

Supporting Information

Nickel-Catalyzed Directed Cross-Electrophile Coupling of Phenolic Esters with Alkyl Bromides

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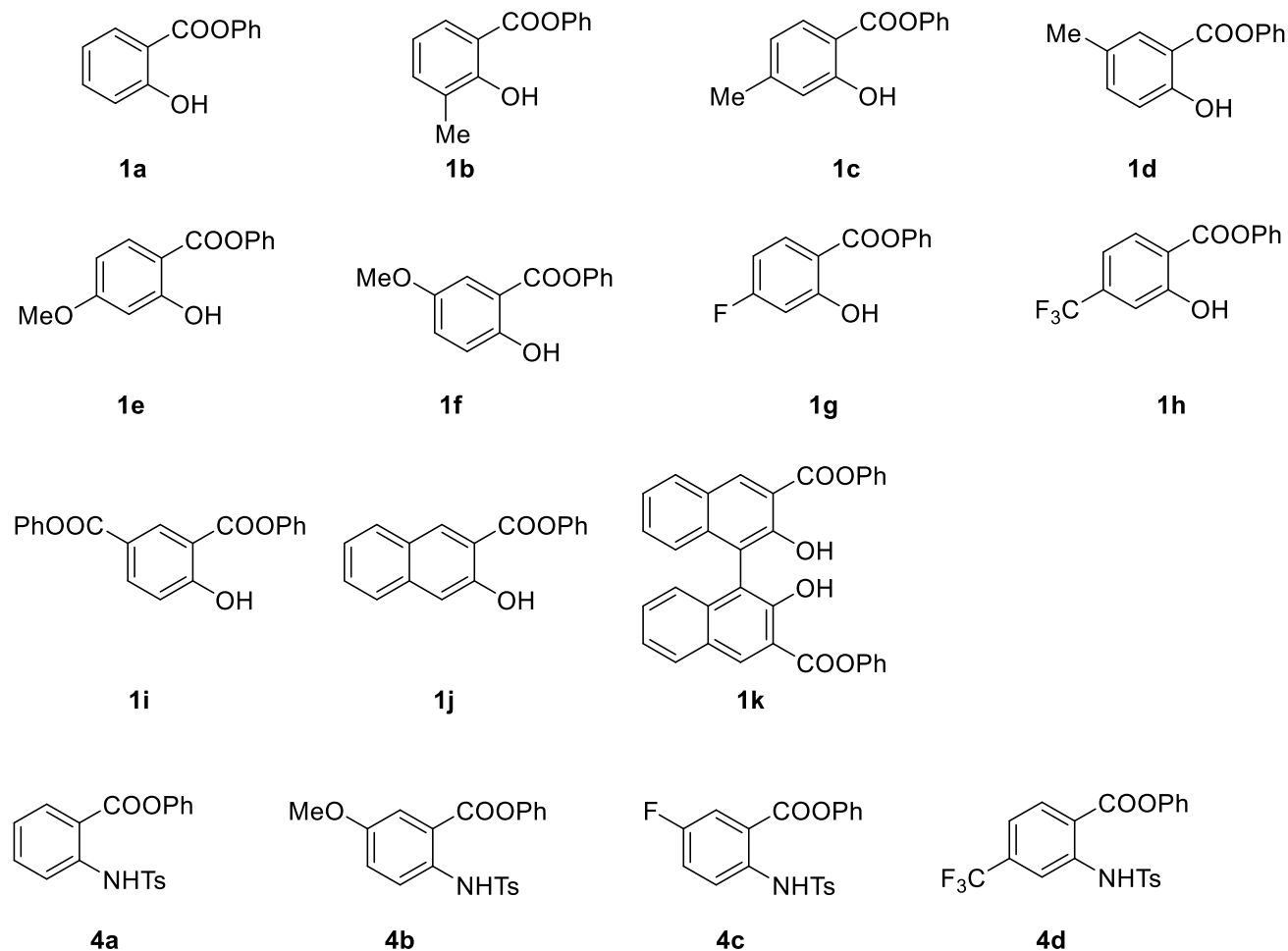
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General Methods and Materials

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M or 500M NMR spectrometers at ambient temperature in CDCl_3 and DMSO-d_6 at 400 and 101 MHz, or 500 and 126 MHz. The chemical shifts are given in ppm relative to tetramethylsilane [^1H : (SiMe_4) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^1H : $\delta(\text{CDCl}_3)$ = 7.26, ^{13}C : $\delta(\text{CDCl}_3)$ = 77.16 ppm; ^1H : $\delta(\text{DMSO-d}_6)$ = 2.50, ^{13}C : $\delta(\text{DMSO-d}_6)$ = 39.52 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as J values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF using ESI technique. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

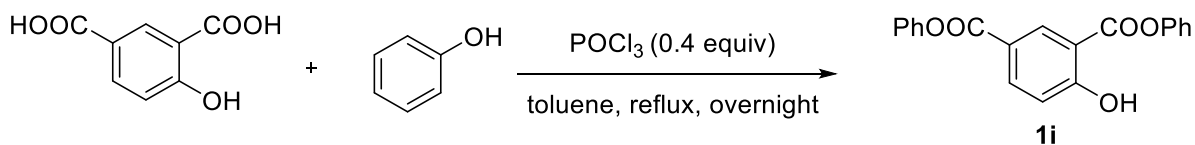
Unless otherwise noted, all the reagents and starting materials were purchased from commercial vendors and used without further purification.

Preparation of Phenolic Esters



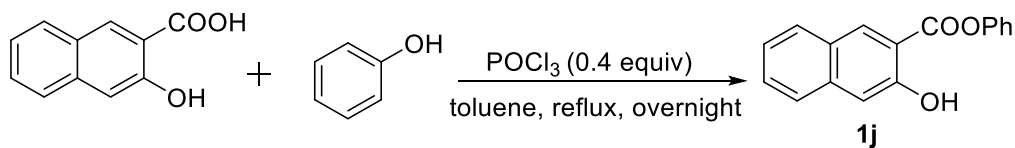
Compounds **1b~1h**¹ are known and their NMR-data are consistent with these reported in the literature.

Preparation of Phenolic Ester 1i



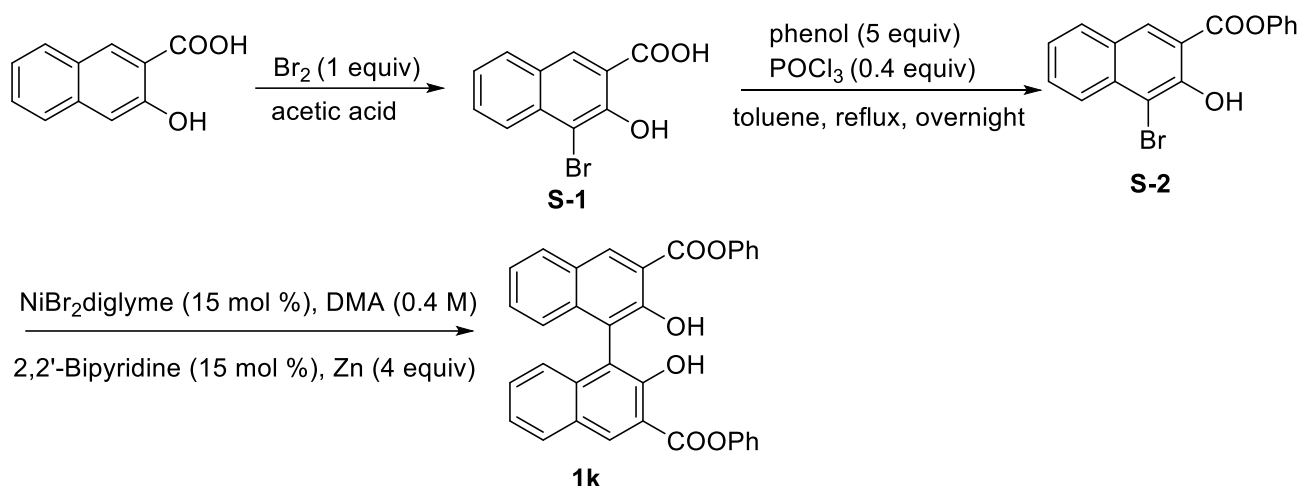
4-Hydroxyisophthalic acid (1.82 g, 10 mmol, 1 equiv) and phenol (9.41 g, 100 mmol, 10 equiv) were dissolved in 20 mL of toluene in a 100 mL round bottle. Phosphorus oxychloride (1.23 g, 0.75 mL, 8 mmol, 0.8 equiv) was added into the solution via syringe dropwise. After the reaction mixture was stirred under reflux (with oil bath at 110 °C) overnight, the mixture was allowed to cool to room temperature, transferred to a separatory funnel, and quenched with saturated aqueous sodium carbonate solution. The aqueous layer was then extracted with ethyl acetate. The organic layers were combined, dried over sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether/ethyl acetate=20:1) on silica gel to give *diphenyl 4-hydroxyisophthalate* (**1i**) as a white solid (1.94 g, 58 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 10.97 (s, 1H), 8.90 (d, *J*= 2.3 Hz, 1H), 8.28 (dd, *J*= 8.7, 2.3 Hz, 1H), 7.45-7.34 (m, 4H), 7.29-7.23 (m, 1H), 7.22-7.14 (m, 5H), 7.08 (d, *J*= 8.8 Hz, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 167.5, 165.1, 163.0, 149.8, 148.8, 136.8, 132.6, 128.7 (2C), 128.5 (2C), 125.7, 125.0, 120.7 (2C), 120.5 (2C), 120.1, 117.4, 110.9 ppm; HRMS (ESI): calcd. for

Preparation of Phenolic Ester **1j**



3-Hydroxy-2-naphthoic acid (1.88 g, 10 mmol, 1 equiv) and phenol (4.71 g, 50 mmol, 5 equiv) were dissolved in 20 mL of toluene in a 100 mL round bottle. Phosphorus oxychloride (0.61 g, 0.4 mL, 4 mmol, 0.4 equiv) was added into the solution via syringe dropwise. After the reaction mixture was stirred under reflux (with oil bath at 110 °C) overnight, the mixture was allowed to cool to room temperature, transferred to a separatory funnel, and quenched with saturated aqueous sodium carbonate solution. The aqueous layer was then extracted with ethyl acetate. The organic layers were combined, dried with sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether/ethyl acetate=10:1) on silica gel to give *phenyl 3-hydroxy-2-naphthoate* (**1j**) as a white solid (1.69 g, 64 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 10.15 (s, 1H), 8.75 (s, 1H), 7.90-7.84 (m, 1H), 7.77-7.70 (m, 1H), 7.58-7.44 (m, 3H), 7.42-7.31 (m, 3H), 7.77-7.70 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 168.7, 156.5, 150.1, 138.3, 133.2, 129.8 (2C), 129.6, 129.4, 127.1, 126.6, 126.4, 124.2, 121.7 (2C), 113.6, 112.0 ppm; HRMS (ESI): calcd. for C₁₇H₁₃O₃ [M+H]⁺: 265.0859 found: 265.0866.

Preparation of Phenolic Ester **1k**



Step1: 3-Hydroxynaphthalene-2-carboxylic acid (3.0 g, 15.9 mmol, 1 equiv) was suspended in acetic acid (40 mL), and with vigorous stirring a solution of bromine (817 μL, 15.9 mmol, 1 equiv) in acetic acid (10 mL) was added drop wise within 30 minutes. After stirring at room temperature for 1 hour, the reaction mixture was filtered and washed with water. Evaporation of the volatiles afforded *4-bromo-3-hydroxynaphthalene-2-carboxylic acid* (**S-1**) as a yellow solid (3.85 g, 90 % yield); ¹H NMR (400 MHz, DMSO-*d*₆) δ= 8.65 (s, 1H), 8.13-8.01 (m, 2H), 7.78-7.67 (m, 1H), 7.54-7.43 (m, 1H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ= 172.0, 153.8, 135.5, 132.8, 131.2, 130.6, 127.6, 125.2, 125.0, 115.7, 105.9 ppm; HRMS (ESI): calcd. for C₁₁H₈BrO₃ [M+H]⁺: 266.9651 found: 266.9654.

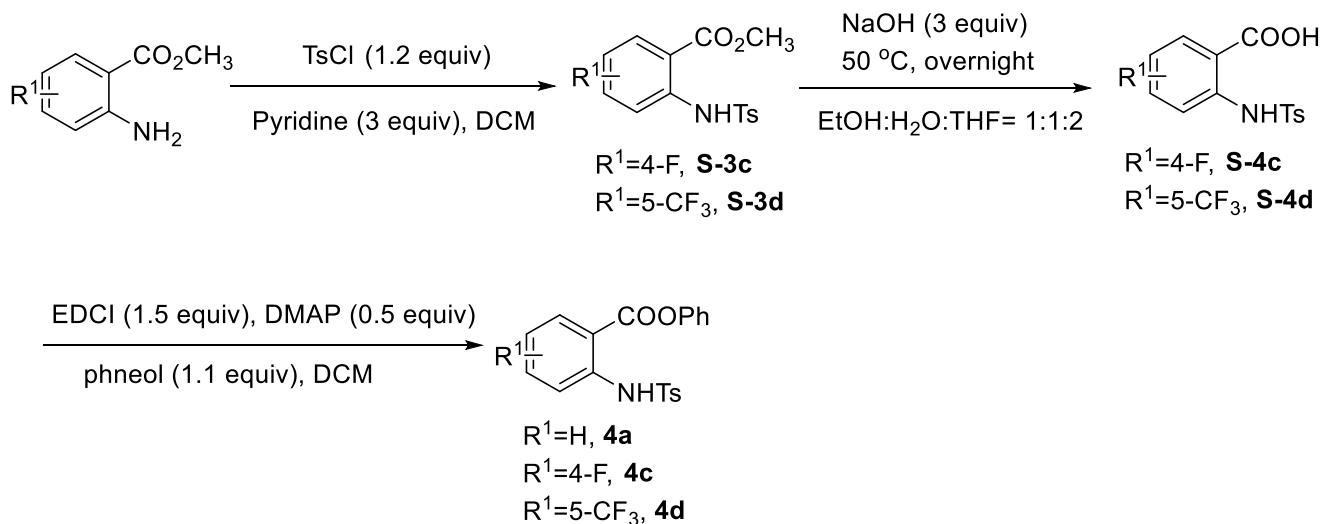
Step2: *4-Bromo-3-hydroxynaphthalene-2-carboxylic acid* (**S-1**) (3.85 g, 14.4 mmol, 1 equiv) and phenol (6.78 g, 72 mmol, 5 equiv) were dissolved in 30 mL of toluene in a 100 mL round bottle. Phosphorus oxychloride (0.88 g, 0.53 mL, 5.76 mmol, 0.4 equiv) was added into the solution via syringe dropwise. After the reaction mixture was stirred under reflux (with oil bath at 110 °C) overnight, the mixture was allowed to cool to room temperature, transferred to a separatory funnel, and

quenched with saturated aqueous sodium carbonate solution. The aqueous layer was then extracted with ethyl acetate. The organic layers were combined, dried with sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether /ethyl acetate=20:1) on silica gel to give *phenyl 4-bromo-3-hydroxy-2-naphthoate* (**S-2**) as a yellow solid (3.76 g, 76 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 10.96 (s, 1H), 8.74 (s, 1H), 8.21 (d, *J* = 8.7, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.75-7.62 (m, 1H), 7.54-7.45 (m, 2H), 7.47-7.41 (m, 1H), 7.40-7.31 (m, 1H), 7.31-7.24 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 168.4, 153.2, 150.0, 136.5, 132.6, 131.0, 129.9, 129.8 (2C), 127.5, 126.7, 126.0, 124.9, 121.5 (2C), 113.7, 107.4 ppm; HRMS (ESI): calcd. for C₁₇H₁₁BrNaO₃ [M+Na]⁺: 364.9784 found: 364.9787.

Step3:

A sealed test tube charged with 2,2'-bipyridine (14.0 mg, 0.03 mmol, 15 mol %), *4-bromo-3-hydroxy-2-naphthoate* (**S-2**) (205.9 mg, 0.6 mmol) and a stir bar was evacuated and filled with nitrogen (three cycles), and then NiBr₂•diglyme (32.0 mg, 0.03 mmol, 15 mol%) and Zn-powder (150.0 mg, 0.8 mmol, 4.0 equiv) were added in the glovebox. Subsequently, DMA (1.2 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 40 °C with oil bath and stirred at this temperature for 10 h. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate= 10:1) to afford *diphenyl 2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarboxylate* (**1k**) as a yellow solid (1.84 g, 32 % yield); ¹H NMR (400 MHz, CDCl₃) δ= 10.94 (s, 1H), 10.14 (s, 1H), 8.70 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 8.3, 3.4 Hz, 2H), 7.71-7.60 (m, 2H), 7.54-7.50 (m, 1H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.47 (d, *J* = 3.2 Hz, 2H), 7.45 (d, *J* = 3.1 Hz, 1H), 7.43-7.38 (m, 1H), 7.36-7.33 (m, 3H), 7.33-7.31 (m, 1H), 7.28-7.26 (m, 1H), 7.26-7.22 (m, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 168.7, 168.4, 156.5, 153.2, 150.2, 150.0, 138.3, 136.5, 133.2, 132.6, 131.0, 129.9, 129.84 (2C), 129.75 (2C), 129.6, 129.4, 127.6, 127.2, 126.8, 126.6, 126.4, 126.0, 124.9, 124.2, 121.7 (2C), 121.6 (2C), 113.7, 113.6, 112.0, 107.4 ppm; HRMS (ESI): calcd. for C₃₄H₂₃O₆ [M+H]⁺: 527.1489 found: 527.1493.

Preparation of Salicylate Esters **4a**, **4c** and **4d**



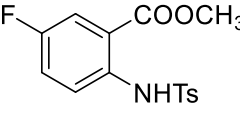
Step1: To a solution of methyl 2-aminobenzoates (10.0 mmol, 1 equiv) in 20 mL of DCM under N₂ atmosphere, were added pyridine (2.4 mL, 30 mmol, 3 equiv) and tosyl chloride (2.3 g, 12 mmol, 1.2 equiv). After the mixture was stirred at room temperature for 1 h, the reaction was quenched by addition of water. The mixture was extracted with EtOAc, and the combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc= 10:1) to give **S-3c** and **S-3d**.

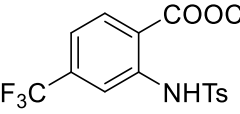
Step2: **S-3** (8 mmol, 1 equiv) and NaOH (0.96 g, 24 mmol, 3 equiv) were dissolved in H₂O (10 mL), EtOH (10 mL) and THF

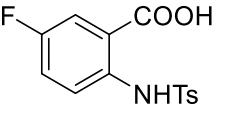
(20 mL). The reaction mixture was stirred for overnight with oil bath at 50 °C. The organic solvent was then removed under vacuum. The residue was extracted with ethyl acetate, The water layer was acidified with concentrated HCl until pH = 2 and extracted with ethyl acetate. The combined organic layers were concentrated under vacuum to afford **S-4c** and **S-4d**.

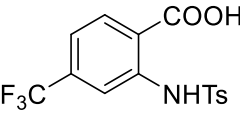
Step3: S-4 (8 mmol, 1 equiv),^a EDCI (2.3 g, 24 mmol, 1.5 equiv), DMAP (488.8 mg, 4 mmol, 0.5 equiv) and phenol (828.2 mg, 8.8 mmol, 1.1 equiv) were dissolved in DCM (20 mL). The reaction mixture was stirred for overnight at room temperature. The reaction was quenched by addition of water. The mixture was extracted with DCM and combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc= 10:1) to give **4a**, **4c**, **4d**.

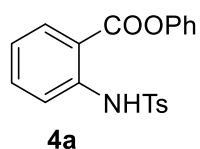
^a **S-4a** was prepared according to the method reported in the literature.^{2,3}


S-3c *Methyl 5-fluoro-2-((4-methylphenyl)sulfonamido)benzoate (S-3c)* was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (2.70 g, 84 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 10.29 (s, 1H), 7.73-7.65 (m, 3H), 7.57 (dd, *J* = 9.0, 3.1 Hz, 1H), 7.23-7.17 (m, 3H), 3.86 (s, 3H), 2.37 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 167.1 (d, *J* = 2.6 Hz), 157.9 (d, *J* = 244.5 Hz), 144.0, 136.6 (d, *J* = 2.7 Hz), 136.0, 129.6 (2C), 127.2 (2C), 121.8, 121.7 (d, *J* = 14.5 Hz), 117.7 (d, *J* = 7.2 Hz), 117.2 (d, *J* = 24.3 Hz), 52.6, 21.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -118.00- -118.86 (m, 1F) ppm; HRMS (ESI): calcd. for C₁₅H₁₄FNO₄SNa [M+Na]⁺: 346.0520 found: 346.0520.

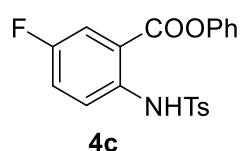

S-3d *Methyl 2-((4-methylphenyl)sulfonamido)-4-(trifluoromethyl)benzoate (S-3d)* was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (1.80 g, 82 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 10.71 (s, 1H), 8.03 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.26-7.23 (m, 3H), 3.93 (s, 3H), 2.38 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 167.4, 144.4, 141.0, 135.9, 135.8 (q, *J* = 32.3 Hz), 131.9, 129.8 (2C), 127.4 (2C), 123.0 (q, *J* = 273.3 Hz), 119.0 (q, *J* = 3.7 Hz), 118.0, 115.5 (q, *J* = 4.0 Hz), 52.9, 21.6 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -63.72 (s, 3F) ppm; HRMS (ESI): calcd. for C₁₆H₁₄F₃NO₄SNa [M+Na]⁺: 396.0488 found: 396.0490.


S-4c *5-Fluoro-2-((4-methylphenyl)sulfonamido)benzoic acid (S-4c)* was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (2:1) as a white solid (2.42 g, 98 % yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ= 7.67-7.56 (m, 3H), 7.46 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.36-7.19 (m, 3H), 2.31 (s, 3H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆) δ= 168.9, 157.0 (d, *J* = 244.5 Hz), 144.6, 136.5 (d, *J* = 3.3 Hz), 136.0, 130.4 (2C), 127.3 (2C), 122.0 (d, *J* = 2.9 Hz), 121.9 (d, *J* = 11.9 Hz), 119.8 (d, *J* = 7.1 Hz), 117.8 (d, *J* = 24.0 Hz), 21.4 ppm; ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ= -118.01 - -118.46 (m, 1F); HRMS (ESI): calcd. for C₁₄H₁₂FNO₄SNa [M+Na]⁺: 332.0363 found: 330.0367.

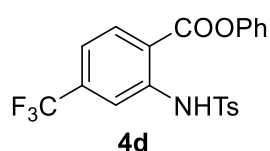

S-4d *2-((4-Methylphenyl)sulfonamido)-4-(trifluoromethyl)benzoic acid (S-4d)* was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (2:1) as a white solid (2.81 g, 98 % yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ= 8.08 (d, *J* = 8.1 Hz, 1H), 7.76-7.63 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 2.31 (s, 3H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ= 168.7, 143.5, 143.4, 137.9, 132.8, 132.3 (q, *J* = 31.8 Hz), 130.1 (2C), 126.9 (2C), 124.5, 124.1 (q, *J* = 272.9 Hz), 117.7 (q, *J* = 3.9 Hz), 114.2 (q, *J* = 4.0 Hz), 21.3; ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ= -61.98 (s, 3F) ppm. HRMS (ESI): calcd. for C₁₅H₁₂F₃NO₄SNa [M+Na]⁺: 382.0331 found: 382.0341.



1-(2-Hydroxyphenyl)nonan-1-one (4a) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (2.20 g, 60 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 10.44 (s, 1H), 8.16 (dd, J = 8.0, 1.7 Hz, 1H), 7.79-7.70 (m, 3H), 7.57-7.47 (m, 1H), 7.46-7.40 (m, 2H), 7.34-7.25 (m, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.16-7.06 (m, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 166.8, 150.1, 144.1, 141.2, 136.4, 135.3, 131.7, 129.74 (2C), 129.69 (2C), 127.4 (2C), 126.5, 123.1, 121.6 (2C), 119.2, 115.1, 21.6 ppm; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 390.0770 found: 390.0779.

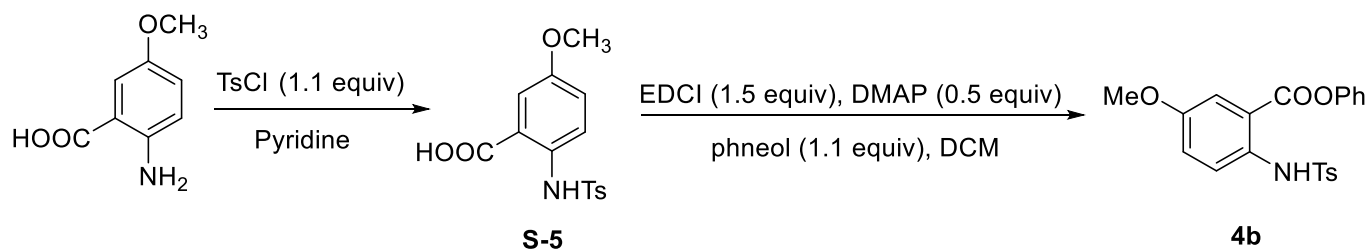


Phenyl 5-fluoro-2-((4-methylphenyl)sulfonamido)benzoate (4c) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (2.64 g, 86 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 10.09 (s, 1H), 7.86-7.76 (m, 2H), 7.72-7.65 (m, 2H), 7.49-7.42 (m, 2H), 7.35-7.28 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.13-7.04 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 165.5 (d, J = 2.6 Hz), 158.0 (d, J = 244.9 Hz), 149.9, 144.1, 137.3 (d, J = 2.7 Hz), 136.1, 129.7 (4C), 127.3 (2C), 126.6, 122.5 (d, J = 22.5 Hz), 122.1 (d, J = 7.6 Hz), 121.4 (2C), 117.6 (d, J = 24.5 Hz), 117.0 (d, J = 7.3 Hz), 21.6 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -114.76 - -125.43 (m, 1F) ppm; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{16}\text{FNO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 408.0676 found: 408.0682

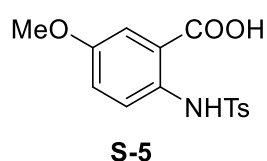


Phenyl 2-((4-methylphenyl)sulfonamido)-4-(trifluoromethyl)benzoate (4d) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (2.34 g, 68 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 10.51 (s, 1H), 8.33-8.24 (m, 1H), 8.06 (s, 1H), 7.81-7.74 (m, 2H), 7.49-7.42 (m, 2H), 7.38-7.30 (m, 2H), 7.29-7.22 (m, 2H), 7.18- 7.07 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 165.8, 149.8, 144.6, 141.7, 136.4 (q, J = 33.2 Hz), 135.9, 132.4, 129.9 (2C), 129.8 (2C), 127.4 (2C), 126.8, 123.0 (q, J =276.7 Hz), 121.4 (2C), 119.1 (q, J = 3.6 Hz), 117.3, 115.6 (q, J = 4.0 Hz), 21.6 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -63.75 (s, 3F) ppm; HRMS (ESI): calcd. for $\text{C}_{21}\text{H}_{16}\text{F}_3\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 458.0644 found: 458.0649

Preparation of Salicylate Ester 4b

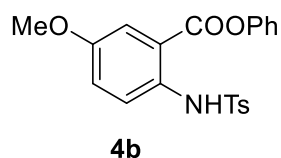


To a solution of a 2-amino-5-methoxybenzoic acid (1.67 g, 10.0 mmol, 1 equiv) in dry pyridine (20 mL), tosyl chloride (2.09 g, 11 mmol, 1.1 equiv) was added at 0 °C under nitrogen atmosphere. After 10 h, the reaction was quenched with ice water, and the aqueous layer was extracted with DCM. The organic layers were combined, washed with HCl 10% (5 mL), brine (10 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc= 1:1) to give **S-5**.



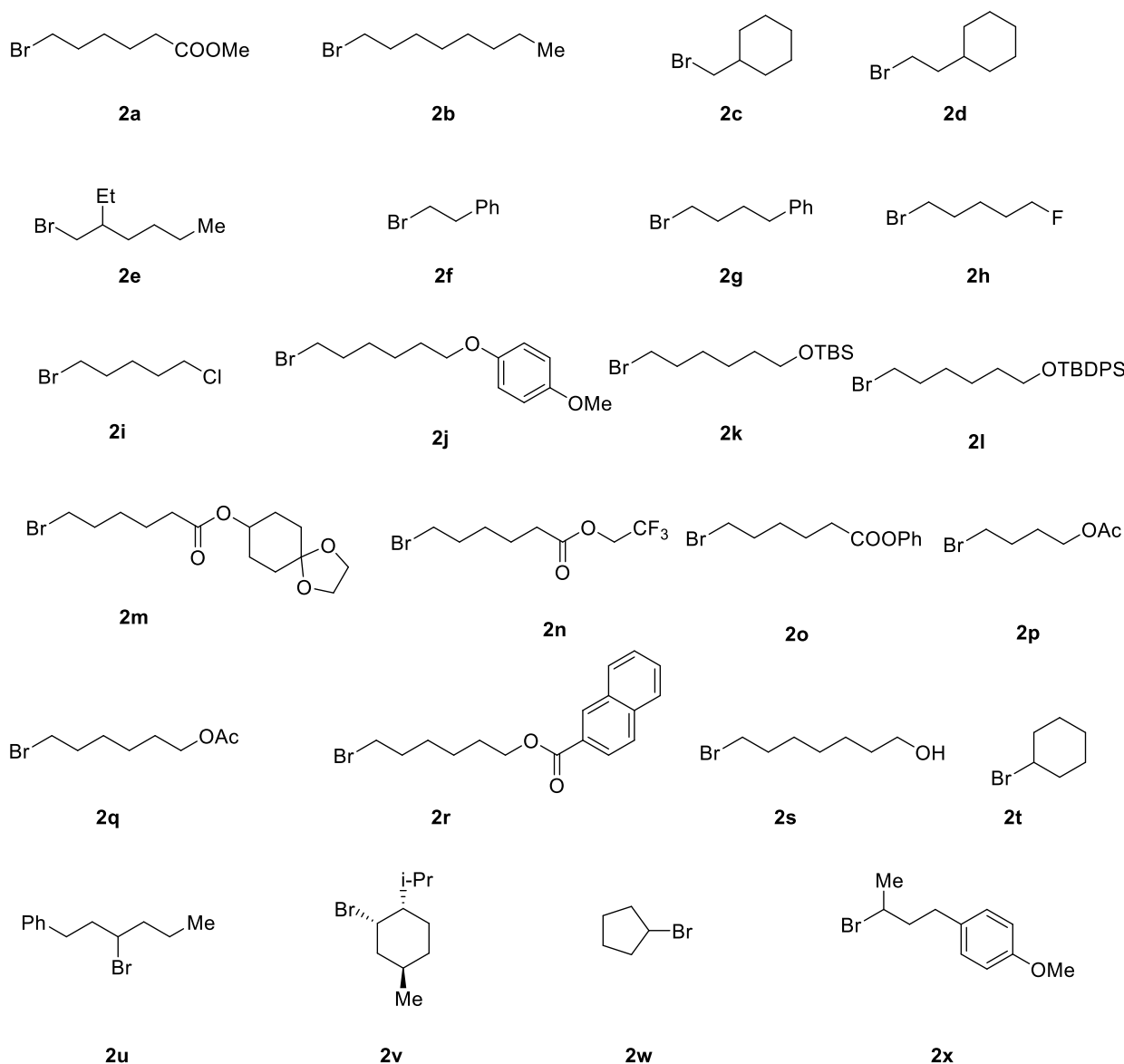
5-Methoxy-2-((4-methylphenyl)sulfonamido)benzoic acid (S-5) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (1:1) as a white solid (2.60 g, 81 % yield). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ = 10.53 (s, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.36-7.30 (m, 3H), 7.18 (dd, J = 9.0, 3.2

Hz, 1H), 3.72 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (126 MHz, DMSO- d_6) δ = 169.6, 155.6, 144.3, 136.2, 133.1, 130.3 (2C), 127.3 (2C), 122.3, 121.0, 119.8, 115.5, 55.9, 21.4 ppm; HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_5\text{SNa}$ $[\text{M}+\text{Na}]^+$: 344.0563 found: 344.0568.



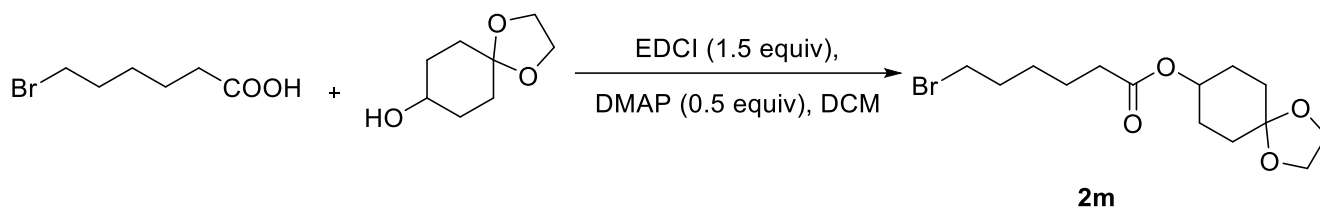
Phenyl 5-methoxy-2-((4-methylphenyl)sulfonamido)benzoate (4b) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a white solid (2.77 g, 87 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 9.82 (s, 1H), 7.74 (d, J = 9.1 Hz, 1H), 7.67-7.61 (m, 2H), 7.59 (d, J = 3.1 Hz, 1H), 7.48-7.41 (m, 2H), 7.34-7.28 (m, 1H), 7.23-7.19 (m, 2H), 7.14 (dd, J = 9.1, 3.1 Hz, 1H), 7.10-7.00 (m, 2H), 3.82 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 166.1, 155.6, 150.0, 143.8, 136.2, 134.1, 129.6 (2C), 129.5 (2C), 127.3 (2C), 126.5, 122.9, 121.7, 121.5 (2C), 117.4, 115.1, 55.7, 21.6 ppm. HRMS (ESI): calcd. for $\text{C}_{21}\text{H}_{19}\text{NO}_5\text{SNa}$ $[\text{M}+\text{Na}]^+$: 420.0876 found: 420.0887.

Preparation of Alkyl Bromides

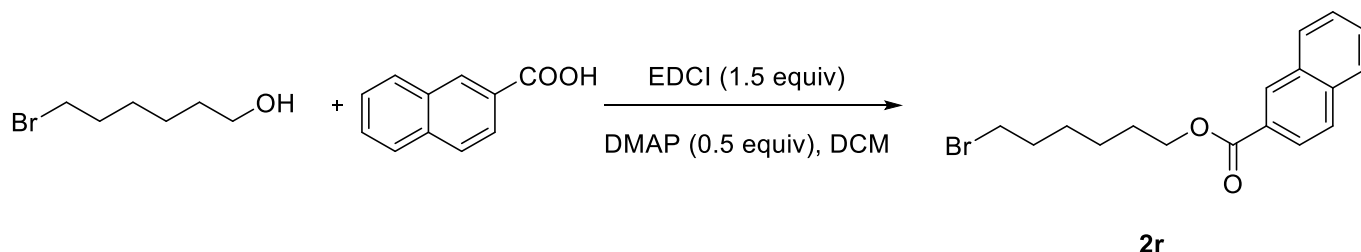


Compounds **2a-i**, **2p**, **2s**, **2t** and **2w** are commercially available. Compounds **2j**⁴, **2k**⁵, **2l**⁶, **2n**⁷, **2o**⁷, **2q**⁷, **2u**⁸, **2v**⁷, **2x**⁹ are known and their NMR-data are consistent with these reported in the literature.

Preparation of Alkyl Bromide 2m and 2r.

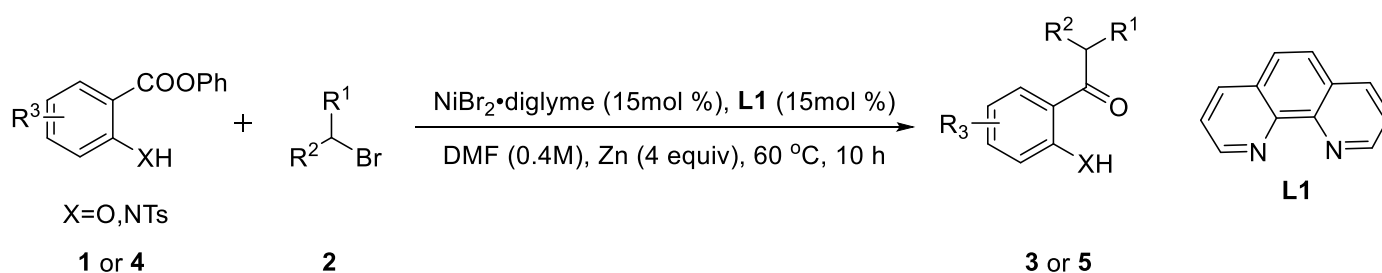


6-Bromohexanoic acid (2.1 g, 11.0 mmol, 1.1 equiv), EDCI (2.9 g, 15 mmol, 1.5 equiv), DMAP (610.0 mg, 5 mmol, 0.5 equiv) and 1,4-dioxaspiro[4.5]decan-8-ol (1.58 g, 10.0 mmol, 1.0 equiv) were dissolved in DCM (20 mL). The reaction mixture was stirred for overnight at room temperature, before it was quenched by addition of water. The mixture was extracted with DCM and combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc= 10:1) to give *1,4-dioxaspiro[4.5]Decan-8-yl 6-bromohexanoate* (**2m**) as a colorless oil (2.74 g, 82% yield). ¹H NMR (500 MHz, CDCl₃) δ= 5.00-4.65 (m, 1H), 4.00-3.82 (m, 4H), 3.41 (t, *J*= 6.8 Hz, 2H), 2.32 (t, *J*= 7.4 Hz, 2H), 1.91-1.84 (m, 4H), 1.82-1.71 (m, 4H), 1.69-1.56 (m, 4H), 1.52-1.43 (m, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 172.8, 107.9, 69.9, 64.29, 64.27, 34.3, 33.5, 32.3, 31.2 (2C), 28.3 (2C), 27.6, 24.1 ppm; HRMS (ESI): calcd. for C₁₄H₂₄BrO₄ [M+H]⁺: 335.0852 found:335.0856.



6-Bromohexan-1-ol (1.8 g, 10.0 mmol, 1.0 equiv), EDCI (2.9 g, 15 mmol, 1.5 equiv), DMAP (610.0 mg, 5 mmol, 0.5 equiv) and 2-naphthoic acid (1.9 g, 11.0 mmol, 1.1 equiv) were dissolved in DCM (20 mL). The reaction mixture was stirred for overnight at room temperature., before it was quenched by addition of water. The mixture was extracted with DCM and combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc= 10:1) to give *6-bromohexyl 2-naphthoate* (**2r**) as a white solid (2.68 g, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ= 8.60 (s, 1H), 8.06 (d, *J*= 8.5 Hz, 1H), 7.96 (d, *J*= 8.1 Hz, 1H), 7.88 (d, *J*= 8.6 Hz, 2H), 7.63 -7.48 (m, 2H), 4.38 (t, *J*= 6.6 Hz, 2H), 3.42 (t, *J*= 6.8 Hz, 2H), 1.92-1.82 (m, 4H), 1.60-1.44 (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 166.8, 135.5, 132.5, 131.0, 129.4, 128.2, 128.2, 127.8, 127.7, 126.7, 125.3, 65.0, 33.8, 32.7, 28.7, 27.9, 25.4 ppm; HRMS (ESI): calcd. for C₁₇H₂₀BrO₂ [M+H]⁺: 335.0641 found:335.0635.

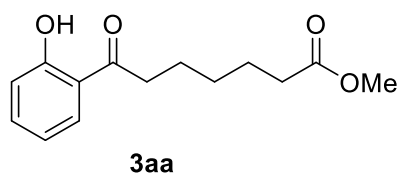
General Procedure for the Ni-Catalyzed Cross-coupling of Phenolic Esters with Alkyl Bromides



A sealed reaction tube charged with the phenolic esters **1** or **4** (0.2 mmol, 1 equiv), ligand **L1** (5.4 mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (10.6 mg, 0.03 mmol, 15 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before alkyl bromides **2** (0.3 mmol, 1.5 equiv)^a were added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding products **3** or **5**. ^a 3 Equiv of the alkyl bromide was used in the case of **3kb**.

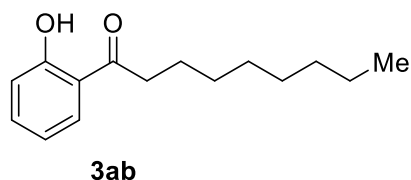
Analytical Data for the Products **3** and **5**

The products **3ab**,¹⁰ **3ac**,¹¹ **3af**,¹² **3ai**¹³ and **3at**¹⁴ are known compounds and their NMR-data are consistent with these reported in the literature.



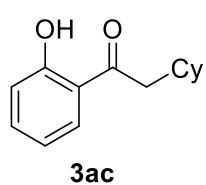
Methyl 7-(2-hydroxyphenyl)-7-oxoheptanoate (3aa) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (46 mg, 92 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 12.36 (s, 1H), 7.75 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.51-7.42 (m, 1H), 7.01-6.95

(m, 1H), 6.93-6.85 (m, 1H), 3.67 (s, 3H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.82-1.62 (m, 4H), 1.48-1.36 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 206.5, 174.1, 162.5, 136.3, 129.9, 119.3, 118.9, 118.5, 51.6, 38.0, 33.8, 28.7, 24.7, 24.0 ppm; HRMS (ESI): calcd. for C₁₄H₁₉O₄ [M+H]⁺: 251.1278 found: 251.1261.



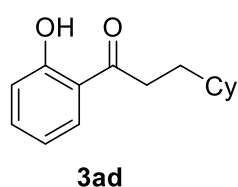
1-(2-Hydroxyphenyl)nonan-1-one (3ab) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (40 mg, 82 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 12.41 (s, 1H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49-7.42 (m, 1H), 6.98 (dd, *J* = 8.4, 1.1

Hz, 1H), 6.93-6.87 (m, 1H), 2.98 (t, *J* = 7.5 Hz, 2H), 1.79-1.68 (m, 2H), 1.44-1.20 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 207.0, 162.5, 136.2, 130.0, 119.4, 118.8, 118.5, 38.4, 31.9, 29.42, 29.35, 29.2, 24.6, 22.7, 14.1 ppm;



2-Cyclohexyl-1-(2-hydroxyphenyl)ethan-1-one (3ac) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a colorless oil (40 mg, 92 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 12.50 (s, 1H), 7.75 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50-7.43 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 2.83 (d, *J* = 6.8 Hz, 2H), 2.01-1.93 (m, 1H), 1.83-1.62 (m, 5H), 1.33-1.24 (m, 2H), 1.22-1.13 (m, 1H), 1.04 (dd, *J* = 12.1, 3.3 Hz,

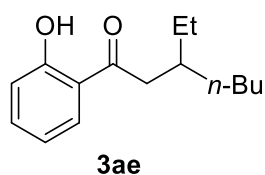
2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 206.8, 162.7, 136.3, 130.3, 119.7, 118.8, 118.6, 45.9, 35.0, 33.4 (2C), 26.2, 26.1 (2C) ppm.



3-Cyclohexyl-1-(2-hydroxyphenyl)propan-1-one (3ad) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a yellow oil (42 mg, 90 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 12.41 (s, 1H), 7.76 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.47-7.42 (m, 1H), 6.98 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.92-6.86 (m, 1H), 3.05-2.96 (m, 2H), 1.79-1.71 (m, 4H), 1.69-1.60 (m, 3H), 1.39-1.12 (m, 4H), 1.01-0.89 (m, 2H) ppm; ¹³C NMR (126

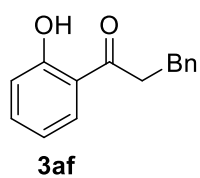
MHz, CDCl₃) δ= 207.4, 162.5, 136.2, 130.0, 119.3, 118.9, 118.6, 37.4, 36.0, 33.2 (2C), 32.0, 26.5, 26.3 (2C) ppm; HRMS

(ESI): calcd. for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1536, found: 233.1536.



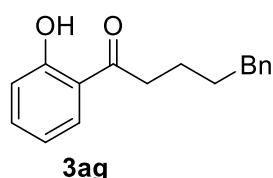
3ae

3-Ethyl-1-(2-hydroxyphenyl)heptan-1-one (3ae) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a yellow oil (41 mg, 87 % yield). 1H NMR (500 MHz, $CDCl_3$) δ = 12.50 (s, 1H), 7.77 (dd, J = 8.1, 1.6 Hz, 1H), 7.50-7.40 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 2.89 (d, J = 6.8 Hz, 2H), 2.07-2.00 (m, 1H), 1.43-1.35 (m, 3H), 1.34-1.24 (m, 5H), 0.91 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 207.3, 162.6, 136.2, 130.1, 119.7, 118.8, 118.6, 42.7, 36.1, 33.2, 28.9, 26.4, 23.0, 14.1, 10.9 ppm; HRMS (ESI): calcd. for $C_{15}H_{23}O_2$ $[M+H]^+$: 235.1693, found: 235.1693.



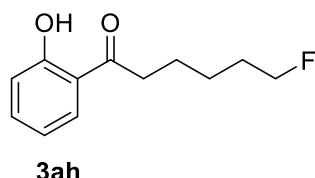
3af

1-(2-Hydroxyphenyl)-3-phenylpropan-1-one (3af) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (32 mg, 71 % yield). 1H NMR (400 MHz, $CDCl_3$) δ = 12.30 (s, 1H), 7.74 (dd, J = 8.1, 1.7 Hz, 1H), 7.49-7.43 (m, 1H), 7.35 -7.28 (m, 2H), 7.27-7.18 (m, 3H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.89-6.83 (m, 1H), 3.33 (t, J = 7.3 Hz, 2H), 3.07 (t, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 205.4, 162.5, 140.7, 136.4, 129.8, 128.6 (2C), 128.4 (2C), 126.4, 119.3, 119.0, 118.6, 40.1, 30.0 ppm.



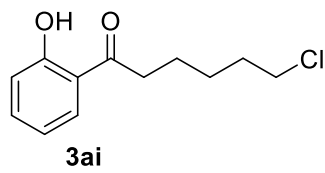
3ag

1-(2-Hydroxyphenyl)-5-phenylpentan-1-one (3ag) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (40 mg, 78 % yield). 1H NMR (400 MHz, $CDCl_3$) δ = 12.38 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.20 -7.13 (m, 3H), 6.97 (d, J = 8.4 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 2.99 (t, J = 7.0 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H), 1.86-1.63 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.6, 162.5, 142.1, 136.3, 130.0, 128.42 (2C), 128.39 (2C), 125.9, 119.3, 118.9, 118.6, 38.2, 35.8, 31.0, 24.1 ppm; HRMS (ESI): calcd. for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found: 255.1378.



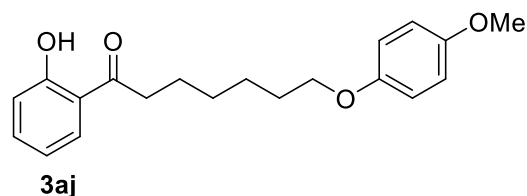
3ah

6-Fluoro-1-(2-hydroxyphenyl)hexan-1-one (3ah) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a yellow oil (35 mg, 83 % yield). 1H NMR (500 MHz, $CDCl_3$) δ = 12.36 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 4.47 (dt, J = 47.3, 6.0 Hz, 2H), 3.02 (t, J = 7.3 Hz, 2H), 1.83-1.76 (m, 3H), 1.76-1.71 (m, 1H), 1.57-1.47 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.5, 162.5, 136.3, 129.9, 119.3, 118.9, 118.6, 84.5 (C-F, $^1J_{C-F}$ = 164.4 Hz), 83.2 (C-F, $^1J_{C-F}$ = 164.4 Hz), 38.1, 30.4 (C-F, $^2J_{C-F}$ = 19.4 Hz), 30.2 (C-F, $^2J_{C-F}$ = 19.4 Hz), 25.03 (C-F, $^3J_{C-F}$ = 5.4 Hz), 24.99 (C-F, $^3J_{C-F}$ = 5.4 Hz), 24.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -218.25 - -218.73 (m, 1F); HRMS (ESI): calcd. for $C_{12}H_{16}FO_2$ $[M+H]^+$: 211.1129, found: 211.1125.

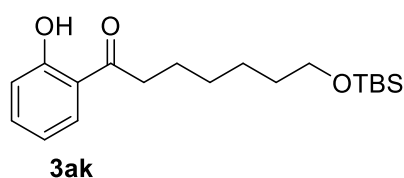


3ai

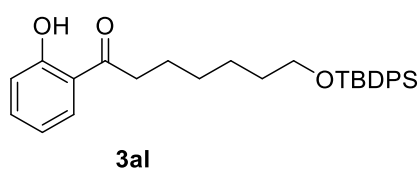
6-Chloro-1-(2-hydroxyphenyl)hexan-1-one (3ai) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a colorless oil (35 mg, 77 % yield). 1H NMR (400 MHz, $CDCl_3$) δ = 12.34 (s, 1H), 7.76 (dd, J = 8.0, 1.7 Hz, 1H), 7.55-7.41 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 3.56 (t, J = 6.6 Hz, 2H), 3.02 (t, J = 7.3 Hz, 2H), 1.88-1.70 (m, 4H), 1.61-1.51 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.3, 162.5, 136.3, 129.9, 119.3, 118.9, 118.6, 44.8, 38.0, 32.4, 26.6, 23.6 ppm;



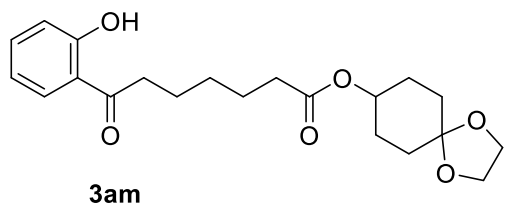
1-(2-Hydroxyphenyl)-7-(4-methoxyphenoxy)heptan-1-one (3aj) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (5:1) (53 mg, 81 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 12.39 (s, 1H), 7.76 (dd, J = 8.0, 1.7 Hz, 1H), 7.46 (t, J = 1.5 Hz, 1H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.82 (s, 4H), 3.91 (t, J = 6.4 Hz, 2H), 3.76 (s, 3H), 3.00 (t, J = 7.4 Hz, 2H), 1.83-1.72 (m, 4H), 1.57-1.42 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 206.8, 162.5, 153.7, 153.2, 136.3, 130.0, 119.3, 118.9, 118.6, 115.4 (2C), 114.6 (2C), 68.4, 55.8, 38.2, 29.2, 29.1, 26.0, 24.4 ppm; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}]^+$: 329.1747, found: 329.1750.



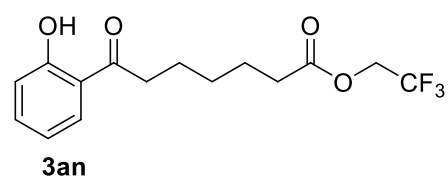
7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxyphenyl)heptan-1-one (3ak) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (66 mg, 98 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 12.41 (s, 1H), 7.76 (dd, J = 8.0, 1.7 Hz, 1H), 7.49-7.42 (m, 1H), 7.00-6.96 (m, 1H), 6.93-6.86 (m, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 1.84-1.66 (m, 2H), 1.60-1.48 (m, 2H), 1.47-1.34 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 206.9, 162.5, 136.2, 130.0, 119.3, 118.8, 118.5, 63.1, 38.3, 32.7, 29.1, 26.0 (3C), 25.7, 24.5, 18.4, -5.6 (2C) ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{33}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 337.2193, found: 337.2189.



7-((tert-Butyldiphenylsilyl)oxy)-1-(2-hydroxyphenyl)heptan-1-one (3al) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (83 mg, 90 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 12.42 (s, 1H), 7.74 (dd, J = 8.1, 1.7 Hz, 1H), 7.67 (dd, J = 7.4, 1.9 Hz, 4H), 7.45-7.32 (m, 7H), 7.00-6.96 (m, 1H), 6.90-6.84 (m, 1H), 3.67 (t, J = 6.3 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 1.75-1.68 (m, 2H), 1.63-1.51 (m, 2H), 1.47-1.32 (m, 4H), 1.05 (s, 9H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 206.9, 162.6, 136.2, 135.6 (4C), 134.2, 134.1, 130.0, 129.6, 129.5, 127.6 (4C), 119.4, 118.9, 118.6, 63.8, 38.3, 24, 29.1, 26.9 (3C), 25.7, 24.5, 19.3 ppm; HRMS (ESI): calcd. for $\text{C}_{29}\text{H}_{37}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 461.2506, found: 461.2536.

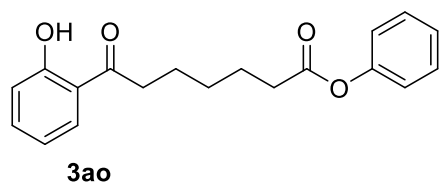


1,4-Dioxaspiro[4.5]decan-8-yl 7-(2-hydroxyphenyl)-7-oxoheptanoate (3am) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (5:1) as a white solid (53 mg, 71 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 12.36 (s, 1H), 7.76 (dd, J = 8.1, 1.7 Hz, 1H), 7.49-7.42 (m, 1H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.93-6.86 (m, 1H), 4.94-4.81 (m, 1H), 3.97-3.87 (m, 4H), 3.00 (t, J = 7.4 Hz, 2H), 2.33 (t, J = 7.4 Hz, 2H), 1.92-1.70 (m, 8H), 1.72-1.55 (m, 4H), 1.48-1.38 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 206.5, 173.1, 162.5, 136.3, 129.9, 118.9, 118.5, 108.0, 70.0, 64.4 (2C), 64.3 (2C), 38.0, 34.5, 31.3, 28.7, 28.4 (2C), 24.8, 24.0 ppm; HRMS (ESI): calcd. for $\text{C}_{21}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 377.1959, found: 377.1963.



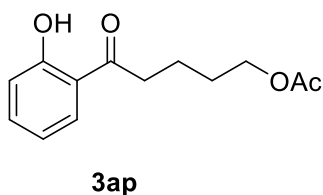
2,2,2-Trifluoroethyl 7-(2-hydroxyphenyl)-7-oxoheptanoate (3an) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a colorless oil (49 mg, 77 % yield). ^1H NMR (500 MHz, CDCl_3) δ = 12.35 (s, 1H), 7.75 (dd, J = 8.1, 1.6 Hz, 1H), 7.50-7.44 (m, 1H), 6.98 (dd, J = 8.4, 1.1 Hz, 1H), 6.93-6.86 (m, 1H), 4.47 (q, J = 8.5 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 2.46 (t, J = 7.5 Hz, 2H), 1.83-1.69 (m, 4H), 1.48-1.39 (m, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ = 206.4, 171.9, 162.5, 136.3, 129.9, 123.0 (q, J = 277.4 Hz), 119.3, 118.9, 118.6, 60.2 (q, J = 36.6 Hz), 37.9,

33.4, 28.5, 24.5, 23.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) $\delta = -73.78 - -73.92$ (m, 3F)ppm; HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_4\text{F}_3\text{Na}[\text{M}+\text{Na}]^+$:341.0971, found:341.0979.



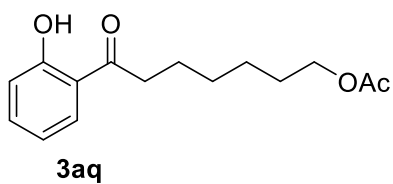
Phenyl 7-(2-hydroxyphenyl)-7-oxoheptanoate (3ao) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) (49 mg, 78 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.37$ (s, 1H), 7.76 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.49-7.44 (m, 1H), 7.40-7.35 (m, 2H), 7.24-7.18 (m, 1H), 7.11-7.05 (m, 2H), 6.99 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.92-6.87 (m, 1H), 3.03 (t, $J = 7.3$ Hz, 2H), 2.60 (t, $J = 7.4$ Hz, 2H), 1.86-1.76 (m,

4H), 1.60-1.48 (m, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3) $\delta = 206.5, 172.1, 162.5, 150.7, 136.3, 130.0, 129.5$ (2C), 125.8, 121.6 (2C), 119.3, 118.9, 118.6, 38.0, 34.2, 29.0, 24.7, 23.9 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$:313.1434, found: 313.1438.



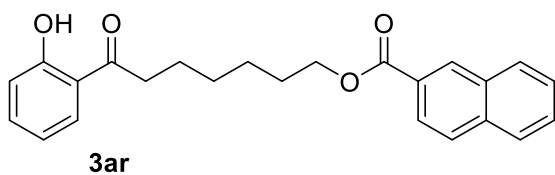
5-(2-Hydroxyphenyl)-5-oxopentyl acetate (3ap) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (34 mg, 73 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.32$ (s, 1H), 7.76 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.52-7.44 (m, 1H), 6.98 (dd, $J = 8.5, 1.2$ Hz, 1H), 6.94-6.86 (m, 1H), 4.12 (t, $J = 6.3$ Hz, 2H), 3.04 (t, $J = 7.1$ Hz, 2H), 2.05 (s, 3H), 1.91-1.71 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 206.1, 171.2, 162.5, 136.4, 129.8, 119.3, 118.9, 118.6, 64.0,$

37.6, 28.1, 21.0, 20.7 ppm; HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{Na}]^+$: 259.0941, found:259.0947.



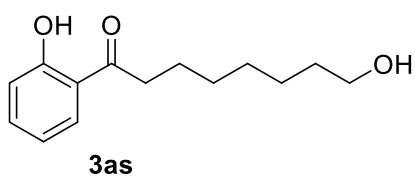
7-(2-Hydroxyphenyl)-7-oxoheptyl acetate (3aq) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (47 mg, 89 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.38$ (s, 1H), 7.76 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.50-7.42 (m, 1H), 6.98 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.94-6.86 (m, 1H), 4.07 (t, $J = 6.7$ Hz, 2H), 3.00 (t, $J = 7.4$ Hz, 2H),

2.05 (s, 3H), 1.85-1.58 (m, 4H), 1.51-1.37 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 206.7, 171.2, 162.5, 136.3, 129.9, 119.3, 118.9, 118.6, 64.4, 38.2, 28.9, 28.5, 25.8, 24.3, 21.0$ ppm; HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 265.1434, found:265.1439.



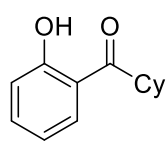
7-(2-Hydroxyphenyl)-7-oxoheptyl 2-naphthoate (3ar) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (48 mg, 64 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.39$ (s, 1H), 8.60 (d, $J = 1.6$ Hz, 1H), 8.06 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.95 (d, $J = 8.0$

Hz, 1H), 7.90-7.85 (m, 2H), 7.74 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.61-7.50 (m, 2H), 7.49-7.41 (m, 1H), 6.98 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.90-6.81 (m, 1H), 4.39 (t, $J = 6.6$ Hz, 2H), 3.00 (t, $J = 7.4$ Hz, 2H), 1.91-1.73 (m, 4H), 1.61-1.42 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 206.7, 166.8, 162.5, 136.3, 135.5, 132.5, 131.0, 130.0, 129.4, 128.22, 128.15, 127.8, 127.7, 126.6, 125.3, 119.3, 118.9, 118.6, 65.1, 38.2, 29.0, 28.7, 26.0, 24.3$ ppm; HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}]^+$: 377.1747, found: 377.1753.



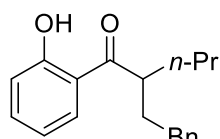
8-Hydroxy-1-(2-hydroxyphenyl)octan-1-one (3as) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (10:1) as a colorless oil (24 mg, 51 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.39$ (s, 1H), 7.77 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.50-7.43 (m, 1H), 6.98 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.94- 6.87 (m, 1H), 3.65 (t, $J = 6.6$ Hz, 2H), 2.99 (t, $J = 7.4$

Hz, 2H), 1.81-1.70 (m, 2H), 1.57 (q, $J = 6.8$ Hz, 2H), 1.44-1.34 (m, 6H) ppm; ^{13}C NMR (126 MHz, CDCl_3) $\delta = 206.9, 162.5, 136.2, 130.0, 119.3, 118.9, 118.6, 63.0, 38.3, 32.7, 29.24, 29.21, 25.6, 24.4$ ppm; HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 237.1485, found: 237.1487.



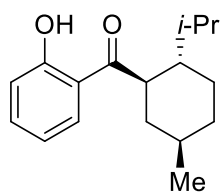
3at

Cyclohexyl(2-hydroxyphenyl)methanone (3at) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (26 mg, 64 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.59$ (s, 1H), 7.81-7.74 (m, 1H), 7.49-7.42 (m, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 6.90 (t, $J = 7.6$ Hz, 1H), 3.38-3.23 (m, 1H), 1.93-1.83 (m, 4H), 1.80-1.71 (m, 1H), 1.55 (dd, $J = 12.1, 3.4$ Hz, 2H), 1.47-1.36 (m, 2H), 1.34-1.20 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 210.2, 163.2, 136.2, 129.8, 118.78, 118.76, 118.2, 45.3, 29.6$ (2C), 25.9, 25.8 (2C) ppm;



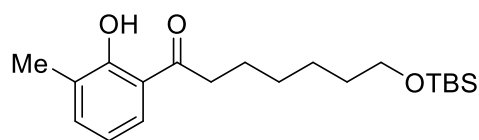
3au

1-(2-Hydroxyphenyl)-2-phenethylpentan-1-one (3au) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (28 mg, 50 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.69$ (s, 1H), 7.60 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.51-7.44 (m, 1H), 7.29-7.23 (m, 2H), 7.22-7.16 (m, 1H), 7.15-7.09 (m, 2H), 7.00 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.90-6.81 (m, 1H), 3.53-3.36 (m, 1H), 2.67-2.52 (m, 2H), 2.19-2.04 (m, 1H), 1.86-1.73 (m, 2H), 1.60-1.47 (m, 1H), 1.29 (q, $J = 7.6$ Hz, 2H), 0.87 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 210.6, 163.1, 141.5, 136.4, 129.9, 128.5$ (2C), 128.4 (2C), 126.0, 119.6, 118.8, 118.7, 44.4, 34.9, 34.0, 33.7, 20.7, 14.2 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: 283.1693 found: 283.1697.



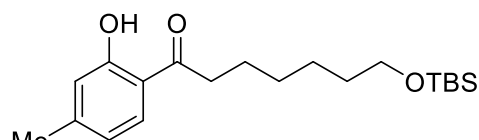
3av

(2-Hydroxyphenyl)((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)methanone (3av) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 5:1) as a colorless oil (37 mg, 71 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.78$ (s, 1H), 7.85 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.50-7.45 (m, 1H), 7.00 (dd, $J = 8.4, 1.1$ Hz, 1H), 6.94-6.87 (m, 1H), 3.40 (d, $J = 3.3$ Hz, 1H), 1.90-1.82 (m, 2H), 1.83-1.75 (m, 2H), 1.61 (s, 1H), 1.55-1.42 (m, 1H), 1.20-1.10 (m, 2H), 1.08-0.97 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.73 (d, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 211.0, 163.2, 136.4, 129.6, 119.2, 118.9, 118.8, 47.4, 43.7, 40.2, 34.6, 32.7, 28.9, 24.1, 22.3, 21.5, 16.6$ ppm; HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$: 261.1849 found: 261.1852.



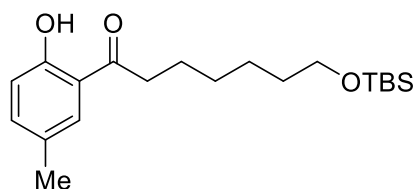
3bk

7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-3-methylphenyl)heptan-1-one (3bk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (30 mg, 43 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.71$ (s, 1H), 7.65-7.55 (m, 1H), 7.33 (d, $J = 7.3$ Hz, 1H), 6.79 (t, $J = 7.7$ Hz, 1H), 3.61 (t, $J = 6.4$ Hz, 2H), 2.98 (t, $J = 7.5$ Hz, 2H), 2.26 (s, 3H), 1.84-1.69 (m, 2H), 1.59-1.48 (m, 2H), 1.44-1.35 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 207.1, 161.0, 136.9, 127.56, 118.6, 118.1, 63.1, 38.4, 32.7, 29.1, 26.0$ (3C), 25.7, 24.7, 18.9, 15.54, -5.3 (2C) ppm; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{35}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 351.2350 found: 351.2352.



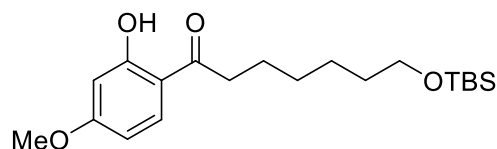
3ck

7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-4-methylphenyl)heptan-1-one (3ck) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (56 mg, 80 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 12.43$ (s, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 6.78 (d, $J = 1.5$ Hz, 1H), 6.70 (dd, $J = 8.2, 1.7$ Hz, 1H), 3.61 (t, $J = 6.4$ Hz, 2H), 2.94 (t, $J = 7.5$ Hz, 2H), 2.34 (s, 3H), 1.80-1.64 (m, 2H), 1.62-1.47 (m, 2H), 1.46-1.31 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 206.3, 162.7, 147.8, 129.9, 120.1, 118.5, 117.1, 63.1, 38.1, 32.7, 29.1, 26.0$ (3C), 25.7, 24.7, 21.9, 18.4, -5.3 (2C) ppm; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{35}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 351.2350 found: 351.2342.



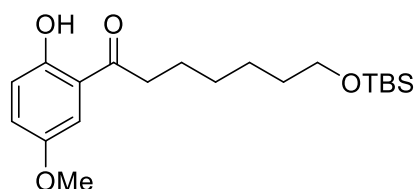
3dk

7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-5-methylphenyl)heptan-1-one (3dk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (68 mg, 97 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 12.22 (s, 1H), 7.63-7.49 (m, 1H), 7.31-7.23 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.84-1.68 (m, 2H), 1.66-1.50 (m, 2H), 1.46-1.28 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 206.7, 160.4, 137.2, 129.7, 127.9, 119.0, 118.3, 63.1, 38.2, 32.7, 29.1, 26.0, 25.7, 24.4, 20.6 (3C), 18.4, -5.6 (2C) ppm; HRMS (ESI): calcd. for C₂₀H₃₅O₃Si [M+H]⁺: 351.2350 found: 351.2356.



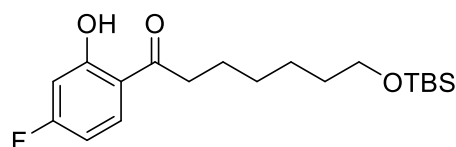
3ek

7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-4-methoxyphenyl)heptan-1-one (3ek) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a colorless oil (31 mg, 42 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 12.90 (s, 1H), 7.80-7.59 (m, 1H), 6.56-6.30 (m, 2H), 3.84 (s, 3H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.80-1.67 (m, 2H), 1.57-1.46 (m, 2H), 1.44-1.35 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 205.1, 165.9, 165.4, 131.6, 113.5, 107.6, 100.9, 63.1, 55.6, 38.0, 32.7, 29.2, 26.0 (3C), 25.7, 24.9, 18.4, -5.3 (2C) ppm; HRMS (ESI): calcd. for C₂₀H₃₅O₄Si [M+H]⁺: 367.2299 found: 367.2300.



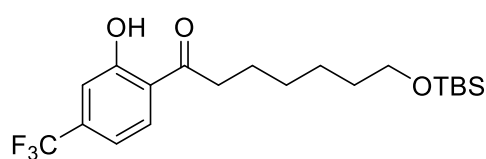
3fk

7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-5-methoxyphenyl)heptan-1-one (3fk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a colorless oil (54 mg, 74 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 11.98 (s, 1H), 7.20 (d, *J* = 3.0 Hz, 1H), 7.10 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.81-1.70 (m, 2H), 1.63-1.48 (m, 2H), 1.48-1.35 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 206.3, 156.8, 151.6, 123.8, 119.3, 118.8, 112.9, 63.1, 56.0, 38.3, 32.7, 29.1, 26.0 (3C), 25.7, 24.3, 18.4, -5.3 (2C) ppm. HRMS (ESI): calcd. for C₂₀H₃₅O₄Si [M+H]⁺: 367.2299 found: 367.2303.



3gk

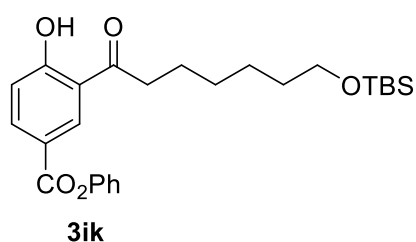
7-((tert-Butyldimethylsilyl)oxy)-1-(4-fluoro-2-hydroxyphenyl)heptan-1-one (3gk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (63 mg, 89 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 12.73 (d, *J* = 1.5 Hz, 1H), 7.82-7.70 (m, 1H), 6.71-6.52 (m, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.80-1.67 (m, 2H), 1.57-1.49 (m, 2H), 1.45-1.33 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 205.7, 168.5 (C-F, ¹*J*_{C-F} = 256.3 Hz), 166.0 (C-F, ¹*J*_{C-F} = 256.3 Hz), 165.2 (C-F, ³*J*_{C-F} = 14.3 Hz), 165.0 (C-F, ³*J*_{C-F} = 14.3 Hz), 132.4 (C-F, ³*J*_{C-F} = 11.8 Hz), 132.3 (C-F, ³*J*_{C-F} = 11.8 Hz), 116.50 (C-F, ⁴*J*_{C-F} = 2.3 Hz), 116.47 (C-F, ⁴*J*_{C-F} = 2.3 Hz), 107.2 (C-F, ²*J*_{C-F} = 22.7 Hz), 107.0 (C-F, ²*J*_{C-F} = 22.7 Hz), 105.2 (C-F, ²*J*_{C-F} = 23.5 Hz), 104.9 (C-F, ²*J*_{C-F} = 23.5 Hz), 63.1, 38.3, 32.6, 29.1, 26.0 (3C), 25.7, 24.5, 18.4, -5.7 (2C) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -93.83- -108.03 (m, 1F) ppm; HRMS (ESI): calcd. for C₁₉H₃₂FO₃Si [M+H]⁺: 355.2099 found: 355.2105



3hk

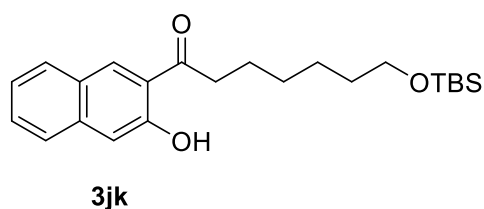
7-((tert-Butyldimethylsilyl)oxy)-1-(2-hydroxy-4-(trifluoromethyl)phenyl)heptan-1-one (3hk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (65 mg, 80 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 12.42 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.38-7.19 (m, 1H), 7.13 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 1.84-1.72 (m, 2H), 1.59-1.50 (m, 2H), 1.47-1.35 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 206.6, 162.3, 137.6 (C-F, ²*J*_{C-F} = 33.0 Hz), 137.3 (C-F, ²*J*_{C-F} = 33.0 Hz),

136.9 (C-F, $^2J_{\text{C-F}} = 33.0$ Hz), 136.6 (C-F, $^2J_{\text{C-F}} = 33.0$ Hz), 130.7, 127.1 (C-F, $^1J_{\text{C-F}} = 273.7$ Hz), 124.4 (C-F, $^1J_{\text{C-F}} = 273.7$ Hz), 121.7 (C-F, $^1J_{\text{C-F}} = 273.7$ Hz), 121.2, 119.0 (C-F, $^1J_{\text{C-F}} = 273.7$ Hz), 116.10 (C-F, $^3J_{\text{C-F}} = 4.0$ Hz), 116.06 (C-F, $^3J_{\text{C-F}} = 4.0$ Hz), 116.02 (C-F, $^3J_{\text{C-F}} = 4.0$ Hz), 115.98 (C-F, $^3J_{\text{C-F}} = 4.0$ Hz), 115.24 (C-F, $^3J_{\text{C-F}} = 3.6$ Hz), 115.21 (C-F, $^3J_{\text{C-F}} = 3.6$ Hz), 115.21 (C-F, $^3J_{\text{C-F}} = 3.6$ Hz), 115.17 (C-F, $^3J_{\text{C-F}} = 3.6$ Hz), 63.1, 38.6, 32.6, 29.0, 26.0 (3C), 25.6, 24.2, 18.4, -5.3 (2C) ppm; ^{19}F NMR (376 MHz, CDCl_3) $\delta = -63.91$ (s, 3F) ppm. HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{32}\text{FO}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 405.2067 found: 405.2068



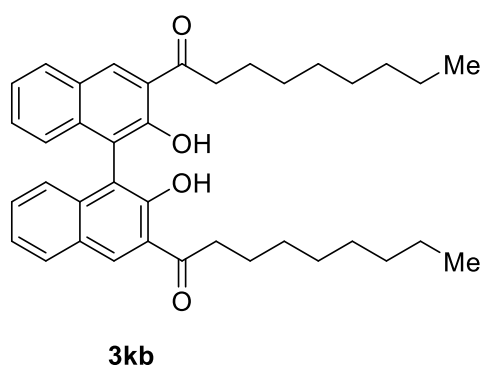
Phenyl 3-(7-((tert-butyldimethylsilyl)oxy)heptanoyl)-4-hydroxybenzoate (3ik) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (65 mg, 71 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.92$ (s, 1H), 8.66 (t, $J = 2.0$ Hz, 1H), 8.36-8.20 (m, 1H), 7.50-7.40 (m, 2H), 7.35-7.18 (m, 3H), 7.13-7.03 (m, 1H), 3.61 (t, $J = 6.5$ Hz, 2H), 3.09 (t, $J = 7.4$ Hz, 2H), 1.85-1.73 (m, 2H), 1.60-1.51 (m, 2H), 1.49-1.37 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (126 MHz, CDCl_3) $\delta = 206.9, 166.7, 164.2, 150.9, 137.4, 133.2, 129.6$ (2C), 126.0,

121.7 (2C), 120.3, 119.04, 118.97, 63.1, 38.3, 32.7, 29.0, 26.0 (3C), 25.7, 24.2, 18.4, -5.3 (2C) ppm. HRMS (ESI): calcd. for $\text{C}_{26}\text{H}_{37}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 457.2405 found: 457.2414



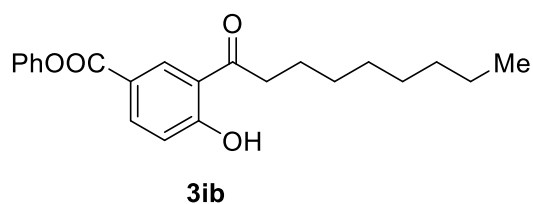
7-((tert-Butyldimethylsilyl)oxy)-1-(3-hydroxynaphthalen-2-yl)heptan-1-one (3jk) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a white solid (46 mg, 60 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 11.70$ (s, 1H), 8.37 (s, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 8.5$ Hz, 1H), 3.62 (t, $J = 6.4$ Hz, 2H), 3.17 (t, $J = 7.4$ Hz, 2H), 1.88-1.76 (m, 2H), 1.64-

1.50 (m, 2H), 1.52-1.39 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 207.1, 157.2, 138.1, 132.7, 129.6, 129.4, 126.8, 126.2, 124.0, 121.0, 112.3, 63.1, 38.5, 32.7, 29.1, 26.0$ (3C), 25.7, 24.6, 18.4, -5.2 (2C) ppm; HRMS (ESI): calcd. for $\text{C}_{23}\text{H}_{35}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 387.2350 found: 387.2357.



1,1'-(2,2'-Dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(nonan-1-one) (3kb) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a yellow solid (55 mg, 48 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 11.70$ (s, 2H), 8.35 (s, 2H), 7.79 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 3.13 (t, $J = 7.5$ Hz, 4H), 1.83-1.72 (m, 4H), 1.46-1.39 (m, 4H), 1.37-1.24 (m, 16H), 0.89 (t, $J = 6.6$ Hz, 6H) ppm; ^{13}C NMR (126 MHz, CDCl_3) $\delta = 207.2$ (2C), 157.3 (2C), 138.1 (2C), 132.7 (2C), 129.6 (2C), 129.4 (2C), 126.8 (2C), 126.2 (2C), 124.0 (2C), 121.0 (2C), 112.3 (2C), 38.5 (2C), 31.9 (2C), 29.5 (2C), 29.4 (2C), 29.2 (2C), 24.6 (2C), 22.7 (2C), 14.1 (2C) ppm; HRMS (ESI): calcd. for $\text{C}_{38}\text{H}_{47}\text{O}_4$ $[\text{M}+\text{H}]^+$: 567.3469

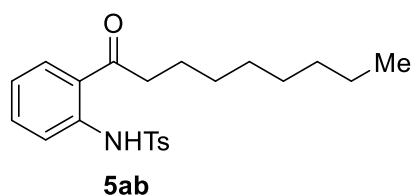
found: 567.3469.



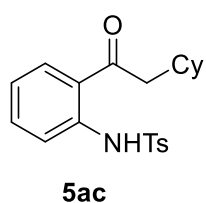
Phenyl 4-hydroxy-3-nonanoylbenzoate (3ib) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 20:1) as a colorless oil (87 mg, 86 % yield). ^1H NMR (500 MHz, CDCl_3) $\delta = 12.93$ (s, 1H), 8.65 (d, $J = 2.1$ Hz, 1H), 8.28 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.21 (dd, $J = 7.4, 1.6$ Hz, 2H), 7.07 (d, $J = 8.8$ Hz, 1H), 3.08 (t, $J = 7.4$ Hz, 2H), 1.85-1.70 (m, 2H), 1.45-1.37 (m, 2H), 1.39-

1.22 (m, 8H), 0.88 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) $\delta = 207.0, 166.7, 164.1, 150.8, 137.4, 133.2, 129.5$ (2C), 126.0, 121.7 (2C), 120.3, 119.00, 118.95, 38.4, 31.8, 29.4, 29.2, 29.1, 24.2, 22.7, 14.1 ppm; HRMS (ESI): calcd. for

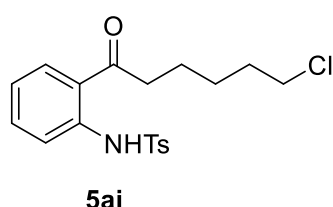
C₂₂H₂₇O₄ [M+H]⁺: 355.1904 found: 355.1901.



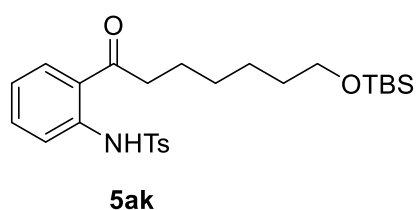
4-Methyl-N-(2-nonanoylphenyl)benzenesulfonamide (5ab) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (40 mg, 52 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 11.45 (s, 1H), 7.80 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.75-7.66 (m, 3H), 7.49-7.38 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.65-1.52 (m, 2H), 1.36-1.25 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 204.8, 143.7, 139.9, 136.6, 134.5, 131.0, 129.6 (2C), 127.2 (2C), 122.7, 122.5, 119.6, 39.7, 31.8, 29.4, 29.21, 29.15, 24.5, 22.7, 21.5, 14.1 ppm; HRMS (ESI): calcd. for C₂₂H₃₀NO₃S [M+H]⁺: 388.1941 found: 388.1945.



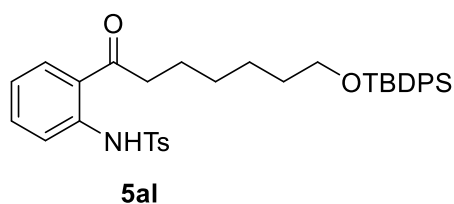
N-(2-(2-cyclohexylacetyl)phenyl)-4-methylbenzenesulfonamide (5ac) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (38 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ= 11.51 (s, 1H), 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76-7.68 (m, 3H), 7.49-7.40 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11-7.02 (m, 1H), 2.73 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 1.91-1.77 (m, 1H), 1.73-1.56 (m, 4H), 1.30-1.10 (m, 4H), 1.01-0.85 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 204.5, 143.7, 140.1, 136.7, 134.6, 131.2, 129.6 (2C), 127.2 (2C), 122.7, 122.6, 119.6, 47.3, 34.8, 33.3 (2C), 26.2, 26.1 (2C), 21.5 ppm; HRMS (ESI): calcd. for C₂₁H₂₅NO₃SNa [M+Na]⁺: 394.1447 found: 394.1445.



N-(2-(6-chlorohexanoyl)phenyl)-4-methylbenzenesulfonamide (5ai) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (46 mg, 61 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 11.41 (s, 1H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.73 (s, 1H), 7.73-7.67 (m, 2H), 7.49-7.41 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 1H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 1.85-1.75 (m, 2H), 1.69-1.62 (m, 2H), 1.53-1.44 (m, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 204.1, 143.8, 140.0, 136.7, 134.7, 130.9, 129.6 (2C), 127.3 (2C), 122.7, 122.4, 119.6, 44.8, 39.4, 32.4, 26.4, 23.5, 21.5 ppm; HRMS (ESI): calcd. for C₁₉H₂₂ClNO₃SNa [M+Na]⁺: 402.0901 found: 402.0904

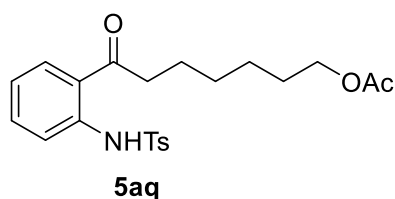


N-(2-(7-((tert-butyldimethylsilyl)oxy)heptanoyl)phenyl)-4-methylbenzenesulfonamide (5ak) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (55 mg, 56 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 11.45 (s, 1H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.75-7.65 (m, 3H), 7.49-7.39 (m, 1H), 7.25- 7.17 (m, 2H), 7.11-7.02 (m, 1H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.35 (s, 3H), 1.68-1.58 (m, 2H), 1.57-1.47 (m, 2H), 1.38-1.31 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 204.7, 143.8, 140.0, 136.6, 134.6, 131.0, 129.6 (2C), 127.3 (2C), 122.7, 122.4, 119.6, 63.1, 39.6, 32.7, 29.0, 26.0 (3C), 25.7, 24.4, 21.5, 18.4, -5.2 (2C) ppm; HRMS (ESI): calcd. for C₂₆H₄₀NO₄SSi [M+H]⁺: 490.2442 found: 490.2437

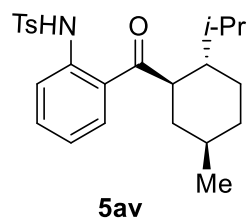


N-(2-(7-((tert-butyldiphenylsilyl)oxy)heptanoyl)phenyl)-4-methylbenzenesulfonamide (5al) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (75 mg, 61 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 11.46 (s, 1H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75-7.63 (m, 7H), 7.48-7.41 (m, 2H), 7.43-7.33 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 1.64-1.53 (m, 4H), 1.42-1.33 (m, 2H), 1.35 -1.22 (m, 2H), 1.05 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 204.6, 143.7, 139.9, 136.6, 135.5 (4C), 134.6, 134.0, 130.9, 129.6 (2C), 129.5 (2C), 127.6 (4C), 127.2 (2C), 122.7 (2C), 122.4, 119.6, 63.8, 39.6, 32.3, 28.9, 26.9 (3C), 25.6,

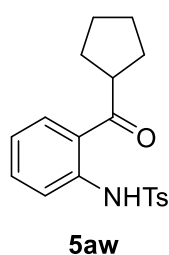
24.3, 21.5, 19.2 ppm; HRMS (ESI): calcd. for C₃₆H₄₃NO₄SSiNa [M+Na]⁺: 636.2574 found: 636.2571



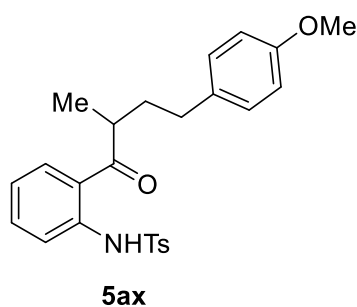
7-(2-((4-Methylphenyl)sulfonamido)phenyl)-7-oxoheptyl acetate (**5aq**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (50 mg, 60 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 11.45 (s, 1H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.75-7.66 (m, 3H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.08-7.02 (m, 1H), 4.07 (t, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 2.05 (s, 3H), 1.70-1.61 (m, 4H), 1.43-1.29 (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 204.4, 171.2, 143.8, 140.0, 136.7, 134.6, 131.0, 129.6 (2C), 127.3 (2C), 122.7, 122.3, 119.5, 64.4, 39.5, 28.8, 28.5, 25.8, 24.2, 21.5, 21.0 ppm; HRMS (ESI): calcd. for C₂₂H₂₇NO₅SSiNa [M+Na]⁺: 440.1502 found: 440.1506



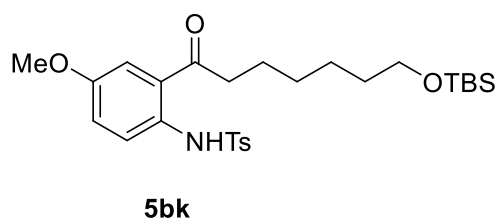
N-(2-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexane-1-carbonyl)phenyl)-4-methylbenzenesulfonamide (**5av**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (56 mg, 68 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 11.55 (s, 1H), 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.72-7.65 (m, 2H), 7.47 (d, *J* = 1.5 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.1 Hz, 1H), 3.28 (d, *J* = 3.2 Hz, 1H), 2.34 (s, 3H), 1.82-1.71 (m, 3H), 1.61-1.52 (m, 1H), 1.44-1.34 (m, 2H), 1.08 (dd, *J* = 12.5, 3.1 Hz, 1H), 1.03-0.93 (m, 1H), 0.91 (d, *J* = 12.6 Hz, 1H), 0.86 (d, *J* = 3.2 Hz, 3H), 0.85 (d, *J* = 3.5 Hz, 3H), 0.61 (d, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 208.8, 143.6, 140.4, 136.8, 134.6, 130.4, 129.6 (2C), 127.2 (2C), 123.0, 122.8, 120.3, 48.9, 43.8, 40.2, 34.5, 32.6, 28.8, 24.0, 22.3, 21.6, 21.5, 16.5 ppm; HRMS (ESI): calcd. for C₂₄H₃₁NO₃SSiNa [M+Na]⁺: 436.1917 found: 436.1926.



N-(2-(cyclopentanecarbonyl)phenyl)-4-methylbenzenesulfonamide (**5aw**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (35 mg, 51 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 11.41 (s, 1H), 7.81 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.73-7.65 (m, 3H), 7.48-7.41 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11-7.04 (m, 1H), 3.75-3.46 (m, 1H), 2.35 (s, 3H), 1.90-1.76 (m, 2H), 1.75-1.53 (m, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 207.0, 143.7, 140.2, 136.7, 134.3, 131.2, 129.6 (2C), 127.2 (2C), 122.9, 122.7, 120.2, 47.1, 30.1 (2C), 26.3 (2C), 21.5 ppm; HRMS (ESI): calcd. for C₁₉H₂₁NO₃SSiNa [M+Na]⁺: 366.1134 found: 366.1147.

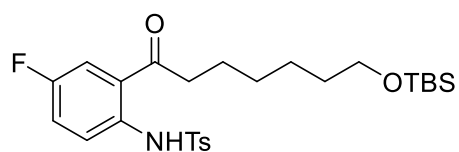


N-(2-(4-(4-methoxyphenyl)-2-methylbutanoyl)phenyl)-4-methylbenzenesulfonamide (**5ax**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a white solid (54 mg, 62 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 11.45 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.03-6.94 (m, 3H), 6.80 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 3H), 3.41-3.32 (m, 1H), 2.50-2.40 (m, 2H), 2.27 (s, 3H), 2.04-1.92 (m, 1H), 1.64-1.50 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 208.4, 158.0, 143.8, 140.4, 136.7, 134.6, 133.4, 130.7, 129.6 (2C), 129.4 (2C), 127.2 (2C), 122.8, 122.1, 120.2, 113.8 (2C), 55.3, 40.3, 35.5, 32.4, 21.5, 17.4 ppm; HRMS (ESI): calcd. for C₂₅H₂₇NO₄SSiNa [M+Na]⁺: 460.1553 found: 460.1559.



N-(2-(7-((*tert*-butyldimethylsilyl)oxy)heptanoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (**5bk**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 5:1) as a white solid (76 mg, 73 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 10.59 (s, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 2.9 Hz, 1H), 7.20-7.13 (m, 2H), 7.04 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.80 (s, 3H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H),

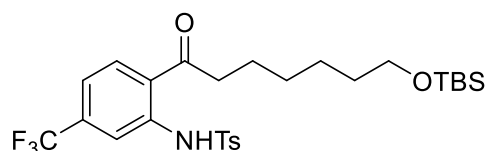
2.34 (s, 3H), 1.57-1.47 (m, 4H), 1.38-1.26 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 204.1, 155.4, 143.5, 136.3, 132.2, 129.4 (2C), 127.2 (2C), 125.3, 123.5, 119.4, 115.8, 63.1, 55.7, 39.6, 32.7, 29.0, 26.0 (3C), 25.7, 24.2, 21.5, 18.4, -5.3 (2C); HRMS (ESI): calcd. for $\text{C}_{27}\text{H}_{41}\text{NO}_5\text{SSiNa}[\text{M}+\text{Na}]^+$: 542.2367 found: 542.2368.



5ck

N-(2-(7-((*tert*-Butyldimethylsilyl)oxy)heptanoyl)-4-fluorophenyl)-4-methylbenzenesulfonamide (**5ck**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc = 10:1) as a white solid (64 mg, 63 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 10.96 (s, 1H), 7.73 (dd, J = 9.2, 4.9 Hz, 1H), 7.67-7.60 (m, 2H), 7.43 (dd, J = 9.1, 3.0 Hz, 1H), 7.24-7.16 (m, 3H), 3.61 (t, J = 6.5 Hz, 2H), 2.77 (t, J = 7.4 Hz, 2H), 2.36 (s, 3H), 1.62-1.48 (m, 4H), 1.39-1.28 (m, 4H), 0.90

(s, 9H), 0.06 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 203.39 (C-F, $^4J_{\text{C-F}}$ = 2.2 Hz), 203.37 (C-F, $^4J_{\text{C-F}}$ = 2.2 Hz), 159.1 (C-F, $^1J_{\text{C-F}}$ = 244.7 Hz), 156.7 (C-F, $^1J_{\text{C-F}}$ = 244.7 Hz), 143.9, 136.2, 135.8 (C-F, $^4J_{\text{C-F}}$ = 2.6 Hz), 135.7 (C-F, $^4J_{\text{C-F}}$ = 2.6 Hz), 129.6 (2C), 127.2 (2C), 124.3 (C-F, $^3J_{\text{C-F}}$ = 5.8 Hz), 124.2 (C-F, $^3J_{\text{C-F}}$ = 5.8 Hz), 122.7 (C-F, $^3J_{\text{C-F}}$ = 7.4 Hz), 122.6 (C-F, $^3J_{\text{C-F}}$ = 7.4 Hz), 121.7 (C-F, $^2J_{\text{C-F}}$ = 22.4 Hz), 121.5 (C-F, $^2J_{\text{C-F}}$ = 22.4 Hz), 116.9 (C-F, $^2J_{\text{C-F}}$ = 23.4 Hz), 116.7 (C-F, $^2J_{\text{C-F}}$ = 23.4 Hz), 63.0, 39.7, 32.6, 28.9, 26.0 (3C), 25.6, 24.1, 21.5, 18.4, -5.3 (2C) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -111.55 - -121.87 (m, 1F) ppm; HRMS (ESI): calcd. for $\text{C}_{26}\text{H}_{39}\text{FNO}_4\text{SSi}[\text{M}+\text{H}]^+$: 508.2353 found: 508.2353.



