

Supplementary Material

Copper-catalyzed silylation of activated alkenes by photoinduced ligand-to-metal charge transfer

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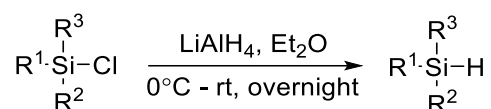
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Table of Contents

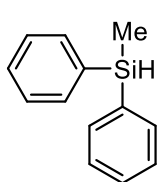
Synthesis of the starting Materials	S2
NMR data	S4

1. Synthesis of the starting Materials



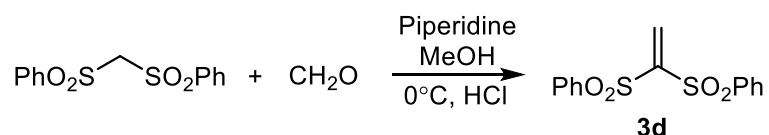
In a Schlenk tube under inert atmosphere chlorosilane (10 mmol, 1.0 equiv.) was dissolved in dry Et₂O (30 mL) and the mixture cooled to 0°C. The lithium aluminium hydride solution (4M, 10 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. Then, H₂O (30 mL) was added dropwise to quench the reaction. Concentrated hydrochloric acid was added dropwise until two layers separated. The organic phases were washed with saturated NaHCO₃ until they gave basic pH, followed by washing with brine (30 mL). The organic phase was dried over Na₂SO₄, filtered and the residue was evaporated by reduced pressure to give product.

Methyldiphenylsilane (4c)¹



Based on general procedure **A**, starting from 2.3 g of chloro(methyl)diphenylsilane, product **4c** has been obtained as oil (1.75 g, 8.8 mmol, 88% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.61 – 7.57 (m, 4H), 7.48 – 7.31 (m, 6H), 4.97 (qd, *J* = 3.8, 1.4 Hz, 1H), 0.66 (dd, *J* = 3.9, 1.1 Hz, 3H). Analytical data are in good agreement with those reported in the literature.¹

Vinyldisulfone (3d)



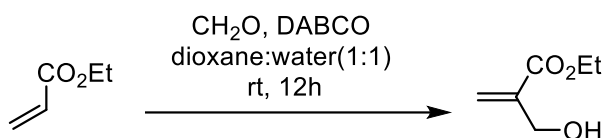
To a methanol (30 mL) solution of paraformaldehyde (40% in water), (2.3 g, 0.03 mol, 3 equiv.), piperidine (4.9 mL, 0.15 mol; 5 equivalents) and bis(phenylsulfonyl)methane (3.05 g, 0.010 mol, 1 equiv.) were successively added slowly at 0°C. After 70 minutes at 0°C, a mixture of icy-water (70 mL) was added and stirred for 10 minutes. The white precipitate was filtered off and washed with additional 50 mL of cold water. The white solid thus obtained was re-dissolved in 30 mL of dichloromethane. 50 mL of HCl (1N) were added and the resulting biphasic mixture was stirred vigorously for 3 hours. Additional 25 mL of HCl (1N) were again added prior to separating the organic layer. The aqueous layer was further extracted 2 times with 50 mL of dichloromethane. The combined organic layers were dried on MgSO₄, filtered and the solvent evaporated to give the crude product (~ 95% pure). Recrystallization from CH₂Cl₂/cyclohexane (alternatively benzene can be used) yielded pure **3d** as a white solid (2.7 g; 8.7 mmol; 87% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.93 (m, 4H), 7.73 – 7.63 (m, 2H), 7.60 – 7.52 (m, 4H), 7.22 (s,

¹ Lesbani, A.; Kondo, H.; Yabusaki, Y.; Nakai, M.; Yamanoi, Y.; Nishihara, H. *Chem. Eur. J.* **2010**, *16*, 13519-13527.

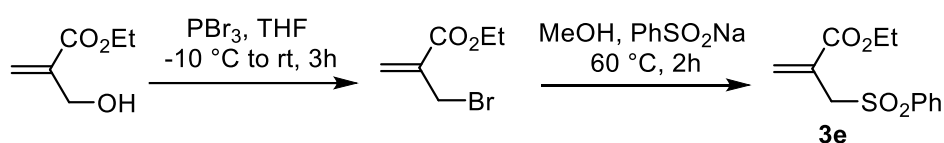
2H). Analytical data are in good agreement with those reported in the literature.²

Allylsulfone (3e)



To a solution of paraformaldehyde (3.98 g, 133.2 mmol) and ethylacrylate (10.8 mL, 100 mmol) in 80 mL of dioxane-water (1:1, v/v) was added DABCO (14.96 g, 133.2 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (200 mL) and water (100 mL). The organic layer was separated and washed with brine (100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product as a colorless oil (6.10 g, 46% yield).³

¹H NMR (300 MHz, CDCl₃) δ: 6.25 (q, *J* = 0.9 Hz, 1H), 5.82 (q, *J* = 1.4 Hz, 1H), 4.35-4.31 (m, 2H), 4.25 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.27 (s, 1H), 1.32 (td, *J* = 7.1, 1.0 Hz, 3H).



First Step: Ethyl 2-(hydroxymethyl)acrylate (1.0 eq., 46.23 mmol, 6.10 g) was dissolved in dry THF (50 mL) at -10°C. To this mixture PBr₃ (0.34 eq., 16.18 mmol, 1.52 mL) was added. The temperature was allowed to rise to rt and stirring was continued for 3 h. Water (20 mL) was then added and the mixture was extracted with petroleum ether (3 × 100 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was used in next step without purification.

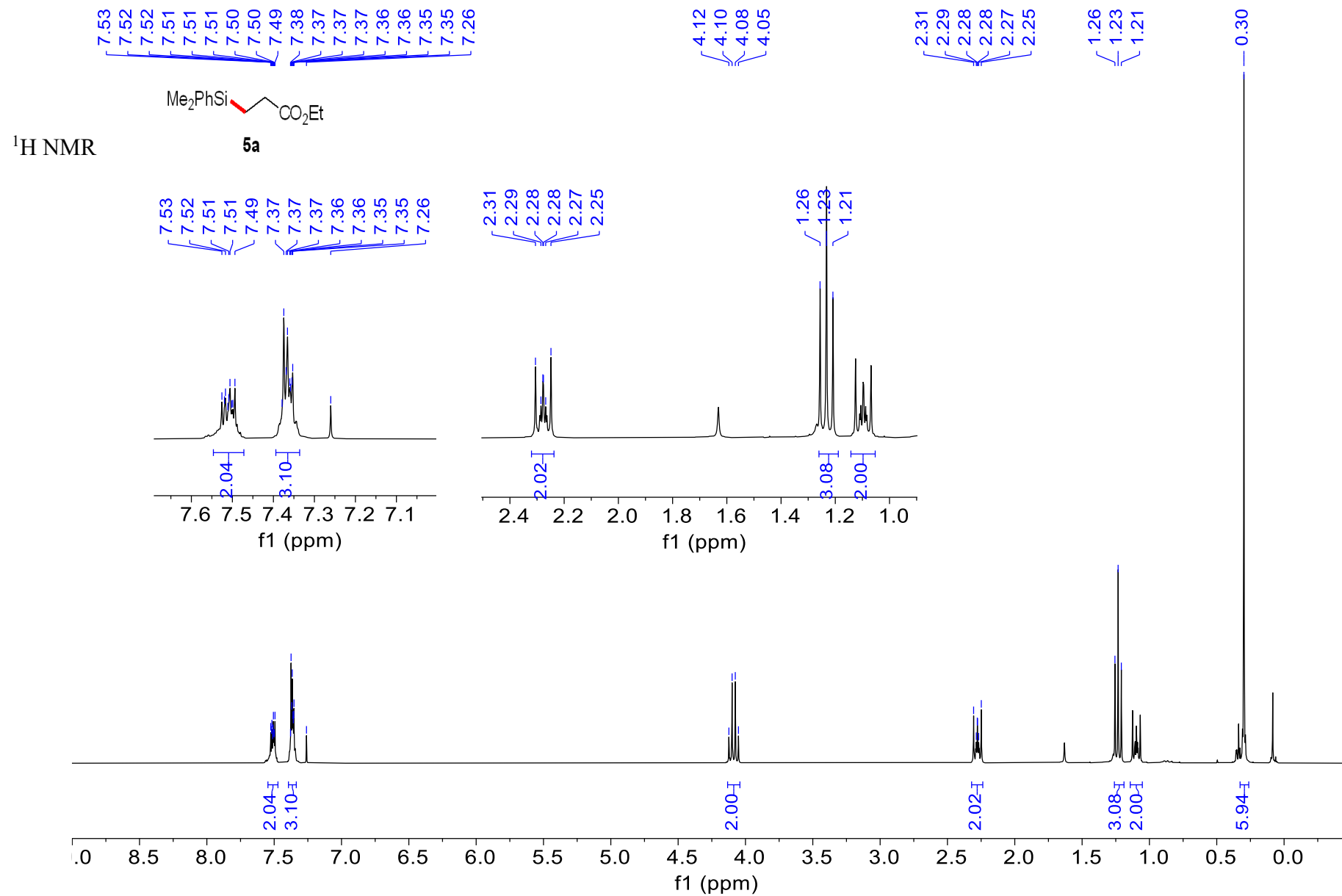
Second Step: To the crude mixture of first step was taken in dry methanol (75 mL) and added sodium phenylsulfinate (1.2 eq., 47.43 mmol, 7.78g). After 2 h of reflux, the mixture was concentrated under reduced pressure. The obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by chromatography in silica gel with 8-10% EtOAc in PE as eluant to afford product **3e** as colorless oil (8.10 g, 69%).³

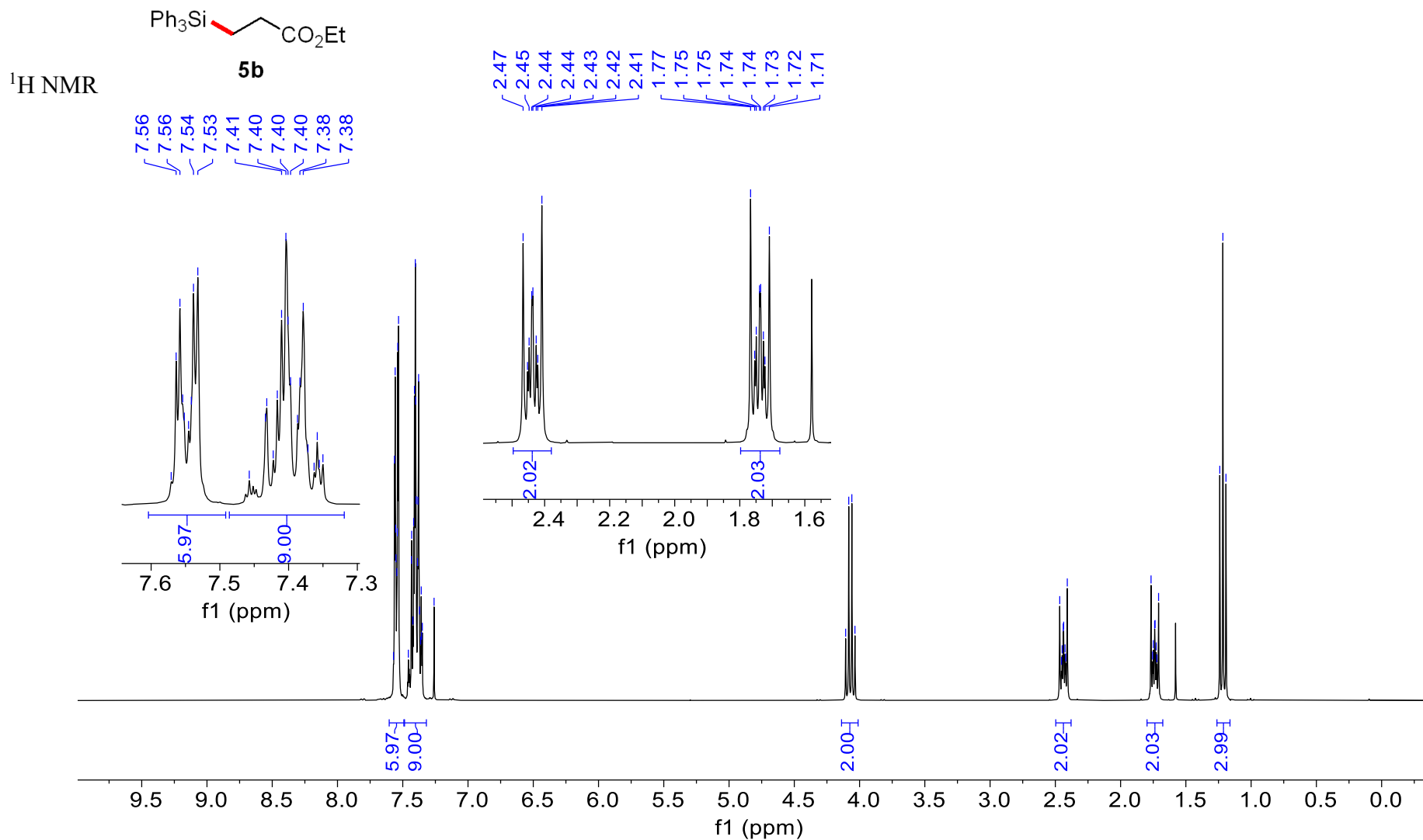
¹H NMR (300 MHz, CDCl₃) δ: 7.91-7.80 (m, 2H), 7.70-7.58 (m, 1H), 7.60-7.47 (m, 2H), 6.50 (d, *J* = 0.7 Hz, 1H), 5.91 (q, *J* = 0.8 Hz, 1H), 4.16 (d, *J* = 0.9 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 164.8, 138.4, 133.9, 133.3, 129.0, 128.8, 61.5, 57.5, 13.9. Analytical data are in good agreement with those reported in the literature.²

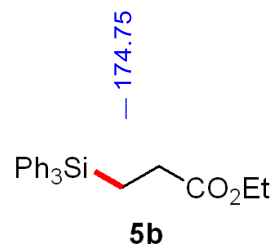
² Quintard, A.; Alexakis, A.; Mazet, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 2354-2358.

