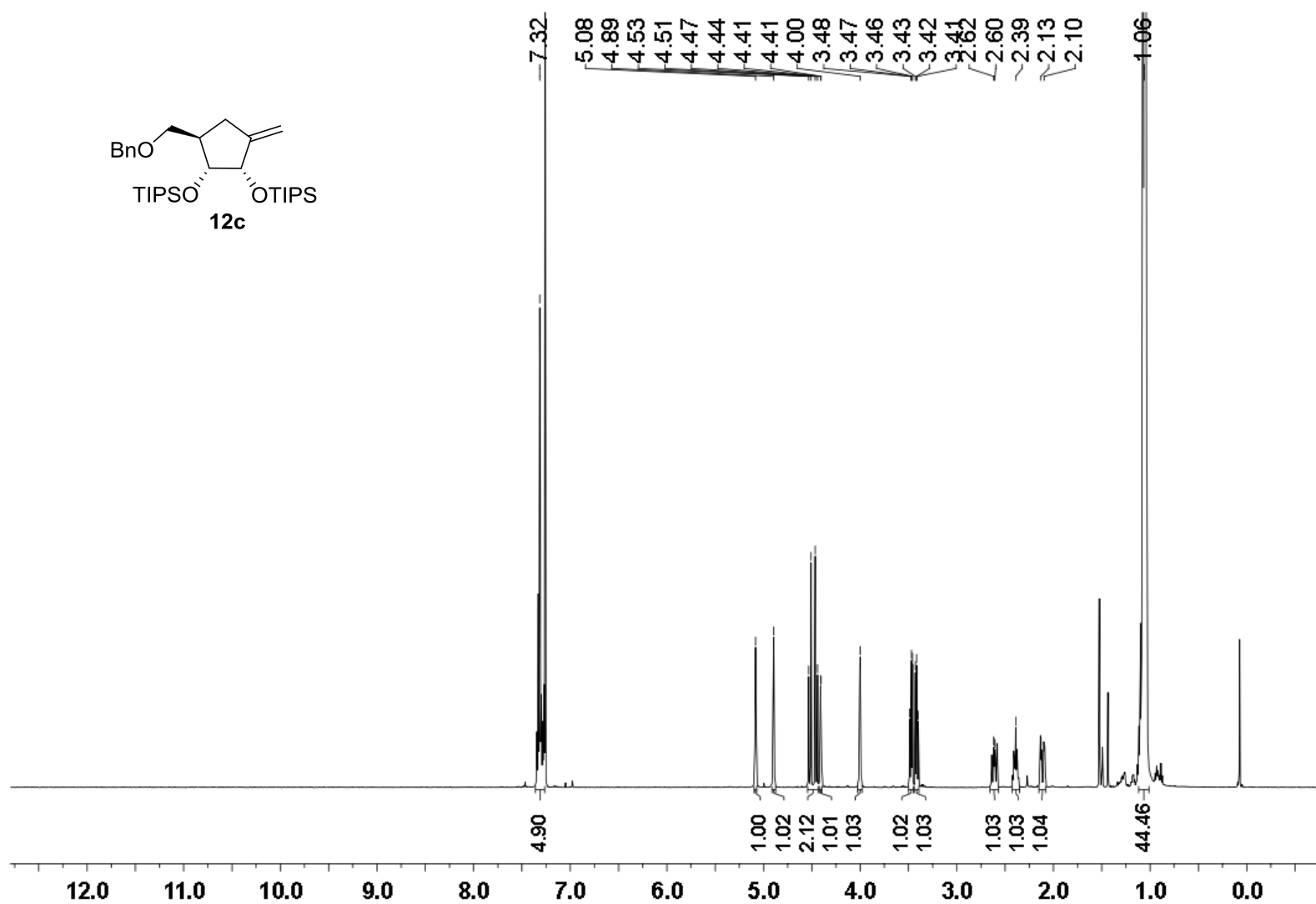
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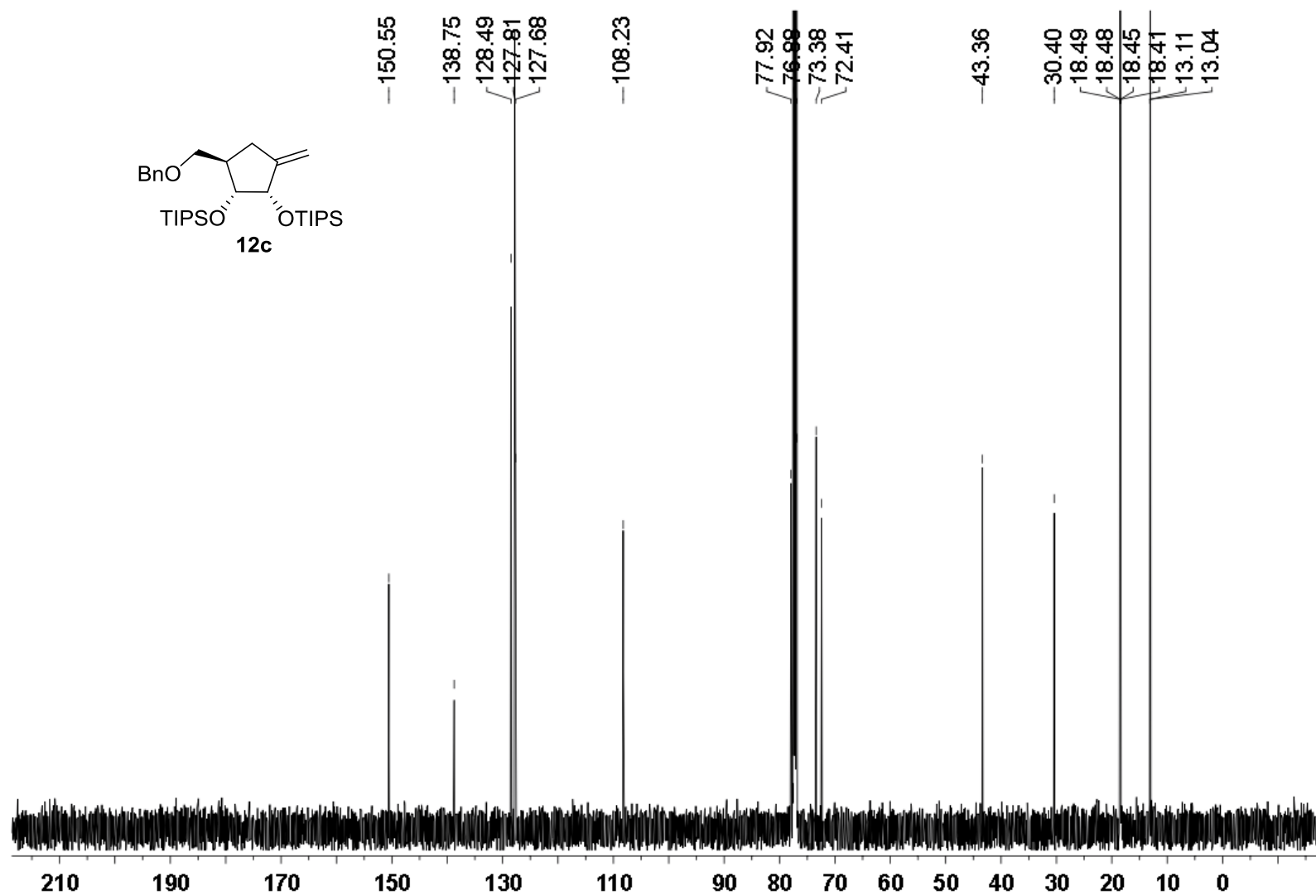
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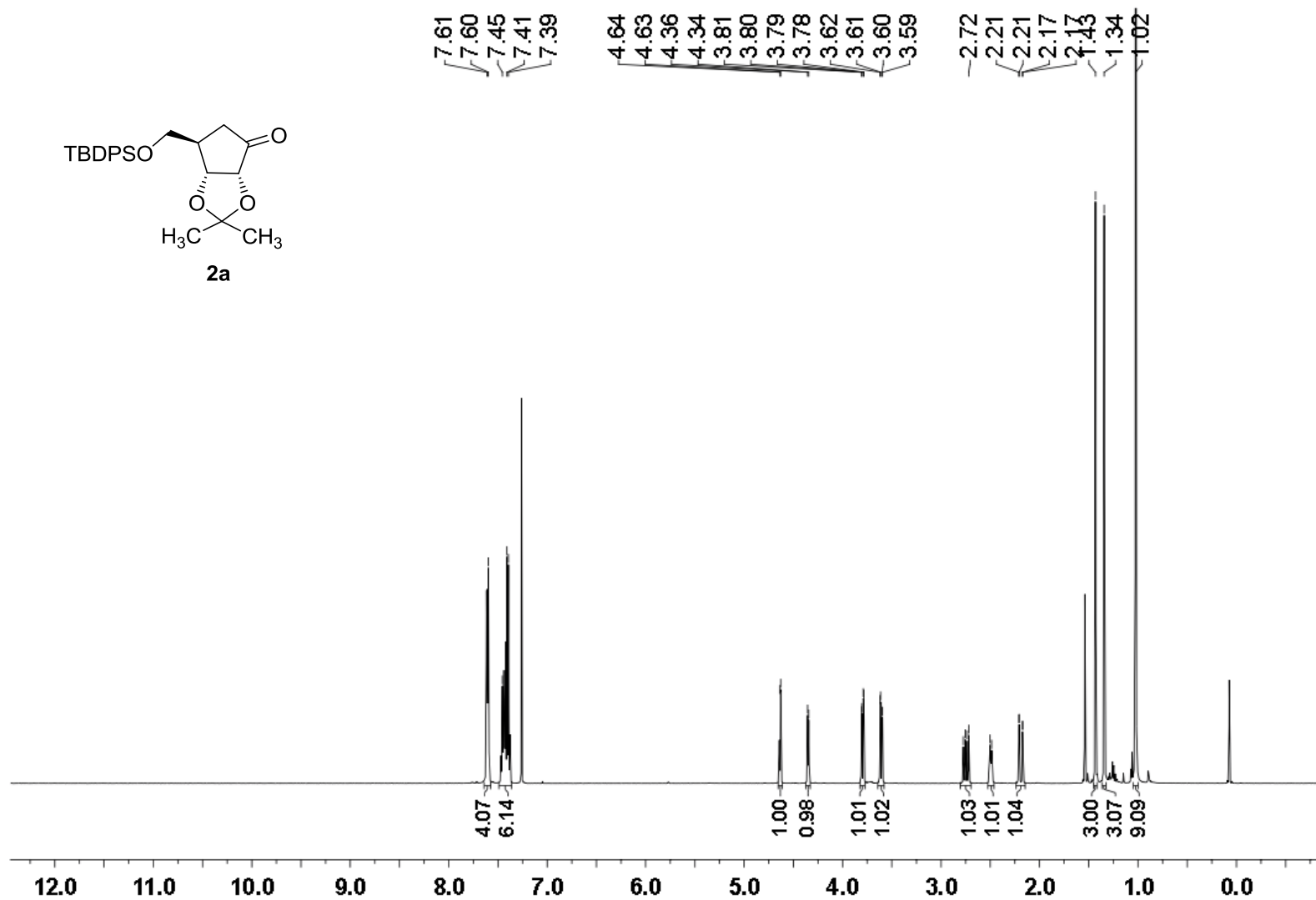
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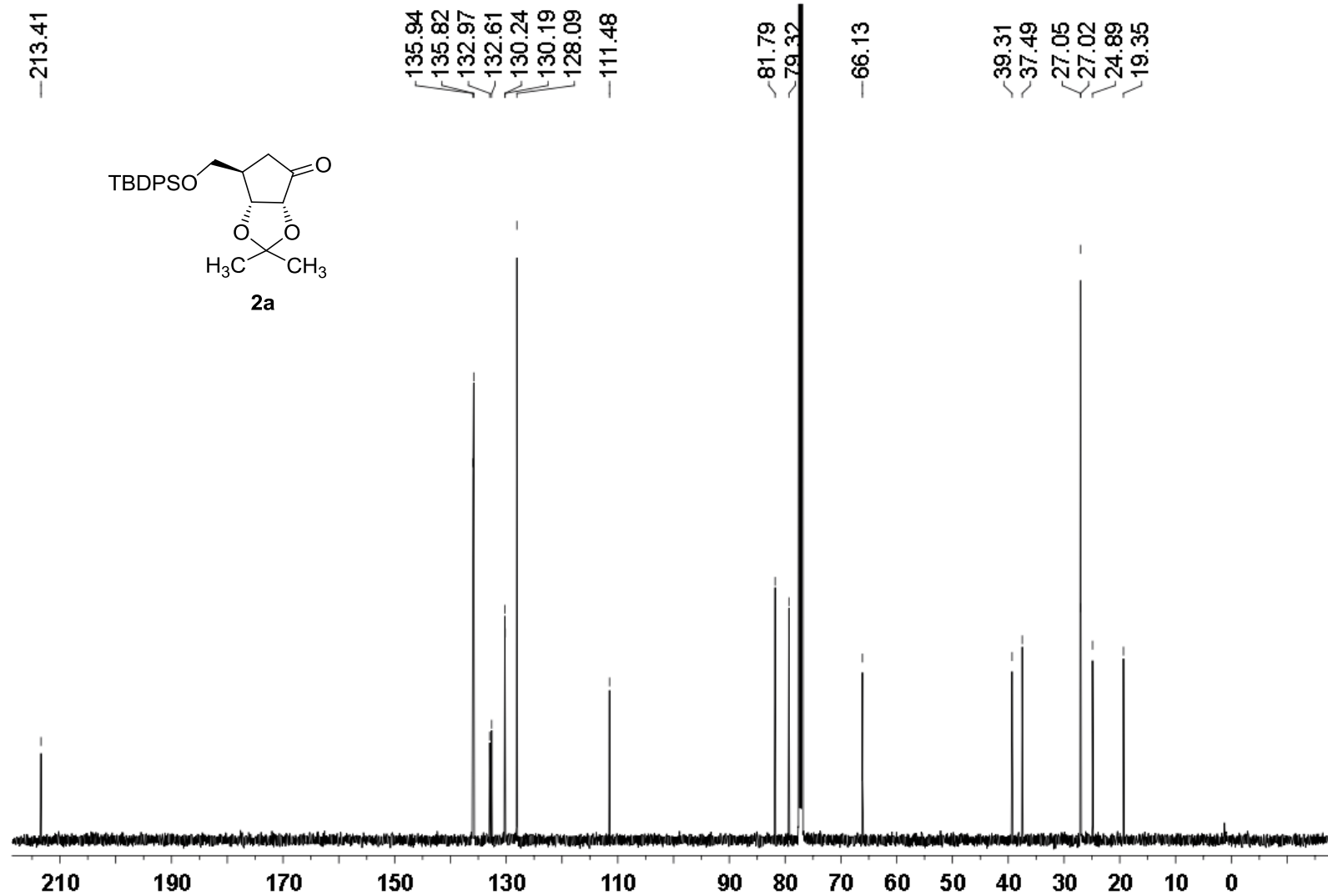
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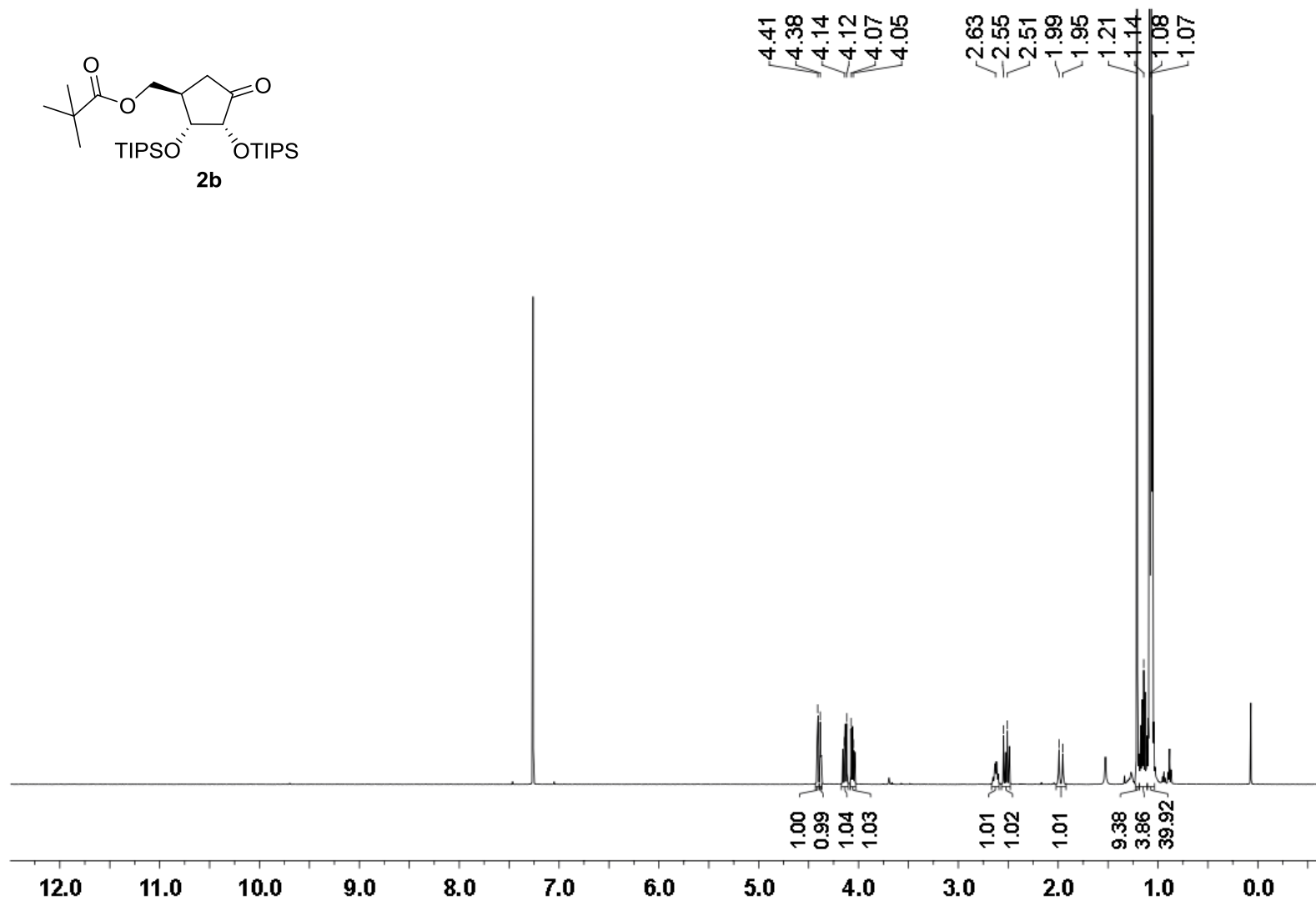
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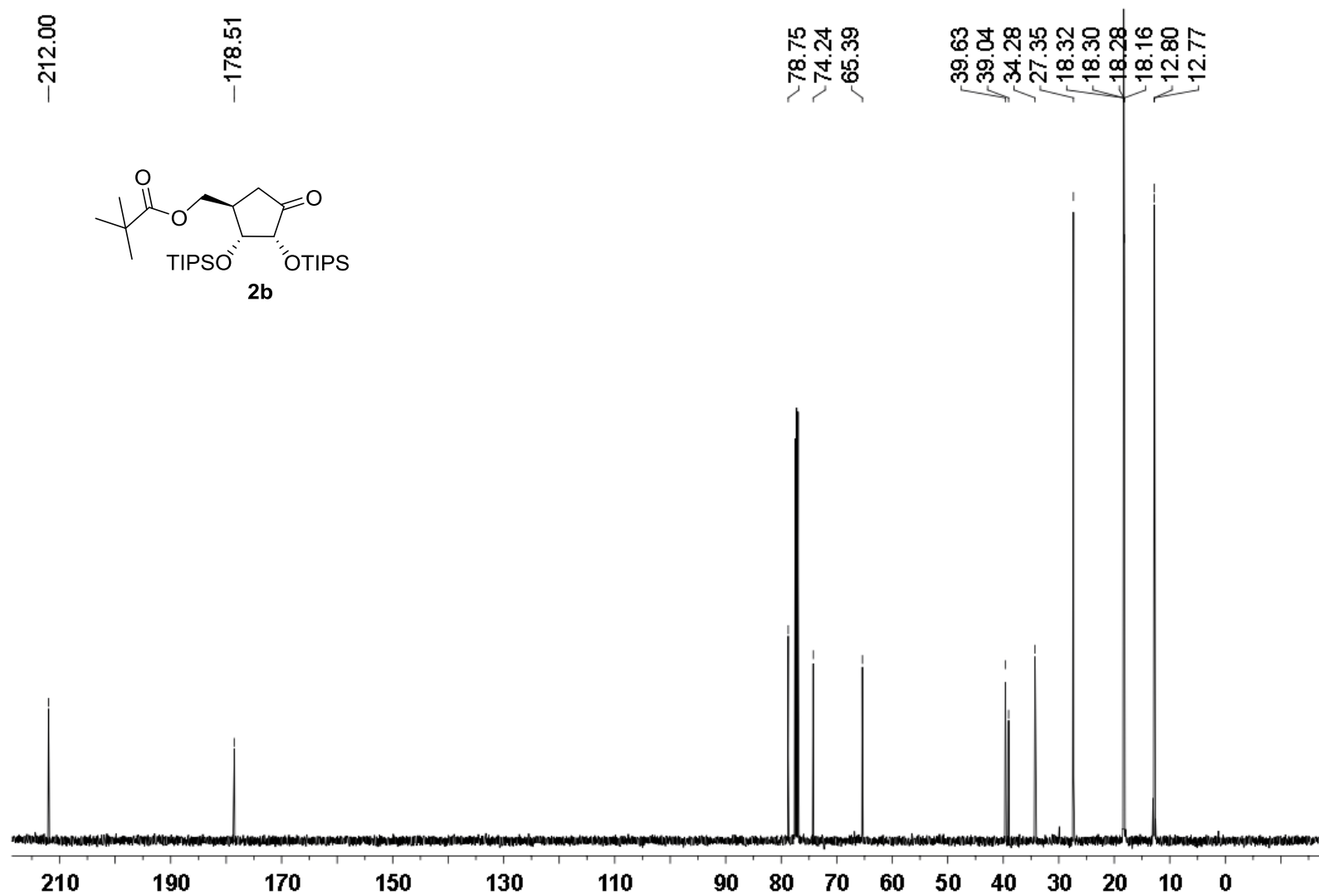
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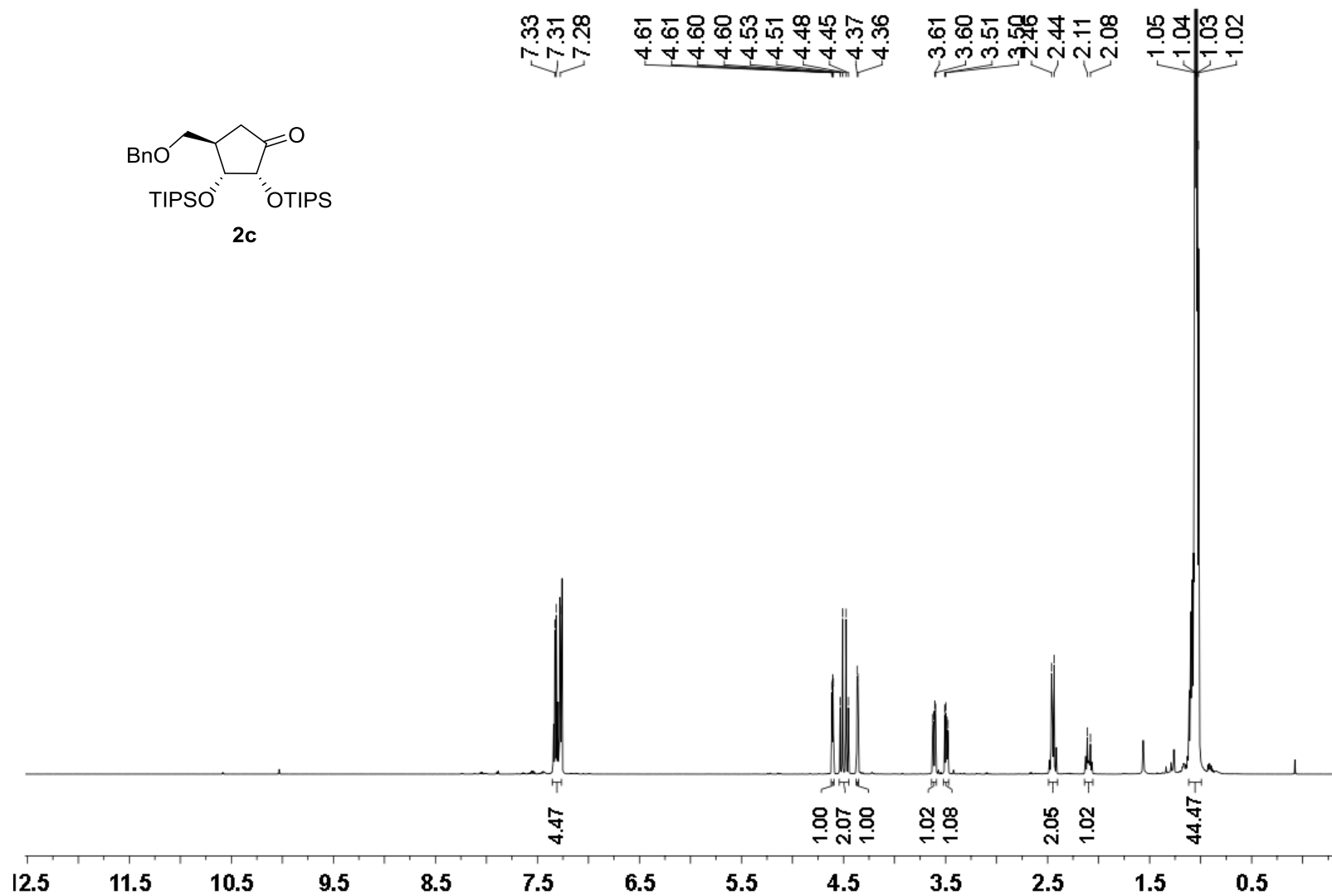
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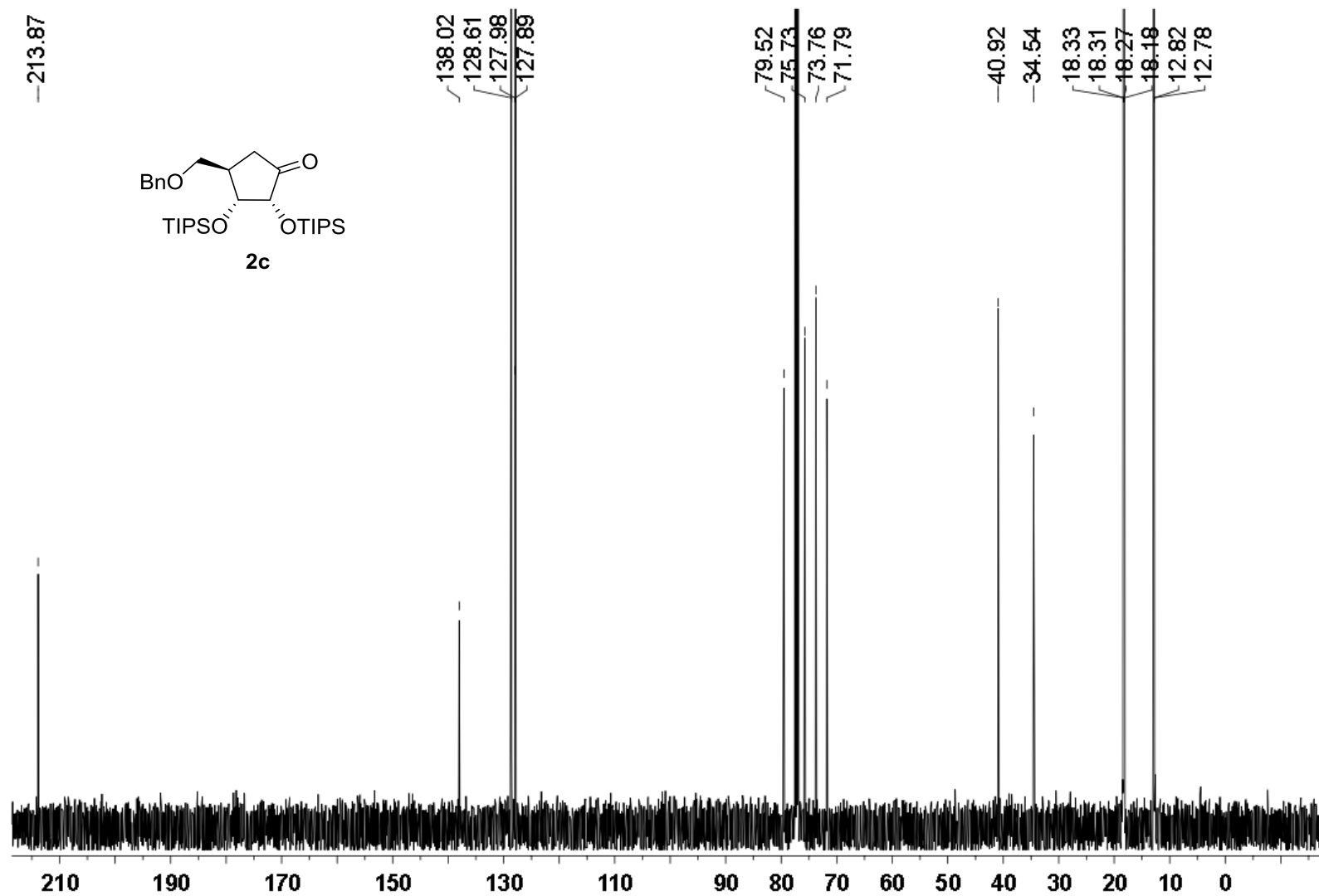
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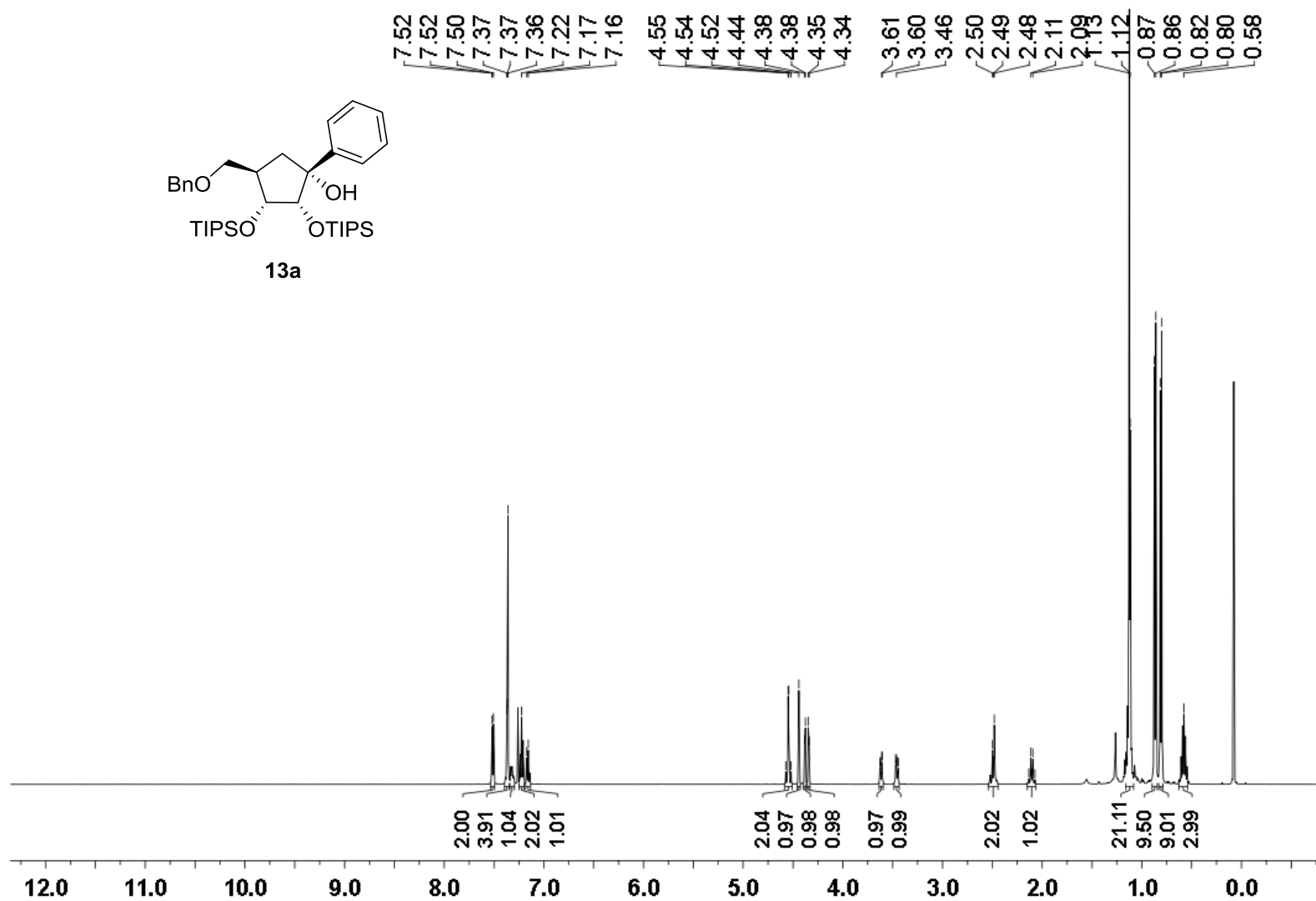
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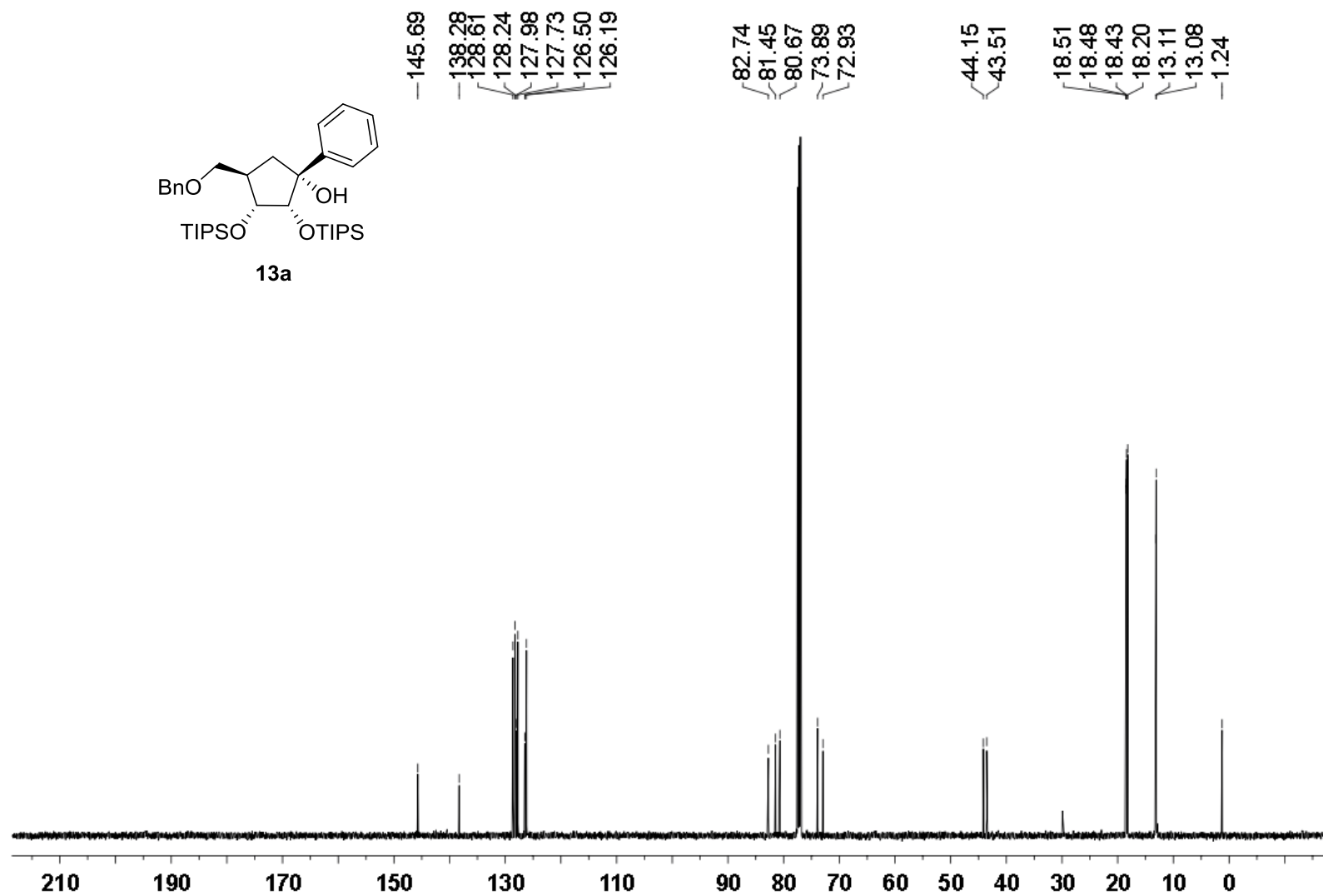
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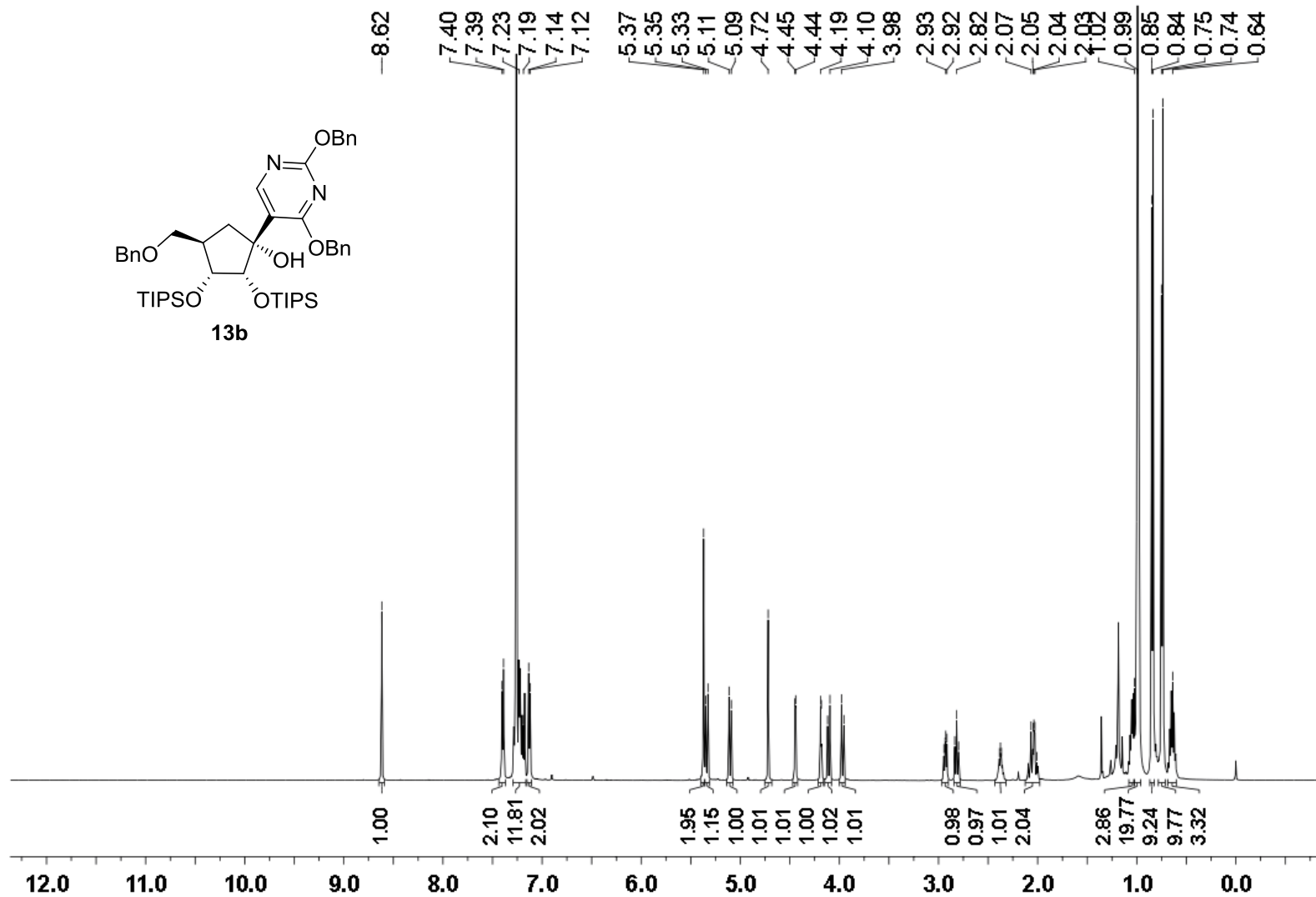
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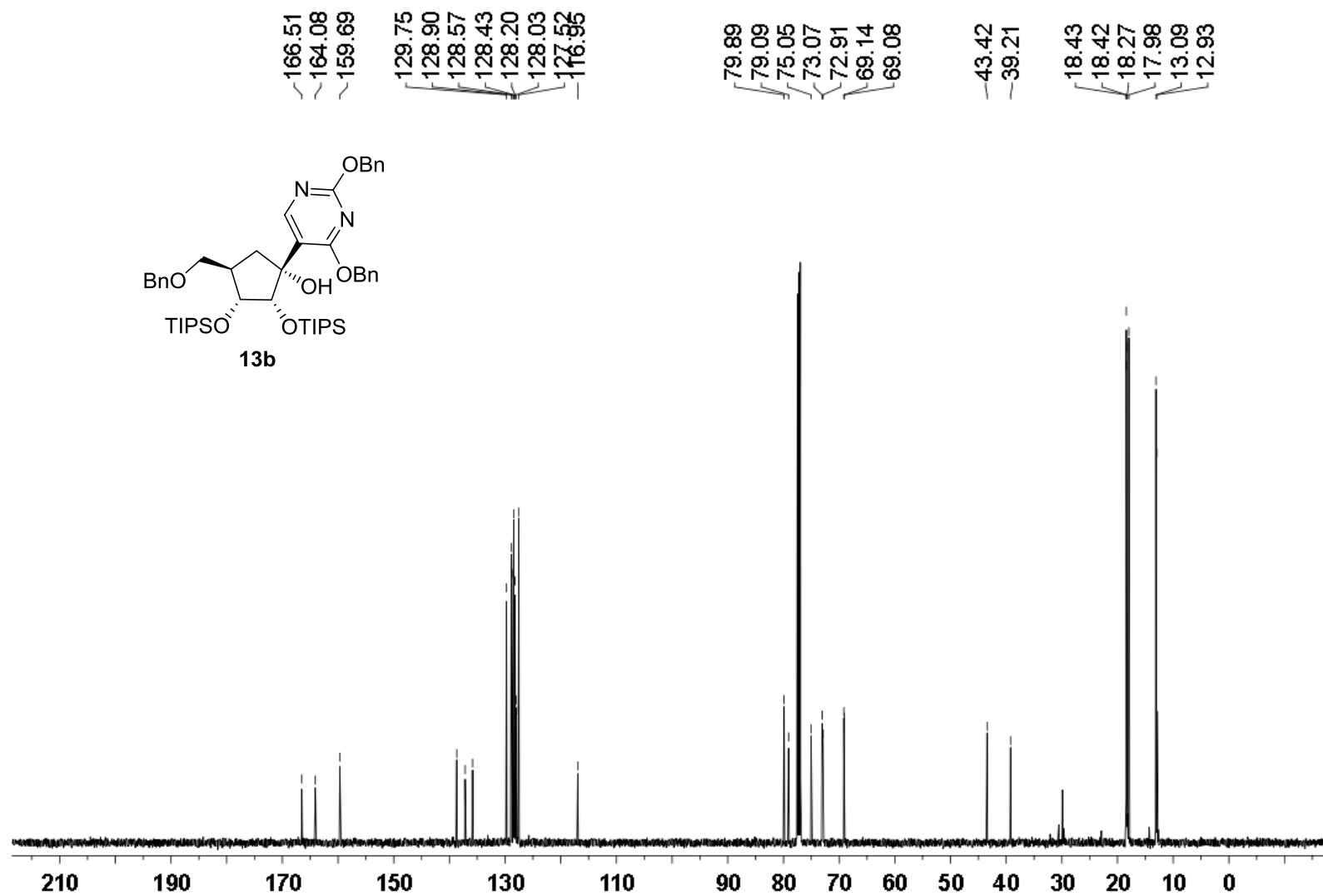
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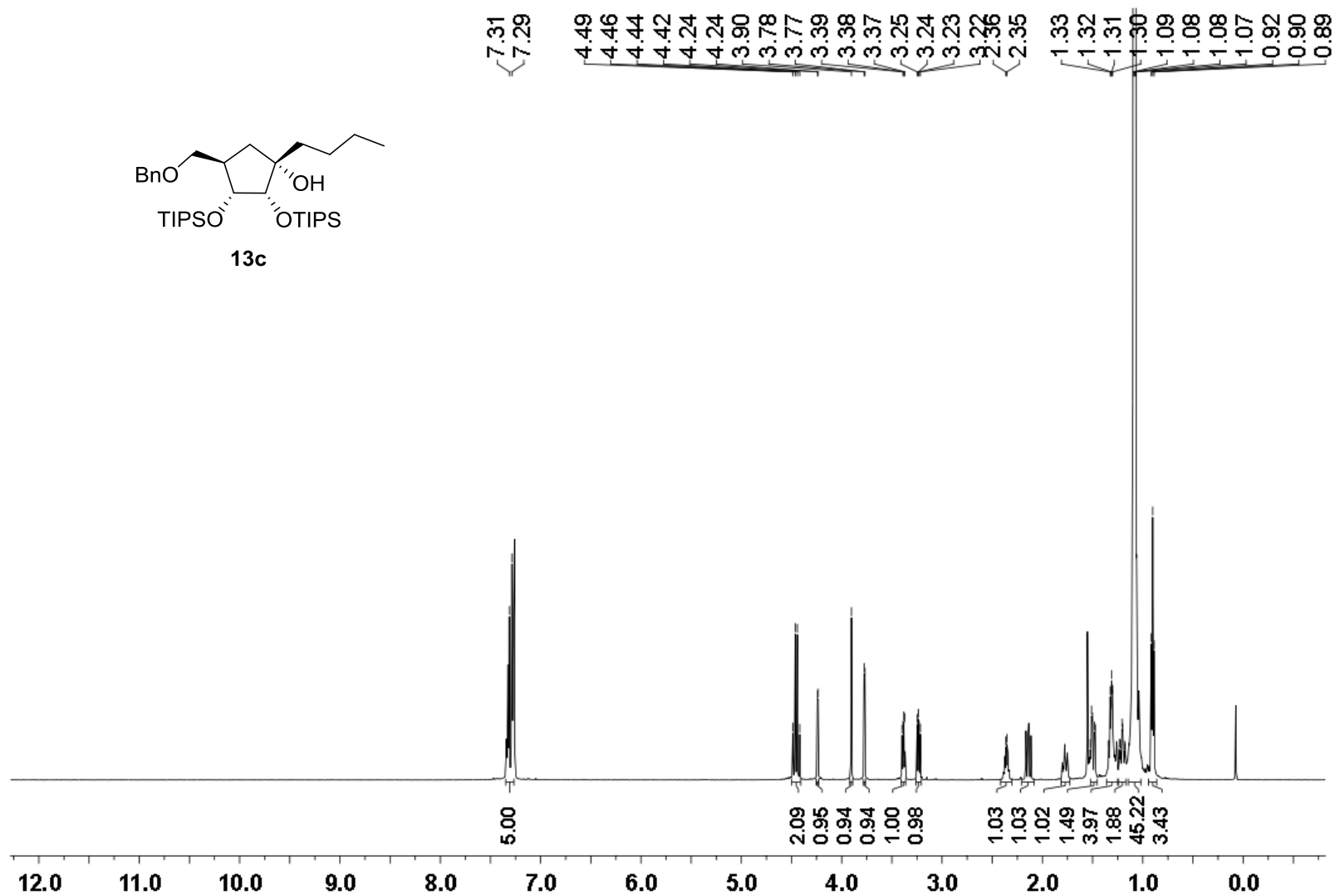
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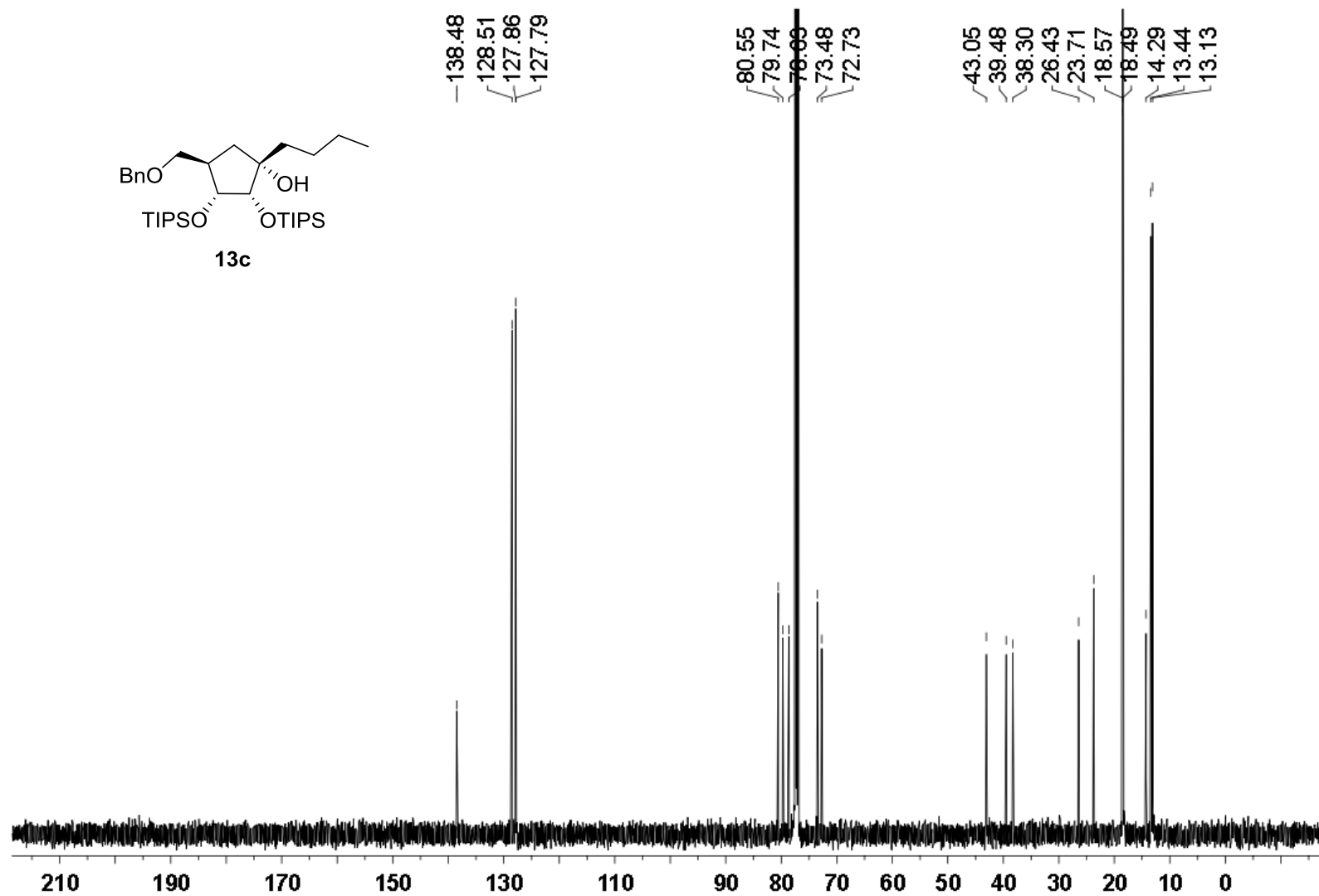
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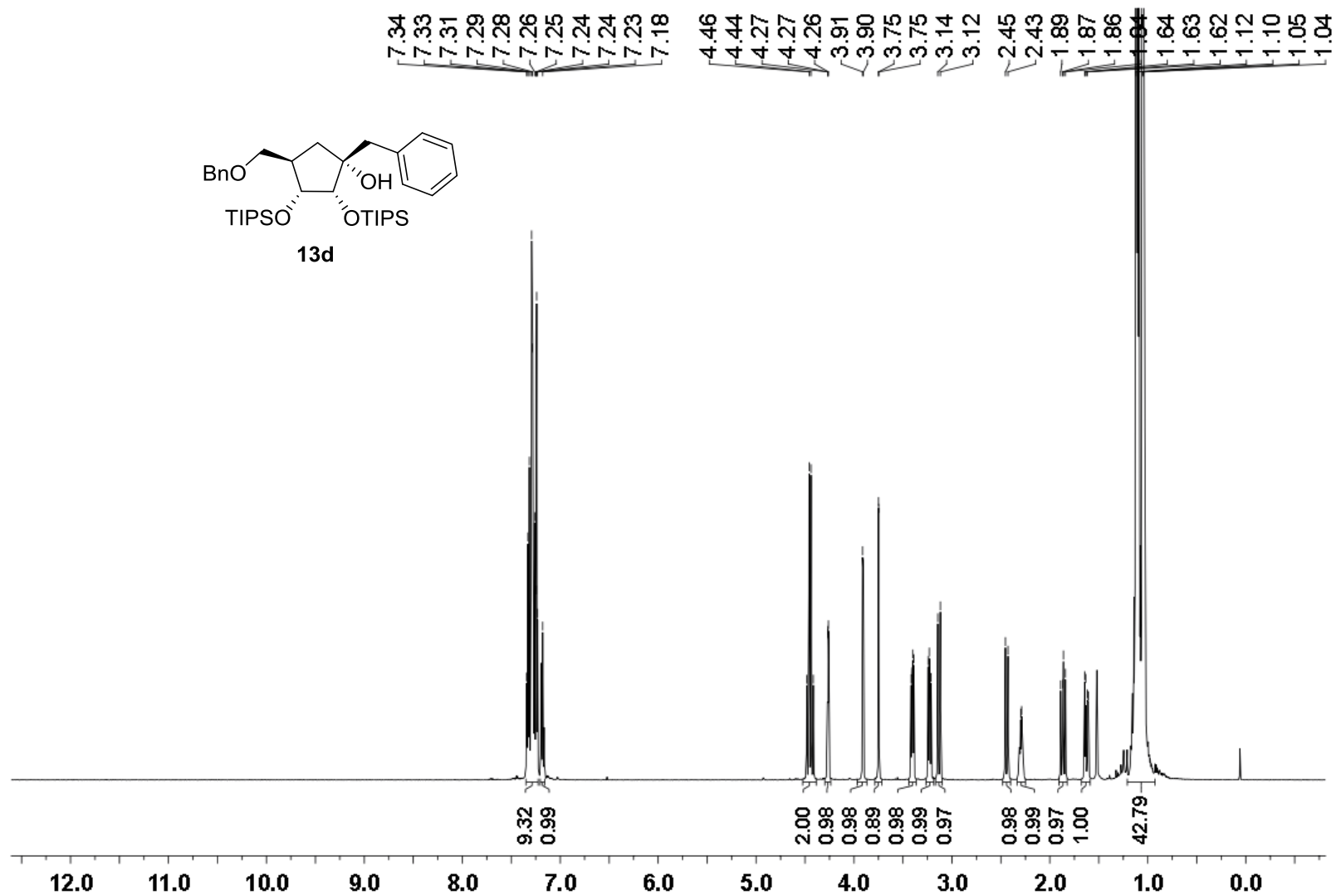
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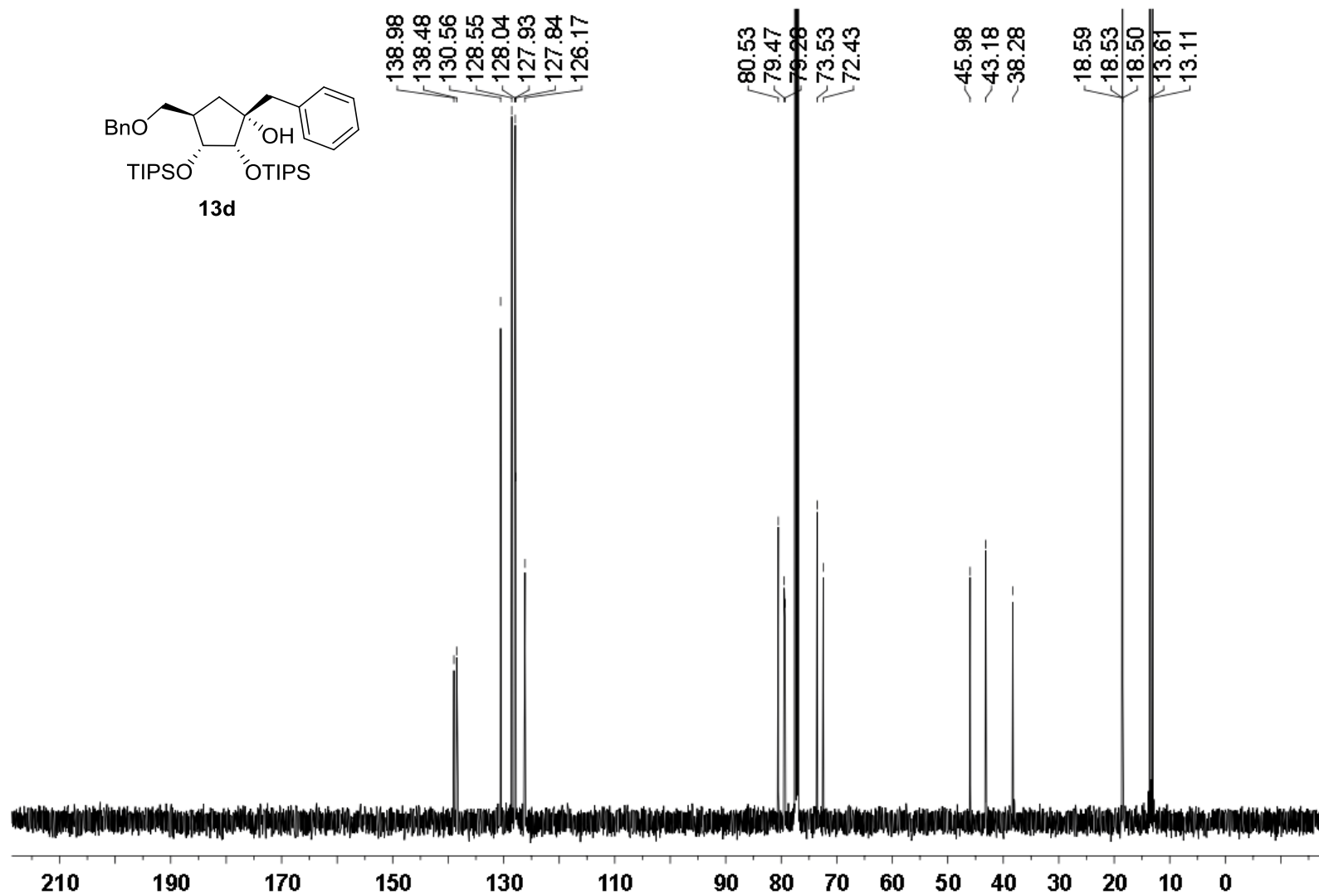
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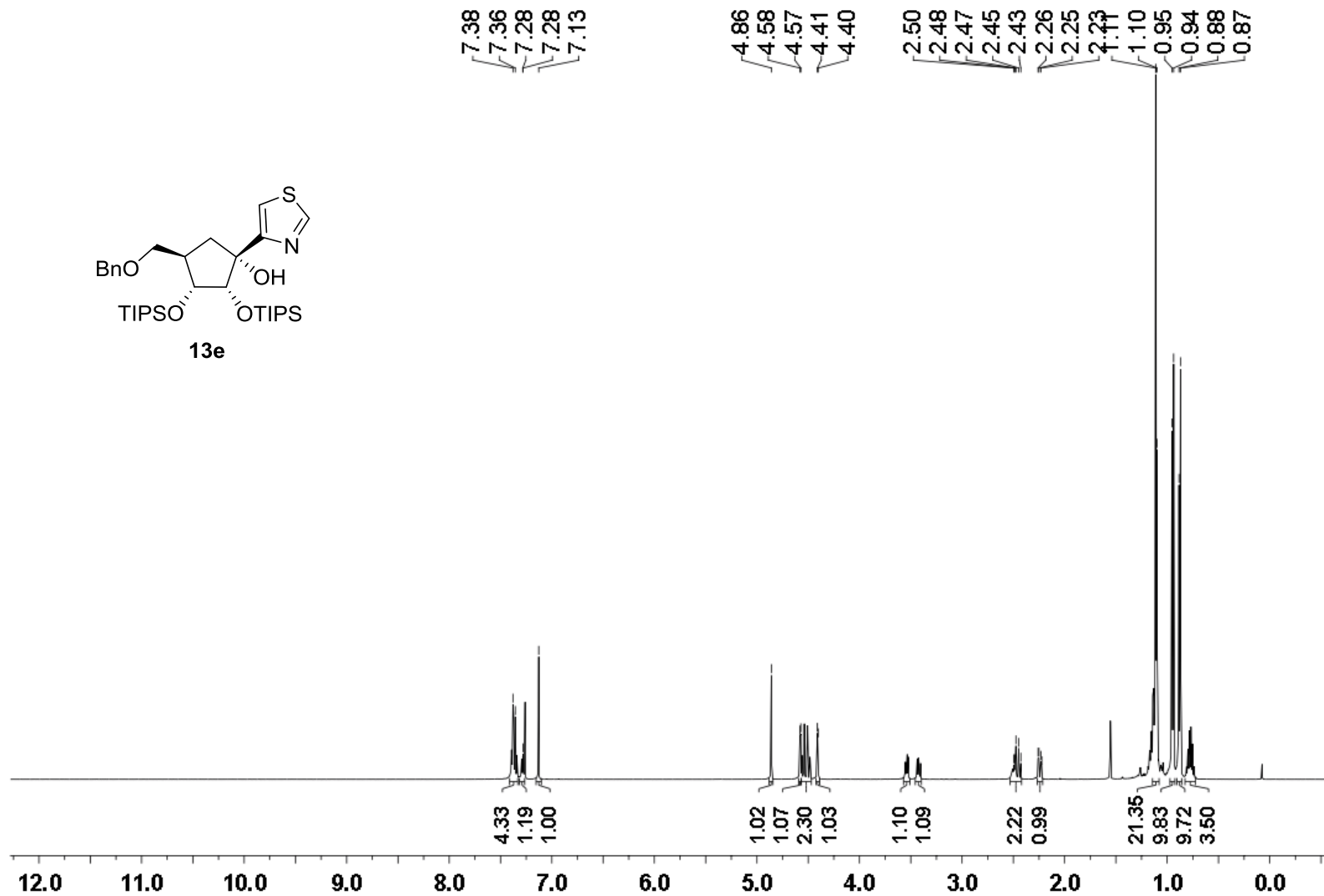
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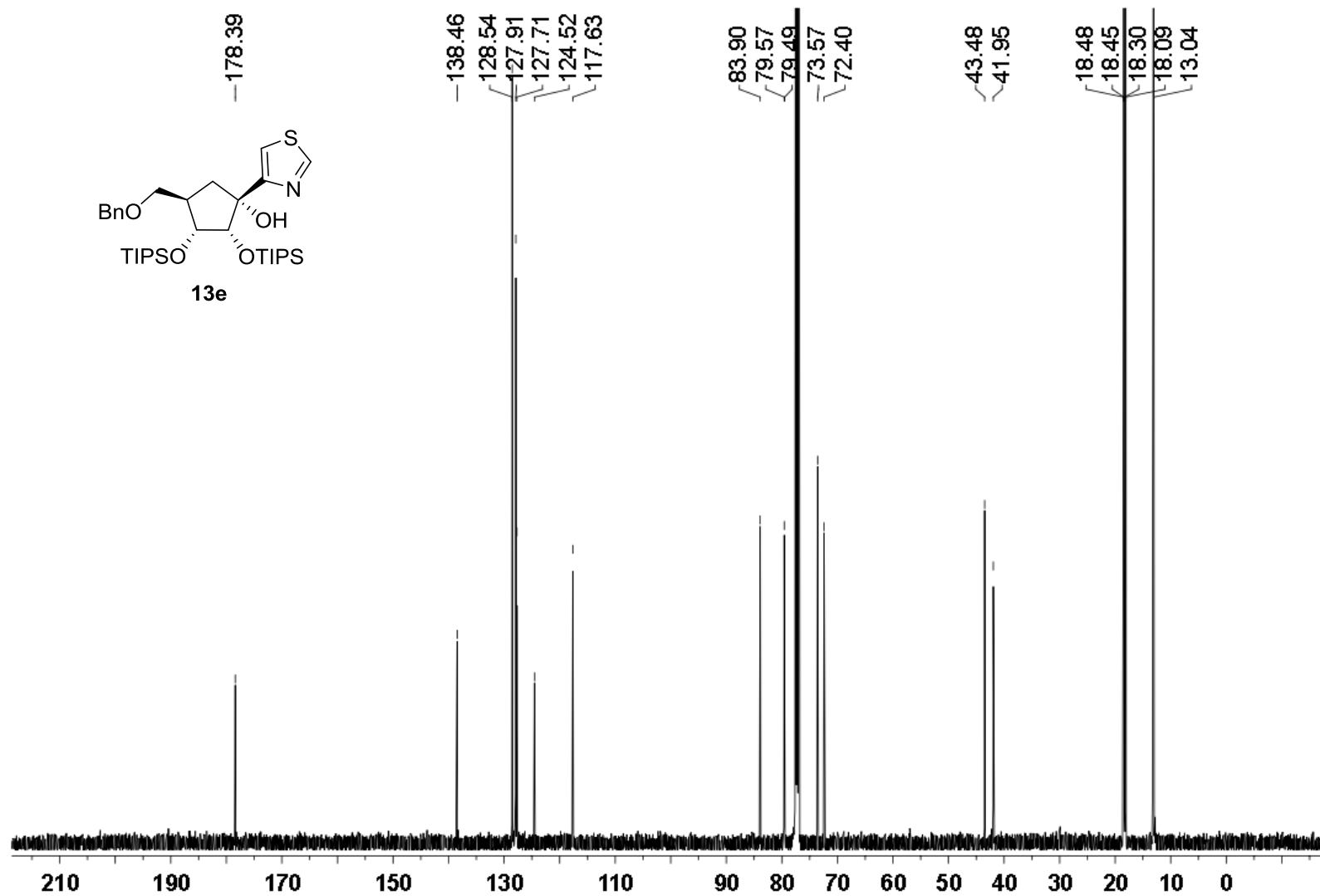
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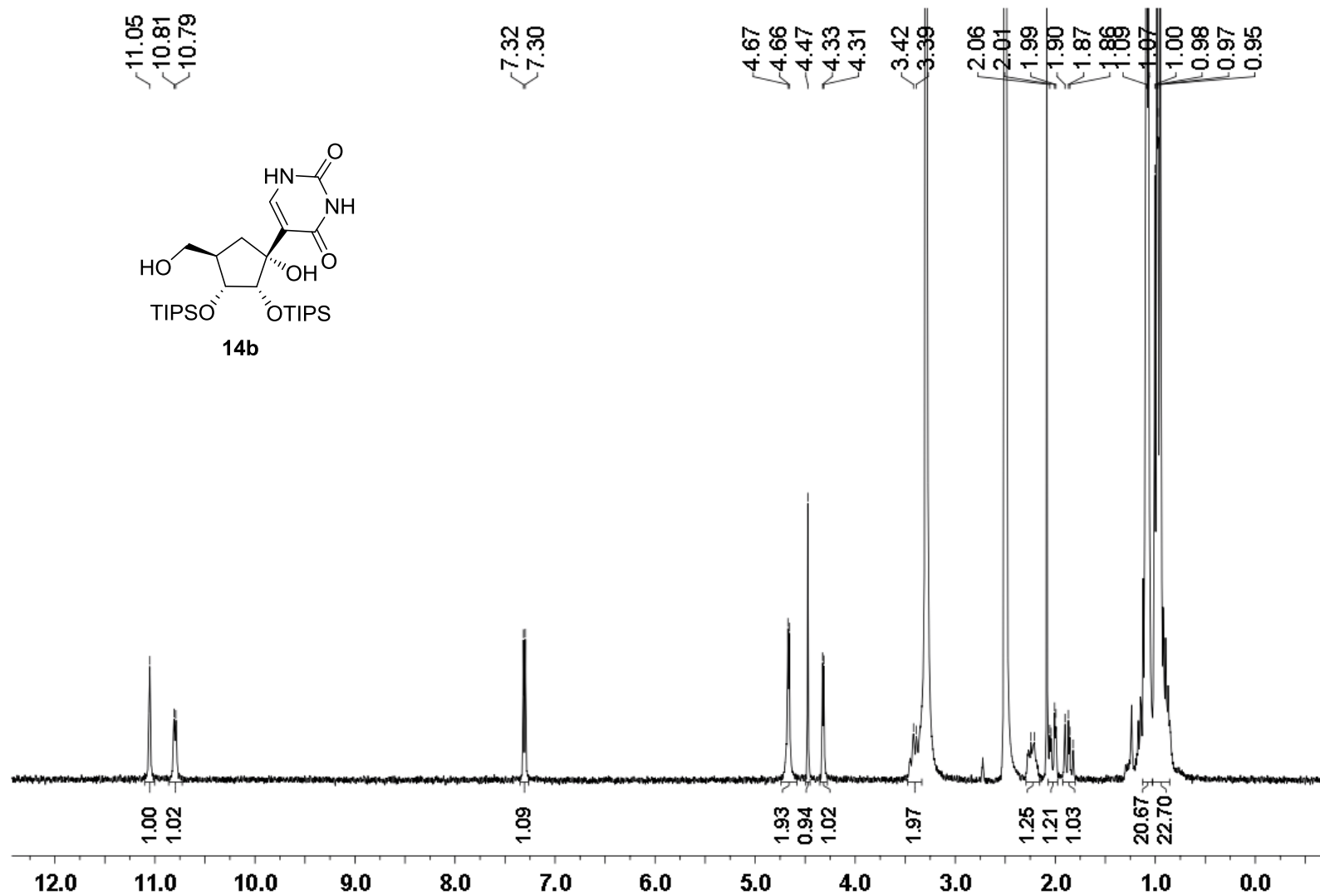
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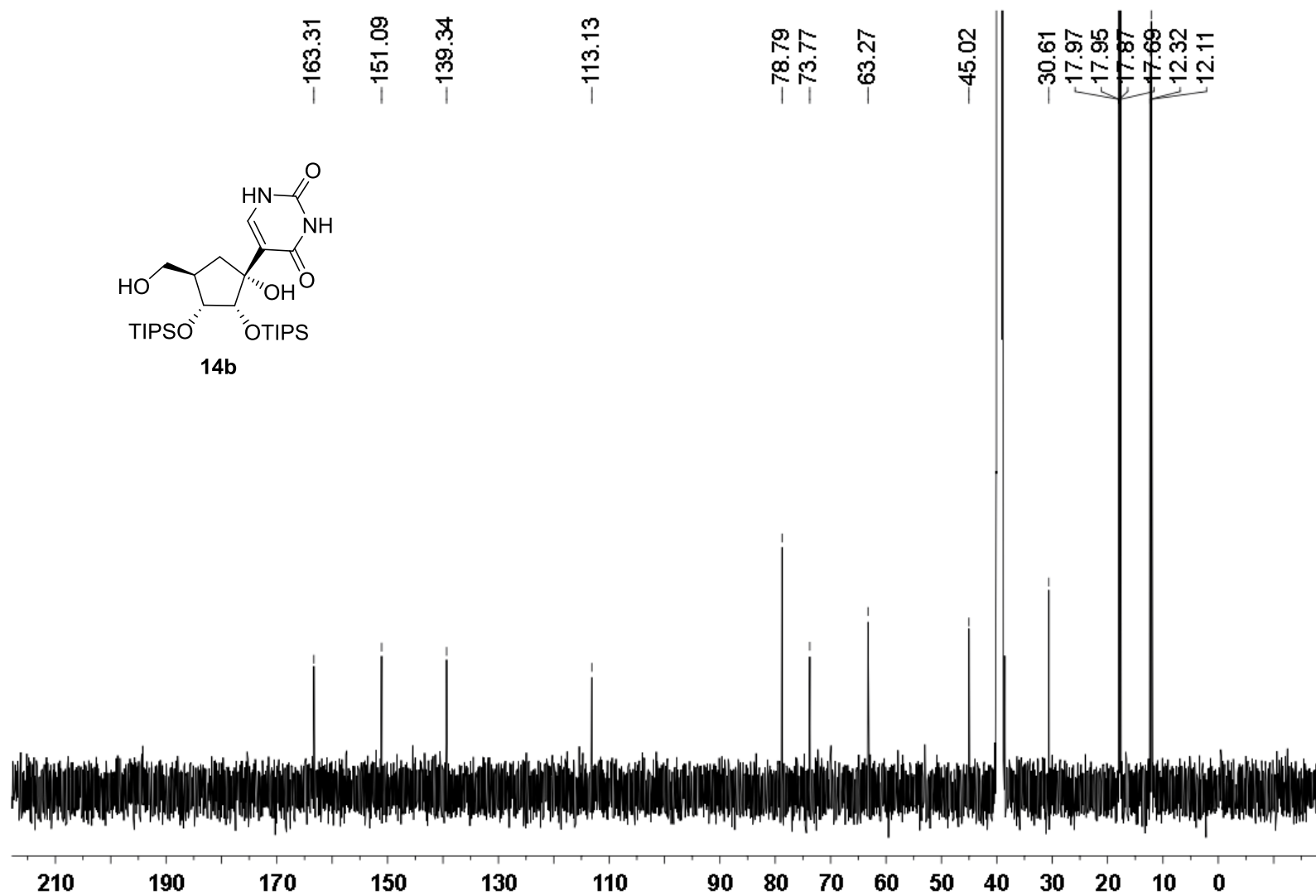
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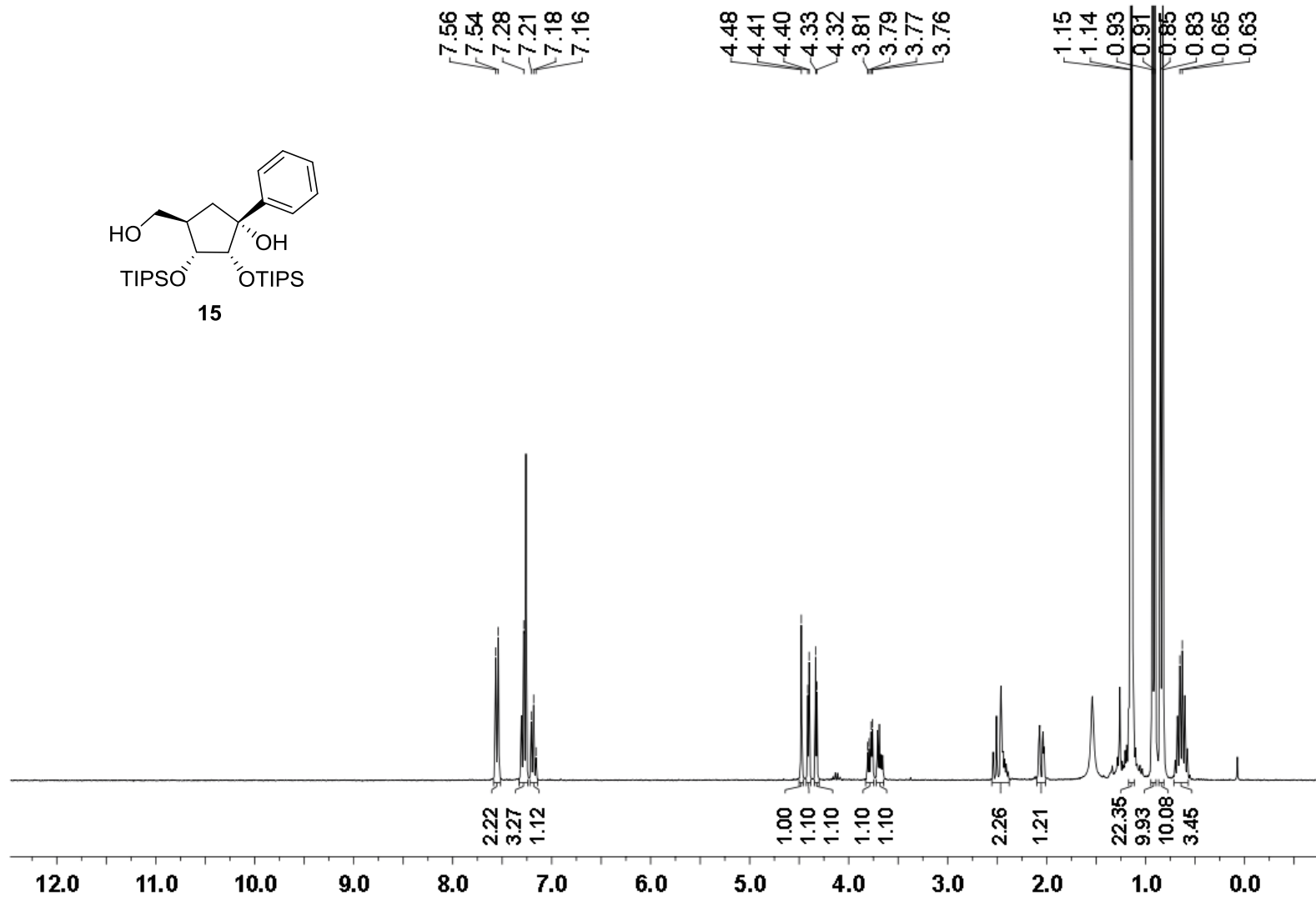
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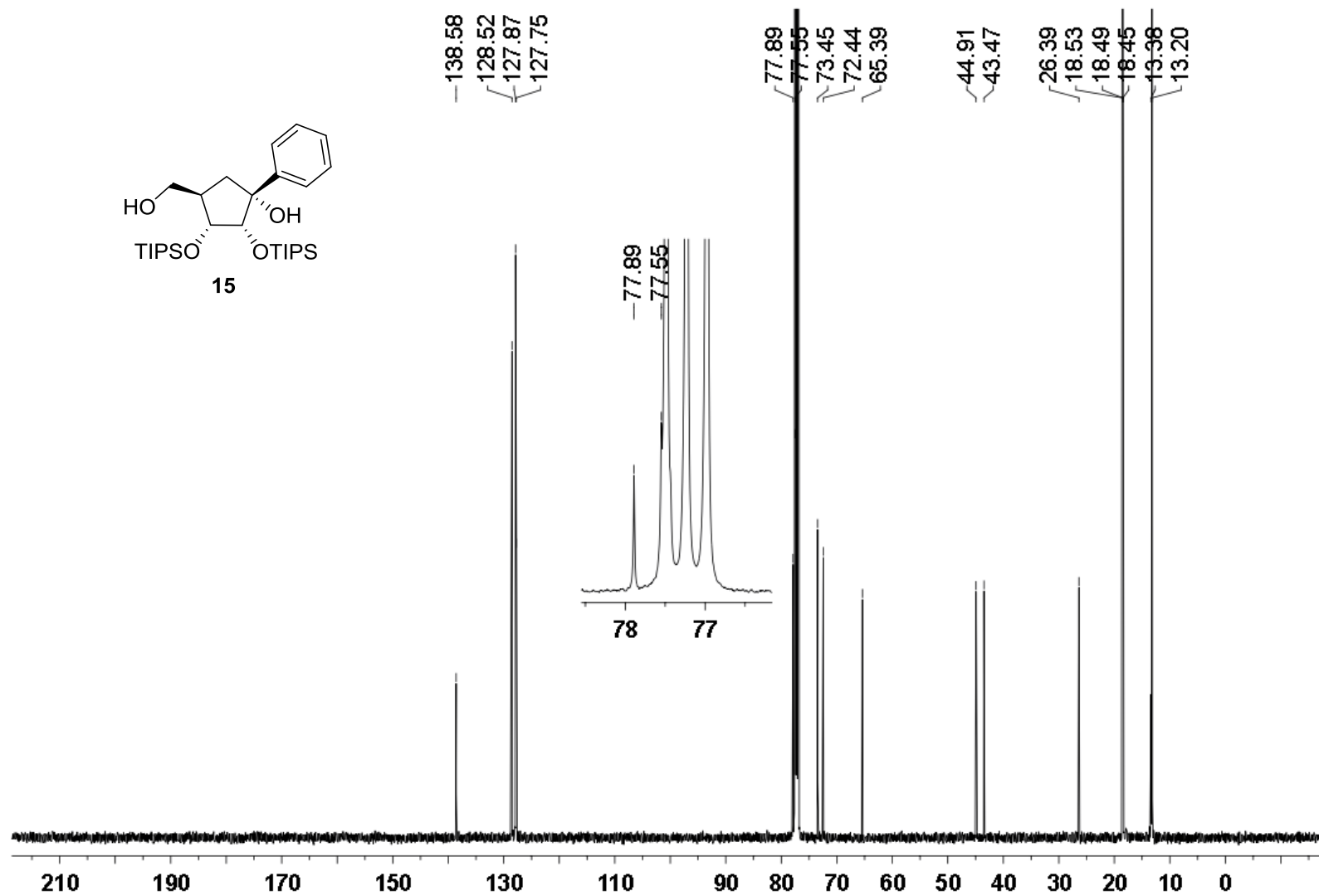
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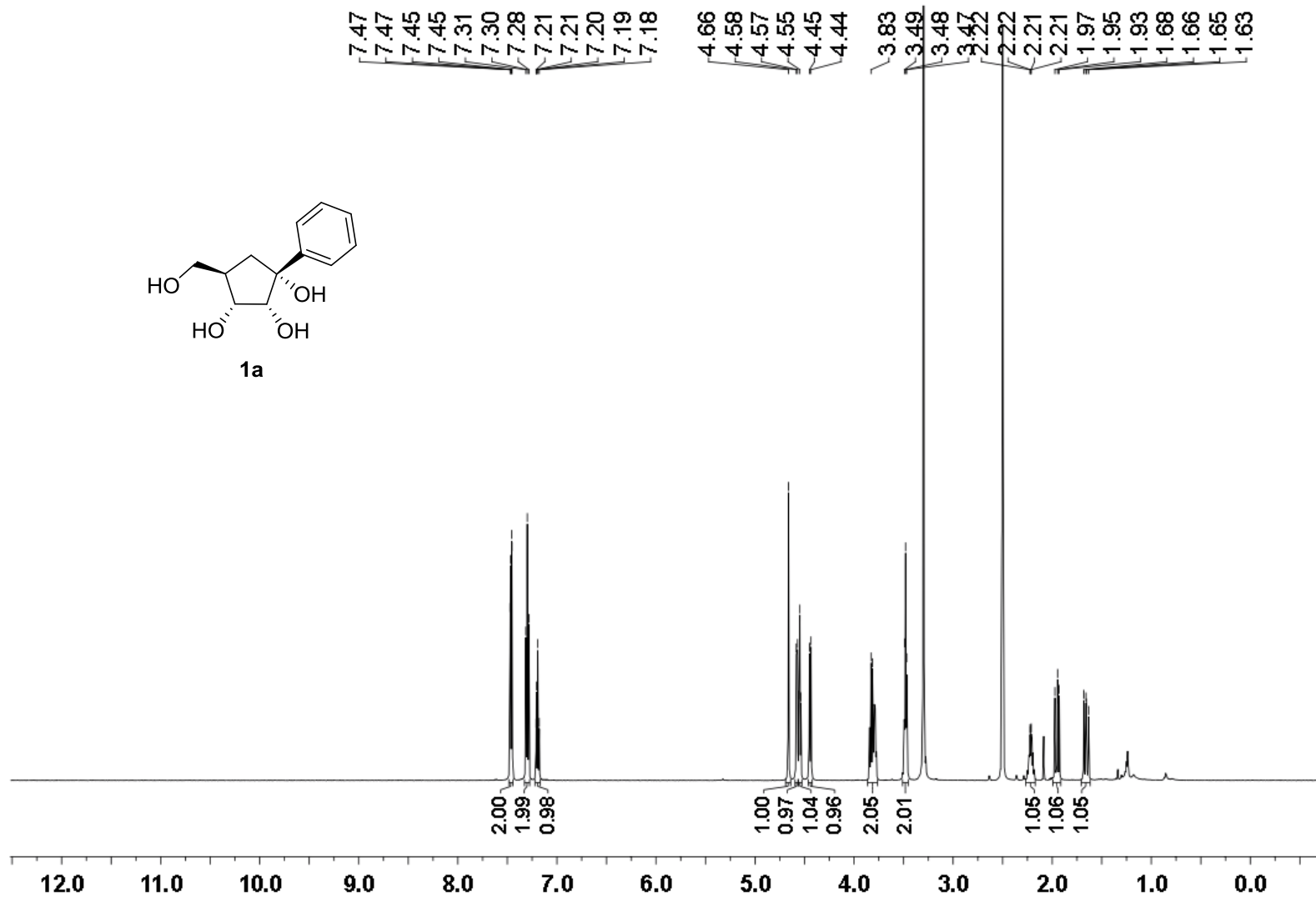
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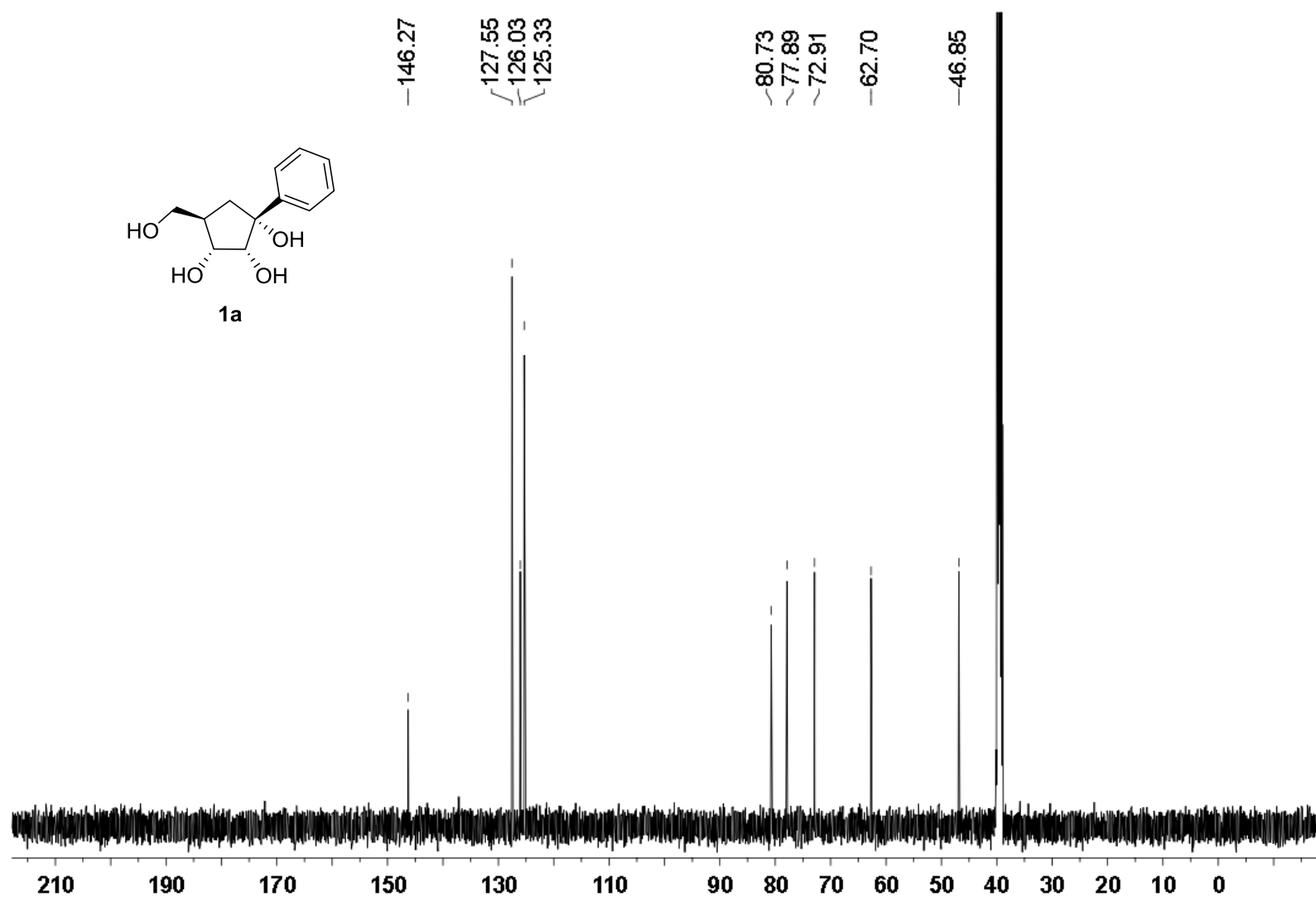
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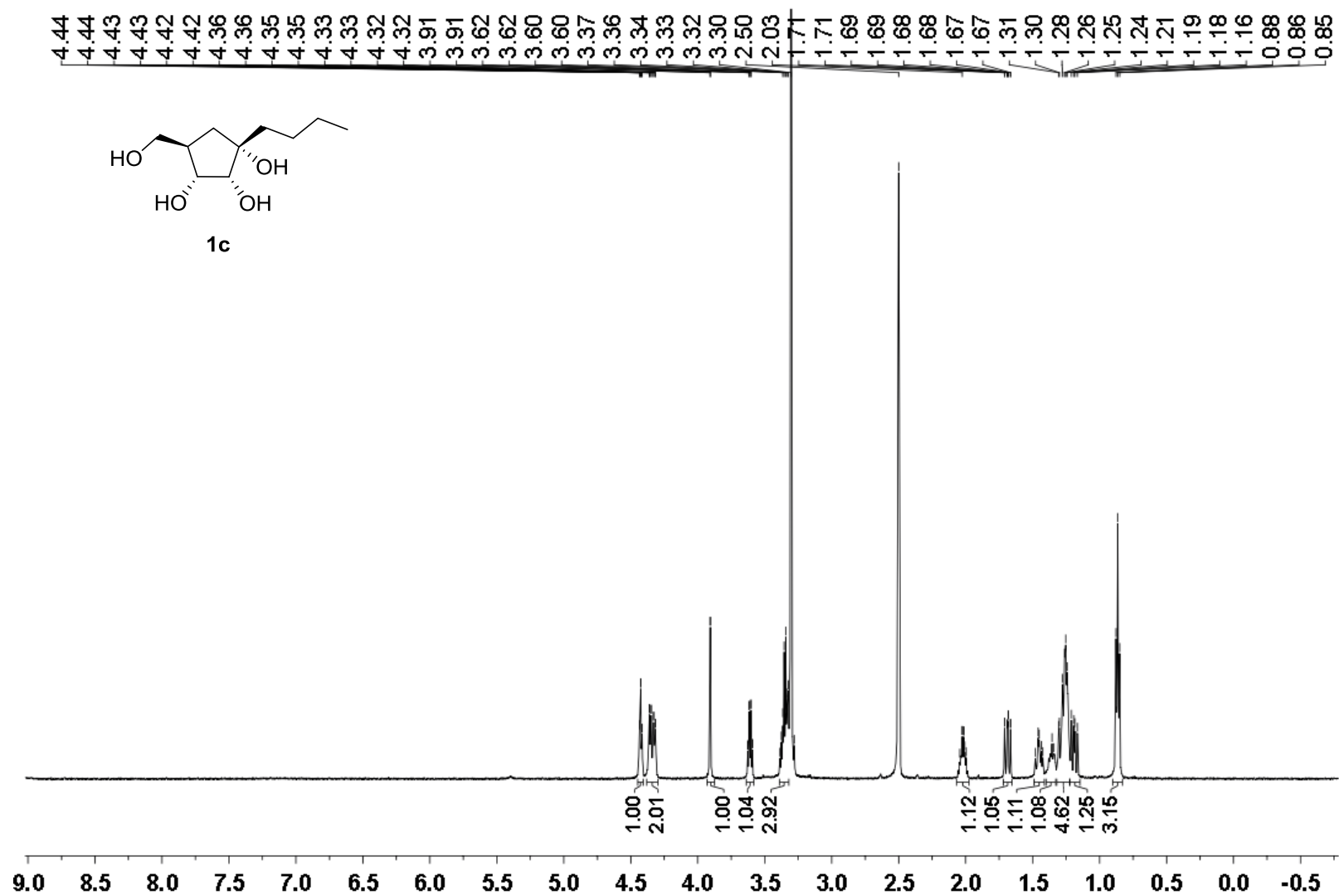
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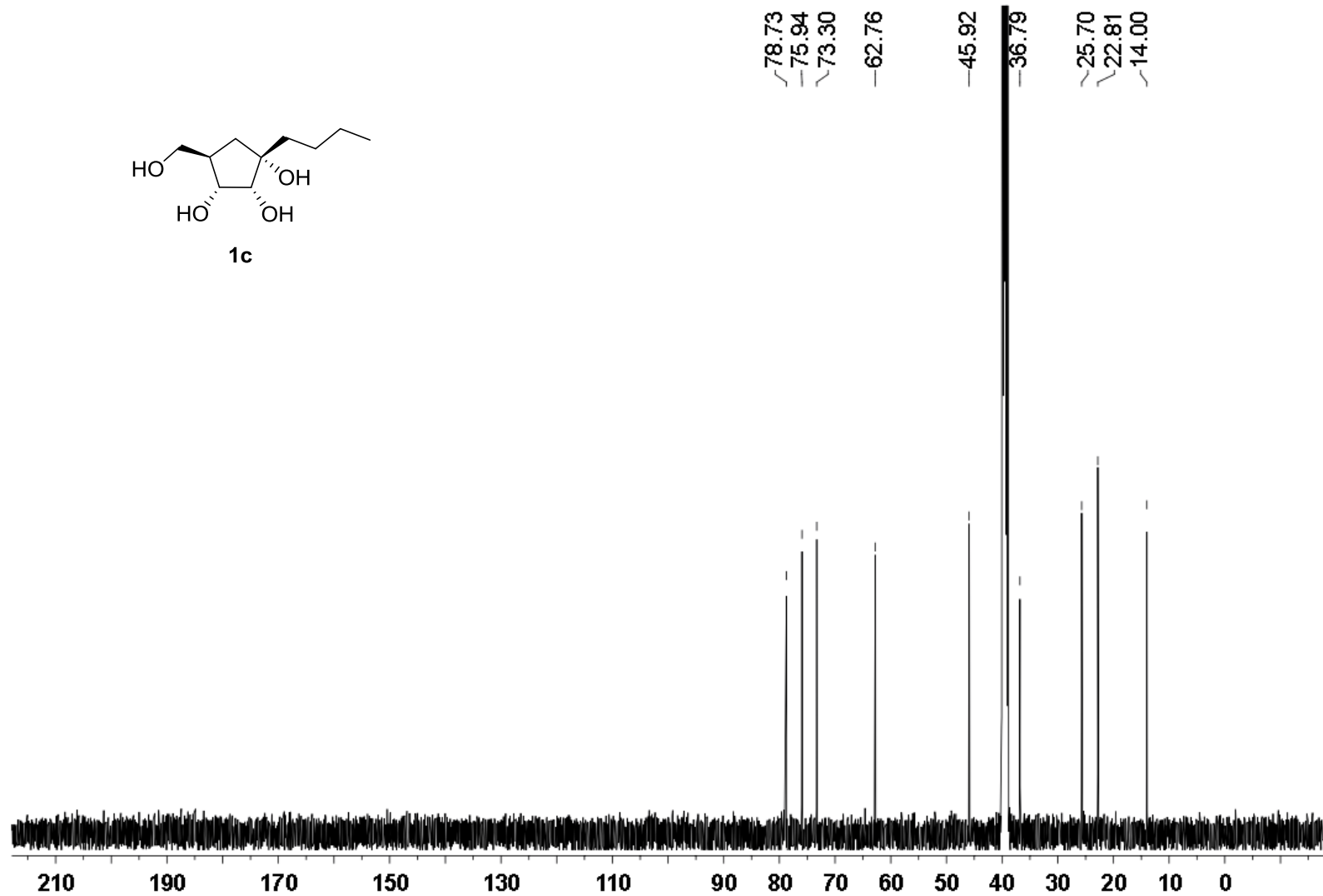
¹H NMR (500 MHz) spectrum of **1a** in DMSO-*d*₆