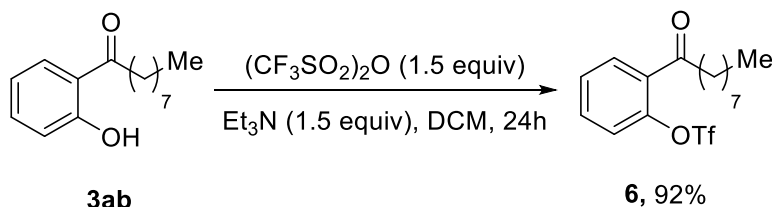
5dk

N-(2-(7-((*tert*-Butyldimethylsilyl)oxy)heptanoyl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (**5dk**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc = 10:1) as a white solid (39 mg, 35 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 11.44 (s, 1H), 8.05-7.96 (m, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.80-7.69 (m, 2H), 7.31-7.21 (m, 3H), 3.61 (t, J = 6.4 Hz, 2H), 2.91 (t, J = 7.4 Hz, 2H), 2.37 (s, 3H), 1.71-1.60 (m, 2H), 1.57-1.47 (m, 2H),

1.39-1.32 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 204.0, 144.3, 140.4, 136.1, 135.8 (C-F, $^2J_{\text{C-F}}$ = 33.2 Hz), 135.5 (C-F, $^2J_{\text{C-F}}$ = 33.2 Hz), 131.5, 129.8 (2C), 127.3 (2C), 124.3 (C-F, $^1J_{\text{C-F}}$ = 274.7 Hz), 124.1, 121.6 (C-F, $^1J_{\text{C-F}}$ = 274.7 Hz), 118.90 (C-F, $^3J_{\text{C-F}}$ = 3.6 Hz), 118.87 (C-F, $^3J_{\text{C-F}}$ = 3.6 Hz), 116.3 (C-F, $^3J_{\text{C-F}}$ = 3.9 Hz), 116.2 (C-F, $^3J_{\text{C-F}}$ = 3.9 Hz), 63.1, 39.9, 32.6, 28.9, 26.0 (3C), 25.6, 24.2, 21.6, 18.4, 5.3 (2C) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -63.76 (s, 3F) ppm; HRMS (ESI): calcd. for $\text{C}_{27}\text{H}_{39}\text{F}_3\text{NO}_4\text{SSi}[\text{M}+\text{H}]^+$: 558.2321 found: 558.2322.

Derivatizations of the Products

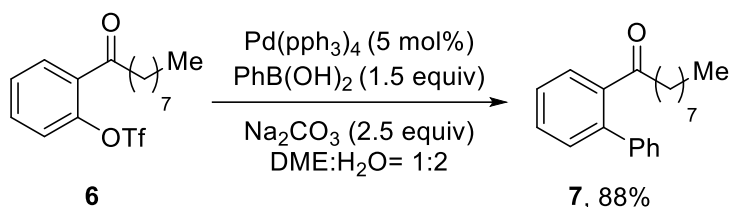
Synthesis of 2-Nonanoylphenyl Trifluoromethanesulfonate (**6**)



The phenol **3ab** (93.7 mg, 0.40 mmol, 1 equiv) was dissolved in DCM (0.8 mL), to which Et_3N (60.7 mg, 0.60 mmol, 1.5 equiv) was added dropwise. After cooling to 0 $^\circ\text{C}$, trifluoromethanesulfonic anhydride (169.3 mg, 0.60 mmol, 1.5 equiv) was added dropwise to the mixture. After stirring at room temperature for 24 h, the reaction was quenched with water. The organic layer was separated and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel with the mixture eluent of petroleum ether and ethyl acetate (50:1) to

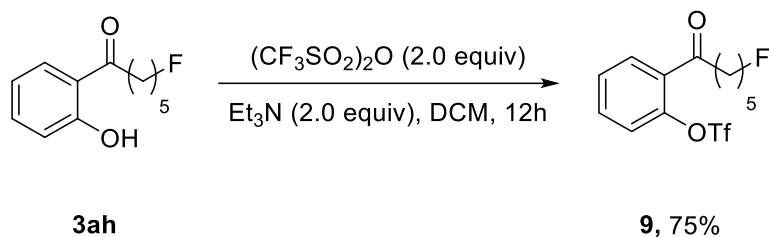
give the title compound **6** as a yellow oil (134.8 mg, 92 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.62-7.55 (m, 1H), 7.51-7.44 (m, 1H), 7.34 (dd, *J* = 8.3, 1.1 Hz, 1H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.78-1.66 (m, 2H), 1.39-1.23 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 199.6, 146.6, 133.2, 132.6, 130.2, 128.5, 122.7, 118.6 (q, *J* = 320.5 Hz), 41.8, 31.8, 29.3, 29.1 (2C), 23.9, 22.6, 14.1 ppm; HRMS (ESI): calcd. for C₁₆H₂₁F₃O₄SNa [M+Na]⁺: 389.1005 found: 389.1011.

Synthesis of 1-([1,1'-Biphenyl]-2-yl)nonan-1-one (**7**)



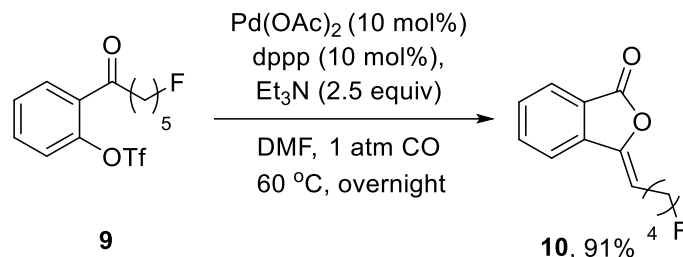
Under nitrogen, the triflate **6** (73.3 mg, 0.20 mmol, 1.0 equiv) and phenylboronic acid (36.6 mg, 0.30 mmol, 1.5 equiv) was dissolved in anhydrous 1,2-dimethoxyethane (0.25 mL) and water (0.50 mL). After addition of Na₂CO₃ (53.0 mg, 0.50 mmol, 2.5 equiv) and Pd(PPh₃)₄ (11.6 mg, 0.01 mmol, 5 mol%), the mixture was stirred at 100 °C (oil bath) for 12 hours. After cooling, the reaction mixture was passed through a plug of silica gel (washed with DCM) and the solvent was removed under reduced pressure. Purification by column chromatography (petroleum ether) afforded the title compound **7** as a yellow oil (52 mg, 88 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.44-7.36 (m, 2H), 7.35-7.28 (m, 5H), 7.27-7.17 (m, 2H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.38-1.24 (m, 2H), 1.20-1.13 (m, 2H), 1.11-1.04 (m, 4H), 1.02-0.88 (m, 4H), 0.78 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 208.4, 141.3, 140.7, 140.0, 130.3, 130.1, 128.9 (2C), 128.7 (2C), 127.8, 127.6, 127.5, 43.0, 31.8, 29.1, 29.04, 28.96, 24.5, 22.6, 14.1 ppm; HRMS (ESI): calcd. for C₂₁H₂₆ONa [M+Na]⁺: 317.1876 found: 317.1876.

Synthesis of 2-(6-Fluorohexanoyl)phenyl Trifluoromethanesulfonate (**9**)



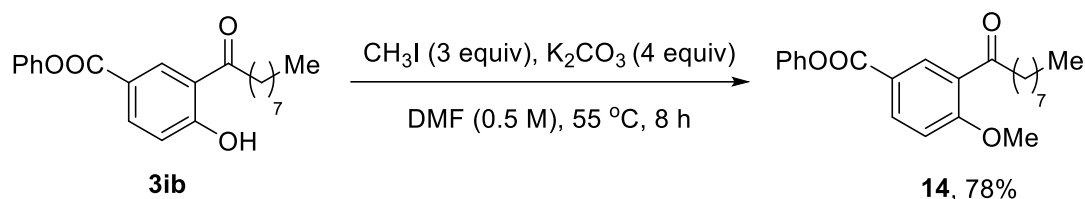
The phenol **3ah** (90.4 mg, 0.43 mmol, 1 equiv) was dissolved in DCM (0.8 mL), to which Et₃N (87.0 mg, 0.86 mmol, 2.0 equiv) was added dropwise. After cooling to 0 °C, trifluoromethanesulfonic anhydride (242.6 mg, 0.86 mmol, 2.0 equiv) was added dropwise. After stirring at room temperature for 12 h, the reaction was quenched with water. The organic layer was separated and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with water and saturated aqueous NaCl solution, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel with the mixture eluent of petroleum ether and ethyl acetate (50:1) to give the title compound **9** as a yellow oil (110.4 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ= 7.77 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64-7.56 (m, 1H), 7.51-7.43 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 4.45 (dt, *J* = 47.3, 6.1 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.84-1.66 (m, 4H), 1.58-1.41 (m, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 199.2, 146.6, 133.4, 132.4, 130.2, 128.6, 122.7, 122.4 (C-F, ¹*J*_{C-F} = 321.3 Hz), 119.9 (C-F, ¹*J*_{C-F} = 321.3 Hz), 117.3 (C-F, ¹*J*_{C-F} = 321.3 Hz), 114.8 (C-F, ¹*J*_{C-F} = 321.3 Hz), 84.5 (C-F, ¹*J*_{C-F} = 164.4 Hz), 83.2 (C-F, ¹*J*_{C-F} = 164.4 Hz), 41.5, 30.3 (C-F, ²*J*_{C-F} = 19.4 Hz), 30.1 (C-F, ²*J*_{C-F} = 19.4 Hz), 24.8 (C-F, ³*J*_{C-F} = 5.4 Hz), 24.7 (C-F, ³*J*_{C-F} = 5.4 Hz), 23.4 ppm; ¹⁹F NMR (471 MHz, CDCl₃) δ= -73.40 (s, 3F), -218.53 (s, 1F) ppm; HRMS (ESI): calcd. for C₁₃H₁₄F₄O₄SNa [M+Na]⁺: 365.0441 found: 365.0453.

Synthesis of (Z)-3-(5-Fluoropentylidene)isobenzofuran-1(3H)-one (**10**)¹⁵



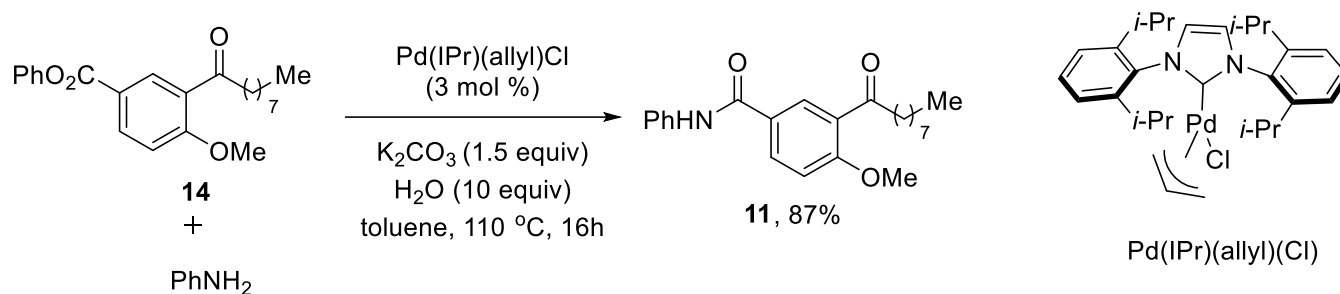
A mixture of the triflate **9** (102.7 mg, 0.3 mmol, 1.0 equiv), Et₃N (60.7 mg, 0.75 mmol, 2.5 equiv), Pd(OAc)₂ (6.7 mg, 0.03 mmol, 10 mol%) and 1,3-bis(diphenylphosphino)propane (12.4 mg, 0.03 mmol, 10 mol%) in DMF (3.0 mL) was degassed by two freeze/pump/thaw cycles. The reaction vessel was filled with CO and stirred at 60 °C (oil bath) under a balloon of CO for 12 h. The reaction mixture was diluted with brine and extracted with Et₂O. The combined organic phases were washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether /ethyl acetate = 20:1) afforded the title compound **10** as a colorless oil (60.1 mg, 91 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.89 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.72-7.62 (m, 2H), 7.55-7.49 (m, 1H), 5.64 (t, *J* = 7.8 Hz, 1H), 4.49 (dt, *J* = 47.2, 5.9 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.86-1.78 (m, 2H), 1.78-1.59 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 167.1, 146.0, 139.4, 134.3, 129.5, 125.3, 124.4, 119.7, 108.7, 84.6 (C-F, ¹*J*_{C-F} = 164.5 Hz), 82.3 (C-F, ¹*J*_{C-F} = 164.5 Hz), 30.1 (C-F, ²*J*_{C-F} = 19.7 Hz), 30.0 (C-F, ²*J*_{C-F} = 19.7 Hz), 25.3, 25.0 (C-F, ³*J*_{C-F} = 4.9 Hz), 24.9 (C-F, ³*J*_{C-F} = 4.9 Hz) ppm; ¹⁹F NMR (471 MHz, CDCl₃) δ= -218.31- -219.04 (m, 1F); HRMS (ESI): calcd. for C₁₃H₁₃FO₂Na [M+Na]⁺: 243.0792 found: 243.0798.

Synthesis of Phenyl 4-Methoxy-3-nonanoylbenzoate (**14**)



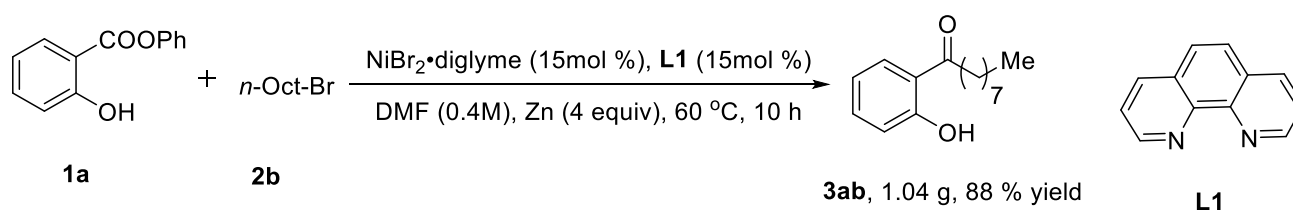
The phenol **3ib** (101.6 mg, 0.3 mmol, 1 equiv), K₂CO₃ (165.9 mg, 1.2 mmol, 4 equiv) was dissolved in DMF (0.6 mL), to which CH₃I (127.7 mg, 0.9 mmol, 3.0 equiv) was added. After stirring at 55 °C (oil bath) for 8 h, the reaction was quenched with water. The mixture was extracted with EtOAc and the combined organic phases were washed with water, brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel with the mixture eluent of petroleum ether and ethyl acetate (10:1) to give the title compound **14** as a colorless oil (86 mg, 78 % yield). ¹H NMR (500 MHz, CDCl₃) δ= 8.46 (d, *J* = 2.3 Hz, 1H), 8.27 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 1H), 3.99 (s, 3H), 2.97 (t, *J* = 7.4 Hz, 2H), 1.76-1.65 (m, 2H), 1.37-1.25 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ= 202.4, 164.4, 162.0, 150.9, 135.2, 132.5, 129.5 (2C), 129.1, 125.9, 122.1, 121.7 (2C), 111.5, 56.0, 43.7, 31.9, 29.5, 29.4, 29.2, 24.3, 22.7, 14.1 ppm; HRMS (ESI): calcd. for C₂₃H₂₉O₄ [M+H]⁺: 369.2060 found: 369.2072.

Synthesis of 4-Methoxy-3-nonanoyl-N-phenylbenzamide (**11**)¹⁶



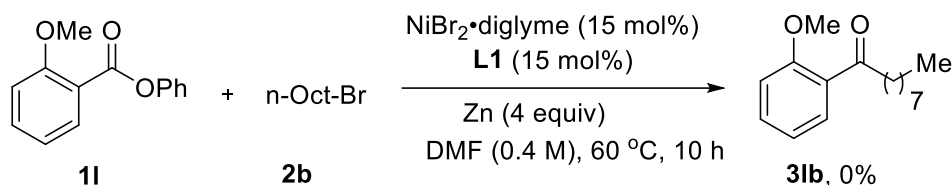
An oven dried screw-capped vial was charged with a magnetic stir bar, powdered K_2CO_3 (41.5 mg, 0.3 mmol 1.5 equiv), $\text{Pd}(\text{IPr})(\text{allyl})\text{Cl}$ (3.44 mg, 0.06 mmol, 3 mol%), the phenolic ester **14** (74.0 mg, 0.2 mmol, 1 equiv) and aniline (23.0 mg, 0.24 mmol, 1.2 equiv). The vial and contents were placed under vacuum and back-filled with N_2 under a Schleck line three times. Dry toluene (1 mL, 0.2 M) and degassed water (36.0 mg, 2.0 mmol, 10 equiv) were then added successively under nitrogen. The vial was sealed and stirred vigorously at 110 °C (oil bath) for 16 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of silica gel (10 mL of EtOAc eluent). The crude mixture was concentrated in vacuo and was purified through column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to give the title compound **11** as a white solid (87 mg, 87 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.20 (s, 1H), 8.16-8.06 (m, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.6 Hz, 1H), 3.95 (s, 3H), 2.96 (t, J = 7.4 Hz, 2H), 1.74-1.55 (m, 2H), 1.35-1.16 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ = 202.6, 164.5, 161.0, 138.0, 133.5, 129.1 (2C), 128.4, 128.0, 127.2, 124.5, 120.3 (2 C), 112.0, 55.9, 43.9, 31.9, 29.5, 29.4, 29.2, 24.3, 22.7, 14.1 ppm; HRMS (ESI): calcd. for $\text{C}_{23}\text{H}_{30}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 368.2220 found: 368.2217.

5 mmol-Scale Reaction of Ni-Catalyzed Cross-Coupling of Phenyl Salicylic Acid Ester with *n*-Octyl Bromide

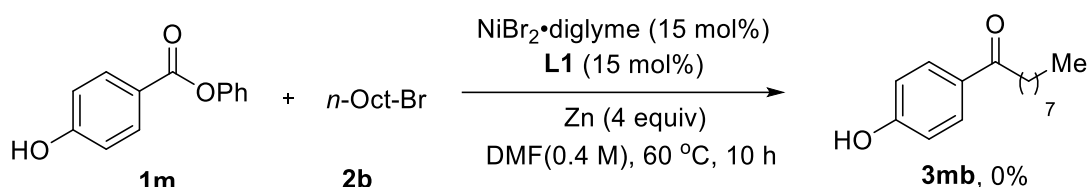


A vial charged with the **1a** (1.1 g, 5.0 mmol, 1 equiv), ligand **L1** (135.0 mg, 0.75 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, $\text{NiBr}_2 \cdot \text{diglyme}$ (265.0 mg, 0.75 mmol, 15 mol%) and Zn-powder (1.3 g, 20.0 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (10 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before alkyl bromides **2b** (1.45 g, 7.5 mmol, 1.5 equiv) were added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford **3ab** (1.04 g, 88 % yield).

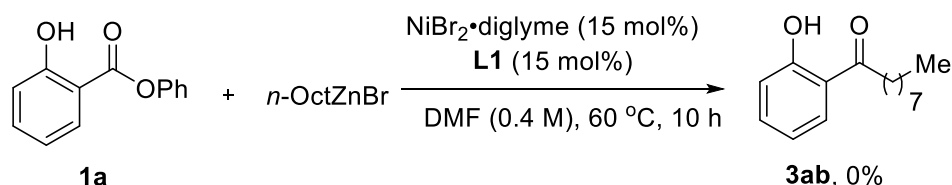
Control Experiments



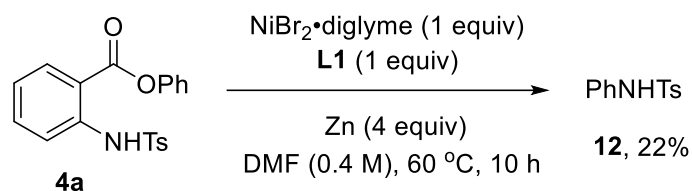
A sealed reaction tube charged with the phenolic esters **1l** (45.7 mg, 0.2 mmol, 1 equiv), ligand **L1** (5.4 mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, $\text{NiBr}_2 \cdot \text{diglyme}$ (10.6 mg, 0.03 mmol, 15 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2b** (57.9 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was subjected to TLC and NMR analysis, indicating that the desired coupling product **3lb** was not formed.



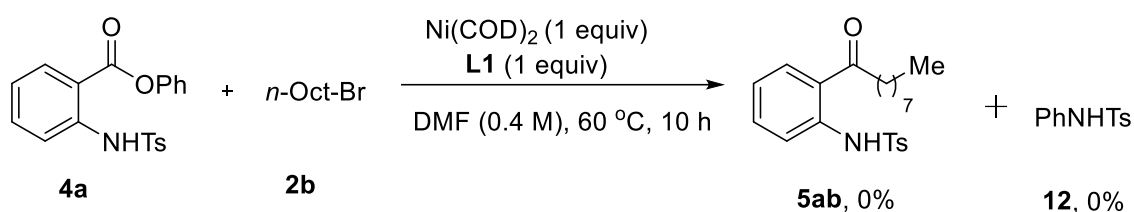
A sealed reaction tube charged with the phenolic esters **1m** (45.7 mg, 0.2 mmol, 1 equiv), ligand **L1** (5.4 mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, $\text{NiBr}_2 \cdot \text{diglyme}$ (10.6 mg, 0.03 mmol, 15 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated with a heating block, before 1-bromooctane **2b** (57.9 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was subjected to TLC and NMR analysis, indicating that the desired coupling product **3mb** was not formed.



A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (5.4 mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, $\text{NiBr}_2 \cdot \text{diglyme}$ (10.6 mg, 0.03 mmol, 15 mol%) was added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before $n\text{-OctZnBr}^{17}$ (0.72 mL, 0.83 M in THF, 3 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was subjected to TLC and NMR analysis, indicating that the desired coupling product **3ab** was not formed.

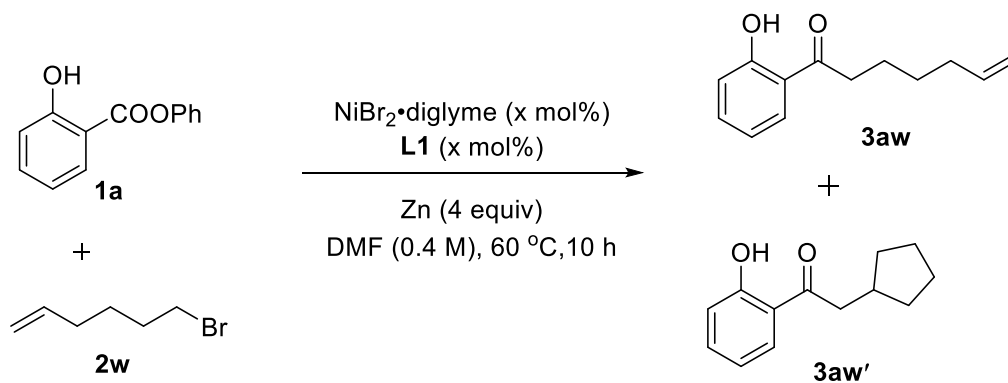


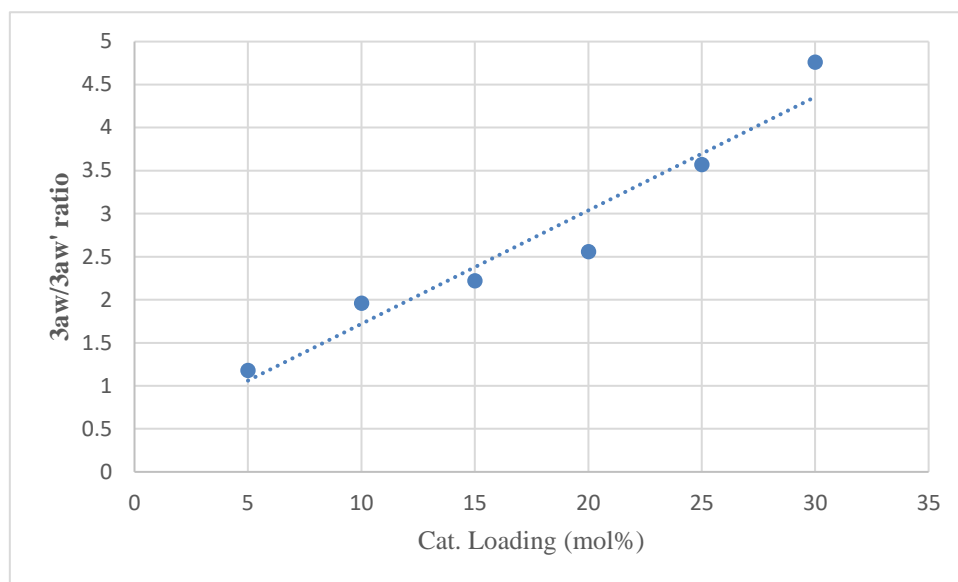
A sealed reaction tube charged with the phenolic esters **4a** (73.5 mg, 0.2 mmol, 1 equiv), ligand **L1** (36.0 mg, 0.2 mmol, 1 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, $\text{NiBr}_2\cdot\text{diglyme}$ (71.0 mg, 0.2 mmol, 1 equiv) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. After stirring at 60 °C with a heating block for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford PhNHTs (**12**) as a colorless oil (11 mg, 22 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.66 (d, J = 8.2 Hz, 2H), 7.24-7.17 (m, 4H), 7.15-7.03 (m, 3H), 6.82 (s, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 143.9, 136.5, 136.1, 129.6 (2C), 129.3 (2C), 127.3 (2C), 125.3, 121.6 (2C), 21.5 ppm. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{SNa}[\text{M}+\text{Na}]^+$: 270.0559 found: 270.0566.



A sealed reaction tube charged with the phenolic esters **4a** (73.5 mg, 0.2 mmol, 1 equiv), ligand **L1** (36.0 mg, 0.2 mmol, 1 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, Ni(COD)_2 (55.0 mg, 0.2 mmol, 1 equiv) was added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) and 1-bromooctane **2b** (57.9 mg, 0.3 mmol, 1.5 equiv) were added to the mixture under nitrogen atmosphere. After stirring at 60 °C with a heating block for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was subjected to TLC and NMR analysis, indicating that neither of the desired coupling product **5ab** and PhNHTs was formed.

Radical Clock Experiment





A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (1.8 mg, 0.015 mmol, 5 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (3.5 mg, 0.015 mmol, 5 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.85**.

A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (3.6 mg, 0.02 mmol, 10 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (7.0 mg, 0.02 mmol, 10 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.51**.

A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (5.4mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (10.6 mg, 0.015 mmol, 15 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.45**.

A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (7.2 mg, 0.04 mmol, 20 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (14.0 mg, 0.04 mmol, 20 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen

atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.39**.

A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (9.0 mg, 0.05 mmol, 25 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (17.5 mg, 0.015 mmol, 25 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.28**.

A sealed reaction tube charged with the phenolic esters **1a** (42.8 mg, 0.2 mmol, 1 equiv), ligand **L1** (10.8 mg, 0.06 mmol, 30 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles). In a nitrogen-filled glovebox, NiBr₂•diglyme (121.0 mg, 0.06 mmol, 30 mol%) and Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) were added to the mixture. The reaction tube was then sealed and removed from the glove box. Subsequently, DMF (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 60 °C with a heating block, before 1-bromooctane **2w** (48.6 mg, 0.3 mmol, 1.5 equiv) was added. After stirring at this temperature for 10 h, the mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether) to afford the corresponding products **3aw:3aw'**= **1:0.21**.

Compound **3aw**: ¹H NMR (400 MHz, CDCl₃) δ= 12.38 (s, 1 H), 7.76 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.51-7.39 (m, 1H), 6.98 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.92-6.85 (m, 1H), 5.89-5.74 (m, 1H), 5.09-4.85 (m, 2H), 3.05-2.91 (m, 2 H), 2.23-2.02 (m, 2H), 1.83-1.69 (m, 2H), 1.55-1.44 (m, 2H) ppm.

Compound **3aw'**: ¹H NMR (400 MHz, CDCl₃) δ= 12.40 (s, 1H), 7.76 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.51-7.39 (m, 1H), 6.98 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.92-6.85 (m, 1H), 3.05-2.91 (m, 2H), 2.23-2.02 (m, 1H), 1.83-1.54 (m, 8H) ppm.

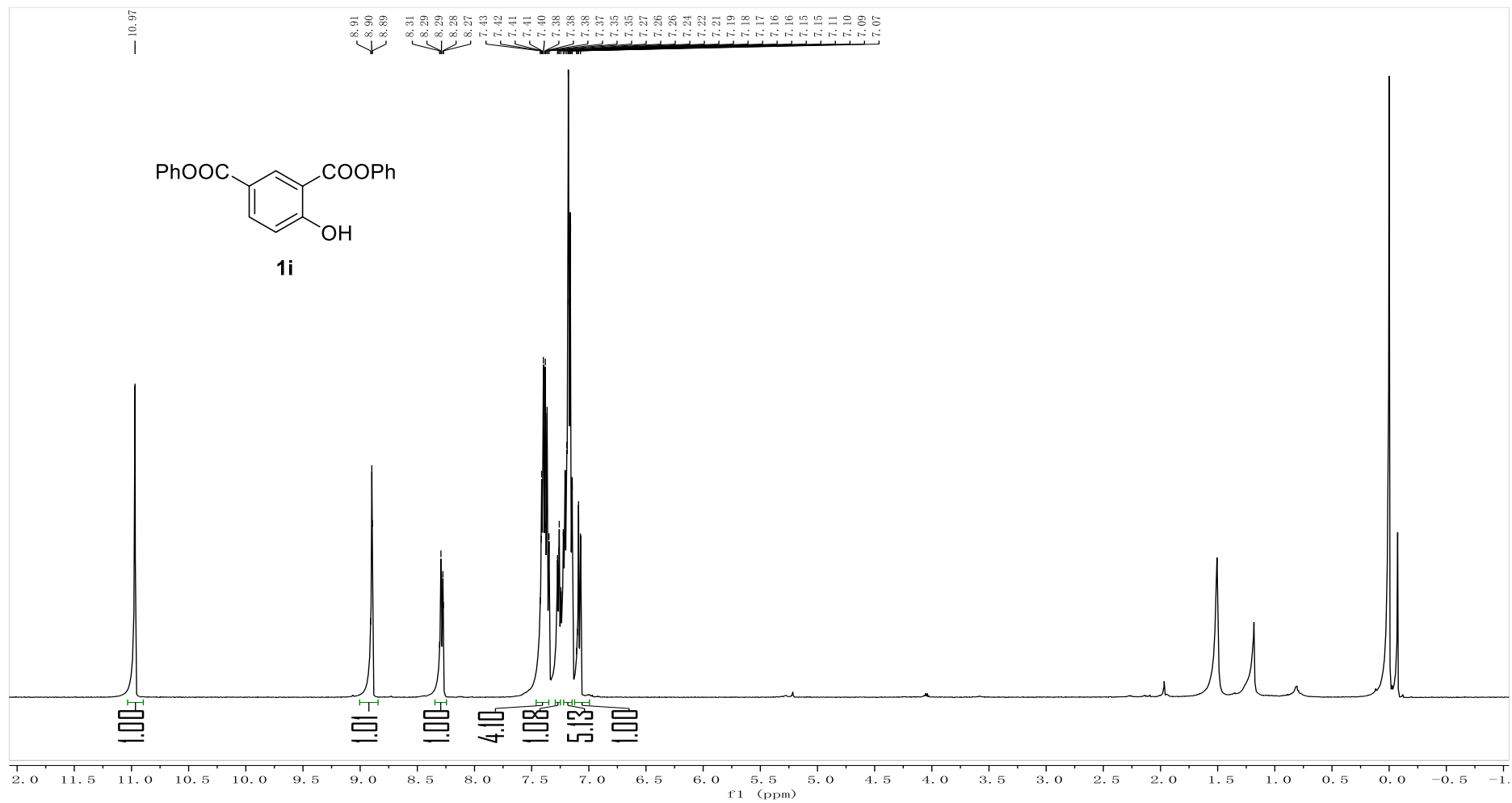
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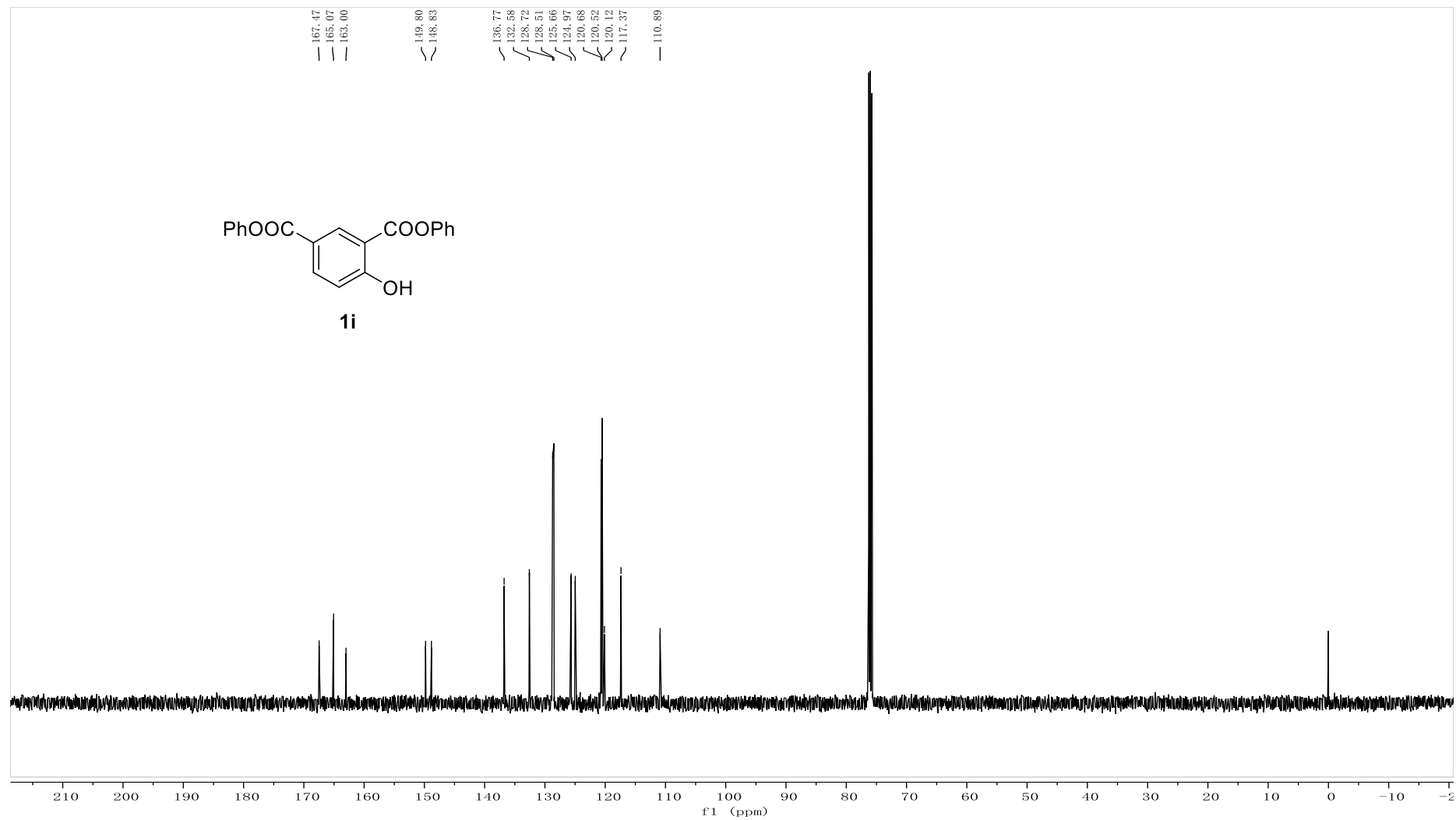
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NMR-Spectra

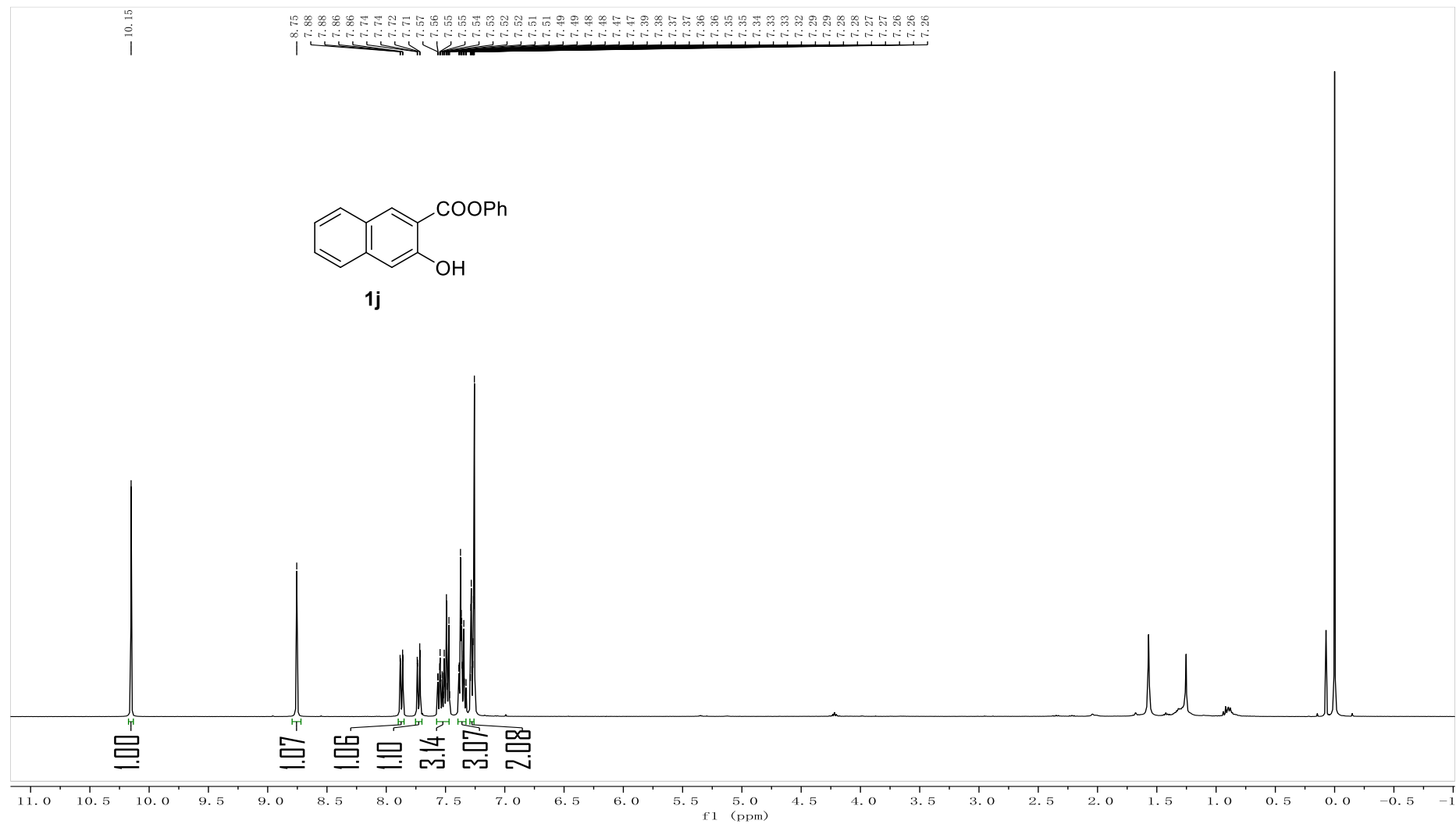
^1H NMR-spectrum (500 MHz, CDCl_3) of **1i**



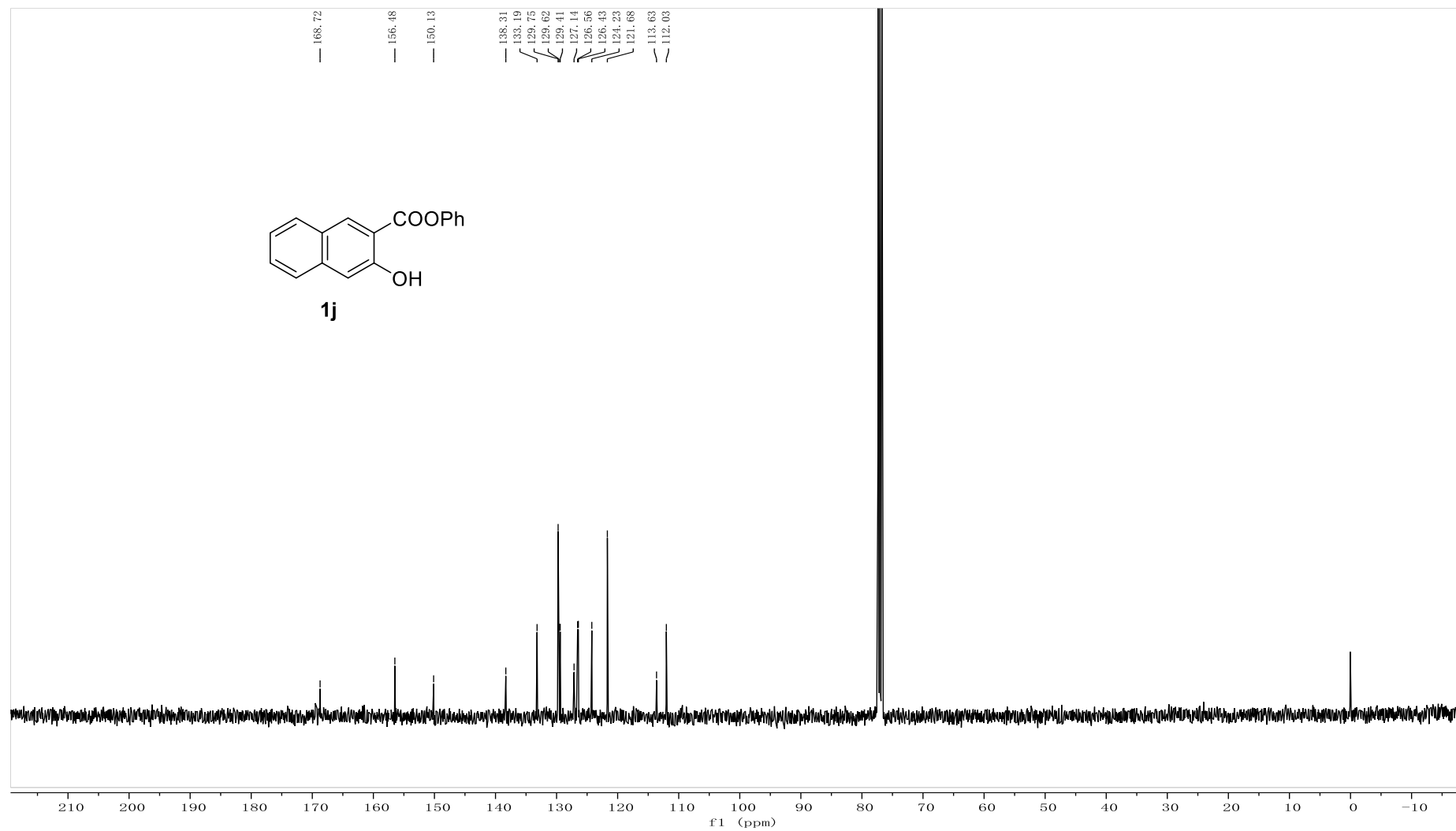
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **1i**



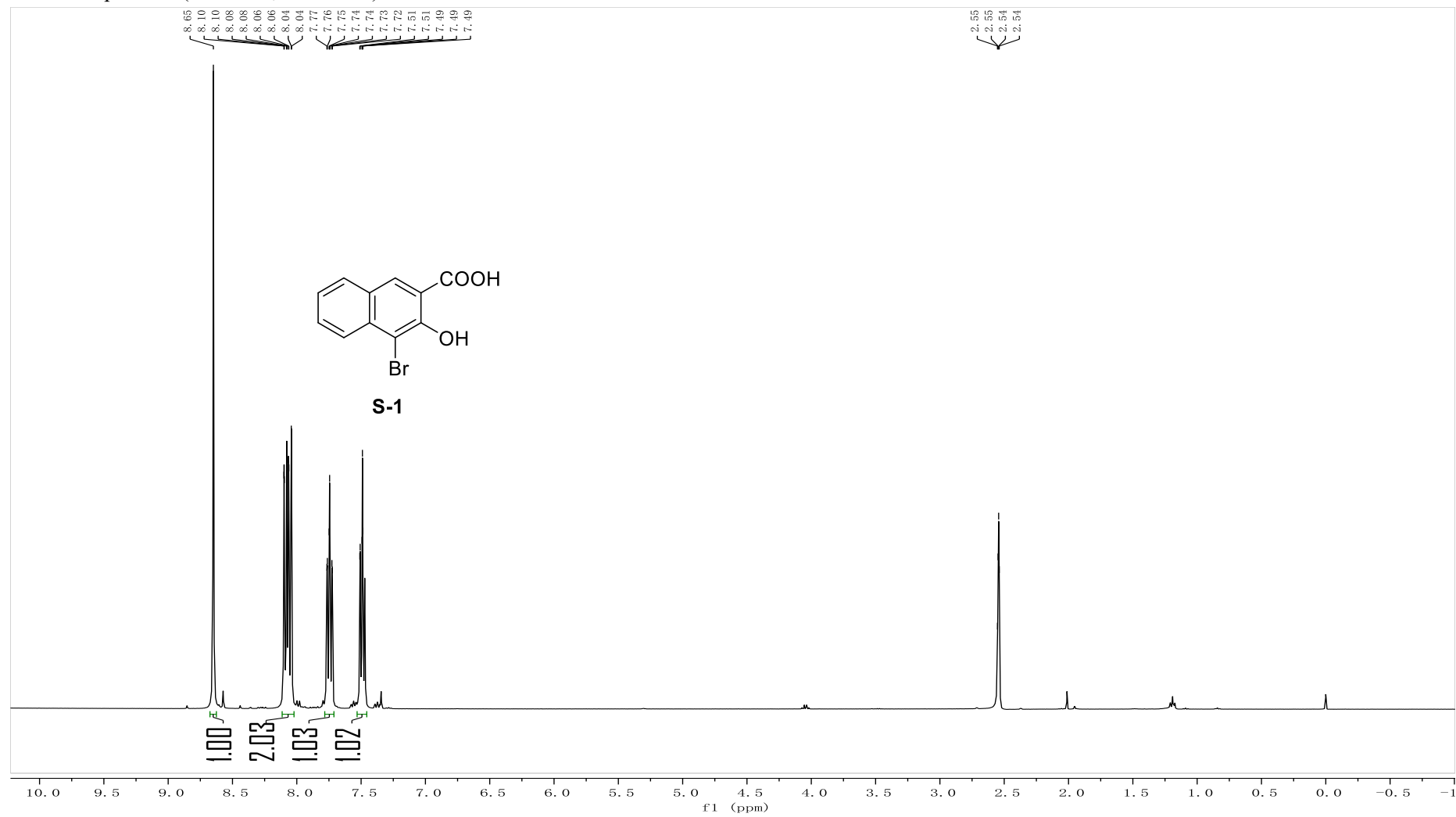
¹H NMR-spectrum (400 MHz, CDCl₃) of **1j**



^{13}C NMR-spectrum (101 MHz, CDCl_3) of **1j**



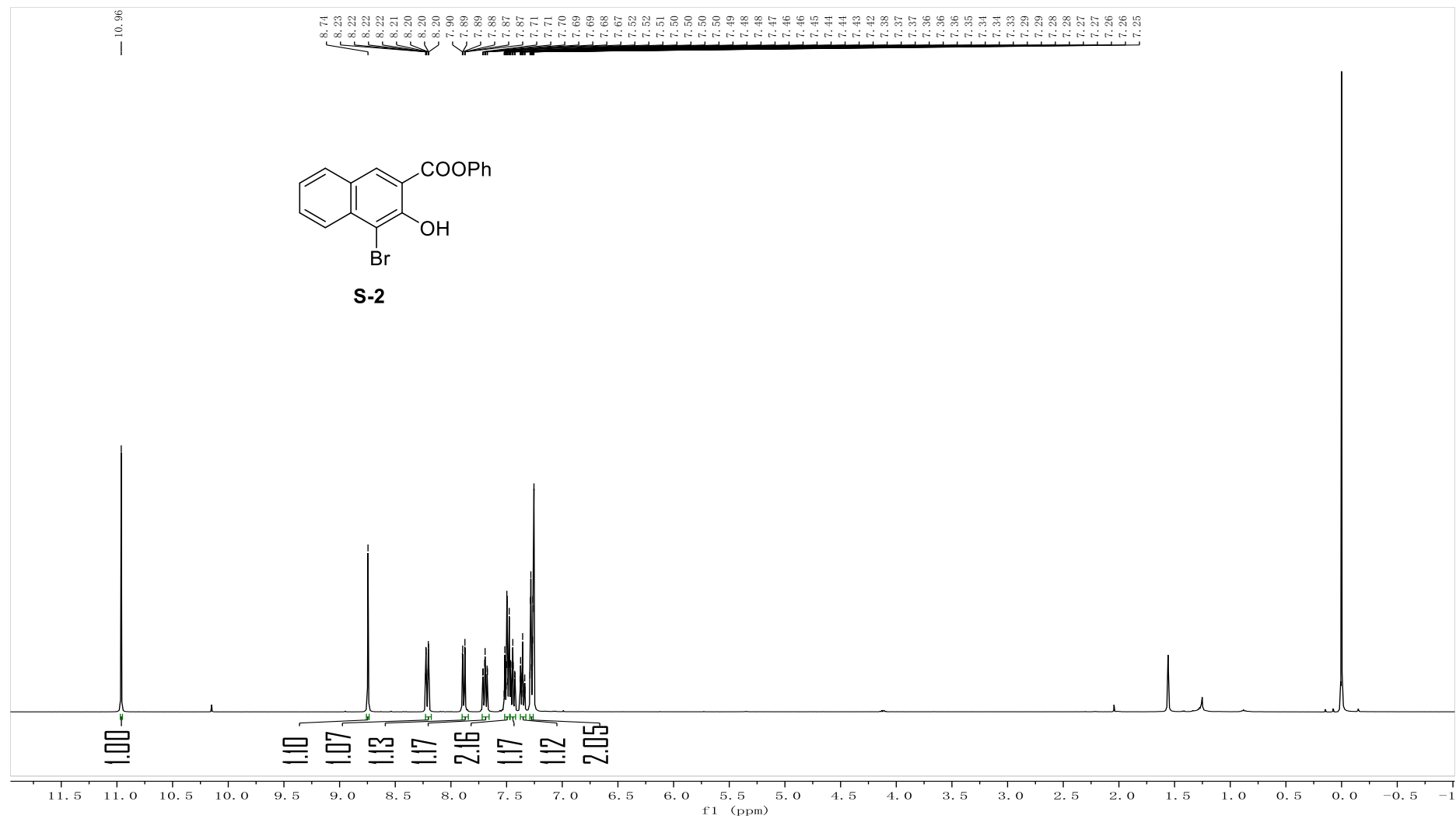
¹H NMR-spectrum (400 MHz, DMSO-*d*₆) of **S-1**



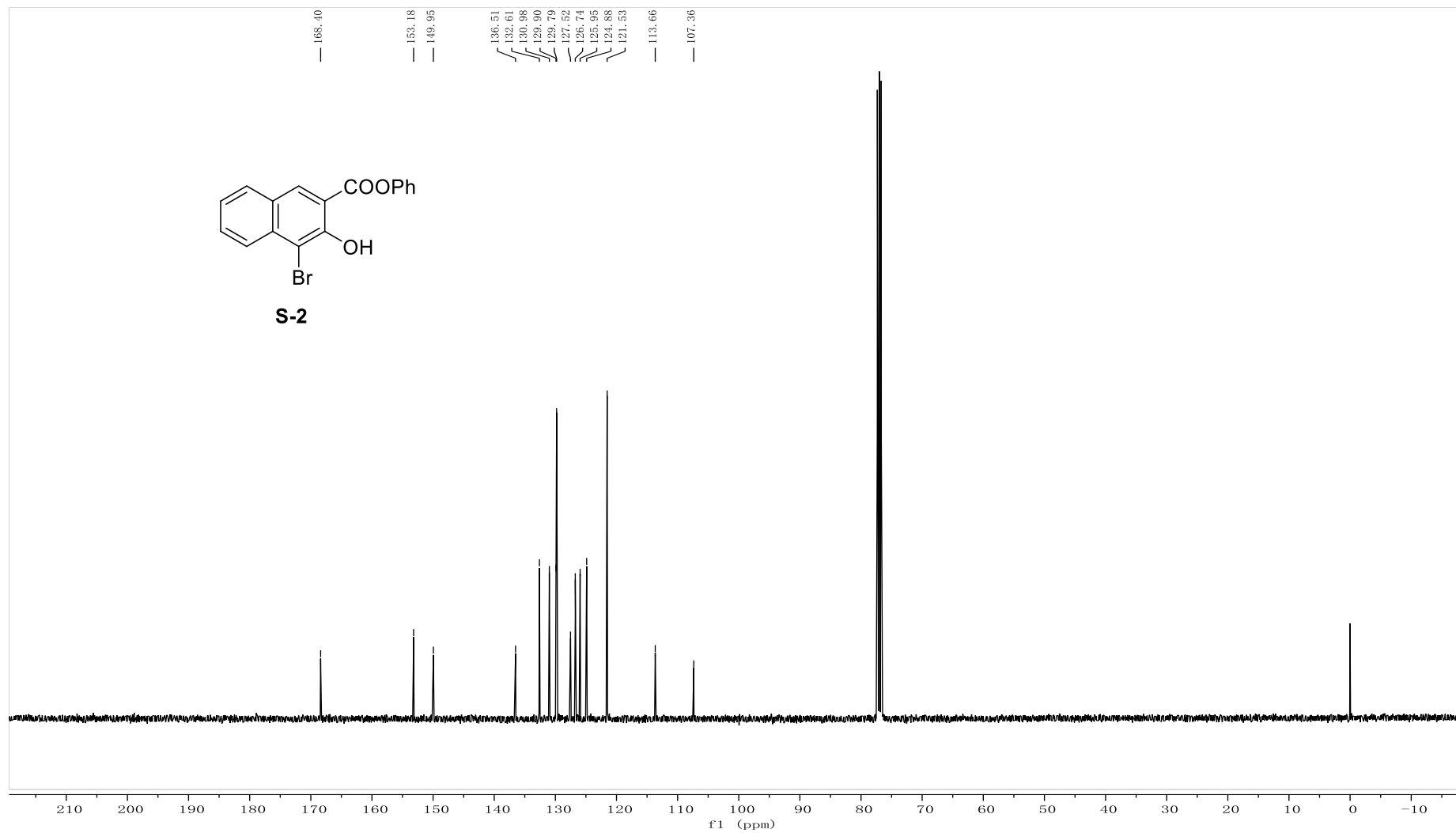
^{13}C NMR-spectrum (101 MHz, $\text{DMSO-}d_6$) of **S-1**



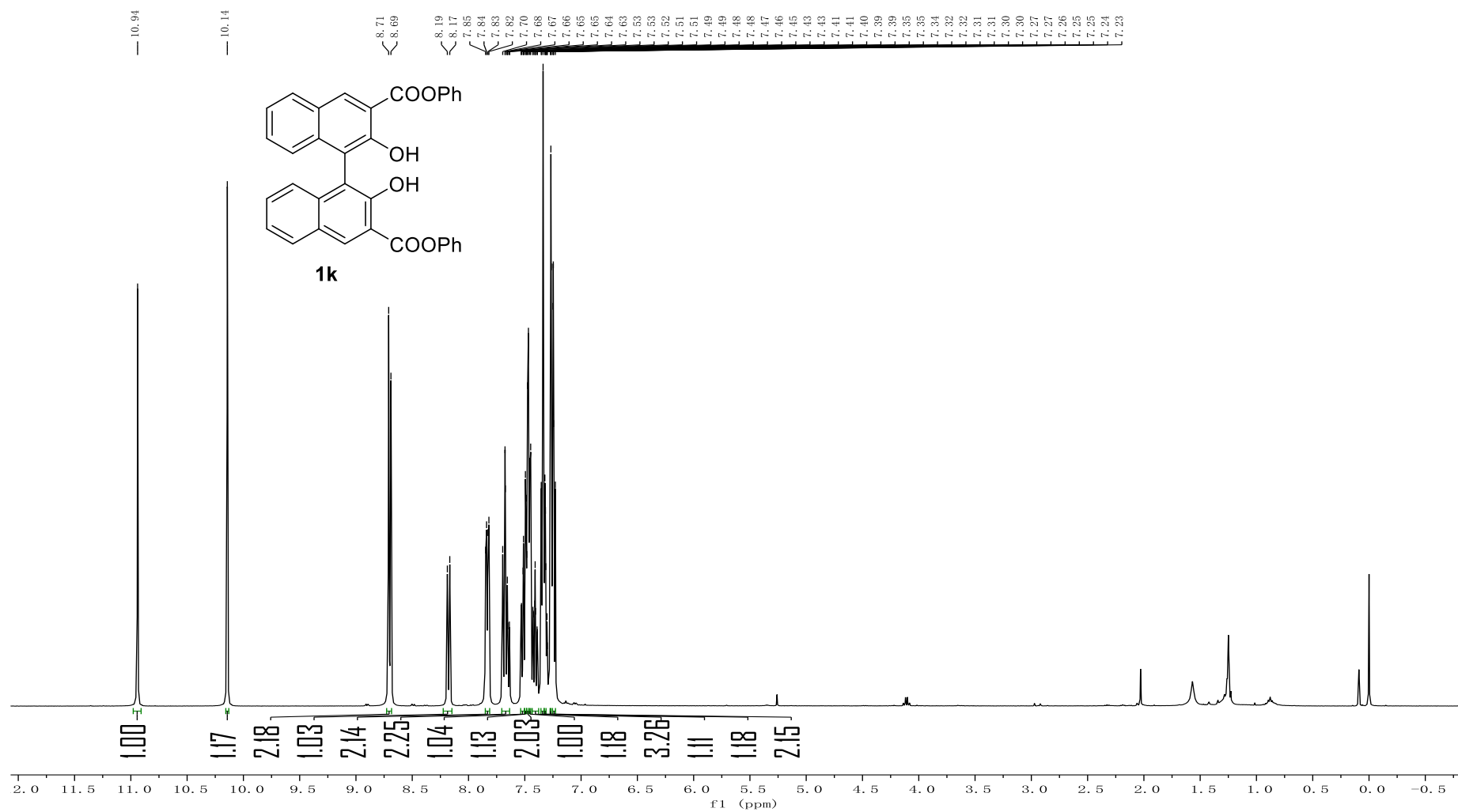
^1H NMR-spectrum (400 MHz, CDCl_3) of **S-2**



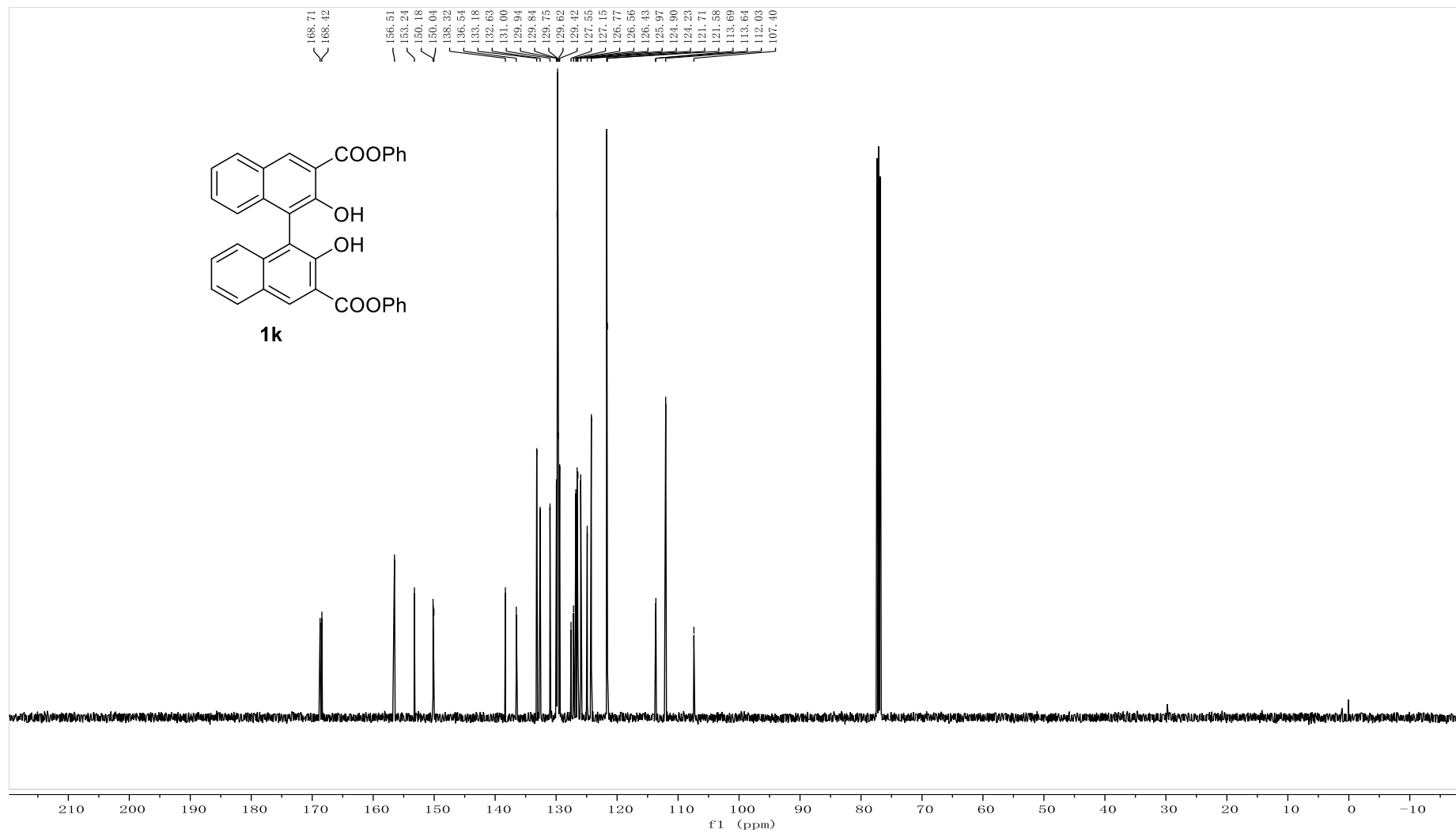
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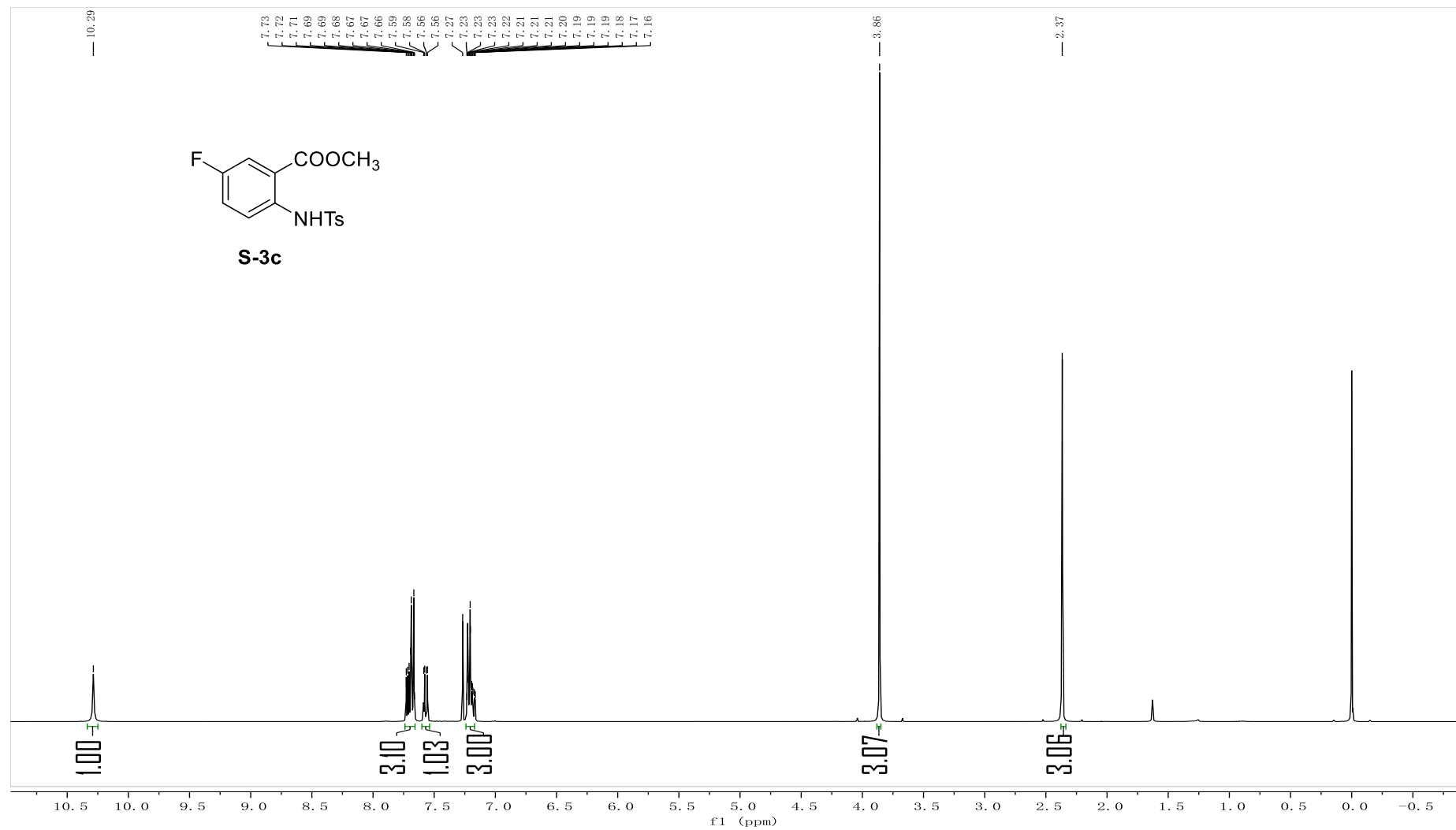
^1H NMR-spectrum (400 MHz, CDCl_3) of **1k**



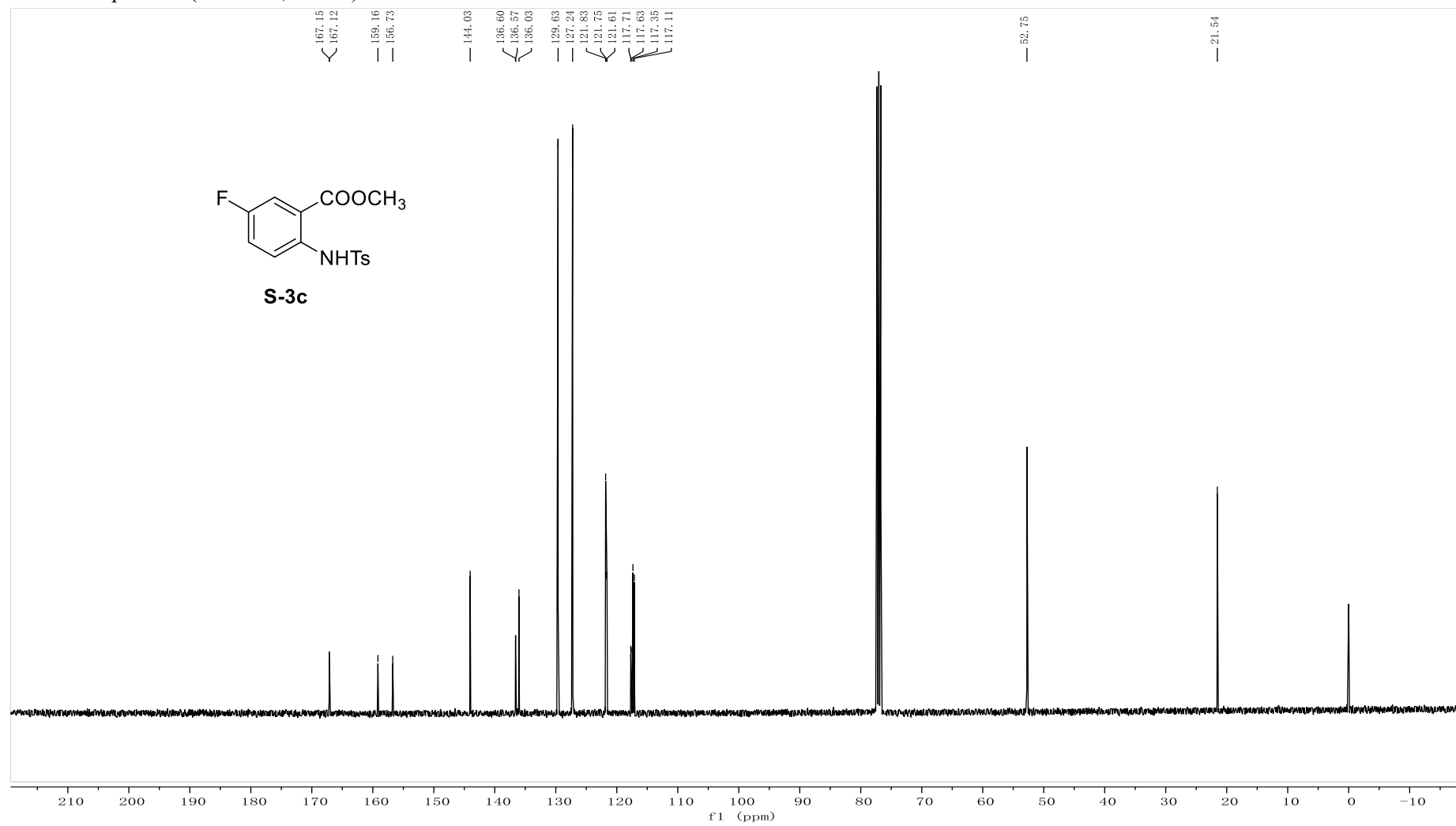
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **1k**



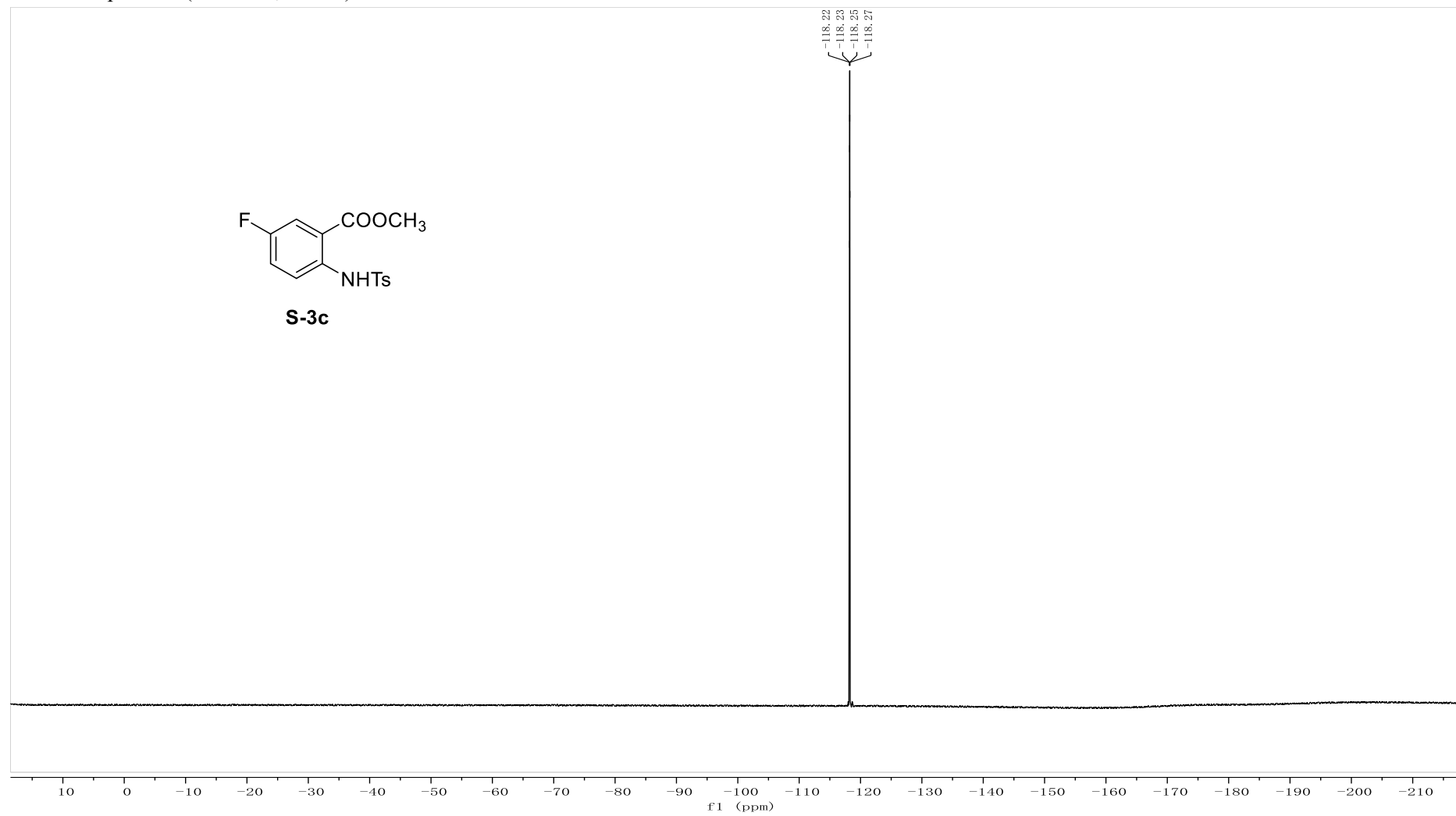
^1H NMR-spectrum (400 MHz, CDCl_3) of **S-3c**



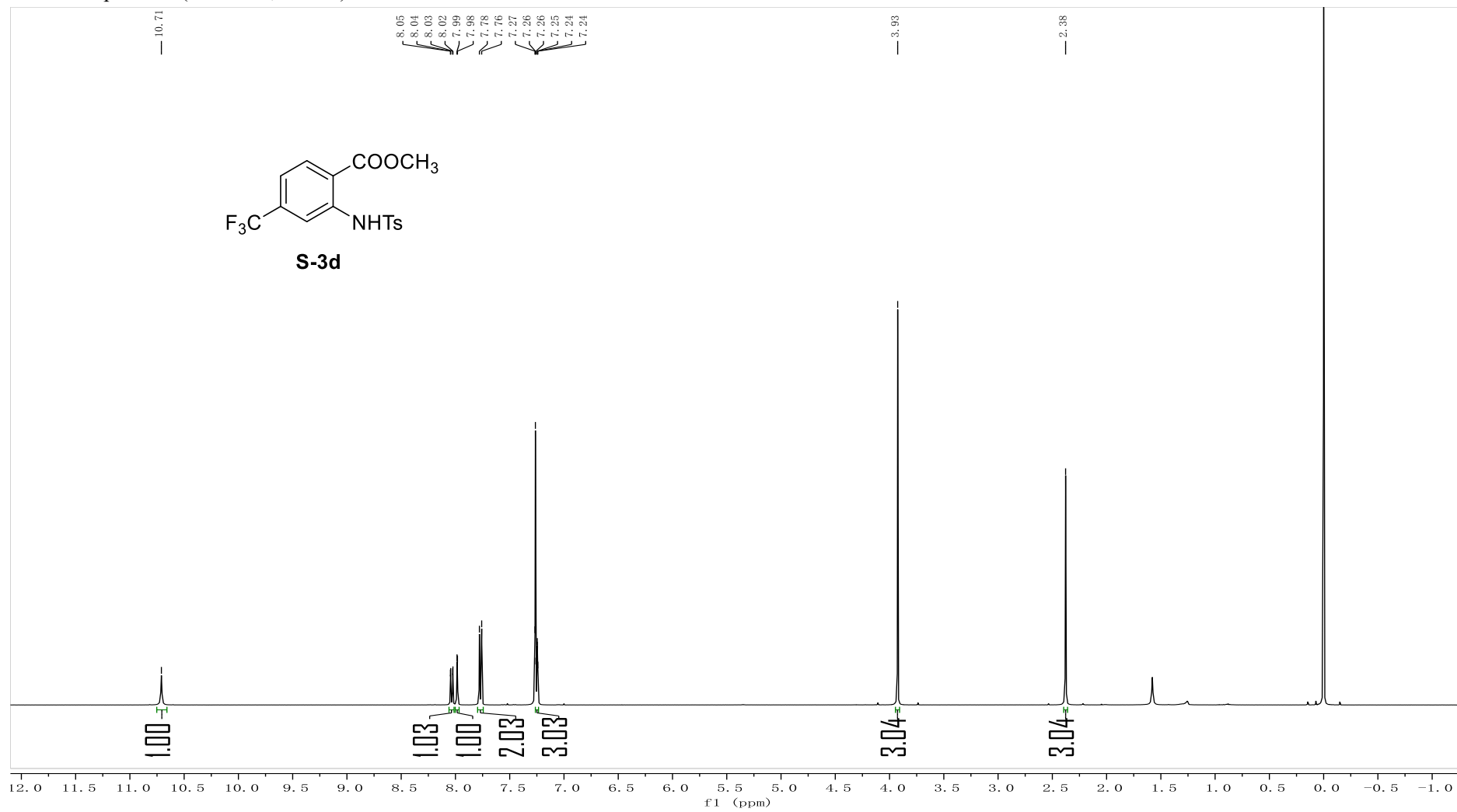
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **S-3c**



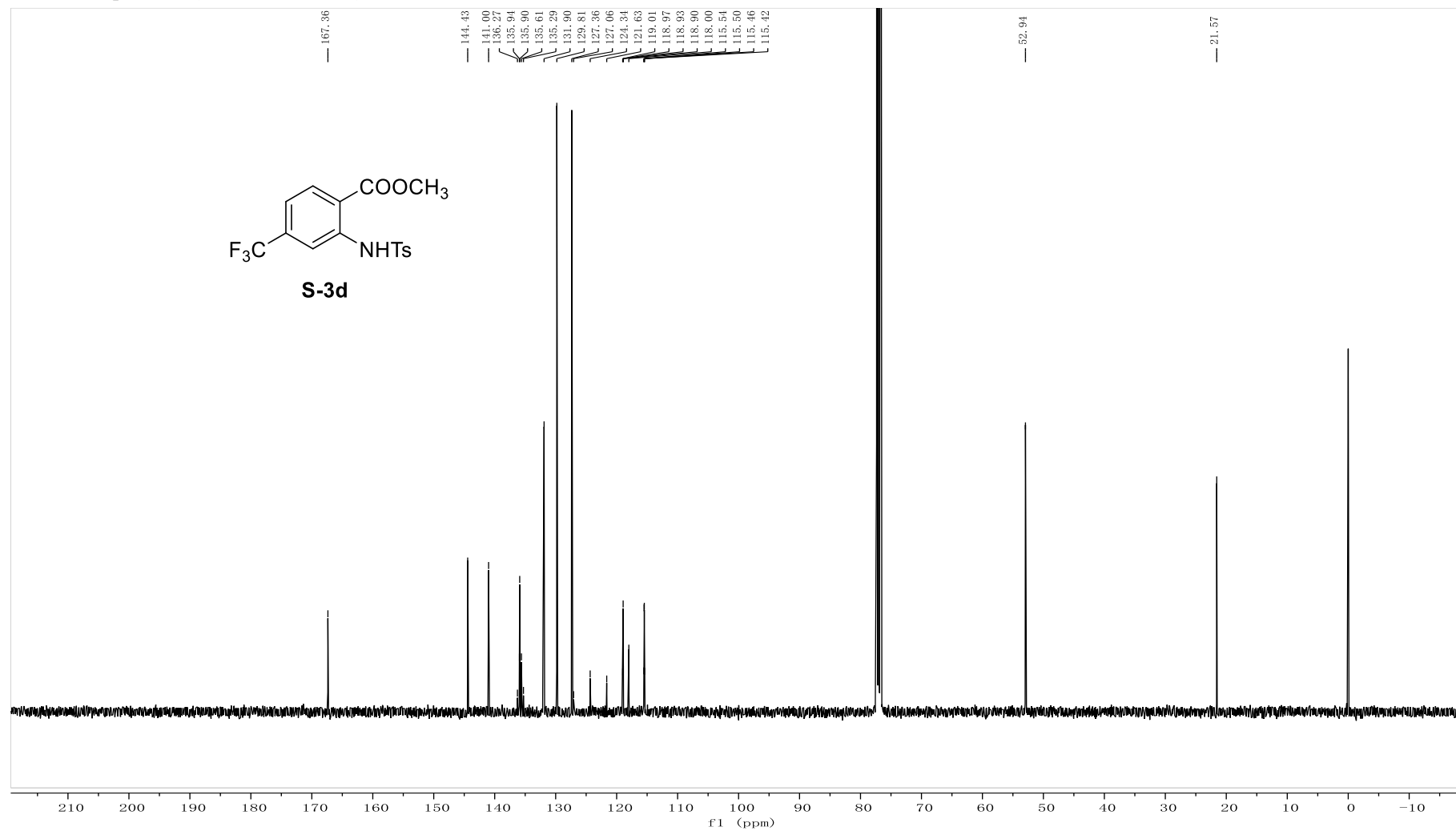
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **S-3c**



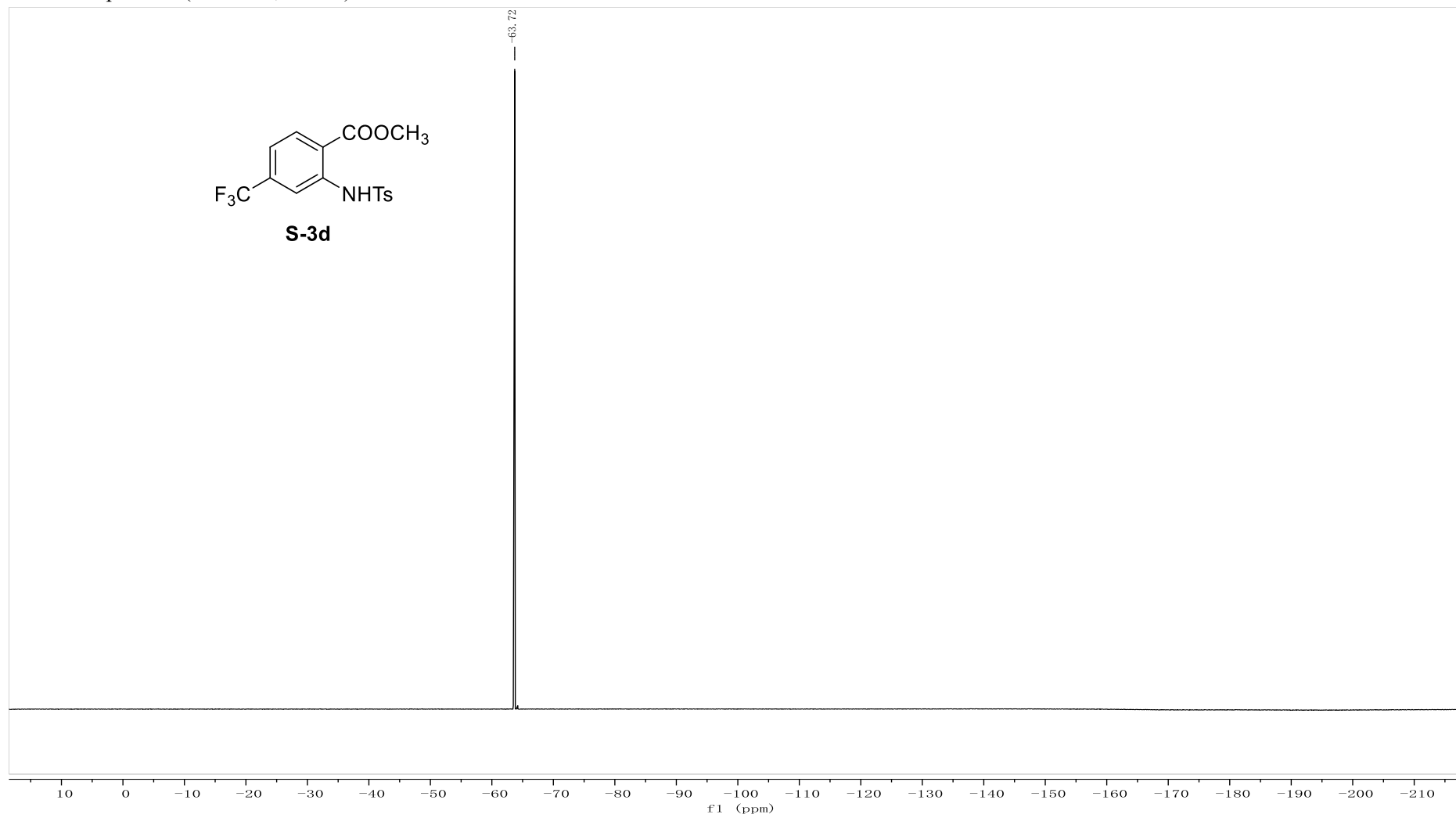
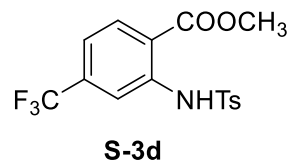
¹H NMR-spectrum (400 MHz, CDCl₃) of **S-3d**



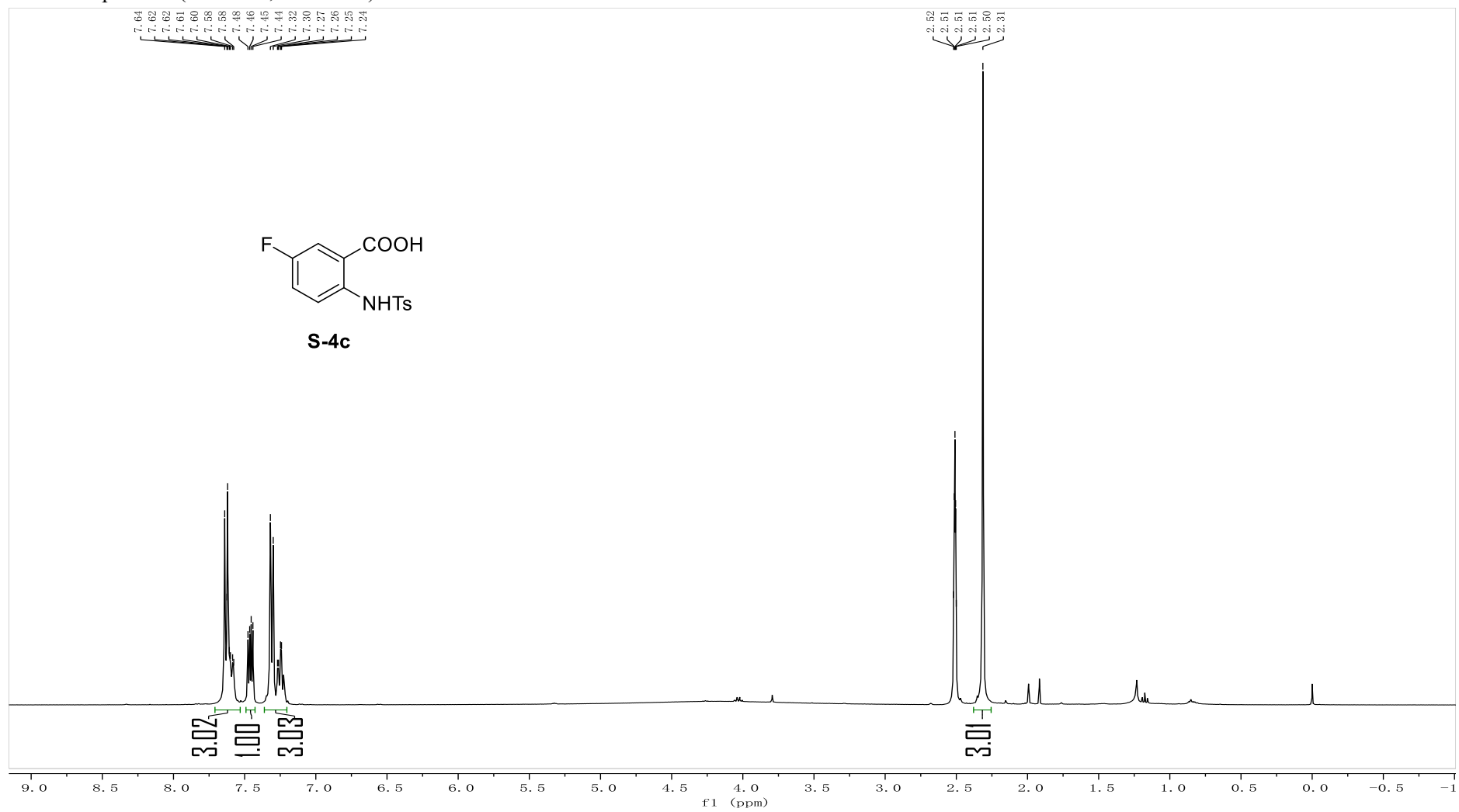
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **S-3d**



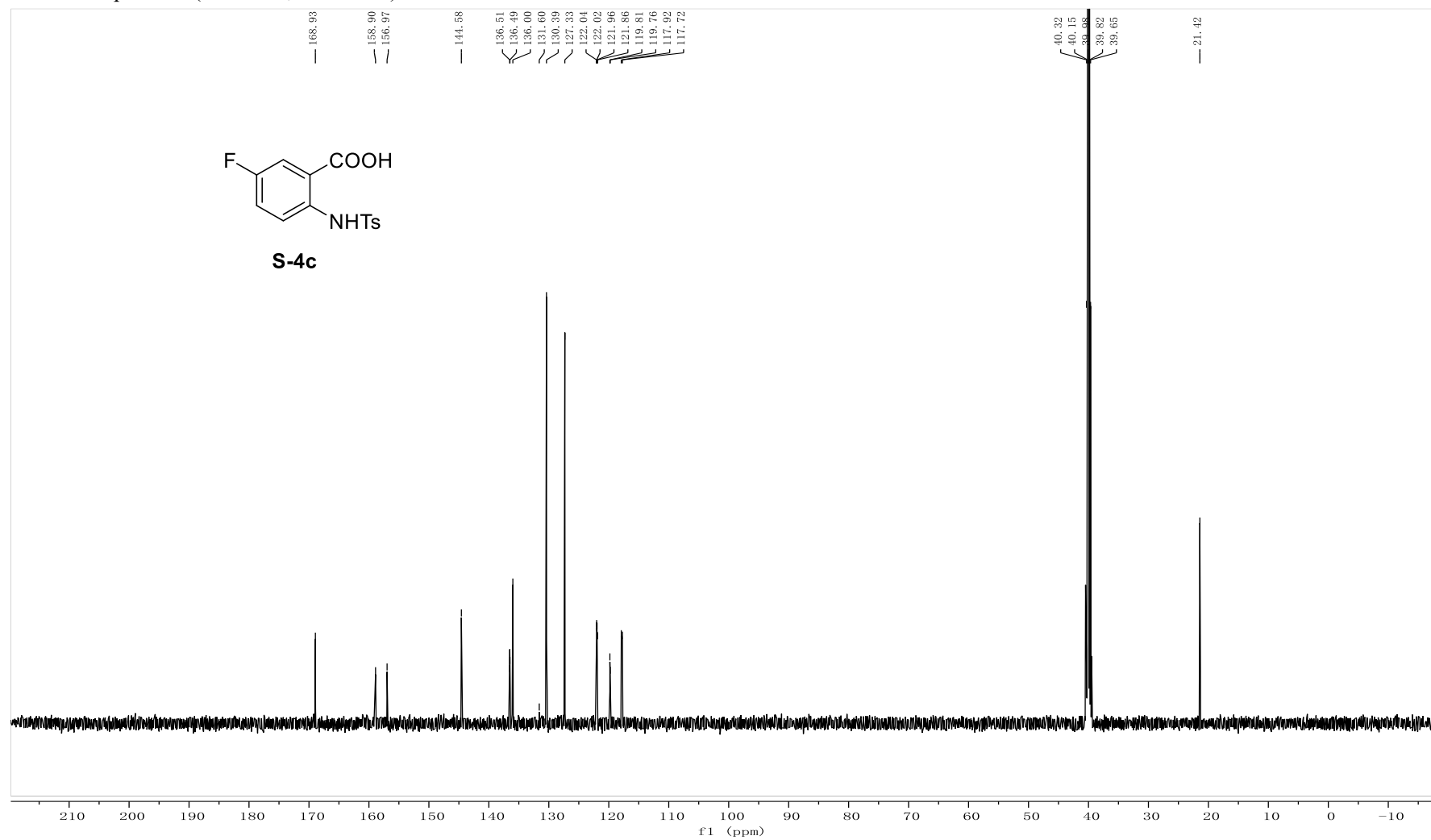
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **S-3d**