³ Li, Y.; Zhang, J.; Liand D. F.; Chen, Y. Y. *Org. Lett.* **2018**, *20*, 3296-3299.

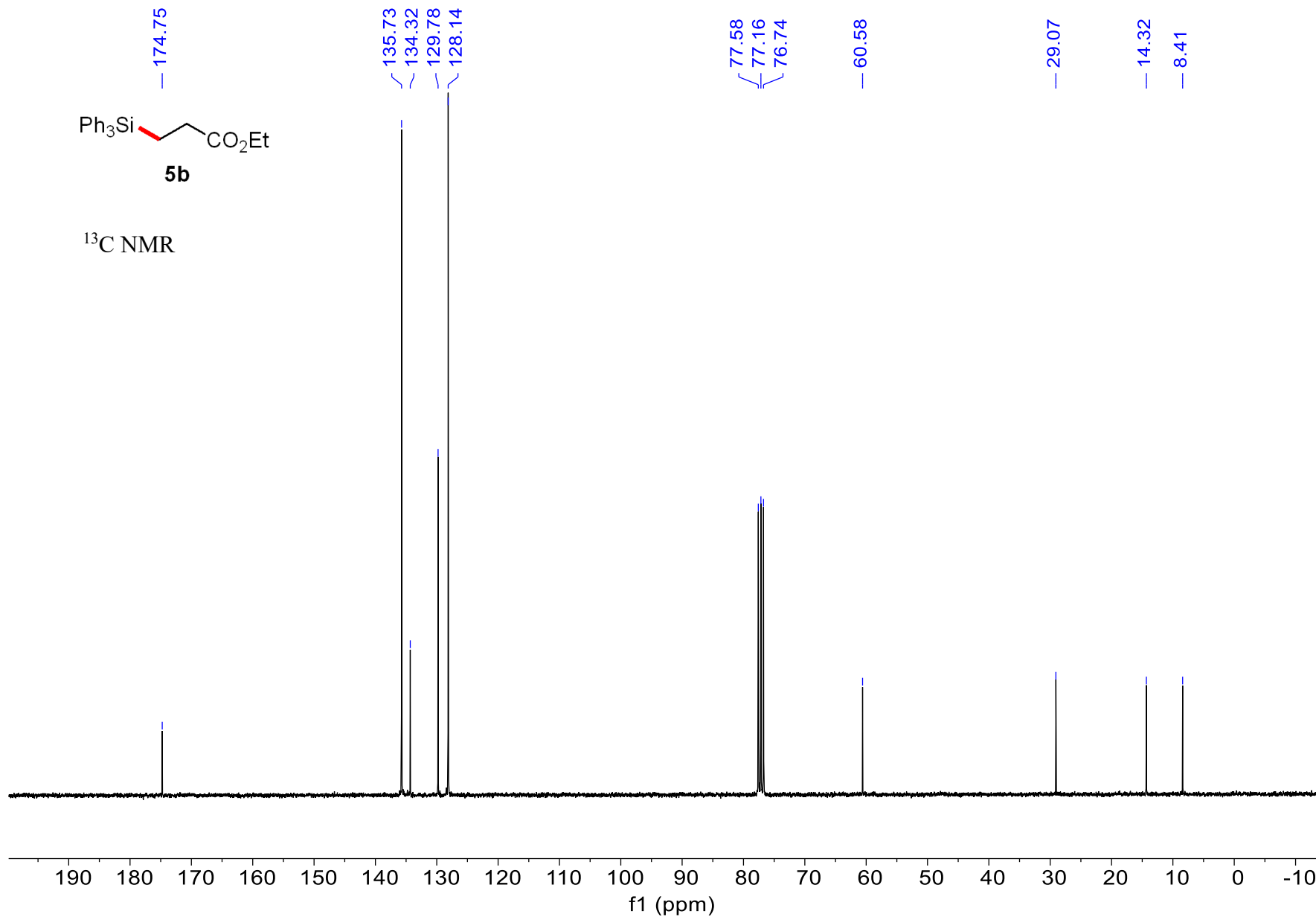
2. NMR data



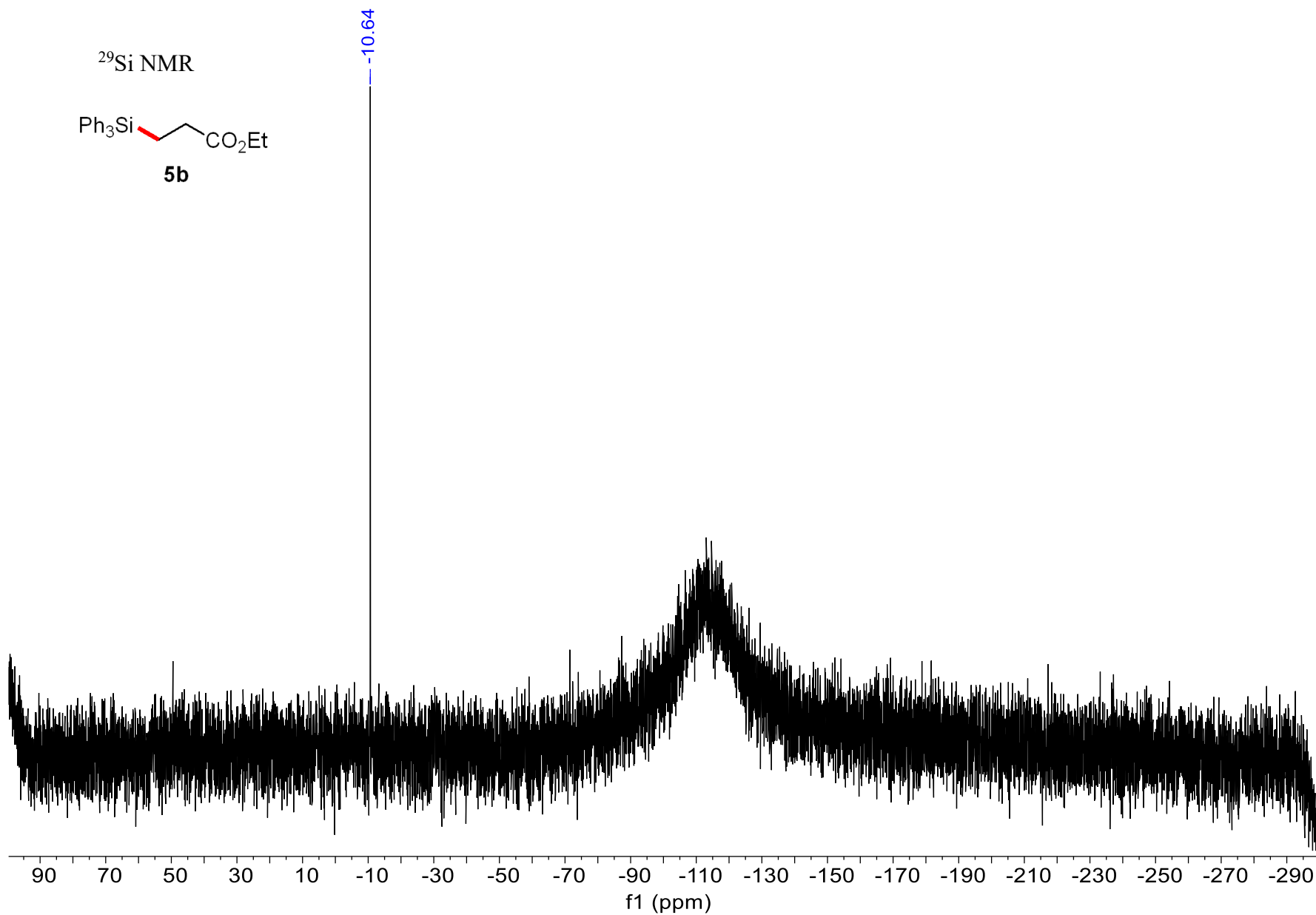
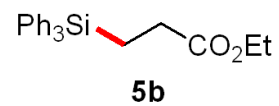