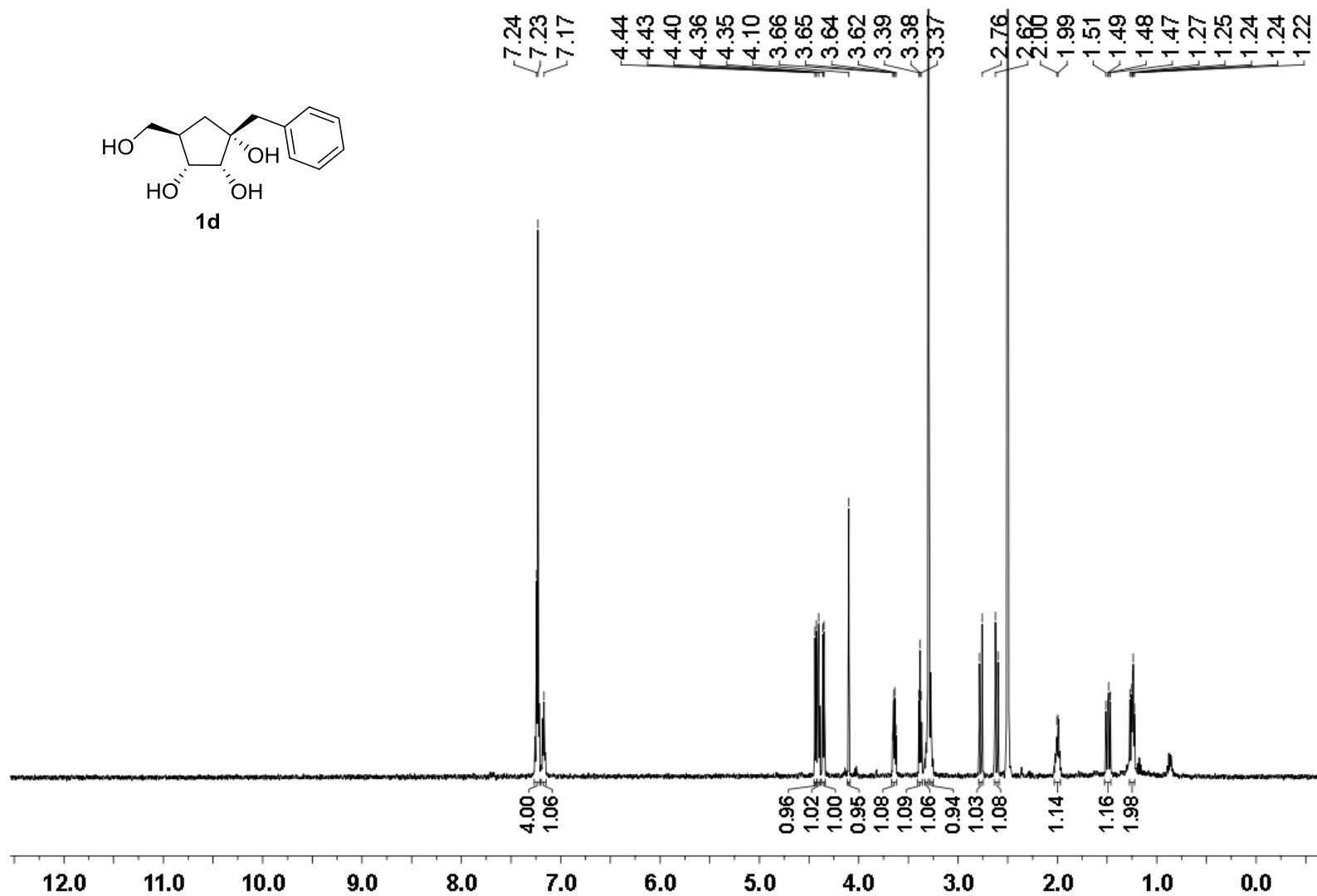
¹³C NMR (126 MHz) spectrum of **1a** in DMSO-*d*₆



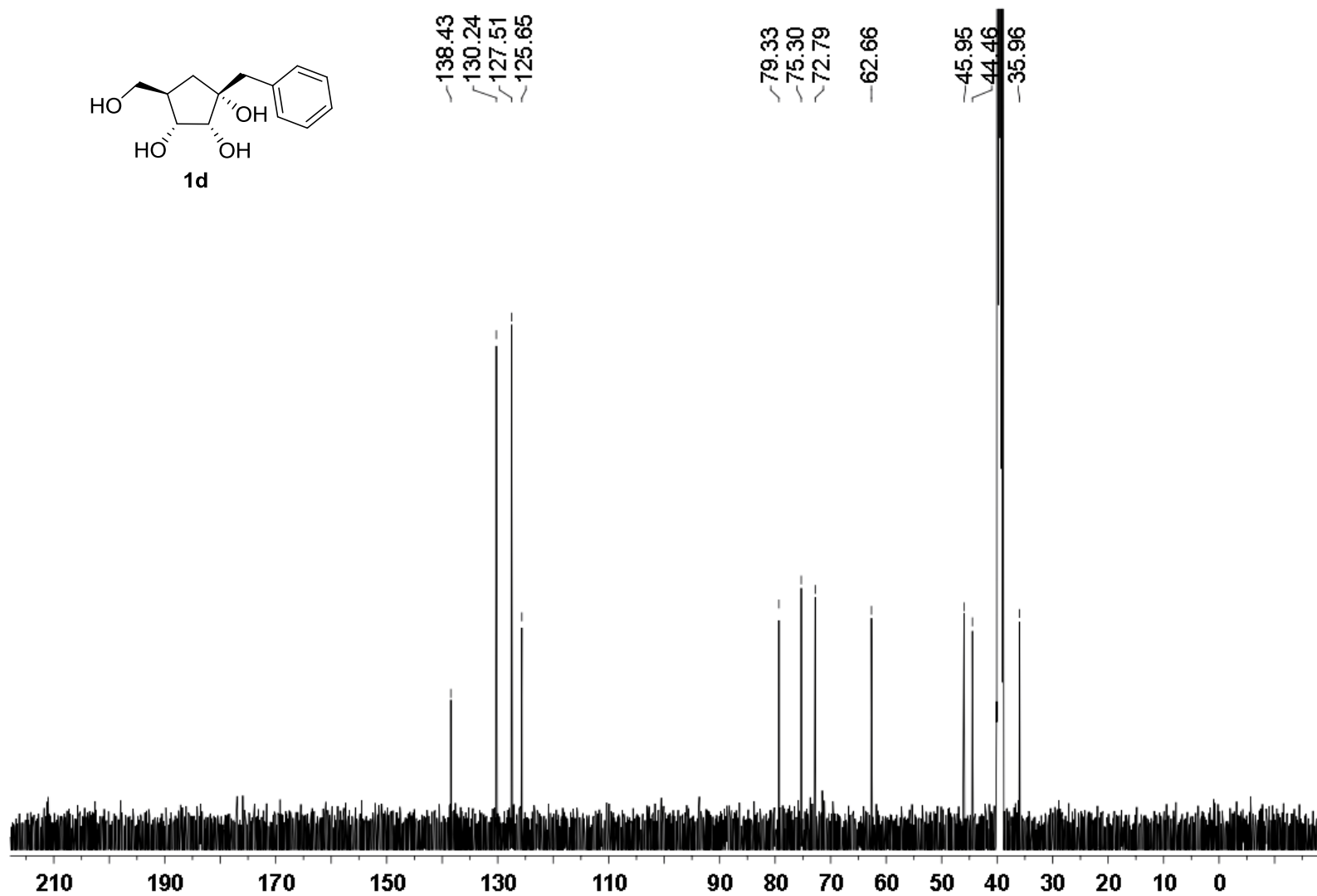
¹H NMR (500 MHz) spectrum of **1c** in DMSO-*d*₆



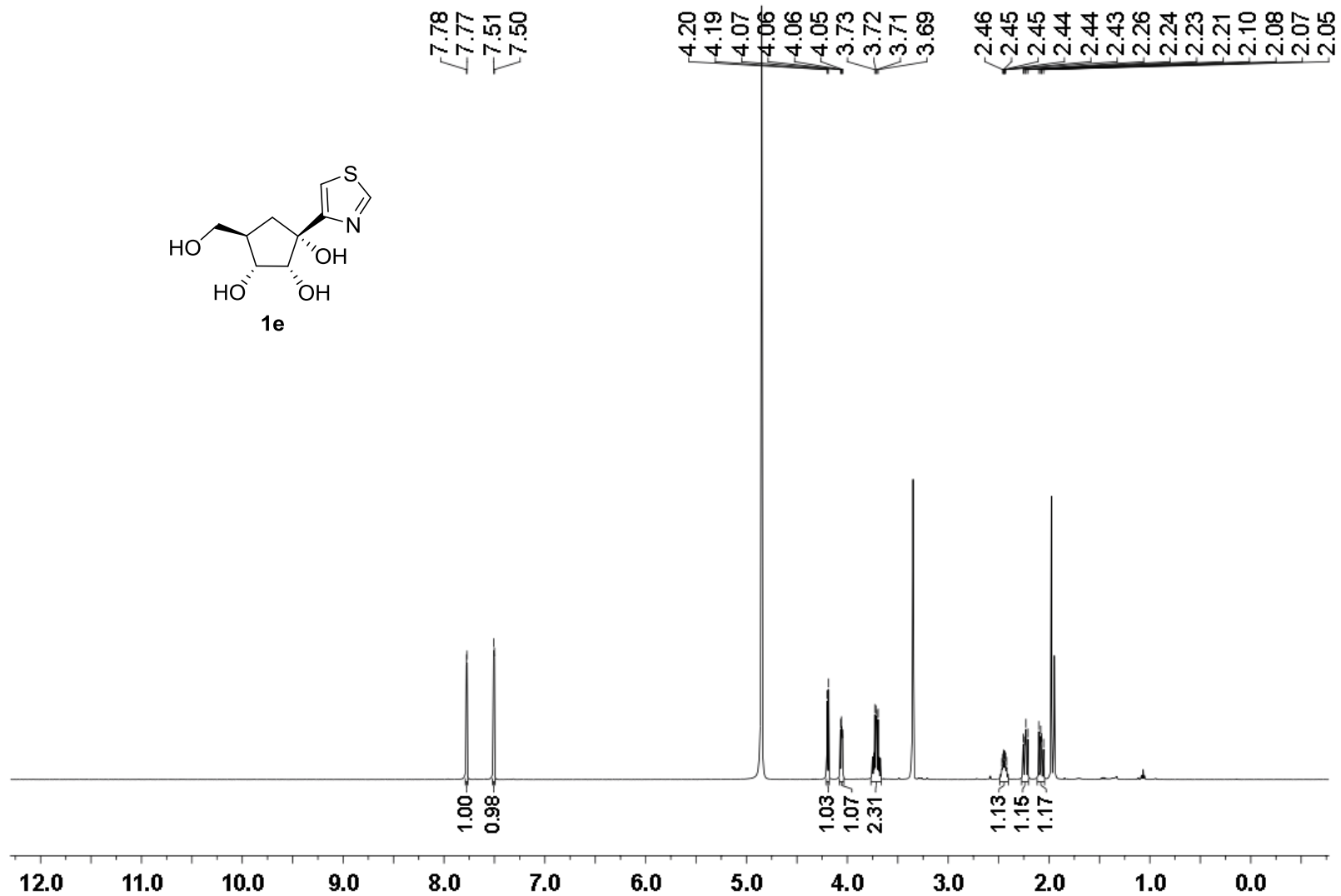
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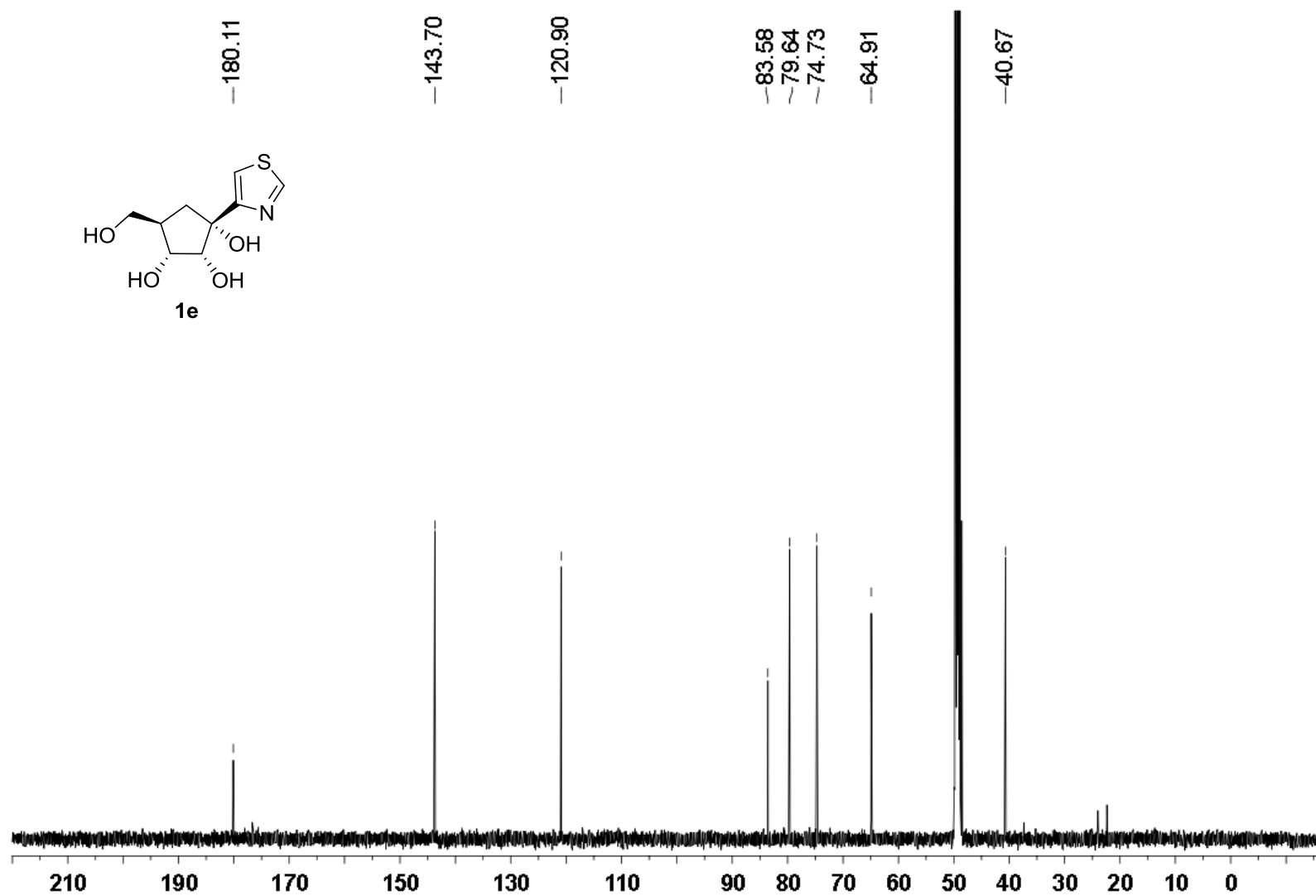
¹H NMR (500 MHz) spectrum of **1d** in DMSO-*d*₆



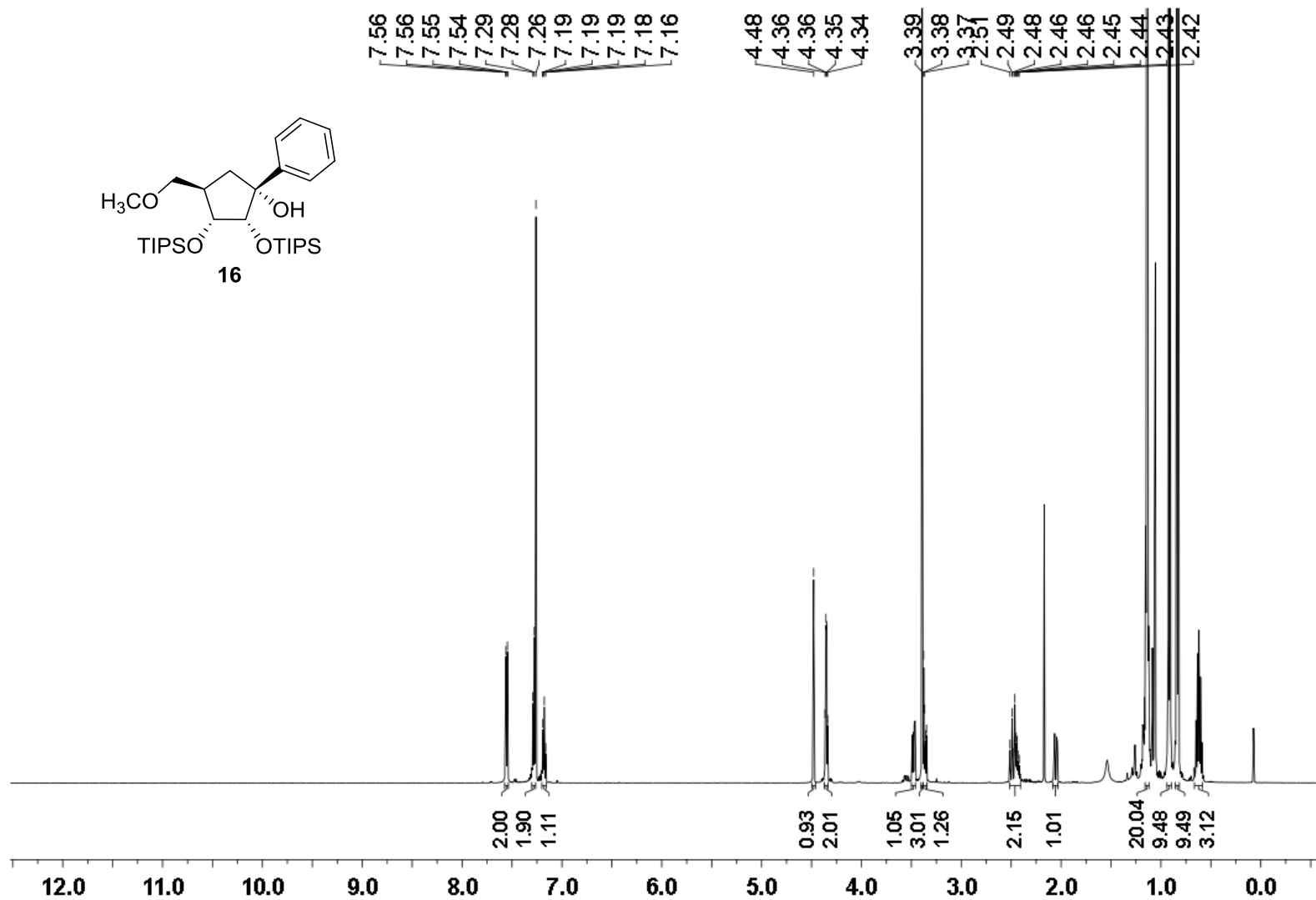
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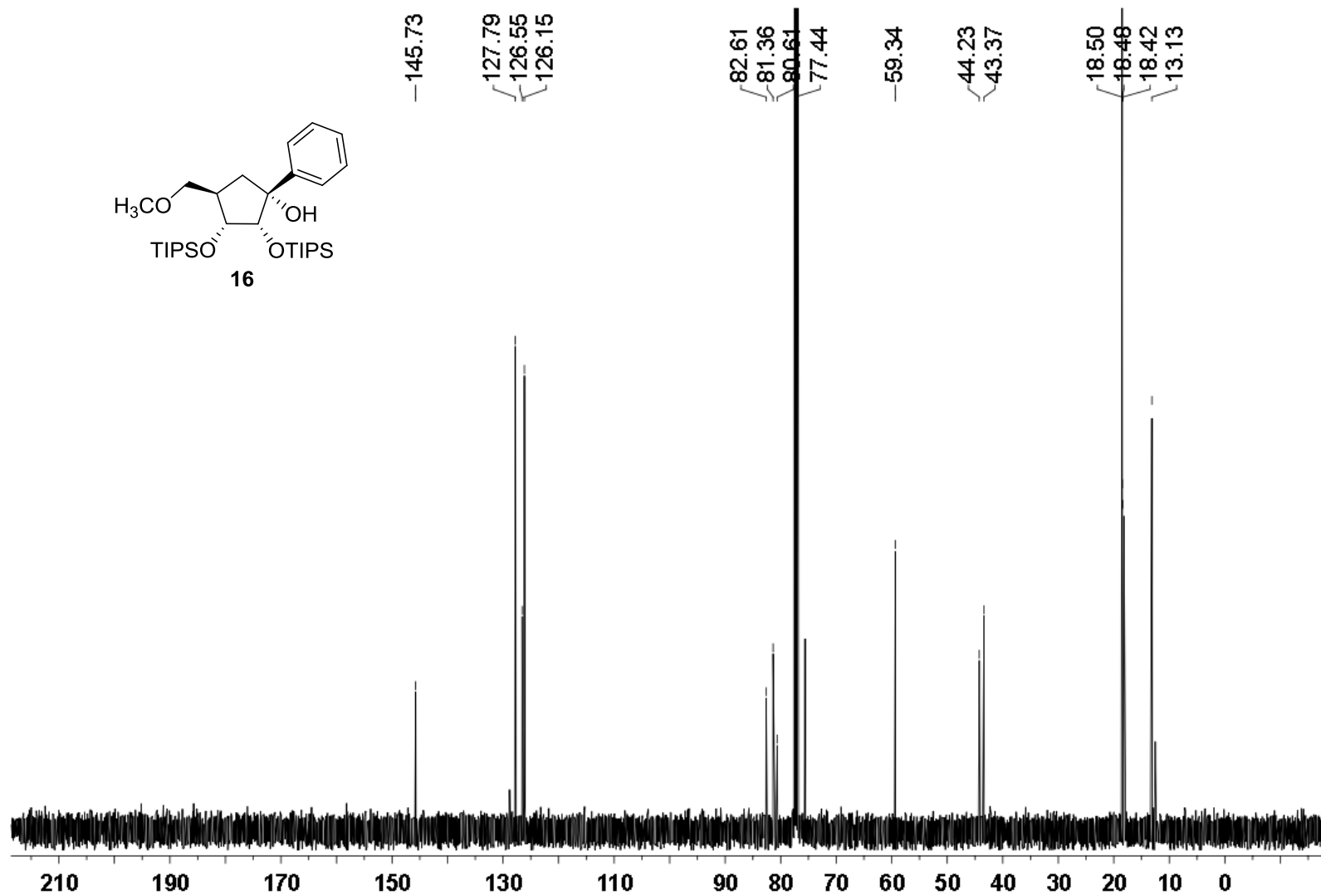
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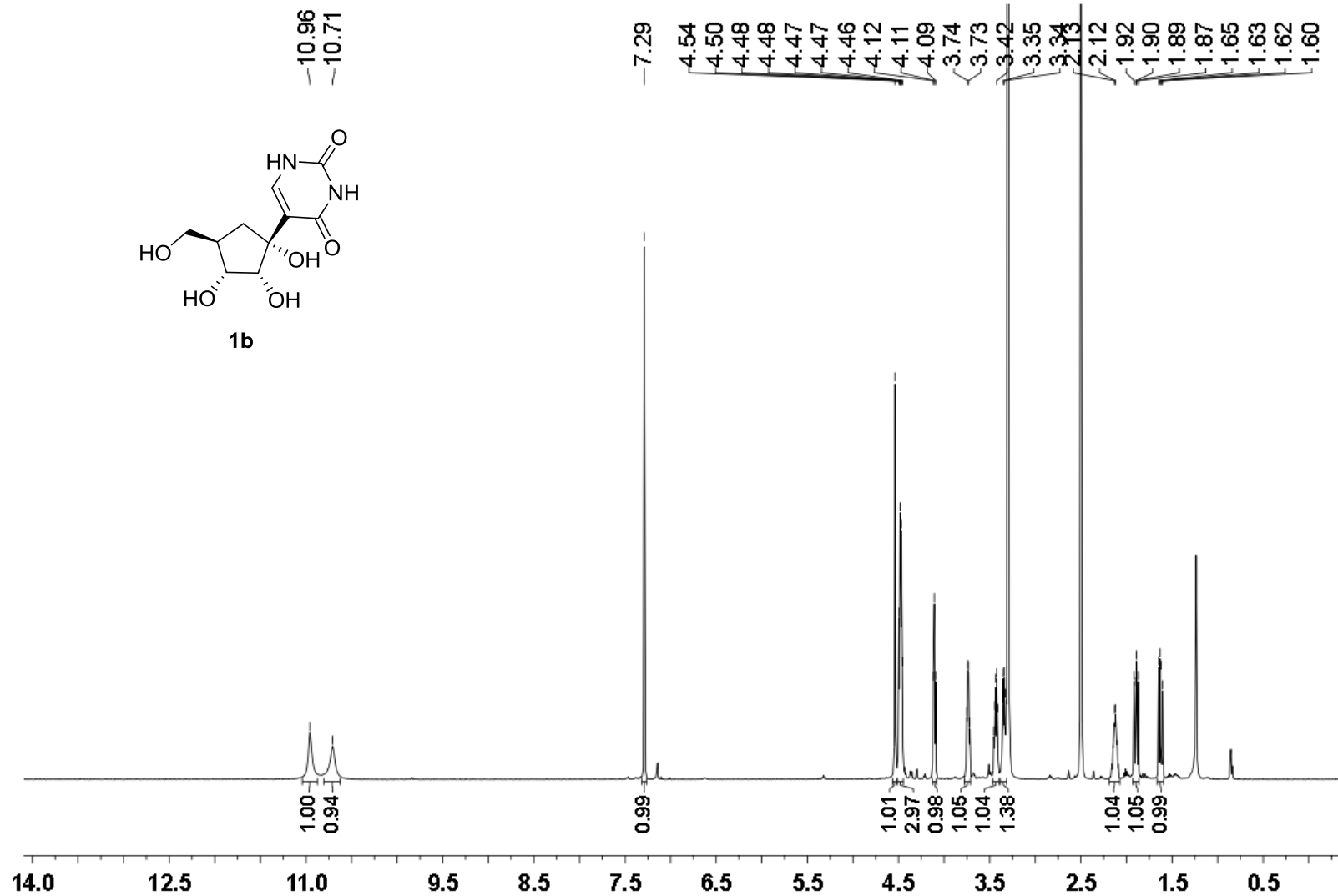
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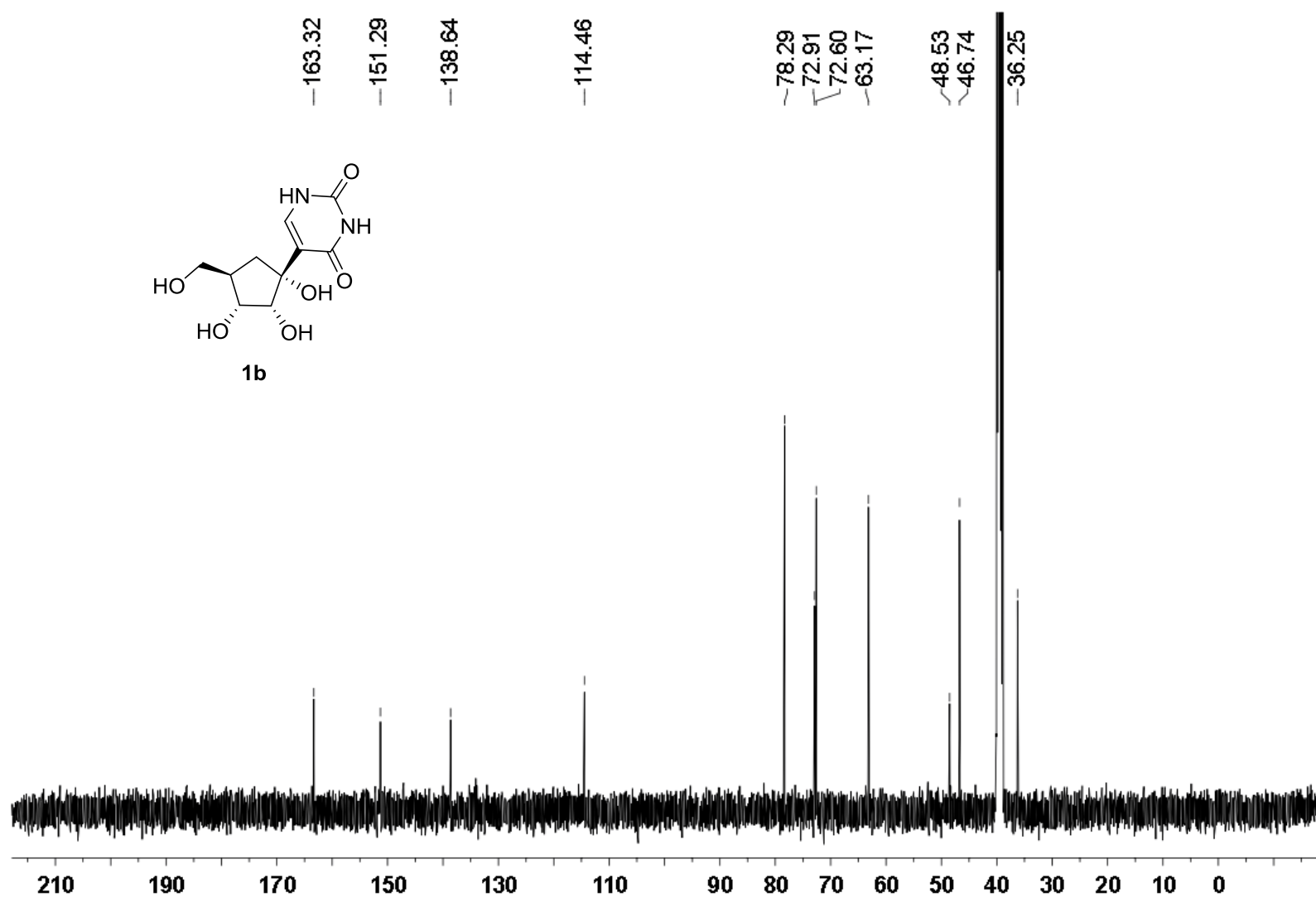
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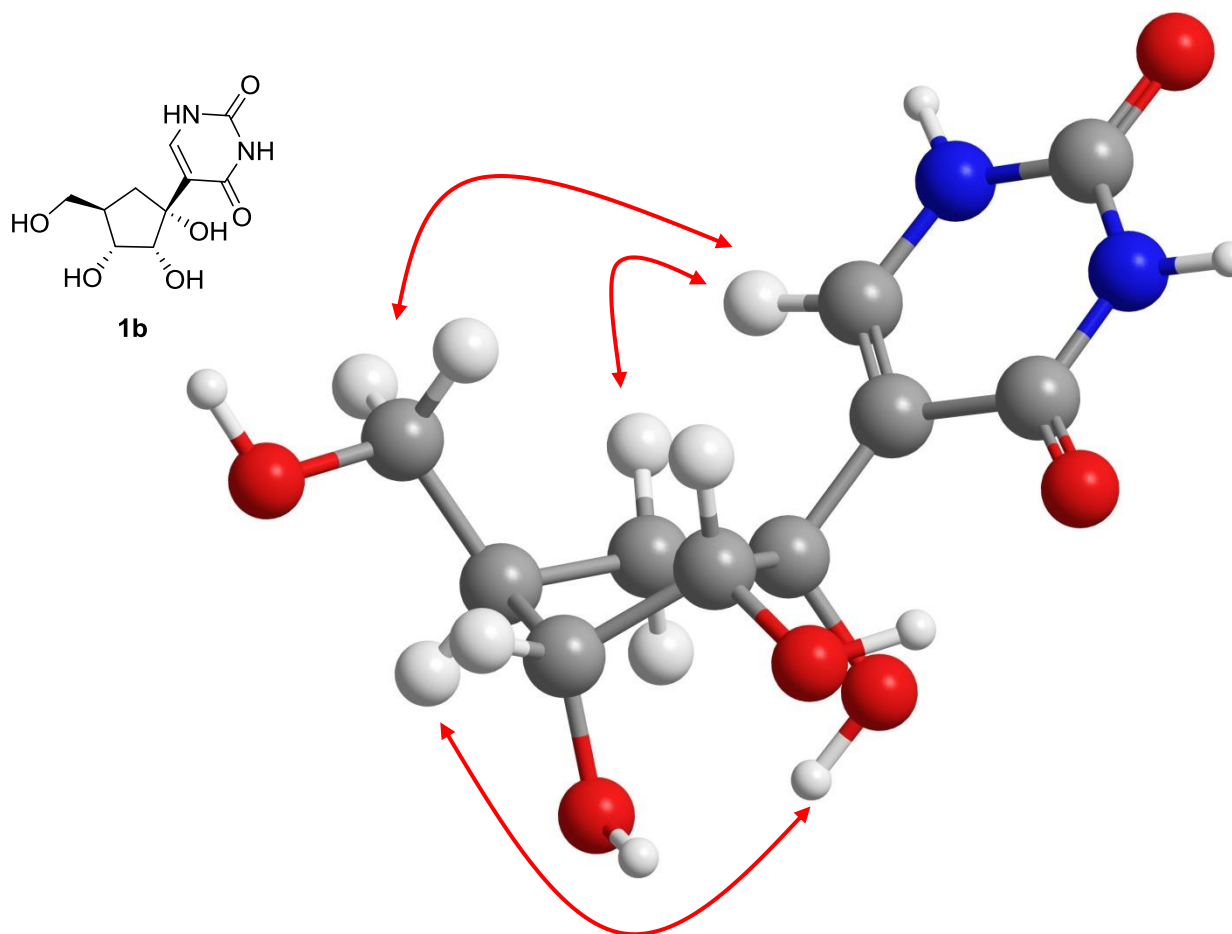
^{13}C NMR (126 MHz) spectrum of **16** in CDCl_3



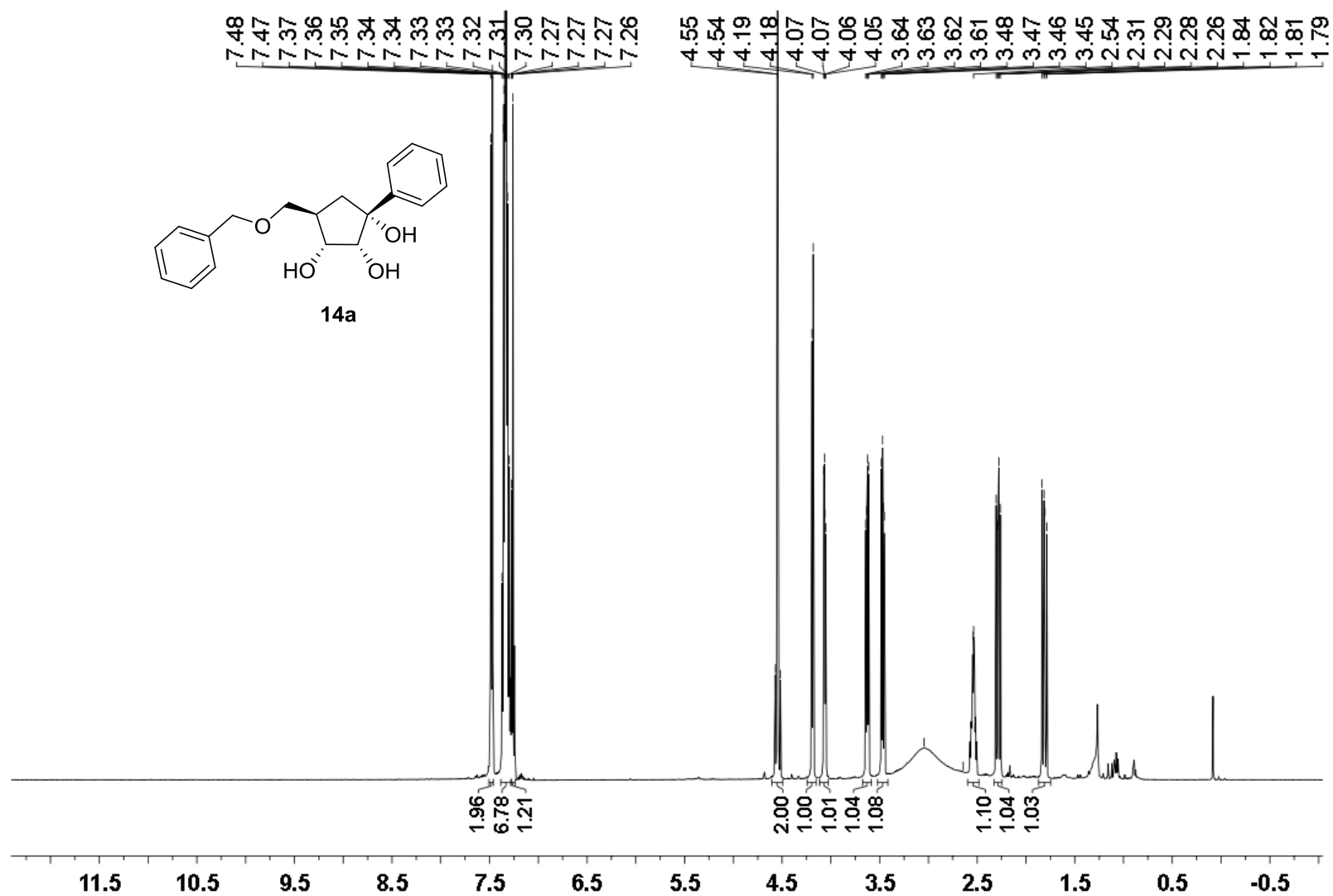
^1H NMR (500 MHz) spectrum of **1b** in $\text{DMSO}-d_6$



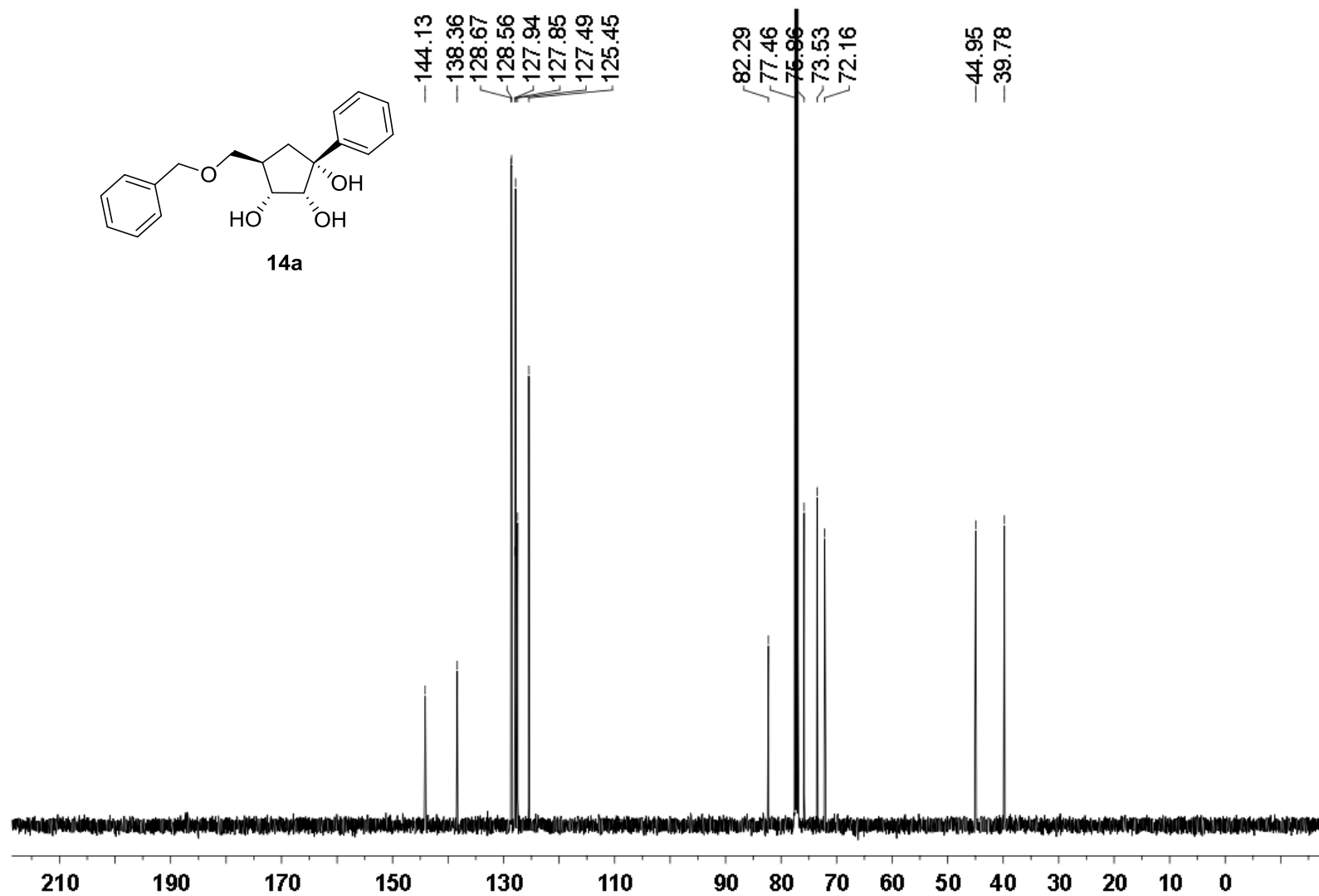
¹³C NMR (126 MHz) spectrum of **1b** in DMSO-*d*₆



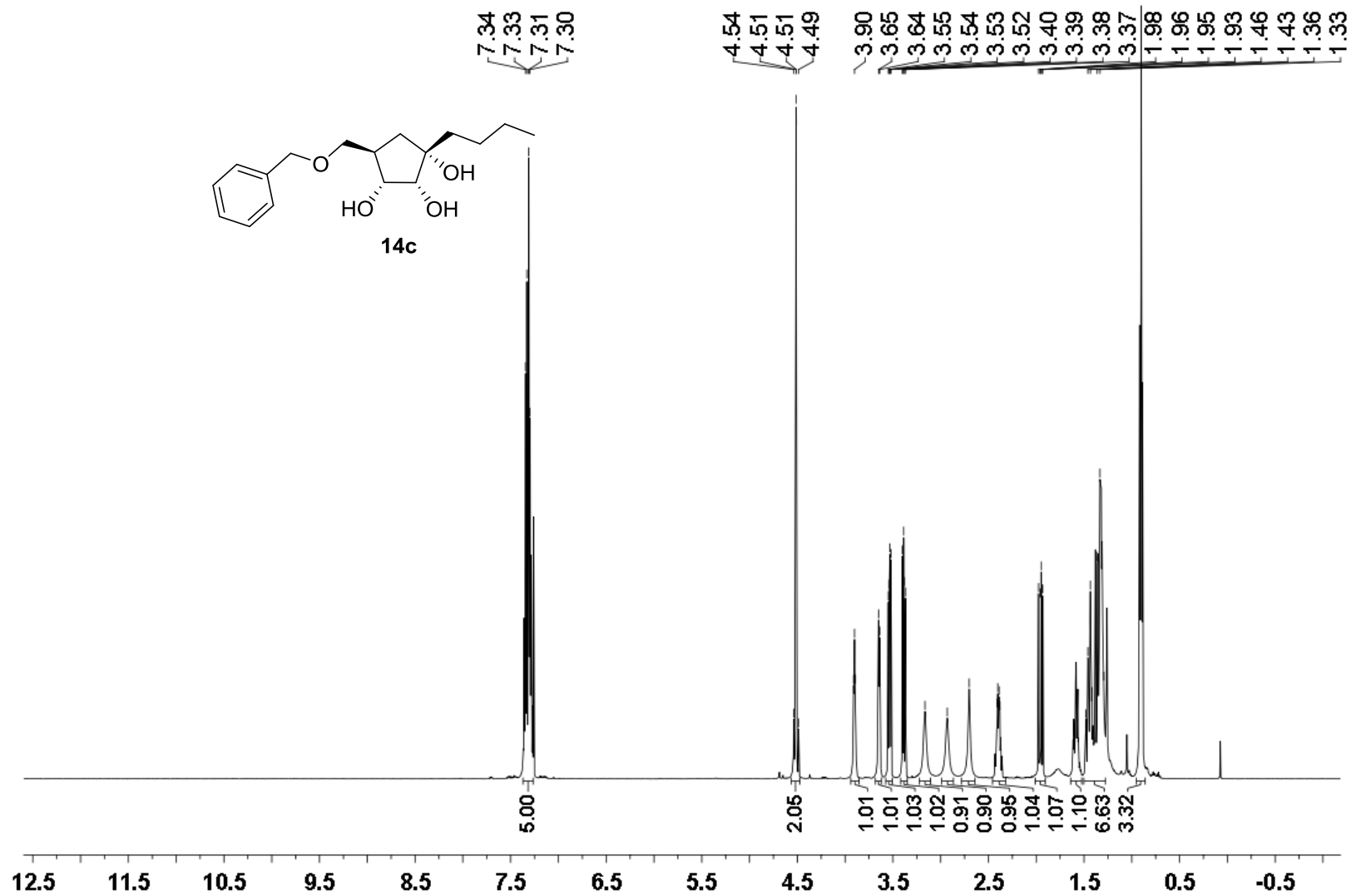
Key NOE interactions observed in molecule **1b**



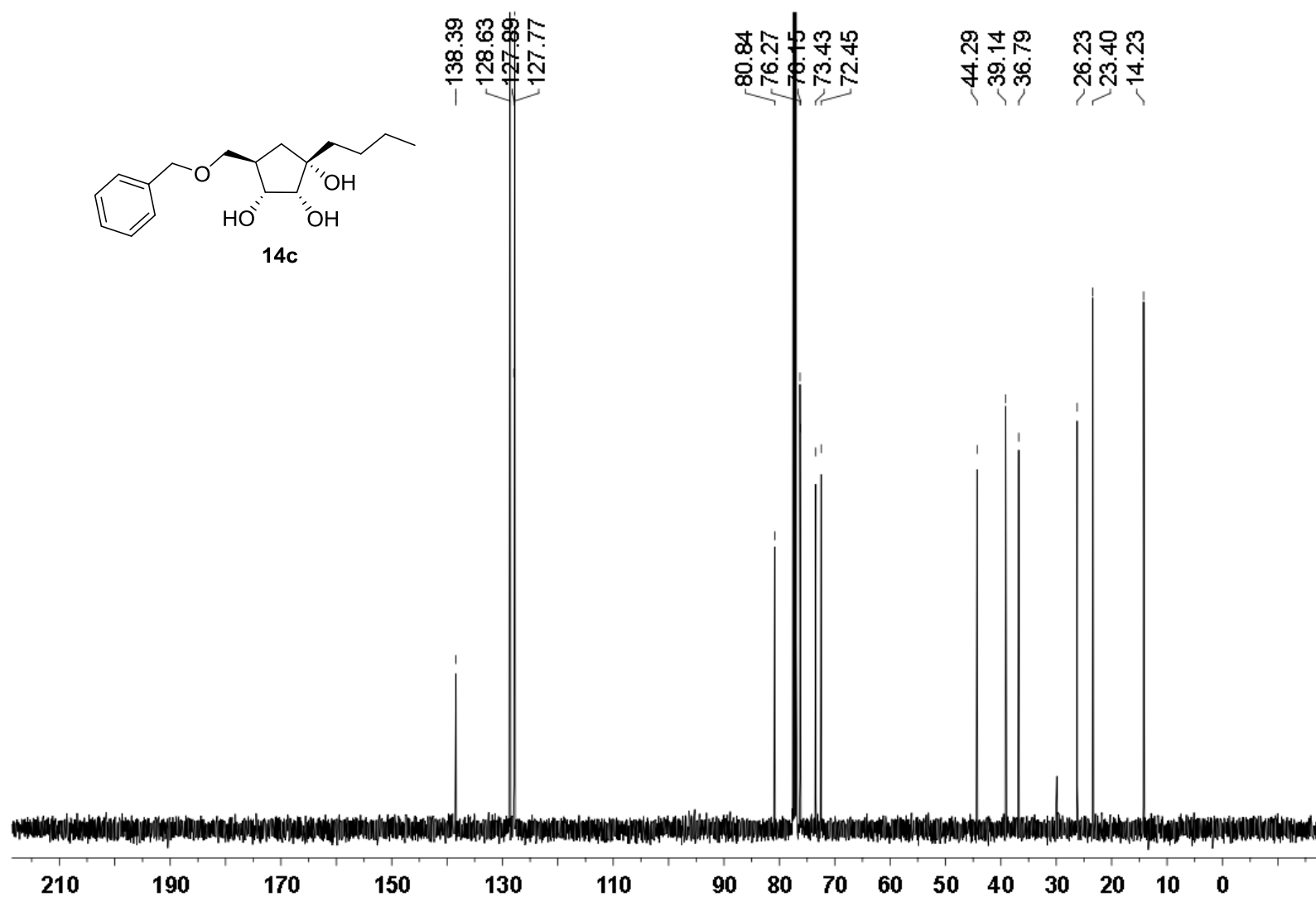
^1H NMR (500 MHz) spectrum of **14a** in CDCl_3



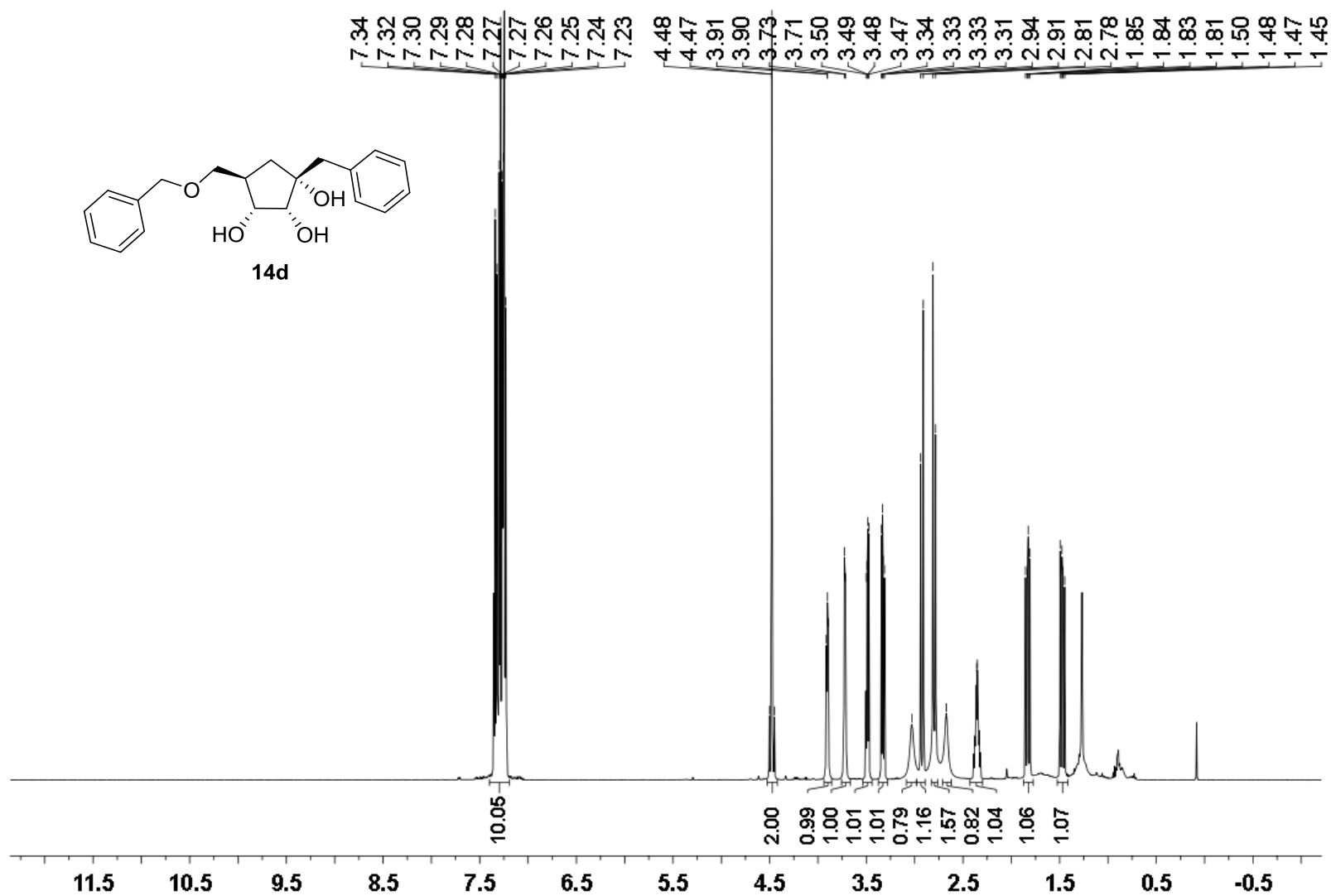
¹³C NMR (126 MHz) spectrum of **14a** in CDCl₃



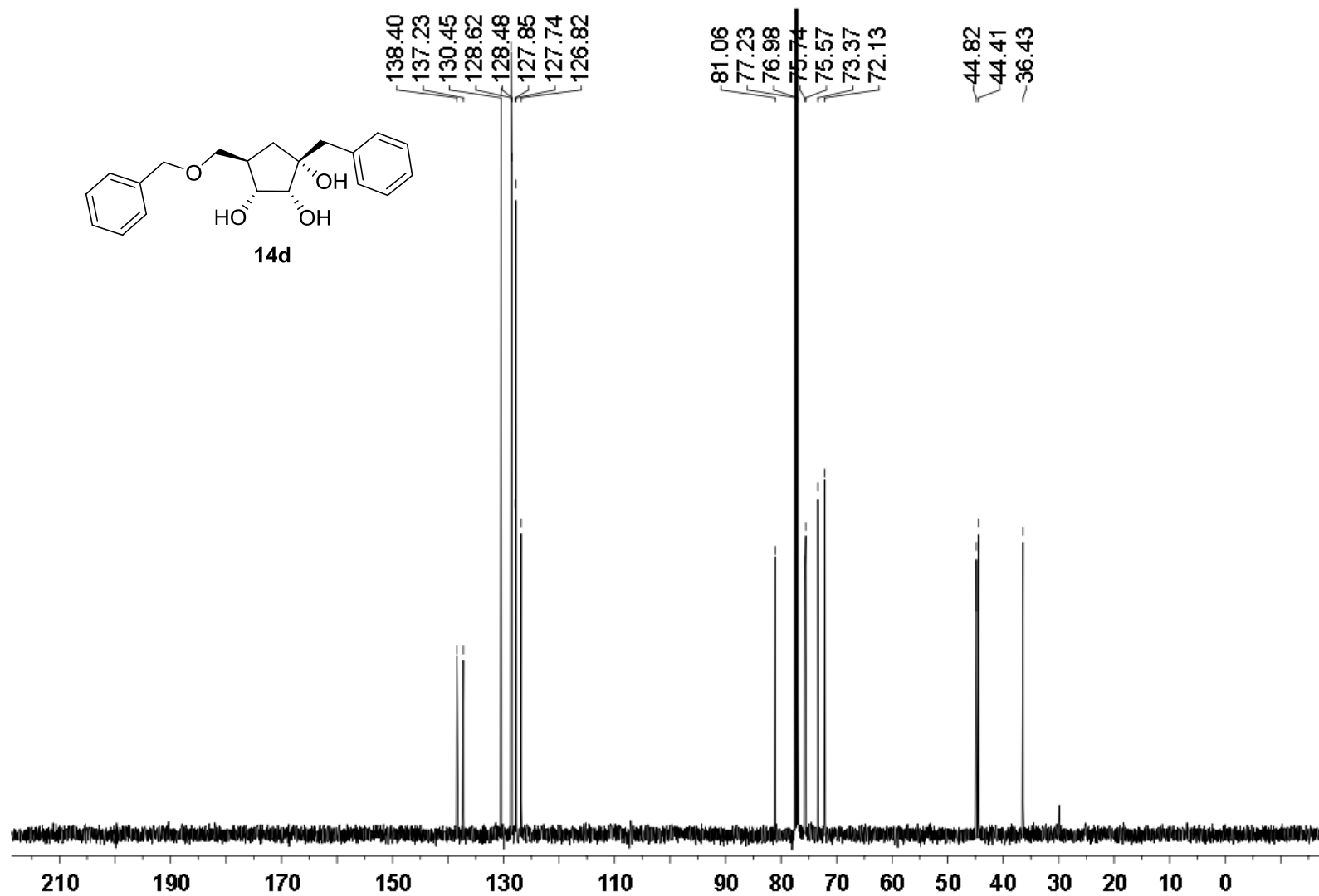
¹H NMR (500 MHz) spectrum of **14c** in CDCl₃



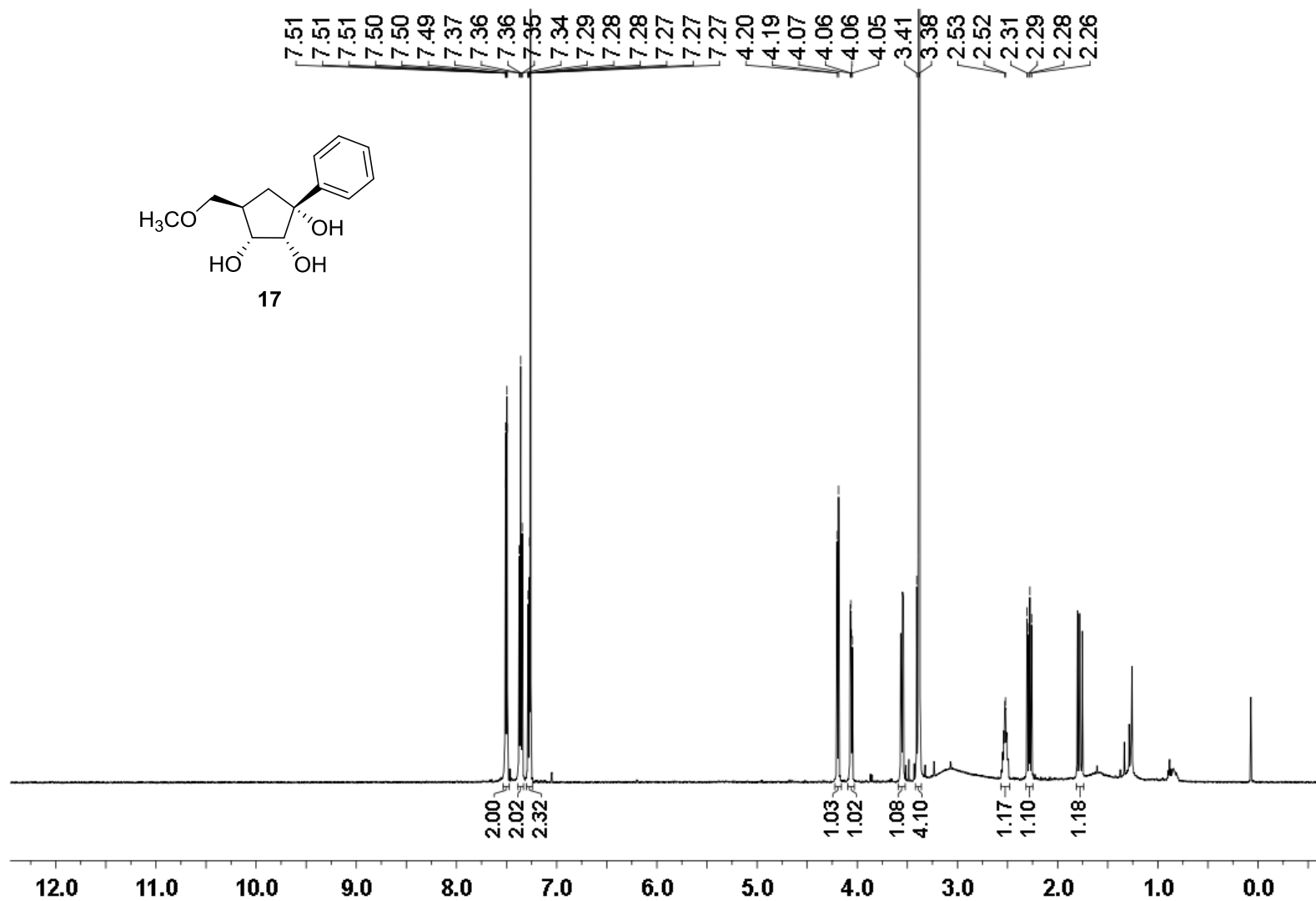
^{13}C NMR (126 MHz) spectrum of **14c** in CDCl_3



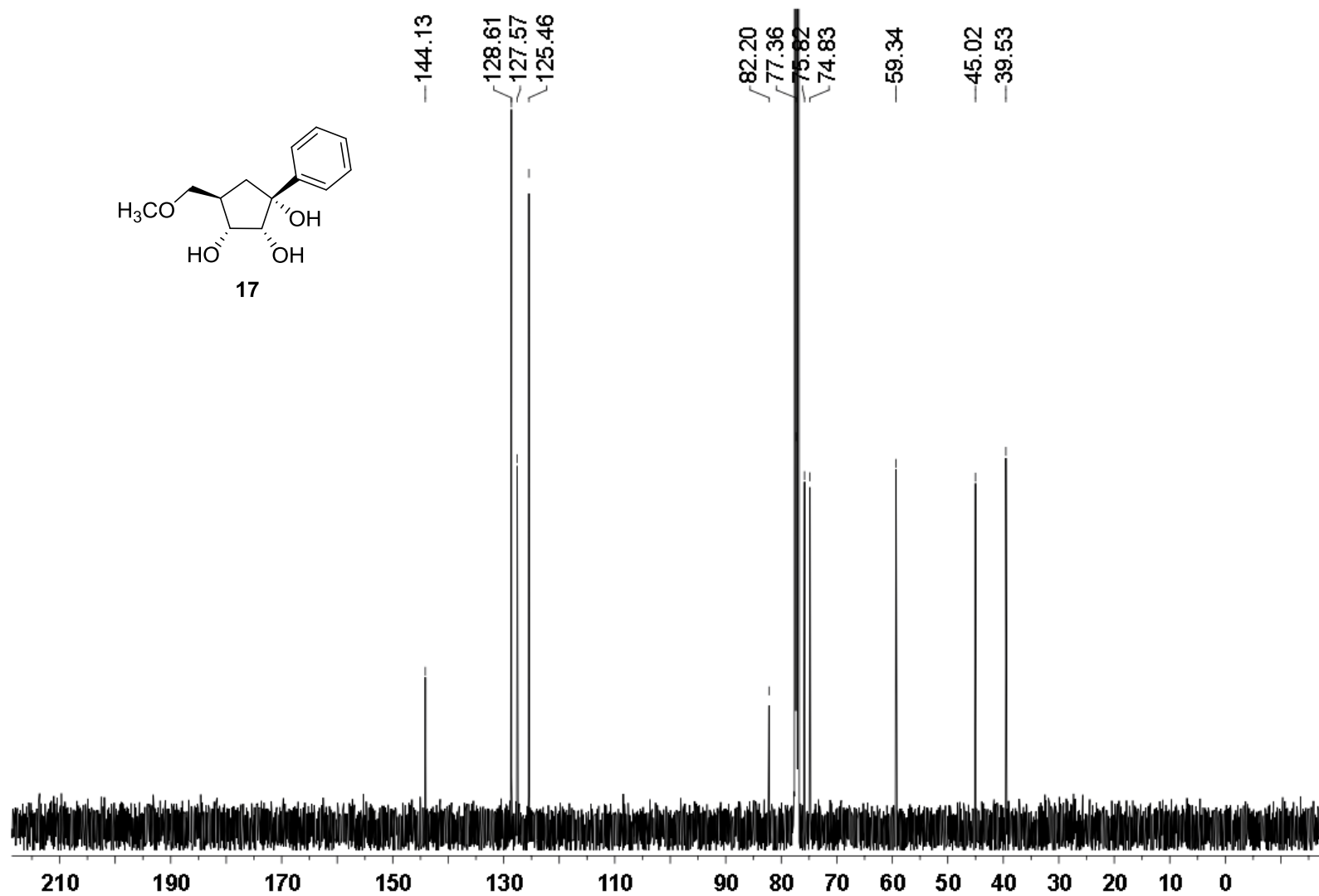
¹H NMR (126 MHz) spectrum of **14d** in CDCl₃



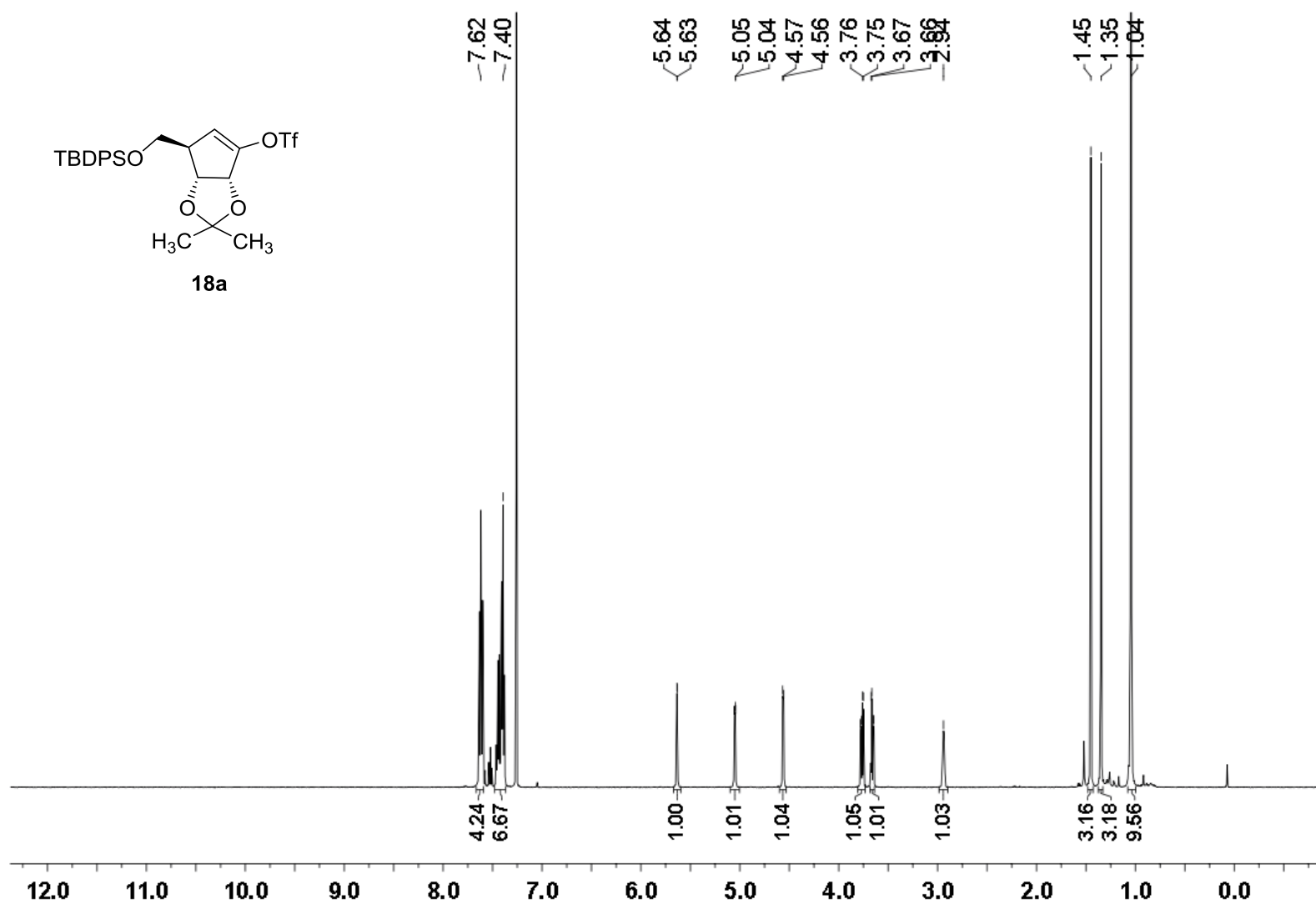
¹³C NMR (126 MHz) spectrum of **14d** in CDCl₃



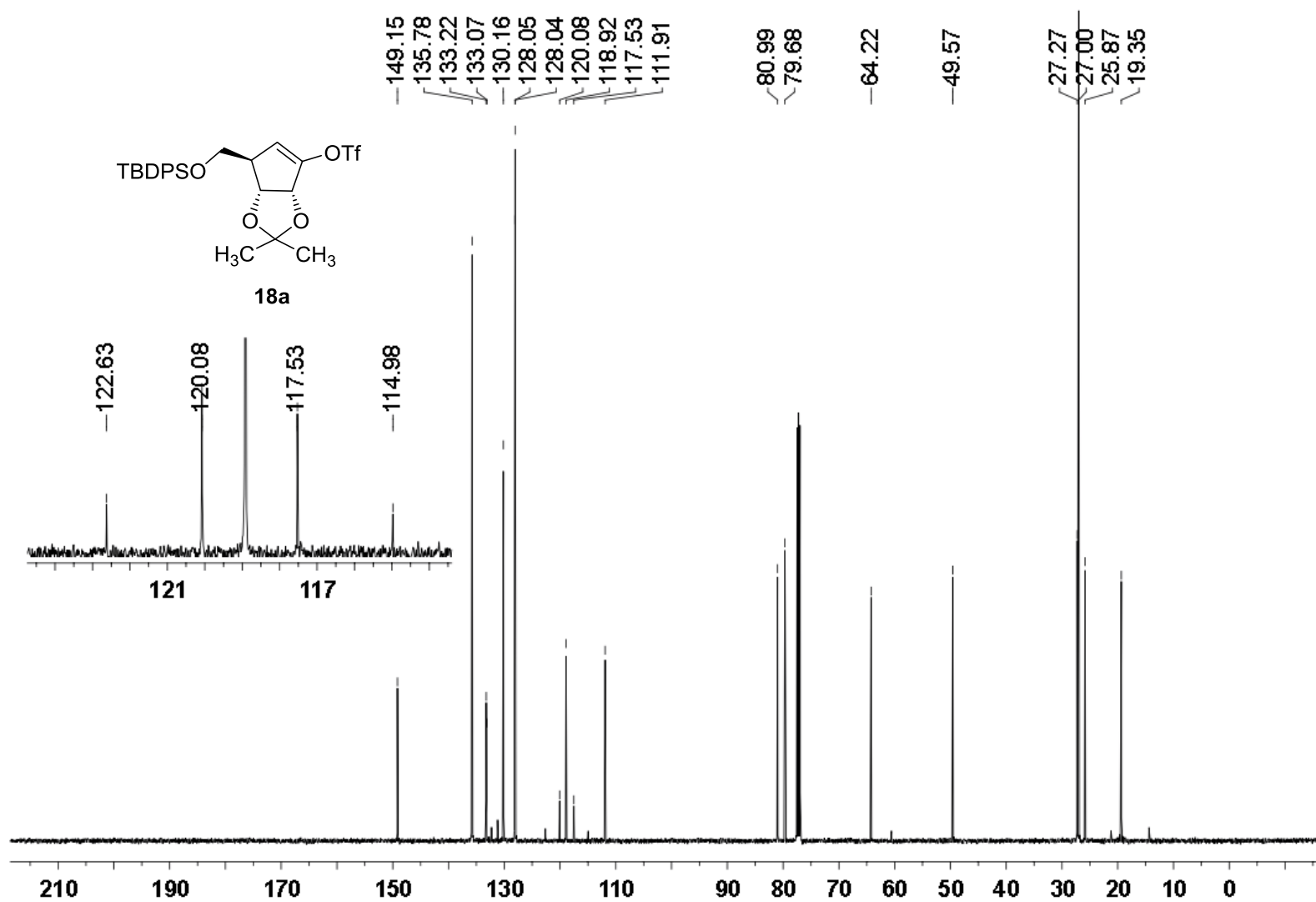
¹H NMR (126 MHz) spectrum of **17** in CDCl₃



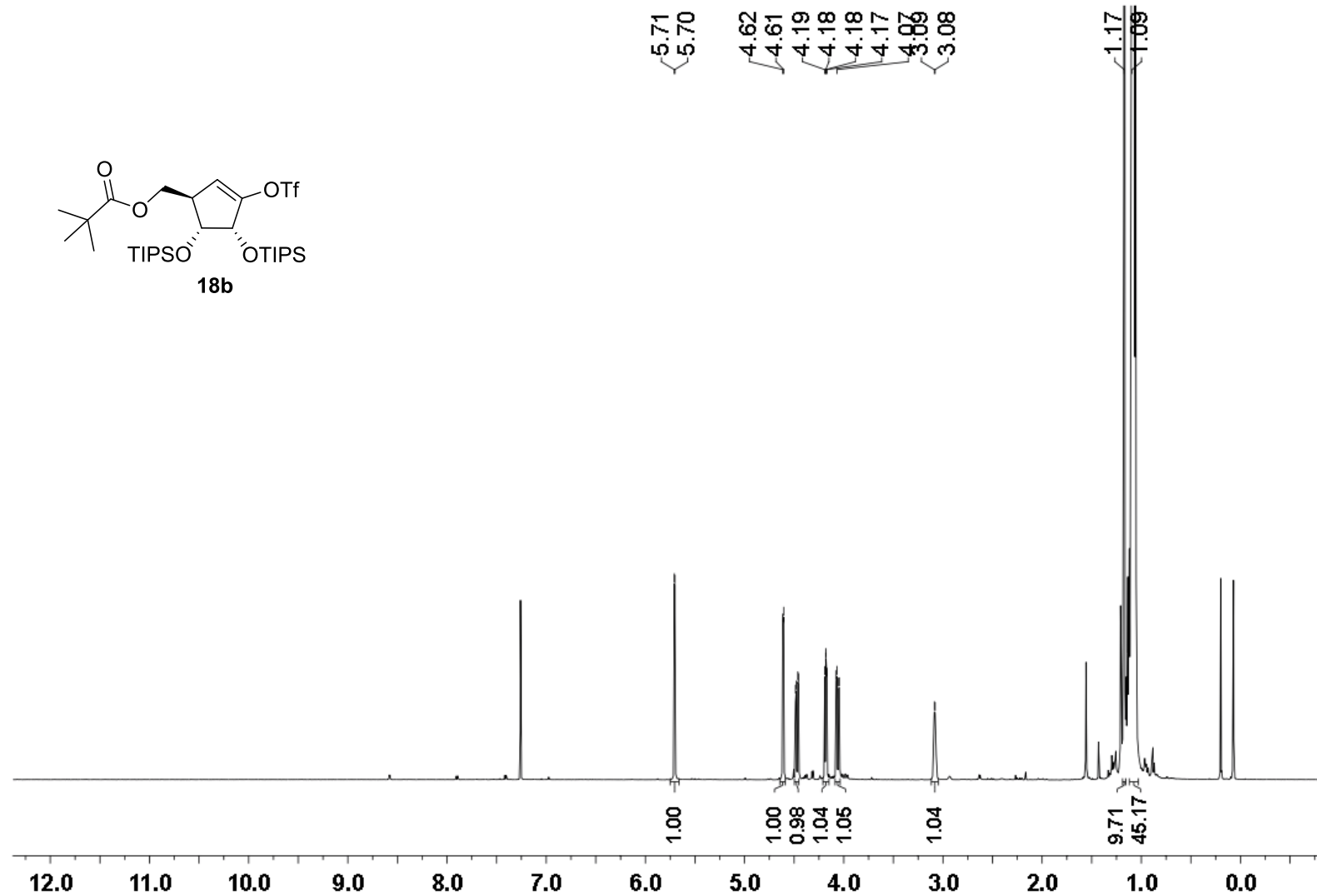
¹³C NMR (126 MHz) spectrum of **17** in CDCl₃



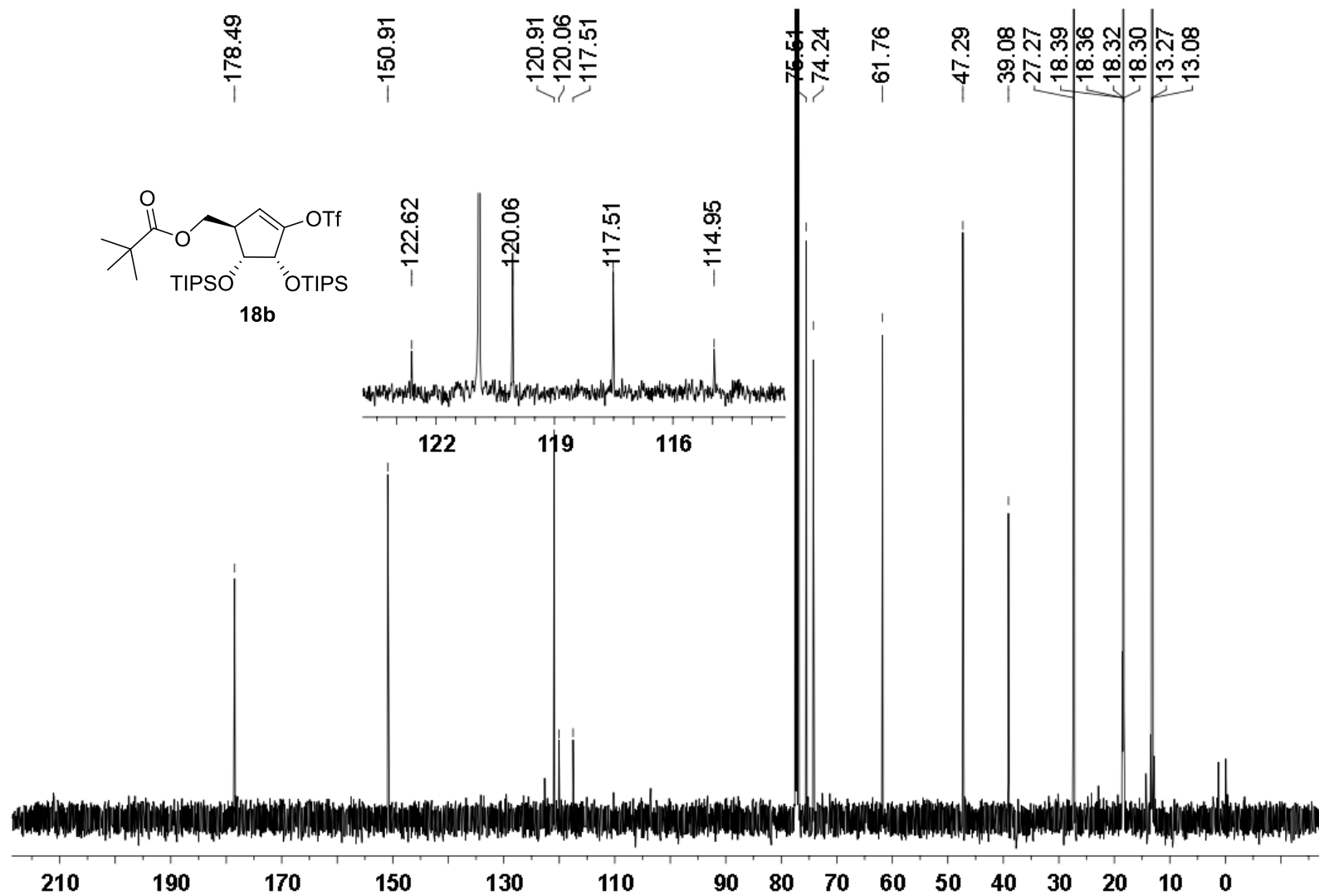
^1H NMR (500 MHz) spectrum of **18a** in CDCl_3



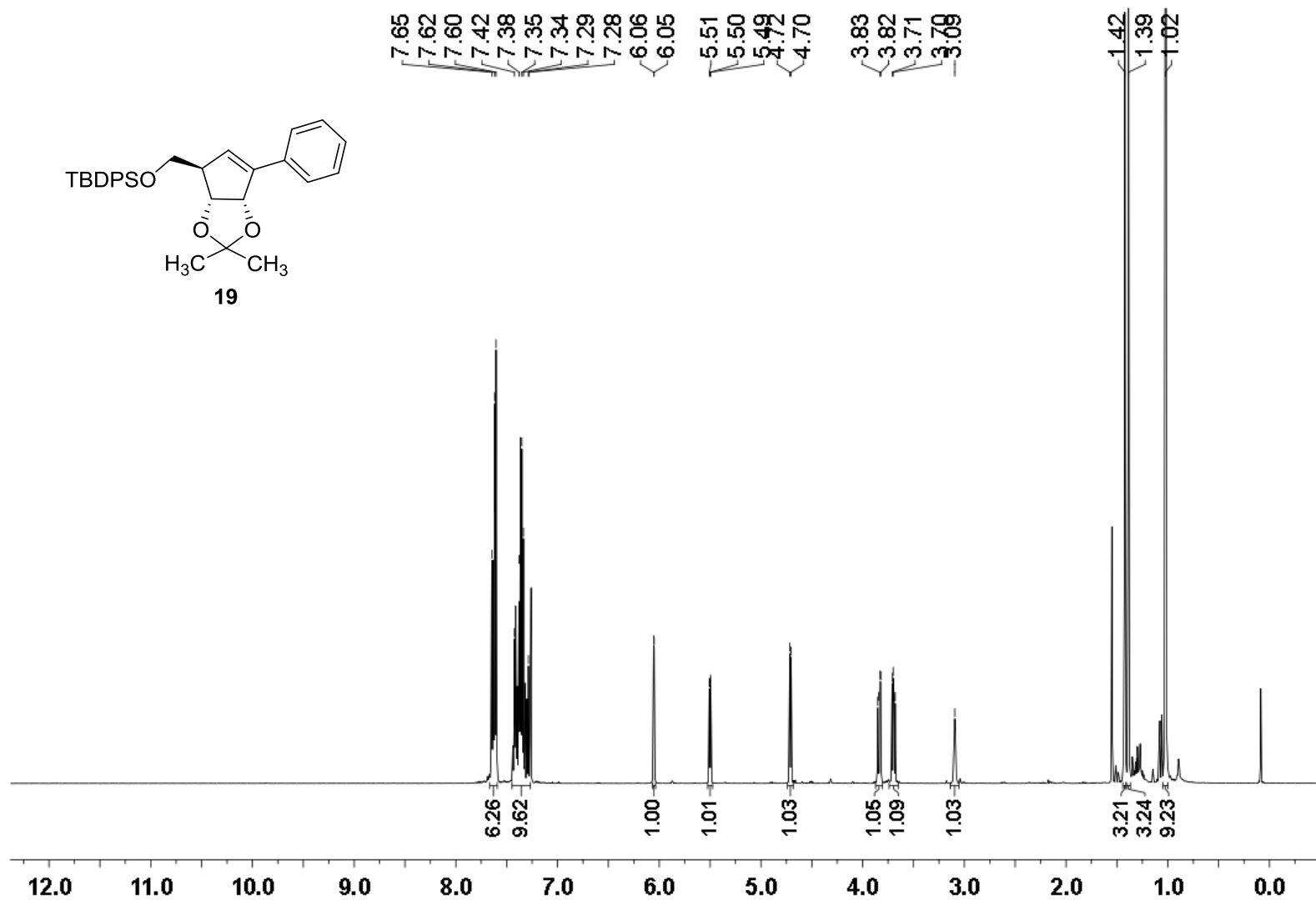
¹³C NMR (126 MHz) spectrum of **18a** in CDCl₃



