

Supporting Information

Acyl Radicals from α -Keto Acids Using a Carbonyl-Photocatalyst: Photoredox-Catalyzed Synthesis of Ketones

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General information: α -Keto acids were synthesized by adapting the reported procedure.^{S1} All reagents were used as purchased without further purification. All solvents were obtained from commercial sources and were purified according to standard procedures. Photochemical reactions were carried with 45 W CFL (Philips), made by Philips Lighting investment (China) Co., Ltd. Column chromatography was performed on silica gel. ¹H, ¹³C and ¹⁹F NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-2600 Spectrophotometer. Photoluminescence spectra were measured on a Hitachi F2500 apparatus. High-performance liquid chromatography (HPLC) was conducted on a LC-20AT with MeOH and H₂O as the mobile phase. High resolution mass spectra (HRMS) were obtained with a MICRO TOF-Q III. Infrared (IR) spectra were recorded on a Varian 1000 spectrometer using KBr disks (4000-400 cm⁻¹).

General procedure for decarboxylative arylation of α -keto acids: A 10 mL test tube was charged with α -keto acid (0.4 mmol, 2.0 equiv), bromoarene (0.2 mmol, 1.0 equiv), NiCl₂ glyme (4.38 mg, 0.02 mmol, 10 mol%), dtbbpy (6.43 mg, 0.024 mmol, 12 mol%), Cl-TXO (9.8 mg, 0.04 mmol, 20 mol%), Li₂CO₃ (29.6 mg, 0.4 mmol, 2.0 equiv) and H₂O (54.0 mg, 3.0 mmol, 15 equiv) in 6 mL degased DMF. The reaction was stirred under a nitrogen atmosphere and irradiated with a household 45 W CFL for 24 h with a fan cooling. The pure product was obtained by column chromatography on silica gel or thin-layer chromatography (TLC) using petroleum ether (PE) and ethyl acetate (EA) as the eluent.

General procedure for hydroacylation of olefins: A 10 mL test tube was charged with α -keto acid (0.4 mmol, 2.0 equiv), Michael acceptor (0.2 mmol, 1.0 equiv), Cl-TXO (9.8 mg, 0.04 mmol, 20 mol%), Cs₂CO₃ (130 mg, 0.4 mmol, 2.0 equiv) and H₂O (0.3 mL) in 6 mL degased DMF. The reaction was stirred under a nitrogen atmosphere and irradiated with a household 45 W CFL for 24 h with a fan cooling. The pure product was obtained by column chromatography on silica gel or TLC using PE and EA as the eluent.

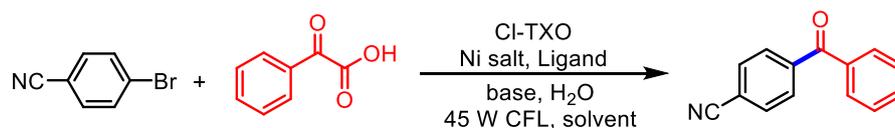
Radical trapping experiment



A 10 mL test tube was charged with phenylglyoxylic acid (30.0 mg, 0.2 mmol, 1.0 equiv), Cl-TXO (9.8 mg, 0.04 mmol, 20 mol%), TEMPO (62.4 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (130 mg, 0.4 mmol, 2.0 equiv) and degased, dried DMF (6 mL). The reaction was stirred under a 45 W CFL for 24 h. The pure 2,2,6,6-tetramethylpiperidin-1-yl benzoate was obtained by column chromatography on silica gel using PE/EA = 50/1 (v/v) as the eluent.^{S2}

Yield: 9.23 mg (18%). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.07 (d, J = 7.4, 2H), 7.57 (t, J = 7.1, 1H), 7.46 (t, J = 7.4, 2H), 1.84–1.73 (m, 2H), 1.68 (d, J = 13.3, 1H), 1.58 (d, J = 12.2, 2H), 1.46 (d, J = 12.3, 1H), 1.27 (s, 6H), 1.12 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 166.5, 132.9, 129.8, 129.6, 128.5, 60.5, 39.1, 32.0, 20.9, 17.1. QTOF-MS m/z [M + H]⁺ Calcd for C₁₆H₂₄NO₂⁺ 262.1801; Found 262.1796.

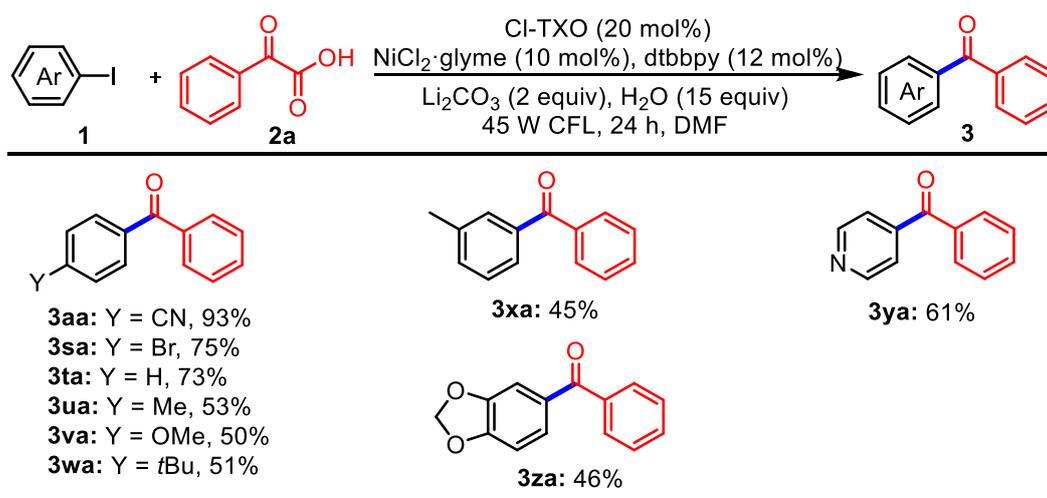
Gram scale reaction: A 100 mL flask was charged with 4-bromobenzonitrile (1.09 g, 6 mmol, 1.0 equiv), phenylglyoxylic acid (1.80 g, 12 mmol, 2.0 equiv), NiCl₂ glyme (0.132 g, 0.6 mmol, 10 mol%), dtbbpy (0.193 g, 0.72 mmol, 12 mol%), Cl-TXO (0.295 g, 1.2 mmol, 20 mol%), Li₂CO₃ (0.887 g, 12 mmol, 2.0 equiv), H₂O (1.62 g, 90 mmol, 15 equiv) and 80 mL degased DMF. The reaction was stirred under a nitrogen atmosphere and irradiated with 2 × 45 W CFLs for 72 h with a fan cooling or sunlight for 8 h. Biphenyl (0.924 g, 6 mmol) as an internal standard was added into the reaction mixture. After stirring for 30 min, the mixture was partitioned between water and ethyl acetate. The organic layer was analyzed by HPLC. Yield: 0.820 g (66% HPLC yield under 2 × 45 W CFLs) or 0.956 g (77% HPLC yield under sunlight).

Table S1. Optimization of decarboxylative arylation reaction conditions

Entry ^a	Base (equiv)	Ligand (12 mol%)	Ni cat. (10 mol%)	H ₂ O (equiv)	Solvent (mL)	Conversion	Yield
1	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	>99%	90%
2	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (4)	>99%	87%
3	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (2)	89%	73%
4	Li ₂ CO ₃ (2)	dtbbpy	Ni(OAc) ₂ ·4H ₂ O	H ₂ O (15)	DMF (6)	69%	48%
5	Li ₂ CO ₃ (2)	dtbbpy	NiSO ₄ ·6H ₂ O	H ₂ O (15)	DMF (6)	79%	53%
6	Li ₂ CO ₃ (2)	dtbbpy	NiBr ₂ ·3H ₂ O	H ₂ O (15)	DMF (6)	78%	49%
7	Li ₂ CO ₃ (2)	dtbbpy	Ni(acac) ₂	H ₂ O (15)	DMF (6)	44%	40%
8	Li ₂ CO ₃ (2)	dtbbpy	NiBr ₂	H ₂ O (15)	DMF (6)	59%	56%
9	Li ₂ CO ₃ (1.5)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	>99%	73%
10	Li ₂ CO ₃ (1.0)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	58%	47%
11	Li ₂ CO ₃ (0.5)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	49%	41%
12	NaF (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	20%	5%
13	K ₂ HPO ₄ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	35%	26%
14	Cs ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	45%	33%
15	K ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	60%	43%
16	Na ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	81%	69%
17	NaOAc (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	23%	17%
18	K ₃ PO ₄ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	36%	30%
19	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	DMSO (6)	87%	18%
20	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	MeCN (6)	19%	10%
21	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	dioxane (6)	30%	21%
22	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	CH ₂ Cl ₂ (6)	10%	7%
23	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (15)	THF (6)	42%	24%
24	Li ₂ CO ₃ (2)	dOMebpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	>99%	76%
25	Li ₂ CO ₃ (2)	dMebpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	>99%	75%
26	Li ₂ CO ₃ (2)	bpy	NiCl ₂ ·glyme	H ₂ O (15)	DMF (6)	>99%	75%
27	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (20)	DMF (6)	>99%	84%
28	Li ₂ CO ₃ (2)	dtbbpy	NiCl ₂ ·glyme	H ₂ O (10)	DMF (6)	73%	65%

^a **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), NiCl₂ glyme (0.02 mmol, 10 mol%), dtbbpy (0.024 mmol, 12 mol%), Li₂CO₃ (0.4 mmol, 2.0 equiv), H₂O (3.0 mmol, 15 equiv), Cl-TXO (20 mol%), in 6 mL DMF under N₂ atmosphere, irradiation under 45 W CFL for 24 h with a fan cooling, HPLC conversion and yield. dOMebpy = 4,4'-di-methoxy-2,2'-bipyridine, dMebpy = 4,4'-di-methyl-2,2'-bipyridine, bpy = 2,2'-bipyridine.

Scheme S1. Scope of aryl iodides^a



^a**1** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), NiCl₂.glyme (0.02 mmol, 10 mol%), dtbbpy (0.024 mmol, 12 mol%), Li₂CO₃ (0.4 mmol, 2.0 equiv), H₂O (3.0 mmol, 15 equiv), Cl-TXO (20 mol%), in 6 mL DMF under N₂ atmosphere, irradiation under 45 W CFL with a fan cooling.

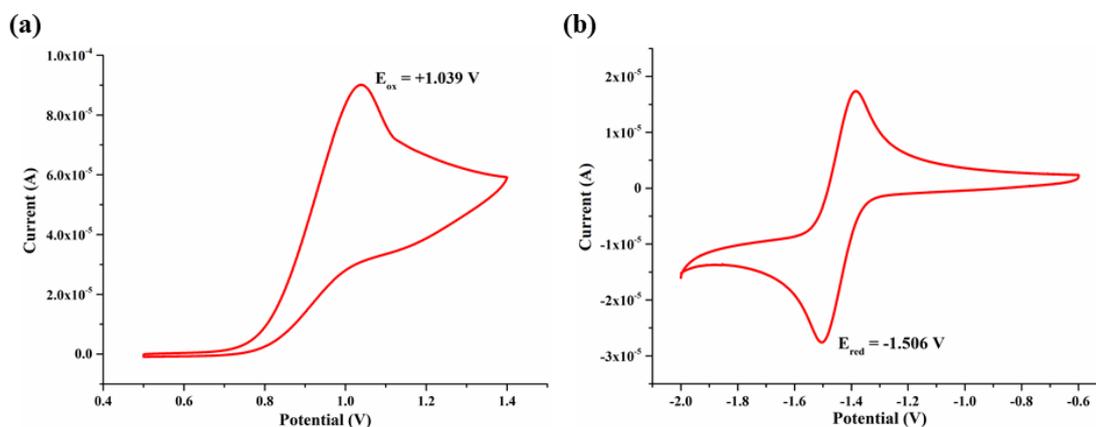


Figure S1. Cyclic voltammograms of **2a**/Li₂CO₃ (a), Cl-TXO (b) using (n-Bu)₄NPF₆ as the electrolyte (0.05 M) in DMF at 100 mV/s scan rate. Working electrode: glassy carbon electrode tip (3 mm diameter); Counter electrode: platinum wire; Reference electrode: Saturated Calomel Electrode (SCE). Upon excitation at $\lambda_{ex} = 374$ nm, the emission maxima of Cl-TXO (Figure S2) is at $\lambda_{em} = 417$ nm, which translates into the excited-state energy $E_{00}(\text{Cl-TXO}^*/\text{Cl-TXO})$ of -2.974 V. The reduction potential of Cl-TXO* was calculated to be 1.468 V employing the equation: $E_{red}^* = E_{red} - E_{00}$.

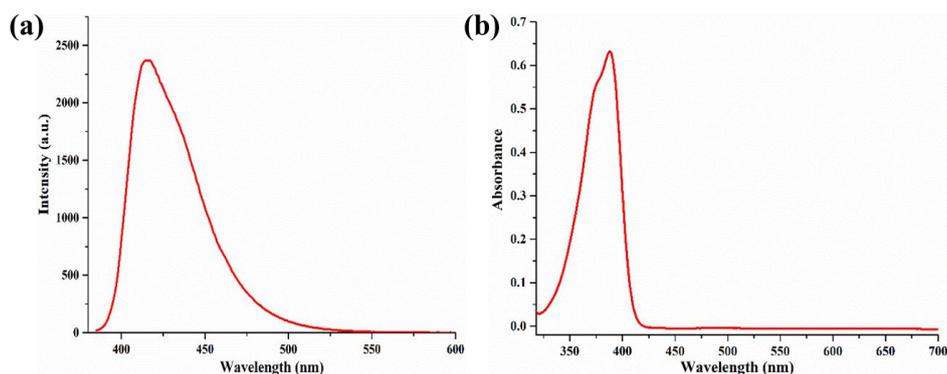


Figure S2. The emission spectrum ($\lambda_{\text{ex}} = 374 \text{ nm}$, $\lambda_{\text{em}} = 417 \text{ nm}$) (a) and absorbance spectrum (b) of Cl-TXO in DMF (10^{-4} M)

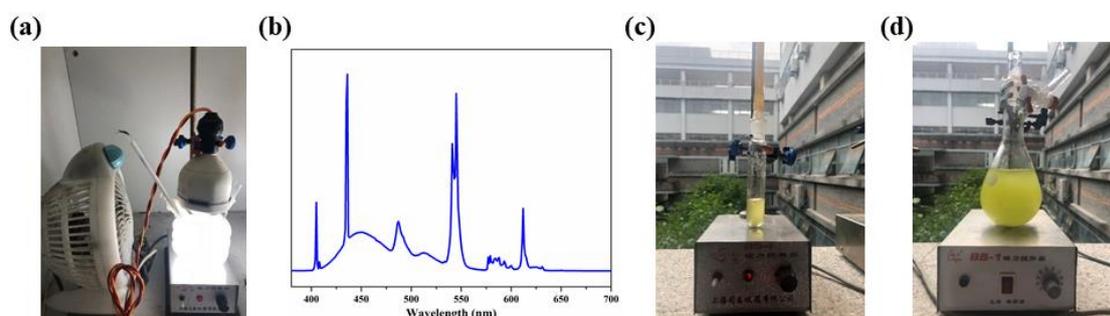


Figure S3. The reaction set-up with 45 W CFL (the power density is about 0.81 mW cm^{-2}) (a), the output spectrum of 45 W CFL (b), the reaction set-up under sunlight (c) and gram scale reaction set-up under sunlight (d)

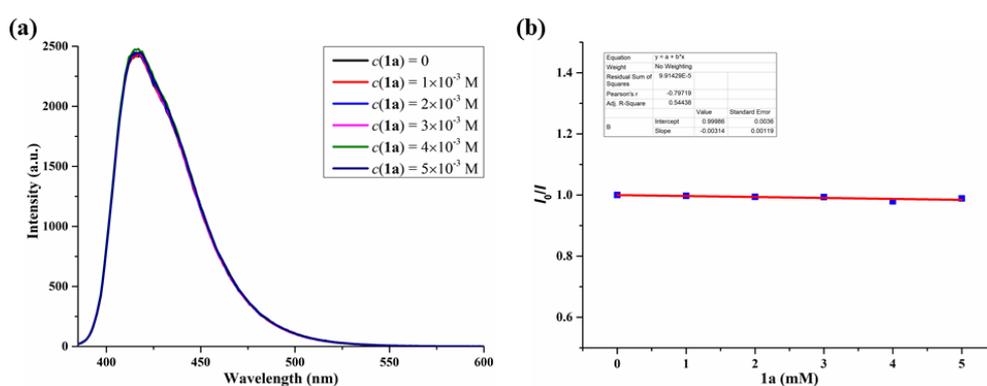


Figure S4. (a) Emission spectra of Cl-TXO in DMF (10^{-4} M) in the presence of increasing **1a** concentrations excited at $\lambda = 374 \text{ nm}$. (b) Stern-Volmer plot of I_0/I versus **1a** concentration in Cl-TXO DMF solution (I_0 and I represent the intensities of the emission in the absence and presence of the quencher)

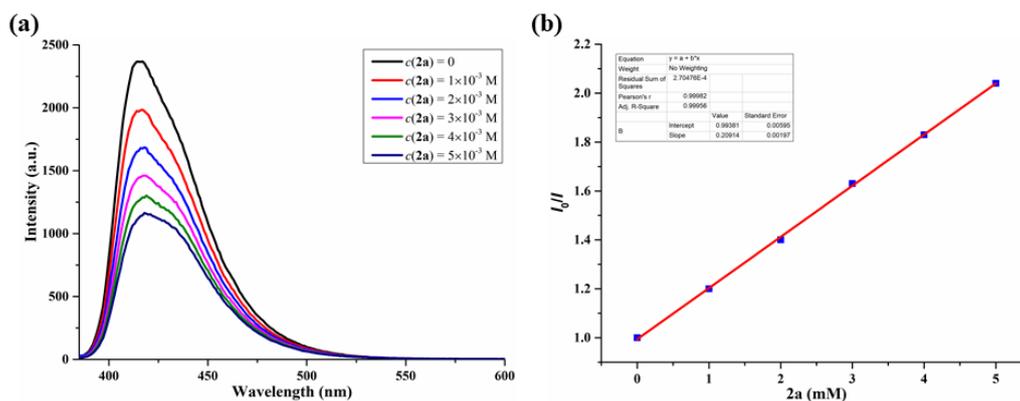


Figure S5. (a) Emission spectra of Cl-TXO in DMF (10^{-4} M) in the presence of increasing **2a** with excess Li_2CO_3 in DMF excited at $\lambda = 374$ nm. (b) Stern-Volmer plot of I_0/I versus **2a** concentration in Cl-TXO DMF solution (I_0 and I represent the intensities of the emission in the absence and presence of the quencher)

Photocatalytic CO_2 evolution reaction. In a top-irradiation Pyrex vessel was added phenylglyoxylic acid (600 mg, 4 mmol, 2.0 equiv), 4-bromobenzonitrile (362 mg, 2 mmol, 1.0 equiv), NiCl_2 glyme (43.8 mg, 0.2 mmol, 10 mol%), dtbbpy (64.3 mg, 0.24 mmol, 12 mol%), Cl-TXO (98 mg, 0.4 mmol, 20 mol%), Li_2CO_3 (296 mg, 4 mmol, 2.0 equiv) and H_2O (540 mg, 30 mmol, 15 equiv) in 60 mL degassed DMF. This dispersion was ultrasonicated for 30 min and the resulting suspension purged with nitrogen for 30 min to remove air. The reaction vessel was linked to a full glass automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfect Light Technology Co., Ltd, China) and the amount of CO_2 was determined using online gas chromatography (GC7900, Tianmei, China) with a TCD detector using argon as carrier gas. The photocatalytic experiments involved direct irradiation of the solution by a 300 W Xe-lamp with a cut-off filter ($\lambda > 400$ nm). The reaction temperature was maintained at 25°C using a water-cooling system.

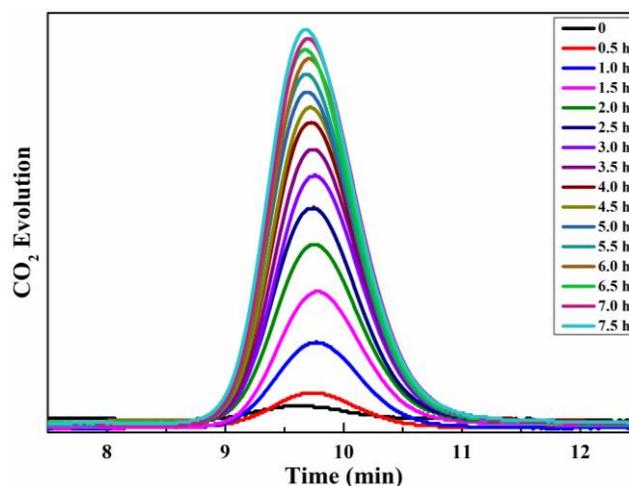
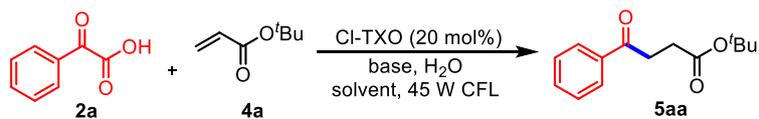
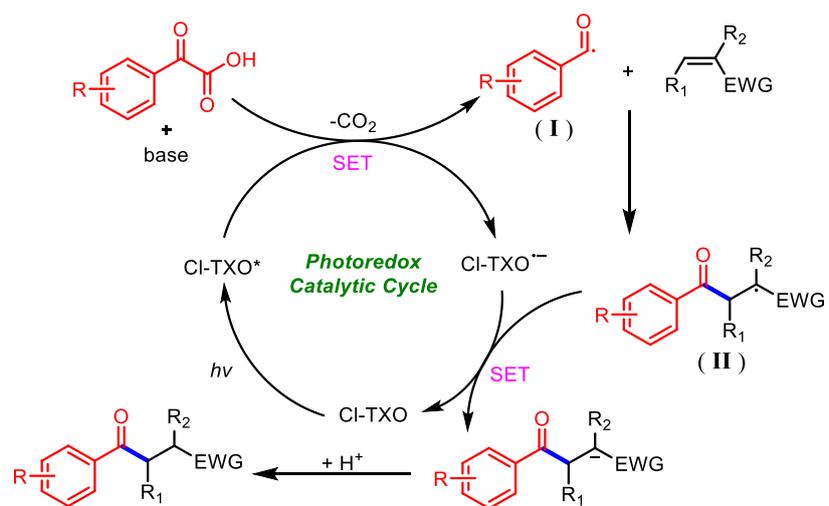


Figure S6. Time-dependent photocatalytic CO_2 production

Table S2. Optimization of photoredox-catalyzed hydroacylation of olefins

Entry ^a	Base (equiv.)	H ₂ O (mL)	Solvent (mL)	Yield
1	Li ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	27%
2	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	71%
3	K ₂ HPO ₄ (2)	H ₂ O (0.3)	DMF (6)	34%
4	K ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	57%
5	Na ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	37%
6	K ₃ PO ₄ (2)	H ₂ O (0.3)	DMF (6)	44%
7	NaF (2)	H ₂ O (0.3)	DMF (6)	7%
8	Cs ₂ CO ₃ (2)	H ₂ O (0.1)	DMF (6)	42%
9	Cs ₂ CO ₃ (2)	H ₂ O (0.2)	DMF (6)	64%
10	Cs ₂ CO ₃ (2)	H ₂ O (0.4)	DMF (6)	54%
11	Cs ₂ CO ₃ (2)	H ₂ O (0.5)	DMF (6)	50%
12	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	DMSO (6)	24%
13	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	MeCN (6)	32%
14	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	CHCl ₃ (6)	2%
15	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	MeOH (6)	11%
16	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	THF (6)	6%
17	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	DME (6)	53%
18	Cs ₂ CO ₃ (2)	-	DMF (6)	40%
19	-	H ₂ O (0.3)	DMF (6)	0
20 ^b	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	<1%
21 ^c	Cs ₂ CO ₃ (2)	H ₂ O (0.3)	DMF (6)	0

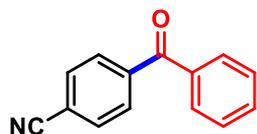
^a **2a** (0.4 mmol, 2 equiv), **4a** (0.2 mmol, 1 equiv), Cs₂CO₃ (0.4 mmol, 2.0 equiv), H₂O (0.3 mL), Cl-TXO (20 mol%), in 6 mL DMF under N₂ atmosphere, irradiation under 45 W CFL for 24 h with a fan cooling, HPLC yield. ^b Without Cl-TXO. ^c In the dark.



Scheme S2. The mechanism of photoredox-catalyzed hydroacylation of olefins

NMR data of products

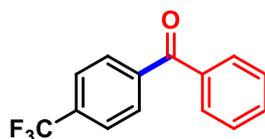
4-benzoylbenzonitrile (**3aa**)^{S3}



Following the General Procedure with 4-bromobenzonitrile or 4-iodobenzonitrile (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3aa** (36.4 mg, 88% for 4-bromobenzonitrile; 38.5 mg, 93% for 4-iodobenzonitrile).

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.88 (d, J = 8.0 Hz, 2H), 7.79 (dd, J = 7.8, 2.8 Hz, 4H), 7.65 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.3, 141.5, 136.6, 133.6, 132.4, 130.5, 130.3, 128.9, 118.3, 115.9. QTOF-MS m/z [M + H]⁺ Calcd for C₁₄H₁₀NO⁺ 208.0757; Found 208.0741.

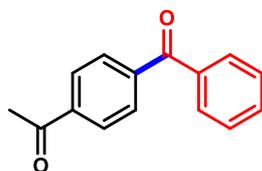
phenyl(4-(trifluoromethyl)phenyl)methanone (**3ba**)^{S3}



Following the General Procedure with 1-bromo-4-(trifluoromethyl)benzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ba** (43.0 mg) in 86% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.90 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.8, 140.9, 136.9, 134.4 (q, J = 32.7 Hz), 133.3, 130.4, 130.3, 128.8, 125.6 (q, J = 3.7 Hz), 123.9 (q, J = 272.6 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ = -63.01. QTOF-MS m/z [M + H]⁺ Calcd for C₁₄H₁₀F₃O⁺ 251.0678; Found 251.0682.

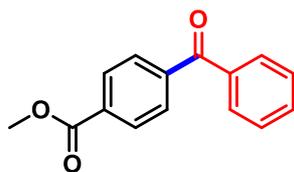
1-(4-benzoylphenyl)ethan-1-one (**3ca**)^{S4}



Following the General Procedure with 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ca** (37.6 mg) in 84% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.05 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 2.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 197.7, 196.1, 141.5, 139.7, 137.1, 133.2, 130.3, 130.2, 128.7, 128.4, 27.1. QTOF-MS m/z [M + H]⁺ Calcd for C₁₅H₁₃O₂⁺ 225.0910; Found 225.0926.

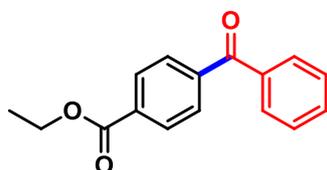
methyl 4-benzoylbenzoate (3da)^{S4}



Following the General Procedure with methyl 4-bromobenzoate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3da** (40.8 mg) in 85% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.14 (d, J = 8.1 Hz, 2H), 7.81 (dd, J = 14.7, 7.8 Hz, 4H), 7.61 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 196.2, 166.5, 141.5, 137.1, 133.4, 133.1, 130.3, 129.9, 129.7, 128.6, 52.6, 1.2. QTOF-MS m/z [M + H]⁺ Calcd for C₁₅H₁₃O₃⁺ 241.0859; Found 241.0831.

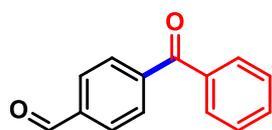
ethyl 4-benzoylbenzoate (3ea)^{S3}



Following the General Procedure with the corresponding ethyl 4-bromobenzoate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **3ea** (44.2 mg) in 87% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.15 (d, J = 8.0 Hz, 2H), 7.81 (dd, J = 13.5, 7.9 Hz, 4H), 7.61 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 4.42 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 196.3, 166.0, 141.4, 137.2, 133.8, 133.1, 130.3, 129.9, 129.6, 128.6, 61.6, 14.5. QTOF-MS m/z [M + H]⁺ Calcd for C₁₆H₁₅O₃⁺ 255.1016; Found 255.1033.

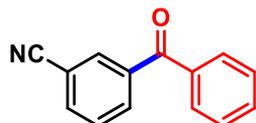
4-benzoylbenzaldehyde (3fa)^{S3}



Following the General Procedure with 4-bromobenzaldehyde (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3fa** (25.6 mg) in 61% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 10.14 (s, 1H), 8.01 (d, J = 7.8 Hz, 2H), 7.93 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 196.1, 191.9, 142.8, 138.7, 136.9, 133.4, 130.6, 130.4, 129.7, 128.7. QTOF-MS m/z [M + H]⁺ Calcd for C₁₄H₁₁O₂⁺ 211.0754; Found 211.0748.

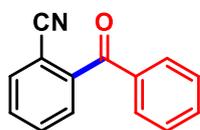
3-benzoylbenzotrile (3ga)^{S5}



Following the General Procedure with 3-bromobenzonitrile (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ga** (29.4 mg) in 71% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.10–8.00 (m, 2H), 7.86 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.68–7.59 (m, 2H), 7.51 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 194.6, 138.8, 136.5, 135.5, 134.0, 133.6, 133.5, 130.2, 129.6, 128.9, 118.1, 113.0. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{NO}^+$ 208.0757; Found 208.0758.

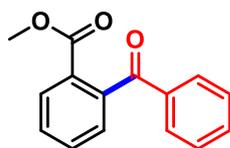
2-benzoylbenzonitrile (**3ha**)^{S6}



Following the General Procedure with 2-bromobenzonitrile (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ha** (24.0 mg) in 58% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.82 (dd, J = 12.7, 7.6 Hz, 3H), 7.74–7.60 (m, 4H), 7.50 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 194.0, 141.7, 136.2, 134.4, 134.1, 132.3, 131.6, 130.5, 130.2, 128.8, 117.2, 112.1, 76.9. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{NO}^+$ 208.0757; Found 208.0764.

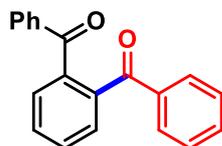
methyl 2-benzoylbenzoate (**3ia**)^{S7}



Following the General Procedure with methyl 2-bromobenzoate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ia** (23.5 mg) in 49% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.05 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.56 (dd, J = 16.0, 7.7 Hz, 2H), 7.43 (t, J = 8.5 Hz, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 197.2, 166.6, 141.9, 137.4, 133.3, 132.6, 130.3, 129.9, 129.5, 128.7, 128.0, 52.4. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3^+$ 241.0859; Found 241.0868.

1,2-phenylenebis(phenylmethanone) (**3ja**)^{S8}

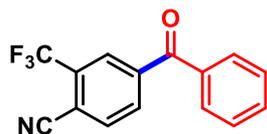


Following the General Procedure with (2-bromophenyl)(phenyl)methanone (0.2 mmol) and

phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **3ja** (23.5 mg) in 41% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.70 (d, J = 7.6 Hz, 4H), 7.62 (s, 4H), 7.52 (t, J = 7.3 Hz, 2H), 7.38 (t, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.8, 140.3, 137.4, 133.2, 130.6, 130.1, 129.9, 128.6, 53.6. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{O}_2^+$ 287.1067; Found 287.1052.

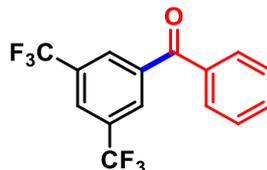
4-benzoyl-2-(trifluoromethyl)benzonitrile (**3ka**)



Following the General Procedure with 4-bromo-2-(trifluoromethyl)benzonitrile (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ka** (46.2 mg) in 84% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.19 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.7, 141.7, 135.8, 135.1, 134.1, 133.5 (d, J = 33.4 Hz), 133.2, 130.3, 129.1, 127.8 (q, J = 4.6 Hz), 122.2 (q, J = 274.4 Hz), 114.9, 113.3 (q, J = 1.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ = -61.98. m.p. = 92.8–93.5 °C. IR (KBr disc, cm^{-1}): 2962, 2927, 2856, 2229, 1746, 1668, 1598, 1498, 1450, 1429, 1319, 1262, 1205, 1176, 1098, 1049, 1023, 963, 924, 863, 798, 747, 719, 698, 666, 585, 559. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_9\text{F}_3\text{NO}^+$ 276.0631; Found 276.0656.

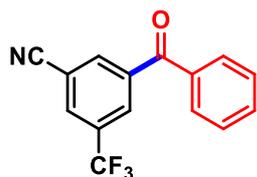
(3,5-bis(trifluoromethyl)phenyl)(phenyl)methanone (**3la**)^{S4}



Following the General Procedure with 1-bromo-3,5-bis(trifluoromethyl)benzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless solid **3la** (54.7 mg) in 86% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.24 (s, 2H), 8.10 (s, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.8, 139.6, 136.1, 133.9, 132.3 (q, J = 34.0 Hz), 130.2, 130.0 (q, J = 3.3 Hz), 129.1, 125.9 (dt, J = 7.4, 3.7 Hz), 123.1 (q, J = 273.1 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ = -62.90. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_9\text{F}_6\text{O}^+$ 319.0552; Found 319.0548.

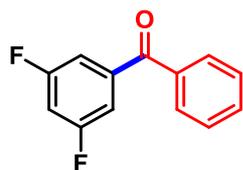
3-benzoyl-5-(trifluoromethyl)benzonitrile (**3ma**)



Following the General Procedure with 3-bromo-5-(trifluoromethyl)benzonitrile (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ma** (42.9 mg) in 78% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.28 (s, 1H), 8.23 (s, 1H), 8.12 (s, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.0, 139.9, 136.5, 135.7, 134.1, 132.8 (q, J = 34.4 Hz), 132.1 (q, J = 3.7 Hz), 130.6 (q, J = 3.5 Hz), 130.2, 129.2, 122.7 (q, J = 273.3 Hz), 116.8, 114.2. ^{19}F NMR (377 MHz, CDCl_3) δ = -63.08. m.p. = 78.1–78.7 °C. IR (KBr disc, cm^{-1}): 3073, 2956, 2924, 2851, 2239, 1732, 1658, 1599, 1579, 1451, 1353, 1323, 1311, 1277, 1262, 1199, 1182, 1164, 1152, 1138, 1109, 1082, 983, 913, 888, 801, 725, 706, 692, 664, 639, 615. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_9\text{F}_3\text{NO}^+$ 276.0631; Found 276.0639.

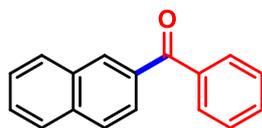
(3,5-difluorophenyl)(phenyl)methanone (**3na**)^{S9}



Following the General Procedure with 1-bromo-3,5-difluorobenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3na** (38.8 mg) in 89% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.79 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 5.7 Hz, 2H), 7.05 (t, J = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 194.1, 164.2 (d, J = 11.7 Hz), 161.7 (d, J = 11.6 Hz), 136.6, 133.4, 130.2, 128.8, 113.2 (q, J = 6.4 Hz), 107.9 (t, J = 24.5 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ = -108.14. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{F}_2\text{O}^+$ 219.0616; Found 219.0631.

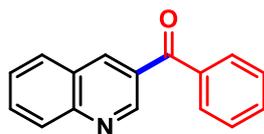
naphthalen-2-yl(phenyl)methanone (**3oa**)^{S5}



Following the General Procedure with 2-bromonaphthalene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3oa** (32.9 mg) in 71% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.27 (s, 1H), 8.00–7.89 (m, 4H), 7.87 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 4.4 Hz, 2H), 7.54 (dt, J = 14.8, 7.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 197.0, 138.1, 135.5, 135.0, 132.6, 132.5, 132.1, 130.3, 129.6, 128.6, 128.5, 128.5, 128.0, 127.0, 126.0. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{13}\text{O}^+$ 233.0961; Found 233.0945.

phenyl(quinolin-3-yl)methanone (**3pa**)^{S10}



Following the General Procedure with 3-bromoquinoline (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the white solid **3pa** (28.0 mg) in 60% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 9.33 (s, 1H), 8.56 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.86 (t, J = 8.0 Hz, 3H), 7.65 (q, J = 7.4 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.1, 150.5, 149.7, 139.0, 137.2, 133.3, 132.1, 130.3, 130.2, 129.7, 129.4, 128.9, 127.8, 126.8. QTOF-MS m/z [M + H]⁺ Calcd for C₁₆H₁₂NO⁺ 234.0913; Found 234.0916.

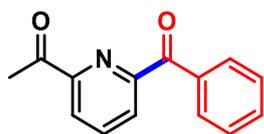
phenyl(6-(trifluoromethyl)pyridin-2-yl)methanone (**3qa**)



Following the General Procedure with 2-bromo-6-(trifluoromethyl)pyridine or 2-chloro-6-(trifluoromethyl)pyridine (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the yellow oil **3qa** (39.2 mg, 78% for 2-bromo-6-(trifluoromethyl)pyridine; 25.6 mg, 51% for 2-chloro-6-(trifluoromethyl)pyridine).

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.24 (d, J = 7.8 Hz, 1H), 8.19 (d, J = 7.6 Hz, 2H), 8.10 (t, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 191.9, 155.4, 147.2 (q, J = 35.4 Hz), 141.1, 138.9, 135.6, 134.4, 133.6, 131.5, 130.7, 128.9, 128.5, 127.3, 122.9 (q, J = 2.5 Hz), 121.4 (q, J = 274.5 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ = -67.89. IR (KBr disc, cm⁻¹): 2958, 2924, 2853, 1735, 1638, 1495, 1459, 1394, 1378, 1347, 1314, 1252, 1189, 1157, 1079, 1066, 1057, 969, 878, 816, 712, 585. QTOF-MS m/z [M + H]⁺ Calcd for C₁₃H₉F₃NO⁺ 252.0631; Found 252.0650.

1-(6-benzoylpyridin-2-yl)ethan-1-one (**3ra**)

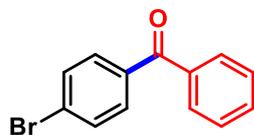


Following the General Procedure with 1-(6-bromopyridin-2-yl)ethan-1-one (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the yellow oil **3ra** (36.0 mg) in 80% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.22 (dd, J = 13.1, 7.8 Hz, 2H), 8.16 (d, J = 7.7 Hz, 2H), 8.04 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 2.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 199.6, 192.7, 154.3, 152.2, 138.3, 136.1, 133.2, 131.3, 128.2, 127.9, 124.0, 25.9. IR (KBr disc, cm⁻¹): 3061, 1702, 1666, 1597, 1577, 1447, 1418, 1358, 1322, 1309,

1238, 1166, 1107, 1080, 995, 952, 836, 814, 786, 739, 716, 692, 642, 628, 594. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{14}H_{12}NO_2^+$ 226.0862; Found 226.0868.

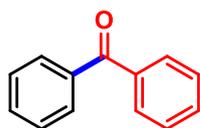
(4-bromophenyl)(phenyl)methanone (3sa)^{S3}



Following the General Procedure with 1-bromo-4-iodobenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3sa** (38.9 mg) in 75% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.77 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.61 (dd, J = 12.9, 7.8 Hz, 3H), 7.49 (t, J = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.9, 137.4, 136.5, 132.9, 131.8, 131.8, 130.2, 128.6, 127.7. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{13}H_{10}BrO^+$ 260.9910; Found 260.9912.

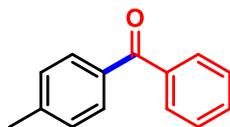
benzophenone (3ta)^{S7}



Following the General Procedure with iodobenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ta** (26.6 mg) in 73% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.81 (d, J = 7.5 Hz, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.49 (t, J = 7.5 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 197.0, 137.8, 132.6, 130.3, 128.5. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{13}H_{11}O^+$ 183.0804; Found 183.0812.

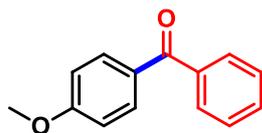
phenyl(p-tolyl)methanone (3ua)^{S3}



Following the General Procedure with 1-iodo-4-methylbenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ua** (20.0 mg) in 51% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.78 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 196.8, 143.5, 138.2, 135.1, 132.4, 130.5, 130.2, 129.2, 128.4, 21.9. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{14}H_{13}O^+$ 197.0961; Found 197.0946.

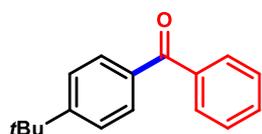
(4-methoxyphenyl)(phenyl)methanone (3va)^{S3}



Following the General Procedure with 1-iodo-4-methoxybenzene (0.2 mmol) phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3va** (22.0 mg) in 52% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.82 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 195.8, 163.4, 138.5, 132.8, 132.1, 130.4, 129.9, 128.4, 113.8, 55.7. QTOF-MS m/z $[M + H]^+$ Calcd for $\text{C}_{14}\text{H}_{13}\text{O}_2^+$ 213.0910; Found 213.0911.

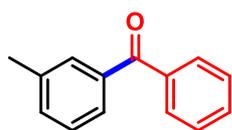
(4-(tert-butyl)phenyl)(phenyl)methanone (**3wa**)^{S5}



Following the General Procedure with 1-(tert-butyl)-4-iodobenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **3wa** (24.3 mg) in 51% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.85 (dd, J = 15.8, 7.8 Hz, 4H), 7.65 (t, J = 7.2 Hz, 1H), 7.60–7.49 (m, 4H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.7, 156.4, 138.2, 135.0, 132.4, 130.4, 130.2, 128.4, 125.5, 35.3, 31.4. QTOF-MS m/z $[M + H]^+$ Calcd for $\text{C}_{17}\text{H}_{19}\text{O}^+$ 239.1430; Found 239.1438.

