Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Highly Diastereoselective C→N Acyl Rearrangement in Polysubstituted Pyrrolidine 2,2-dicarboxylates. Stereocontrolled Synthesis of Densely Functionalized Prolines

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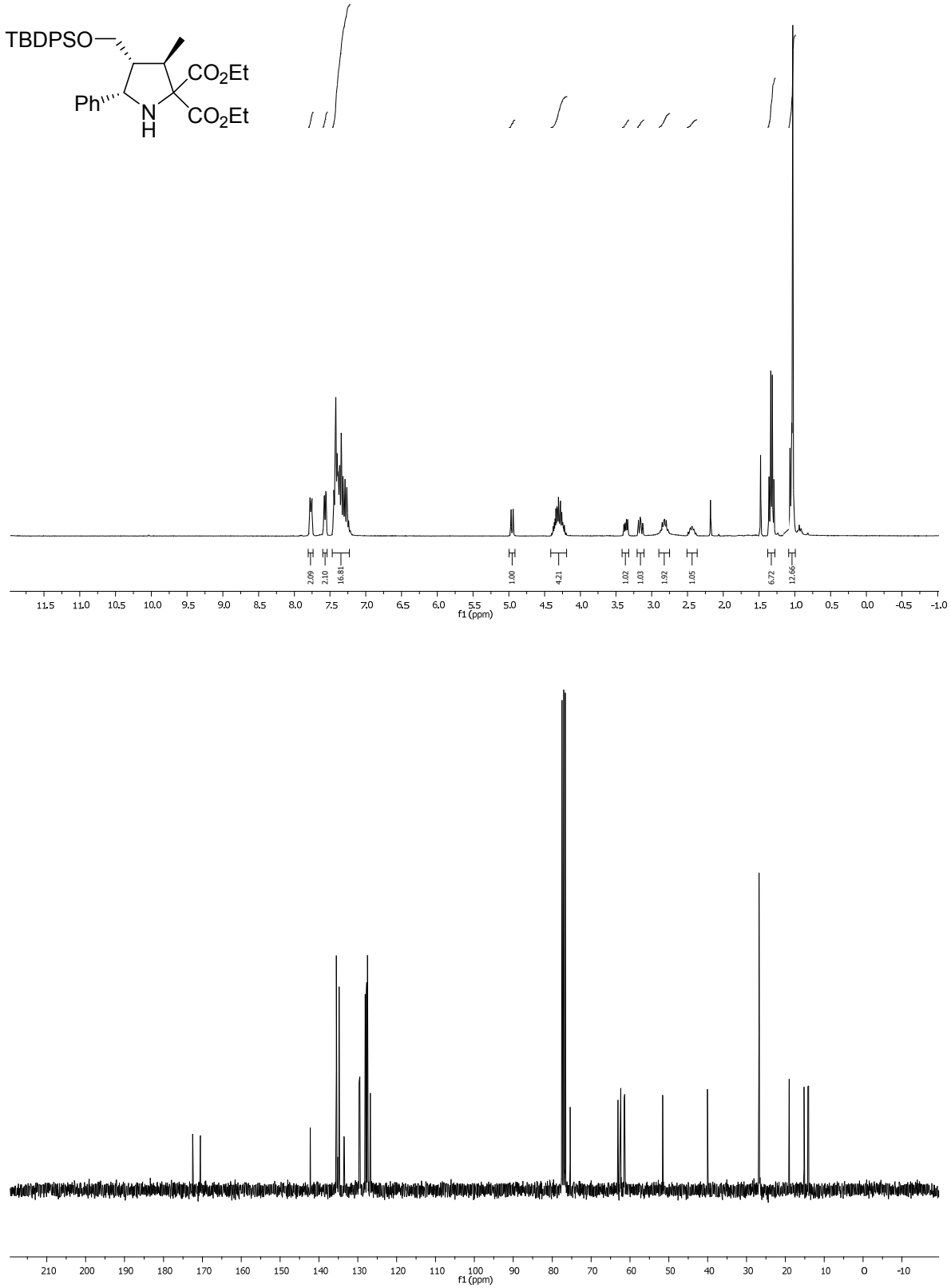

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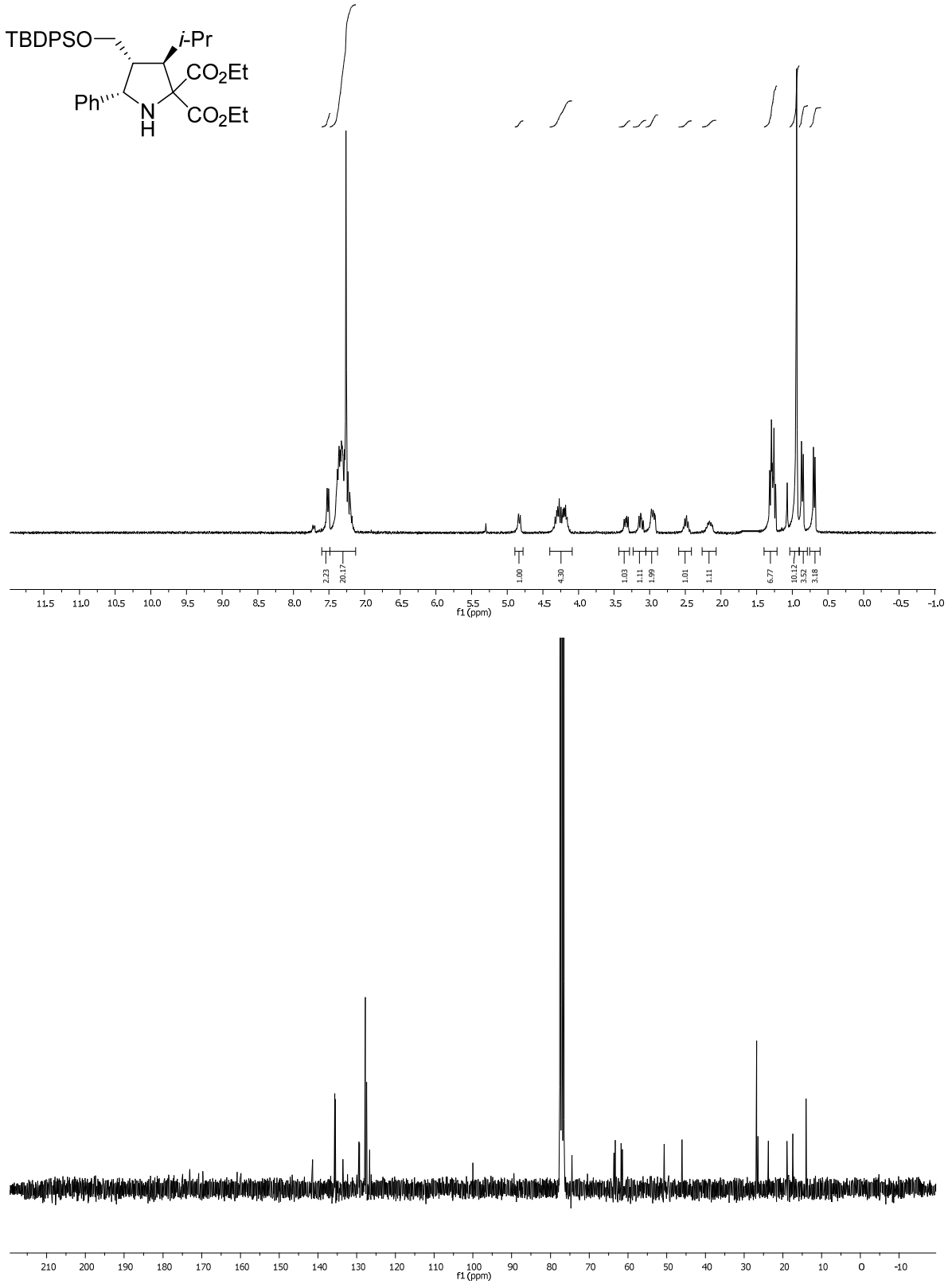

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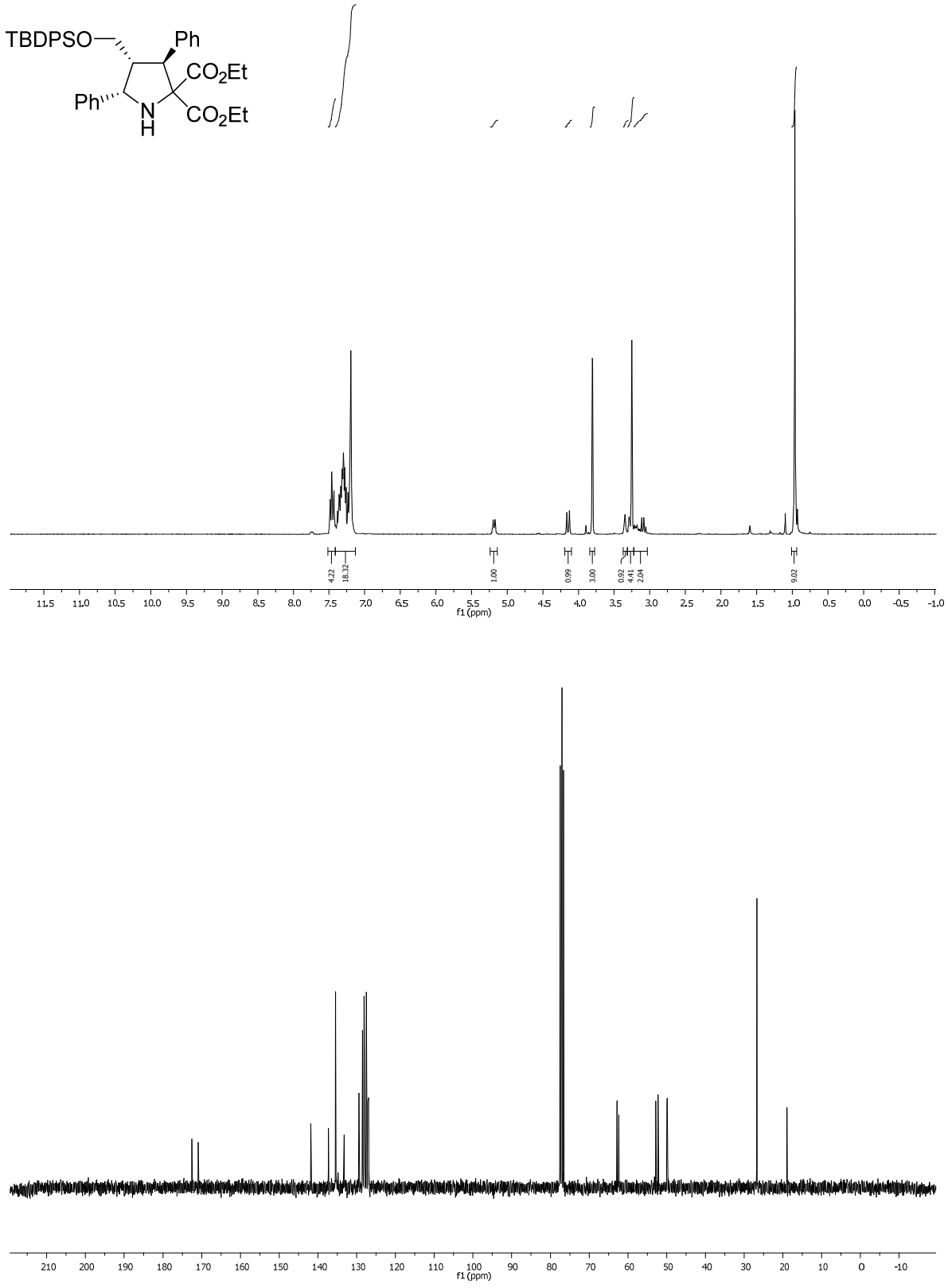

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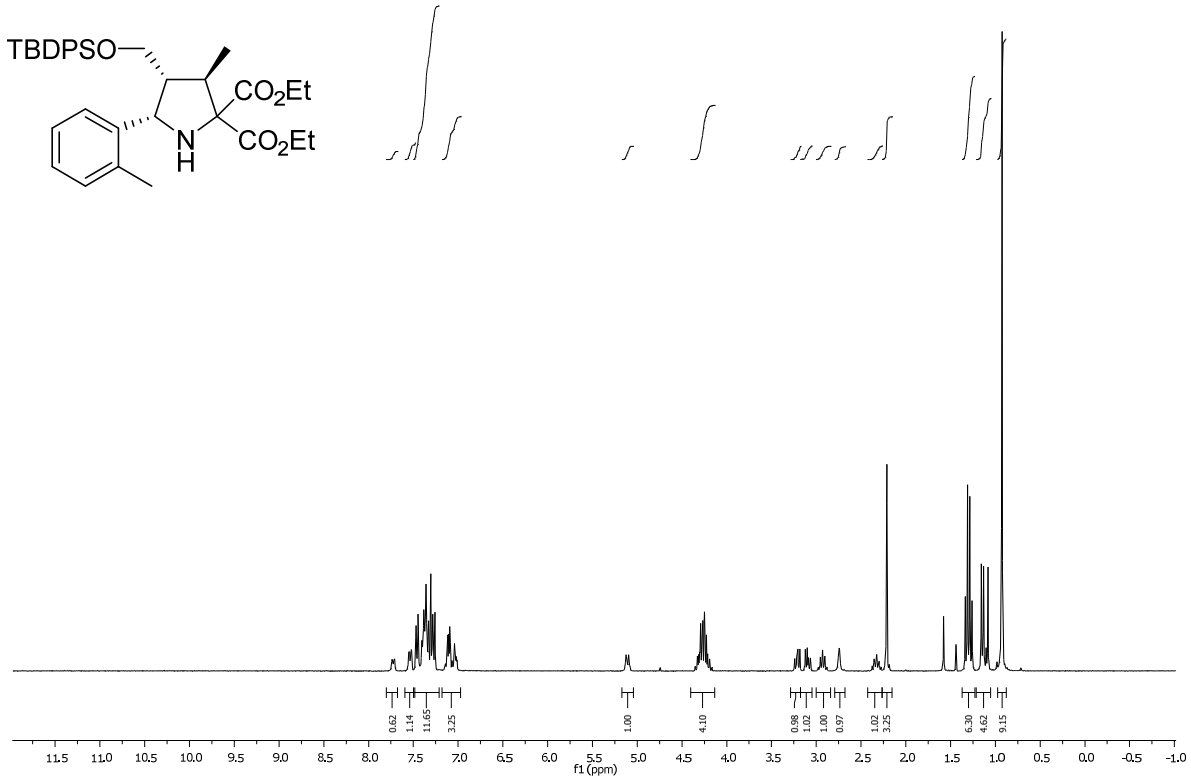