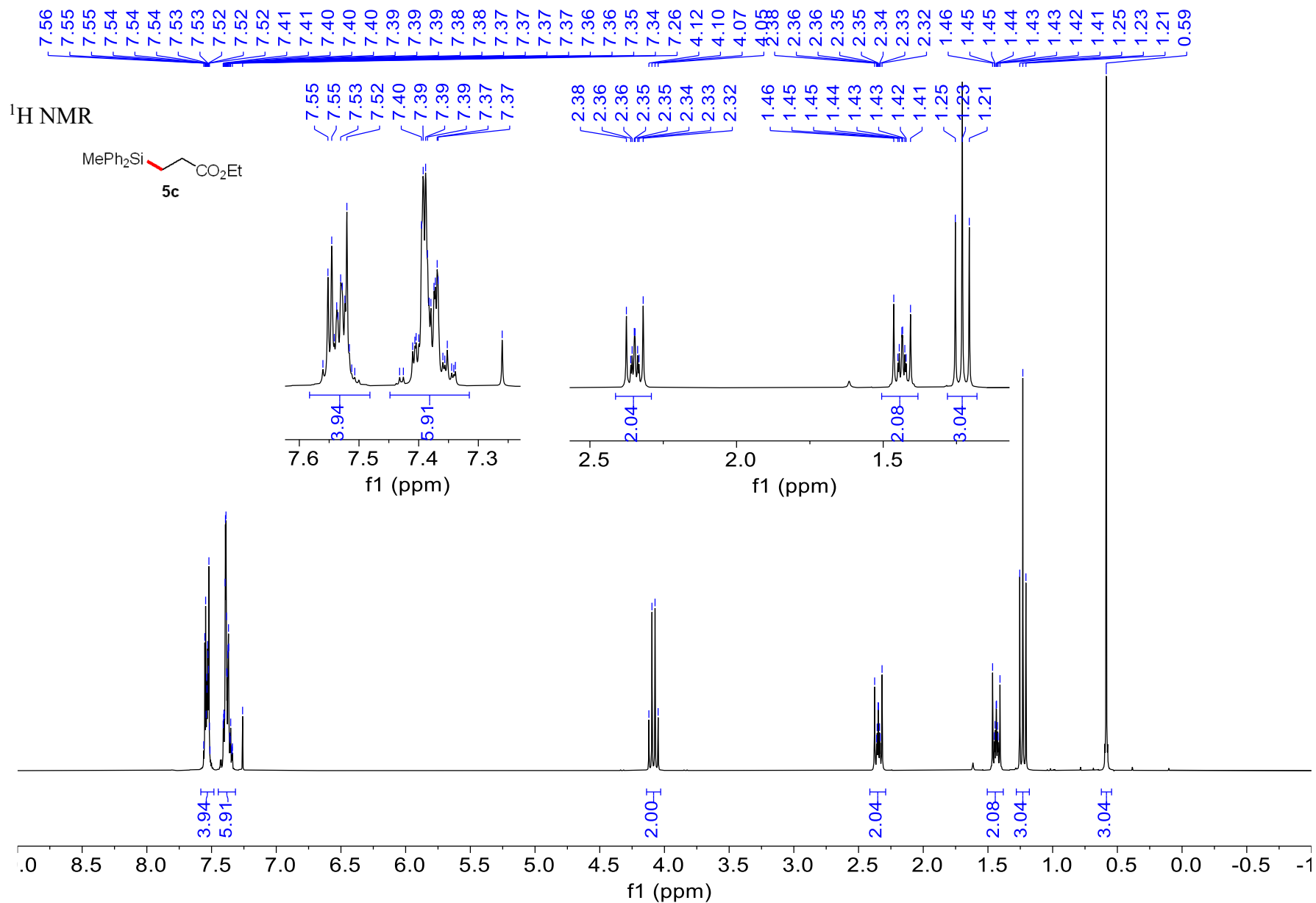


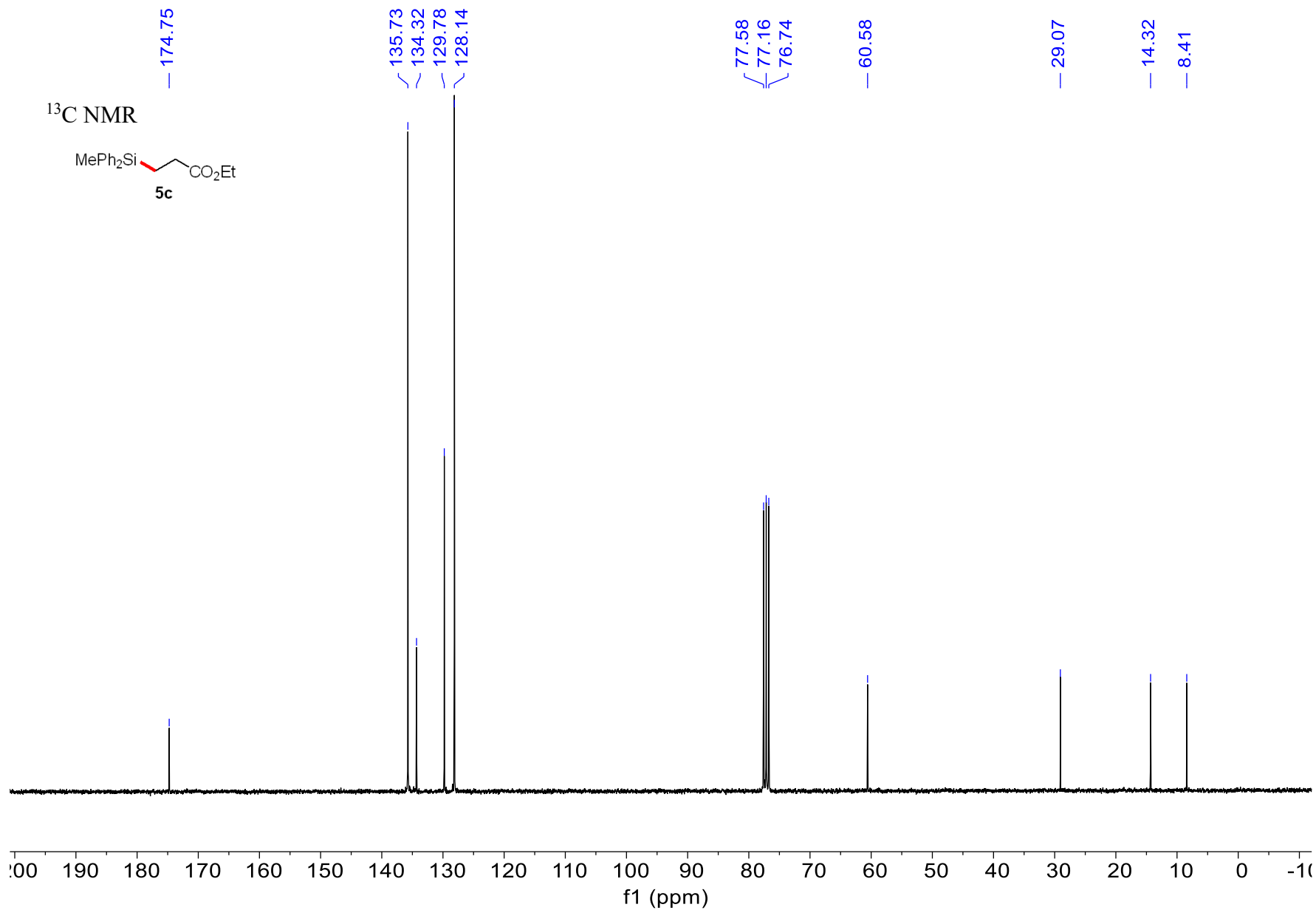
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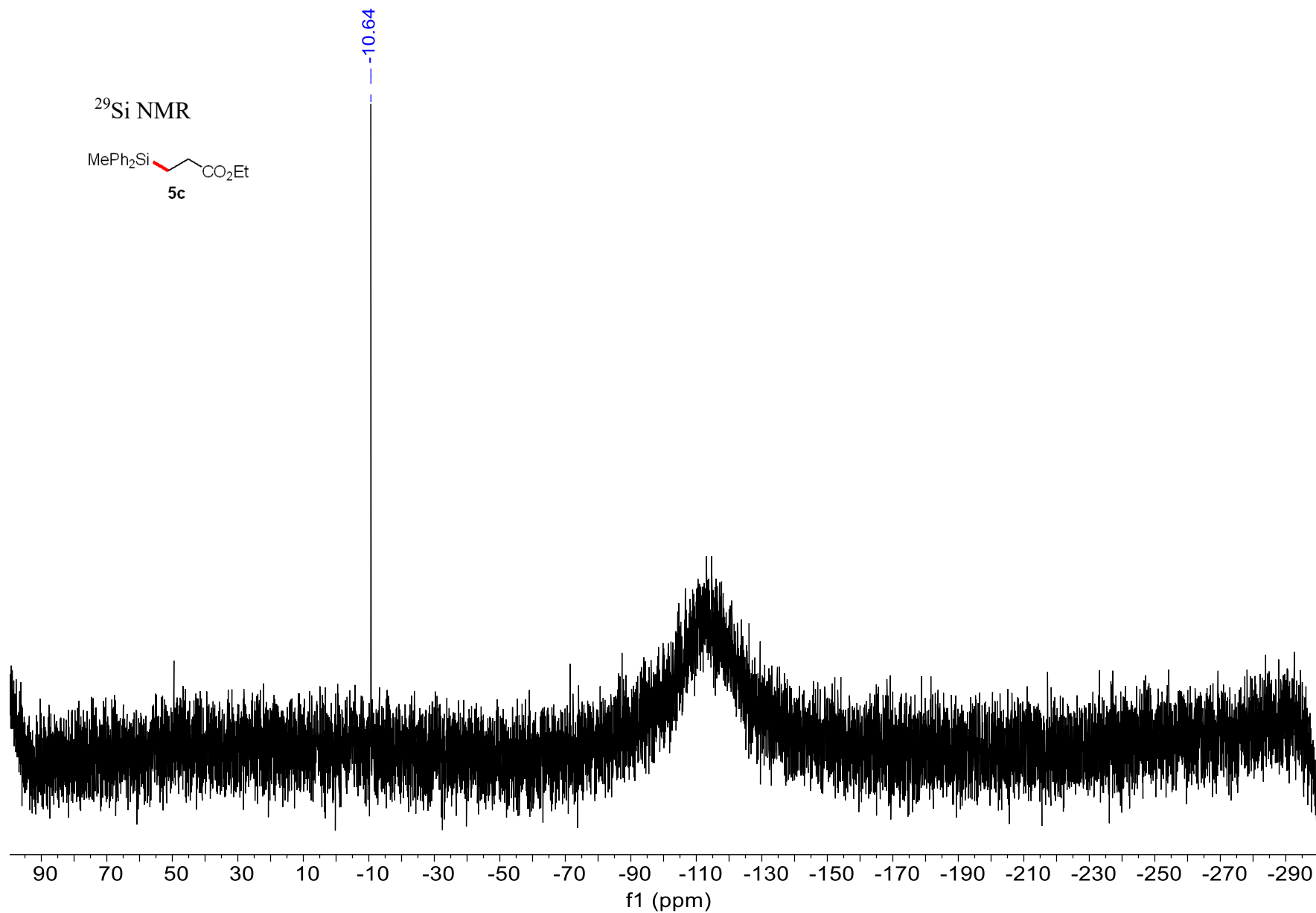


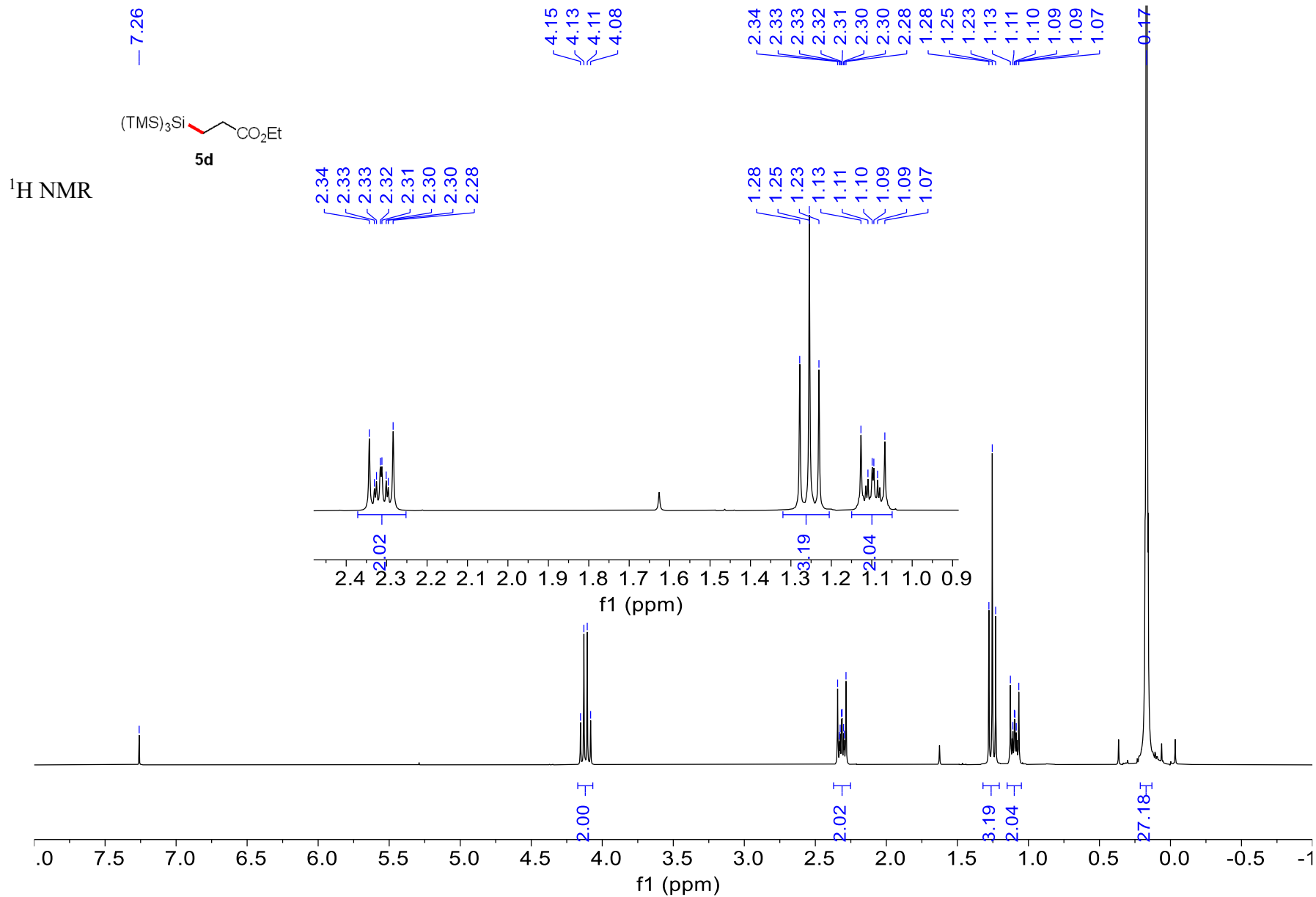
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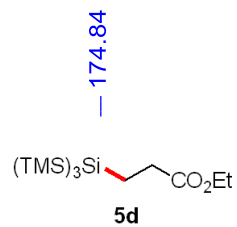




