Supporting information

Titanium-catalyzed Highly Stereoselective Anti-Markovnikov Intermolecular Hydroalkoxylation of Alkynes to Prepare Z-Enol Ethers

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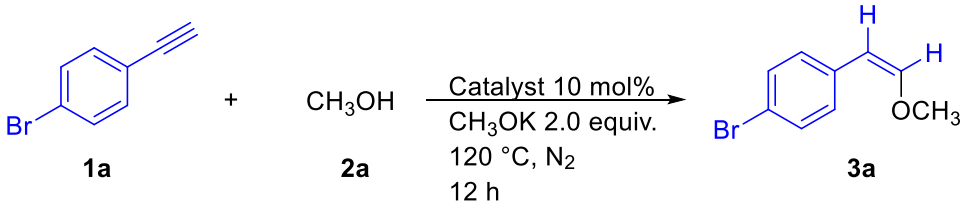
1. General Information

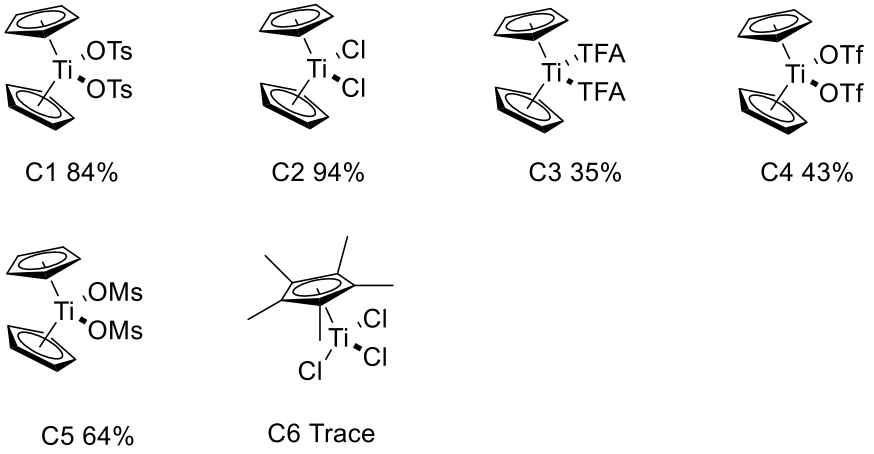
All experiments were performed under a nitrogen atmosphere unless stated otherwise. All solvents are purchased from the highest commercial grades without further purification. Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F254 plates. ^{1}H NMR spectra were recorded on a Bruker-500 MHz spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ=77.00 ppm). Abbreviations for NMR data are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sxt (sextet). Synthesis of alkenyl ether compounds was carried out in 10 mL Schlenk tubes under nitrogen atmosphere at 120 ℃, while gram level synthesis was carried out in 50 mL Schlenk tubes. The reaction is carried out in a heating plate.

2. Optimization of the reaction condition

General procedure for Reaction Optimization: An oven-dried 10 mL Schlenk tube containing 4-bromophenylacetylene **1a** (0.2 mmol, 1.0 equiv.), Ti-catalyst (0.02 mmol, 10 mol%), base (0.4 mmol, 2.0 equiv.), methanol **2a** (0.5 mL). Then the tube is filled with nitrogen and sealed. The reaction was placed on a magnetic stirrer at 120 ℃ for 12 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography.

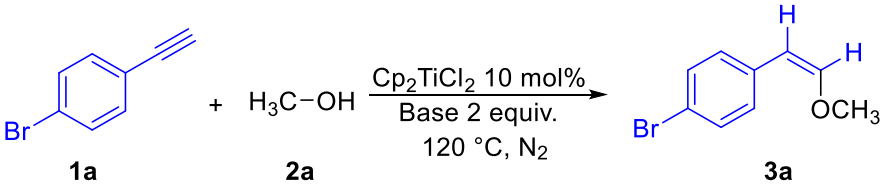
Table S1 Evaluation of catalysts.





Reaction conditions:**1a** (0.2 mmol), **2a** (0.5 mL), Catalyst (10 mol%) and CH_3OK (2.0 equiv.) were stirred with 120 ℃ under N_2 for 12 h.

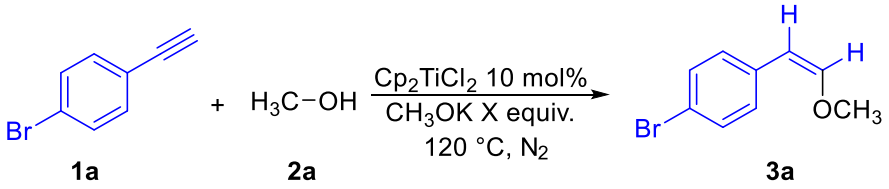
Table S2 Evaluation of different base.



Entry	Base	Yield/%
1	CH_3OK	94
2	CH_3OLi	84
3	NaH	66
4	K_2CO_3	25
5	KF	Trace
6	NaOH	84
7	KOH	87

Reaction conditions:**1a** (0.2 mmol), **2a** (0.5 mL), Cp_2TiCl_2 (10 mol%) and Base (2.0 equiv.) were stirred with 120 ℃ under N_2 for 12 h.

Table S3 Evaluation of different amount of alkali.

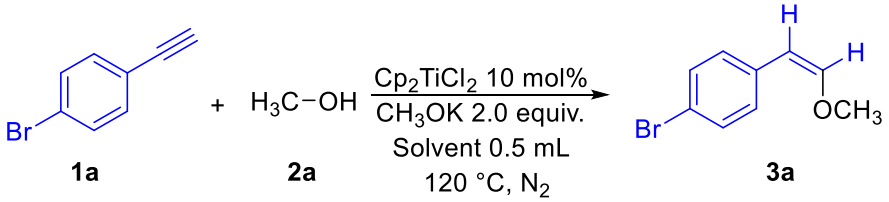


1a **2a** **3a**

Entry	X/equiv.	Yield/%
1	0.5	trace
2	1.0	24
3	1.5	67
4	1.8	79
5	2.0	94
6	3.0	93

Reaction conditions:**1a** (0.2 mmol), **2a** (0.5 mL), Cp_2TiCl_2 (10 mol%) and Base (2.0 equiv.) were stirred with 120 ℃ under N_2 for 12 h.

Table S4 Evaluation of different solvents.

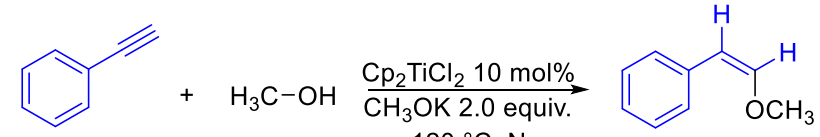


1a **2a** **3a**

Entry	Solvent	Yield/%
1	DMSO	43
2	DMF	36
3	THF	32
4	1,4-dioxane	0
5	CH_3CN	88

Reaction conditions:**1a** (0.2 mmol), **2a** (5.0 equiv.), Cp_2TiCl_2 (10 mol%) and CH_3OK (2.0 equiv.) were stirred with 120 ℃ under N_2 for 12 h.

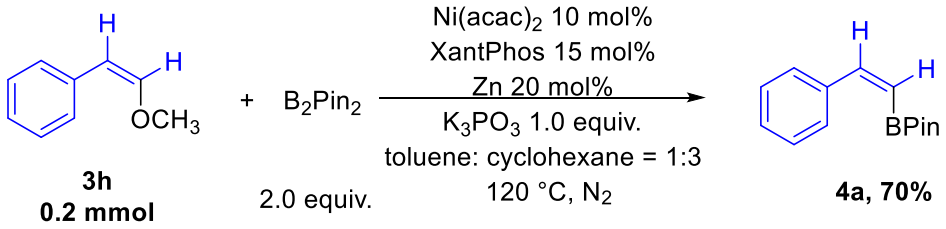
3. Gram-scale Reaction and Derivatizations



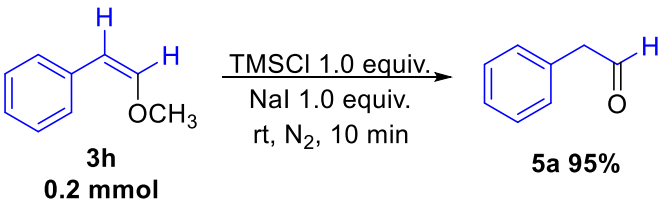
1h **15 mmol** **2a** **10 mL** **3h**

A mixture of phenylacetylene **1h** (1.53 g, 15 mmol, 1.0 equiv.), methanol **2a** (10 mL), Cp_2TiCl_2 (0.375 g, 1.5 mmol, 10 mol%), and CH_3OK (2.1 g, 30 mmol, 2.0

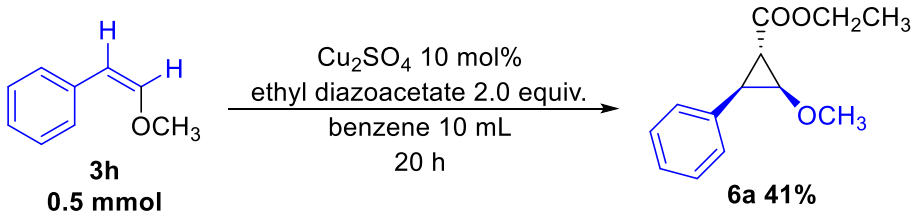
equiv.) was added to a 50 mL Schlenk tube and stirred at 120 ℃, N_2 for 24 h. After the reaction was completed, the reaction was concentrated under reduced pressure to give a crude residue which was purified by column chromatography to give 1.85 g of **3h**, 92% yield of a pale yellow oil liquid.



To a flame dried 10 mL Schlenk tube was added $Ni(acac)_2$ (5.14 mg, 0.02 mmol, 10 mol%), XantPhos (17.4 mg, 0.03 mmol, 15 mol%) and Zn (2.6 mg, 0.04 mmol, 20 mol%), then B_2Pin_2 (101.6 mg, 0.4 mmol, 2.0 equiv.) and K_3PO_4 (42.4 mg, 0.2 mmol, 1.0 equiv.) were added. The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (0.5 mL) and cyclohexane (1.5 mL). Substrates **3h** (26.8 mg, 0.2 mmol, 1.0 equiv.) was also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, the reaction was stirred under 120 ℃ in the heating module for 24 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether and ethyl actate as the eluent to afford the pure product **4a** as a color less oil in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.06 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 7.0 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.54, 135.11, 131.18, 129.68, 118.93, 88.50, 23.22. Spectroscopic data in agreement with the literature[1].



To a flame dried 10 mL Schlenk tube was added TMSCl (21.7 mg, 0.2 mmol, 1.0 equiv.), NaI (29.9 mg, 0.2 mmol, 1.0 equiv.) **3h** (26.8 mg, 0.2 mmol, 1.0 equiv.). The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous CH_3CN (1.0 mL). After that, the reaction was stirred under 25 ℃ in the heating module for 10 min. At the end of the reaction, it was extracted three times with ether, the organic phases were combined, the organic phases were washed with saturated sodium chloride and dried with anhydrous Na_2SO_4. Decompression concentration to obtain yellow oily liquid. The target product **5a** was obtained by column chromatography separation as light yellow oil in 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), δ 7.29 – 7.15 (m, 5H), 3.69 (d, *J* = 1.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.57, 131.84, 129.64, 129.04, 127.45, 77.30, 77.05, 76.79, 50.60. Spectroscopic data in agreement with the literature[2].

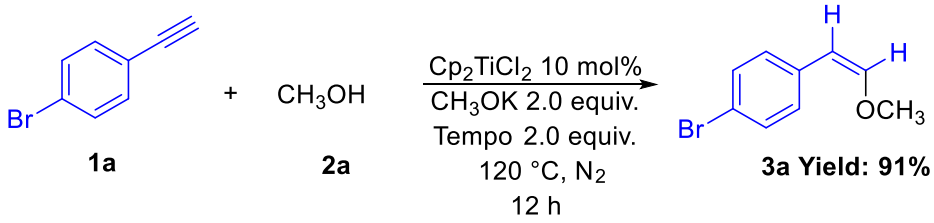


To a flame dried 25 mL round bottom flask was added Cu_2SO_4 (0.008g, 0.05 mmol, 10 mol%), **3h** (26.8 mg, 0.2 mmol, 1.0 equiv.) and benzene (10 mL). Stirring was done at 75 ℃ and ethyl diazoacetate dissolved in benzene was slowly added to the system. The reaction was continued for 1 h. The reaction was then cooled to room temperature and continued for 16 h. At the end of the reaction, the reaction was quenched by the addition of water, extracted three times with ether, the organic phases were combined, the organic phases were washed with saturated sodium chloride and dried with anhydrous Na_2SO_4. Decompression concentration to obtain bownish yellow oily liquid. The target product **6a** was obtained by column chromatography separation as light yellow oil in 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 6.9 Hz, 3H), 5.53 (t, *J* = 7.6 Hz, 1H),

4.57 (q, *J* = 7.9 Hz, 2H), 3.76 (s, 3H), 3.14 (t, *J* = 7.2 Hz, 1H), 2.42 (t, *J* = 6.3 Hz, 1H), 1.23 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.21, 147.94, 128.19, 128.18, 125.74, 77.30, 77.04, 76.79, 60.67, 53.35, 50.61, 39.69, 29.73, 26.63. Spectroscopic data in agreement with the literature[3].

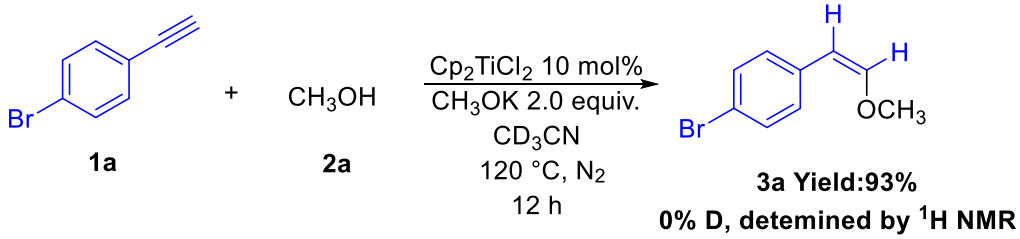
4. Mechanism Studies

a. Radical inhibition experiment



To a flame dried 10 mL Schlenk tube was added 4-bromophenylacetylene **1a** (0.0362g, 0.2 mmol, 1.0 equiv.), Cp_2TiCl_2 (0.005g, 0.02 mmol, 10 mol%), CH_3OK (0.028g, 0.4 mmol, 2.0 equiv.), Tempo (0.0625g, 0.4 mmol, 2.0 equiv.) and methanol **2a** (0.5 mL). Then the tube is filled with nitrogen and sealed. The reaction was placed on a magnetic stirrer at 120 ℃ for 12 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography, affording product **3a** (38.8 mg, 91% yield).

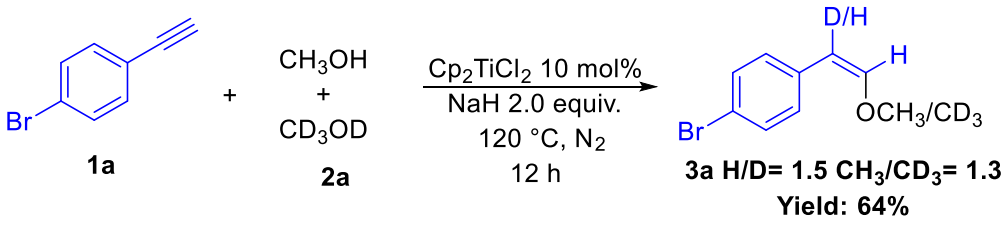
b. Deuterium labeled experiment



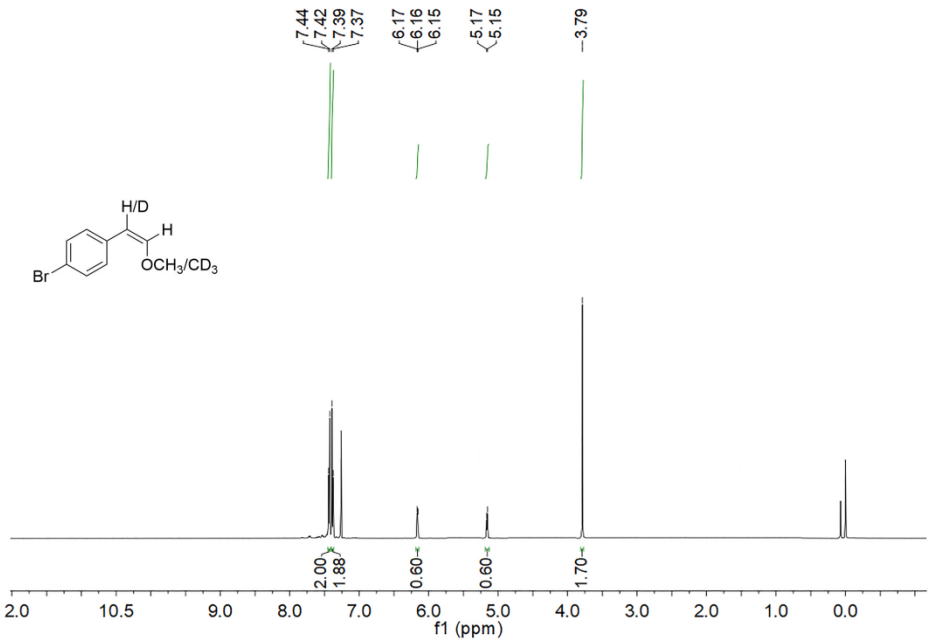
To a flame dried 10 mL Schlenk tube was added 4-bromophenylacetylene **1a** (0.0362g, 0.2 mmol, 1.0 equiv.), 2a (0.032g, 1.0 mmol, 5.0 equiv.), Cp_2TiCl_2 (0.005g, 0.02 mmol, 10 mol%), CH_3OK (0.028g, 0.4 mmol, 2.0 equiv.) and CD_3CN (0.5 mL). Then the tube is filled with nitrogen and sealed. The reaction was placed on a

magnetic stirrer at 120 ℃ for 12 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography, affording product **3a** (39.7 mg, 93% yield).

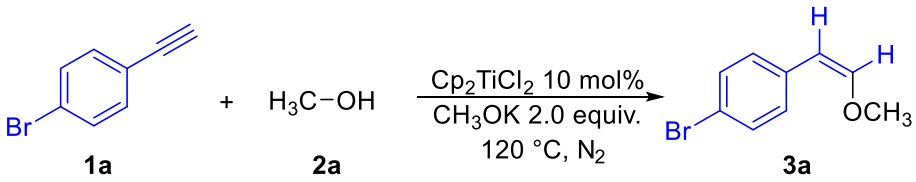
c. Deuterium labeled experiment



To a flame dried 10 mL Schlenk tube was added 4-bromophenylacetylene **1a** (0.0362g, 0.2 mmol, 1.0 equiv.), Cp_2TiCl_2 (0.005g, 0.02 mmol, 10 mol%), NaH (0.0096g, 0.4 mmol, 2.0 equiv.), CH_3OH (0.25 mL) and CD_3OD (0.25 mL). Then the tube is filled with nitrogen and sealed. The reaction was placed on a magnetic stirrer at 120 ℃ for 12 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography, the value of KH/KD is obtained as 1.5.



5. General Procedures



An oven-dried 10 mL Schlenk tube containing 4-bromophenylacetylene **1a** (0.2 mmol, 1.0 equiv.), Cp_2TiCl_2 (0.02 mmol, 10 mol%), CH_3OK (0.4 mmol, 2.0 equiv.), methanol **2a** (0.5 mL). Then the tube is filled with nitrogen and sealed. The reaction was placed on a magnetic stirrer at 120 ℃ for 12 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography, affording product **3a** (40.1 mg, 94% yield, *Z/E*:100:0) The *Z/E* value was determined by ^{1}H NMR analysis using the relative of the product.

When re-expanding the substrate of benzyl alcohol and derivatives, we added benzyl alcohol and derivative **2a** (5.0 equiv.), with acetonitrile as solvent.

All catalysts related to titanium are obtained through methods obtained from published articles[12]. All sources of alkynes are also based on methods obtained from published articles[5, 11, 13].

6. References

1. X. D. Qiu, Y. Y. Li, L. Zhou, P. S. Chen, F. Li, Y. N. Zhang and Y. Li, *Org. Lett.*, 2020, **22**, 6424-6428.

2. Z. Kosarych and T. Cohen, *Tetrahedron Letters*, 1980, 21, 3959-3962.

3. M. J. Rawling, J. H. Rowley, M. Campbell, A. R. Kennedy, J. A. Parkinson and N. C. O. Tomkinson, *Chem. Sci.*, 2014, **5**, 1777-1785.

4. J. Cuthbertson and J. D. Wilden, *Tetrahedron*, 2015, **71**, 4385-4392.

5. M. Kondo, T. Kochi and F. Kakiuchi. *J. Am. Chem. Soc.*, 2011, **133**, 32-34.

6. M. F. Zheng, L. B. Huang, W. Q. Wu and H. F. Jiang, *Org. Lett.*, 2013, **15**, 1838-1841.

7. C. E. Brown, J. Mcnulty, C. Bordón, R. Yolken and L. Jones-Brando, *Org. Biomol. Chem.*, 2016, **00**, 1-3.

8. P. Molina, M. Alajarin, A. Vidal and P. Sánchez-Andrada, *J. Org. Chem.*, 1992, **57**, 929-939.

9. B. M. Trost and G. R. Dake, *J. Am. Chem. Soc.*, 1997, **119**, 7595-7596.

10. R. H. Lam, D. B. Walker, M. H. Tucker, M. R. D. Gatus, M. Bhadbhade and B. A. Messerle, *Organometallics*, 2015, **34**, 4312 – 4317.

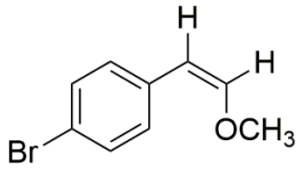
11. M. Patel, R. K. Saunthwal, D. K. Dhaked, P. V. Bharatam and A. K. Verma, *Asian J. Org. Chem.*, 2016, **5**, 213-221.

12. R. B. Richrath, T. Olyschl-ger, S. Hildebrandt, D. G. Enny, G. D. Fianu, R. A. Flowers II and A. Gansauer, Chem. Eur. J., 2018, **24**, 6371-6379.

13. S. Zhao, X. Y. Wang, P. F. Wang, G. W. Wang, W. T. Zhao, X. Y. Tang and M. J. Guo, Org. Lett., 2019, **21**, 3990-3993.

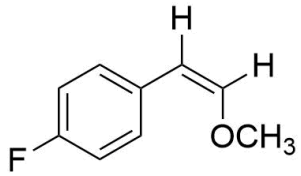
7. Product Synthesis and Characterization

(*Z*)-1-bromo-4-(2-methoxyvinyl)benzene. (**3a**)



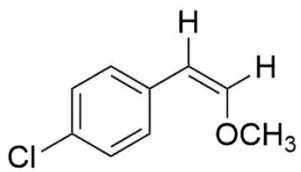
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), methanol (0.5 mL) afforded compound **3a** (40.1 mg, 94% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.40 – 7.37 (m, 2H), 6.16 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.55, 134.83, 131.20, 129.76, 119.14, 104.58, 60.81. Spectroscopic data in agreement with the literature[4].

(*Z*)-1-fluoro-4-(2-methoxyvinyl)benzene. (**3b**)



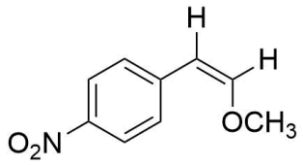
Following the general procedure described above, the reaction of 1-ethynyl-4-fluorobenzene (0.2 mmol, 24.6 mg), methanol (0.5 mL) afforded compound **3b** (25.4 mg, 84% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 6.99 – 6.94 (m, 2H), 6.11 (d, *J* = 7.0 Hz, 1H), 5.19 (d, *J* = 7.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.75, 147.43, 147.41, 130.94, 128.85, 115.03, 114.86, 104.60, 65.59. Spectroscopic data in agreement with the literature[5].

(*Z*)-1-chloro-4-(2-methoxyvinyl)benzene. (**3c**)



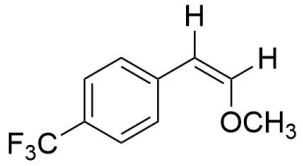
Following the general procedure described above, the reaction of 1-chloro-4-ethynylbenzene (0.2 mmol, 27.3 mg), methanol (0.5 mL) afforded compound **3c** (32.3 mg, 96% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 6.15 (d, *J* = 7.0 Hz, 1H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.37, 134.40, 131.03, 129.41, 128.25, 104.56, 60.78. Spectroscopic data in agreement with the literature[6].

(*Z*)-1-(2-methoxyvinyl)-4-nitrobenzene. (**3d**)



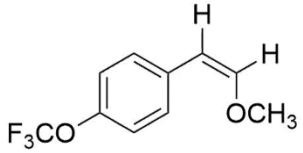
Following the general procedure described above, the reaction of 1-ethynyl-4-nitrobenzene (0.2 mmol, 29.4 mg), methanol (0.5 mL) afforded compound **3d** (30.8 mg, 86% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 6.21 (d, *J* = 7.0 Hz, 1H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.96, 130.25, 126.61, 125.17, 114.55, 99.99, 56.22. Spectroscopic data in agreement with the literature[5].

(*Z*)-1-(2-methoxyvinyl)-4-(trifluoromethyl)benzene. (**3e**)



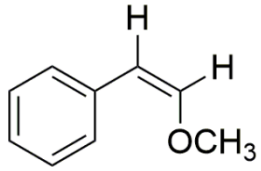
Following the general procedure described above, the reaction of 1-ethynyl-4-(trifluoromethyl)benzene (0.2 mmol, 34.0 mg), methanol (0.5 mL) afforded compound **3e** (37.2 mg, 92% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 6.24 (d, *J* = 7.0 Hz, 1H), 5.25 (d, *J* = 7.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.86, 129.92, 128.13, 126.14, 126.11, 126.05, 125.04, 125.01, 104.45, 60.97. Spectroscopic data in agreement with the literature[4].

(*Z*)-1-(2-methoxyvinyl)-4-(trifluoromethoxy)benzene. (**3f**)



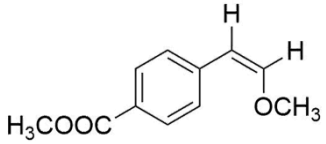
Following the general procedure described above, the reaction of 1-ethynyl-4-(trifluoromethoxy)benzene (0.2 mmol, 37.2 mg), methanol (0.5 mL) afforded compound **3f** (35.8 mg, 82% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.16 (d, *J* = 7.0 Hz, 1H), 5.21 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.42, 144.22, 127.26, 124.06, 112.00, 111.50, 103.11, 58.37. Spectroscopic data in agreement with the literature[5].

(*Z*)-(2-methoxyvinyl)benzene. (**3g**)



Following the general procedure described above, the reaction of ethynyl benzene (0.2 mmol, 20.4 mg), methanol (0.5 mL) afforded compound **3g** (26.5 mg, 99% yield) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.06 (s, 1H), 6.06 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 7.0 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.94, 129.64, 129.44, 129.03, 128.18, 125.74, 105.69, 60.67. Spectroscopic data in agreement with the literature[4].

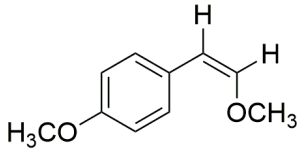
methyl (*Z*)-4-(2-methoxyvinyl)benzoate. (**3h**)



Following the general procedure described above, the reaction of methyl 4-ethynylbenzoate (0.2 mmol, 32.0 mg), methanol (0.5 mL) afforded compound **3h** (13.8 mg, 36% yield) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8

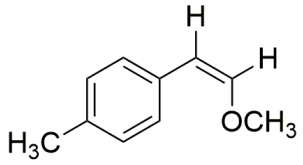
Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.98 (d, *J* = 7.0 Hz, 1H), 5.10 (d, *J* = 7.0 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.55, 147.28, 146.08, 129.12, 125.92, 113.86, 113.36, 104.97, 104.35, 55.04, 54.97. Spectroscopic data in agreement with the literature[5].

(*Z*)-1-methoxy-4-(2-methoxyvinyl)benzene. (**3i**)



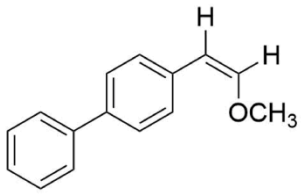
Following the general procedure described above, the reaction of 1-ethynyl-4-methoxybenzene (0.2 mmol, 26.4 mg), methanol (0.5 mL) afforded compound **3i** (22.0 mg, 67% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 6.88 – 6.81 (m, 2H), 6.06 (d, *J* = 7.0 Hz, 1H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.82, 145.30, 128.34, 125.14, 112.58, 104.19, 59.45, 55.43. Spectroscopic data in agreement with the literature[4].

(*Z*)-1-(2-methoxyvinyl)-4-methylbenzene. (**3j**)



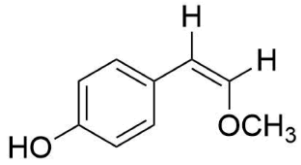
Following the general procedure described above, the reaction of 1-ethynyl-4-methylbenzene (0.2 mmol, 23.2 mg), methanol (0.5 mL) afforded compound **3j** (24.3 mg, 82% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.10 (d, *J* = 7.0 Hz, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.25, 135.36, 133.02, 128.88, 128.11, 105.63, 60.58, 21.20. Spectroscopic data in agreement with the literature[4].

(*Z*)-4-(2-methoxyvinyl)-1,1'-biphenyl. (**3k**)



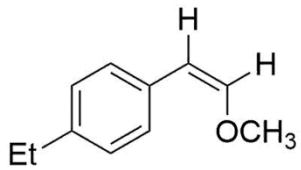
Following the general procedure described above, the reaction of 4-ethynyl-1,1'-biphenyl (0.2 mmol, 35.6 mg), methanol (0.5 mL) afforded compound **3k** (26.5 mg, 63% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.61 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.46 – 7.41 (m, 2H), 7.33 (ddd, *J* = 7.4, 4.0, 1.2 Hz, 1H), 6.18 (d, *J* = 7.0 Hz, 1H), 5.28 (d, *J* = 7.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.20, 141.12, 138.36, 135.07, 128.73, 128.59, 126.91, 126.87, 105.31, 60.76. Spectroscopic data in agreement with the literature[6].

(*Z*)-4-(2-methoxyvinyl)phenol. (**3l**)



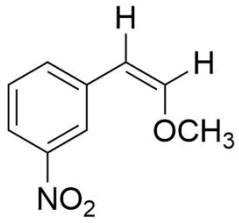
Following the general procedure described above, the reaction of 4-ethynylphenol (0.2 mmol, 23.6 mg), methanol (0.5 mL) afforded compound **3l** (11.7 mg, 39% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.23 (d, *J* = 7.0 Hz, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.05, 141.15, 138.82, 134.67, 133.90, 111.42, 66.37. Spectroscopic data in agreement with the literature[7].

(*Z*)-1-ethyl-4-(2-methoxyvinyl)benzene. (**3m**)



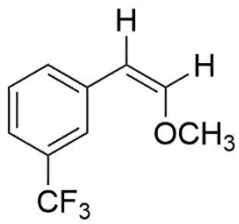
Following the general procedure described above, the reaction of 1-ethyl-4-ethynylbenzene (0.2 mmol, 23.6 mg), methanol (0.5 mL) afforded compound **3m** (28.9 mg, 89% yield) as pale yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.10 (d, *J* = 7.0 Hz, 1H), 5.21 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.28, 141.82, 133.29, 128.17, 127.68, 105.63, 60.57, 28.62, 15.65. Spectroscopic data in agreement with the literature[6].

(Z)-1-(2-methoxyvinyl)-3-nitrobenzene. (**3n**)



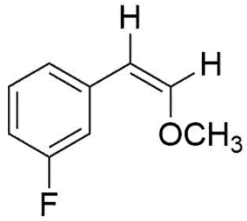
Following the general procedure described above, the reaction of 1-ethynyl-3-nitrobenzene (0.2 mmol, 29.4 mg), methanol (0.5 mL) afforded compound 3n (31.9 mg, 89% yield) as yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 8.44 (t, J = 1.9 Hz, 1H), 7.96 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 6.28 (d, J = 7.0 Hz, 1H), 5.28 (d, J = 7.0 Hz, 1H), 3.85 (s, 3H). 13C NMR (125 MHz, $CDCl_3$) δ 150.25, 137.57, 133.85, 128.88, 122.68, 120.28, 103.60, 77.30, 77.04, 76.79, 61.19.

(Z)-1-(2-methoxyvinyl)-3-(trifluoromethyl)benzene. (**3o**)



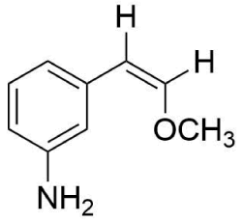
Following the general procedure described above, the reaction of 1-ethynyl-3-(trifluoromethyl)benzene (0.2 mmol, 34.0 mg), methanol (0.5 mL) afforded compound **3o** (39.6 mg, 98% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.62 (t, *J* = 3.8 Hz, 6.7 Hz, 1H), 7.30 (d, *J* = 5.0 Hz, 2H), 6.14 (d, *J* = 7.0 Hz, 1H), 5.17 (d, *J* = 7.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.30, 136.61, 131.20, 131.20, 128.49, 124.73, 124.70, 122.17, 122.14, 104.39, 60.95. Spectroscopic data in agreement with the literature[5].

(*Z*)-1-fluoro-3-(2-methoxyvinyl)benzene. (**3p**)



Following the general procedure described above, the reaction of 1-ethynyl-3-fluorobenzene (0.2 mmol, 24.1 mg), methanol (0.5 mL) afforded compound **3p** (26.1 mg, 86% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 11.0 Hz, 1H), 7.22 (t, *J* = 5.2 Hz, 2H), 6.87 – 6.76 (m, 1H), 6.17 (d, *J* = 7.0 Hz, 1H), 5.21 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.80, 161.87, 148.92, 138.08, 138.01, 129.42, 129.35, 123.84, 123.82, 114.82, 114.64, 112.57, 112.40, 104.75, 104.73, 60.84. Spectroscopic data in agreement with the literature[5].

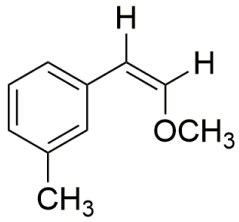
(*Z*)-3-(2-methoxyvinyl)aniline. (**3q**)



Following the general procedure described above, the reaction of 3-ethynylaniline (0.2 mmol, 23.4 mg), methanol (0.5 mL) afforded compound **3q** (21.4 mg, 72% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 1H), 7.02 – 7.01

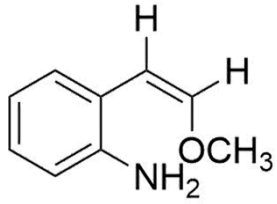
(m, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.53 – 6.49 (m, 1H), 6.10 (d, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.88, 146.14, 136.81, 129.04, 119.12, 114.91, 113.04, 105.78, 60.67. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(2-methoxyvinyl)-3-methylbenzene. (**3r**)



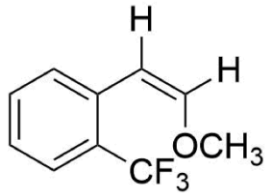
Following the general procedure described above, the reaction of 1-ethynyl-3-methylbenzene (0.2 mmol, 23.2 mg), methanol (0.5 mL) afforded compound **3r** (20.7 mg, 70% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 6.7 Hz, 2H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.04 (d, *J* = 7.0 Hz, 1H), 5.12 (d, *J* = 7.0 Hz, 1H), 3.70 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.46, 135.56, 133.23, 129.08, 128.31, 105.83, 60.78, 21.41. Spectroscopic data in agreement with the literature[4].

(*Z*)-2-(2-methoxyvinyl)aniline. (**3s**)



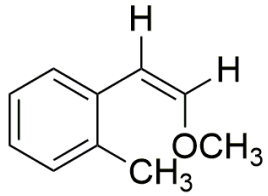
Following the general procedure described above, the reaction of 2-ethynylaniline (0.2 mmol, 23.4 mg), methanol (0.5 mL) afforded compound **3s** (26.8 mg, 90% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.9 Hz, 2H), 6.16 (d, *J* = 7.0 Hz, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.11, 142.54, 130.12, 127.44, 121.54, 119.11, 116.54, 101.50, 60.48. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(2-methoxyvinyl)-2-(trifluoromethyl)benzene. (**3t**)



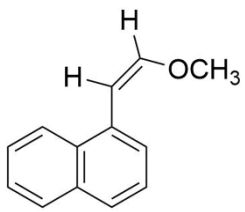
Following the general procedure described above, the reaction of 1-ethynyl-2-(trifluoromethyl)benzene (0.2 mmol, 34 mg), methanol (0.5 mL) afforded compound **3t** (20.6 mg, 51% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 7.3 Hz, 1H), 5.47 (dd, *J* = 7.2, 1.8 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.52, 133.93, 133.92, 131.36, 130.65, 125.57, 125.52, 125.41, 100.55, 100.53, 60.87. Spectroscopic data in agreement with the literature[9].

(*Z*)-1-(2-methoxyvinyl)-2-methylbenzene. (**3u**)



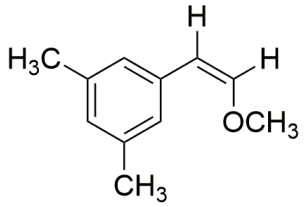
Following the general procedure described above, the reaction of 1-ethynyl-2-methylbenzene (0.2 mmol, 23.2 mg), methanol (0.5 mL) afforded compound **3u** (13.3 mg, 45% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.05(t, *J* = 7.7 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.09 (d, *J* = 7.0 Hz, 1H), 5.19 (d, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.81, 134.91, 132.58, 128.43, 127.66, 105.18, 60.13, 20.76. Spectroscopic data in agreement with the literature[6].

(*Z*)-1-(2-methoxyvinyl)naphthalene. (**3v**)



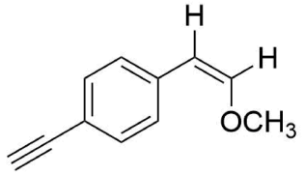
Following the general procedure described above, the reaction of 1-ethynylnaphthalene (0.2 mmol, 23.2 mg), methanol (0.5 mL) afforded compound **3v** (23.5 mg, 64% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 8.9 Hz, 1H), 7.54 – 7.44 (m, 3H), 6.39 (d, *J* = 7.2 Hz, 1H), 5.92 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.66, 126.74, 126.73, 126.47, 126.10, 125.33, 123.90, 101.57, 53.60. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(2-methoxyvinyl)-3,5-dimethylbenzene. (**3w**)



Following the general procedure described above, the reaction of 1-ethynyl-3,5-dimethylbenzene (0.2 mmol, 26.0 mg), methanol (0.5 mL) afforded compound **3w** (26.5 mg, 72% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.80 (s, 1H), 6.10 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.10, 136.20, 133.87, 129.72, 128.95, 106.47, 61.42, 22.05. Spectroscopic data in agreement with the literature[8].

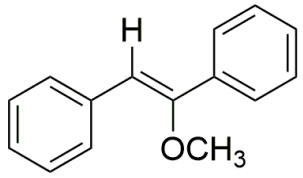
(*Z*)-1-ethynyl-4-(2-methoxyvinyl)benzene. (**3x**)



Following the general procedure described above, the reaction of 1,4-diethynylbenzene (0.2 mmol, 25.2 mg), methanol (0.5 mL) afforded compound **3x** (14.9 mg, 47% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.17 (d, *J* = 7.0 Hz, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 3.07 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.98, 136.59, 131.97,

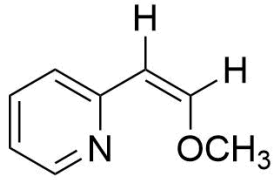
127.97, 118.90, 105.09, 84.22, 60.88. Spectroscopic data in agreement with the literature[7].

(*Z*)-(1-methoxyethene-1,2-diyl)dibenzene. (**3y**)



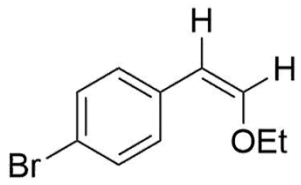
Following the general procedure described above, the reaction of 1,2-diphenylethyne (0.2 mmol, 35.6 mg), methanol (0.5 mL) afforded compound **3y** (14.7 mg, 35% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 4H), 7.21 (t, *J* = 7.7 Hz, 5H), 7.06 (t, *J* = 7.4 Hz, 2H), δ 5.67 (s, 1H), δ 4.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.85, 132.22, 130.84, 129.64, 128.25, 106.21, 60.58. Spectroscopic data in agreement with the literature[10].

(*Z*)-2-(2-methoxyvinyl)pyridine. (**3z**)



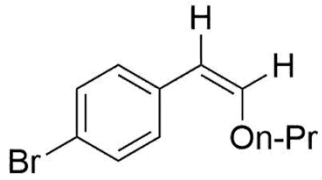
Following the general procedure described above, the reaction of 2-ethynylpyridine (0.2 mmol, 20.6 mg), methanol (0.5 mL) afforded compound **3z** (22.4 mg, 83% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.6 Hz, 1H), 7.59 (td, *J* = 7.7, 1.6 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.12 (dd, *J* = 7.1, 5.3 Hz, 1H), 6.34 (d, *J* = 7.2 Hz, 1H), 5.50 (d, *J* = 7.2 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.33, 150.95, 149.23, 136.36, 124.15, 121.51, 104.45, 53.56. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-4-(2-ethoxyvinyl)benzene. (**3aa**)



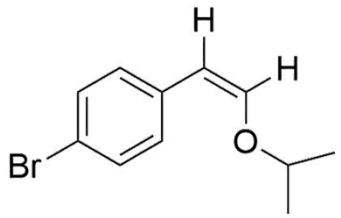
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), ethanol (0.5 mL) afforded compound **3aa** (42.4 mg, 94% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.23 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.18, 132.47, 131.18, 129.71, 118.98, 104.38, 69.30, 15.45. Spectroscopic data in agreement with the literature[4].

(*Z*)-1-bromo-4-(2-propoxyvinyl)benzene. (**3ab**)



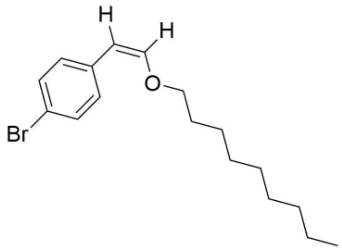
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), propanol (0.5 mL) afforded compound **3ab** (39.8 mg, 83% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.23 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 7.0 Hz, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.75 (dd, *J* = 8.3, 3.1 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.54, 131.18, 129.68, 118.93, 104.21, 75.44, 23.22, 10.41. Spectroscopic data in agreement with the literature[5].

(*Z*)-1-bromo-4-(2-isopropoxyvinyl)benzene. (**3ac**)



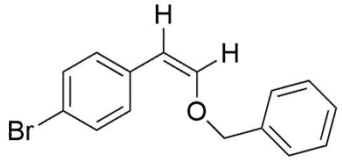
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), isopropanol (0.5 mL) afforded compound **3ac** (21.6 mg, 45% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.22 (d, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 4.33 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.22, 136.78, 132.85, 131.35, 120.60, 105.88, 77.11, 24.89. Spectroscopic data in agreement with the literature[4].

(*Z*)-1-bromo-4-(2-(nonyloxy)vinyl)benzene. (**3ad**)



Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), nonyl alcohol (0.5 mL) afforded compound **3ad** (21.6 mg, 39% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.22 (d, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.27 (s, 12H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.56, 135.10, 131.17, 129.66, 118.91, 104.19, 73.98, 31.87, 29.86, 29.50, 29.30, 29.24, 25.84, 22.68, 14.12. Spectroscopic data in agreement with the literature[8].

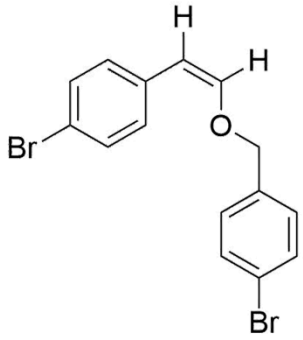
(*Z*)-1-(2-(benzyloxy)vinyl)-4-bromobenzene. (**3ae**)



Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), phenylmethanol (1.0 mmol, 108.1 mg) afforded compound **3ae** (46.1 mg, 80% yield) as pale yellow oil. ^{1}H NMR (500

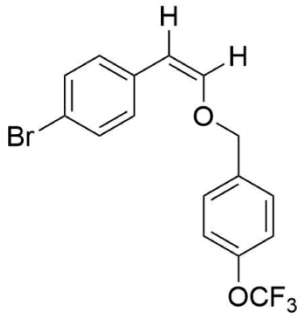
MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.35 (m, 7H), 6.31 (d, *J* = 7.0 Hz, 1H), 5.22 (d, *J* = 7.0 Hz, 1H), 5.00 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.89, 136.99, 134.82, 131.26, 129.88, 128.68, 128.20, 127.29, 119.24, 105.25, 75.11. Spectroscopic data in agreement with the literature[6]. Spectroscopic data in agreement with the literature[11].

(*Z*)-1-bromo-4-(2-((4-bromobenzyl)oxy)vinyl)benzene. (**3af**)



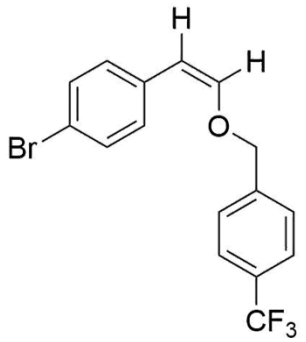
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (4-bromophenyl)methanol (1.0 mmol, 185.9 mg) afforded compound **3af** (50.0 mg, 68% yield) as pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.4 Hz, 2.1 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.14 (m, 2H), 6.19 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 7.0 Hz, 1H), 4.86 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.52, 135.95, 134.61, 131.84, 131.30, 129.89, 128.94, 122.19, 119.43, 105.67, 74.32. Spectroscopic data in agreement with the literature[11].

(*Z*)-1-bromo-4-(2-((4-(trifluoromethoxy)benzyl)oxy)vinyl)benzene. (**3ag**)



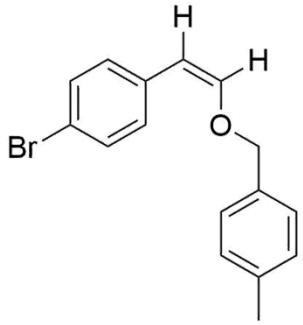
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (4-(trifluoromethoxy)phenyl)methanol (1.0 mmol, 192.0 mg) afforded compound **3ag** (47.6 mg, 64% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.20 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 4.90 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.52, 135.68, 134.60, 131.31, 129.90, 128.63, 121.18, 119.46, 105.71, 74.16. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-4-(2-((4-(trifluoromethyl)benzyl)oxy)vinyl)benzene. (**3ah**)



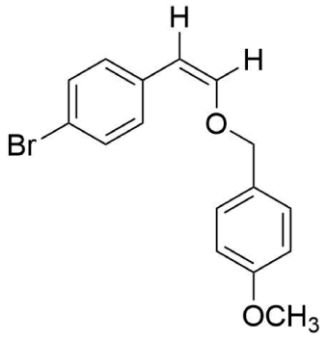
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (4-(trifluoromethyl)phenyl)methanol (1.0 mmol, 176.1 mg) afforded compound **3ah** (35.6 mg, 50% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.46 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.27 (d, *J* = 7.0 Hz, 1H), 5.26 (d, *J* = 7.0 Hz, 1H), 5.05 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.41, 139.94, 133.45, 130.29, 128.88, 126.16, 124.63, 124.60, 118.50, 104.88, 73.14. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-4-(2-((4-methylbenzyl)oxy)vinyl)benzene. (**3ai**)



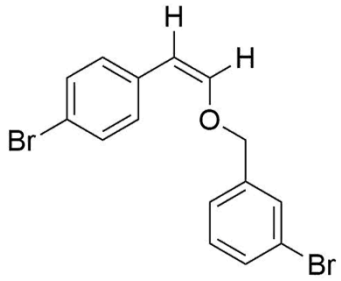
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), p-tolylmethanol (1.0 mmol, 122.1 mg) afforded compound **3ai** (29.5 mg, 49% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.22 (d, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 7.0 Hz, 1H), 4.87 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.88, 138.04, 134.89, 133.94, 131.23, 129.85, 129.35, 127.49, 119.16, 105.11, 75.05, 21.22. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-4-(2-((4-methoxybenzyl)oxy)vinyl)benzene. (**3aj**)



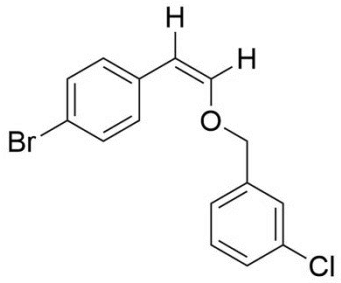
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (4-methoxyphenyl)methanol (1.0 mmol, 138.7 mg) afforded compound **3aj** (41.3 mg, 65% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 7.0 Hz, 1H), 5.12 (d, *J* = 7.0 Hz, 1H), 4.84 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.61, 146.77, 134.89, 131.22, 129.83, 129.12, 129.01, 119.14, 114.05, 105.08, 74.86, 55.31. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-3-(((4-bromostyryl)oxy)methyl)benzene. (**3ak**)



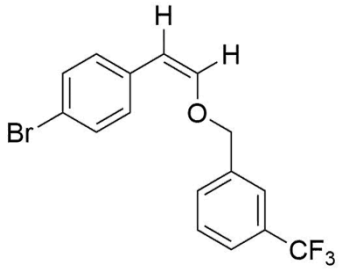
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (3-bromophenyl)methanol (1.0 mmol, 185.9 mg) afforded compound **3ak** (43.4 mg, 59% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 4.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.47, 139.24, 134.57, 131.31, 130.31, 130.26, 129.92, 125.77, 122.75, 119.47, 105.76, 74.15. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(((4-bromostyryl)oxy)methyl)-3-chlorobenzene. (**3al**)



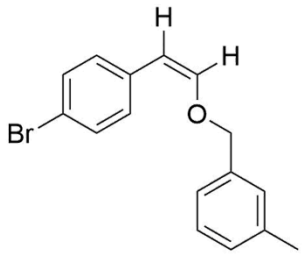
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (3-chlorophenyl)methanol (1.0 mmol, 142.3 mg) afforded compound **3al** (32.8 mg, 51% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.15 (m, 4H), 6.19 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 4.88 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.49, 138.98, 134.61, 134.58, 131.67, 131.31, 130.02, 129.92, 128.36, 127.33, 126.74, 125.28, 119.46, 105.74, 74.23. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(((4-bromostyryl)oxy)methyl)-3-(trifluoromethyl)benzene. (**3am**)



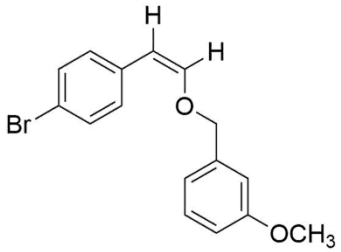
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (3-(trifluoromethyl)phenyl)methanol (1.0 mmol, 176.6 mg) afforded compound **3am** (32.7 mg, 46% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 4H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.27 (d, *J* = 7.0 Hz, 1H), 5.26 (d, *J* = 6.9 Hz, 1H), 5.05 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.44, 134.48, 131.69, 131.34, 129.92, 127.45, 127.21, 126.74, 125.68, 125.65, 119.56, 105.95, 74.20. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(((4-bromostyryl)oxy)methyl)-3-methylbenzene. (**3an**)



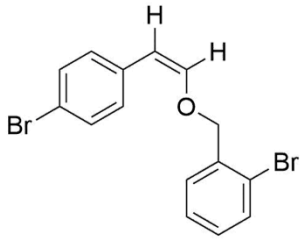
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), m-tolylmethanol (1.0 mmol, 122.1 mg) afforded compound **3an** (34.4 mg, 57% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.15 (dd, *J* = 12.4, 7.2 Hz, 3H), 6.29 (d, *J* = 7.0 Hz, 1H), 5.19 (d, *J* = 7.0 Hz, 1H), 4.94 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.93, 138.38, 136.88, 134.86, 131.24, 129.87, 128.97, 128.59, 128.10, 124.45, 119.19, 105.12, 75.16, 21.45. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(((4-bromostyryl)oxy)methyl)-3-methoxybenzene. (**3ao**)



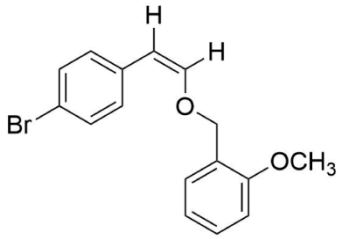
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (3-methoxyphenyl)methanol (1.0 mmol, 138.2 mg) afforded compound **3ao** (23.5 mg, 37% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.22 (d, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 4.89 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.87, 146.85, 138.58, 134.80, 131.25, 129.89, 129.74, 119.41, 113.66, 112.69, 105.35, 74.91, 55.24. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-2-(((4-bromostyryl)oxy)methyl)benzene. (**3ap**)



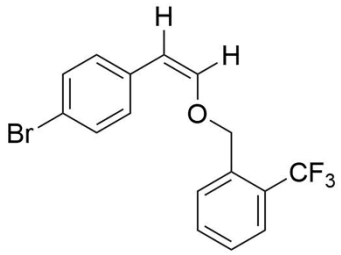
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (2-bromophenyl)methanol (1.0 mmol, 185.9 mg) afforded compound **3ap** (47.8 mg, 65% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.43 (dd, *J* = 7.6, 2.4 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 7.0 Hz, 1H), 5.26 (d, *J* = 7.0 Hz, 1H), 5.07 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.30, 136.61, 131.20, 131.20, 130.58, 130.33, 128.49, 124.73, 124.70, 122.17, 122.14, 104.39, 60.95. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-(((4-bromostyryl)oxy)methyl)-2-methoxybenzene. (**3aq**)



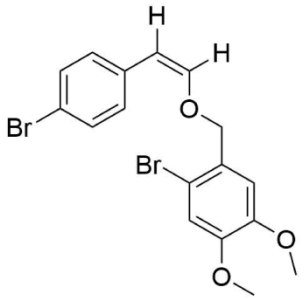
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (2-methoxyphenyl)methanol (1.0 mmol, 138.1 mg) afforded compound **3aq** (46.4 mg, 73% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.27 (d, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 7.0 Hz, 1H), 4.96 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.63, 135.04, 131.20, 129.82, 129.28, 128.57, 125.52, 120.60, 119.02, 110.30, 104.77, 70.65, 55.36. Spectroscopic data in agreement with the literature[8].