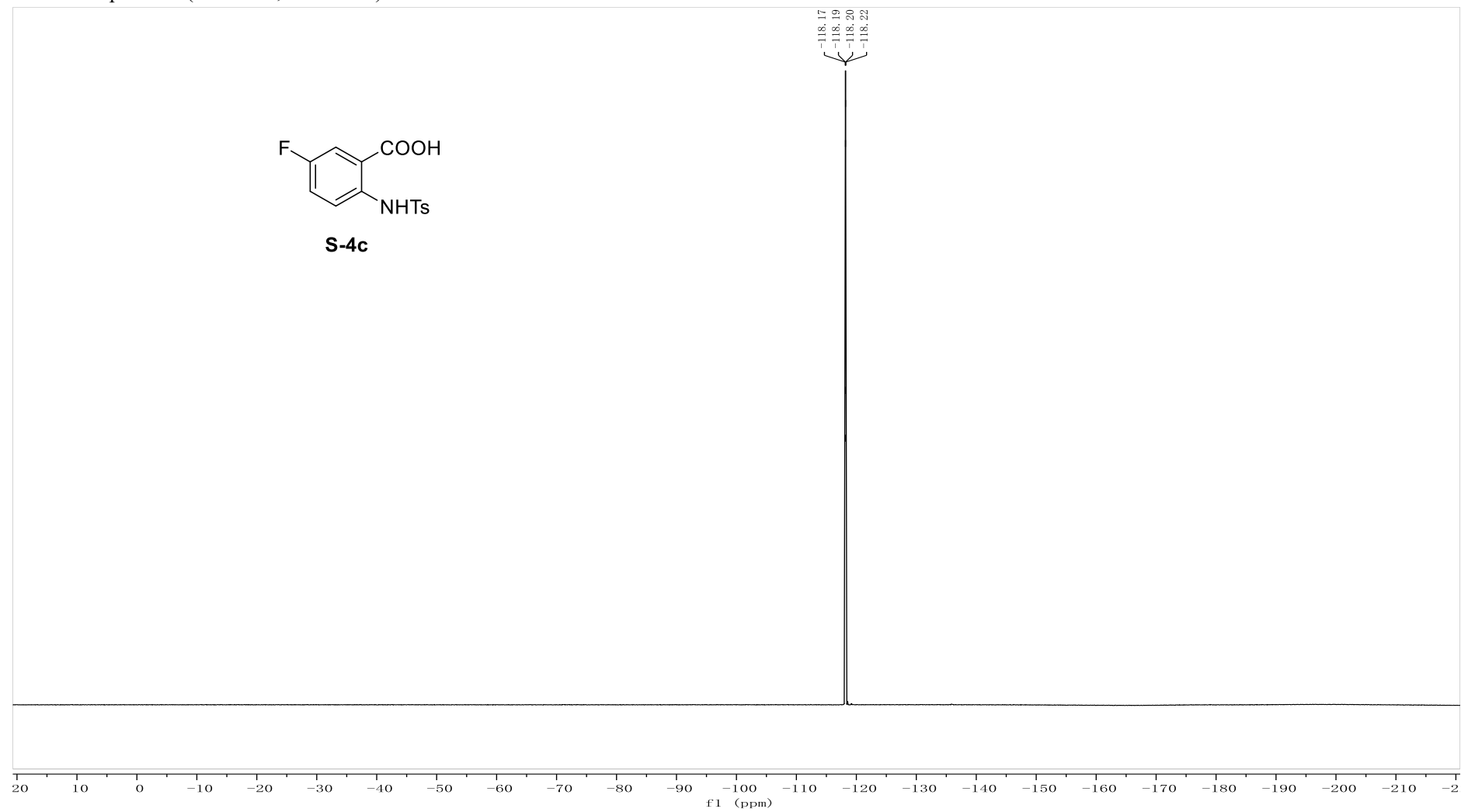
¹H NMR-spectrum (400 MHz, DMSO-*d*₆) of **S-4c**



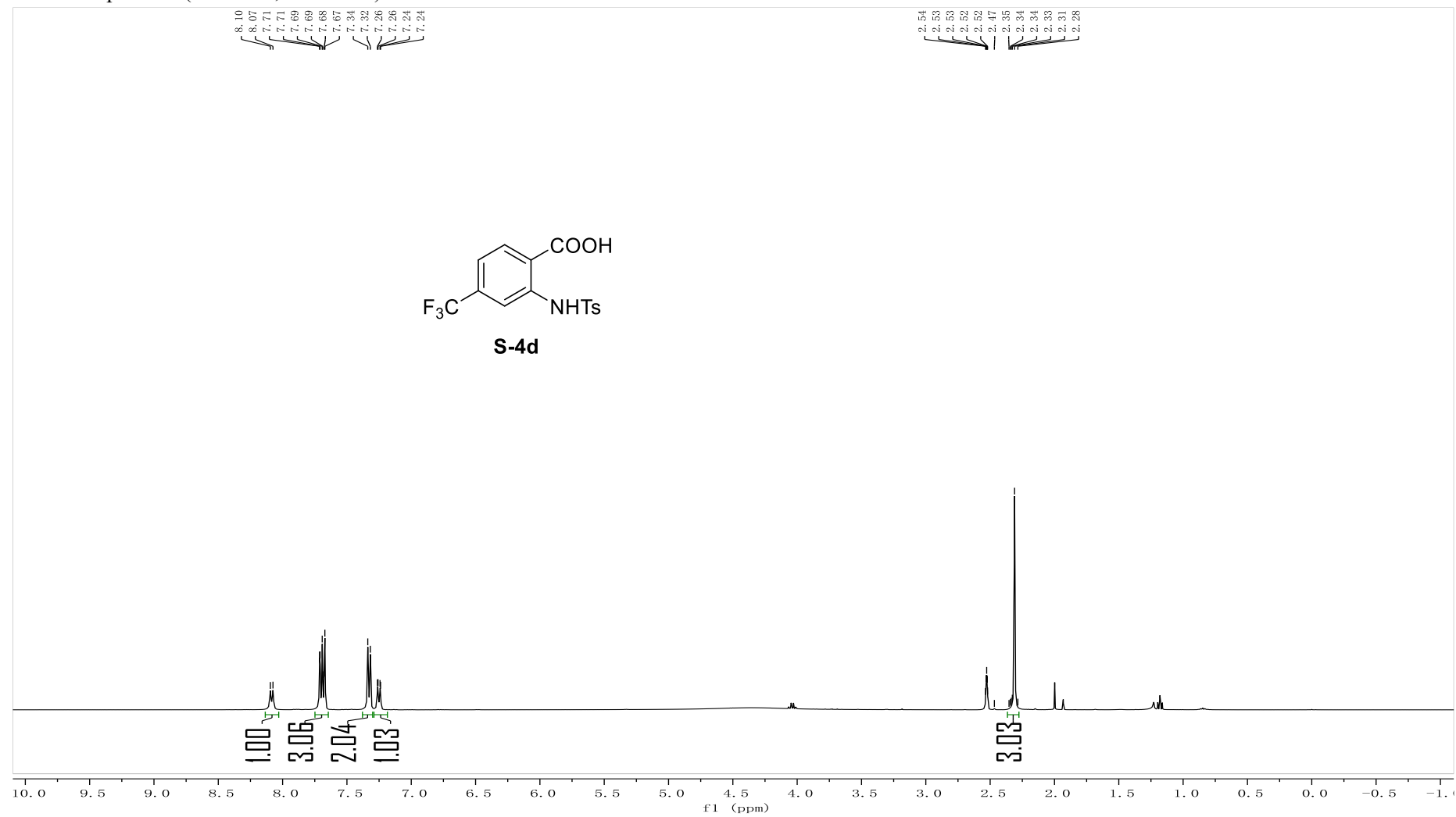
^{13}C NMR-spectrum (126 MHz, $\text{DMSO-}d_6$) of **S-4c**



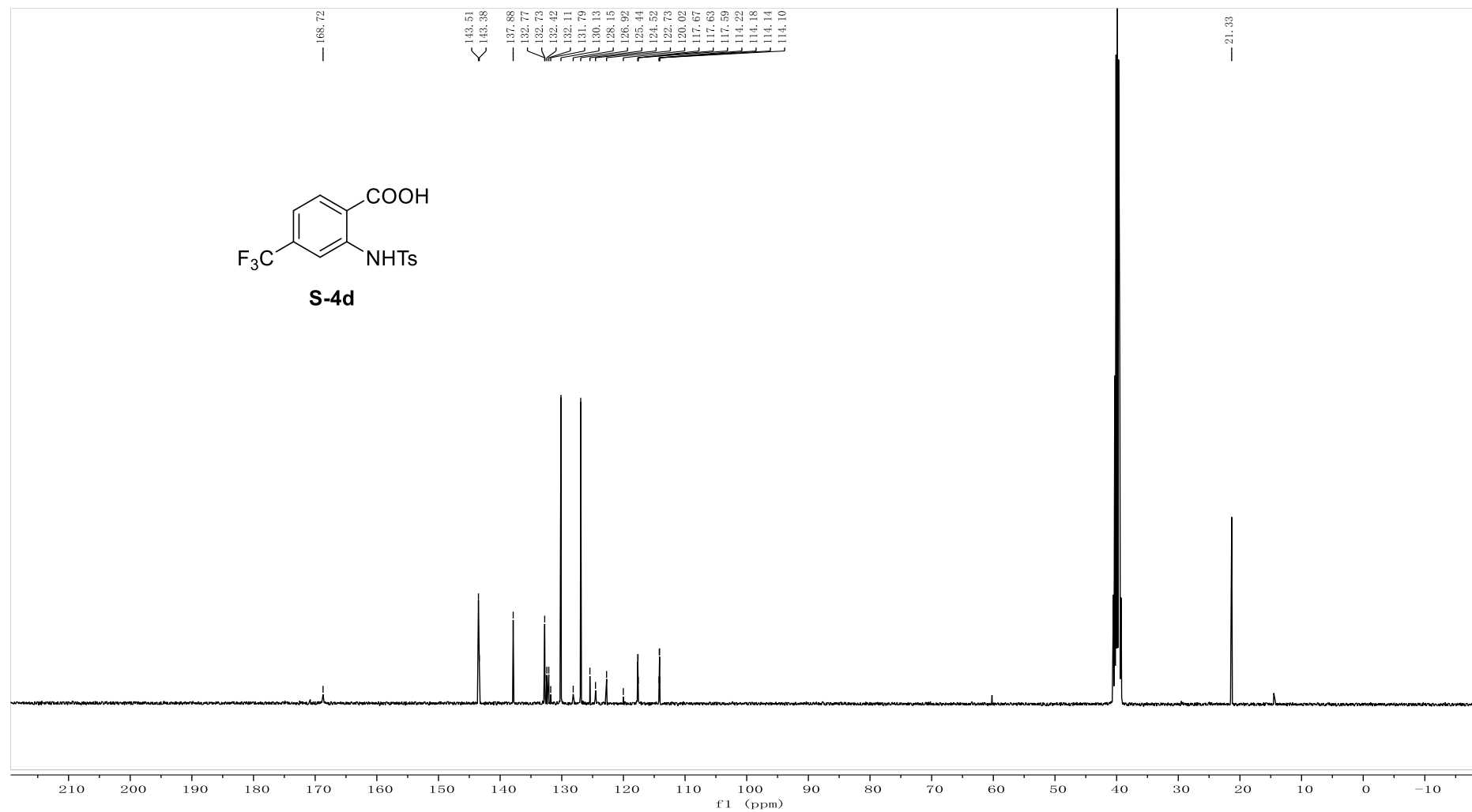
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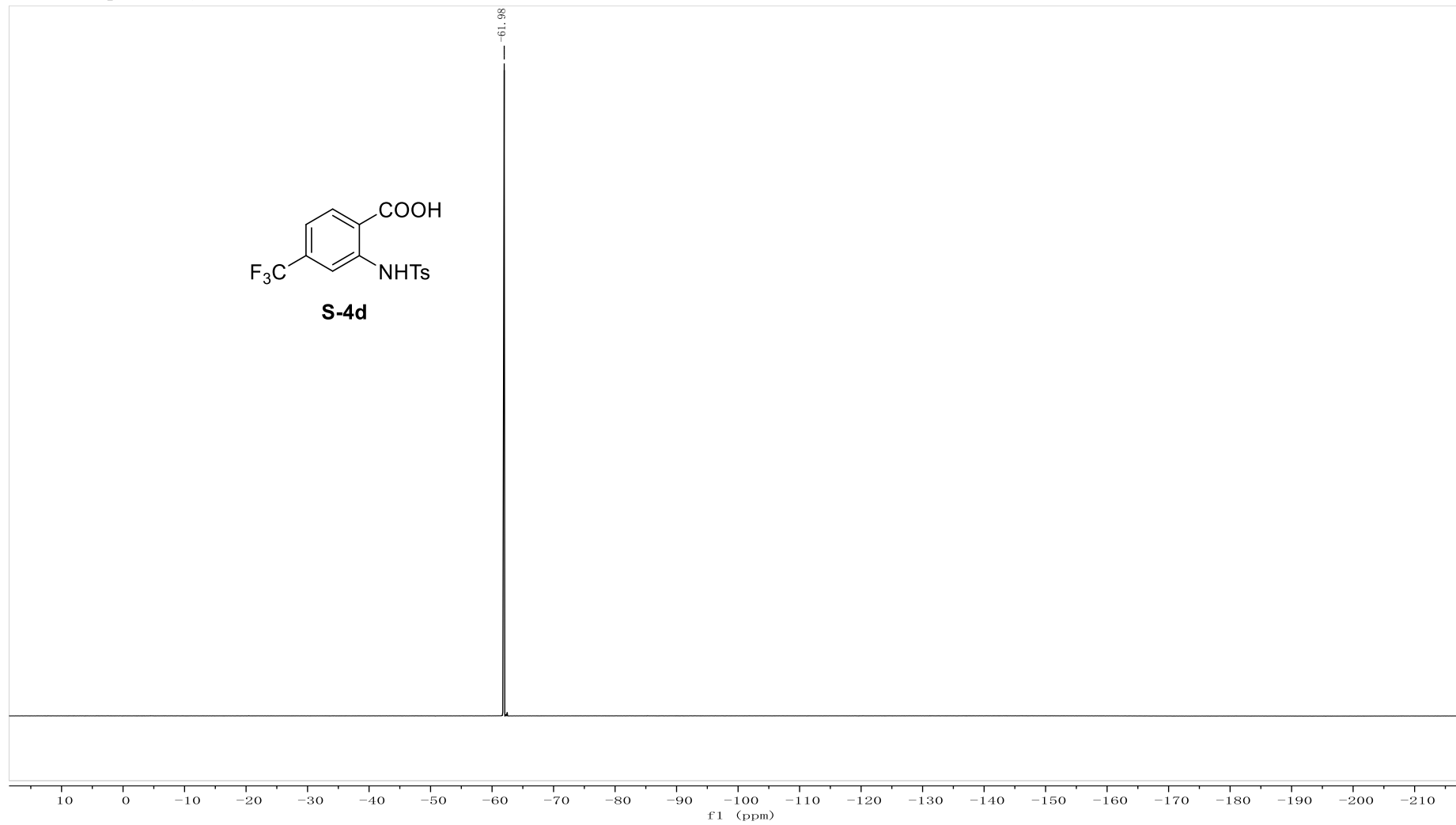
¹H NMR-spectrum (400 MHz, DMSO-*d*₆) of **S-4d**



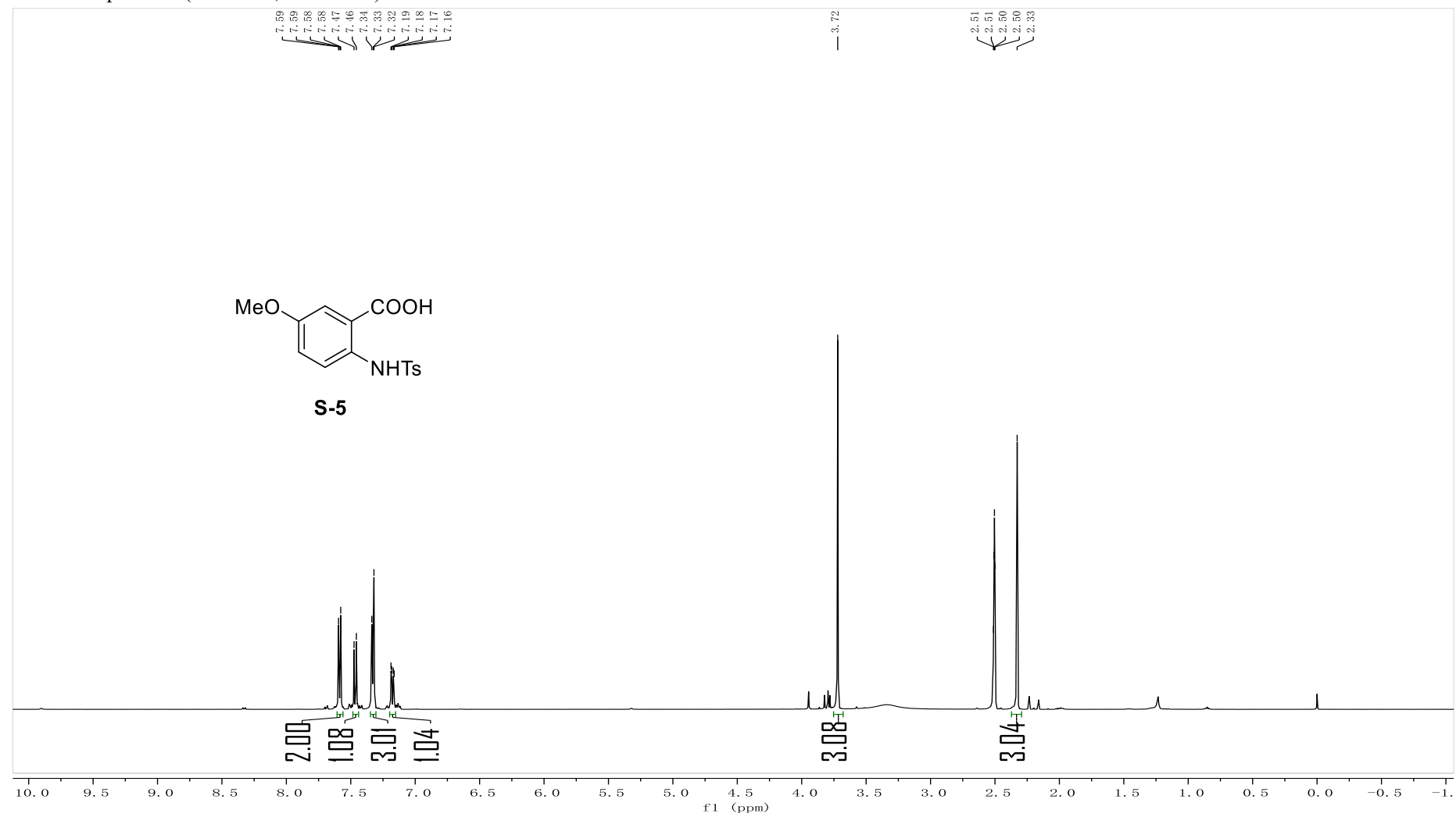
^{13}C NMR-spectrum (101 MHz, $\text{DMSO-}d_6$) of **S-4d**



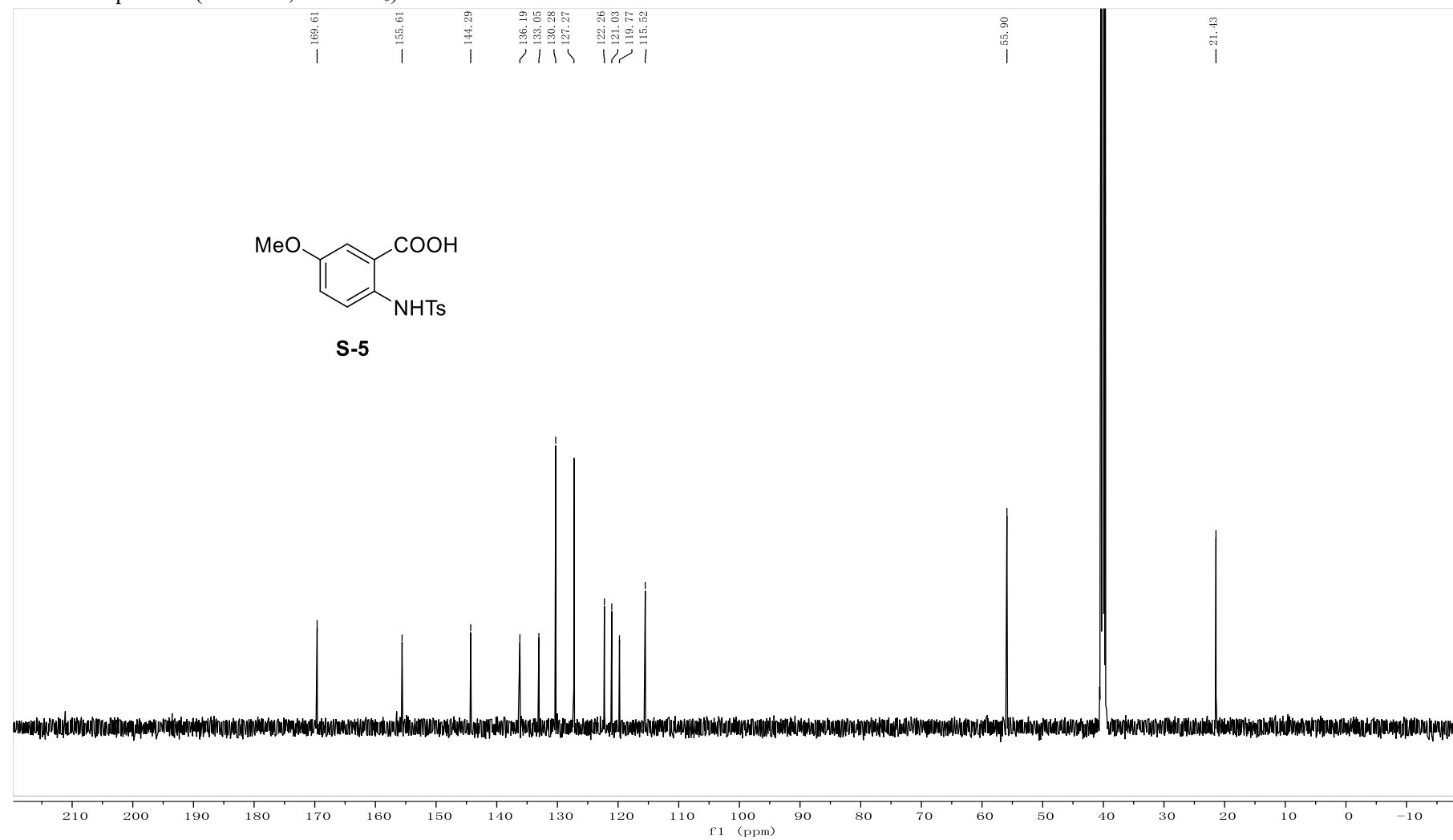
^{19}F NMR-spectrum (376 MHz, $\text{DMSO-}d_6$) of **S-4d**



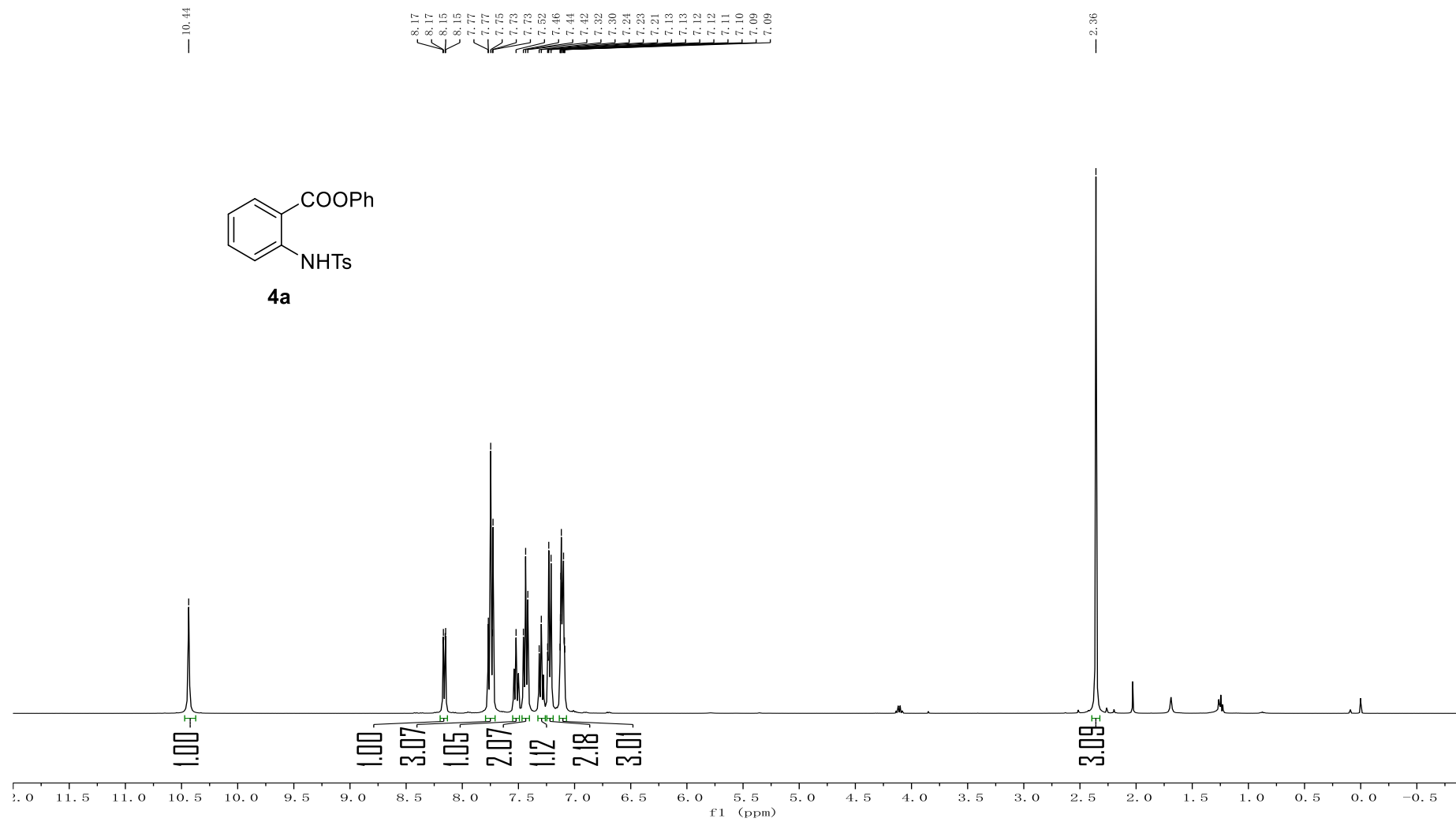
¹H NMR-spectrum (500 MHz, DMSO-*d*₆) of **S-5**



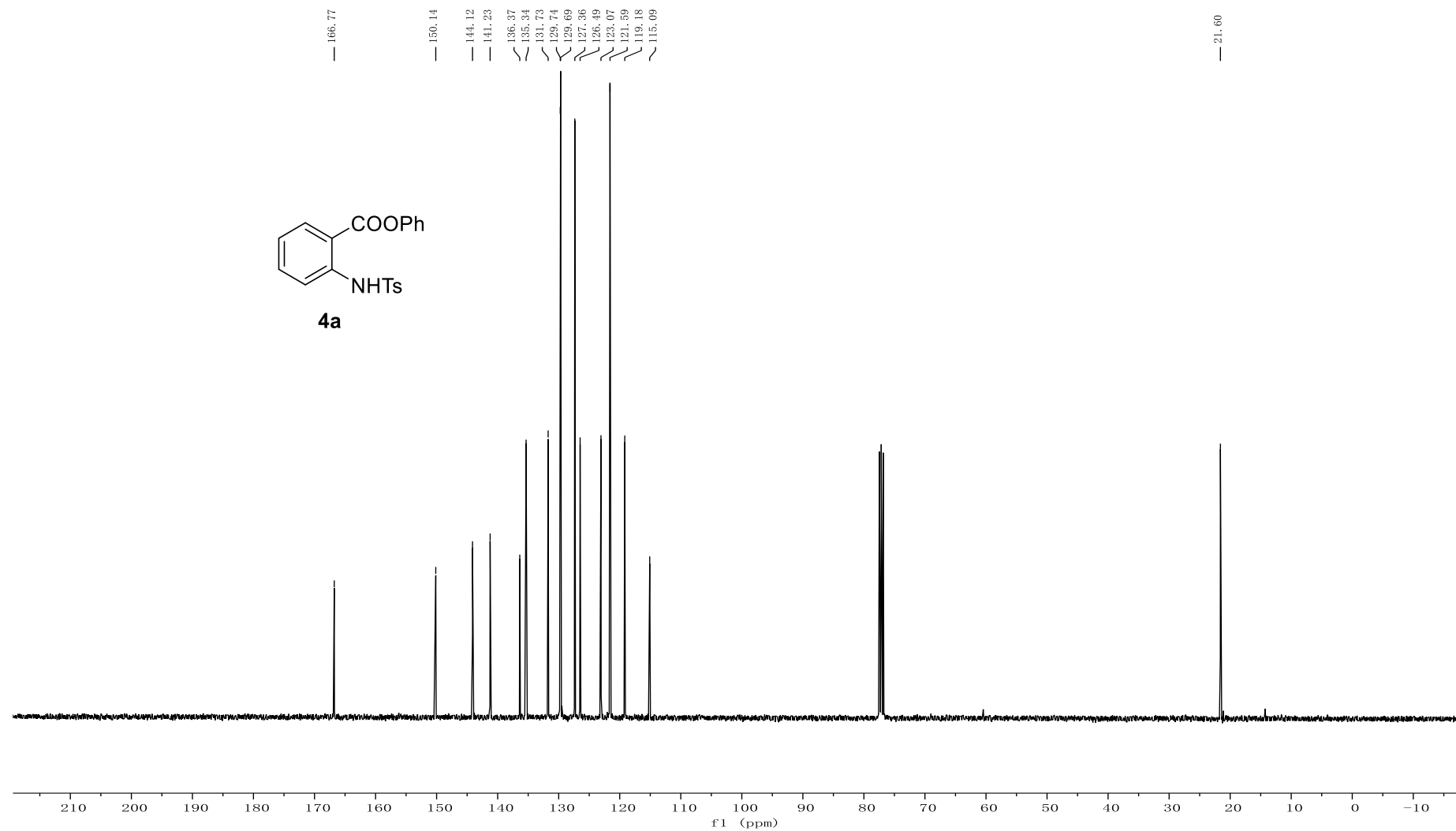
¹³C NMR-spectrum (126 MHz, DMSO-*d*₆) of **S-5**



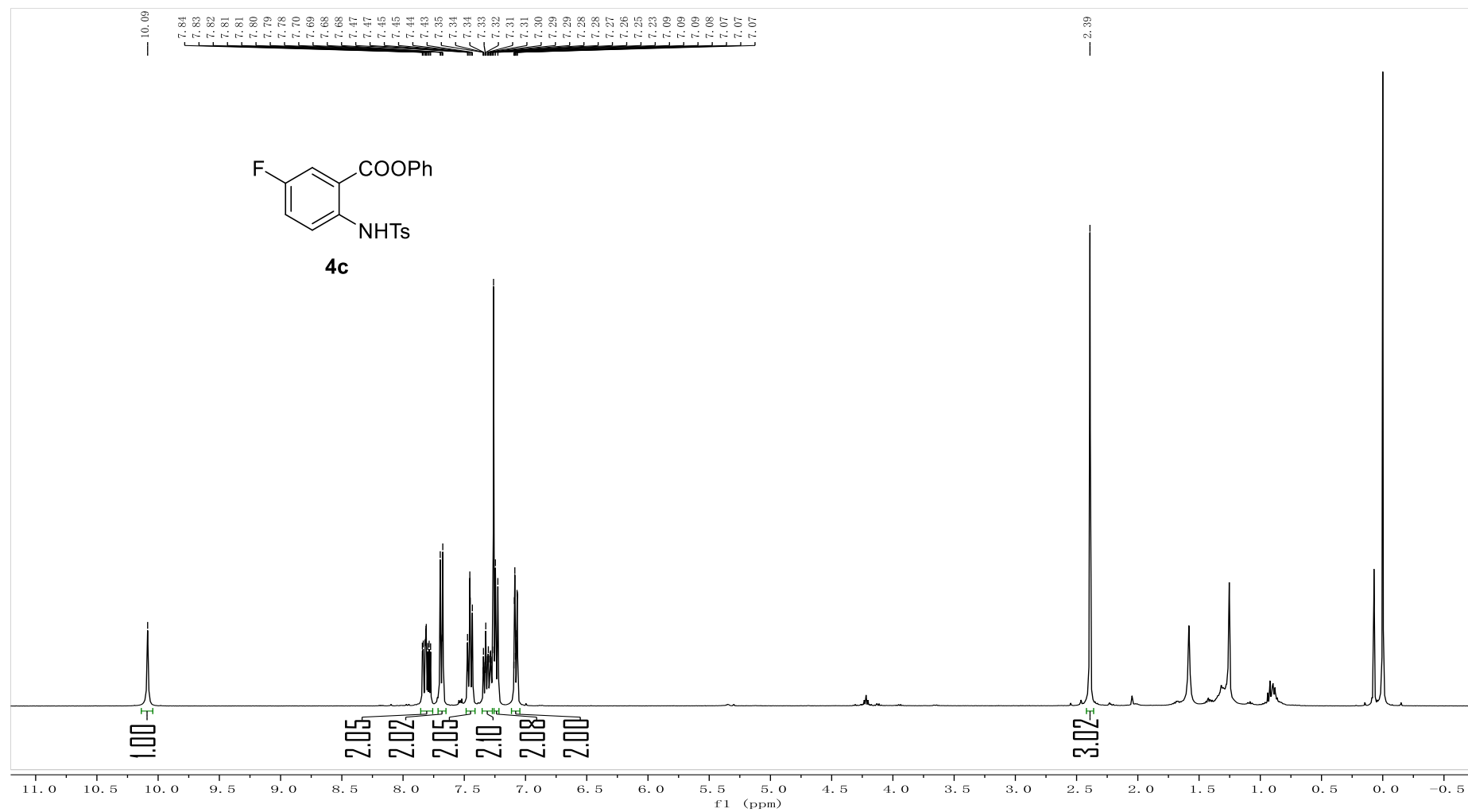
¹H NMR-spectrum (400 MHz, CDCl₃) of **4a**



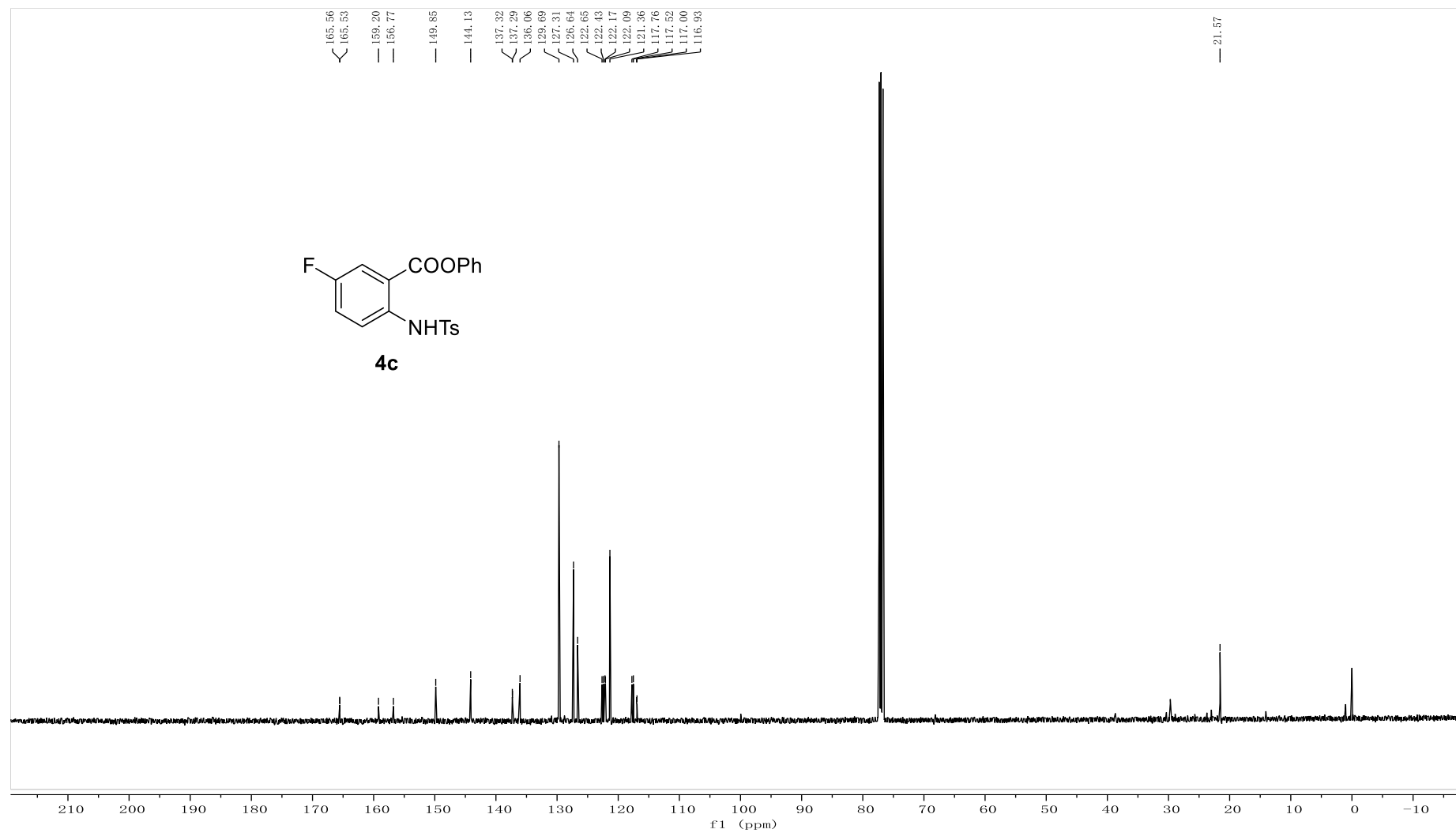
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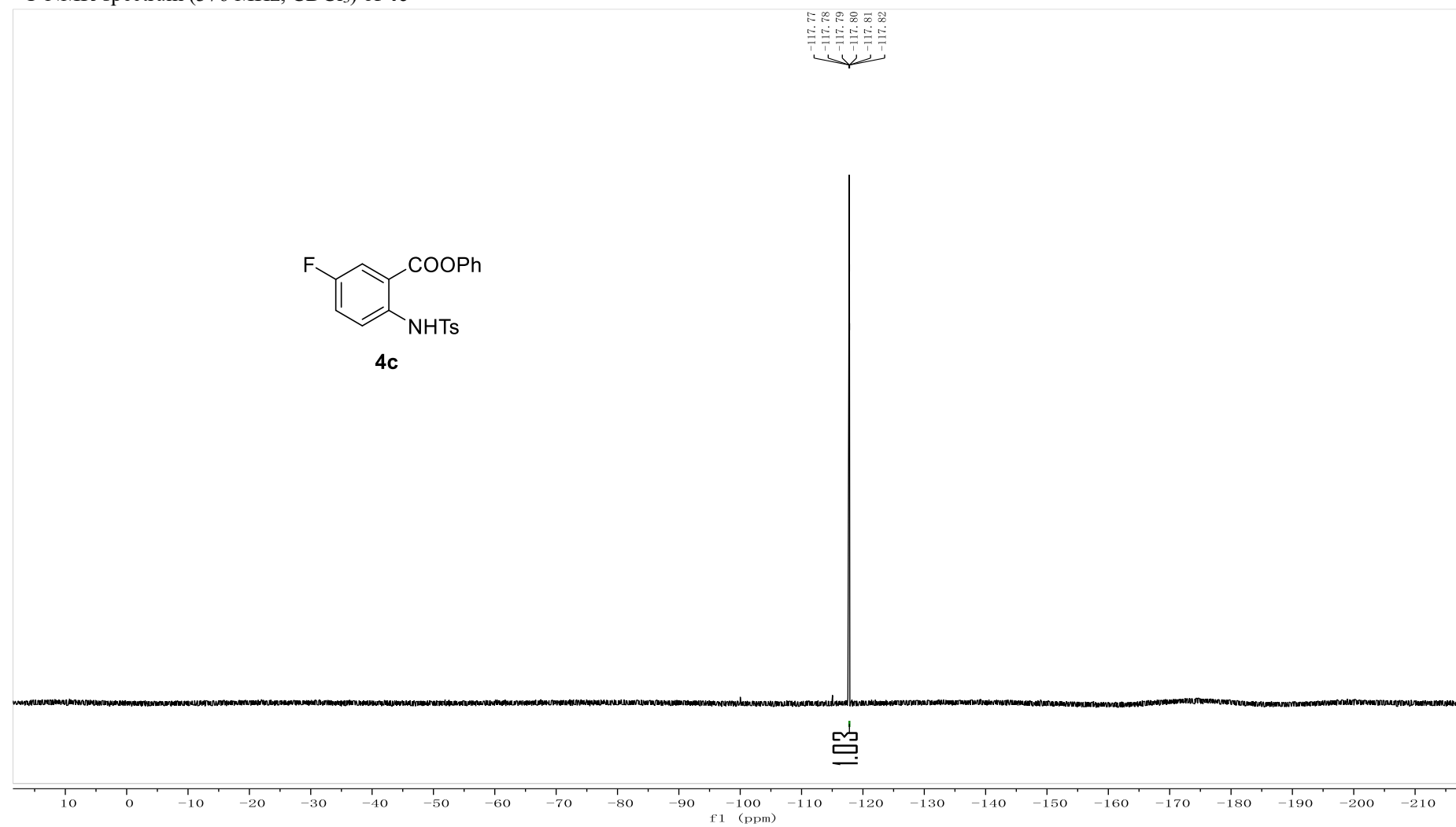
^1H NMR-spectrum (400 MHz, CDCl_3) of **4c**



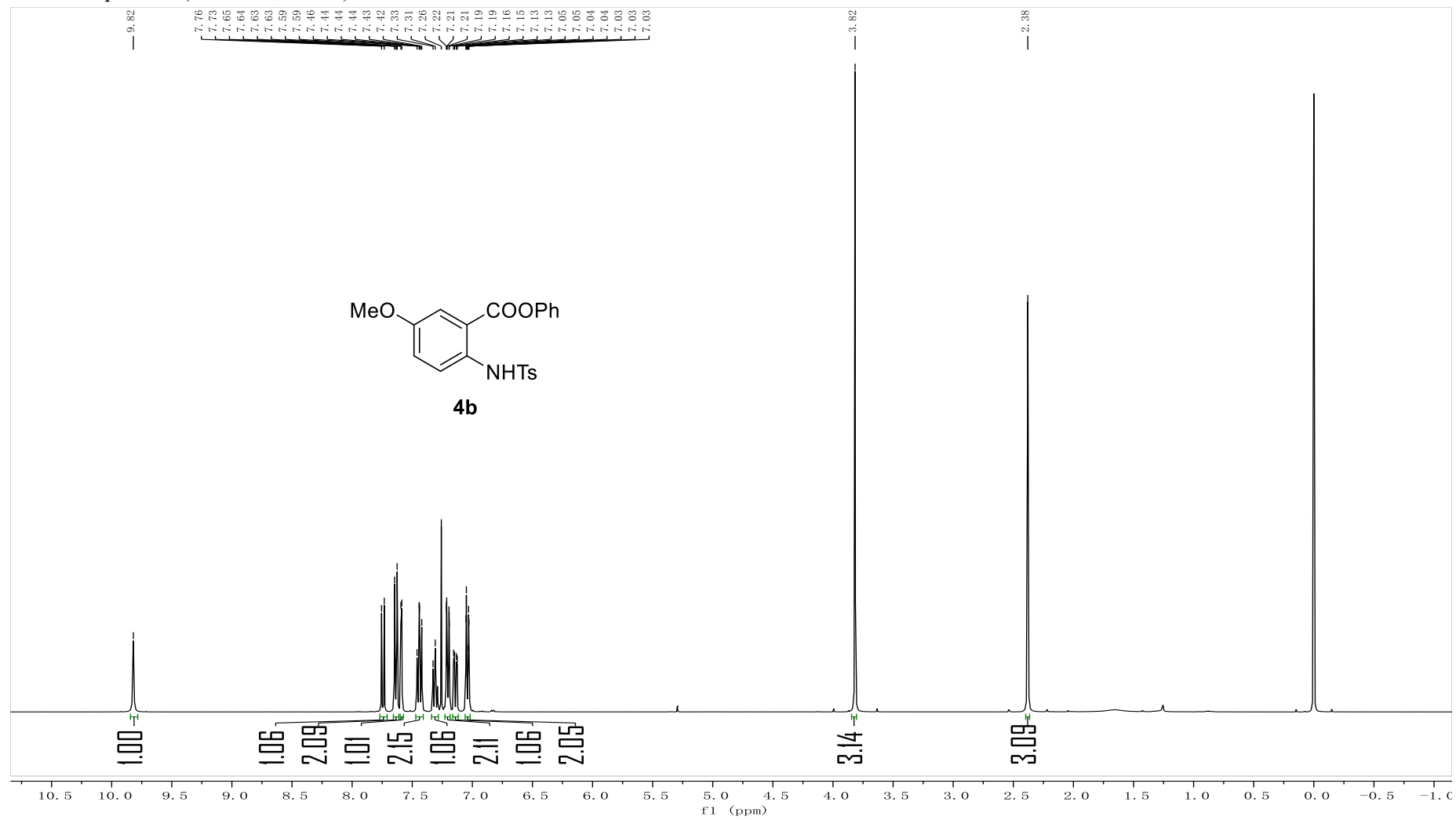
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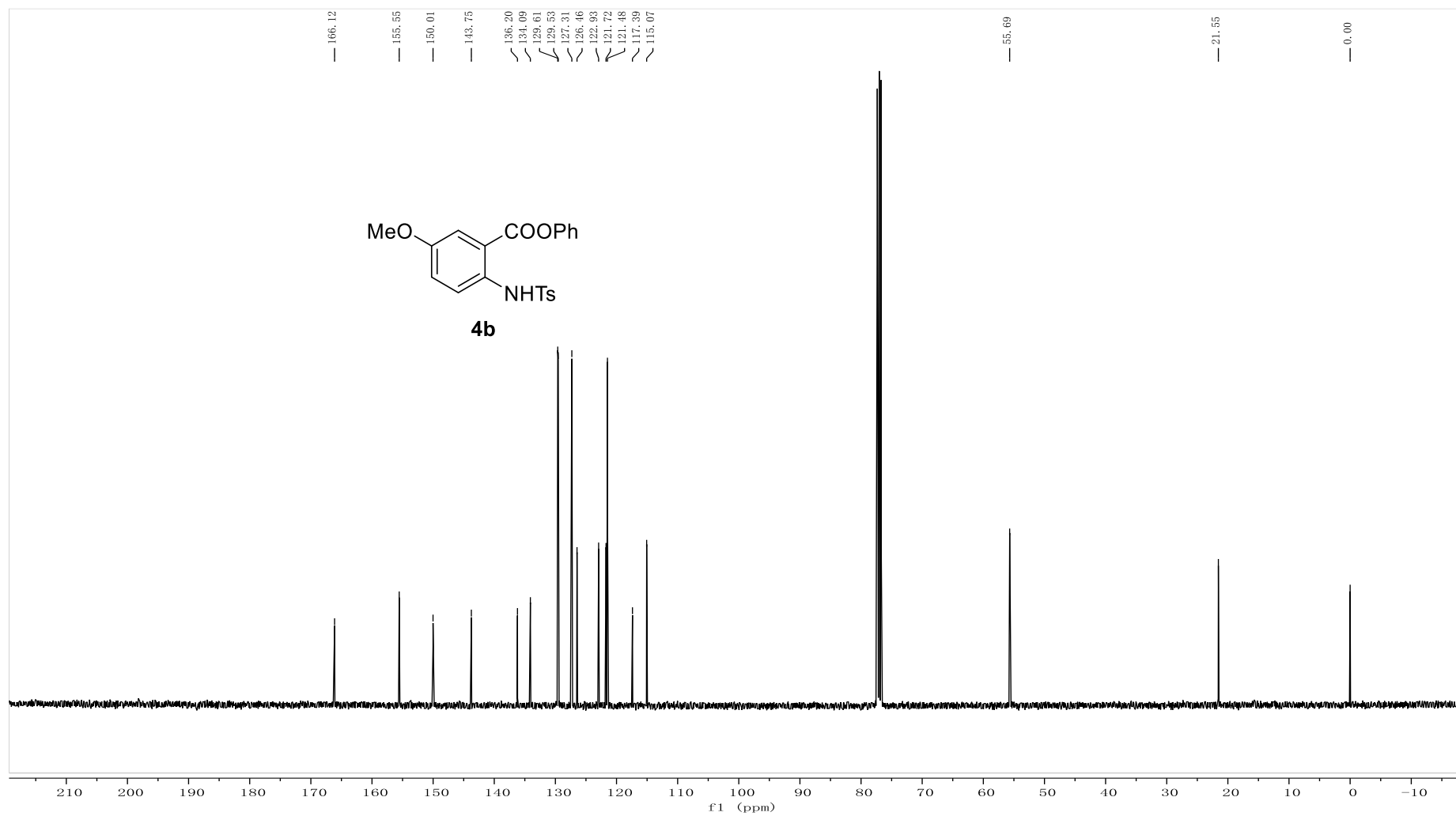
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **4c**



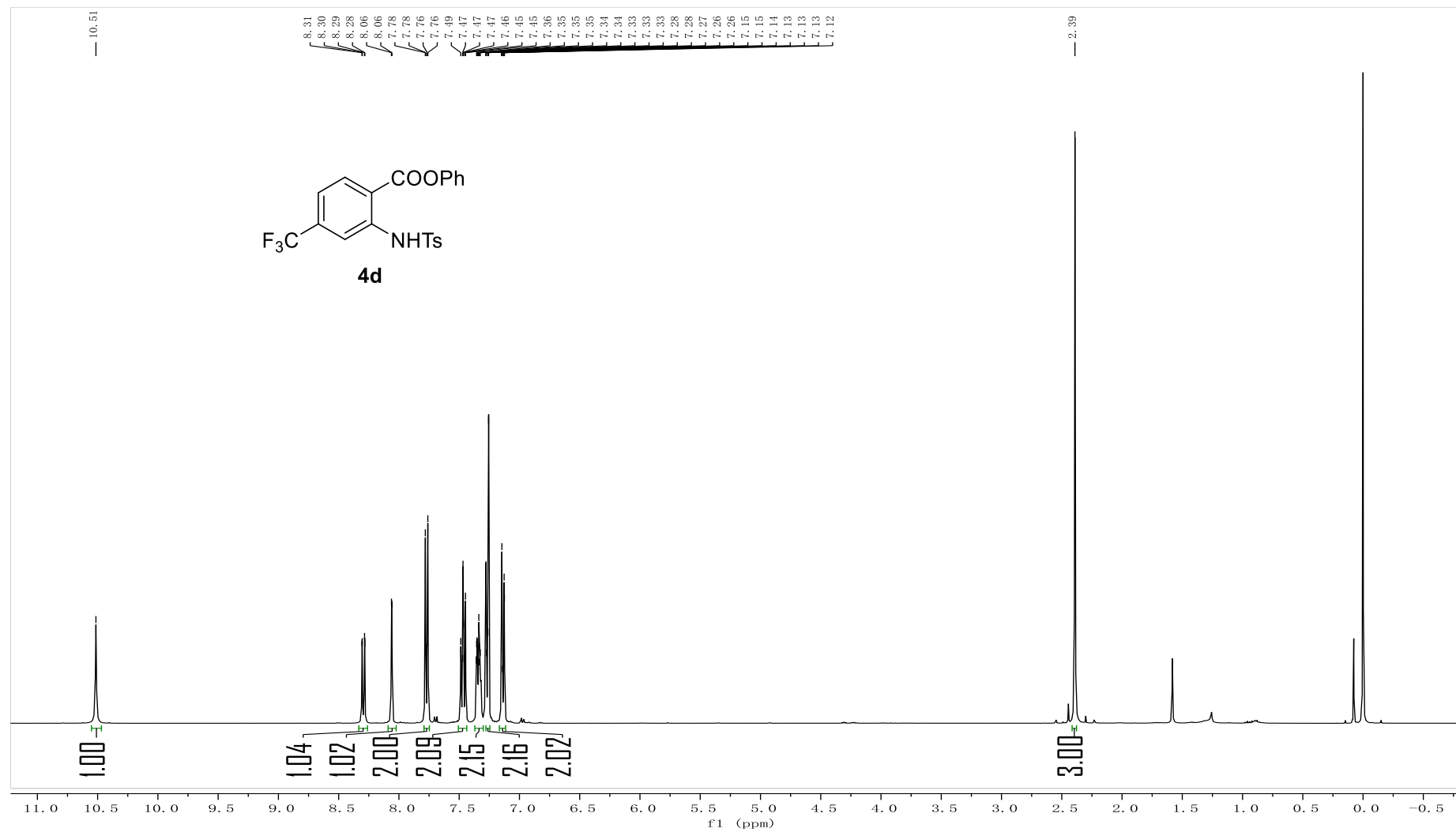
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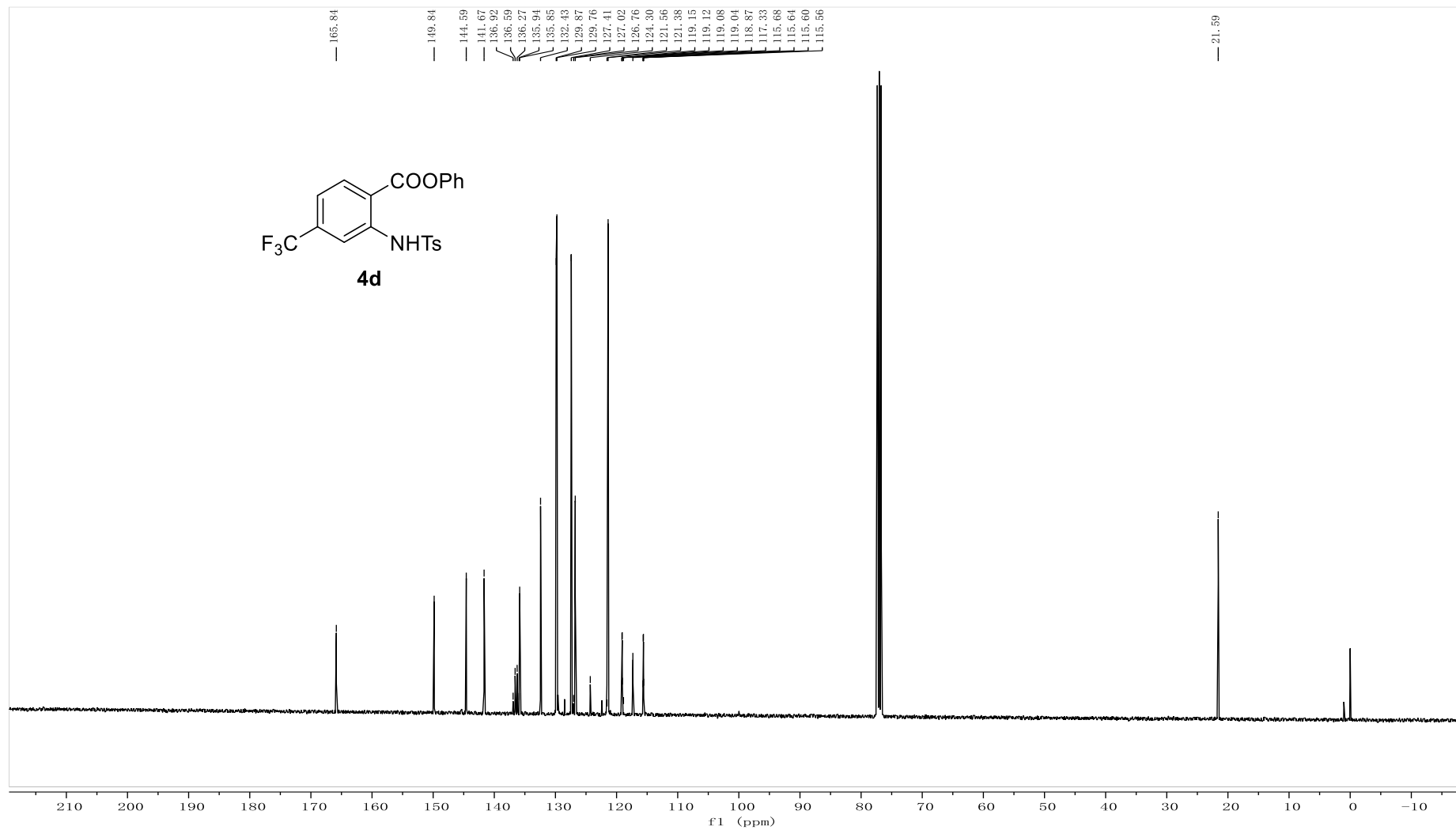
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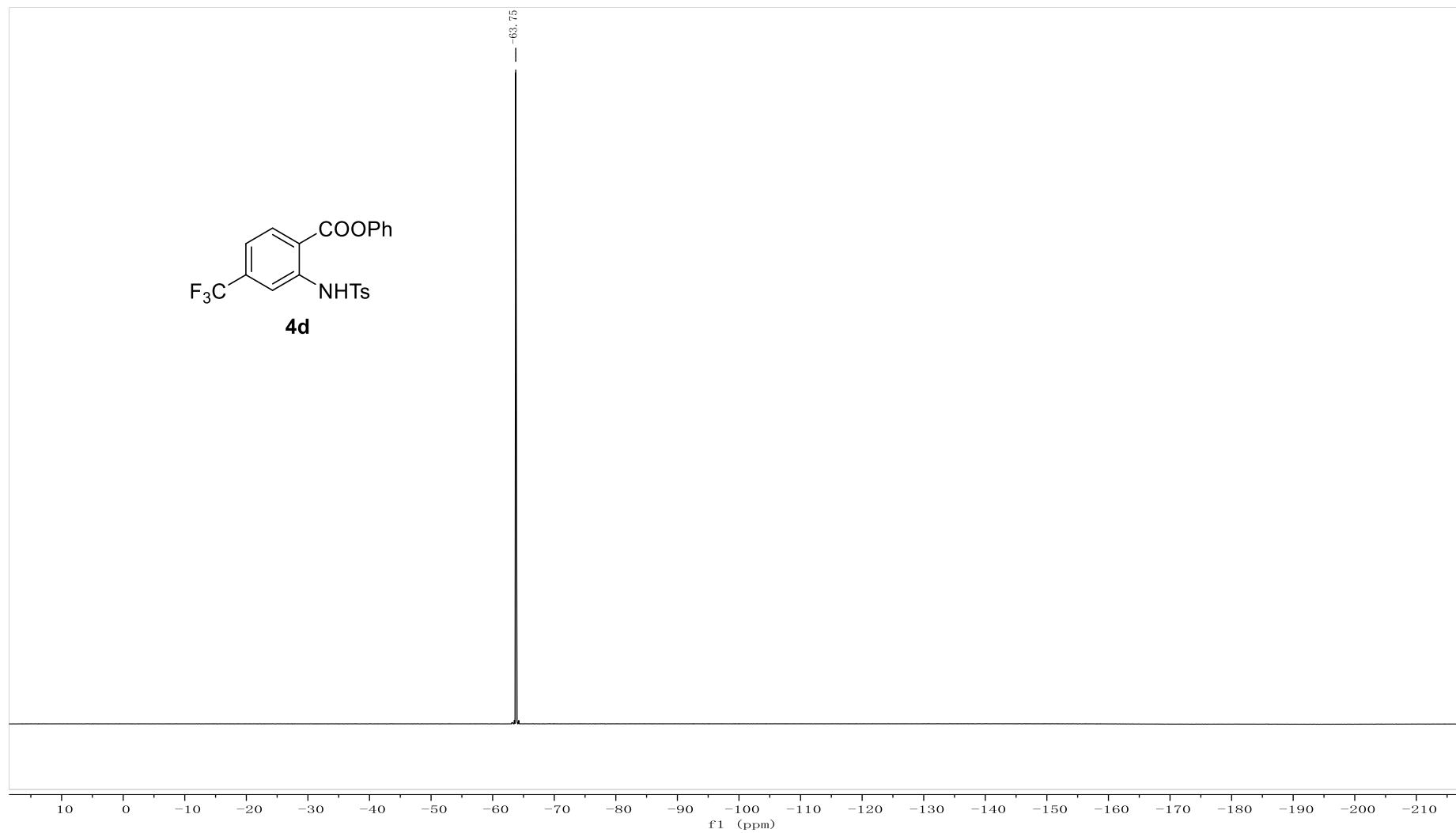
¹H NMR-spectrum (400 MHz, CDCl₃) of **4d**



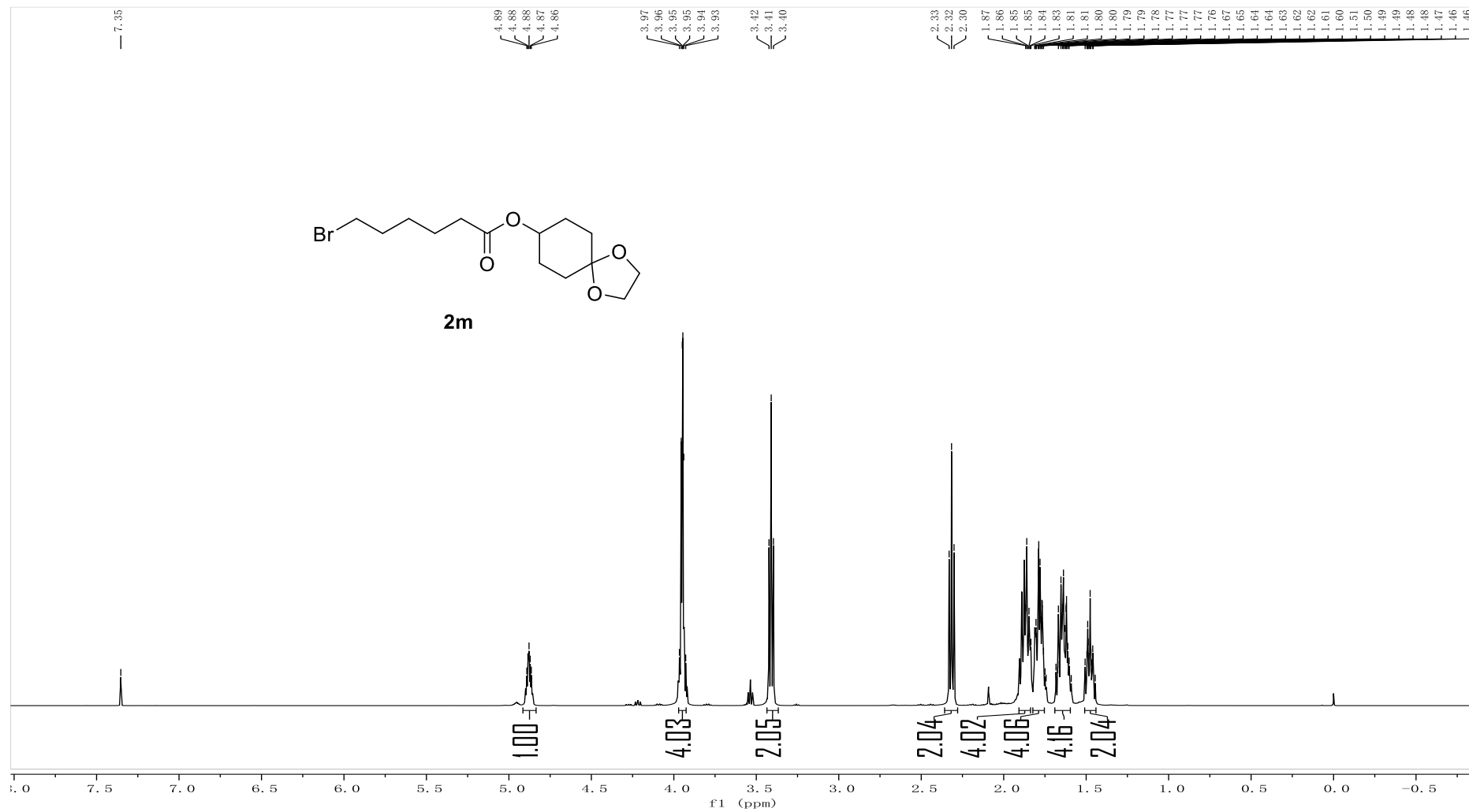
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **4d**



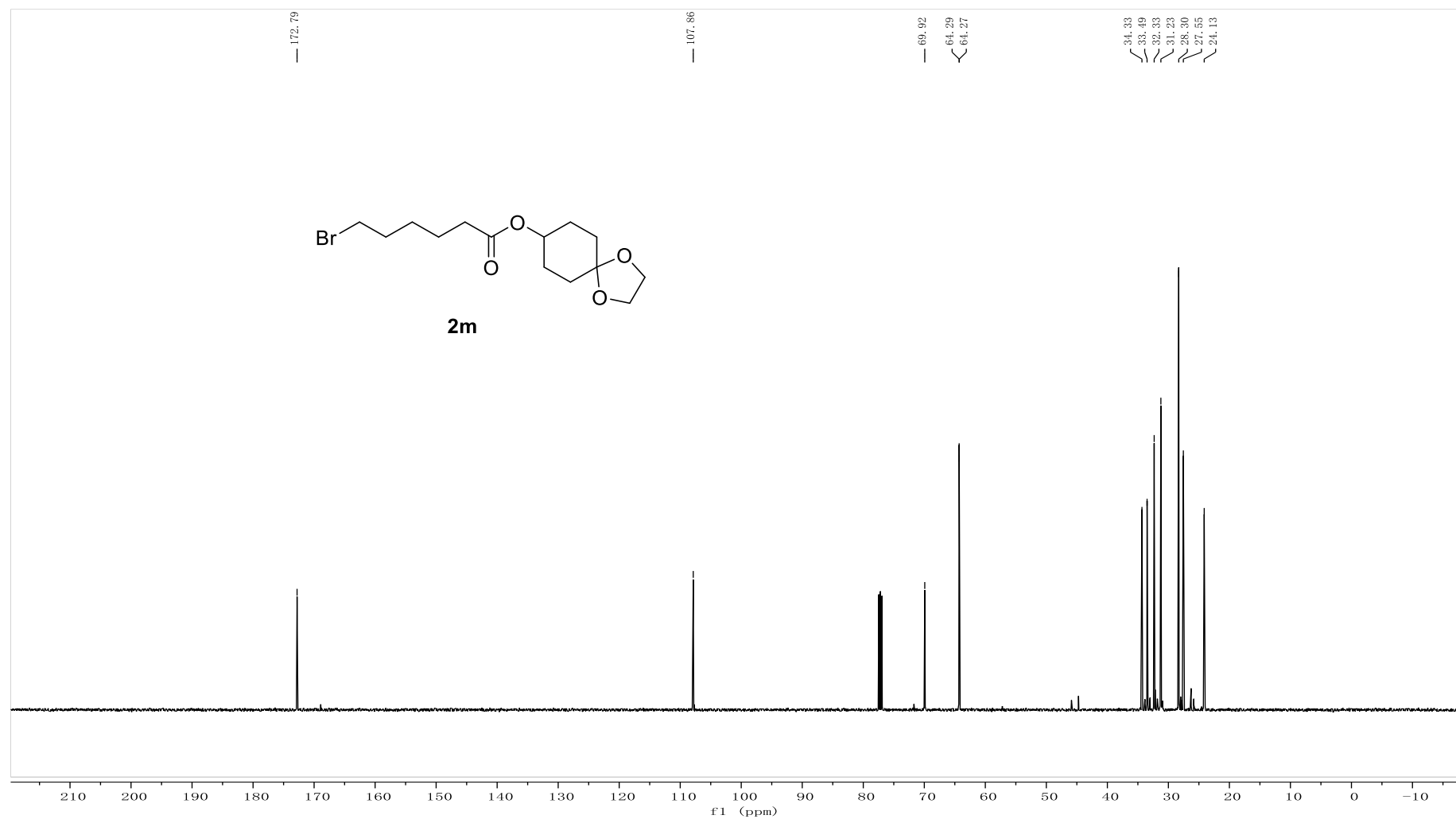
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **4d**



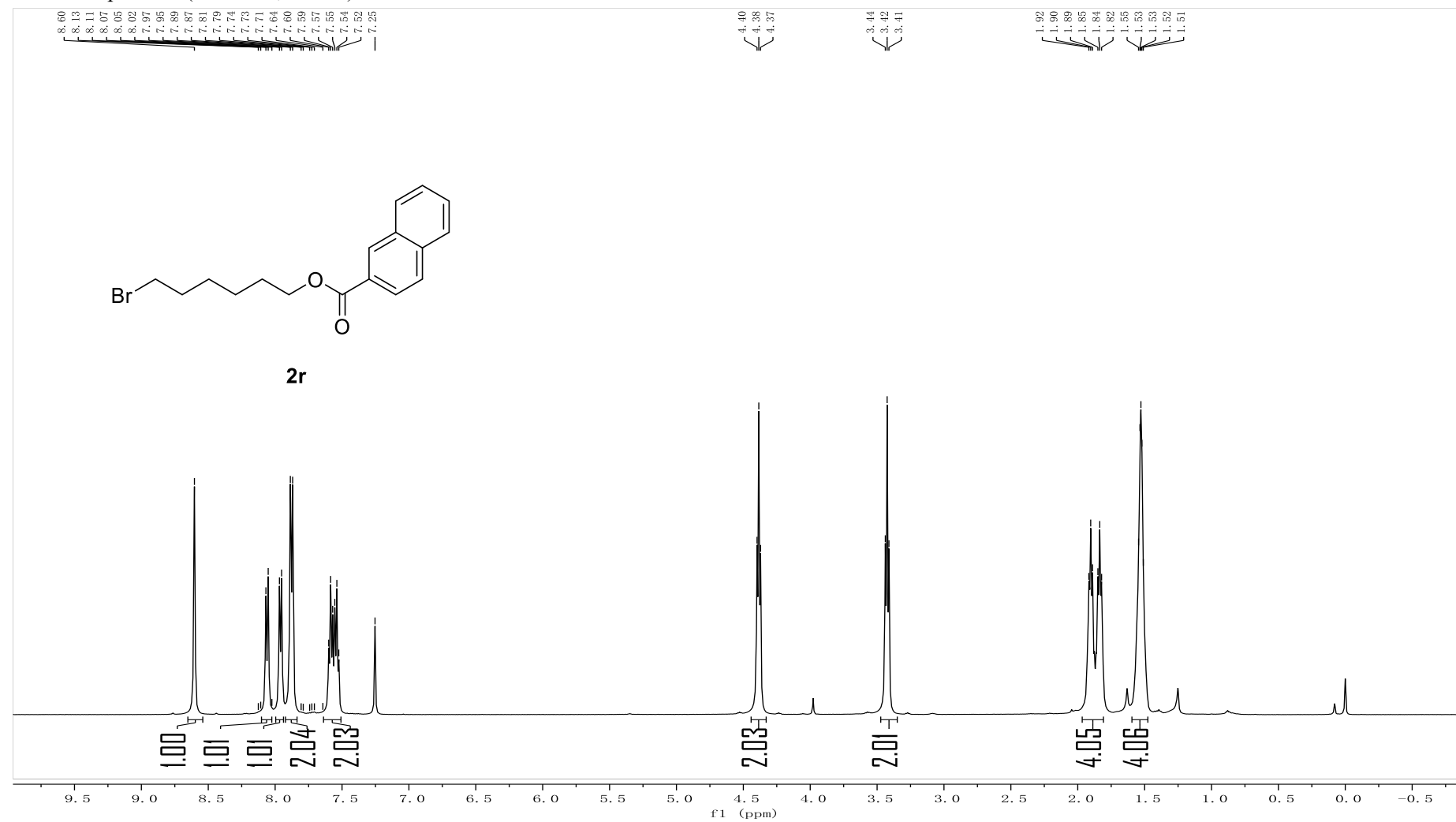
^1H NMR-spectrum (500 MHz, CDCl_3) of **2m**



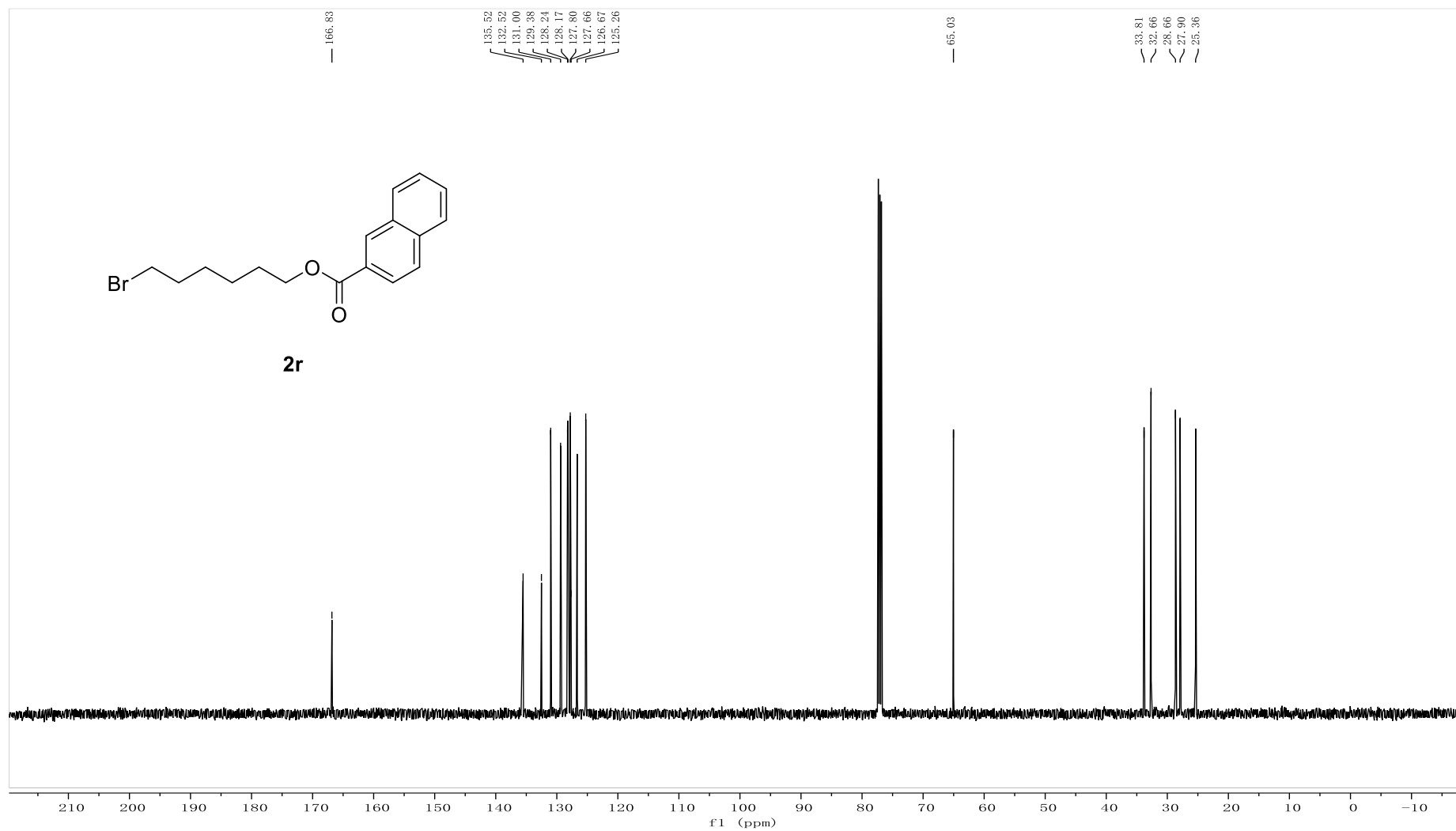
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **2m**



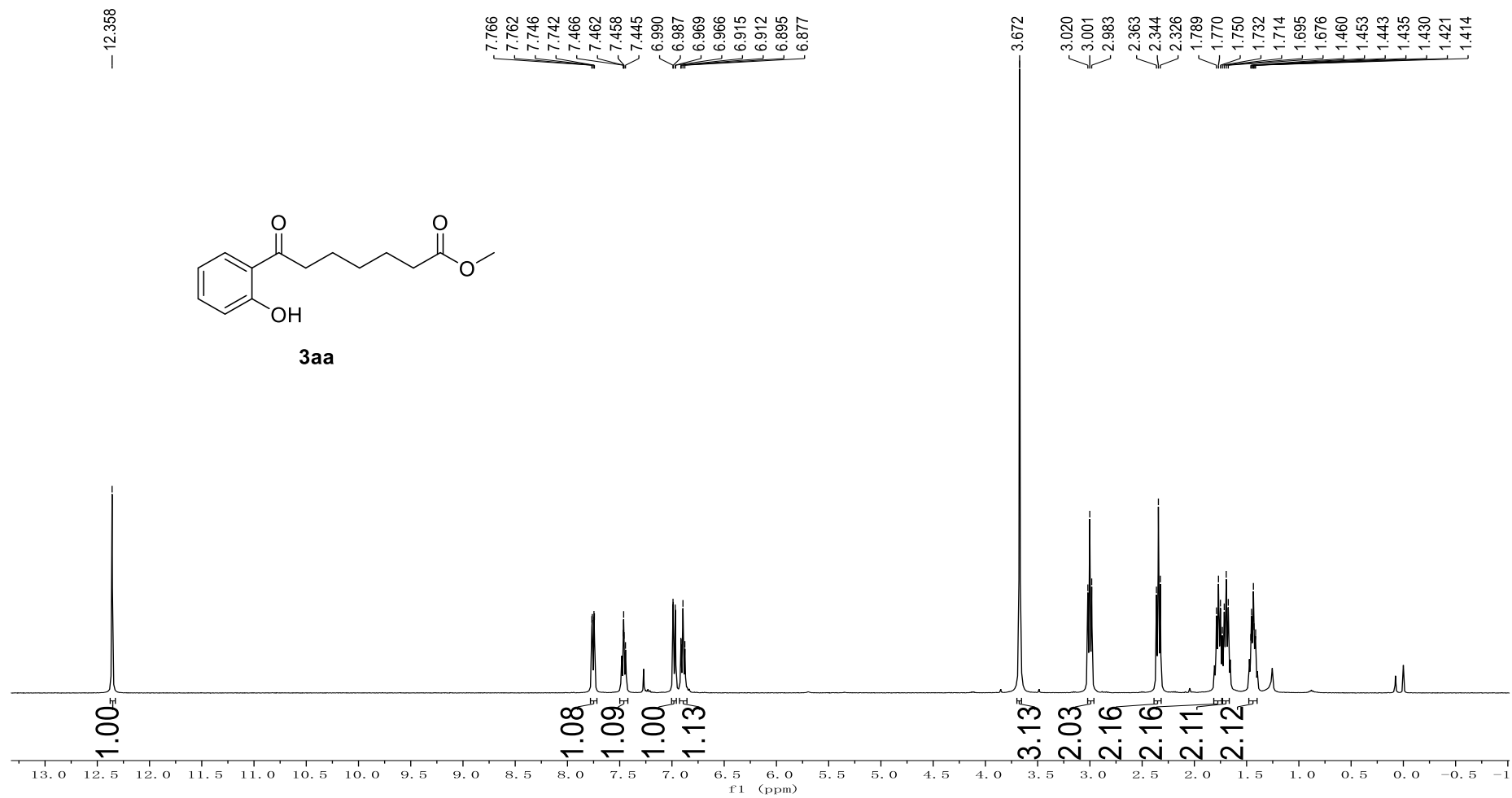
^1H NMR-spectrum (500 MHz, CDCl_3) of **2r**



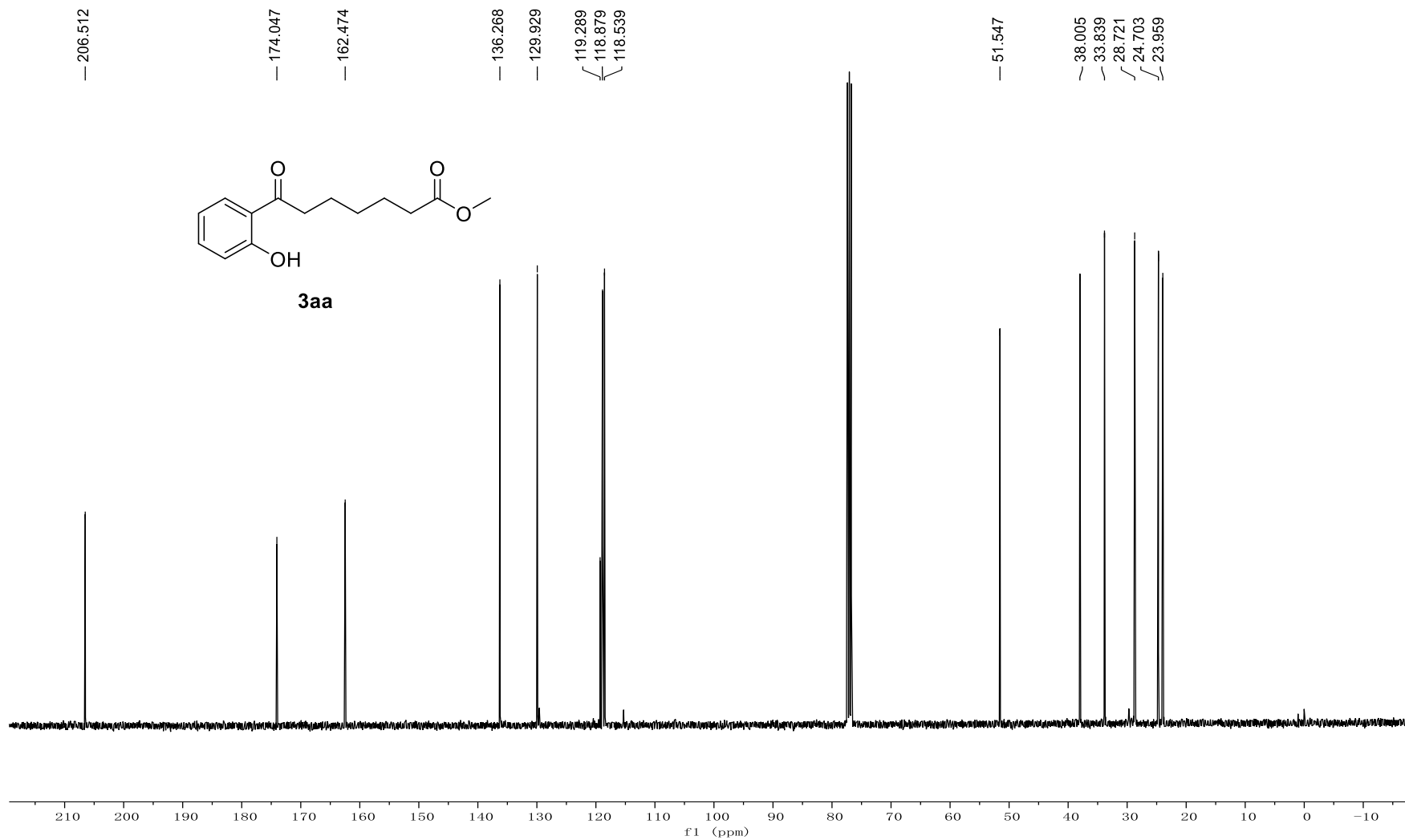
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **2r**



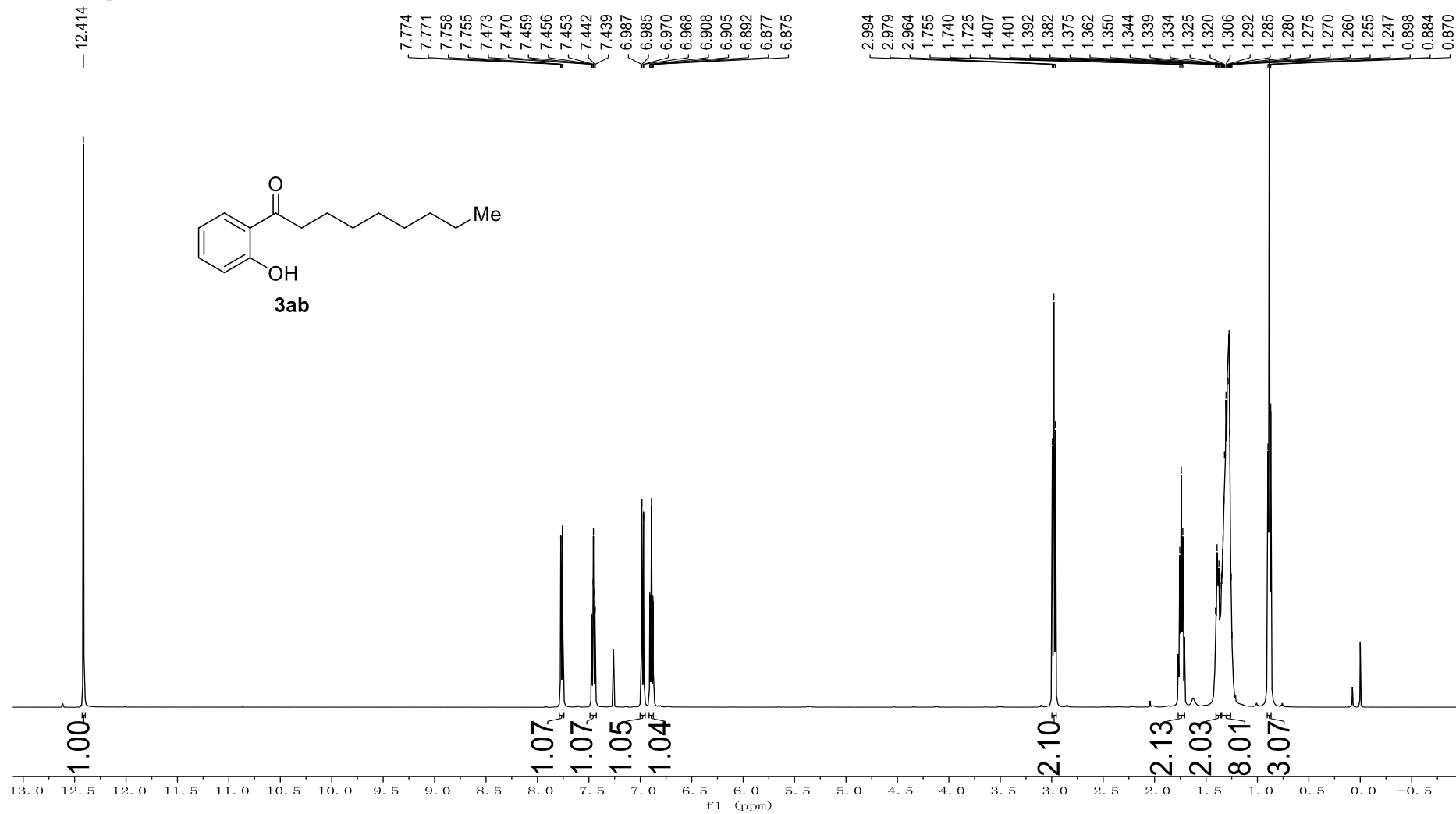
^1H NMR-spectrum (400 MHz, CDCl_3) of **3aa**



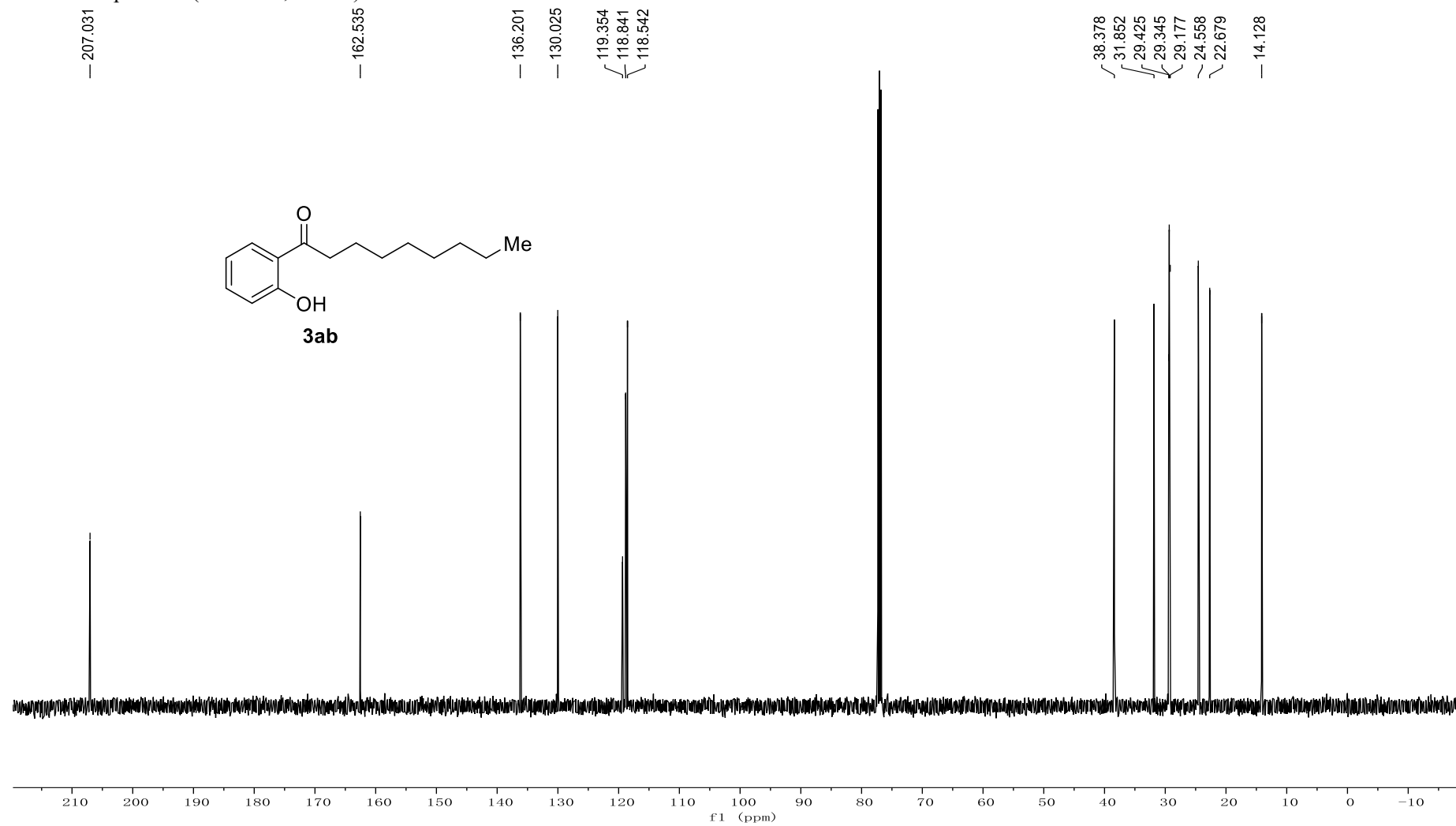
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3aa**