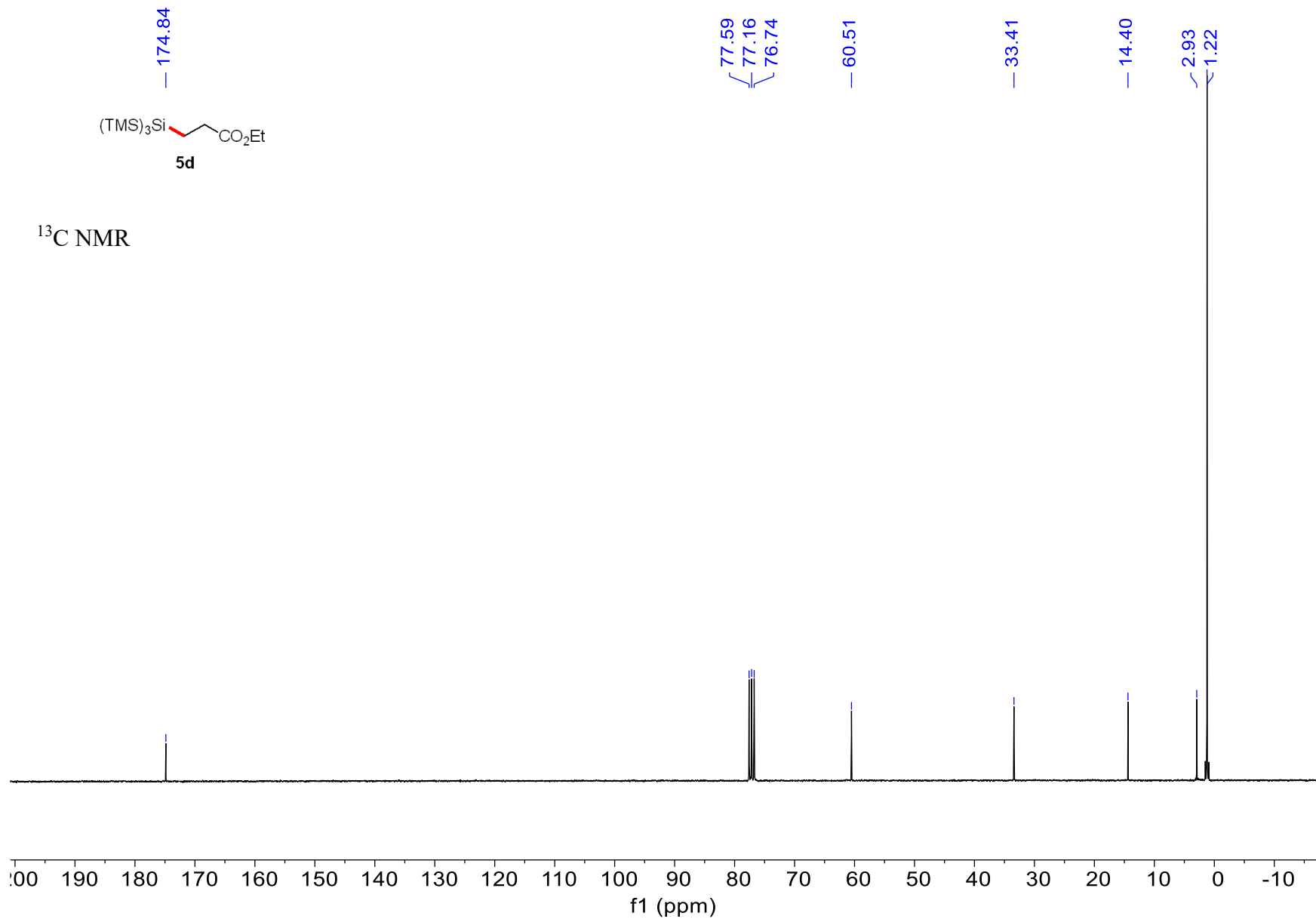


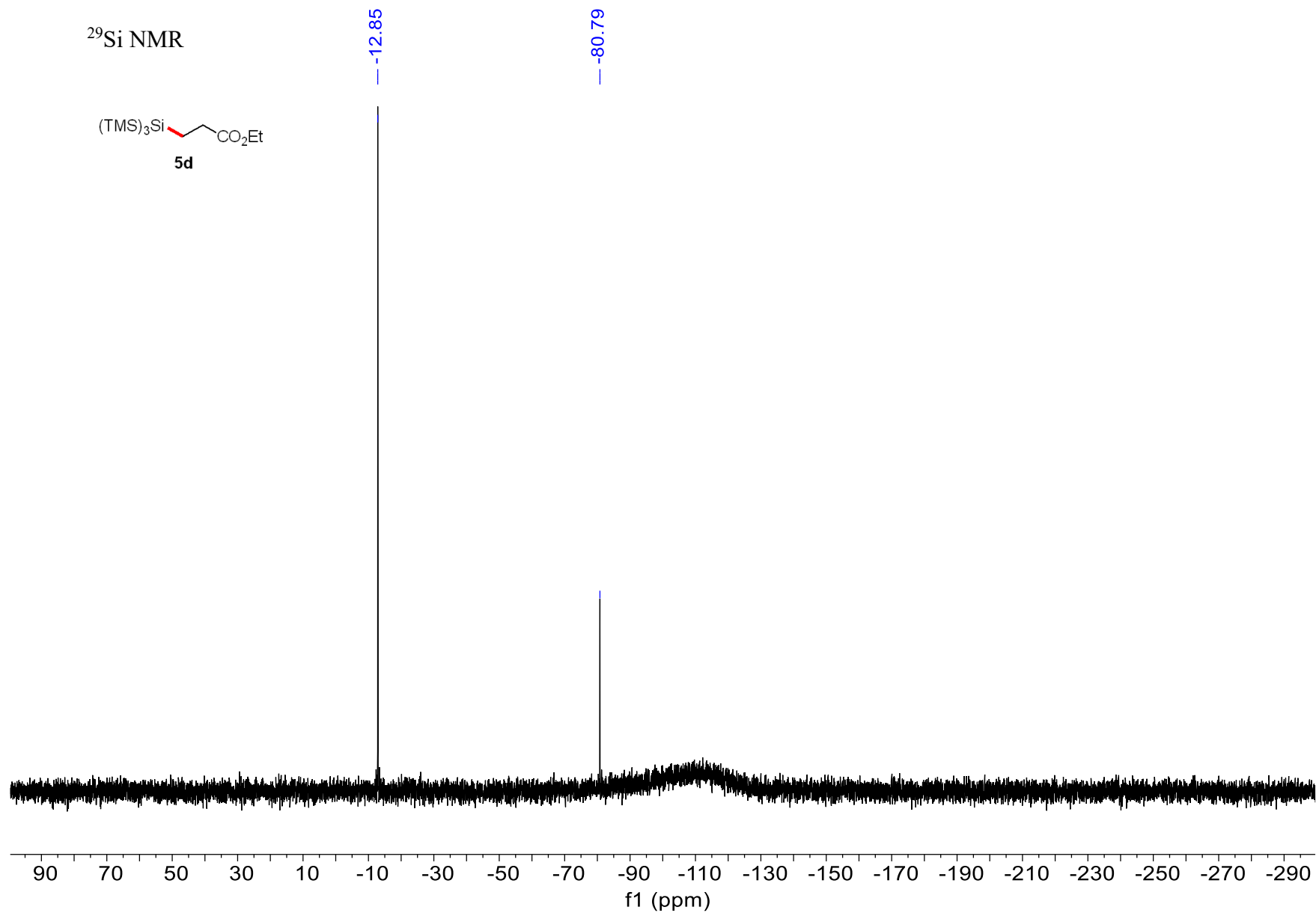


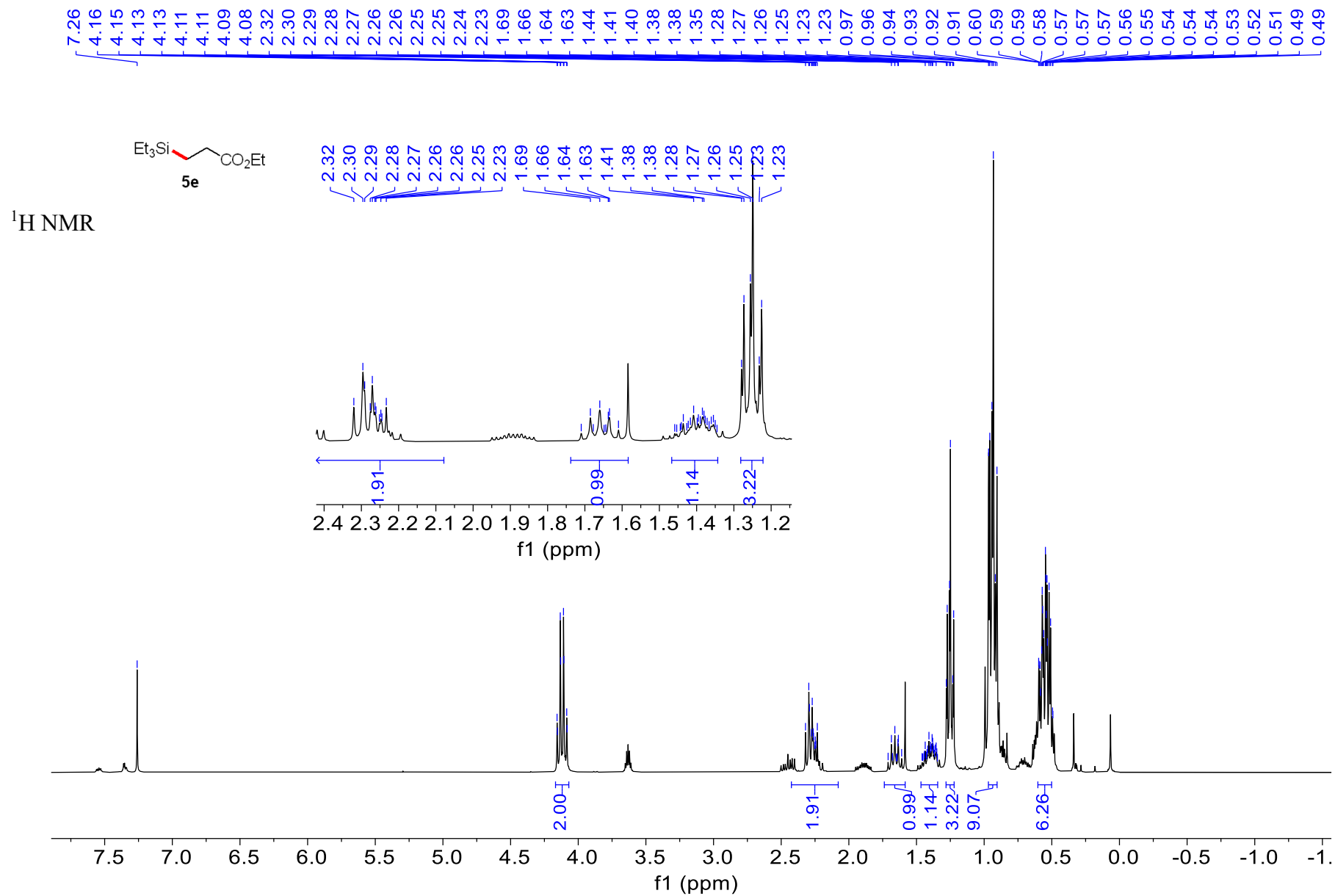


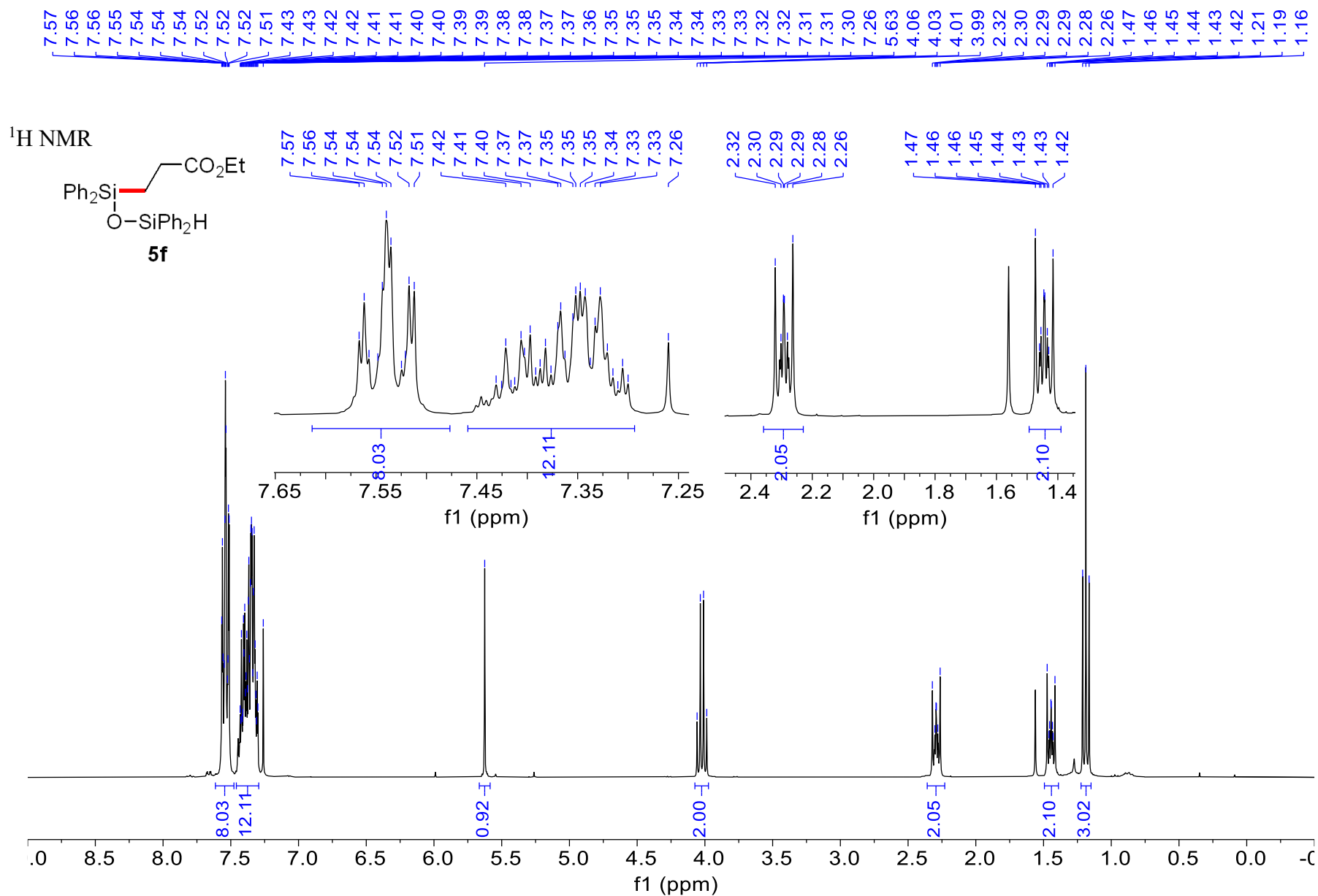


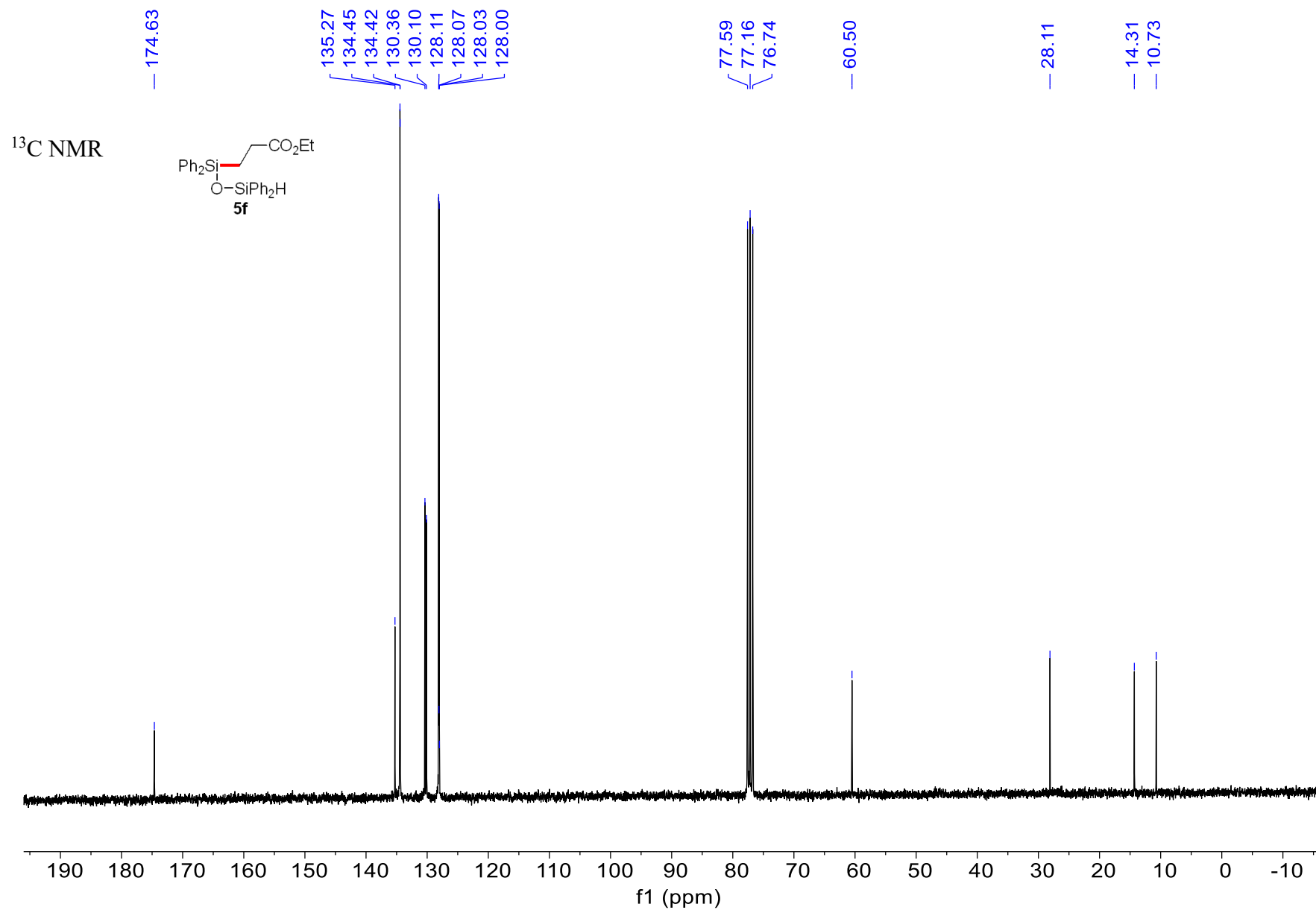
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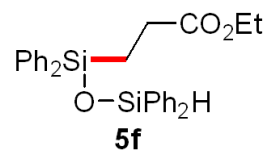