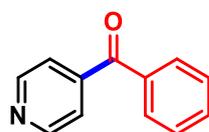
phenyl(m-tolyl)methanone (**3xa**)^{S3}



Following the General Procedure with 1-iodo-3-methylbenzene (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3xa** (17.6 mg) in 45% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.79 (d, J = 7.6 Hz, 2H), 7.62 (s, 1H), 7.56 (d, J = 6.1 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.35 (dt, J = 15.0, 7.3 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 197.0, 138.2, 137.8, 137.7, 133.3, 132.4, 130.5, 130.1, 128.3, 128.2, 127.5, 21.4. QTOF-MS m/z $[M + H]^+$ Calcd for $\text{C}_{14}\text{H}_{13}\text{O}^+$ 197.0961; Found 197.0973.

phenyl(pyridin-4-yl)methanone (**3ya**)^{S11}

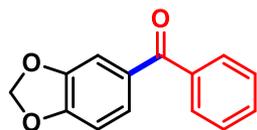


Following the General Procedure with 4-iodopyridine (0.2 mmol) and phenylglyoxylic acid (0.4

mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the white solid **3ya** (22.3 mg) in 61% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.80 (d, J = 4.5 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.57 (d, J = 5.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 195.4, 150.6, 144.6, 136.1, 133.7, 130.3, 128.9, 123.1. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{10}\text{NO}^+$ 184.0757; Found 184.0736.

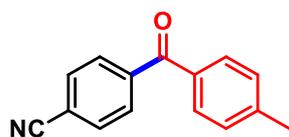
benzo[*d*][1,3]dioxol-5-yl(phenyl)methanone (**3za**)^{S3}



Following the General Procedure with 5-iodobenzo[*d*][1,3]dioxole (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3za** (20.3 mg) in 45% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.74 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.7 Hz, 2H), 6.86 (d, J = 8.1 Hz, 1H), 6.06 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 195.3, 151.7, 148.1, 138.3, 132.2, 132.1, 129.9, 128.4, 127.1, 110.1, 107.9, 102.0. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{O}_3^+$ 227.0703; Found 227.0698.

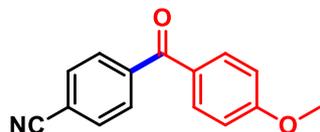
4-(4-methylbenzoyl)benzonitrile (**3ab**)^{S12}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-oxo-2-(*p*-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ab** (40.7 mg) in 92% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.84 (d, J = 7.9 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 194.9, 144.6, 141.8, 133.8, 132.3, 130.5, 130.3, 129.5, 118.3, 115.6, 21.9. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{NO}^+$ 222.0913; Found 222.0913.

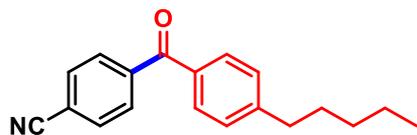
4-(4-methoxybenzoyl)benzonitrile (**3ac**)^{S5}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(4-methoxyphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ac** (44.1 mg) in 93% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.79 (q, J = 8.0 Hz, 6H), 6.98 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.9, 164.1, 142.3, 132.8, 132.3, 130.1, 129.1, 118.3, 115.3, 114.1, 55.8. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{NO}_2^+$ 238.0863; Found 238.0867.

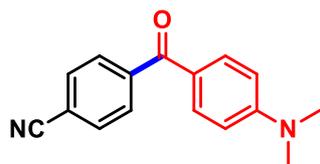
4-(4-pentylbenzoyl)benzonitrile (**3ad**)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-oxo-2-(4-pentylphenyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **3ad** (49.9 mg) in 90% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.88 – 7.84 (m, 2H), 7.80 – 7.76 (m, 2H), 7.73–7.69 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 2.74–2.65 (m, 2H), 1.66 (dt, J = 15.1, 7.5 Hz, 2H), 1.35 (dd, J = 7.2, 3.8 Hz, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 195.0, 149.6, 141.9, 134.0, 132.3, 130.5, 130.3, 128.9, 118.3, 115.6, 36.2, 31.6, 31.0, 22.7, 14.2. IR (KBr disc, cm^{-1}): 2956, 2929, 2858, 2231, 1741, 1661, 1606, 1557, 1466, 1413, 1403, 1310, 1277, 1177, 1144, 1110, 1019, 930, 861, 763, 684, 634, 585, 543. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}^+$ 278.1539; Found 278.1540.

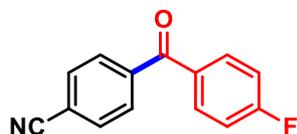
4-(4-(dimethylamino)benzoyl)benzonitrile (**3ae**)^{S13}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(4-(dimethylamino)phenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the yellow solid **3ae** (41.0 mg) in 82% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.76 (dt, J = 8.9, 6.9 Hz, 6H), 6.68 (d, J = 9.0 Hz, 2H), 3.10 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.3, 154.0, 143.6, 133.0, 132.2, 129.9, 123.7, 118.6, 114.6, 110.9, 40.3. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}^+$ 251.1179; Found 251.1172.

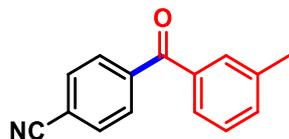
4-(4-fluorobenzoyl)benzonitrile (**3af**)^{S14}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(4-fluorophenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3af** (23.4 mg) in 52% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.82 (q, J = 8.1 Hz, 6H), 7.19 (t, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 193.7, 166.1 (d, J = 256.0 Hz), 141.3, 133.0 (d, J = 9.3 Hz), 132.8 (d, J = 2.9 Hz), 132.5, 130.3, 117.0 (d, J = 217.2 Hz), 116.2, 116.0. ^{19}F NMR (377 MHz, CDCl_3) δ = -104.00. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_9\text{FNO}^+$ 226.0663; Found 226.0675.

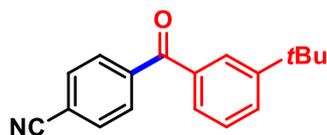
4-(3-methylbenzoyl)benzonitrile (**3ag**)^{S15}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-oxo-2-(m-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ag** (36.2 mg) in 82% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.86 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.60 (s, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.4, 141.6, 138.8, 136.6, 134.3, 132.3, 130.6, 130.4, 128.6, 127.6, 118.2, 115.7, 21.5. QTOF-MS m/z [M + H]⁺ Calcd for C₁₅H₁₂NO⁺ 222.0913; Found 222.0919.

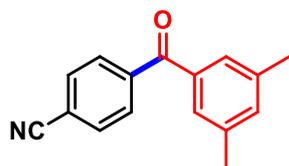
4-(3-(tert-butyl)benzoyl)benzonitrile (**3ah**)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(3-(tert-butyl)phenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ah** (42.1 mg) in 80% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.87 (t, J = 6.8 Hz, 3H), 7.79 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.6, 152.2, 141.7, 136.3, 132.3, 130.7, 130.4, 128.4, 127.8, 127.0, 118.3, 115.8, 35.1, 31.4. m.p. = 97.3–98.0 °C. IR (KBr disc, cm⁻¹): 2960, 2924, 2869, 2229, 1733, 1656, 1605, 1458, 1395, 1379, 1364, 1315, 1298, 1248, 1081, 952, 855, 816, 766, 745, 712, 605, 547. QTOF-MS m/z [M + H]⁺ Calcd for C₁₈H₁₈NO⁺ 264.1383; Found 264.1366.

4-(3,5-dimethylbenzoyl)benzonitrile (**3ai**)

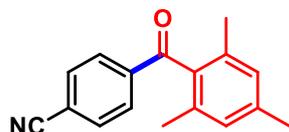


Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(3,5-dimethylphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ai** (39.5 mg) in 84% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.86 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.37 (s, 2H), 7.26 (s, 1H), 2.38 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 195.7, 141.8, 138.6, 136.7, 135.2, 132.3, 130.4, 128.0, 118.3, 115.7, 21.4. m.p. = 104.1–104.9 °C. IR (KBr disc, cm⁻¹): 2958,

2923, 2229, 1732, 1668, 1632, 1457, 1382, 1317, 1228, 1066, 1050, 866, 851, 763, 716, 605, 549. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{16}H_{14}NO^+$ 236.1070; Found 236.1073.

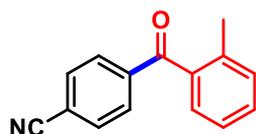
4-(2,4,6-trimethylbenzoyl)benzonitrile (**3aj**)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-mesityl-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3aj** (36.4 mg) in 73% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.88 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.9 Hz, 2H), 6.91 (s, 2H), 2.33 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 199.5, 140.4, 139.5, 135.8, 134.4, 132.9, 129.8, 128.8, 118.1, 116.9, 21.4, 19.6. m.p. = 127.5–128.2 °C. IR (KBr disc, cm^{-1}): 2954, 2923, 2229, 1670, 1608, 1568, 1455, 1406, 1378, 1313, 1292, 1265, 1171, 1034, 959, 911, 861, 848, 769, 740, 692, 561, 549, 534. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{17}H_{16}NO^+$ 250.1226; Found 250.1234.

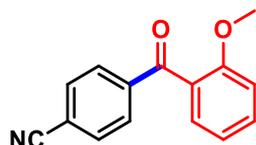
4-(2-methylbenzoyl)benzonitrile (**3ak**)^{S16}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-oxo-2-(o-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless oil **3ak** (33.2 mg) in 75% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.89 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 6.7 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.31–7.24 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.0, 141.3, 137.7, 137.2, 132.5, 131.6, 131.4, 130.5, 129.1, 125.6, 118.2, 116.4, 20.3. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{15}H_{12}NO^+$ 222.0913; Found 222.0906.

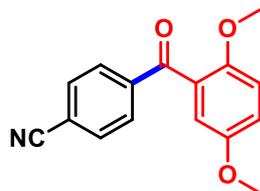
4-(2-methoxybenzoyl)benzonitrile (**3al**)^{S17}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(2-methoxyphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **3al** (36.5 mg) in 77% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.85 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.54–7.50 (m, 1H), 7.43 (dd, J = 7.5, 1.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 195.2, 157.8, 141.7, 133.3, 132.3, 130.4, 129.9, 127.6, 121.1, 118.41, 115.9, 111.7, 55.7. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{15}H_{12}NO_2^+$ 238.0863; Found 238.0879.

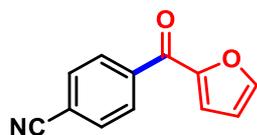
4-(2,5-dimethoxybenzoyl)benzonitrile (**3am**)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(2,5-dimethylphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **3am** (38.4 mg) in 72% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.86 (d, J = 7.9 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 8.9 Hz, 1H), 6.98 (s, 1H), 6.93 (d, J = 9.0 Hz, 1H), 3.80 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 195.0, 154.0, 152.0, 141.6, 132.3, 130.0, 128.1, 119.0, 118.4, 116.0, 114.9, 113.3, 56.3, 56.1. m.p. = 72.8–73.4 °C. IR (KBr disc, cm^{-1}): 2957, 2924, 2852, 2229, 1734, 1676, 1605, 1587, 1495, 1467, 1422, 1316, 1287, 1265, 1221, 1185, 1153, 1081, 1049, 1022, 967, 865, 850, 811, 771, 721, 693. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_3^+$ 268.0968; Found 268.0981.

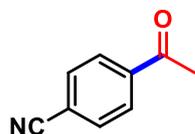
4-(furan-2-carbonyl)benzonitrile (**3an**)^{S18}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(furan-2-yl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **3an** (20.1 mg) in 51% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.08 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 1.0 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 6.65 (dd, J = 3.6, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 180.8, 152.1, 148.0, 140.8, 132.5, 129.9, 121.5, 118.2, 116.1, 112.9. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_8\text{NO}_2^+$ 198.0550; Found 198.0538.

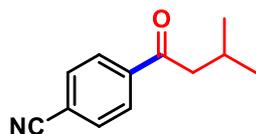
4-acetylbenzonitrile (**3ao**)^{S19}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-oxopropanoic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **3ao** (12.8 mg) in 44% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.04 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.7, 140.1, 132.7, 128.9, 118.1, 116.6, 26.9. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_9\text{H}_8\text{NO}^+$ 146.0600; Found 146.0612.

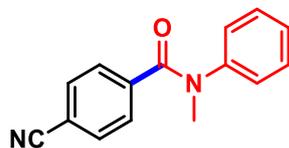
4-(3-methylbutanoyl)benzonitrile (**3ap**)^{S20}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-methyl-2-oxopentanoic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless oil **3ap** (17.2 mg) in 46% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.02 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 2.84 (d, J = 6.8 Hz, 2H), 2.36–2.20 (m, 1H), 0.99 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 198.9, 140.5, 132.7, 128.7, 118.2, 116.3, 47.9, 25.1, 22.8. QTOF-MS m/z [M + H]⁺ Calcd for C₁₂H₁₄NO⁺ 188.1070; Found 188.1073.

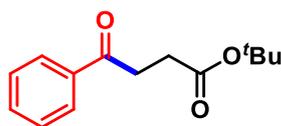
4-cyano-N-methyl-N-phenylbenzamide (**3aq**)^{S21}



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-(methyl(phenyl)amino)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the yellow solid **3aq** (29.3 mg) in 62% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.46 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.26–7.23 (m, 2H), 7.22–7.17 (m, 1H), 7.02 (d, J = 7.4 Hz, 2H), 3.51 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 168.8, 144.1, 140.5, 131.8, 129.7, 129.4, 127.5, 127.1, 118.3, 113.4, 38.5. QTOF-MS m/z [M + H]⁺ Calcd for C₁₅H₁₃N₂O⁺ 237.1022; Found 237.1018.

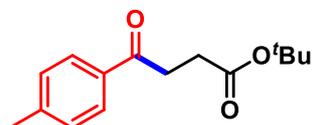
tert-butyl 4-oxo-4-phenylbutanoate (**5aa**)^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5aa** (31.4 mg) in 67% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.97 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.9 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 3.24 (t, J = 6.7 Hz, 2H), 2.67 (t, J = 6.7 Hz, 2H), 1.44 (s, 9H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 198.5, 172.3, 136.9, 133.2, 128.7, 128.2, 80.7, 33.6, 29.6, 28.2. QTOF-MS m/z [M + H]⁺ Calcd for C₁₄H₁₉O₃⁺ 235.1329; Found 235.1335.

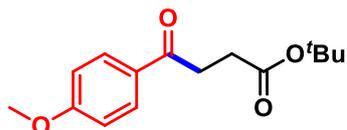
tert-butyl 4-oxo-4-(*p*-tolyl)butanoate (**5ab**)^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-oxo-2-(*p*-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **5ab** (33.7 mg) in 68% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.88 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.23 (t, J = 6.6 Hz, 2H), 2.67 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 198.2, 172.4, 144.0, 134.5, 129.4, 128.3, 80.7, 33.5, 29.7, 28.3, 21.8. QTOF-MS m/z [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ $^+$ 249.1485; Found 249.1482.

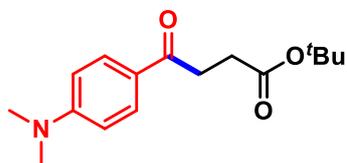
***tert*-butyl 4-(4-methoxyphenyl)-4-oxobutanoate (5ac)**^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(4-methoxyphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **5ac** (37.5 mg) in 71% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.96 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.20 (t, J = 6.7 Hz, 2H), 2.65 (t, J = 6.7 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 197.1, 172.5, 163.7, 130.5, 130.1, 113.9, 80.7, 55.6, 33.3, 29.8, 28.3. QTOF-MS m/z [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_4$ $^+$ 265.1434; Found 265.1430.

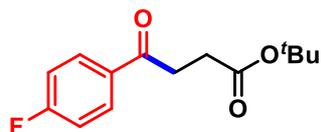
***tert*-butyl 4-(4-(dimethylamino)phenyl)-4-oxobutanoate (5ad)**



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(4-(dimethylamino)phenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ad** (38.8 mg) in 70% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.89 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H), 3.05 (s, 6H), 2.65 (t, J = 6.8 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.6, 172.8, 153.6, 130.4, 125.1, 110.9, 80.6, 40.3, 32.9, 30.1, 28.3. IR (KBr disc, cm^{-1}): 2957, 2924, 2853, 1726, 1663, 1601, 1554, 1529, 1457, 1366, 1259, 1232, 1188, 1152, 1081, 945, 852, 817, 807. QTOF-MS m/z [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_3$ $^+$ 278.1751; Found 278.1746.

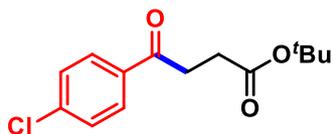
***tert*-butyl 4-(4-fluorophenyl)-4-oxobutanoate (5ae)**^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(4-fluorophenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative

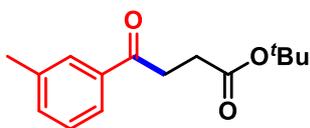
TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **5ae** (21.2 mg) in 42% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.05–7.95 (m, 2H), 7.12 (t, J = 8.5 Hz, 2H), 3.22 (t, J = 6.5 Hz, 2H), 2.67 (t, J = 6.5 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.9, 172.3, 165.9 (d, J = 254.4 Hz), 133.4 (d, J = 3.2 Hz), 130.9 (d, J = 9.2 Hz), 115.9 (d, J = 21.9 Hz), 80.9, 33.6, 29.6, 28.3. ^{19}F NMR (377 MHz, CDCl_3 , ppm) δ = -105.31. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{18}\text{FO}_3^+$ 253.1234; Found 253.1245.

***tert*-butyl 4-(4-chlorophenyl)-4-oxobutanoate (**5af**)**^{S22}



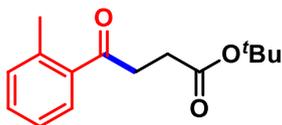
Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(4-chlorophenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **5af** (23.6 mg) in 44% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.92 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 3.22 (t, J = 6.4 Hz, 2H), 2.67 (t, J = 6.4 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 197.4, 172.2, 139.8, 135.3, 129.7, 129.1, 80.9, 33.6, 29.6, 28.3. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{18}\text{ClO}_3^+$ 269.0939; Found 269.0946.

***tert*-butyl 4-oxo-4-(*m*-tolyl)butanoate (**5ag**)**^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-oxo-2-(*m*-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ag** (31.2 mg) in 63% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.77 (d, J = 8.8 Hz, 2H), 7.41–7.29 (m, 2H), 3.24 (t, J = 6.6 Hz, 2H), 2.67 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 198.8, 172.4, 138.5, 136.9, 134.0, 128.8, 128.6, 125.4, 80.8, 33.7, 29.7, 28.3, 21.5. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3^+$ 249.1485; Found 249.1473.

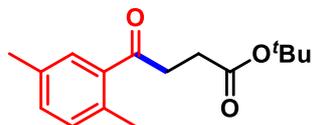
***tert*-butyl 4-oxo-4-(*o*-tolyl)butanoate (**5ah**)**^{S22}



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-oxo-2-(*o*-tolyl)acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ah** (29.8 mg) in 60% yield. ^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.70 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.26 (dd, J = 12.7, 6.6 Hz, 2H), 3.16 (t, J = 6.5 Hz, 2H), 2.66 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 202.6, 172.4, 138.2, 137.9, 132.1, 131.5, 128.6, 125.9,

80.8, 36.5, 29.9, 28.3, 21.4. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{15}H_{21}O_3^+$ 249.1485; Found 249.1490.

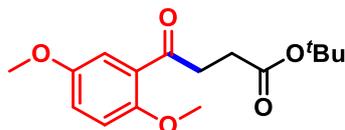
***tert*-butyl 4-(2,5-dimethylphenyl)-4-oxobutanoate (5ai)**



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(2,5-dimethylphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless oil **5ai** (32.0 mg) in 61% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.49 (s, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 3.15 (t, J = 6.6 Hz, 2H), 2.65 (t, J = 6.6 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 202.7, 172.4, 137.9, 135.4, 135.0, 132.2, 132.0, 129.2, 80.8, 36.5, 29.9, 28.3, 21.1, 20.9. IR (KBr disc, cm^{-1}): 2961, 2925, 1731, 1689, 1638, 1571, 1496, 1457, 1393, 1367, 1290, 1259, 1236, 1154, 1081, 1038, 971, 848, 814. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{16}H_{23}O_3^+$ 263.1642; Found 263.1638.

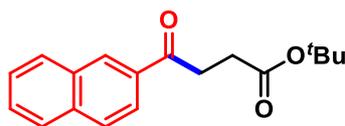
***tert*-butyl 4-(2,5-dimethoxyphenyl)-4-oxobutanoate (5aj)^{S23}**



Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(2,5-dimethoxyphenyl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **5aj** (36.5 mg) in 62% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.29 (d, J = 3.2 Hz, 1H), 7.01 (dd, J = 9.0, 3.2 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.26 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 6.7 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.1, 172.6, 153.6, 153.6, 128.0, 120.5, 114.1, 113.3, 80.5, 56.2, 56.0, 39.1, 30.1, 28.3. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{16}H_{23}O_5^+$ 295.1540; Found 295.1540.

***tert*-butyl 4-(naphthalen-2-yl)-4-oxobutanoate (5ak)^{S22}**

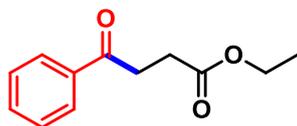


Following the General Procedure with *tert*-butyl acrylate (0.2 mmol) and 2-(naphthalen-2-yl)-2-oxoacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow solid **5ak** (29.0 mg) in 51% yield.

1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.52 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.9 Hz,

1H), 7.89 (t, $J = 8.1$ Hz, 2H), 7.58 (dt, $J = 14.7, 6.9$ Hz, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 2.74 (t, $J = 6.7$ Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 198.5, 172.5, 135.8, 134.3, 132.8, 129.9, 129.8, 128.7, 128.0, 127.0, 124.0, 80.9, 33.8, 29.8, 28.3$. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3^+$ 285.1485; Found 285.1480.

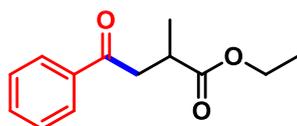
ethyl 4-oxo-4-phenylbutanoate (5ba)^{S22}



Following the General Procedure with ethyl acrylate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ba** (27.6 mg) in 67% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.98$ (d, $J = 7.5$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.31 (t, $J = 6.6$ Hz, 2H), 2.76 (t, $J = 6.6$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 198.4, 173.1, 136.8, 133.4, 128.8, 128.2, 60.9, 33.6, 28.5, 14.4$. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3^+$ 207.1016; Found 207.1023.

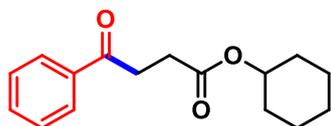
ethyl 2-methyl-4-oxo-4-phenylbutanoate (5ca)^{S24}



Following the General Procedure with ethyl methacrylate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ca** (28.2 mg) in 64% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.97$ (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.48 (dd, $J = 17.5, 7.8$ Hz, 1H), 3.20 – 3.06 (m, 1H), 3.01 (dd, $J = 17.5, 5.4$ Hz, 1H), 1.26 (dd, $J = 15.1, 7.3$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 198.3, 176.2, 136.9, 133.4, 128.8, 128.2, 77.6, 77.2, 76.9, 60.8, 42.1, 35.2, 17.5, 14.4$. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3^+$ 221.1172; Found 221.1170.

cyclohexyl 4-oxo-4-phenylbutanoate (5da)^{S25}

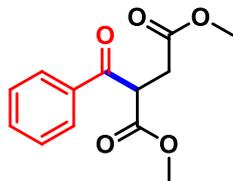


Following the General Procedure with cyclohexyl acrylate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless oil **5da** (34.8 mg) in 67% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.98$ (d, $J = 7.7$ Hz, 2H), 7.56 (t, $J = 7.1$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 2H), 4.77 (dd, $J = 10.0, 6.4$ Hz, 1H), 3.30 (t, $J = 6.5$ Hz, 2H), 2.74 (t, $J = 6.4$ Hz, 2H), 1.83 (d, $J = 5.1$ Hz, 2H), 1.71 (d, $J = 10.7$ Hz, 2H), 1.58–1.48 (m, 1H), 1.46–1.29 (m, 4H), 1.24 (t, $J = 10.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) $\delta = 198.4, 172.5, 136.9, 133.3, 128.8, 128.2,$

73.1, 33.6, 31.8, 28.9, 25.6, 23.9. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{16}H_{21}O_3^+$ 261.1485; Found 261.1470.

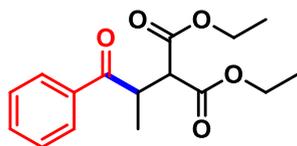
dimethyl 2-benzoylsuccinate (5ea)^{S26}



Following the General Procedure with dimethyl fumarate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the yellow oil **5ea** (36.0 mg) in 72% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.04 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 4.89 (t, J = 7.2 Hz, 1H), 3.68 (d, J = 1.7 Hz, 6H), 3.07 (qd, J = 17.4, 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 194.2, 171.9, 169.4, 135.9, 134.0, 129.1, 129.0, 53.1, 52.3, 49.5, 33.3. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{13}H_{15}O_5^+$ 251.0914; Found 251.0929.

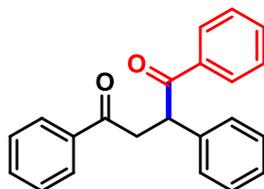
diethyl 2-(1-oxo-1-phenylpropan-2-yl)malonate (5fa)^{S27}



Following the General Procedure with diethyl 2-ethylidenemalonate (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the colorless oil **5fa** (42.6 mg) in 73% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.00 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 4.26 (dd, J = 13.9, 6.9 Hz, 2H), 4.22–4.15 (m, 1H), 4.15–4.03 (m, 2H), 3.99 (d, J = 10.8 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H), 1.17 (dd, J = 15.2, 7.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 201.8, 169.0, 168.6, 135.8, 133.4, 128.9, 128.7, 61.9, 61.9, 55.1, 40.7, 16.1, 14.4, 14.1. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{16}H_{21}O_5^+$ 293.1384; Found 293.1383.

1,2,4-triphenylbutane-1,4-dione (5ga)^{S28}

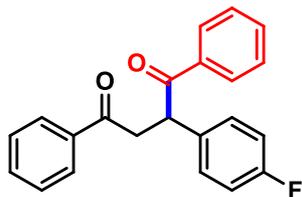


Following the General Procedure with chalcone (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **5ga** (38.3 mg) in 61% yield.

¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.04 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (ddd, J = 32.6, 16.7, 7.5 Hz, 7H), 7.31 (t, J = 7.3 Hz, 2H), 7.26–7.20 (m, 1H), 5.33 (dd, J = 9.8, 2.6 Hz, 1H), 4.22 (dd, J = 18.0, 10.1 Hz, 1H), 3.30 (dd, J = 18.0, 2.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ = 199.1, 198.3, 138.8, 136.7, 133.4, 133.1, 129.4, 129.1, 128.8, 128.7, 128.4, 128.4, 127.6, 48.9, 44.1. QTOF-MS m/z $[M + H]^+$ Calcd for $C_{22}H_{19}O_2^+$

315.1380; Found 315.1369.

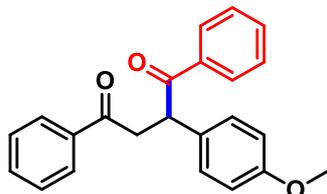
2-(4-fluorophenyl)-1,4-diphenylbutane-1,4-dione (**5ha**)



Following the General Procedure with 3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **5ha** (48.5mg) in 73% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.00 (dd, J = 15.5, 7.6 Hz, 4H), 7.56 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.43 (dt, J = 14.8, 7.6 Hz, 4H), 7.33 (dd, J = 7.9, 5.6 Hz, 2H), 7.00 (t, J = 8.5 Hz, 2H), 5.32 (dd, J = 9.8, 3.7 Hz, 1H), 4.17 (dd, J = 18.0, 9.8 Hz, 1H), 3.31 (dd, J = 18.0, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 199.1, 198.1, 162.3 (d, J = 246.4 Hz), 136.6 (d, J = 9.2 Hz), 134.5 (d, J = 3.4 Hz), 133.6, 133.3, 130.0 (d, J = 8.0 Hz), 129.1, 128.8 (d, J = 3.5 Hz), 128.4, 116.4, 116.2, 48.0, 44.0. ^{19}F NMR (377 MHz, CDCl_3) δ = -114.96. m.p. = 115.6–116.2 °C. IR (KBr disc, cm^{-1}): 1684, 1672, 1596, 1509, 1447, 1382, 1338, 1314, 1232, 1205, 1185, 1160, 1003, 951, 842, 794, 780, 746, 739, 716, 688, 551, 503. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{18}\text{FO}_2^+$ 333.1285; Found 333.1292.

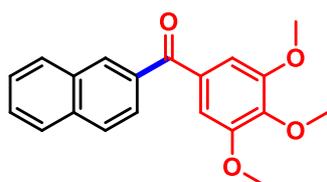
2-(4-methoxyphenyl)-1,4-diphenylbutane-1,4-dione (**5ia**)^{S28}



Following the General Procedure with 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (0.2 mmol) and phenylglyoxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **5ia** (37.2 mg) in 54% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.03 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.52–7.36 (m, 5H), 7.28 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 5.28 (dd, J = 9.9, 3.5 Hz, 1H), 4.18 (dd, J = 18.0, 10.0 Hz, 1H), 3.75 (s, 3H), 3.29 (dd, J = 18.0, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 199.4, 198.5, 159.1, 136.7, 136.7, 133.4, 133.0, 130.7, 129.5, 129.1, 128.8, 128.7, 128.4, 114.8, 55.5, 48.0, 44.1. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3^+$ 345.1485; Found 345.1482.

naphthylphenstatin^{S29}

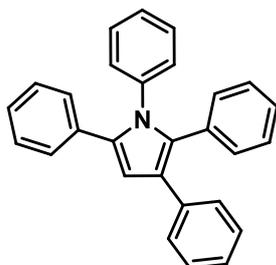


Following the General Procedure with 2-bromonaphthalene (0.2 mmol) and 2-oxo-2-(3,4,5-trimethoxyphenyl)acetic acid (0.4 mmol). The crude product was purified by

preparative TLC, using PE/EA = 10/1 (v/v) as the eluent, to yield the white solid naphthylphenstatin (31.6 mg) in 49% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.29 (s, 1H), 7.99–7.89 (m, 4H), 7.60 (dt, J = 14.6, 7.0 Hz, 2H), 7.12 (s, 2H), 3.96 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 196.1, 153.1, 142.2, 135.4, 135.3, 133.1, 132.5, 131.7, 129.6, 128.5, 128.7, 128.1, 127.1, 126.1, 108.0, 61.2, 56.6. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_4^+$ 323.1278; Found 323.1254.

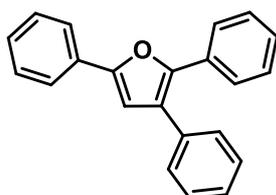
1,2,3,5-tetraphenyl-1H-pyrrole (6)^{S28}



A solution of **5ga** (62.8 mg, 0.2mmol), aniline (50 mg, 0.54 mmol) in ionic liquid $[\text{bmim}]\text{HSO}_4$ (1.6 mL) was stirred at 150 °C for 3h in oil bath. After cooling to room temperature, water (10 mL) was added and the aqueous solution extracted with ethyl acetate (3×10 mL). The combined extracts were dried over anhydrous Na_2SO_4 , concentrated *in vacuo*. The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **6** (70.5 mg) in 95% yield.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.26 (d, J = 7.4 Hz, 2H), 7.21 (d, J = 7.4 Hz, 2H), 7.13 (dd, J = 13.2, 7.9 Hz, 12H), 7.04 (d, J = 6.1 Hz, 2H), 6.98 (d, J = 4.5 Hz, 2H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 139.0, 136.3, 135.0, 133.1, 132.9, 132.4, 131.7, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.3, 127.2, 126.6, 125.7, 123.7, 110.2. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747; Found 372.1773.

2,3,5-triphenylfuran (7)^{S28}



A solution of **5ga** (62.8 mg, 0.2mmol) in ionic liquid $[\text{bmim}]\text{HSO}_4$ (0.4mL) was stirred at 150 °C for 4h in oil bath. After cooling to room temperature, water (10 mL) was added and the aqueous solution extracted with ethyl acetate (3×10 mL). The combined extracts were dried over anhydrous Na_2SO_4 , concentrated *in vacuo*. The crude product was purified by preparative TLC, using PE/EA = 50/1 (v/v) as the eluent, to yield the white solid **7** (56.8 mg) in 96%.

^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.75 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.3 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.30 (dd, J = 15.3, 7.6 Hz, 4H), 7.25 – 7.18 (m, 1H), 6.80 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ = 152.7, 148.1, 134.5, 131.3, 130.7, 128.9, 128.9, 128.9, 128.6, 127.7, 127.7, 127.5, 126.3, 124.7, 124.0, 109.7. QTOF-MS m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{17}\text{O}^+$ 297.1274; Found 297.1303.

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NMR spectra

Figure S7. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzotrile in CDCl_3

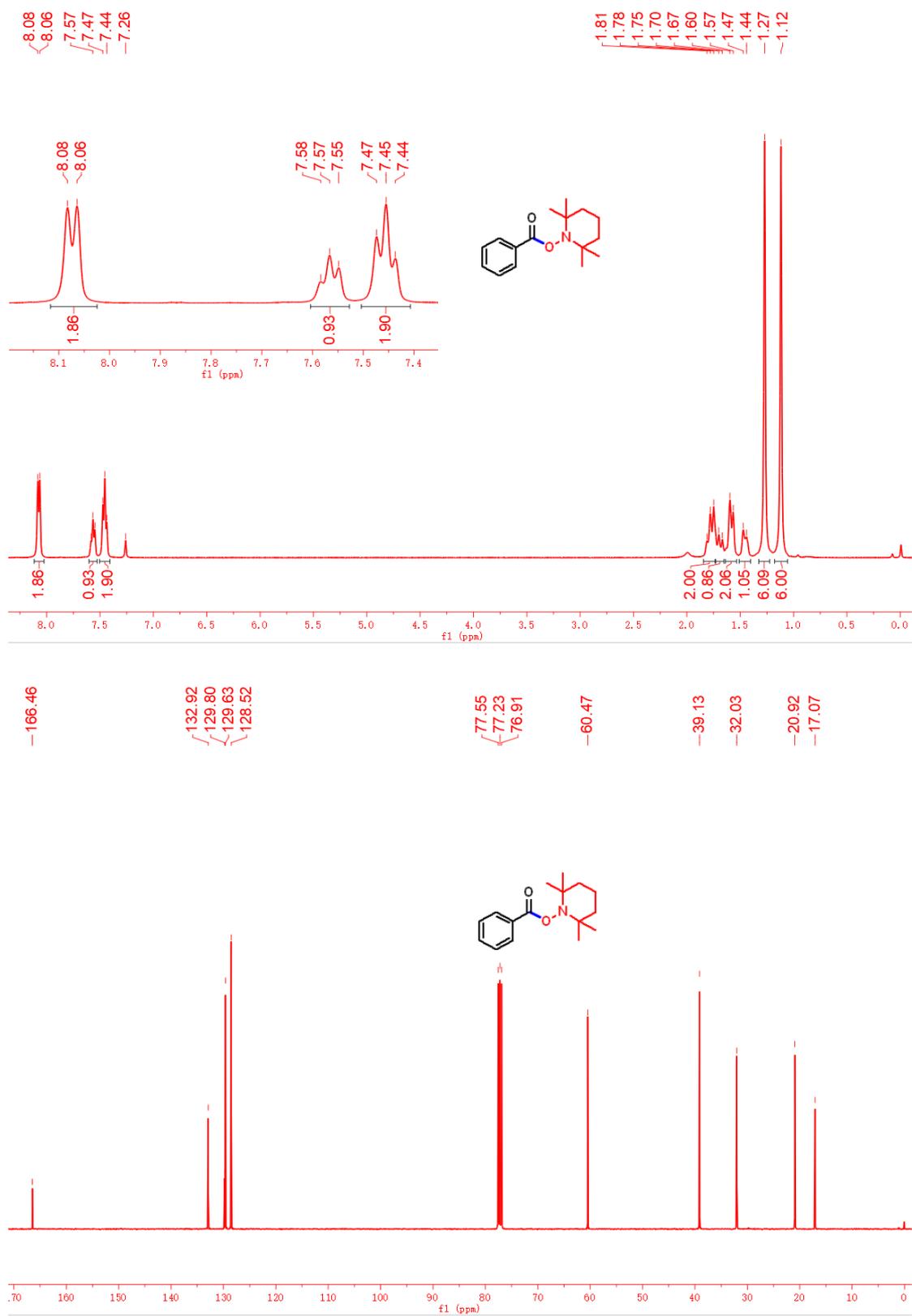


Figure S8. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-benzoylbenzonitrile (**3aa**) in CDCl_3

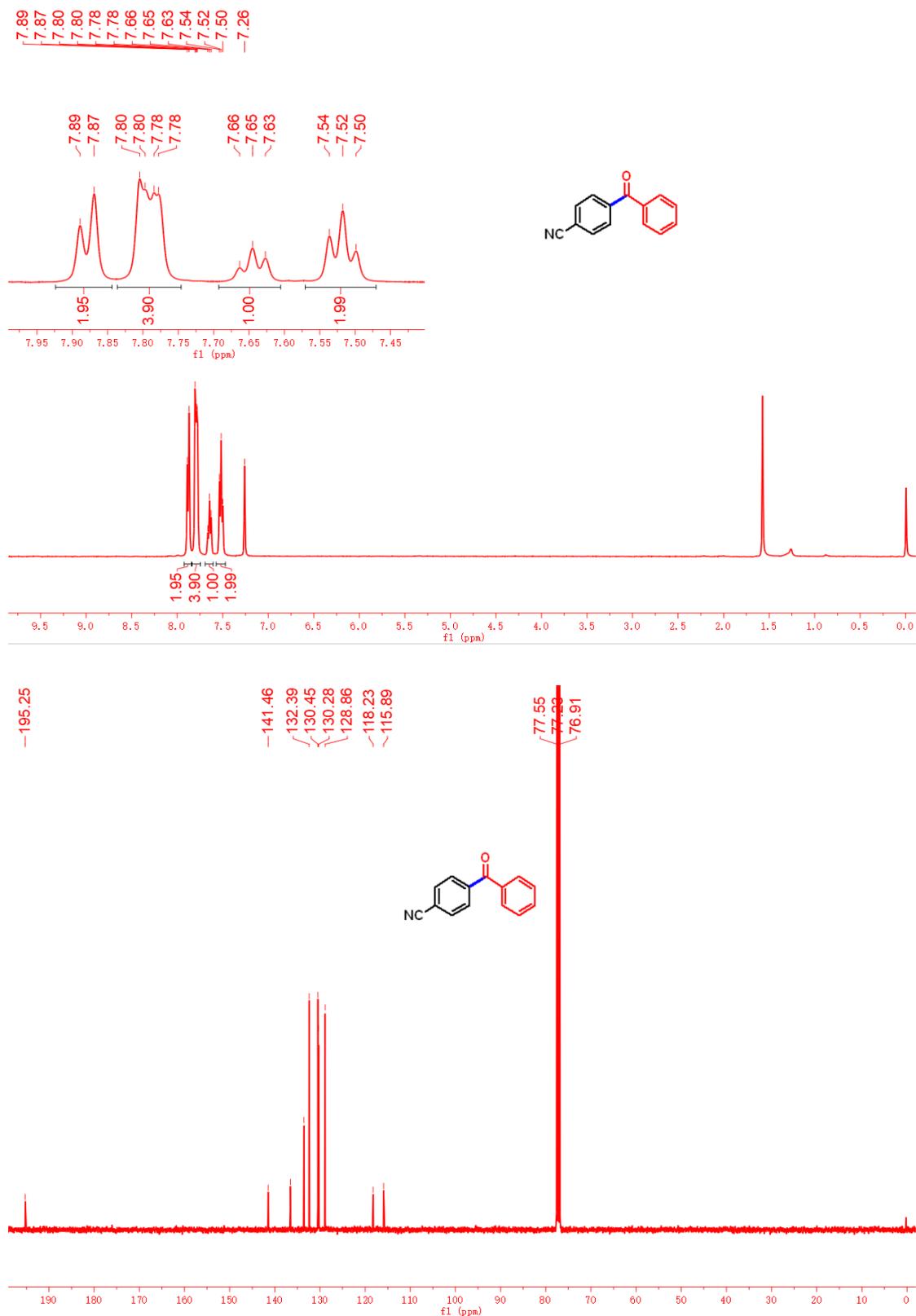
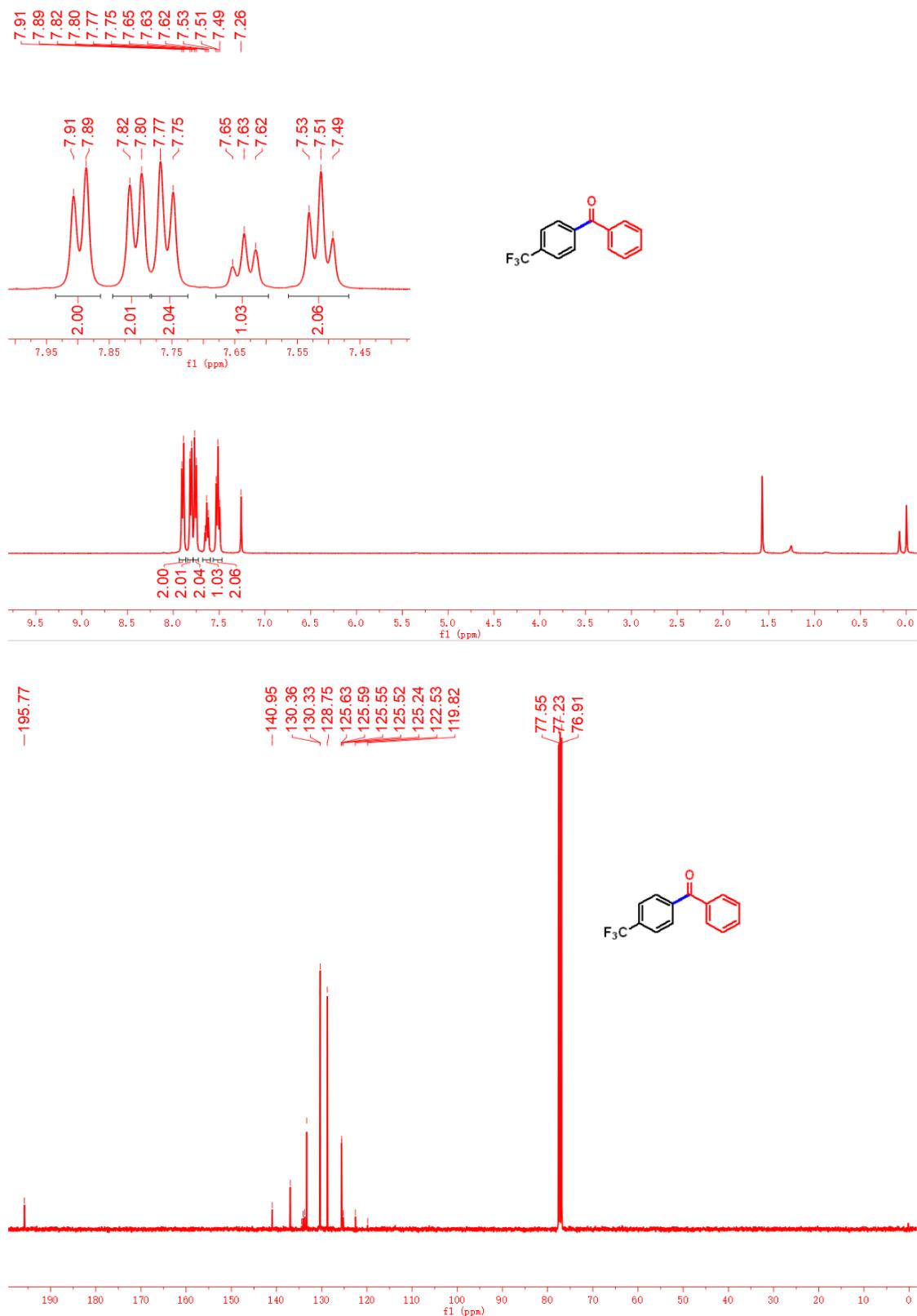


