Supplementary Information (SI) for RSC Advances.
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Supporting Information

for

Selective Oxidation of Benzyl Ethers to Esters Catalyzed by Cu_2O/C_3N_4 with TBHP & Oxygen as Co-oxidant

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Contents

1. General Information

Unless otherwise noted, materials were obtained from commercial suppliers, and all the solvents were used without any purification. The surface morphology and structure of the samples were characterized using scanning electron microscopy (SEM, Hitachi S-4800, with an acceleration voltage of 5 kV). An *X*-ray diffractometer (Bruker, D8) with Cu *K*α radiation is used to obtain the *X*-ray diffraction spectra (XRD). *X*-ray photo-electron spectroscopy (XPS: PHI Quantera II, Japan) was used to examine the surface properties of the catalysts. The catalytic activity was determined by gas chromatography (GC, Beijing Beifen-Ruili Analytic Instrument (Group) Co., Ltd. SP-3420A) with a SE-54 capillary column and a FID detector.

NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm; ^{13}C NMR: $CDCl_3$ 77.16 ppm,). And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). All of the known compounds described in the paper were characterized by comparing their ^{1}H & ^{13}C NMR to the previously reported data.

2. Catalyst preparation

Preparation of bulk g-C_3N_4:

7.20 g of melamine, 20 mL of hydrogen peroxide (30%), and 30 mL of distilled water were added in a 100 mL hydrothermal reactor. After stirring at room temperature for 10 minutes, place the reactor in a 140°C oven for 12 hours and then cool down to room temperature. The obtained white solid was washed several times with distilled water and ethanol, and dried in an oven at 80°C for 12 hours, and then grind it uniformly. The dry powder was then put in a muffle furnace and heat it at a high temperature of 550°C for two hours under a nitrogen flow (2 L/min) to obtain a yellow powdery solid g-C_3N_4 (4.32 g). The heating program is: the initial temperature is 25°C, the heating rate is 2°C/min, the temperature is increased to 550°C, the holding time is 120 min, and the cooling rate is 2°C/min, finally down to 25°C. Grind the calcined block g-C_3N_4 material for later use.

Preparation of Cu_2O:

Under a nitrogen atmosphere, 100 mL of distilled water and 26.3 mg of polyethylene glycol 400 (approximately 22 μL) were introduced into a 500 mL three-necked flask. The mixture was stirred until the polyethylene glycol fully dissolved. Then, 500.0 mg of hydrated copper acetate was added into the flask and stir at 30°C for 10 minutes to ensure complete dissolution. While stirring vigorously, 8.5 mL of 0.6 M sodium hydroxide aqueous solution was incorporated and allowed to react for an additional 20 minutes. Following this, 0.75 mL of 2 M hydrazine hydrate aqueous solution was gradually introduced. As the hydrazine hydrate was added, the blue-green reaction mixture transitioned to a red-brown hue. After stirring for 5 hours, stop stirring and let the mixture stand for 10 minutes. A red-brown solid precipitates on the bottom of the flask. Proceed with centrifugal separation, followed by washing with distilled water, absolute ethanol, and anhydrous ether three times (5 mL each). Place the powder in a vacuum drying oven at 50°C for 6 hours to obtain the Cu_2O catalyst (red-brown powder).

Preparation of Cu_2O/C_3N_4:

Under a nitrogen atmosphere, 100 mL of distilled water and 26.3 mg of polyethylene glycol 400 (approximately 22 μL) were introduced into a 500 mL three-necked flask. The mixture was stirred until the polyethylene glycol fully dissolved. Subsequently, 500.0 mg of hydrated copper acetate (2.5 mmol) and 1.4400 g of g-C_3N_4 material were added to the flask. The resultant mixture was then stirred at 30 °C for 10 minutes. While stirring vigorously, 8.5 mL of 0.6 M sodium hydroxide aqueous solution was incorporated and allowed to react for an additional 20 minutes. Following this, 0.75 mL of 2 M hydrazine hydrate aqueous solution was gradually introduced. As the hydrazine hydrate was added, the blue-green reaction mixture transitioned to a red-brown hue. After a continuous stirring period of 5 hours, the mixture was left to settle for 10 minutes, during which time reddish-brown solid precipitates formed at the flask's bottom. The Cu_2O/C_3N_4 (20 wt%) catalyst, appearing as a reddish-brown powder, was subsequently harvested via centrifugation. The powder was then washed in succession with distilled water, anhydrous ethanol, and anhydrous diethyl ether (each wash involved 5 mL X 3). Finally, the powder was dried in a vacuum oven at 50 °C for a duration of 6 hours.

3. Other data

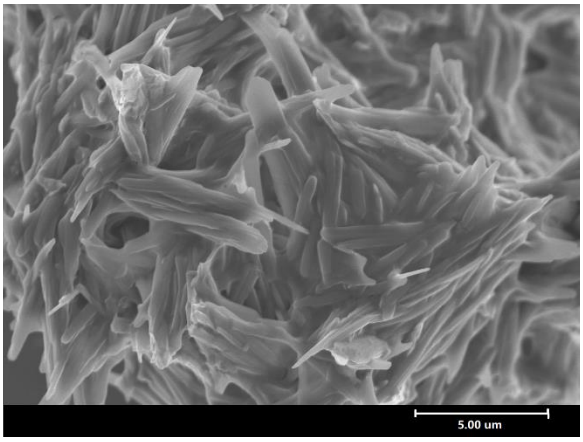
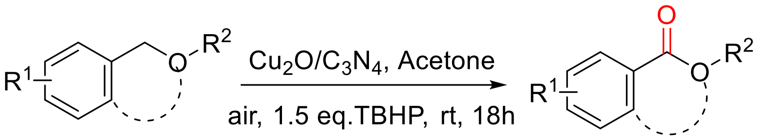
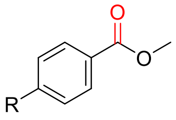


Figure S1. SEM of g-C_3N_4

Table S1. Scope exploration of the substrates.[a]





2a, R = H, 88% Y, 99% S

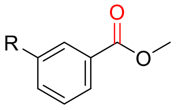
2b, R = CH_3, 80% Y, 98% S

2c, R = MeO, 80% Y, 99% S

2d, R = I, 80% Y, 99% S

2e, R = F, 82% Y, 99% S

2f, R = CF_3, 82% Y, 99% S



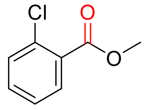
2g, R = CH_3, 88% Y, 99% S

2h, R = MeO, 87% Y, 98% S

2i, R = Cl, 86% Y

2j, R = F, 75% Y, 99% S

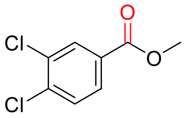
2k[b], R = NO_2, 80% Y



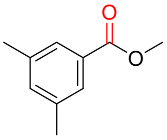
2l, R = Cl, 85% Y, 90% S[c]

2m, R = Me, 81% Y

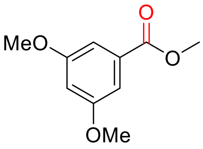
2n, R = OMe, 83% Y



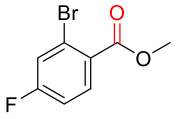
2o, 78% Y



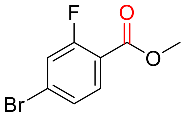
2p, 84% Y



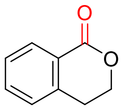
2q, 87% Y



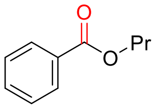
2r, 83% Y



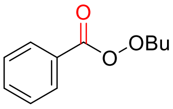
2s, 82% Y



2t, 97% Y



2u, 90% Y, 97% S



2v, 91% Y, 97% S

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[a] Reaction conditions: substrate (0.20 mmol), solvent (1.0 mL), catalyst 10%mol, TBHP (70 wt.% in H_2O) 0.3 mmol, at room temperature in air for 18 h; Y: isolated yield; S: selectivity, detected by GC.

[b] 50°C, *ca.* 85% conversion.

[c] The major side-product is acid

Table S2 comparison the current reaction with previous reports with TBHP as oxidant.

entry	**Reaction condition**	**Yield**	**reference**
1	Cu_2O/C_3N_4 10%mol; TBHP 1.5 equiv.; room temperature; 18 h.	97-75%	This paper
2	di-Rh cat. 1 mol%; TBHP 5equiv.; $NaHCO_3$ 0.5 equiv.; 40 ºC, 20 h.	80-46%	Ref. 5a
3	MnOx-N@C 2 mol% of Mn; TBHP 2-3 equiv.; 60 ºC, 24 h	87-53%	Ref. 6c
4	DIB (1.5 equiv.)/TBHP (6 equiv.)/ $Mg(OAc)_2 \cdot 4H_2O$ (1 equiv), 0 ºC	93-25%	Ref. 5b
5	Cu-neocuproin 5 mol%; TBHP 7 equiv.; room temperature; 1h	78-24%	Ref. 5e

4. ^{1}H and ^{13}C NMR Data of Compounds 2

Benzyl methyl ether (2a): Yield 88%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.96 (m, 2H), 7.56 – 7.49 (m, 1H), 7.41 (t, J = 7.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.08, 132.91, 130.19, 129.58, 128.37, 52.06.[S1]

Methyl 4-methylbenzoate (2b)： Yield 80%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 143.34, 129.63, 129.11, 127.46, 51.98, 21.76. [S1]

Methyl 4-methoxybenzoate (2c)： Yield 80%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 163.36, 131.60, 122.62, 113.62, 55.41, 51.85. [S1]

Methyl 4-iodobenzoate (2d)： Yield 80%; light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 143.34, 129.63, 129.11, 127.46, 51.98, 21.76. [S1]

Methyl 4-fluorobenzoate (2e): Yield 82%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, J = 1.7 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.44 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.01, 166.13, 164.49, 132.17, 132.07, 126.40, 115.61, 115.39, 52.17. [S1]

Methyl 4-(trifluoromethyl)benzoate (2f): Yield 82%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86, 134.59, 134.26, 133.36, 129.98, 125.45, 125.41, 125.37, 125.34, 122.29, 52.48. [S1]

Methyl 3-methylbenzoate (2g): Yield 88%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.34 – 7.30 (m, 2H), 3.89 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 138.16, 133.70, 130.15, 130.11, 128.28, 126.73, 52.06, 21.28. [S1]

Methyl 3-methoxybenzoate (2h): Yield 87%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.03 (dd, J = 8.2, 2.6 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 159.59, 131.49, 129.41, 122.02, 119.55, 113.98, 55.47, 52.20. [S1]

Methyl 3-chlorobenzoate (2i): Yield 86%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, J = 1.7 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.44 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.92, 134.53, 132.99, 131.84, 129.73, 129.70, 127.73, 52.45. [S2]

Methyl 3-fluorobenzoate (2j): Yield 75%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 9.3 Hz, 1H), 7.33 (dd, J = 13.6, 7.9 Hz, 1H), 7.20 – 7.13 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01, 165.98, 163.77, 161.32, 132.33, 132.25, 130.08, 130.00, 125.35, 125.32, 120.13, 119.92, 116.62, 116.39, 52.42. [S3]

Methyl 3-nitrobenzoate (2k): Yield 80%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.35 (dd, J = 8.2, 2.1 Hz, 1H), 8.30 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.99, 148.31, 135.31, 131.90, 129.68, 127.43, 124.64, 52.84. [S4]

Methyl 2-chlorobenzoate (2l): Yield 85%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 133.70, 132.58, 131.41, 131.09, 130.09, 126.64, 52.44. [S1]

Methyl 2-methylbenzoate (2m): Yield 81%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, 1H), 7.29-7.27 (m, 2H), 3.93 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 140.24, 132.02, 131.73, 130.61, 129.54, 125.74, 51.86, 21.80.[S1]

Methyl 2-methoxybenzoate (2n): Yield 83%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 4Hz, 1H), 7.49 - 7.45 (m, 1H), 6.99 - 6.97 (m, 2H), 3.894 (s, 3H), 3.891 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 159.10, 133.58, 131.66, 120.12, 199.93, 111.97, 55.95, 52.03. [S1]

Methyl 3,4-dichlorobenzoate (2o): Yield 78%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.22, 137.59, 132.95, 131.56, 130.55, 129.98, 128.67, 52.58. [S4]

Methyl 3,5-dimethylbenzoate (2p): Yield 84%; white oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.18 (s, 1H), 3.90 (d, *J* = 4.4 Hz, 3H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.48, 138.03, 134.60, 130.03, 127.32, 52.02, 21.17. [S5]

Methyl 3,5-dimethoxybenzoate (2q): Yield 87%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.4 Hz, 2H), 6.64 (t, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 160.65, 132.01, 107.13, 105.77, 55.56, 52.24. [S2]

Methyl 2-bromo-4-fluorobenzoate (2r): Yield 83%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.45 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.00 (ddd, *J* = 8.9, 7.7, 3.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44, 162.57, 160.09, 135.89, 135.82, 120.15, 119.92, 118.70, 118.45, 116.13, 116.10, 52.79. [S6]

Methyl 4-bromo-2-fluorobenzoate (2s): Yield 82%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.38 – 7.32 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.24, 164.20, 162.95, 160.32, 133.20, 133.18, 127.99, 127.90, 127.60, 127.56, 120.85, 120.59, 117.74, 117.64, 52.53. [S7]

Isochroman-1-one (2t): Yield 97%; white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 7.5, 1.1 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.26 (m, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.07 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.22, 139.61, 133.74, 130.42, 127.73, 127.31, 125.32, 67.37, 27.85. [S1]

Propyl benzoate (2u)： Yield 90%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.58 – 7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.74, 132.83, 130.56, 129.57, 128.35, 77.39, 77.07, 76.75, 66.58, 22.15, 10.56. [S7]

Butyl benzoate (2v)： Yield 91%; colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.44 – 1.32 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.68, 132.81, 130.57, 129.55, 128.33, 64.83, 30.82, 19.31, 13.79. [S8]

Reference:

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[S2] Y.-F. Cao, L.-J. Li, M. Liu, H. Xu and H.-X. Dai, *J. Org. Chem.*, 2020, **85**, 4475.