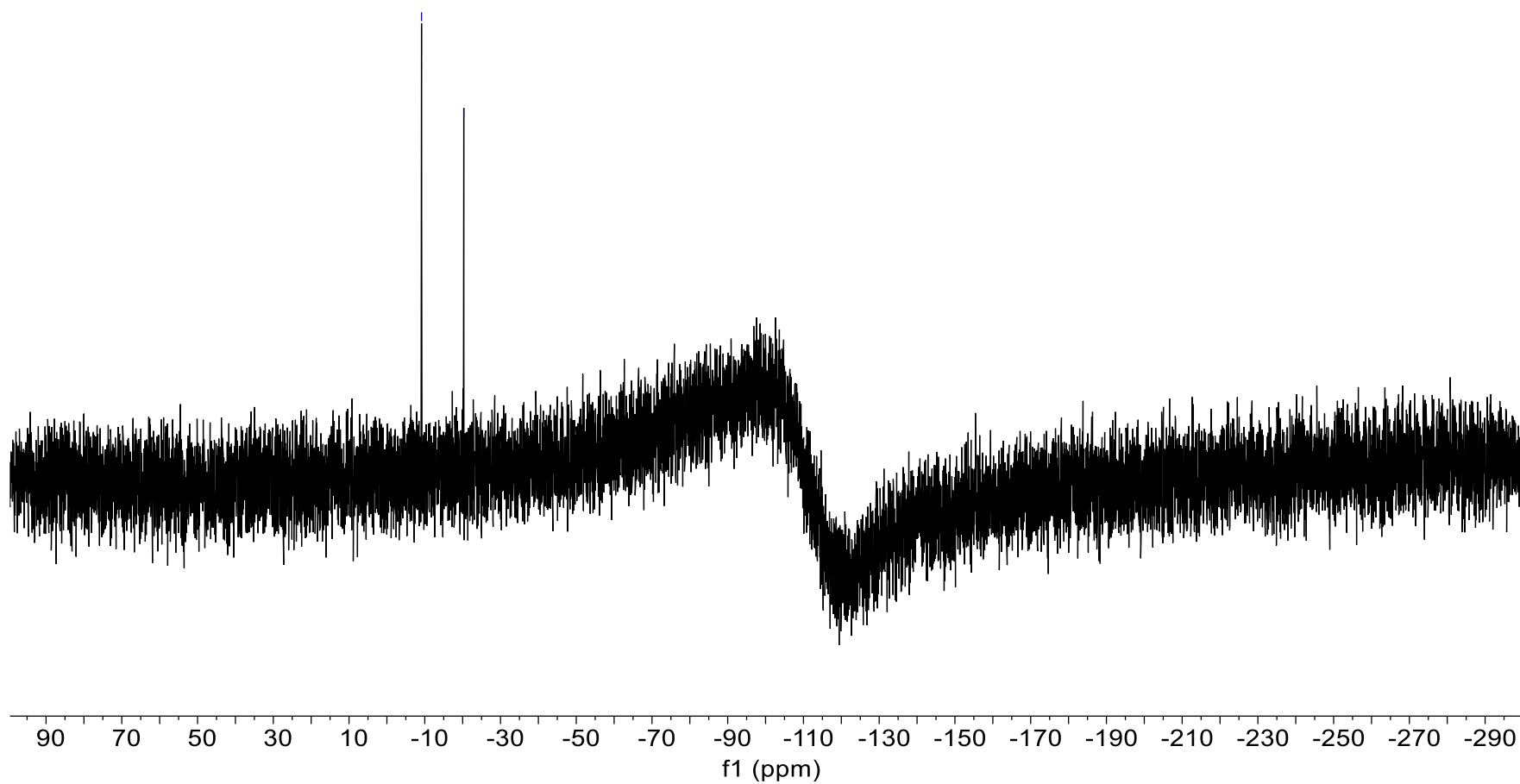


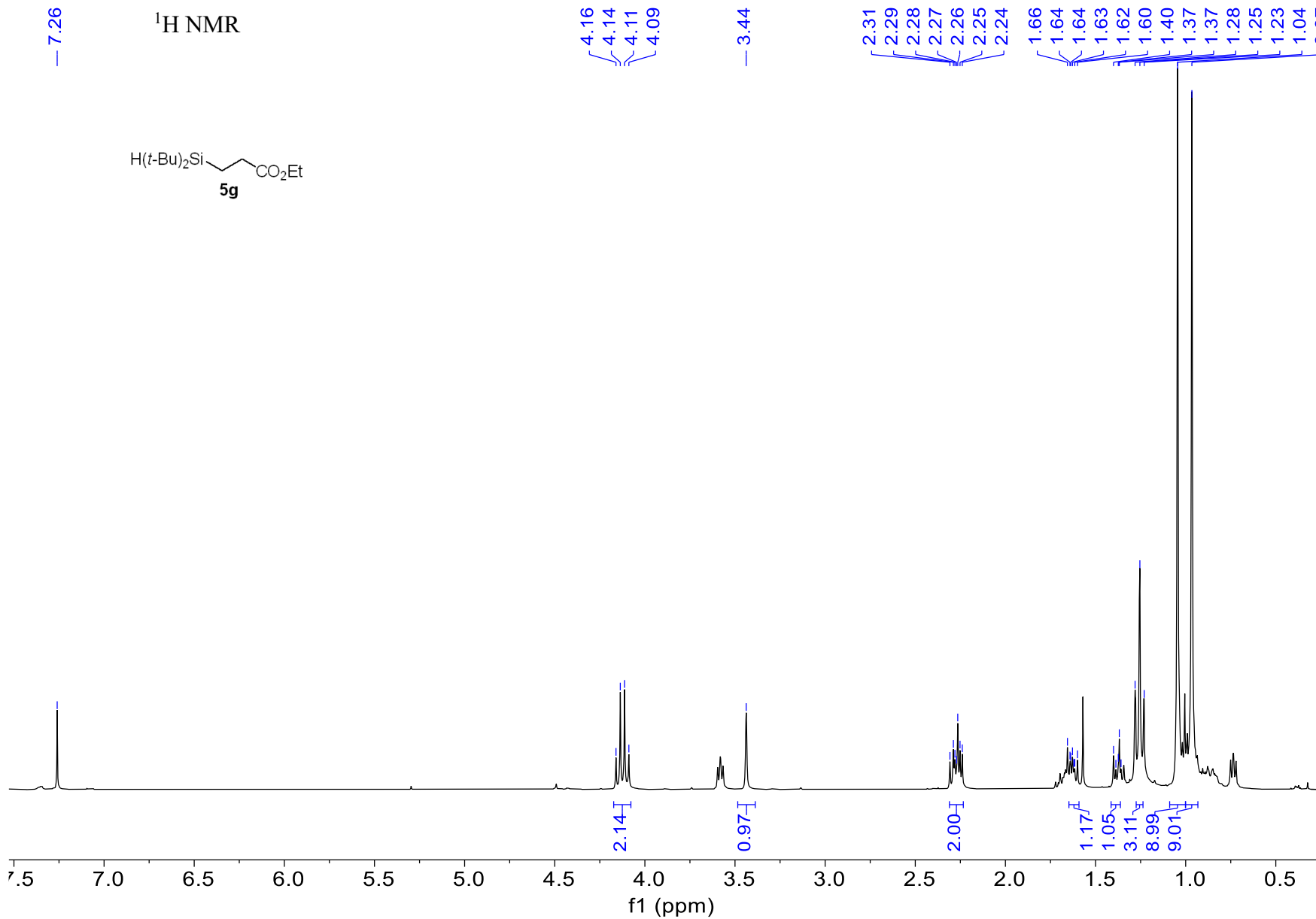




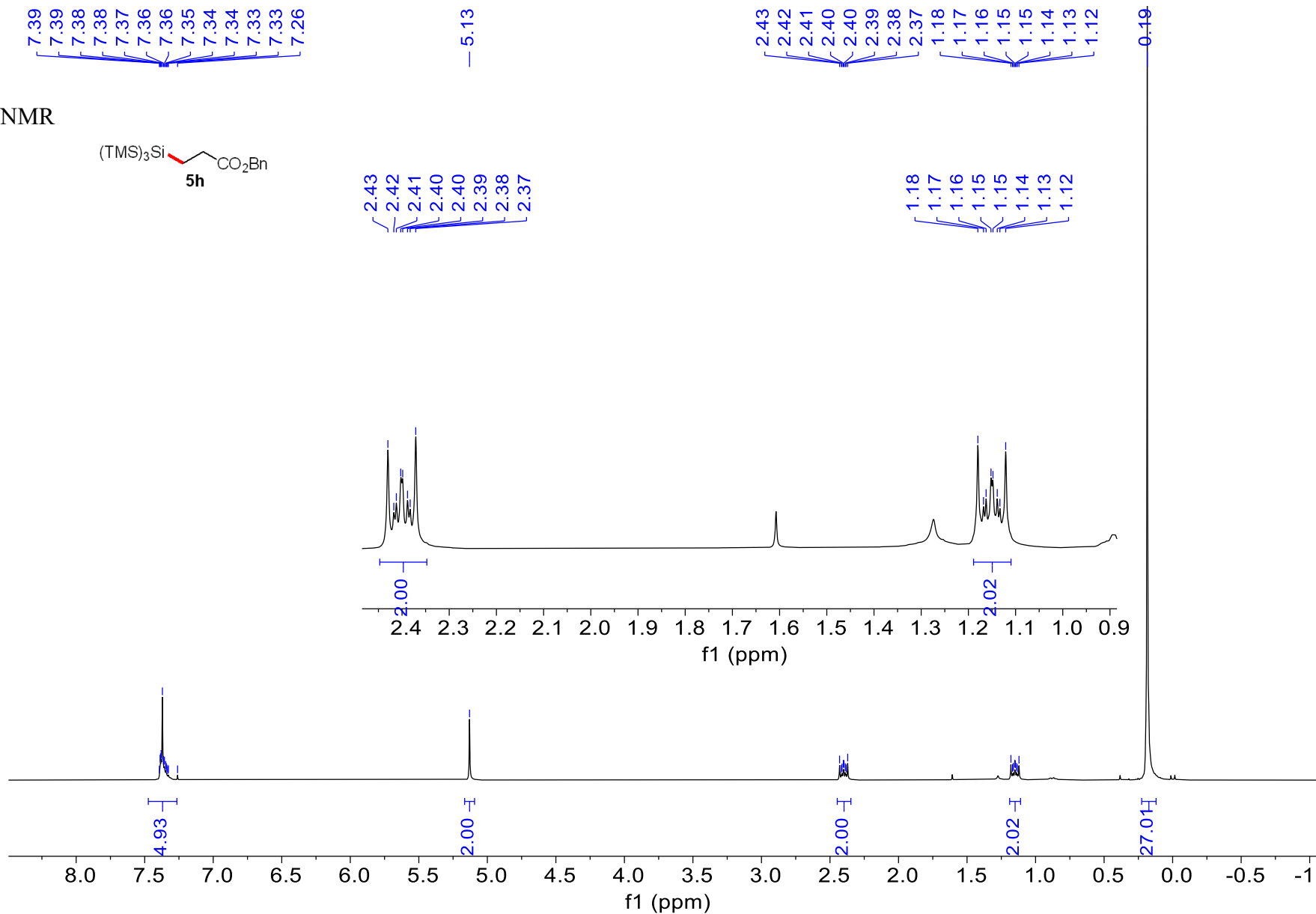
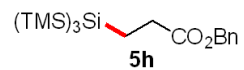
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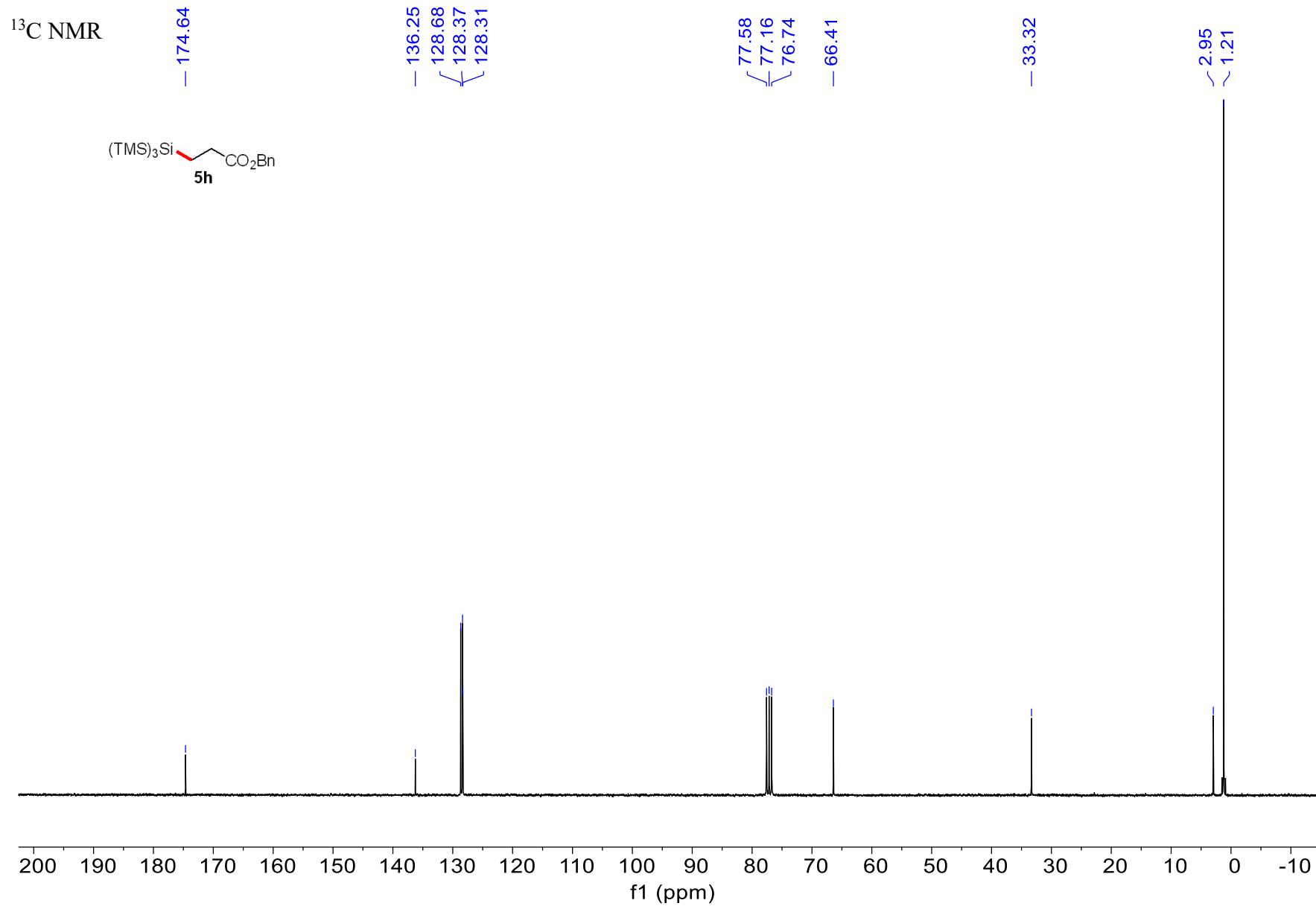
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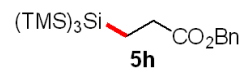


