Synthesis Chiral Hexacyclic Steroids via [8π+2π] Cycloaddition of Diazafulvenium methides

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Electronic Supplementary Information

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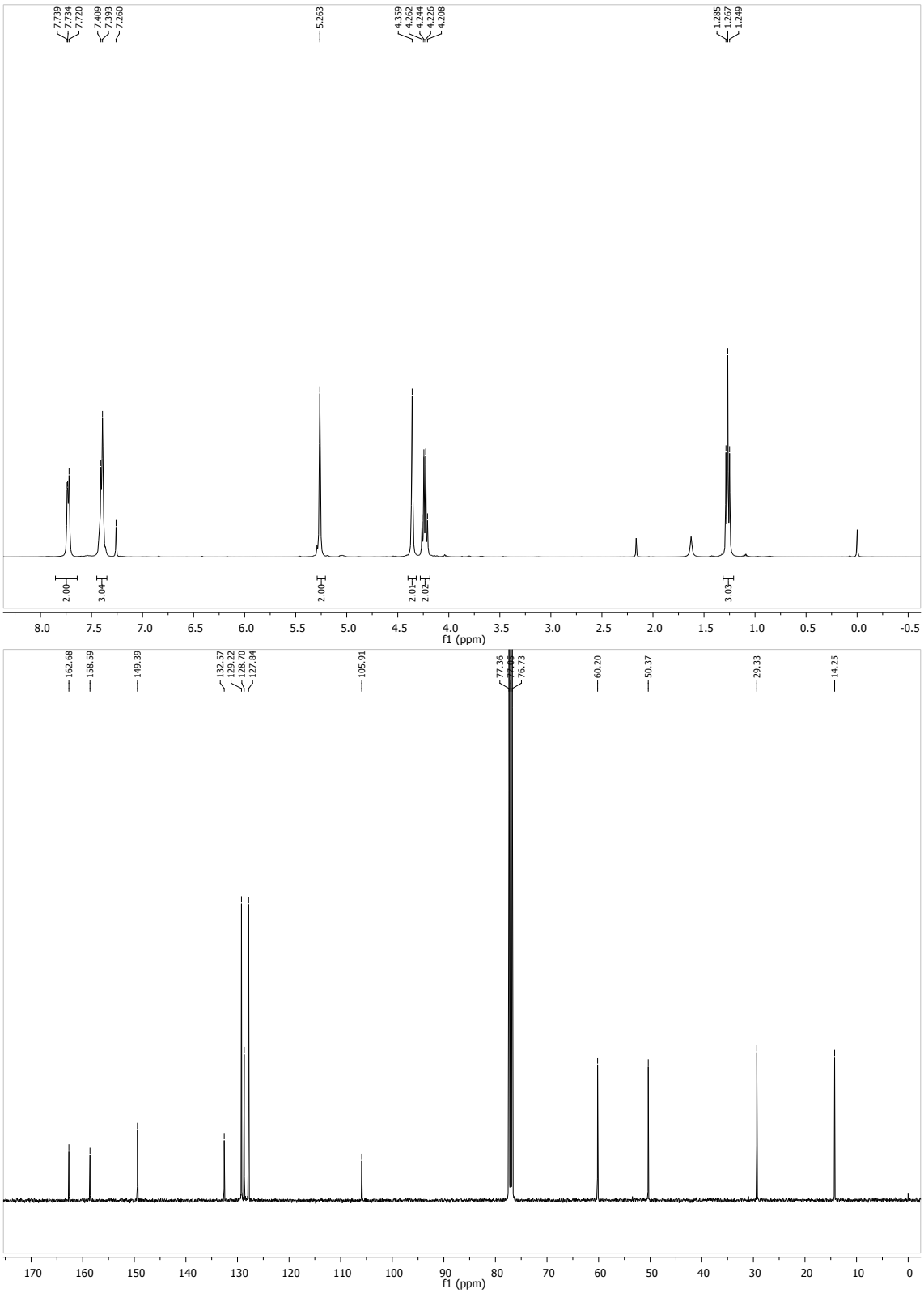

Figure 1. ^{1}H NMR and ^{13}C NMR spectra of compound **16a** ($CDCl_3$).

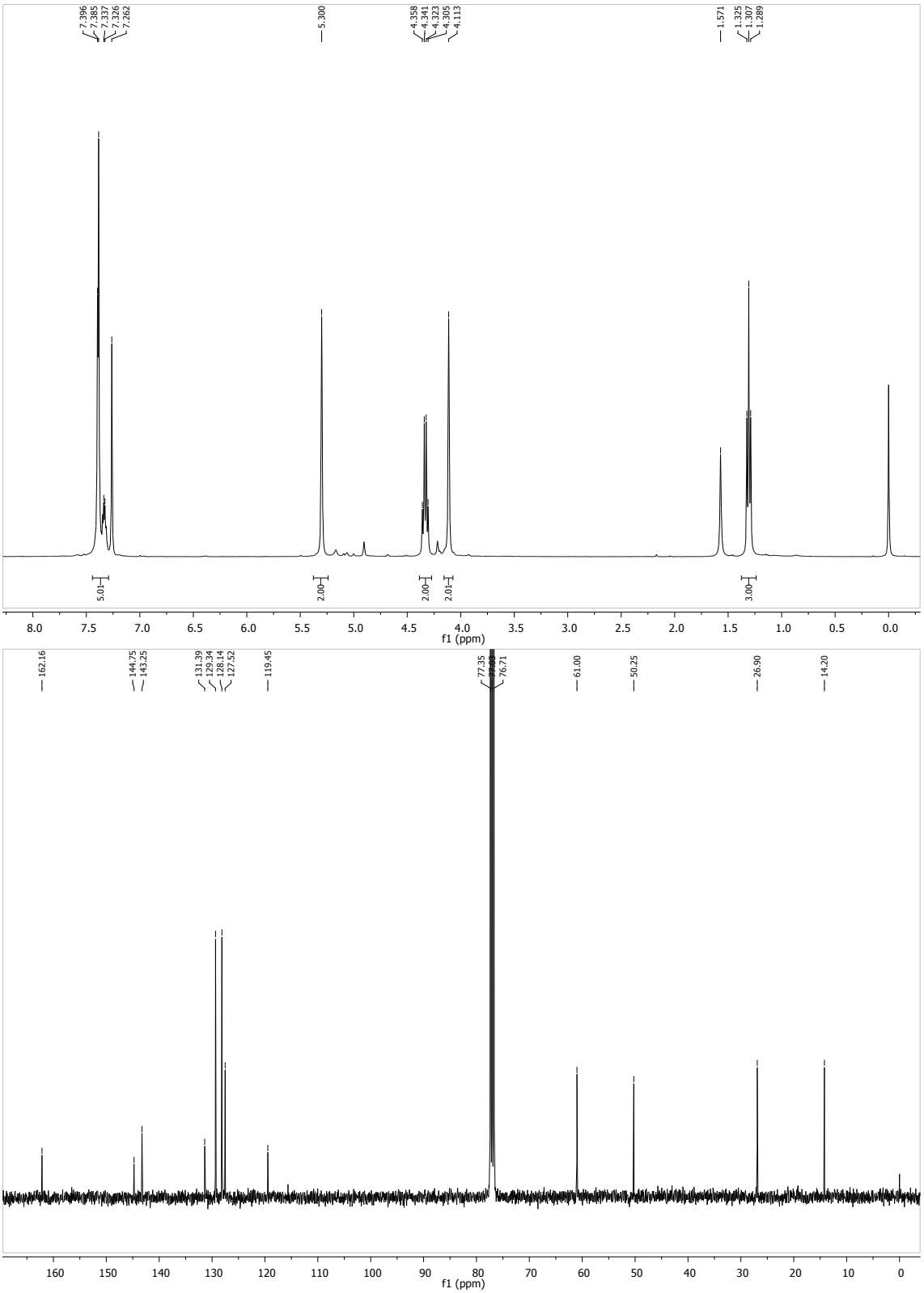

Figure 2. ^{1}H NMR and ^{13}C NMR spectra of compound **17a** ($CDCl_3$).

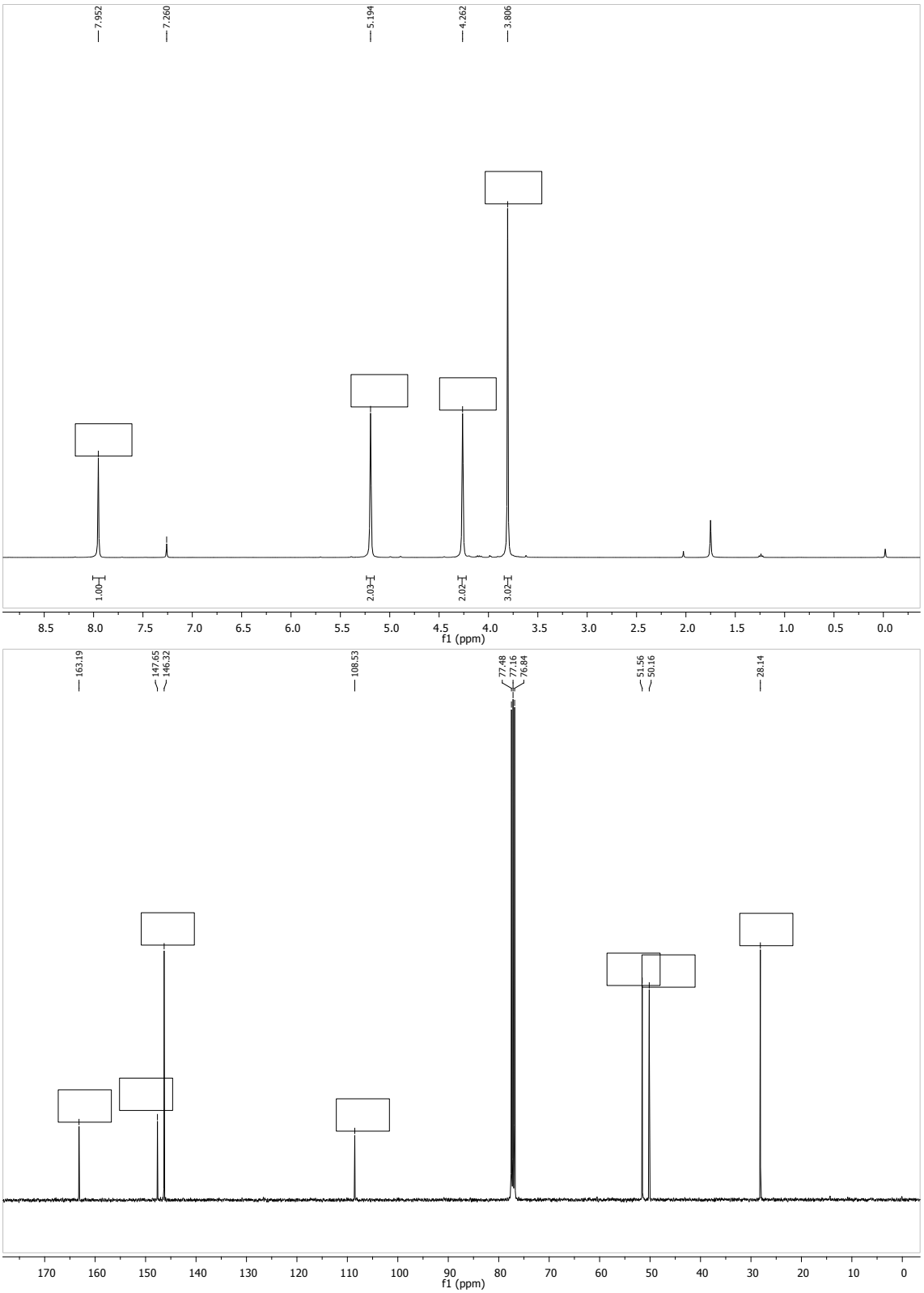

Figure 3. ^{1}H NMR and ^{13}C NMR spectra of compound **16b** ($CDCl_3$).

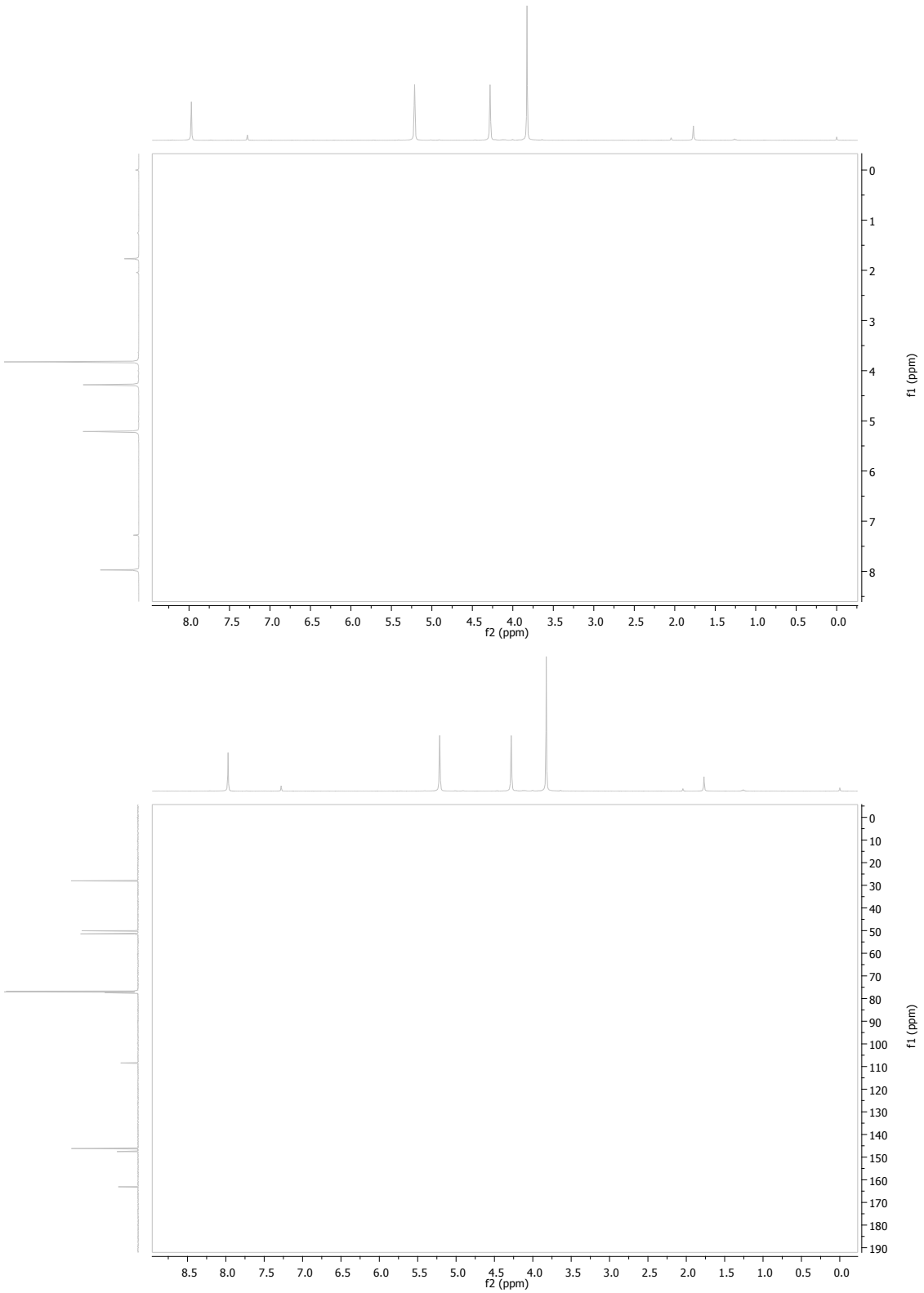

Figure 4. COSY and HMQC spectra of compound **16b** ($CDCl_3$).

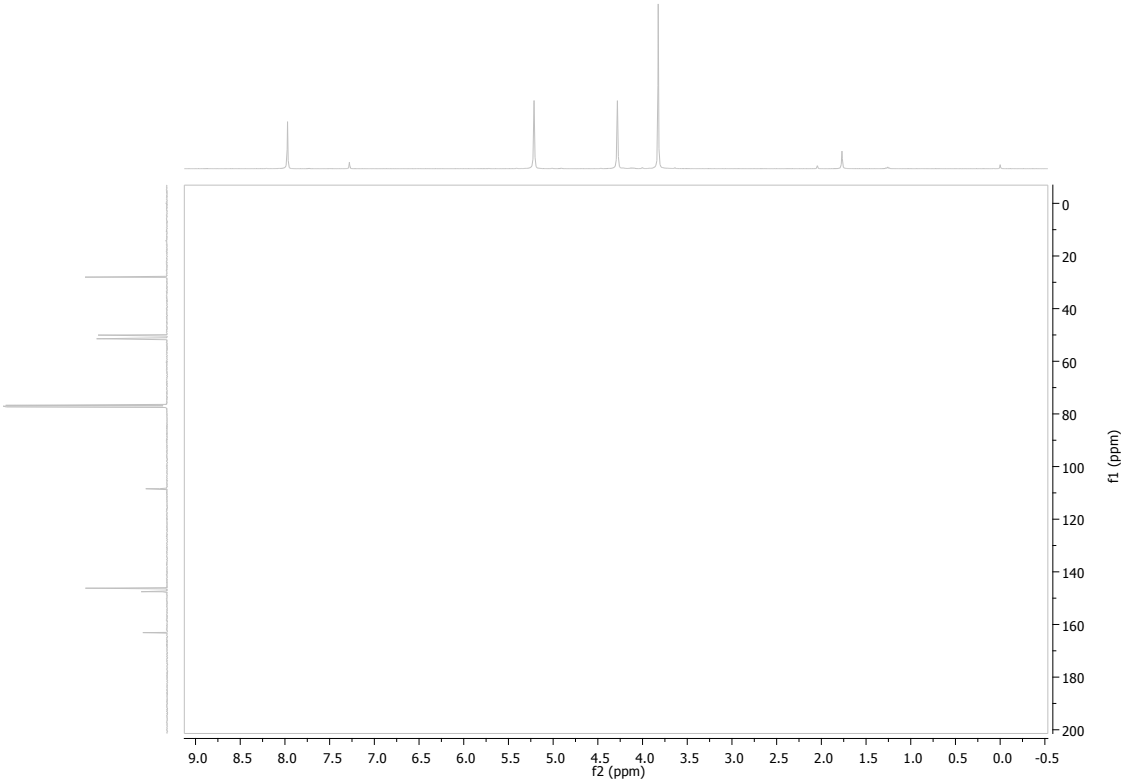

Figure 5. HMBC spectrum of compound **16b** ($CDCl_3$).

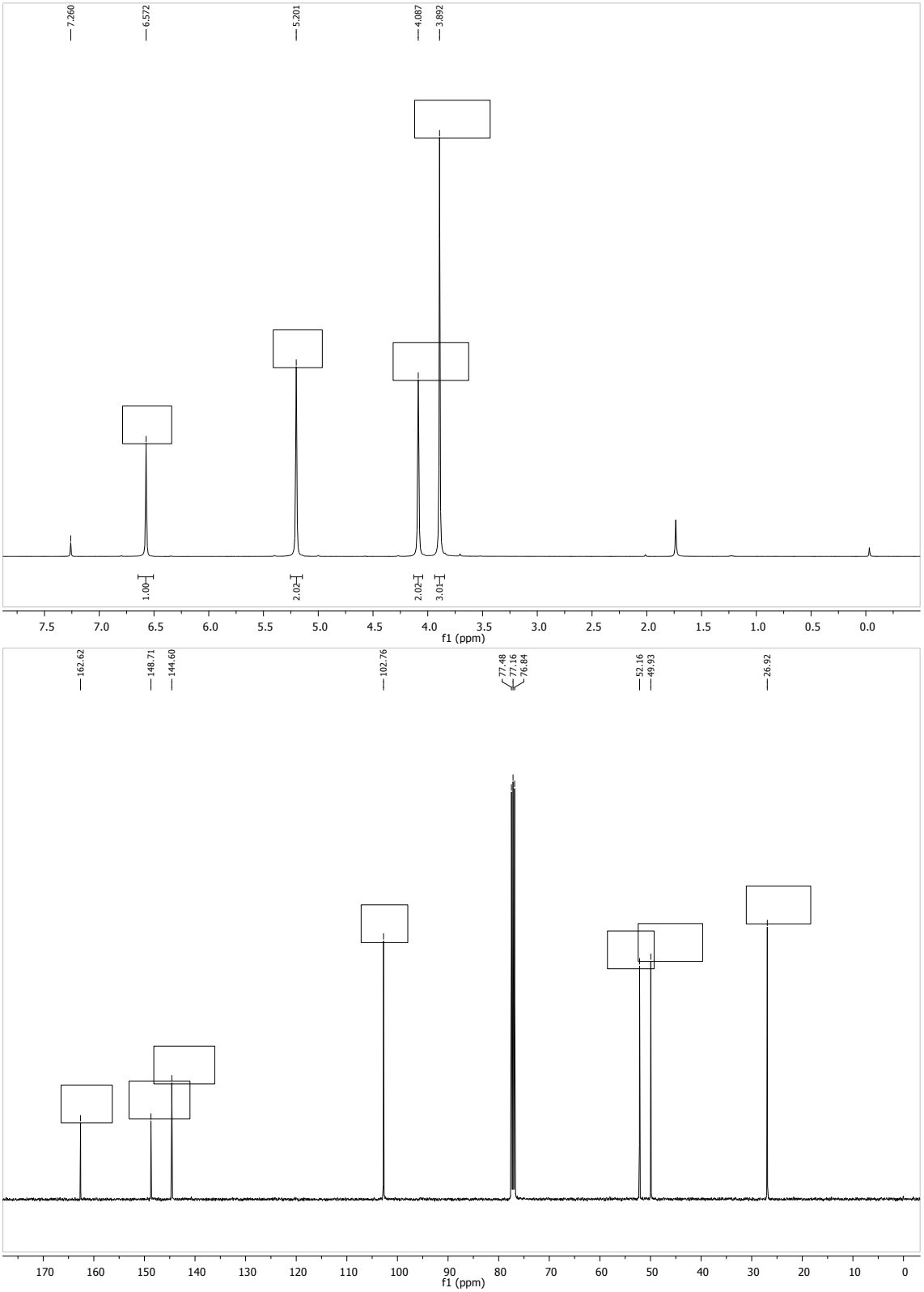

Figure 6. ^{1}H NMR and ^{13}C NMR spectra of compound **17b** ($CDCl_3$).