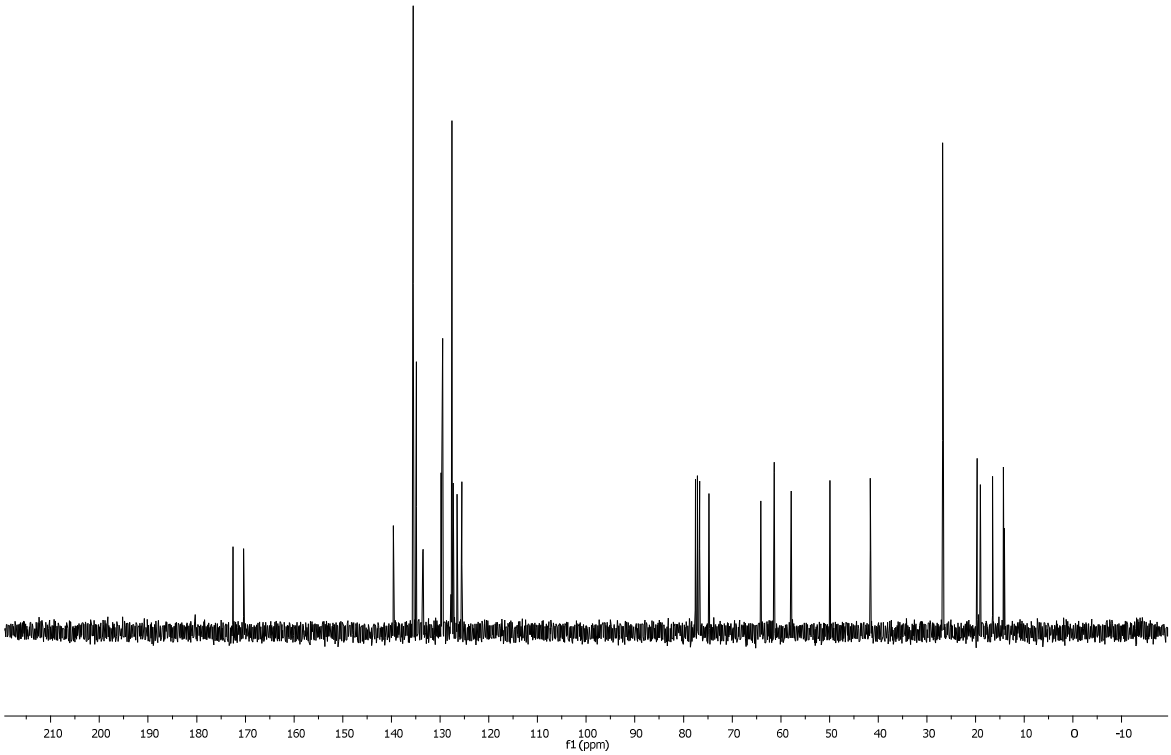

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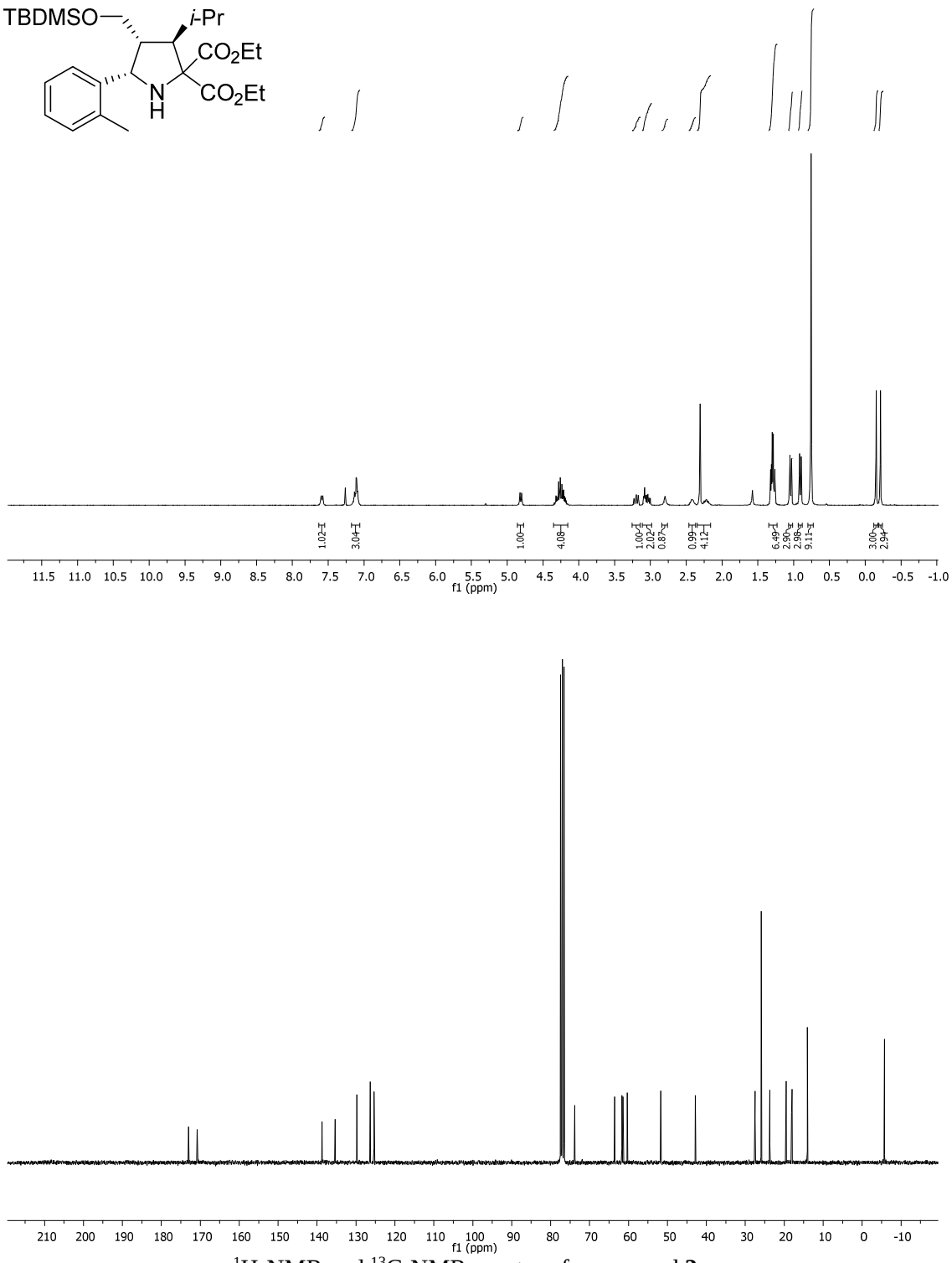

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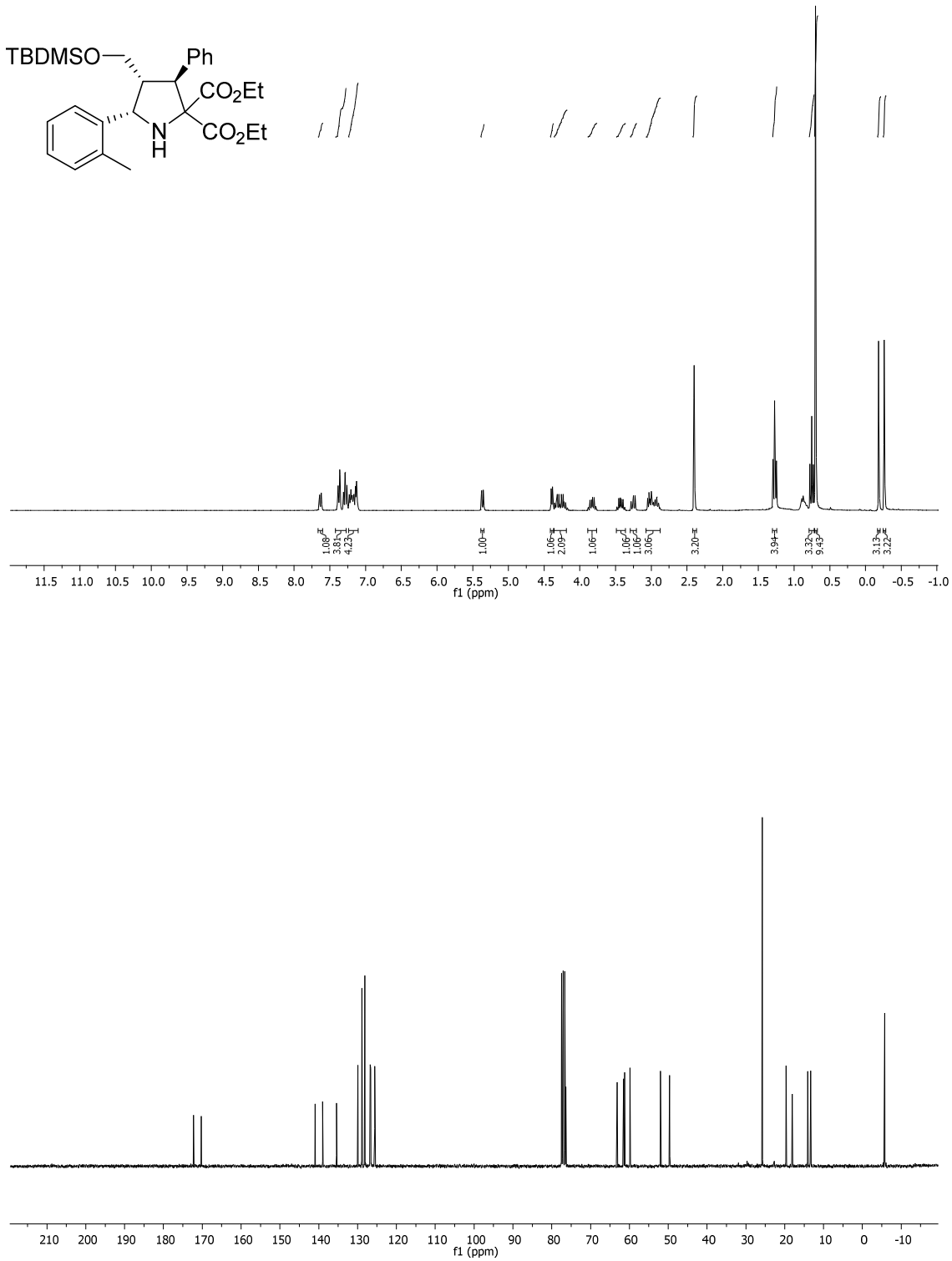

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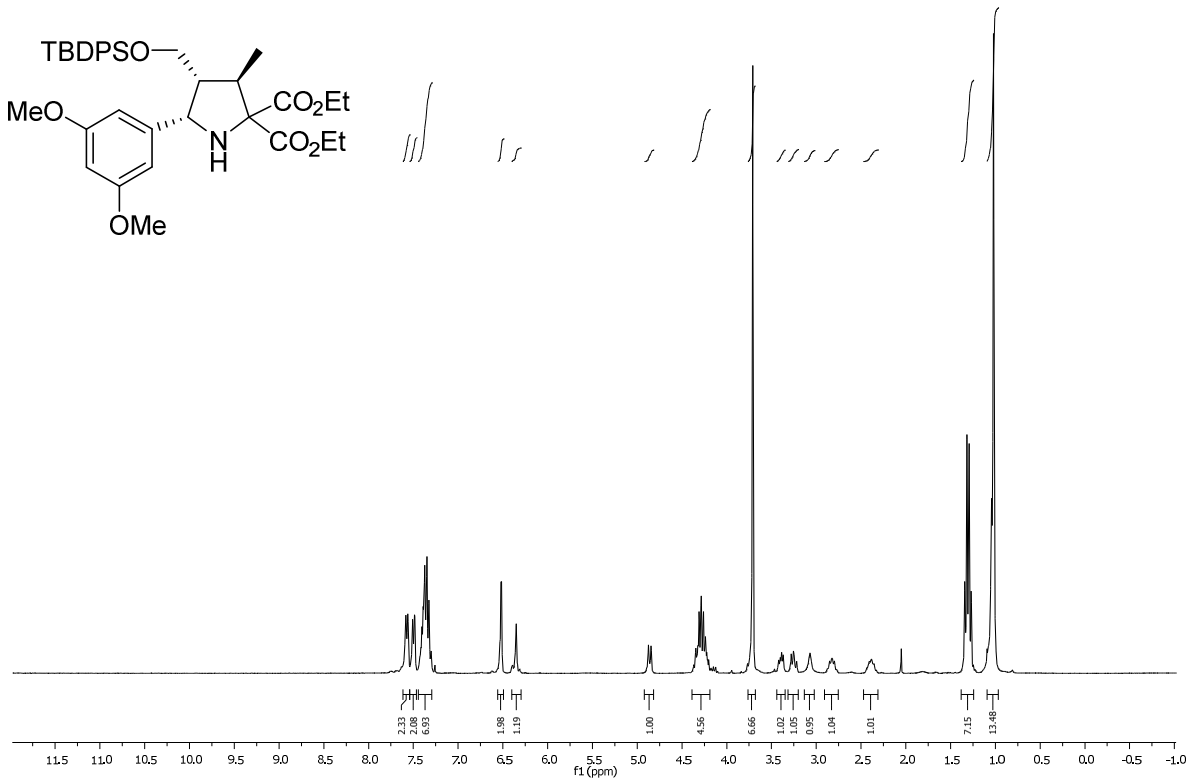

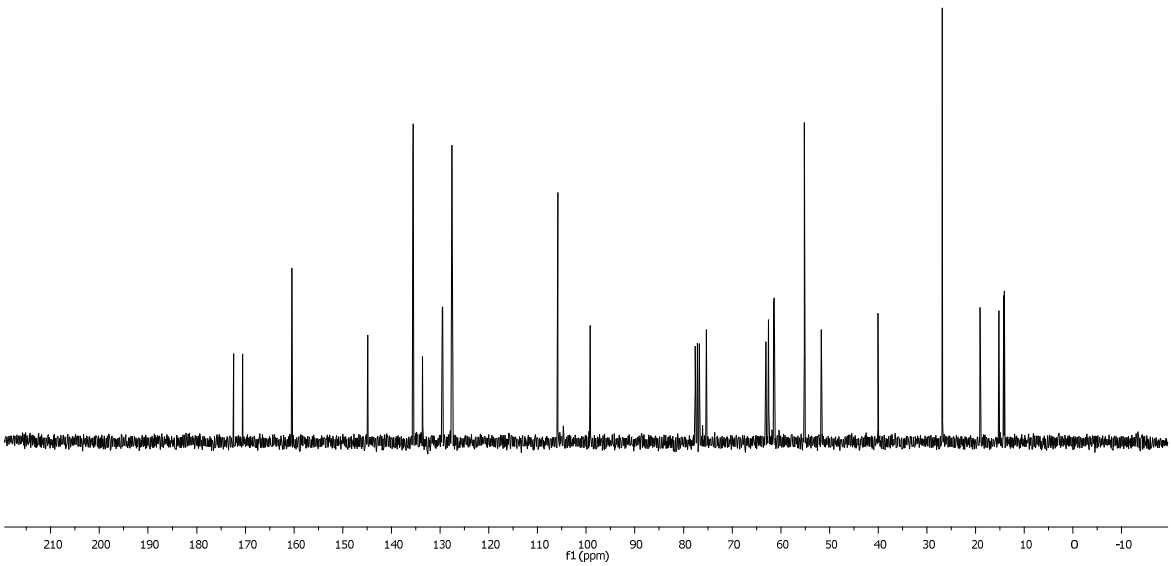

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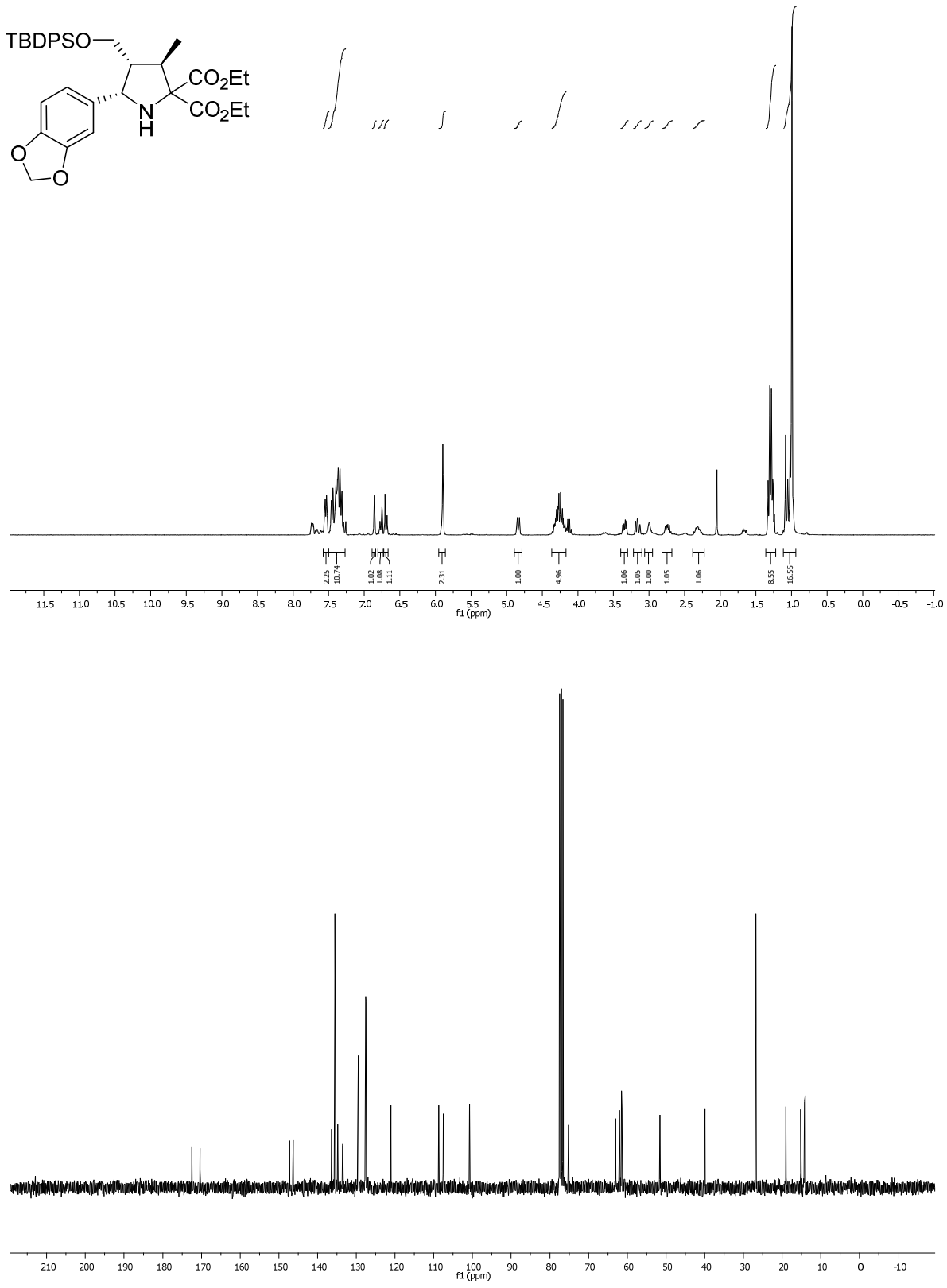