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[S7] S. S. Zimmerman, A. Khatri, E. C. Garnier-Amblard, P. Mullasseril, N. L. Kurtkaya, S. Gyoneva, K. B. Hansen, S. F. Traynelis and D. C. Liotta, *J. Med. Chem.,* 2014, **57**, 2334.

[S8] L. Ren, M.-M. Yang, C.-H. Tung, L.-Z. Wu and H. Cong, *ACS Catal.*, 2017, **7**, 8134.

4. ^{1}H and ^{13}C NMR Spectra of Compounds 2

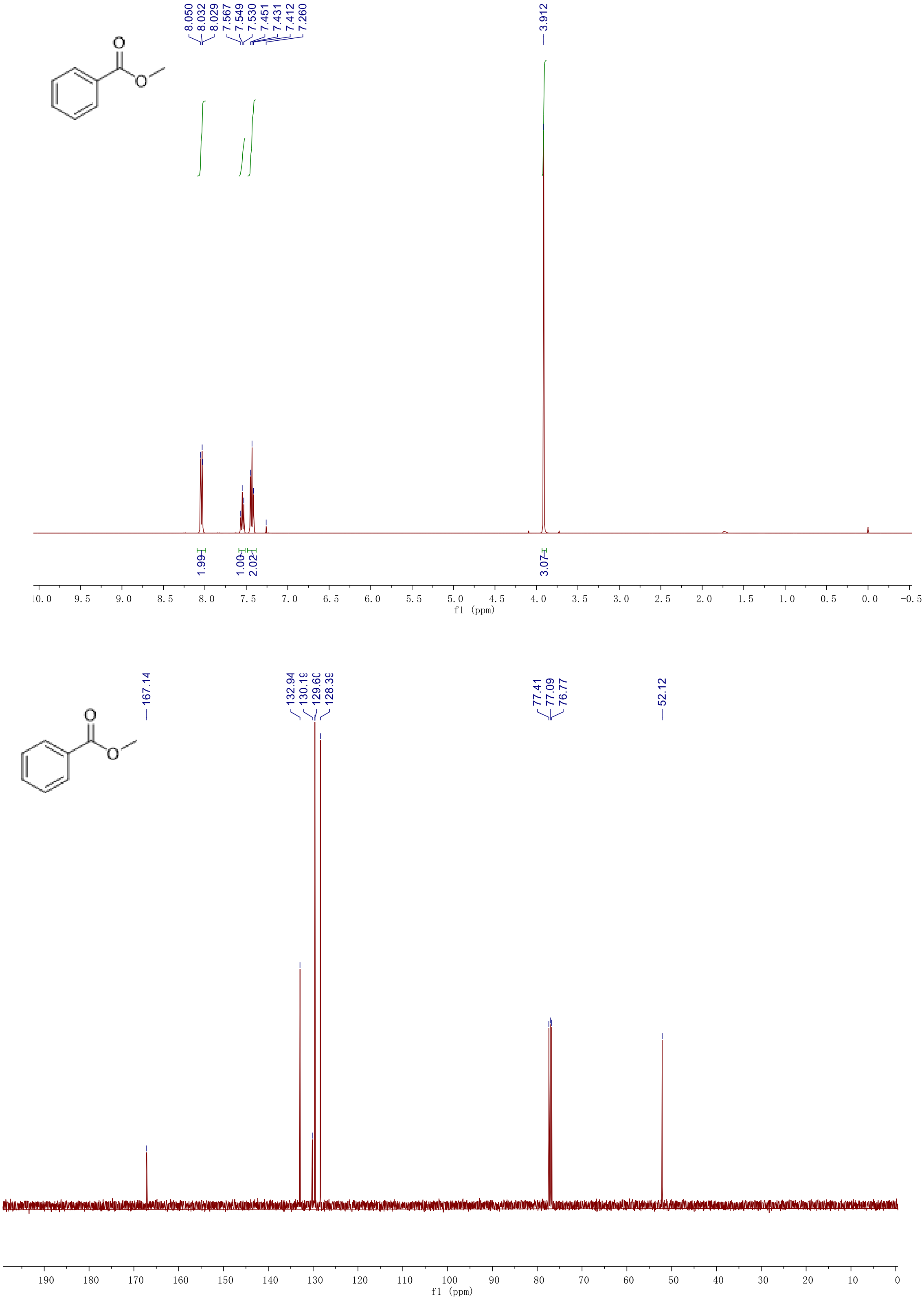

Figure S2. ^{1}H and ^{13}C NMR Spectra of Compound **2a**.

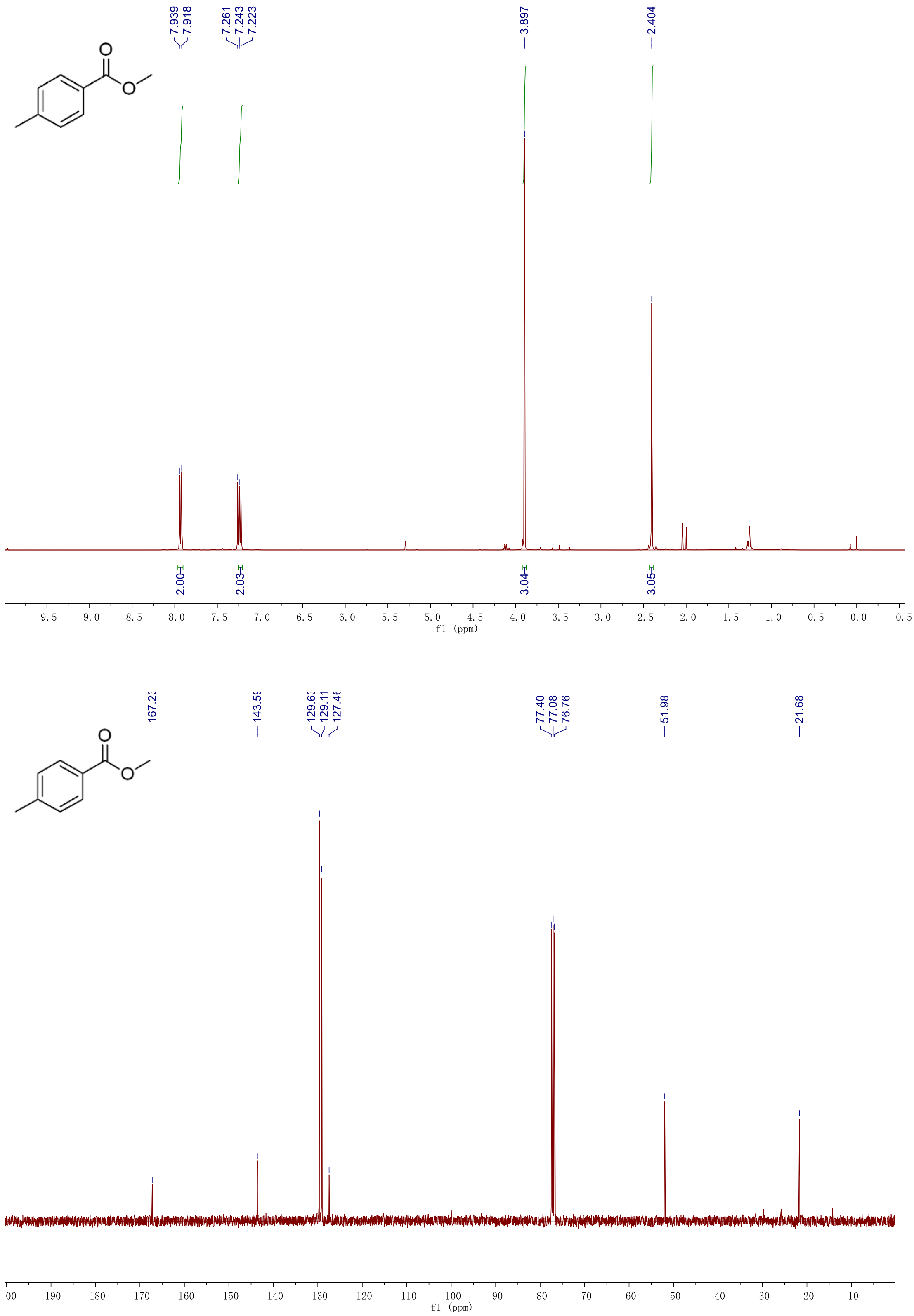

Figure S3. ^{1}H and ^{13}C NMR Spectra of Compound **2b**.

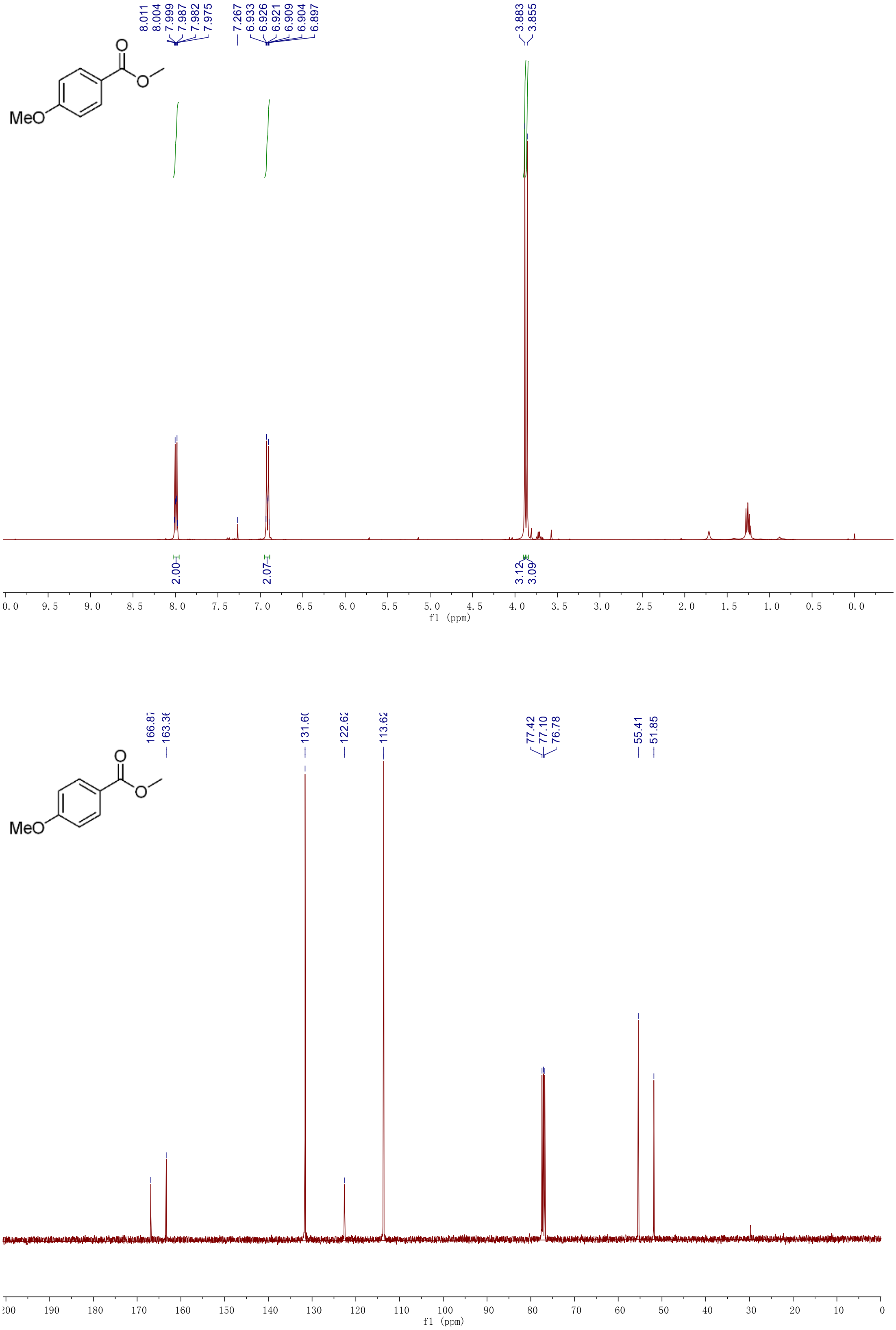

Figure S4. ^{1}H and ^{13}C NMR Spectra of Compound **2c**.

