

One-pot sequence of Staudinger/aza-Wittig/Castagnoli-Cushman reactions provides facile access to novel natural-like polycyclic ring system

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Crystallographic data

X-ray Single Crystal analysis was performed on Rigaku XtaLAB Synergy-S diffractometer with monochromated CuK α radiation. Crystal growth was performed by slow dilution of solution in DMSO at room temperature. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structures were solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization. Crystallographic data: CCDC 2207932 (**6a**), 2207933 (**6c**), 2207934 (**6d**), 2207935 (**6e**), 2207937 (**6f**), 2178410 (**6m**), 2207930 (**13**), 2207931 (**16**), 2207936 (**6a'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* 2009, 42, (2), 339-341, 10.1107/s0021889808042726.
2. Sheldrick, G. M., SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr A Found Adv* 2015, 71, (Pt 1), 3-8, 10.1107/S2053273314026370.
3. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr C Struct Chem* 2015, 71, (Pt 1), 3-8, 10.1107/S2053229614024218.

Table S1. Crystal data and ORTEP representation for 6a (CCDC 2207932)	
Empirical formula	C ₁₈ H ₁₅ NO ₄
Formula weight	309.31
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	8.8480(4)
b/Å	8.8775(4)
c/Å	11.0352(5)
α /°	68.579(4)
β /°	66.496(4)
γ /°	65.896(4)
Volume/Å ³	704.05(6)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.459
μ/mm^{-1}	0.857
F(000)	324.0
Crystal size/mm ³	0.1 × 0.08 × 0.04
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	9.006 to 138.454
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -11 ≤ l ≤ 13
Reflections collected	5951
Independent reflections	2625 [R _{int} = 0.0194, R _{sigma} = 0.0276]
Data/restraints/parameters	2625/0/209
Goodness-of-fit on F ²	1.055
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0336, wR ₂ = 0.0872
Final R indexes [all data]	R ₁ = 0.0378, wR ₂ = 0.0904
Largest diff. peak/hole / e Å ⁻³	0.26/-0.21

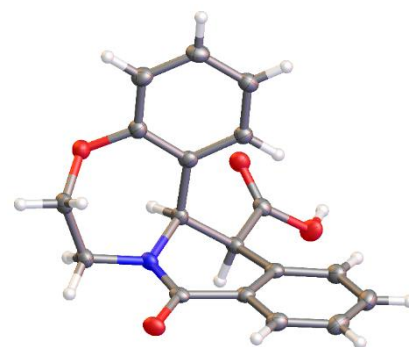


Figure S1. ORTEP representation of compound **6a** (thermal ellipsoids are shown at 50% probability)

Table S2. Crystal data and ORTEP representation for 6d (2207933)	
Empirical formula	C ₁₈ H ₁₄ ClNO ₄
Formula weight	343.75
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	8.7472(6)
b/Å	9.9319(8)
c/Å	10.2459(8)
α/°	69.488(7)
β/°	69.344(7)
γ/°	72.157(7)
Volume/Å ³	762.94(11)
Z	2
ρ _{calc} /cm ³	1.496
μ/mm ⁻¹	2.427
F(000)	356
Crystal size/mm ³	0.1 × 0.07 × 0.03
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.586 to 152.44
Index ranges	-10 ≤ h ≤ 10, -8 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	5927
Independent reflections	3117 [R _{int} = 0.0360, R _{sigma} = 0.0415]
Data/restraints/parameters	3117/0/218
Goodness-of-fit on F ²	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0396, wR2 = 0.1018
Final R indexes [all data]	R1 = 0.0487, wR2 = 0.1087
Largest diff. peak/hole / e Å ⁻³	0.34/-0.40

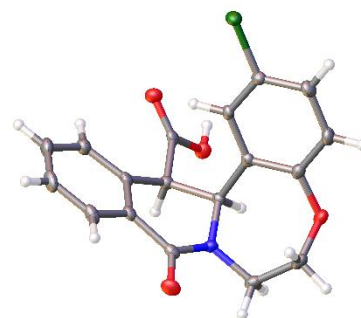


Figure S2. ORTEP representation of compound **6c** (thermal ellipsoids are shown at 50% probability)

Table S3. Crystal data and ORTEP representation for 6d (2207934)	
Empirical formula	C ₂₀ H ₂₀ BrNO ₅ S
Formula weight	466.34
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.4897(5)
b/Å	9.8117(5)
c/Å	11.0978(4)
α/°	98.873(4)
β/°	97.974(4)
γ/°	98.680(5)
Volume/Å ³	995.28(8)
Z	2
ρ _{calc} /cm ³	1.556
μ/mm ⁻¹	4.074
F(000)	476
Crystal size/mm ³	0.2 × 0.16 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.176 to 152.868
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 11, -13 ≤ l ≤ 8
Reflections collected	7904
Independent reflections	4058 [R _{int} = 0.0323, R _{sigma} = 0.0387]
Data/restraints/parameters	4058/0/256
Goodness-of-fit on F ²	1.036
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0321, wR ₂ = 0.0811
Final R indexes [all data]	R ₁ = 0.0379, wR ₂ = 0.0859
Largest diff. peak/hole / e Å ⁻³	0.47/-0.72

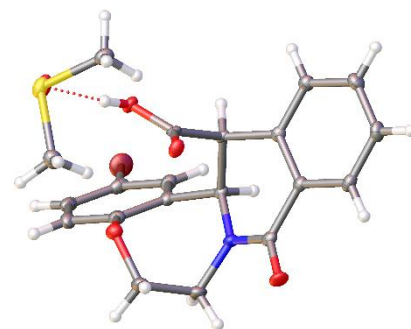


Figure S3. ORTEP representation of compound **6d** (thermal ellipsoids are shown at 50% probability)

Table S4. Crystal data and ORTEP representation for 6e (2207935)	
Empirical formula	C ₂₄ H _{18.67} N _{2.67} O ₈
Formula weight	472.41
Temperature/K	100.15
Crystal system	monoclinic
Space group	Cc
a/Å	14.1681(3)
b/Å	12.9329(3)
c/Å	8.3714(2)
$\alpha/^\circ$	90
$\beta/^\circ$	94.263(2)
$\gamma/^\circ$	90
Volume/Å ³	1529.69(6)
Z	3
$\rho_{\text{calc}}/\text{cm}^3$	1.538
μ/mm^{-1}	0.993
F(000)	736
Crystal size/mm ³	? × ? × ?
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/ $^\circ$	9.27 to 160.626
Index ranges	-17 \leq h \leq 17, -16 \leq k \leq 16, -10 \leq l \leq 10
Reflections collected	7704
Independent reflections	2624 [R _{int} = 0.0396, R _{sigma} = 0.0400]
Data/restraints/parameters	2624/2/236
Goodness-of-fit on F ²	1.094
Final R indexes [I \geq 2 σ (I)]	R ₁ = 0.0326, wR ₂ = 0.0857
Final R indexes [all data]	R ₁ = 0.0346, wR ₂ = 0.0867
Largest diff. peak/hole / e Å ⁻³	0.20/-0.17

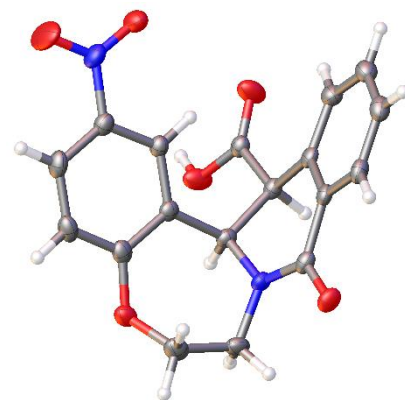


Figure S4. ORTEP representation of compound **6e** (thermal ellipsoids are shown at 50% probability)

Table S5. Crystal data and ORTEP representation for 6f (2207937)	
Empirical formula	C ₂₀ H ₂₂ NO _{6.5} S _{0.5}
Formula weight	396.41
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2
a/Å	24.8119(3)
b/Å	7.35890(10)
c/Å	20.2825(3)
α /°	90
β /°	97.5290(10)
γ /°	90
Volume/Å ³	3671.42(9)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.434
μ/mm^{-1}	1.405
F(000)	1672
Crystal size/mm ³	0.15 × 0.09 × 0.05
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	7.188 to 152.338
Index ranges	-31 ≤ h ≤ 31, -9 ≤ k ≤ 8, -25 ≤ l ≤ 22
Reflections collected	8474
Independent reflections	5471 [R_{int} = 0.0332, R_{sigma} = 0.0380]
Data/restraints/parameters	5471/1/517
Goodness-of-fit on F ²	1.05
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0362, wR_2 = 0.0958
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0979
Largest diff. peak/hole / e Å ⁻³	0.51/-0.37

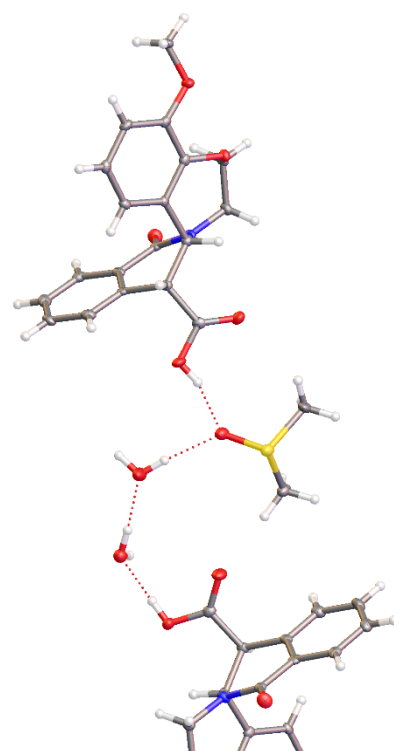


Figure S5. ORTEP representation of compound **6f** (thermal ellipsoids are shown at 50% probability)

Table S6. Crystal data and ORTEP representation for 6m (2178410)	
Empirical formula	C ₂₂ H ₁₇ NO ₄
Formula weight	359.36
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	8.3167(3)
b/Å	9.0975(4)
c/Å	11.7175(7)
α/°	73.755(4)
β/°	75.582(4)
γ/°	87.460(3)
Volume/Å ³	824.05(7)
Z	2
ρ _{calc} /g/cm ³	1.448
μ/mm ⁻¹	0.82
F(000)	376
Crystal size/mm ³	0.16 × 0.12 × 0.04
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.11 to 160.482
Index ranges	-8 ≤ h ≤ 10, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	10082
Independent reflections	3430 [R _{int} = 0.0513, R _{sigma} = 0.0439]
Data/restraints/parameters	3430/0/245
Goodness-of-fit on F ²	1.122
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0982, wR ₂ = 0.3030
Final R indexes [all data]	R ₁ = 0.1037, wR ₂ = 0.3048
Largest diff. peak/hole / e Å ⁻³	0.85/-0.52

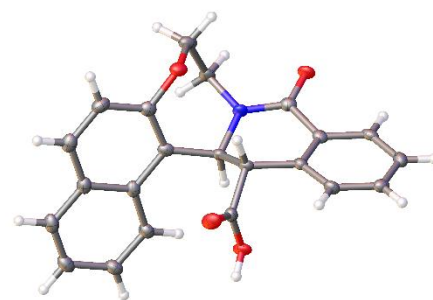


Figure S6. ORTEP representation of compound **6m** (thermal ellipsoids are shown at 50% probability)

Table S7. Crystal data and ORTEP representation for 13 (2207930)	
Empirical formula	C _{16.8} H ₁₆ N _{1.6} O _{3.2}
Formula weight	291.51
Temperature/K	100.15
Crystal system	monoclinic
Space group	Ia
a/Å	13.1227(3)
b/Å	8.3329(2)
c/Å	16.2683(3)
α/°	90
β/°	93.697(2)
γ/°	90
Volume/Å ³	1775.24(7)
Z	5
ρ _{calc} /cm ³	1.363
μ/mm ⁻¹	0.78
F(000)	768
Crystal size/mm ³	0.28 × 0.18 × 0.12
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	10.9 to 152.632
Index ranges	-13 ≤ h ≤ 16, -10 ≤ k ≤ 10, -19 ≤ l ≤ 20
Reflections collected	7455
Independent reflections	2852 [R _{int} = 0.0213, R _{sigma} = 0.0208]
Data/restraints/parameters	2852/2/246
Goodness-of-fit on F ²	1.057
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0288, wR ₂ = 0.0756
Final R indexes [all data]	R ₁ = 0.0289, wR ₂ = 0.0758
Largest diff. peak/hole / e Å ⁻³	0.30/-0.17

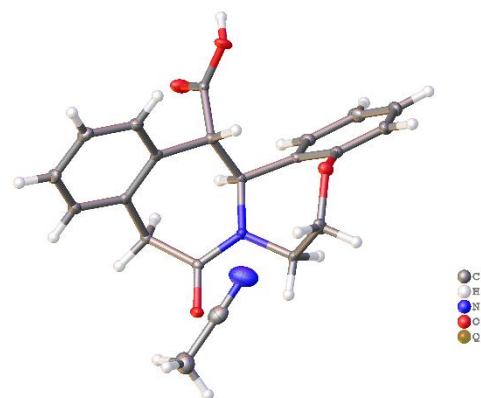


Figure S7. ORTEP representation of compound **13** (thermal ellipsoids are shown at 50% probability)

Table S8. Crystal data and ORTEP representation for 16 (2207931)	
Empirical formula	C ₁₃ H ₁₃ NO ₄ S
Formula weight	279.3
Temperature/K	100.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	13.3435(2)
b/Å	8.09740(10)
c/Å	11.9013(2)
α/°	90
β/°	109.952(2)
γ/°	90
Volume/Å ³	1208.73(3)
Z	4
ρ _{calc} /cm ³	1.535
μ/mm ⁻¹	2.494
F(000)	584
Crystal size/mm ³	0.14 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.048 to 138.17
Index ranges	-16 ≤ h ≤ 15, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	5547
Independent reflections	2252 [R _{int} = 0.0271, R _{sigma} = 0.0261]
Data/restraints/parameters	2252/0/173
Goodness-of-fit on F ²	1.051
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0319, wR ₂ = 0.0858
Final R indexes [all data]	R ₁ = 0.0329, wR ₂ = 0.0869
Largest diff. peak/hole / e Å ⁻³	0.27/-0.28

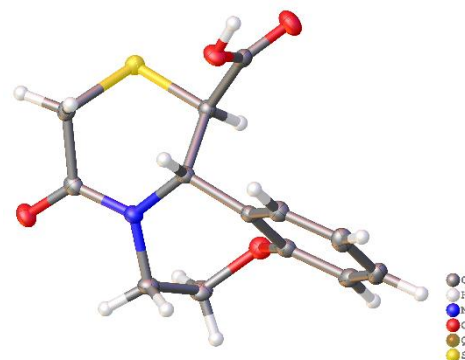


Figure S8. ORTEP representation of compound **16** (thermal ellipsoids are shown at 50% probability)

Table S9. Crystal data and ORTEP representation for 6a' (2207936)	
Empirical formula	C ₁₈ H ₁₅ NO ₄
Formula weight	309.31
Temperature/K	100.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.9679(3)
b/Å	9.2236(2)
c/Å	14.4744(3)
α/°	90
β/°	100.629(2)
γ/°	90
Volume/Å ³	1439.16(6)
Z	4
ρ _{calc} /g/cm ³	1.428
μ/mm ⁻¹	0.839
F(000)	648.0
Crystal size/mm ³	0.06 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.202 to 159.218
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	10838
Independent reflections	3036 [R _{int} = 0.0495, R _{sigma} = 0.0406]
Data/restraints/parameters	3036/0/209
Goodness-of-fit on F ²	1.035
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0415, wR ₂ = 0.1040
Final R indexes [all data]	R ₁ = 0.0487, wR ₂ = 0.1081
Largest diff. peak/hole / e Å ⁻³	0.22/-0.23

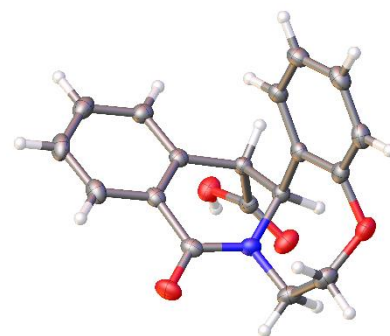
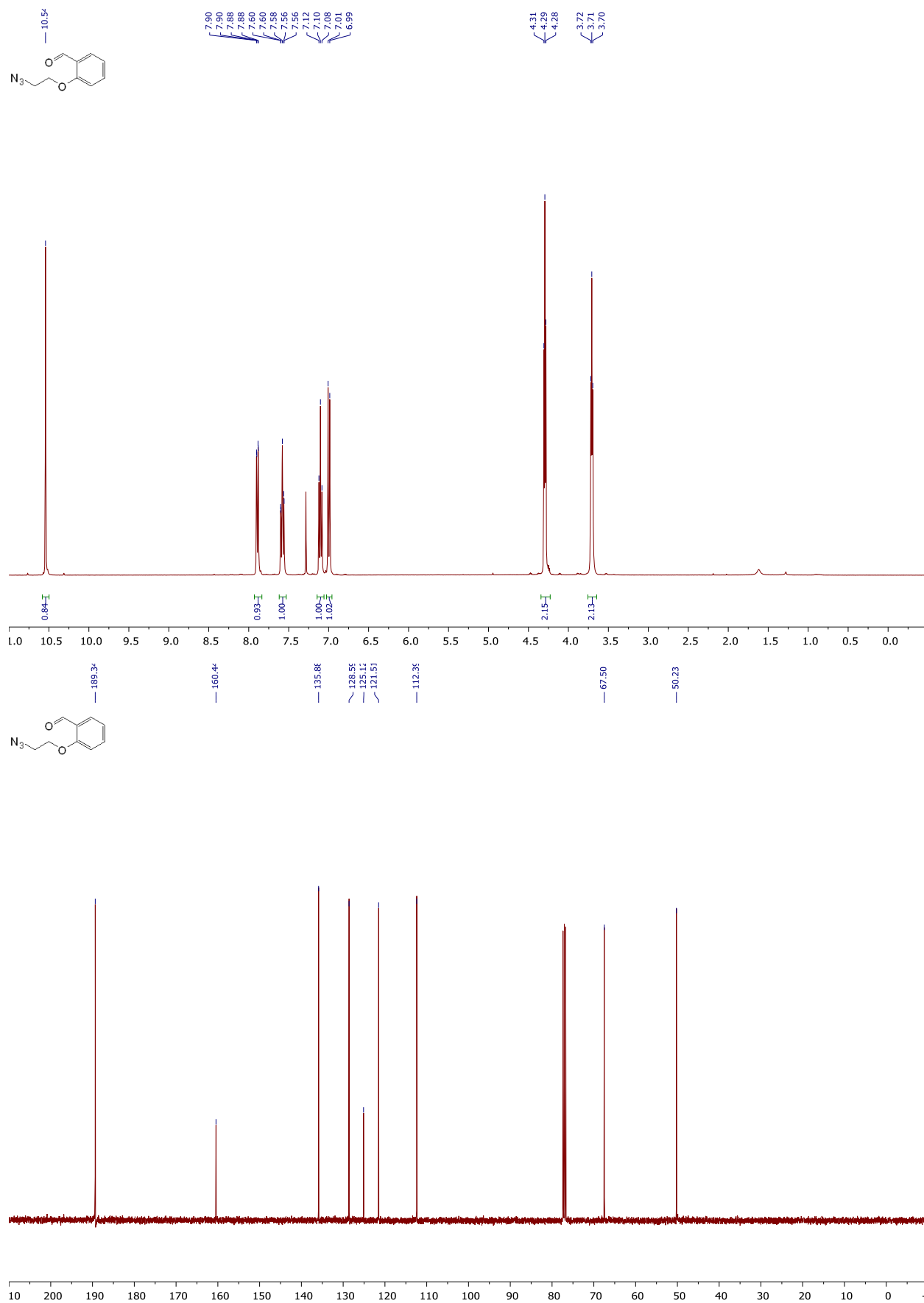
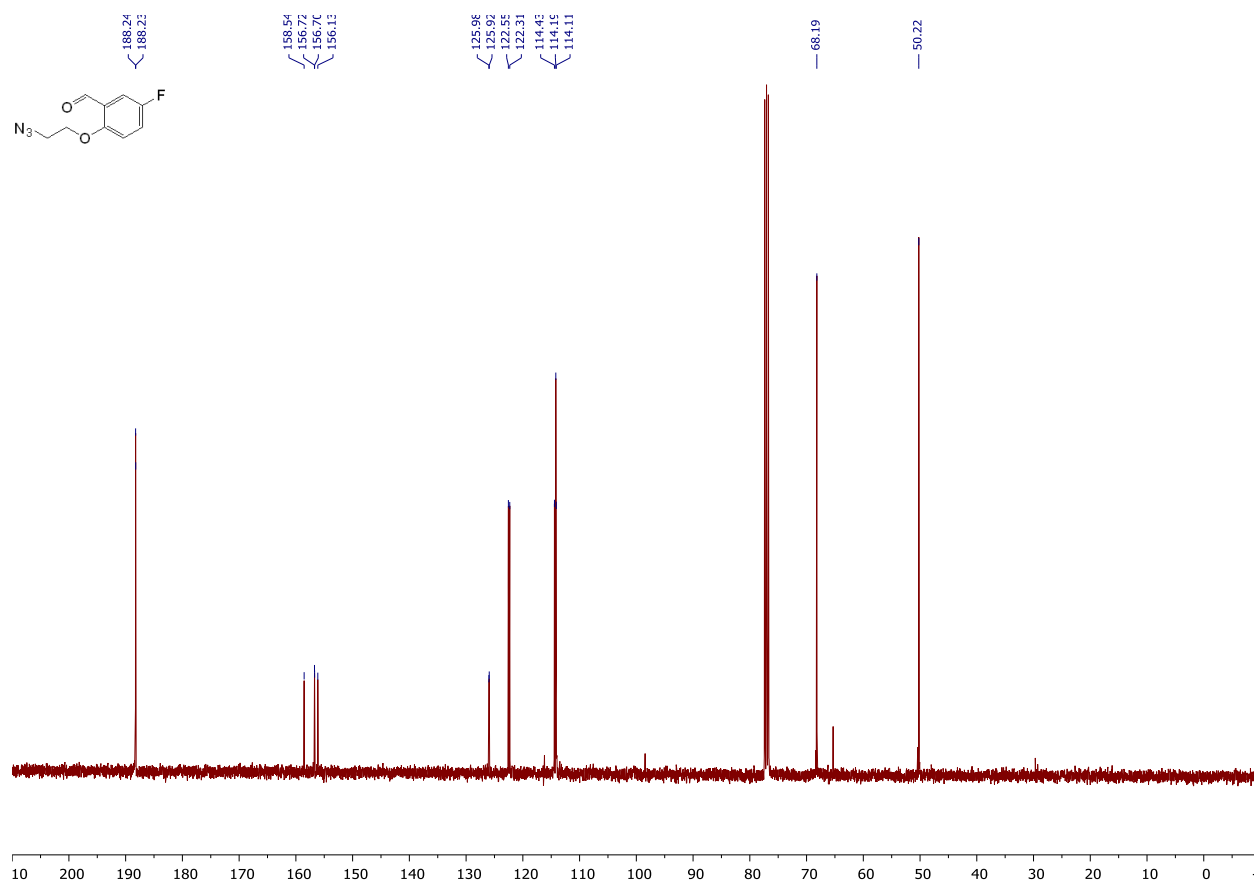
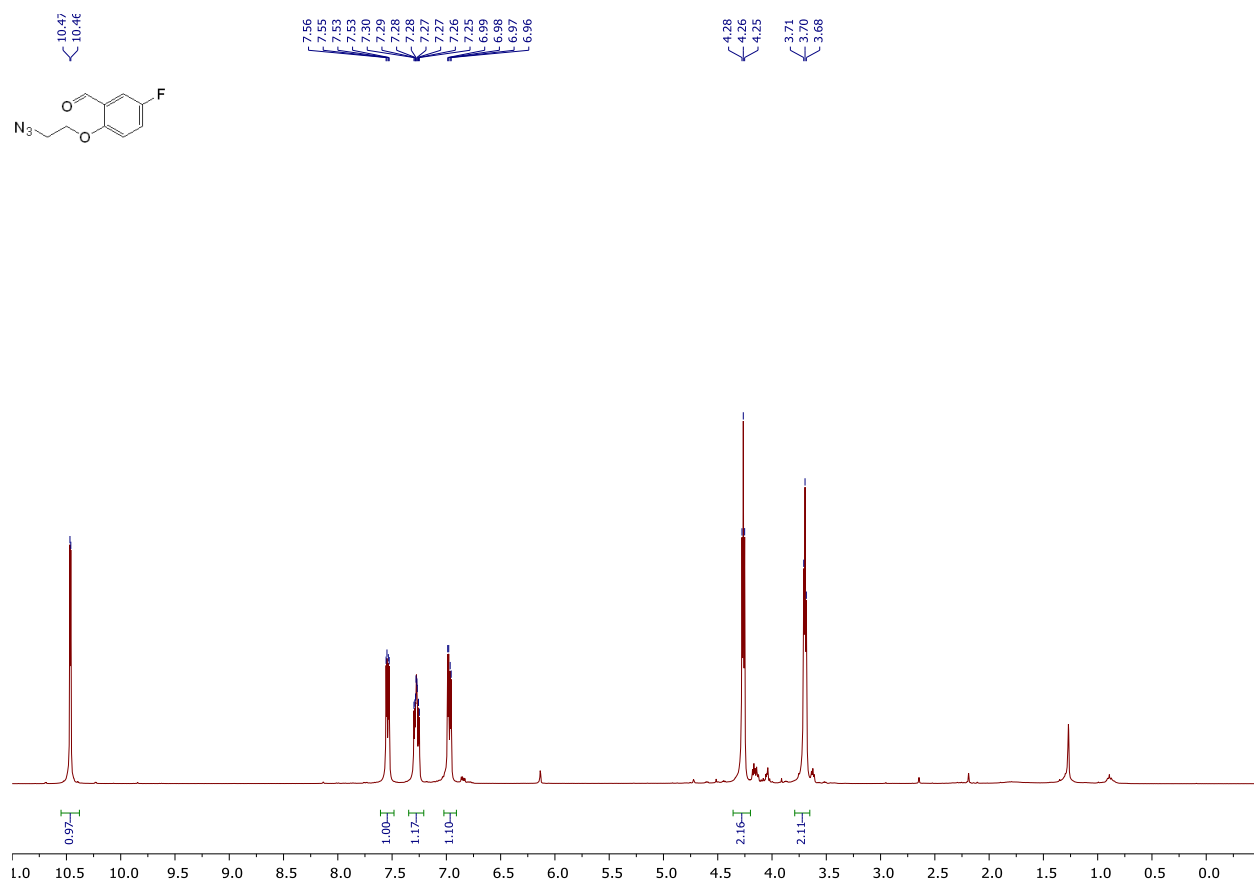