(Z)-1-(((4-bromostyryl)oxy)methyl)-2-(trifluoromethyl)benzene. (**3ar**)



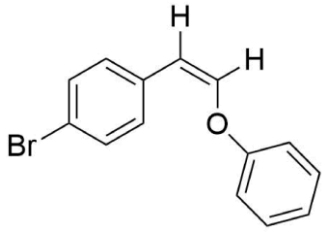
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (2-(trifluoromethyl)phenyl)methanol (1.0 mmol, 176.5 mg) afforded compound **3ar** (44.1 mg, 62% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 8.5 Hz, 3H), 6.27 (d, *J* = 7.0 Hz, 1H), 5.27 (d, *J* = 7.0 Hz, 1H), 5.20 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.80, 146.71, 134.55, 132.29, 131.66, 131.33, 129.93, 128.79, 128.37, 127.94, 126.76, 126.01, 125.97, 119.50, 105.82, 71.34, 71.31. Spectroscopic data in agreement with the literature[8].

(Z)-1-bromo-2-(((4-bromostyryl)oxy)methyl)-4,5-dimethoxybenzene. (**3as**)



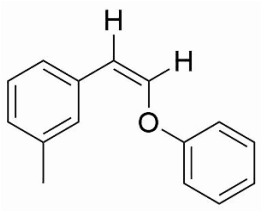
Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), (2-bromo-4,5-dimethoxyphenyl)methanol (1.0 mmol, 245.3 mg) afforded compound **3as** (63.3 mg, 74% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.31 (d, *J* = 7.0 Hz, 1H), 5.27 (d, *J* = 7.0 Hz, 1H), 4.99 (s, 2H), 3.87 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.85, 146.83, 138.56, 134.78, 131.23, 129.87, 129.72, 119.39, 119.24, 113.64, 112.67, 105.33, 77.28, 77.03, 76.77, 74.89, 55.22. Spectroscopic data in agreement with the literature[8].

(*Z*)-1-bromo-4-(2-phenoxyvinyl)benzene. (**3at**)



Following the general procedure described above, the reaction of 1-bromo-4-ethynylbenzene (0.2 mmol, 36.2 mg), phenol (1.0 mmol, 94.4 mg) afforded compound **3at** (43.8 mg, 80% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 9.5 Hz, 3H), 6.64 (d, *J* = 6.9 Hz, 1H), 5.56 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.13, 142.42, 133.86, 131.41, 130.22, 129.82, 123.63, 120.23, 116.99, 109.16. Spectroscopic data in agreement with the literature[11].

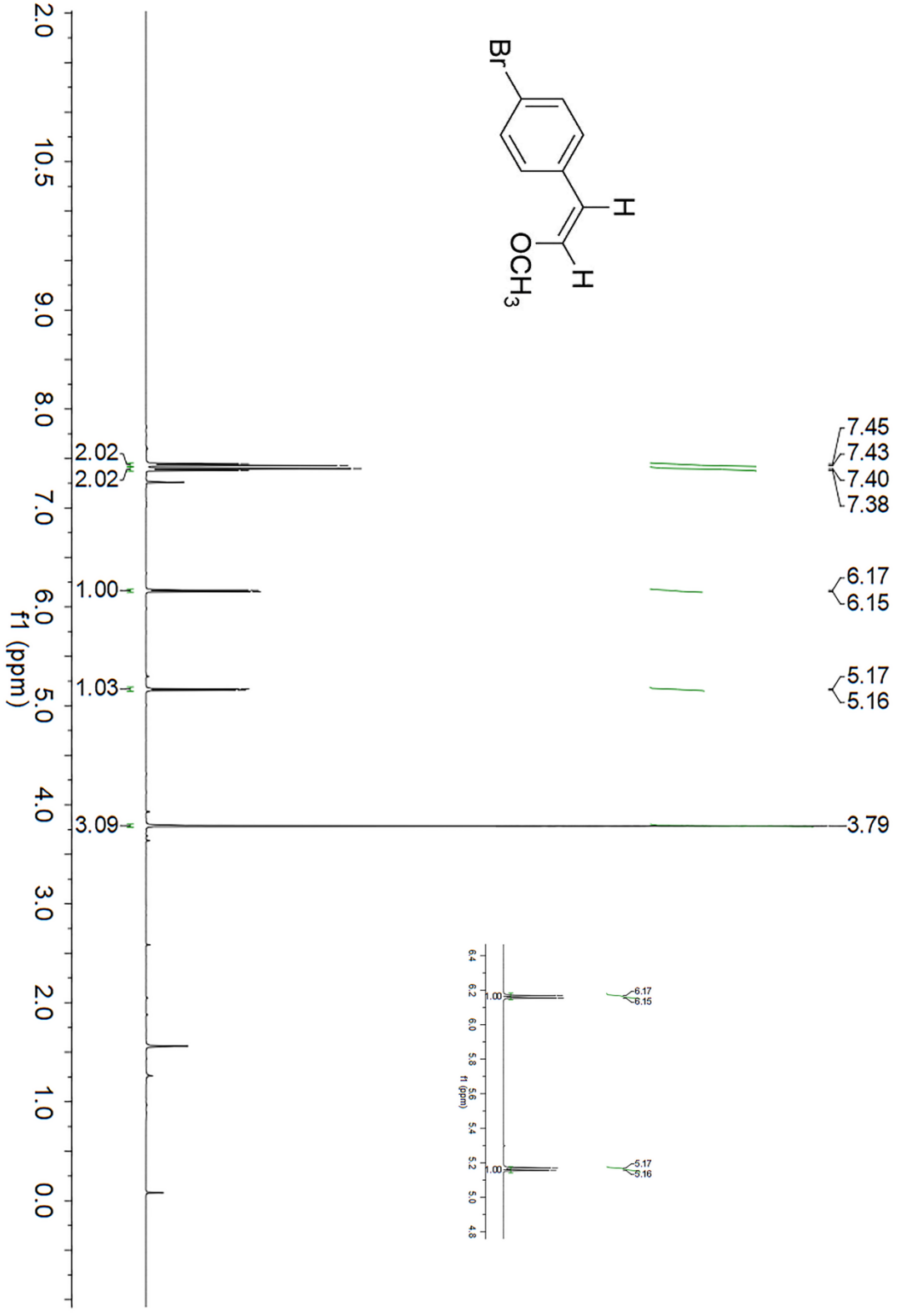
(Z)-1-methyl-3-(2-phenoxyvinyl)benzene. (3au)



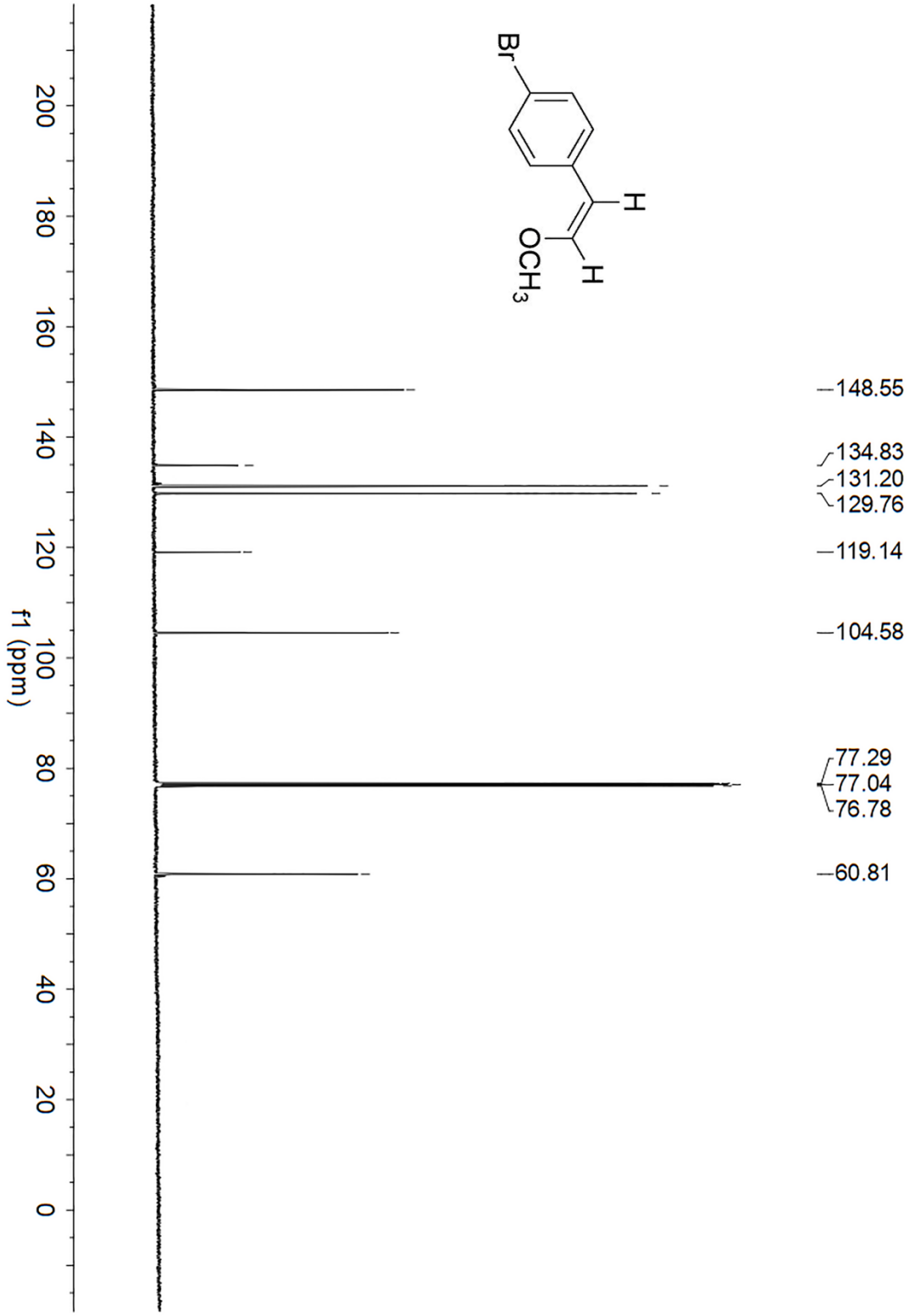
Following the general procedure described above, the reaction of 1-ethynyl-3-methylbenzene (0.2 mmol, 23.2 mg), phenol (1.0 mmol, 94.4 mg) afforded compound **3au** (31.1 mg, 74% yield) as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 – 7.02 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 6.9 Hz, 1H), 5.52 (d, *J* = 6.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.87, 146.85, 138.58, 134.80, 131.25, 129.89, 129.74, 119.41, 119.26, 113.66, 112.69, 105.35, 23.22. Spectroscopic data in agreement with the literature[11].

8. Spectroscopic Data

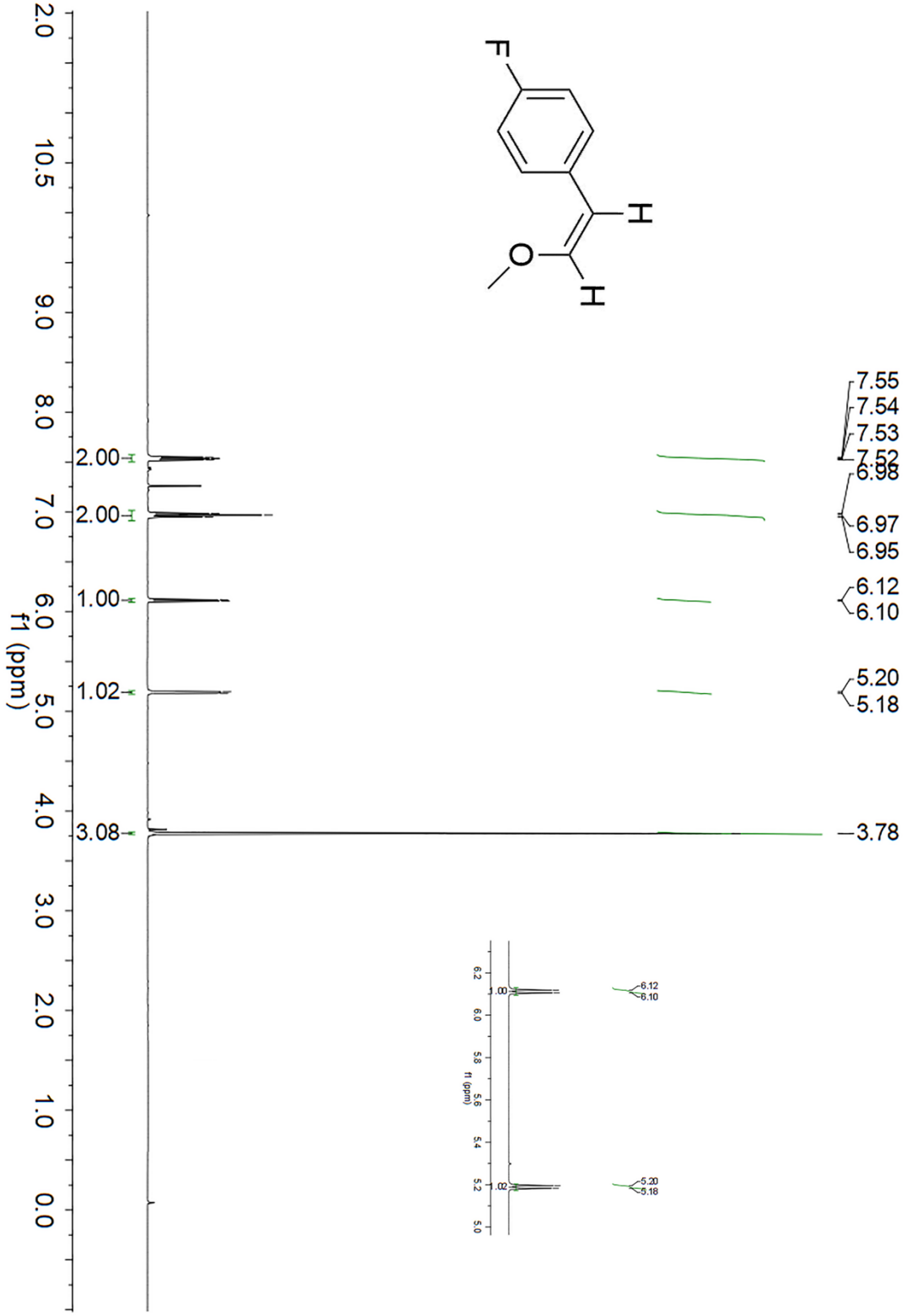
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**.



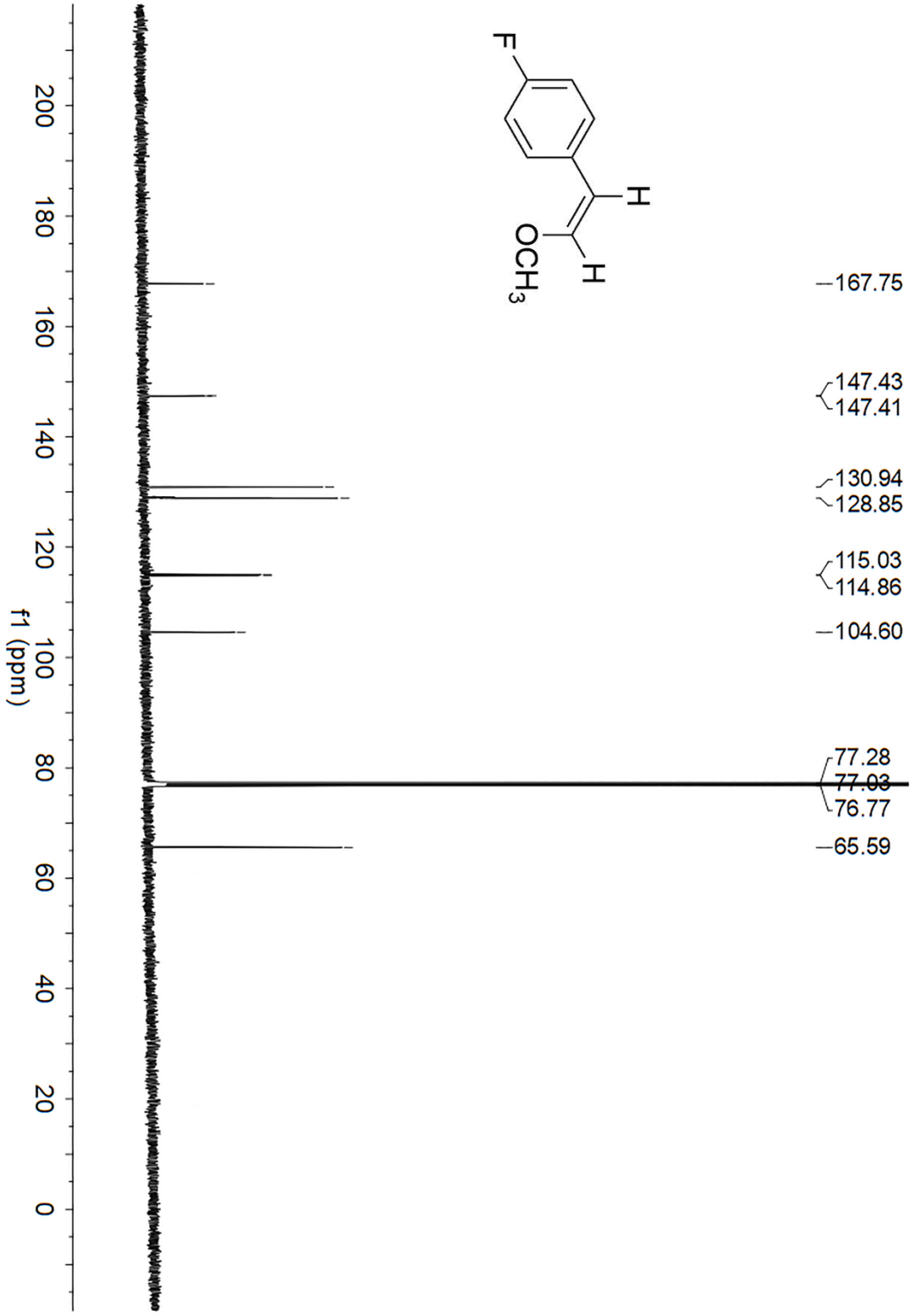
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3a**.



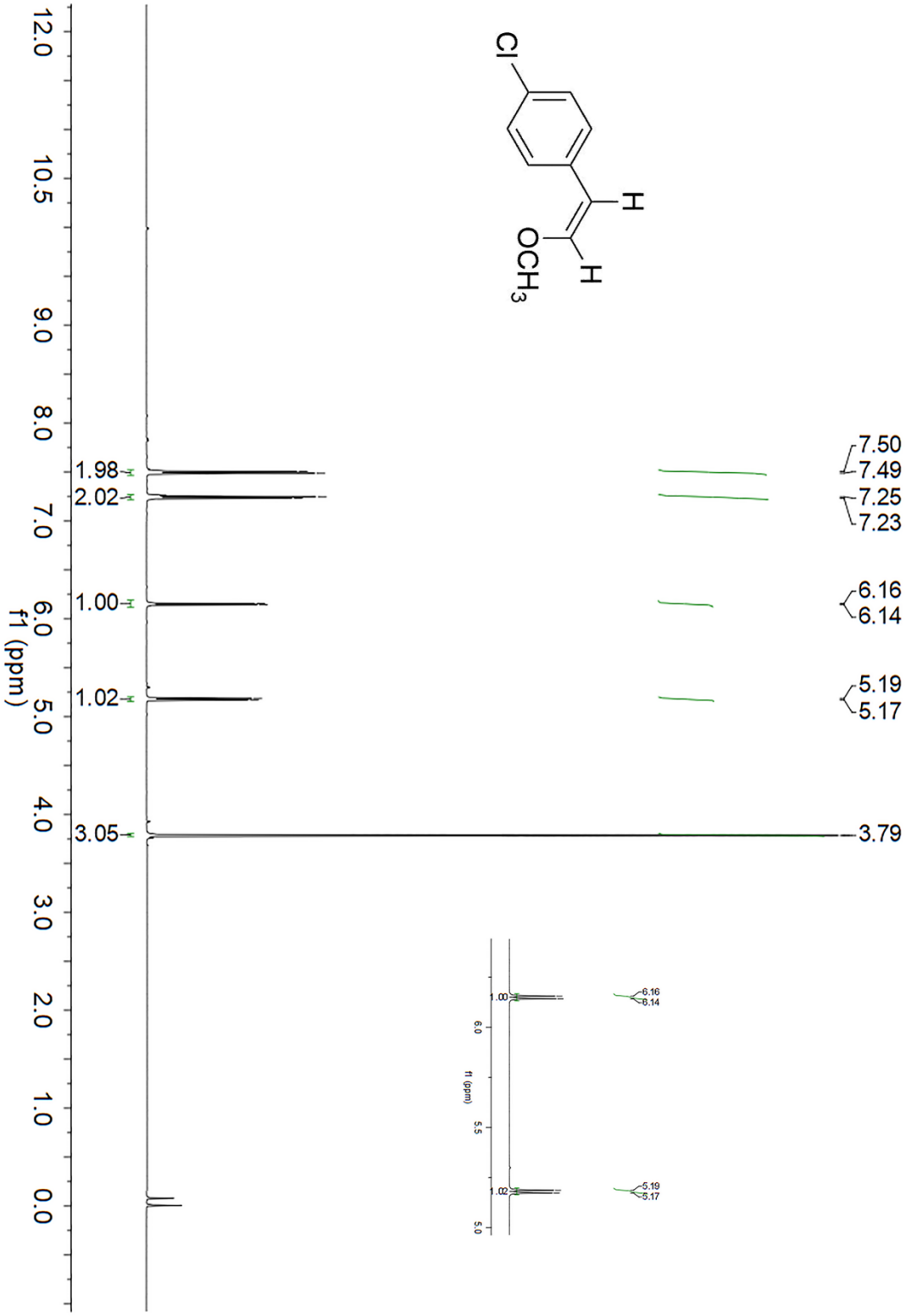
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**.



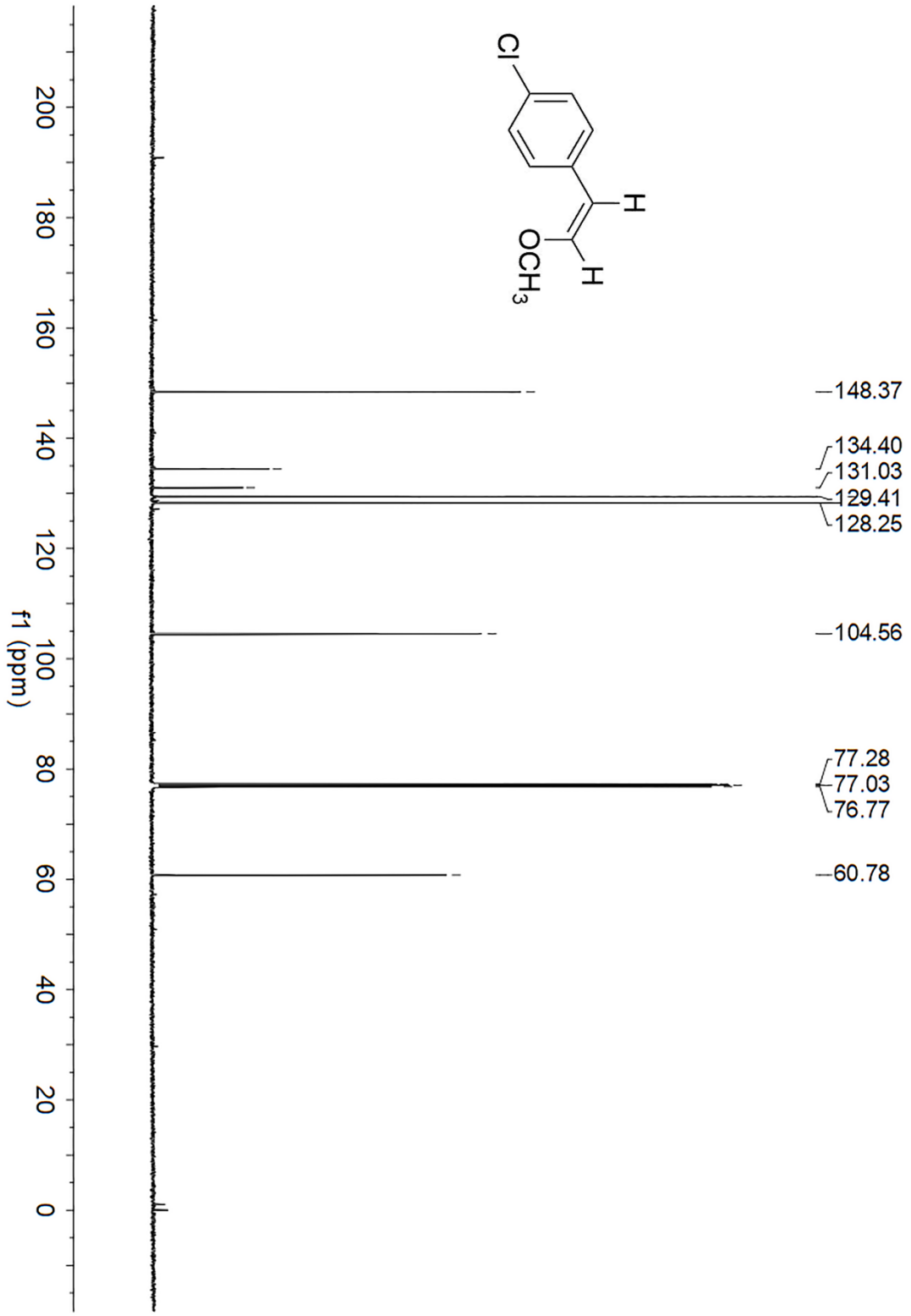
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3b**.



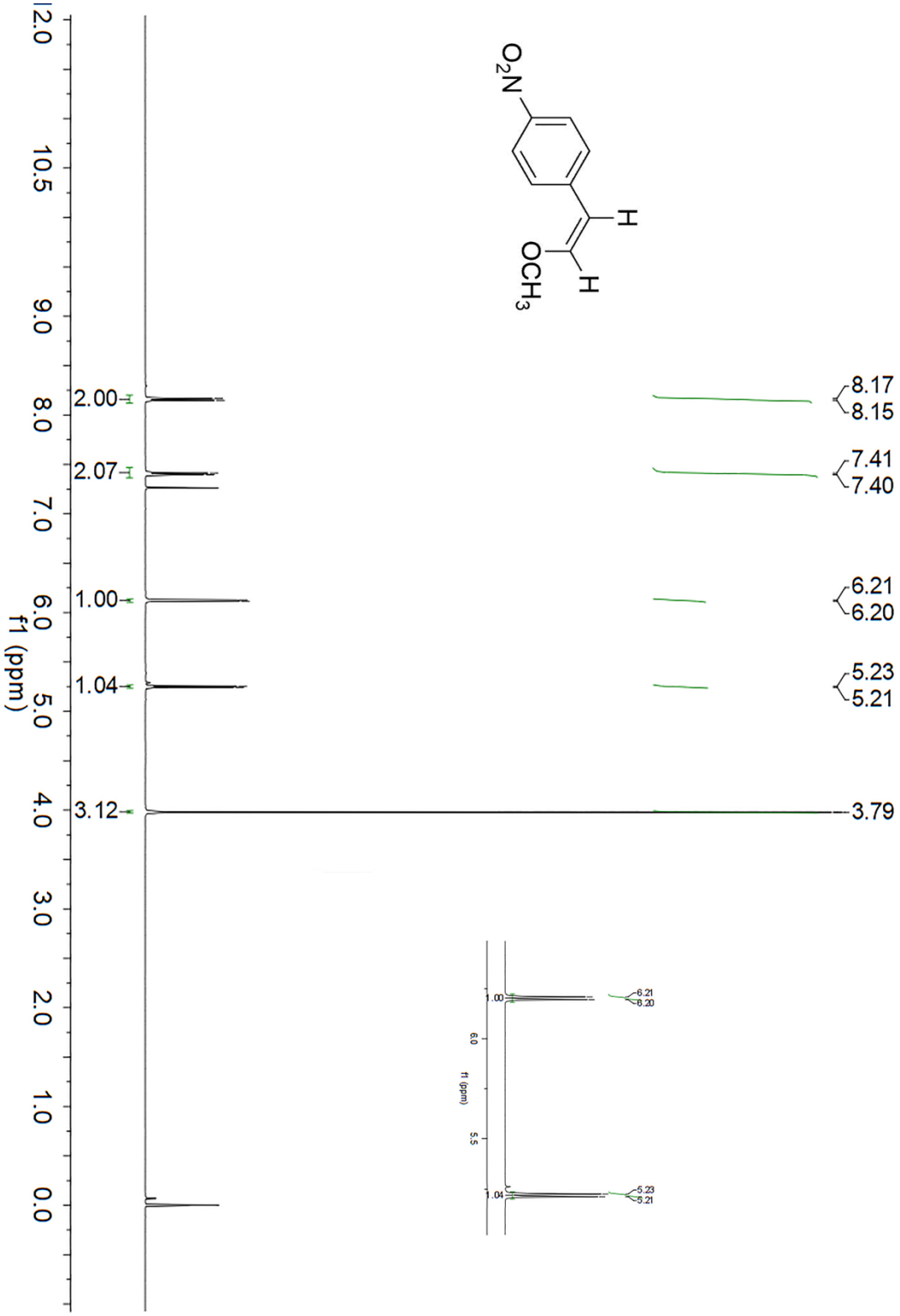
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**.



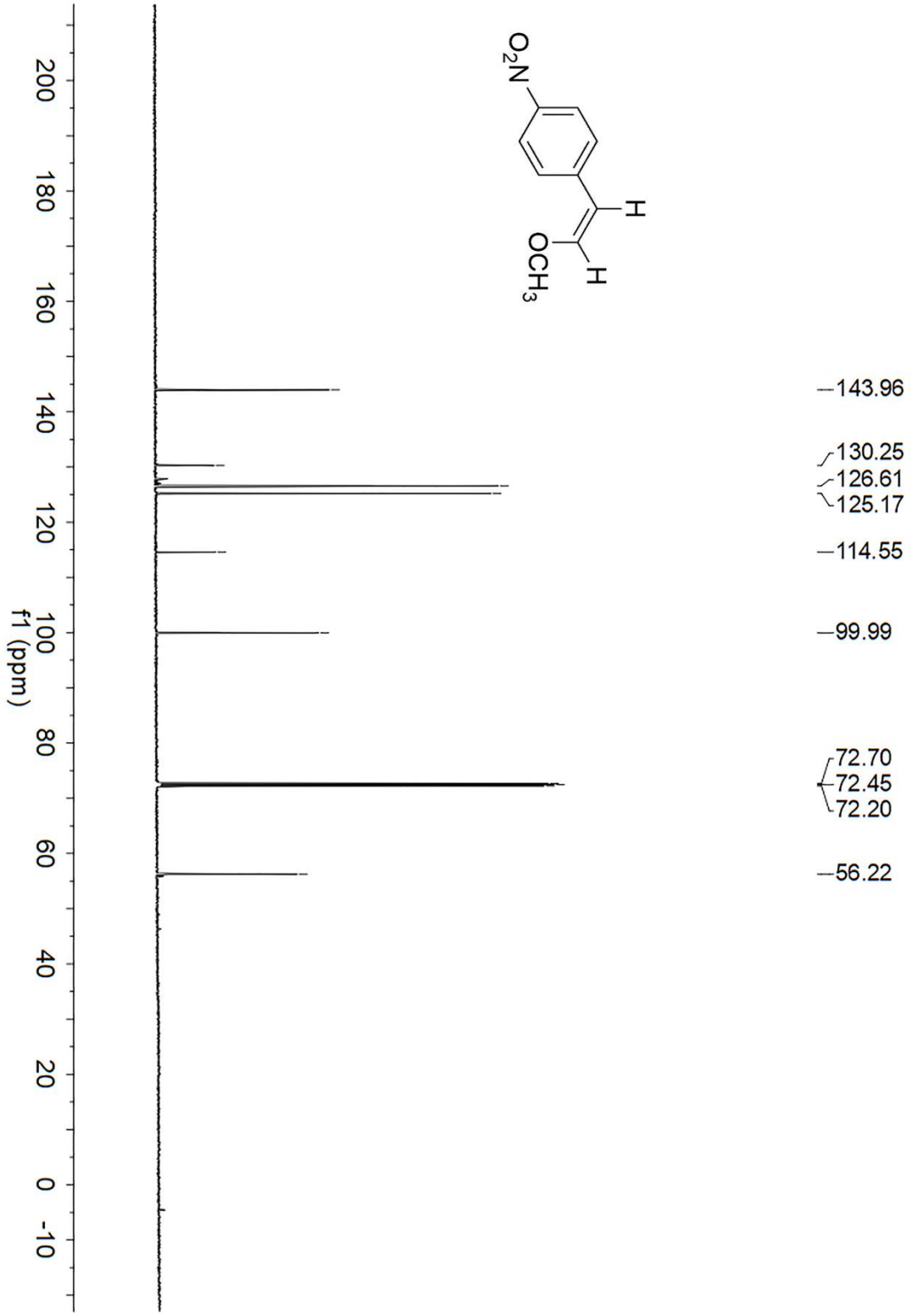
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3c**.



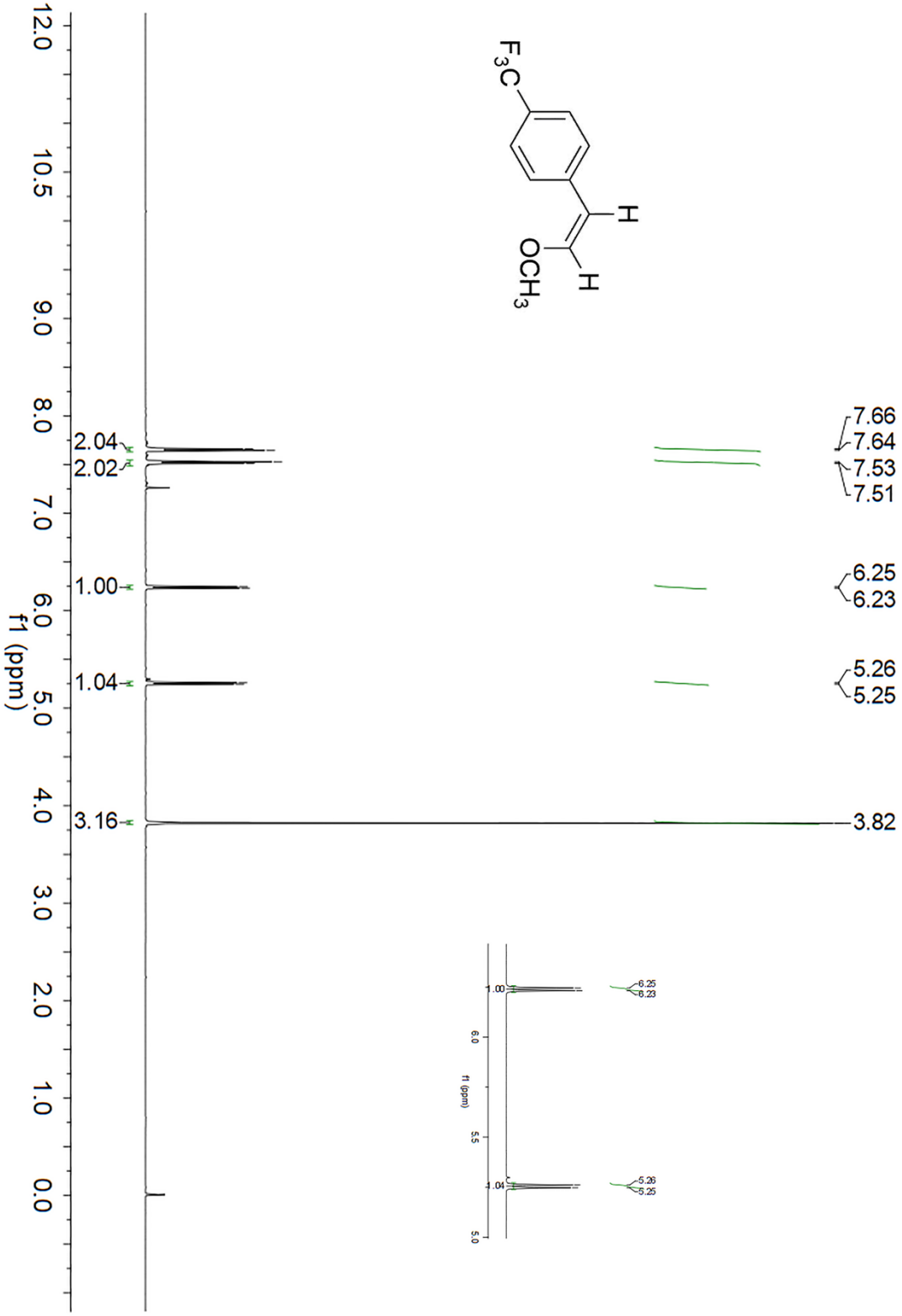
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**.



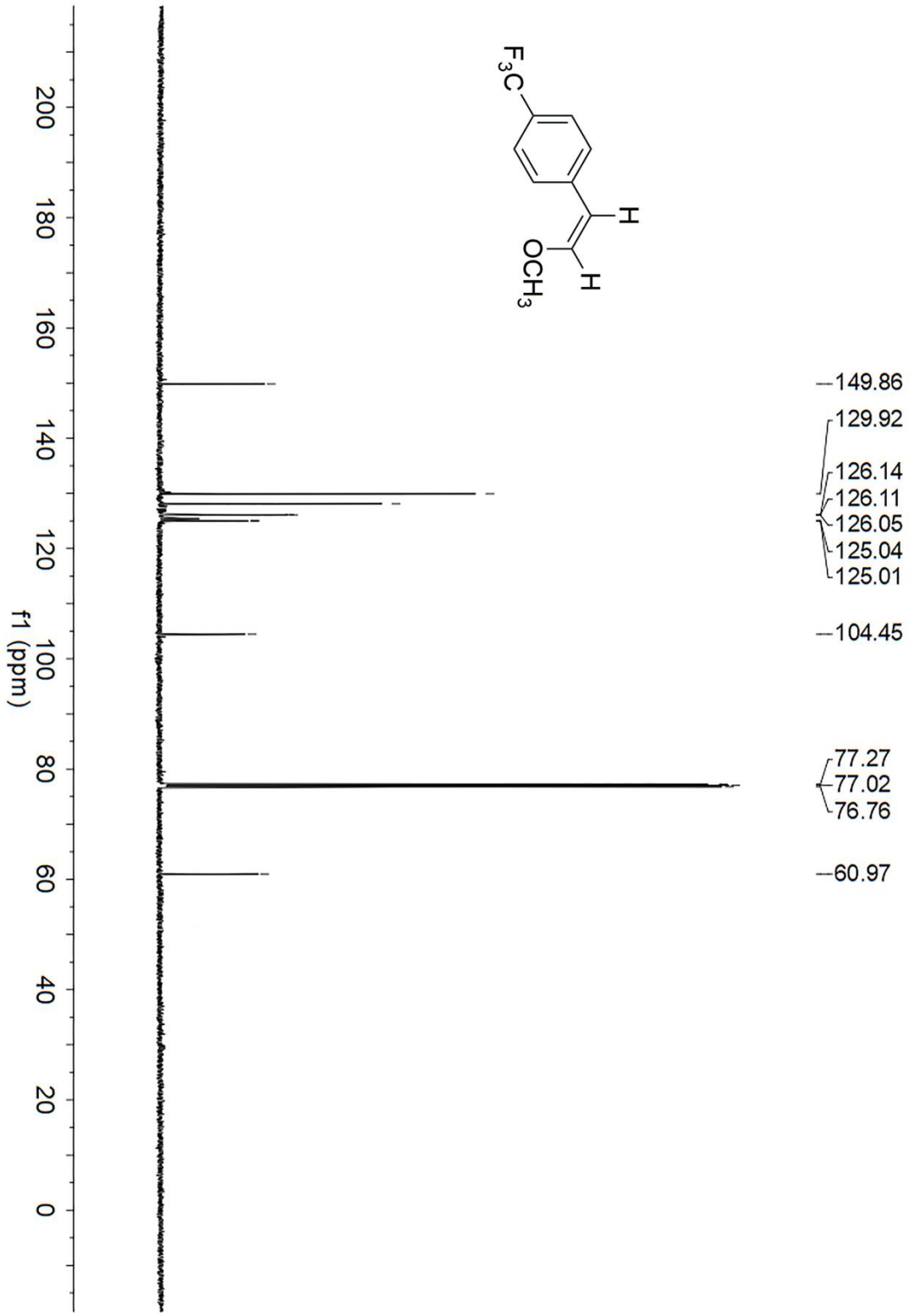
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3d**.



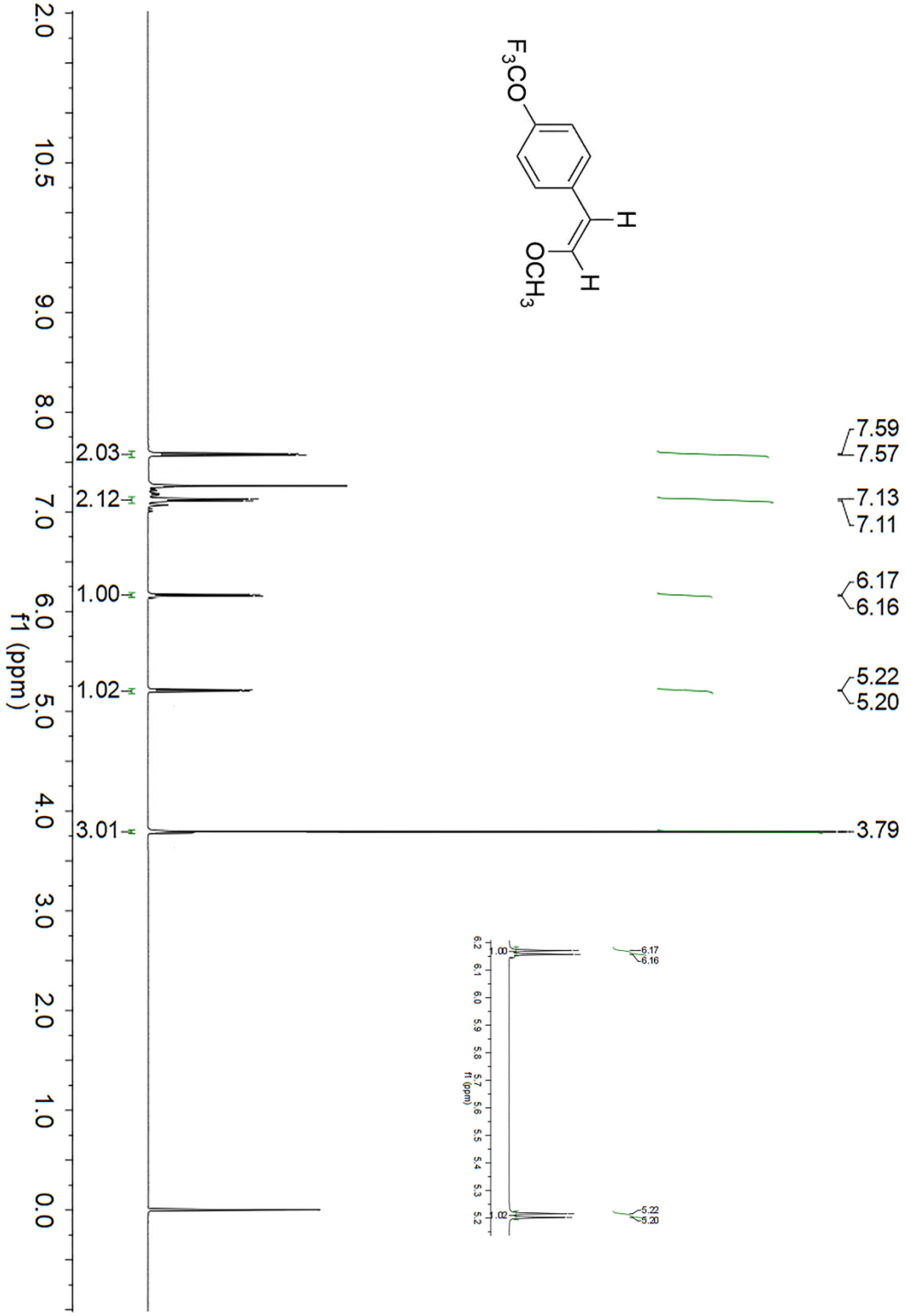
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**.



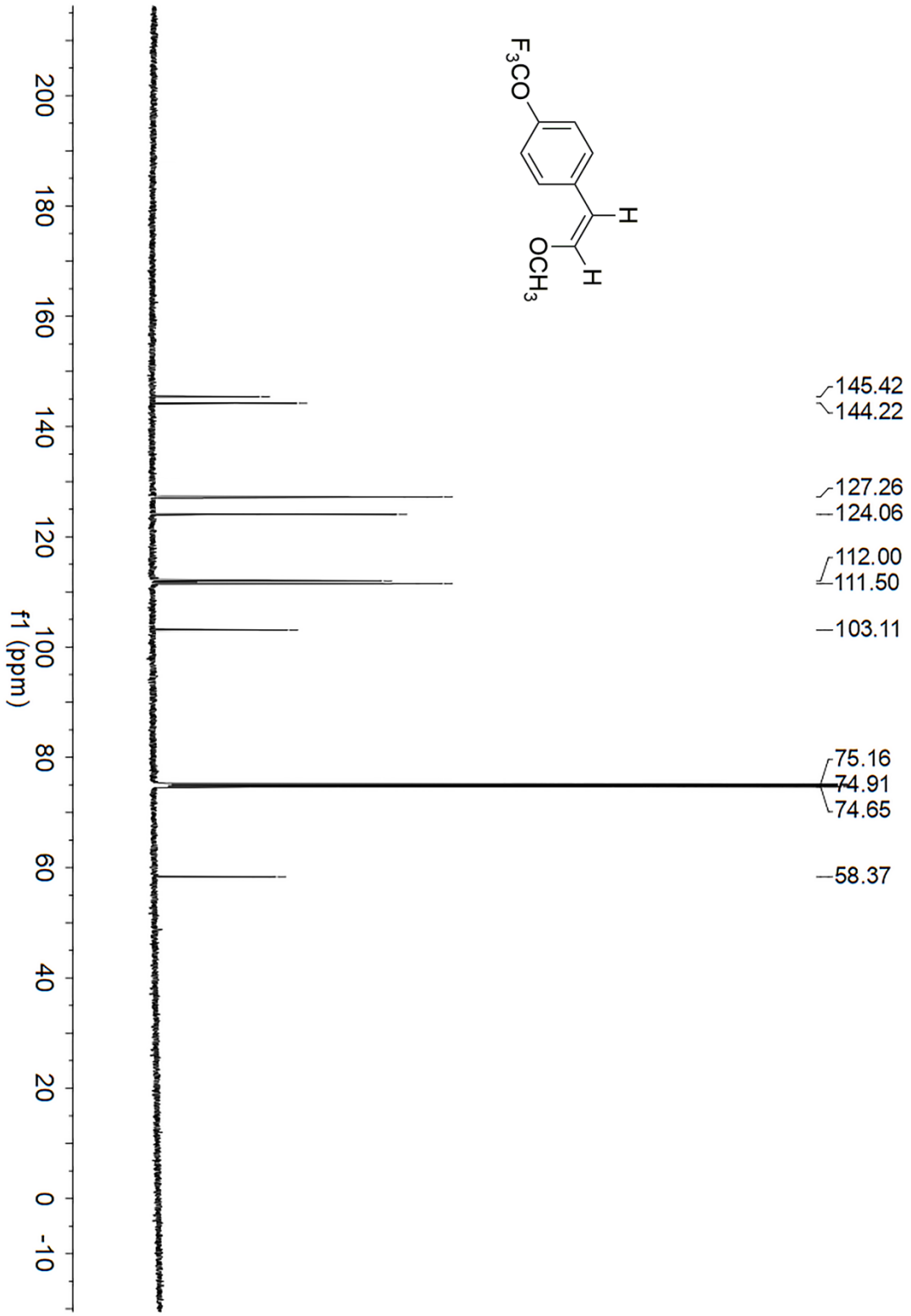
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3e**.