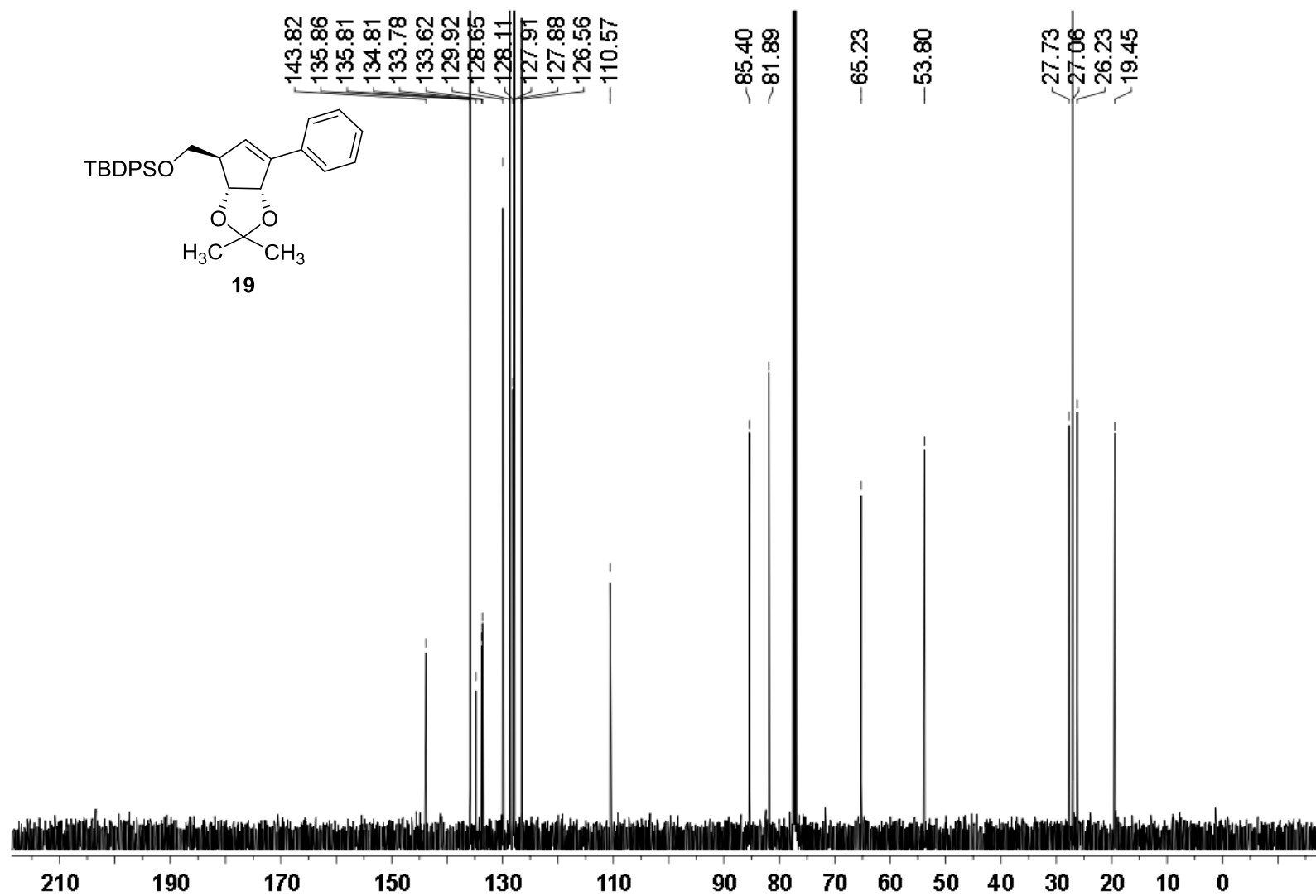
^1H NMR (500 MHz) spectrum of **18b** in CDCl_3



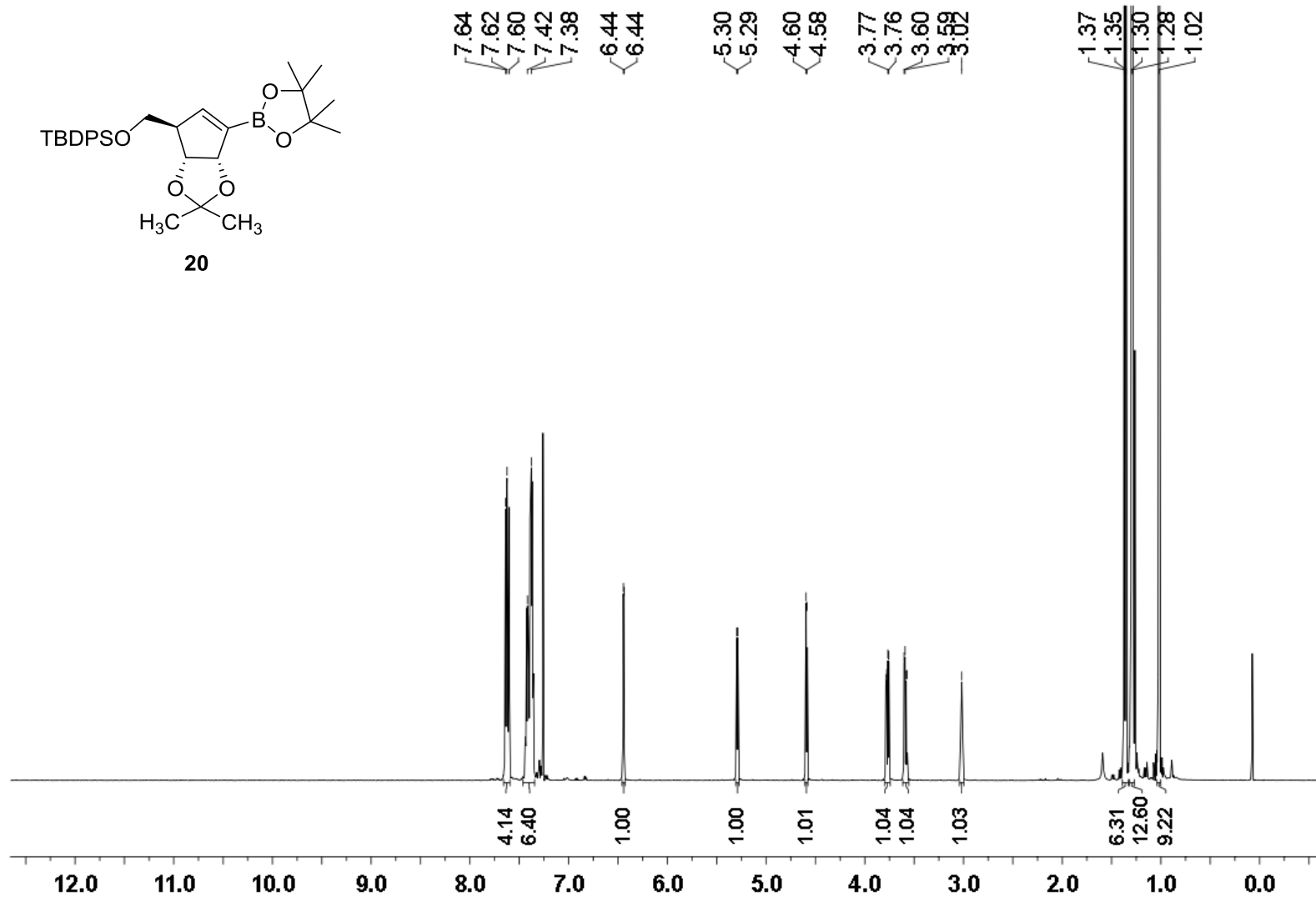
^{13}C NMR (126 MHz) spectrum of **18b** in CDCl_3



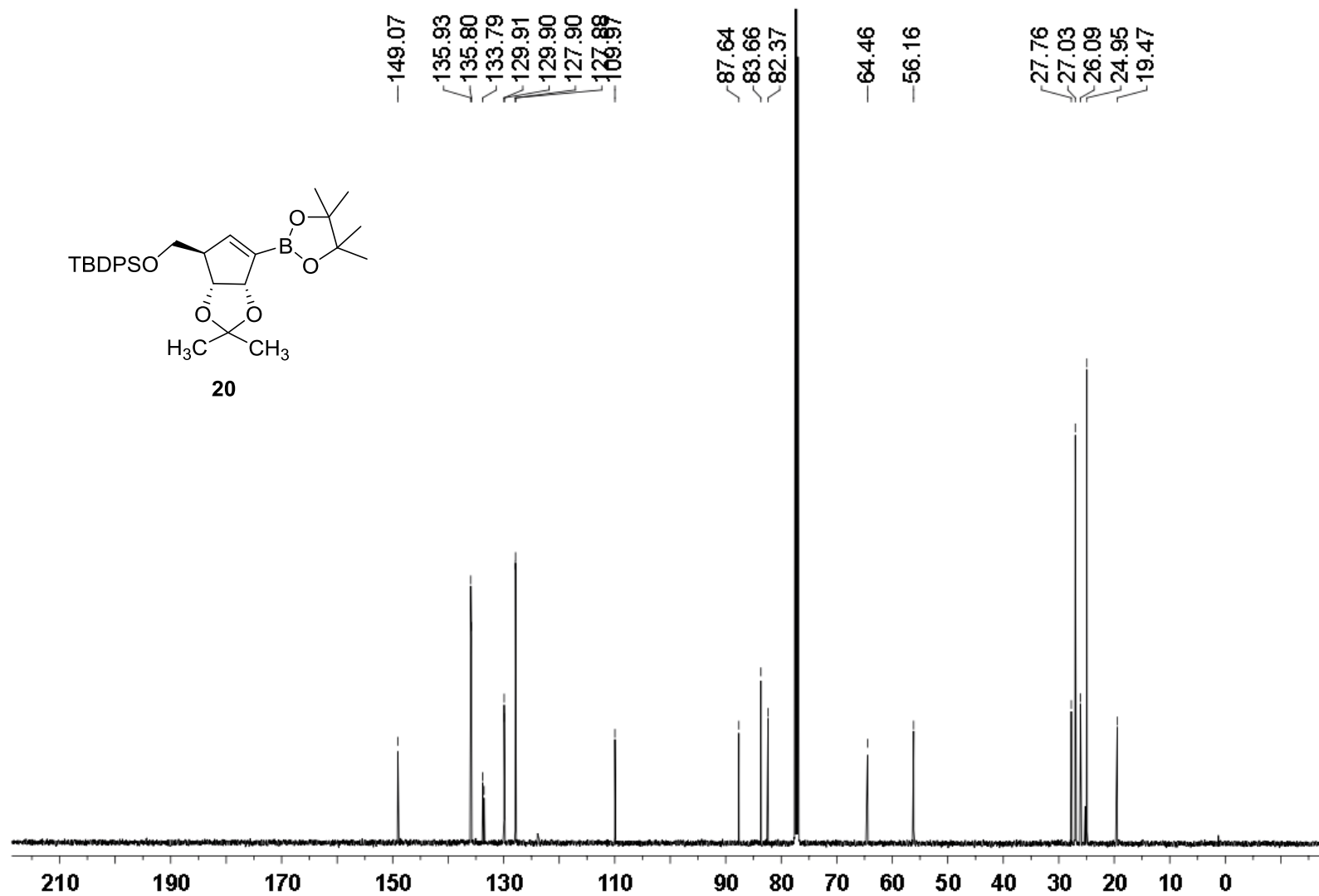
¹H NMR (500 MHz) spectrum of **19** in CDCl₃



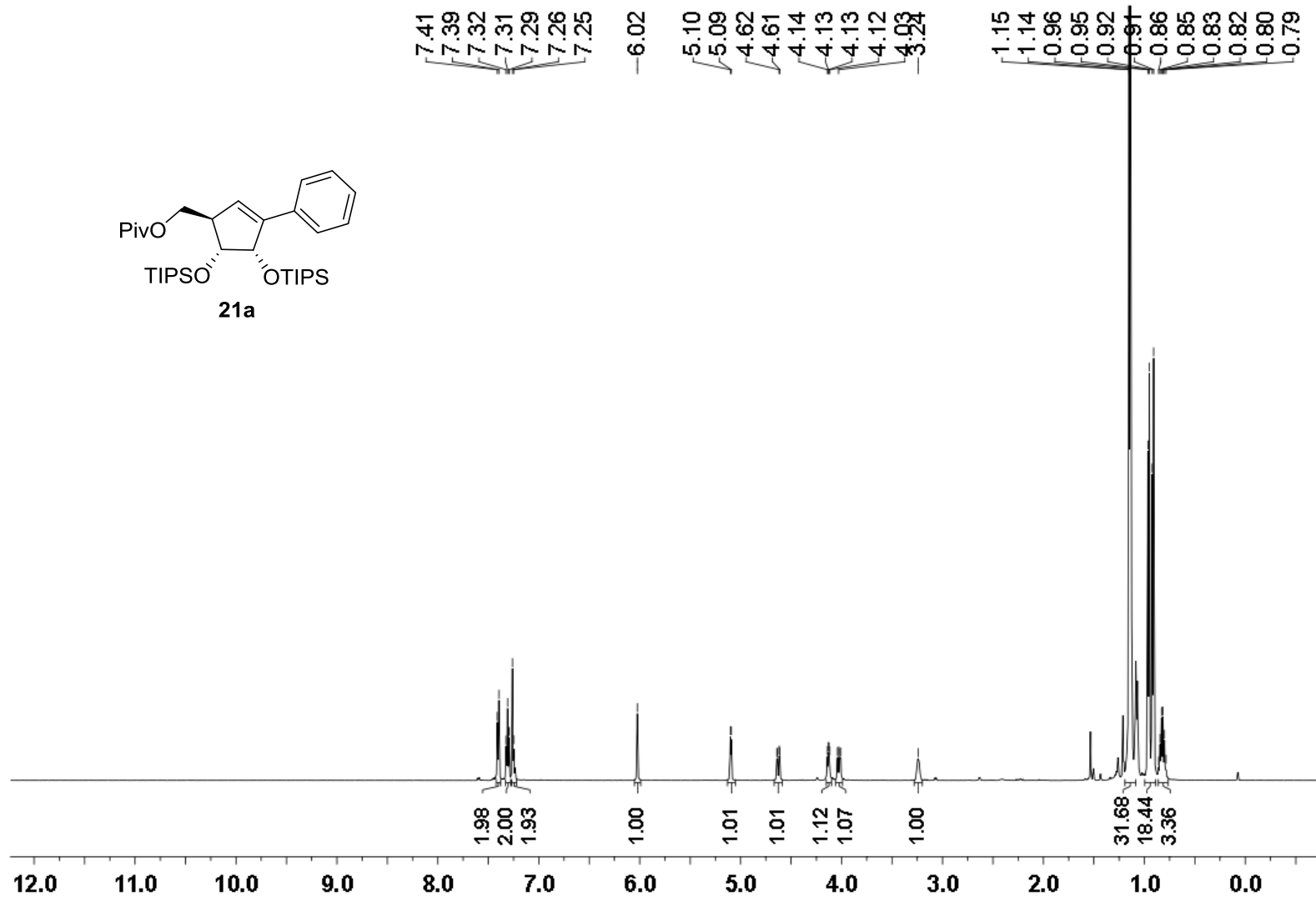
^{13}C NMR (126 MHz) spectrum of **19** in CDCl_3



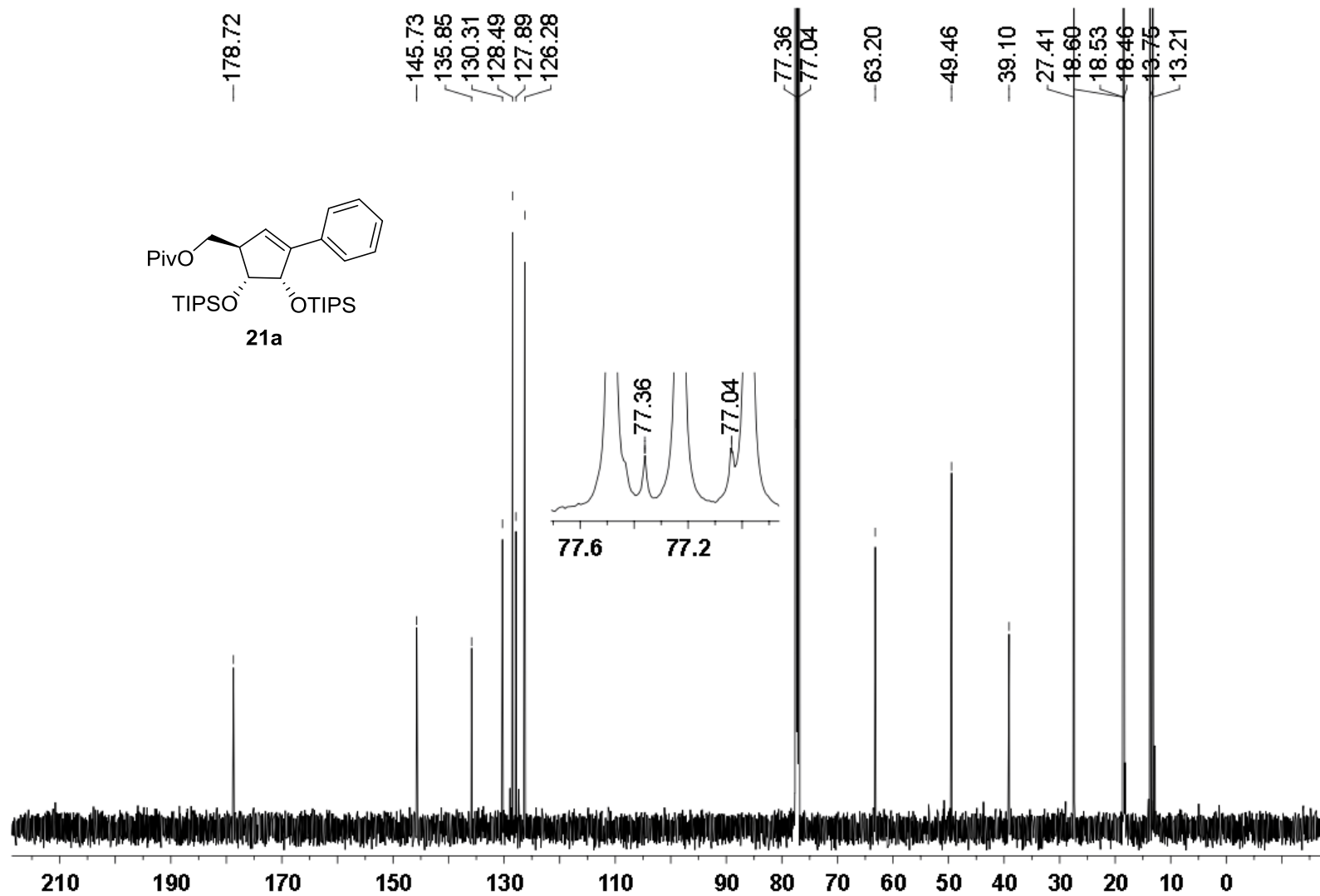
^1H NMR (500 MHz) spectrum of **20** in CDCl_3



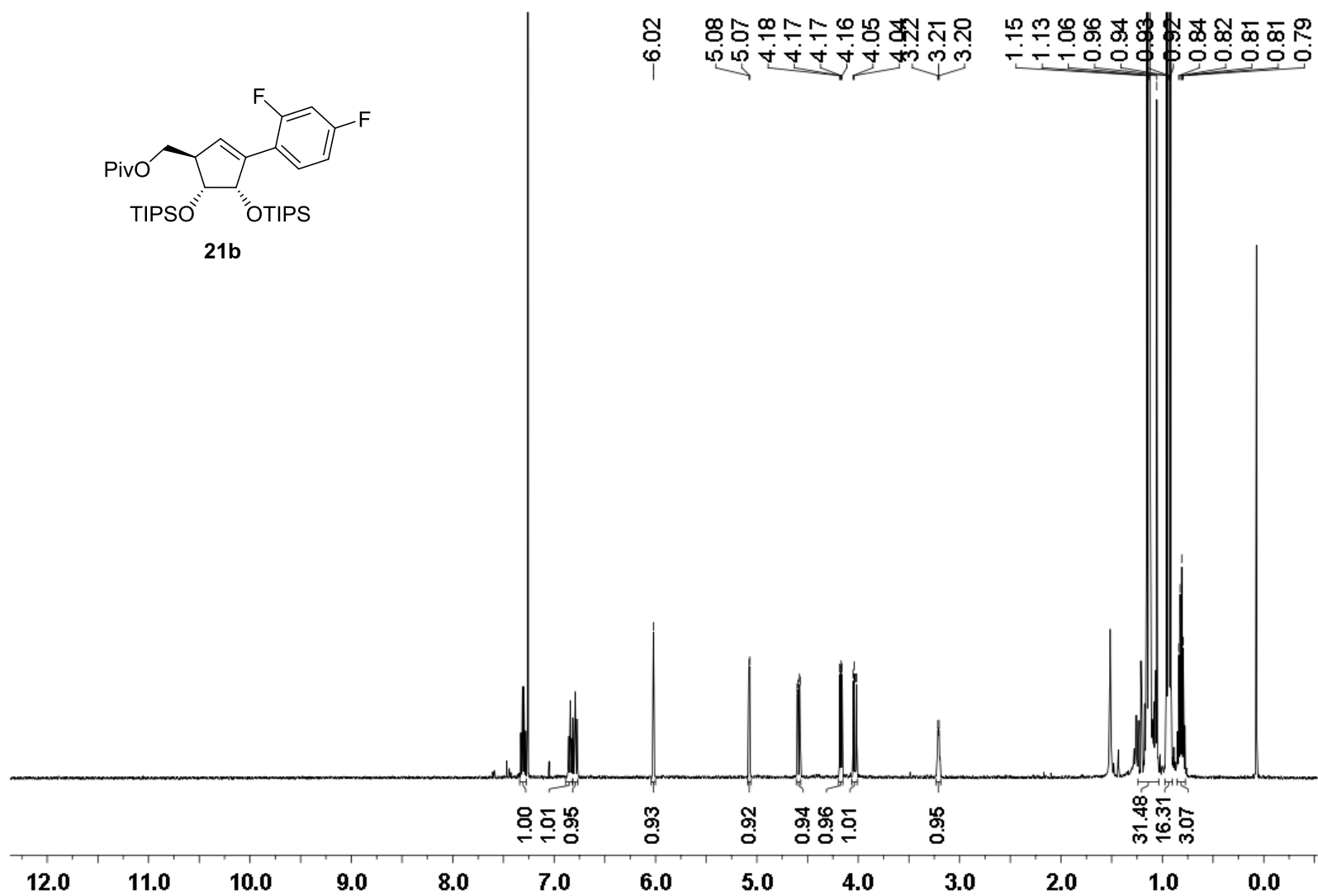
^{13}C NMR (126 MHz) spectrum of **20** in CDCl_3



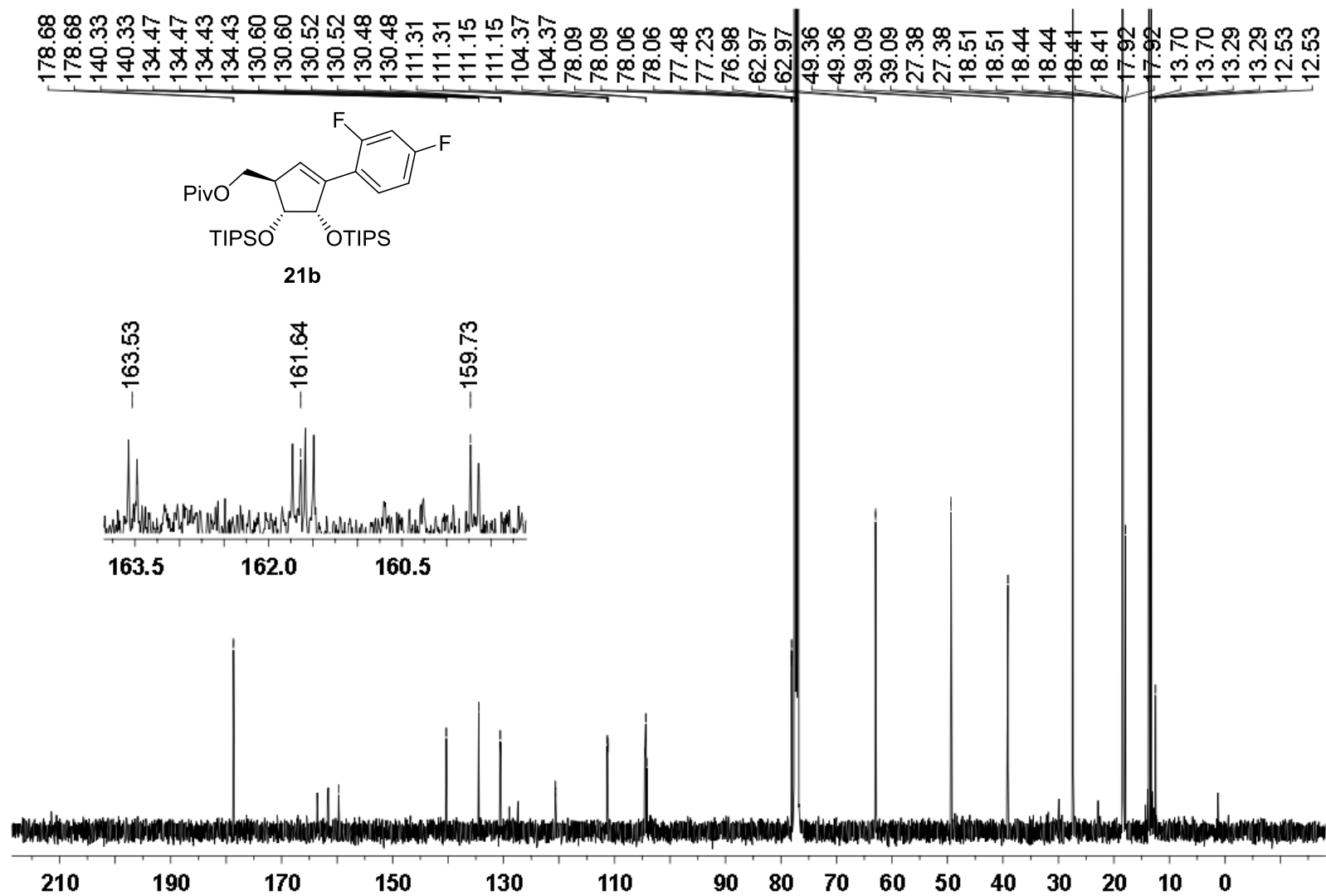
¹H NMR (500 MHz) spectrum of **21a** in CDCl₃



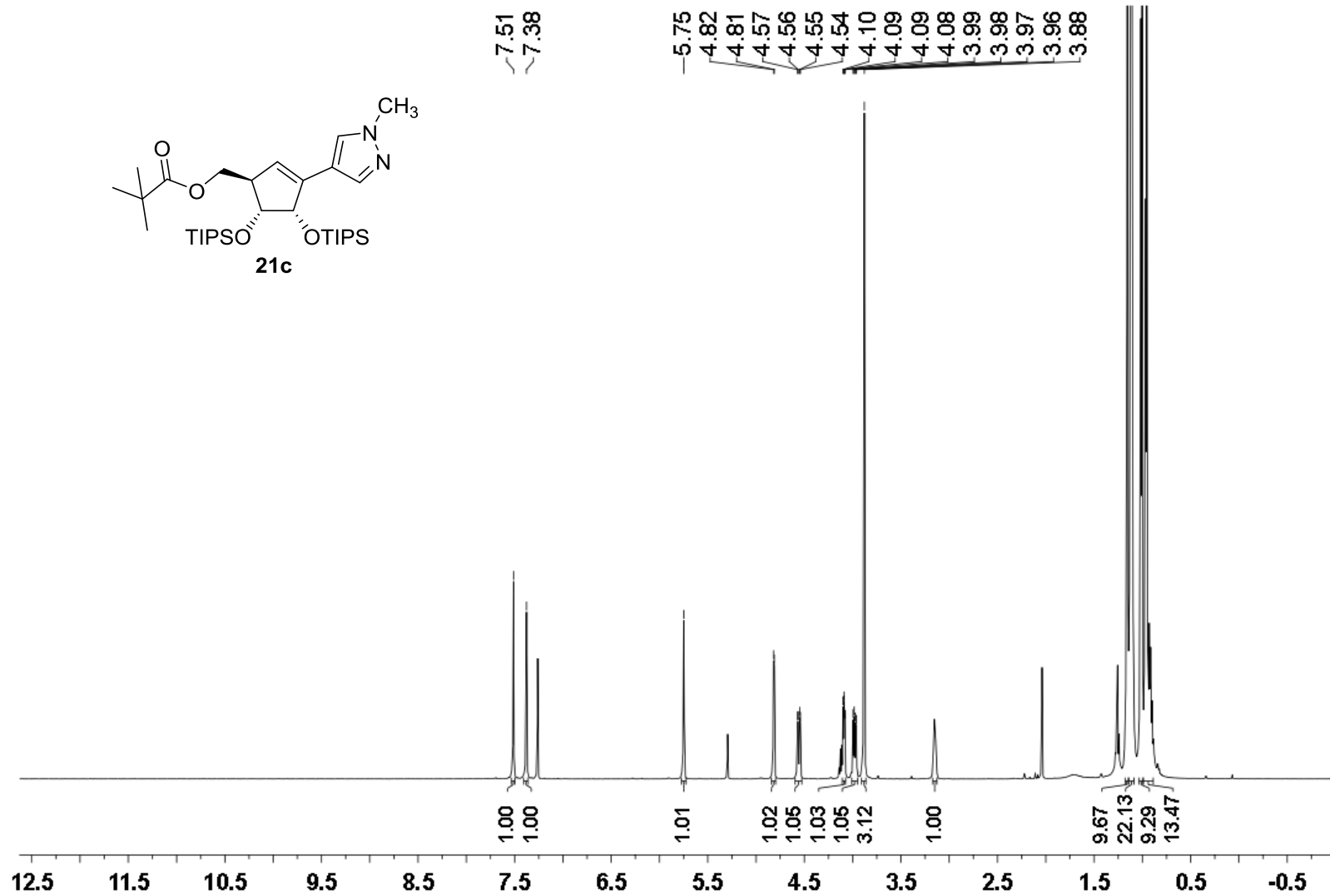
¹³C NMR (126 MHz) spectrum of **21a** in CDCl₃



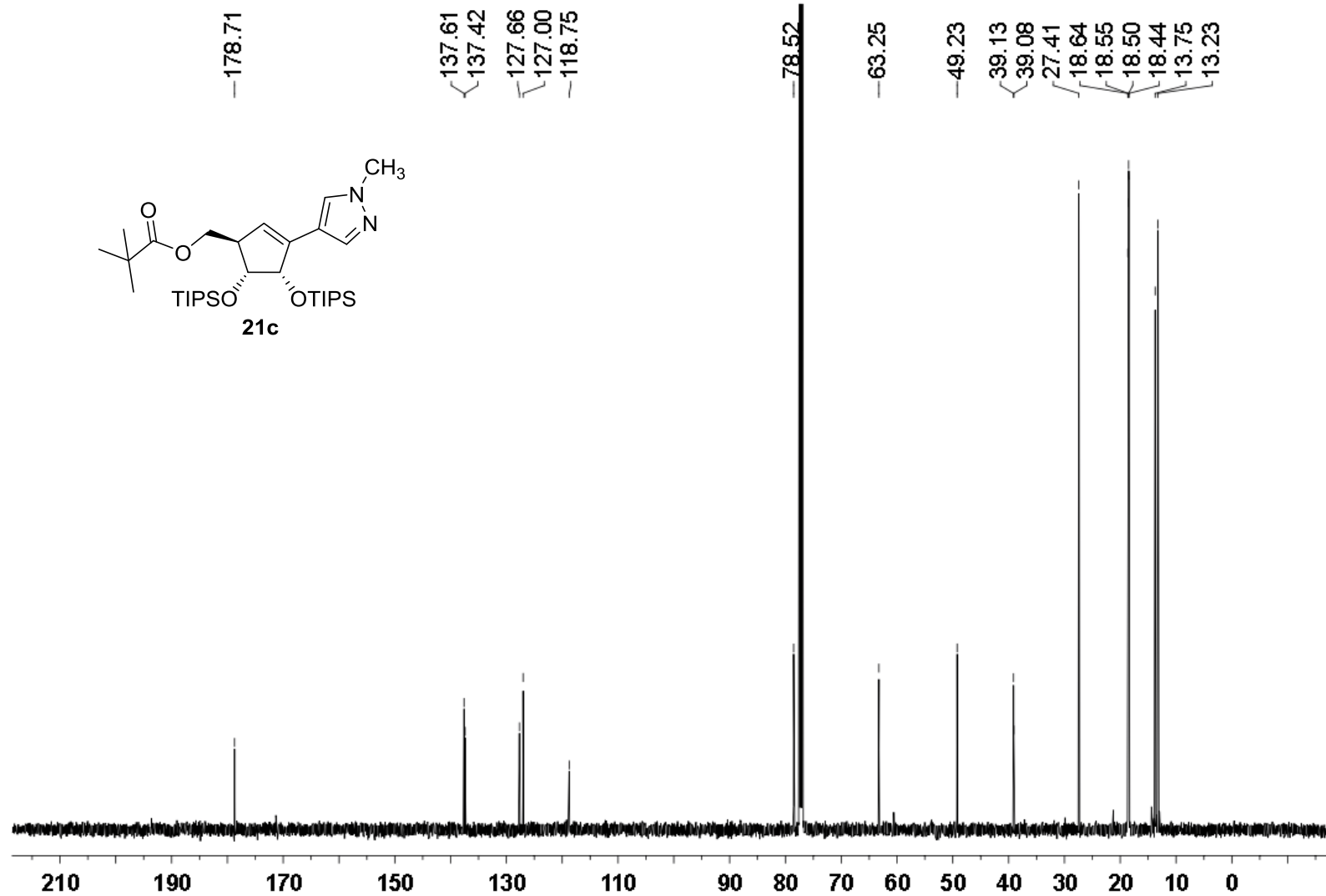
¹H NMR (500 MHz) spectrum of **21b** in CDCl₃



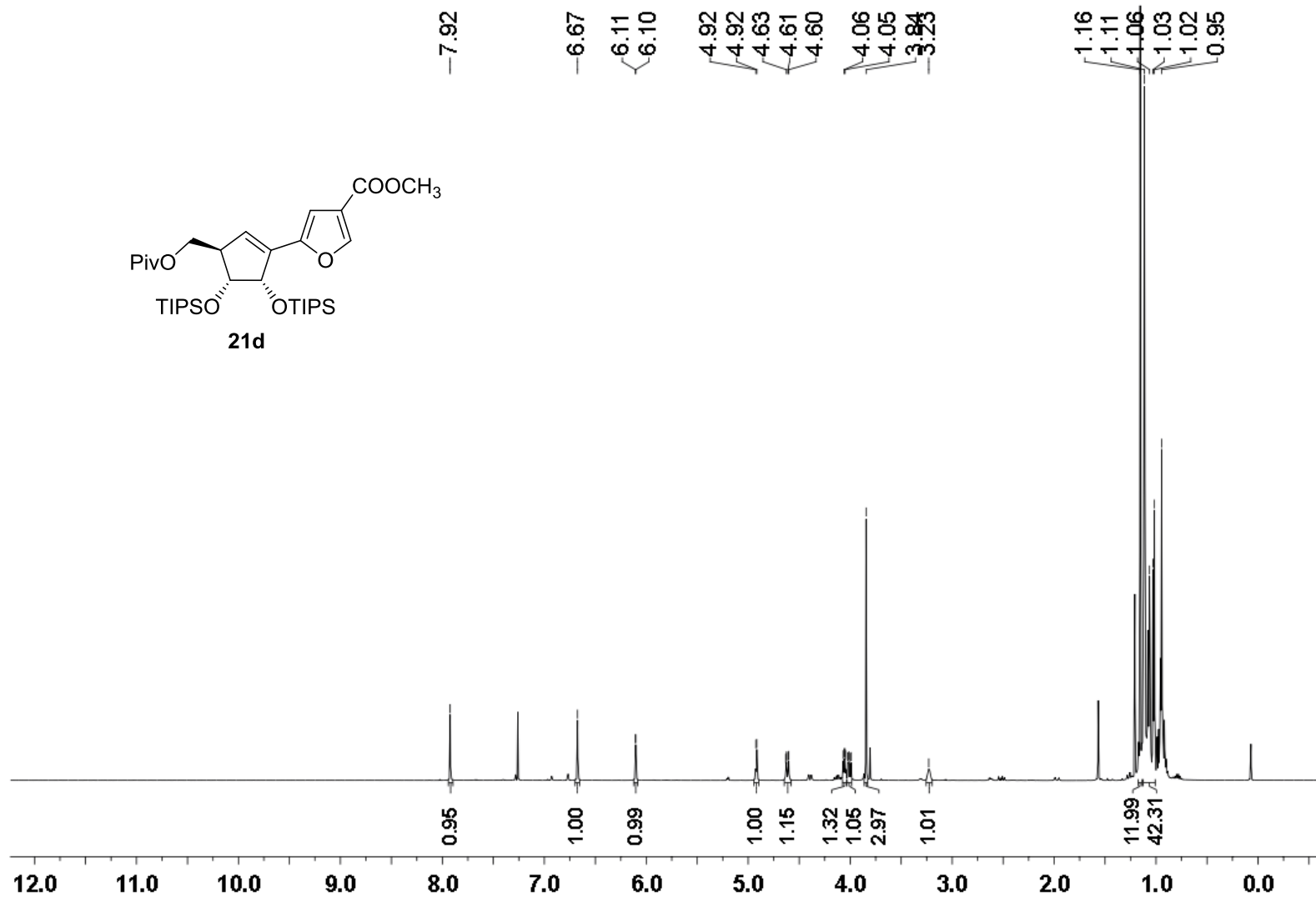
¹³C NMR (126 MHz) spectrum of **21b** in CDCl₃



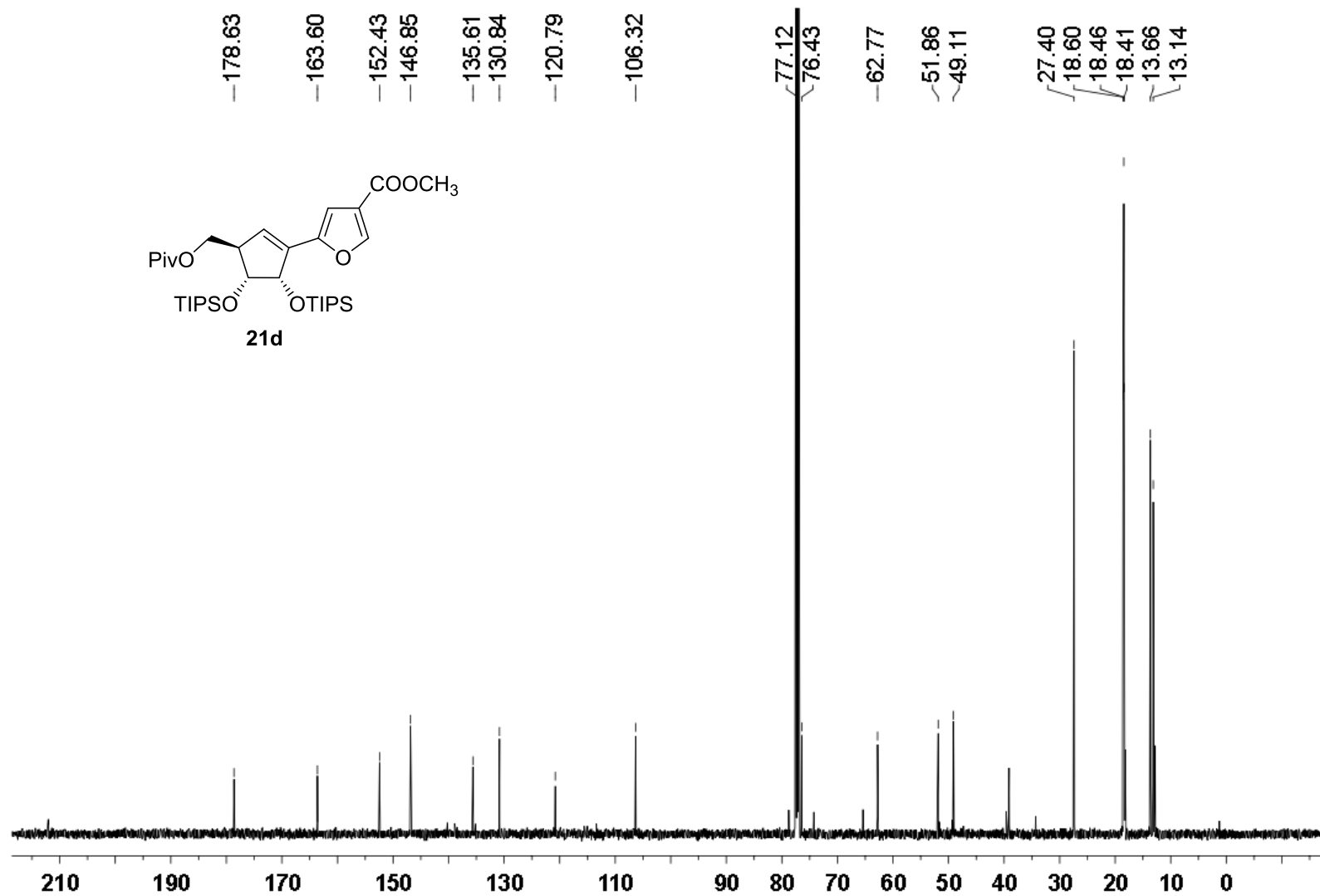
^1H NMR (500 MHz) spectrum of **21c** in CDCl_3



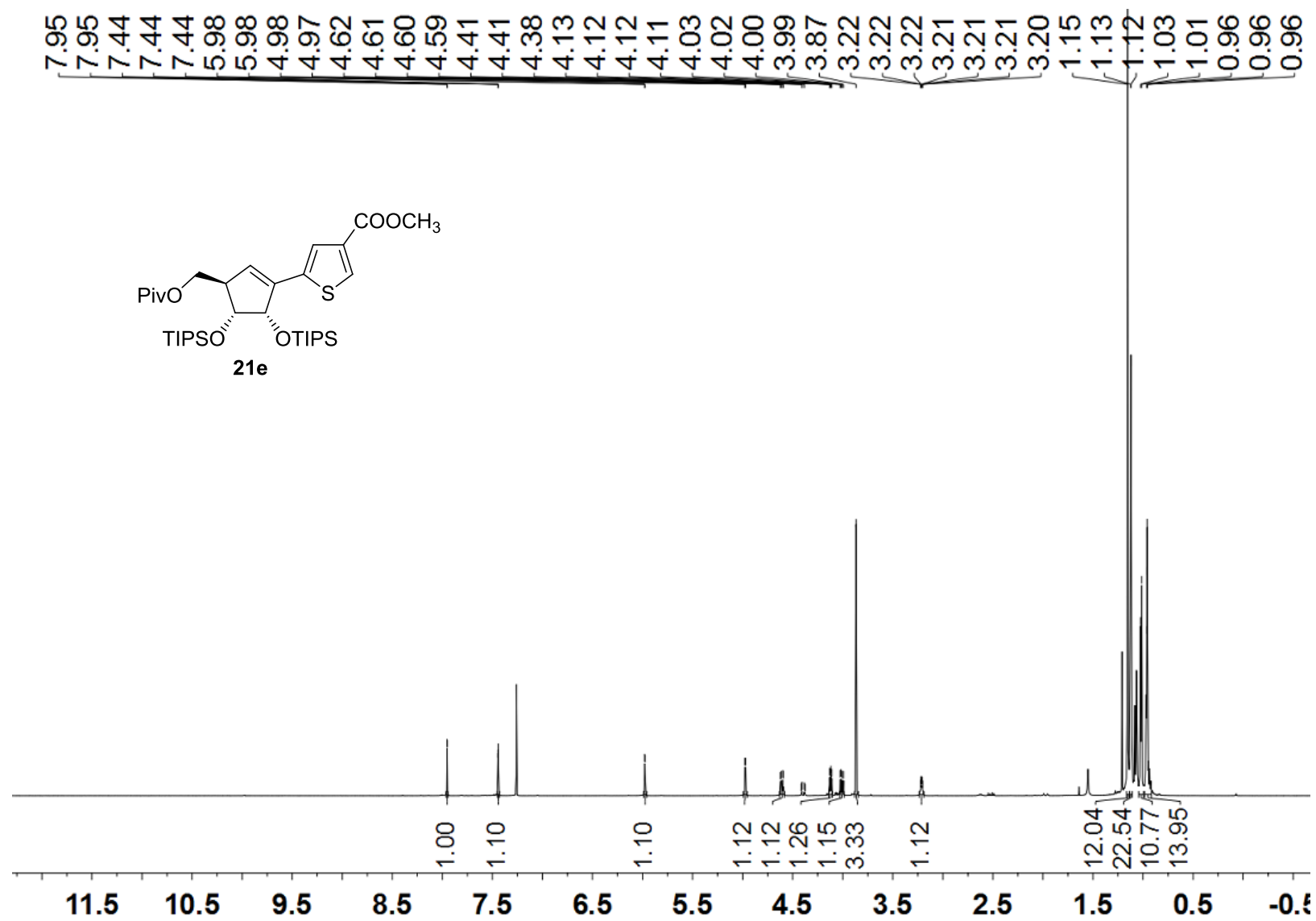
^{13}C NMR (126 MHz) spectrum of **21c** in CDCl_3



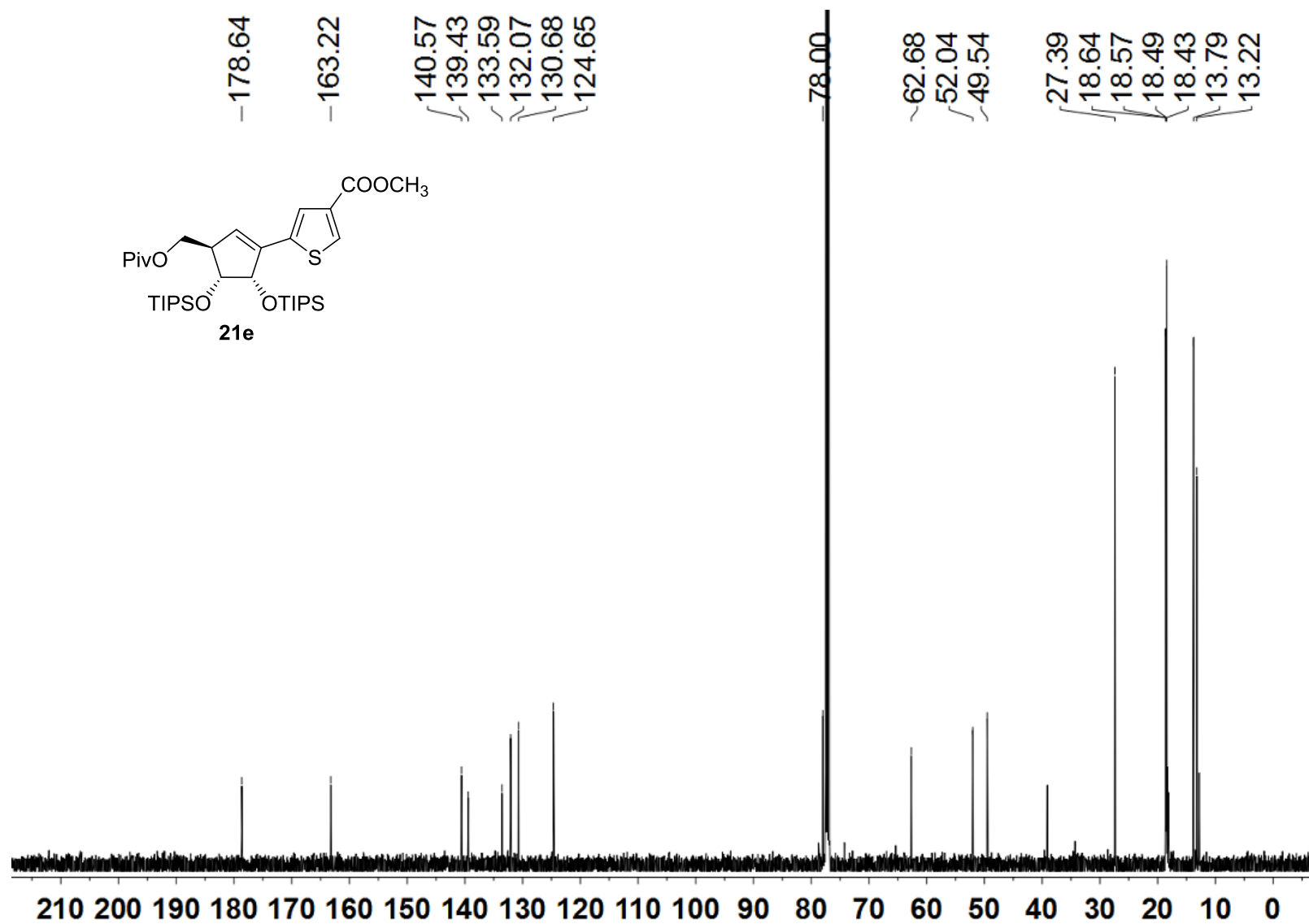
¹H NMR (500 MHz) spectrum of **21d** in CDCl₃



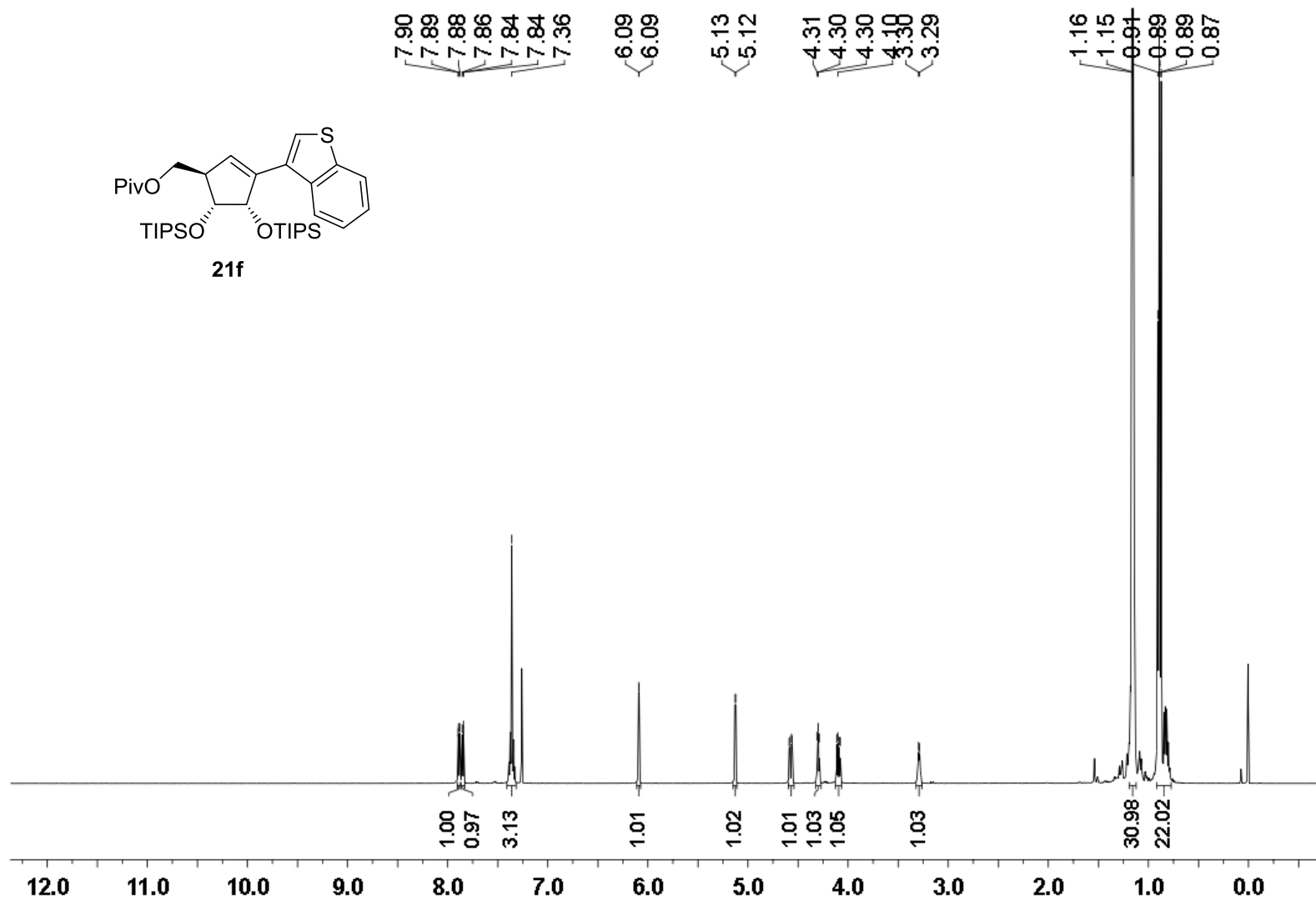
¹³C NMR (126 MHz) spectrum of **21d** in CDCl₃



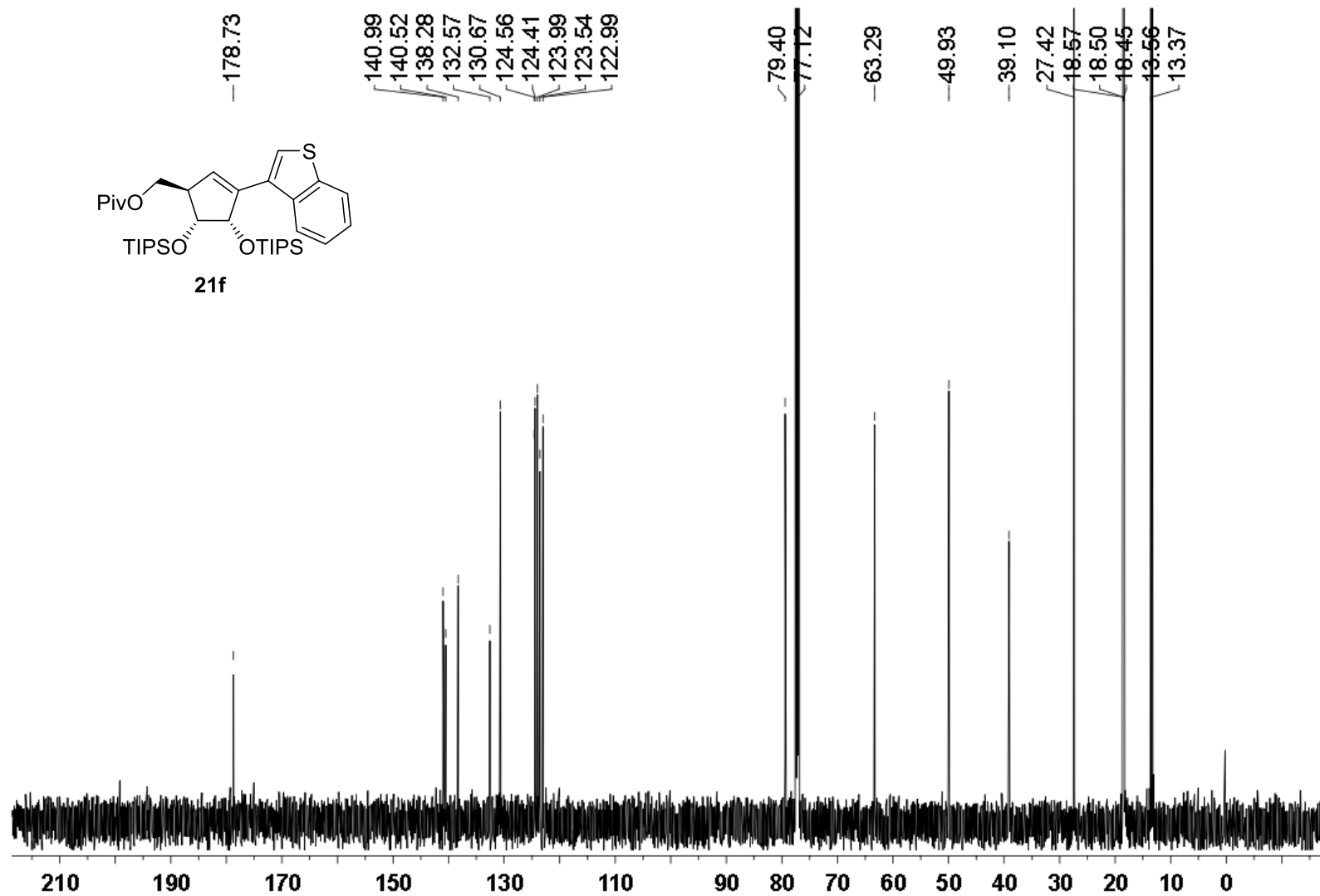
¹H NMR (500 MHz) spectrum of **21e** in CDCl₃



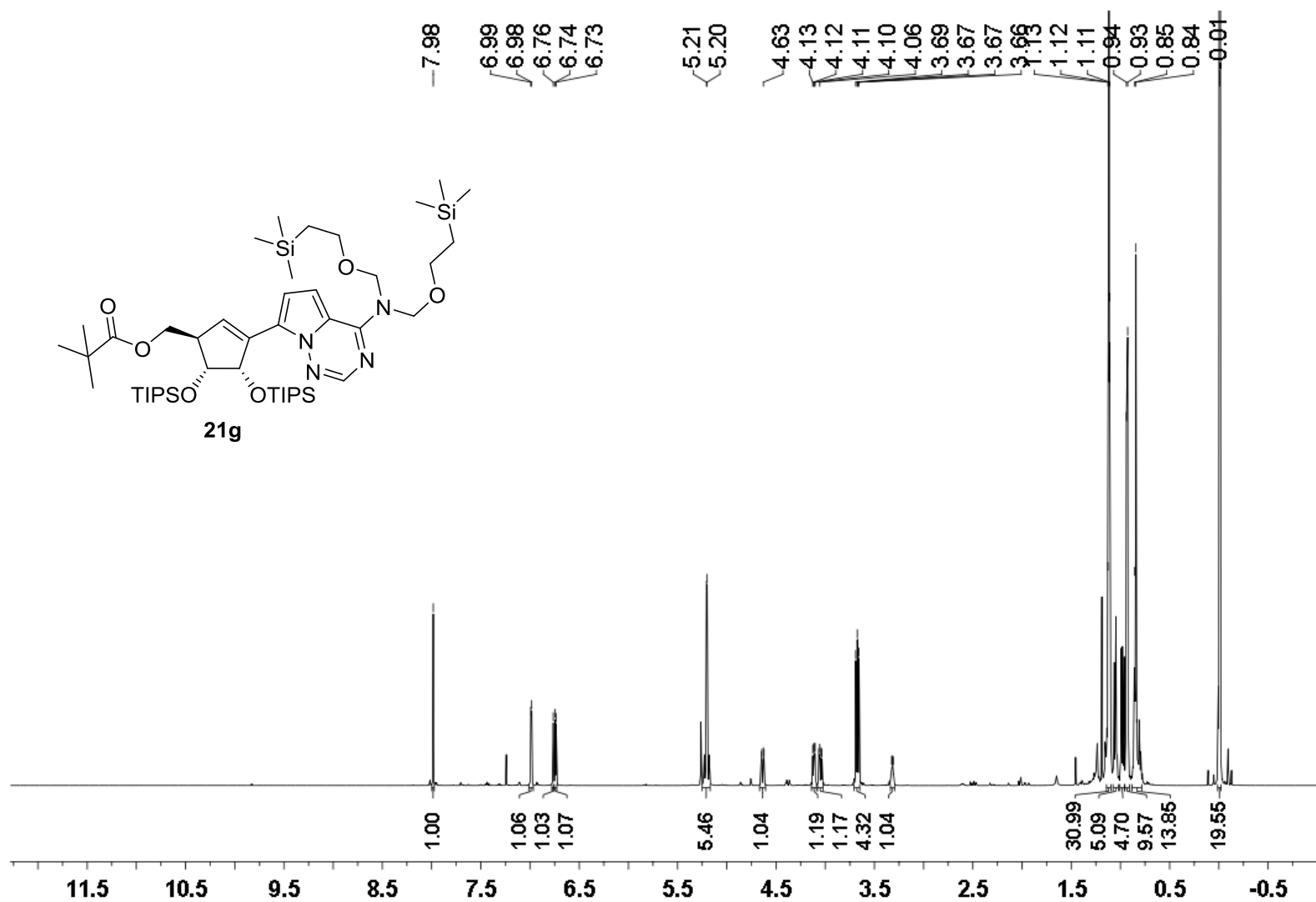
¹³C NMR (126 MHz) spectrum of **21e** in CDCl₃



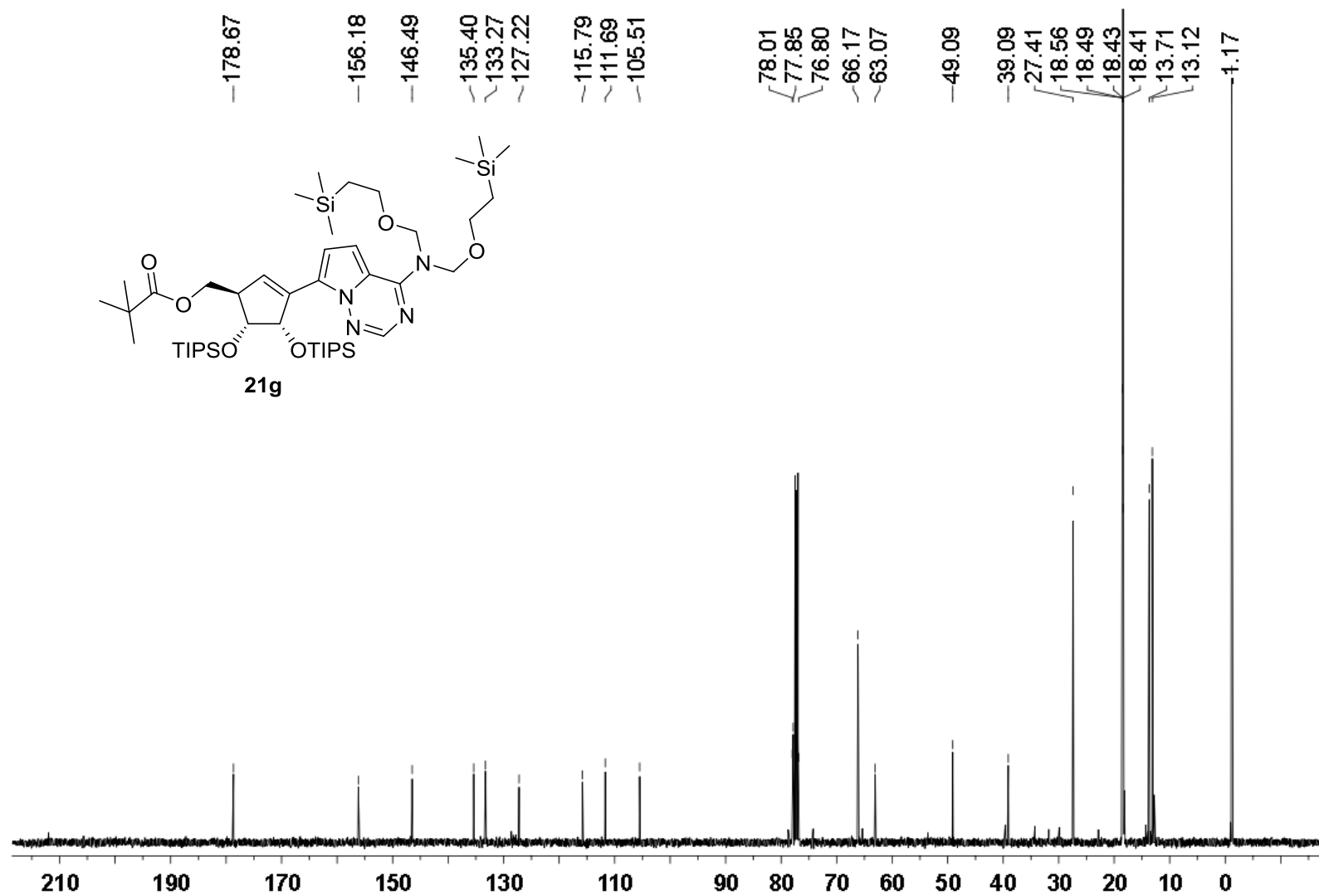
^1H NMR (500 MHz) spectrum of **21f** in CDCl_3



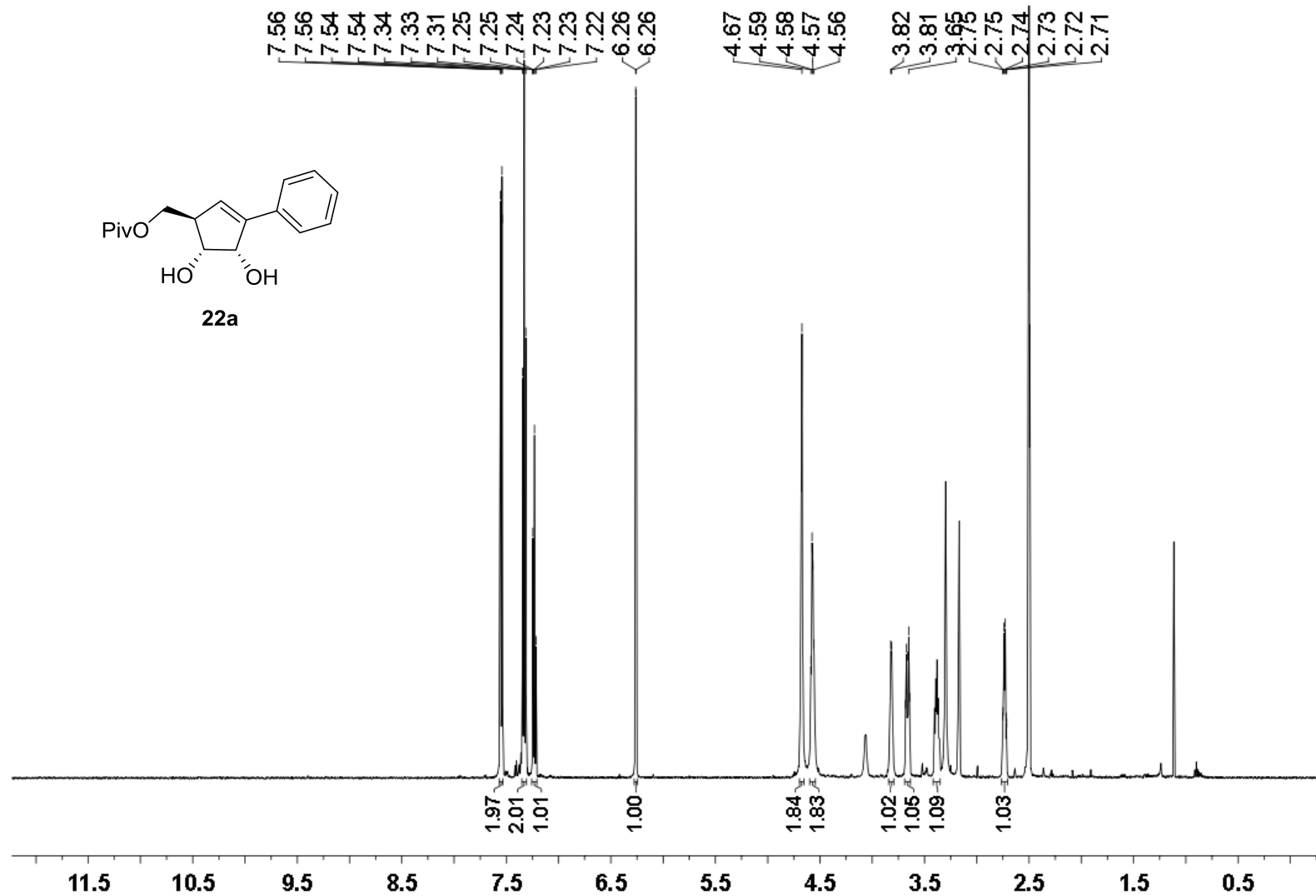
¹³C NMR (126 MHz) spectrum of **21f** in CDCl₃



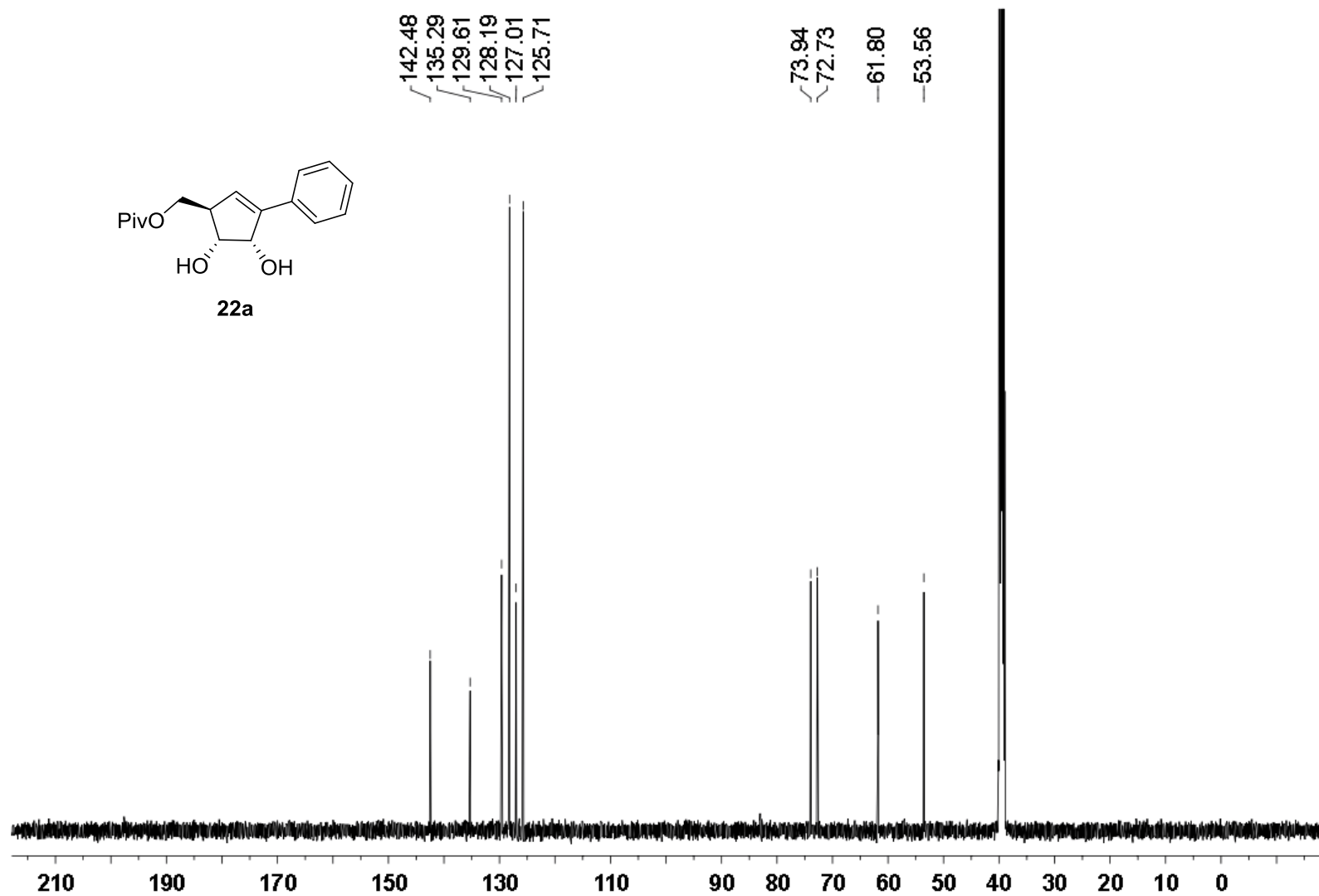
¹H NMR (500 MHz) spectrum of **21g** in CDCl₃



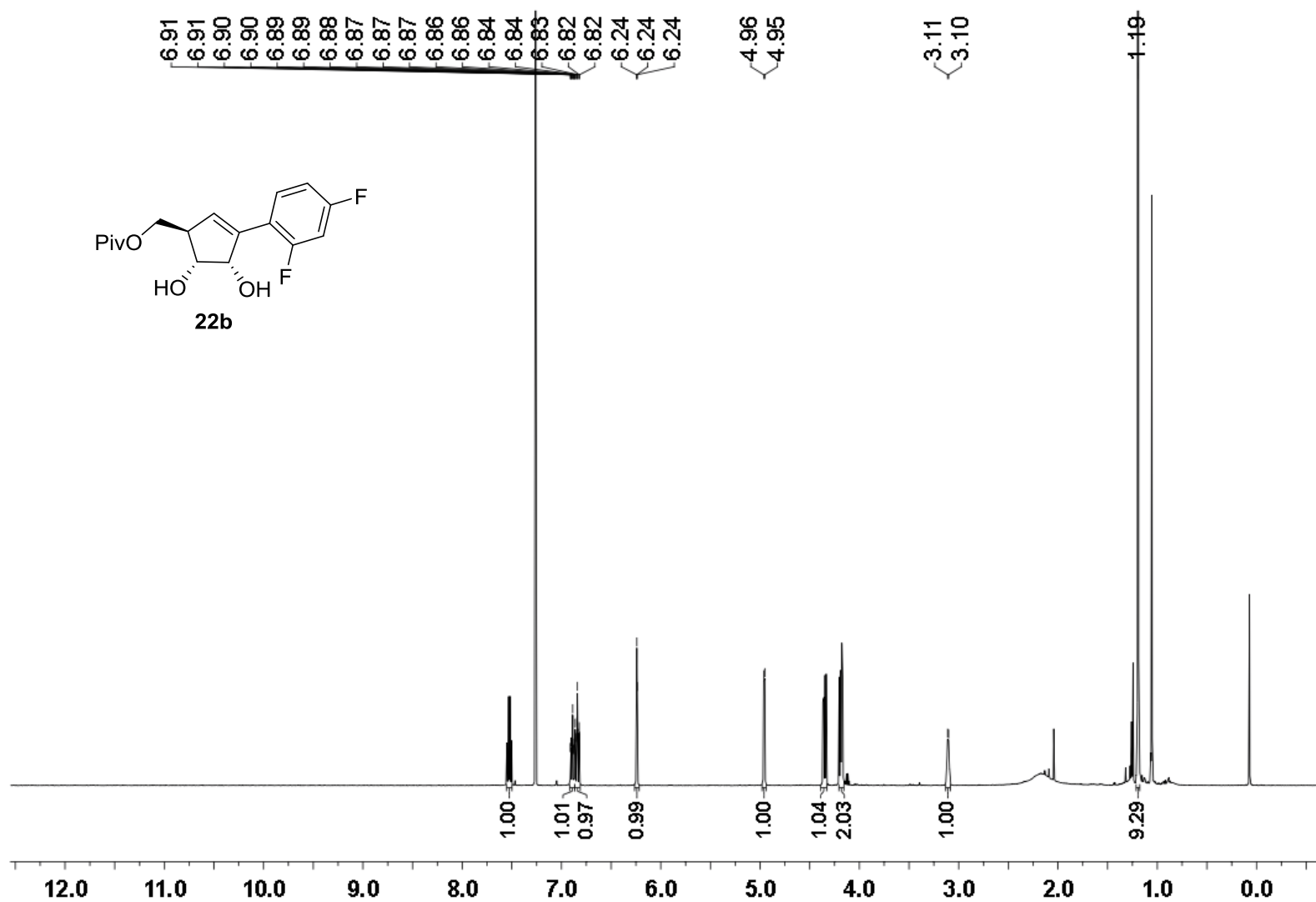
^{13}C NMR (126 MHz) spectrum of **21g** in CDCl_3



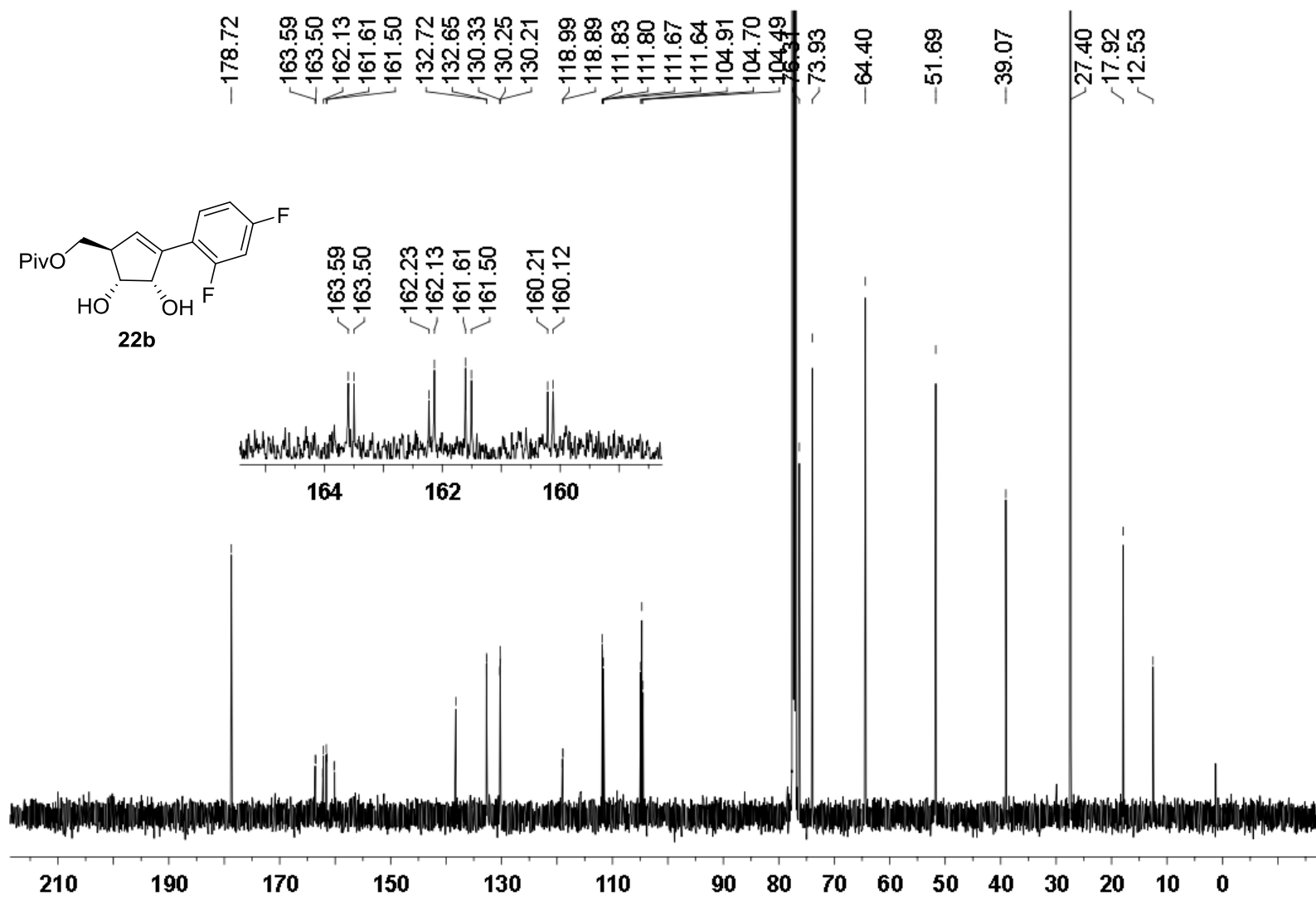
^1H NMR (500 MHz) spectrum of **22a** in DMSO- d_6



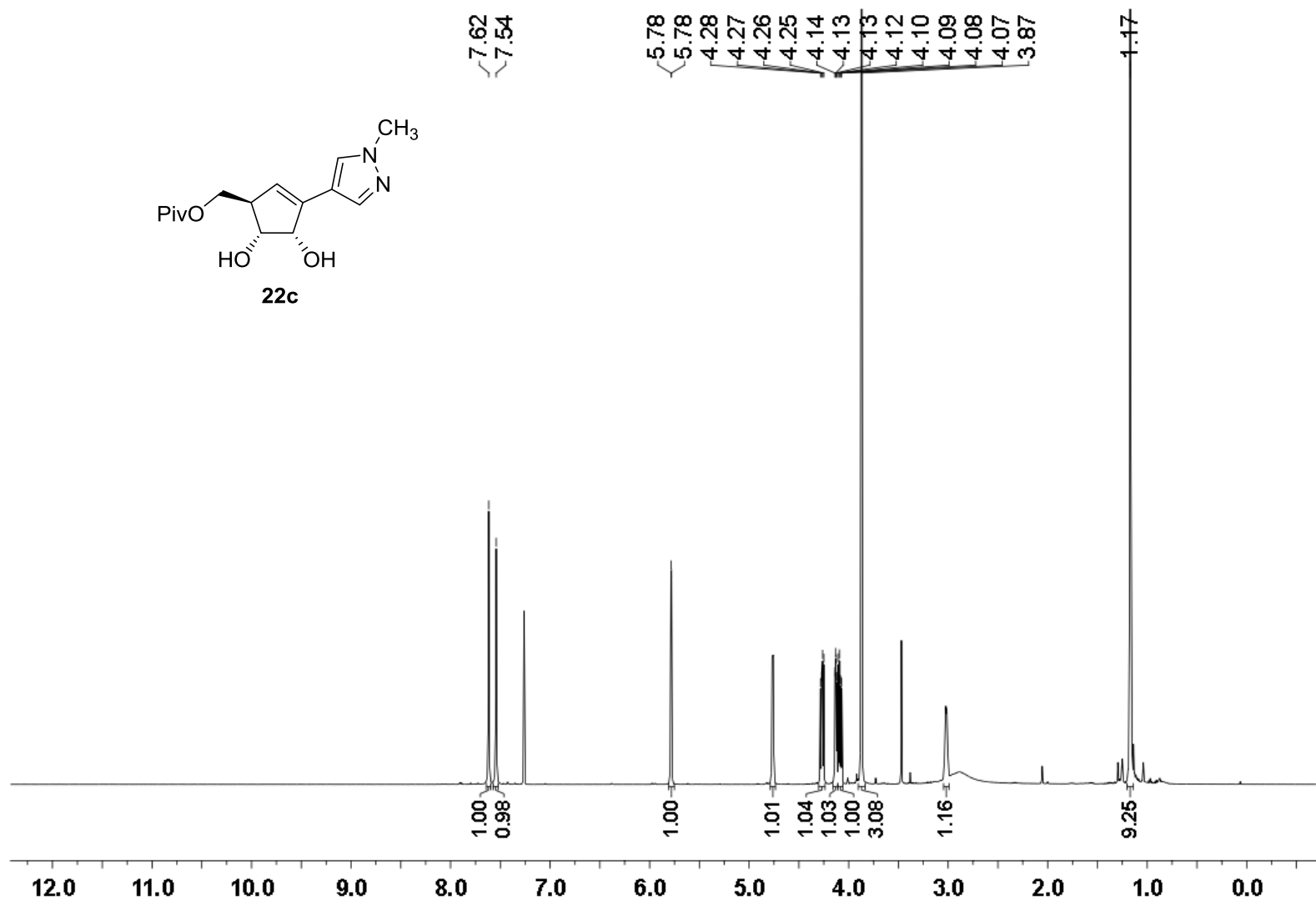
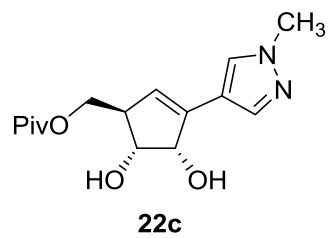
^{13}C NMR (126 MHz) spectrum of **22a** in DMSO- d_6



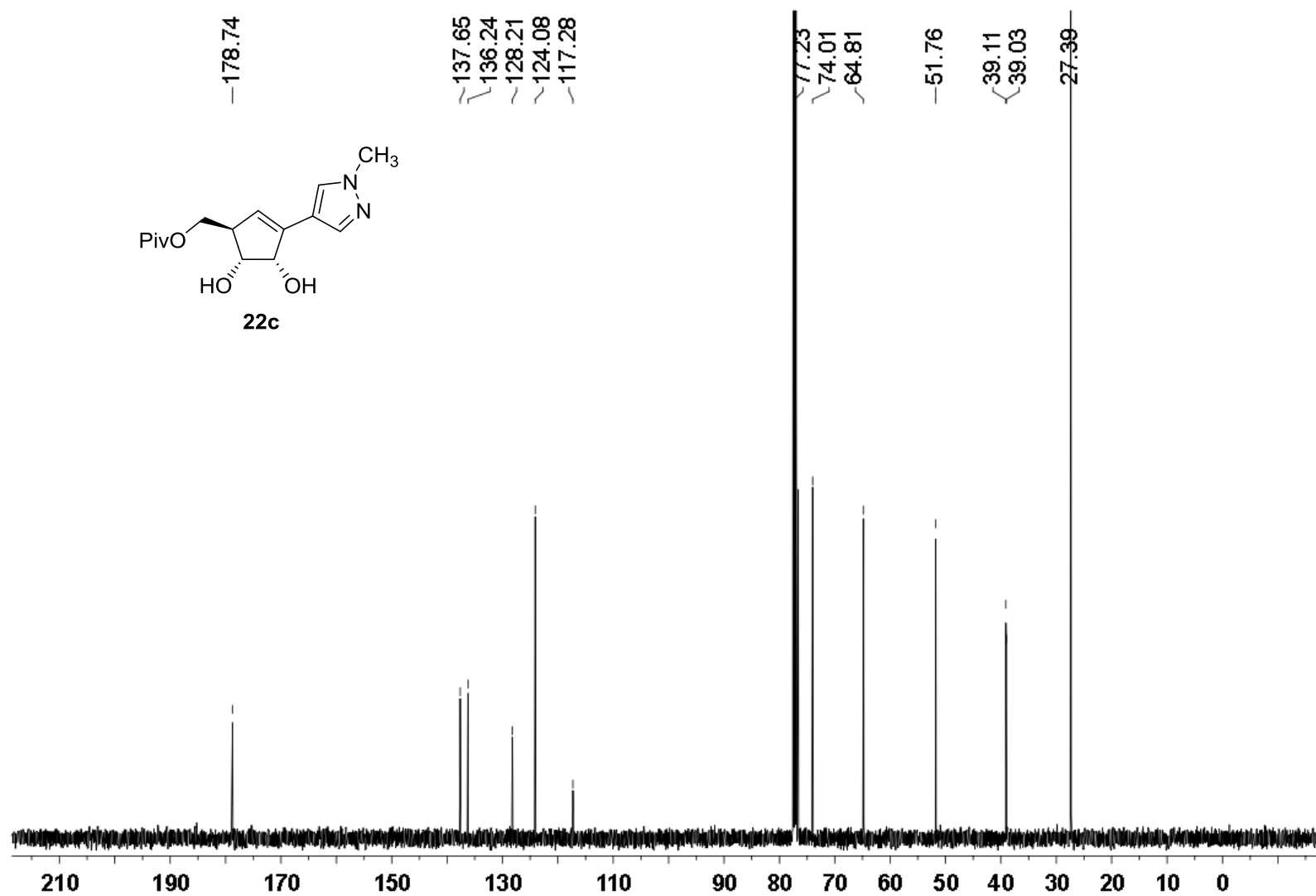
¹H NMR (500 MHz) spectrum of **22b** in CDCl₃



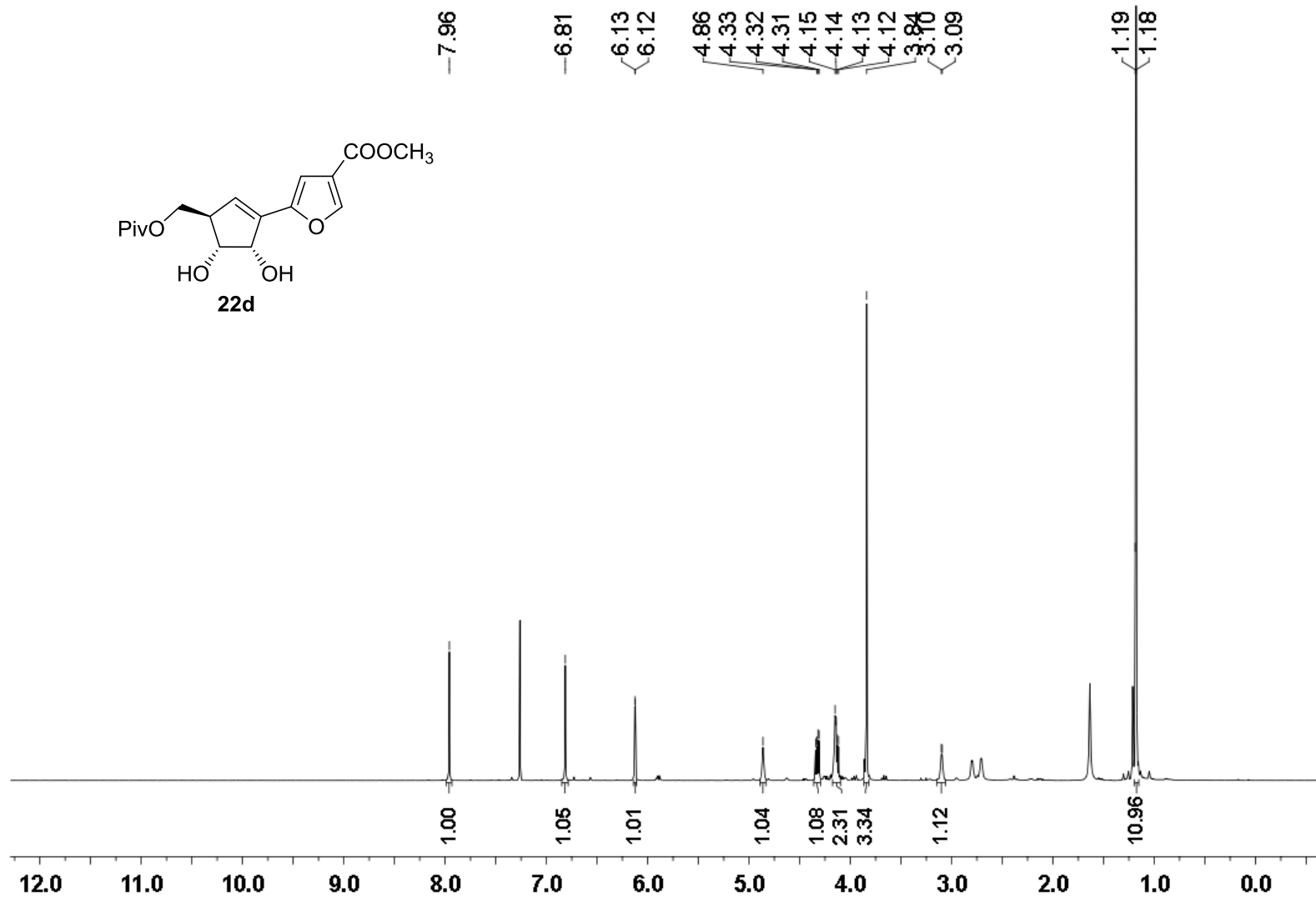
¹³C NMR (126 MHz) spectrum of **22b** in CDCl₃