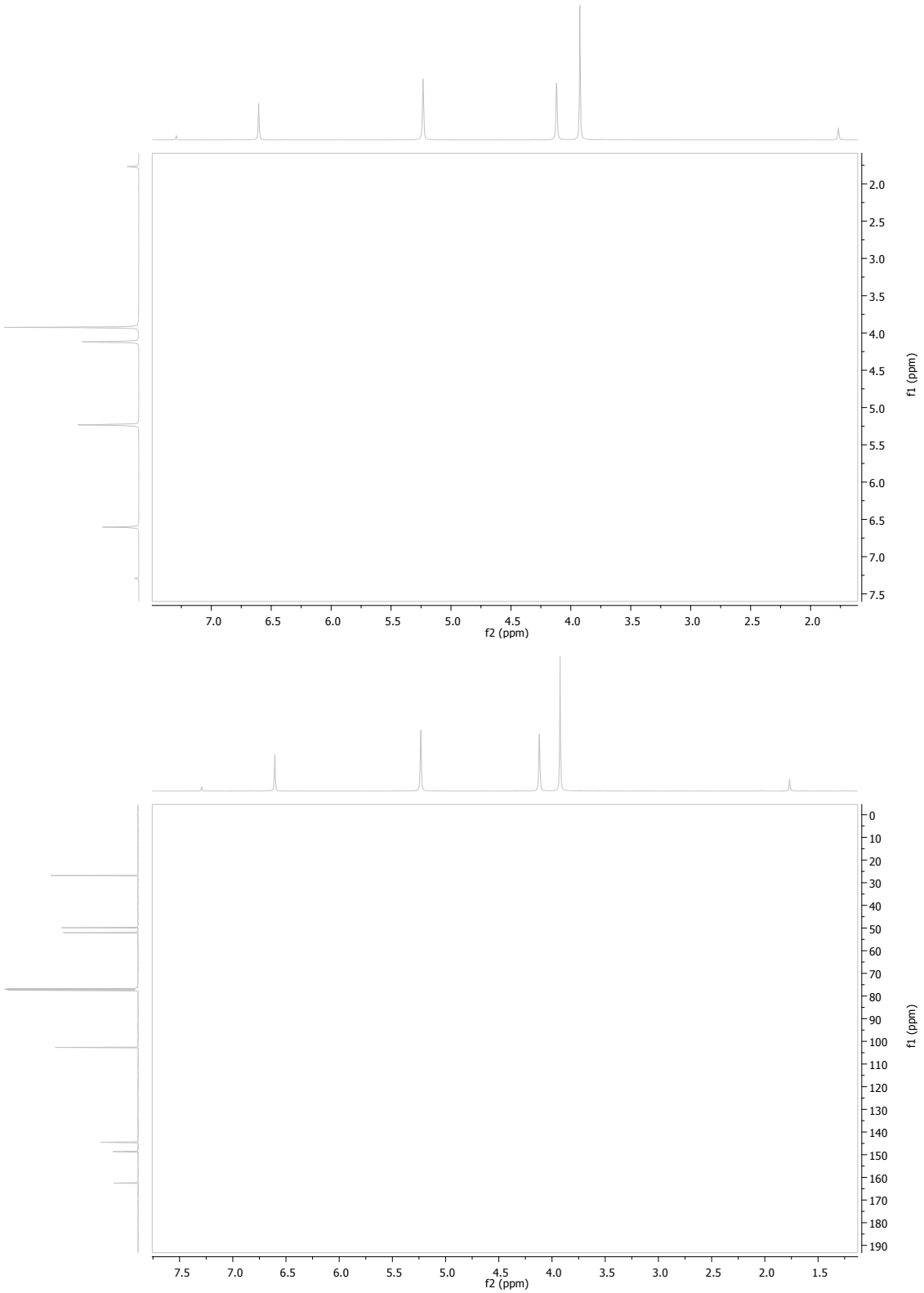

Figure 7. COSY and HMQC spectra of compound **17b** ($CDCl_3$).

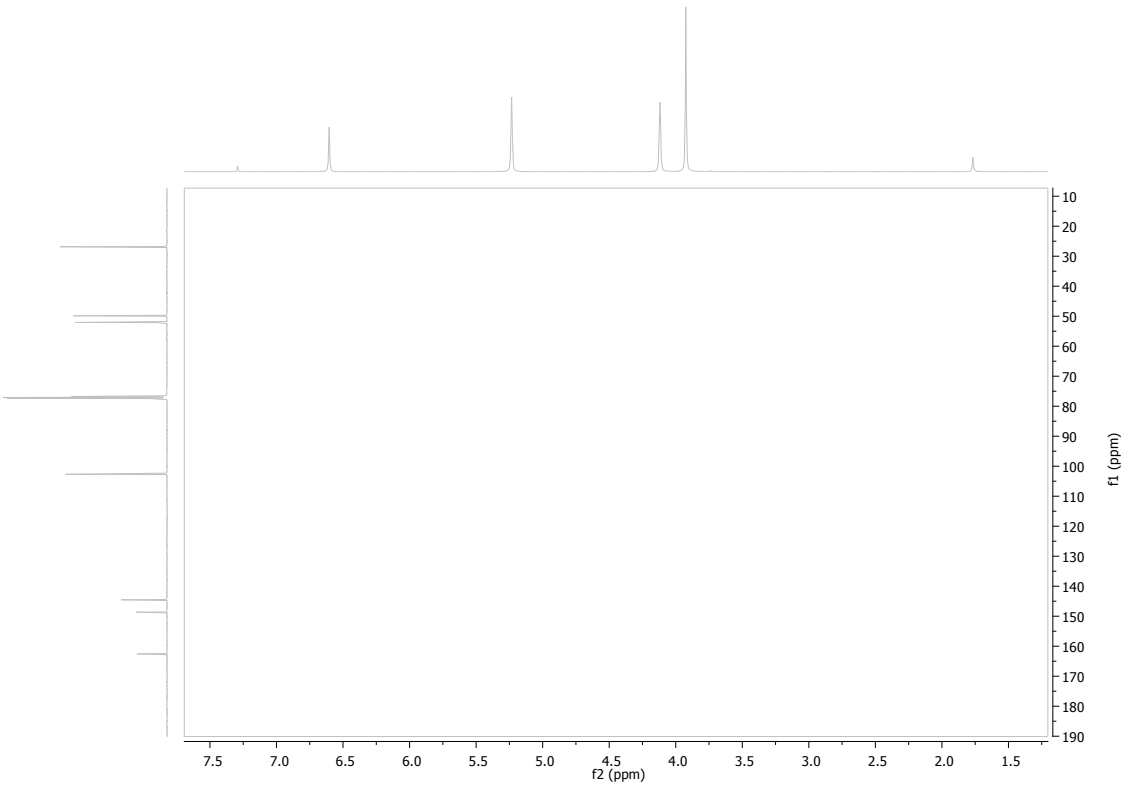

Figure 8. HMBC spectrum of compound **17b** ($CDCl_3$).

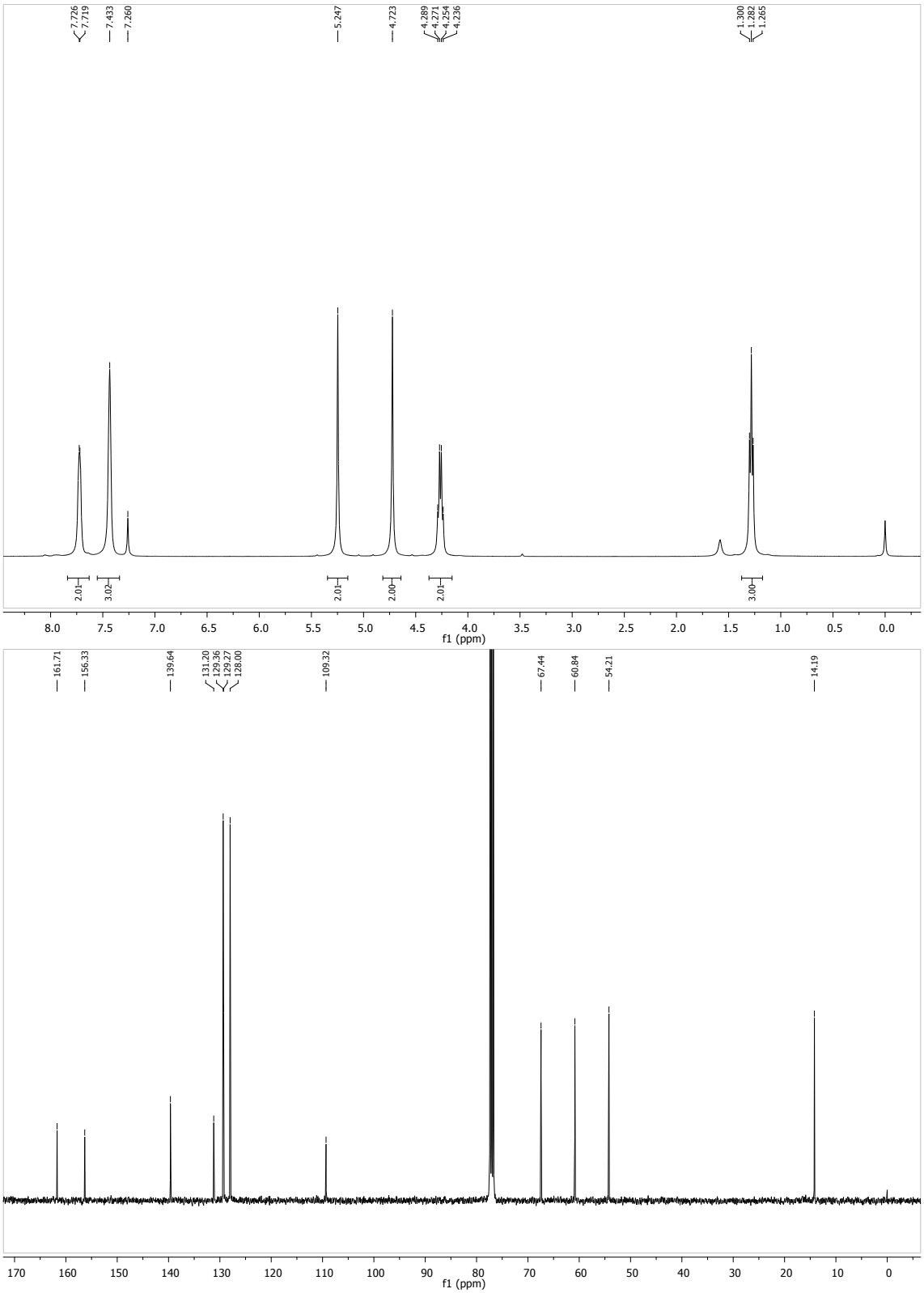

Figure 9. ^{1}H NMR and ^{13}C NMR spectra of compound **18a** ($CDCl_3$).

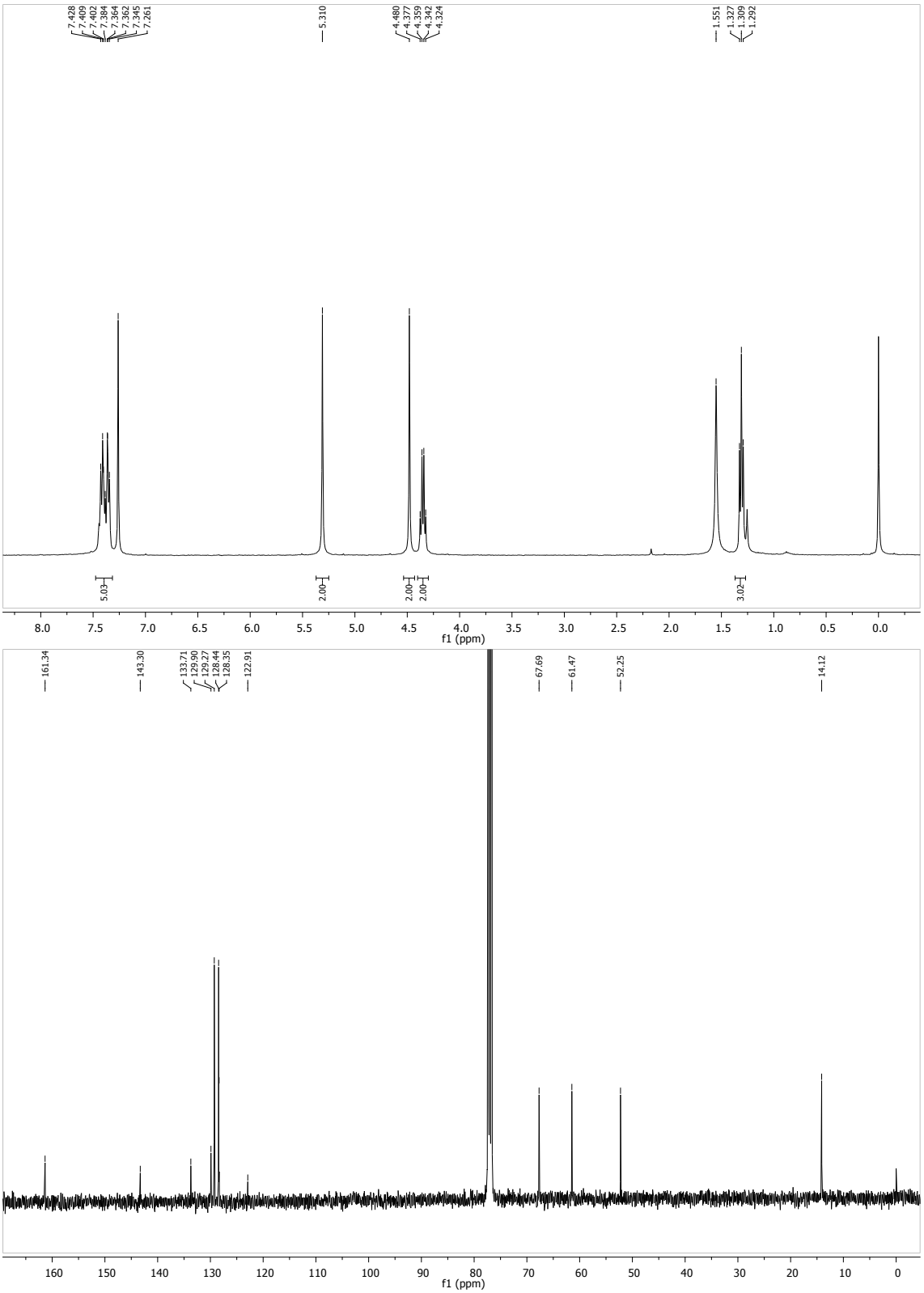

Figure 10. ^{1}H NMR and ^{13}C NMR spectra of compound **19a** ($CDCl_3$).

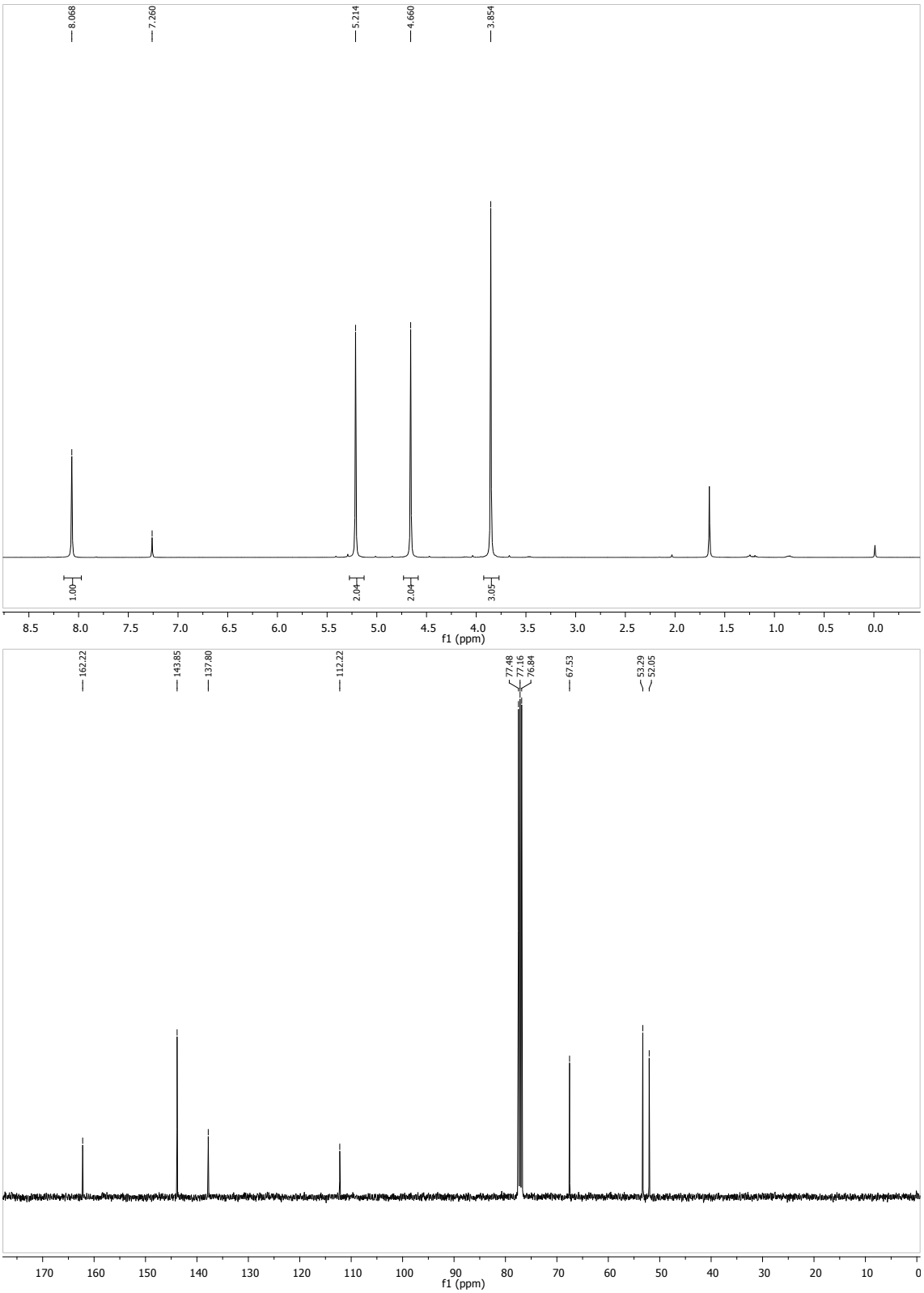

Figure 11. ^{1}H NMR and ^{13}C NMR spectra of compound **18b** ($CDCl_3$).

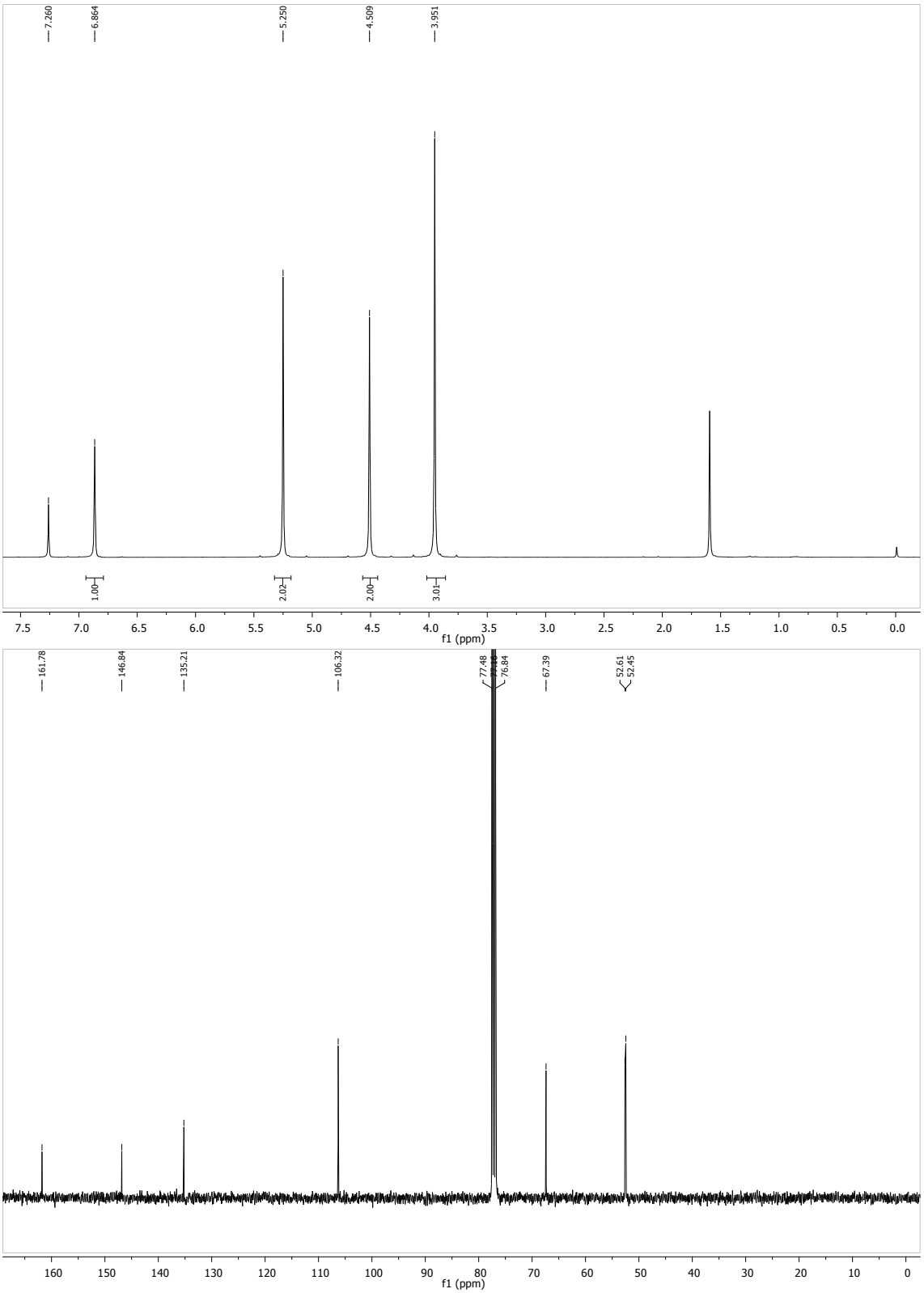

Figure 12. ^{1}H NMR and ^{13}C NMR spectra of compound **19b** ($CDCl_3$).

Figure 13. ^{1}H NMR spectrum of compound **21** ($CDCl_3$).