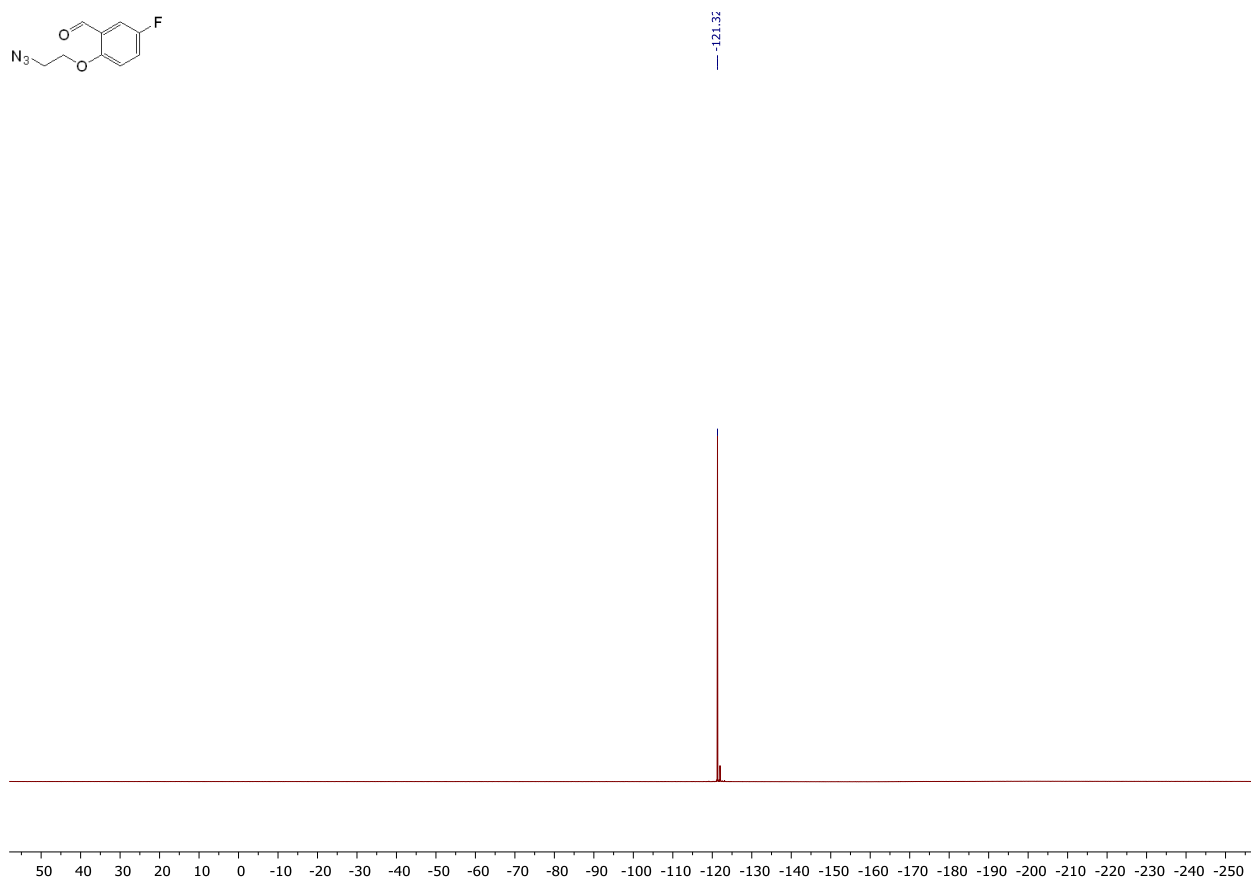
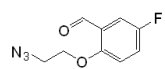
Figure S9. ORTEP representation of compound **6a'** (thermal ellipsoids are shown at 50% probability)

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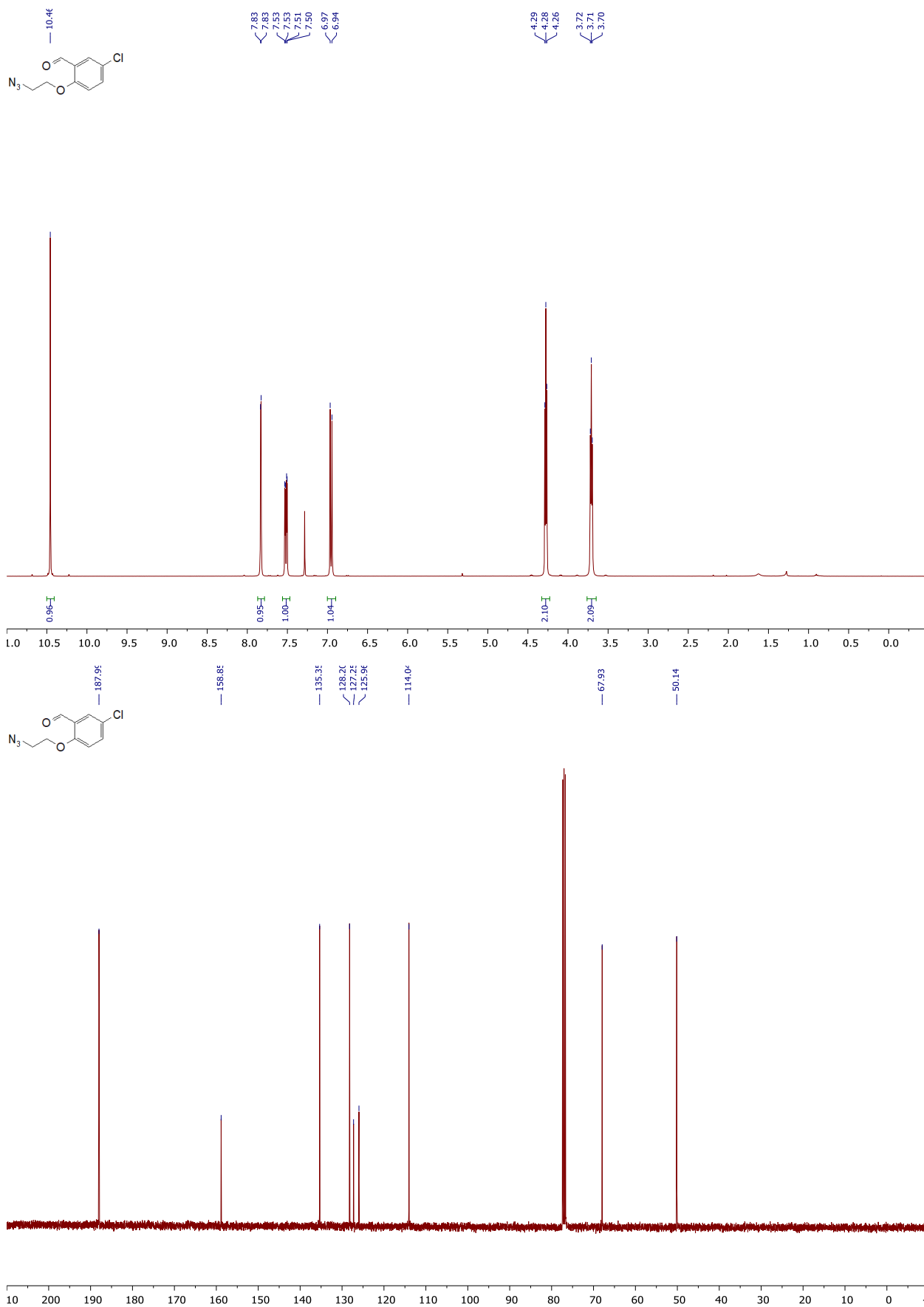


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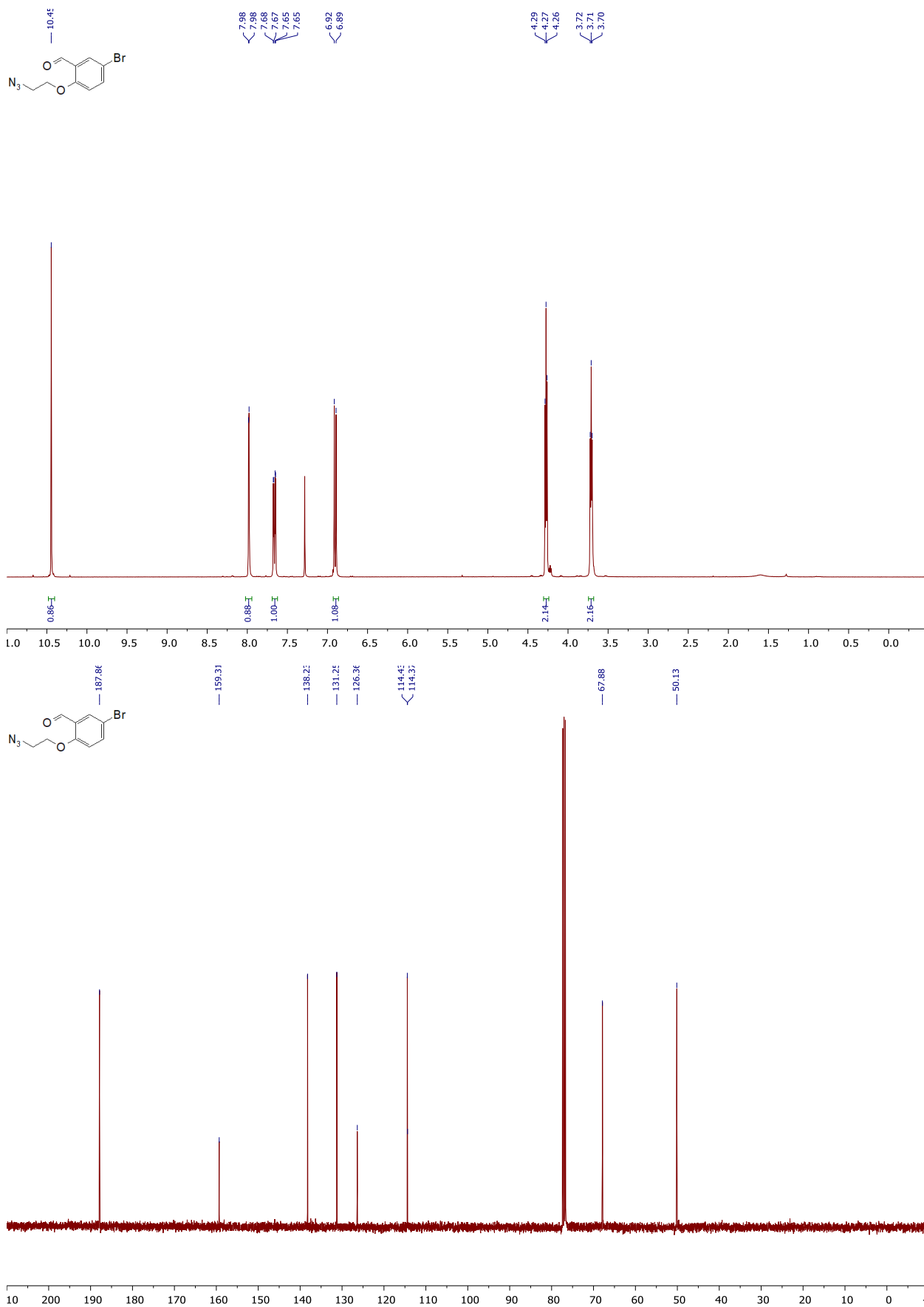