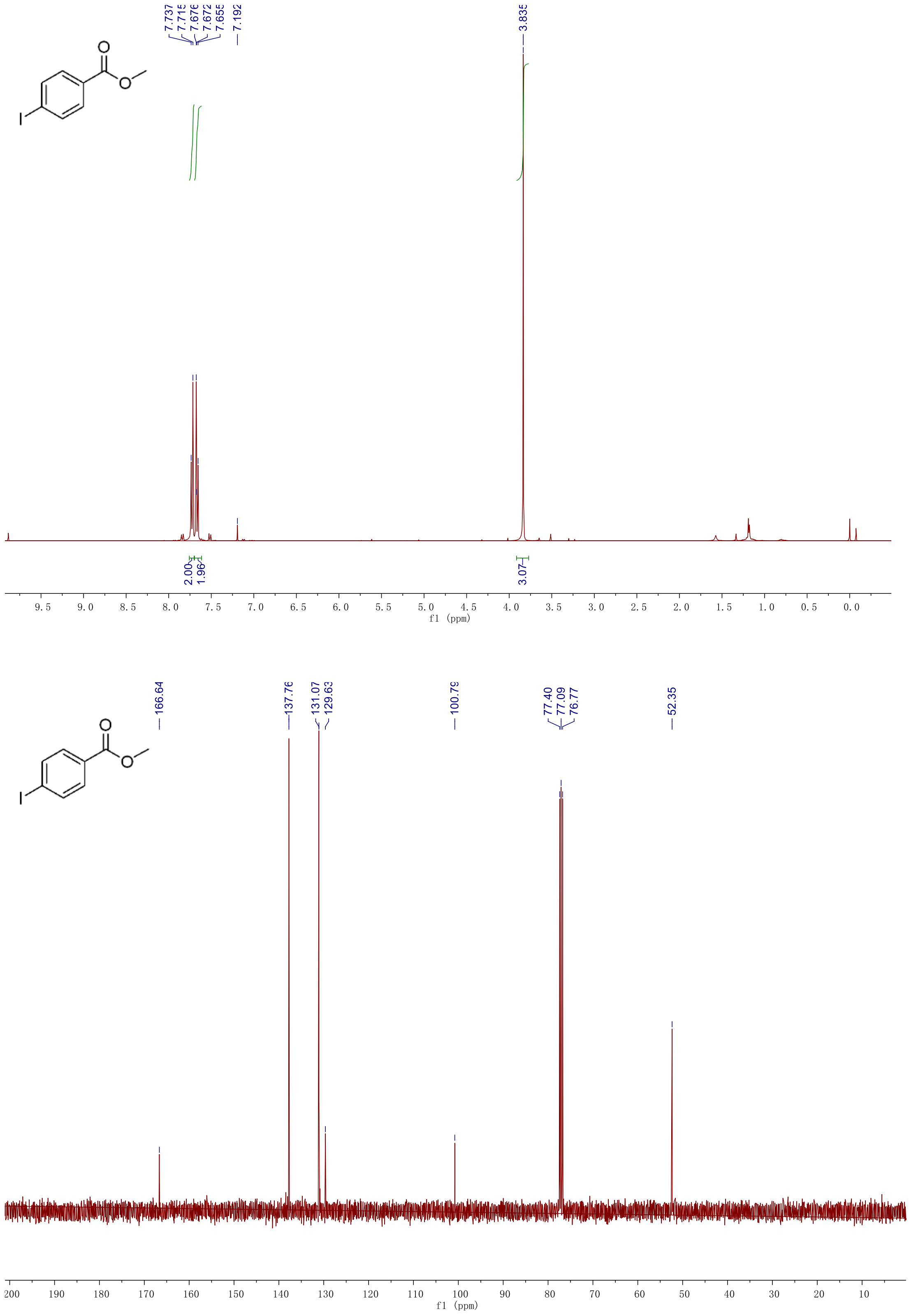

Figure S5. ^{1}H and ^{13}C NMR Spectra of Compound **2d**.

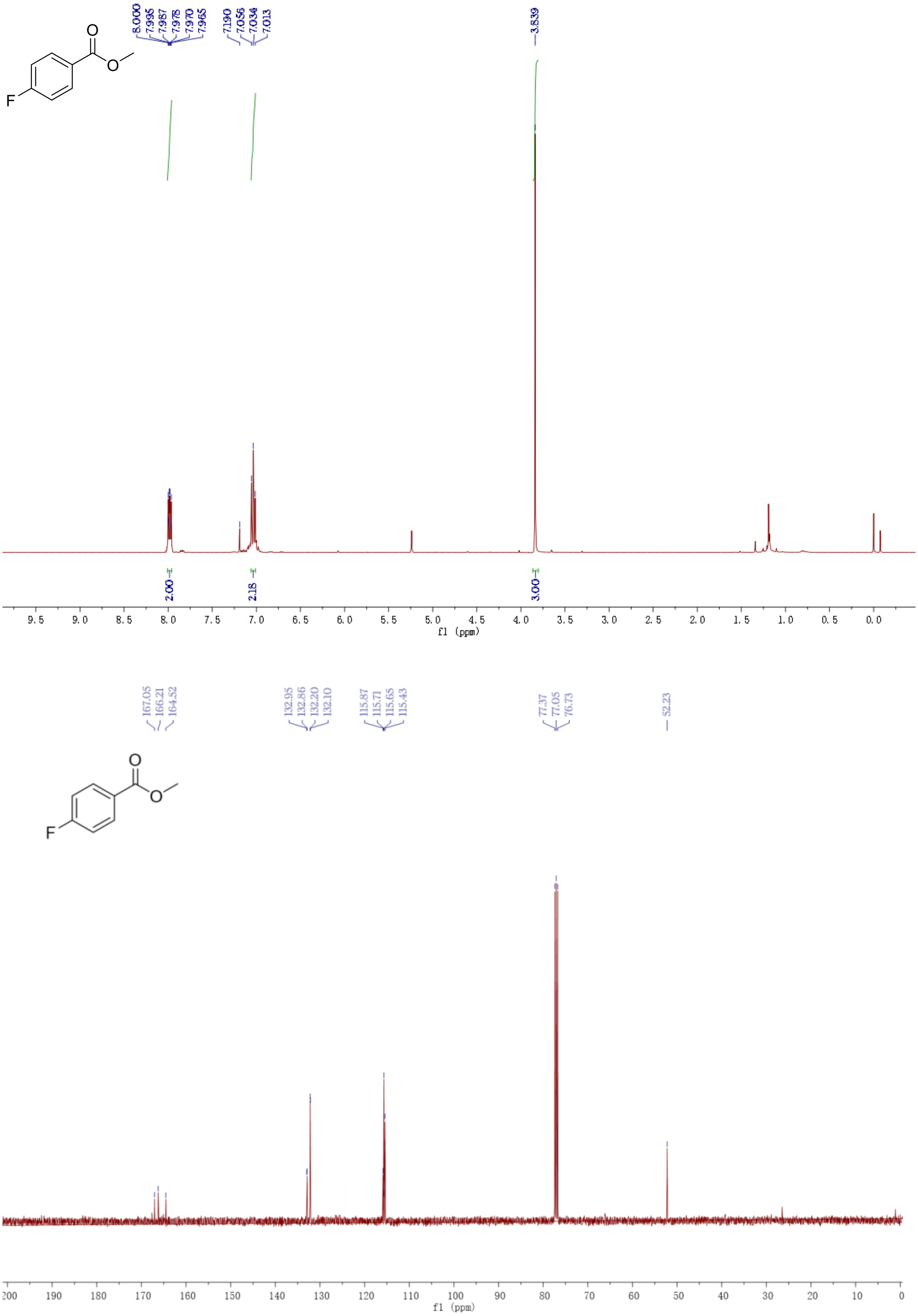

Figure S6. ^{1}H and ^{13}C NMR Spectra of Compound **2e**.

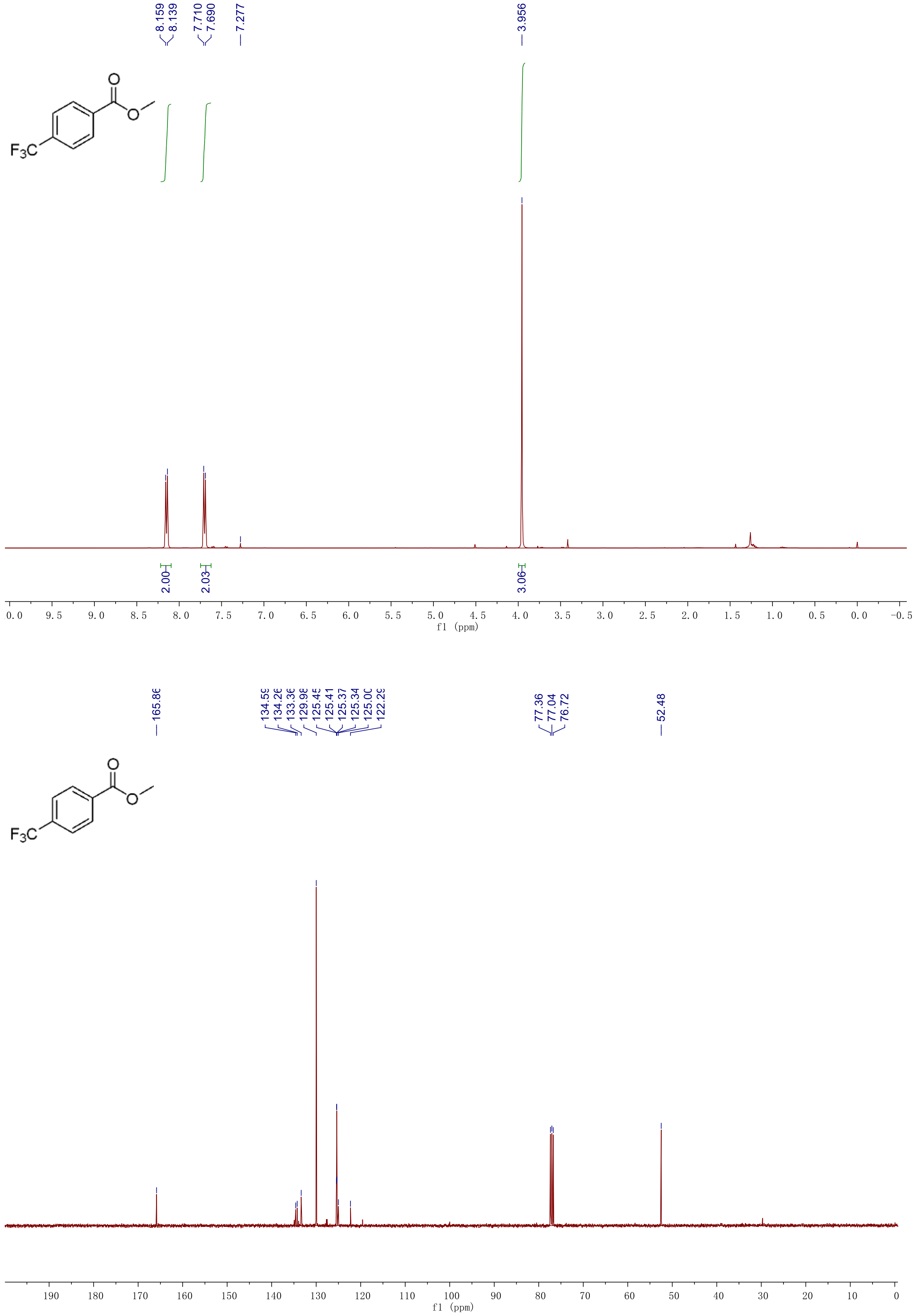

Figure S7. ^{1}H and ^{13}C NMR Spectra of Compound **2f**.