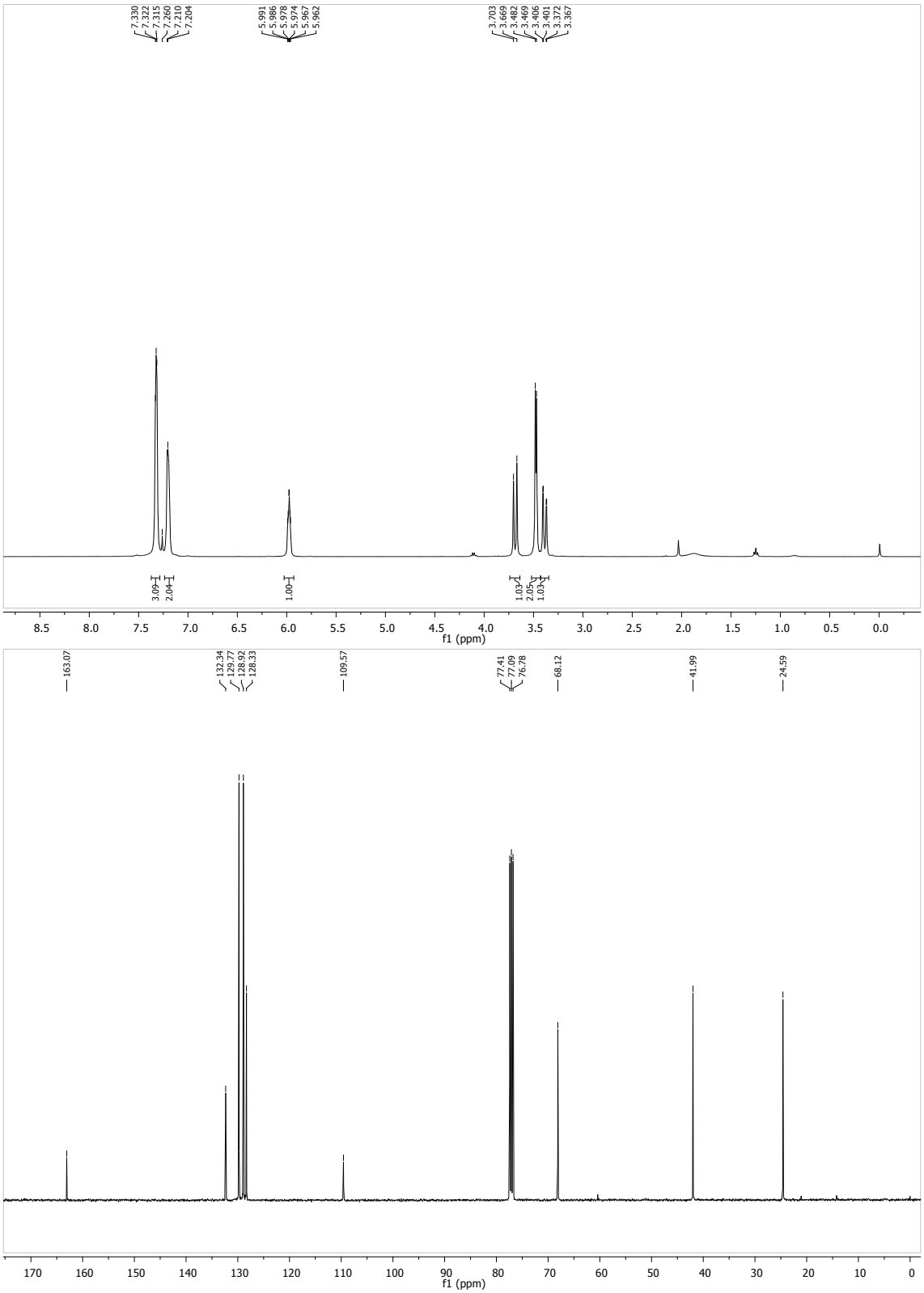

Figure 14. ^{1}H NMR and ^{13}C NMR spectra of compound **22** ($CDCl_3$).

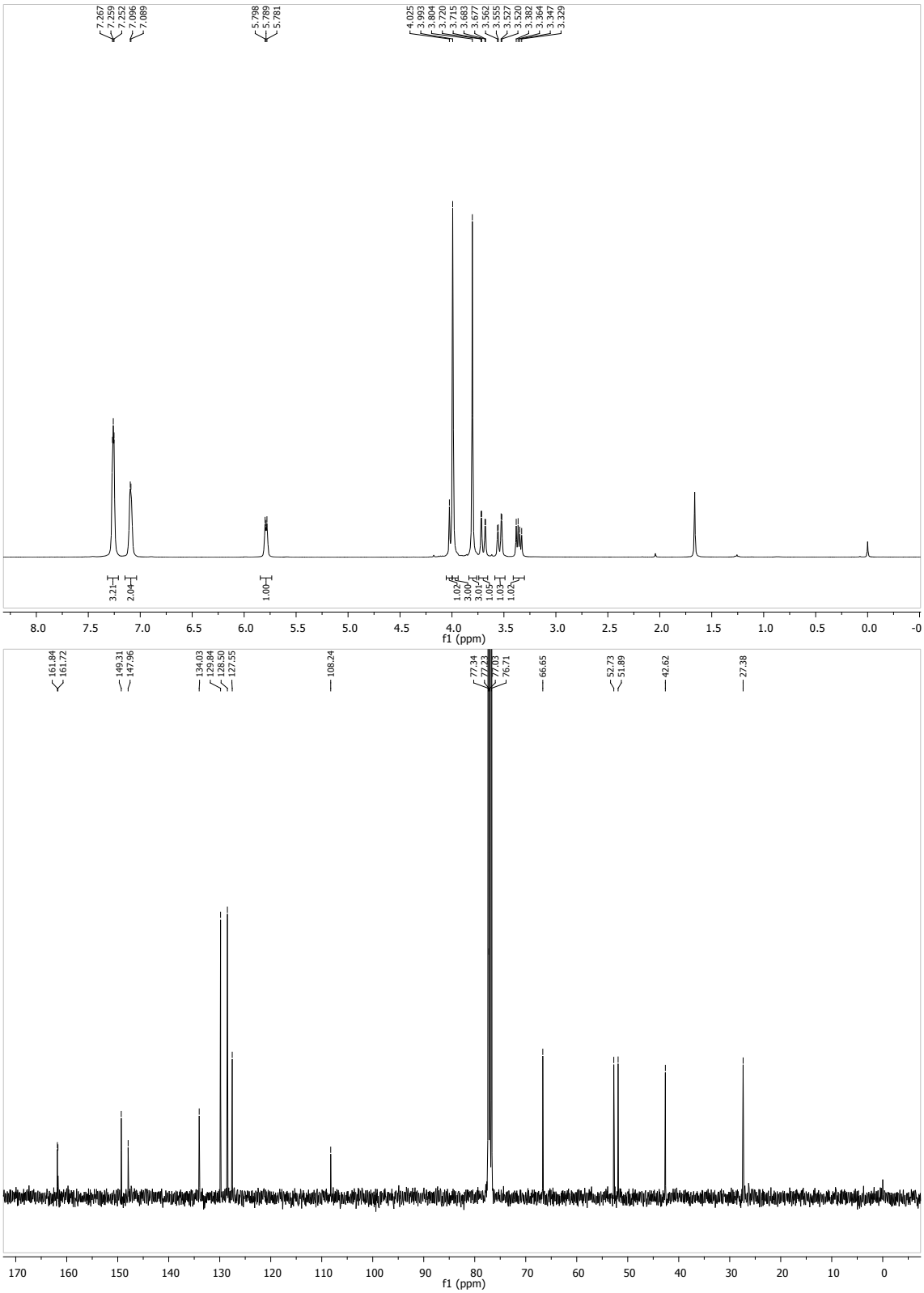

Figure 15. ^{1}H NMR and ^{13}C NMR spectra of compound **23** ($CDCl_3$).

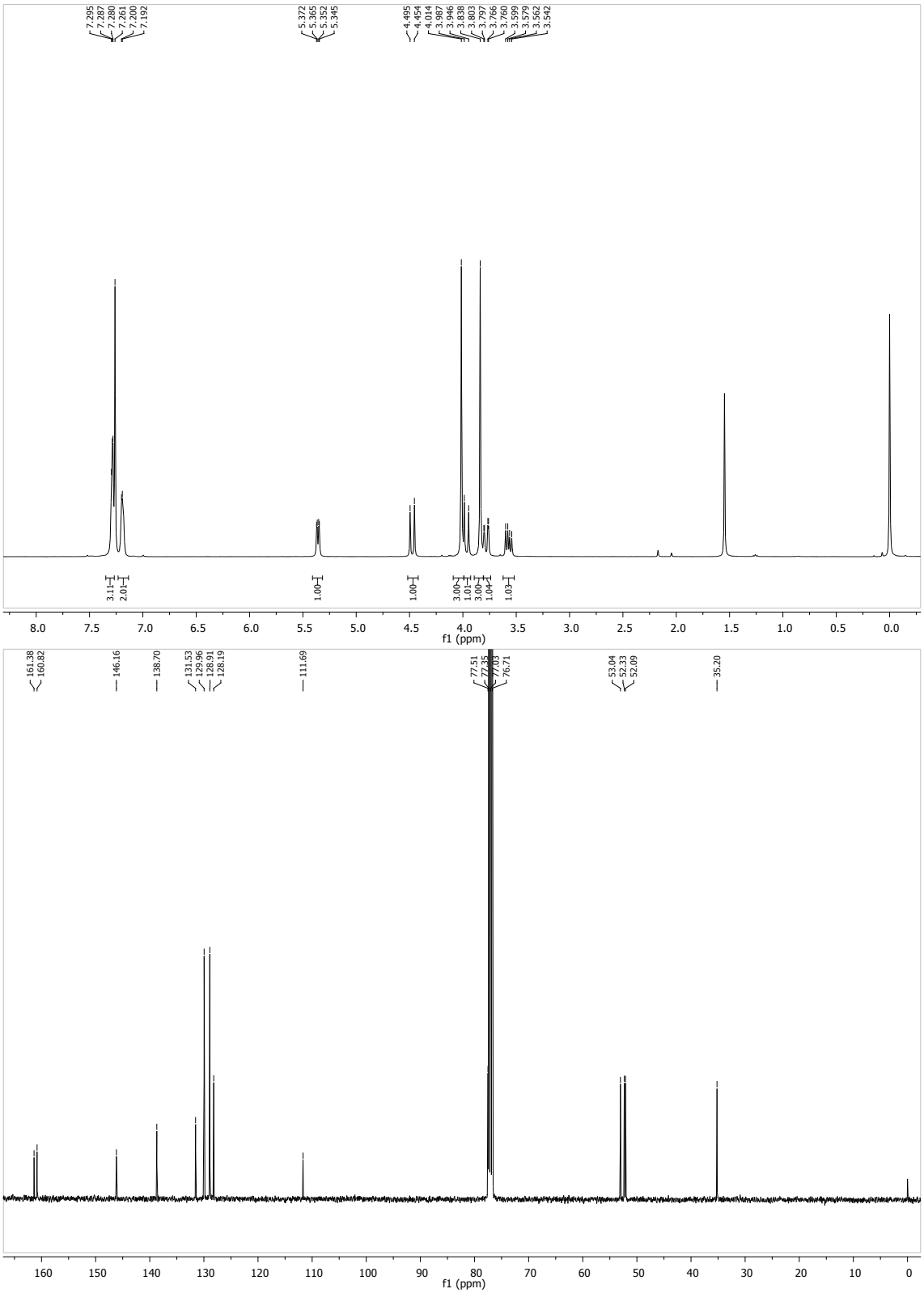

Figure 16. ^{1}H NMR and ^{13}C NMR spectra of compound **24** ($CDCl_3$).

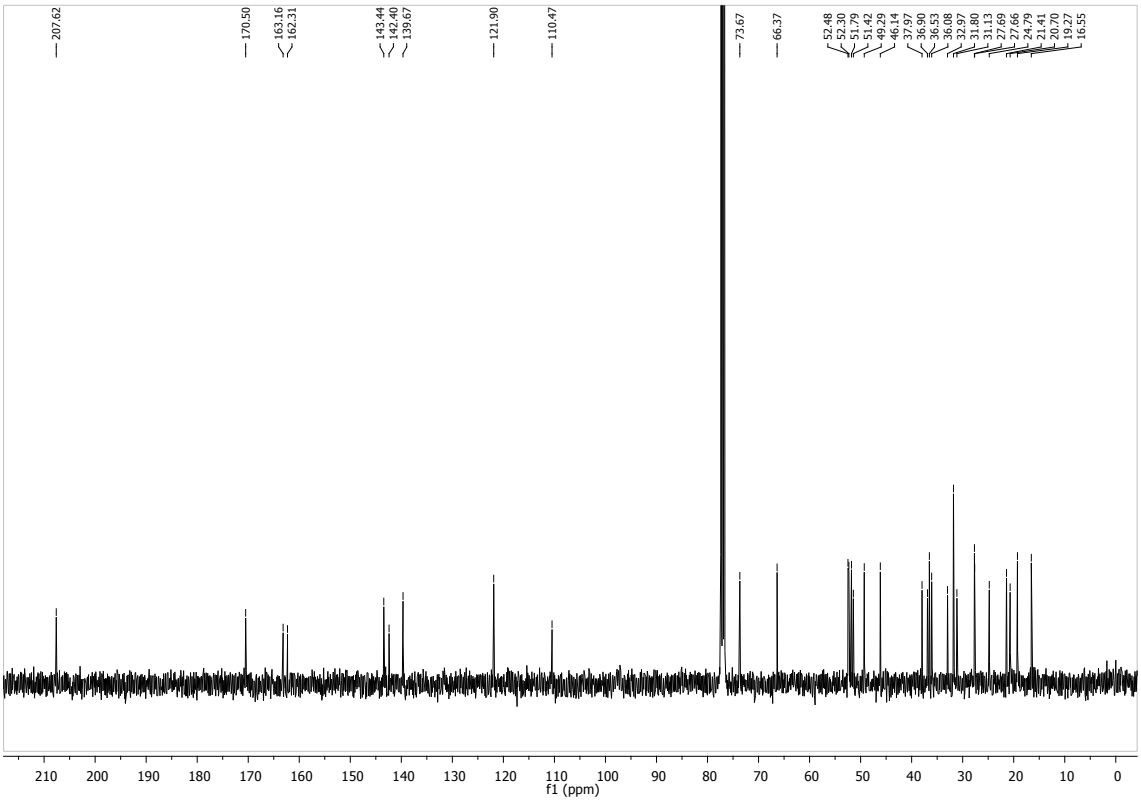

Figure 17. ^{1}H NMR and ^{13}C NMR spectra of compound **27** ($CDCl_3$).

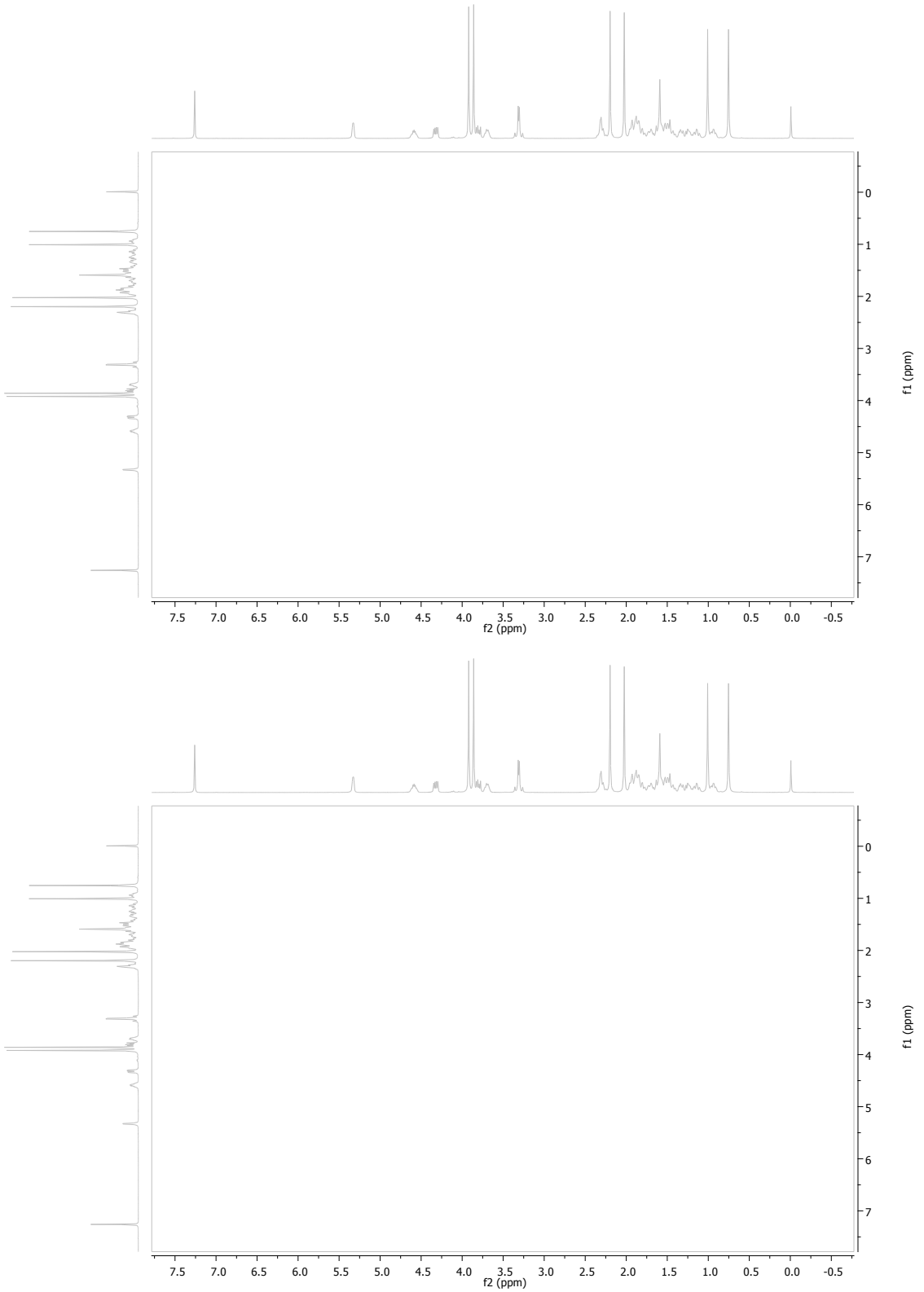

Figure 18. COSY and NOESY spectra of compound **27** ($CDCl_3$).

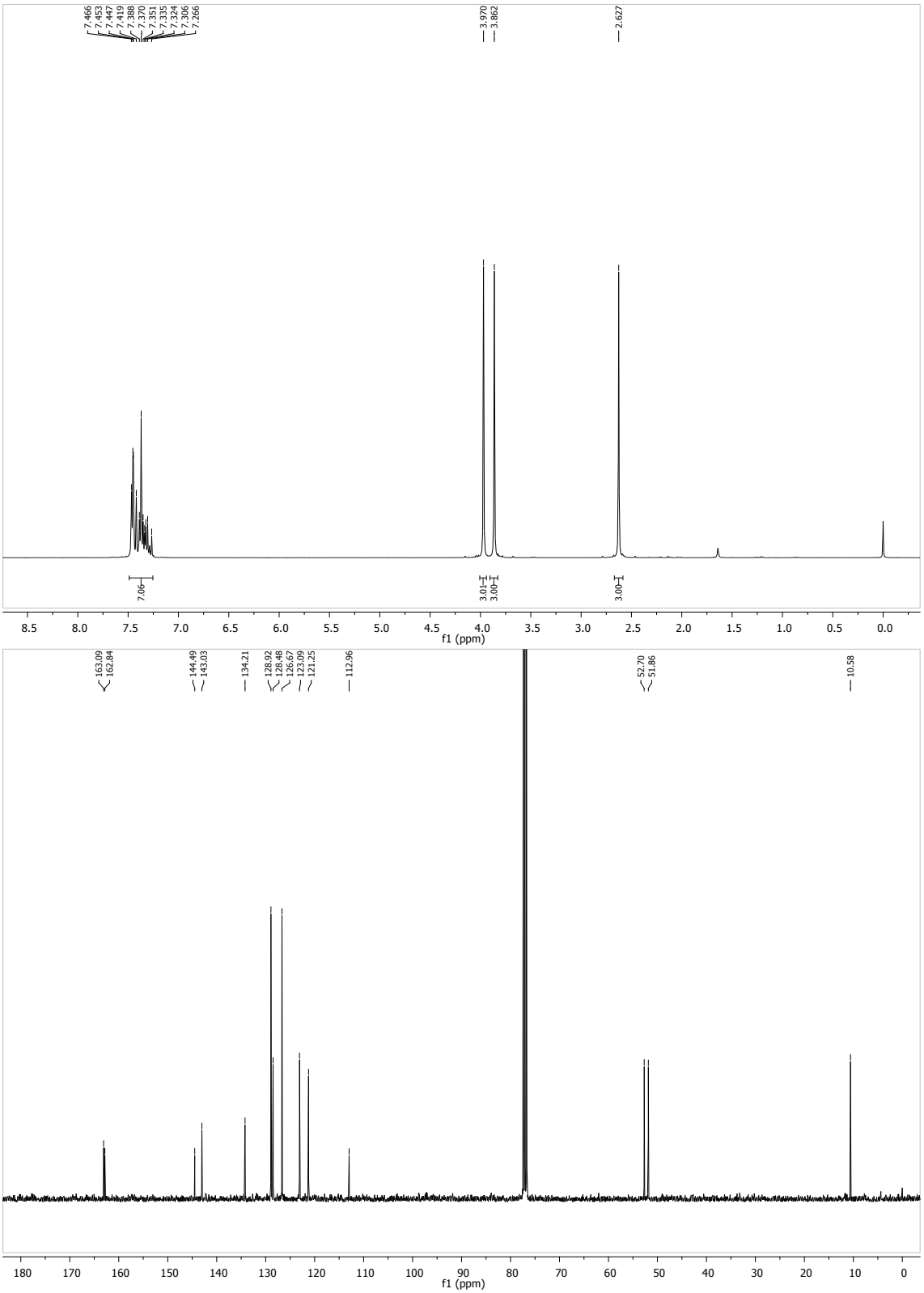

Figure 19. ^{1}H NMR and ^{13}C NMR spectra of compound **29** ($CDCl_3$).

Figure 20. ^{1}H NMR and ^{13}C NMR spectra of compound **30** ($CDCl_3$).