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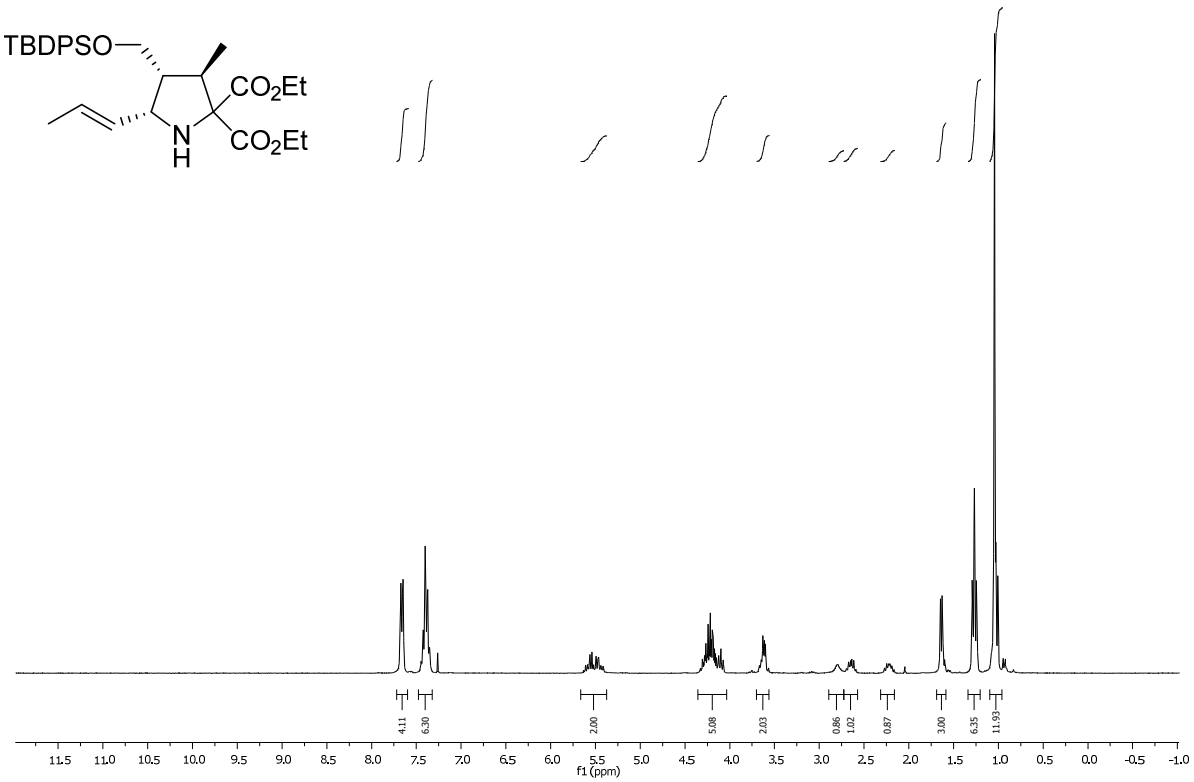

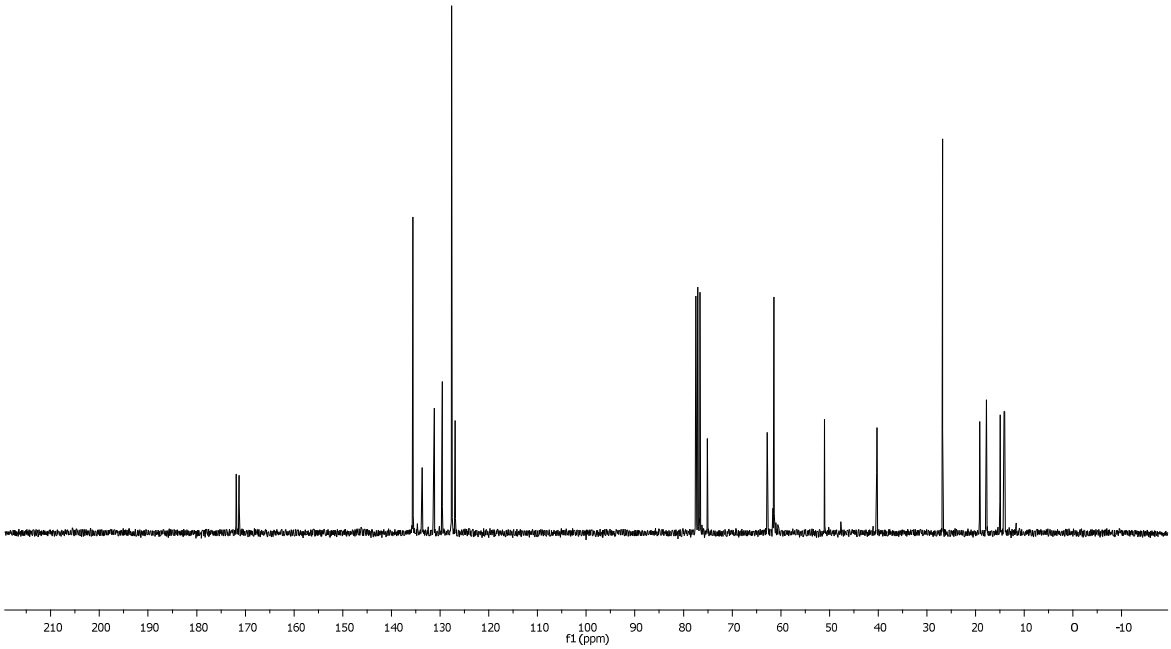

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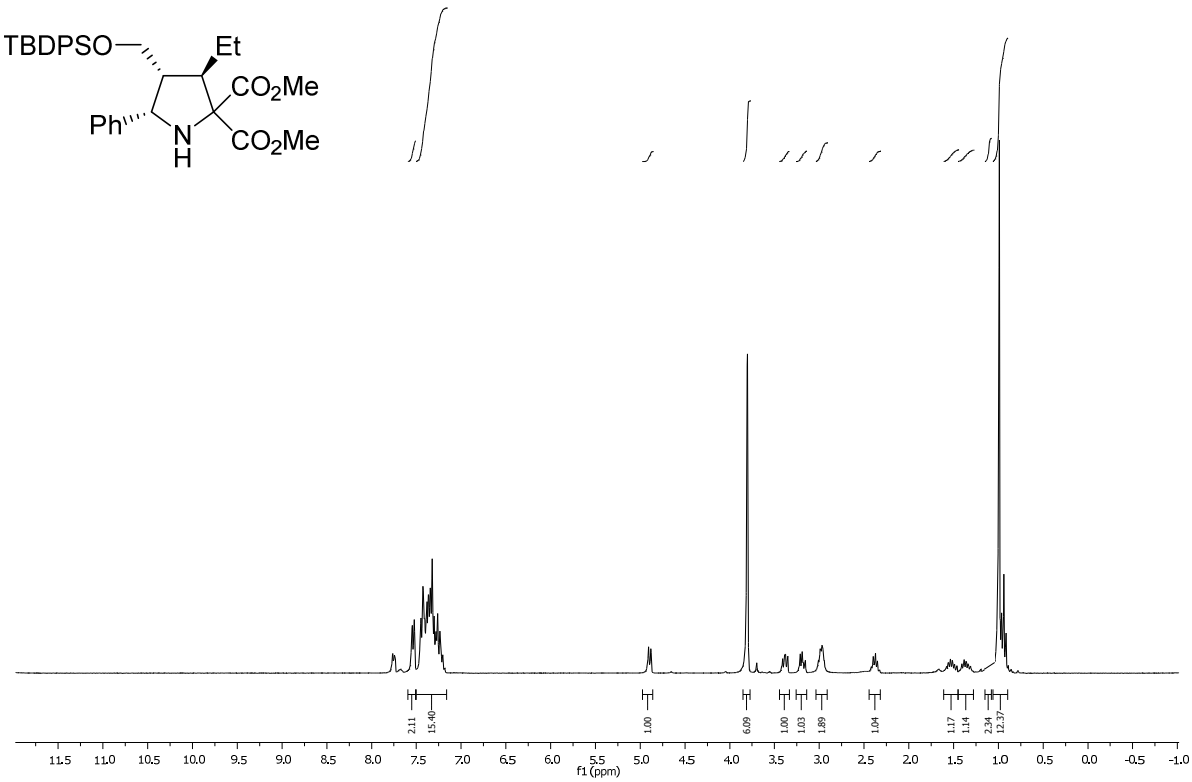

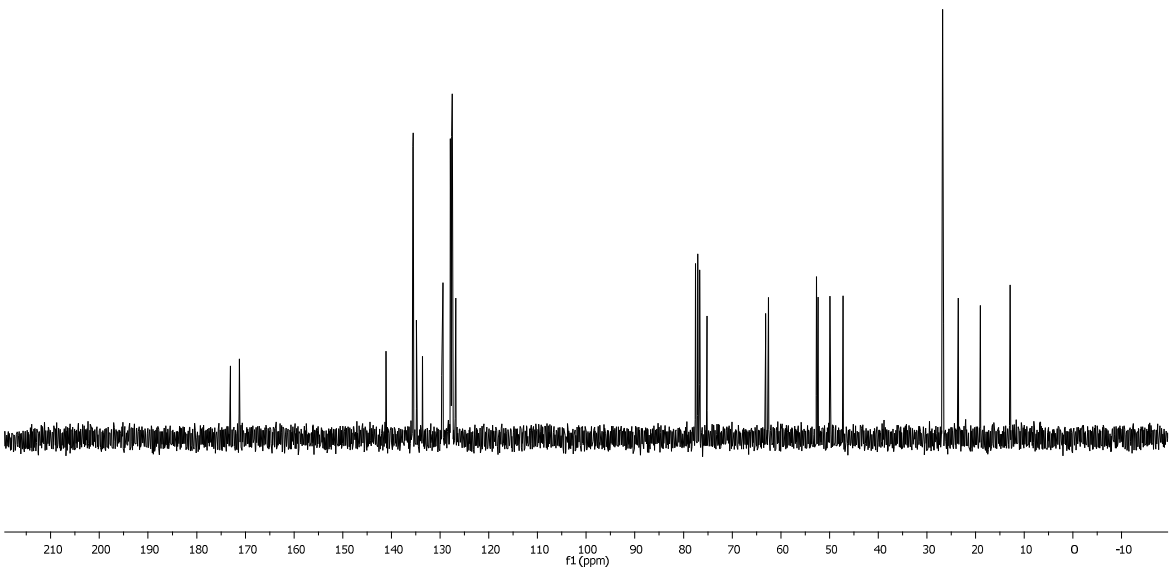

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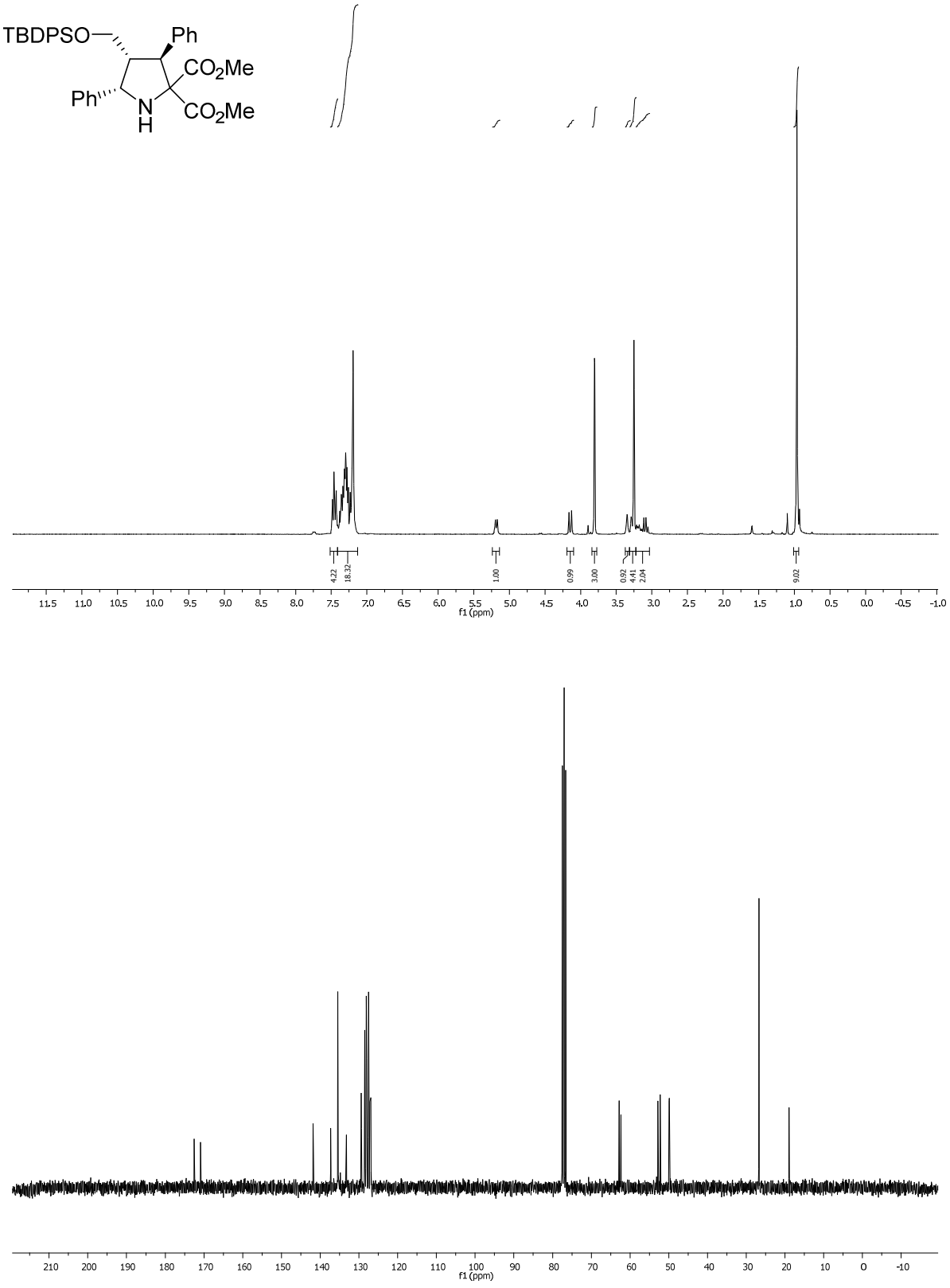

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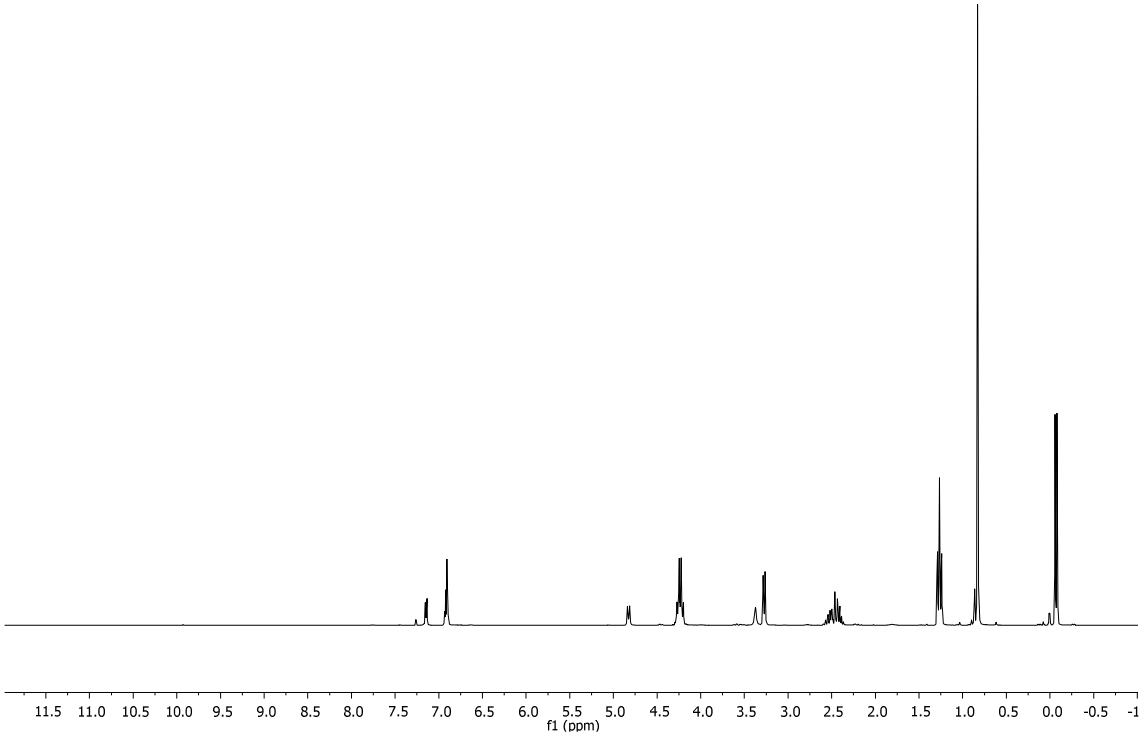