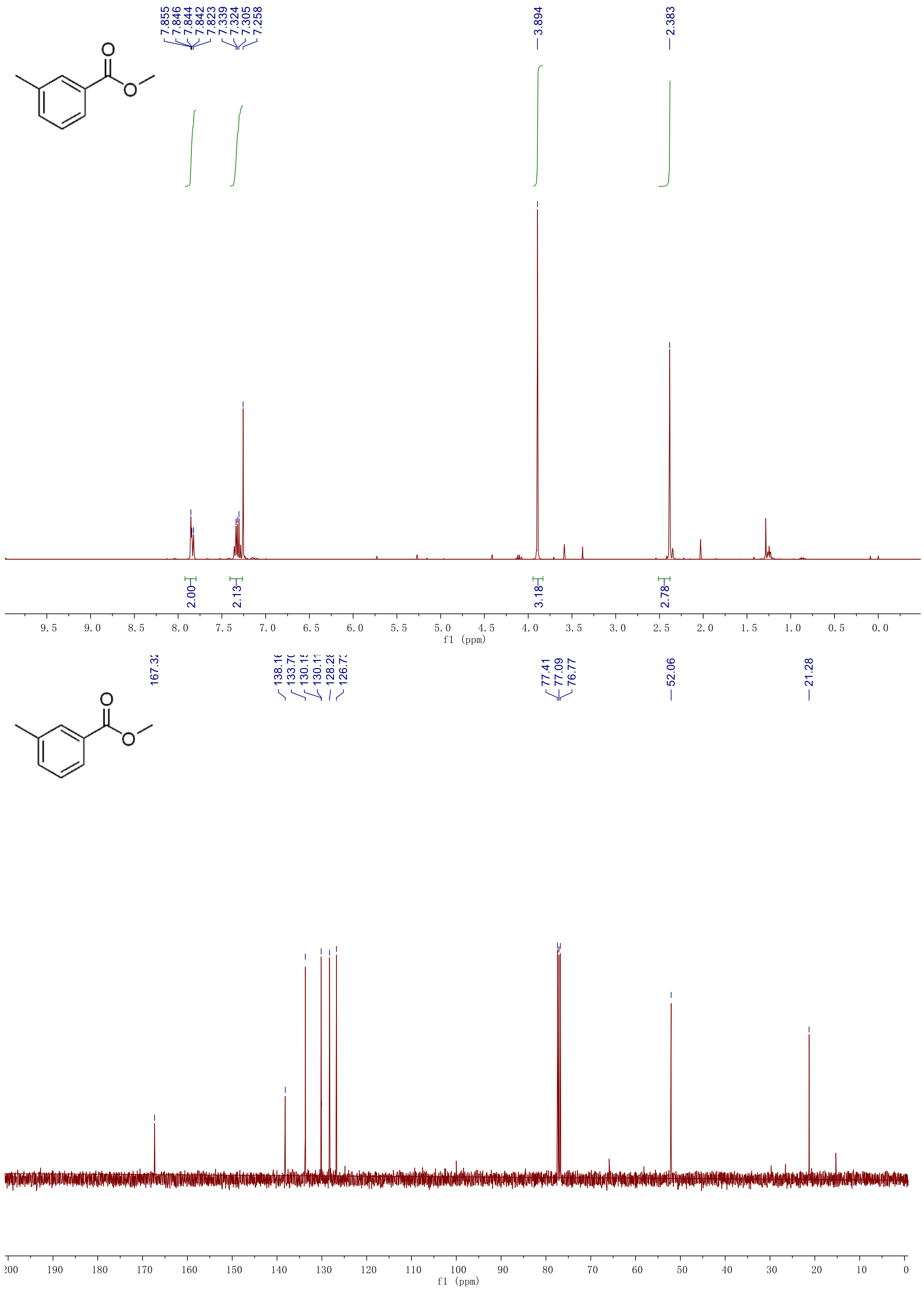

Figure S8. ^{1}H and ^{13}C NMR Spectra of Compound **2g**.

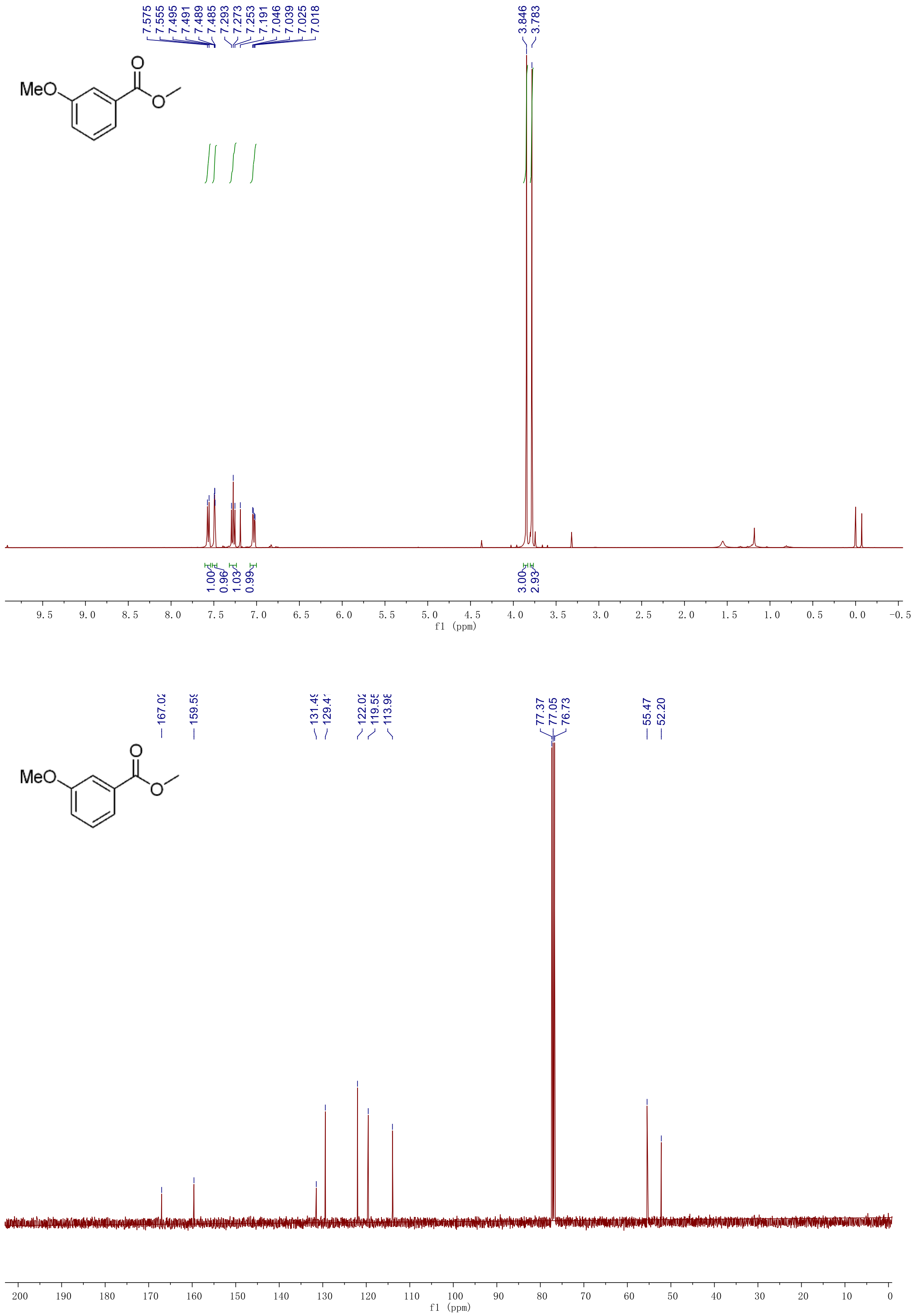

Figure S9. ^{1}H and ^{13}C NMR Spectra of Compound **2h**.

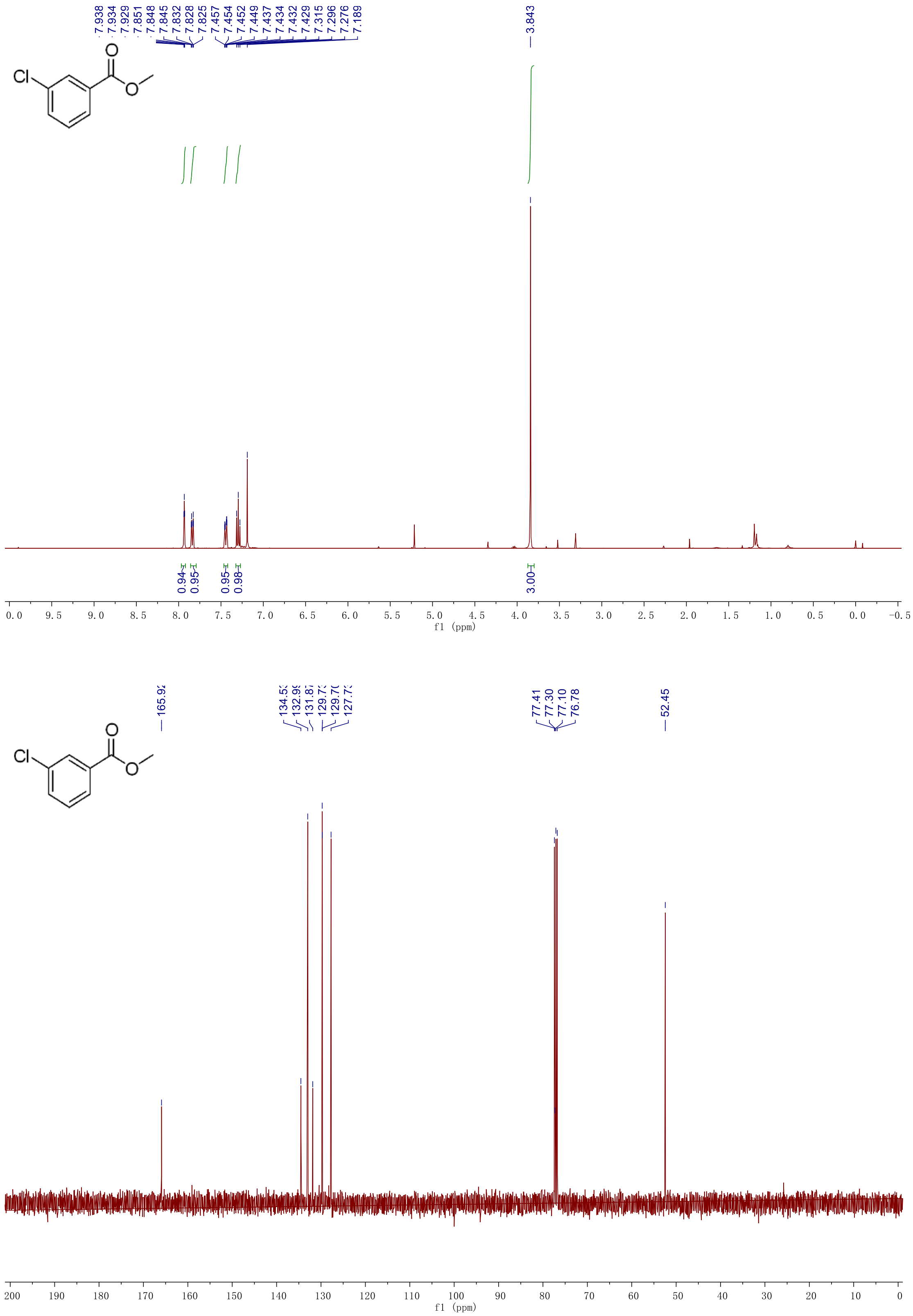

Figure S10. ^{1}H and ^{13}C NMR Spectra of Compound **2i**.