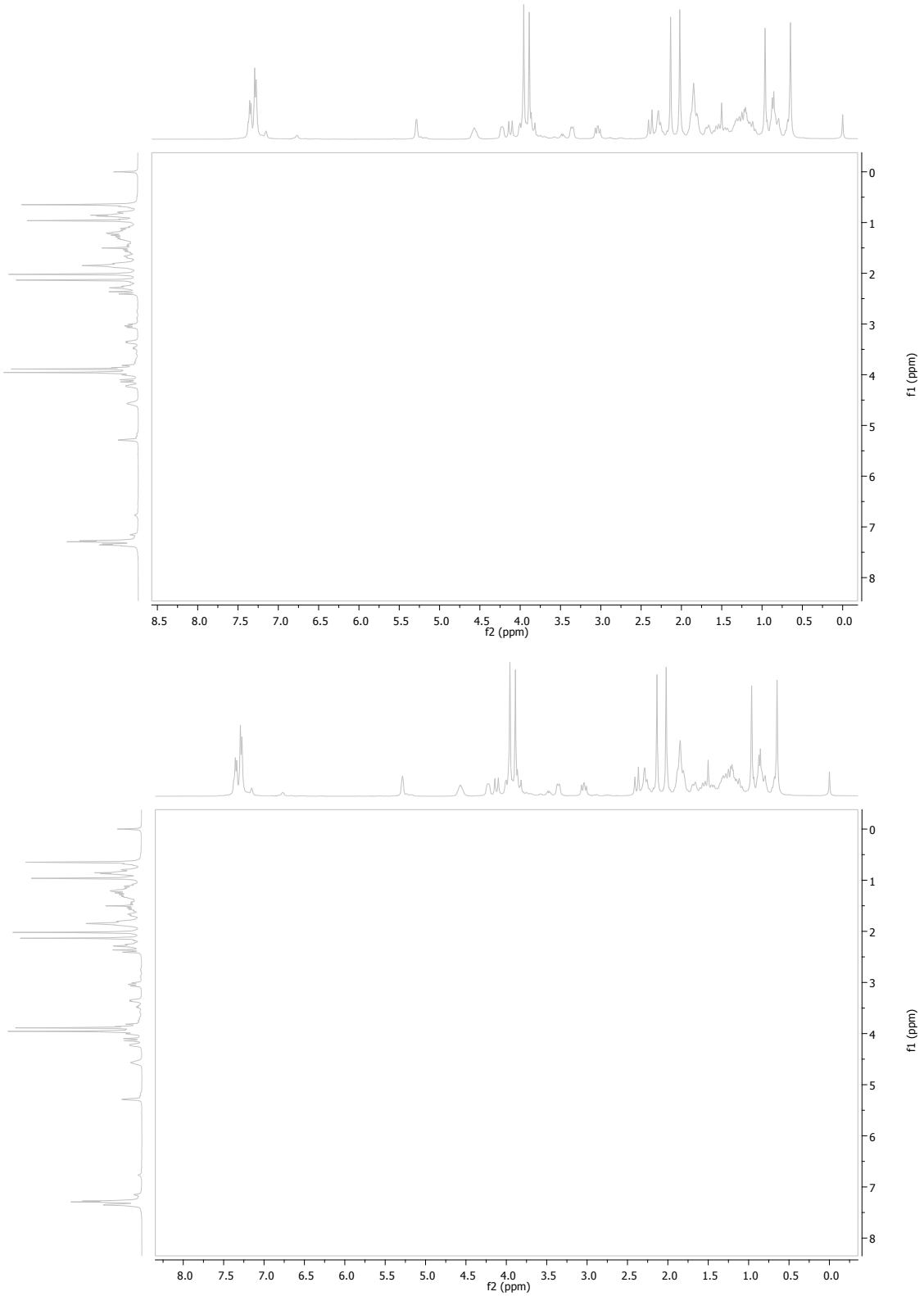

Figure 21. COSY and NOESY spectra of compound **30** ($CDCl_3$).

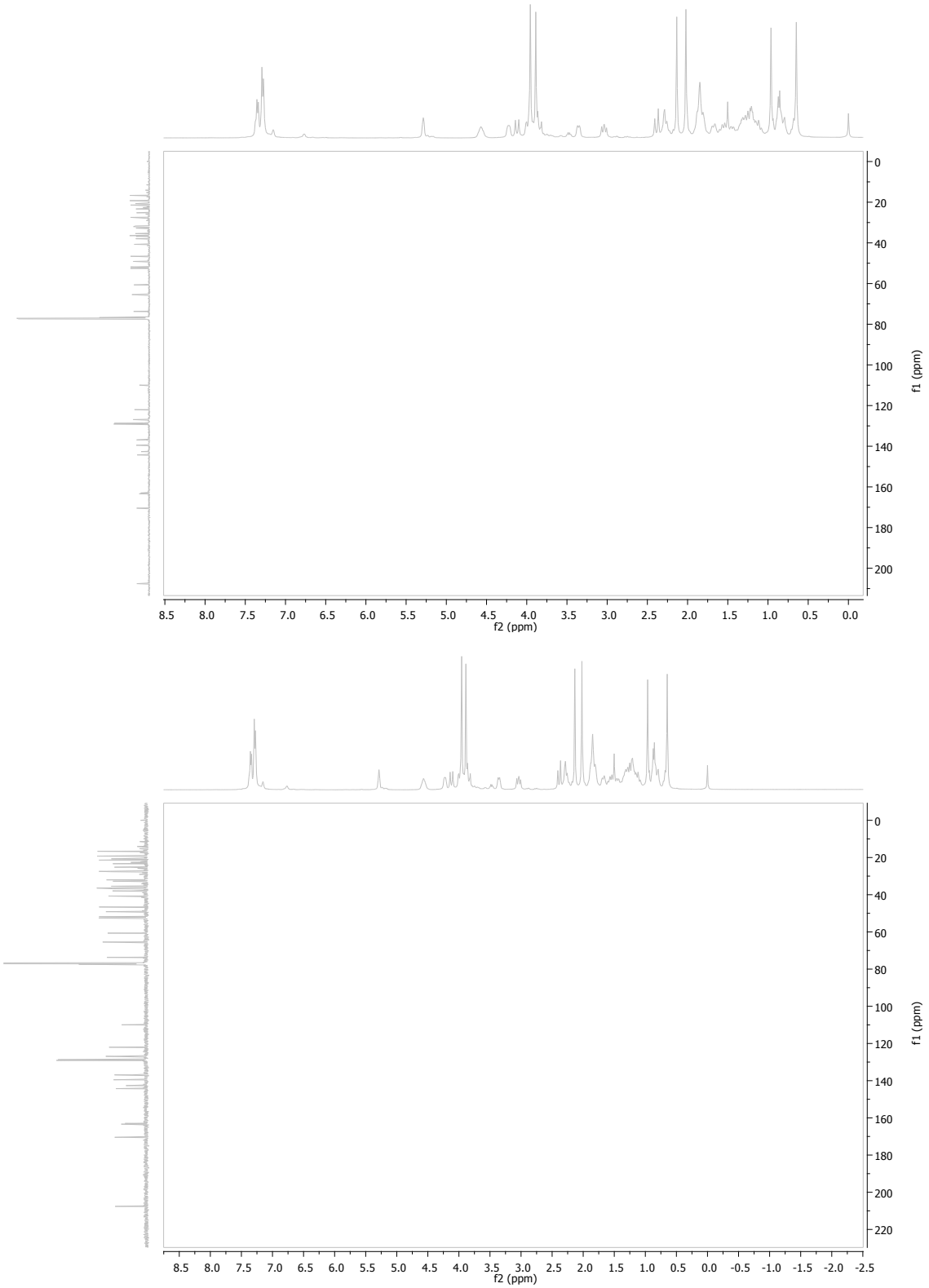

Figure 22. HMQC and HMBC spectra of compound **30** ($CDCl_3$).

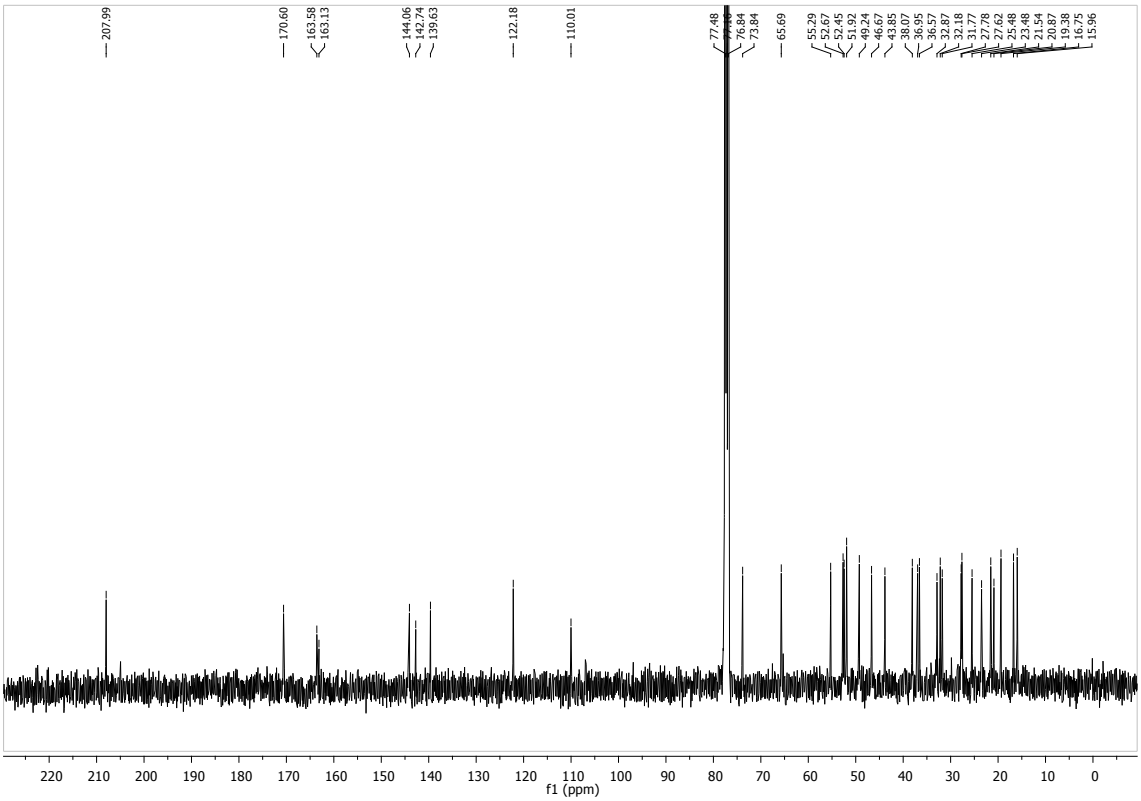

Figure 23. ^{1}H NMR and ^{13}C NMR spectra of compound **34** ($CDCl_3$).

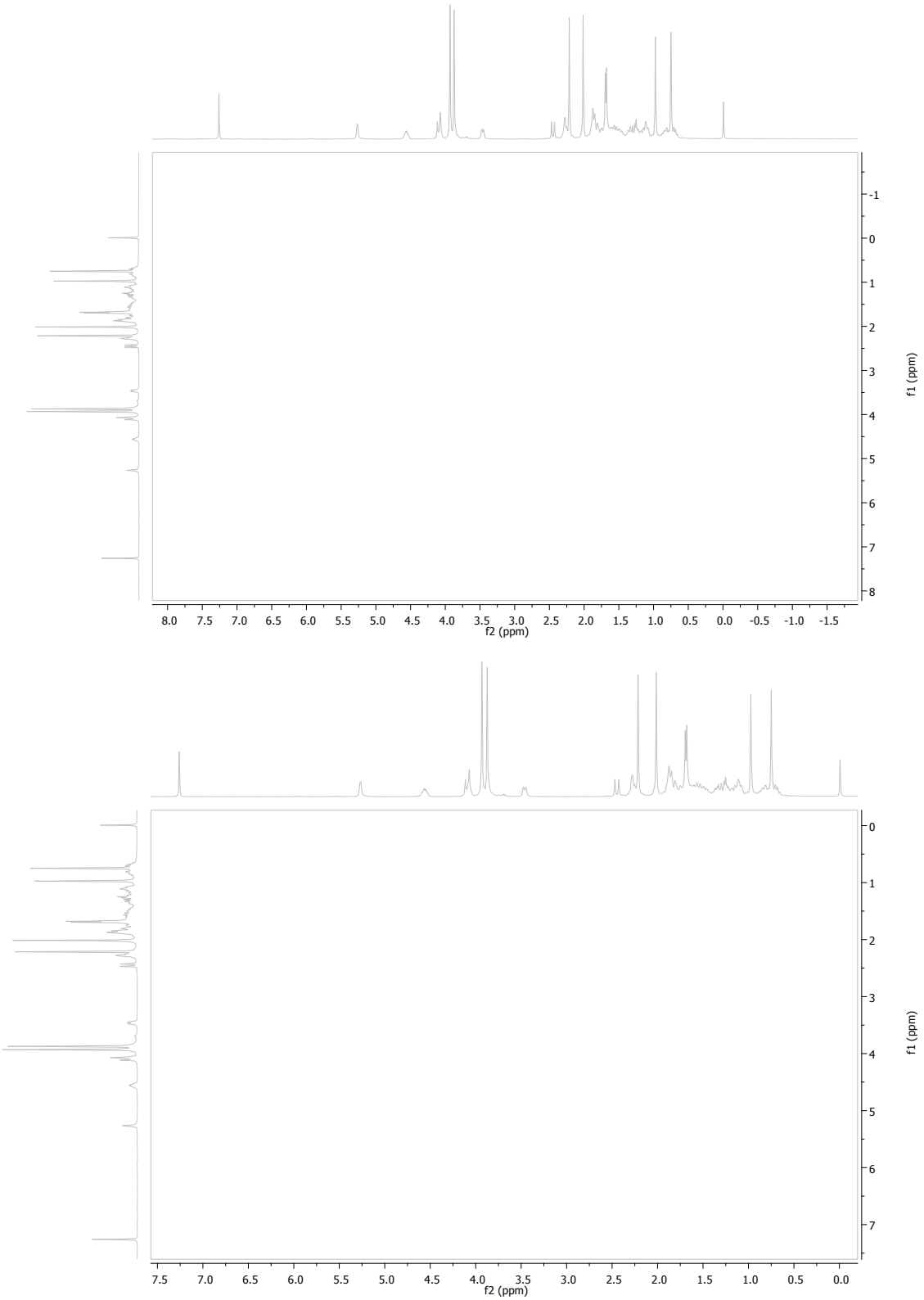

Figure 24. COSY and NOESY spectra of compound **34** ($CDCl_3$).

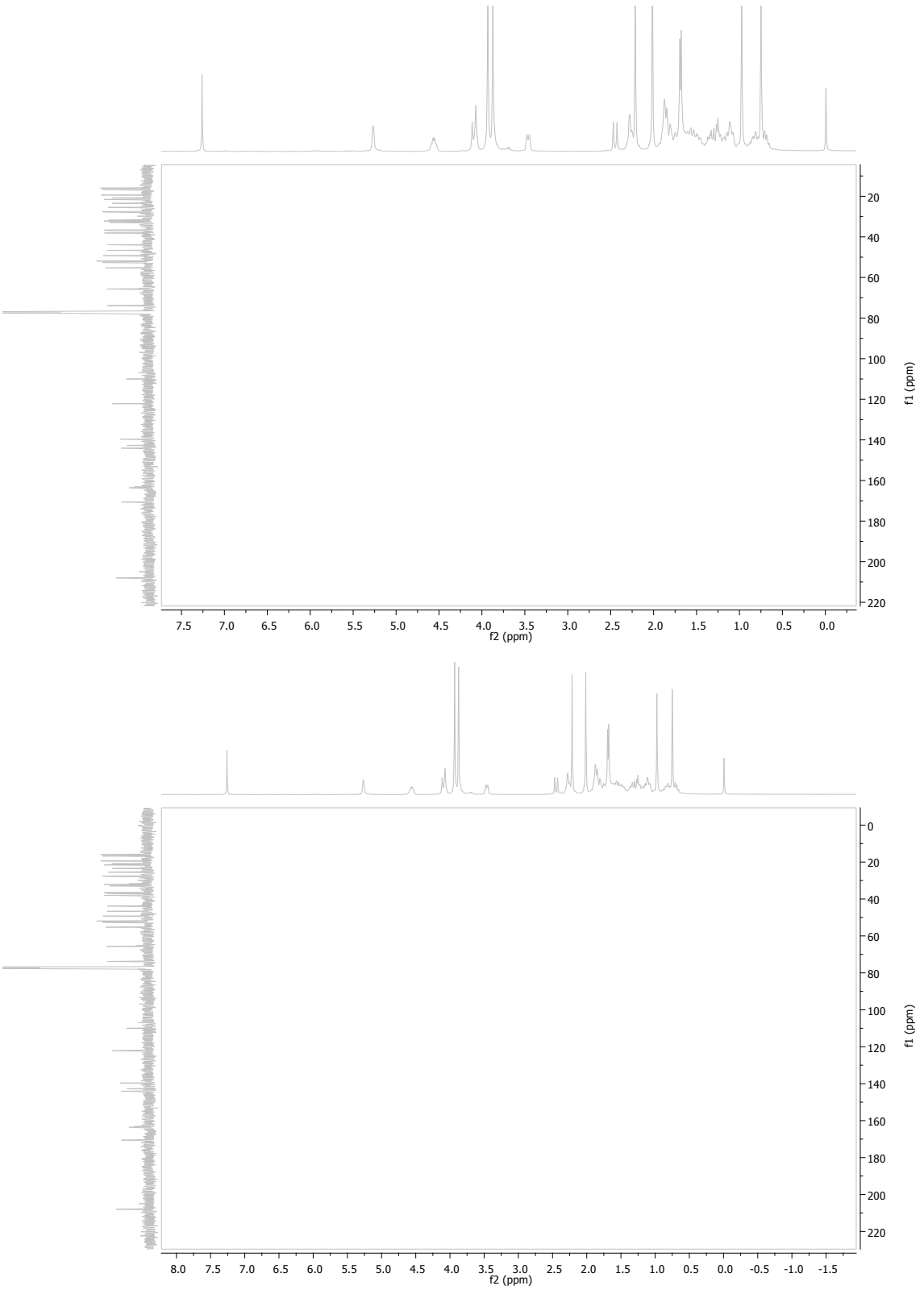

Figure 25. HMQC and HMBC spectra of compound **34** ($CDCl_3$).

Figure 26. ^{1}H MNR spectrum of the mixture compounds **34**/**35** ($CDCl_3$).

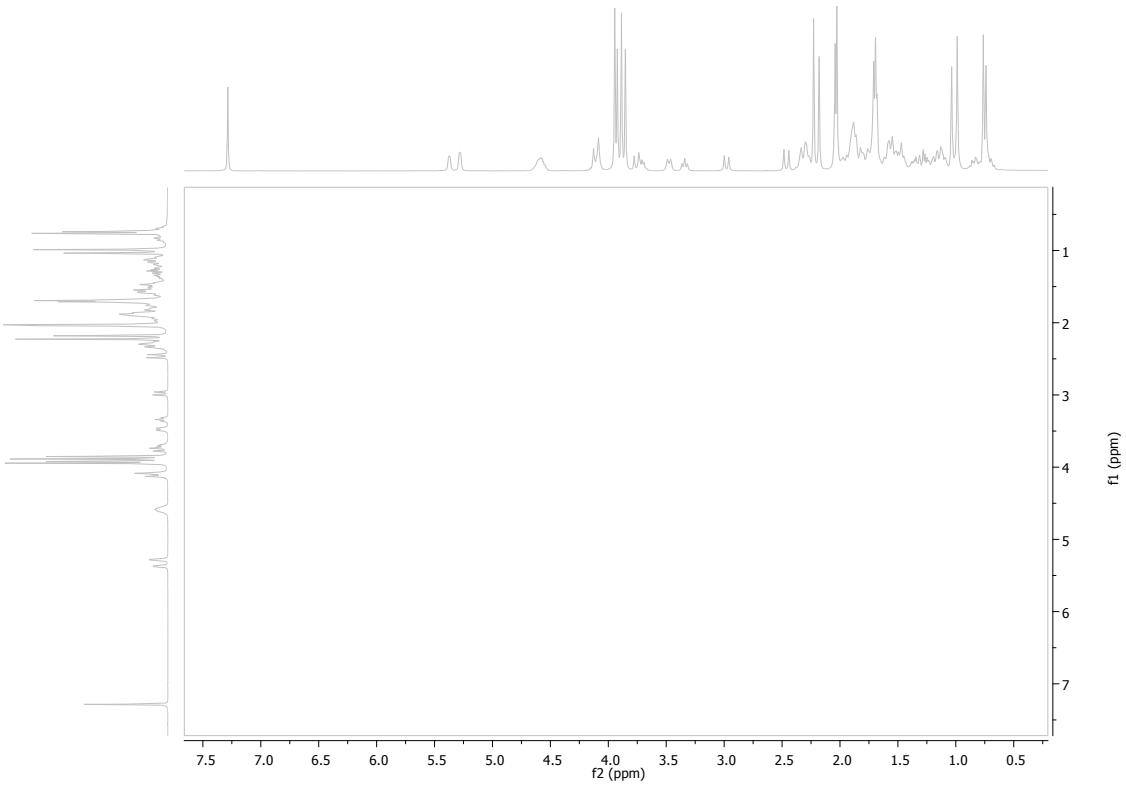

Figure 27. COSY spectrum of compounds **34**/**35** ($CDCl_3$).

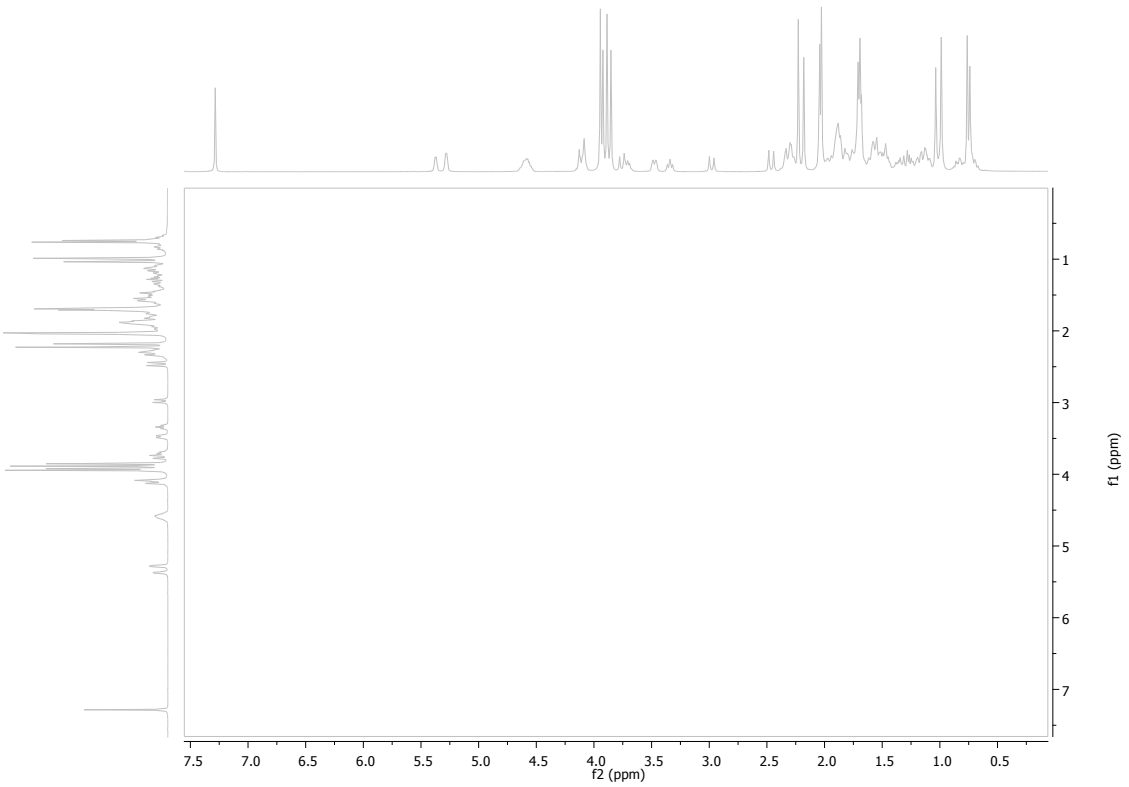

Figure 28. NOESY spectrum of compounds **34**/**35** ($CDCl_3$).