¹H NMR



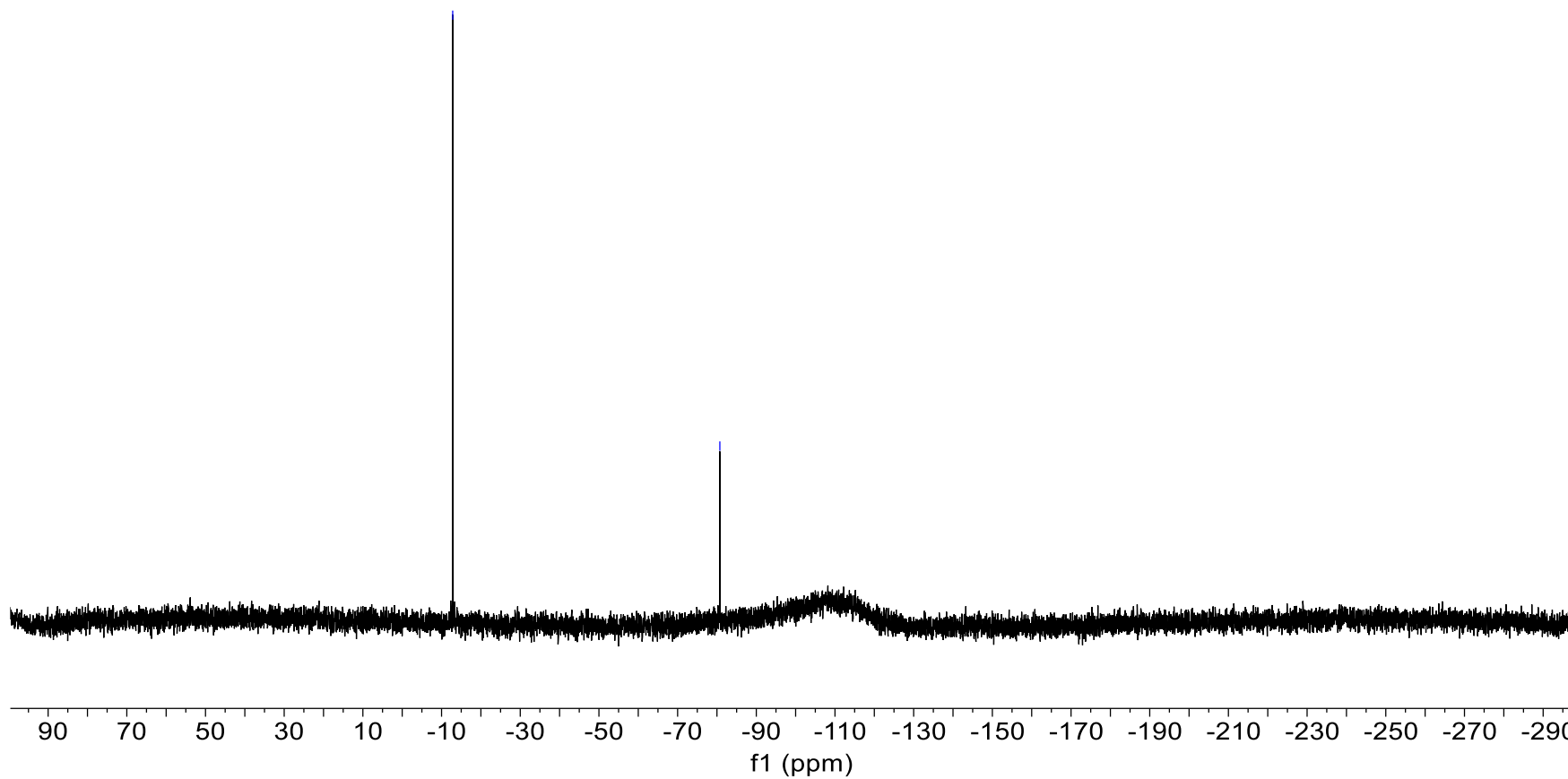


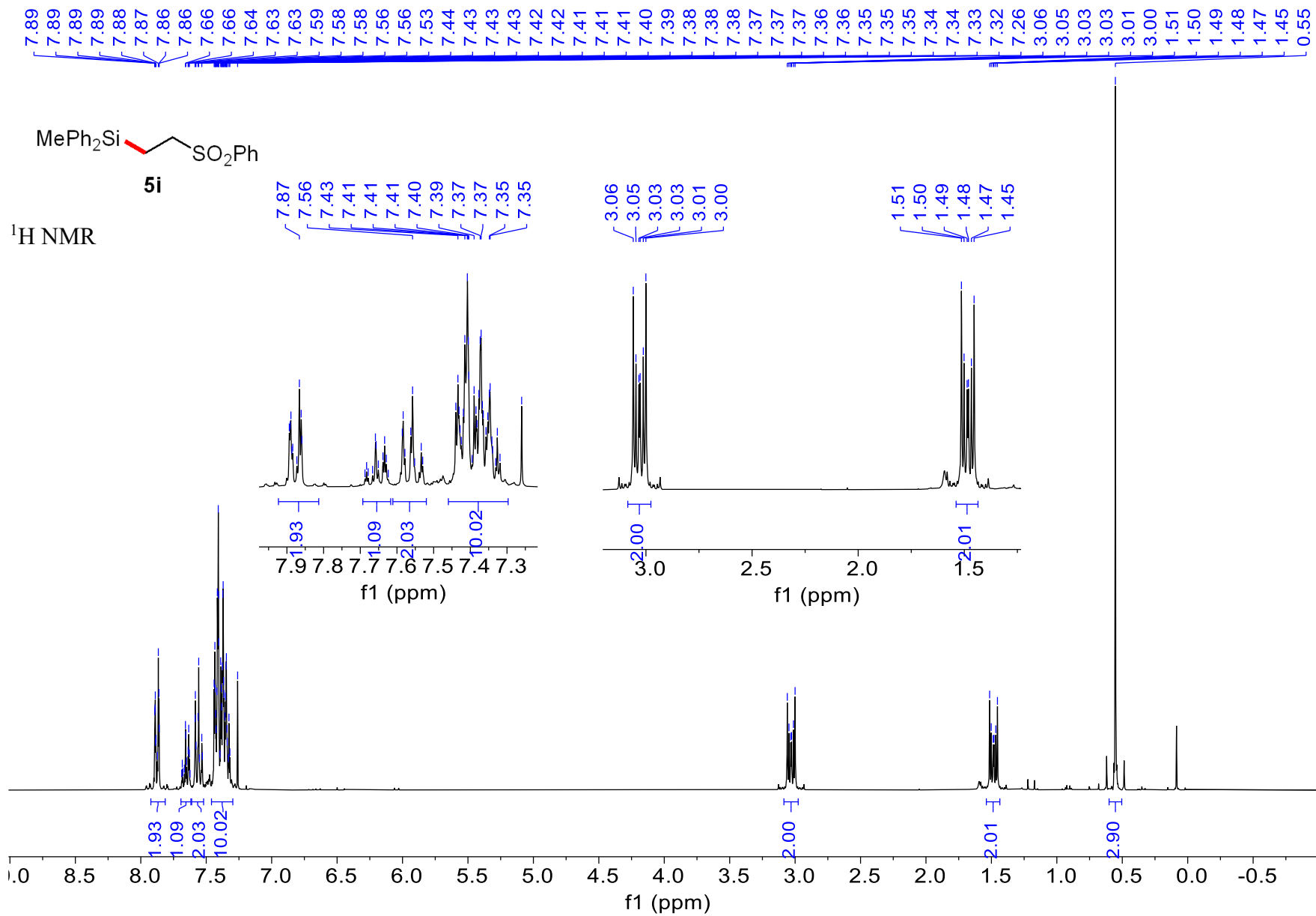
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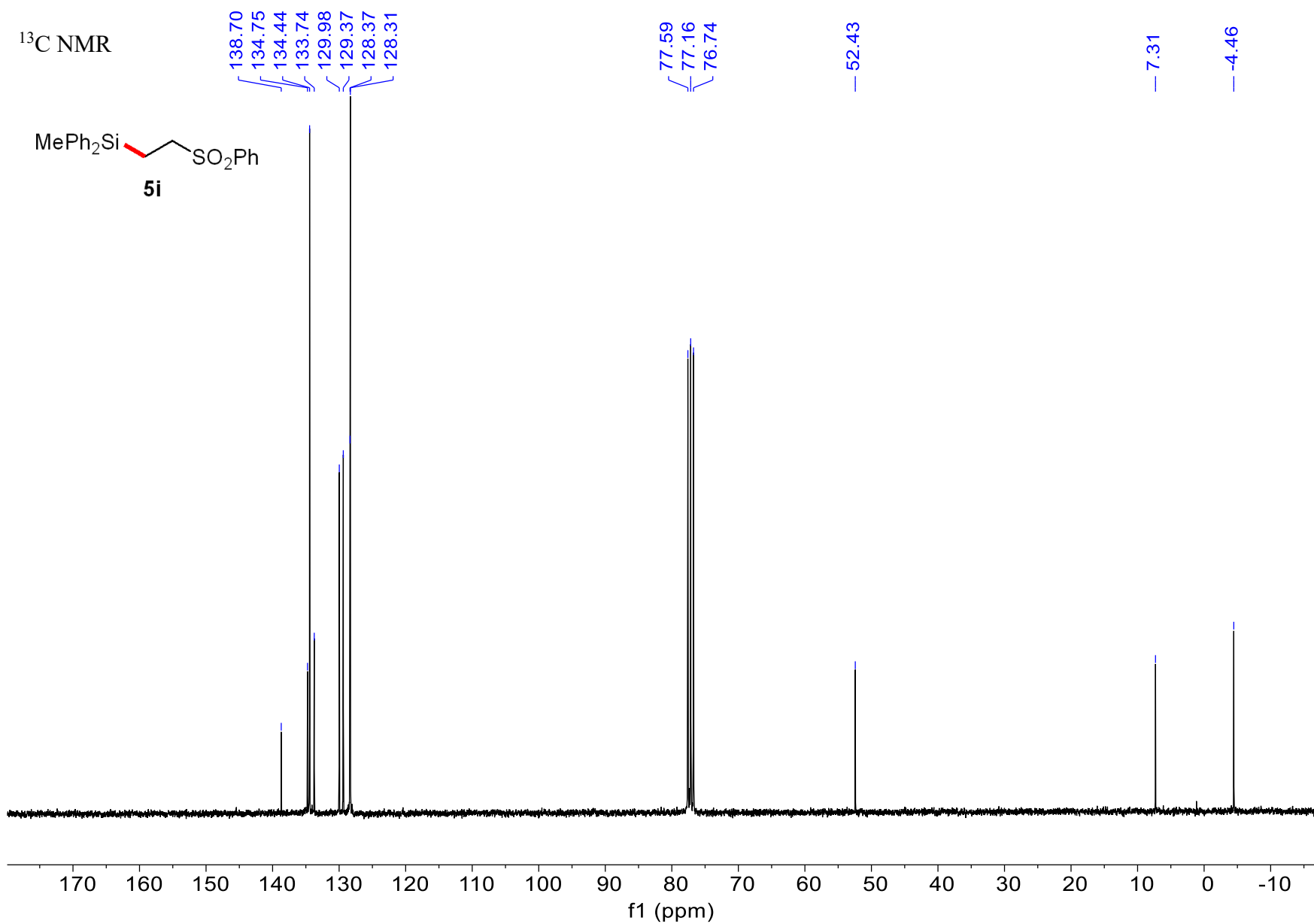