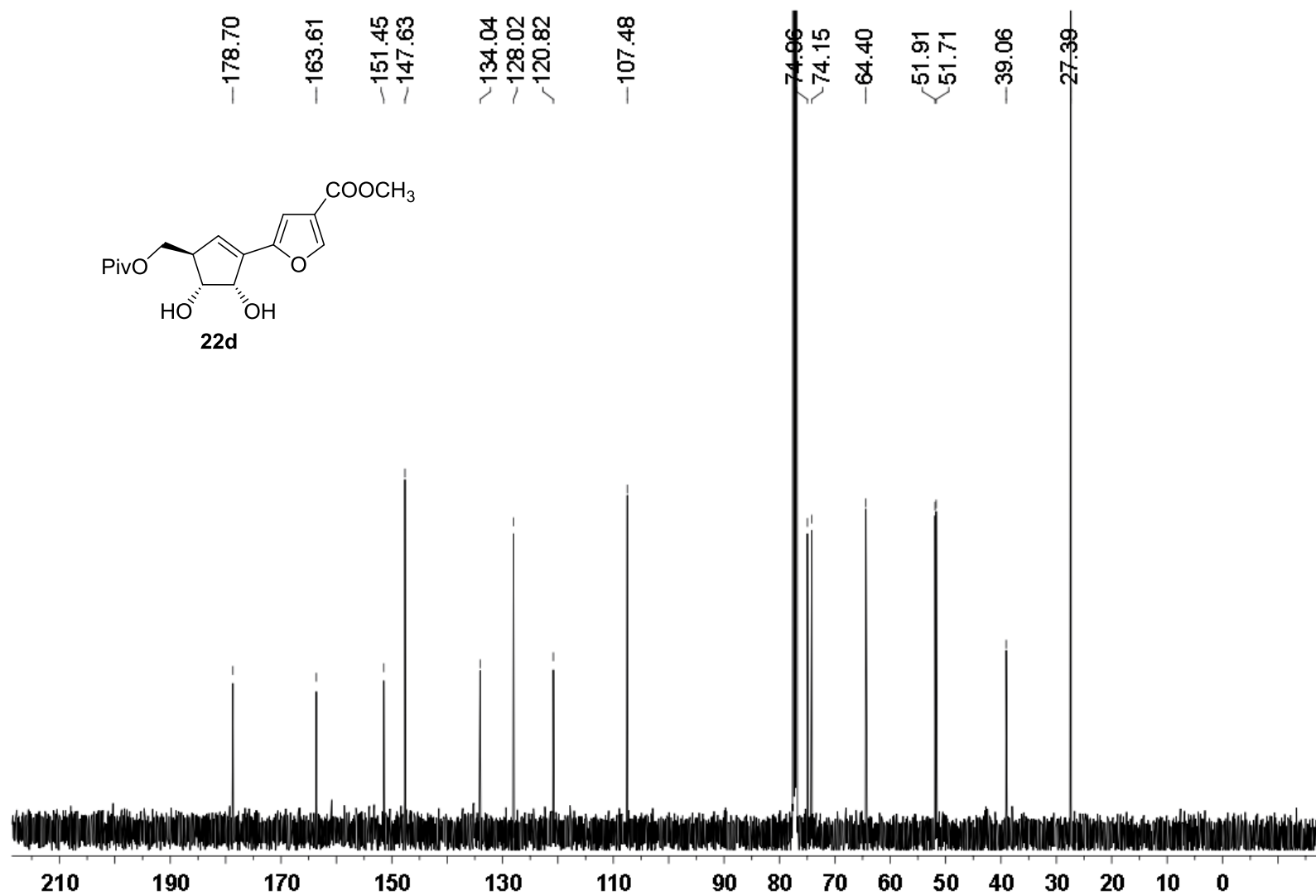
¹H NMR (500 MHz) spectrum of **22c** in CDCl₃



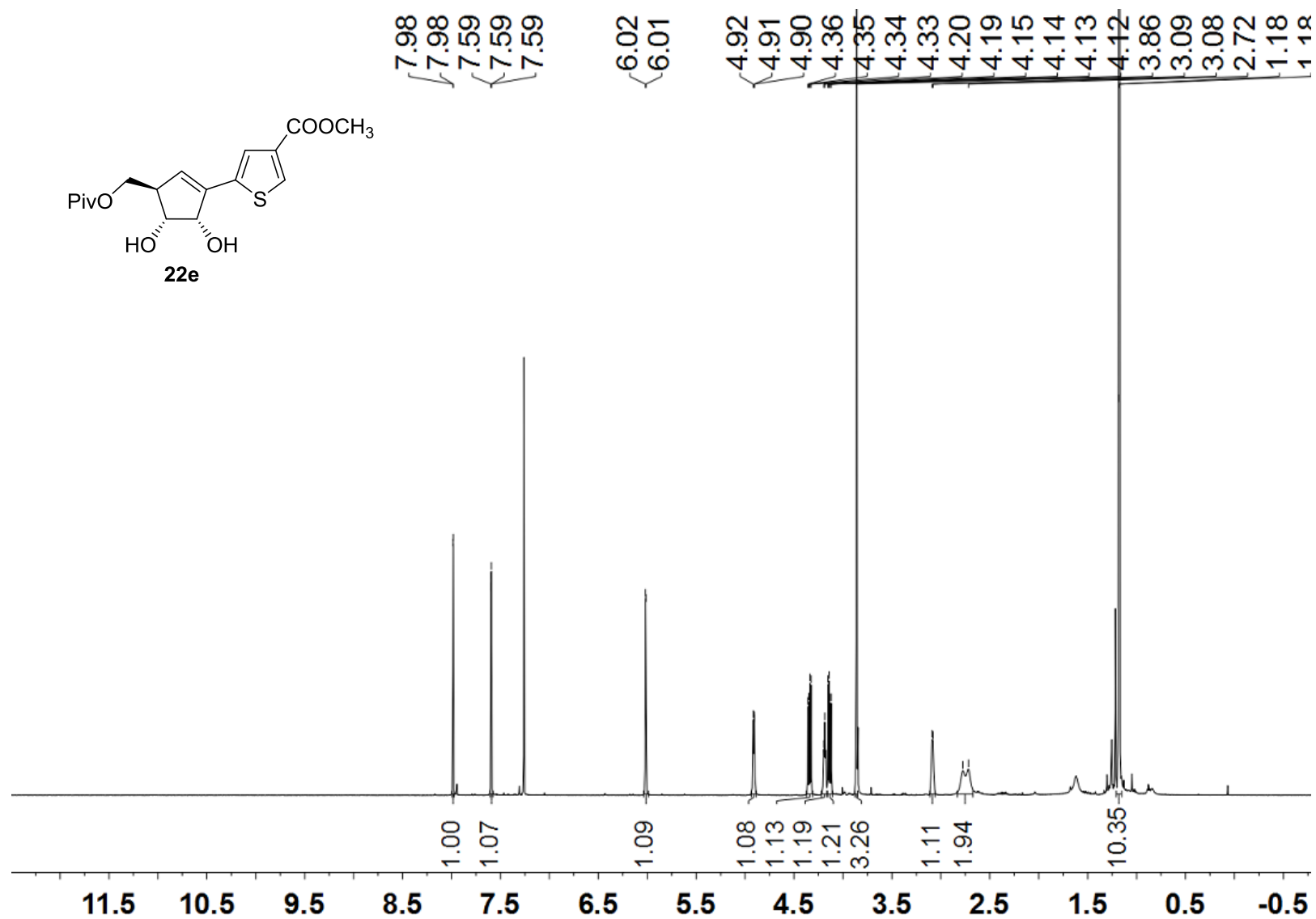
^{13}C NMR (126 MHz) spectrum of **22c** in CDCl_3



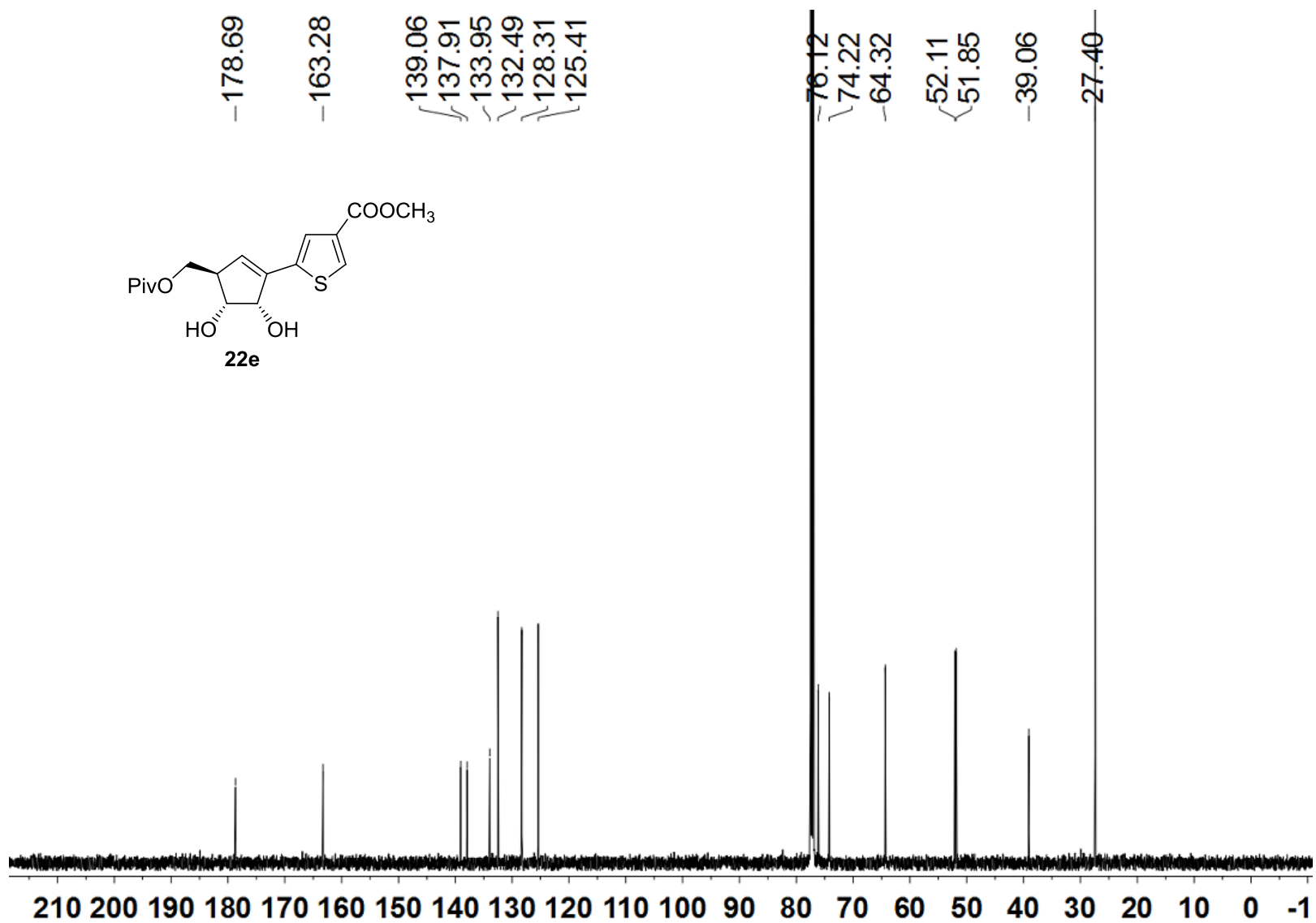
¹H NMR (500 MHz) spectrum of **22d** in CDCl₃



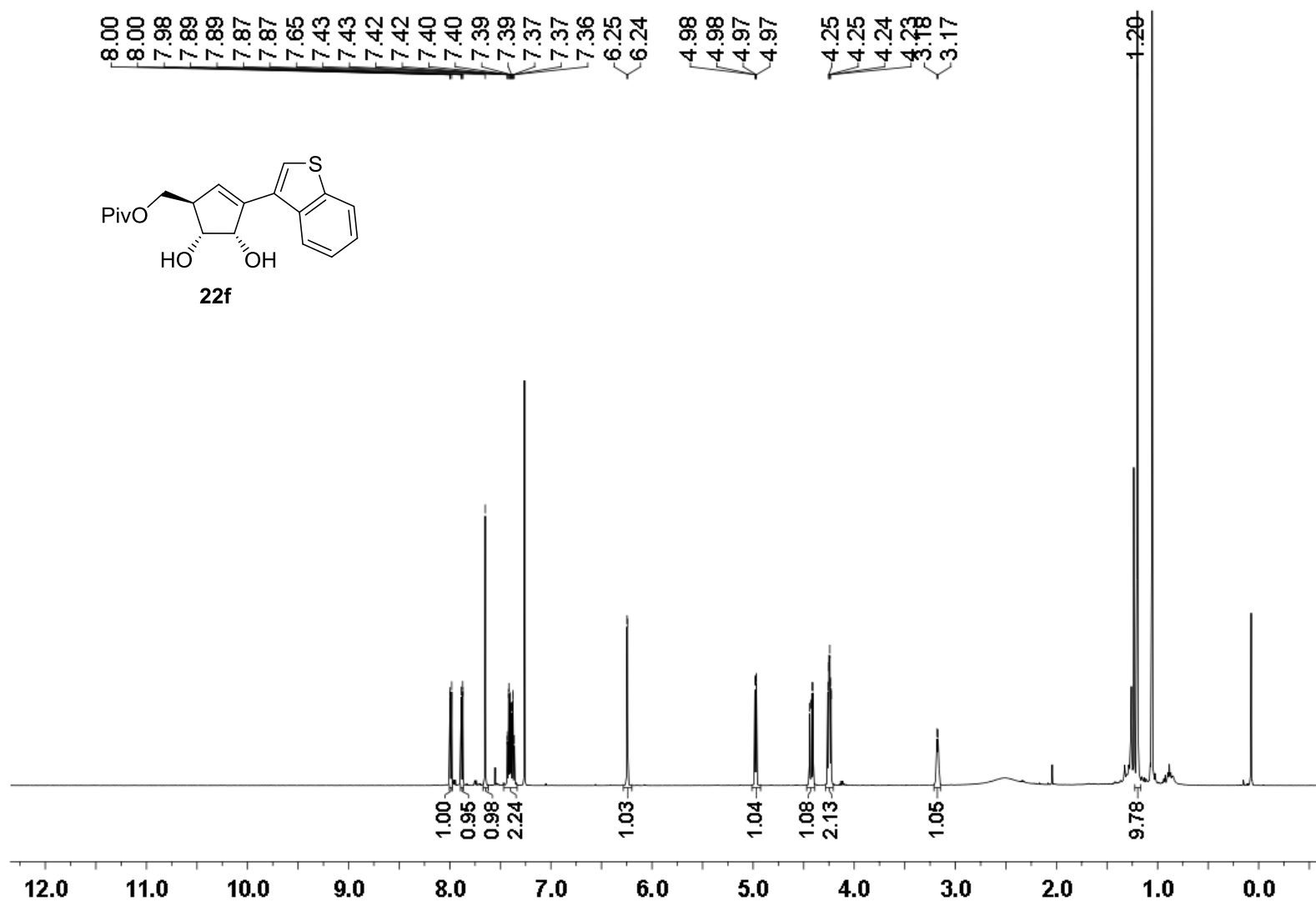
^{13}C NMR (126 MHz) spectrum of **22d** in CDCl_3



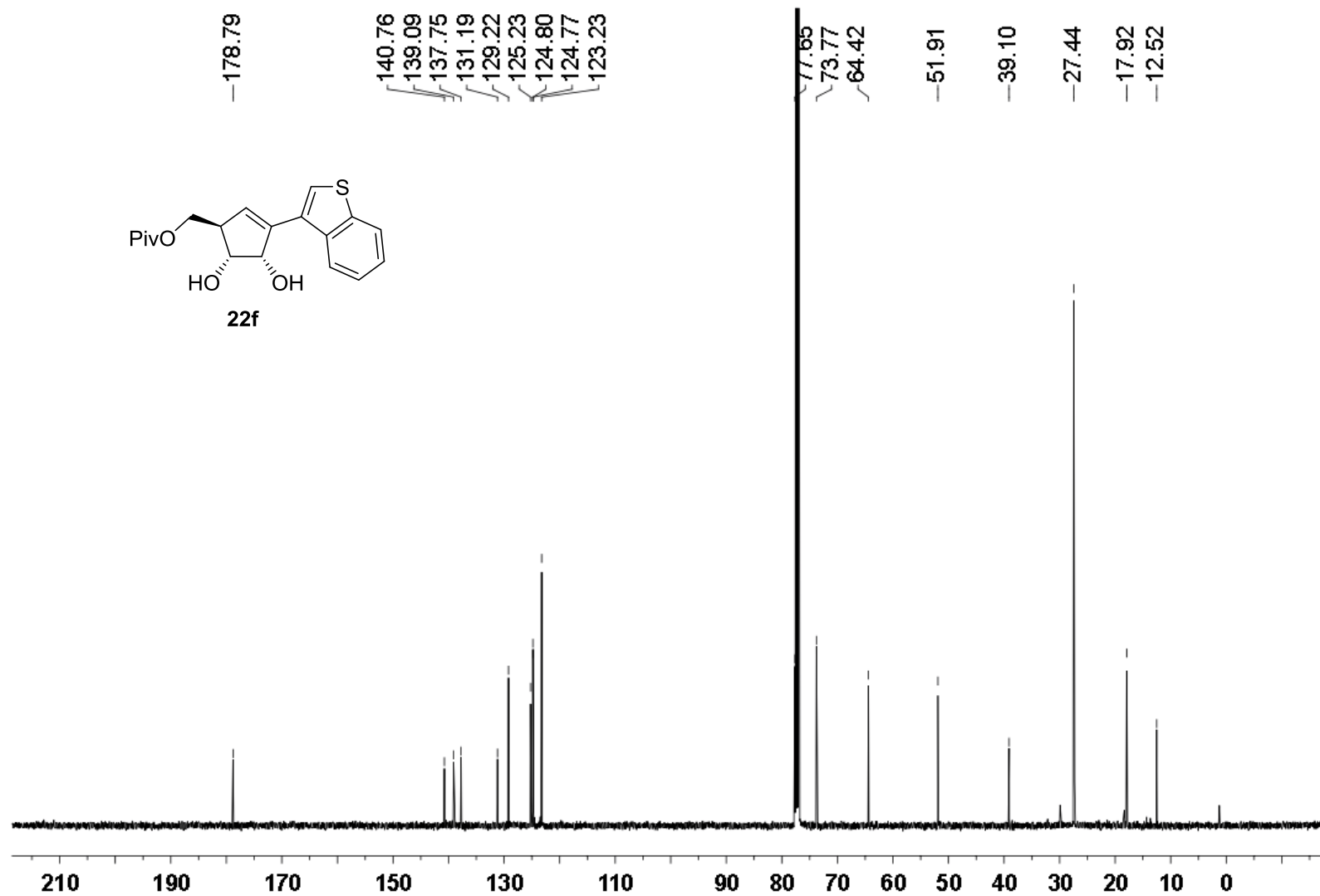
^1H NMR (500 MHz) spectrum of **22e** in CDCl_3



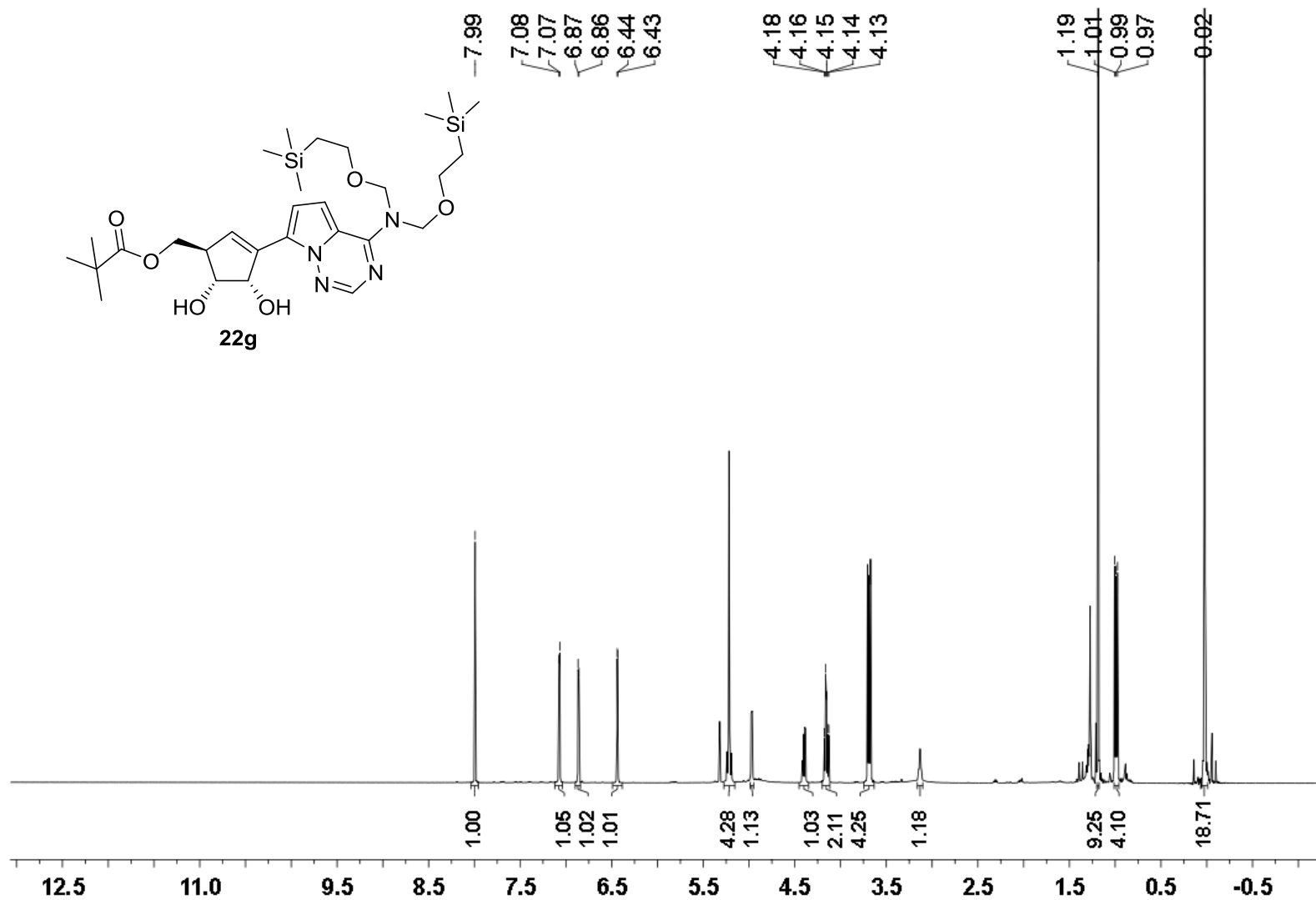
¹³C NMR (126 MHz) spectrum of **22e** in CDCl₃



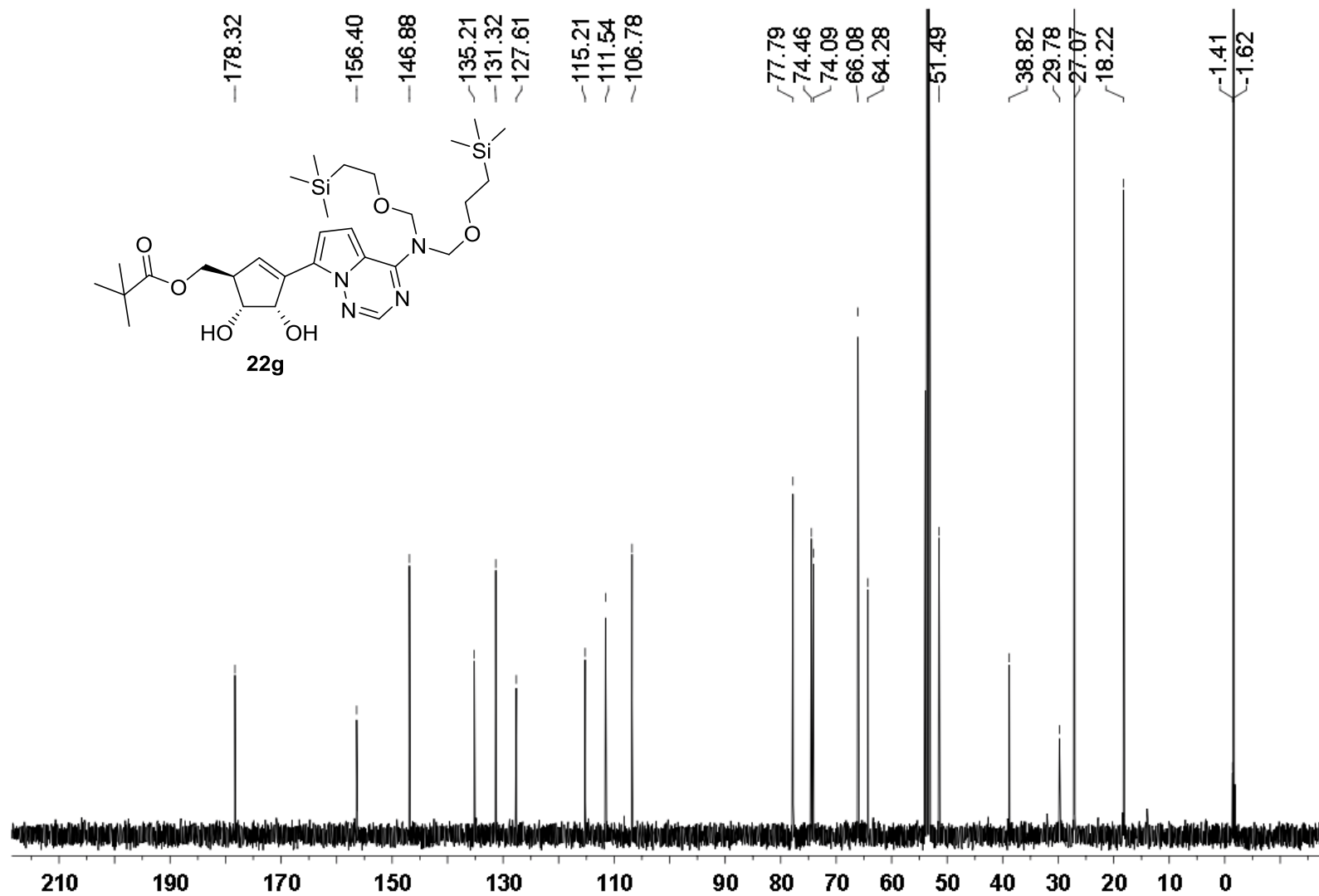
¹H NMR (500 MHz) spectrum of **22f** in CDCl₃



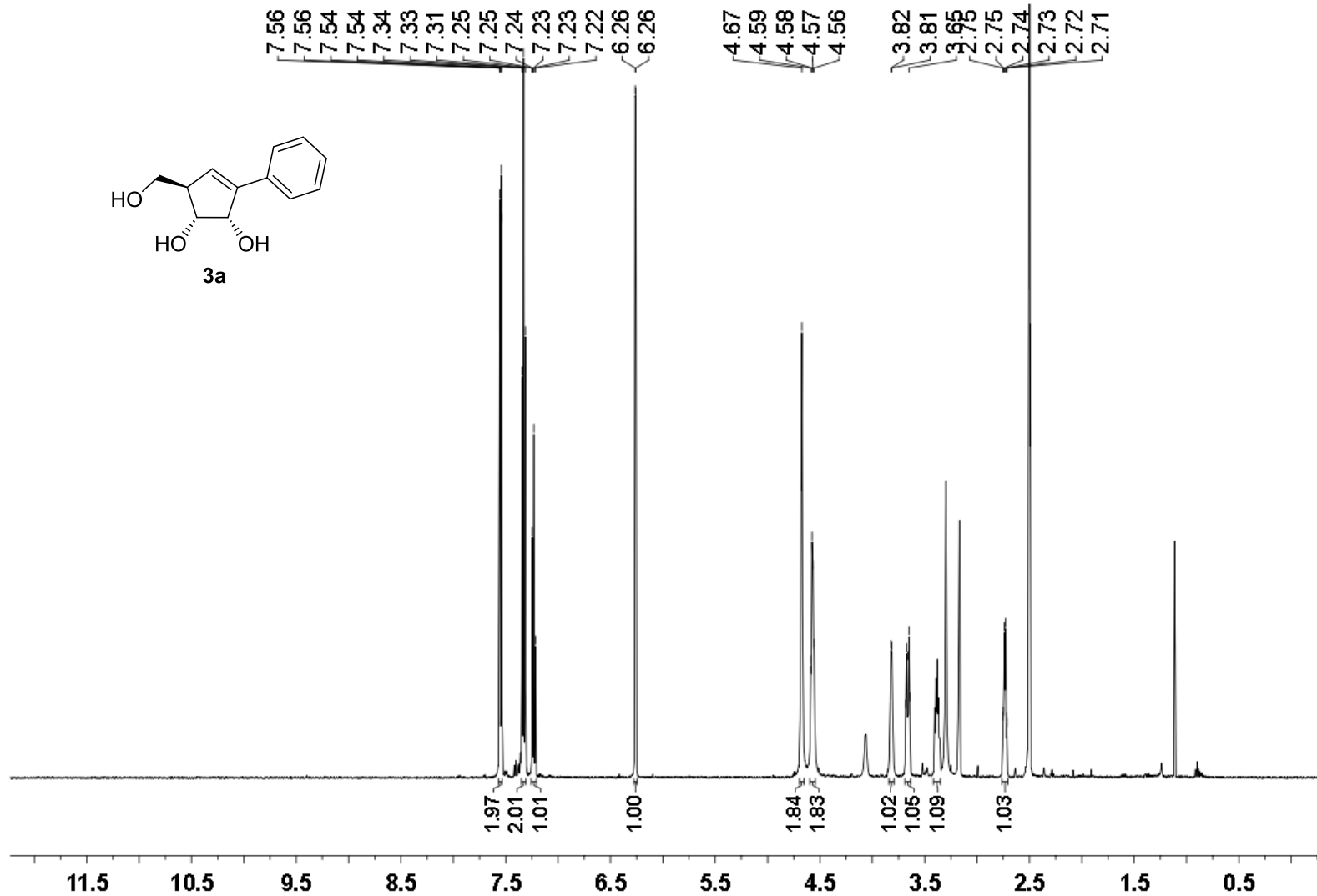
¹³C NMR (126 MHz) spectrum of **22f** in CDCl₃



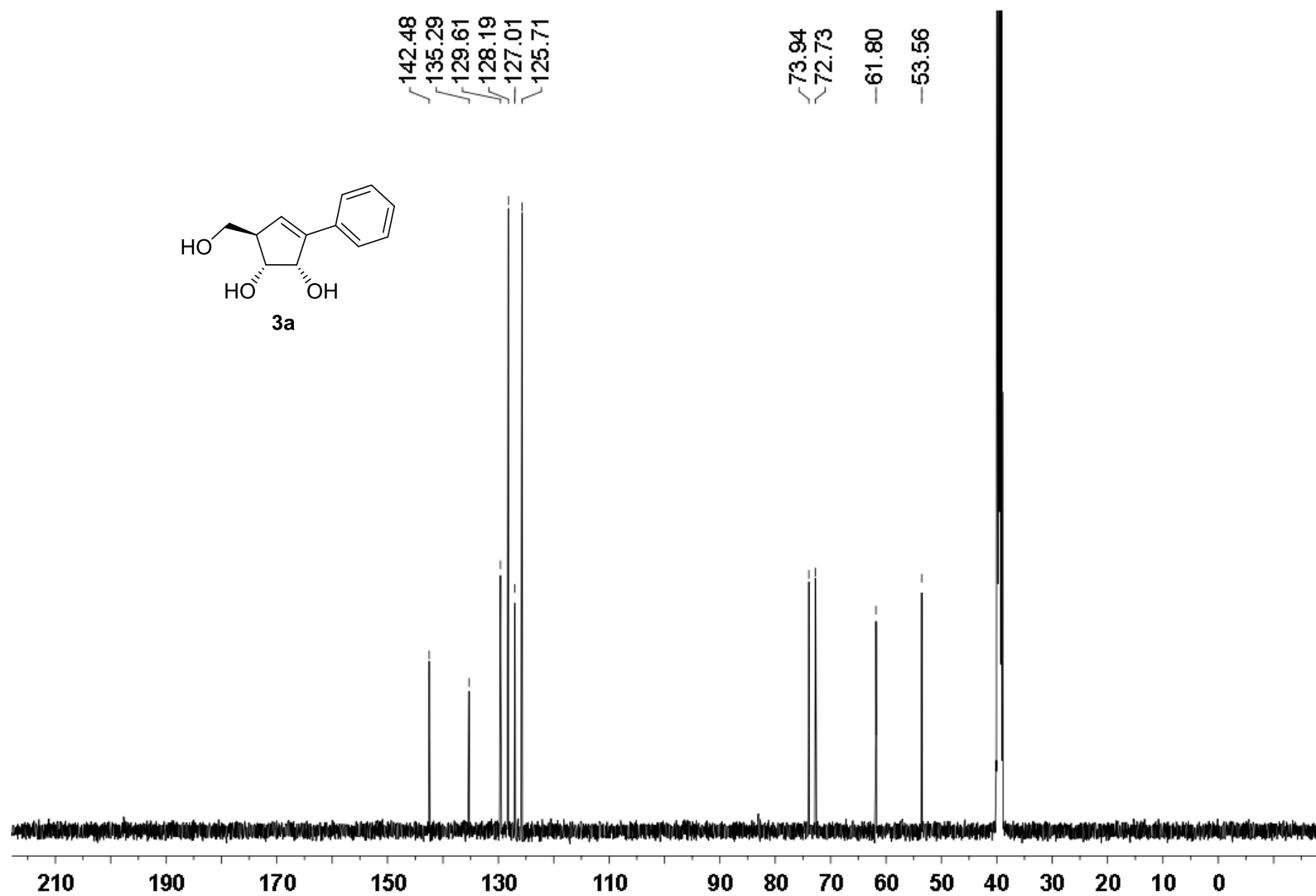
^1H NMR (500 MHz) spectrum of **22g** in CD_2Cl_2



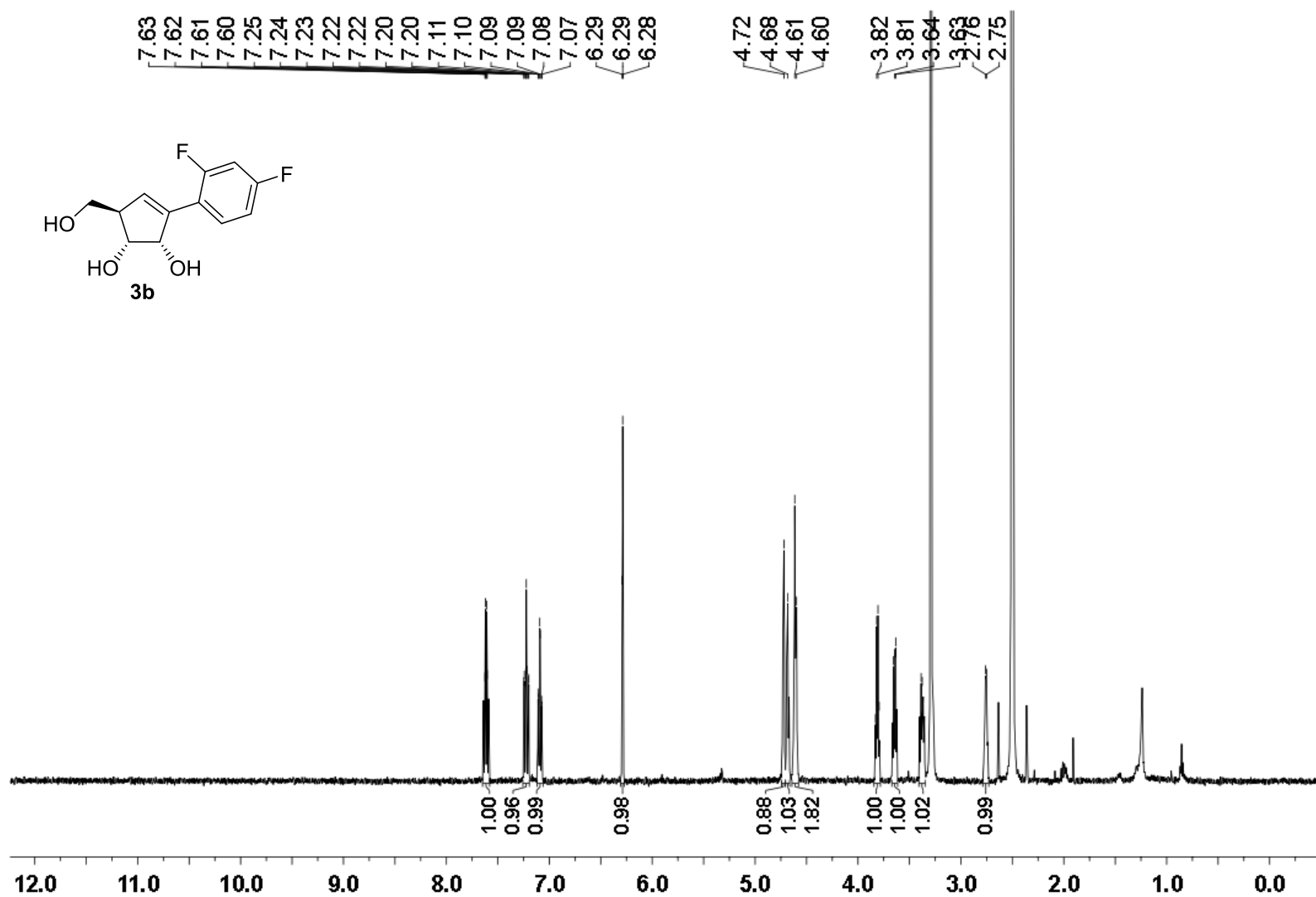
¹³C NMR (126 MHz) spectrum of **22g** in CD₂Cl₂



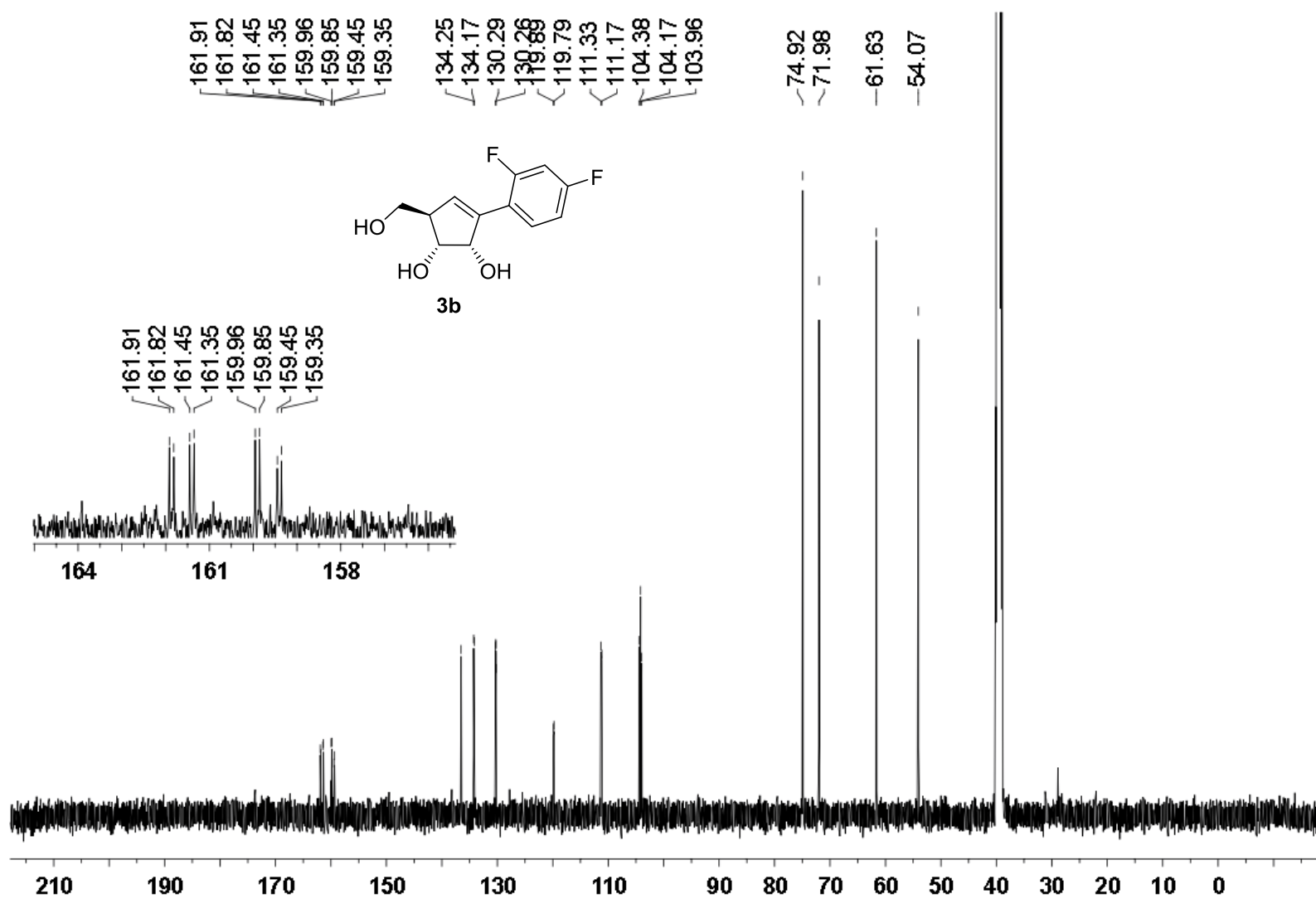
¹H NMR (500 MHz) spectrum of **3a** in DMSO-*d*₆



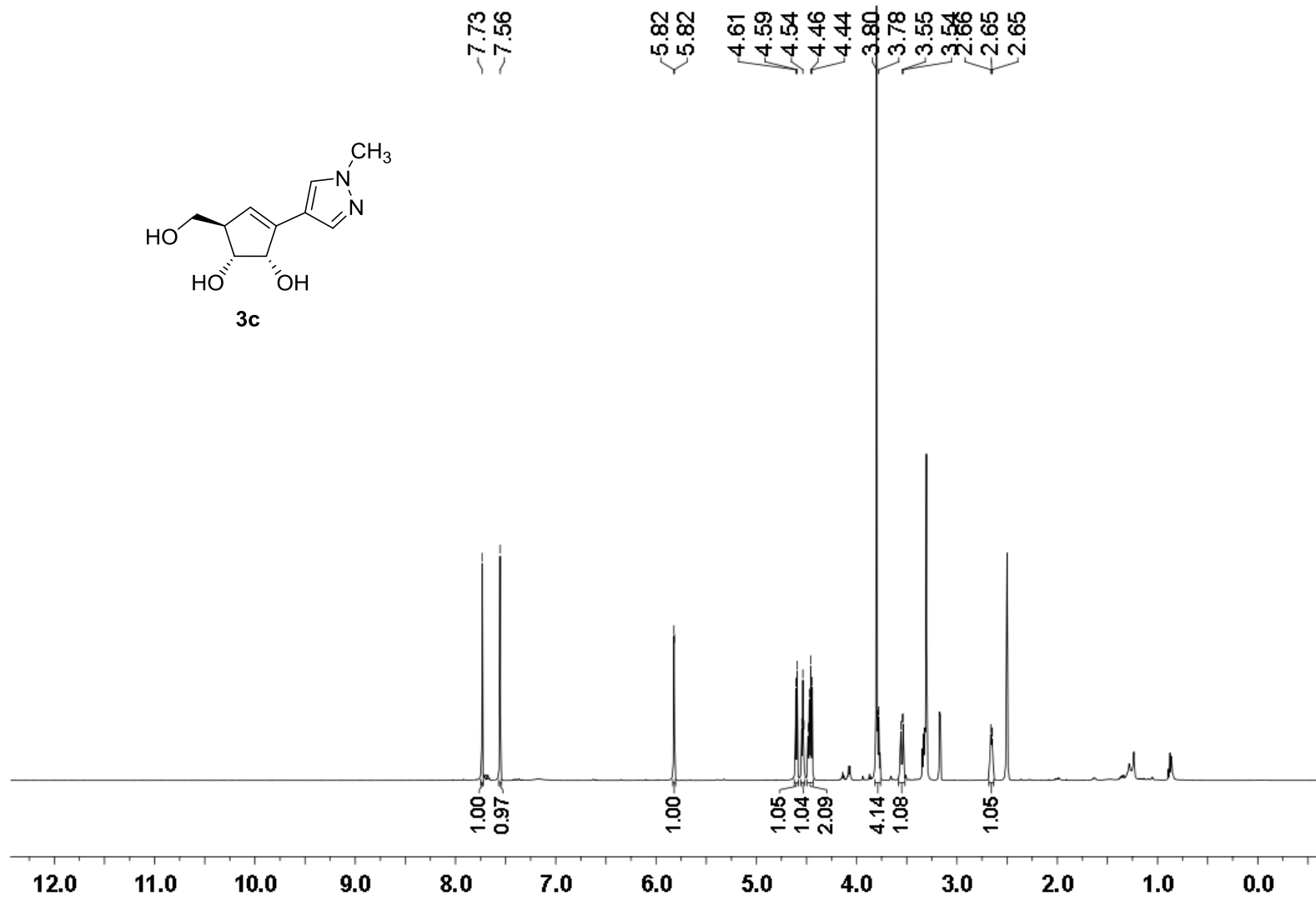
^{13}C NMR (126 MHz) spectrum of **3a** in $\text{DMSO}-d_6$



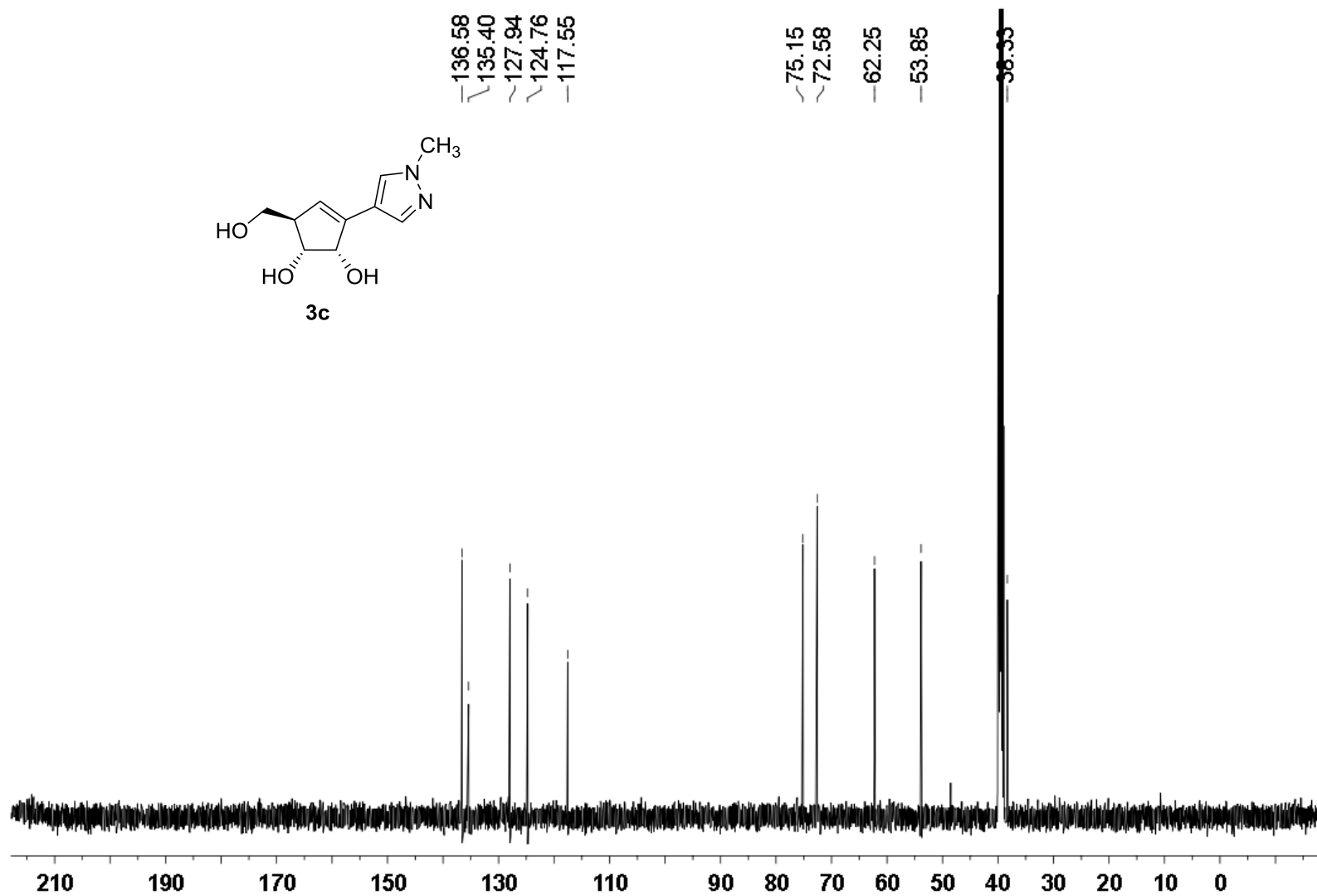
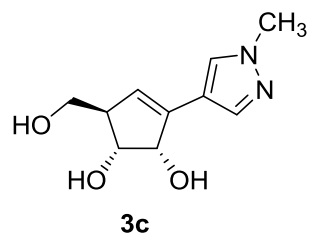
¹H NMR (500 MHz) spectrum of **3b** in DMSO-*d*₆



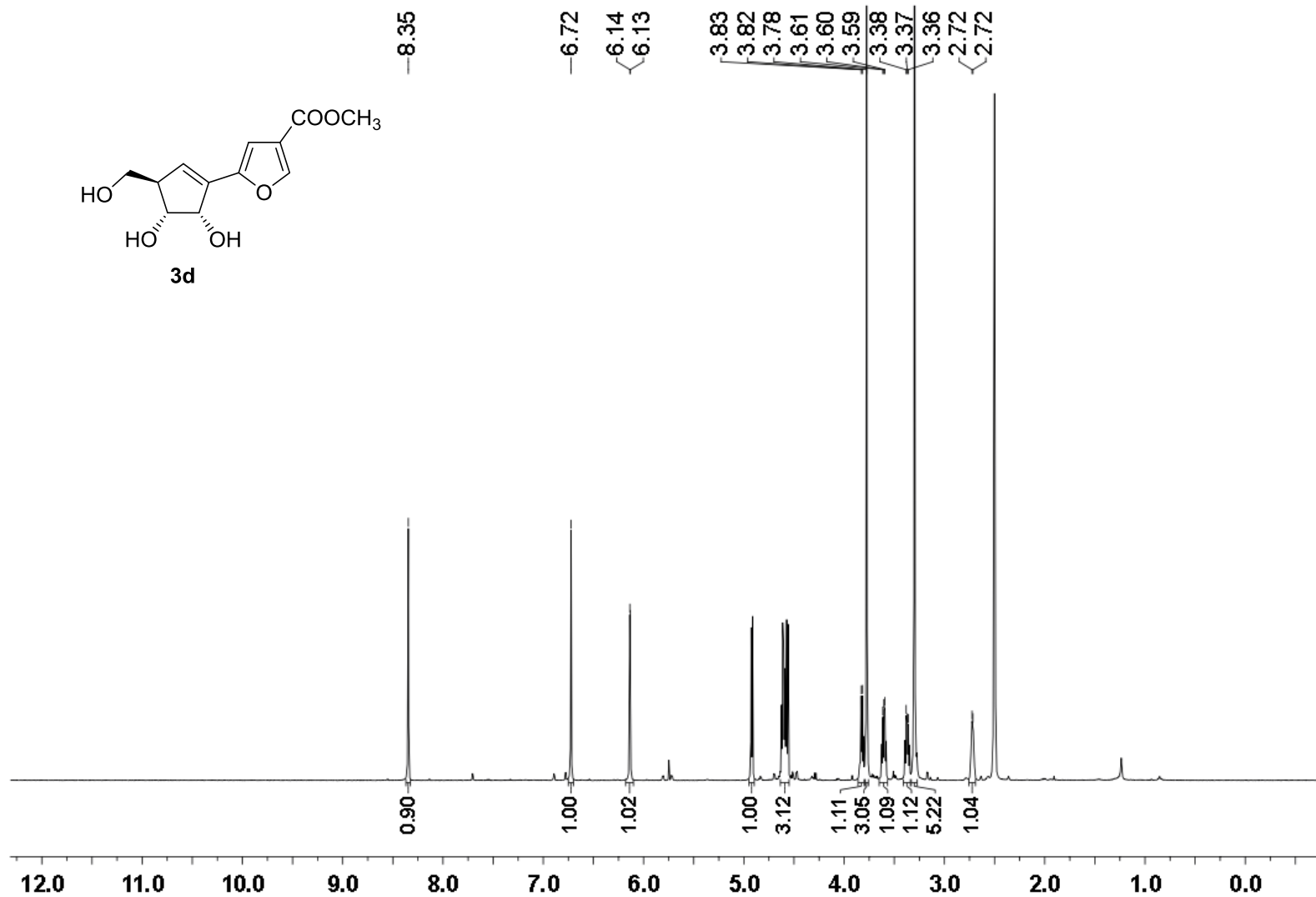
¹³C NMR (126 MHz) spectrum of **3b** in DMSO-*d*₆



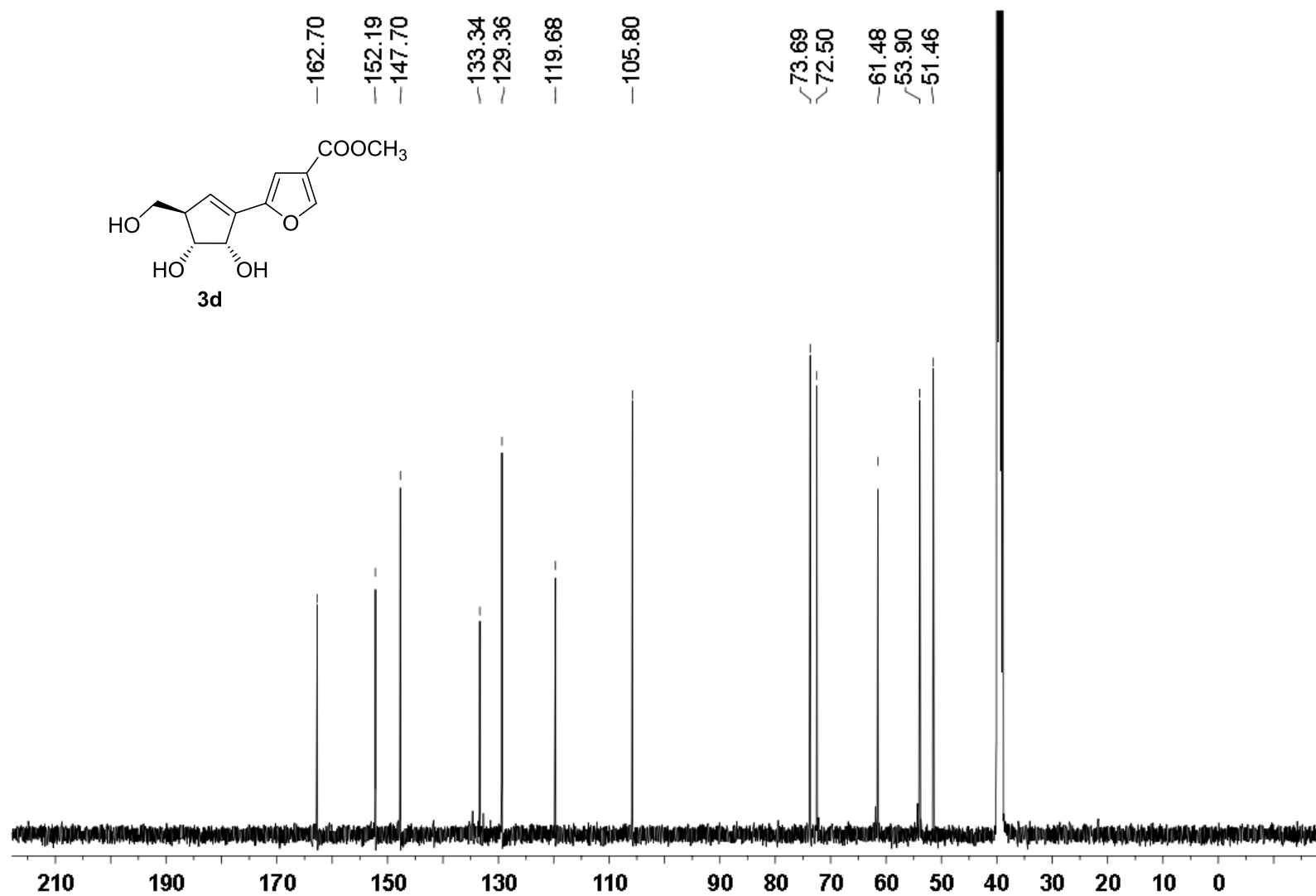
¹H NMR (500 MHz) spectrum of **3c** in DMSO-*d*₆



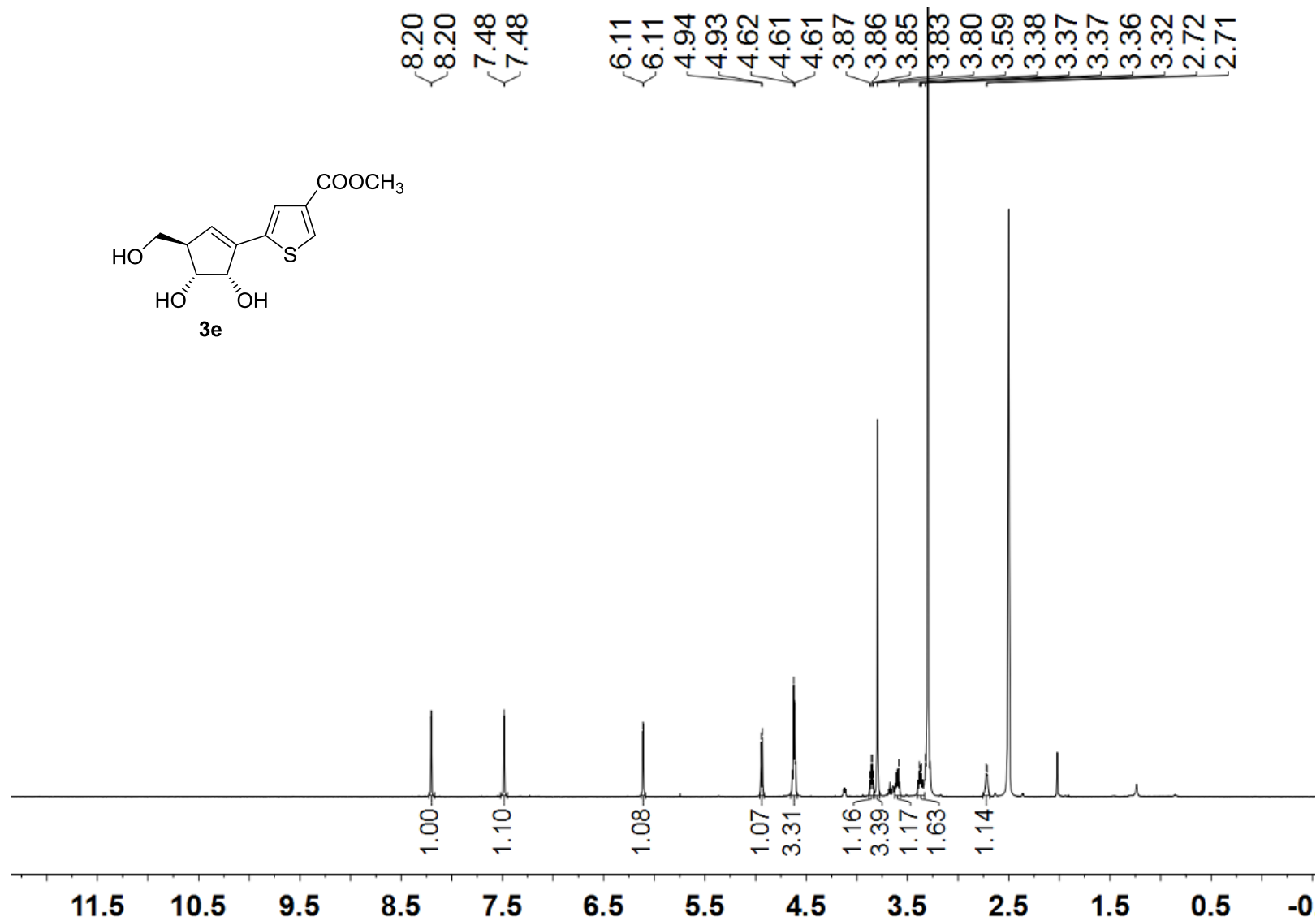
^{13}C NMR (126 MHz) spectrum of **3c** in $\text{DMSO}-d_6$



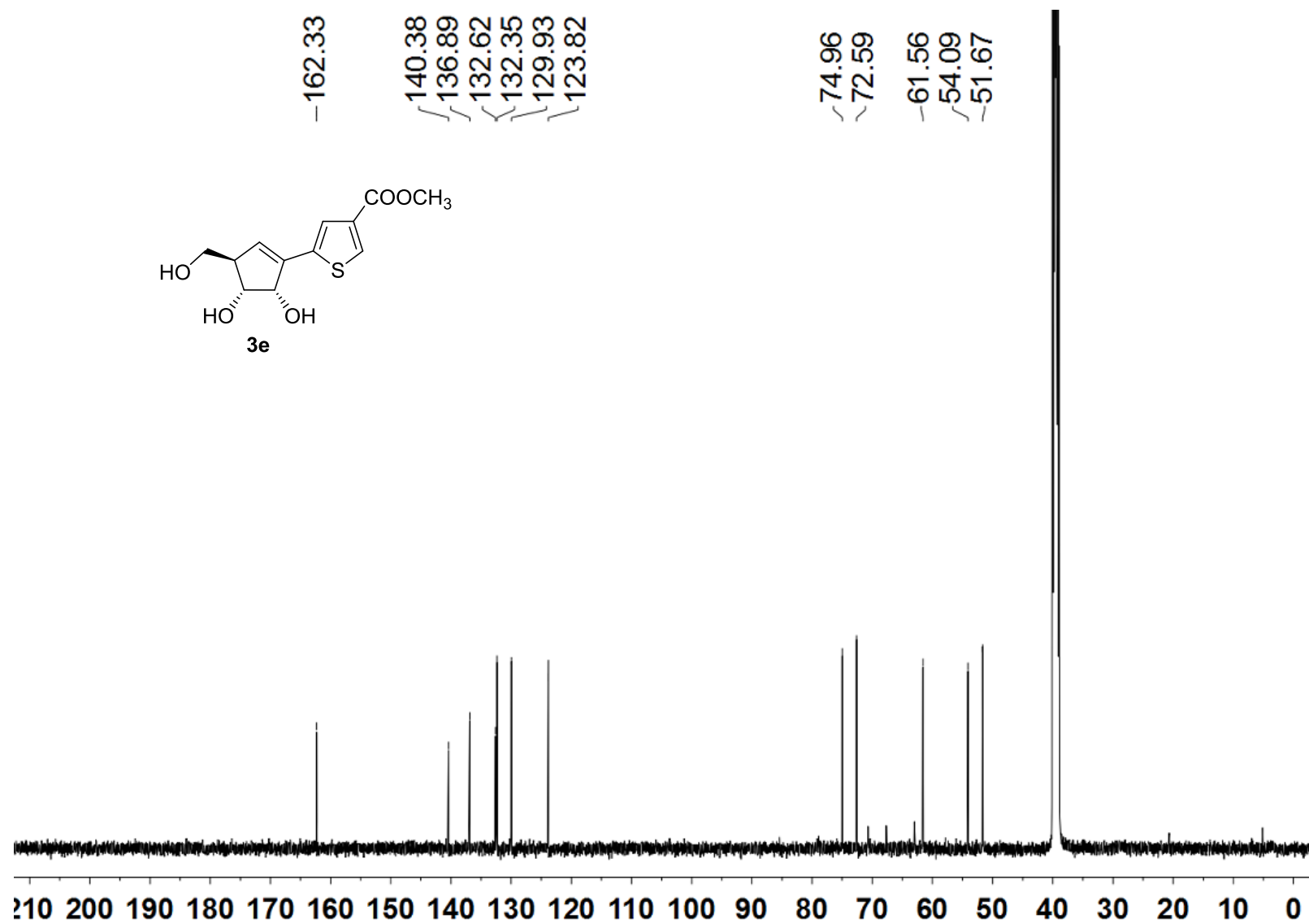
^1H NMR (500 MHz) spectrum of **3d** in $\text{DMSO}-d_6$

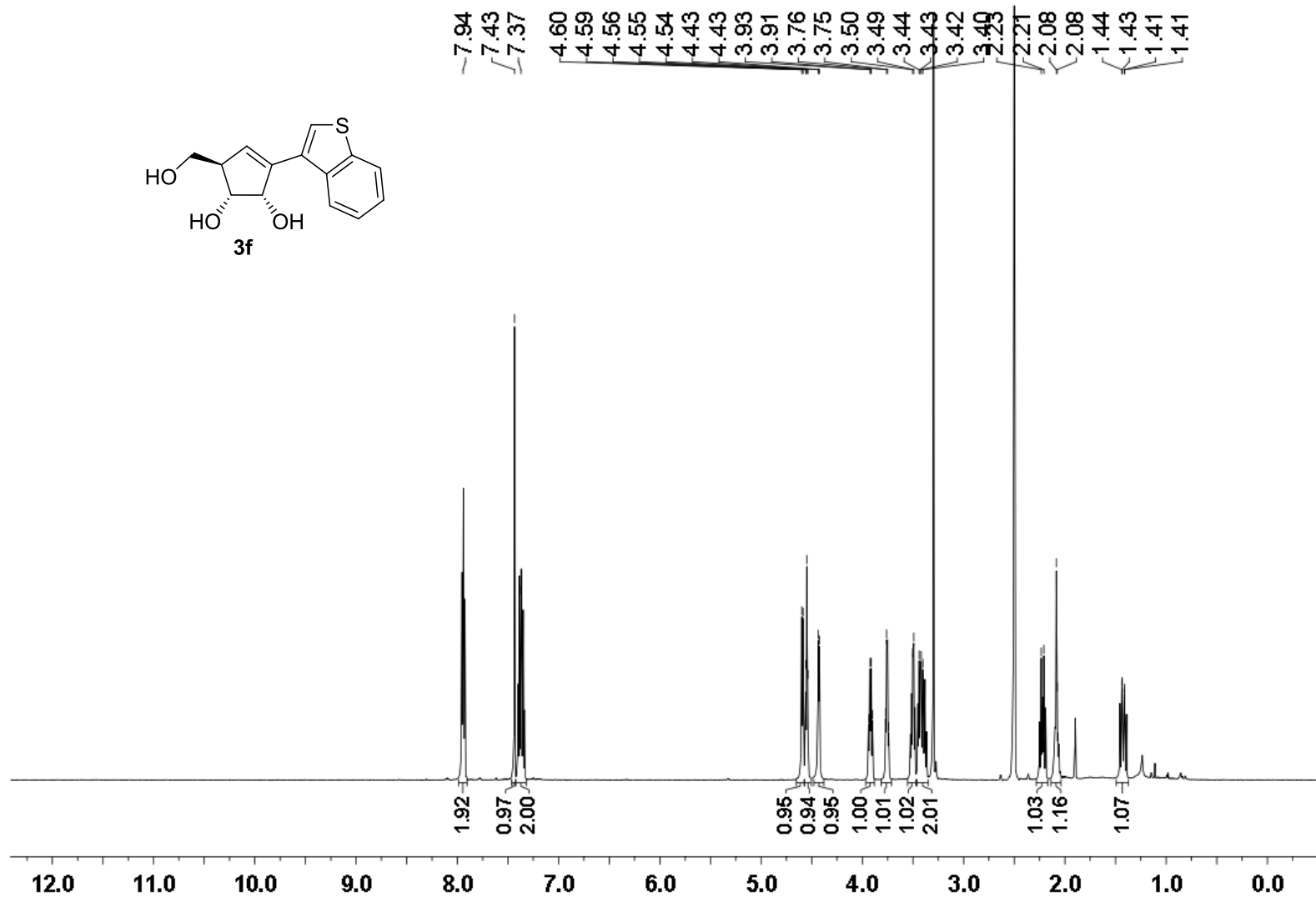


¹³C NMR (126 MHz) spectrum of **3d** in DMSO-*d*₆

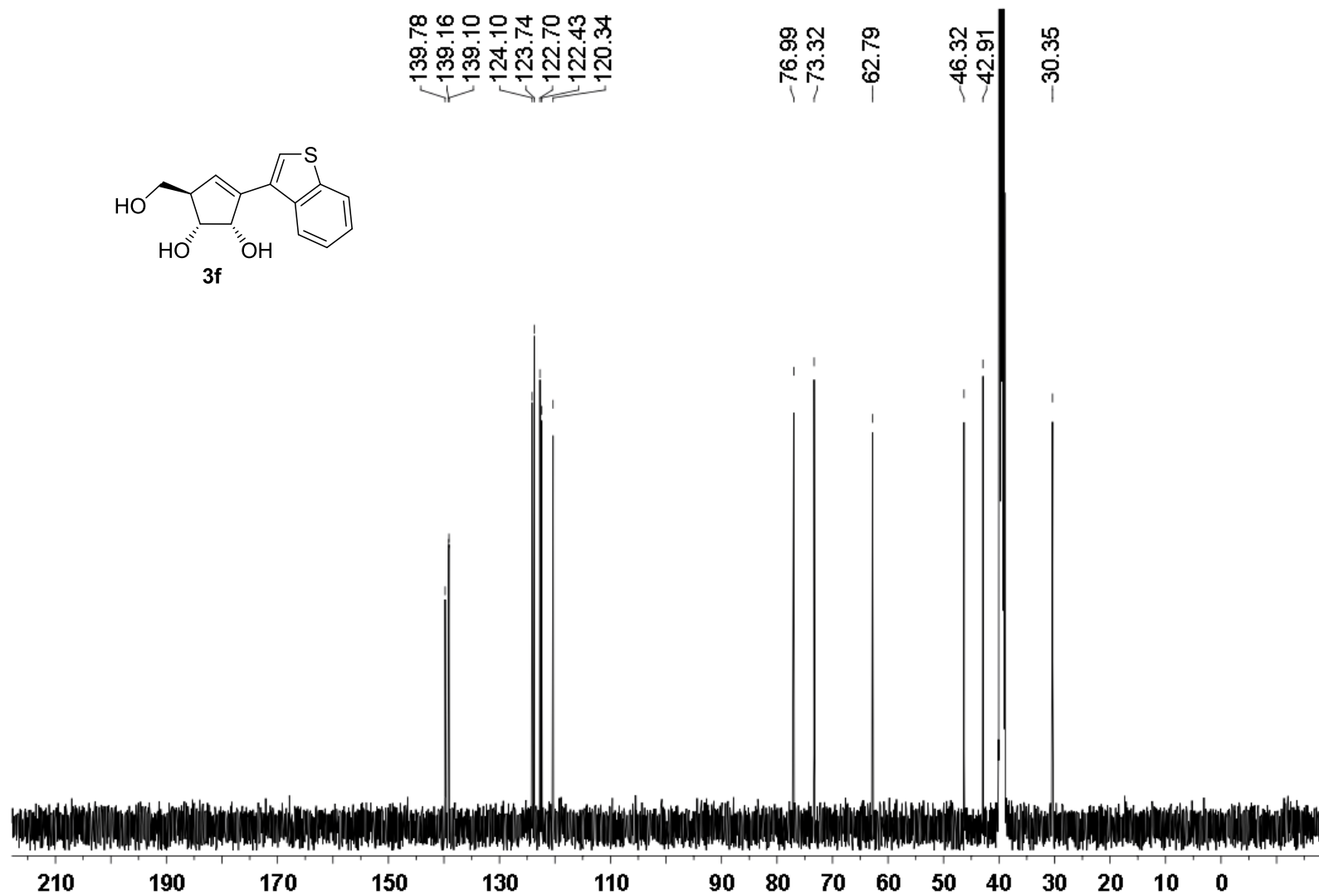


^1H NMR (500 MHz) spectrum of **3e** in $\text{DMSO}-d_6$

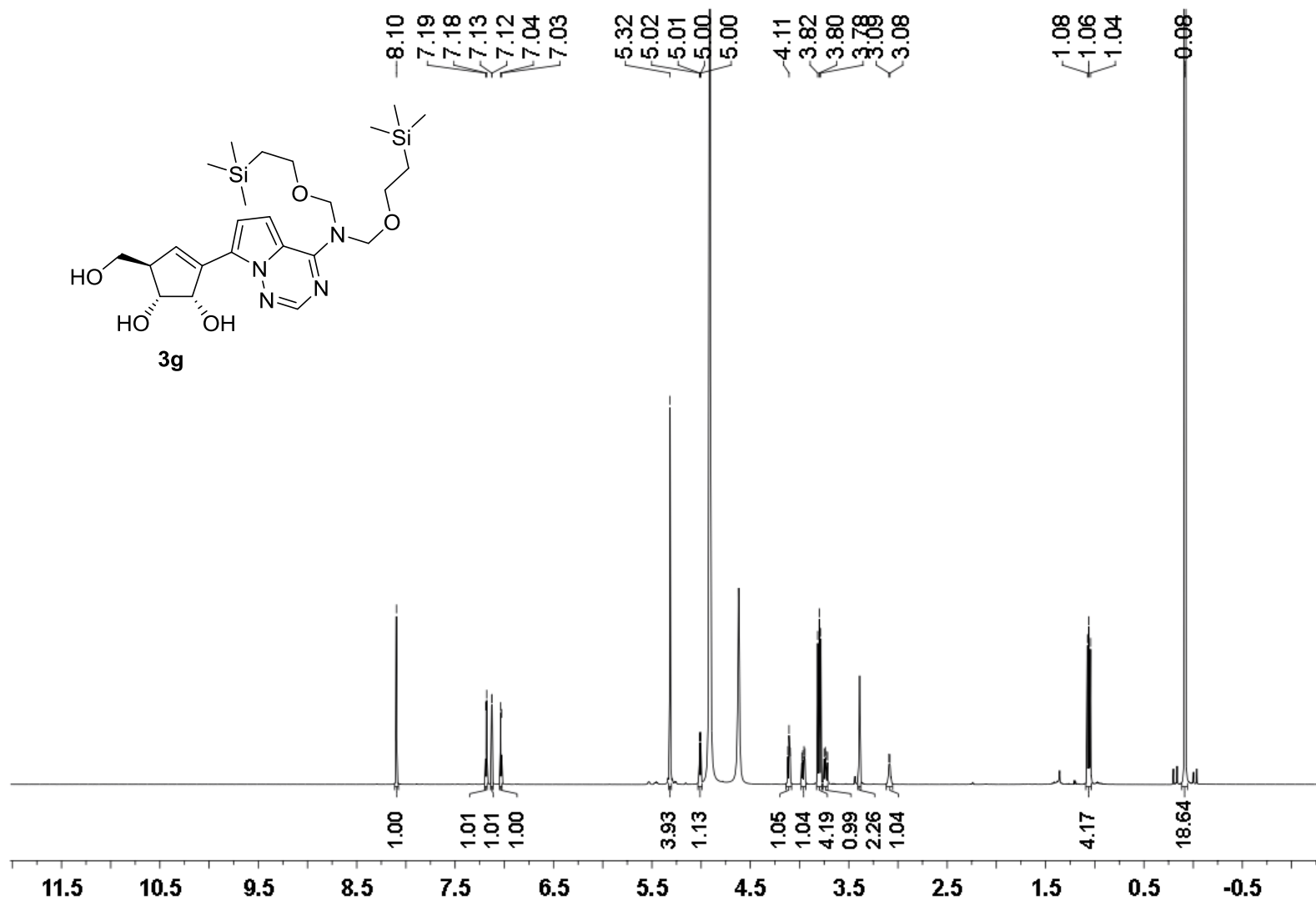




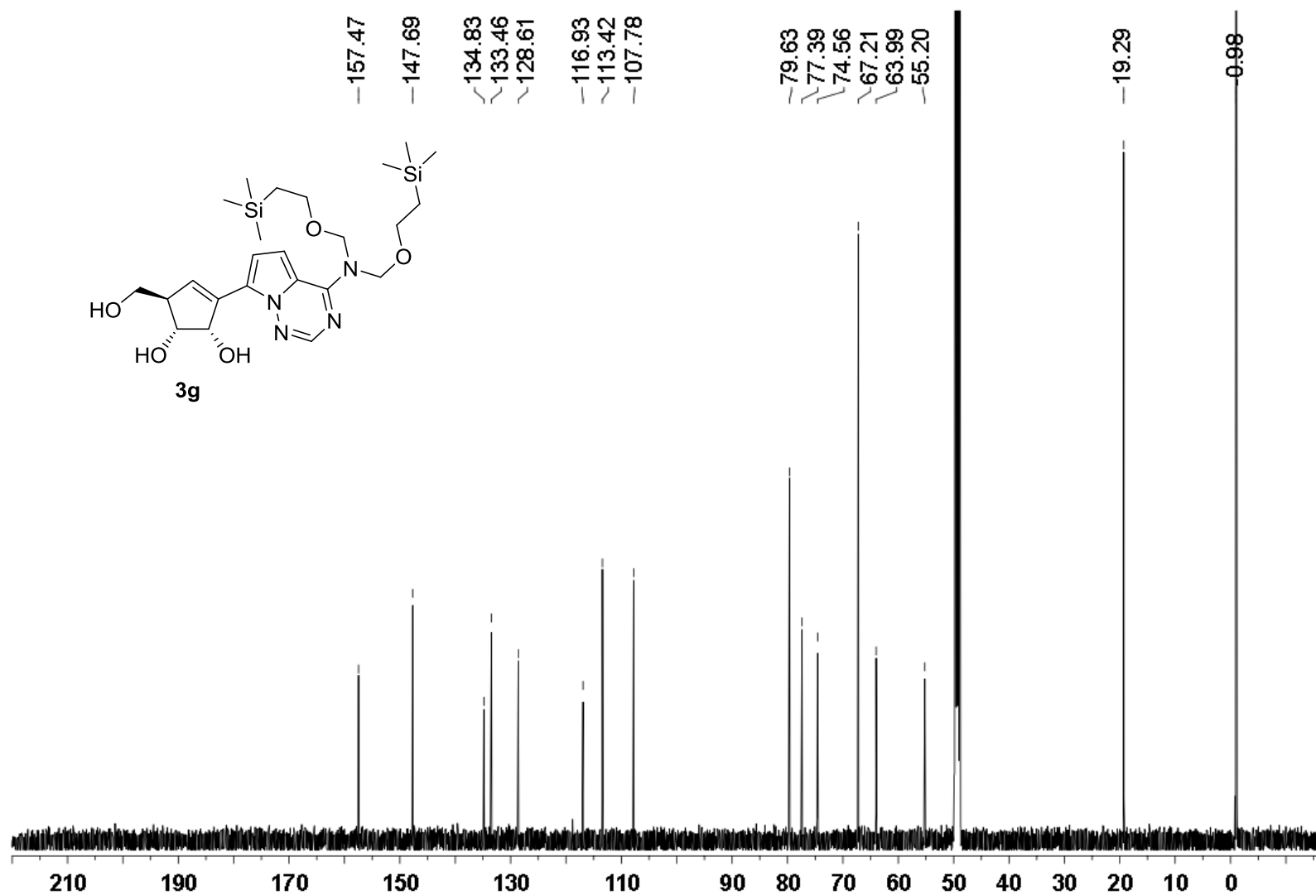
¹H NMR (500 MHz) spectrum of **3f** in DMSO-*d*₆



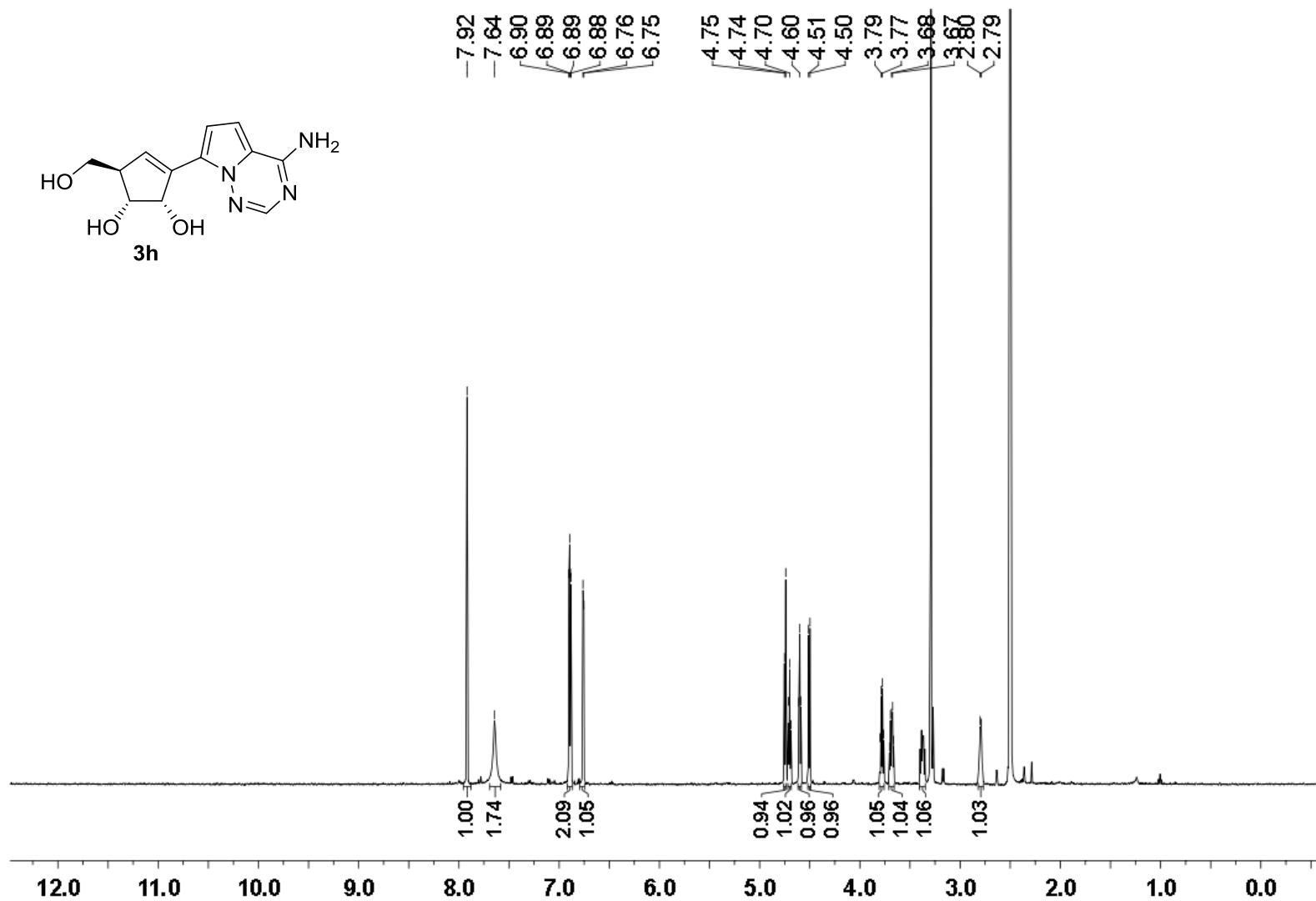
¹³C NMR (126 MHz) spectrum of **3f** in DMSO-*d*₆



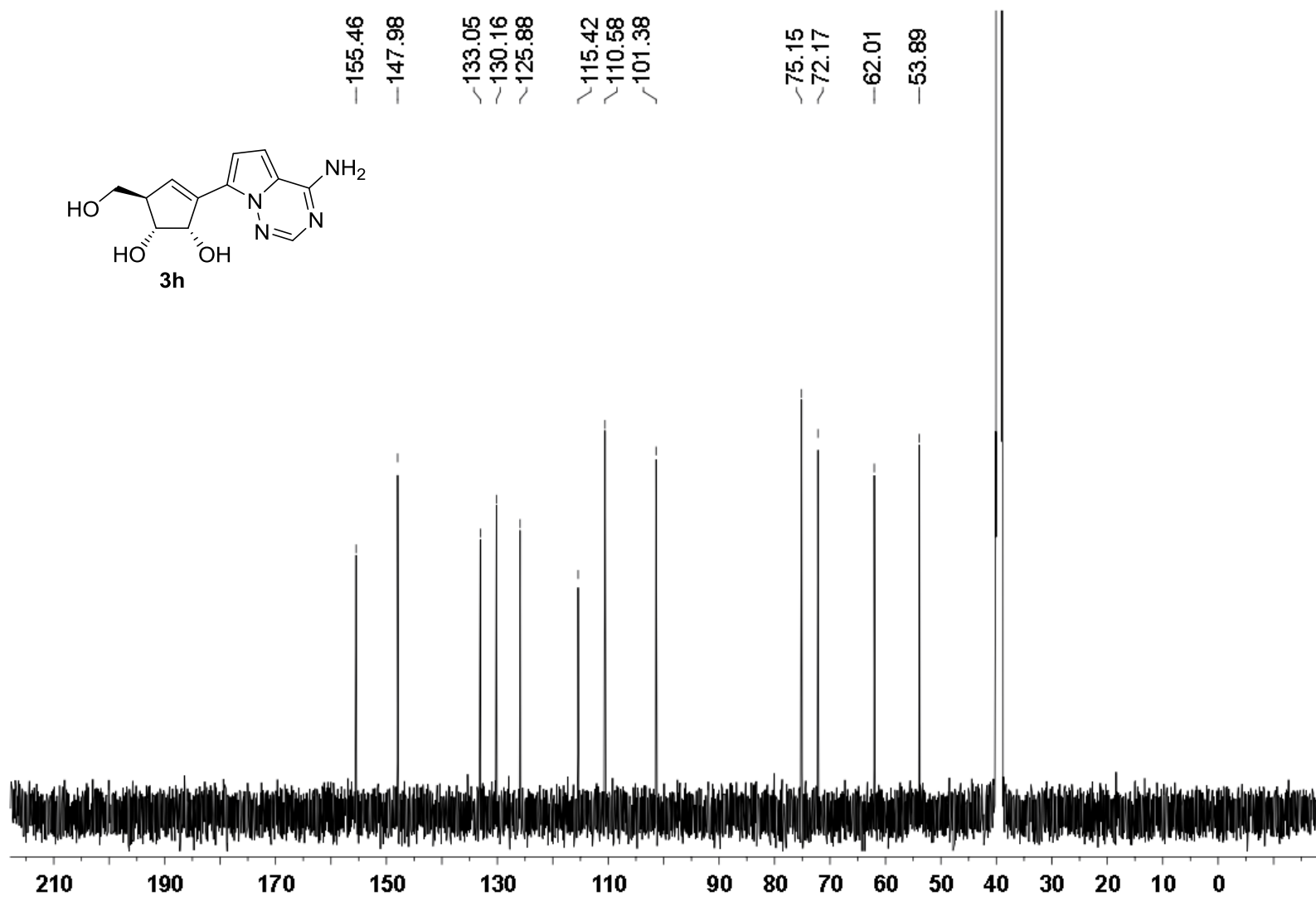
^1H NMR (500 MHz) spectrum of **3g** in CD_3OD



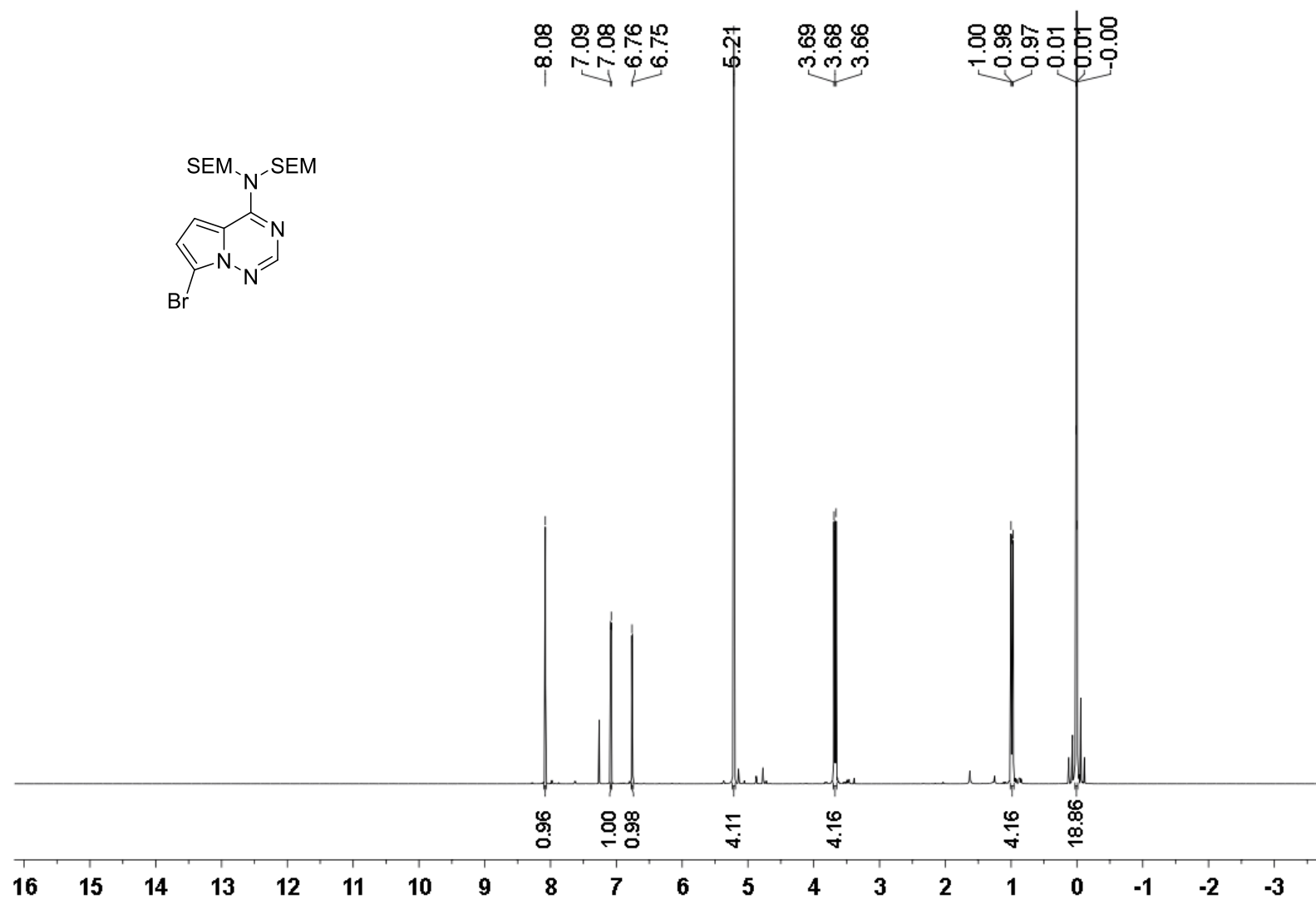
¹³C NMR (126 MHz) spectrum of **3g** in CD₃OD