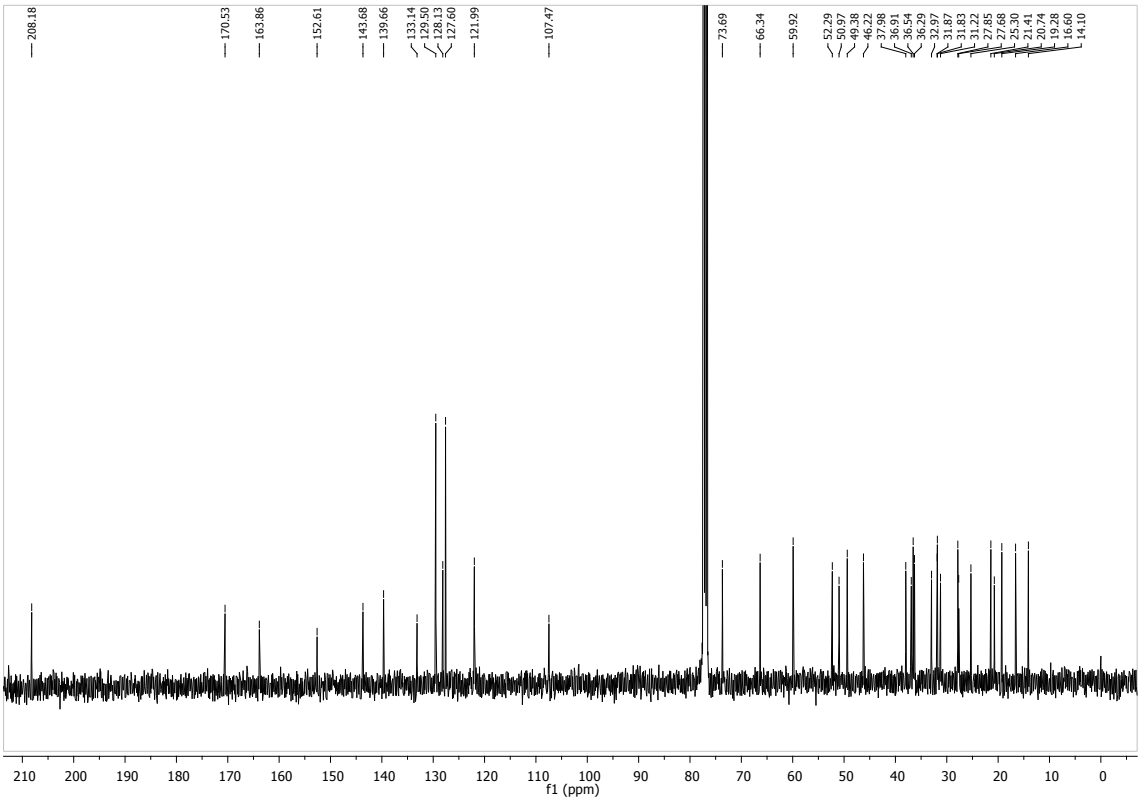

Figure 29. ^{1}H NMR and ^{13}C NMR spectra of compound **36a** ($CDCl_3$).

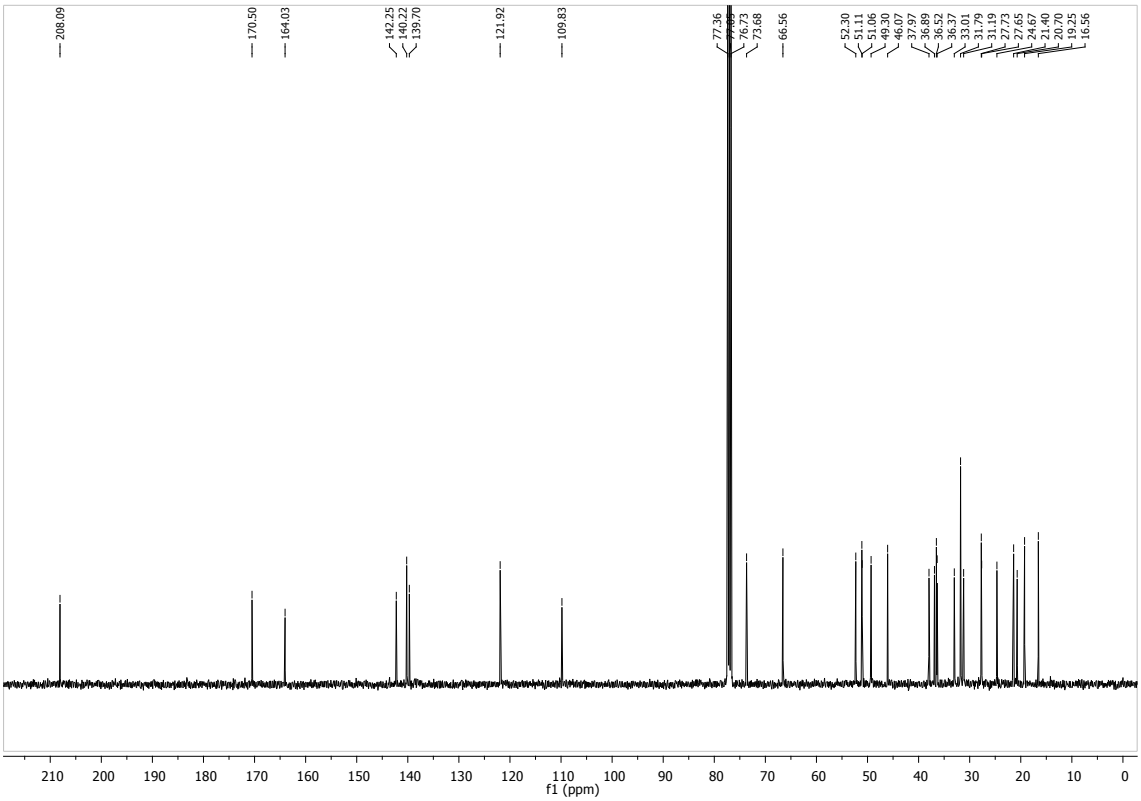

Figure 30. ^{1}H NMR and ^{13}C NMR spectra of compound **36b** ($CDCl_3$).

Figure 31. ^{1}H NMR and ^{13}C NMR spectra of compounds **37**/**38** ($CDCl_3$).

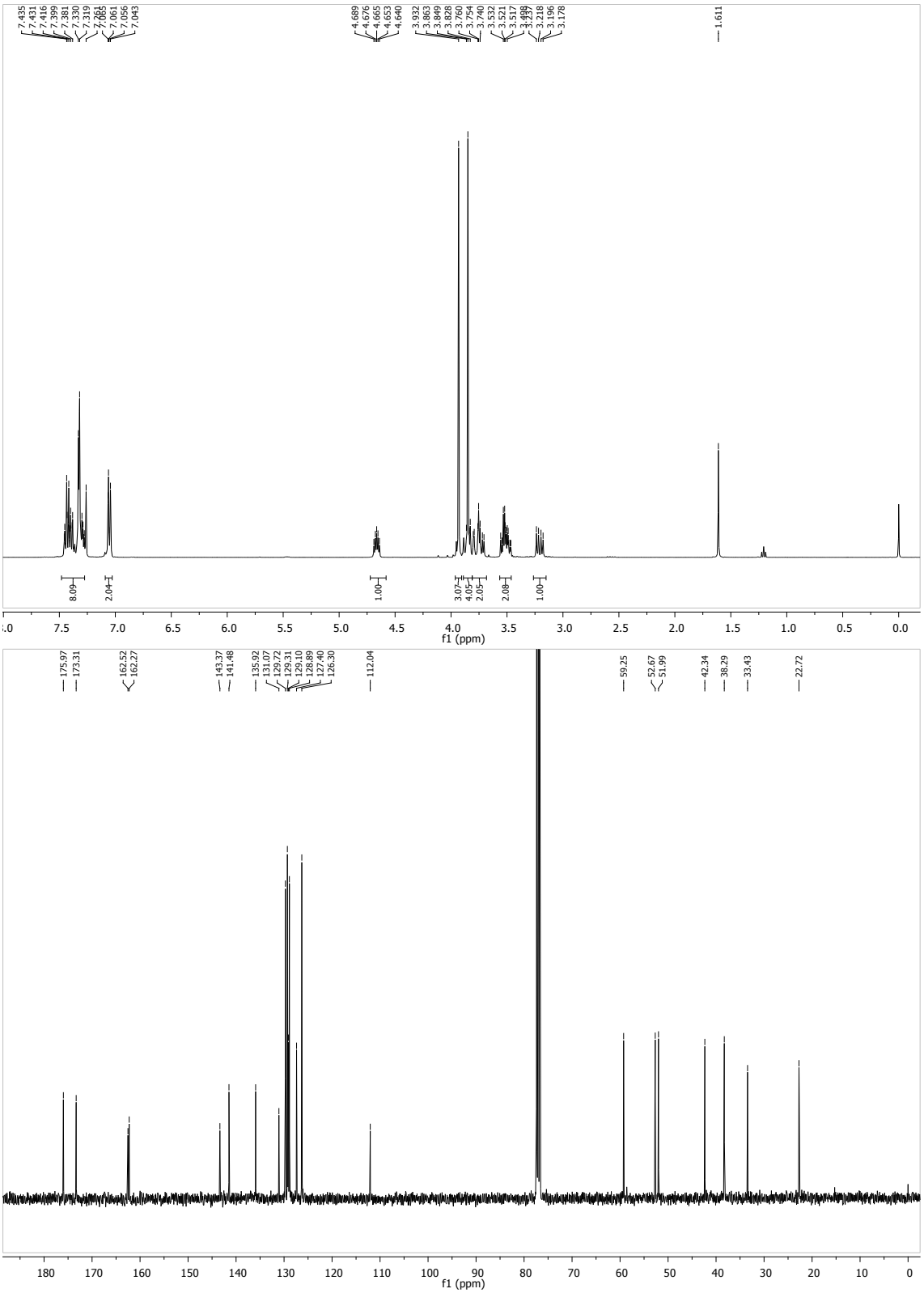

Figure 32. ^{1}H NMR and ^{13}C NMR spectra of compound **44** ($CDCl_3$).

Crystallographic data for Ethyl 6-phenyl-2,2-dioxo-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-7-carboxylate (18a) and (4a*R*,7a*R*,8a*R*)-Dimethyl 8-benzyl-5,7-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-1*H*,3*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*d*]pyridine-2,3-dicarboxylate (44)

X-ray Diffraction. Crystals of compounds **18a** and **44** were selected, covered with polyfluoroether oil, and mounted on a nylon loop. Crystallographic data for this compound was collected at the IST using graphite monochromated Mo-Kα radiation (λ=0.71073Å) on diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat, at 150 K. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.[1] Structure solution and refinement were performed using direct methods with the programs SIR2004[2] or SIR2014[3] included in the package of programs WINGX-Version 2014.1[4] and SHELXL.[5] All hydrogen atoms were inserted in idealised positions and allowed to refine riding on the parent carbon atom, with C–H distances of 0.95Å, 0.98 Å, 0.99 Å and 1.00 Å for aromatic, methyl, methylene and methine H atoms, respectively, and with U_{iso}(H) = 1.2U_{eq}(C). The figures of the molecular structure were generated using ORTEP-III.[6]

Table 1. Crystallographic data and details about refinement for structures **18a** and **44**.

	18a	**44**
Formula	C_{14} H_{14} N_2 O_4 S	C_{26} H_{23} N_3 O_6
M	306.33	473.47
λ (Å)	0.71073	0.71073
T (K)	150(2)	150(2)
crystal system	Monoclinic	Triclinic
space group	*P* $2_1/c$	*P* -1
a (Å)	8.7862(3)	12.8055(17)
b (Å)	20.9598(7)	14.5445(19)
c (Å)	8.5716(3)	14.594(2)
α (°)	90	98.060(6)
β (°)	117.059(2)	99.289(7)
γ (°)	90	115.517(6)
V (Å^3)	1405.73(8)	2352.8(6)
Z	4	4
ρ_{calc} (g.cm^{-3})	1.447	1.337
μ (mm^{-1})	0.248	0.096
Crystal size	0.50×0.40×0.40	0.40×0.20×0.10
Crystal colour	Colourless	Colourless
Crystal description	Block	Plate
θ_{max} (°)	31.97	25.909
total data	18485	25820
unique data	3803	4179
R_{int}	0.0302	0.1036
R [I>2σ(I)]	0.0408	0.0614
R_w	0.1048	0.1206
Goodness of fit	1.046	0.872
ρ_{min}	-0.347	-0.321
ρ_{max}	0.350	0.377

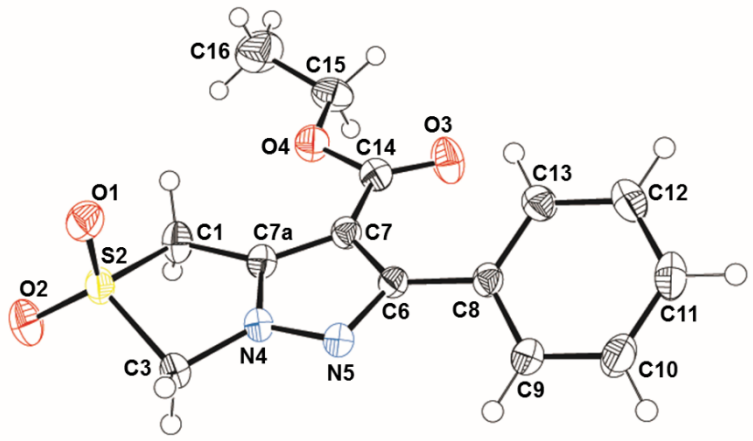

Figure 33. ORTEP-3 diagram of compound **18a**, using 50% probability level ellipsoids. Selected bond lengths (Å): C1−S2, 1.8080(13); S2−C3, 1.8108(13); S2−O1, 1.4309(10); S2−O2, 1.4265(10); C3−N4, 1.4432(14); N4−C7a, 1.3403(15); N4−N5, 1.3511(14); N5−C6, 1.3431(14); C6−C7, 1.4269(17); C7−C7a, 1.3849(15); Selected bond angles (º): C1–C7a–N4 113.67(10); C1–S2–C3, 107.96(6); S2–C3–N4, 99.54(8).

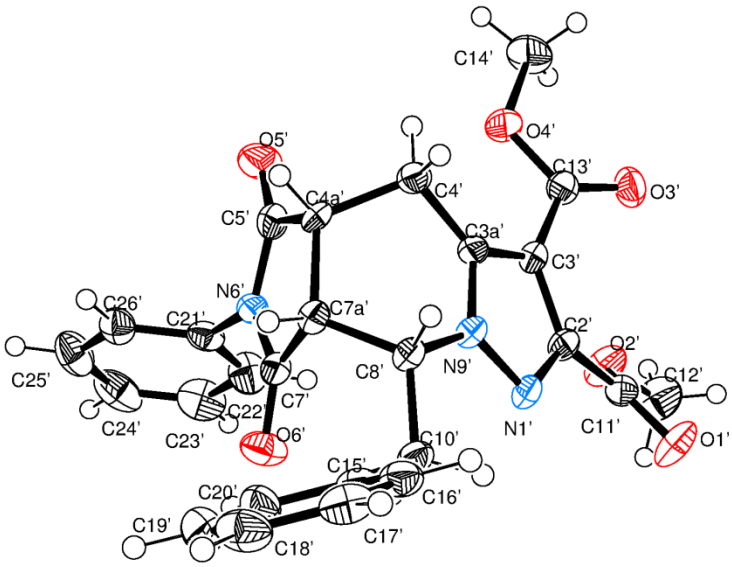

Figure 34. ORTEP-3 diagram of compound **44**, using 50% probability level ellipsoids. Selected bond lengths (Å): N6−C5, 1.383(4); C5−C4a, 1.504(4); C4a−C7a, 1.550(4); C7−C7a, 1.504(5); C7−N6, 1.405(4); N9−N1, 1.356(4); N1−C2, 1.329(4); C2−C3, 1.407(4); C3−C3a, 1.387(5); C3a−N9, 1.343(4); C8−C7a, 1.541(4); C4−C4a, 1.532(5); Selected bond angles (º): C5–C4a–C4, 109.9(3); C7–C7a–C8, 112.5(3); C8–N9–N1, 124.8(3);); C4–C3a–C3, 137.6(3).

Table 2. Crystal data and structure refinement for **18a**.

Identification code	**18a**	
Empirical formula	C14 H14 N2 O4 S	
Formula weight	306.33	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.7862(3) Å	α= 90°.
	b = 20.9598(7) Å	β= 117.059(2)°.
	c = 8.5716(3) Å	γ = 90°.
Volume	1405.73(9) $Å^3$	
Z	4	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	0.248 mm^{-1}	
F(000)	640	
Crystal size	0.500 x 0.400 x 0.400 mm^3	
Theta range for data collection	1.943 to 31.969°.	
Index ranges	-13<=h<=12, -31<=k<=30, -12<=l<=12	
Reflections collected	18485	
Independent reflections	4845 [R(int) = 0.0308]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.907 and 0.886	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4845 / 0 / 191	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1048	
R indices (all data)	R1 = 0.0561, wR2 = 0.1105	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.350 and -0.347 $e.Å^{-3}$	

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **18a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(2)	2539(1)	1517(1)	5927(1)	29(1)
O(1)	965(1)	1779(1)	5753(1)	36(1)
O(2)	3392(2)	1823(1)	5059(1)	44(1)
O(3)	4507(1)	225(1)	12959(1)	41(1)
O(4)	4969(1)	1150(1)	11925(1)	34(1)
N(4)	2386(1)	433(1)	7051(1)	27(1)
N(5)	1710(1)	-112(1)	7310(1)	27(1)
C(1)	3938(2)	1386(1)	8227(2)	33(1)
C(3)	2205(2)	676(1)	5400(2)	30(1)
C(6)	2249(1)	-131(1)	9048(1)	24(1)
C(7)	3270(1)	413(1)	9883(2)	25(1)
C(7A)	3297(2)	763(1)	8525(2)	26(1)
C(8)	1642(1)	-668(1)	9729(2)	24(1)
C(9)	1145(2)	-1235(1)	8767(2)	31(1)
C(10)	434(2)	-1728(1)	9284(2)	38(1)
C(11)	233(2)	-1672(1)	10789(2)	39(1)
C(12)	744(2)	-1117(1)	11764(2)	35(1)
C(13)	1434(2)	-615(1)	11237(2)	30(1)
C(14)	4272(2)	571(1)	11740(2)	28(1)
C(15)	6111(2)	1350(1)	13696(2)	38(1)
C(16)	6365(3)	2049(1)	13648(3)	59(1)

Table 4. Bond lengths [Å] and angles [°] for **18a**.

S(2)-O(2)	1.4265(10)
S(2)-O(1)	1.4309(10)
S(2)-C(1)	1.8080(13)
S(2)-C(3)	1.8108(13)
O(3)-C(14)	1.2092(15)
O(4)-C(14)	1.3361(15)
O(4)-C(15)	1.4495(16)
N(4)-C(7A)	1.3403(15)
N(4)-N(5)	1.3511(14)
N(4)-C(3)	1.4432(14)
N(5)-C(6)	1.3431(14)
C(1)-C(7A)	1.4890(17)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(6)-C(7)	1.4269(17)
C(6)-C(8)	1.4749(15)
C(7)-C(7A)	1.3849(15)
C(7)-C(14)	1.4635(16)
C(8)-C(13)	1.3899(16)
C(8)-C(9)	1.3970(17)
C(9)-C(10)	1.3809(18)
C(9)-H(9)	0.9500
C(10)-C(11)	1.385(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.383(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.3883(18)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(15)-C(16)	1.487(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800

C(16)-H(16C)	0.9800
O(2)-S(2)-O(1)	119.06(6)
O(2)-S(2)-C(1)	112.28(6)
O(1)-S(2)-C(1)	108.49(6)
O(2)-S(2)-C(3)	111.82(6)
O(1)-S(2)-C(3)	107.96(6)
C(1)-S(2)-C(3)	94.39(6)
C(14)-O(4)-C(15)	116.69(10)
C(7A)-N(4)-N(5)	113.60(9)
C(7A)-N(4)-C(3)	119.62(10)
N(5)-N(4)-C(3)	126.78(10)
C(6)-N(5)-N(4)	104.38(9)
C(7A)-C(1)-S(2)	101.40(8)
C(7A)-C(1)-H(1A)	111.5
S(2)-C(1)-H(1A)	111.5
C(7A)-C(1)-H(1B)	111.5
S(2)-C(1)-H(1B)	111.5
H(1A)-C(1)-H(1B)	109.3
N(4)-C(3)-S(2)	99.54(8)
N(4)-C(3)-H(3A)	111.9
S(2)-C(3)-H(3A)	111.9
N(4)-C(3)-H(3B)	111.9
S(2)-C(3)-H(3B)	111.9
H(3A)-C(3)-H(3B)	109.6
N(5)-C(6)-C(7)	110.86(10)
N(5)-C(6)-C(8)	116.98(10)
C(7)-C(6)-C(8)	132.08(10)
C(7A)-C(7)-C(6)	104.44(10)
C(7A)-C(7)-C(14)	124.27(11)
C(6)-C(7)-C(14)	130.95(10)
N(4)-C(7A)-C(7)	106.71(10)
N(4)-C(7A)-C(1)	113.67(10)
C(7)-C(7A)-C(1)	139.52(11)
C(13)-C(8)-C(9)	118.67(11)
C(13)-C(8)-C(6)	122.05(11)
C(9)-C(8)-C(6)	119.12(10)
C(10)-C(9)-C(8)	120.79(12)

C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	120.28(13)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(12)-C(11)-C(10)	119.33(13)
C(12)-C(11)-H(11)	120.3
C(10)-C(11)-H(11)	120.3
C(11)-C(12)-C(13)	120.72(12)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-C(8)	120.20(12)
C(12)-C(13)-H(13)	119.9
C(8)-C(13)-H(13)	119.9
O(3)-C(14)-O(4)	123.50(12)
O(3)-C(14)-C(7)	125.94(12)
O(4)-C(14)-C(7)	110.51(10)
O(4)-C(15)-C(16)	107.33(13)
O(4)-C(15)-H(15A)	110.2
C(16)-C(15)-H(15A)	110.2
O(4)-C(15)-H(15B)	110.2
C(16)-C(15)-H(15B)	110.2
H(15A)-C(15)-H(15B)	108.5
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **18a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(2)	32(1)	26(1)	30(1)	7(1)	17(1)	1(1)
O(1)	37(1)	33(1)	40(1)	6(1)	18(1)	8(1)
O(2)	52(1)	44(1)	46(1)	11(1)	31(1)	-6(1)
O(3)	40(1)	48(1)	26(1)	8(1)	8(1)	-9(1)
O(4)	37(1)	32(1)	29(1)	-2(1)	11(1)	-5(1)
N(4)	33(1)	24(1)	25(1)	4(1)	15(1)	0(1)
N(5)	33(1)	23(1)	27(1)	2(1)	16(1)	1(1)
C(1)	31(1)	31(1)	32(1)	6(1)	11(1)	-5(1)
C(3)	38(1)	29(1)	26(1)	5(1)	18(1)	2(1)
C(6)	26(1)	22(1)	25(1)	3(1)	13(1)	4(1)
C(7)	24(1)	25(1)	25(1)	3(1)	11(1)	2(1)
C(7A)	25(1)	25(1)	26(1)	3(1)	11(1)	1(1)
C(8)	24(1)	23(1)	27(1)	5(1)	12(1)	5(1)
C(9)	39(1)	24(1)	32(1)	4(1)	18(1)	4(1)
C(10)	47(1)	24(1)	43(1)	3(1)	20(1)	-1(1)
C(11)	41(1)	32(1)	46(1)	13(1)	22(1)	-1(1)
C(12)	33(1)	43(1)	34(1)	9(1)	19(1)	1(1)
C(13)	29(1)	32(1)	30(1)	2(1)	15(1)	0(1)
C(14)	24(1)	30(1)	28(1)	1(1)	11(1)	1(1)
C(15)	35(1)	47(1)	31(1)	-11(1)	13(1)	-6(1)
C(16)	64(1)	46(1)	63(1)	-20(1)	27(1)	-16(1)

Table 6. Torsion angles [°] for **18a**.