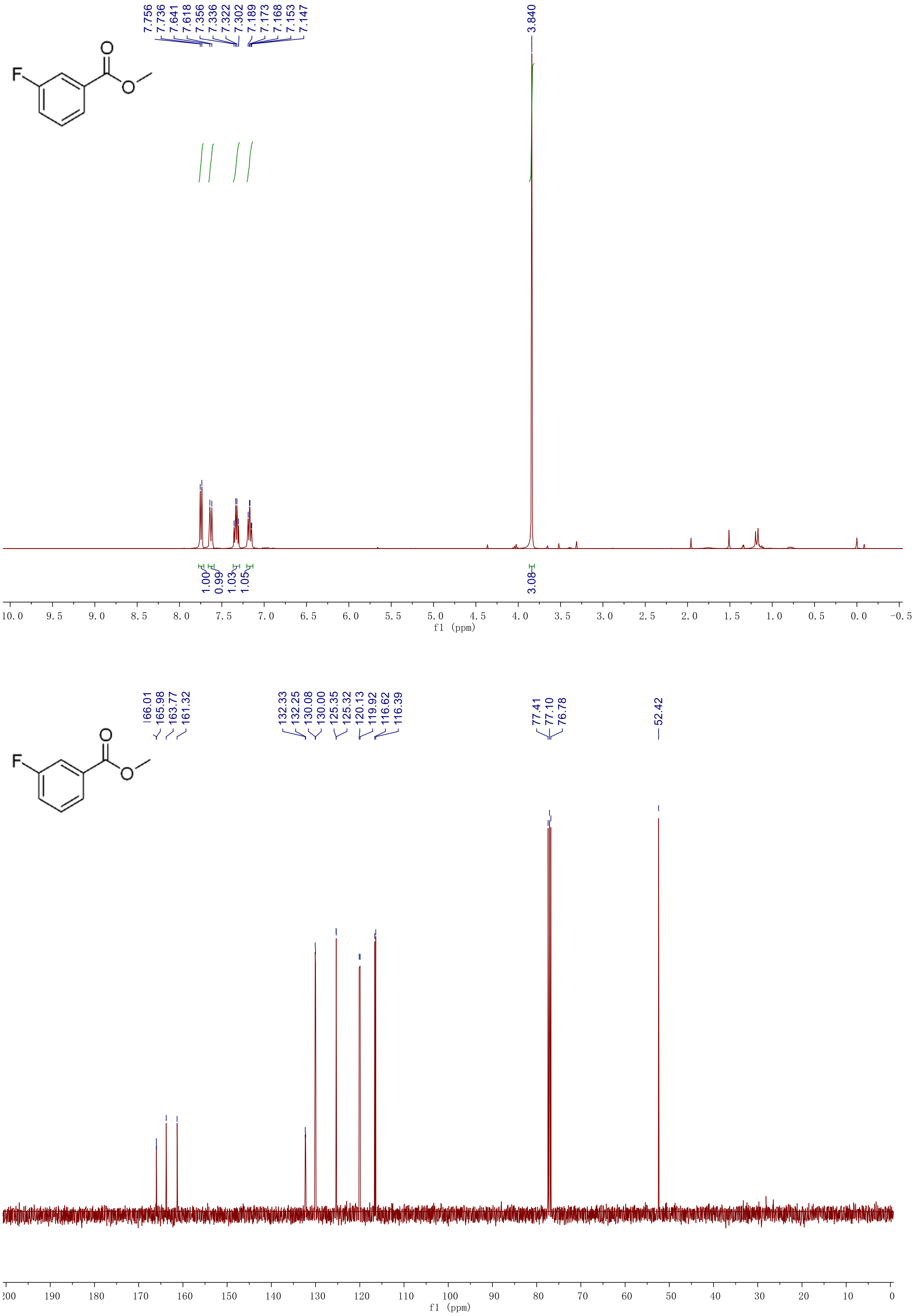

Figure S11. ^{1}H and ^{13}C NMR Spectra of Compound **2j**.

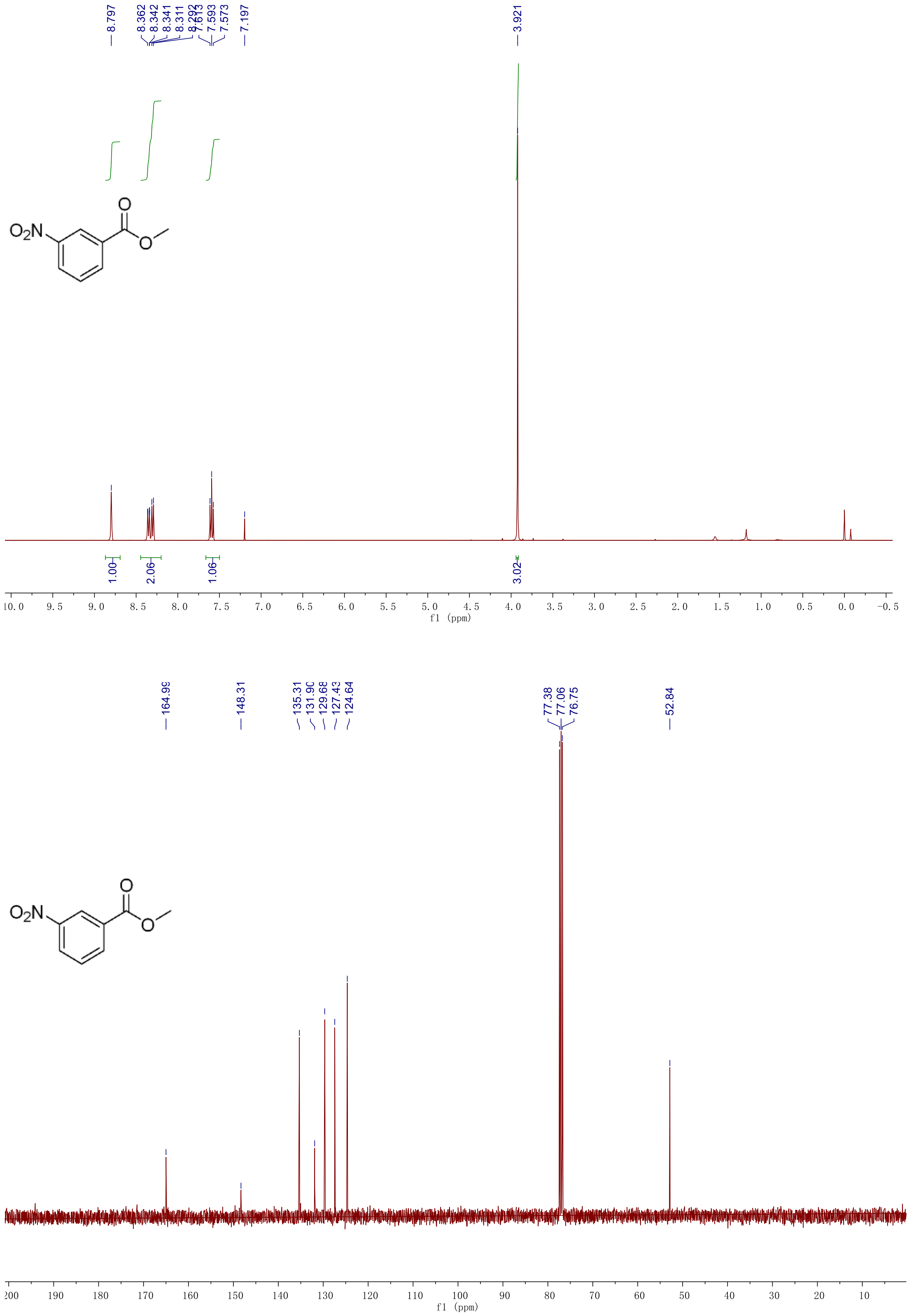

Figure S12. ^{1}H and ^{13}C NMR Spectra of Compound **2k.**

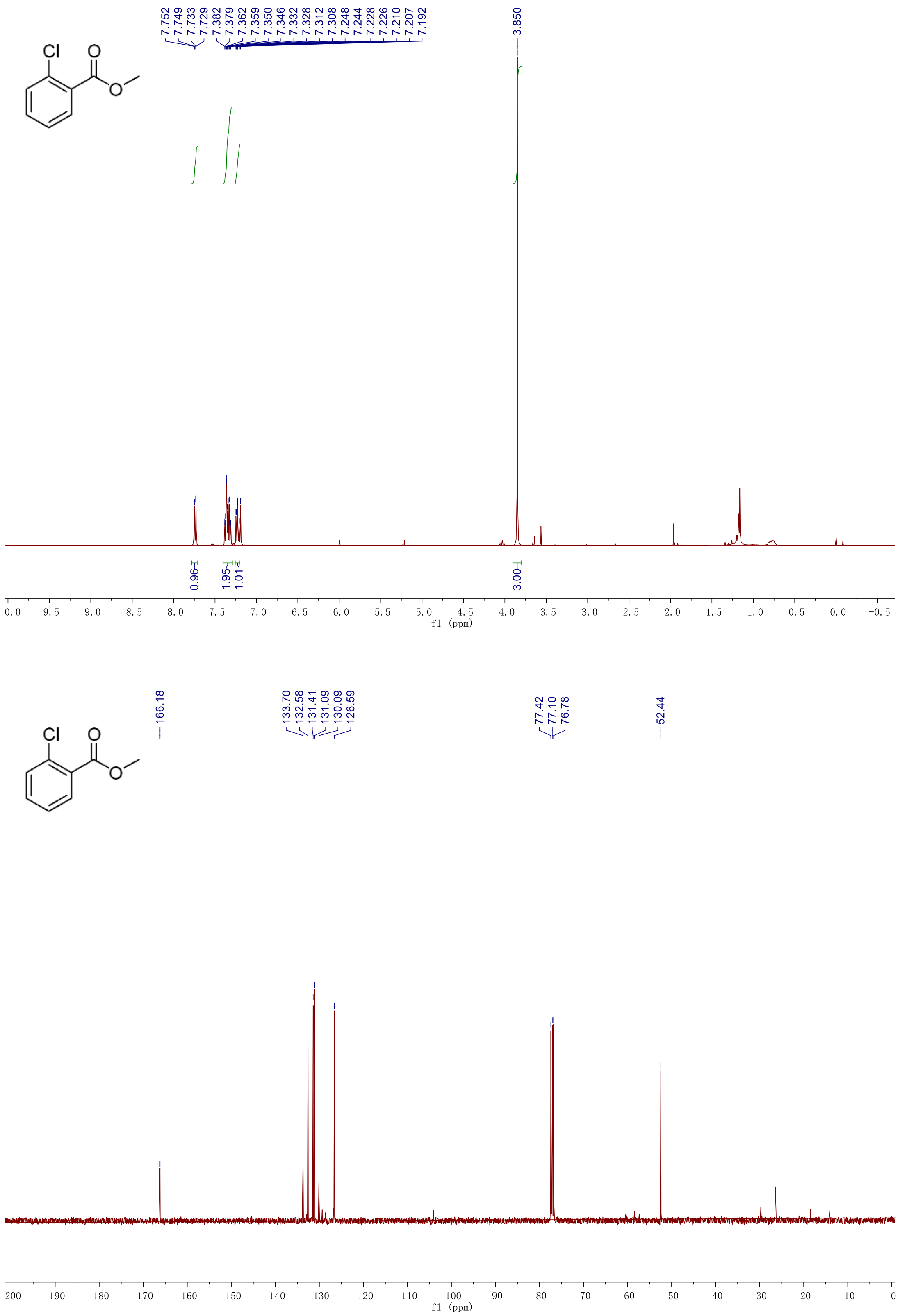

Figure S13. ^{1}H and ^{13}C NMR Spectra of Compound **2l**.