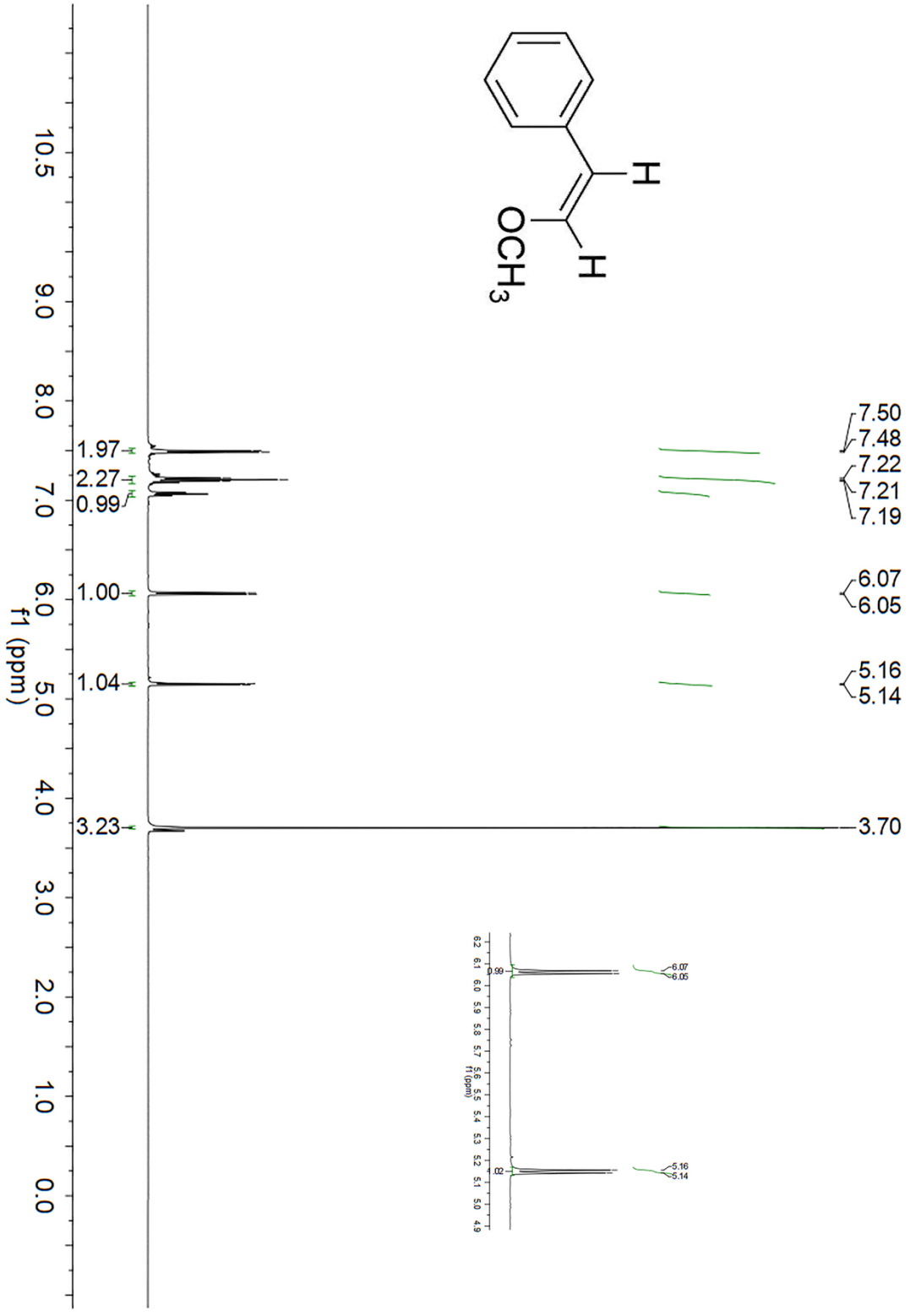
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.



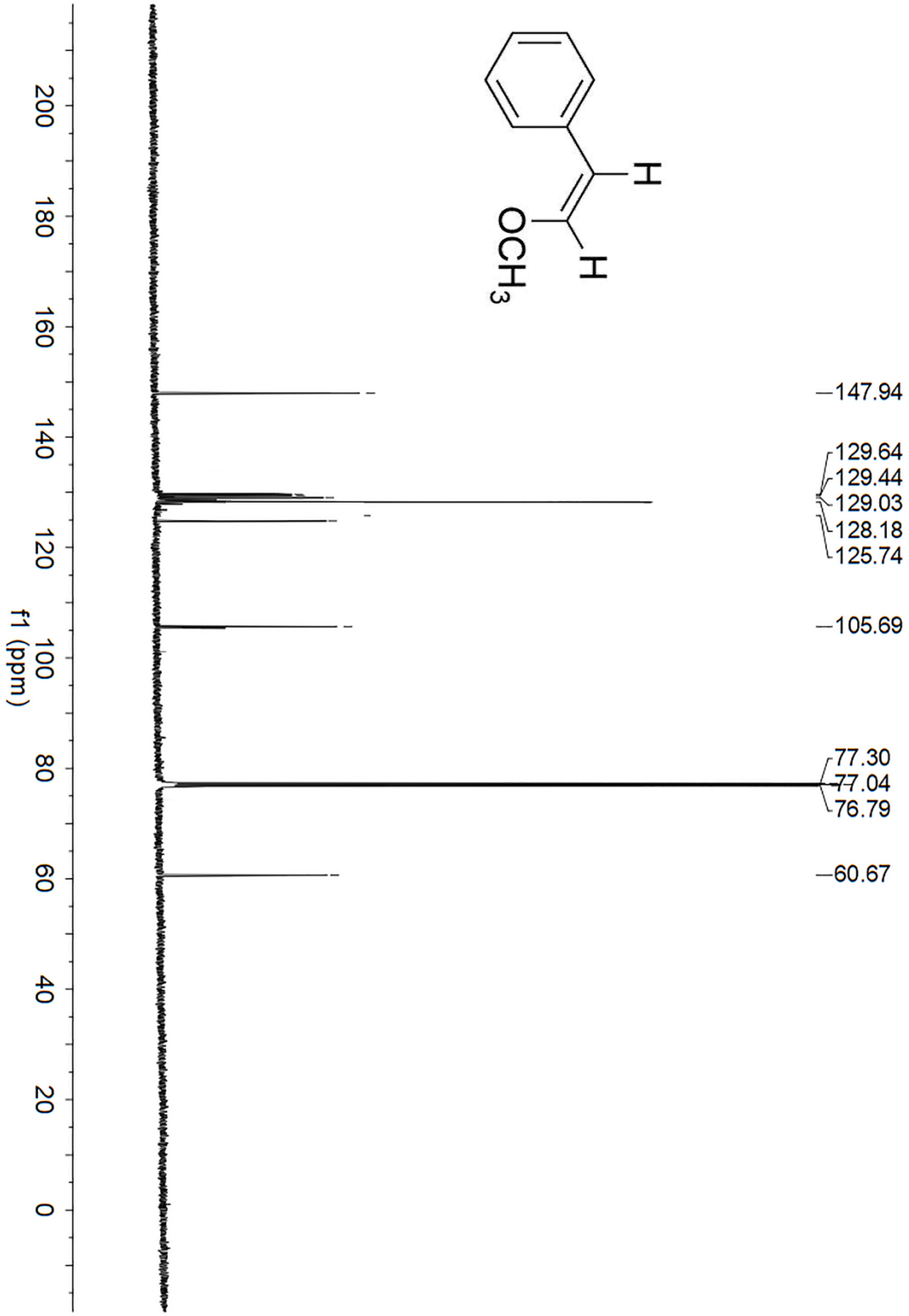
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3f**.



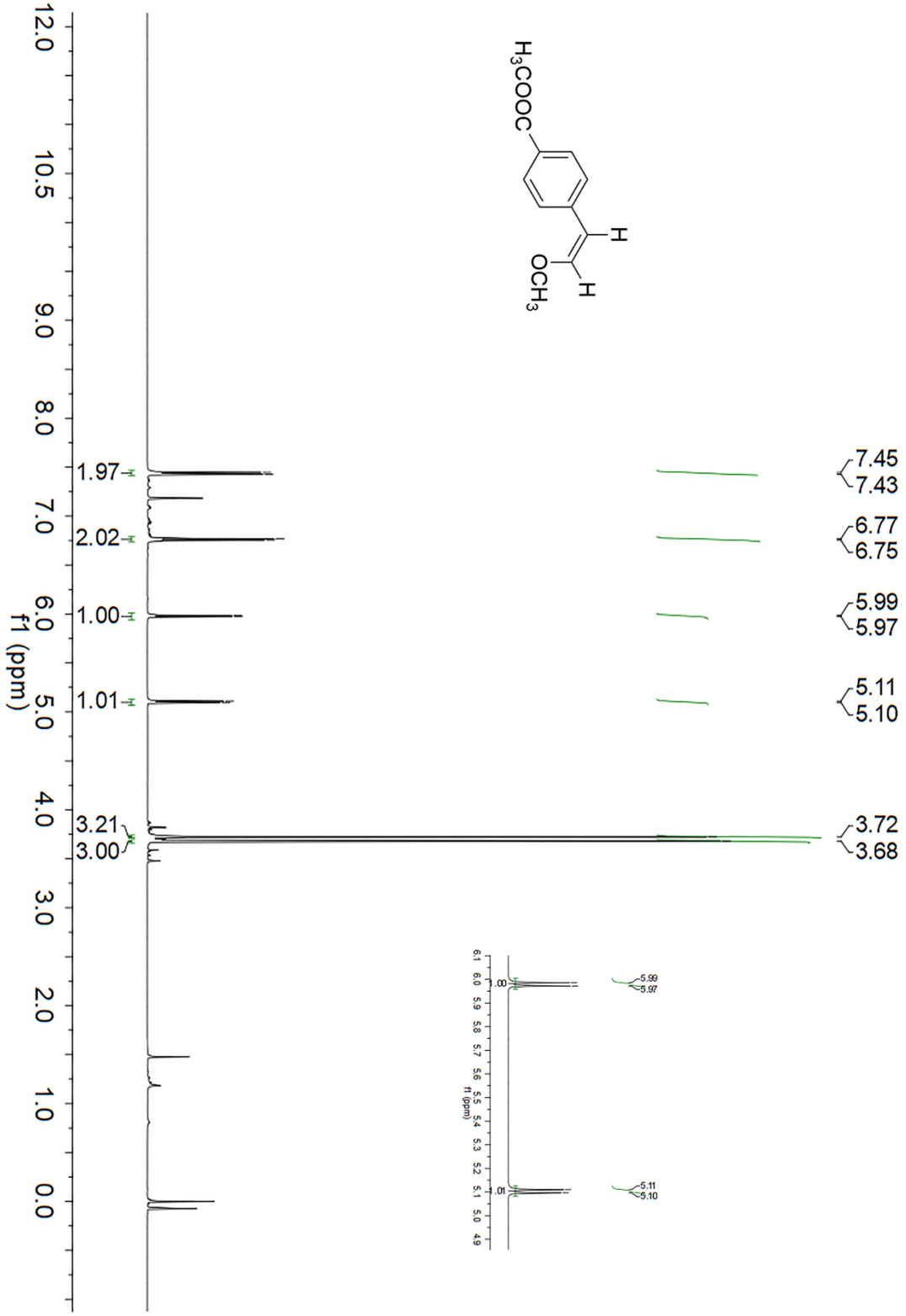
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**.



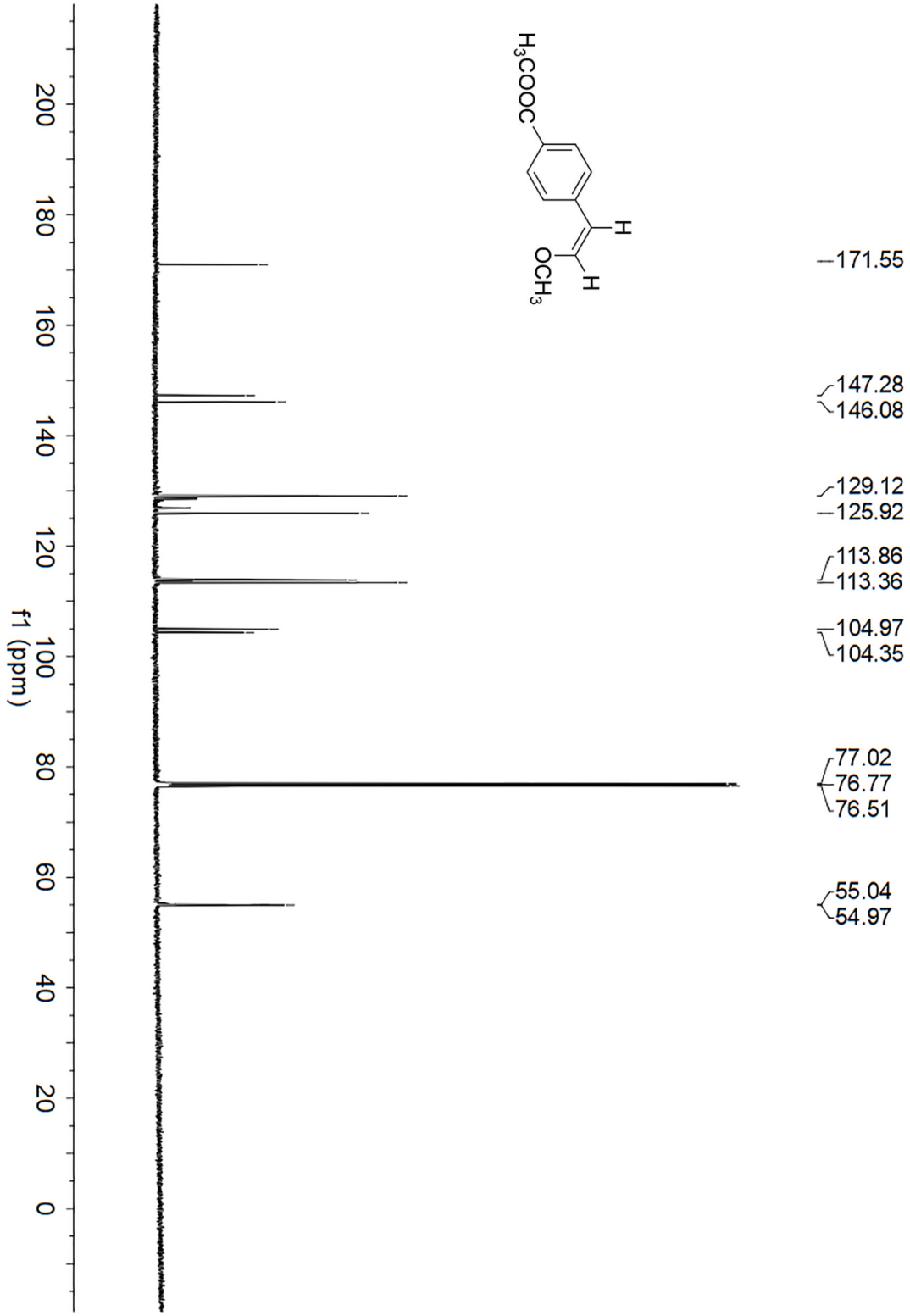
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3g**.



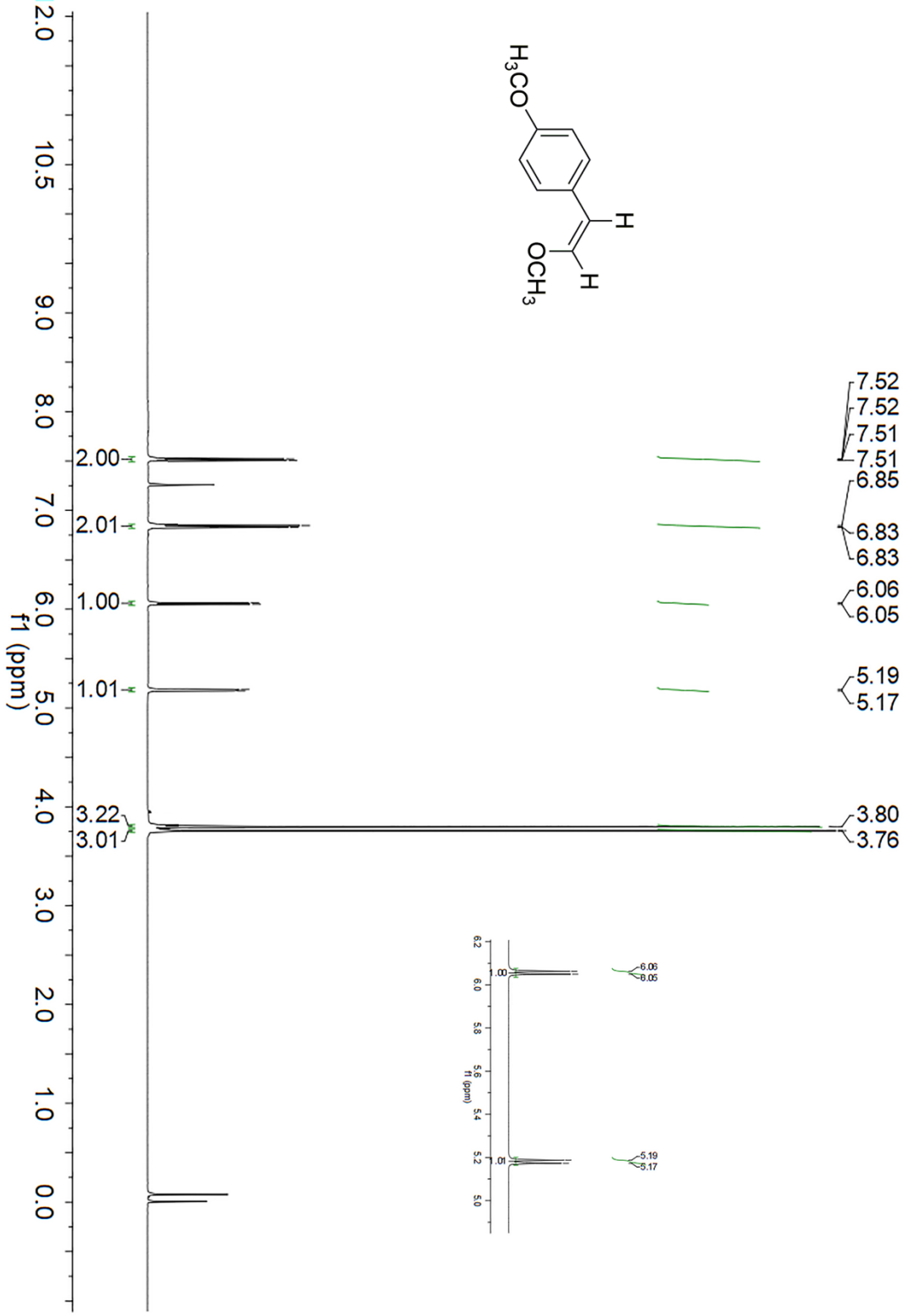
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h**.



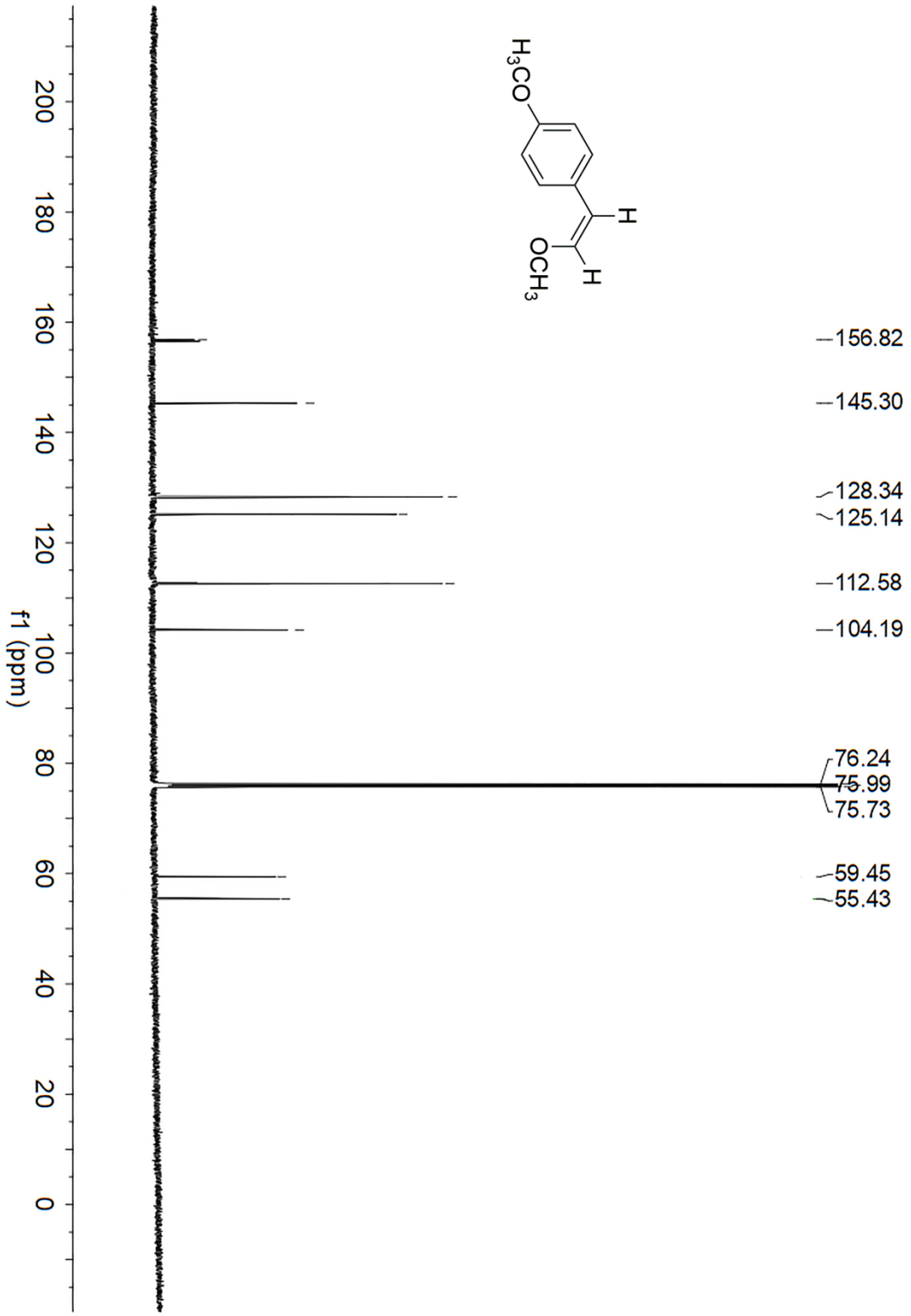
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3h**.



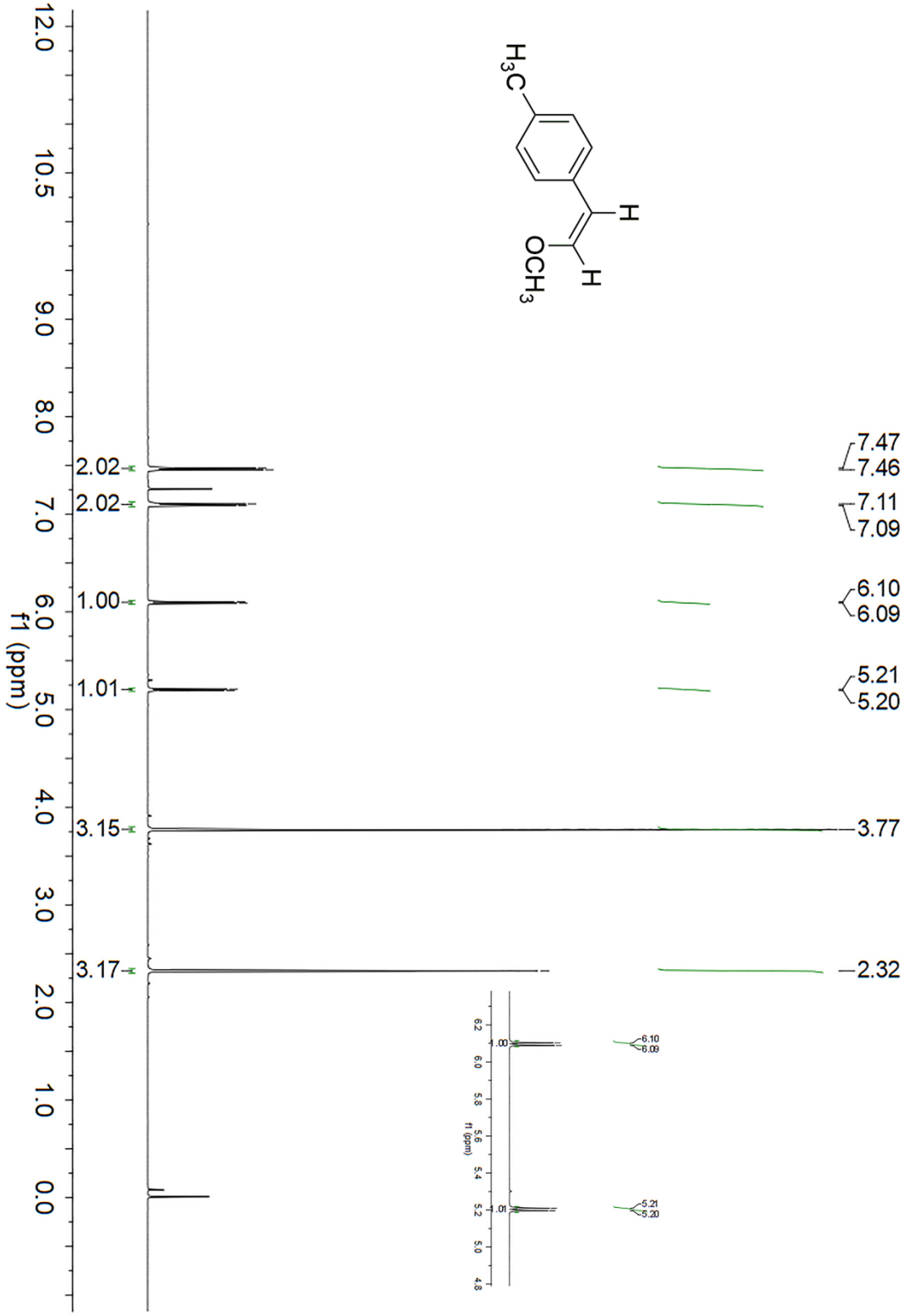
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**.



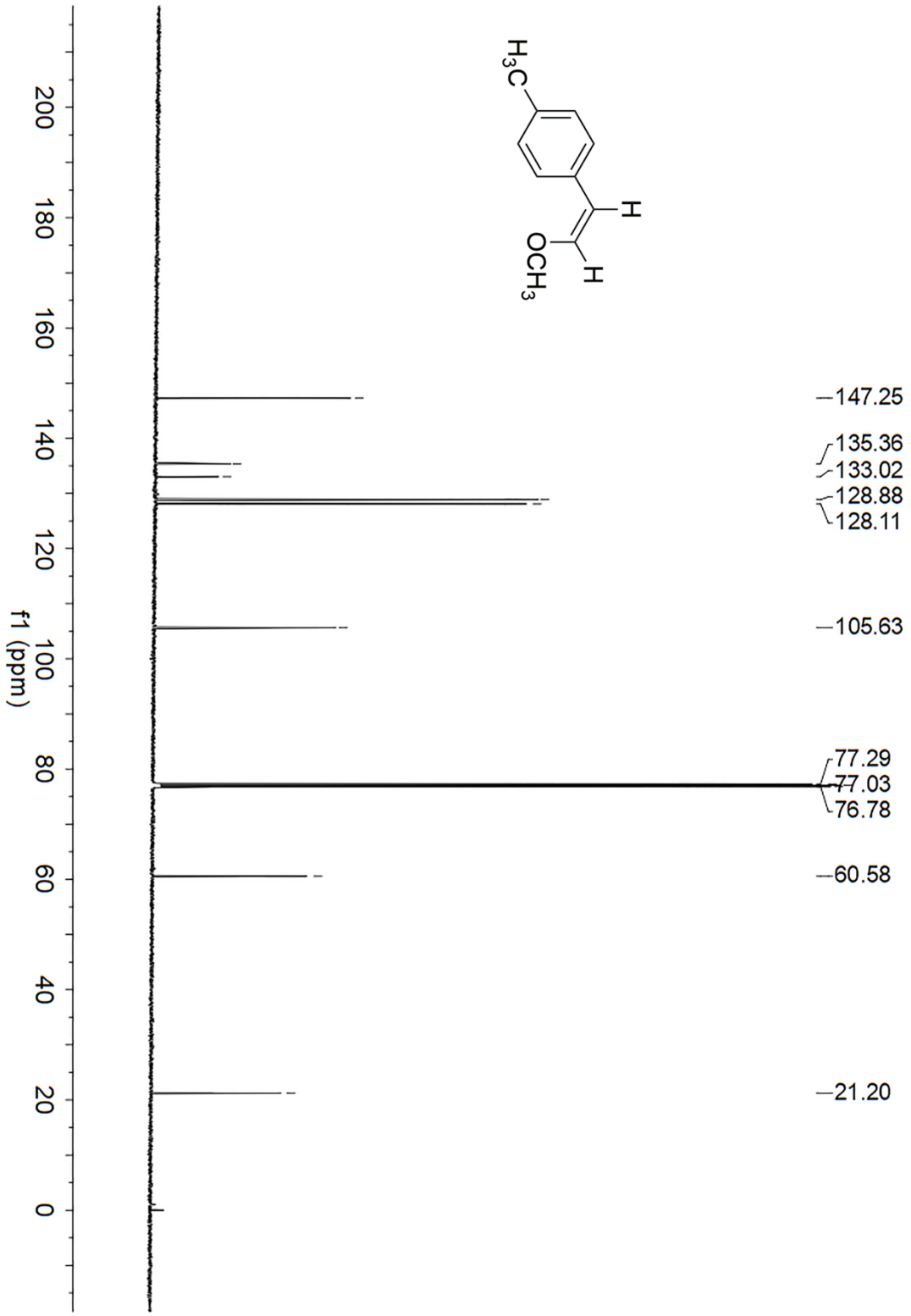
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3i**.



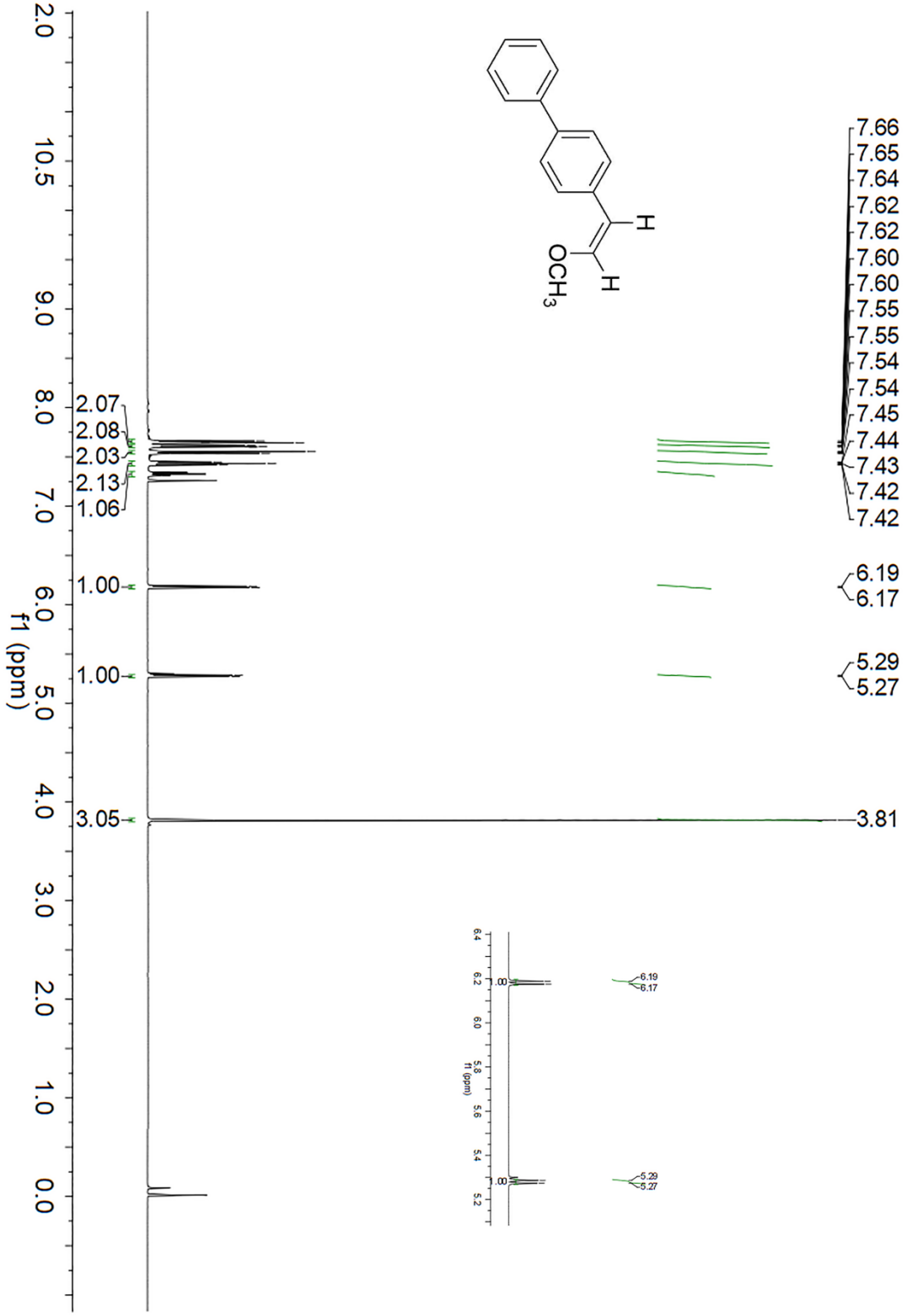
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j**.



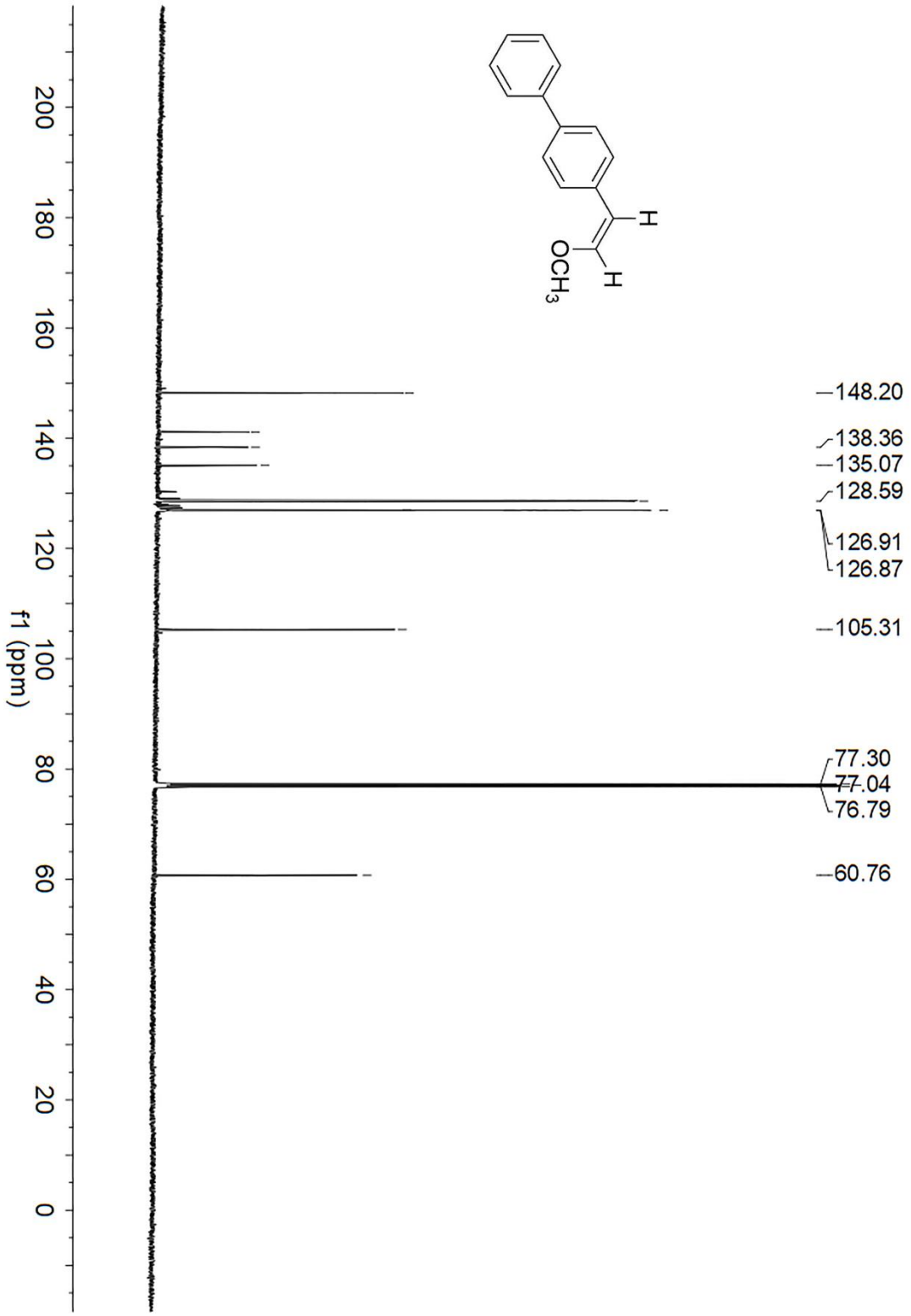
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3j**.



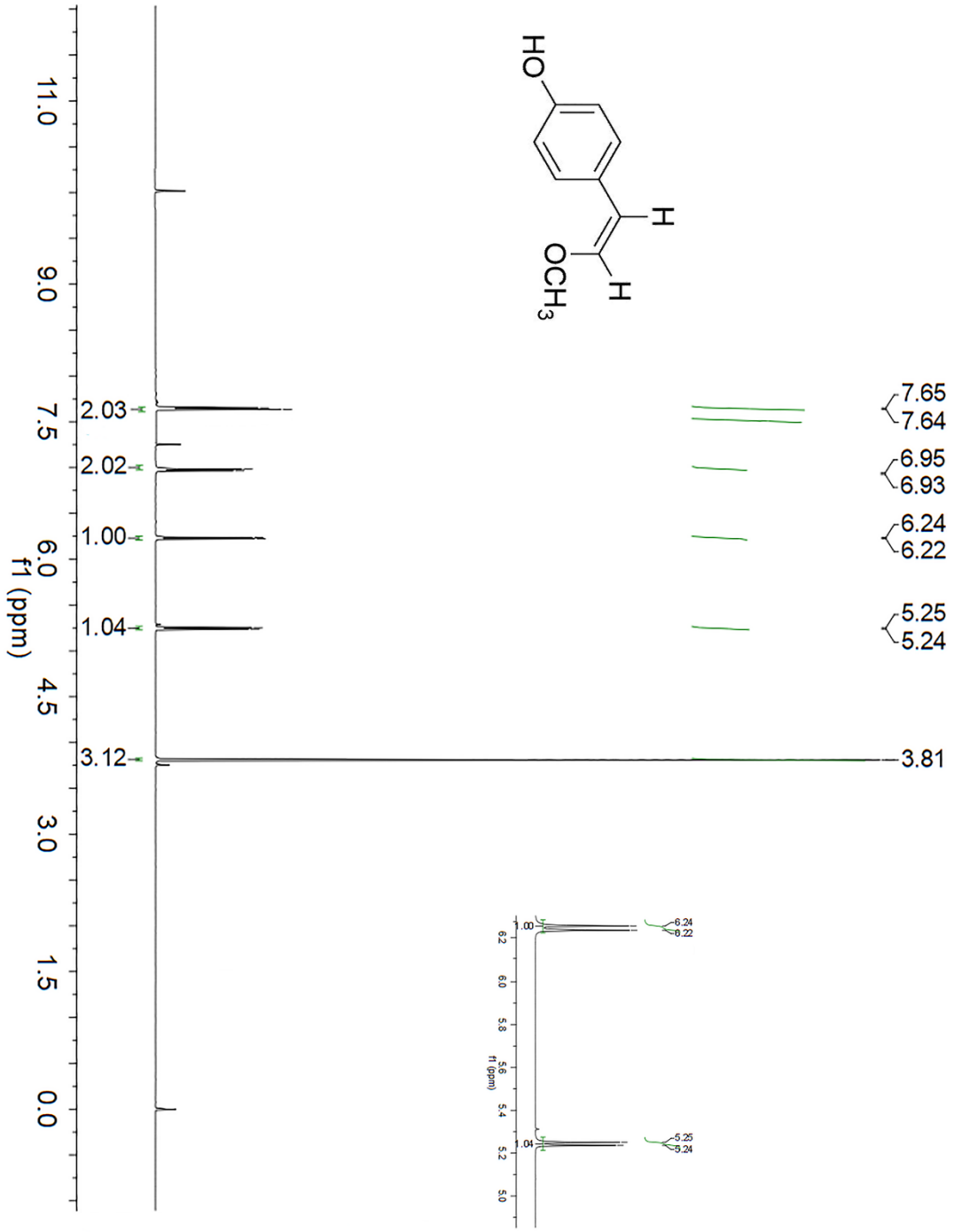
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**.



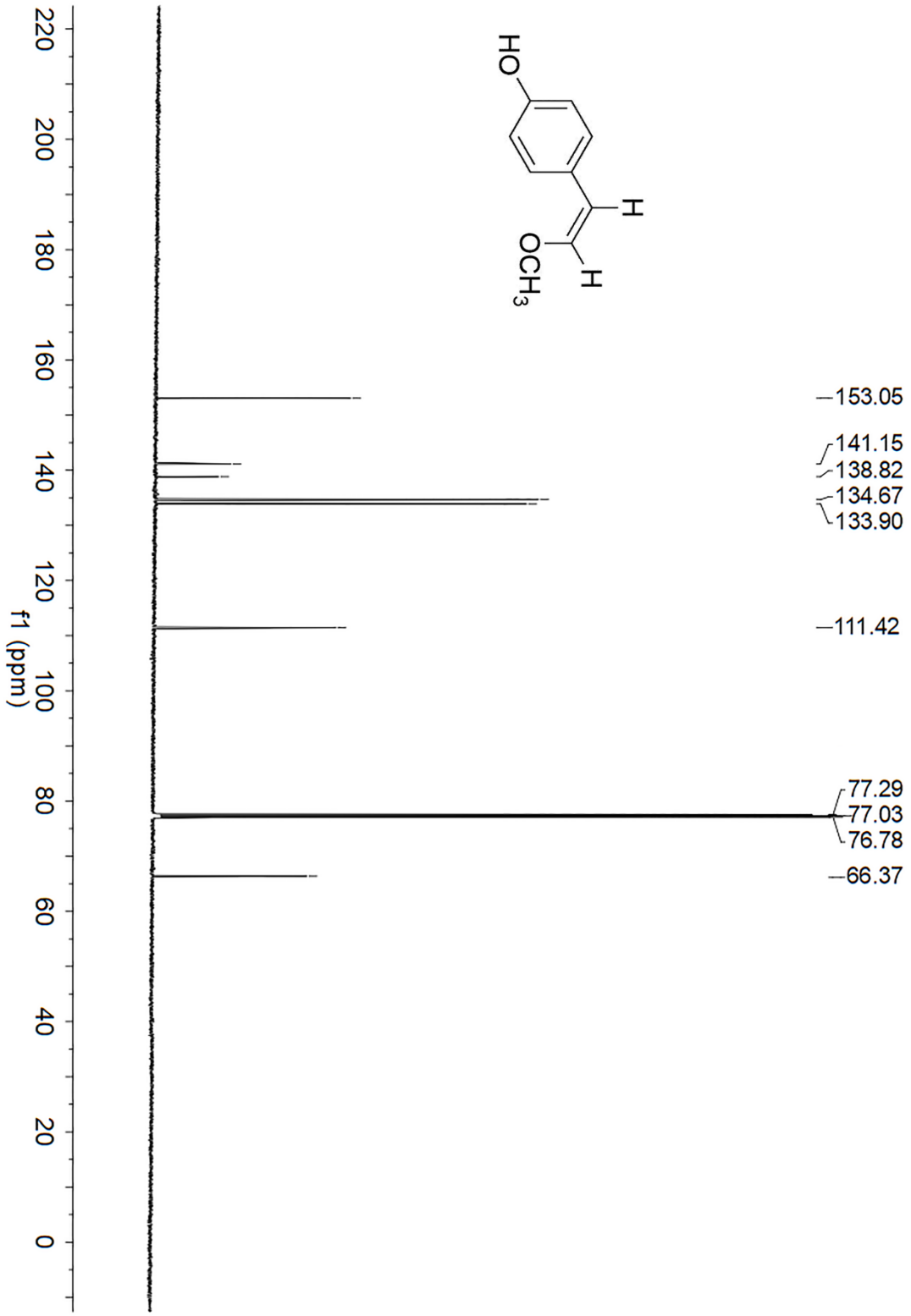
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3k**.



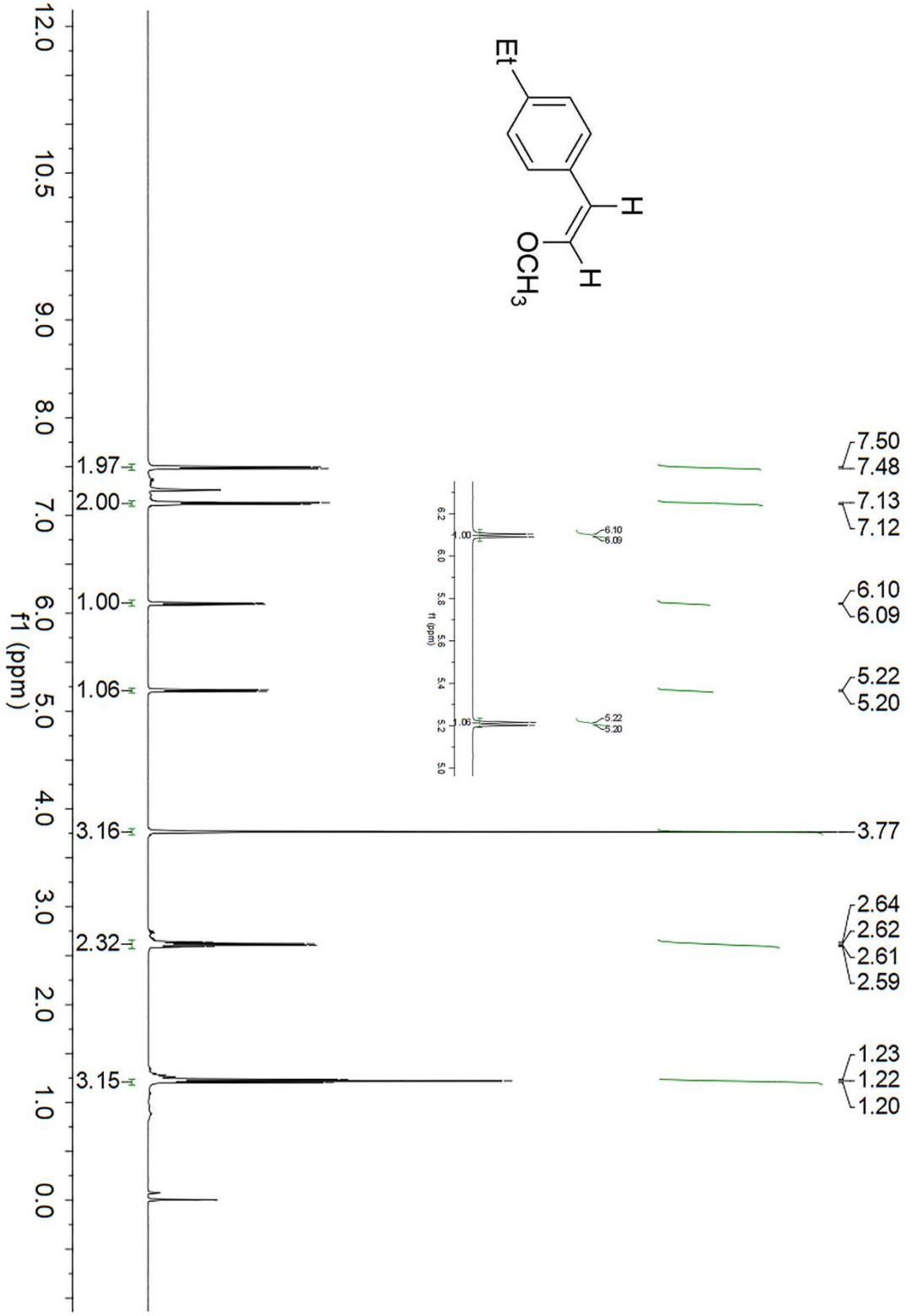
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**.