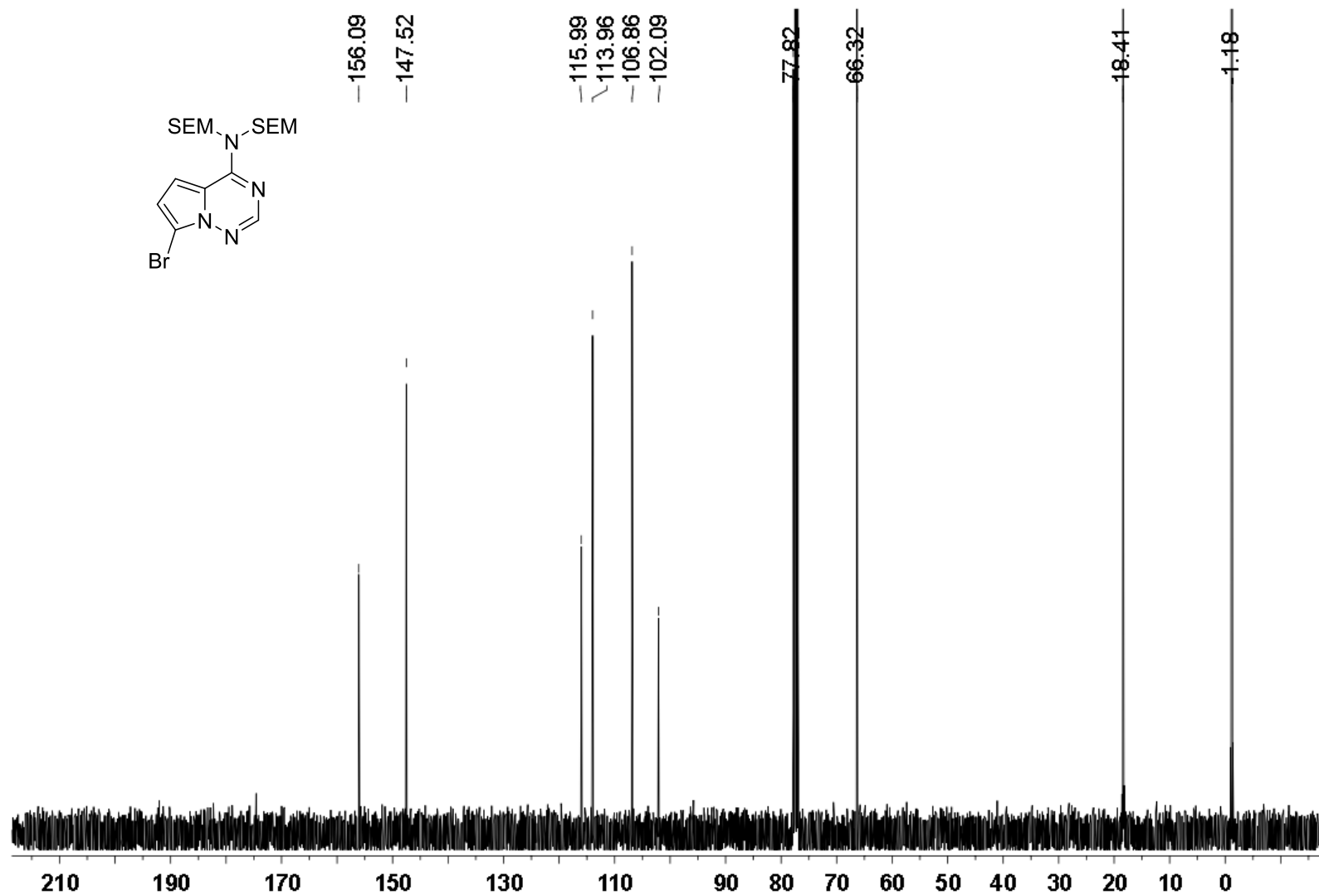
^1H NMR (500 MHz) spectrum of **3h** in $\text{DMSO}-d_6$



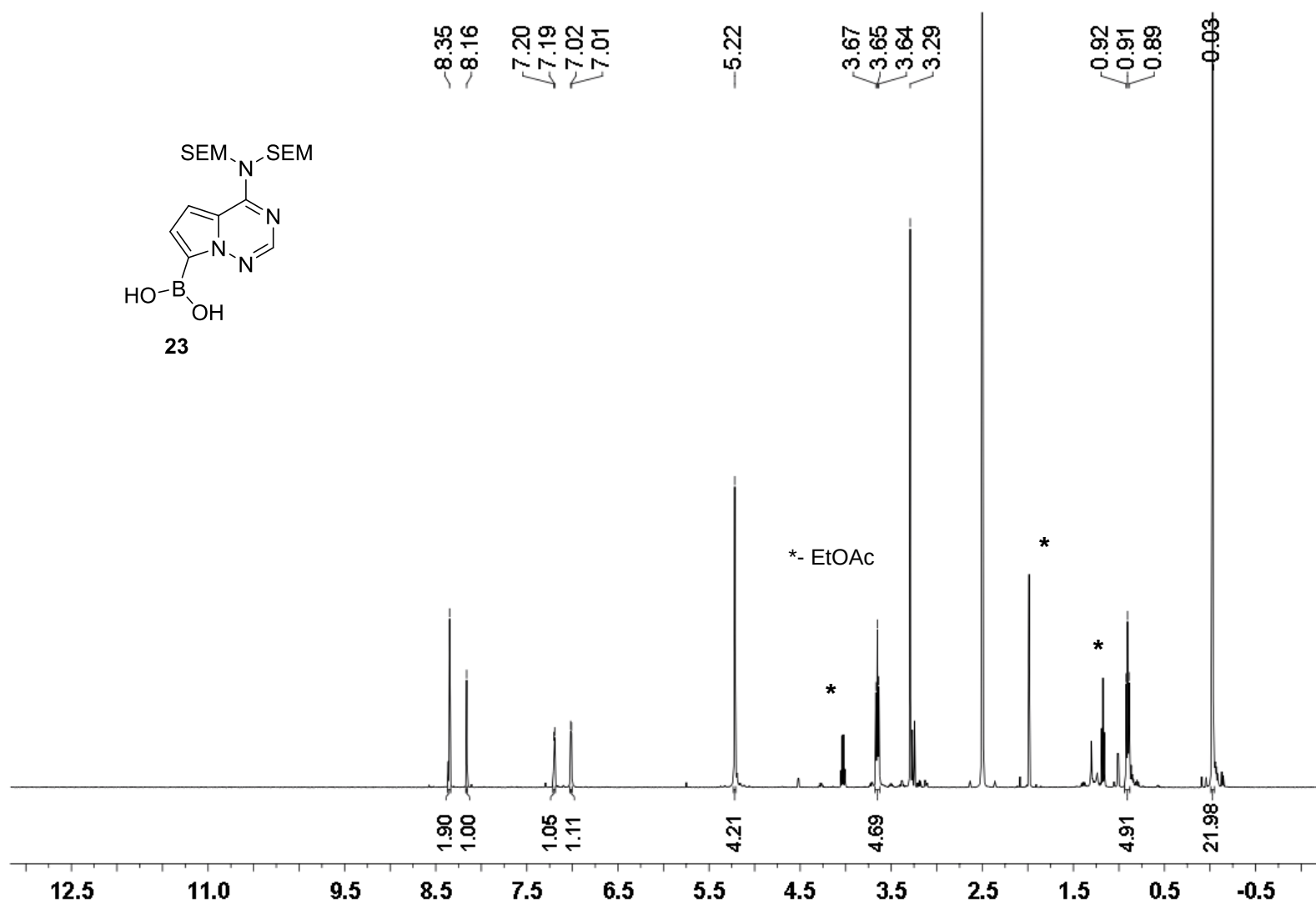
^{13}C NMR (500 MHz) spectrum of **3h** in DMSO- d_6



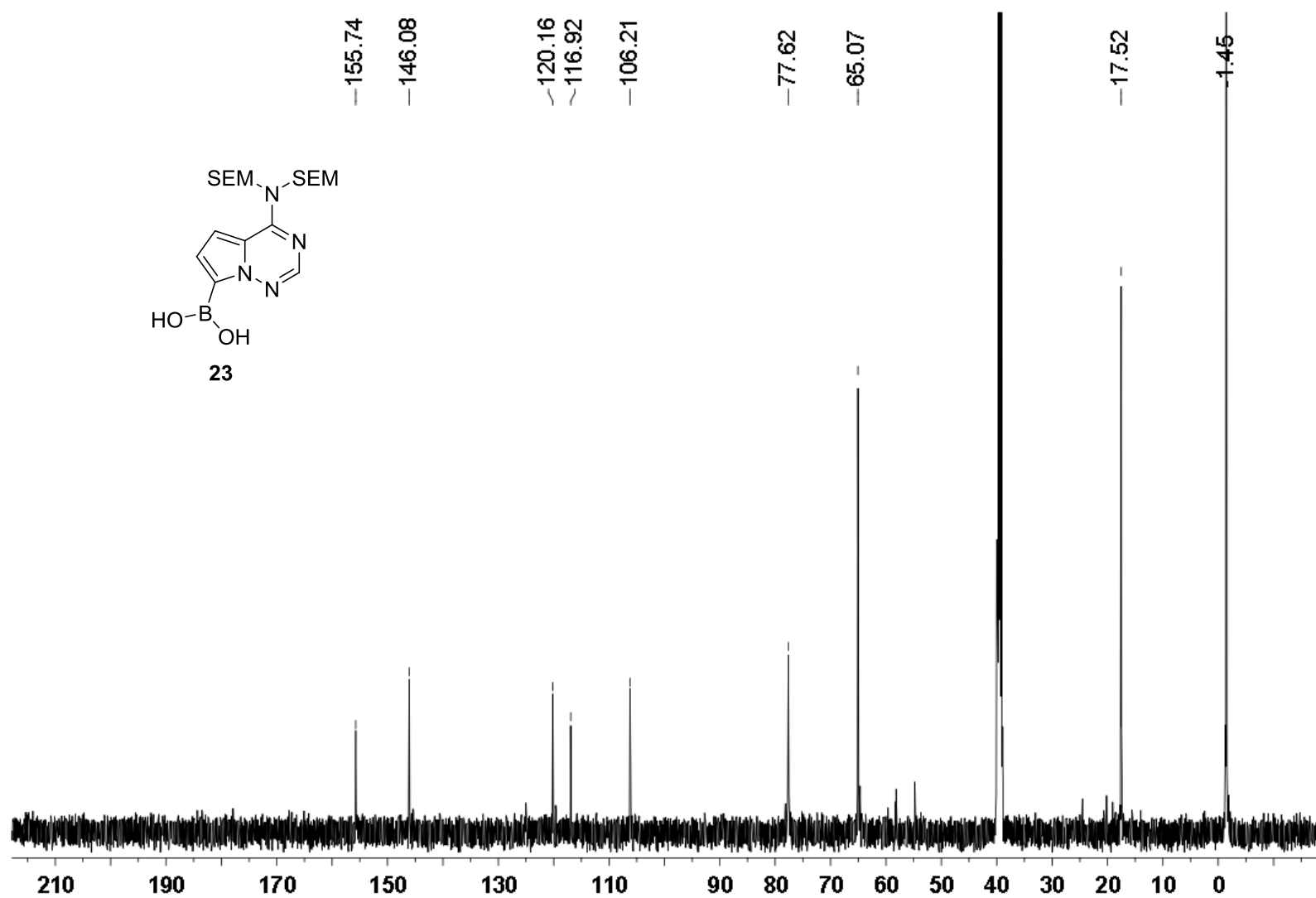
^1H NMR (500 MHz) spectrum in CDCl_3



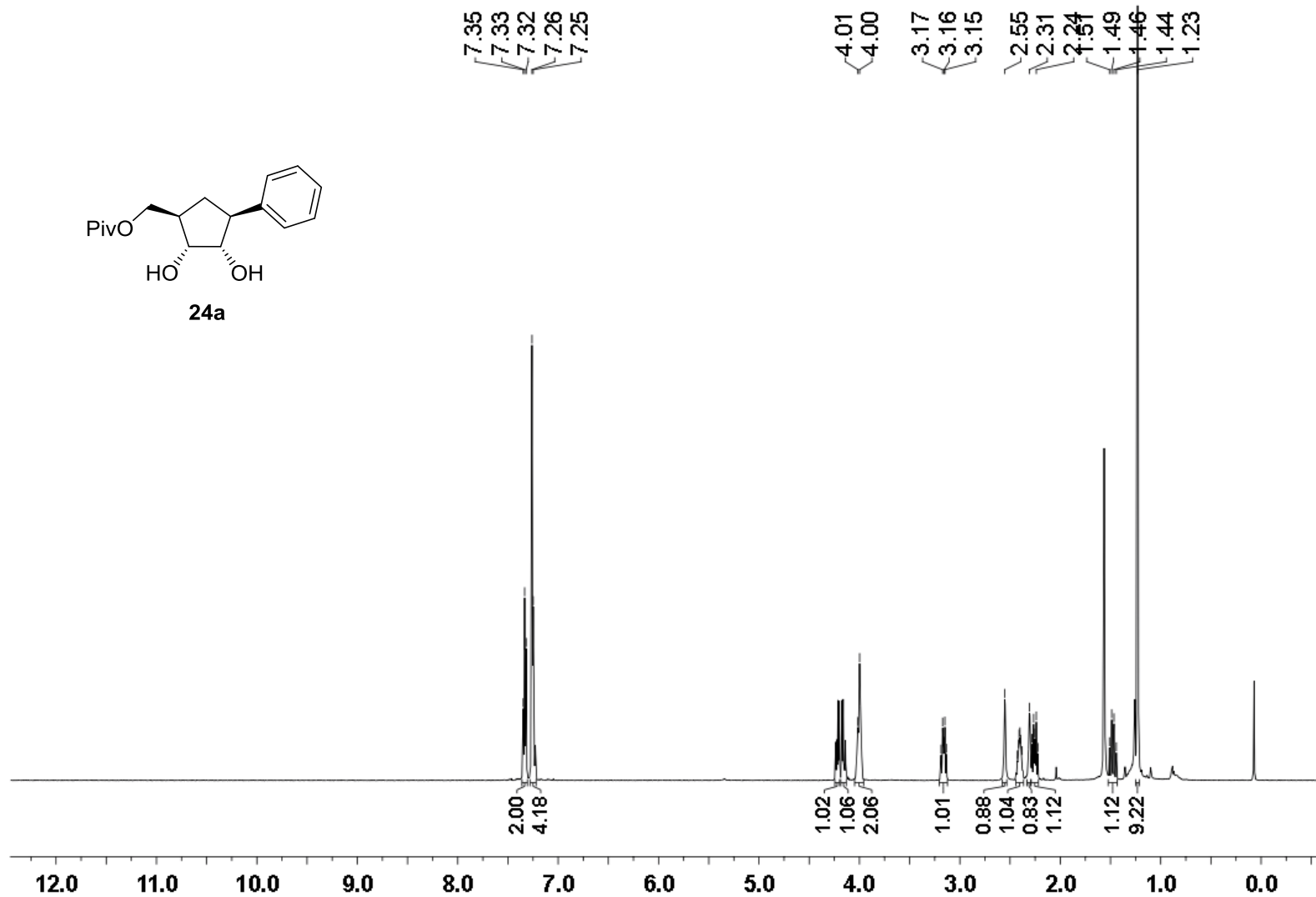
^{13}C NMR (126 MHz) spectrum in CDCl_3



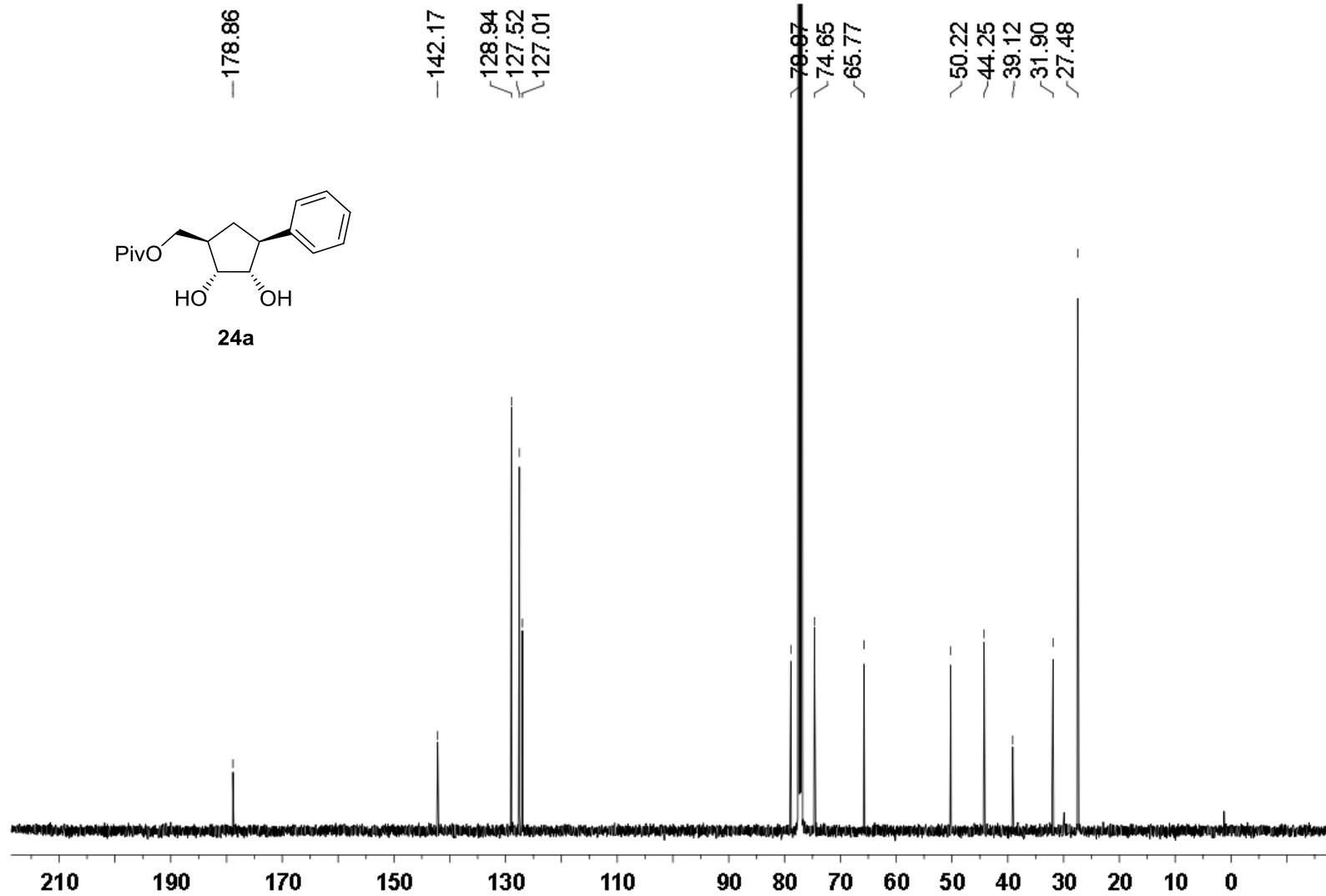
¹H NMR (500 MHz) spectrum of **23** in DMSO-*d*₆



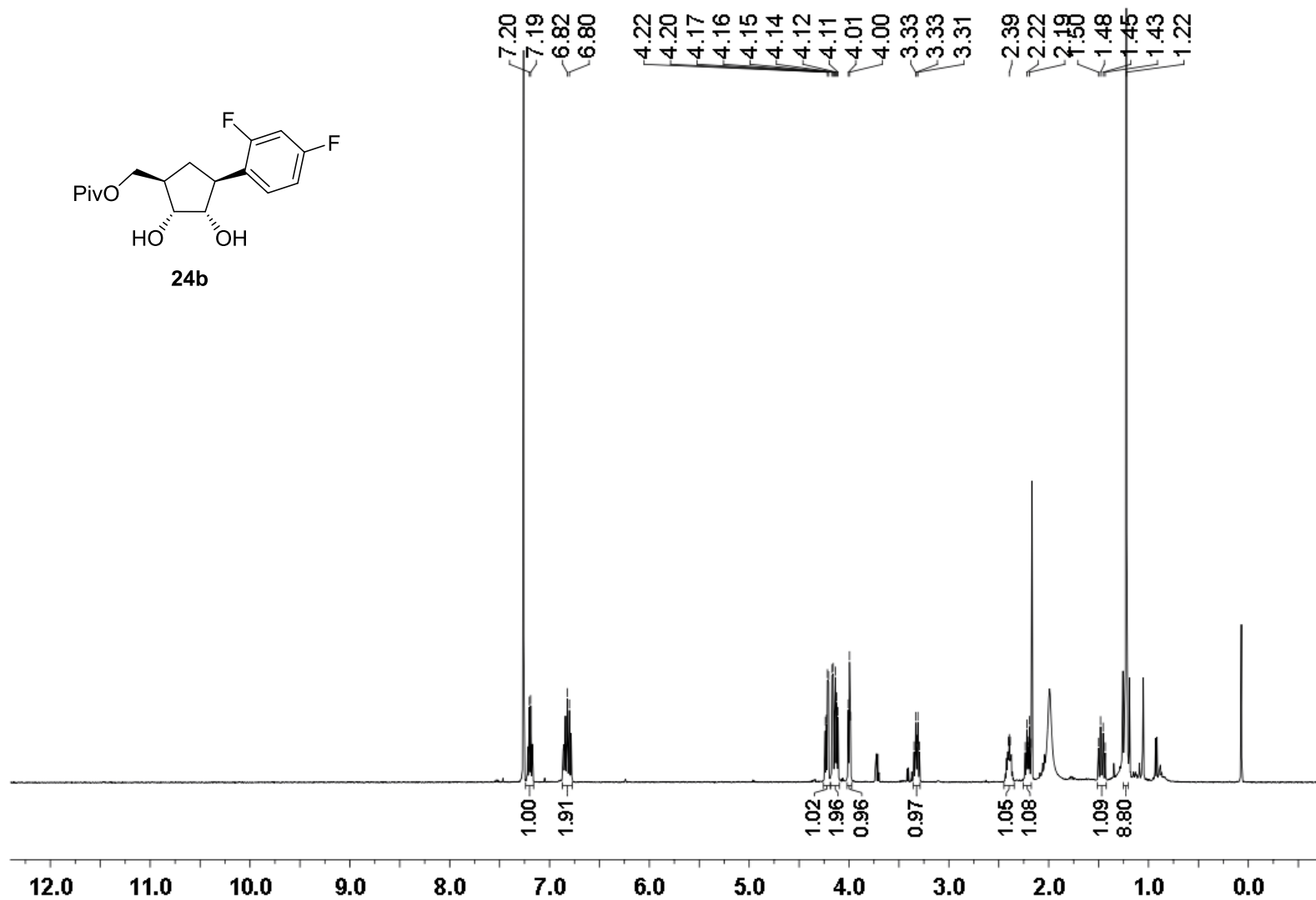
^{13}C NMR (126 MHz) spectrum of **23** in DMSO- d_6



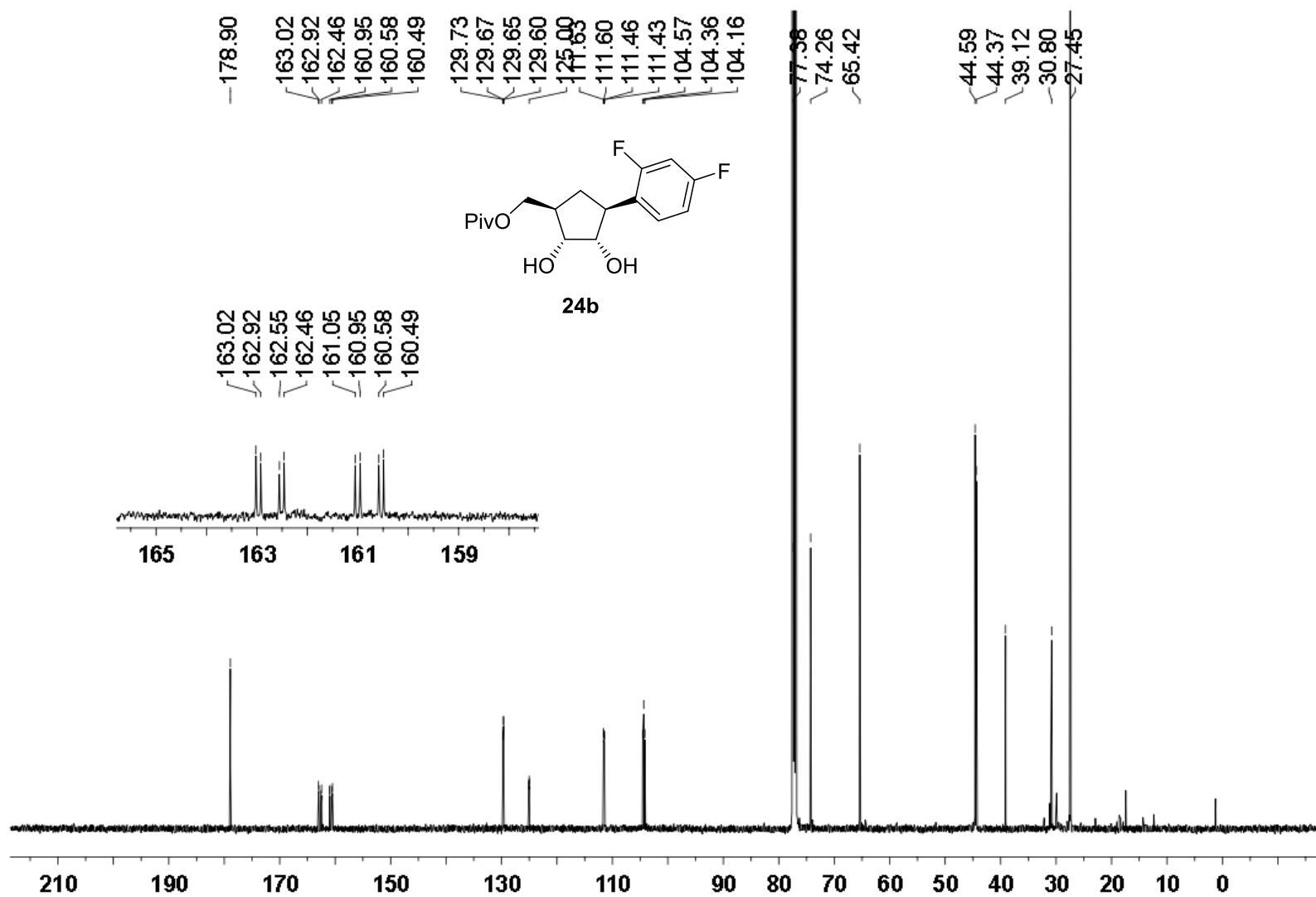
^1H NMR (500 MHz) spectrum of **24a** in CDCl_3



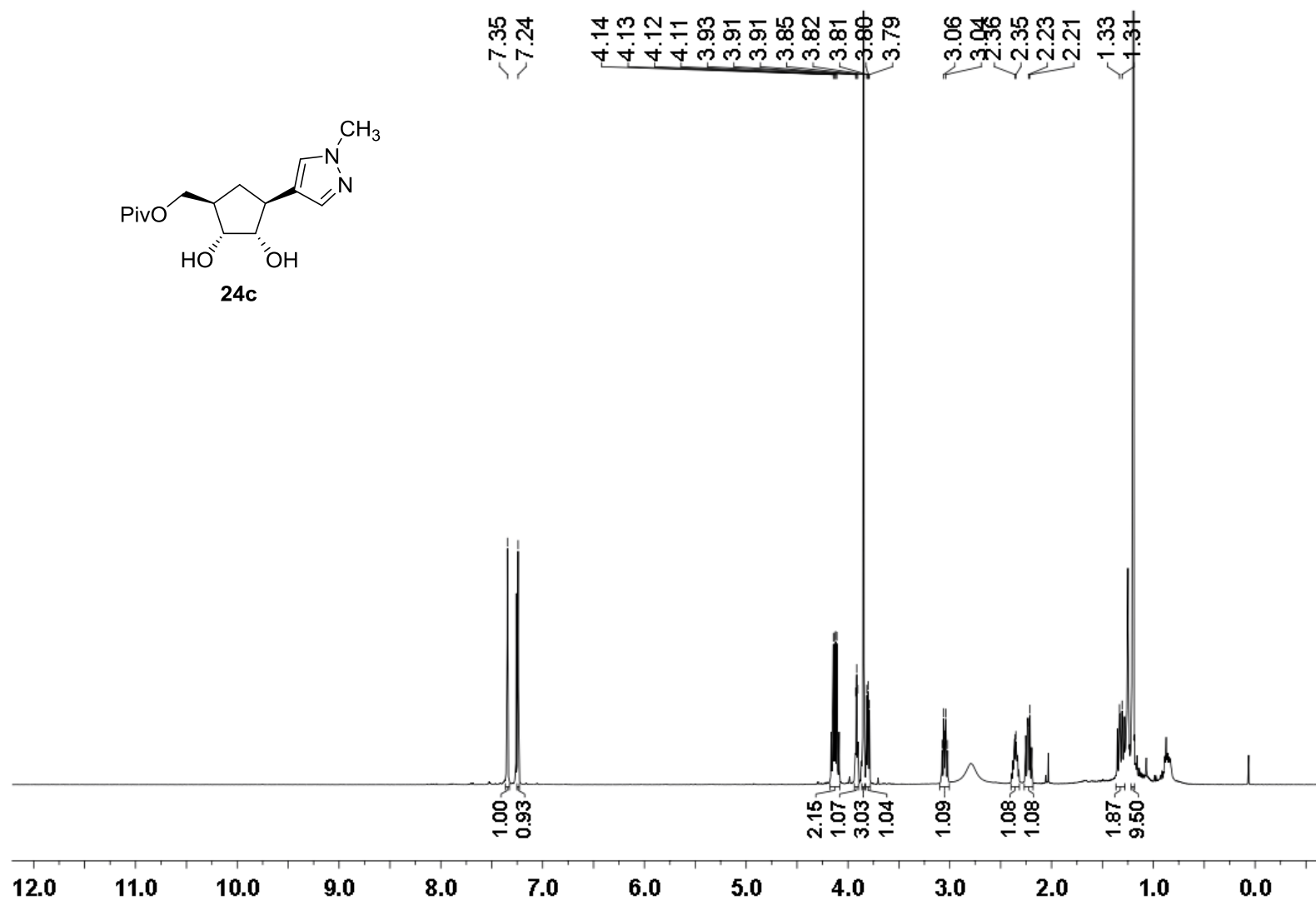
¹³C NMR (126 MHz) spectrum of **24a** in CDCl₃



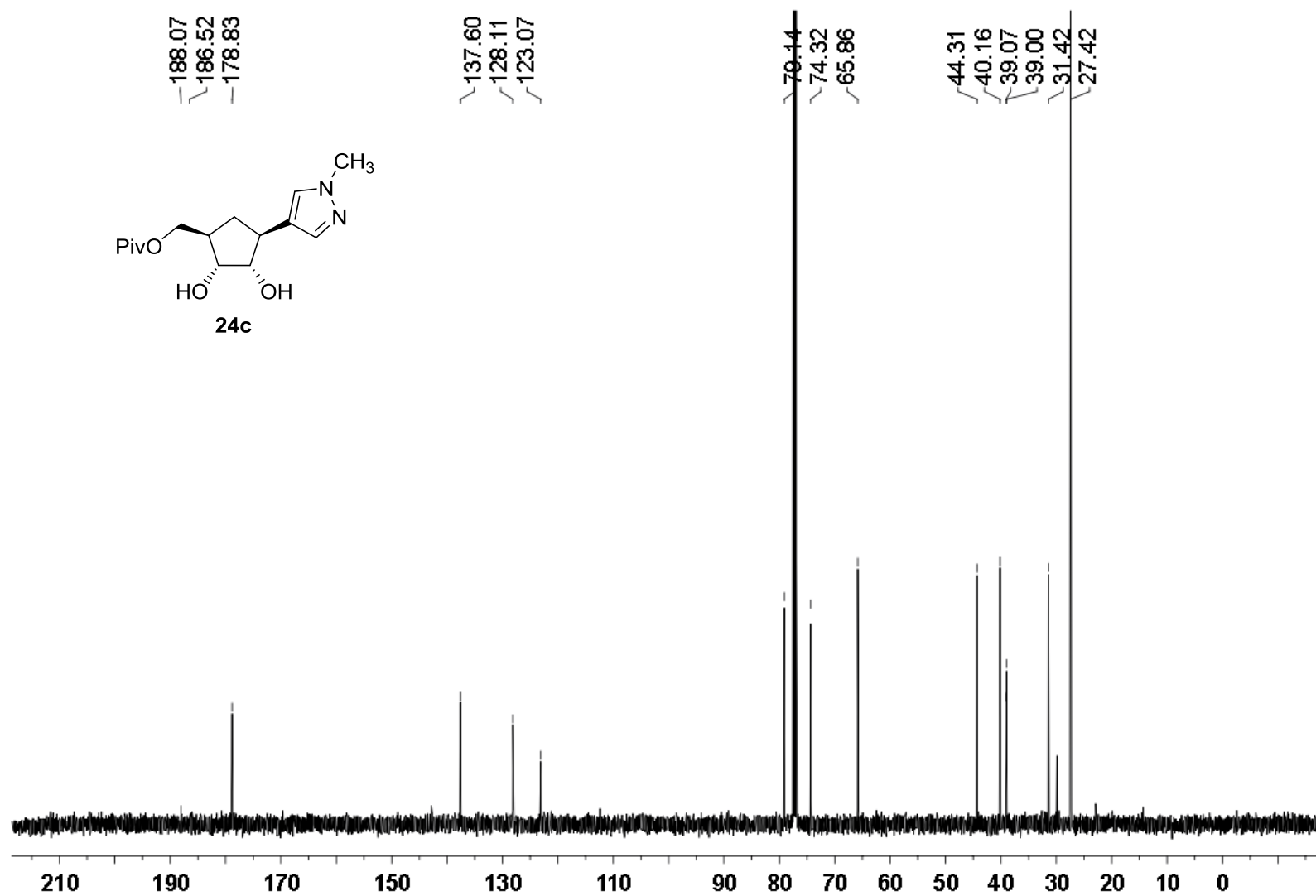
^1H NMR (500 MHz) spectrum of **24b** in CDCl_3



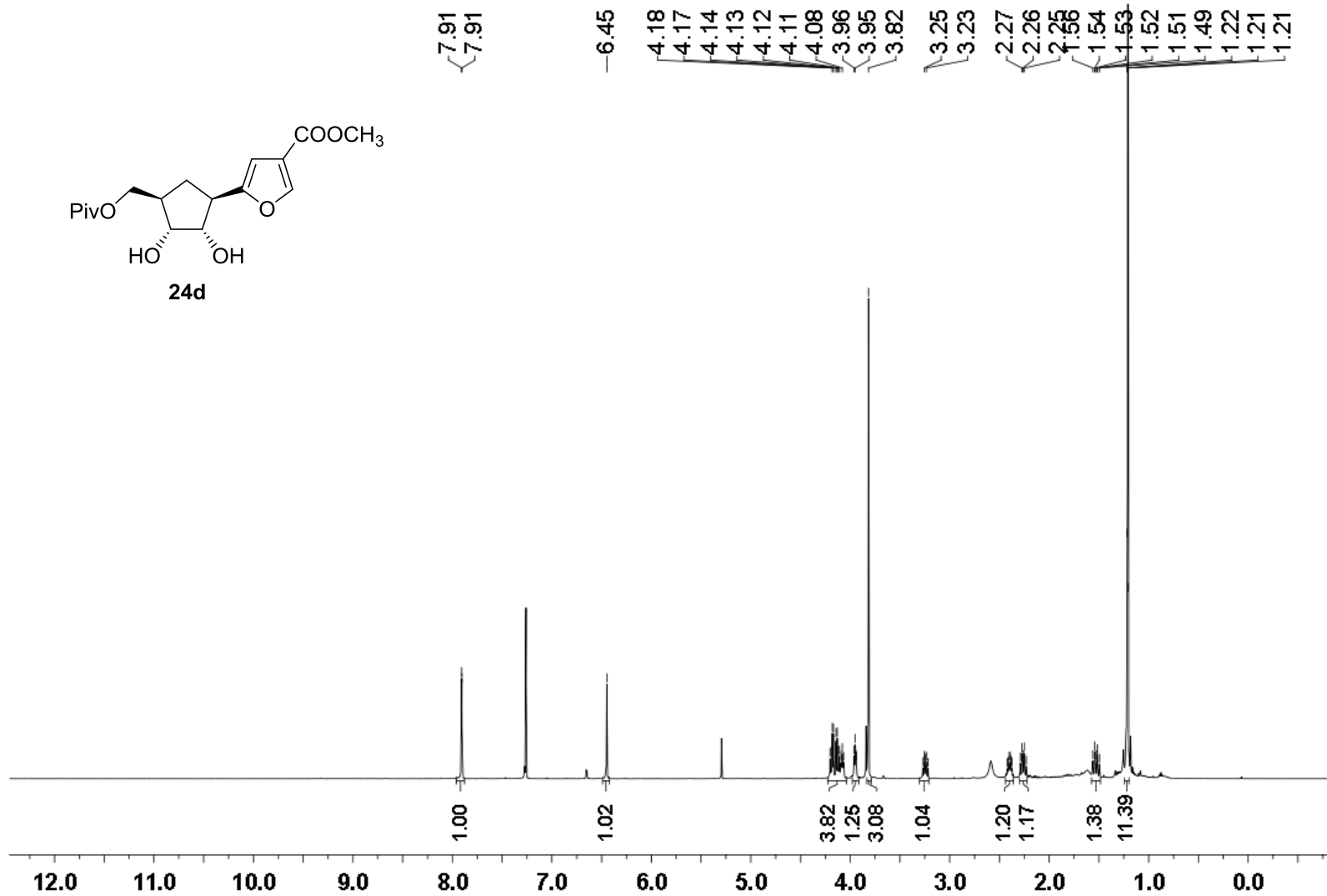
¹³C NMR (126 MHz) spectrum of **24b** in CDCl₃



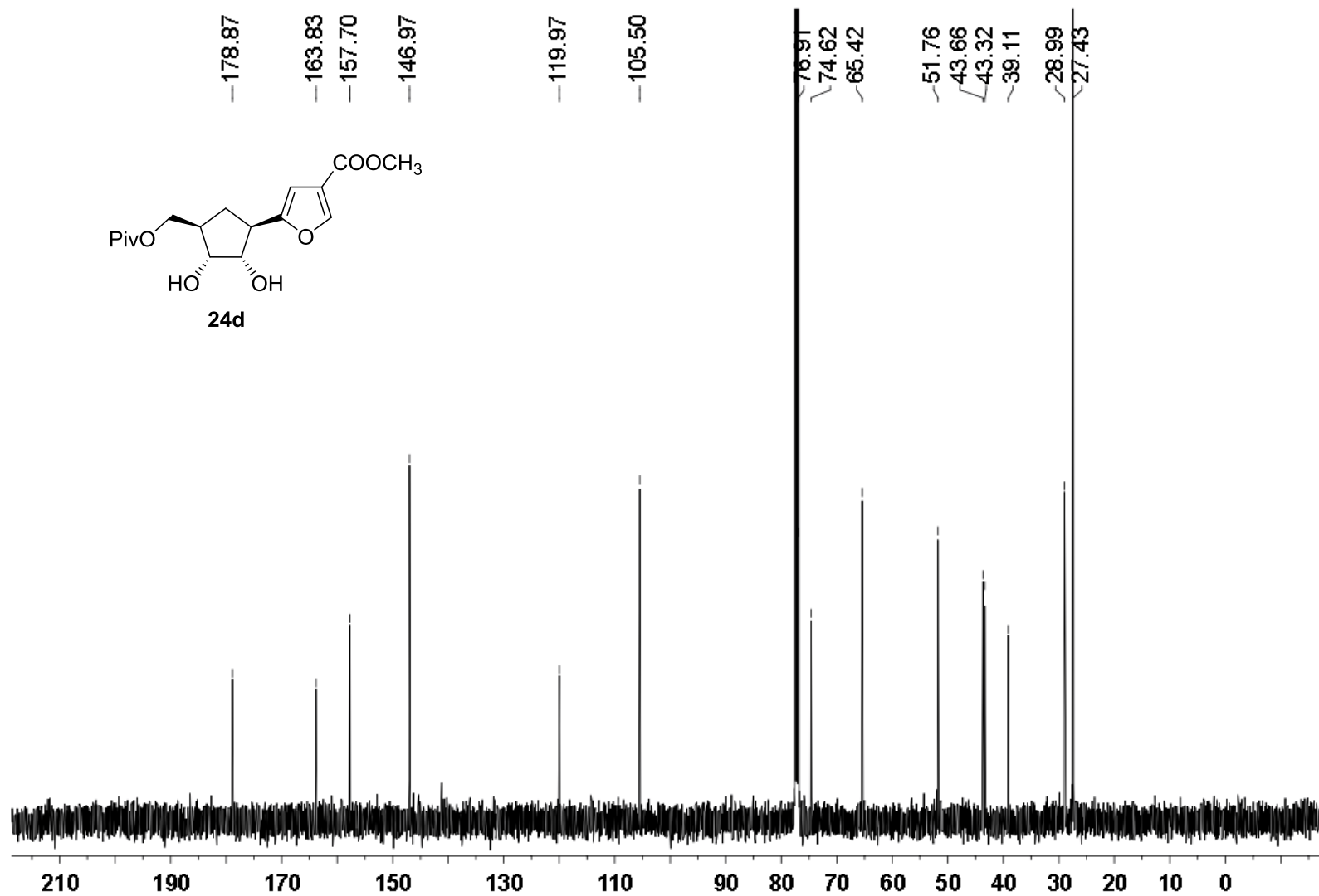
¹H NMR (500 MHz) spectrum of **24c** in CDCl₃



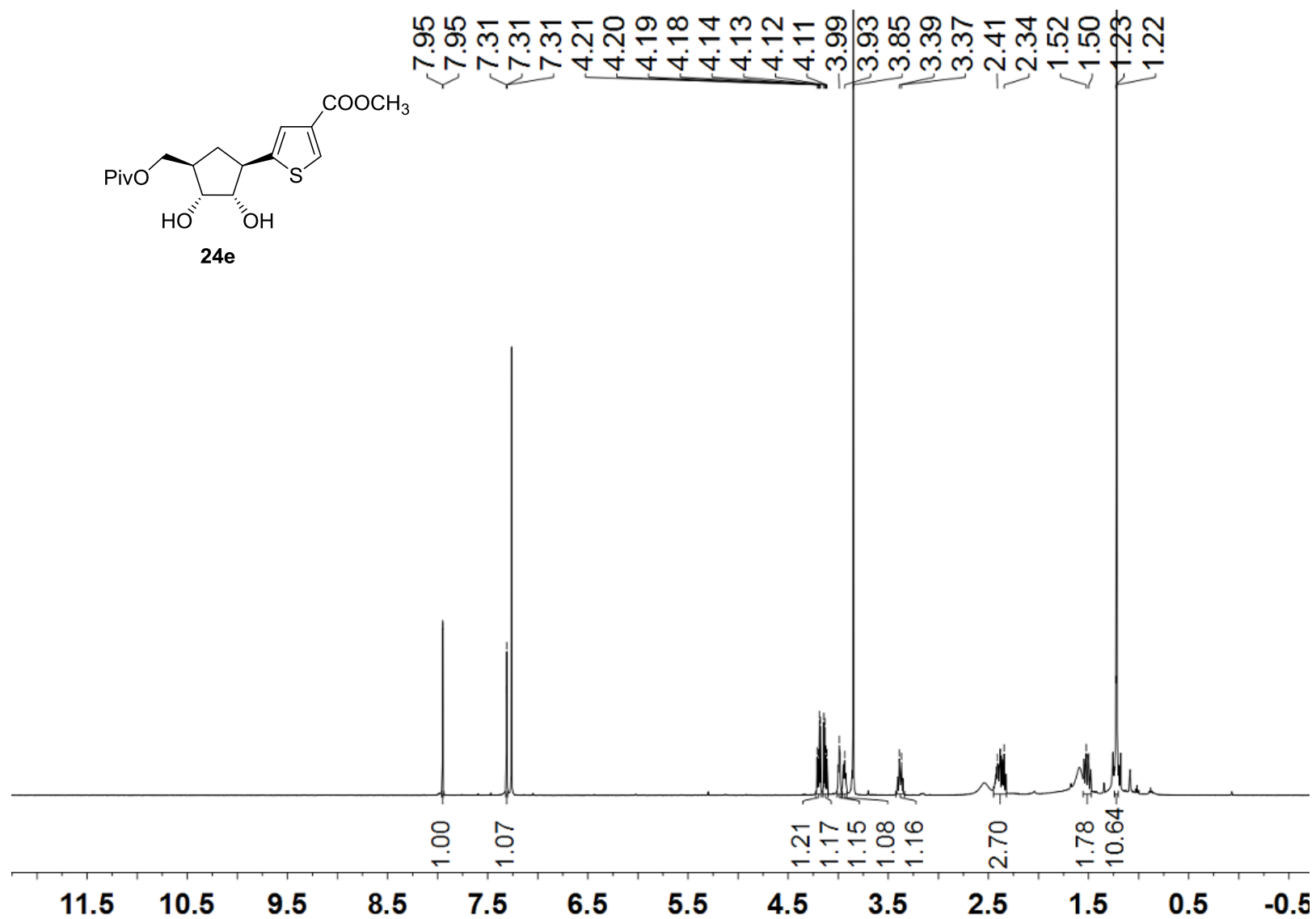
¹³C NMR (126 MHz) spectrum of **24c** in CDCl₃



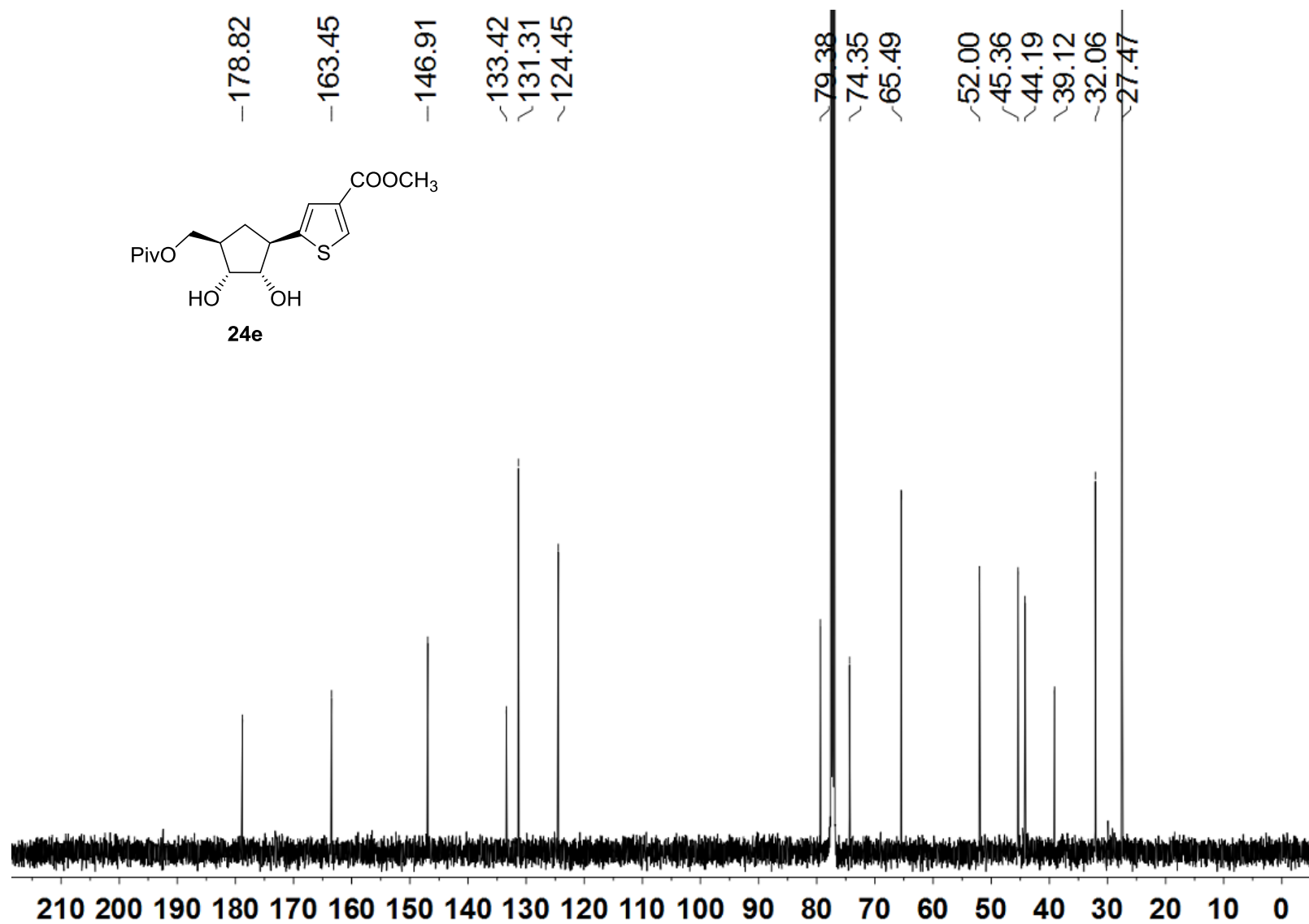
^1H NMR (500 MHz) spectrum of **24d** in CDCl_3



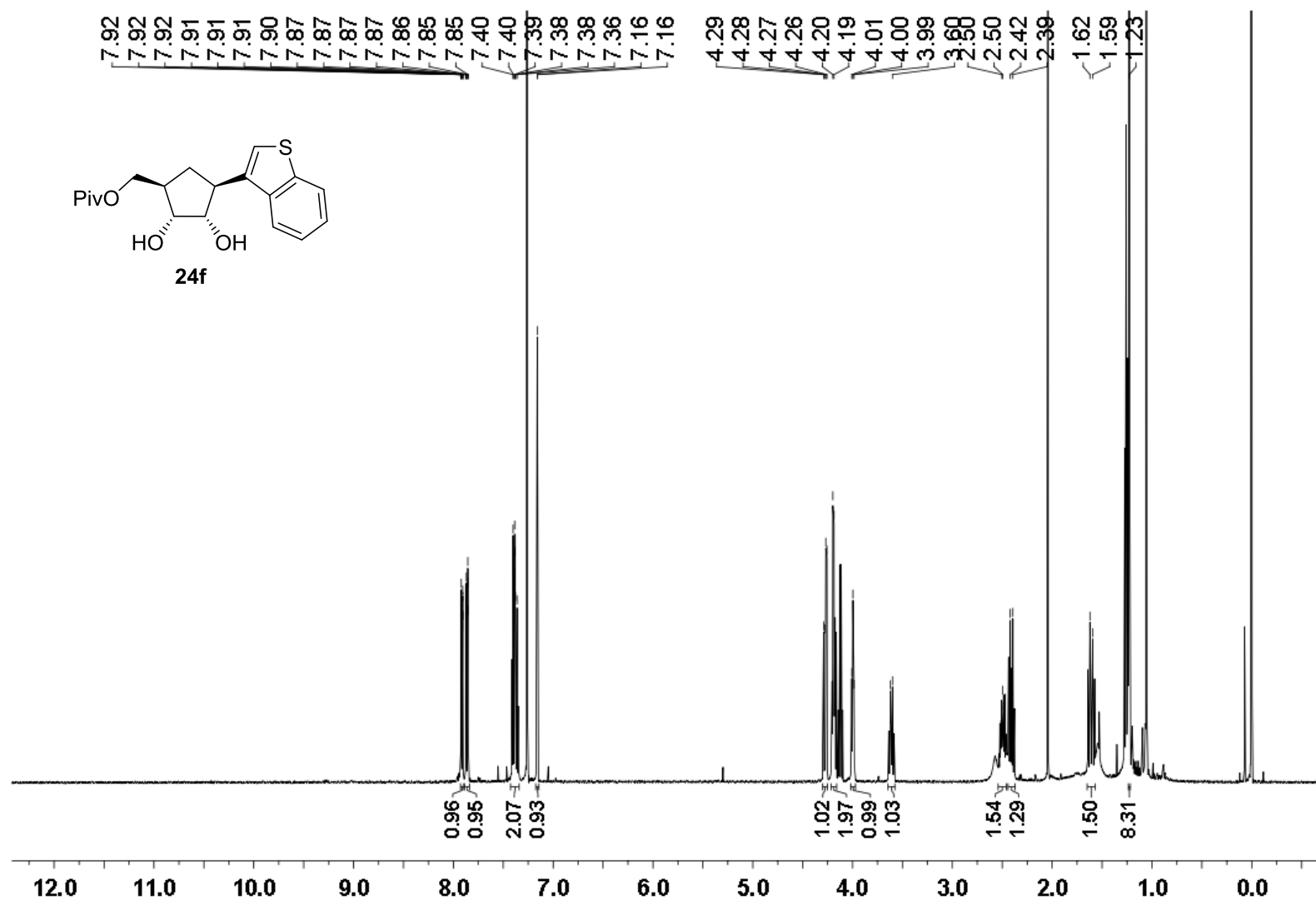
¹³C NMR (126 MHz) spectrum of **24d** in CDCl₃



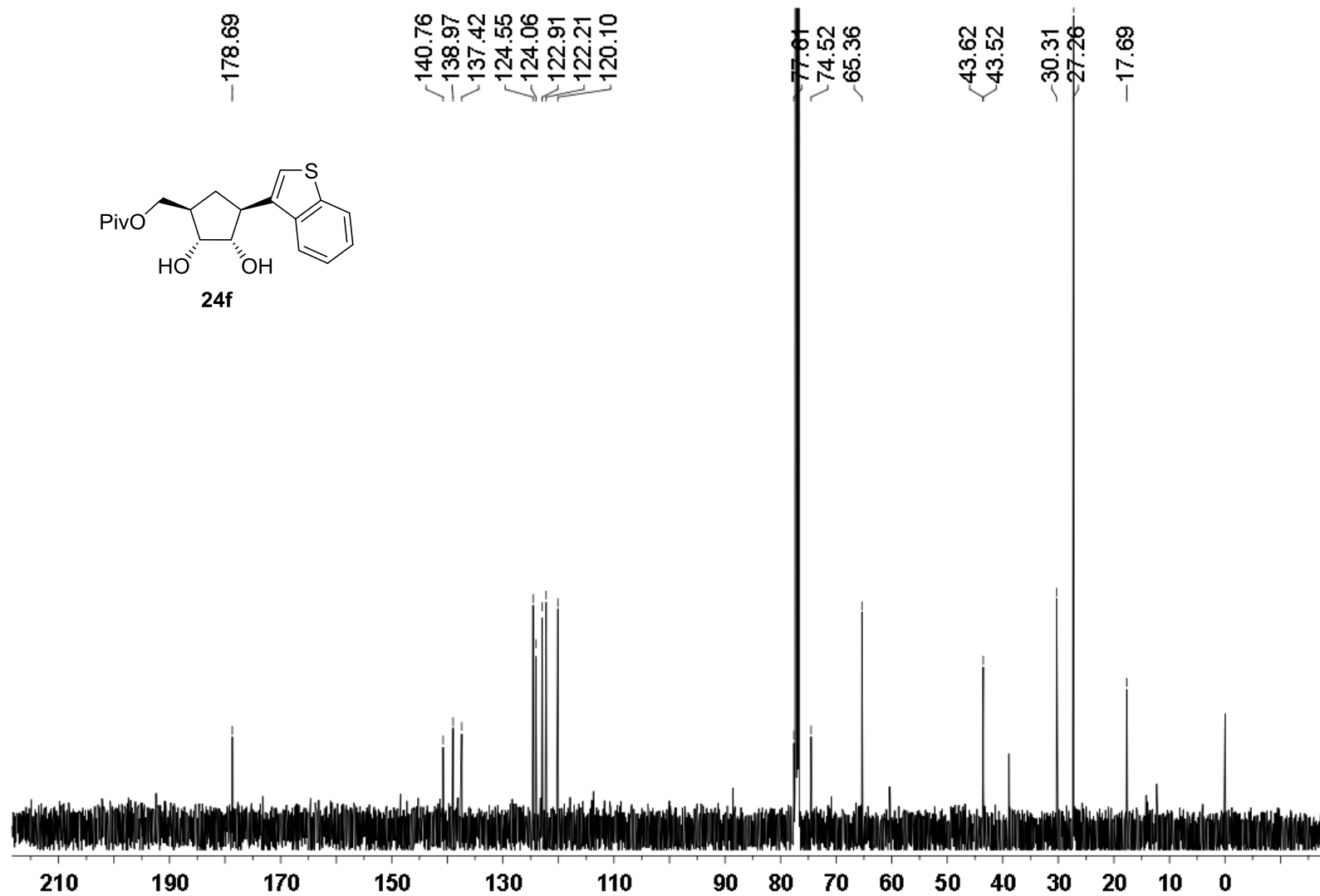
^1H NMR (500 MHz) spectrum of **24e** in CDCl_3



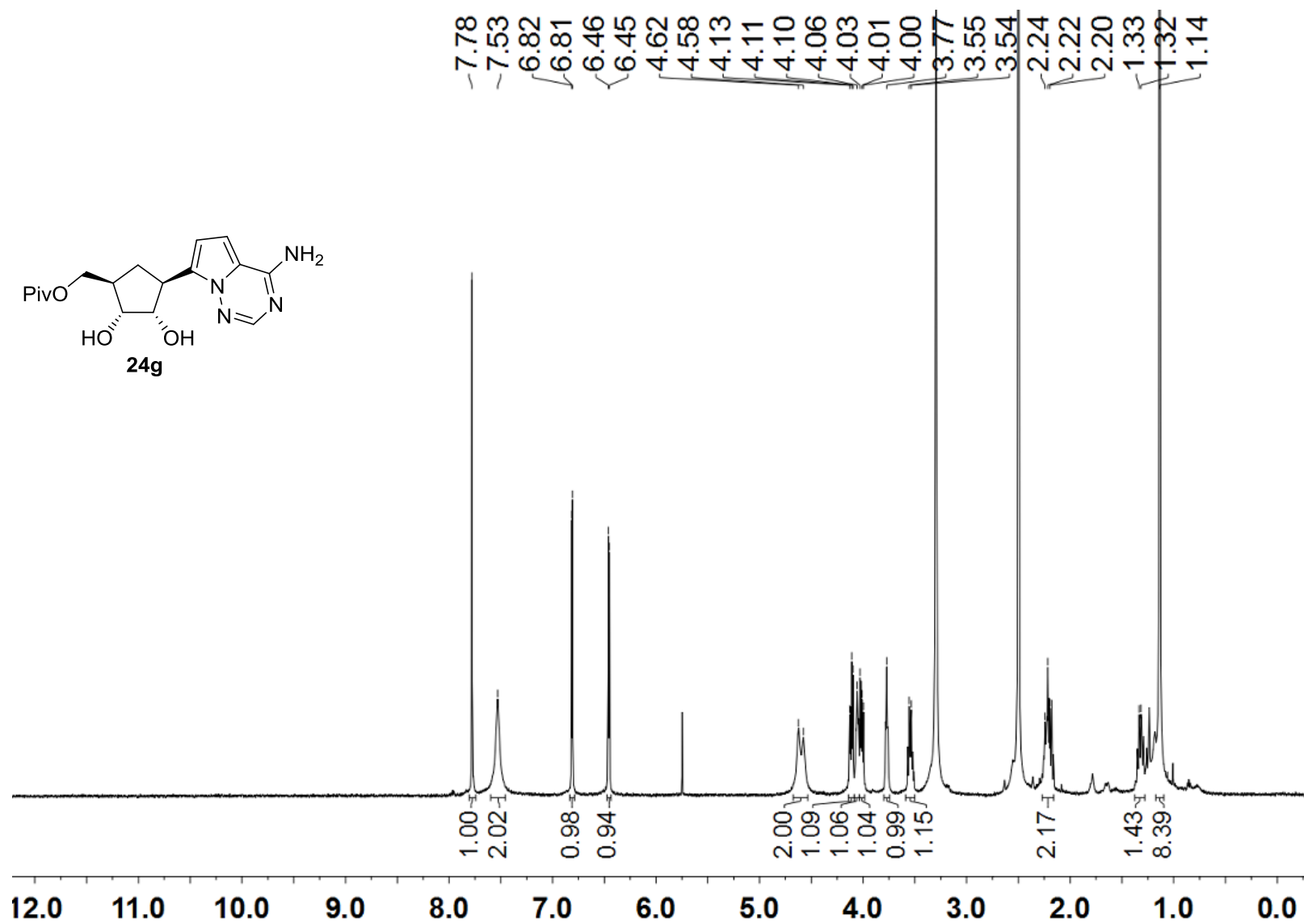
¹³C NMR (500 MHz) spectrum of **24e** in CDCl₃



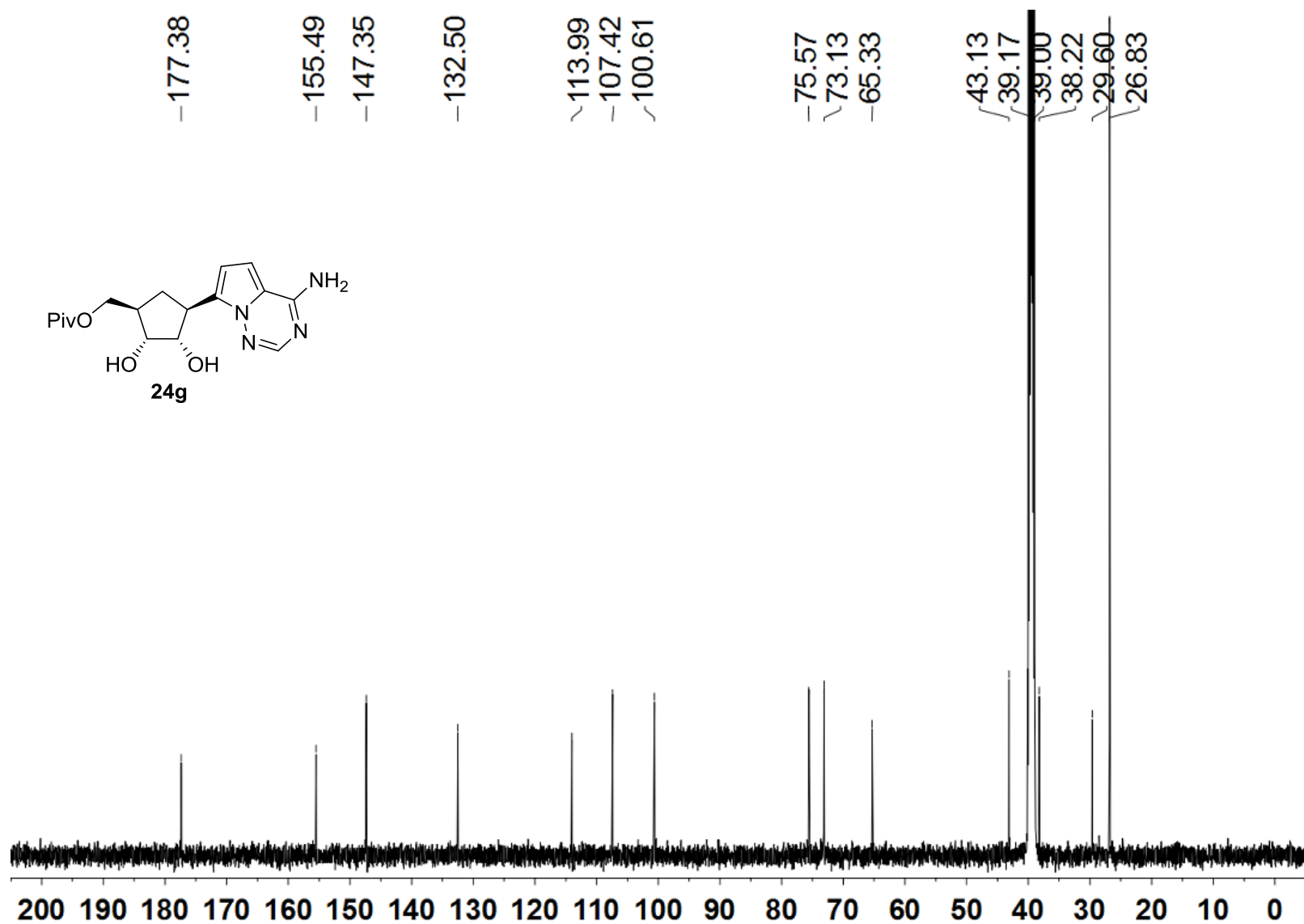
¹H NMR (500 MHz) spectrum of **24f** in CDCl₃



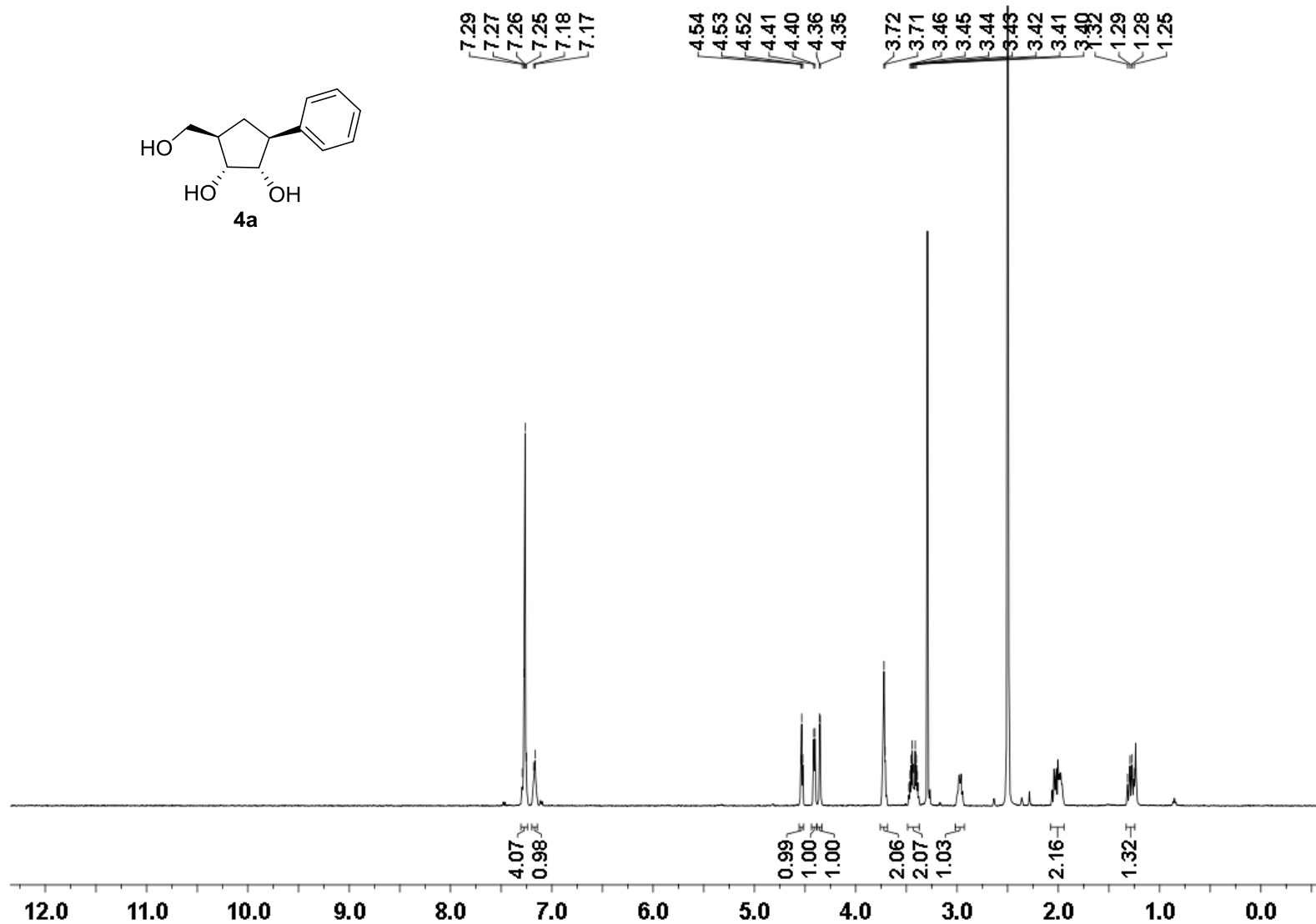
¹³C NMR (126 MHz) spectrum of **24f** in CDCl₃



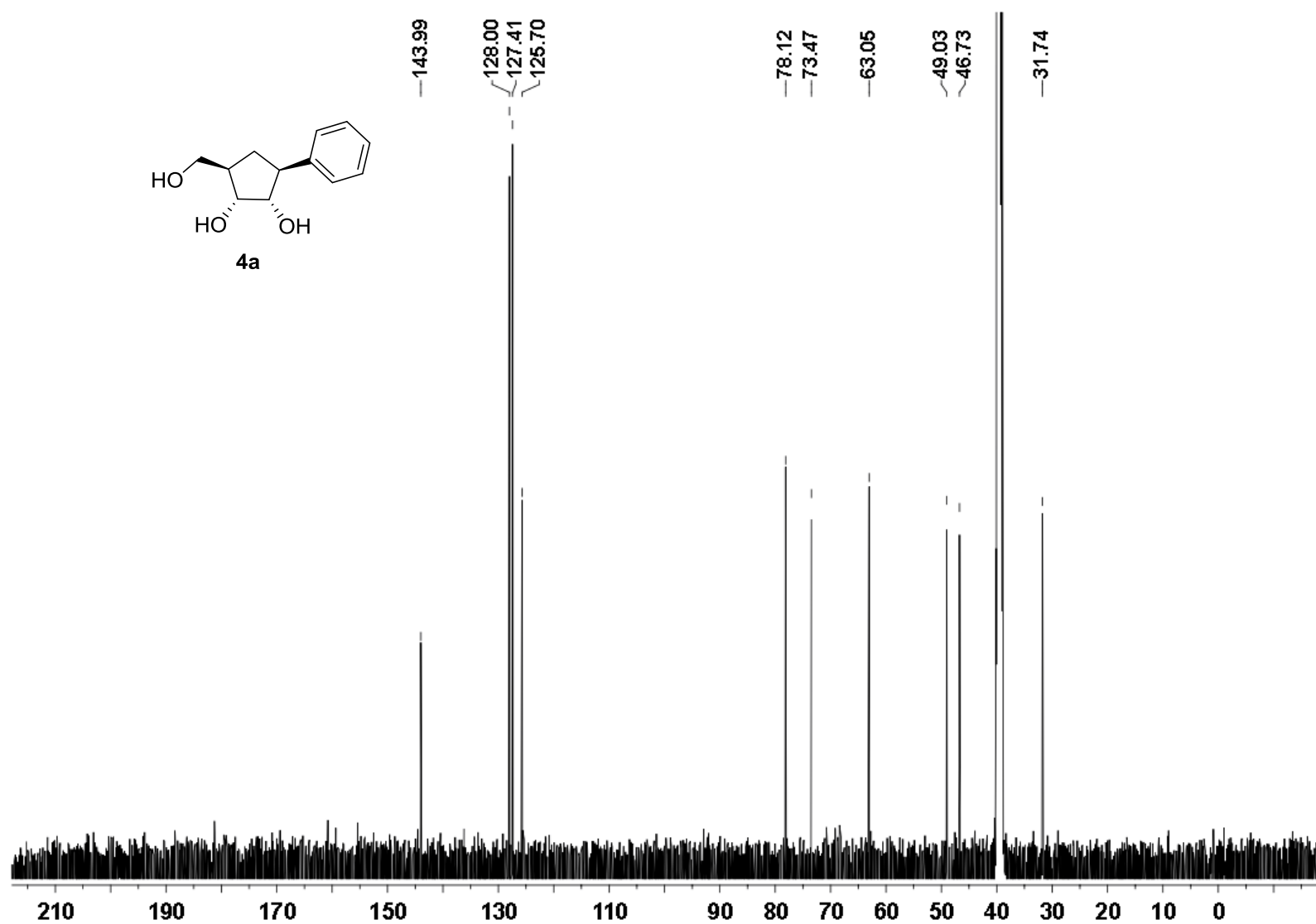
^1H NMR (500 MHz) spectrum of **24g** in $\text{DMSO}-d_6$



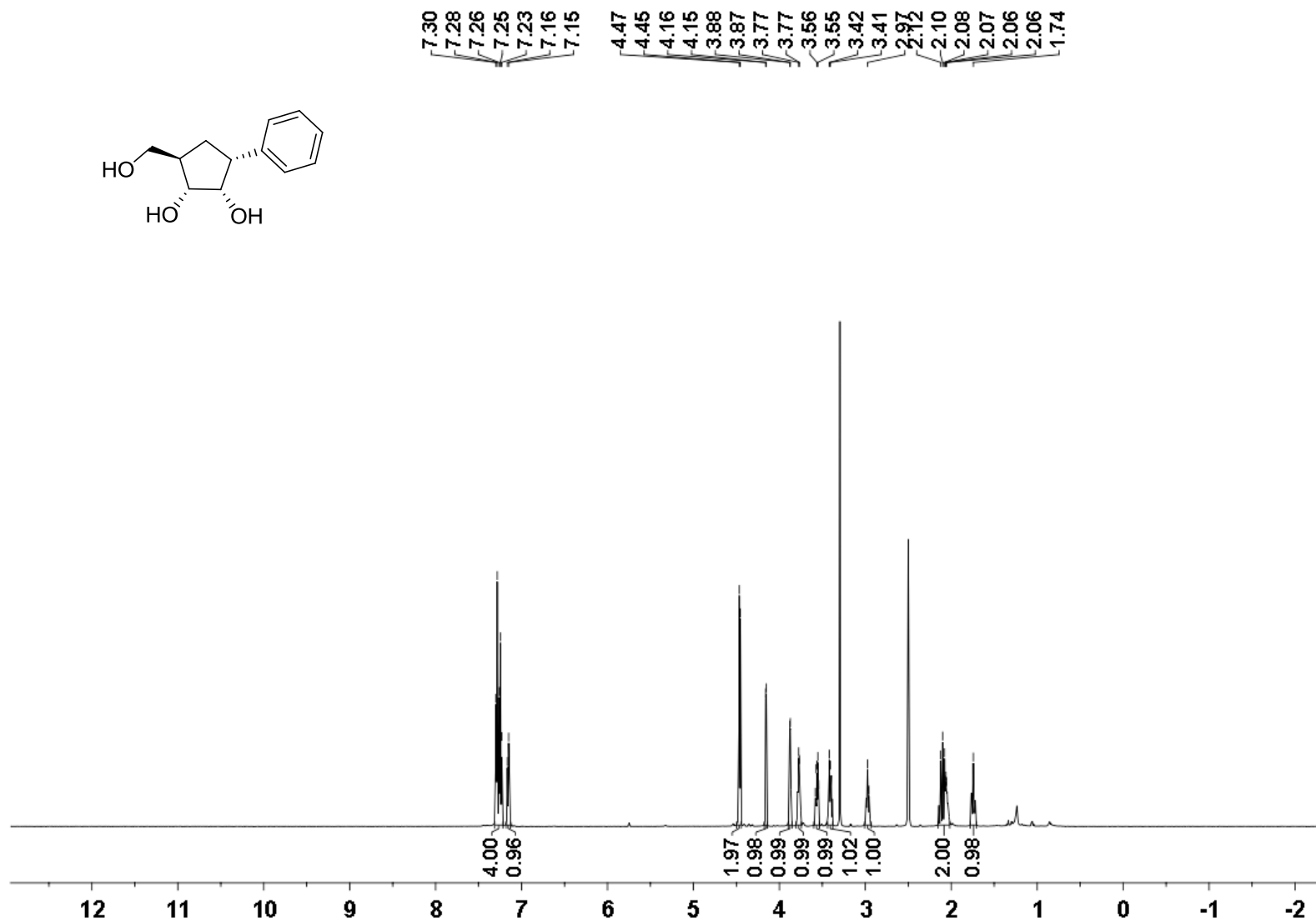
^1H NMR (500 MHz) spectrum of **24g** in $\text{DMSO}-d_6$



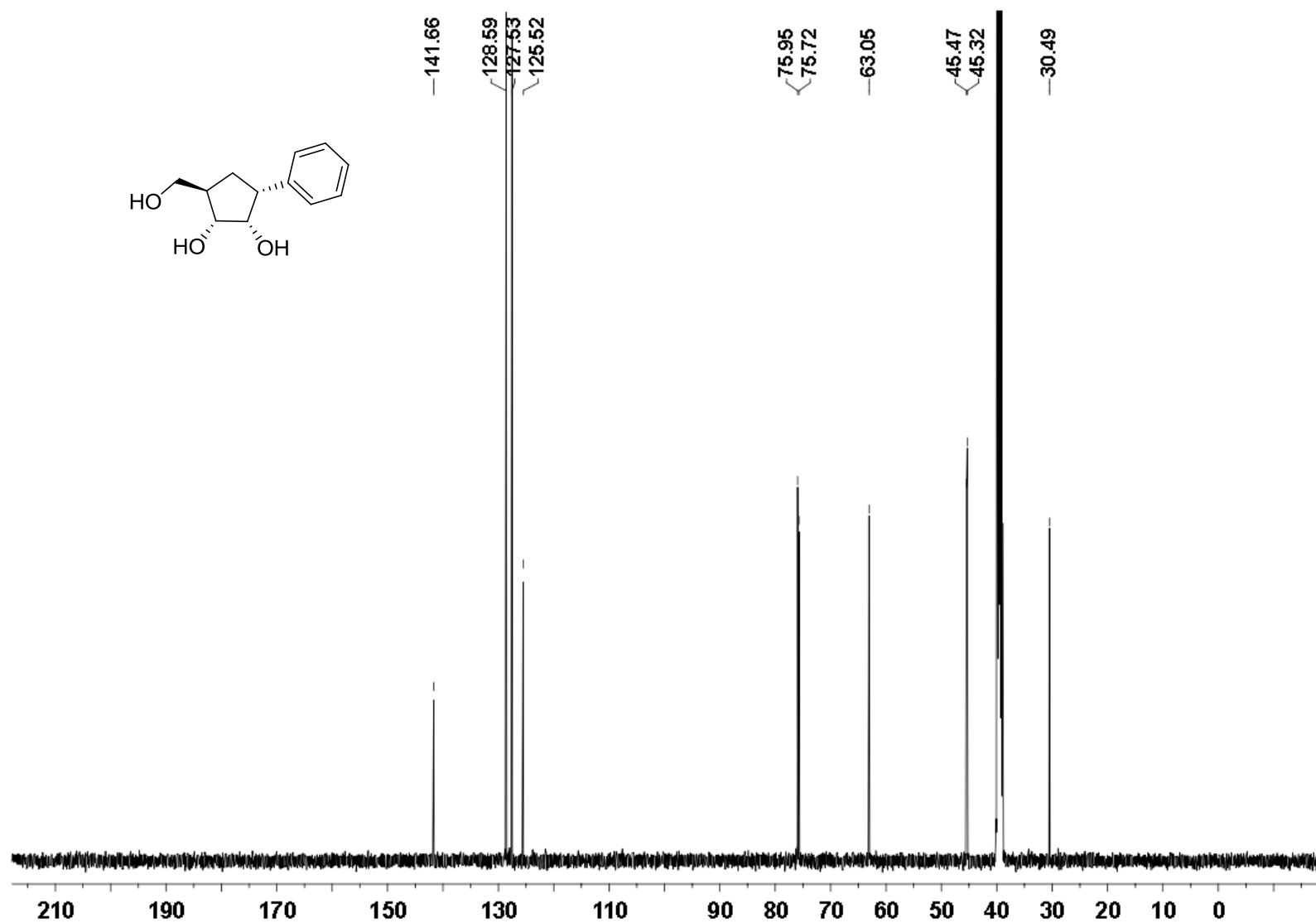
^1H NMR (500 MHz) spectrum of **4a** in $\text{DMSO}-d_6$



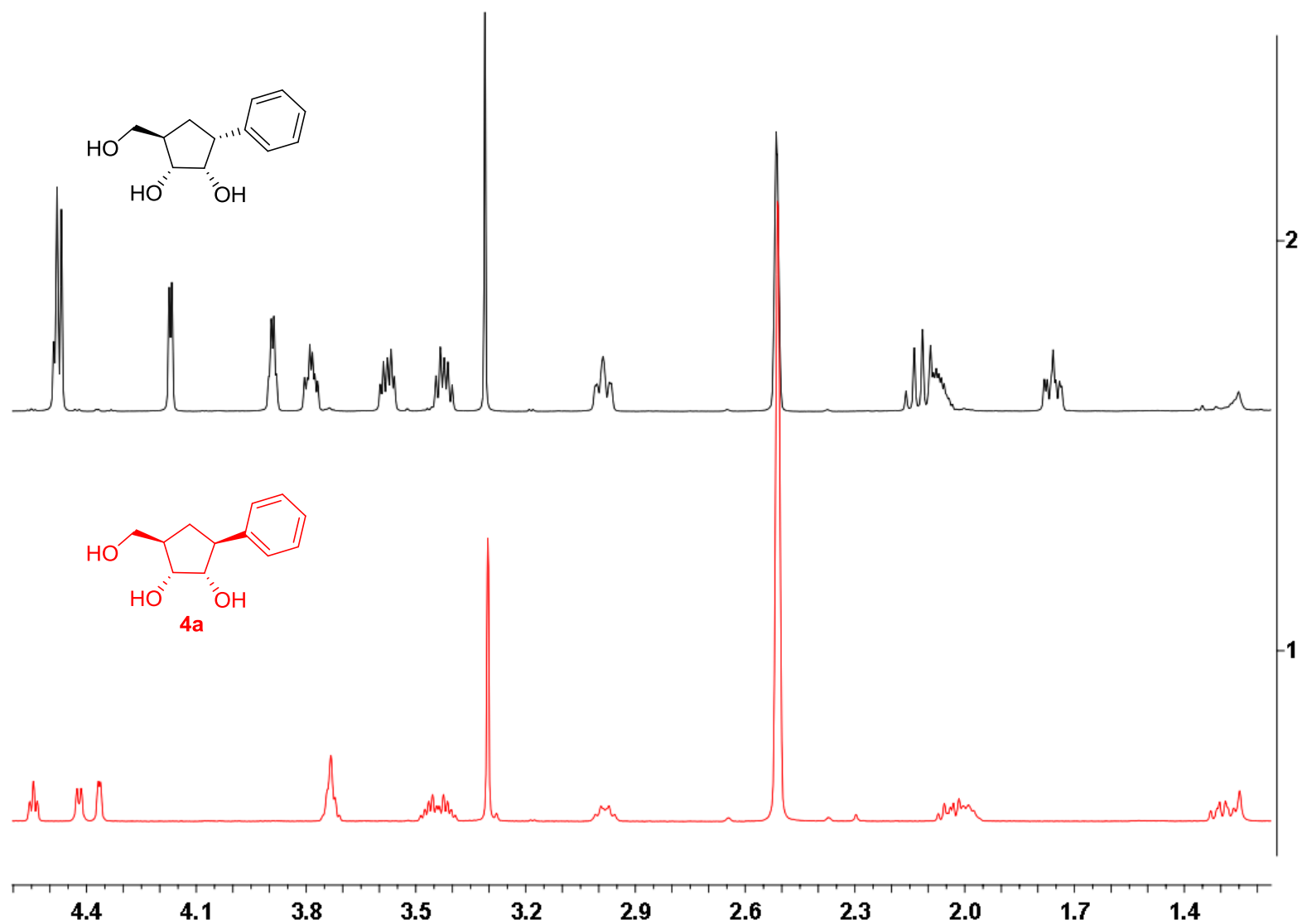
^{13}C NMR (126 MHz) spectrum of **4a** in $\text{DMSO}-d_6$



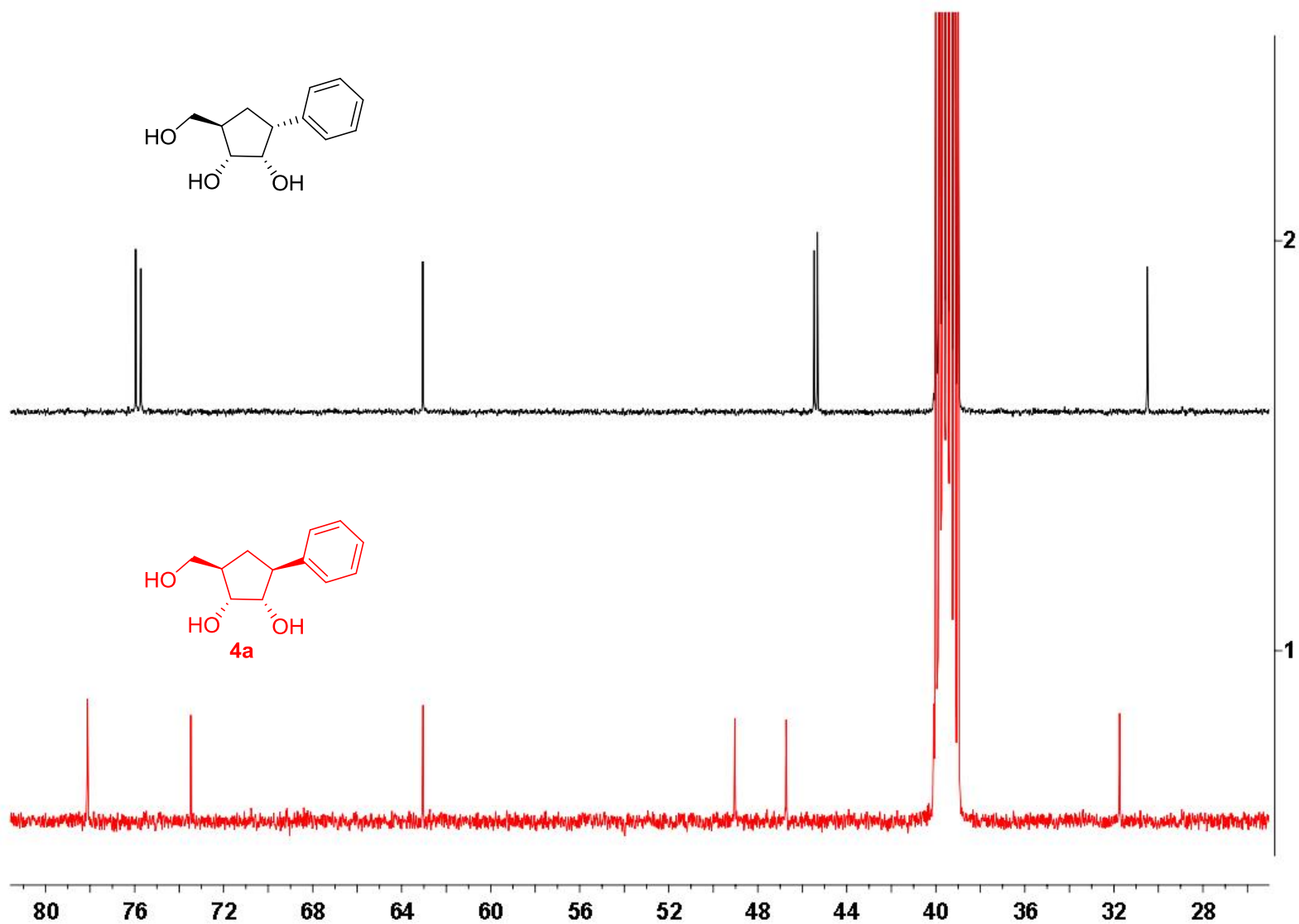
^1H NMR (500 MHz) spectrum in $\text{DMSO}-d_6$



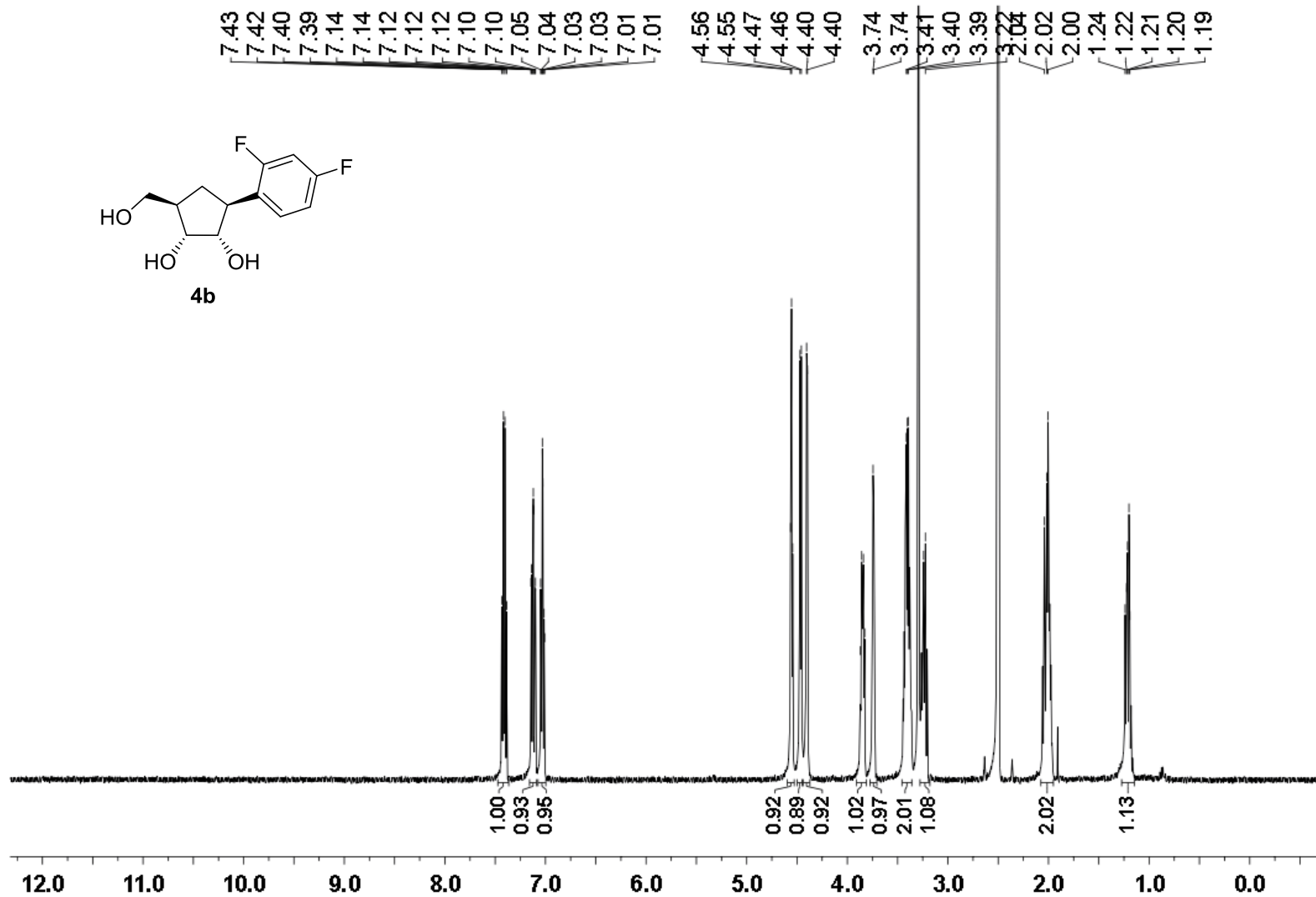
^{13}C NMR (126 MHz) spectrum in DMSO- d_6



