

Supplementary Information

Addition of benzyl ethers to alkynes: a metal-free synthesis of 1*H*- isochromenes.

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Jhong-li, Taoyuan, Taiwan, 32001.

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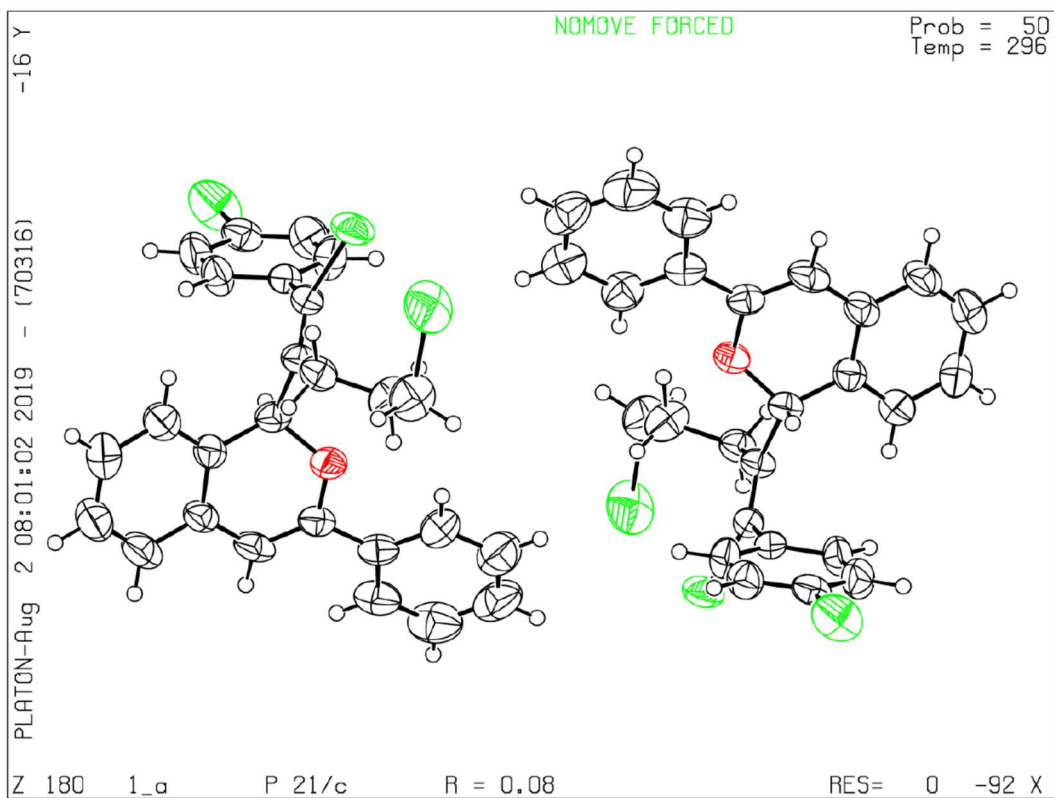
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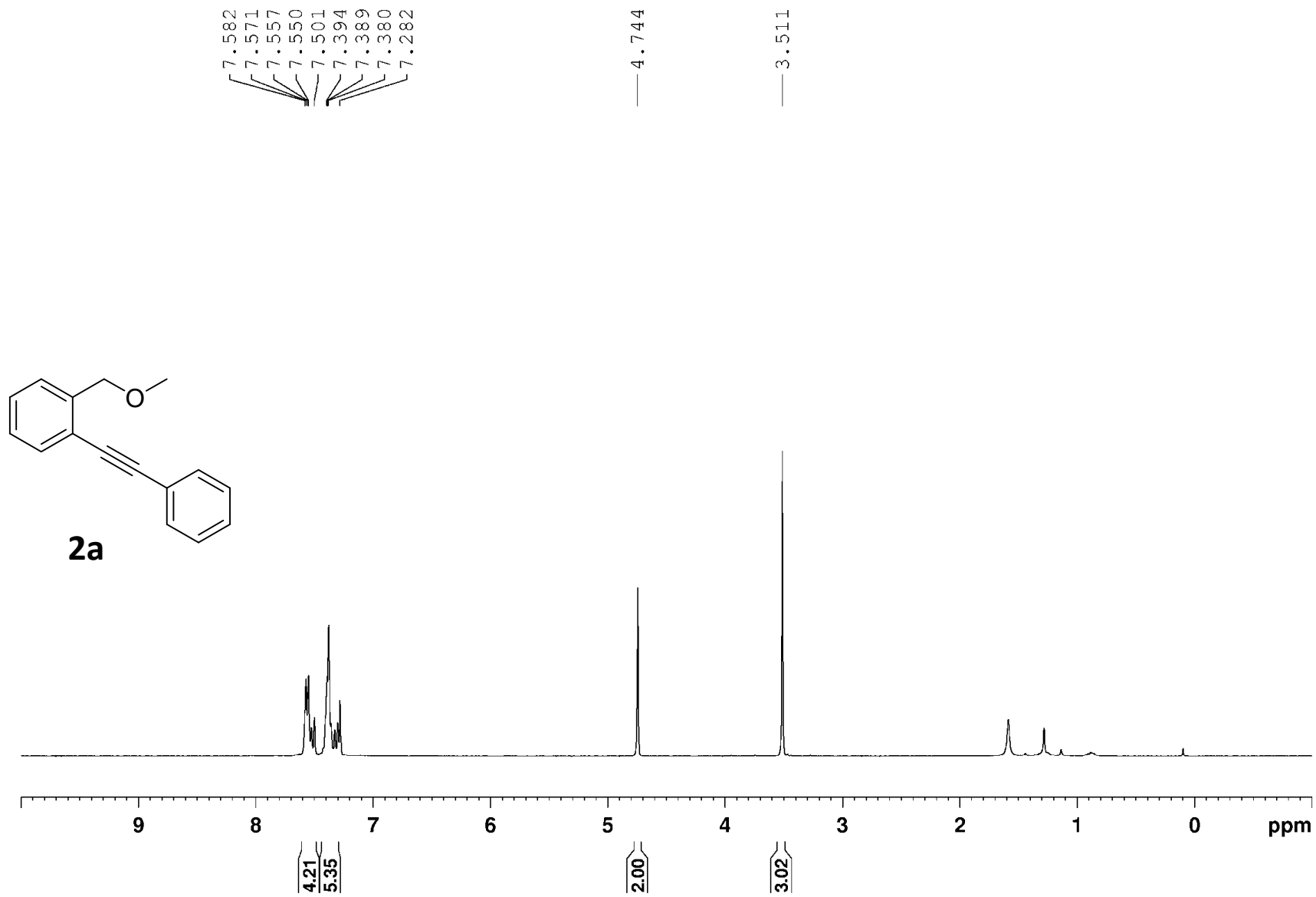
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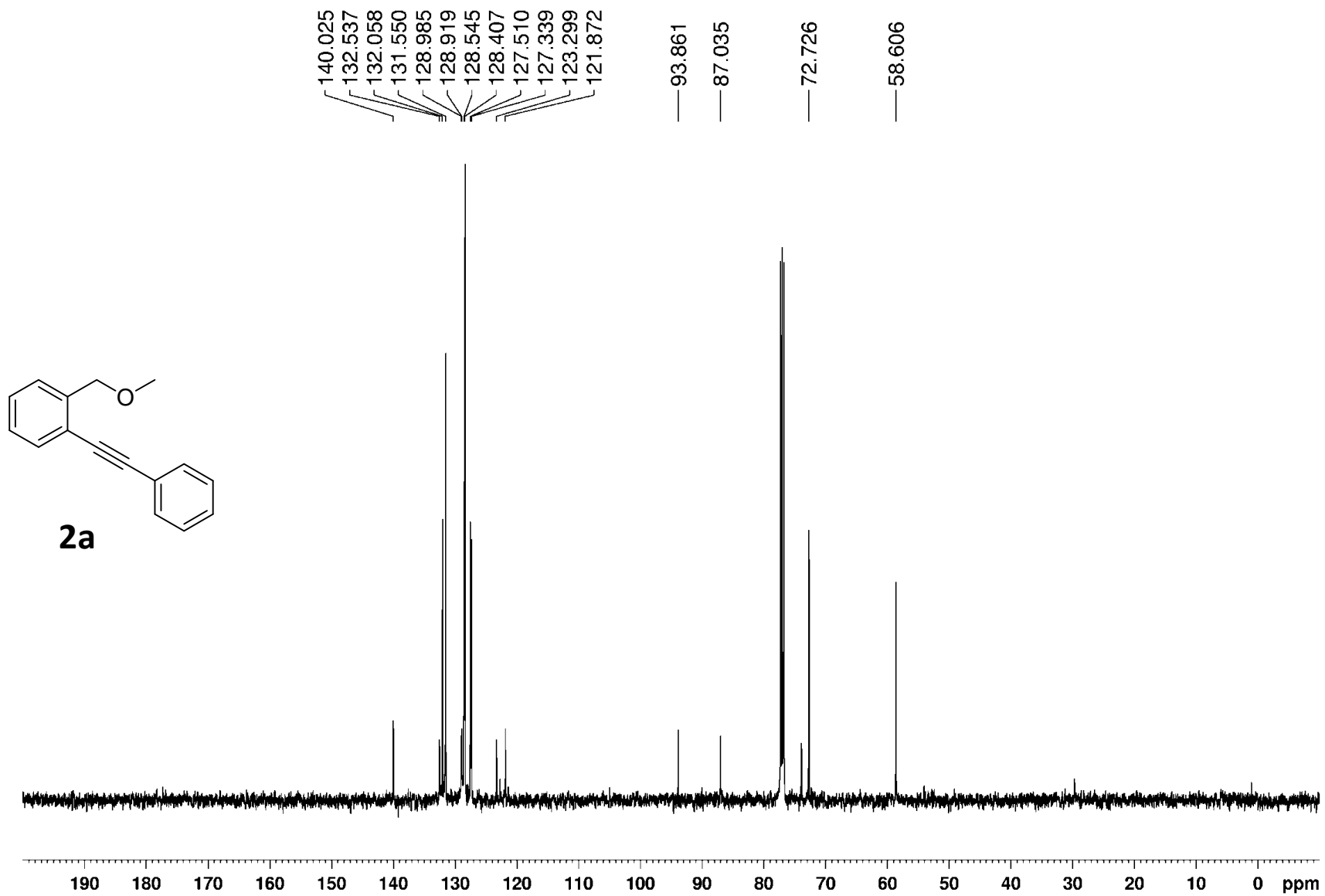
Table S1. Crystal data and structure refinement for **6ad (CCDC2068139)**.

Identification code	1_a	
Empirical formula	C ₂₆ H ₂₁ Br ₂ Cl O	
Formula weight	544.70	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 18.6040(8) Å	α = 90°.
	b = 12.3733(4) Å	β = 97.6430(10)°.
	c = 20.0612(8) Å	γ = 90°.
Volume	4576.9(3) Å ³	
Z	8	
Density (calculated)	1.581 Mg/m ³	
Absorption coefficient	3.675 mm ⁻¹	
F(000)	2176	
Crystal size	0.443 x 0.050 x 0.025 mm ³	
Theta range for data collection	2.194 to 28.309°.	
Index ranges	-24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26	
Reflections collected	202295	
Independent reflections	11380 [R(int) = 0.1153]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Numerical Mu Calculated	
Max. and min. transmission	0.7457 and 0.6638	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11380 / 0 / 541	
Goodness-of-fit on F ²	1.021	
Final R indices [I > 2σ(I)]	R1 = 0.0827, wR2 = 0.2047	
R indices (all data)	R1 = 0.1548, wR2 = 0.2544	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.722 and -1.165 e.Å ⁻³	

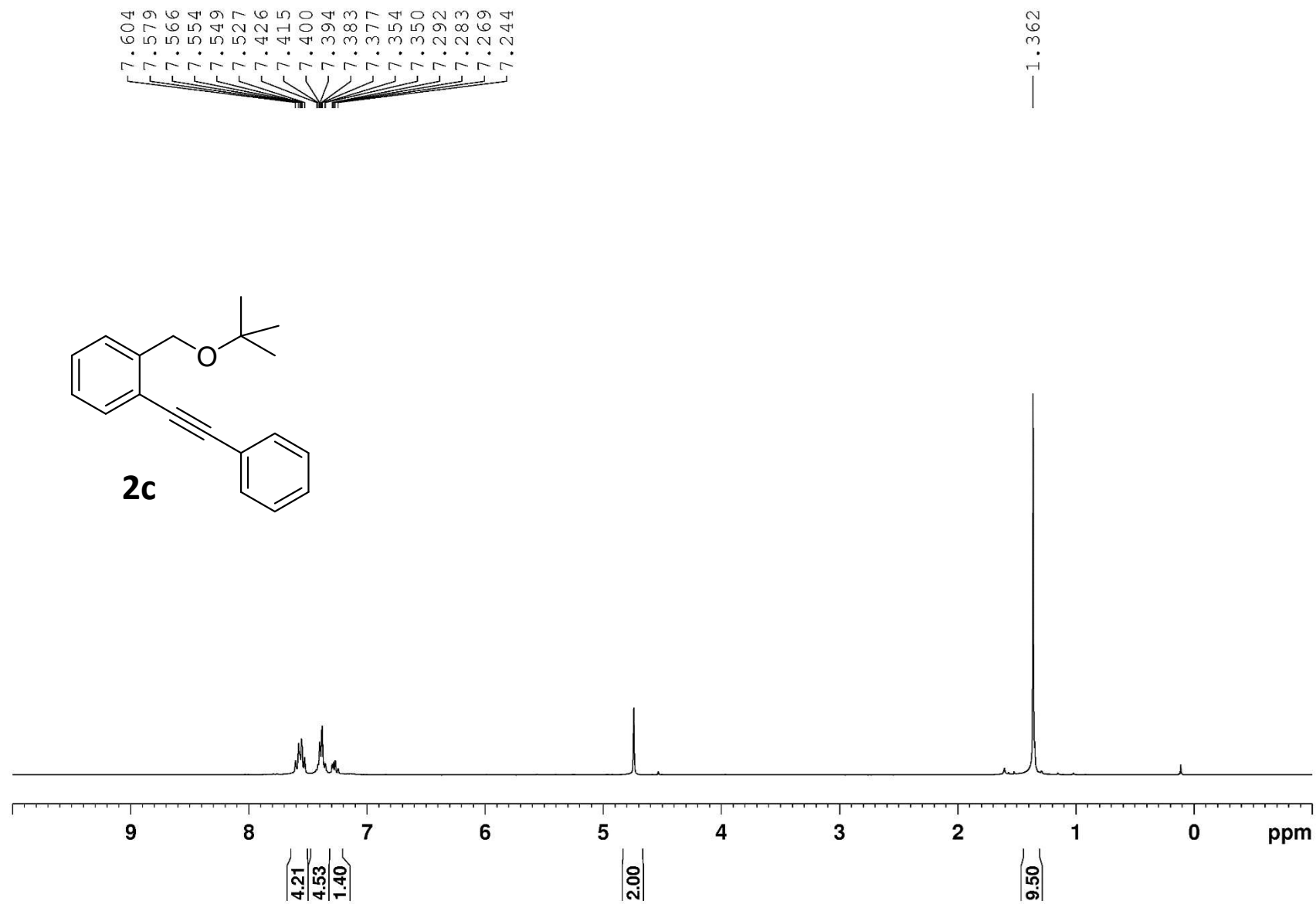




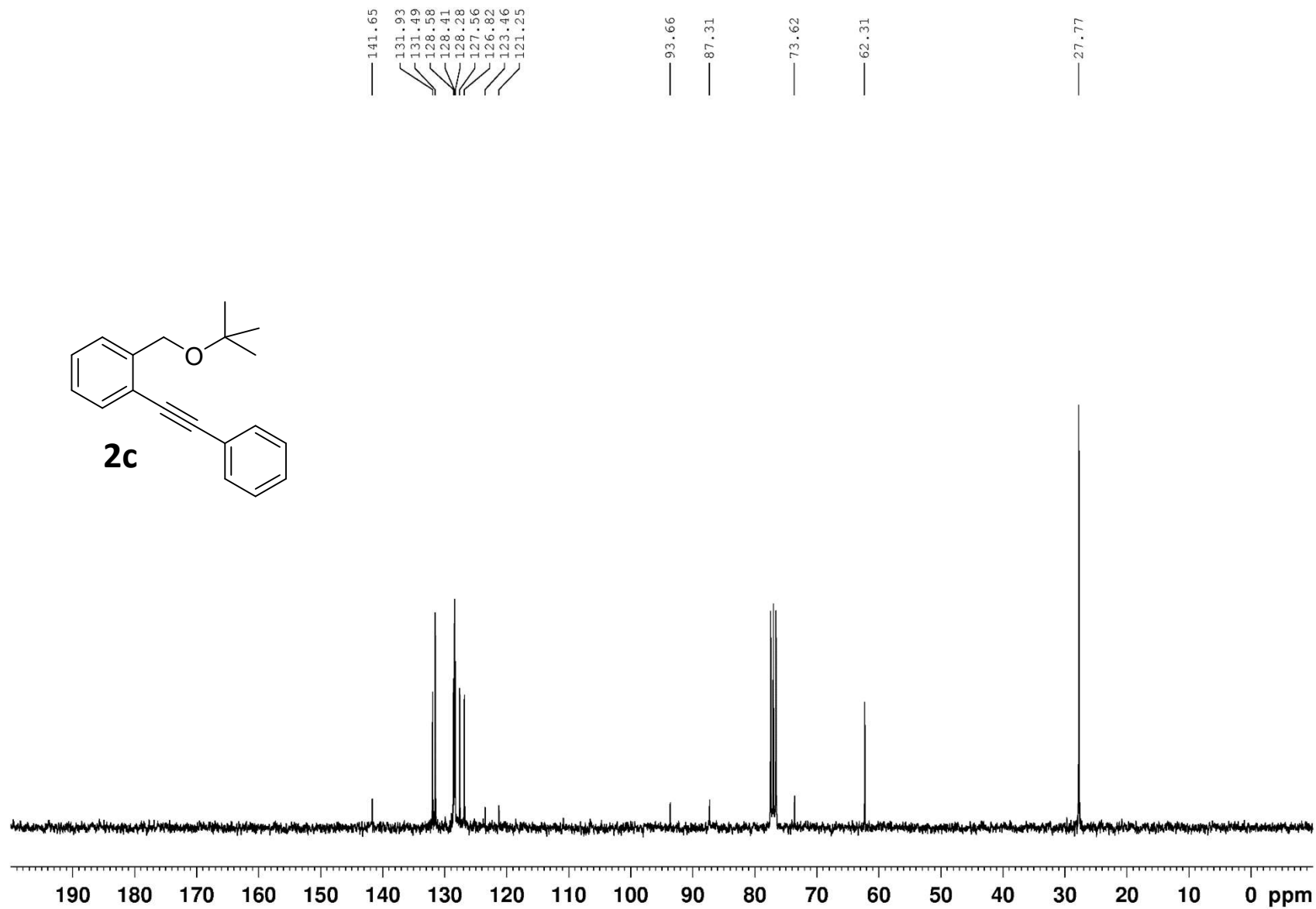
¹H NMR of compound **2a** (300 MHz, CDCl₃)



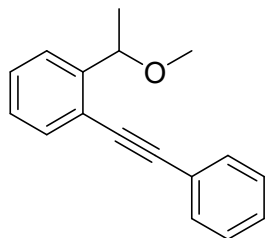
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2a** (75 MHz, CDCl_3)



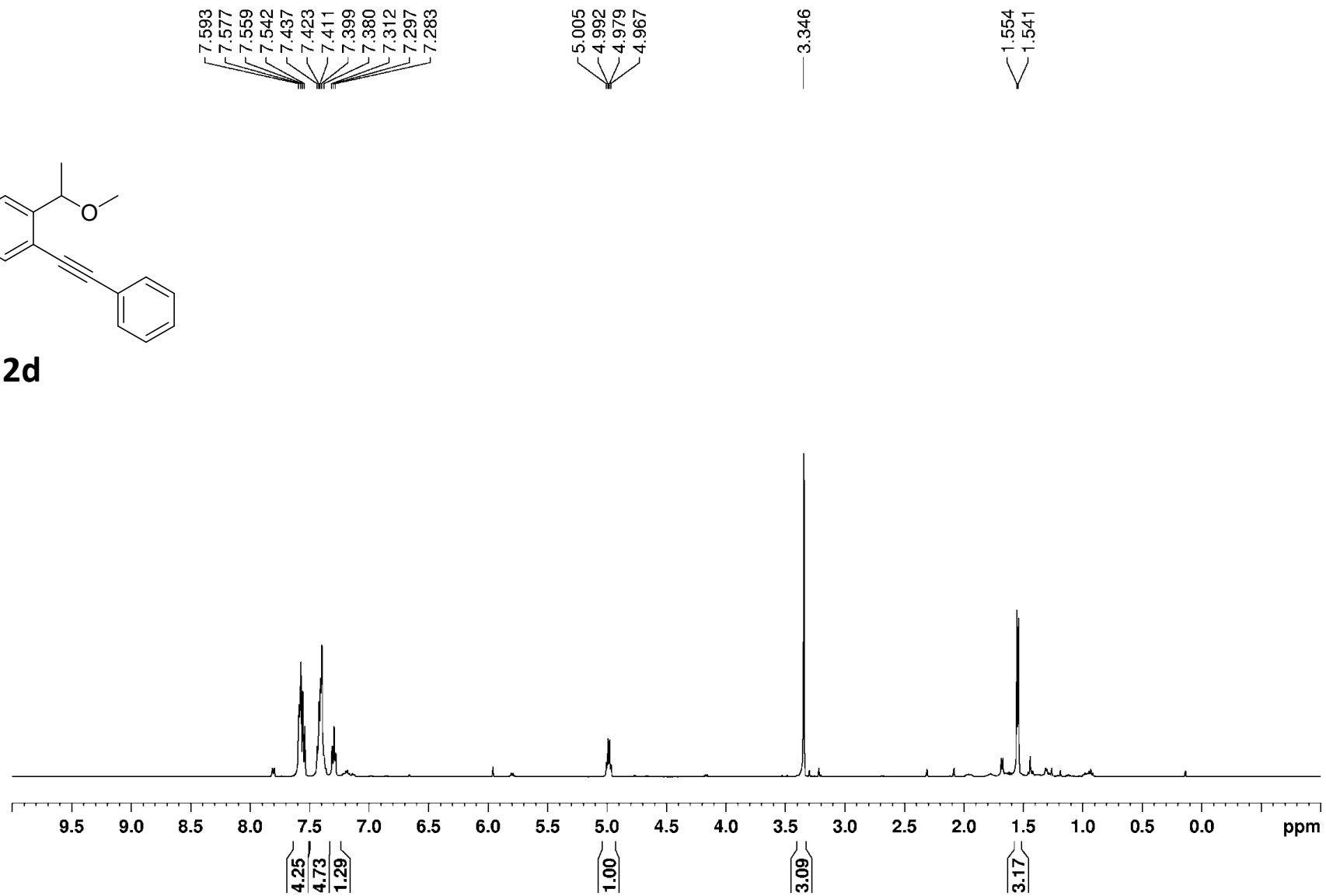
^1H NMR of compound **2c** (300 MHz, CDCl_3)



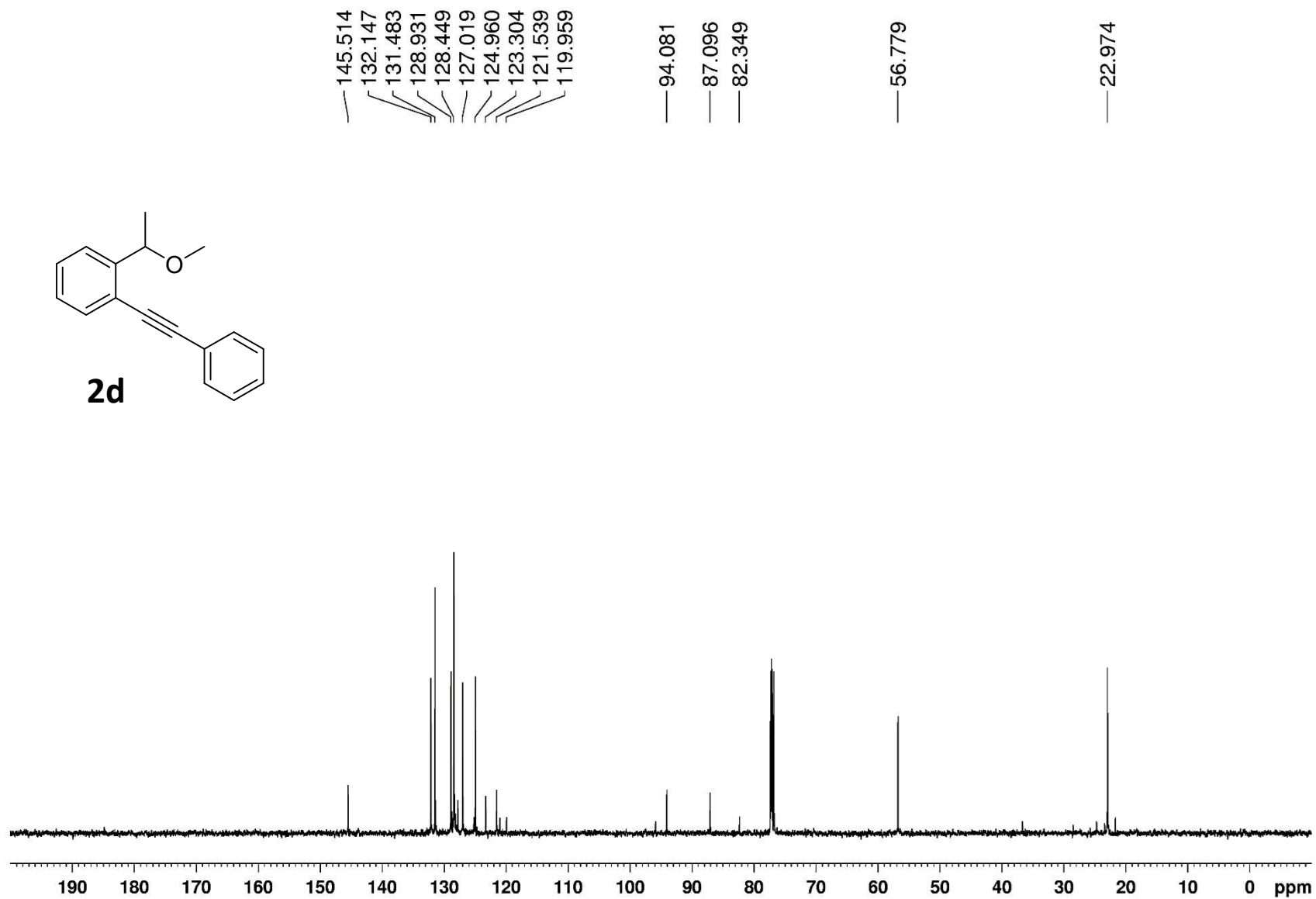
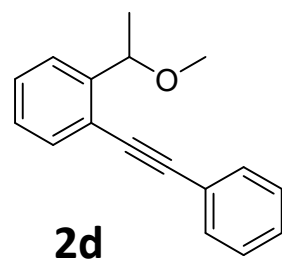
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2c** (75 MHz, CDCl_3)



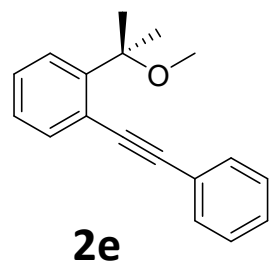
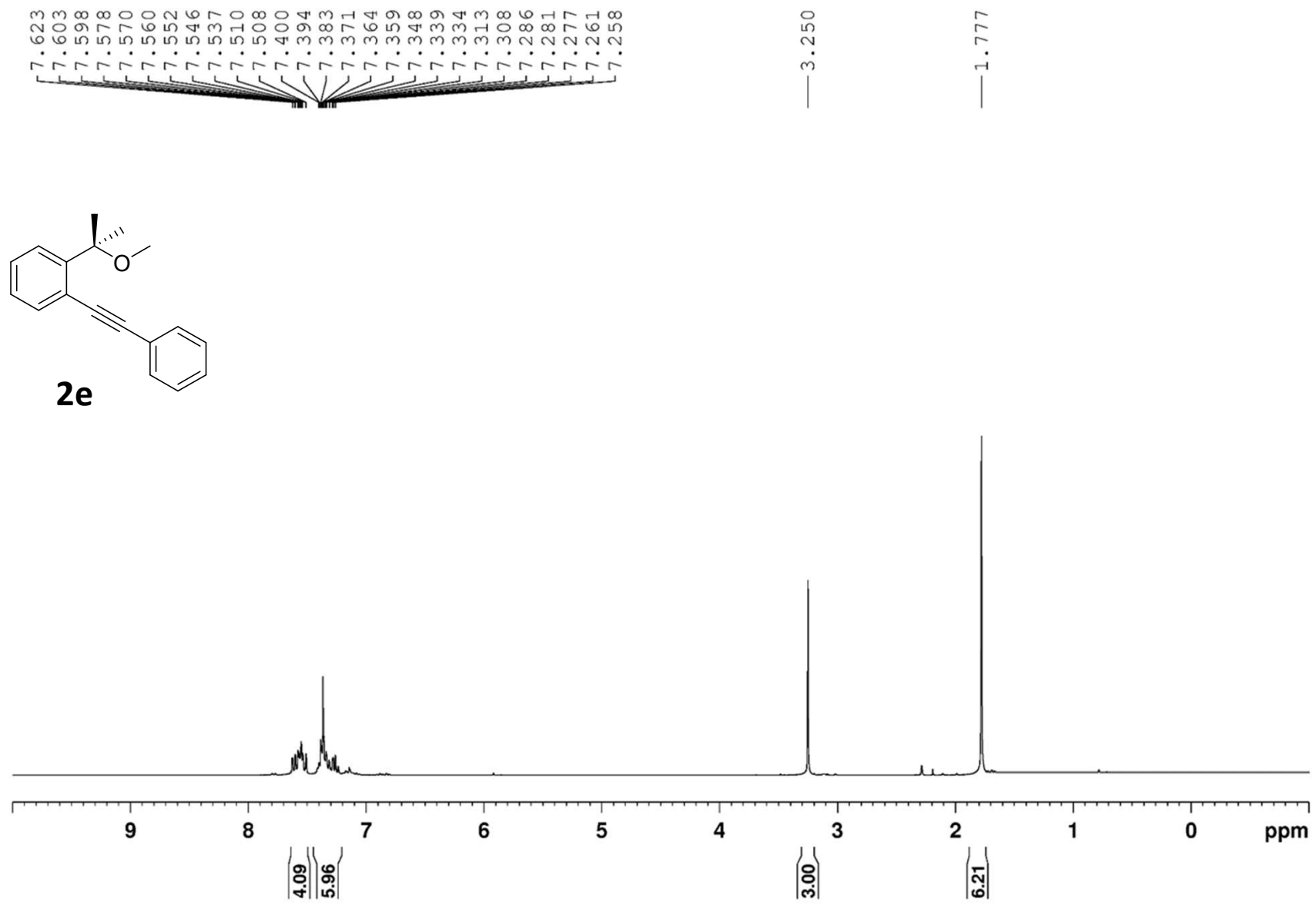
2d