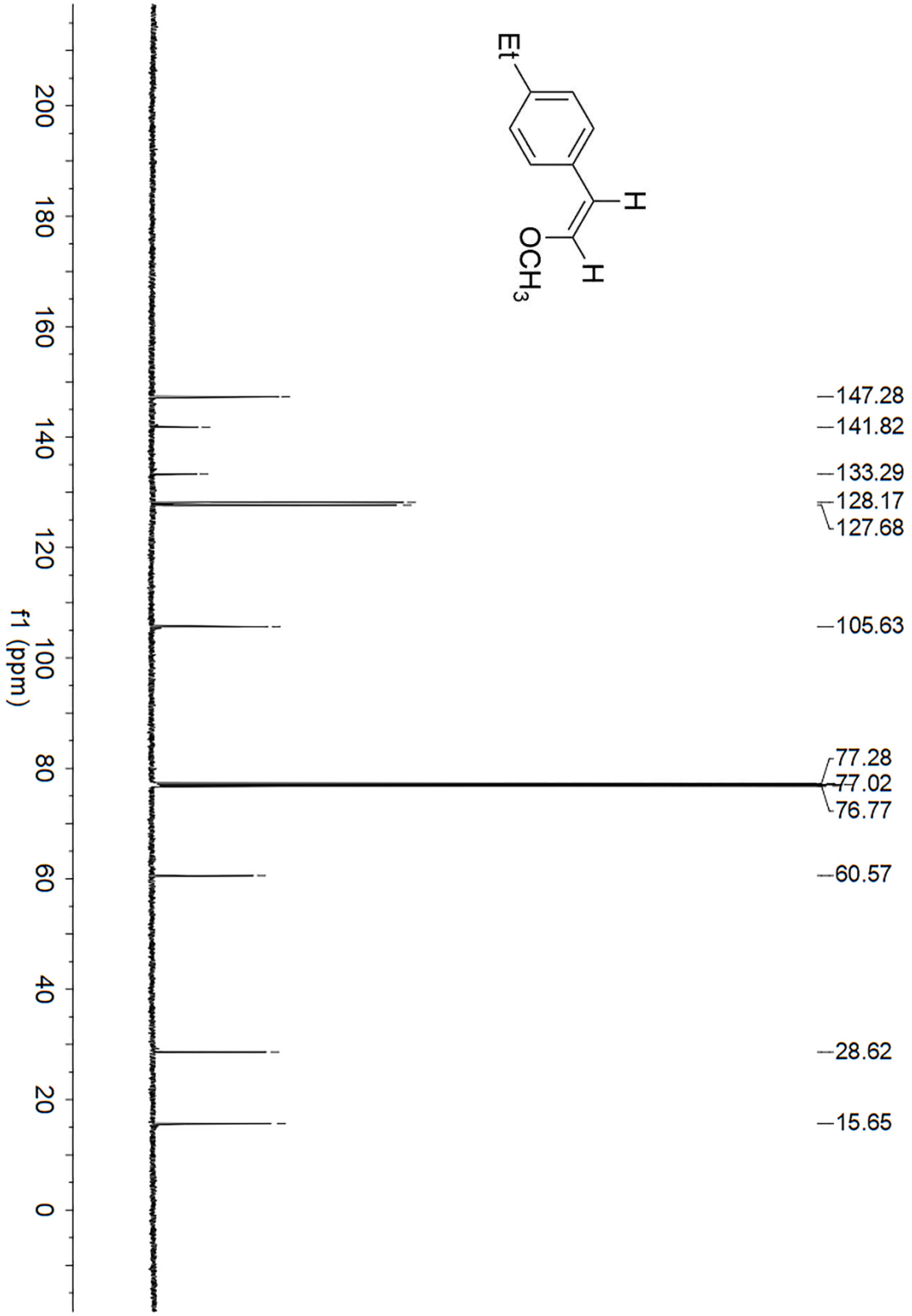
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3l**.



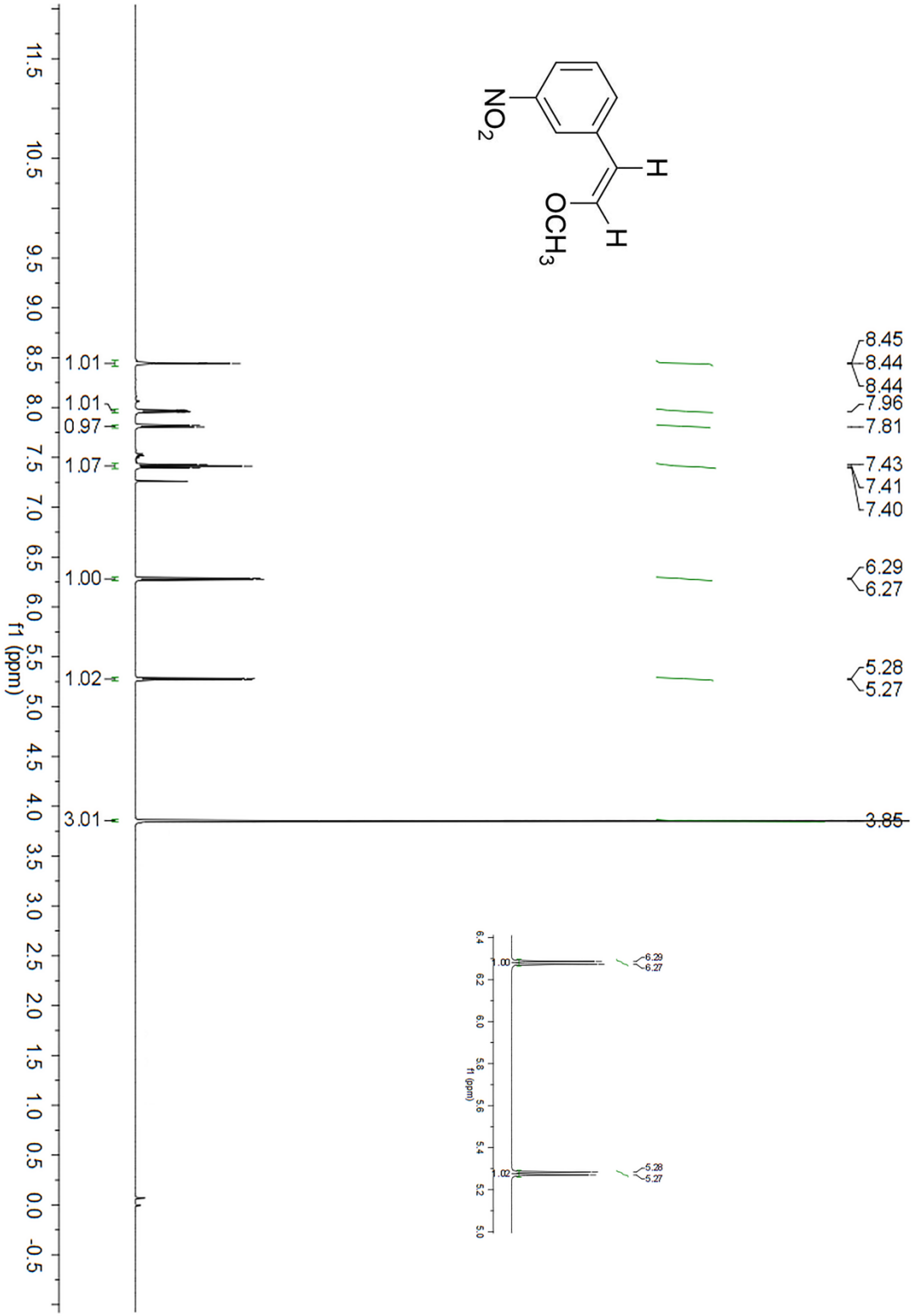
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**.



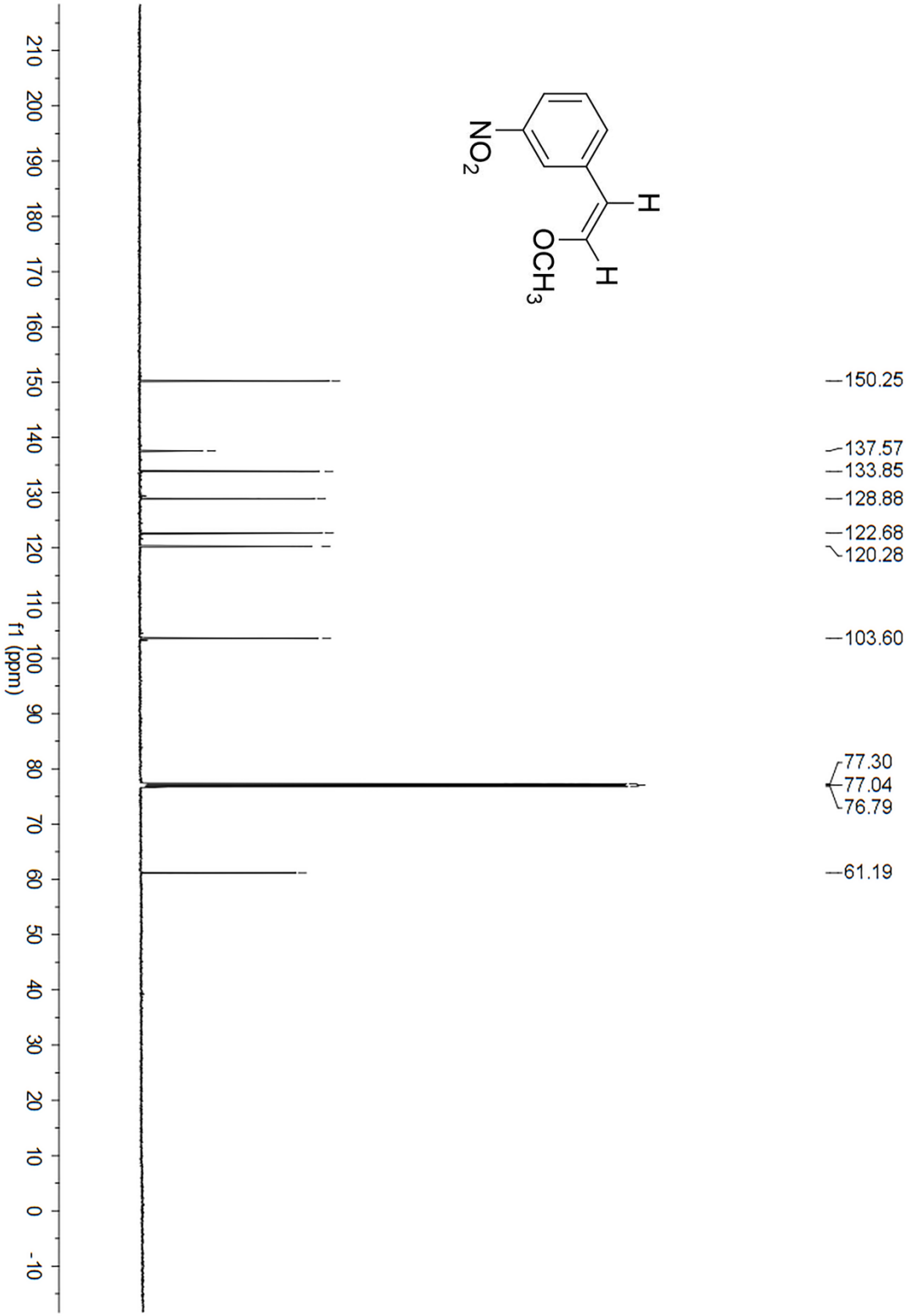
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3m**.



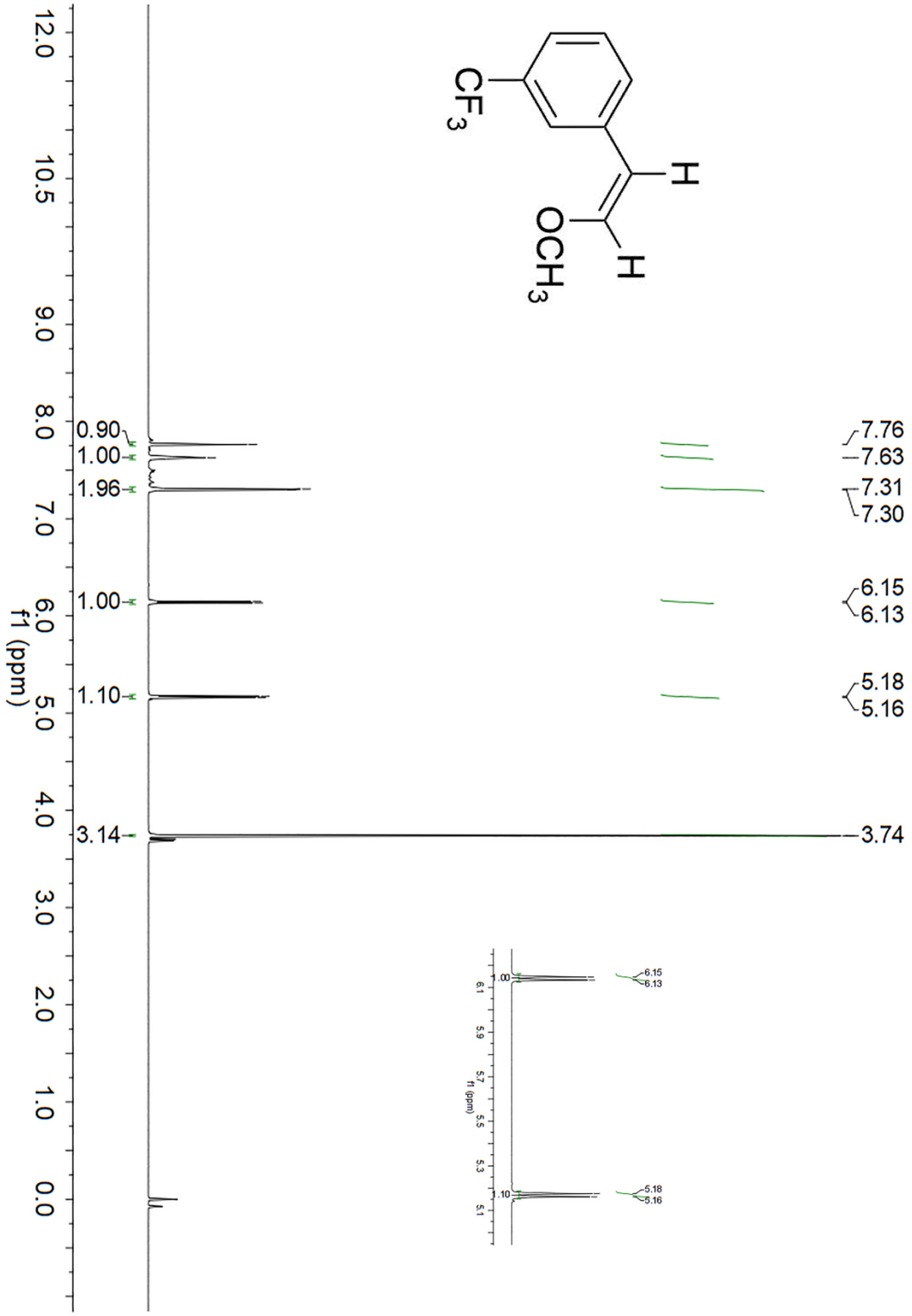
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**.



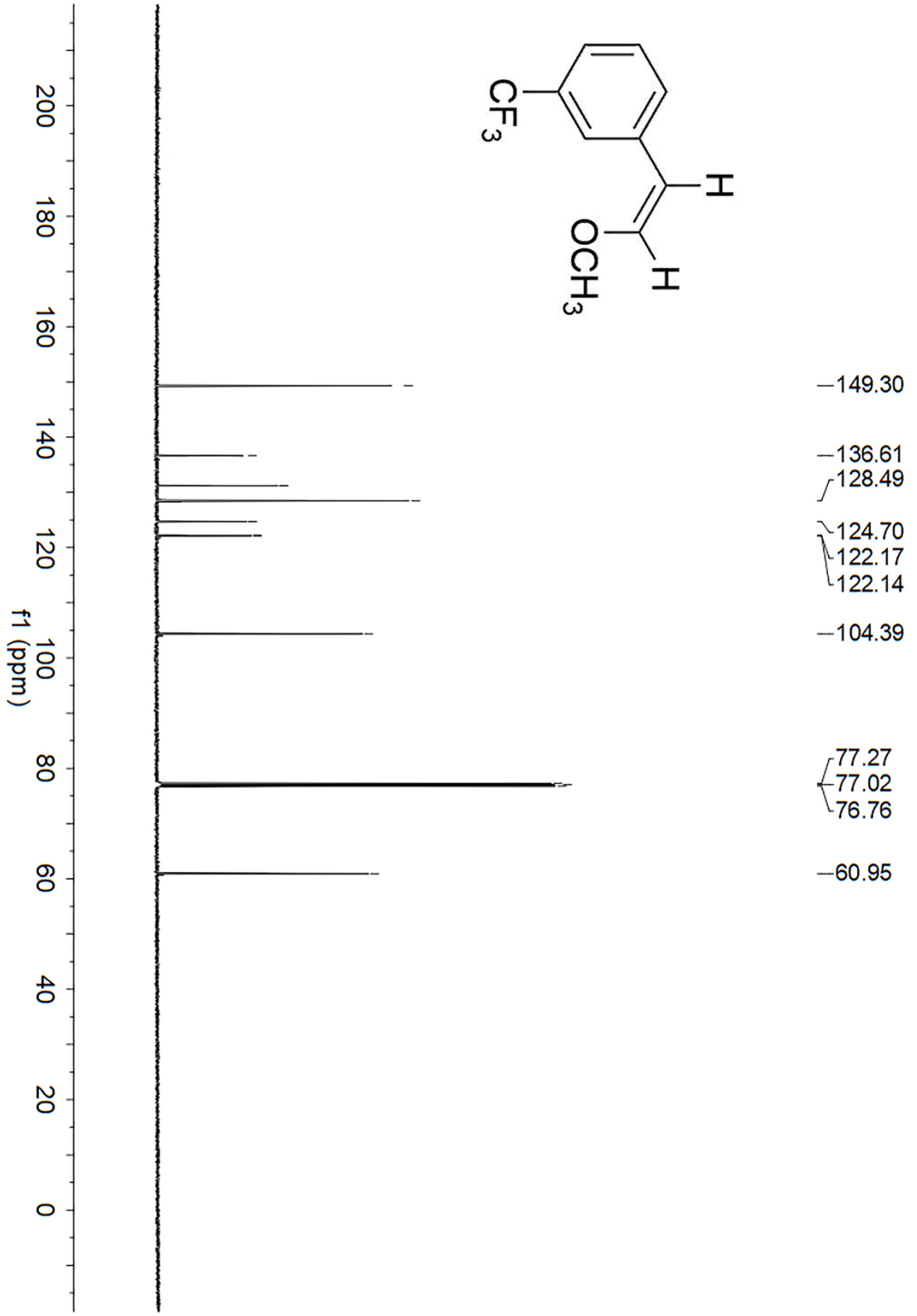
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3n**.



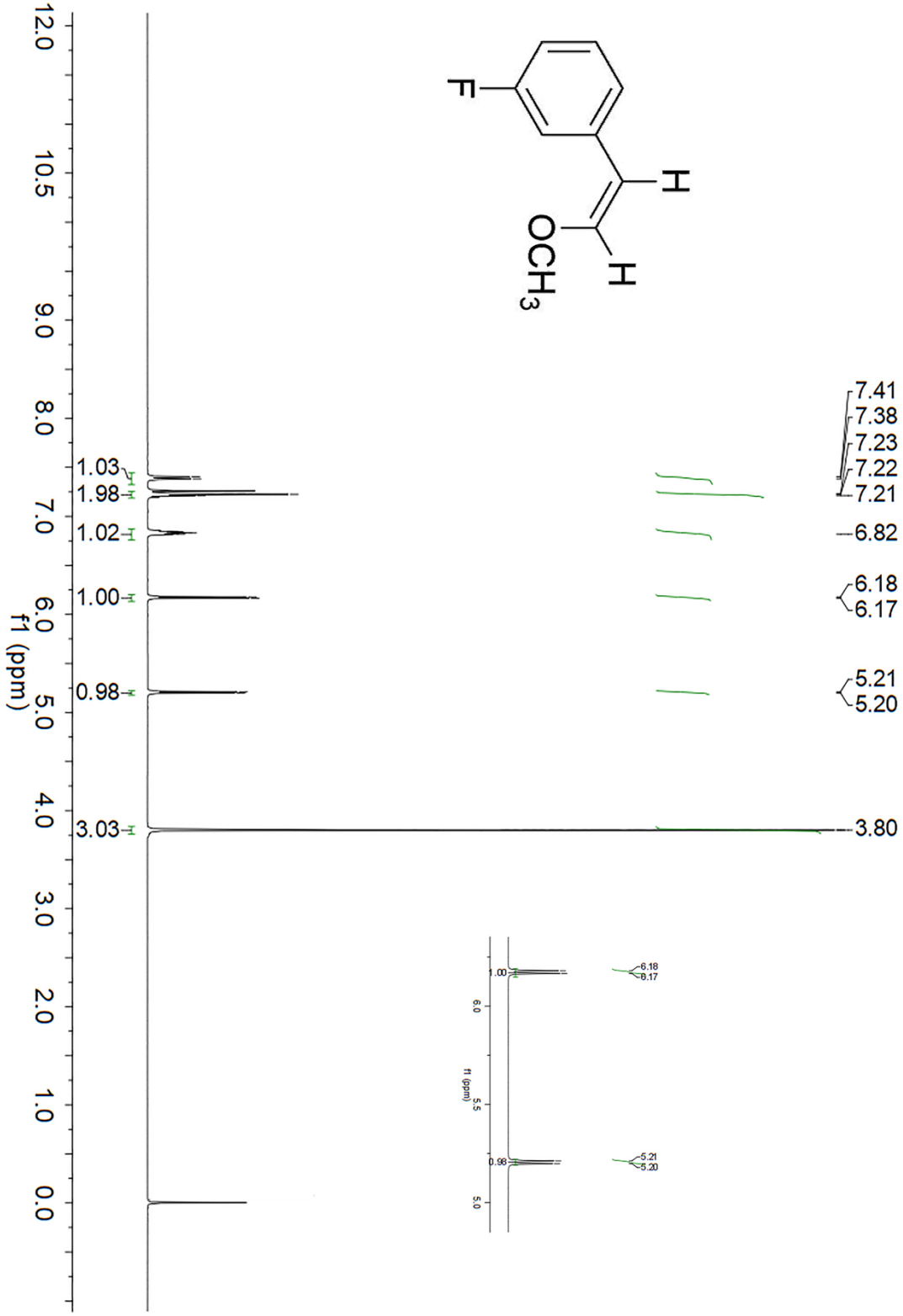
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**.



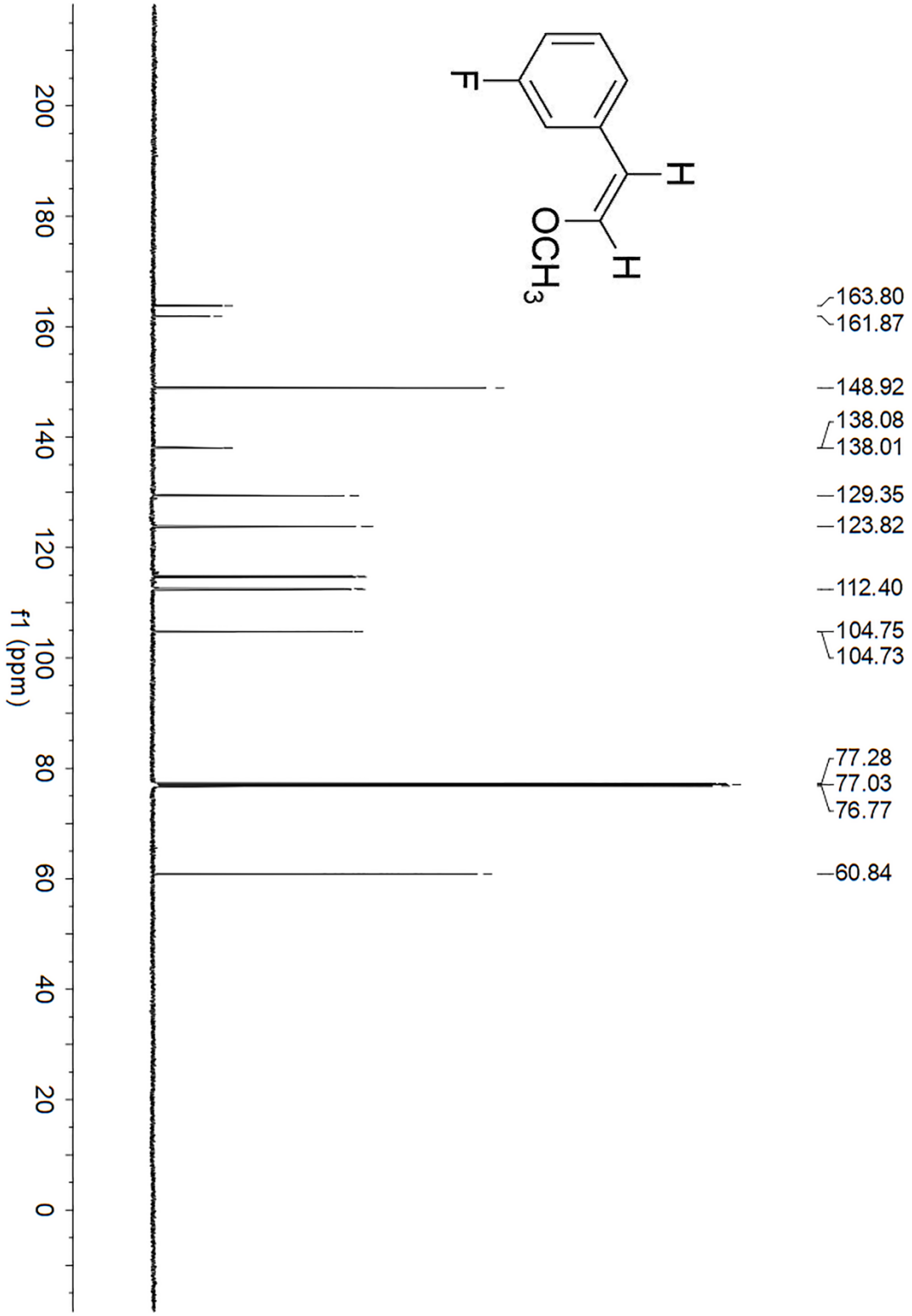
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3o**.



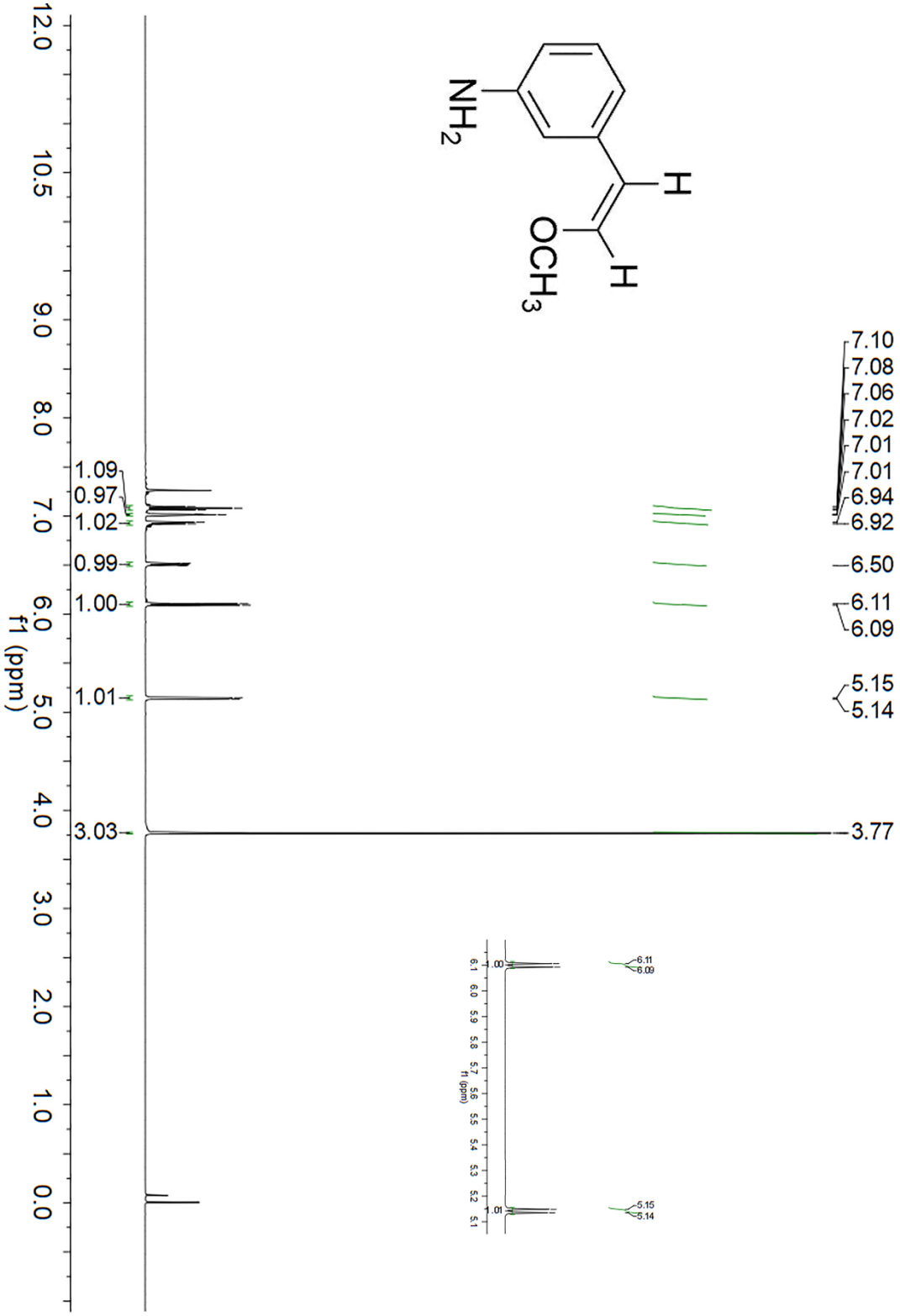
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**.



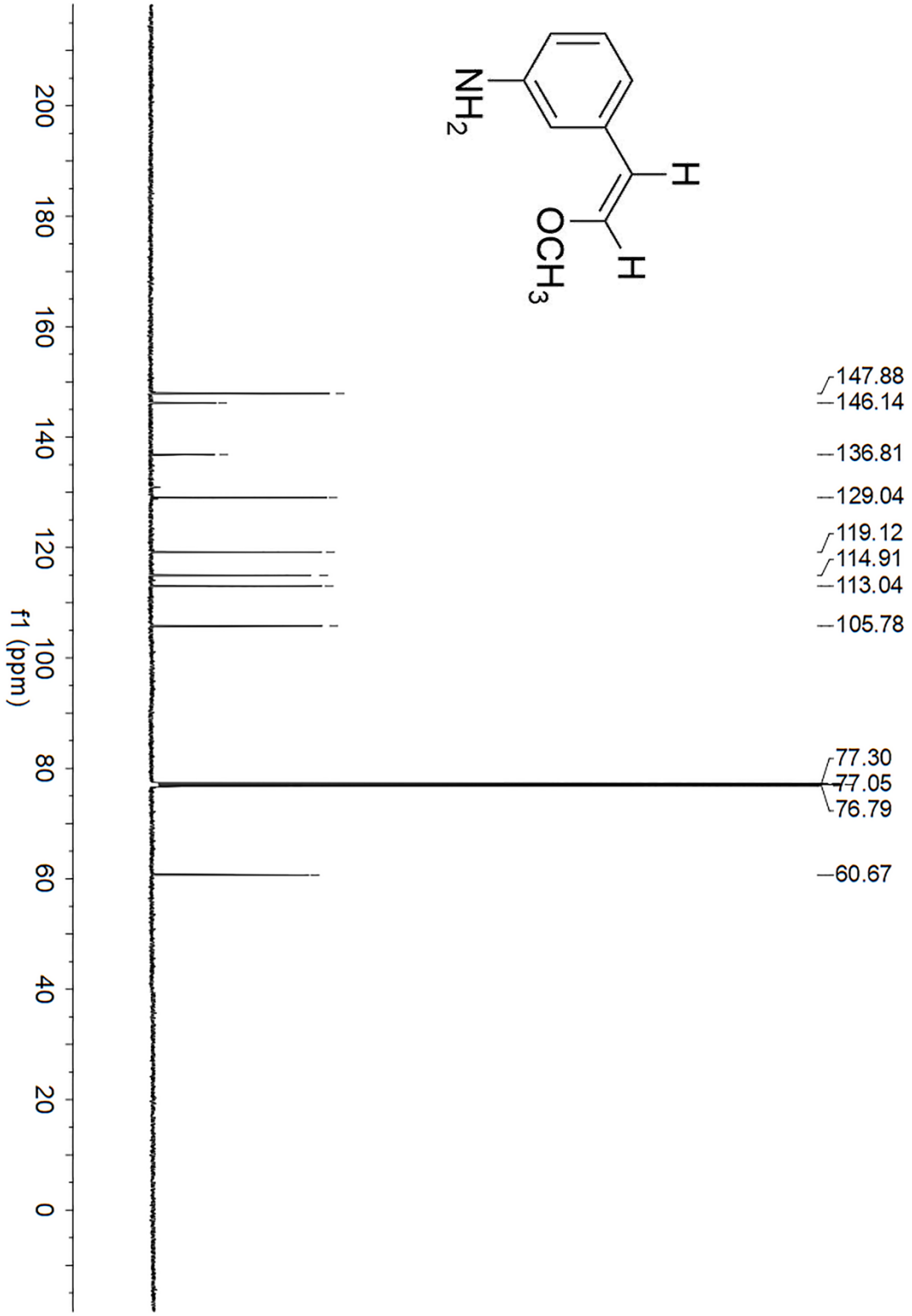
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3p**.



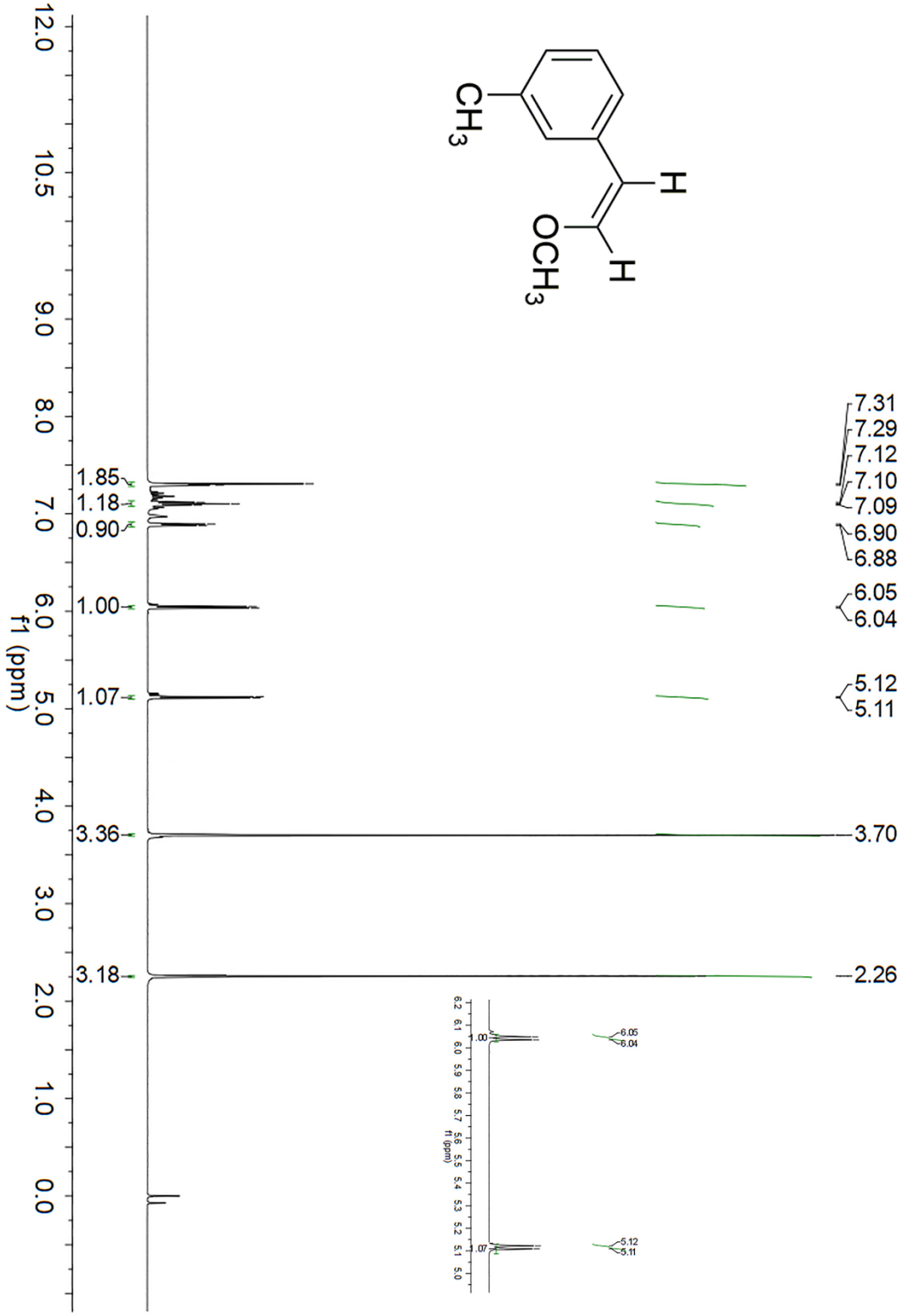
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**.



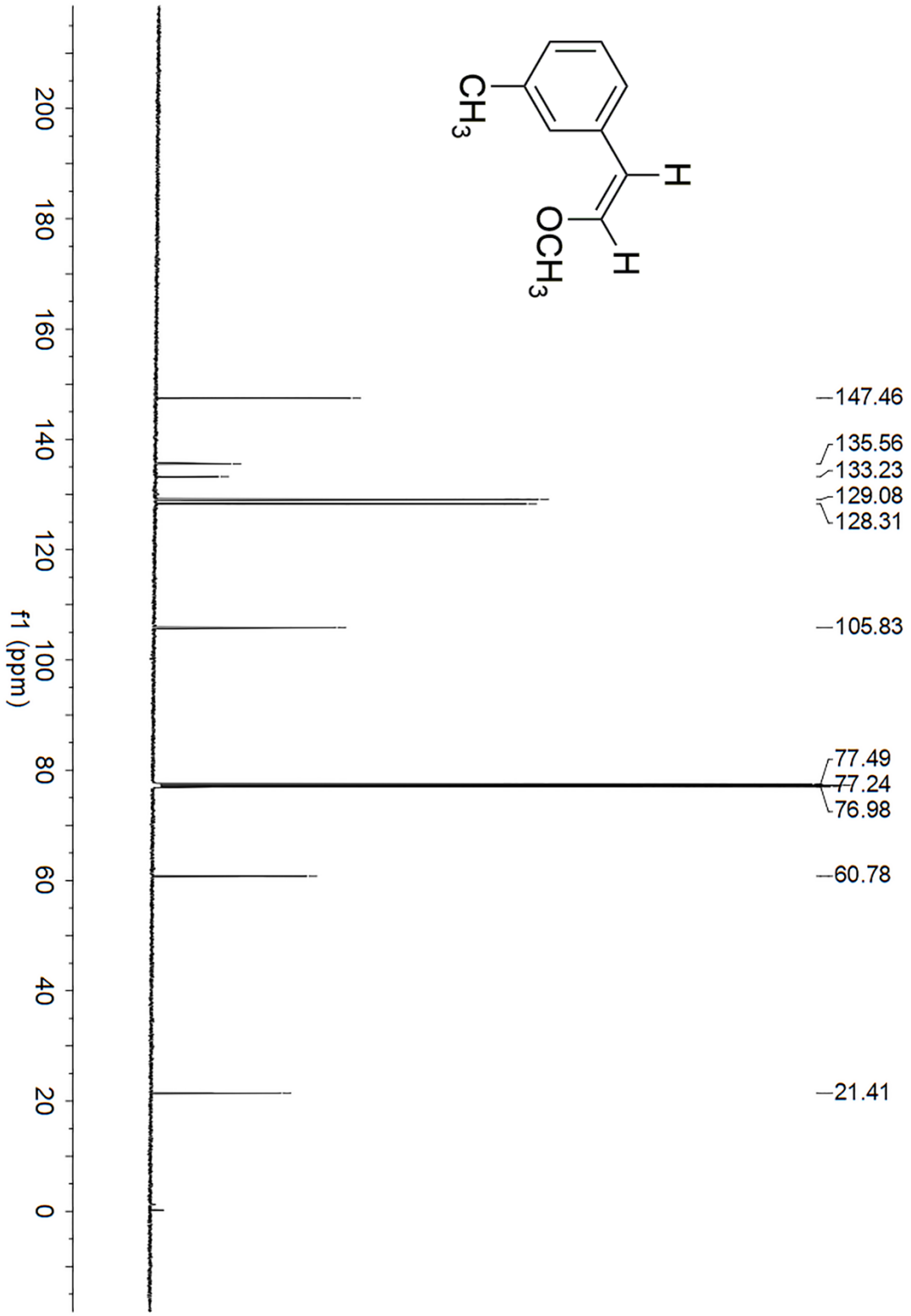
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3q**.



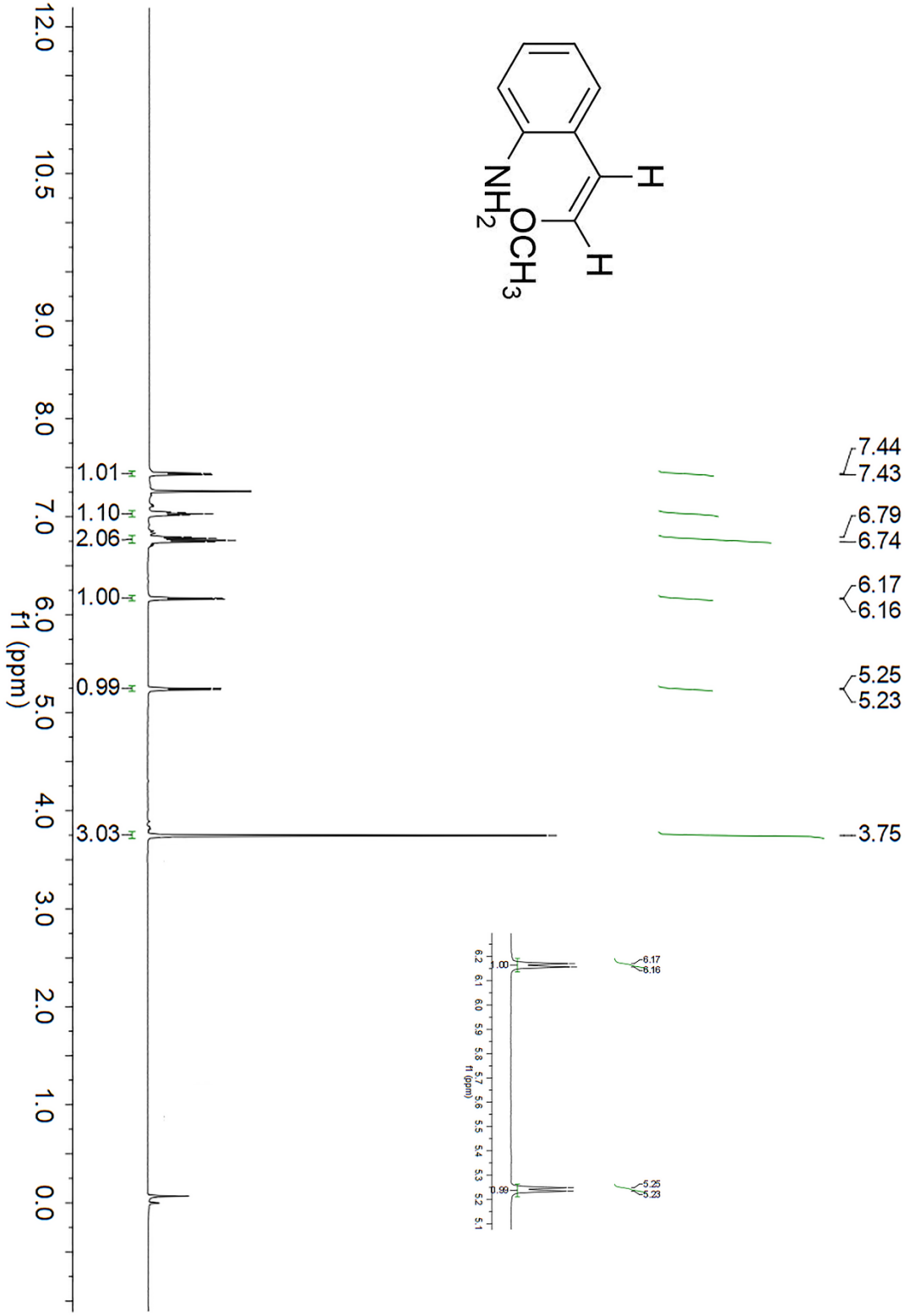
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**.



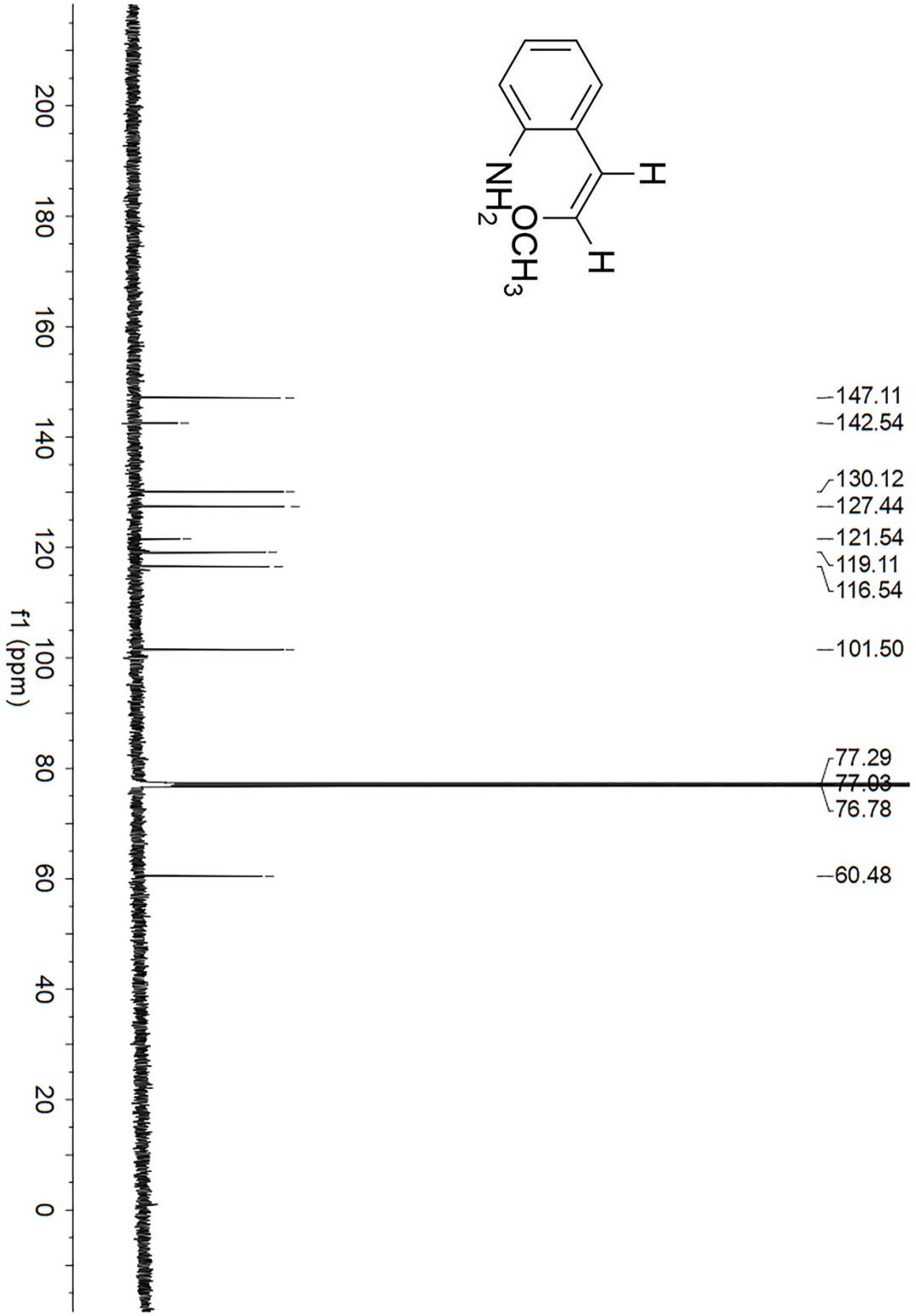
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3r**.



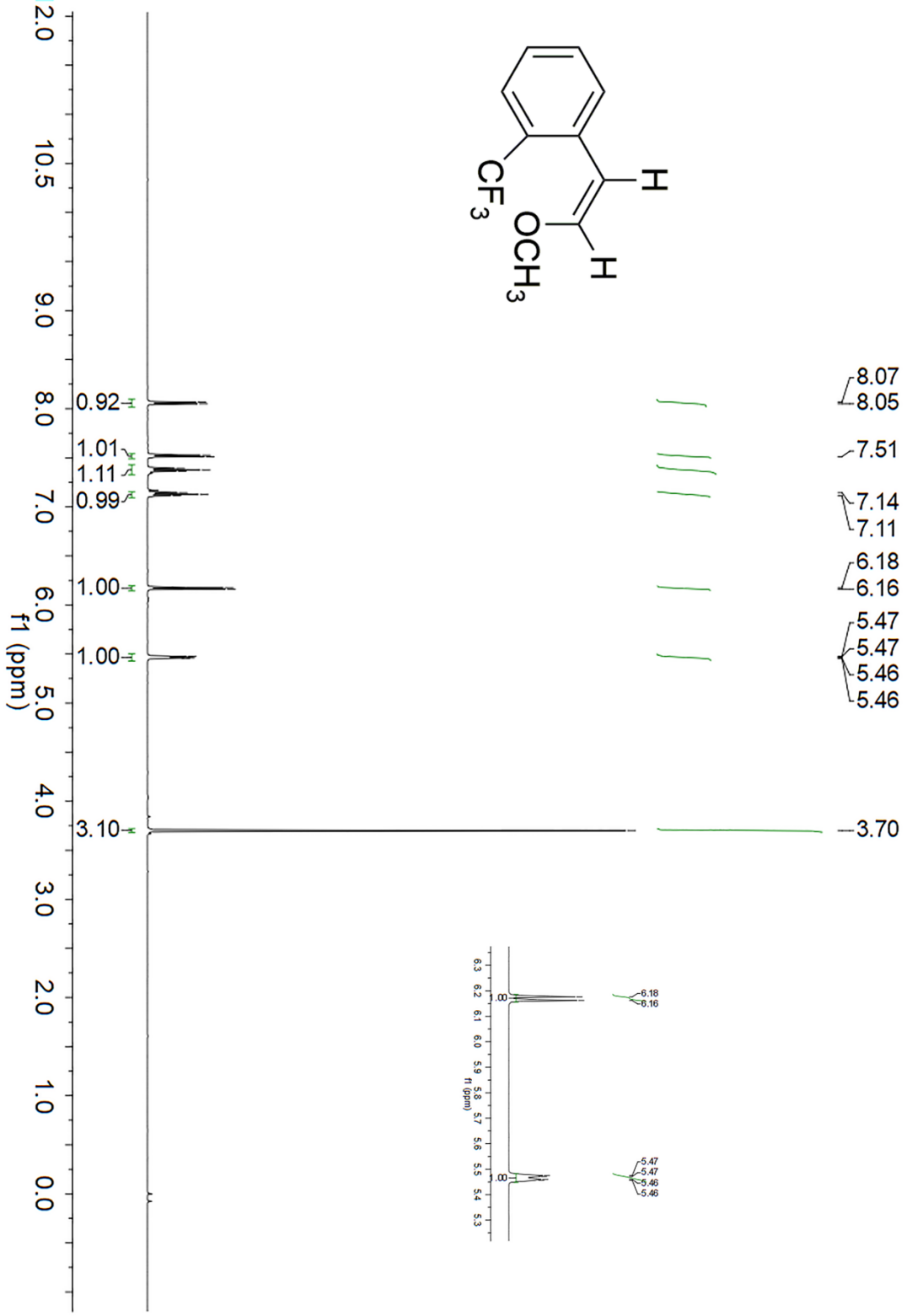
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3s**.