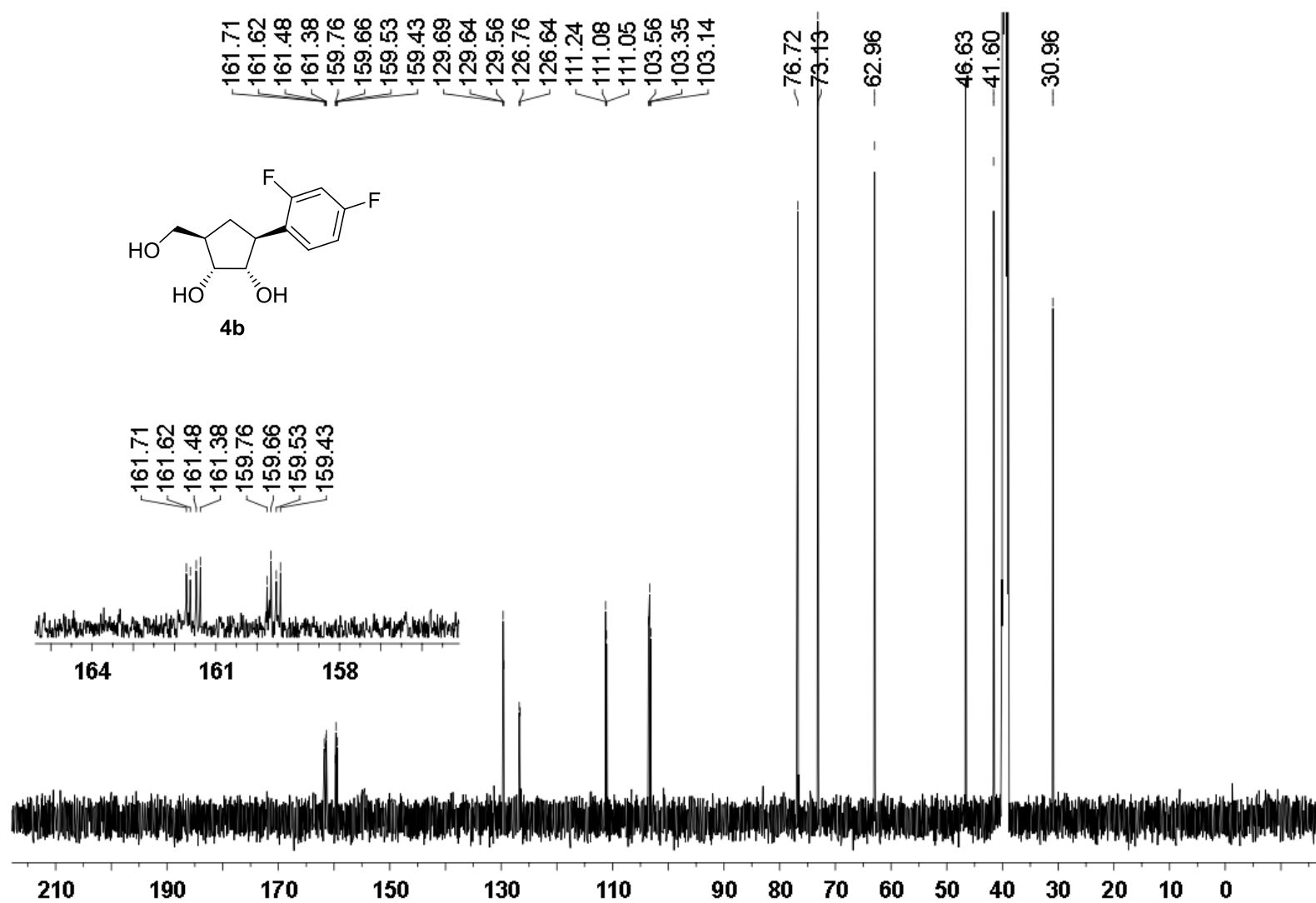
Comparison of ^1H NMR resonances for **4a** and corresponding epimer



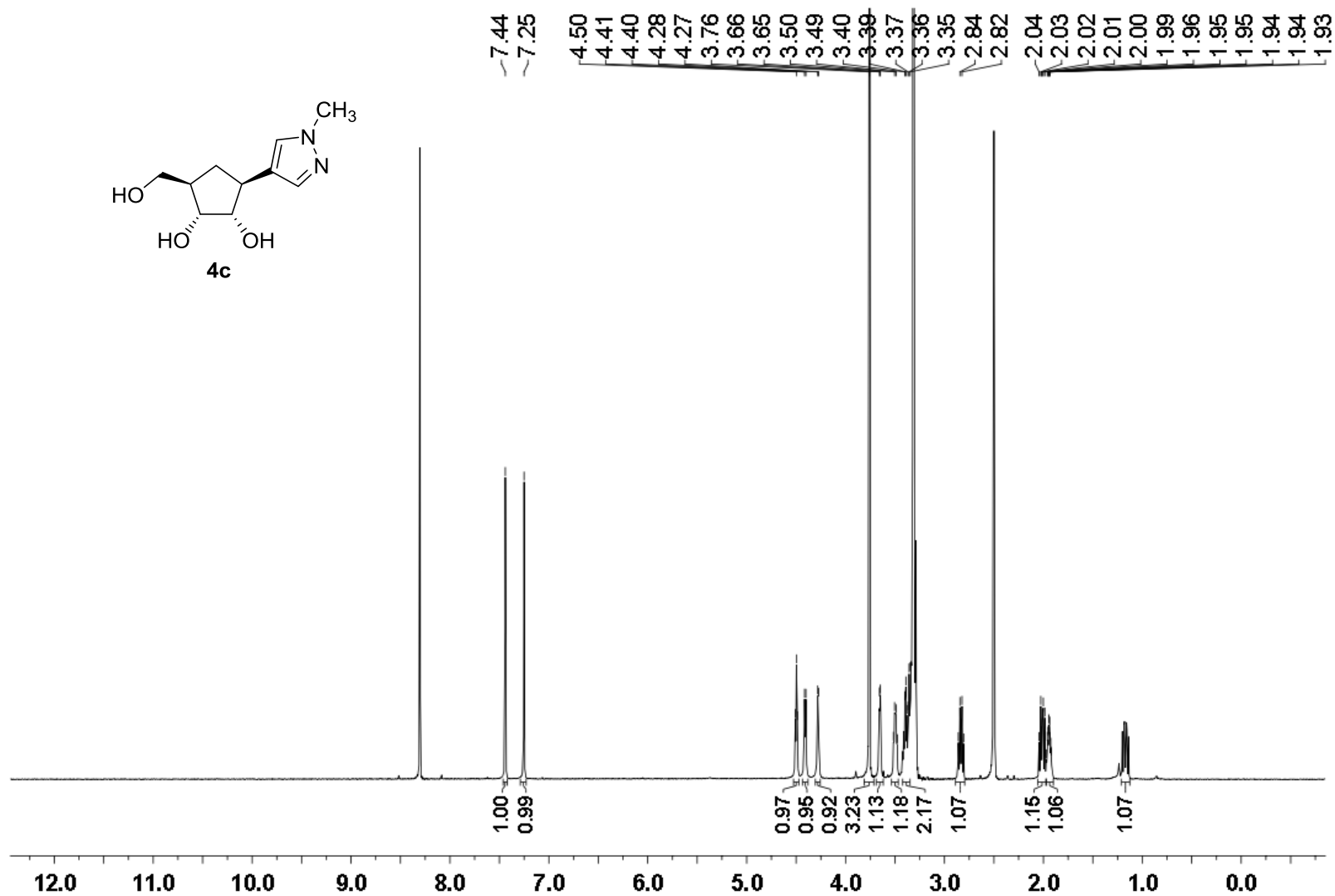
Comparison of ^{13}C NMR resonances for 5a and corresponding epimer



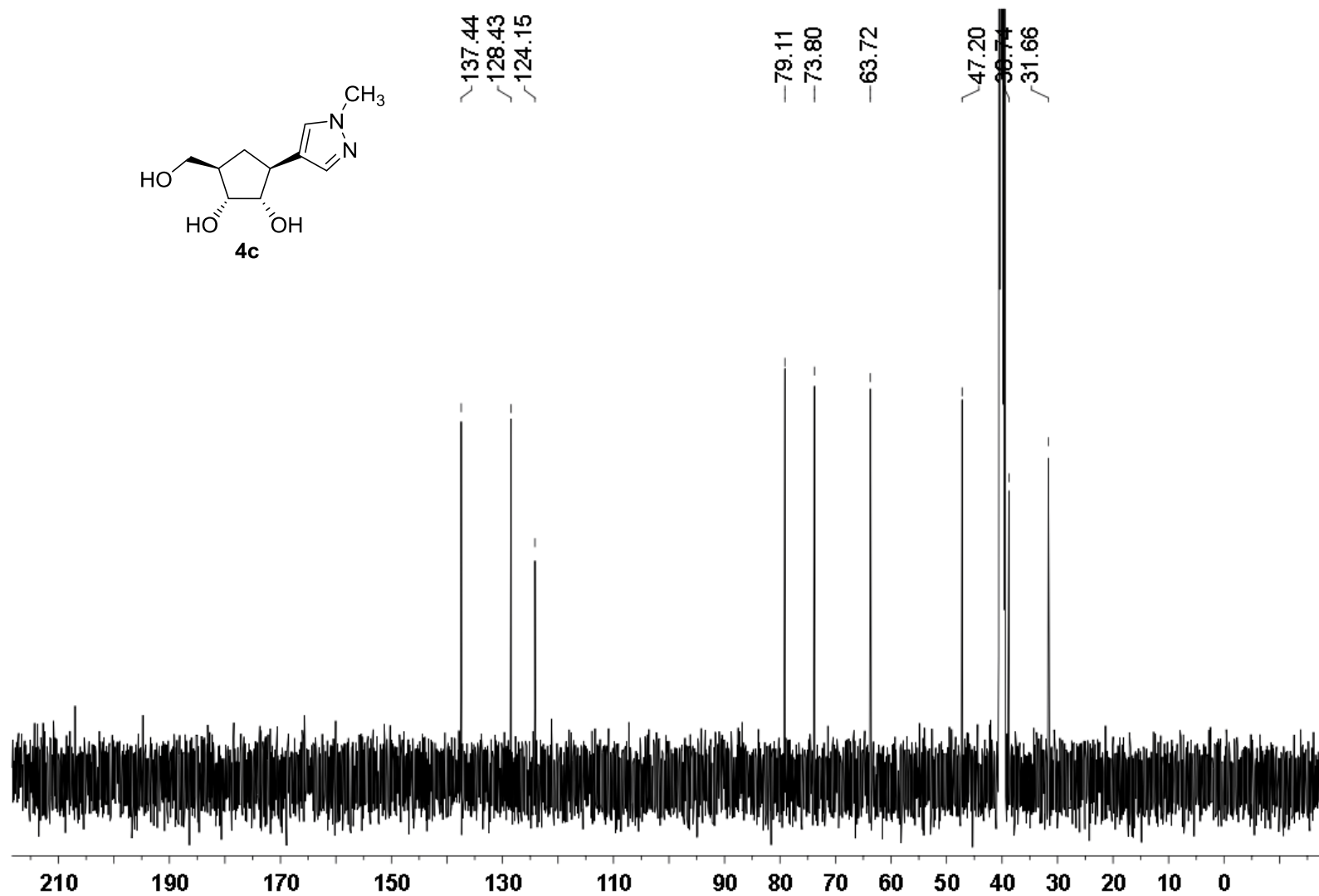
¹H NMR (500 MHz) spectrum of **4b** in DMSO-*d*₆



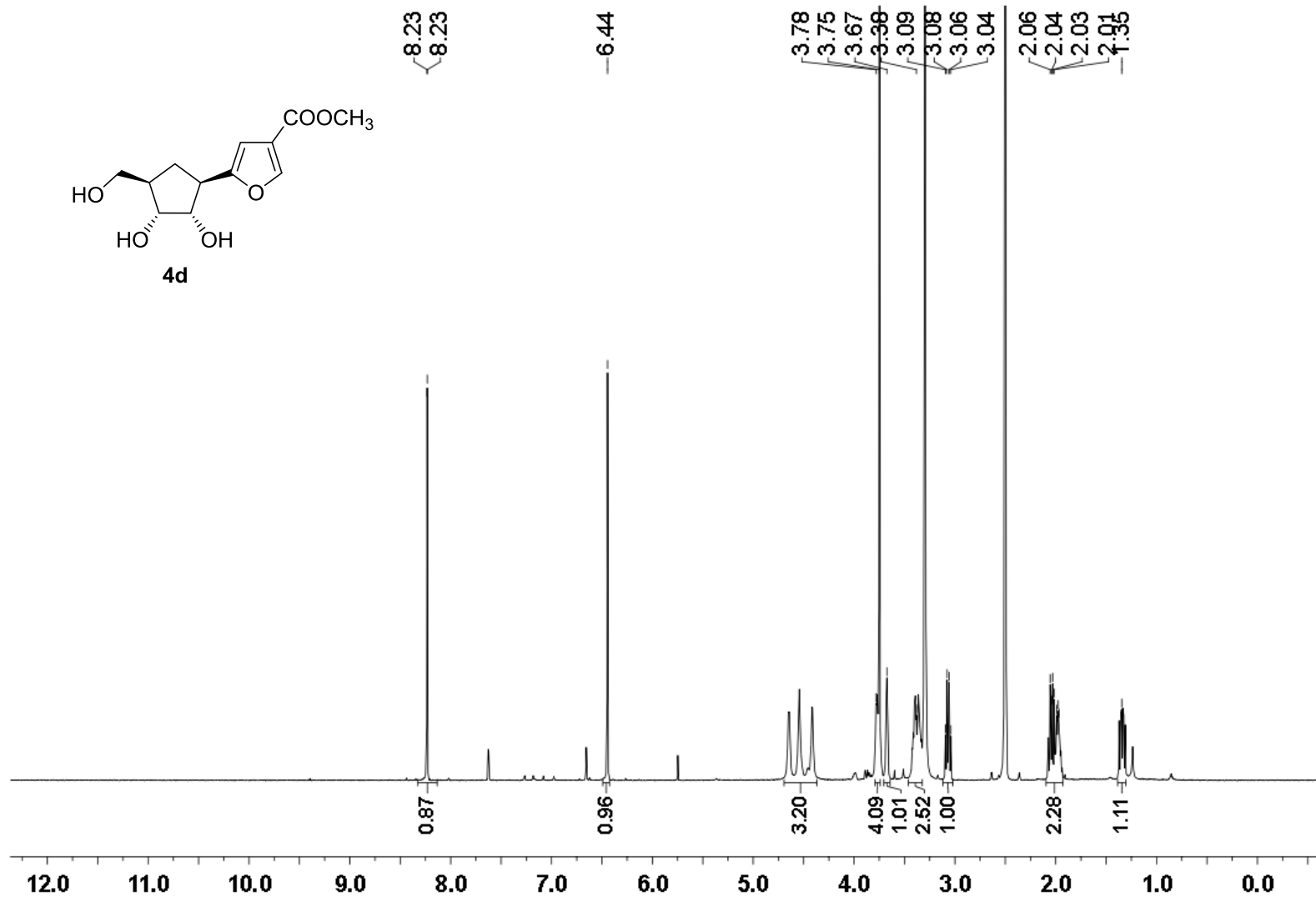
^{13}C NMR (126 MHz) spectrum of **4b** in DMSO- d_6



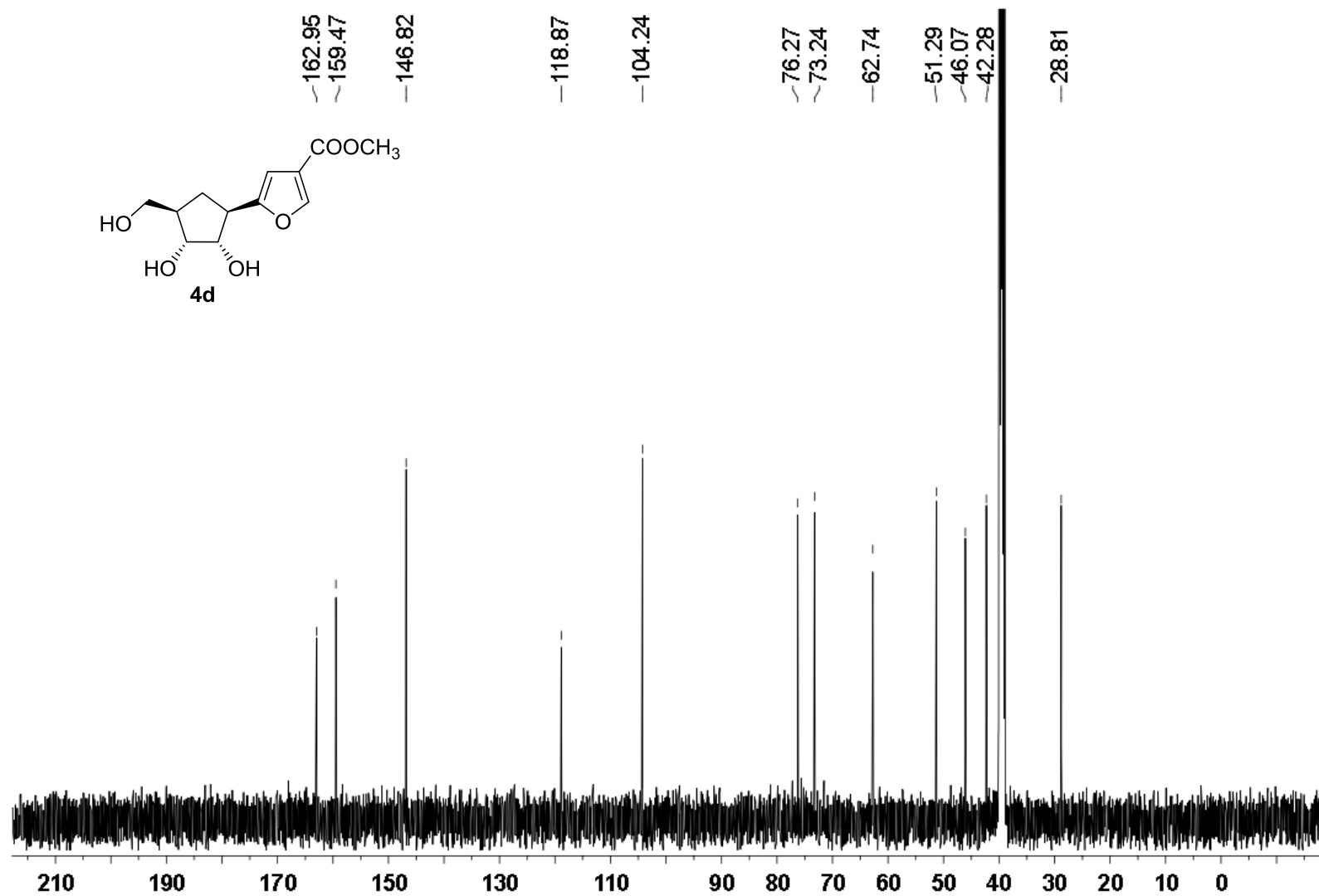
¹H NMR (500 MHz) spectrum of **4c** in DMSO-*d*₆ + CDCl₃



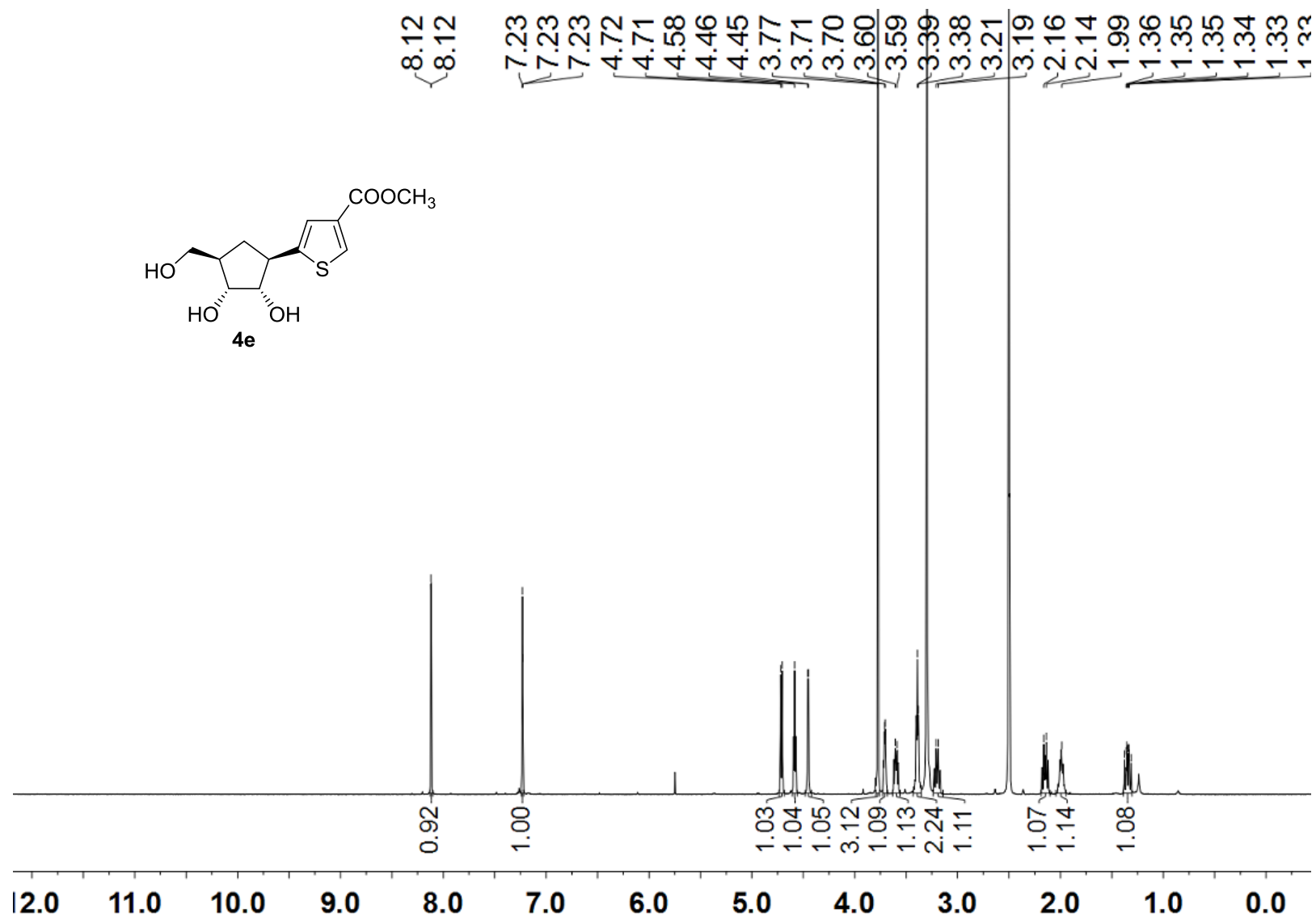
^{13}C NMR (126 MHz) spectrum of **4c** in $\text{DMSO}-d_6$



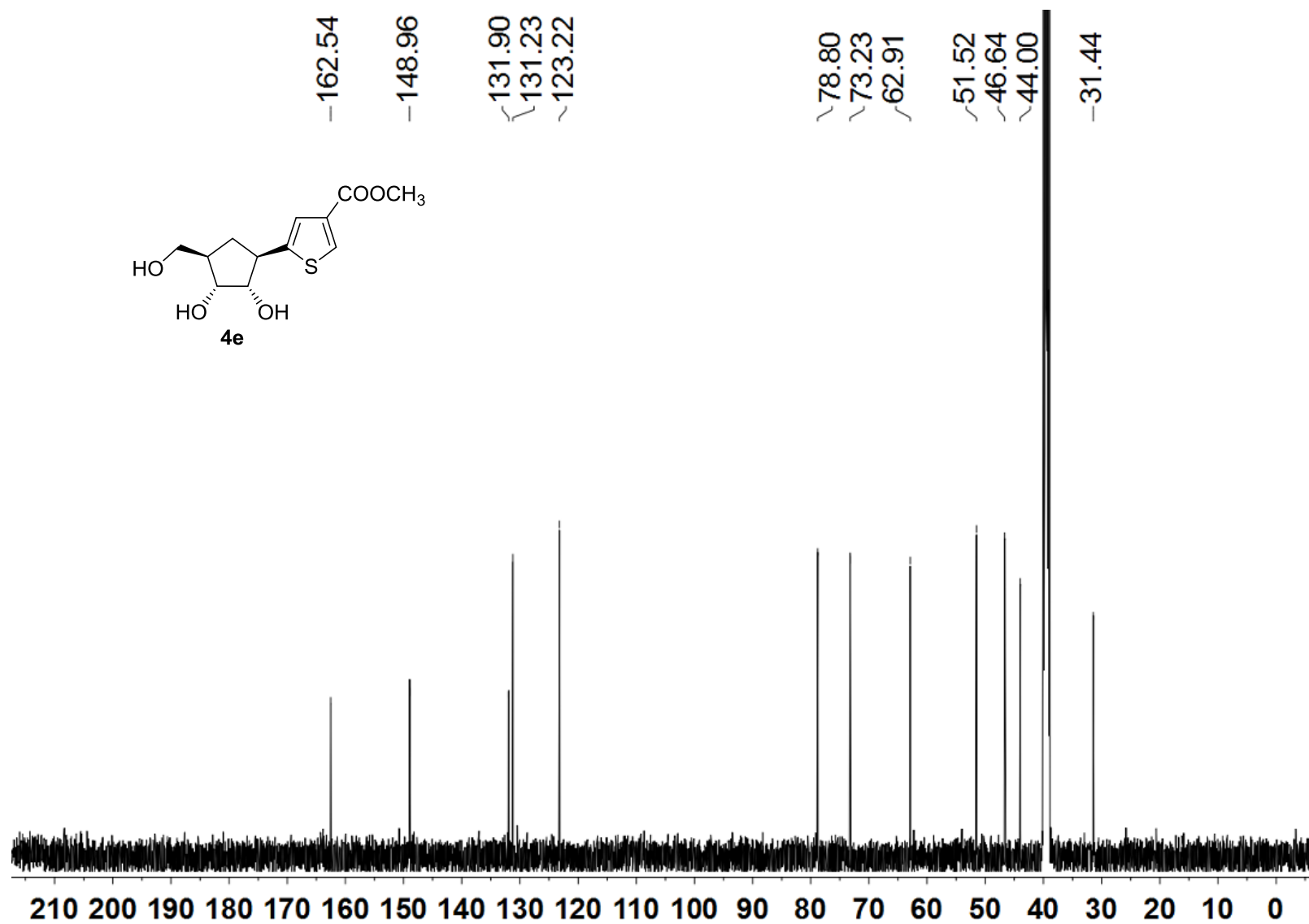
¹H NMR (500 MHz) spectrum of **4d** in DMSO-*d*₆



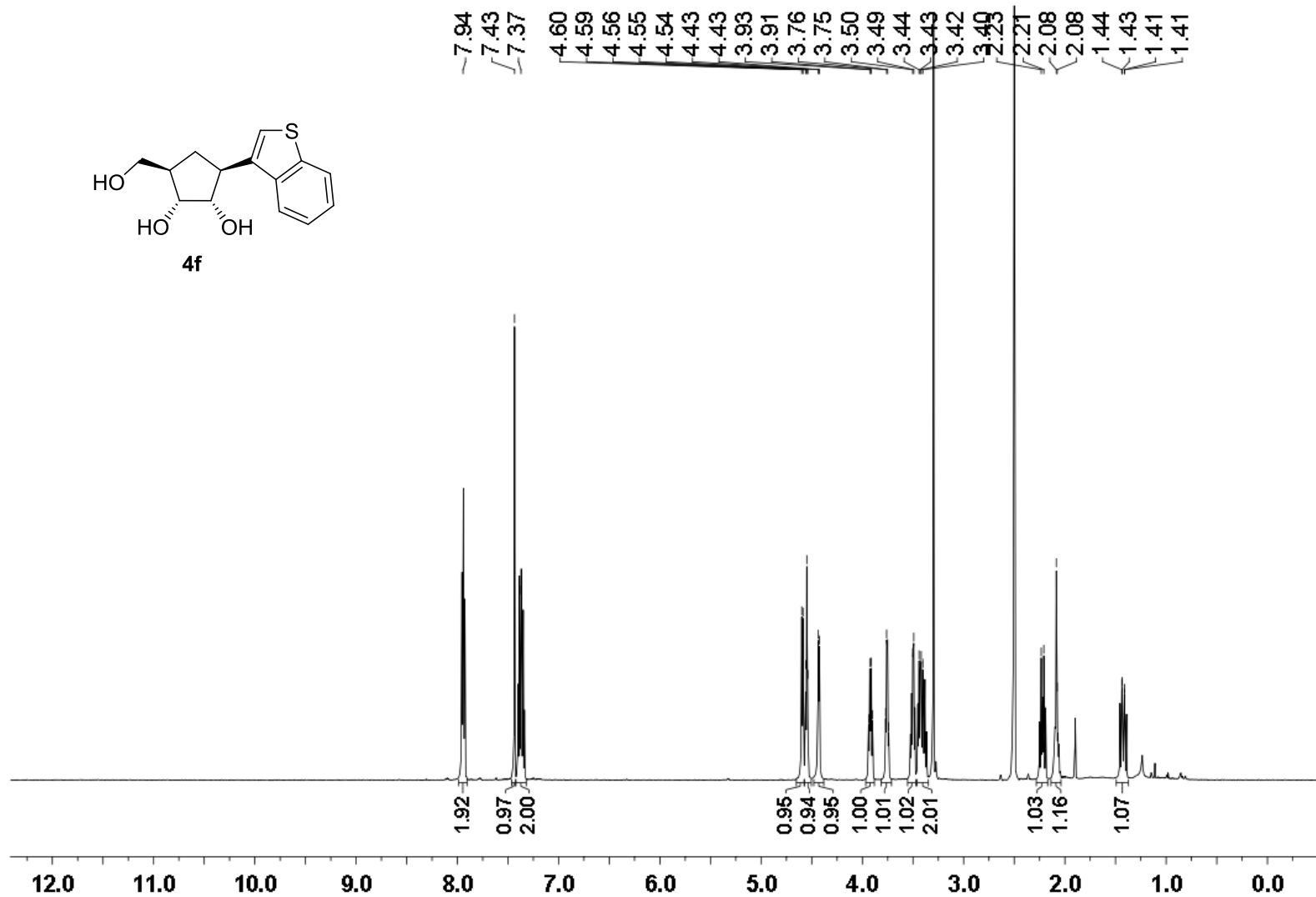
^{13}C NMR (126 MHz) spectrum of **4d** in $\text{DMSO}-d_6$



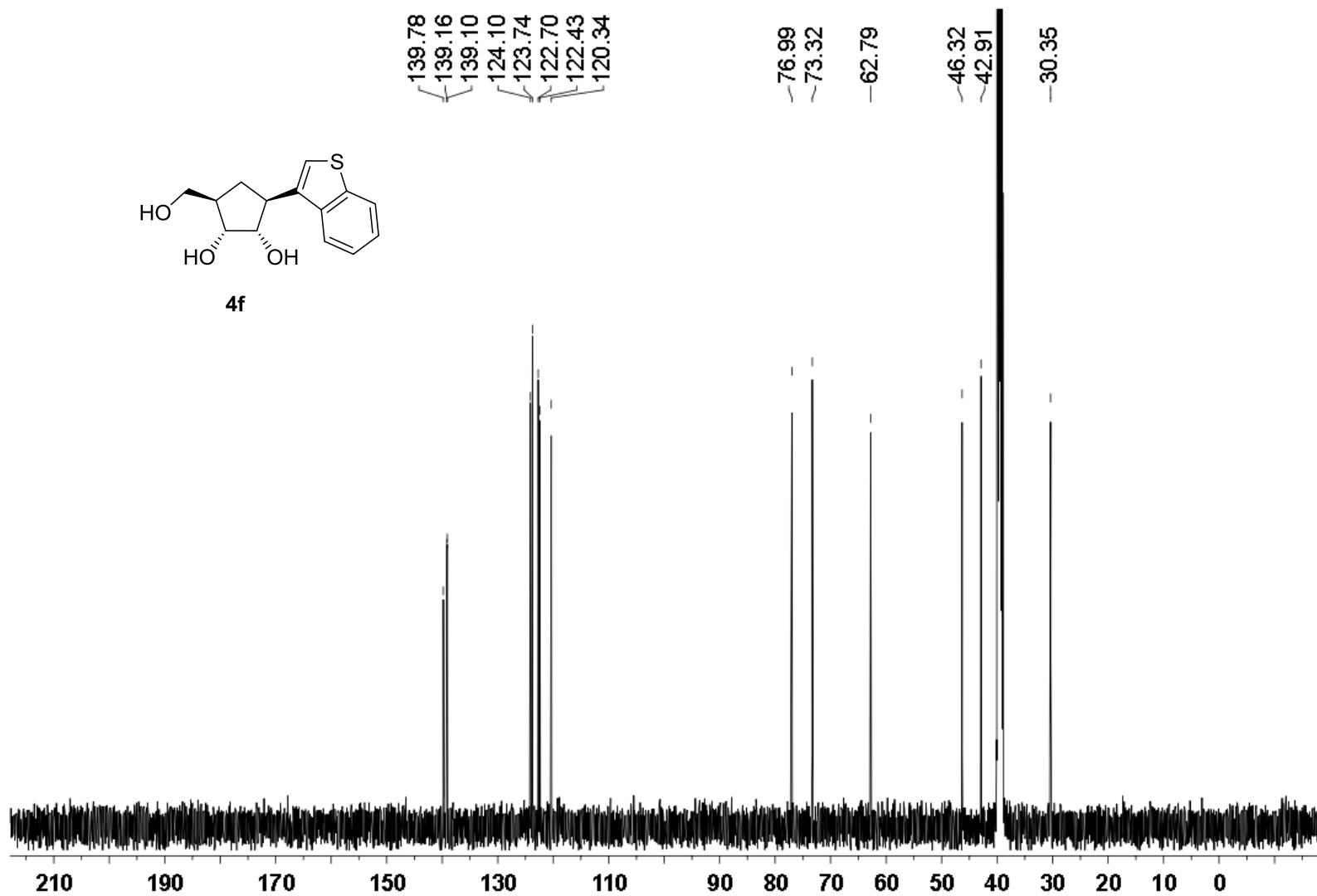
^1H NMR (500 MHz) spectrum of **4e** in $\text{DMSO}-d_6$



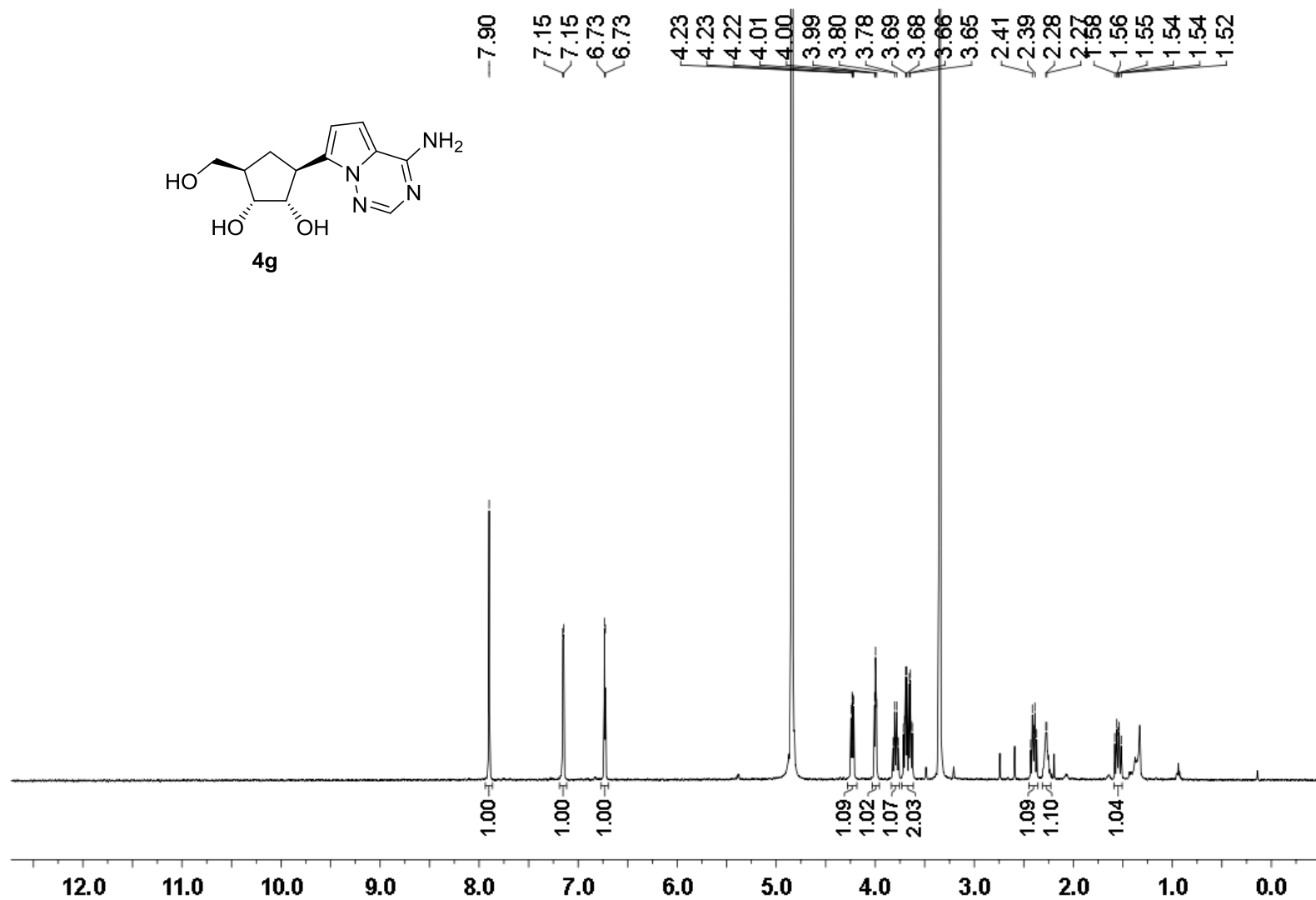
¹³C NMR (126 MHz) spectrum of **4e** in DMSO-*d*₆



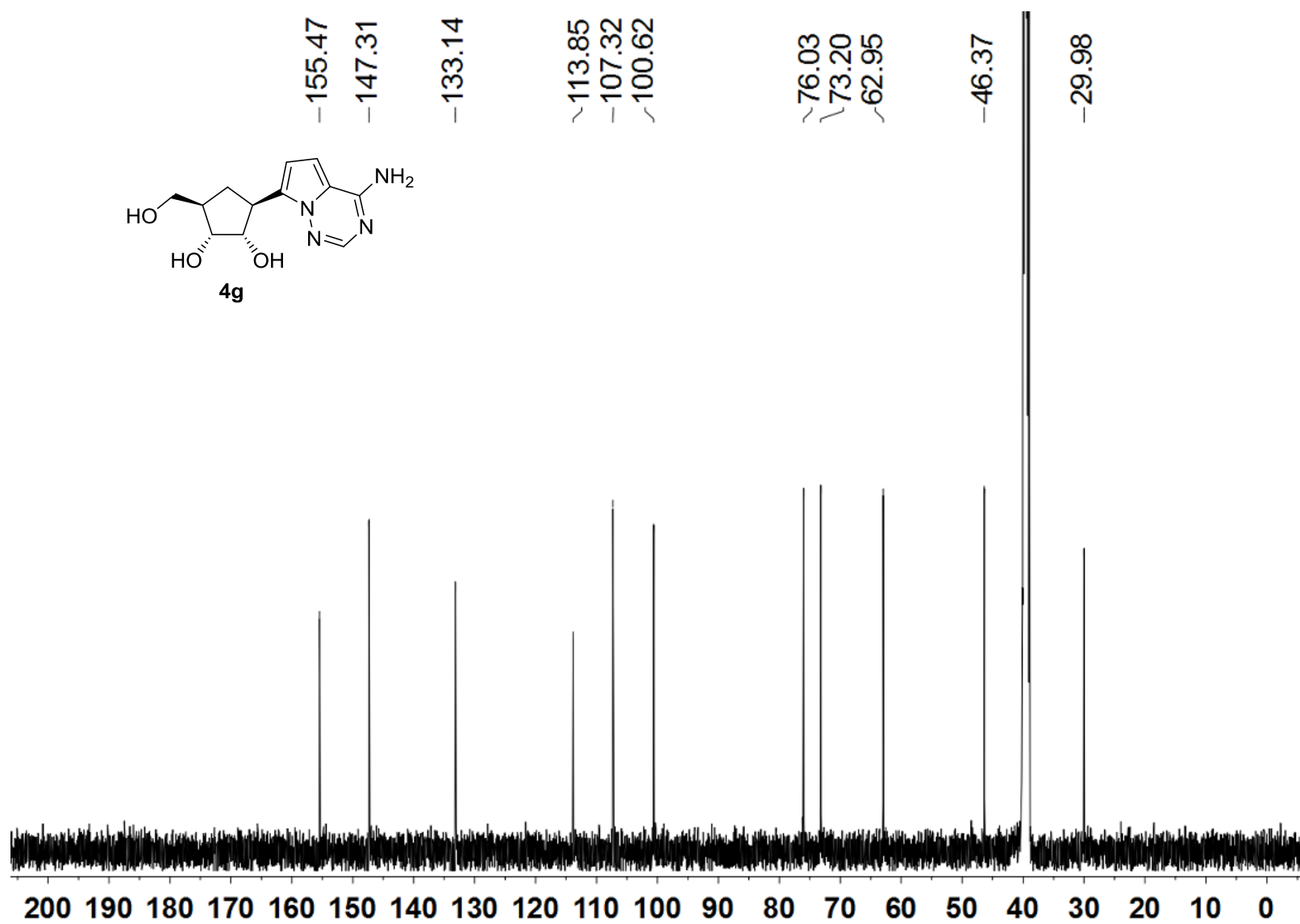
¹H NMR (500 MHz) spectrum of **4f** in DMSO-*d*₆

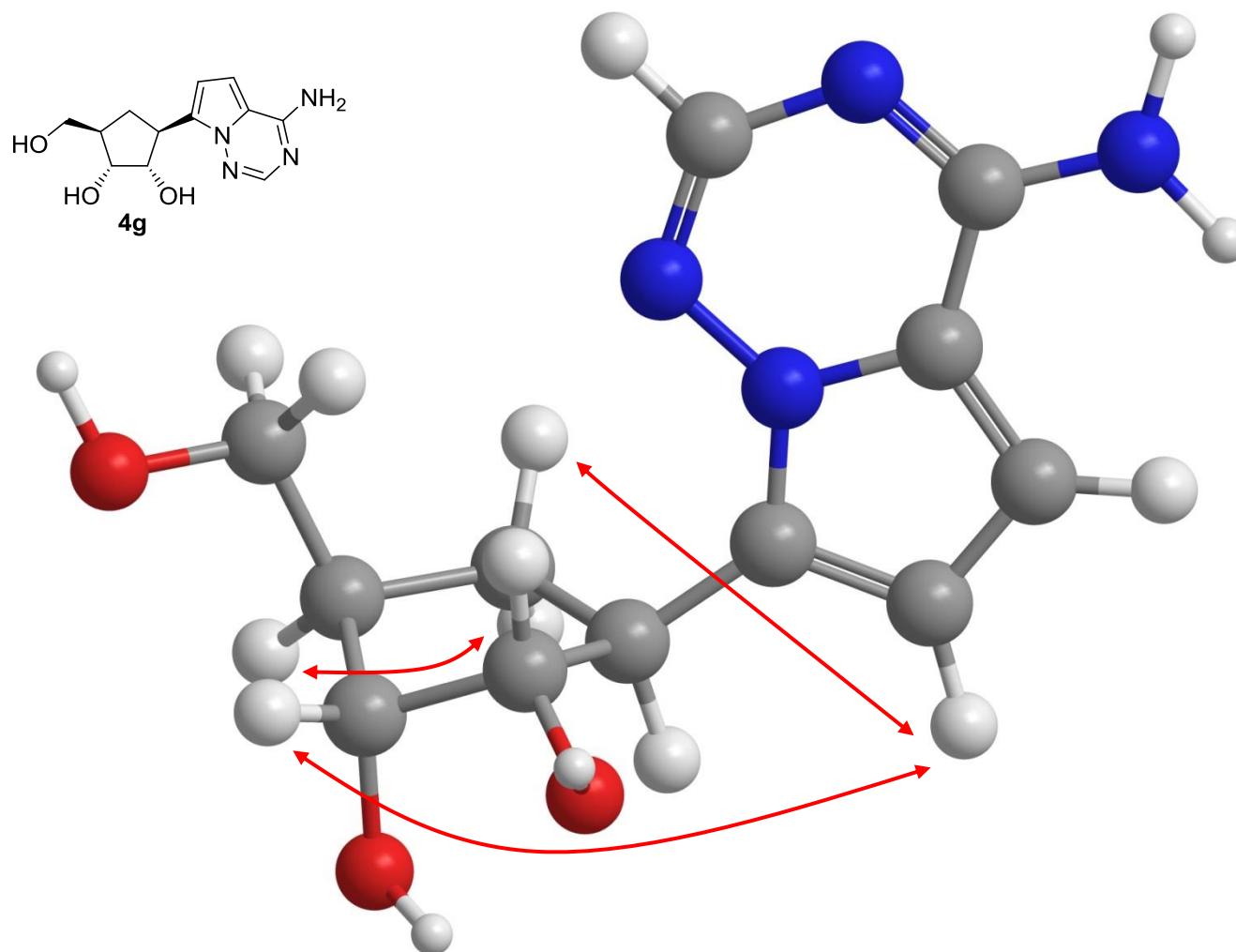


^{13}C NMR (126 MHz) spectrum of **4f** in $\text{DMSO}-d_6$

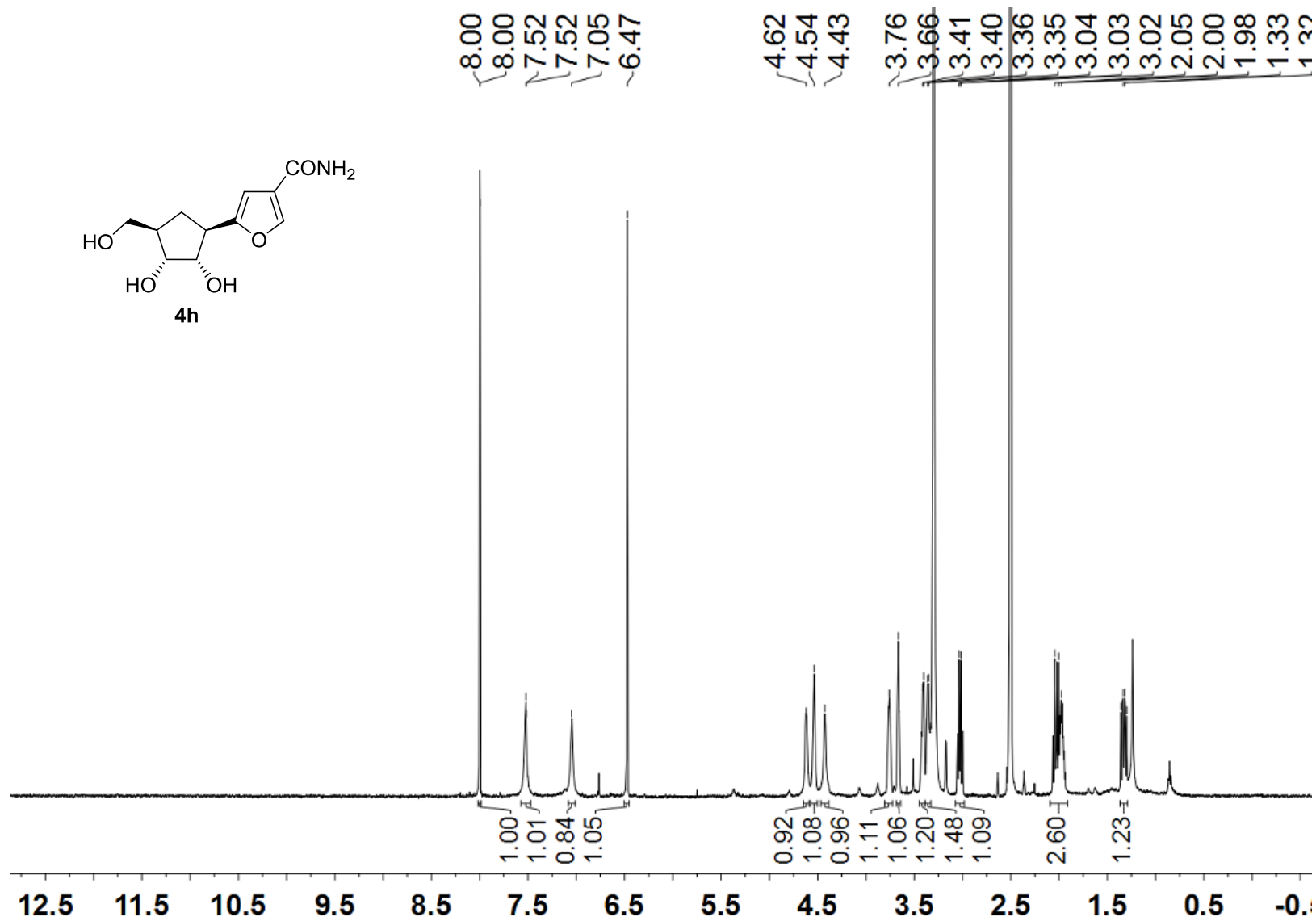


¹H NMR (500 MHz) spectrum of **4g** in CD₃OD

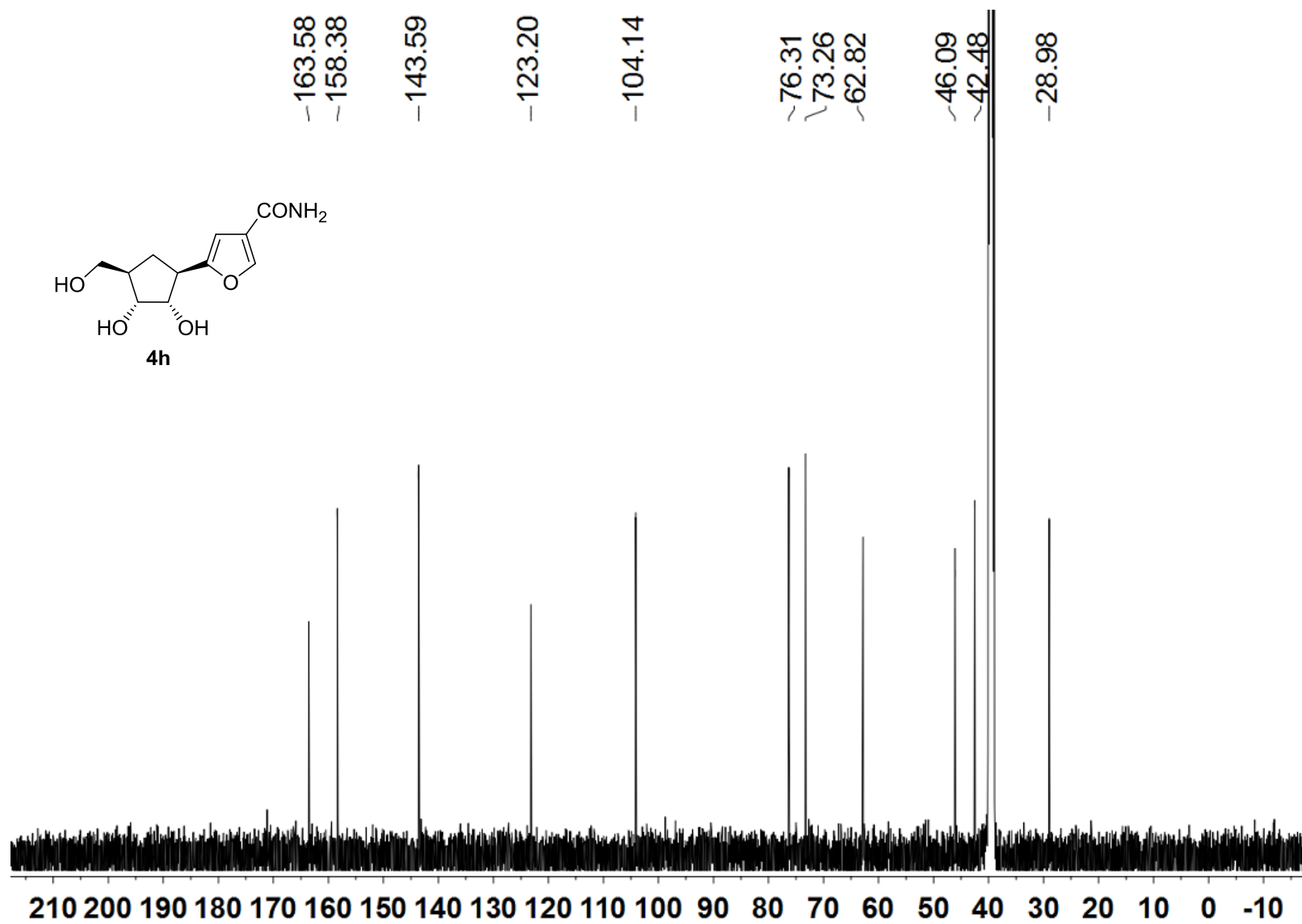




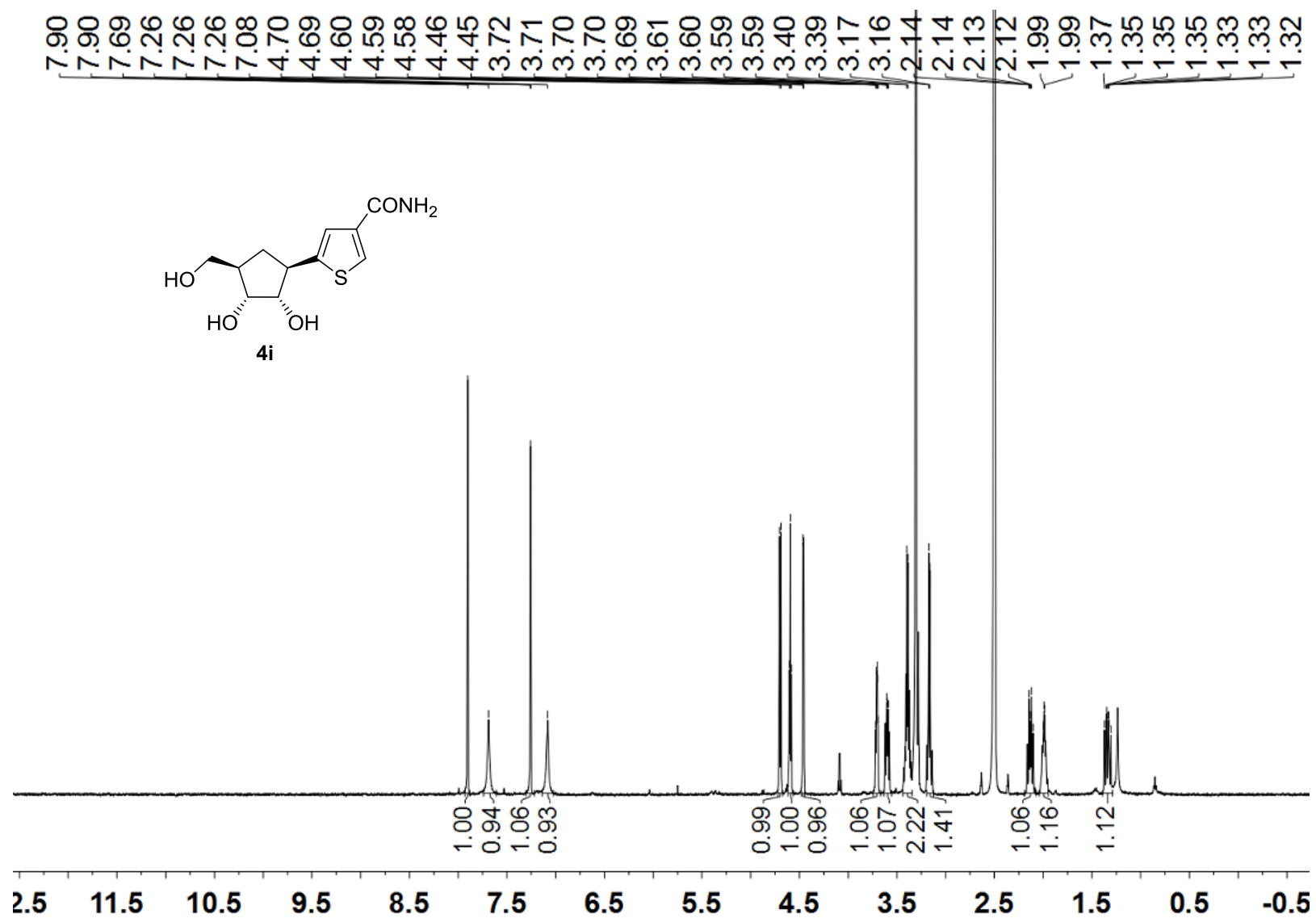
Important NOE interactions observed in compound **4g**



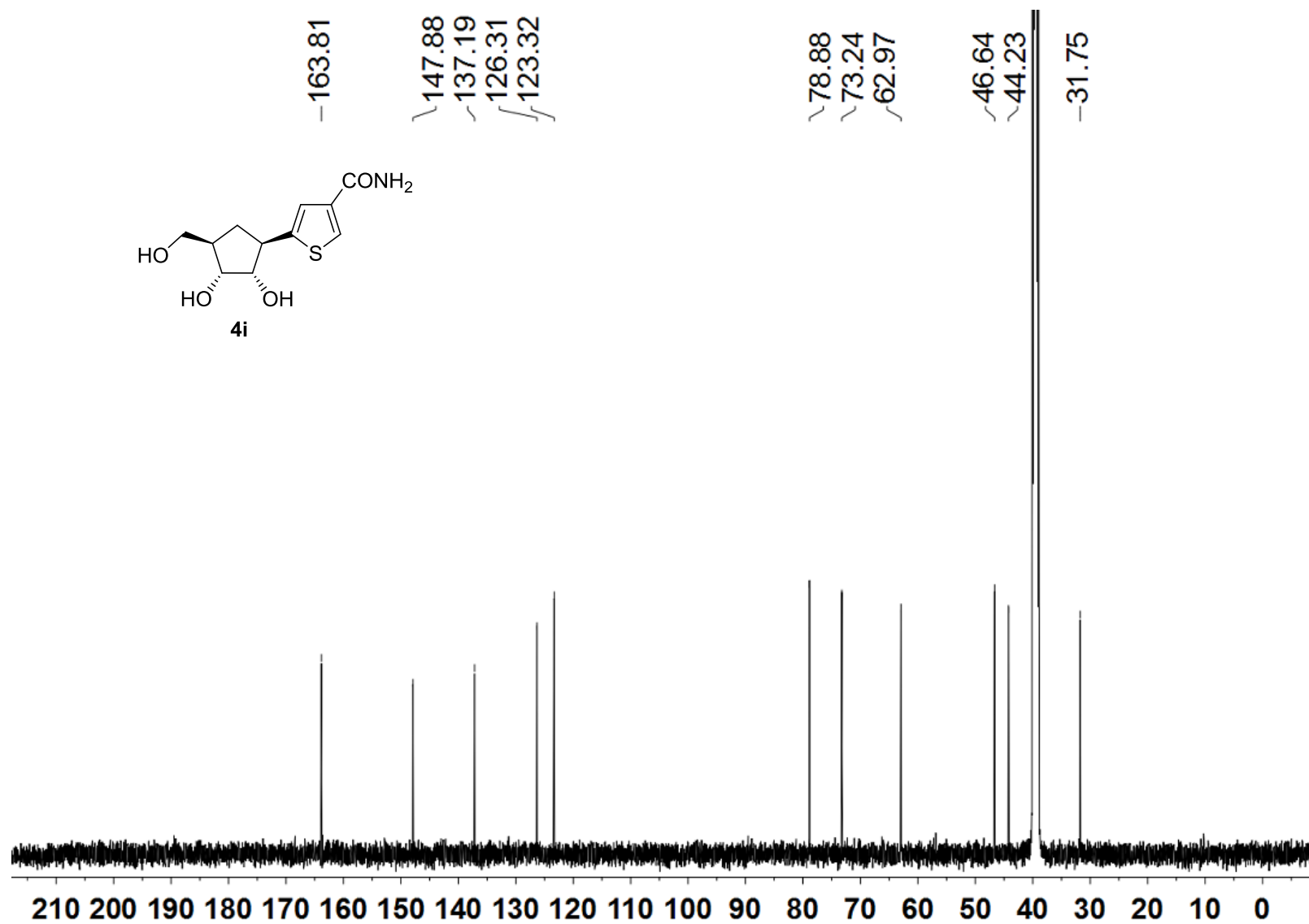
¹H NMR (126 MHz) spectrum of **4h** in DMSO-*d*₆



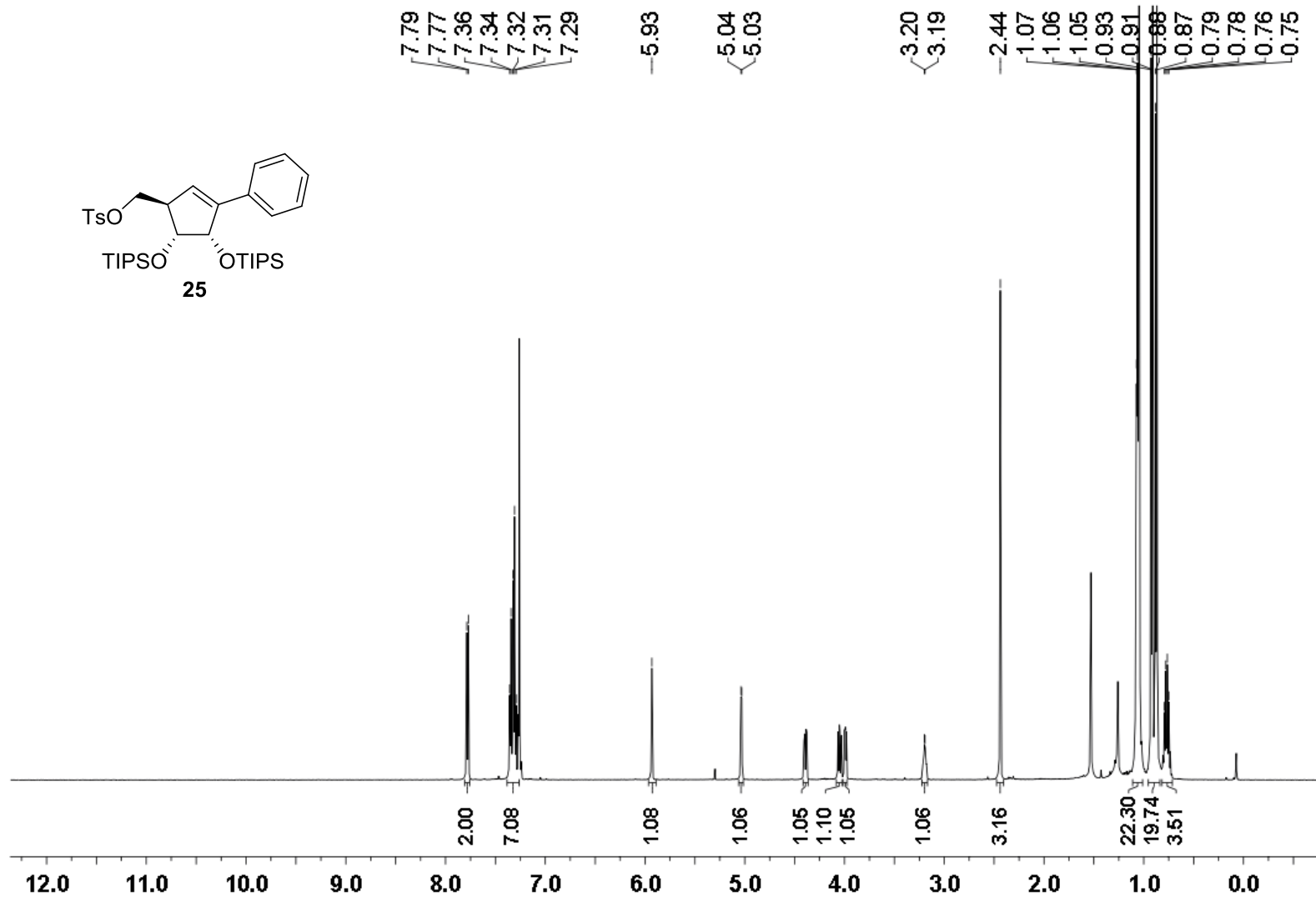
¹³C NMR (126 MHz) spectrum of **4h** in DMSO-*d*₆



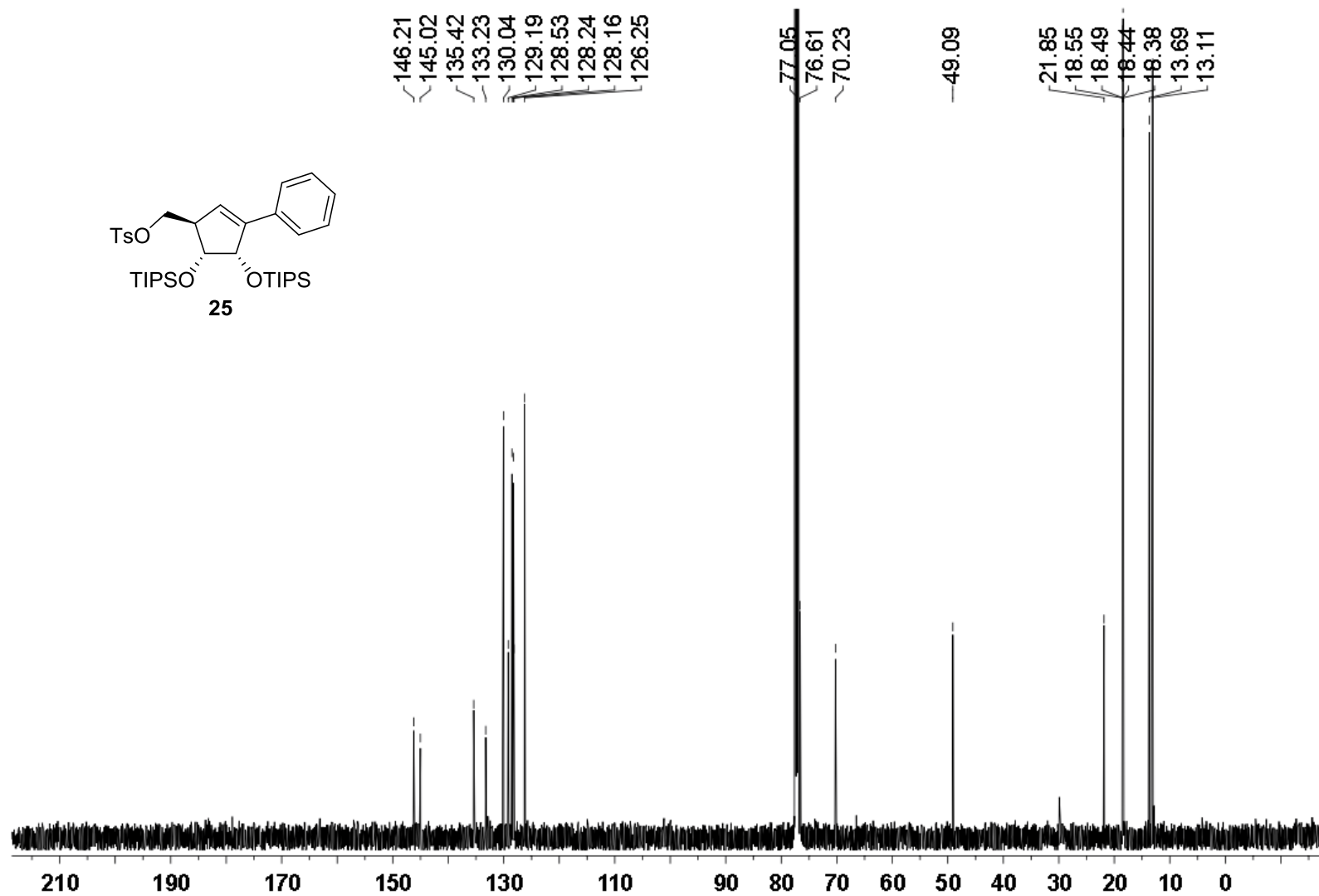
¹H NMR (126 MHz) spectrum of **4i** in DMSO-*d*₆



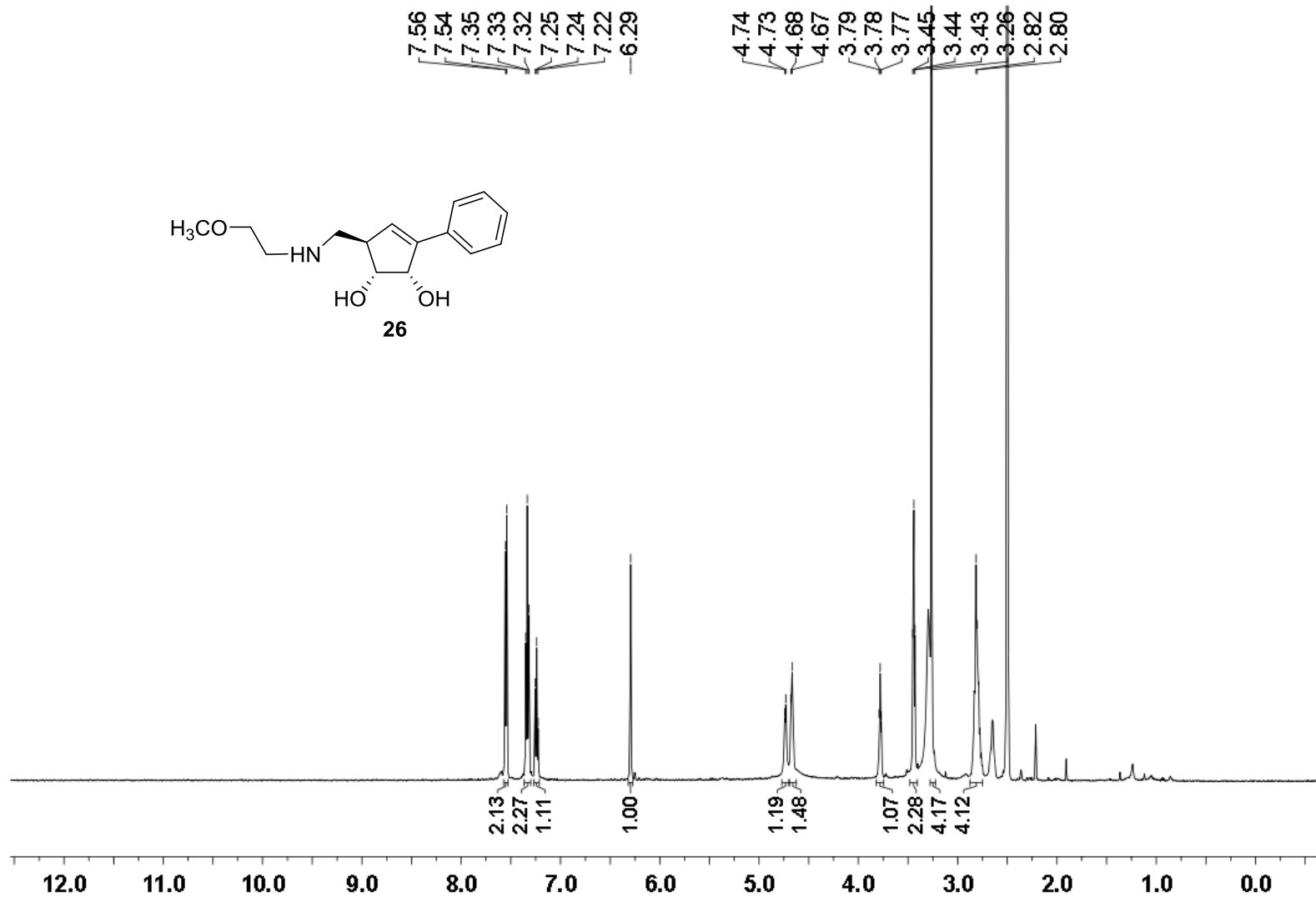
^{13}C NMR (126 MHz) spectrum of **4i** in $\text{DMSO}-d_6$



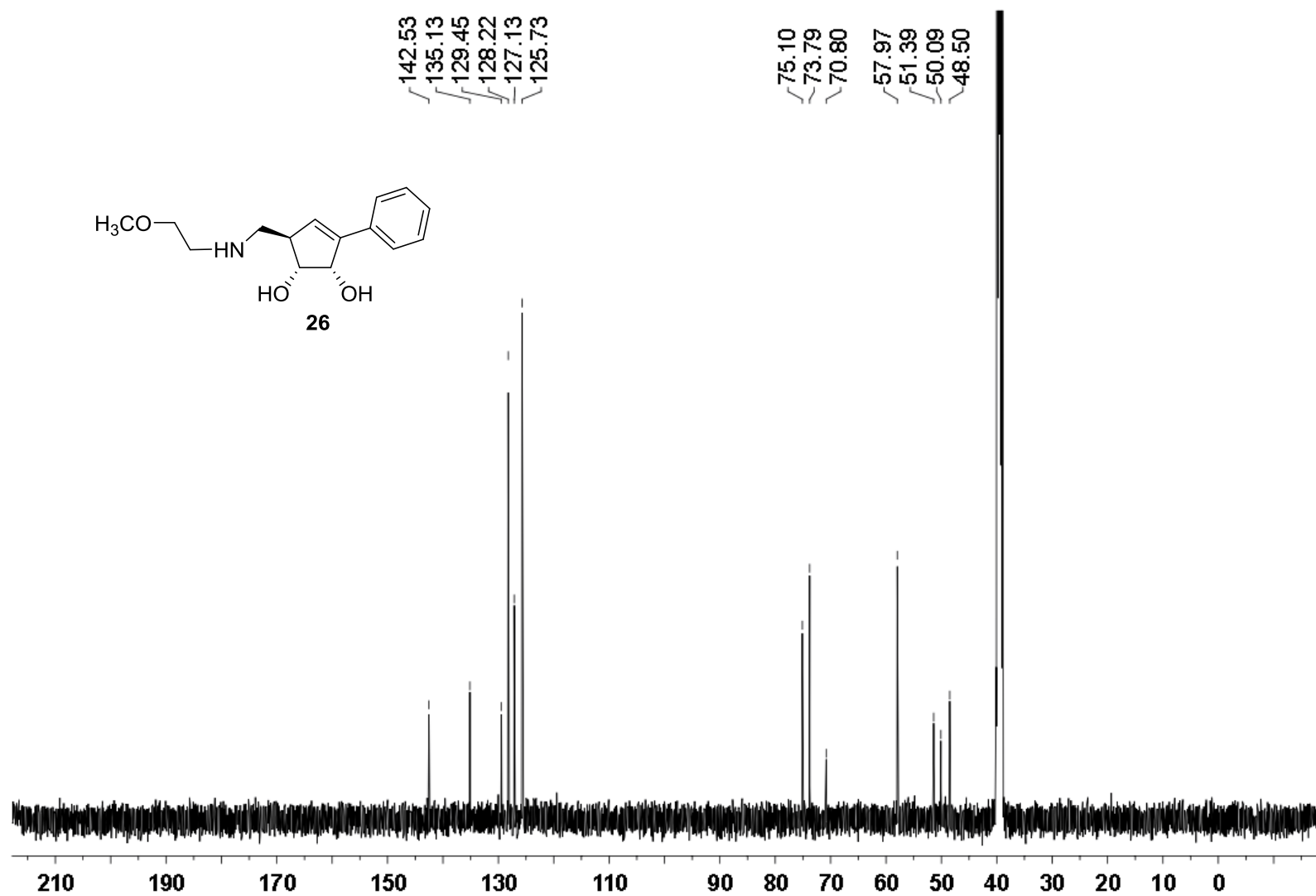
¹H NMR (500 MHz) spectrum of **25** in CDCl₃



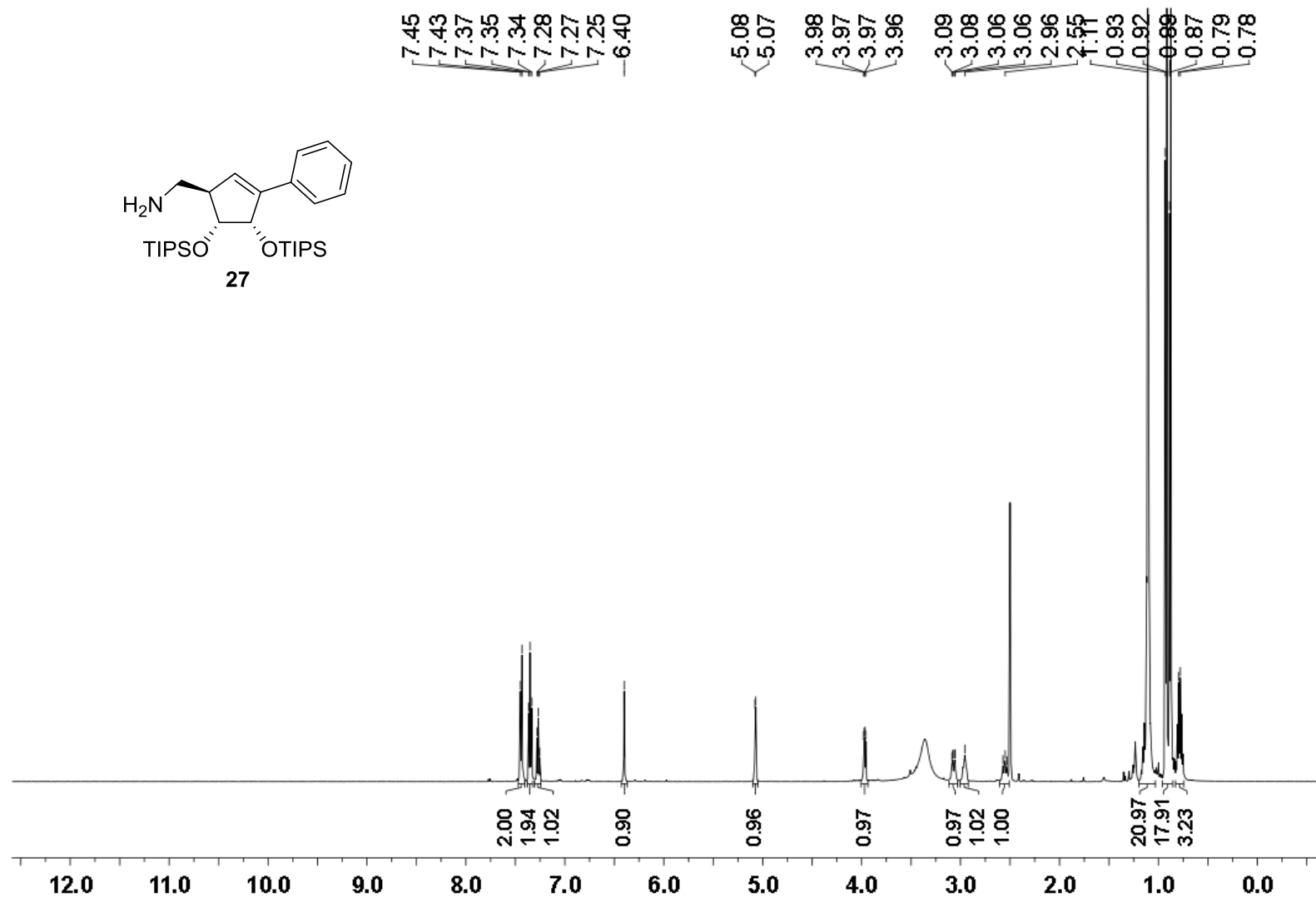
^{13}C NMR (126 MHz) spectrum of **25** in CDCl_3



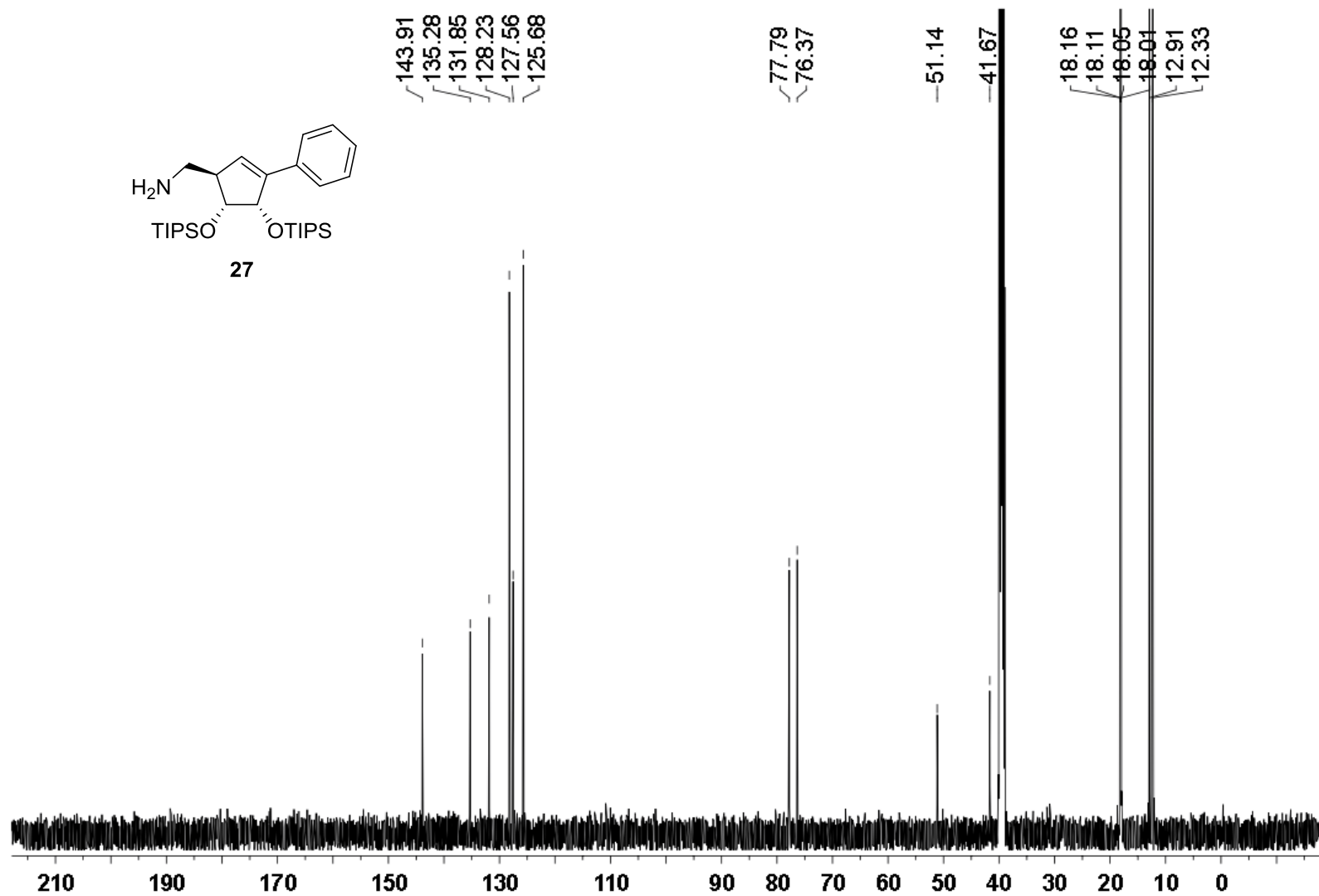
^1H NMR (500 MHz) spectrum of **26** in $\text{DMSO}-d_6$



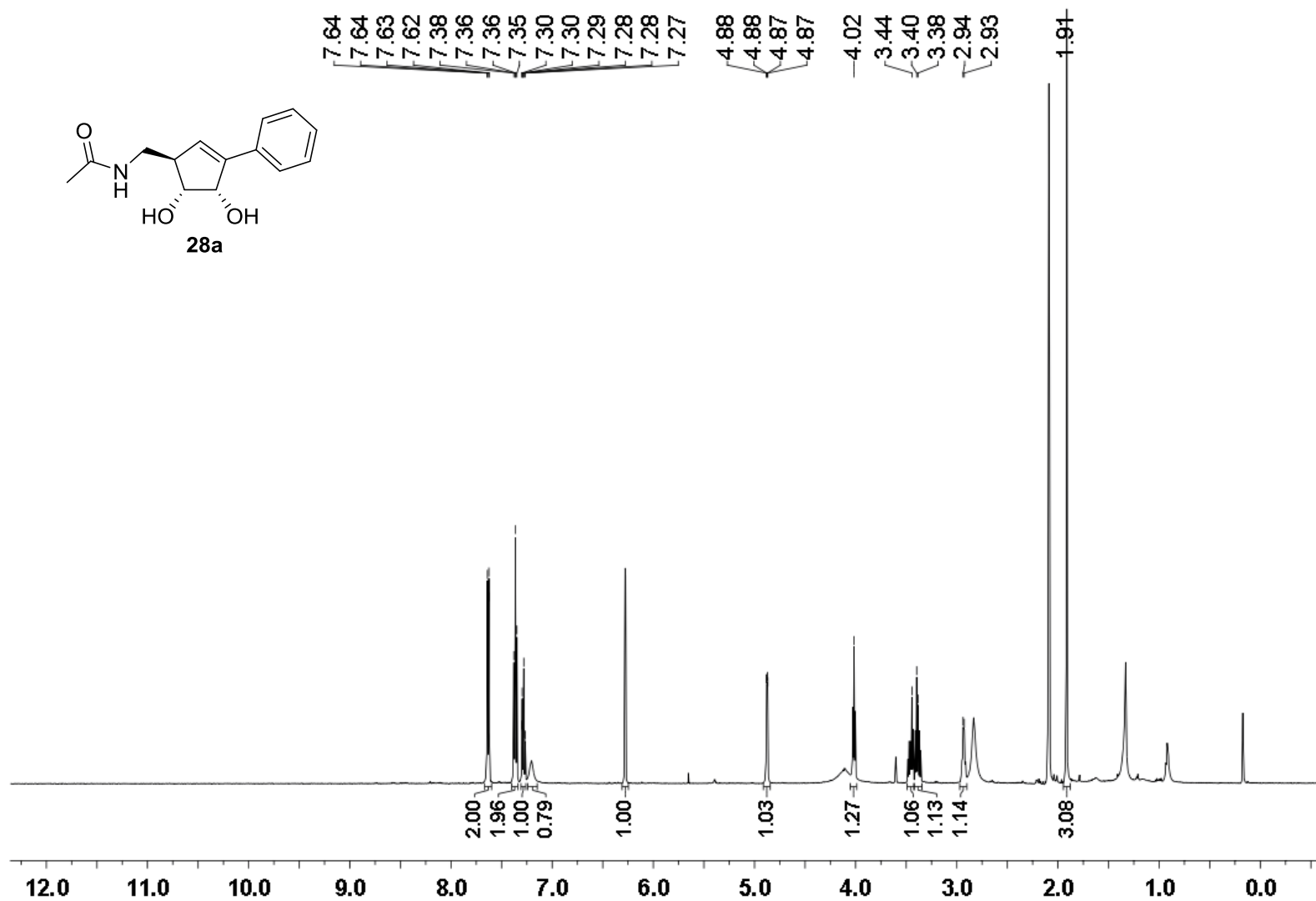
^{13}C NMR (126 MHz) spectrum of **26** in $\text{DMSO}-d_6$



