Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Rhodium(III)-catalyzed CF_3-Carbenoid C-H Functionalization of 6-Arylpurines

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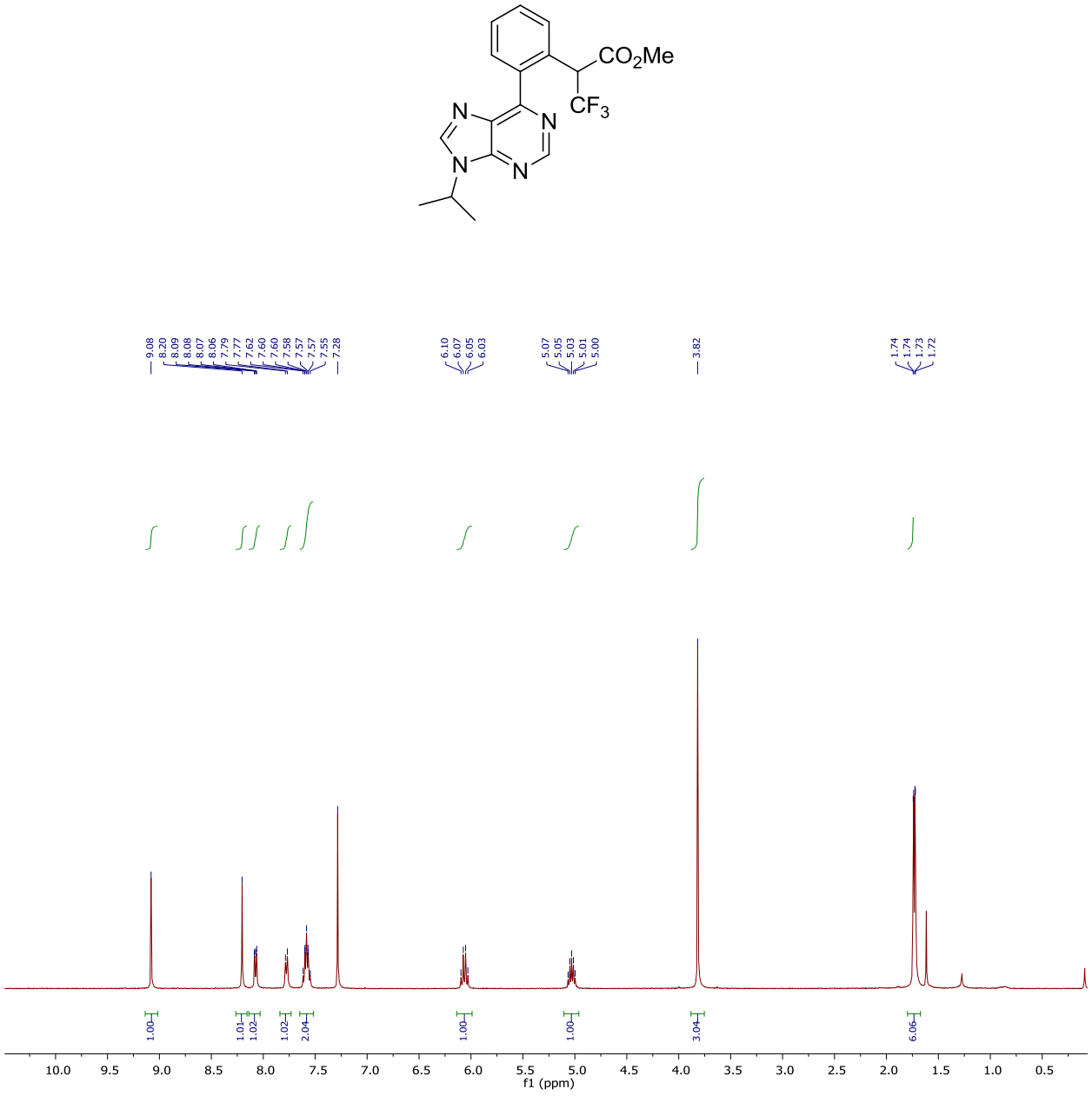
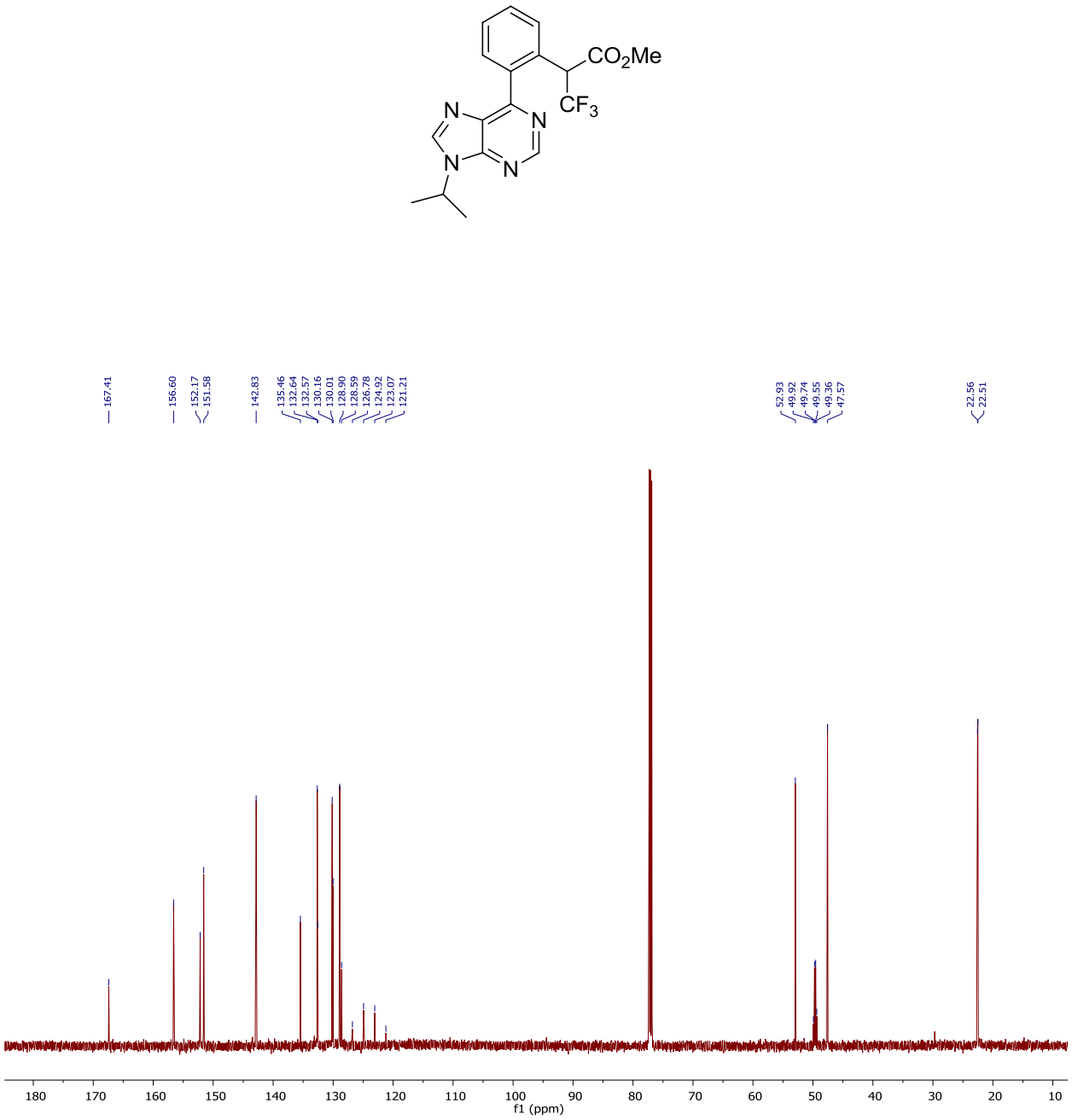
Table of contents

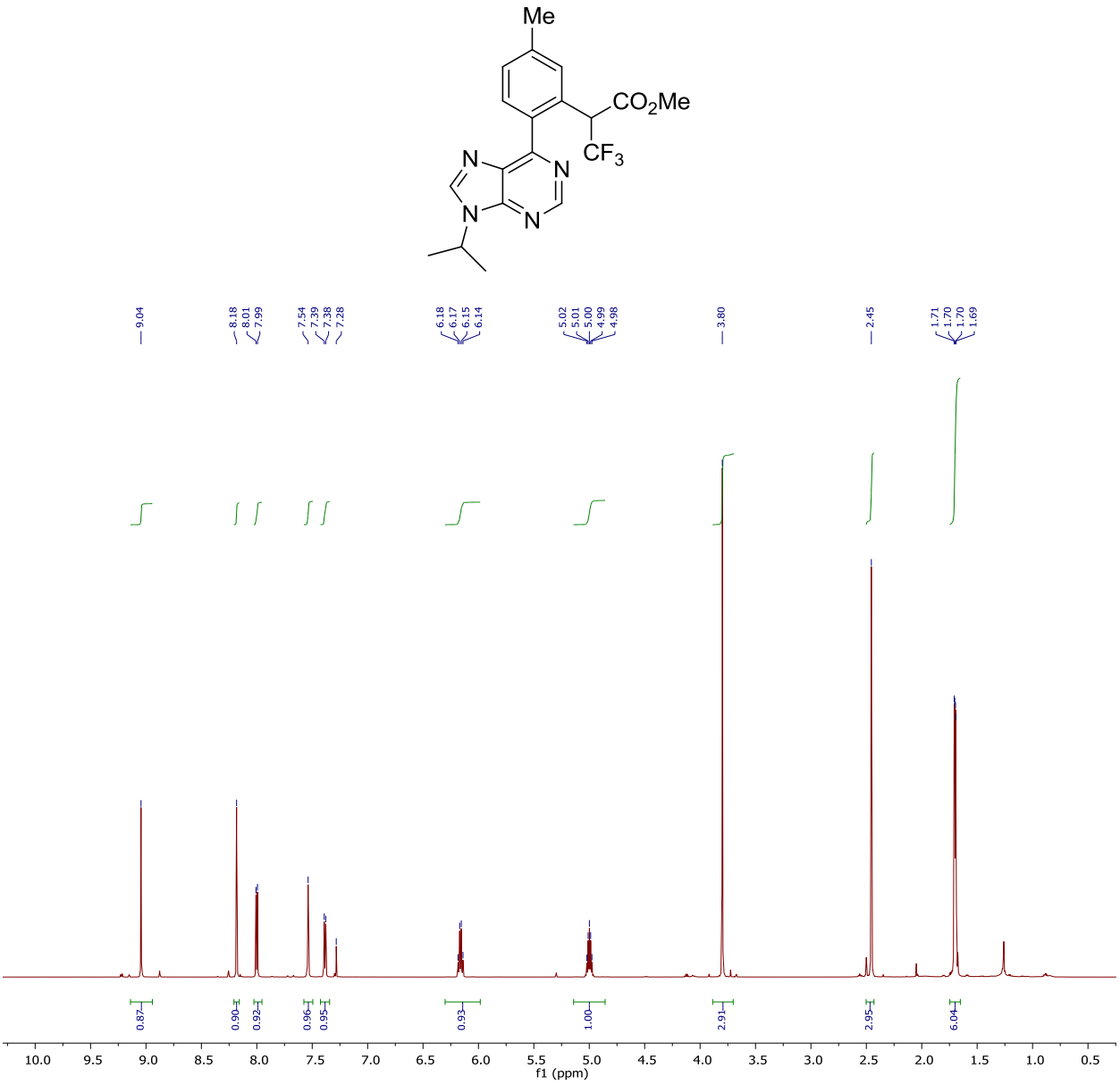
1. ^{1}H and ^{13}C NMR Spectra



^{1}H NMR spectra of compound **2a** in CDCl3



^{13}C NMR spectra of compound **2a** in $CDCl_3$



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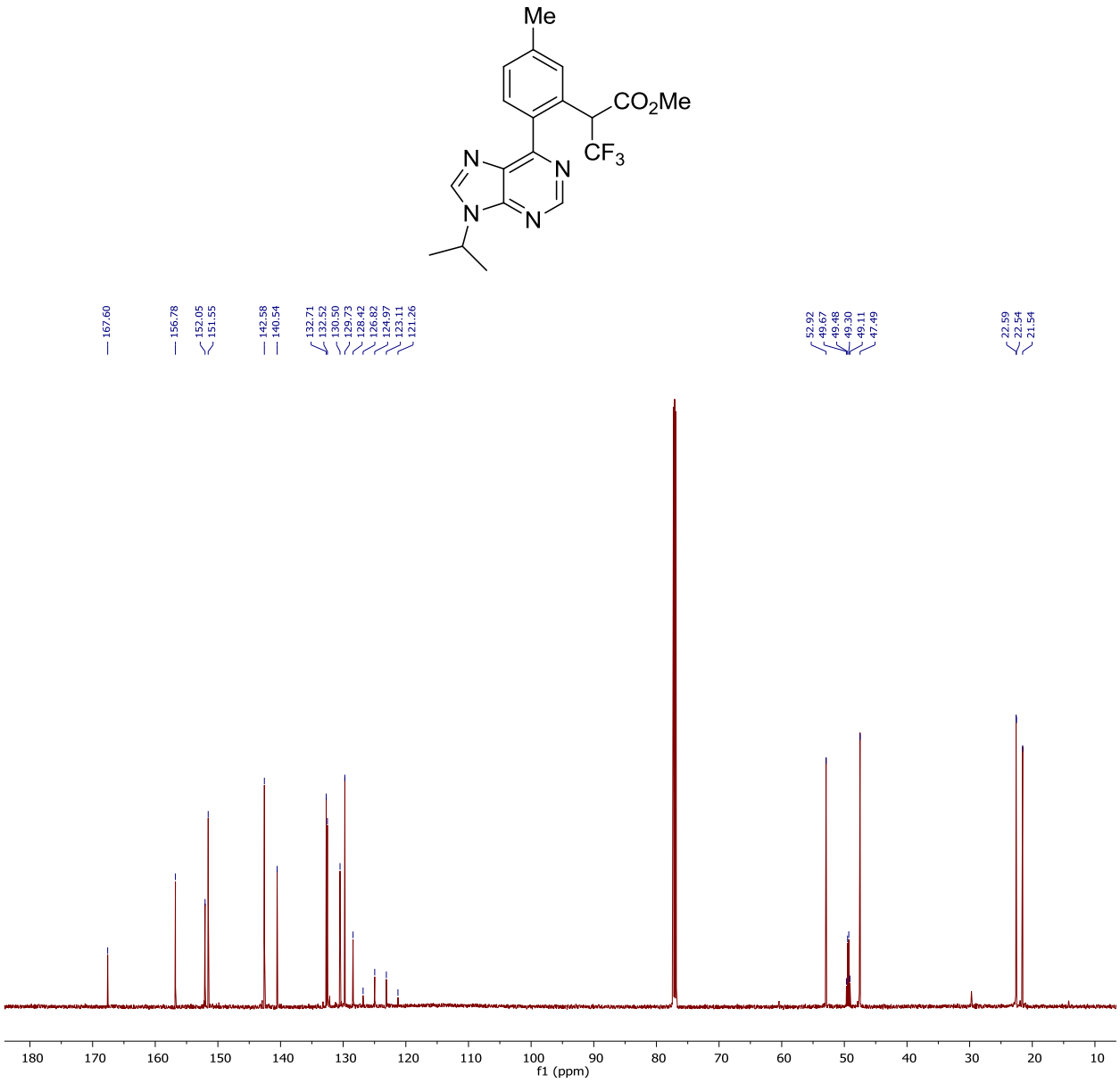

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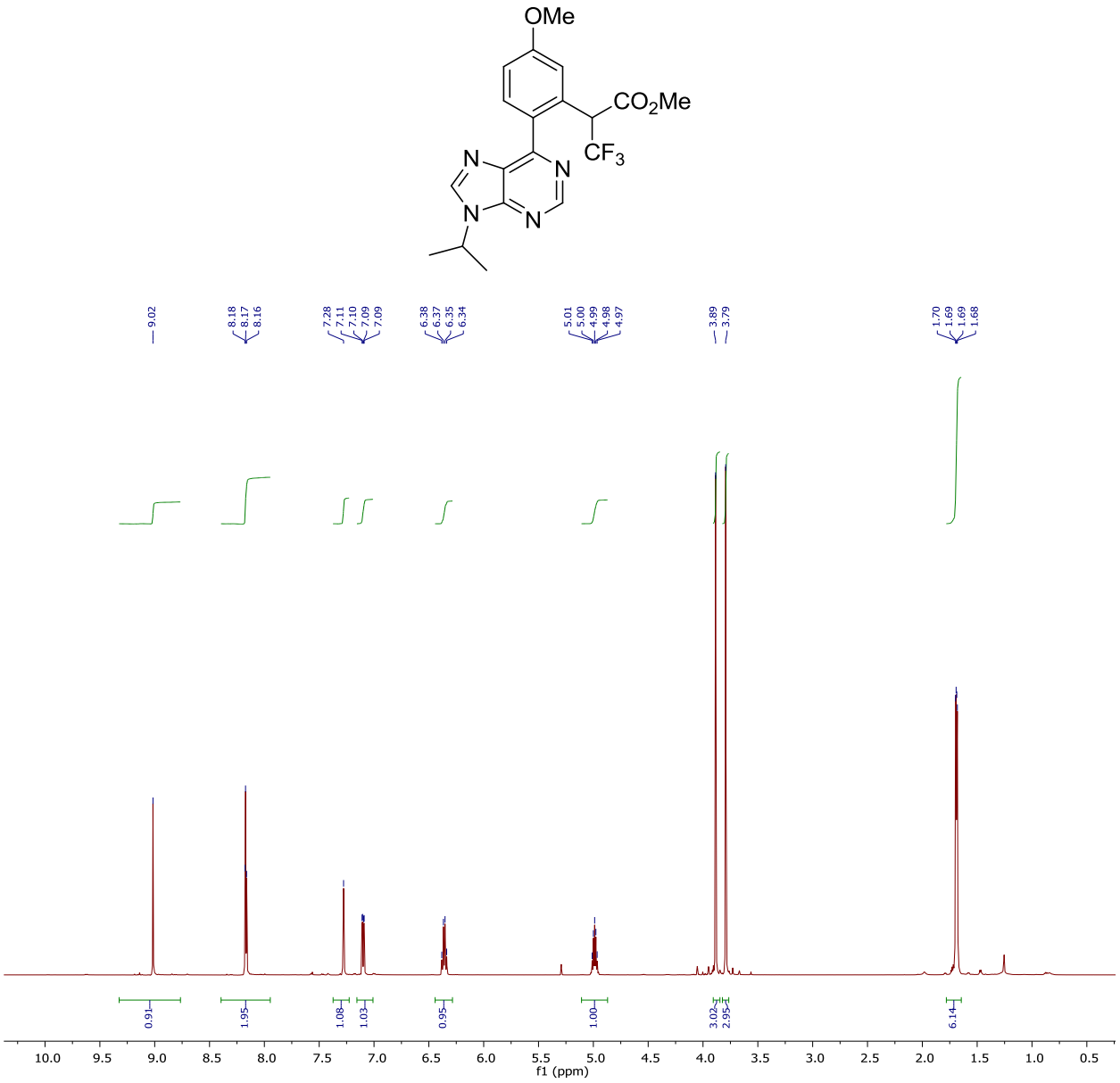

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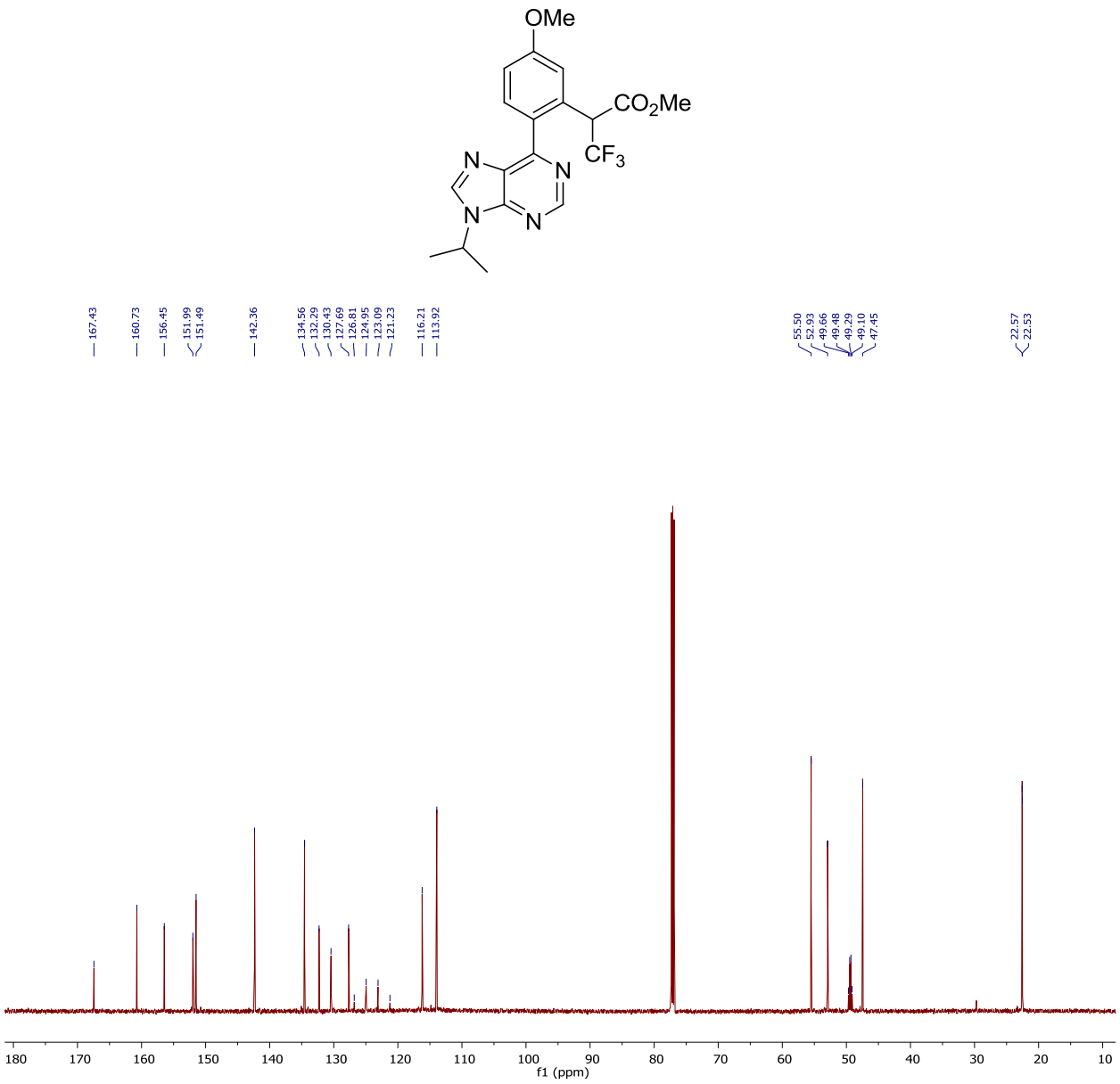