C(7A)-N(4)-N(5)-C(6)	-1.01(13)
C(3)-N(4)-N(5)-C(6)	179.33(11)
O(2)-S(2)-C(1)-C(7A)	-144.49(9)
O(1)-S(2)-C(1)-C(7A)	81.83(9)
C(3)-S(2)-C(1)-C(7A)	-28.76(9)
C(7A)-N(4)-C(3)-S(2)	-24.58(13)
N(5)-N(4)-C(3)-S(2)	155.06(10)
O(2)-S(2)-C(3)-N(4)	146.01(8)
O(1)-S(2)-C(3)-N(4)	-81.16(9)
C(1)-S(2)-C(3)-N(4)	29.89(9)
N(4)-N(5)-C(6)-C(7)	0.30(12)
N(4)-N(5)-C(6)-C(8)	177.38(9)
N(5)-C(6)-C(7)-C(7A)	0.45(13)
C(8)-C(6)-C(7)-C(7A)	-176.04(11)
N(5)-C(6)-C(7)-C(14)	-172.86(11)
C(8)-C(6)-C(7)-C(14)	10.6(2)
N(5)-N(4)-C(7A)-C(7)	1.32(14)
C(3)-N(4)-C(7A)-C(7)	-178.99(10)
N(5)-N(4)-C(7A)-C(1)	-175.89(10)
C(3)-N(4)-C(7A)-C(1)	3.79(16)
C(6)-C(7)-C(7A)-N(4)	-1.02(13)
C(14)-C(7)-C(7A)-N(4)	172.87(10)
C(6)-C(7)-C(7A)-C(1)	175.05(14)
C(14)-C(7)-C(7A)-C(1)	-11.1(2)
S(2)-C(1)-C(7A)-N(4)	19.37(12)
S(2)-C(1)-C(7A)-C(7)	-156.52(14)
N(5)-C(6)-C(8)-C(13)	-150.84(11)
C(7)-C(6)-C(8)-C(13)	25.48(19)
N(5)-C(6)-C(8)-C(9)	24.56(16)
C(7)-C(6)-C(8)-C(9)	-159.12(12)
C(13)-C(8)-C(9)-C(10)	1.13(19)
C(6)-C(8)-C(9)-C(10)	-174.43(11)
C(8)-C(9)-C(10)-C(11)	-1.3(2)
C(9)-C(10)-C(11)-C(12)	0.3(2)
C(10)-C(11)-C(12)-C(13)	0.8(2)
C(11)-C(12)-C(13)-C(8)	-0.9(2)

C(9)-C(8)-C(13)-C(12)	-0.05(18)
C(6)-C(8)-C(13)-C(12)	175.37(11)
C(15)-O(4)-C(14)-O(3)	2.32(18)
C(15)-O(4)-C(14)-C(7)	-175.28(10)
C(7A)-C(7)-C(14)-O(3)	-166.77(13)
C(6)-C(7)-C(14)-O(3)	5.4(2)
C(7A)-C(7)-C(14)-O(4)	10.76(16)
C(6)-C(7)-C(14)-O(4)	-177.09(11)
C(14)-O(4)-C(15)-C(16)	-165.42(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Crystal data and structure refinement for **44**.

Identification code	**44**	
Empirical formula	C26 H23 N3 O6	
Formula weight	473.47	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.8055(17) Å	α= 98.060(6)°.
	b = 14.5445(19) Å	β= 99.289(7)°.
	c = 14.594(2) Å	γ = 115.517(6)°.
Volume	2352.8(6) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	992	
Crystal size	0.400 x 0.200 x 0.100 mm^3	
Theta range for data collection	1.596 to 25.909°.	
Index ranges	-11<=h<=15, -17<=k<=16, -17<=l<=17	
Reflections collected	25820	
Independent reflections	9063 [R(int) = 0.1036]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.990 and 0.962	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9063 / 0 / 635	
Goodness-of-fit on F^2	0.872	
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1206	
R indices (all data)	R1 = 0.1744, wR2 = 0.1581	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.377 and -0.321 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **44**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-963(2)	2028(2)	4497(2)	43(1)
O(2)	567(2)	2952(2)	5780(2)	37(1)
O(3)	512(2)	1212(2)	6649(2)	33(1)
O(4)	1968(2)	759(2)	6583(2)	33(1)
O(5)	4895(2)	1695(2)	5736(2)	39(1)
O(6)	4054(2)	2801(2)	3082(2)	36(1)
N(1)	852(2)	1603(2)	3828(2)	25(1)
N(6)	4644(2)	2484(2)	4520(2)	25(1)
N(9)	1496(2)	1068(2)	3815(2)	22(1)
C(2)	704(3)	1694(2)	4711(2)	23(1)
C(3)	1246(3)	1221(3)	5259(2)	23(1)
C(3A)	1734(3)	806(2)	4641(2)	21(1)
C(4)	2374(3)	162(3)	4657(2)	22(1)
C(4A)	3450(3)	660(3)	4233(2)	23(1)
C(5)	4413(3)	1639(3)	4932(3)	27(1)
C(7)	3970(3)	2190(3)	3572(2)	25(1)
C(7A)	3177(3)	1025(2)	3316(2)	21(1)
C(8)	1845(3)	731(3)	2980(2)	25(1)
C(10)	1490(3)	1134(3)	2134(2)	28(1)
C(11)	3(3)	2232(3)	4963(2)	26(1)
C(12)	-108(4)	3437(3)	6144(3)	55(1)
C(13)	1180(3)	1079(3)	6226(2)	25(1)
C(14)	1896(3)	472(3)	7485(2)	38(1)
C(15)	5462(3)	3537(3)	5026(2)	28(1)
C(16)	6500(4)	4053(3)	4769(3)	49(1)
C(17)	7289(4)	5086(3)	5260(3)	65(1)
C(18)	7009(4)	5554(3)	6003(3)	52(1)
C(19)	5968(4)	5026(3)	6245(3)	39(1)
C(20)	5184(3)	4016(3)	5754(2)	33(1)
C(21)	1741(3)	702(3)	1242(2)	29(1)
C(22)	2556(3)	1342(3)	822(2)	36(1)
C(23)	2779(4)	942(4)	6(3)	51(1)
C(24)	2200(5)	-116(4)	-392(3)	63(2)

C(25)	1386(6)	-757(4)	10(3)	84(2)
C(26)	1149(5)	-354(3)	828(3)	66(2)
O(1')	8852(3)	4226(2)	12323(2)	45(1)
O(2')	9123(2)	2898(2)	11667(2)	38(1)
O(3')	10953(2)	3758(2)	10629(2)	36(1)
O(4')	10180(2)	3062(2)	9055(2)	37(1)
O(5')	7308(2)	1474(2)	7019(2)	44(1)
O(6')	4620(2)	1868(2)	8482(2)	38(1)
N(1')	7662(2)	3958(2)	10366(2)	25(1)
N(6')	5841(2)	1441(2)	7747(2)	24(1)
N(9')	7590(2)	3934(2)	9432(2)	23(1)
C(2')	8580(3)	3775(3)	10639(2)	24(1)
C(3')	9090(3)	3630(3)	9886(2)	24(1)
C(3A')	8414(3)	3748(3)	9108(2)	23(1)
C(4')	8403(3)	3741(3)	8086(2)	26(1)
C(4A')	7114(3)	3057(3)	7468(2)	24(1)
C(5')	6802(3)	1908(3)	7359(2)	30(1)
C(7')	5440(3)	2134(3)	8108(2)	26(1)
C(7A')	6158(3)	3184(3)	7911(2)	24(1)
C(8')	6678(3)	4088(3)	8799(2)	24(1)
C(10')	5813(3)	4223(3)	9325(2)	27(1)
C(11')	8867(3)	3680(3)	11636(2)	27(1)
C(12')	9497(4)	2764(3)	12600(3)	52(1)
C(13')	10170(3)	3505(3)	9918(3)	29(1)
C(14')	11248(4)	2973(4)	9004(3)	58(1)
C(15')	4977(3)	4508(3)	8709(2)	25(1)
C(16')	5289(3)	5547(3)	8753(2)	31(1)
C(17')	4541(4)	5837(3)	8213(3)	38(1)
C(18')	3482(4)	5090(3)	7609(3)	41(1)
C(19')	3172(4)	4049(3)	7550(3)	43(1)
C(20')	3919(3)	3764(3)	8104(3)	35(1)
C(21')	5208(3)	339(3)	7703(3)	29(1)
C(22')	5362(4)	-36(3)	8496(3)	42(1)
C(23')	4684(4)	-1106(3)	8431(3)	48(1)
C(24')	3887(4)	-1757(3)	7596(3)	49(1)
C(25')	3754(3)	-1371(3)	6804(3)	43(1)
C(26')	4407(3)	-316(3)	6857(3)	32(1)

Table 9. Bond lengths [Å] and angles [°] for **44**.

O(1)-C(11)	1.198(4)
O(2)-C(11)	1.327(4)
O(2)-C(12)	1.448(4)
O(3)-C(13)	1.196(4)
O(4)-C(13)	1.344(4)
O(4)-C(14)	1.442(4)
O(5)-C(5)	1.209(4)
O(6)-C(7)	1.197(4)
N(1)-C(2)	1.329(4)
N(1)-N(9)	1.356(4)
N(6)-C(5)	1.383(4)
N(6)-C(7)	1.405(4)
N(6)-C(15)	1.428(4)
N(9)-C(3A)	1.343(4)
N(9)-C(8)	1.457(4)
C(2)-C(3)	1.407(4)
C(2)-C(11)	1.478(5)
C(3)-C(3A)	1.387(5)
C(3)-C(13)	1.465(5)
C(3A)-C(4)	1.487(4)
C(4)-C(4A)	1.532(5)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4A)-C(5)	1.504(4)
C(4A)-C(7A)	1.550(4)
C(4A)-H(40A)	1.0000
C(7)-C(7A)	1.504(5)
C(7A)-C(8)	1.541(4)
C(7A)-H(7A)	1.0000
C(8)-C(10)	1.525(4)
C(8)-H(8)	1.0000
C(10)-C(21)	1.508(5)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800

C(12)-H(12C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.361(5)
C(15)-C(20)	1.367(5)
C(16)-C(17)	1.395(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.377(6)
C(17)-H(17)	0.9500
C(18)-C(19)	1.356(6)
C(18)-H(18)	0.9500
C(19)-C(20)	1.371(5)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.364(5)
C(21)-C(26)	1.374(5)
C(22)-C(23)	1.377(5)
C(22)-H(22)	0.9500
C(23)-C(24)	1.373(6)
C(23)-H(23)	0.9500
C(24)-C(25)	1.346(7)
C(24)-H(24)	0.9500
C(25)-C(26)	1.391(6)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
O(1')-C(11')	1.197(4)
O(2')-C(11')	1.318(4)
O(2')-C(12')	1.437(4)
O(3')-C(13')	1.207(4)
O(4')-C(13')	1.336(4)
O(4')-C(14')	1.440(4)
O(5')-C(5')	1.197(4)
O(6')-C(7')	1.202(4)
N(1')-C(2')	1.326(4)
N(1')-N(9')	1.346(4)
N(6')-C(5')	1.381(5)
N(6')-C(7')	1.394(4)

N(6')-C(21')	1.437(4)
N(9')-C(3A')	1.335(4)
N(9')-C(8')	1.484(4)
C(2')-C(3')	1.401(5)
C(2')-C(11')	1.483(5)
C(3')-C(3A')	1.391(4)
C(3')-C(13')	1.465(5)
C(3A')-C(4')	1.487(5)
C(4')-C(4A')	1.543(4)
C(4')-H(4'1)	0.9900
C(4')-H(4'2)	0.9900
C(4A')-C(5')	1.518(5)
C(4A')-C(7A')	1.539(5)
C(4A')-H(4A')	1.0000
C(7')-C(7A')	1.503(5)
C(7A')-C(8')	1.530(4)
C(7A')-H(7A')	1.0000
C(8')-C(10')	1.508(5)
C(8')-H(8')	1.0000
C(10')-C(15')	1.517(4)
C(10')-H(10C)	0.9900
C(10')-H(10D)	0.9900
C(12')-H(12D)	0.9800
C(12')-H(12E)	0.9800
C(12')-H(12F)	0.9800
C(14')-H(14D)	0.9800
C(14')-H(14E)	0.9800
C(14')-H(14F)	0.9800
C(15')-C(20')	1.368(5)
C(15')-C(16')	1.375(5)
C(16')-C(17')	1.383(5)
C(16')-H(16')	0.9500
C(17')-C(18')	1.369(5)
C(17')-H(17')	0.9500
C(18')-C(19')	1.376(5)
C(18')-H(18')	0.9500
C(19')-C(20')	1.388(5)
C(19')-H(19')	0.9500

C(20')-H(20')	0.9500
C(21')-C(22')	1.368(5)
C(21')-C(26')	1.379(5)
C(22')-C(23')	1.397(5)
C(22')-H(22')	0.9500
C(23')-C(24')	1.366(6)
C(23')-H(23')	0.9500
C(24')-C(25')	1.371(6)
C(24')-H(24')	0.9500
C(25')-C(26')	1.378(5)
C(25')-H(25')	0.9500
C(26')-H(26')	0.9500

C(11)-O(2)-C(12)	115.5(3)
C(13)-O(4)-C(14)	116.4(3)
C(2)-N(1)-N(9)	103.6(2)
C(5)-N(6)-C(7)	112.6(3)
C(5)-N(6)-C(15)	122.8(3)
C(7)-N(6)-C(15)	124.6(3)
C(3A)-N(9)-N(1)	113.8(3)
C(3A)-N(9)-C(8)	121.3(3)
N(1)-N(9)-C(8)	124.8(3)
N(1)-C(2)-C(3)	112.1(3)
N(1)-C(2)-C(11)	117.7(3)
C(3)-C(2)-C(11)	130.2(3)
C(3A)-C(3)-C(2)	104.7(3)
C(3A)-C(3)-C(13)	127.1(3)
C(2)-C(3)-C(13)	127.8(3)
N(9)-C(3A)-C(3)	105.8(3)
N(9)-C(3A)-C(4)	116.5(3)
C(3)-C(3A)-C(4)	137.6(3)
C(3A)-C(4)-C(4A)	108.7(3)
C(3A)-C(4)-H(4A)	110.0
C(4A)-C(4)-H(4A)	110.0
C(3A)-C(4)-H(4B)	110.0
C(4A)-C(4)-H(4B)	110.0
H(4A)-C(4)-H(4B)	108.3
C(5)-C(4A)-C(4)	109.9(3)

C(5)-C(4A)-C(7A)	104.7(3)
C(4)-C(4A)-C(7A)	114.1(3)
C(5)-C(4A)-H(40A)	109.3
C(4)-C(4A)-H(40A)	109.3
C(7A)-C(4A)-H(40A)	109.3
O(5)-C(5)-N(6)	124.7(3)
O(5)-C(5)-C(4A)	126.1(3)
N(6)-C(5)-C(4A)	109.2(3)
O(6)-C(7)-N(6)	123.2(3)
O(6)-C(7)-C(7A)	128.3(3)
N(6)-C(7)-C(7A)	108.5(3)
C(7)-C(7A)-C(8)	112.5(3)
C(7)-C(7A)-C(4A)	104.9(3)
C(8)-C(7A)-C(4A)	112.4(3)
C(7)-C(7A)-H(7A)	109.0
C(8)-C(7A)-H(7A)	109.0
C(4A)-C(7A)-H(7A)	109.0
N(9)-C(8)-C(10)	111.6(3)
N(9)-C(8)-C(7A)	106.6(2)
C(10)-C(8)-C(7A)	117.0(3)
N(9)-C(8)-H(8)	107.1
C(10)-C(8)-H(8)	107.1
C(7A)-C(8)-H(8)	107.1
C(21)-C(10)-C(8)	111.8(3)
C(21)-C(10)-H(10A)	109.3
C(8)-C(10)-H(10A)	109.3
C(21)-C(10)-H(10B)	109.3
C(8)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	107.9
O(1)-C(11)-O(2)	124.4(3)
O(1)-C(11)-C(2)	124.2(3)
O(2)-C(11)-C(2)	111.4(3)
O(2)-C(12)-H(12A)	109.5
O(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
O(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

O(3)-C(13)-O(4)	123.6(3)
O(3)-C(13)-C(3)	125.5(3)
O(4)-C(13)-C(3)	110.9(3)
O(4)-C(14)-H(14A)	109.5
O(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	121.0(3)
C(16)-C(15)-N(6)	119.5(3)
C(20)-C(15)-N(6)	119.5(3)
C(15)-C(16)-C(17)	119.1(4)
C(15)-C(16)-H(16)	120.4
C(17)-C(16)-H(16)	120.4
C(18)-C(17)-C(16)	119.4(4)
C(18)-C(17)-H(17)	120.3
C(16)-C(17)-H(17)	120.3
C(19)-C(18)-C(17)	120.5(4)
C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(20)	120.2(4)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(15)-C(20)-C(19)	119.8(4)
C(15)-C(20)-H(20)	120.1
C(19)-C(20)-H(20)	120.1
C(22)-C(21)-C(26)	118.1(4)
C(22)-C(21)-C(10)	121.3(3)
C(26)-C(21)-C(10)	120.6(4)
C(21)-C(22)-C(23)	121.0(4)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(24)-C(23)-C(22)	120.4(4)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(25)-C(24)-C(23)	119.2(4)
C(25)-C(24)-H(24)	120.4

C(23)-C(24)-H(24)	120.4
C(24)-C(25)-C(26)	120.5(5)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(21)-C(26)-C(25)	120.7(5)
C(21)-C(26)-H(26)	119.6
C(25)-C(26)-H(26)	119.6
C(11')-O(2')-C(12')	116.5(3)
C(13')-O(4')-C(14')	115.4(3)
C(2')-N(1')-N(9')	103.6(3)
C(5')-N(6')-C(7')	112.9(3)
C(5')-N(6')-C(21')	125.3(3)
C(7')-N(6')-C(21')	121.4(3)
C(3A')-N(9')-N(1')	114.0(3)
C(3A')-N(9')-C(8')	121.9(3)
N(1')-N(9')-C(8')	124.1(3)
N(1')-C(2')-C(3')	112.3(3)
N(1')-C(2')-C(11')	117.9(3)
C(3')-C(2')-C(11')	129.6(3)
C(3A')-C(3')-C(2')	104.2(3)
C(3A')-C(3')-C(13')	126.8(3)
C(2')-C(3')-C(13')	128.6(3)
N(9')-C(3A')-C(3')	105.8(3)
N(9')-C(3A')-C(4')	116.7(3)
C(3')-C(3A')-C(4')	137.5(3)
C(3A')-C(4')-C(4A')	109.2(3)
C(3A')-C(4')-H(4'1)	109.8
C(4A')-C(4')-H(4'1)	109.8
C(3A')-C(4')-H(4'2)	109.8
C(4A')-C(4')-H(4'2)	109.8
H(4'1)-C(4')-H(4'2)	108.3
C(5')-C(4A')-C(7A')	105.1(3)
C(5')-C(4A')-C(4')	109.3(3)
C(7A')-C(4A')-C(4')	114.1(3)
C(5')-C(4A')-H(4A')	109.4
C(7A')-C(4A')-H(4A')	109.4
C(4')-C(4A')-H(4A')	109.4
O(5')-C(5')-N(6')	125.0(3)

O(5')-C(5')-C(4A')	126.7(4)
N(6')-C(5')-C(4A')	108.3(3)
O(6')-C(7')-N(6')	122.2(3)
O(6')-C(7')-C(7A')	128.7(3)
N(6')-C(7')-C(7A')	109.0(3)
C(7')-C(7A')-C(8')	113.1(3)
C(7')-C(7A')-C(4A')	104.5(3)
C(8')-C(7A')-C(4A')	113.5(3)
C(7')-C(7A')-H(7A')	108.5
C(8')-C(7A')-H(7A')	108.5
C(4A')-C(7A')-H(7A')	108.5
N(9')-C(8')-C(10')	111.4(3)
N(9')-C(8')-C(7A')	105.6(2)
C(10')-C(8')-C(7A')	117.3(3)
N(9')-C(8')-H(8')	107.4
C(10')-C(8')-H(8')	107.4
C(7A')-C(8')-H(8')	107.4
C(8')-C(10')-C(15')	110.9(3)
C(8')-C(10')-H(10C)	109.5
C(15')-C(10')-H(10C)	109.5
C(8')-C(10')-H(10D)	109.5
C(15')-C(10')-H(10D)	109.5
H(10C)-C(10')-H(10D)	108.0
O(1')-C(11')-O(2')	124.1(3)
O(1')-C(11')-C(2')	125.0(3)
O(2')-C(11')-C(2')	110.9(3)
O(2')-C(12')-H(12D)	109.5
O(2')-C(12')-H(12E)	109.5
H(12D)-C(12')-H(12E)	109.5
O(2')-C(12')-H(12F)	109.5
H(12D)-C(12')-H(12F)	109.5
H(12E)-C(12')-H(12F)	109.5
O(3')-C(13')-O(4')	123.7(3)
O(3')-C(13')-C(3')	124.9(3)
O(4')-C(13')-C(3')	111.4(3)
O(4')-C(14')-H(14D)	109.5
O(4')-C(14')-H(14E)	109.5
H(14D)-C(14')-H(14E)	109.5

O(4')-C(14')-H(14F)	109.5
H(14D)-C(14')-H(14F)	109.5
H(14E)-C(14')-H(14F)	109.5
C(20')-C(15')-C(16')	118.5(3)
C(20')-C(15')-C(10')	122.1(3)
C(16')-C(15')-C(10')	119.4(3)
C(15')-C(16')-C(17')	121.0(3)
C(15')-C(16')-H(16')	119.5
C(17')-C(16')-H(16')	119.5
C(18')-C(17')-C(16')	120.3(4)
C(18')-C(17')-H(17')	119.8
C(16')-C(17')-H(17')	119.8
C(17')-C(18')-C(19')	119.0(3)
C(17')-C(18')-H(18')	120.5
C(19')-C(18')-H(18')	120.5
C(18')-C(19')-C(20')	120.3(4)
C(18')-C(19')-H(19')	119.8
C(20')-C(19')-H(19')	119.8
C(15')-C(20')-C(19')	120.8(4)
C(15')-C(20')-H(20')	119.6
C(19')-C(20')-H(20')	119.6
C(22')-C(21')-C(26')	121.3(4)
C(22')-C(21')-N(6')	120.4(3)
C(26')-C(21')-N(6')	118.3(3)
C(21')-C(22')-C(23')	118.3(4)
C(21')-C(22')-H(22')	120.9
C(23')-C(22')-H(22')	120.9
C(24')-C(23')-C(22')	120.7(4)
C(24')-C(23')-H(23')	119.7
C(22')-C(23')-H(23')	119.7
C(23')-C(24')-C(25')	120.4(4)
C(23')-C(24')-H(24')	119.8
C(25')-C(24')-H(24')	119.8
C(24')-C(25')-C(26')	119.8(4)
C(24')-C(25')-H(25')	120.1
C(26')-C(25')-H(25')	120.1
C(25')-C(26')-C(21')	119.6(4)
C(25')-C(26')-H(26')	120.2