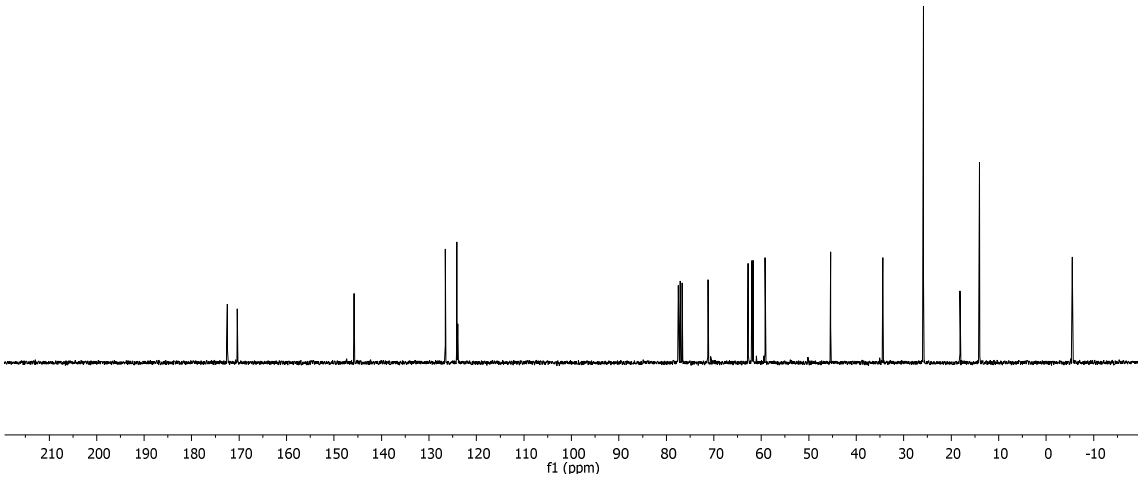

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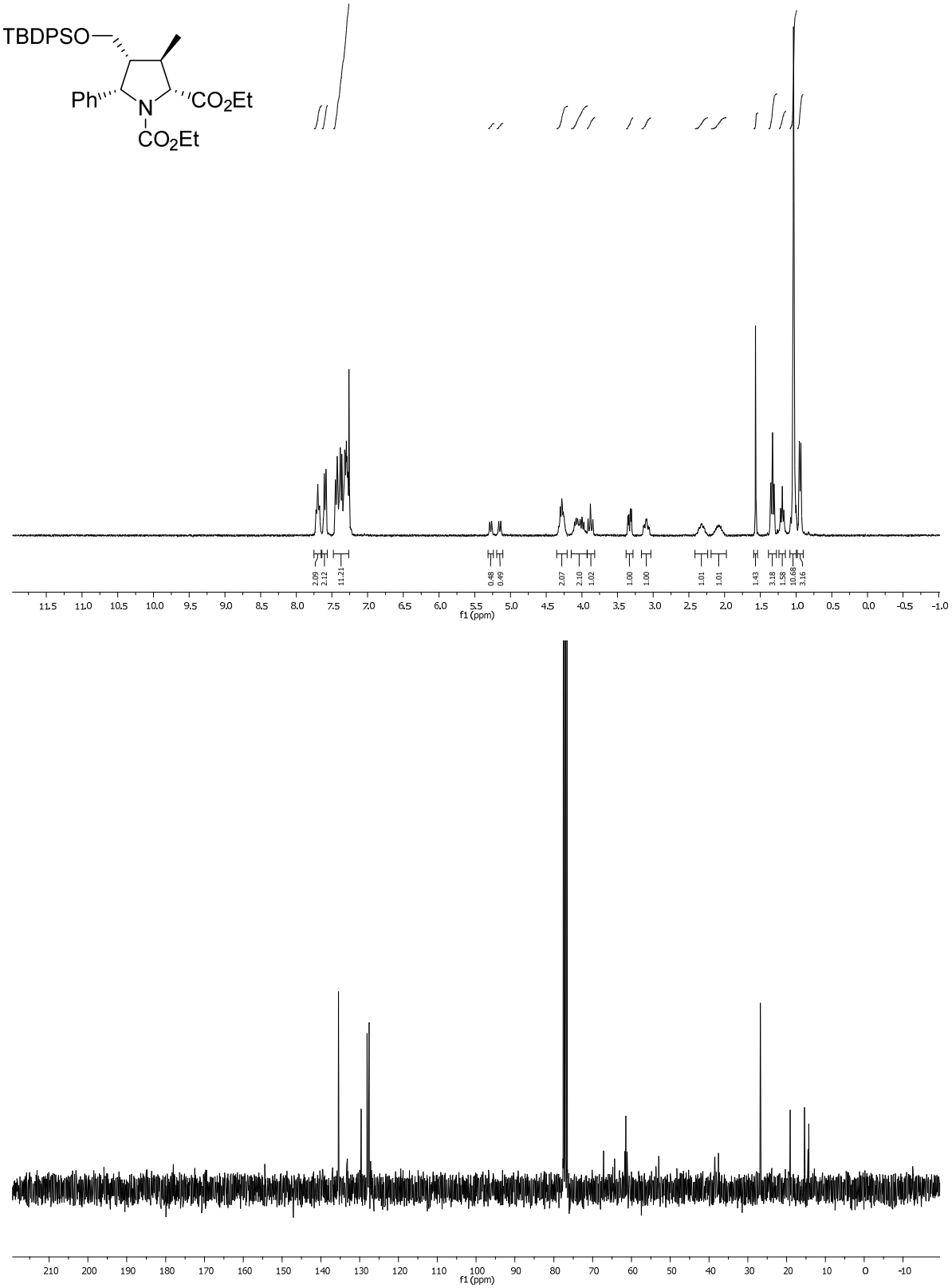

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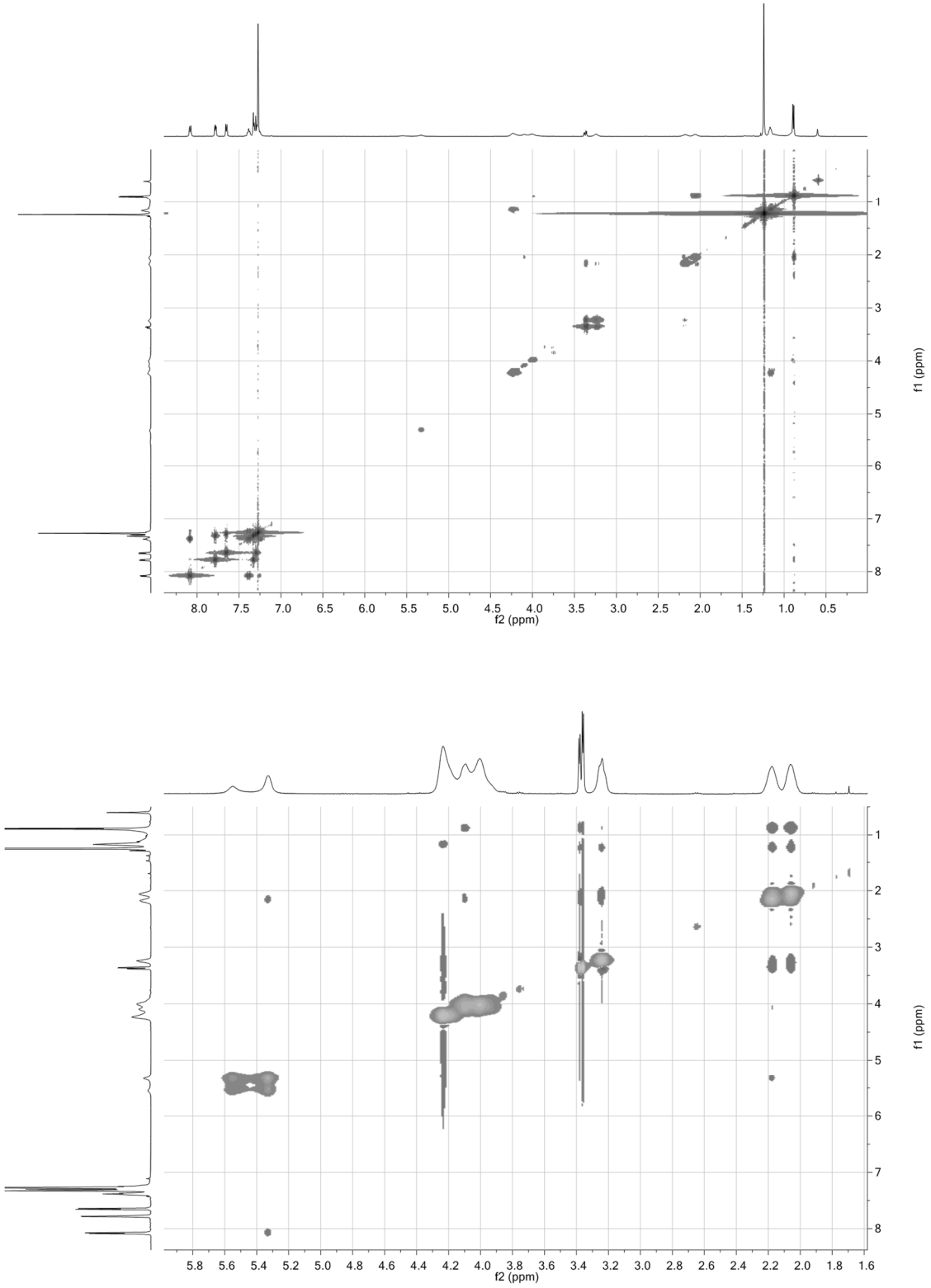

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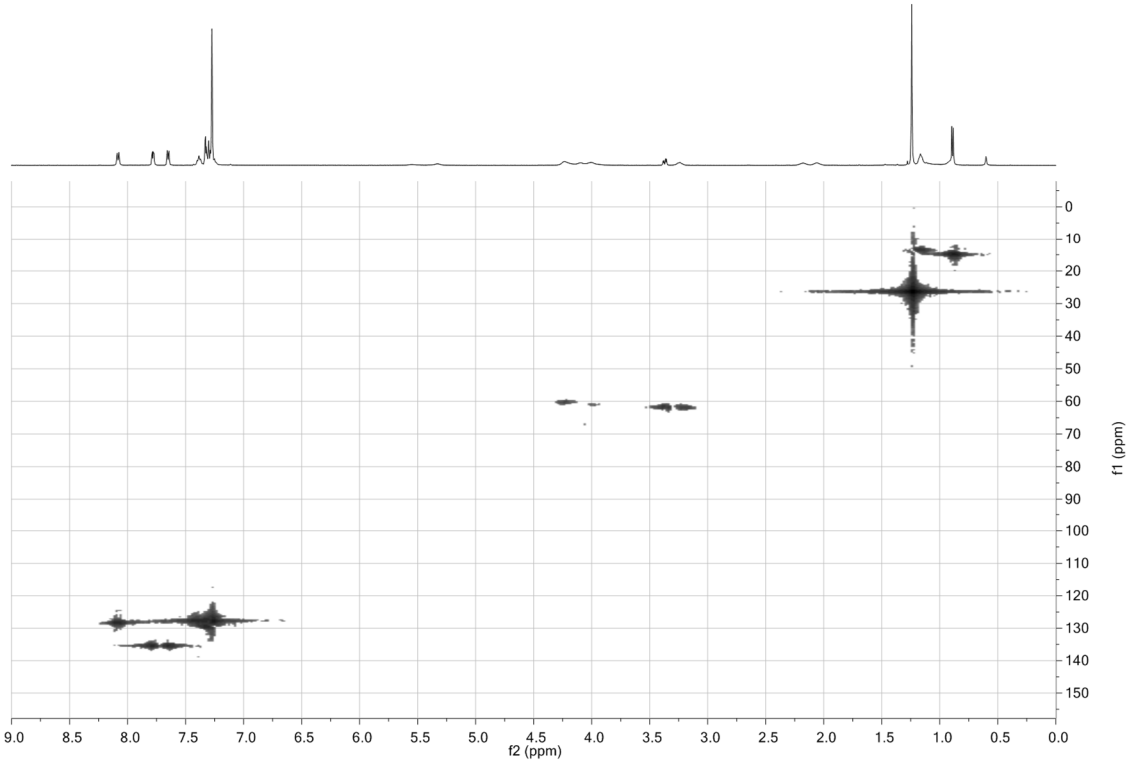

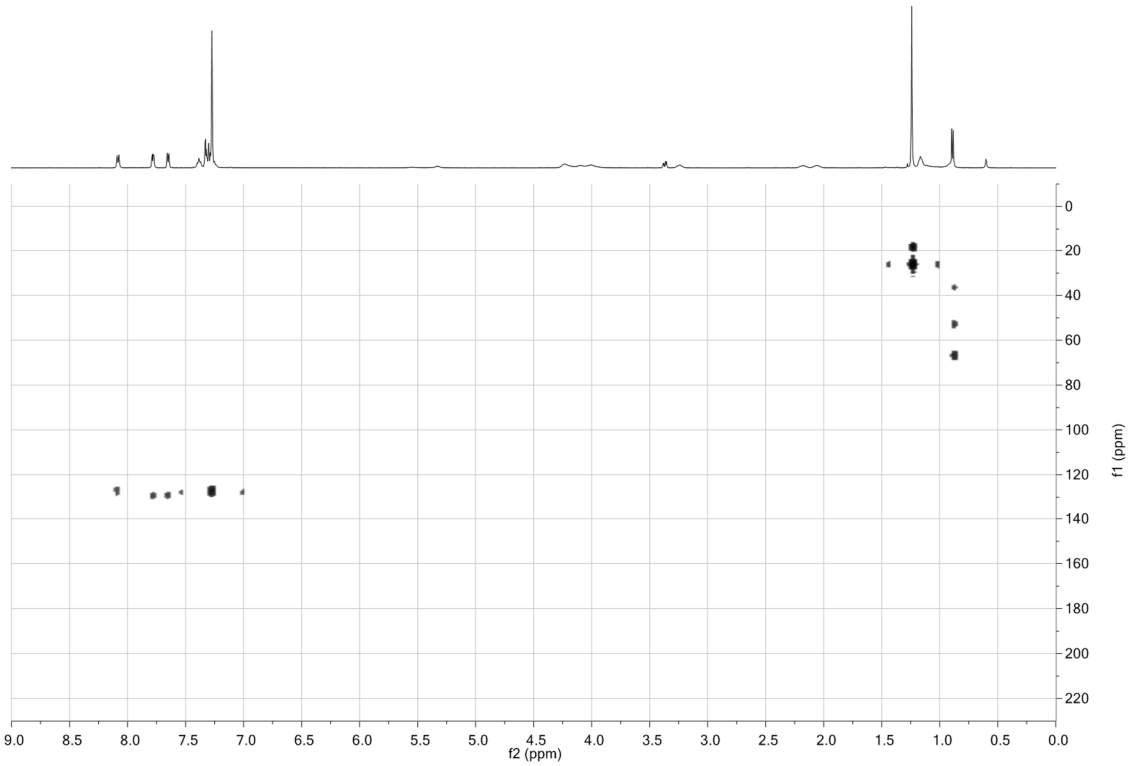

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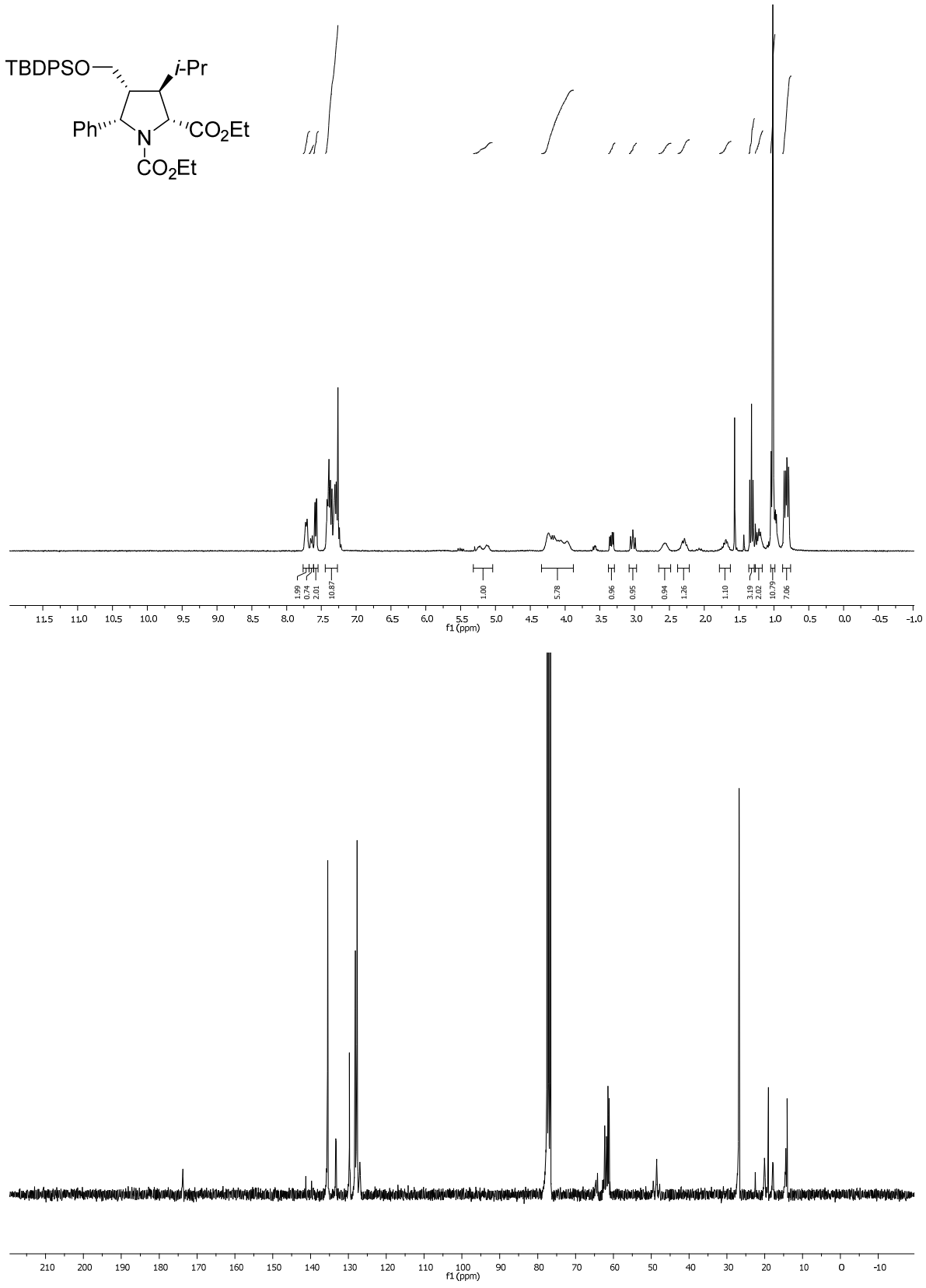