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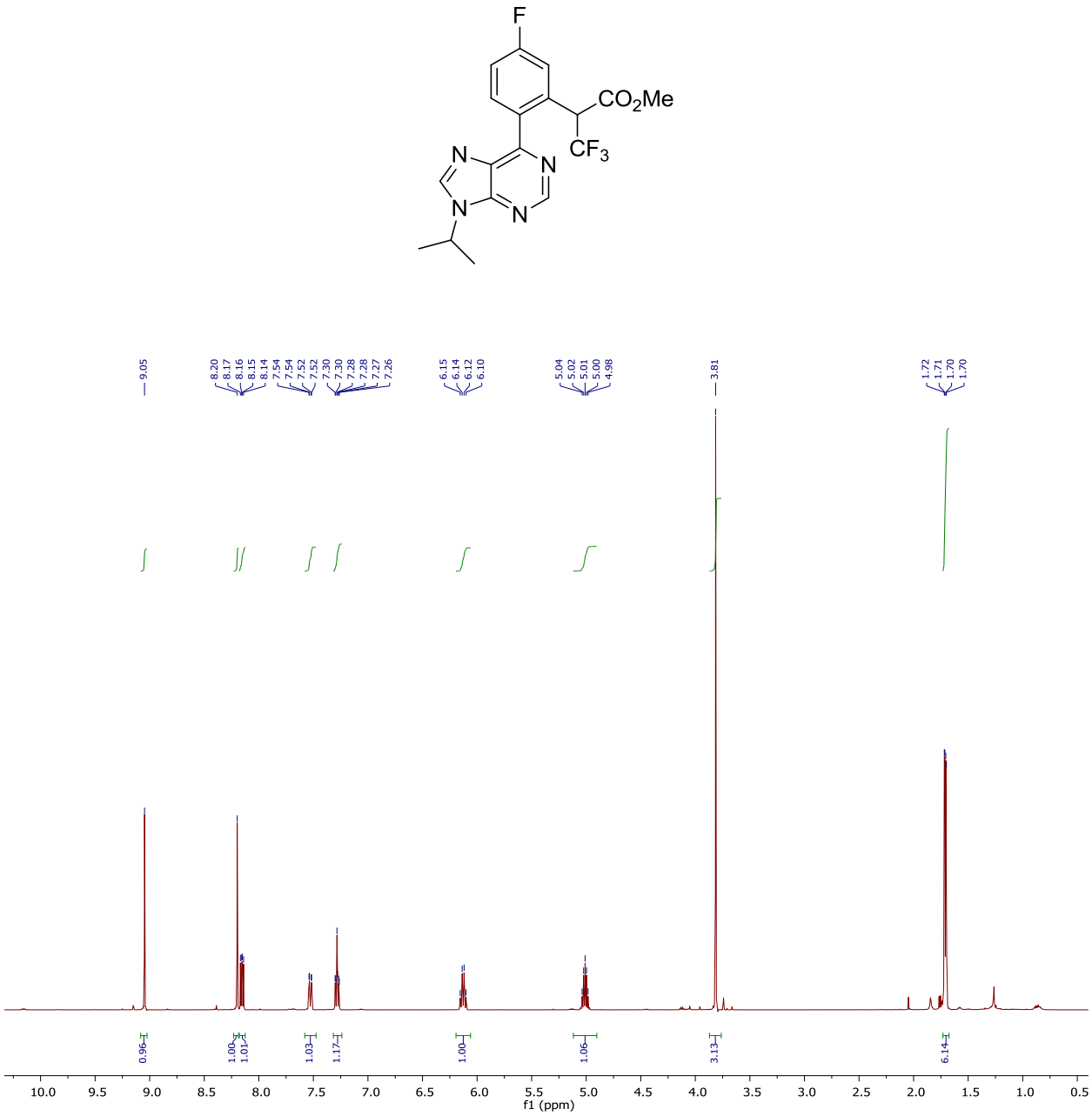

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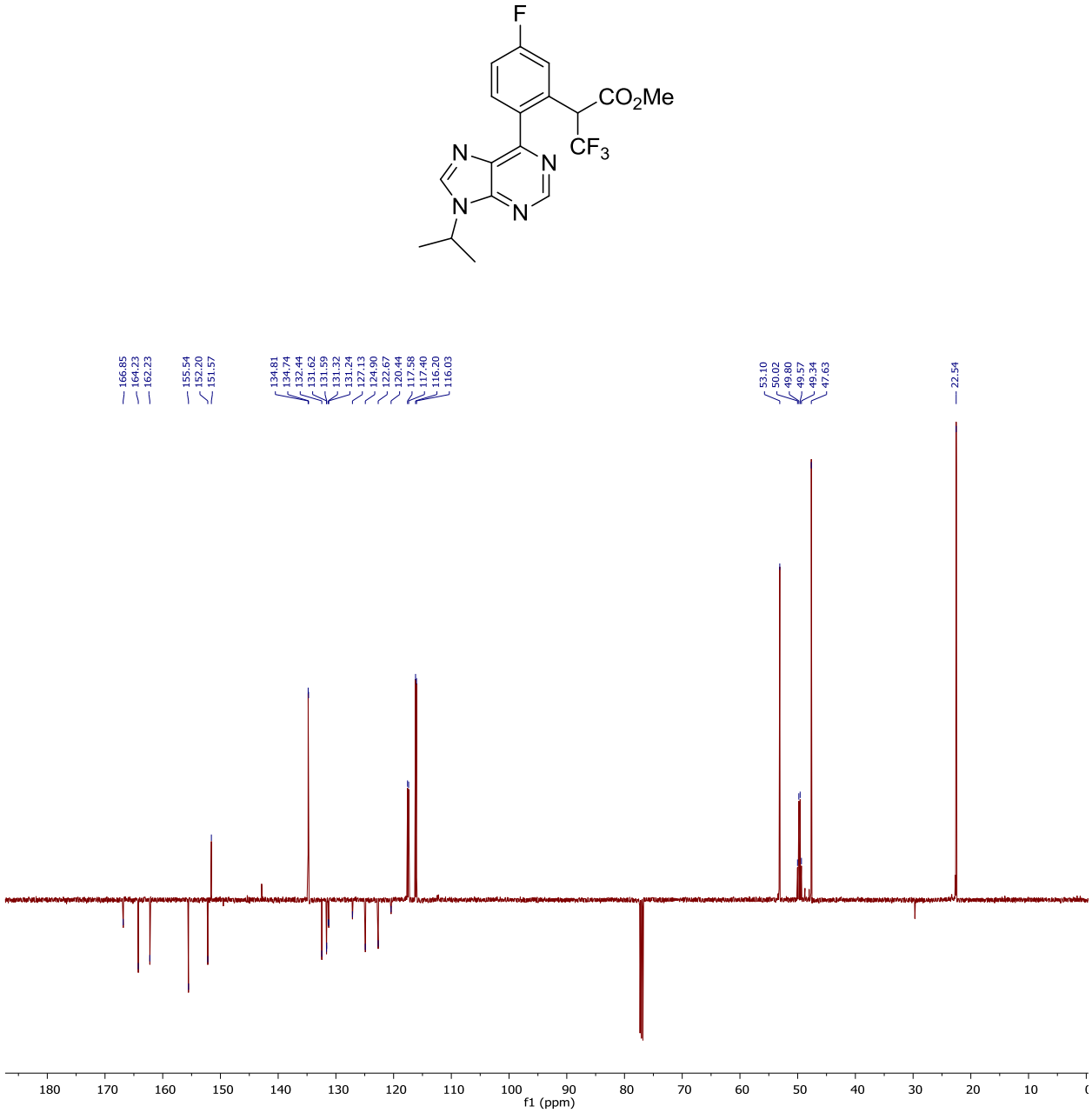
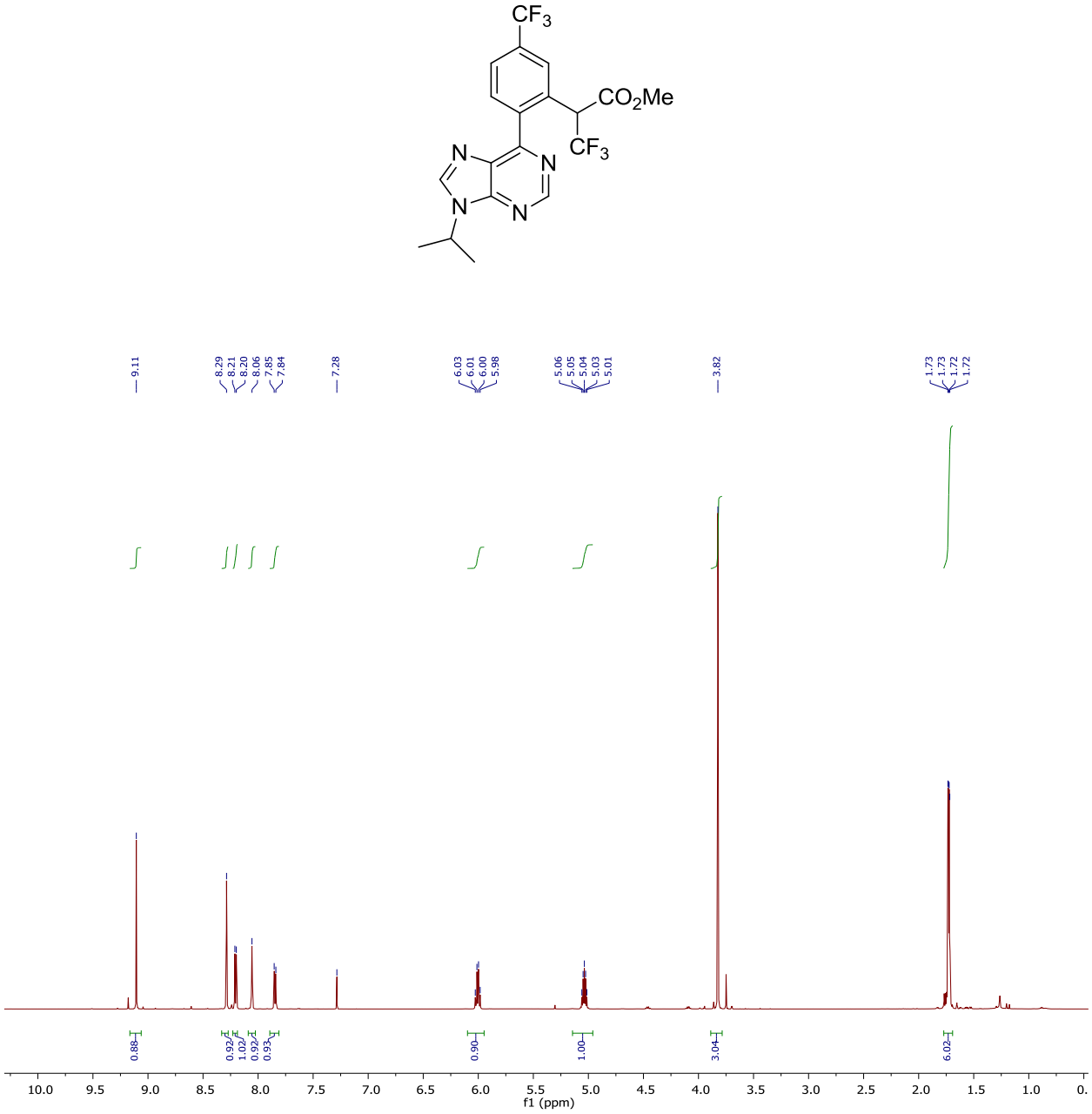


^{13}C NMR spectra (*J*-mod) of compound **2d** in $CDCl_3$



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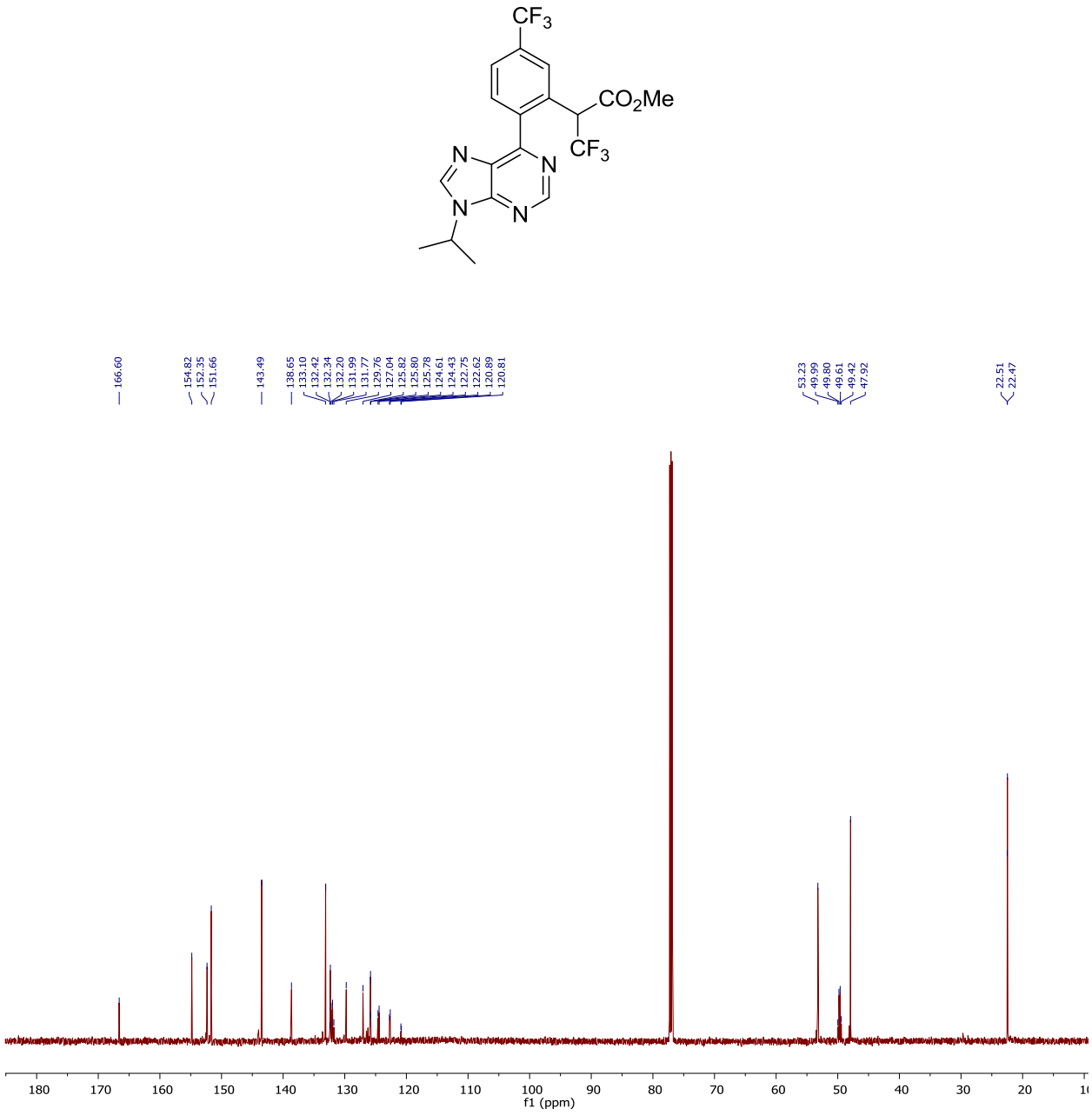

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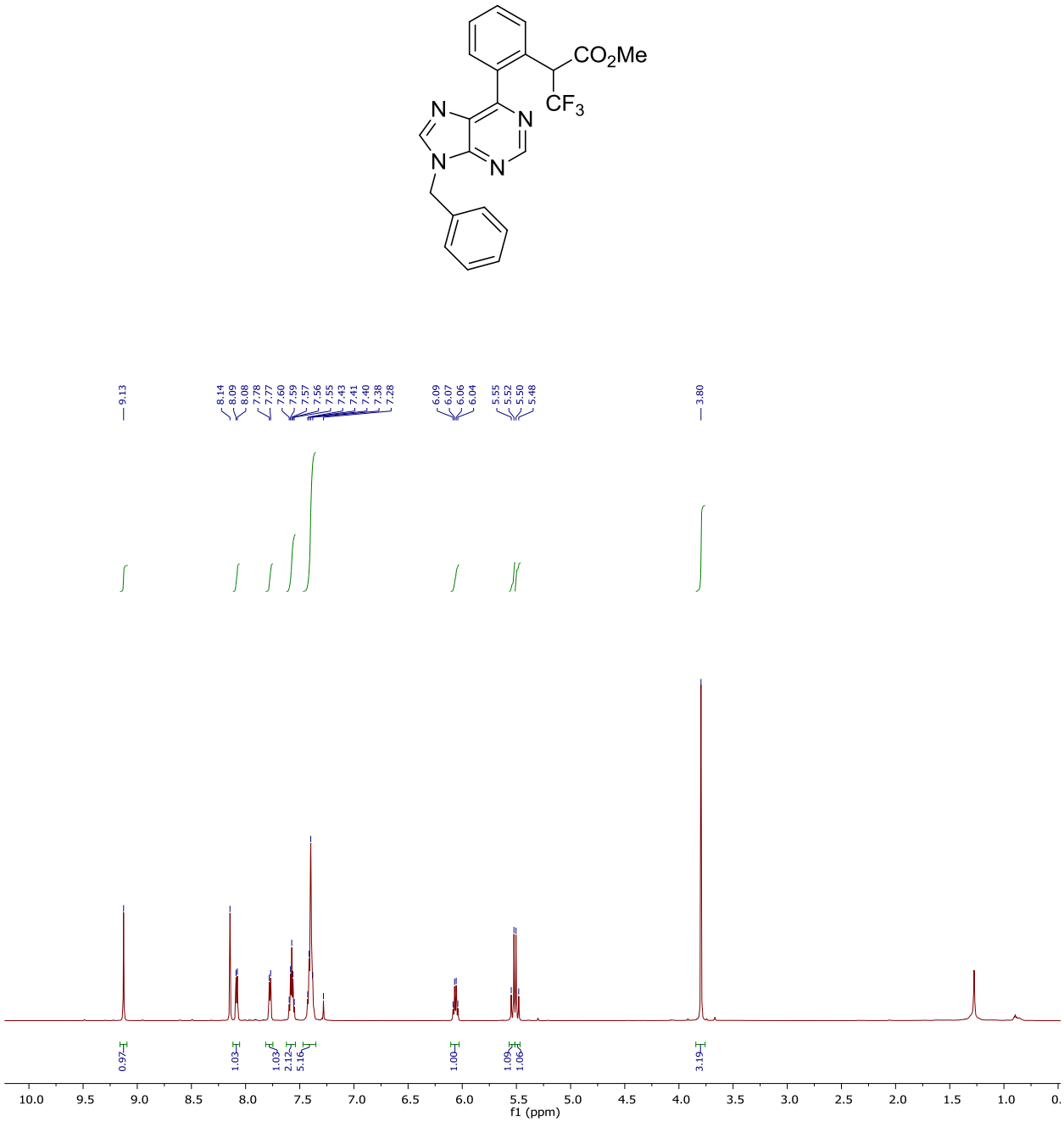