Figure S9. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for phenyl(4-(trifluoromethyl)phenyl)methanone (**3ba**) in CDCl_3



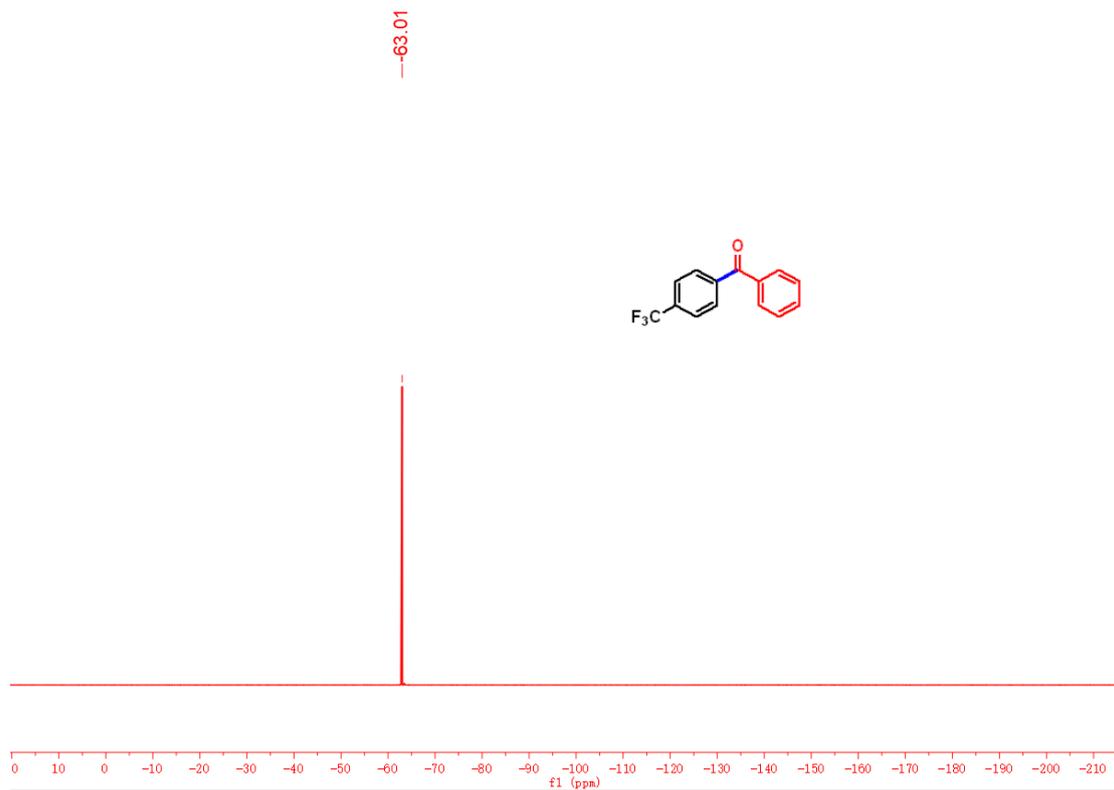


Figure S10. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(4-benzoylphenyl)ethan-1-one (**3ca**) in CDCl_3

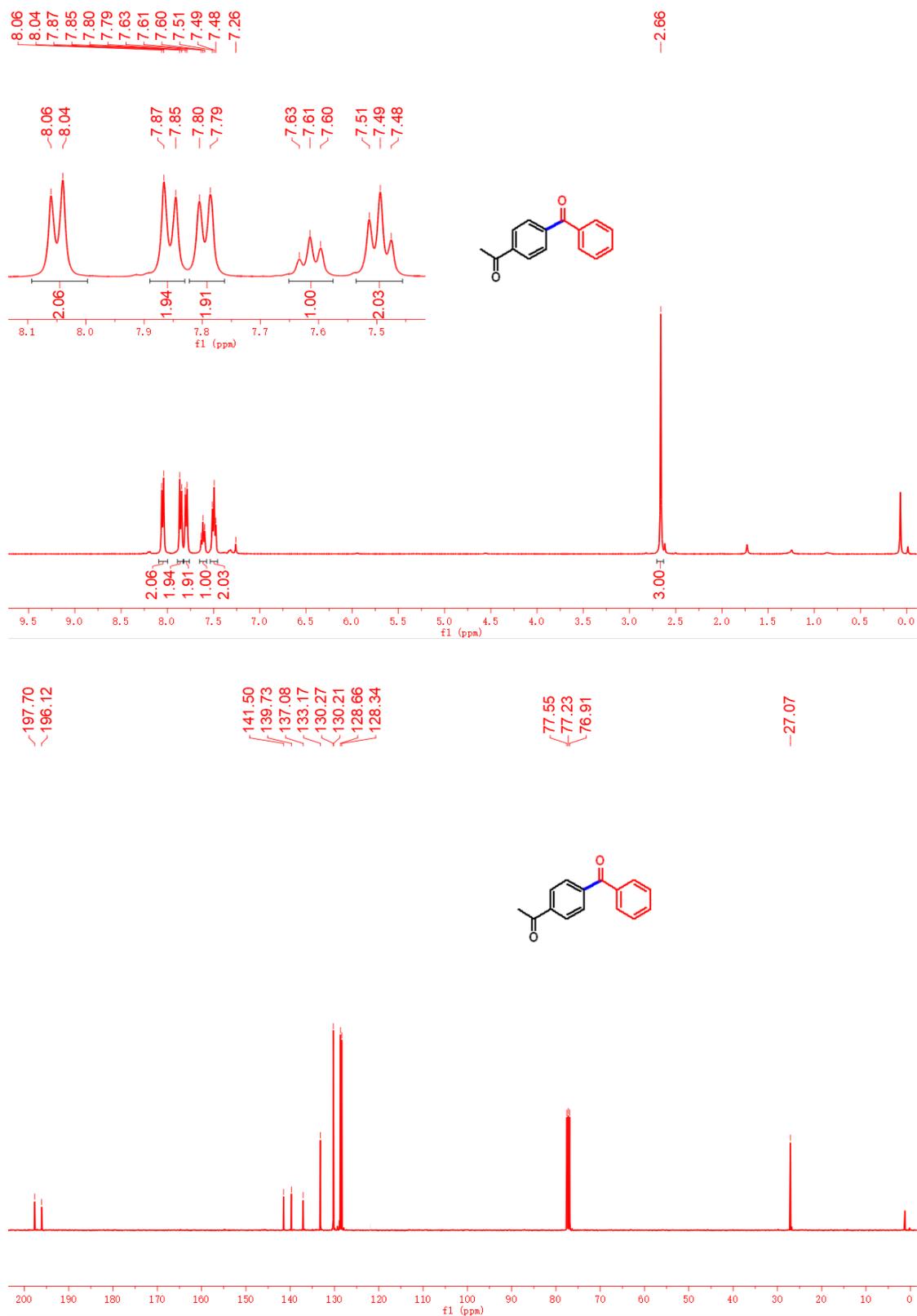


Figure S11. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4-benzoylbenzoate (**3da**) in CDCl_3

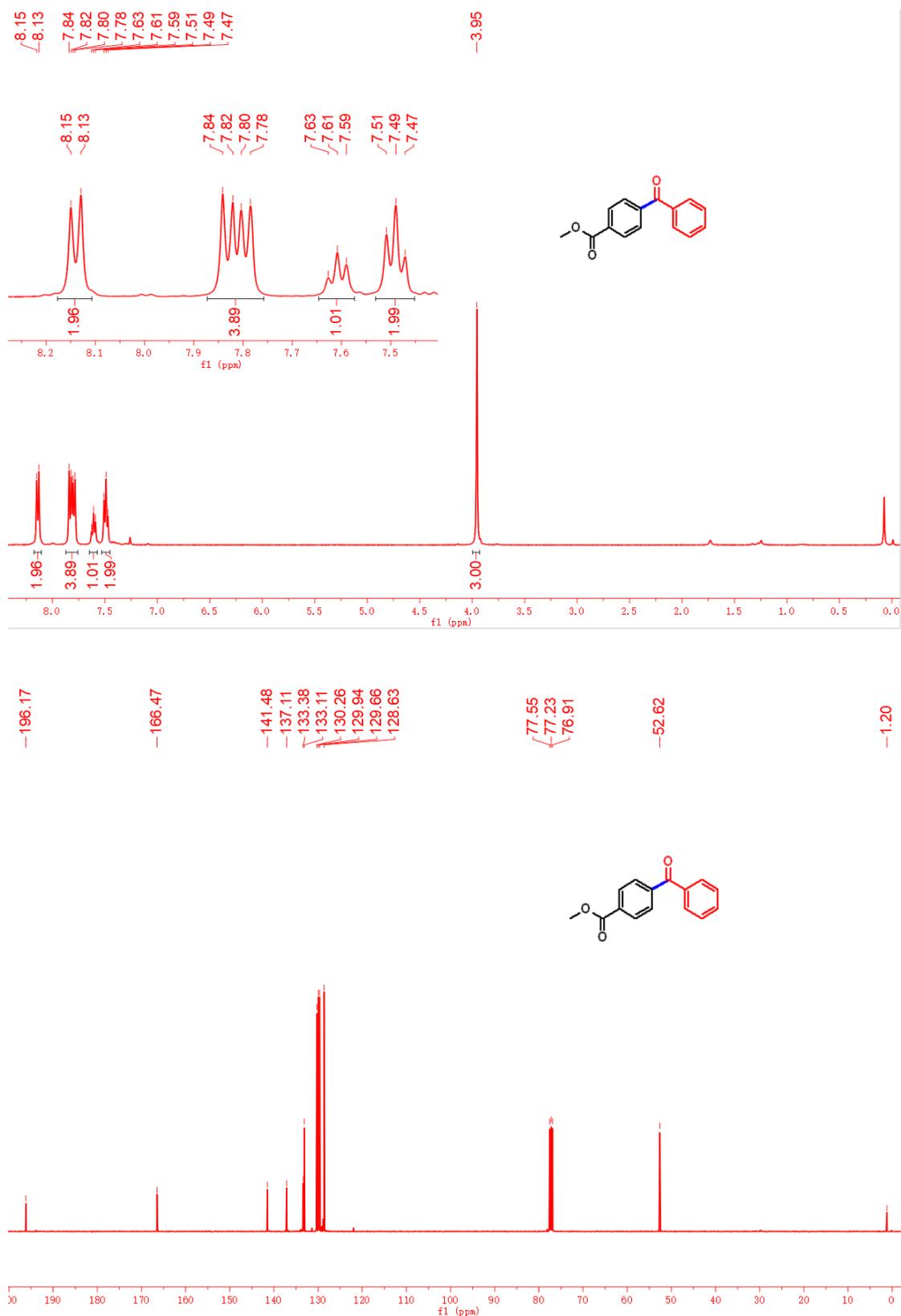


Figure S12. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for ethyl 4-benzoylbenzoate (**3ea**) in CDCl_3

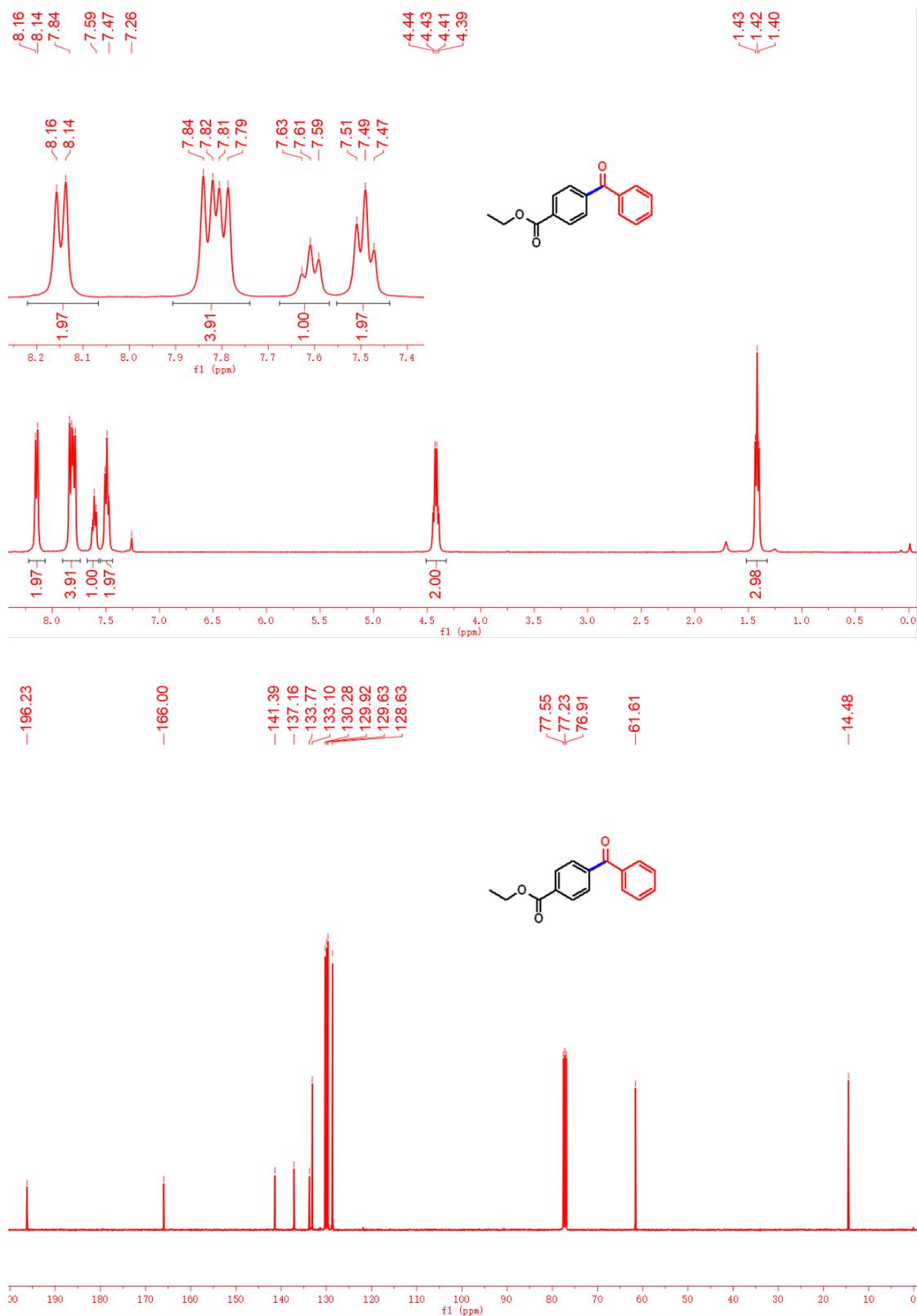


Figure S13. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-benzoylbenzaldehyde (**3fa**) in CDCl_3

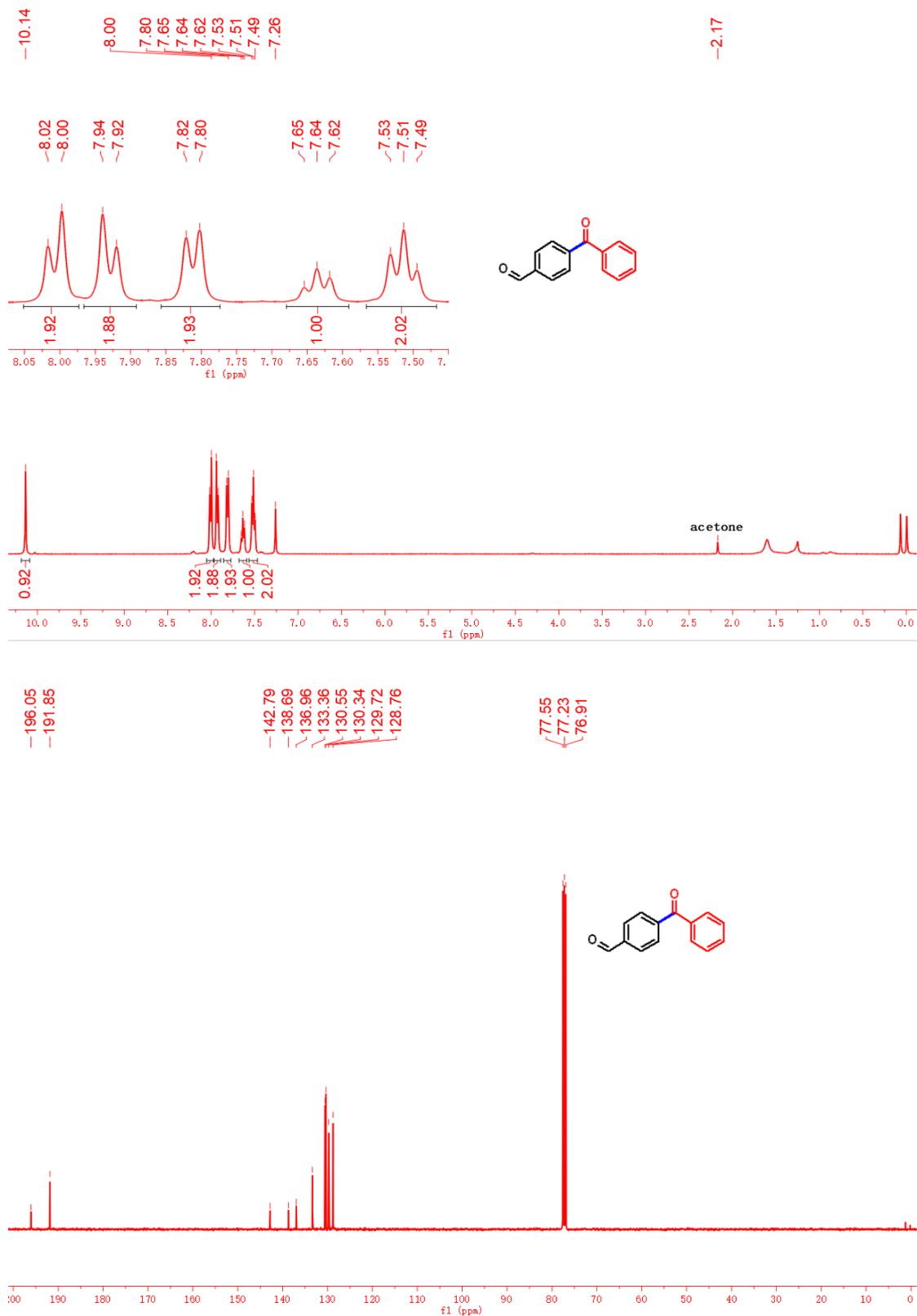


Figure S14. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 3-benzoylbenzonitrile (**3ga**) in CDCl_3

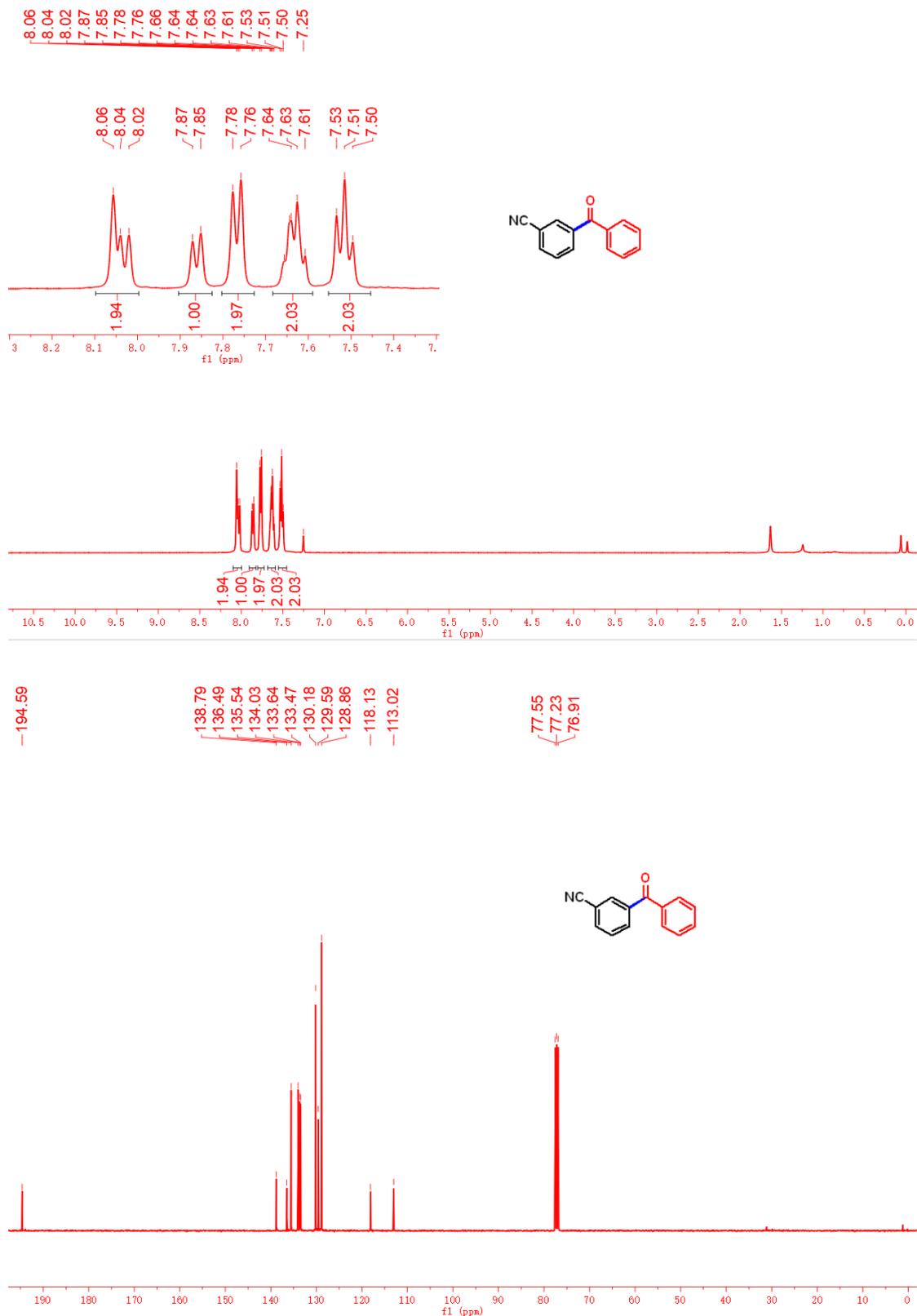


Figure S15. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 2-benzoylbenzotrile (**3ha**) in CDCl_3

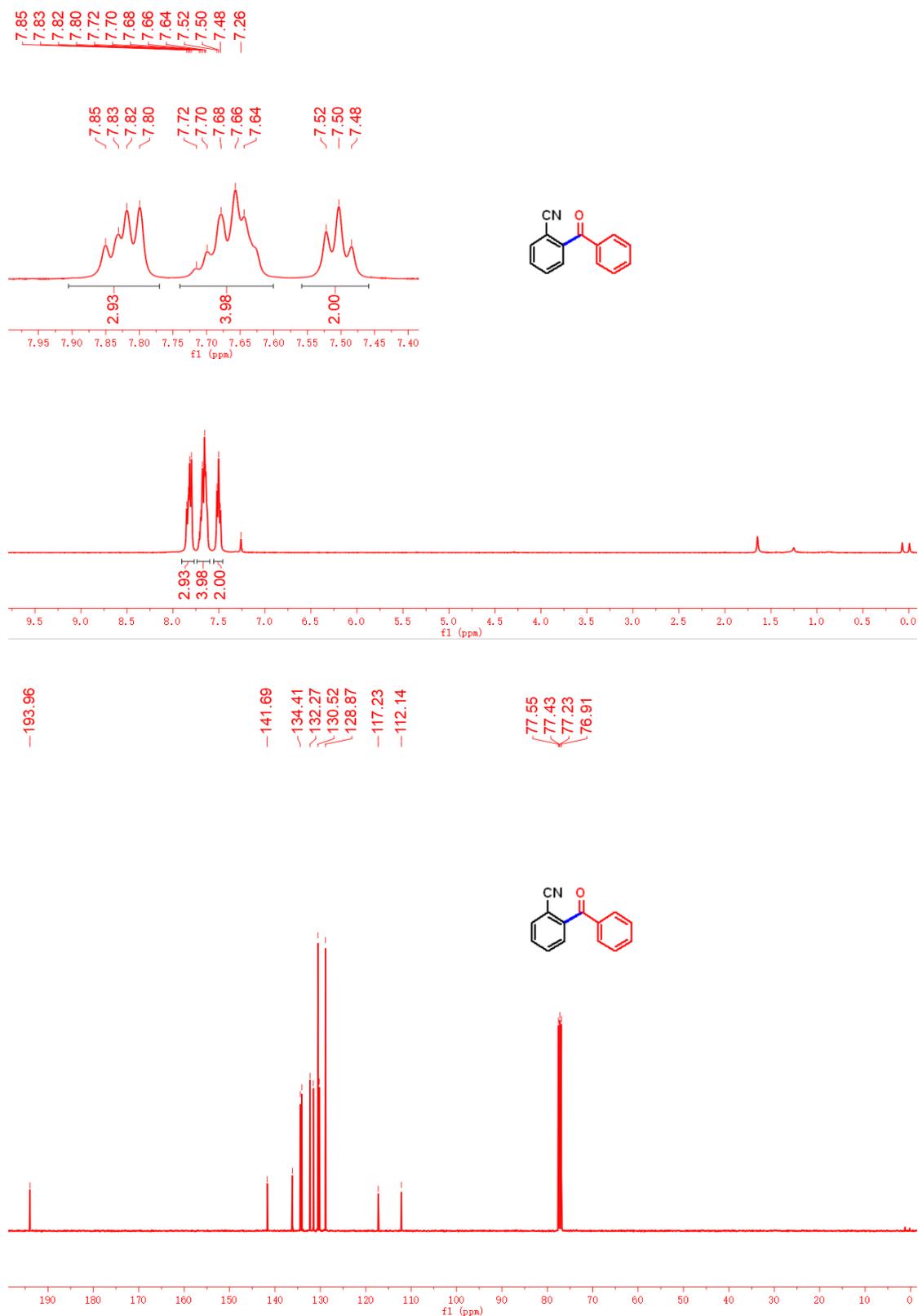


Figure S16. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 2-benzoylbenzoate (**3ia**) in CDCl_3

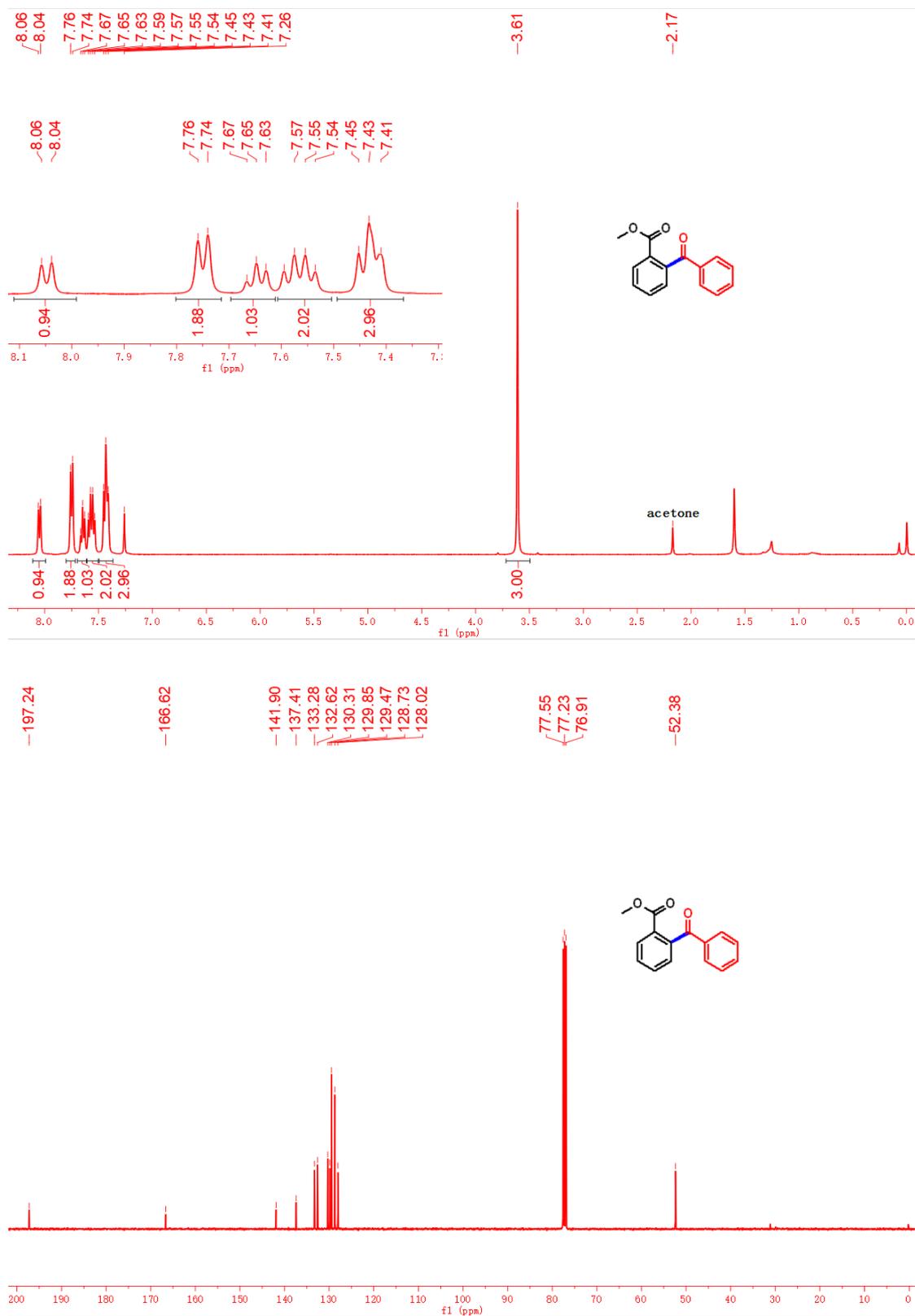


Figure S17. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1,2-phenylenebis(phenylmethanone) (**3ja**) in CDCl_3

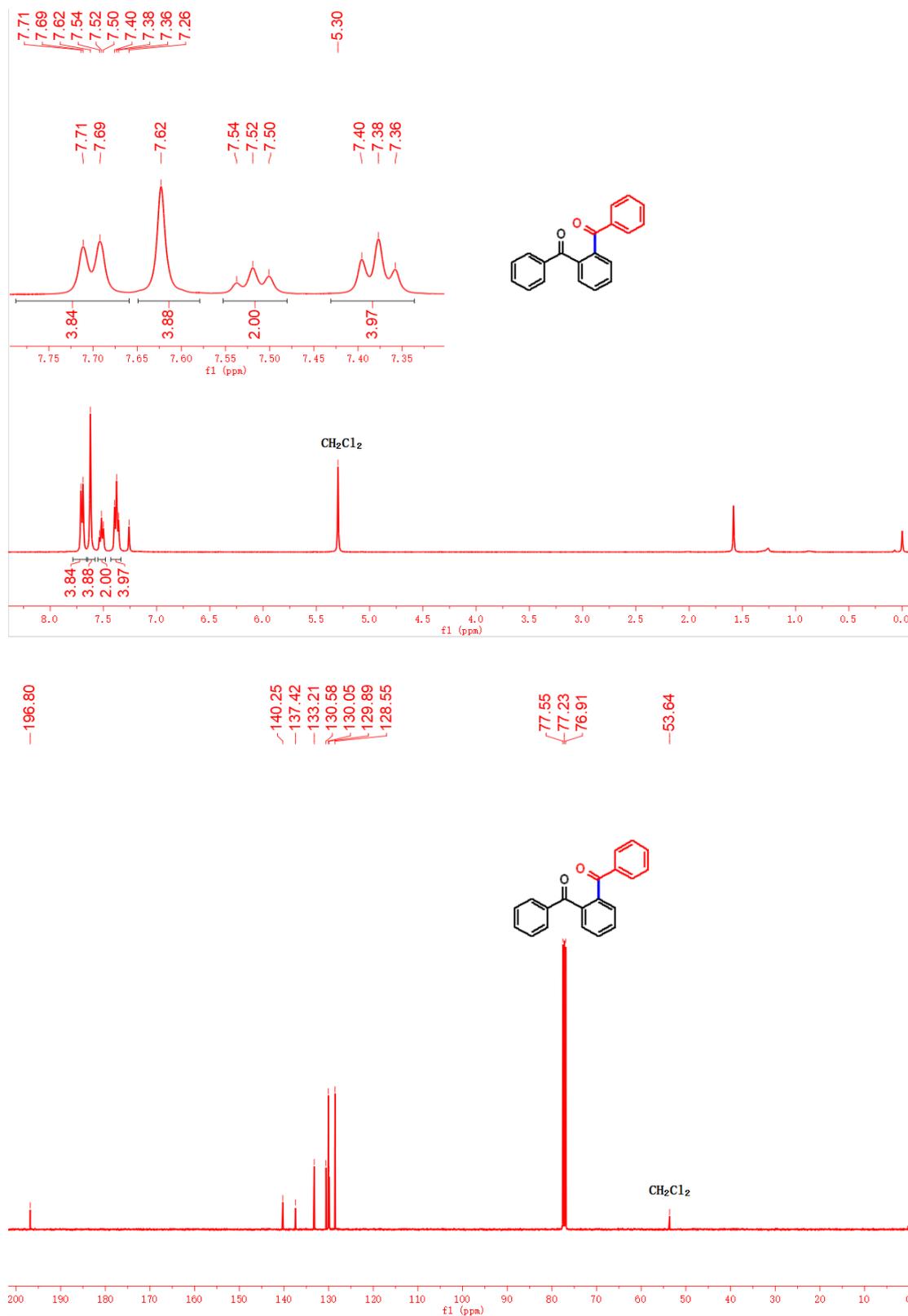
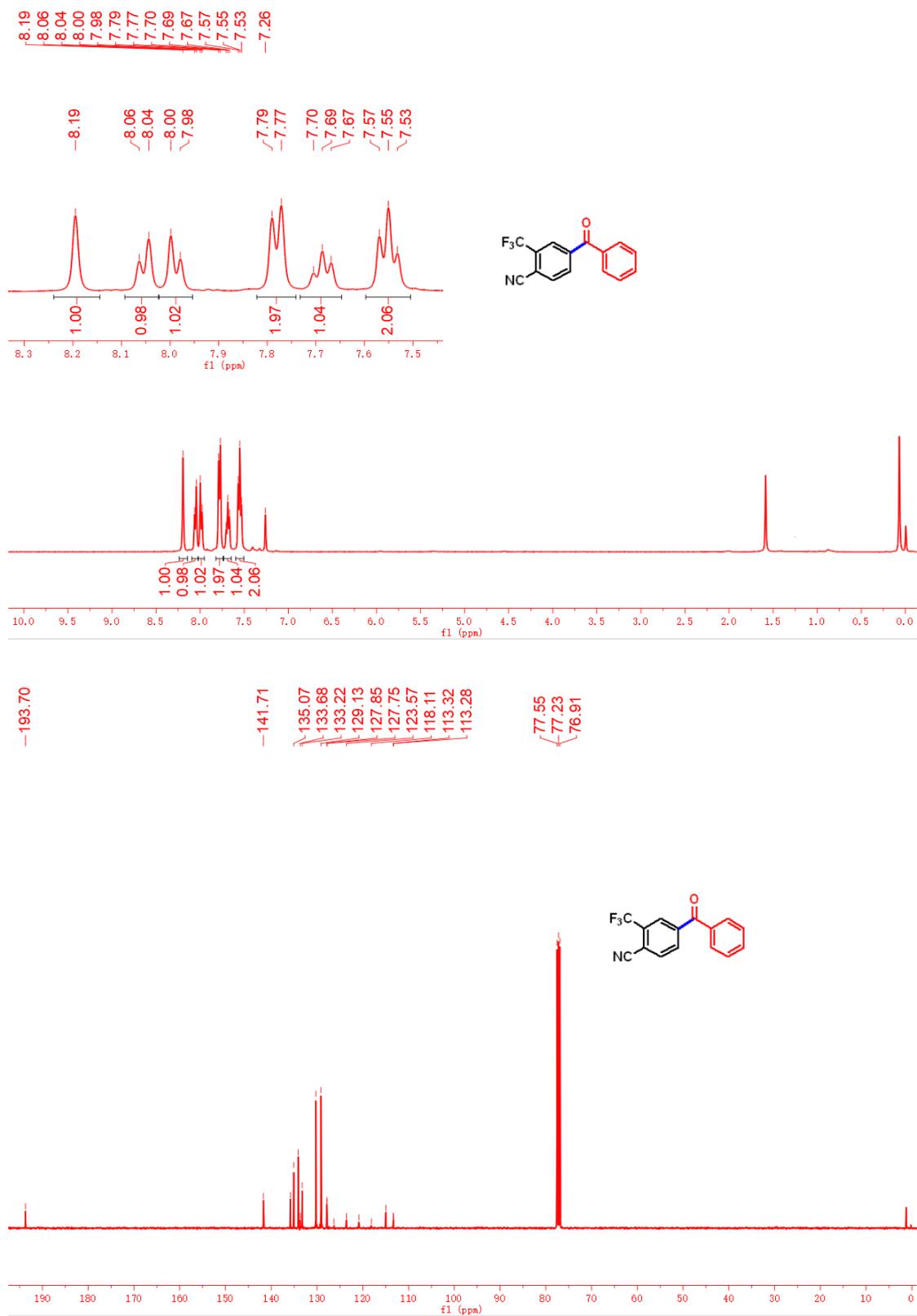


Figure S18. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 4-benzoyl-2-(trifluoromethyl)benzonitrile (**3ka**) in CDCl_3



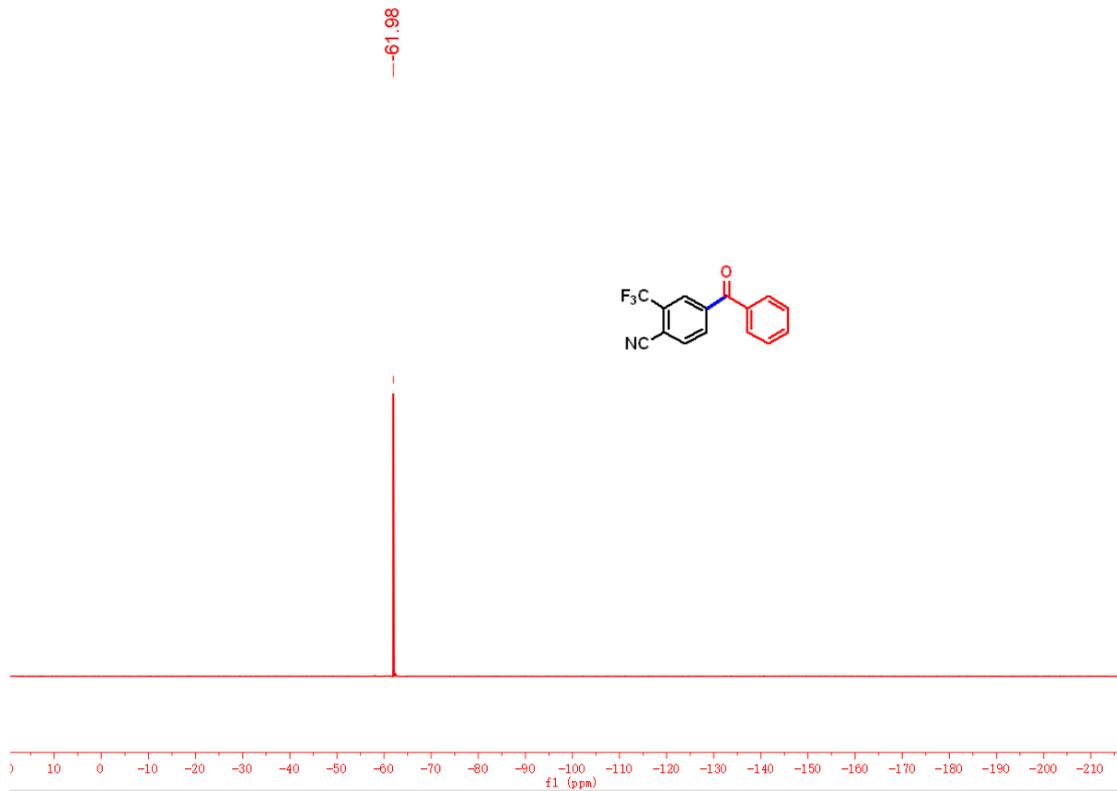


Figure S19. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for (3,5-bis(trifluoromethyl)phenyl)(phenyl)methanone (**3la**) in CDCl_3