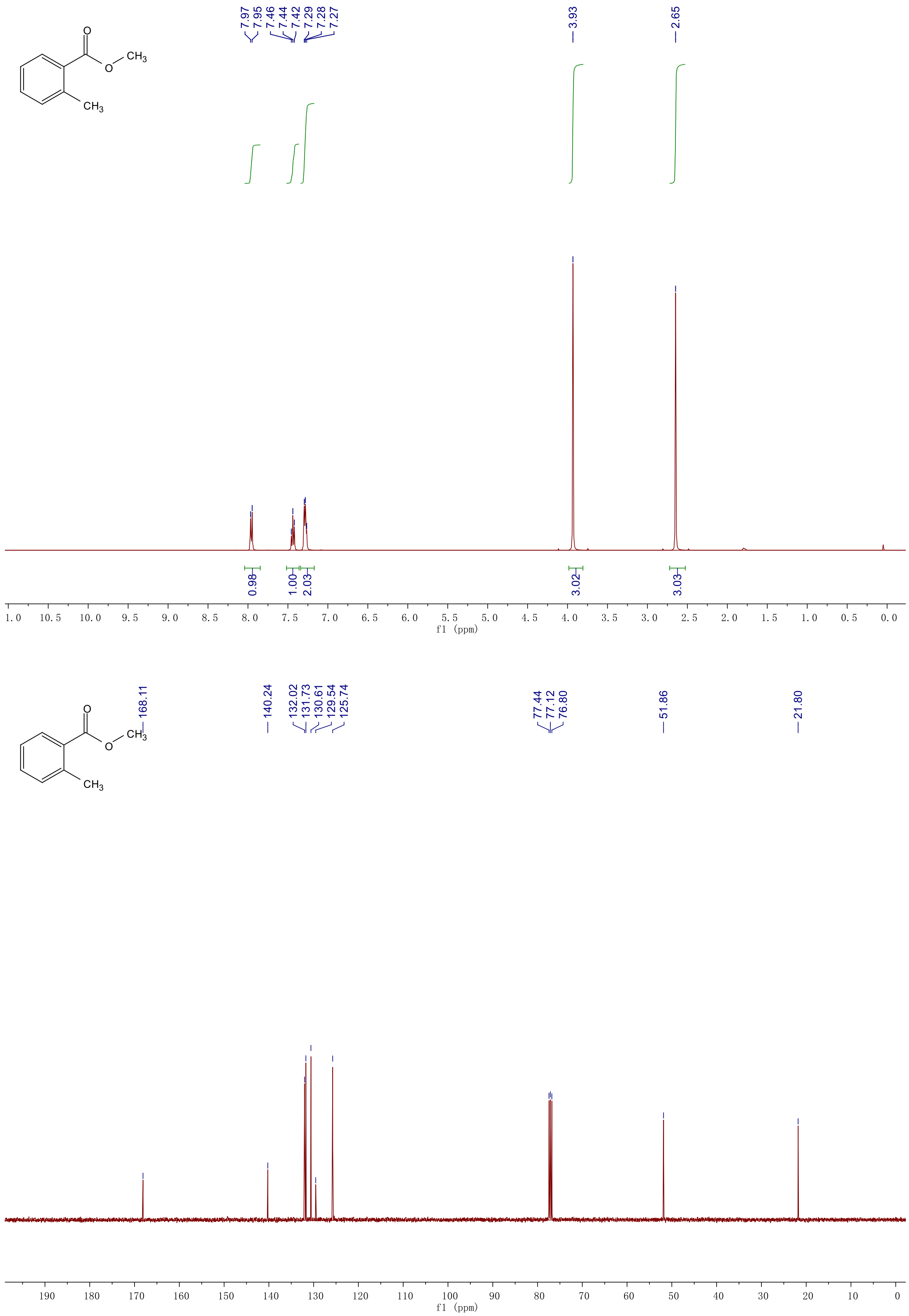

Figure S14. ^{1}H and ^{13}C NMR Spectra of Compound **2m**.

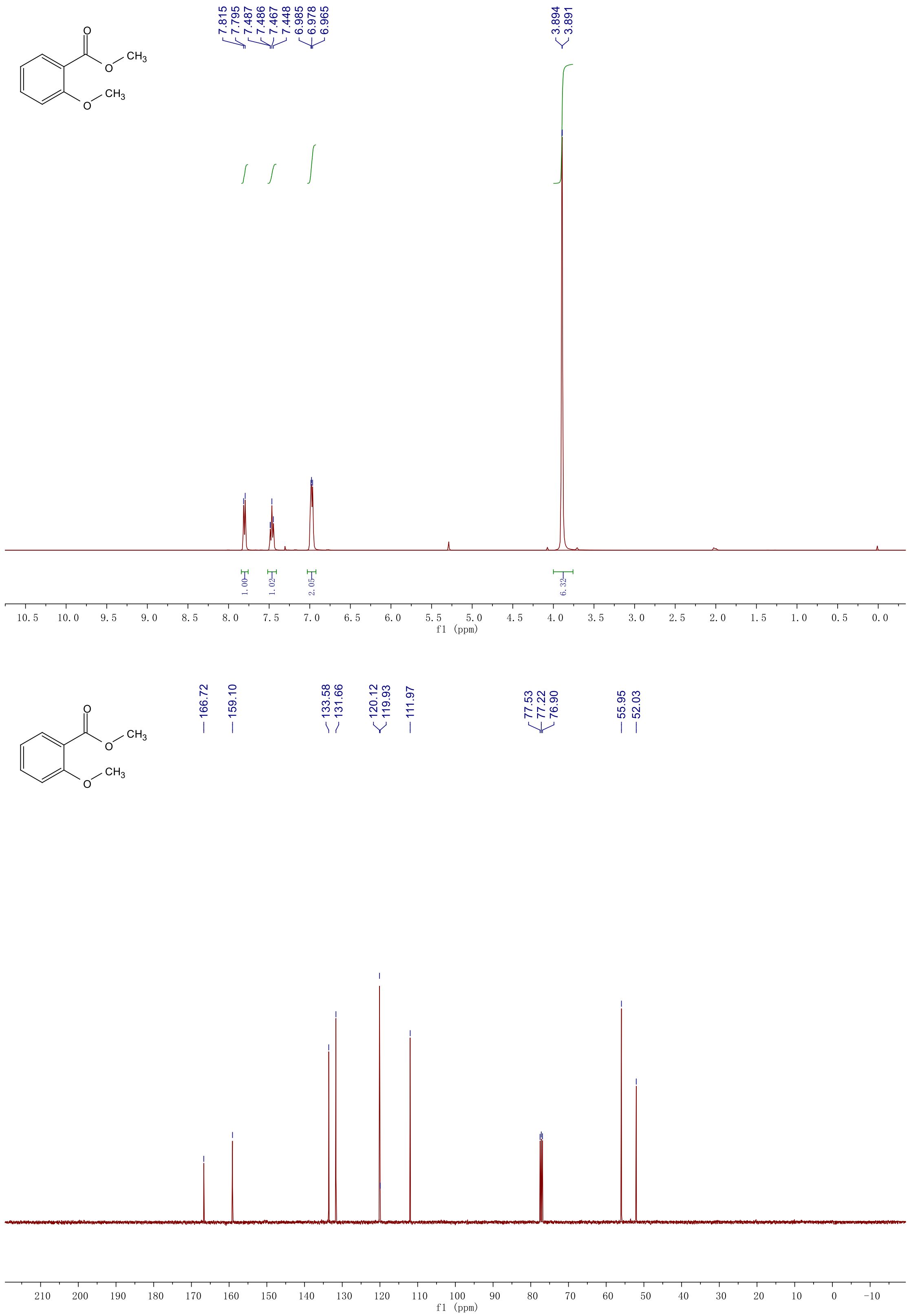

Figure S15. ^{1}H and ^{13}C NMR Spectra of Compound **2n**.

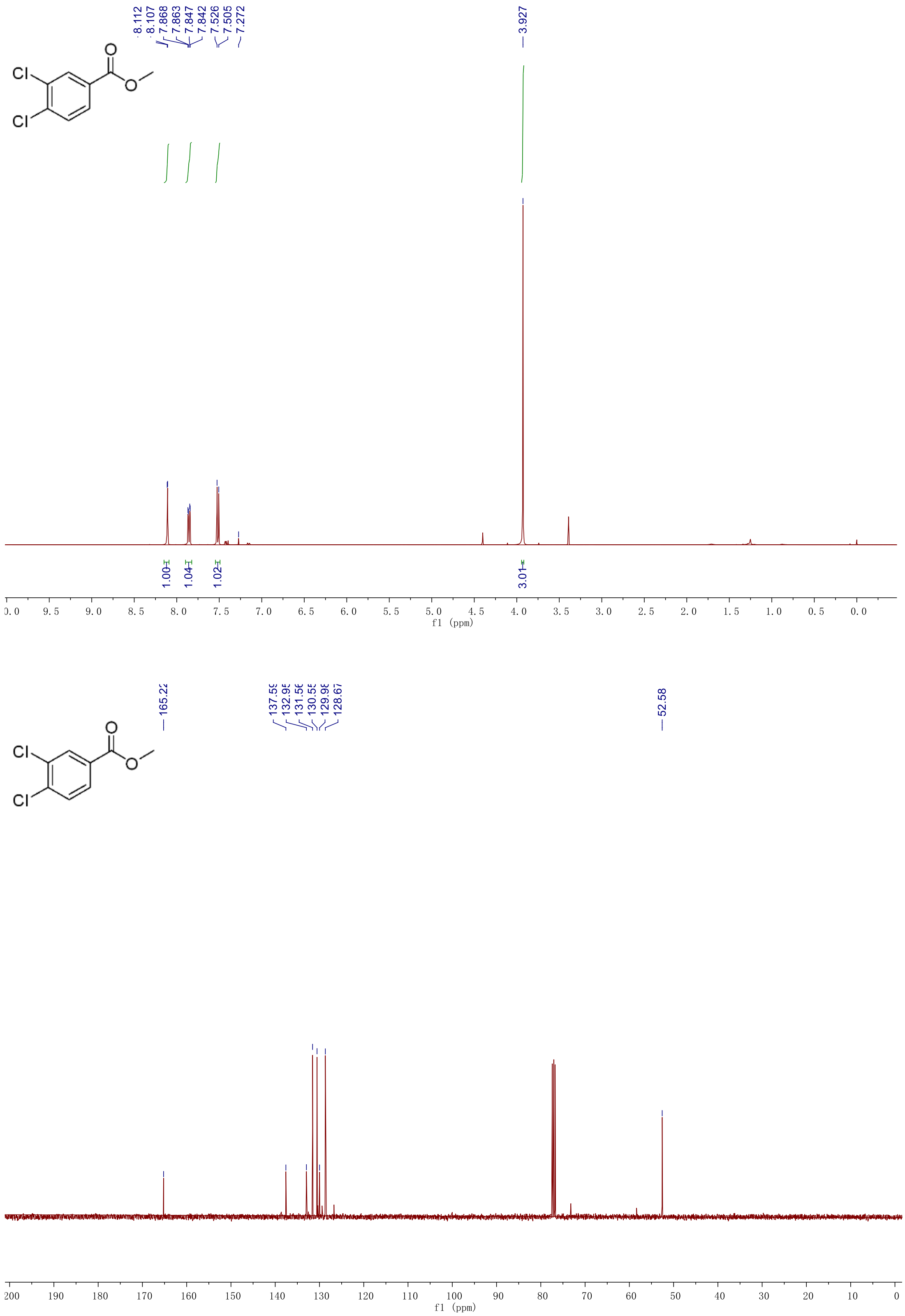

Figure S16. ^{1}H and ^{13}C NMR Spectra of Compound **2o**.

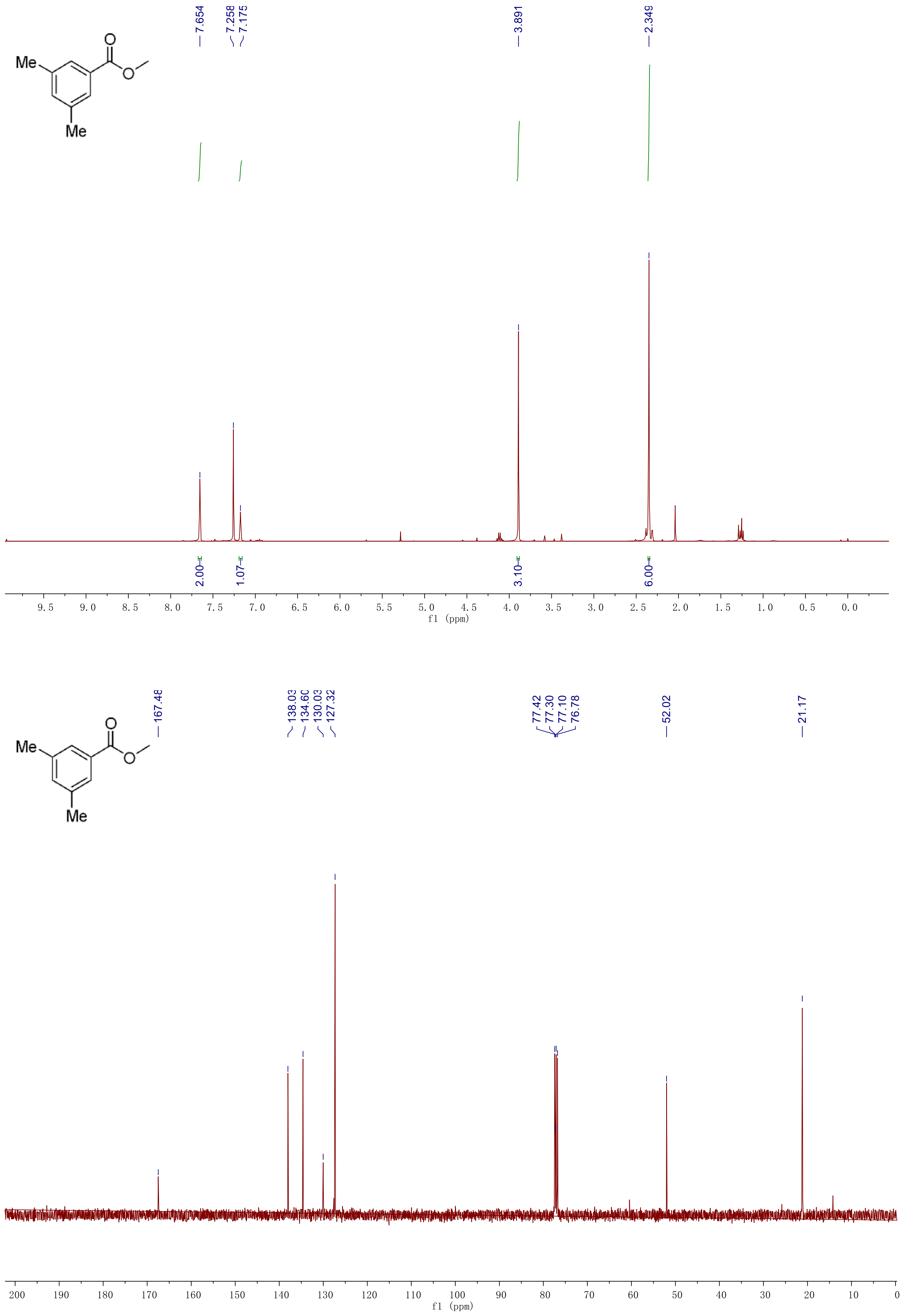

Figure S17. ^{1}H and ^{13}C NMR Spectra of Compound **2p**.

