Cascade deprotonation/intramolecular aldol reaction of *α*-carbonyl sulfonium ylides with 2-mercaptoindole-3-carbaldehydes and 2-mercaptobenzaldehydes to access thieno[2,3-*b*]indoles and benzothiophenes

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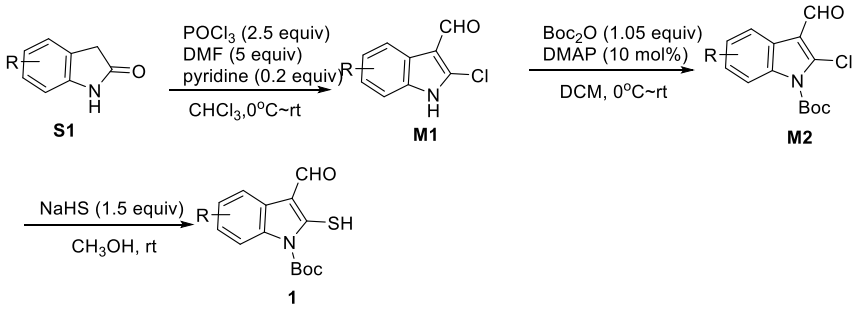
Supporting Information

Contents

1. General procedure for the preparation of substrates 1.[1]

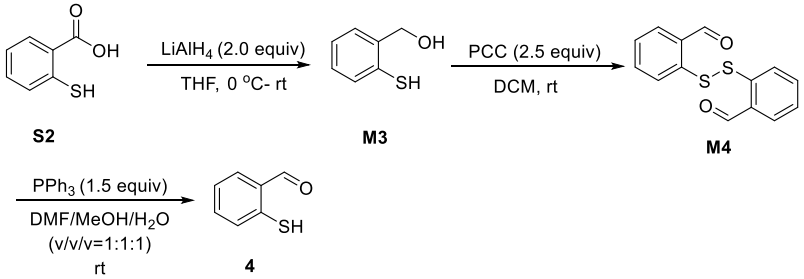


The substrate **1** is known compound, which can be synthesized according reference [1]. To a mixture of DMF (5 equiv., 20 mL) and $CHCl_3$ (10mL) was added $POCl_3$ (2.5 equiv., 20 mL) via a funnel drop by drop over 20 min at 0°C. After 30 min a mixture Oxindoles **S1** (6.4 g 48 mmol) pyridine (0.2 equiv., 10 mL), $CHCl_3$ (50 mL) was added via a funnel at 0 °C. The mixture was stirred overnight at room temperature. The mixture was poured in to ice-cold H_2O and the solid compounds was filtered and dried. The crude product **M1** was obtained (6.9 g, 80% yield).

The crude product **M1** (5 g, 27.84 mmol) was dissolved in 50 mL DCM, and the Boc_2O (29.23 mmol, 1.05 equiv.) was added dropwise via funnel at 0 ℃ and the reaction temperature was allowed to warm up to room temperature, and the mixture was stirred at room temperature until the reaction was complete monitored by TLC. The mixture was concentrated under reduced pressure and the residue purified by flash chromatography to afford the desired product **M2** (9.5 g, 82% yield).

The above product **M2** (4g, 14.28 mmol) was dissolved in methanol (20 mL), the sodium hydrogensulfide hydrate (1.77 g, 1.5 equiv.) was added. After stirring for 3 h at room temperature the reaction mixture was poured into water. Then 1M HCl was added to it until the pH to 1~2. Then the resulting mixture was extracted three times with DCM (30 mL), the combined organic phase washed with brine and dried by Na_2SO_4, filtered, concentrated under reduced pressure to afford the crude product and the crude product recrystallization from ethyl acetate and petroleum ether. The yellow needles solid **1** was obtained.

2. General procedure for the preparation of substrates 4.[2]



Substrate **4** is prepared according to the reference [2]. $LiAlH_4$ (2.3 g, 52.0 mmol) was added carefully in portions to a solution of 2-mercaptobenzoic acid (4.6 g, 30 mmol) in THF at 0 °C. The reaction temperature was allowed to warm up to room temperature, then the mixture was stirred at room temperature until the reaction was complete monitored by TLC, 10% aq. H_2SO_4 (43.0 mL) was added dropwise followed by EtOAc (50.0 mL). The mixture was separated and the aqueous layer was extracted three times with EtOAc (30 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under vacuum to give 2-mercaptobenzenemethanol(**M3**) as a light brown oil in 85% yield (3.58 g, 25.6 mmol).

PCC (13.7 g, 64.0 mmol) was added slowly in portions to a solution of 2-mercaptobenzenemethanol (3.37 g, 25.6 mmol) in CH_2Cl_2. After complete conversion of the starting material monitored by TLC, the suspension was filtered through celite bed, filtrate was collected and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography. The combined organic solution was passed through a short silica column with CH_2Cl_2 (100 mL) as eluent. Evaporation of the solvent at room temperature gave 2,2'-dithiodibenzaldehyde (**M4**) in 62% yield, 4.35 g.

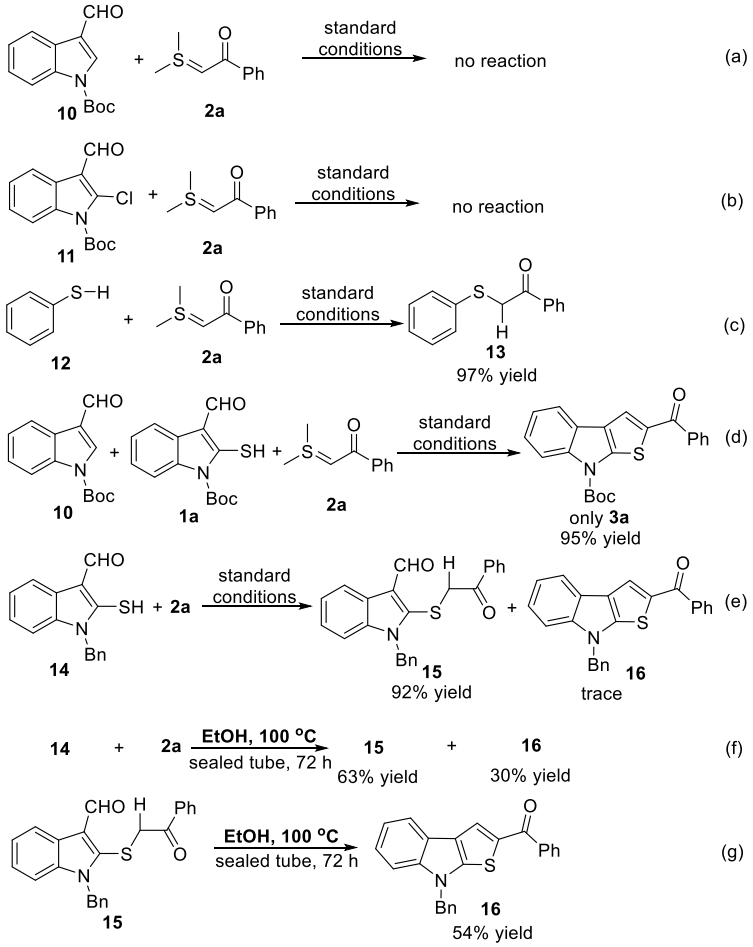
PPh_3 (2.53 g, 9.68 mmol) was added slowly in portions to a solution of crude 2,2'-dithiodibenzaldehyde (**M4**) (1.76 g, 6.45 mmol) in DMF (60.0 mL), MeOH (60.0 mL) and water (30.0 mL), the stirring was continued for 30 min at room temperature. The mixture was cooled in an ice-water bath and stirring was continued at that temperature for 30 min, then cold water (120 mL) and Et_2O (100 mL) was added. The mixture was separated and aqueous layer was extracted three times with Et_2O (50 mL). The combined Et_2O layer was washed with cold water and dried by $Na_2S_2O_4$. The solution was filtered and concentrated by rotary evaporation to afford the crude oil, then the crude oil was directly purified by flash chromatography on silica gel quickly to afford 2-mercaptobenzaldehyde as a yellow oil in 72% yield, 1.2 g.

References

[1] L. Wu, Y. Wang and Z. Zhou, *Tetrahedron: Asymmetry*, 2014, ***25***, 1389.

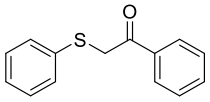
[2] M.-H. Li, J. L. Petersen, J. M. Hoover, *Org. Lett.* 2017, **19**, 638.

3. Control experiments



Control experiments (c)

To a reaction tube were added thiophenol **12** (0.1 mmol, 1.0 equiv.), sulfonium ylide **2a** (0.12 mmol, 1.2 equiv.), and EtOH (1.0 mL). The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure, and the residue directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the compound **13** (22.2 mg, 97% yield).

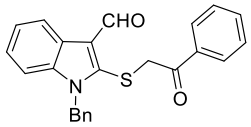


1-phenyl-2-(phenylthio)ethan-1-one (13)[1]

^{1}H NMR (300 MHz, $CDCl_3$) (known compound) δ 7.98 – 7.90 (m, 2H), 7.63 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.21 (m, 3H), 4.28 (s, 2H).

Control experiments (e)

To a reaction tube were added the *N*-Bn-2-mercaptoindole-3-carbaldehyde **14** (0.1 mmol, 1.0 equiv.), sulfonium ylide **2a** (0.12 mmol, 1.2 equiv.) and EtOH (1.0 mL). The reaction mixture was stirred at room temperature for 5 h. the reaction mixture was concentrated under reduced pressure, and the residue directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 ~ 8:1) to afford the compound **15** as a brown yellow solid (35.5 mg, 92% yield).



benzyl-2-((2-oxo-2-phenylethyl)thio)-1*H*-indole-3-carbaldehyde (15)

Brown yellow solid, 35.5 mg, 92% yield, m.p. 123.5-124.4 ℃

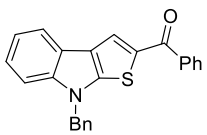
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.36 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.18 (m, 6H), 7.08 (d, *J* = 7.5 Hz, 2H), 5.64 (s, 2H), 4.09 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 186.8, 140.4, 137.9, 136.4, 134.8, 134.0, 129.1, 128.9, 128.4, 127.9, 126.4, 125.4, 125.2, 123.5, 121.9, 121.1, 110.8, 47.5, 44.3.

HRMS (ESI) Calcd. For $C_{24}H_{19}NNaO_2S$ $[M+Na]^+$: 408.1029; found: 408.1031.

Control experiments (f)

To a reaction tube were added *N*-Bn-2-mercaptoindole-3-carbaldehyde **14** (0.2 mmol, 1.0 equiv.), sulfonium ylide **2a** (0.24 mmol, 1.2 equiv.) and EtOH (2.0 mL). The reaction mixture was stirred at 100^{o}C in sealed tube for 72 h. The reaction mixture was concentrated under reduced pressure, and the residue directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 ~ 8:1) to afford the compound **15** as a brown yellow solid (48.5 mg, 63% yield) and **16** as a yellow solid (22.1 mg, 30% yield).



(8-benzyl-8H-thieno[2,3-*b*]indol-2-yl)(phenyl)methanone (16)

Yellow solid, 19.5 mg, 54% yield, m.p. 126.1-127.4 ℃

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.53 (dd, *J* = 8.1, 6.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.35 (m, 5H), 7.27 (m, 2H), 5.40 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 150.5, 142.9, 138.8, 136.8, 134.7, 131.7, 129.2, 129.0, 128.6, 128.5, 128.2, 127.9, 124.9, 123.8, 122.9, 121.0, 120.0, 110.1, 50.2.

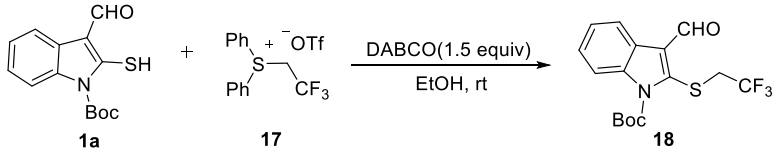
HRMS (ESI) Calcd. For $C_{24}H_{17}NNaOS$ $[M+Na]^+$: 390.0923; found: 390.0925.

Control experiments (g)

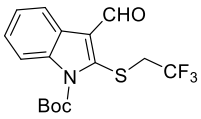
To a reaction sealed tube were added compound **15** (0.1 mmol, 1.0 equiv.) and EtOH (1.0 mL). The reaction mixture was stirred at 100 ^{o}C in sealed tube for 72 h. The reaction mixture was concentrated in vacuo, and the residue directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 ~ 10:1) to afford the compound **15** as a yellow solid (21 mg, 54% yield, recovered **15**, 12.2 mg, 32% yield).

[1] Dias, R. M. P.; Burtoloso, A. C. B. *Org. Lett.* **2016**, *18*, 3034.

The reaction of 1a with diphenyl(2,2,2-trifluoroethyl)sulfonium ylide (17) for the synthesis of 18.



The 2-mercaptoindole-3-carbaldehydes **1a** (0.1 mmol, 1.0 equiv.), diphenyl(2,2,2-trifluoroethyl)sulfonium ylides **17** (0.12 mmol, 1.2 equiv.), DABCO (0.15 mmol, 1.5 equiv) and EtOH (1.0 mL) were added to a reaction tube. The reaction mixture was stirred at room temperature. After complete conversion of the starting material monitored by TLC and the reaction mixture concentrated by rotary evaporation then the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1).



***tert*-butyl 3-formyl-2-((2,2,2-trifluoroethyl)thio)-1*H*-indole-1-carboxylate (18).**

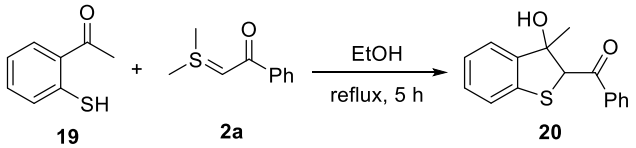
White solid, 33.4 mg, 93% yield, m.p. 87.8-88.2 – 167.2 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.42 – 8.31 (m, 1H), 8.03 – 7.92 (m, 1H), 7.49 – 7.31 (m, 2H), 3.64 (q, *J* = 9.7 Hz, 2H), 1.76 (s, 9H);

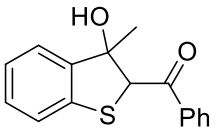
^{13}C NMR (75 MHz, $CDCl_3$) δ 188.5, 148.9, 138.1, 137.0, 127.0, 126.6, 125.3, 125.2 (q, *J* = 274.5 Hz) 124.9, 122.1, 115.1, 86.7, 39.2 (q, *J* = 32.3 Hz), 28.2.

HRMS (ESI) Calcd. For $C_{16}H_{16}F_3NNaO_3S$ $[M+Na]^+$: 382.0695; found: 382.0677.

The reaction of 1-(2-mercaptophenyl)ethan-1-one (19) with 2a for the synthesis of 20.



The 1-(2-mercaptophenyl)ethan-1-one **19** (0.1 mmol, 1.0 equiv.), sulfonium ylides **2a** (0.12 mmol, 1.2 equiv.) and EtOH (1.0 mL) were added to a reaction tube. The reaction was carried out in reflux EtOH for 5 h. After complete conversion of the starting material monitored by TLC and the reaction mixture concentrated by rotary evaporation then the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1).



(3-hydroxy-3-methyl-2,3-dihydrobenzo[b]thiophen-2-yl)(phenyl)methanone (20)

Yellow oil, 25.7 mg, 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 7.1, 1.4 Hz, 2H), 7.70 – 7.56 (m, 1H), 7.56 – 7.45 (m, 2H), 7.45 – 7.36 (m, 1H), 7.33 – 7.16 (m, 2H), 7.15 – 7.05 (m, 1H), 4.82 (s, 1H), 4.75 (s, 1H), 1.75 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 145.1, 135.1, 134.5, 133.9, 129.0, 128.9, 128.6, 126.3, 123.2, 123.0, 84.4, 56.8, 27.3.;

HRMS (ESI) Calcd. For $C_{16}H_{14}NaO_2S$ $[M+Na]^+$: 293.0607; found: 293.0601.

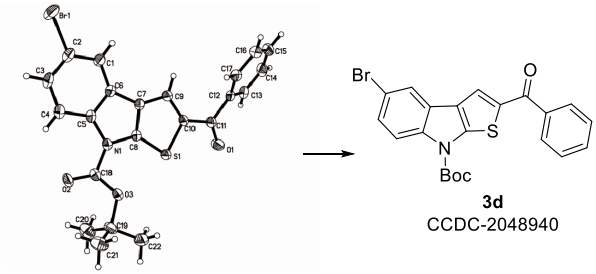
4. X-ray crystal structure of 3d.

Single crystals of compound **3d** were prepared from the mixture solvent of dichloromethane and EtOH. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[3] Sheldrick, G. M. *Acta Cryst*. **2015**, C71, 3-8.



Crystal data and structure refinement for **3d (**CCDC 2048940**)**

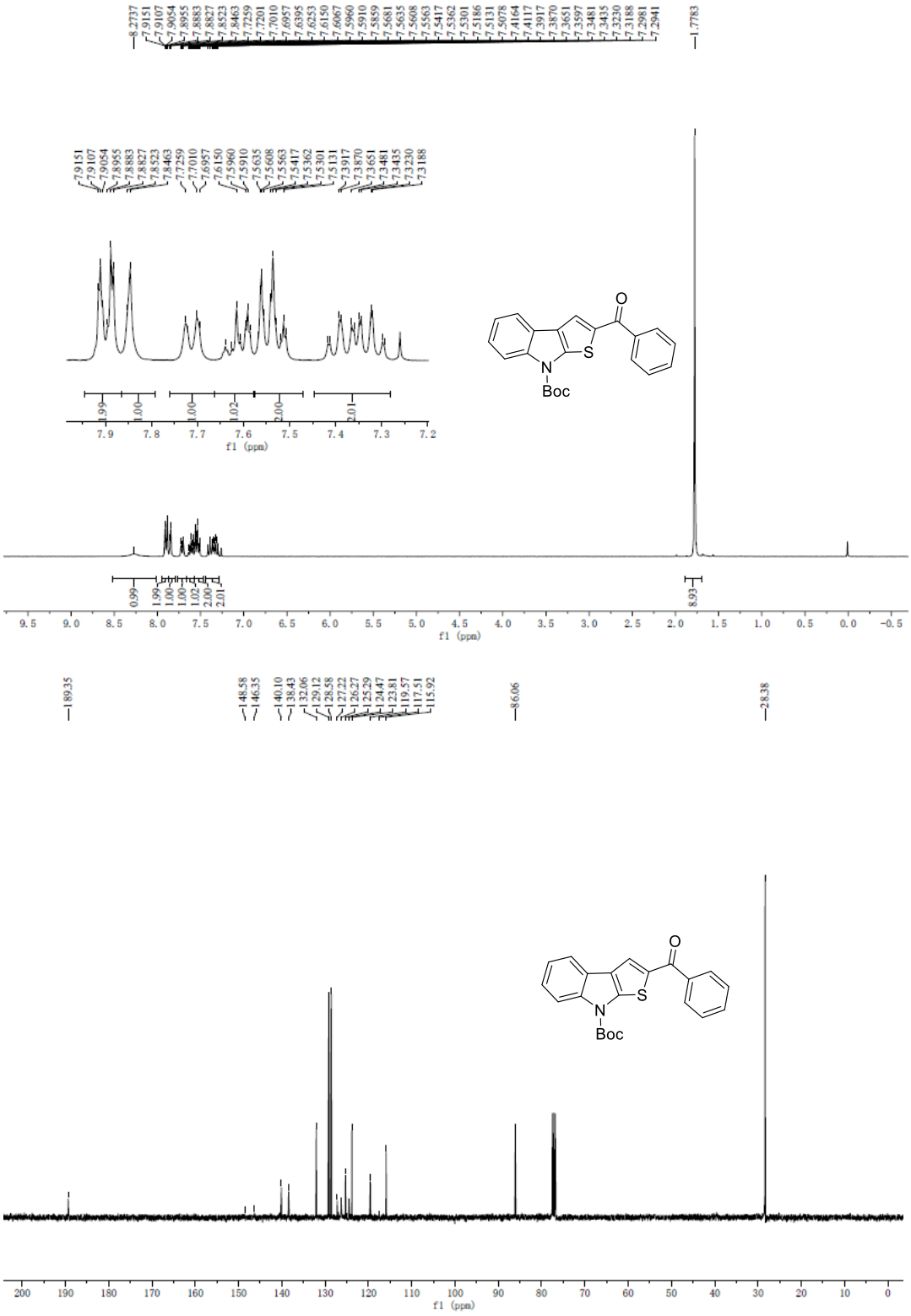
Identification code	**3d**
Empirical formula	$C_{22}H_{18}BrNO_3S$
Formula weight	456.34
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6907(12)
b/Å	10.3979(10)
c/Å	11.4082(13)
α/°	88.986(9)

β/°	65.263(11)
γ/°	80.064(9)
Volume/Å^3	1026.5(2)
Z	2
ρ_{calc}g/cm^3	1.476
μ/mm^{-1}	3.867
F(000)	464.0
Crystal size/mm^3	0.21 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.55 to 134.198
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	7270
Independent reflections	3682 [R_{int} = 0.0231, R_{sigma} = 0.0348]
Data/restraints/parameters	3682/0/256
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1026
Final R indexes [all data]	R_1 = 0.0490, wR_2 = 0.1104
Largest diff. peak/hole / e Å^{-3}	0.42/-0.54

5. ^{1}H, ^{13}C NMR, for compounds 3, 5, 6-9, 15 and 16, 18, 20.