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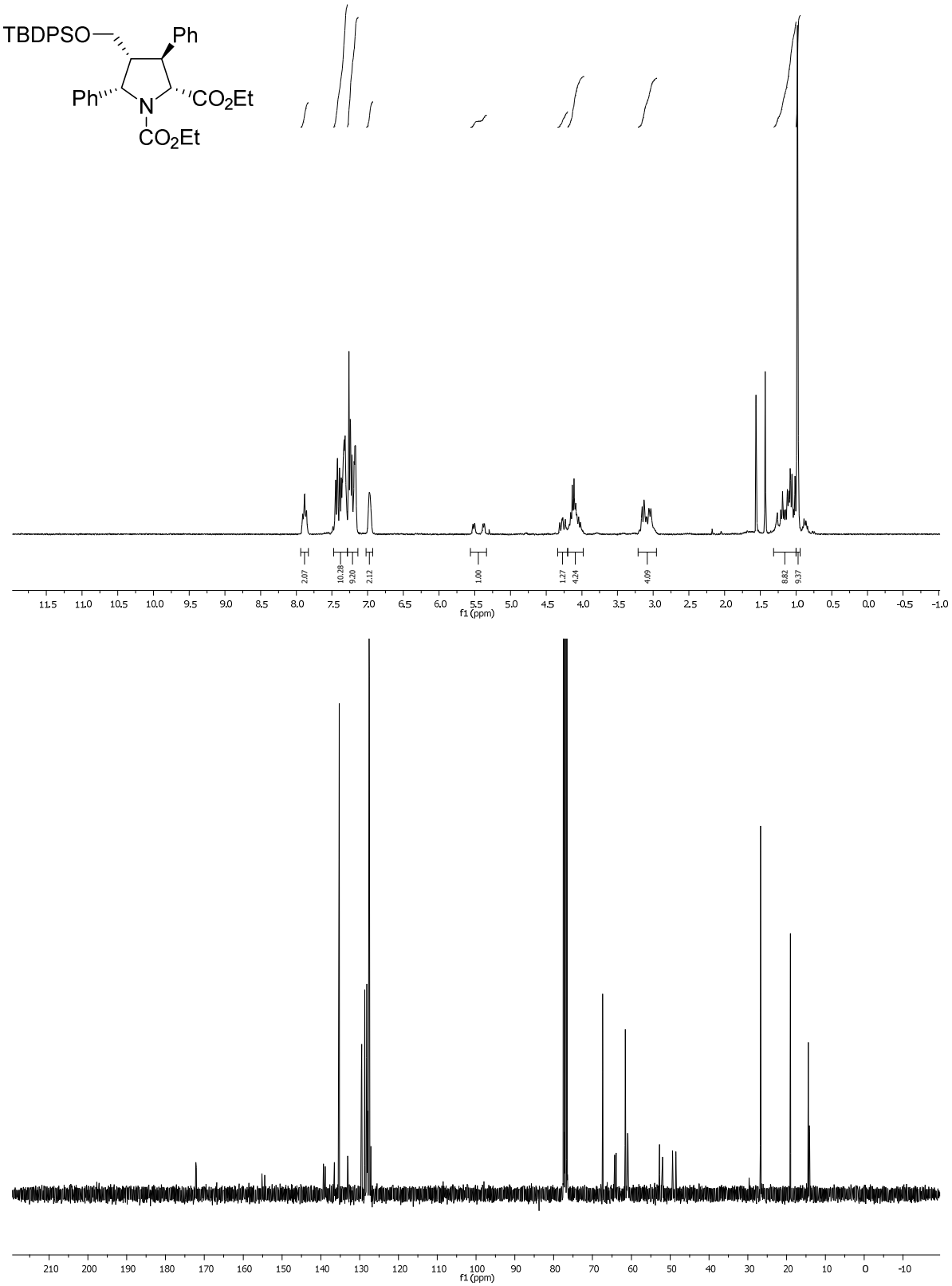
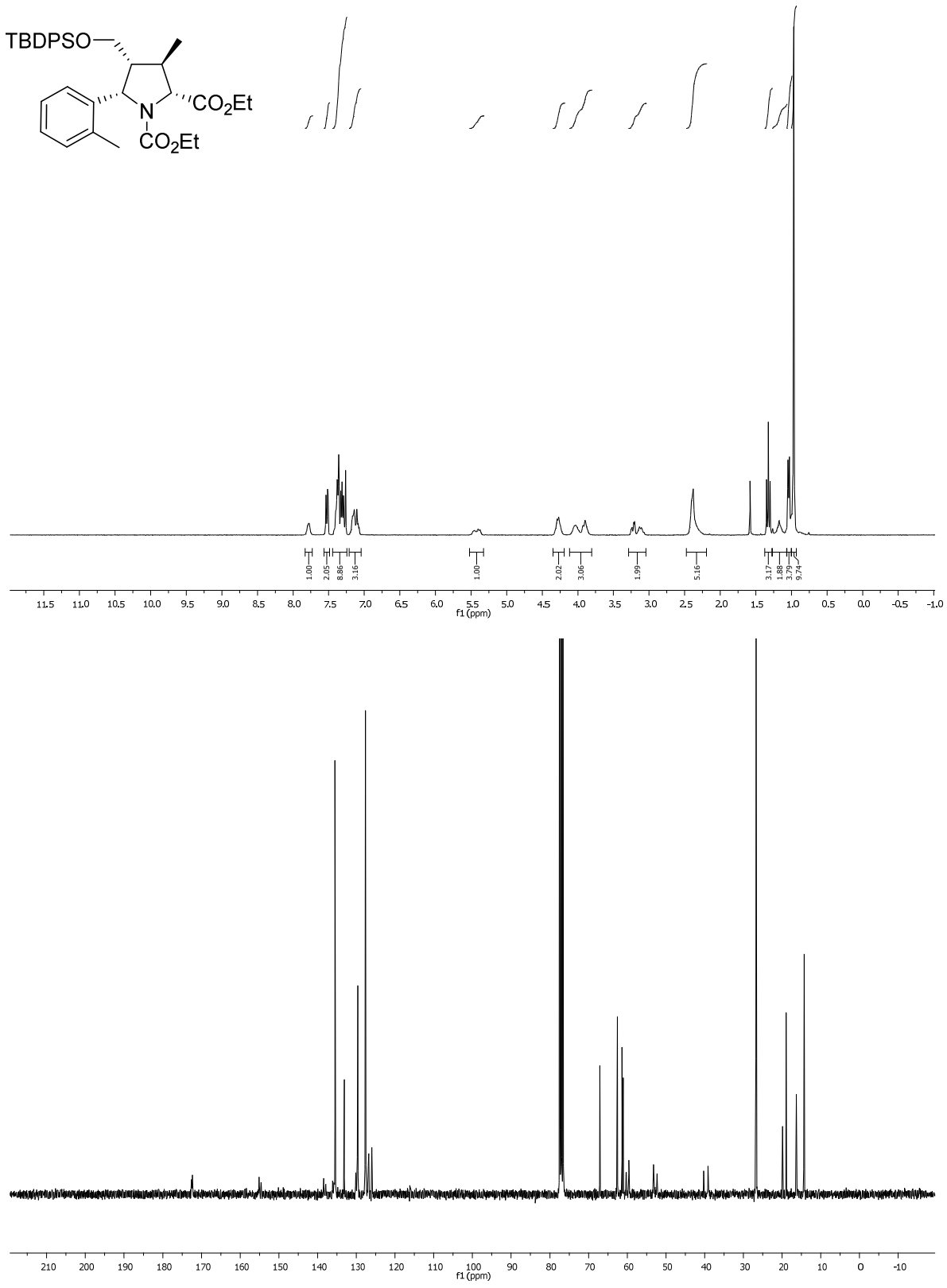


^{1}H-NMR and ^{13}C-NMR spectra of compound **4c**



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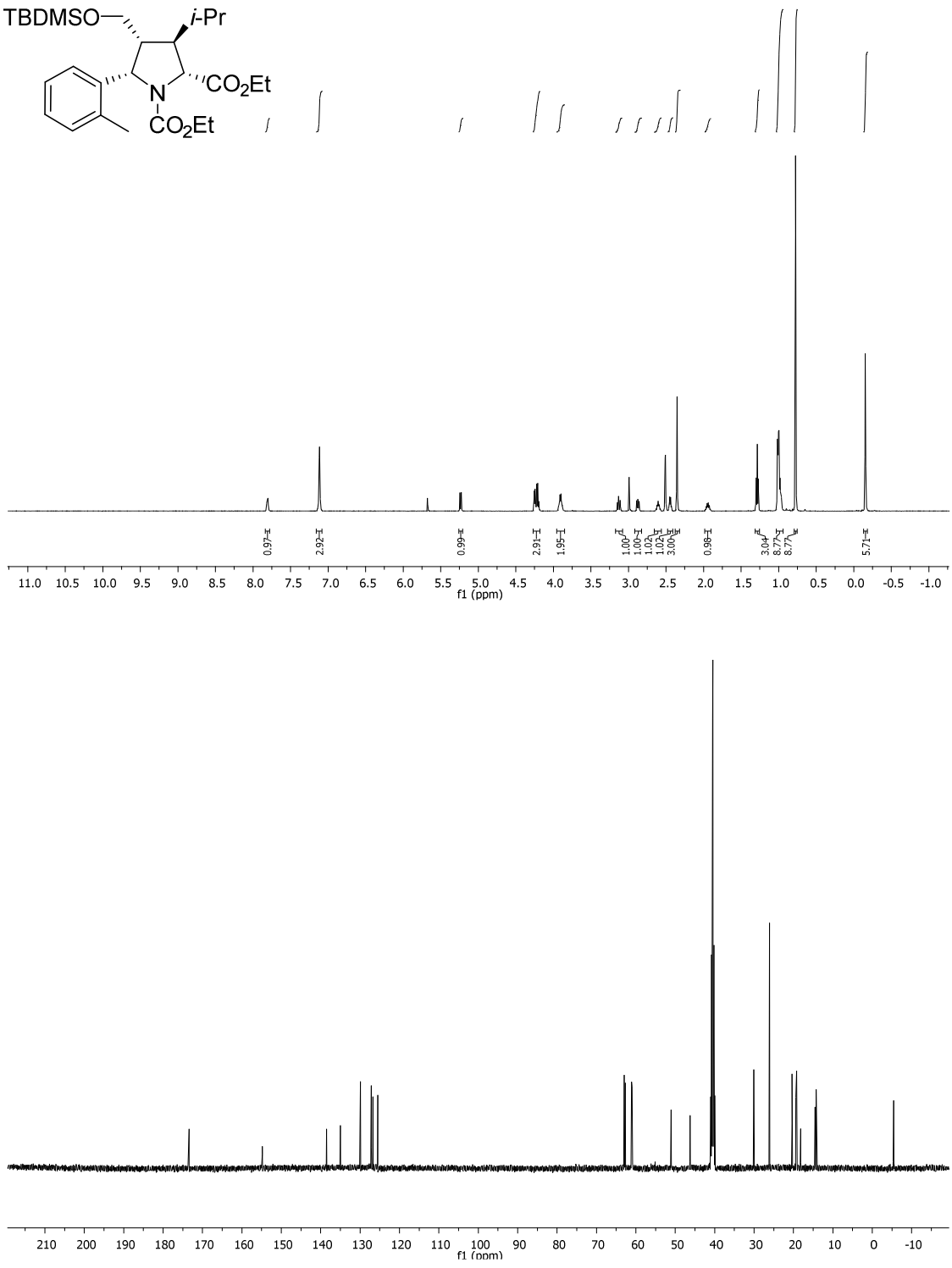

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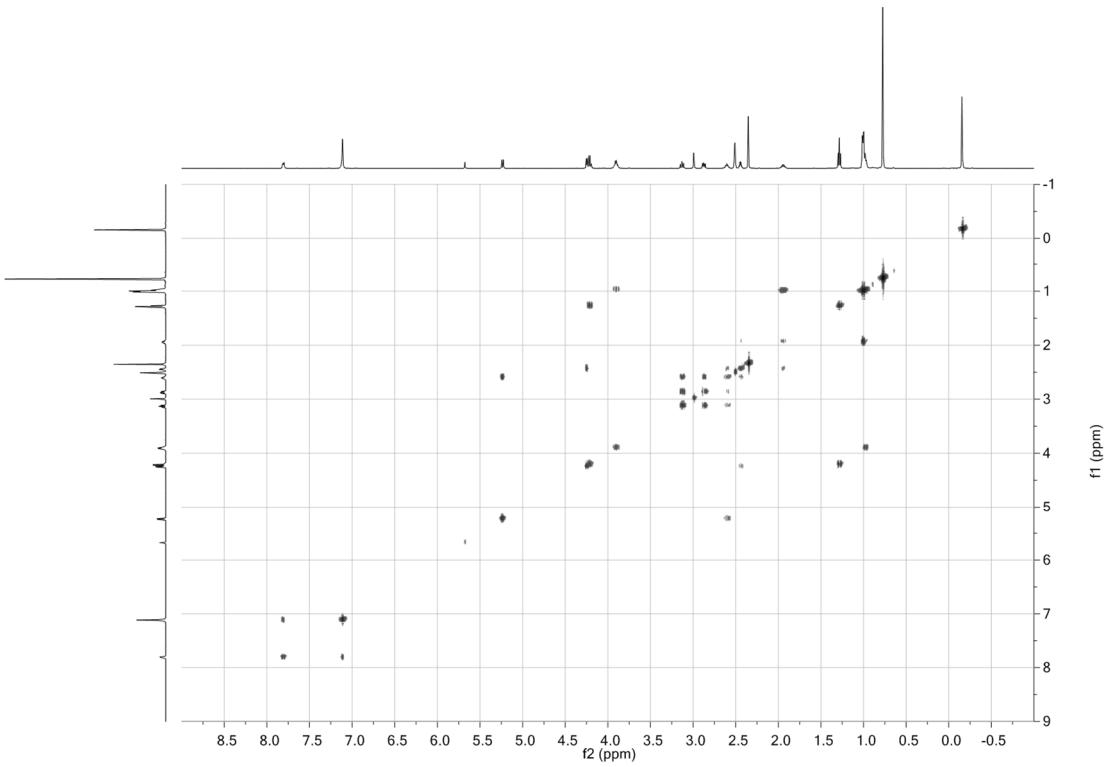