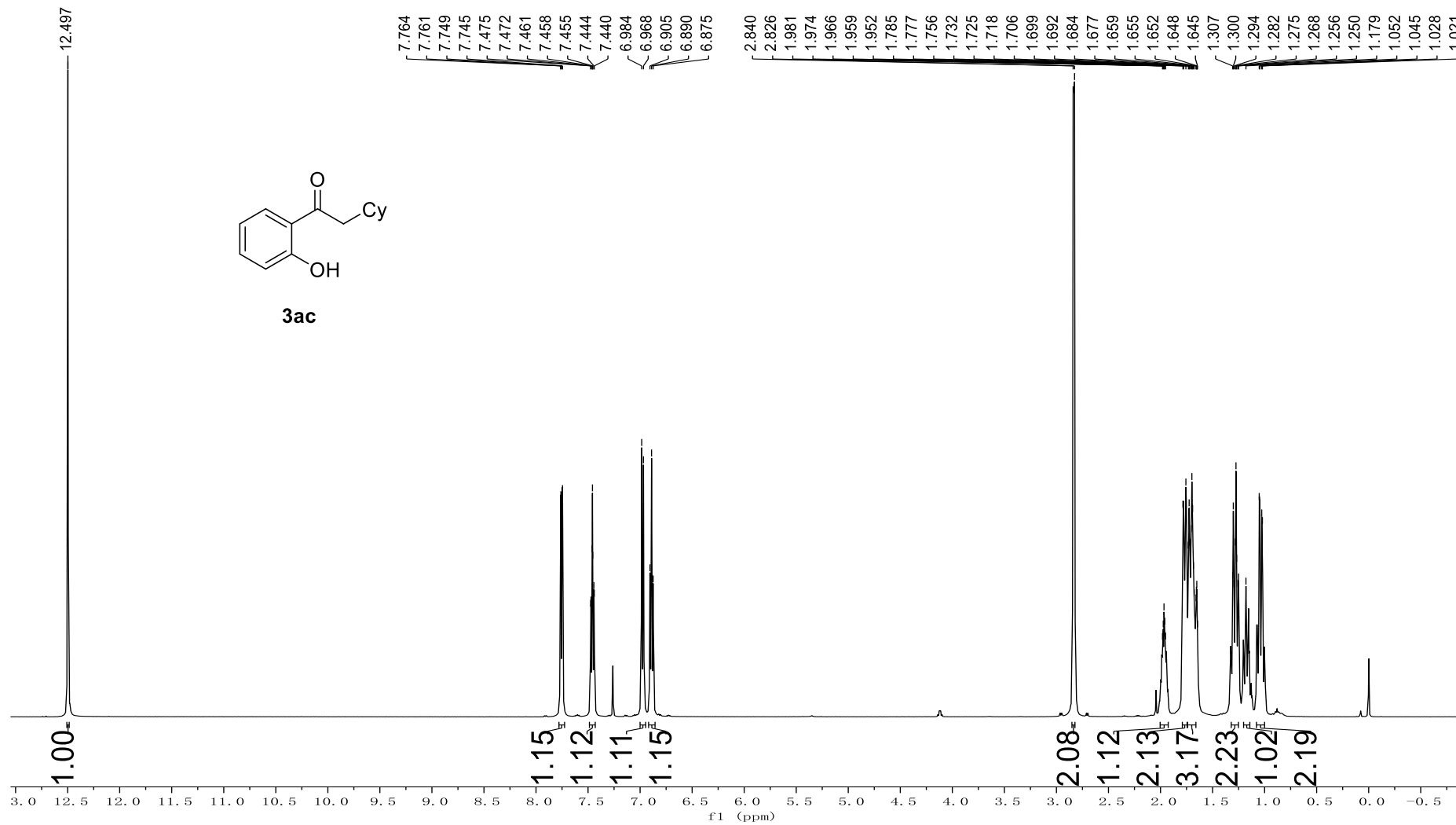
^1H NMR-spectrum (500 MHz, CDCl_3) of **3ab**



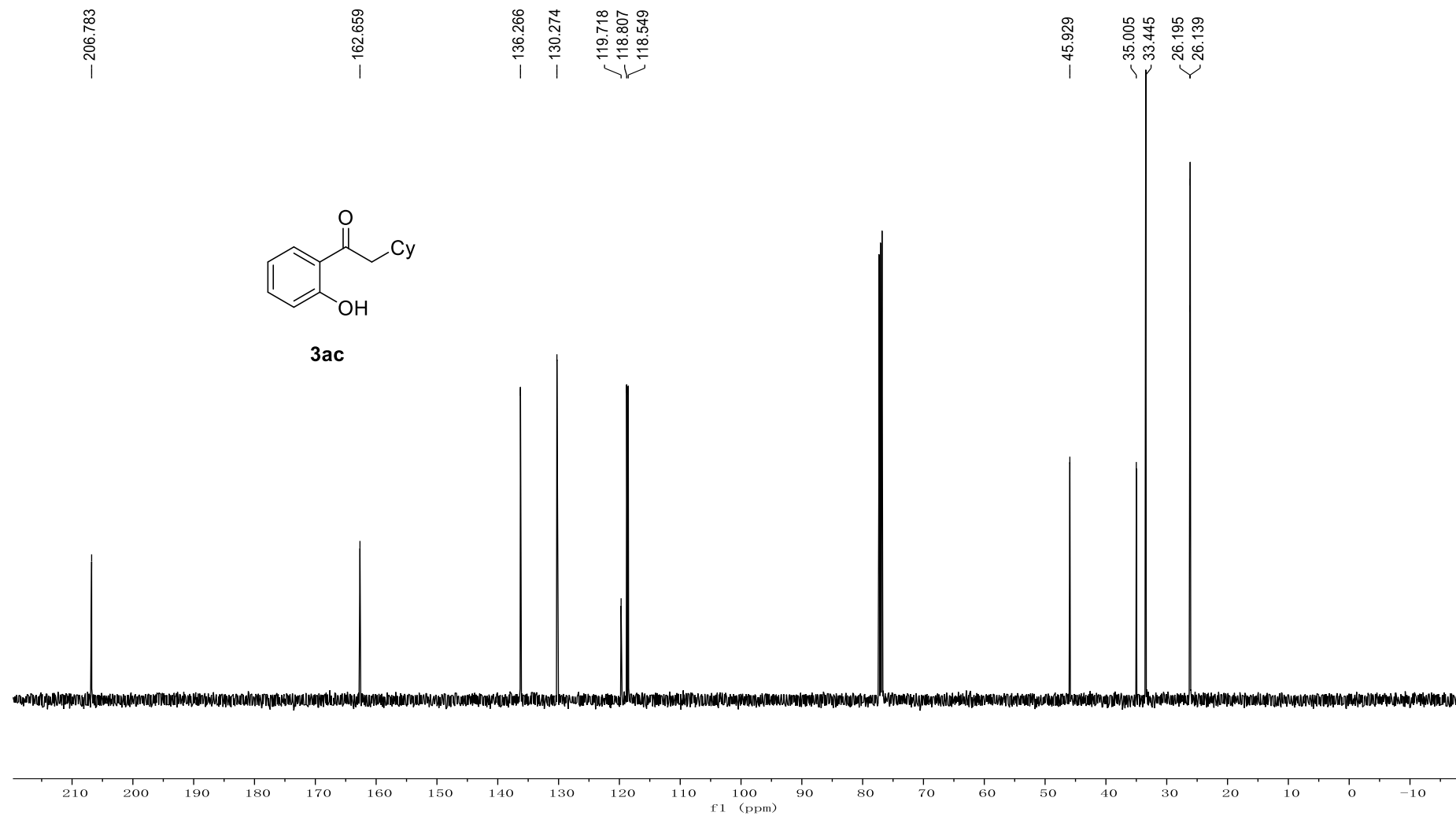
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ab**



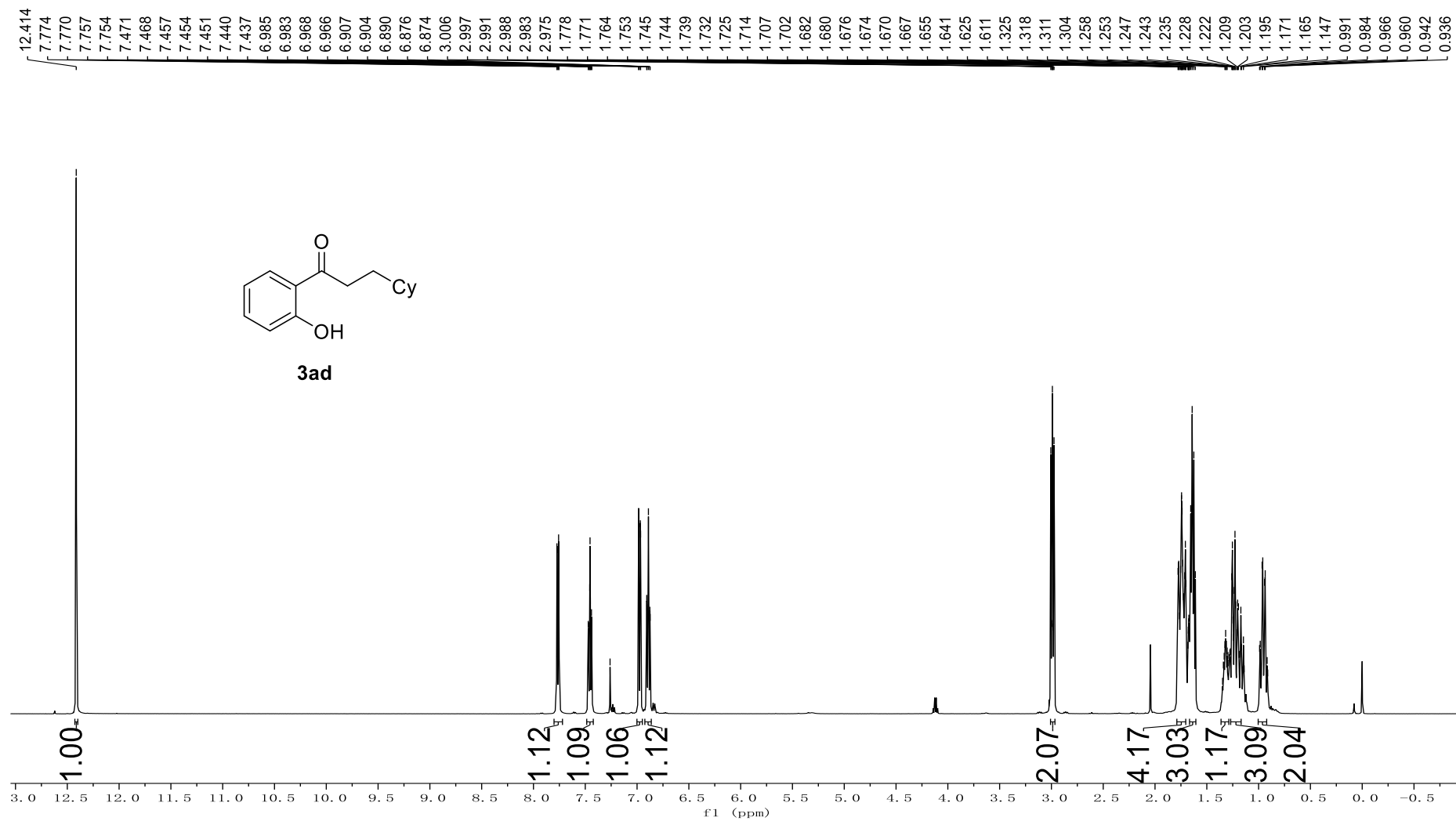
^1H NMR-spectrum (500 MHz, CDCl_3) of **3ac**



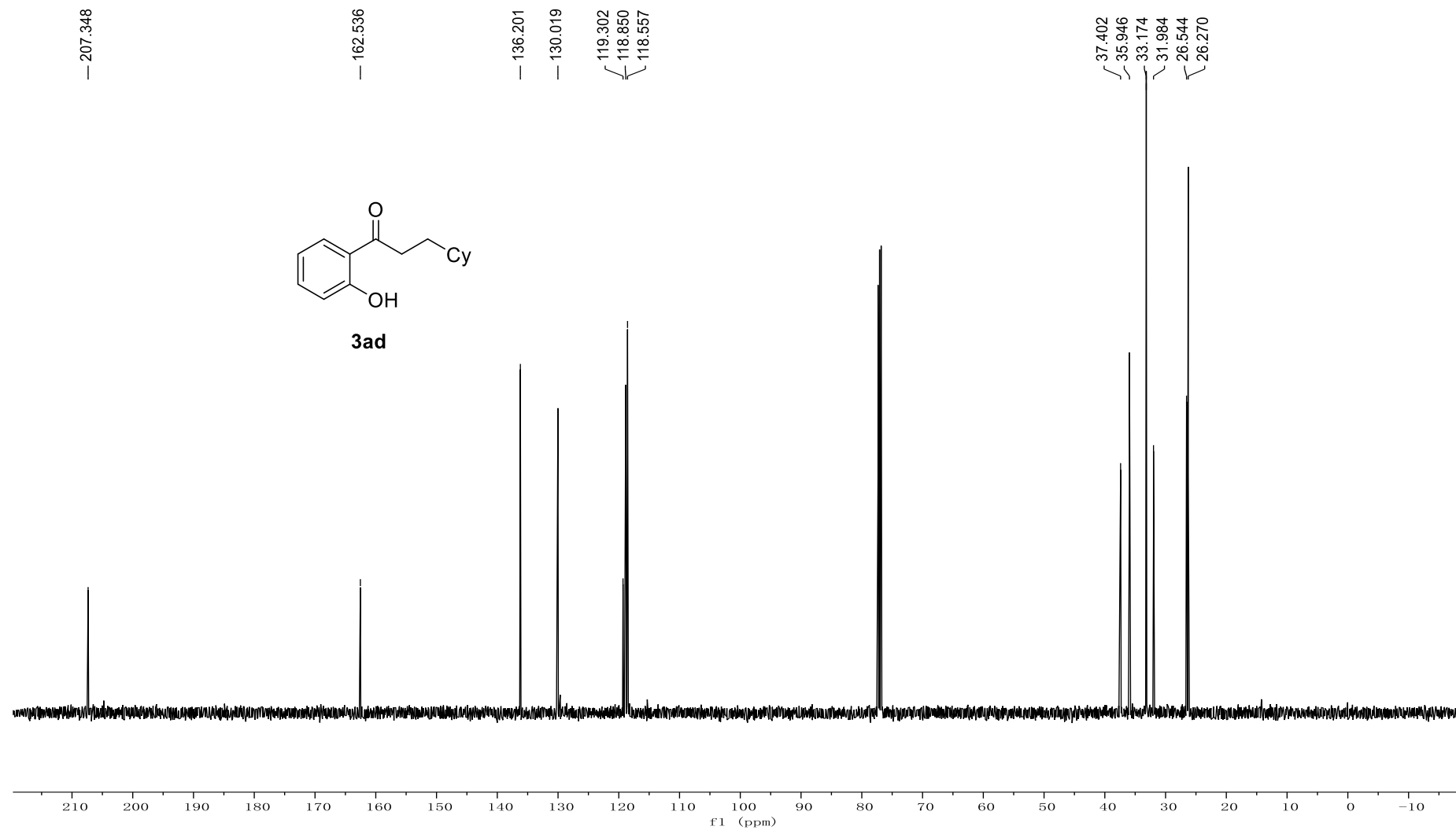
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ac**



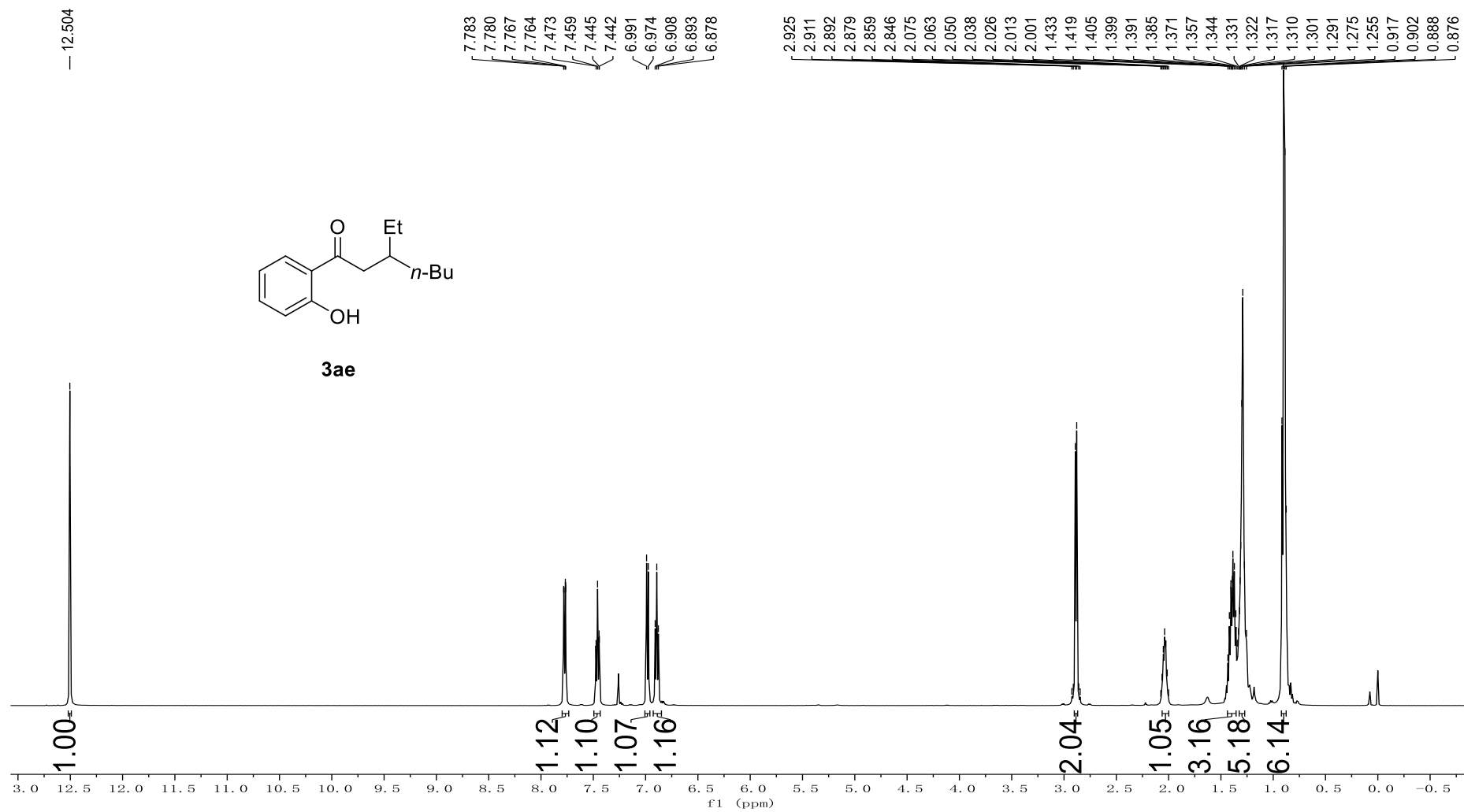
¹H NMR-spectrum (500 MHz, CDCl₃) of **3ad**



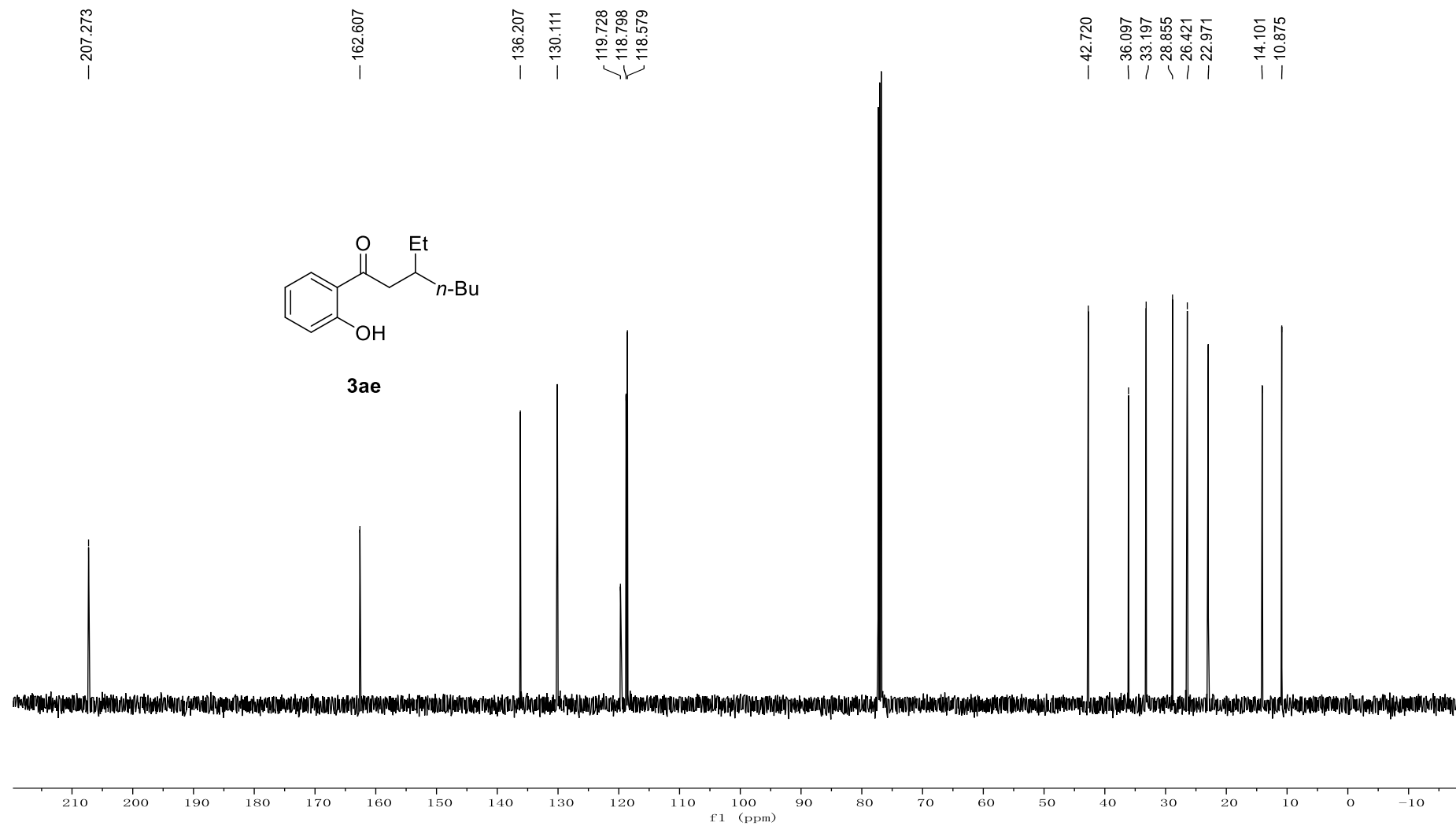
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ad**



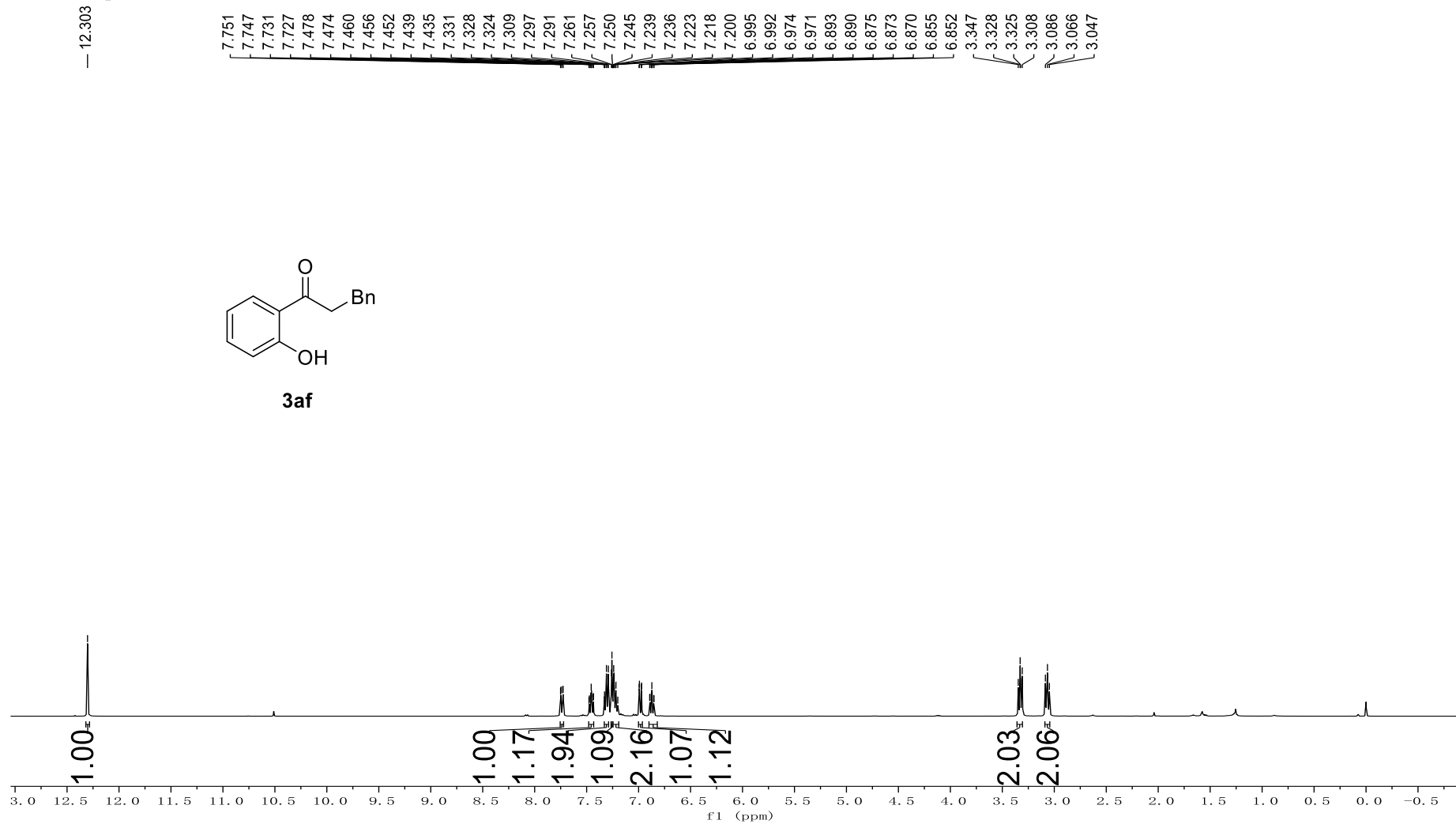
^1H NMR-spectrum (500 MHz, CDCl_3) of **3ae**



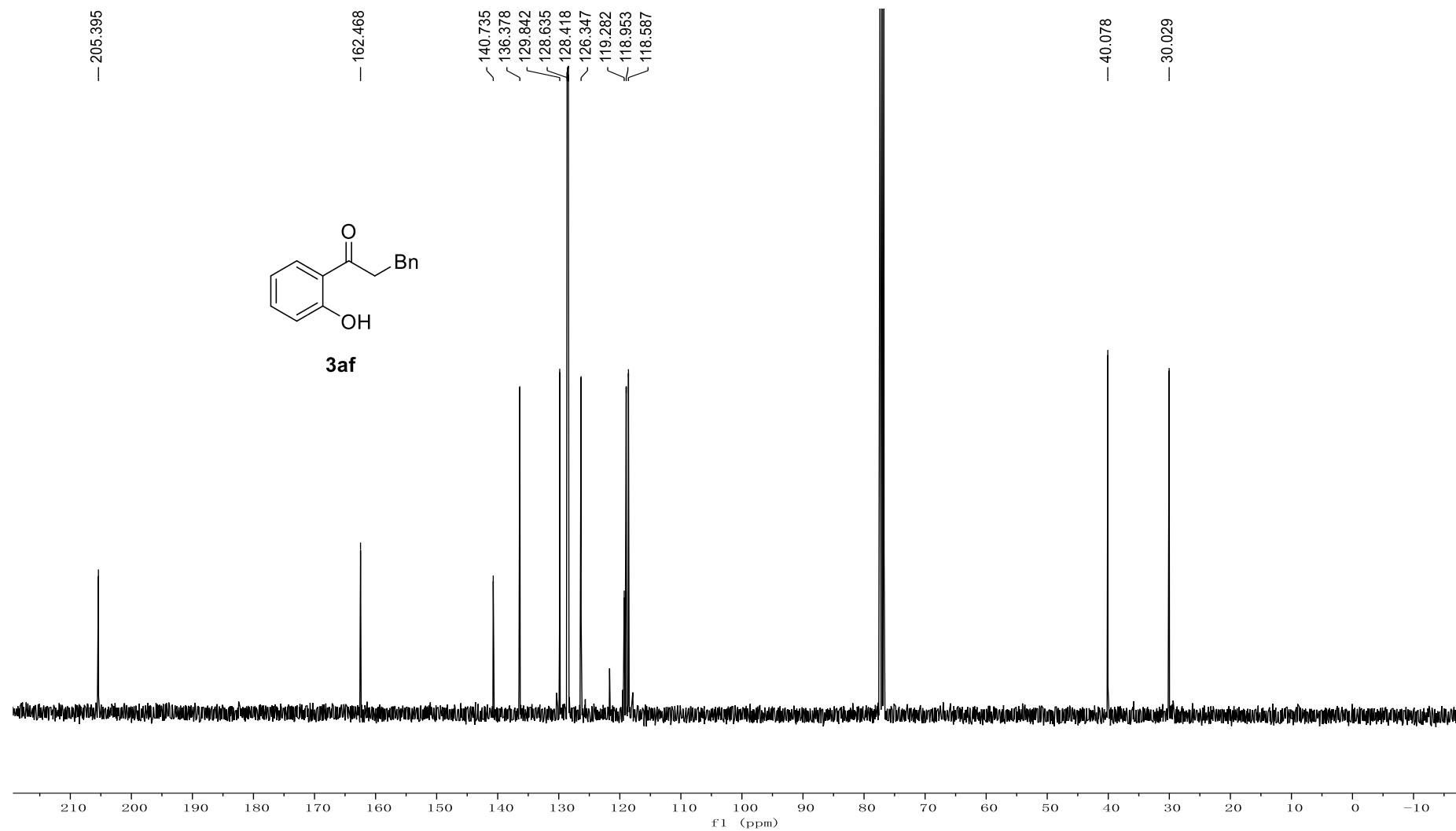
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ae**



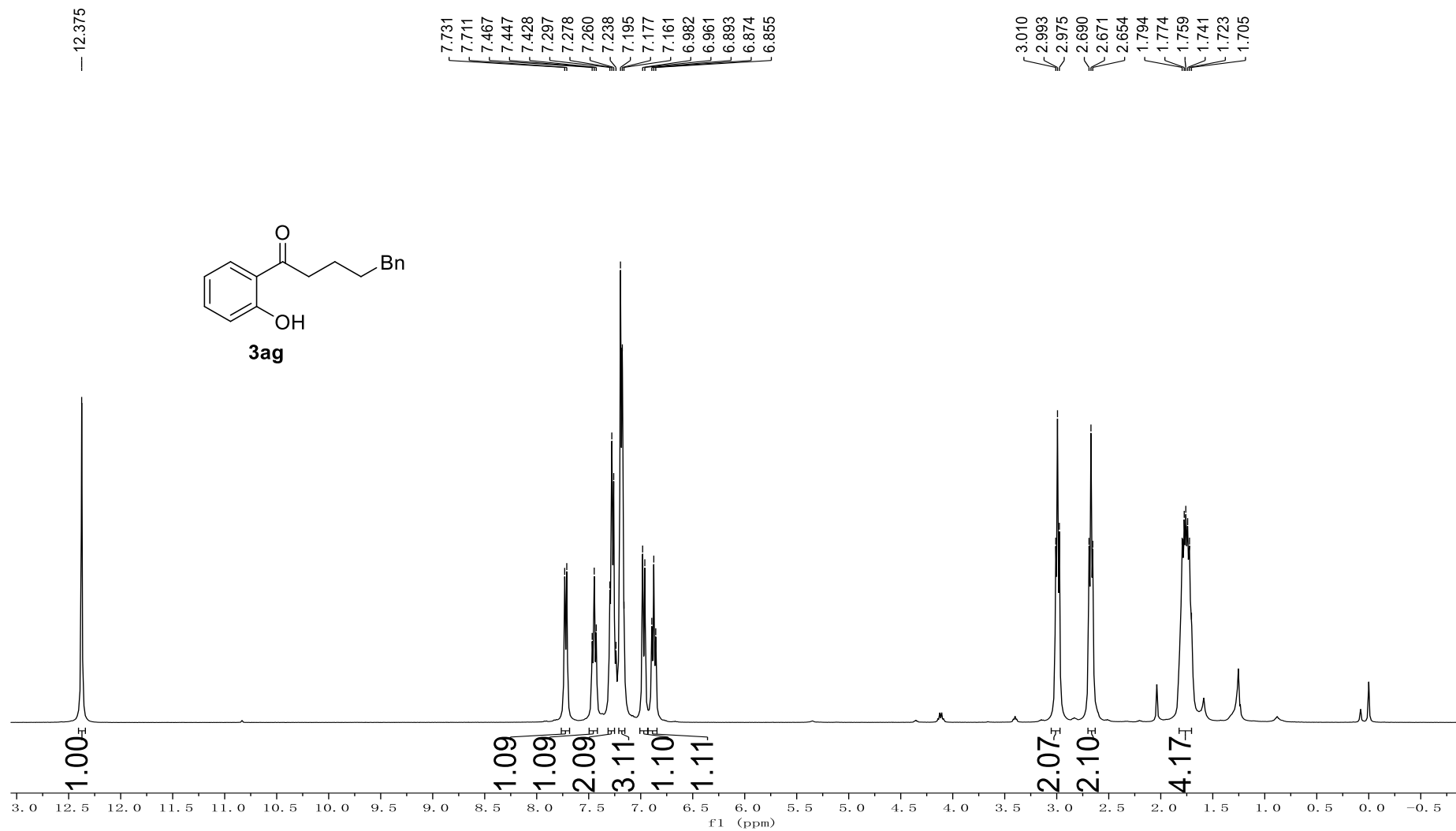
¹H NMR-spectrum (400 MHz, CDCl₃) of **3af**



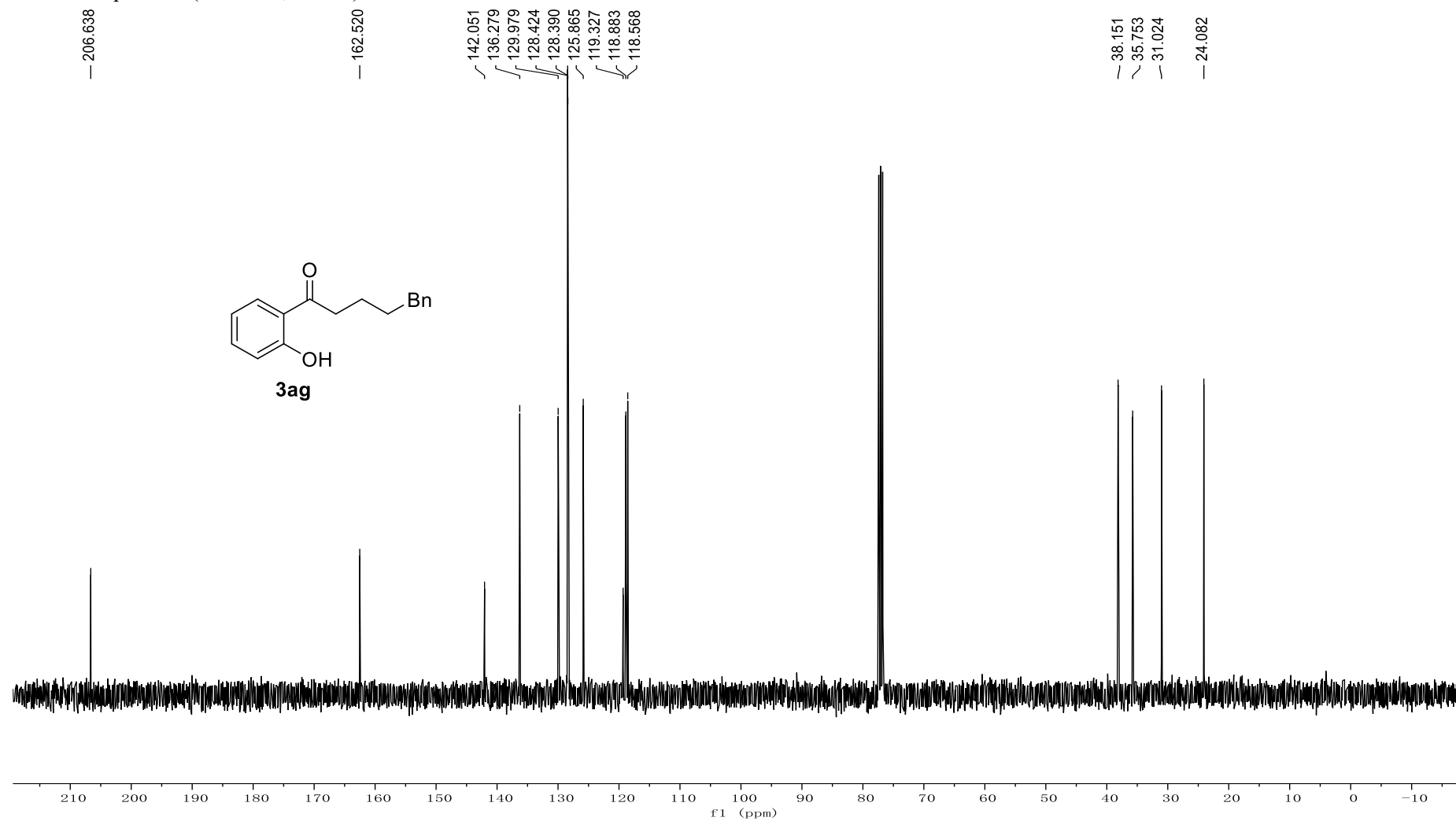
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3af**



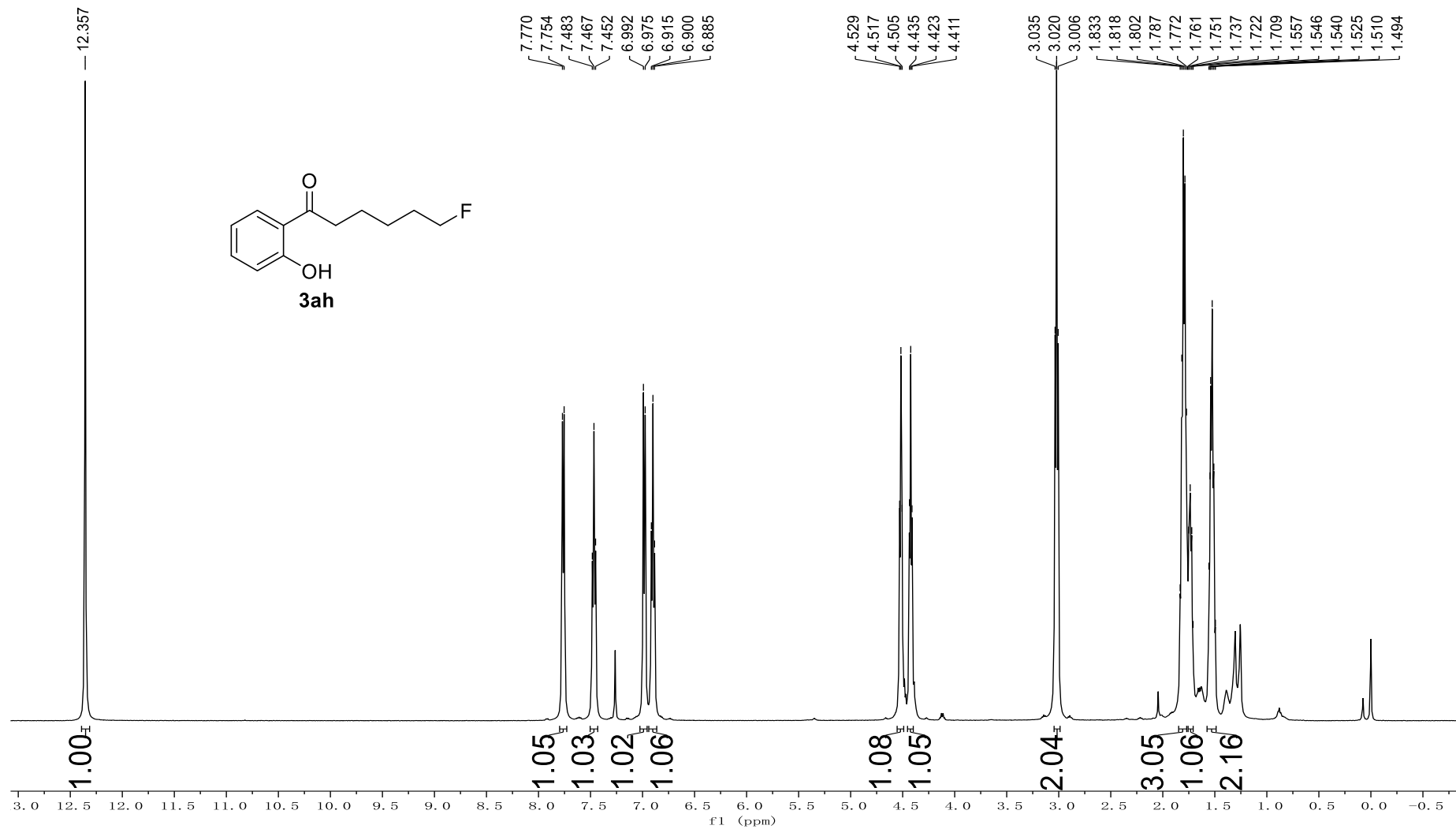
^1H NMR-spectrum (400 MHz, CDCl_3) of **3ah**



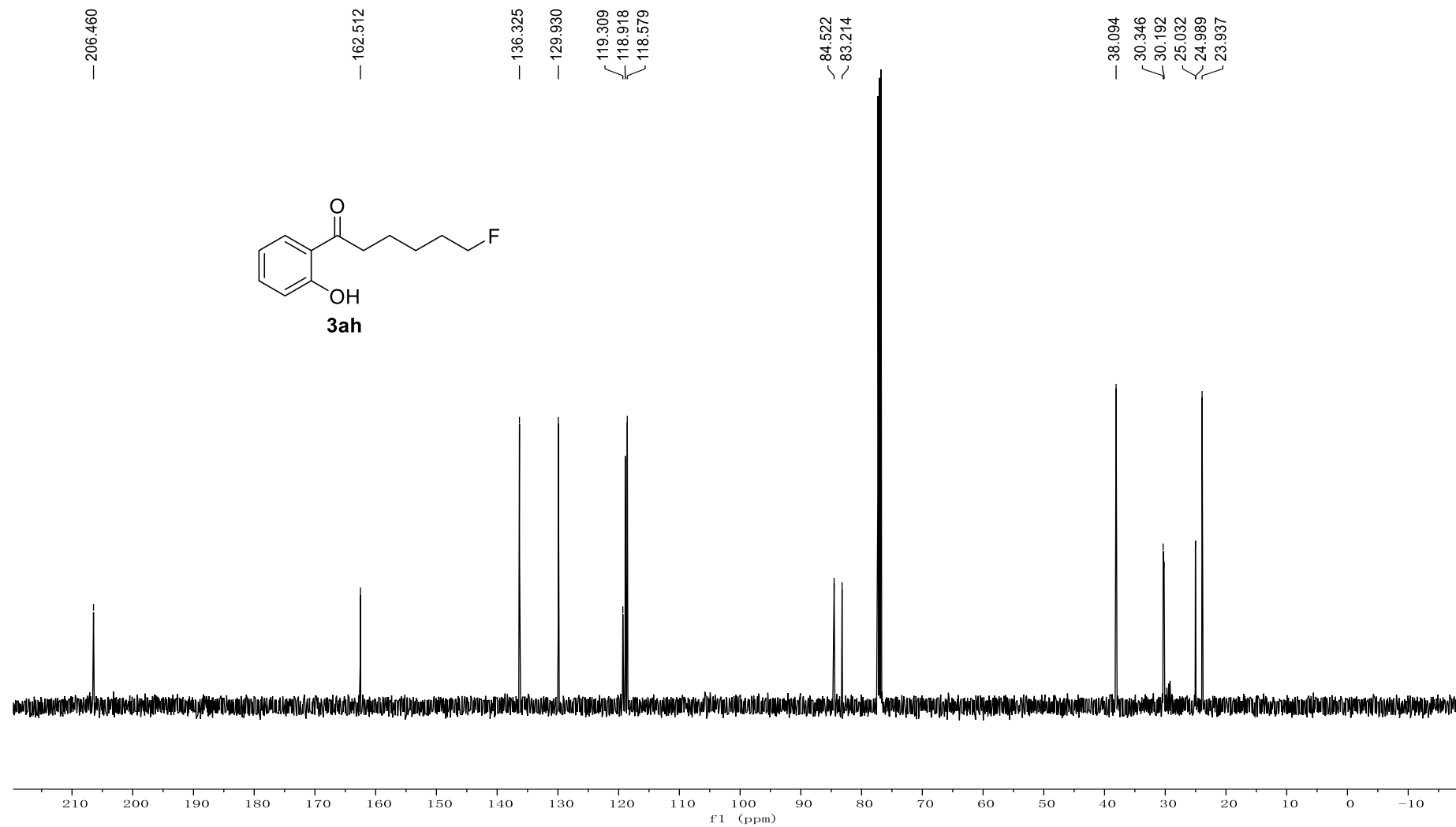
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ah**



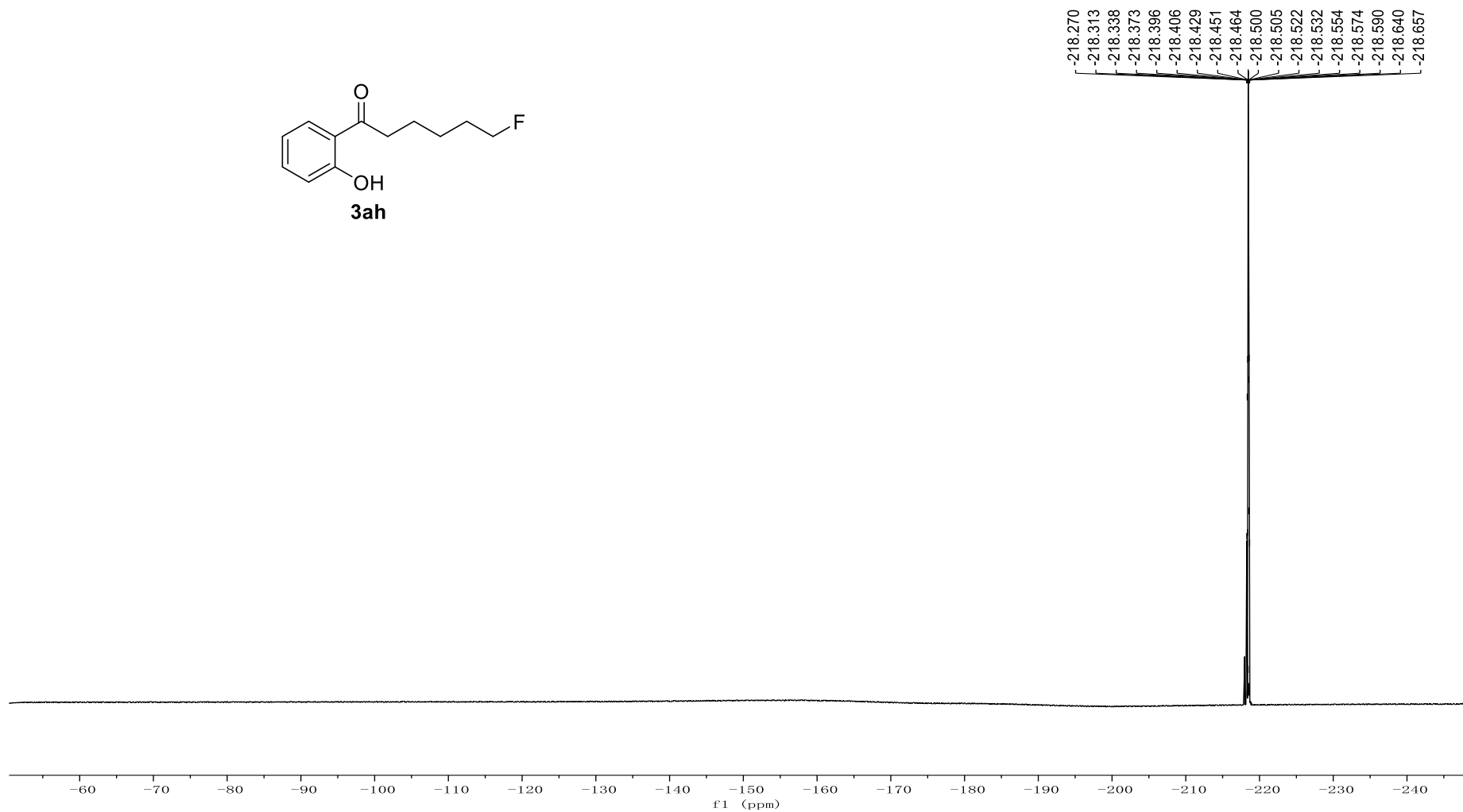
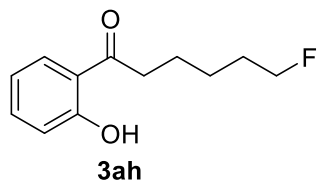
^1H NMR-spectrum (500 MHz, CDCl_3) of **3ah**



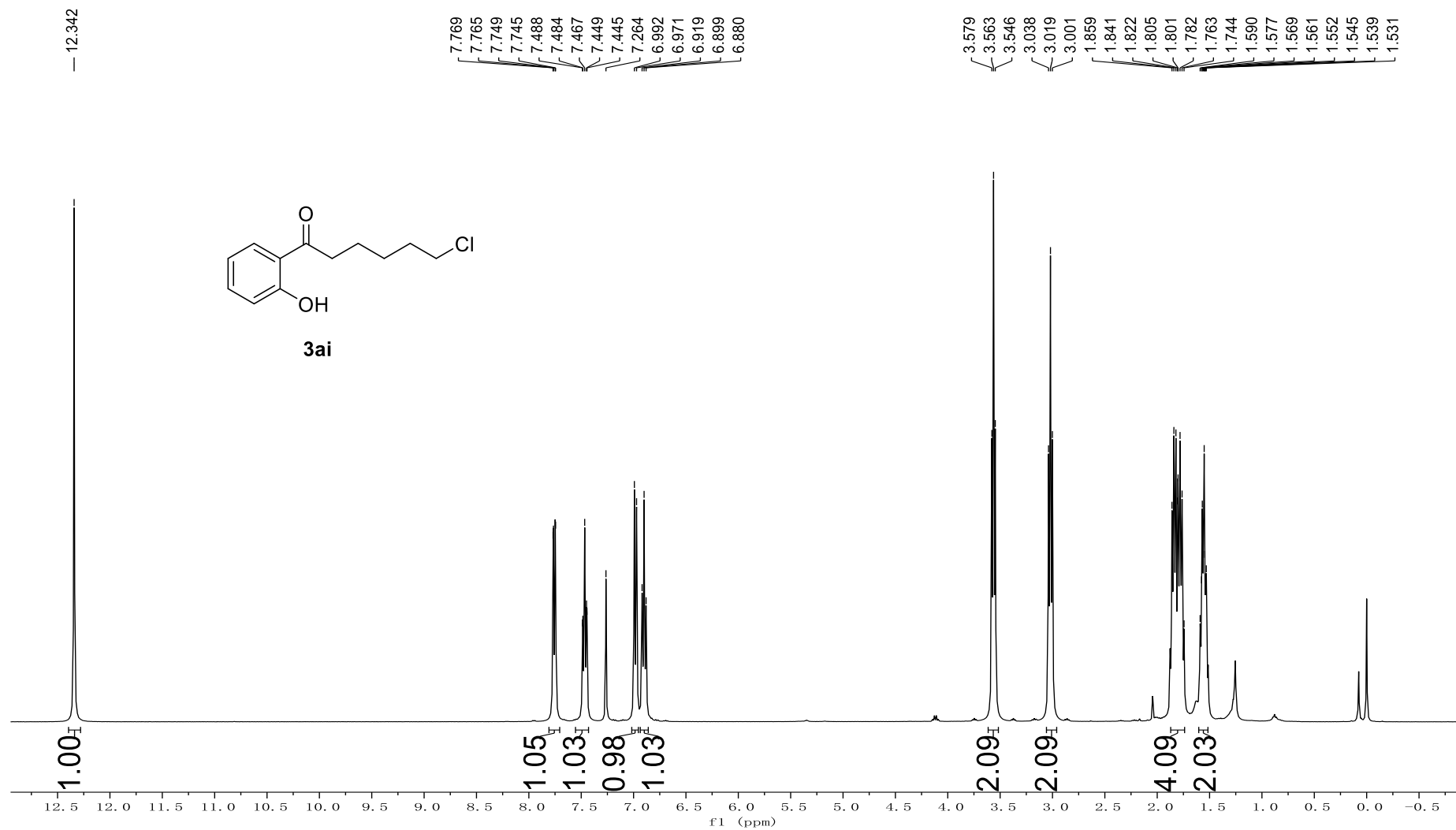
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ah**



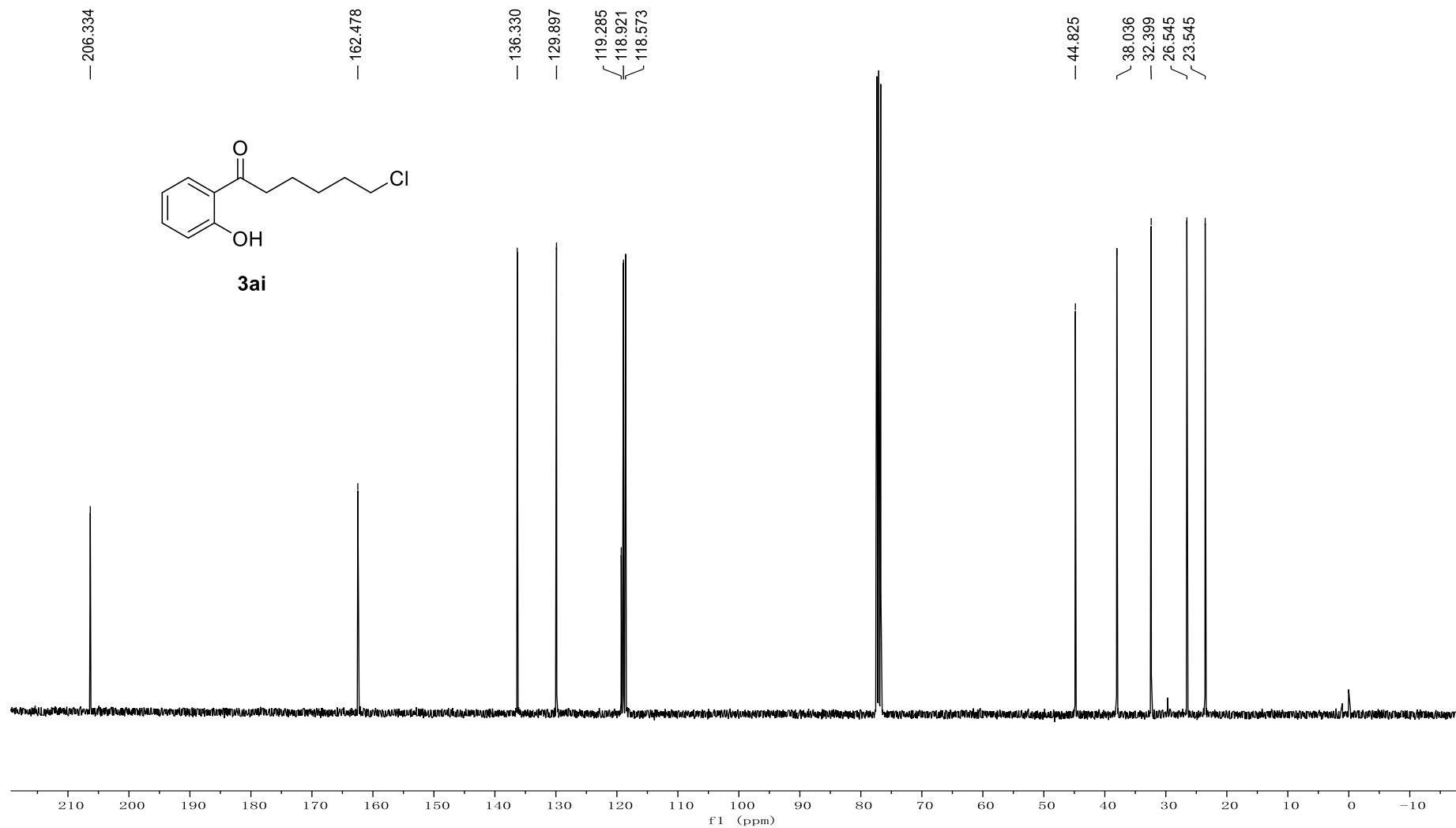
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **3ah**



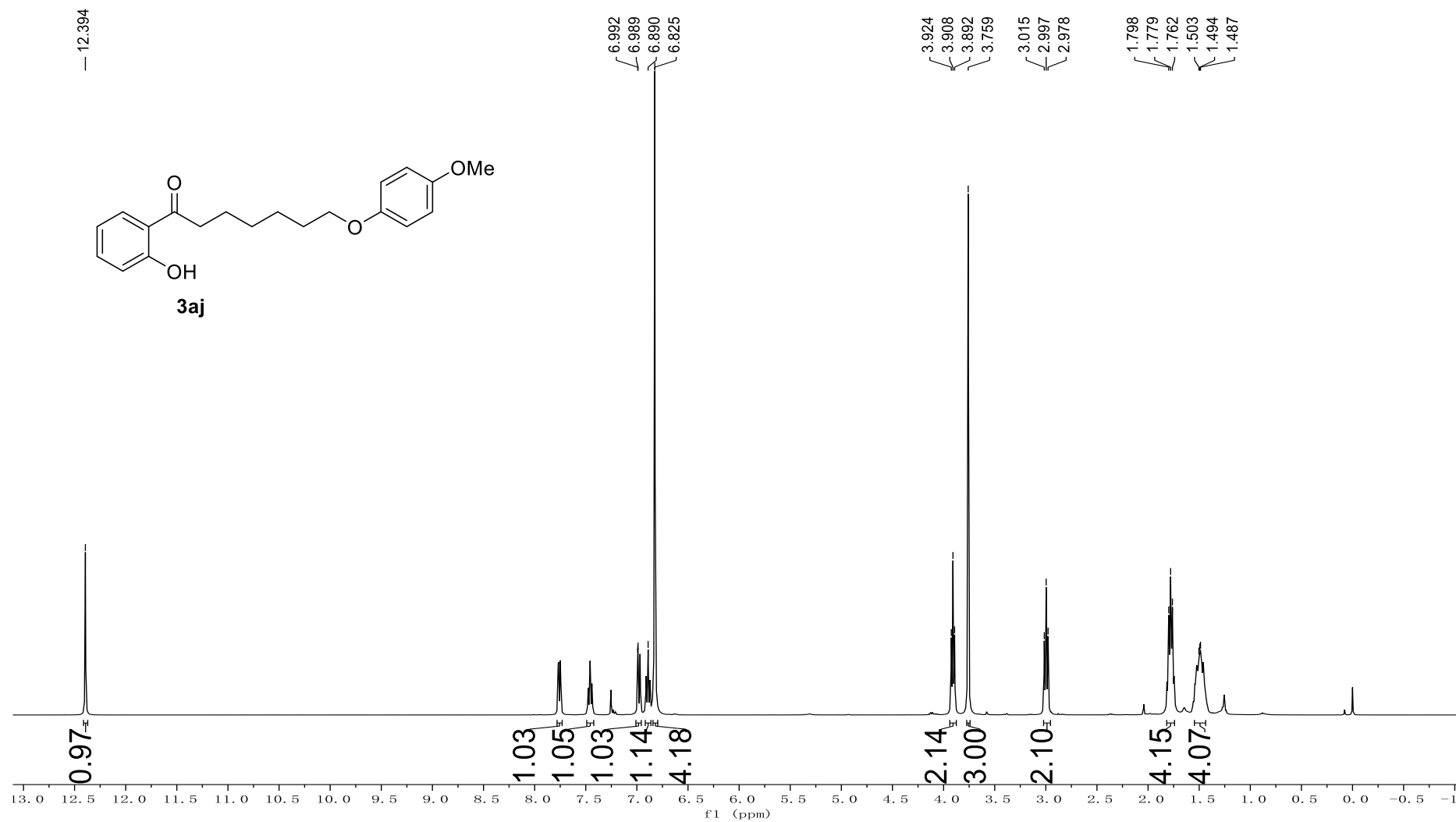
^1H NMR-spectrum (400 MHz, CDCl_3) of **3ai**



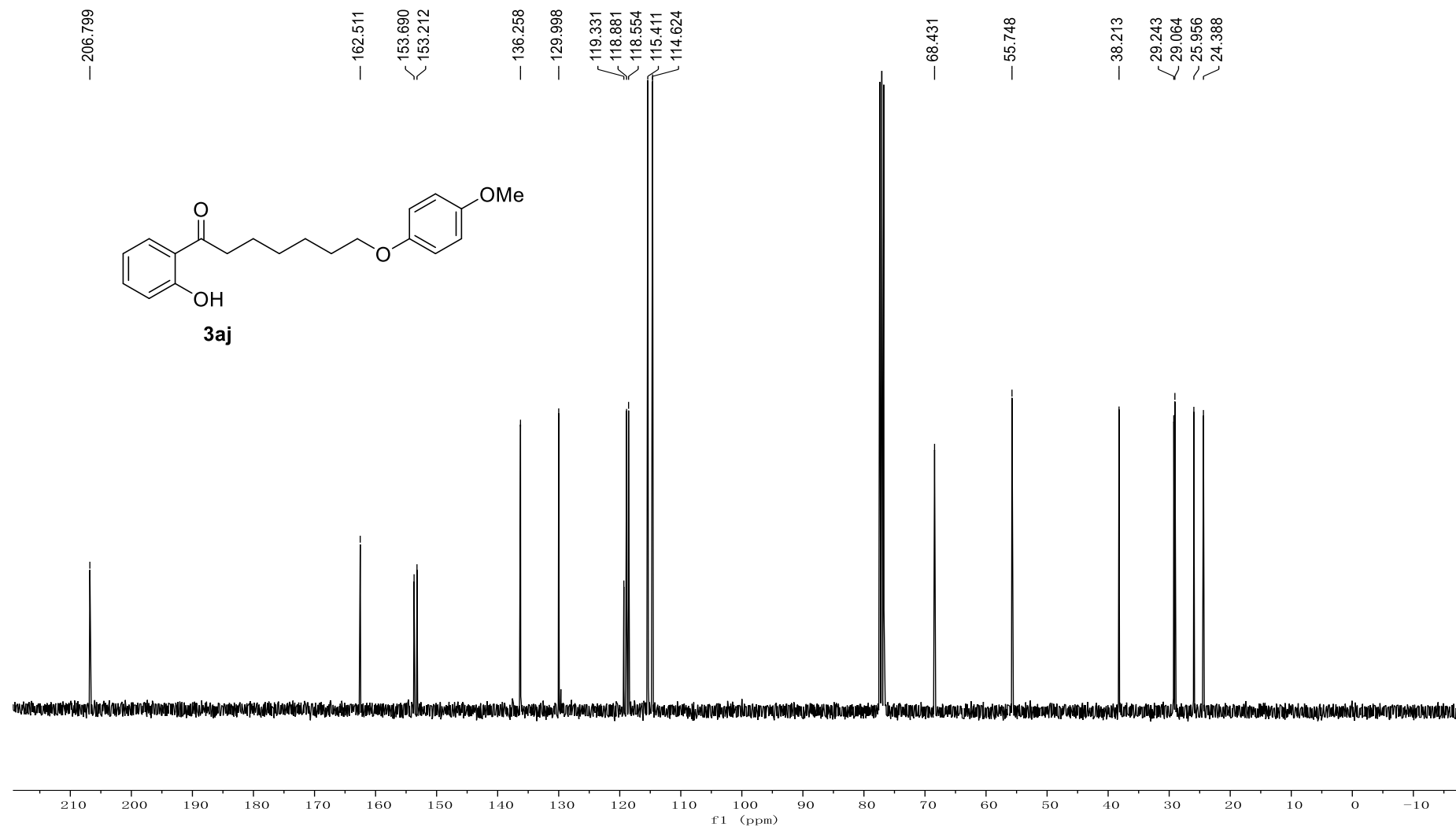
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ai**



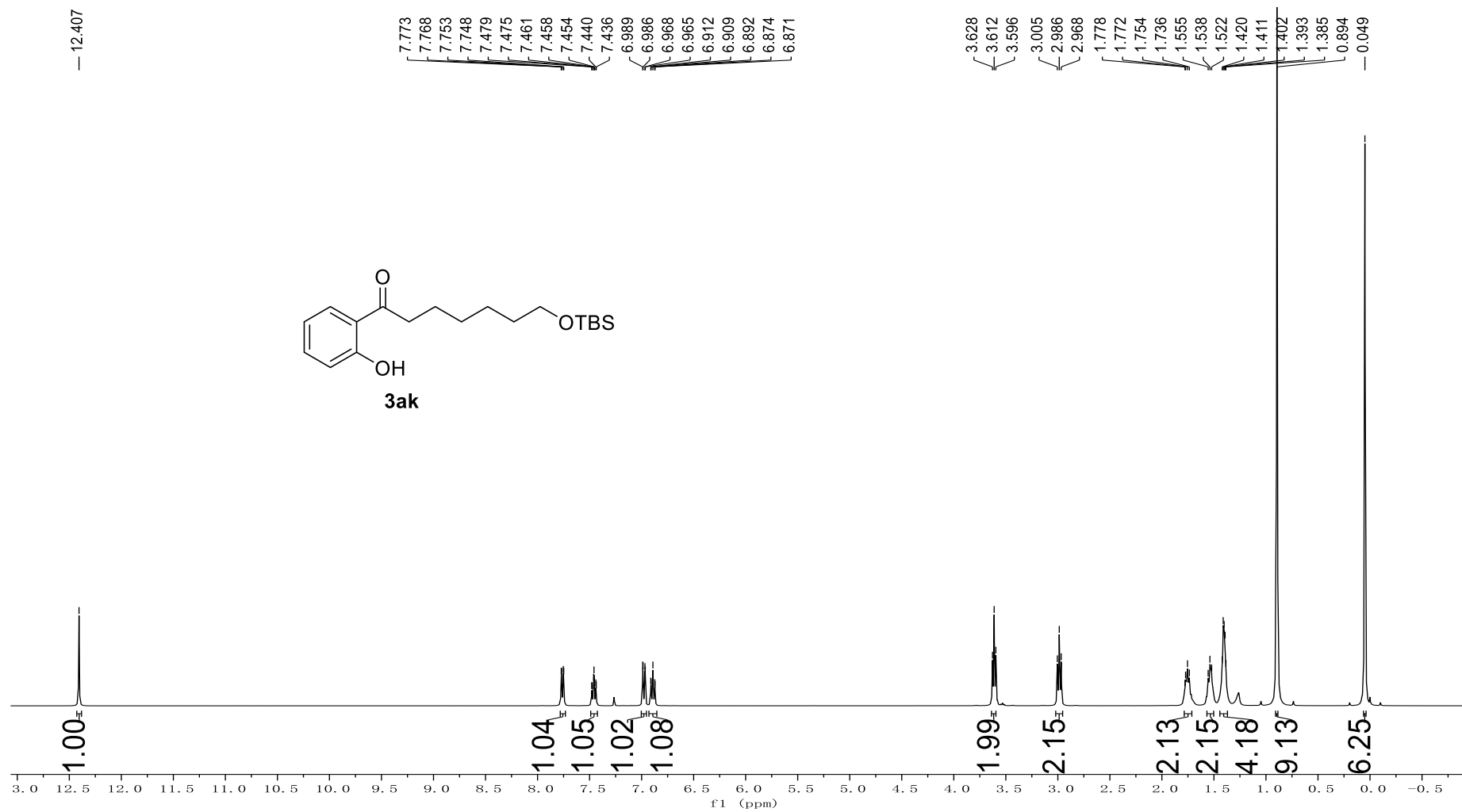
¹H NMR-spectrum (400 MHz, CDCl₃) of **3aj**



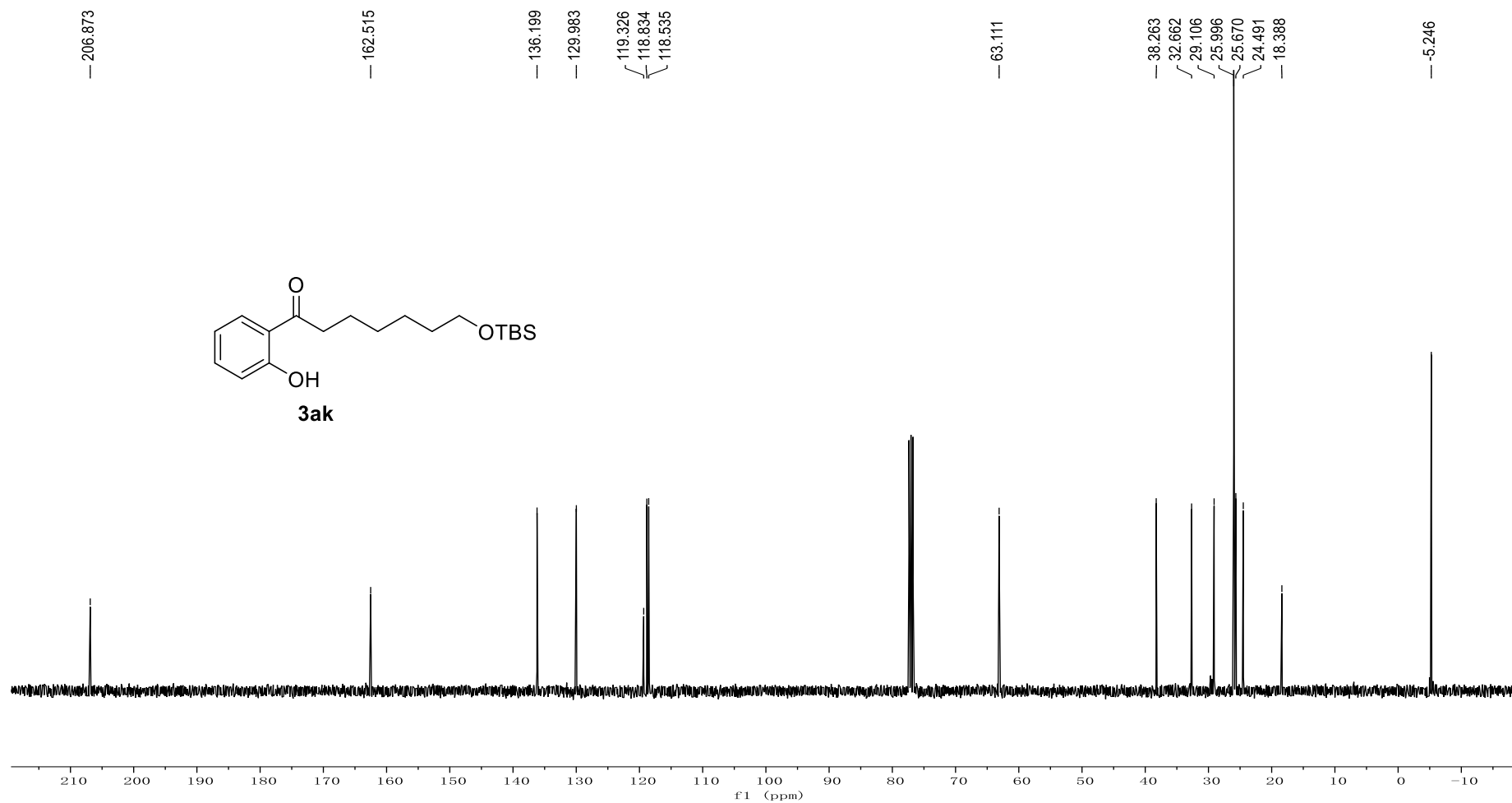
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3aj**



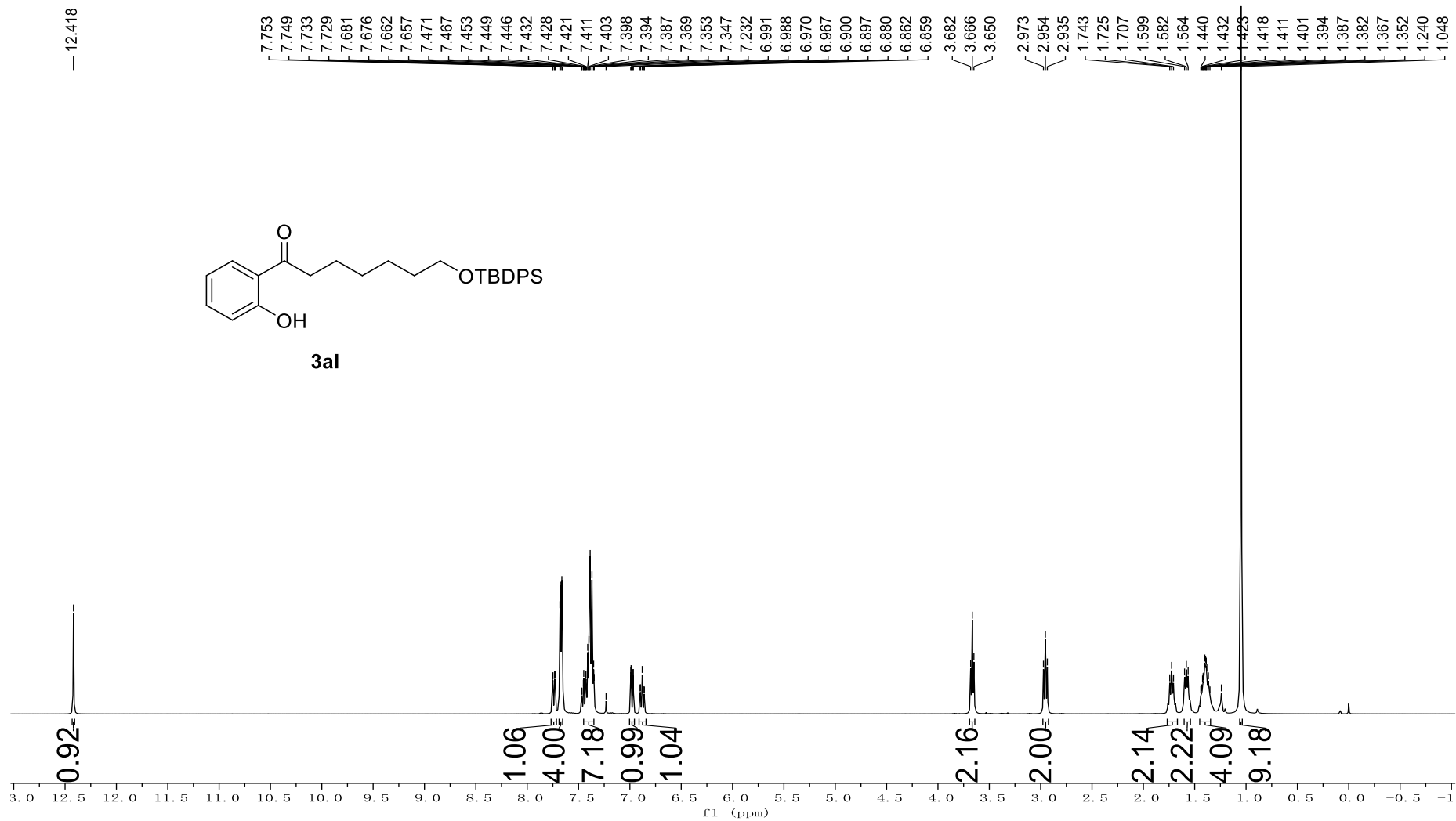
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ak**



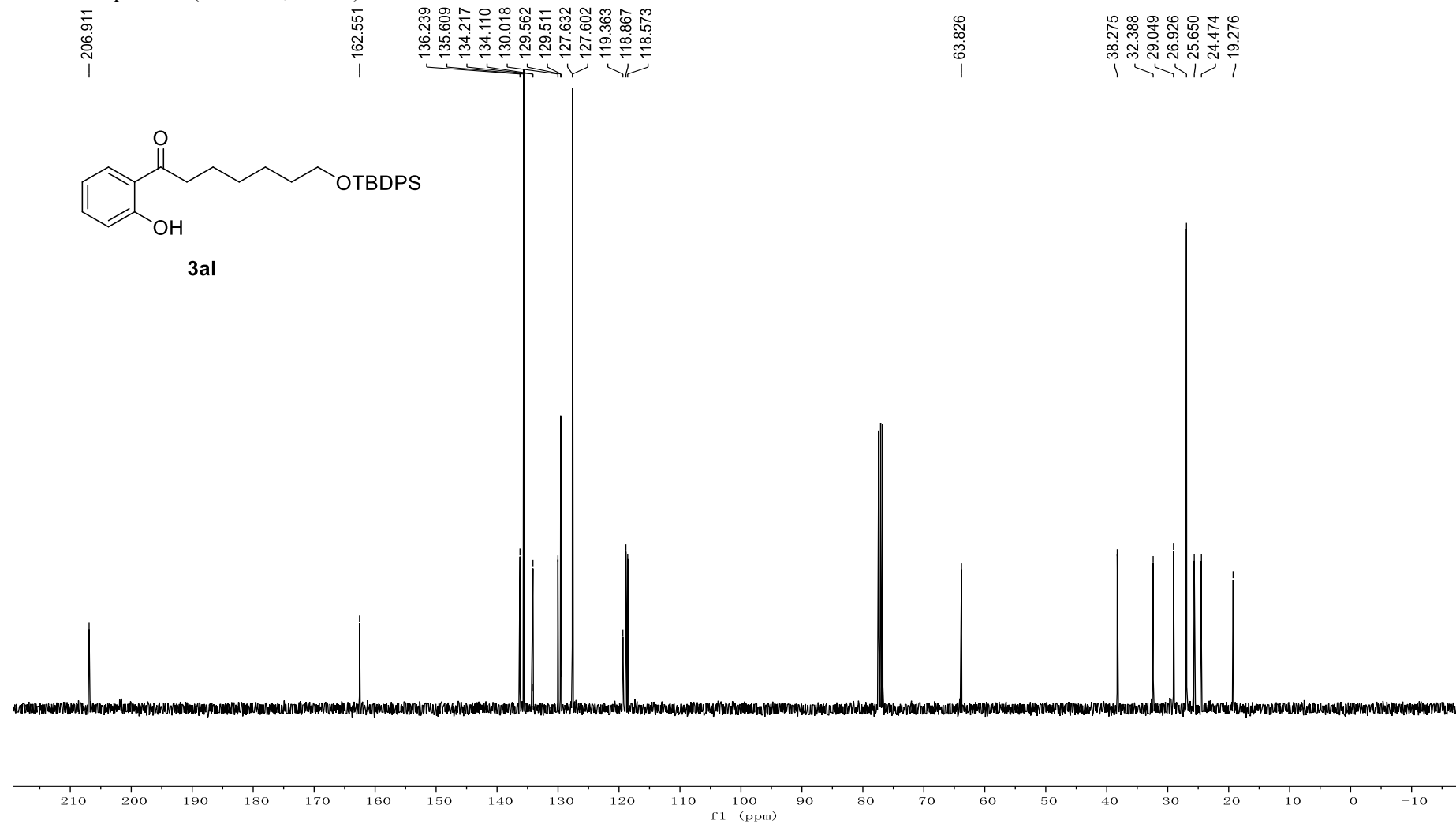
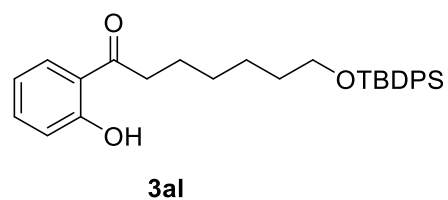
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ak**



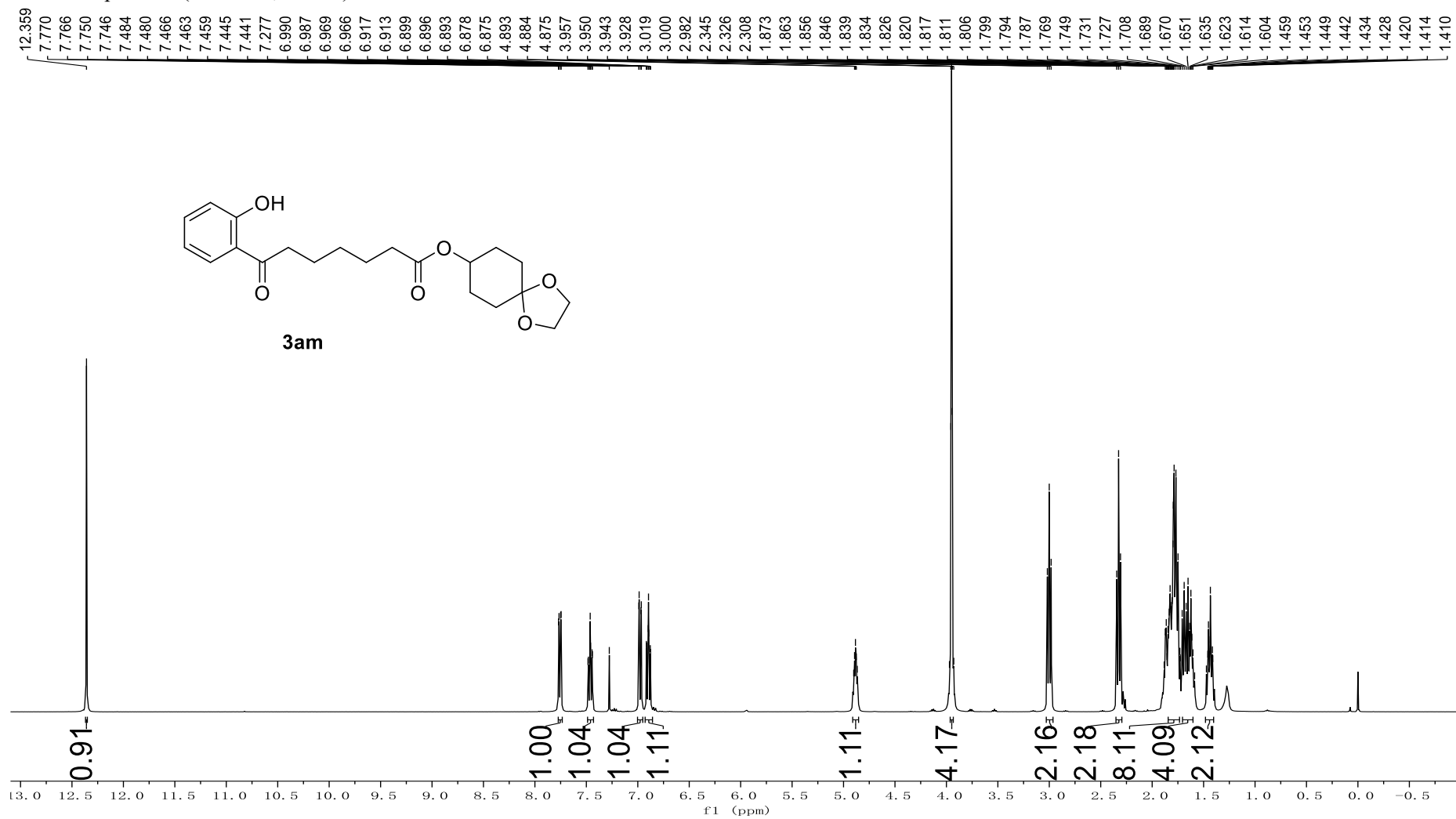
^1H NMR-spectrum (400 MHz, CDCl_3) of **3al**



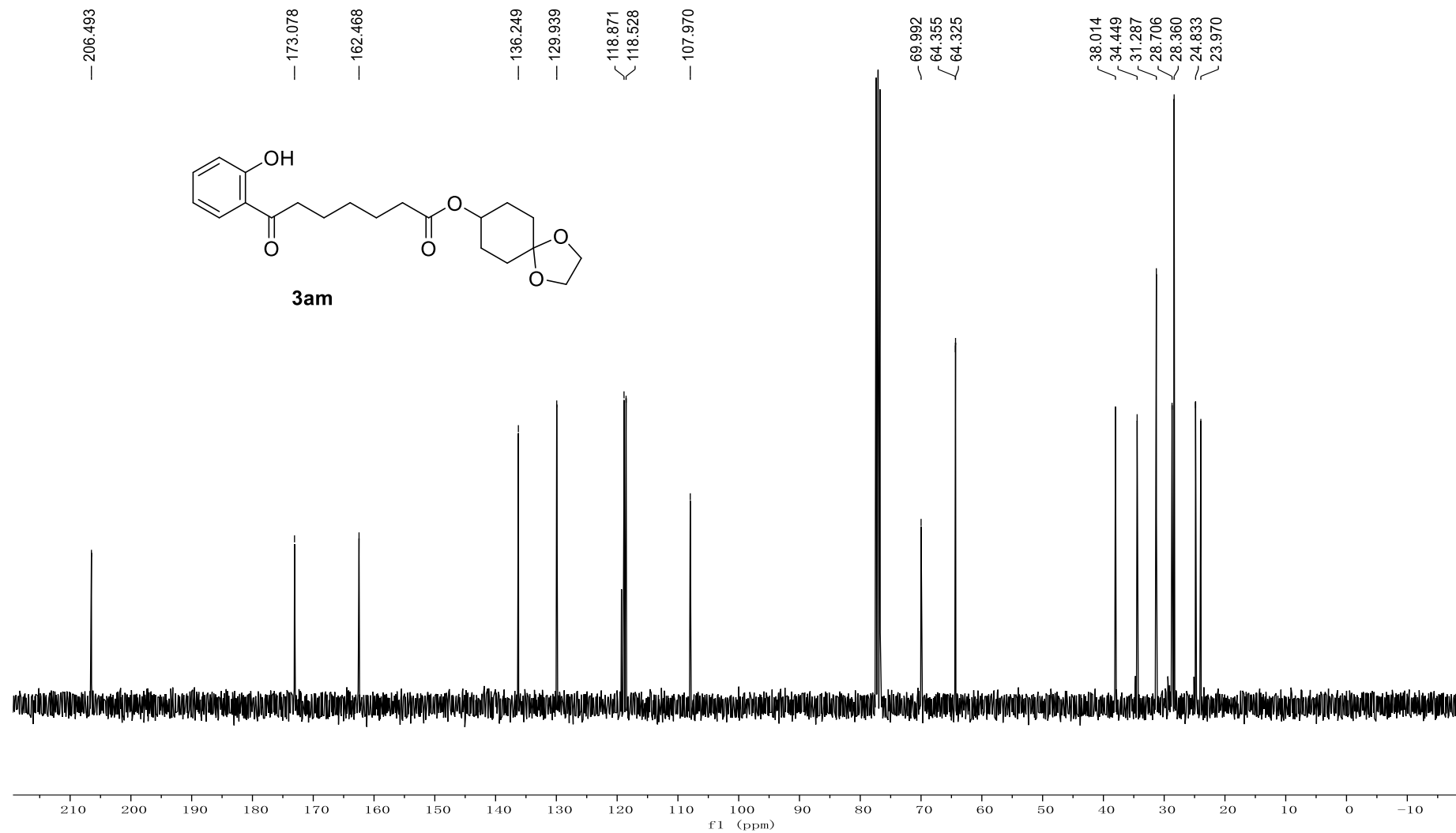
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3al**



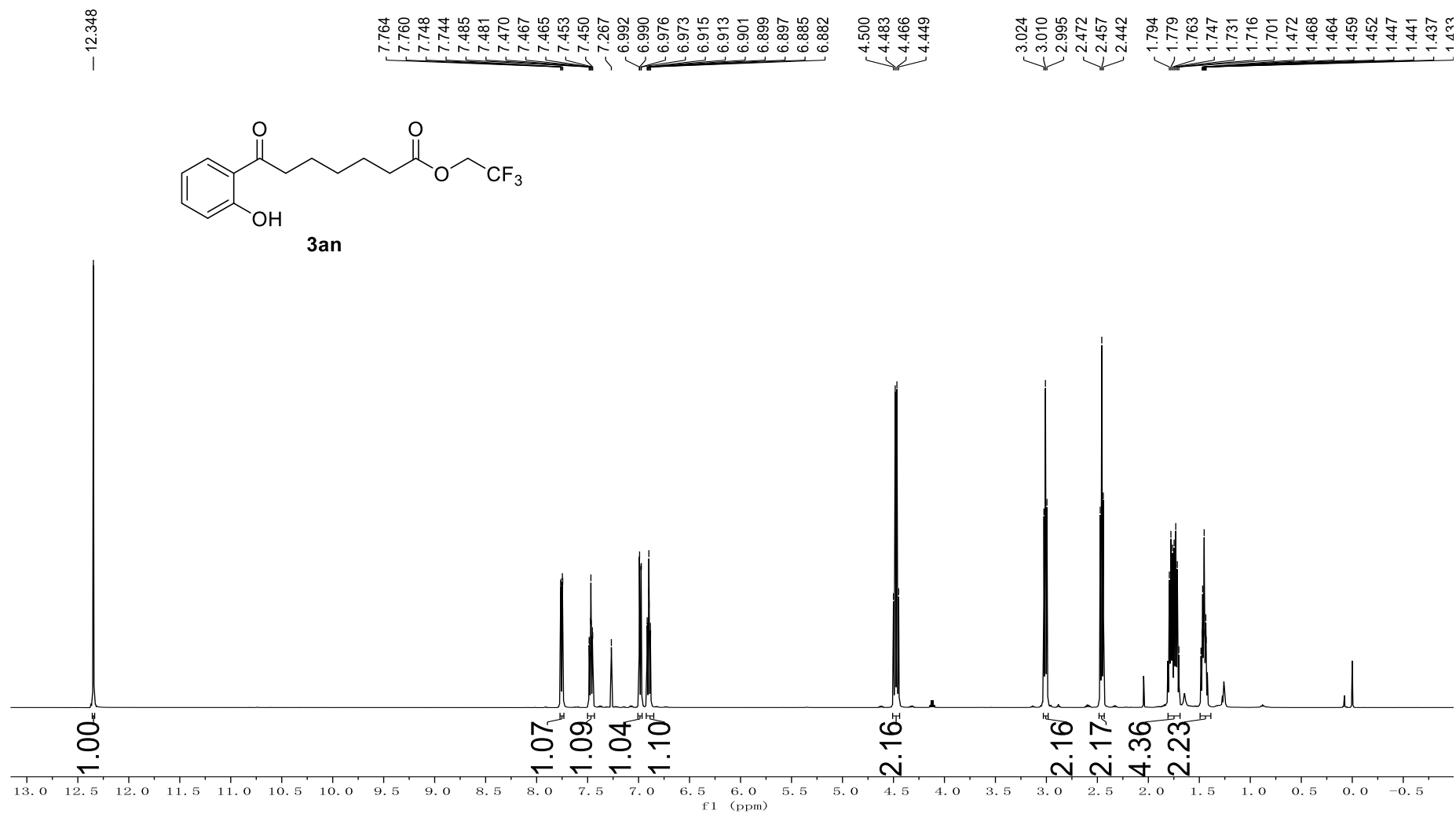
¹H NMR-spectrum (400 MHz, CDCl₃) of **3am**