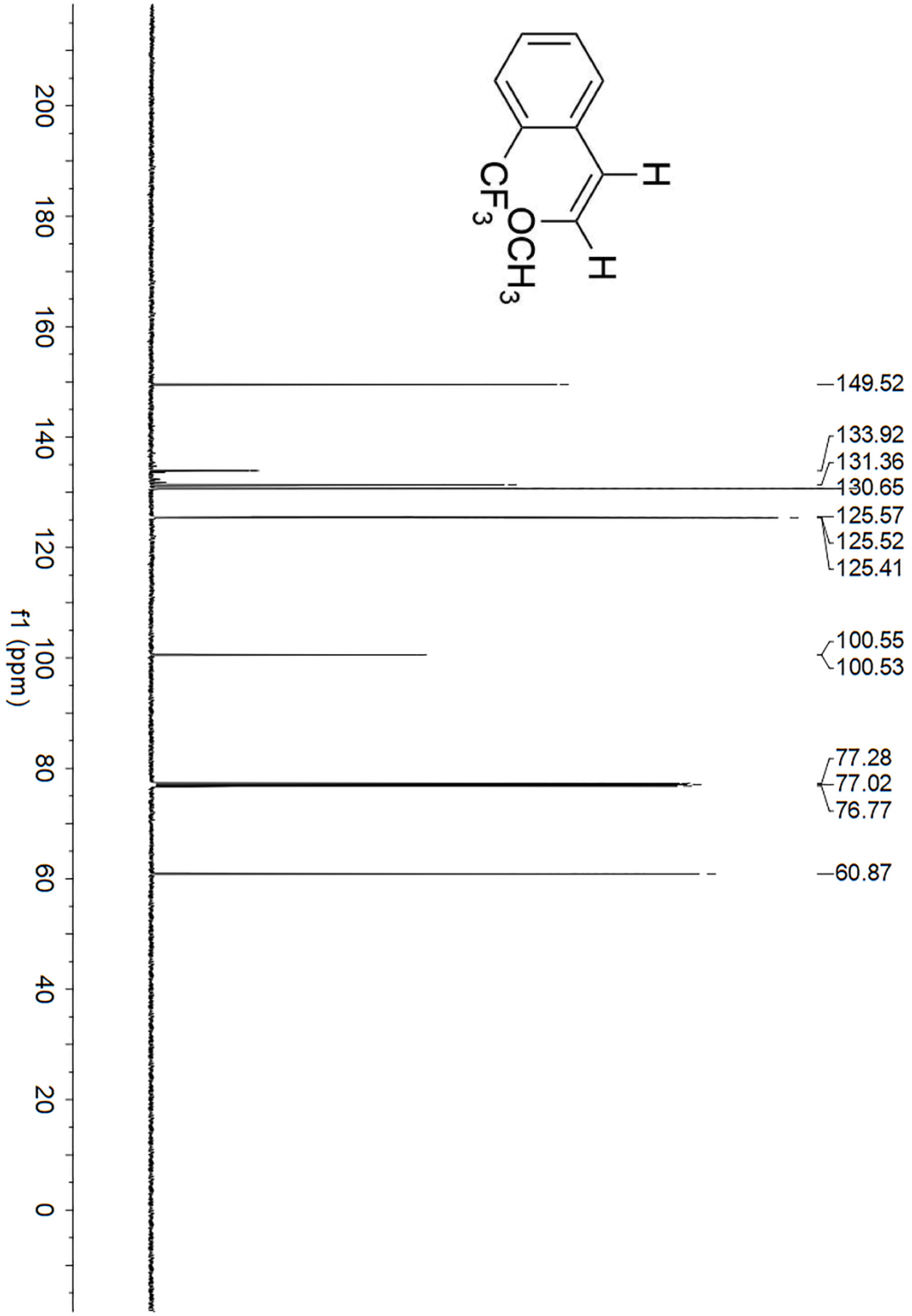
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3s**.



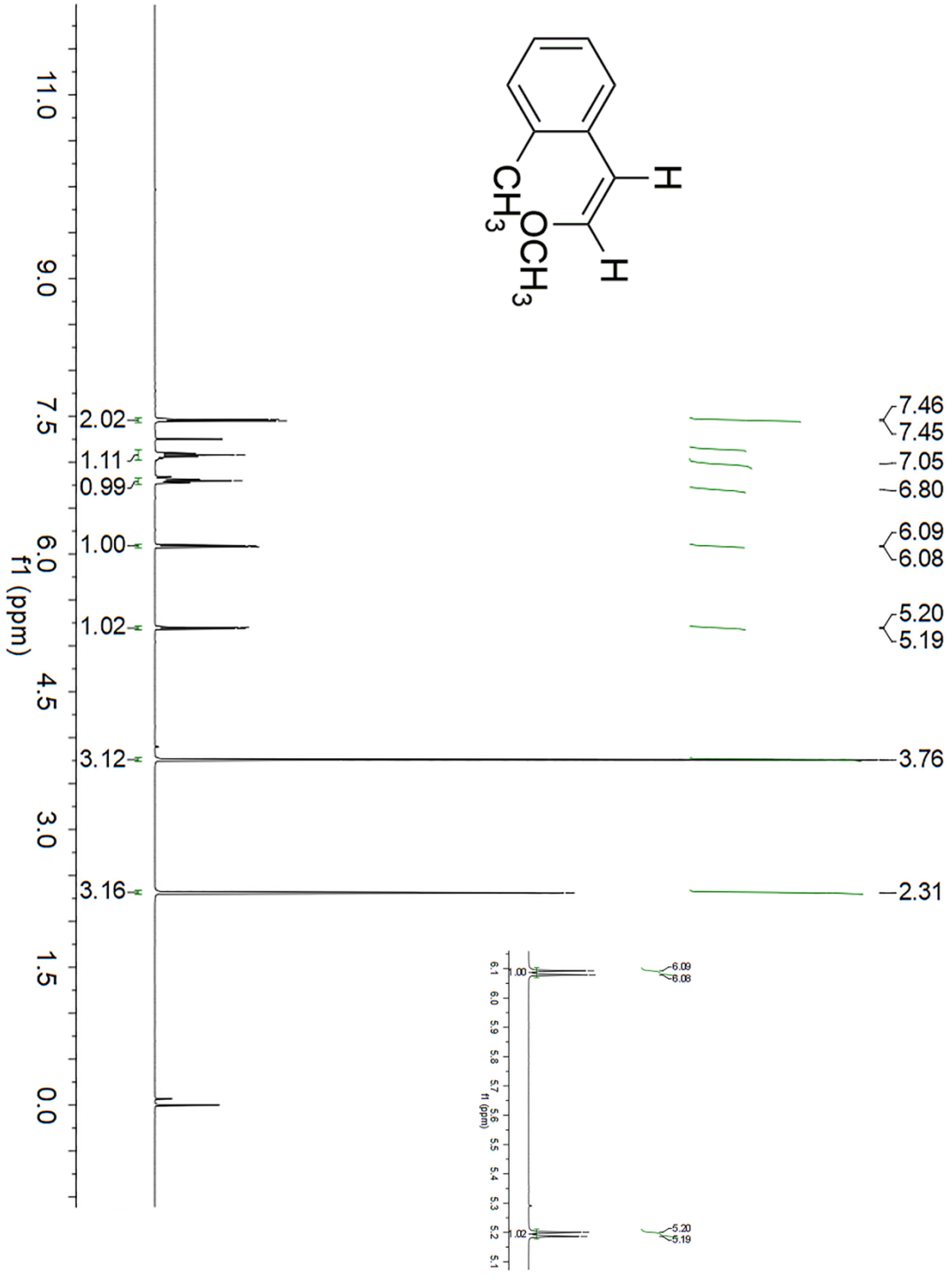
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**.



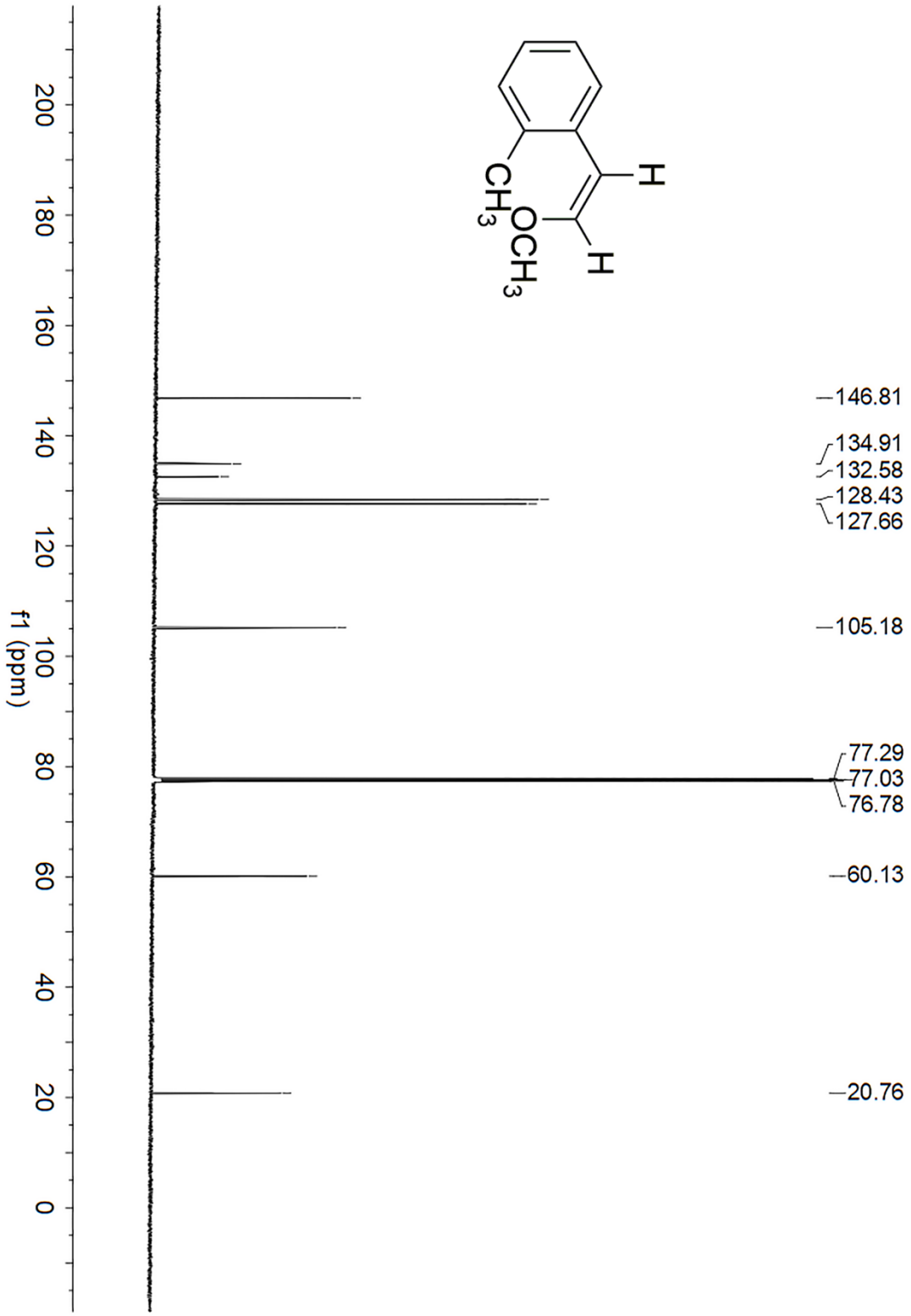
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3t**.



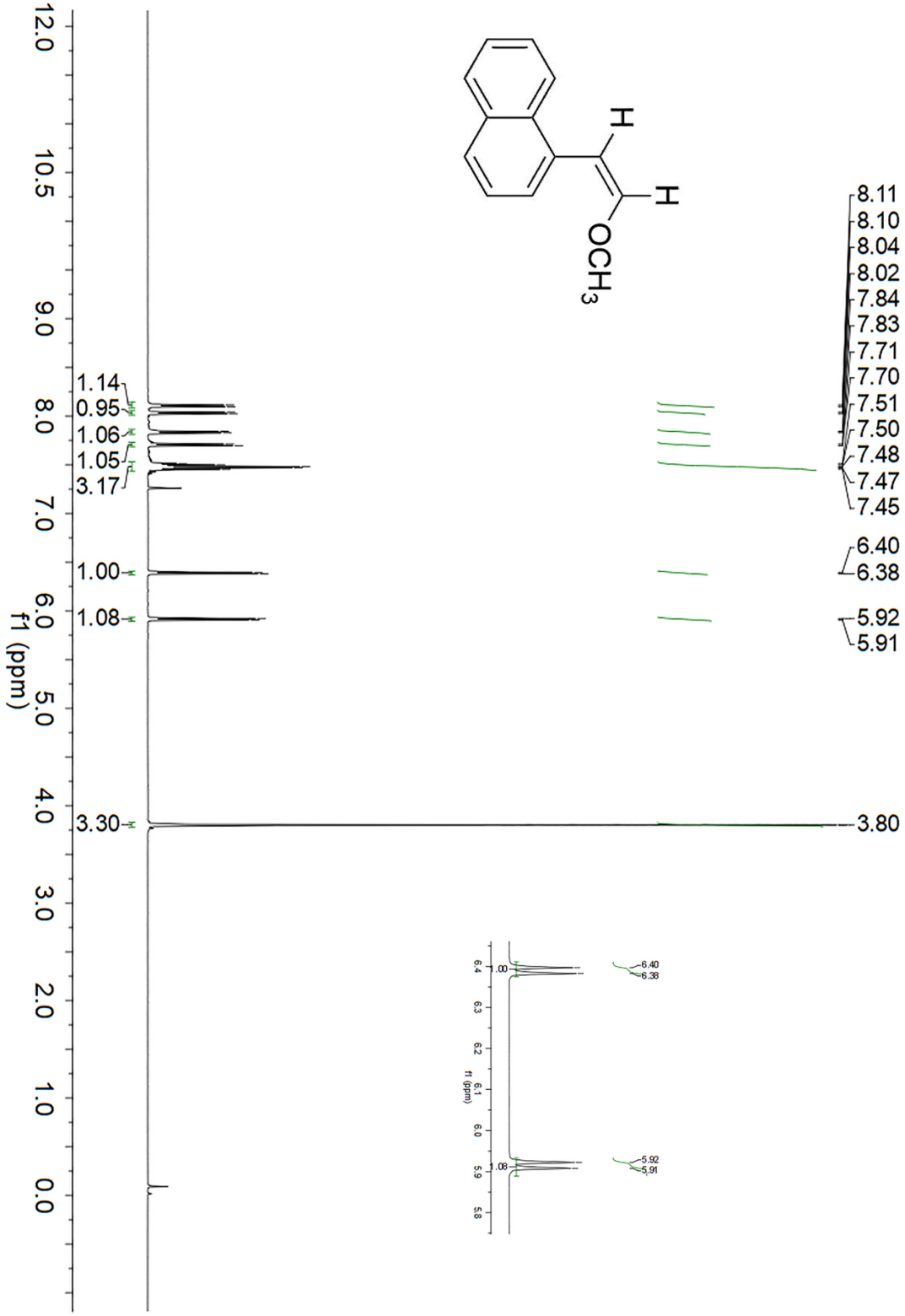
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**.



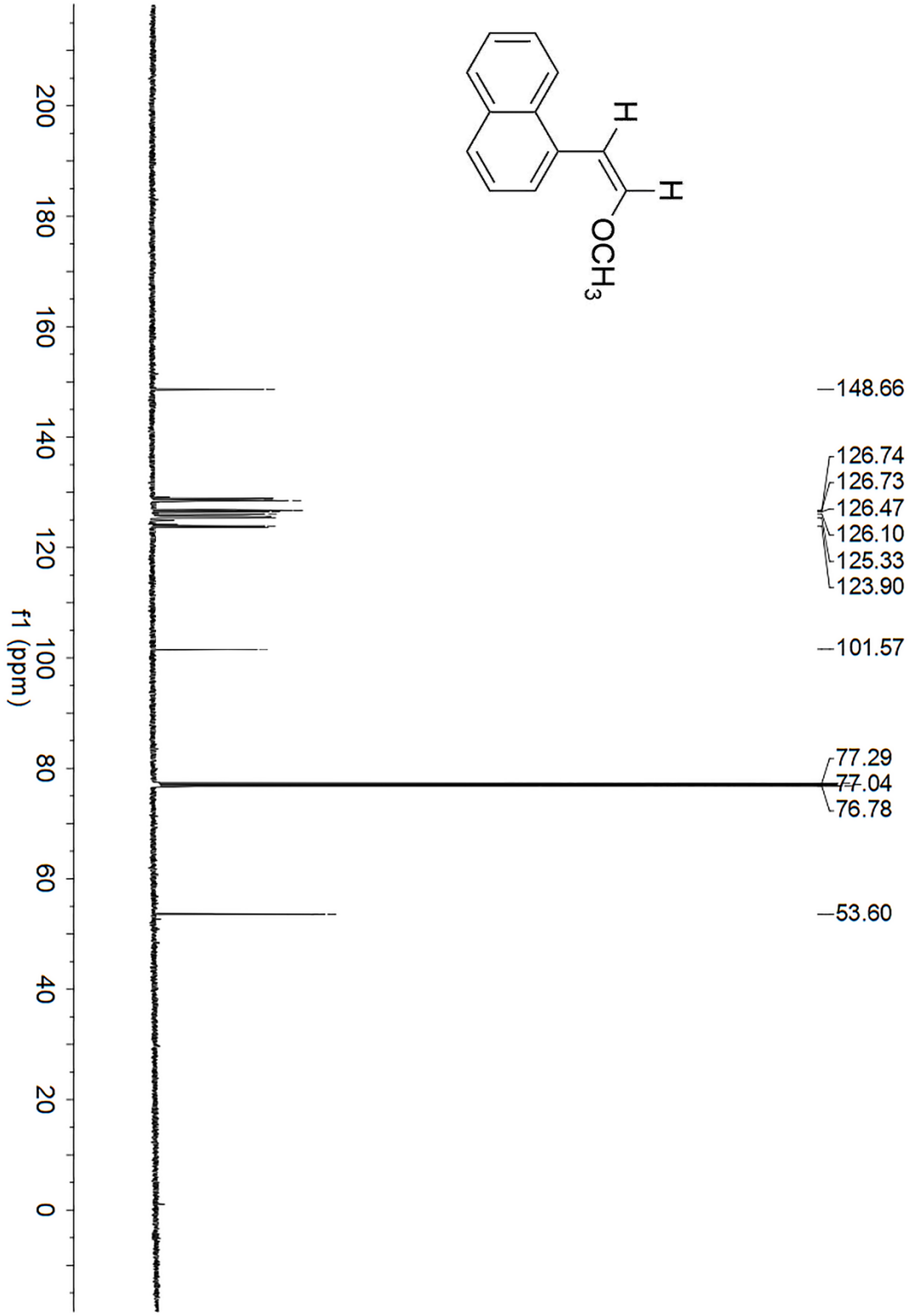
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3u**.



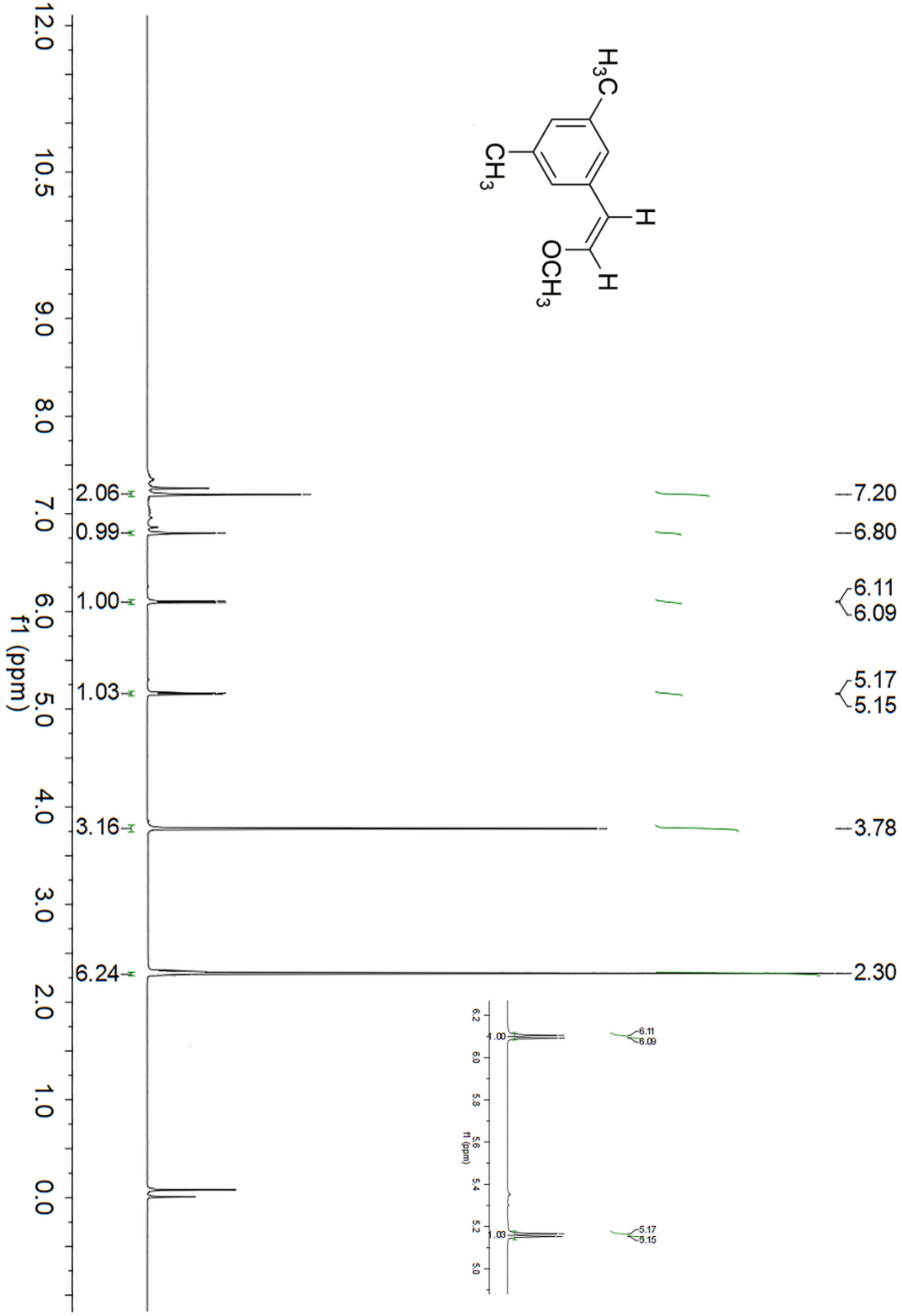
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**.



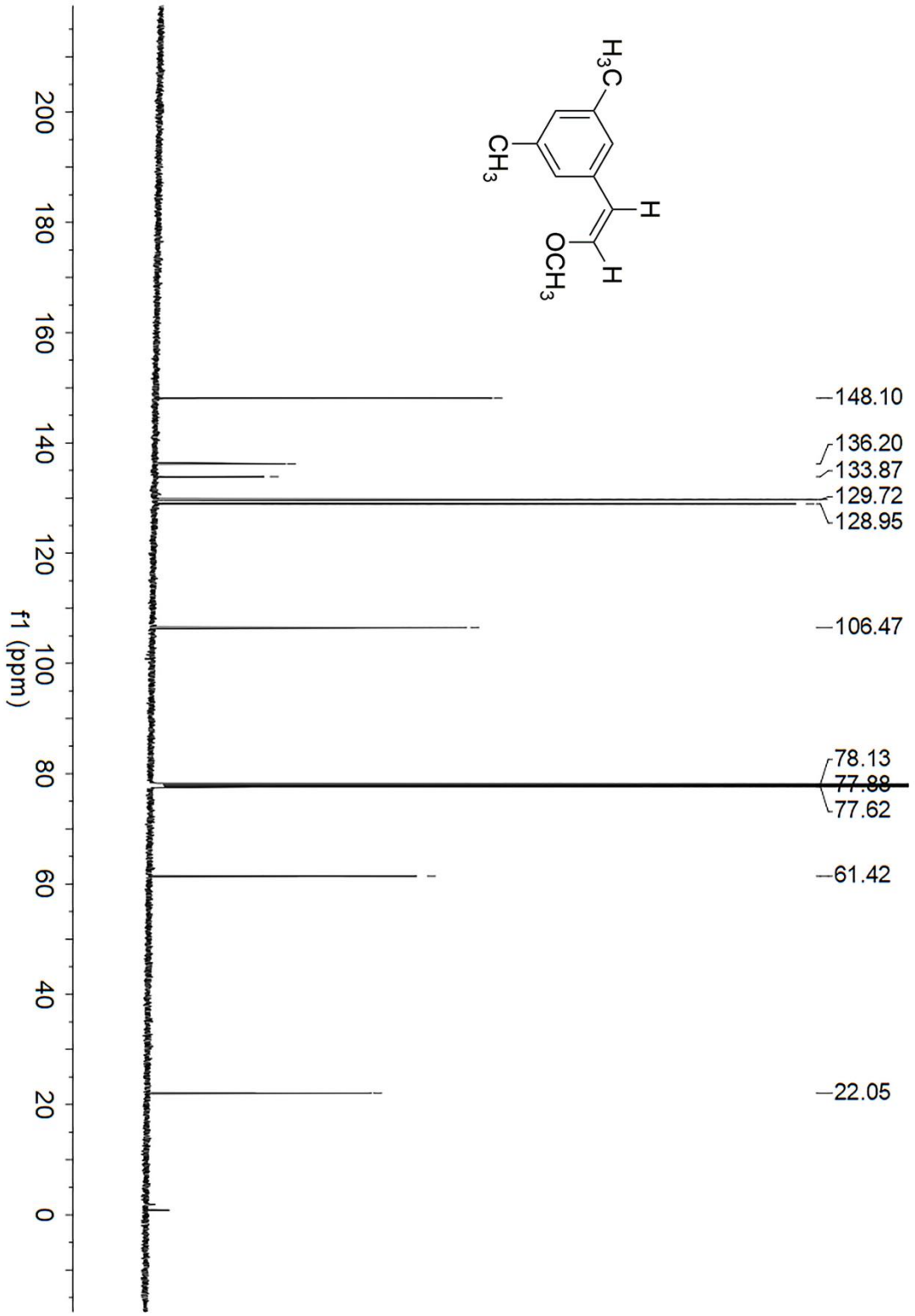
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3v**.



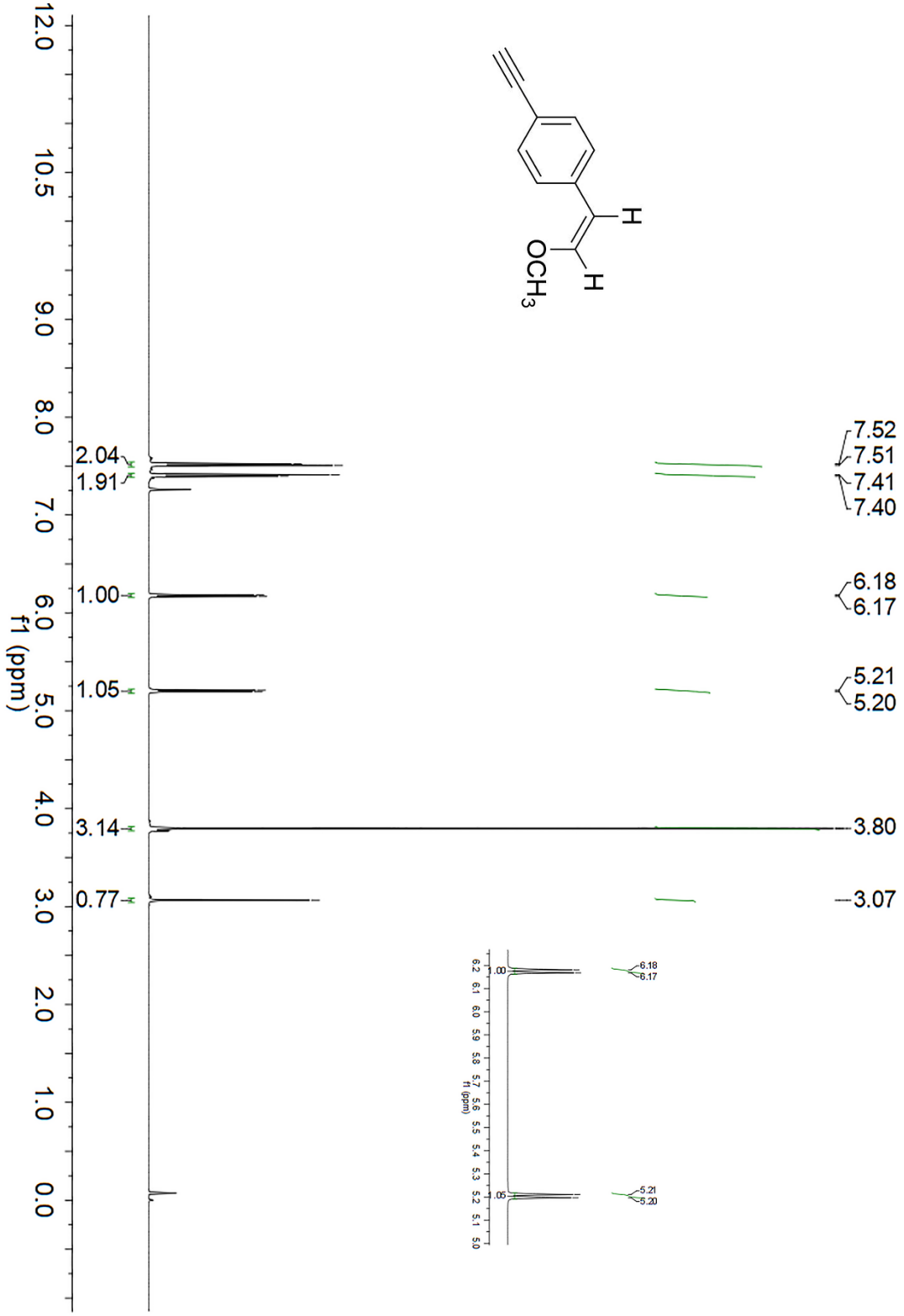
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**.



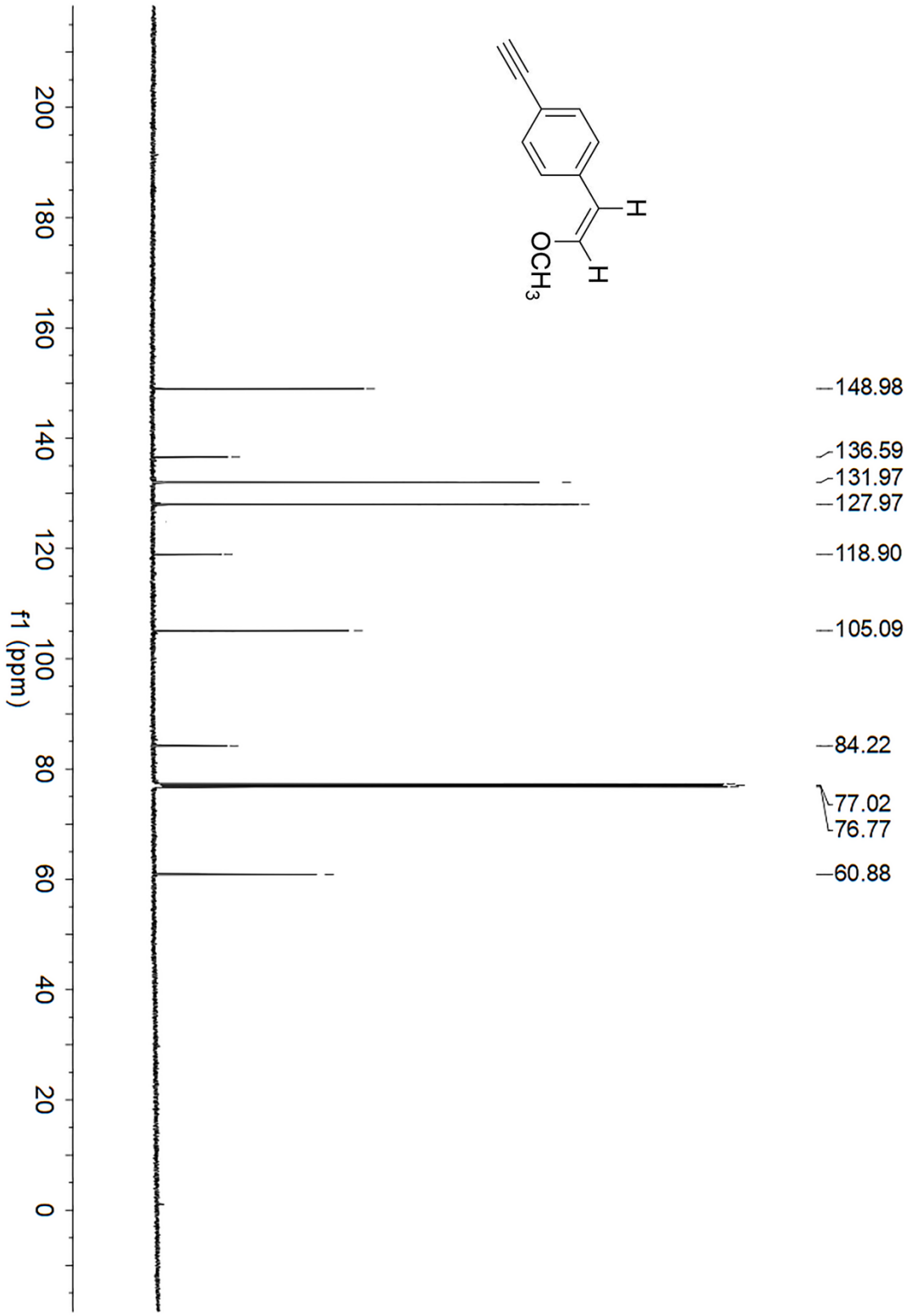
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3w**.



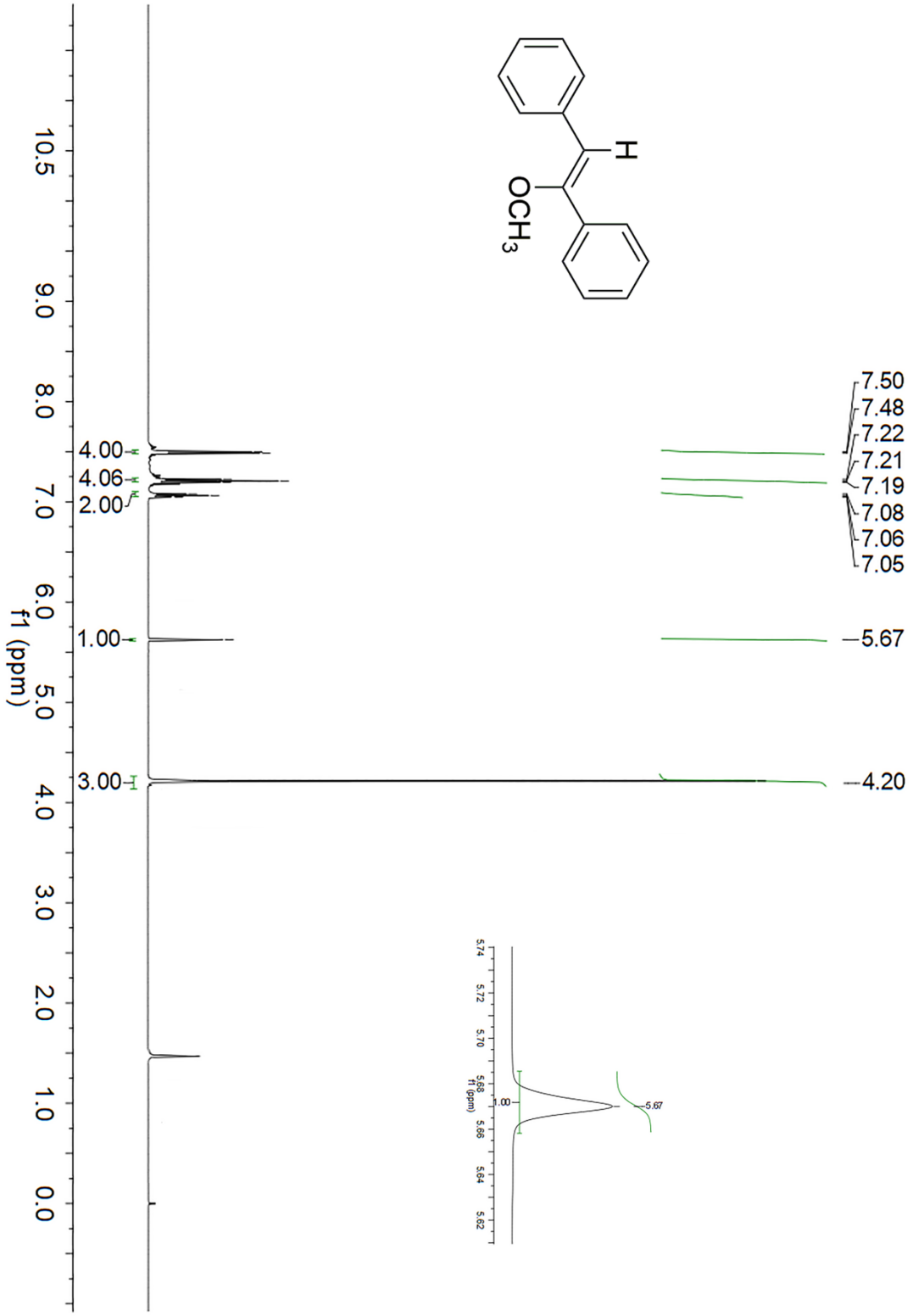
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x**.



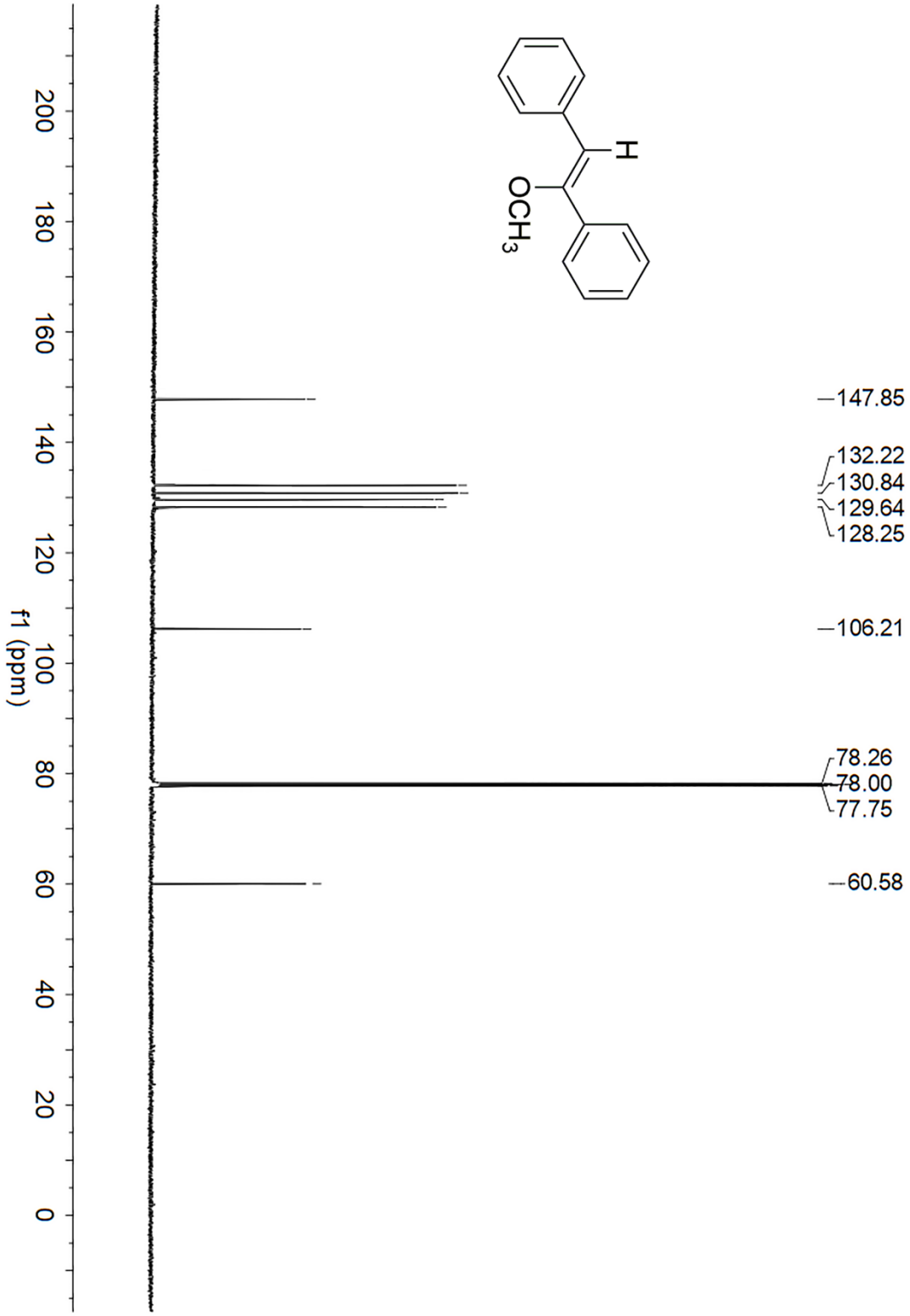
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3x**.



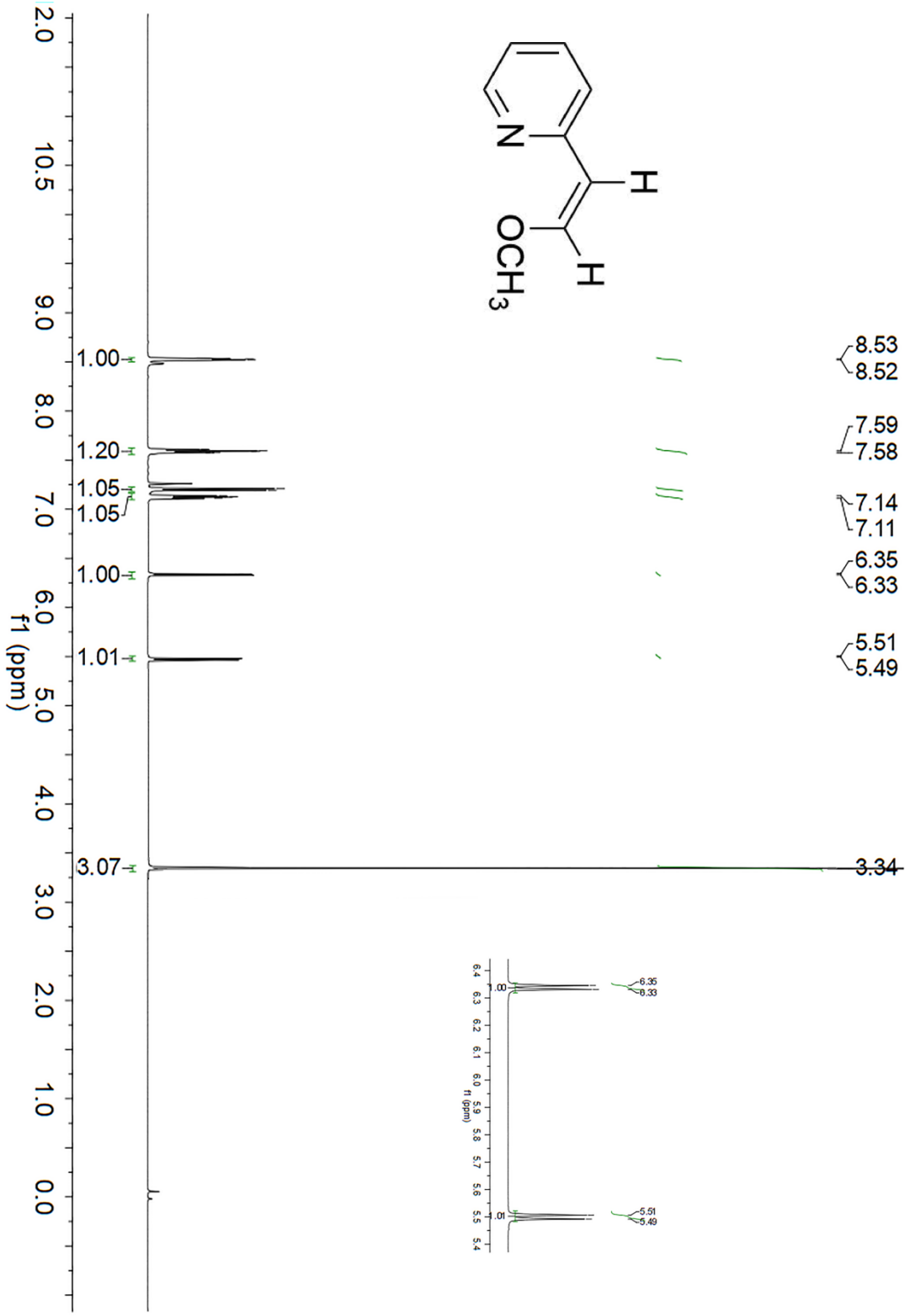
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y**.



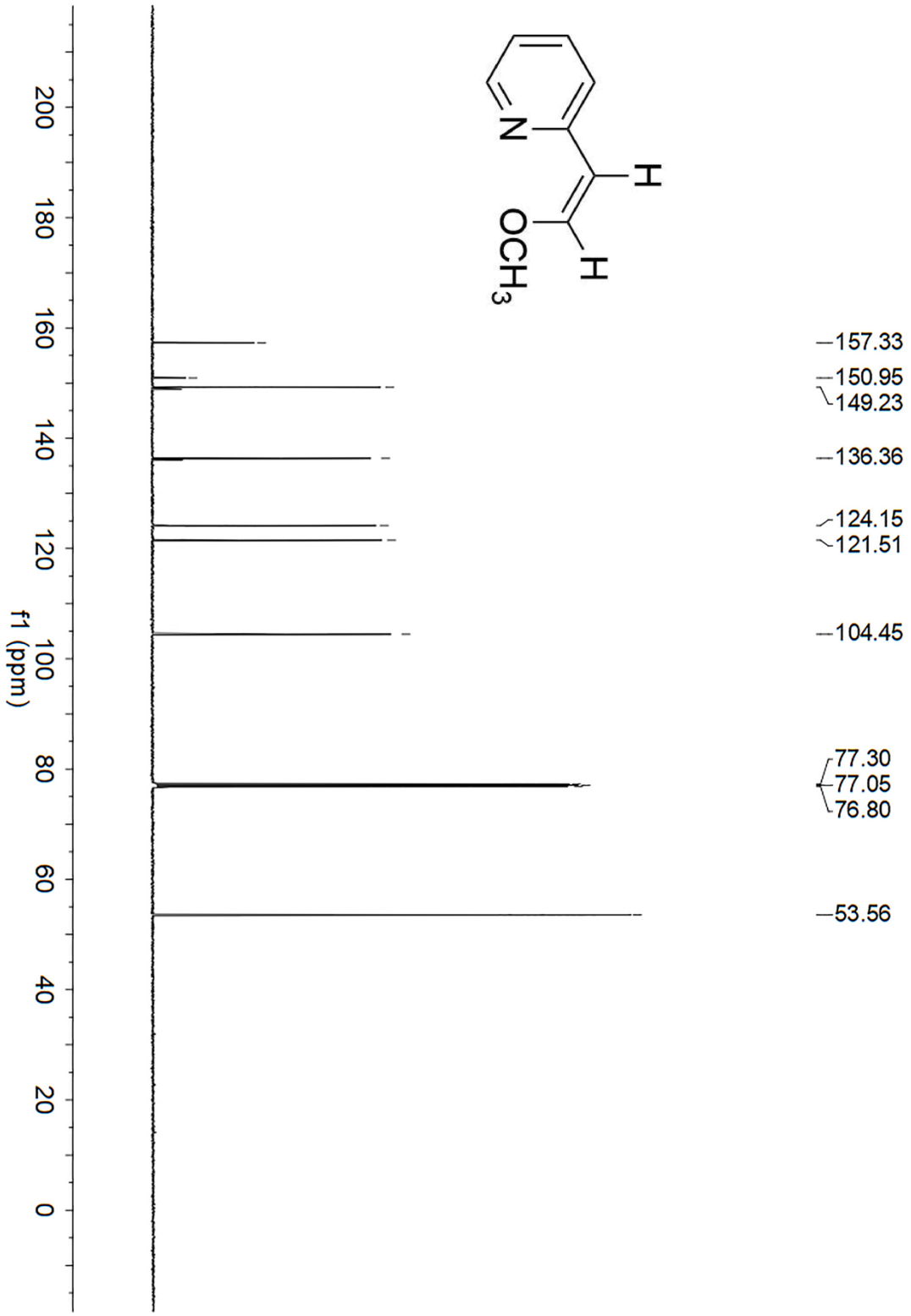
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3y**.