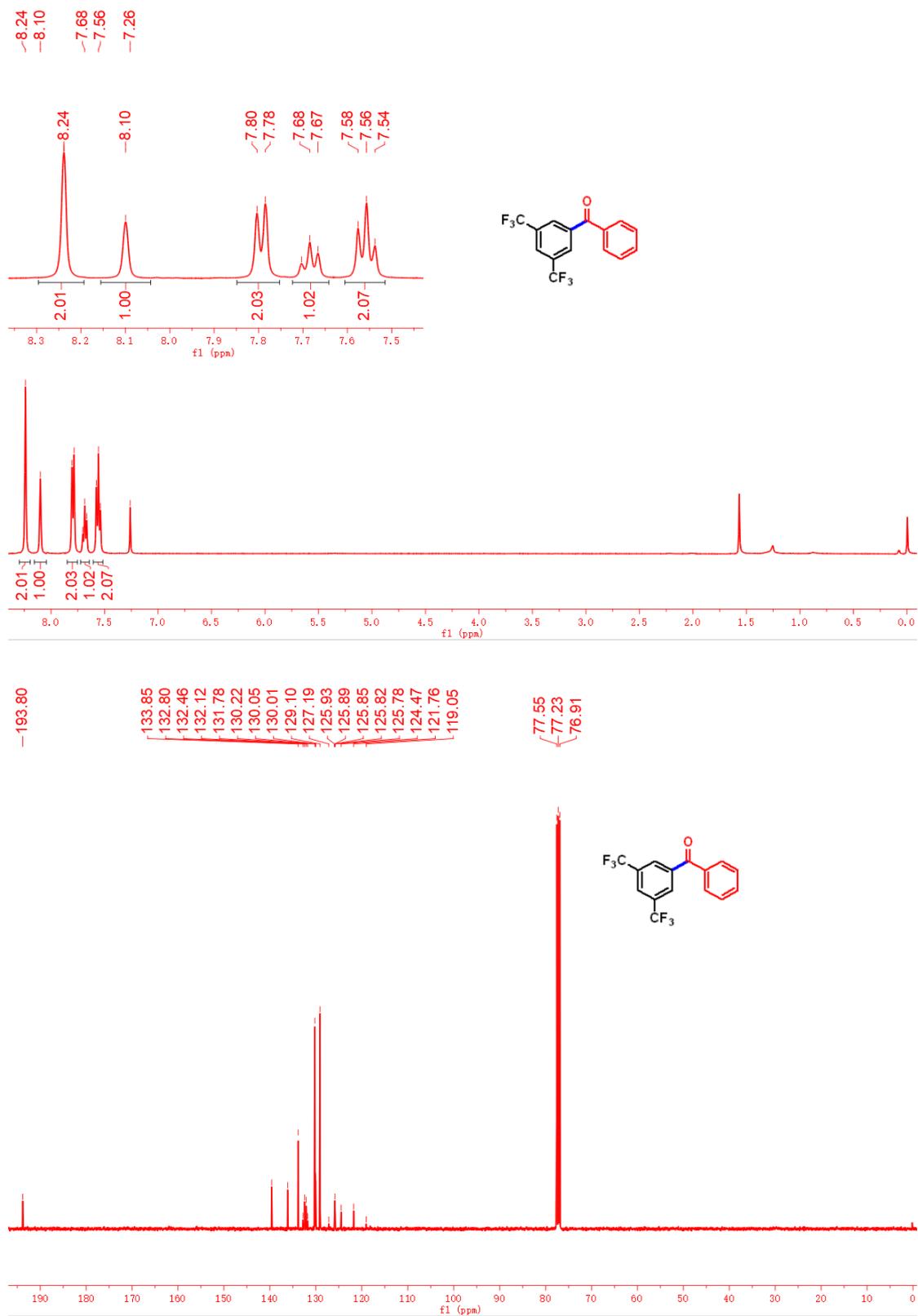
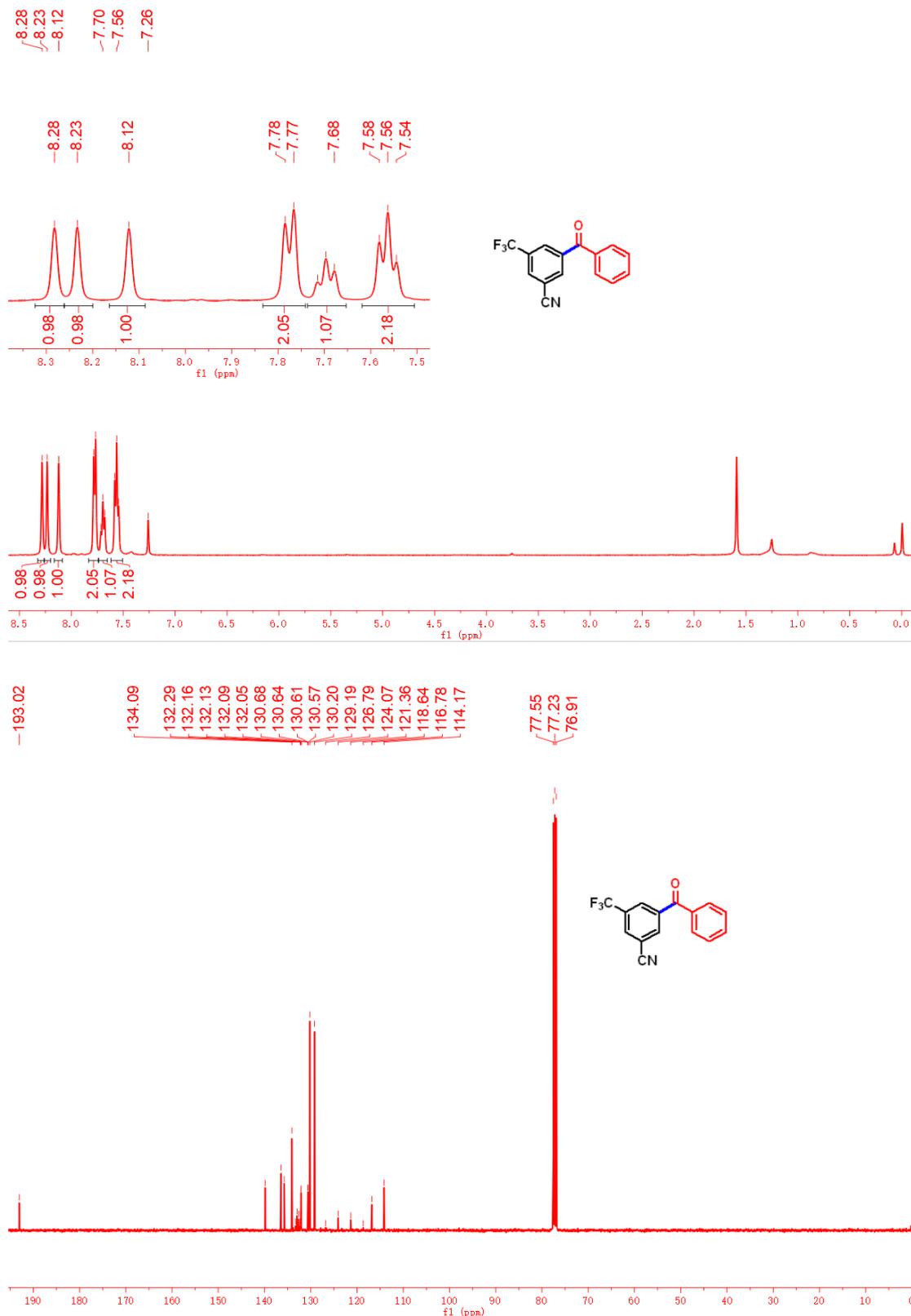




Figure S20. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 3-benzoyl-5-(trifluoromethyl)benzonitrile (**3ma**) in CDCl_3



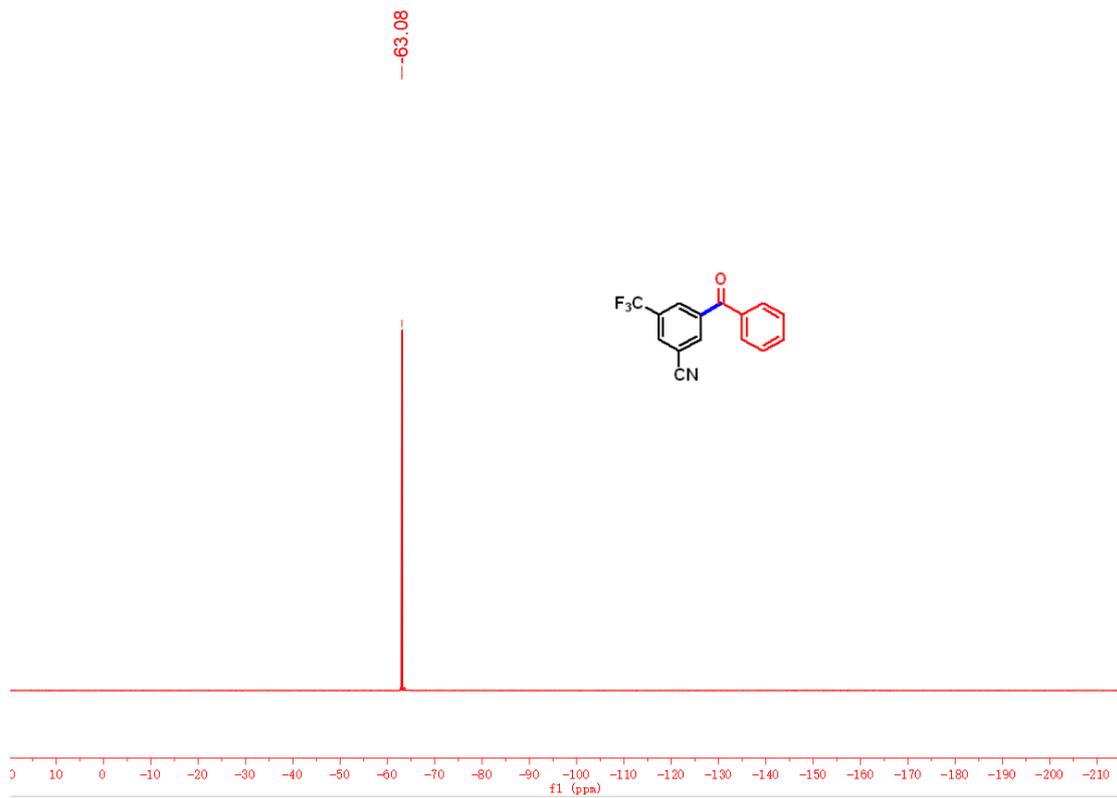


Figure S21. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for (3,5-difluorophenyl)(phenyl)methanone (**3na**) in CDCl_3

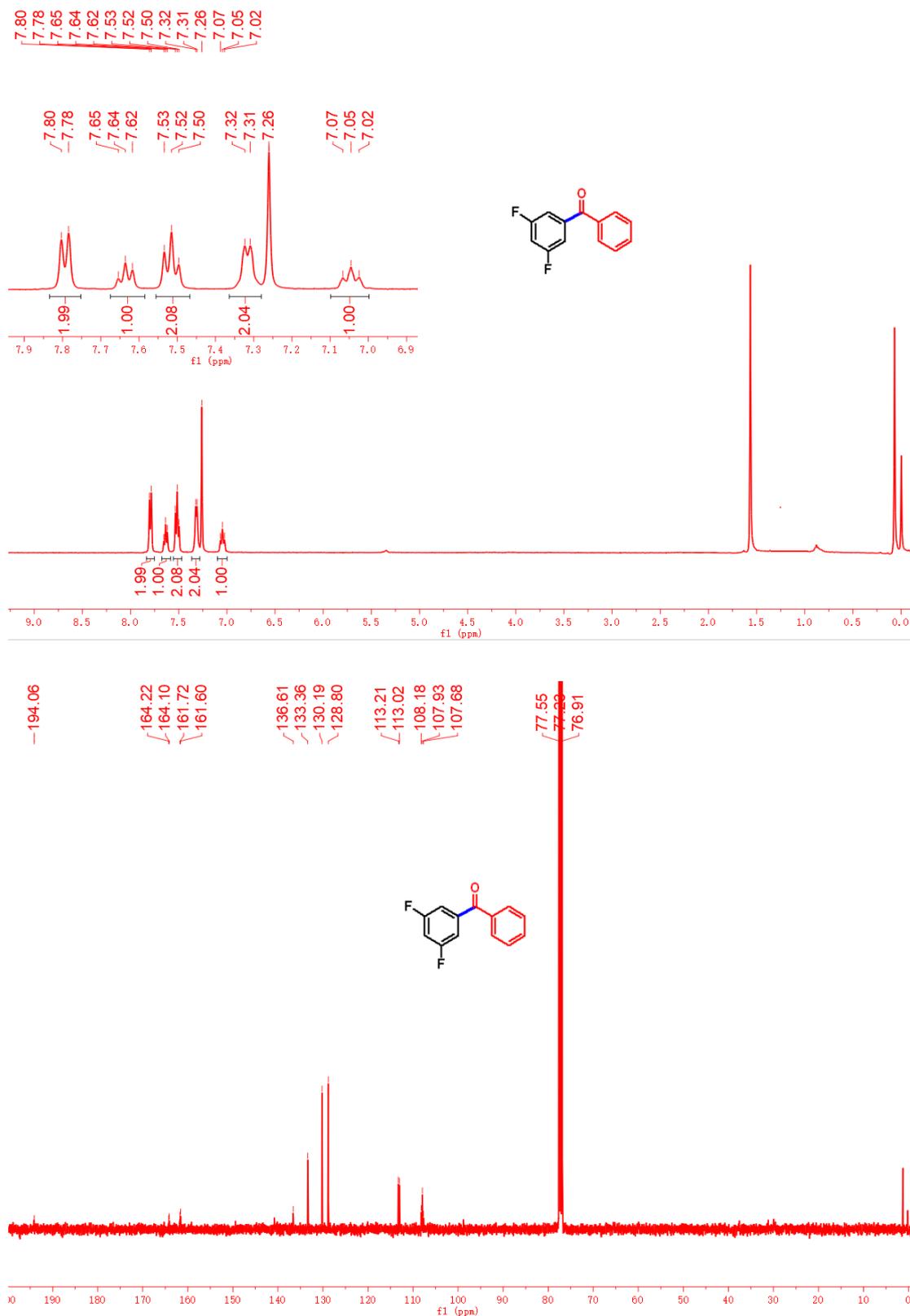




Figure S22. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for naphthalen-2-yl(phenyl)methanone (**30a**) in CDCl_3

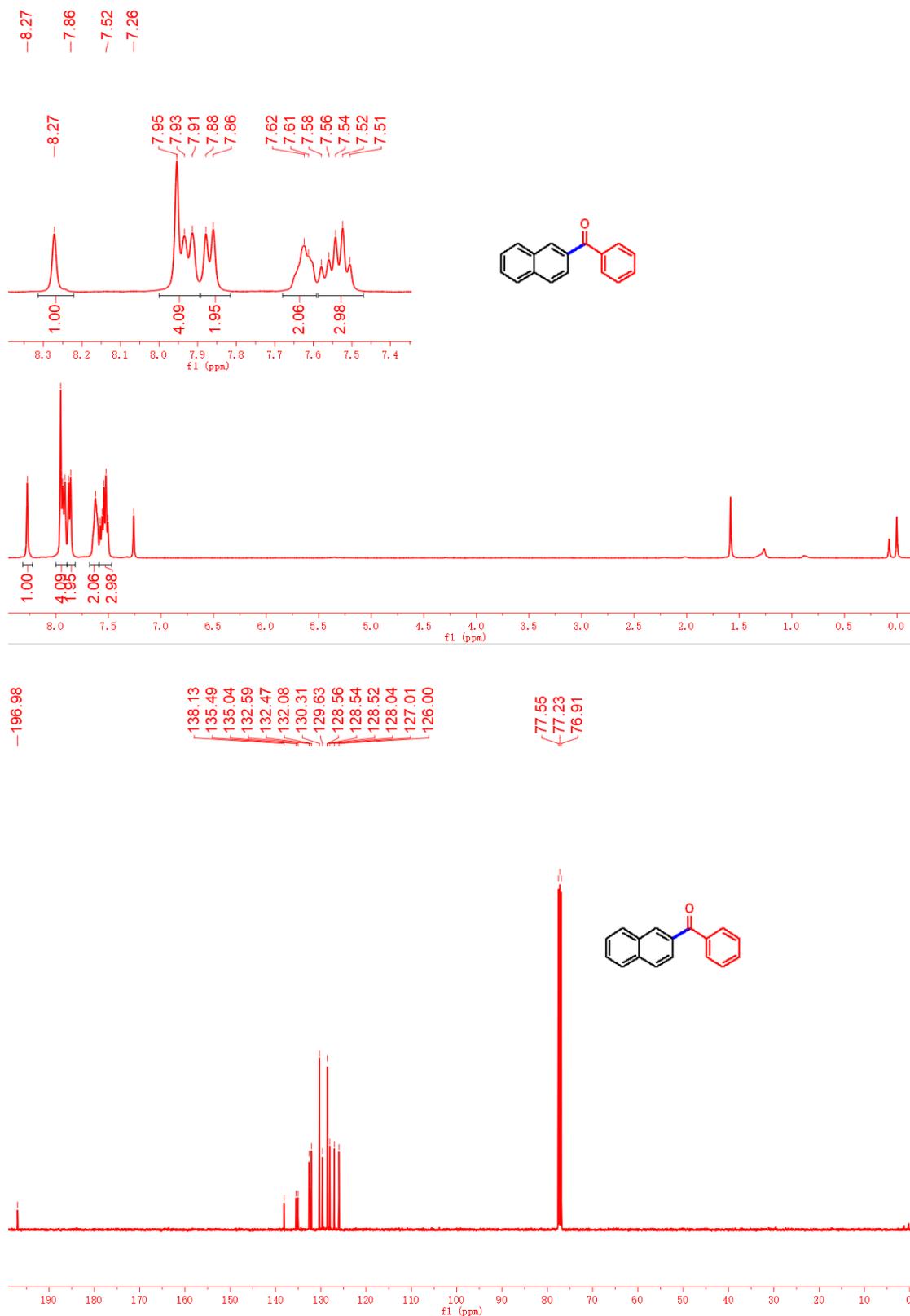


Figure S23. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for phenyl(quinolin-3-yl)methanone (**3pa**) in CDCl_3

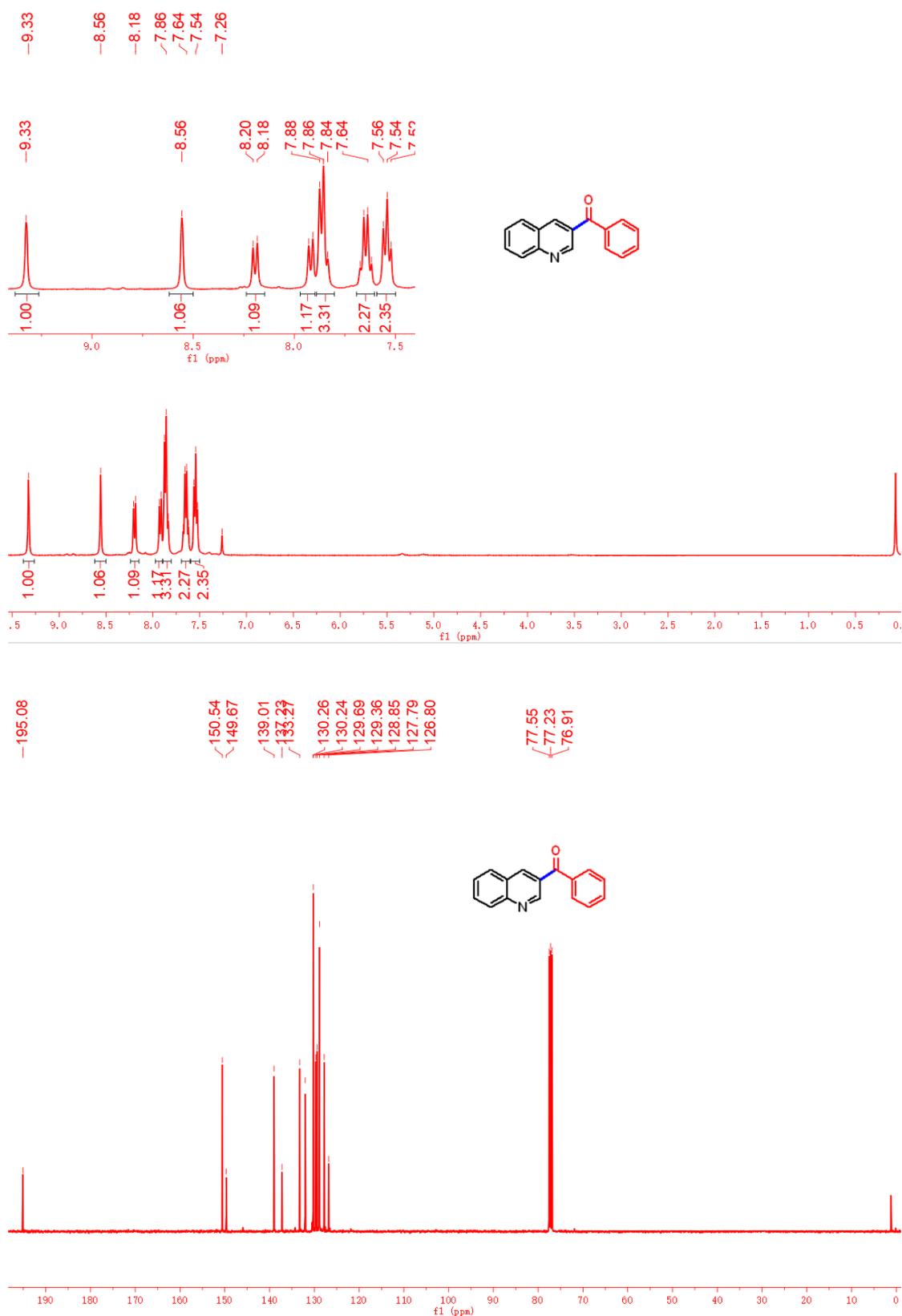
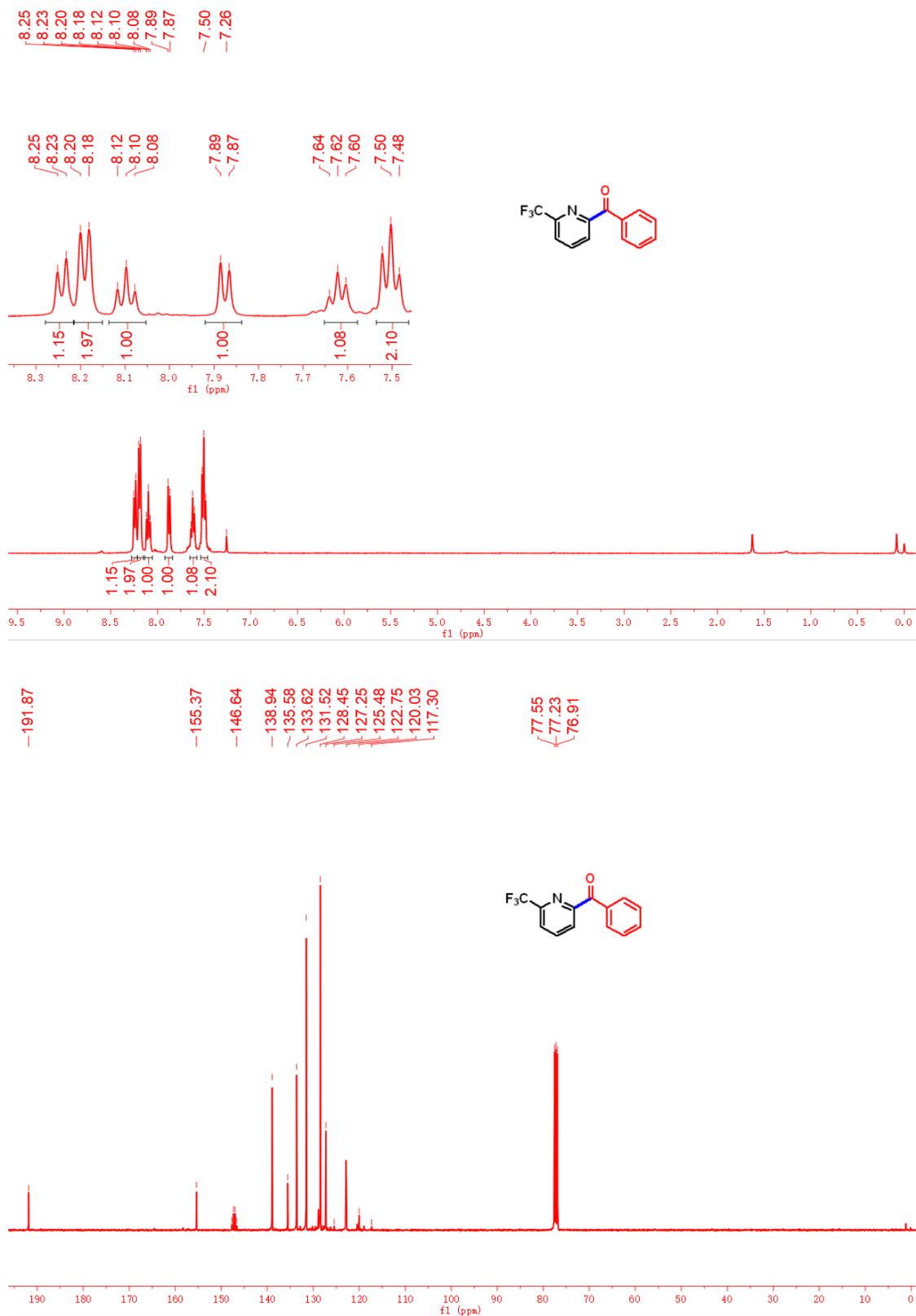


Figure S24. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for phenyl(6-(trifluoromethyl)pyridin-2-yl)methanone (**3qa**) in CDCl_3



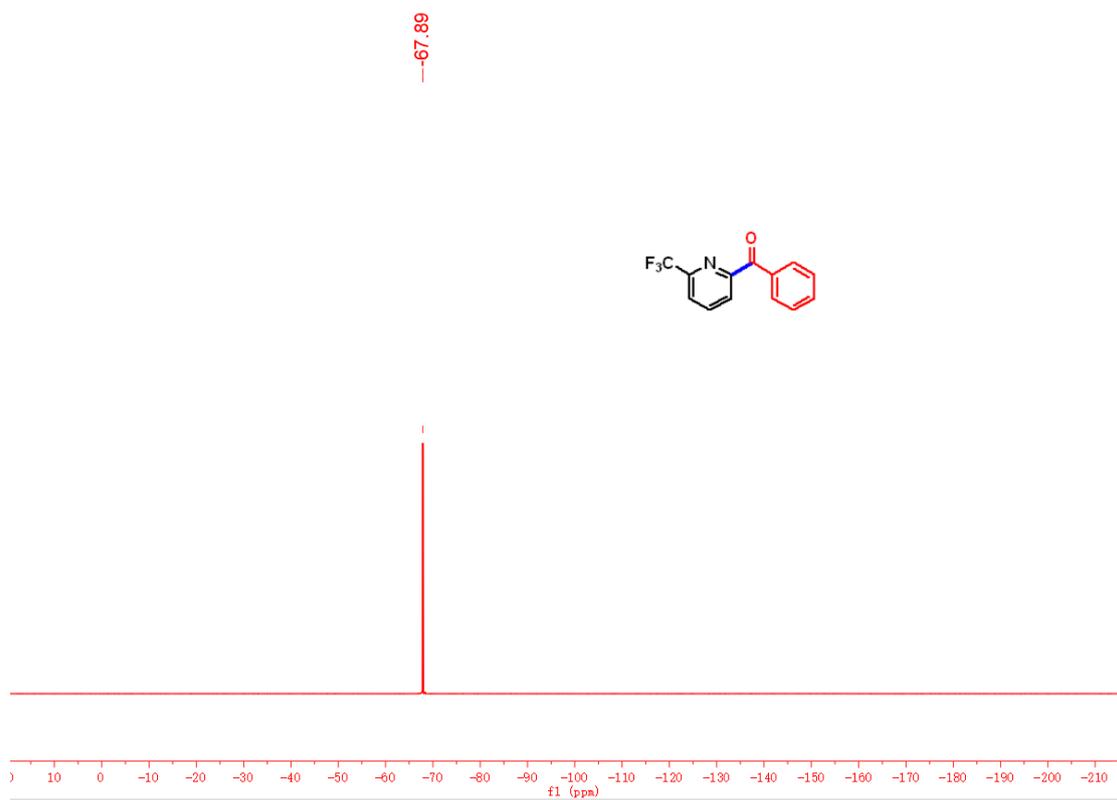


Figure S25. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(6-benzoylpyridin-2-yl)ethan-1-one (**3ra**) in CDCl_3

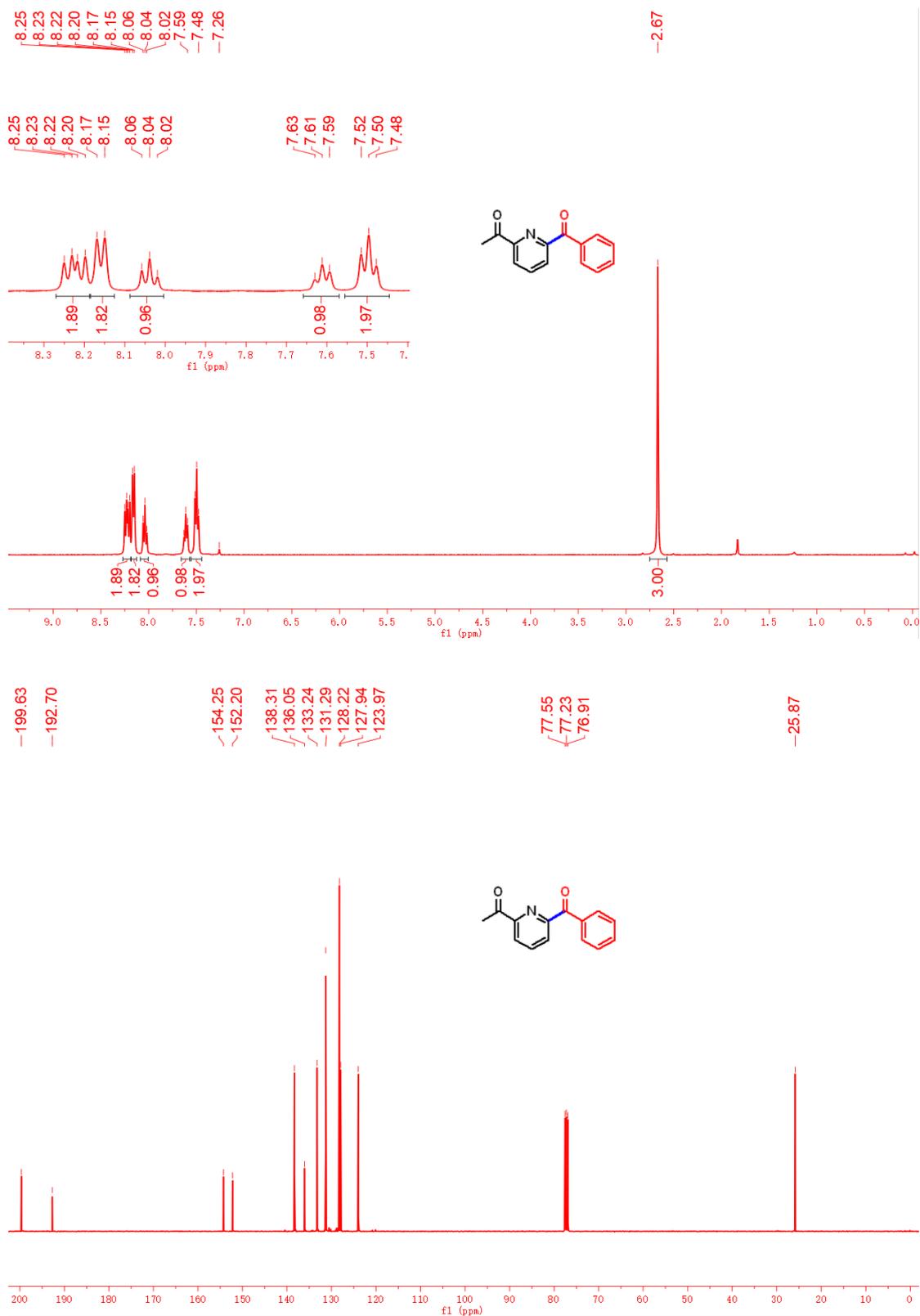


Figure S26. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for (4-bromophenyl)(phenyl)methanone (**3sa**) in CDCl_3

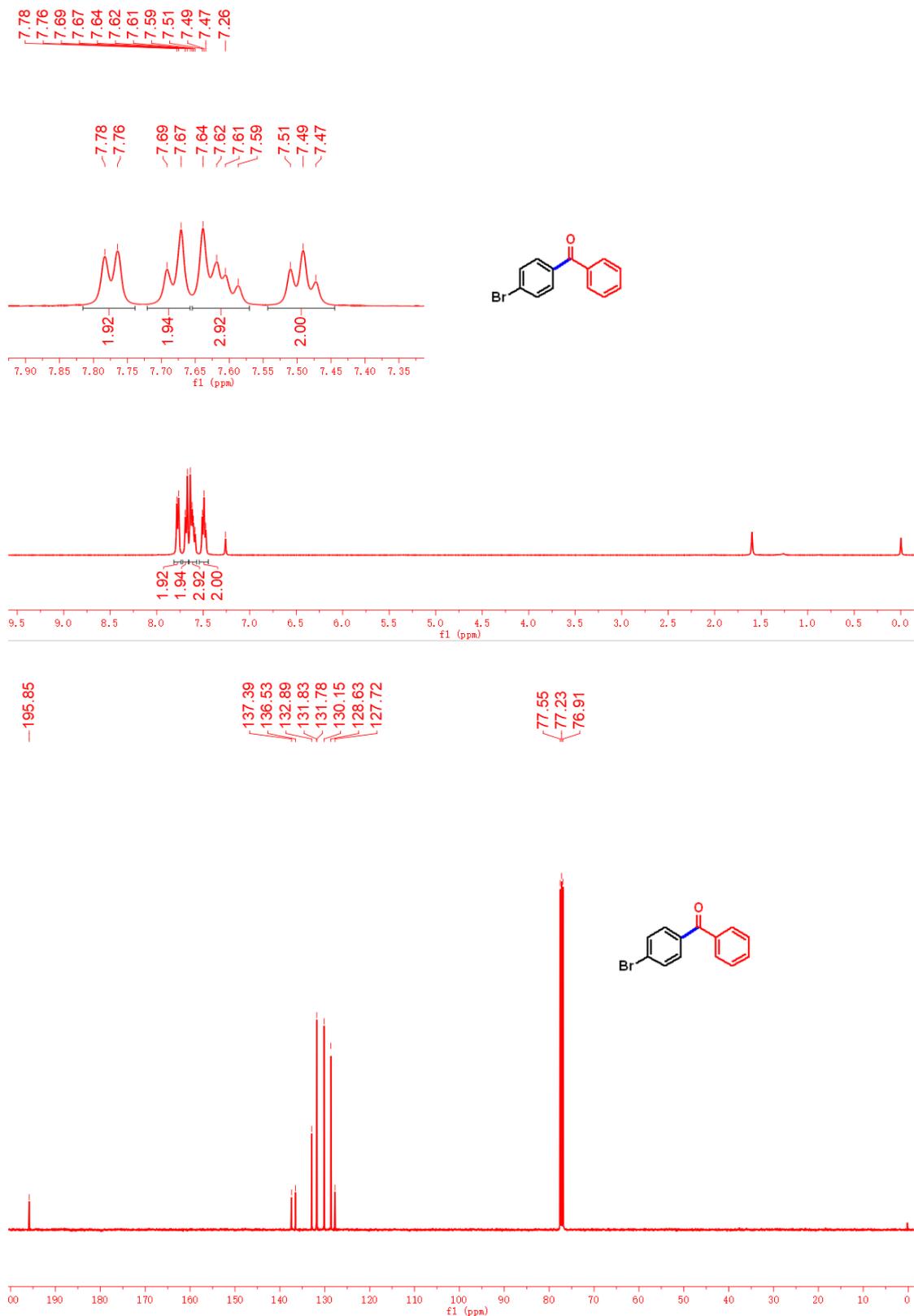


Figure S27. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for benzophenone (**3ta**) in CDCl_3

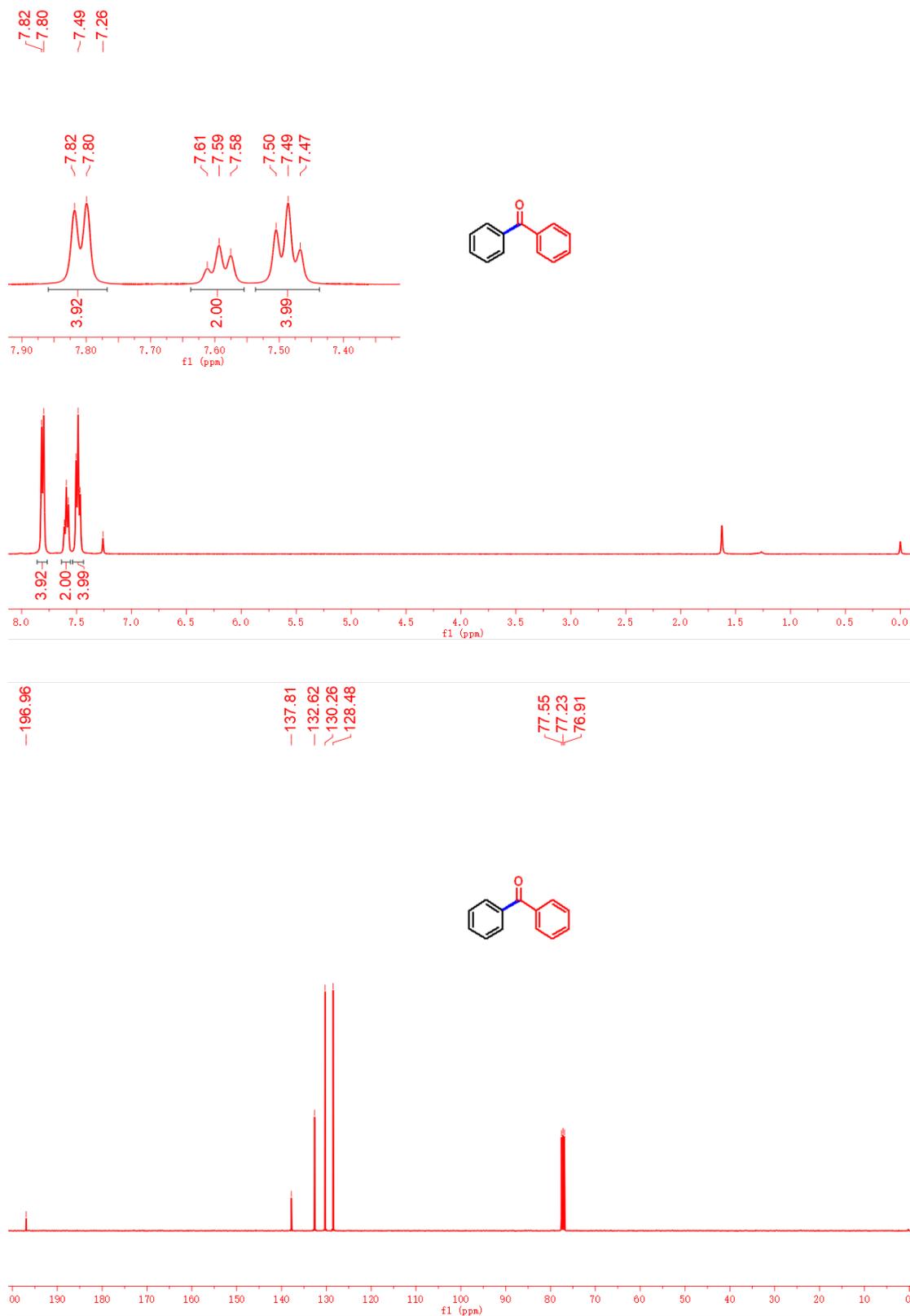


Figure S28. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for phenyl(p-tolyl)methanone (**3ua**) in CDCl_3