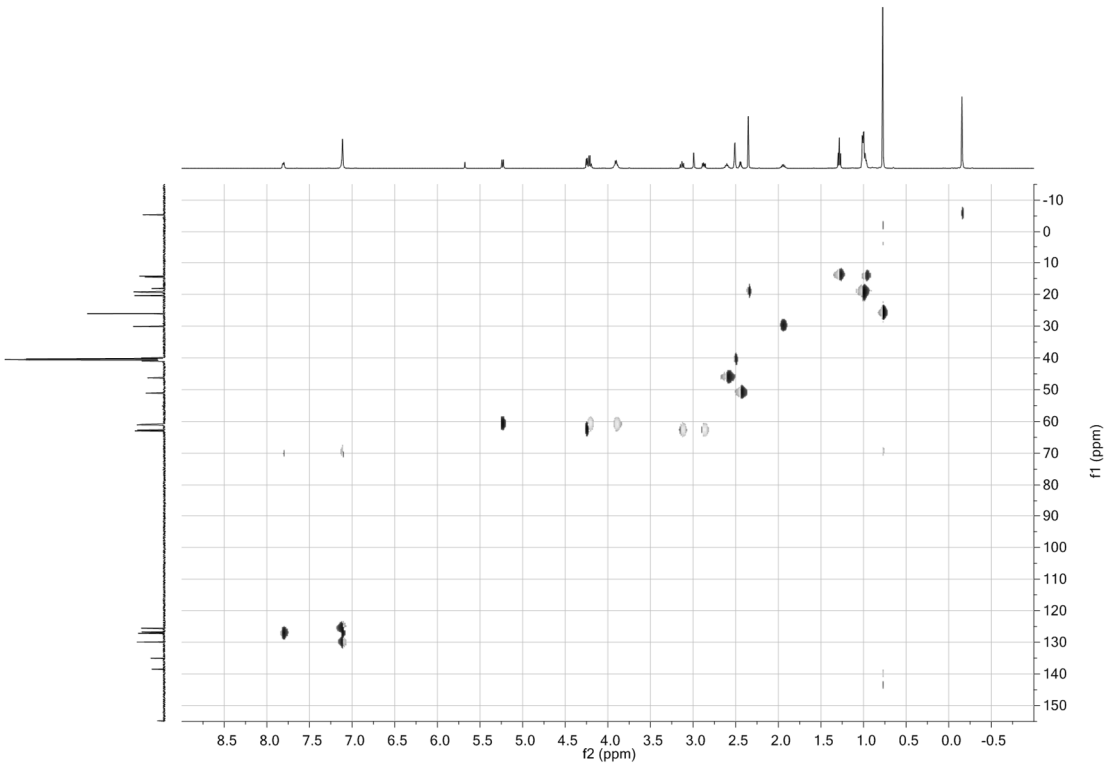

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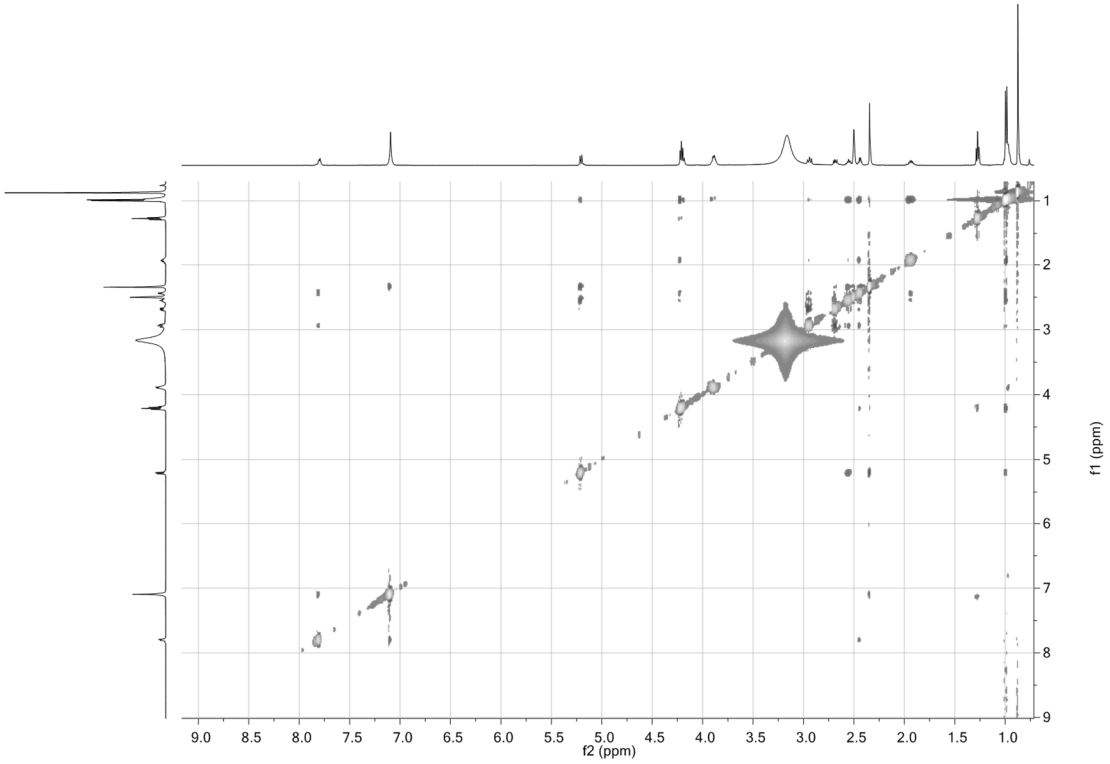

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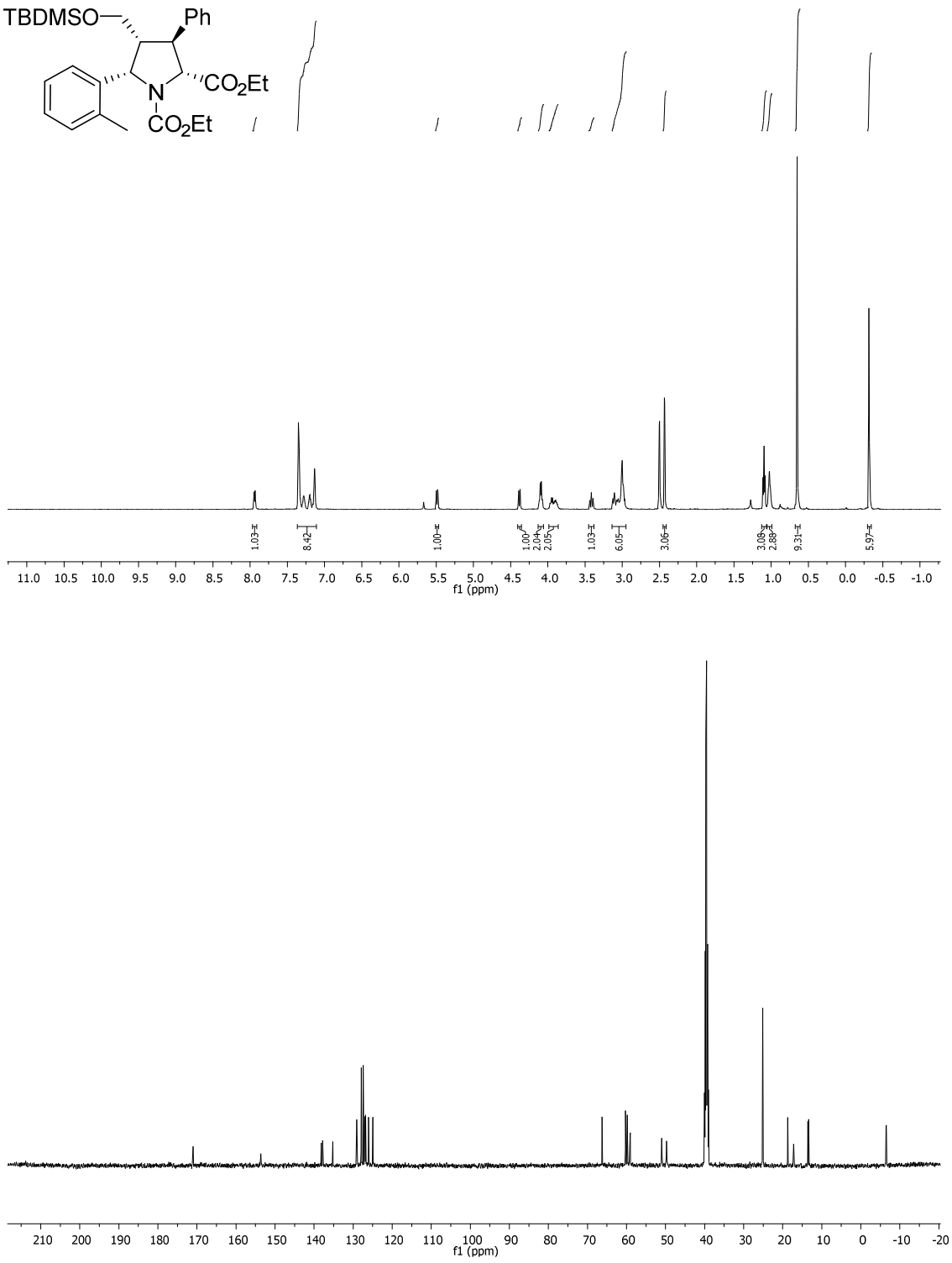
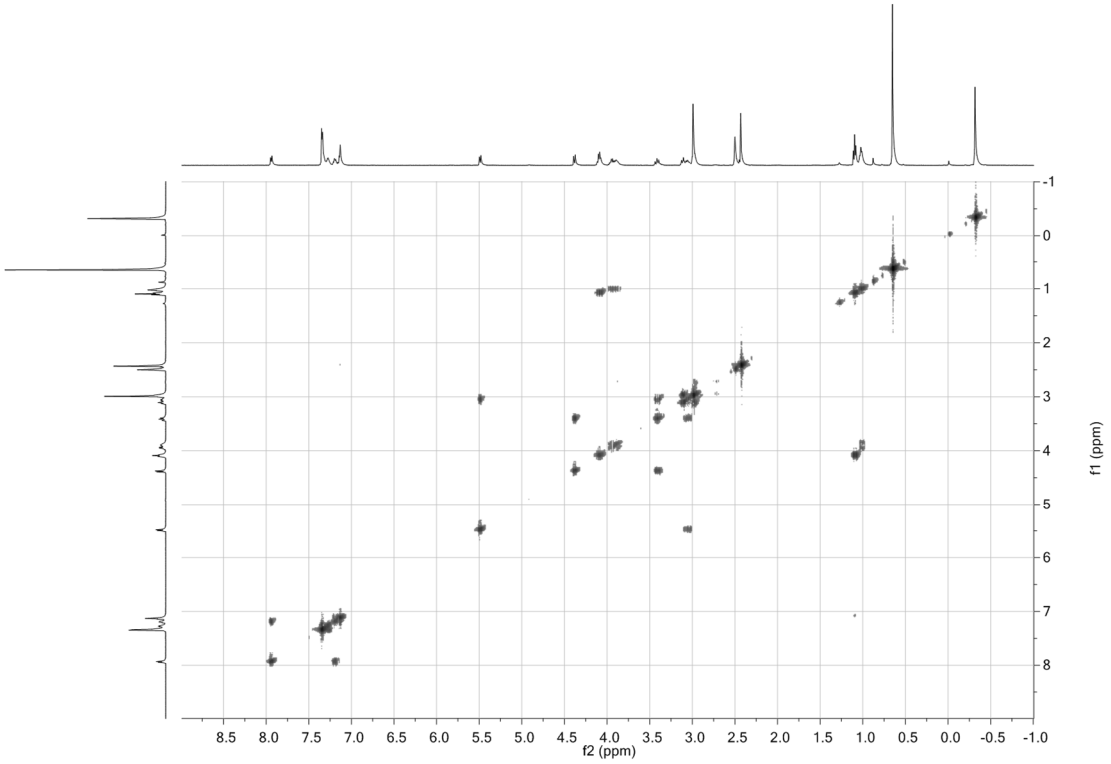
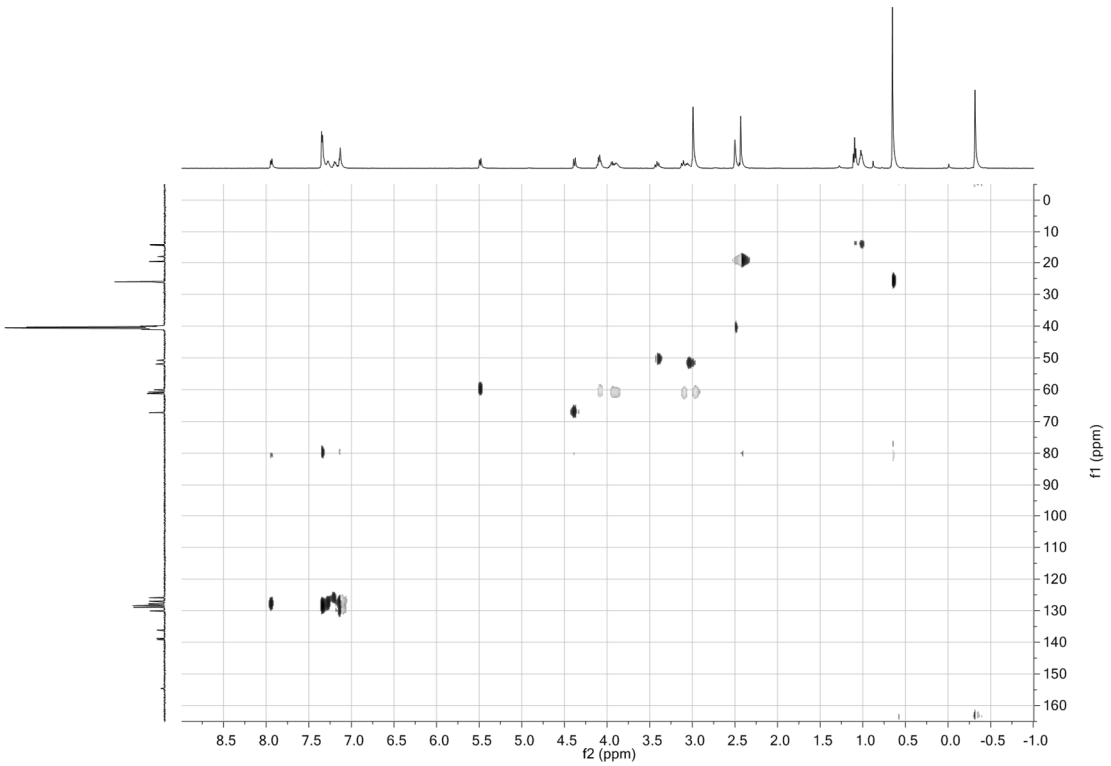
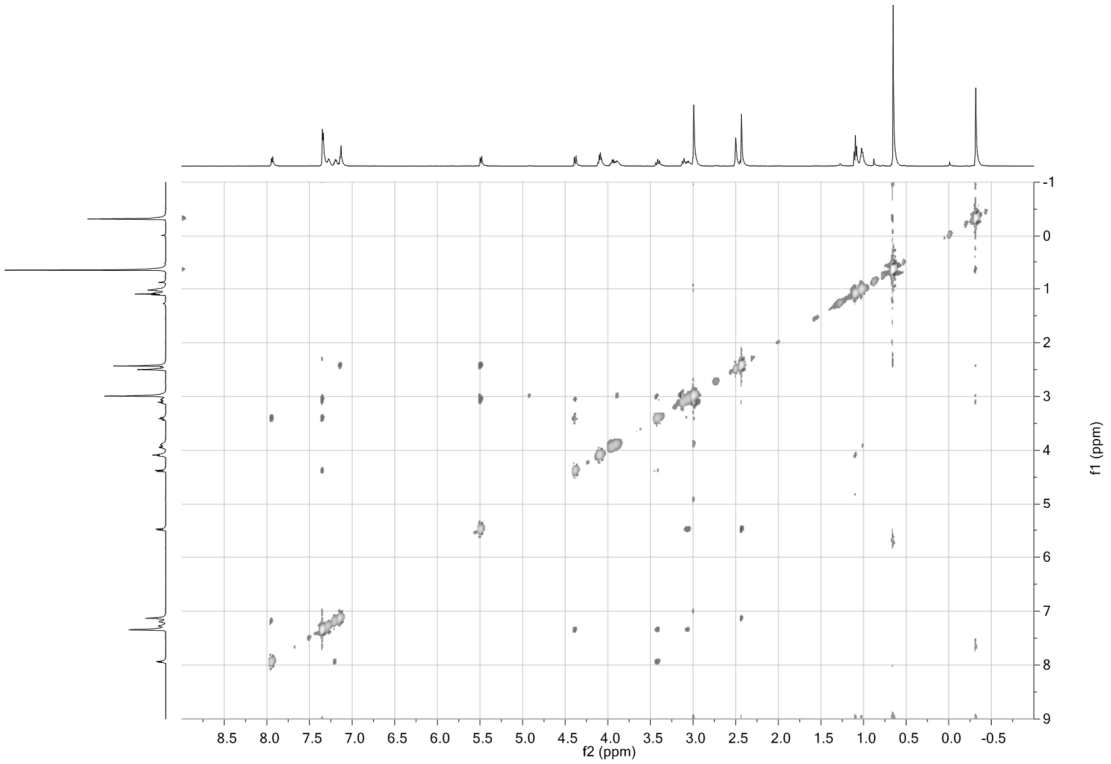