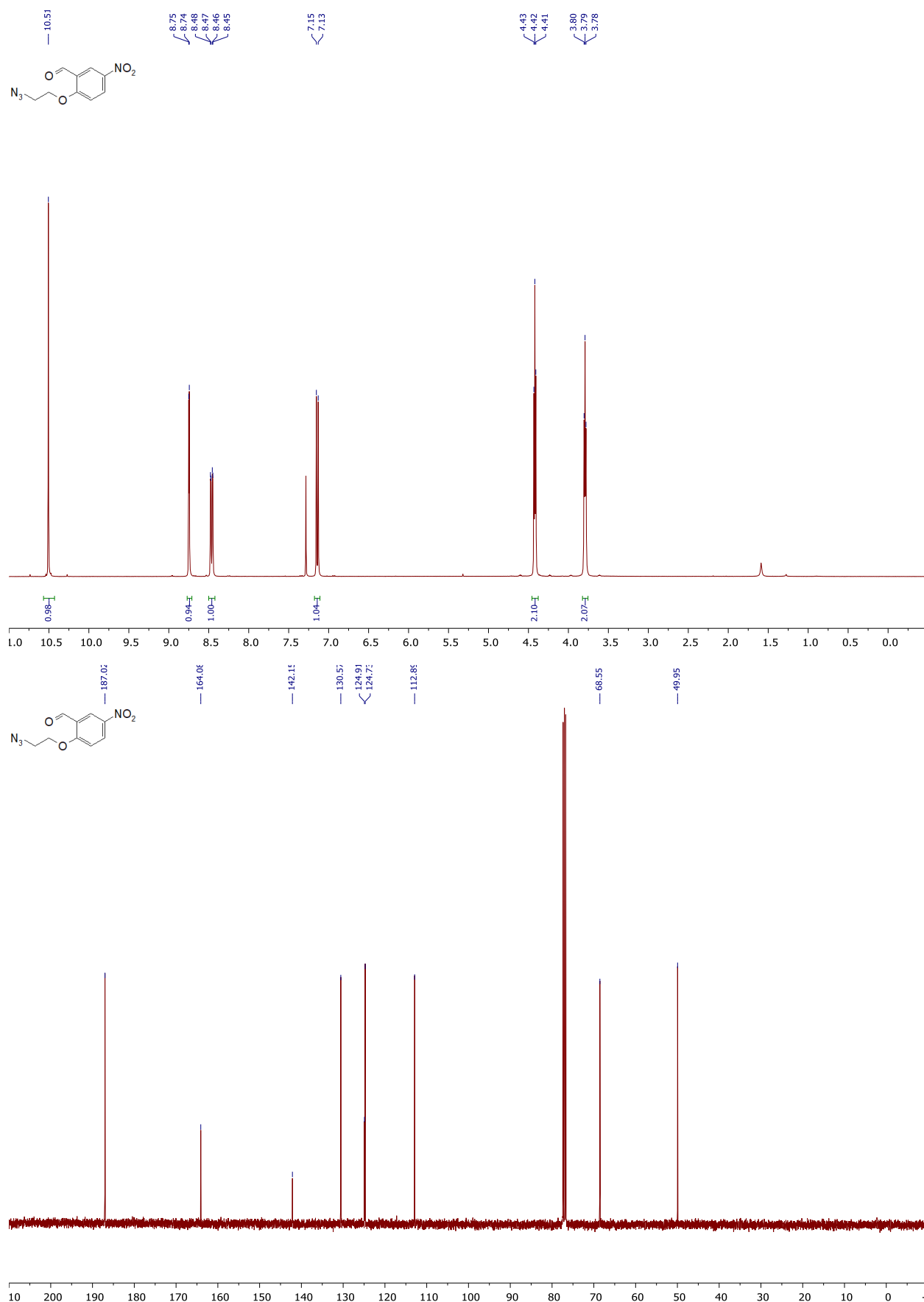
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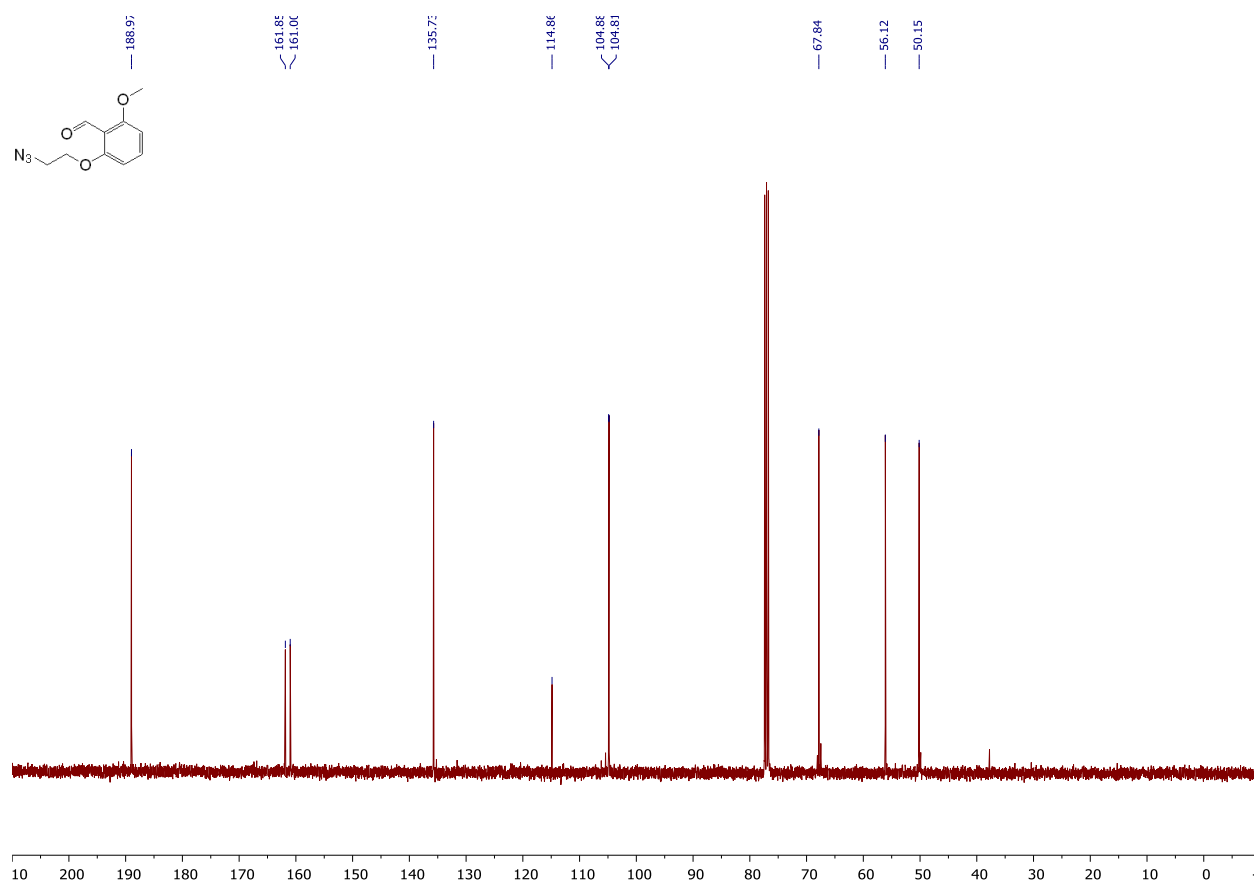
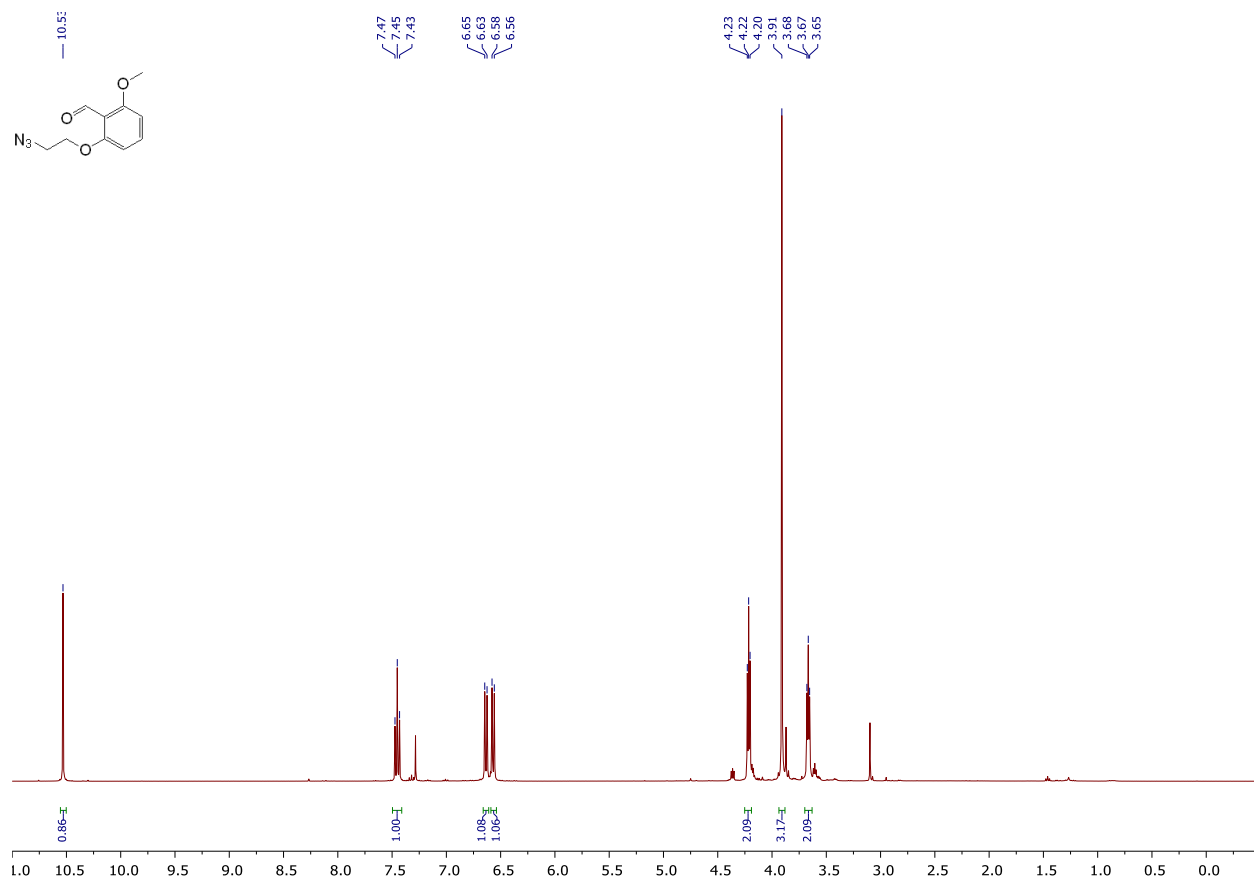
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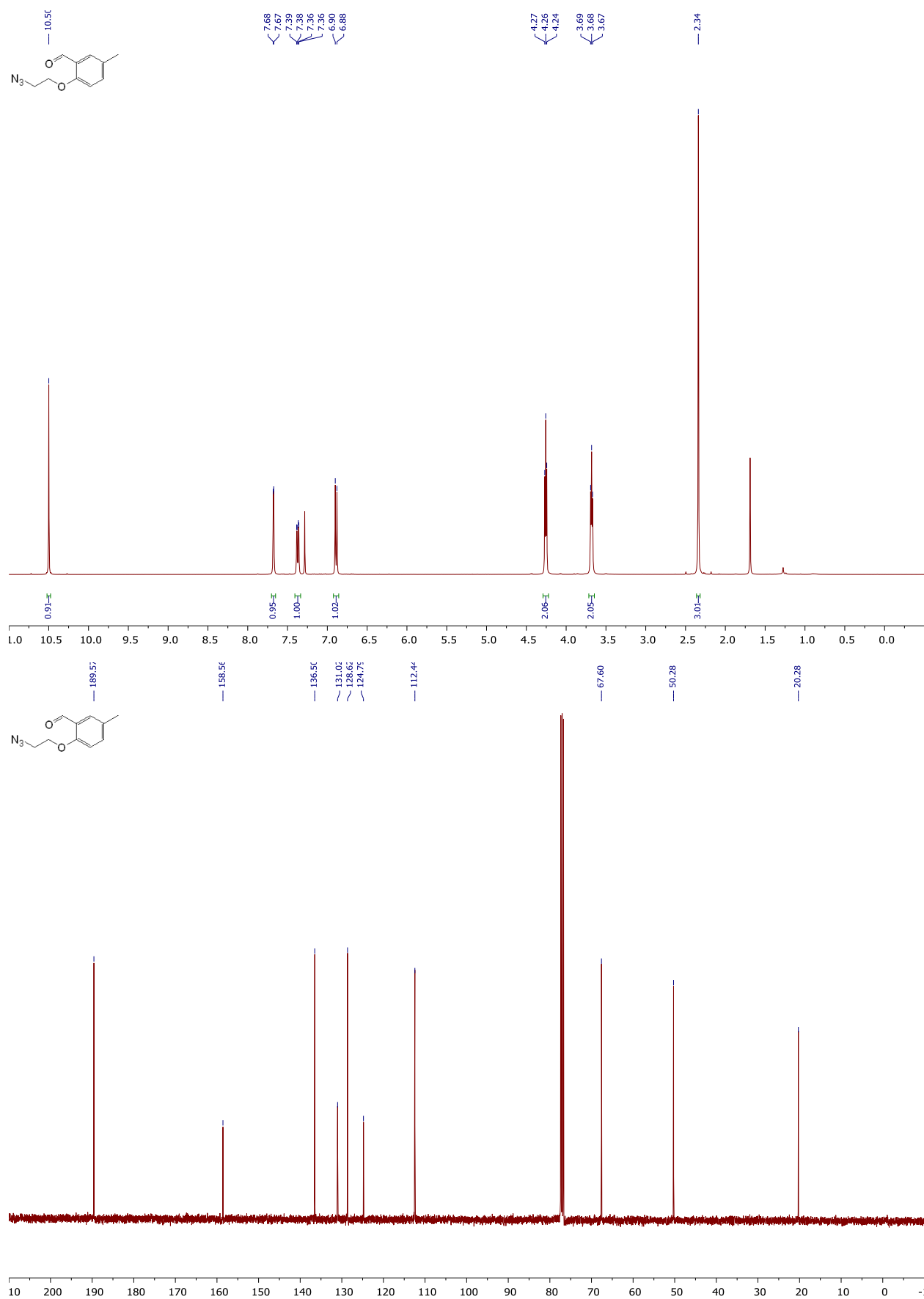
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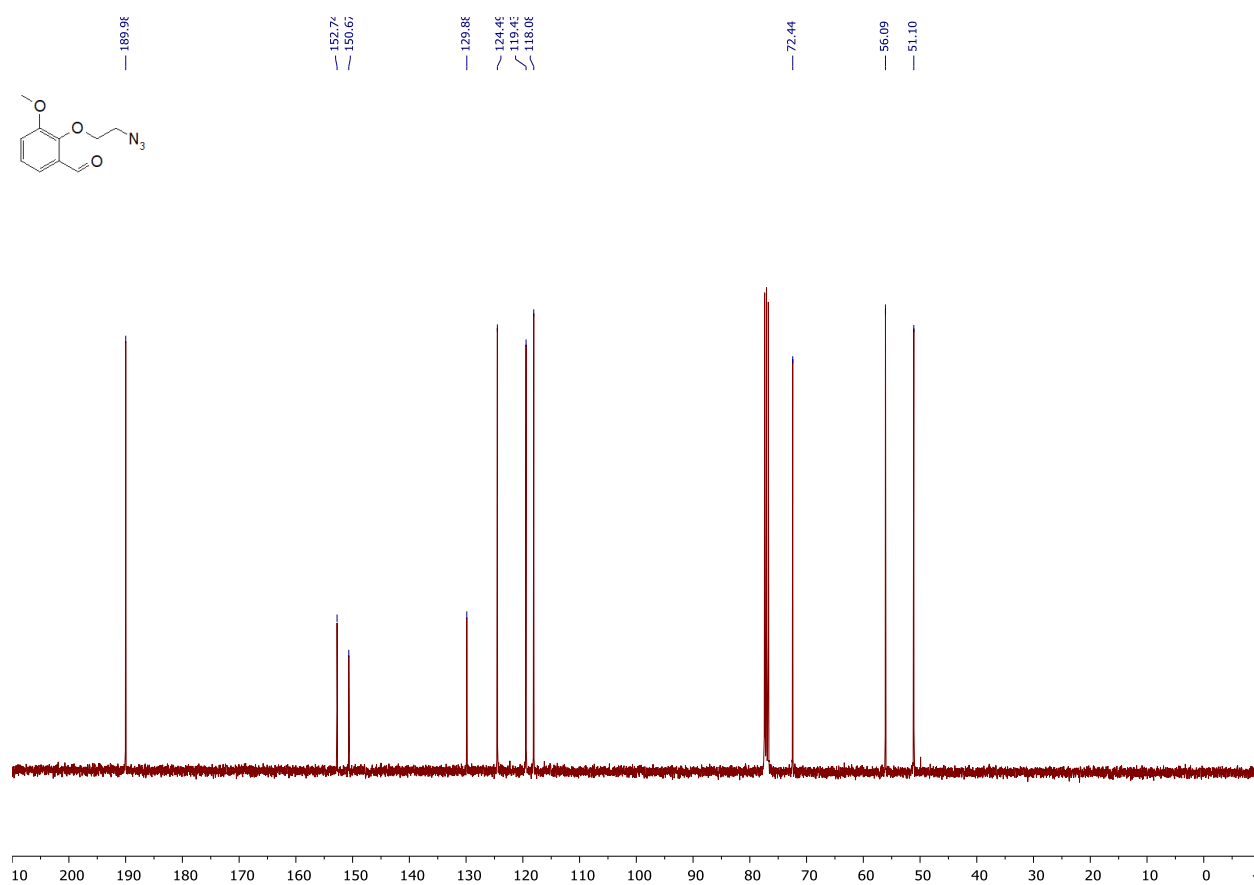
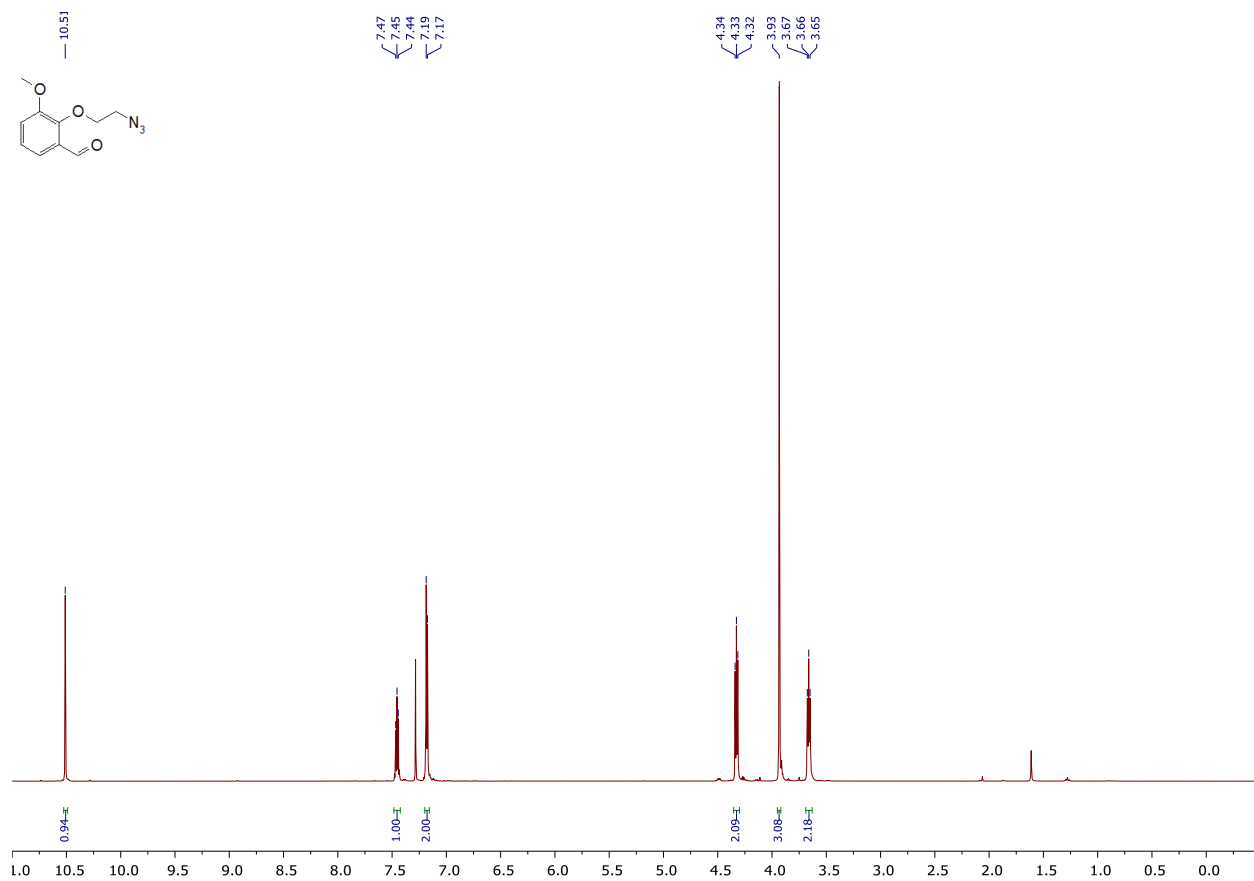
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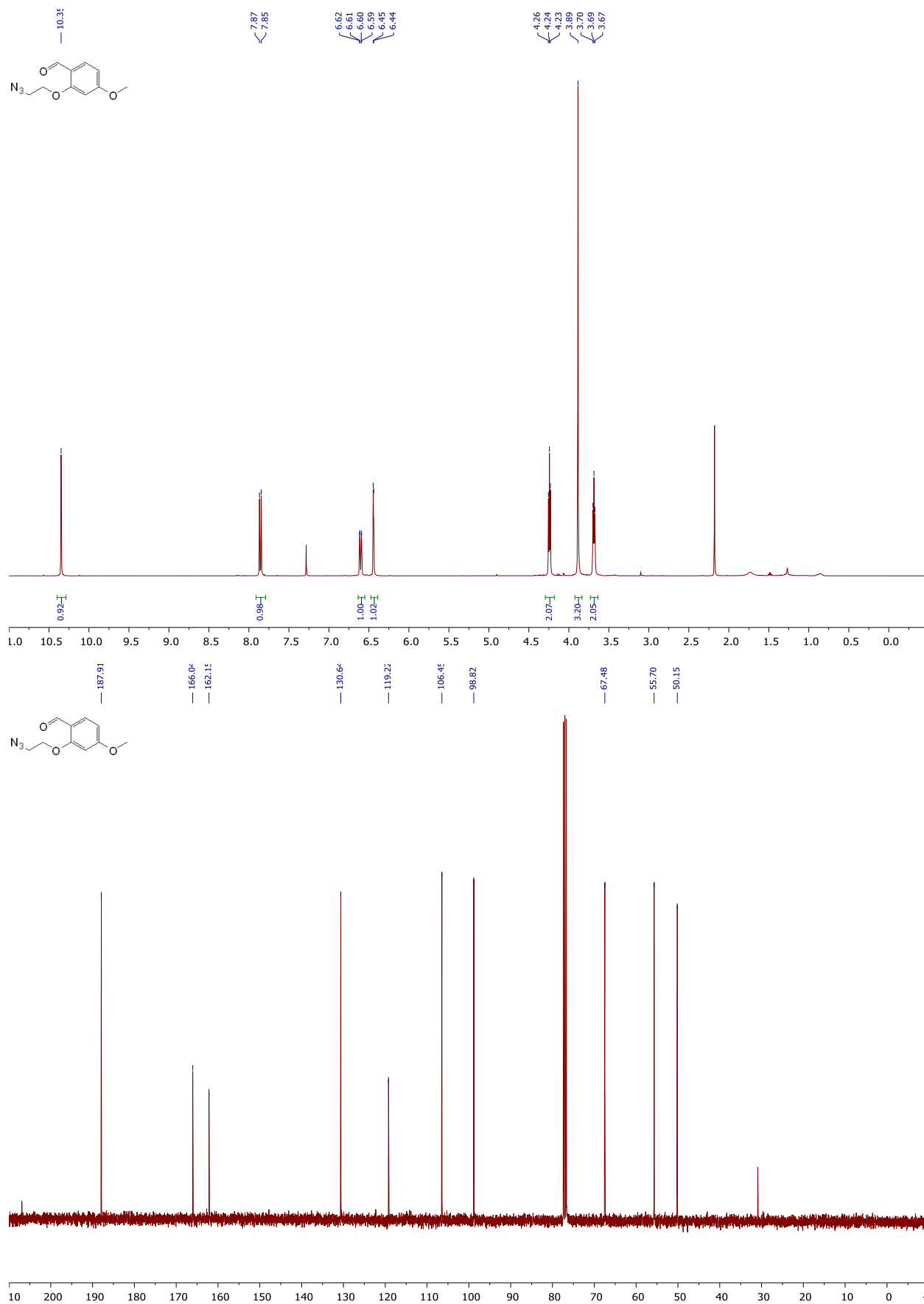
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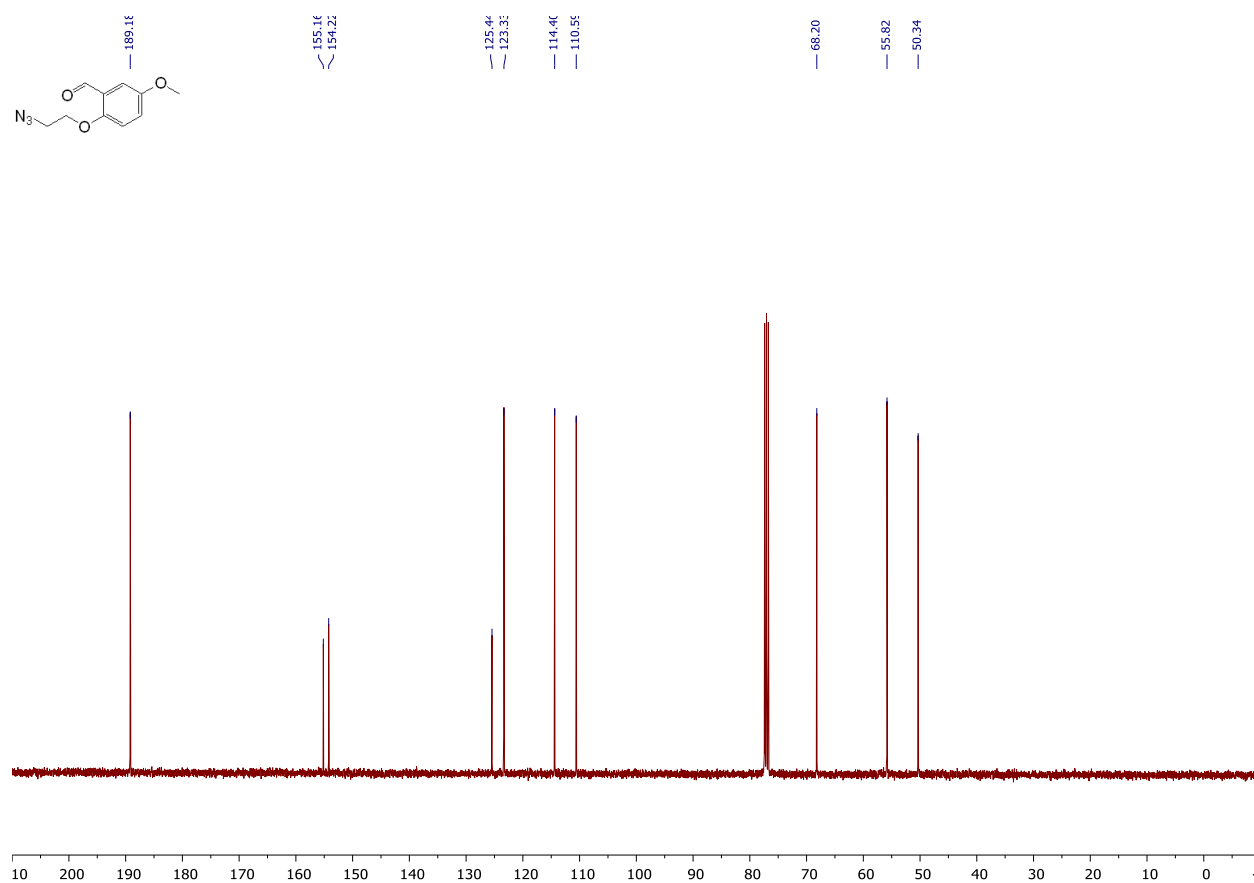
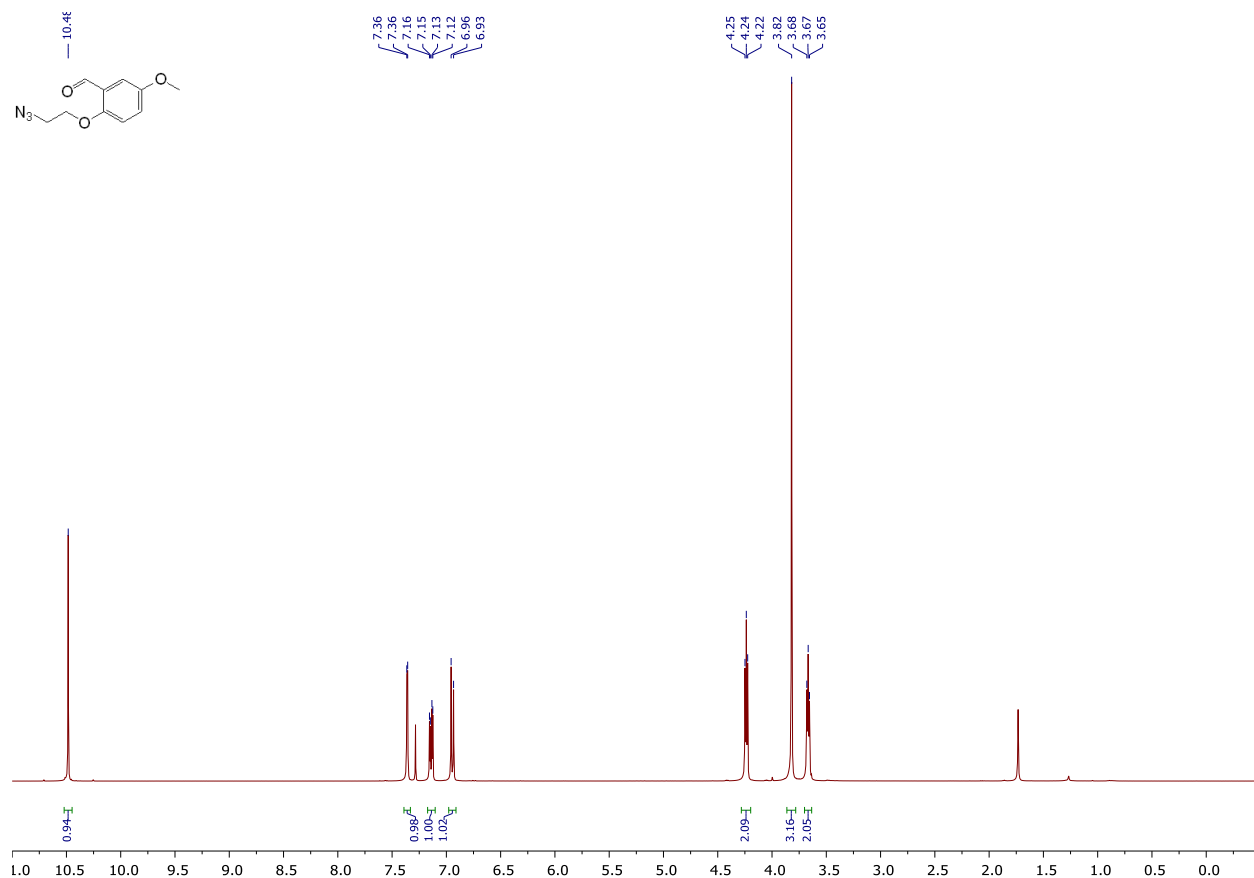
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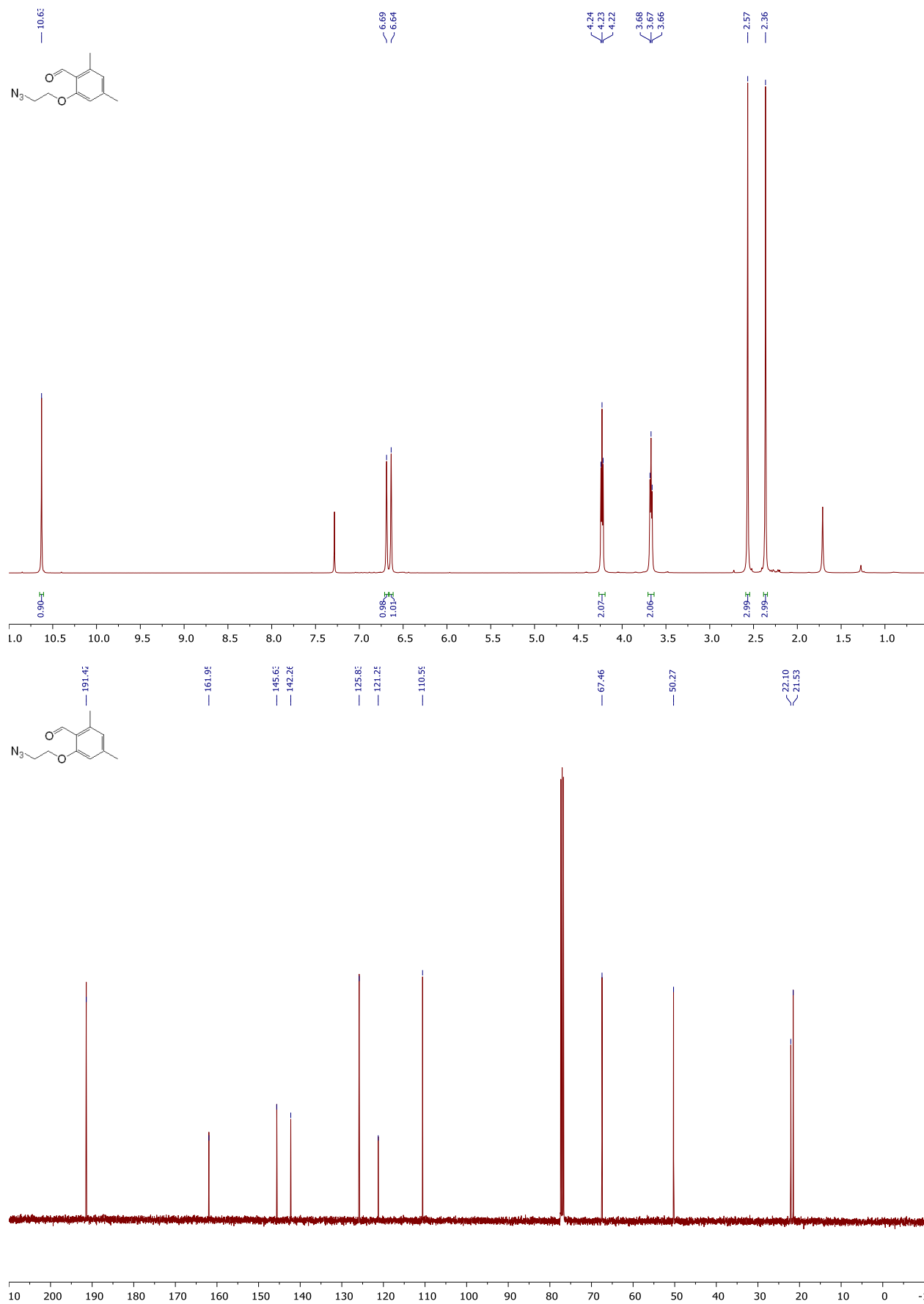