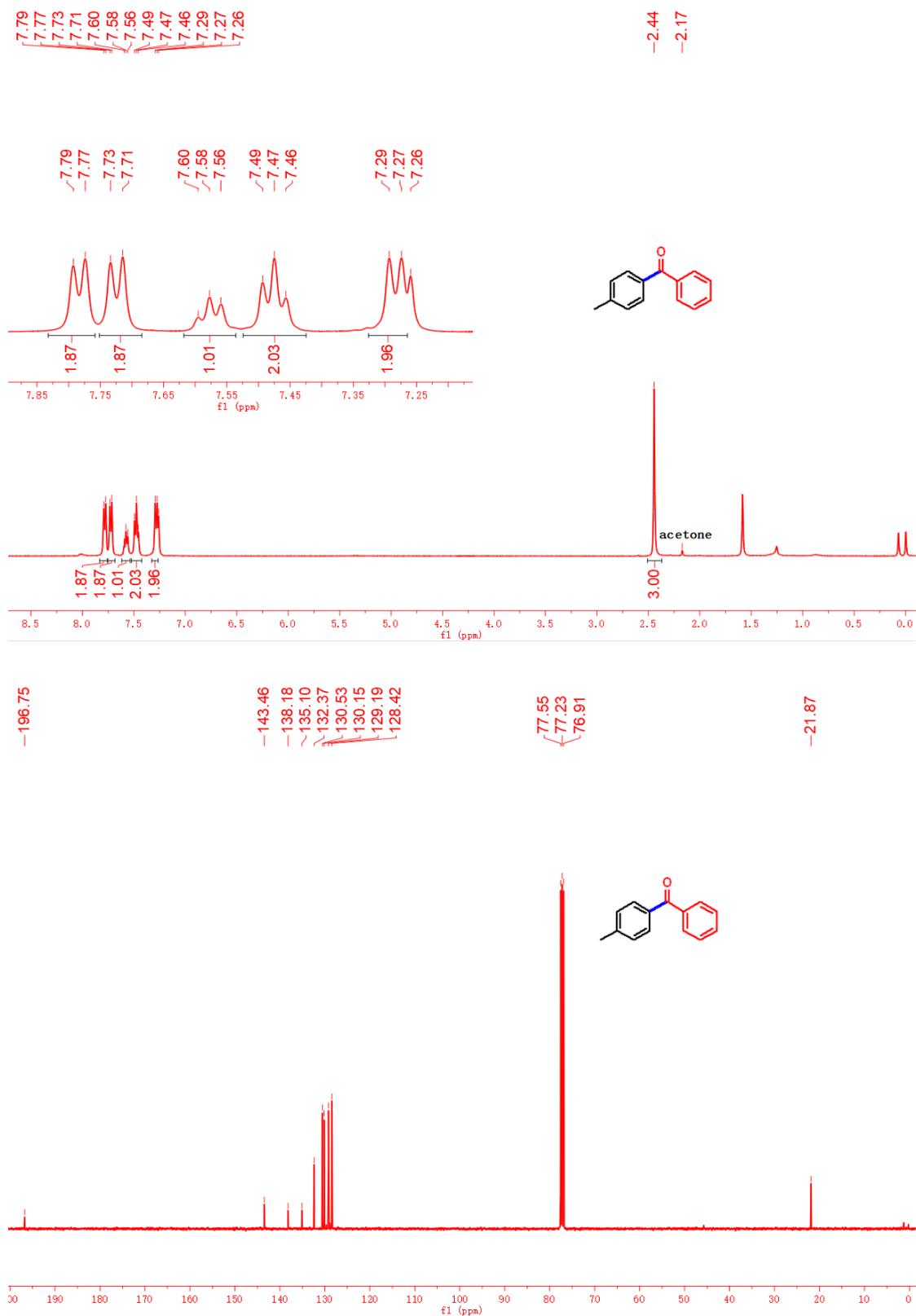


Figure S29. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for (4-methoxyphenyl)(phenyl)methanone (**3va**) in CDCl_3

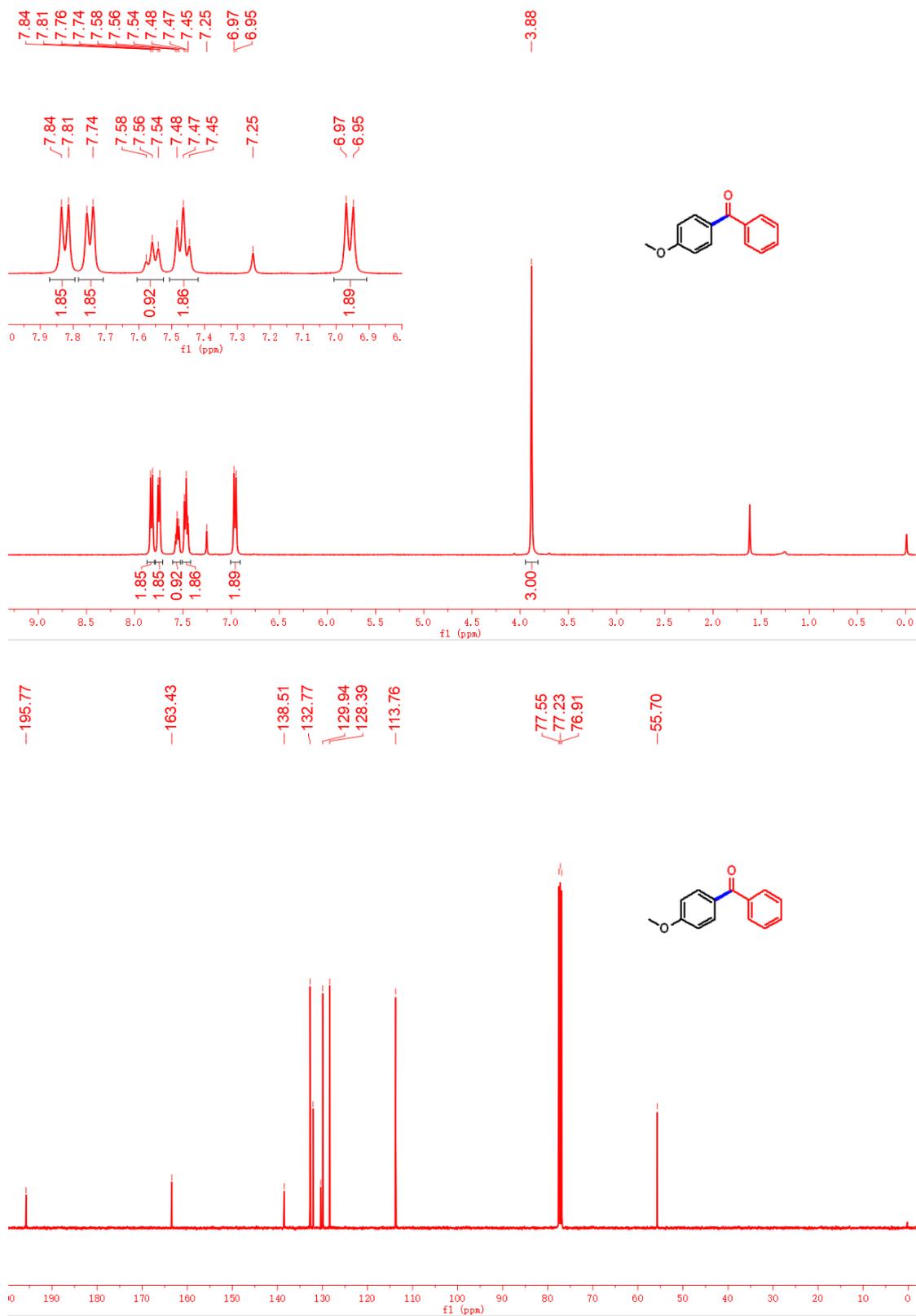


Figure S30. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for (4-(tert-butyl)phenyl)(phenyl)methanone (**3wa**) in CDCl_3

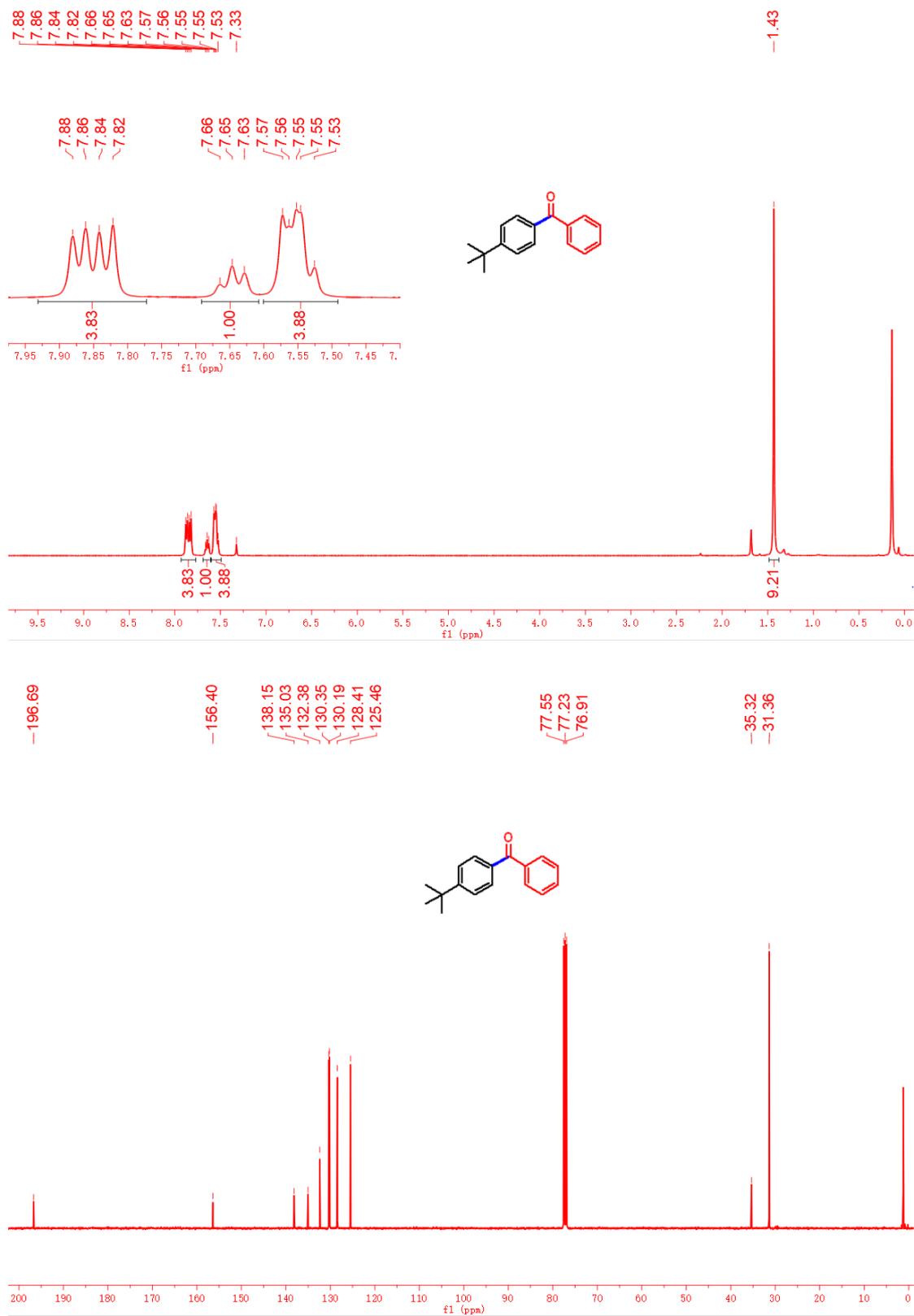


Figure S31. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for phenyl(m-tolyl)methanone (**3xa**) in CDCl_3

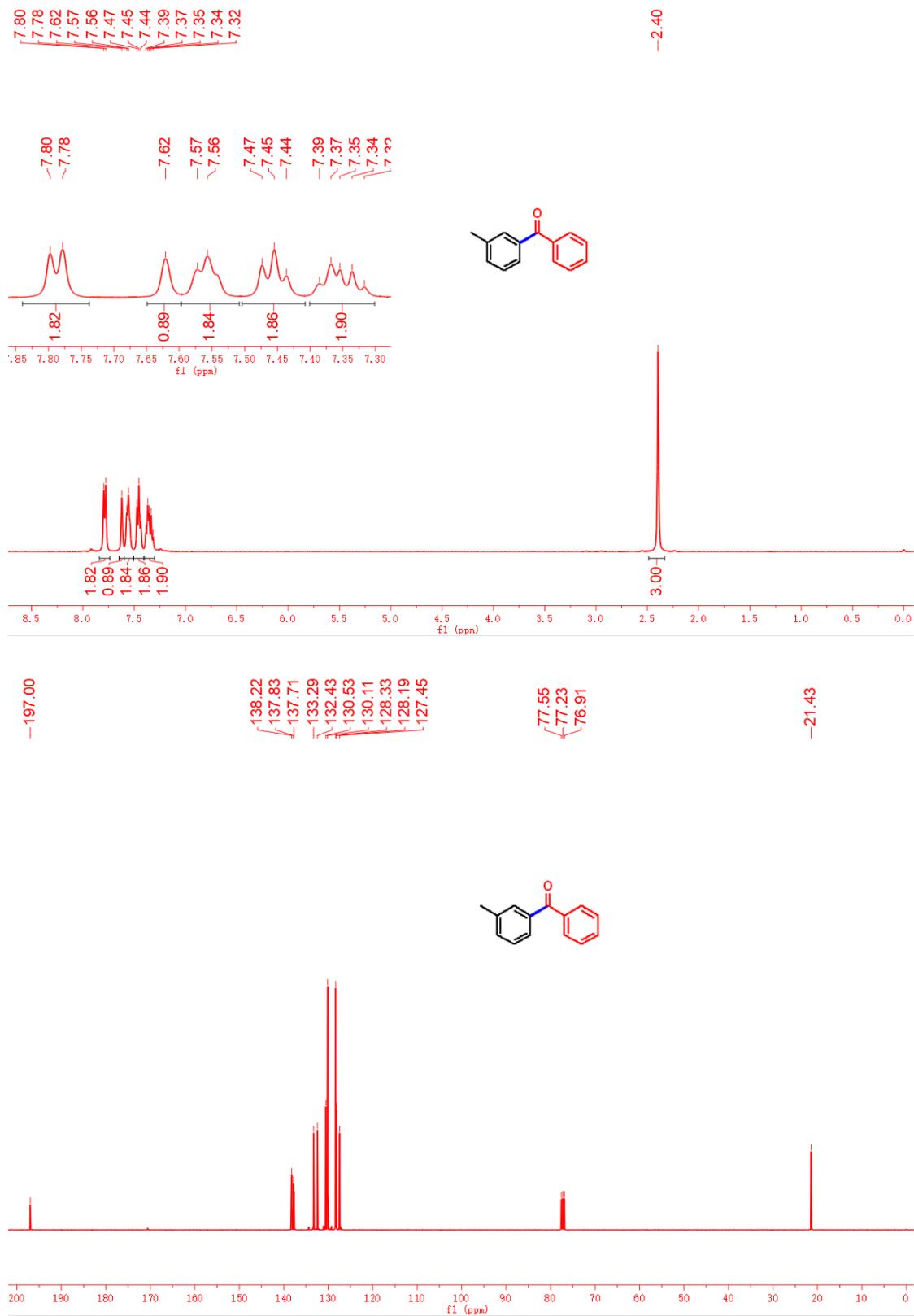


Figure S32. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for phenyl(pyridin-4-yl)methanone (**3ya**) in CDCl_3

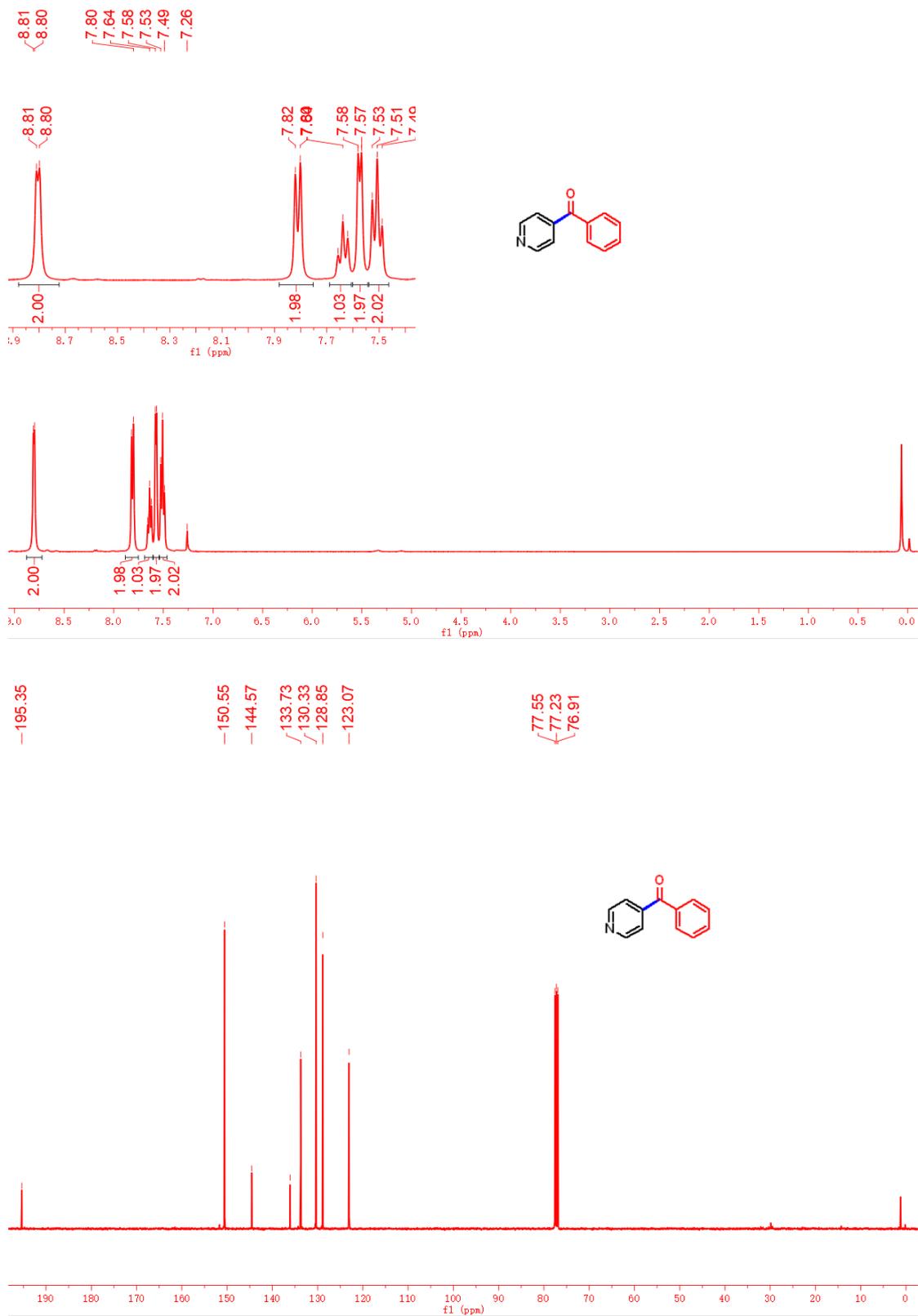


Figure S33. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for benzo[*d*][1,3]dioxol-5-yl(phenyl)methanone (**3za**) in CDCl_3

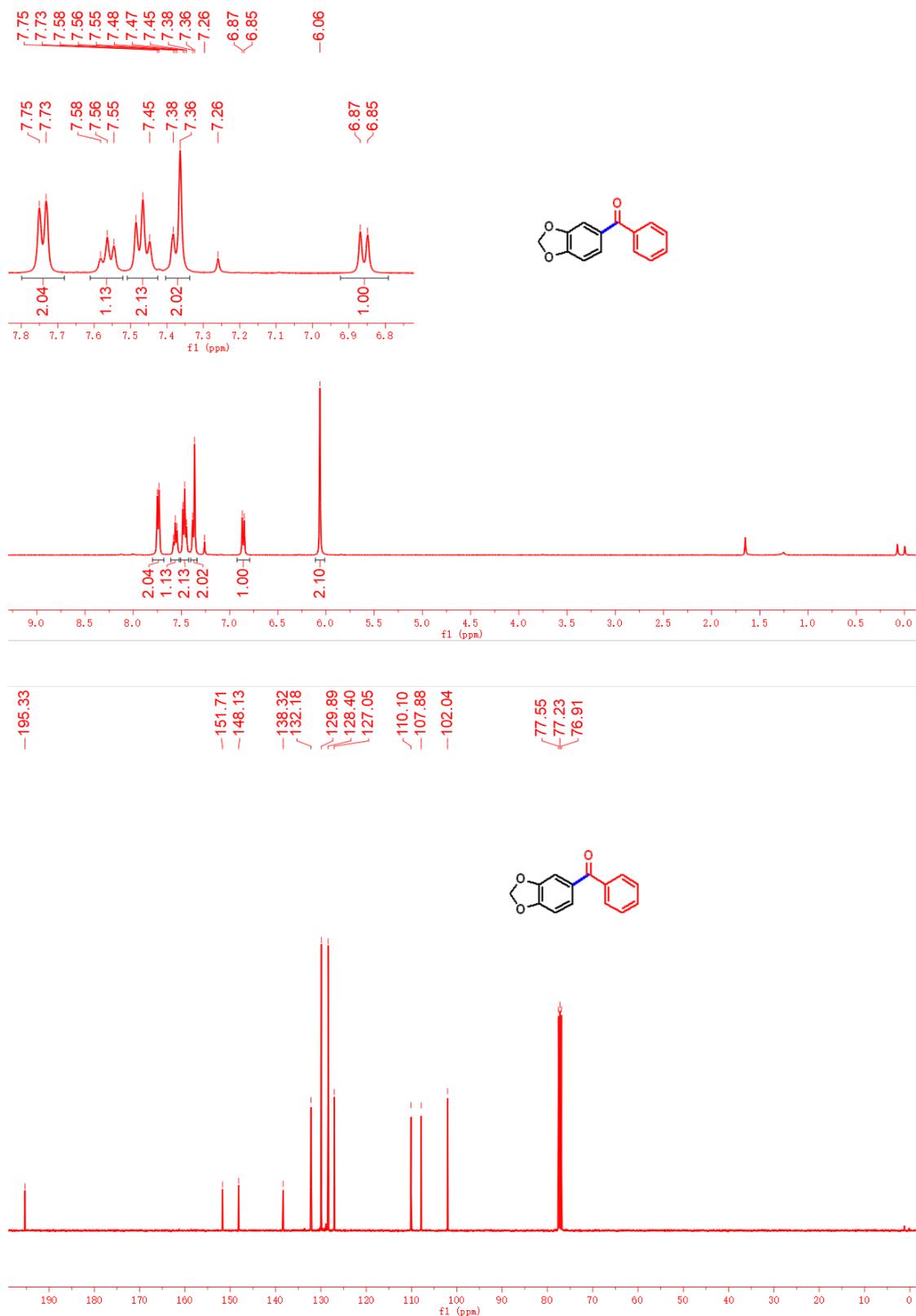


Figure S34. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(4-methylbenzoyl)benzonitrile (**3ab**) in CDCl_3

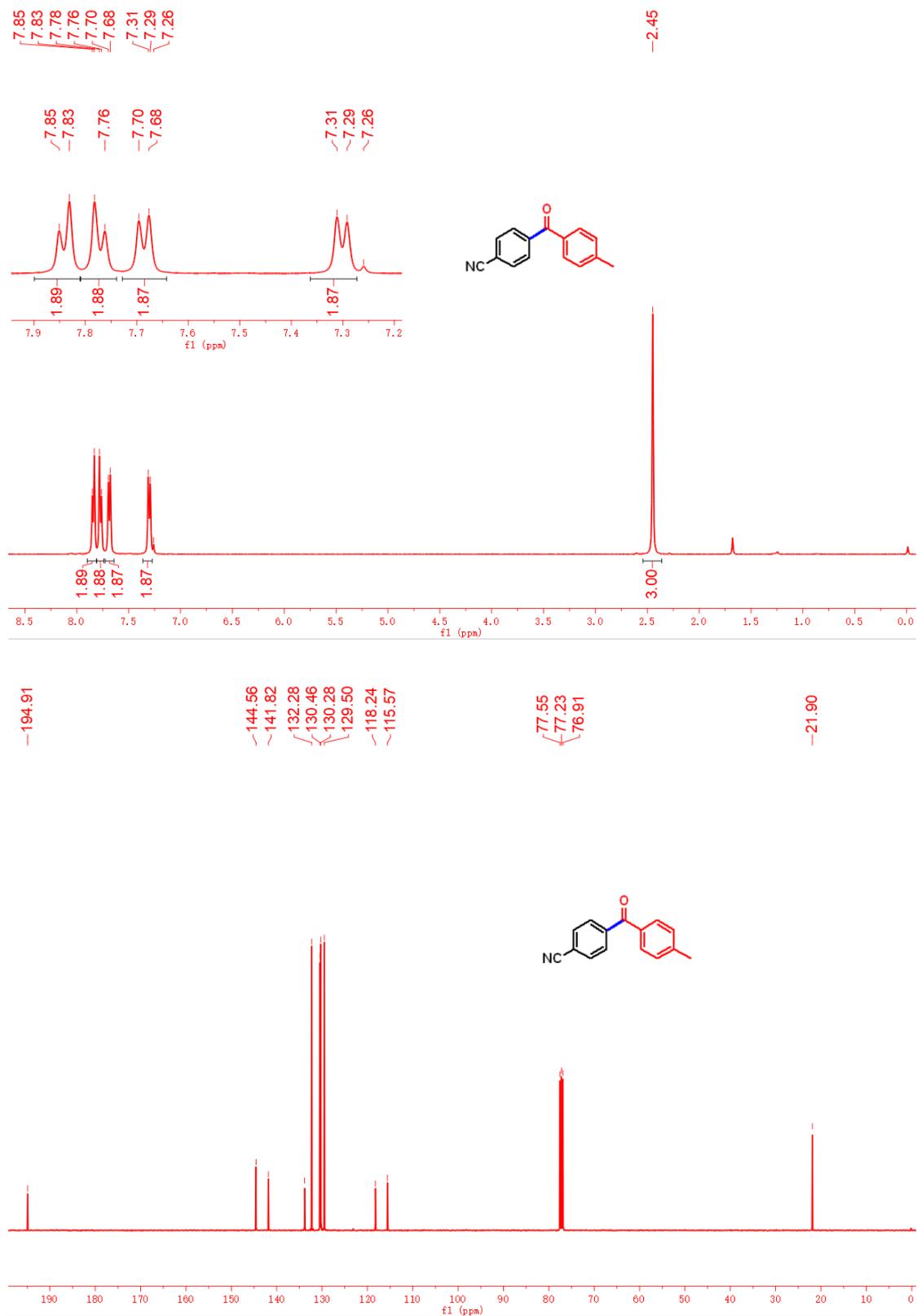


Figure S35. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(4-methoxybenzoyl)benzonitrile (**3ac**) in CDCl_3

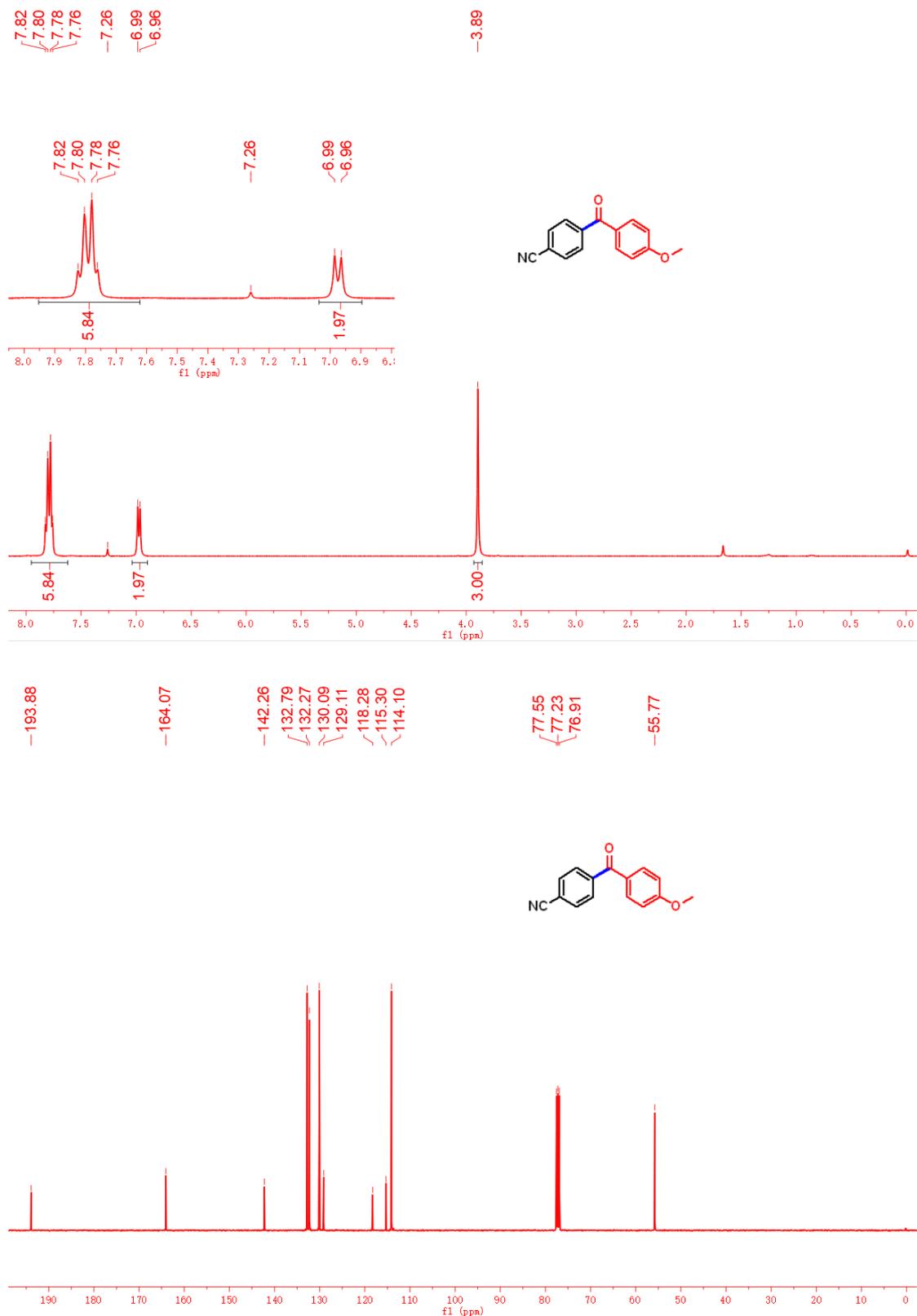


Figure S36. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(4-pentylbenzoyl)benzonitrile (**3ad**) in CDCl_3

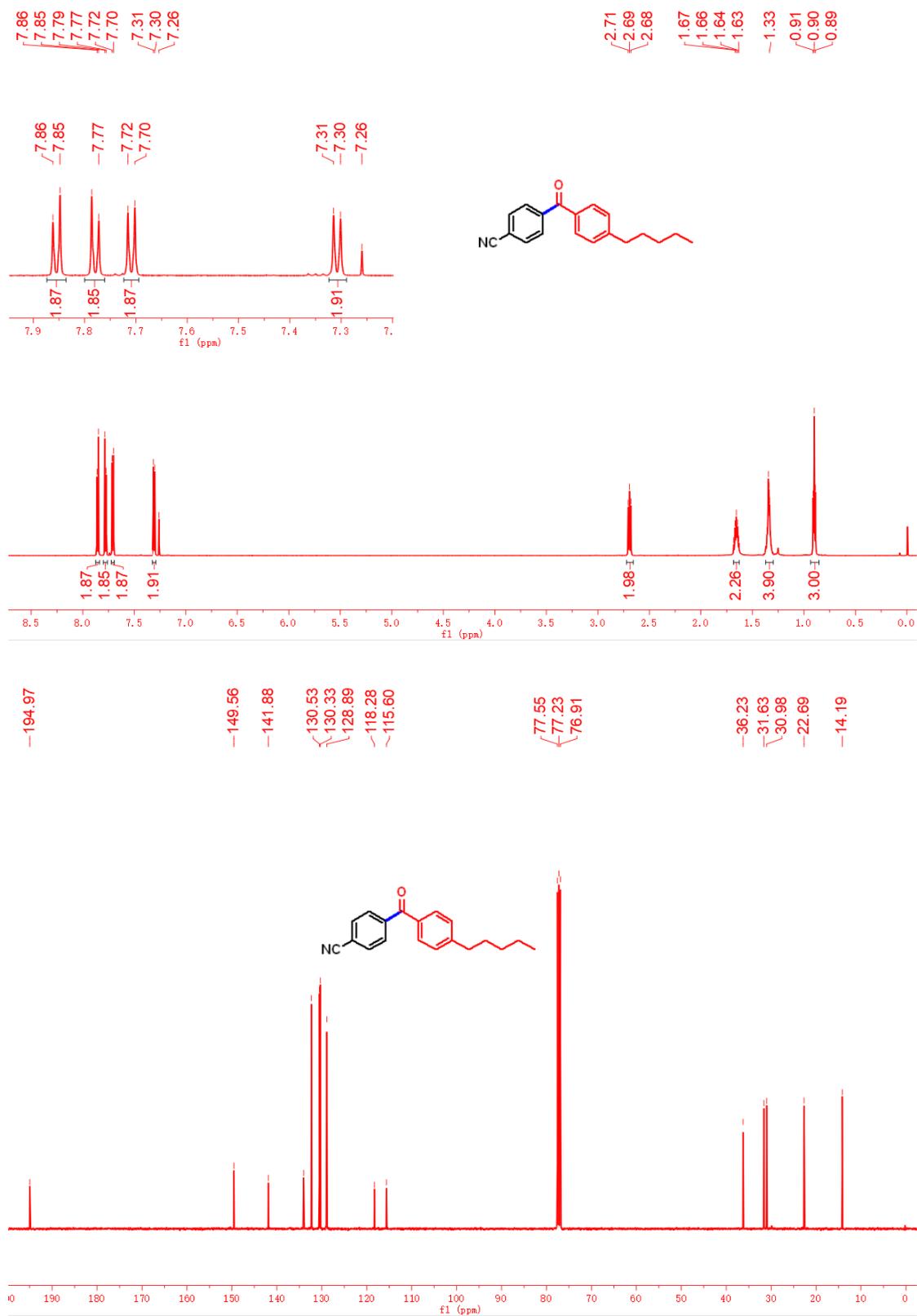


Figure S37. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(4-(dimethylamino)benzoyl)benzonitrile (**3ae**) in CDCl_3

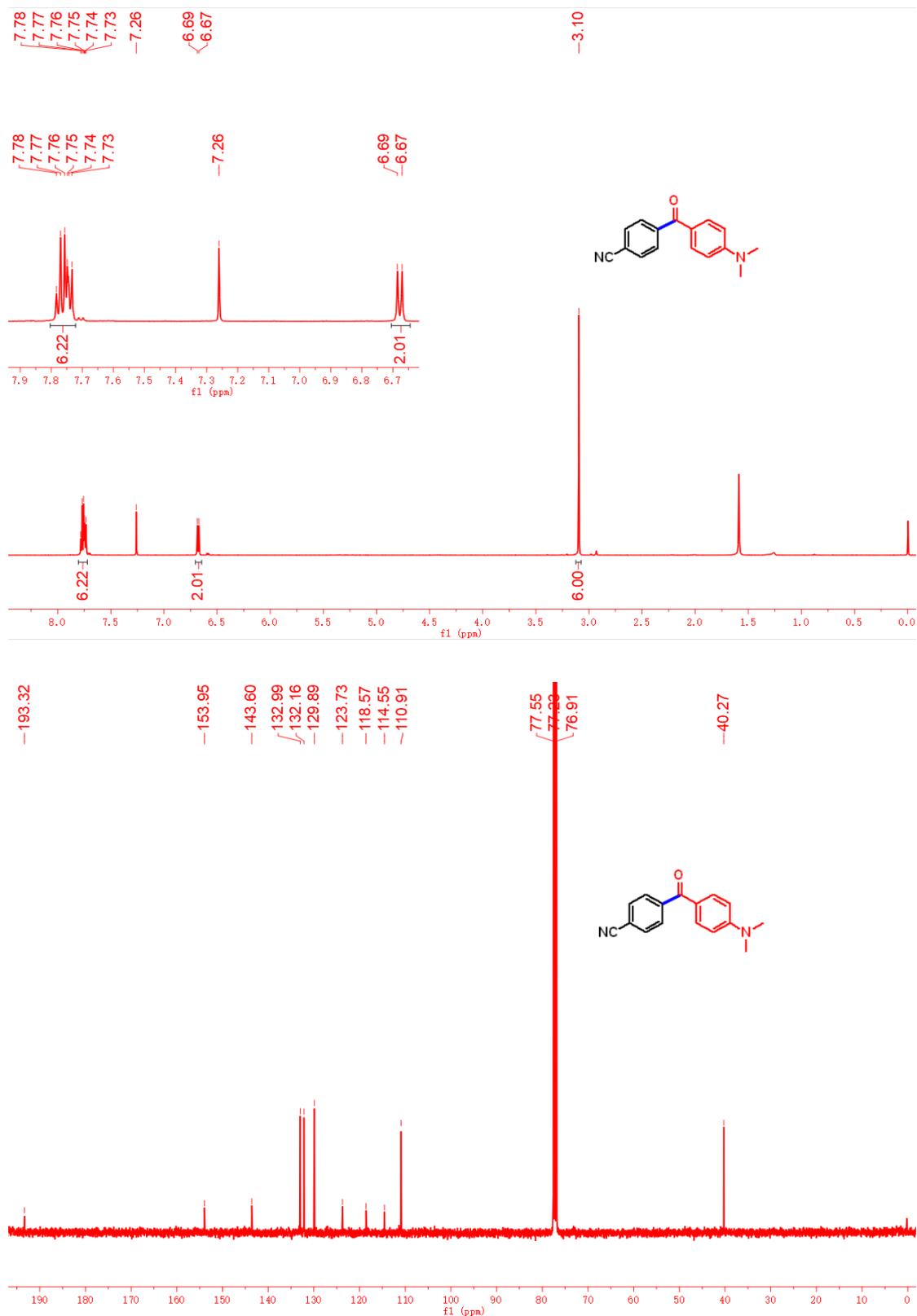
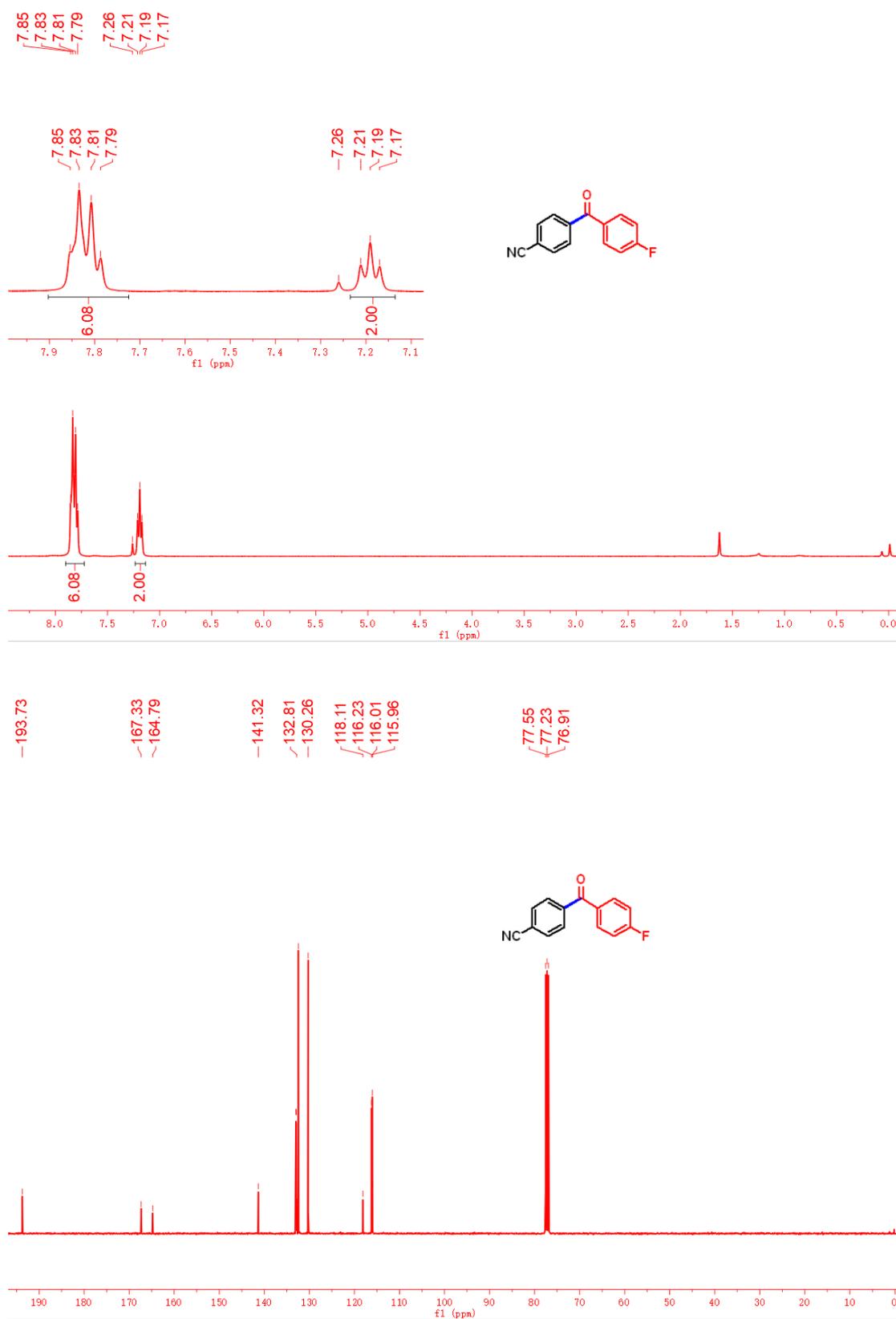


Figure S38. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 4-(4-fluorobenzoyl)benzonitrile (**3af**) in CDCl_3



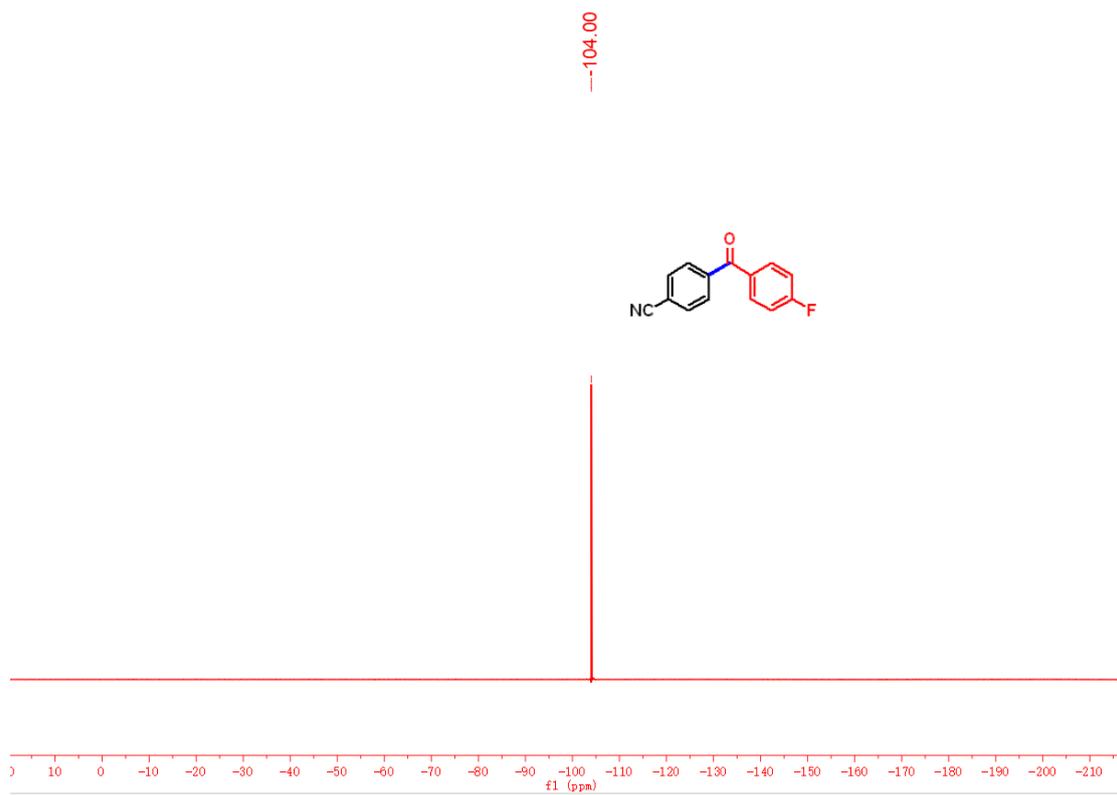


Figure S39. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(3-methylbenzoyl)benzonitrile (**3ag**) in CDCl_3