C(21')-C(26')-H(26') 120.2

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **44**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	39(2)	65(2)	34(2)	4(1)	4(1)	36(2)
O(2)	34(2)	37(2)	37(2)	-7(1)	11(1)	19(1)
O(3)	33(2)	42(2)	24(1)	4(1)	14(1)	16(1)
O(4)	39(2)	53(2)	20(1)	18(1)	14(1)	27(1)
O(5)	43(2)	34(2)	28(2)	9(1)	-2(1)	10(1)
O(6)	44(2)	32(2)	27(1)	12(1)	9(1)	11(1)
N(1)	24(2)	32(2)	21(2)	3(1)	8(1)	15(1)
N(6)	28(2)	20(2)	22(2)	5(1)	7(1)	8(1)
N(9)	24(2)	26(2)	19(2)	4(1)	9(1)	13(1)
C(2)	21(2)	23(2)	20(2)	2(2)	5(2)	8(2)
C(3)	24(2)	26(2)	15(2)	3(2)	7(2)	10(2)
C(3A)	23(2)	24(2)	13(2)	6(2)	6(1)	7(2)
C(4)	25(2)	22(2)	22(2)	3(2)	10(2)	13(2)
C(4A)	24(2)	21(2)	24(2)	4(2)	9(2)	10(2)
C(5)	26(2)	25(2)	26(2)	2(2)	6(2)	10(2)
C(7)	30(2)	32(2)	18(2)	4(2)	11(2)	17(2)
C(7A)	28(2)	20(2)	17(2)	2(2)	10(2)	11(2)
C(8)	29(2)	30(2)	17(2)	1(2)	8(2)	15(2)
C(10)	33(2)	34(2)	17(2)	3(2)	7(2)	15(2)
C(11)	32(2)	26(2)	22(2)	8(2)	13(2)	10(2)
C(12)	61(3)	54(3)	62(3)	-6(2)	32(2)	37(3)
C(13)	20(2)	20(2)	23(2)	0(2)	3(2)	1(2)
C(14)	40(2)	50(3)	21(2)	16(2)	10(2)	15(2)
C(15)	31(2)	22(2)	25(2)	1(2)	8(2)	8(2)
C(16)	43(3)	36(3)	54(3)	-4(2)	24(2)	5(2)
C(17)	44(3)	40(3)	79(4)	-5(3)	23(3)	-6(2)
C(18)	52(3)	34(3)	50(3)	-6(2)	8(2)	8(2)
C(19)	56(3)	32(2)	26(2)	-2(2)	6(2)	21(2)
C(20)	38(2)	27(2)	32(2)	3(2)	7(2)	15(2)

C(21)	35(2)	31(2)	17(2)	2(2)	5(2)	15(2)
C(22)	40(2)	46(3)	18(2)	6(2)	7(2)	16(2)
C(23)	44(3)	91(4)	27(2)	22(3)	18(2)	34(3)
C(24)	119(5)	97(4)	18(2)	19(3)	31(3)	85(4)
C(25)	185(7)	48(3)	28(3)	7(2)	35(3)	59(4)
C(26)	116(4)	33(3)	34(3)	8(2)	34(3)	15(3)
O(1')	71(2)	51(2)	23(2)	-1(1)	10(1)	40(2)
O(2')	59(2)	46(2)	26(2)	12(1)	10(1)	37(2)
O(3')	25(2)	39(2)	37(2)	-3(1)	-2(1)	14(1)
O(4')	30(2)	45(2)	37(2)	-4(1)	12(1)	22(1)
O(5')	38(2)	34(2)	57(2)	-5(1)	22(1)	16(1)
O(6')	34(2)	28(2)	57(2)	10(1)	24(1)	13(1)
N(1')	29(2)	27(2)	17(2)	1(1)	3(1)	14(1)
N(6')	21(2)	22(2)	27(2)	0(1)	7(1)	9(1)
N(9')	27(2)	25(2)	17(2)	4(1)	6(1)	13(1)
C(2')	28(2)	22(2)	23(2)	1(2)	7(2)	13(2)
C(3')	24(2)	24(2)	20(2)	0(2)	4(2)	10(2)
C(3A')	22(2)	23(2)	24(2)	1(2)	8(2)	9(2)
C(4')	27(2)	23(2)	26(2)	4(2)	11(2)	10(2)
C(4A')	28(2)	27(2)	16(2)	0(2)	7(2)	13(2)
C(5')	28(2)	26(2)	28(2)	-4(2)	4(2)	9(2)
C(7')	25(2)	31(2)	21(2)	2(2)	4(2)	13(2)
C(7A')	26(2)	23(2)	21(2)	4(2)	6(2)	12(2)
C(8')	28(2)	26(2)	18(2)	3(2)	6(2)	14(2)
C(10')	29(2)	32(2)	24(2)	4(2)	8(2)	18(2)
C(11')	24(2)	29(2)	28(2)	4(2)	6(2)	13(2)
C(12')	67(3)	72(3)	37(3)	21(2)	11(2)	48(3)
C(13')	30(2)	19(2)	35(2)	-1(2)	11(2)	10(2)
C(14')	32(3)	76(3)	67(3)	-7(3)	19(2)	32(3)
C(15')	26(2)	33(2)	24(2)	8(2)	14(2)	18(2)
C(16')	30(2)	37(2)	33(2)	8(2)	12(2)	20(2)
C(17')	48(3)	40(2)	40(2)	16(2)	23(2)	27(2)
C(18')	39(3)	58(3)	46(3)	24(2)	18(2)	34(2)
C(19')	32(2)	51(3)	41(2)	5(2)	4(2)	20(2)
C(20')	27(2)	37(2)	41(2)	3(2)	5(2)	18(2)
C(21')	25(2)	29(2)	37(2)	9(2)	13(2)	15(2)
C(22')	42(3)	39(3)	42(3)	12(2)	8(2)	17(2)
C(23')	51(3)	42(3)	61(3)	26(2)	21(2)	25(2)

C(24')	33(2)	32(2)	87(4)	16(3)	18(2)	18(2)
C(25')	32(2)	28(2)	61(3)	4(2)	3(2)	13(2)
C(26')	30(2)	34(2)	37(2)	6(2)	6(2)	20(2)

Table 11. Torsion angles [°] for **44**.

C(2)-N(1)-N(9)-C(3A)	1.2(4)
C(2)-N(1)-N(9)-C(8)	177.2(3)
N(9)-N(1)-C(2)-C(3)	-0.1(4)
N(9)-N(1)-C(2)-C(11)	-178.8(3)
N(1)-C(2)-C(3)-C(3A)	-0.9(4)
C(11)-C(2)-C(3)-C(3A)	177.5(3)
N(1)-C(2)-C(3)-C(13)	-173.9(3)
C(11)-C(2)-C(3)-C(13)	4.6(6)
N(1)-N(9)-C(3A)-C(3)	-1.8(4)
C(8)-N(9)-C(3A)-C(3)	-178.0(3)
N(1)-N(9)-C(3A)-C(4)	176.4(3)
C(8)-N(9)-C(3A)-C(4)	0.2(4)
C(2)-C(3)-C(3A)-N(9)	1.6(4)
C(13)-C(3)-C(3A)-N(9)	174.6(3)
C(2)-C(3)-C(3A)-C(4)	-176.0(4)
C(13)-C(3)-C(3A)-C(4)	-3.0(6)
N(9)-C(3A)-C(4)-C(4A)	48.4(4)
C(3)-C(3A)-C(4)-C(4A)	-134.2(4)
C(3A)-C(4)-C(4A)-C(5)	73.7(3)
C(3A)-C(4)-C(4A)-C(7A)	-43.6(4)
C(7)-N(6)-C(5)-O(5)	179.1(4)
C(15)-N(6)-C(5)-O(5)	-2.4(6)
C(7)-N(6)-C(5)-C(4A)	-2.6(4)
C(15)-N(6)-C(5)-C(4A)	175.9(3)
C(4)-C(4A)-C(5)-O(5)	58.2(5)
C(7A)-C(4A)-C(5)-O(5)	-178.9(4)
C(4)-C(4A)-C(5)-N(6)	-120.1(3)
C(7A)-C(4A)-C(5)-N(6)	2.8(4)
C(5)-N(6)-C(7)-O(6)	-178.4(3)
C(15)-N(6)-C(7)-O(6)	3.1(5)
C(5)-N(6)-C(7)-C(7A)	1.2(4)
C(15)-N(6)-C(7)-C(7A)	-177.3(3)

O(6)-C(7)-C(7A)-C(8)	-57.2(5)
N(6)-C(7)-C(7A)-C(8)	123.2(3)
O(6)-C(7)-C(7A)-C(4A)	-179.7(4)
N(6)-C(7)-C(7A)-C(4A)	0.6(4)
C(5)-C(4A)-C(7A)-C(7)	-2.1(3)
C(4)-C(4A)-C(7A)-C(7)	118.1(3)
C(5)-C(4A)-C(7A)-C(8)	-124.6(3)
C(4)-C(4A)-C(7A)-C(8)	-4.4(4)
C(3A)-N(9)-C(8)-C(10)	-179.4(3)
N(1)-N(9)-C(8)-C(10)	4.9(4)
C(3A)-N(9)-C(8)-C(7A)	-50.5(4)
N(1)-N(9)-C(8)-C(7A)	133.8(3)
C(7)-C(7A)-C(8)-N(9)	-69.0(3)
C(4A)-C(7A)-C(8)-N(9)	49.2(3)
C(7)-C(7A)-C(8)-C(10)	56.7(4)
C(4A)-C(7A)-C(8)-C(10)	174.8(3)
N(9)-C(8)-C(10)-C(21)	-174.5(3)
C(7A)-C(8)-C(10)-C(21)	62.4(4)
C(12)-O(2)-C(11)-O(1)	5.5(5)
C(12)-O(2)-C(11)-C(2)	-173.2(3)
N(1)-C(2)-C(11)-O(1)	50.1(5)
C(3)-C(2)-C(11)-O(1)	-128.3(4)
N(1)-C(2)-C(11)-O(2)	-131.3(3)
C(3)-C(2)-C(11)-O(2)	50.3(5)
C(14)-O(4)-C(13)-O(3)	6.2(5)
C(14)-O(4)-C(13)-C(3)	-173.0(3)
C(3A)-C(3)-C(13)-O(3)	-160.1(3)
C(2)-C(3)-C(13)-O(3)	11.3(6)
C(3A)-C(3)-C(13)-O(4)	19.1(5)
C(2)-C(3)-C(13)-O(4)	-169.5(3)
C(5)-N(6)-C(15)-C(16)	112.1(4)
C(7)-N(6)-C(15)-C(16)	-69.6(5)
C(5)-N(6)-C(15)-C(20)	-68.8(4)
C(7)-N(6)-C(15)-C(20)	109.6(4)
C(20)-C(15)-C(16)-C(17)	0.2(6)
N(6)-C(15)-C(16)-C(17)	179.4(4)
C(15)-C(16)-C(17)-C(18)	1.0(7)
C(16)-C(17)-C(18)-C(19)	-1.2(7)

C(17)-C(18)-C(19)-C(20)	0.3(6)
C(16)-C(15)-C(20)-C(19)	-1.2(5)
N(6)-C(15)-C(20)-C(19)	179.7(3)
C(18)-C(19)-C(20)-C(15)	0.9(6)
C(8)-C(10)-C(21)-C(22)	-115.8(4)
C(8)-C(10)-C(21)-C(26)	64.3(5)
C(26)-C(21)-C(22)-C(23)	0.0(6)
C(10)-C(21)-C(22)-C(23)	-179.8(3)
C(21)-C(22)-C(23)-C(24)	-1.3(6)
C(22)-C(23)-C(24)-C(25)	1.8(7)
C(23)-C(24)-C(25)-C(26)	-1.1(8)
C(22)-C(21)-C(26)-C(25)	0.7(7)
C(10)-C(21)-C(26)-C(25)	-179.5(4)
C(24)-C(25)-C(26)-C(21)	-0.2(8)
C(2')-N(1')-N(9')-C(3A')	-0.1(4)
C(2')-N(1')-N(9')-C(8')	179.3(3)
N(9')-N(1')-C(2')-C(3')	-0.3(4)
N(9')-N(1')-C(2')-C(11')	-176.2(3)
N(1')-C(2')-C(3')-C(3A')	0.5(4)
C(11')-C(2')-C(3')-C(3A')	175.8(3)
N(1')-C(2')-C(3')-C(13')	174.1(3)
C(11')-C(2')-C(3')-C(13')	-10.6(6)
N(1')-N(9')-C(3A')-C(3')	0.4(4)
C(8')-N(9')-C(3A')-C(3')	-179.0(3)
N(1')-N(9')-C(3A')-C(4')	-178.4(3)
C(8')-N(9')-C(3A')-C(4')	2.2(4)
C(2')-C(3')-C(3A')-N(9')	-0.5(4)
C(13')-C(3')-C(3A')-N(9')	-174.3(3)
C(2')-C(3')-C(3A')-C(4')	177.8(4)
C(13')-C(3')-C(3A')-C(4')	4.1(6)
N(9')-C(3A')-C(4')-C(4A')	-48.0(4)
C(3')-C(3A')-C(4')-C(4A')	133.8(4)
C(3A')-C(4')-C(4A')-C(5')	-77.3(3)
C(3A')-C(4')-C(4A')-C(7A')	39.9(4)
C(7')-N(6')-C(5')-O(5')	178.9(3)
C(21')-N(6')-C(5')-O(5')	-7.9(5)
C(7')-N(6')-C(5')-C(4A')	0.5(4)
C(21')-N(6')-C(5')-C(4A')	173.8(3)

C(7A')-C(4A')-C(5')-O(5')	178.0(3)
C(4')-C(4A')-C(5')-O(5')	-59.2(5)
C(7A')-C(4A')-C(5')-N(6')	-3.6(3)
C(4')-C(4A')-C(5')-N(6')	119.2(3)
C(5')-N(6')-C(7')-O(6')	-179.2(3)
C(21')-N(6')-C(7')-O(6')	7.3(5)
C(5')-N(6')-C(7')-C(7A')	2.9(4)
C(21')-N(6')-C(7')-C(7A')	-170.6(3)
O(6')-C(7')-C(7A')-C(8')	53.3(5)
N(6')-C(7')-C(7A')-C(8')	-129.0(3)
O(6')-C(7')-C(7A')-C(4A')	177.3(3)
N(6')-C(7')-C(7A')-C(4A')	-5.0(3)
C(5')-C(4A')-C(7A')-C(7')	5.1(3)
C(4')-C(4A')-C(7A')-C(7')	-114.5(3)
C(5')-C(4A')-C(7A')-C(8')	128.8(3)
C(4')-C(4A')-C(7A')-C(8')	9.2(4)
C(3A')-N(9')-C(8')-C(10')	176.7(3)
N(1')-N(9')-C(8')-C(10')	-2.6(4)
C(3A')-N(9')-C(8')-C(7A')	48.3(4)
N(1')-N(9')-C(8')-C(7A')	-131.0(3)
C(7')-C(7A')-C(8')-N(9')	68.0(3)
C(4A')-C(7A')-C(8')-N(9')	-50.8(4)
C(7')-C(7A')-C(8')-C(10')	-56.7(4)
C(4A')-C(7A')-C(8')-C(10')	-175.5(3)
N(9')-C(8')-C(10')-C(15')	173.2(3)
C(7A')-C(8')-C(10')-C(15')	-65.0(4)
C(12')-O(2')-C(11')-O(1')	-5.2(5)
C(12')-O(2')-C(11')-C(2')	175.9(3)
N(1')-C(2')-C(11')-O(1')	-41.4(5)
C(3')-C(2')-C(11')-O(1')	143.5(4)
N(1')-C(2')-C(11')-O(2')	137.5(3)
C(3')-C(2')-C(11')-O(2')	-37.6(5)
C(14')-O(4')-C(13')-O(3')	-4.7(5)
C(14')-O(4')-C(13')-C(3')	175.9(3)
C(3A')-C(3')-C(13')-O(3')	153.1(4)
C(2')-C(3')-C(13')-O(3')	-19.2(6)
C(3A')-C(3')-C(13')-O(4')	-27.5(5)
C(2')-C(3')-C(13')-O(4')	160.3(3)

C(8')-C(10')-C(15')-C(20')	88.8(4)
C(8')-C(10')-C(15')-C(16')	-90.8(4)
C(20')-C(15')-C(16')-C(17')	1.3(5)
C(10')-C(15')-C(16')-C(17')	-179.0(3)
C(15')-C(16')-C(17')-C(18')	-1.2(6)
C(16')-C(17')-C(18')-C(19')	0.2(6)
C(17')-C(18')-C(19')-C(20')	0.6(6)
C(16')-C(15')-C(20')-C(19')	-0.5(6)
C(10')-C(15')-C(20')-C(19')	179.9(3)
C(18')-C(19')-C(20')-C(15')	-0.5(6)
C(5')-N(6')-C(21')-C(22')	105.9(4)
C(7')-N(6')-C(21')-C(22')	-81.3(4)
C(5')-N(6')-C(21')-C(26')	-76.9(4)
C(7')-N(6')-C(21')-C(26')	95.8(4)
C(26')-C(21')-C(22')-C(23')	0.0(6)
N(6')-C(21')-C(22')-C(23')	177.0(3)
C(21')-C(22')-C(23')-C(24')	-0.2(6)
C(22')-C(23')-C(24')-C(25')	1.0(7)
C(23')-C(24')-C(25')-C(26')	-1.5(6)
C(24')-C(25')-C(26')-C(21')	1.3(6)
C(22')-C(21')-C(26')-C(25')	-0.5(6)
N(6')-C(21')-C(26')-C(25')	-177.6(3)

Symmetry transformations used to generate equivalent atoms:

Computational Methodology

Calculations were performed resorting to the Gamess[7] program package. All the calculations were conducted in gas phase. The two conformers of the diazafulvenium methides **28** and **32** considered to be relevant (I and II) and the structure of NPM previously[8] identified as the most stale conformer, were fully optimized at the DFT level of theory, using the B3LYP hybrid functional[8] and the standard 6-31G(d) basis set. The energy values are given in Table 12. Furthermore, the transition states resulting from the *endo*- and *exo*-cycloadditions of **NPM** and with **28** and **32** were considered and also optimized at the DFT level. Full geometry optimizations were performed followed by harmonic frequency calculations, at the same level of theory. This allowed establishing the nature of the stationary points which, in the case of the located transition states, were characterized by having a single imaginary frequency. Inspection of the corresponding imaginary frequency allowed confirming that the transition states connect the reactants with the expected products. All the individual contribution to the energy barriers corresponding to all the transitions states identified are reported in Table 13, considering both zero-point-energy (ZPE) and basis set superposition error corrections (BSSE).

Table 12. Total energy, E, zero-point vibration energy, ZPE and relative energy, ΔE, of each conformer of the diazafulvenium methides **28** and **32**. Energy and ZPE values for NPM are also given. All values were obtained by optimization at B3LYP/6-31G(d) level of theory. The value ΔE includes ZPE.

Structure	E/hartree	ZPE/hartree	ΔE /(kJ mol^{-1})
NPM	-590.1449729478	0.149086	-------
32-*II*	-798.1787191647	0.216676	0.00
32-*I*	-798.1739413769	0.217452	14.58
28-*II*	-1029.0802311281	0.298133	0.00
28-*I*	-1029.0745703072	0.298686	16.31

Table 13. Total energy, E, zero-point vibration energy, ZPE, basis set superposition error correction, BSSE, and energy relative to the reactants, ΔE, of the transition states identified for the addition of **32** and **28** with NPM, calculated at the B3LYP/6-31G(d) level of theory. The value ΔE includes both ZPE and BSSE corrections.