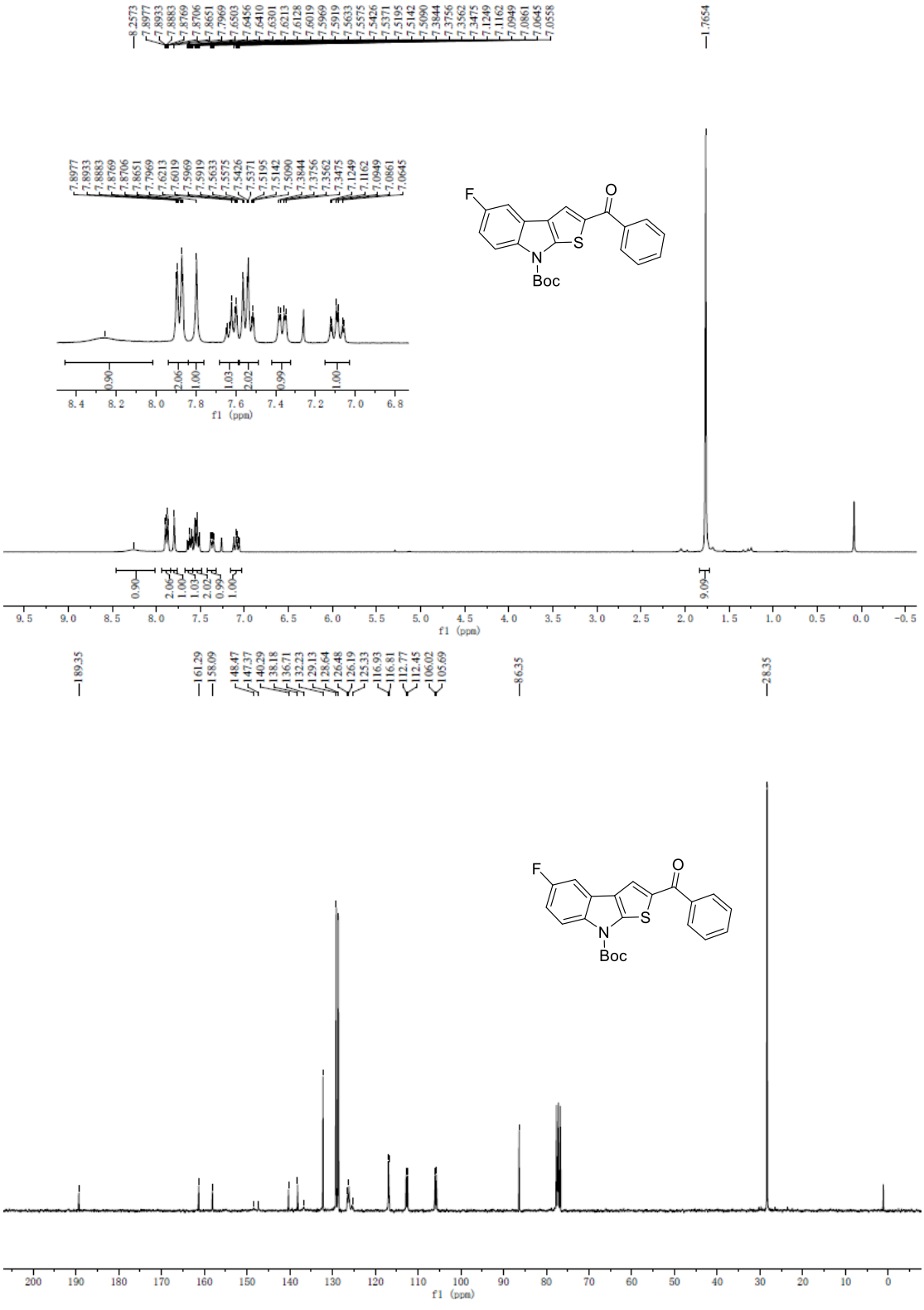
^{1}H and ^{13}C NMR of **3a**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



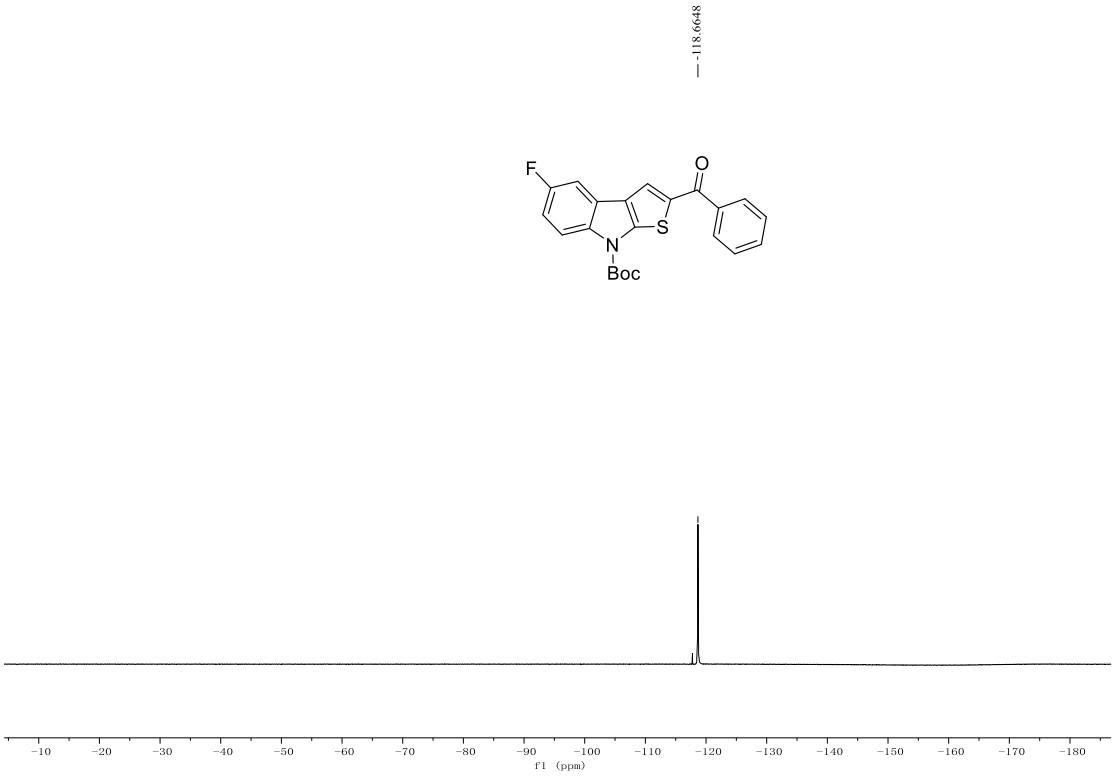
^{1}H and ^{13}C NMR of **3b**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



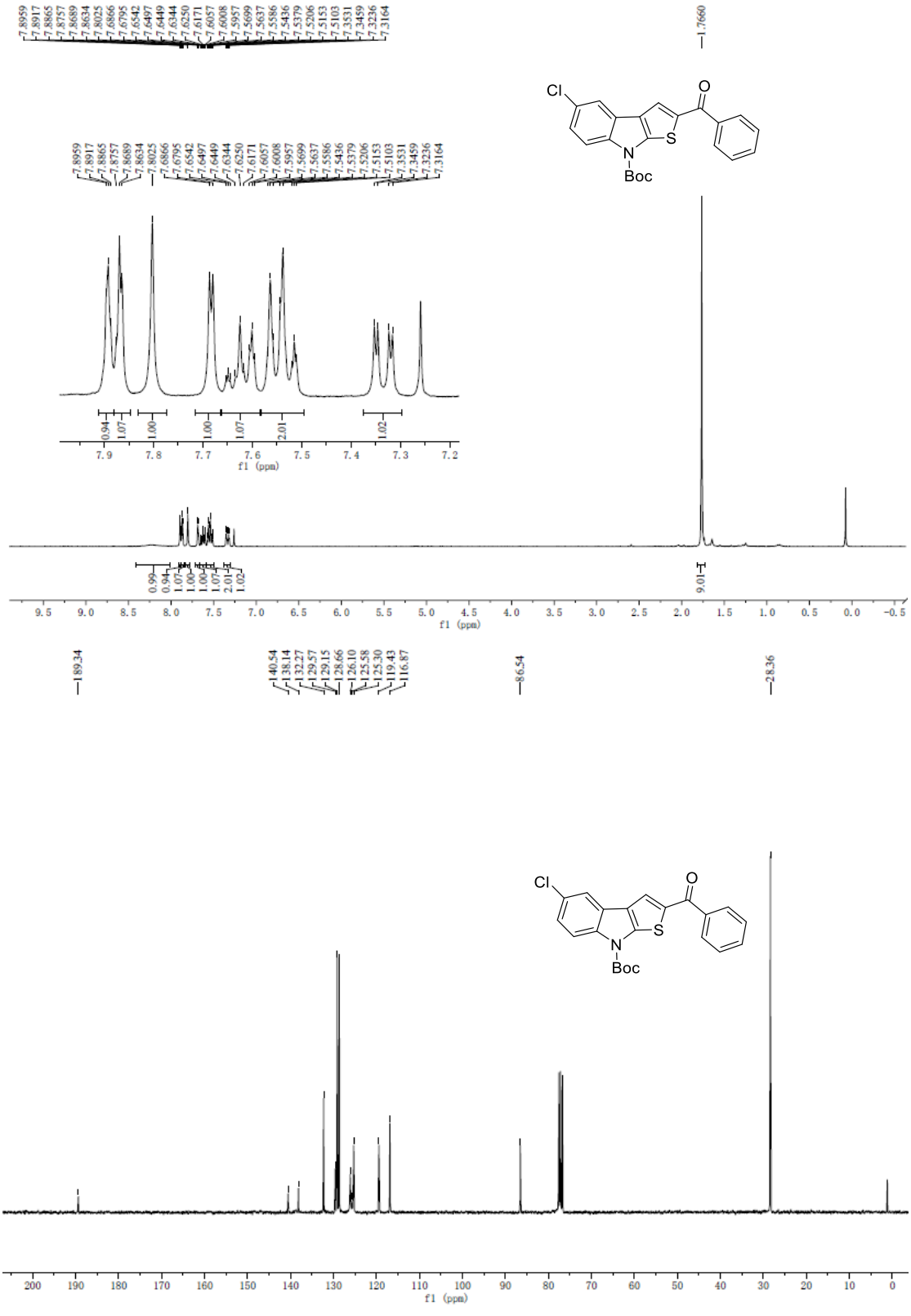
^{19}F NMR of **3b**

(376 MHz, $CDCl_3$)



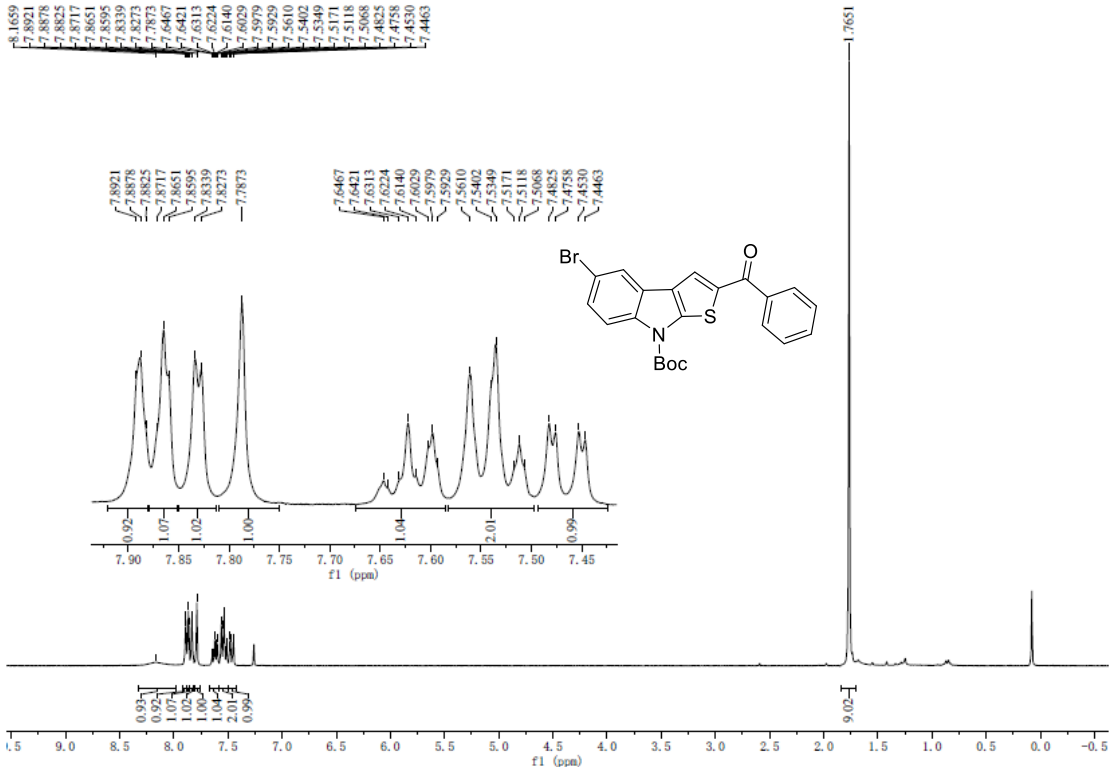
^{1}H and ^{13}C NMR of **3c**

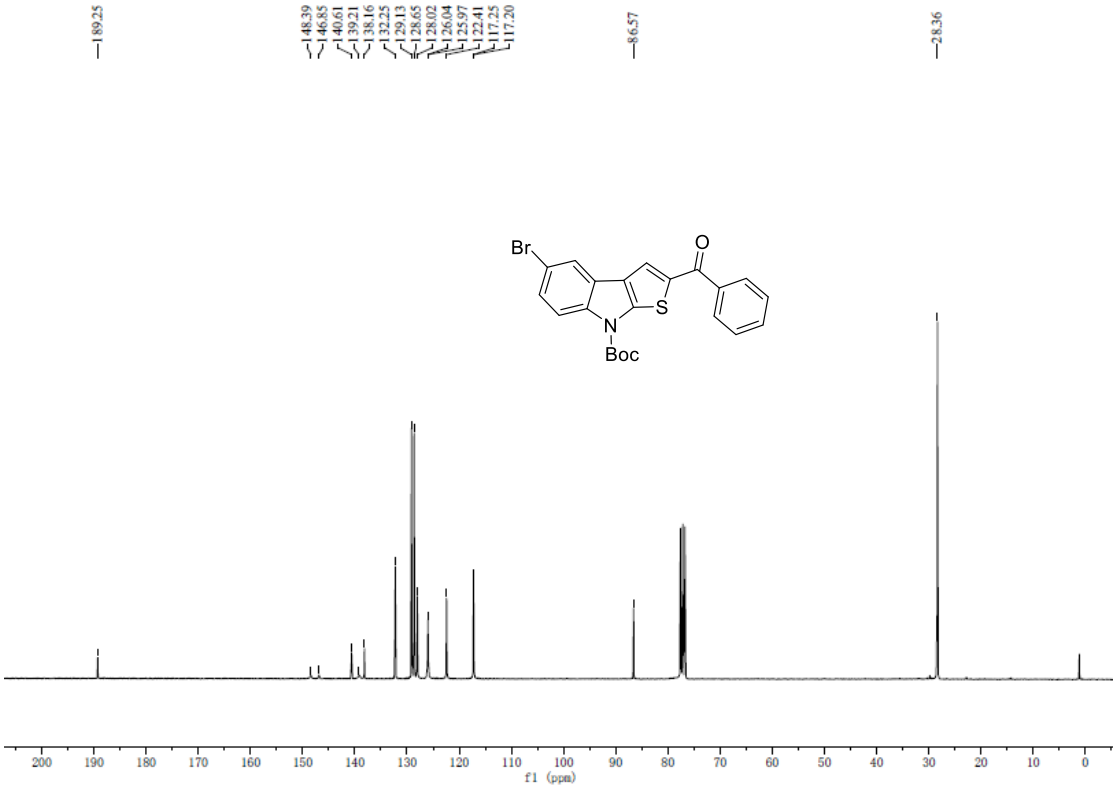
^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR of **3d**

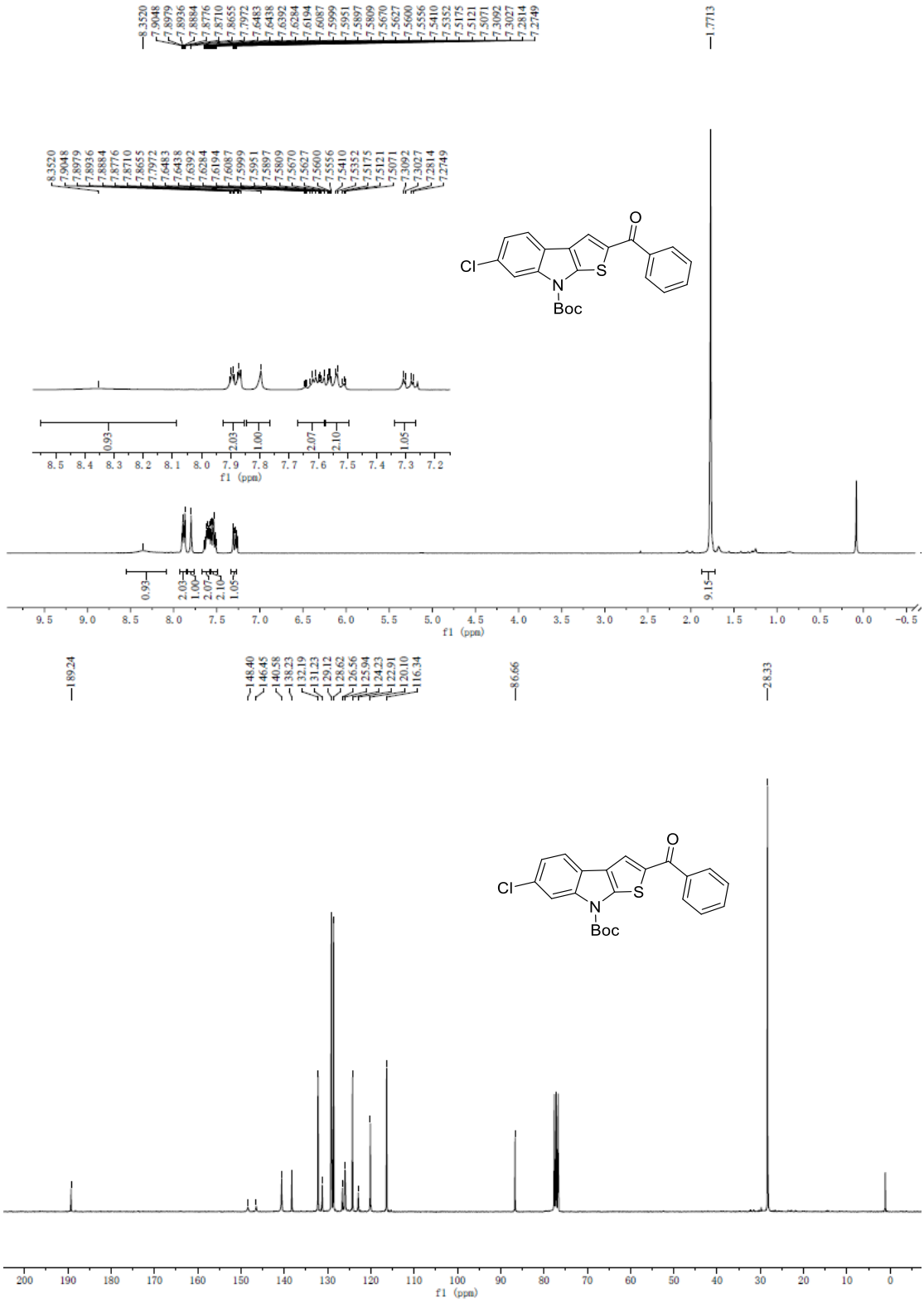
^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)