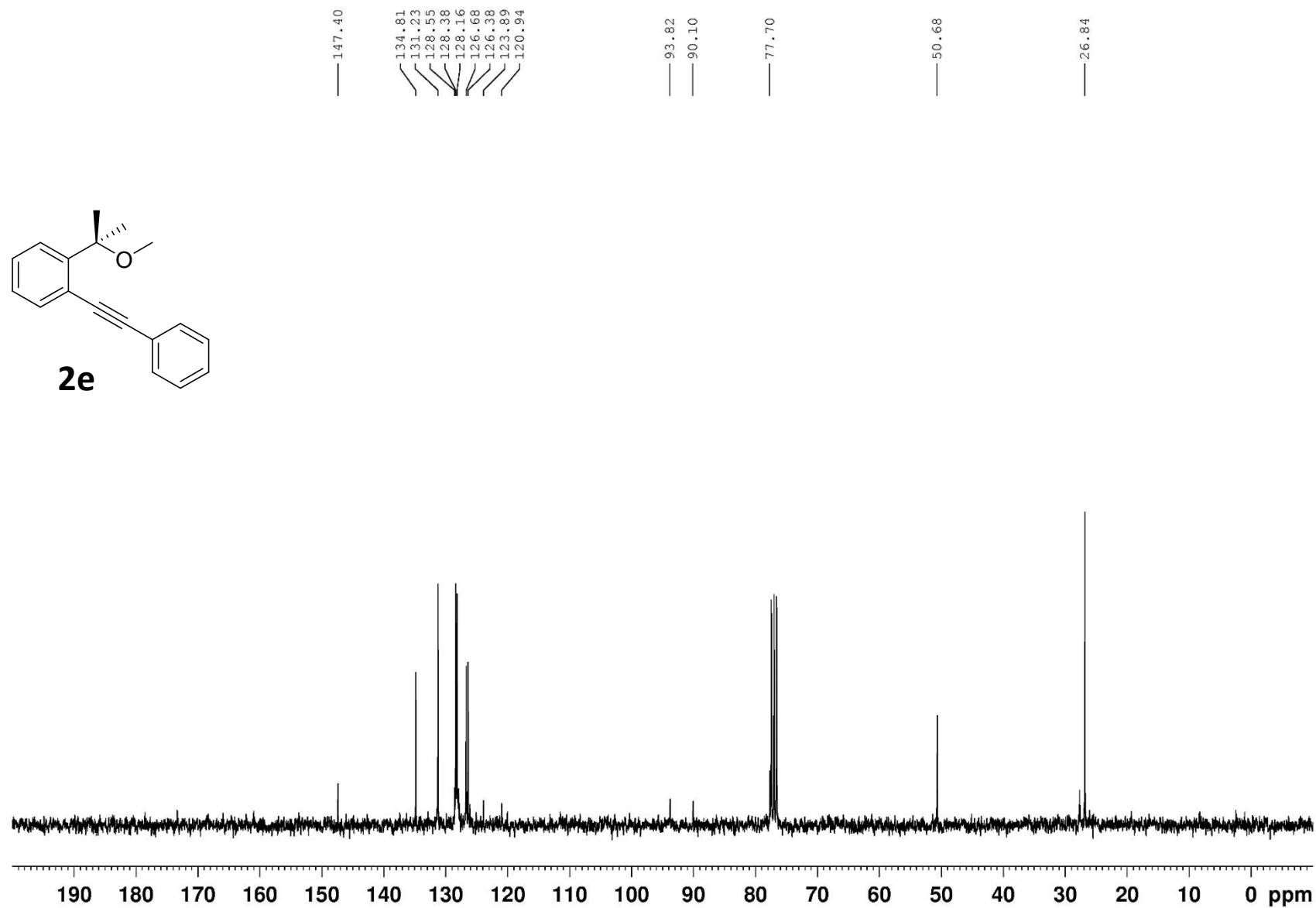
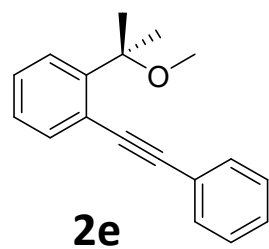
^1H NMR of compound **2d** (500 MHz, CDCl_3)



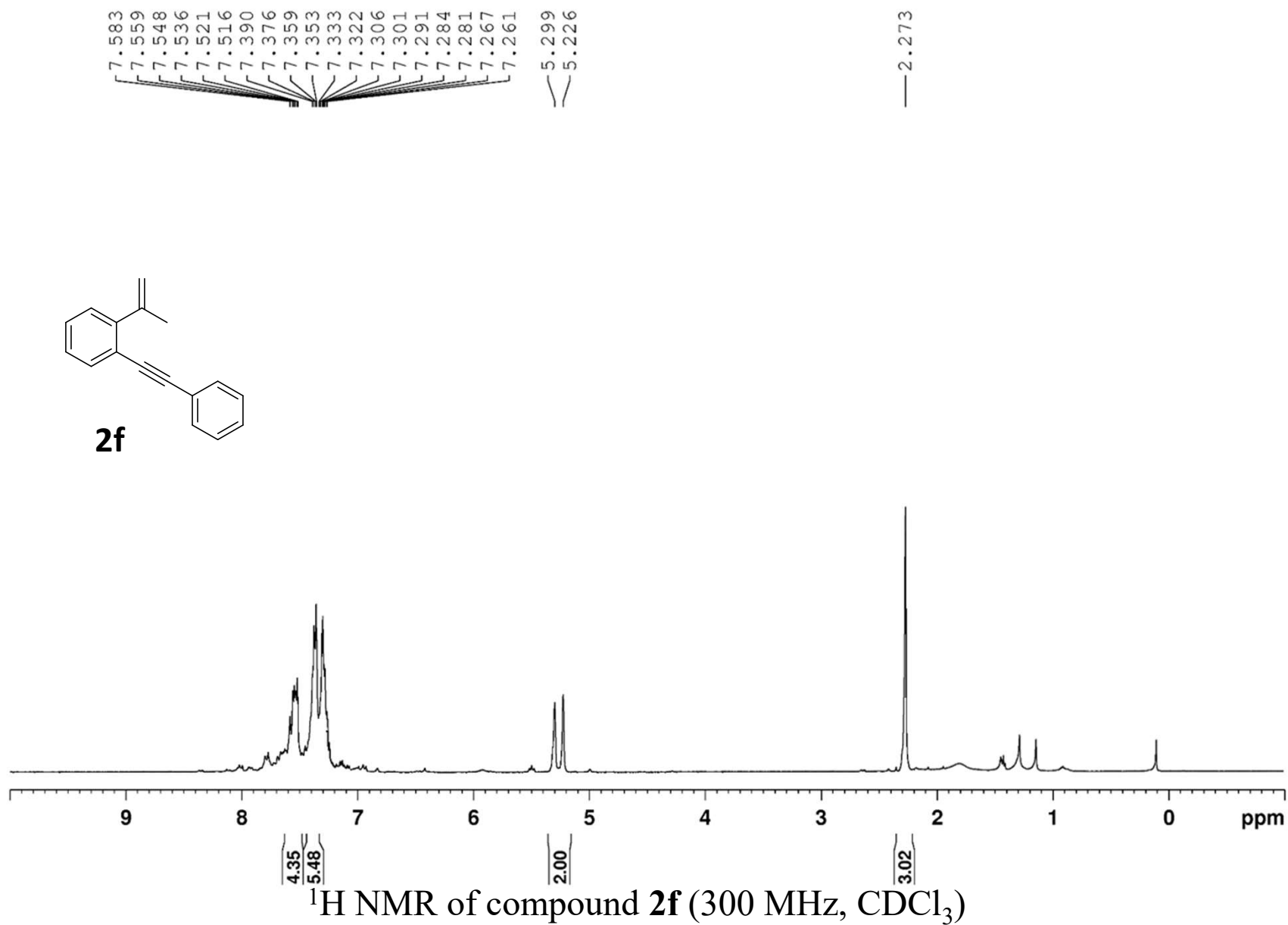
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2d** (126 MHz, CDCl_3)

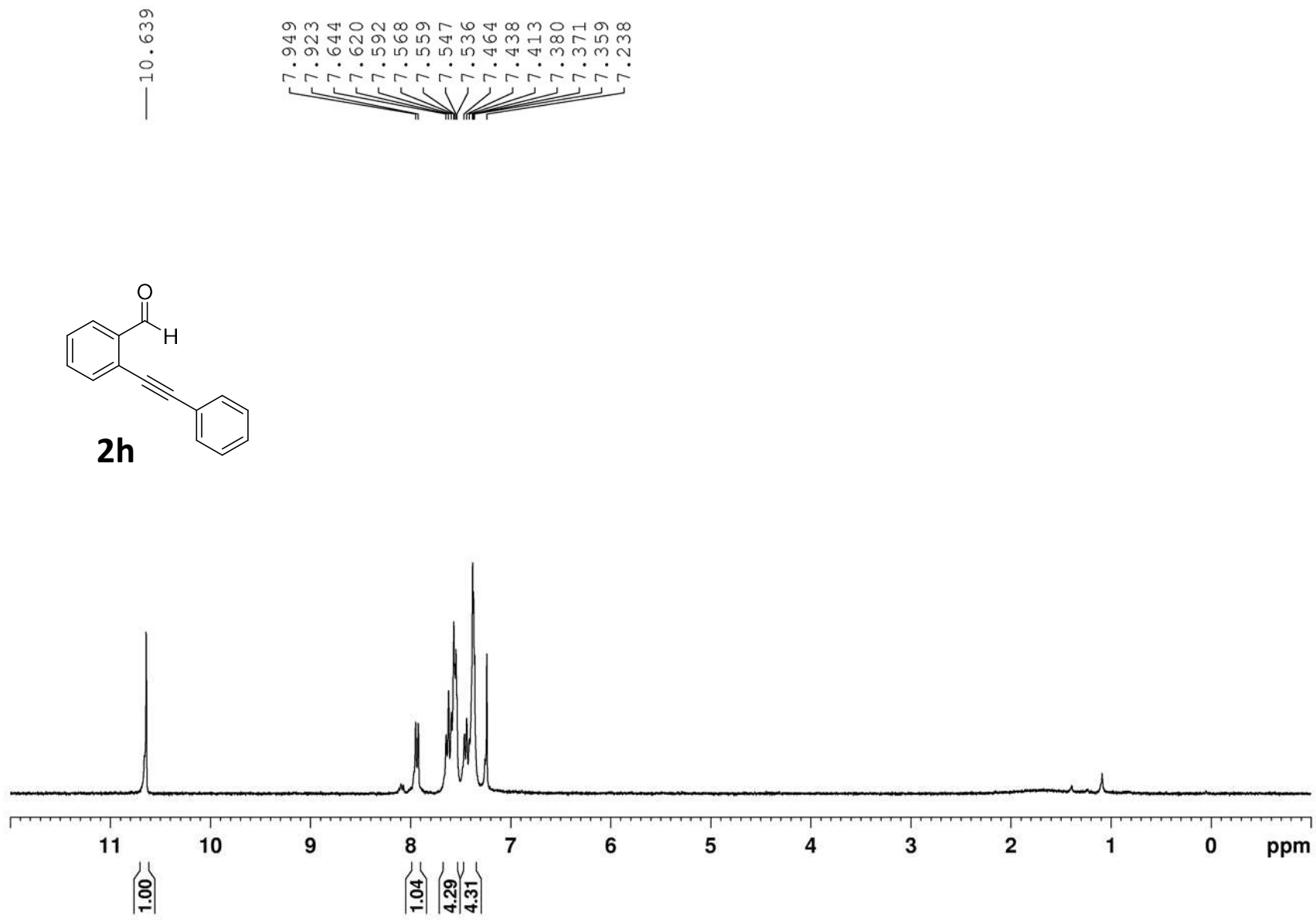


¹H NMR of compound **2e** (300 MHz, CDCl₃)

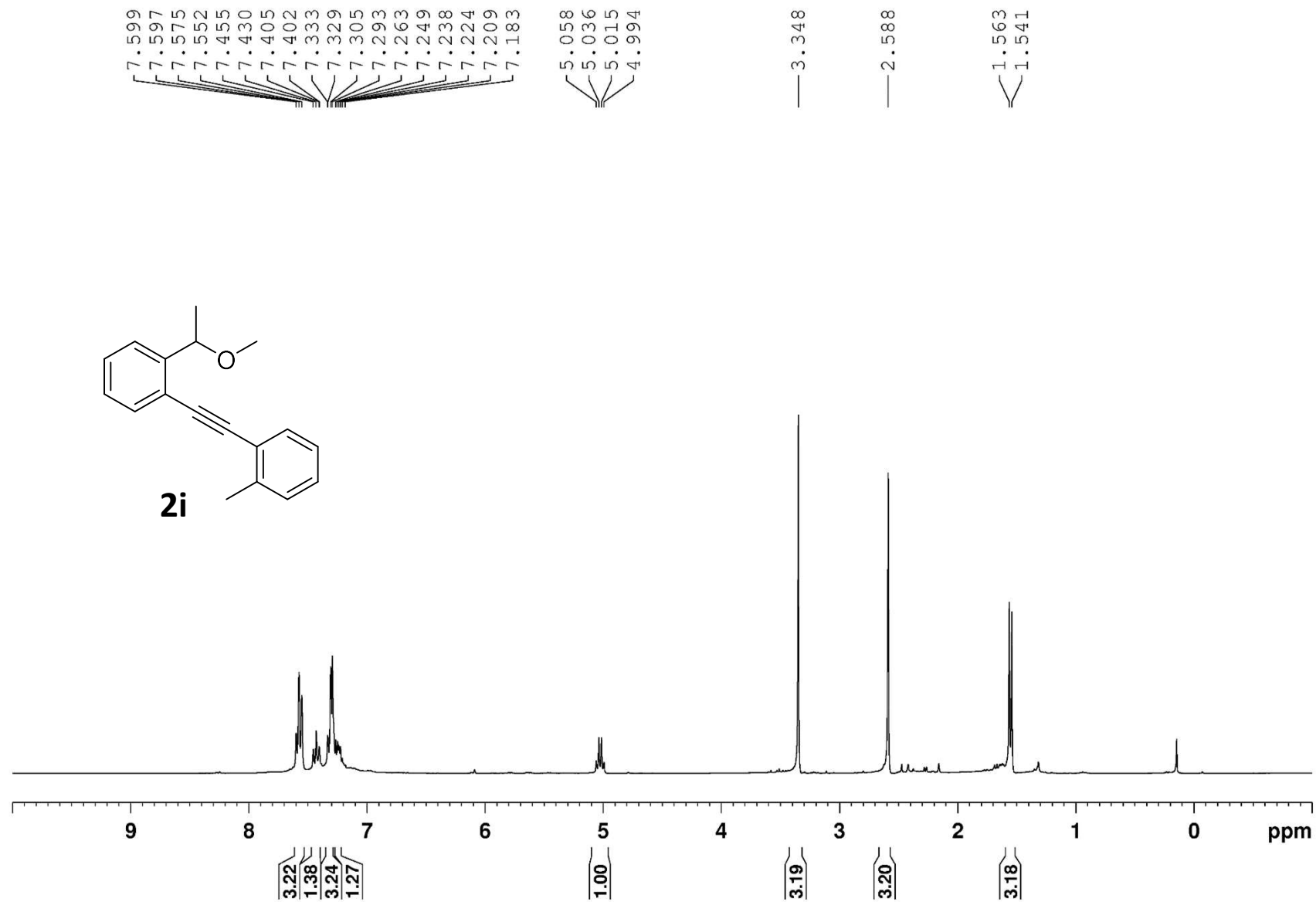


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2e** (75 MHz, CDCl_3)

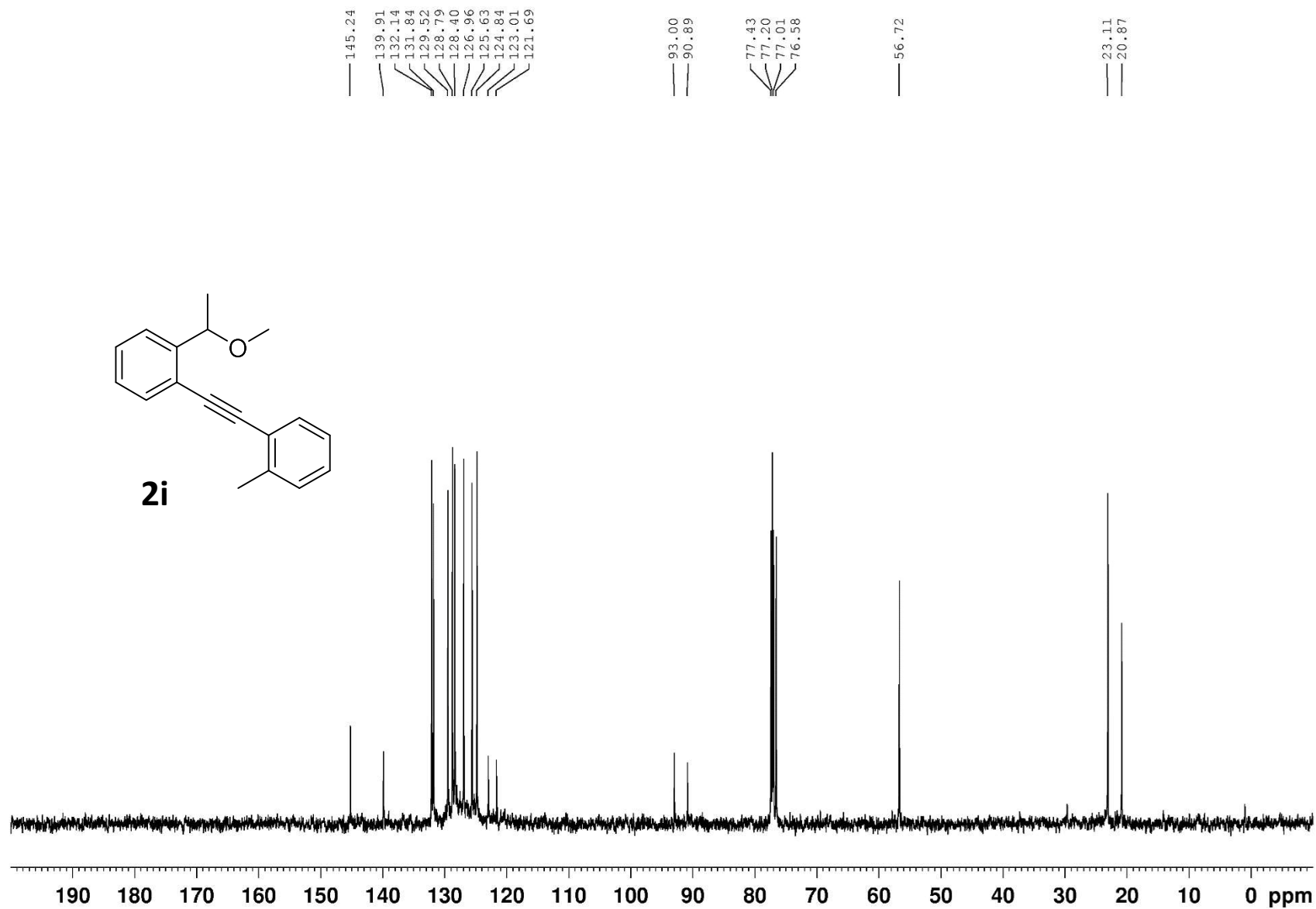




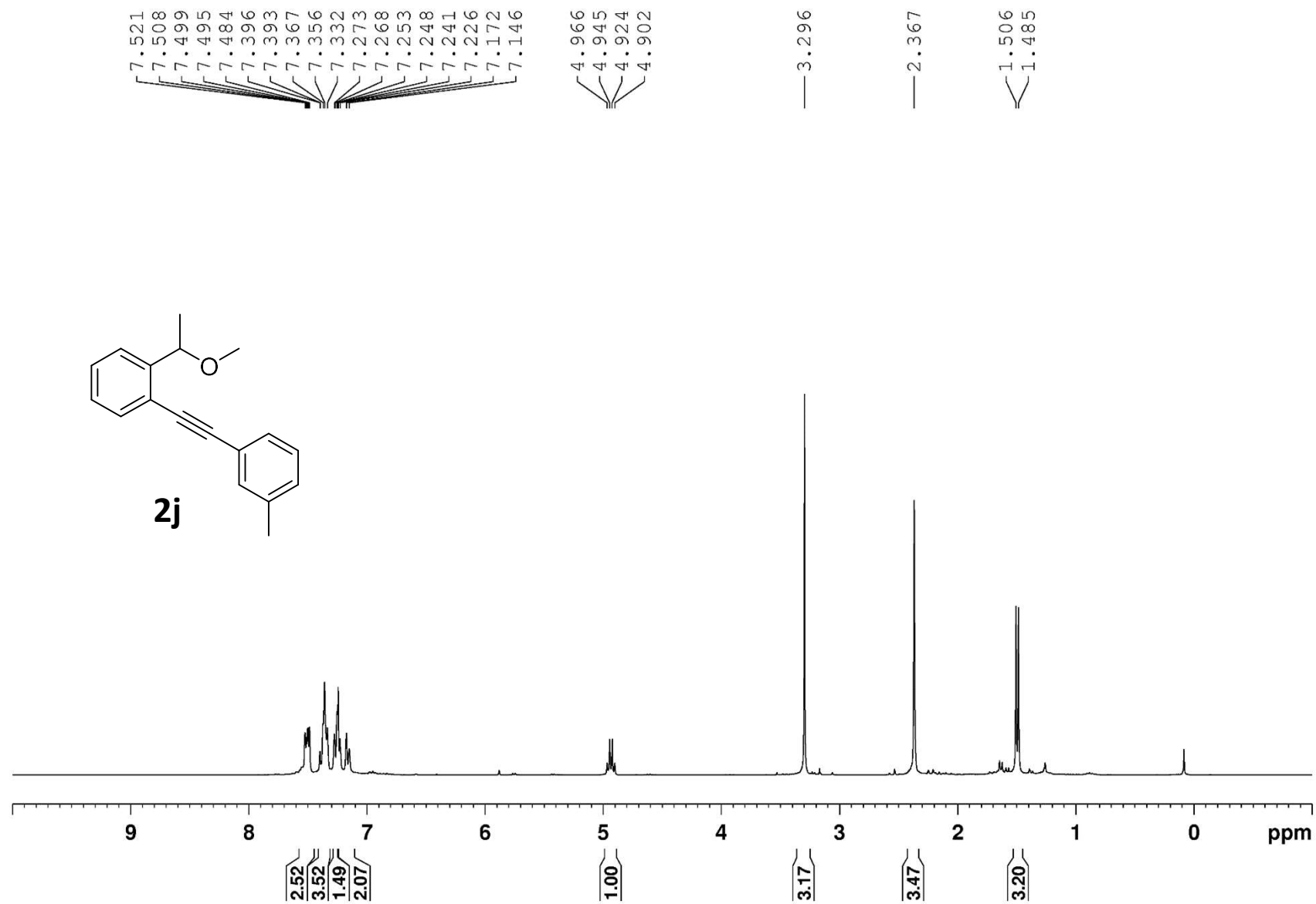
^1H NMR of compound **2h** (300 MHz, CDCl_3)



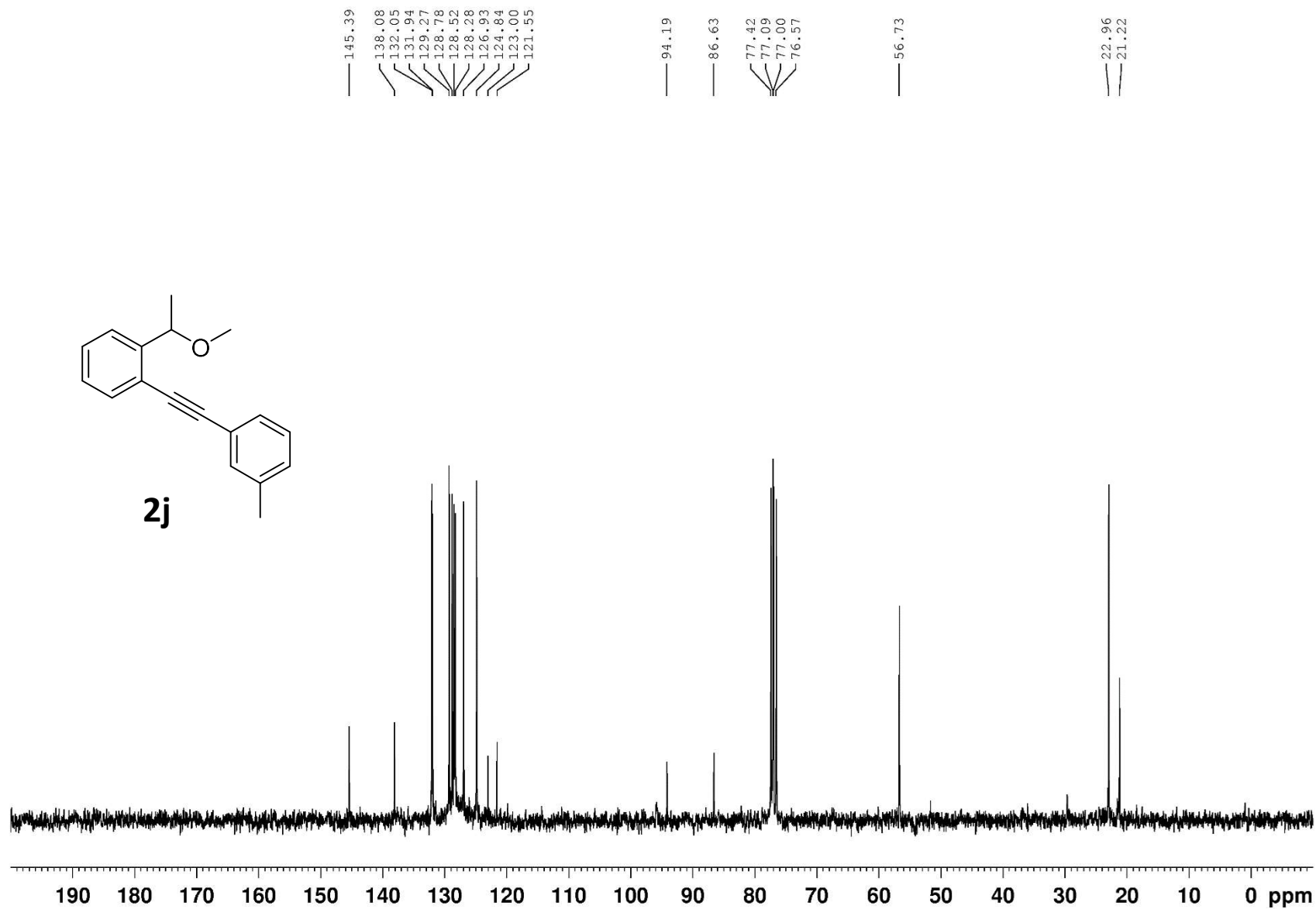
^1H NMR of compound **2i** (300 MHz, CDCl_3)



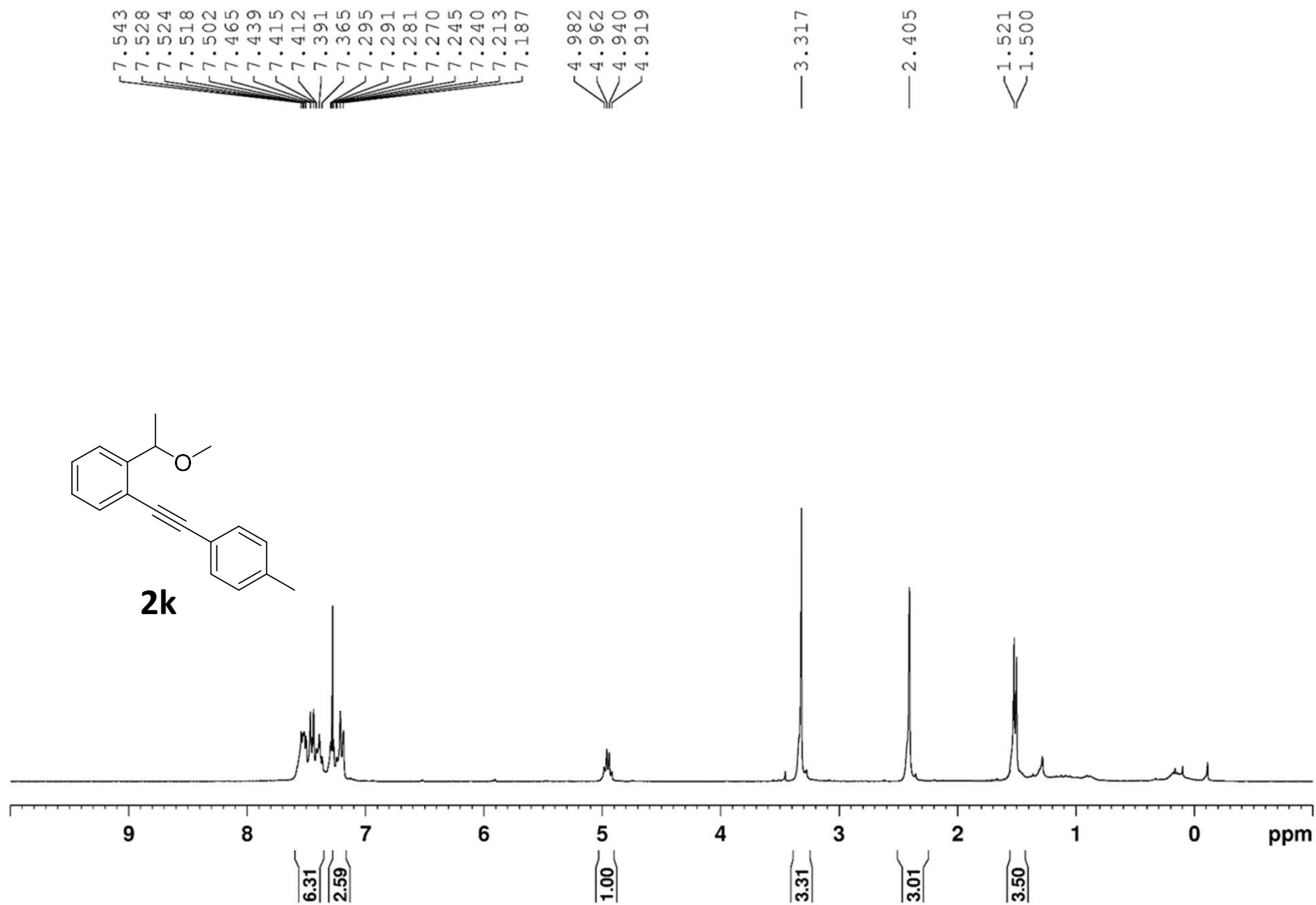
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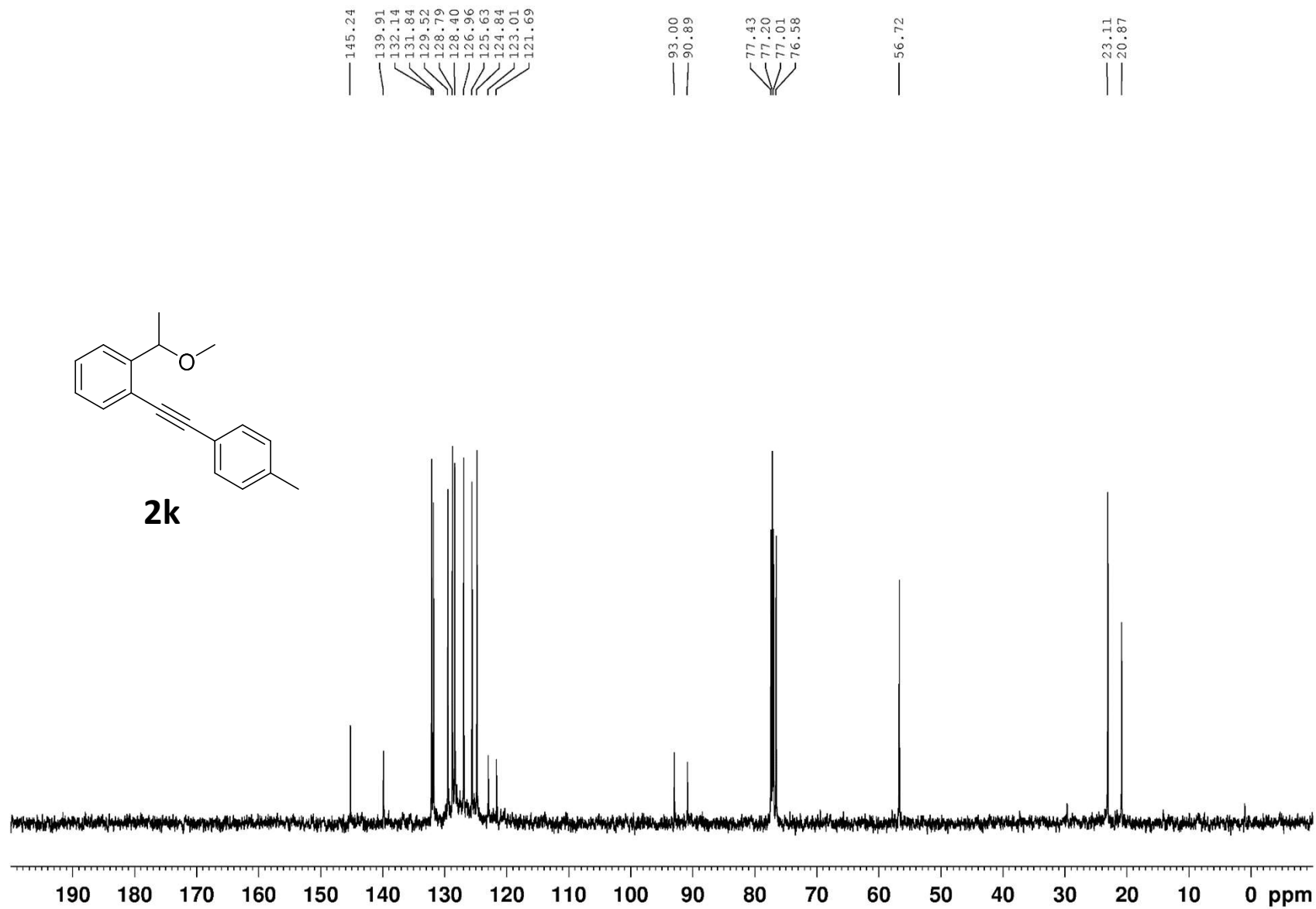
^1H NMR of compound **2j** (300 MHz, CDCl_3)