Structure	E/hartree	ZPE/hartree	BSSE/hartree	ΔE /(kJ mol^{-1})
$TS1_{endo}$[**32** + NPM]	-1388.3224380991	0.368021	0.008156128398	30.64
$TS2_{endo}$[**32** + NPM]	-1388.3209849762	0.367863	0.007843068381	33.22
TS_{exo}[**32** + NPM]	-1388.3099301748	0.367924	0.00488534641	54.63
TS_{endo}[**28** + NPM]	-1619.2267275912	0.449649	0.009912802799	28.41
TS_{exo}[**28** + NPM]	-1619.2123540183	0.44959	0.005813636314	55.23

Cartesian coordinates (Å) obtained from the B3LYP/6-31G(d) calculations

NPM

C	2.9952014448	0.6530949814	-0.1370670412
C	2.9951804476	-0.6534195407	0.1368984906
C	1.5765277413	1.1298903939	-0.2352848461
C	1.5764765399	-1.1300703680	0.2353382489
N	0.7624514294	-0.0000823306	-0.0000089483
O	1.1964342068	2.2570733963	-0.4677028551
O	1.1963740263	-2.2572069349	0.4678928365
H	3.8281612616	-1.3301509755	0.2800913250
H	3.8281151365	1.3298944734	-0.2802771931
C	-0.6660995050	0.0000125838	0.0000532262
C	-1.3633375112	1.0706852857	0.5718927596
C	-1.3632285000	-1.0706705075	-0.5719352758
C	-2.7577369073	1.0680297965	0.5604123405

H	-0.8201283029	1.9005593520	1.0073413764
C	-2.7576382963	-1.0680869241	-0.5607222559
H	-0.8200739398	-1.9005389793	-1.0074852315
C	-3.4601473839	-0.0000283658	-0.0001959954
H	-3.2942167562	1.9051383739	0.9991993275
H	-3.2940982550	-1.9051083443	-0.9996690590
H	-4.5468168765	-0.0000153663	-0.0003712298

32-*II*

N	-2.4460443006	-0.9106406257	-0.2188397004
C	-3.6247205825	-1.4678354715	-0.3179365297
N	-1.3255279105	-1.6701271077	0.0002153496
C	-2.1256025810	0.5217186714	-0.3164818032
C	-0.3140930393	-0.7774502986	0.0405667429
C	-0.6881103765	0.5473907123	-0.1365388229
C	-3.0289147862	1.4941647064	-0.5222709222
H	-2.6741011338	2.5154474882	-0.5759099105
H	-4.0910498569	1.3064286919	-0.6364924035
C	0.1036526718	1.7593833276	-0.1150865184
O	-0.3303691235	2.8881234024	-0.3007354535
O	1.4183213924	1.5149452780	0.1502564304
C	2.2549690074	2.6770884101	0.1947552304
H	1.9147499148	3.3713530847	0.9685088886
H	3.2552173439	2.3082958579	0.4278569276
H	2.2534457322	3.1942450340	-0.7692566689
C	1.0562528806	-1.3265897472	0.3220575185
O	1.4108606502	-1.7173507386	1.4099043090
O	1.8049540044	-1.3577108149	-0.7921375701
C	3.1413526954	-1.8583910451	-0.6130325326
H	3.1195736504	-2.8817162796	-0.2287886705

H	3.5985808126	-1.8271435476	-1.6026660914
H	3.6931226815	-1.2243577735	0.0863155644
C	-3.7936496133	-2.9376462014	-0.1926709467
H	-3.3986498220	-3.2916953105	0.7689470659
H	-3.2142315489	-3.4618784841	-0.9651610227
H	-4.8473589076	-3.2118127844	-0.2801608617
H	-4.4601298550	-0.8019384344	-0.4935175984

32-*I*

N	-2.4236930320	-0.8149891870	-0.1790191726
C	-3.5834756868	-1.4232060985	-0.2571714670
N	-1.2941744730	-1.5805127947	0.0307994296
C	-2.0898791435	0.6091117643	-0.2847129433
C	-0.2820415938	-0.7019642160	0.0535029991
C	-0.6521043357	0.6273791168	-0.1261716438
C	-2.9605765505	1.6229037738	-0.4796267488
H	-2.5380213798	2.6191808518	-0.5326214470
H	-4.0270615124	1.5104411010	-0.5802513219
C	0.1558517795	1.8270415952	-0.1218490908
O	-0.2591195246	2.9651356072	-0.2989916231
O	1.4723258030	1.5597409960	0.1163420865
C	2.3292809470	2.7068449869	0.1513486769
H	2.0018057997	3.4126933895	0.9198605584
H	3.3229850147	2.3218984353	0.3862837566
H	2.3361749908	3.2172209555	-0.8165402188
C	1.0896752671	-1.2583201371	0.3171630498
O	1.4732517278	-1.6118287654	1.4076564707
O	1.8026047122	-1.3438588934	-0.8178175476
C	3.1360140589	-1.8597518067	-0.6608496410
H	3.1099860215	-2.8688358509	-0.2409658680

H	3.5634643442	-1.8707628595	-1.6639414368
H	3.7181272434	-1.2117125107	-0.0000703977
C	-4.8997386395	-0.7783247087	-0.4798550088
H	-4.9282297084	-0.2191389044	-1.4269157179
H	-5.1473171192	-0.0633571719	0.3194728370
H	-5.6776125036	-1.5444755662	-0.5076631751
H	-3.5020025073	-2.4980531022	-0.1385953945

28-*II*

N	2.2158607871	-0.6052243414	-0.5905000347
C	3.4884138270	-0.8100176455	-0.8096753380
N	1.2834787195	-1.5535851051	-0.9265566288
C	1.5920135859	0.5897667945	-0.0009116833
C	0.0999125121	-0.9997282815	-0.5886959899
C	0.1793520244	0.2687242840	-0.0309667895
C	2.2674824404	1.6657218756	0.4346369178
H	1.7008808728	2.4897679563	0.8490657915
H	3.3481706202	1.7471942132	0.3917662508
C	-0.8593347935	1.1356049968	0.4858467546
O	-0.6793699897	2.2557057508	0.9436187260
O	-2.0935020192	0.5609595464	0.4186247592
C	-3.1676765878	1.3705828553	0.9117438369
H	-3.2582026638	2.2917852431	0.3287372379
H	-4.0662546334	0.7609048838	0.8040756674
H	-3.0076743903	1.6316746782	1.9617913775
C	-1.1229170840	-1.8458611468	-0.8068159680
O	-1.4045177105	-2.8040616745	-0.1253279785
O	-1.8254485501	-1.4198807391	-1.8690689322
C	-3.0221001194	-2.1679472306	-2.1454470054
H	-3.7096010477	-2.1112932174	-1.2970633109

H	-3.4606782996	-1.7004953281	-3.0277311082
H	-2.7821225528	-3.2163020757	-2.3424626702
C	3.9734894109	-2.0764419201	-1.4355260945
H	3.7457897131	-2.9165845977	-0.7616918218
H	3.3573500111	-2.2707763594	-2.3266079408
H	4.1718658666	-0.0224682996	-0.5173181046
C	6.3725806373	-2.8222390526	-1.0793227416
C	7.7321587224	-2.7761702634	-1.3958378967
C	5.4487337732	-2.0369233680	-1.7780909701
H	6.0245209289	-3.4782392444	-0.2843264491
C	8.1853160596	-1.9387546135	-2.4161841311
H	8.4358642353	-3.3951189975	-0.8450671538
C	5.9144036952	-1.2010176764	-2.8032176221
C	7.2719959661	-1.1501769038	-3.1199350854
H	9.2429406646	-1.9024898341	-2.6639261554
H	5.2063666014	-0.5910322021	-3.3612875893
H	7.6161587666	-0.4980629596	-3.9186441257

28-*I*

N	2.4456087335	-0.2290772753	0.4747572690
C	3.6706978960	-0.6437140801	0.6940463789
N	1.6512921919	-0.9537767975	-0.3950139561
C	1.7009702984	0.8801338991	1.0763491964
C	0.4383619415	-0.3941356795	-0.2941101893
C	0.3568112793	0.6868771177	0.5802237978
C	2.2196086348	1.8573656053	1.8516453251
H	1.5267994105	2.6042615742	2.2202787146
H	3.2676771229	1.9712783320	2.0763757212
C	-0.7637724618	1.5436578212	0.8994078898
O	-0.7344801327	2.4963869648	1.6675217407

O	-1.8992408097	1.1724609507	0.2402184427
C	-3.0512269437	1.9793336706	0.5100206660
H	-2.8743635195	3.0200714817	0.2230062447
H	-3.8549030517	1.5512540255	-0.0914342814
H	-3.3095794560	1.9458937985	1.5727125085
C	-0.6480715257	-0.9625507751	-1.1652436038
O	-0.7643783476	-0.7164350033	-2.3428989962
O	-1.4367151932	-1.7969971781	-0.4686218819
C	-2.5218695944	-2.3739863502	-1.2161026746
H	-2.1435130517	-2.9282985915	-2.0791732226
H	-3.0296689593	-3.0430726255	-0.5208025401
H	-3.2004608601	-1.5896957113	-1.5624713258
C	4.6422866234	-0.0622800669	1.6653179937
H	3.9376548745	-1.5204899760	0.1138459060
C	5.7932254232	-1.0117365215	1.9431333757
C	7.0127228498	-0.8861632214	1.2678908020
C	5.6354784008	-2.0495907716	2.8707717229
C	8.0566272687	-1.7803088086	1.5151436927
H	7.1491115553	-0.0839563272	0.5454836659
C	6.6773559037	-2.9436545606	3.1204660759
H	4.6922906110	-2.1555145993	3.4027783807
C	7.8909772097	-2.8105430507	2.4424286767
H	8.9987998568	-1.6702135735	0.9844080179
H	6.5407073570	-3.7416096023	3.8454559838
H	8.7036858522	-3.5055350479	2.6361112513
H	4.1120598140	0.1818199193	2.5998917997
H	5.0267327982	0.8999410342	1.2887814314

TS1$_{endo}$[**32** +NPM]

Imaginary frequency = -260.7 cm^{-1}

N	-0.0029298138	-2.1096248517	-1.3658935894
C	-0.9900279703	-2.7492425505	-1.9920376463
H	-1.3175753070	-3.6668374602	-1.5257078390
C	-2.9716709026	-1.9522896531	-0.6064456324
C	0.3292157392	-2.2259658702	0.0236939587
C	1.4799960207	-0.6019812780	-1.0134713925
C	1.3077530800	-1.2078908892	0.2370596466
C	-0.3312539288	-3.0720891415	0.8755397012
H	-0.8635541571	-3.9438967483	0.5175699516
H	-0.0791526689	-3.0266992938	1.9279666806
C	-2.6427124936	-2.0903970168	0.7167183516
N	0.6961501089	-1.1095923199	-1.9795237669
C	-2.7784623849	-0.5287438911	-0.9986528137
C	-2.2440967784	-0.7503699538	1.2501313654
N	-2.2879806097	0.1333688920	0.1487213498
O	-2.9957550814	-0.0132906696	-2.0791954939
O	-1.9606042664	-0.4542936299	2.3917398585
H	-2.9067023754	-2.8938941676	1.3910350589
H	-3.5502332915	-2.6271466256	-1.2237539395
C	-1.9416677306	1.5193032554	0.2021538692
C	-1.0953780333	2.0580107577	-0.7715063465
C	-2.4437045442	2.3221006049	1.2322255966
C	-0.7562577214	3.4094364796	-0.7126840121
H	-0.6963869449	1.4304615499	-1.5591604578
C	-2.0910609761	3.6701152486	1.2840824022
H	-3.0904004000	1.8900921274	1.9872854040
C	-1.2512595517	4.2182228292	0.3117485752
H	-0.0881858223	3.8179777852	-1.4651597191
H	-2.4769684787	4.2929913596	2.0868882179
H	-0.9806069475	5.2701183694	0.3563220477

C	1.9143066922	-0.9278382546	1.5359990394
O	1.7986036728	-1.6366264795	2.5225309345
O	2.6089417011	0.2352320326	1.5385681681
C	3.2197427430	0.5769201026	2.7915709127
H	3.9577337718	-0.1776600902	3.0793575286
H	3.7024176689	1.5411393899	2.6261946880
H	2.4653690870	0.6552911550	3.5790154716
C	2.4070797043	0.5048070824	-1.4232575293
O	2.0397274948	1.5344508910	-1.9436208909
O	3.6868160940	0.1815136212	-1.1815616177
C	4.6479050607	1.1975668459	-1.5198156265
H	4.4654751565	2.1009706369	-0.9316699775
H	5.6203792006	0.7686440469	-1.2767130501
H	4.5877529017	1.4432404801	-2.5833913432
C	-1.3057644401	-2.4388957450	-3.4104098567
H	-1.6752945003	-1.4100866908	-3.5035359388
H	-2.0631341397	-3.1288207535	-3.7899257023
H	-0.4000836373	-2.5128015191	-4.0273245967

TS2$_{endo}$[**32** +NPM]

Imaginary frequency = -262.4 cm^{-1}

N	0.0091192763	-2.0683638120	-1.3163859217
C	-0.9619698426	-2.7139197760	-1.9589818509
H	-1.2921901433	-3.6321193495	-1.4959763232
C	-2.9816816150	-1.9571222458	-0.6002804132
C	0.3188224501	-2.1858208965	0.0783332516
C	1.4842677713	-0.5602414043	-0.9386754041
C	1.2959990611	-1.1725908478	0.3062965153
C	-0.3558413960	-3.0313394352	0.9205269108
H	-0.8763998222	-3.9078210399	0.5565885008

H	-0.1194616041	-2.9814524260	1.9766335027
C	-2.6527335927	-2.0587360781	0.7268911356
N	0.7190680757	-1.0646183743	-1.9183700683
C	-2.8298555788	-0.5401981136	-1.0212843068
C	-2.2919575790	-0.6974021785	1.2327151852
N	-2.3564970723	0.1629590065	0.1119562345
O	-3.0639196697	-0.0525888025	-2.1118152819
O	-2.0240514259	-0.3708945855	2.3695209147
H	-2.9067957716	-2.8492924872	1.4197438495
H	-3.5390331783	-2.6602479764	-1.2052919322
C	-2.0881875494	1.5653405767	0.1346548348
C	-1.3741763462	2.1484361366	-0.9175656031
C	-2.5506644863	2.3508619232	1.1972219703
C	-1.1398530975	3.5229819285	-0.9099954418
H	-1.0103710558	1.5310988514	-1.7296280080
C	-2.2943004765	3.7214320374	1.2004318956
H	-3.0927014287	1.8894168624	2.0138647933
C	-1.5959028962	4.3136837910	0.1461685600
H	-0.5942421672	3.9736688718	-1.7349922326
H	-2.6505528423	4.3281723979	2.0288148544
H	-1.4083735677	5.3843573680	0.1488942355
C	1.9829620391	-0.9628339354	1.5748441760
O	1.7629721188	-1.5841814166	2.6015110615
O	2.9229293443	0.0118280081	1.4847092283
C	3.6430910165	0.2830836192	2.6959114052
H	4.1760873045	-0.6090173618	3.0367374833
H	4.3483254131	1.0758869964	2.4422460712
H	2.9607222020	0.6136386234	3.4842820645
C	2.4704784543	0.5140344393	-1.3069930096
O	3.4930726661	0.3084206030	-1.9181728053

O	2.0442656214	1.7151352489	-0.8903161534
C	2.9309226544	2.8140385913	-1.1643029157
H	3.1312765069	2.8888218478	-2.2365305712
H	2.4087145112	3.7006750969	-0.8039897482
H	3.8757348260	2.6782050668	-0.6307892961
C	-1.2550733628	-2.4114845629	-3.3837181745
H	-1.6259563619	-1.3846239237	-3.4895125023
H	-2.0055894781	-3.1043043593	-3.7714223283
H	-0.3390979051	-2.4885625038	-3.9849083425

TS$_{exo}$[**32** +NPM]

Imaginary frequency = -298.9cm^{-1}

N	-0.9374556555	-0.8952953227	-0.9665386221
C	0.2624220674	-1.4535126447	-1.1922306764
H	0.2524030990	-2.5220809845	-1.0070040718
C	1.1748008597	-0.8433605187	0.9482272676
C	-1.2406350960	0.4929183505	-0.8172026640
C	-2.9299694720	-0.8363024276	-0.1630530632
C	-2.5773880541	0.5111478534	-0.3082590444
C	-0.3114969829	1.4943487483	-0.9370744330
H	0.6176389093	1.3879866215	-1.4716147109
H	-0.6182425739	2.4921634459	-0.6468918511
C	1.0927053643	0.5195766197	1.0911997030
H	0.3269202546	1.0975543331	1.5869298335
H	0.4933287623	-1.5837278746	1.3482851244
N	-1.9669797781	-1.6887343852	-0.5329598018
C	2.4279021628	1.1114885564	0.7950134132
C	2.5884474010	-1.2021740504	0.6251113442
N	3.2884091934	0.0190979390	0.4950855709

O	2.7531312120	2.2803971675	0.8075476722
O	3.0572200928	-2.3136698283	0.4803141586
C	4.6675249373	0.1391627713	0.1457032399
C	5.0811884999	1.1465470888	-0.7342544724
C	5.6030772011	-0.7513910164	0.6860892731
C	6.4305414393	1.2597275153	-1.0674509804
H	4.3567408416	1.8451768887	-1.1364612395
C	6.9471626595	-0.6356966402	0.3334043719
H	5.2772181984	-1.5310642051	1.3635153089
C	7.3671066069	0.3685166480	-0.5403243888
H	6.7471815550	2.0476176797	-1.7457028805
H	7.6681942769	-1.3331904470	0.7514220637
H	8.4167400156	0.4575359085	-0.8072485899
C	-3.3432995603	1.7229380677	-0.0542215169
O	-2.8960460797	2.8581196811	-0.1216482450
O	-4.6328896699	1.4564838861	0.2732173565
C	-5.4385866975	2.6071582360	0.5688109920
H	-5.4877391274	3.2756458700	-0.2950077403
H	-6.4286765097	2.2157422828	0.8061189164
H	-5.0276236343	3.1562303616	1.4206272584
C	-4.2366431409	-1.4232750765	0.2924338434
O	-5.0116608846	-1.9962884446	-0.4364817999
O	-4.4011211722	-1.2507263110	1.6145536571
C	-5.6343056809	-1.7668098037	2.1479280135
H	-5.7155109678	-2.8398393748	1.9555763287
H	-5.5929021663	-1.5683614075	3.2191905444
H	-6.4868576277	-1.2553383274	1.6929121417
C	1.2561929993	-0.9047273696	-2.1734247109
H	0.7403986419	-0.4454506169	-3.0268468440
H	1.9331007755	-0.1519986138	-1.7569148150

H	1.8790325049	-1.7254668297	-2.5375002346

TS$_{endo}$[**28** +NPM]

Imaginary frequency = -261.8cm^{-1}

C	-3.3132365587	-2.1070245380	-0.8578290359
C	-3.0792847757	-2.1390249961	0.4926479457
C	-3.1427251445	-0.7095870773	-1.3353740182
C	-2.7731886025	-0.7491203075	0.9552473865
N	-2.7611024038	0.0518610956	-0.2100948687
O	-3.2998858180	-0.2764910450	-2.4642068016
O	-2.5926739940	-0.3580810885	2.0888746325
H	-3.3701620296	-2.9024168314	1.2015546073
H	-3.8046077616	-2.8514084891	-1.4701232517
C	-2.4610951104	1.4494842269	-0.2340194236
C	-1.5658648001	1.9471945827	-1.1854844843
C	-3.0536584940	2.3049355859	0.7011524055
C	-1.2689539628	3.3096627170	-1.2009722050
H	-1.0943442608	1.2797305127	-1.8964305414
C	-2.7415478852	3.6638229540	0.6808326171
H	-3.7400458815	1.9071033448	1.4396885996
C	-1.8534644426	4.1705760265	-0.2707418155
H	-0.5614474725	3.6861460175	-1.9338160190
H	-3.1974512822	4.3273804591	1.4110599874
H	-1.6148685355	5.2310269951	-0.2828480734
H	3.0021727358	1.8020167093	2.6906211343
C	2.4686942397	0.8708128644	2.8866551000
O	2.0098512369	0.4159555587	1.6050991946
H	3.1347850451	0.1339188905	3.3440877229
H	1.6221602231	1.0492006429	3.5557164801
C	1.3315184780	-0.7571264943	1.6208705065

C	0.8591119442	-1.1408204889	0.2936056967
O	1.1274405691	-1.3947324860	2.6410381082
C	-0.0656822642	-2.2028338930	0.0574843077
C	1.1296694744	-0.6058063927	-0.9717547344
N	-0.2708239155	-2.1823707823	-1.3609815291
C	-0.7782648609	-3.0197147851	0.8966209300
N	0.4543756781	-1.1968856117	-1.9710189959
C	2.0584539294	0.5069490994	-1.3618860644
C	-1.1757959572	-2.8908590386	-2.0339901047
H	-0.6258470876	-2.9040733098	1.9627047763
H	-1.2450593169	-3.9307502482	0.5448264039
O	1.7061515106	1.5050637756	-1.9493265159
O	3.3248877267	0.2233887202	-1.0198443840
C	-1.3710693184	-2.6733668053	-3.5001813236
H	-1.5283432888	-3.7924562376	-1.5542213390
C	4.2881599086	1.2445113848	-1.3357292484
H	-1.6852835153	-1.6331375871	-3.6562796908
H	-0.3863890749	-2.7554170291	-3.9868107848
C	-2.3647913308	-3.6440714716	-4.1063638606
H	4.0809133320	2.1496376207	-0.7582295989
H	5.2559895985	0.8253868021	-1.0587863845
H	4.2586586736	1.4831299680	-2.4019021297
C	-3.6781876226	-3.2387695295	-4.3808919427
C	-1.9899129206	-4.9654364309	-4.3865645222
C	-4.5977747191	-4.1406217830	-4.9216812292
H	-3.9705117196	-2.2144551436	-4.1632583285
C	-2.9087239383	-5.8670454538	-4.9254107718
H	-0.9685218810	-5.2865133674	-4.1898336277
C	-4.2164410644	-5.4560187403	-5.1936825760
H	-5.6124367741	-3.8135545650	-5.1340316659

H	-2.6028380452	-6.8874161539	-5.1421049125
H	-4.9322864723	-6.1560883526	-5.6167817388

TS_{exo}[**28** +NPM]

Imaginary frequency = -290.6cm^{-1}

N	-0.4233858265	-0.7456244582	-0.8814365107
C	0.8190065538	-1.2235462218	-1.0353818122
H	0.8713420523	-2.2972457325	-0.8892042545
C	1.4909798277	-0.6444785983	1.2742363587
C	-0.8173071172	0.6160167377	-0.6943474218
C	-2.5000886502	-0.8282091556	-0.3381659842
C	-2.2090274463	0.5424318606	-0.3801868650
C	0.0770391484	1.6527520494	-0.5919277529
H	1.0854508969	1.6065129299	-0.9706359963
H	-0.3141199259	2.6226370854	-0.3078530505
C	1.2016399876	0.6774489424	1.5049891728
H	0.3202841061	1.0992719997	1.9656452937
H	0.8840692324	-1.5031049290	1.5306474817
N	-1.4519779586	-1.6121636661	-0.6139389034
C	2.4658449411	1.4634231632	1.4113001776
C	2.9589962065	-0.7792422231	1.0645081282
N	3.4925468950	0.5292036520	1.1004022681
O	2.6220343204	2.6556840039	1.5699869004
O	3.5937681918	-1.8013513457	0.8789310429
C	4.8645349043	0.8656968892	0.8888911258
C	5.1935801624	2.0324412926	0.1869196525
C	5.8769083229	0.0326722252	1.3815008362
C	6.5332746248	2.3626305083	-0.0132576846
H	4.4092879909	2.6826865507	-0.1809769987
C	7.2124515515	0.3673188806	1.1589493251

H	5.6203318003	-0.8705417895	1.9206743782
C	7.5472584802	1.5318742120	0.4659588431
H	6.7814045001	3.2732939601	-0.5519545397
H	7.9936509590	-0.2860320307	1.5383603477
H	8.5899251737	1.7905257128	0.3022848503
C	-3.0760888865	1.6958203475	-0.1874128813
O	-2.7004618006	2.8570918500	-0.1366389132
O	-4.3804465139	1.3364064938	-0.0726030279
C	-5.3001838456	2.4189419719	0.1293225817
H	-5.2256928768	3.1456693697	-0.6841316078
H	-6.2899731125	1.9606768042	0.1442146122
H	-5.0988330106	2.9266791335	1.0773659322
C	-3.8200528622	-1.5019086291	-0.0875011566
O	-4.4578301069	-2.0762596396	-0.9383028427
O	-4.1686674267	-1.4048955065	1.2063928075
C	-5.4314150934	-2.0080824788	1.5431758524
H	-5.4168655542	-3.0779622451	1.3189360574
H	-5.5568234720	-1.8396865834	2.6131316192
H	-6.2396658321	-1.5344019724	0.9794807490
C	1.8403332885	-0.5881858693	-1.9561406362
H	1.3525476450	0.2112031120	-2.5263435852
H	2.6646119585	-0.1217030294	-1.4055872709
C	1.7327029052	-1.9019683685	-4.1173934269
C	2.2103216527	-2.8851163728	-4.9847471402
C	2.3895784290	-1.6407262843	-2.9078479884
H	0.8456026224	-1.3305682138	-4.3825830760
C	3.3481046510	-3.6206949834	-4.6471746242
H	1.6937695087	-3.0763274837	-5.9216665600
C	3.5286473400	-2.3844812916	-2.5724681725
C	4.0050652904	-3.3679810894	-3.4406616603

H	3.7209934233	-4.3872310971	-5.3214606427
H	4.0355875662	-2.1971480290	-1.6290622514
H	4.8912302074	-3.9375424205	-3.1732111555

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