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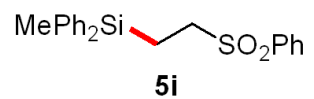
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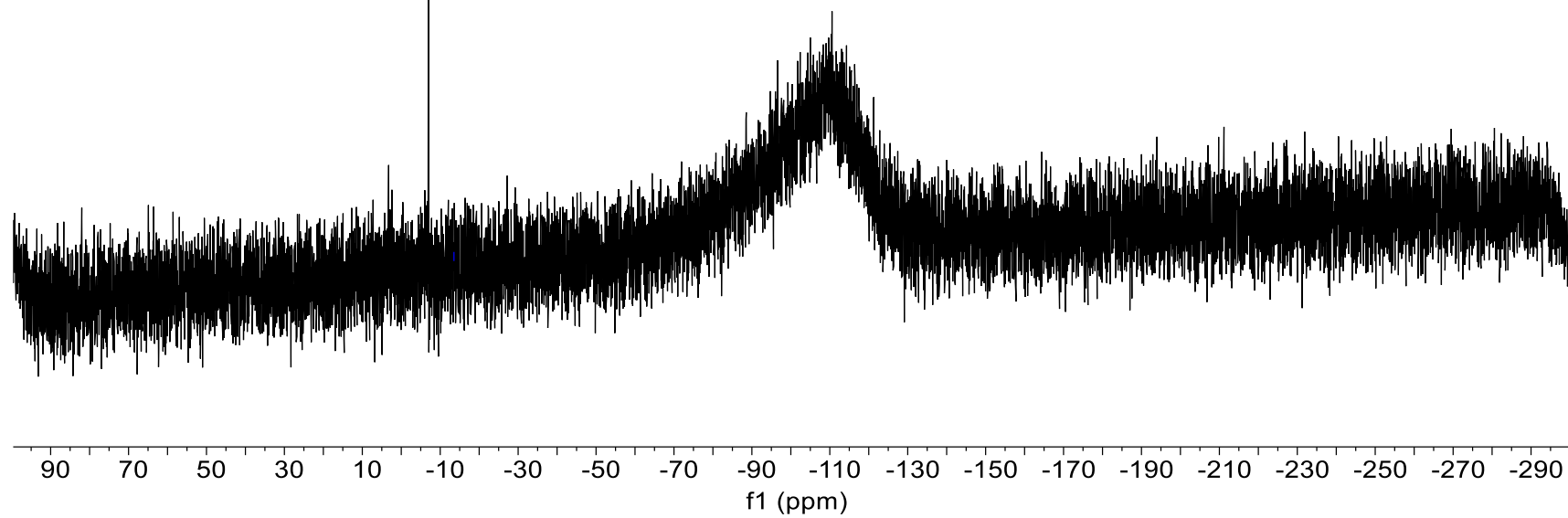




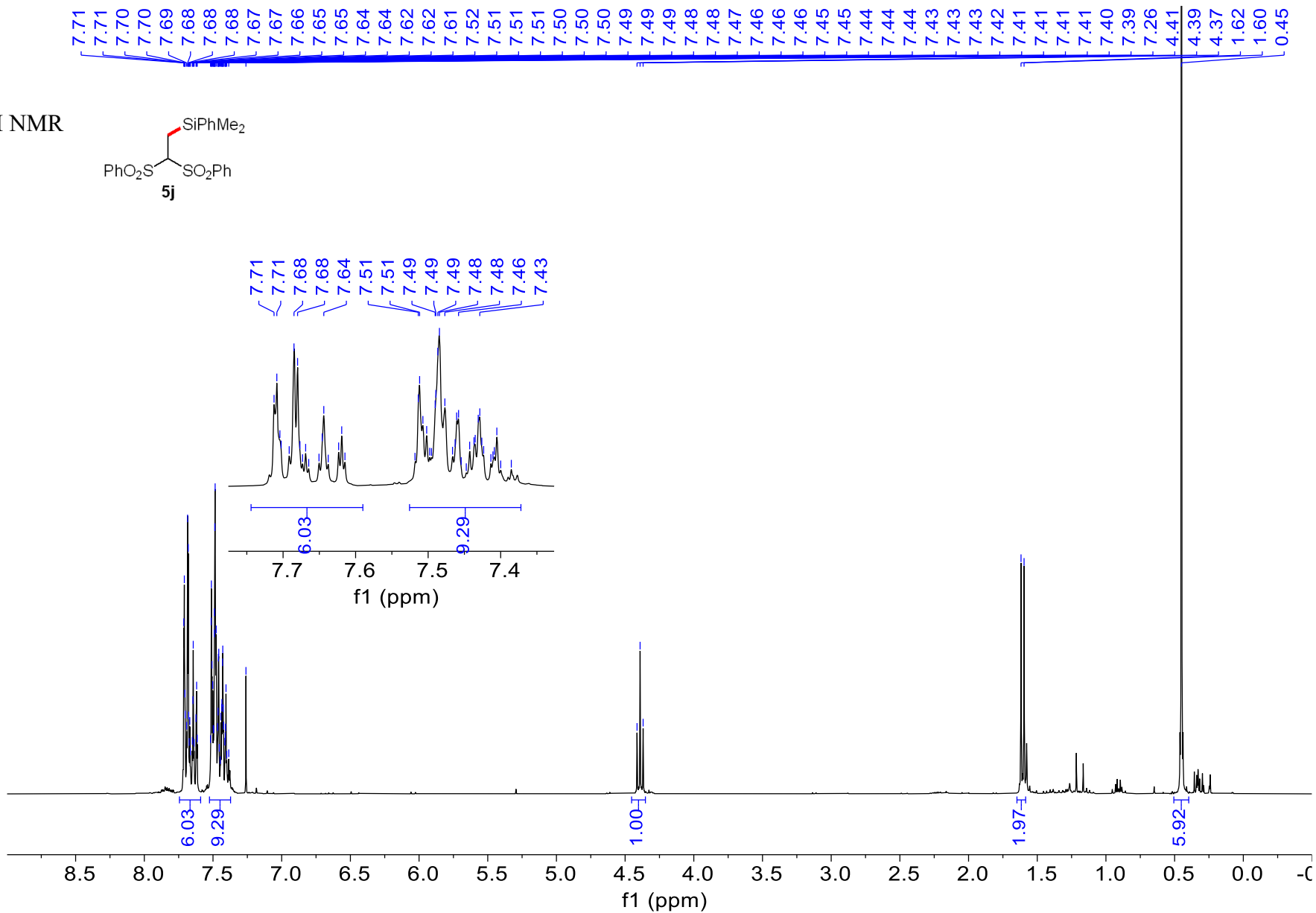
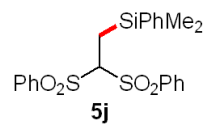
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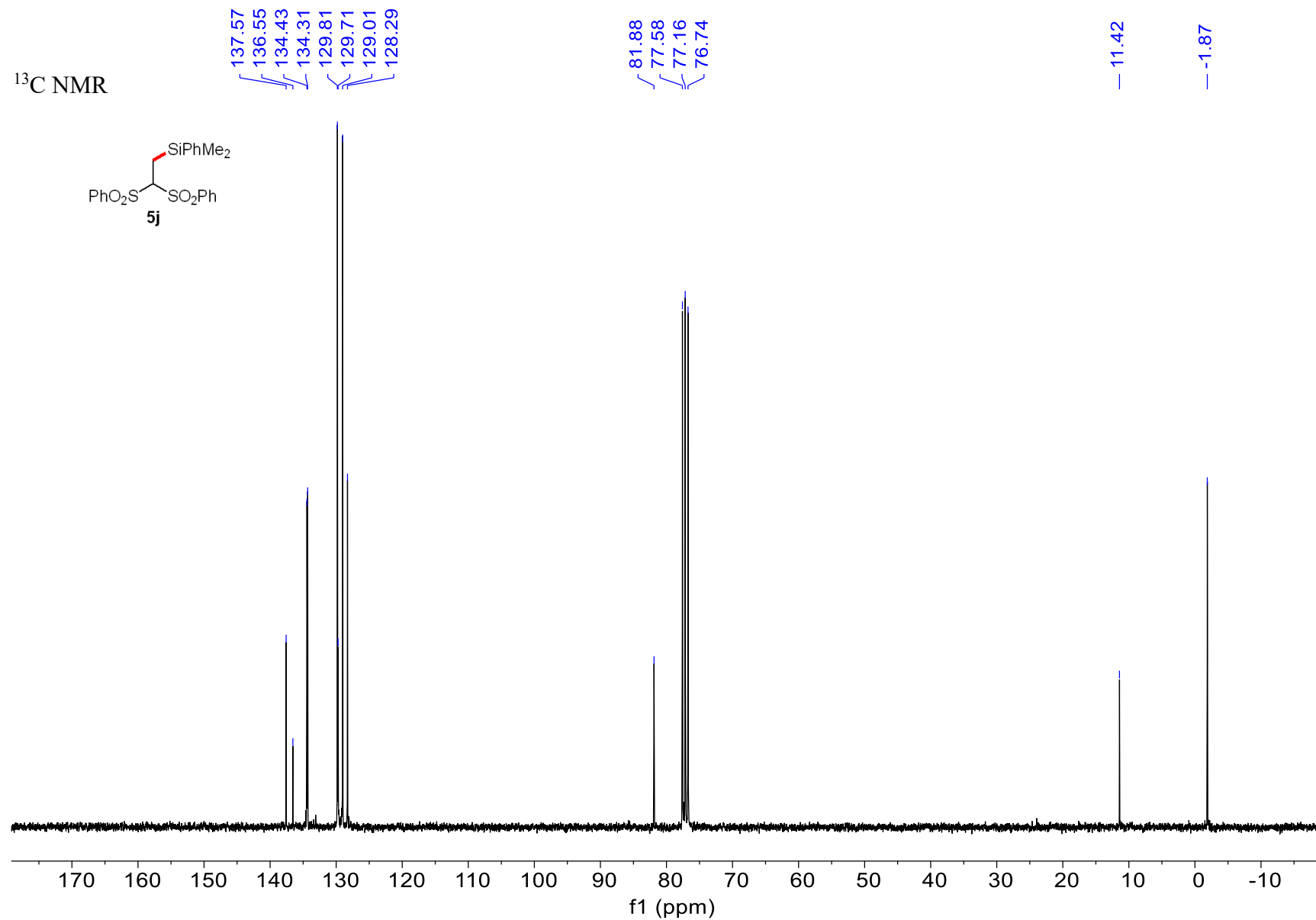


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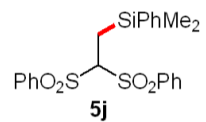