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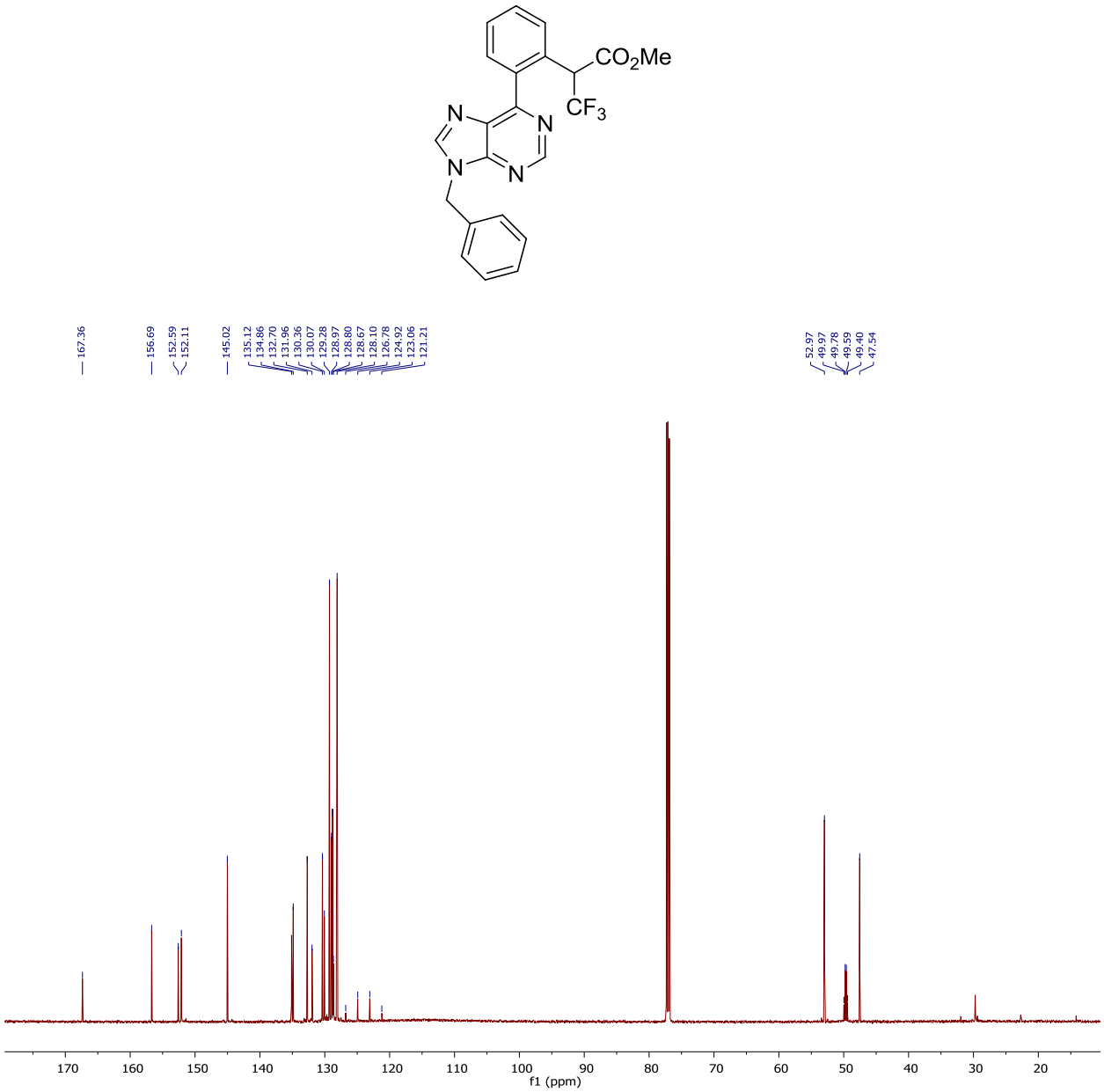

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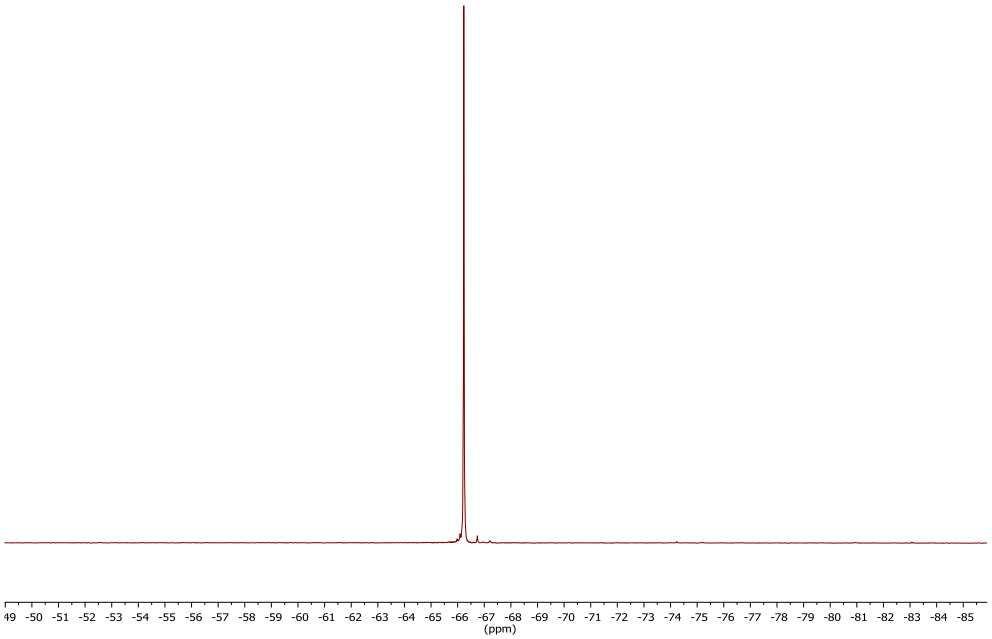

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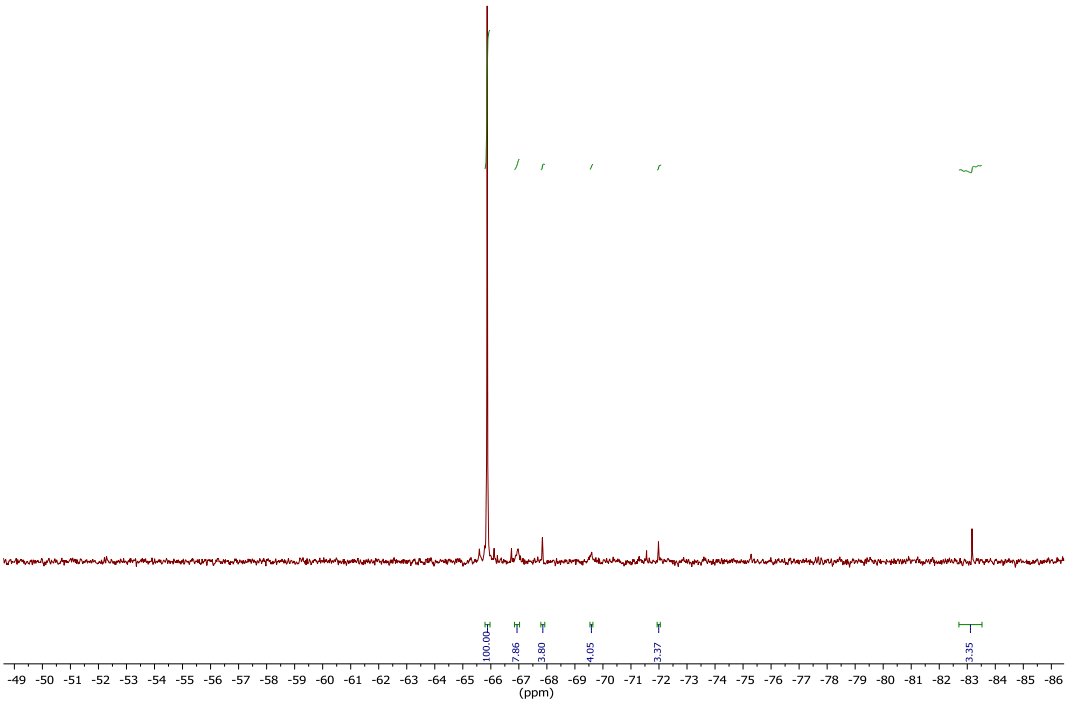
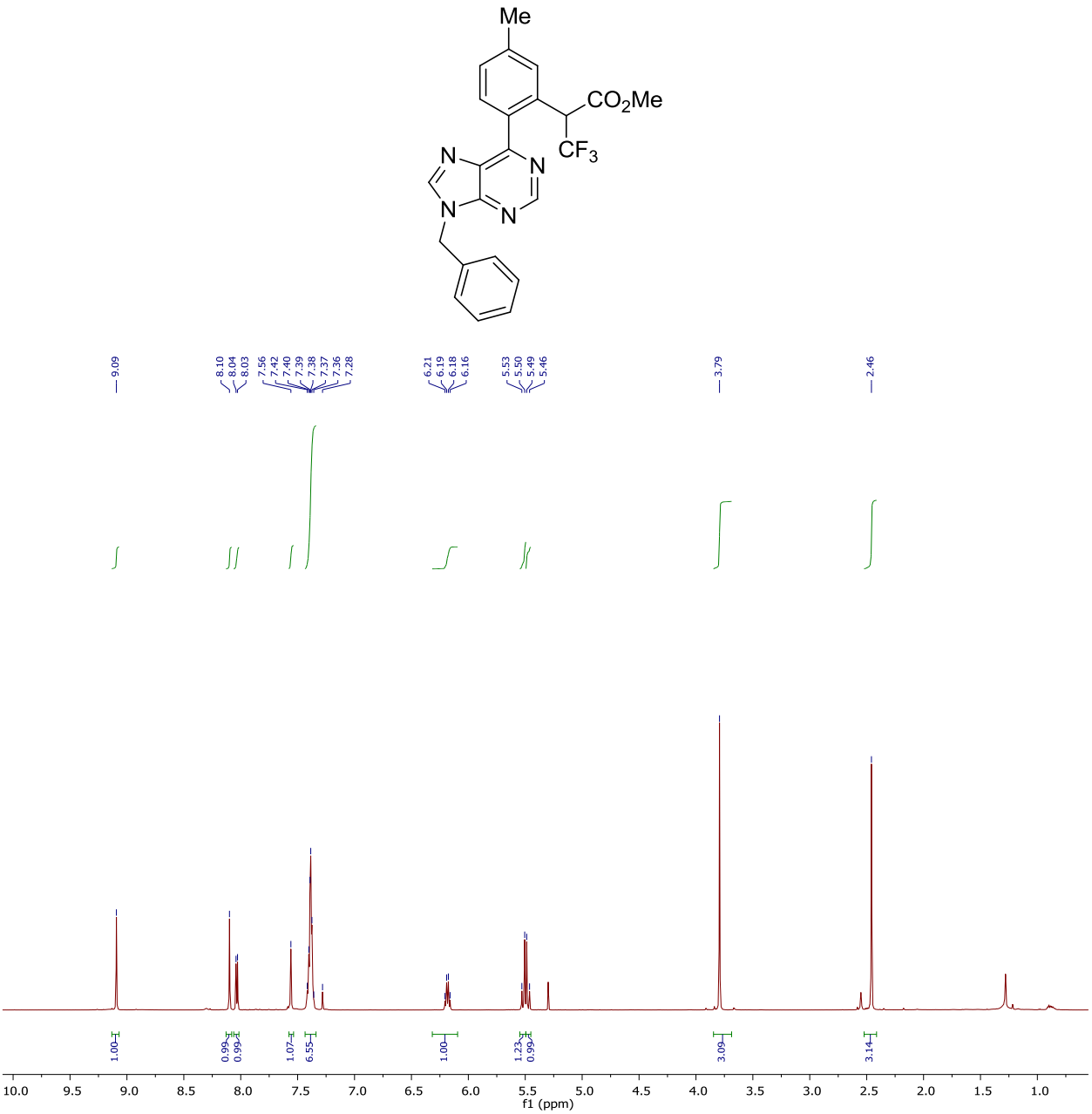


^{19}F NMR spectra of reaction mixture for **2f** in $CDCl_3$



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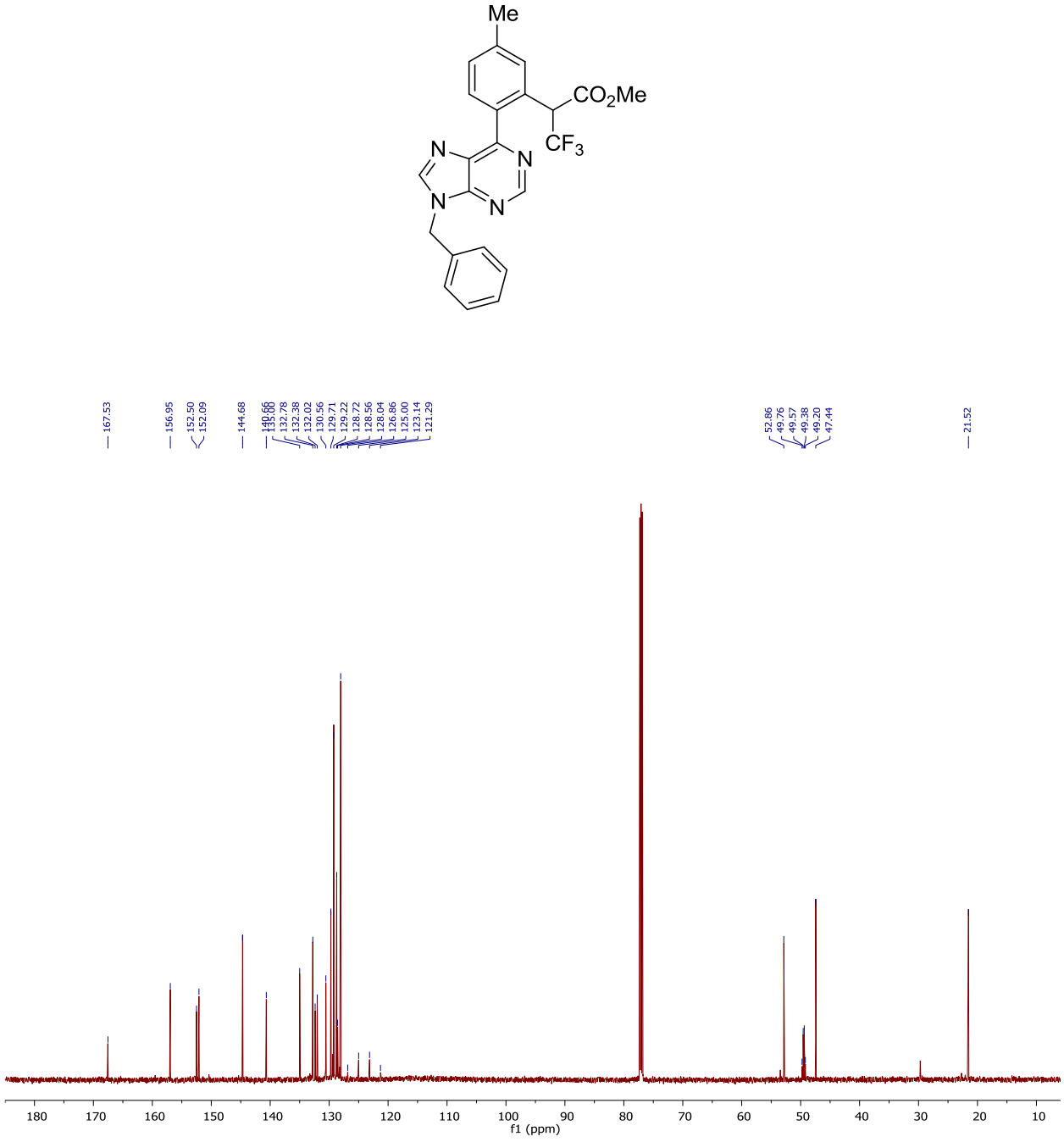

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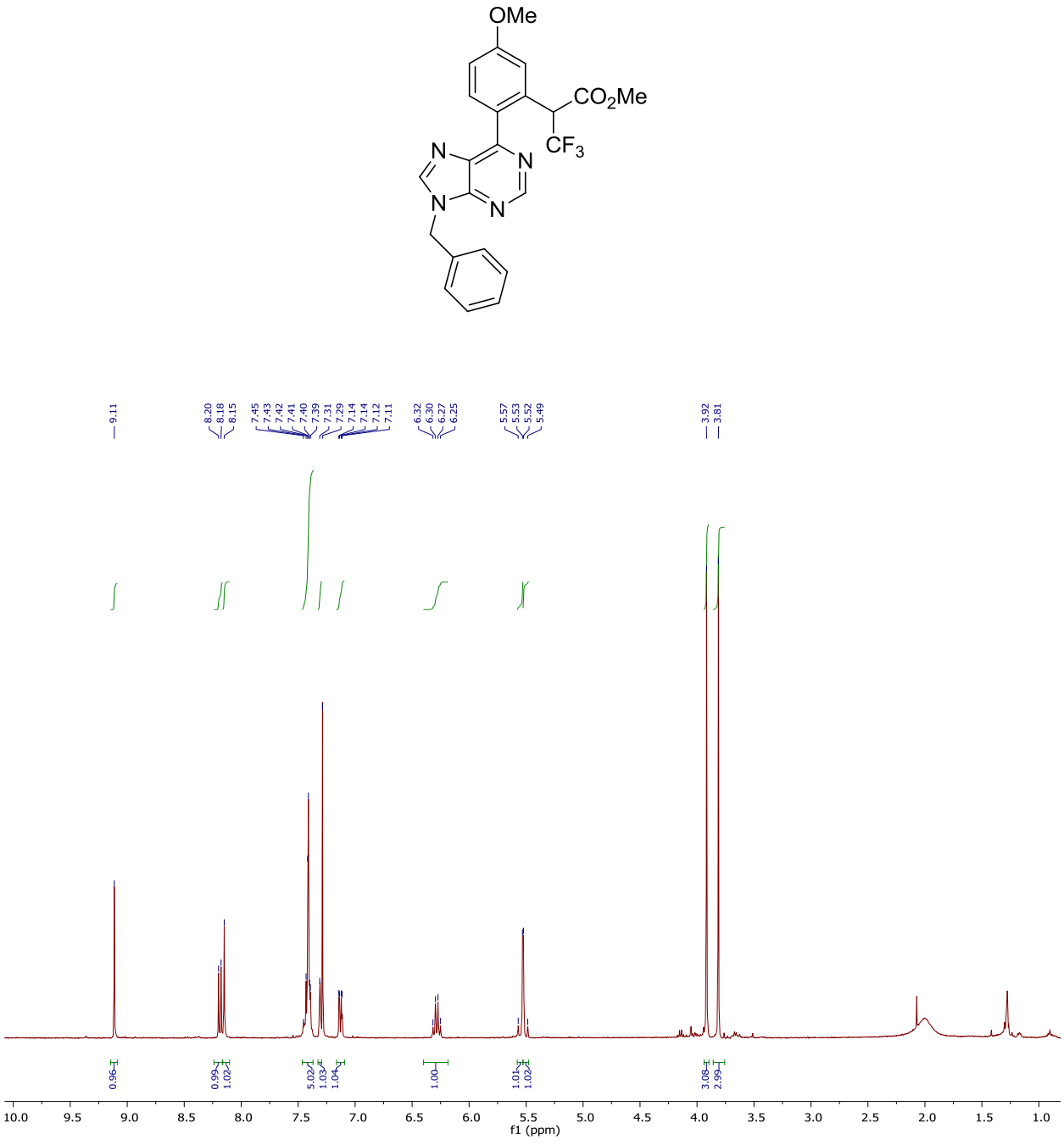

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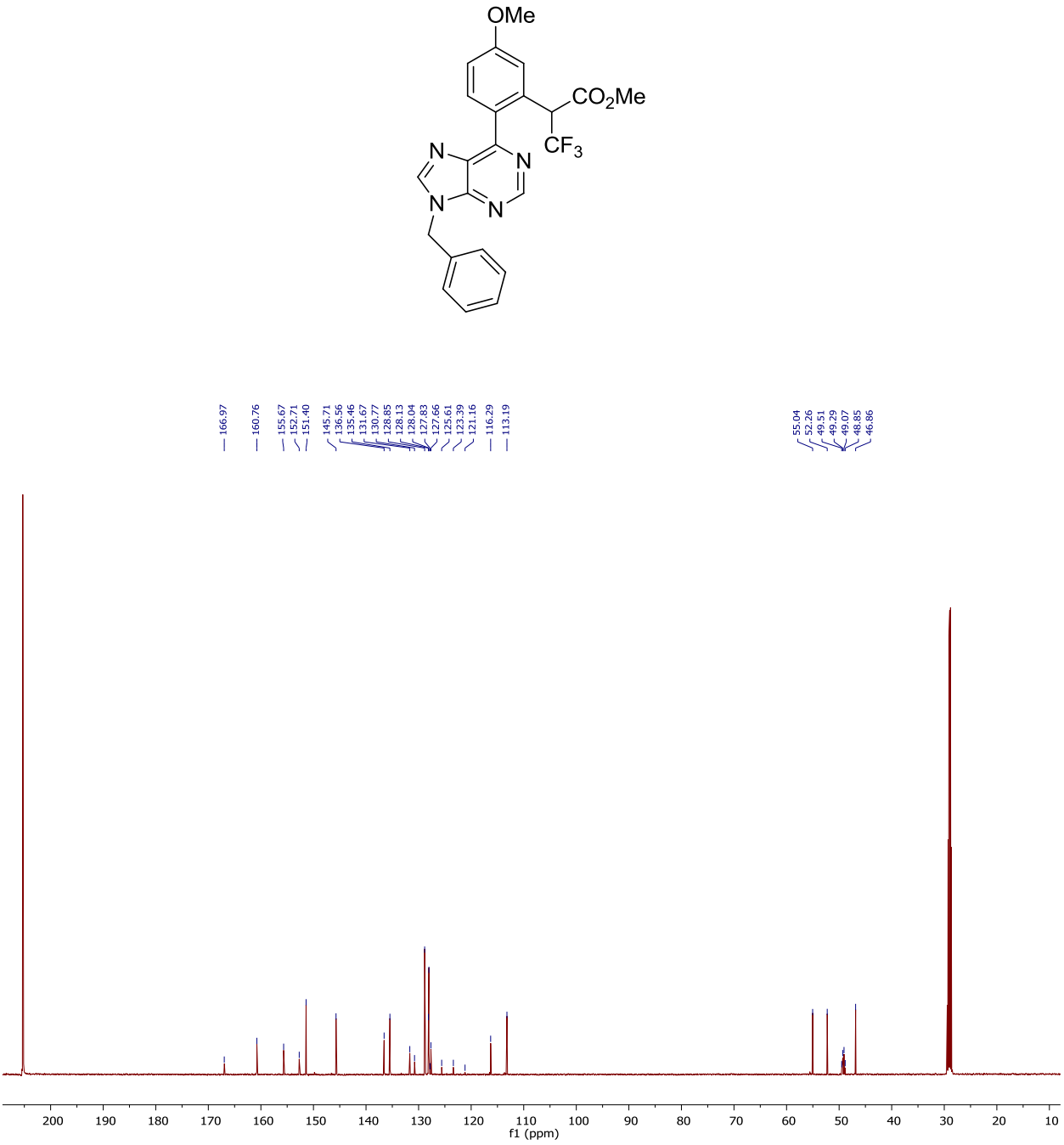