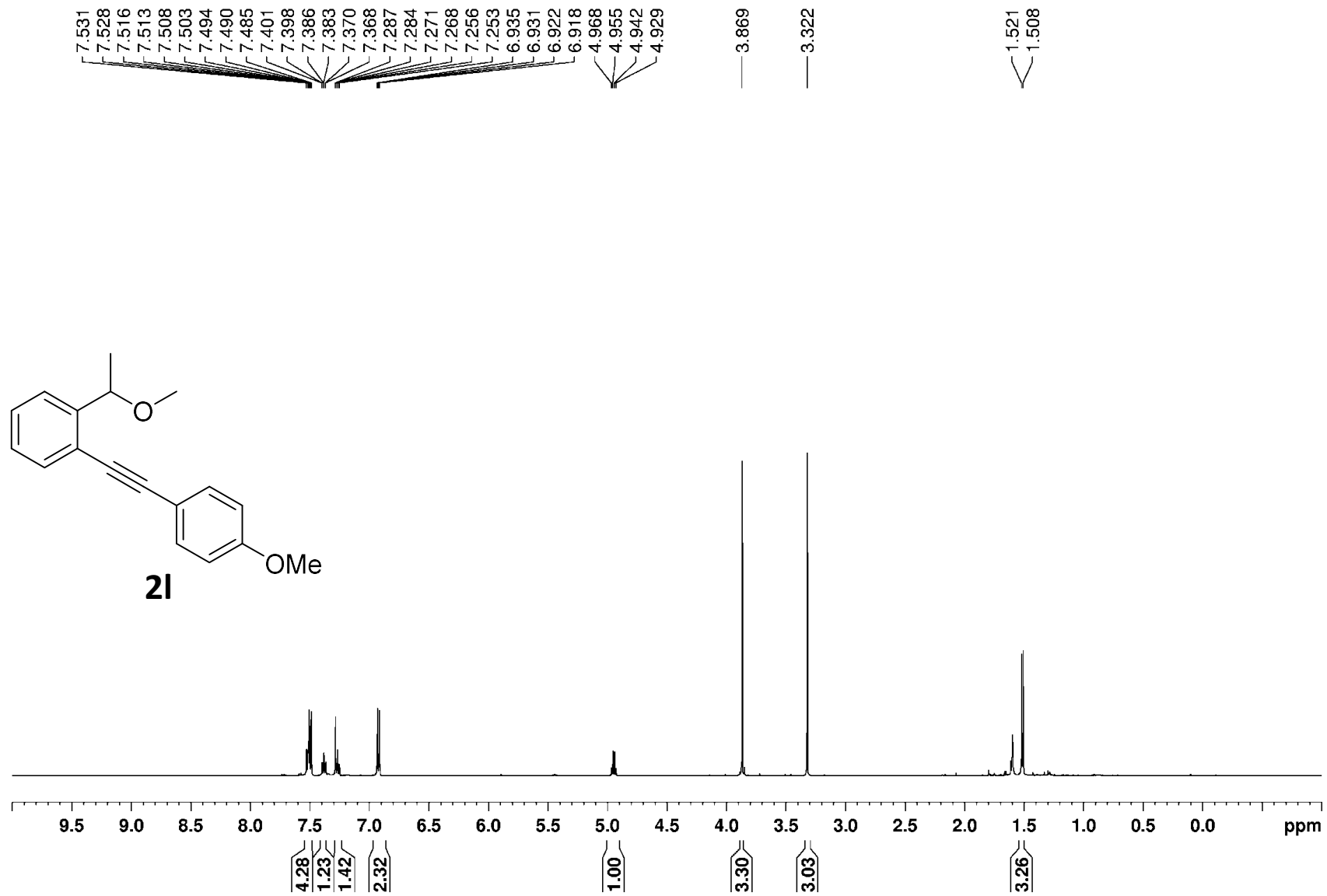
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2j** (75 MHz, CDCl_3)



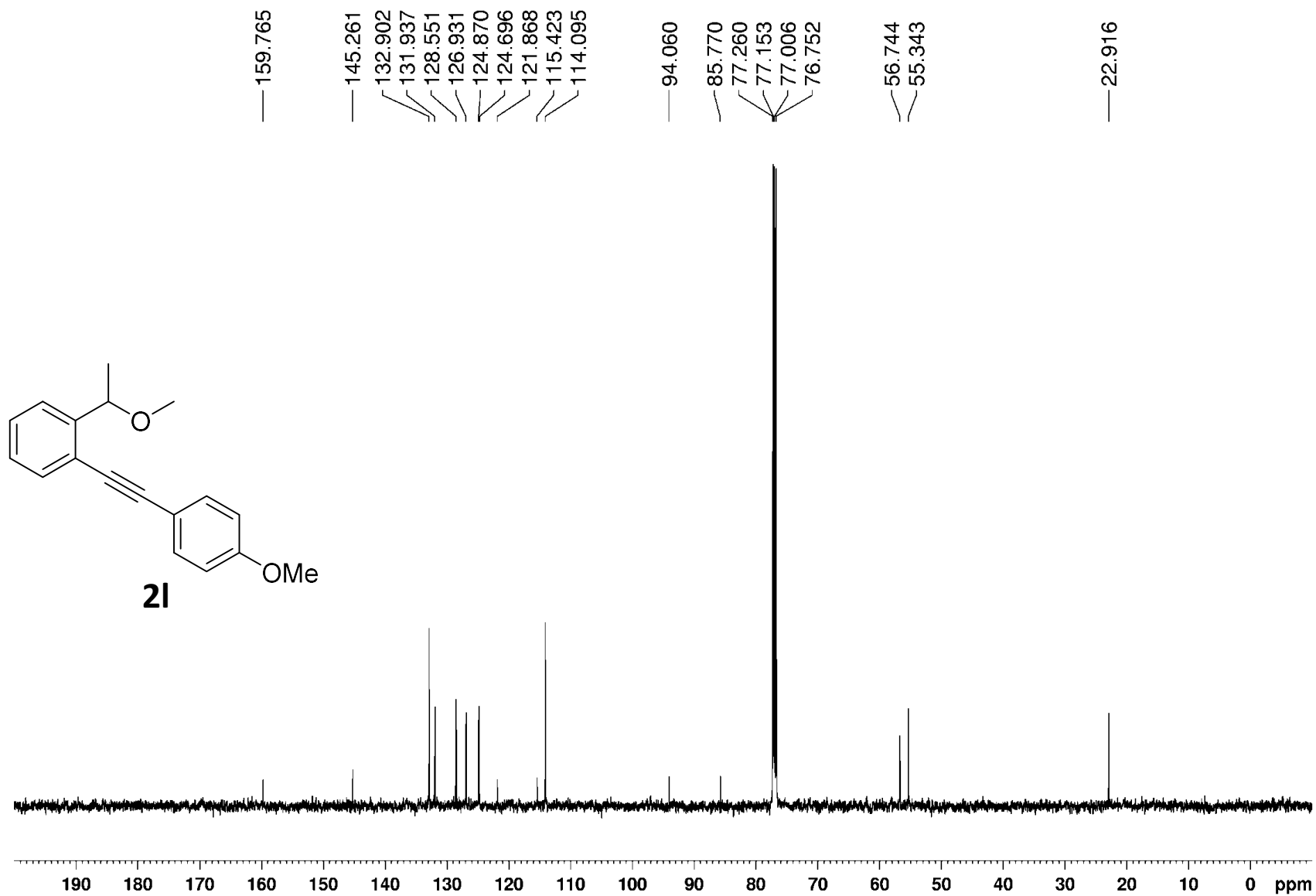
¹H NMR of compound **2k** (300 MHz, CDCl₃)



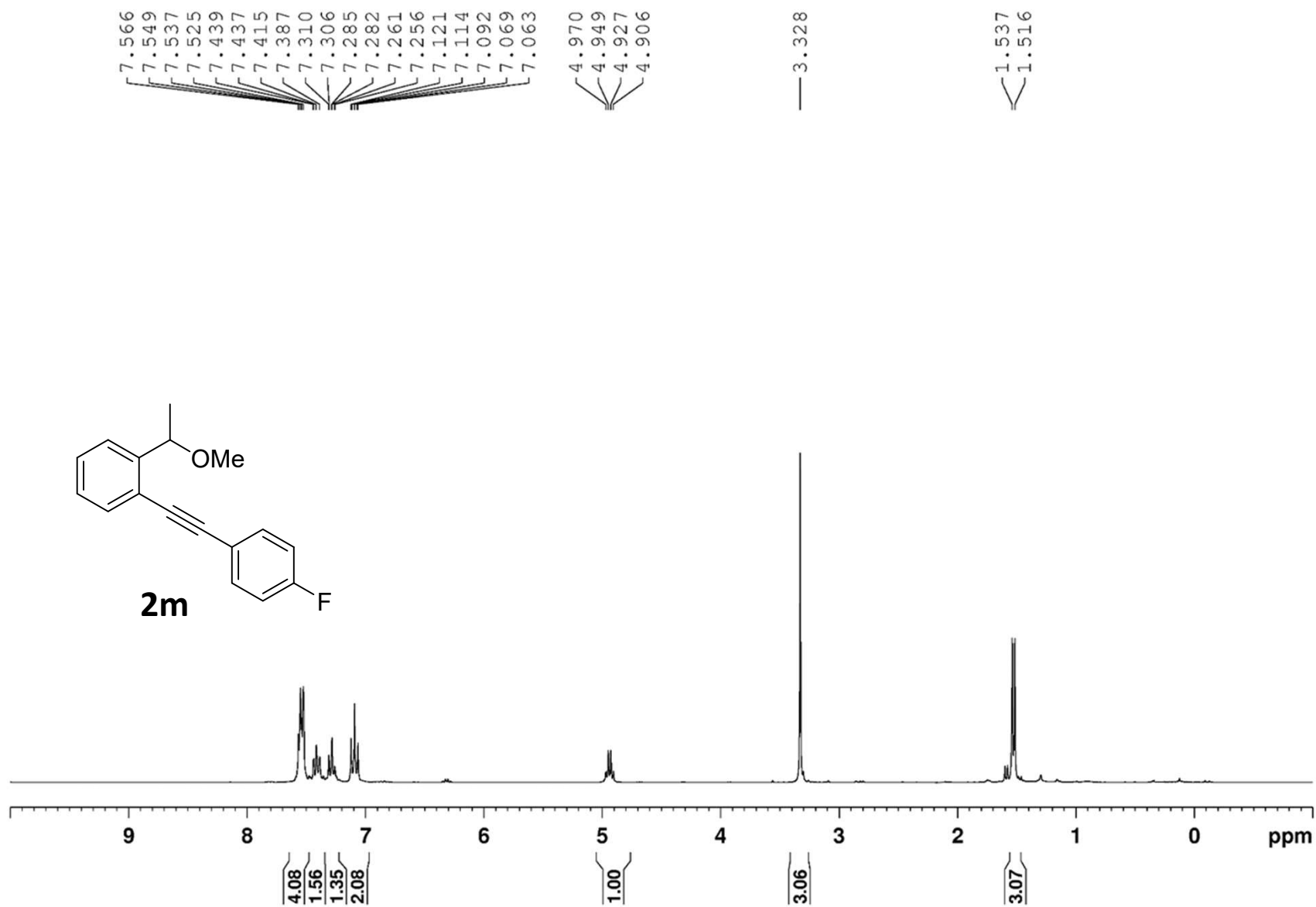
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2k** (75 MHz, CDCl_3)



¹H NMR of compound **21** (500 MHz, CDCl₃)

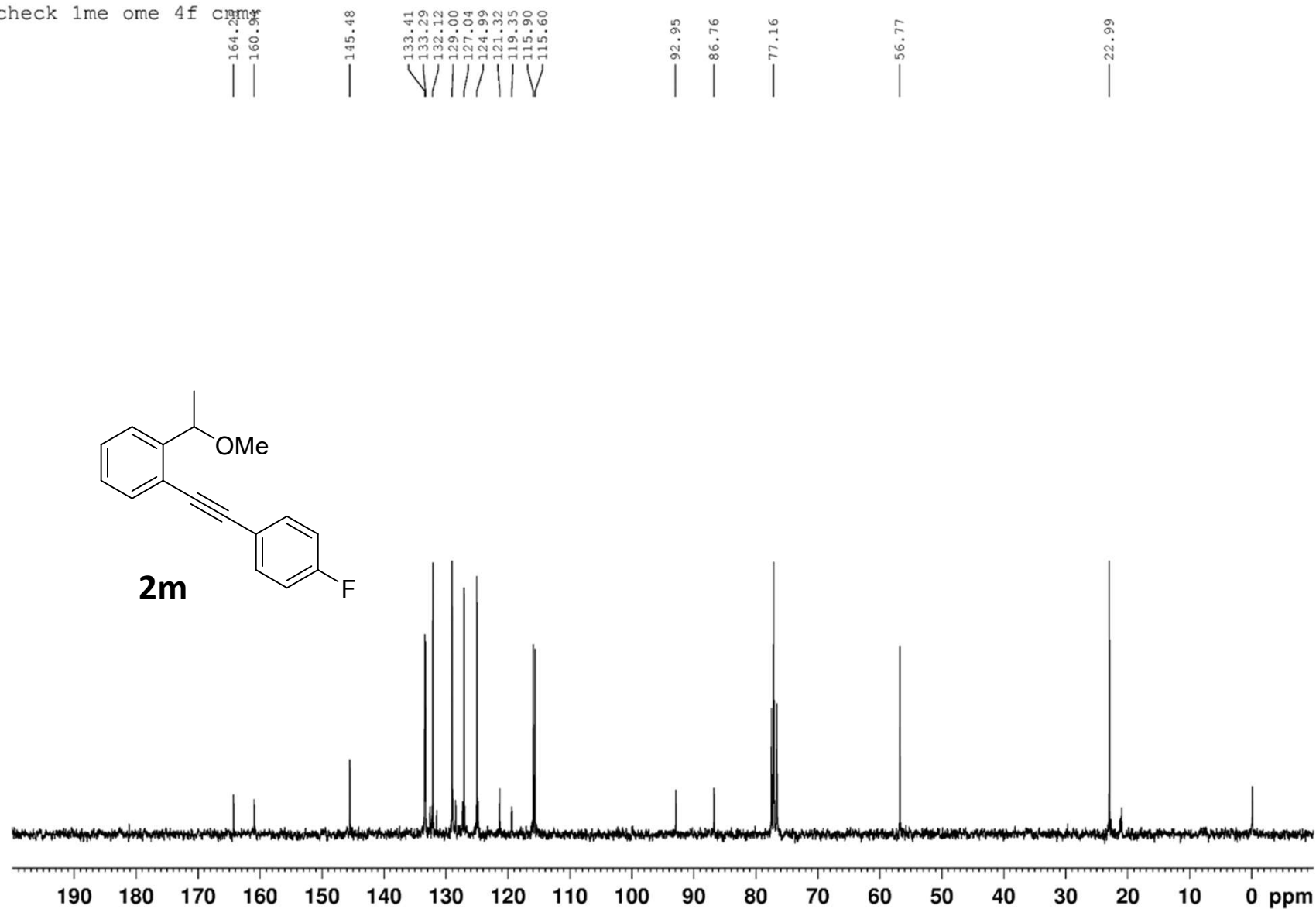


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **21** (126 MHz, CDCl_3)



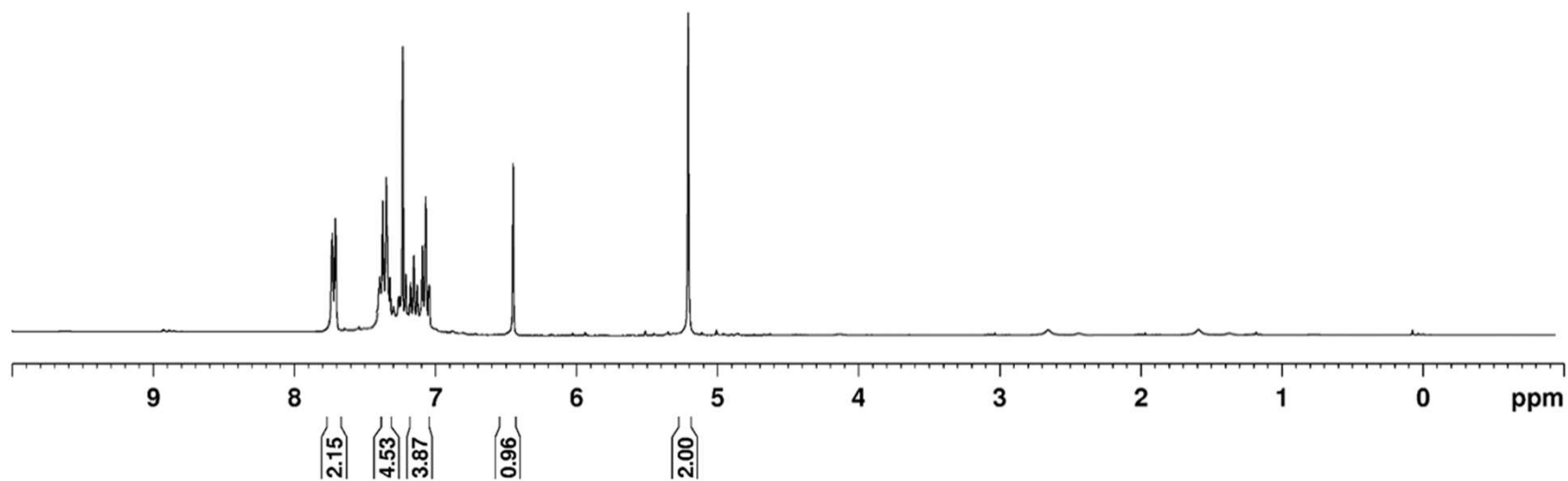
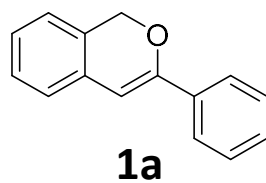
¹H NMR of compound **2m** (500 MHz, CDCl₃)

check 1me ome 4f cm

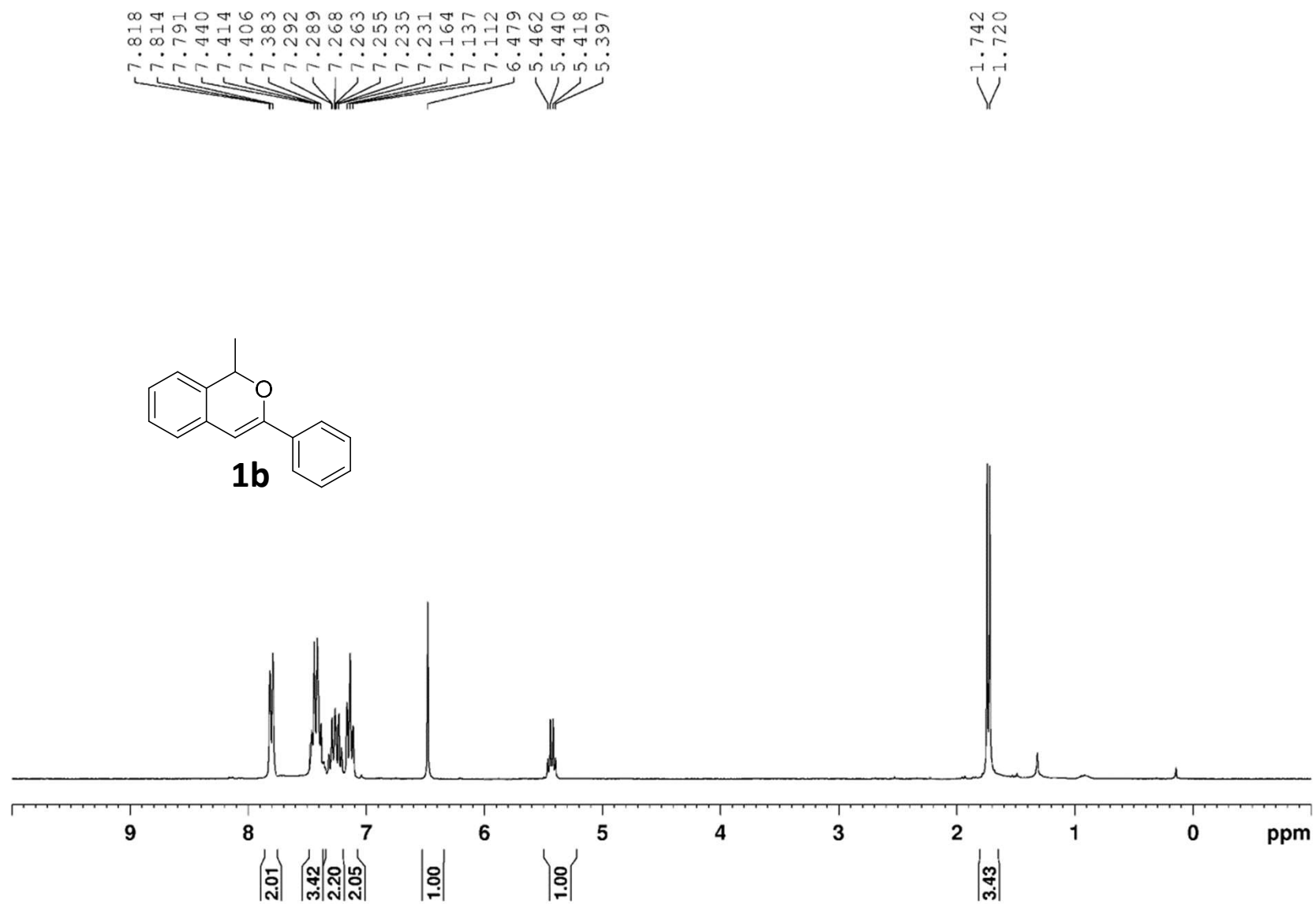


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **2m** (126 MHz, CDCl_3)

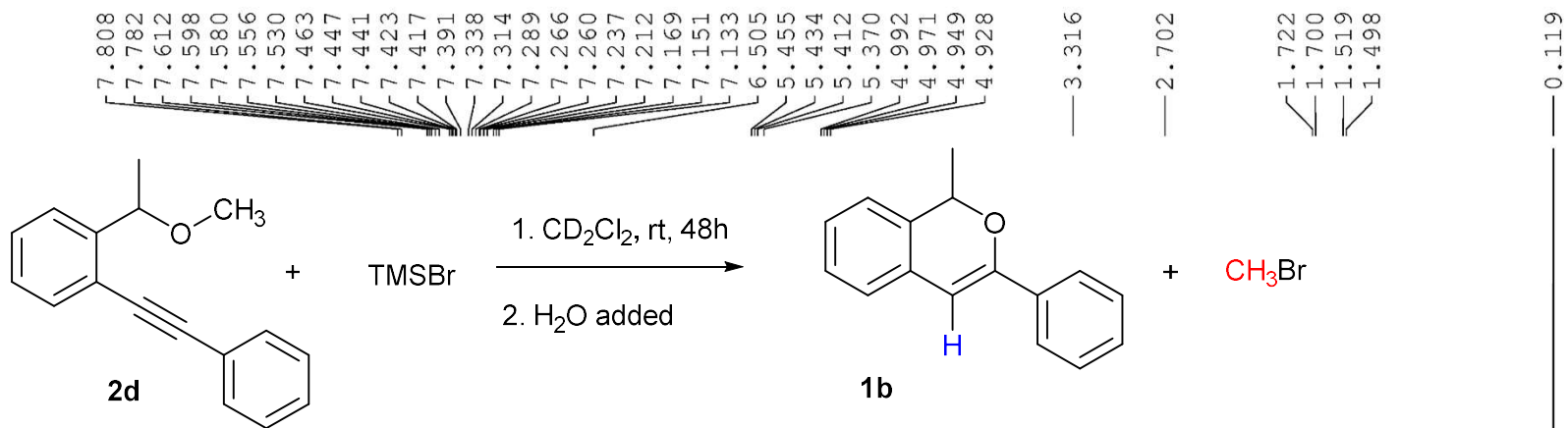
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7.145
7.120
7.084
7.061
7.038
6.440
— 5.203



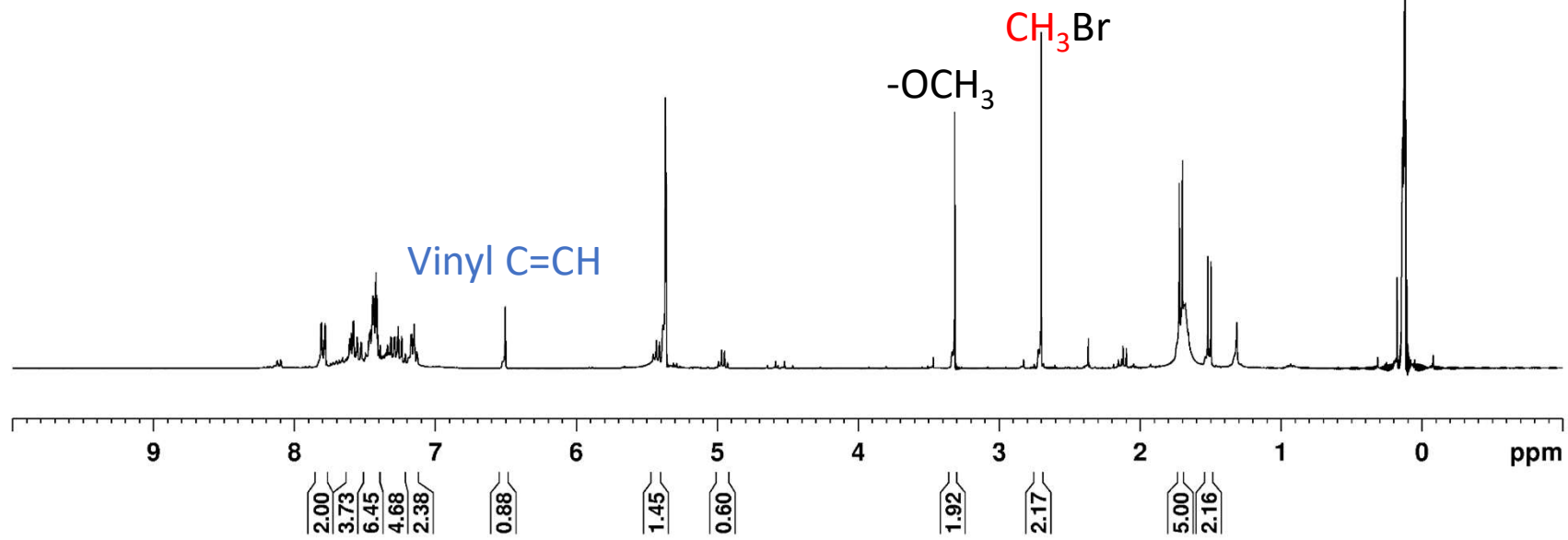
¹H NMR of compound **1a** (300 MHz, CDCl₃)



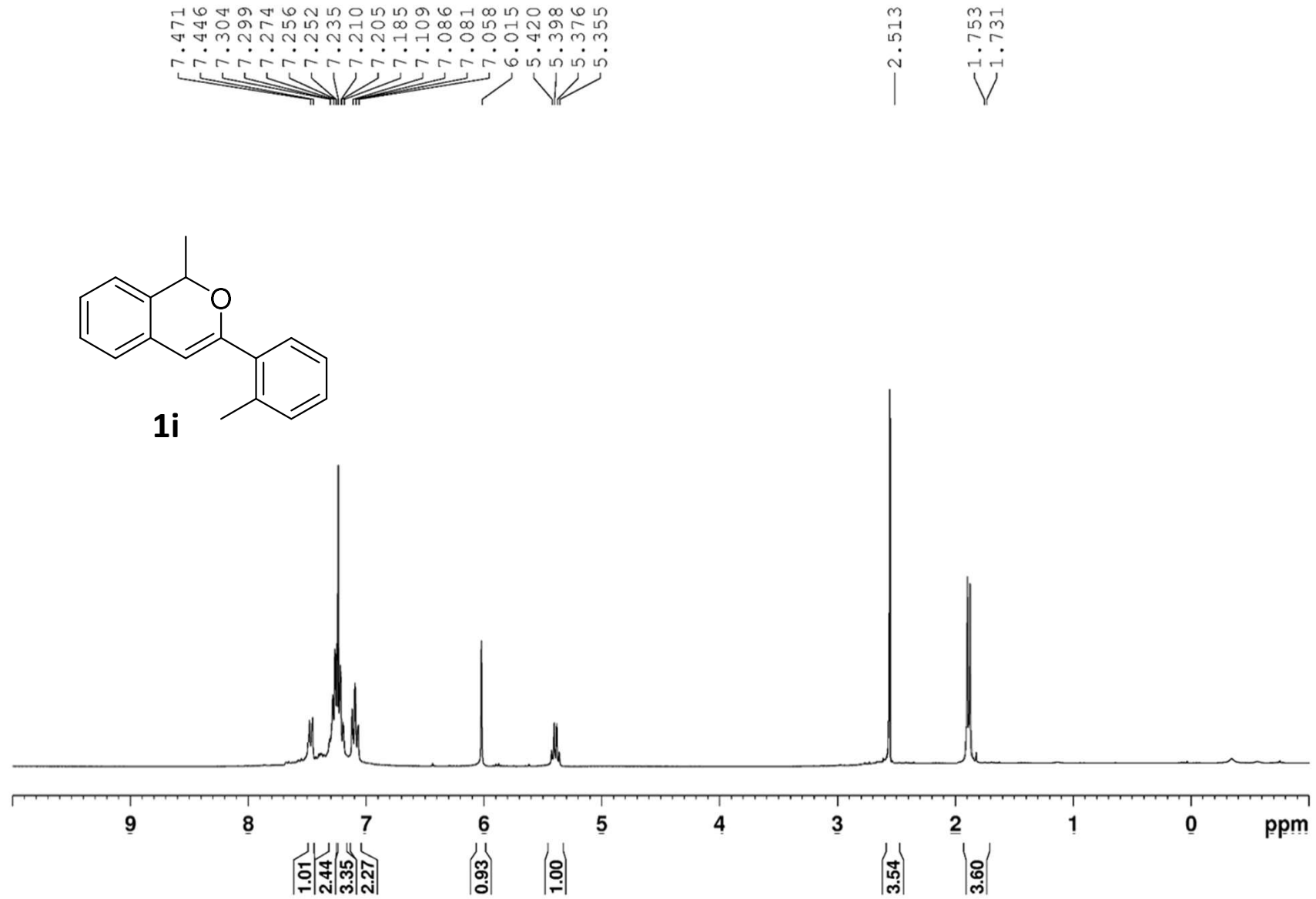
¹H NMR of compound **1b** (300 MHz, CDCl₃)



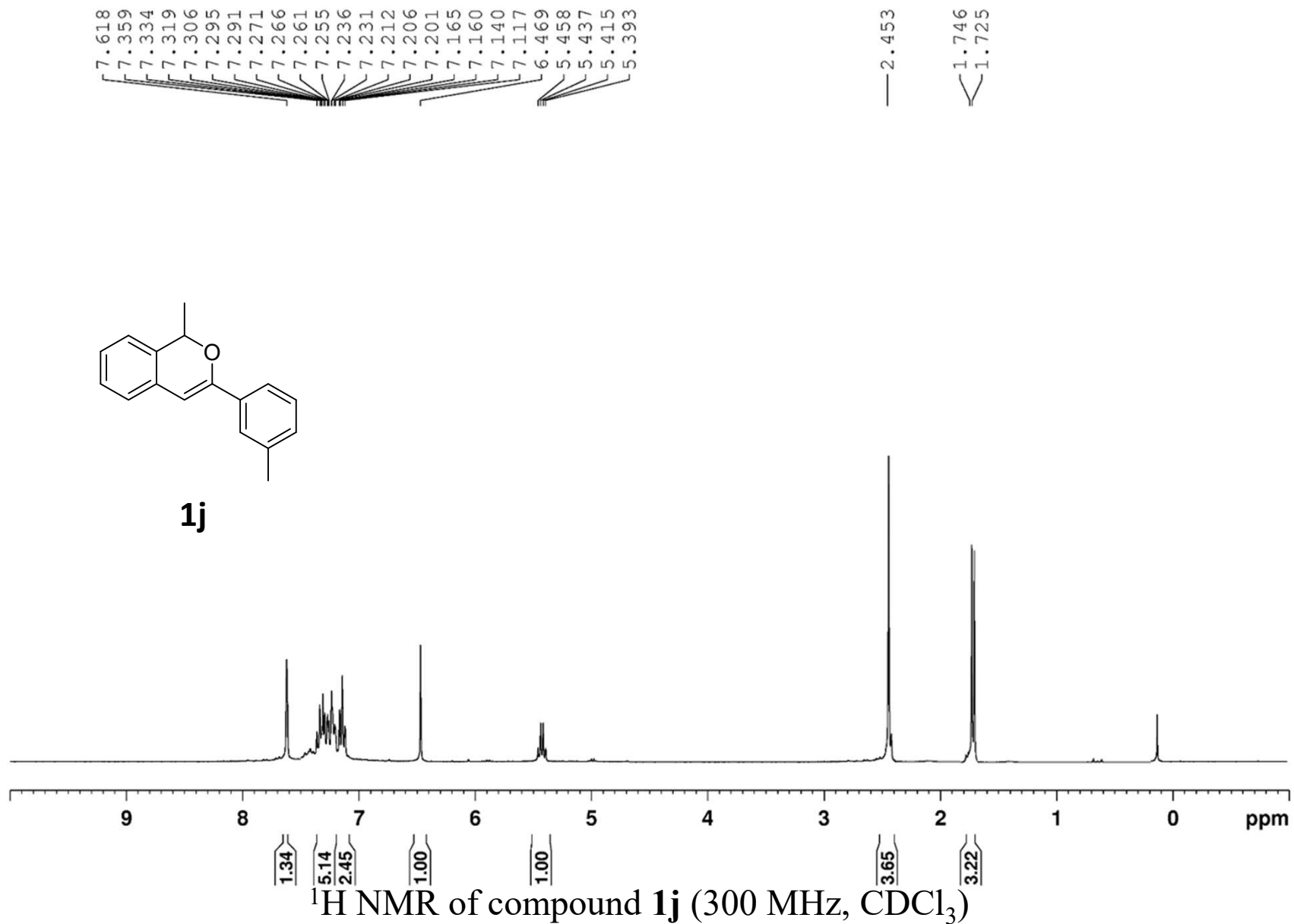
After 62% conversion of **2d**,
1b : **CH₃Br** = 1 : 0.72.