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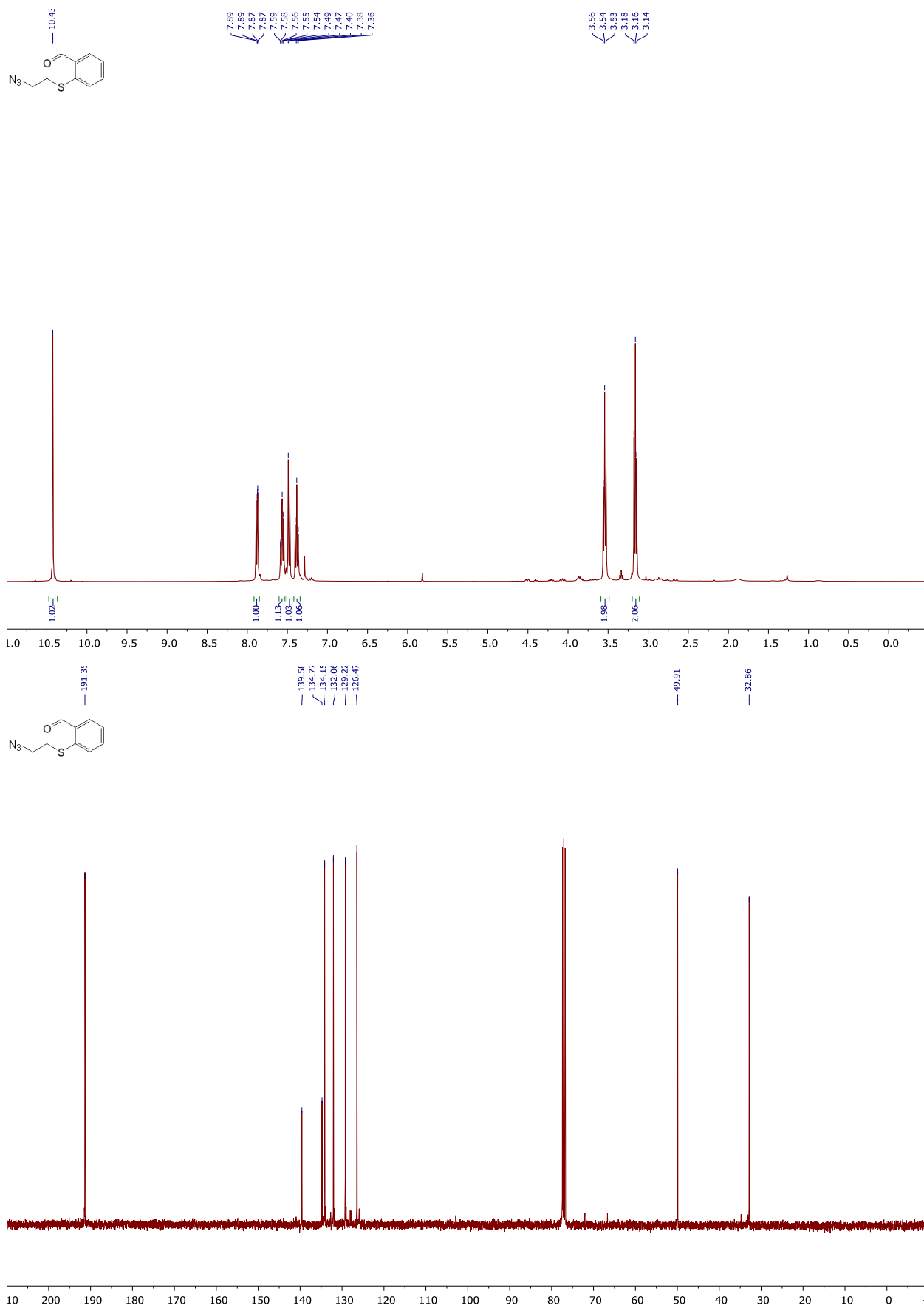
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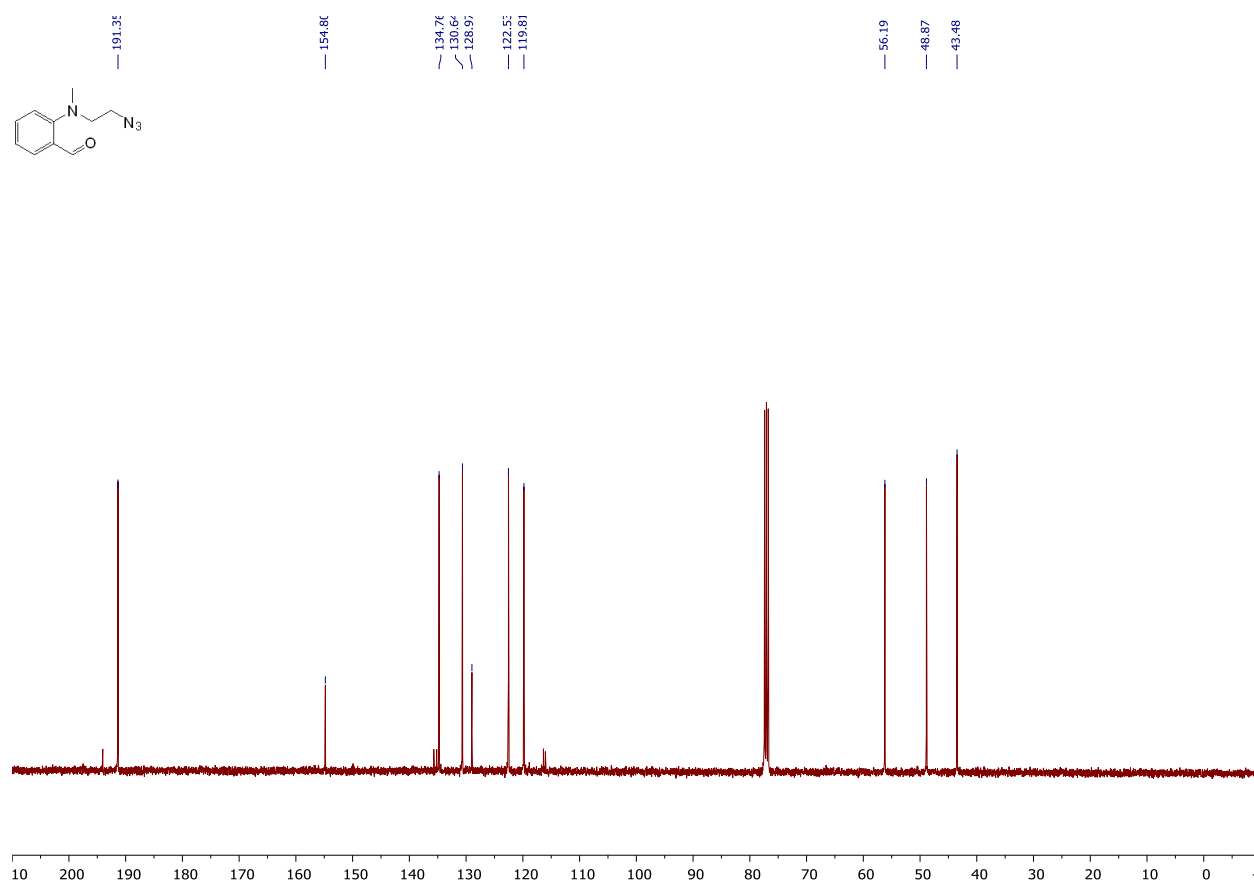
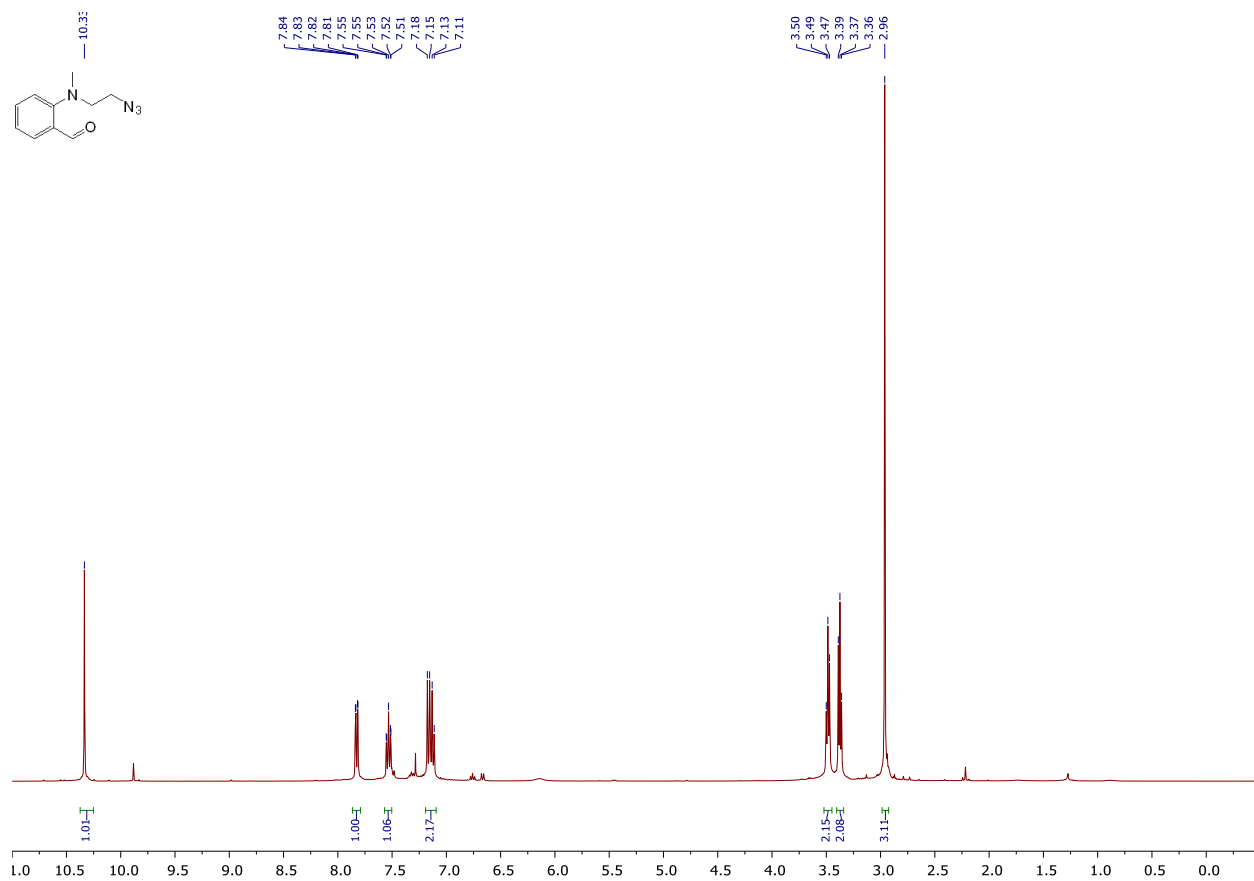
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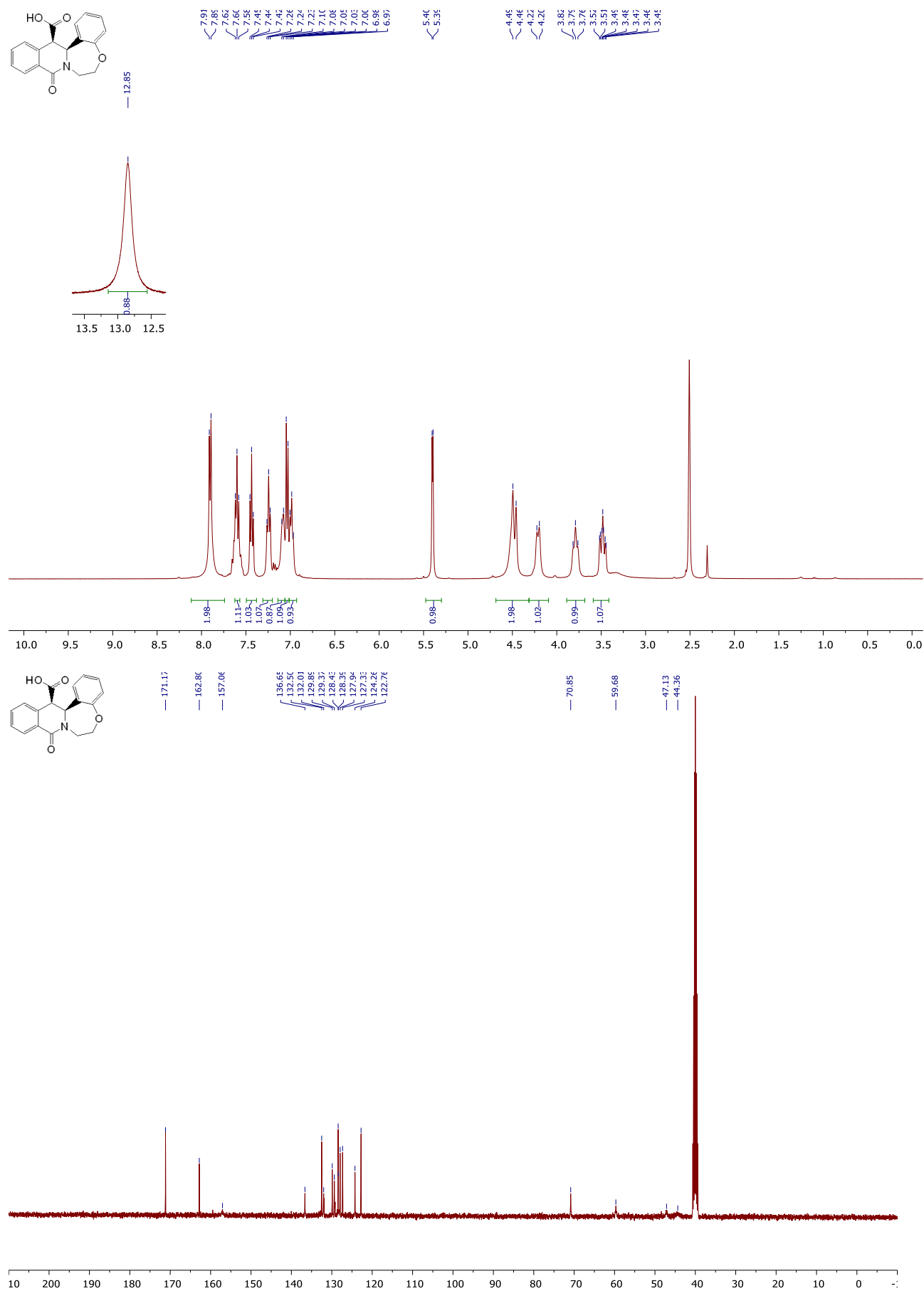
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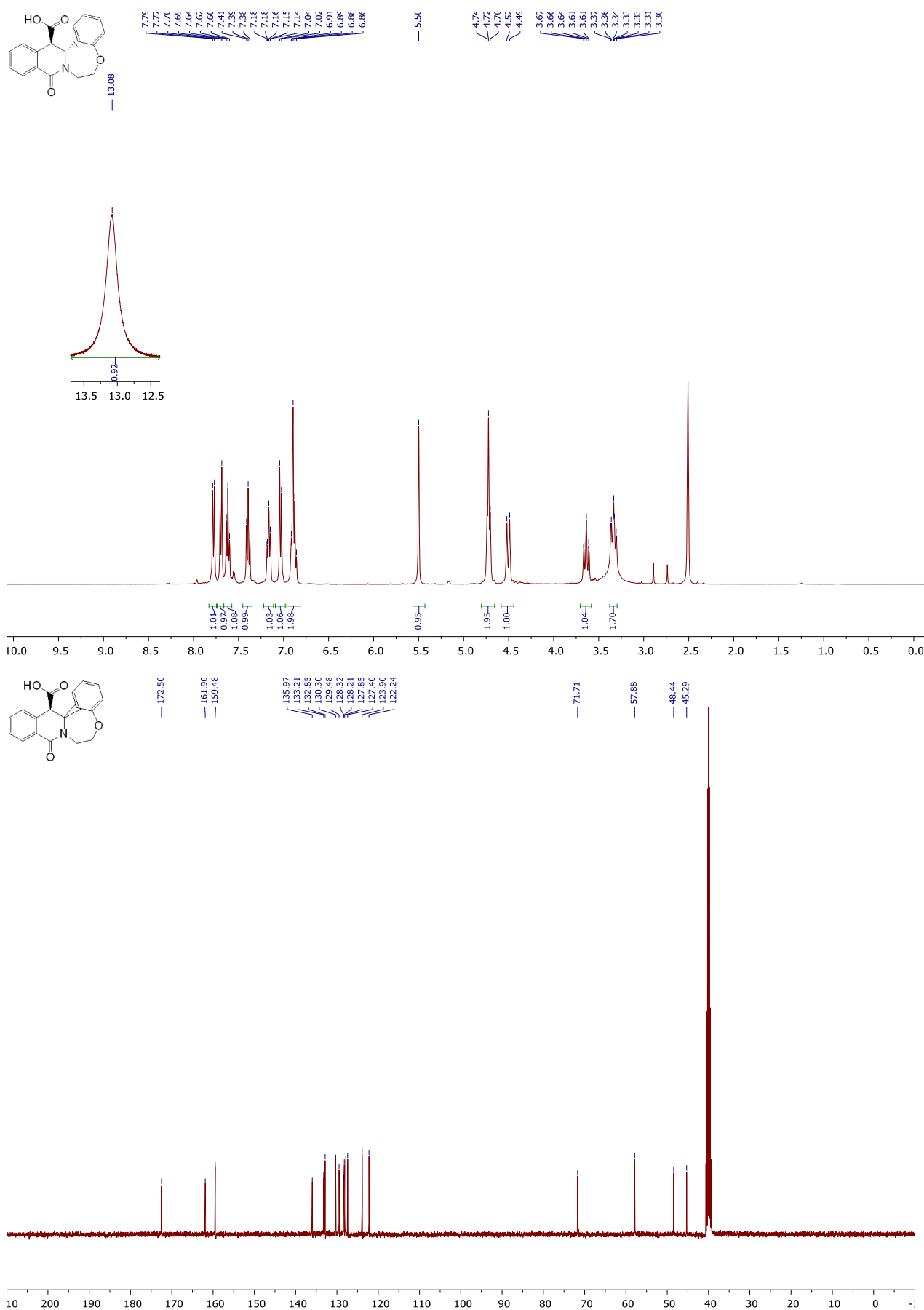
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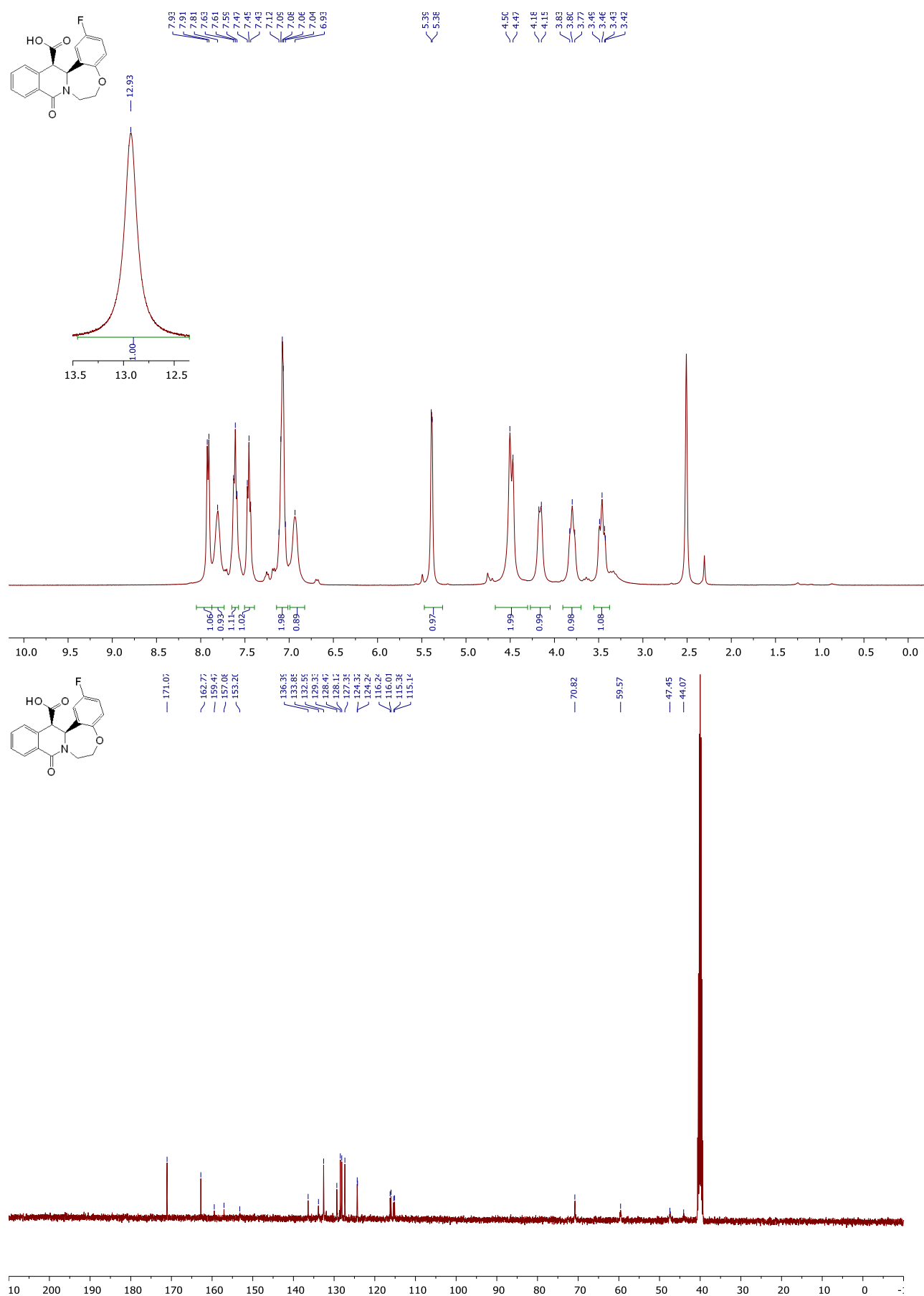
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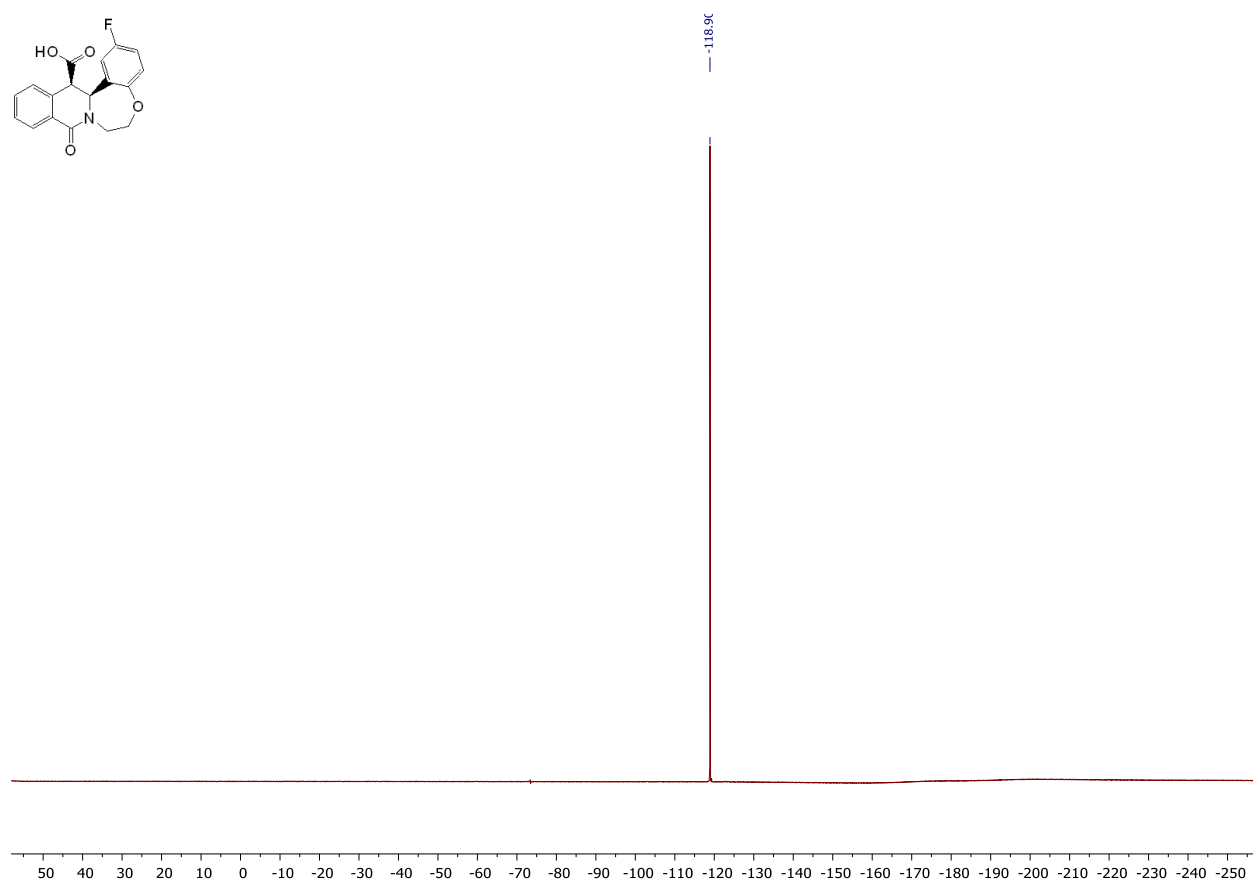
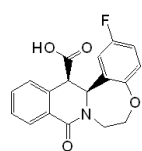


Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6a'**



Copies of ^1H 400.13 MHz, CDCl_3 , ^{13}C 100.61 MHz, CDCl_3 and ^{19}F 376.50 MHz, CDCl_3 spectra of **6b**





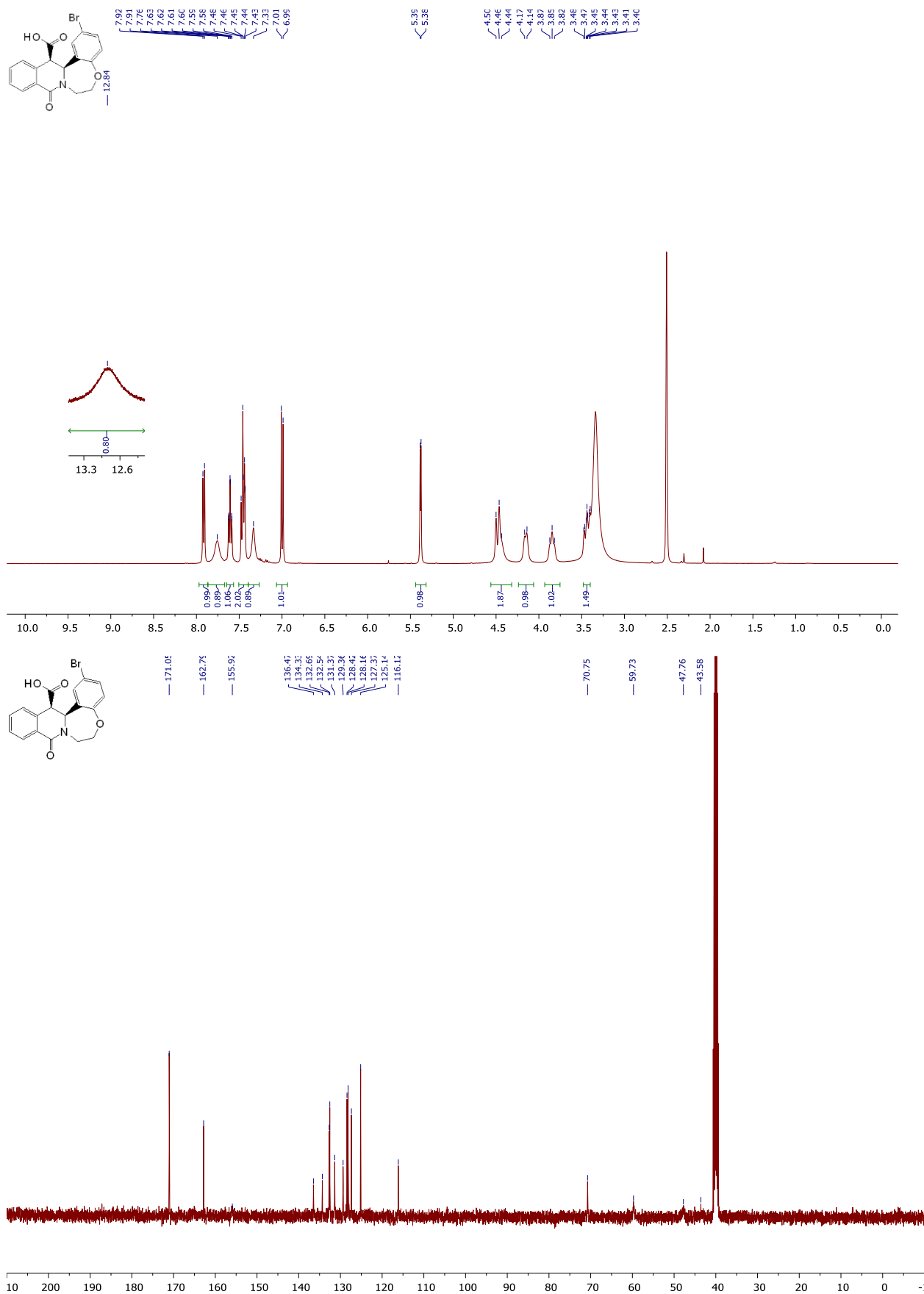
The figure displays the ^1H and ^{13}C NMR spectra of compound 10, along with its chemical structure.

Chemical Structure: The structure of compound 10 is shown, featuring a benzodioxane core with a chlorine substituent and a carboxylic acid group.

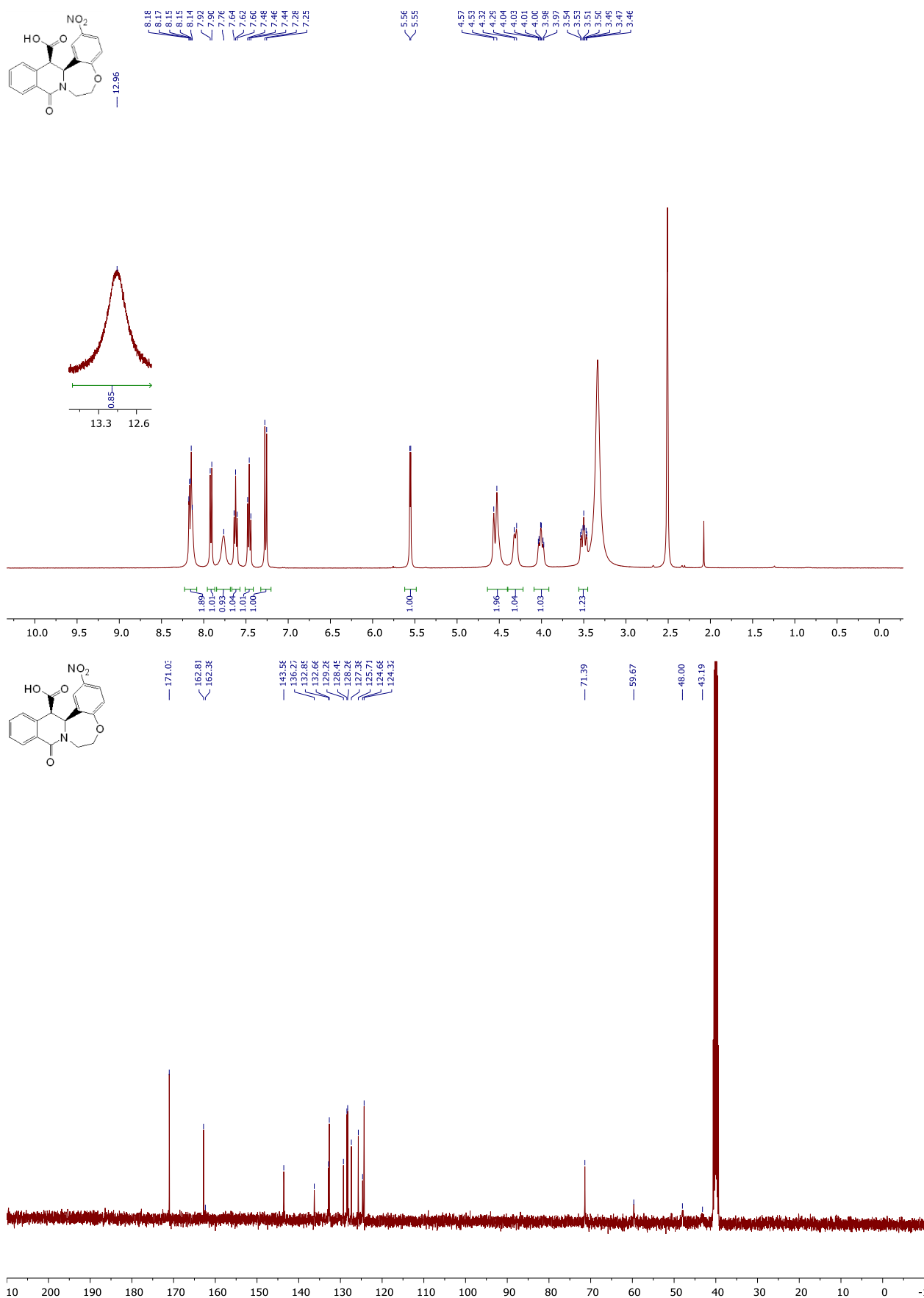
^1H NMR Spectrum (Top): The ^1H NMR spectrum (400 MHz, CDCl_3) shows peaks in the aromatic region (7.05–7.91 ppm) and aliphatic region (3.41–5.38 ppm). Integration values are provided below the peaks.

^{13}C NMR Spectrum (Bottom): The ^{13}C NMR spectrum (100 MHz, CDCl_3) shows peaks in the aromatic region (124.71–136.44 ppm) and aliphatic region (43.52–70.80 ppm).