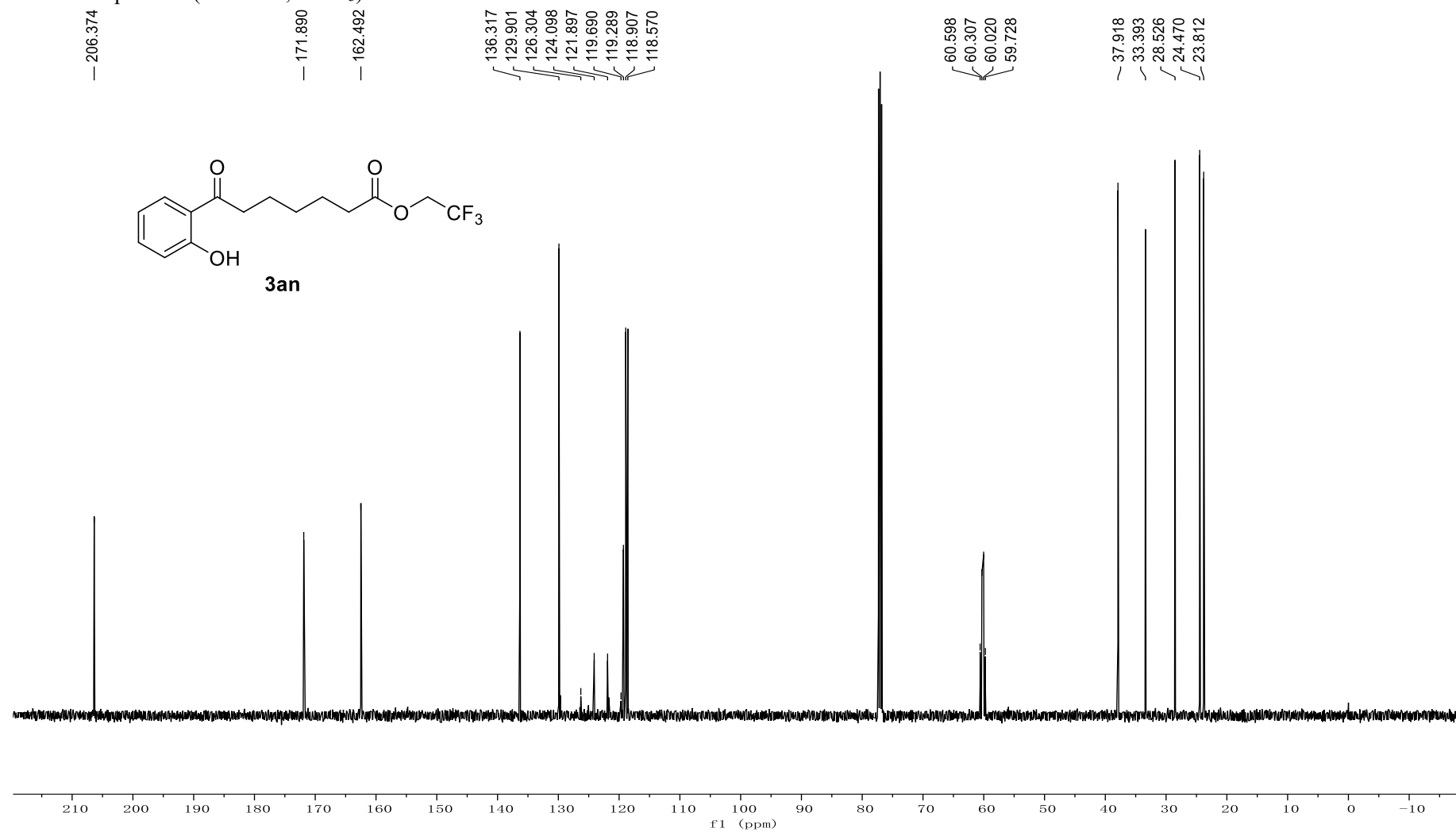
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3am**



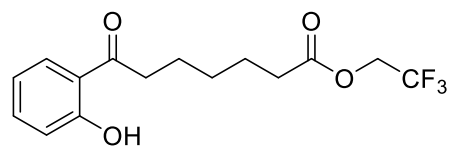
¹H NMR-spectrum (500 MHz, CDCl₃) of **3an**



^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3an**

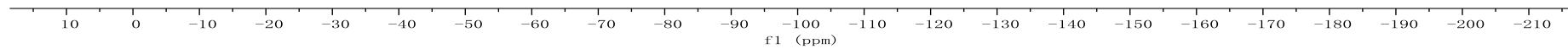


^{19}F NMR-spectrum (376 MHz, CDCl_3) of **3an**

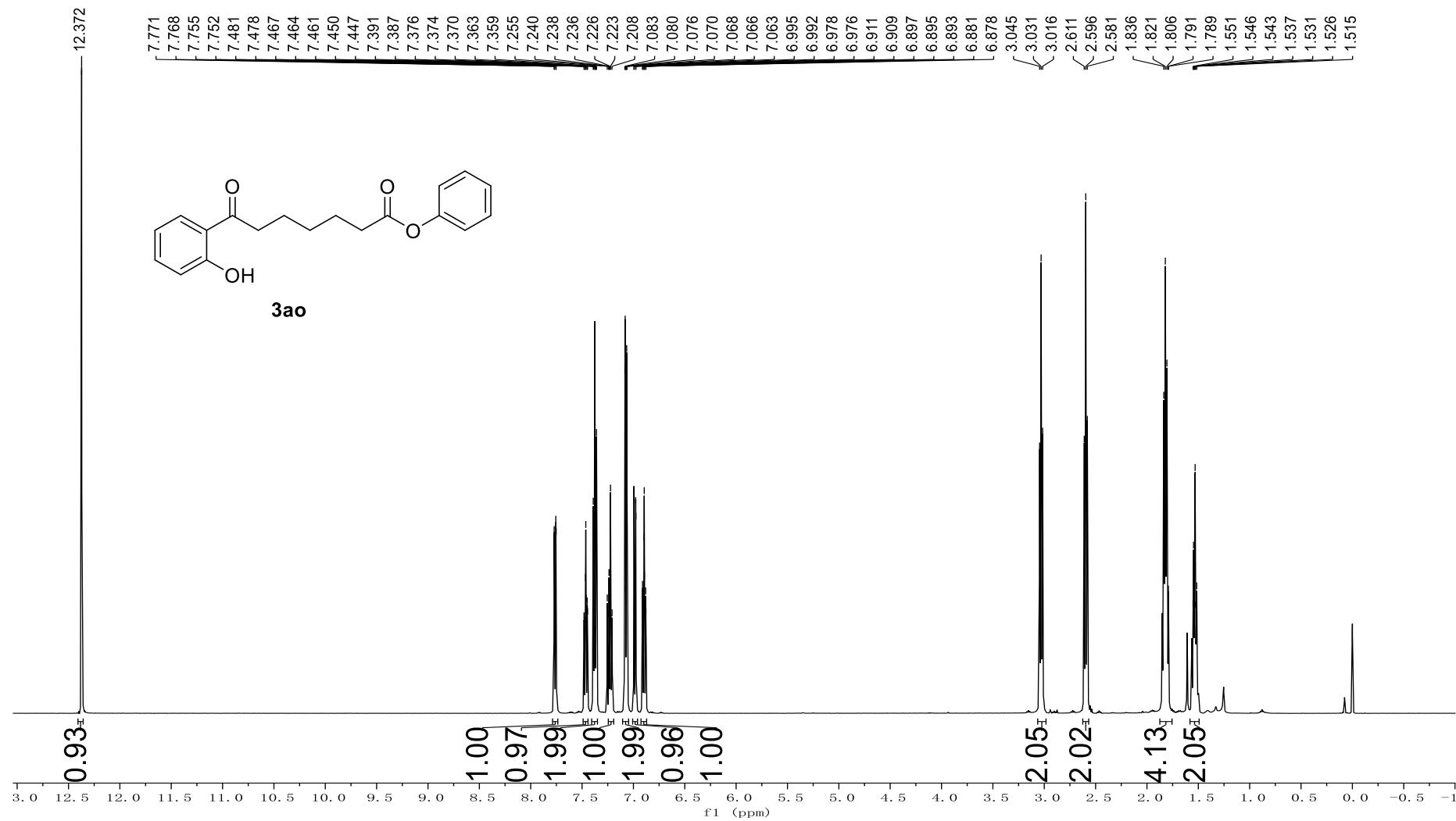


3an

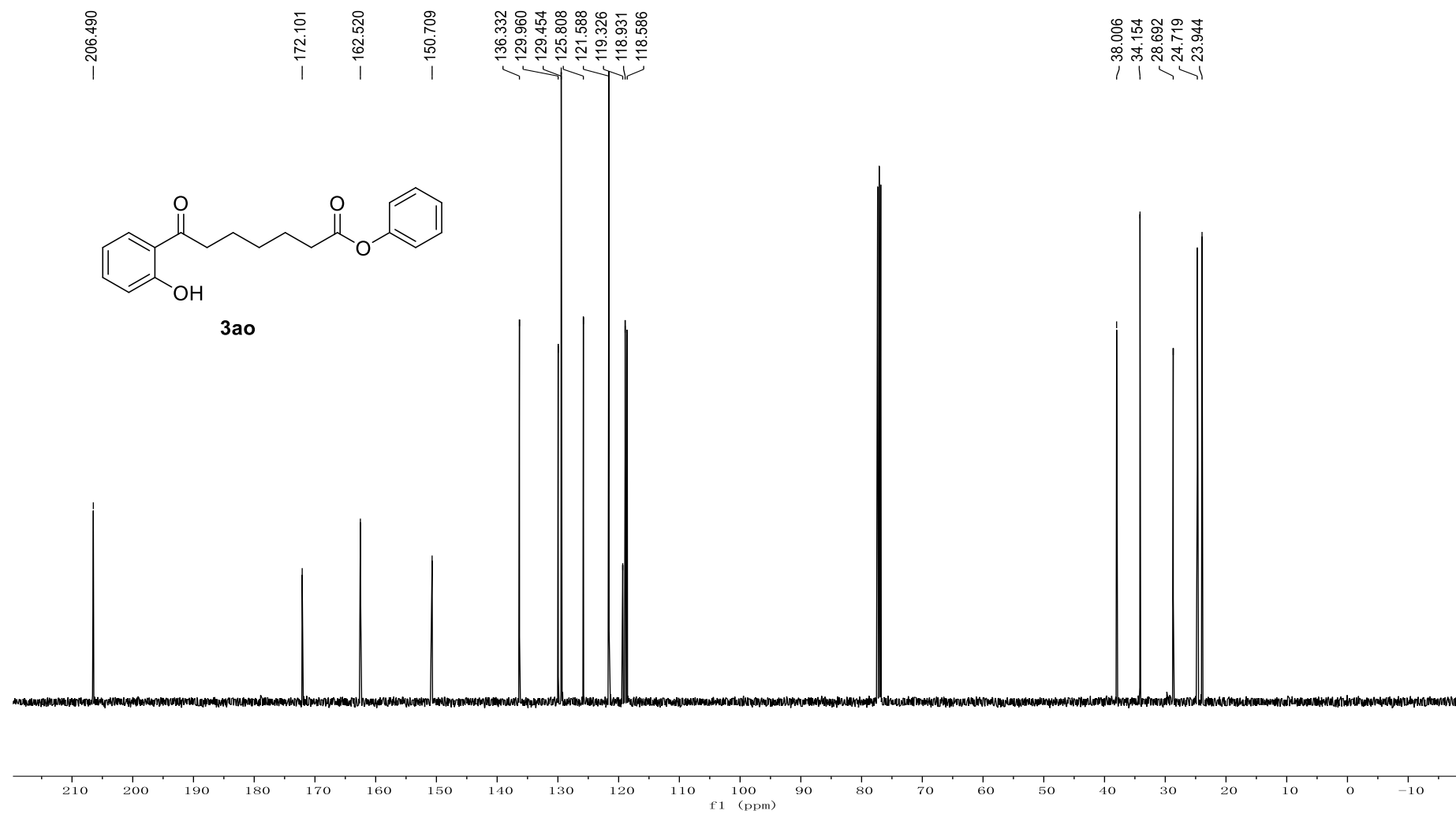
-73.811
-73.833
-73.858



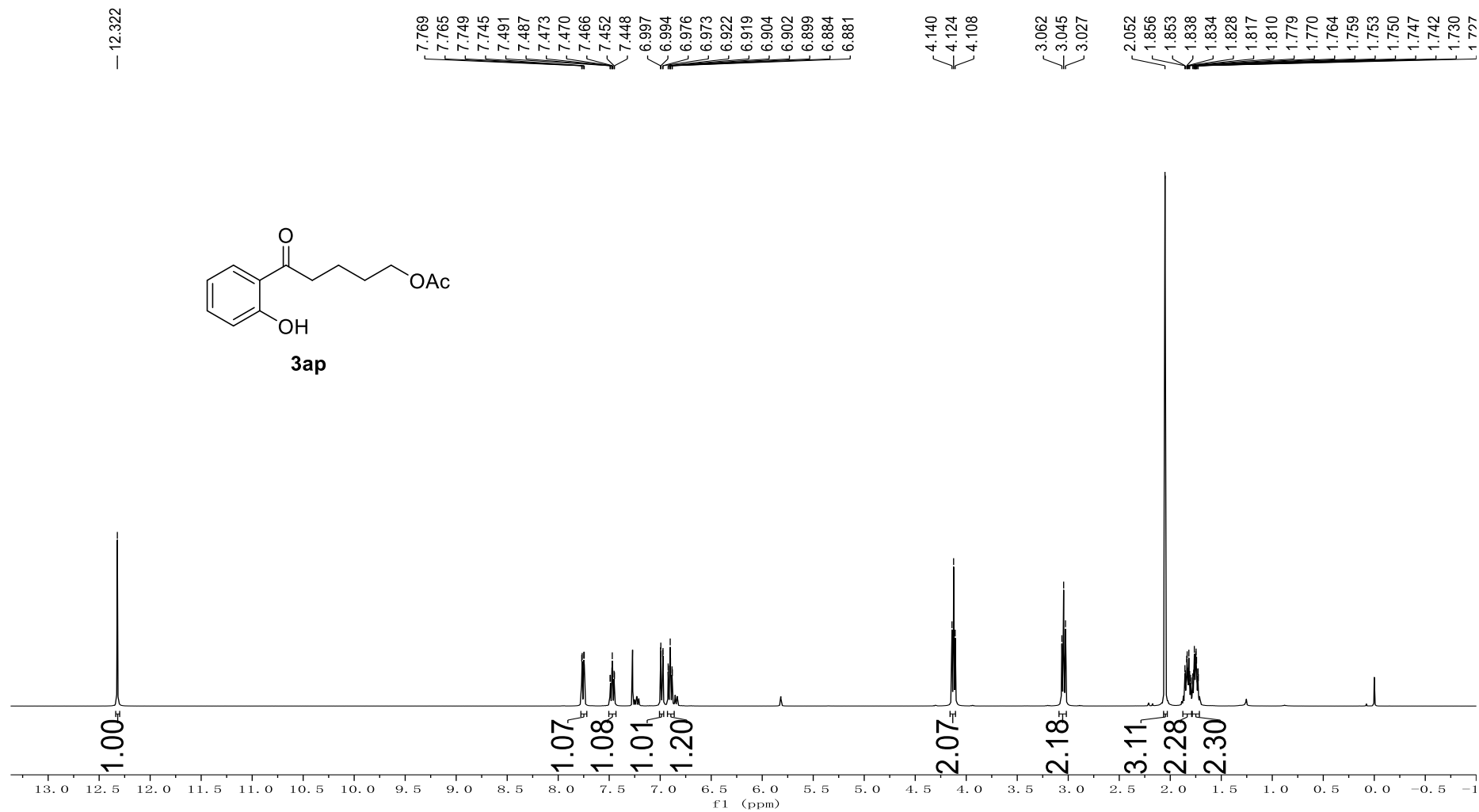
¹H NMR-spectrum (500 MHz, CDCl₃) of **3ao**



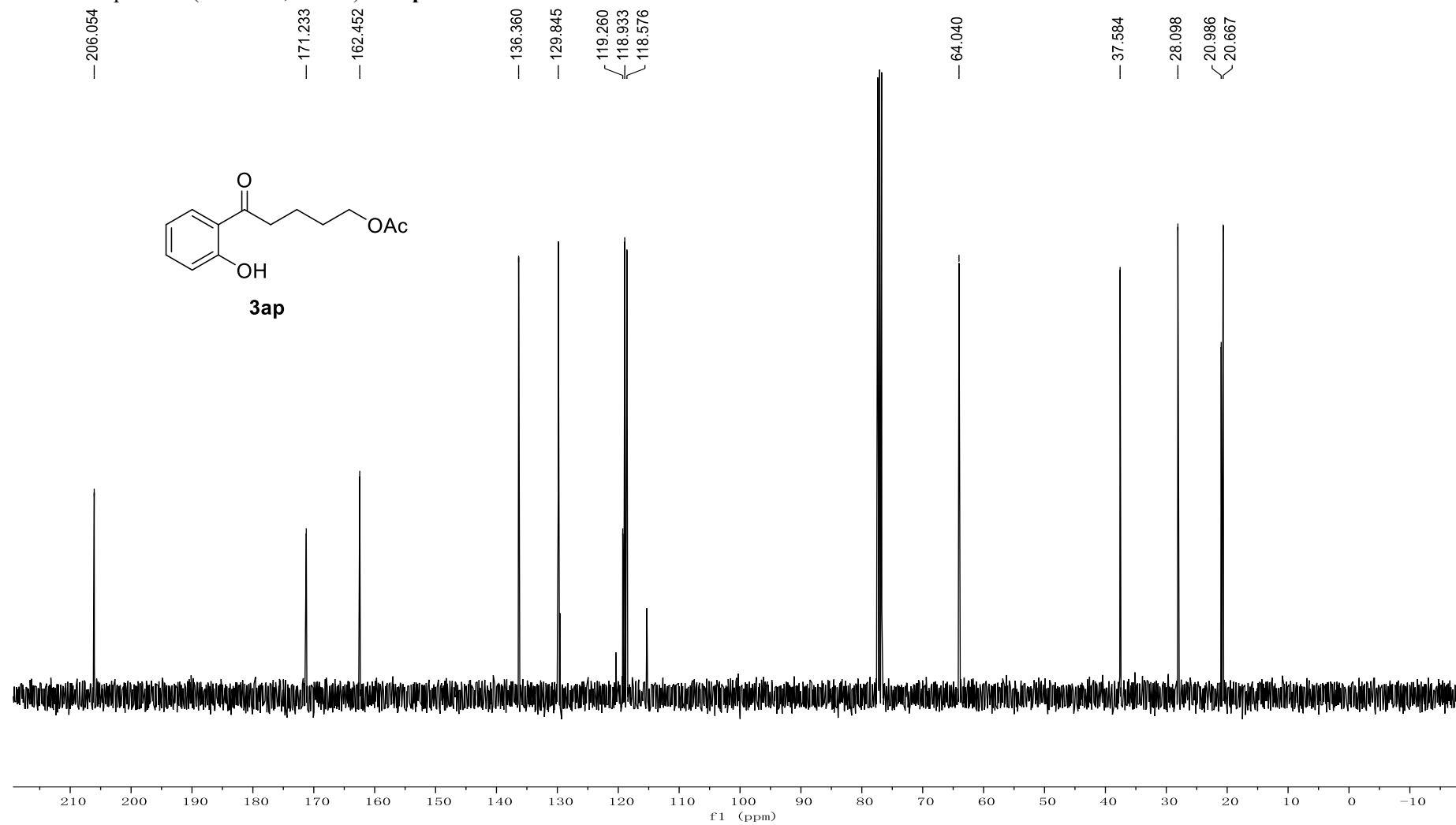
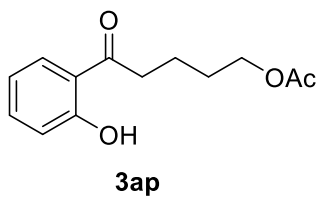
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ao**



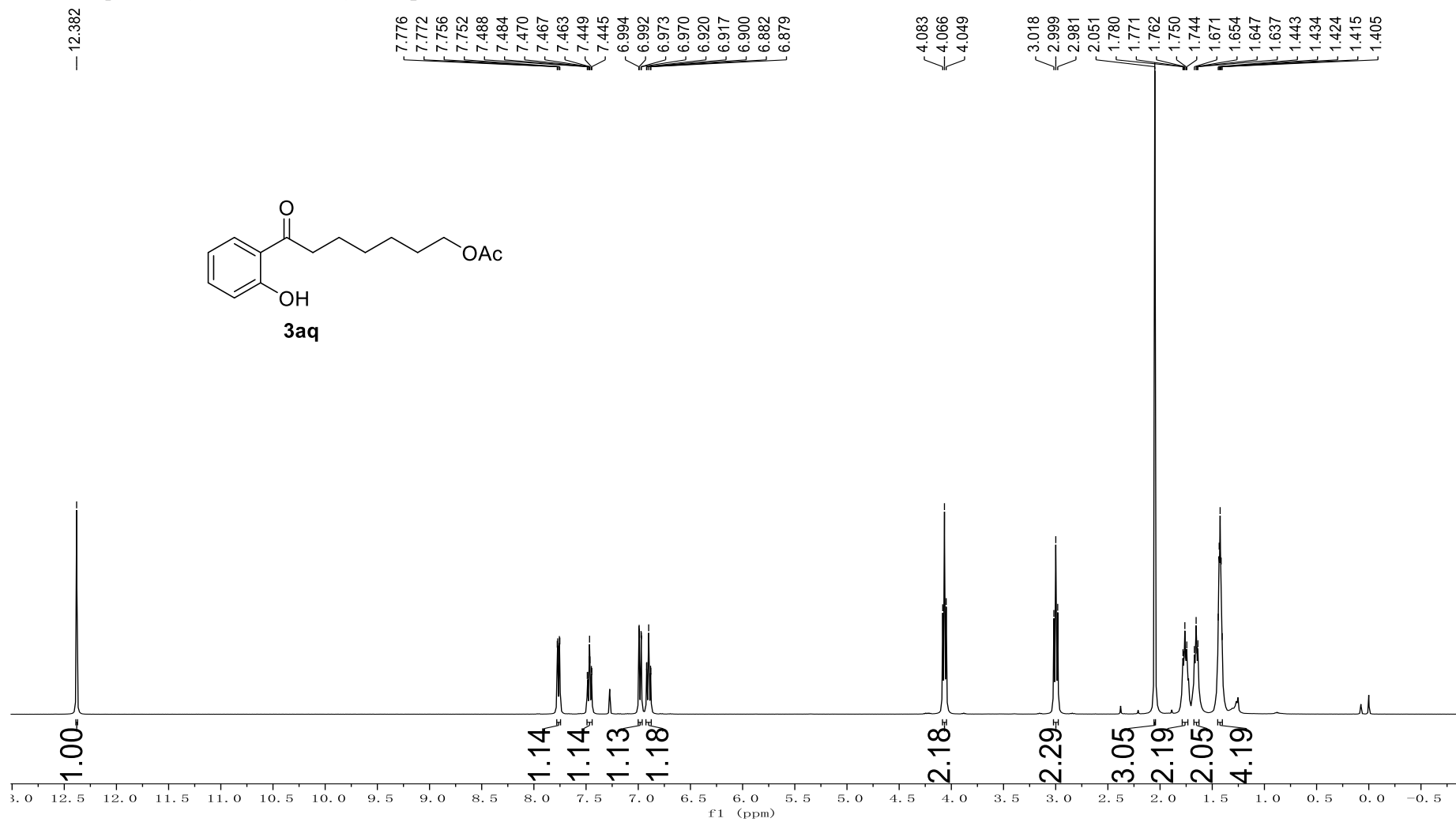
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ap**



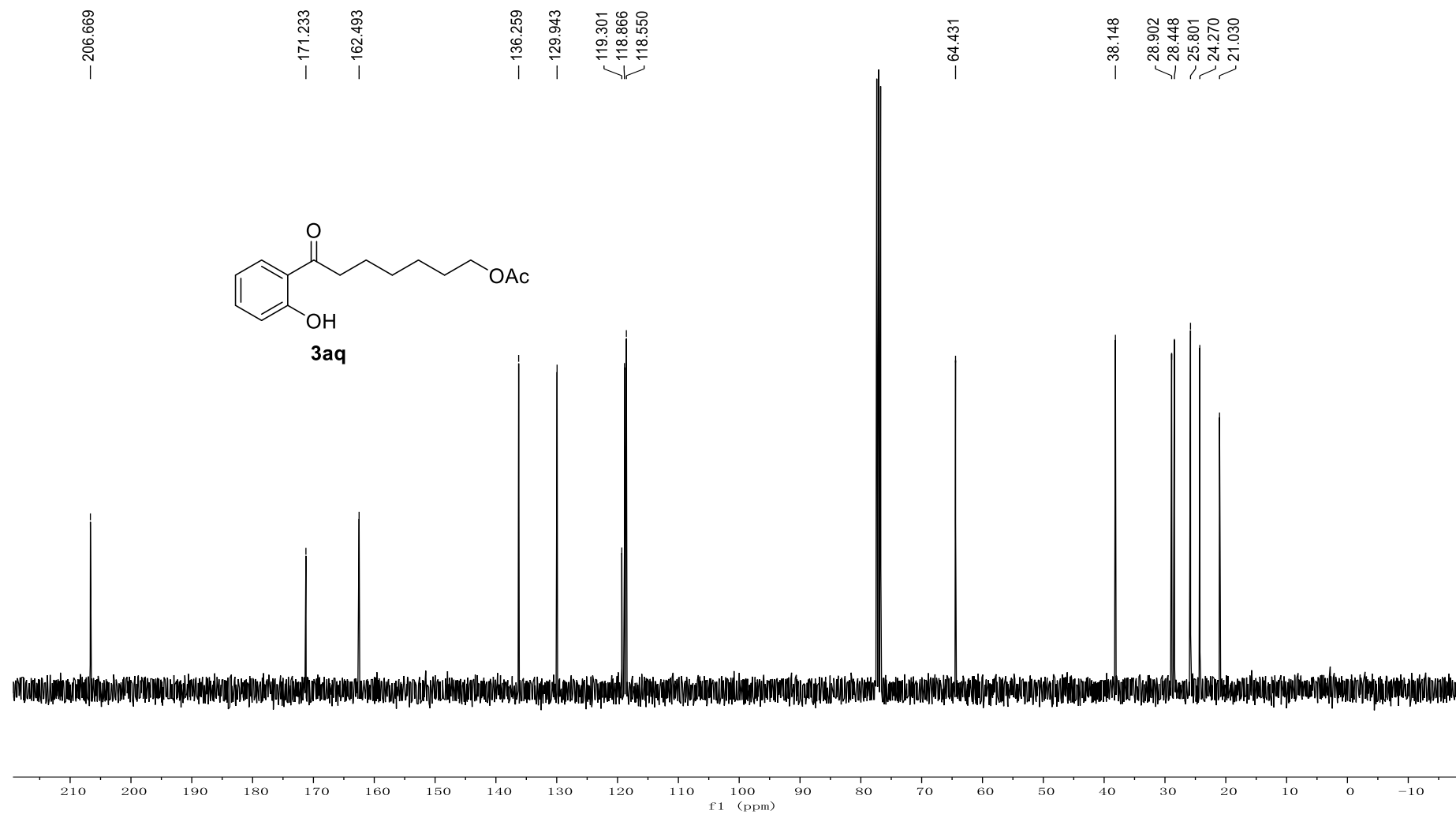
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ap**



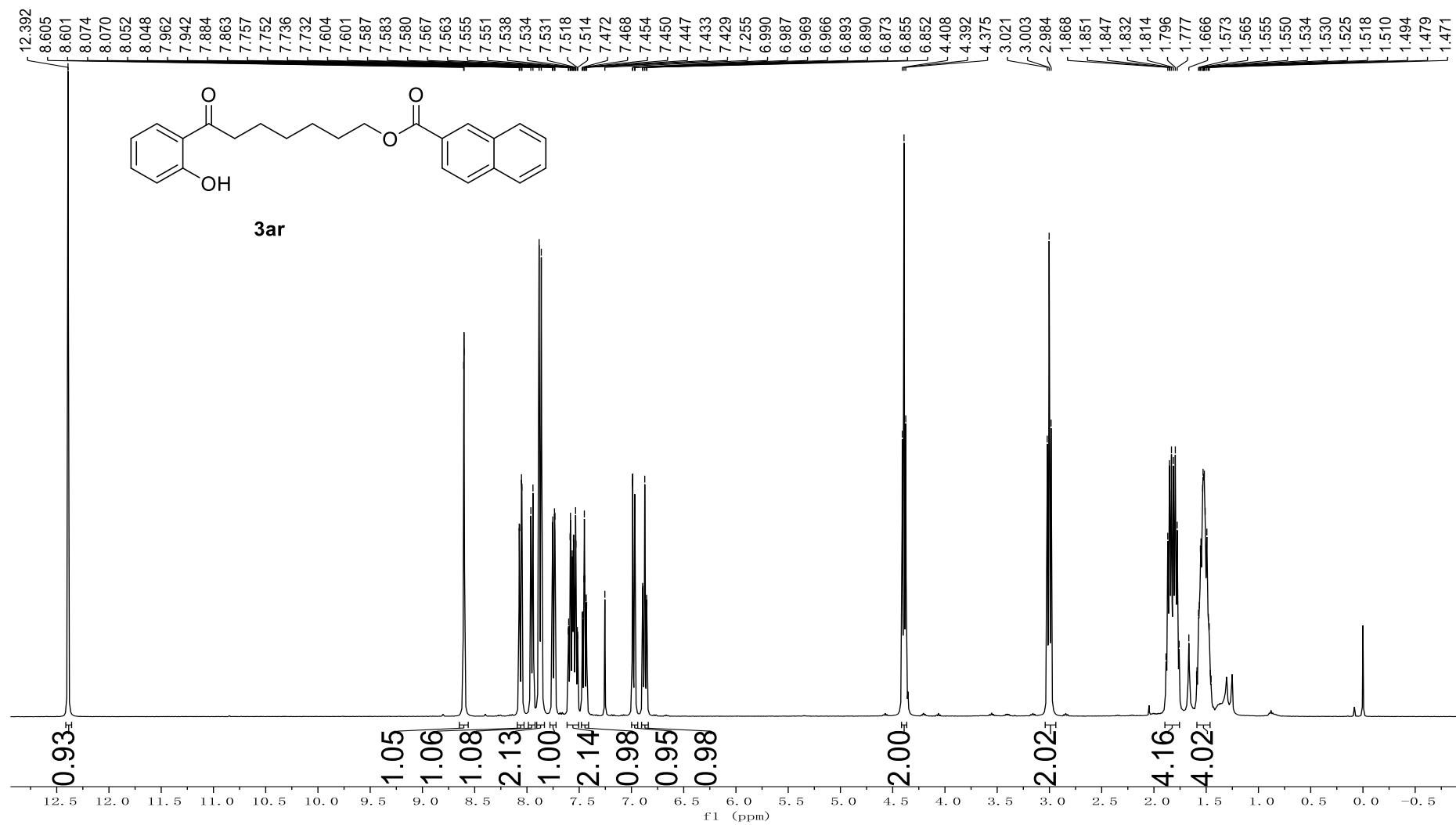
^1H NMR-spectrum (400 MHz, CDCl_3) of **3aq**



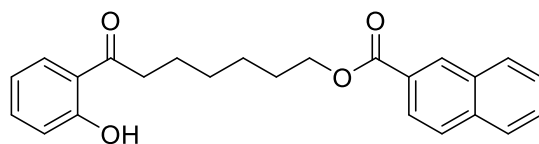
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3aq**



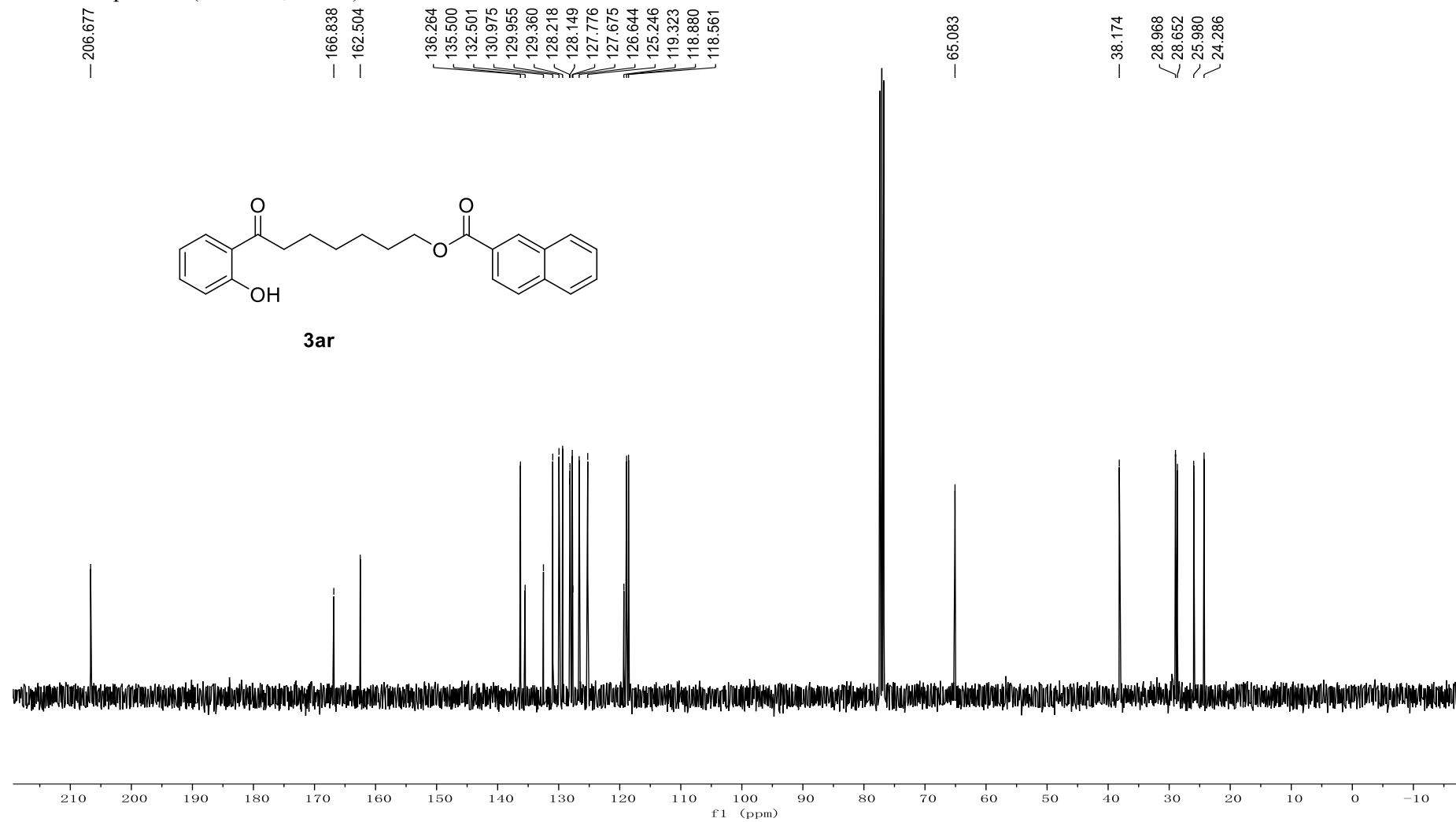
^1H NMR-spectrum (400 MHz, CDCl_3) of **3ar**



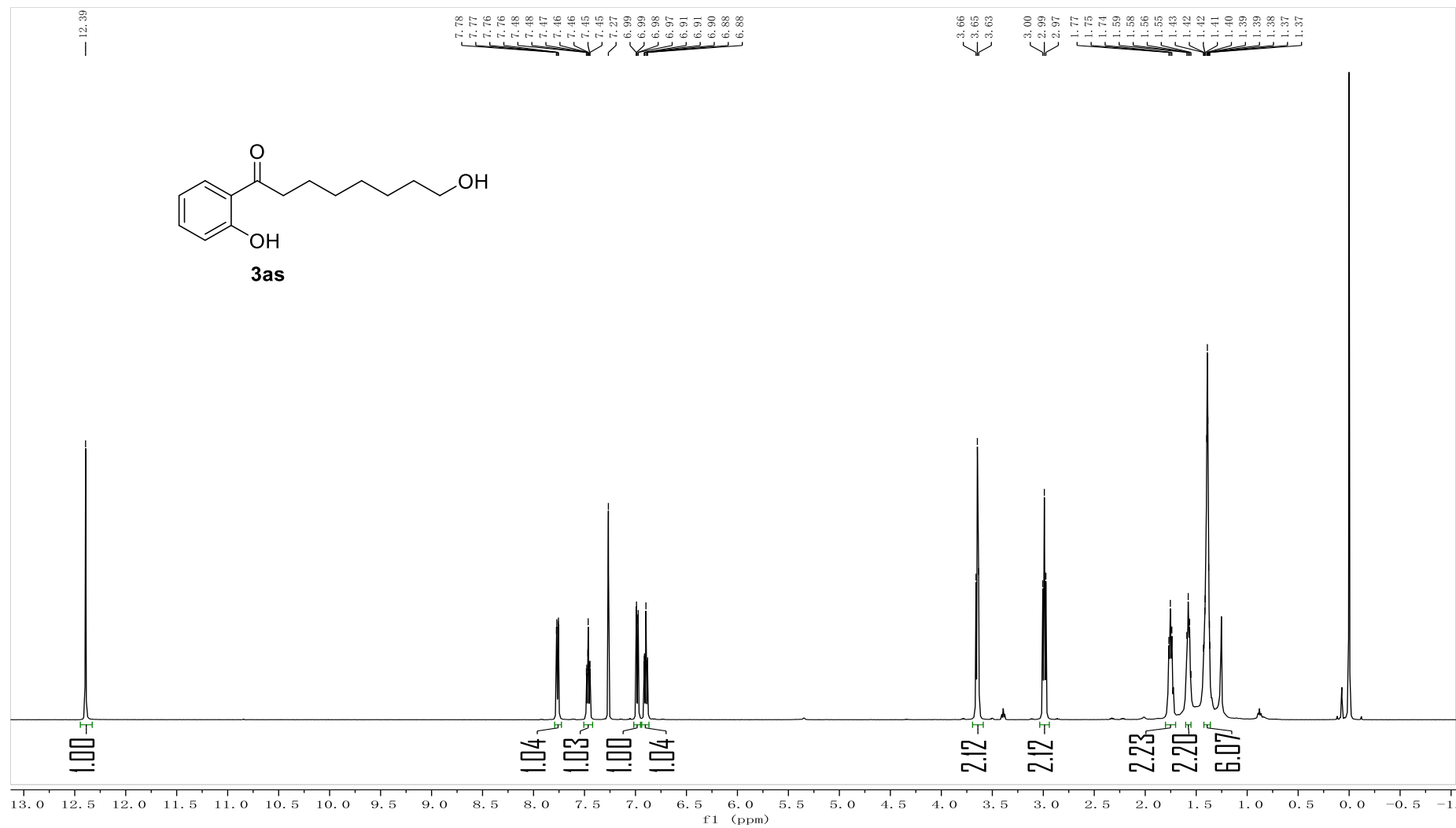
¹³C NMR-spectrum (101 MHz, CDCl₃) of **3ar**



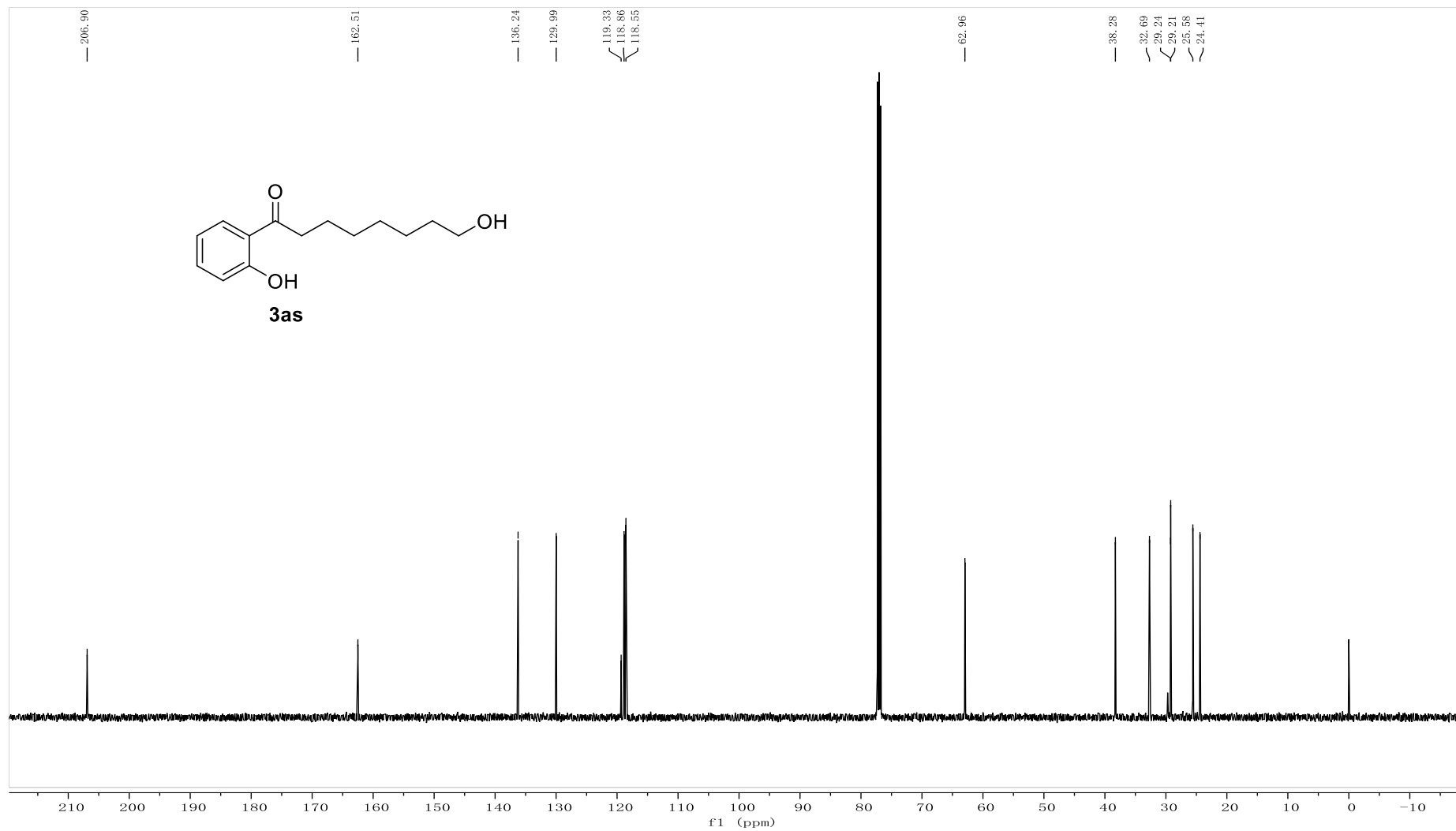
3ar



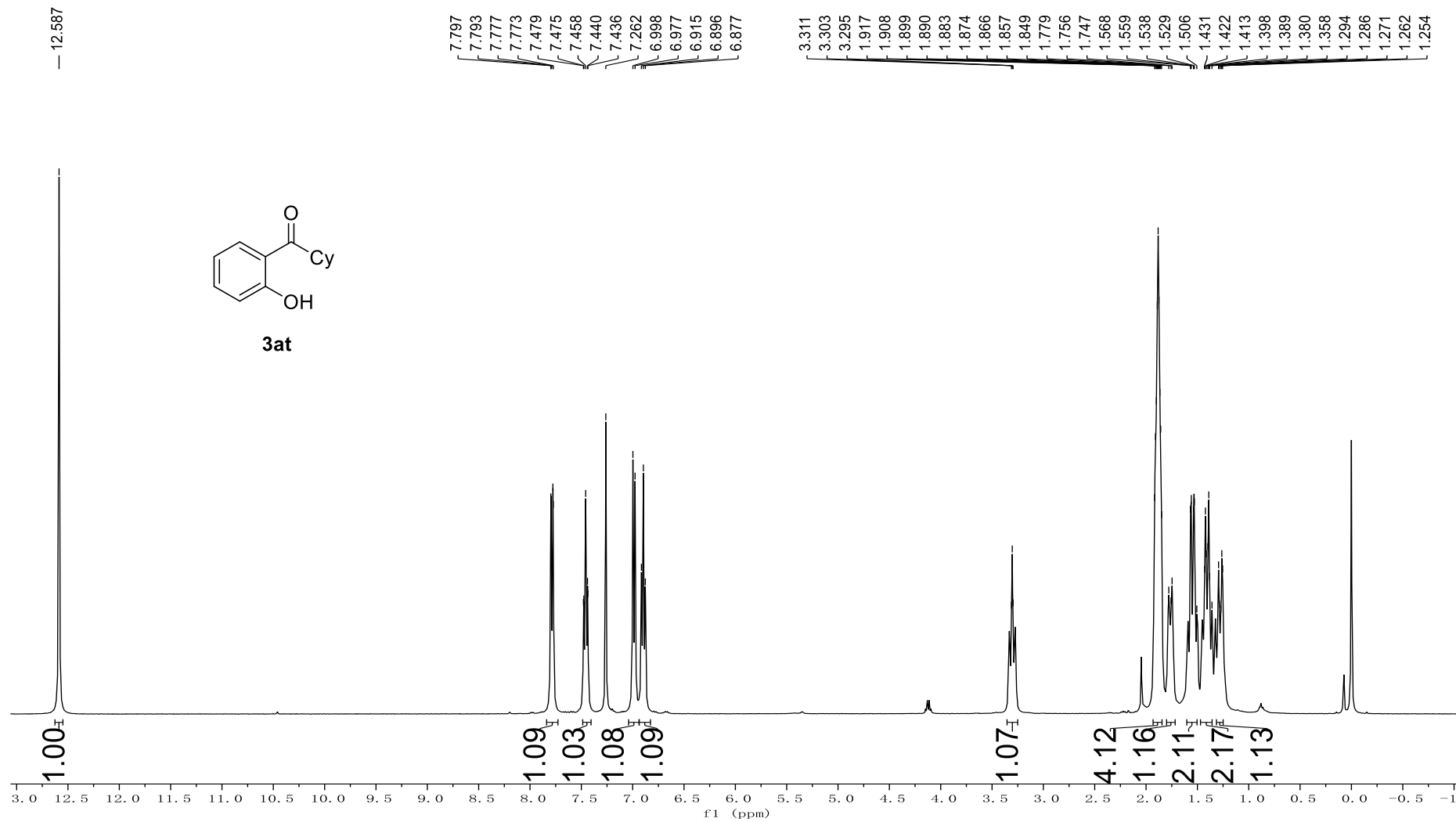
^1H NMR-spectrum (500 MHz, CDCl_3) of **3as**



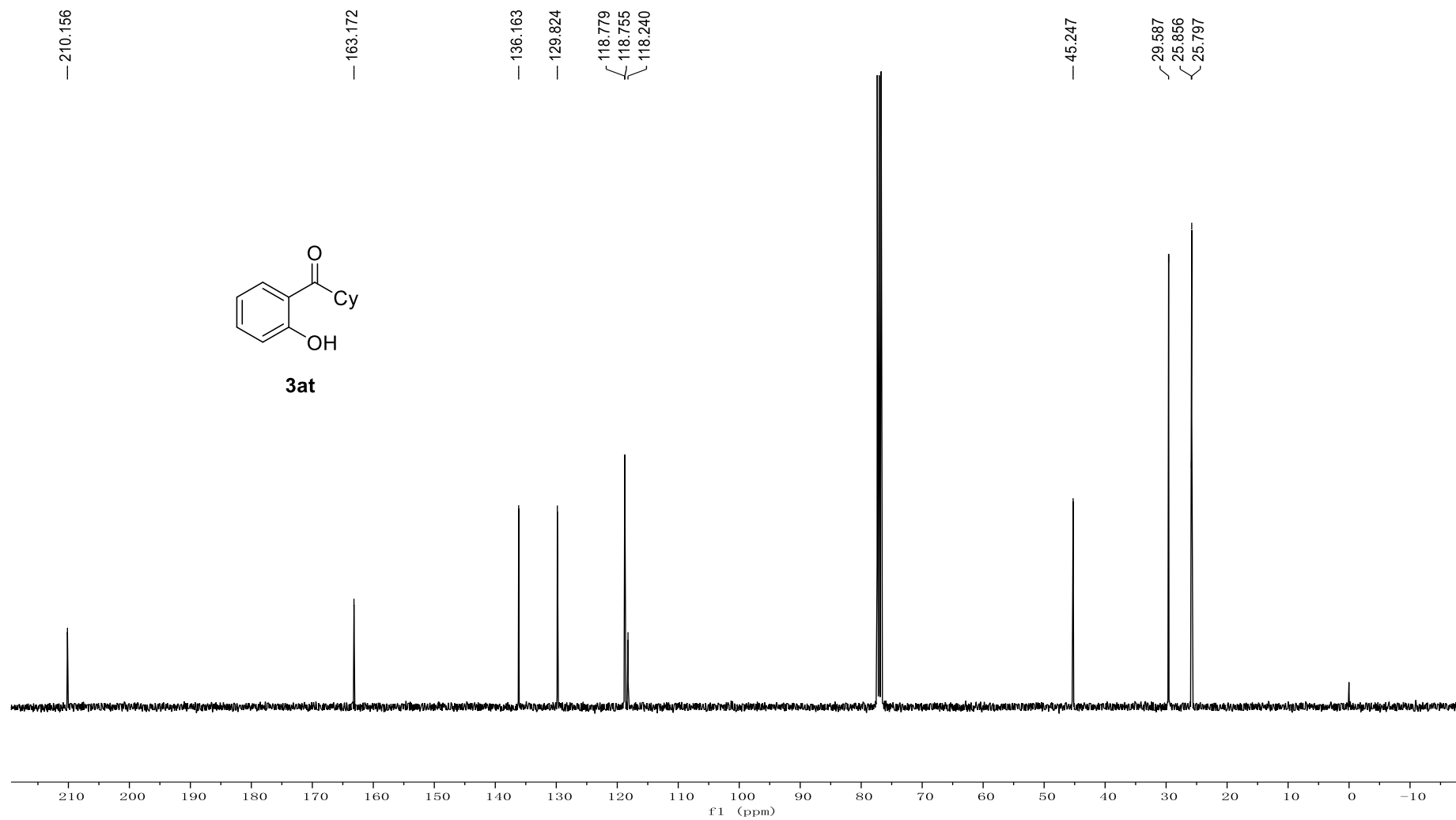
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3as**



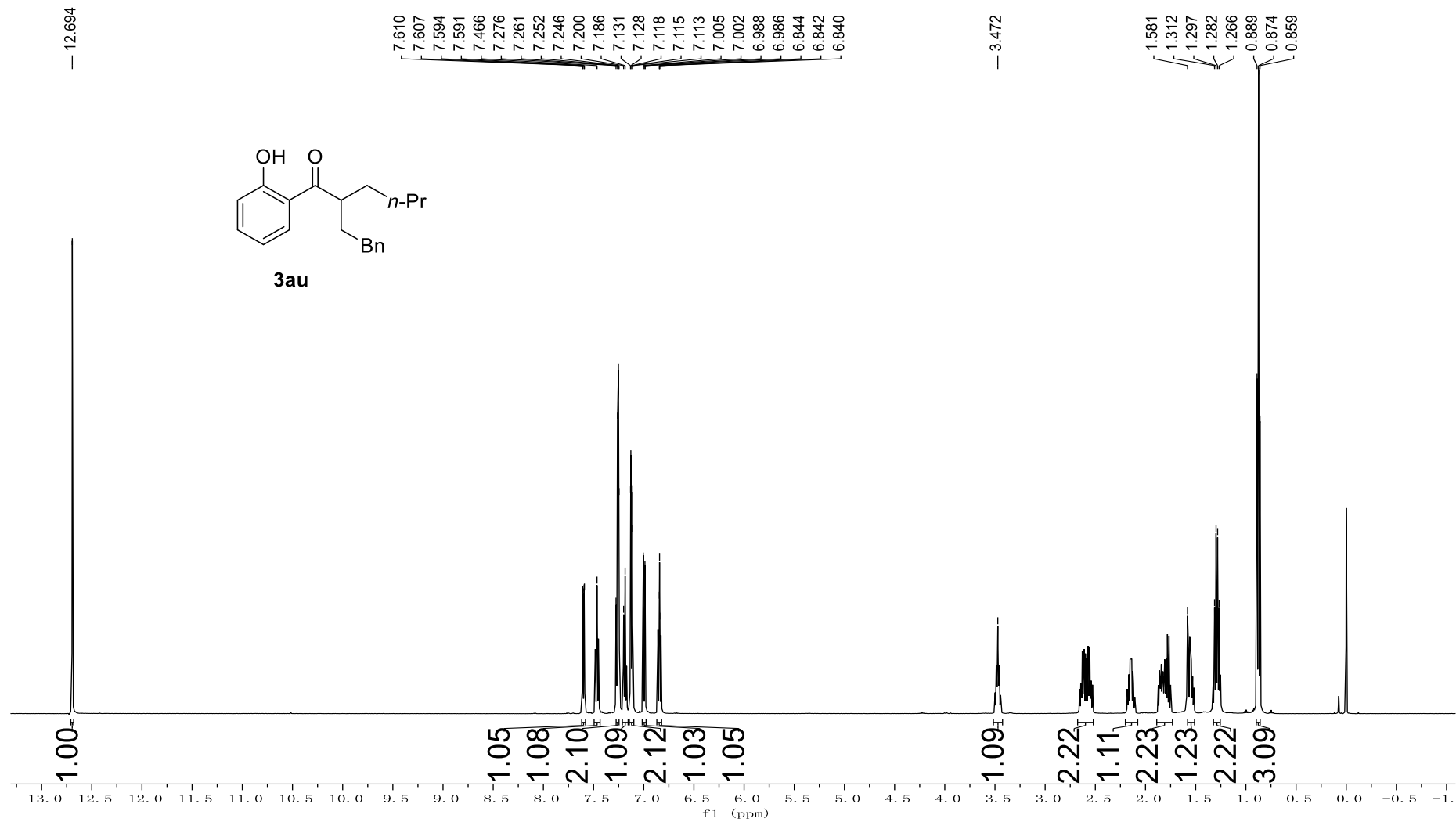
^1H NMR-spectrum (400 MHz, CDCl_3) of **3at**



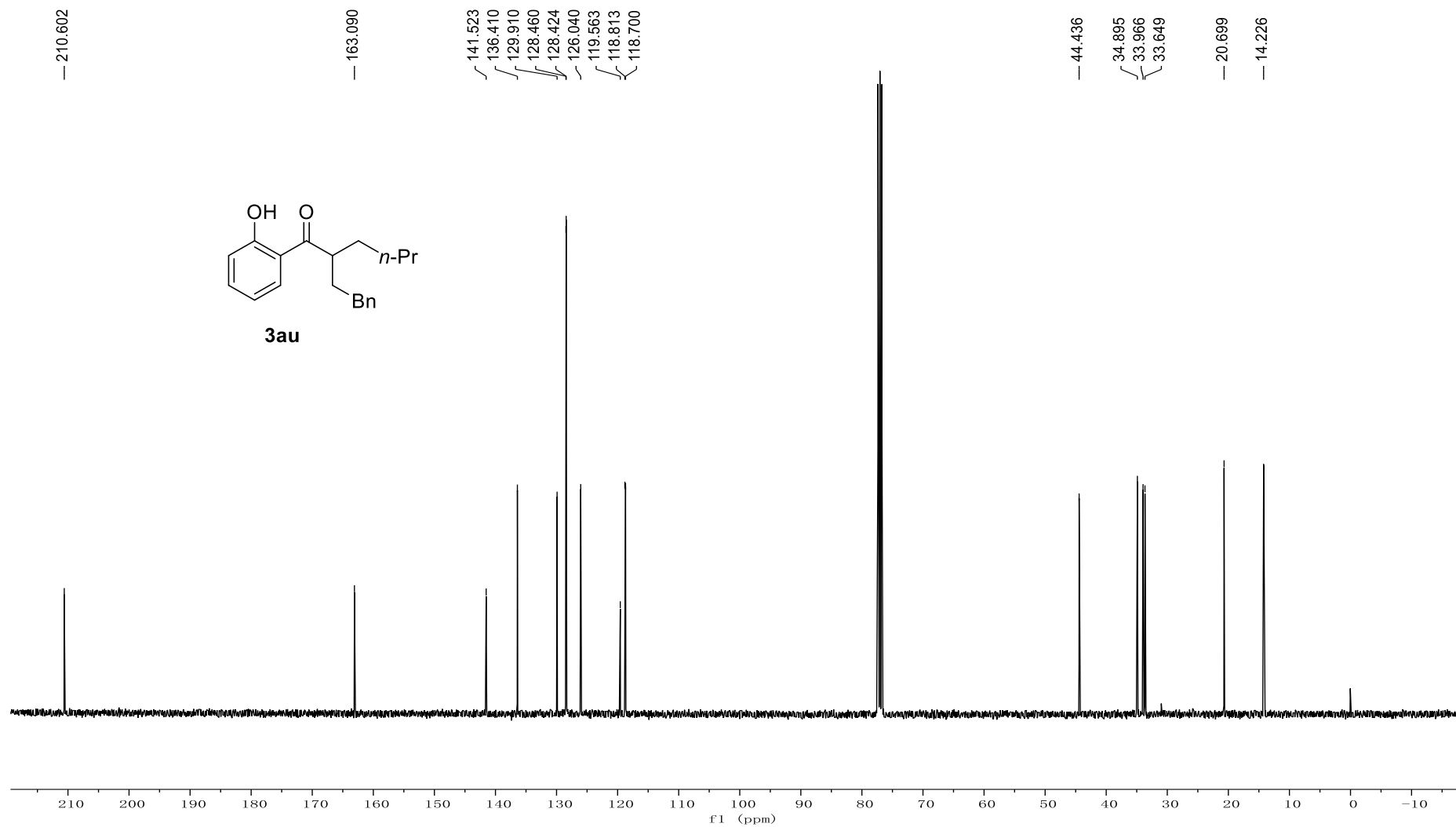
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3at**



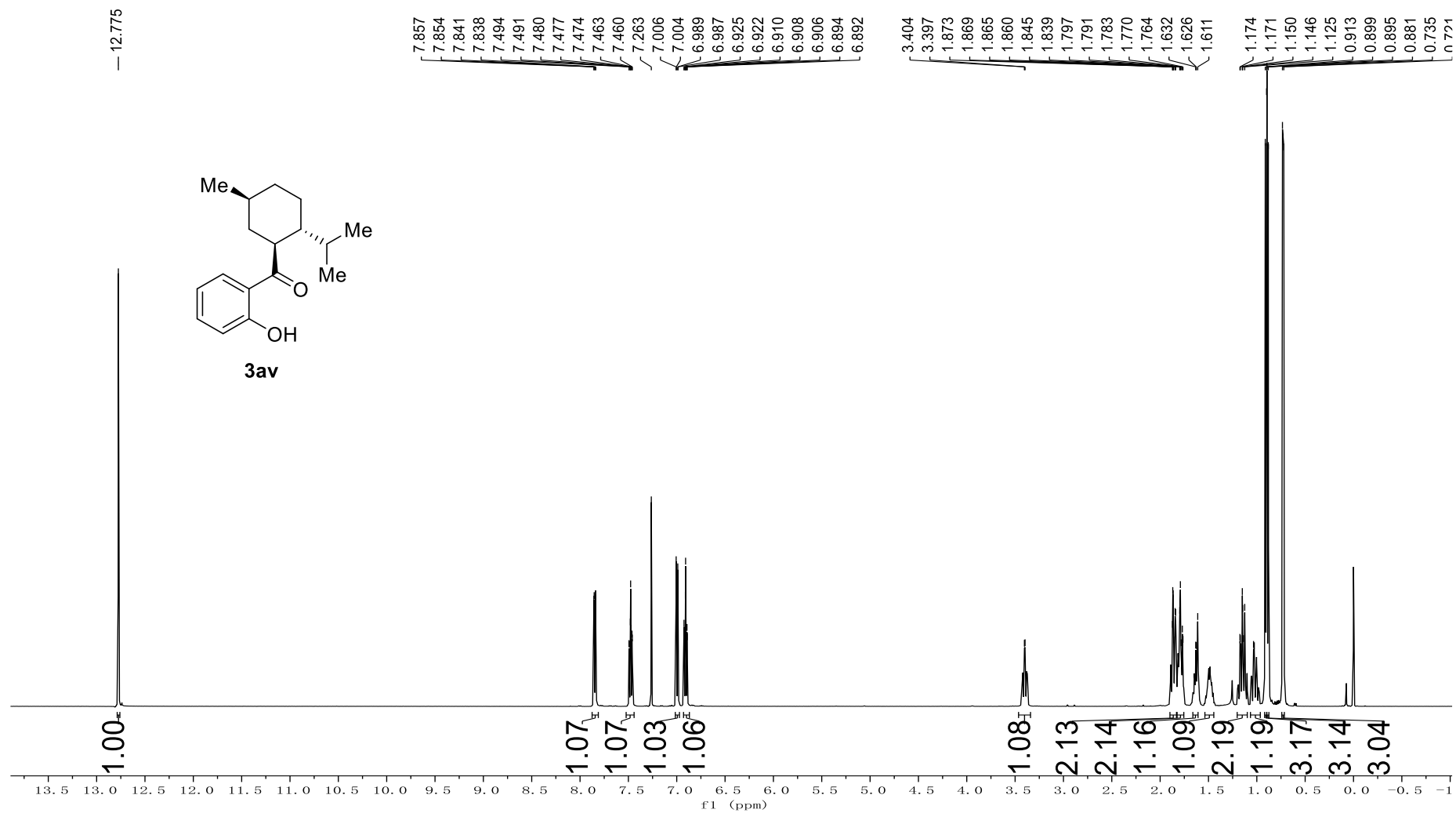
^1H NMR-spectrum (500 MHz, CDCl_3) of **3au**



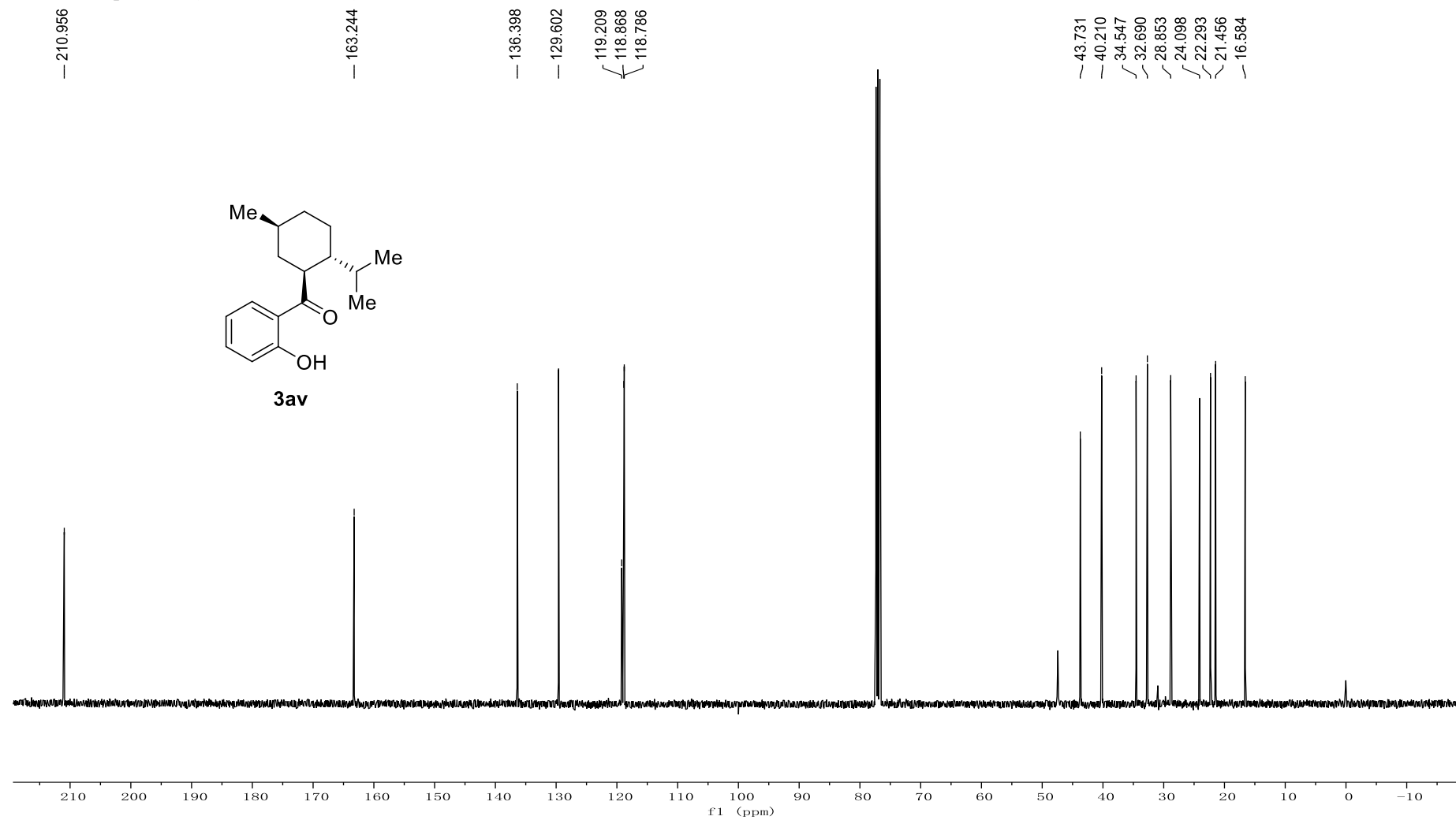
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3au**



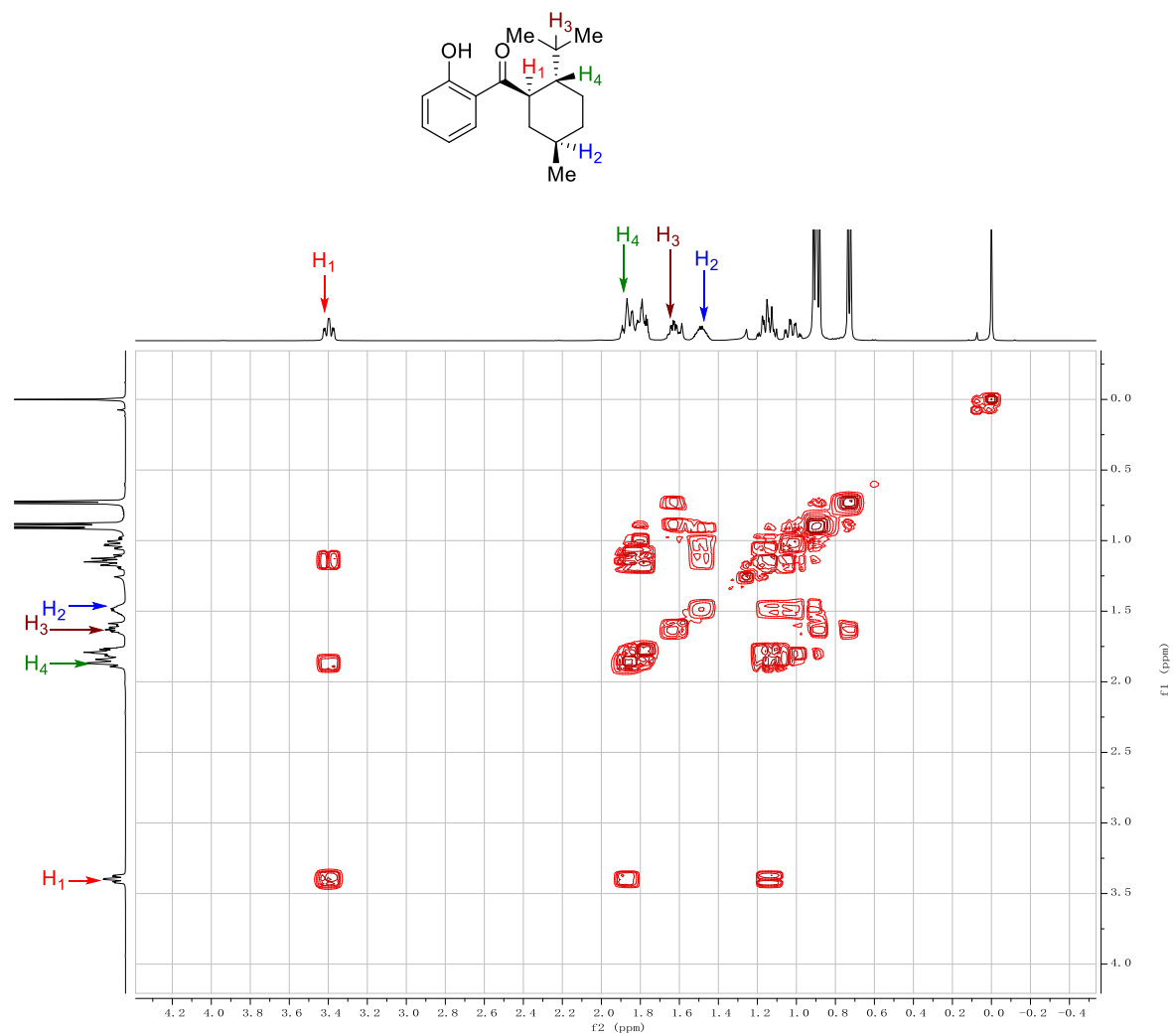
¹H NMR-spectrum (500 MHz, CDCl₃) of **3av**



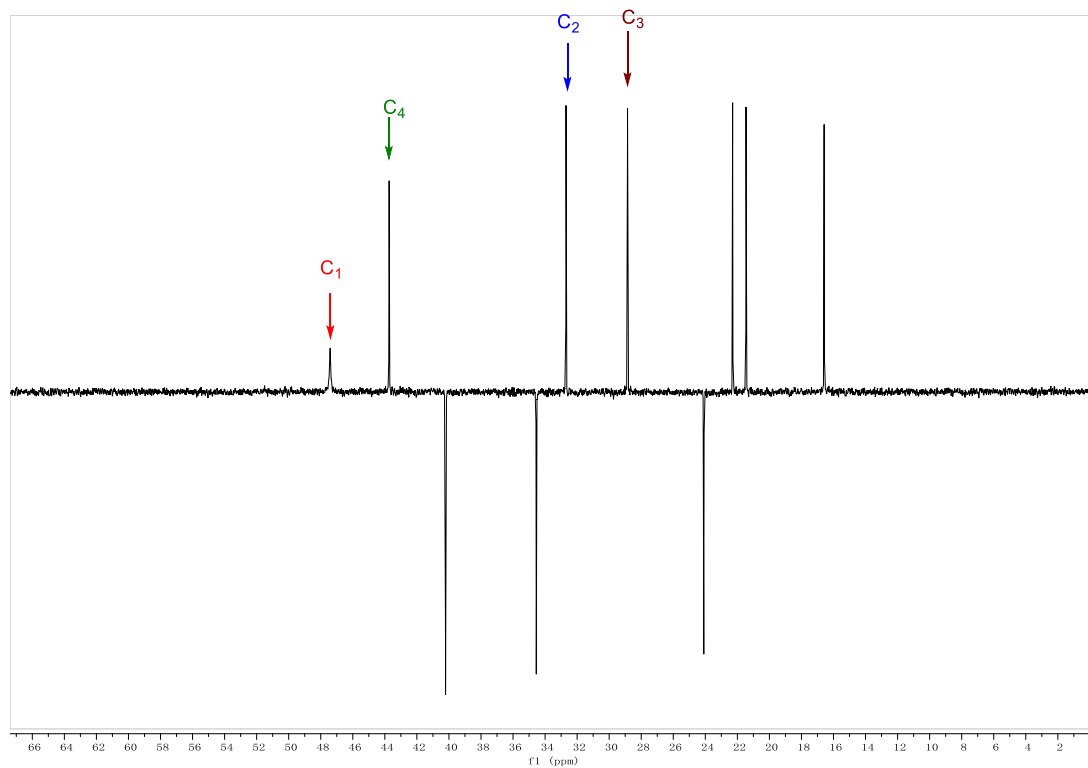
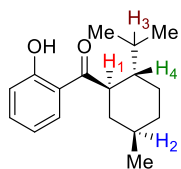
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3av**



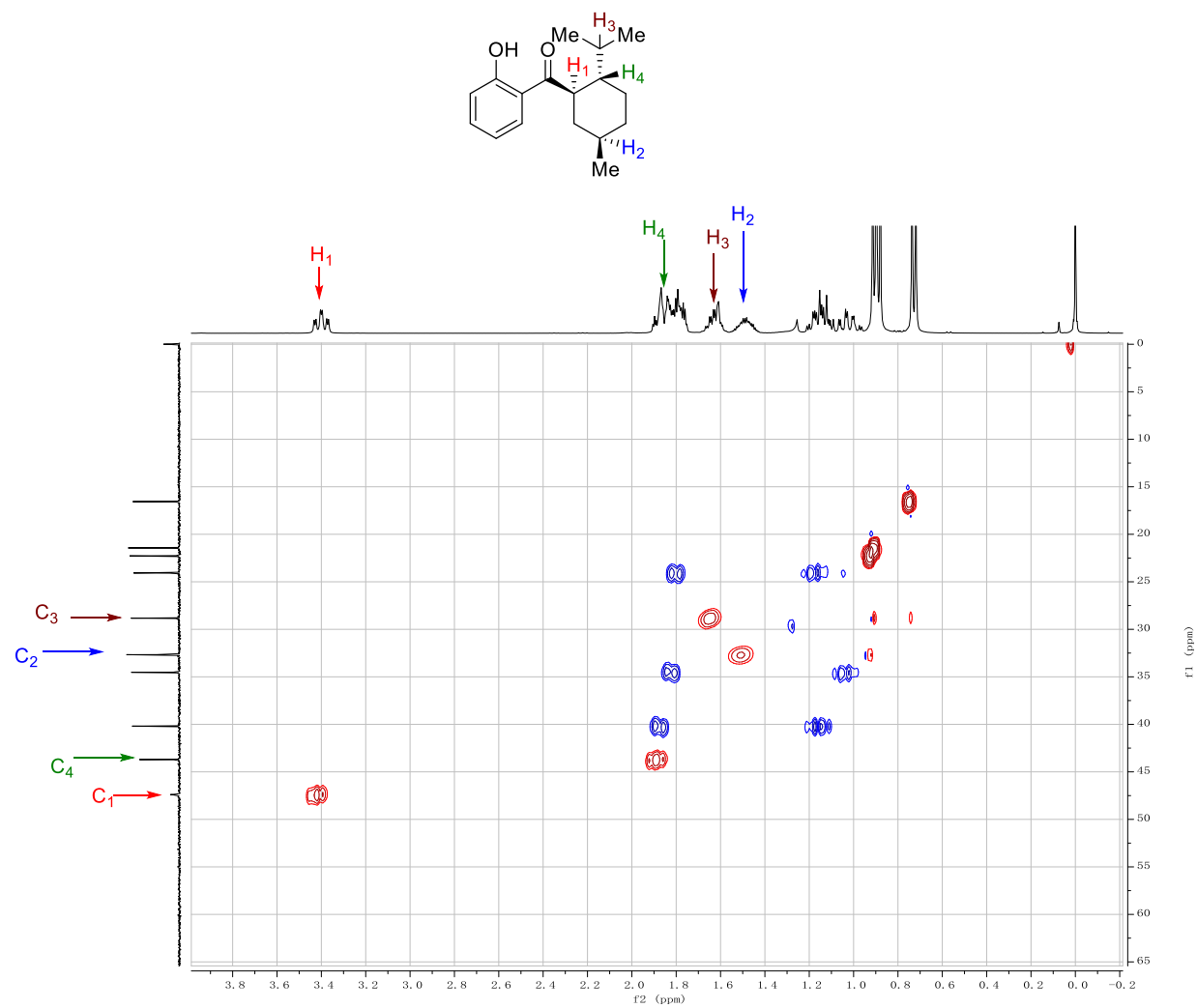
COSY-spectrum of **3av**



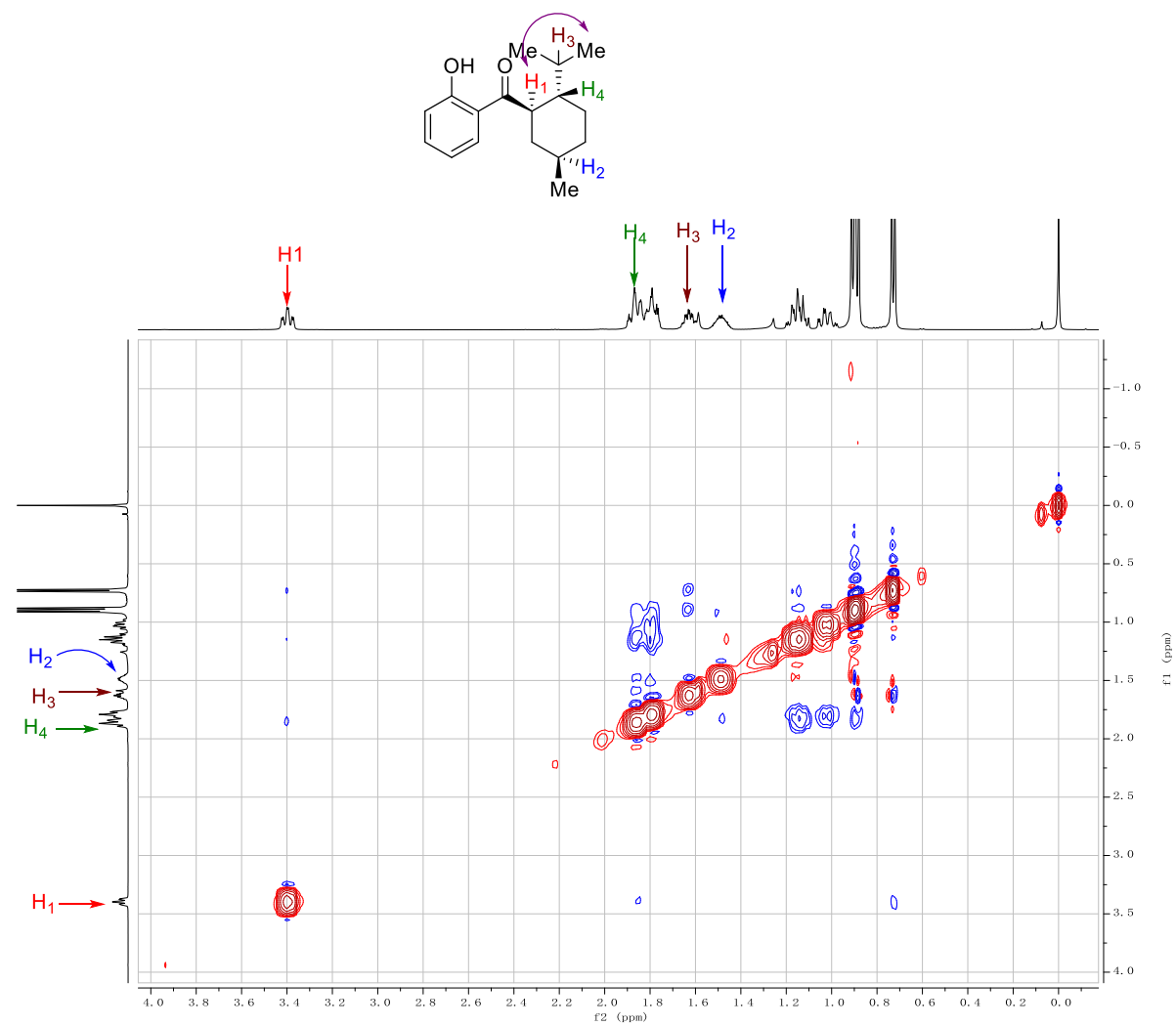
DEPT-135°-spectrum of **3av**



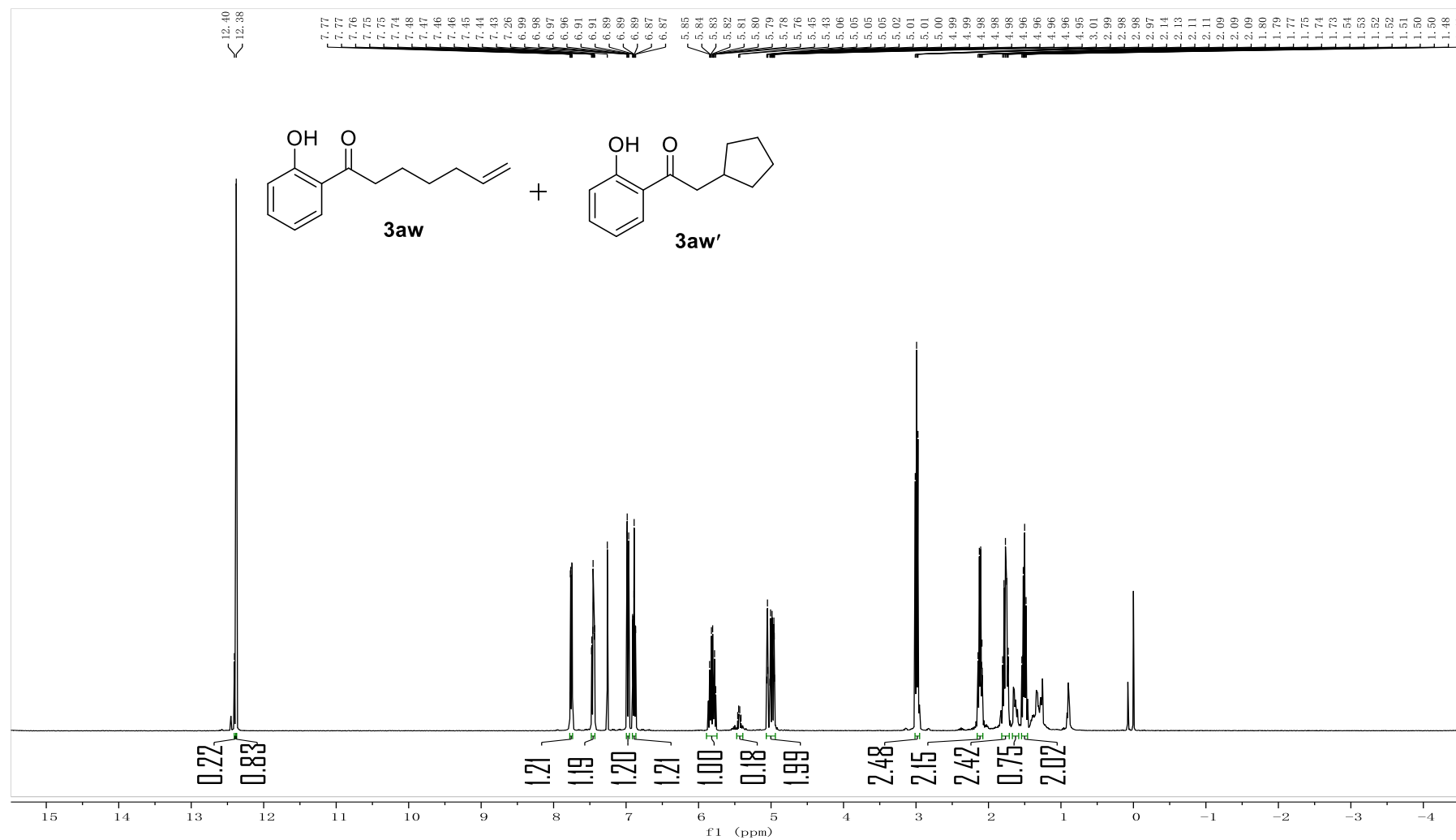
HSQC-spectrum of **3av**



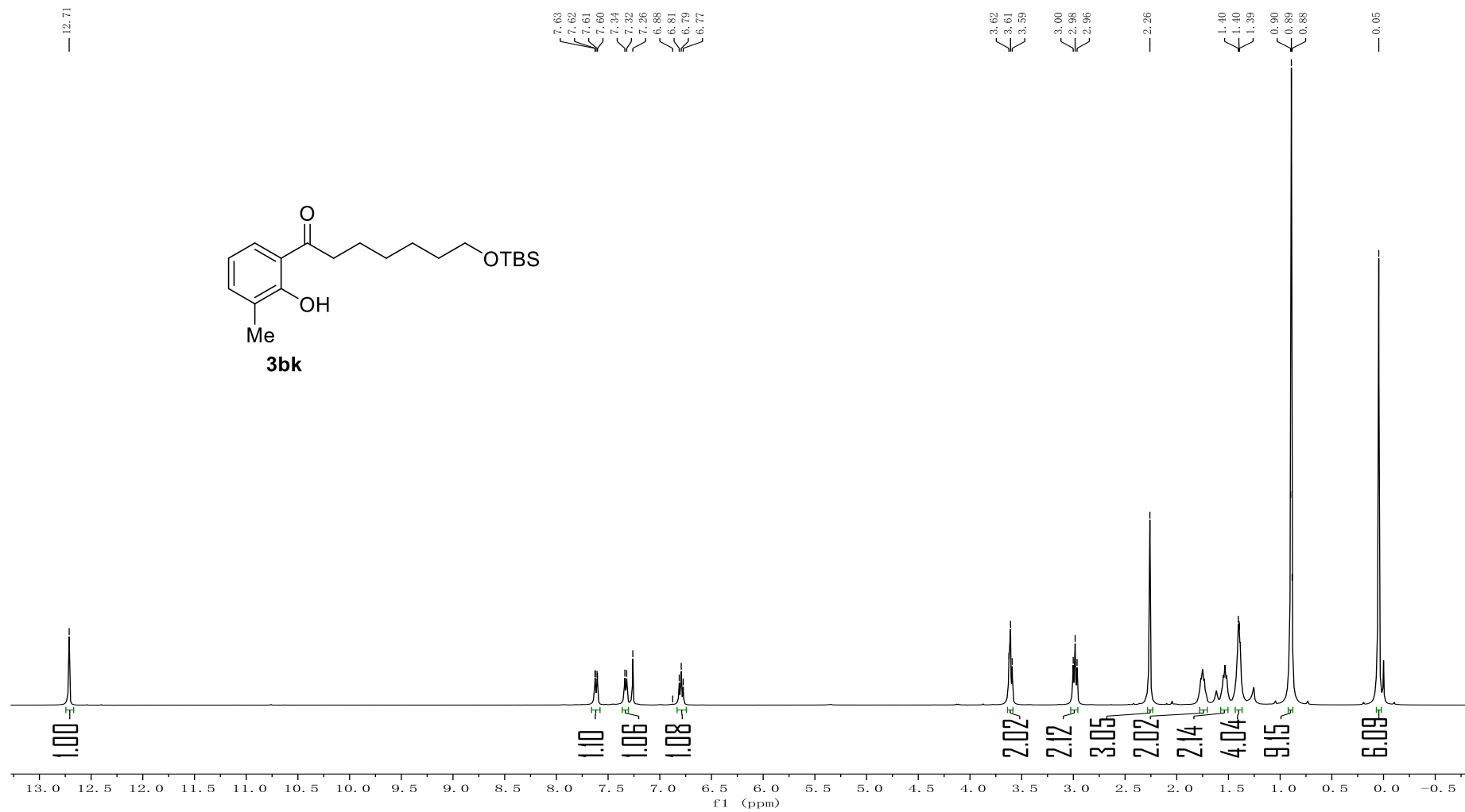
NOSEY-spectrum of **3av**



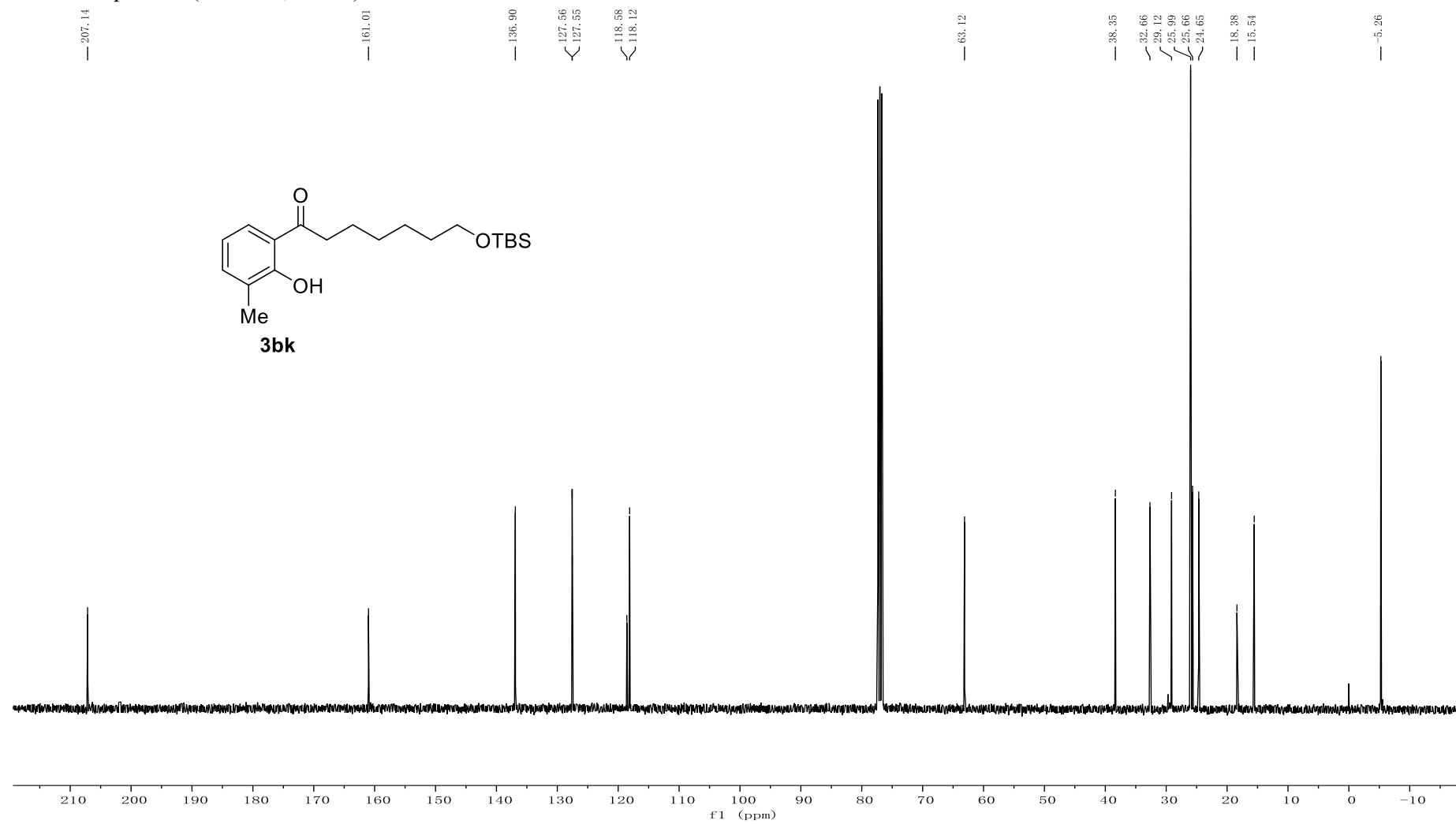
¹H NMR-spectrum (500 MHz, CDCl₃) of **3aw** and **3aw'**