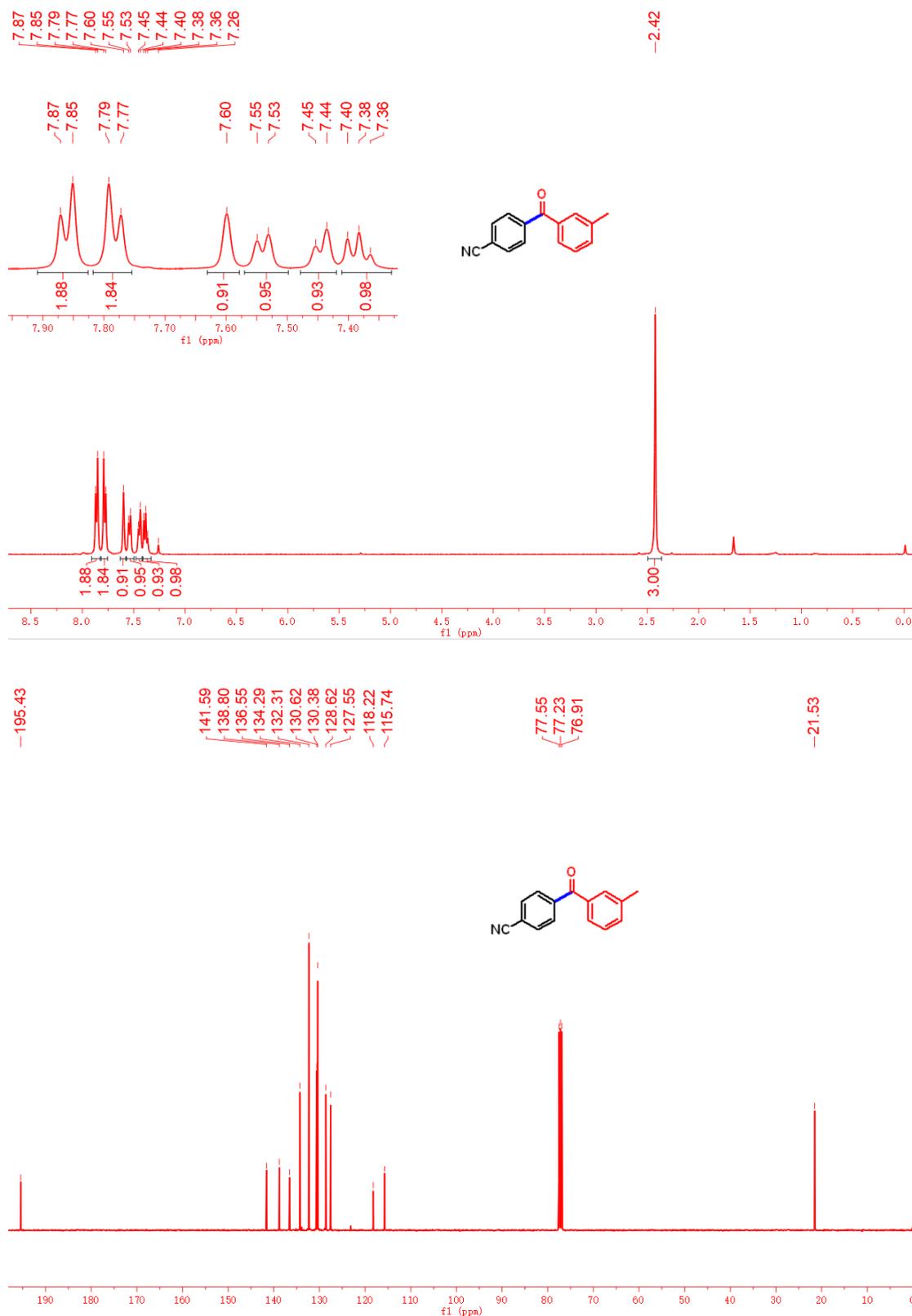


Figure S40. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(3-(tert-butyl)benzoyl)benzonitrile (**3ah**) in CDCl_3

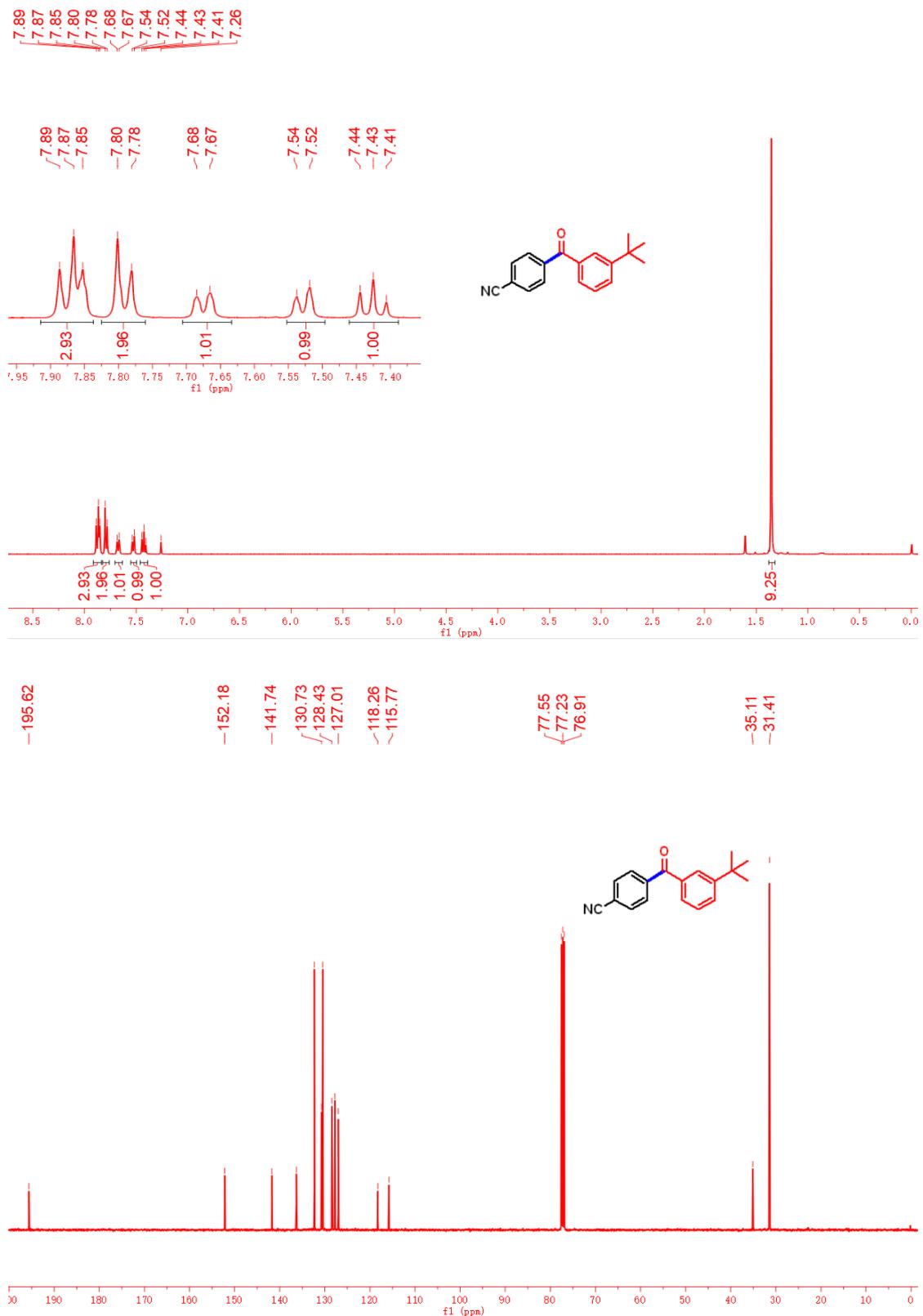


Figure S41. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(3,5-dimethylbenzoyl)benzonitrile (**3ai**) in CDCl_3

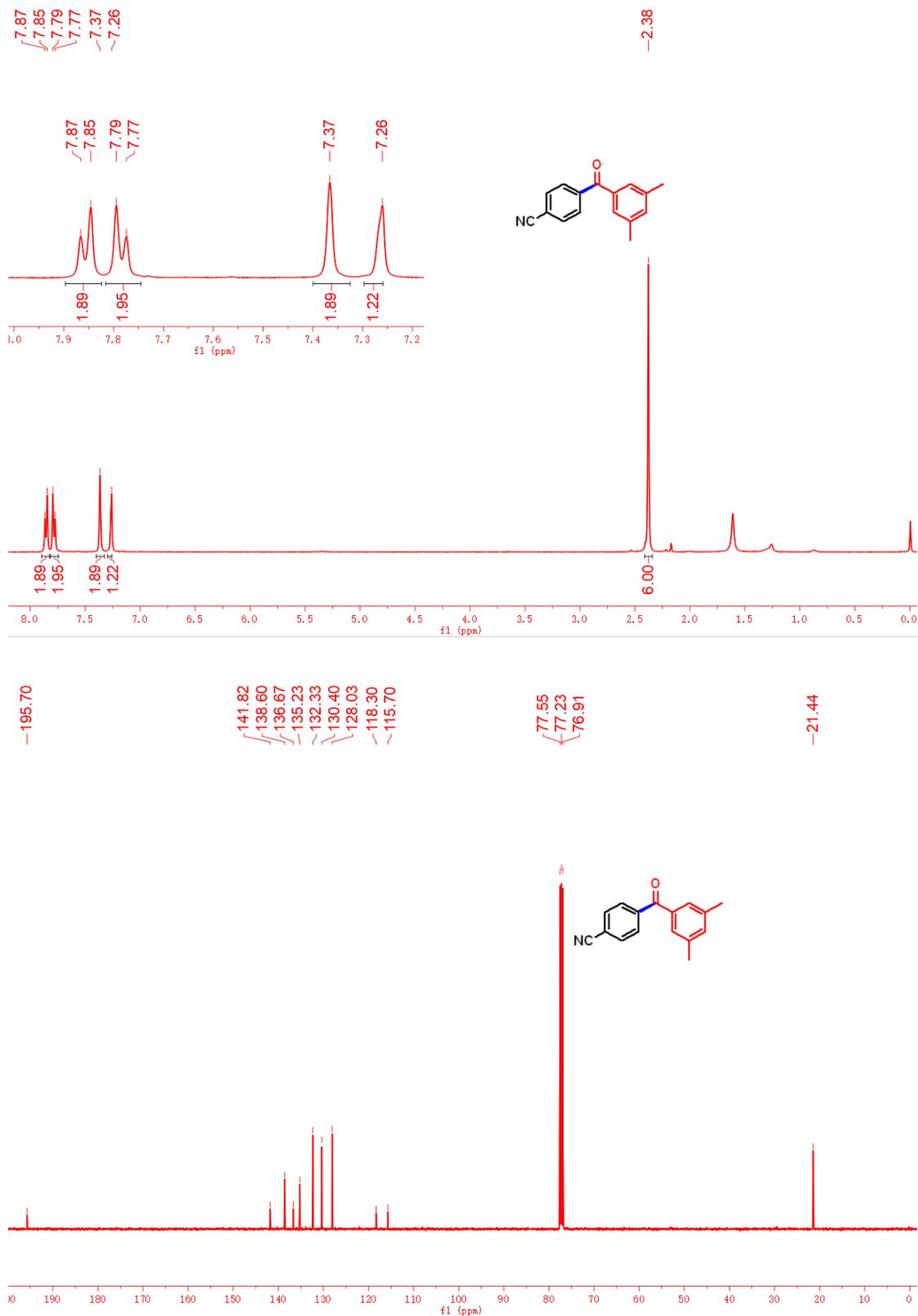


Figure S42. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(2,4,6-trimethylbenzoyl)benzonitrile (**3aj**) in CDCl_3

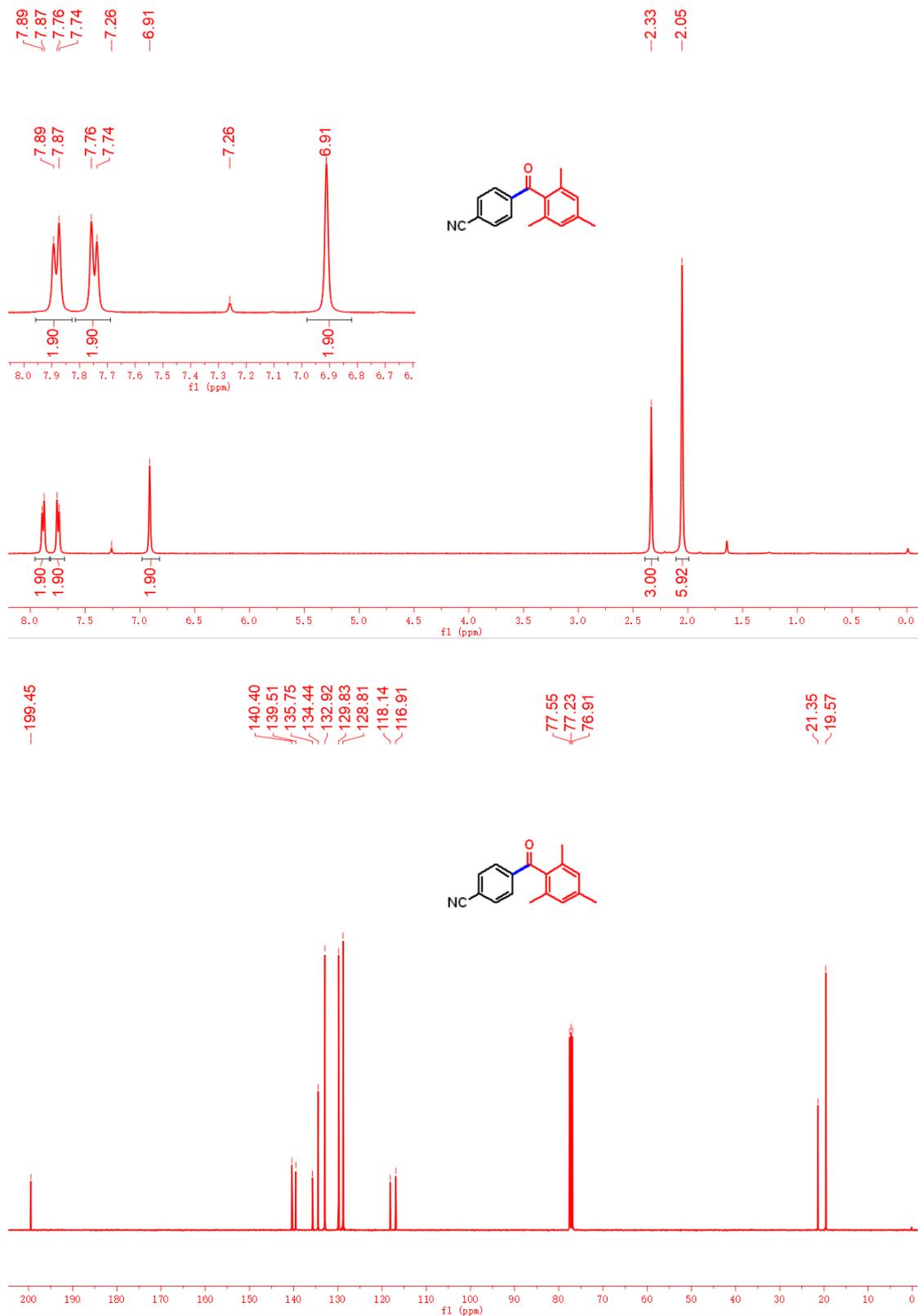


Figure S43. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(2-methylbenzoyl)benzonitrile (**3ak**) in CDCl_3

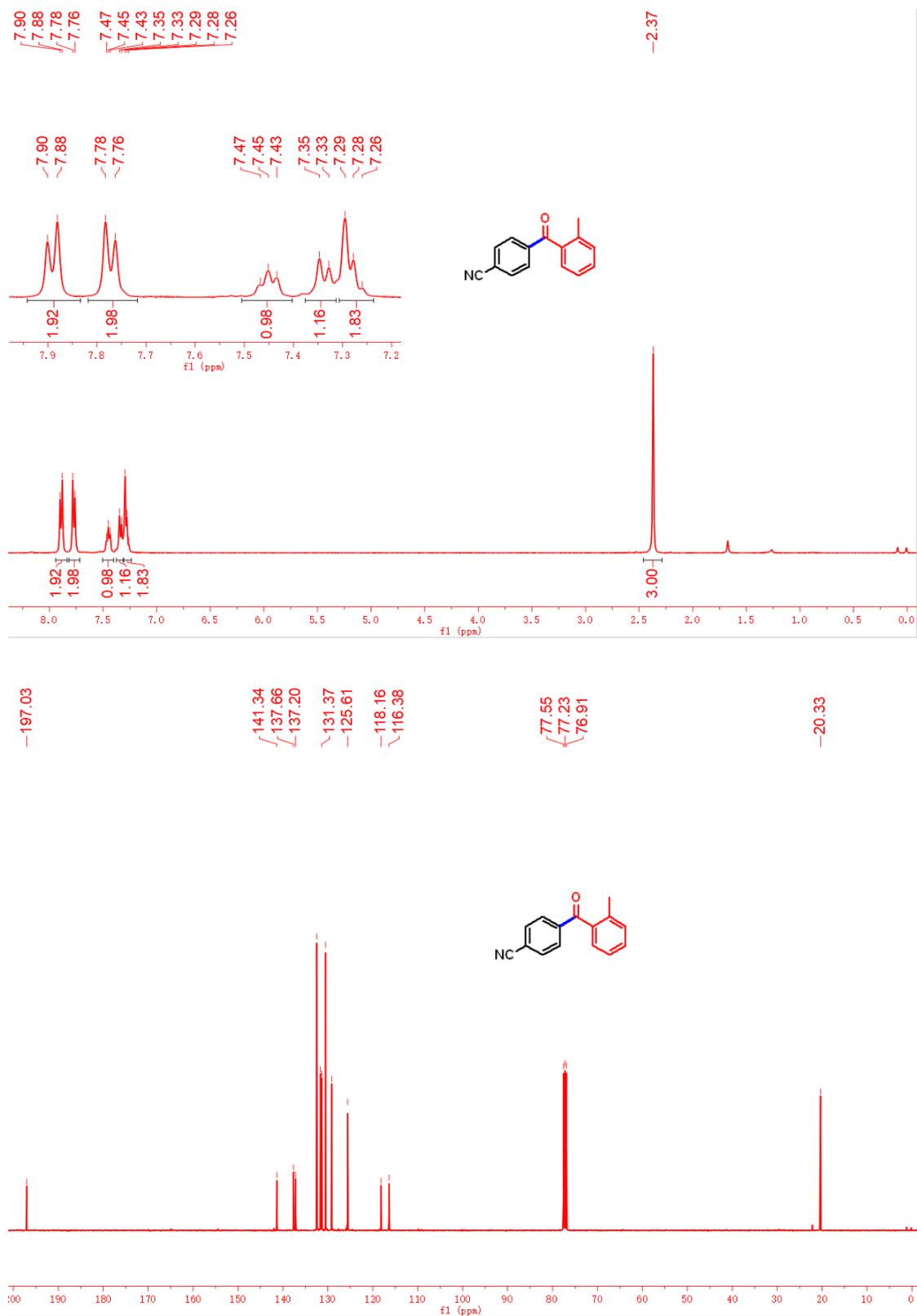


Figure S44. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(2-methoxybenzoyl)benzonitrile (**3a**) in CDCl_3

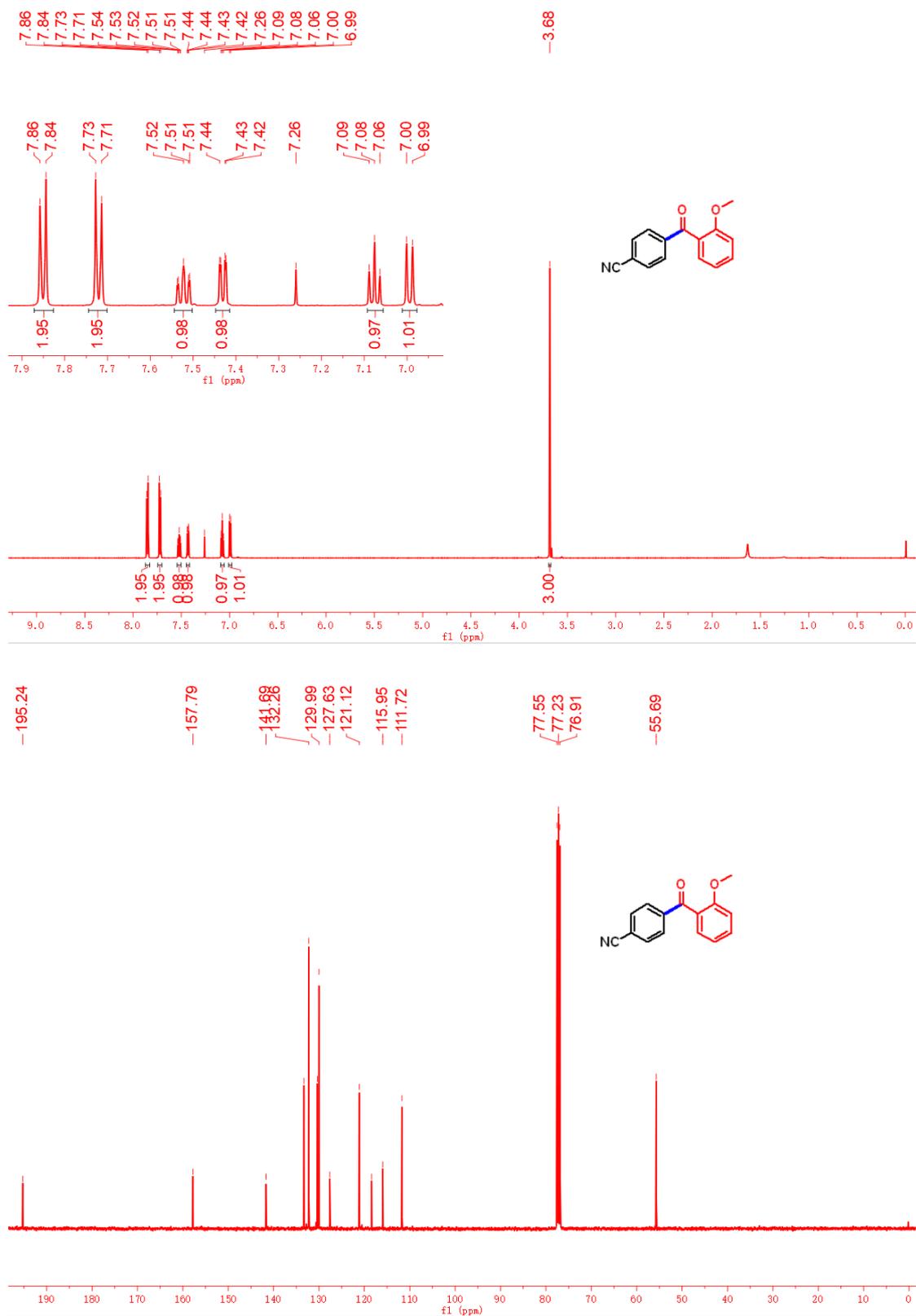


Figure S45. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(2,5-dimethoxybenzoyl)benzonitrile (**3am**) in CDCl_3

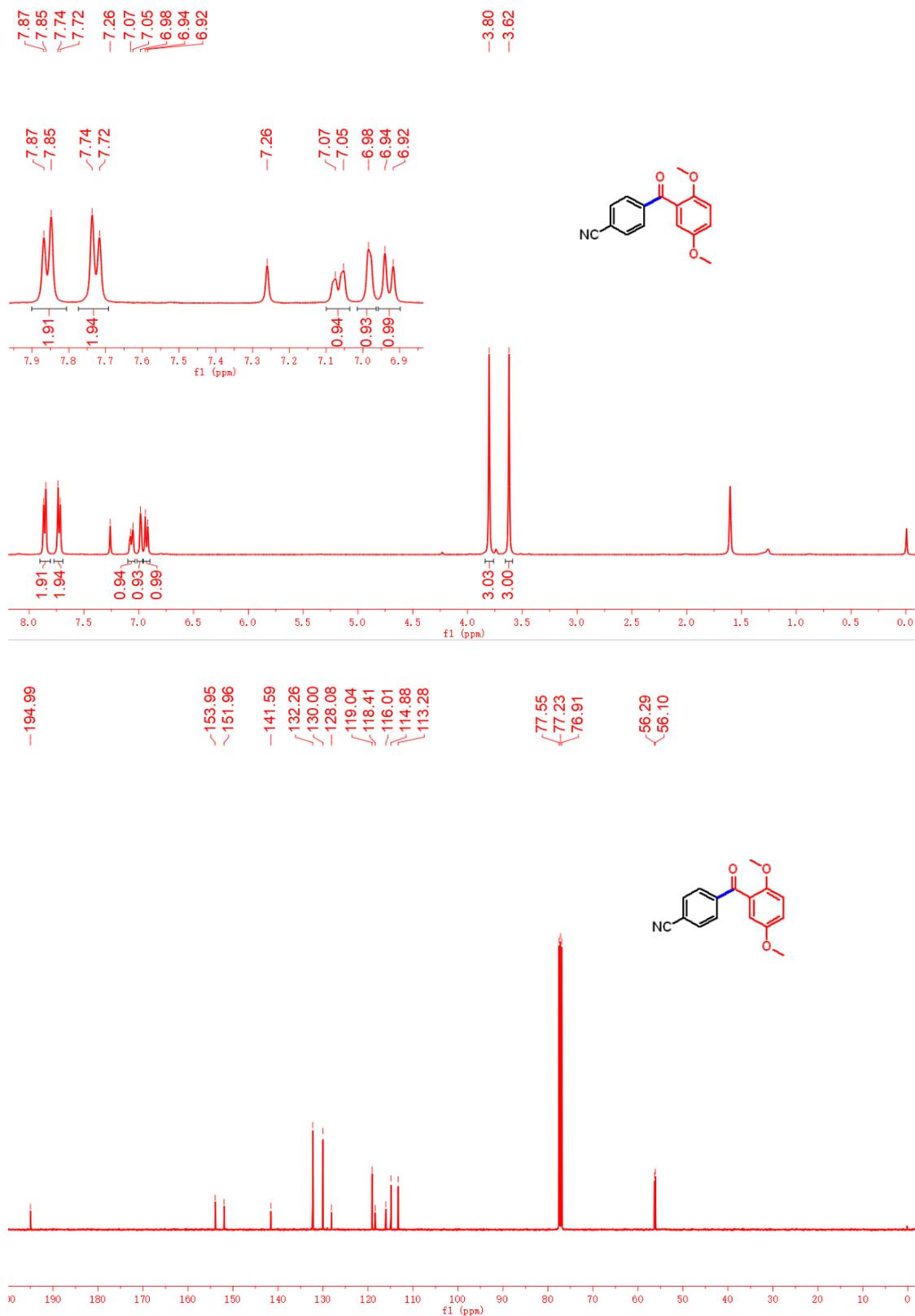


Figure S46. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(furan-2-carbonyl)benzotrile (**3an**) in CDCl_3

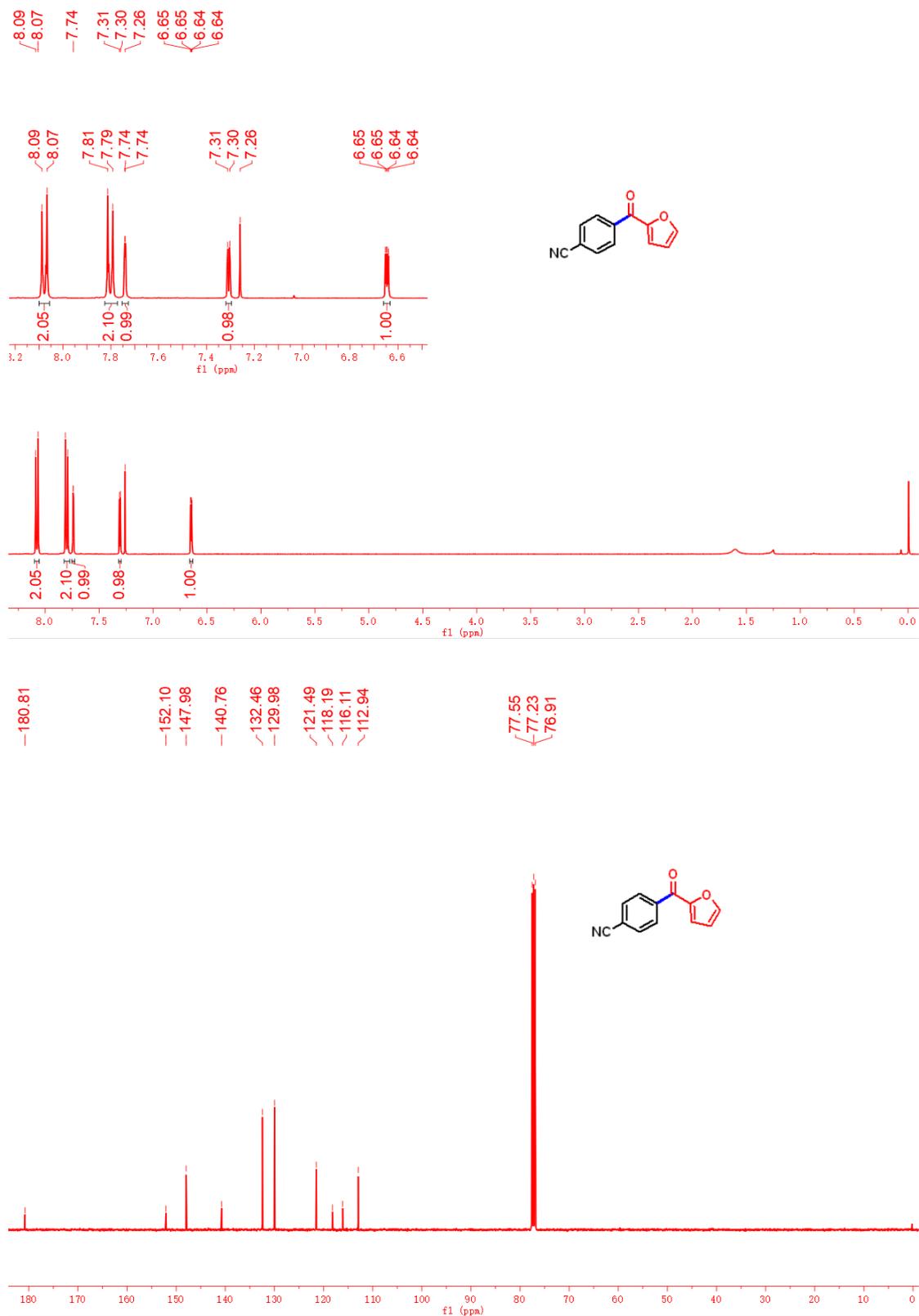


Figure S47. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-acetylbenzotrile (**3ao**) in CDCl_3

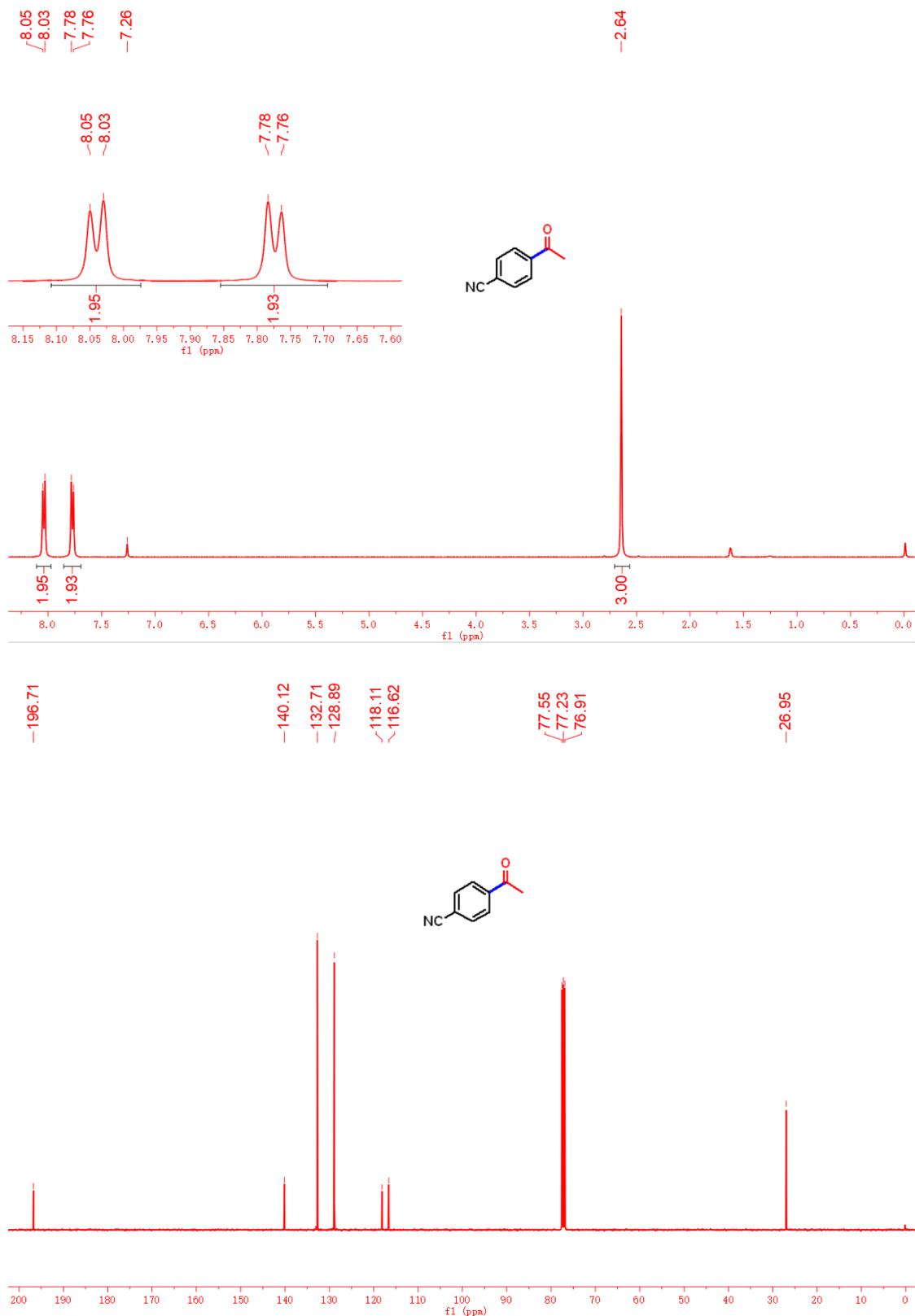


Figure S48. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-(3-methylbutanoyl)benzonitrile (**3ap**) in CDCl_3

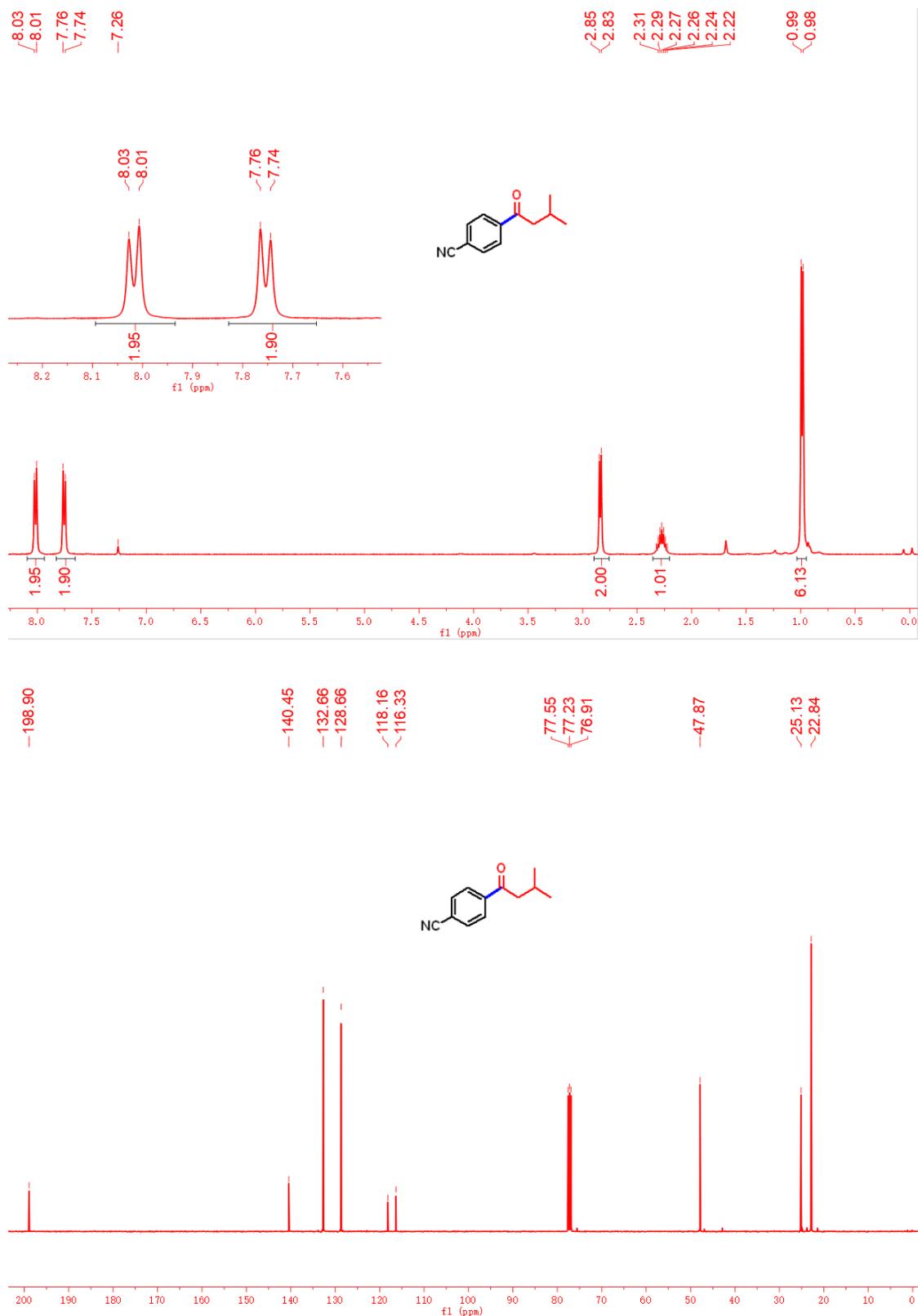


Figure S49. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4-cyano-N-methyl-N-phenylbenzamide (**3aq**) in CDCl_3

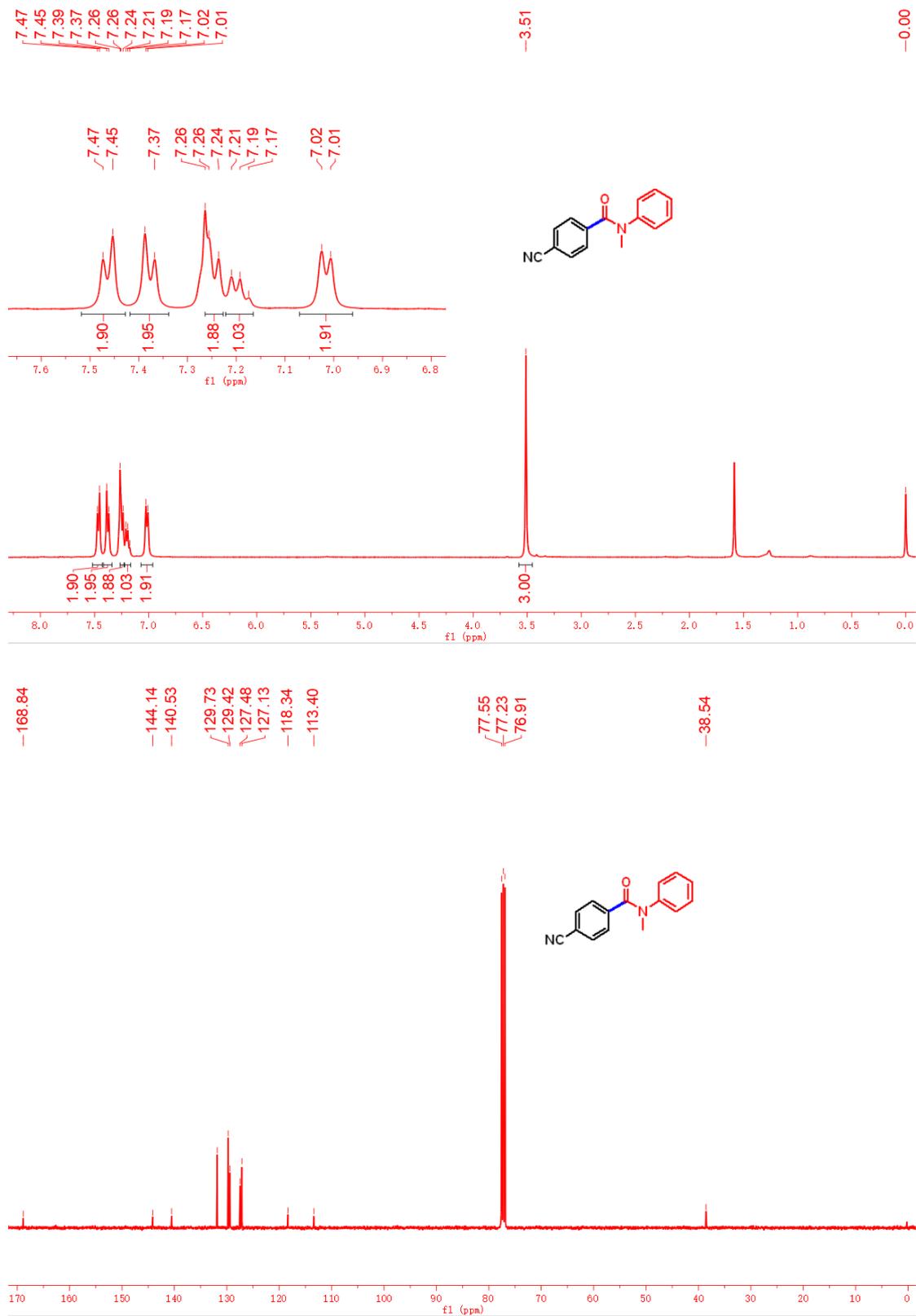


Figure S50. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-oxo-4-phenylbutanoate (**5aa**) in CDCl_3