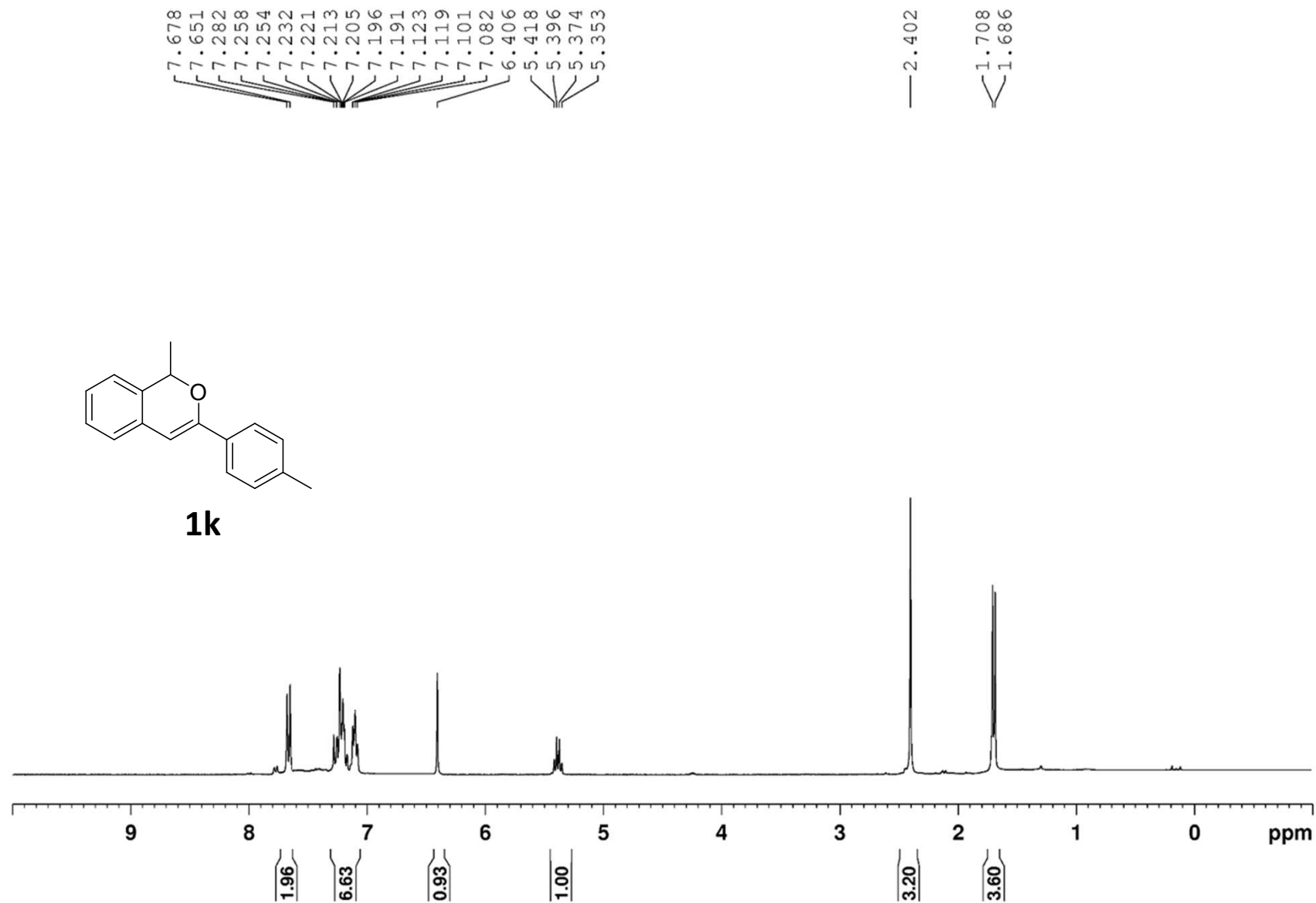


¹H NMR for the reaction of **2d** to **1b** (300 MHz, CD₂Cl₂)

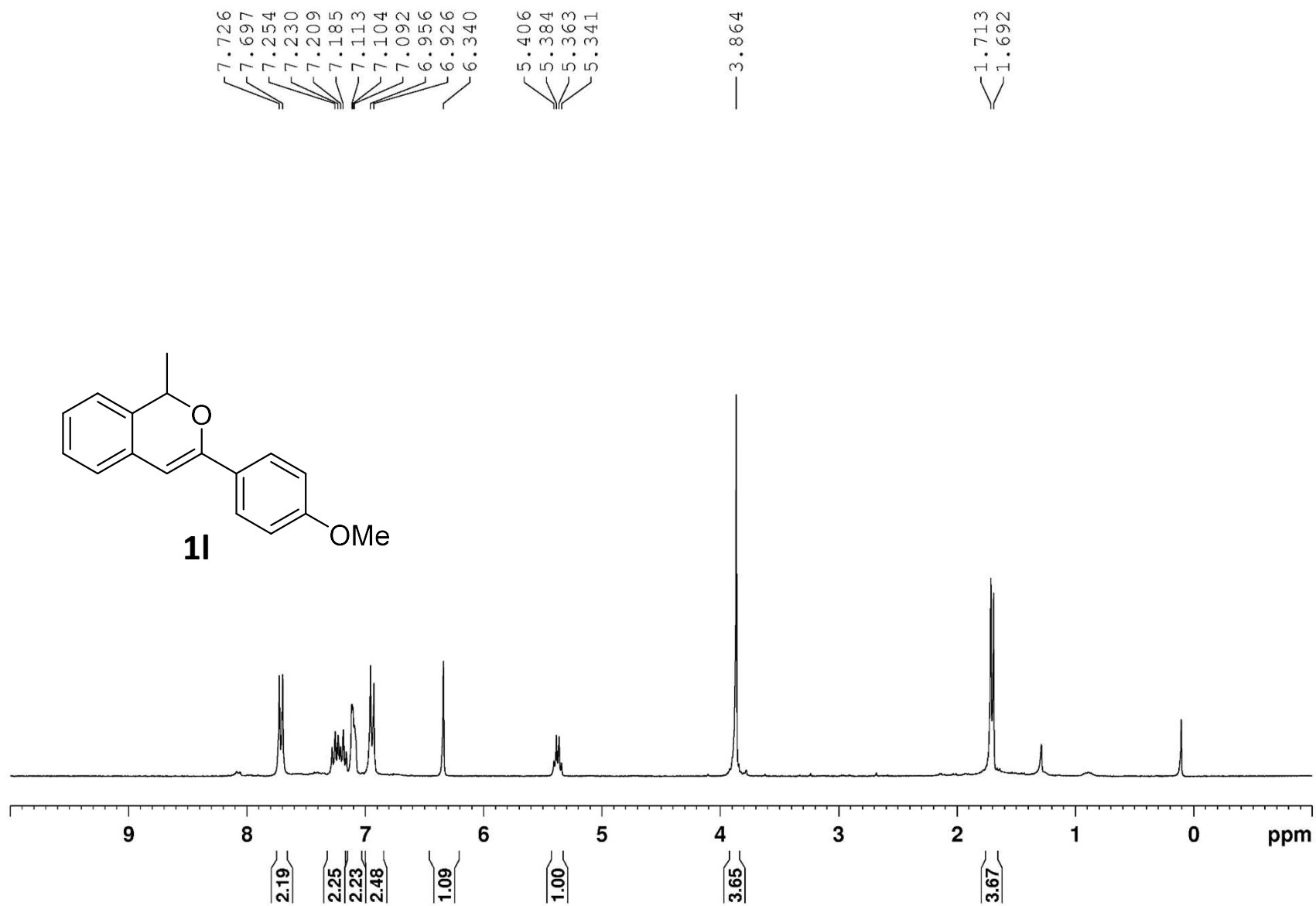


¹H NMR of compound **1i** (300 MHz, CDCl₃)

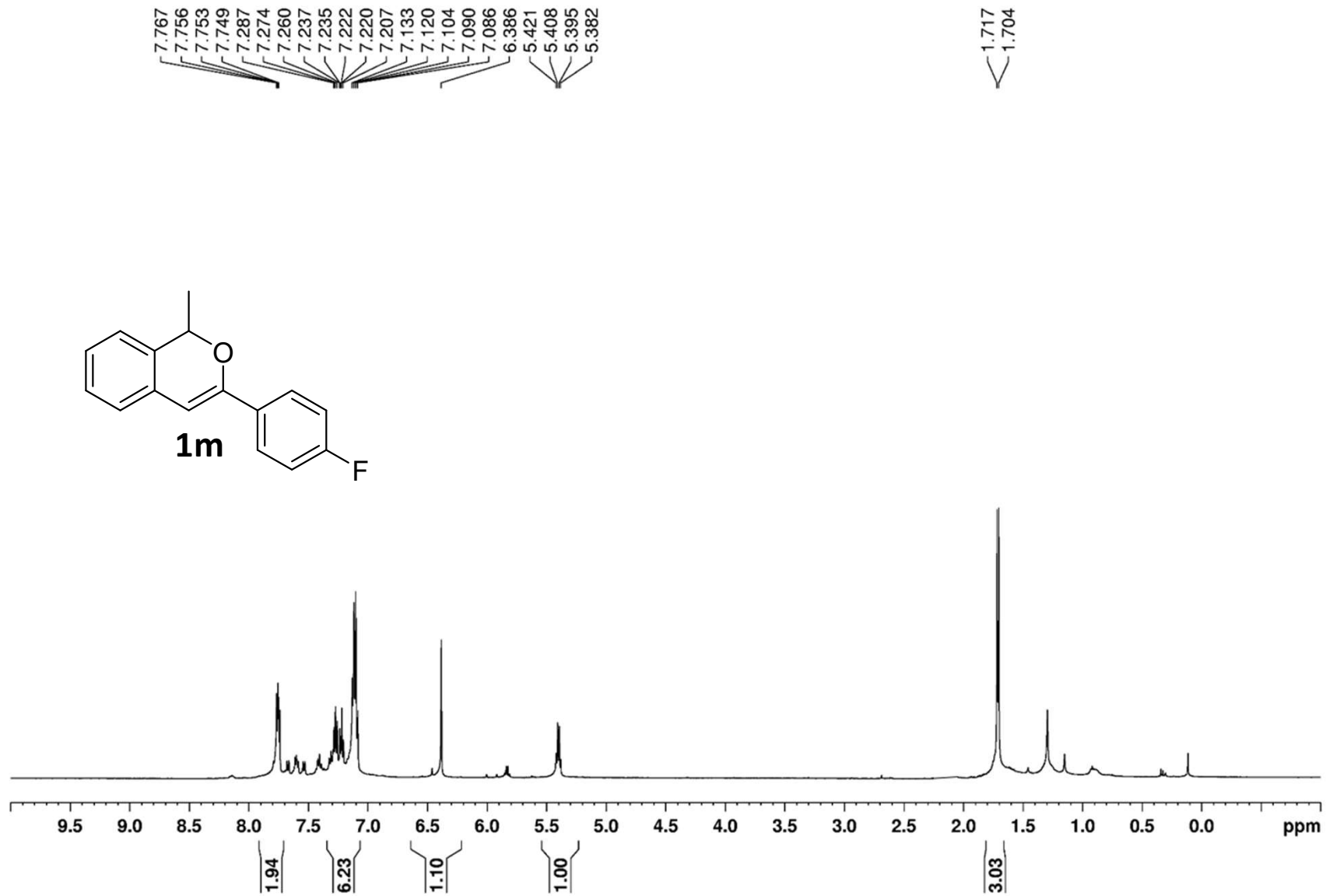




¹H NMR of compound **1k** (500 MHz, CDCl₃)

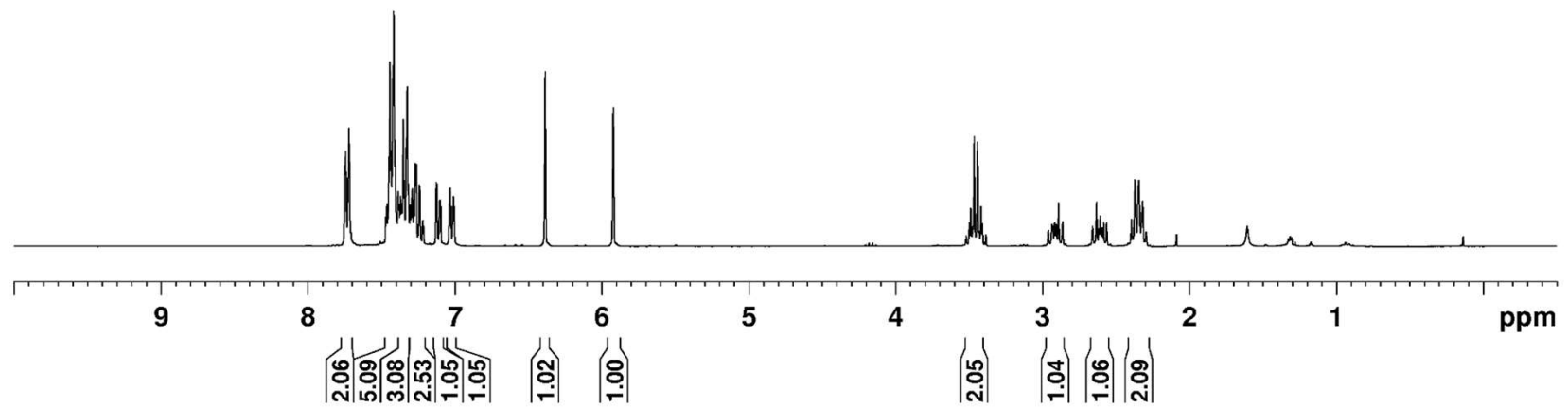
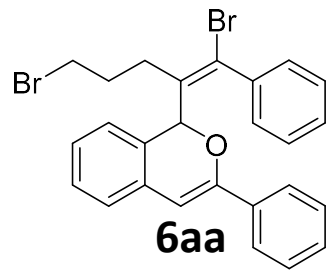


^1H NMR of compound **11** (300 MHz, CDCl_3)

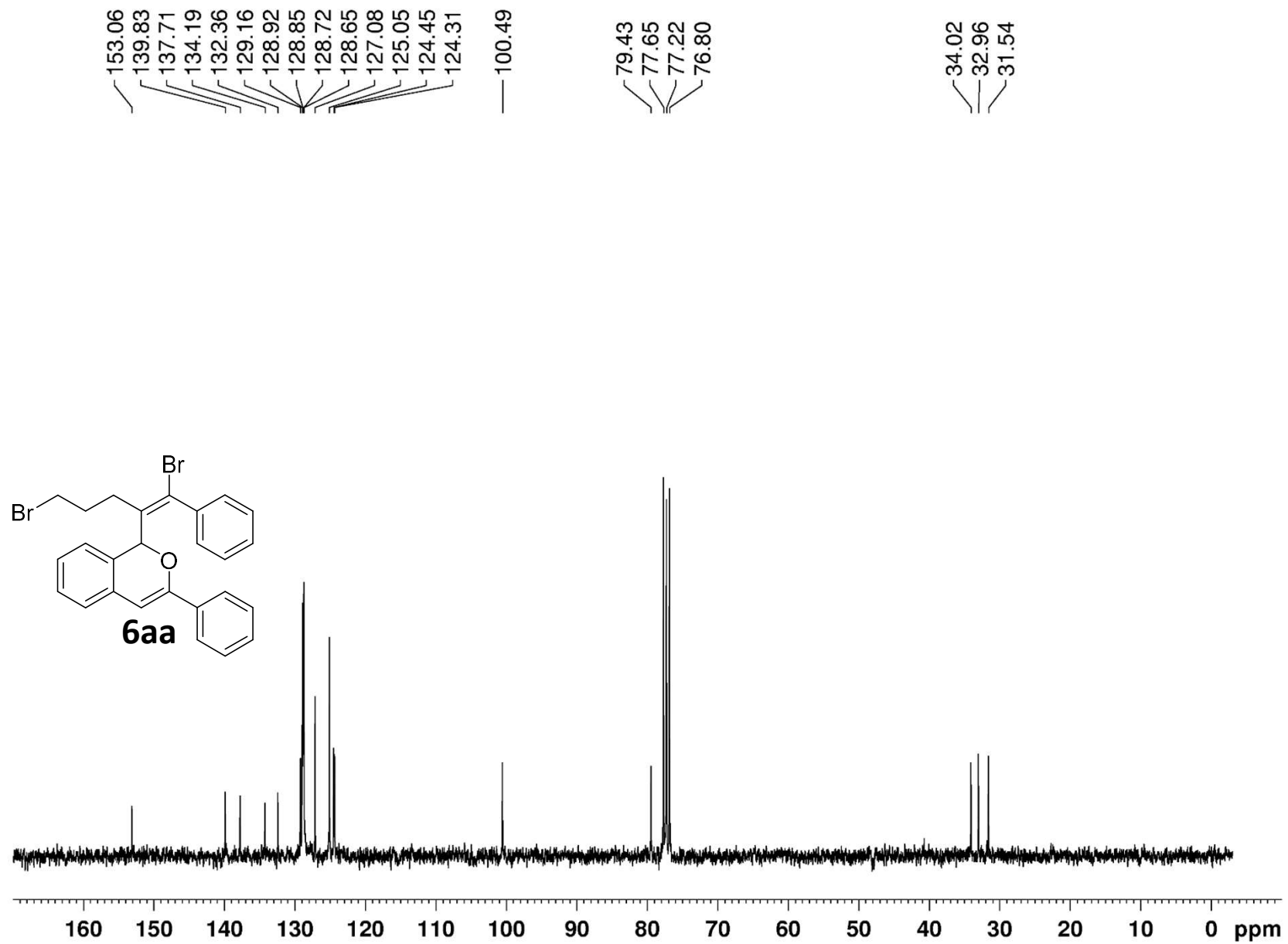


¹H NMR of compound **1m** (300 MHz, CDCl₃)

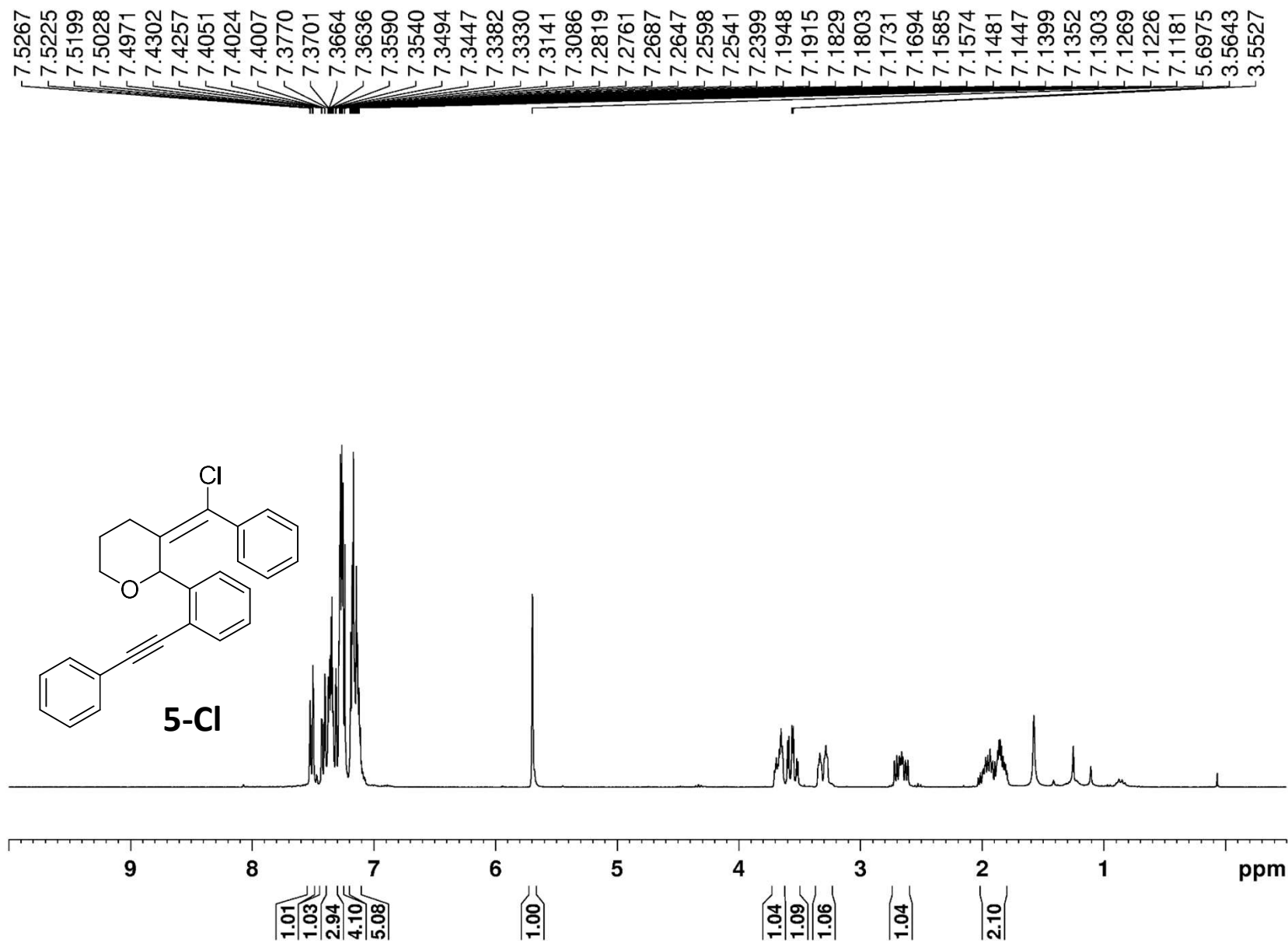
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7.3814
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7.3041
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7.2701
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2.3451
2.3201



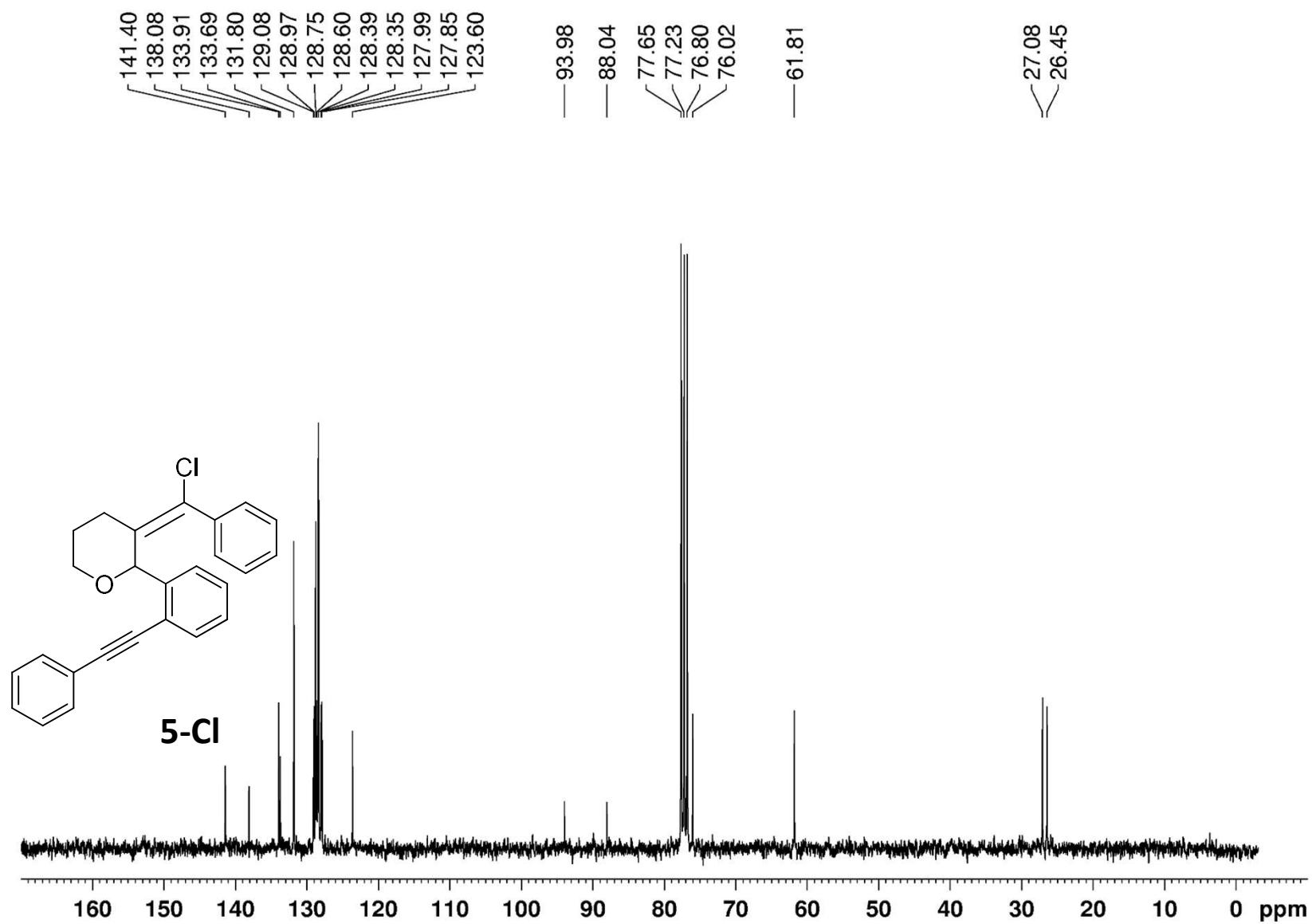
¹H NMR of compound **6aa** (300 MHz, CDCl₃)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6aa** (75 MHz, CDCl_3)

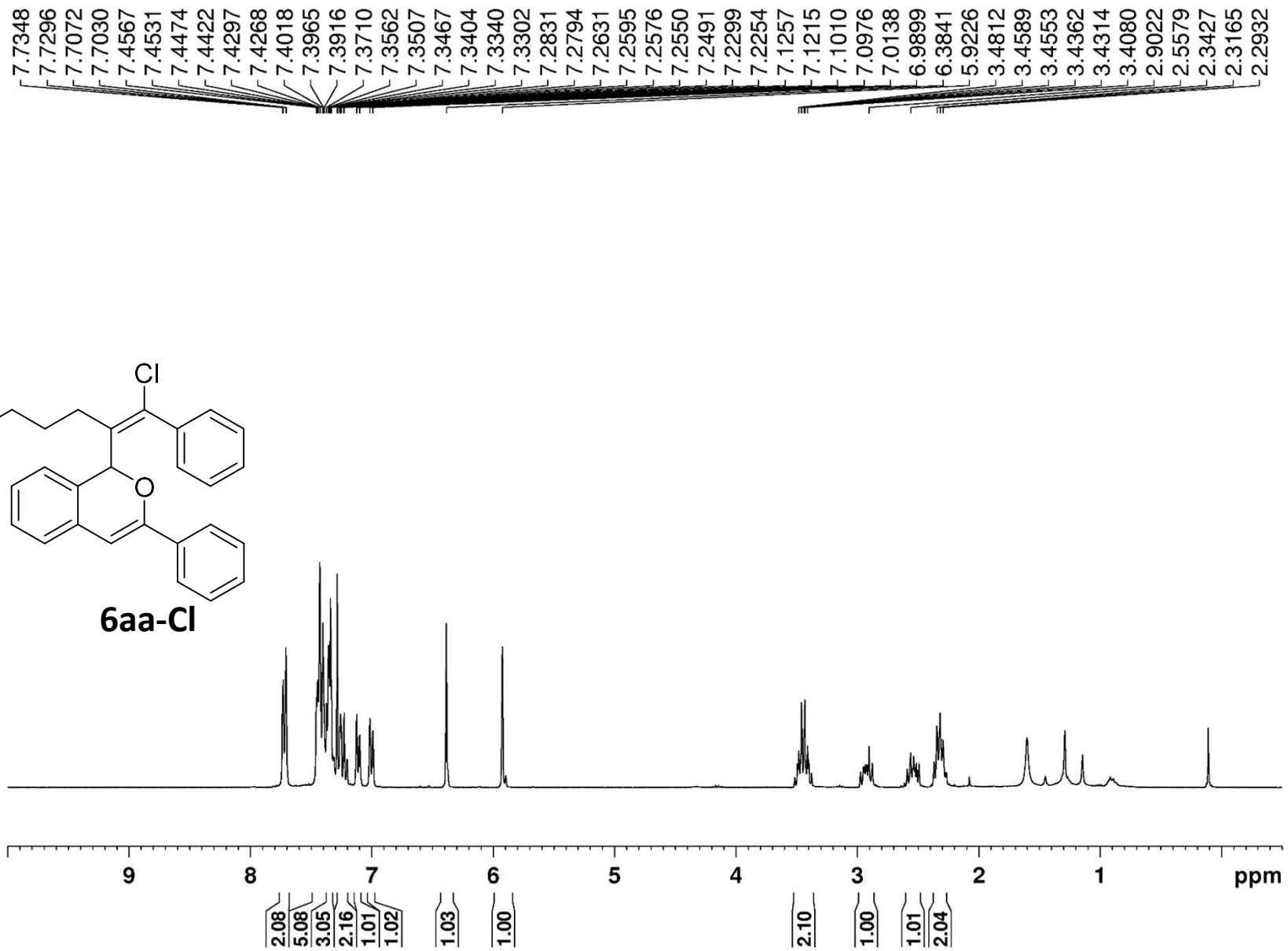
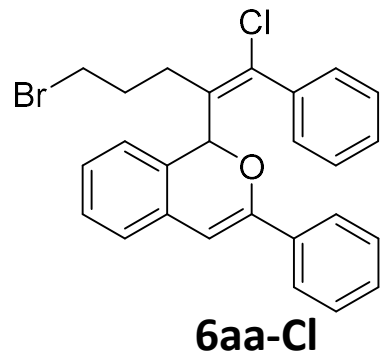


¹H NMR of compound **5-Cl** (300 MHz, CDCl₃)