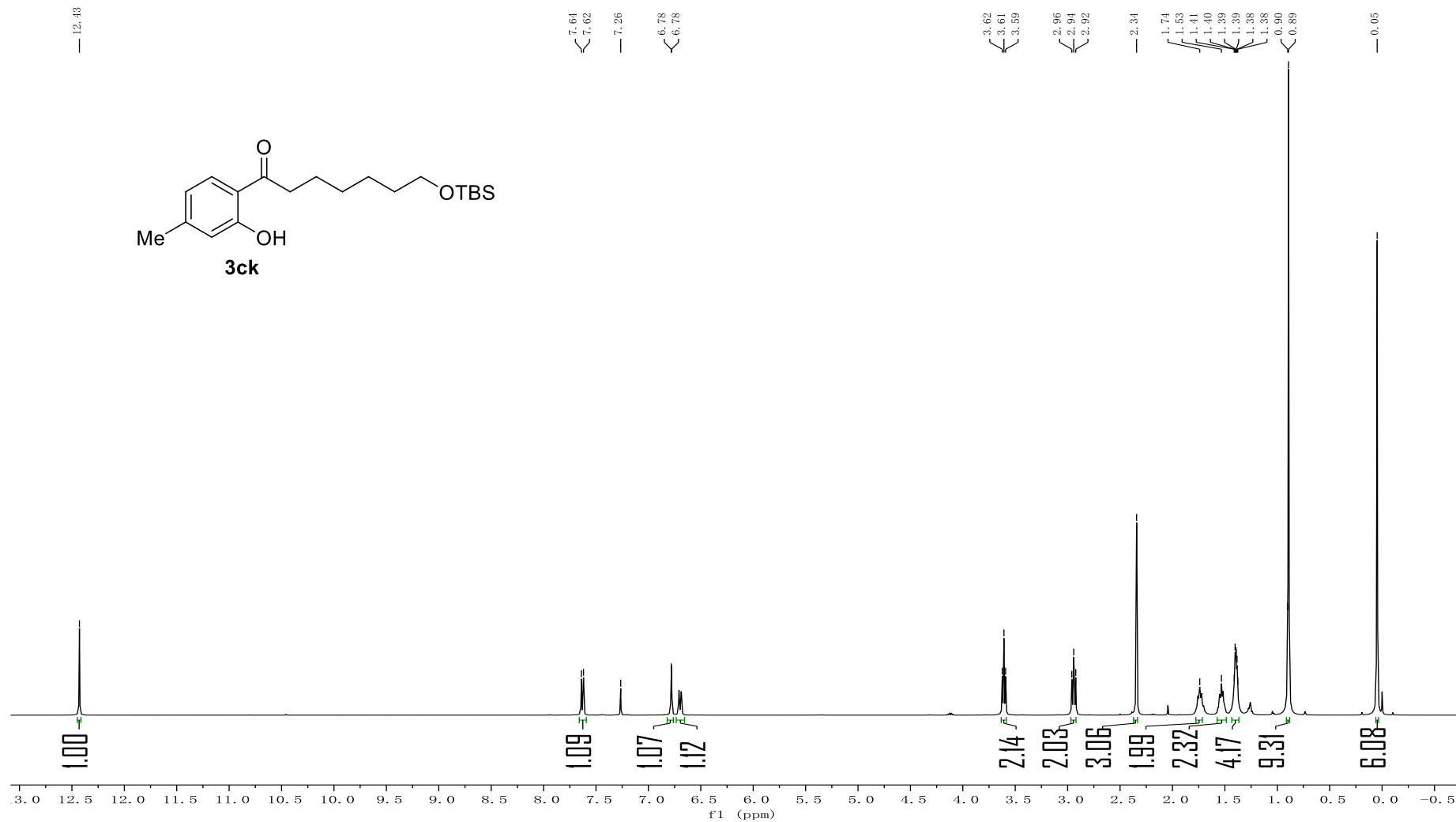
^1H NMR-spectrum (400 MHz, CDCl_3) of **3bk**



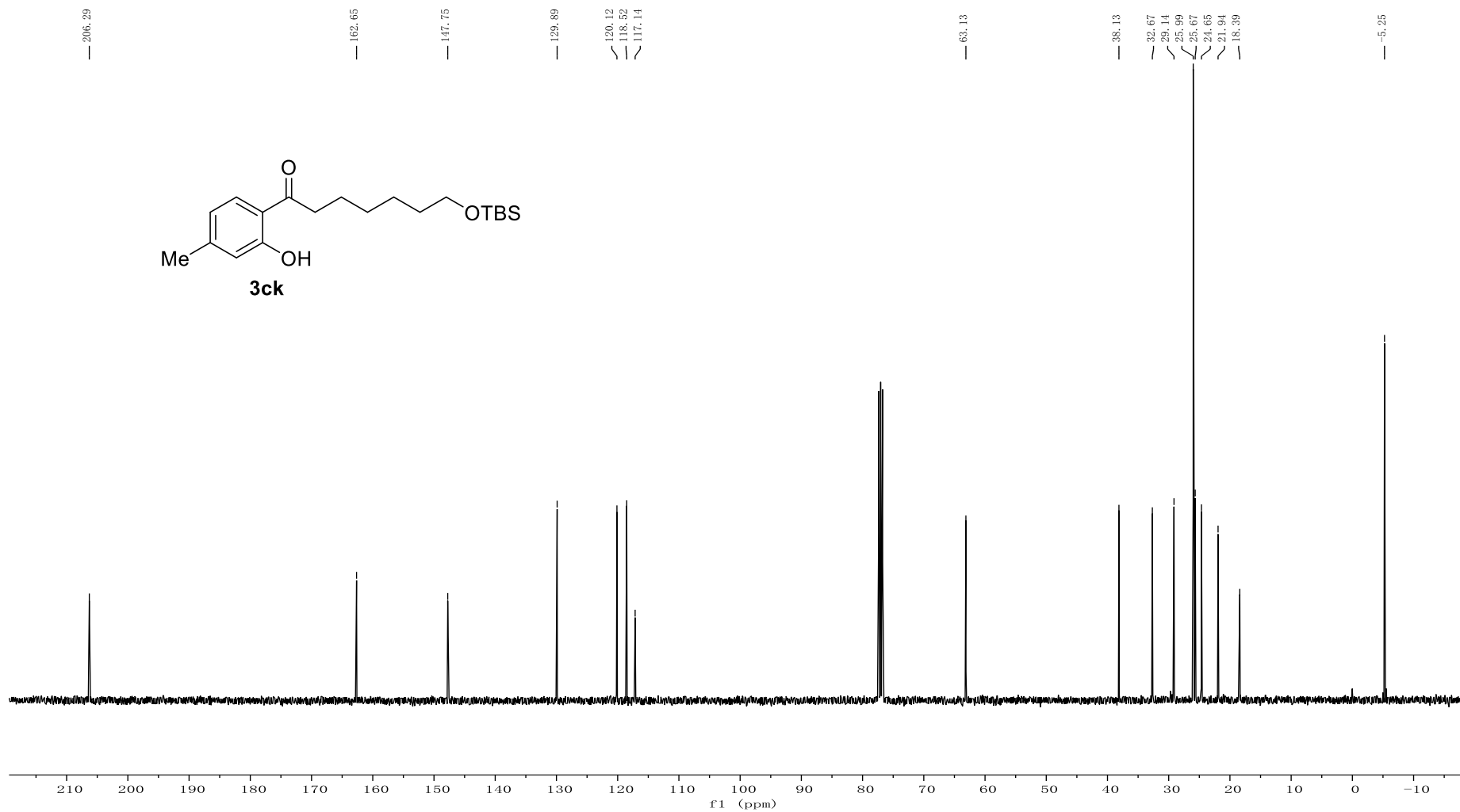
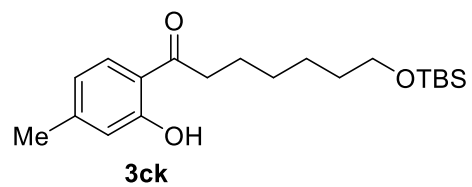
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3bk**



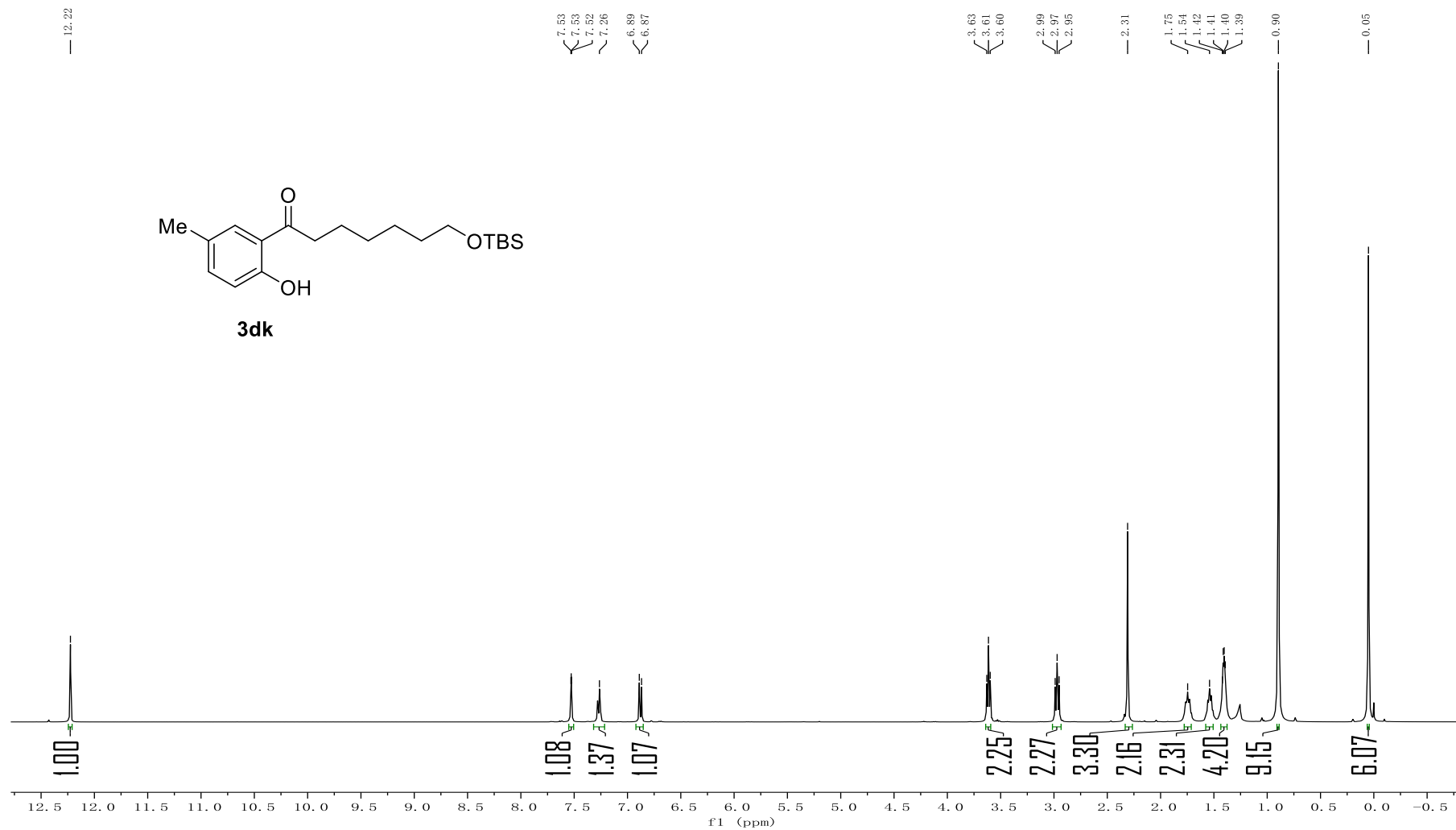
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ck**



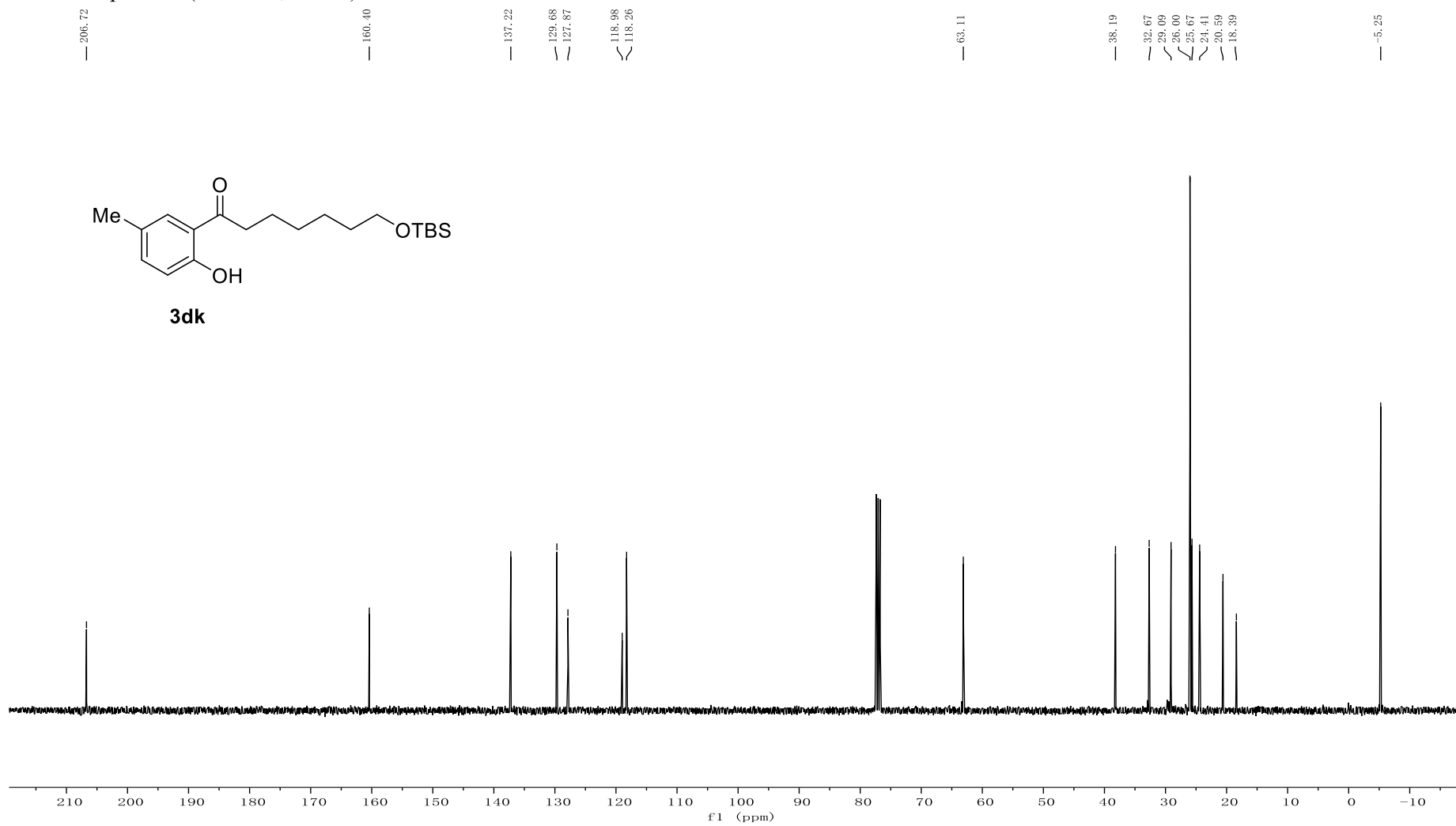
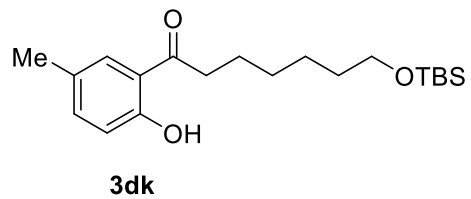
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ck**



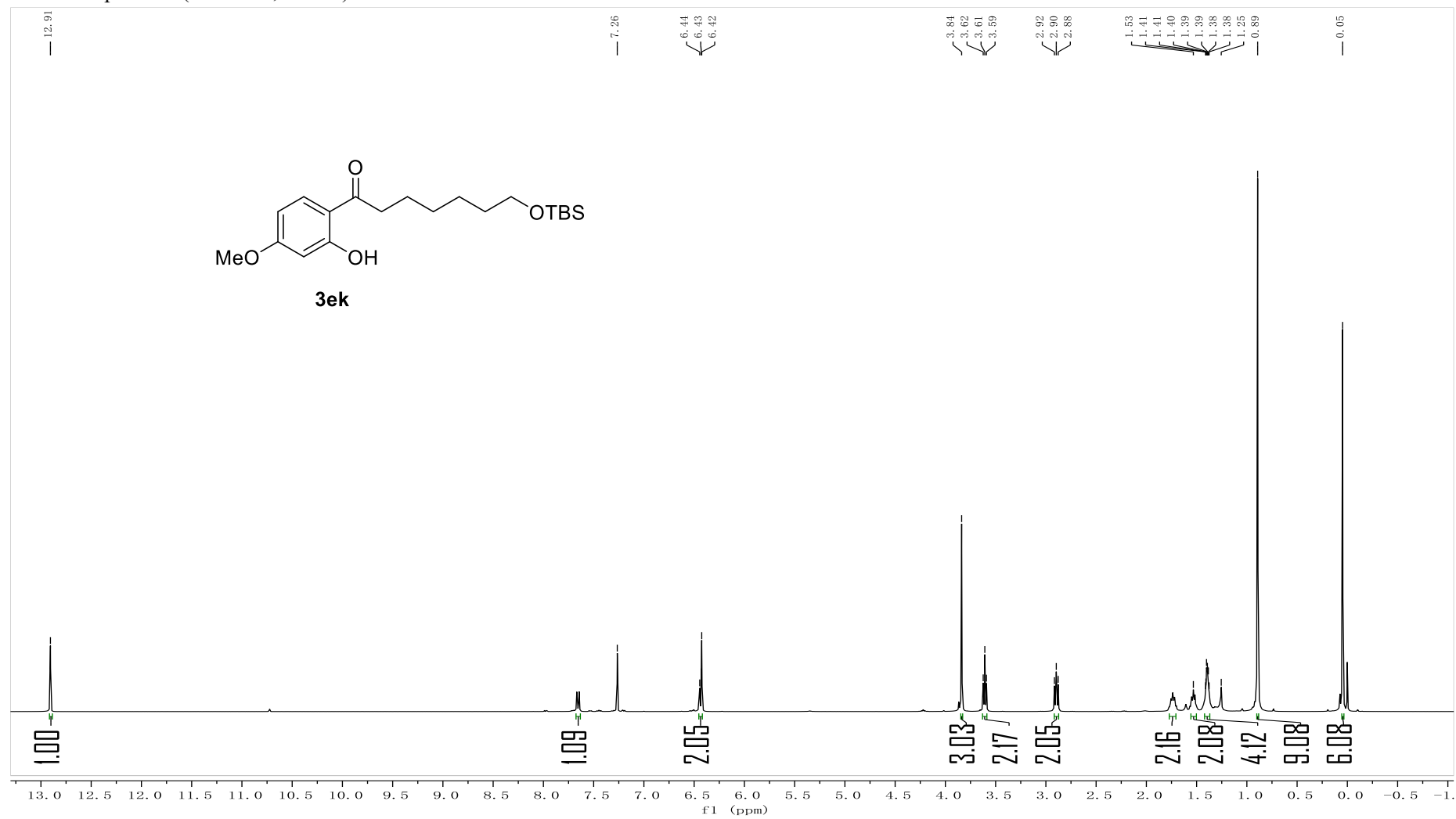
^1H NMR-spectrum (400 MHz, CDCl_3) of **3dk**



^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3dk**



^1H NMR-spectrum (400 MHz, CDCl_3) of **3ek**



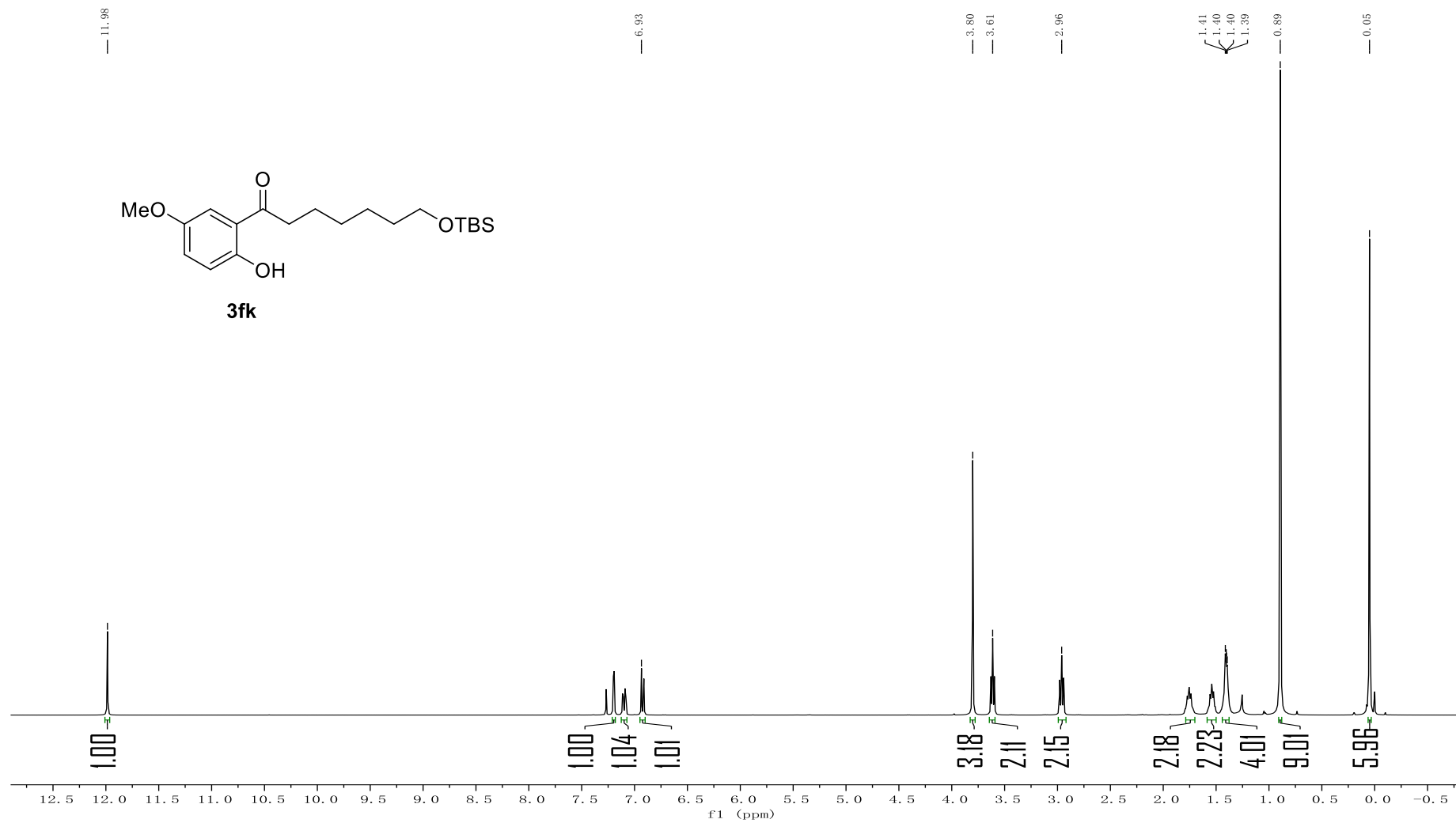
Chemical structure of compound **3ek** is shown above the spectrum:

COc1ccc(cc1C(=O)CCCCCO[Si](C)(C)C)O

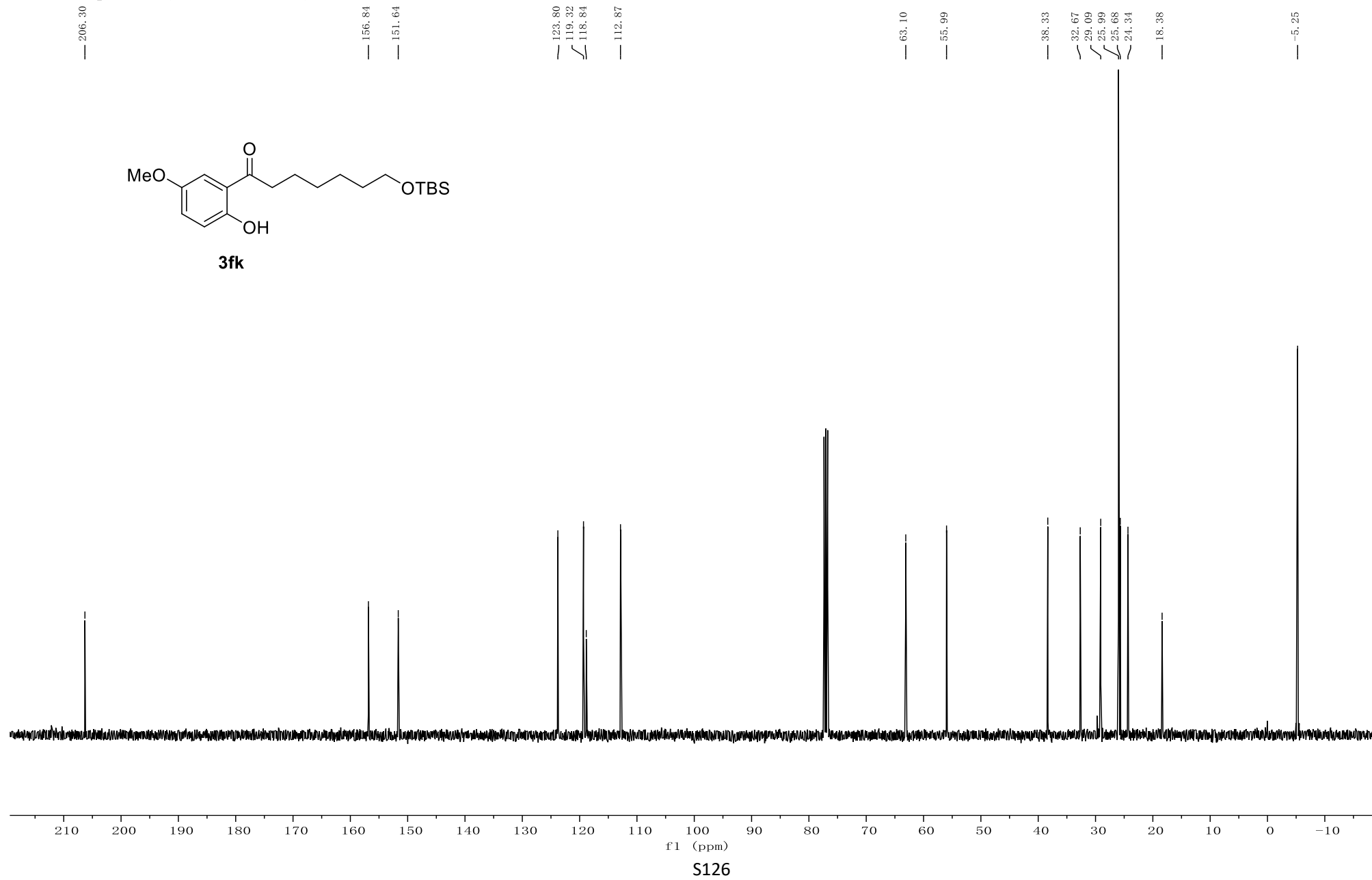
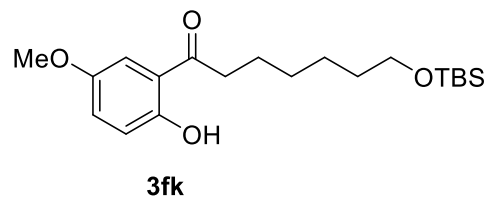
The spectrum displays the following chemical shifts (ppm):

Chemical Shift (ppm)
205.10
165.89
165.44
131.61
113.47
107.56
100.93
63.14
55.56
37.95
32.68
29.18
26.00
25.67
24.86
18.40
-5.25

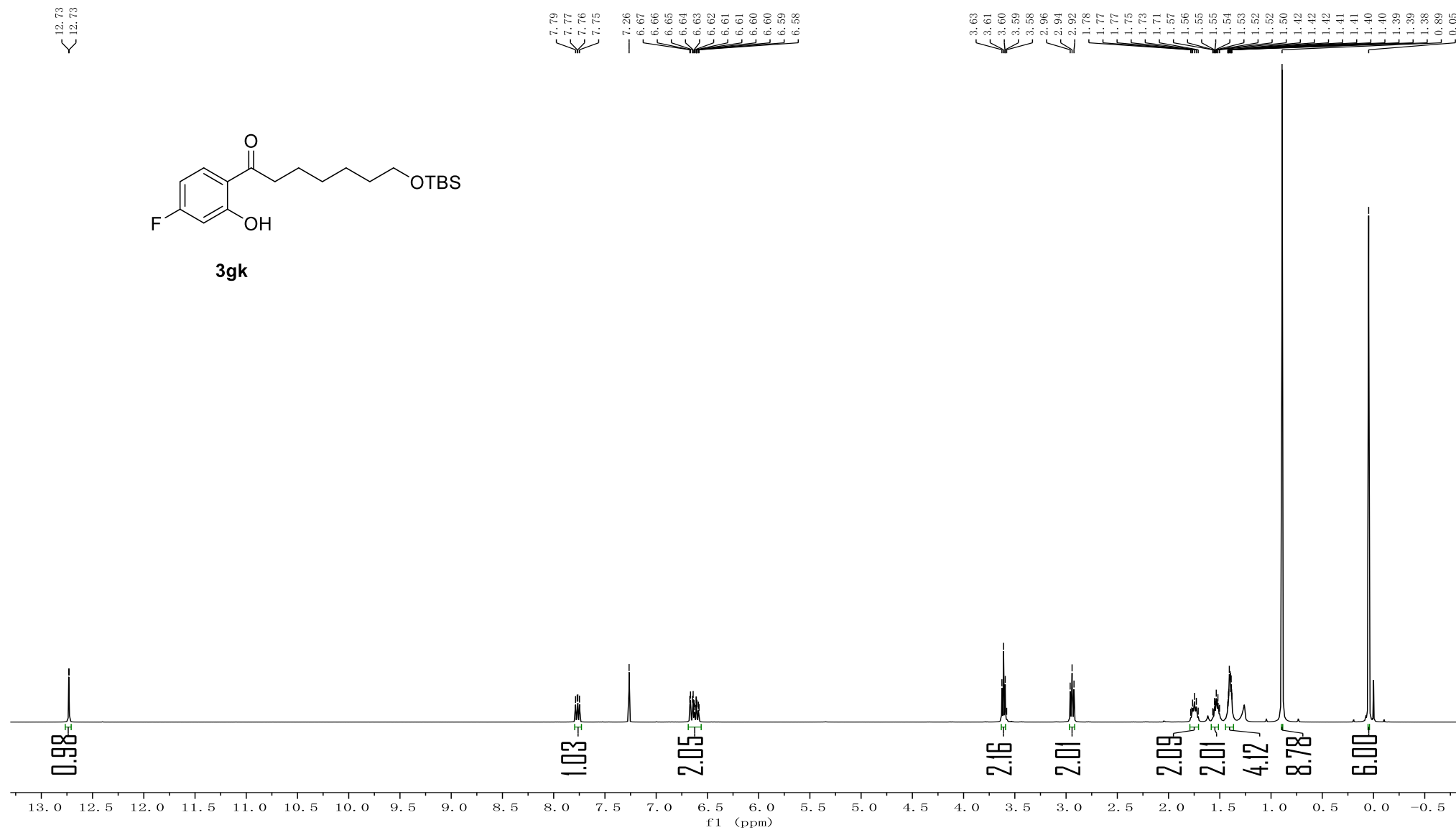
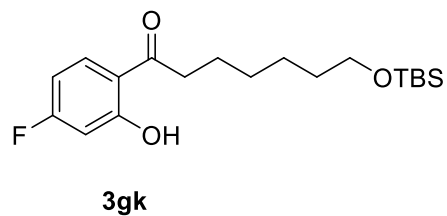
^1H NMR-spectrum (400 MHz, CDCl_3) of **3fk**



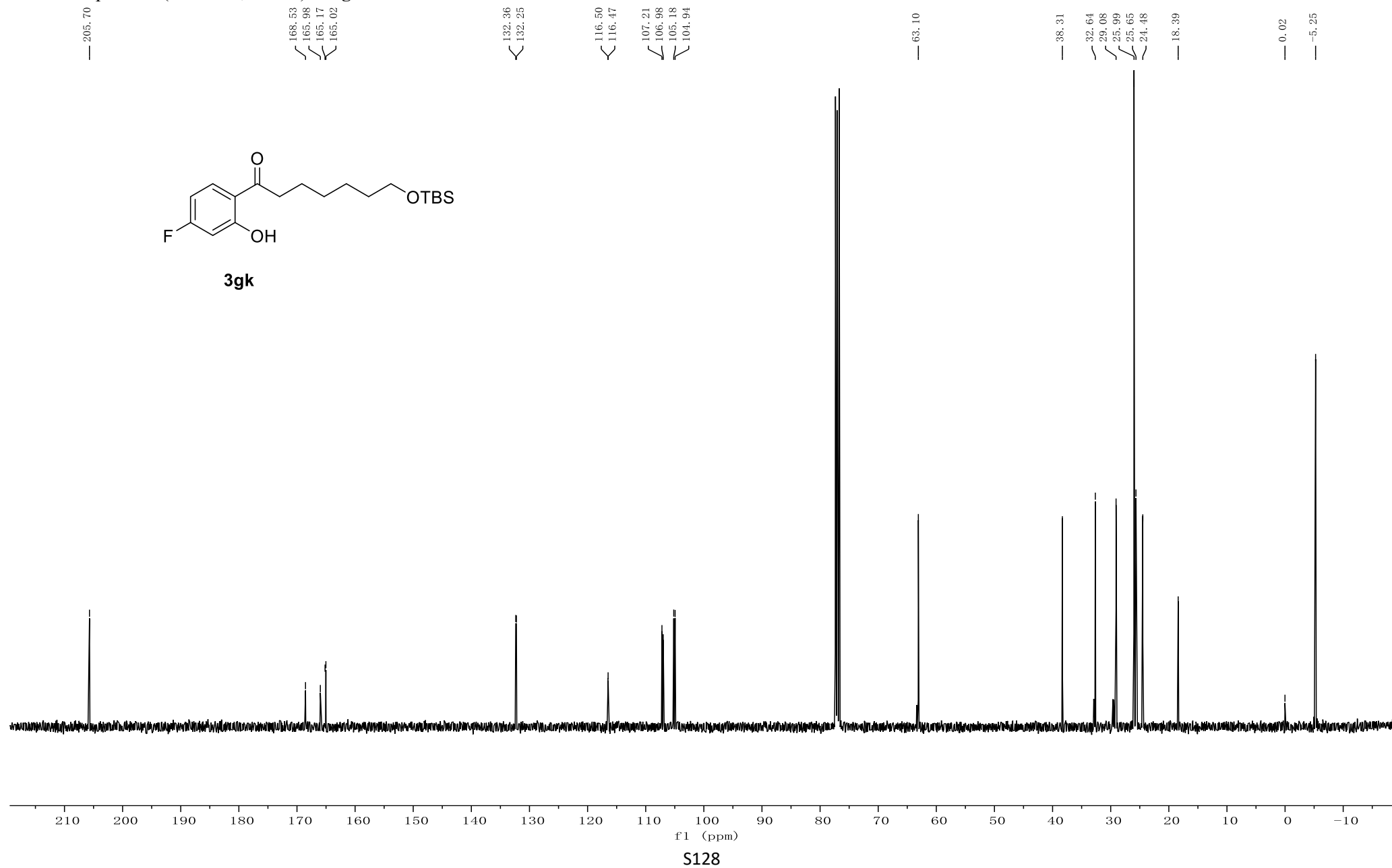
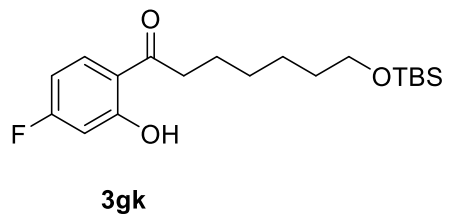
¹³C NMR-spectrum (101 MHz, CDCl₃) of **3fk**



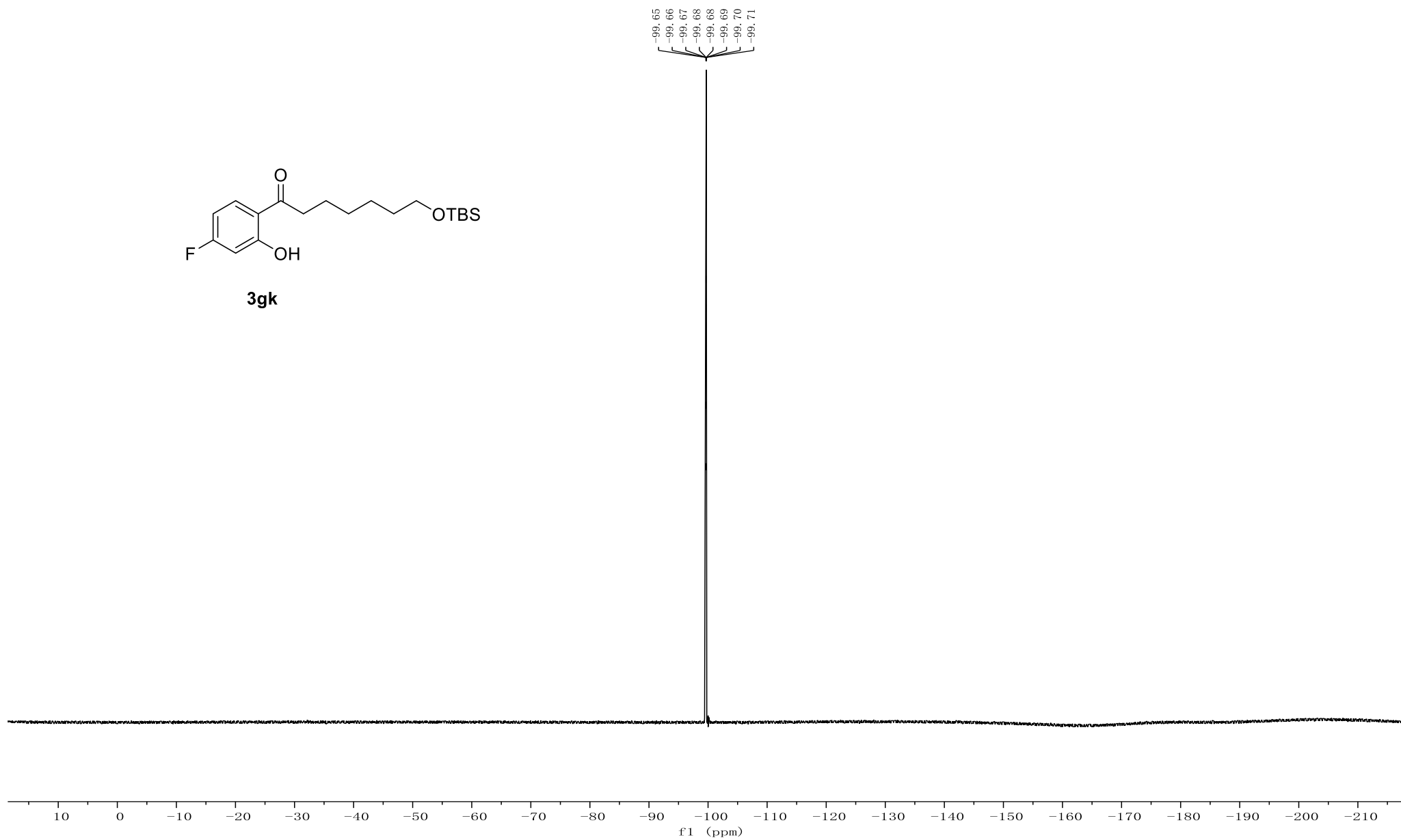
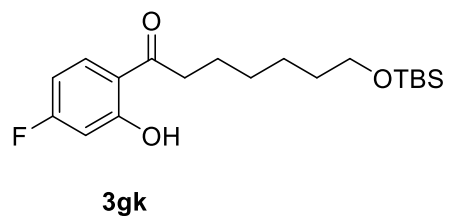
¹H NMR-spectrum (400 MHz, CDCl₃) of **3gk**



^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3gk**

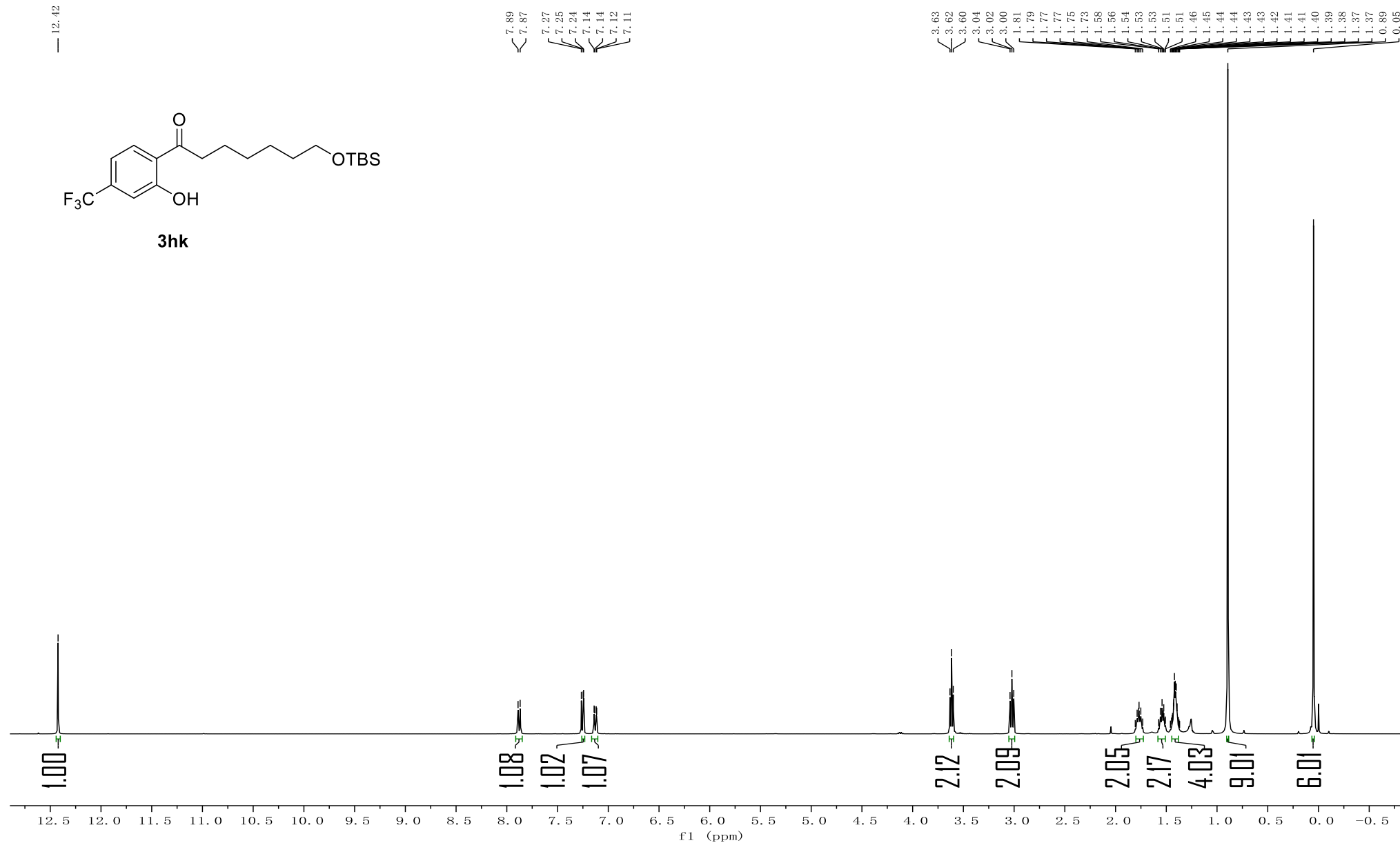


^{19}F NMR-spectrum (376 MHz, CDCl_3) of **3gk**

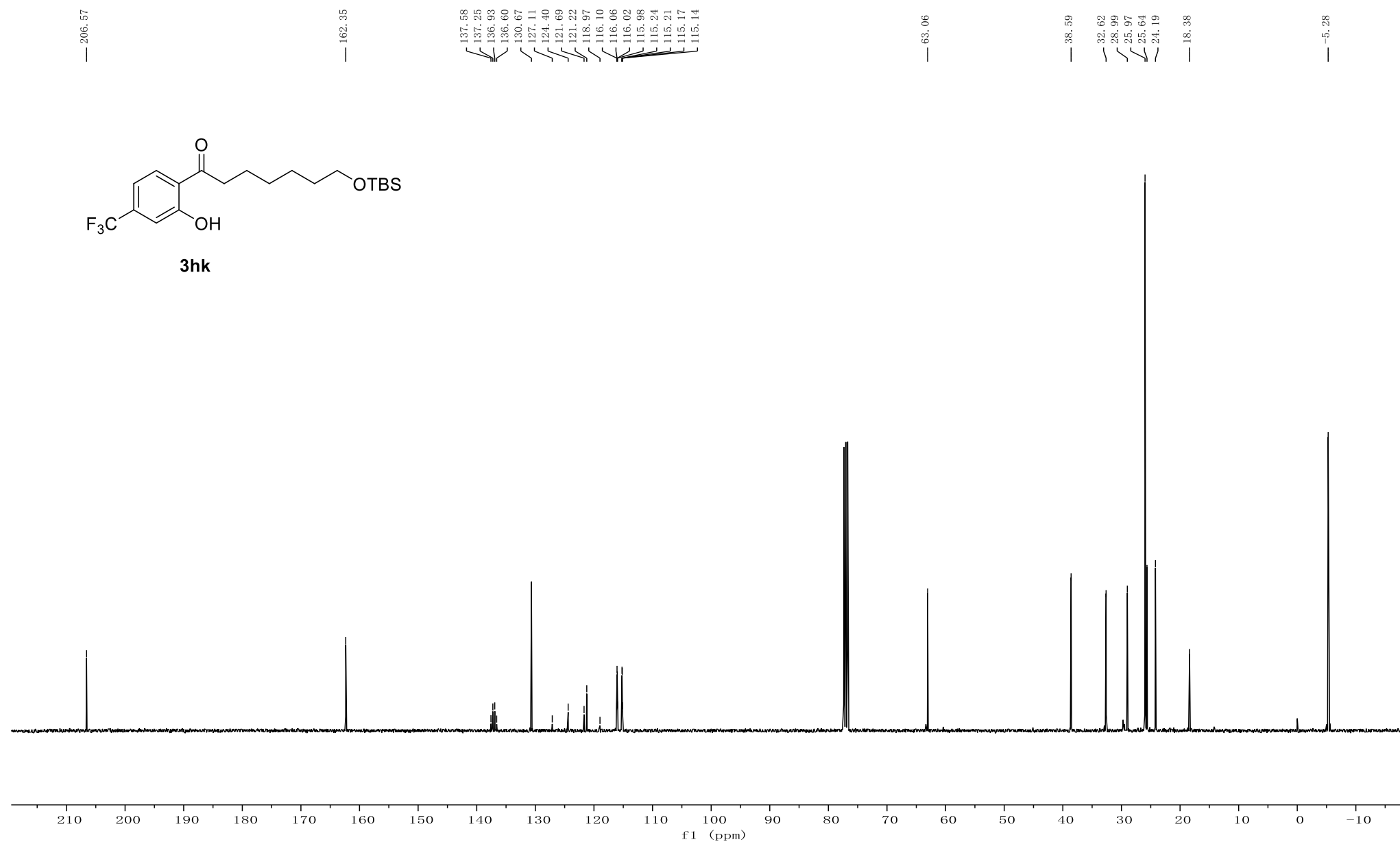


S129

¹H NMR-spectrum (400 MHz, CDCl₃) of **3hk**

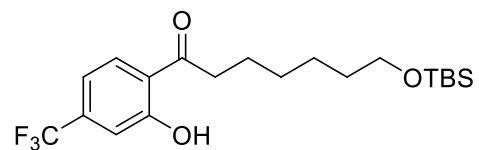


¹³C NMR-spectrum (101 MHz, CDCl₃) of **3hk**



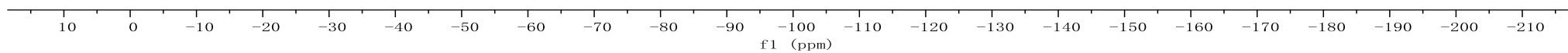
S131

^{19}F NMR-spectrum (376 MHz, CDCl_3) of **3hk**



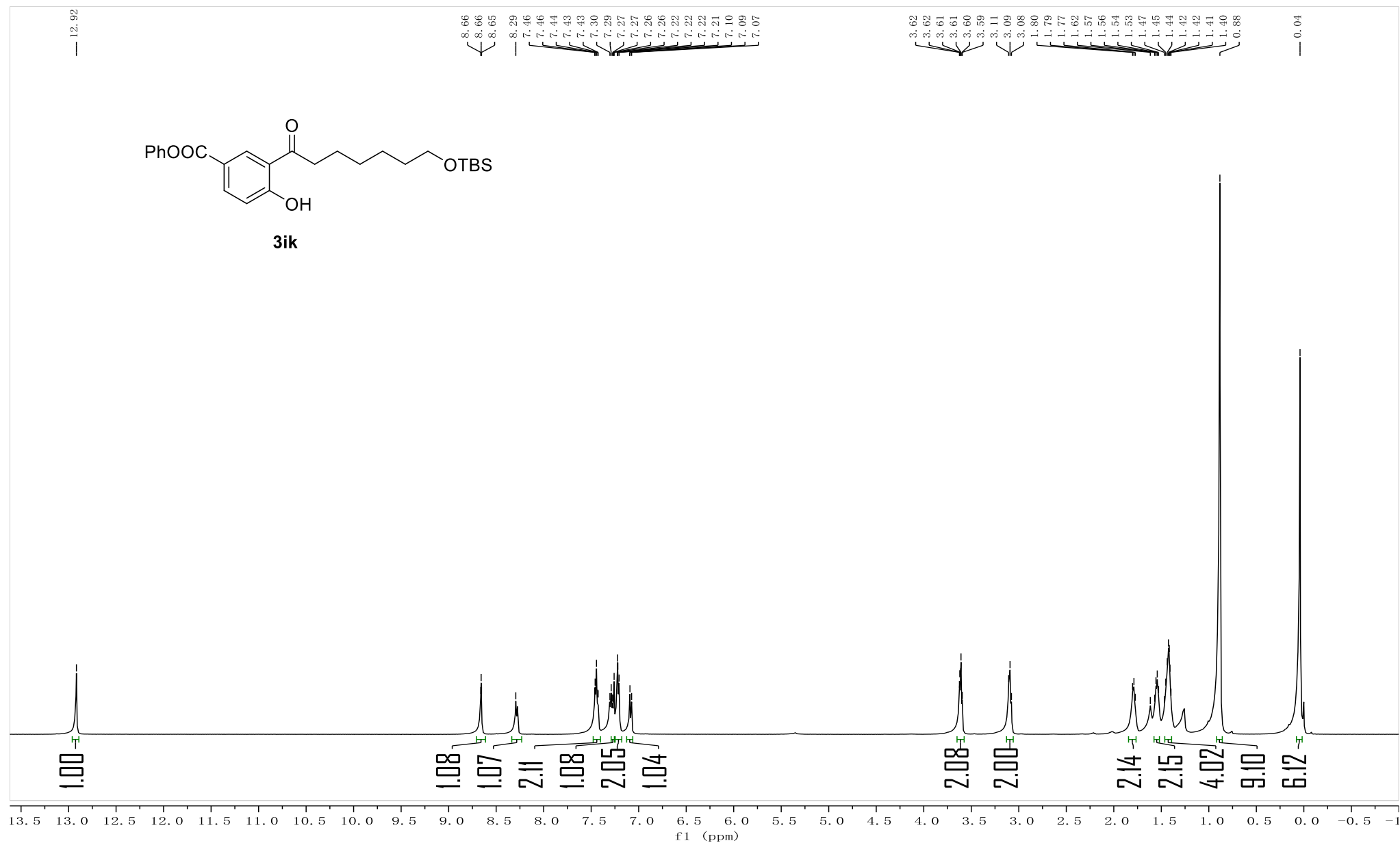
3hk

-63.91



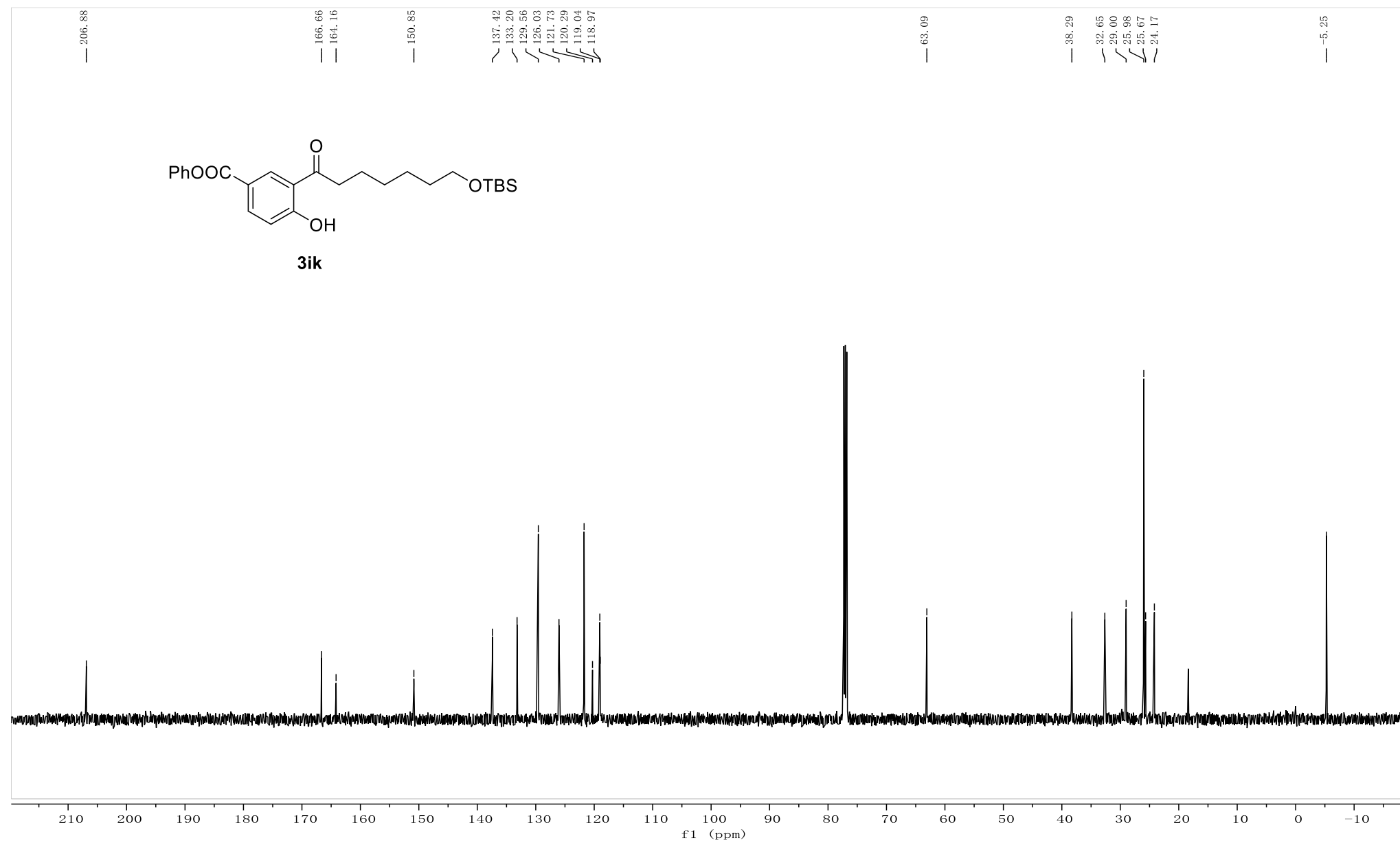
S132

¹H NMR-spectrum (500 MHz, CDCl₃) of **3ik**



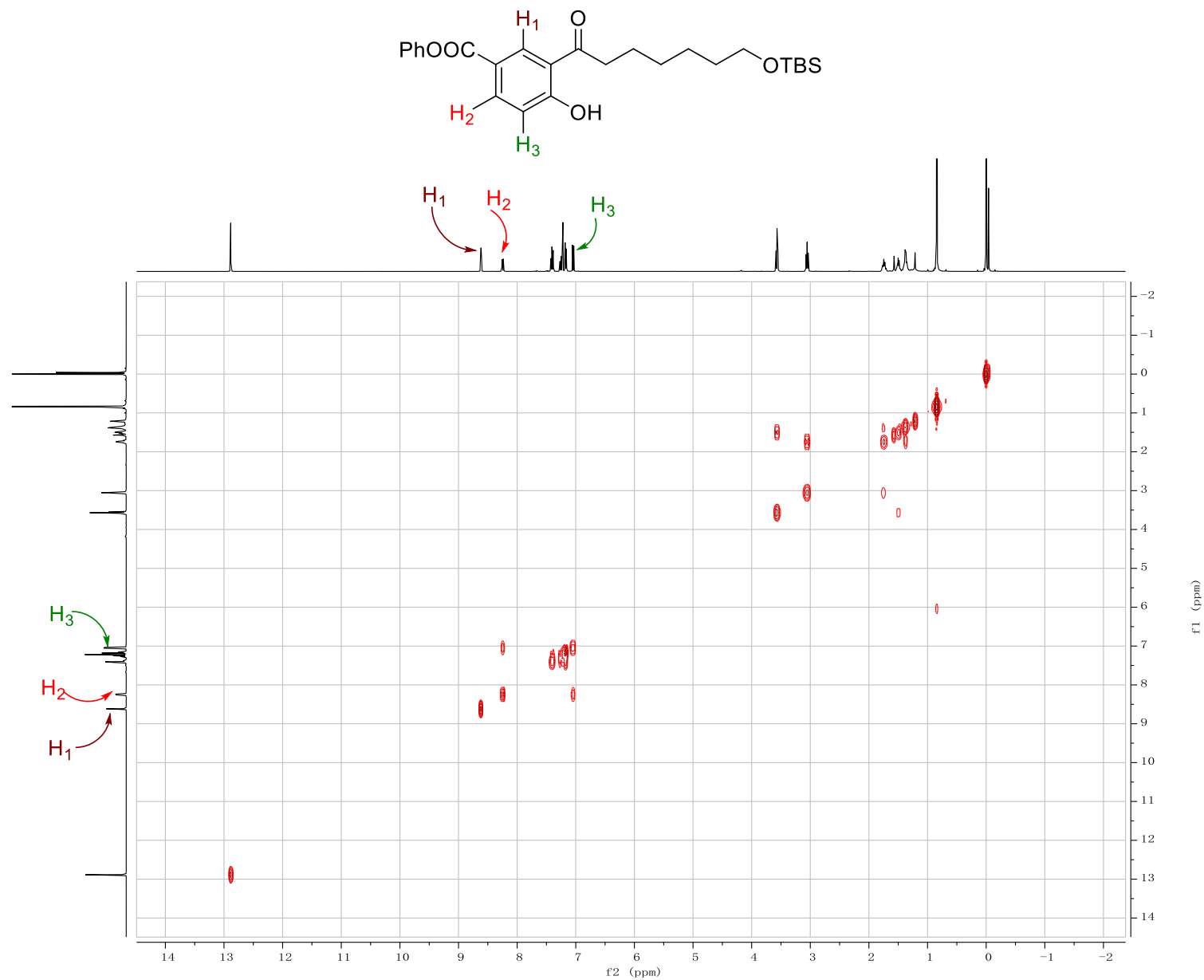
S133

^{13}C NMR-spectrum (101 MHz, CDCl_3) of **3ik**



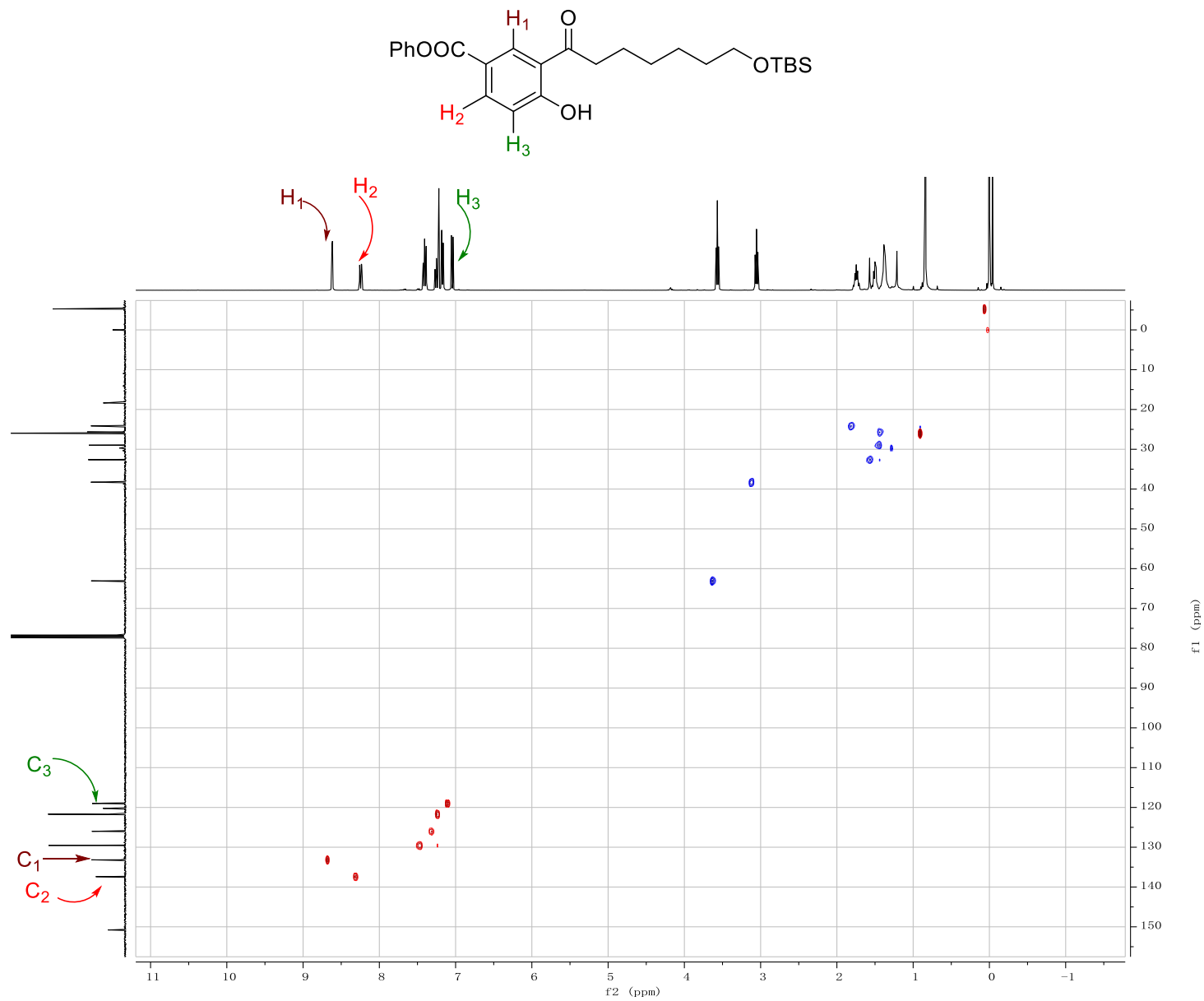
S134

COSY-spectrum of **3ik**

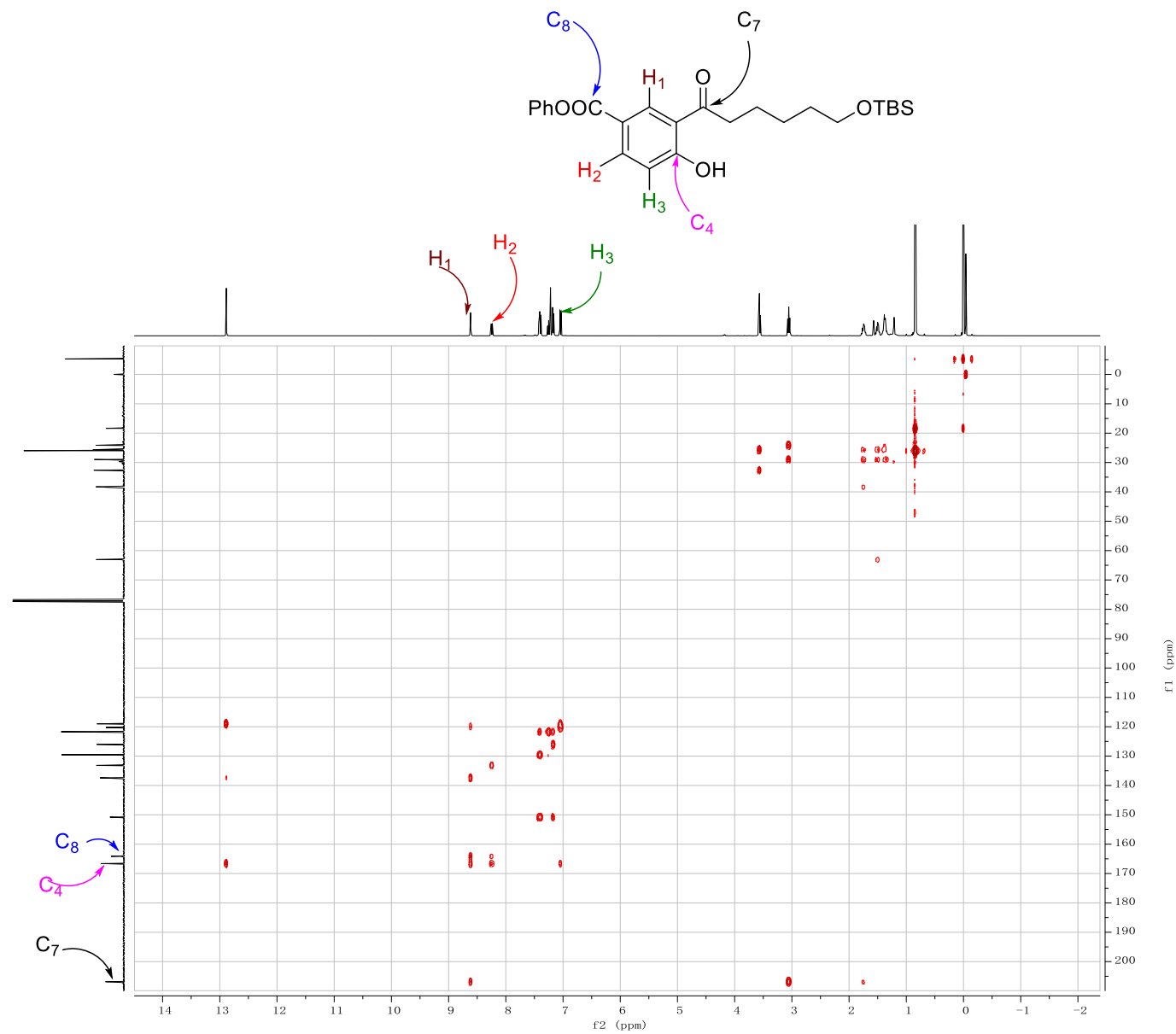


S135

HSQC-spectrum of **3ik**

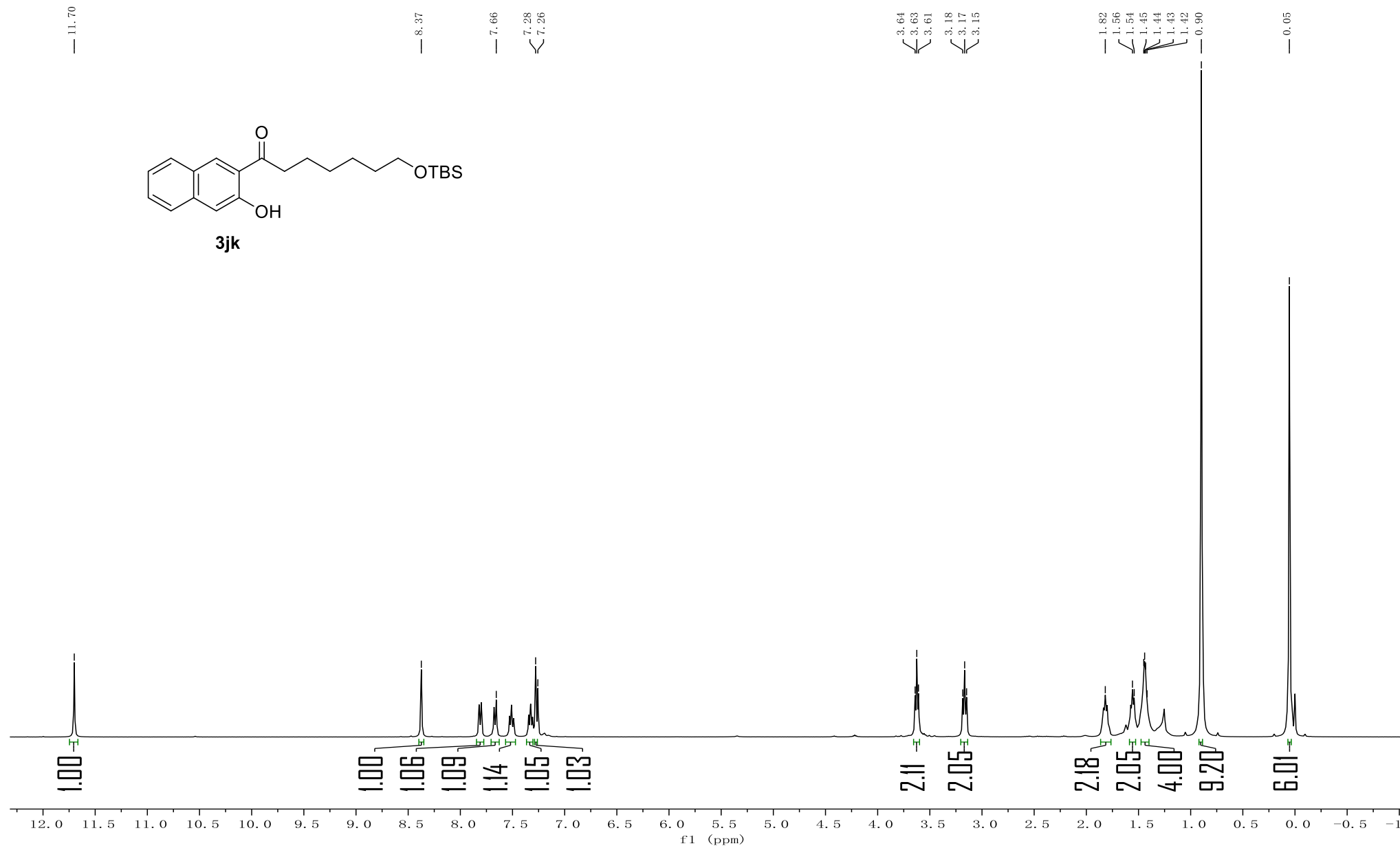


HMBC-spectrum of **3ik**

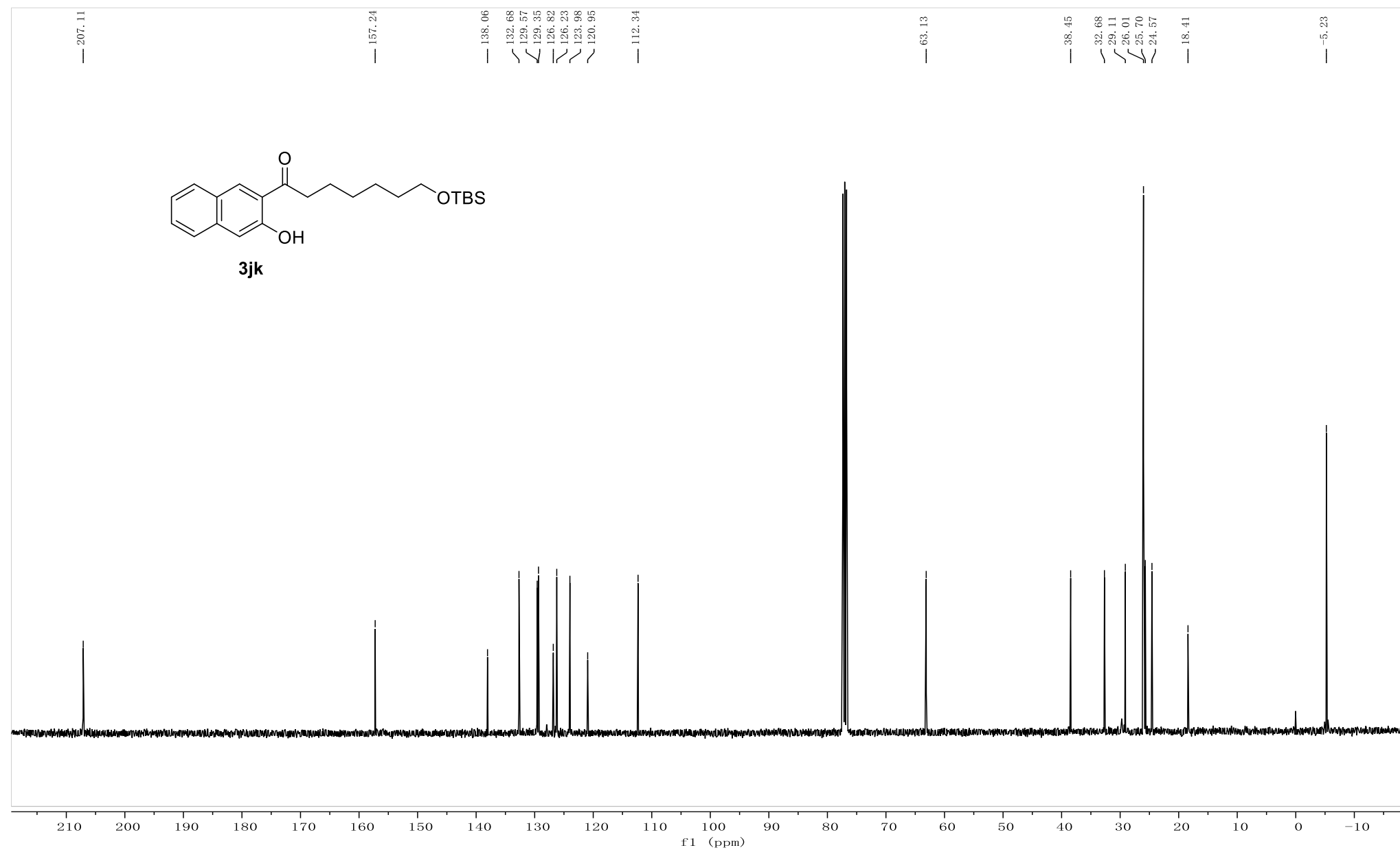


S137

¹H NMR-spectrum (400 MHz, CDCl₃) of **3jk**

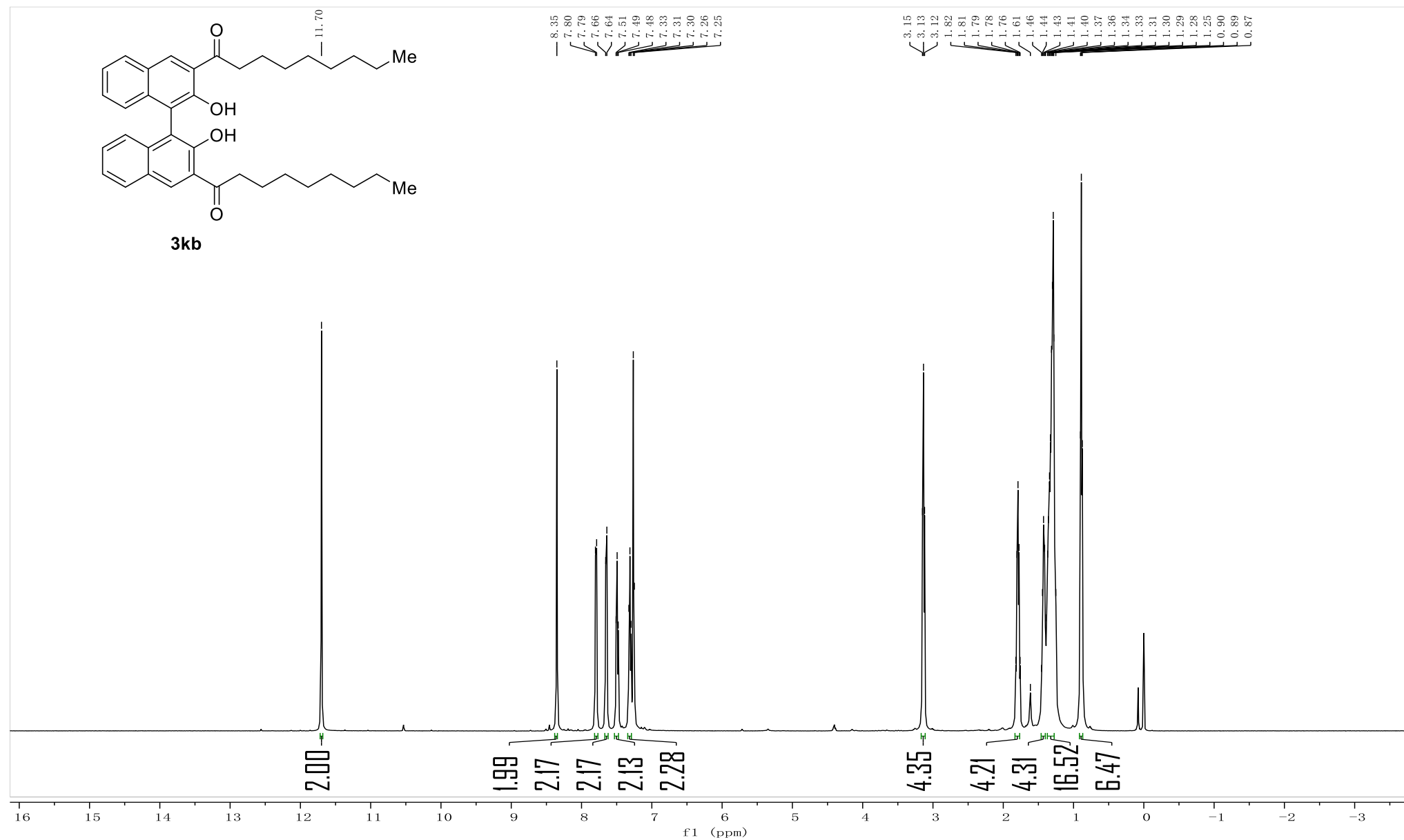


¹³CNMR-spectrum (101 MHz, CDCl₃) of **3jk**

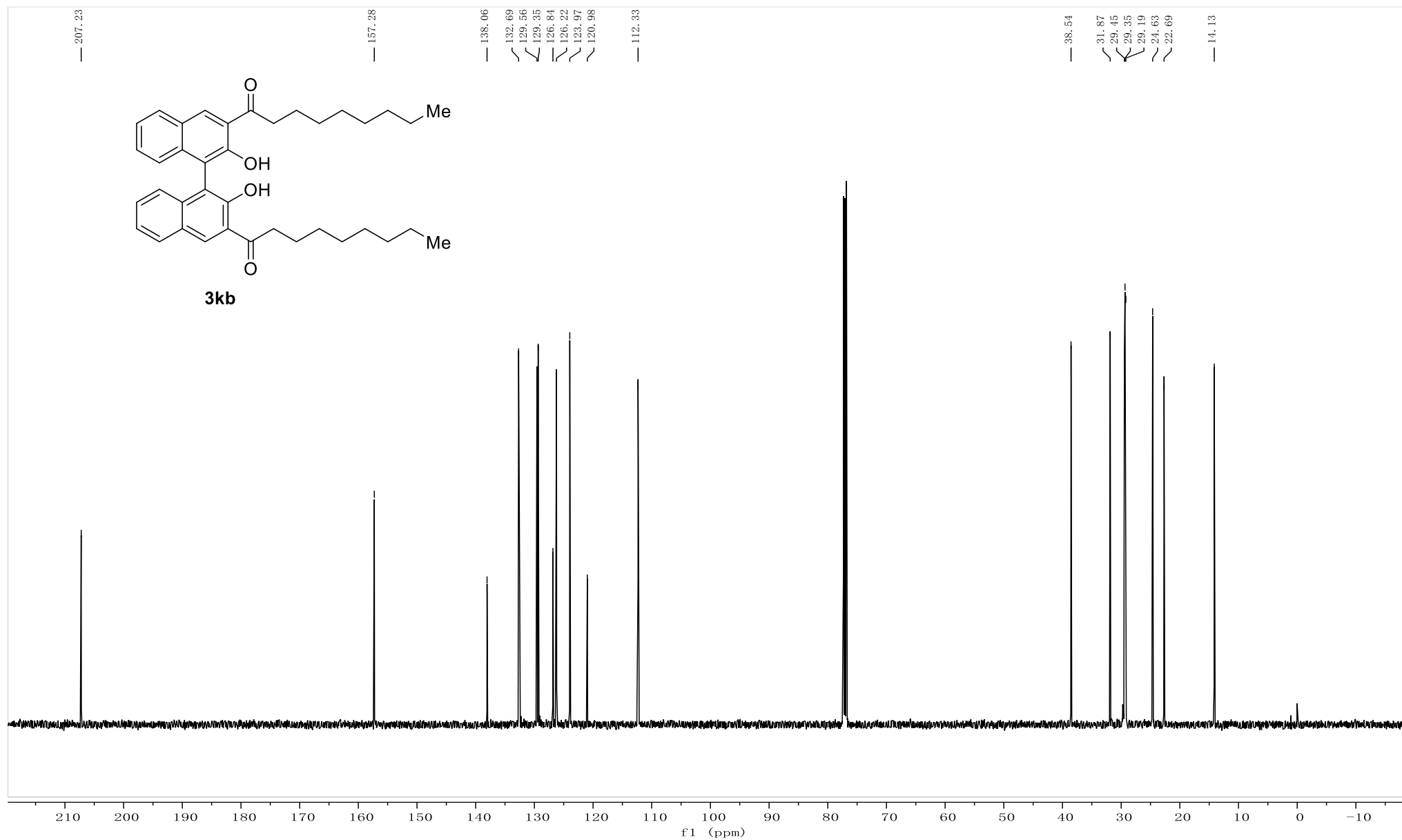


S139

¹H NMR-spectrum (500 MHz, CDCl₃) of **3kb**

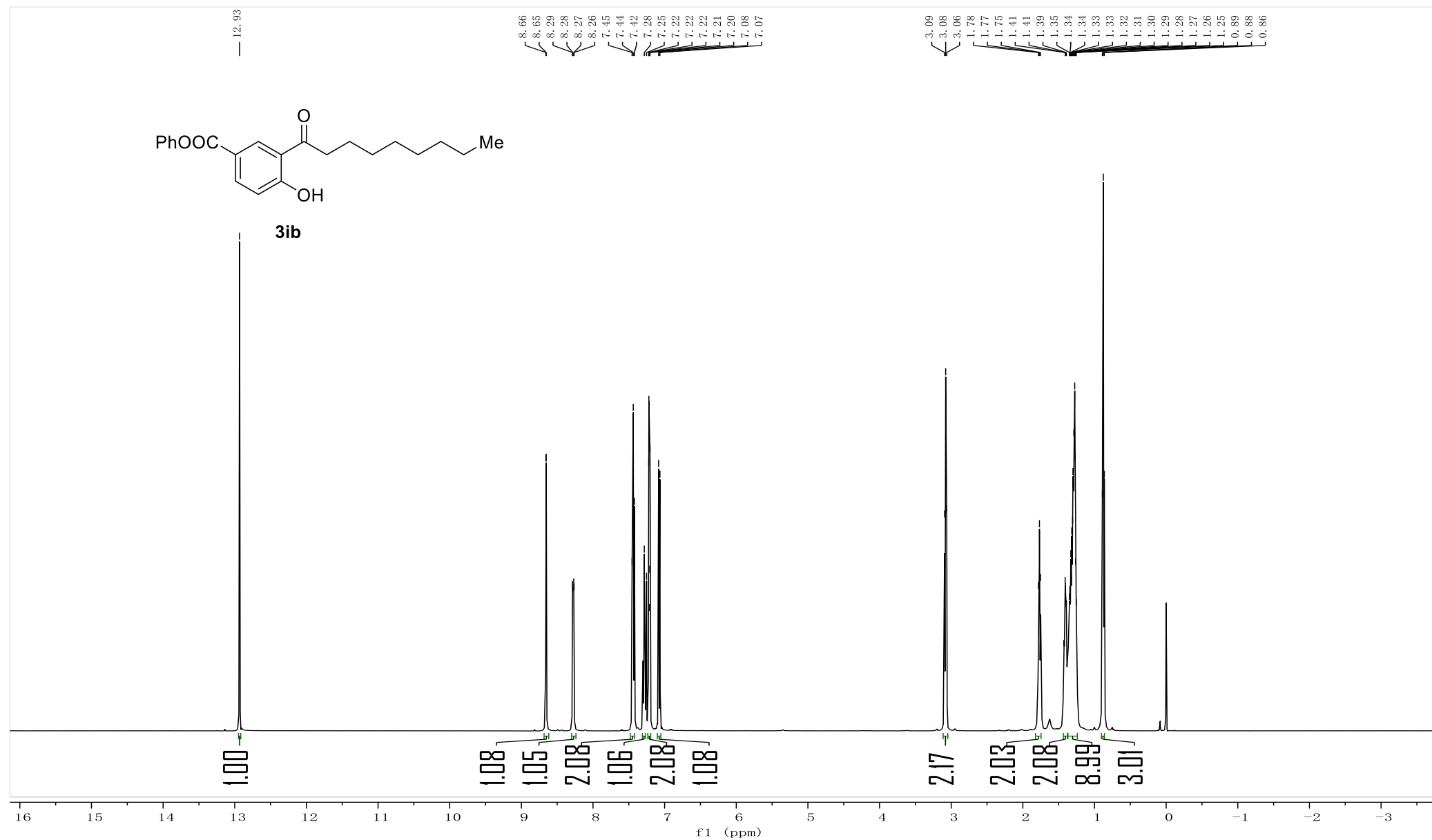


^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3kb**

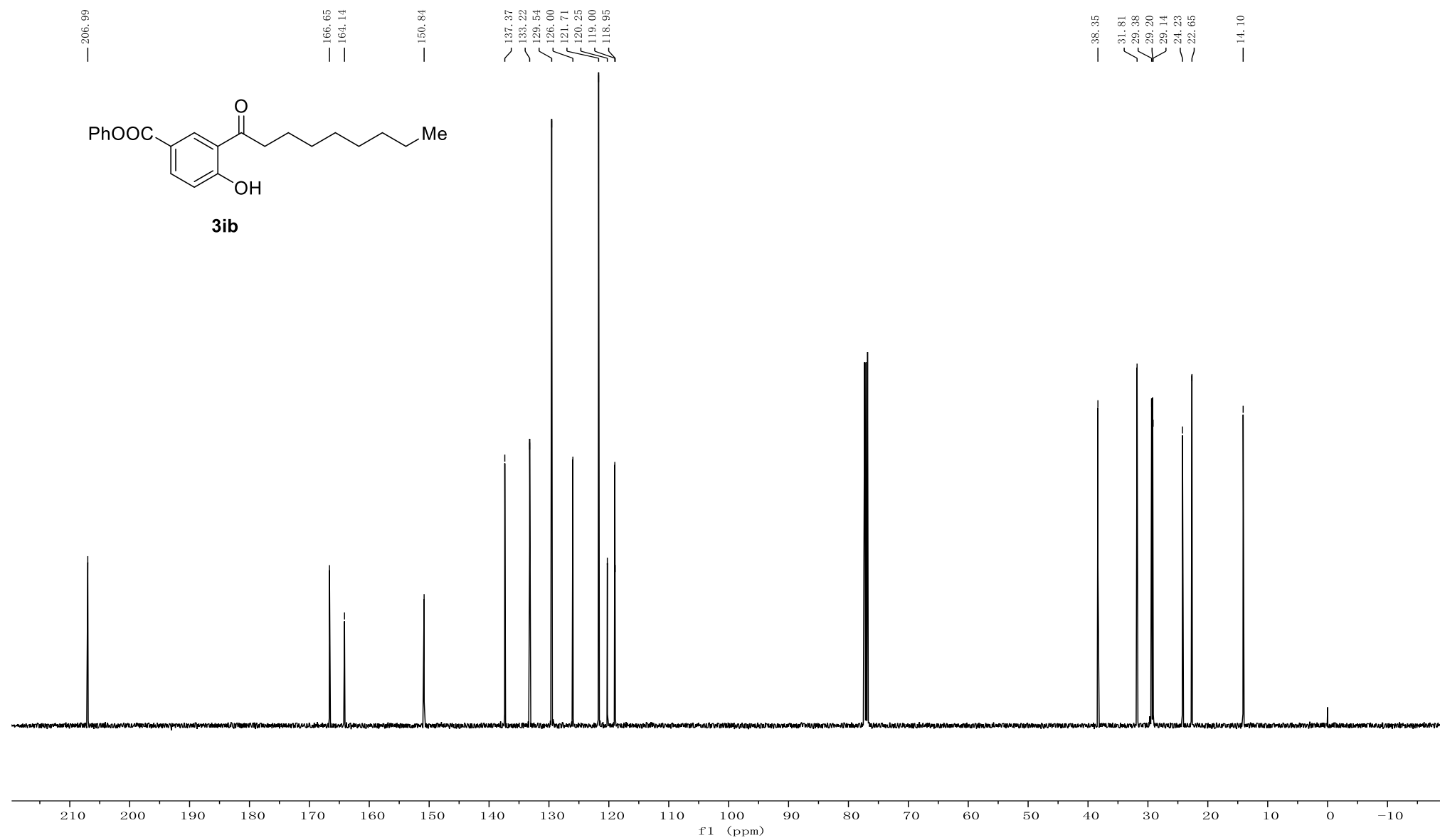


S141

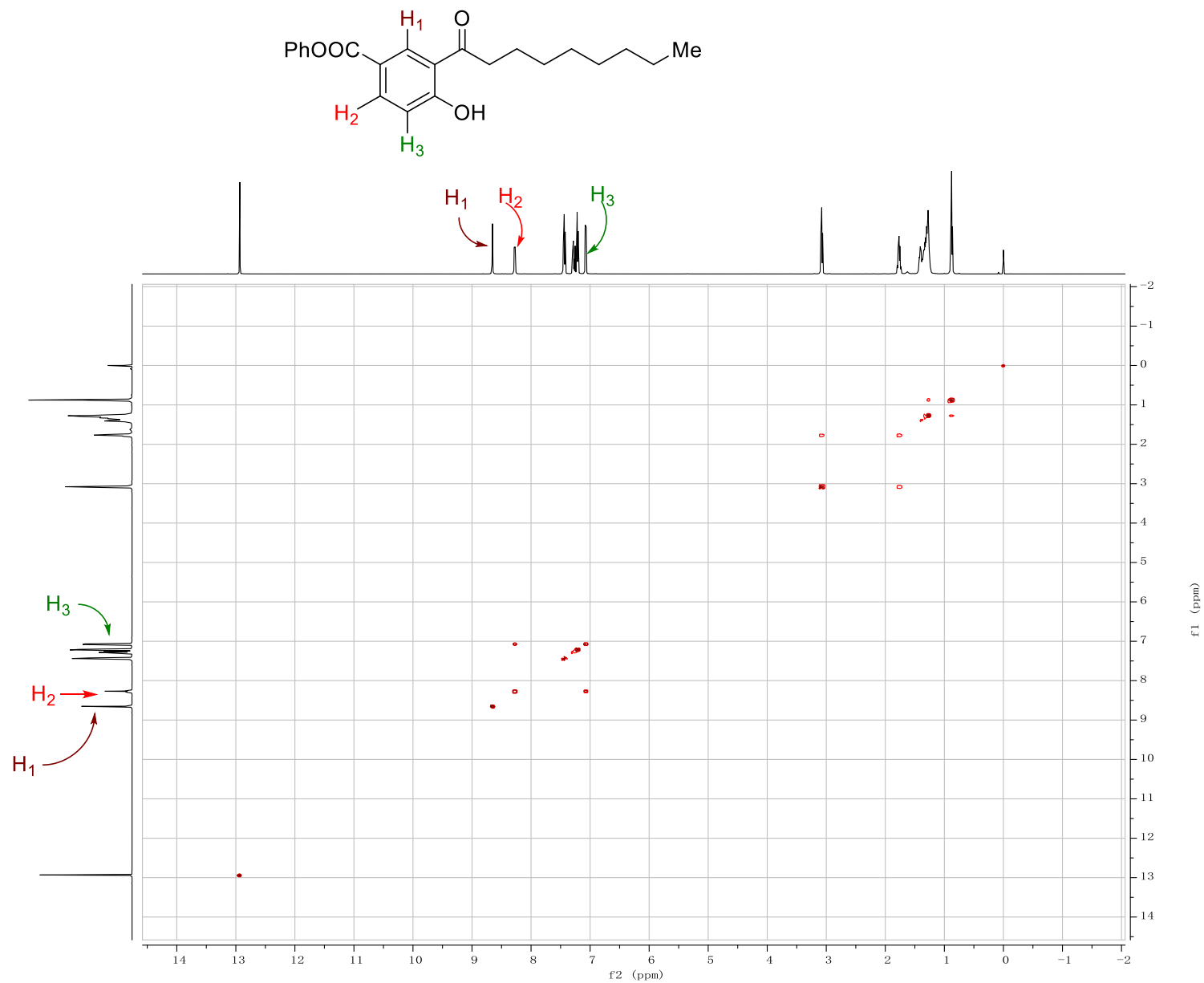
¹H NMR-spectrum (500 MHz, CDCl₃) of **3ib**