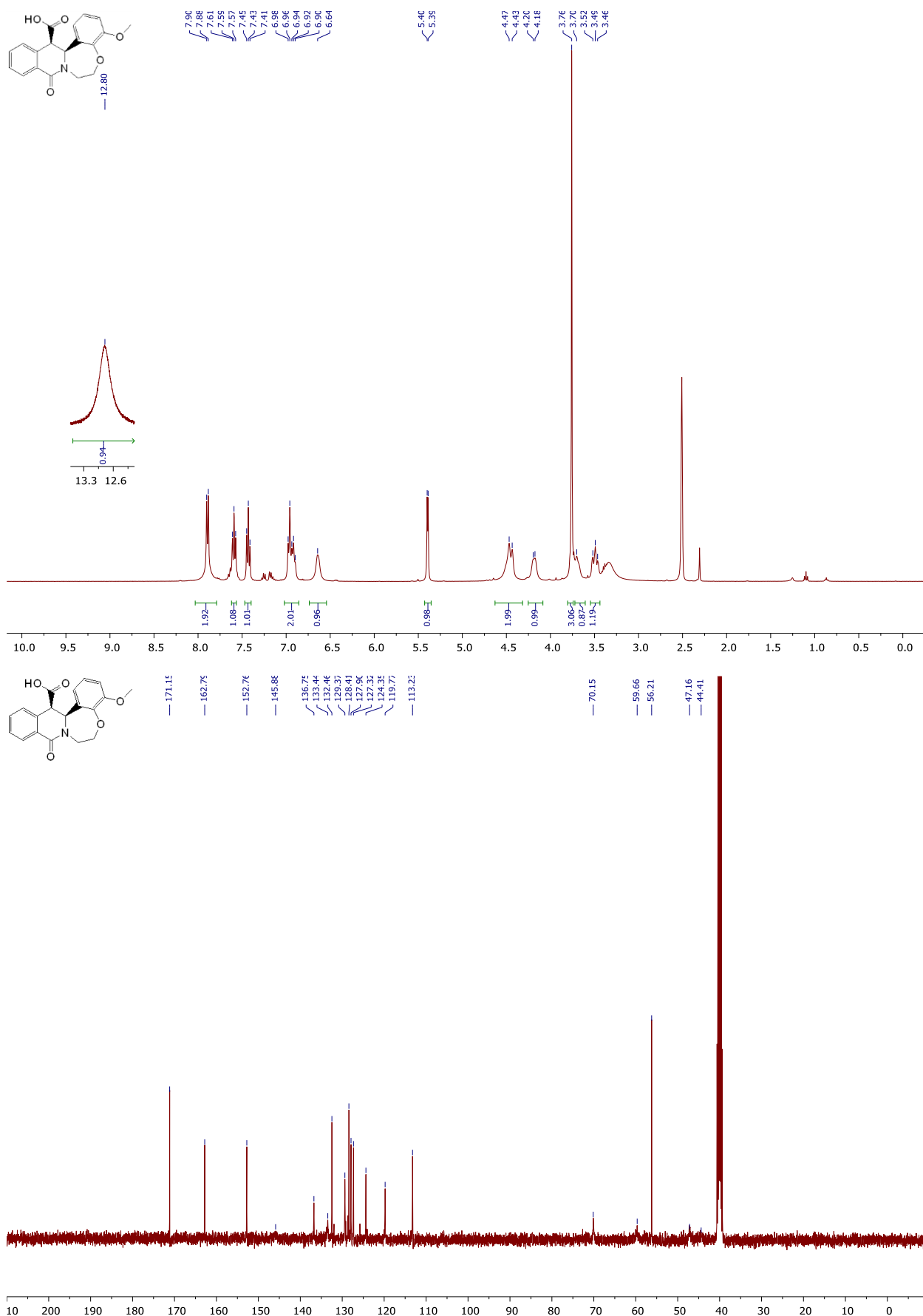
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6d**



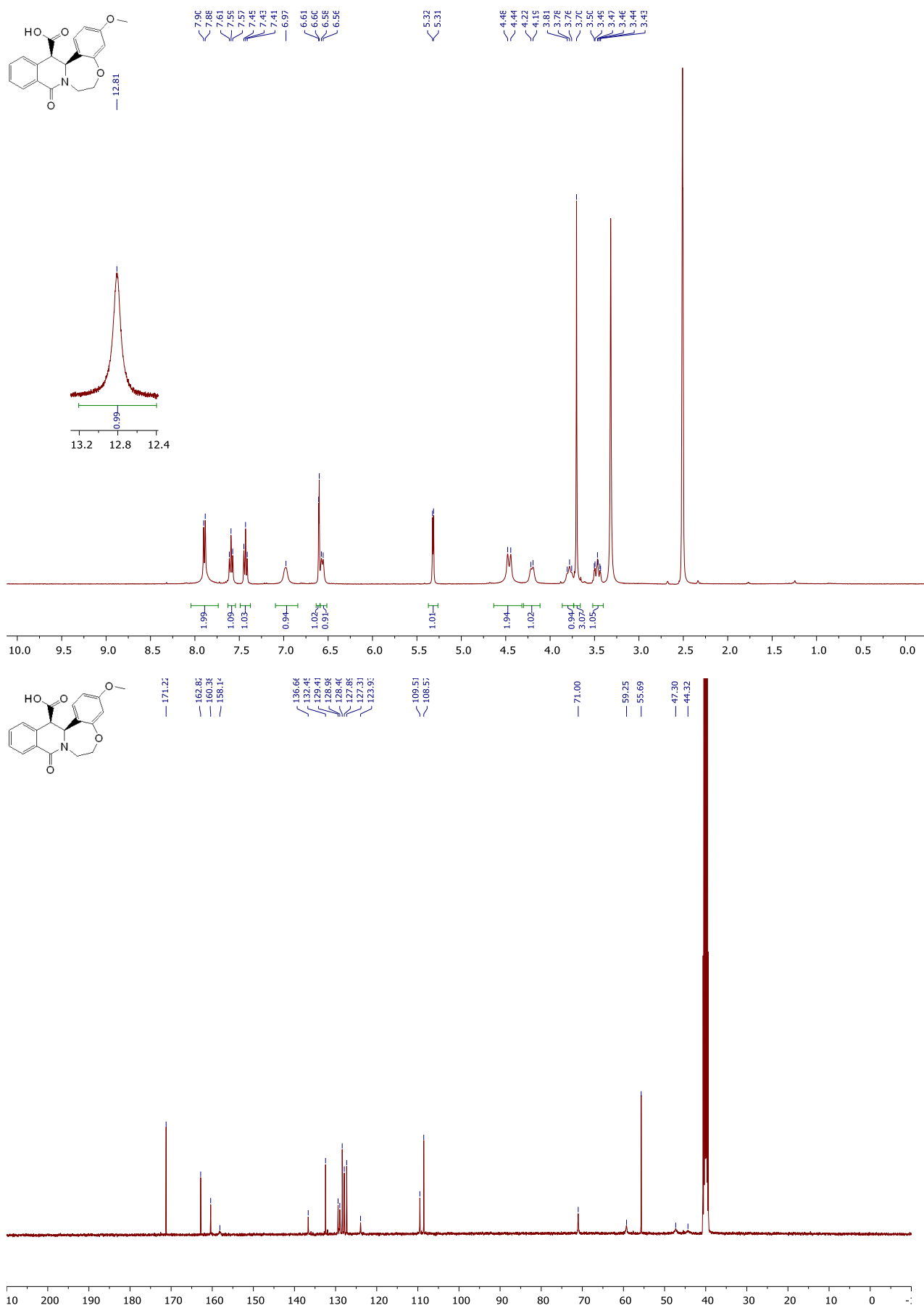
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6e**



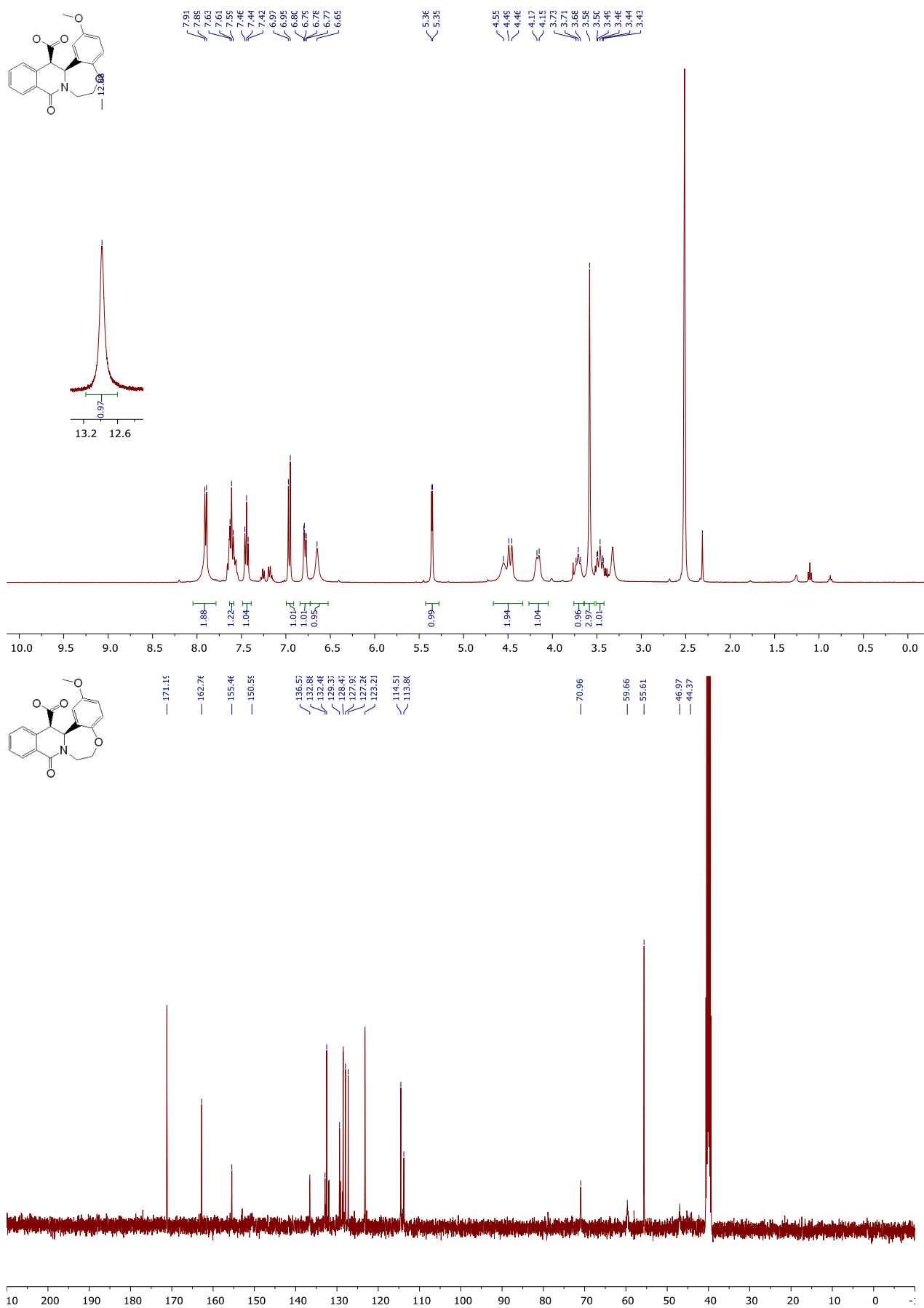
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6f**



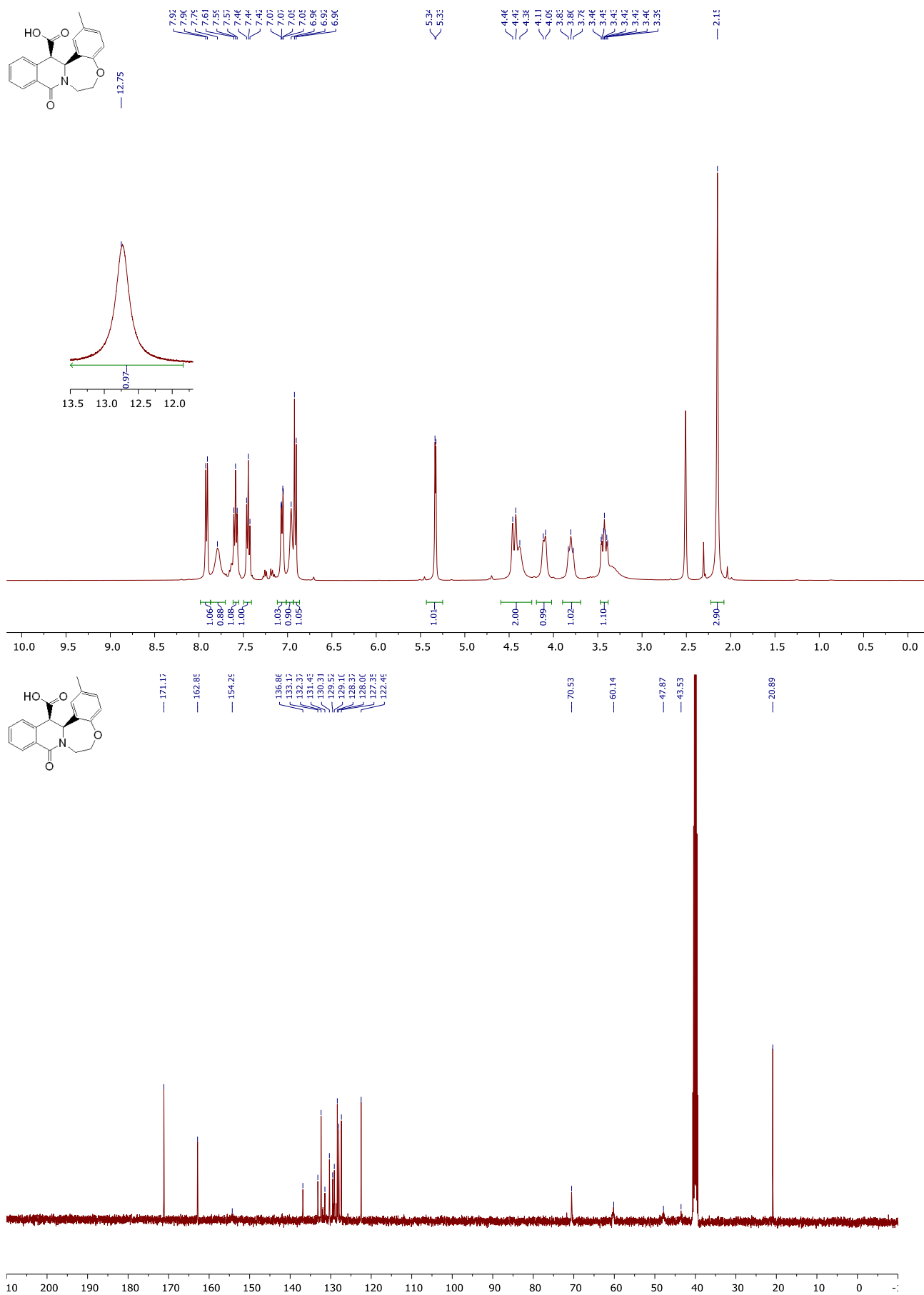
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6g**



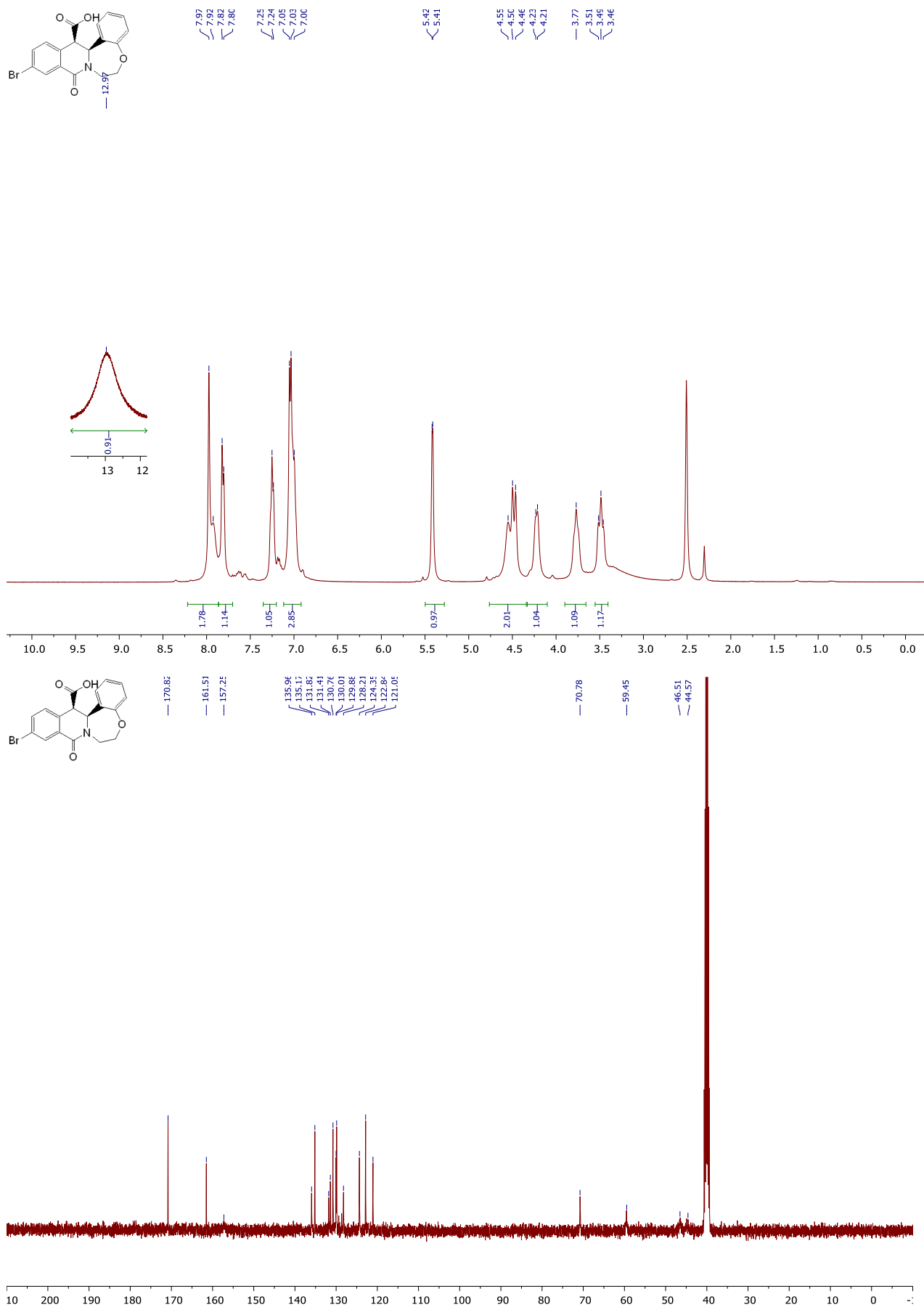
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6h**



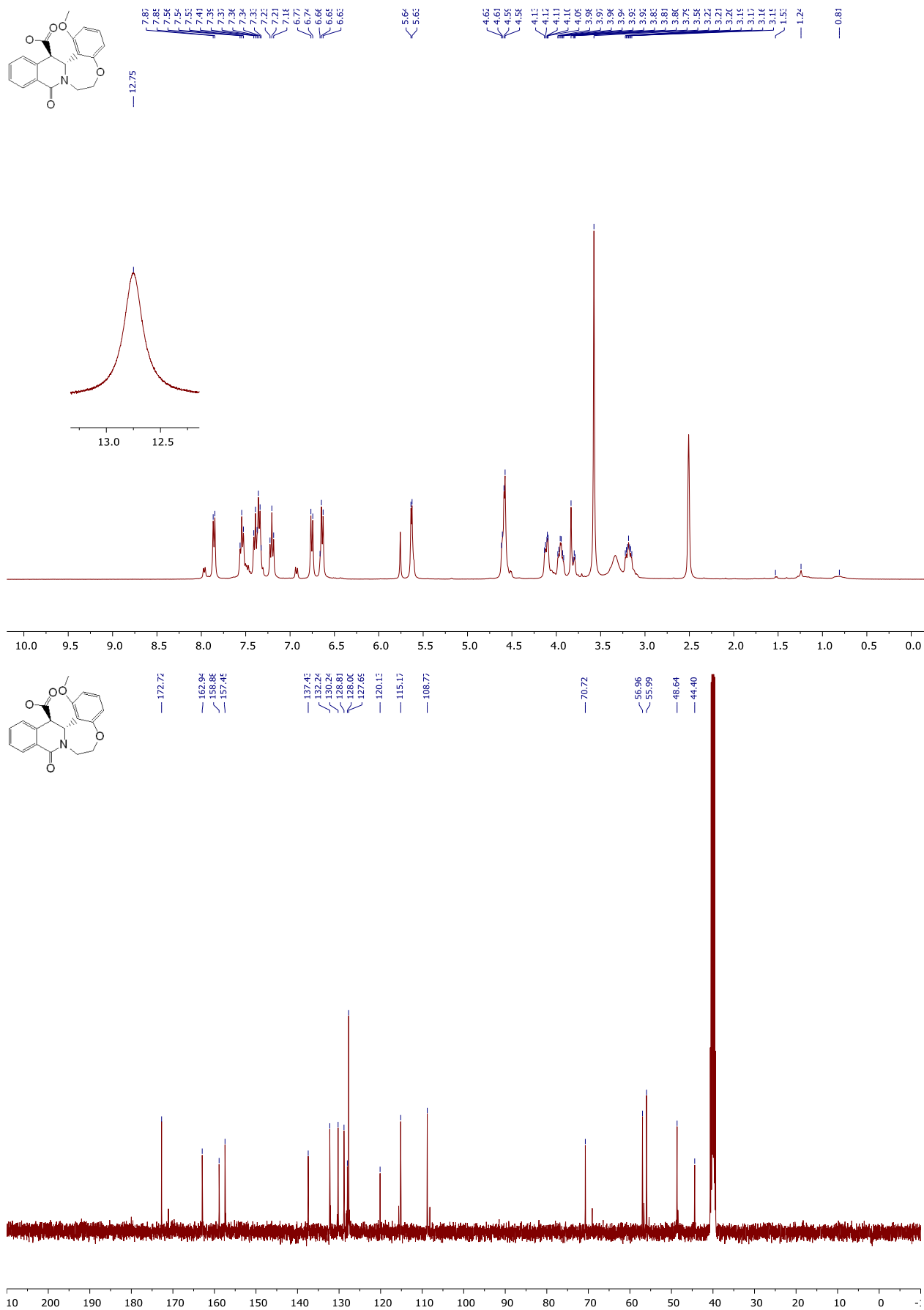
Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **6i**