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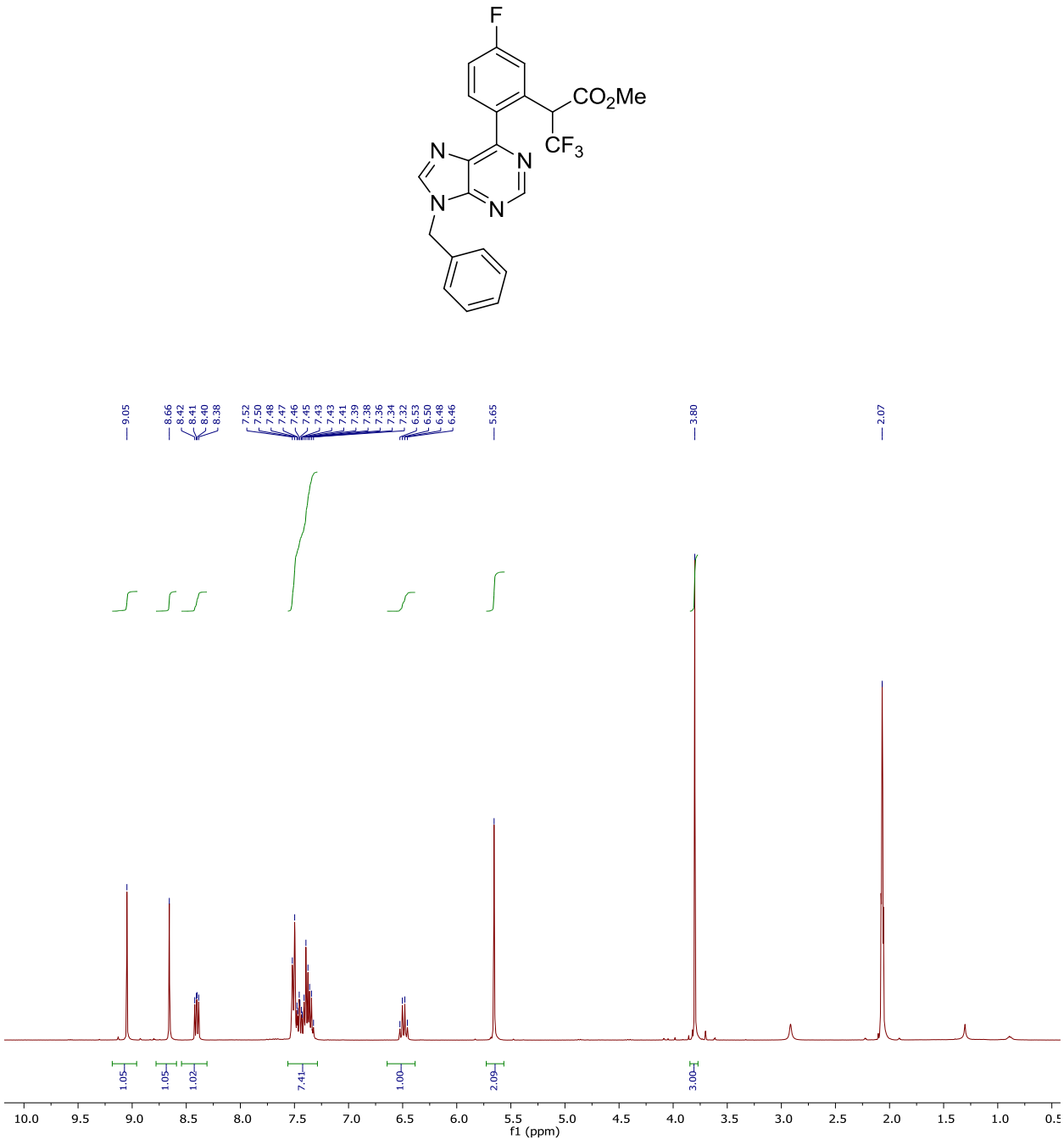

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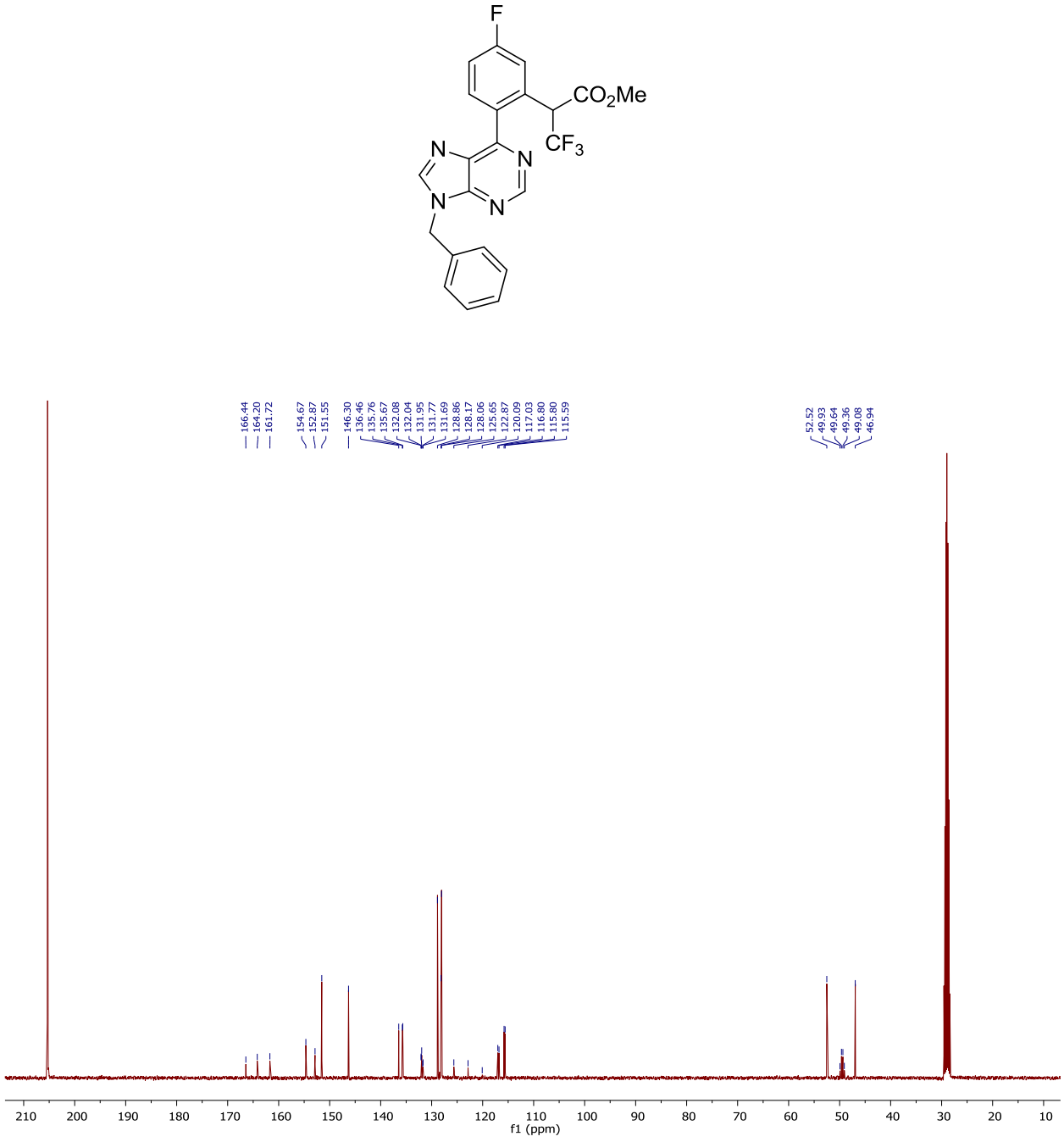

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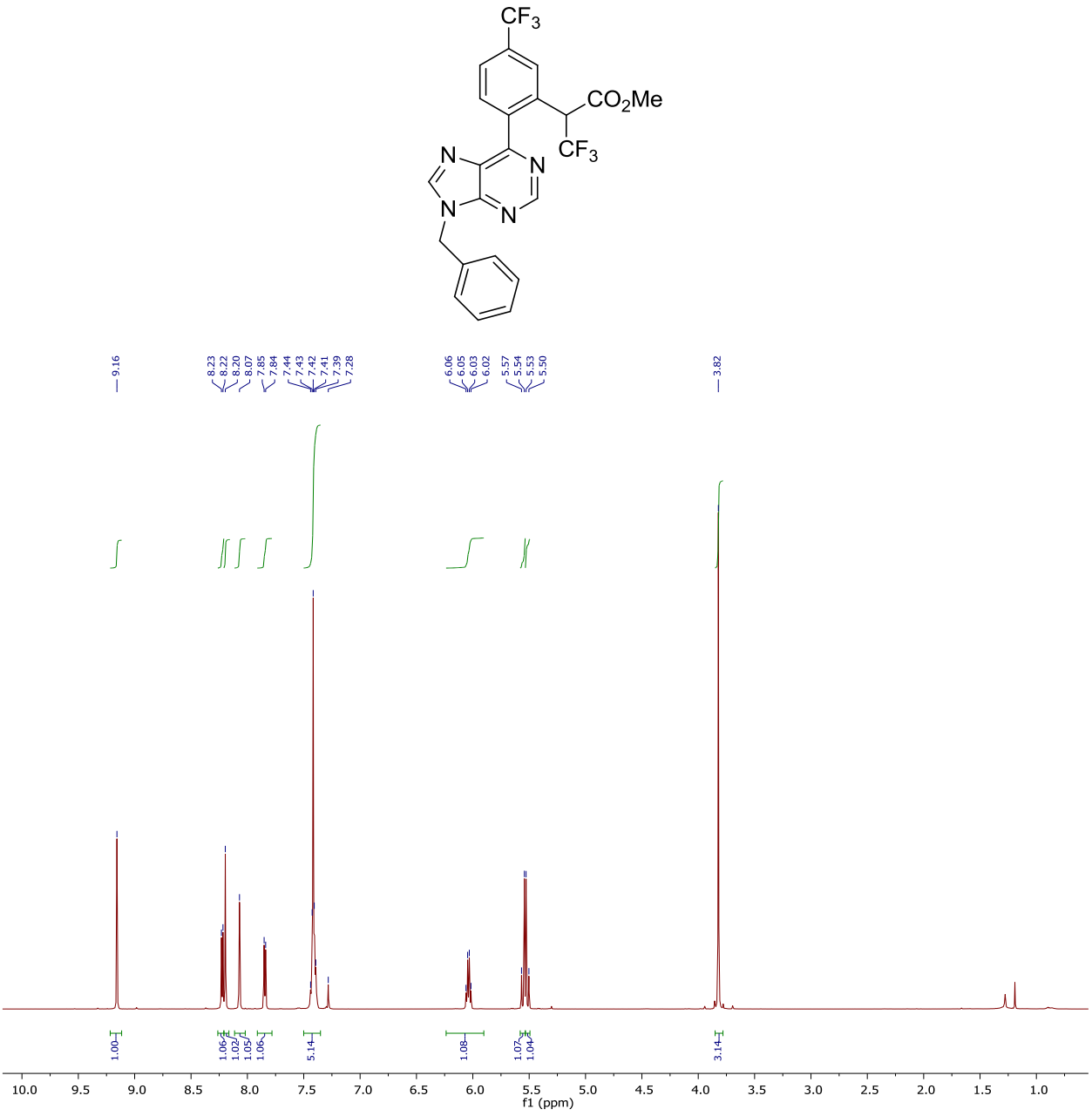

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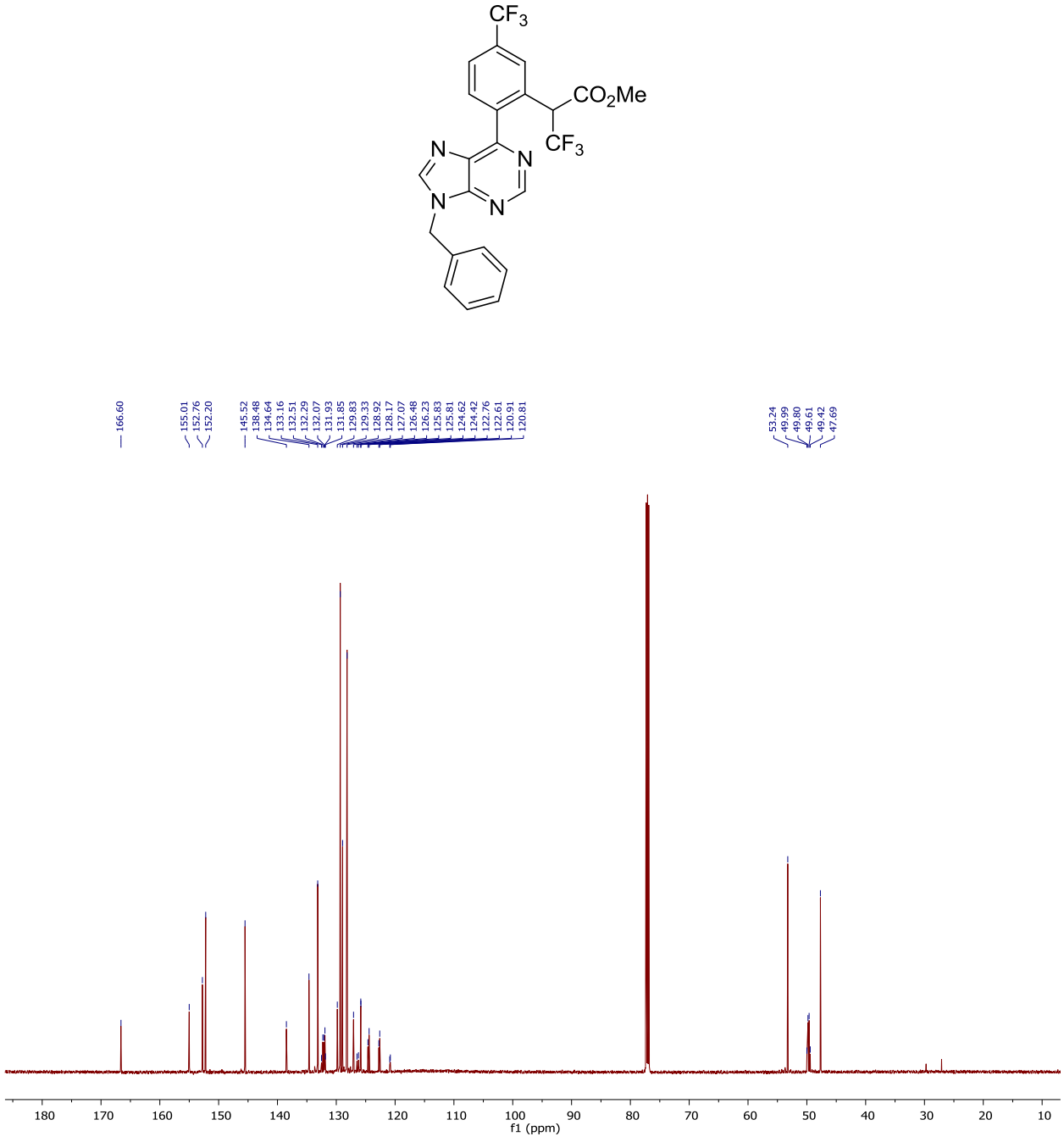

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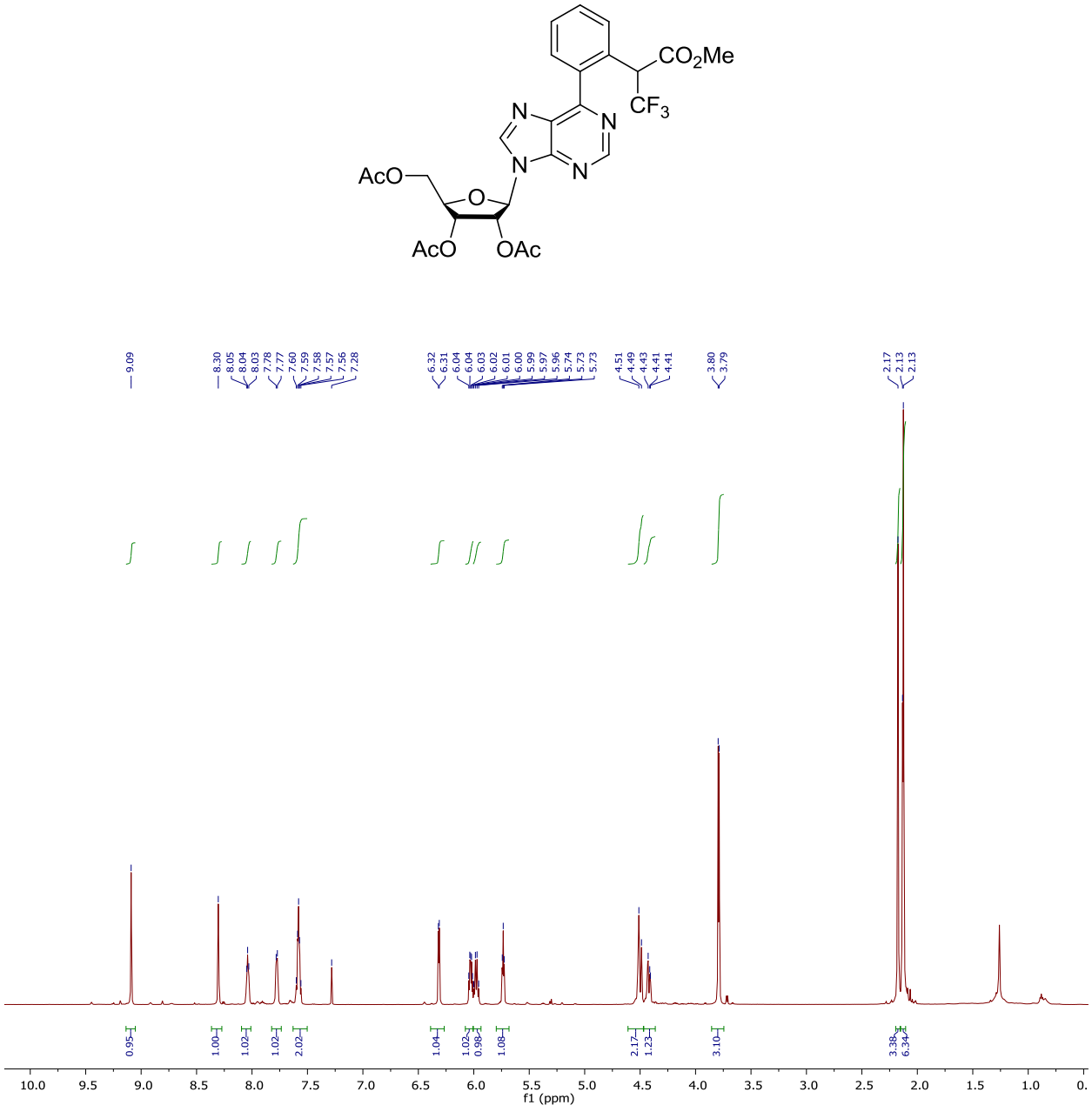

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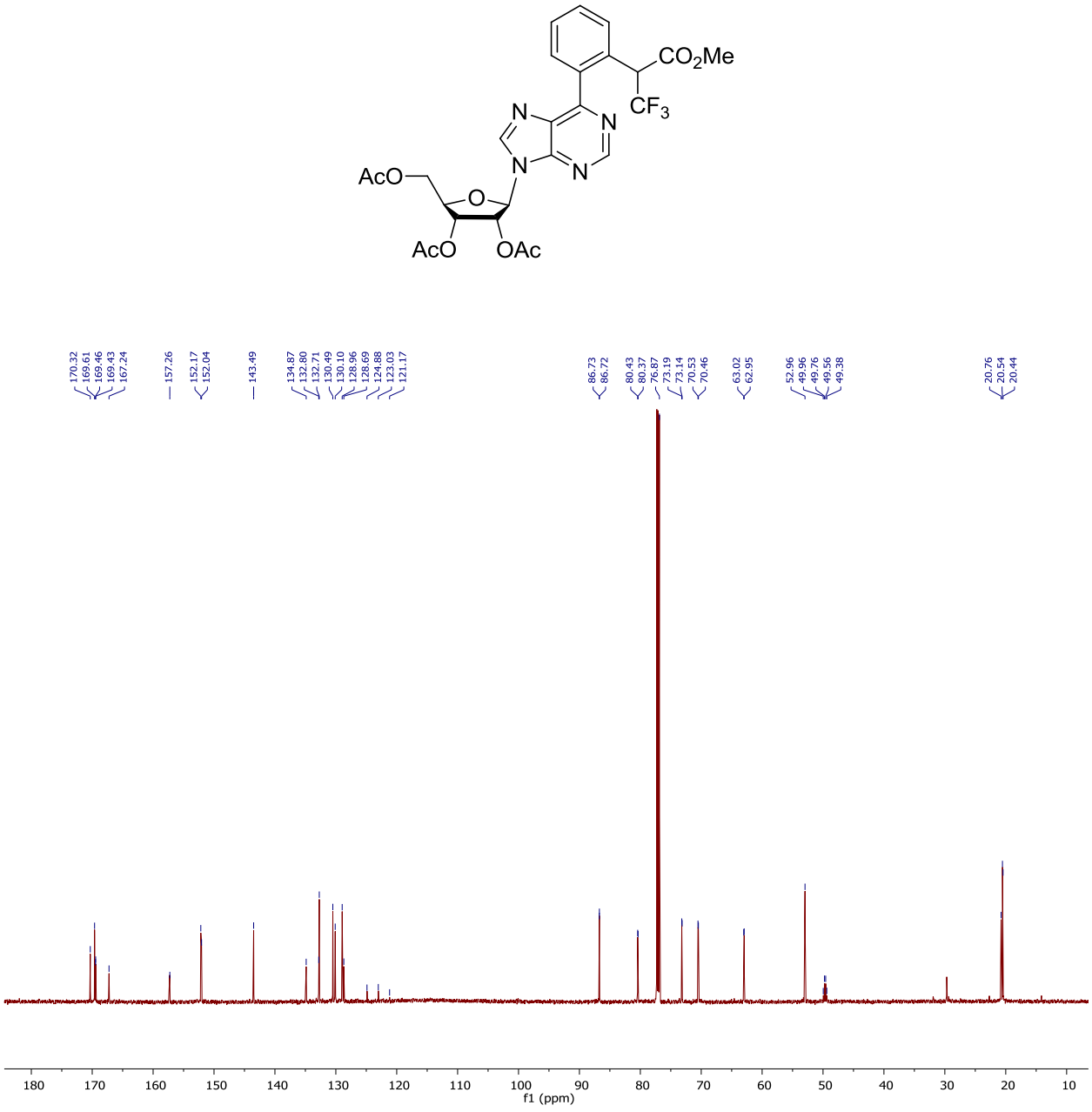