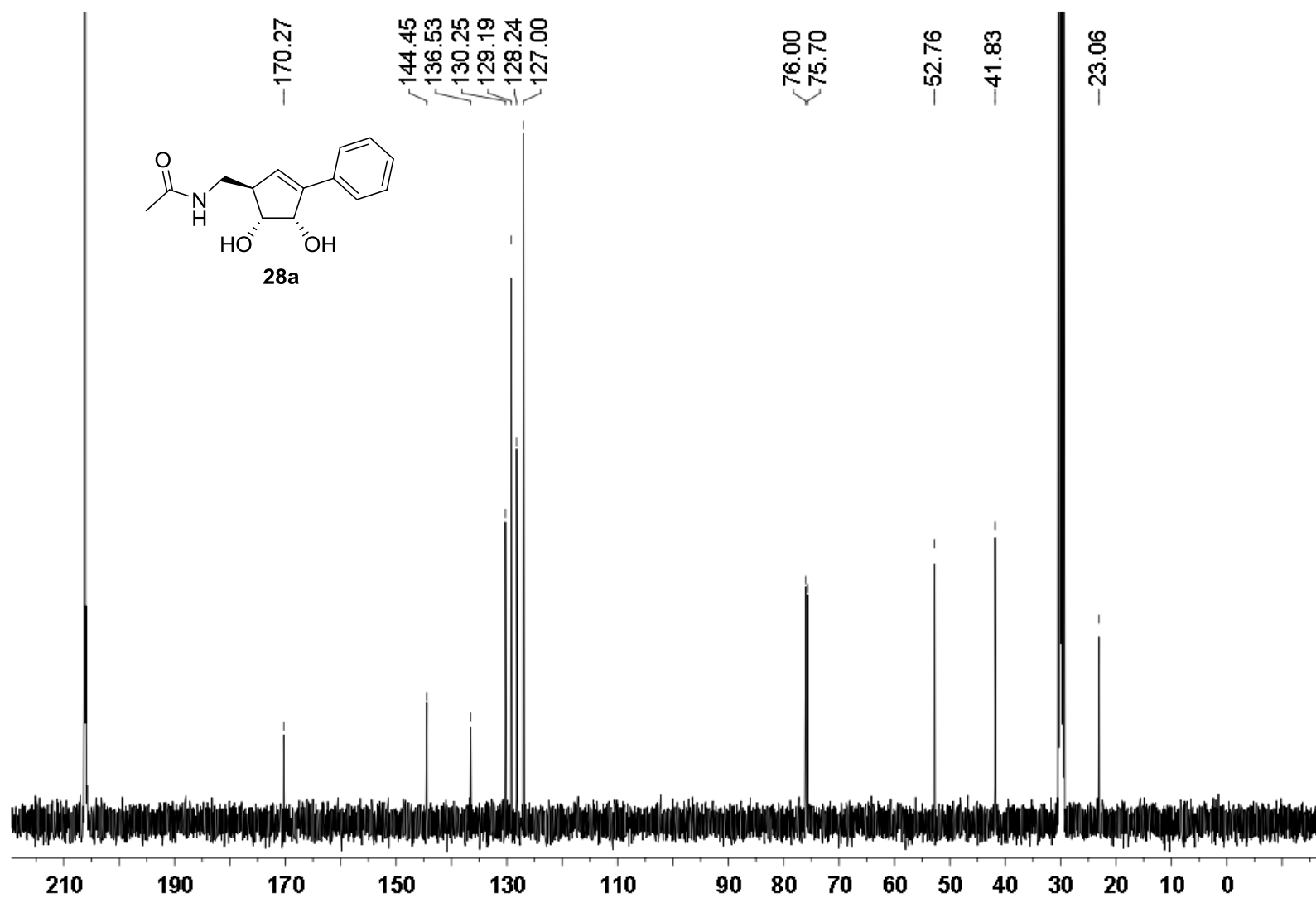
¹H NMR (500 MHz) spectrum of **27** in DMSO-*d*₆



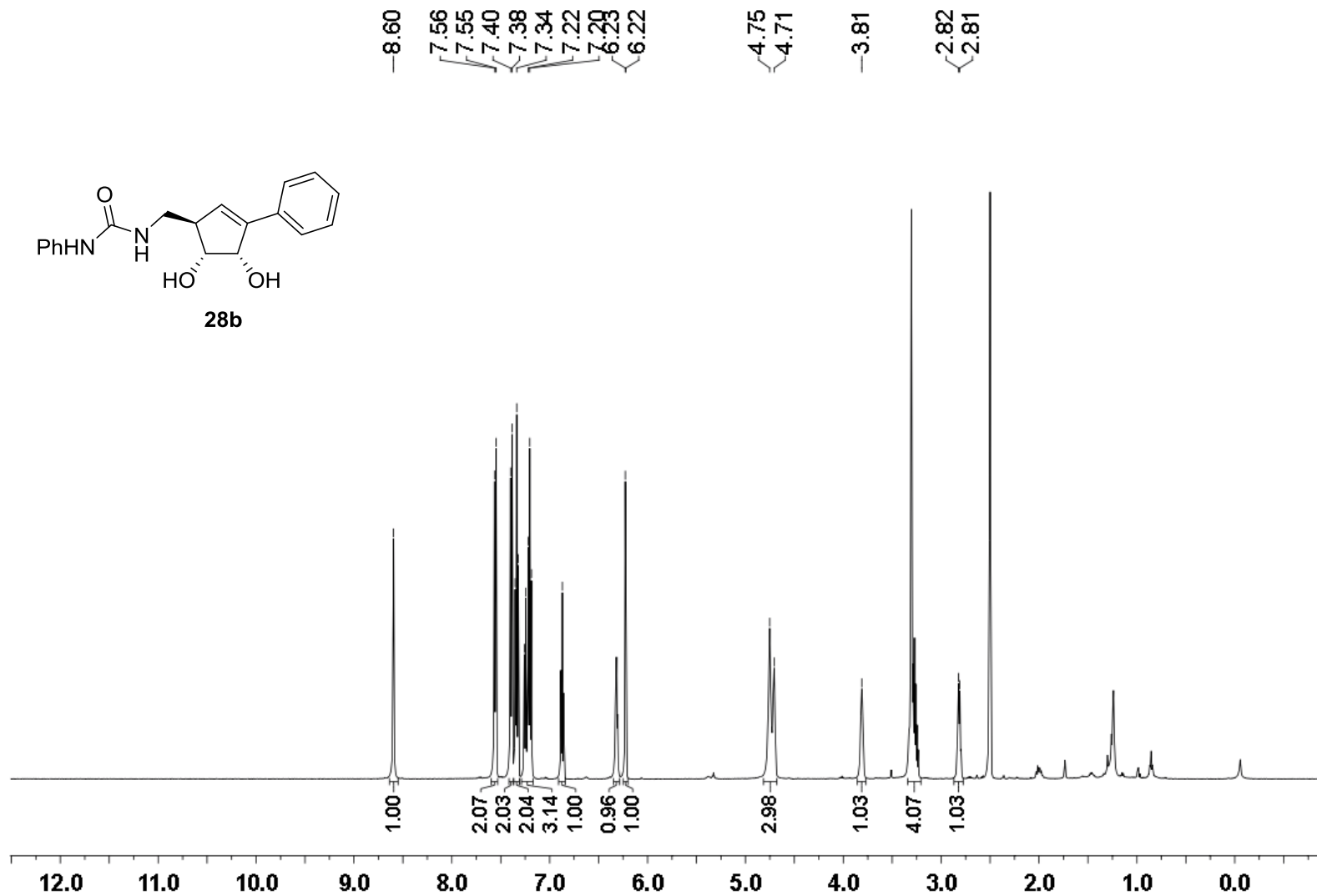
^{13}C NMR (126 MHz) spectrum of **27** in $\text{DMSO}-d_6$



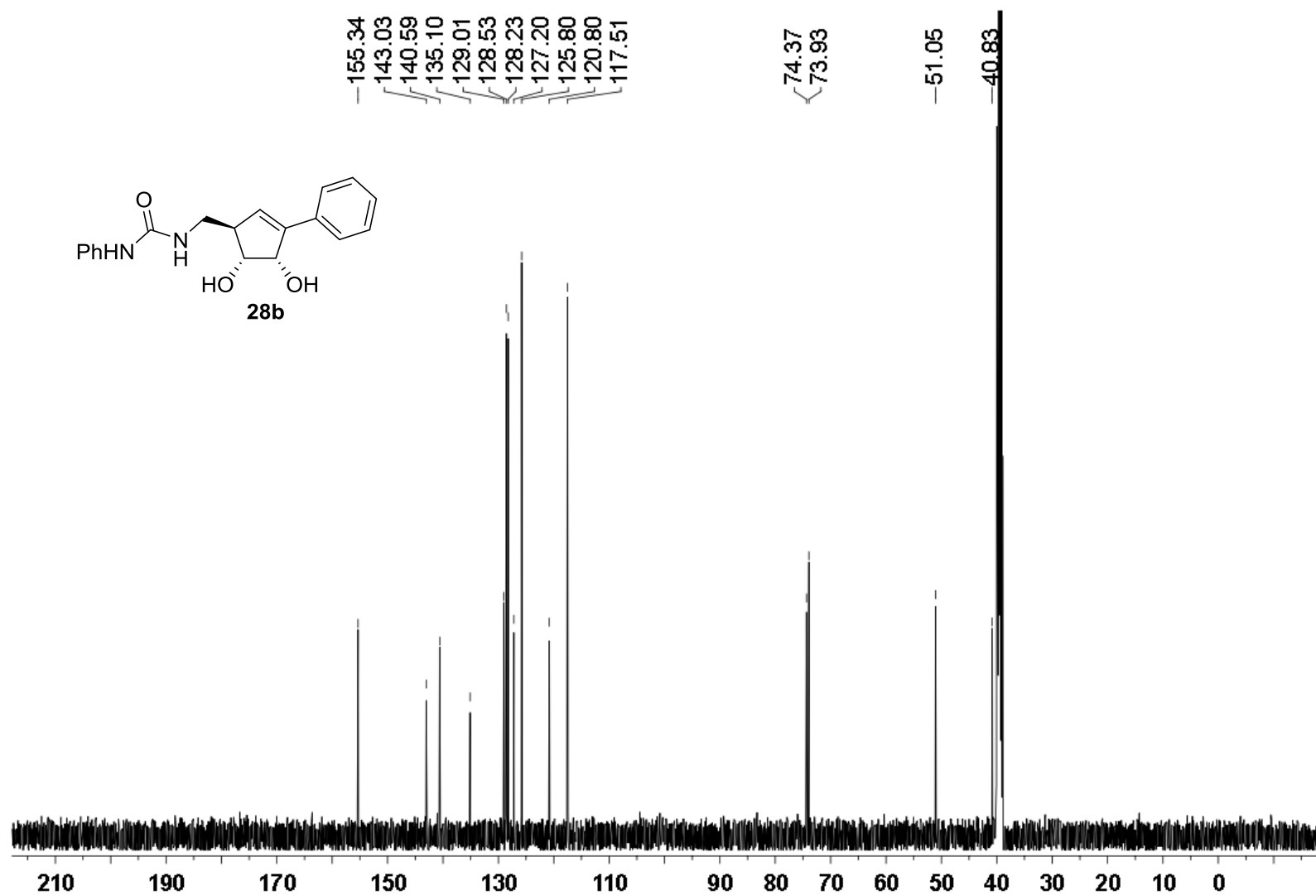
^1H NMR (500 MHz) spectrum of **28a** in acetone- d_6



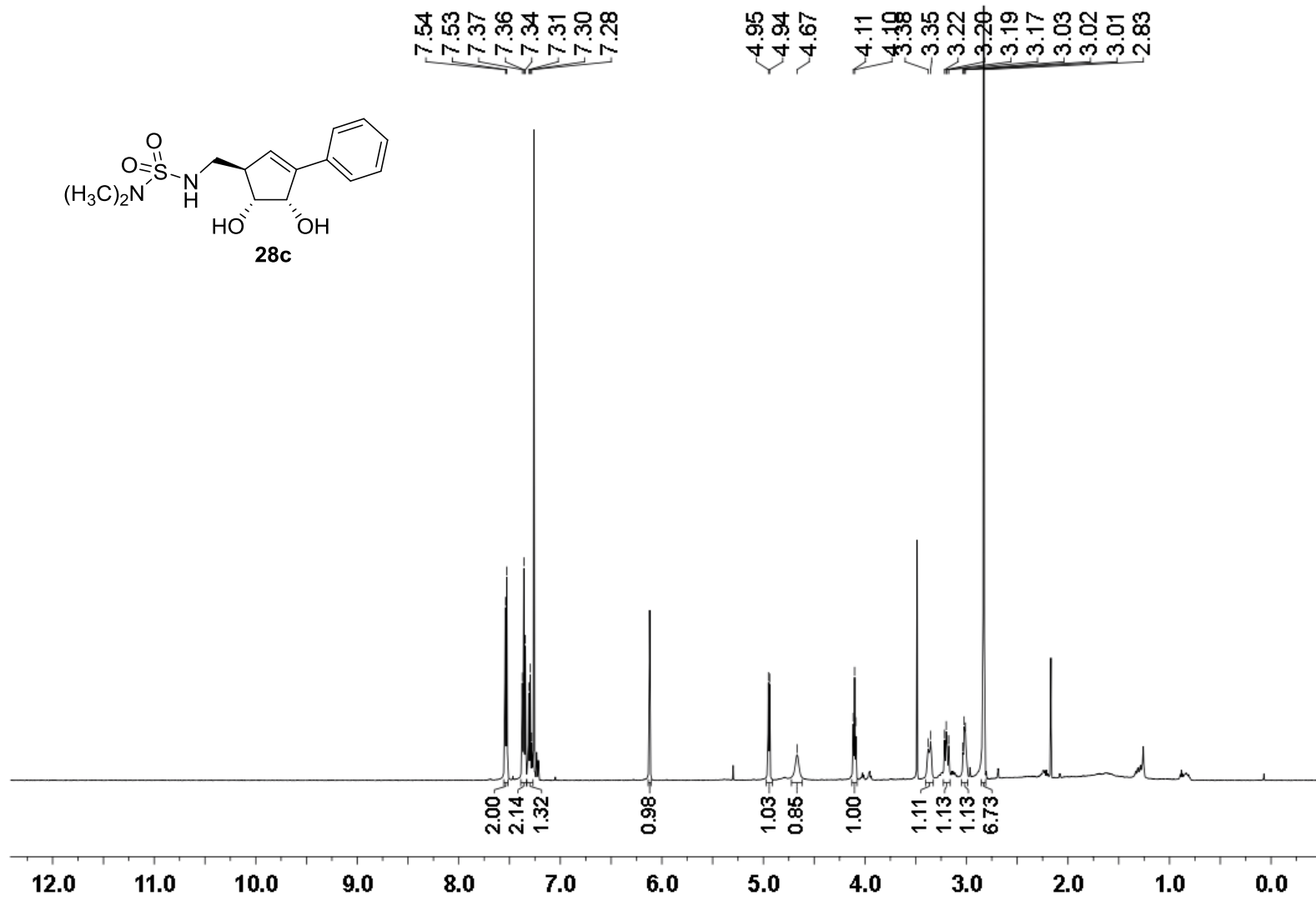
^{13}C NMR (126 MHz) spectrum of **28a** in acetone- d_6



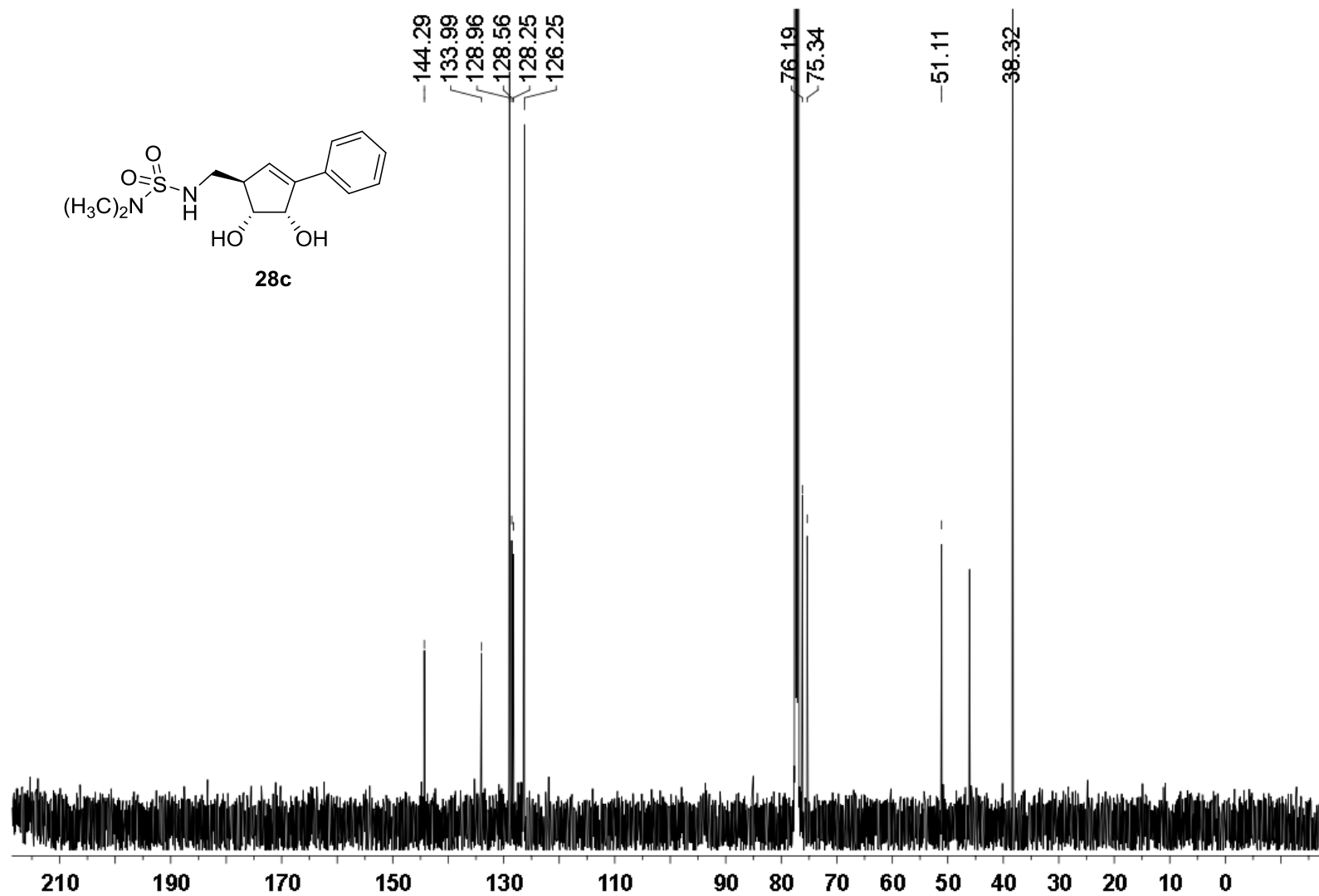
¹H NMR (500 MHz) spectrum of **28b** in DMSO-*d*₆



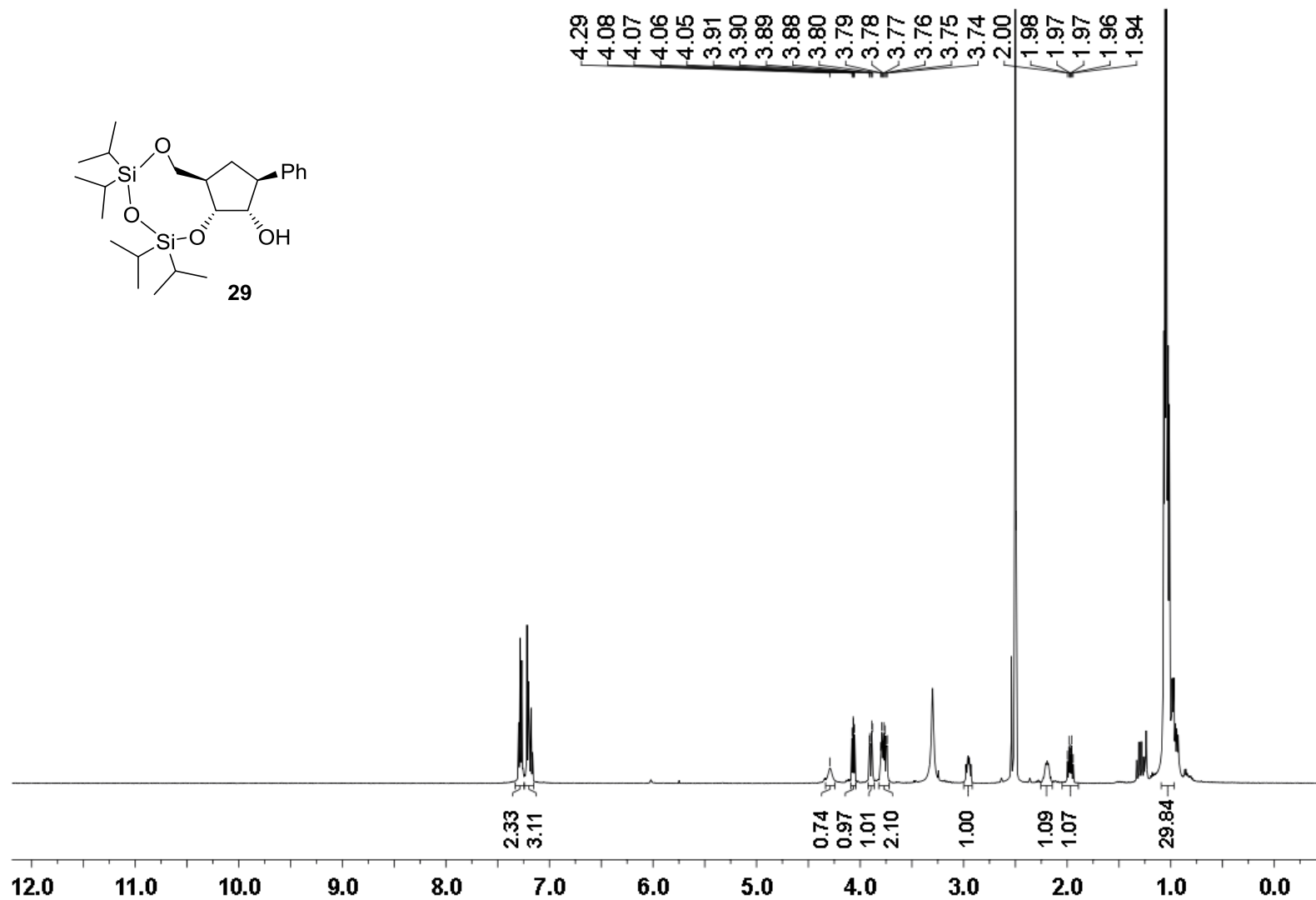
^{13}C NMR (126 MHz) spectrum of **28b** in $\text{DMSO}-d_6$



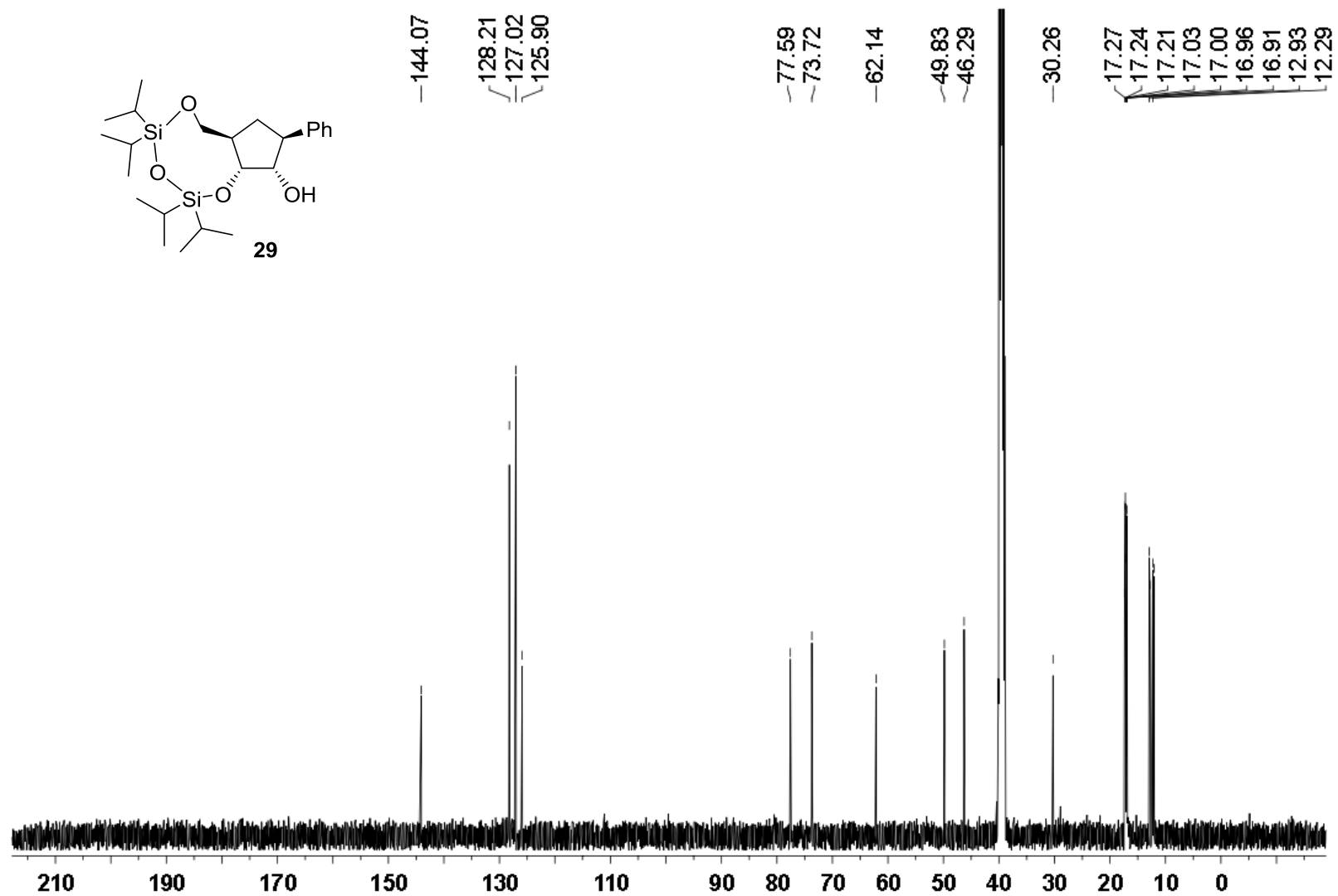
¹H NMR (500 MHz) spectrum of **28c** in CDCl₃



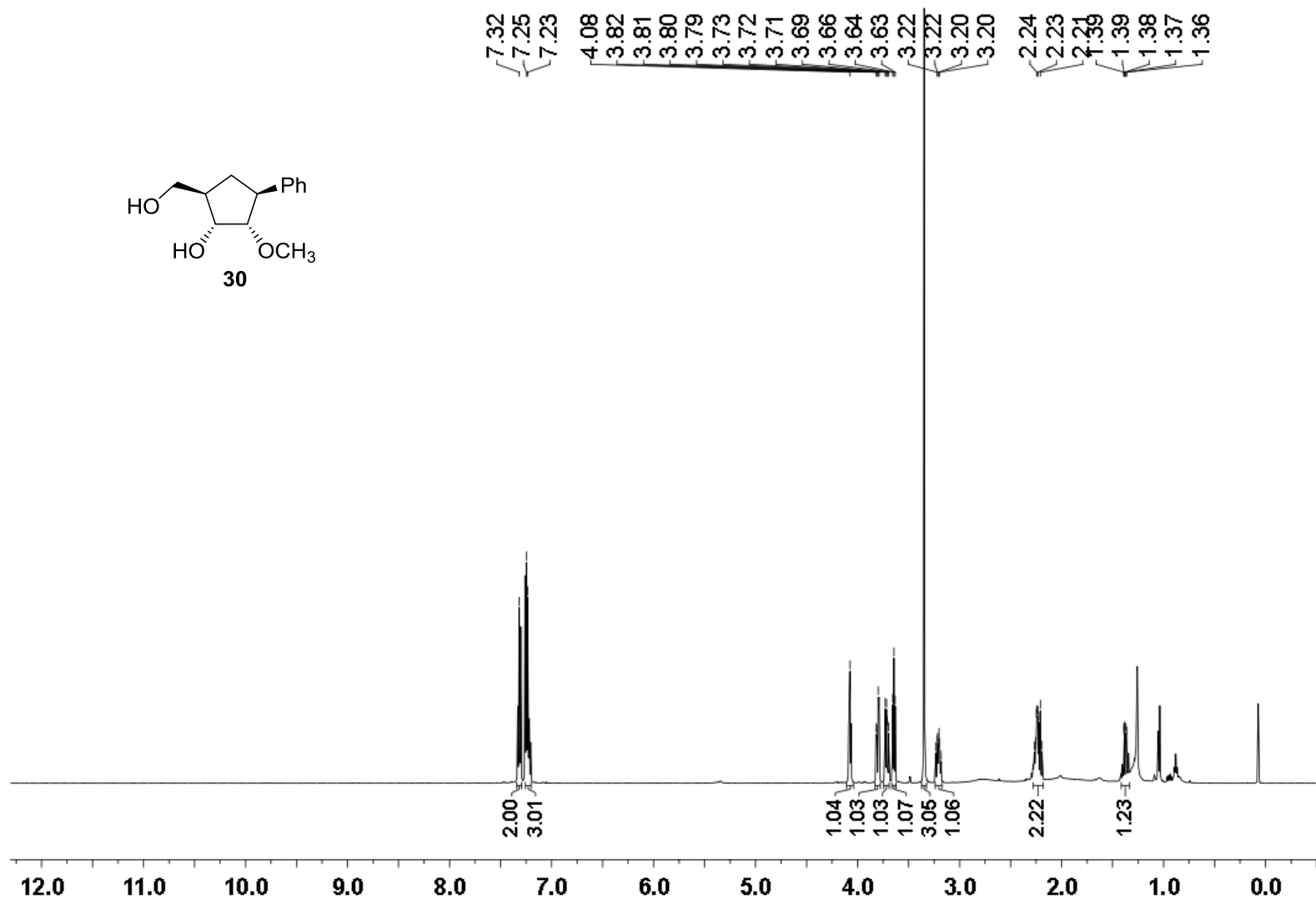
^{13}C NMR (126 MHz) spectrum of **28c** in CDCl_3



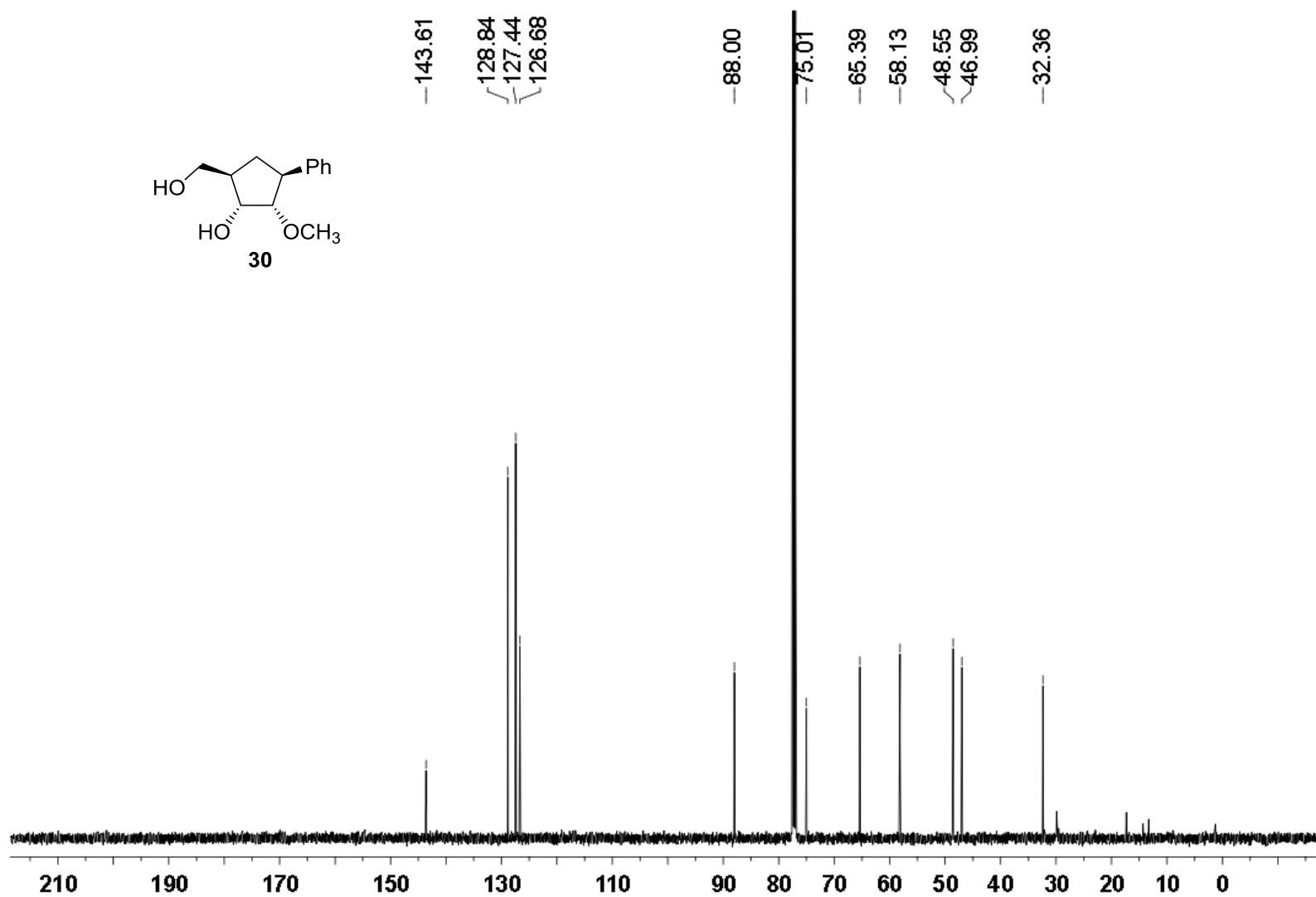
^1H NMR (500 MHz) spectrum of **29** in $\text{DMSO}-d_6$



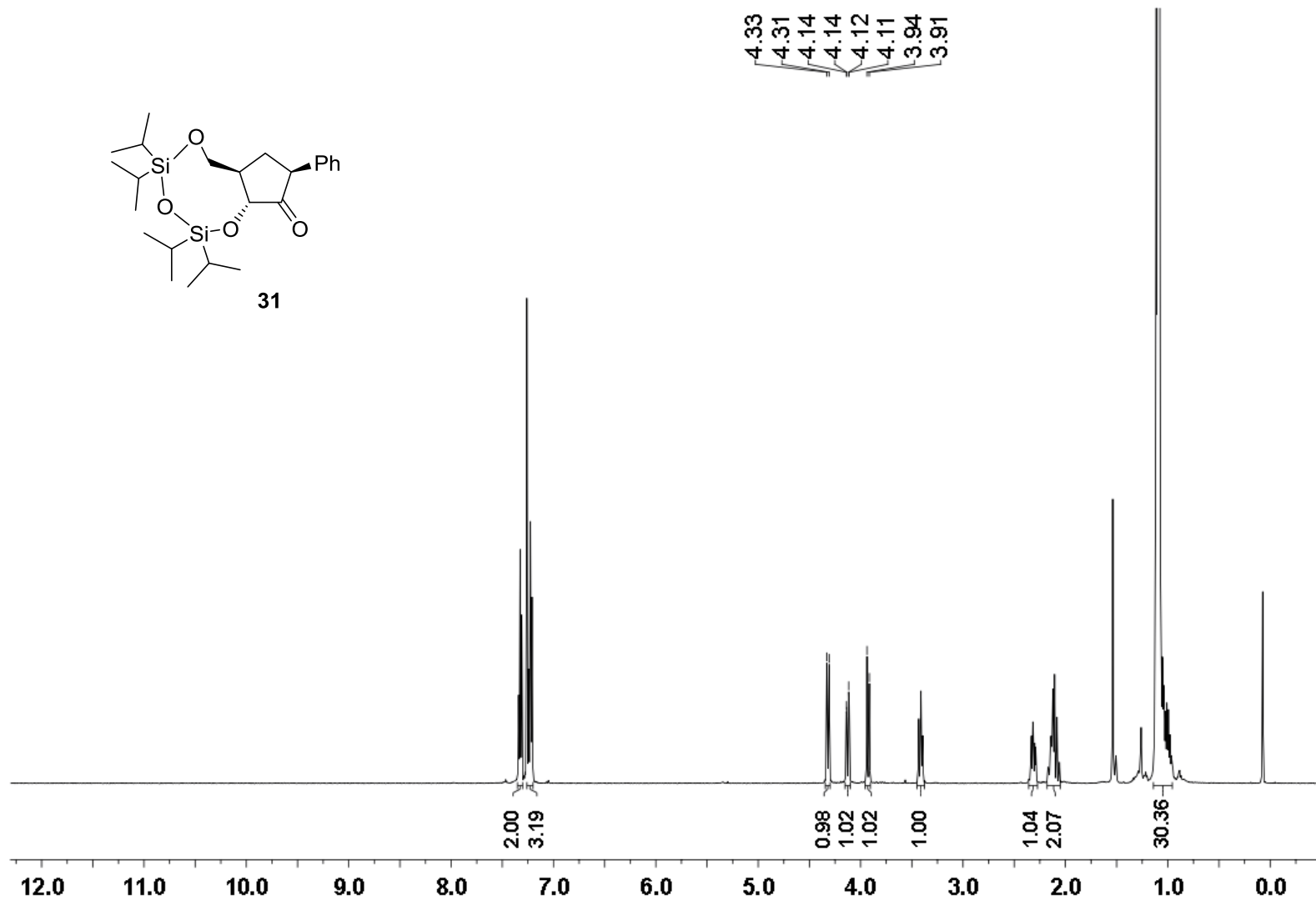
^{13}C NMR (126 MHz) spectrum of **29** in $\text{DMSO}-d_6$



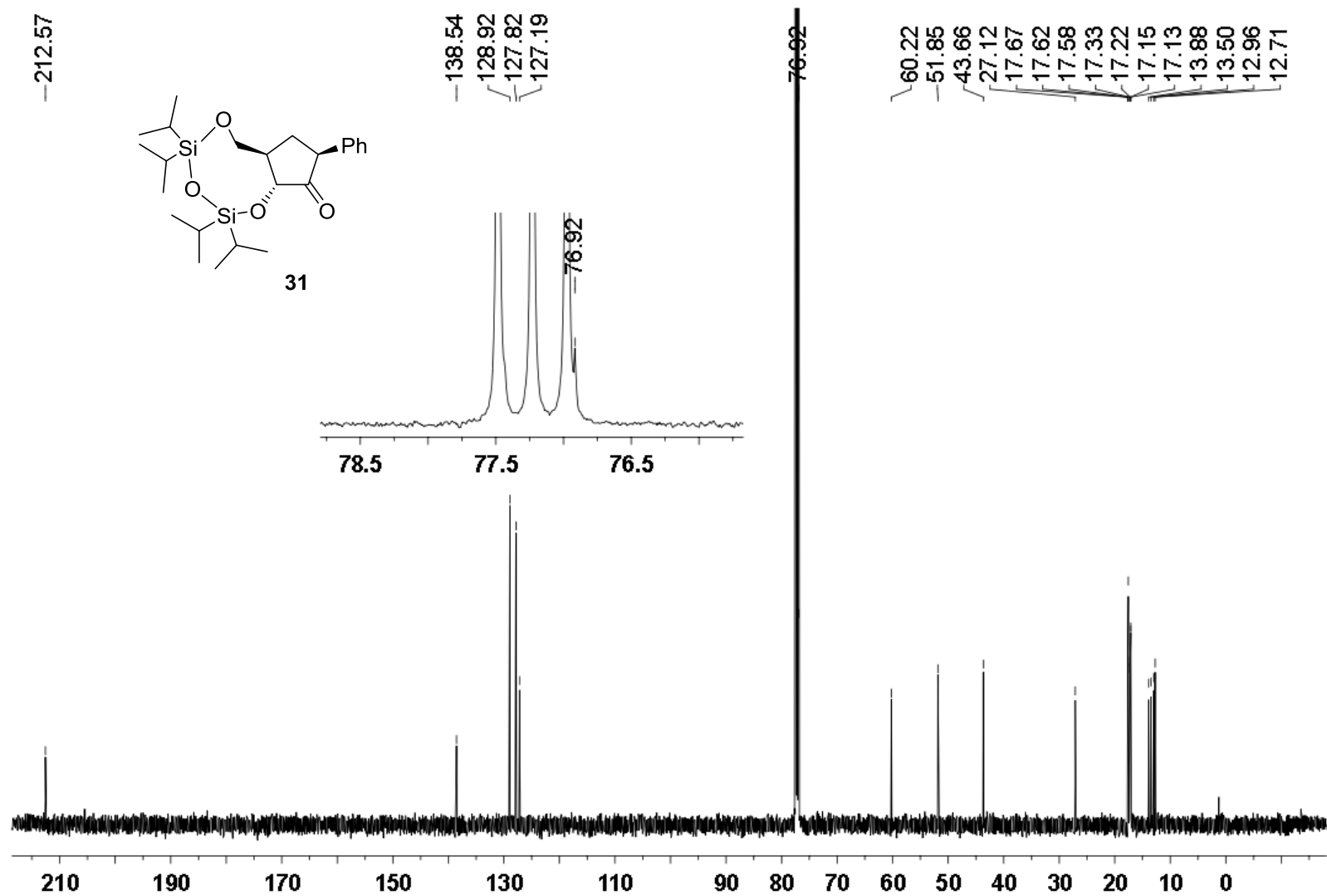
¹H NMR (500 MHz) spectrum of **30** in CDCl₃



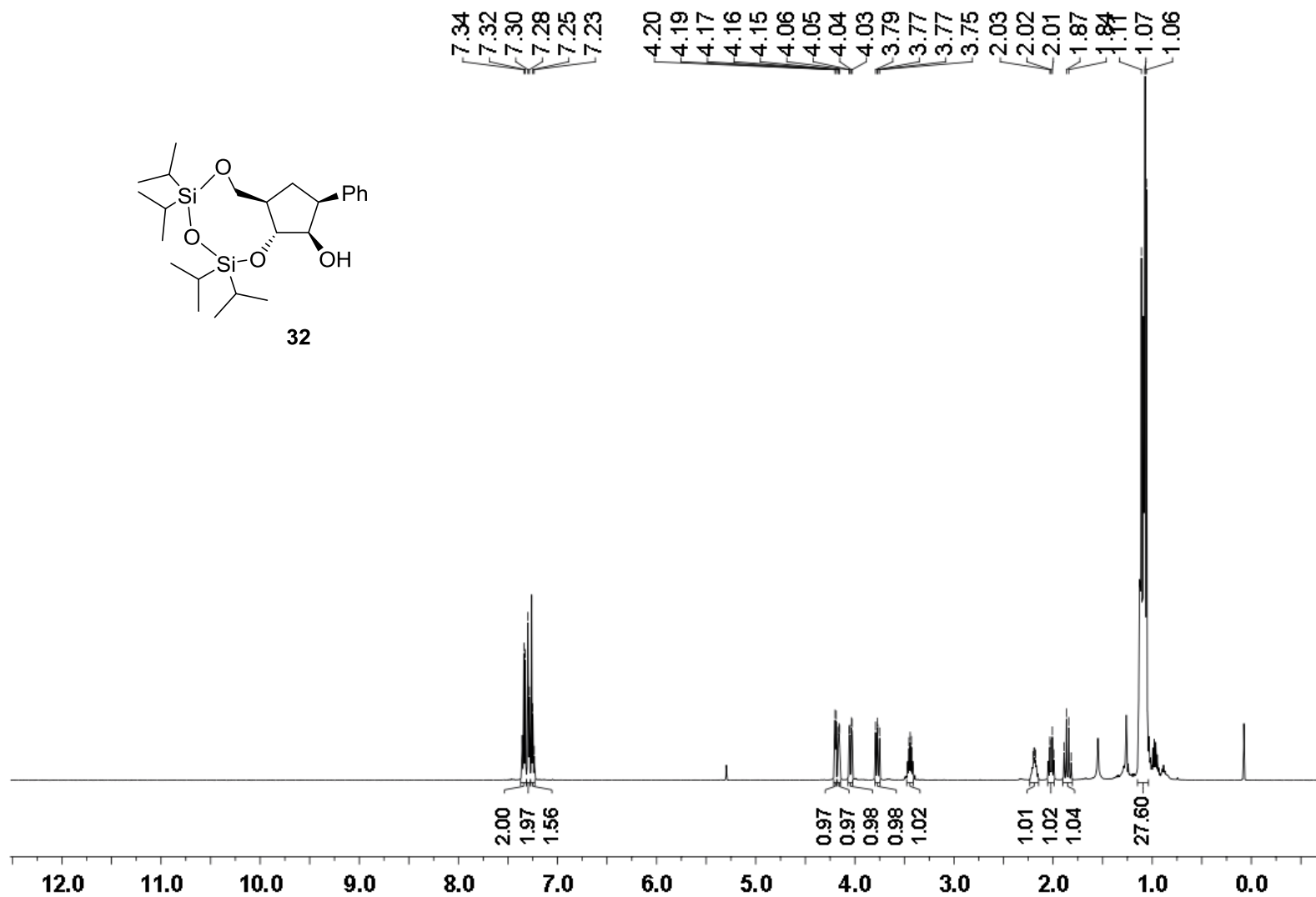
¹³C NMR (126 MHz) spectrum of **30** in CDCl₃



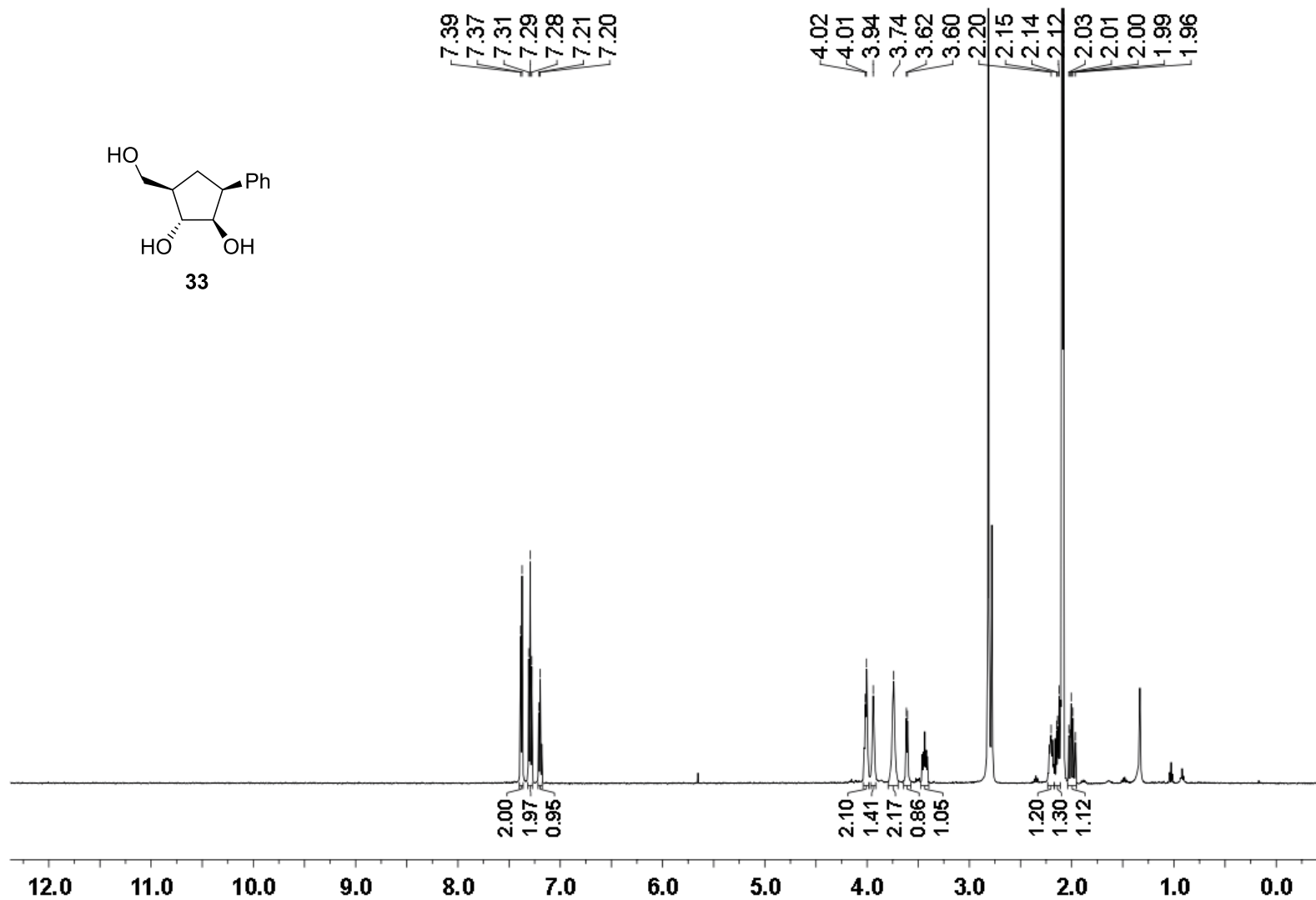
^1H NMR (500 MHz) spectrum of **31** in CDCl_3



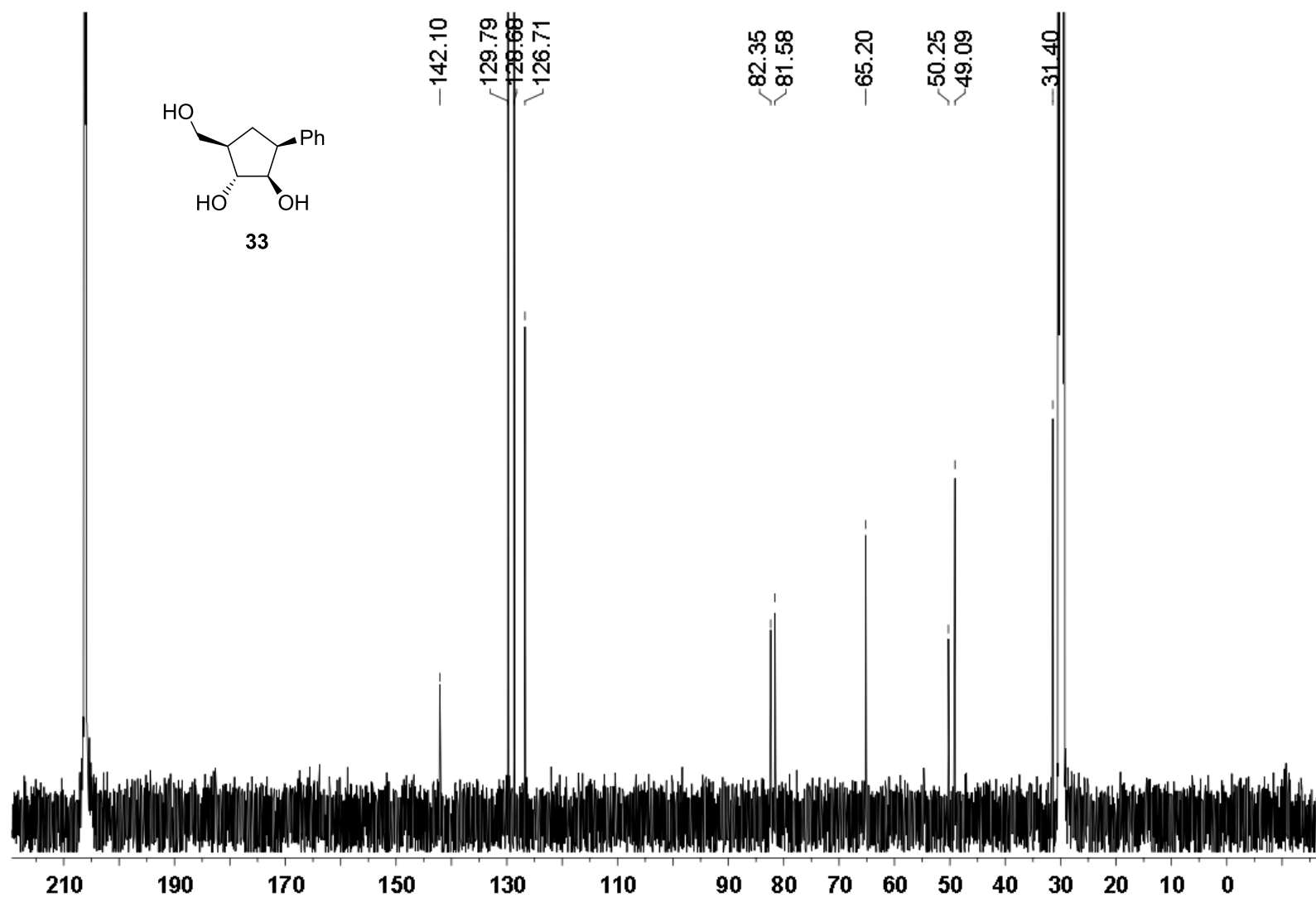
^{13}C NMR (126 MHz) spectrum of **31** in CDCl_3



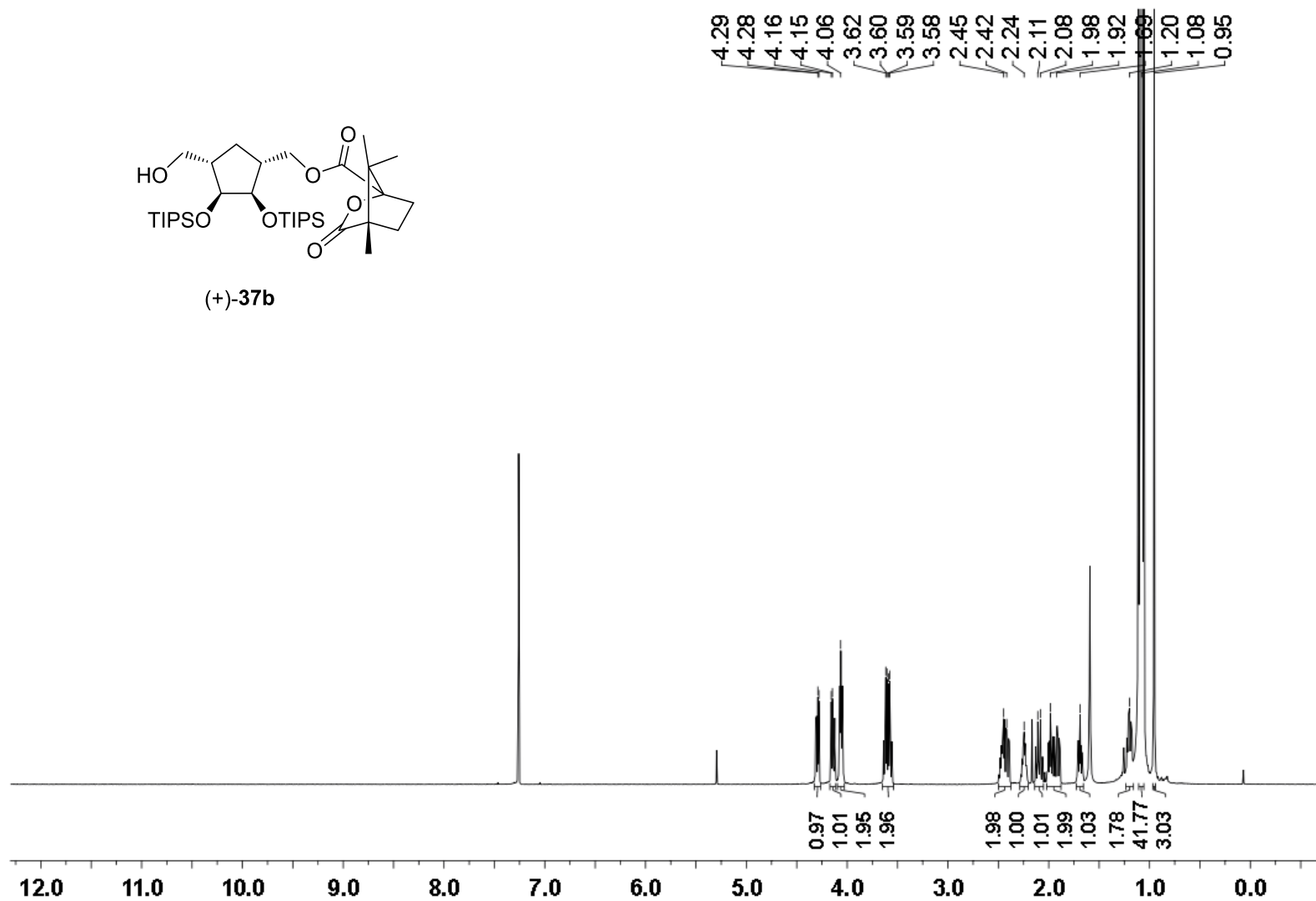
¹H NMR (500 MHz) spectrum of **32** in CDCl₃



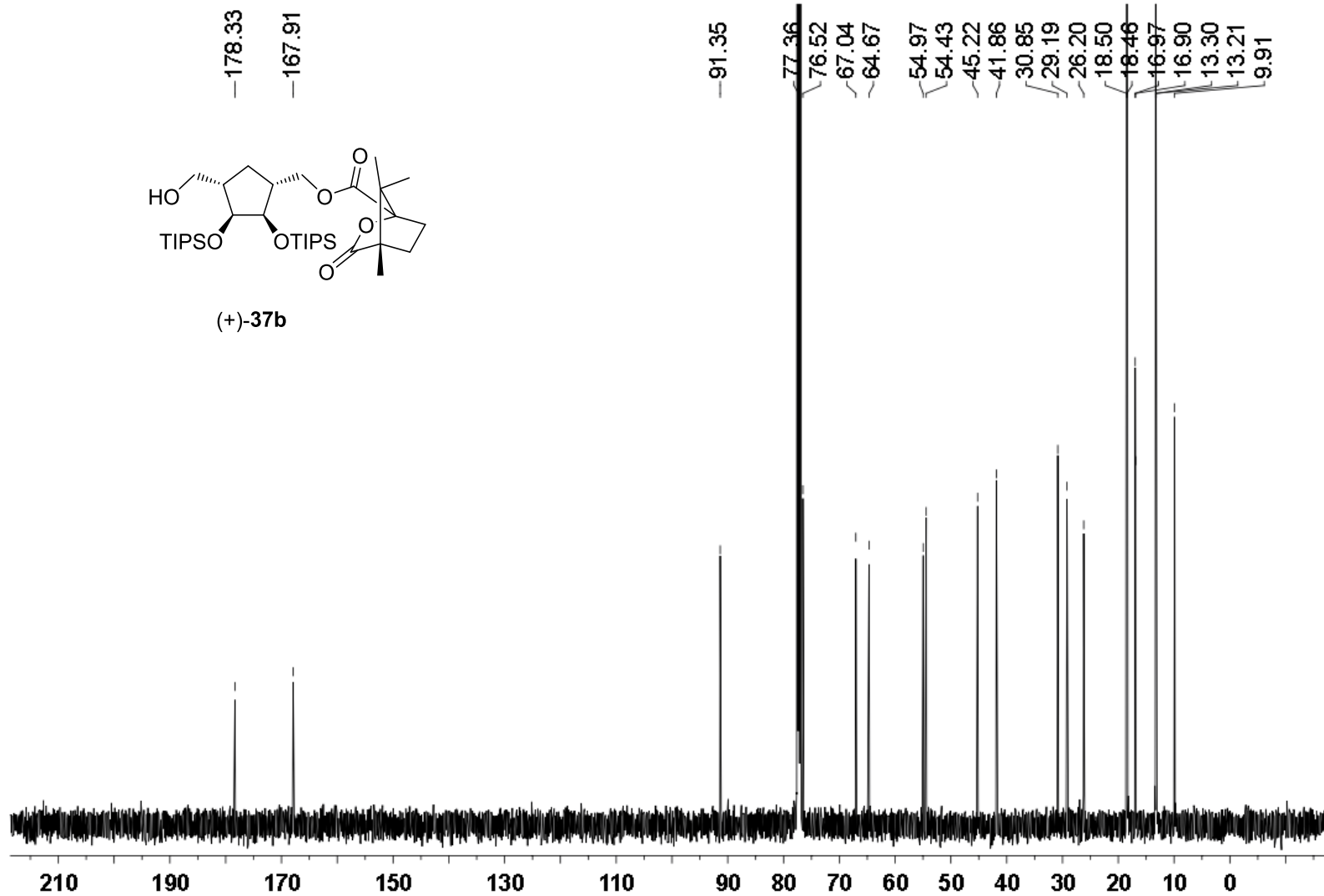
^1H NMR (500 MHz) spectrum of **33** in acetone- d_6



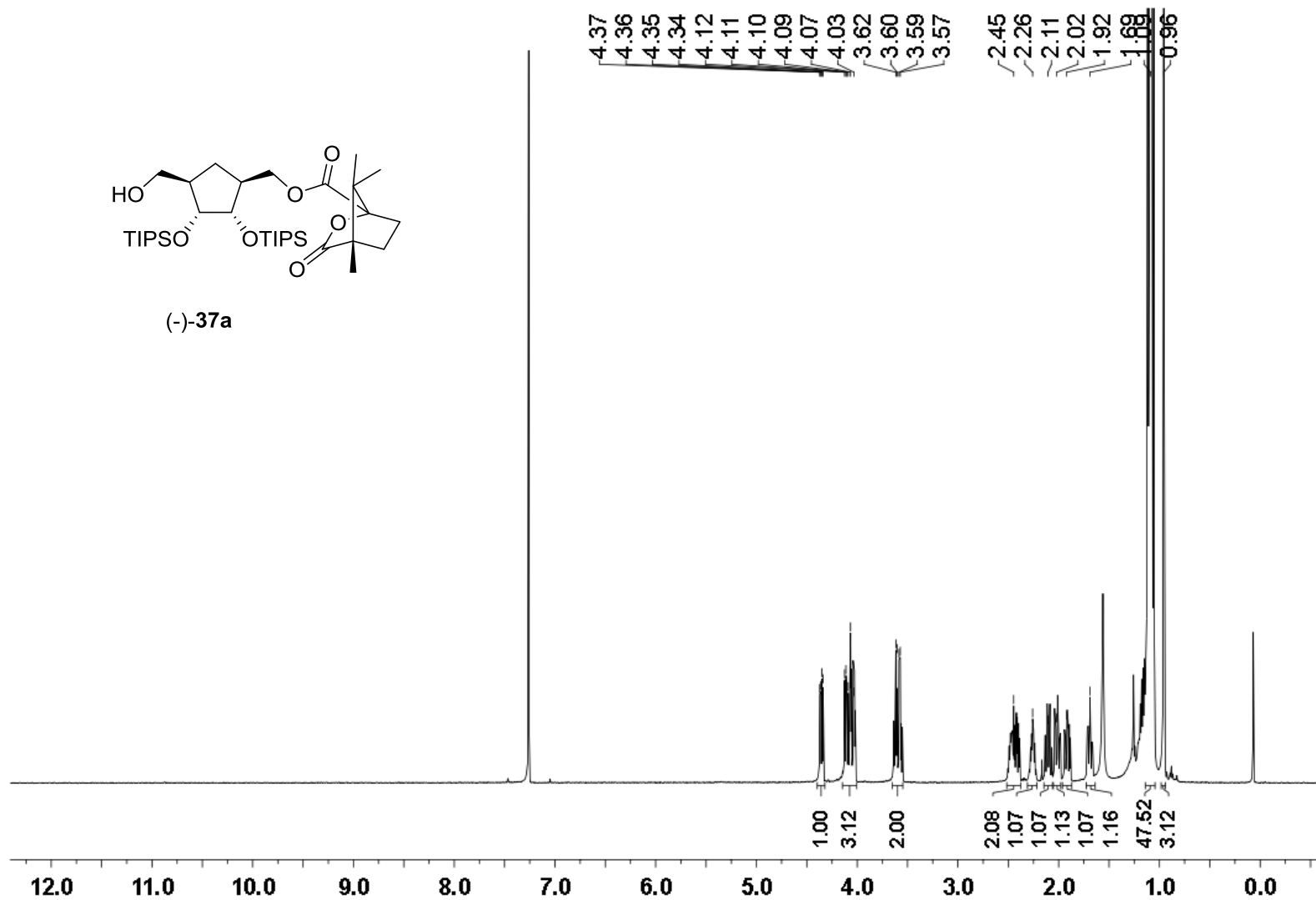
^{13}C NMR (126 MHz) spectrum of **33** in acetone- d_6



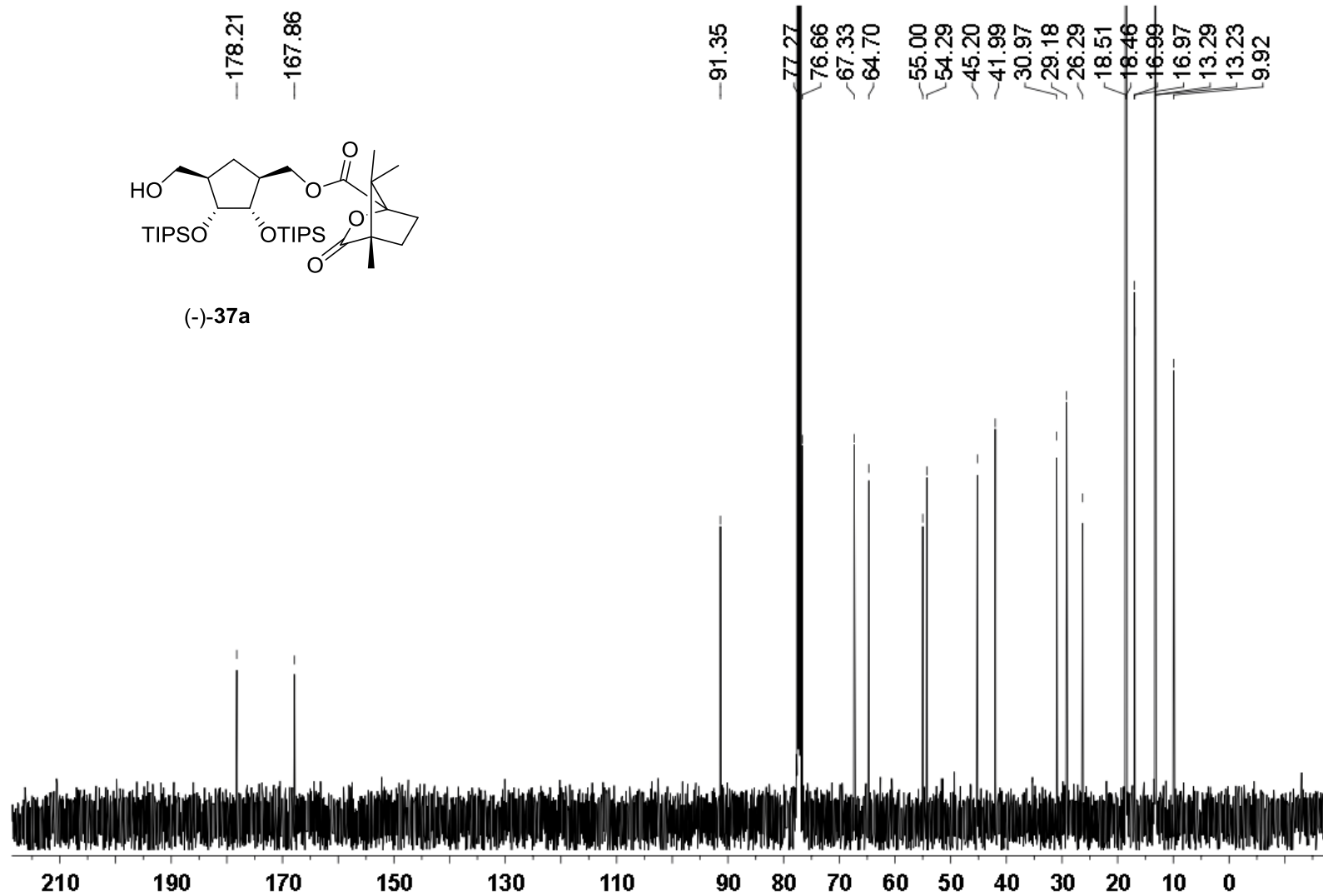
¹H NMR (500 MHz) spectrum of (+)-**37b** in CDCl₃



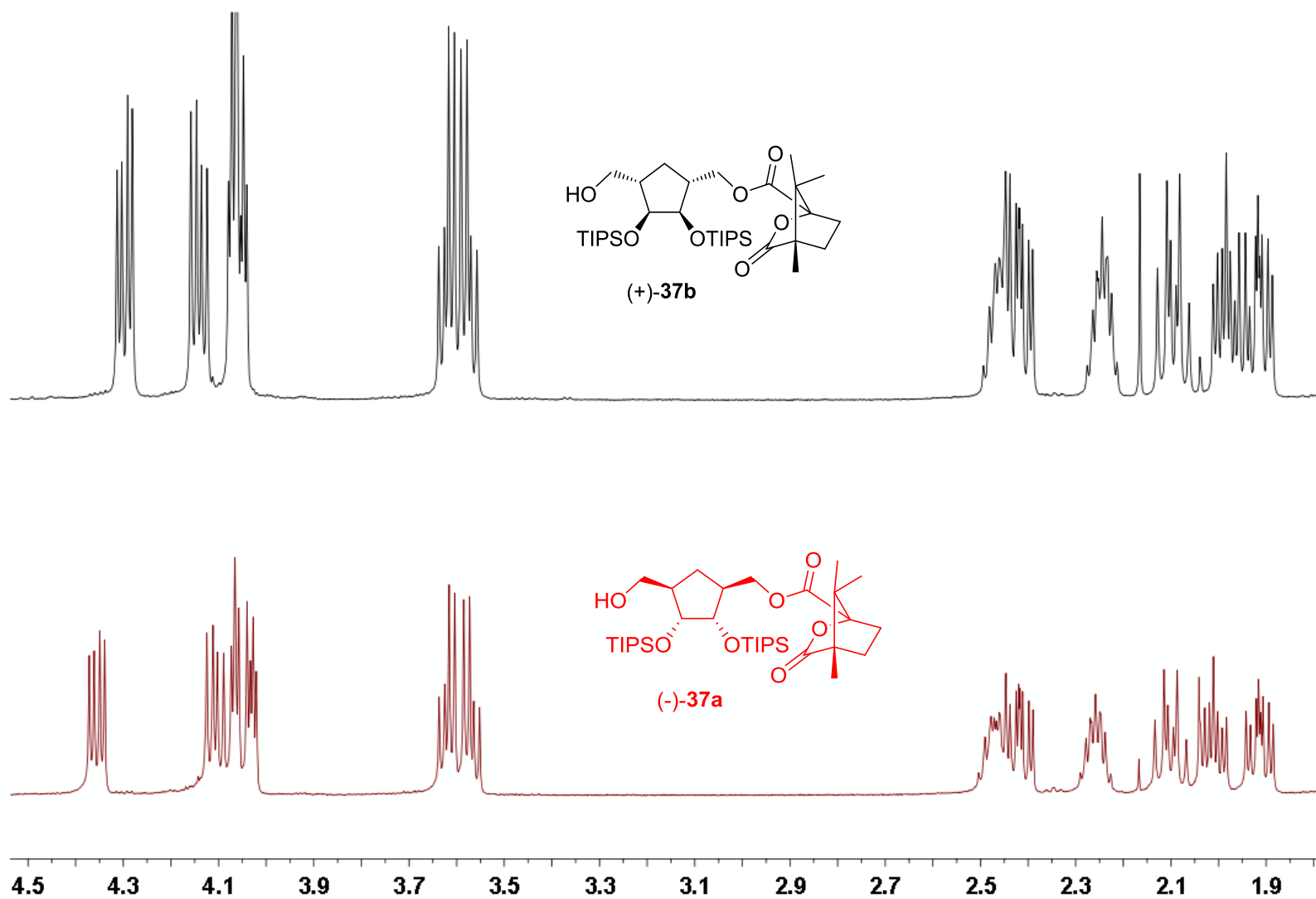
^{13}C NMR (126 MHz) spectrum of (+)-**37b** in CDCl_3



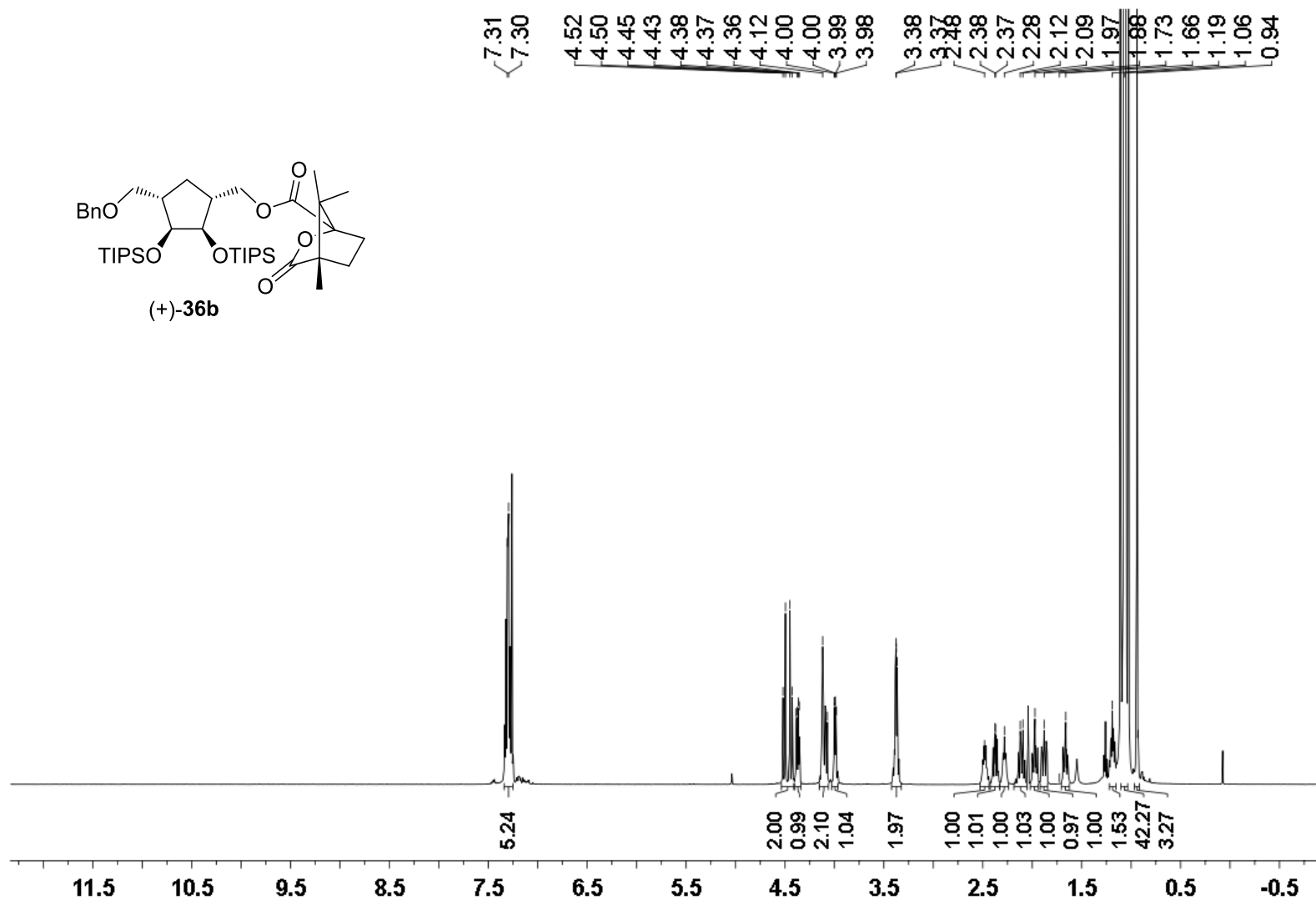
¹H NMR (500 MHz) spectrum of (-)-37a in CDCl₃



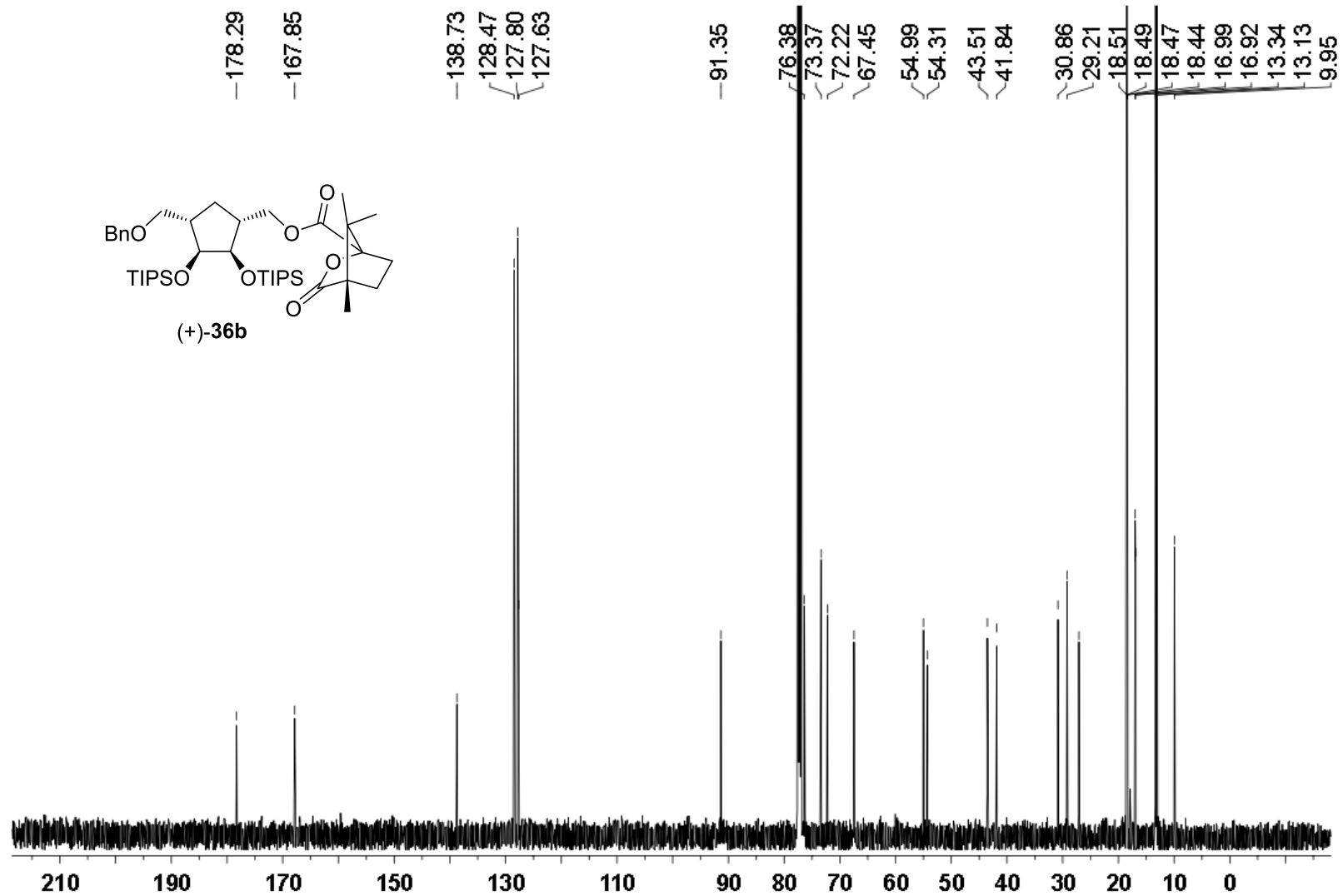
^{13}C NMR (126 MHz) spectrum of (-)-**37a** in CDCl_3



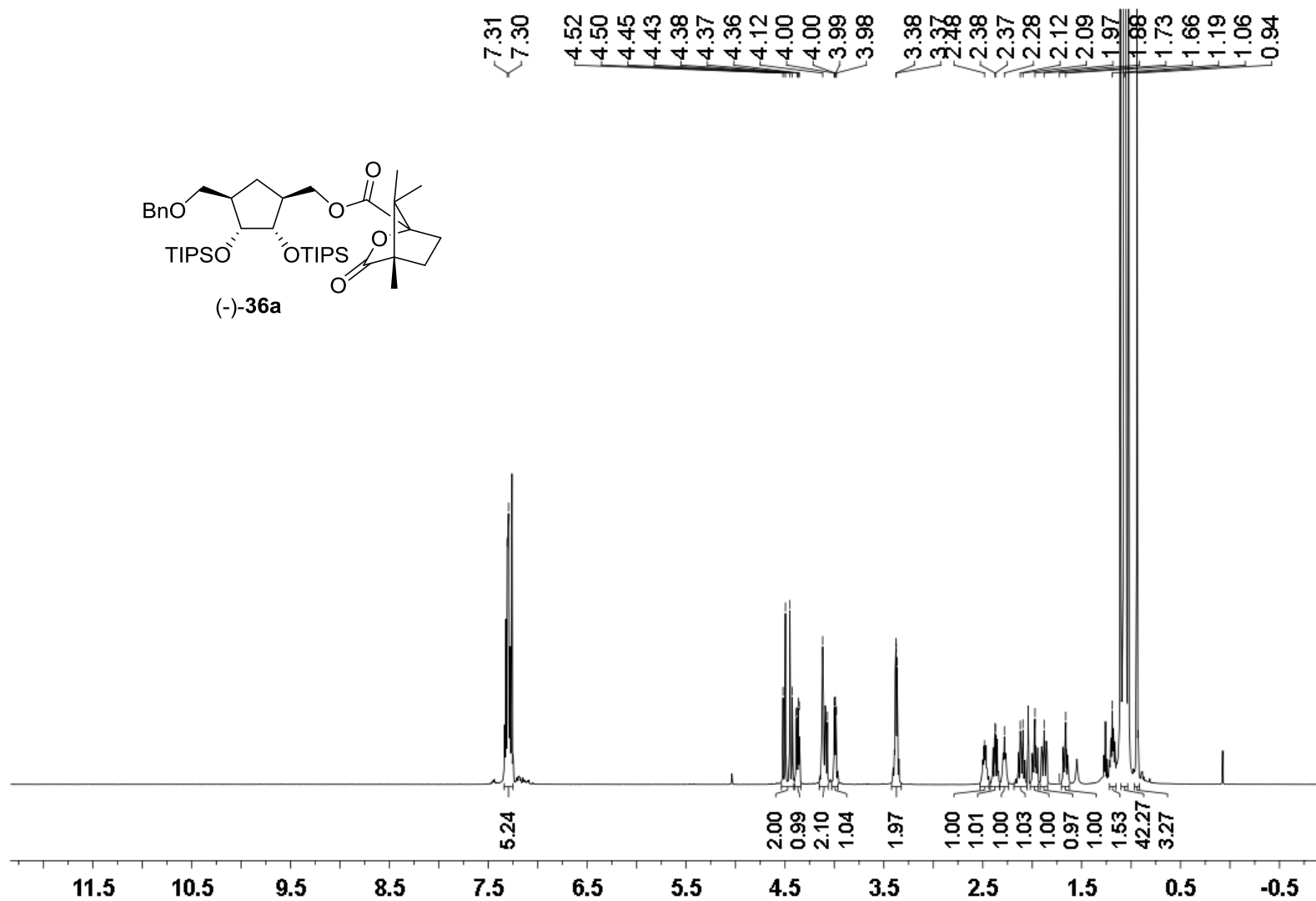
Portion of ^1H NMR spectrum of diastereomers **(+)-37b** and **(-)-37a** in CDCl_3



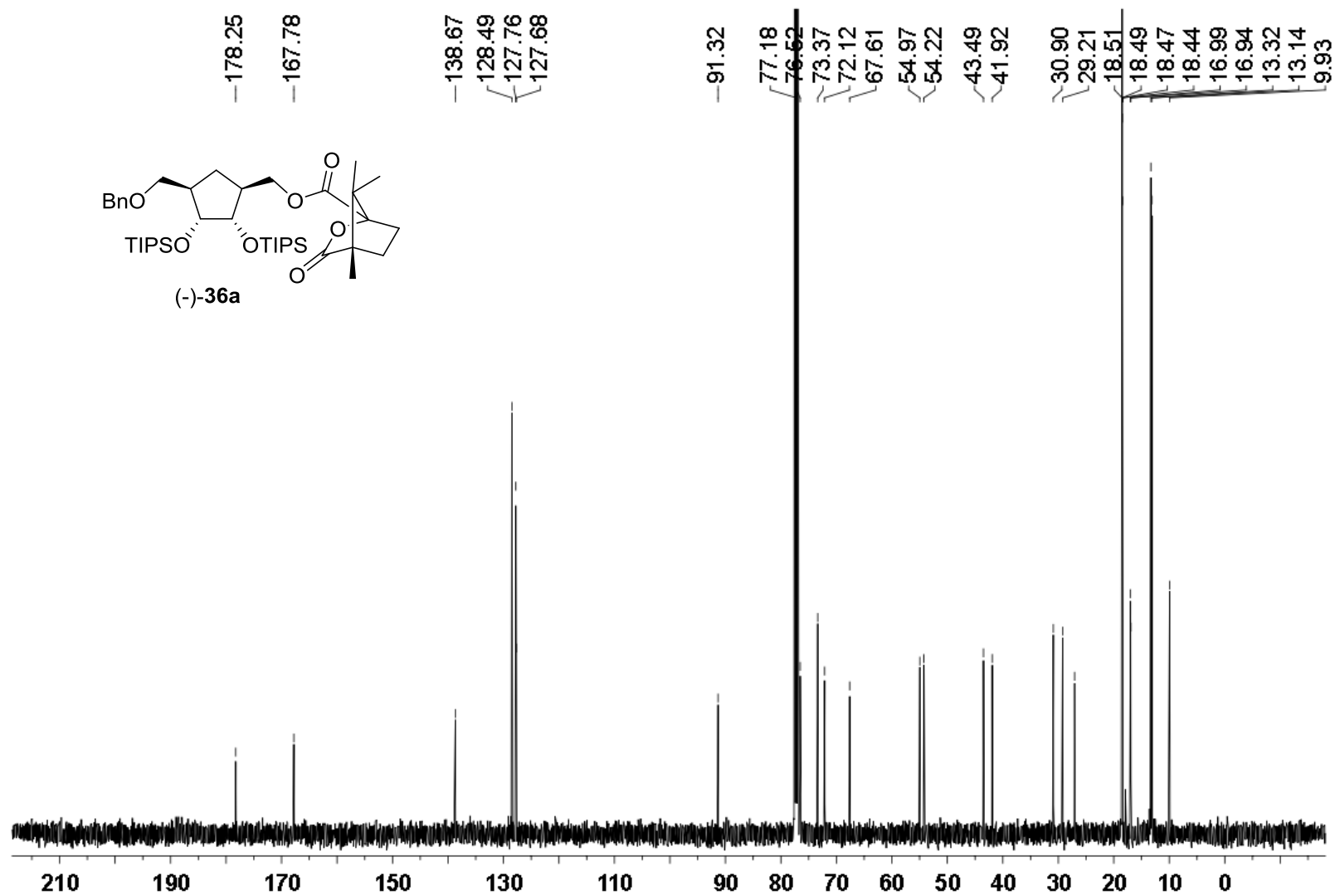
^1H NMR (500 MHz) spectrum of (+)-**36b** in CDCl_3



¹³C NMR (126 MHz) spectrum (+)-36b in CDCl₃



¹H NMR (500 MHz) spectrum of (-)-36a in CDCl₃



^{13}C NMR (126 MHz) spectrum of **(-)-36a** in CDCl_3

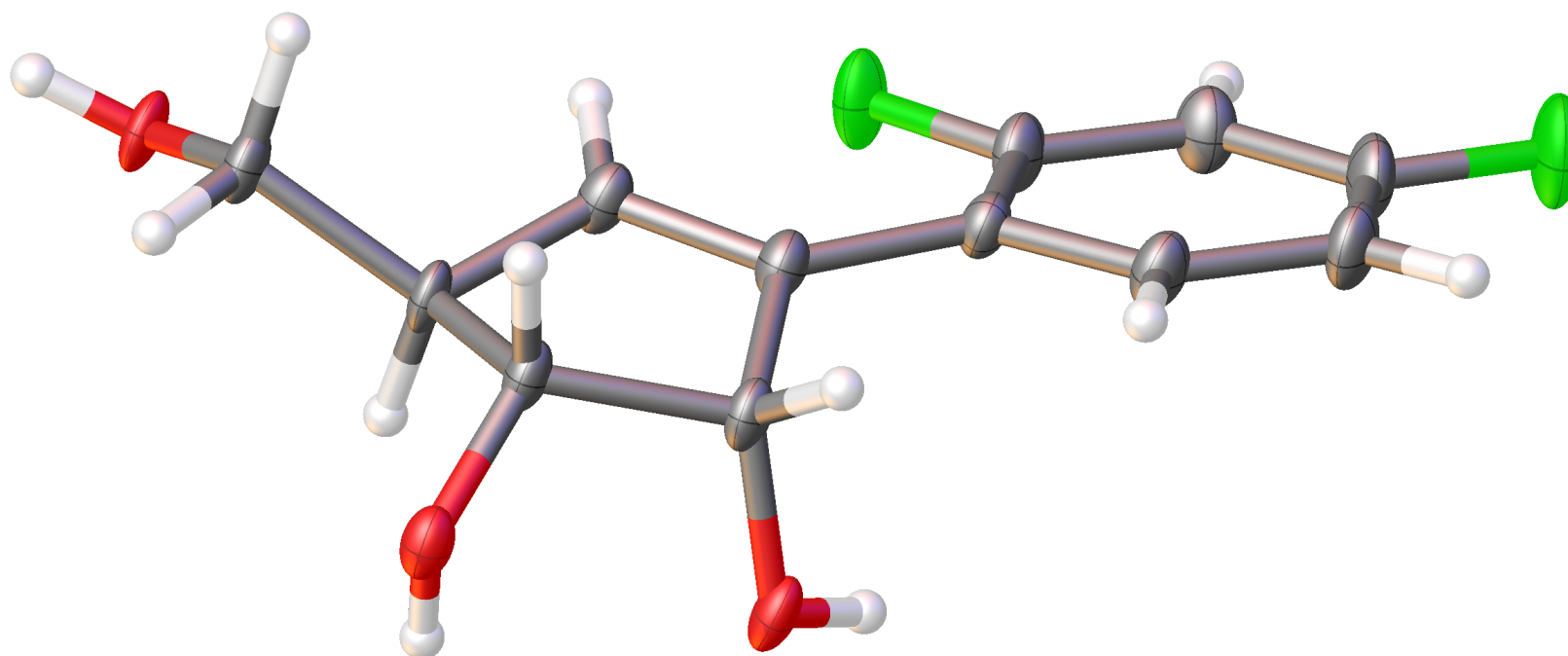
X-ray crystallographic analysis

The diffraction data were collected at 120 K with a partial χ geometry diffractometer equipped with a CCD detector. Cu K α radiation (λ = 1.54184 Å, rotating anode source, multilayer optic) was used. Data reduction and final cell refinement were carried out using the CrysAlisPro software (CrysAlisPRO, Agilent Technologies UK Ltd).

Table S1. Sample and crystal data for compound **3b**.