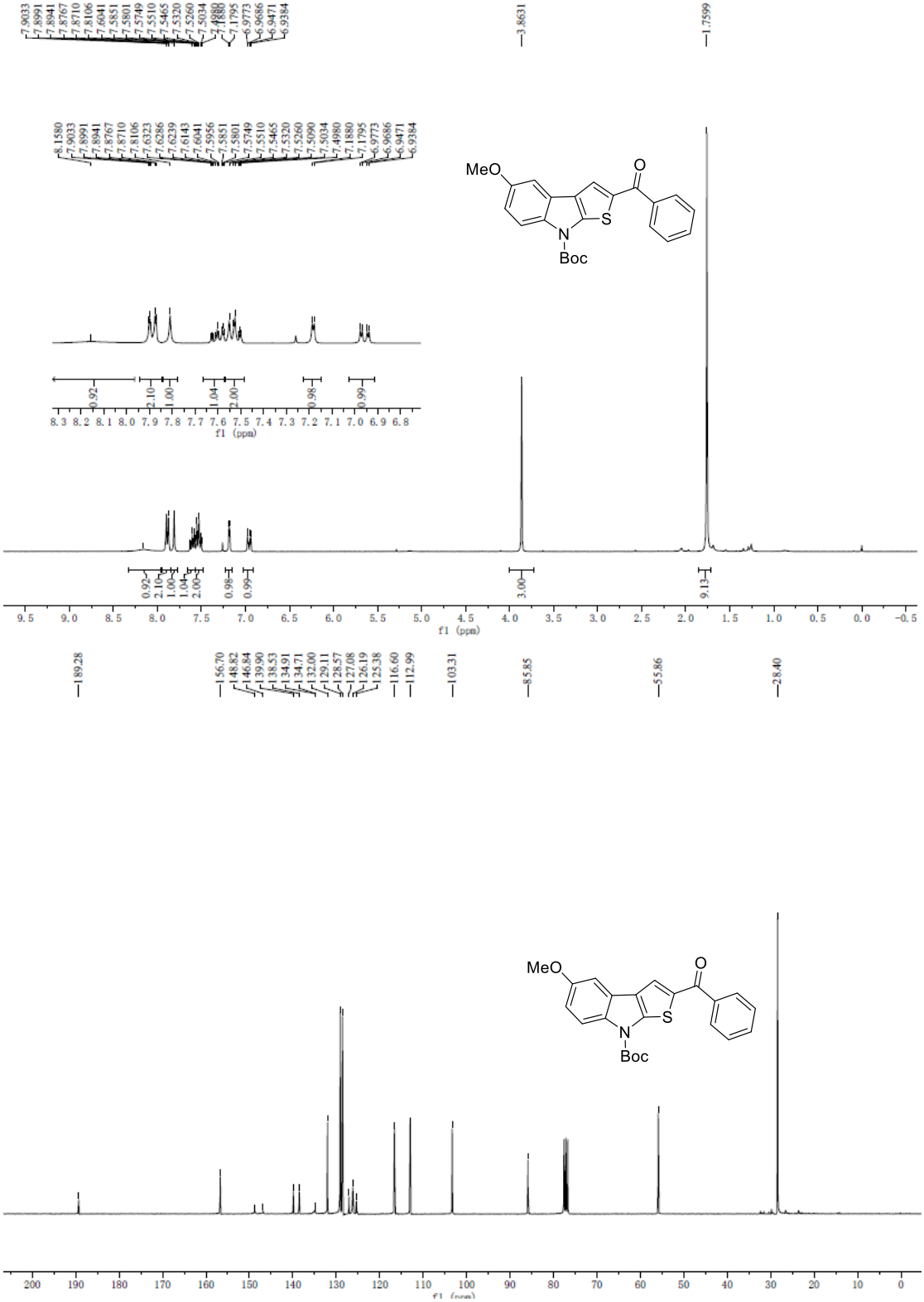
^{1}H and ^{13}C NMR of **3e**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



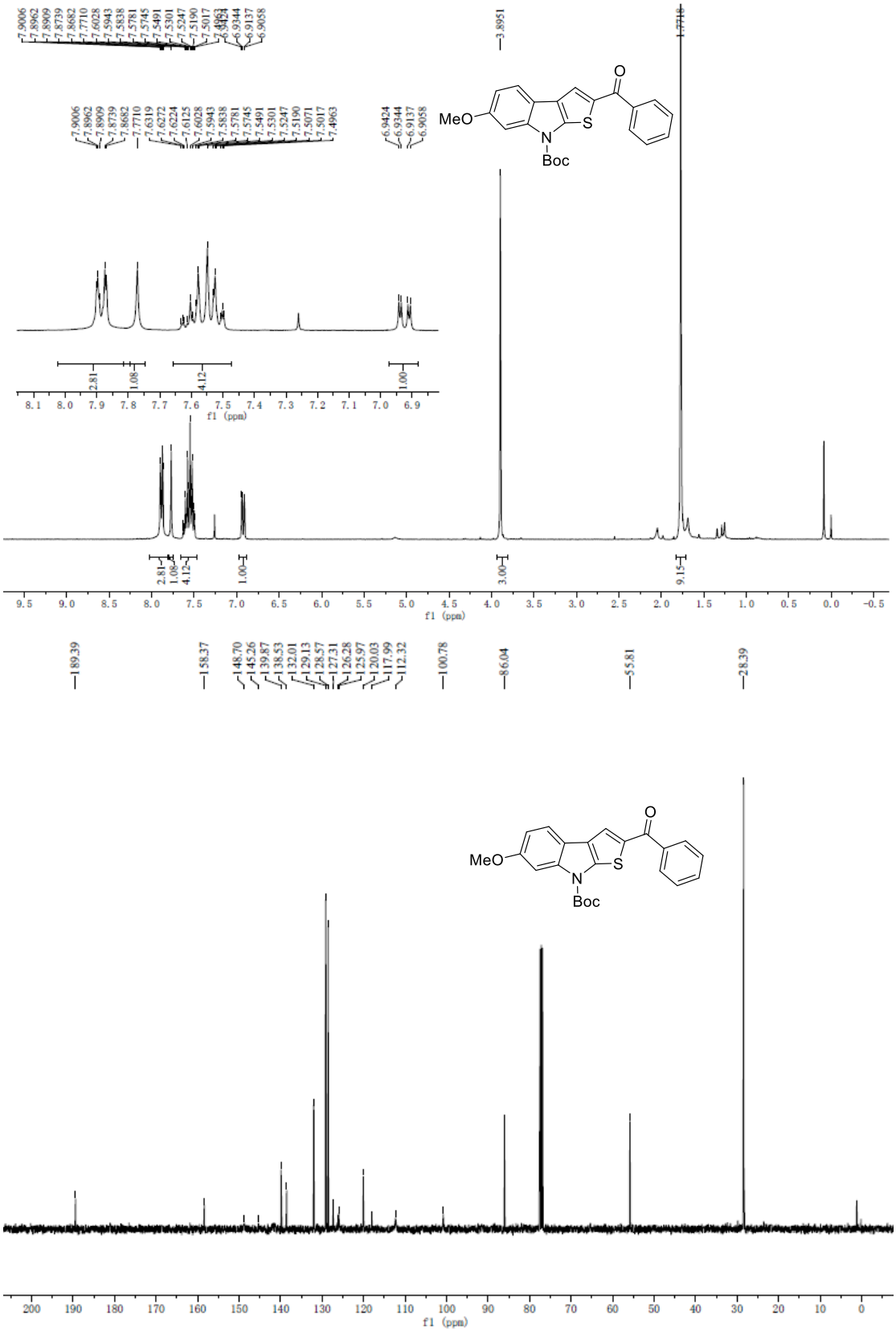
^{1}H and ^{13}C NMR of **3f**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



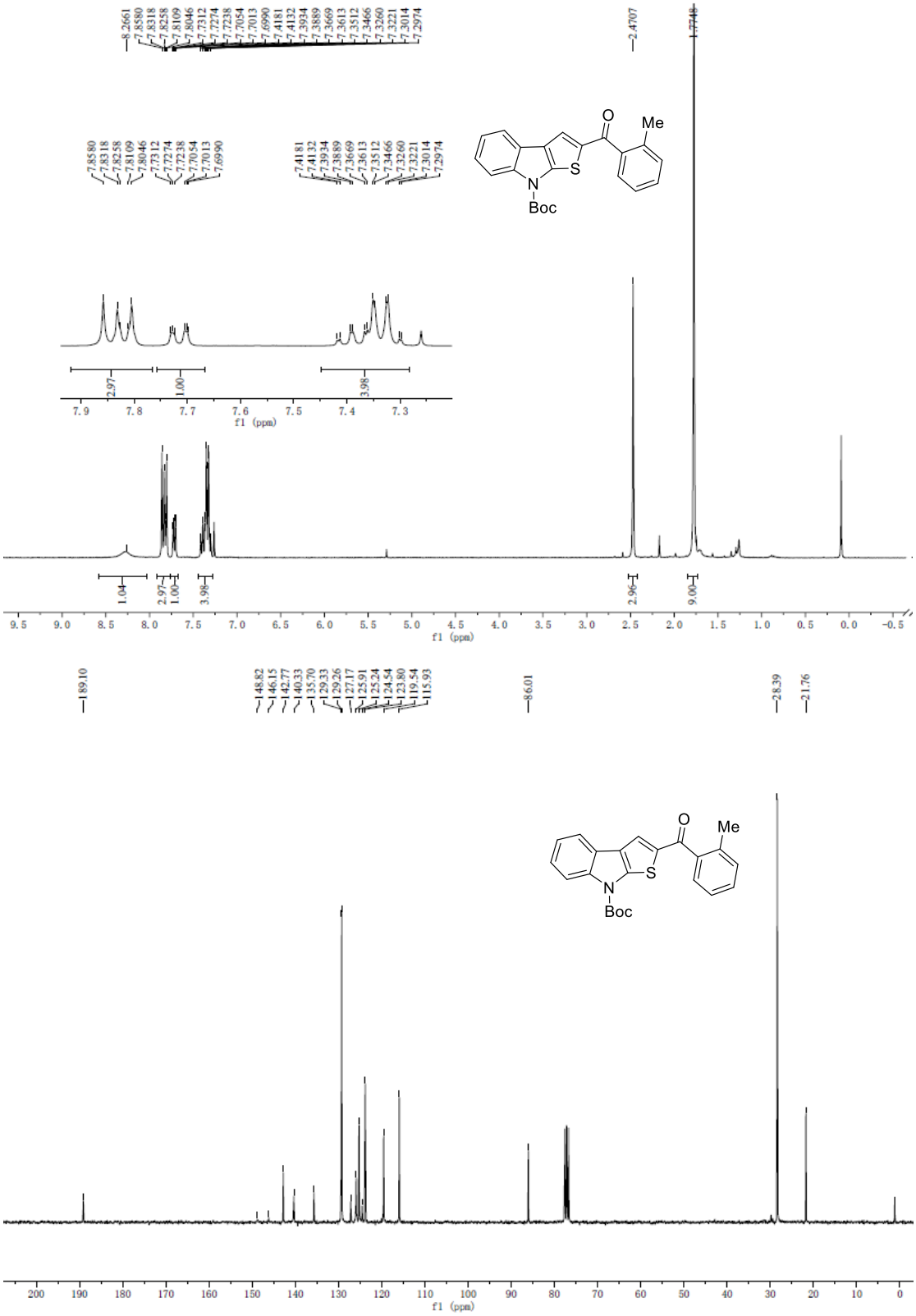
^{1}H and ^{13}C NMR of **3g**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



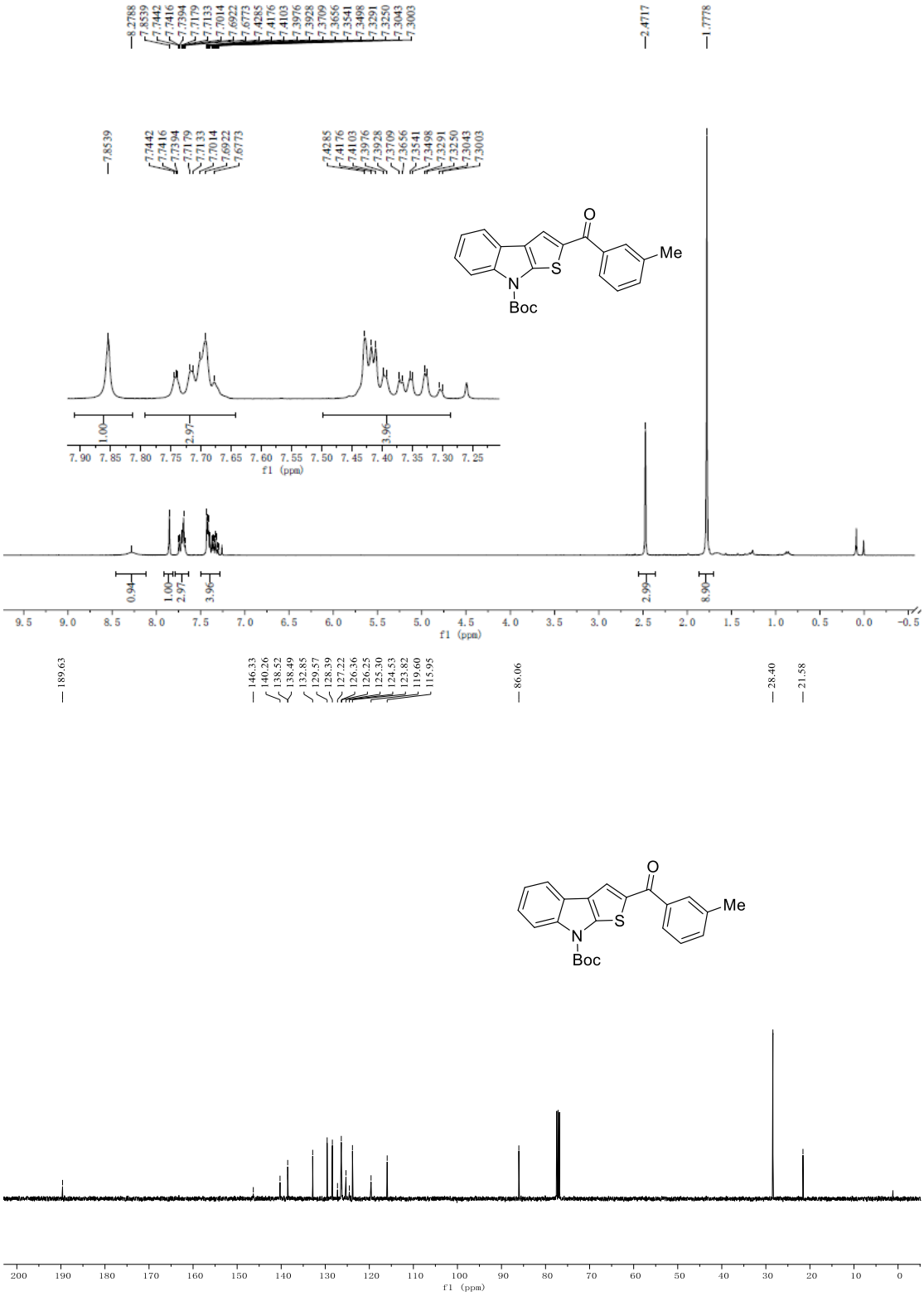
^{1}H and ^{13}C NMR of **3h**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



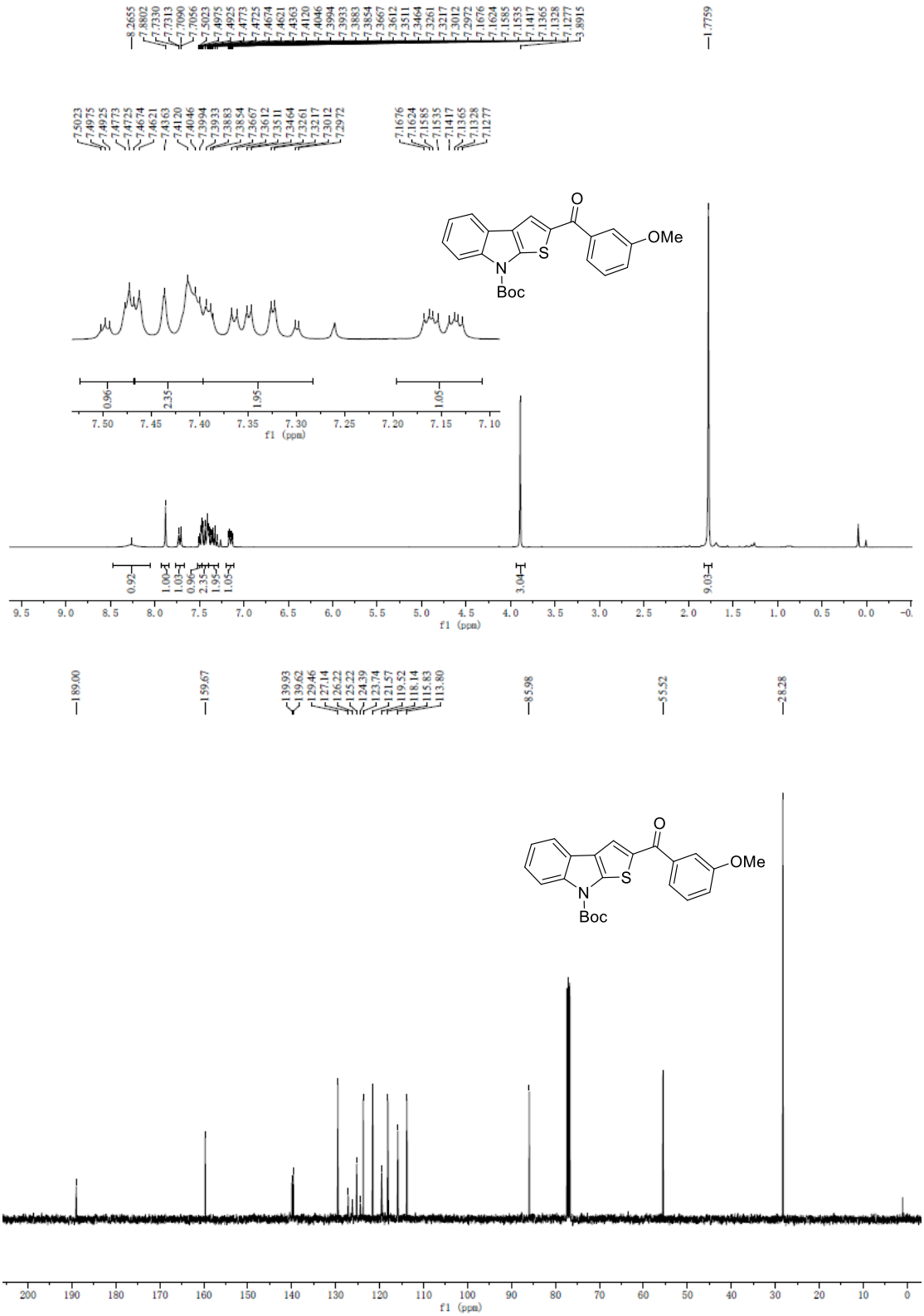
^{1}H and ^{13}C NMR of **3i**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