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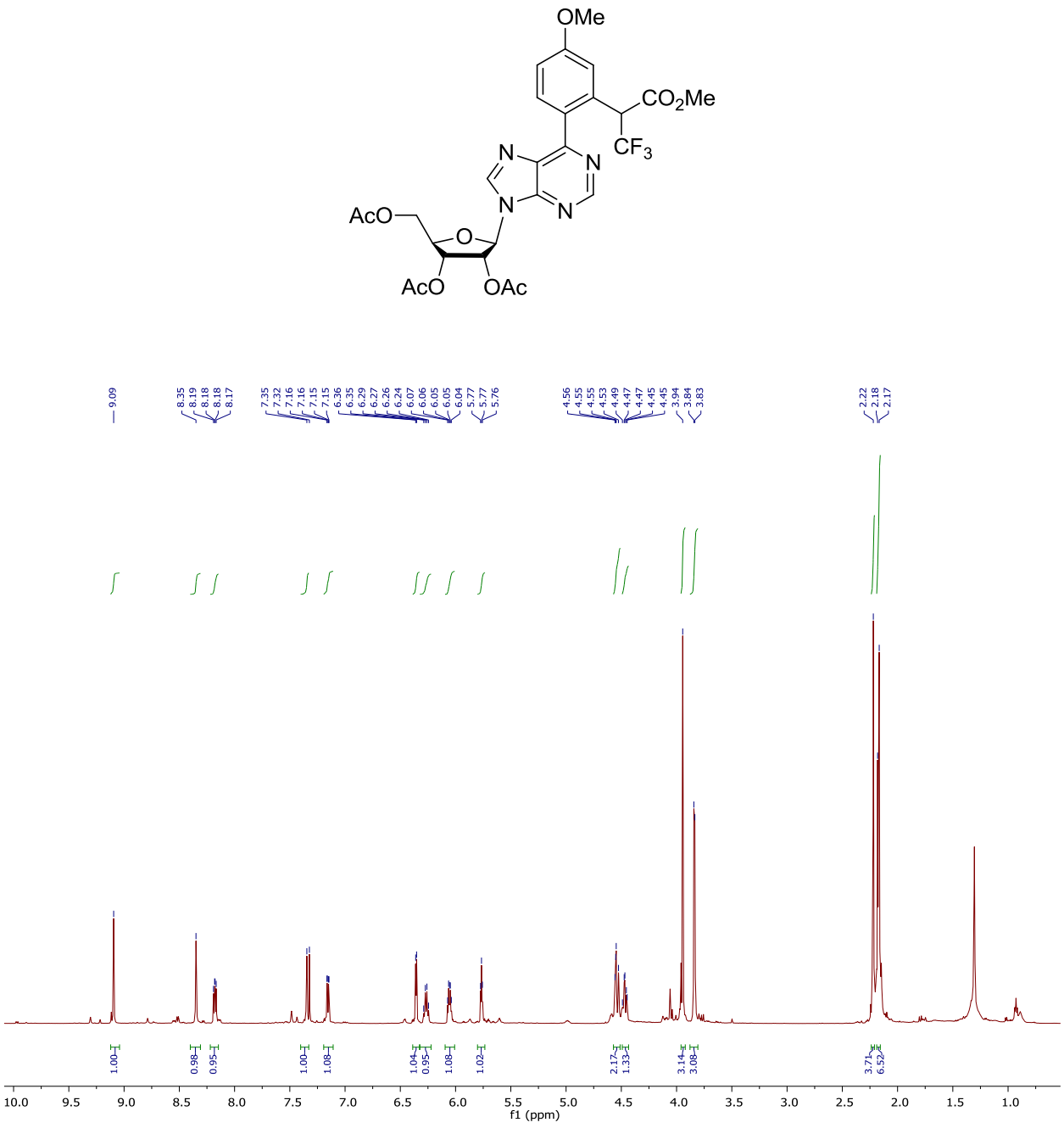

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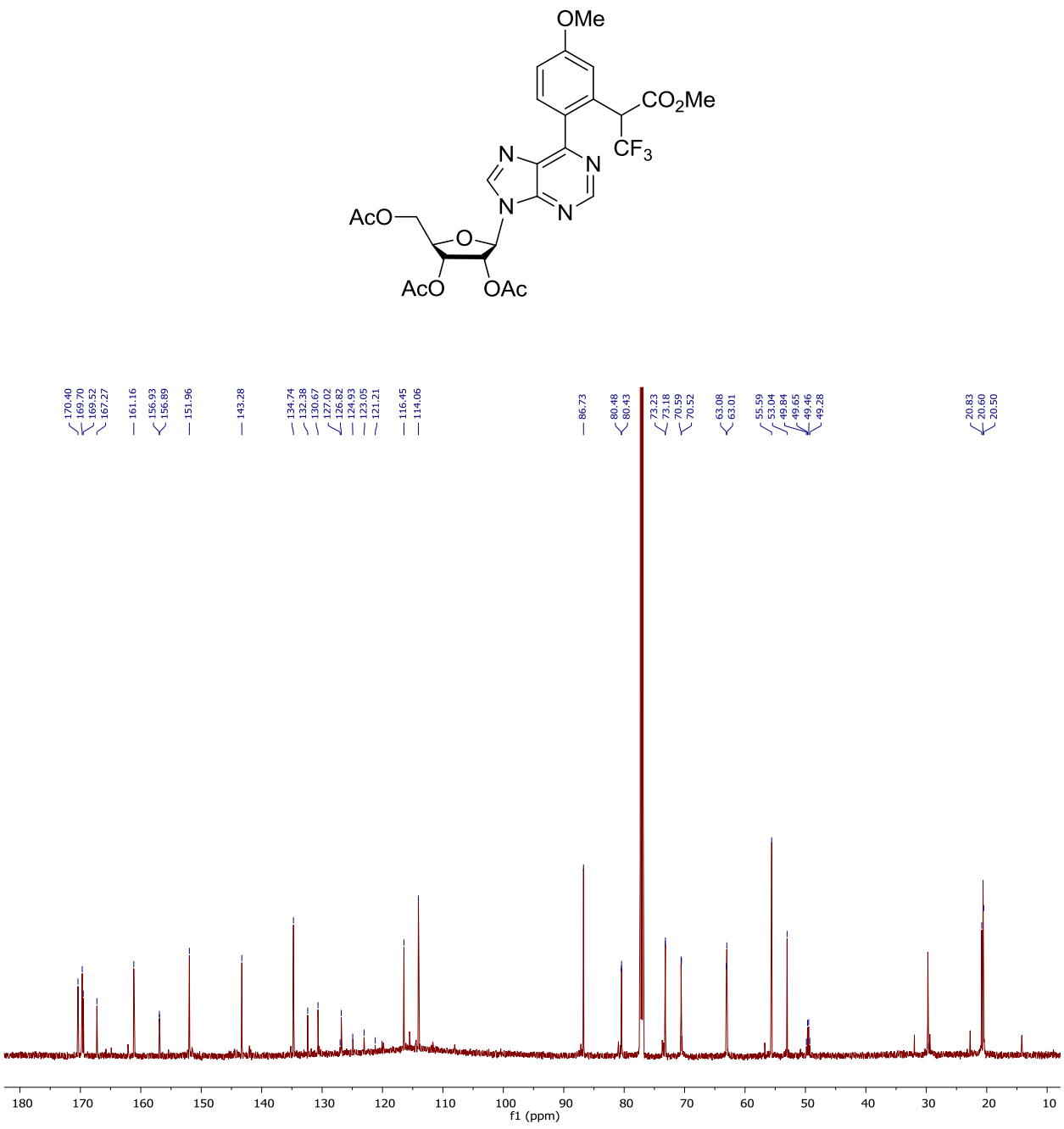
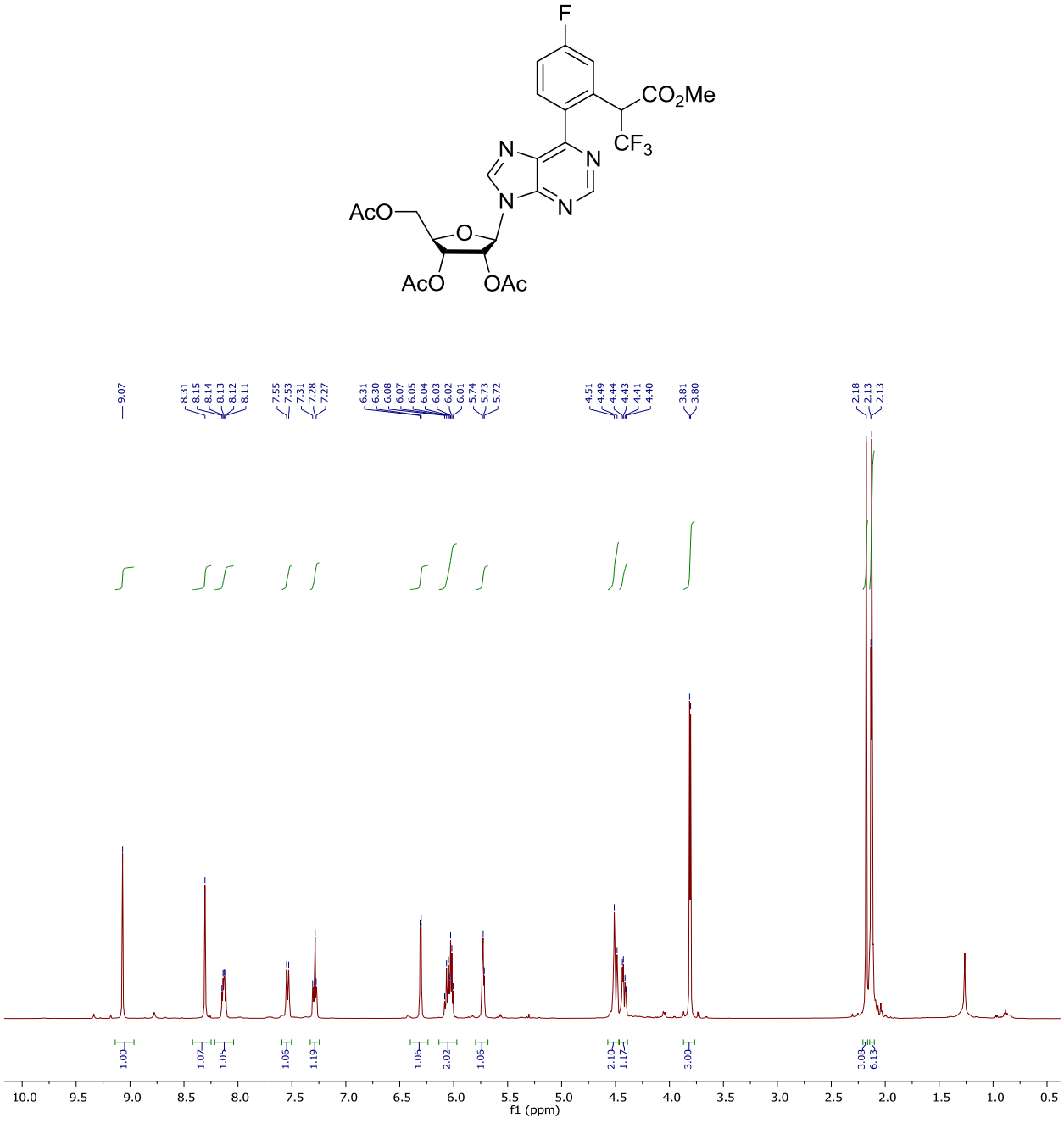


^{13}C NMR spectra of compound **2l** in $CDCl_3$



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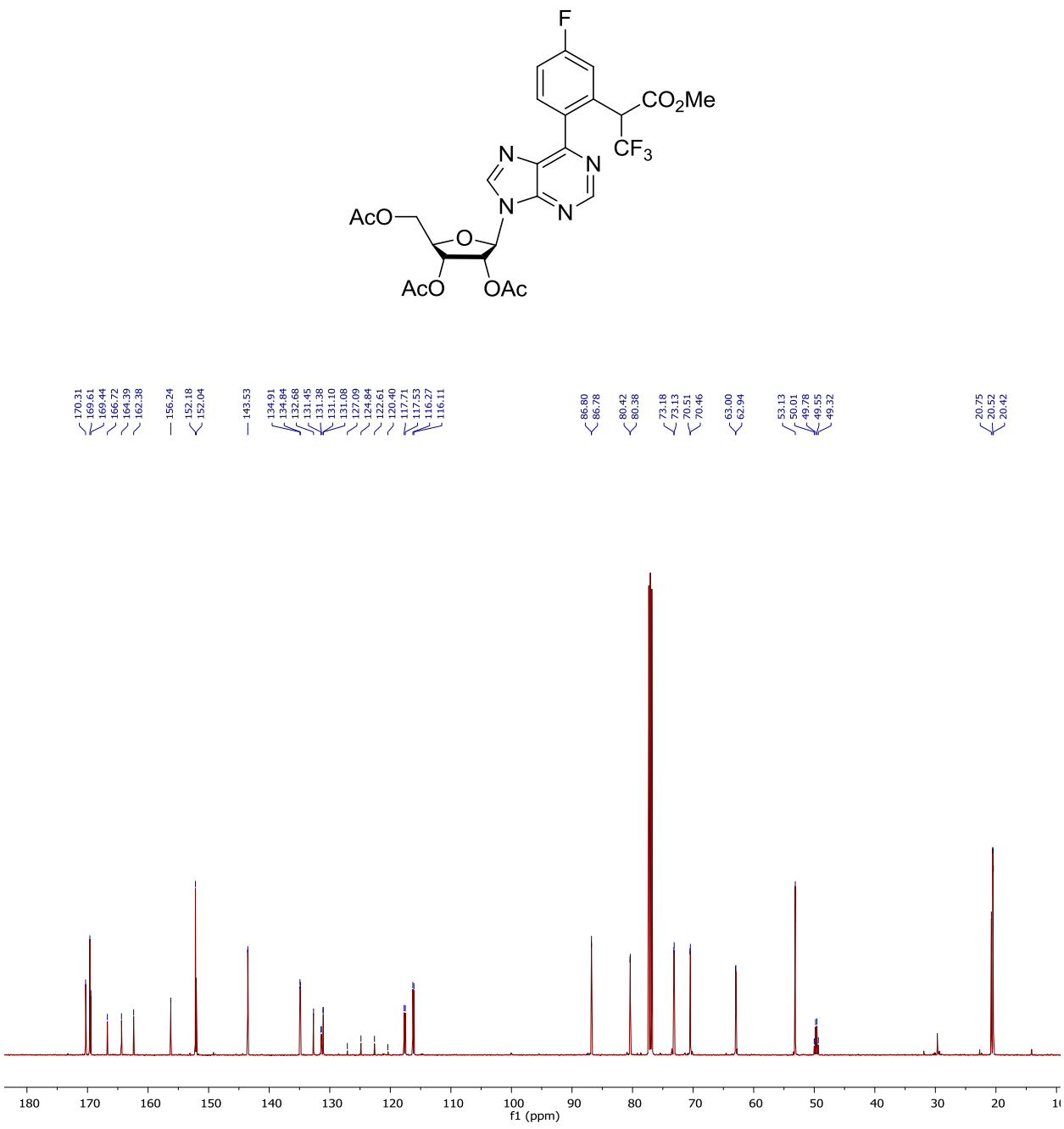
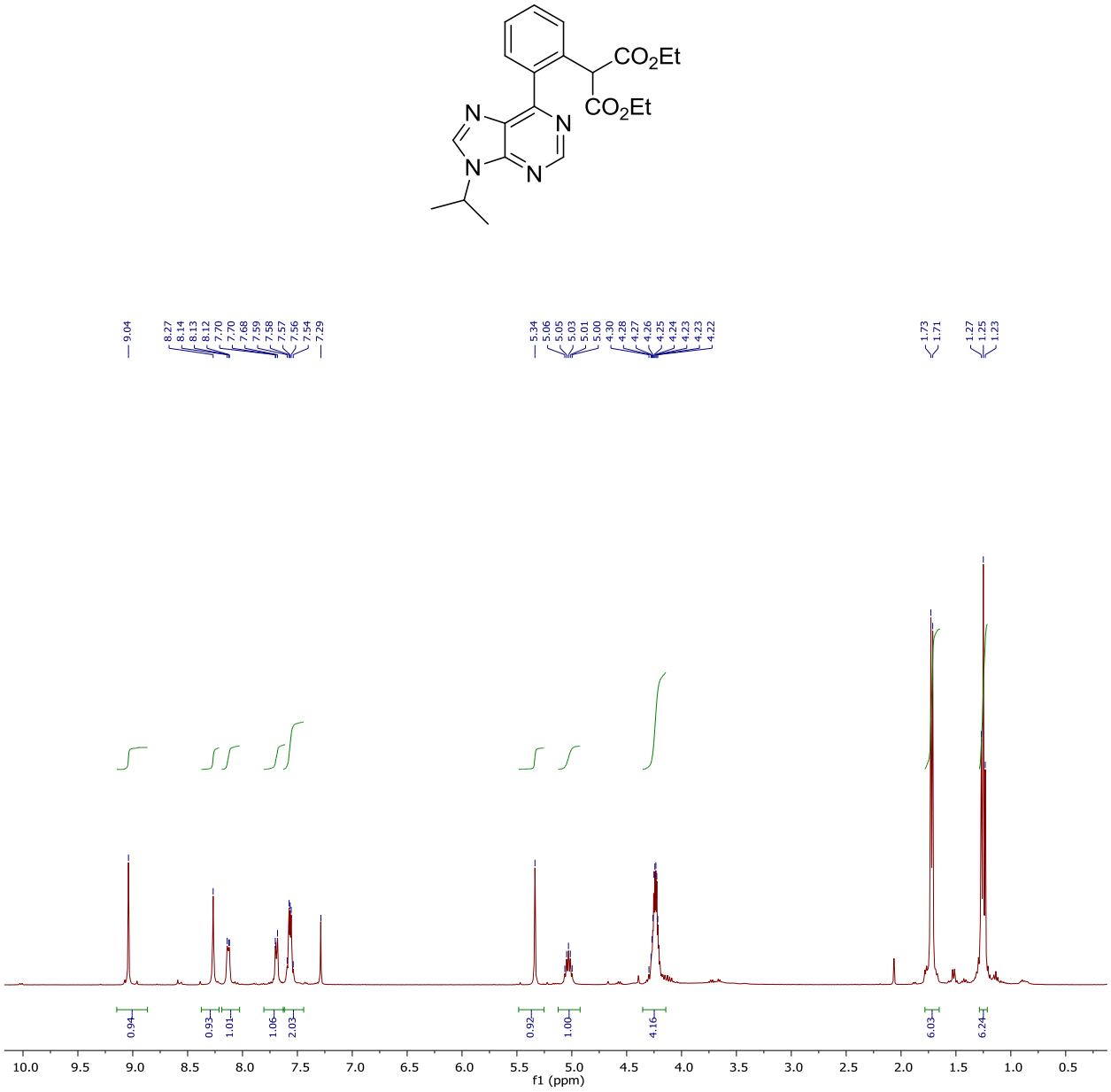
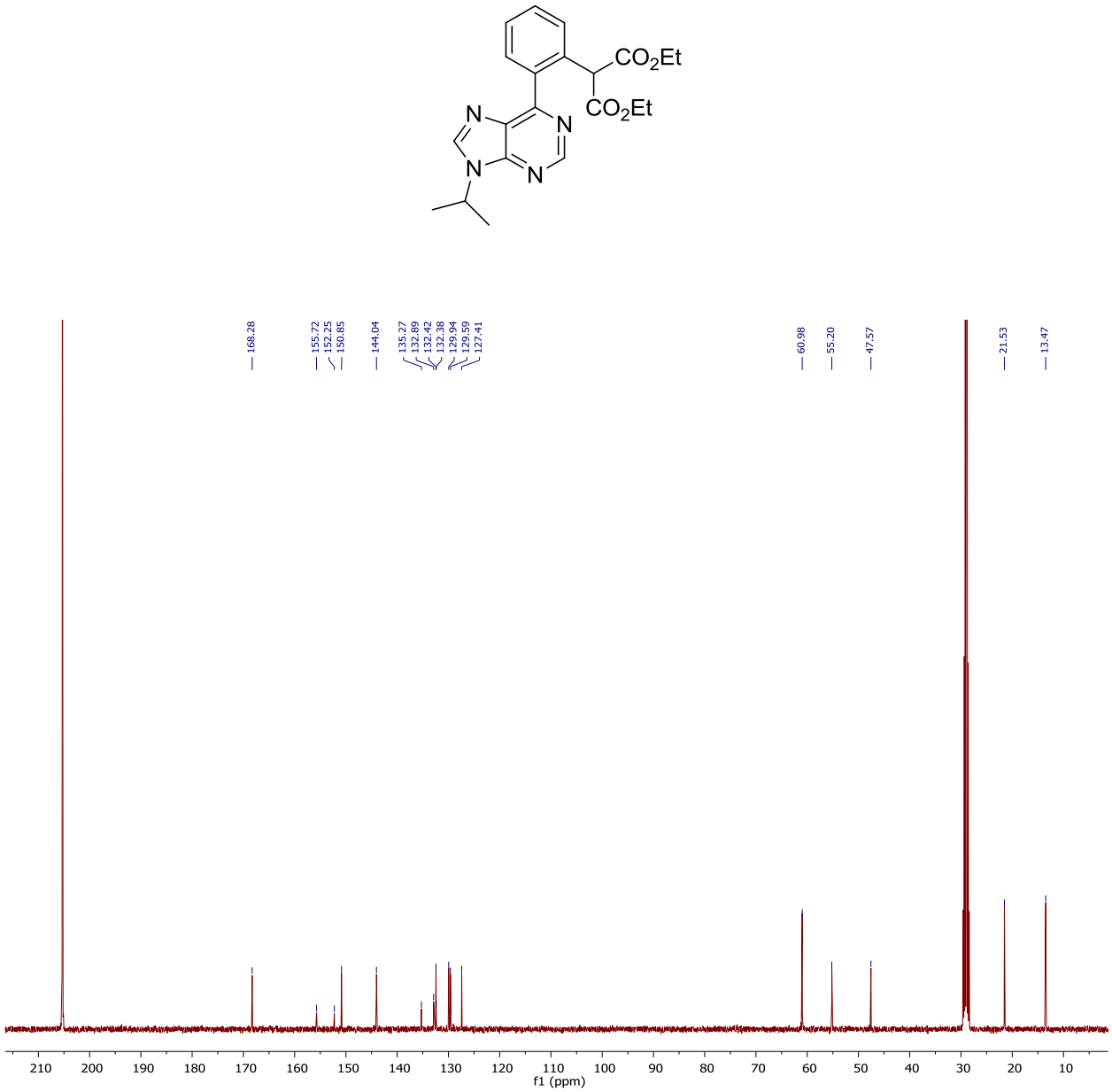