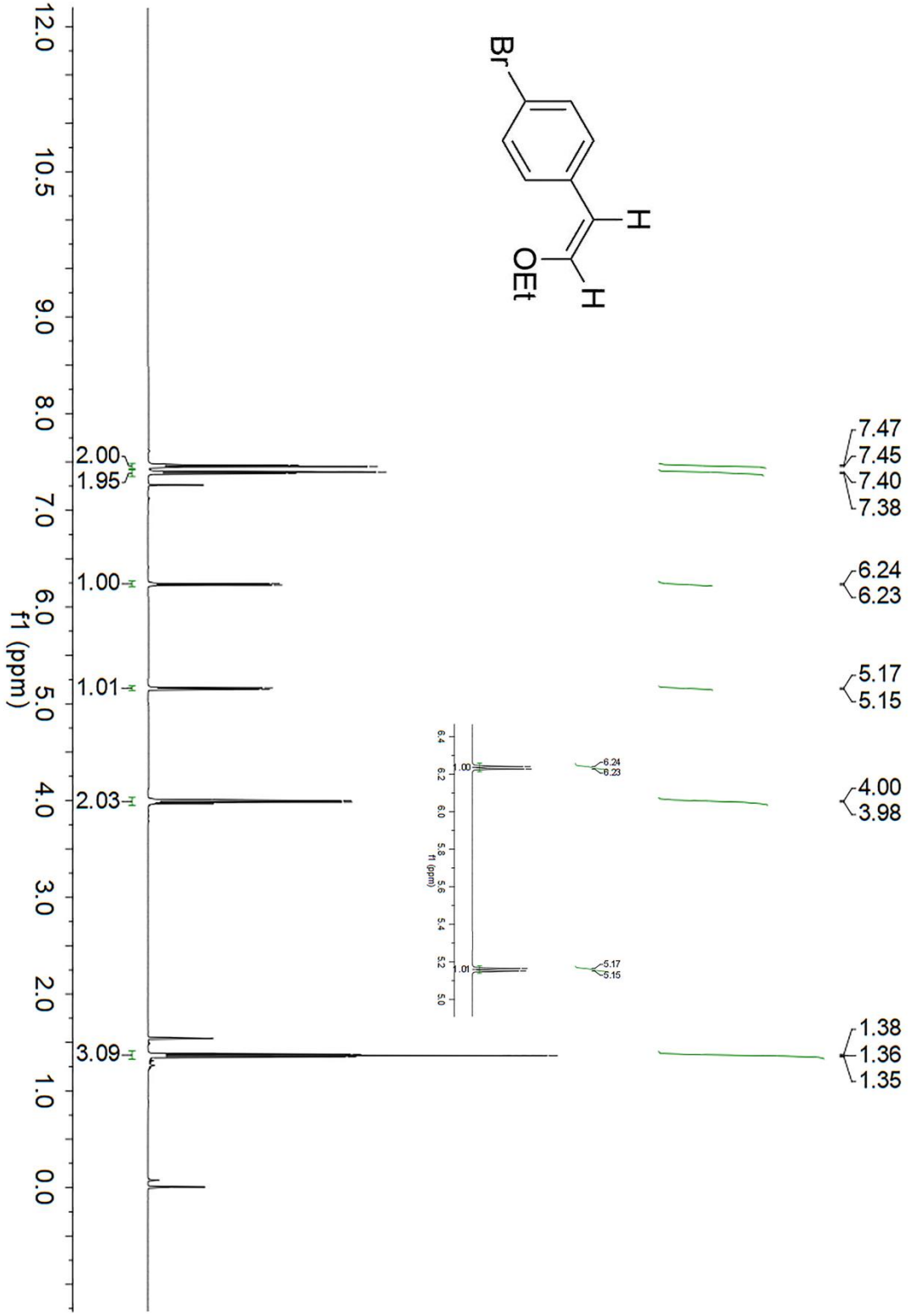
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**.



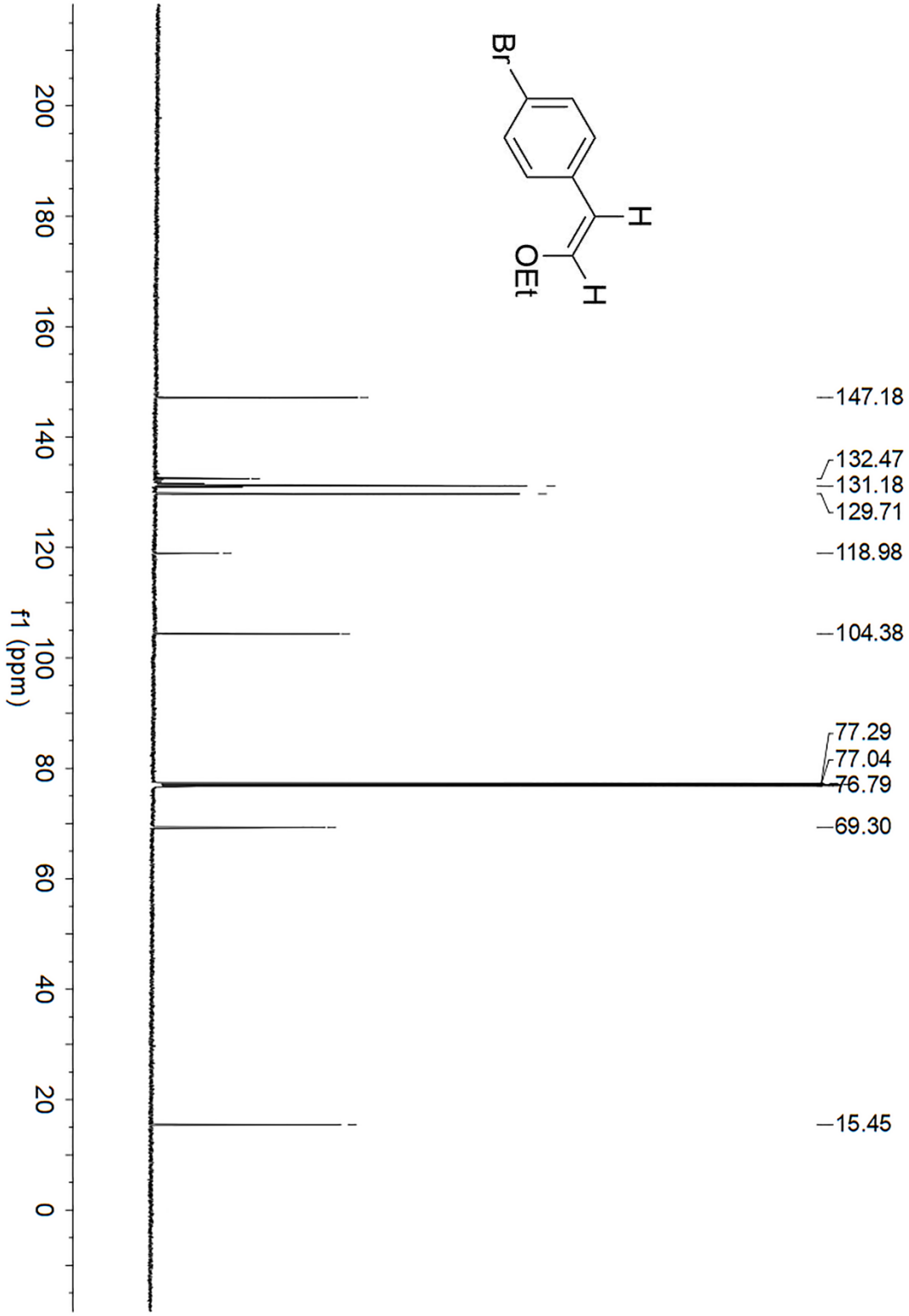
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3z**.



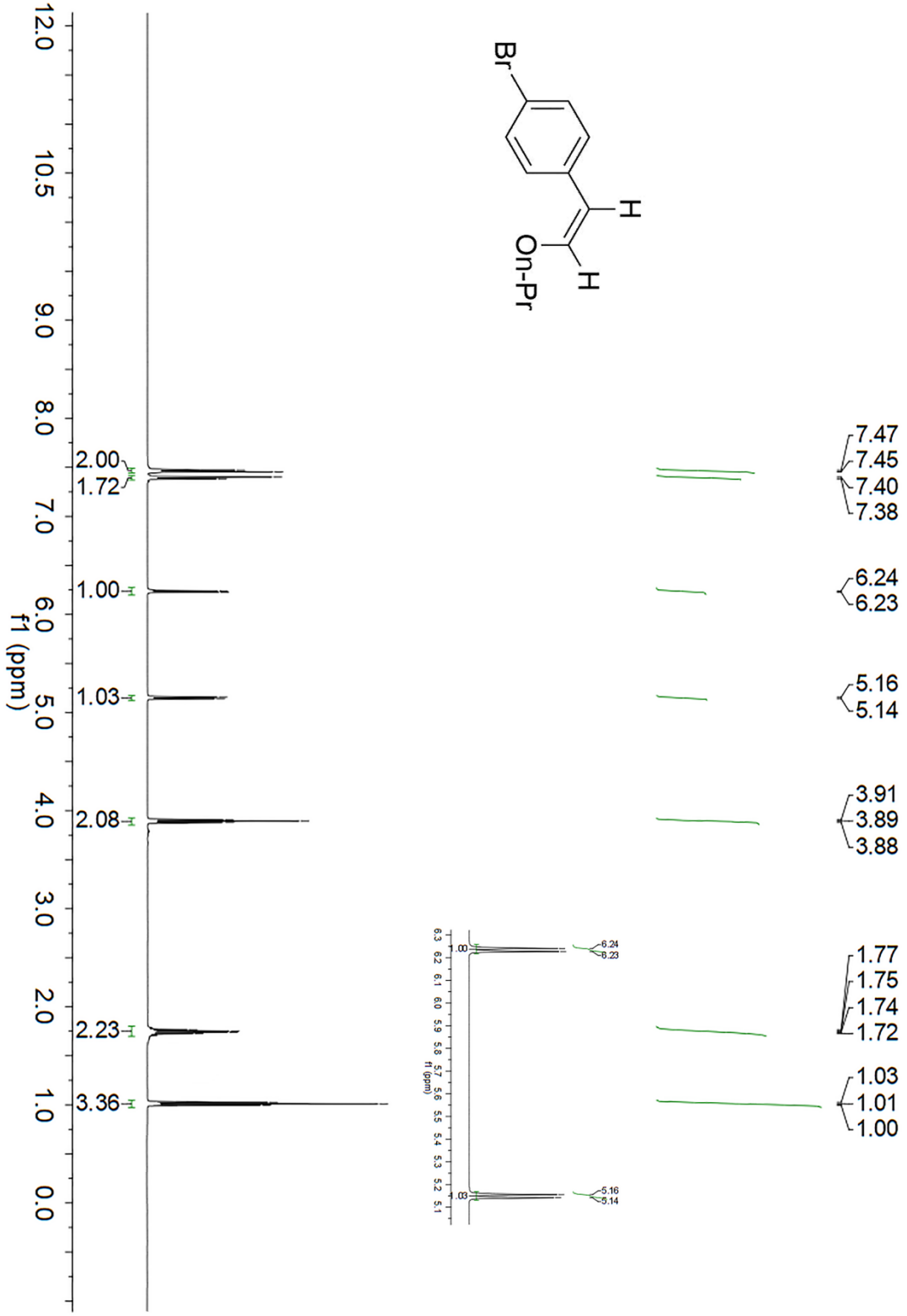
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aa**.



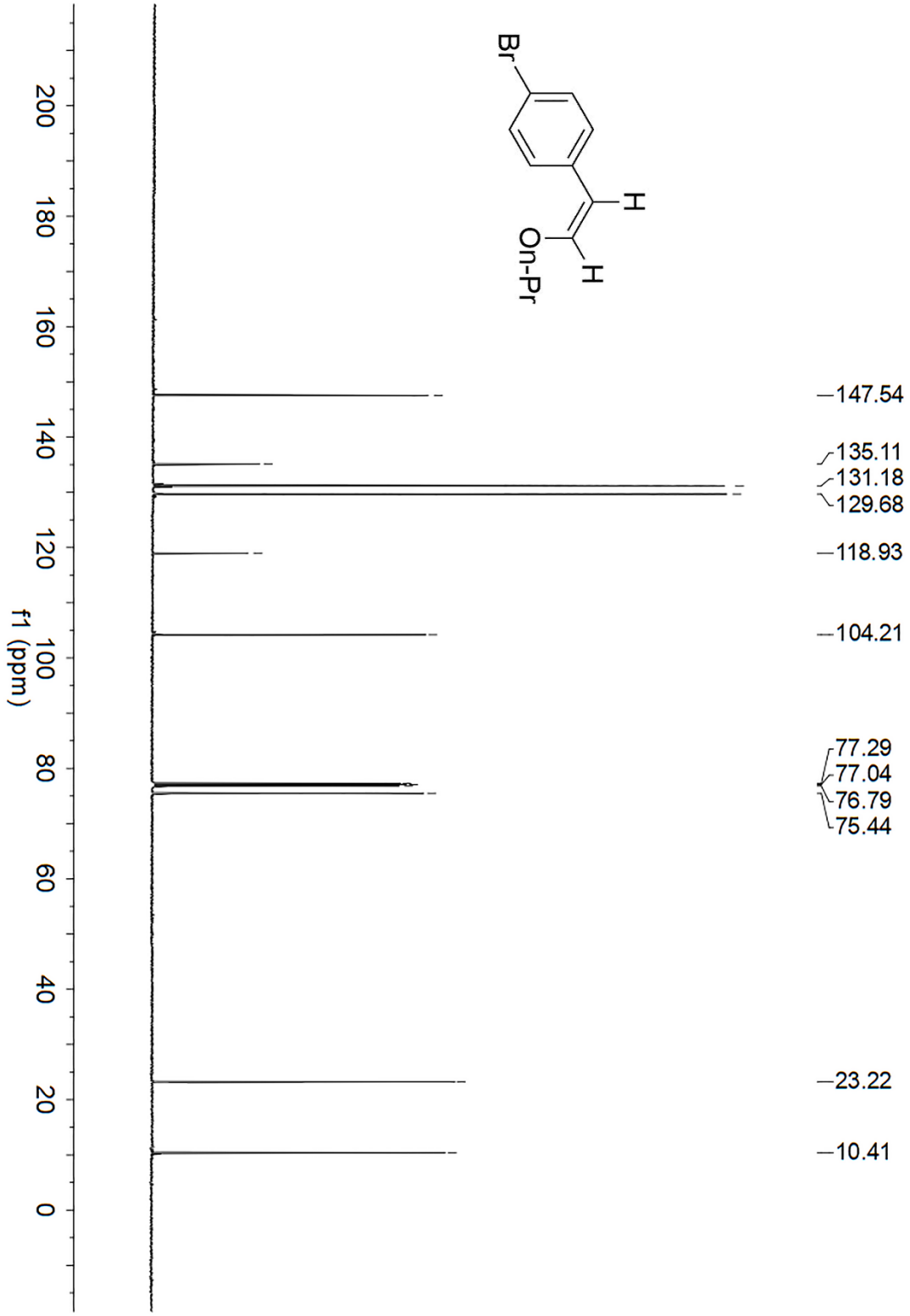
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3aa**.



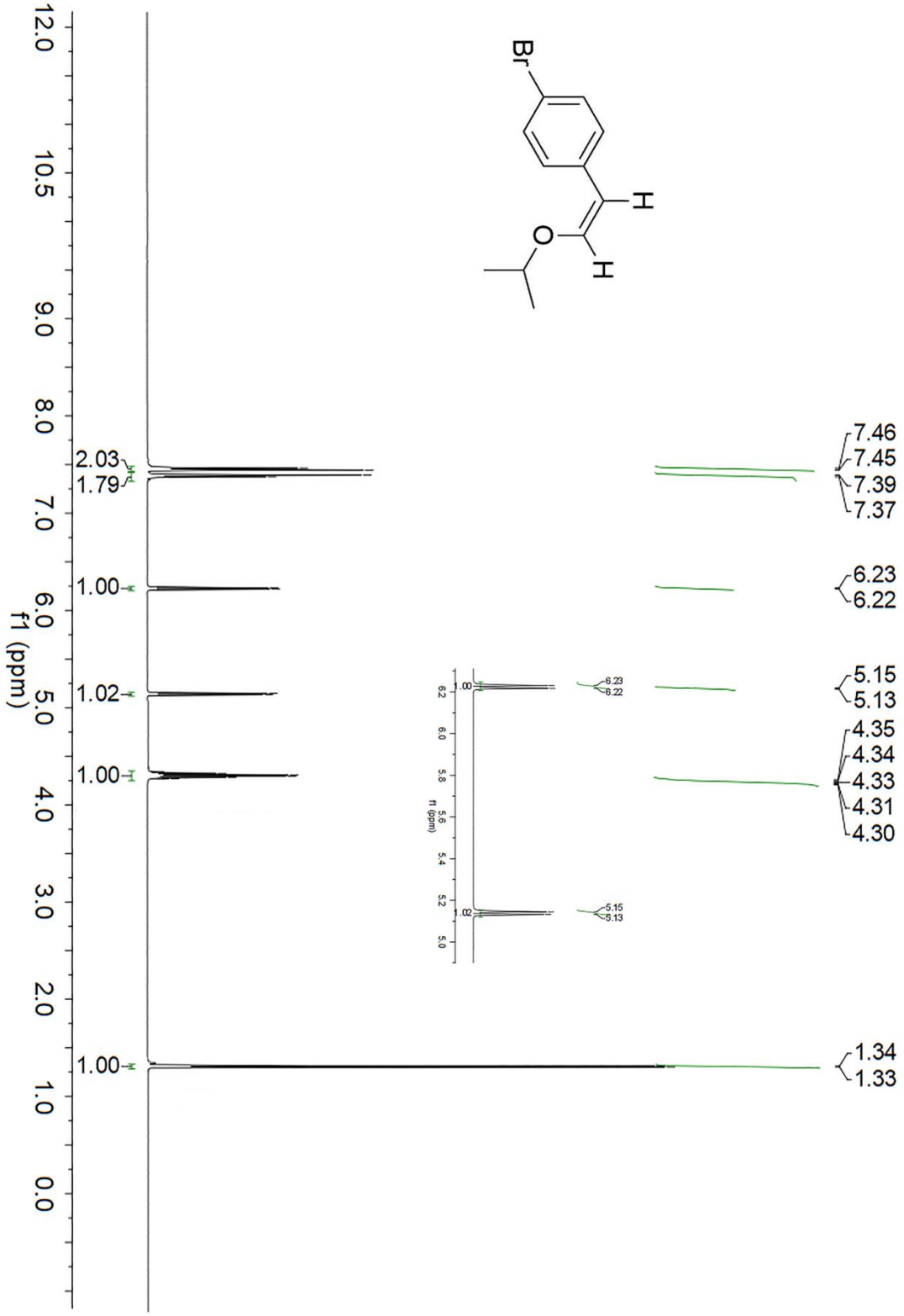
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ab**.



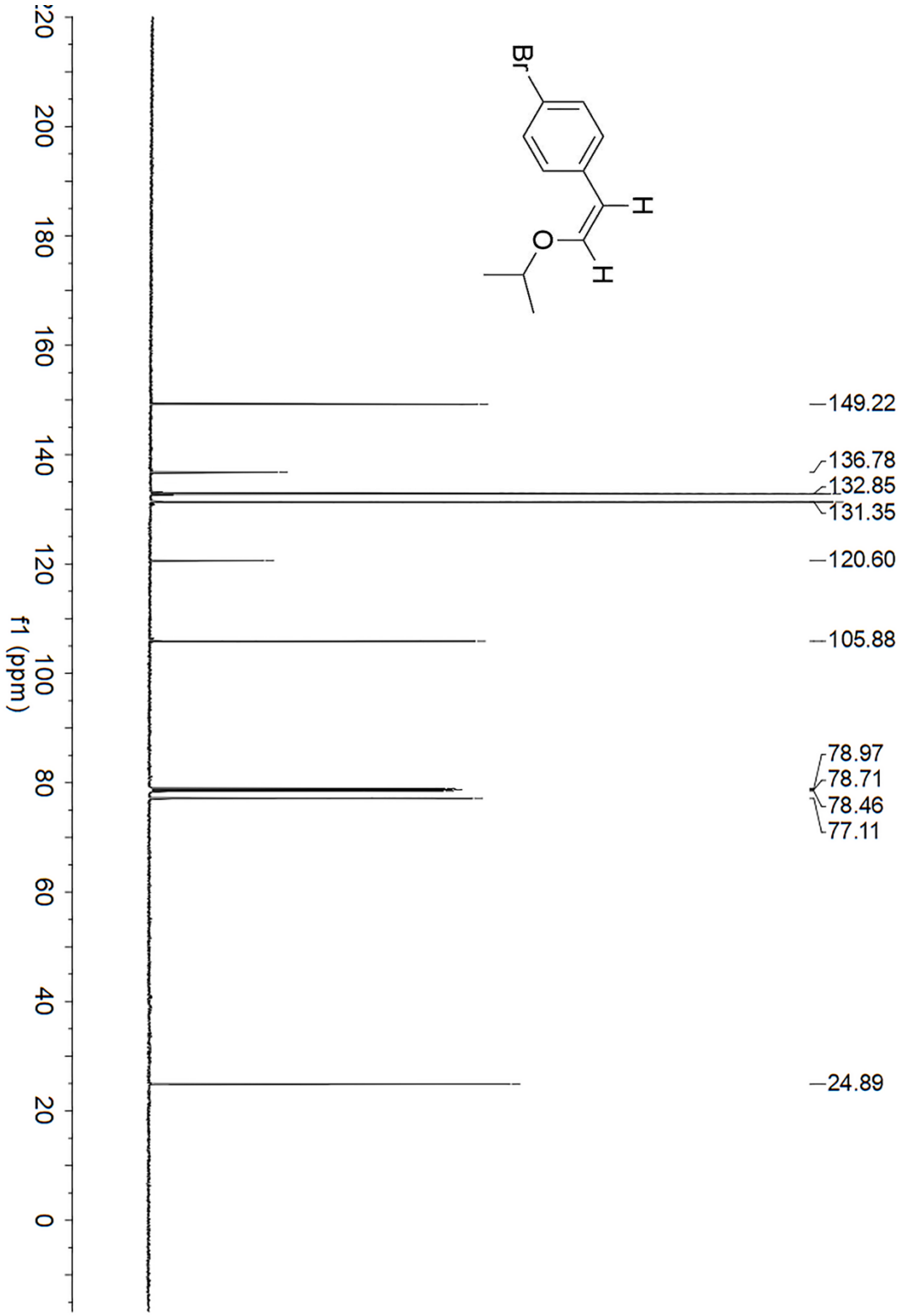
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ab**.



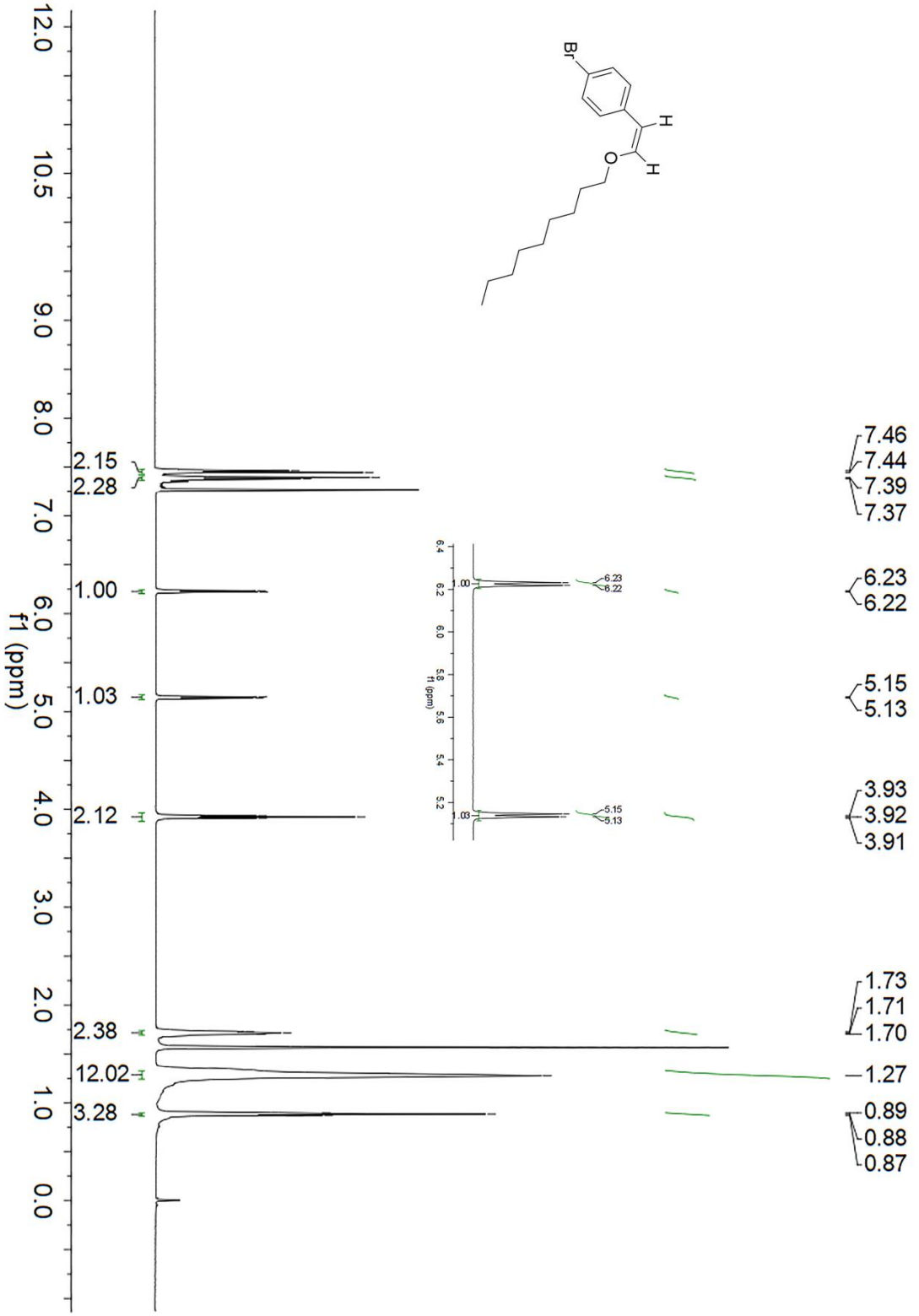
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ac**.



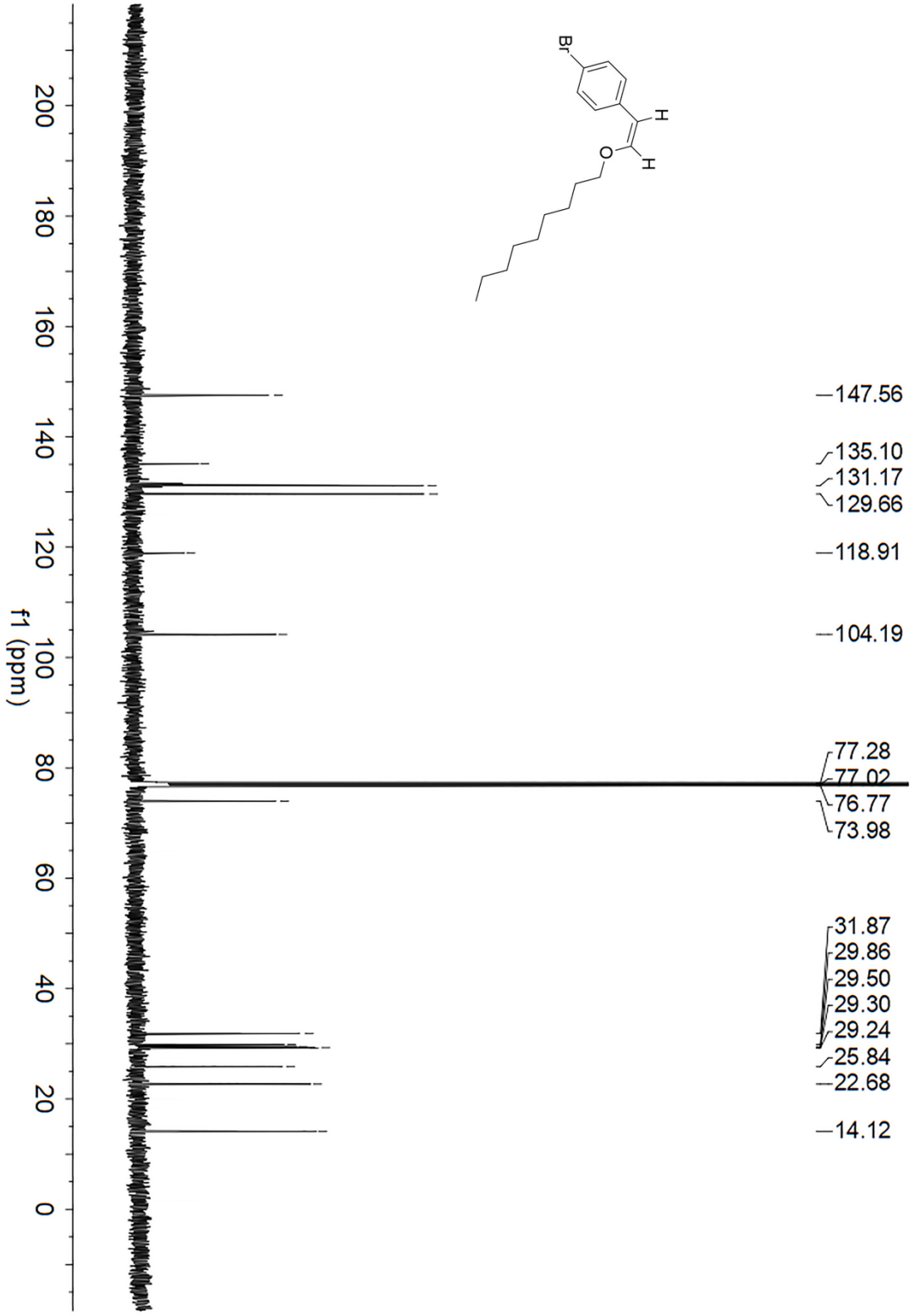
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ac**.



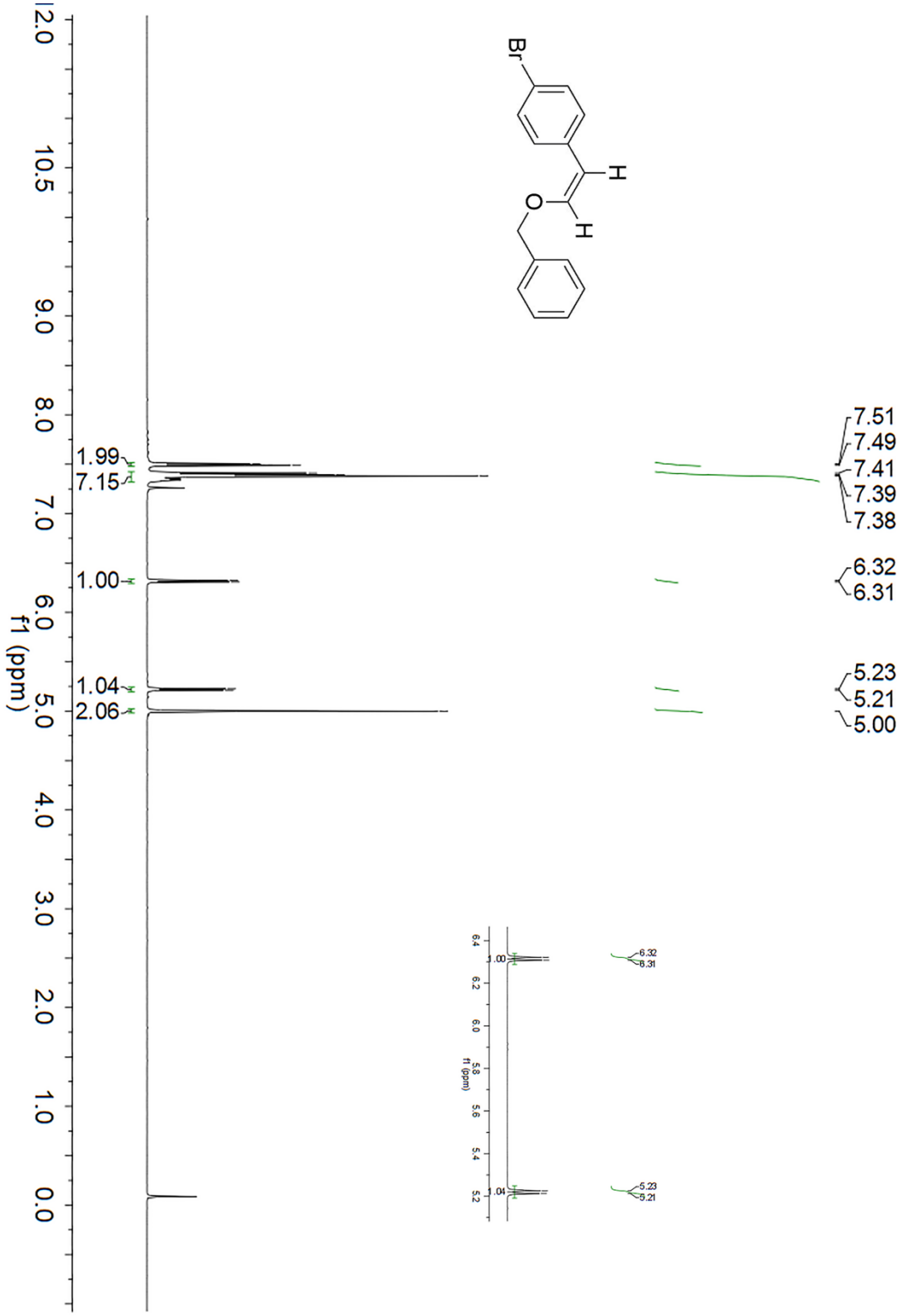
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ad**.



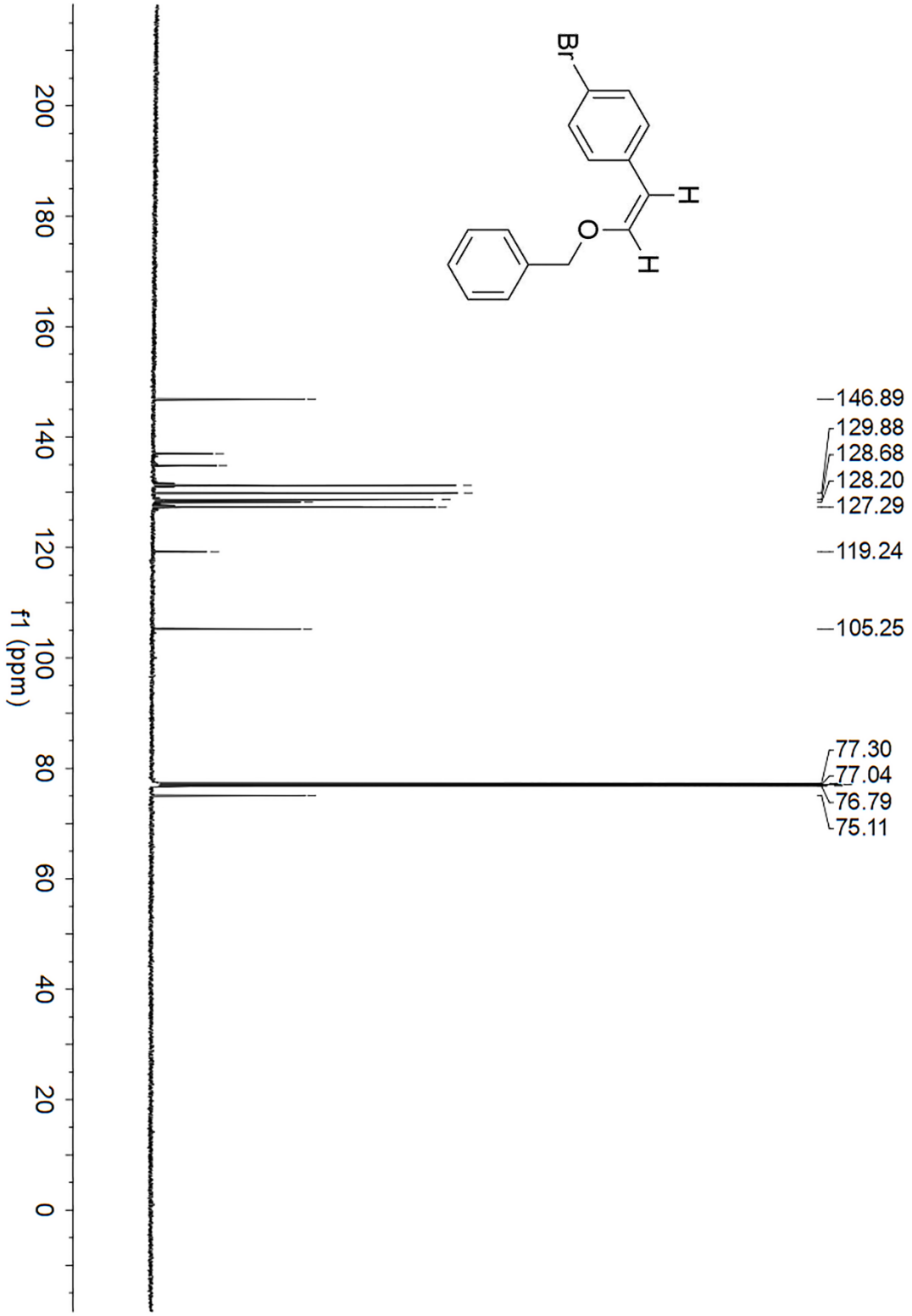
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ad**.



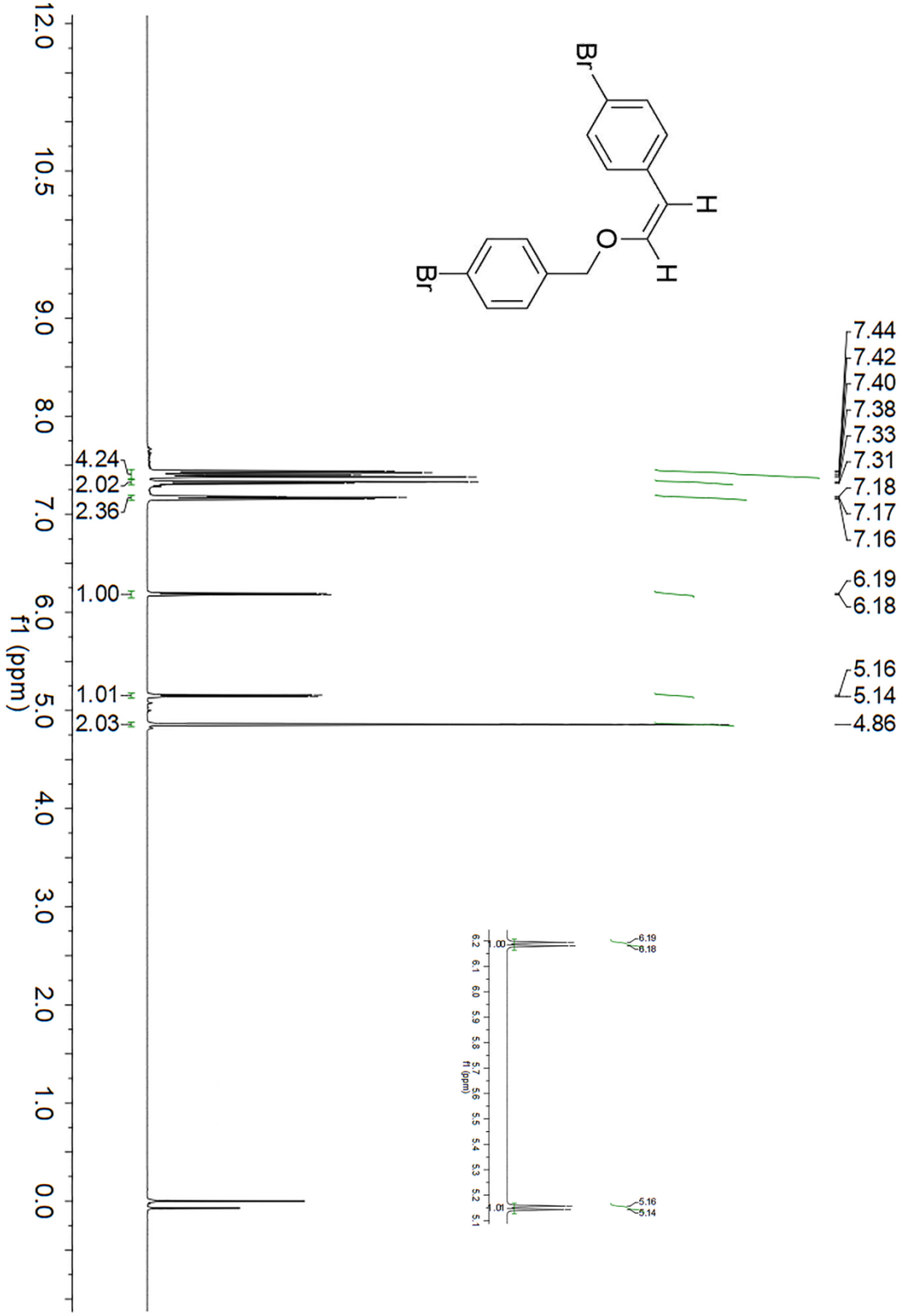
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ae**.



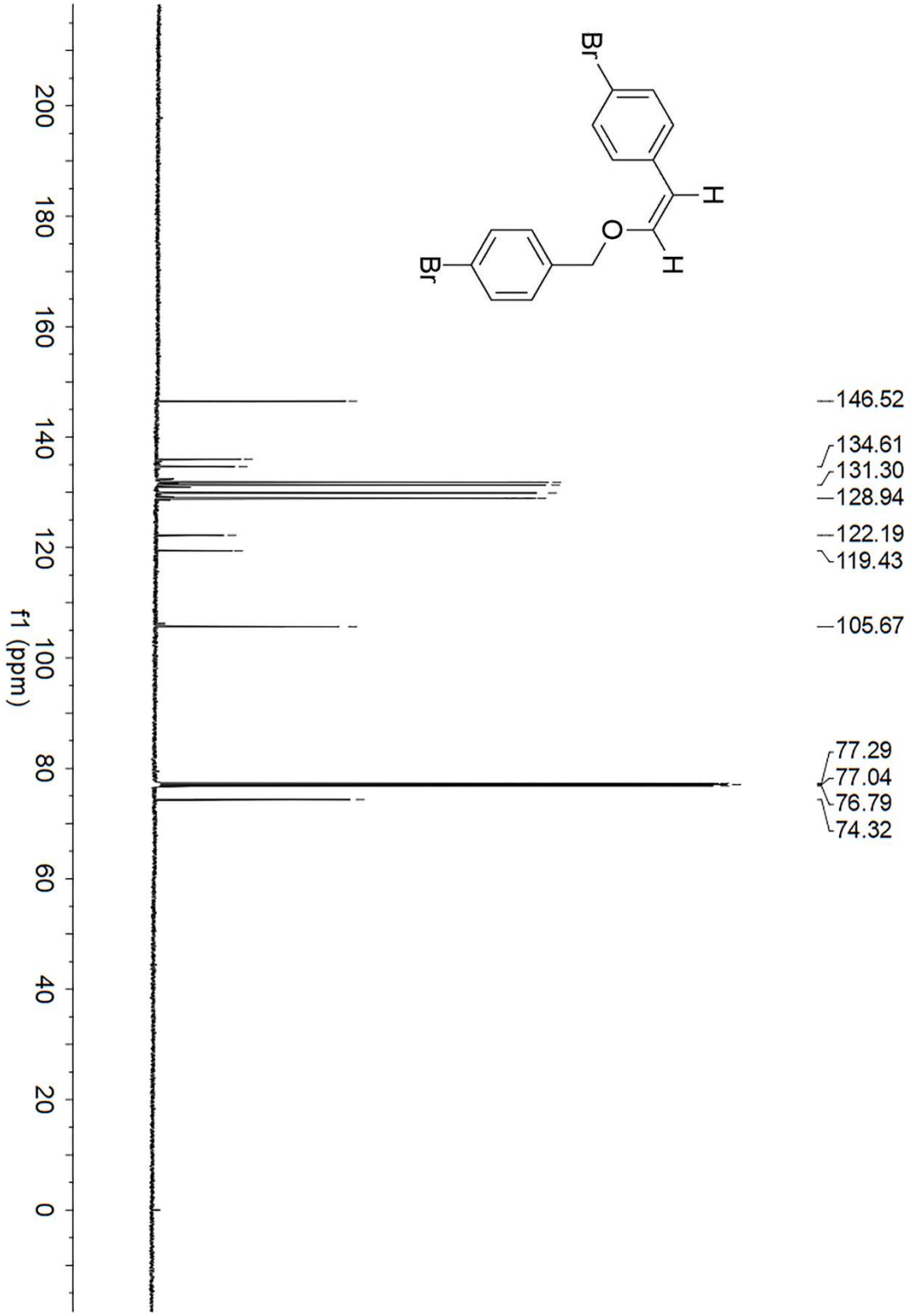
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ae**.



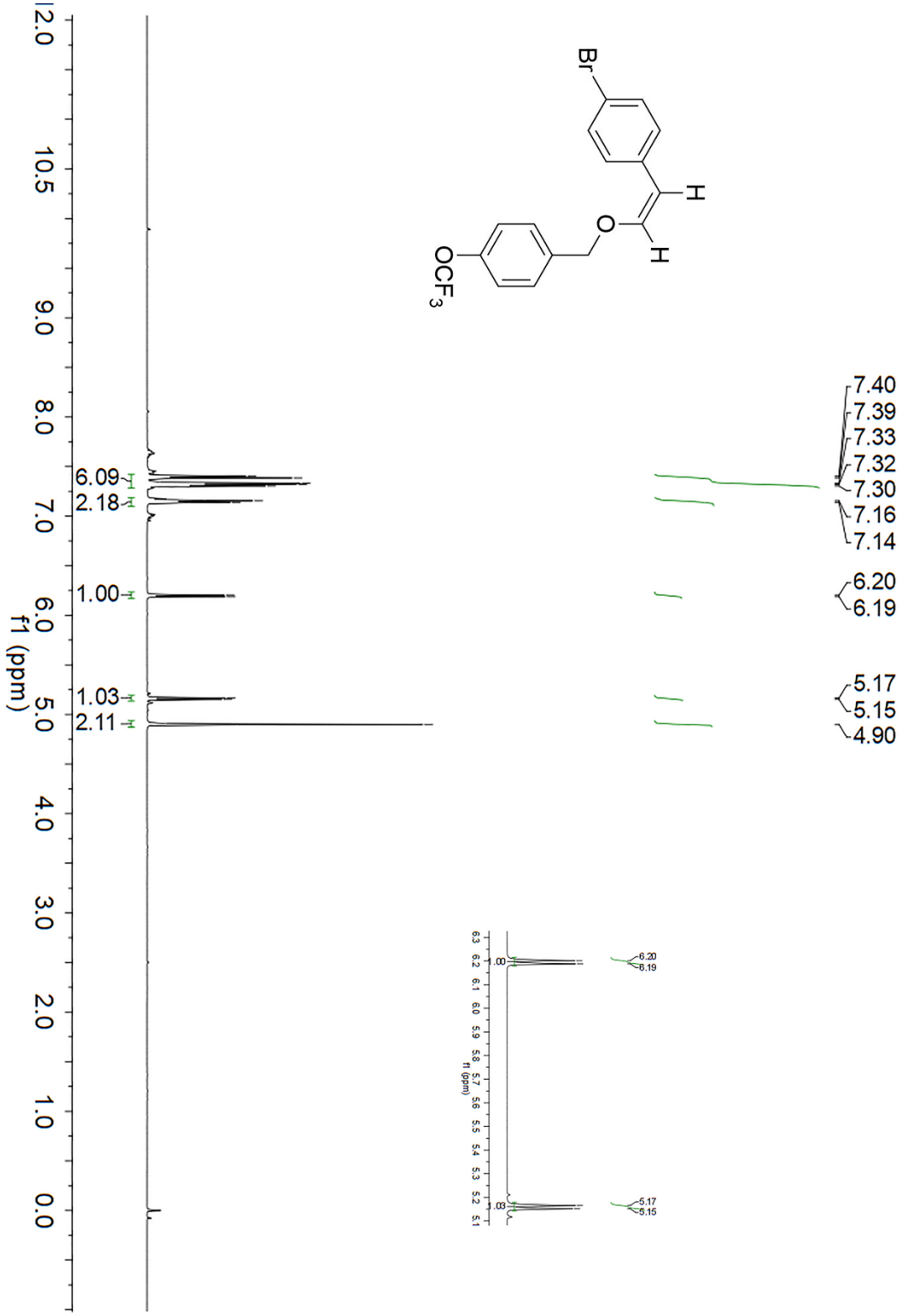
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3af**.



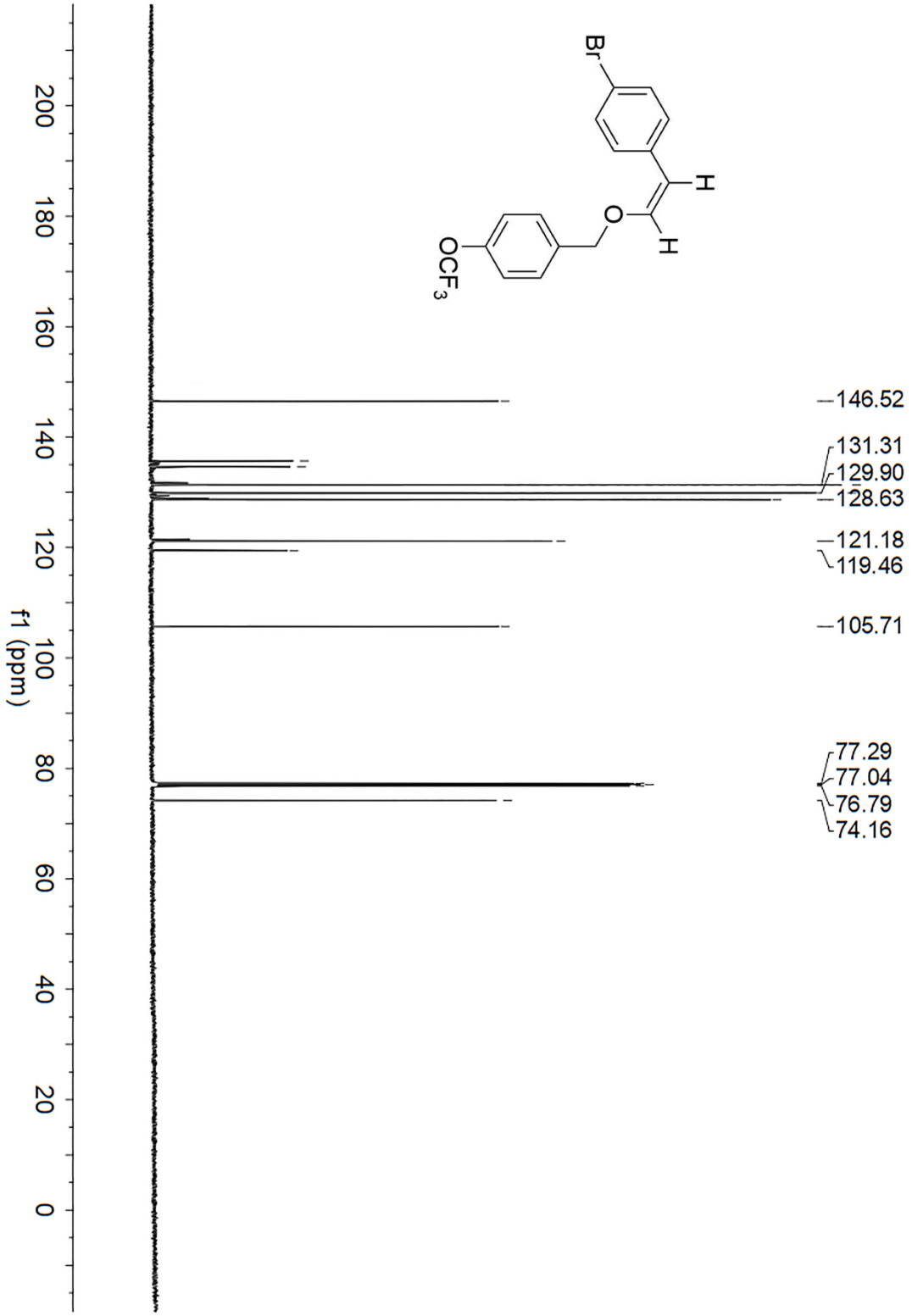
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3af**.