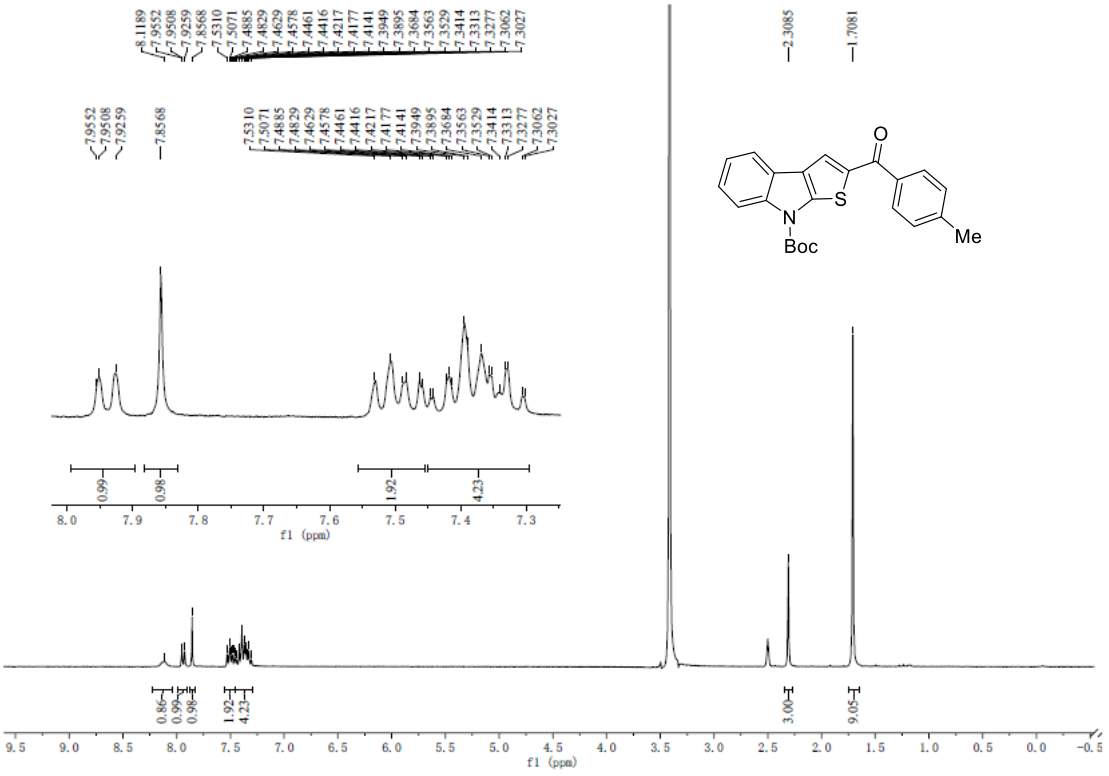
^{1}H and ^{13}C NMR of **3j**

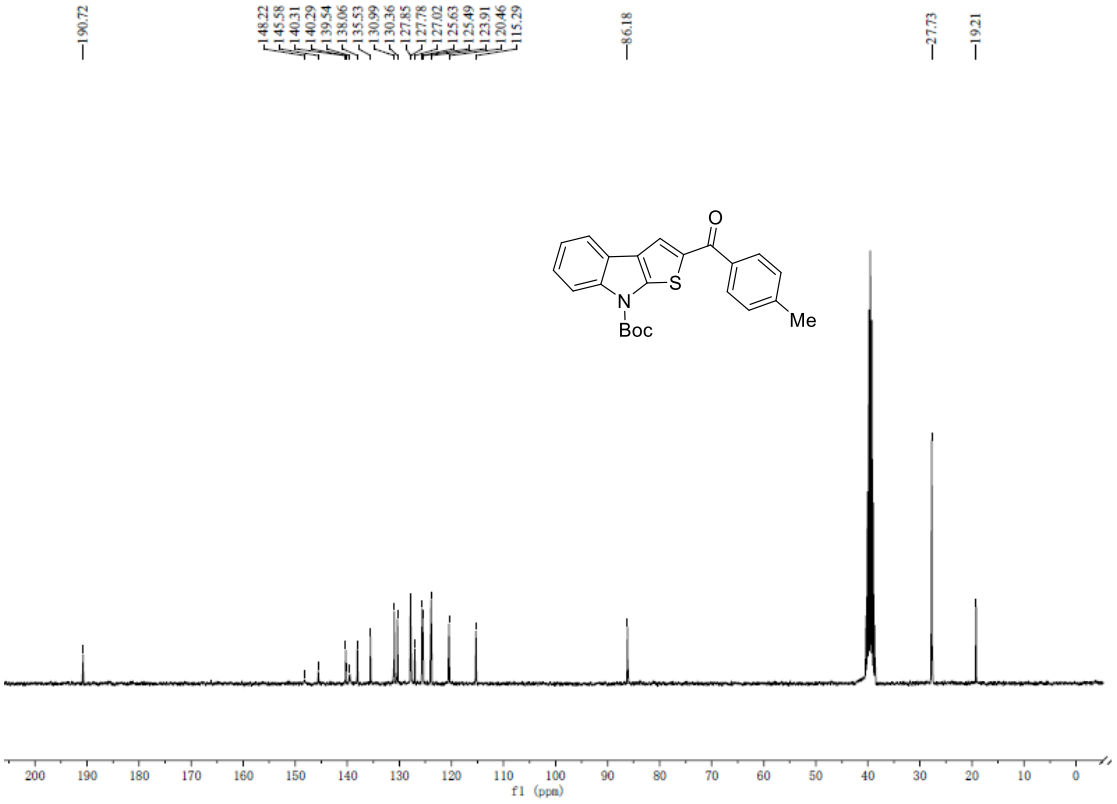
^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR of **3k**

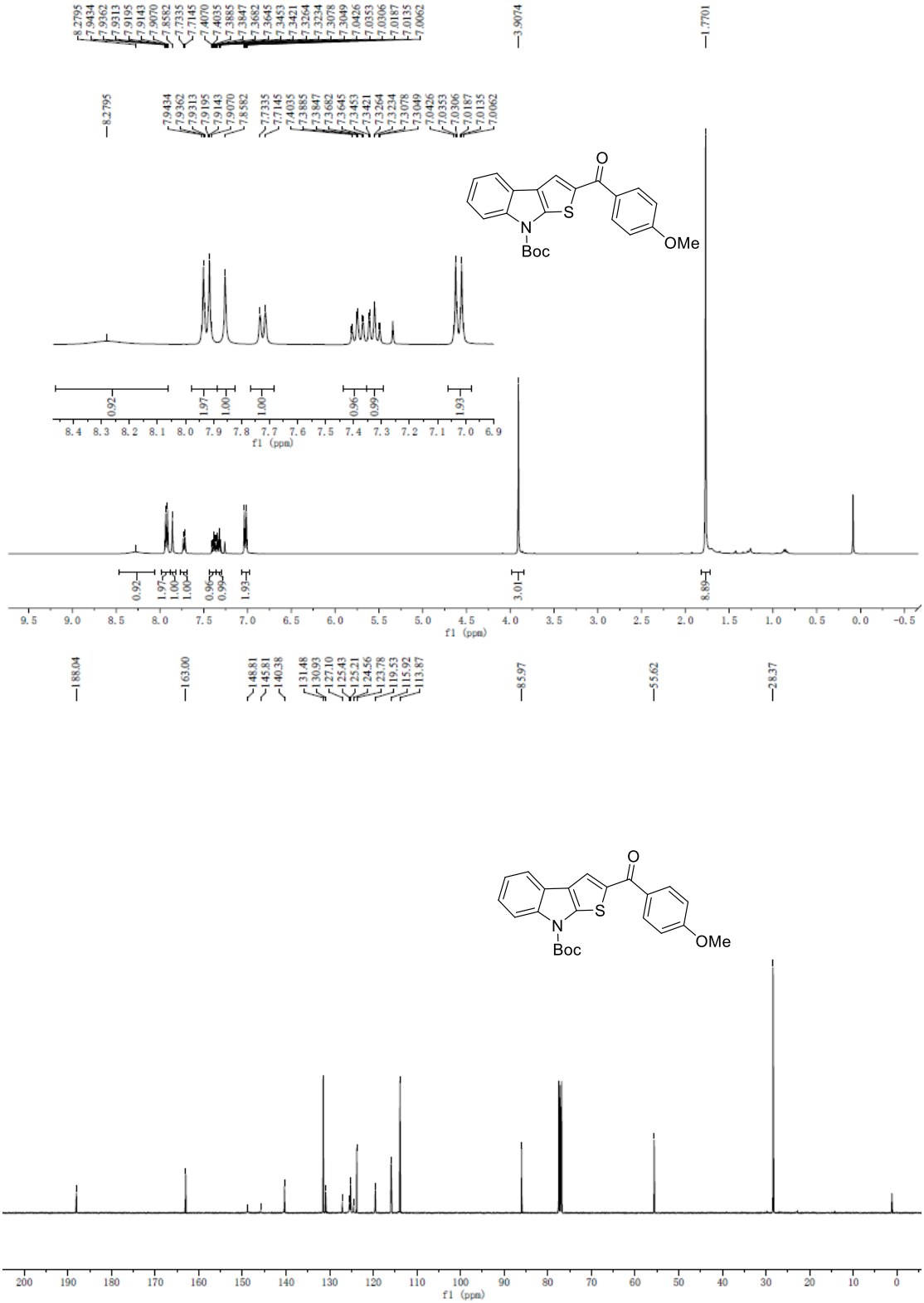
^{1}H NMR (300 MHz, DMSO-d$_6$), ^{13}C NMR (75 MHz, DMSO-d_6)





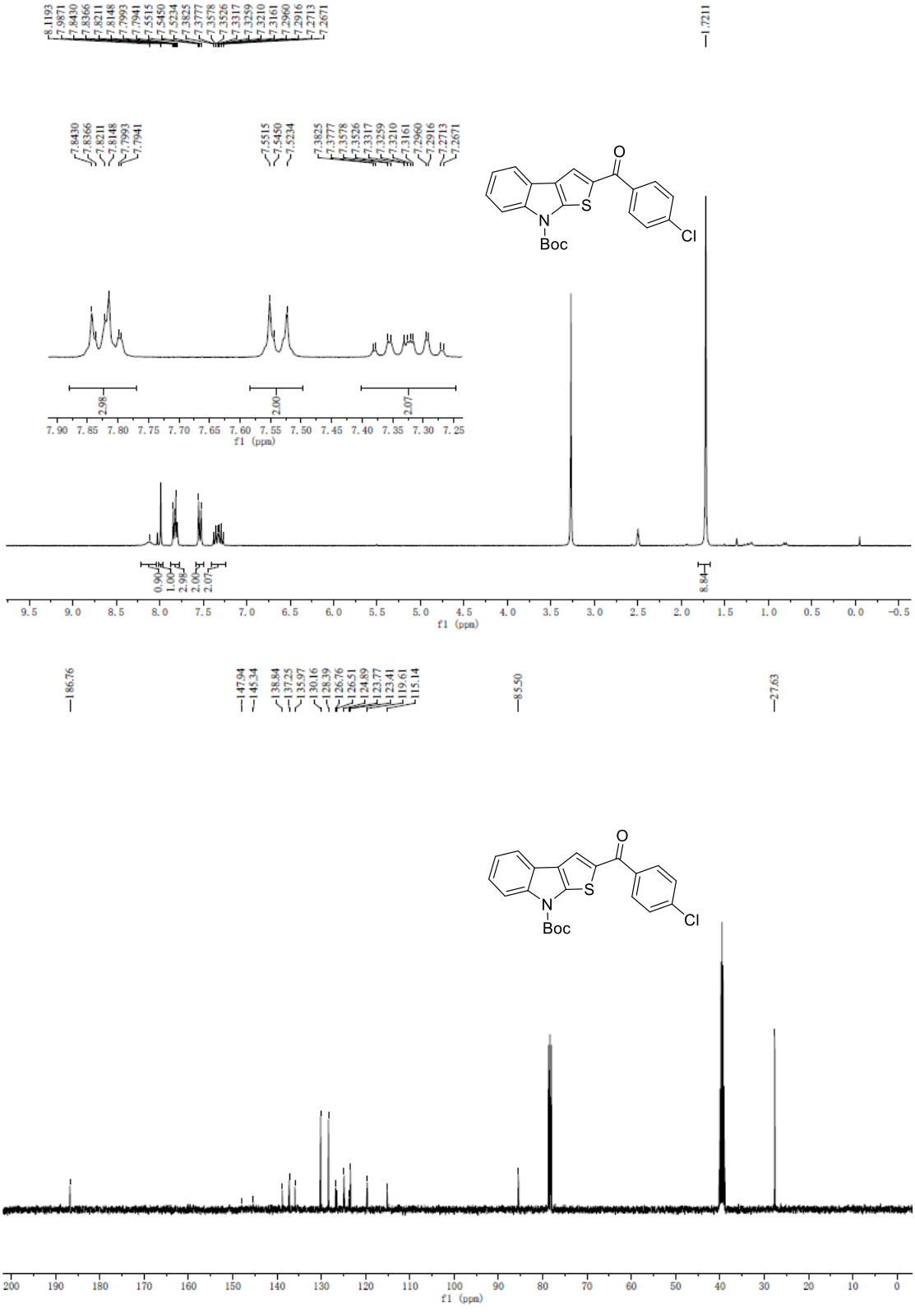
^{1}H and ^{13}C NMR of **3l**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



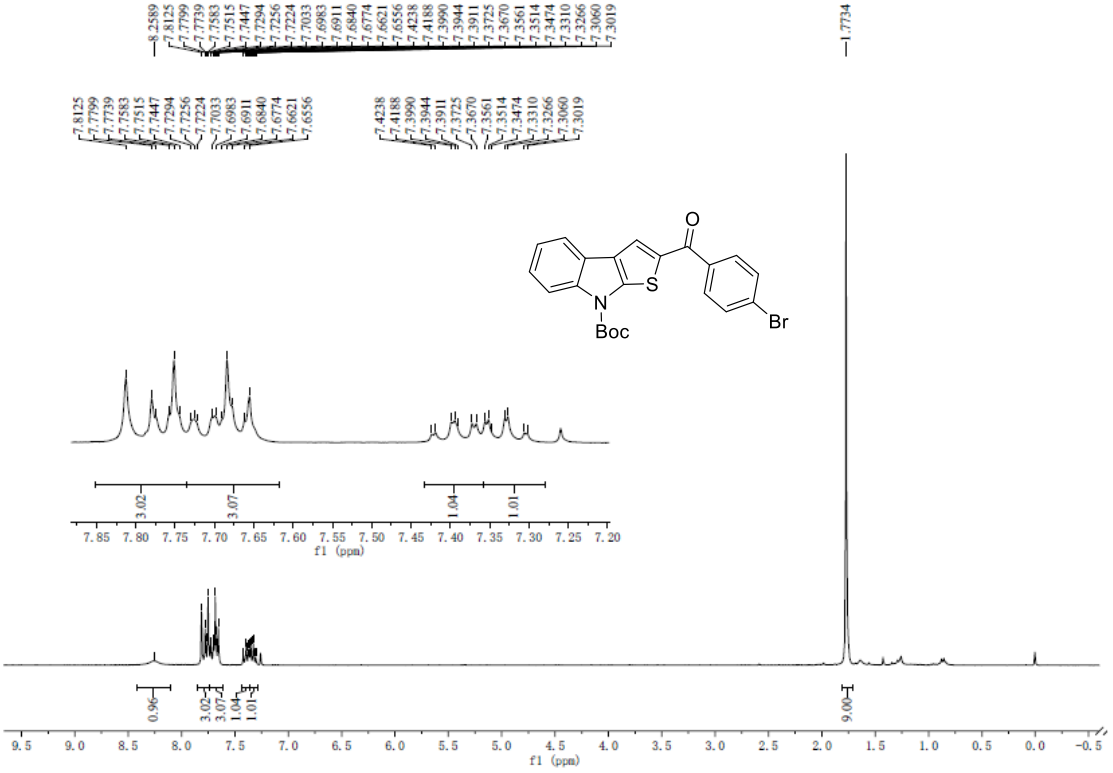
^{1}H and ^{13}C NMR of **3m**

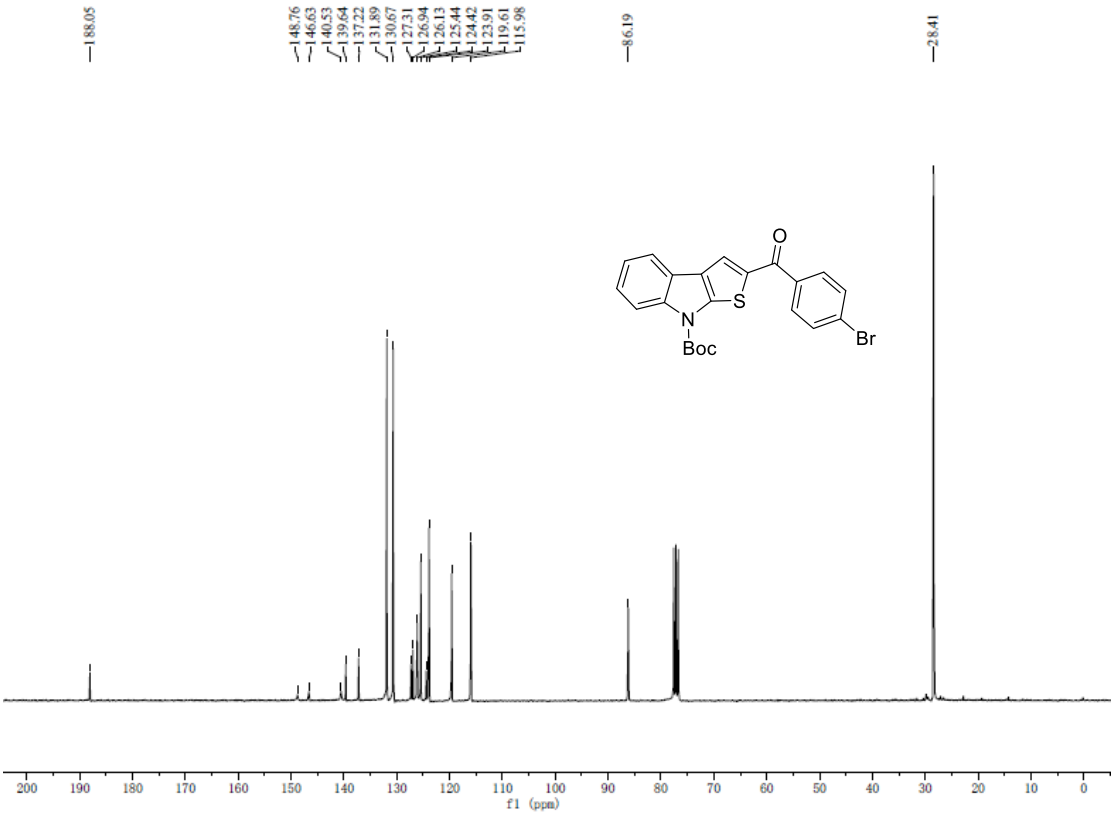
^{1}H NMR (300 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6)



^{1}H and ^{13}C NMR of **3n**

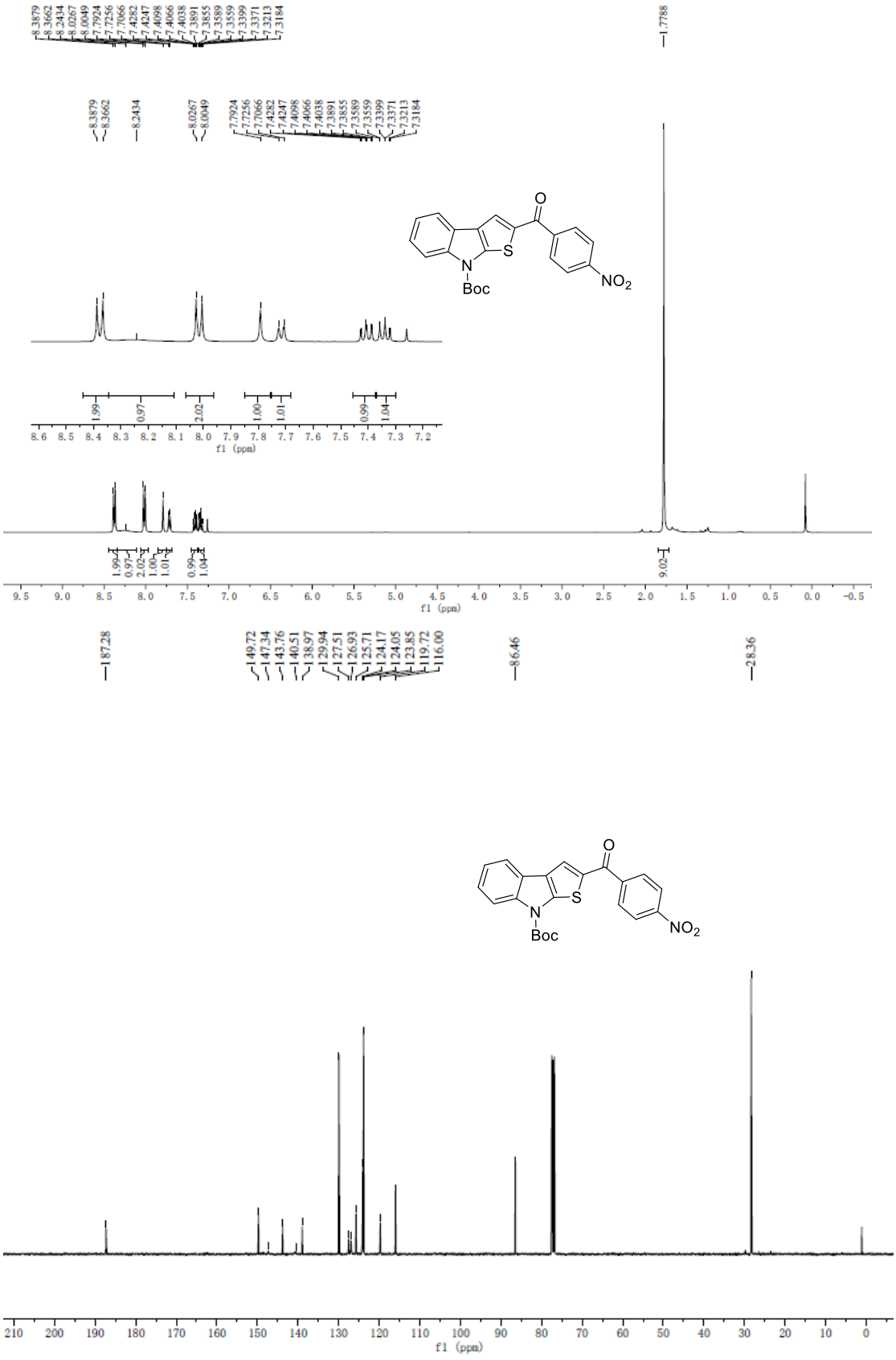
^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)