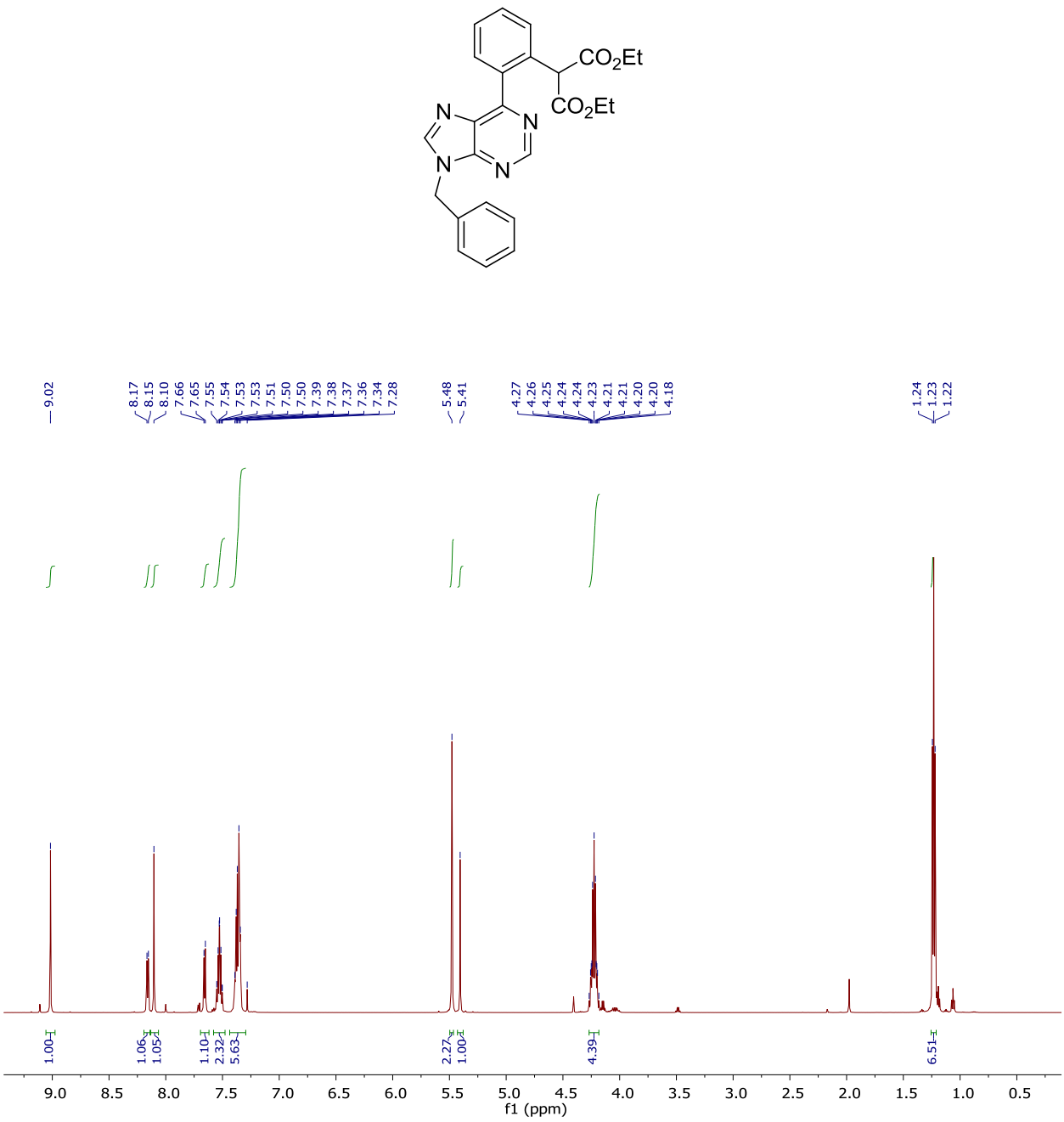
^{13}C NMR spectra of compound **2m** in $CDCl_3$



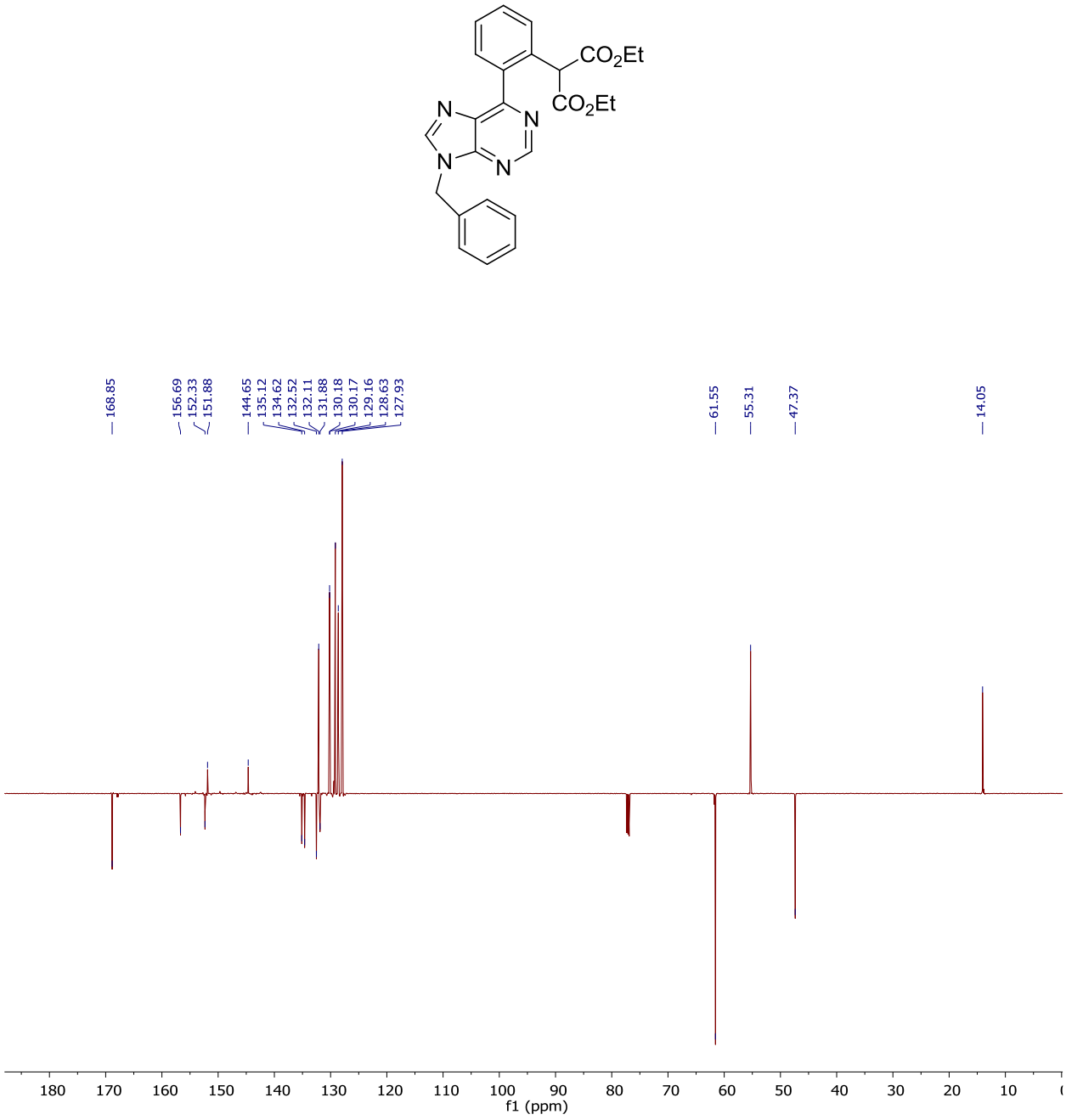
^{1}H NMR spectra of compound **3a** in $CDCl_3$



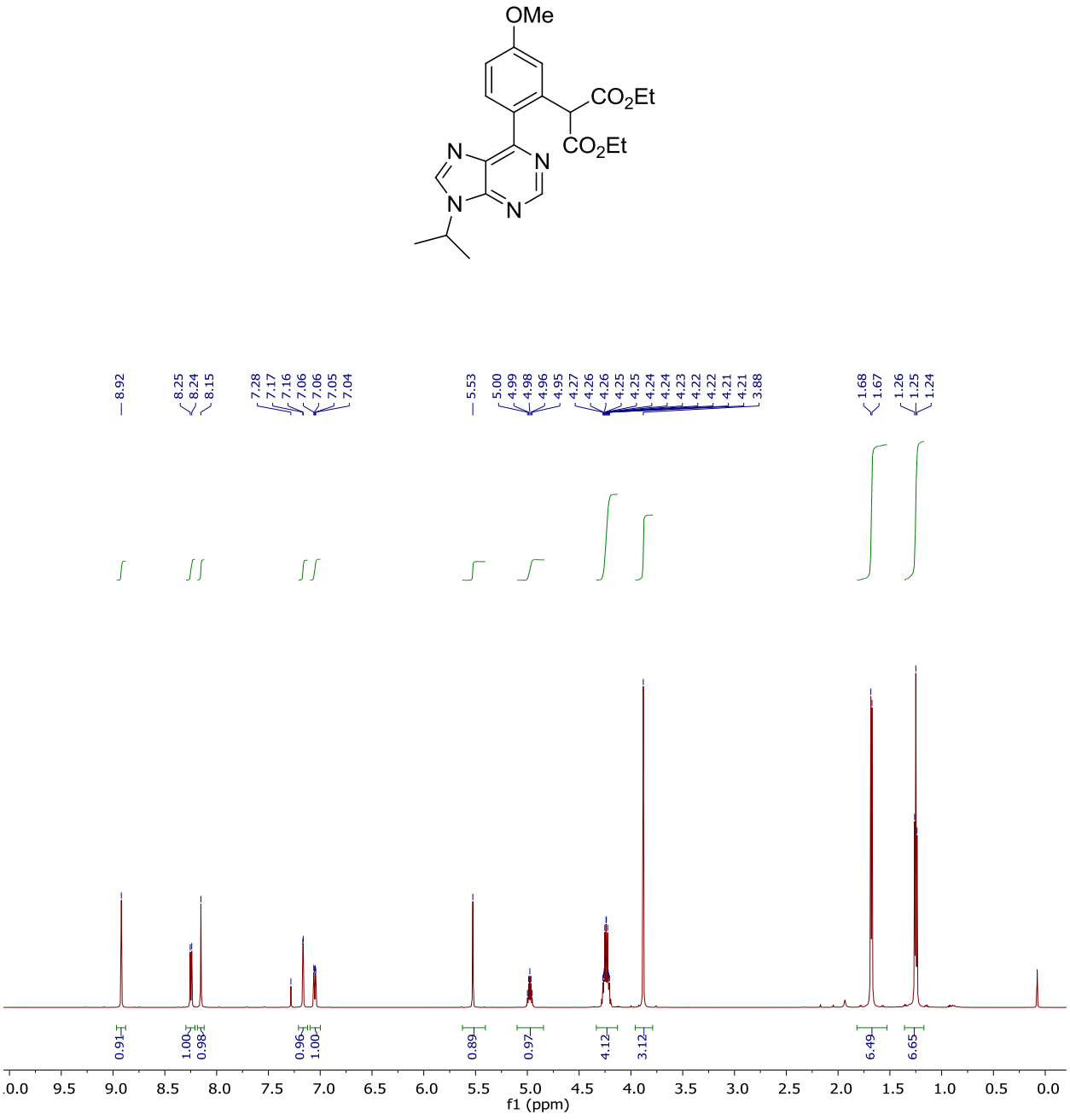
^{13}C NMR spectra of compound **3a** in $(CD_3)_2CO$



^{1}H NMR spectrum of compound **3b** in $CDCl_3$



^{13}C NMR spectrum (*J*-mod) of compound **3b** in $CDCl_3$



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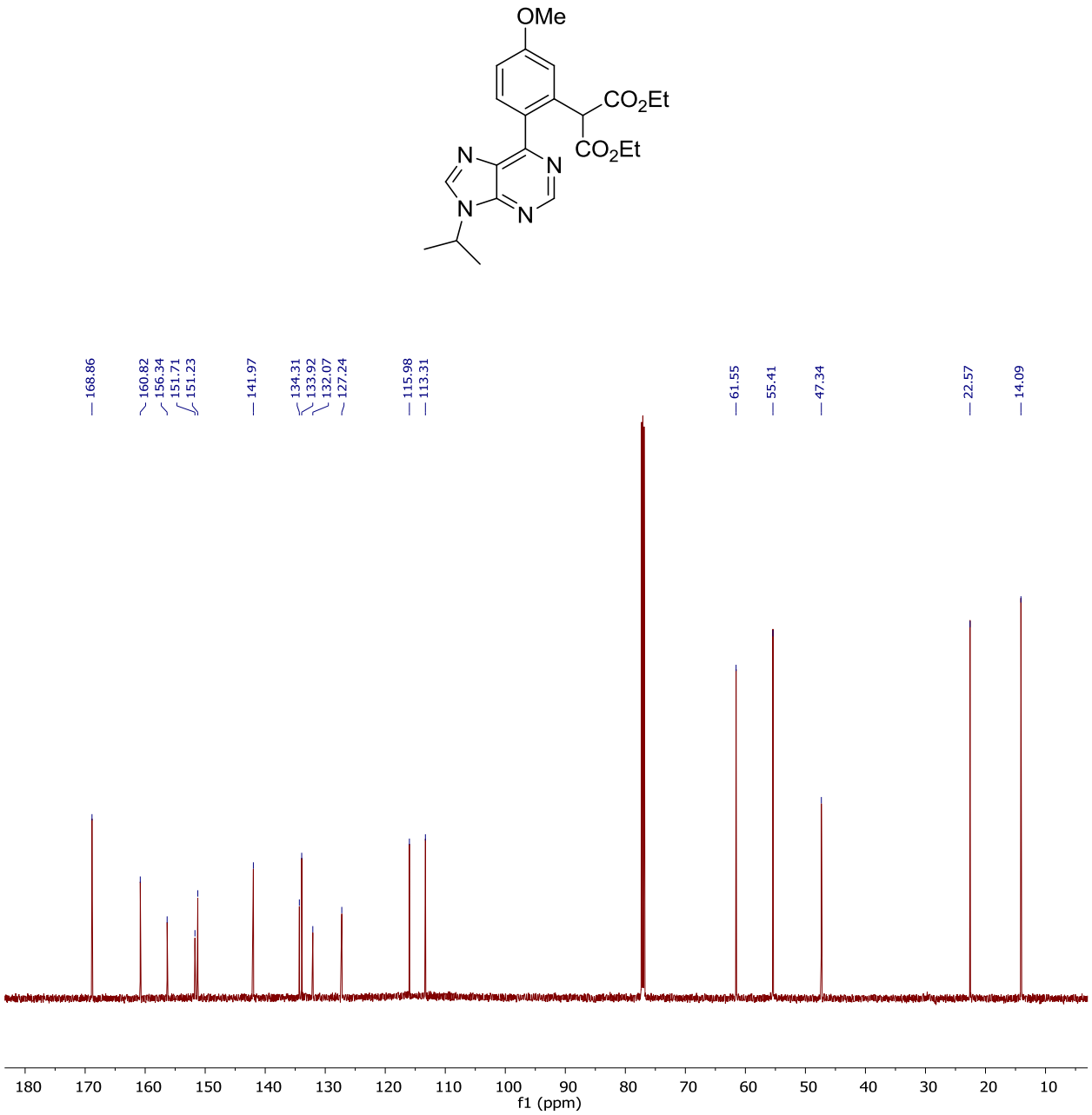

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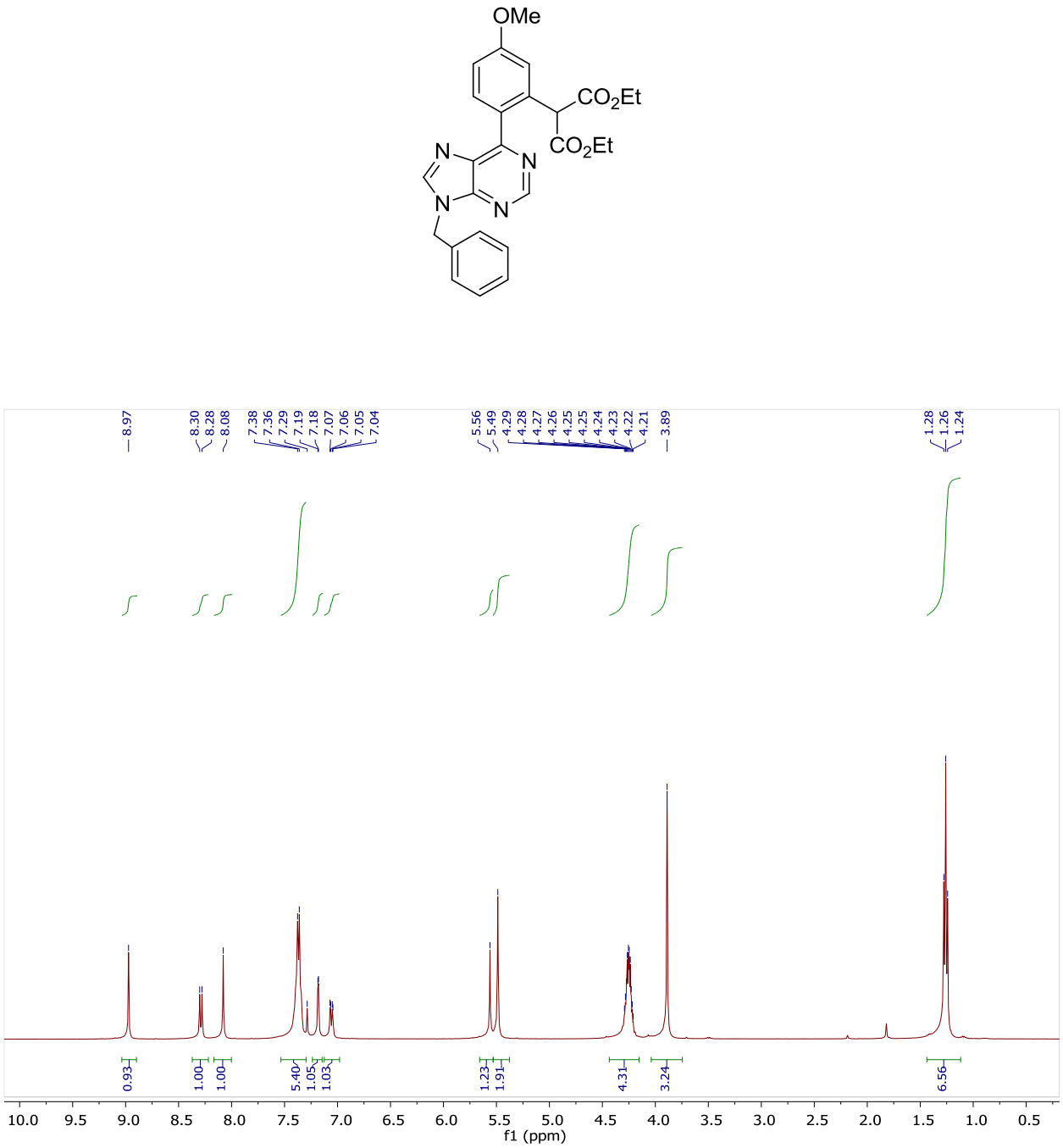