^{1}H-NMR and ^{13}C-NMR spectra of compound **4f.**





COSY and HSQC spectra of compound **4f.**



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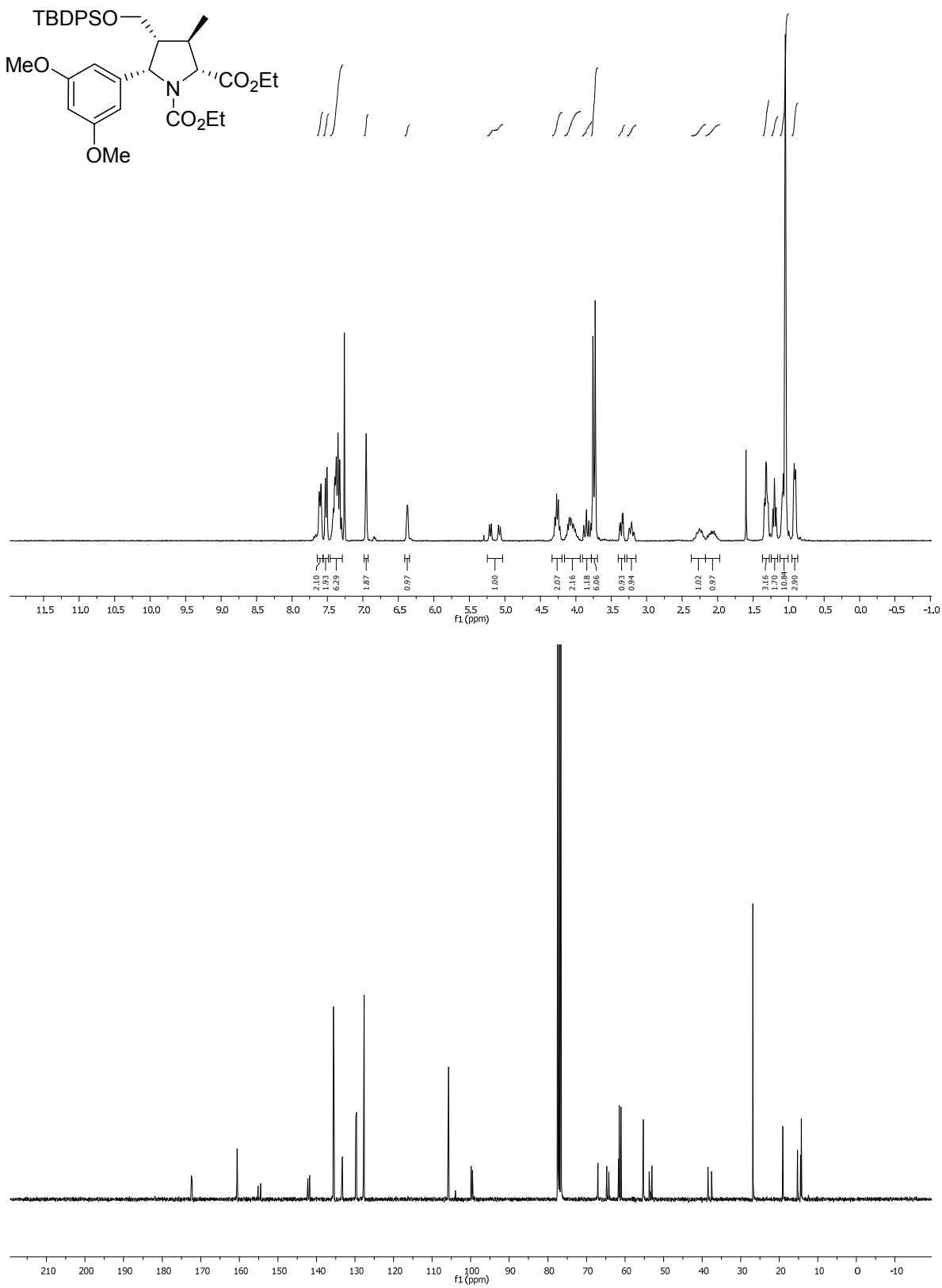
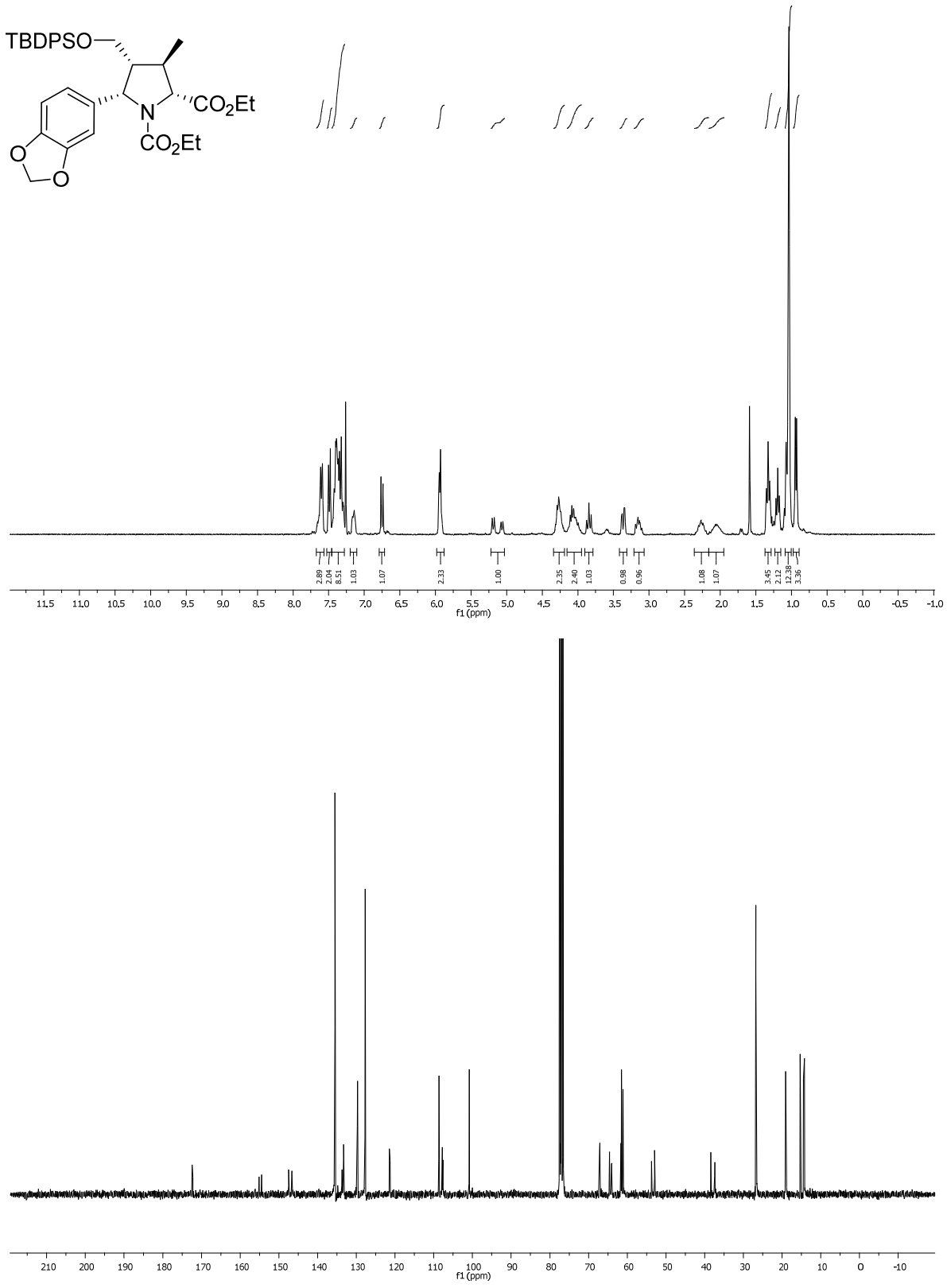
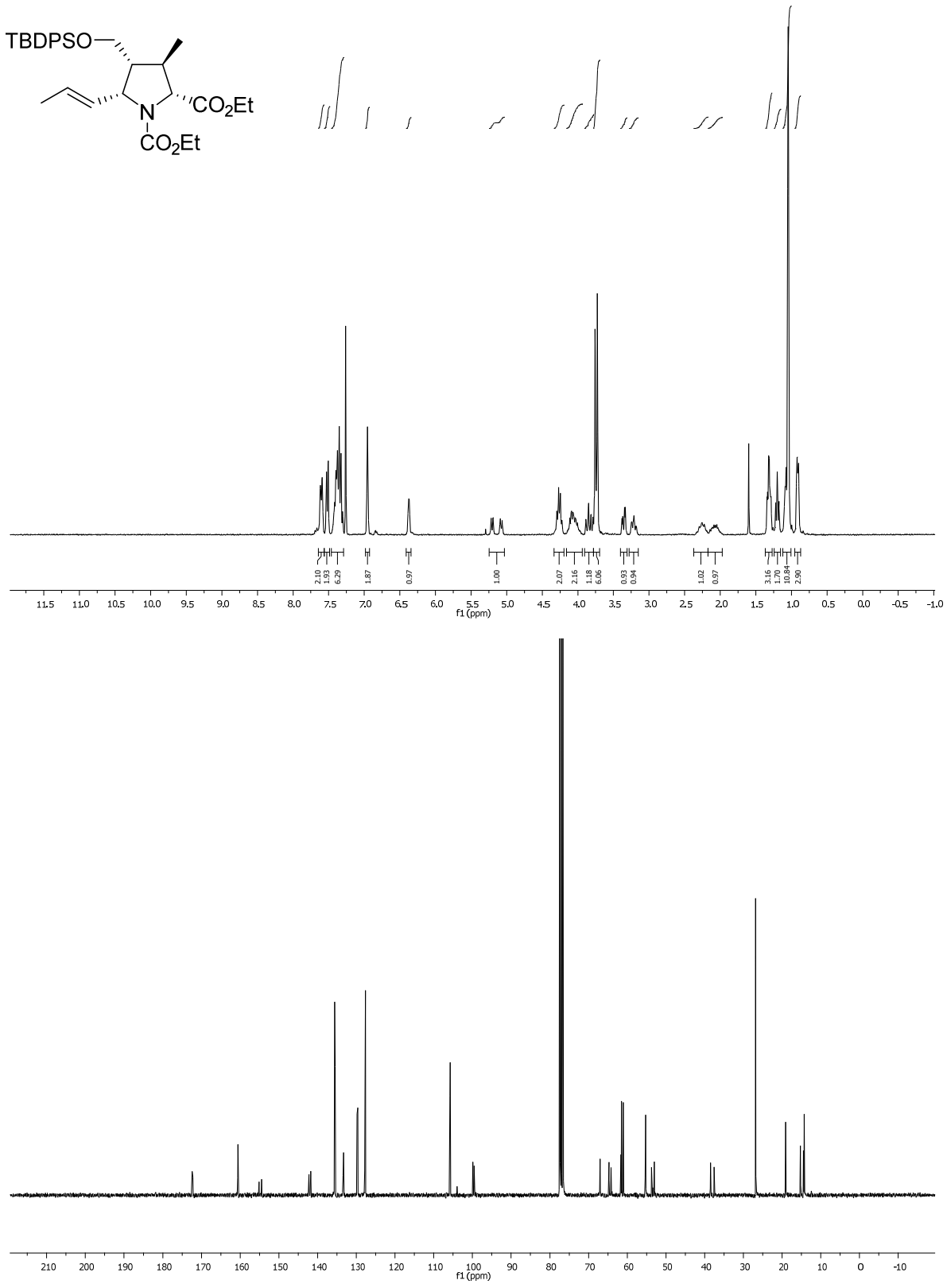