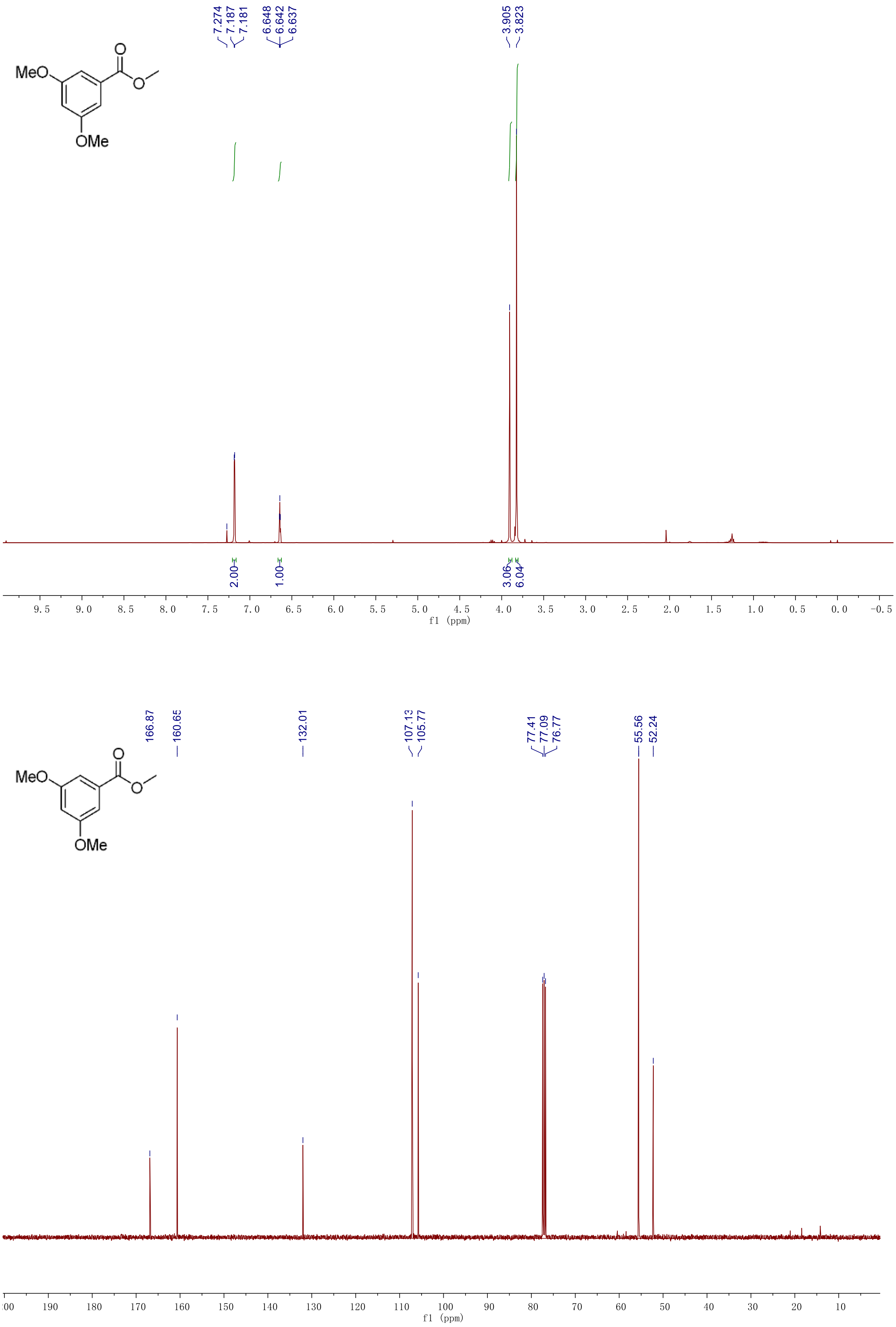

Figure S18. ^{1}H and ^{13}C NMR Spectra of Compound **2q**.

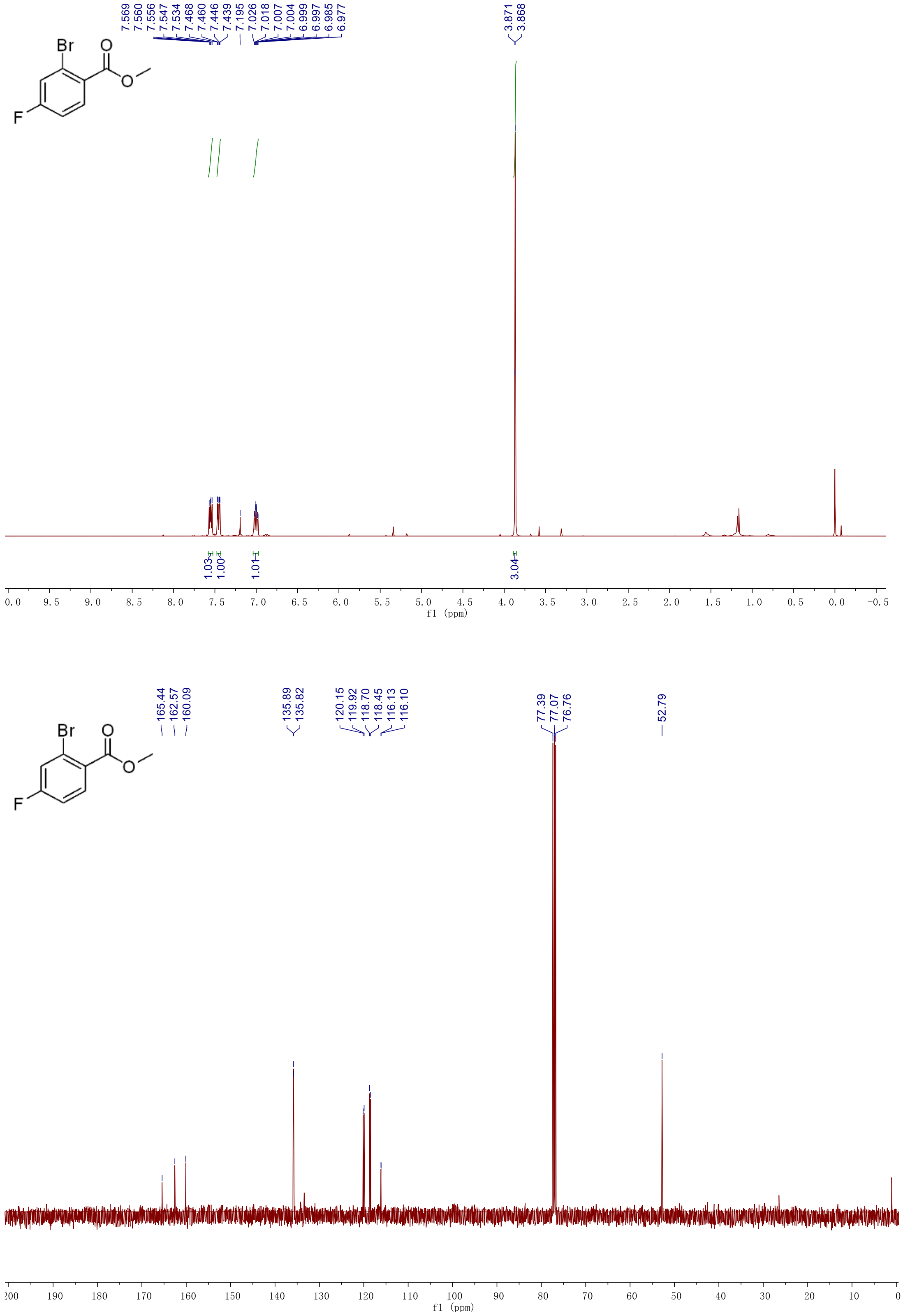

Figure S19. ^{1}H and ^{13}C NMR Spectra of Compound **2r**.

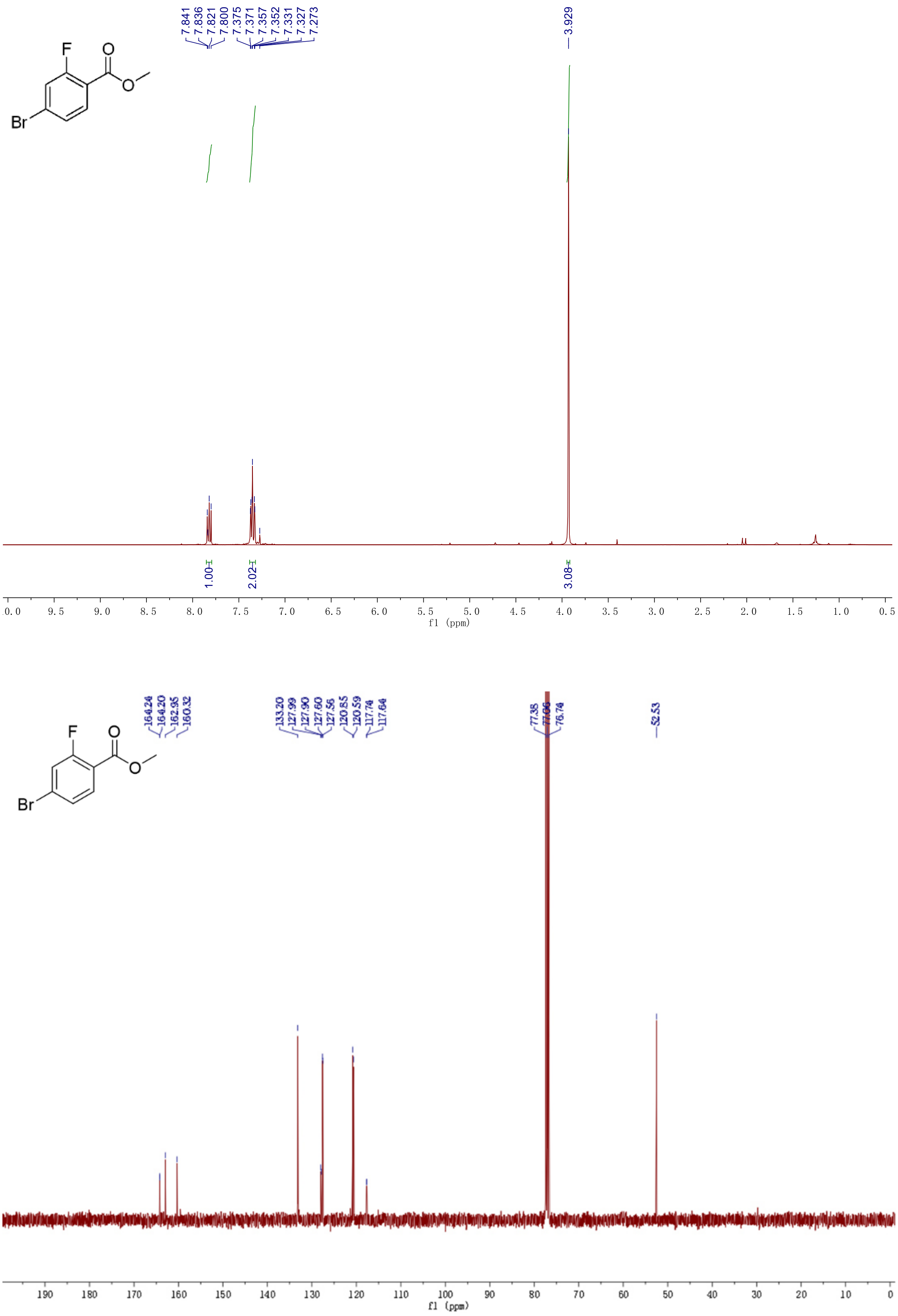

Figure S20. ^{1}H and ^{13}C NMR Spectra of Compound **2s**.