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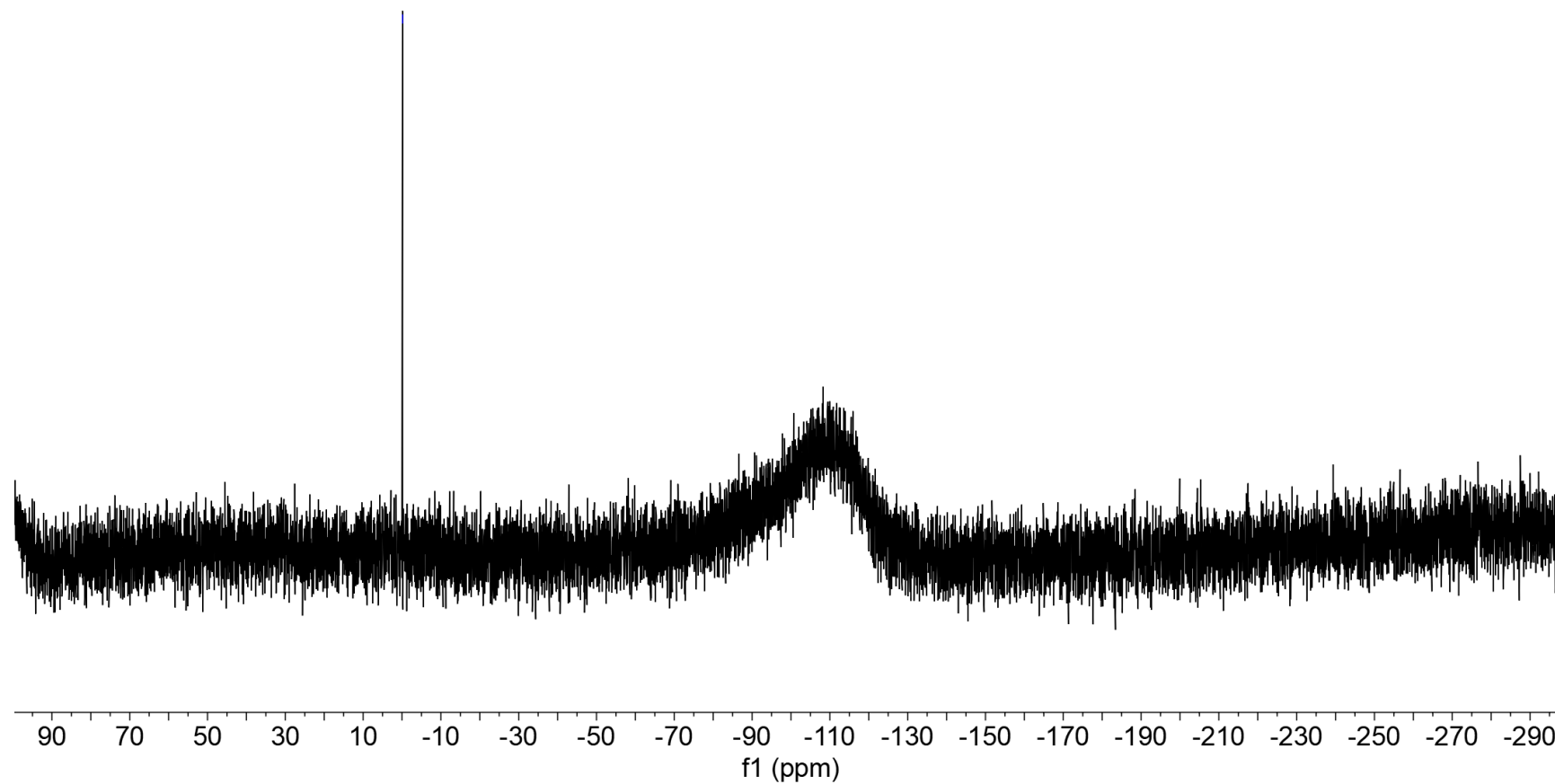


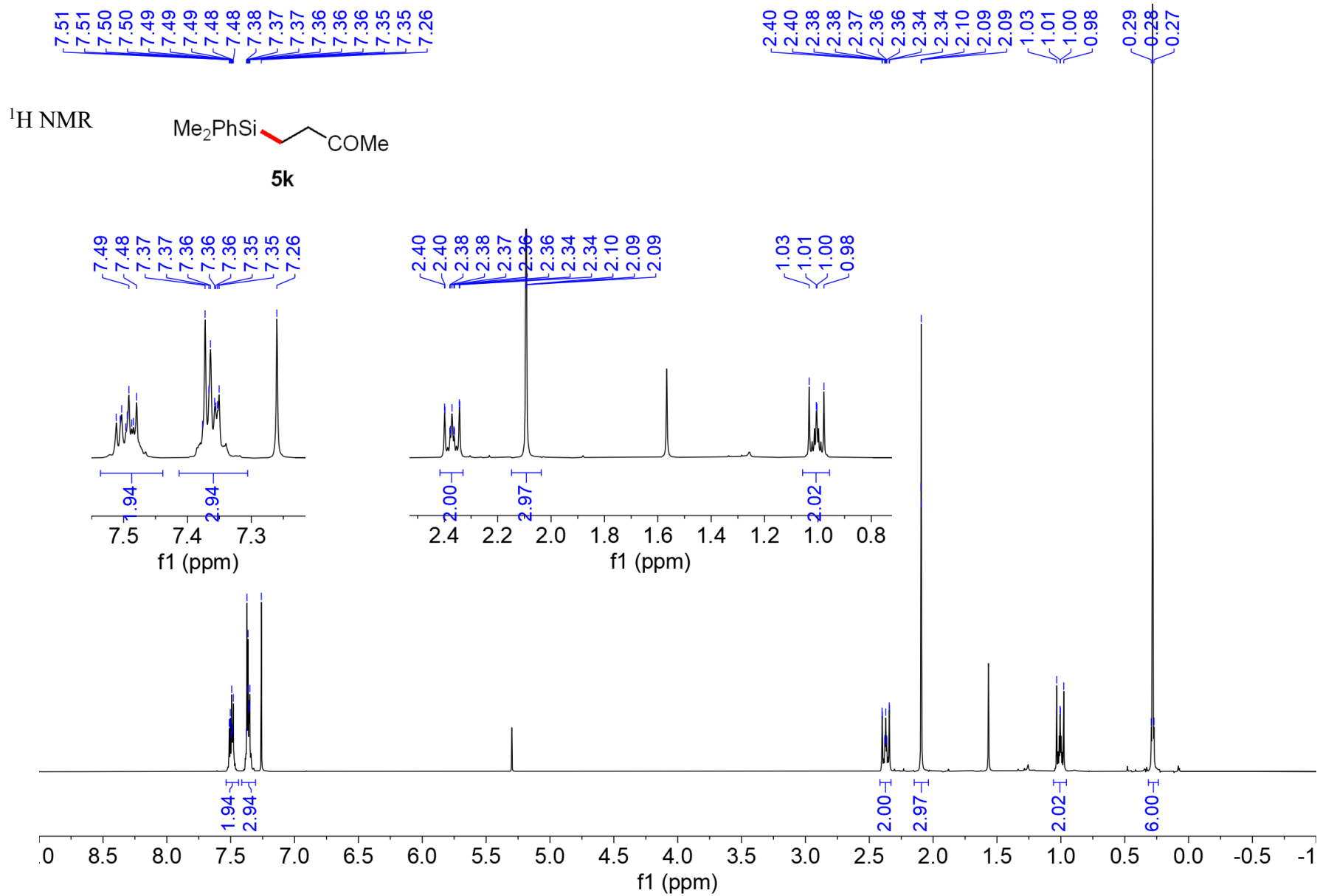


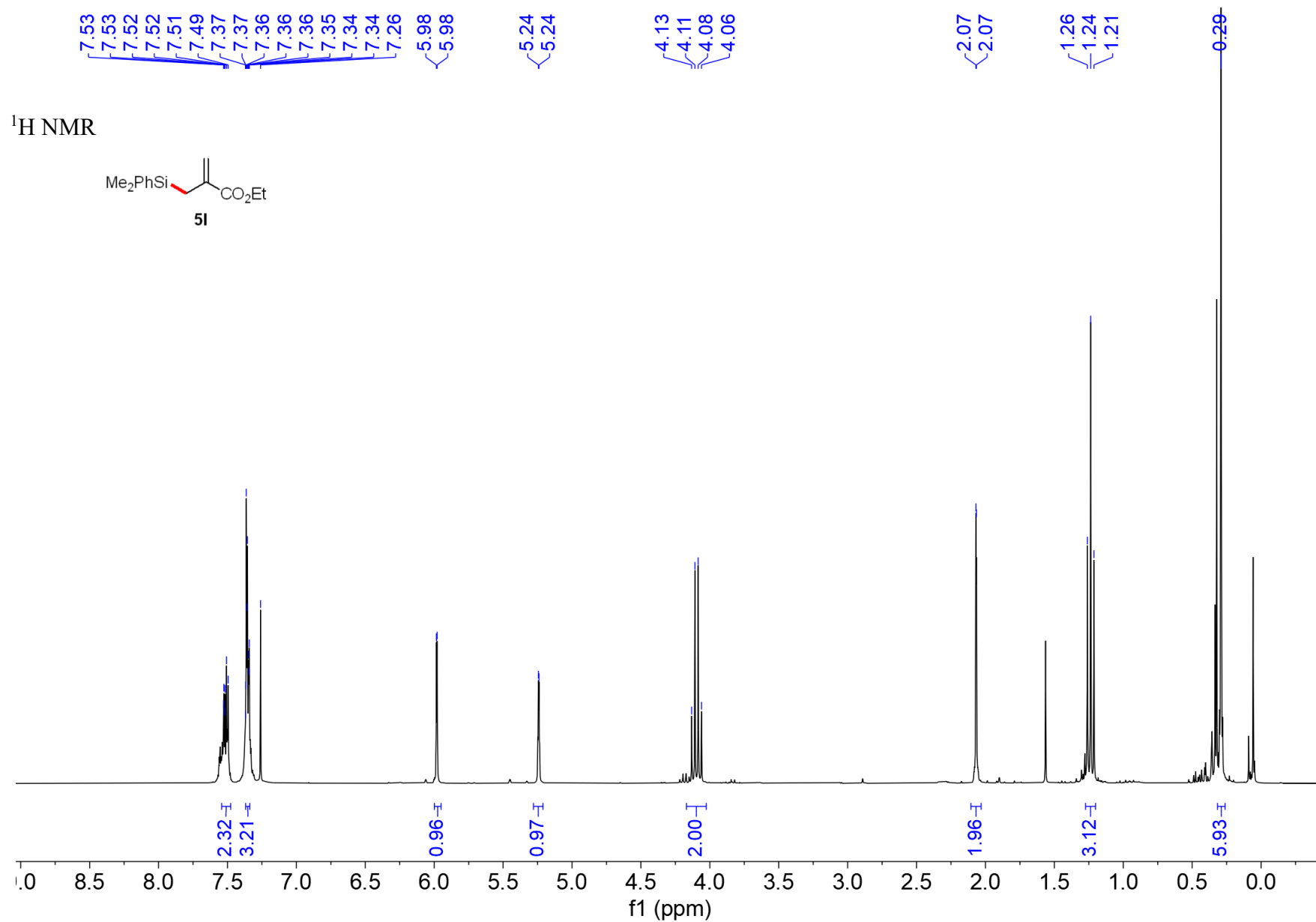
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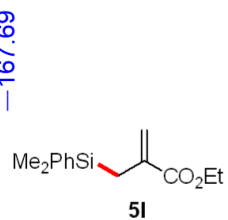


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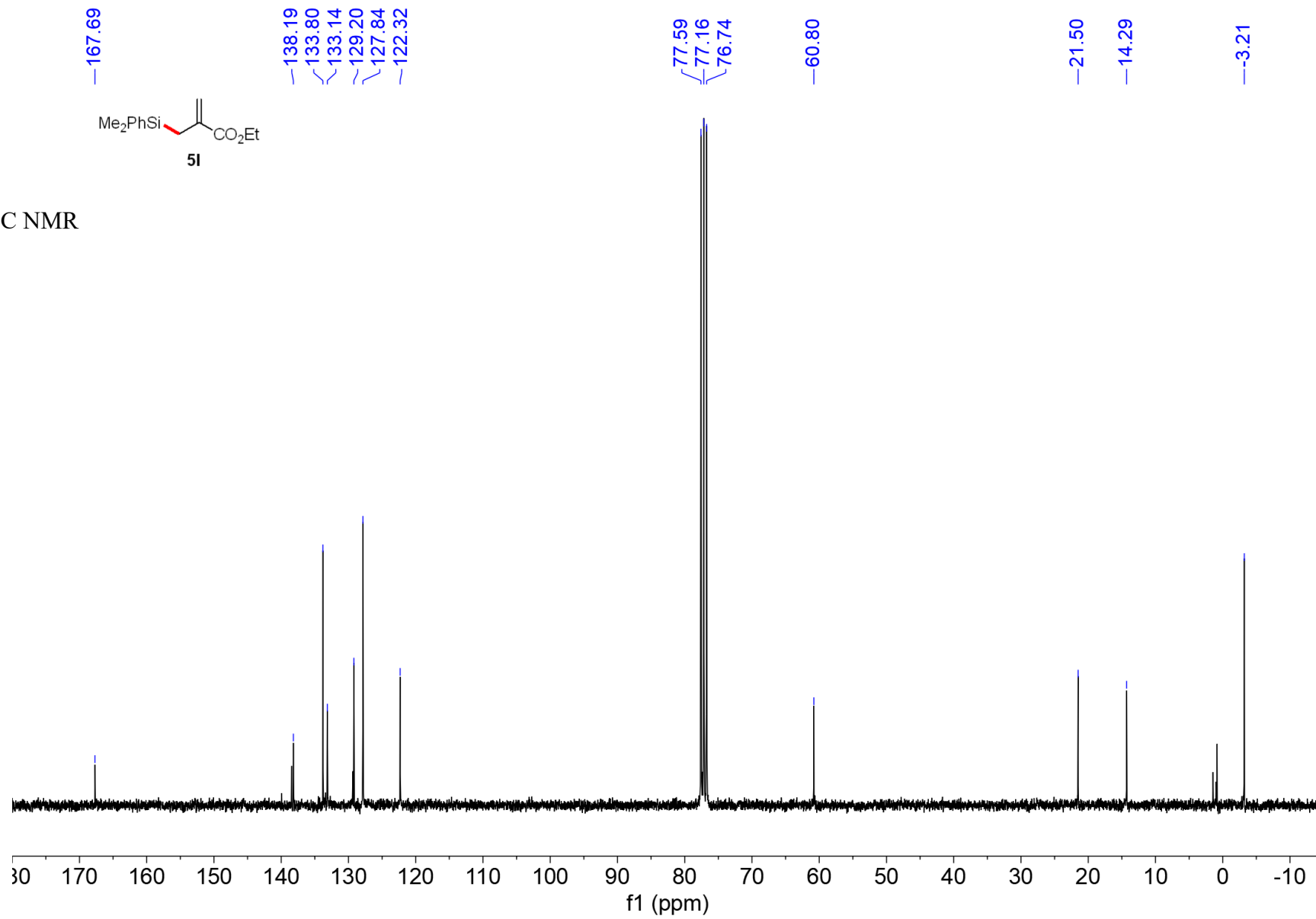




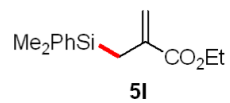




¹³C NMR



^{29}Si NMR



-3.57