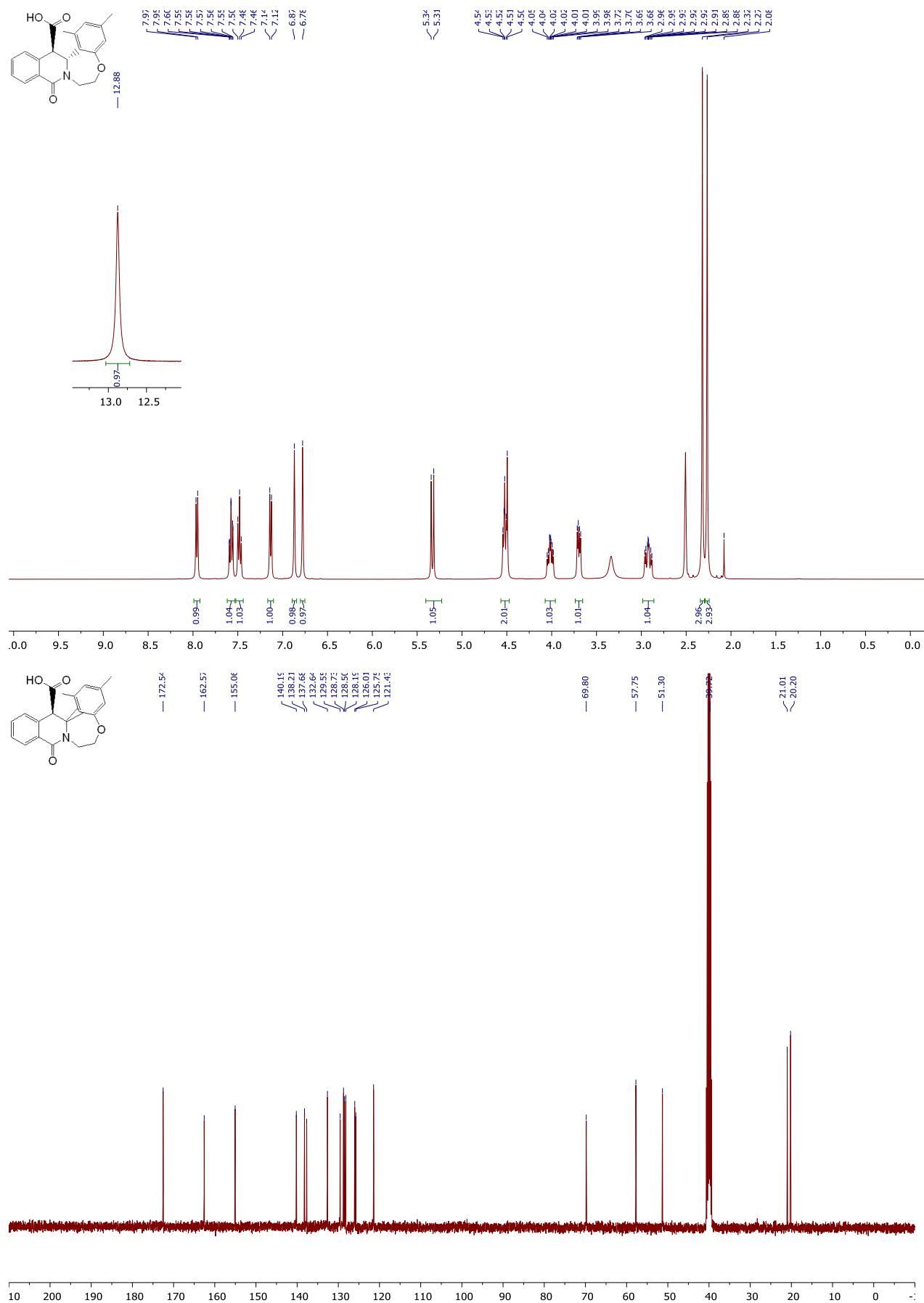
Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **6j**



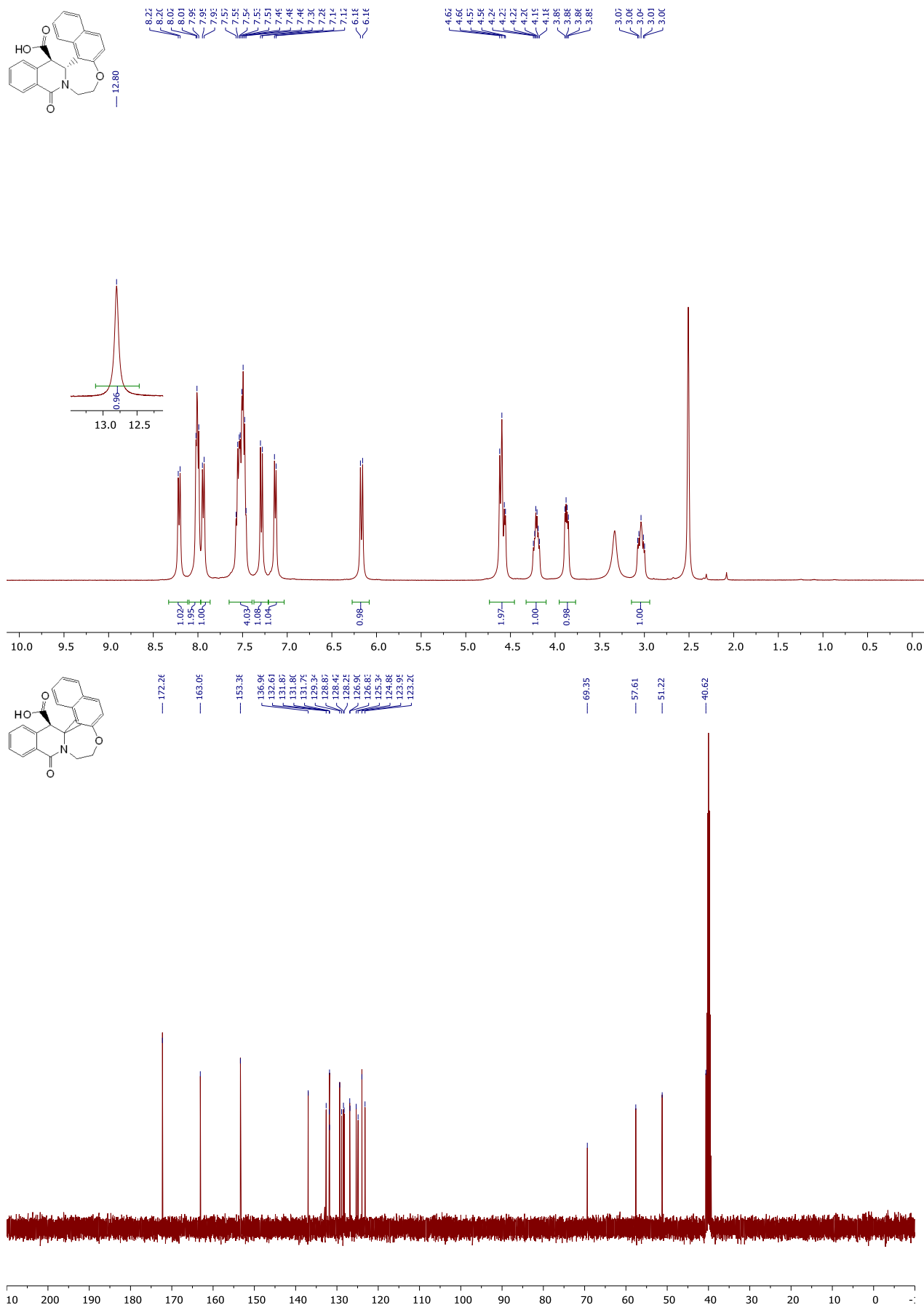
Copies of ^1H 400.13 MHz, $\text{DMSO}-d_6$ and ^{13}C 100.61 MHz, $\text{DMSO}-d_6$ spectra of **6k**



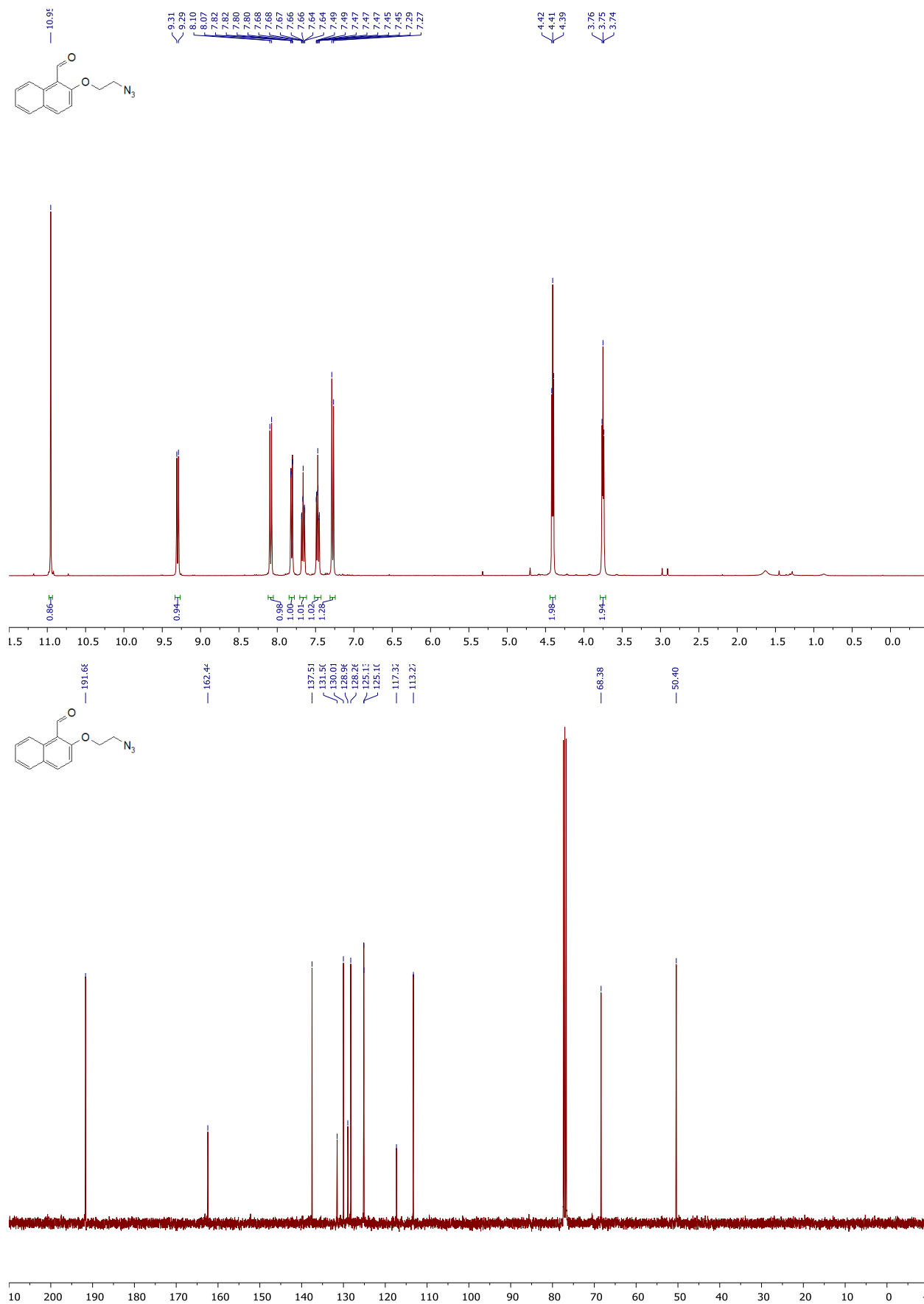
Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **6l**



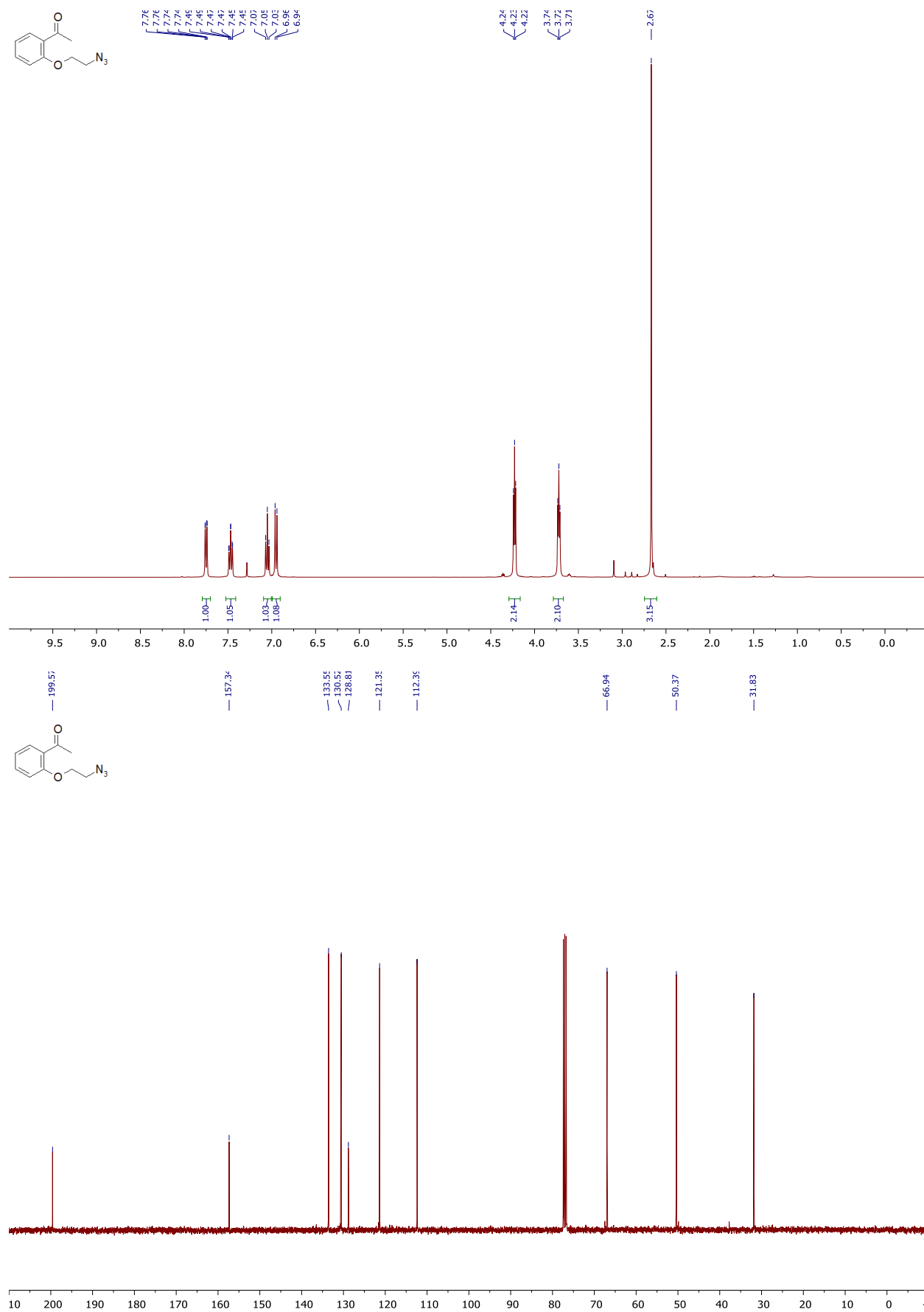
Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **6m**



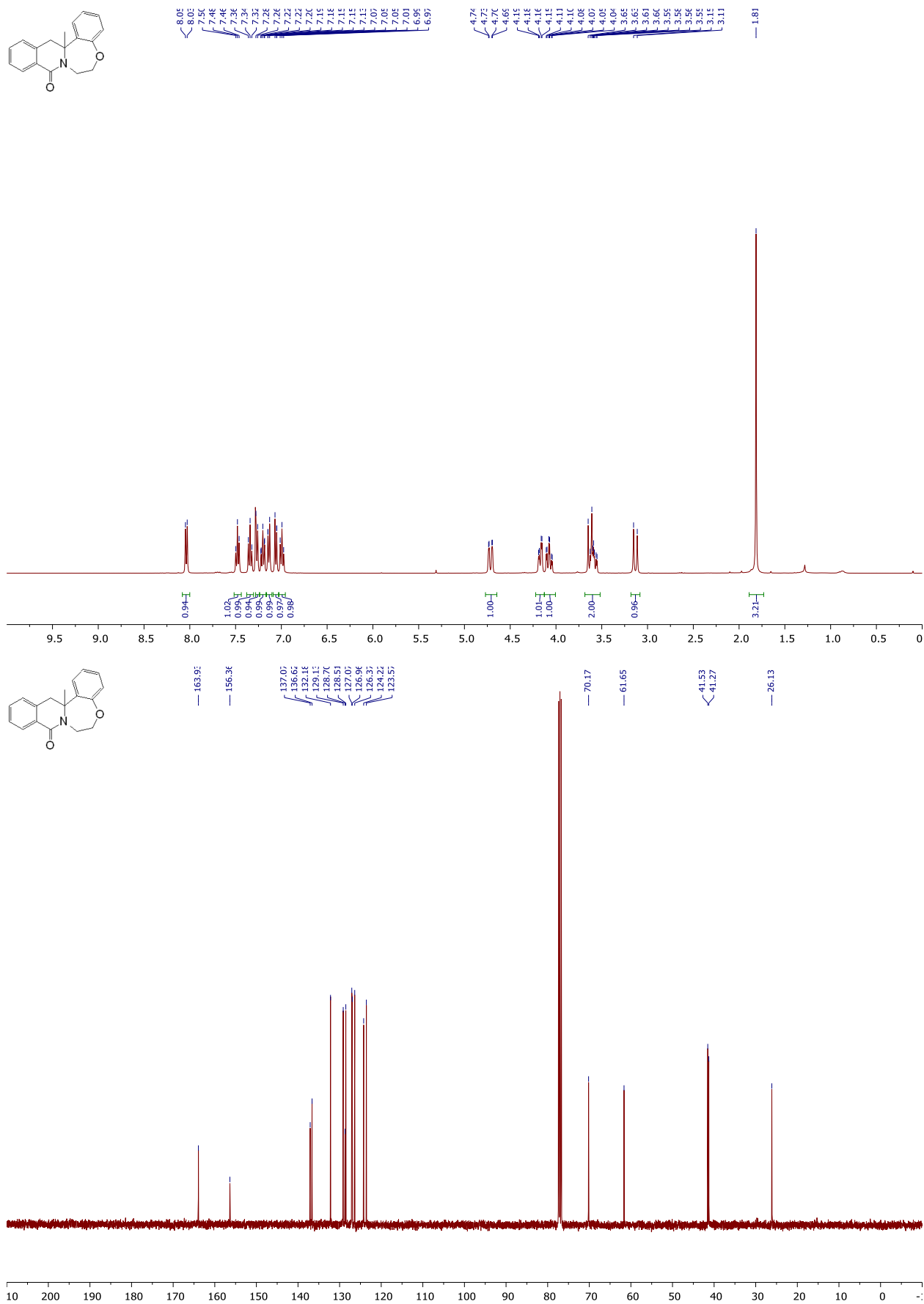
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **7**



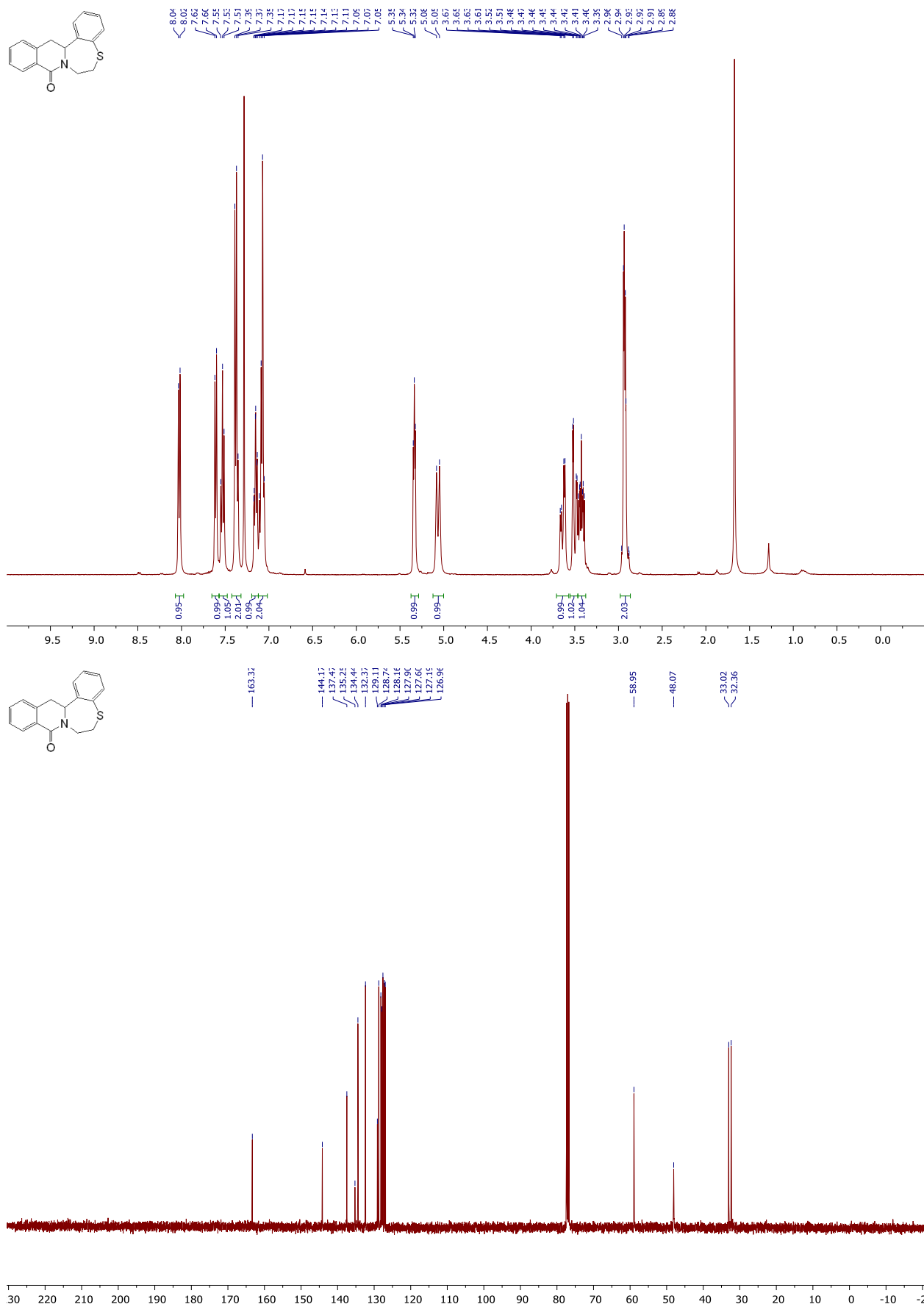
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **8**