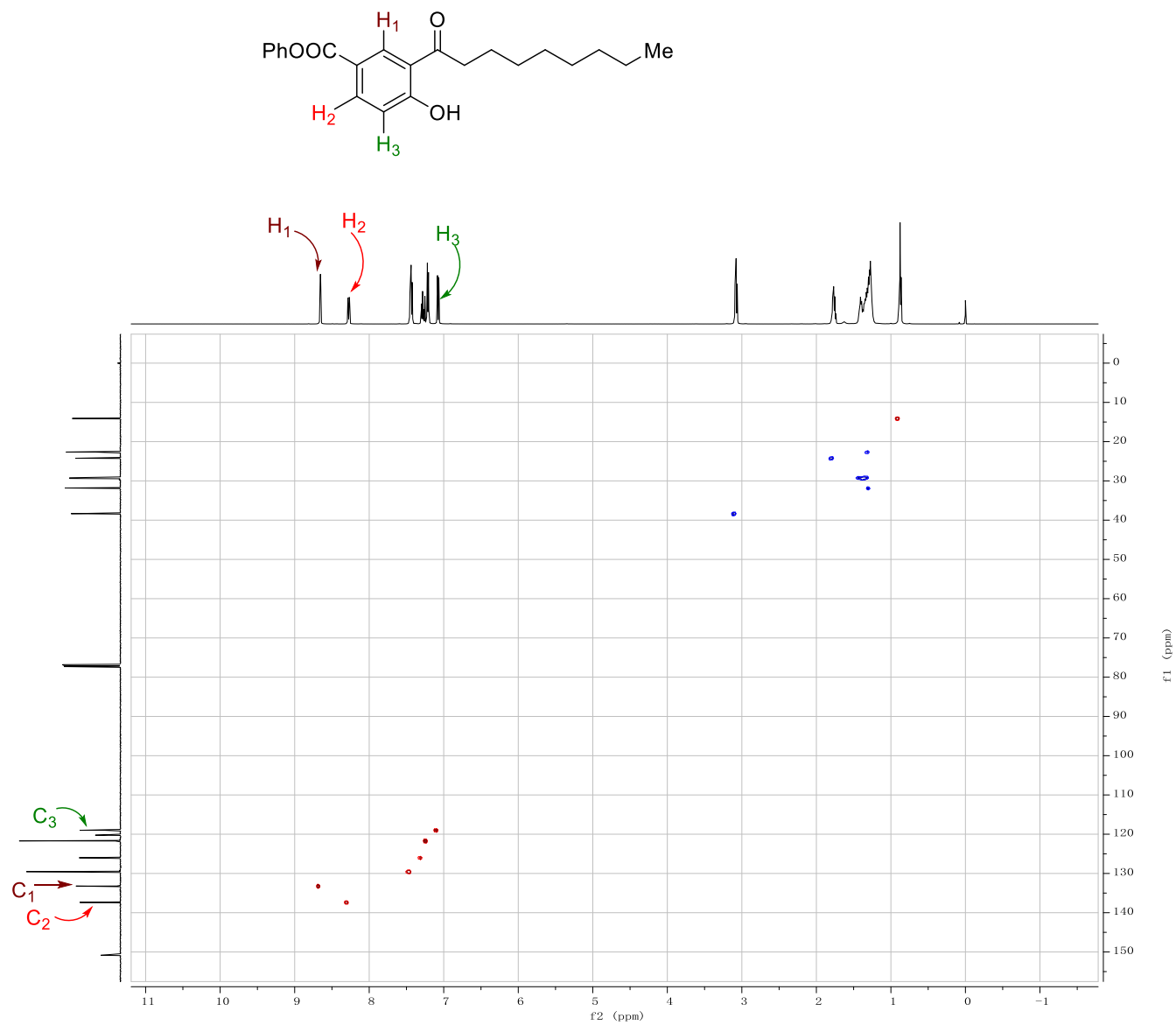
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **3ib**



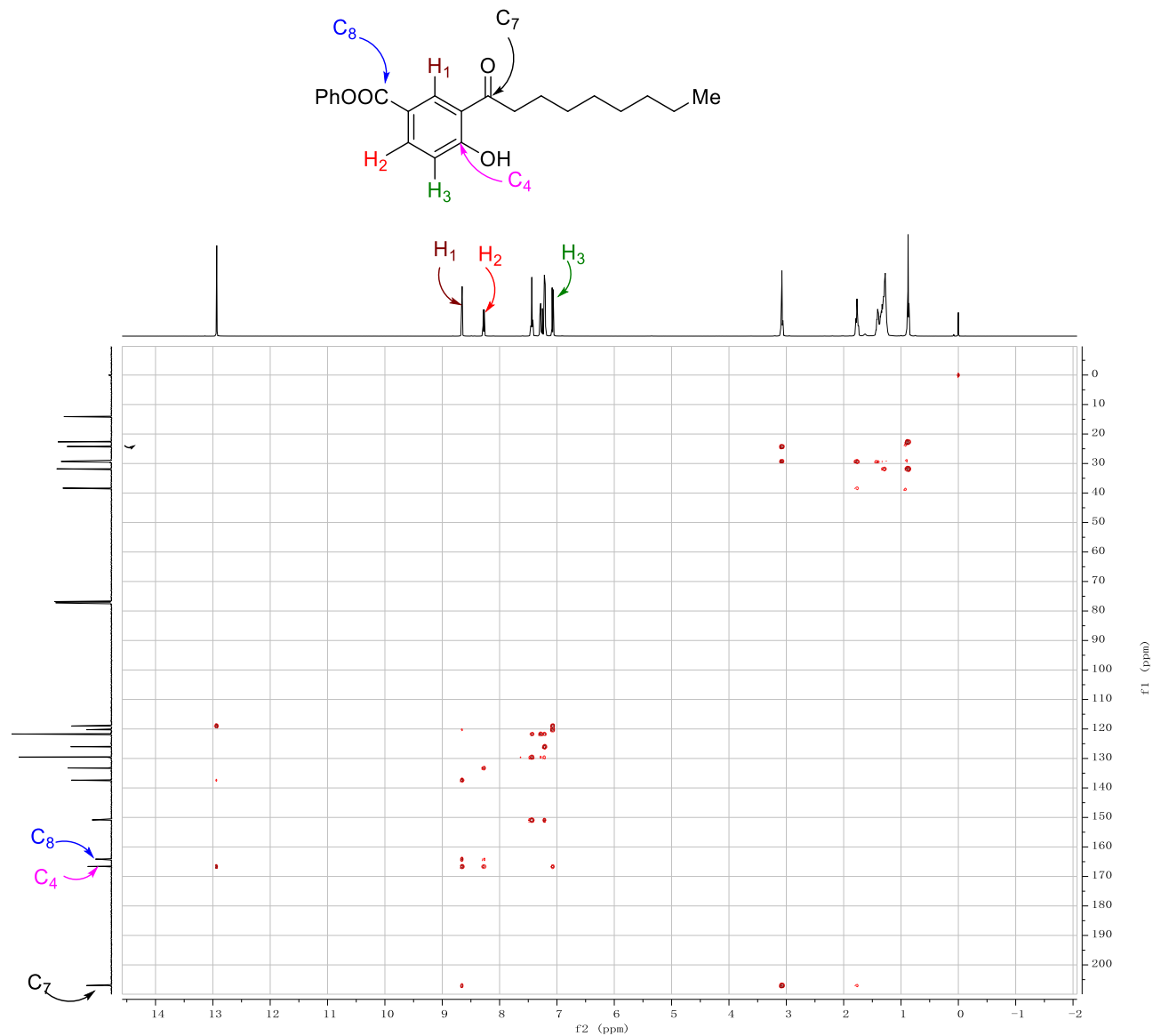
COSY-spectrum of **3ib**



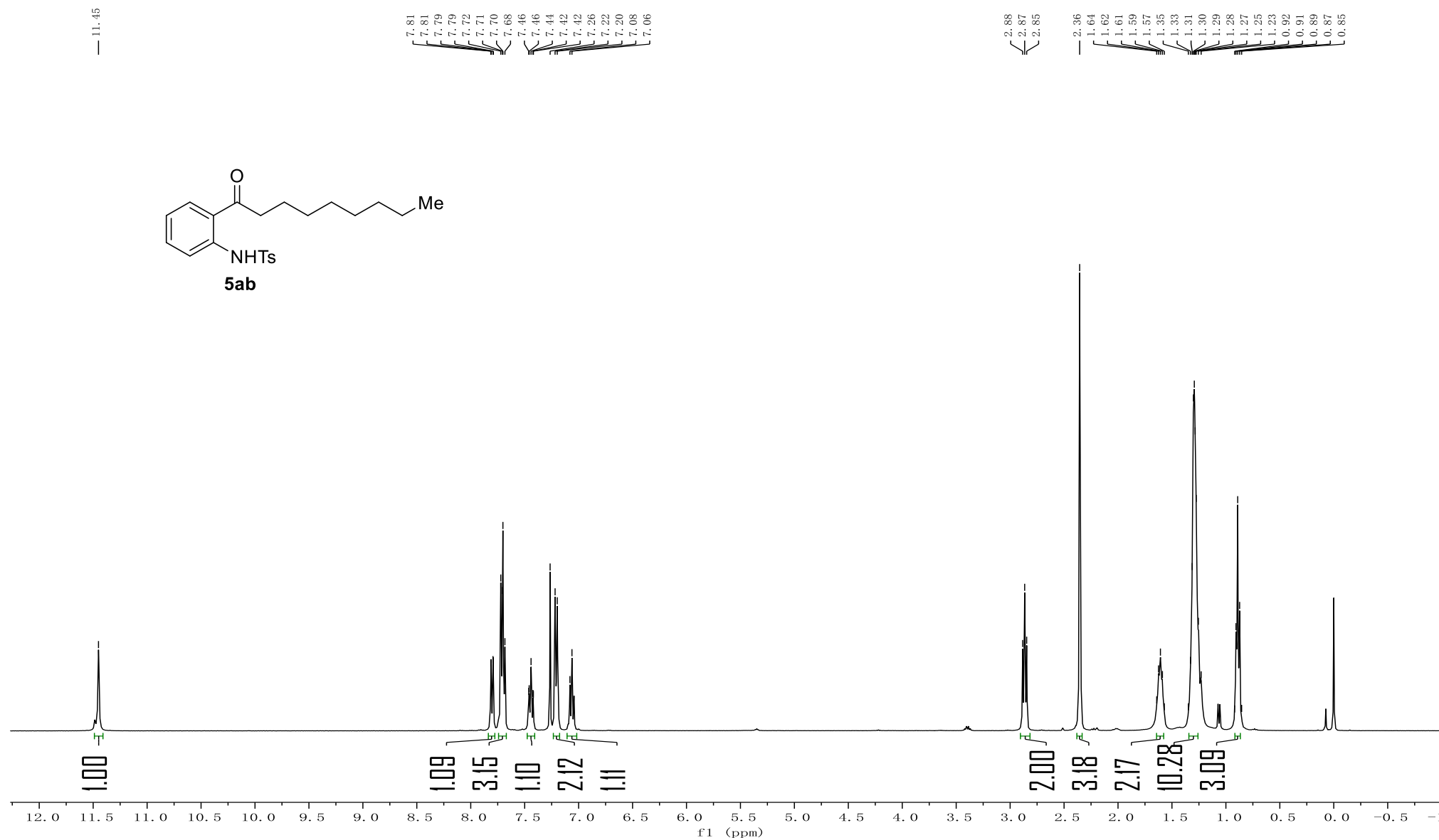
HSQC-spectrum of **3ib**



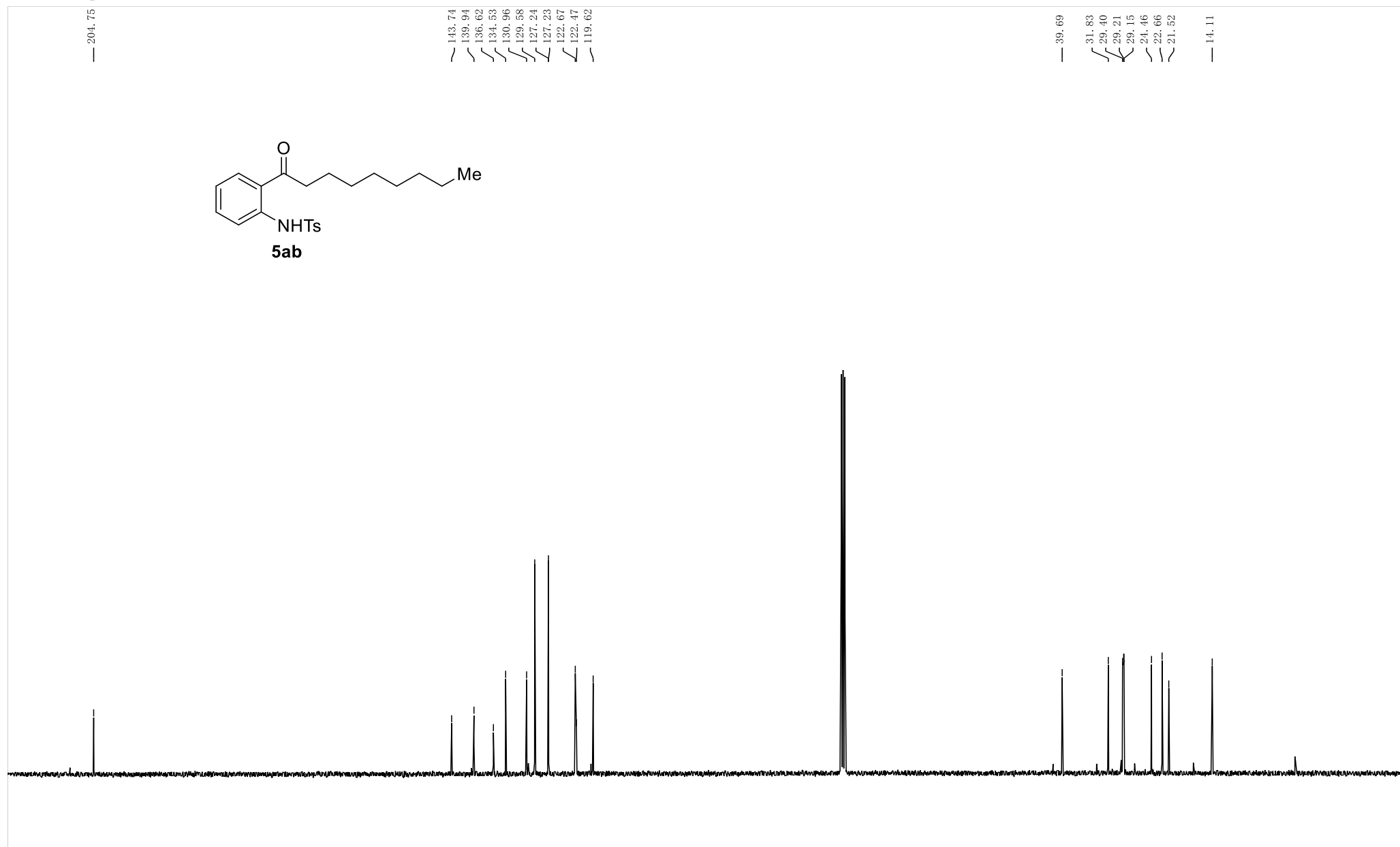
HMBC-spectrum of **3ib**



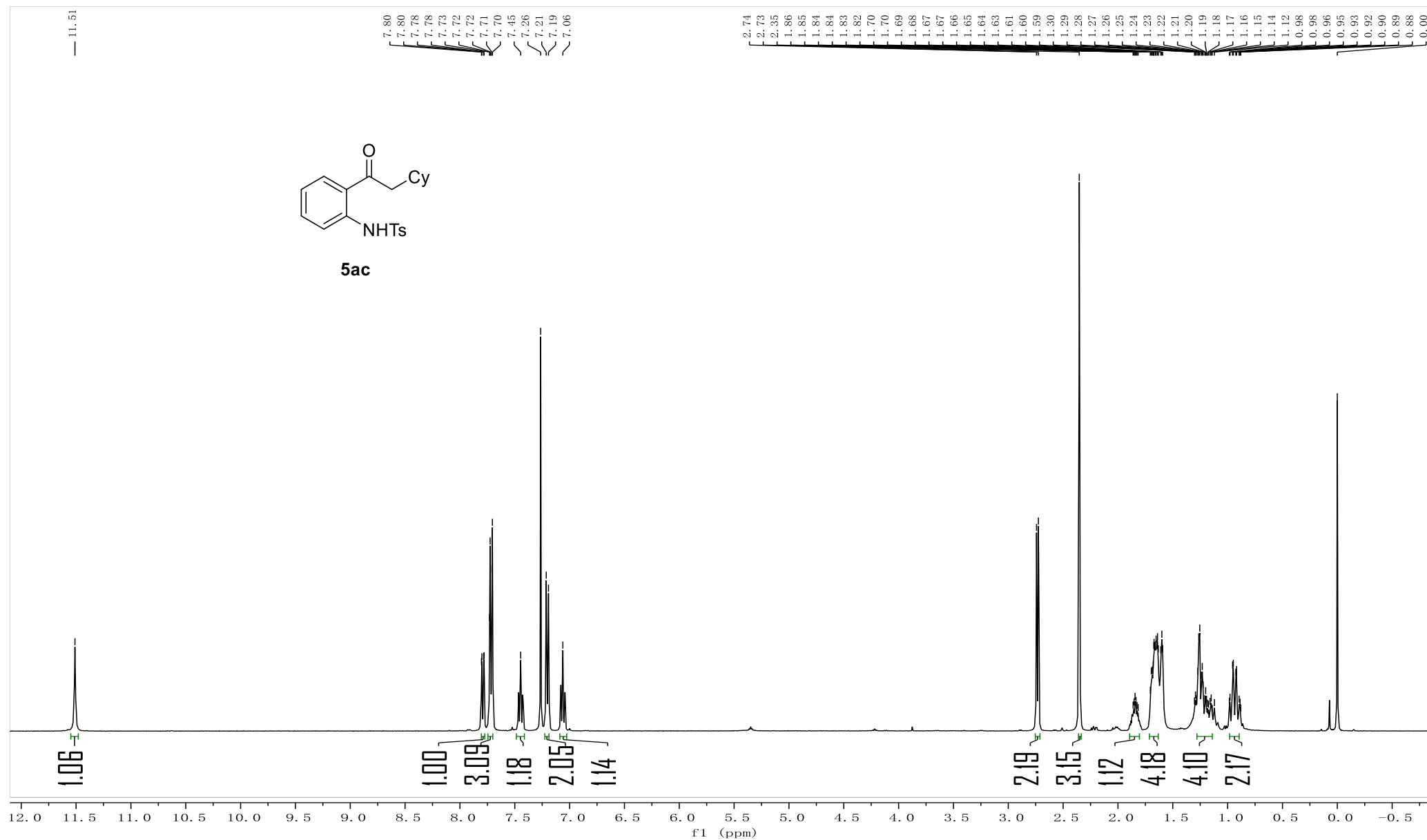
¹H NMR-spectrum (400 MHz, CDCl₃) of **5ab**



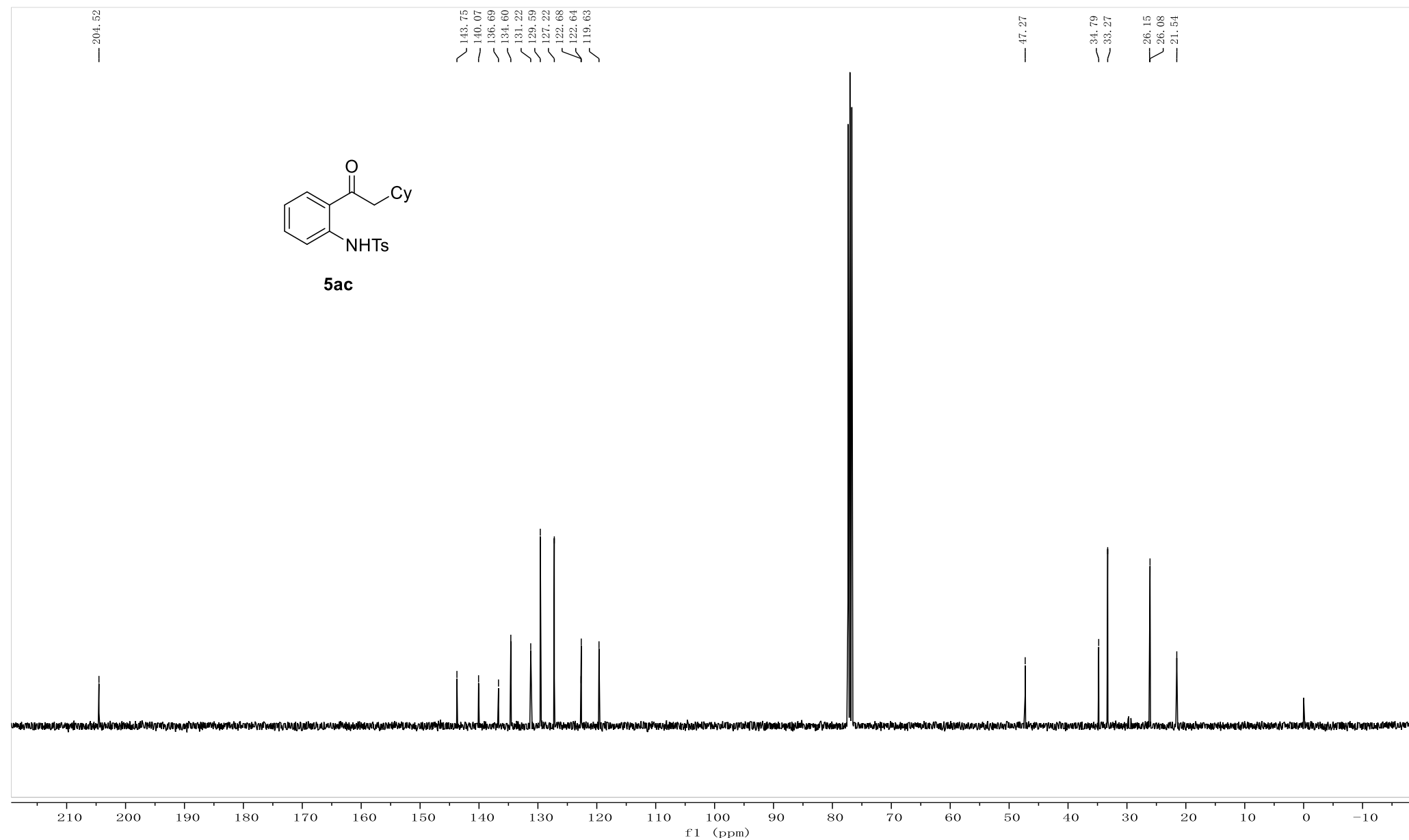
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **5ab**



¹H NMR-spectrum (400 MHz, CDCl₃) of **5ac**

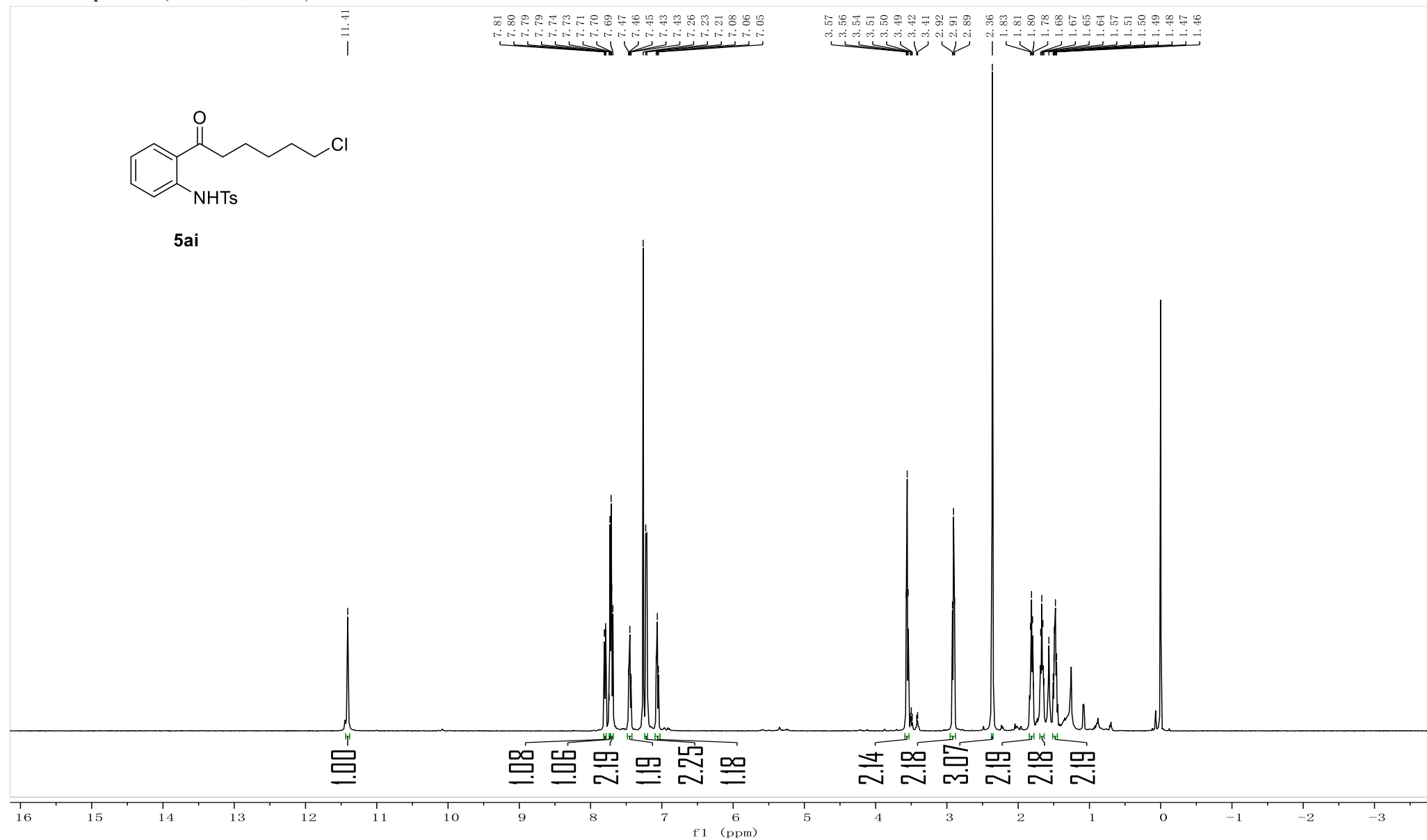


^{13}C NMR-spectrum (101 MHz, CDCl_3) of **5ac**

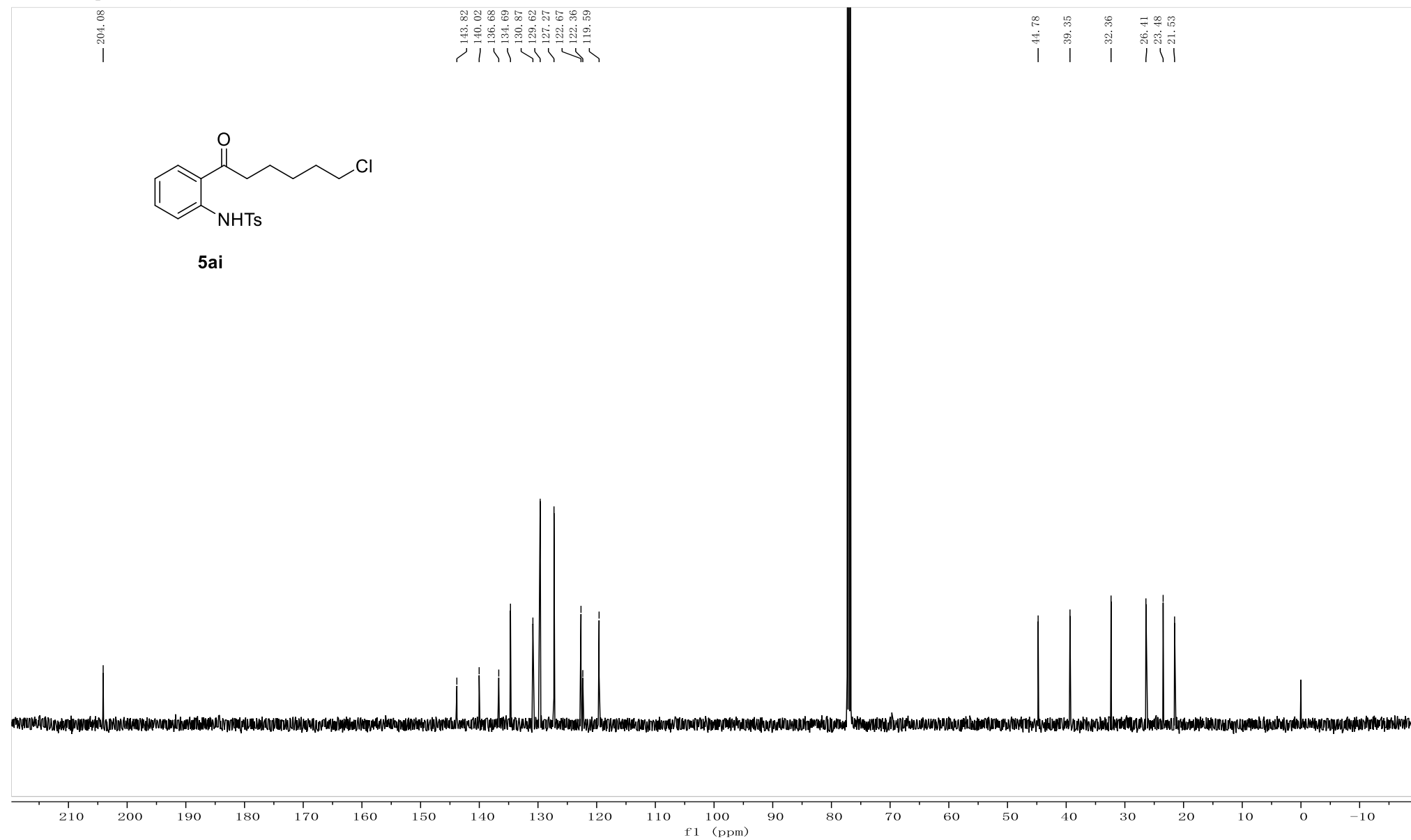


S150

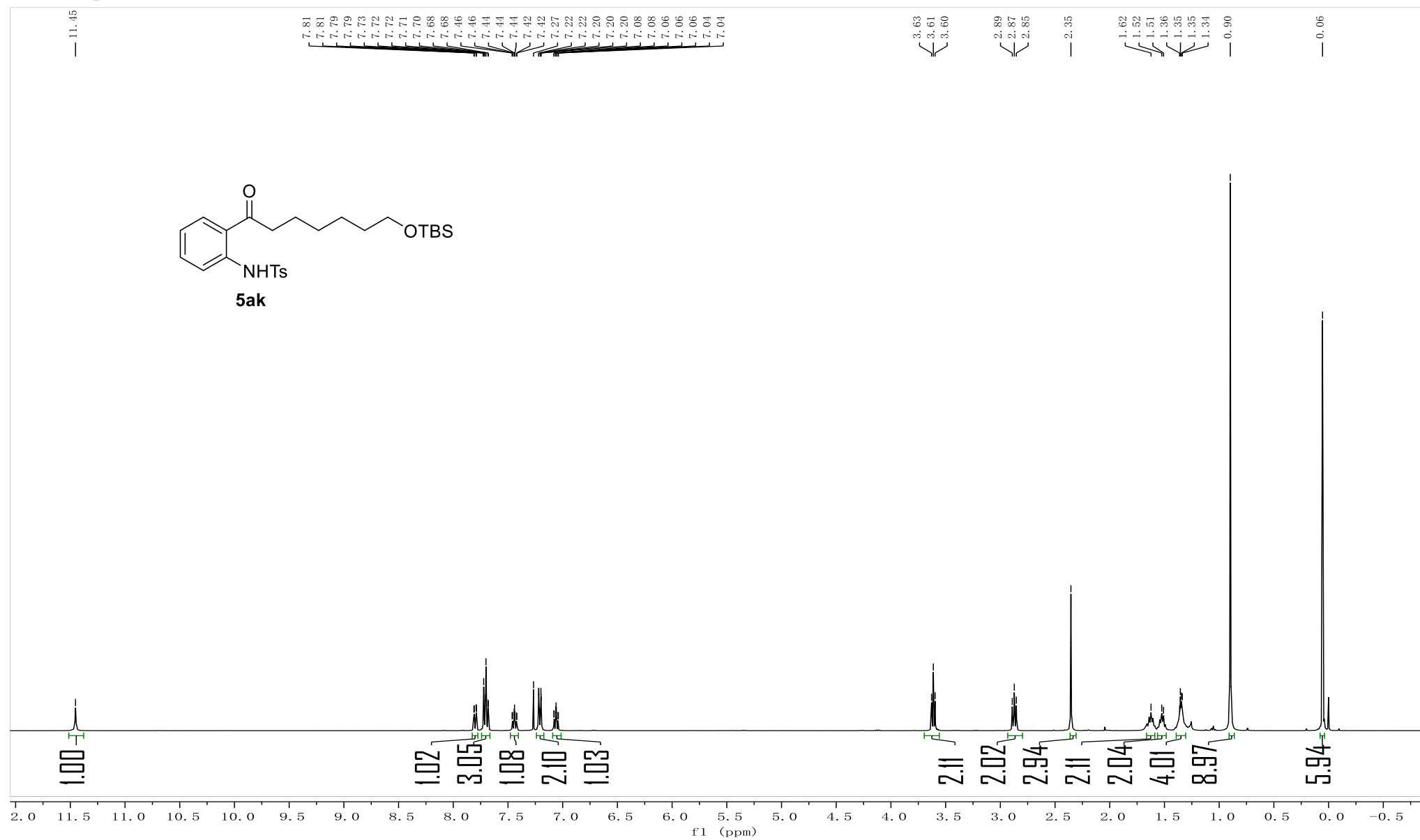
¹H NMR-spectrum (500 MHz, CDCl₃) of **5ai**



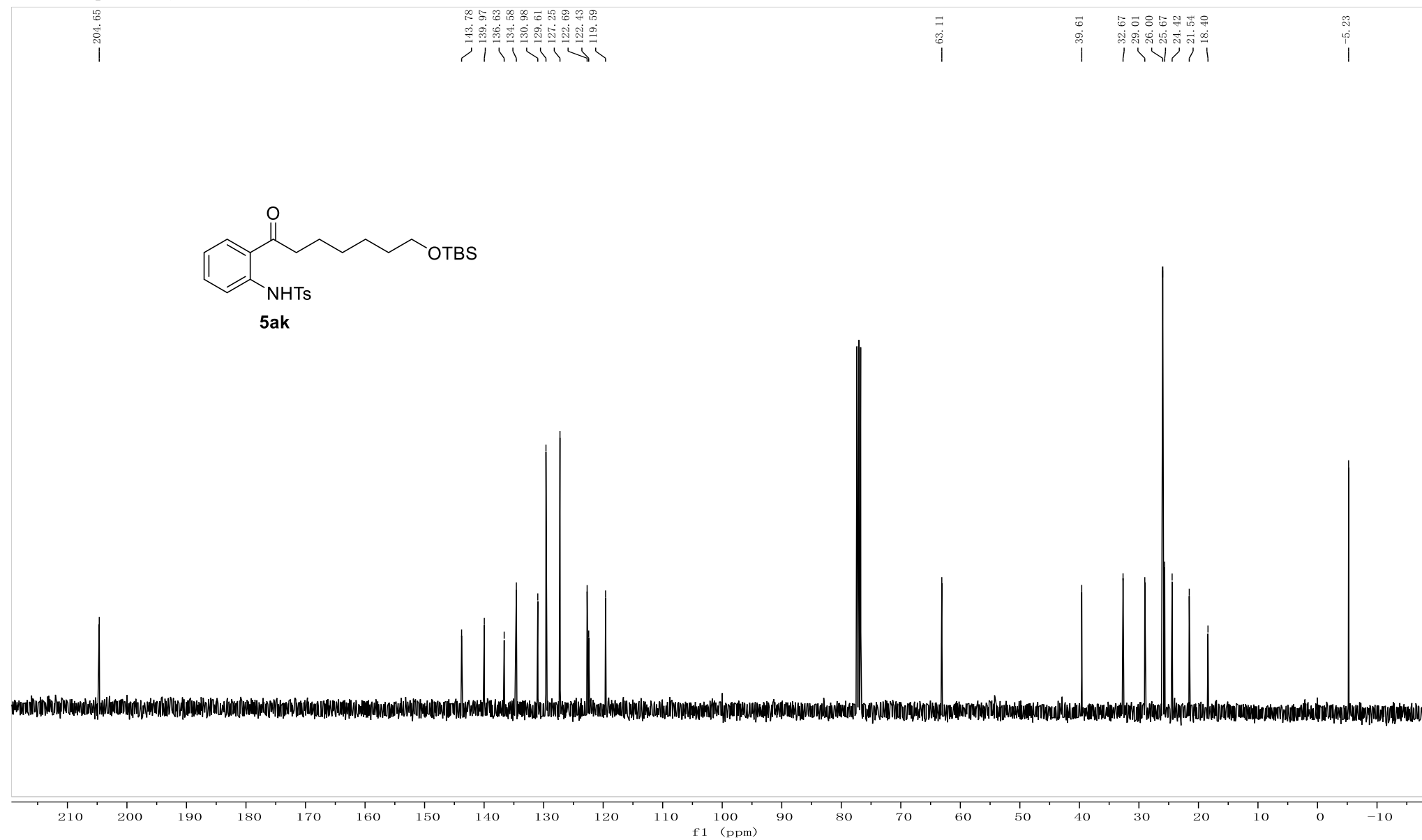
¹³CNMR-spectrum (126 MHz, CDCl₃) of **5ai**



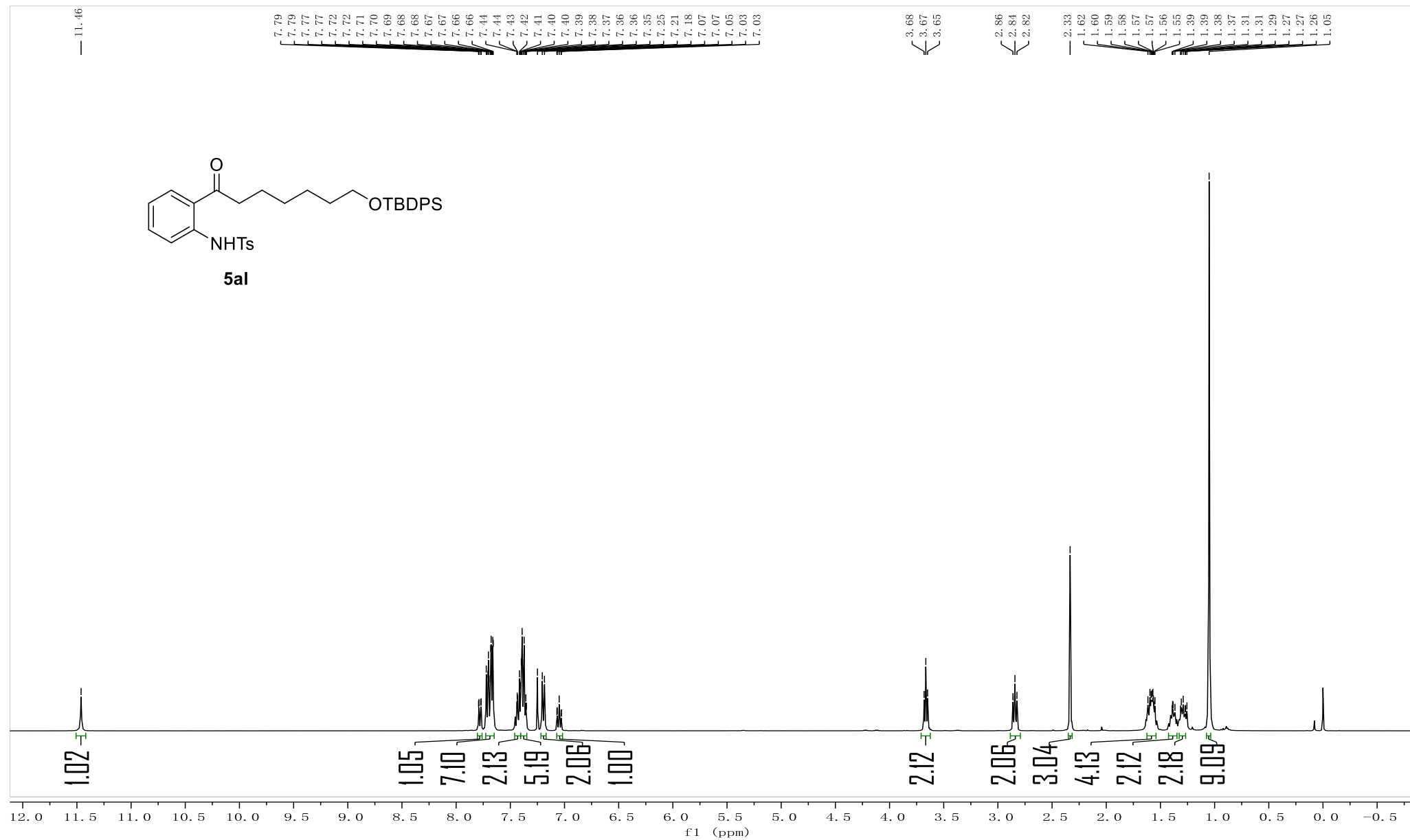
¹H NMR-spectrum (400 MHz, CDCl₃) of **5ak**



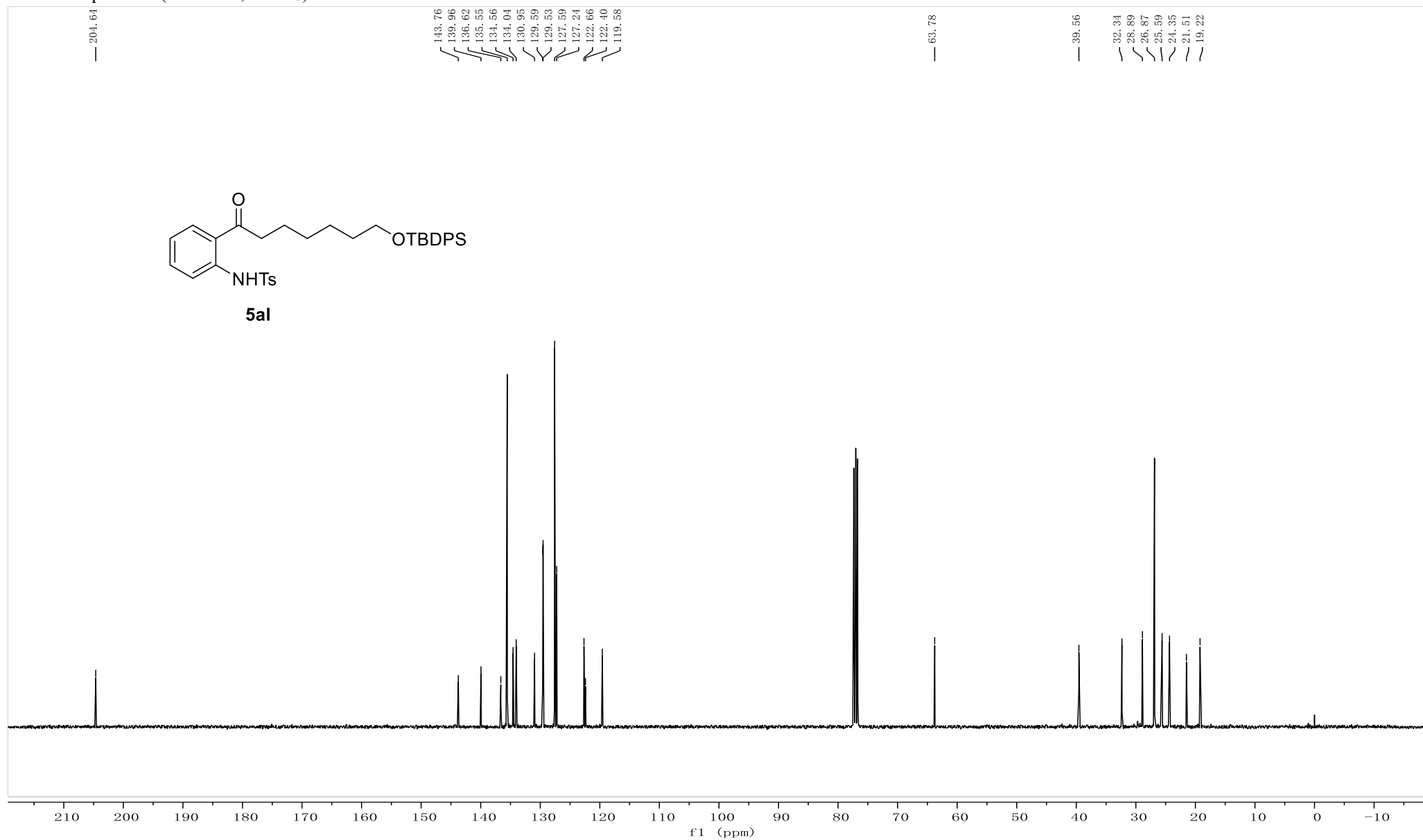
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **5ak**



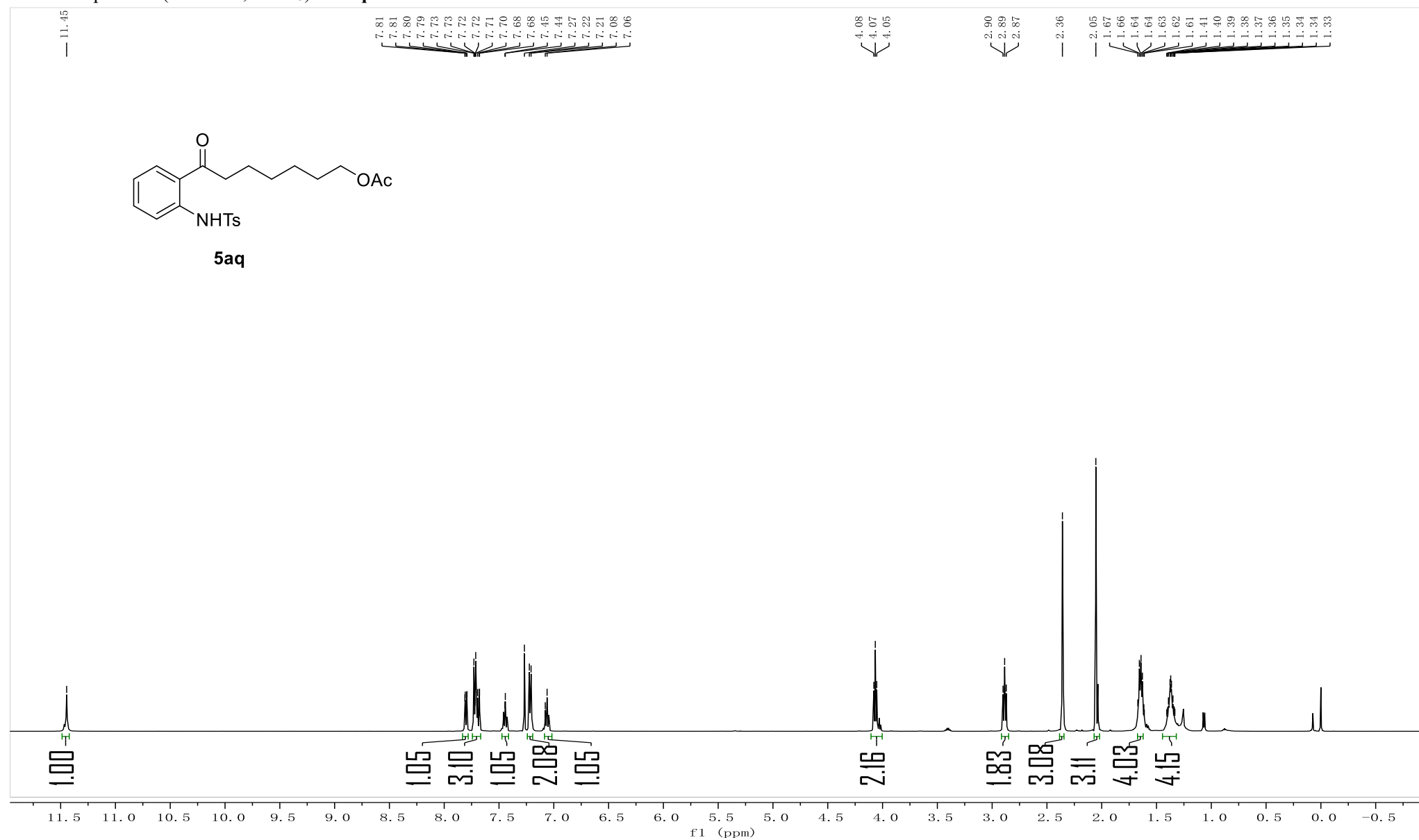
¹H NMR-spectrum (400 MHz, CDCl₃) of **5al**



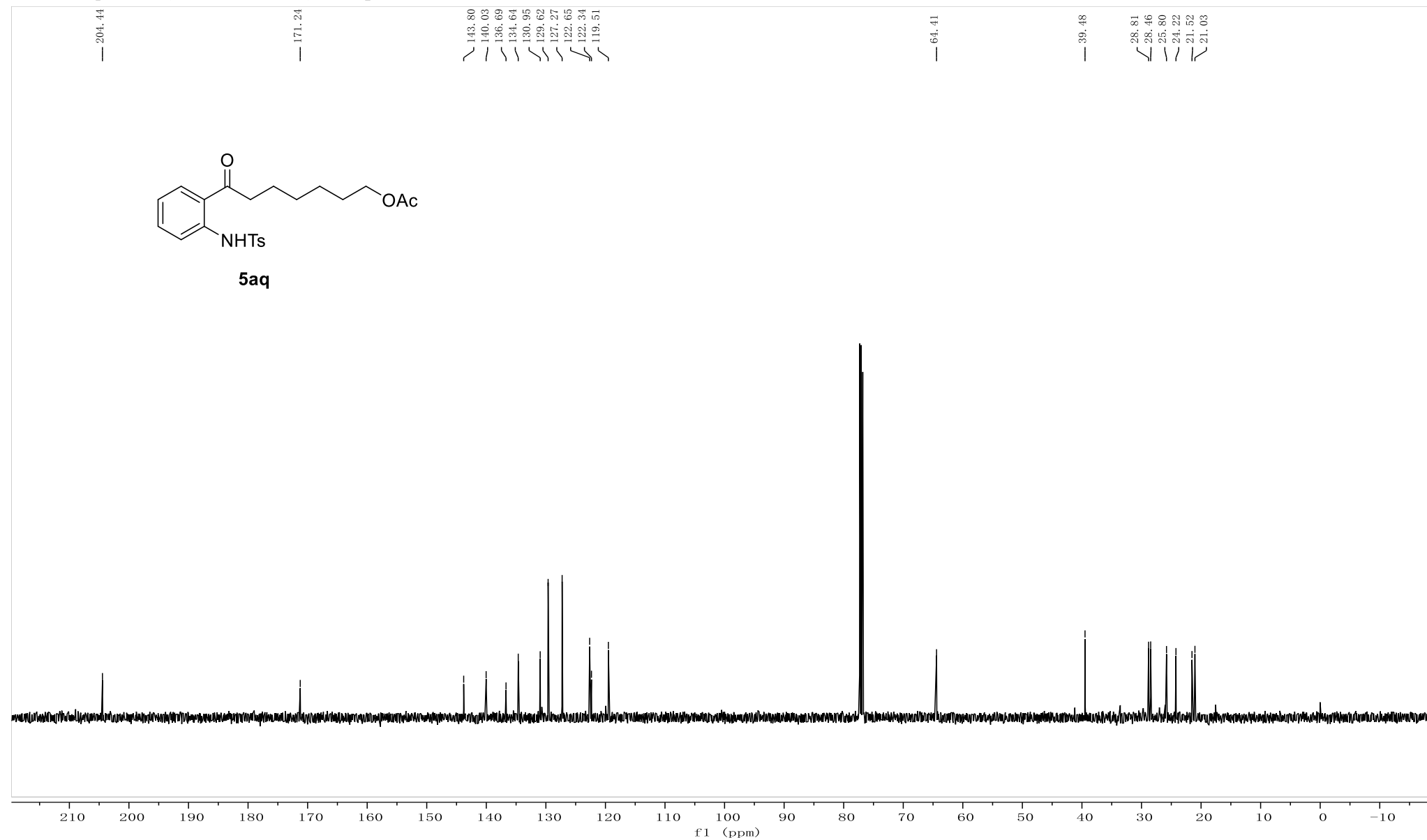
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **5al**



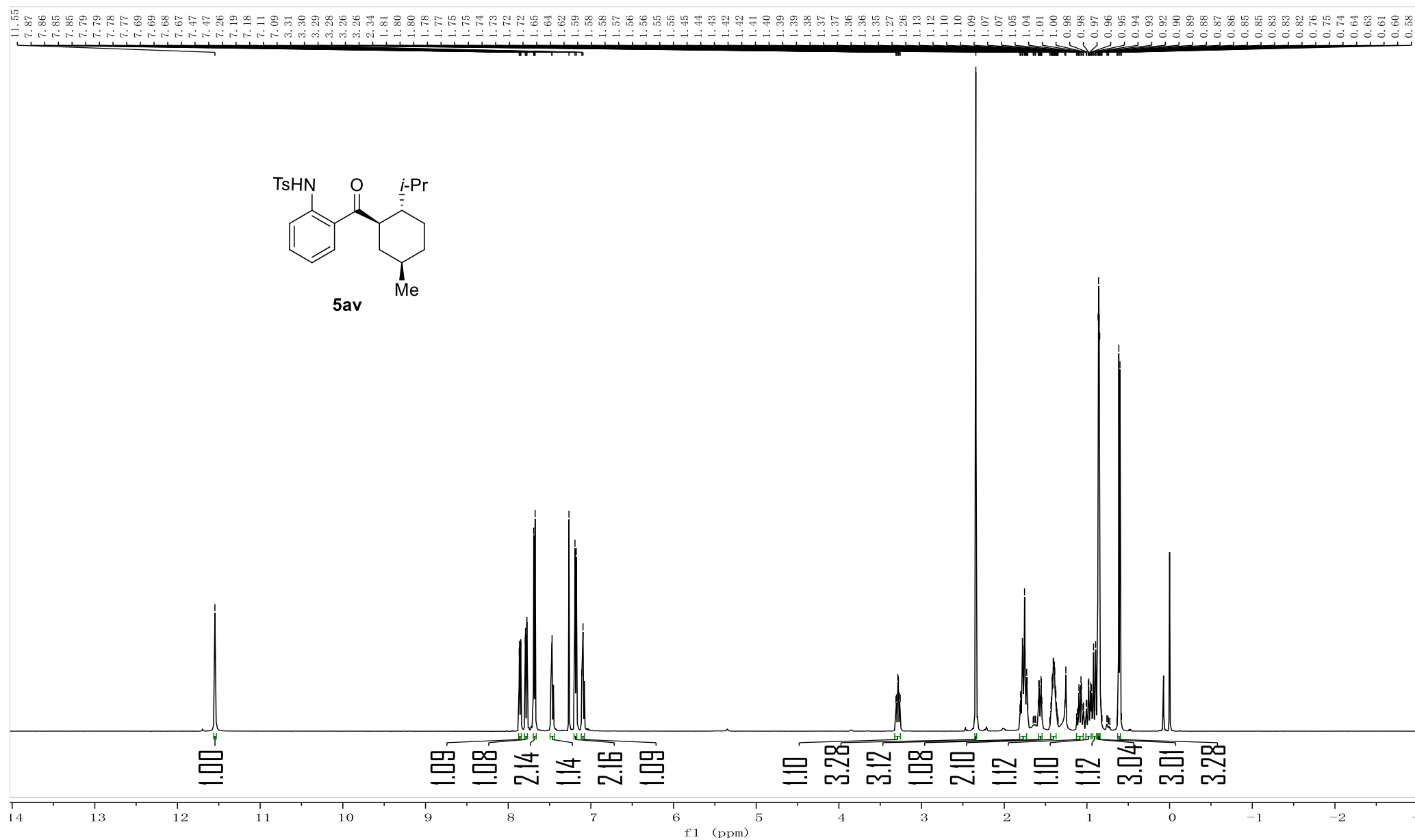
¹H NMR-spectrum (500 MHz, CDCl₃) of **5aq**



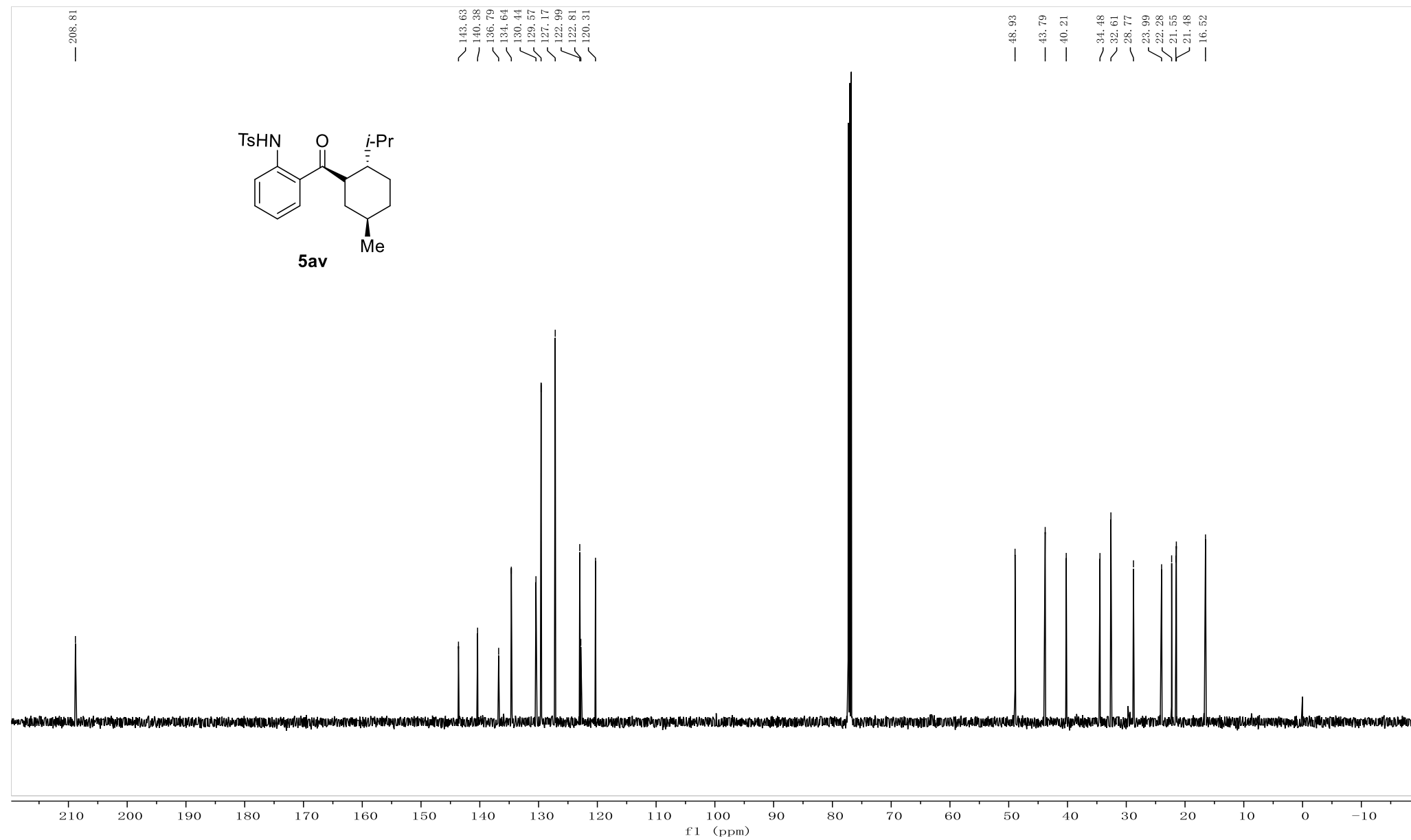
^{13}C NMR-spectrum (126 MHz, CDCl_3) of **5aq**



¹H NMR-spectrum (500 MHz, CDCl₃) of **5av**

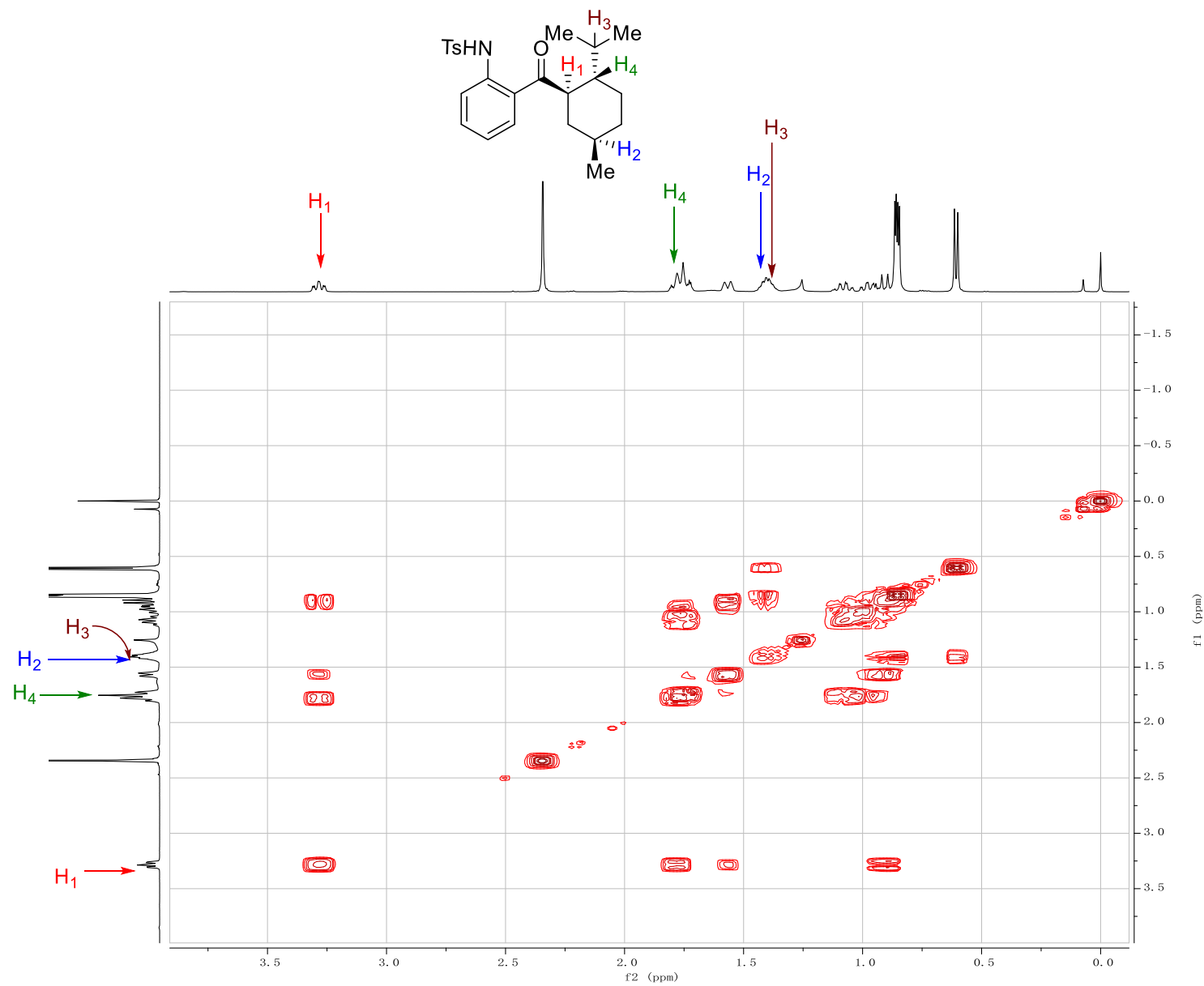


^{13}C NMR-spectrum (126 MHz, CDCl_3) of **5av**



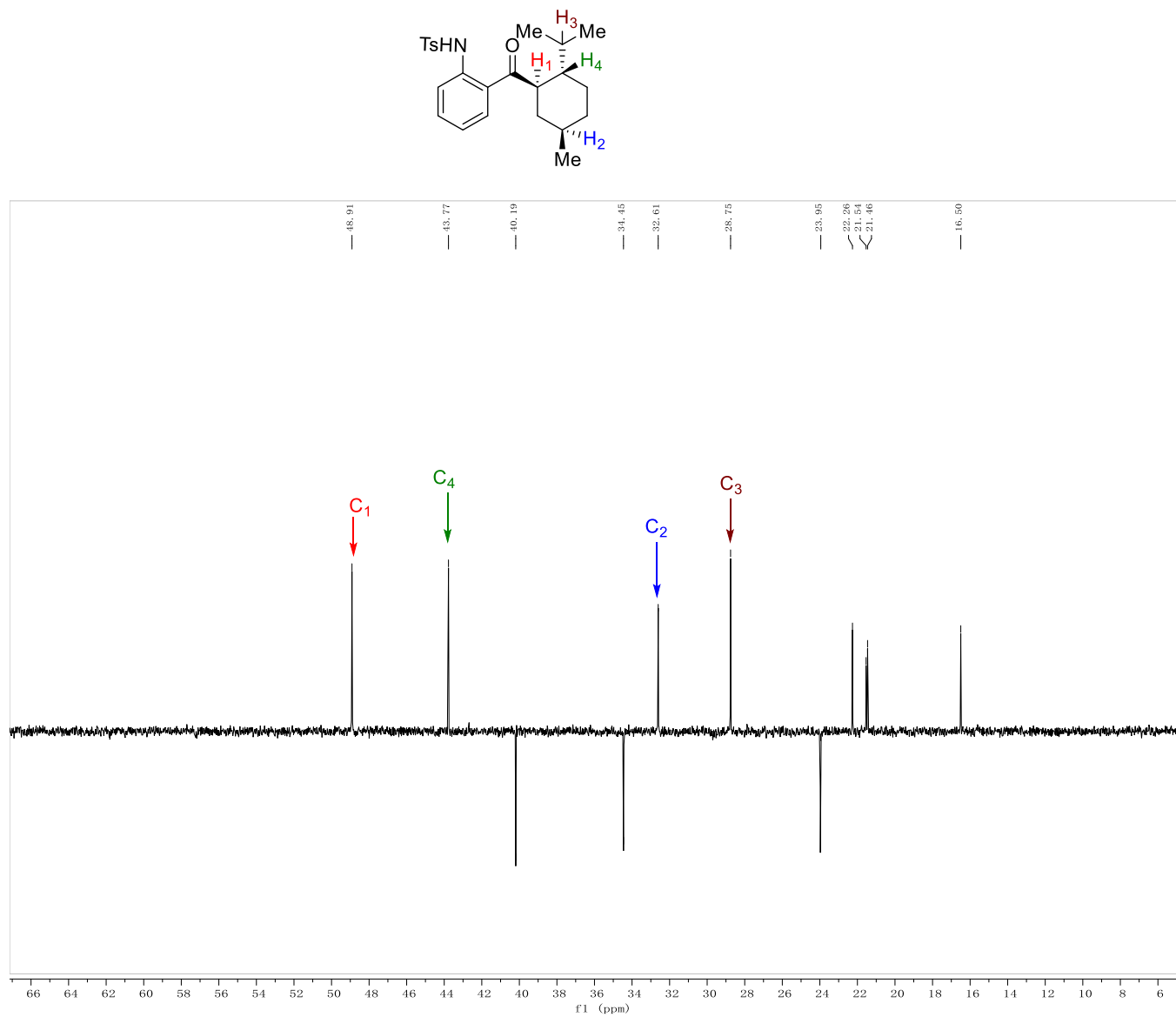
S160

COSY-spectrum of **5av**

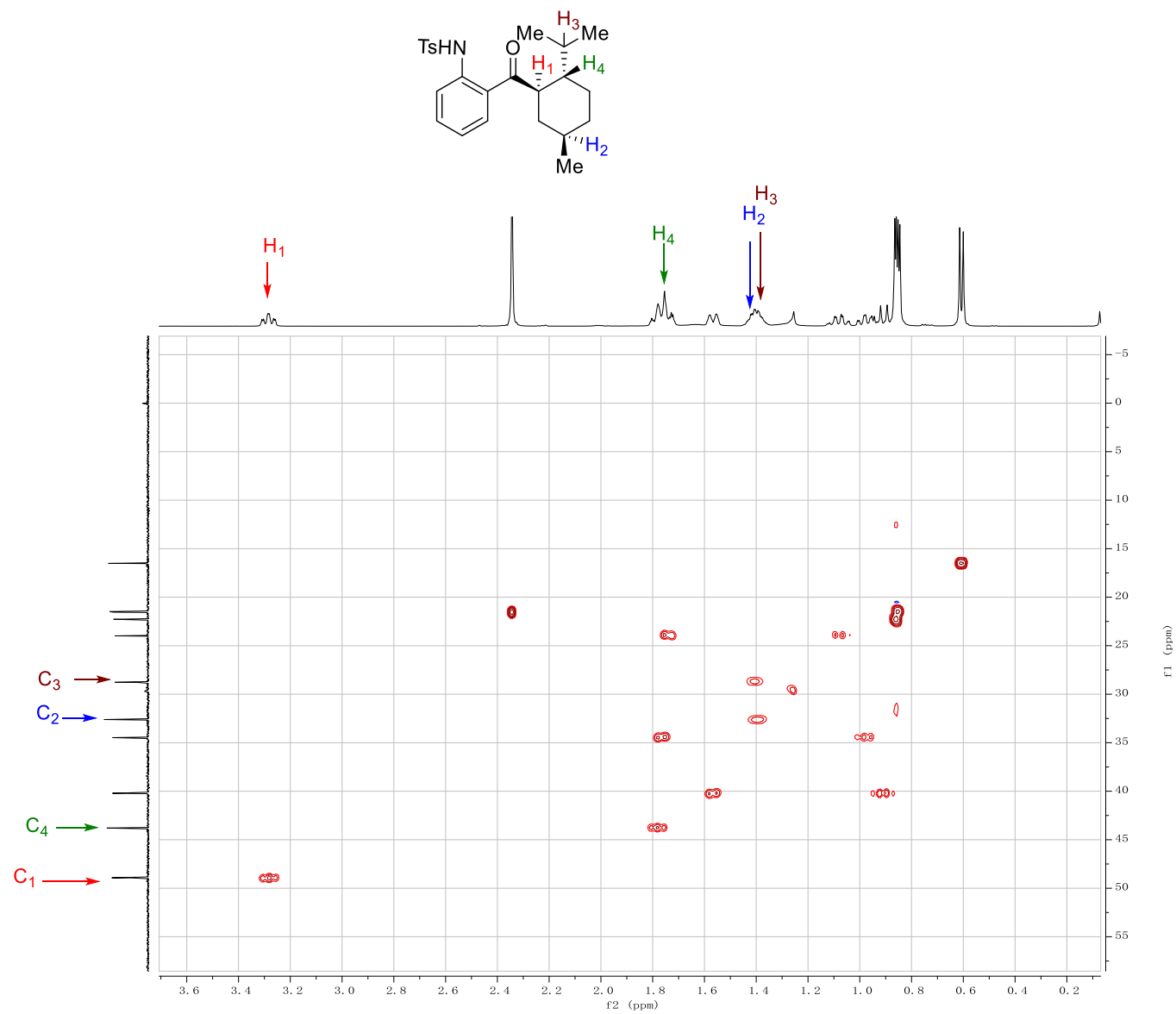


S161

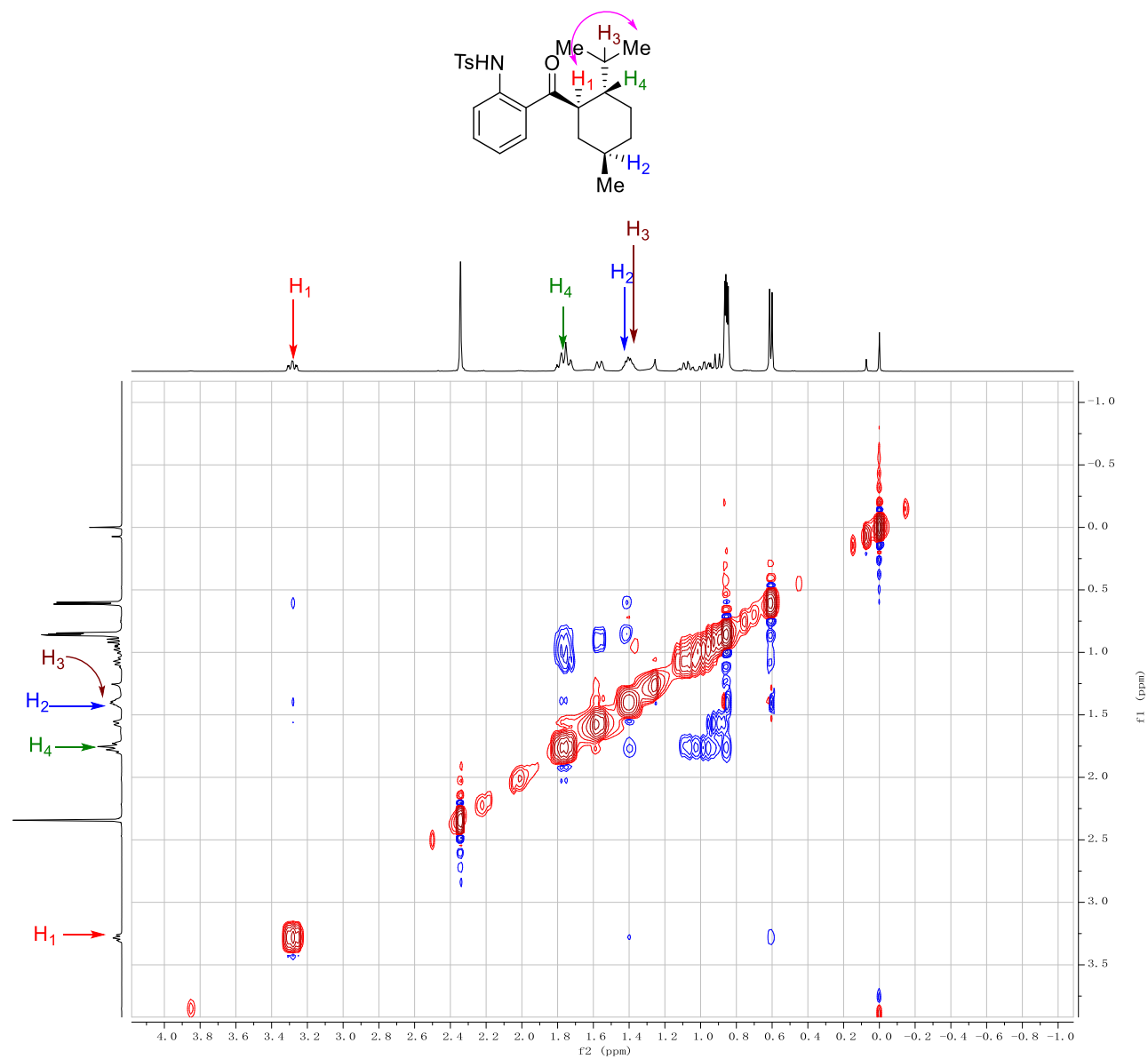
DEPT-135°-spectrum of **5av**



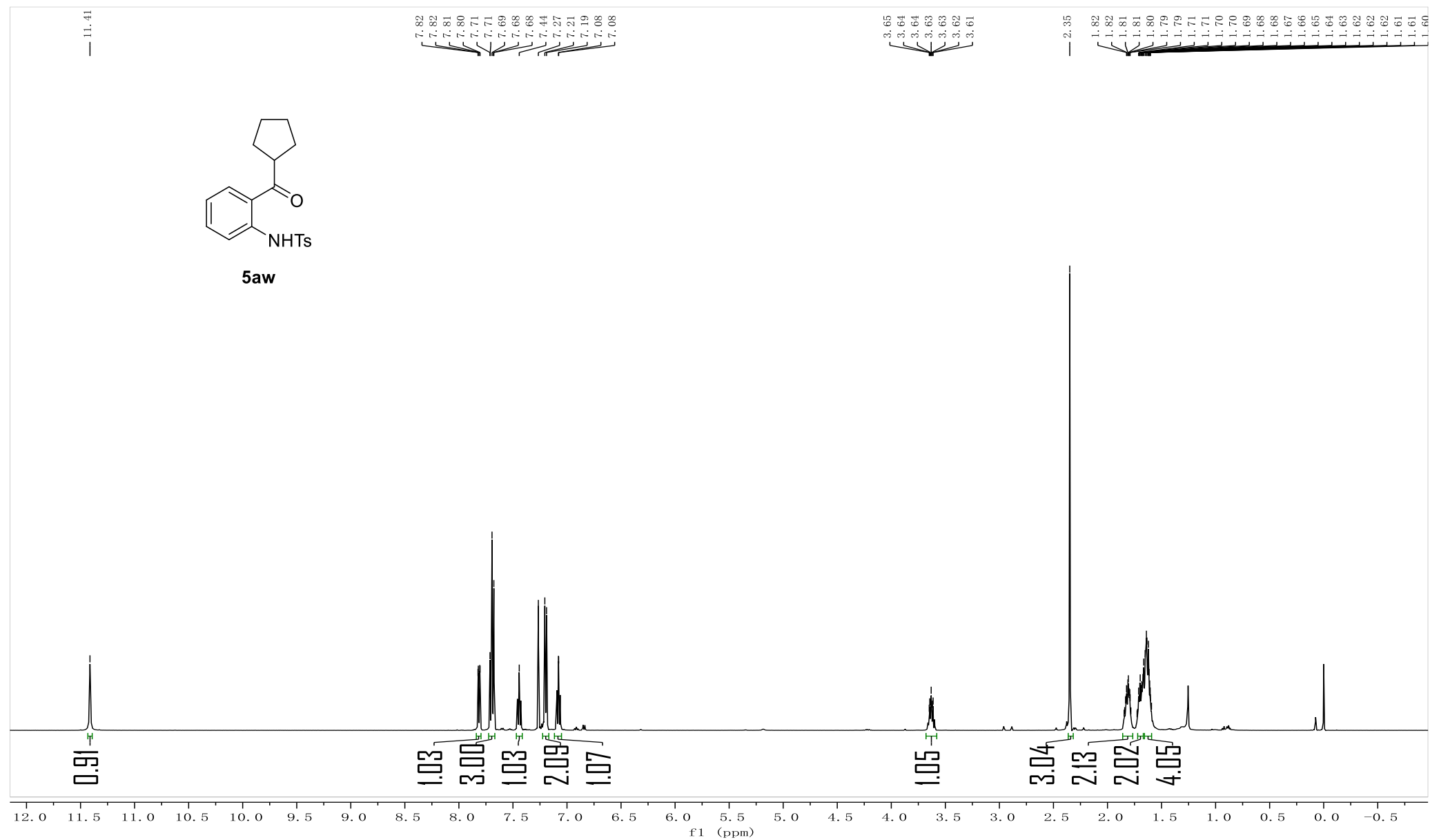
HSQC-spectrum of **5av**



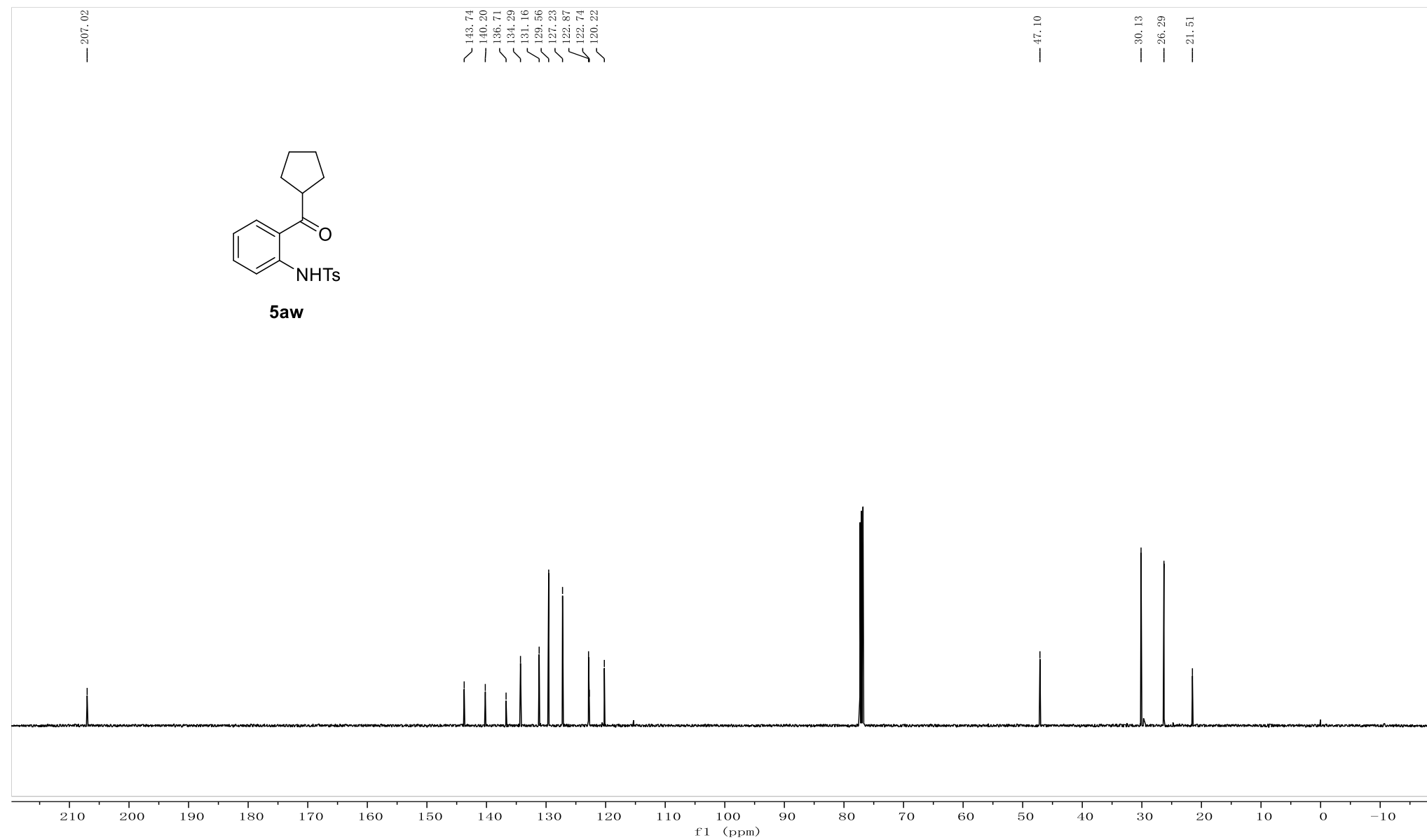
NOSEY-spectrum of **5av**



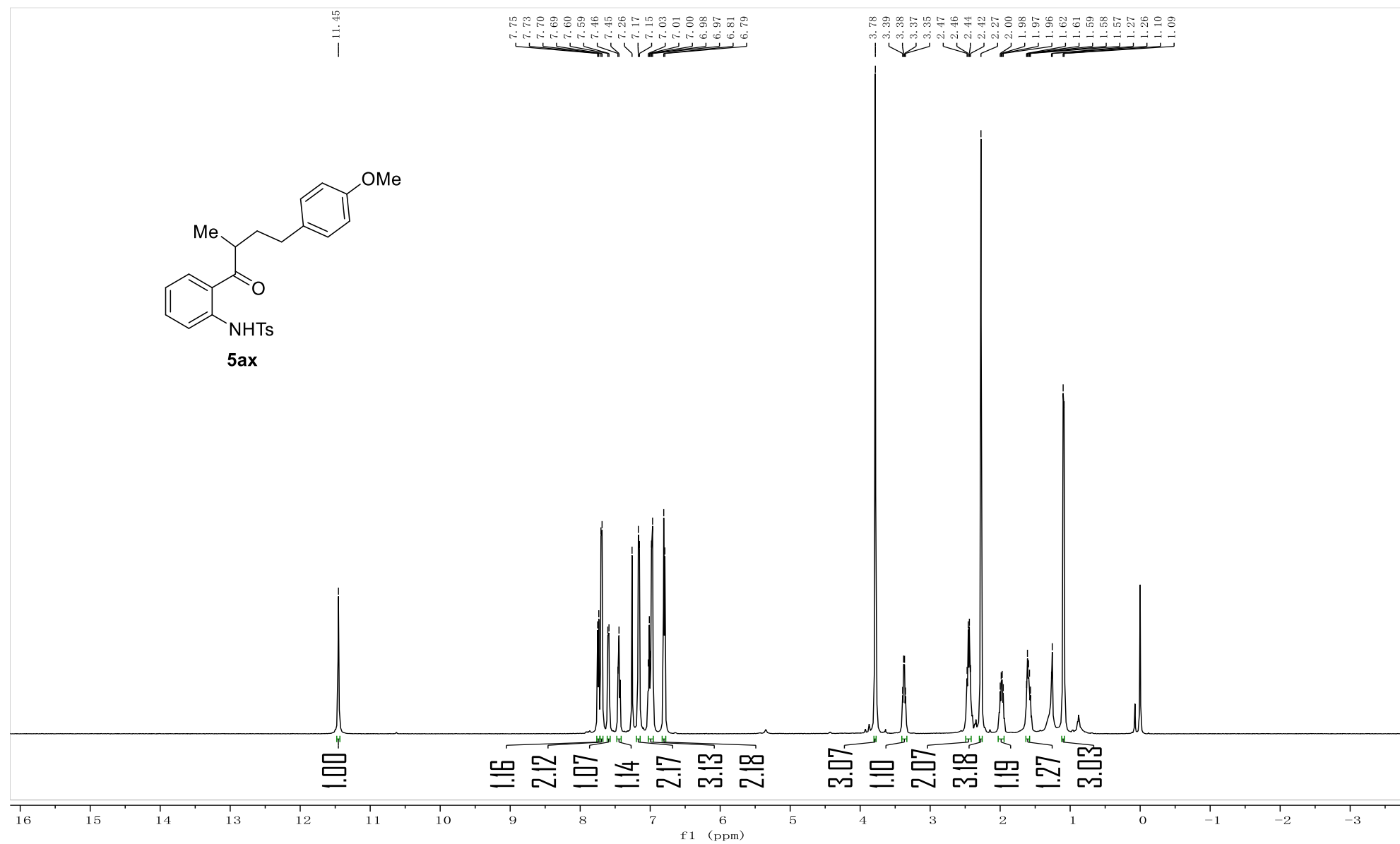
¹H NMR-spectrum (500 MHz, CDCl₃) of **5aw**



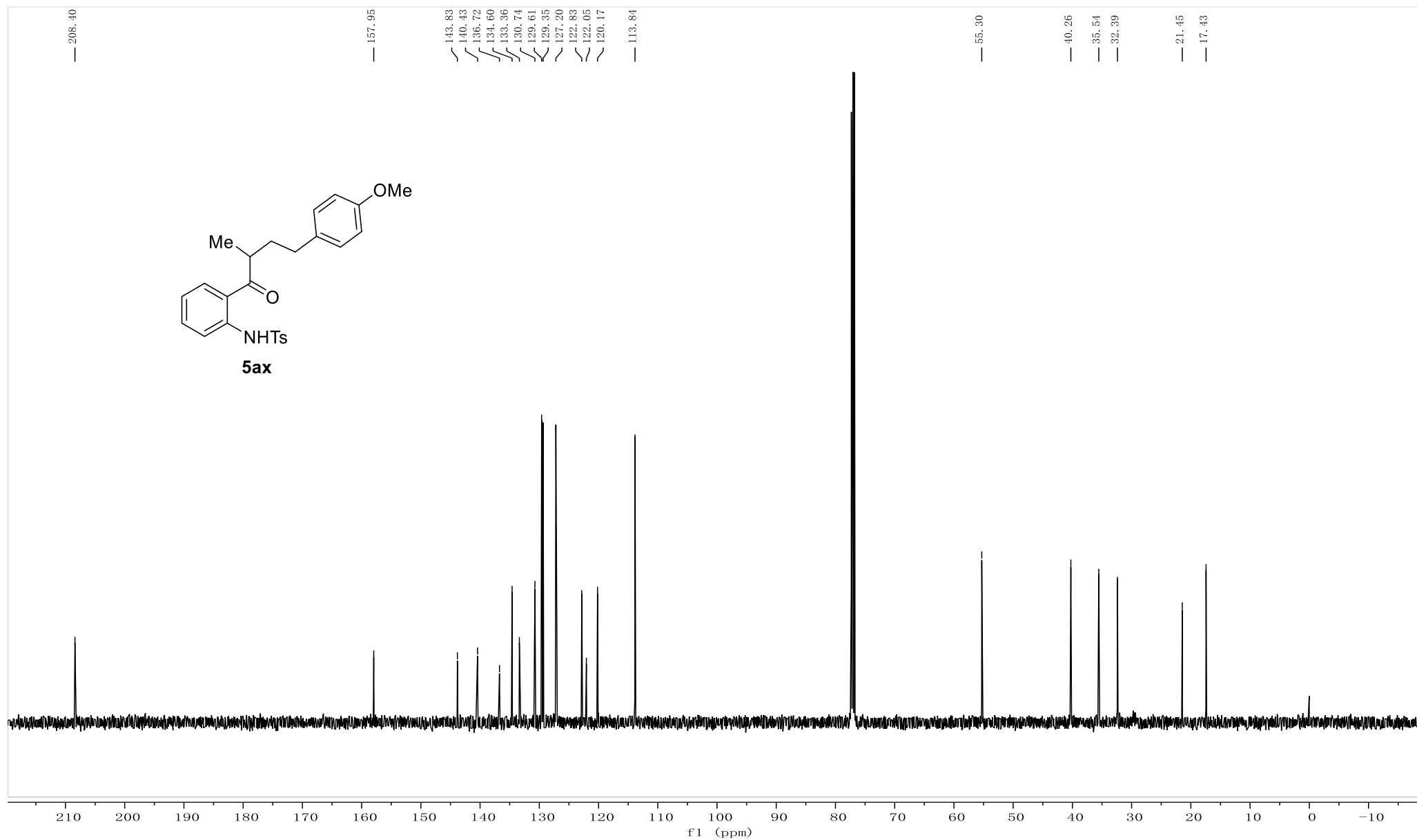
¹³C NMR-spectrum (126 MHz, CDCl₃) of **5aw**