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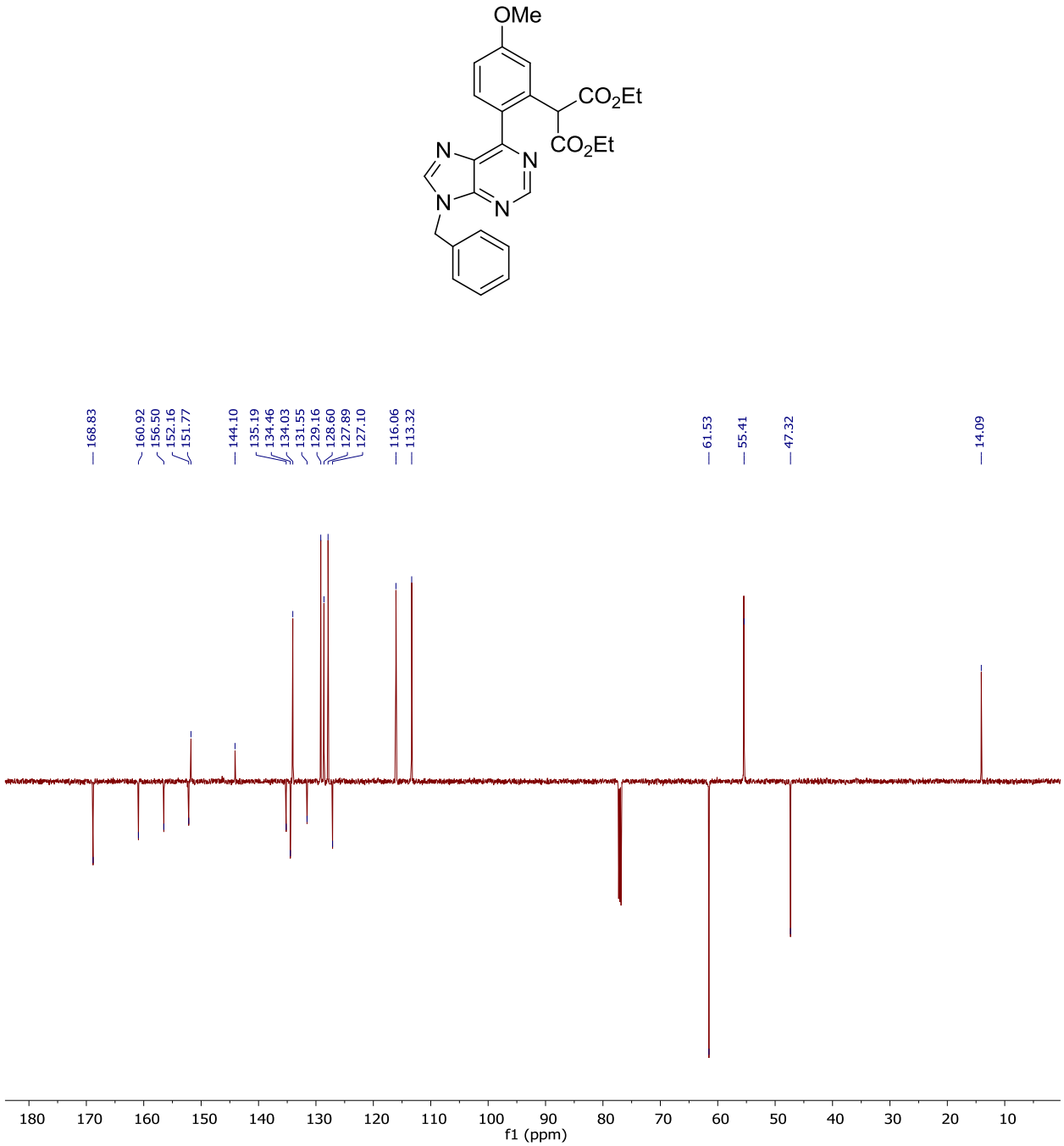

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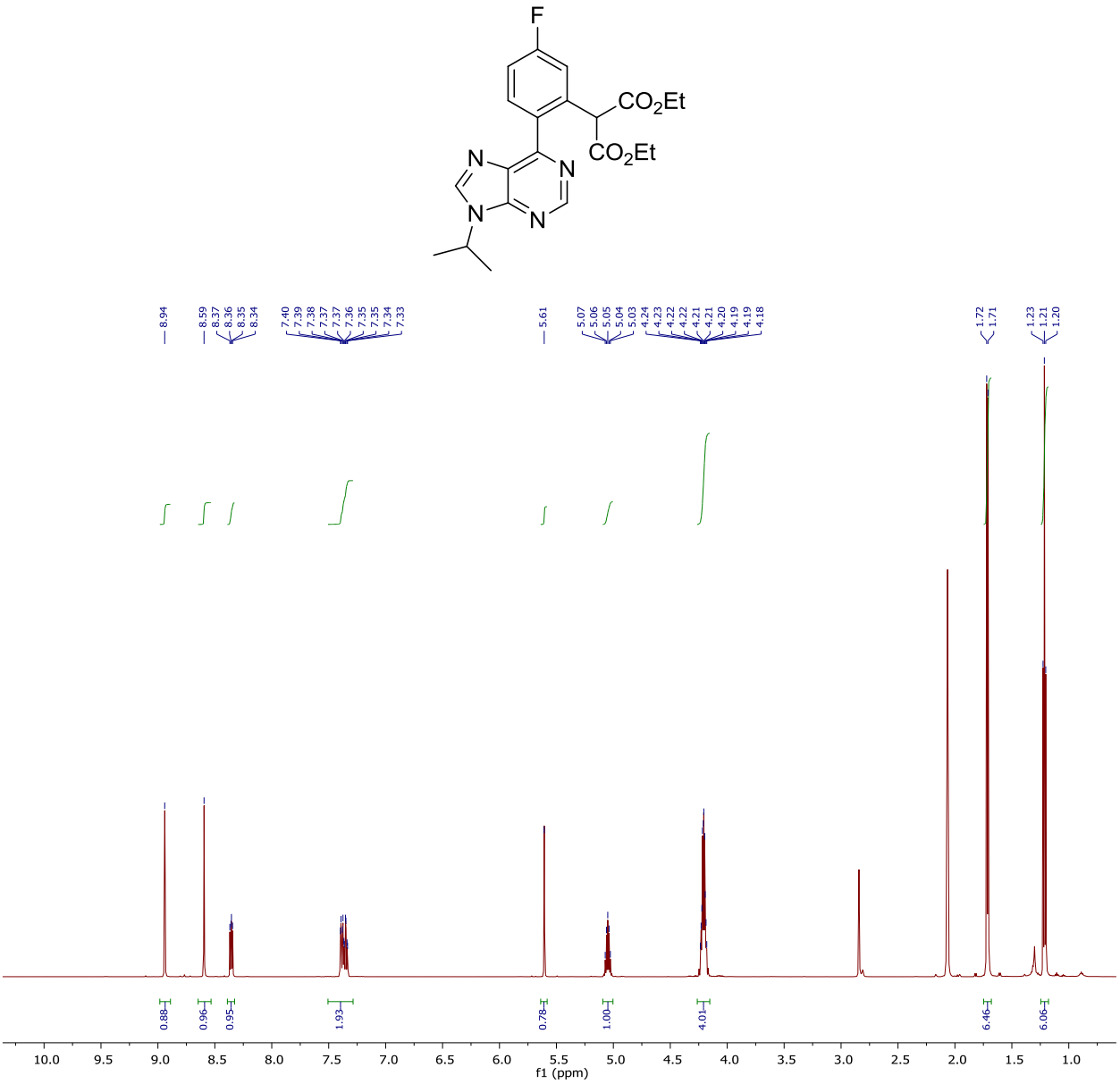
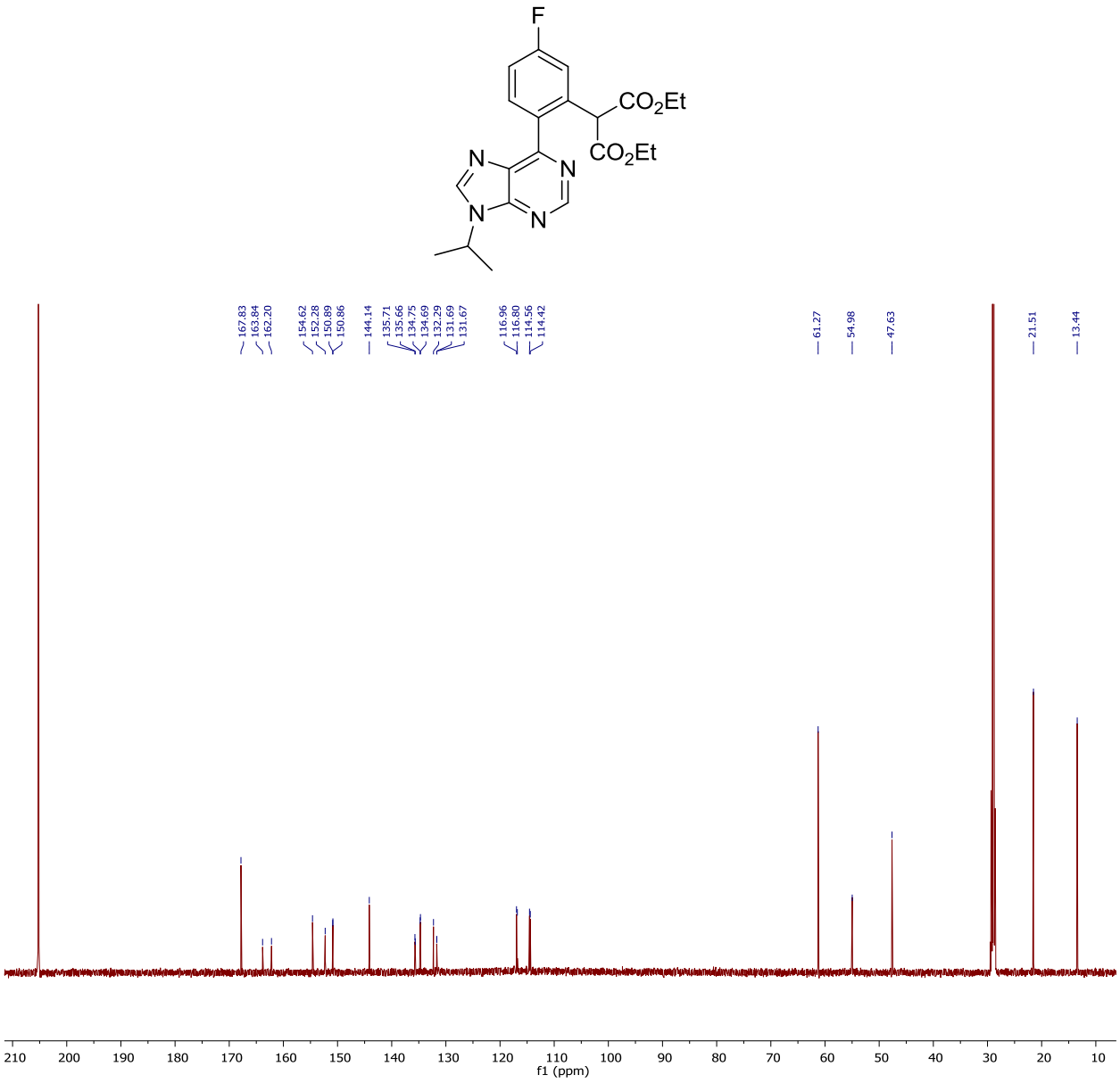


^{1}H NMR spectra of compound **3e** in $(CD_3)_2CO$



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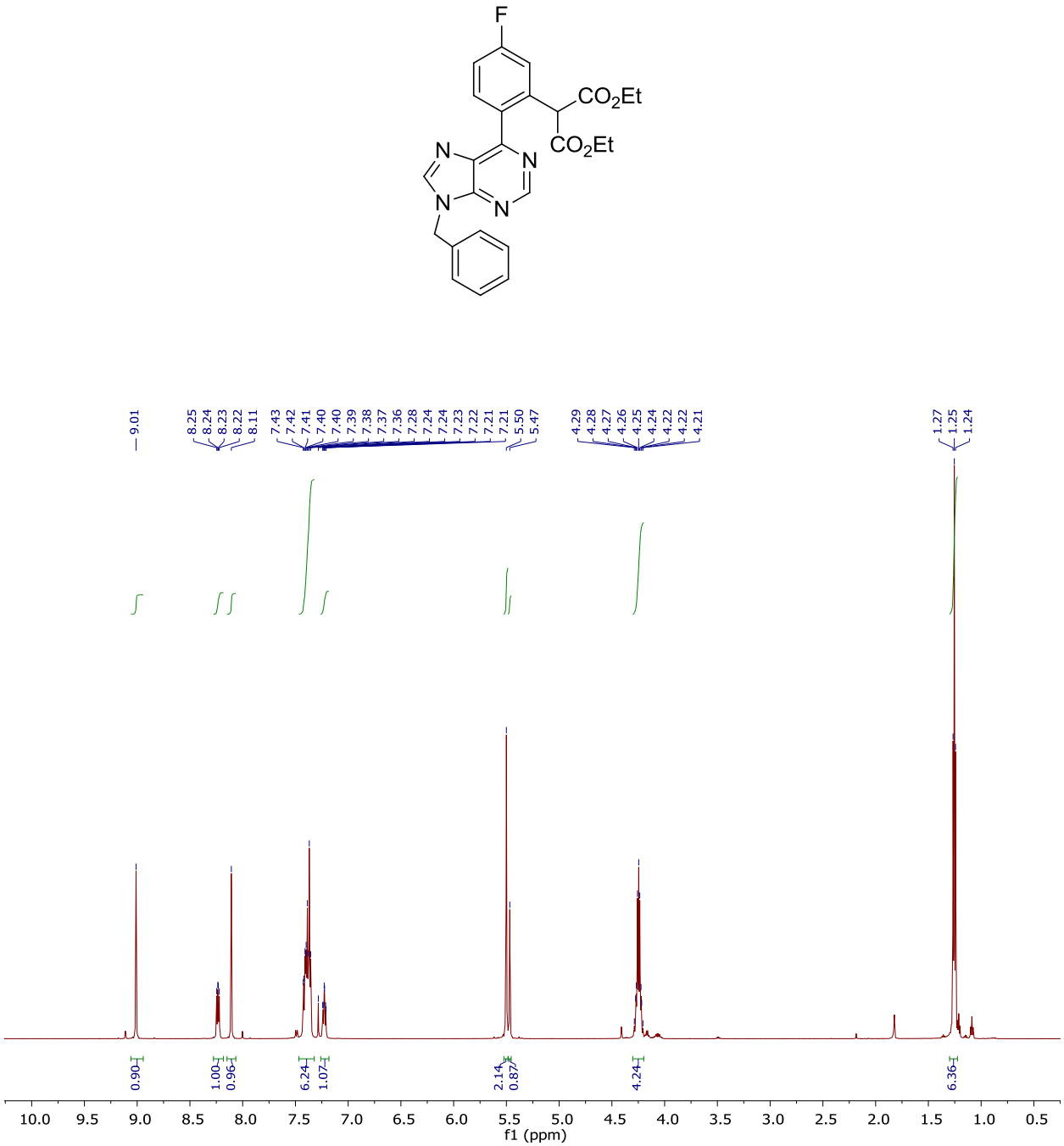
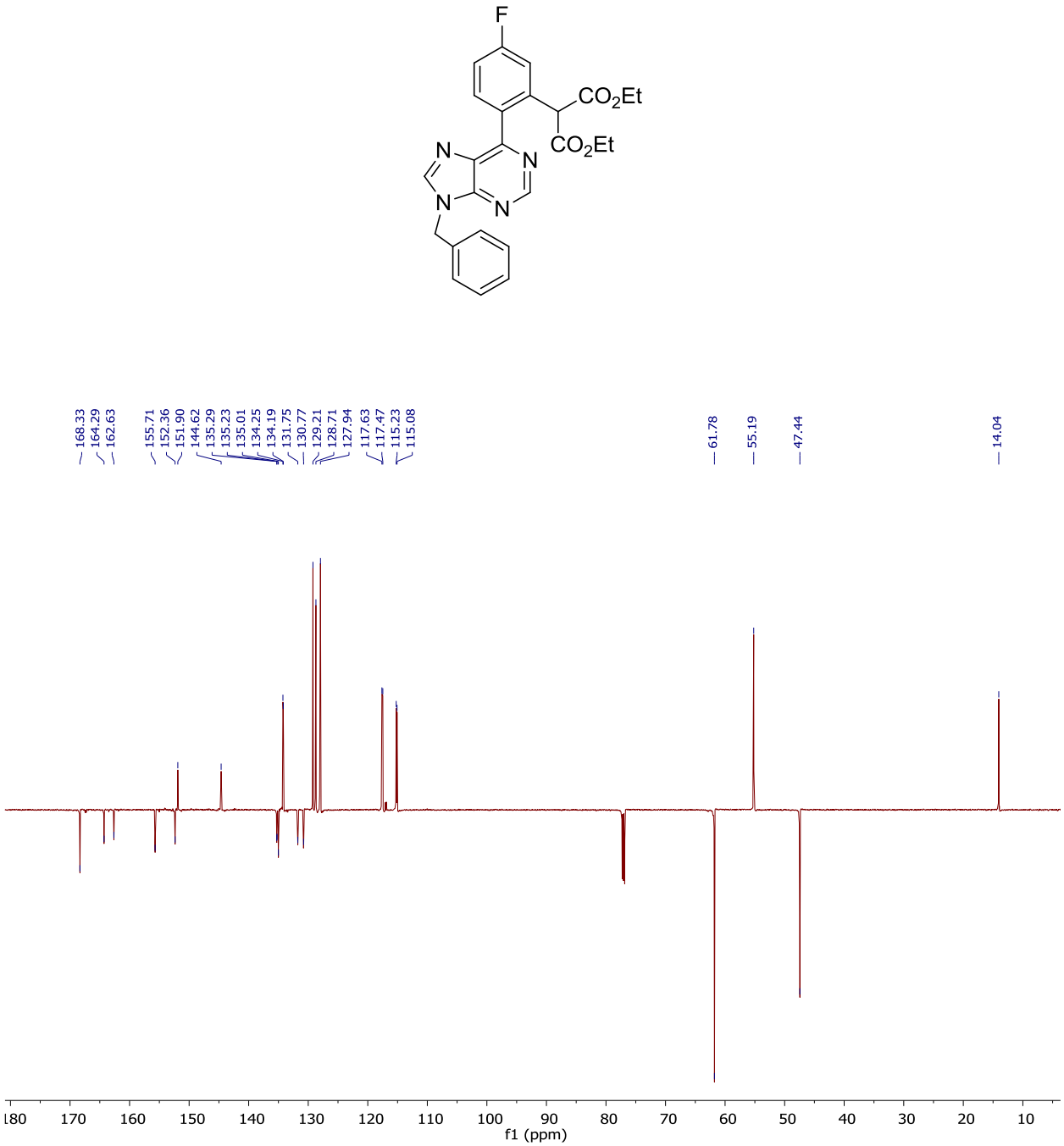


^{1}H NMR spectrum of compound **3f** in $CDCl_3$



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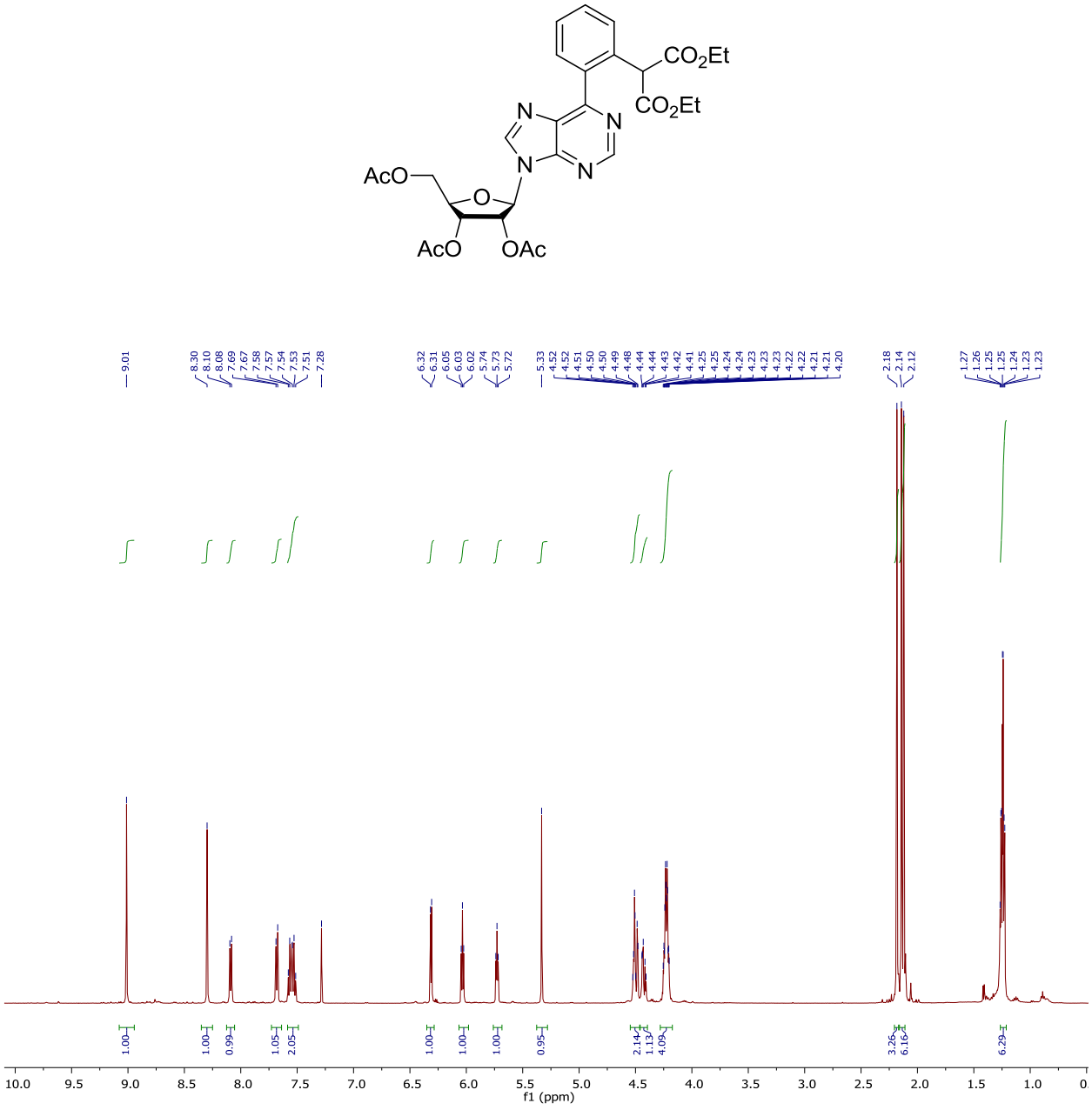
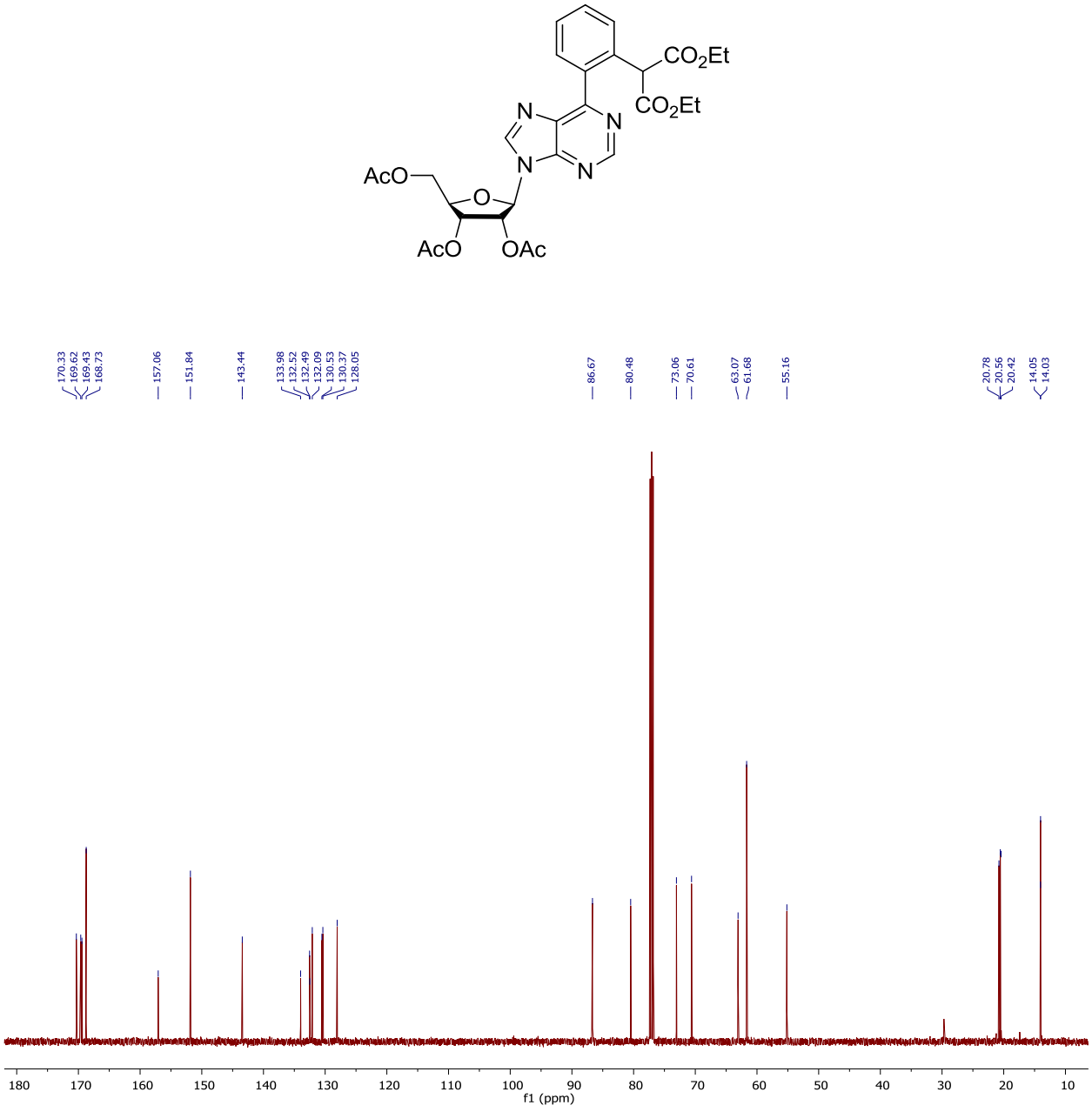