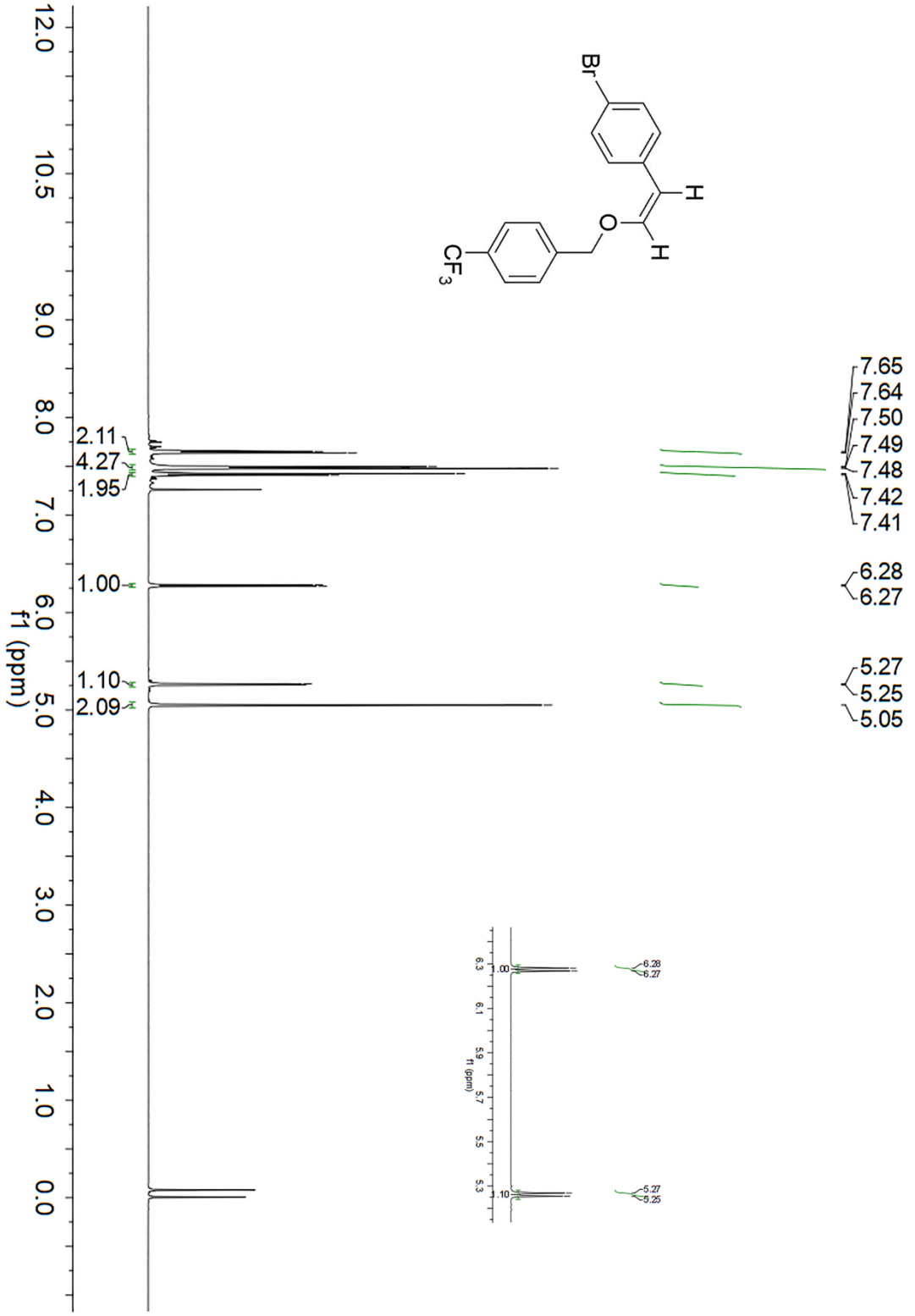
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ag**.



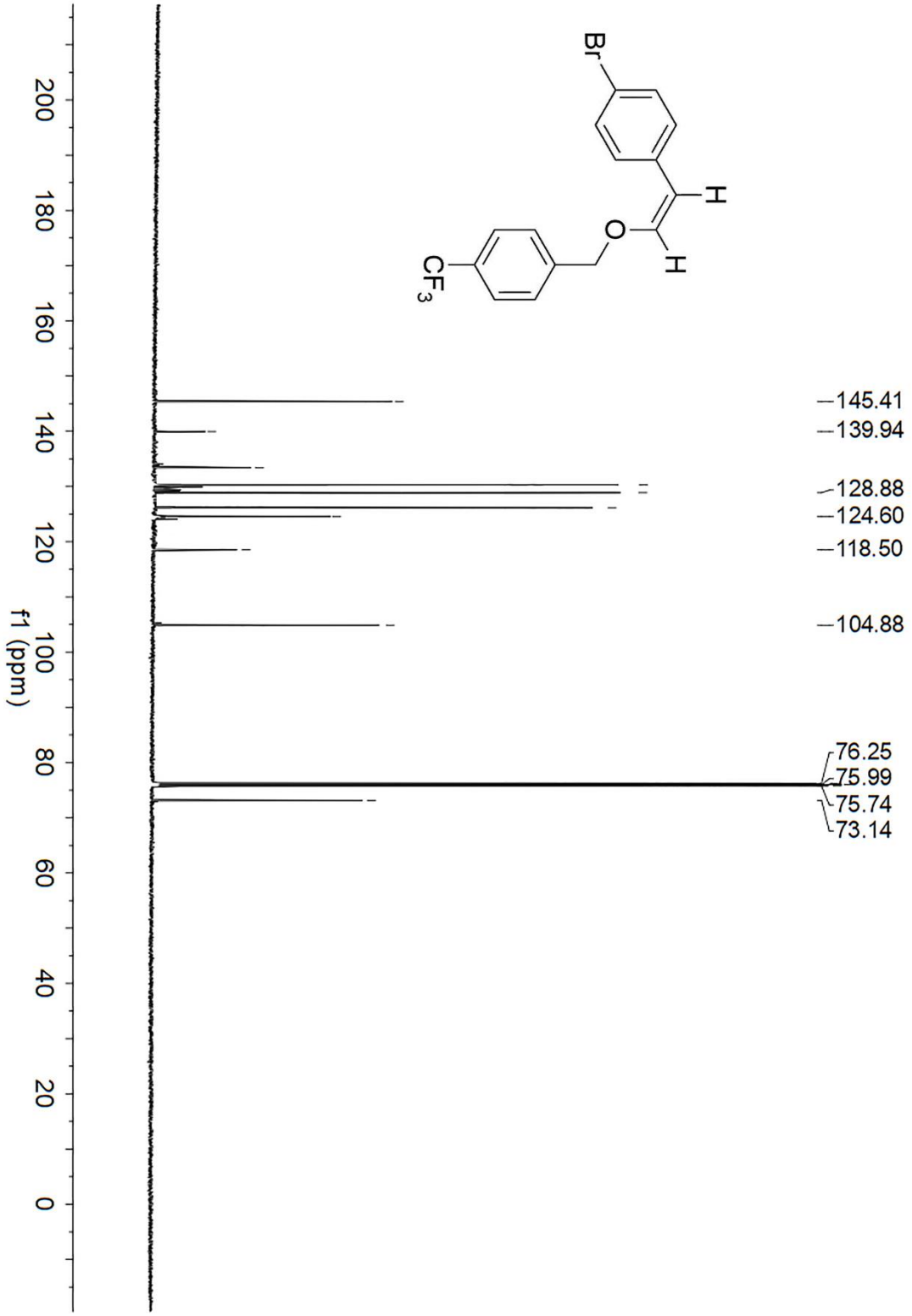
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ag**.



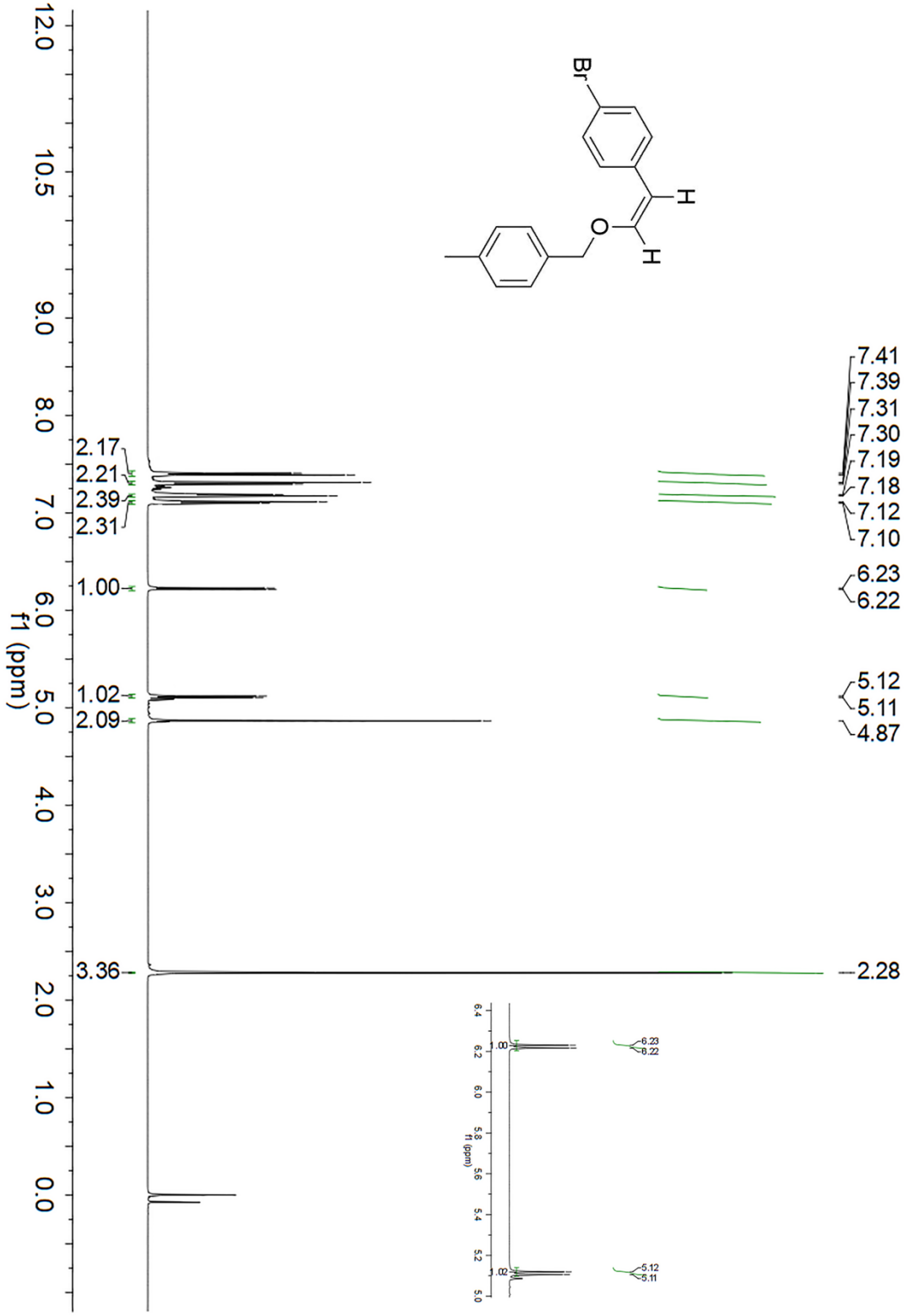
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ah**.



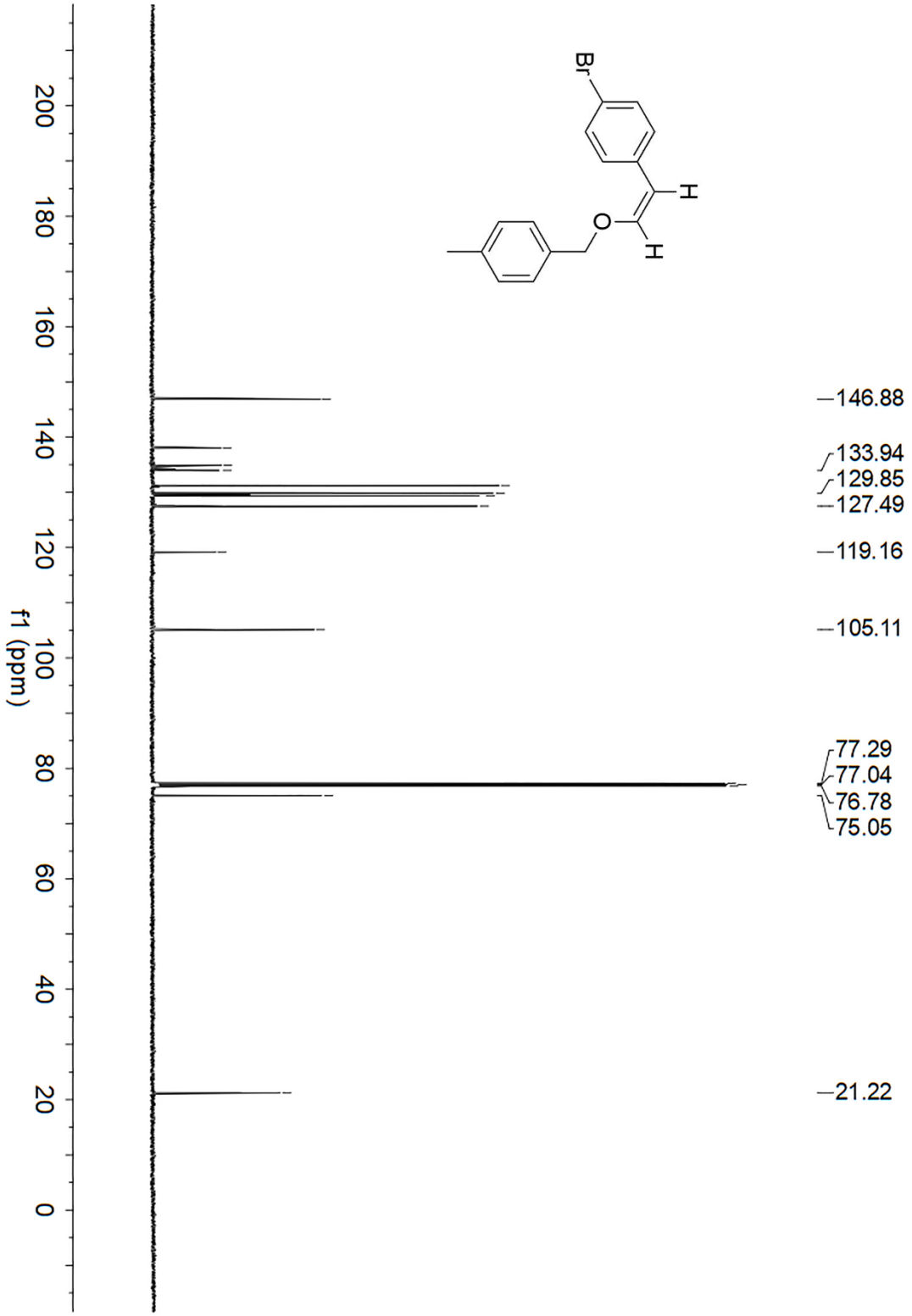
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ah**.



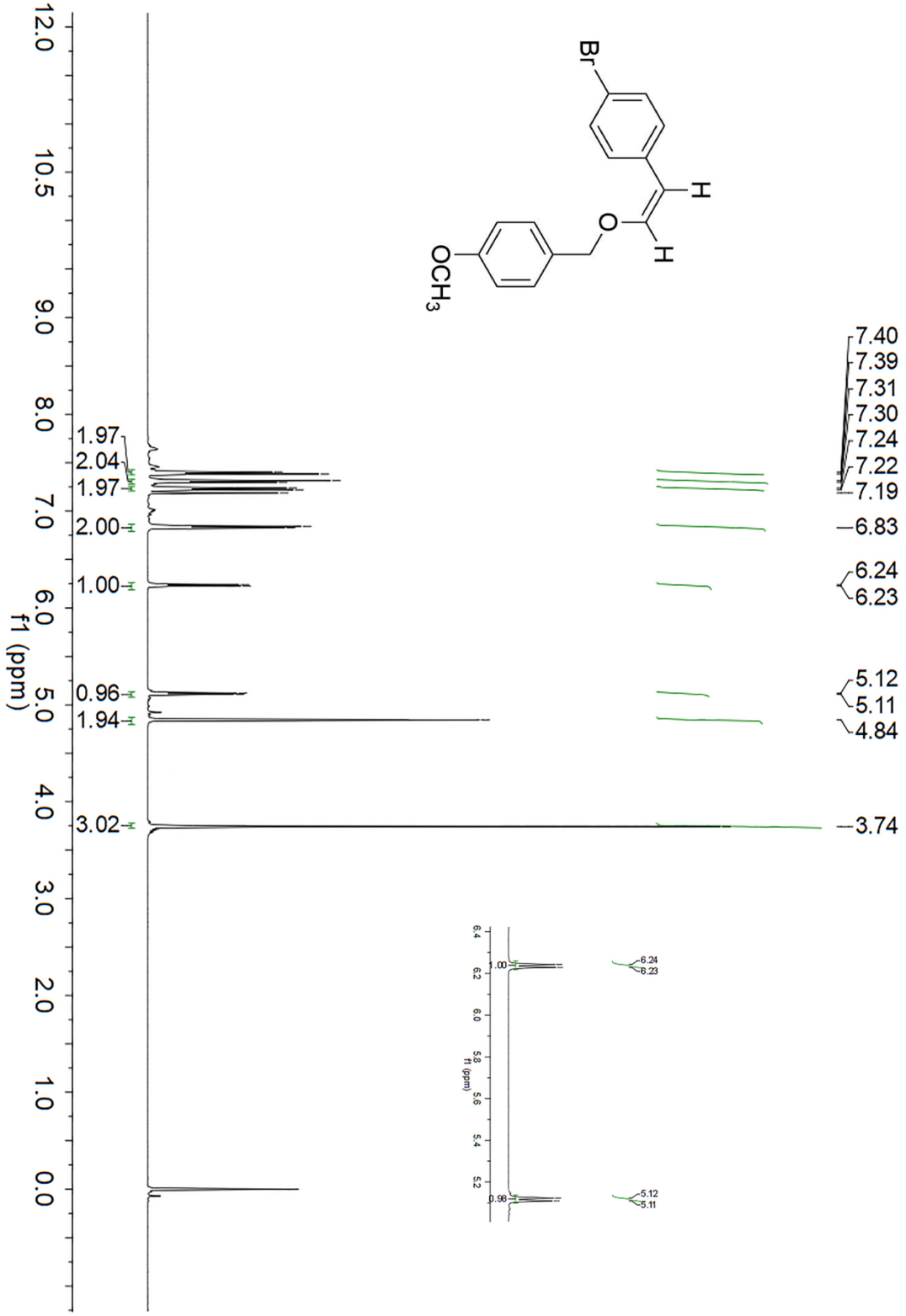
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ai**.



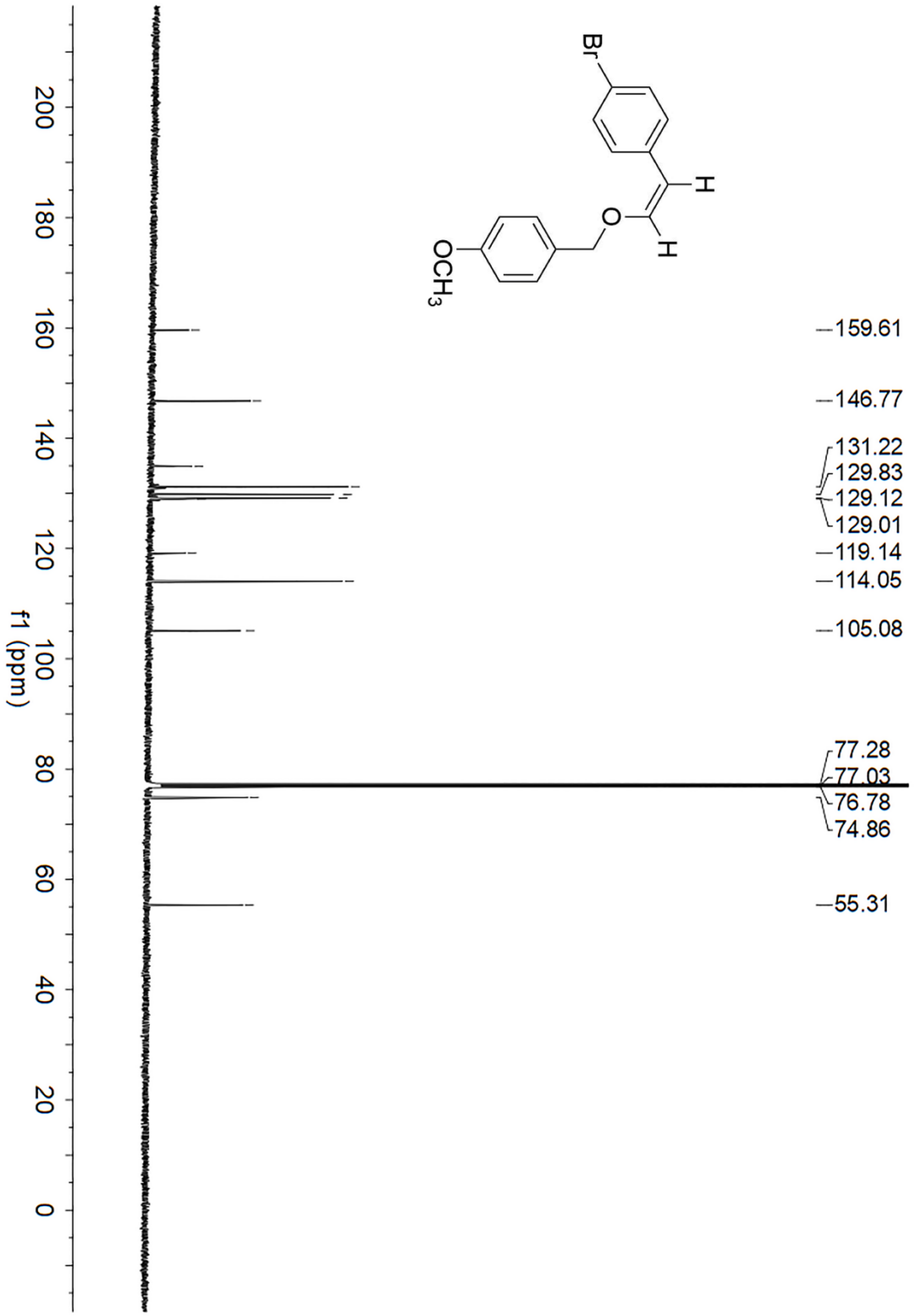
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ai**.



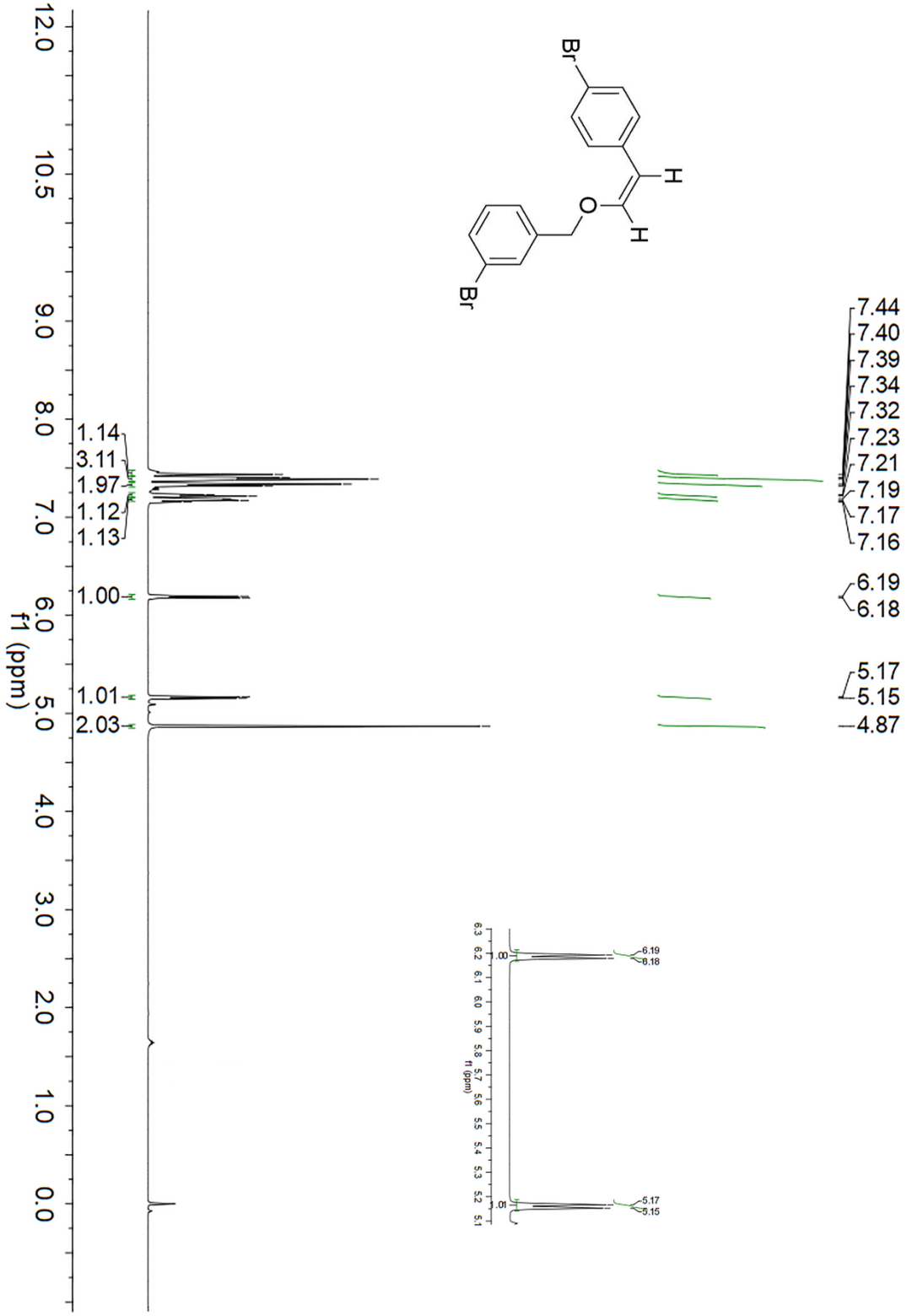
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aj**.



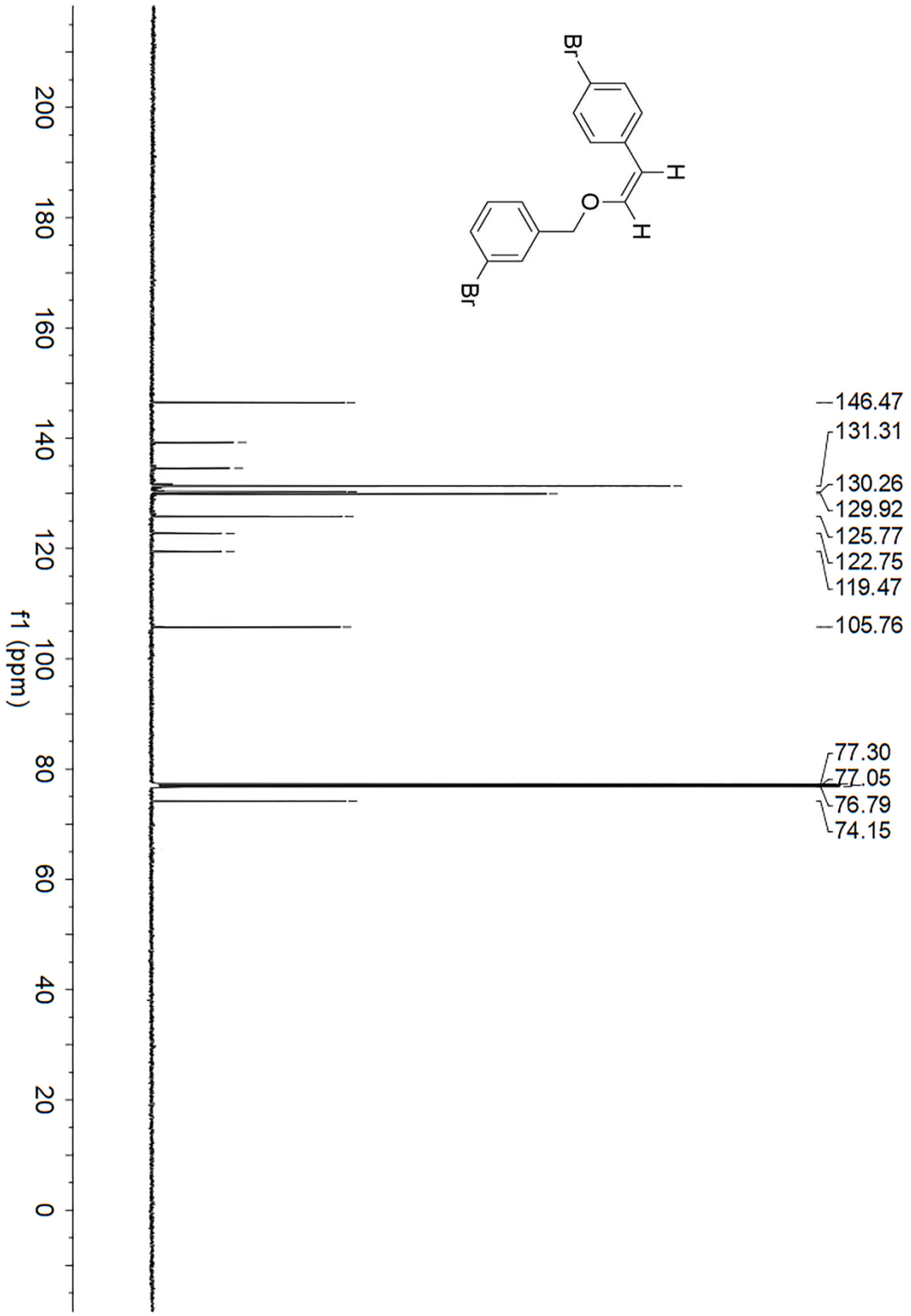
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3aj**.



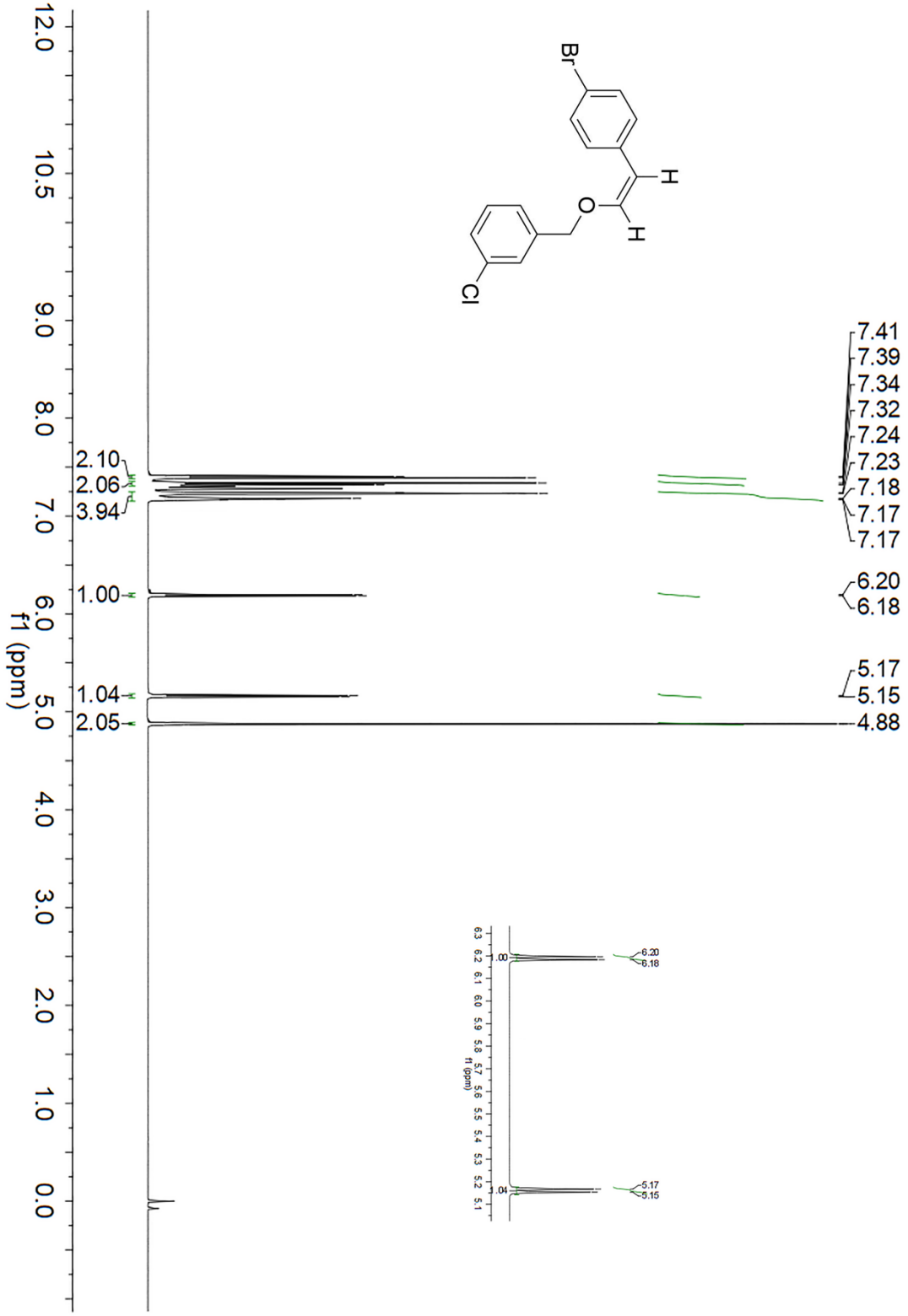
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ak**.



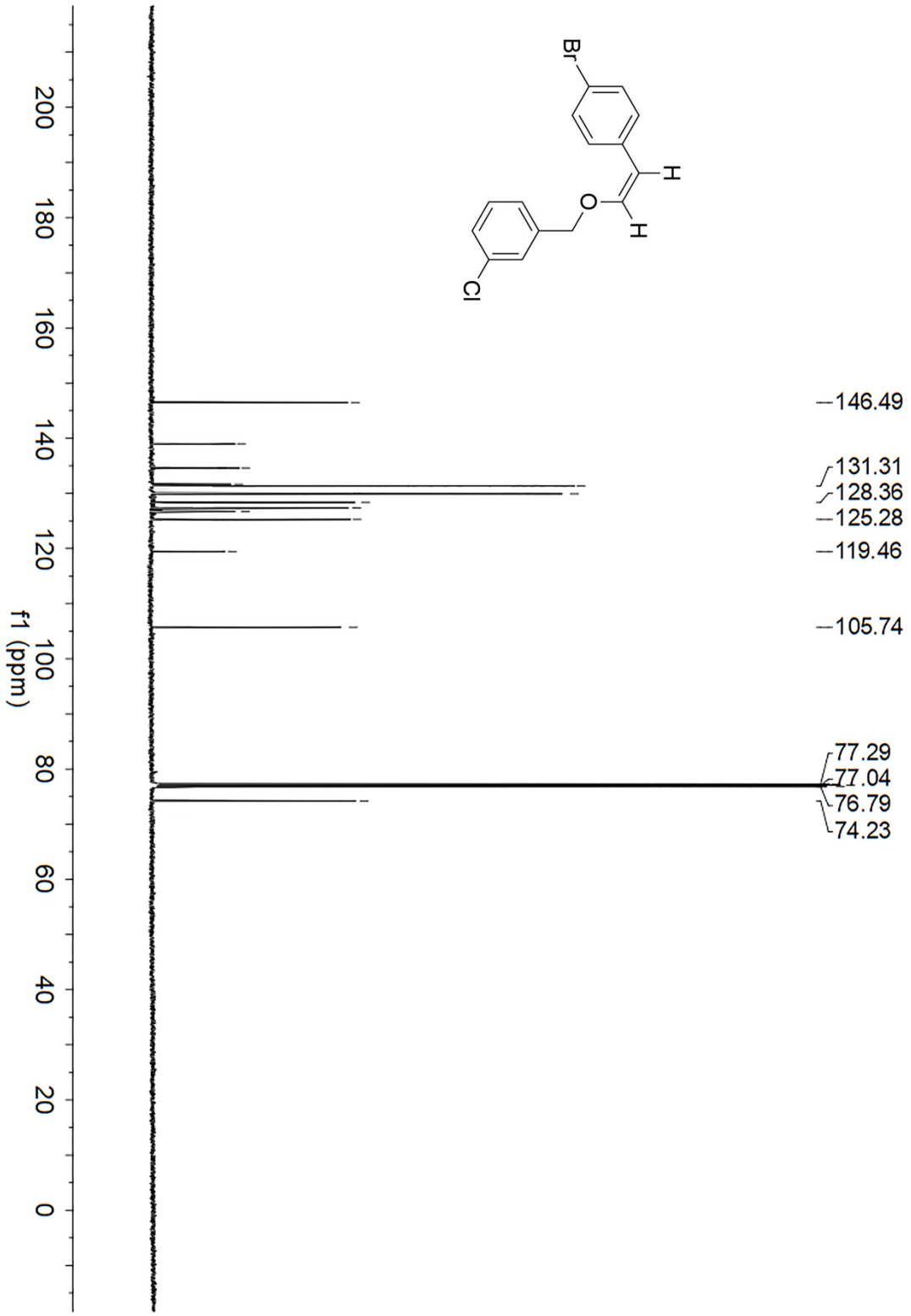
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ak**.



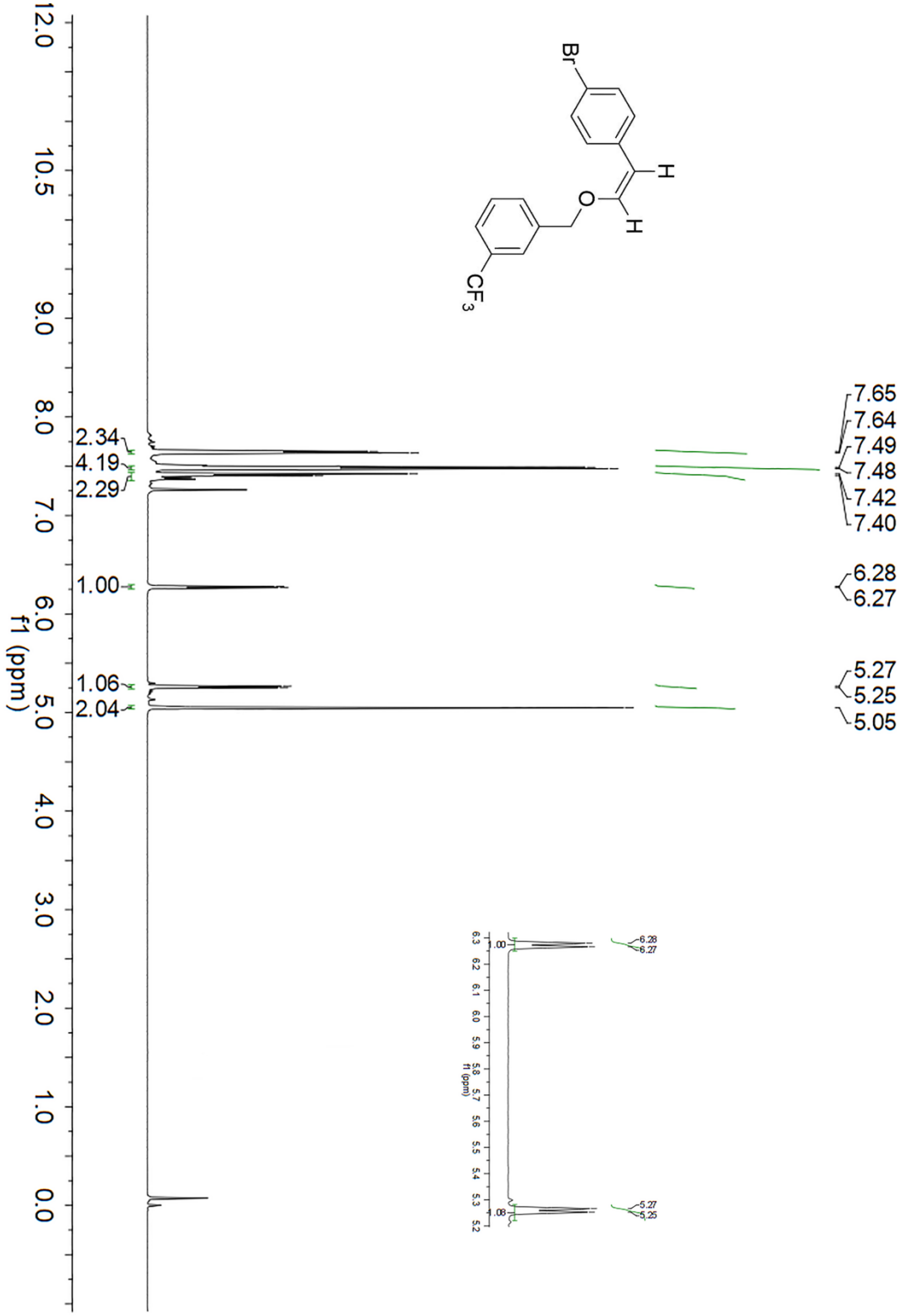
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3al**.



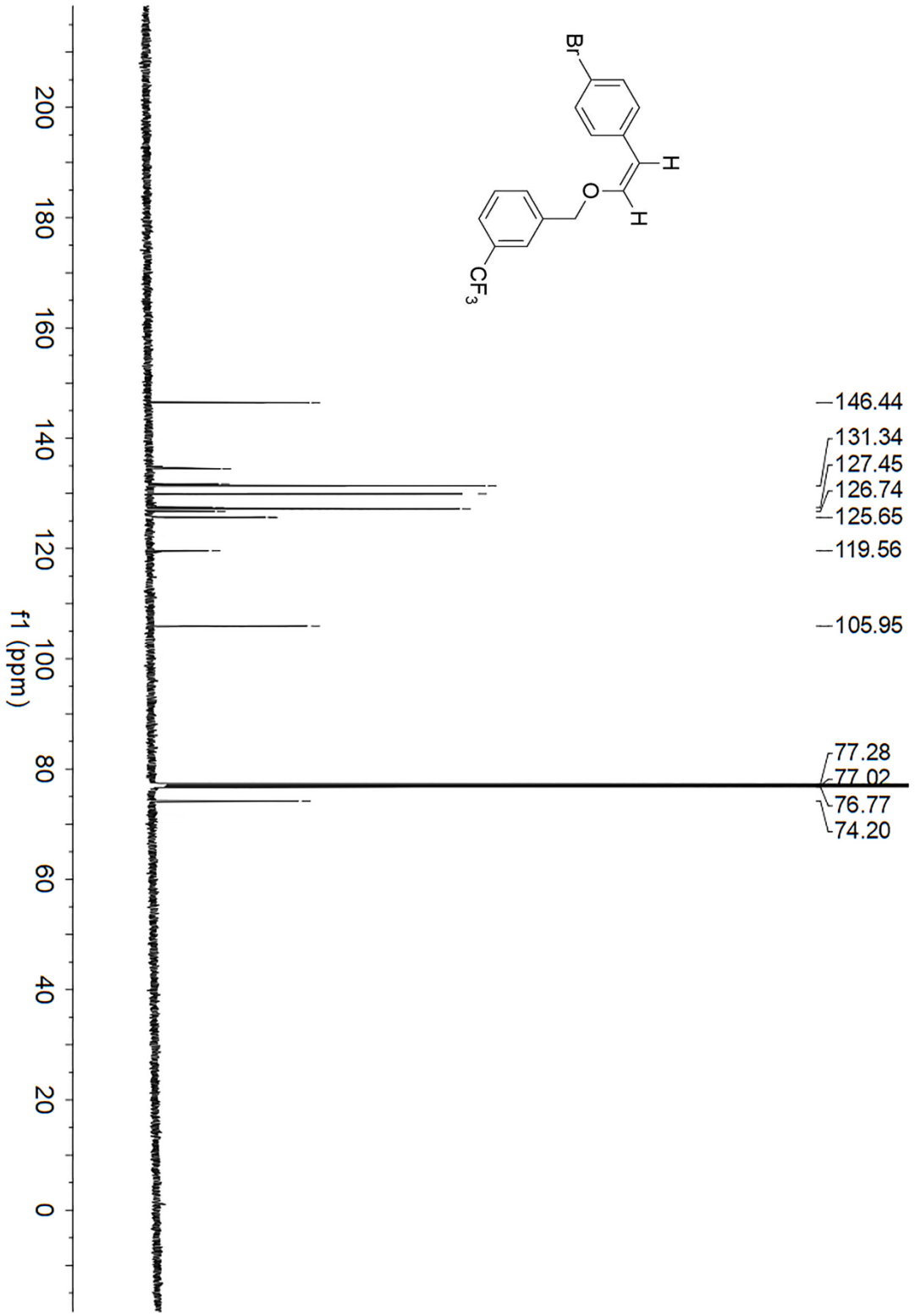
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3al**.



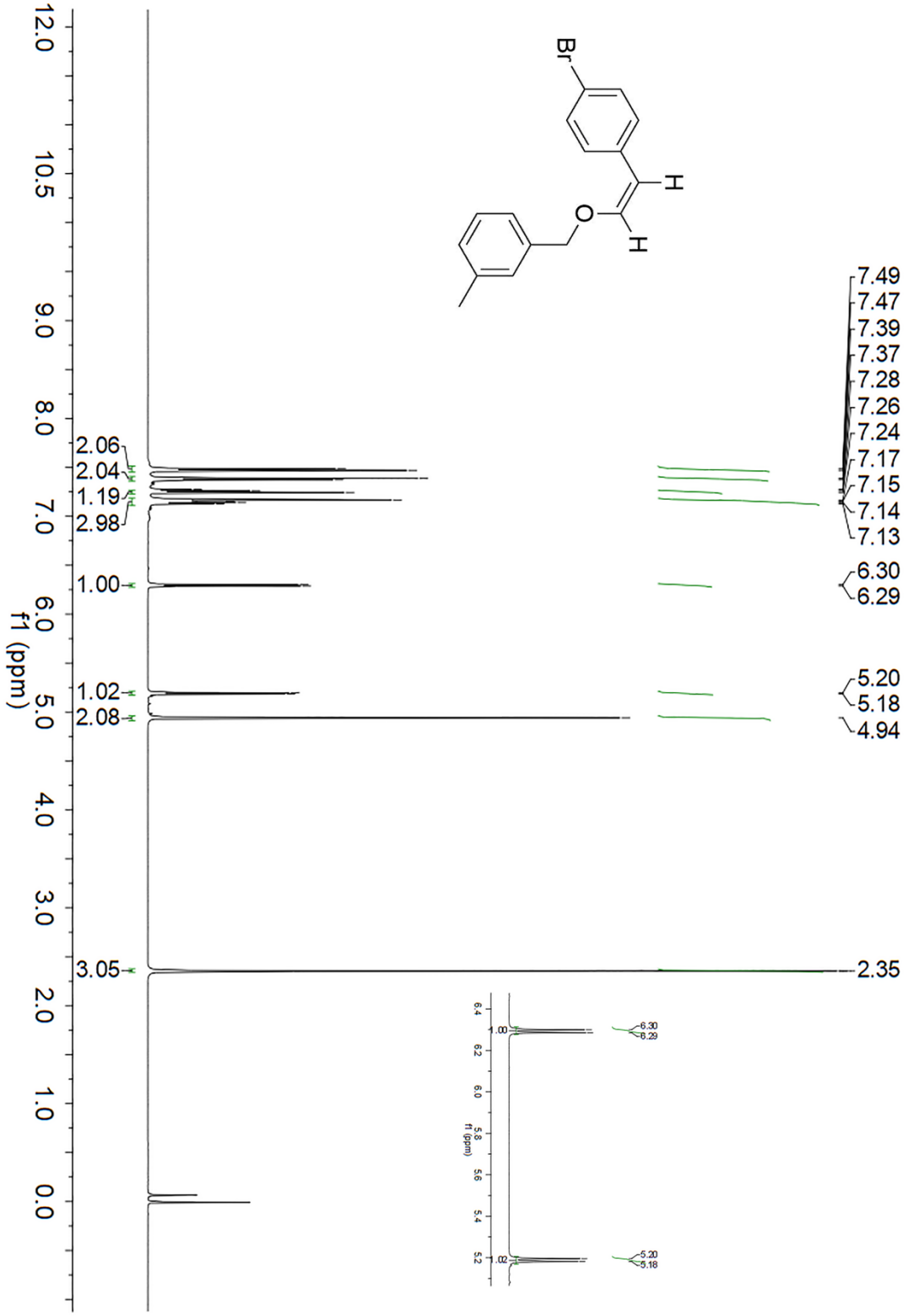
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3am**.