¹H NMR-spectrum (500 MHz, CDCl₃) of **5ax**

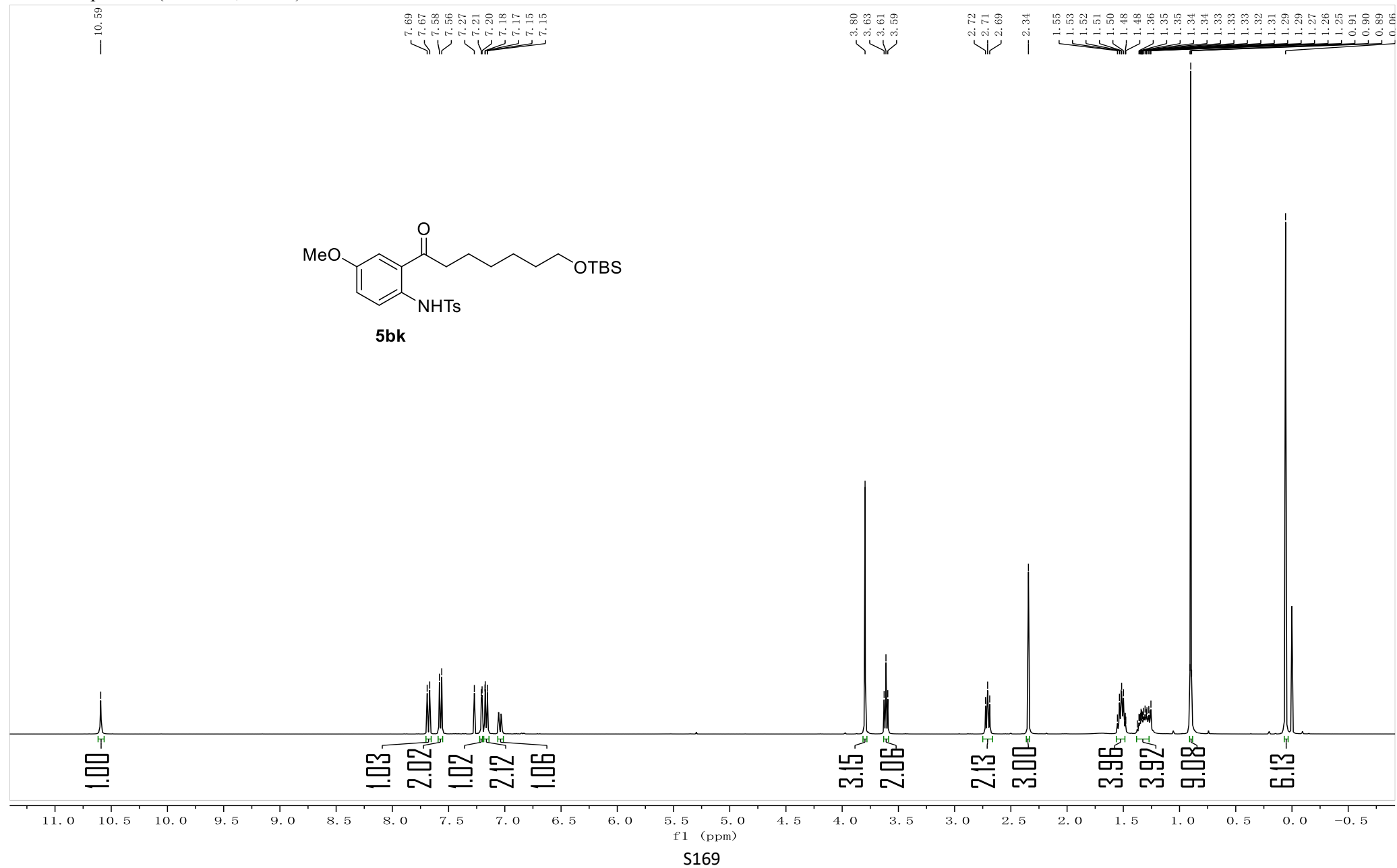


^{13}C NMR-spectrum (126 MHz, CDCl_3) of **5ax**

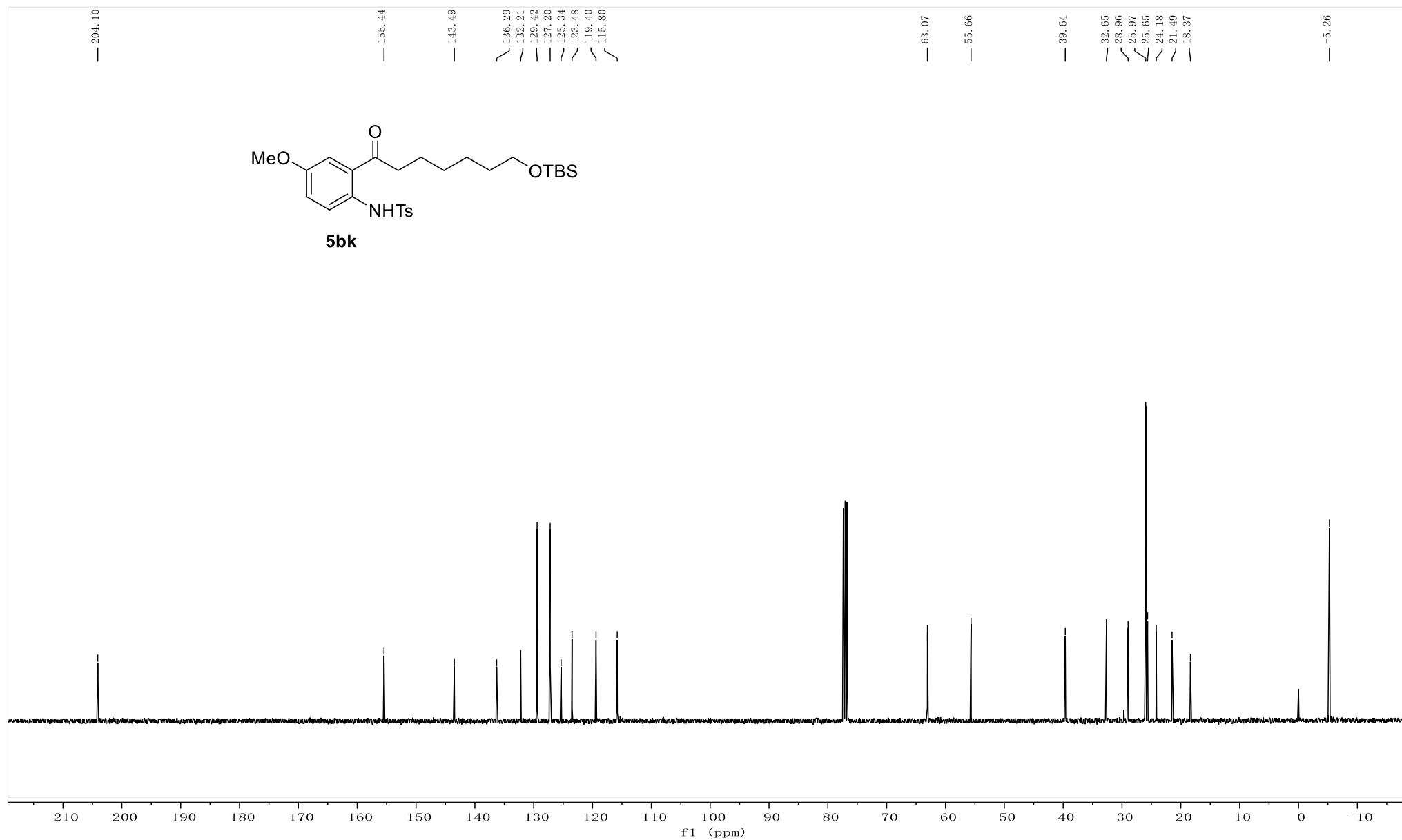


S168

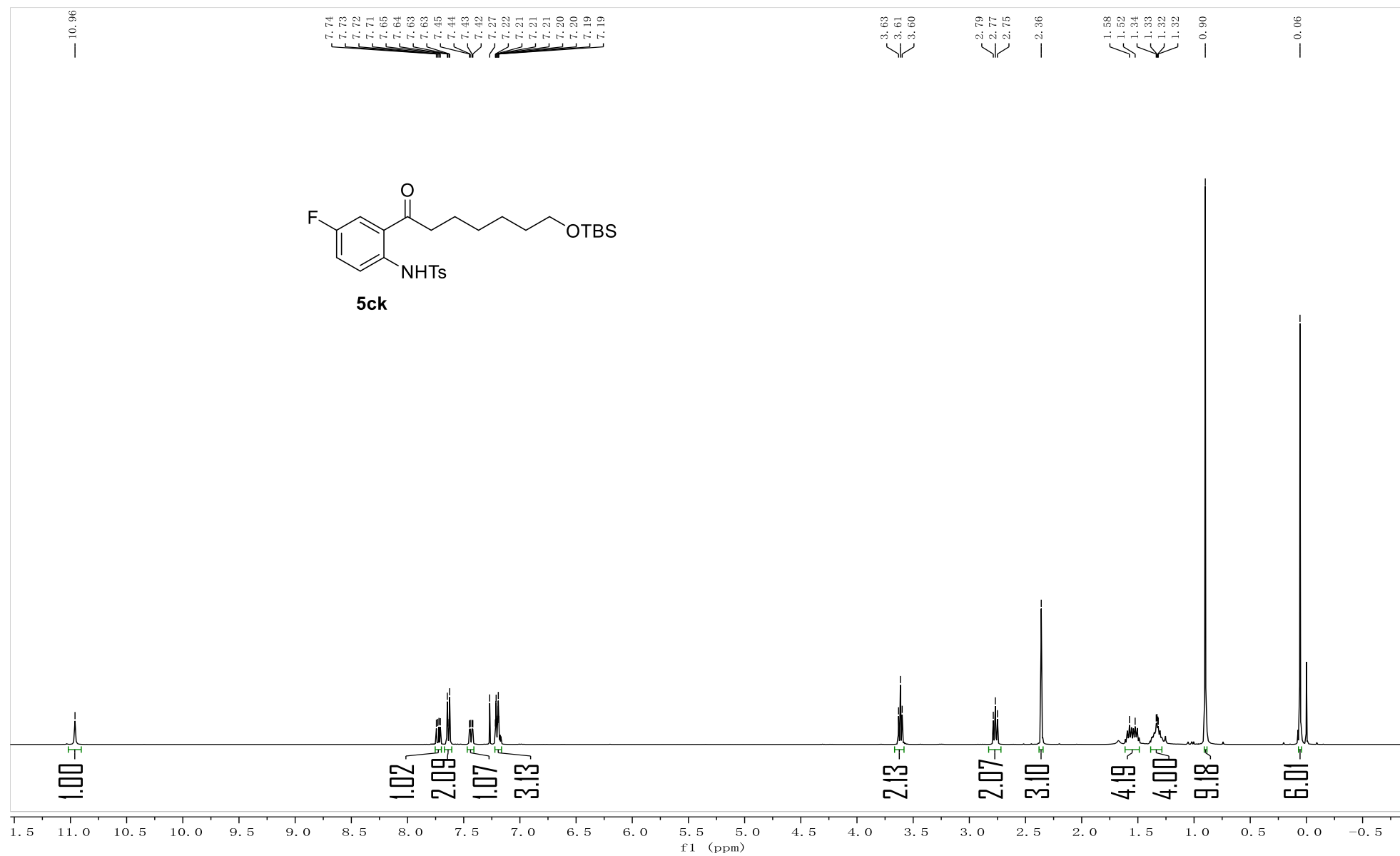
¹H NMR-spectrum (400 MHz, CDCl₃) of **5bk**



¹³C NMR-spectrum (101 MHz, CDCl₃) of **5bk**

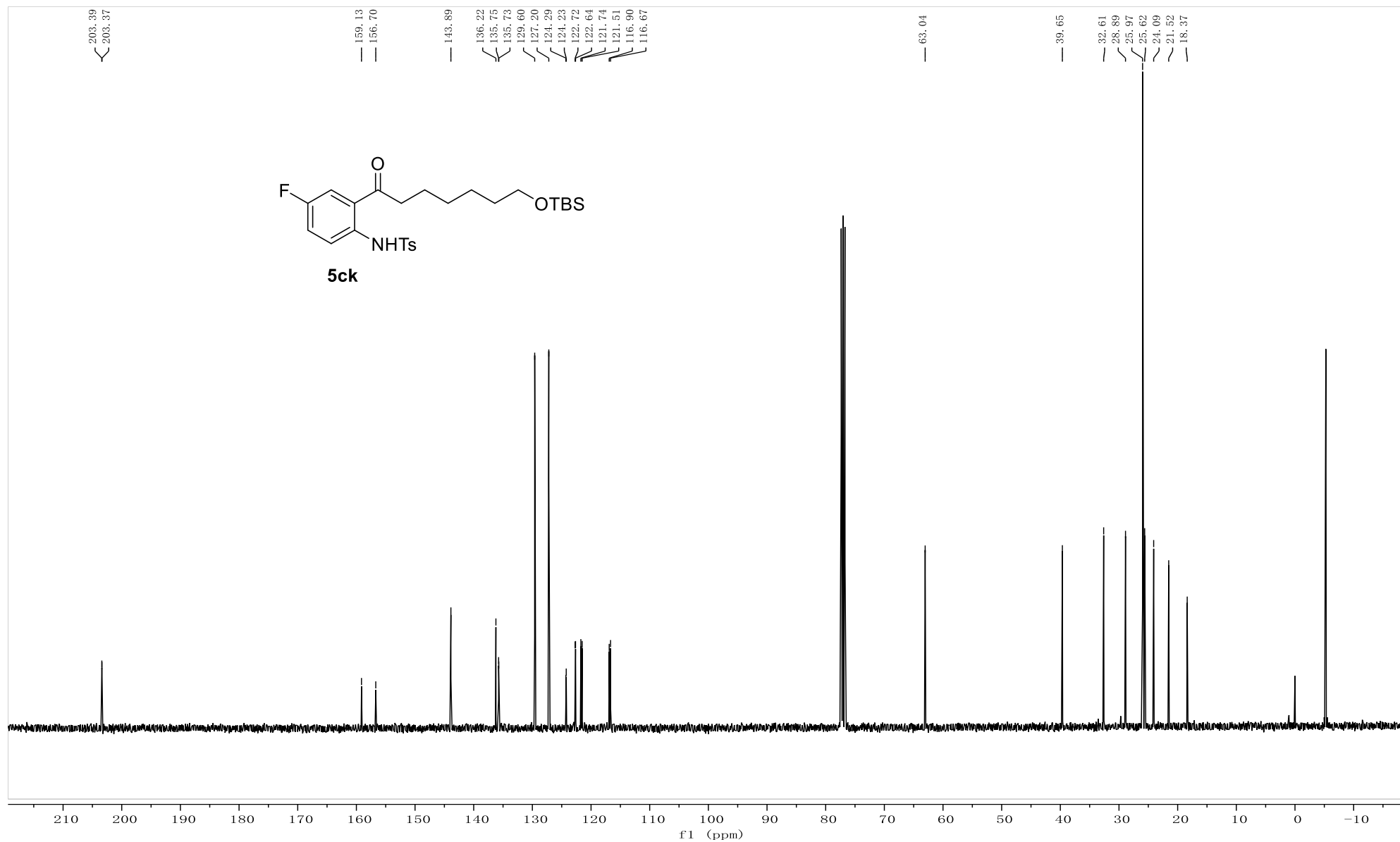


¹H NMR-spectrum (400 MHz, CDCl₃) of **5ck**

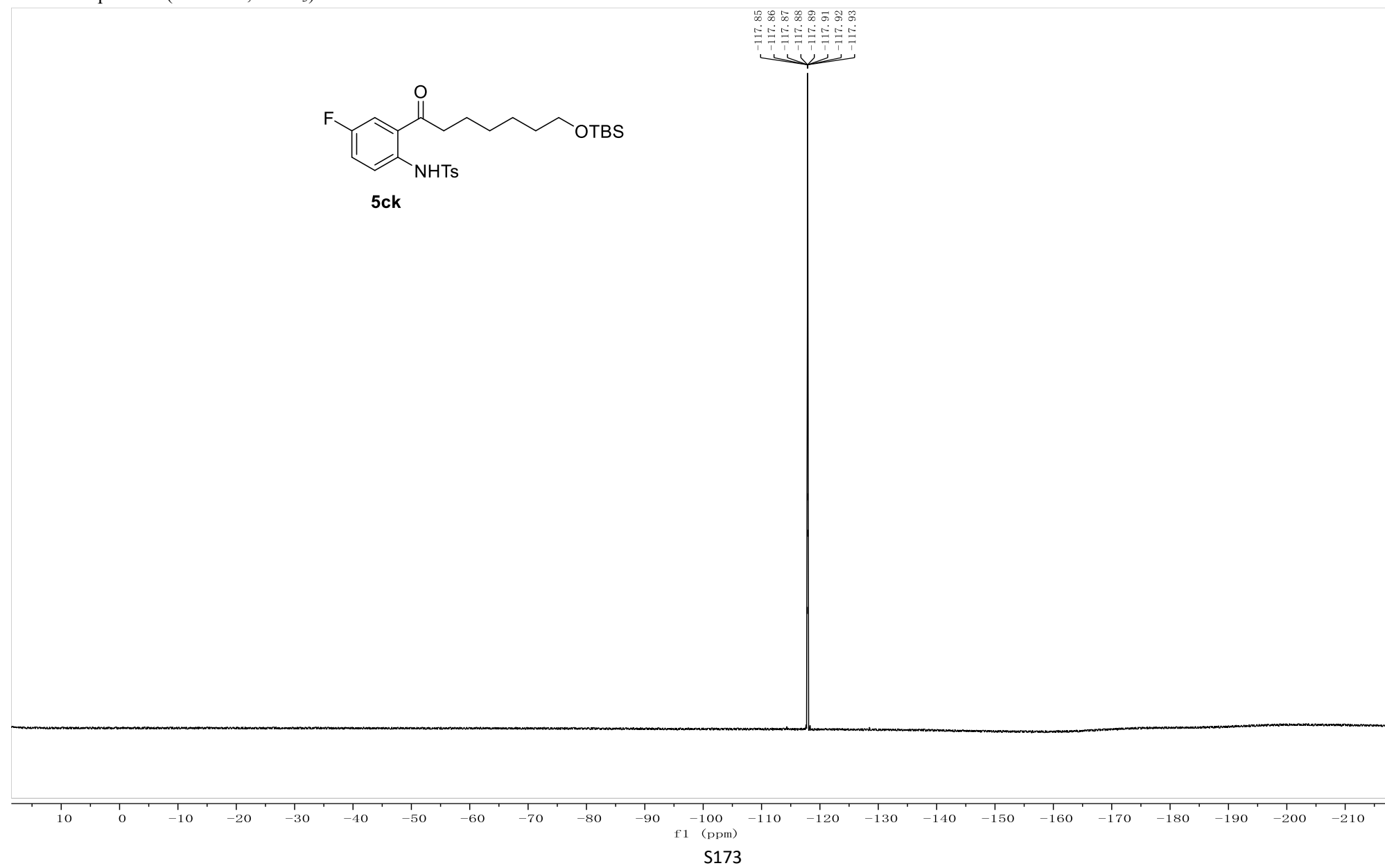


S171

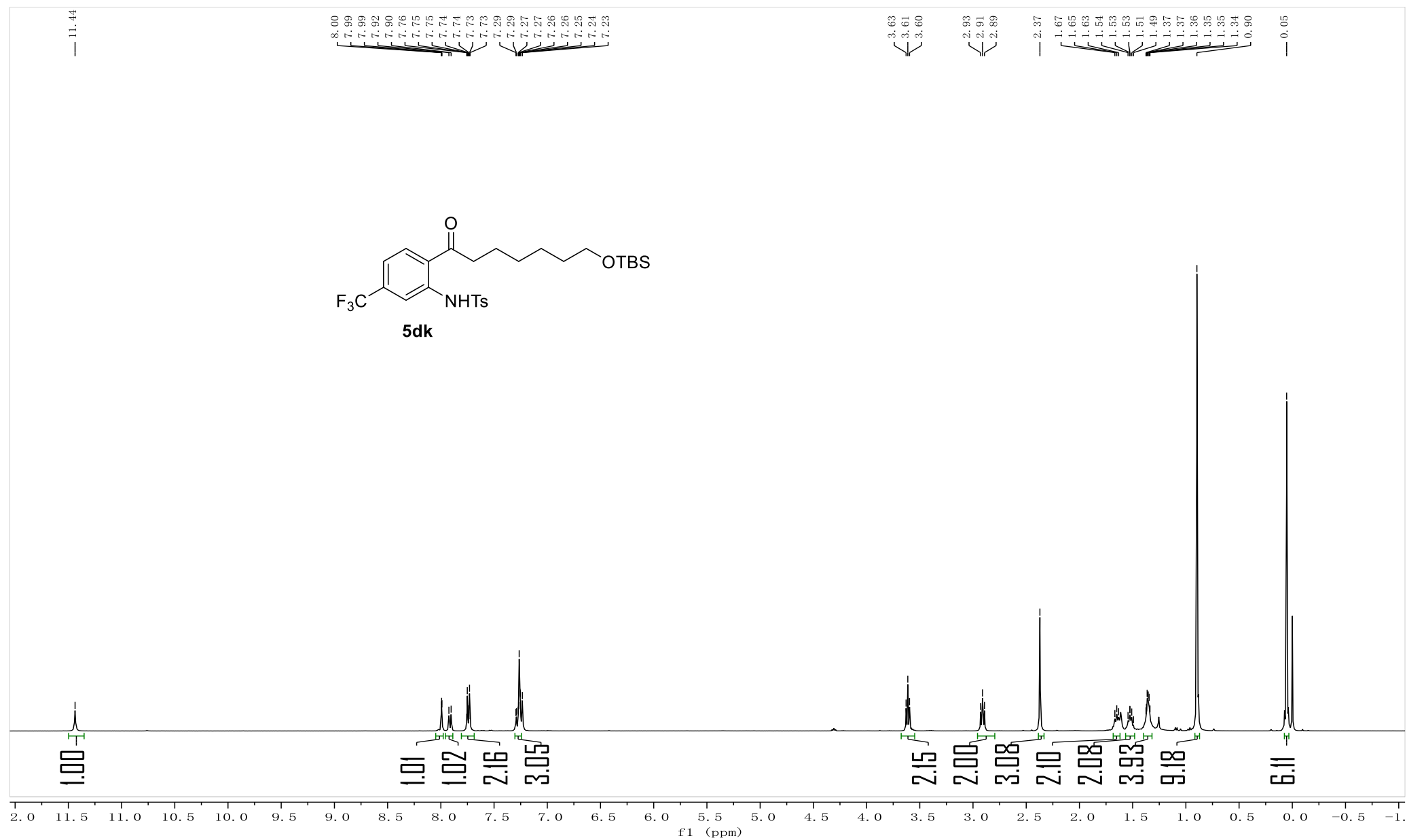
^{13}C NMR-spectrum (101 MHz, CDCl_3) of **5ck**



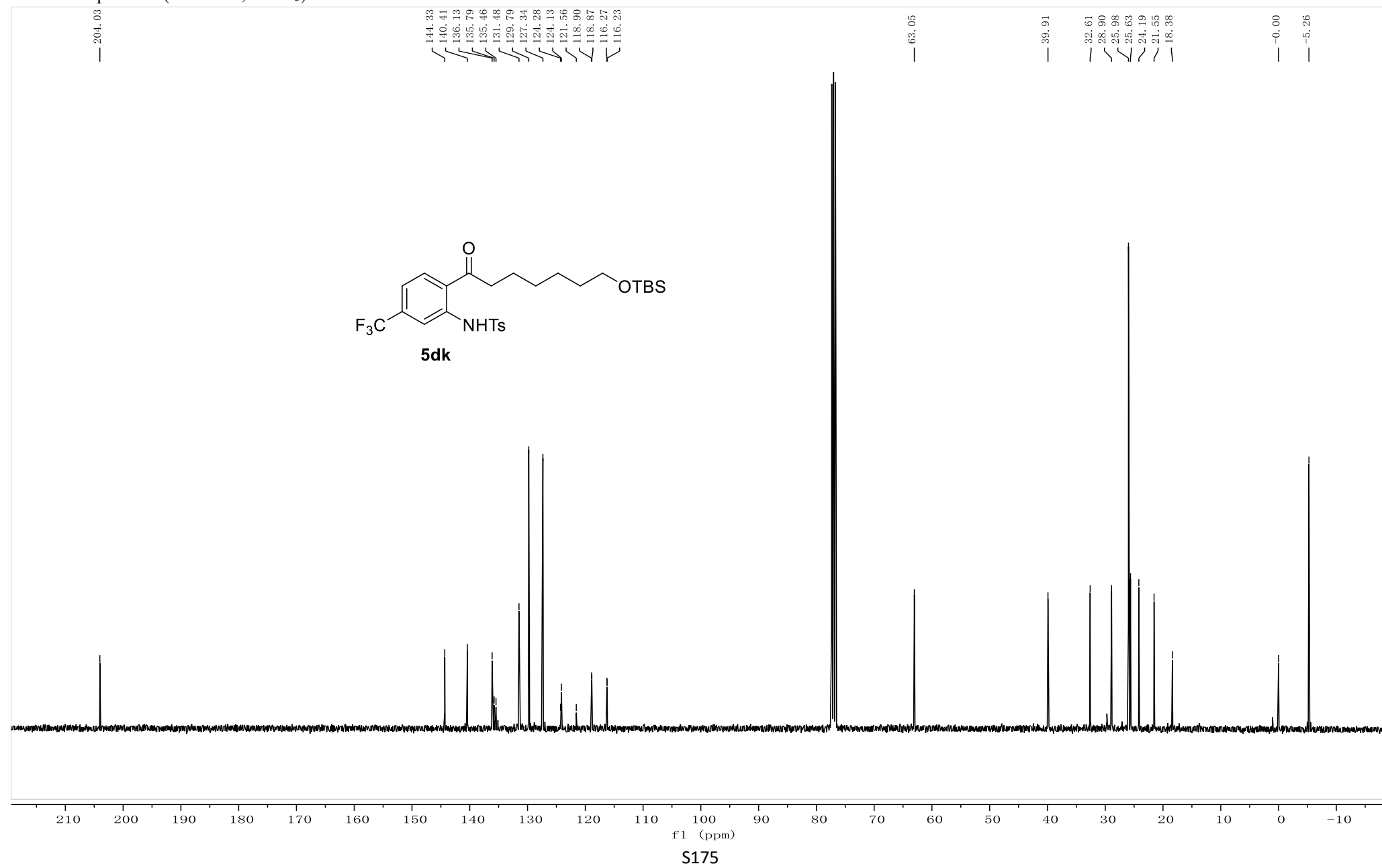
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **5ck**



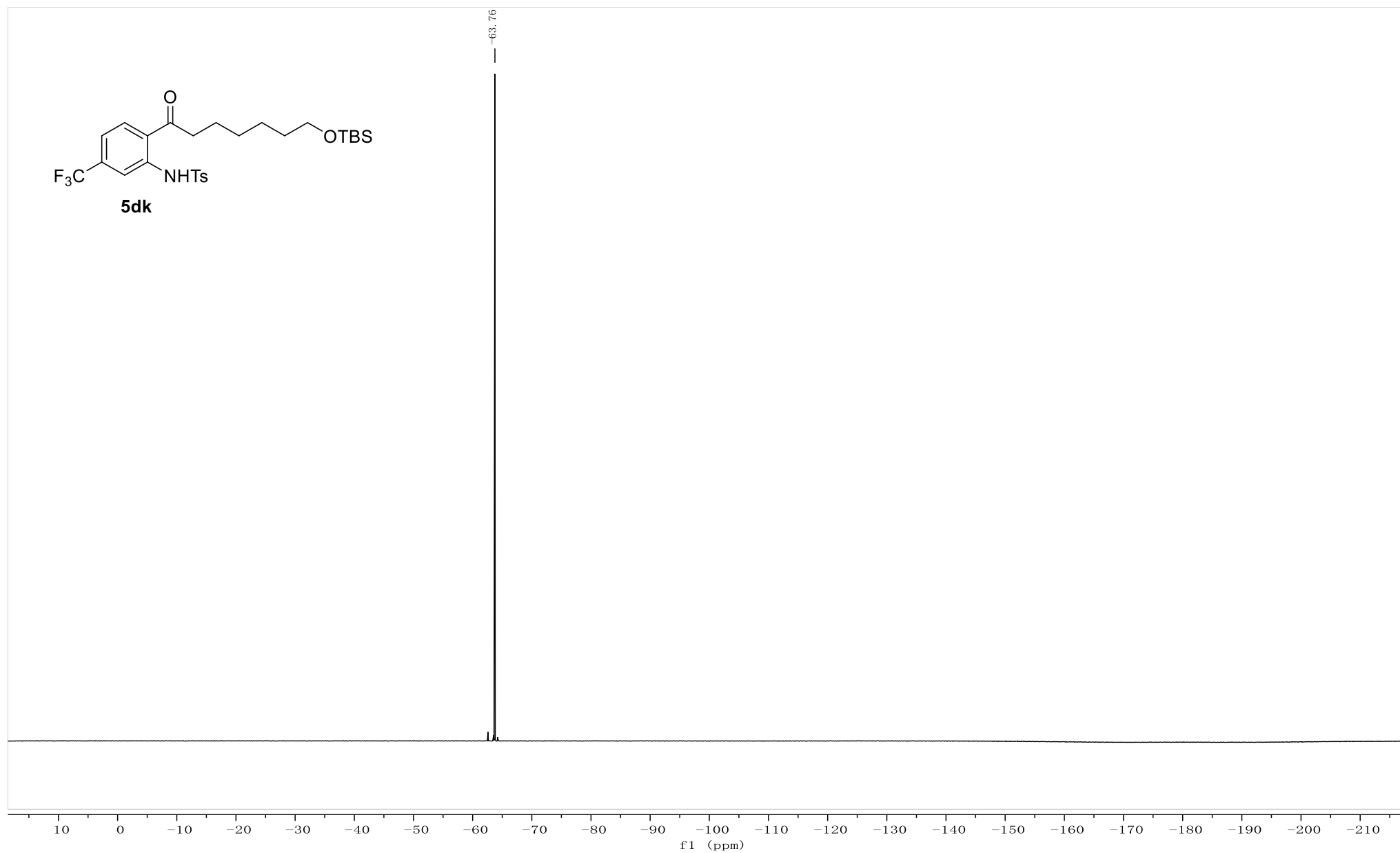
¹H NMR-spectrum (400 MHz, CDCl₃) of **5dk**



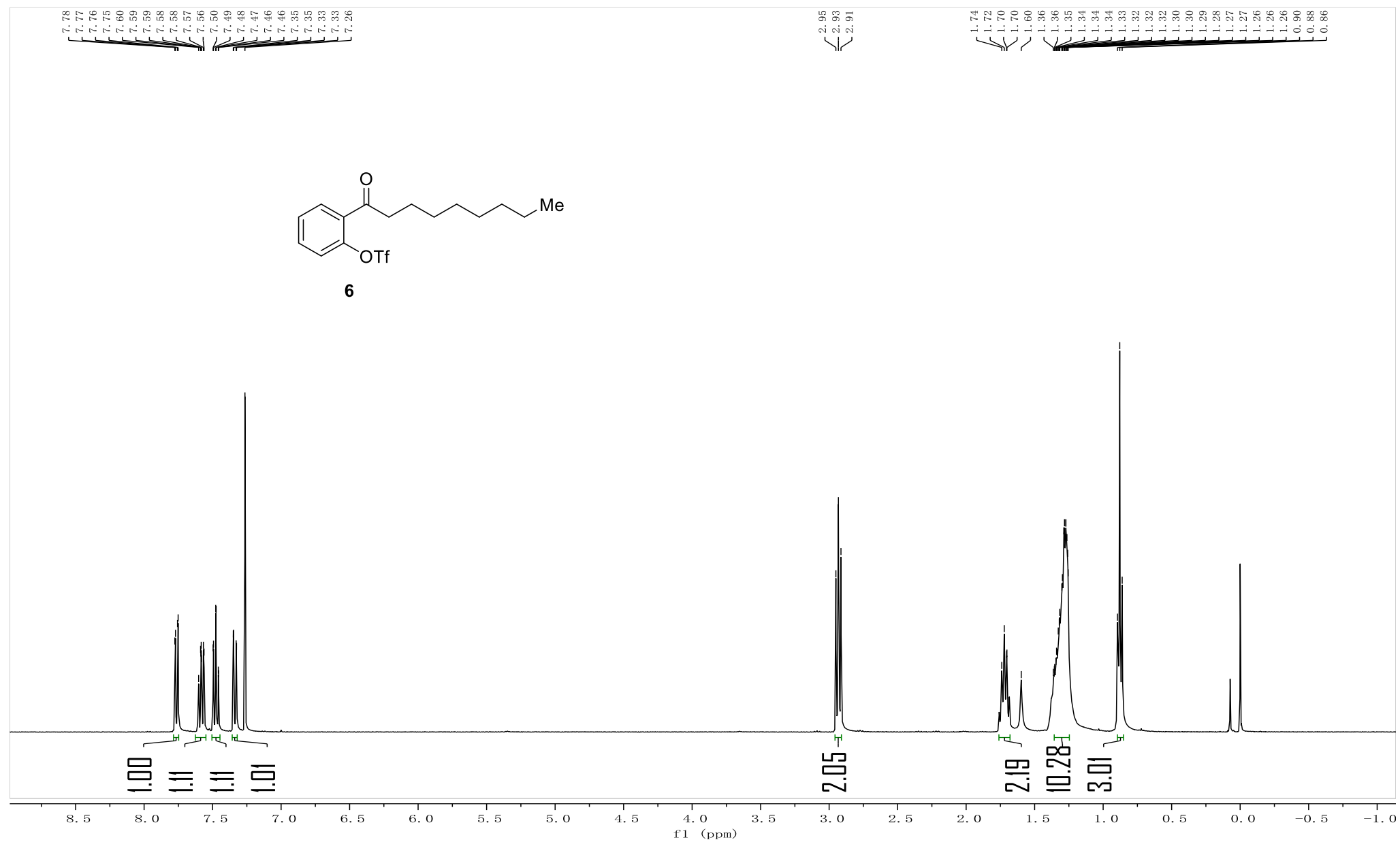
¹³C NMR-spectrum (101 MHz, CDCl₃) of **5dk**



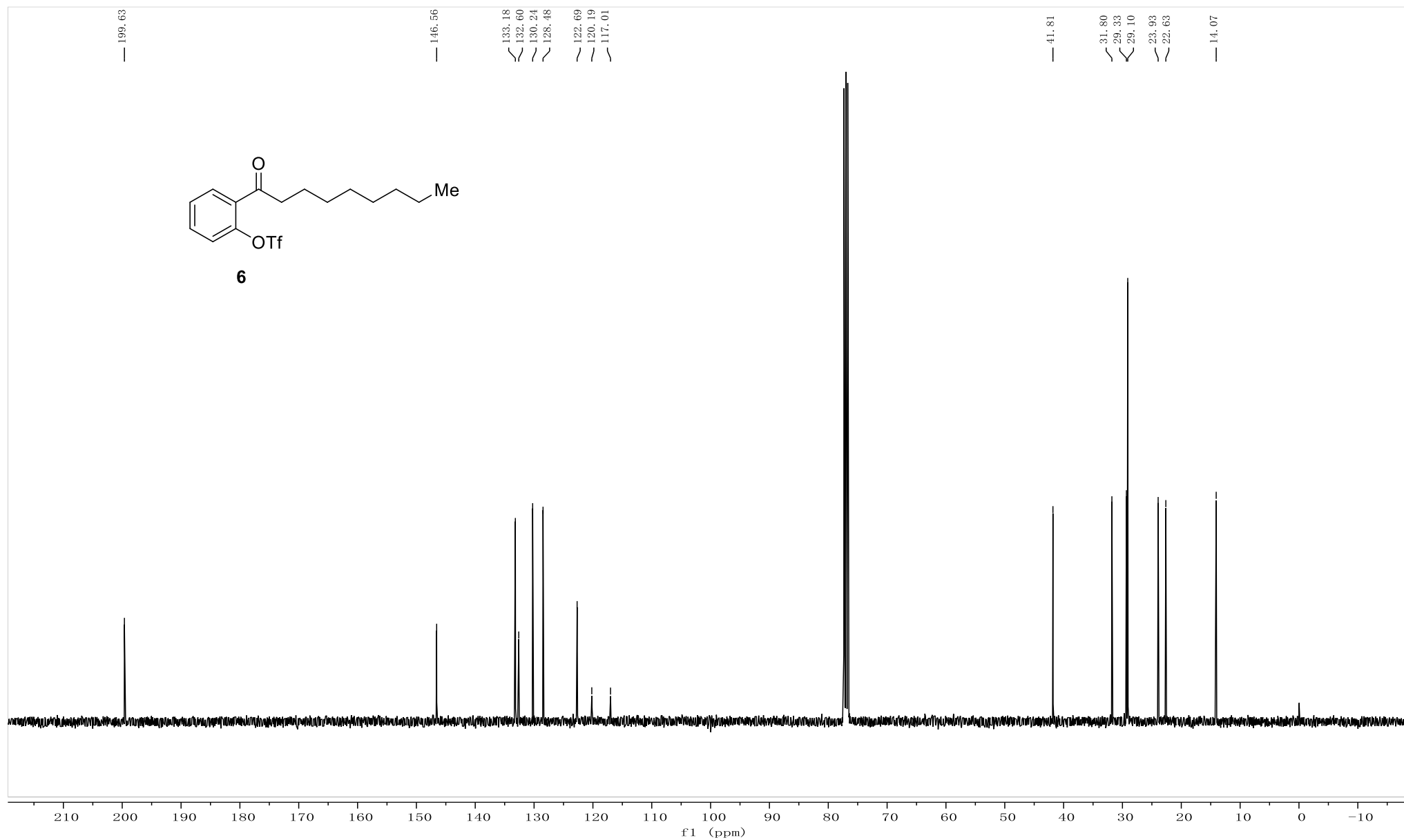
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **5dk**



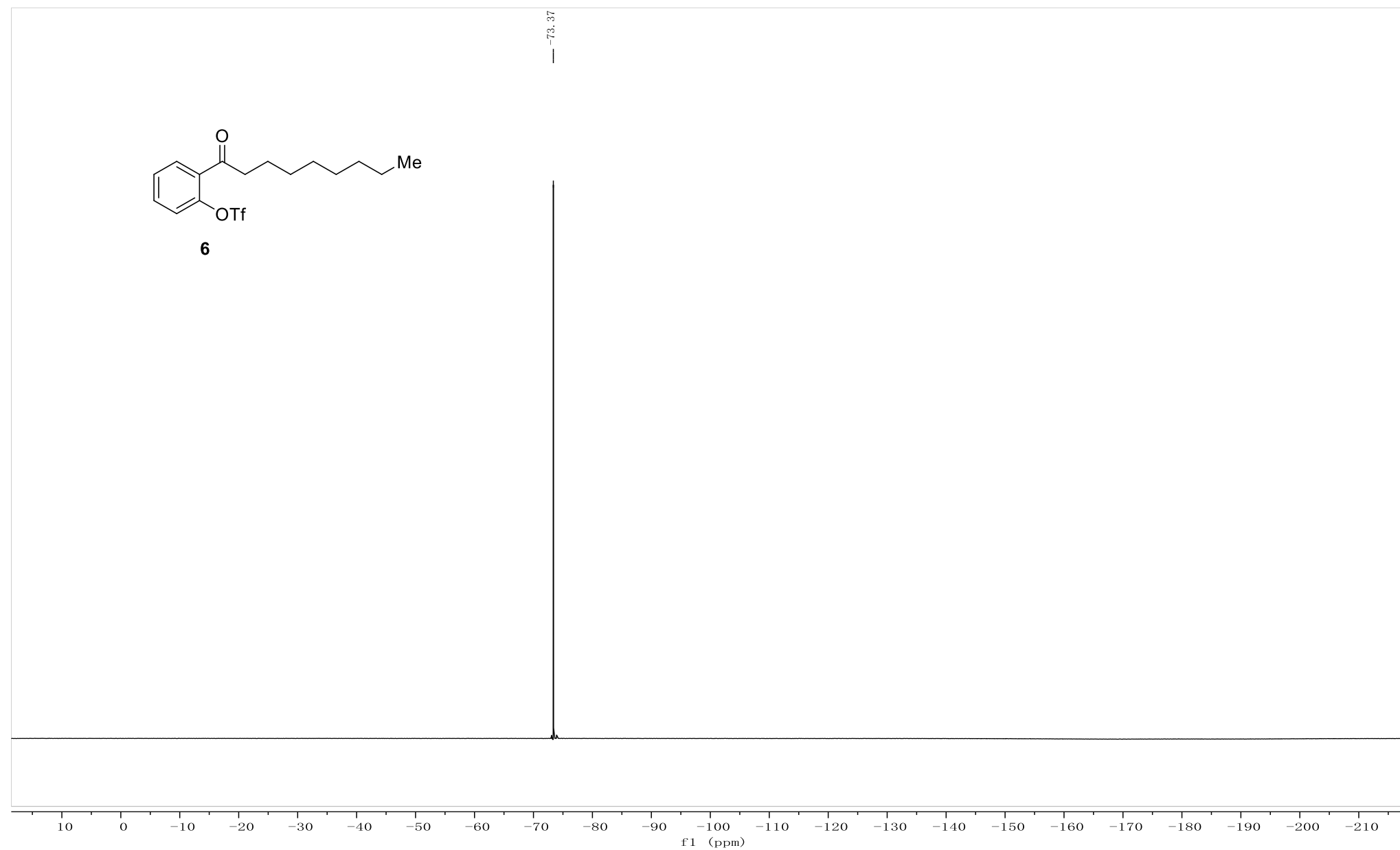
¹H NMR-spectrum (400 MHz, CDCl₃) of **6**



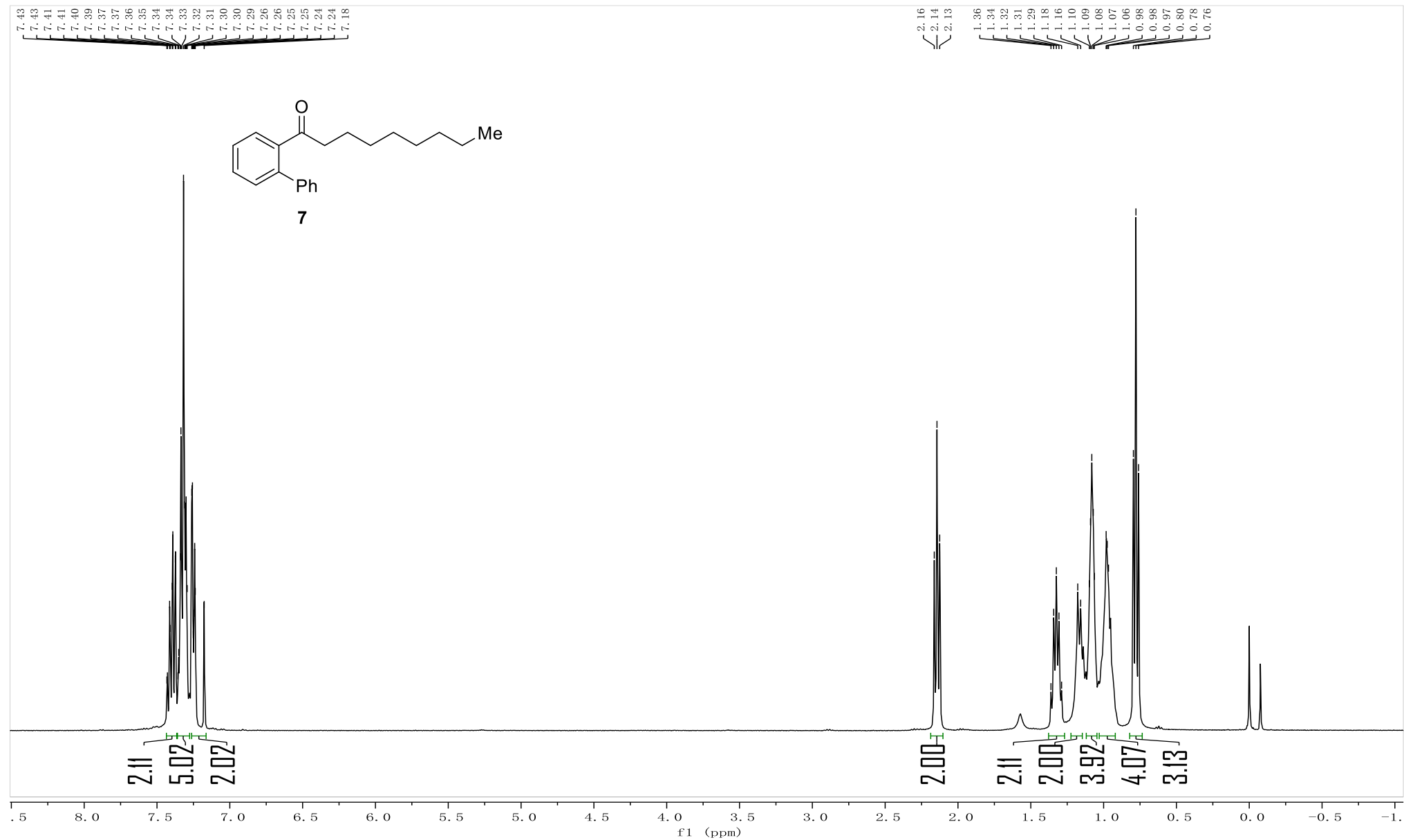
¹³C NMR-spectrum (101 MHz, CDCl₃) of **6**



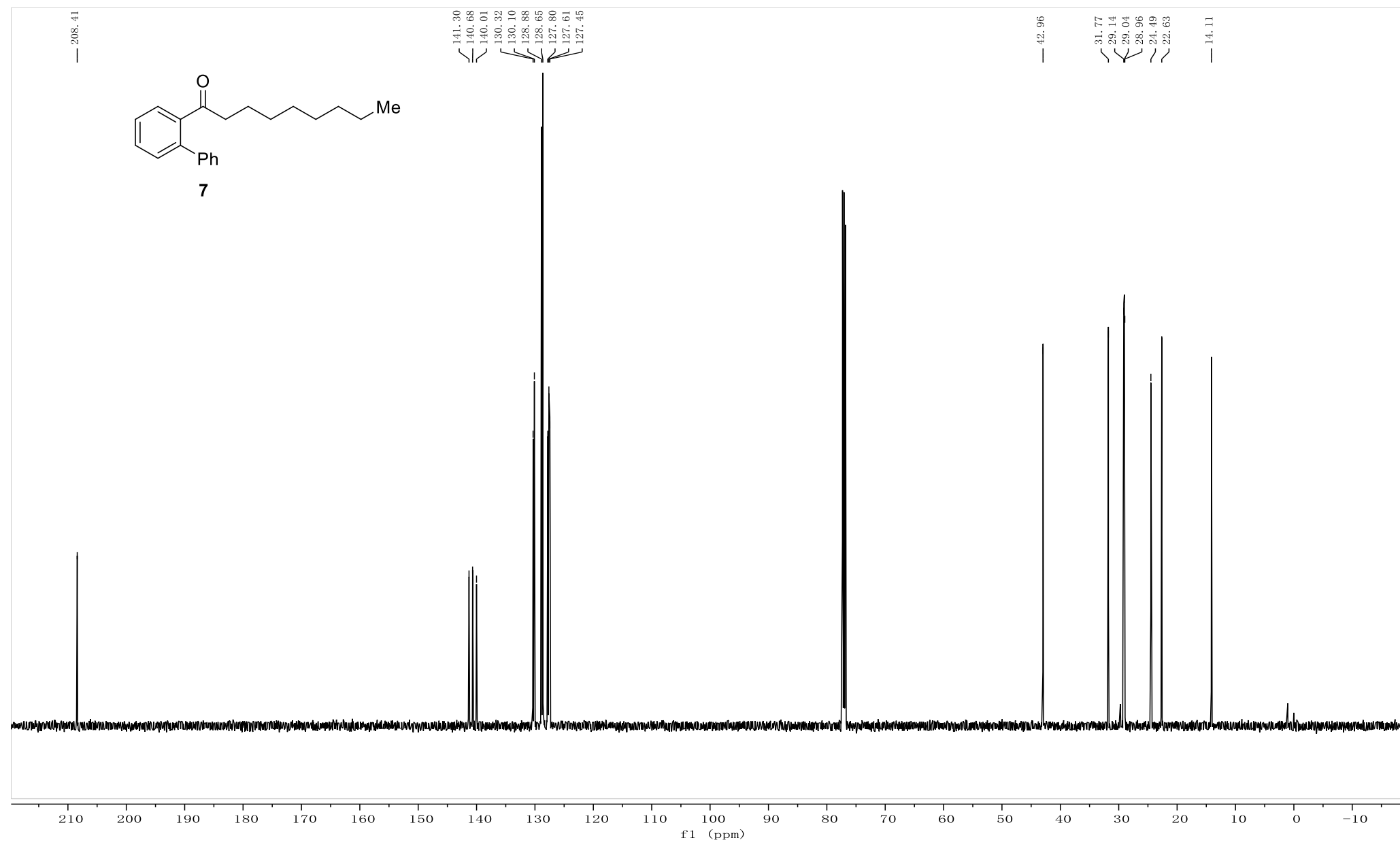
^{19}F NMR-spectrum (376 MHz, CDCl_3) of **6**



¹H NMR-spectrum (400 MHz, CDCl₃) of **7**

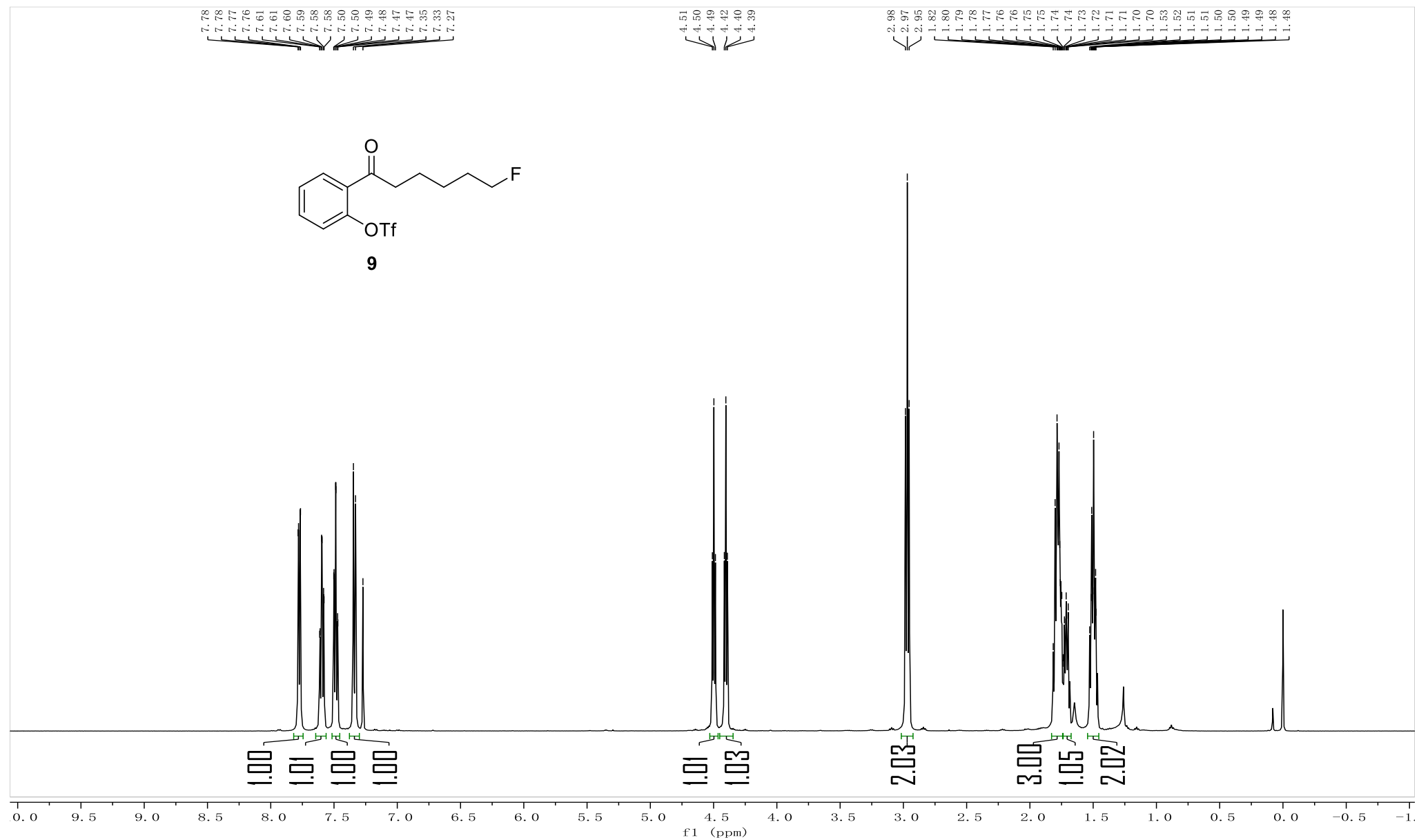


^{13}C NMR-spectrum (126 MHz, CDCl_3) of **7**



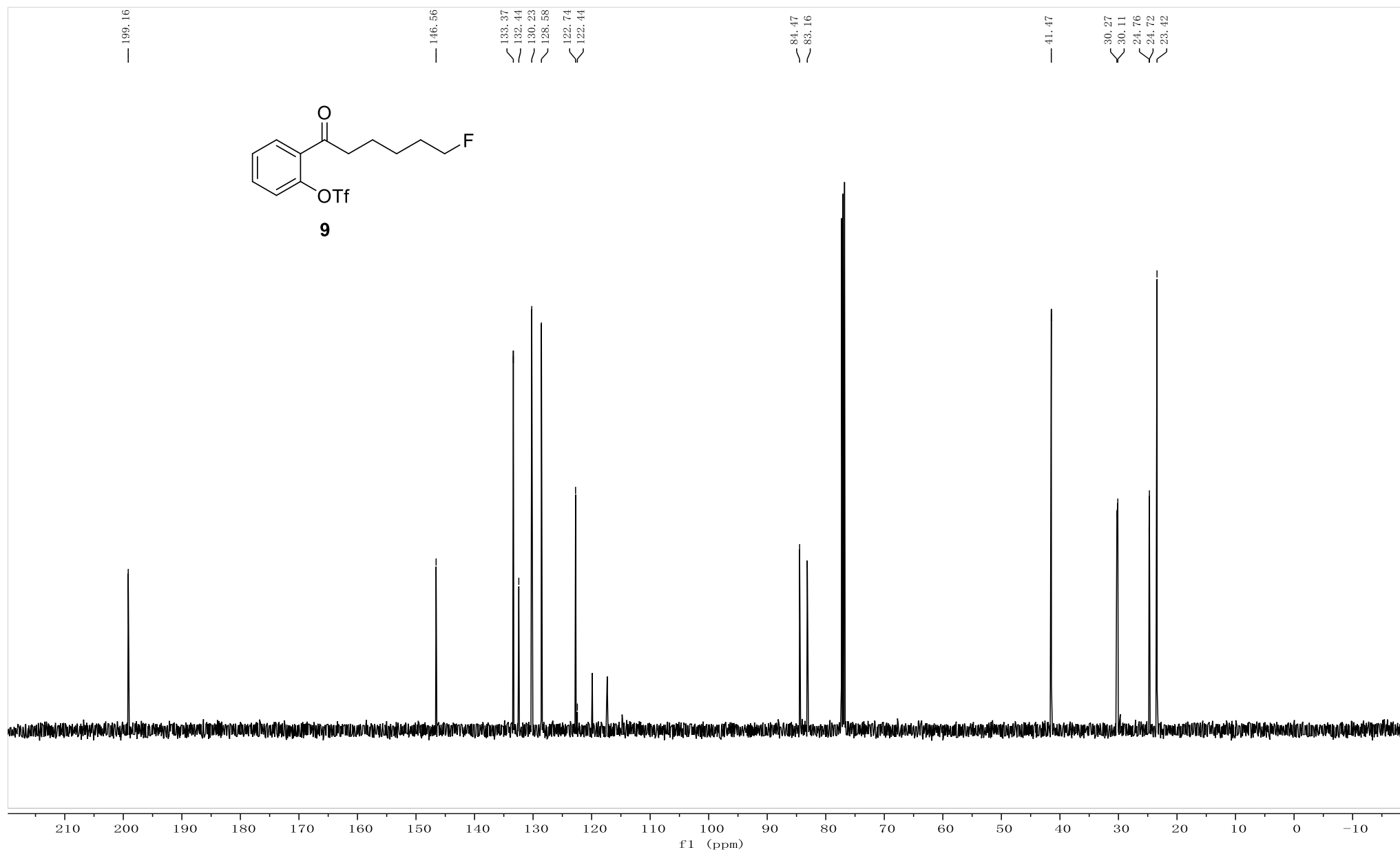
S181

¹H NMR-spectrum (500 MHz, CDCl₃) of **9**



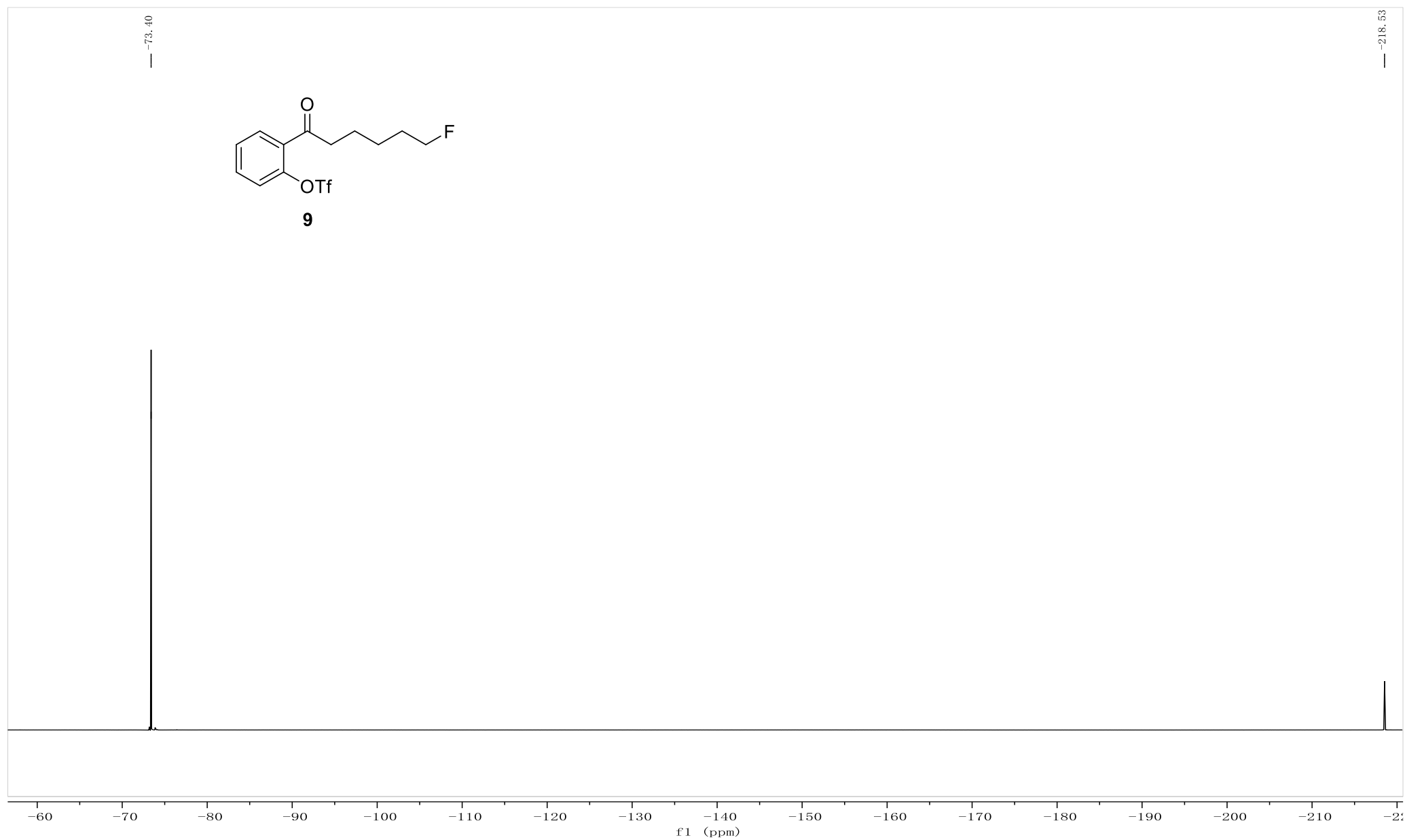
S182

¹³C NMR-spectrum (126 MHz, CDCl₃) of **9**

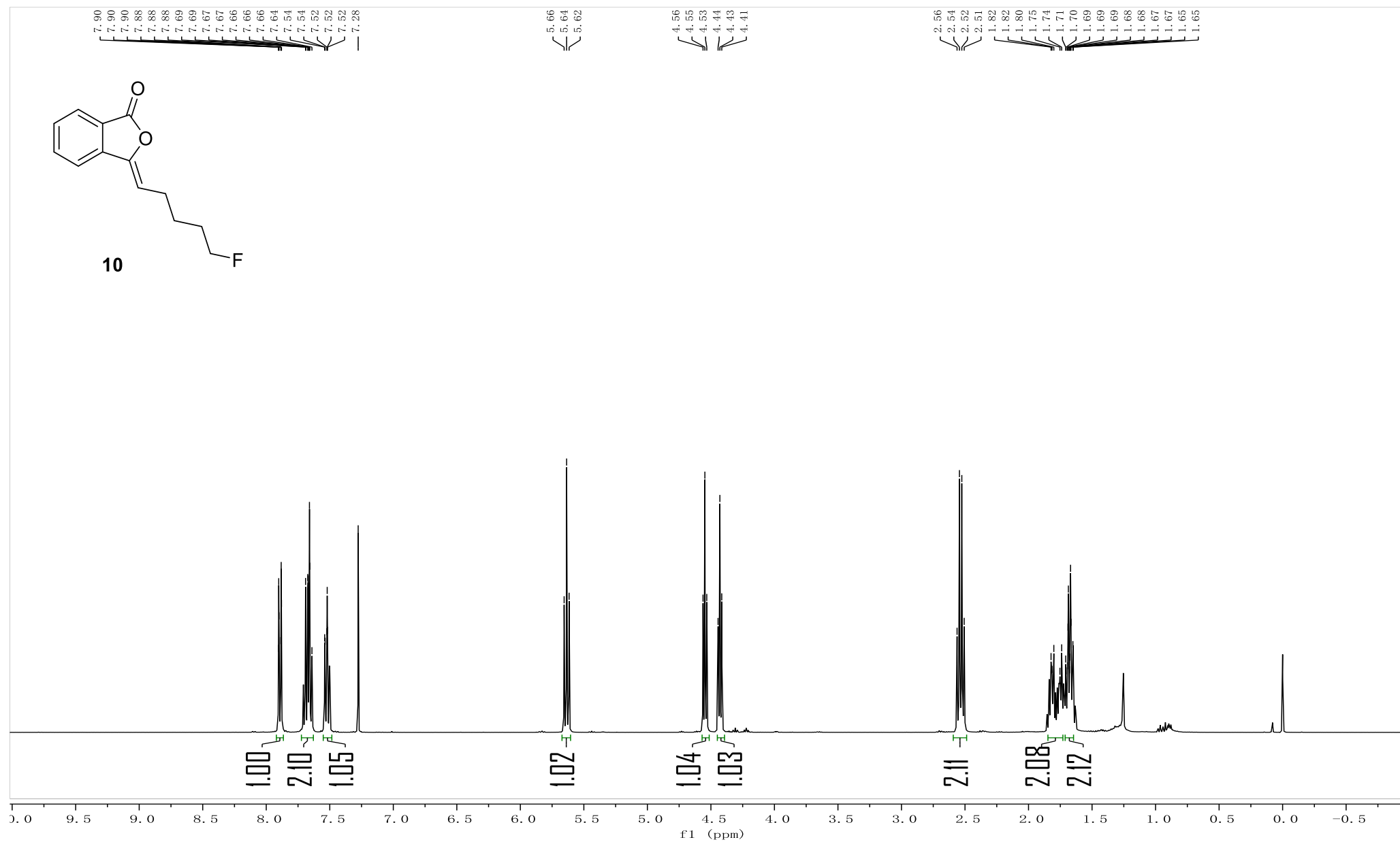


S183

^{19}F NMR-spectrum (471 MHz, CDCl_3) of **9**



¹H NMR-spectrum (400 MHz, CDCl₃) of **10**

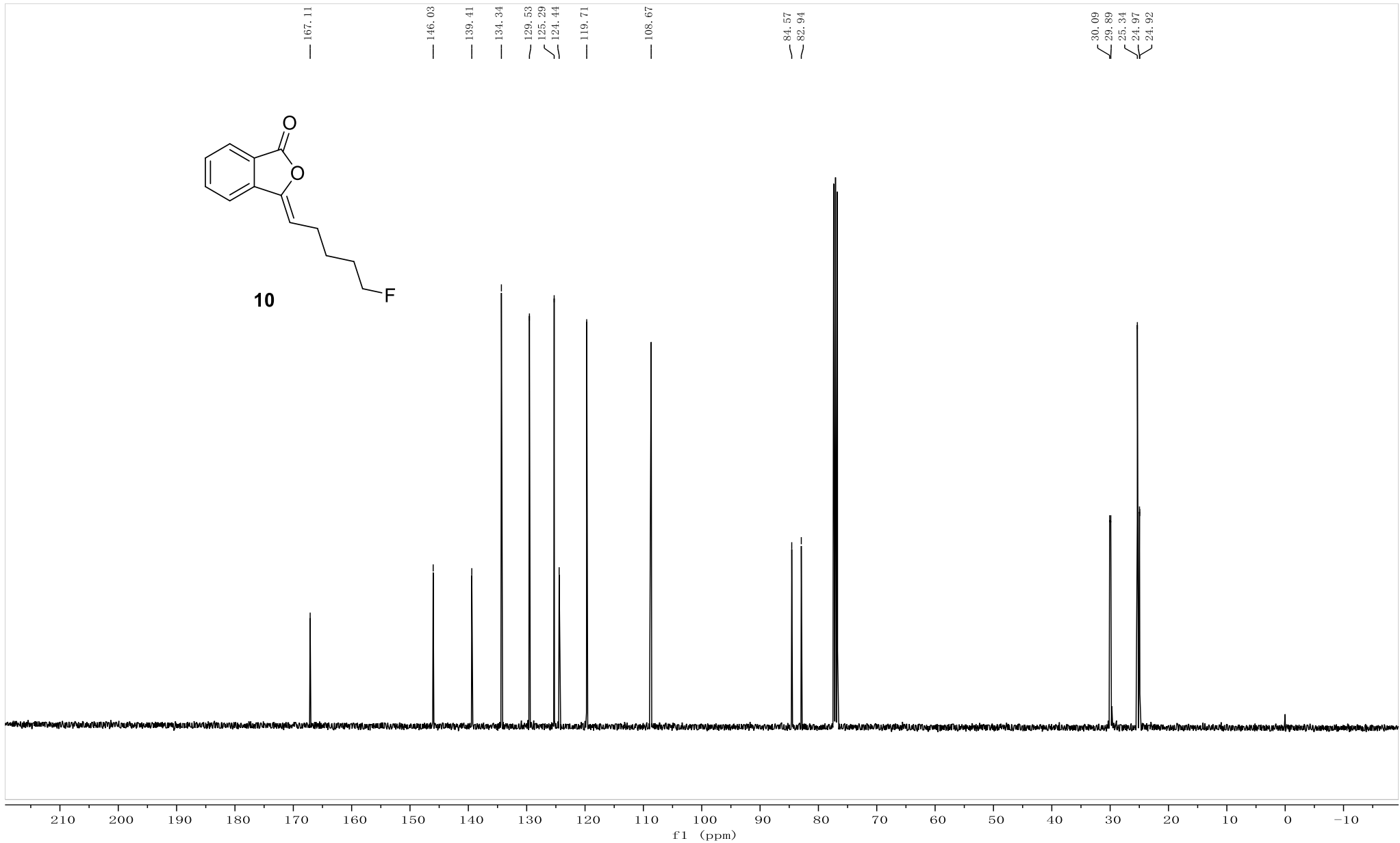


S185

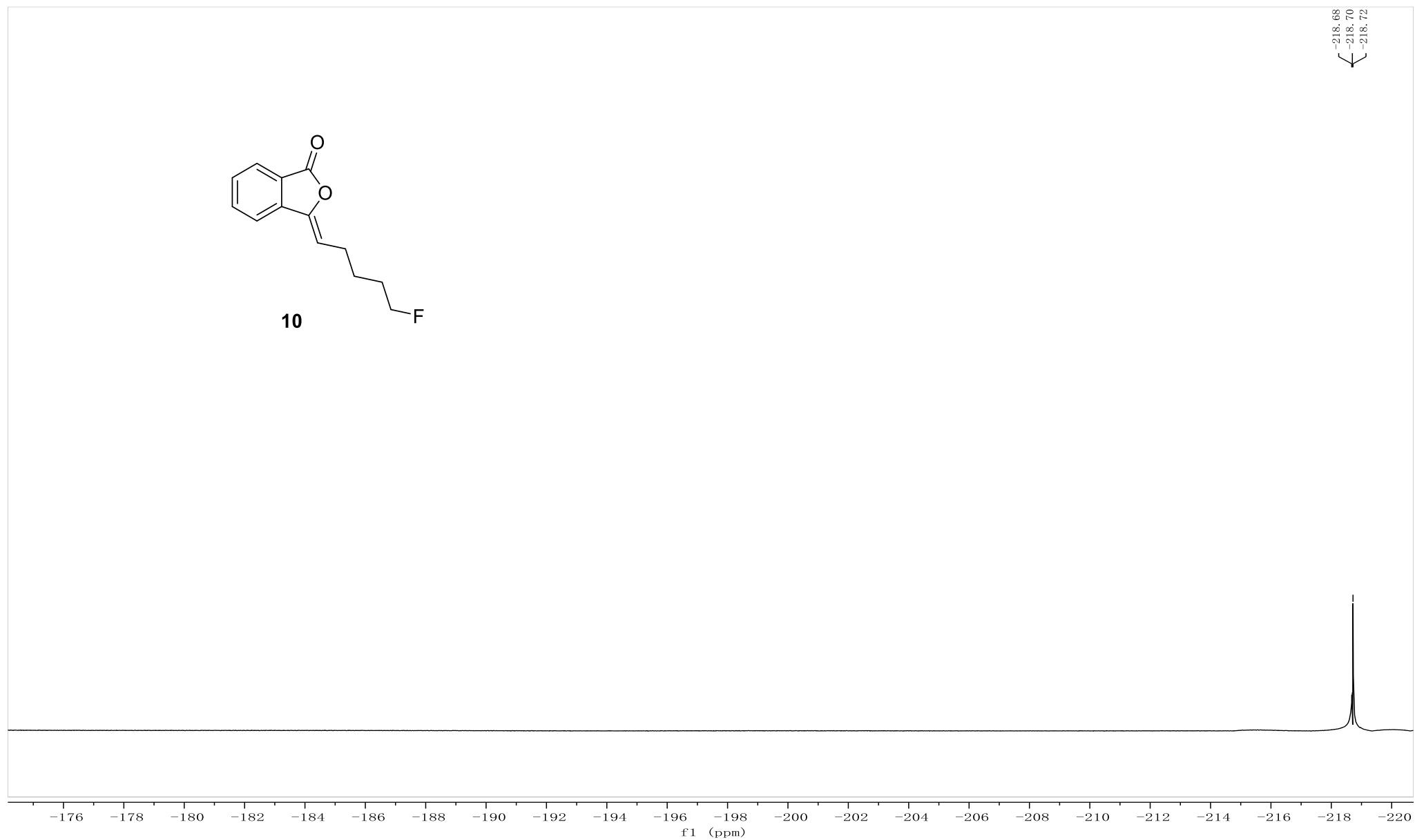
CCCCC=C1OC(=O)c2ccccc12

10

167.11, 146.03, 139.41, 134.34, 129.53, 125.29, 124.44, 119.71, 108.67, 84.57, 82.91, 30.09, 29.89, 25.34, 24.97, 24.92



^{19}F NMR-spectrum (471 MHz, CDCl_3) of **10**

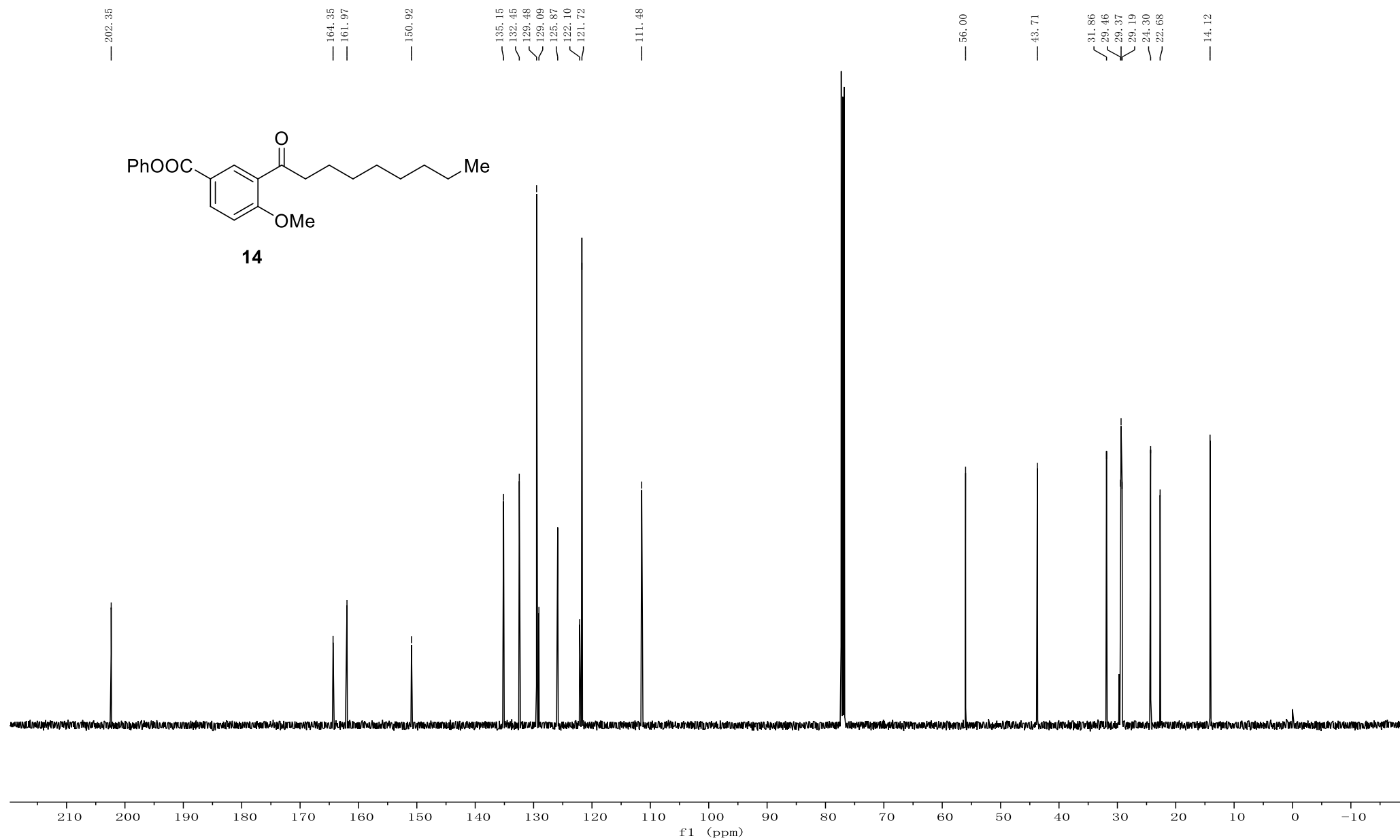


S187

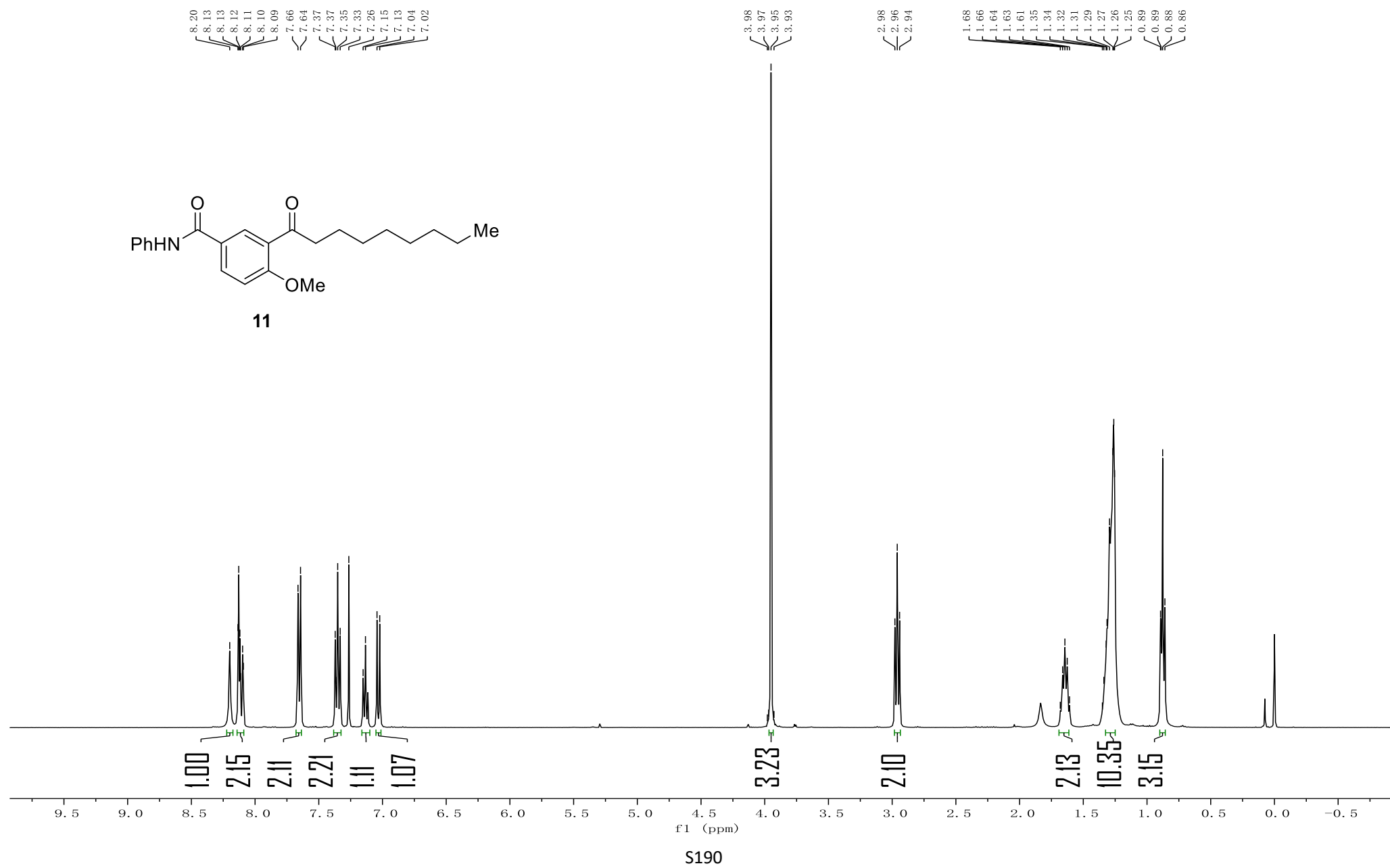
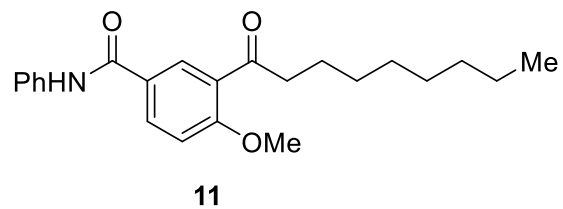
¹H NMR-spectrum (500 MHz, CDCl₃) of **14**



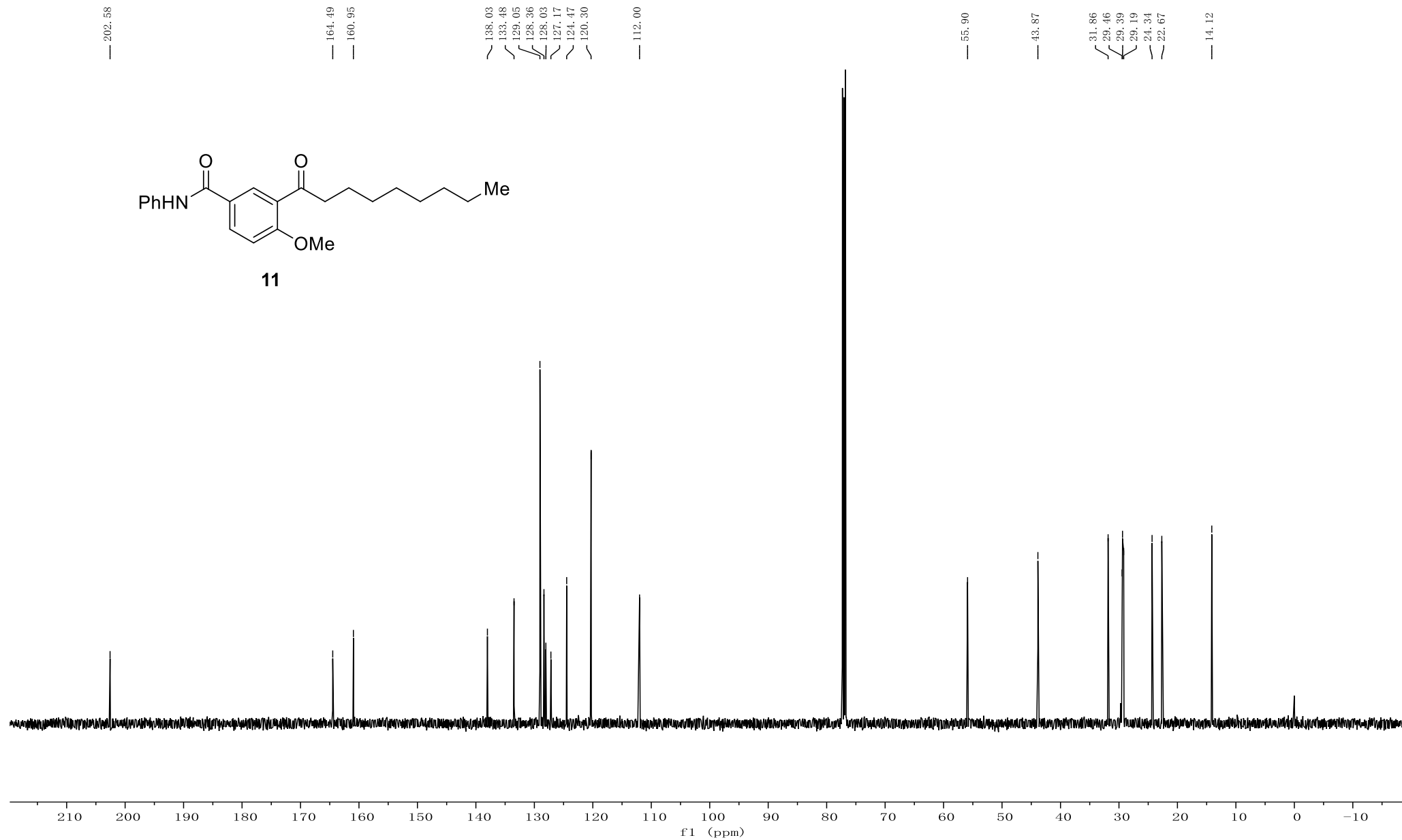
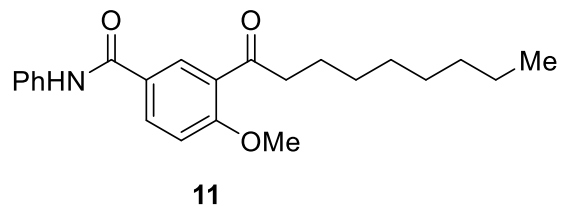
¹³C NMR-spectrum (126 MHz, CDCl₃) of **14**



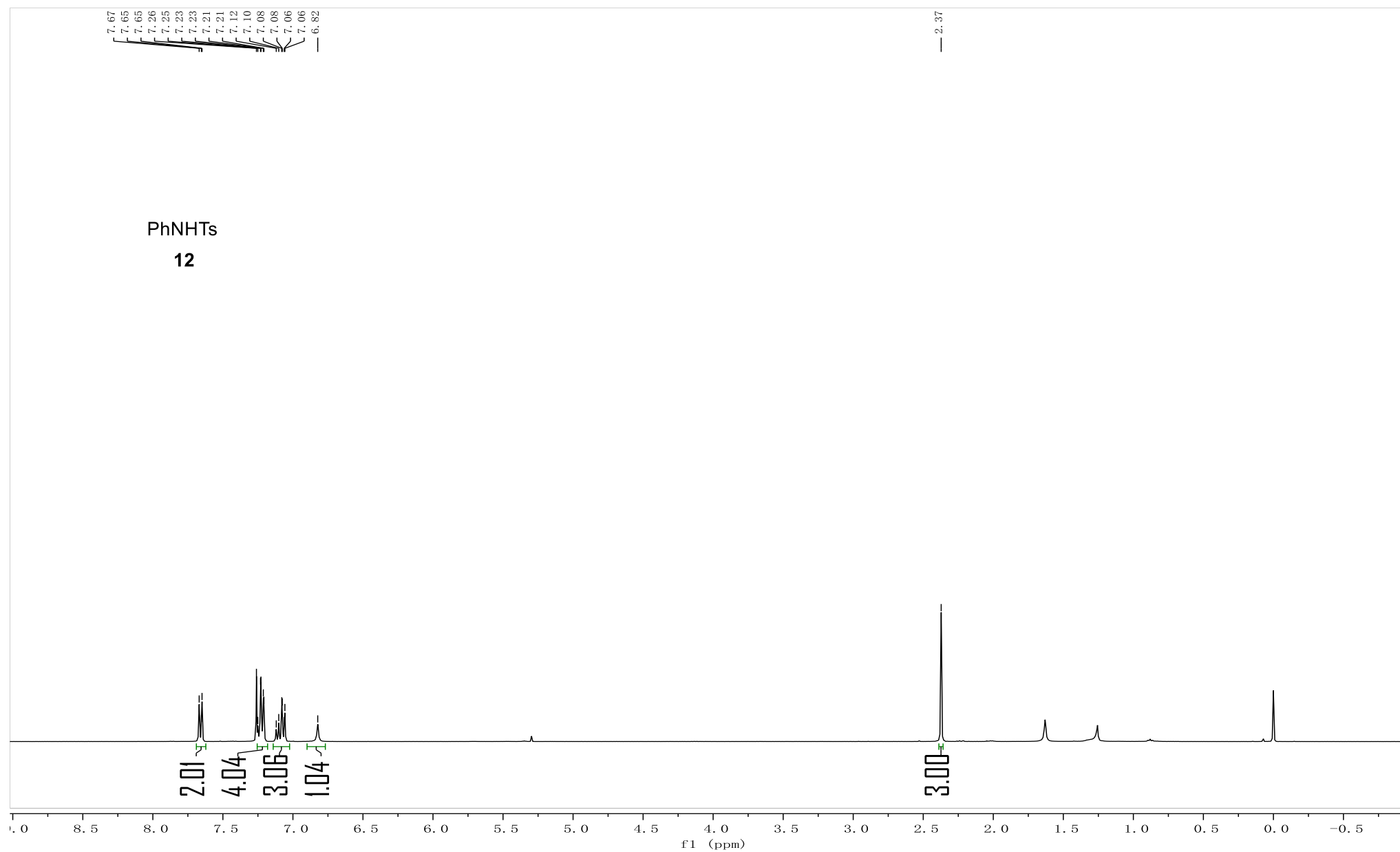
¹H NMR-spectrum (400 MHz, CDCl₃) of **11**



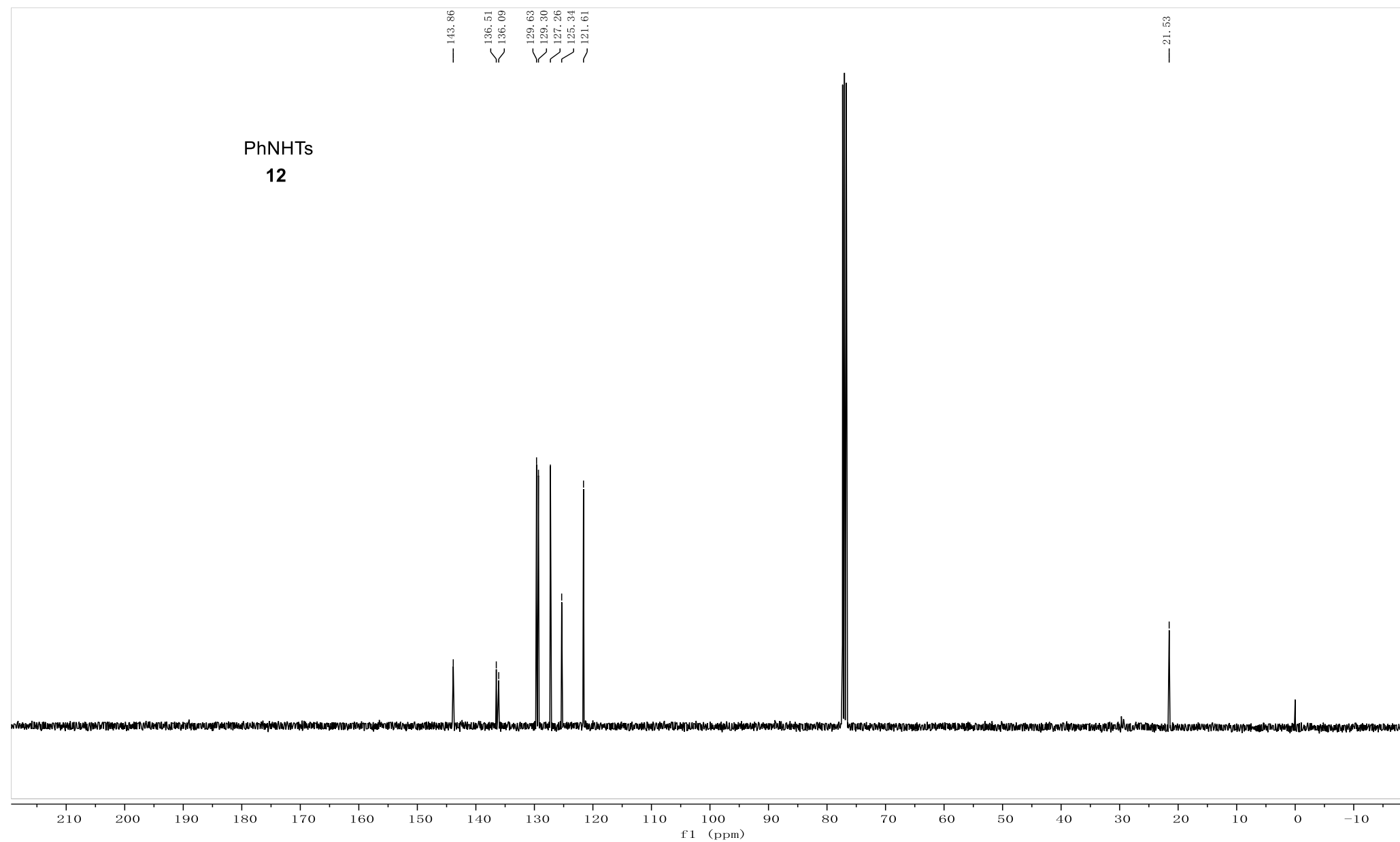
¹³C NMR-spectrum (126 MHz, CDCl₃) of **11**



¹H NMR-spectrum (400 MHz, CDCl₃) of **12**



^{13}C NMR-spectrum (101 MHz, CDCl_3) of **12**



S193