^{1}H-NMR and ^{13}C-NMR spectra of compound **4g**



^{1}H-NMR and ^{13}C-NMR spectra of compound **4h.**



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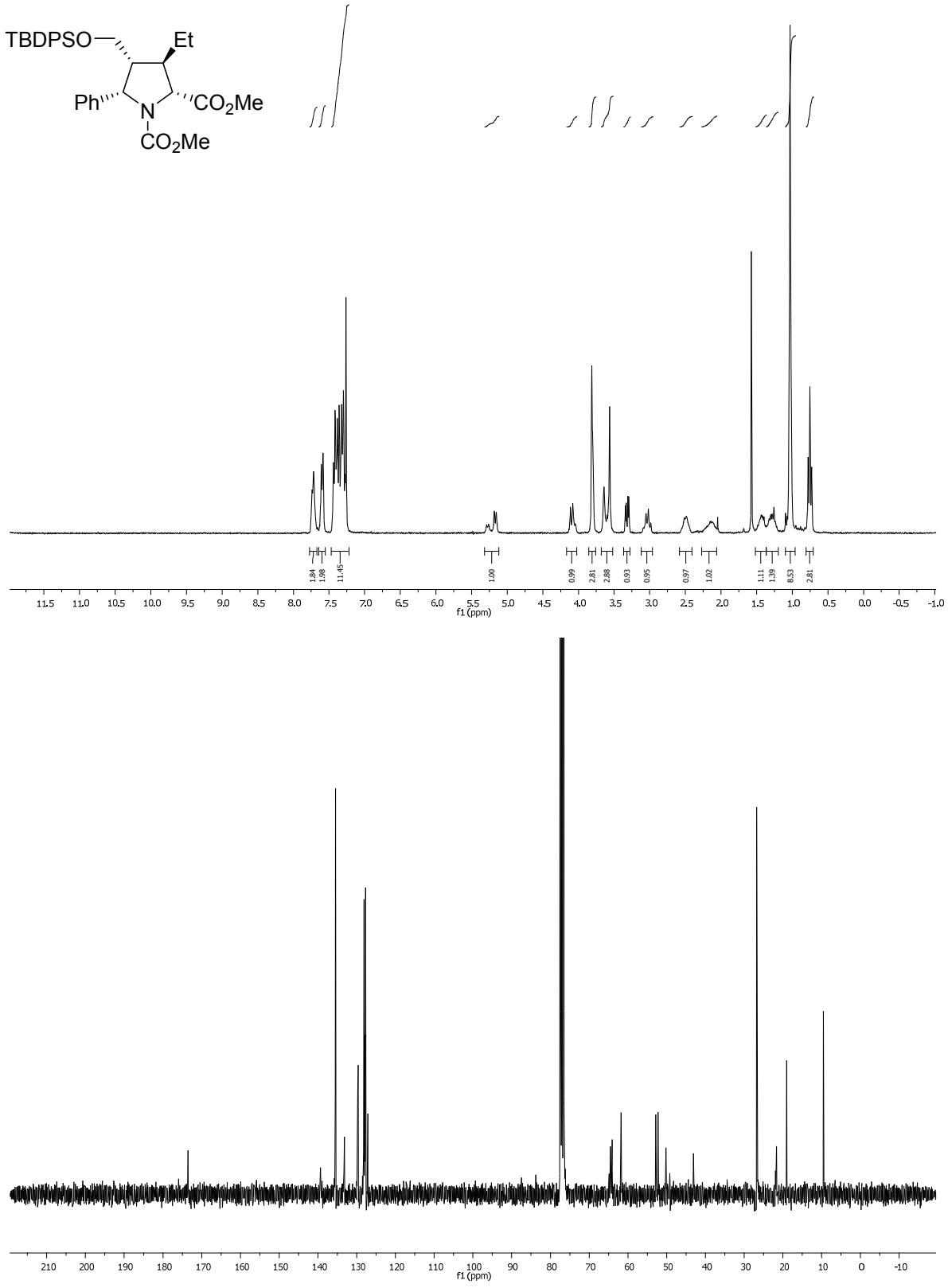
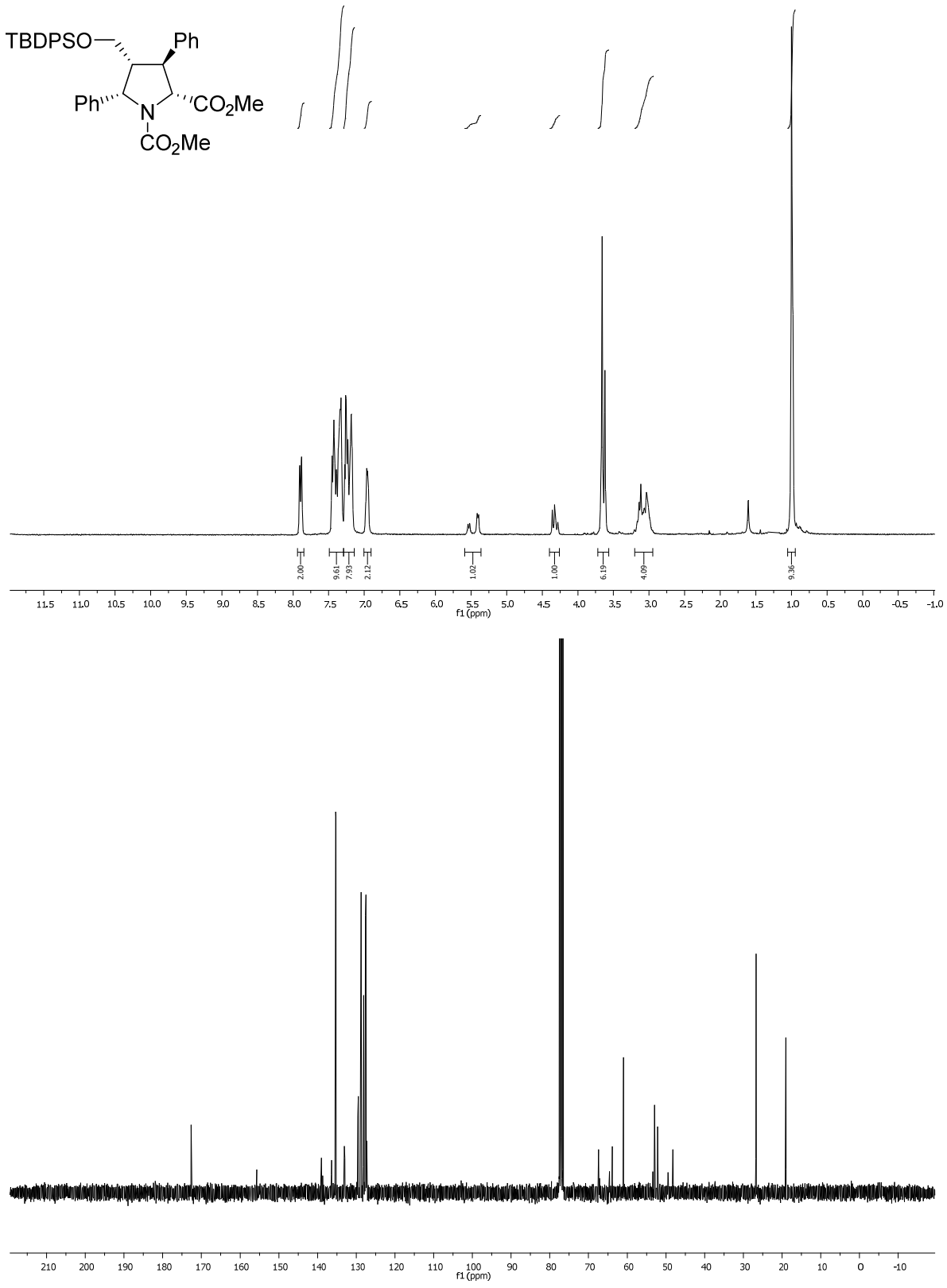
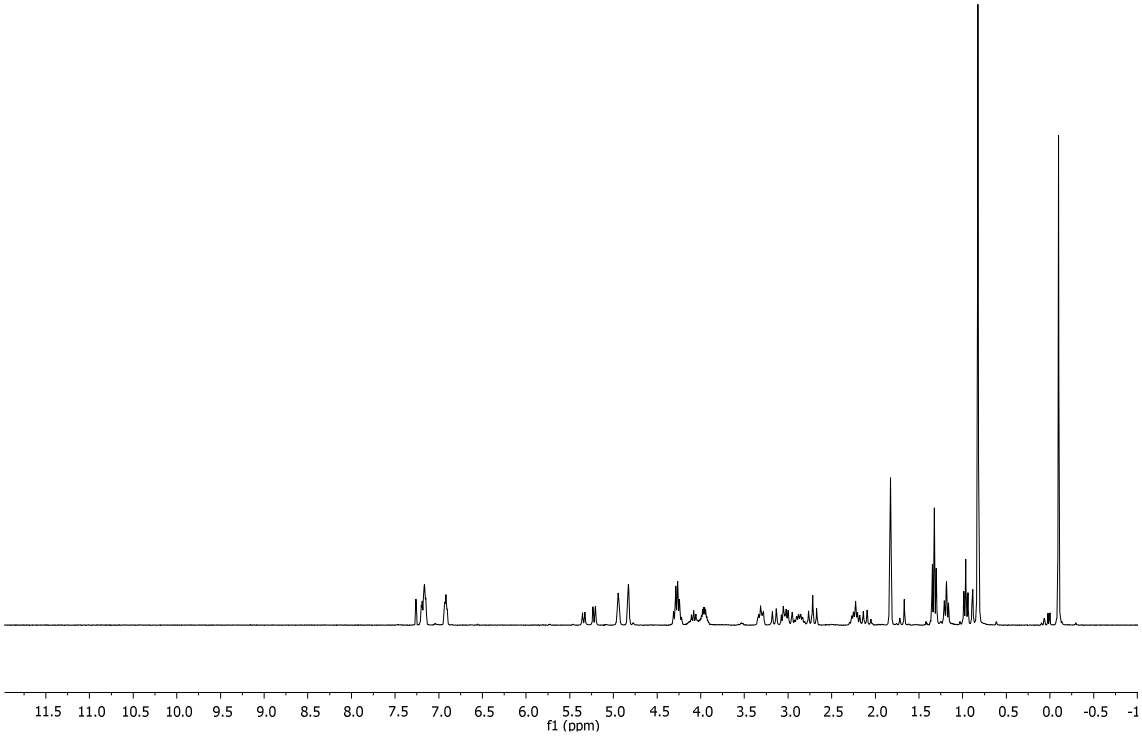
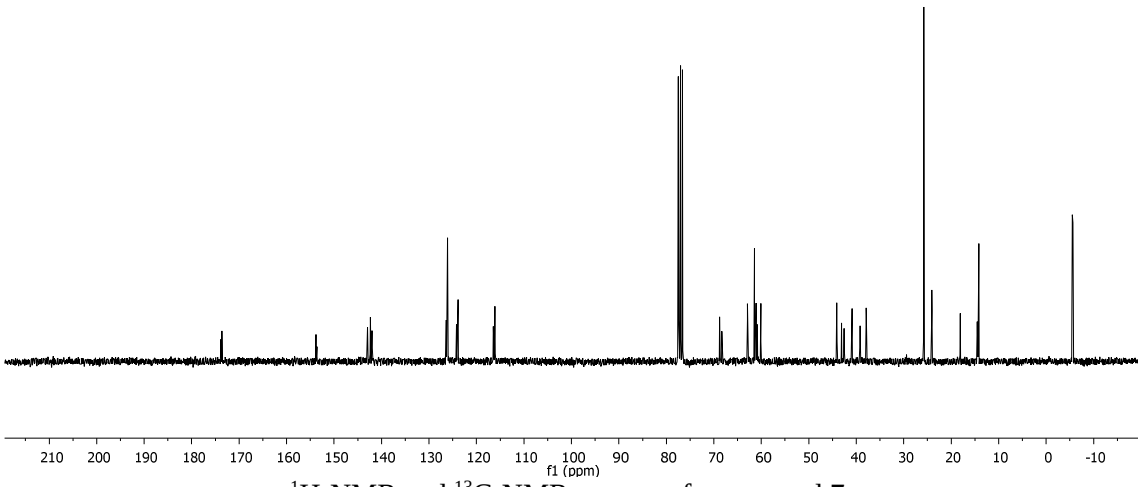


^{1}H-NMR and ^{13}C-NMR spectra of compound **4j.**

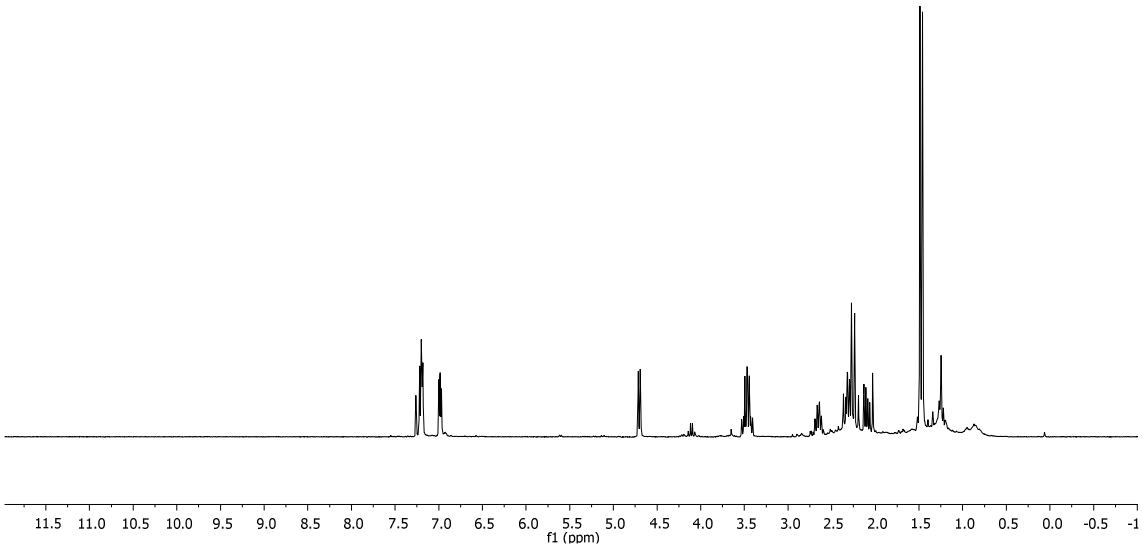


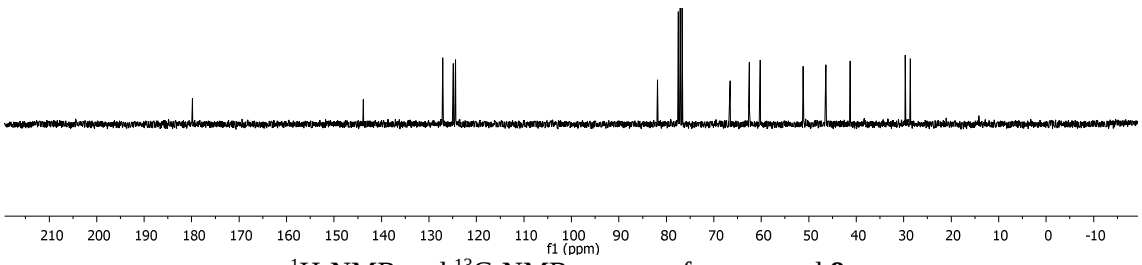
^{1}H-NMR and ^{13}C-NMR spectra of compound **4k.**





^{1}H-NMR and ^{13}C-NMR spectra of compound **7.**





^{1}H-NMR and ^{13}C-NMR spectra of compound **8.**

2. X-Ray data for compound 8

Crystal Data for $C_{14}H_{19}NO_3S$ (*M* = 281.36) (**8**) (CCDC number 1584197): orthorhombic, space group $P2_12_12_1$, *a* = *b* =5.36821(6) Å, *b* = 11.71337(15) Å, *c* = 21.6232(3) Å, α = *β* = γ = 90.00°, *V* = 1359.66(3) Å^3, *Z* = 8, *T* = 100.00(10) K, μ(Cu Kα) = 1.814 mm^{-1}, *Dcalc* = 1.374 g/cm^3, 9152 reflections measured (8.178° ≤ 2Θ ≤ 139.996°), 2586 unique (R_{int} = 0.0258, R_{sigma} = 0.0222) which were used in all calculations. The final R_1 was 0.0254 (I>=2u(I)) and wR_2 was 0.0620 (all data).

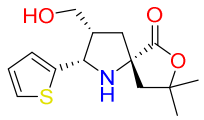


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Figure SI-1. ORTEP diagram for compound **(2*R*,4*S*,5*R*)-8**

Table SI-1 Crystal data and structure refinement for compound **8.**

Identification code	IU706
Empirical formula	$C_{14}H_{19}NO_3S$
Formula weight	281.36
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.36821(6)
b/Å	11.71337(15)
c/Å	21.6232(3)
α/°	90.0
β/°	90.0
γ/°	90.0
Volume/Å^3	1359.66(3)
Z	4
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	2.157
F(000)	600.0
Crystal size/mm^3	0.349 × 0.239 × 0.038
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.178 to 139.996
Index ranges	-6 ≤ h ≤ 3, -13 ≤ k ≤ 14, -25 ≤ l ≤ 26
Reflections collected	9152
Independent reflections	2586 [R_{int} = 0.0258, R_{sigma} = 0.0222]
Data/restraints/parameters	2586/25/191
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0254, wR_2 = 0.0615
Final R indexes [all data]	R_1 = 0.0263, wR_2 = 0.0620
Largest diff. peak/hole / e Å^{-3}	0.17/-0.18
Flack parameter	-0.005(9)

Table SI-2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for IU706. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7793.3(12)	9449.2(6)	3869.8(3)	15.4(2)
S1B	3847(11)	8591(6)	4642(2)	17.2(14)
O1	8752(3)	9653.2(12)	2192.8(7)	18.3(3)
O2	7550(3)	8619.9(11)	1383.8(6)	16.4(3)
O3	7260(3)	5173.7(12)	3603.9(7)	23.6(3)
N1	4291(3)	8738.0(14)	2804.2(8)	14.5(3)
C0BG	7860(30)	9730(20)	4533(6)	19.6(4)
C0BJ	6160(30)	9413(19)	4963(7)	19.6(4)
C1	7470(4)	8895.4(16)	1981.8(9)	14.3(4)
C2	5709(4)	8108.2(16)	2338.9(9)	12.8(4)
C3	4012(4)	8061.7(16)	3378.4(9)	14.7(4)
C4	5302(4)	6916.3(17)	3227.0(9)	14.8(4)
C5	7203(4)	7258.9(15)	2733.1(9)	14.1(4)
C6	4233(4)	7535.4(17)	1813.4(9)	14.8(4)
C7	5917(4)	7626.6(16)	1244.7(9)	15.4(4)
C8	5081(3)	8679.1(17)	3929.2(9)	14.7(4)
C9	7780(7)	9744(4)	4653.6(11)	19.6(4)
C10	5749(6)	9289(4)	4937.0(15)	19.6(4)
C11	4253(9)	8684(4)	4523.2(19)	21.4(10)
C11B	7200(20)	9312(15)	3968(6)	17.2(14)
C12	6420(4)	6284.6(17)	3774.2(9)	19.1(4)
C13	7649(4)	6612.6(16)	1146.5(10)	19.2(4)
C14	4526(4)	7896.0(19)	657.5(9)	19.7(4)

Table SI-3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for IU706. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	13.9(3)	15.8(3)	16.5(3)	-2.5(2)	1.1(2)	-3.8(2)
S1B	16.6(16)	17.3(15)	17.8(15)	0.2(9)	1.3(9)	-1.7(9)
O1	16.8(7)	15.4(7)	22.9(7)	-1.7(6)	-0.8(6)	-4.5(6)
O2	17.7(7)	14.8(6)	16.7(6)	-0.5(5)	2.3(6)	-4.4(6)
O3	27.7(8)	14.8(7)	28.3(8)	4.9(6)	7.5(7)	5.3(6)
N1	14.8(8)	15.1(8)	13.7(8)	0.9(7)	-0.3(7)	3.3(7)
C0BG	23.9(9)	18.8(9)	16.2(8)	-2.0(8)	-2.9(8)	-0.3(7)
C0BJ	23.9(9)	18.8(9)	16.2(8)	-2.0(8)	-2.9(8)	-0.3(7)
C1	12.4(10)	13.6(9)	16.9(9)	1.3(7)	0.1(8)	3.1(8)
C2	11.6(9)	11.0(8)	15.7(9)	-1.4(8)	-0.4(7)	-0.1(8)
C3	14.6(9)	13.5(9)	16.0(9)	1.2(8)	-0.2(8)	-0.2(8)
C4	16.1(9)	11.4(9)	16.8(9)	-0.1(8)	0.2(8)	-0.5(8)
C5	13.7(9)	13.4(9)	15.2(8)	0.8(7)	-0.5(8)	1.0(8)
C6	12.8(9)	16.0(9)	15.5(9)	-0.3(7)	-0.5(8)	-1.5(8)
C7	16.1(9)	12.8(9)	17.2(10)	-2.4(7)	0.4(8)	-2.4(8)
C8	15.1(9)	10.9(9)	18.2(10)	0.6(8)	-0.3(8)	1.4(7)
C9	23.9(9)	18.8(9)	16.2(8)	-2.0(8)	-2.9(8)	-0.3(7)
C10	23.9(9)	18.8(9)	16.2(8)	-2.0(8)	-2.9(8)	-0.3(7)
C11	16.9(19)	20.3(18)	27(2)	4.7(16)	3.3(15)	-4.0(15)
C11B	16.6(16)	17.3(15)	17.8(15)	0.2(9)	1.3(9)	-1.7(9)
C12	23.8(11)	14.3(9)	19.2(10)	2.1(8)	2.5(8)	4.0(8)
C13	18.4(10)	18.3(10)	21.1(9)	-3.1(8)	2.9(9)	0.7(8)
C14	23.4(10)	20.8(11)	15.0(9)	-0.8(8)	0.2(8)	-0.2(9)