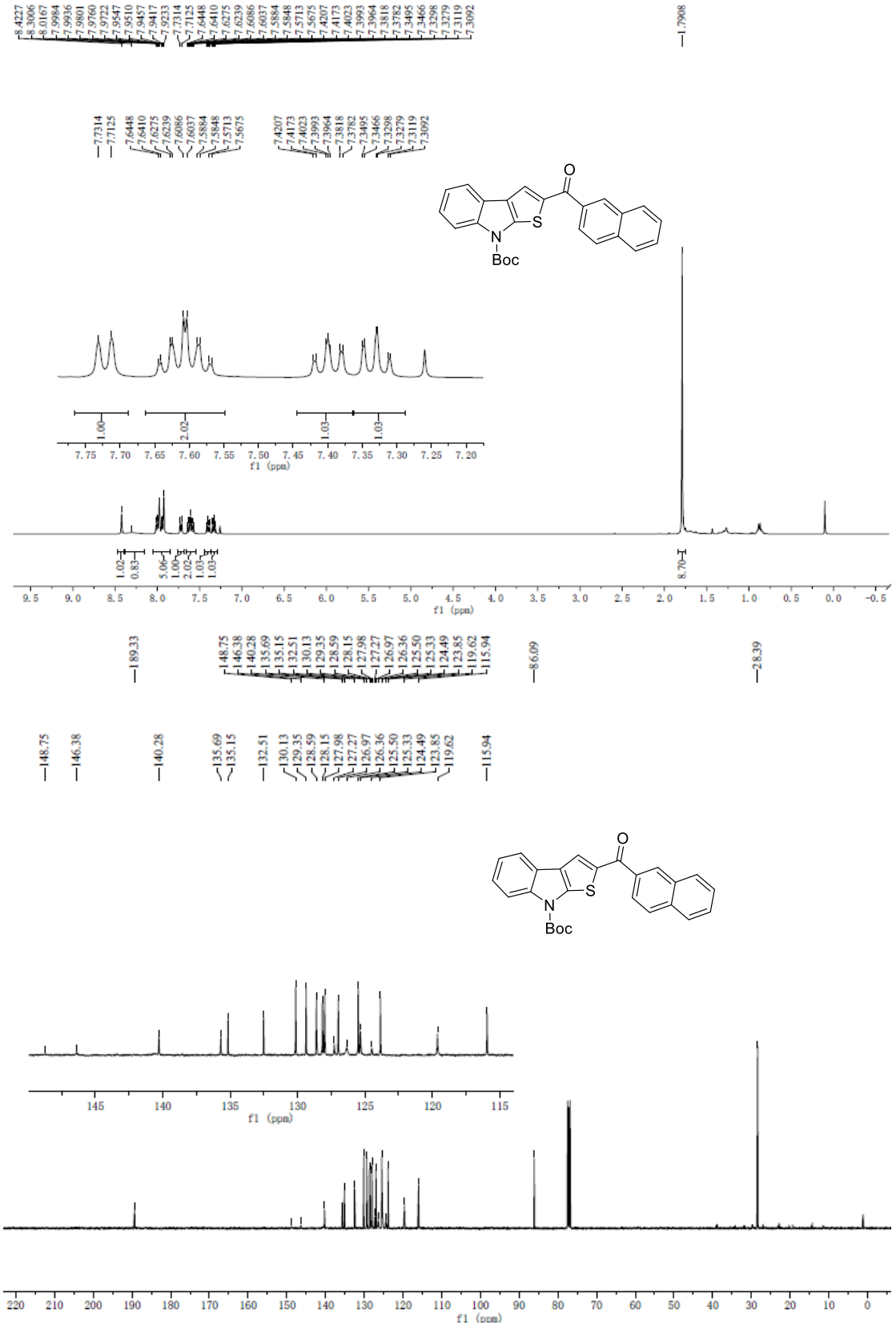
^{1}H and ^{13}C NMR of **3o**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



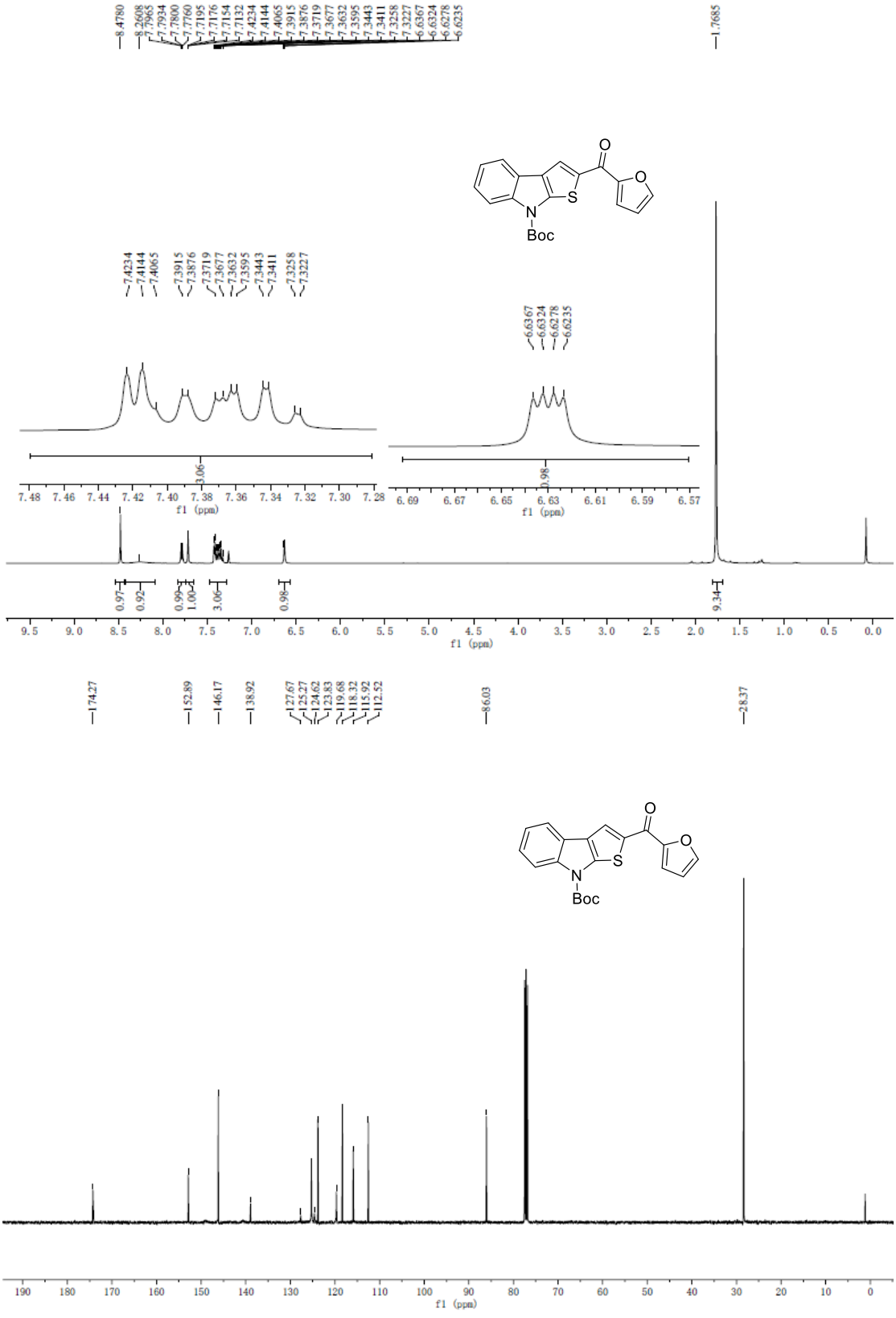
^{1}H and ^{13}C NMR of **3p**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



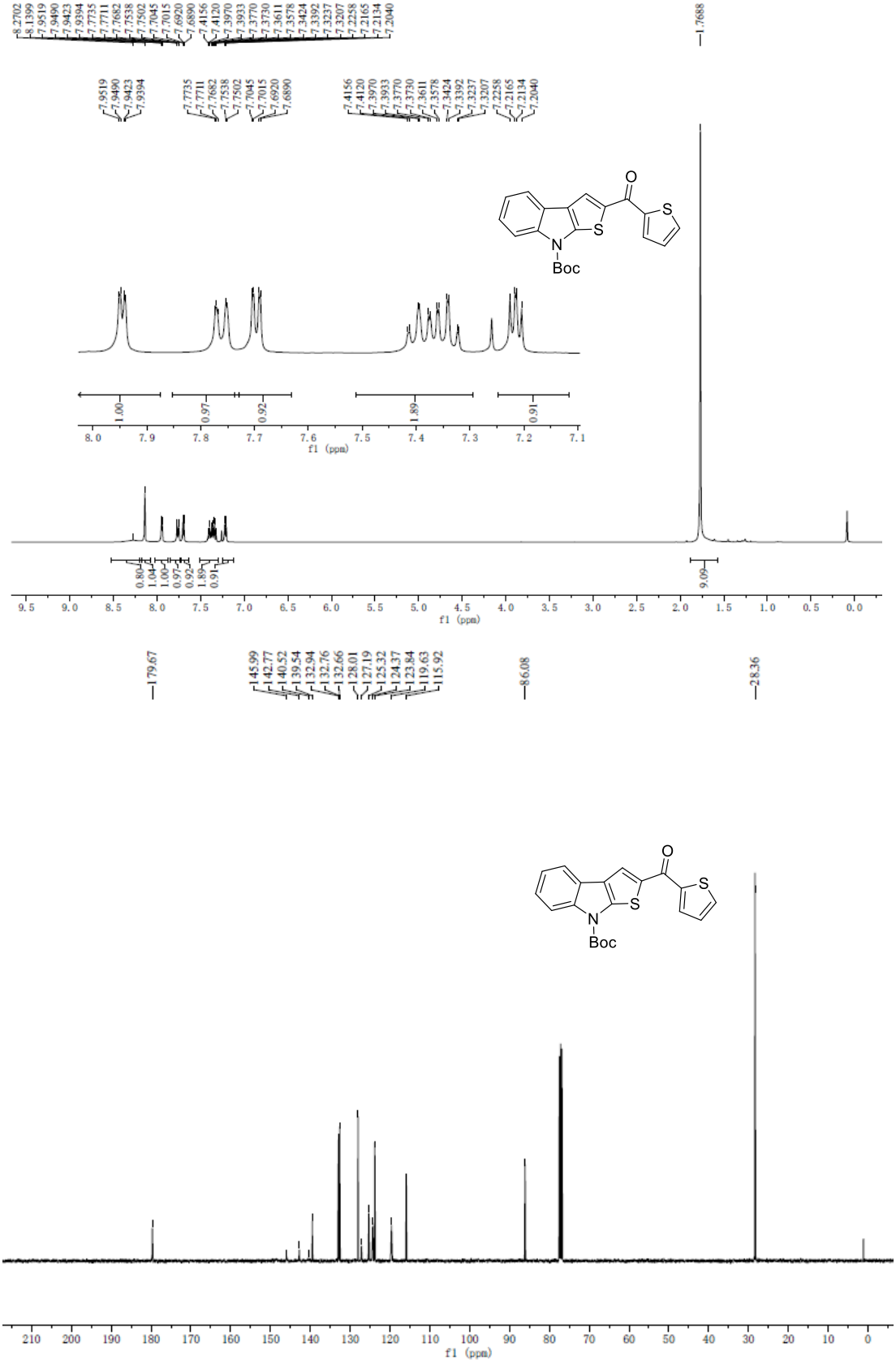
^{1}H and ^{13}C NMR of **3q**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



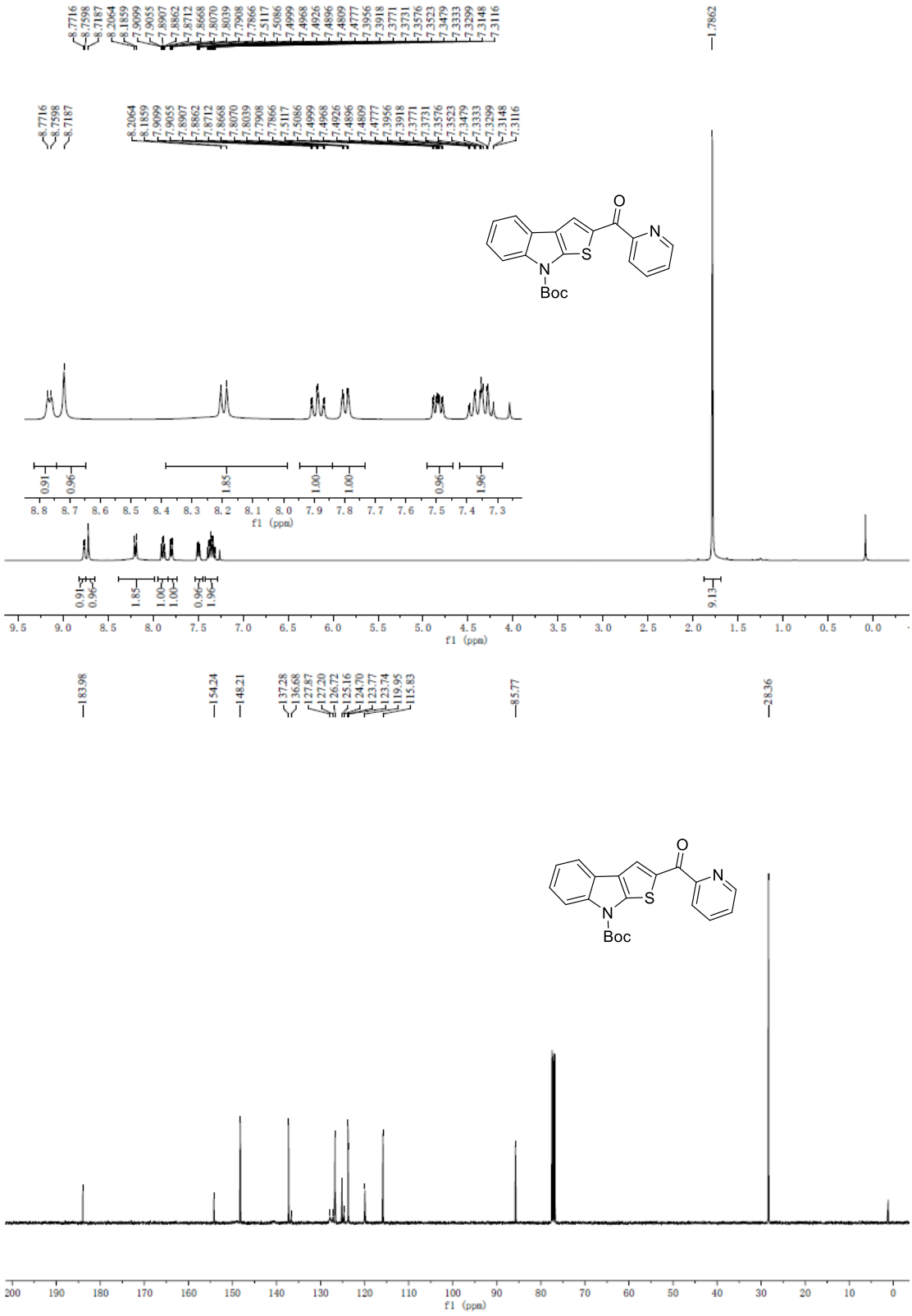
^{1}H and ^{13}C NMR of **3r**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



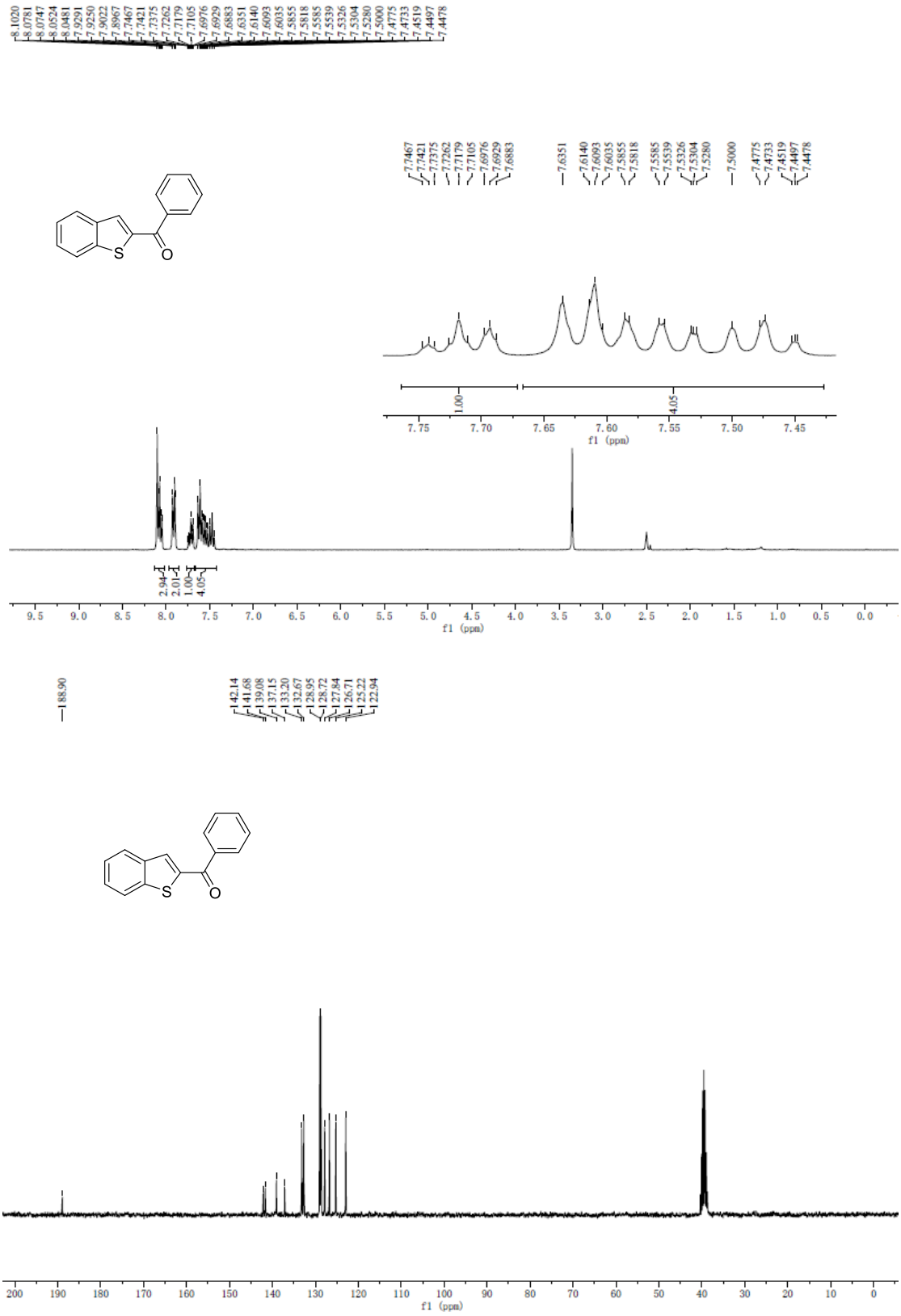
^{1}H and ^{13}C NMR of **3s**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



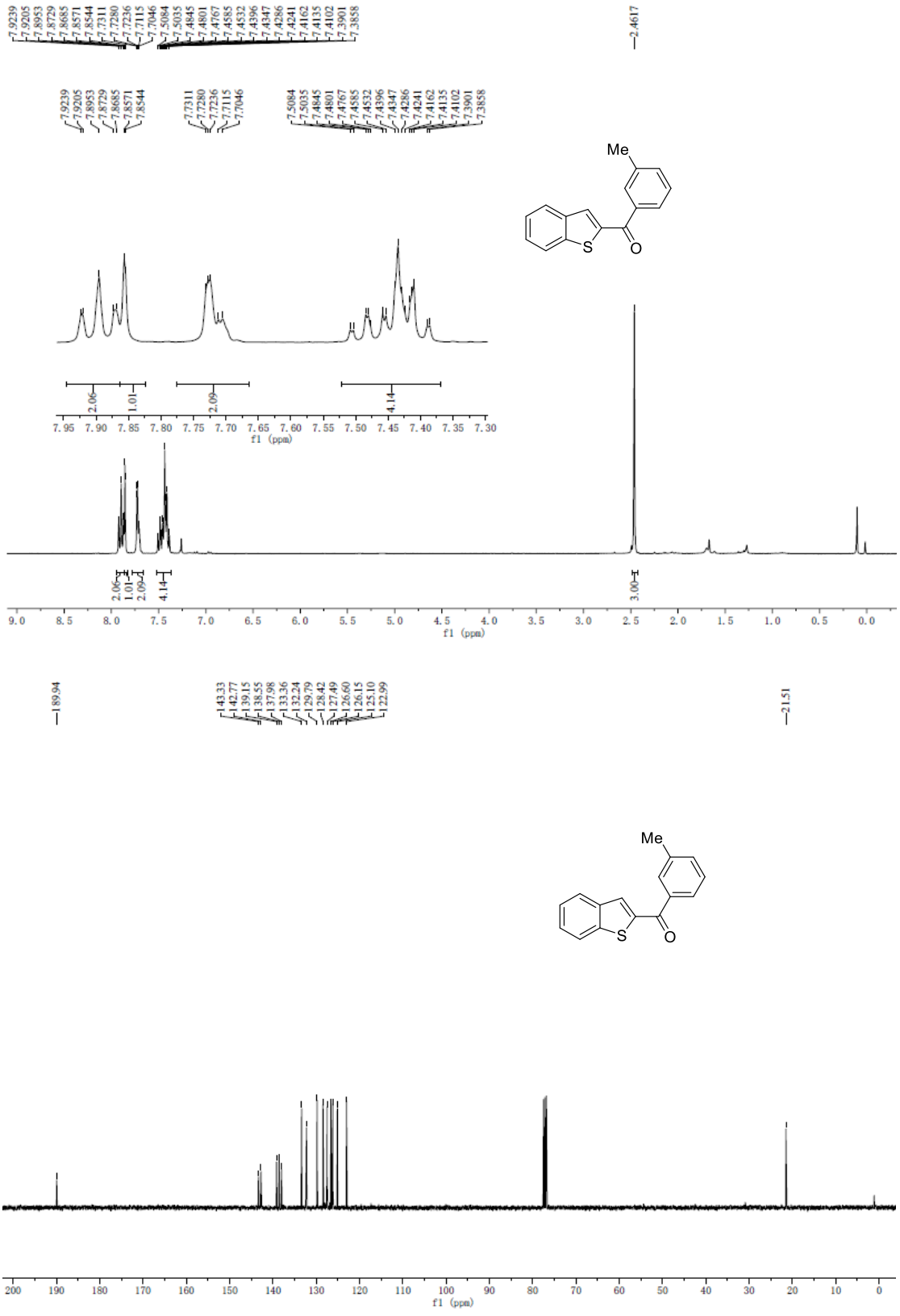
^{1}H and ^{13}C NMR of **5a**

^{1}H NMR (300 MHz, DMSO-d_6), ^{13}C NMR (75 MHz, DMSO-d_6)