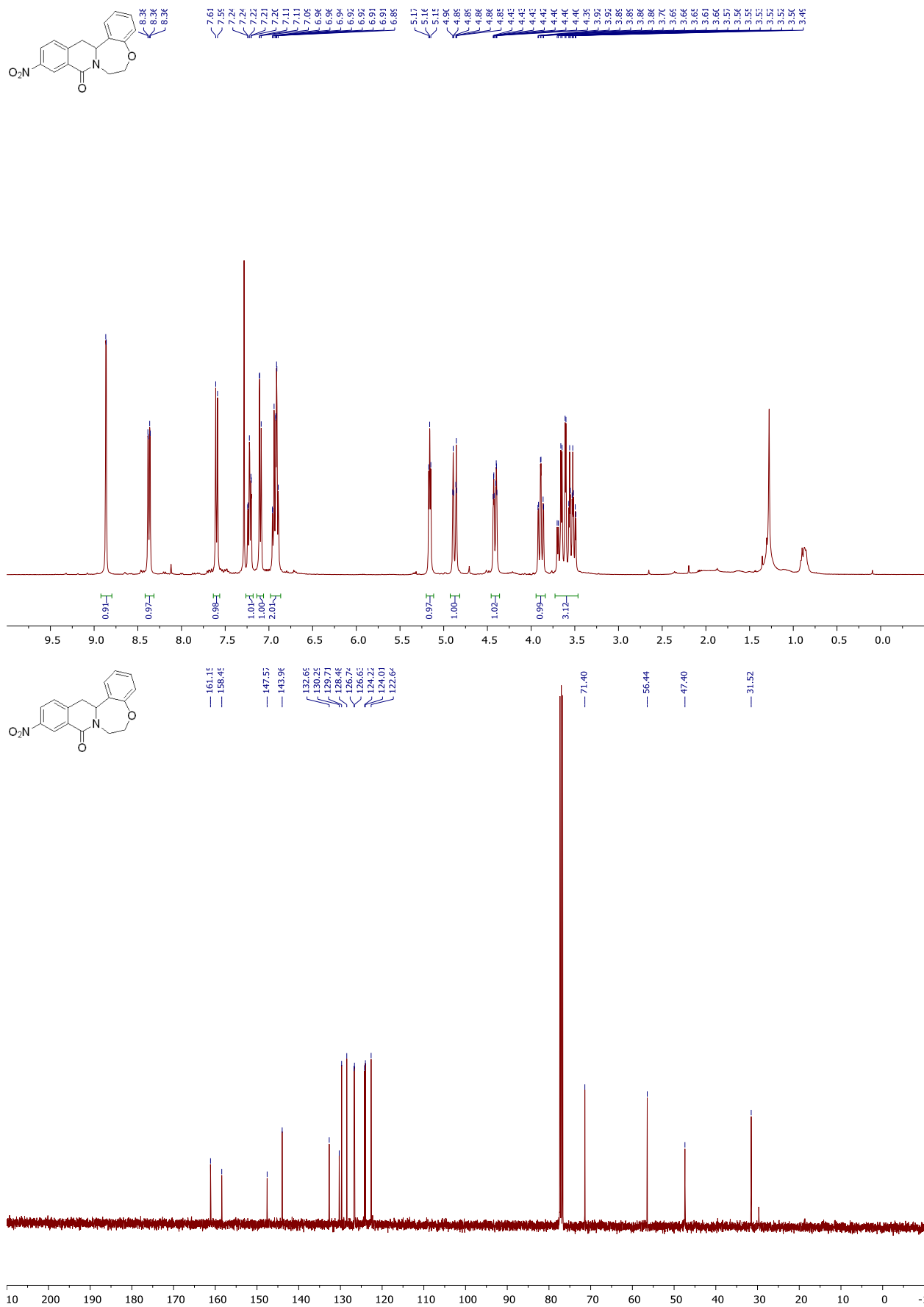
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **10a**



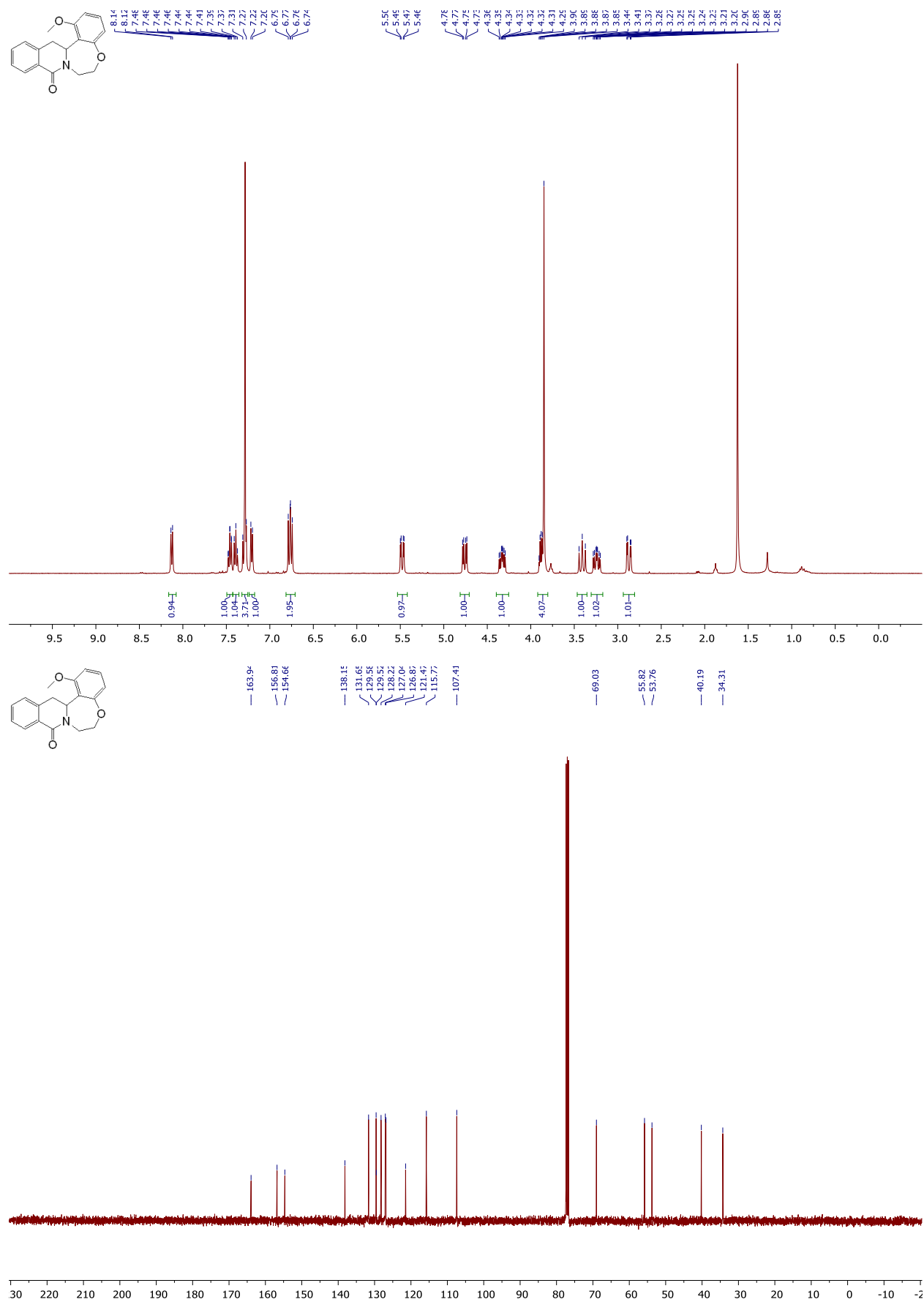
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **10b**



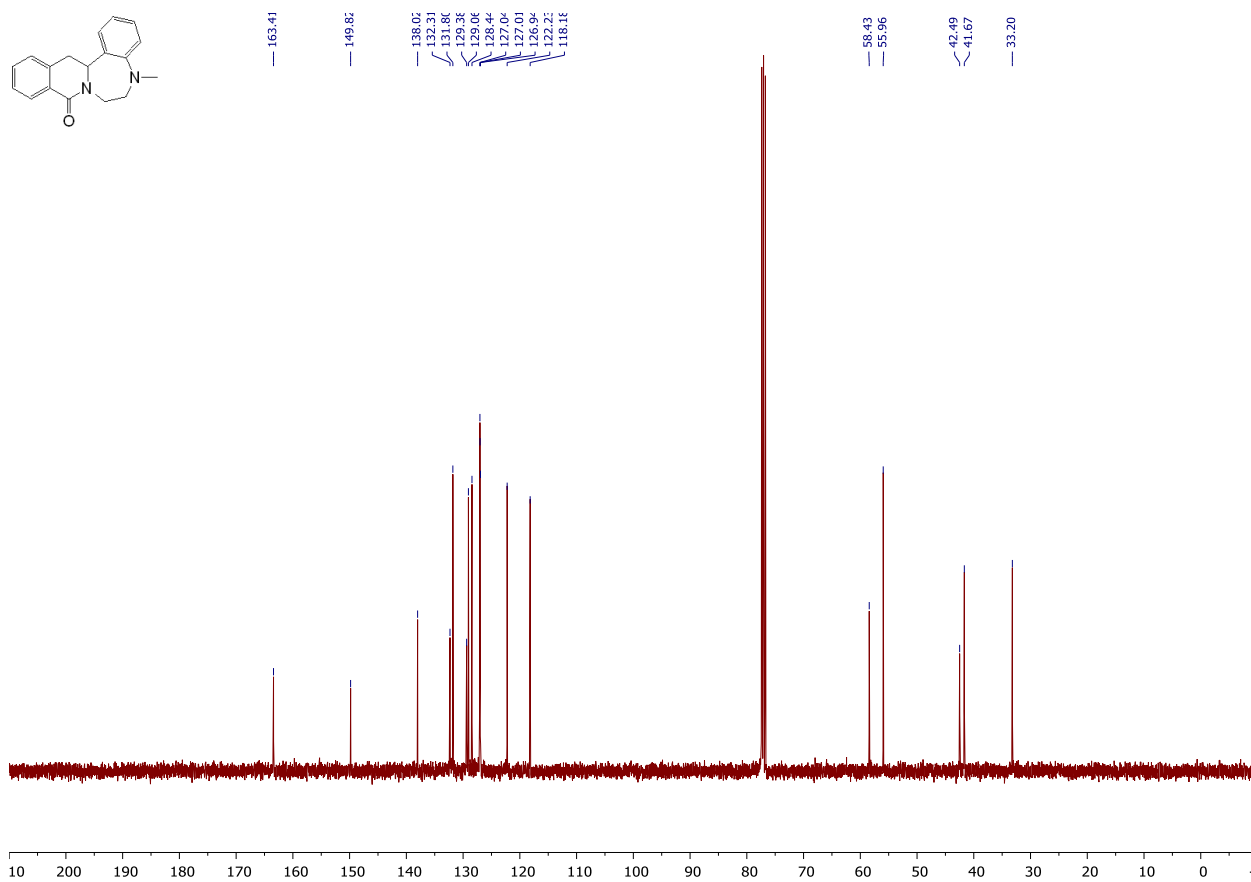
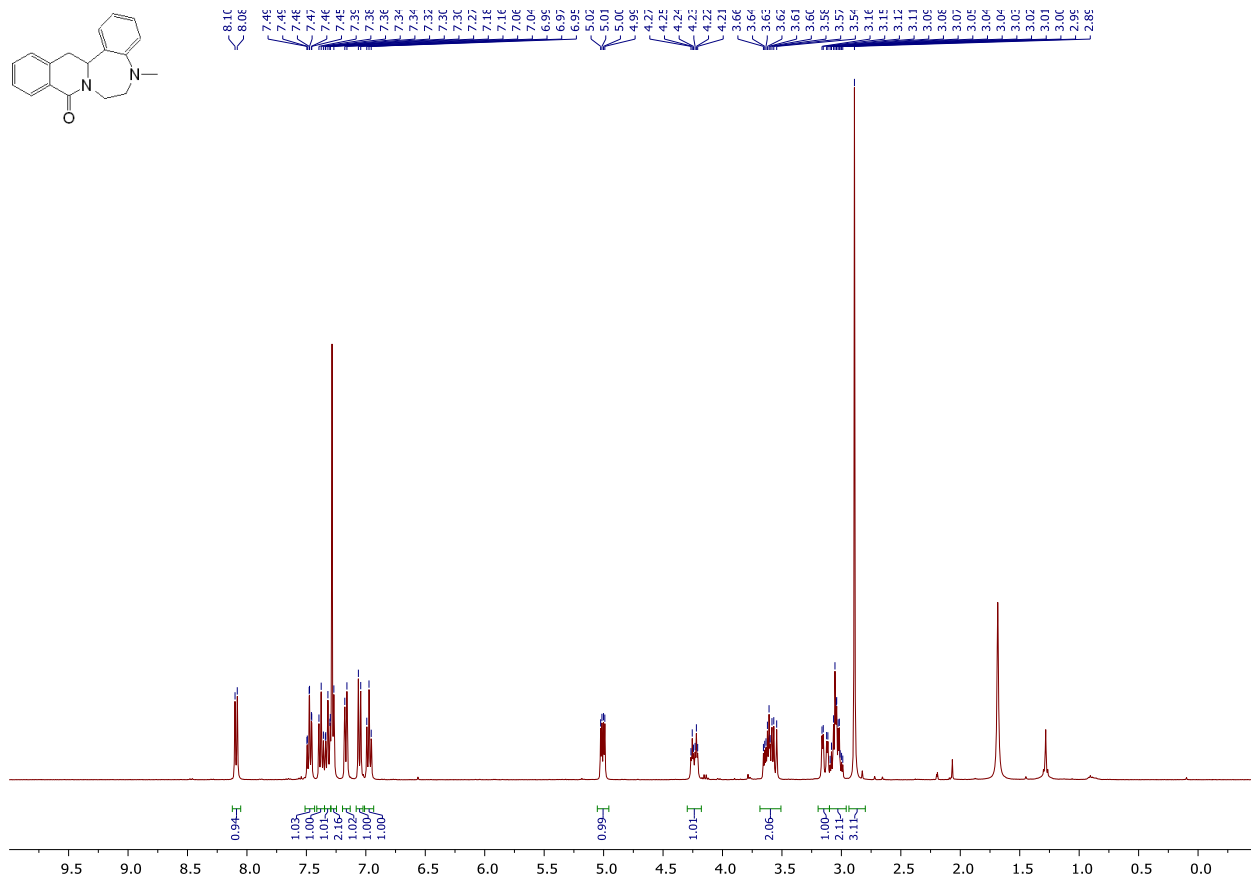
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **10c**



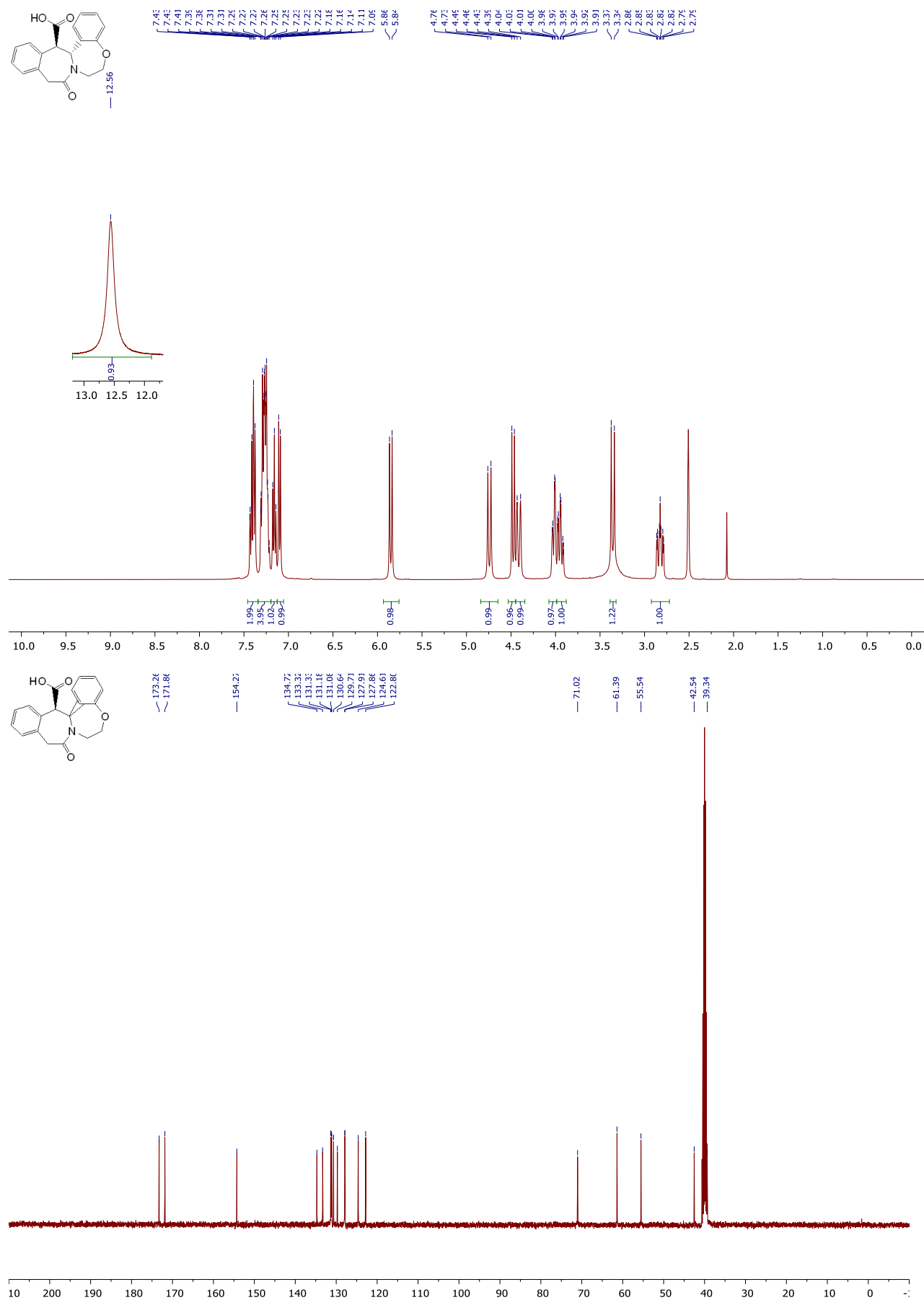
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **10d**



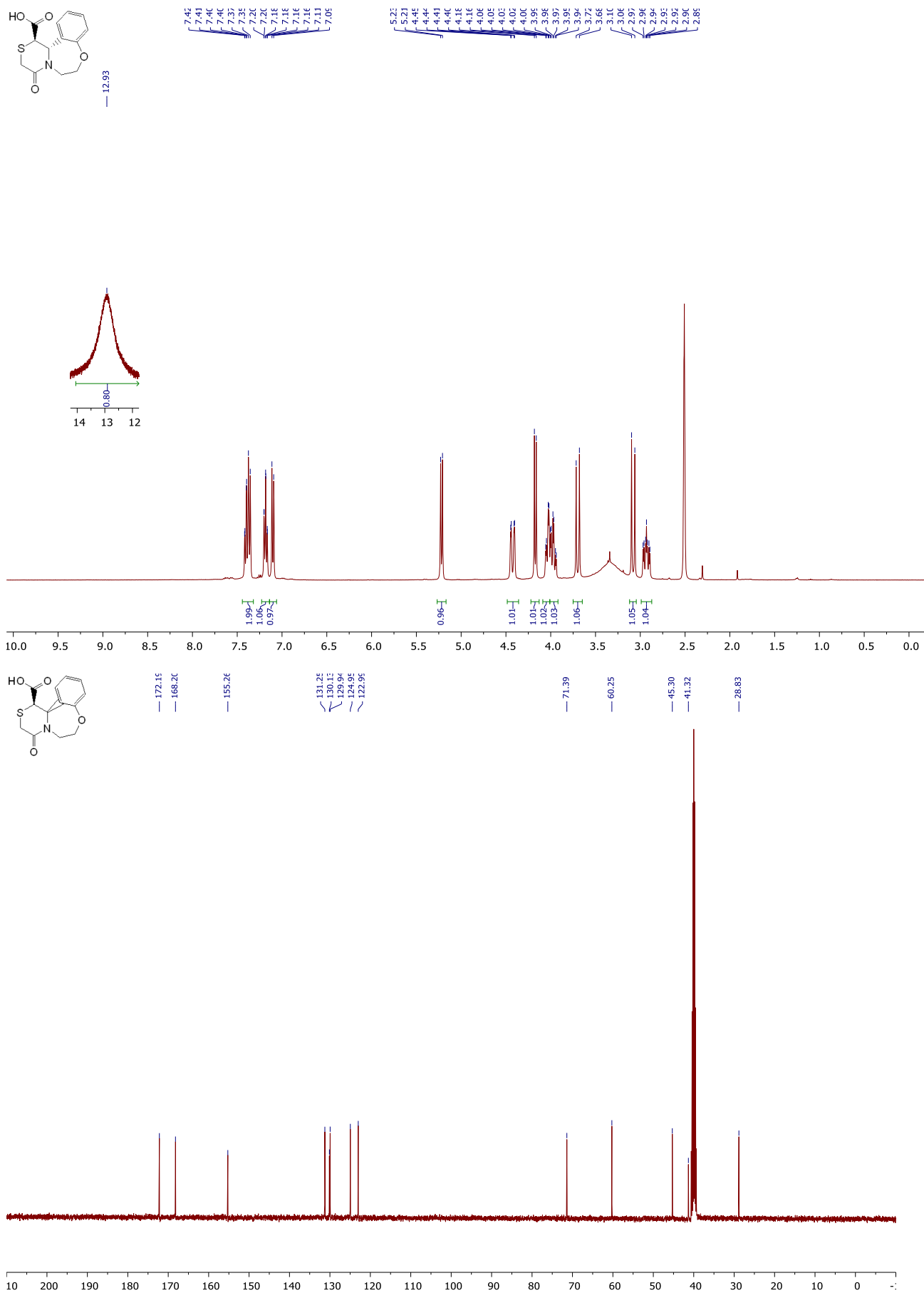
Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **10e**



Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **13**



Copies of ^1H 400.13 MHz, DMSO- d_6 and ^{13}C 100.61 MHz, DMSO- d_6 spectra of **16**



Copies of ^1H 400.13 MHz, CDCl_3 and ^{13}C 100.61 MHz, CDCl_3 spectra of **17**