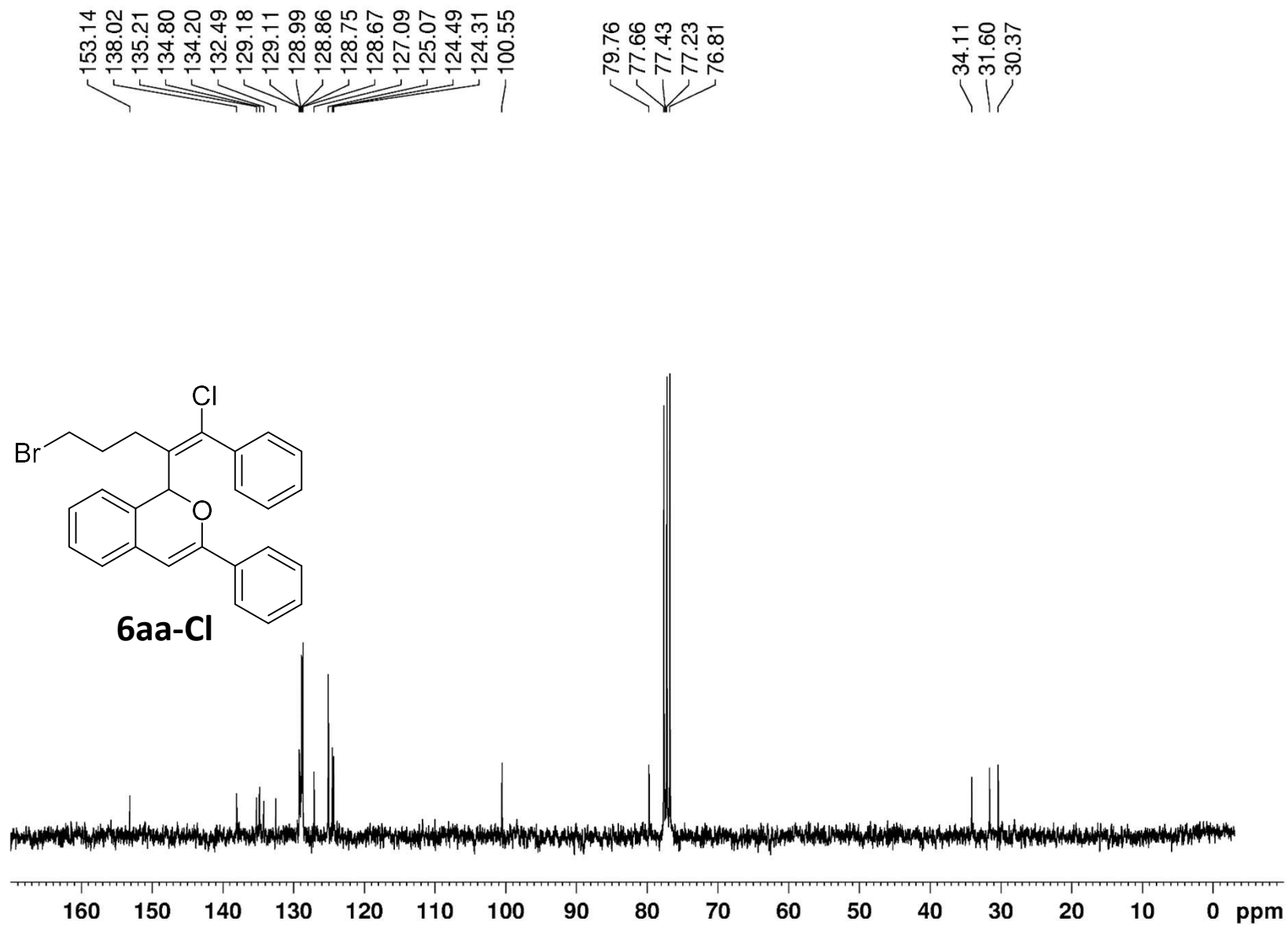


5-Cl

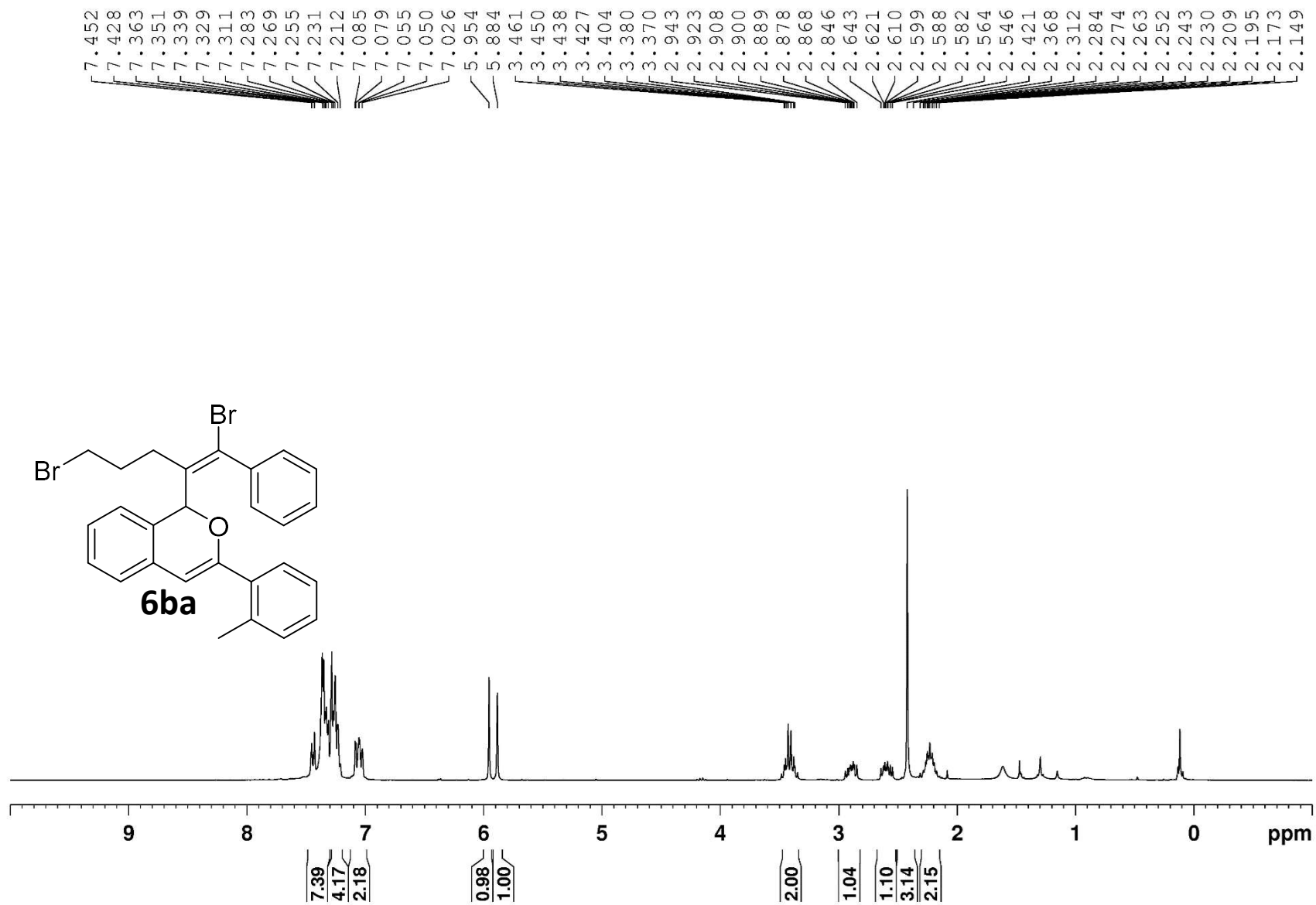
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **5-Cl** (75 MHz, CDCl_3)



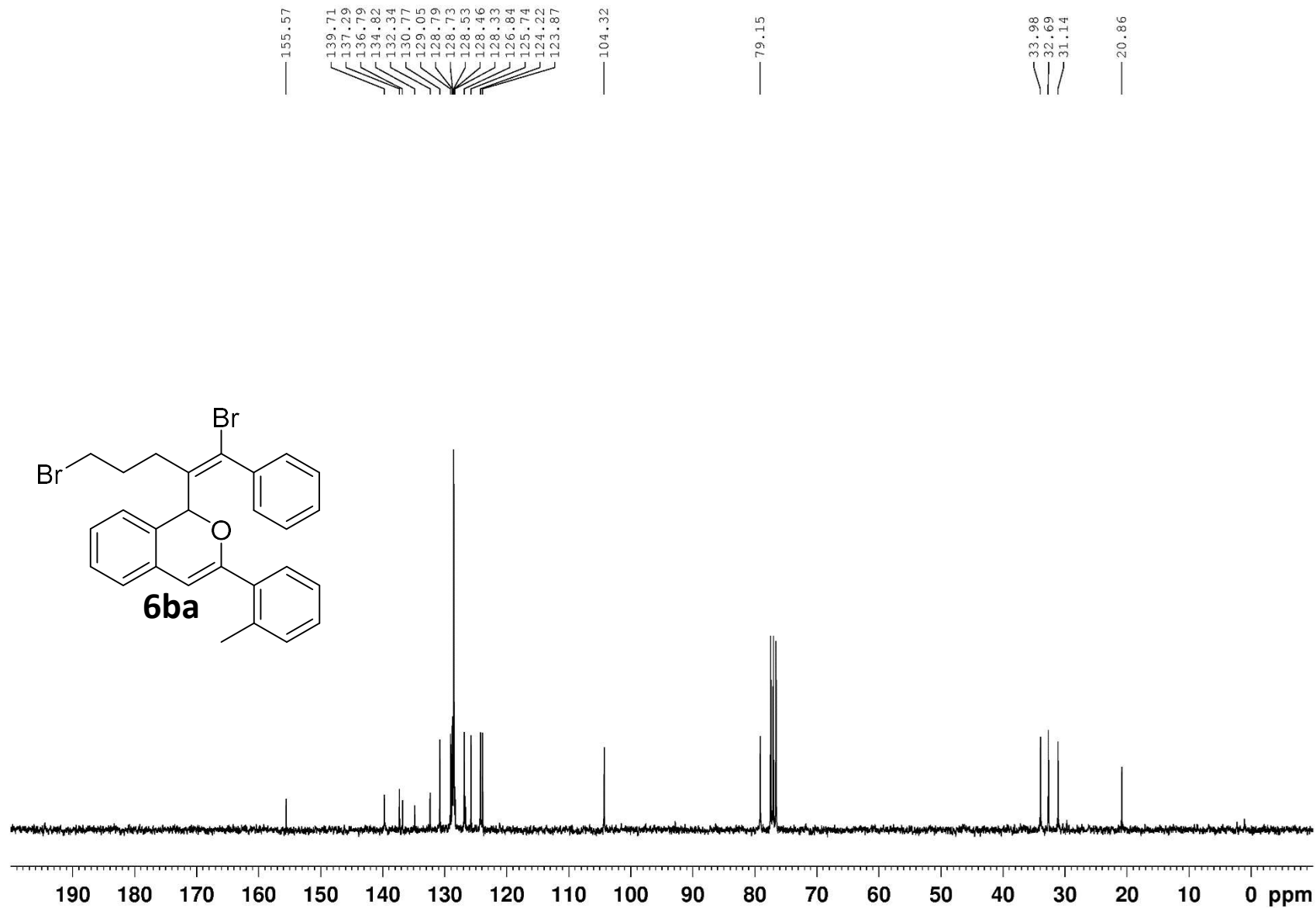
^1H NMR of compound **6aa-Cl** (300 MHz, CDCl_3)



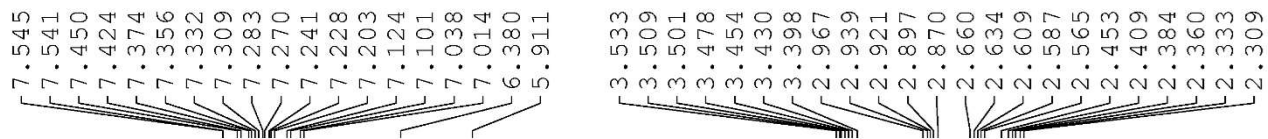
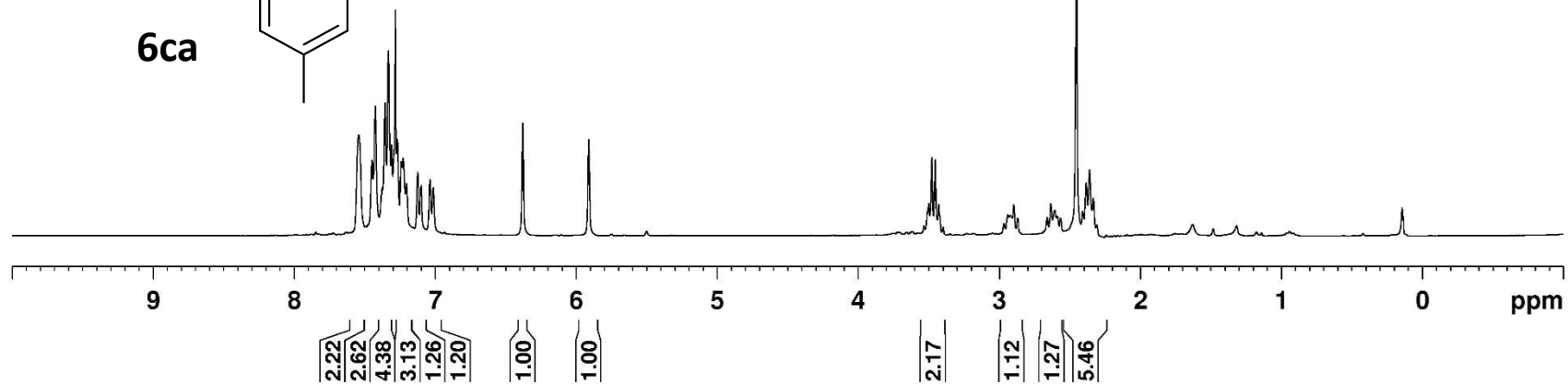
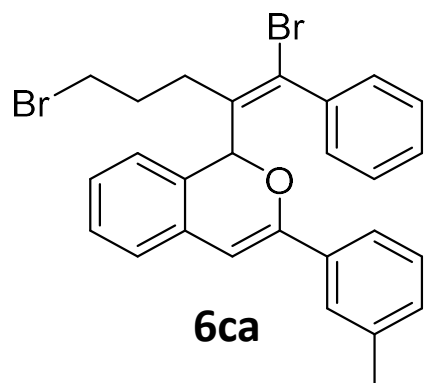
^{13}C NMR of compound **6aa-Cl** (75 MHz, CDCl_3)



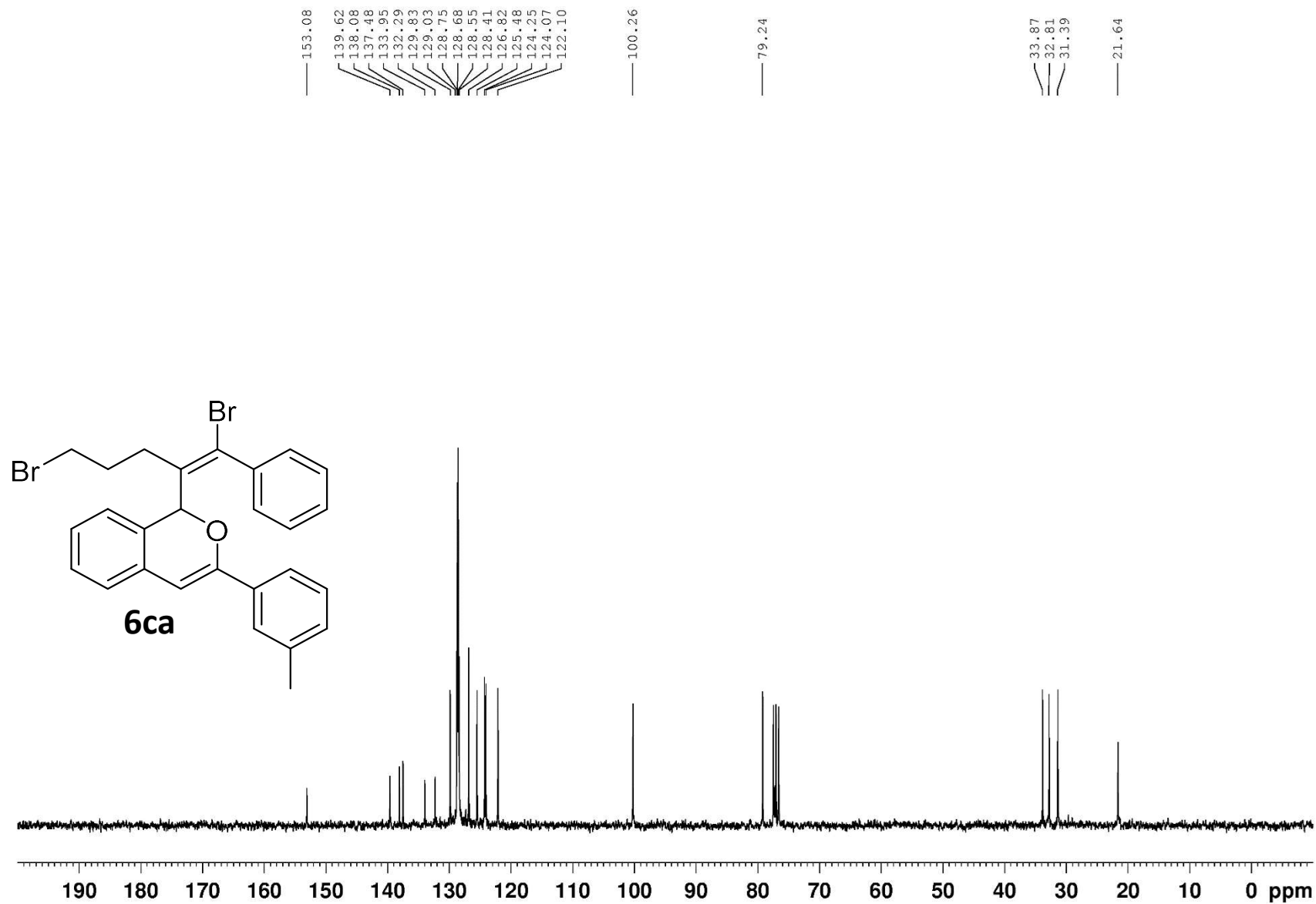
^1H NMR of compound **6ba** (300 MHz, CDCl_3)



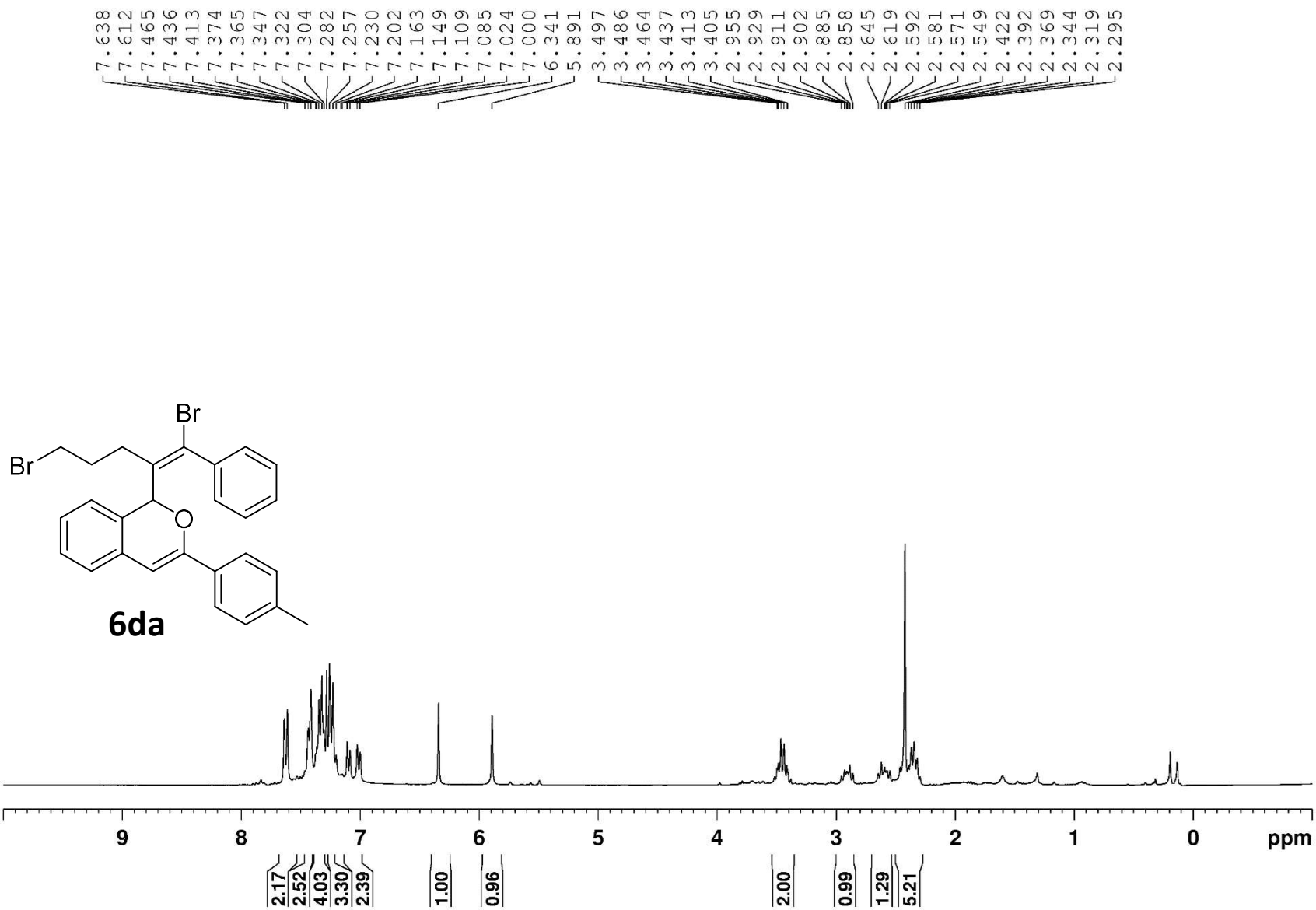
¹³C {¹H} NMR of compound **6ba** (75 MHz, CDCl₃)



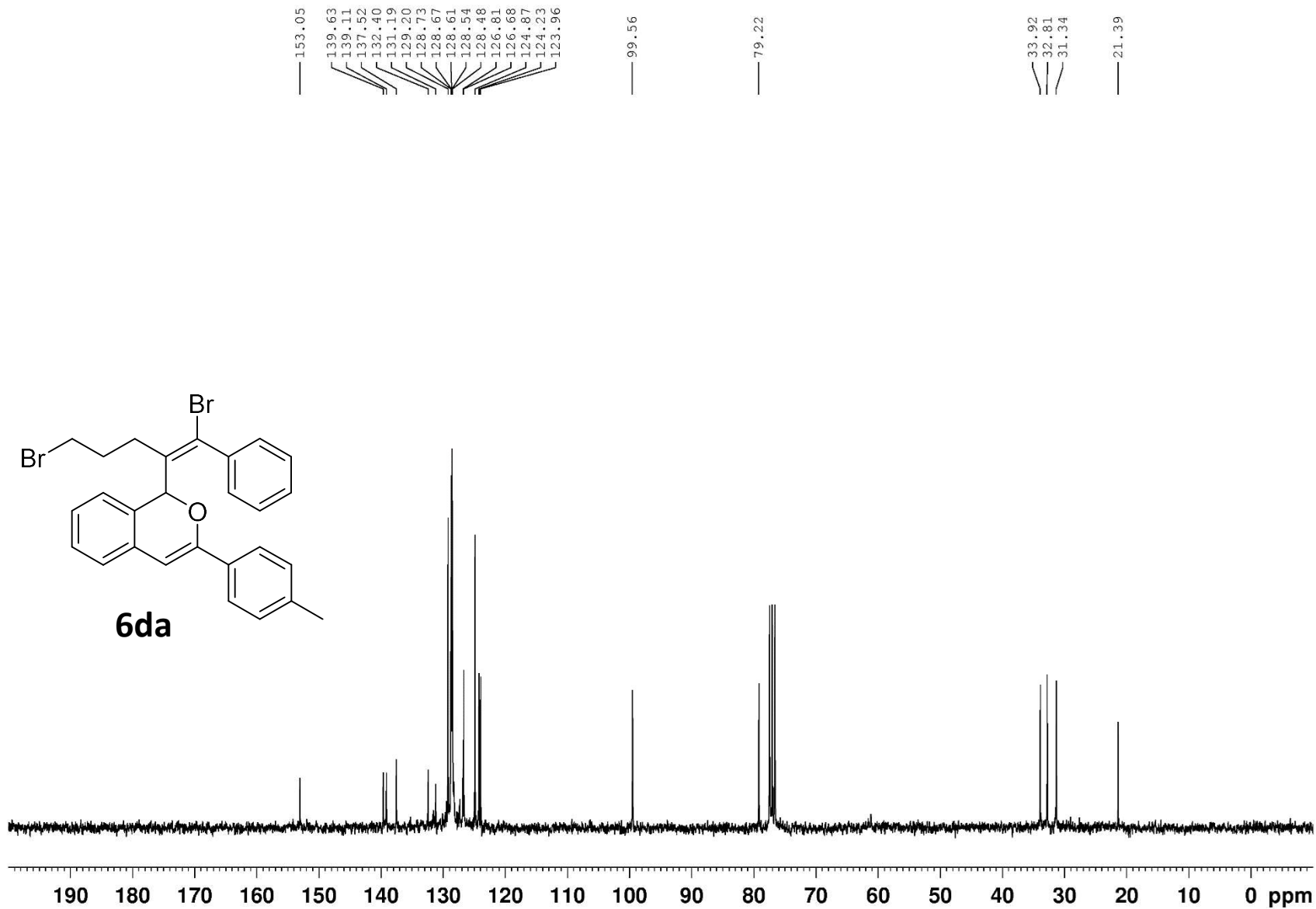
^1H NMR of compound **6ca** (300 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ca** (75 MHz, CDCl_3)

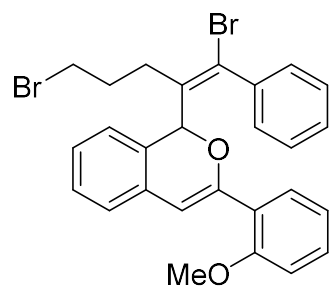


^1H NMR of compound **6da** (300 MHz, CDCl_3)

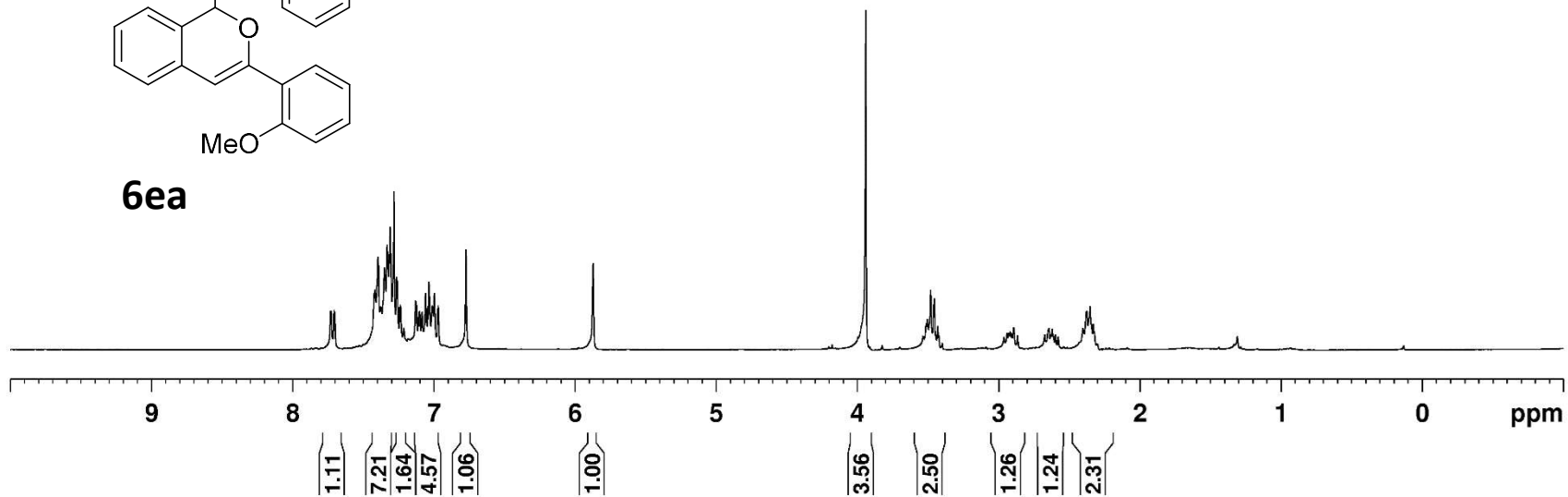


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6da** (75 MHz, CDCl_3)

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7.701
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7.418
7.398
7.393
7.383
7.378
7.372
7.350
7.331
7.309
7.282
7.264
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7.239
7.234
7.214
7.209
7.129
7.124
7.105
7.101
7.085
7.083
7.058
7.035
7.011
6.997
6.969
6.773
5.872
3.941
3.513
3.503
3.481
3.455
3.432
3.422
2.940
2.929
2.919
2.908
2.893
2.865
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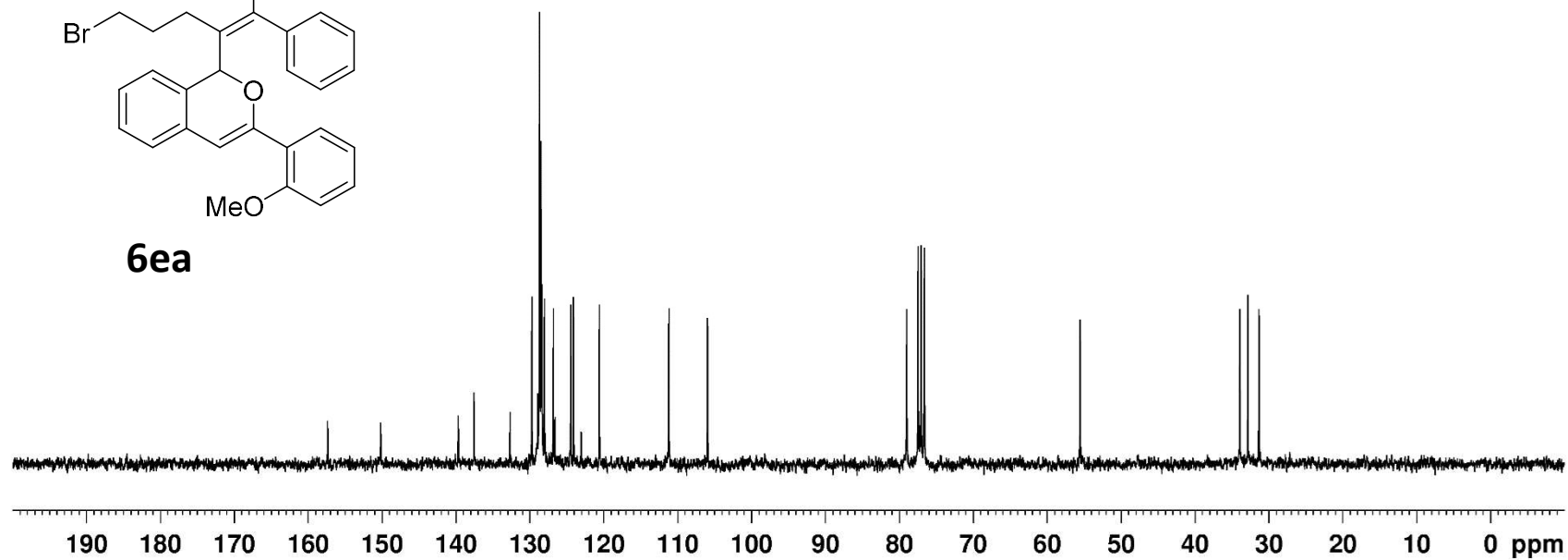
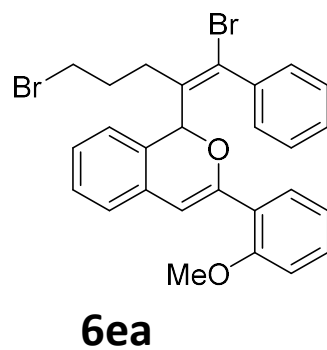