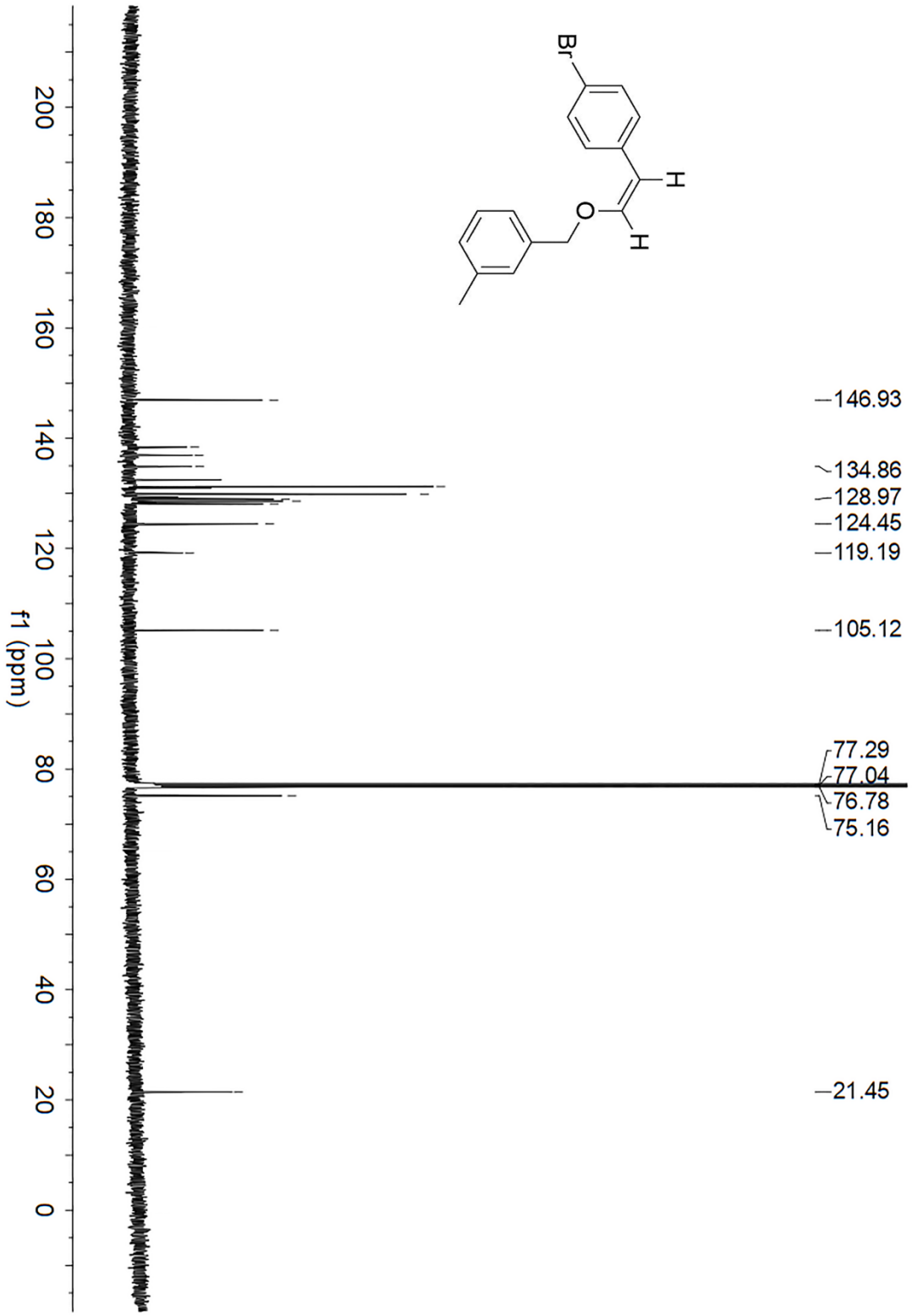
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3am**.



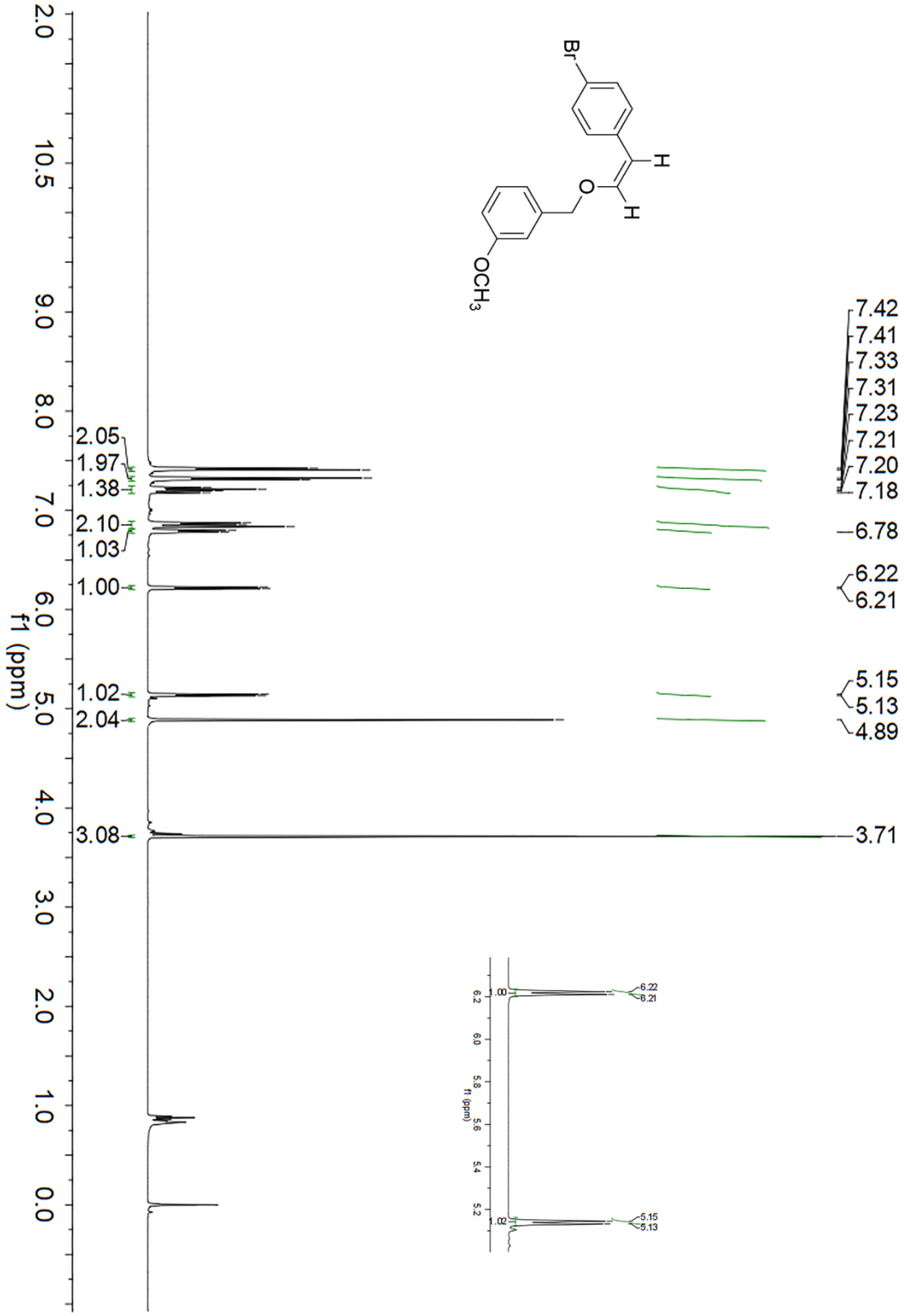
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3an**.



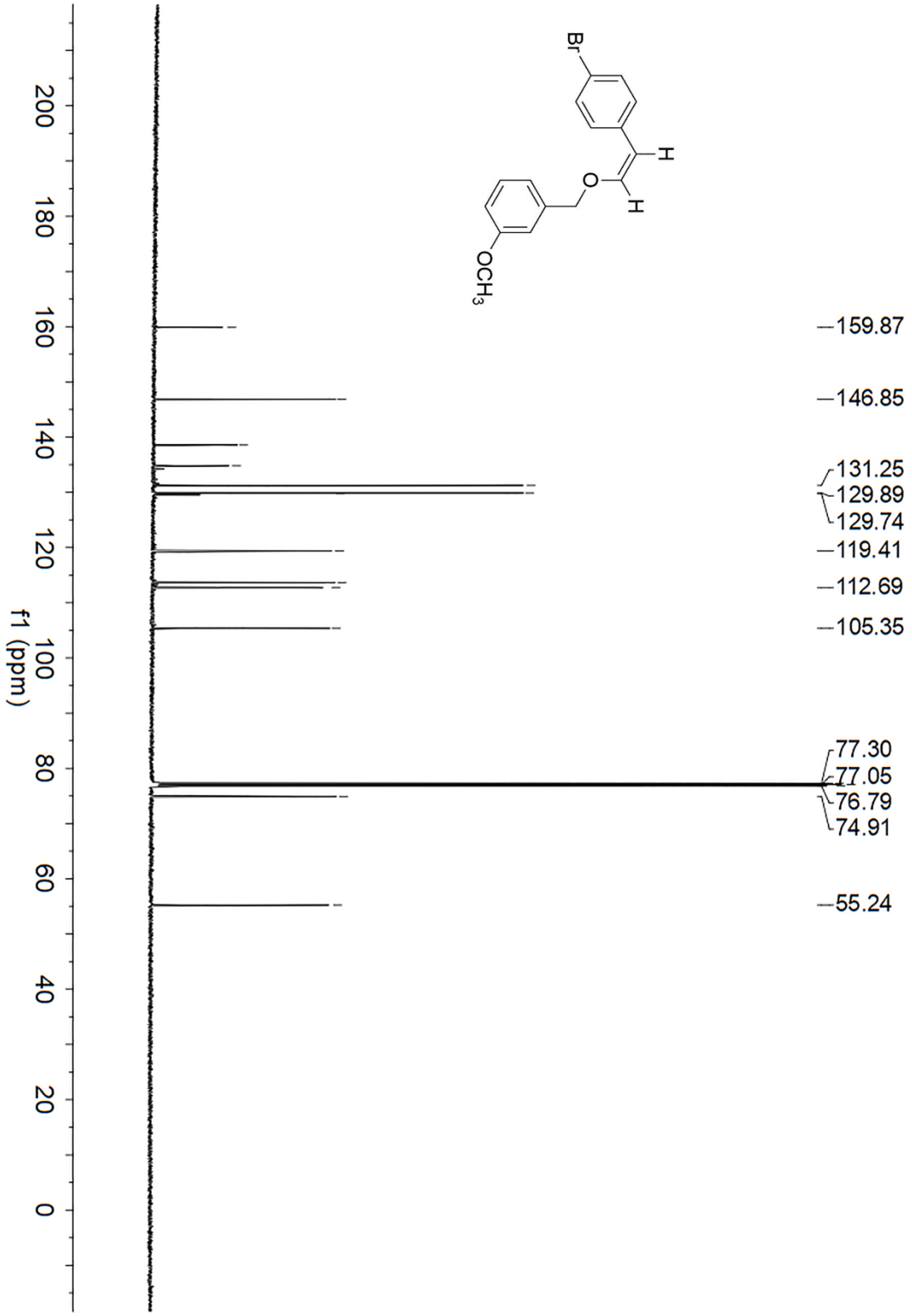
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3an**.



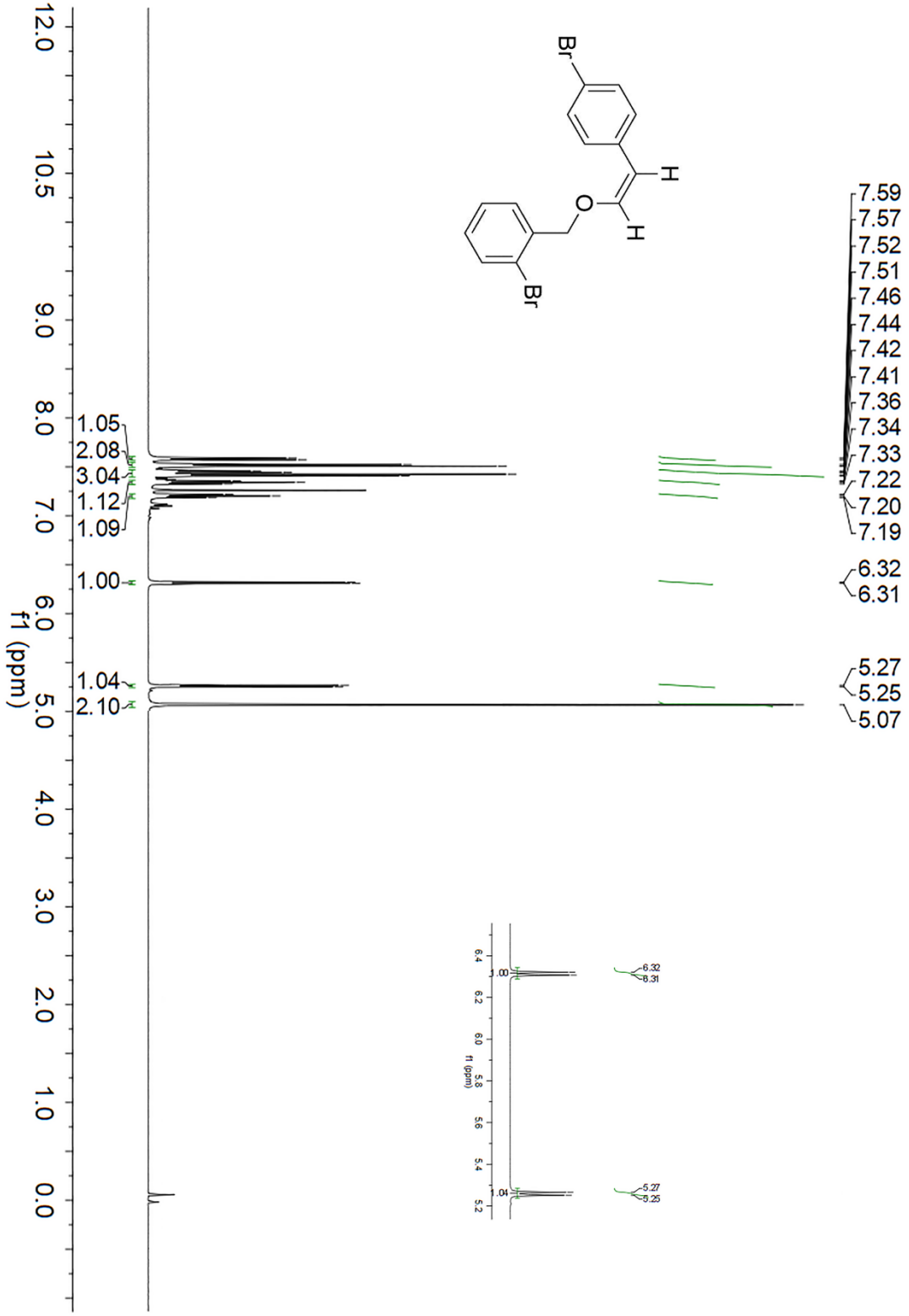
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ao**.



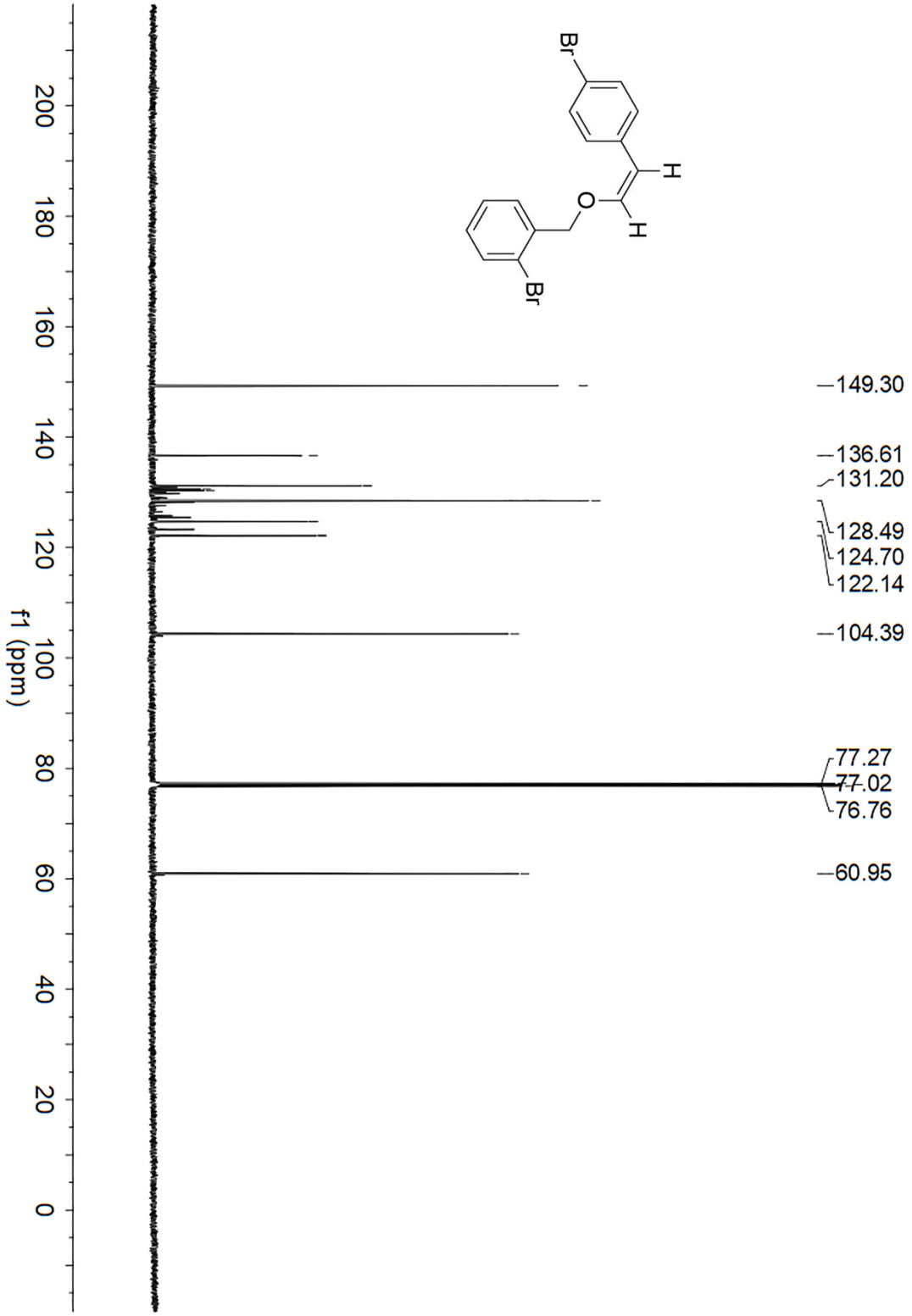
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ao**.



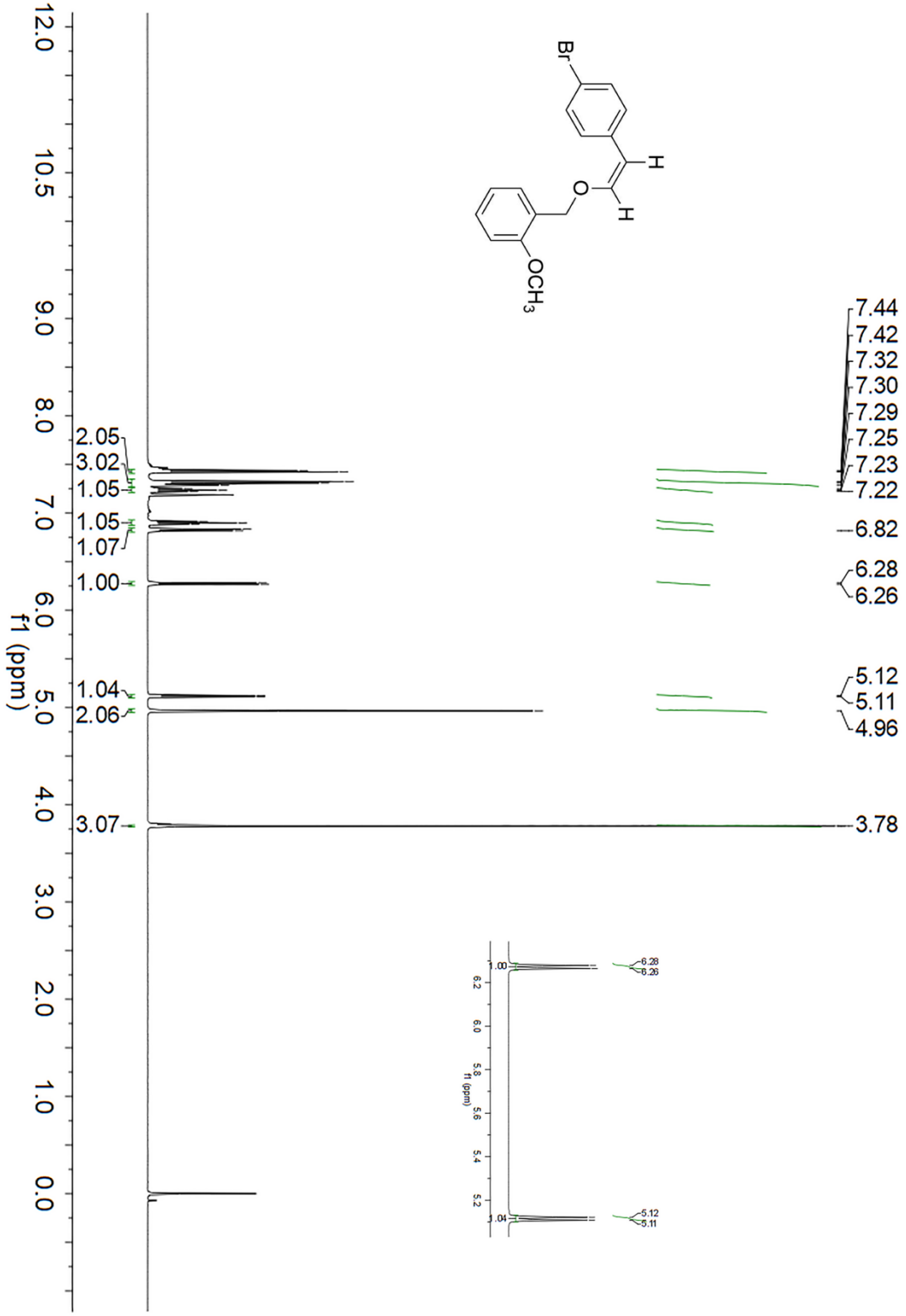
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ap**.



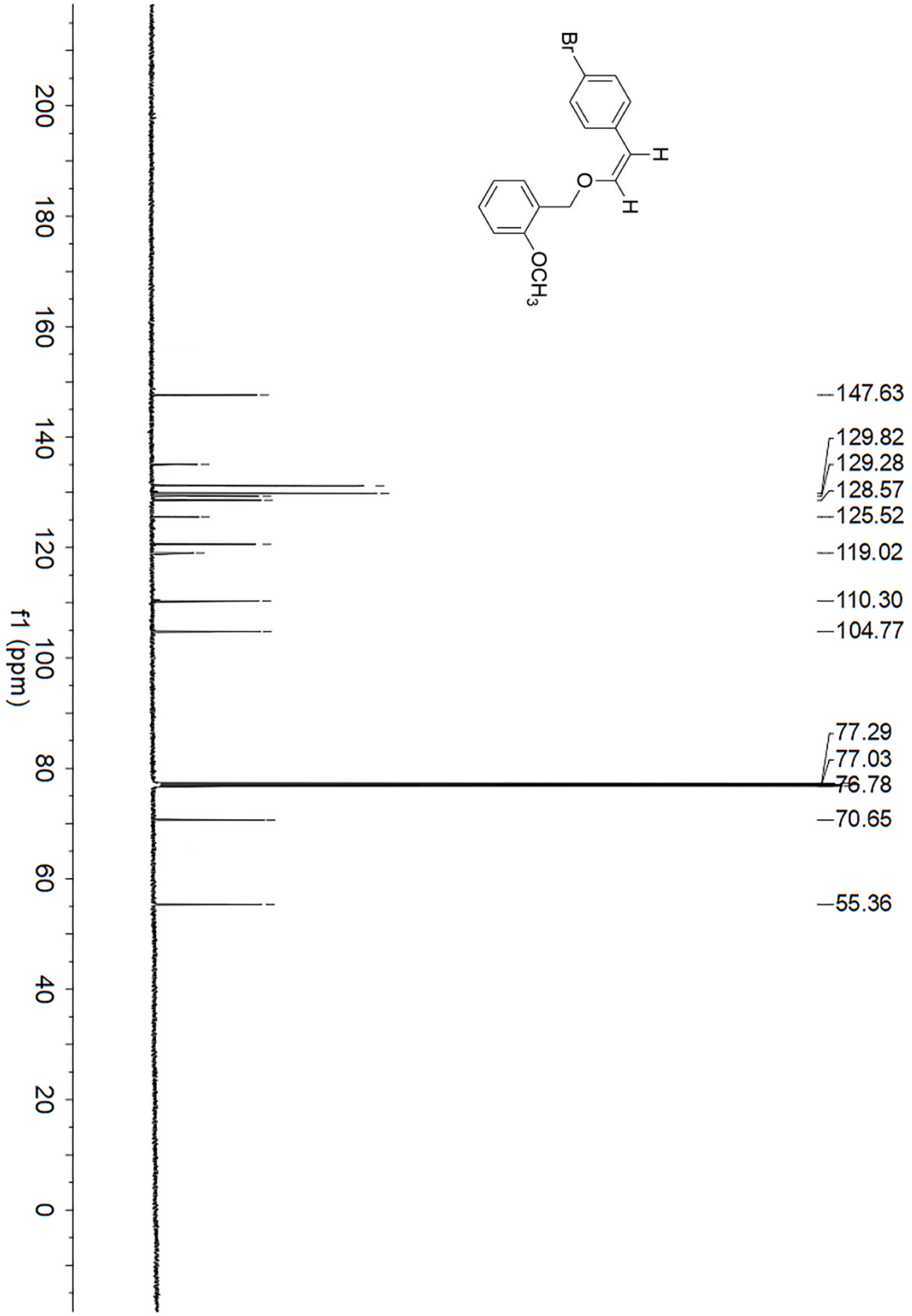
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ap**.



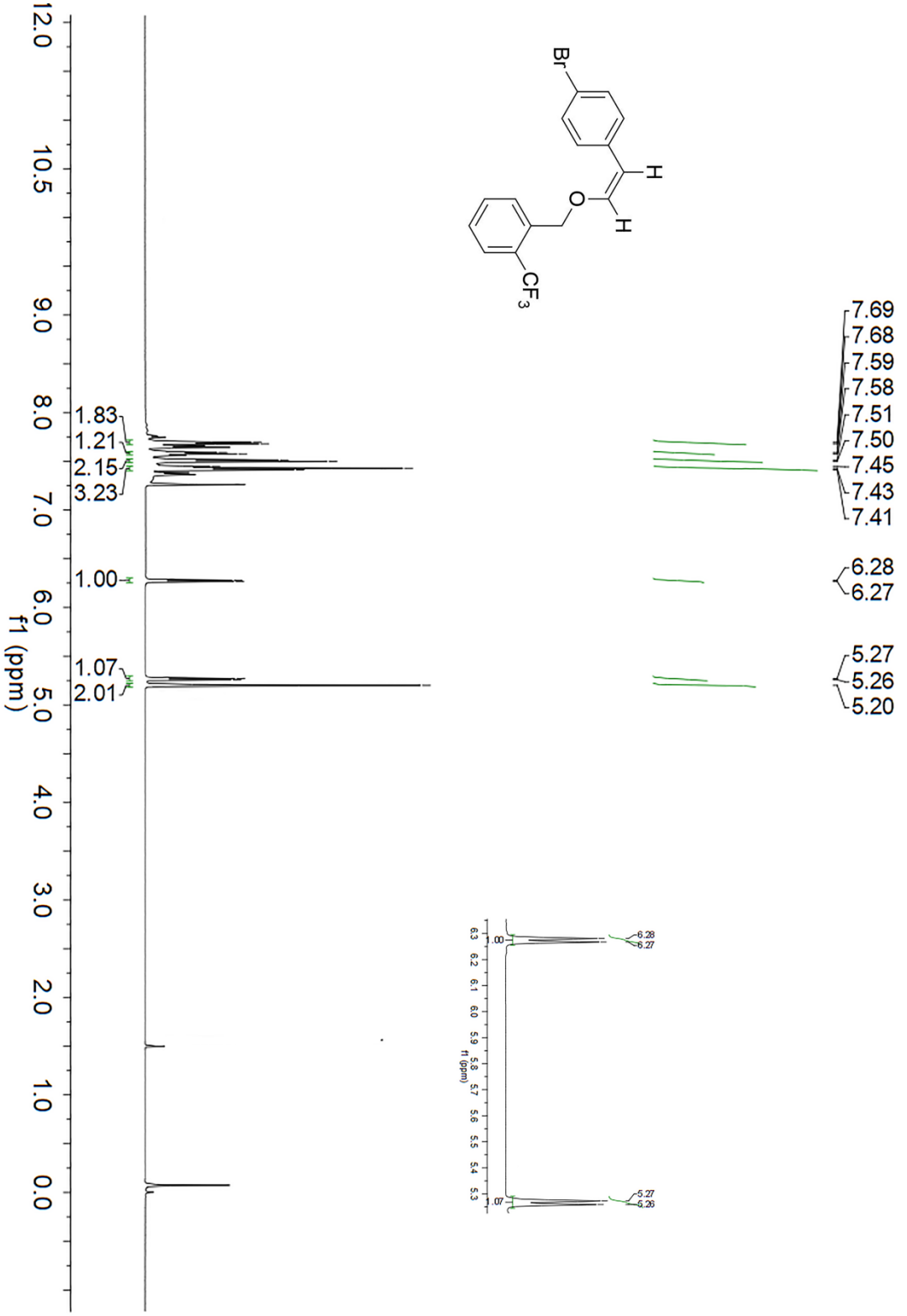
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aq**.



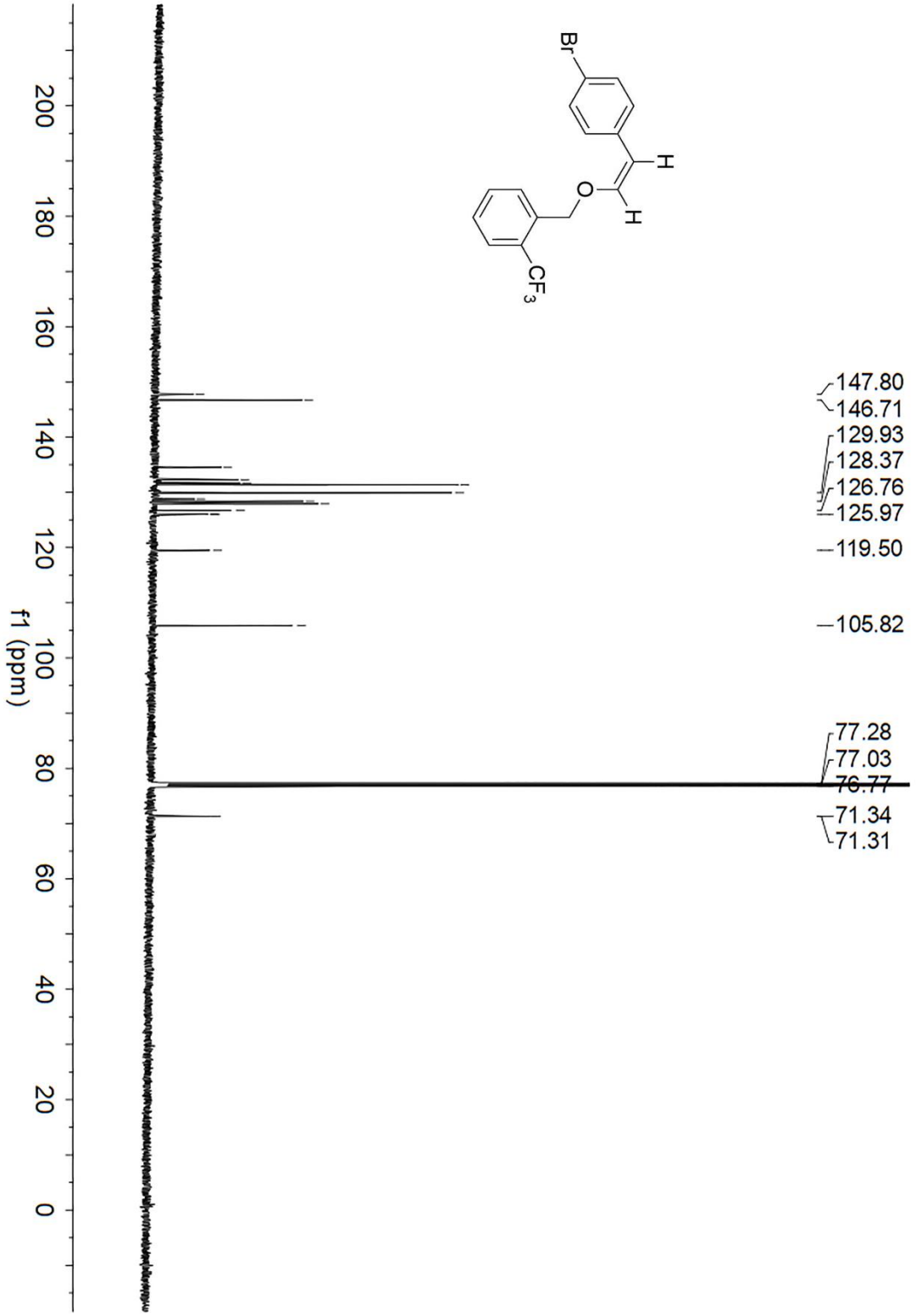
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3aq**.



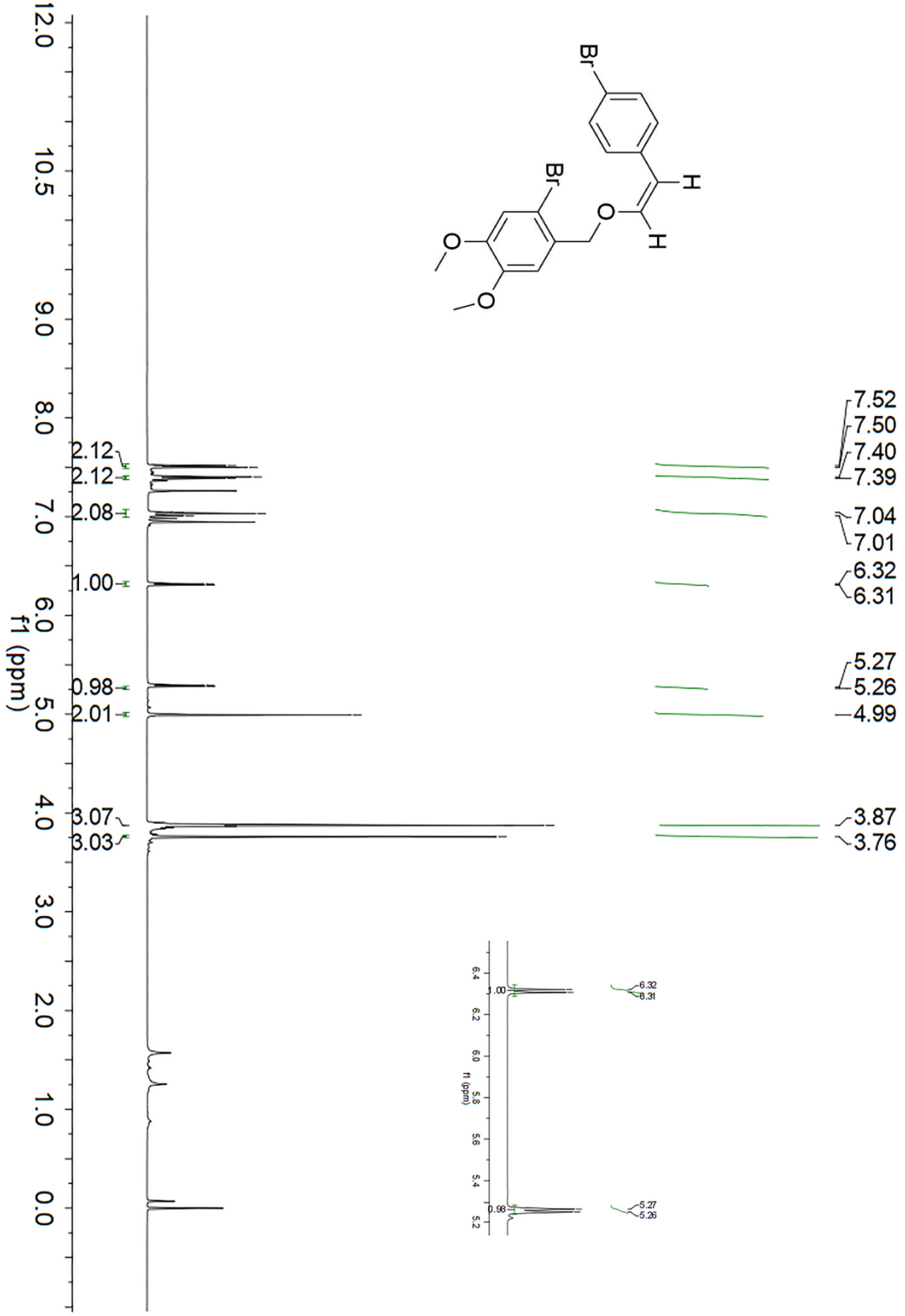
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ar**.



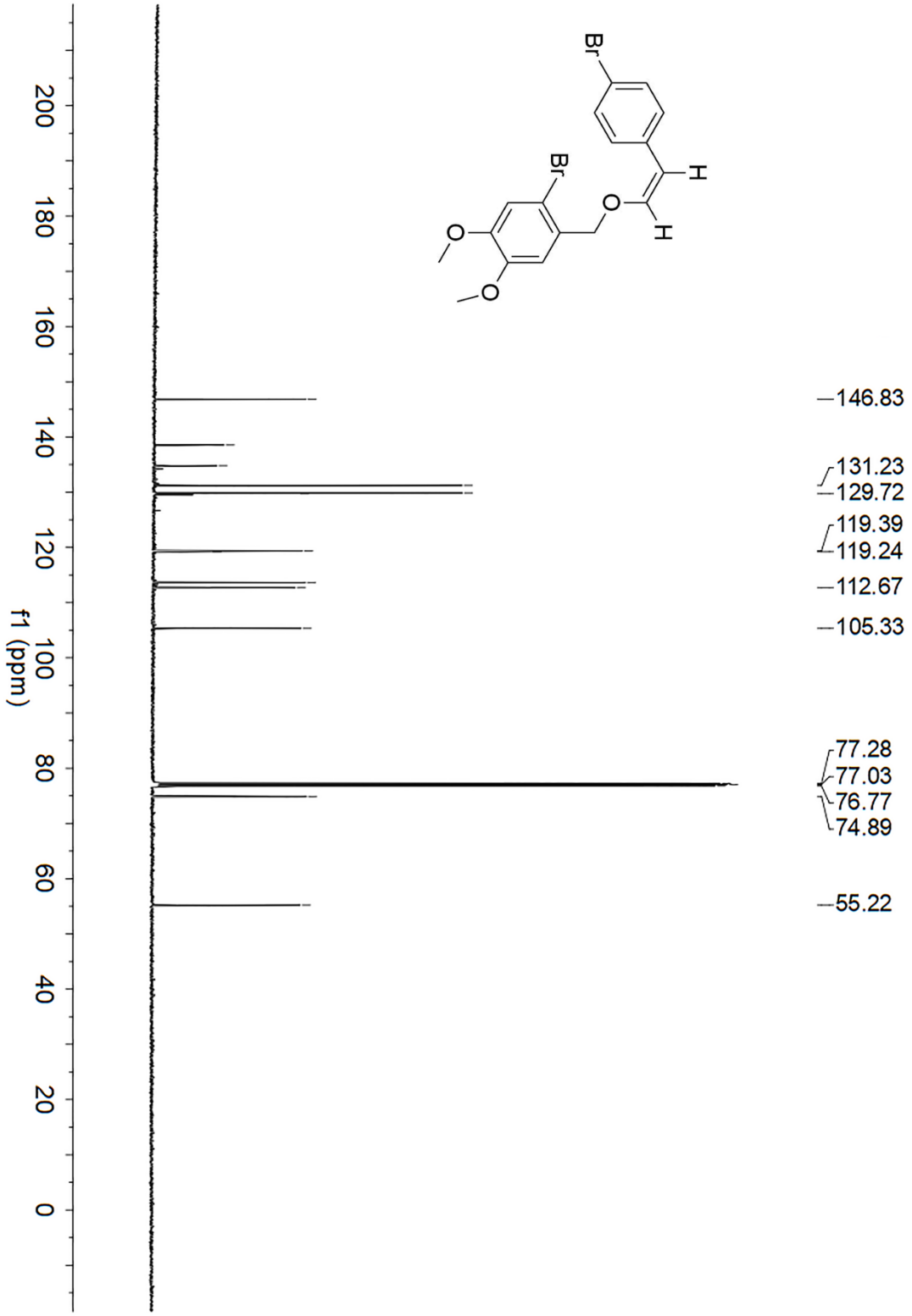
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3ar**.



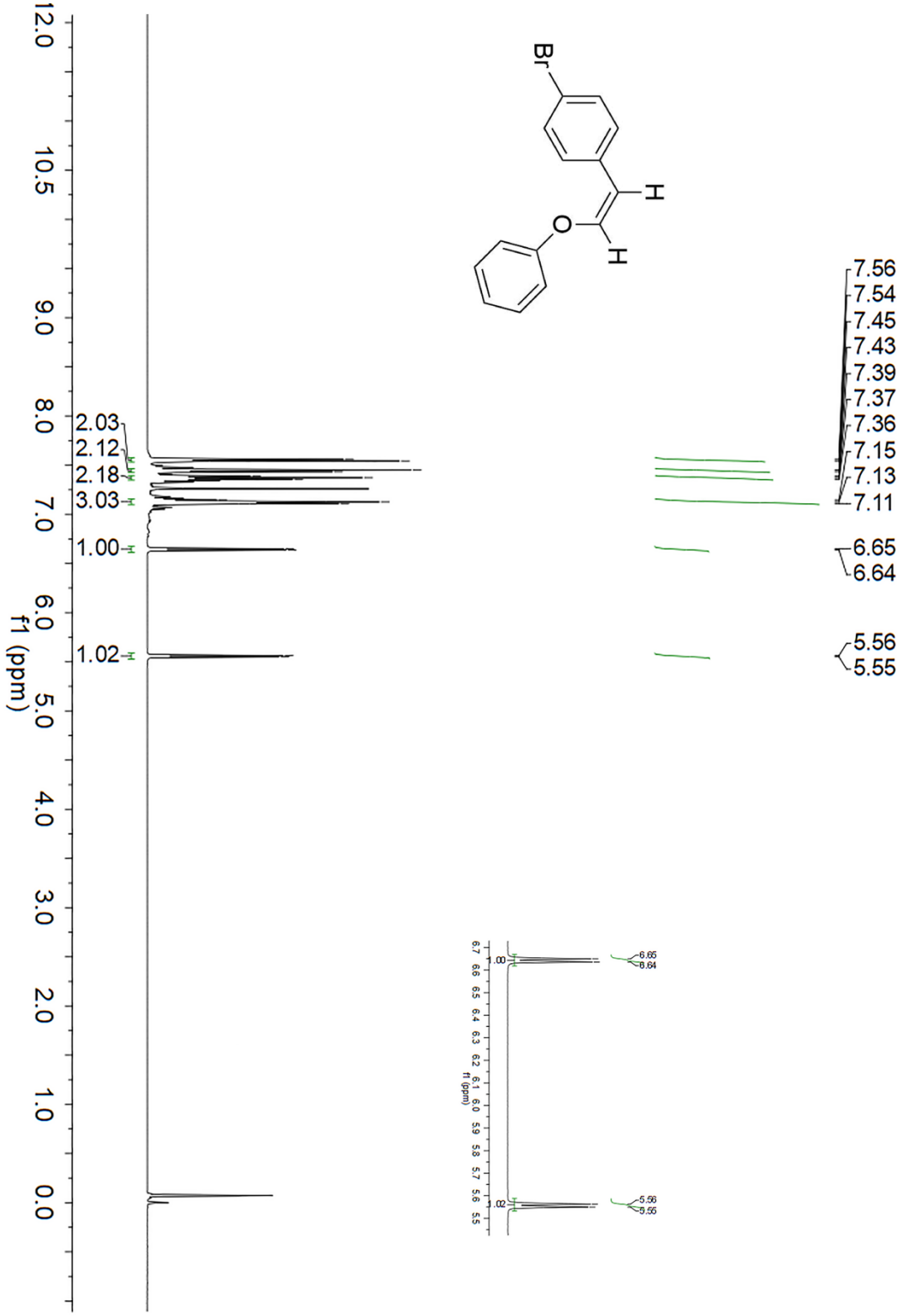
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3as**.



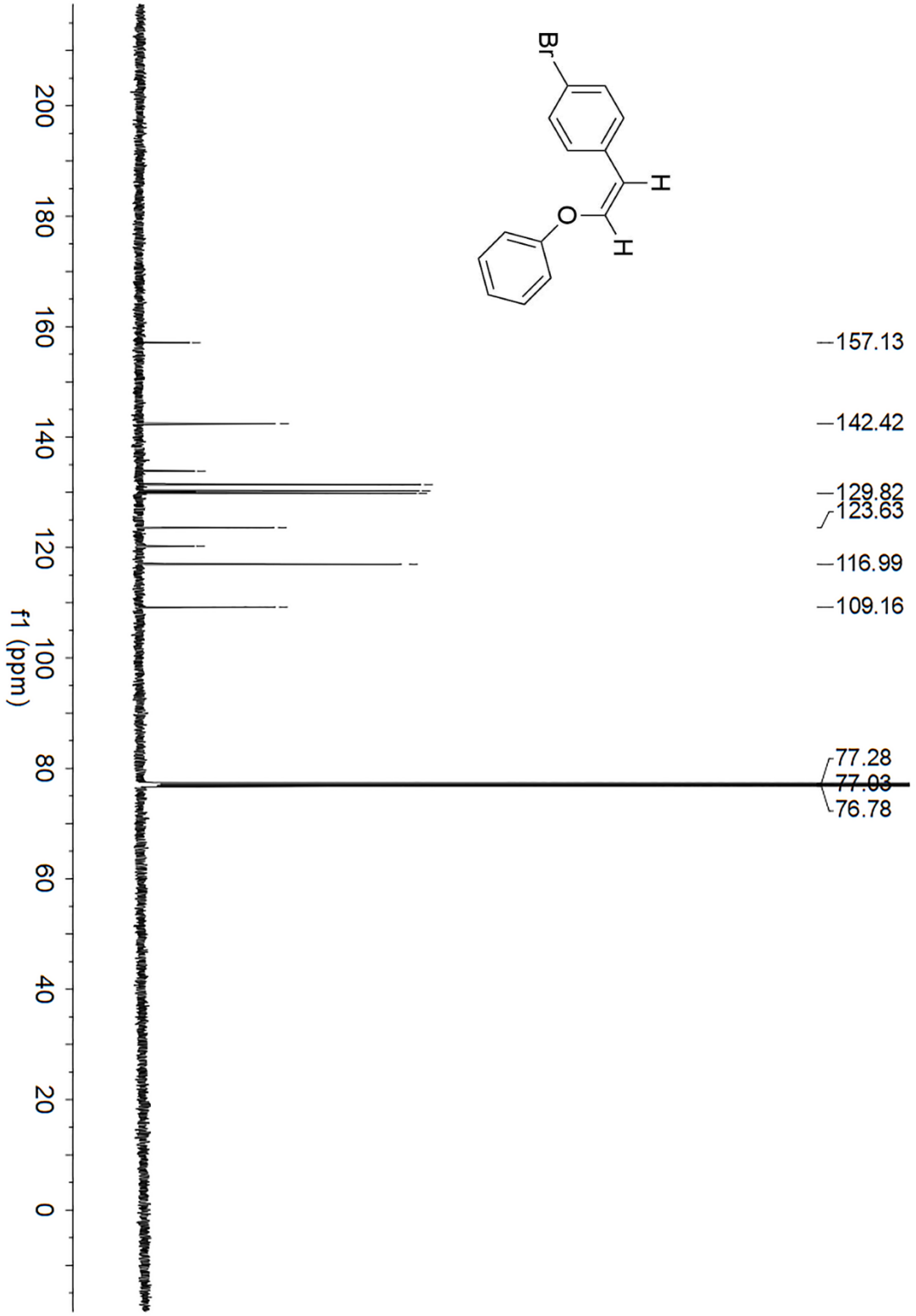
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3as**.



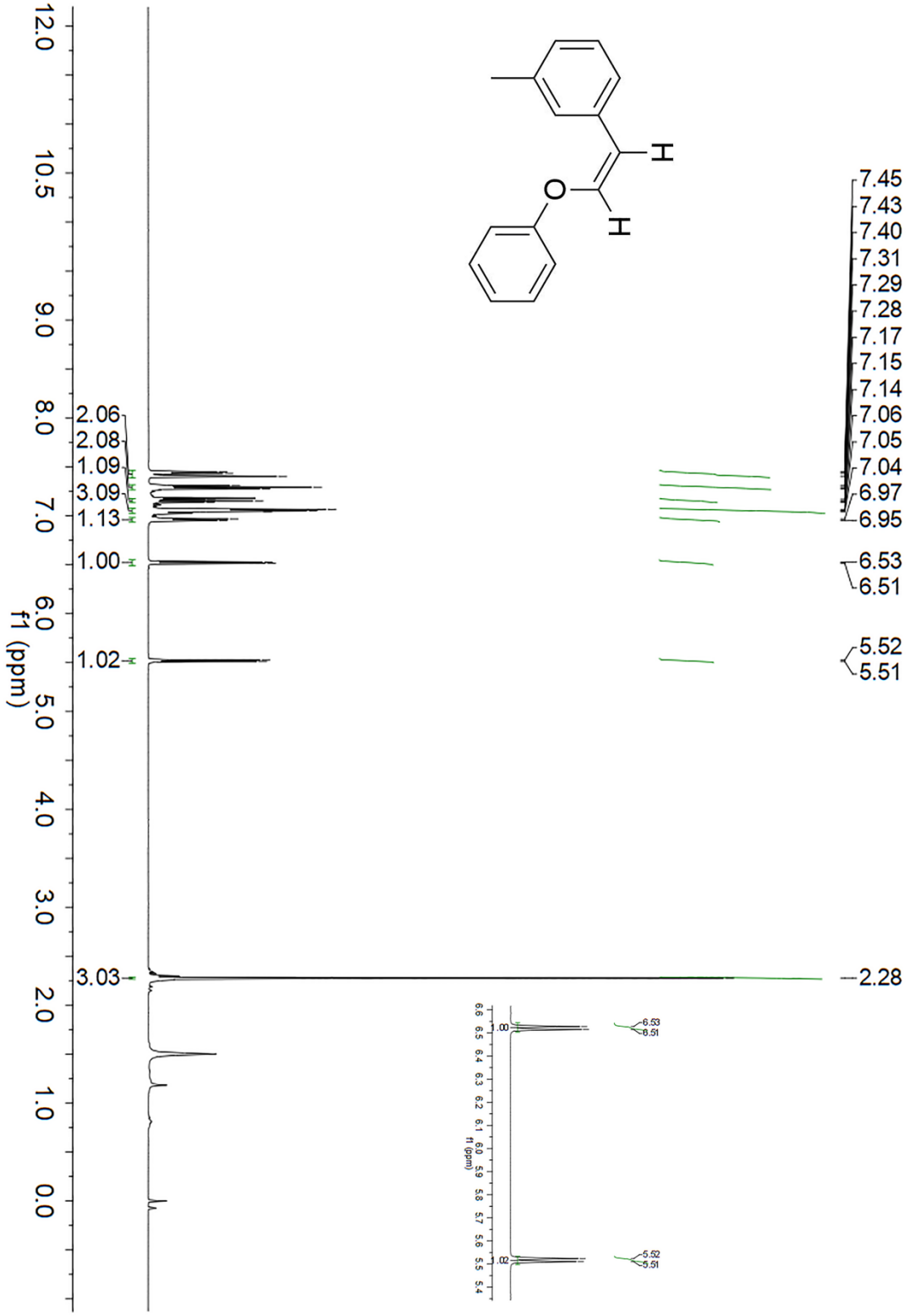
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3at**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **3at**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **3au**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **3au**.