CCDC NO.	1452238	
Empirical formula	C ₁₂ H ₁₂ F ₂ O ₃	
Formula weight	242.22	
Crystal system	Triclinic	
Space group	<i>P</i> 1	
<i>a</i> [Å]	5.2120(4)	α = 80.834(6)
<i>b</i> [Å]	7.4380(5)	β = 85.227(6)
<i>c</i> [Å]	14.3549(9)	γ = 74.865(6)
Volume [Å ³]	529.826	
<i>Z</i>	2	
Crystal size [mm]	0.30 × 0.25 × 0.15	
2 range [°]	6.036 to 50.696	
Reflections collected/unique	4567 / 1931	
<i>R</i> _{int}	0.0207	
Data/restraints/parameters	1931 / 11 / 173	

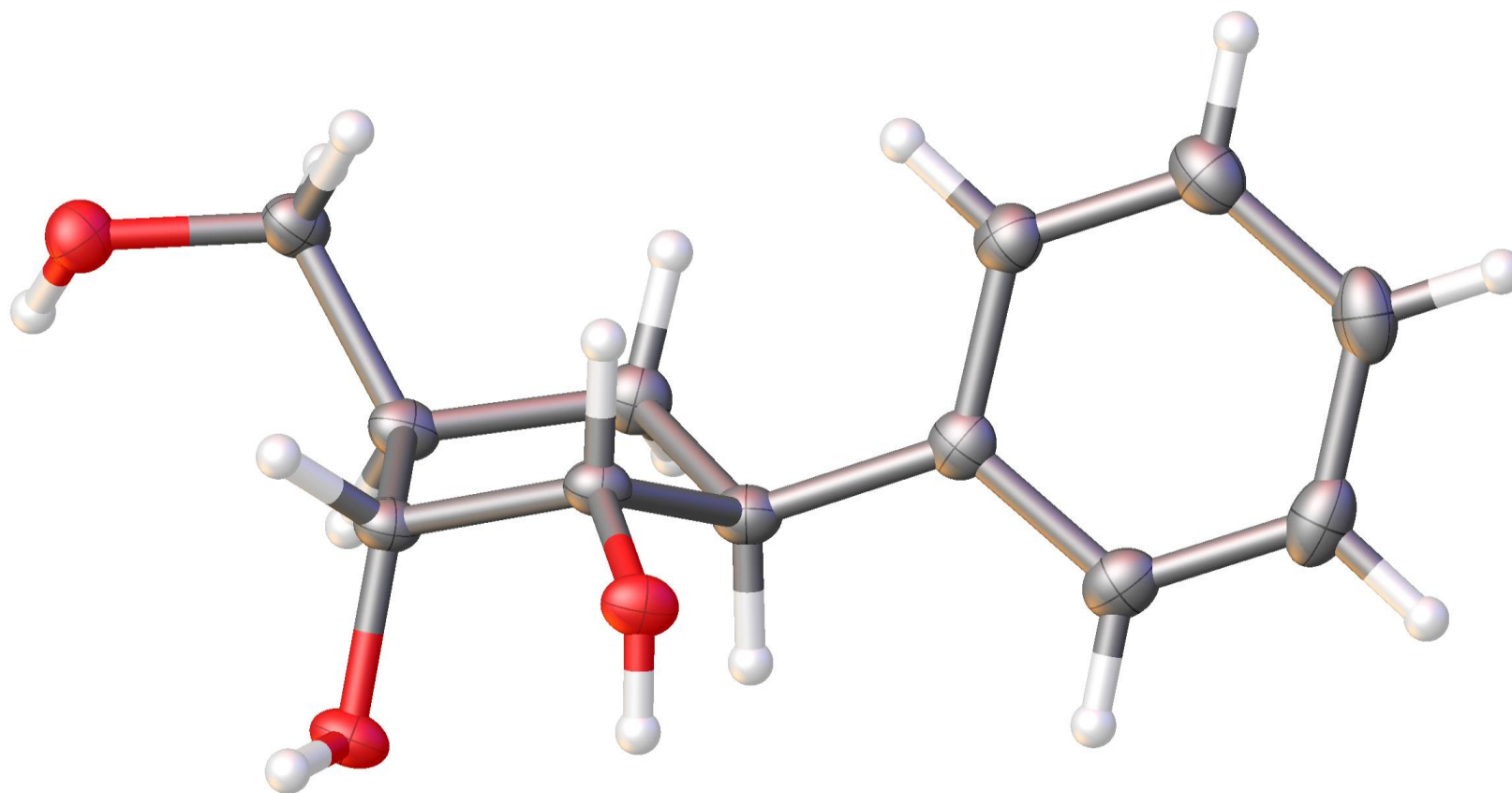
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0503$ $wR_2 = 0.1343$
Final R indices [all data]	$R_1 = 0.0534$ $wR_2 = 0.1389$
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$ [$\text{e } \text{\AA}^{-3}$]	0.30 / -0.39



ORTEP Figure of **3b**. The ellipsoid contour probability level is 50%.

Table S2. Sample and crystal data for compound **4a**.

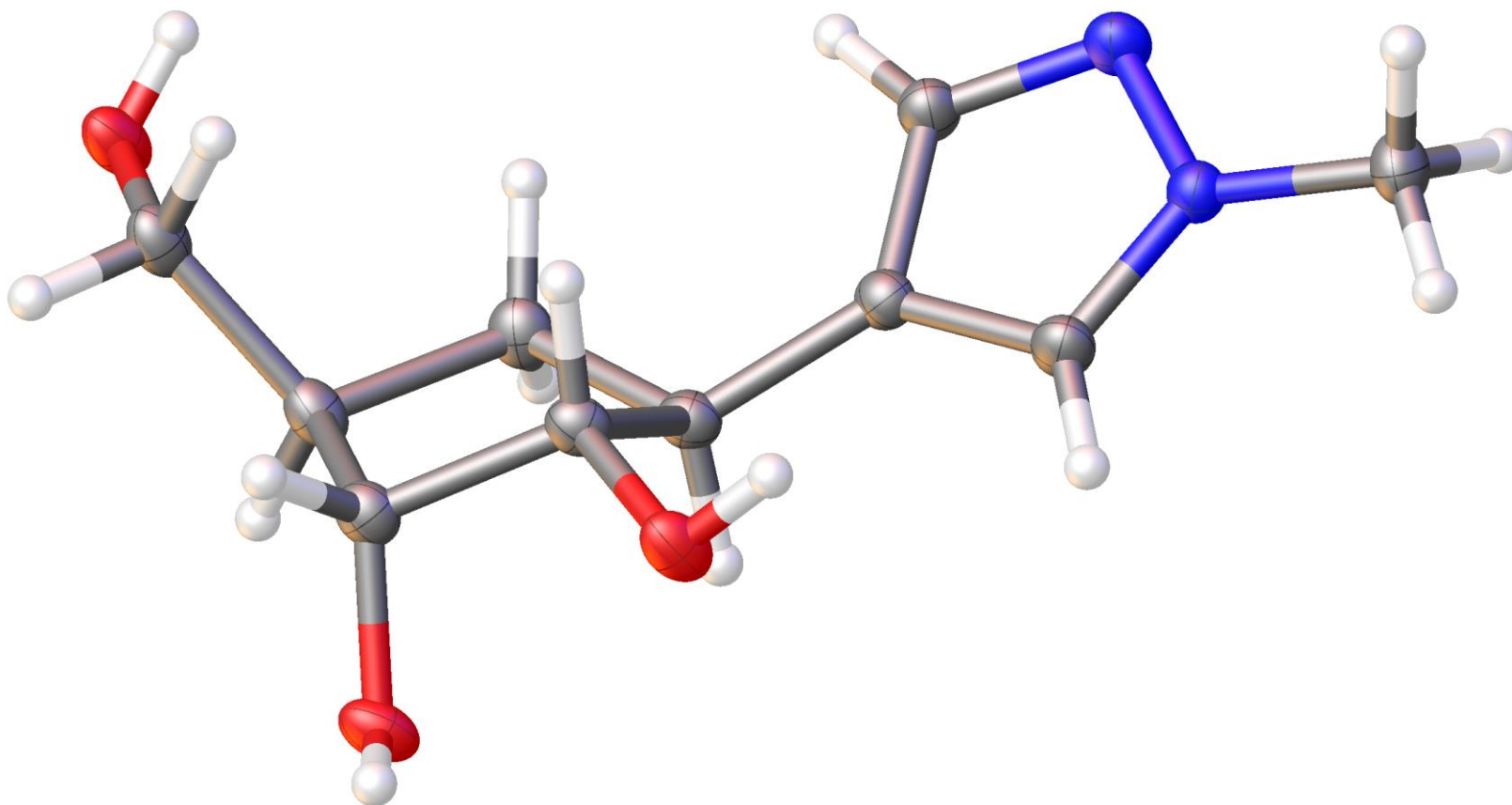
CCDC NO.	1452773	
Empirical formula	C ₁₂ H ₁₆ O ₃	
Formula weight	208.25	
Crystal system	Orthorhombic	
Space group	<i>Pbca</i>	
<i>a</i> [Å]	9.8445(4)	$\alpha = 90$
<i>b</i> [Å]	6.9522(3)	$\beta = 90$
<i>c</i> [Å]	30.4659(12)	$\gamma = 90$
Volume [Å ³]	2085.11	
<i>Z</i>	8	
Crystal size [mm]	0.20 × 0.20 × 0.15	
2 θ range [°]	6.764 to 50.696	
Reflections collected/unique	10308 / 1892	
<i>R</i> _{int}	0.0164	
Data/restraints/parameters	1892 / 3 / 145	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0331 <i>wR</i> ₂ = 0.0835	
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.0342 <i>wR</i> ₂ = 0.0844	
$\Delta\rho$ max / $\Delta\rho$ min [e Å ⁻³]	0.31 / -0.20	



ORTEP Figure of **4a**. The ellipsoid contour probability level is 50%.

Table S3. Sample and crystal data for compound **4c**.

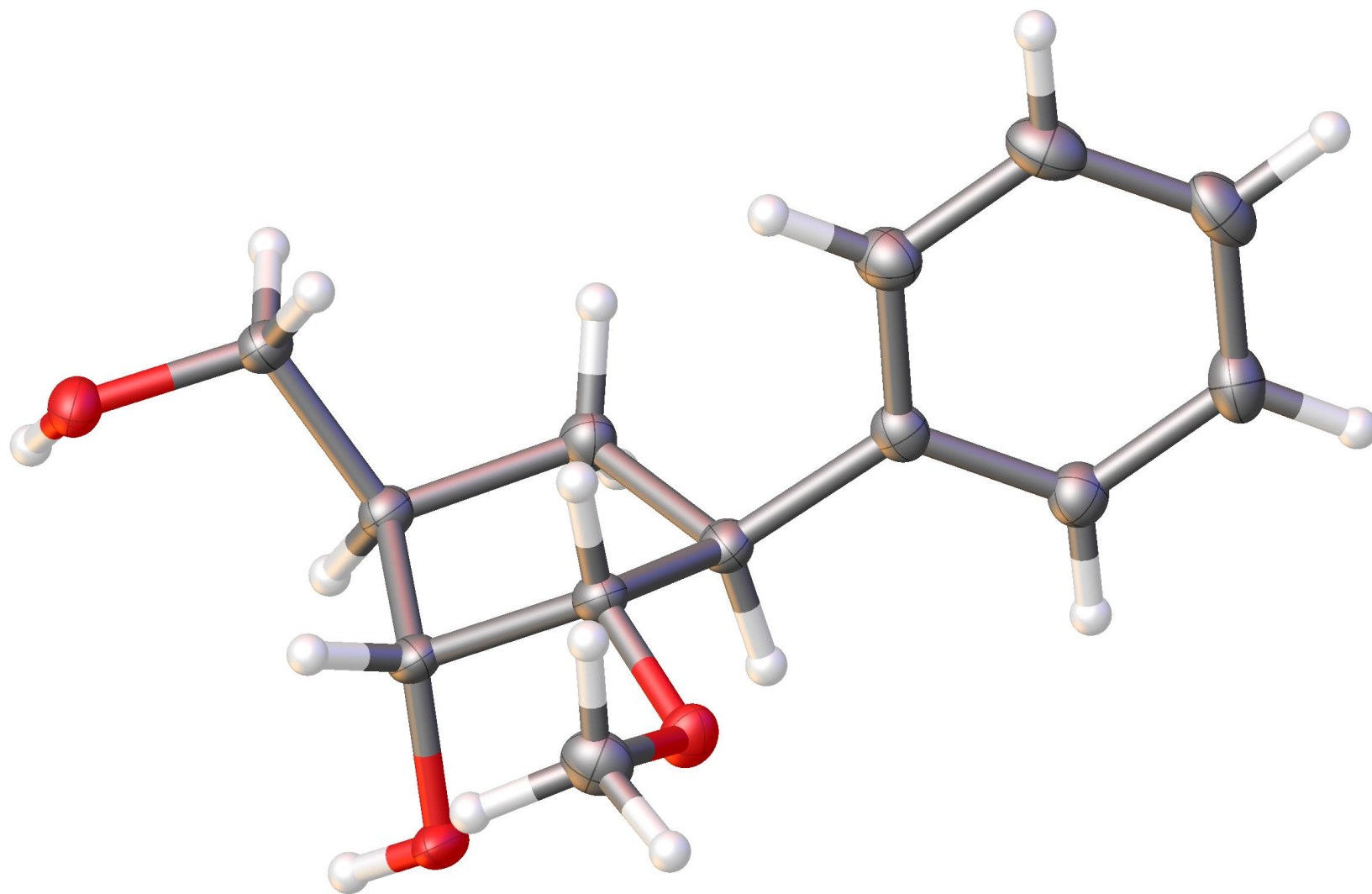
CCDC NO.	1452237	
Empirical formula	C ₁₀ H ₁₆ N ₂ O ₃	
Formula weight	212.24	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
<i>a</i> [Å]	7.2069(4)	$\alpha = 80.466(4)$
<i>b</i> [Å]	7.7420(3)	$\beta = 79.403(4)$
<i>c</i> [Å]	9.5826(4)	$\gamma = 77.127(4)$
Volume [Å ³]	507.987	
<i>Z</i>	2	
Crystal size [mm]	0.15 × 0.06 × 0.06	
2 θ range [°]	4.362 to 51.36	
Reflections collected/unique	4995 / 1929	
<i>R</i> _{int}	0.0178	
Data/restraints/parameters	1929 / 3 / 146	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0409 <i>wR</i> ₂ = 0.0995	
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.0455 <i>wR</i> ₂ = 0.1027	
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$ [e Å ⁻³]	0.38 / -0.21	



ORTEP Figure of **4c**. The ellipsoid contour probability level is 50%.

Table S4. Sample and crystal data for compound **30**.

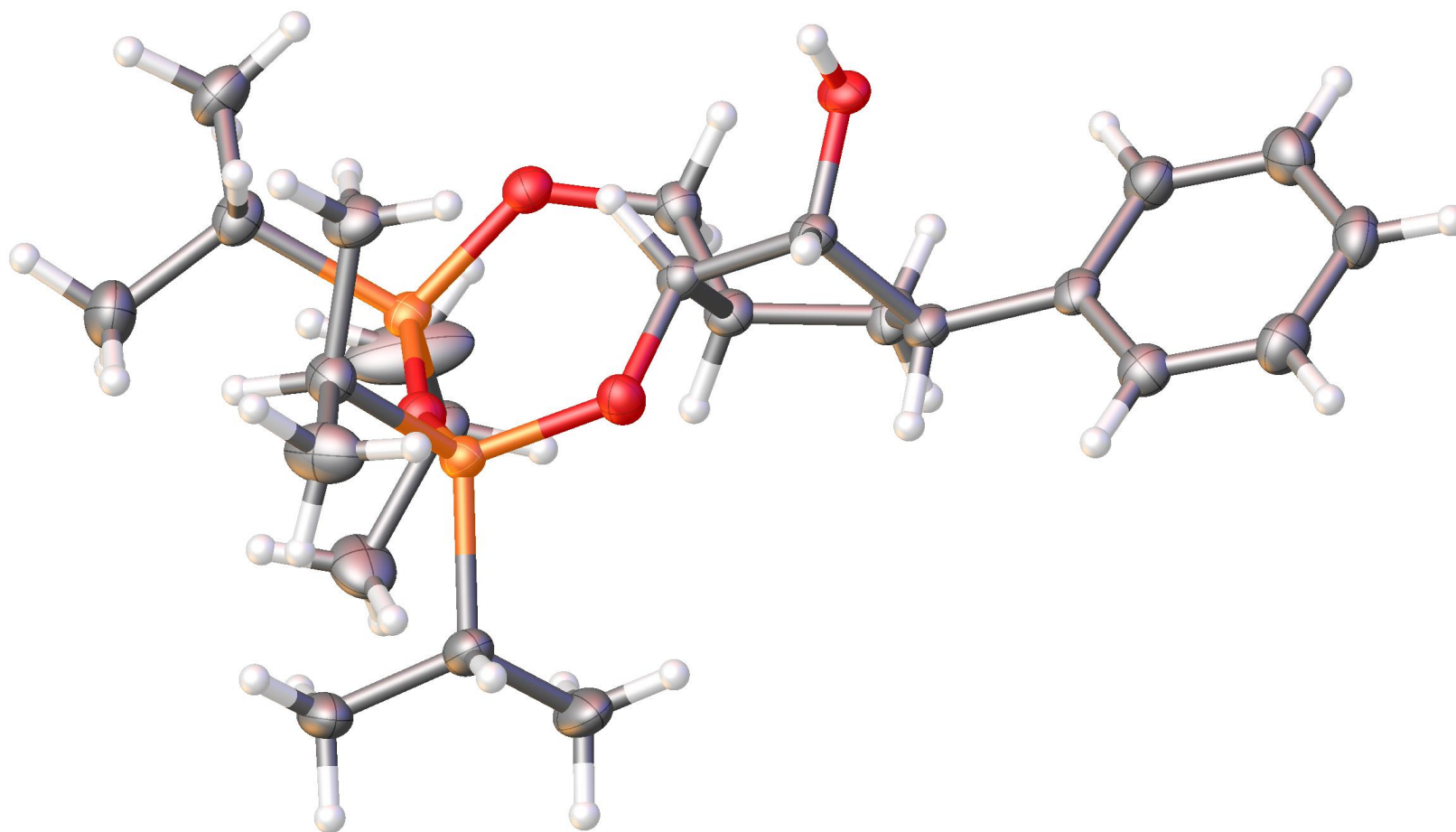
CCDC NO.	1452235	
Empirical formula	C ₁₃ H ₁₈ O ₃	
Formula weight	222.28	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> [Å]	12.5947(2)	$\alpha = 90$
<i>b</i> [Å]	6.74830(10)	$\beta = 105.382(2)$
<i>c</i> [Å]	14.1169(3)	$\gamma = 90$
Volume [Å ³]	1156.86	
<i>Z</i>	4	
Crystal size [mm]	0.25 × 0.20 × 0.20	
2 θ range [°]	5.986 to 50.698	
Reflections collected/unique	9291 / 2102	
<i>R</i> _{int}	0.0197	
Data/restraints/parameters	2102 / 2 / 152	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0331 <i>wR</i> ₂ = 0.0843	
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.0349 <i>wR</i> ₂ = 0.0858	
$\Delta\rho$ max / $\Delta\rho$ min [e Å ⁻³]	0.26 / -0.17	



ORTEP Figure of **30**. The ellipsoid contour probability level is 50%.

Table S5. Sample and crystal data for compound **32**.

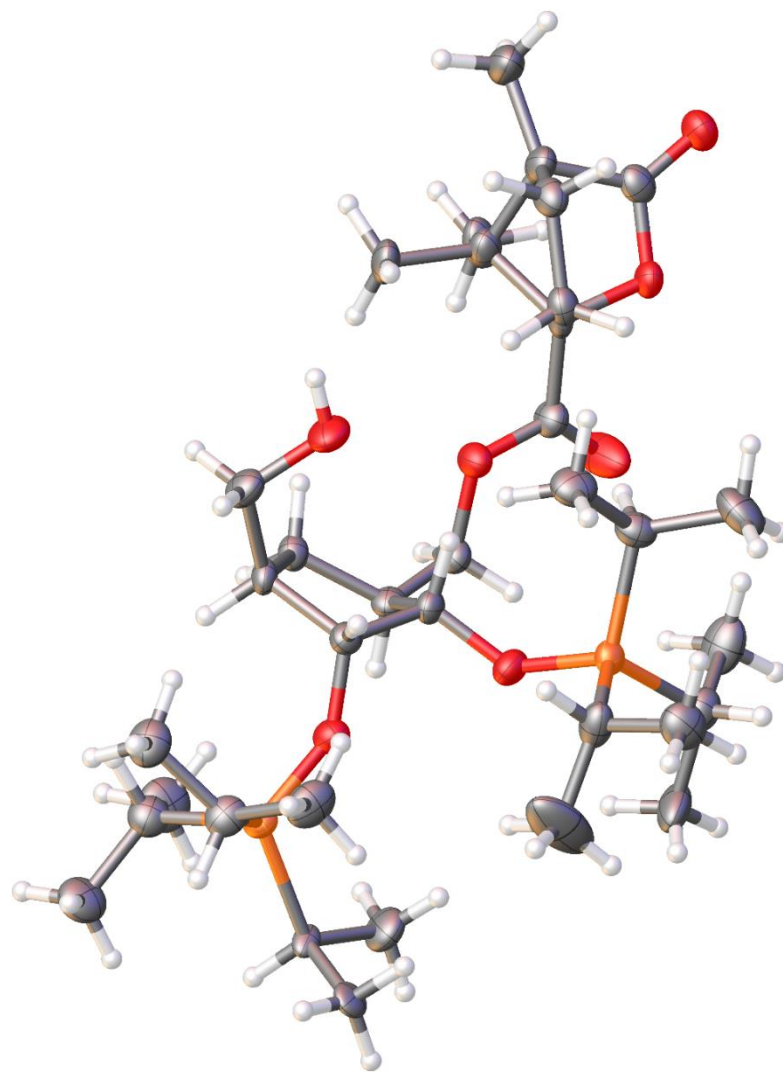
CCDC NO.	1452236	
Empirical formula	C ₂₄ H ₄₂ O ₄ Si ₂	
Formula weight	450.76	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> [Å]	9.6577(2)	$\alpha = 90$
<i>b</i> [Å]	26.6774(5)	$\beta = 109.914(2)$
<i>c</i> [Å]	10.5938(2)	$\gamma = 90$
Volume [Å ³]	2566.21	
<i>Z</i>	4	
Crystal size [mm]	0.25 × 0.25 × 0.15	
2 θ range [°]	6.108 to 50.698	
Reflections collected/unique	23480 / 4677	
<i>R</i> _{int}	0.0399	
Data/restraints/parameters	4677 / 1 / 274	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0458 <i>wR</i> ₂ = 0.1203	
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.0497 <i>wR</i> ₂ = 0.1251	
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$ [e Å ⁻³]	0.47 / -0.44	



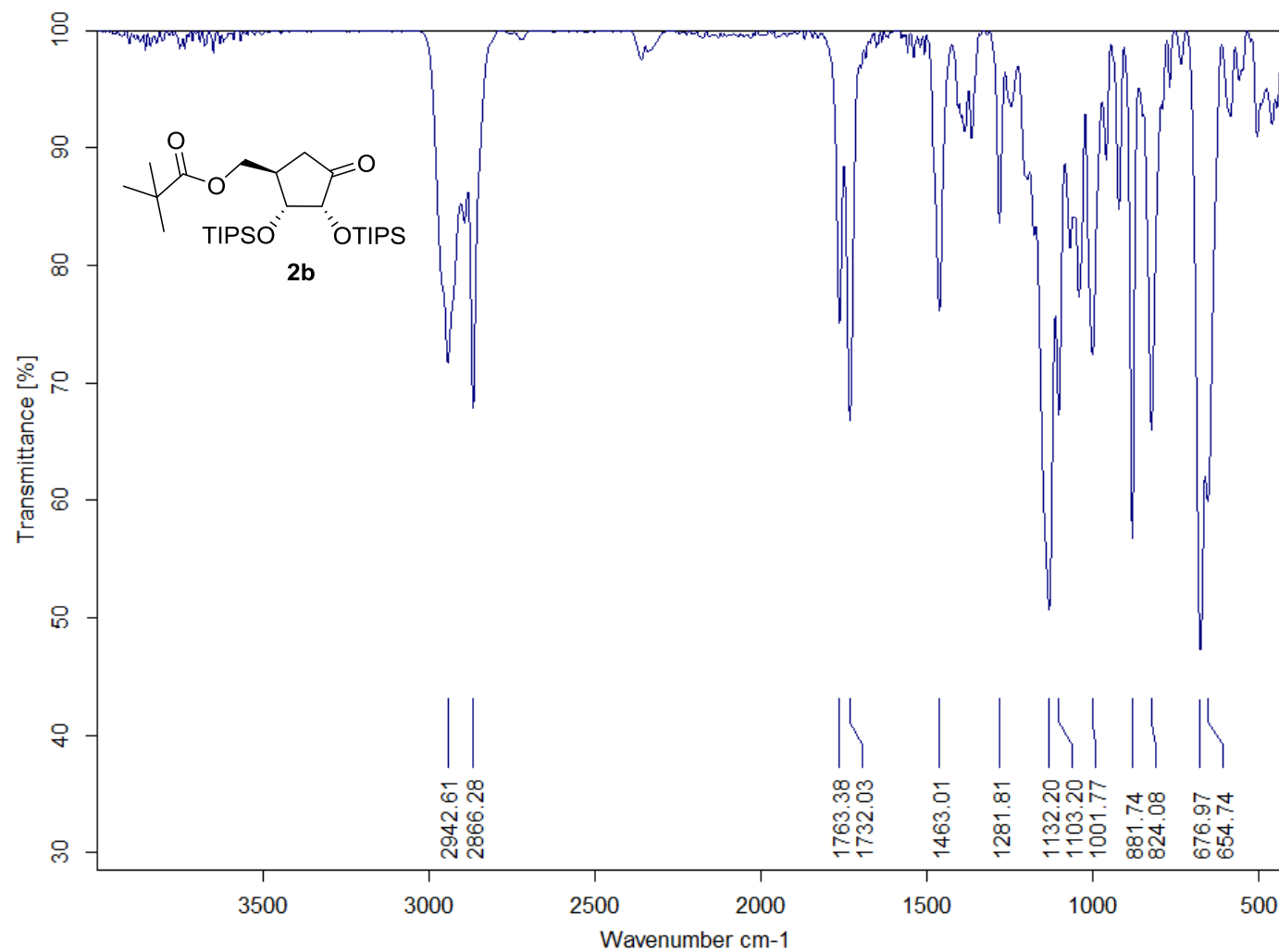
ORTEP Figure of **32**. The ellipsoid contour probability level is 50%.

Table S6. Sample and crystal data for compound (-)**37a**.

CCDC NO.	1452234	
Empirical formula	C ₃₅ H ₆₆ O ₇ Si ₂	
Formula weight	655.06	
Crystal system	Orthorhombic	
Space group	<i>P</i> 2 ₁ 2 ₁ 2	
<i>a</i> [Å]	11.0527(3)	$\alpha = 90$
<i>b</i> [Å]	44.5049(19)	$\beta = 90$
<i>c</i> [Å]	7.8273(3)	$\gamma = 90$
Volume [Å ³]	3850.24	
<i>Z</i>	4	
Crystal size [mm]	0.22 × 0.22 × 0.08	
2 θ range [°]	3.66 to 51.362	
Reflections collected/unique	41693 / 7346	
<i>R</i> _{int}	0.0449	
Data/restraints/parameters	7346 / 110 / 433	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0755 <i>wR</i> ₂ = 0.1566	
Final <i>R</i> indices [all data]	<i>R</i> ₁ = 0.0756 <i>wR</i> ₂ = 0.1566	
$\Delta\rho$ max / $\Delta\rho$ min [e Å ⁻³]	0.40 / -0.35	

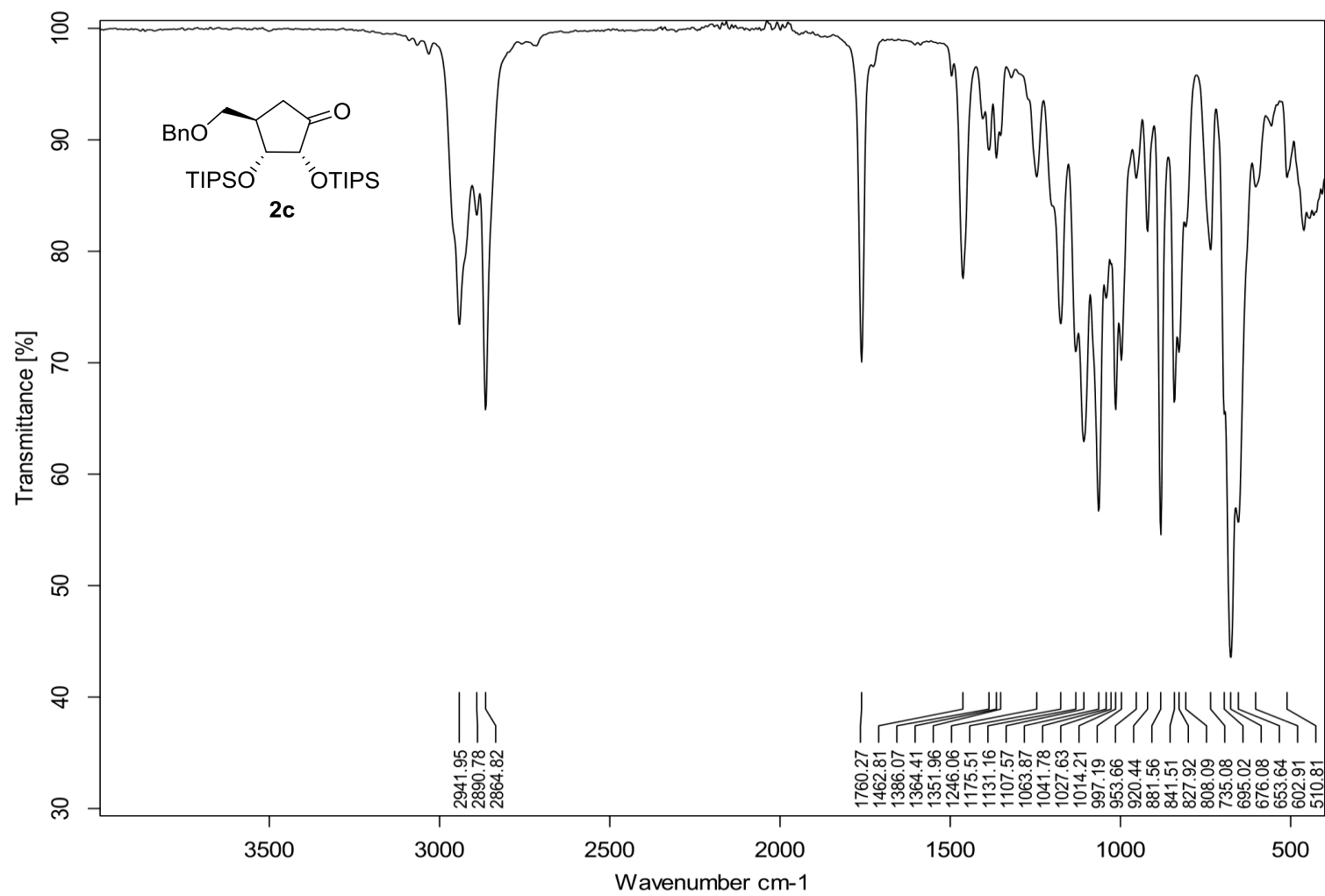


ORTEP Figure of (-)**37a**. The ellipsoid contour probability level is 50%.

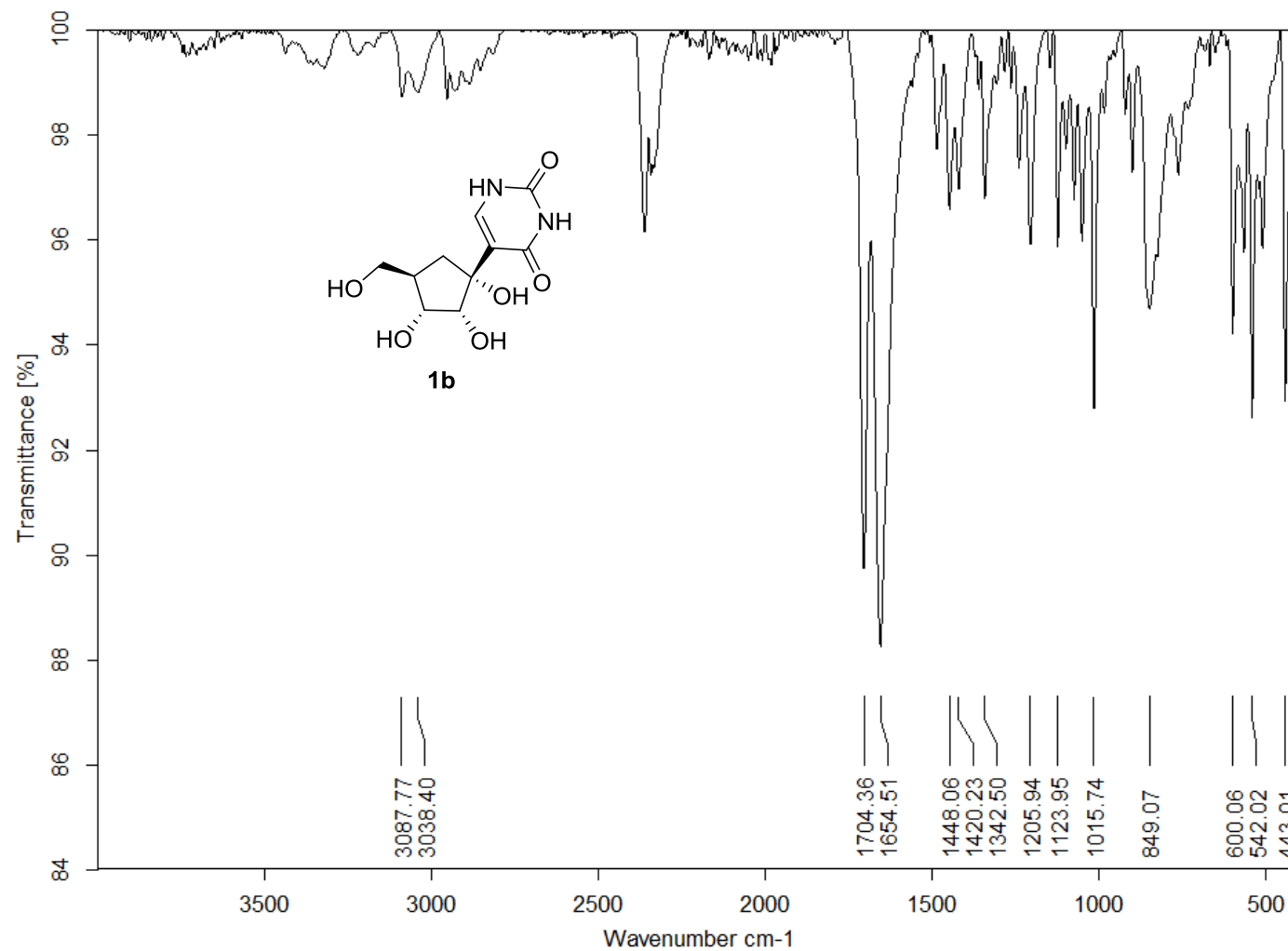


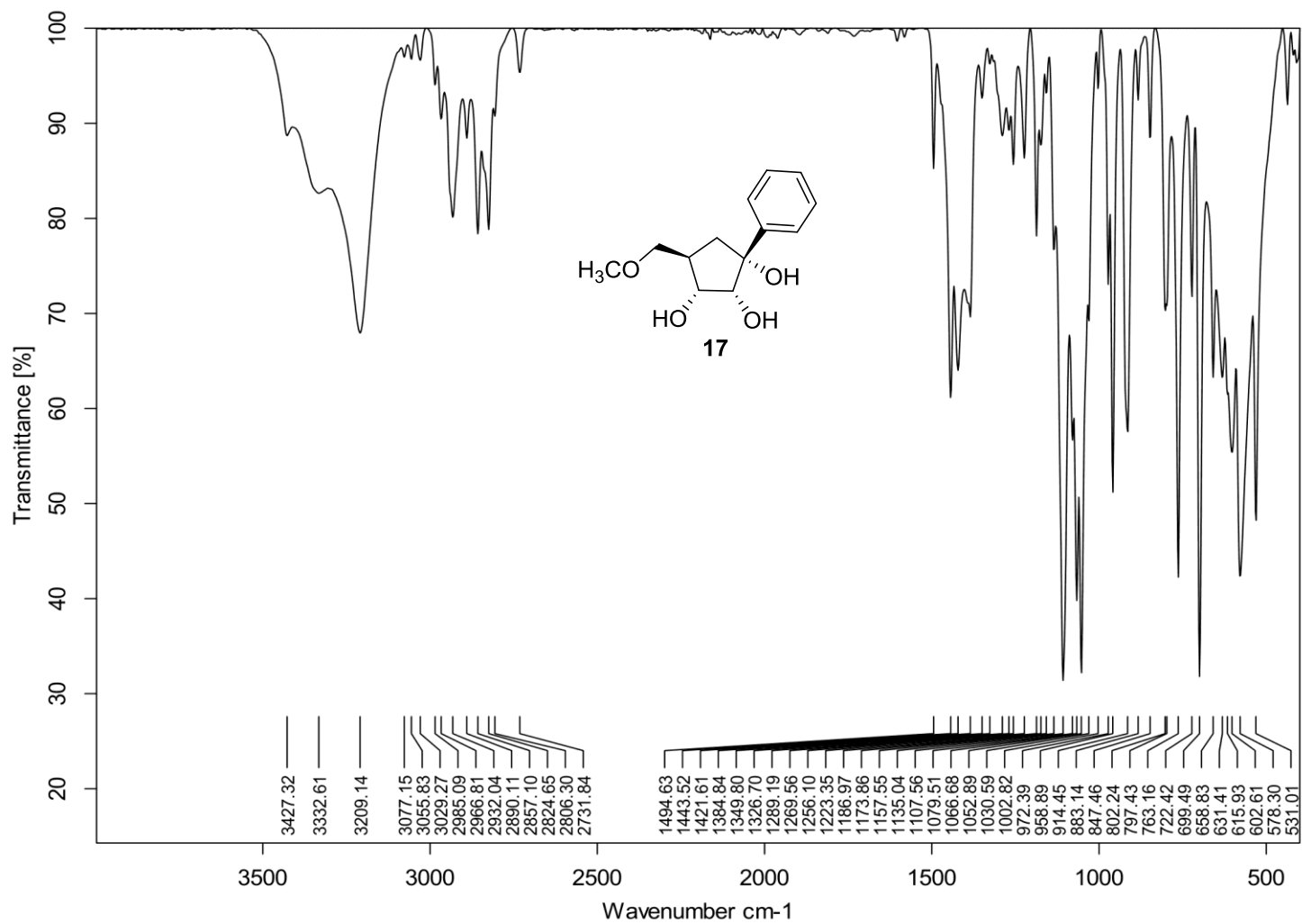
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IR spectrum (neat) of **2b**.

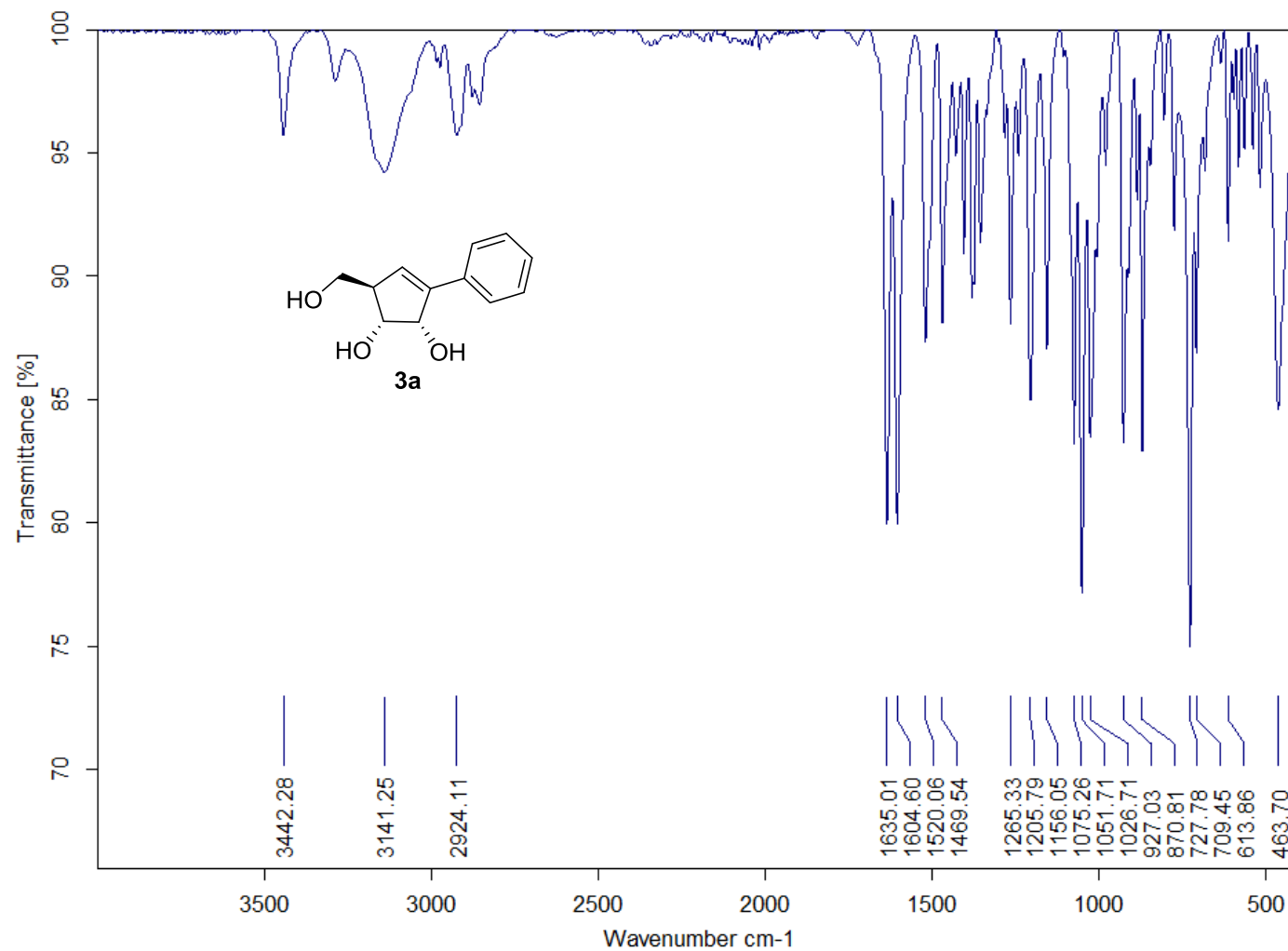


IR spectrum (neat) of **2c**.



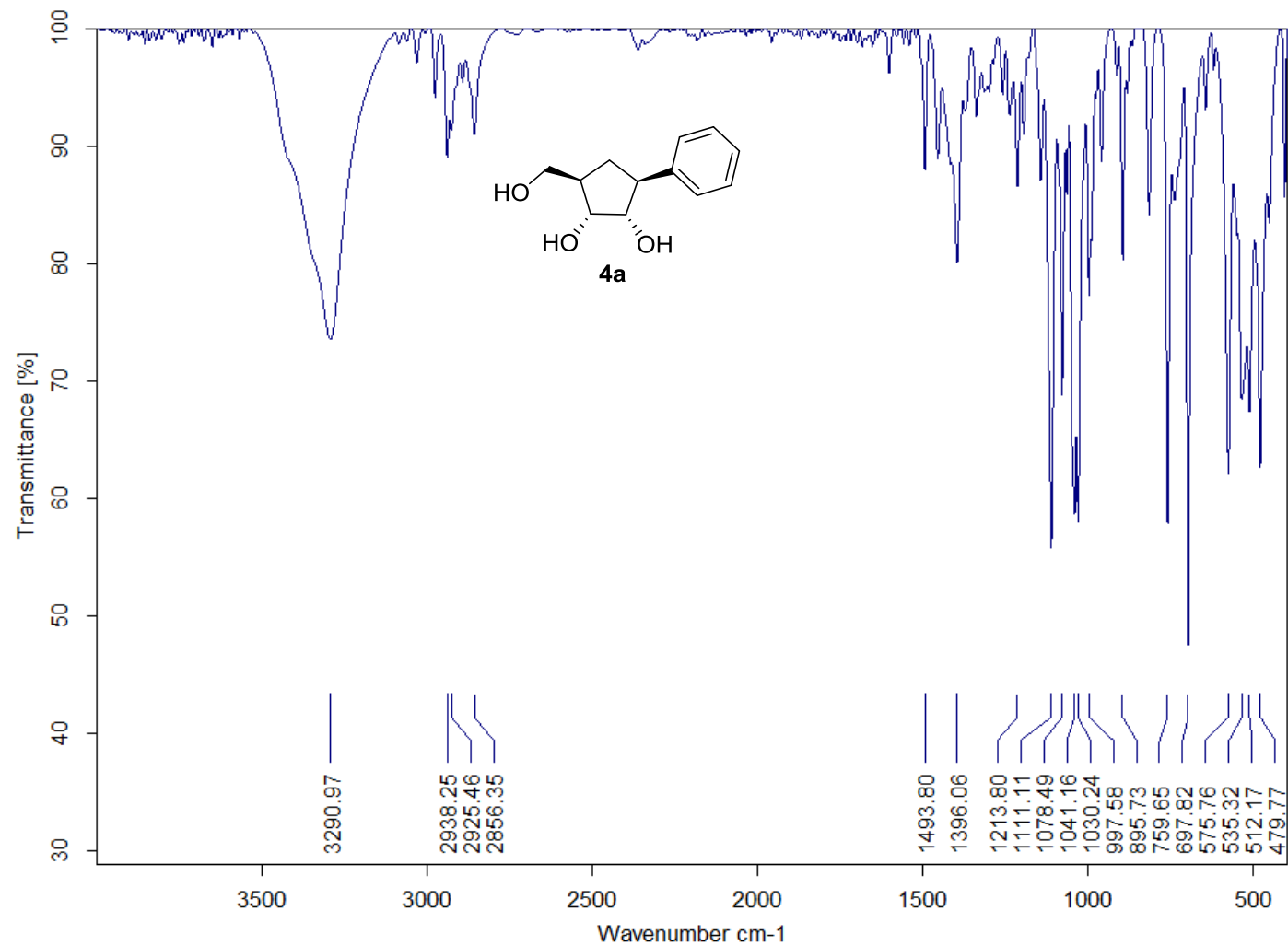


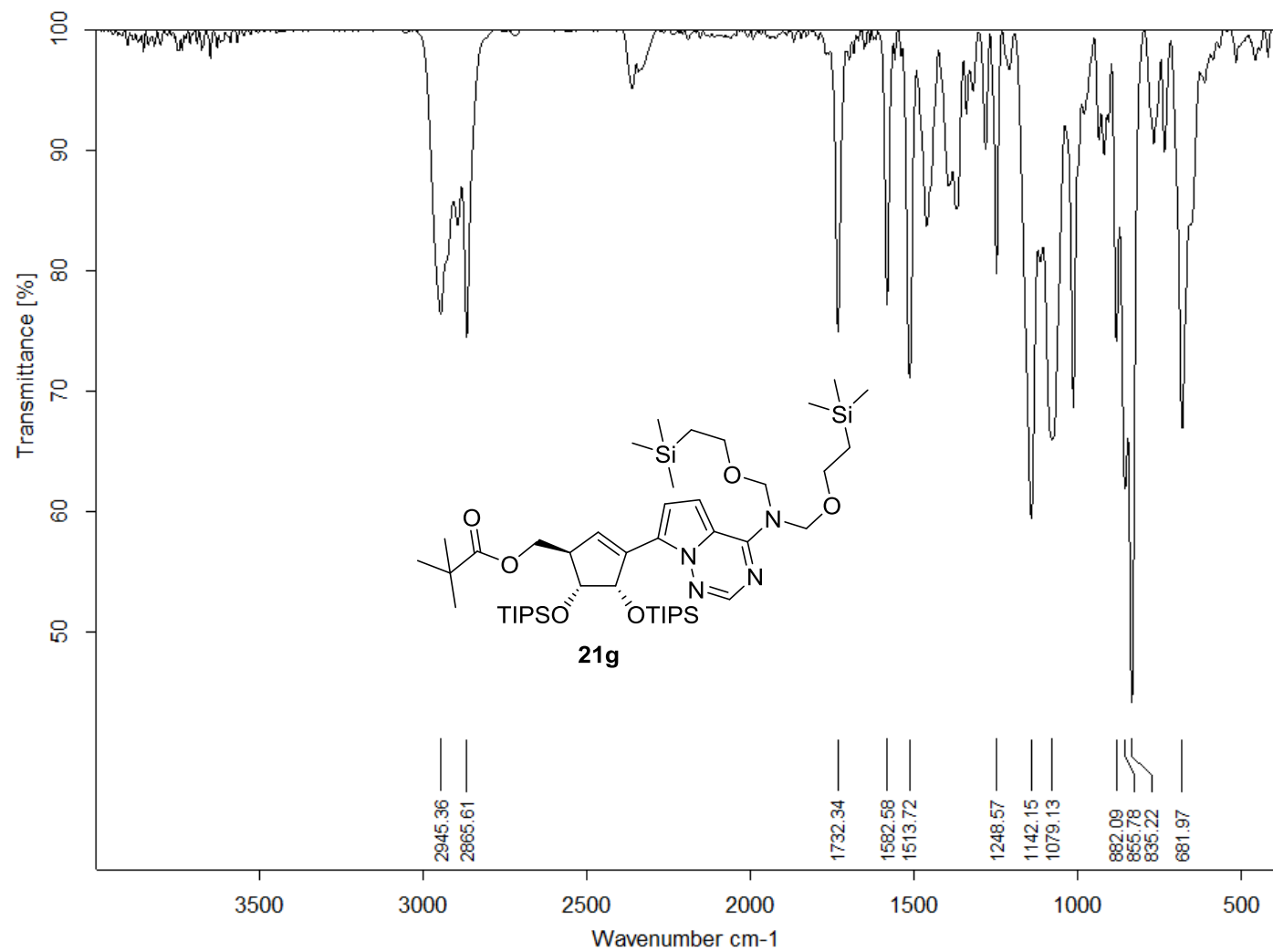
IR spectrum (neat) of 17.



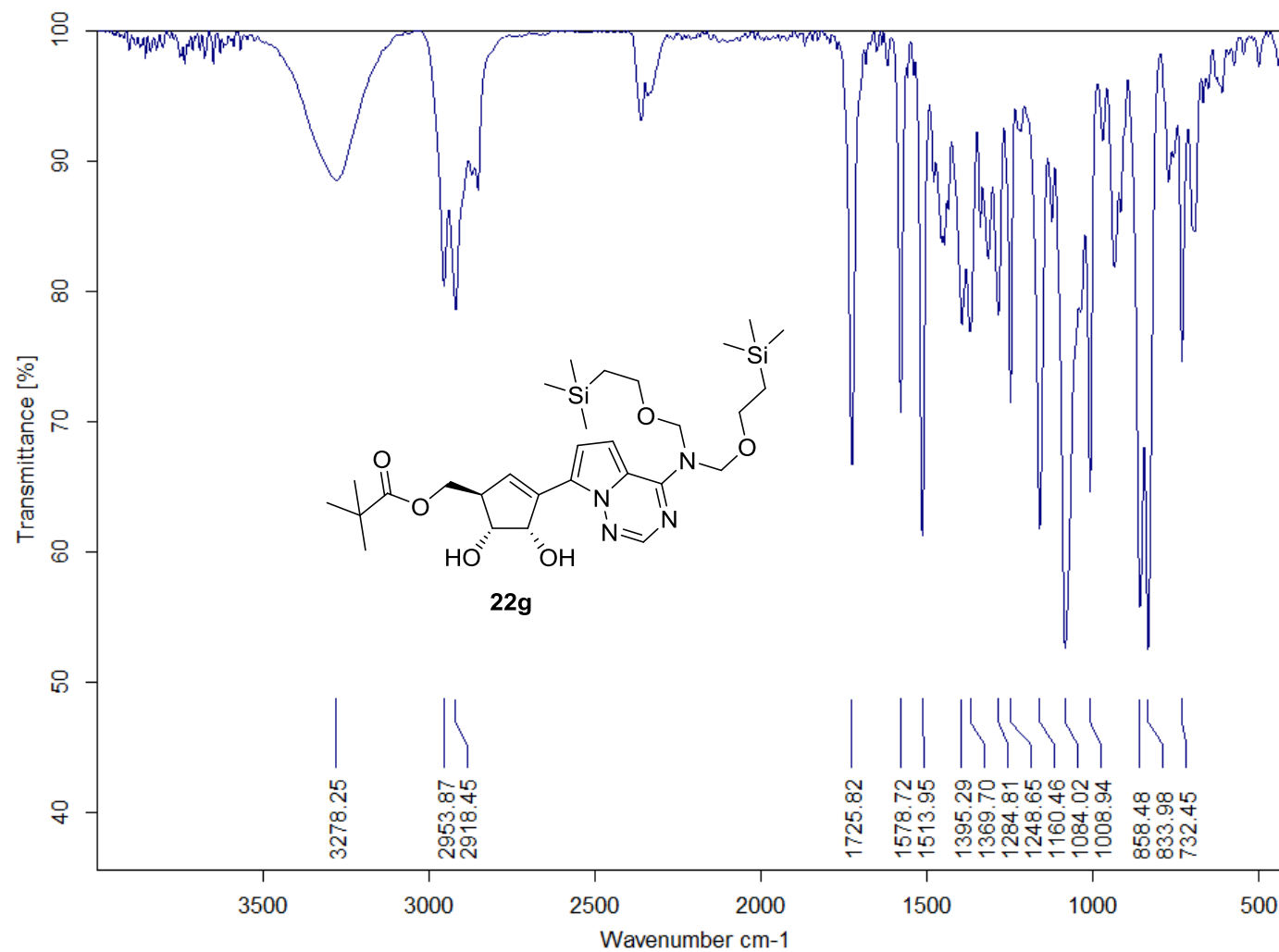
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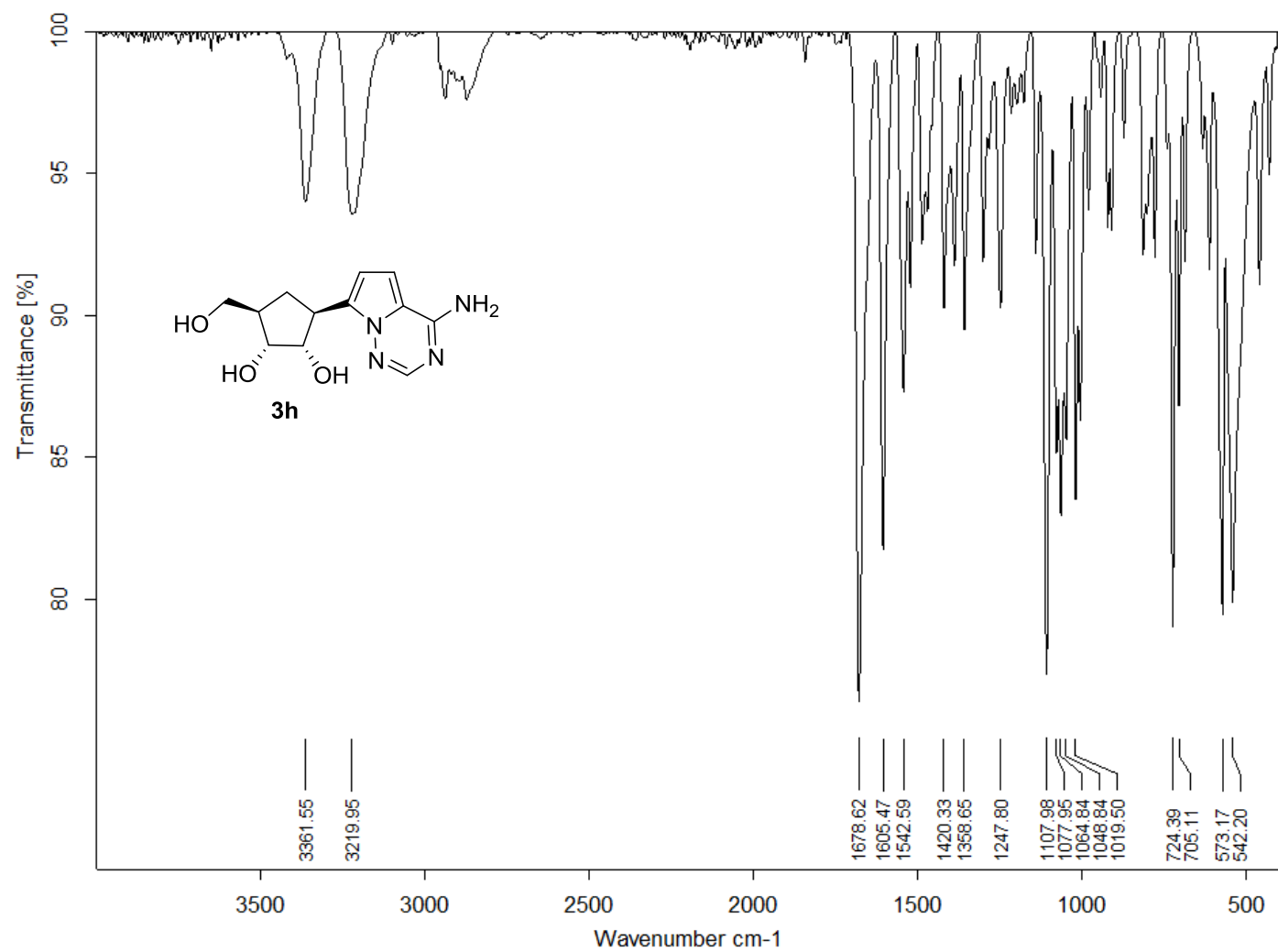
IR spectrum (neat) of **3a**.





IR spectrum (neat) of **21g**.

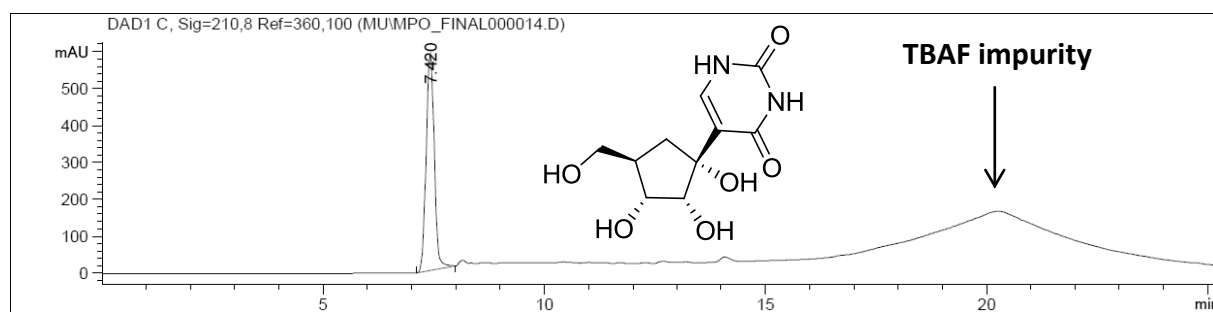




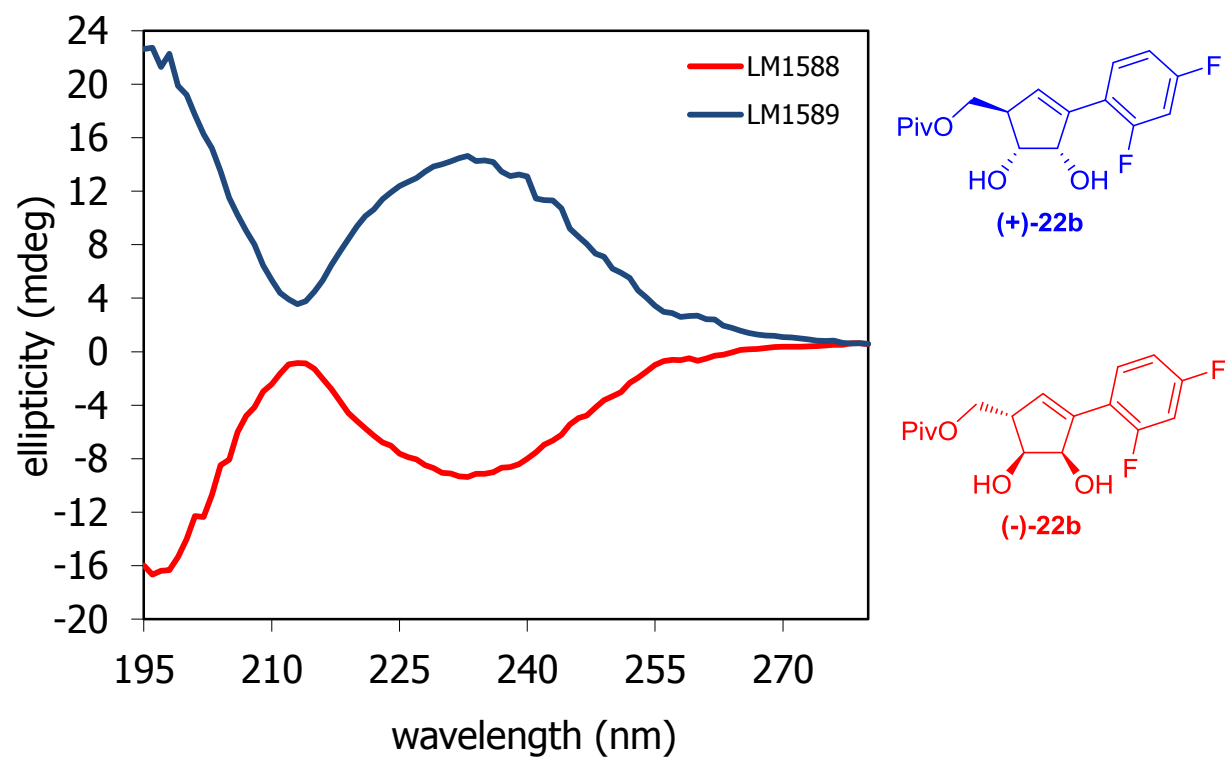
IR spectrum (neat) of **3h**.

Table S7. Gradient elution profile for RP-HPLC (Nucleodur[®] C18 HTec, 5µm, 250 mm × 50 mm) purification of **1b** and **1e** (solvent A – MeOH, solvent B – H₂O).

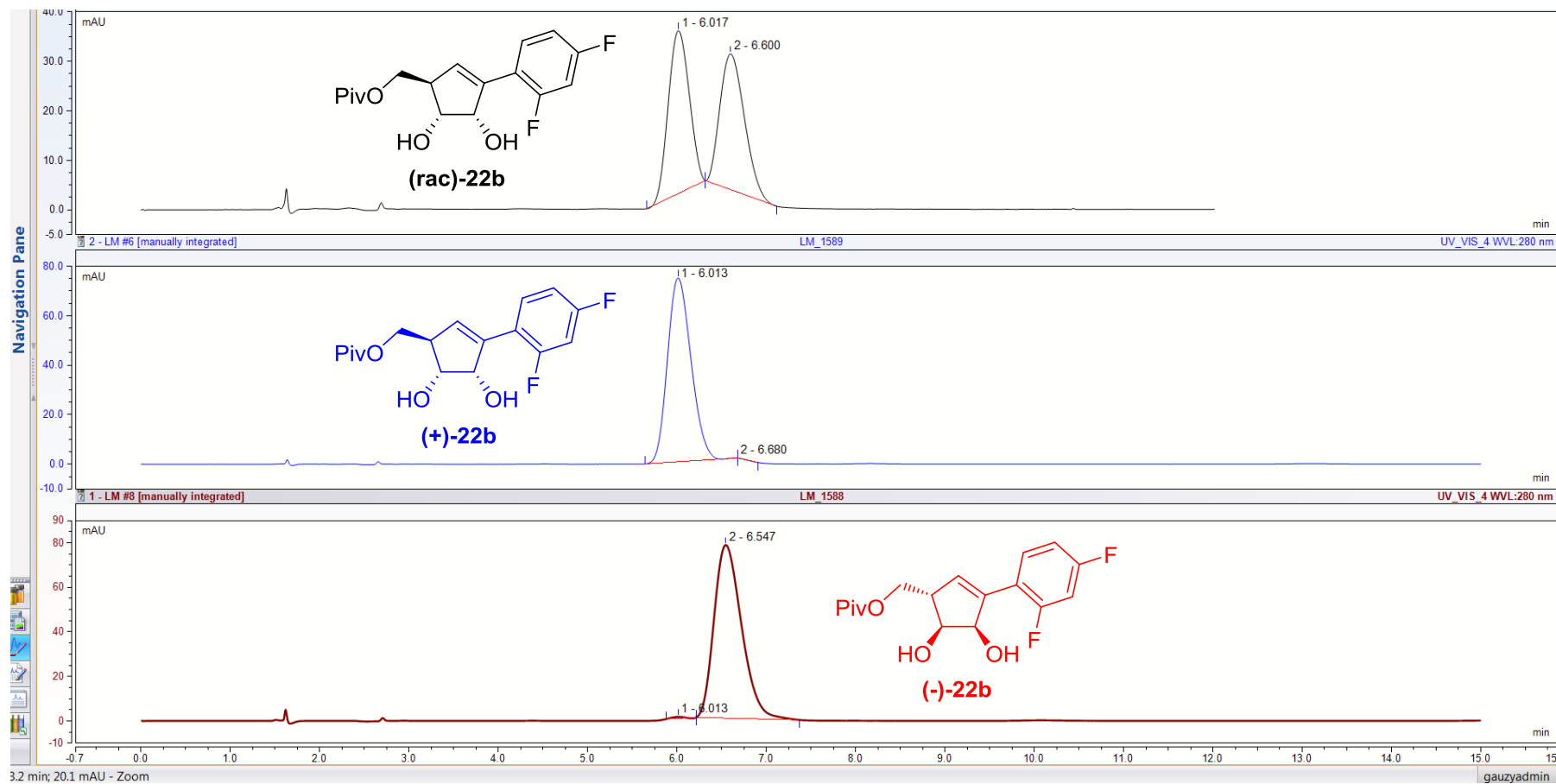
Time [min]	Solvent B [%]	Flow [ml/min]
0.00	90.0	10.00
2.00	60.0	10.00
4.00	55.0	10.00
6.00	50.0	10.00
8.00	45.0	10.00
10.00	40.0	10.00
12.00	30.0	10.00
14.00	15.0	10.00
25.00	90.0	10.00



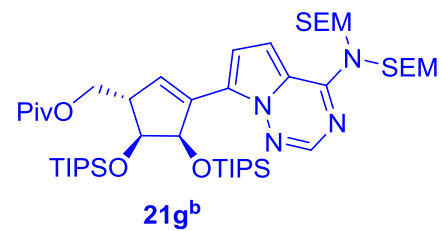
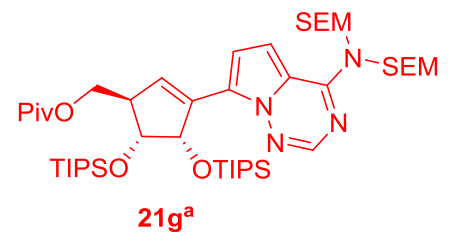
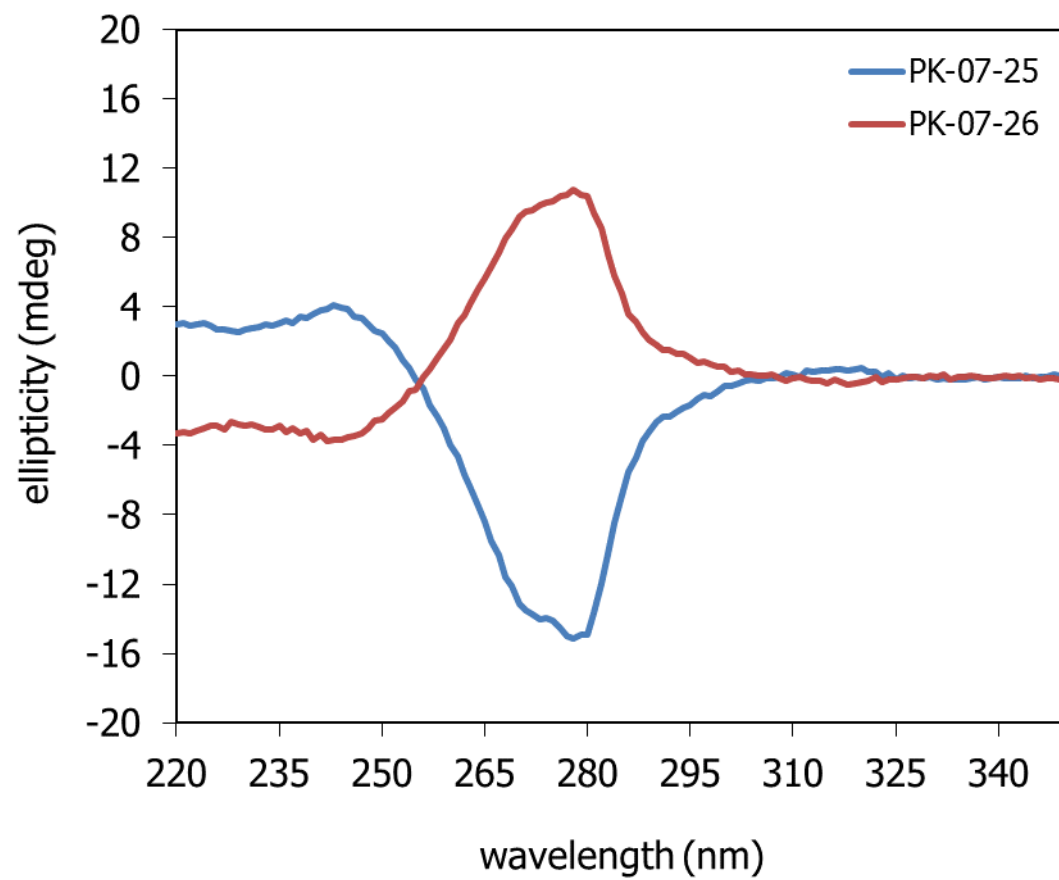
HPLC Chromatogram of compound **1b** (UV detection at 210 nm).



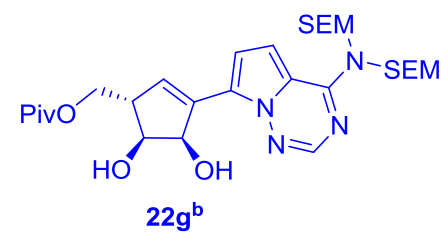
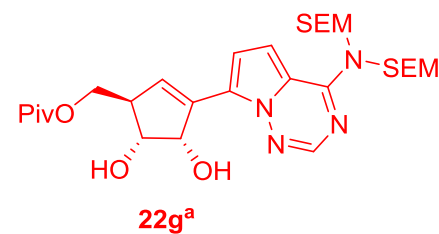
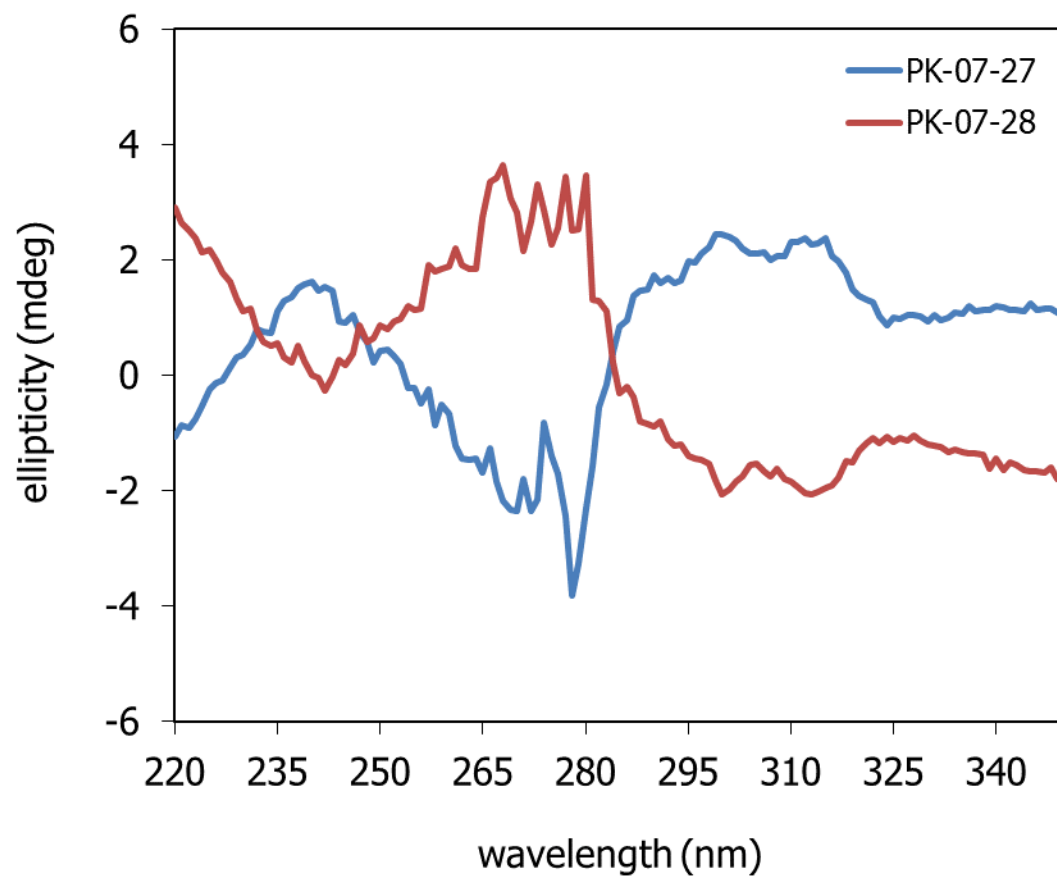
CD spectra of enantiomers of compound **22b** (EtOH, 10^{-3} M).



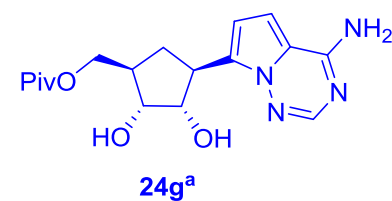
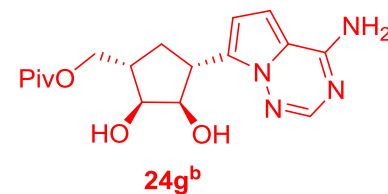
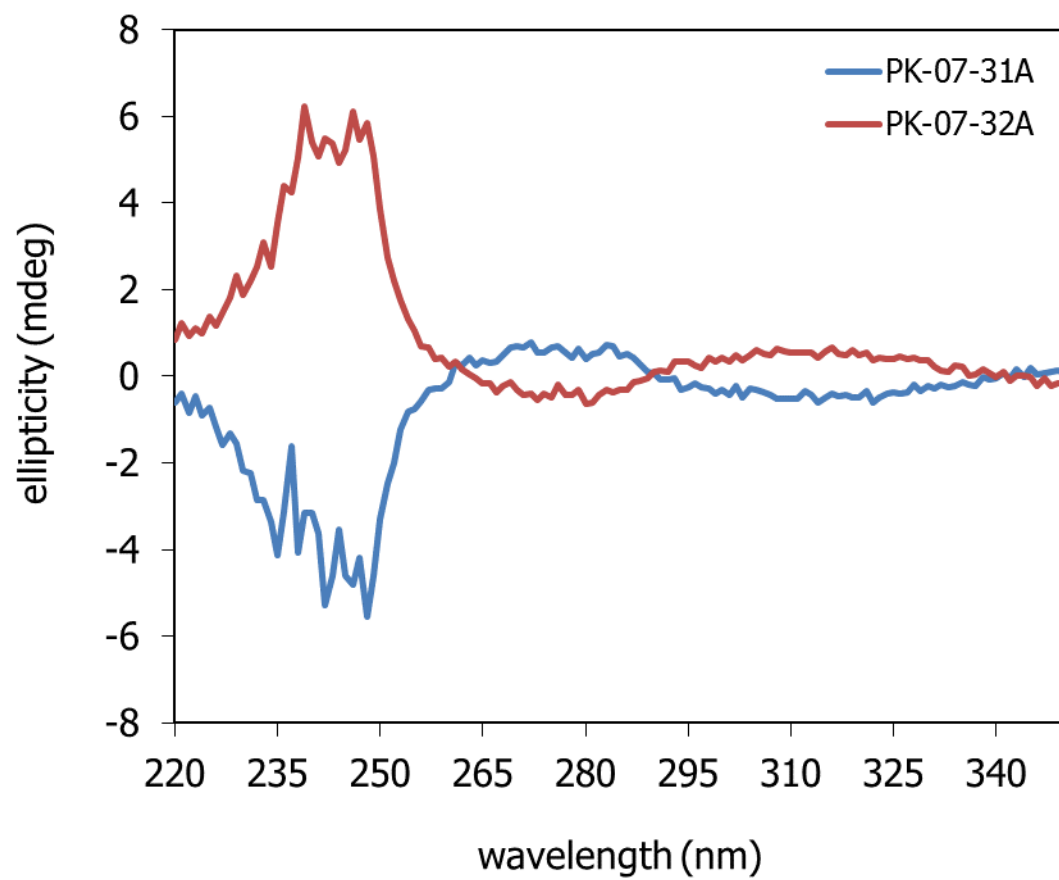
HPLC chromatogram of racemic compound **22b** and corresponding HPLC analysis of enantiomers (+)-**22b** and (-)-**22b**. (Daicel-CHIRALPAK AS 4.6 mm × 250 mm; hexane/EtOH = 96.5 / 3.5; 2 mL/min; rt; t_R = 6.02 min for (+)-**22b**, 6.60 min for (-)-**22b**).



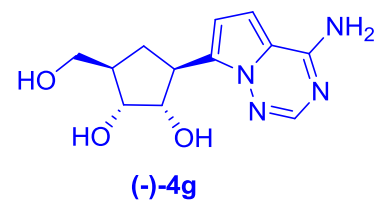
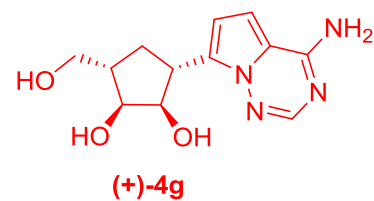
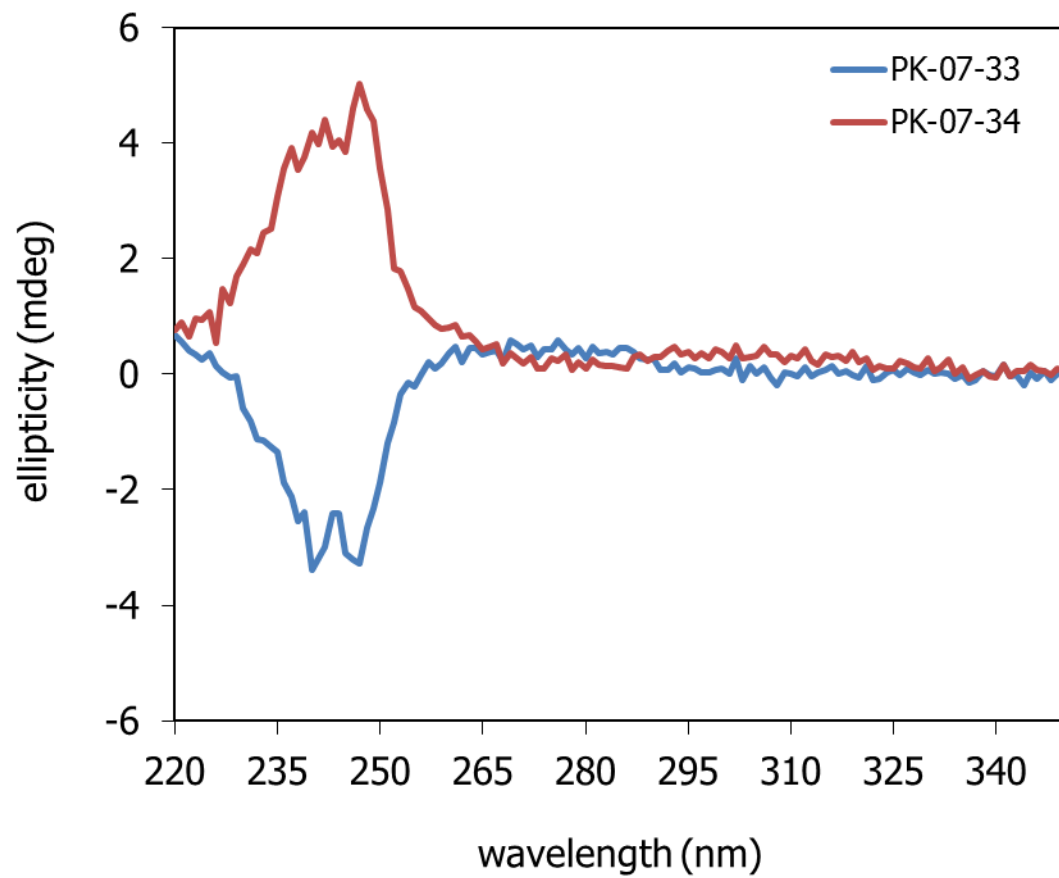
CD spectra of enantiomers of compound **21g** (CH_2Cl_2 , 10^{-3} M).



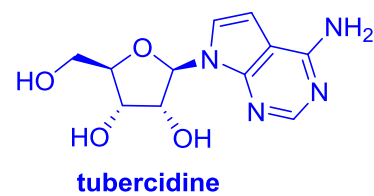
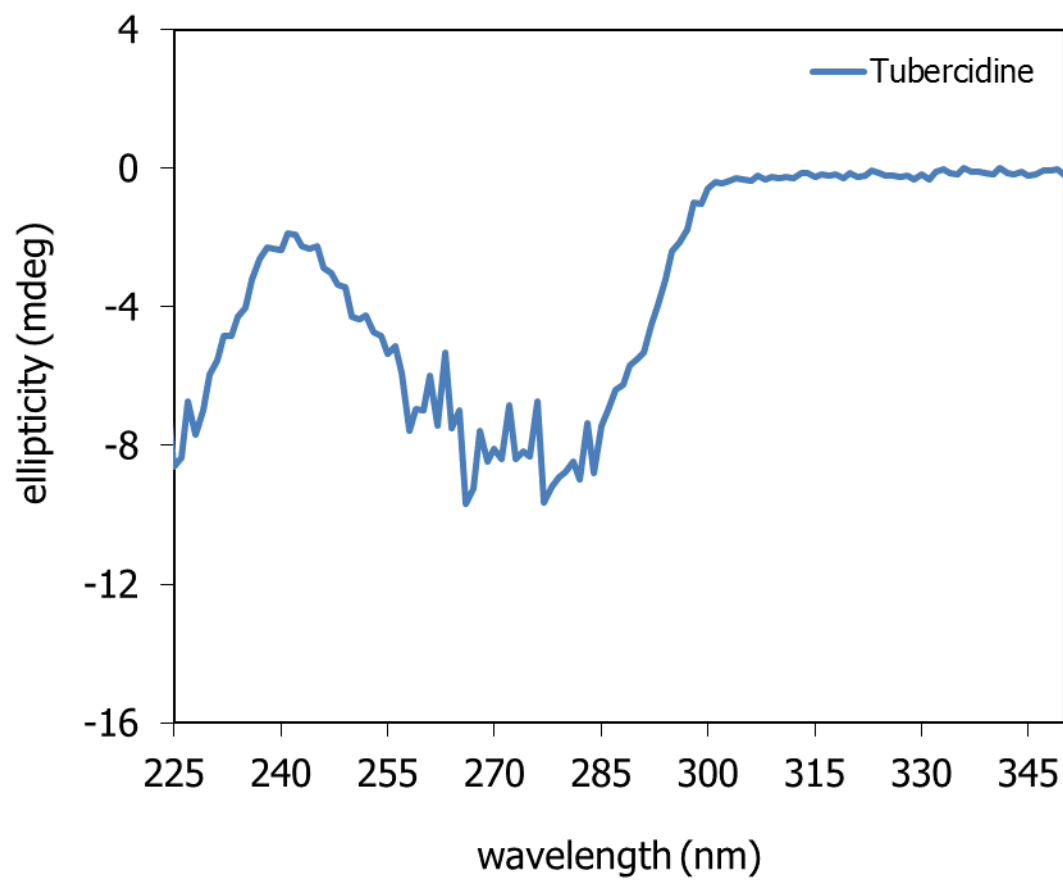
CD spectra of enantiomers of compound **22g** (CH_2Cl_2 , 10^{-3} M).



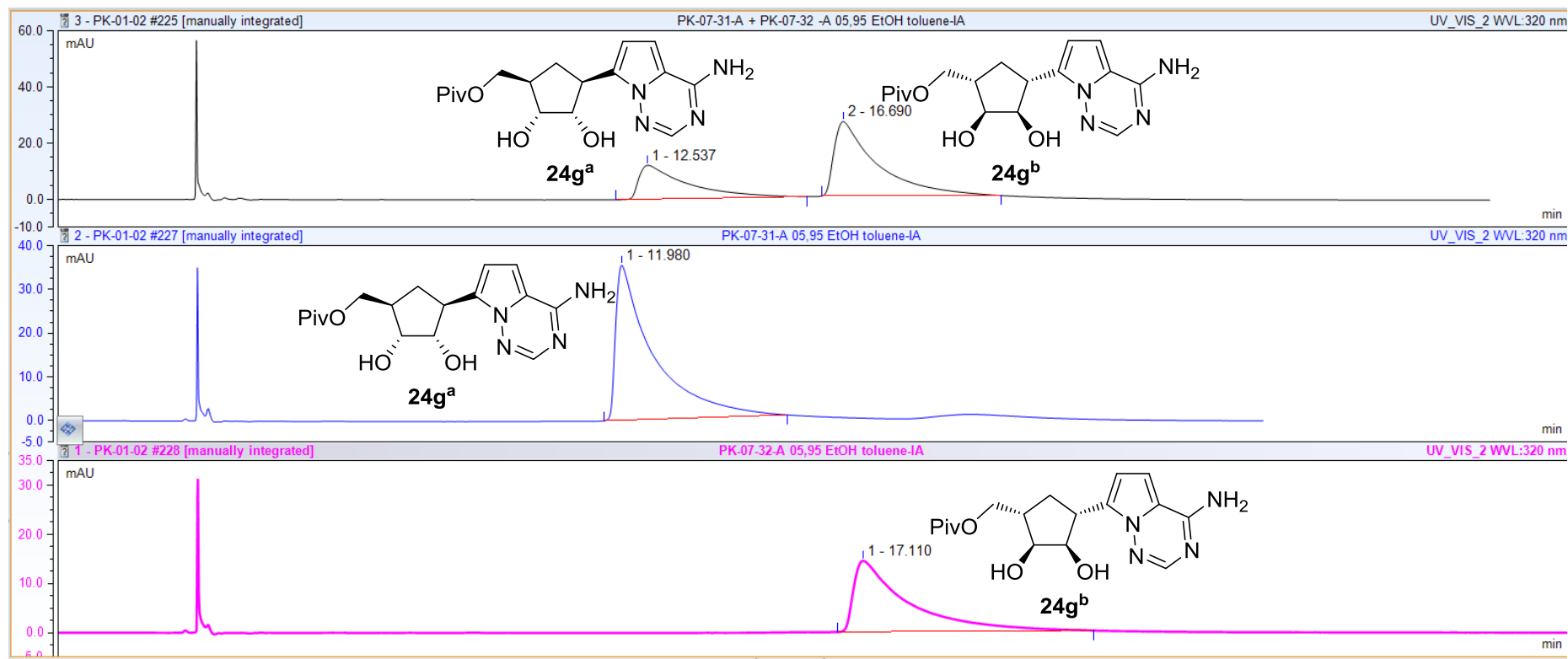
CD spectra of enantiomers of compound **24g** ($\text{CH}_2\text{Cl}_2\text{:CH}_3\text{OH}$ 1:1, 10^{-3} M).



CD spectra of enantiomers of compound **4g** ($\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ 1:1, 10^{-3} M).



CD spectra of natural tubercidine (CH₃OH, 10⁻³ M).



HPLC chromatogram of 2:1 mixture of individual enantiomers of compound **24g** and corresponding HPLC analysis of enantiomers **24g^a** and **24g^b** (Daicel-CHIRALPAK IA 4.6 mm × 250 mm; toluene/EtOH = 95 / 5; 1 mL/min).

Cell cultures

MCF7 breast cancer cells was cultivated in Minimum Essential Media (MEM) with L-Glutamine, Proline and Pyruvate (Gibco) supplemented with penicillin (100 U/mL), streptomycin (0.1 mg/mL) and 10% fetal bovine serum (Gibco).

Human foreskin fibroblasts HFF1 were maintained in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 15% fetal bovine serum (Gibco).

All cells were harvested after a brief incubation in 0.05% ethylenediaminetetraacetic acid (EDTA) in phosphate-buffered saline (PBS), followed by trypsinization (0.25% w/v trypsin/0.53 mM EDTA in PBS). They were then counted by using a CASY TT automatic cell counter (Roche Diagnostics, Prague, Czech Republic), diluted in the appropriate volume and seeded for experimental procedure.

MCF7 and HFF1 cell lines were obtained from American Type Culture Collection (LGC Standards, Warsaw, Poland).

Cell proliferation assays

For cytotoxicity screening the cells were seeded at the density of 20 000 cells/cm² on black Corning 96 well plates with clear flat bottom. After 24 hrs, cells were treated with tubercidine or compound **4g** (3 wells per concentration, range 0,0015 uM to 100 uM using 9 points). Vehicle (DMSO) was added at the same time as the control. The cells were grown during next 24 hrs. The medium was then gently removed, the cells were refurbished with fresh medium and allowed to proliferate for 48 hrs. Finally, the cells were harvested and analysed using the CyQuant assay. The CyQuant cell proliferation assay (Invitrogen) was performed according to the manufacturer's recommendations and the results were analysed using a Fluostar Galaxy reader (BMG Labtech, Ortenberg, Germany).

Data analysis

The data were evaluated as % of viable cell normalized to the control (DMSO). For calculation of IC₅₀ values, a four-parameter logistic dose-response model with a sigmoidal shape was used: $Y = \text{Bottom} + (\text{Top} - \text{Bottom}) / (1 + (x / \text{IC}_{50})^{\text{HillSlope}})$ where IC₅₀ denoted the concentration of the inhibitor that gave a response that was halfway between Bottom and Top. HillSlope described the steepness of the curve, and the Top and Bottom denoted plateaus in the units of the Y-axis. Lower and upper bound of a 95% confidence interval for IC₅₀ was calculated.