6ea

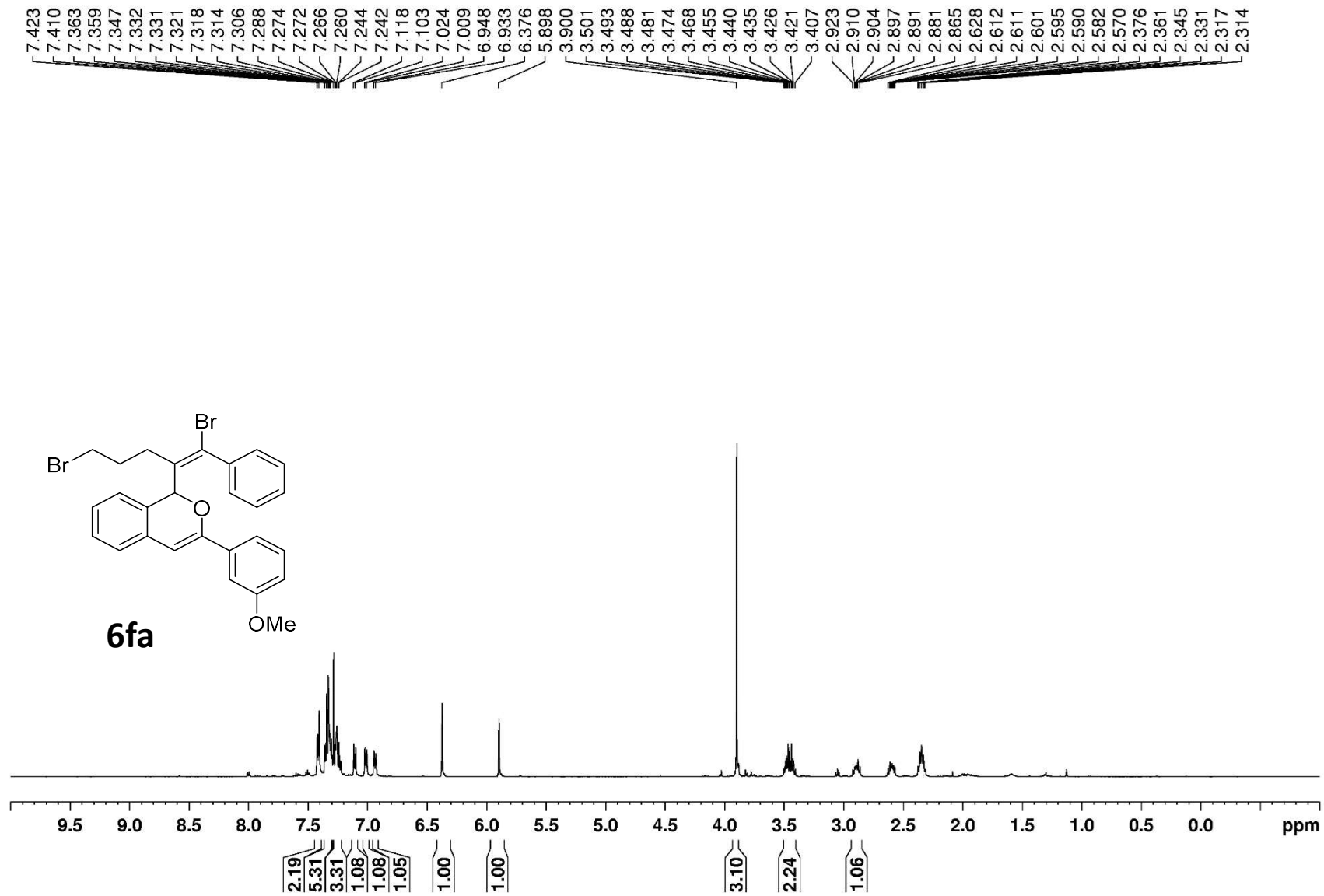


¹H NMR of compound **6ea** (300 MHz, CDCl₃)

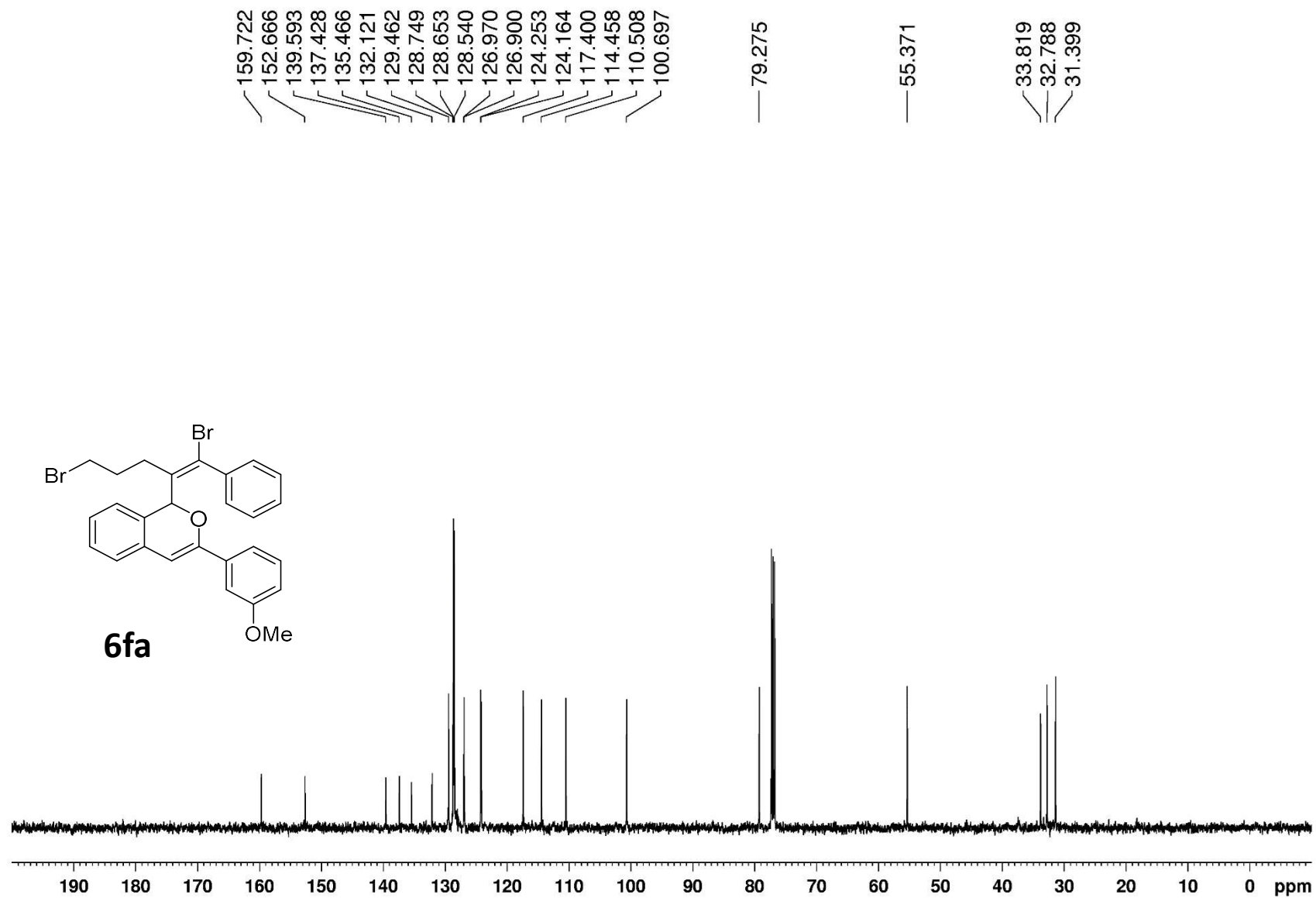
2ome



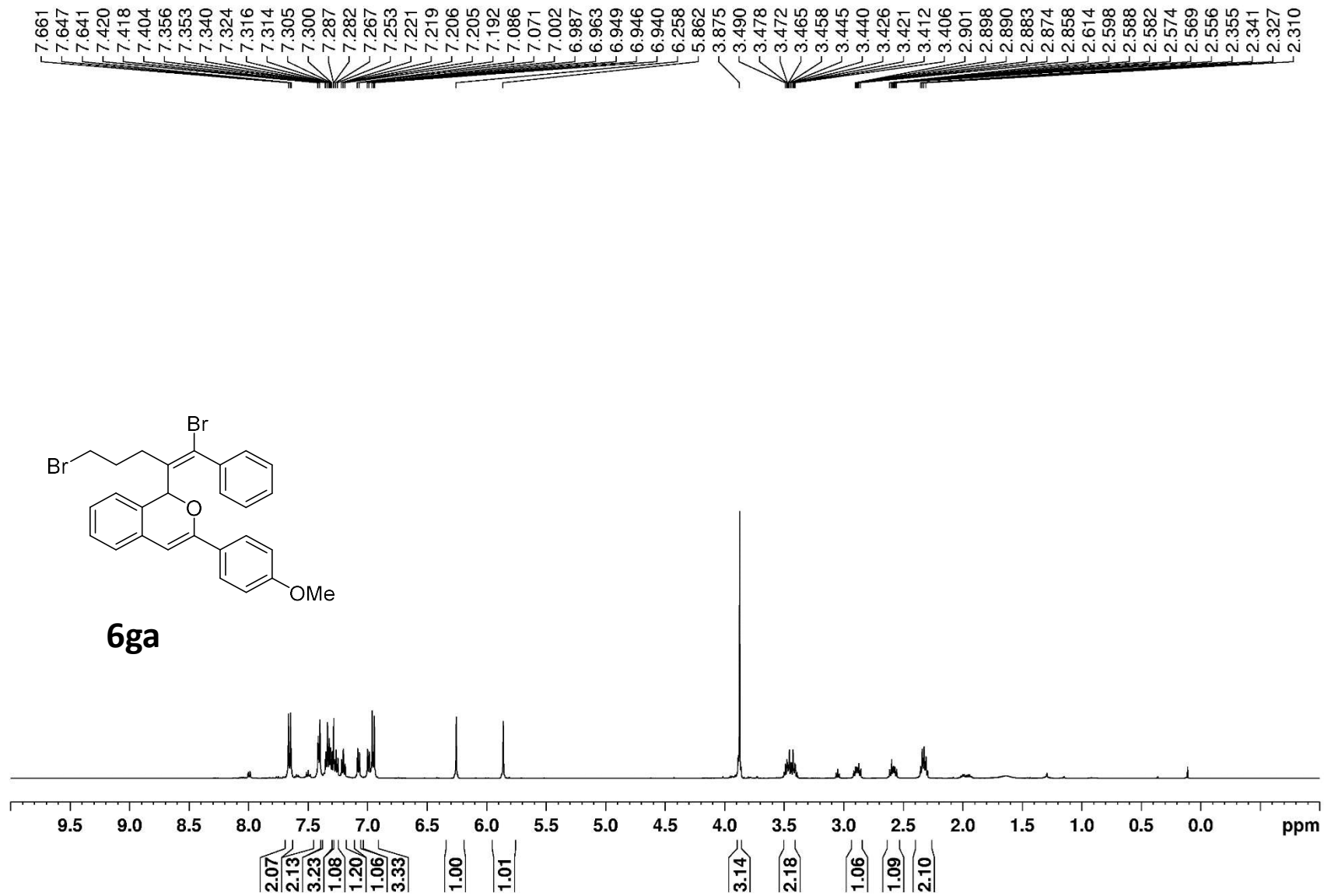
¹³C {¹H} NMR of compound **6ea** (75 MHz, CDCl₃)



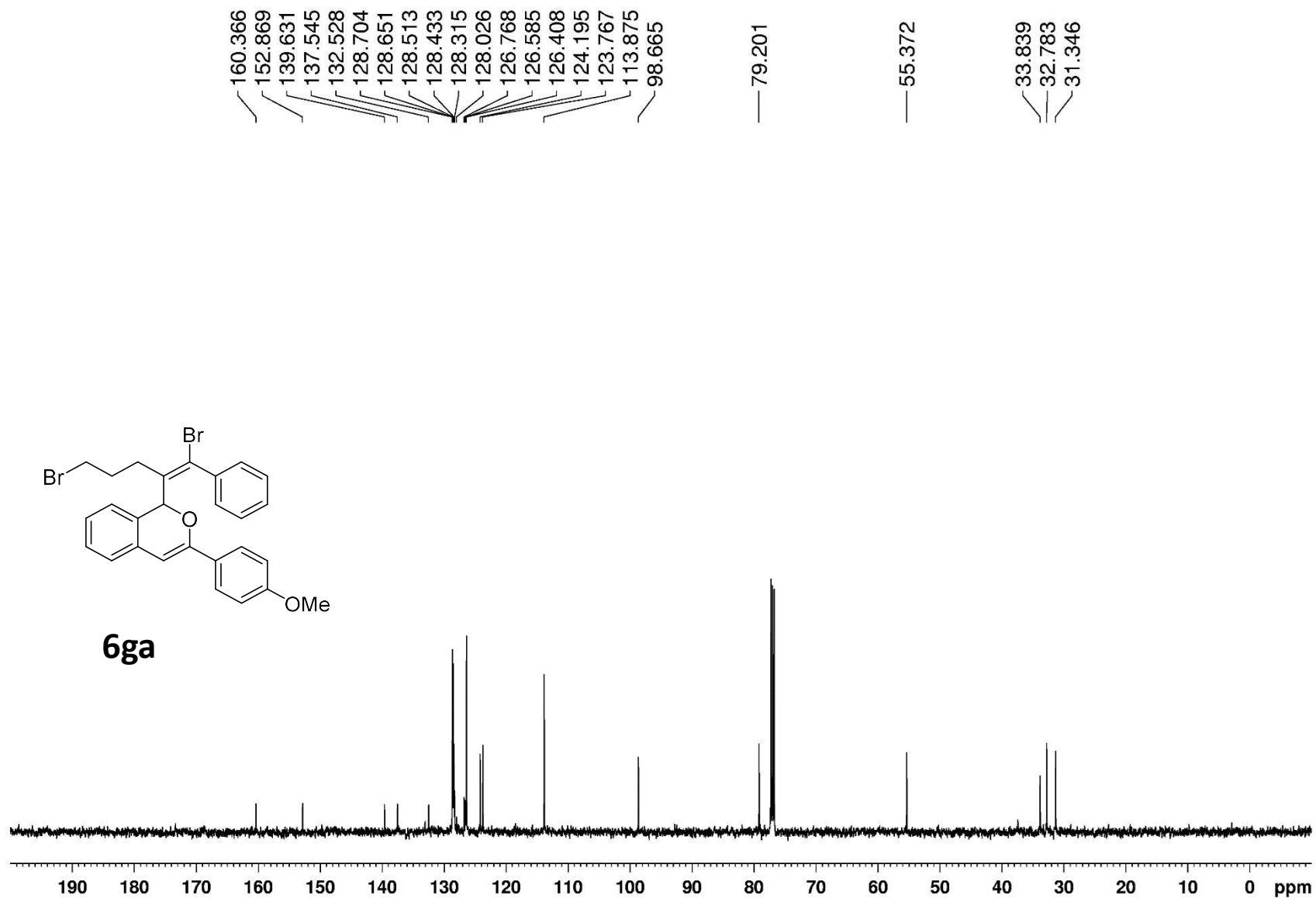
¹H NMR of compound **6fa** (300 MHz, CDCl₃)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6fa** (75 MHz, CDCl_3)

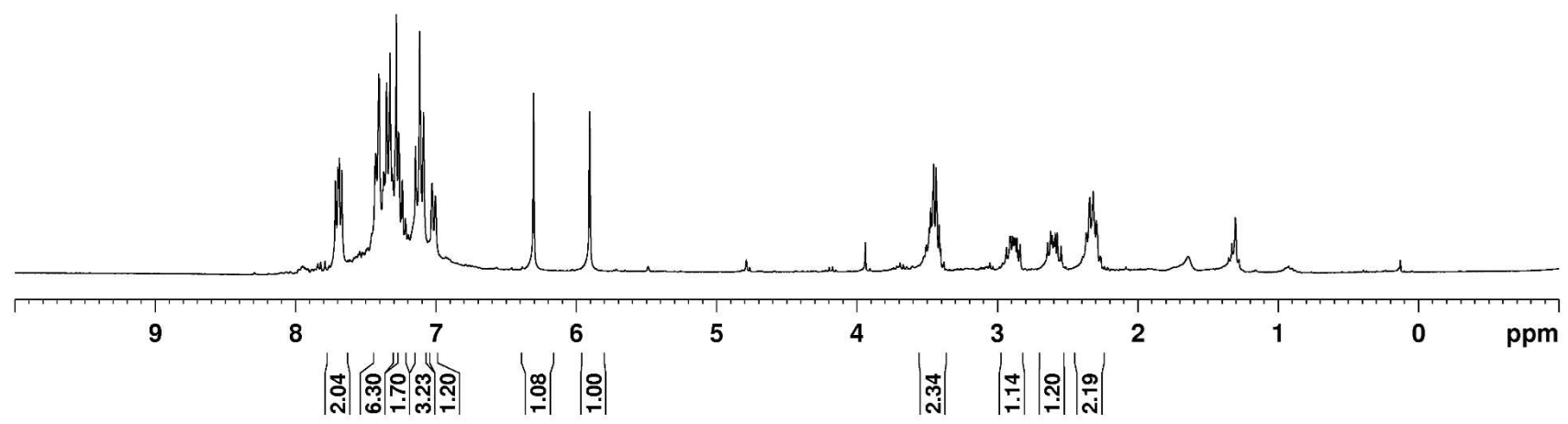
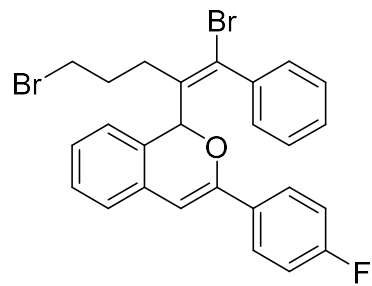


¹H NMR of compound **6ga** (300 MHz, CDCl₃)



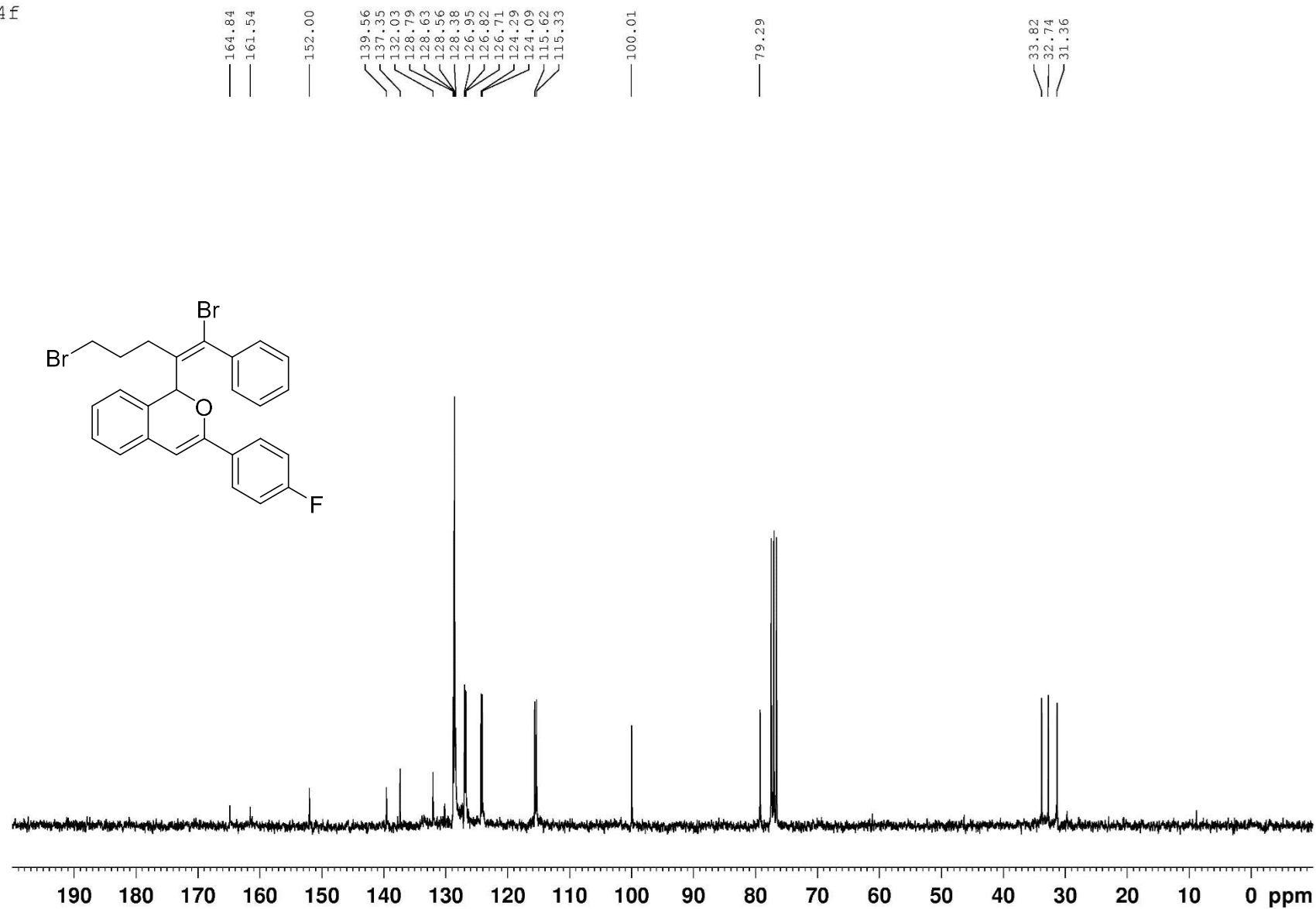
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ga** (75 MHz, CDCl_3)

7.718
7.711
7.699
7.692
7.688
7.677
7.670
7.434
7.429
7.408
7.403
7.380
7.371
7.351
7.327
7.309
7.282
7.268
7.262
7.243
7.238
7.218
7.214
7.196
7.146
7.139
7.116
7.088
7.027
7.004
6.304
5.904
3.506
3.485
3.475
3.453
3.437
3.414
3.404
2.935
2.906
2.892
2.881
2.872
2.858
2.838
2.642
2.620
2.610
2.599
2.588
2.573
2.545
2.366
2.342
2.316
2.308
2.293

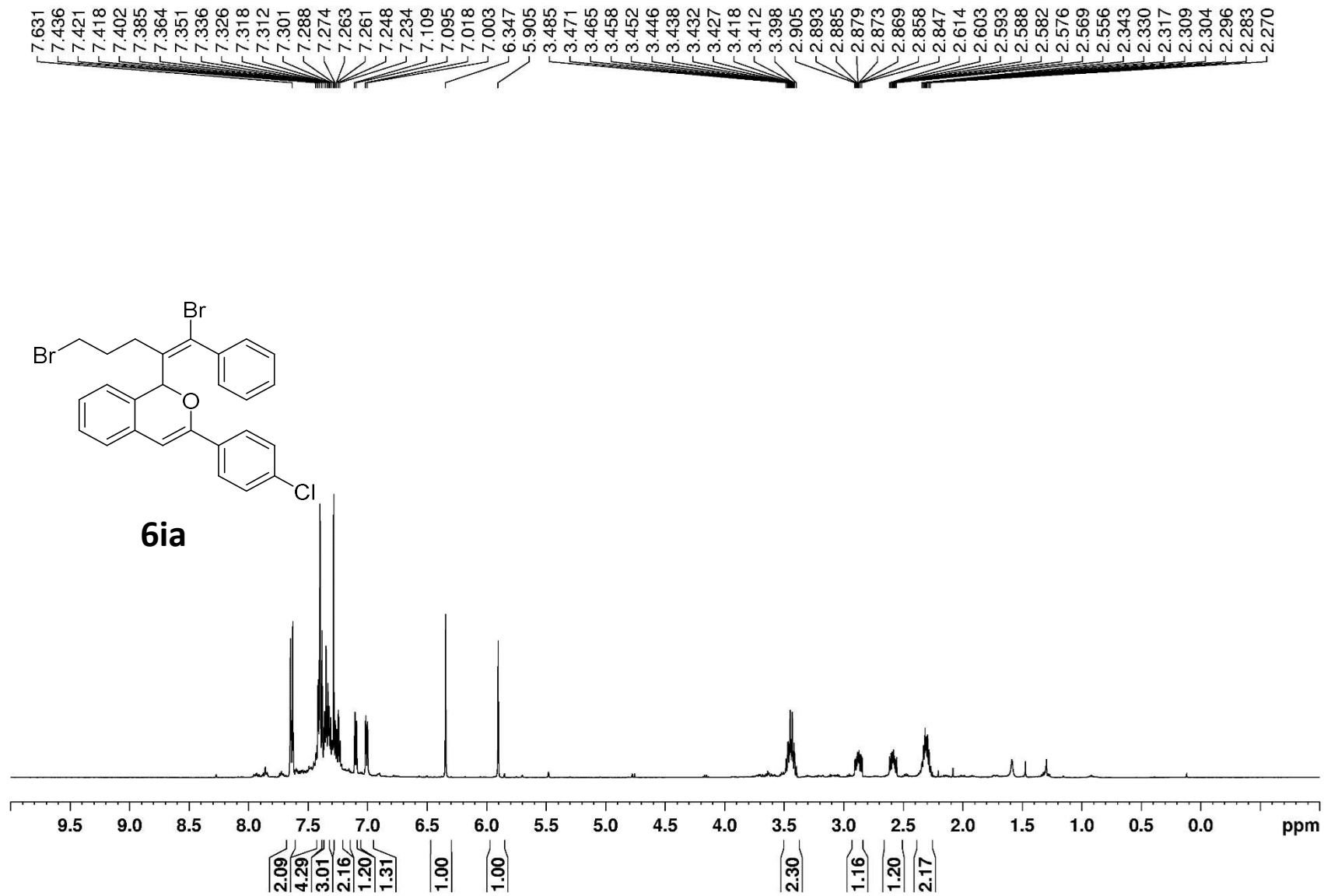


¹H NMR of compound **6ha** (300 MHz, CDCl₃)

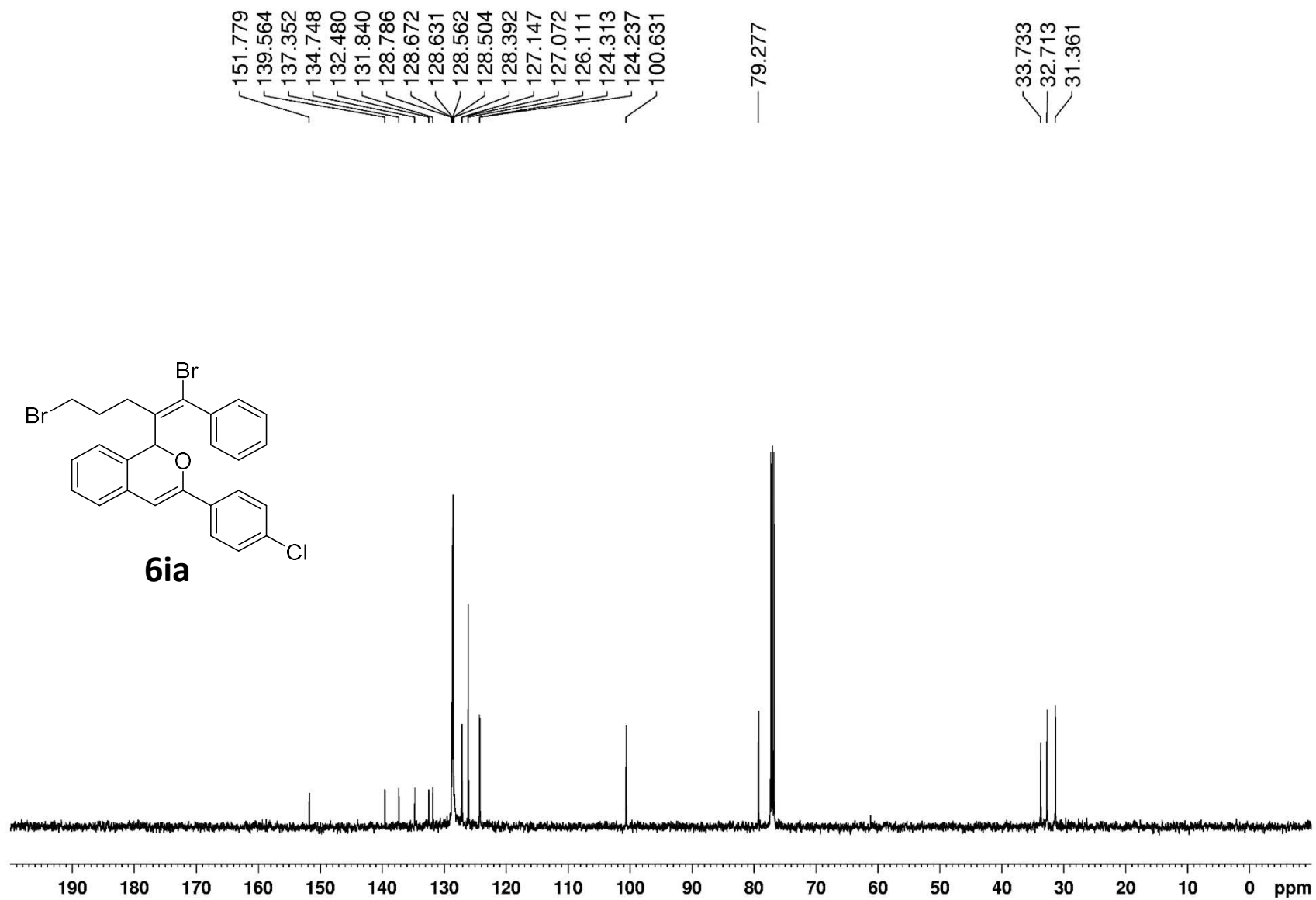
4 f



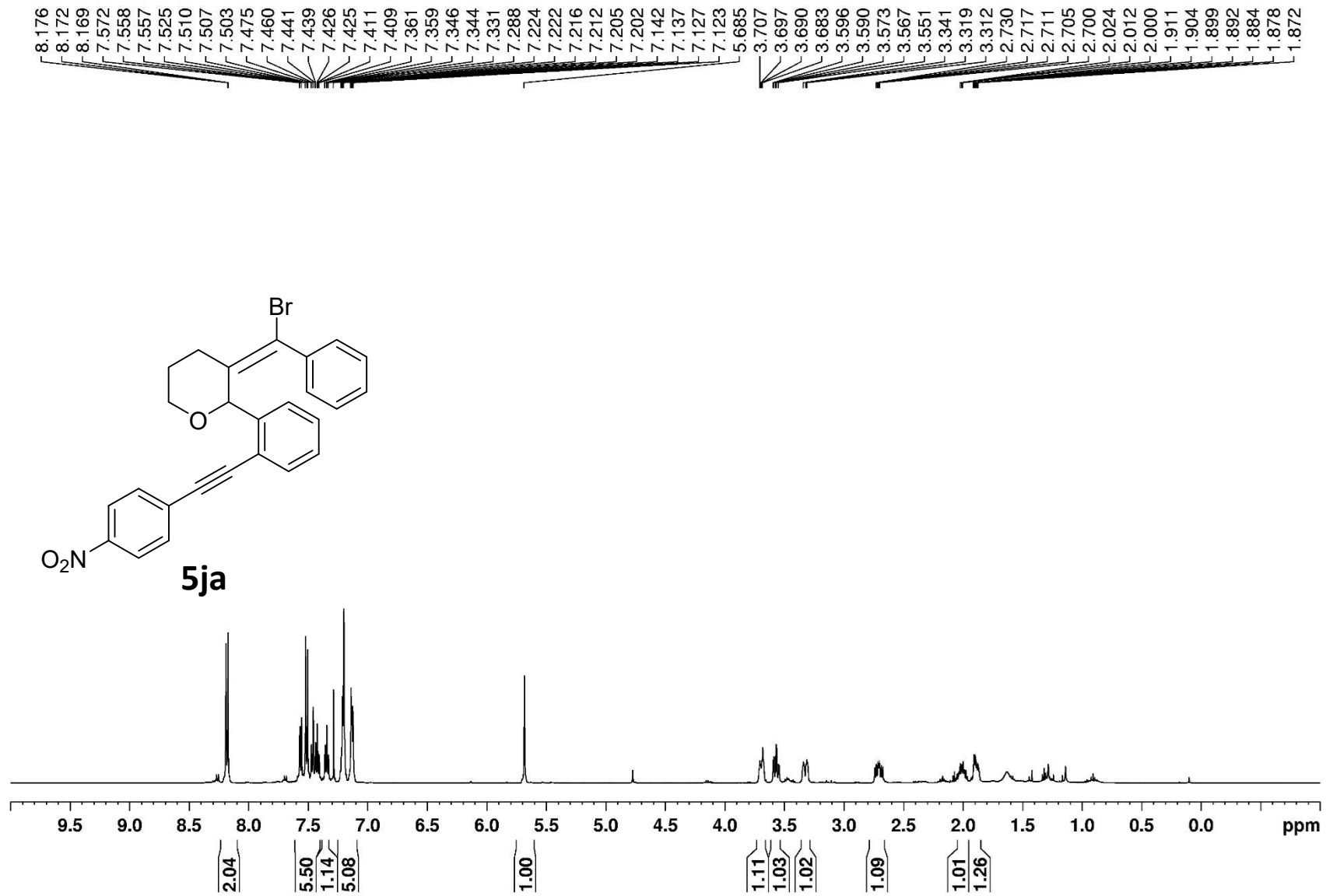
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ha** (75 MHz, CDCl_3)