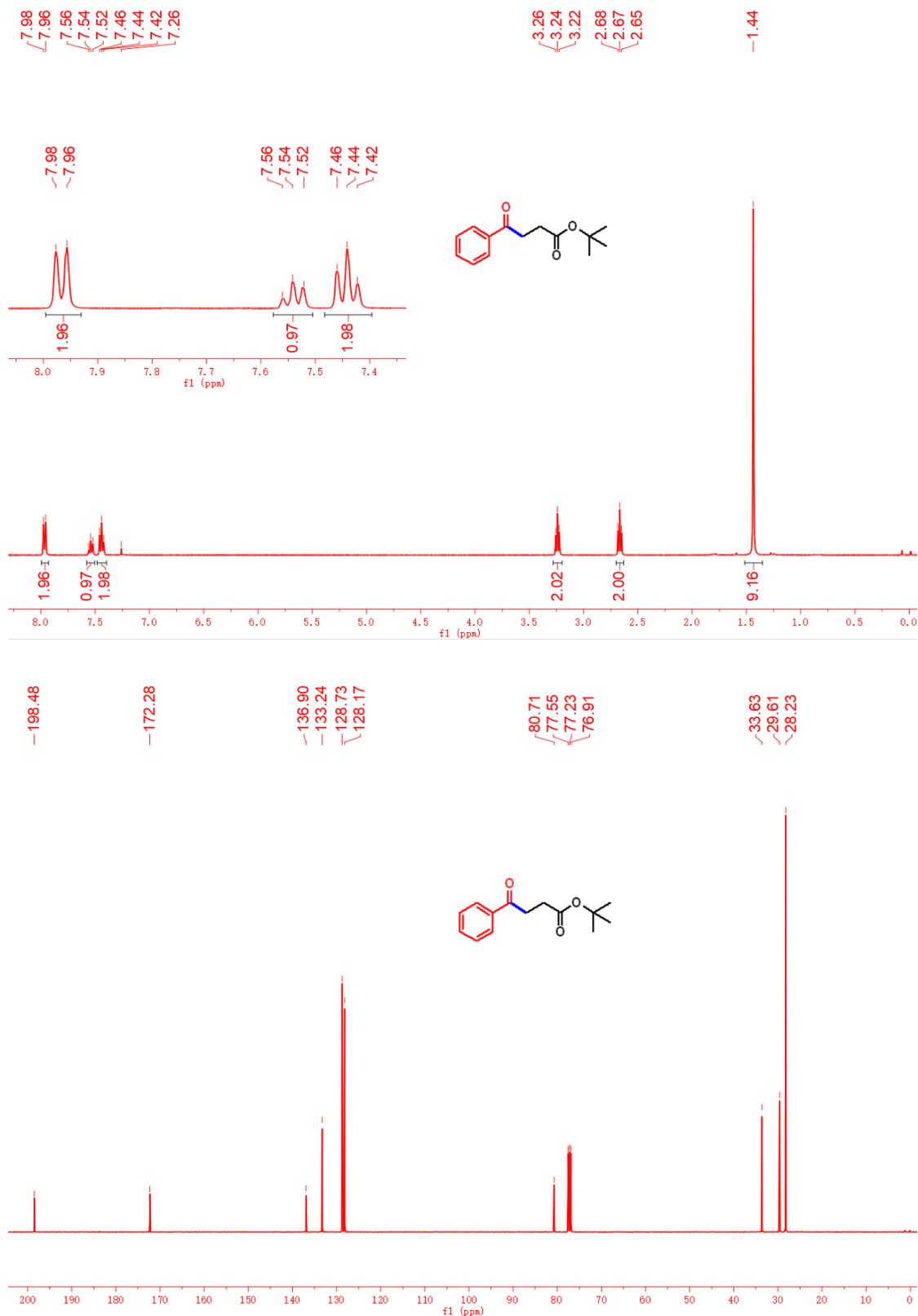


Figure S51. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-oxo-4-(*p*-tolyl)butanoate (**5ab**) in CDCl_3

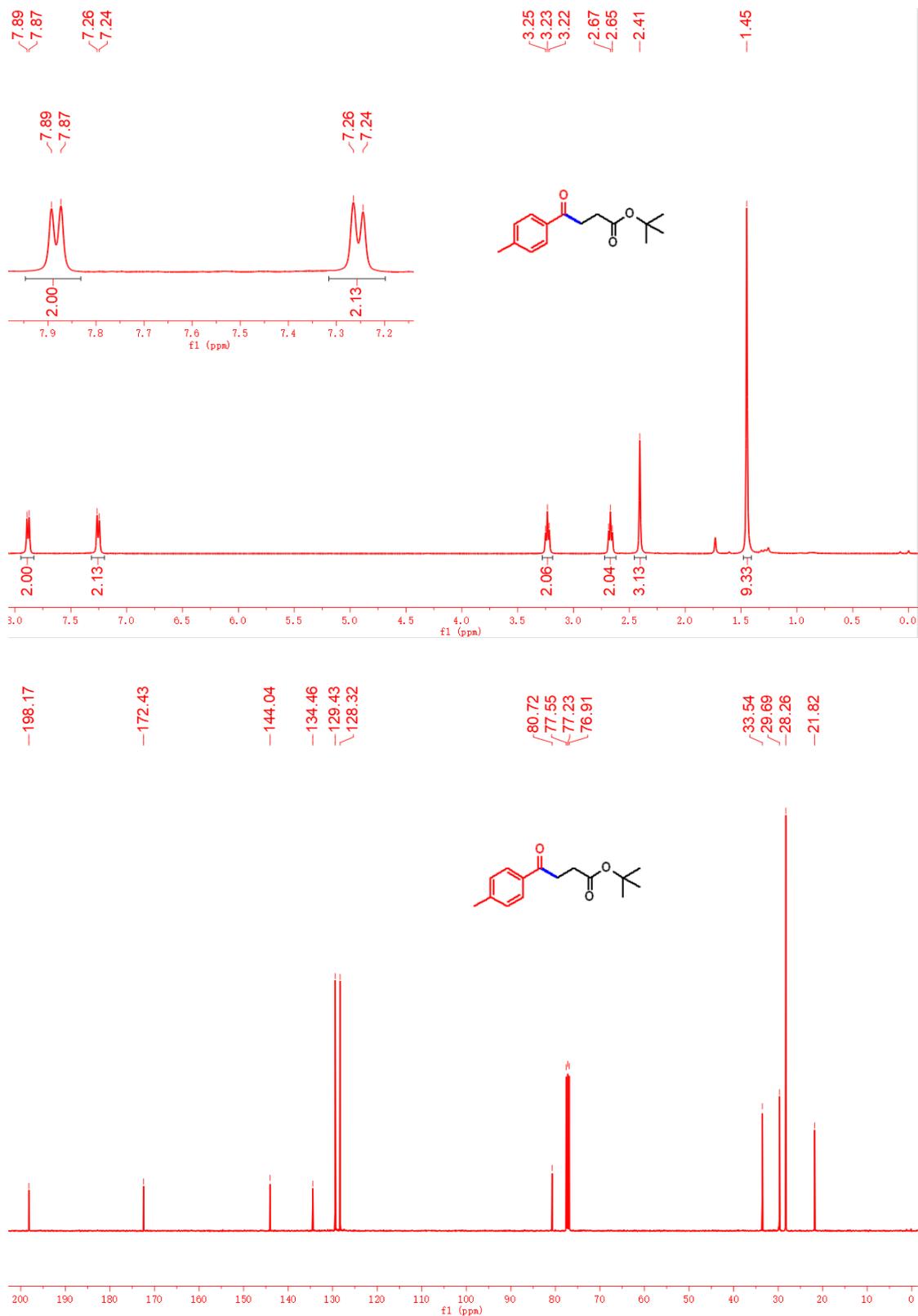


Figure S52. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(4-methoxyphenyl)-4-oxobutanoate (**5ac**) in CDCl_3

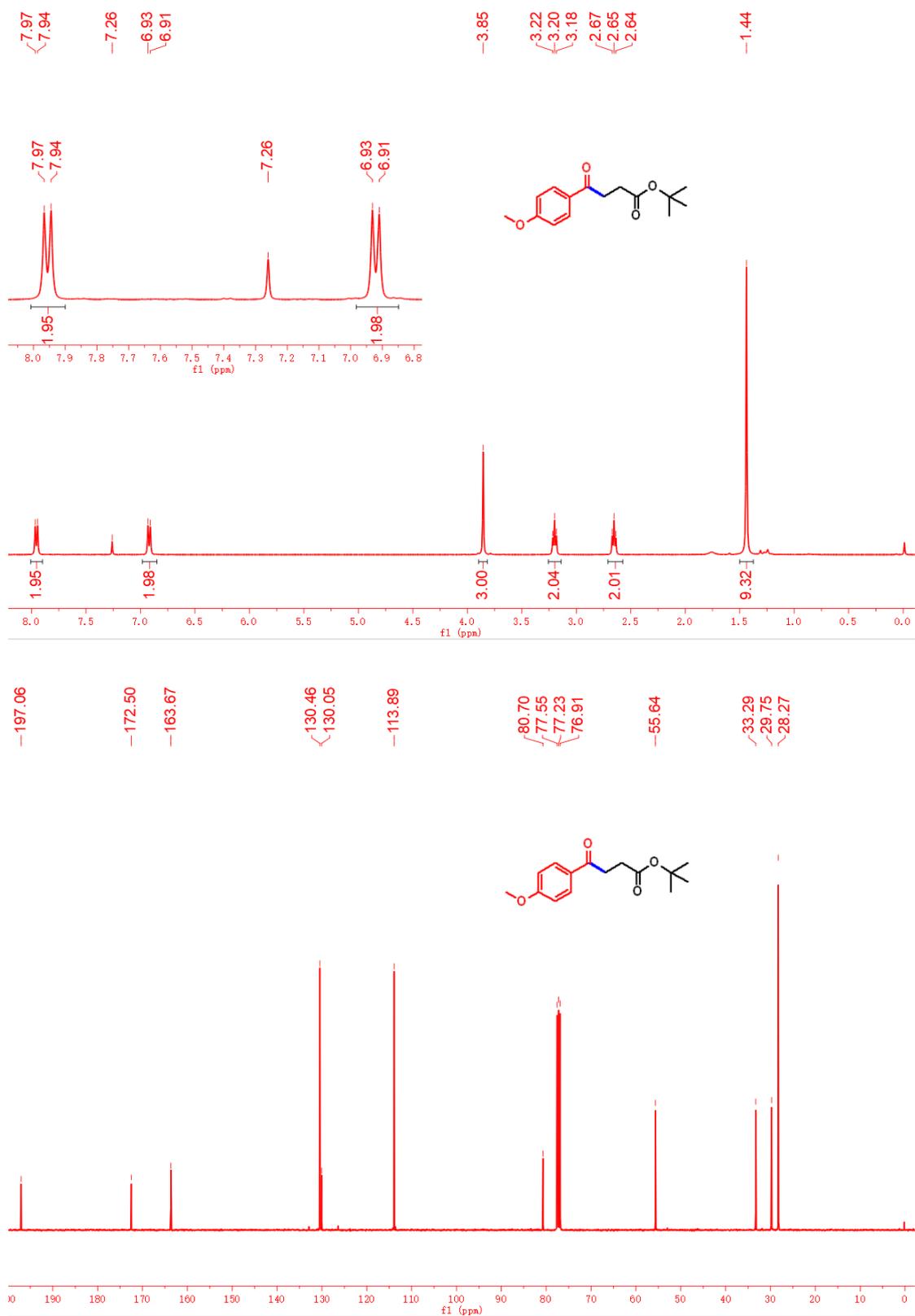


Figure S53. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(4-(dimethylamino)phenyl)-4-oxobutanoate (**5ad**) in CDCl_3

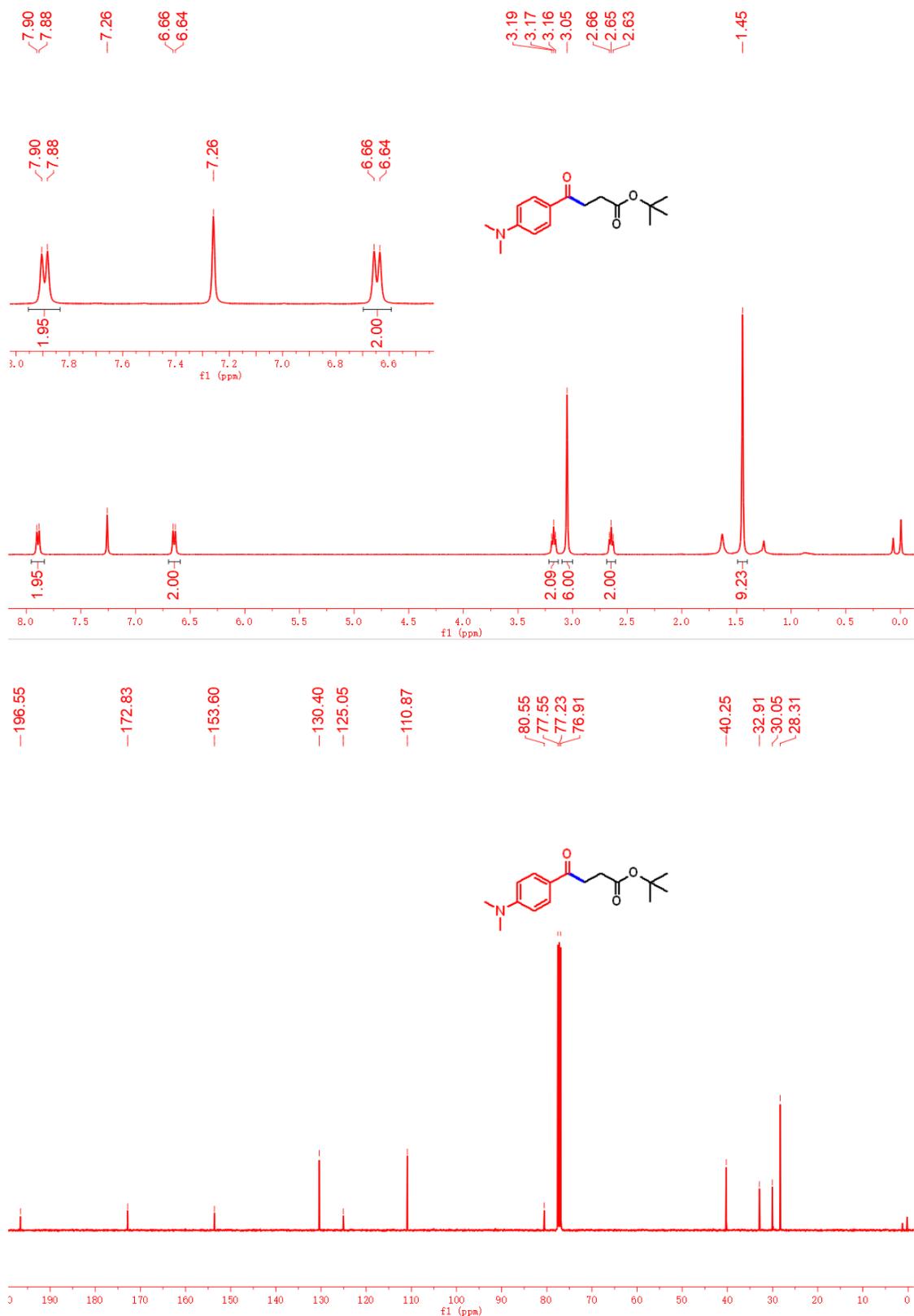
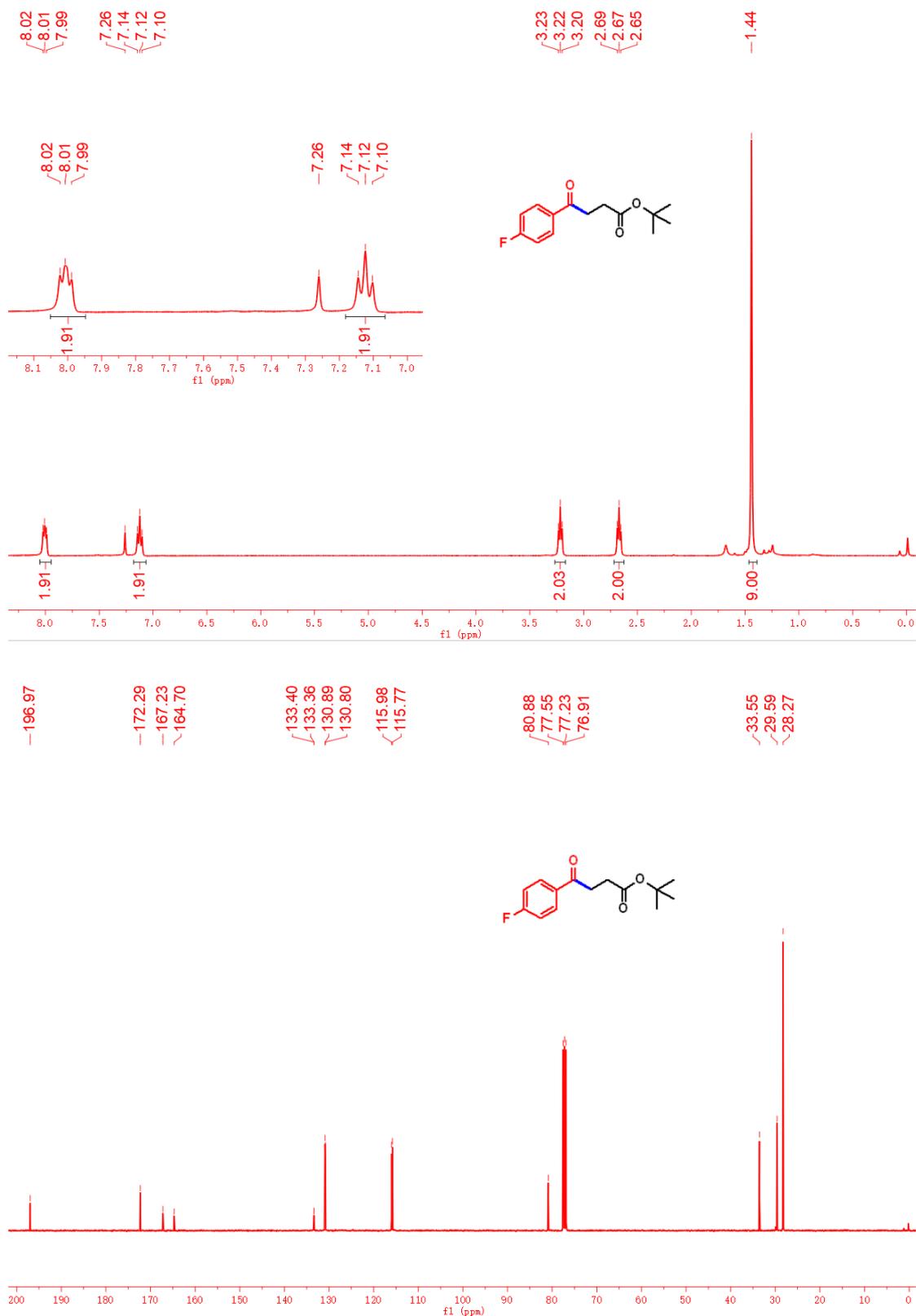


Figure S54. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for *tert*-butyl 4-(4-fluorophenyl)-4-oxobutanoate (**5ae**) in CDCl_3



--105.31

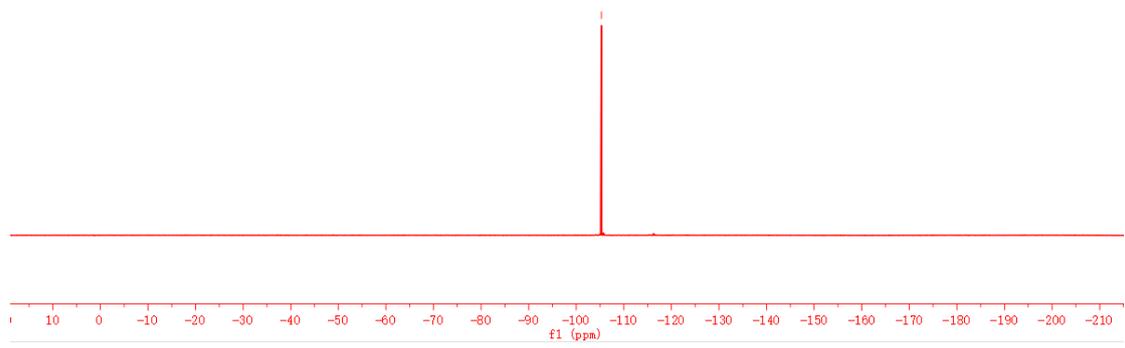
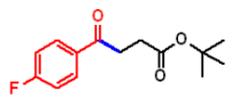


Figure S55. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(4-chlorophenyl)-4-oxobutanoate (**5af**) in CDCl_3

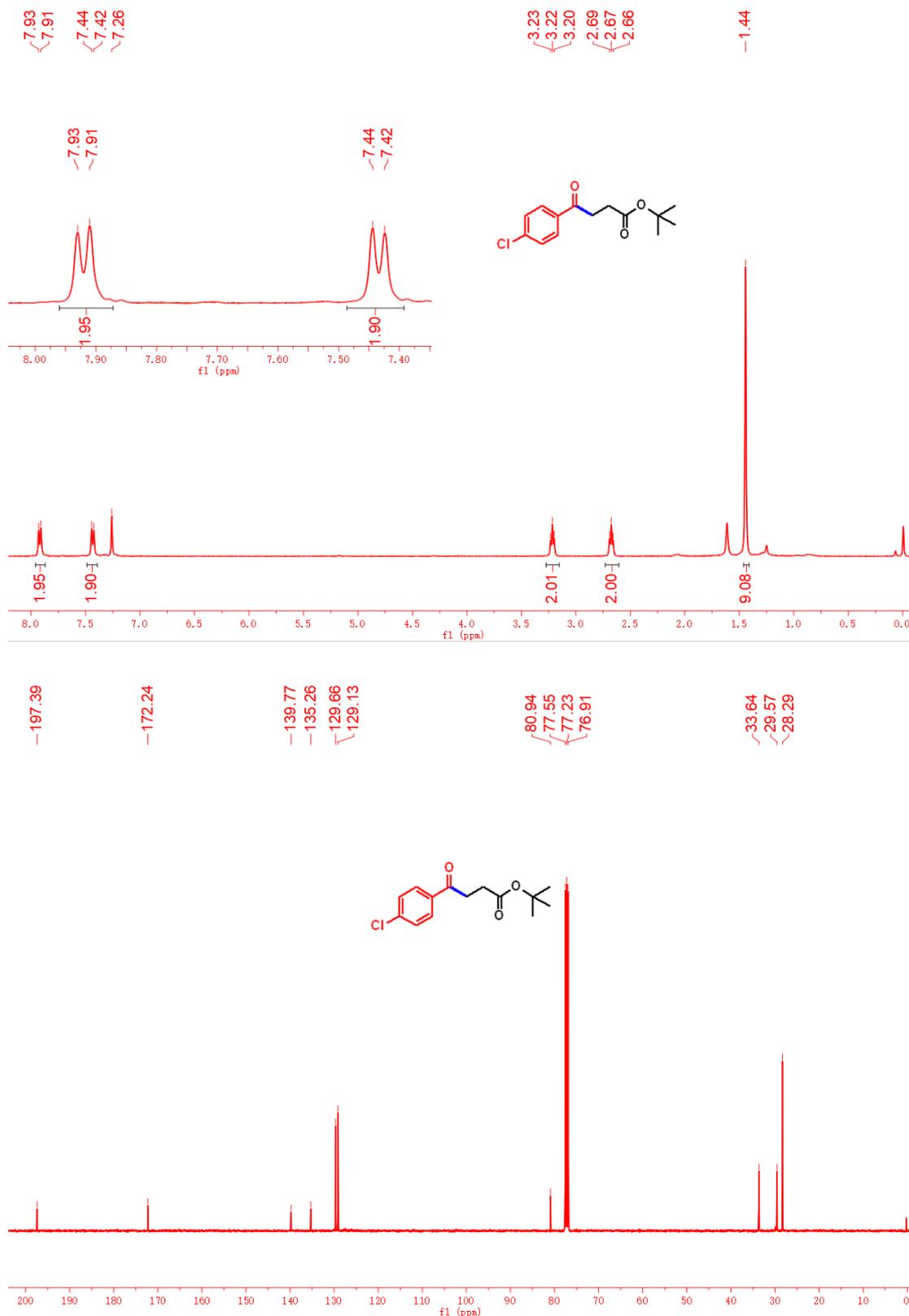


Figure S56. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-oxo-4-(*m*-tolyl)butanoate (**5ag**) in CDCl_3

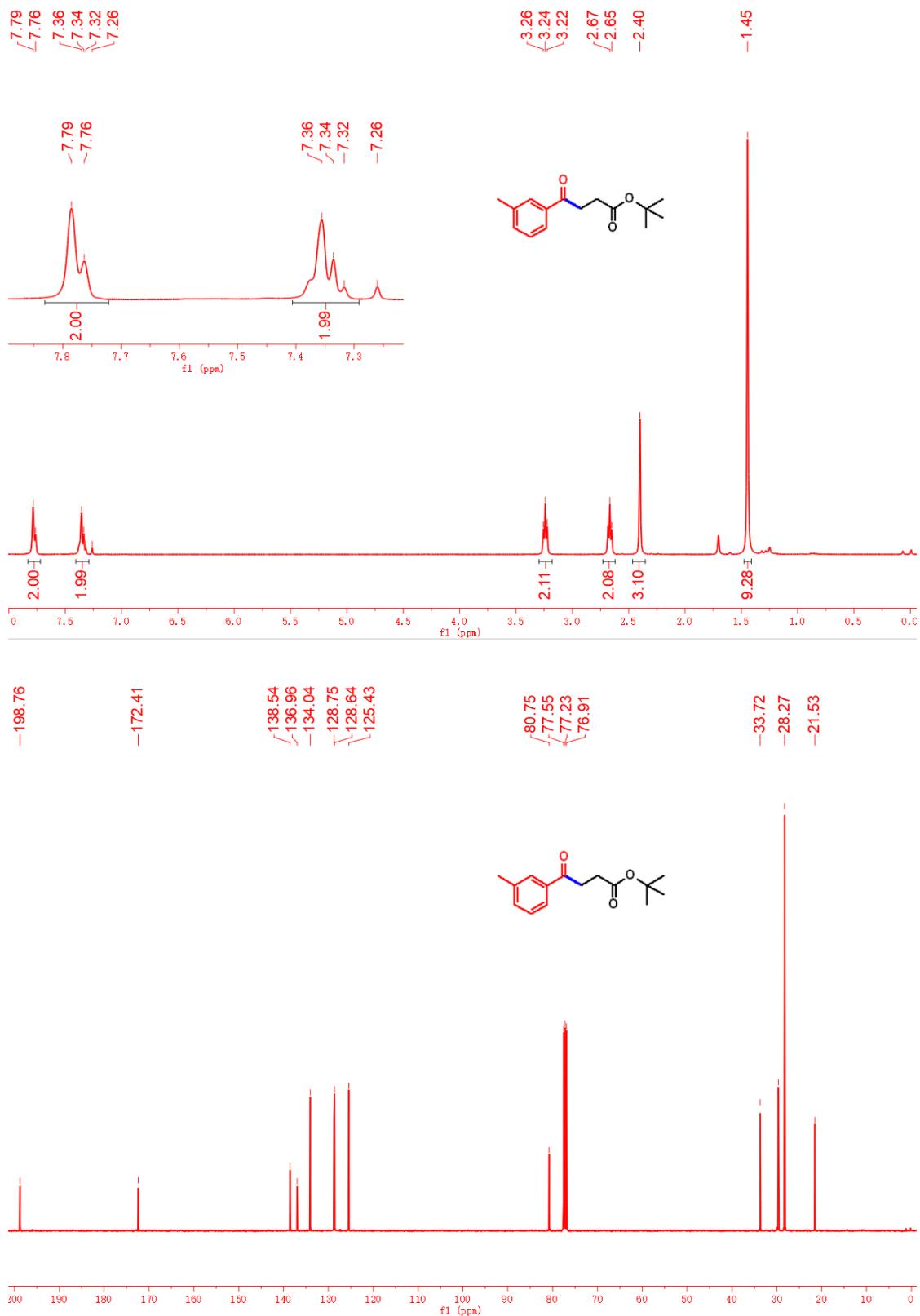


Figure S57. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-oxo-4-(*o*-tolyl)butanoate (**5ah**) in CDCl_3

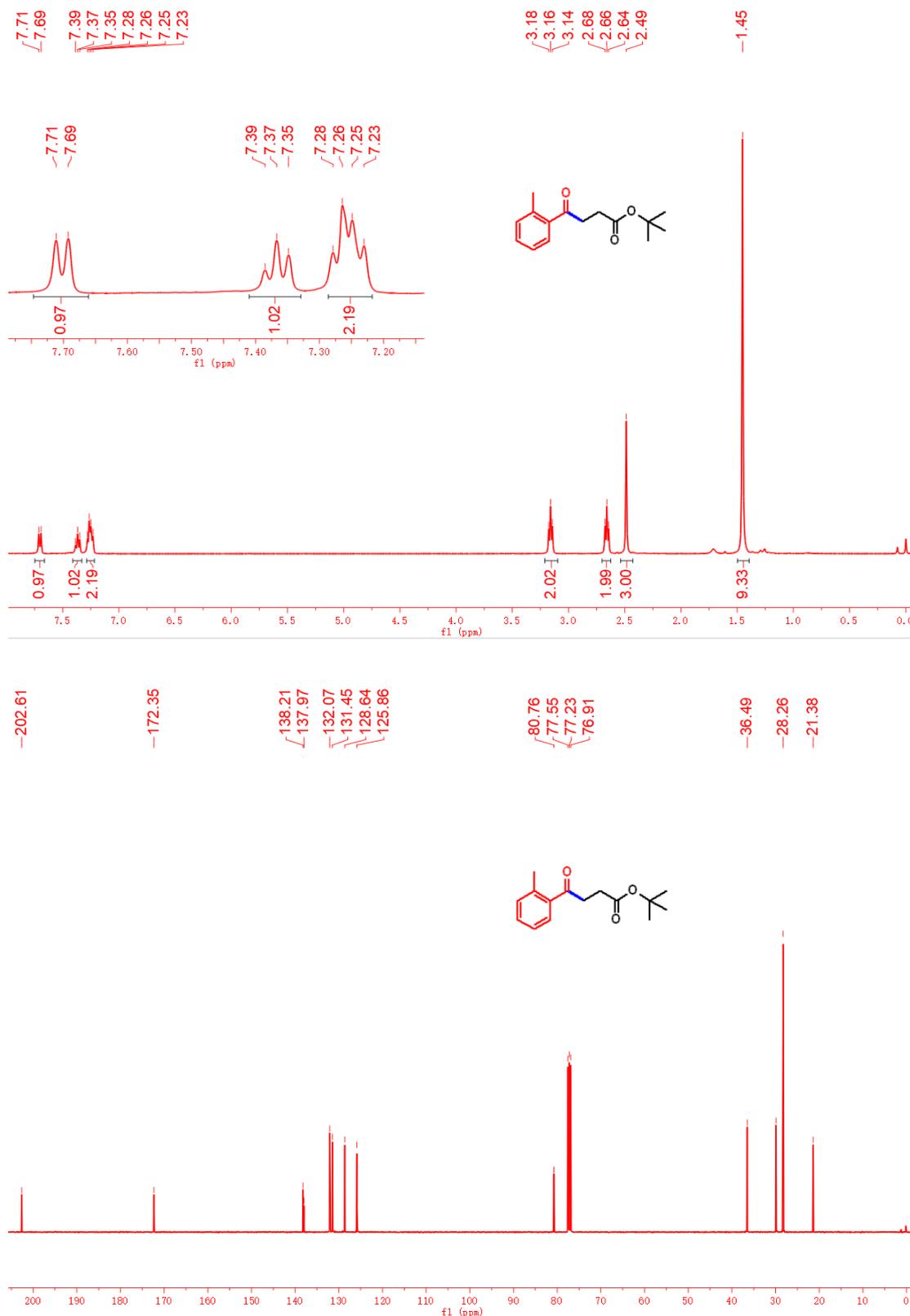


Figure S58. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(2,5-dimethylphenyl)-4-oxobutanoate (**5ai**) in CDCl_3

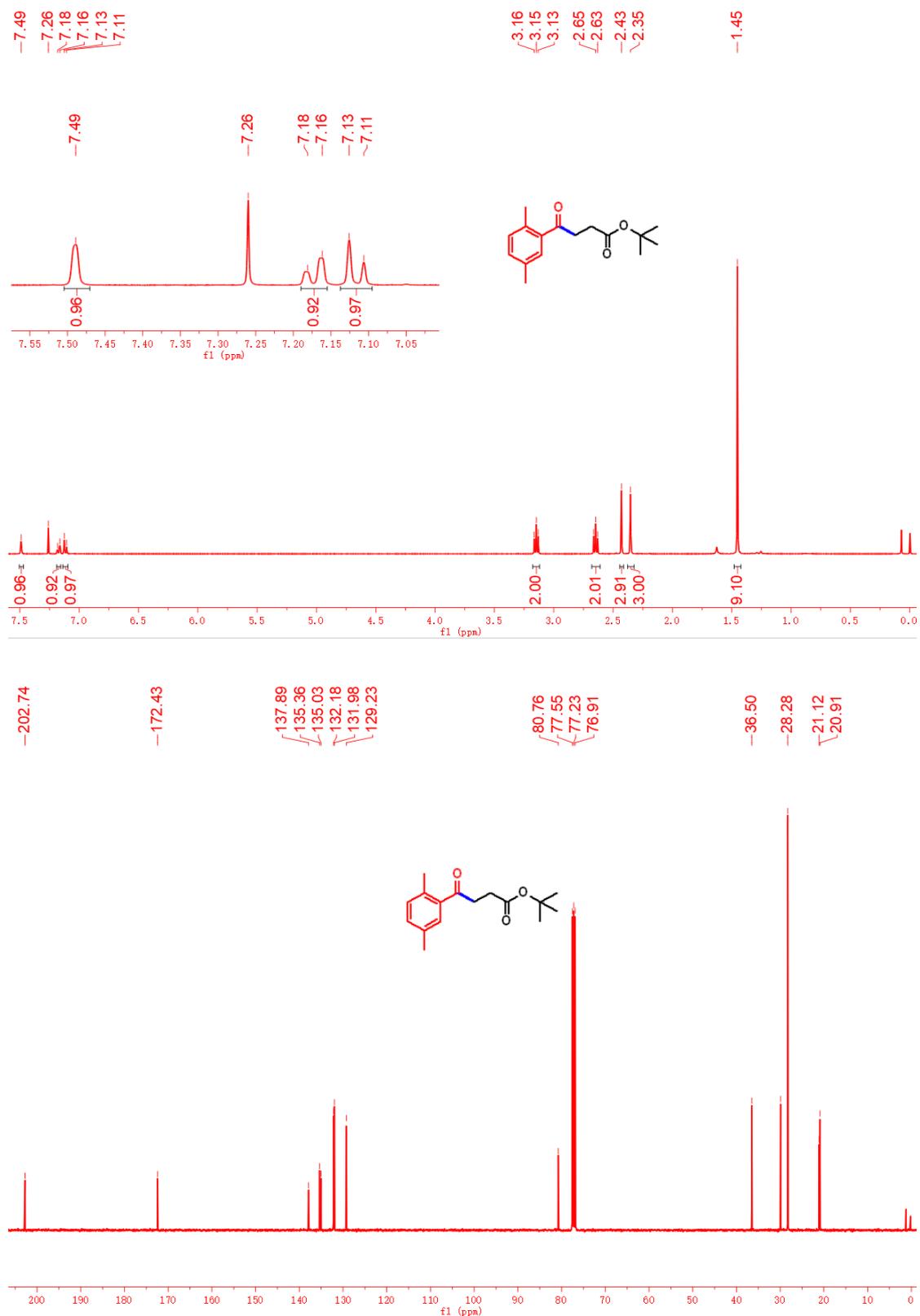


Figure S59. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(2,5-dimethoxyphenyl)-4-oxobutanoate (**5aj**) in CDCl_3

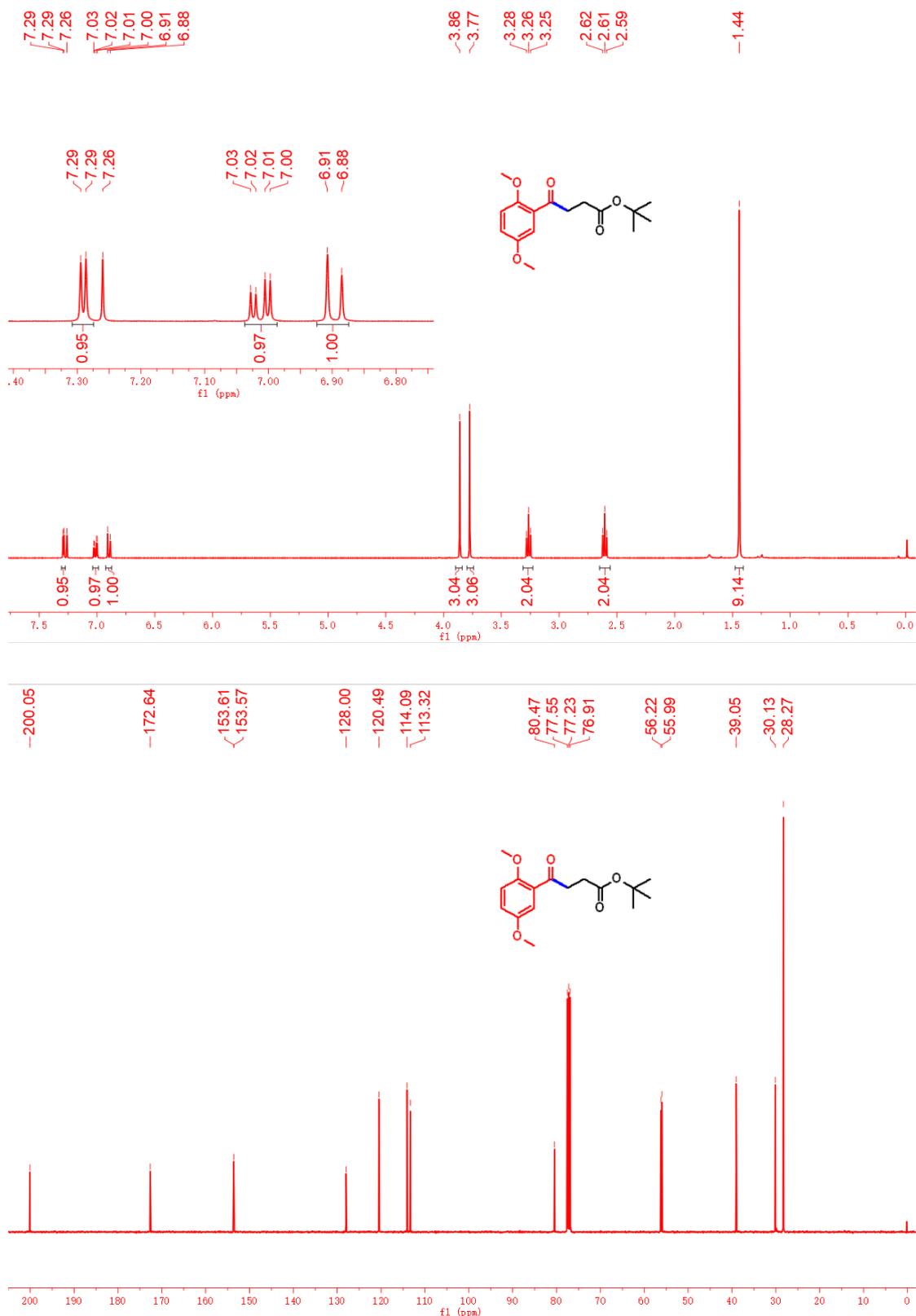


Figure S60. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for *tert*-butyl 4-(naphthalen-2-yl)-4-oxobutanoate (**5ak**) in CDCl_3