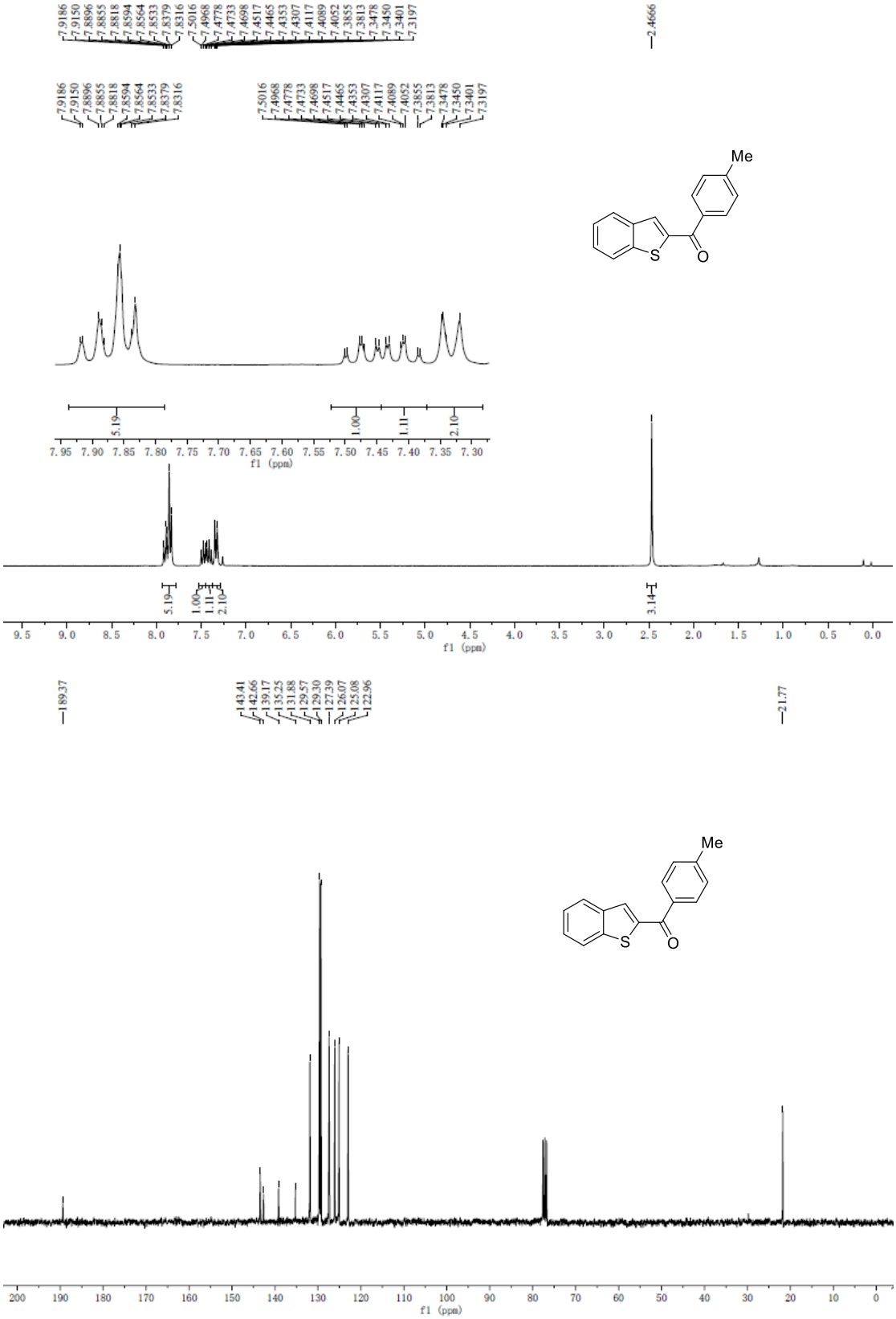
^{1}H and ^{13}C NMR of **5b**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



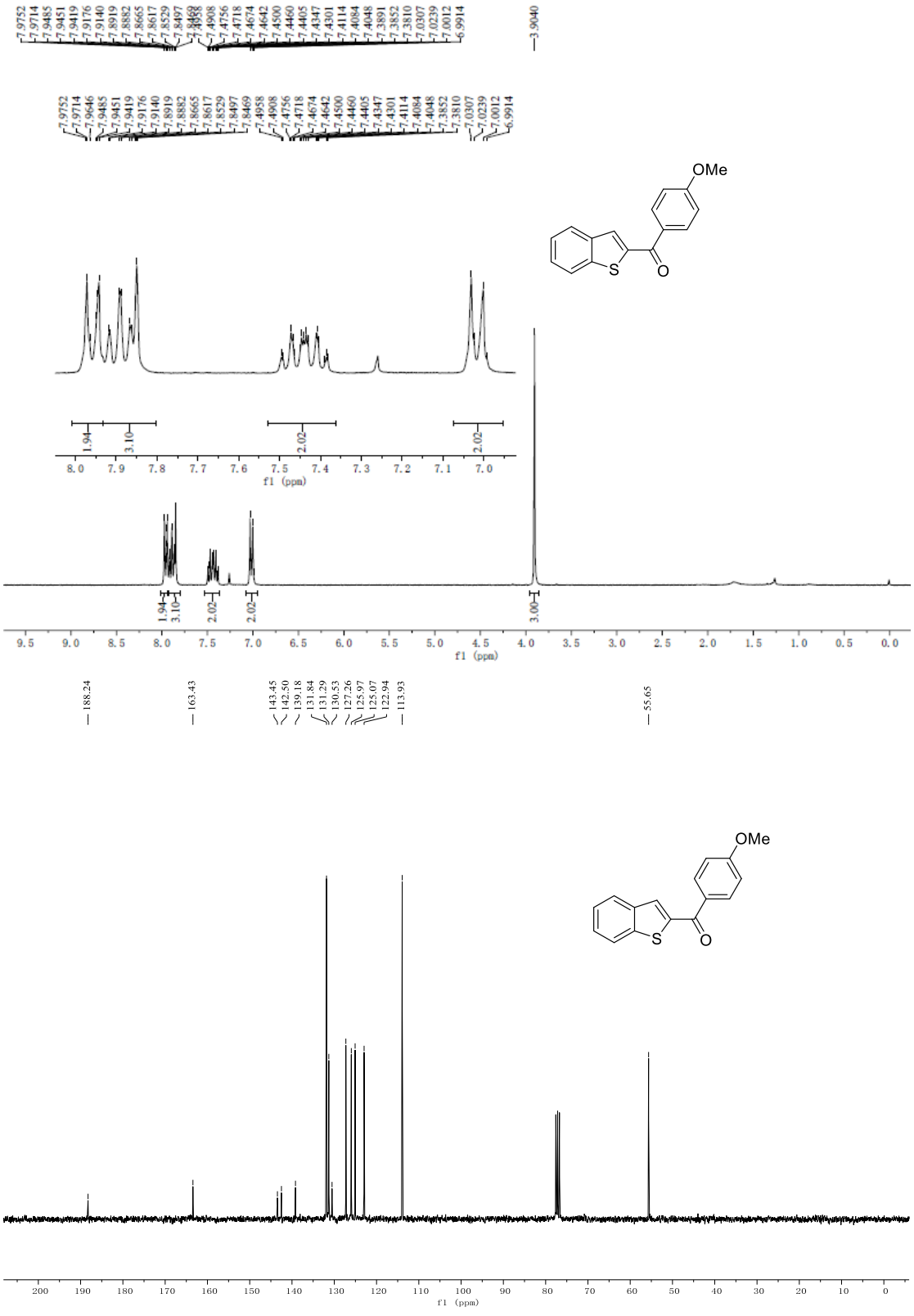
^{1}H and ^{13}C NMR of **5c**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



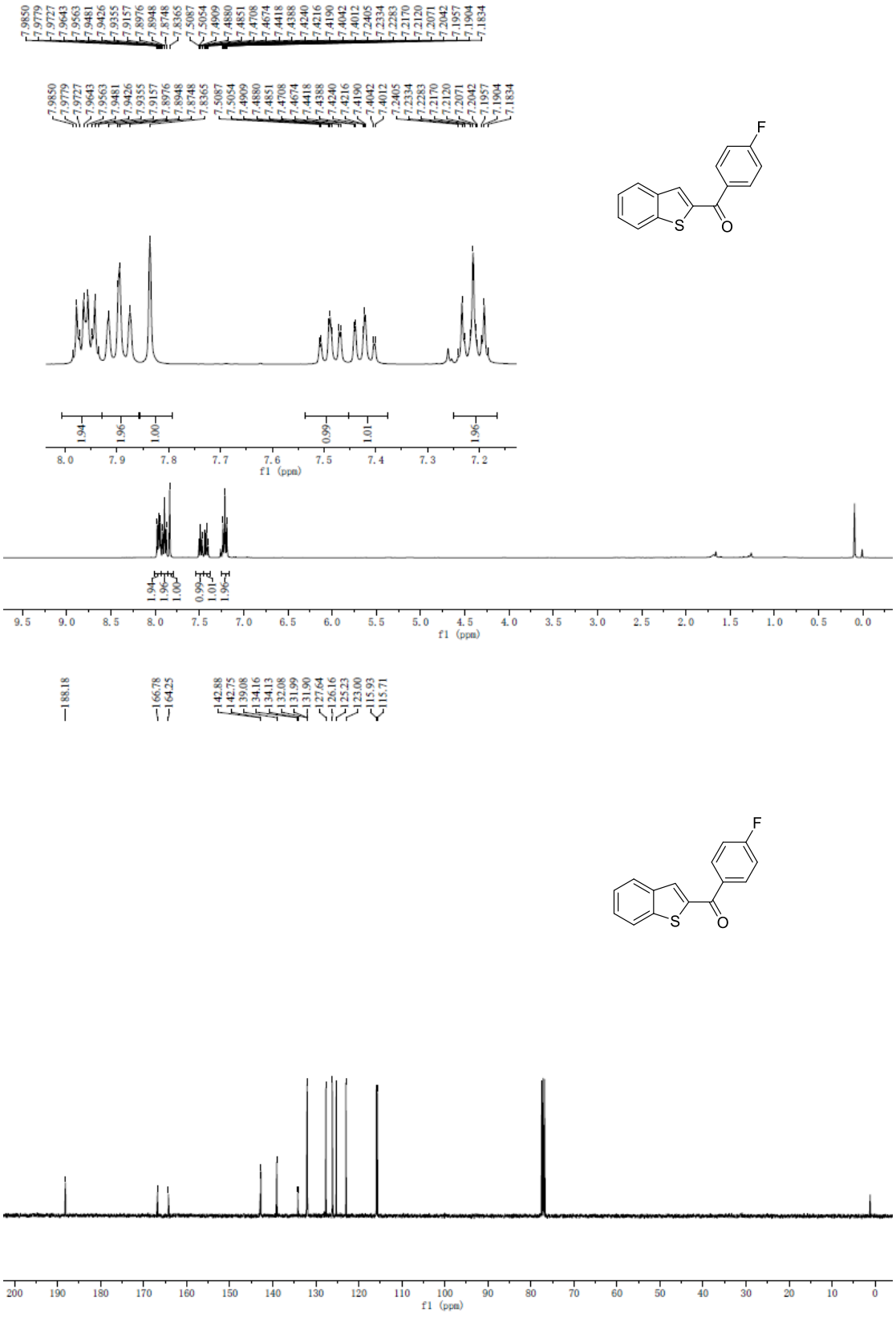
^{1}H and ^{13}C NMR of **5d**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



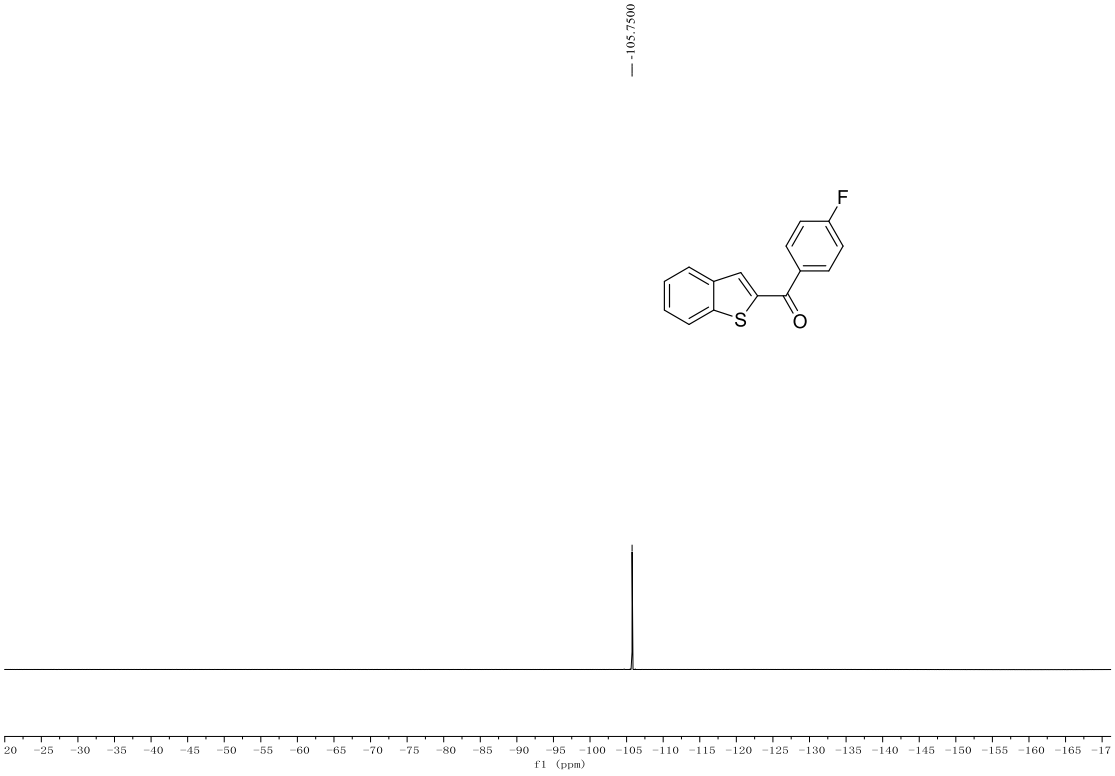
^{1}H and ^{13}C NMR of **5e**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



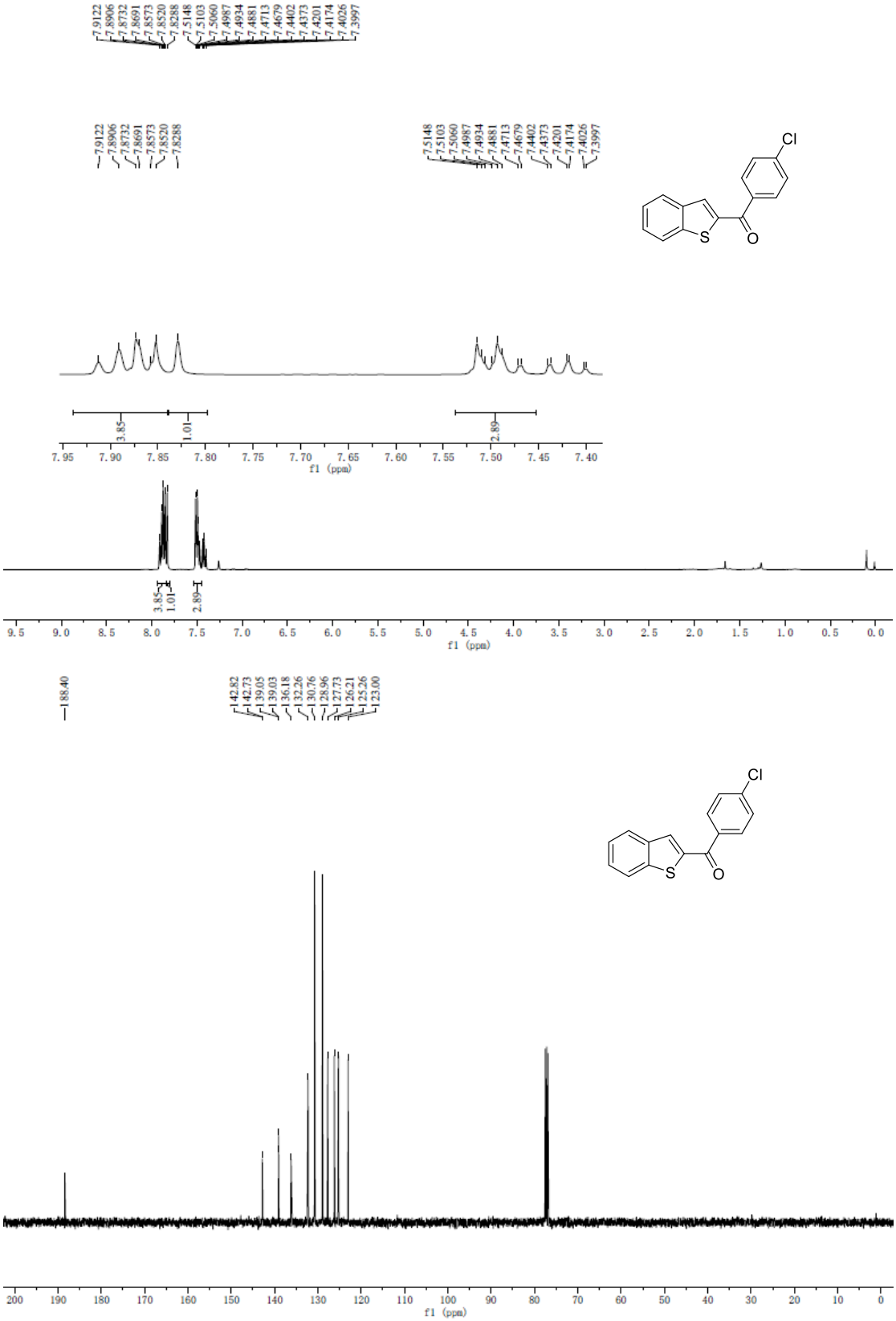
^{19}F NMR of **5e**

(376 MHz, $CDCl_3$)