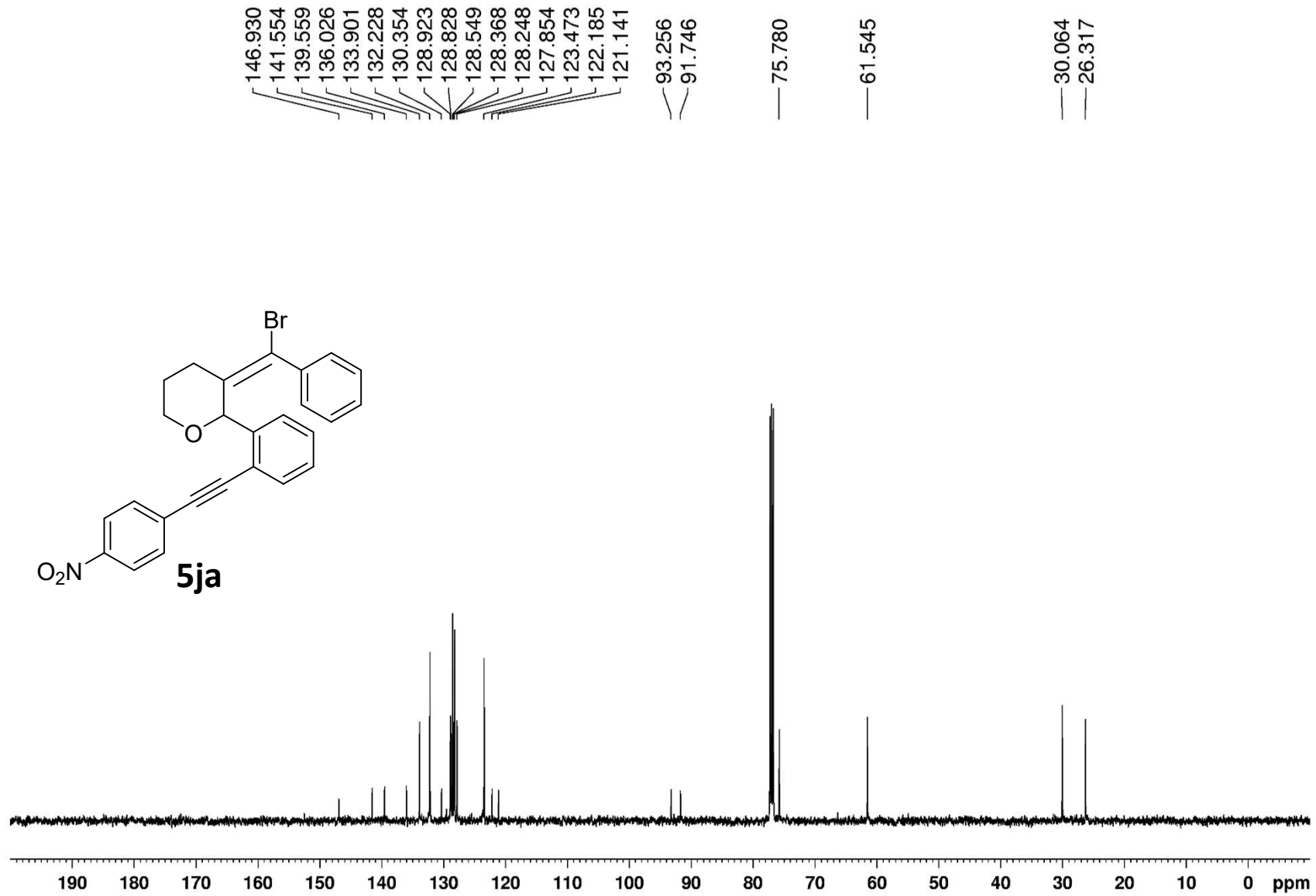


$^1\text{H NMR}$ of compound **6ia** (300 MHz, CDCl_3)

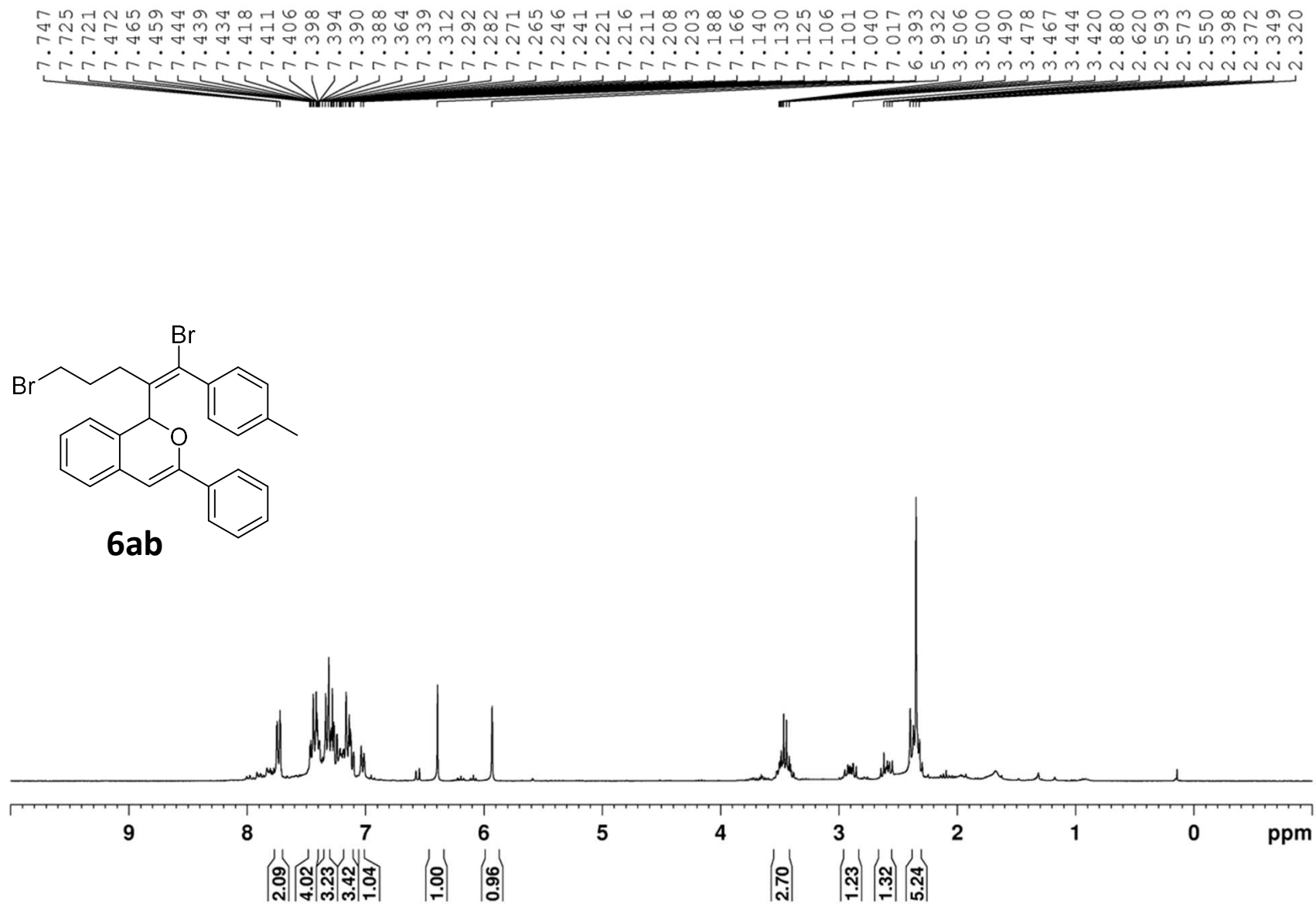


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ia** (75 MHz, CDCl_3)

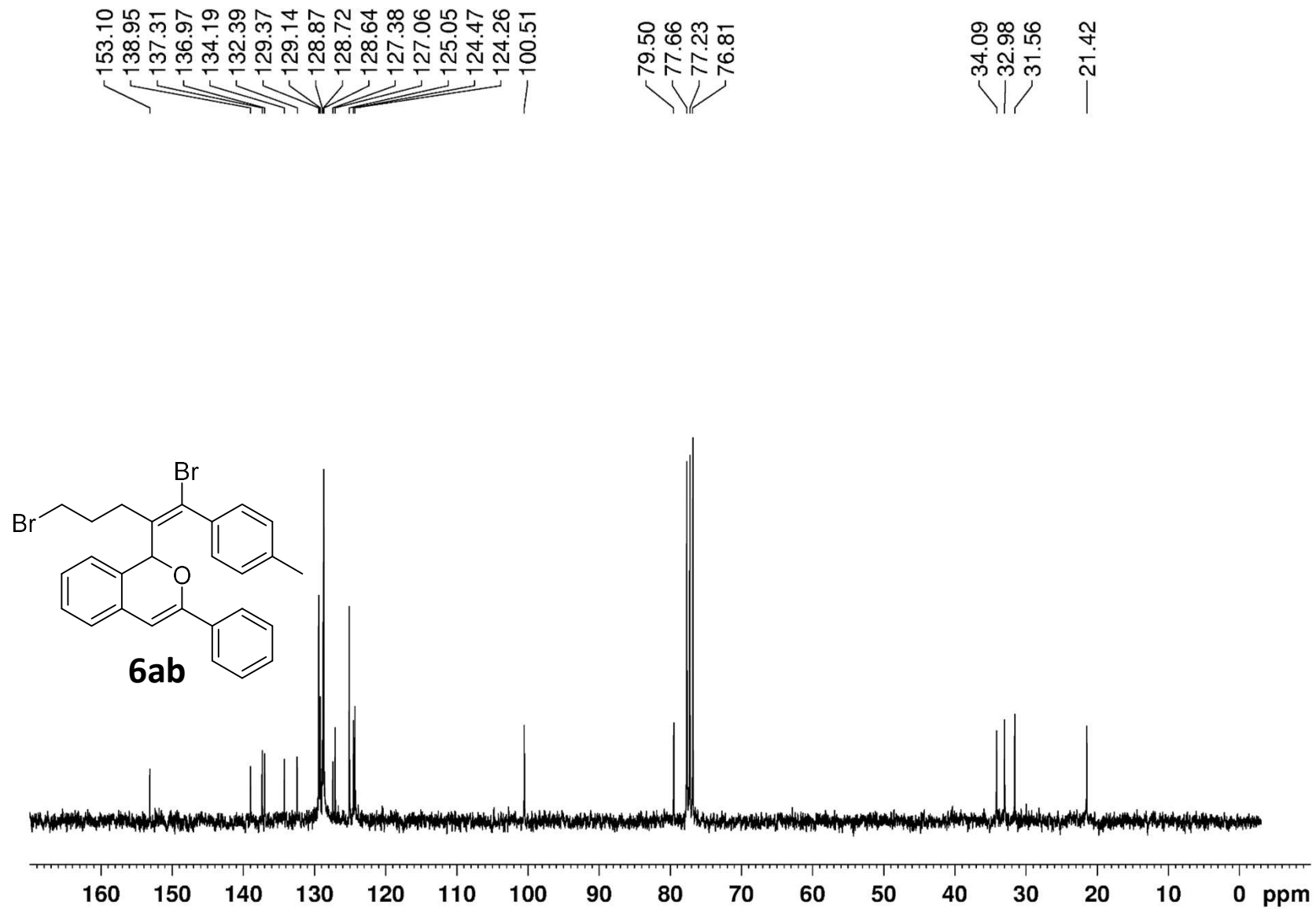




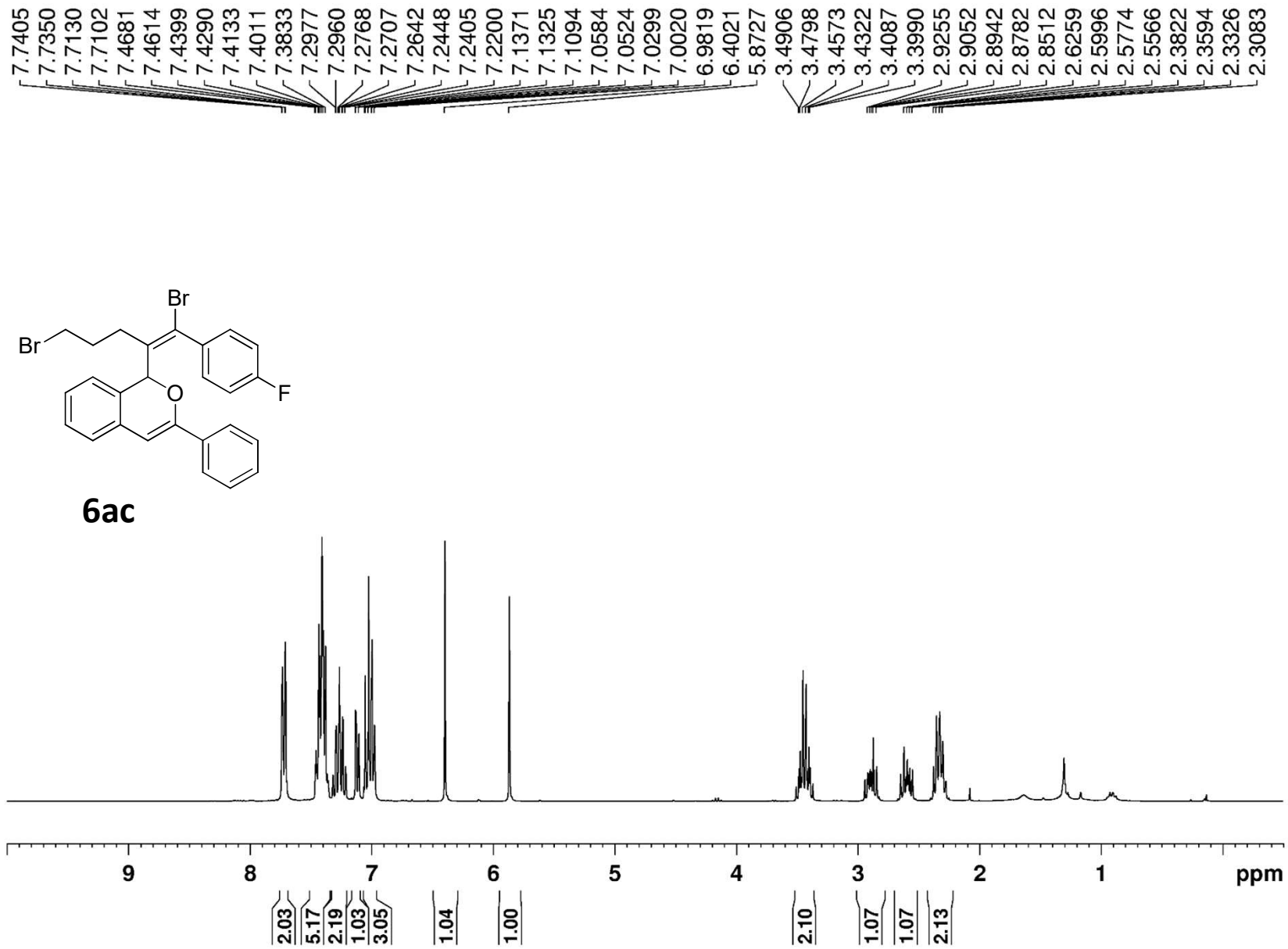
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **5ja** (75 MHz, CDCl_3)



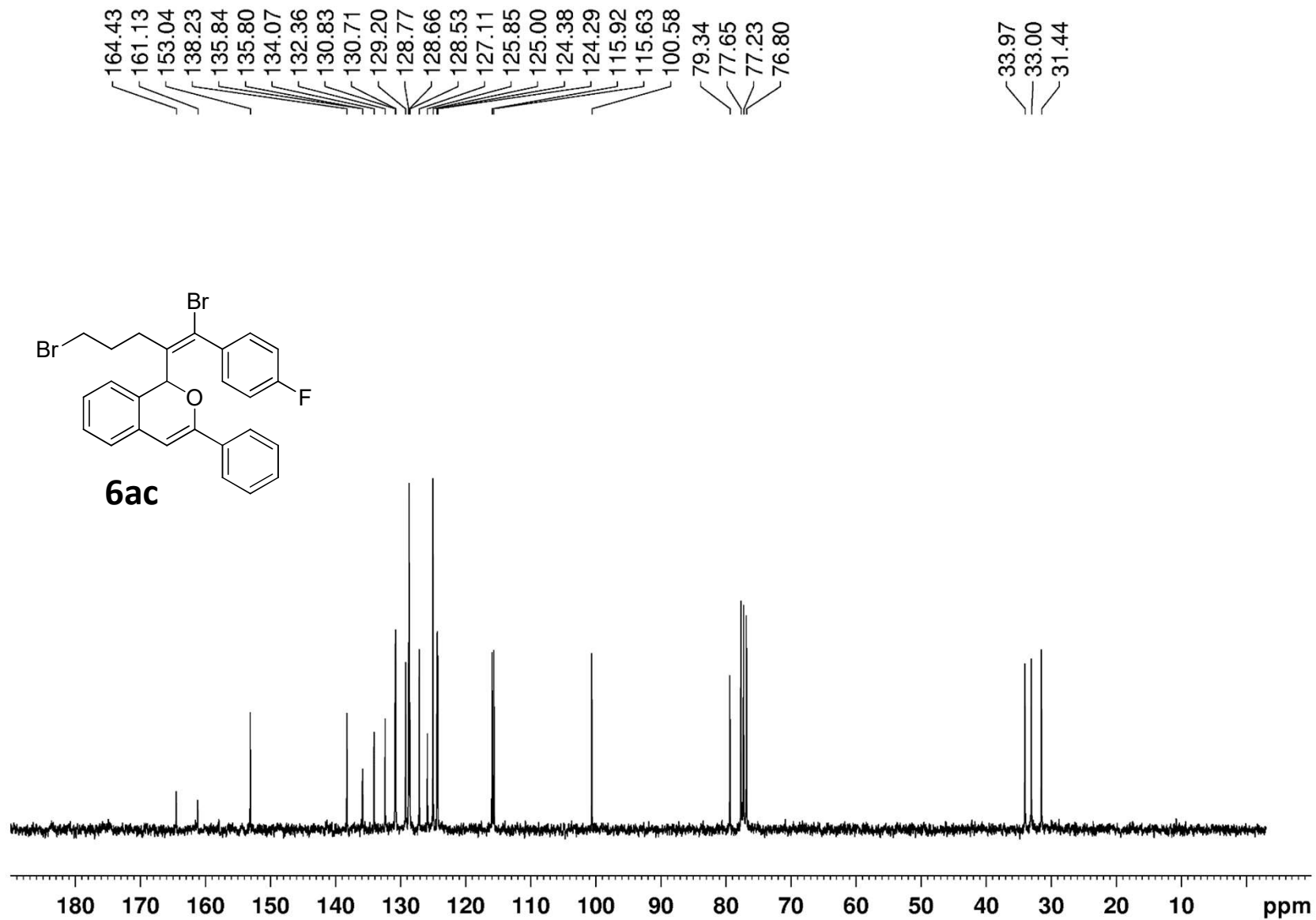
¹H NMR of compound **6ab** (300 MHz, CDCl₃)



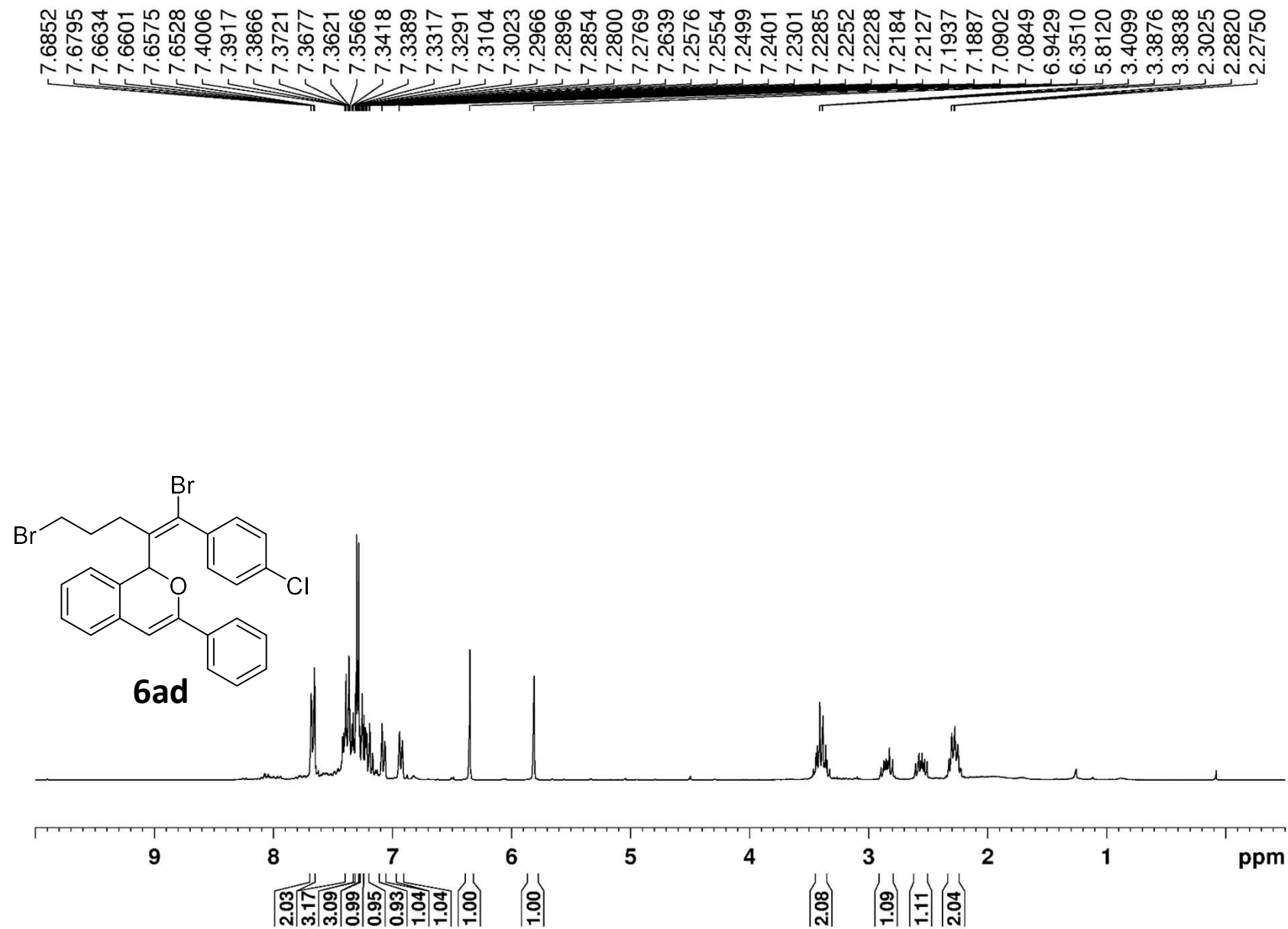
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ab** (75 MHz, CDCl_3)



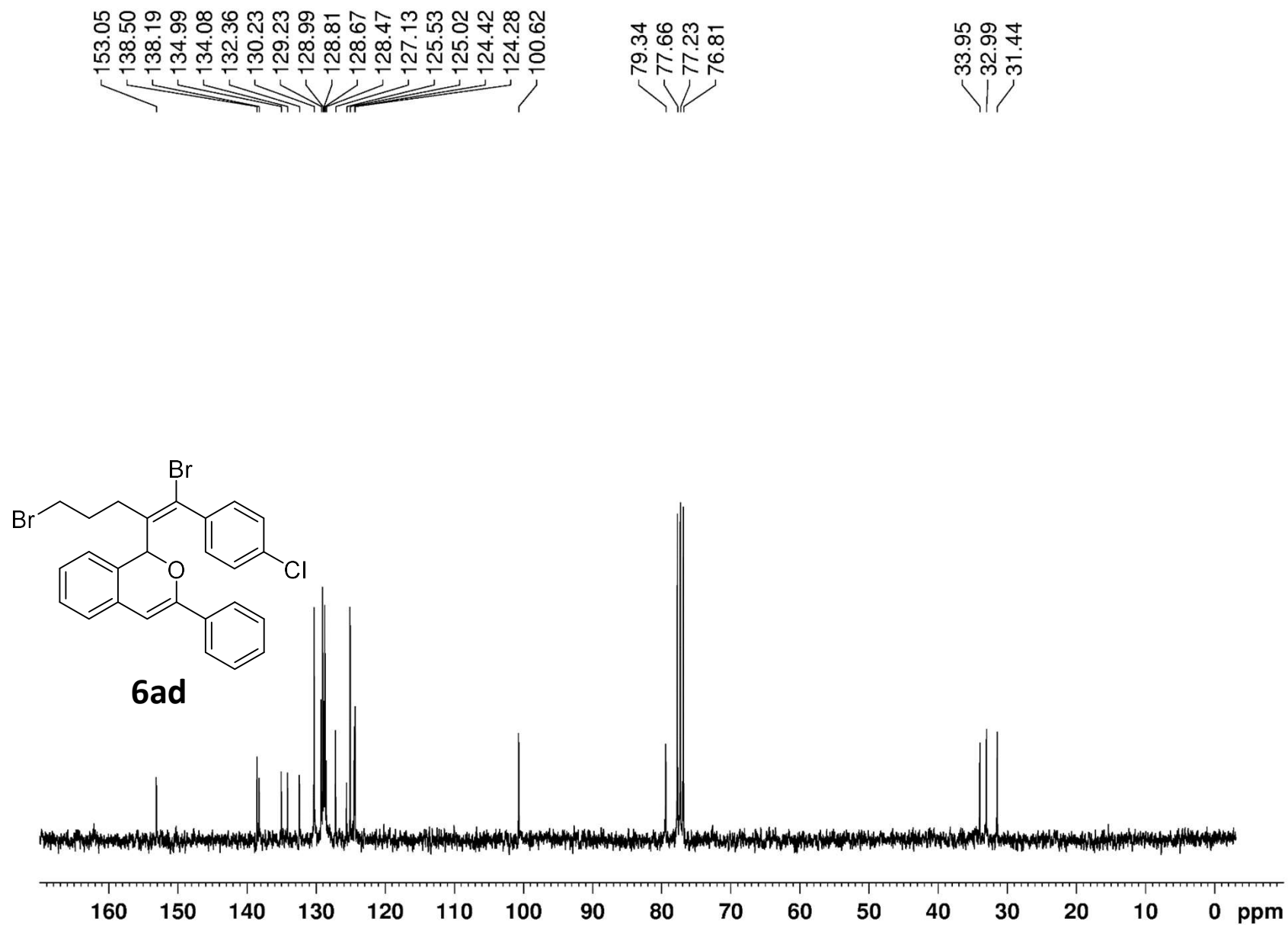
¹H NMR of compound **6ac** (300 MHz, CDCl₃)



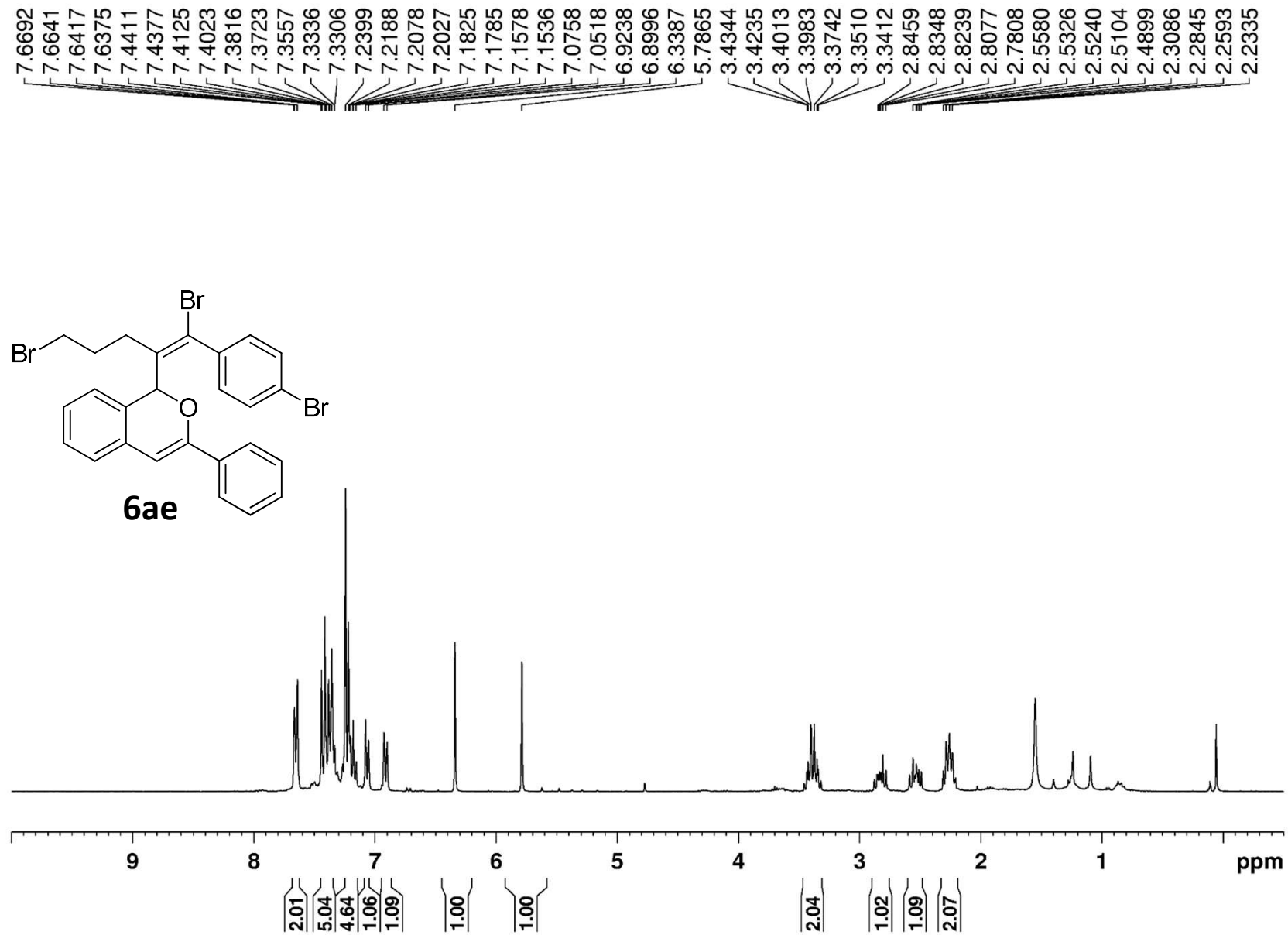
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ac** (75 MHz, CDCl_3)



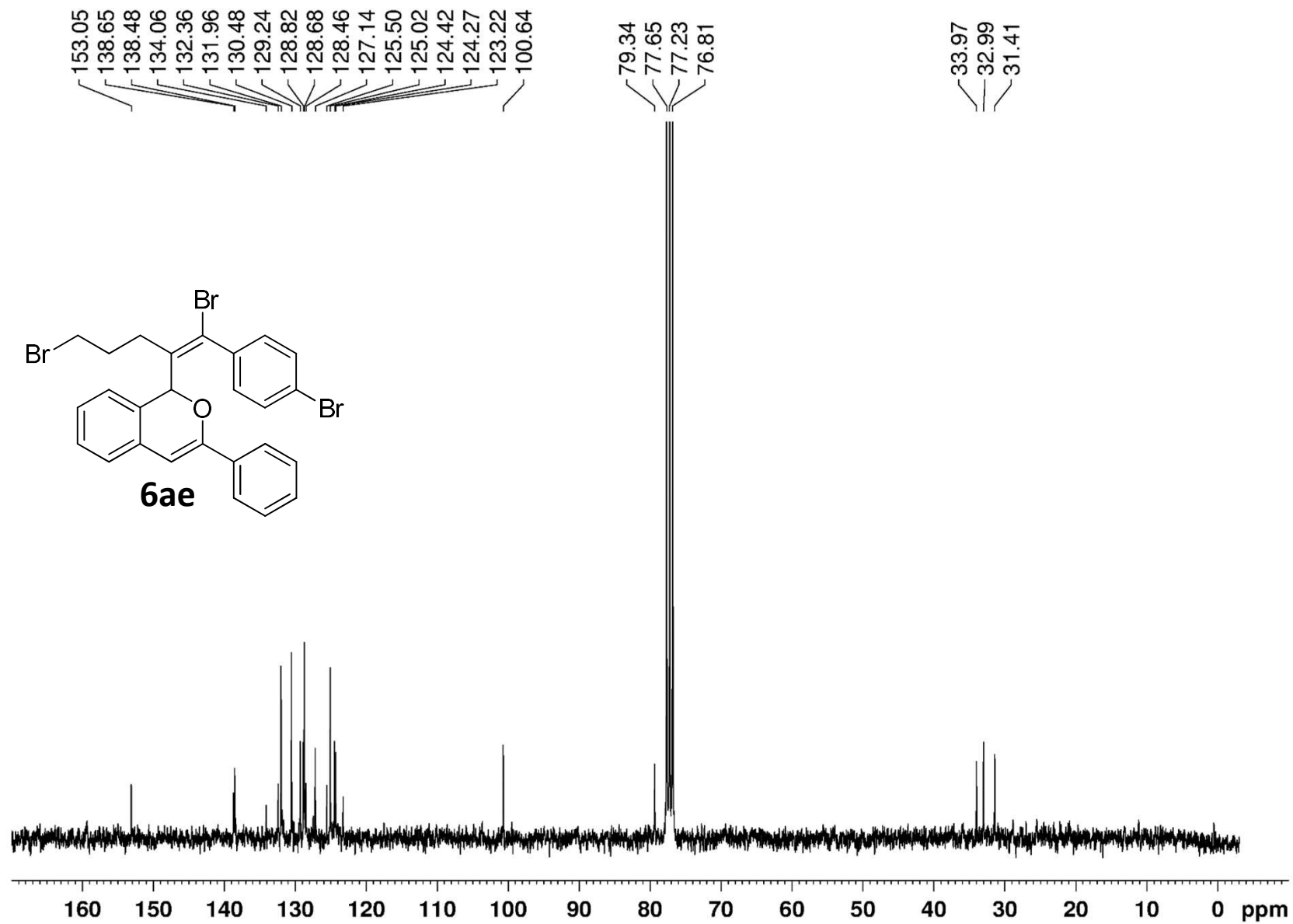
^1H NMR of compound **6ad** (300 MHz, CDCl_3)