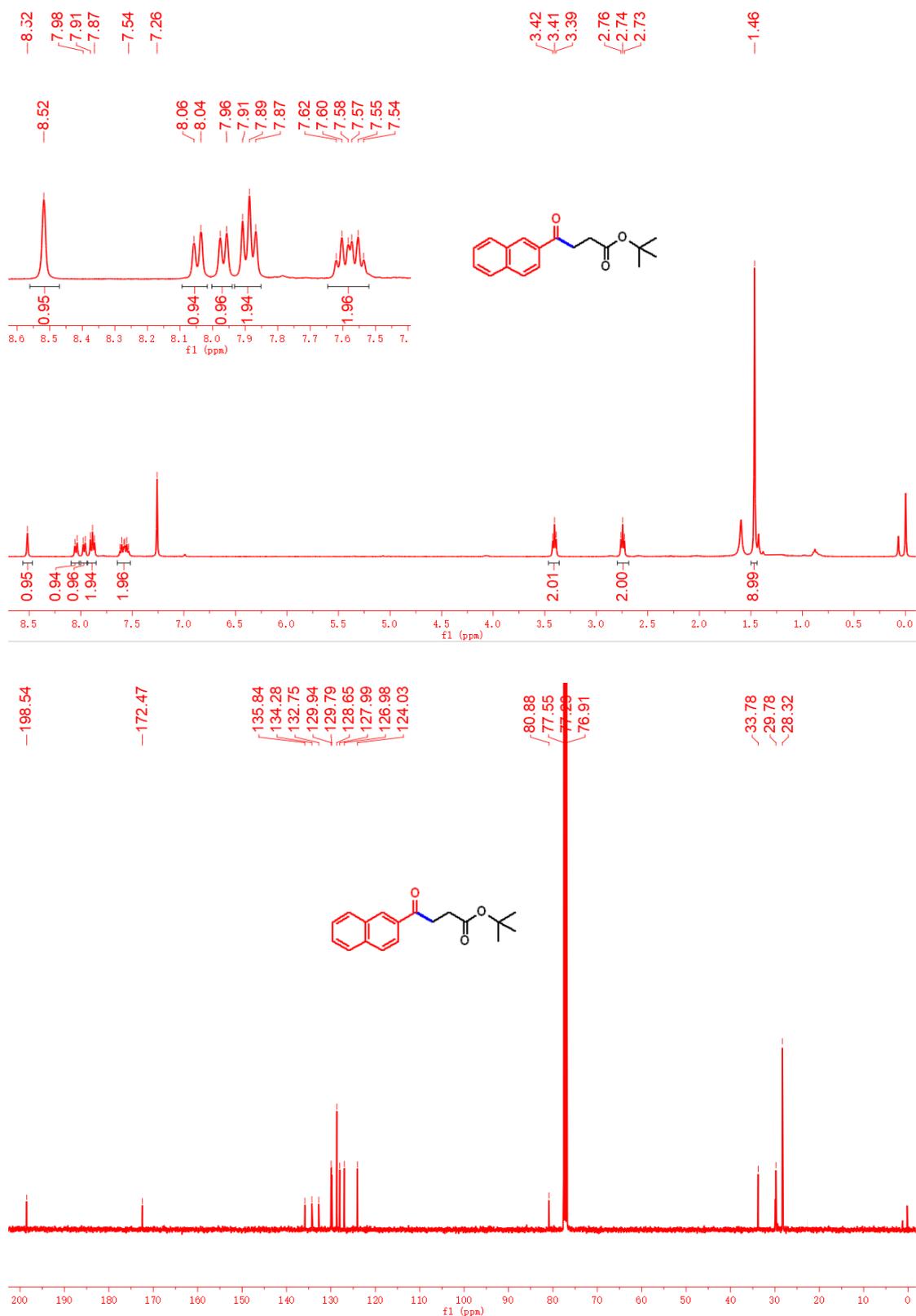


Figure S61. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for ethyl 4-oxo-4-phenylbutanoate (**5ba**) in CDCl_3

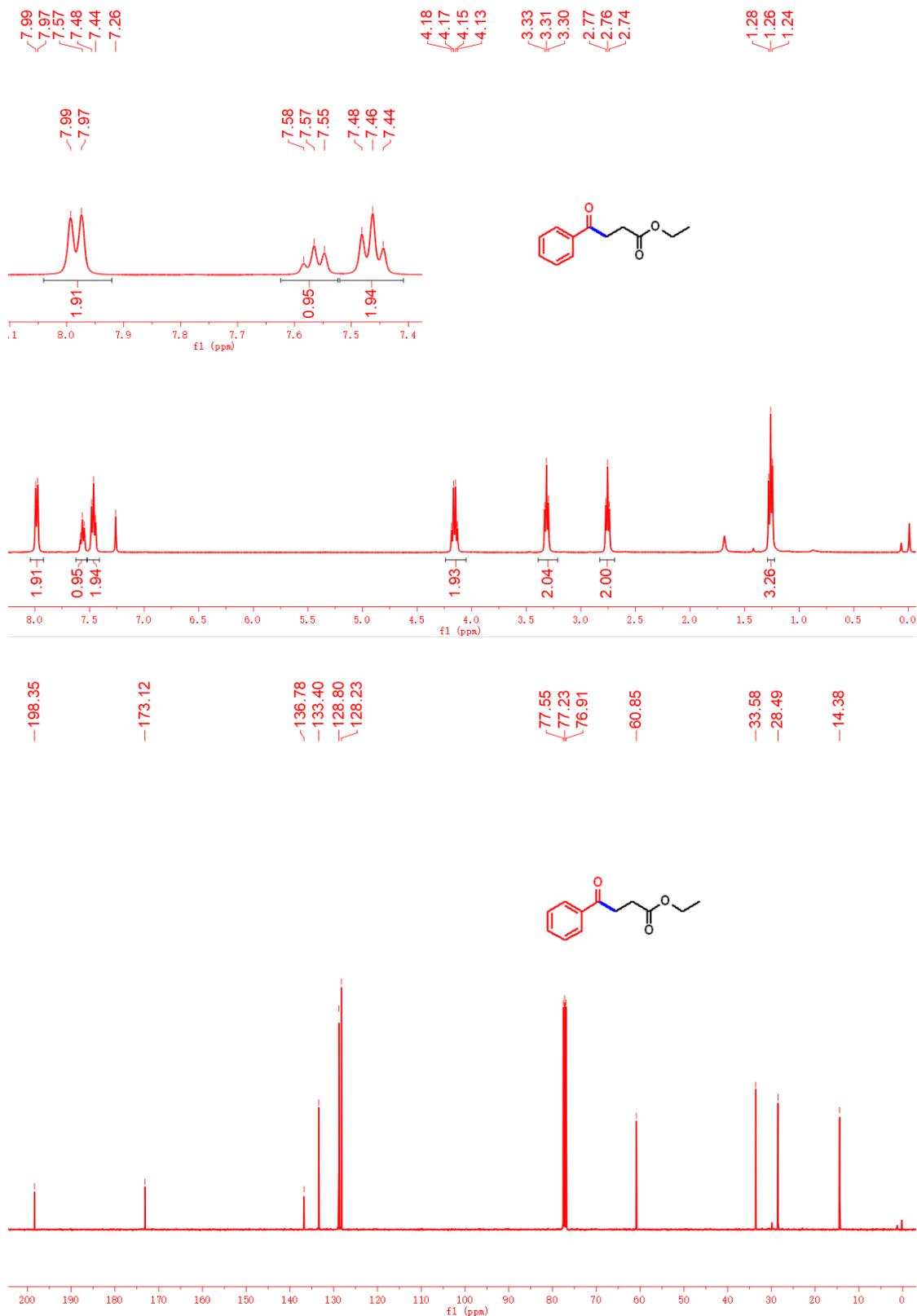


Figure S62. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for ethyl 2-methyl-4-oxo-4-phenylbutanoate (**5ca**) in CDCl_3

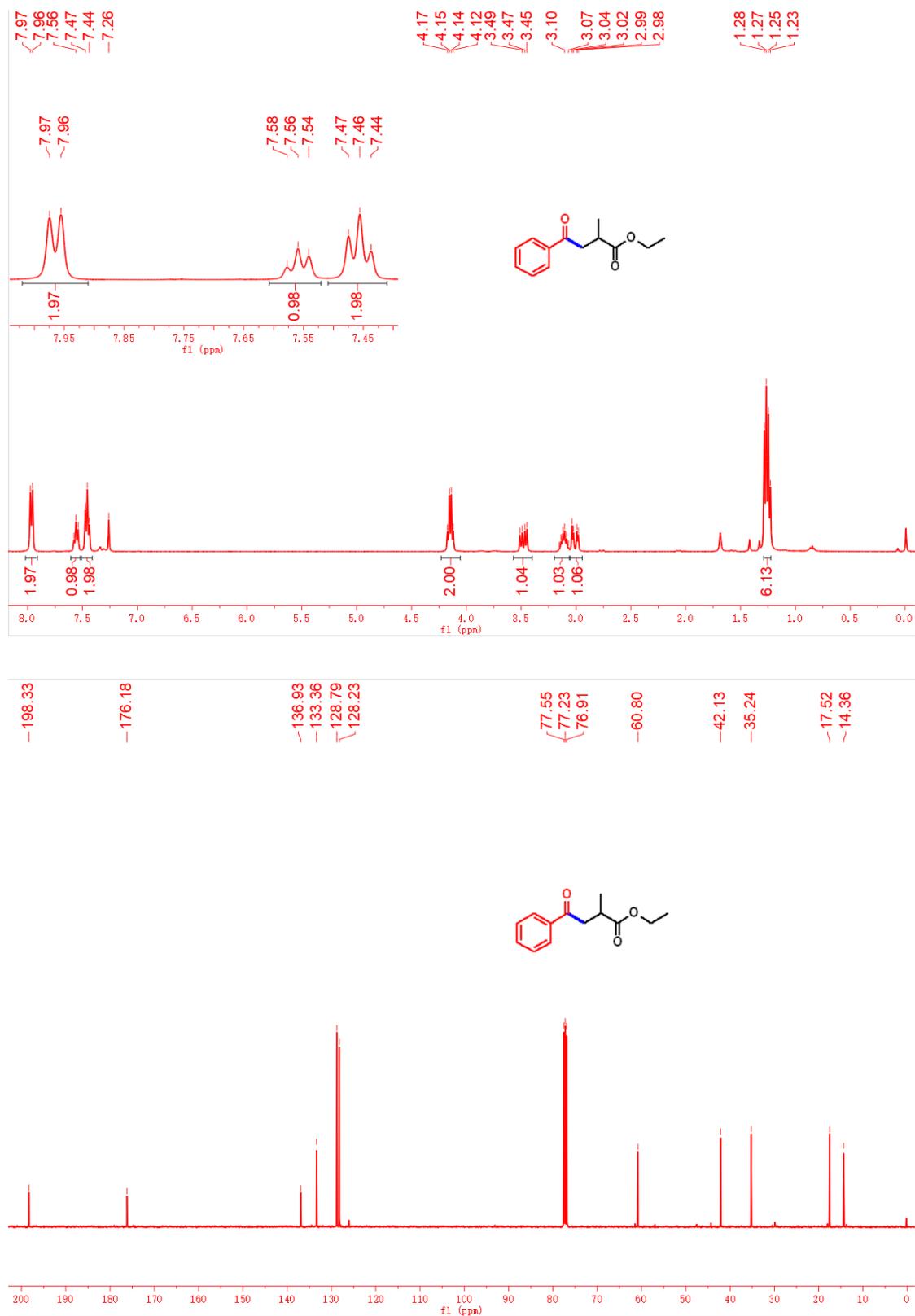


Figure S63. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for cyclohexyl 4-oxo-4-phenylbutanoate (**5da**) in CDCl_3

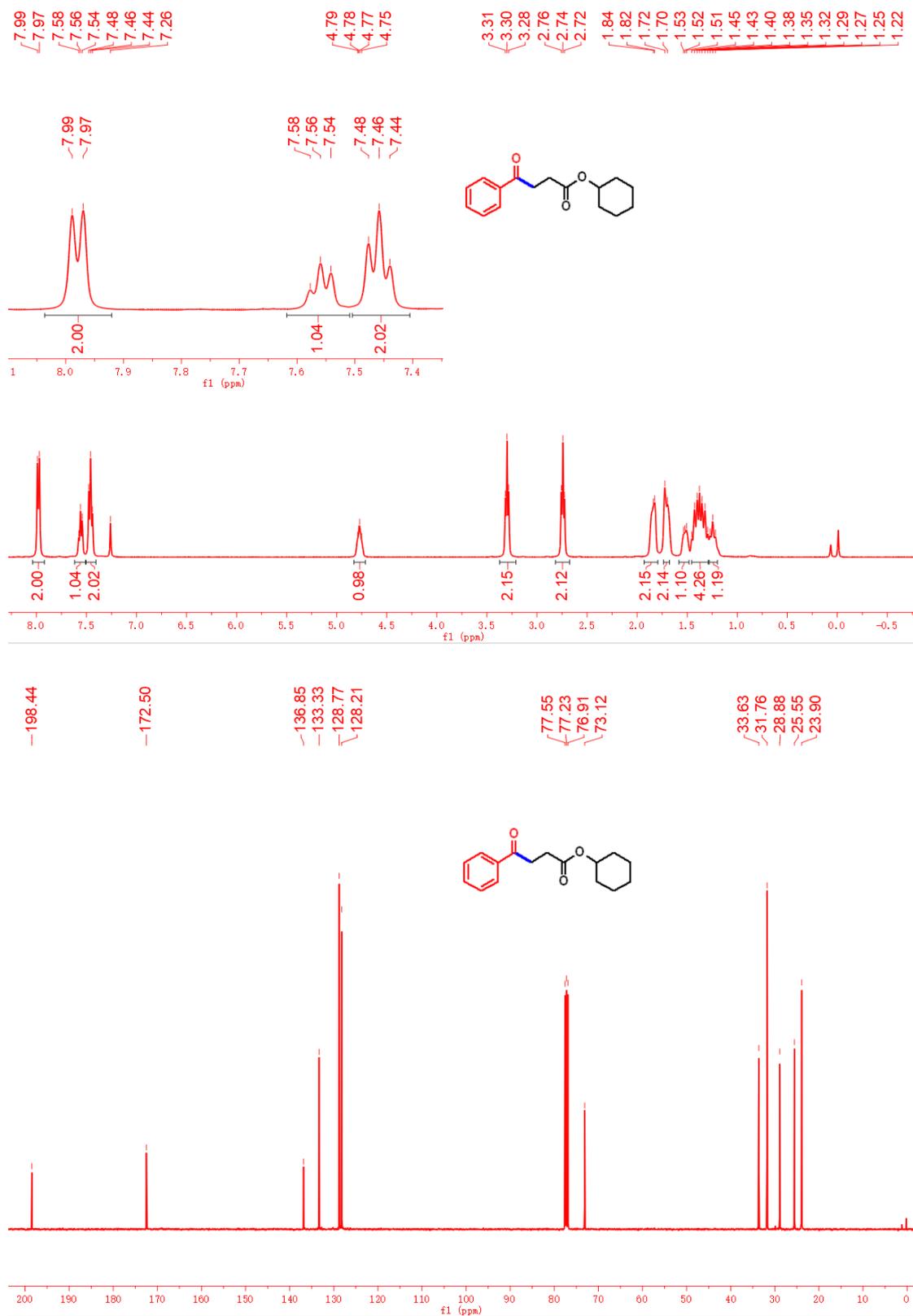


Figure S64. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for dimethyl 2-benzoylsuccinate (**5ea**) in CDCl_3

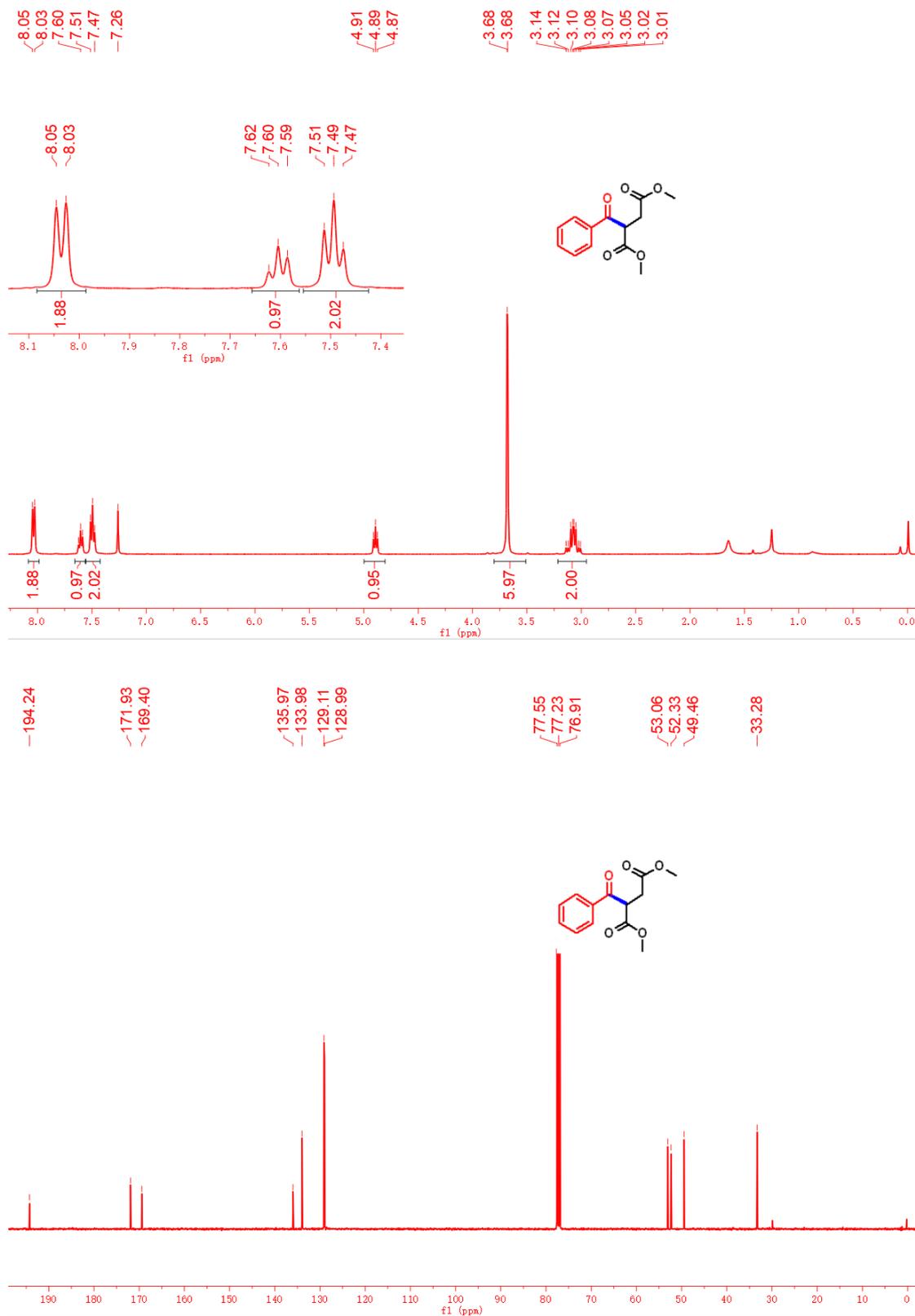


Figure S65. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for diethyl 2-(1-oxo-1-phenylpropan-2-yl)malonate (**5fa**) in CDCl_3

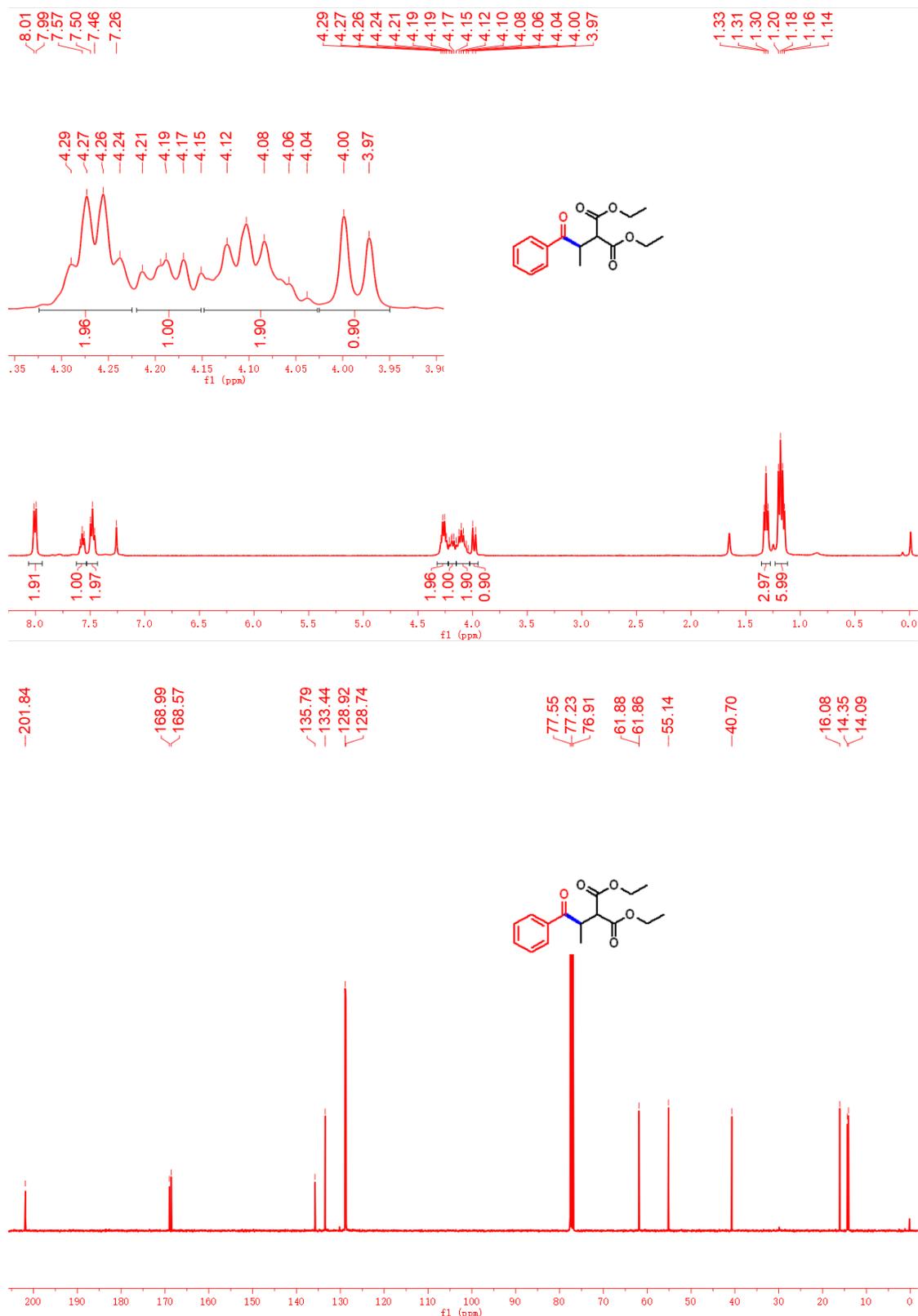


Figure S66. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1,2,4-triphenylbutane-1,4-dione (**5ga**) in CDCl_3

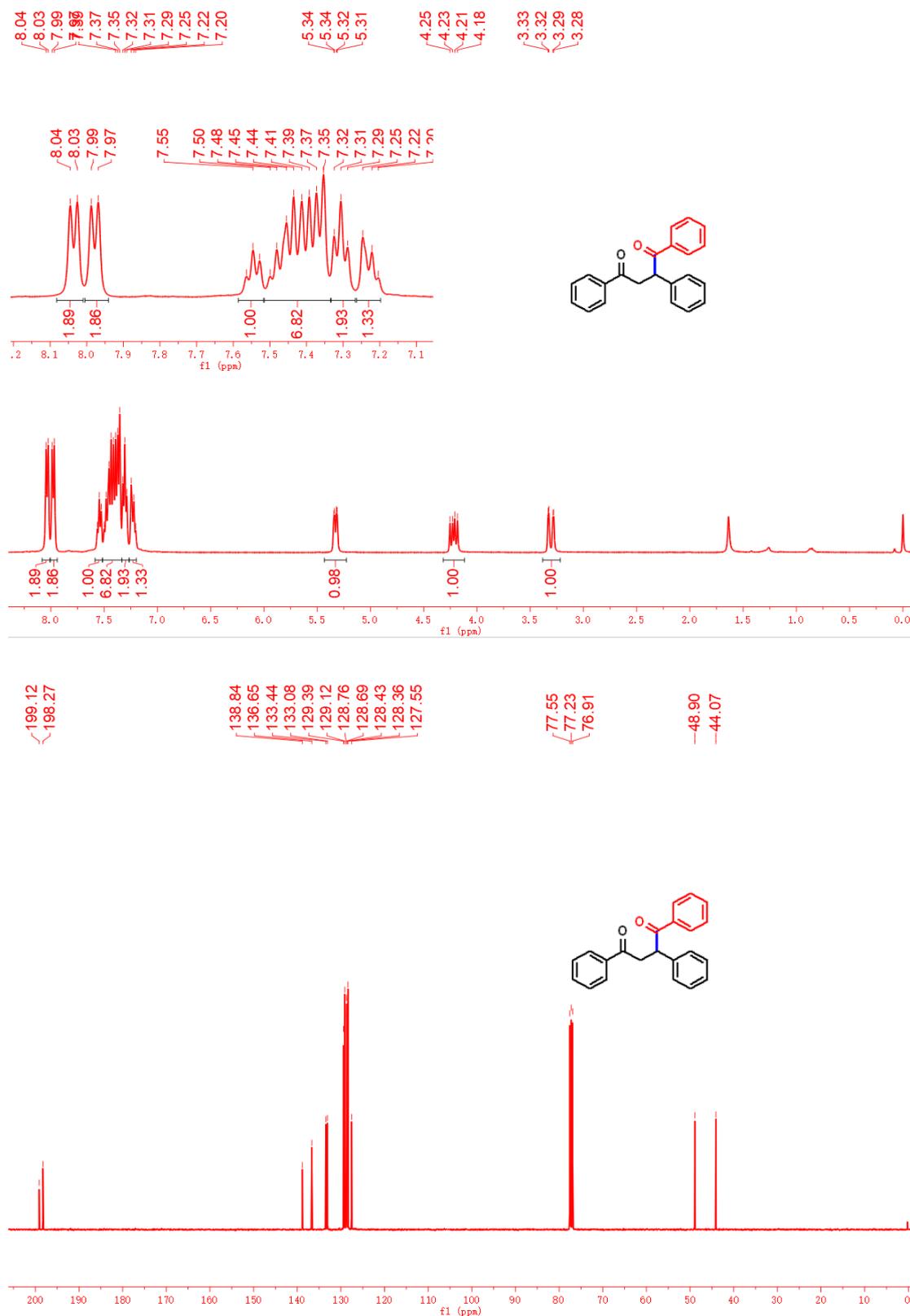


Figure S67. The ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for 2-(4-fluorophenyl)-1,4-diphenylbutane-1,4-dione (**5ha**) in CDCl_3

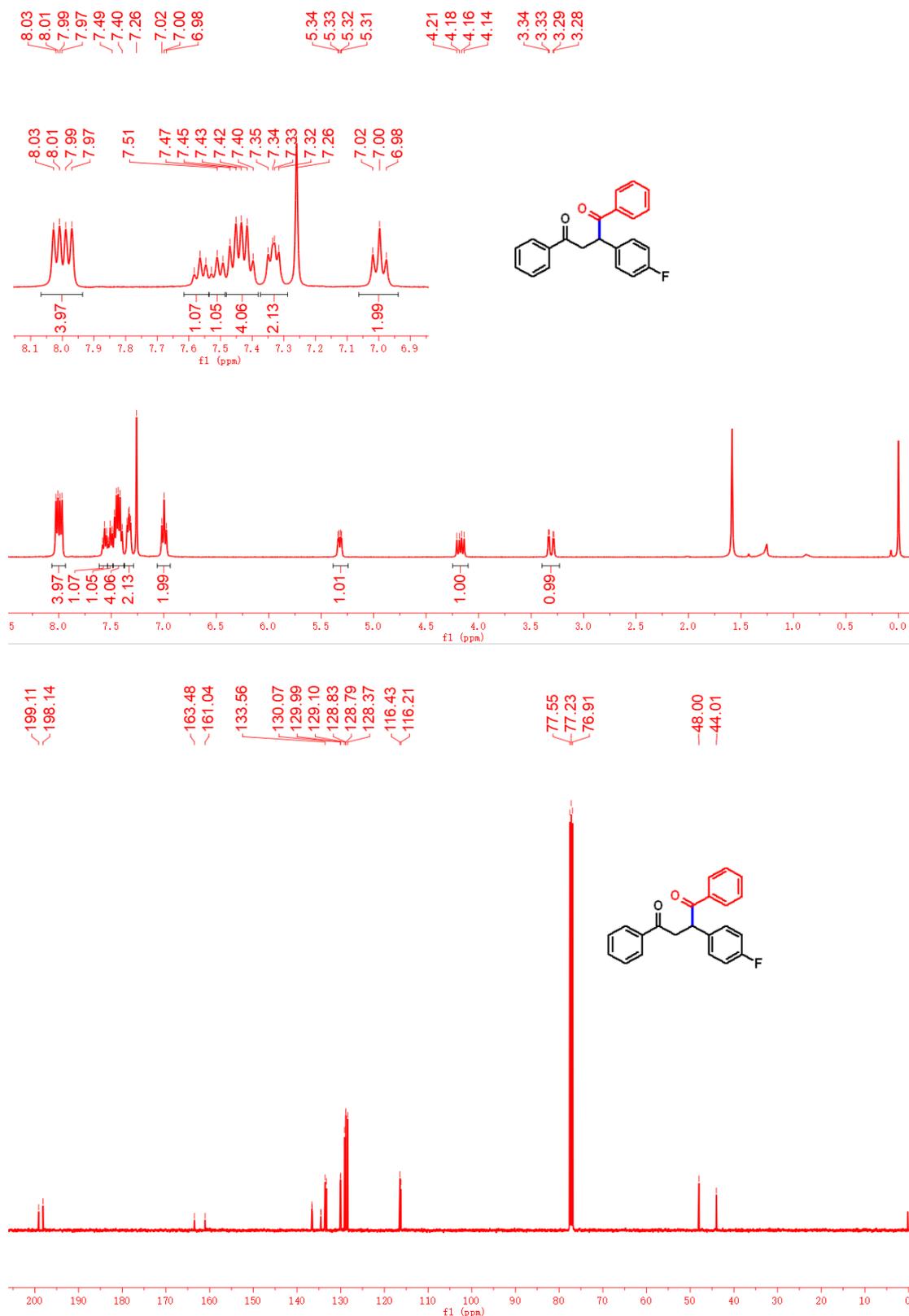




Figure S68. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 2-(4-methoxyphenyl)-1,4-diphenylbutane-1,4-dione (**5ia**) in CDCl_3

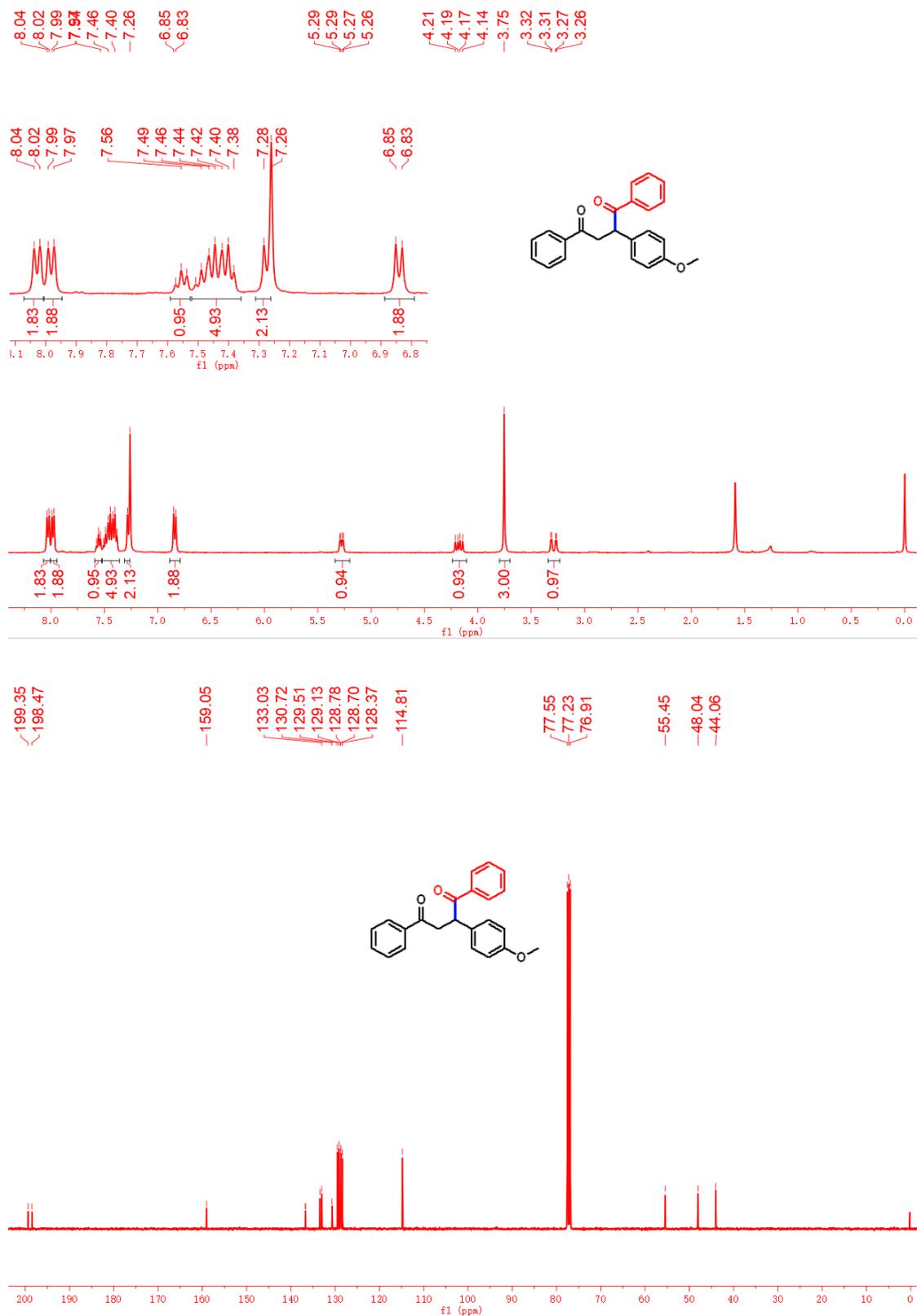


Figure S69. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for naphthylphenstatin in CDCl_3

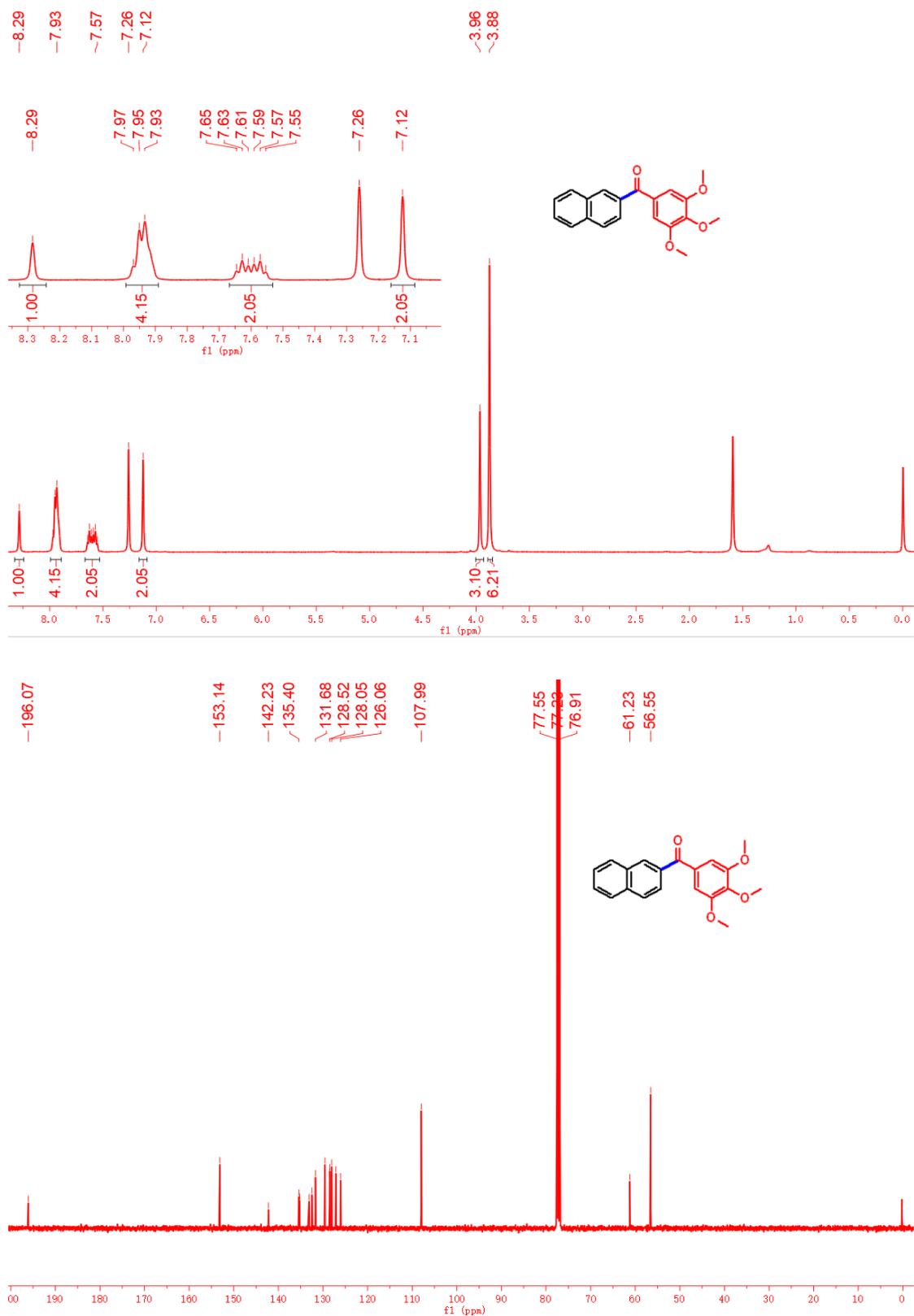


Figure S70. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1,2,3,5-tetraphenyl-1H-pyrrole (**6**) in CDCl_3

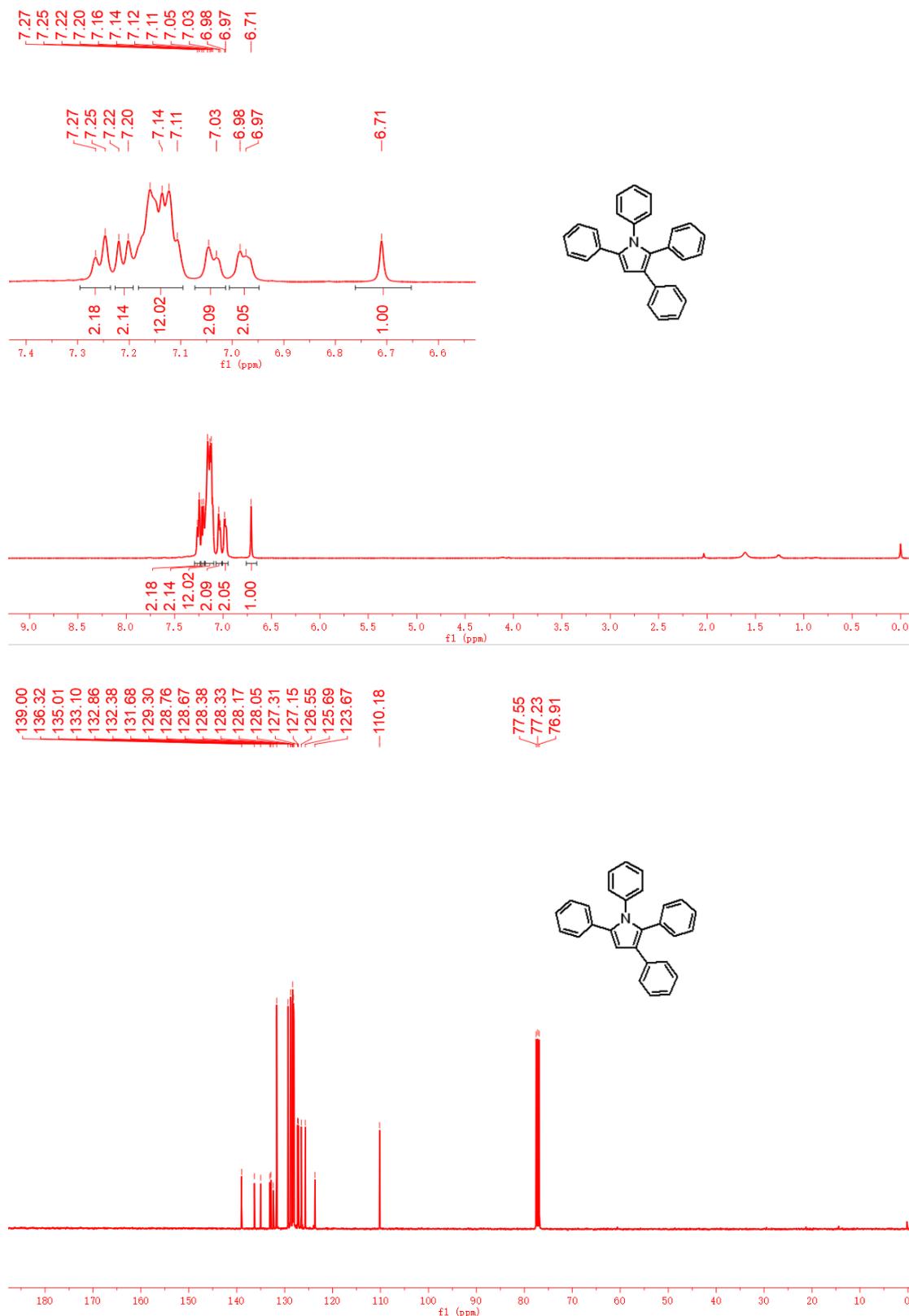


Figure S71. The ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 2,3,5-triphenylfuran (**7**) in CDCl_3