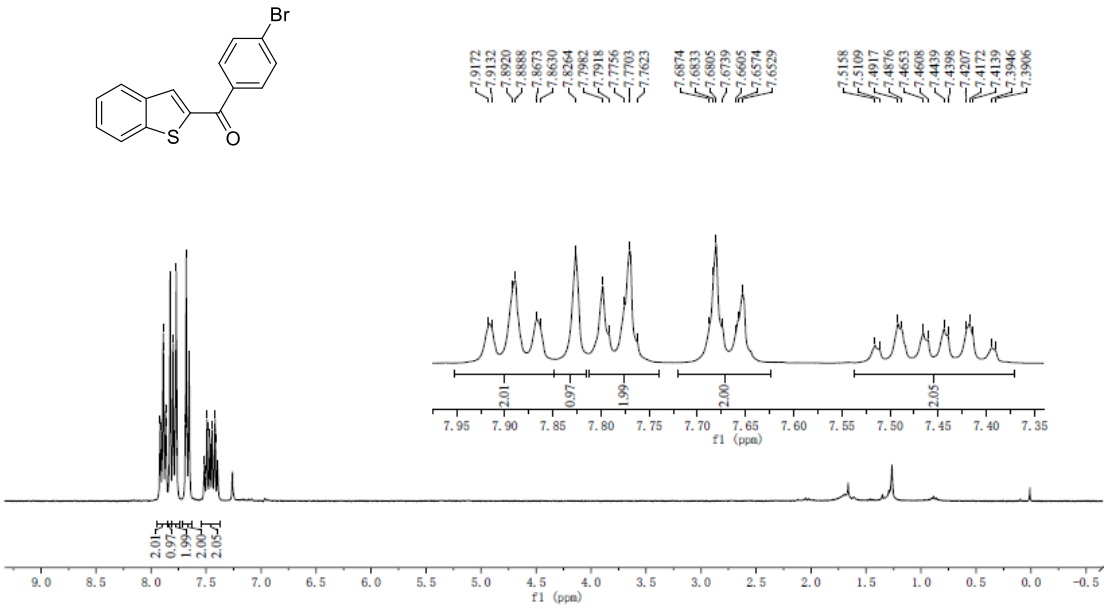
^{1}H and ^{13}C NMR of **5f**

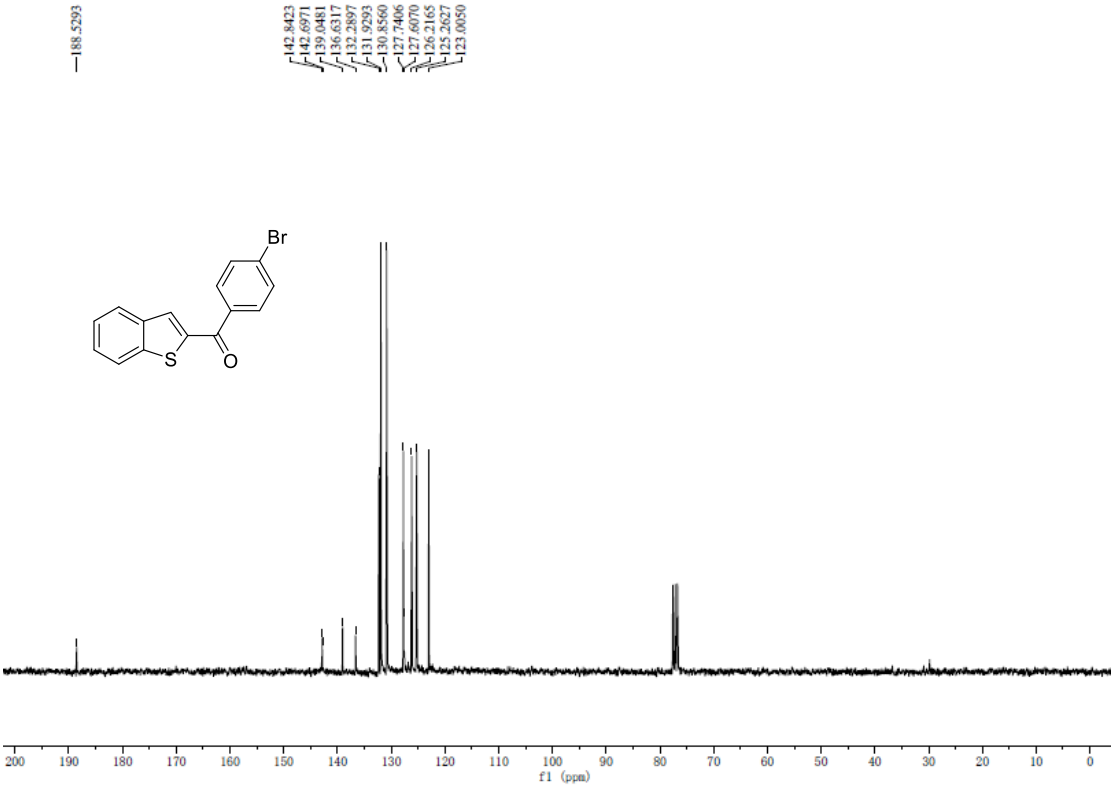
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR of **5g**

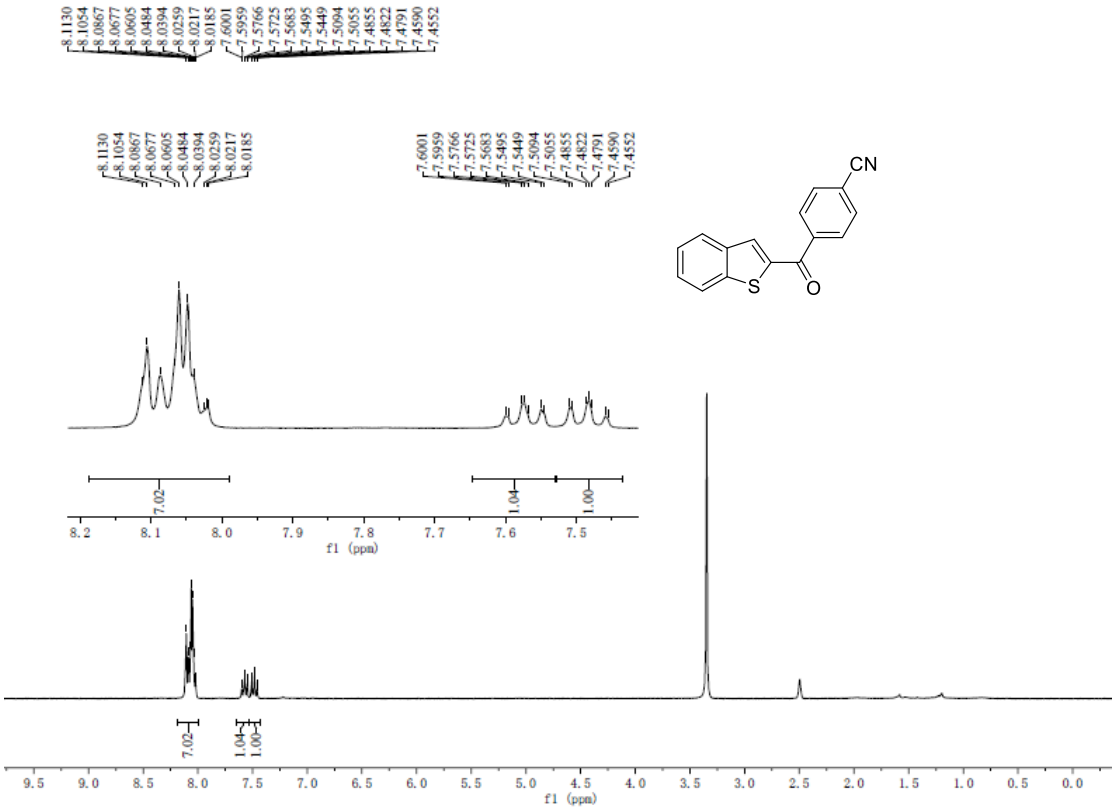
^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)

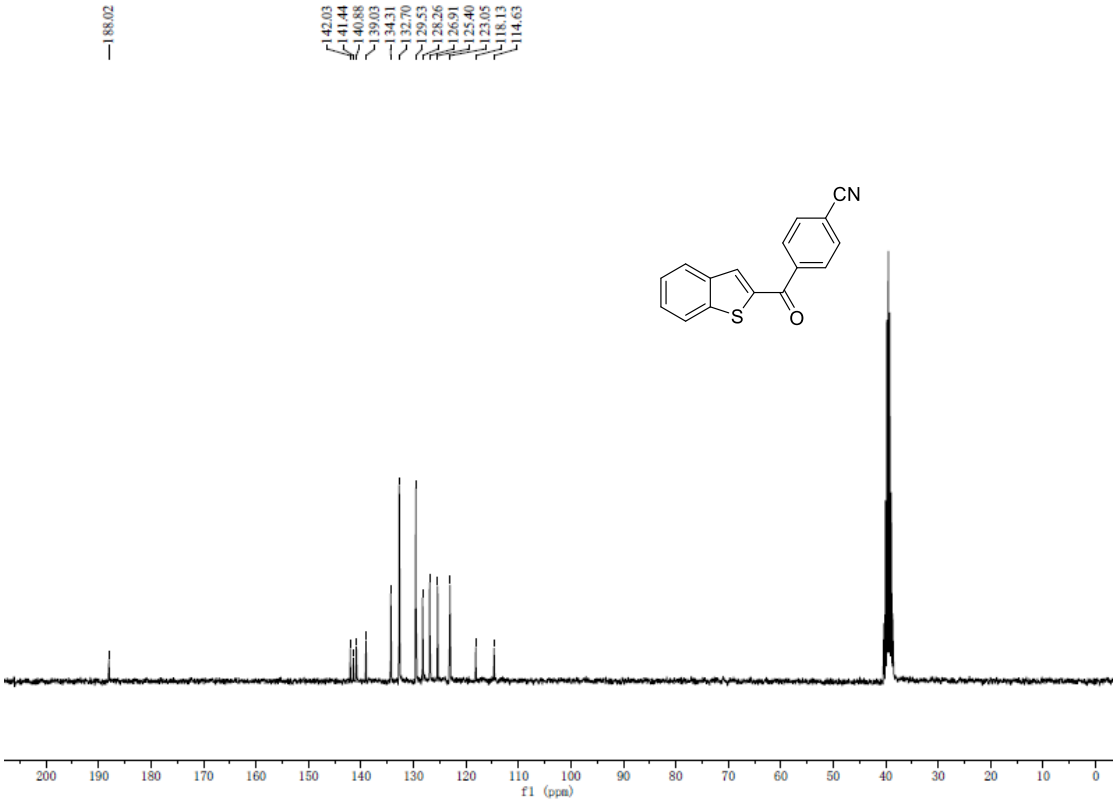




^{1}H and ^{13}C NMR of **5h**

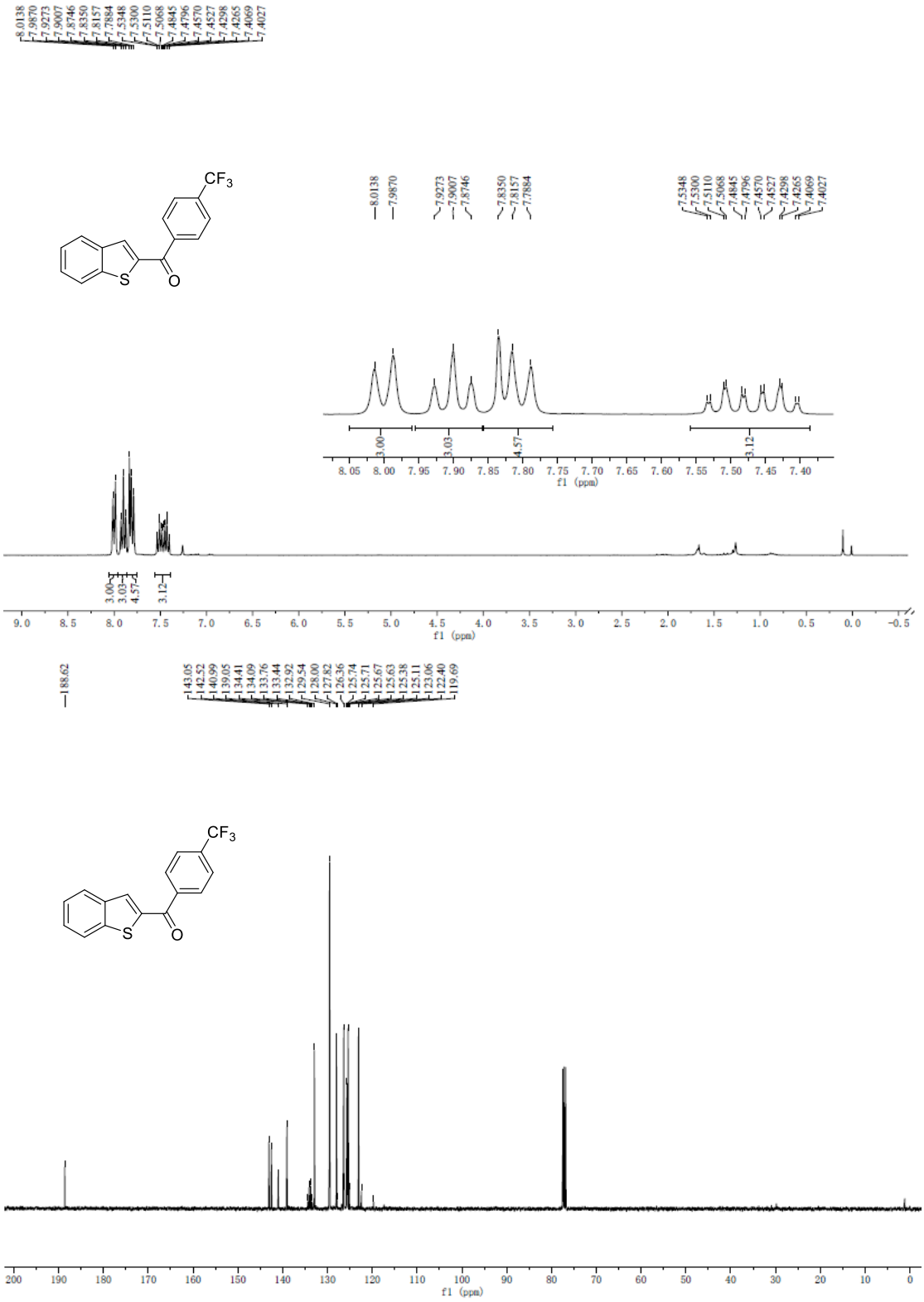
^{1}H NMR (300 MHz, DMSO-d_6), ^{13}C NMR (75 MHz, DMSO-d_6)





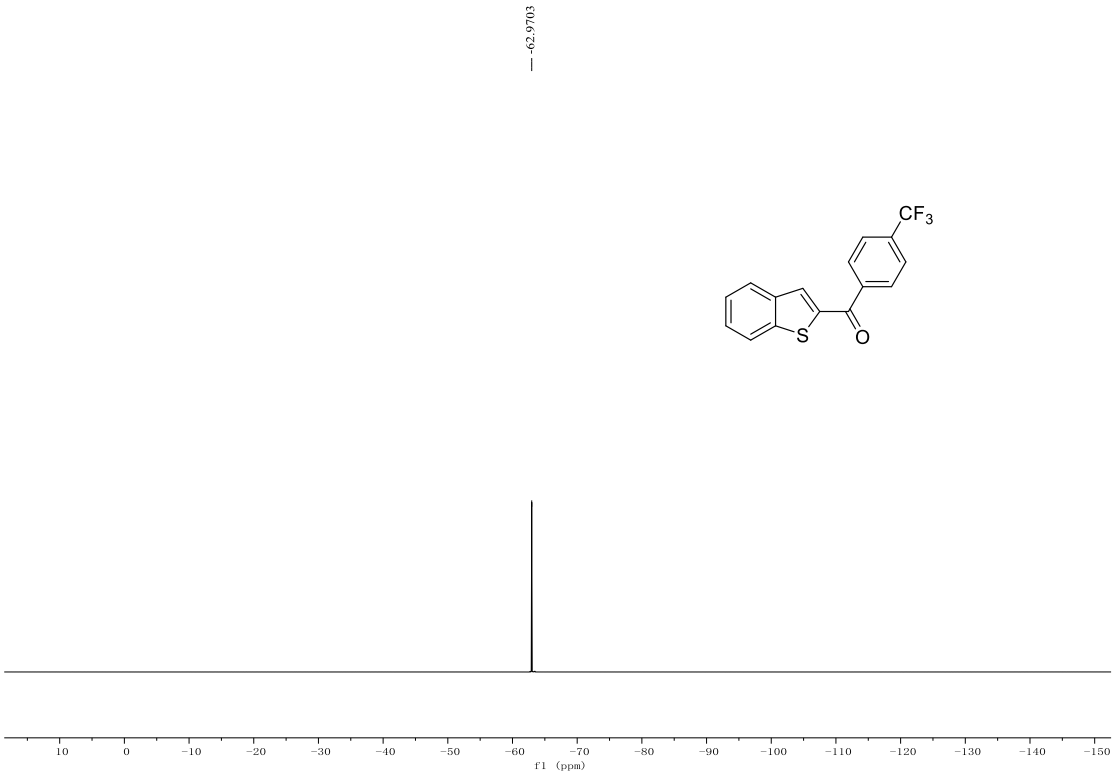
^{1}H and ^{13}C NMR of **5i**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



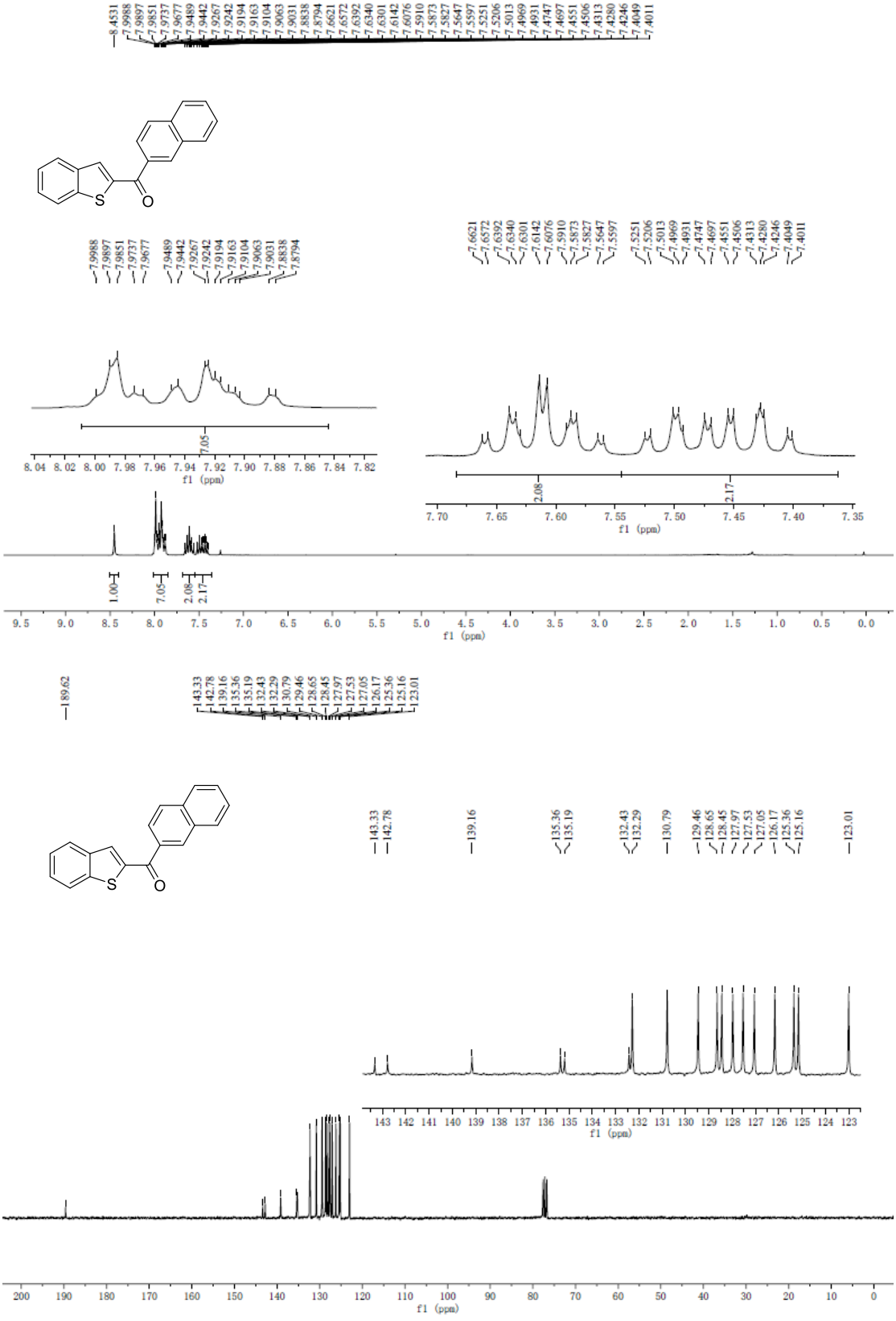
^{19}F NMR of **5i**

(376 MHz, $CDCl_3$)