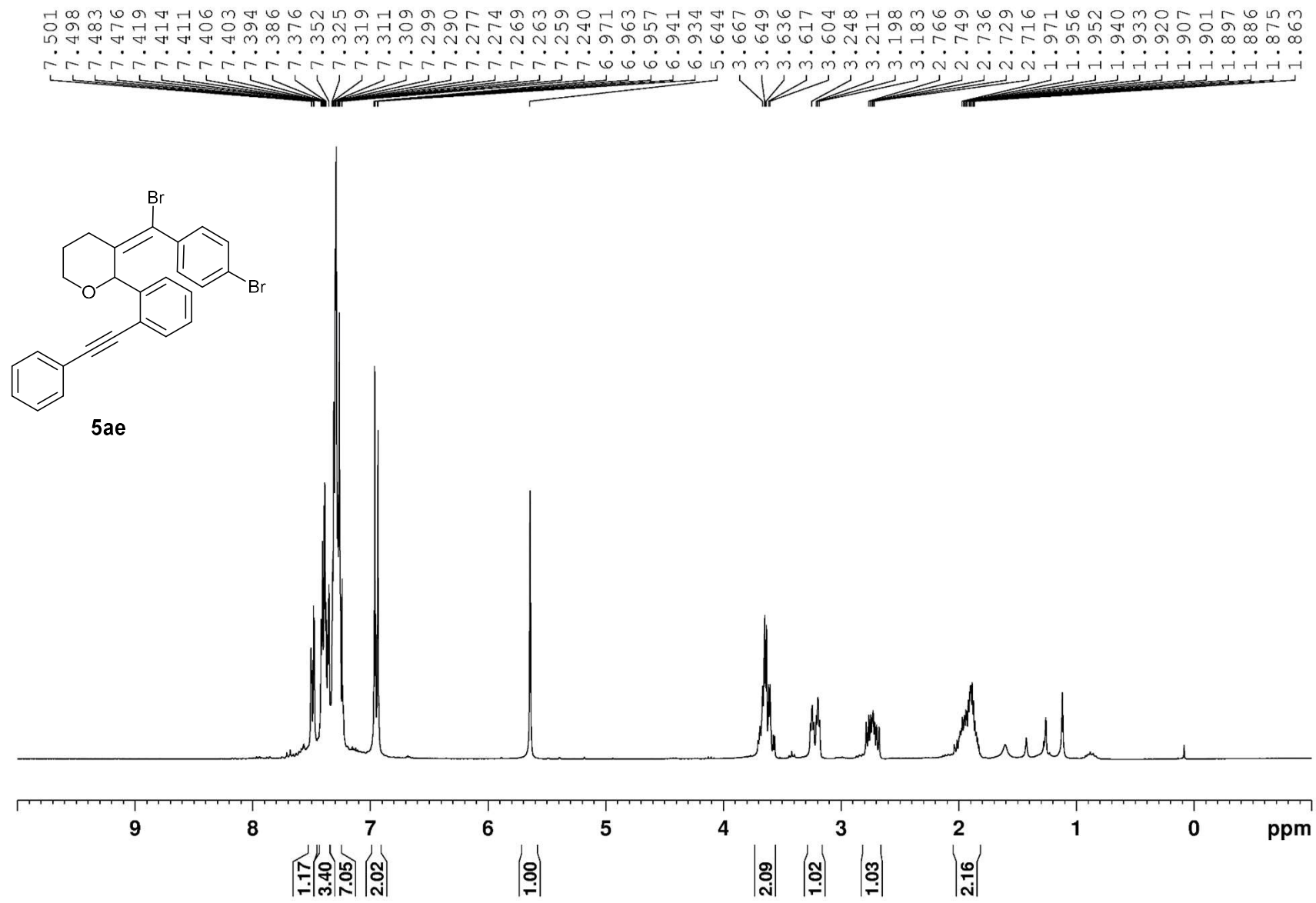
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ad** (75 MHz, CDCl_3)



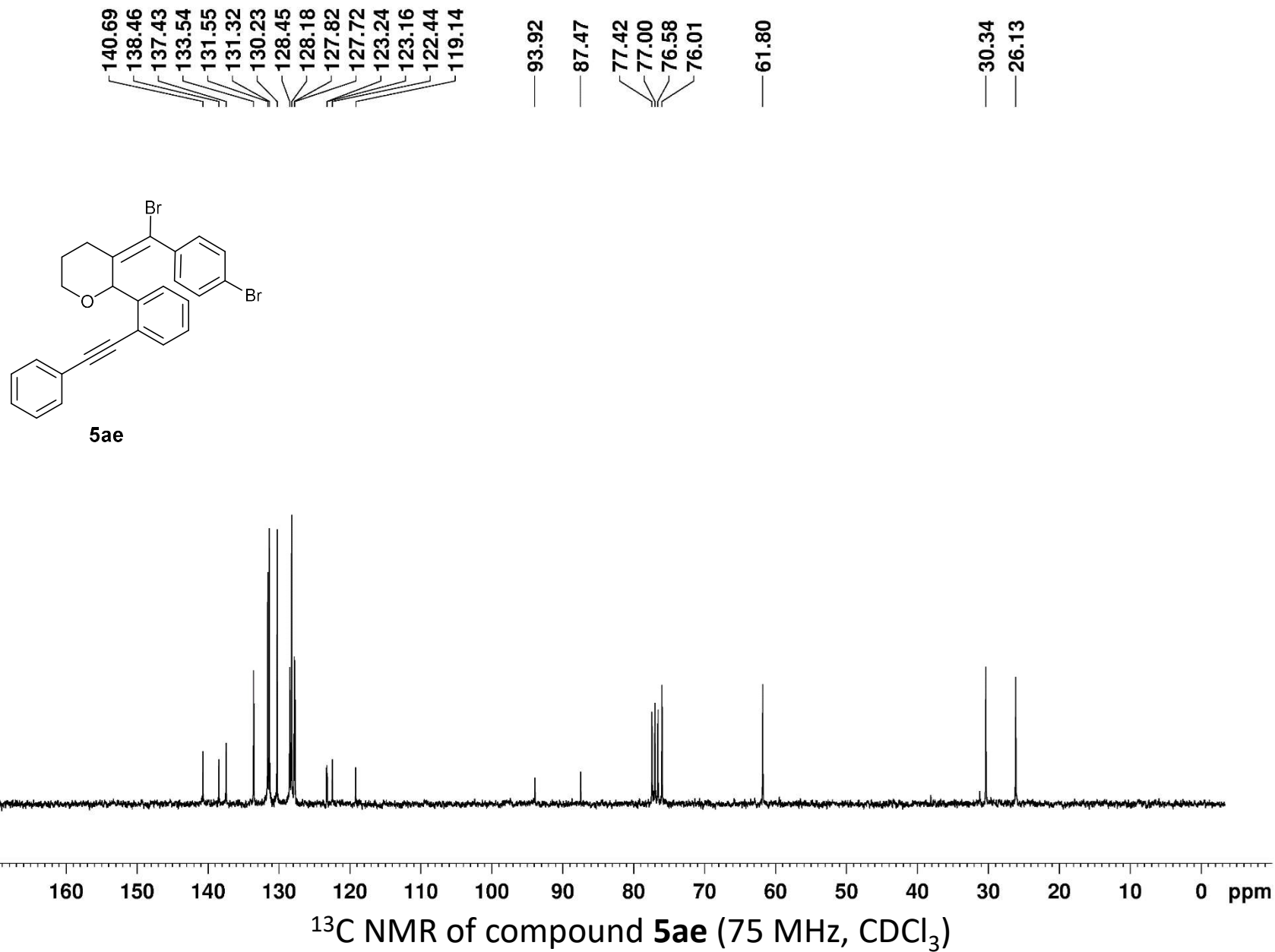
^1H NMR of compound **6ae** (300 MHz, CDCl_3)

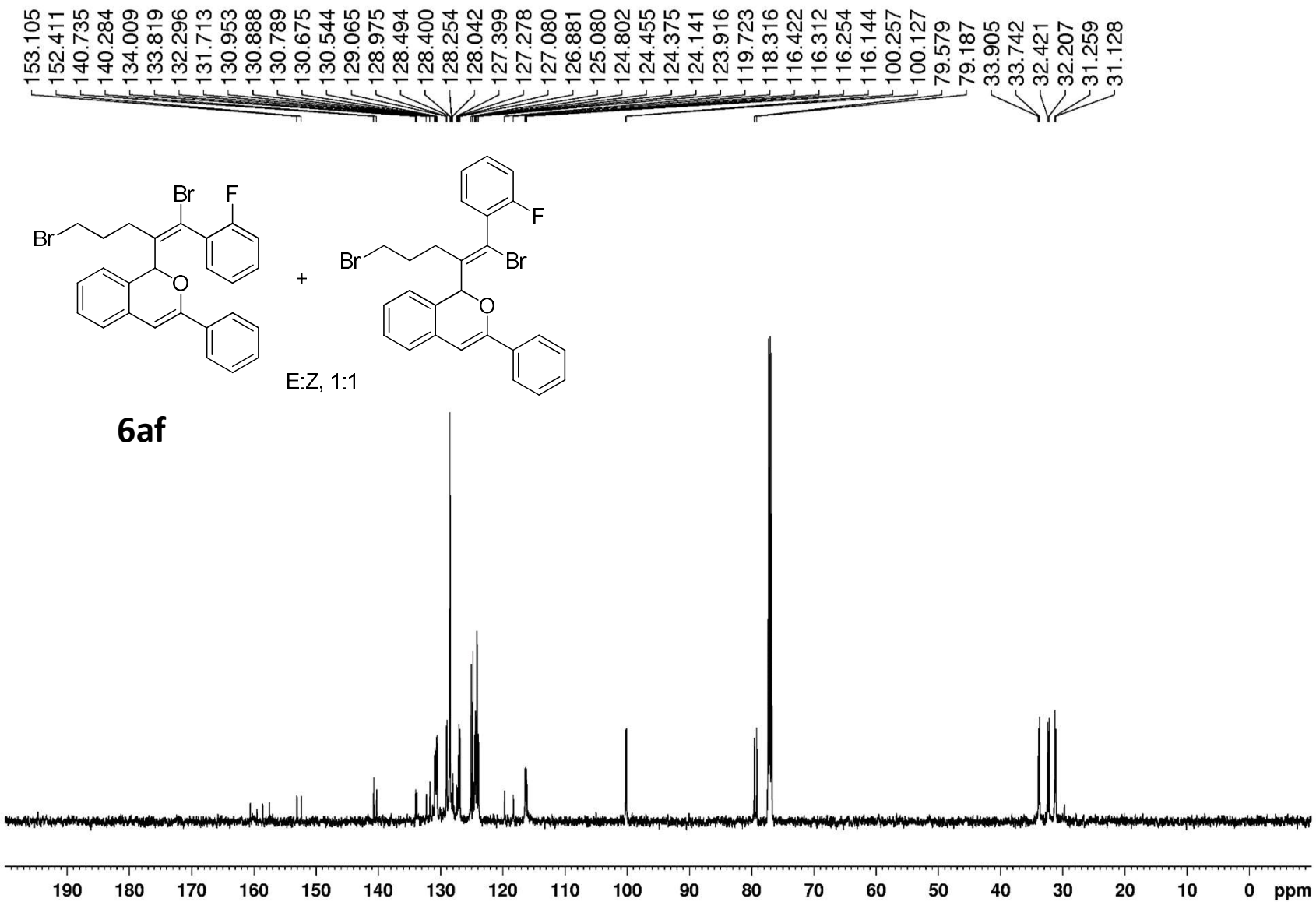


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ae** (75 MHz, CDCl_3)

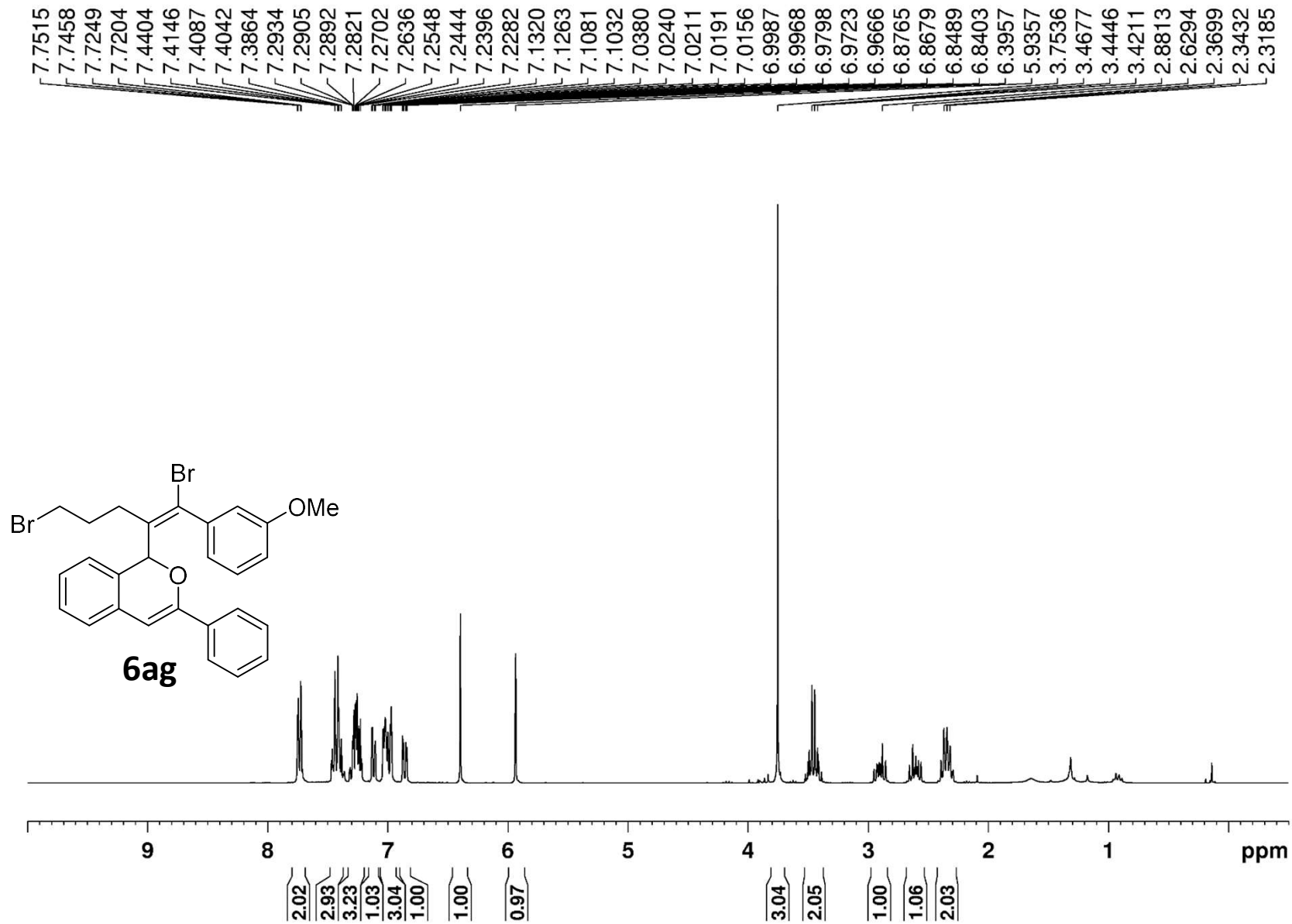


$^1\text{H NMR}$ of compound **5ae** (300 MHz, CDCl_3)

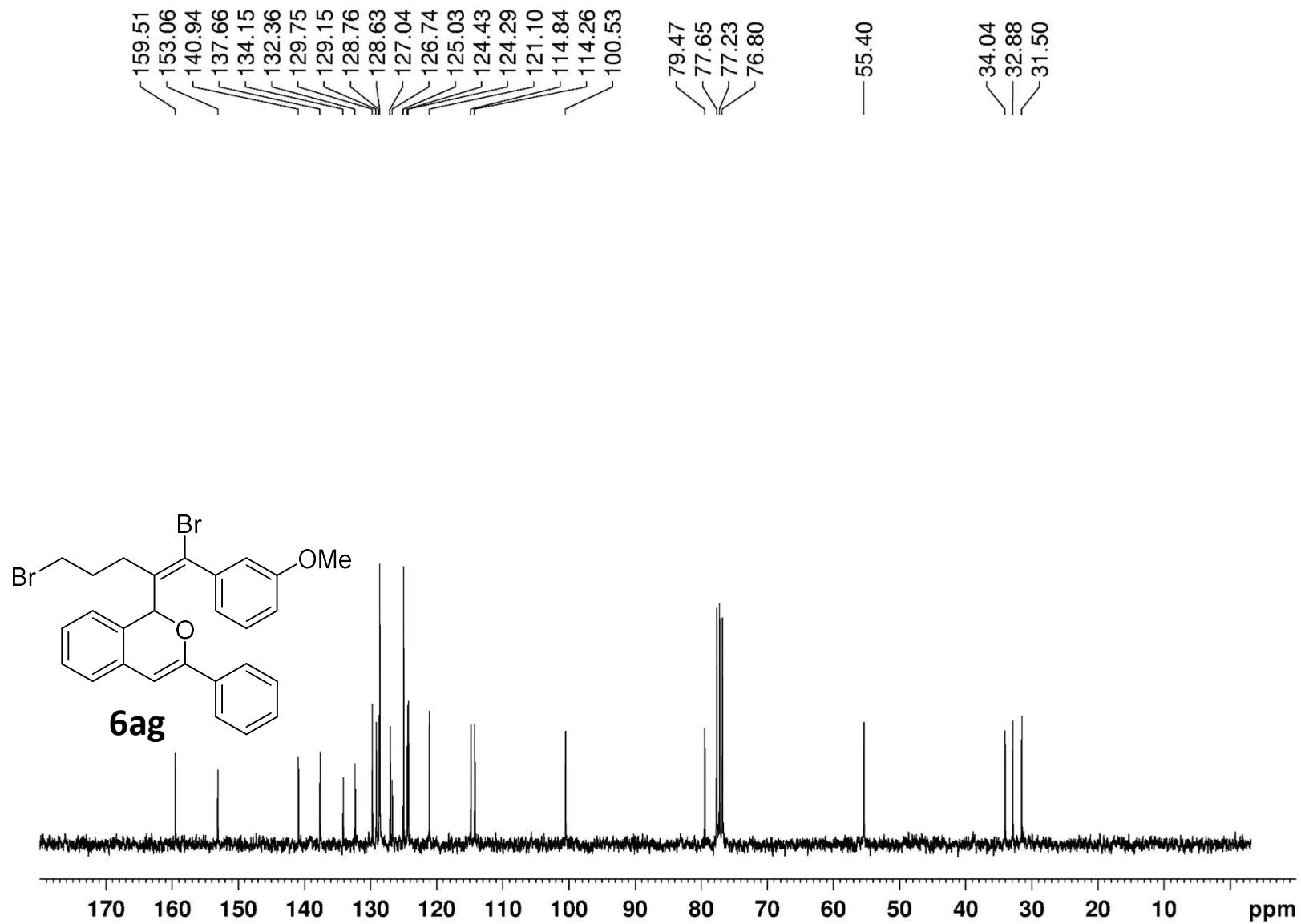




$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6af** (75 MHz, CDCl_3)

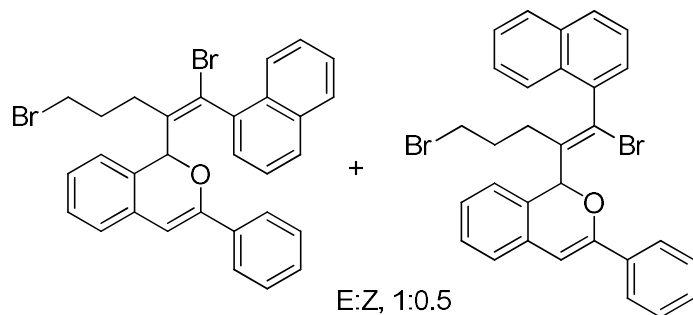


¹H NMR of compound **6ag** (300 MHz, CDCl₃)

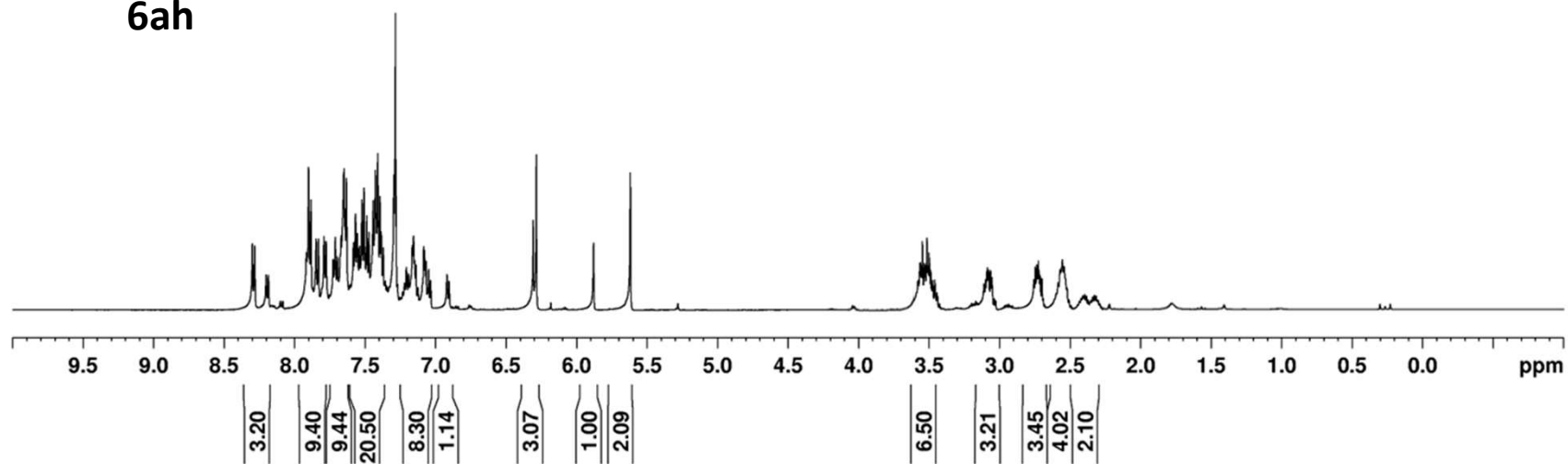


$^{13}\text{C}\{^1\text{H}\}$ NMR of compound **6ag** (75 MHz, CDCl_3)

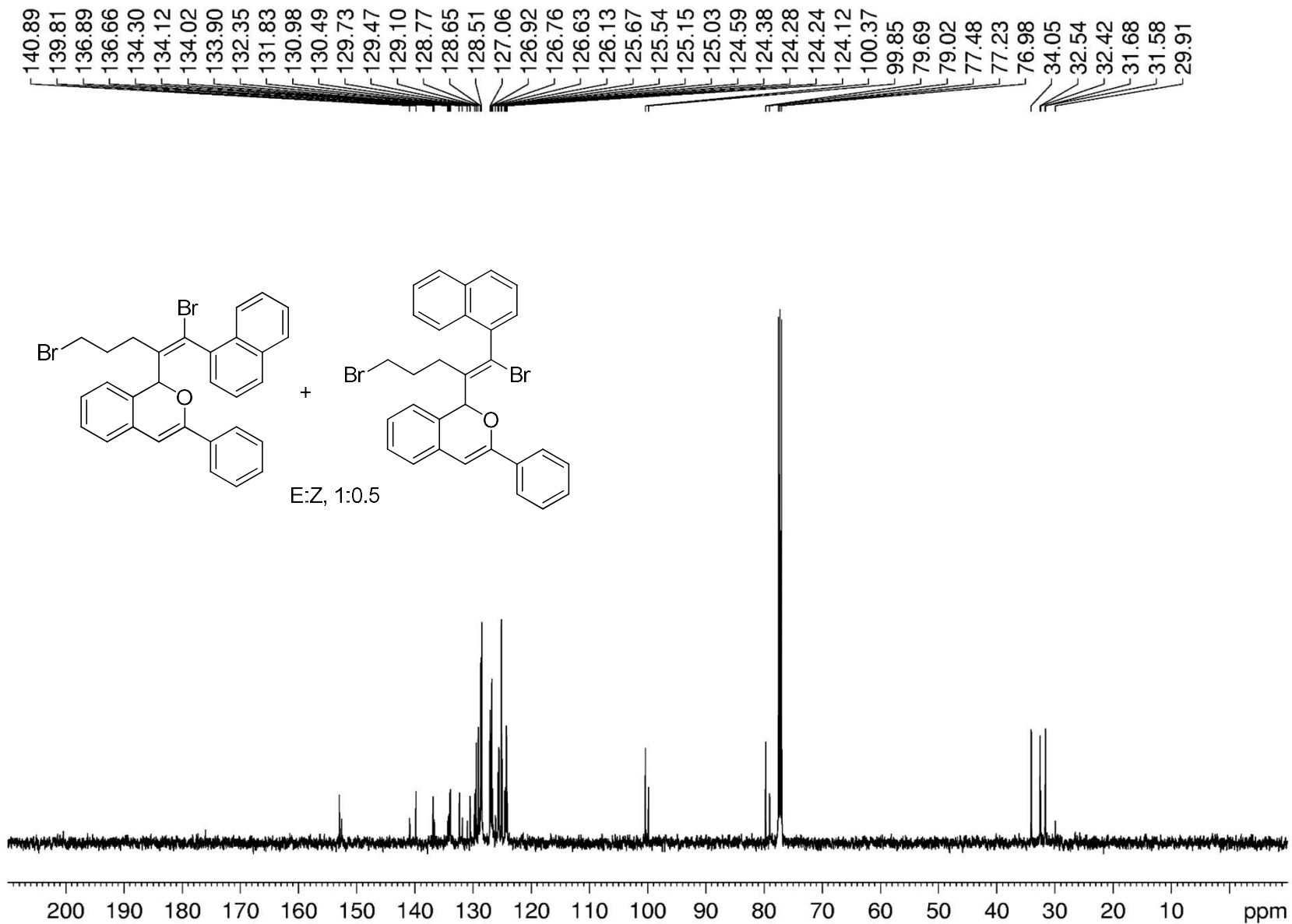
8.282
7.916
7.899
7.883
7.846
7.830
7.792
7.789
7.775
7.725
7.710
7.696
7.673
7.668
7.652
7.649
7.635
7.584
7.570
7.556
7.541
7.524
7.510
7.490
7.474
7.458
7.444
7.428
7.422
7.412
7.396
7.386
7.372
7.298
7.291
7.287
7.281
7.168
7.158
7.151
7.142
7.087
7.080
7.077
7.070
6.310
6.287
6.287
5.881
5.621
3.568
3.561
3.548
3.535
3.530
3.516
3.509
3.502
3.496
2.738
2.726
2.556
2.543



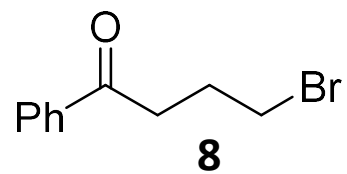
6ah



¹H NMR of compound **6ah** (300 MHz, CDCl₃)

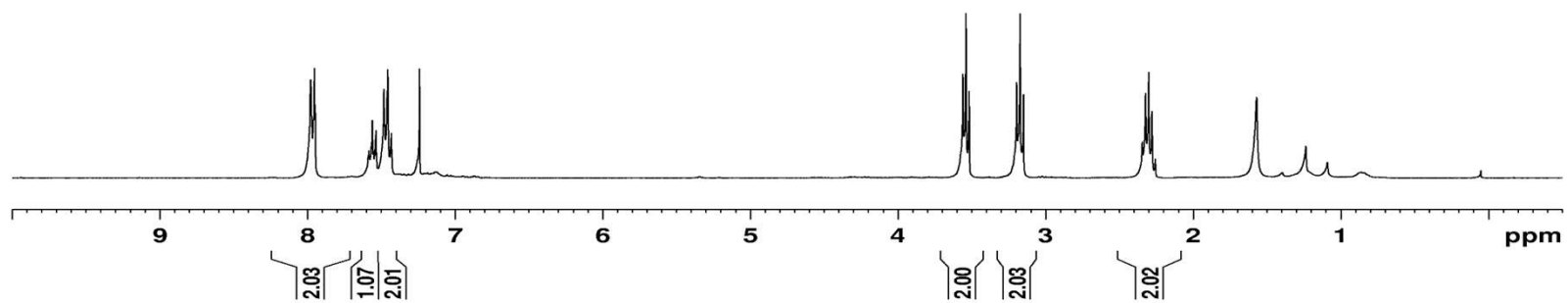


¹³C {¹H} NMR of compound **6ah** (75 MHz, CDCl₃)

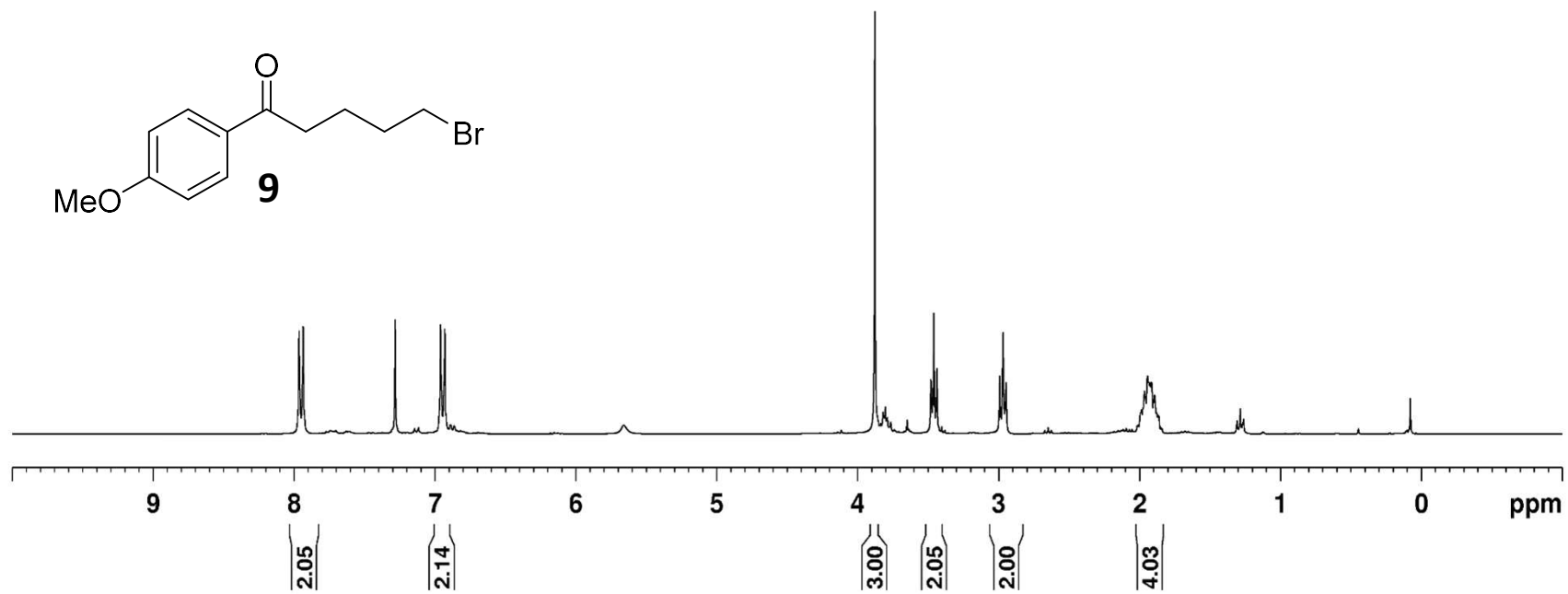


7.9791
7.9756
7.9584
7.9520
7.9471
7.5880
7.5841
7.5796
7.5673
7.5601
7.5523
7.5397
7.5353
7.5307
7.4808
7.4760
7.4597
7.4552
7.4365
7.4314
7.4279
7.2401

3.5593
3.5383
3.5172
3.1947
3.1716
3.1626
3.1485
2.3436
2.3220
2.2998
2.2781



^1H NMR of compound **8** (300 MHz, CDCl_3)



^1H NMR of compound **9** (300 MHz, CDCl_3)