^{1}H NMR spectra of compound **3g** in $CDCl_3$



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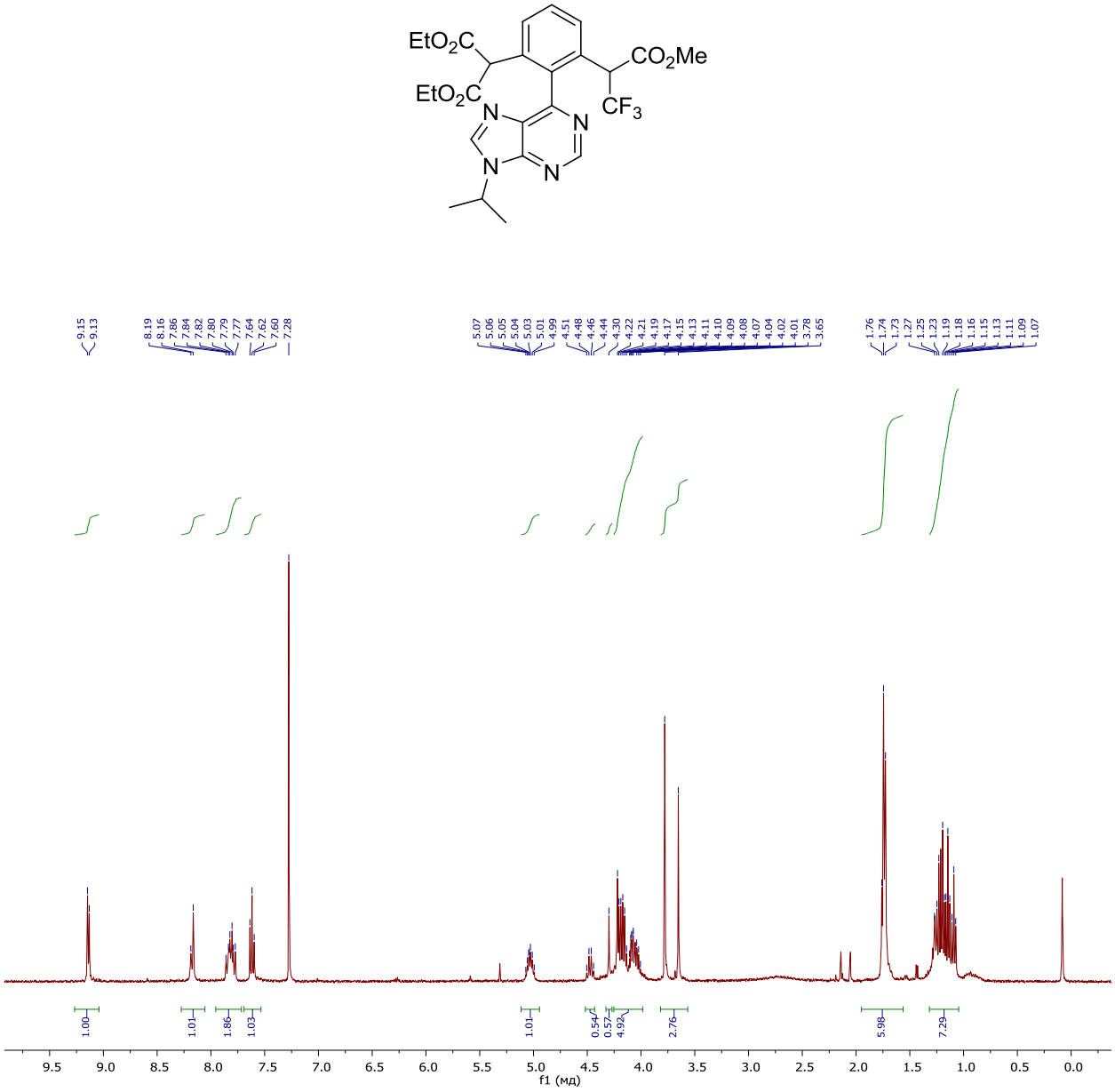
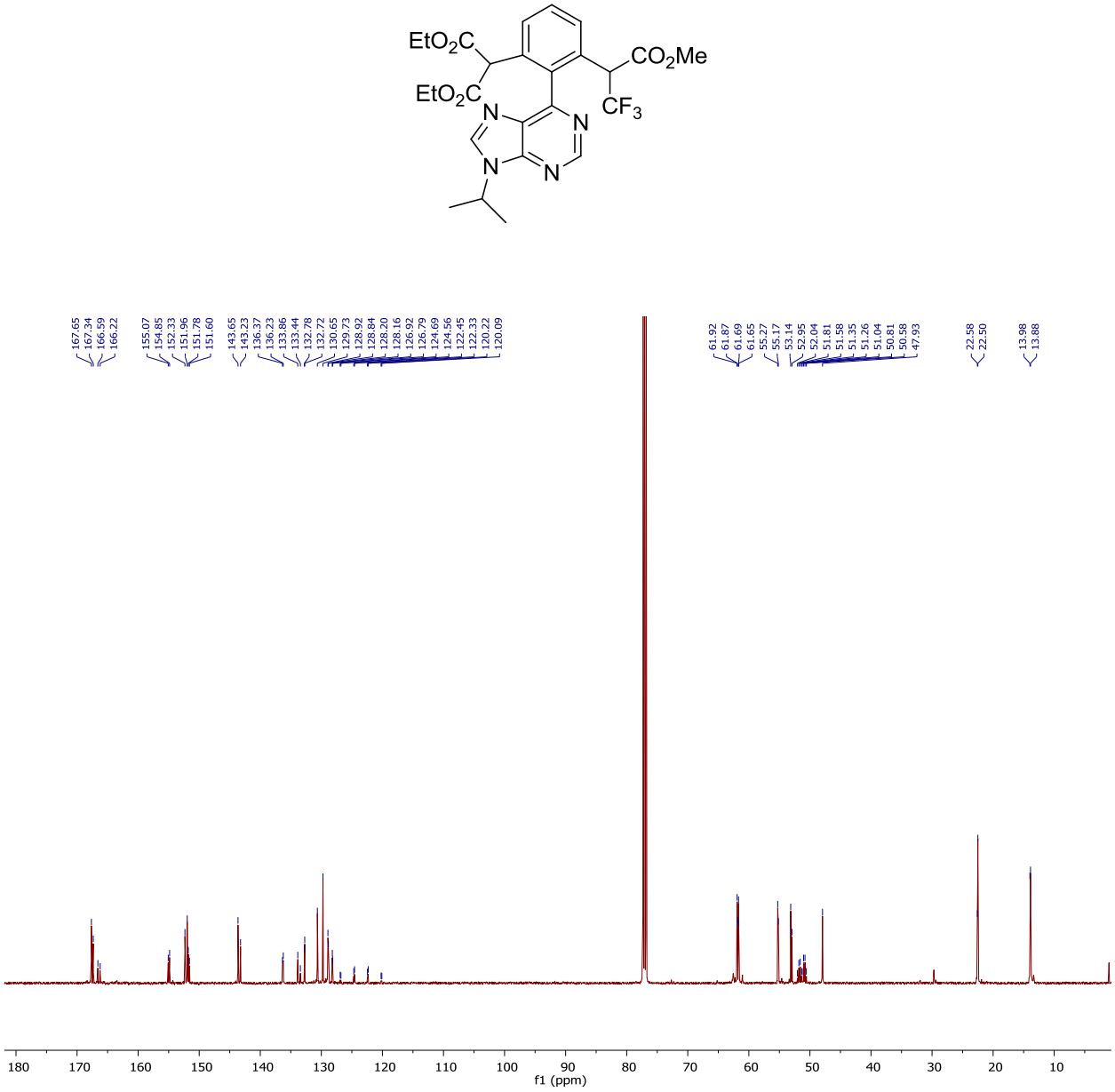


^{1}H NMR spectra of compound **4** in $CDCl_3$



^{13}C NMR spectra of compound **4** in $CDCl_3$

2. Scale up synthesis of 2a

A dried 50 mL Schlenk flask equipped with a magnetic stirrer was charged with 6-phenylpurine (2.01 g, 8.4 mmol), DCE (20 mL), $[Cp^*RhCl_2]_2$ (0.13 g, 0.21 mmol), $AgSbF_6$ (0.29 g, 0.84 mmol), and diazo compound (1.69 g, 10 mmol) under Ar. The reaction mixture was stirred at 80 °C for 4 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) to give 1.81 g (57% yield) of the analytically pure product.

3. X-ray Diffraction Study of Compounds 3a and 4

Experimental details: Intensities of 25772 and 15832 reflections were measured for **3a** and **4** with a Bruker APEX2 CCD and APEX2 DUO CCD diffractometers [λ(MoKα) = 0.71072Å, ω-scans, $2\theta<60$ and $2\theta<58°$], respectively; 6036 and 6752 independent reflections [R_{int} = 0.0396 and 0.0275] were used in further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. For **3a**, the refinement converged to wR2 = 0.1180 and GOF = 1.007 for all the independent reflections (R1 = 0.0460 was calculated against F for 4931 observed reflections with $I>2\sigma(I)$)**. 4**, the refinement converged to wR2 = 0.1261 and GOF = 1.005 for all the independent reflections (R1 = 0.0457 was calculated against F for 5494 observed reflections with $I>2\sigma(I)$)**.** All calculations were performed using SHELXTL PLUS 5.0 [G.M. Sheldrick. A short history of SHELX. *Acta Cryst. A*, 2008, **64**, 112-122].

*Crystal data for **3a**:* $C_{21}H_{24}N_4O_4$, M = 396.44, monoclinic, space group $P2_1/n$, at 120 K: a = 9.7486(10), b = 10.5135(11), c = 19.312(2) Å, β = 100.750(2)˚, V = 1944.6(4) $Å^3$, Z = 4 (Z' = 1), d_{calc} = 1.354 gcm^{-3}, μ(MoKα) = 0.96 cm^{-1}, F(000) = 840.

*Crystal data for **4**:* $C_{25}H_{27}F_3N_4O_6$, M = 536.50, triclinic, space group P-1, at 120 K: a = 9.0578(5), b = 9.3785(5), c = 15.7048(9) Å, α = 103.1670(10), β = 101.3370(10), γ = 91.8400(10)˚, V = 1269.54(12) $Å^3$, Z = 2 (Z' = 1), d_{calc} = 1.403 gcm^{-3}, μ(MoKα) = 1.15 cm^{-1}, F(000) = 560.

CCDC 1826774 and 1826773 contain the supplementary crystallographic information for **3a** and **4.**

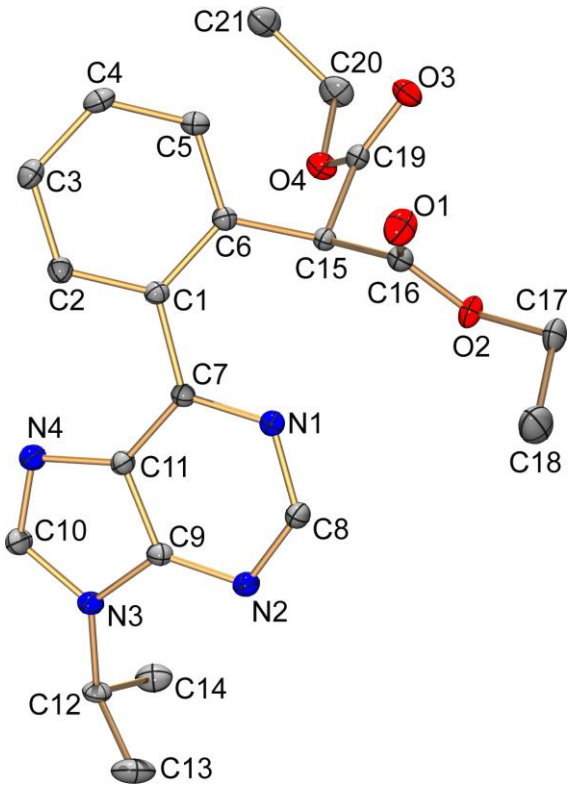


Figure S1. Structure of compound **3a**. Ellipsoids are shown at 50% level. Selected bond lengths [Å] and angles [º]: O1−C16 1.2013(14), O2−C16 1.3412(14), O2−C17 1.4537(14), O3−C19 1.2055(14), O4−C19 1.3368(14), O4−C20 1.4608(14), N1−C8 1.3443(14), N1−C7 1.3484(14), N2−C9 1.3345(14), N2−C8 1.3355(15), N3−C10 1.3673(15), N3−C9 1.3758(14), N3−C12 1.4742(14), N4−C10 1.3156(15), N4−C11 1.3903(14), C1−C2 1.3992(15), C1−C6 1.4112(15), C1−C7 1.4833(14), C2−C3 1.3867(15), C3−C4 1.3868(16), C4−C5 1.3913(16), C5−C6 1.3958(15), C6−C15 1.5257(15), C7−C11 1.3980(15), C9−C11 1.4068(15), C15−C16 1.5221(15), C15−C19 1.5269(15), C8−N1−C7 118.61(10), C9−N2−C8 111.78(9), C10−N3−C9 105.48(9), C10−N3−C12 123.99(9), C9−N3−C12 129.21(10), C10−N4−C11 103.33(10), C2−C1−C6 119.57(10), C2−C1−C7 118.25(9), C6−C1−C7 122.17(10), C3−C2−C1 121.00(10), C2−C3−C4 119.54(10), C3−C4−C5 120.08(10), C4−C5−C6 121.25(10), C5−C6−C1 118.47(10), C5−C6−C15 119.90(9), C1−C6−C15 121.53(9), N1−C7−C11 118.39(10), N1−C7−C1 117.97(9), C11−C7−C1 123.63(10), N2−C8−N1 128.48(10), N2−C9−N3 128.31(10), N2−C9−C11 125.93(10), N3−C9−C11 105.76(9), N4−C10−N3 115.08(10), N4−C11−C7 132.86(10), N4−C11−C9 110.35(9), C7−C11−C9 116.75(10), C16−C15−C6 114.04(9), C16−C15−C19 108.49(9), C6−C15−C19 109.57(9).

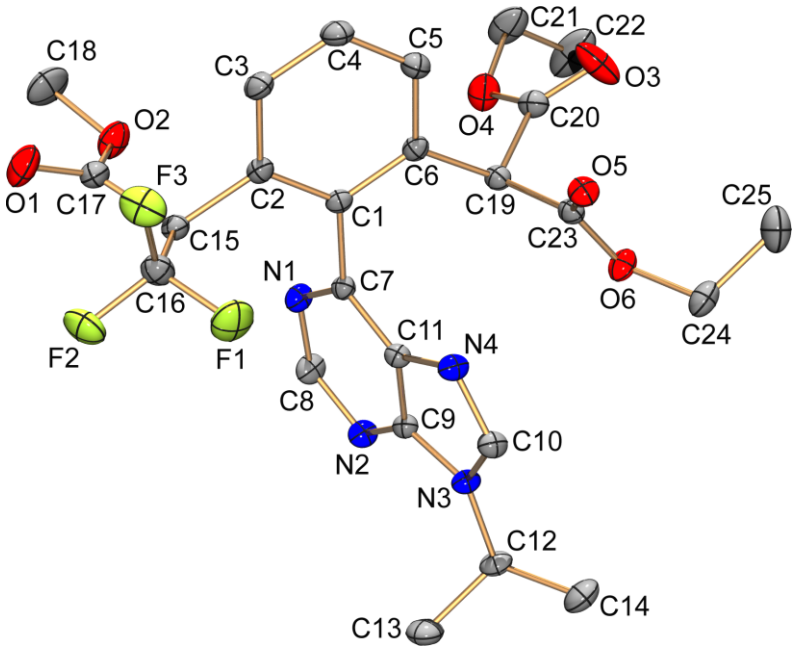


Figure S2. Structure of compound **4**. Ellipsoids are shown at 50% level. Selected bond lengths [Å] and angles [º]: F1−C16 1.3473(19), F2−C16 1.3316(18), F3−C16 1.3472(18), N1−C8 1.3455(18), N1−C7 1.3473(17), N2−C9 1.3328(18), N2−C8 1.3407(19), N3−C9 1.3717(17), N3−C10 1.3743(17), N3−C12 1.4800(17), N4−C10 1.3152(18), N4−C11 1.3838(17), O1−C17 1.1991(19), O2−C17 1.3317(19), O2−C18 1.449(2), O3−C20 1.196(2), O4−C20 1.3365(19), O4−C21 1.467(2), O5−C23 1.2008(17), O6−C23 1.3423(16), O6−C24 1.4608(18), C1−C6 1.4030(19), C1−C2 1.4058(18), C1−C7 1.4978(18), C2−C3 1.3961(19), C2−C15 1.5227(19), C3−C4 1.384(2), C4−C5 1.385(2), C5−C6 1.4011(19), C6−C19 1.5178(18), C7−C11 1.3906(18), C9−C11 1.4081(18), C15−C16 1.515(2), C15−C17 1.523(2), C19−C20 1.5274(19), C19−C23 1.528(2), C8−N1−C7 118.12(12), C9−N2−C8 111.73(12), C9−N3−C10 105.64(11), C9−N3−C12 126.01(11), C10−N3−C12 128.34(12), C10−N4−C11 103.81(11), C6−C1−C2 119.24(12), C6−C1−C7 118.85(12), C2−C1−C7 121.90(12), C3−C2−C1 119.60(13), C3−C2−C15 118.79(12), C1−C2−C15 121.54(12), C4−C3−C2 120.91(13), C3−C4−C5 119.89(13), C4−C5−C6 120.24(13), C5−C6−C1 120.08(12), C5−C6−C19 118.96(12), C1−C6−C19 120.96(12), N1−C7−C11 118.62(12), N1−C7−C1 119.44(12), C11−C7−C1 121.84(12), N2−C8−N1 128.65(13), N2−C9−N3 128.79(12), N2−C9−C11 125.48(12), N3−C9−C11 105.73(11), N4−C10−N3 114.45(12), N4−C11−C7 132.39(12), N4−C11−C9 110.35(12), C7−C11−C9 117.16(12), N3−C12−C13 110.13(12), C16−C15−C2 110.46(12), C16−C15−C17 111.16(12), C2−C15−C17 111.84(11), C6−C19−C20 110.65(11), C6−C19−C23 112.76(11), C20−C19−C23 108.66(11).