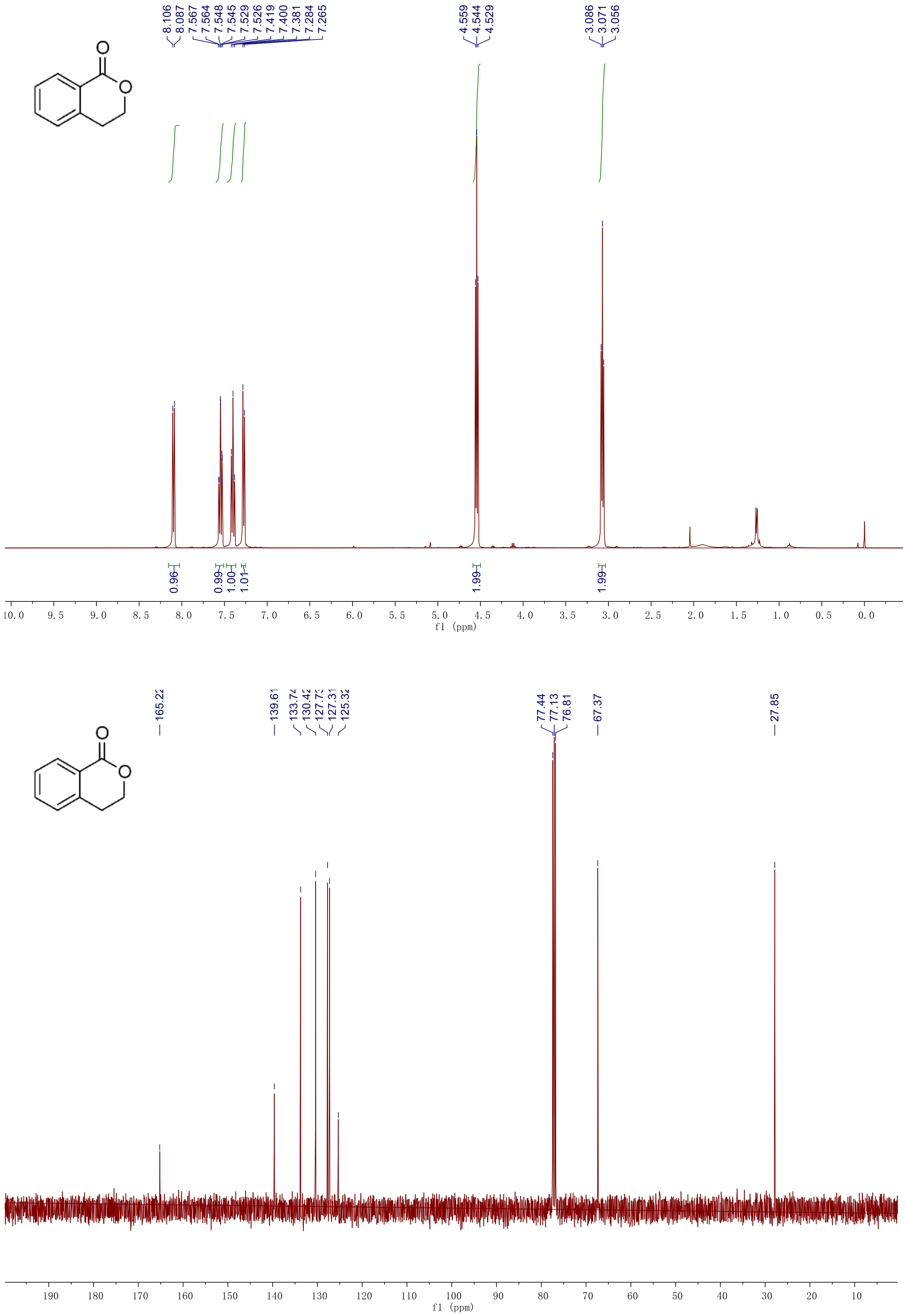

Figure S21. ^{1}H and ^{13}C NMR Spectra of Compound **2t**.

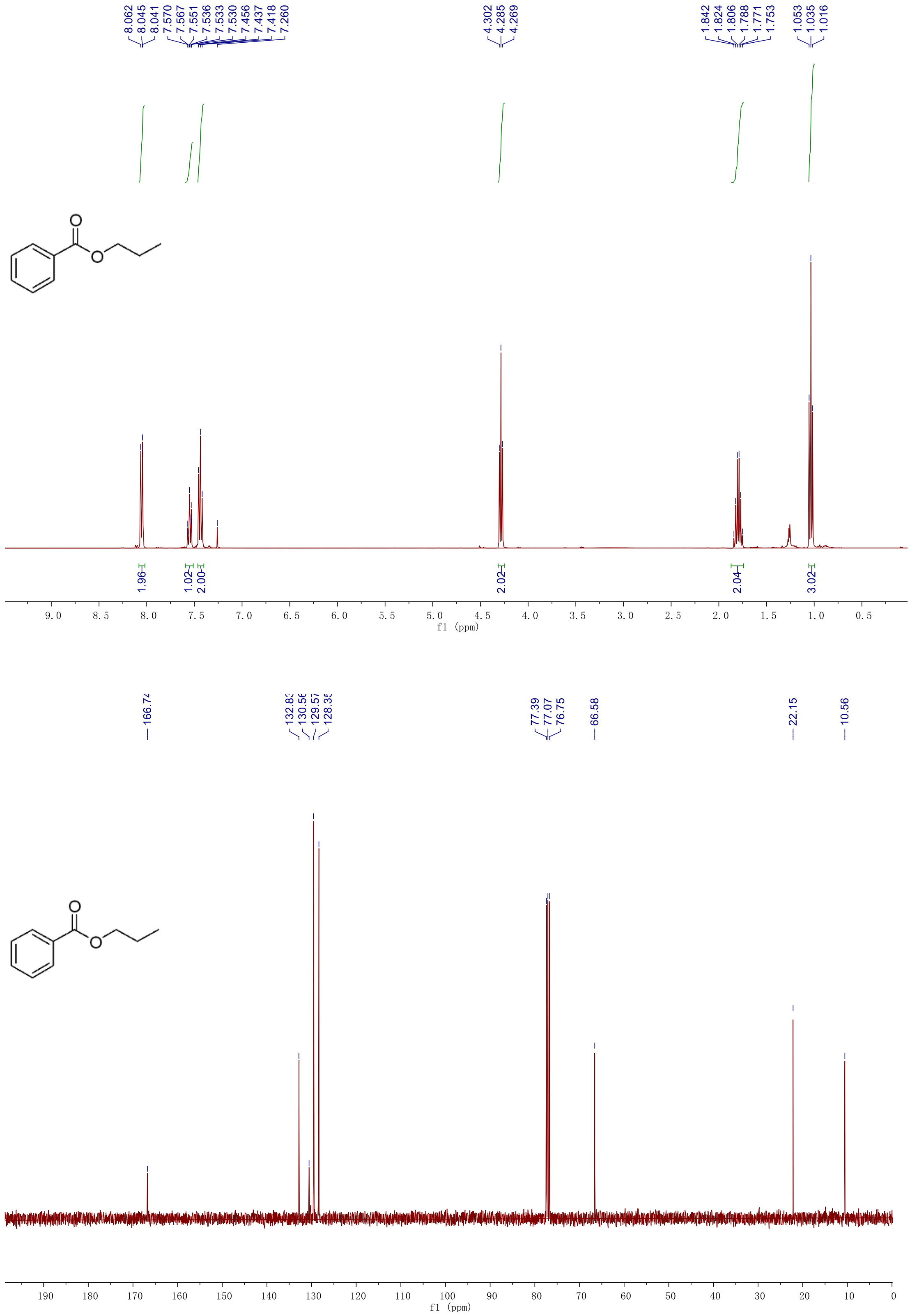

Figure S22. ^{1}H and ^{13}C NMR Spectra of Compound **2u**.

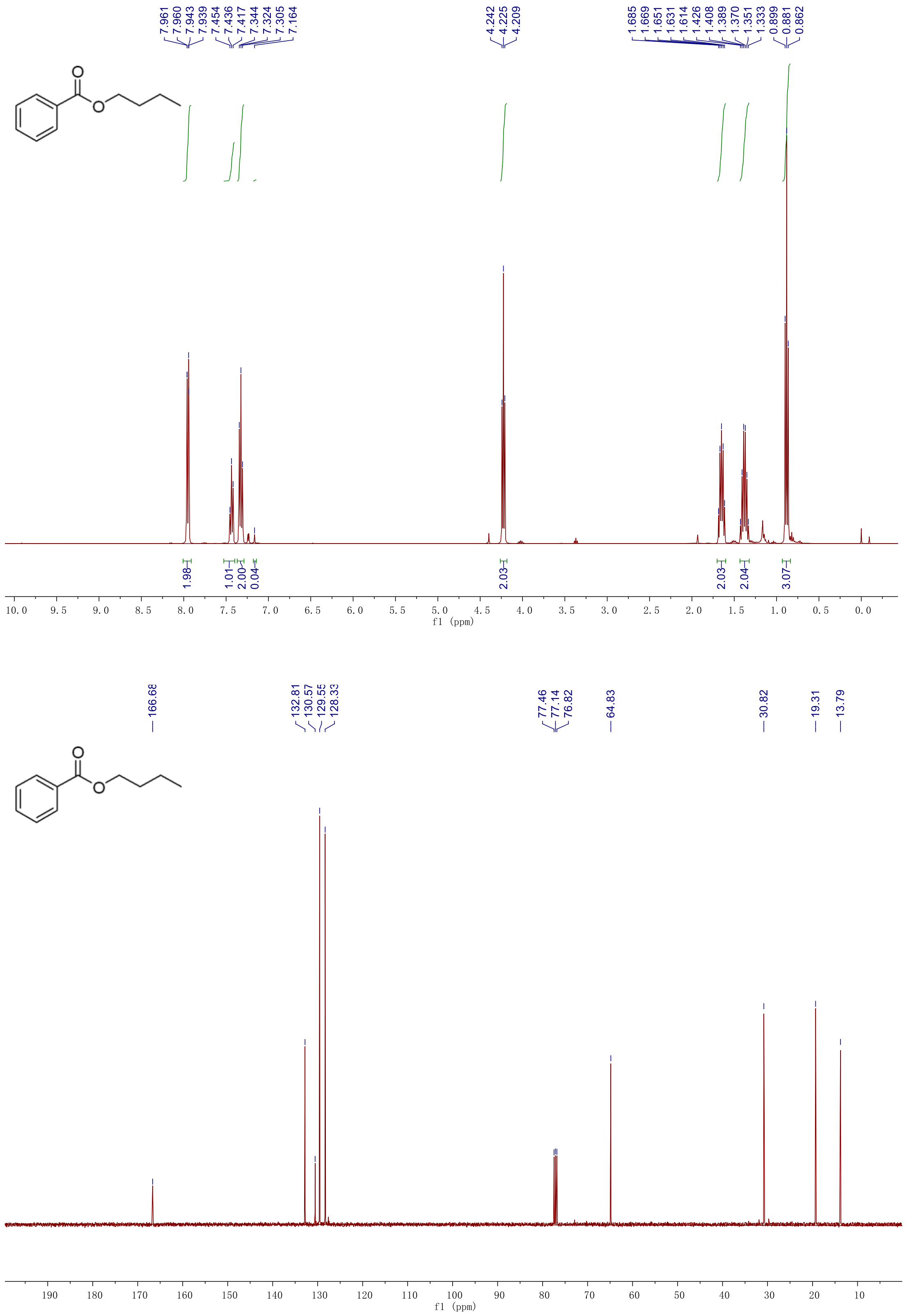

Figure S23. ^{1}H and ^{13}C NMR Spectra of Compound **2v**.