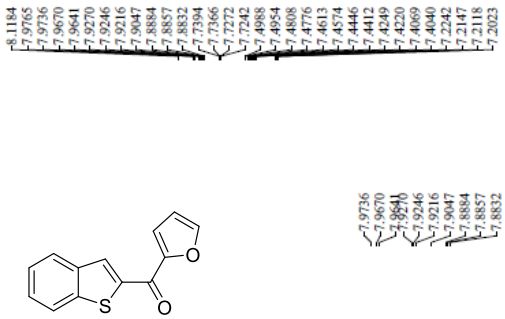
^{1}H and ^{13}C NMR of **5j**

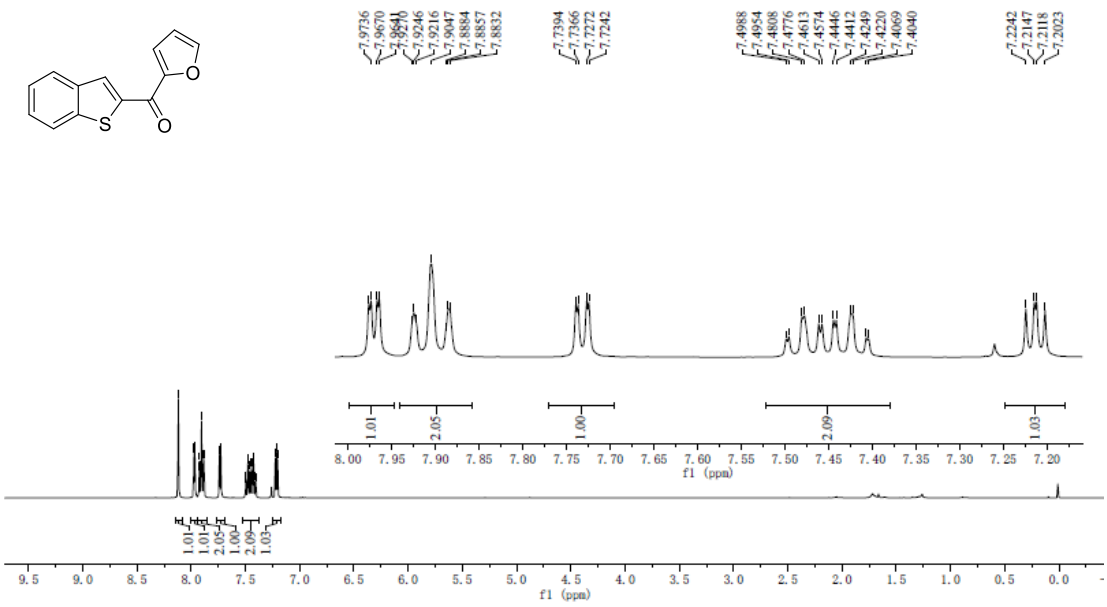
^{1}H NMR (300 MHz, $CDCl_3$), ^{1}H NMR (75 MHz, $CDCl_3$)

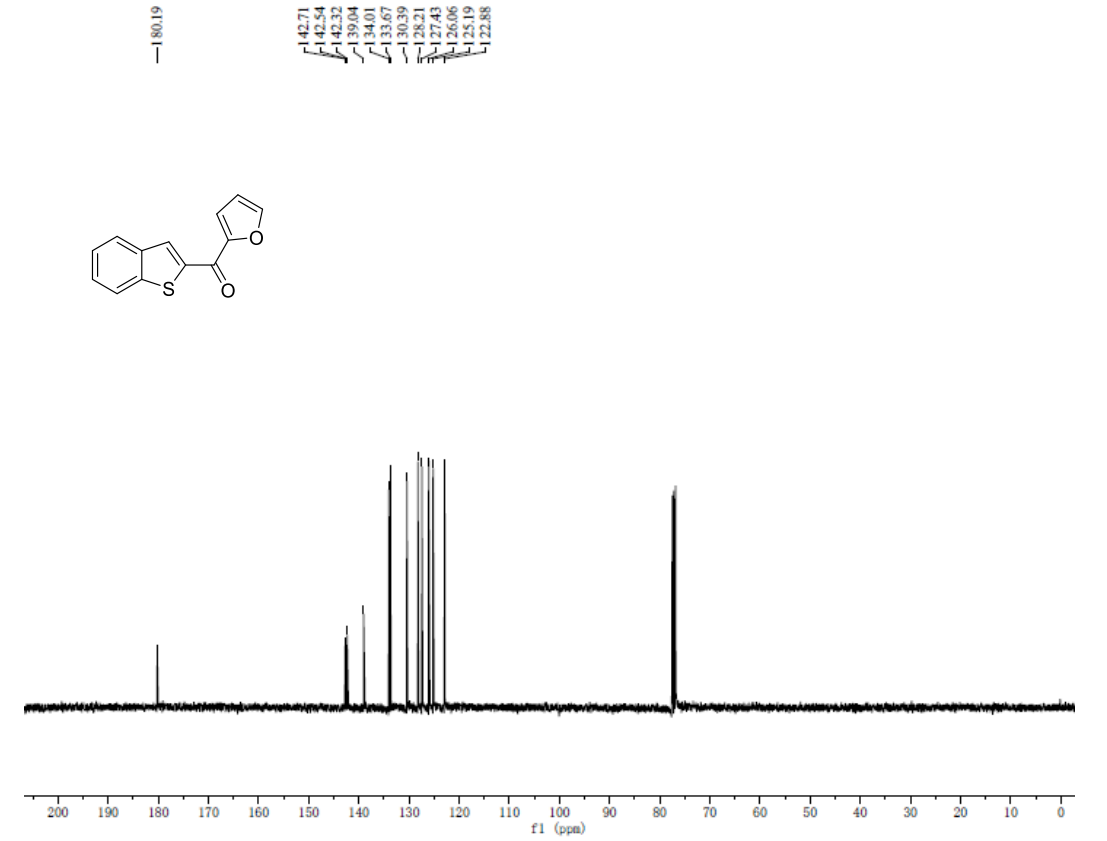


^{1}H and ^{13}C NMR of **5k**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)

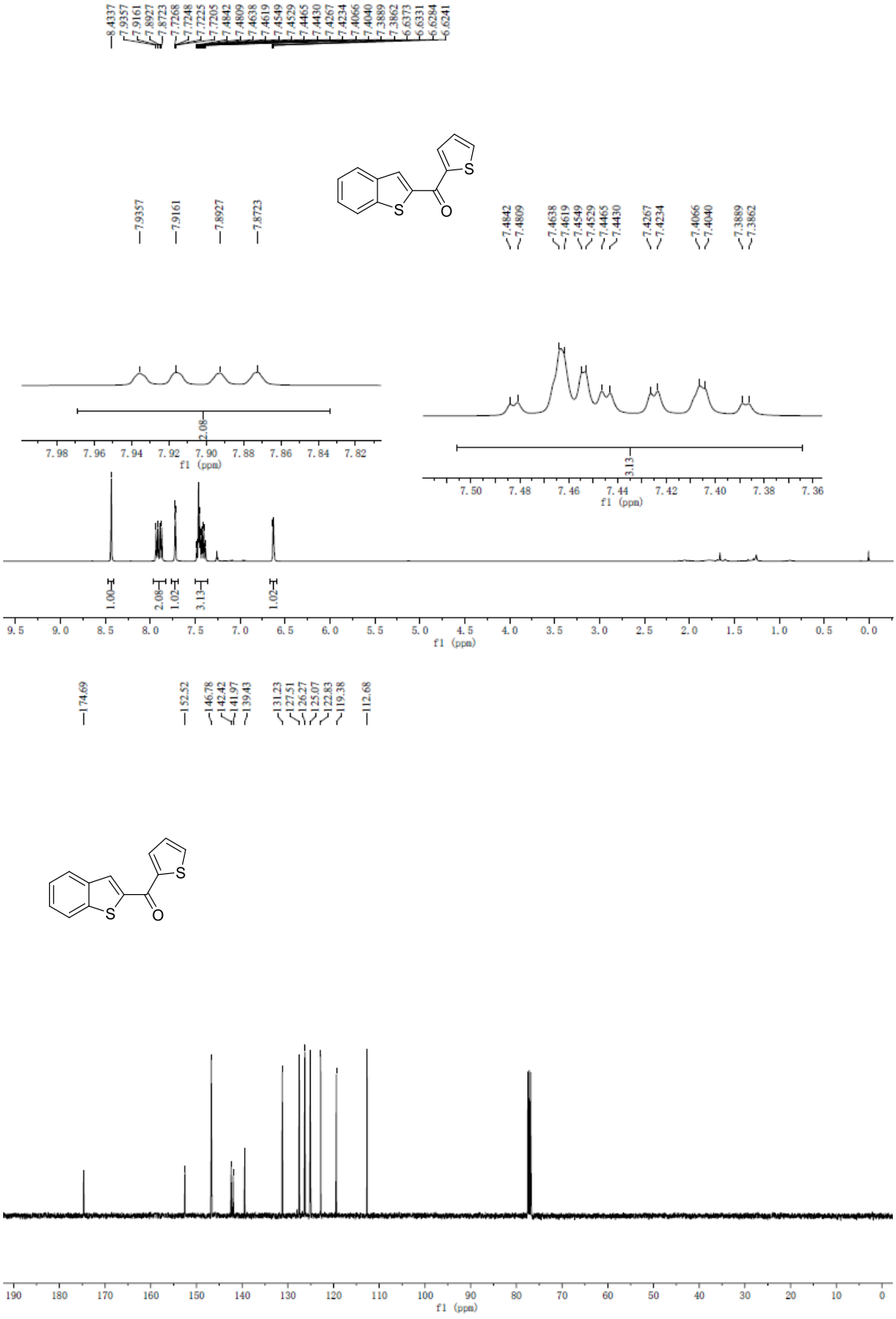






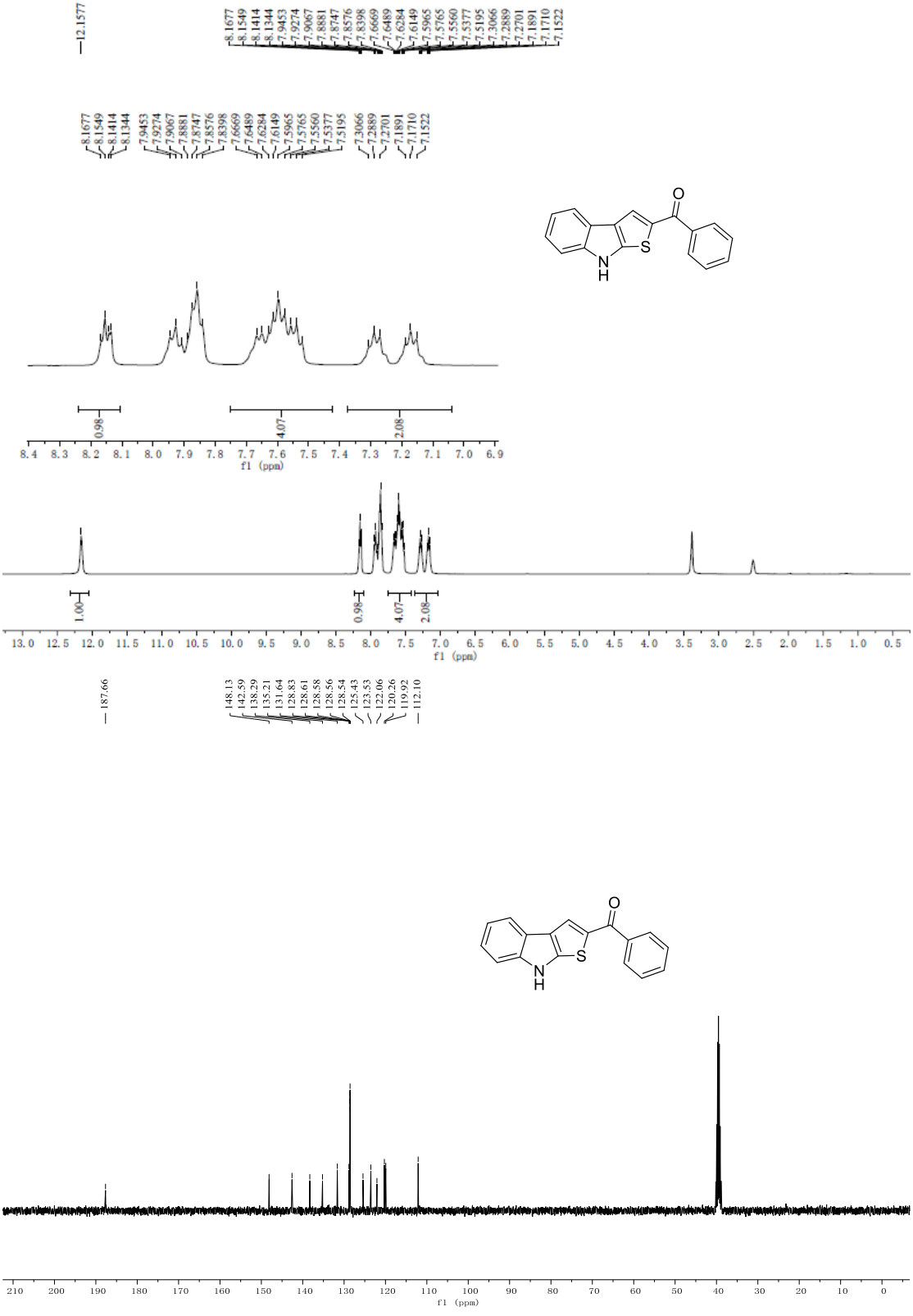
^{1}H and ^{13}C NMR of **5l**

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



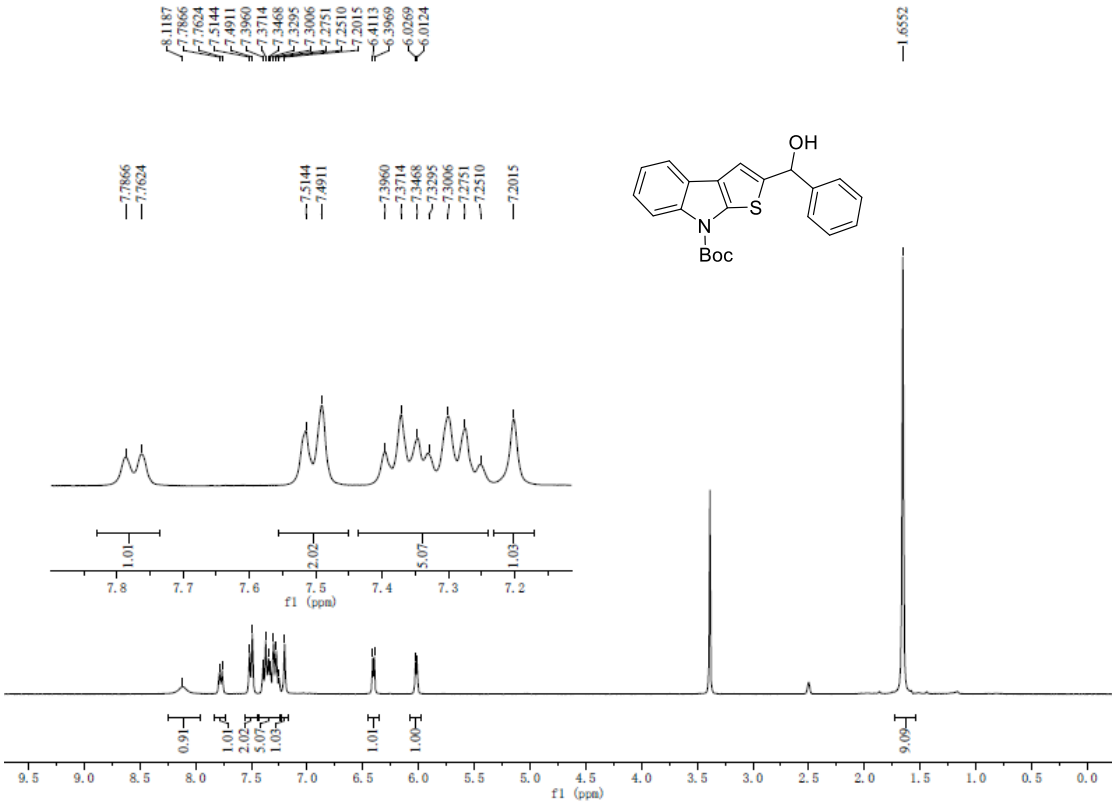
^{1}H and ^{13}C NMR of **6**

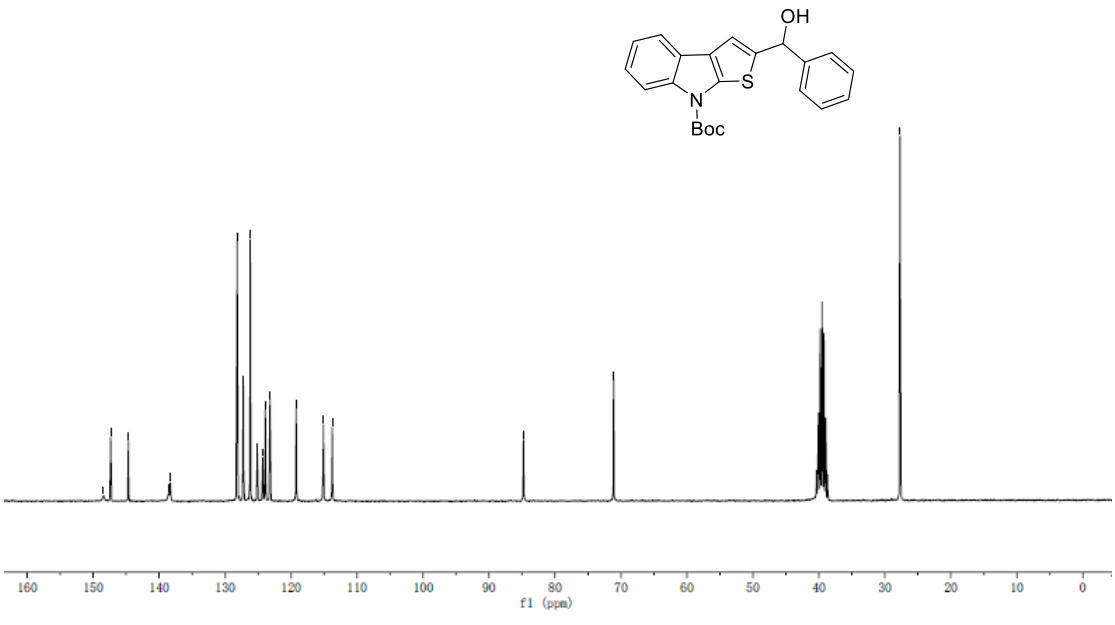
^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (101 MHz, DMSO-d_6)



^{1}H and ^{13}C NMR of **7**

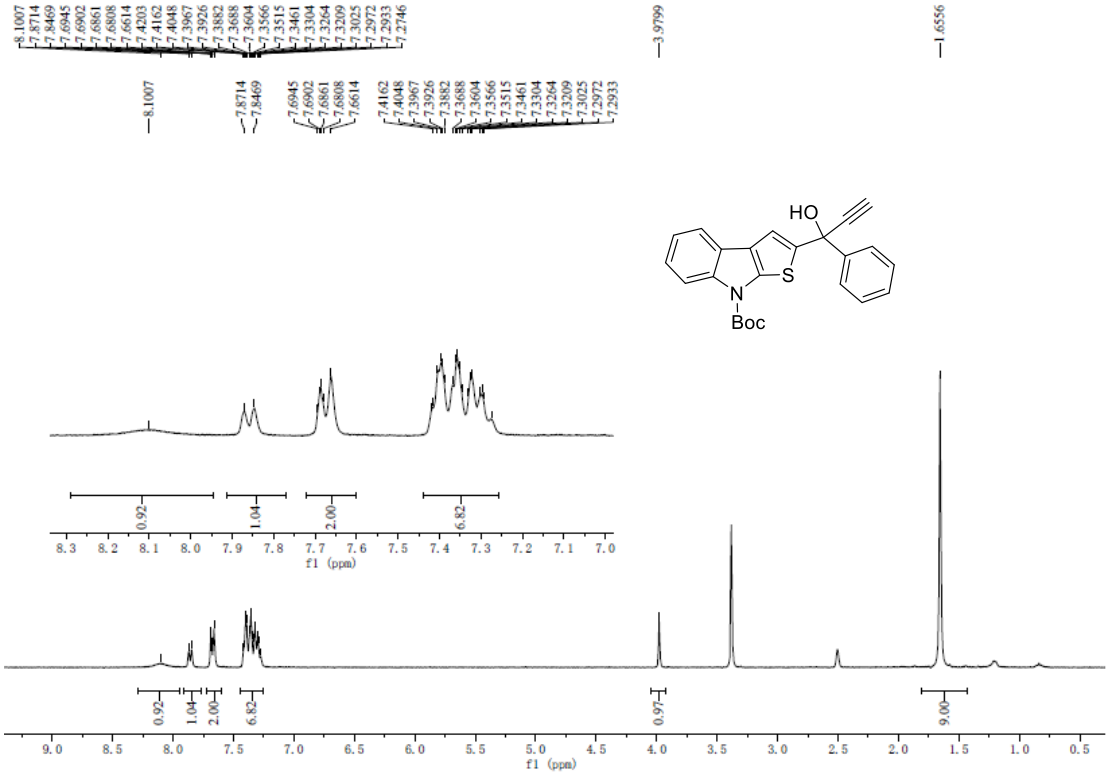
^{1}H NMR (300 MHz, DMSO-d_6), ^{13}C NMR (75 MHz, DMSO-d_6)

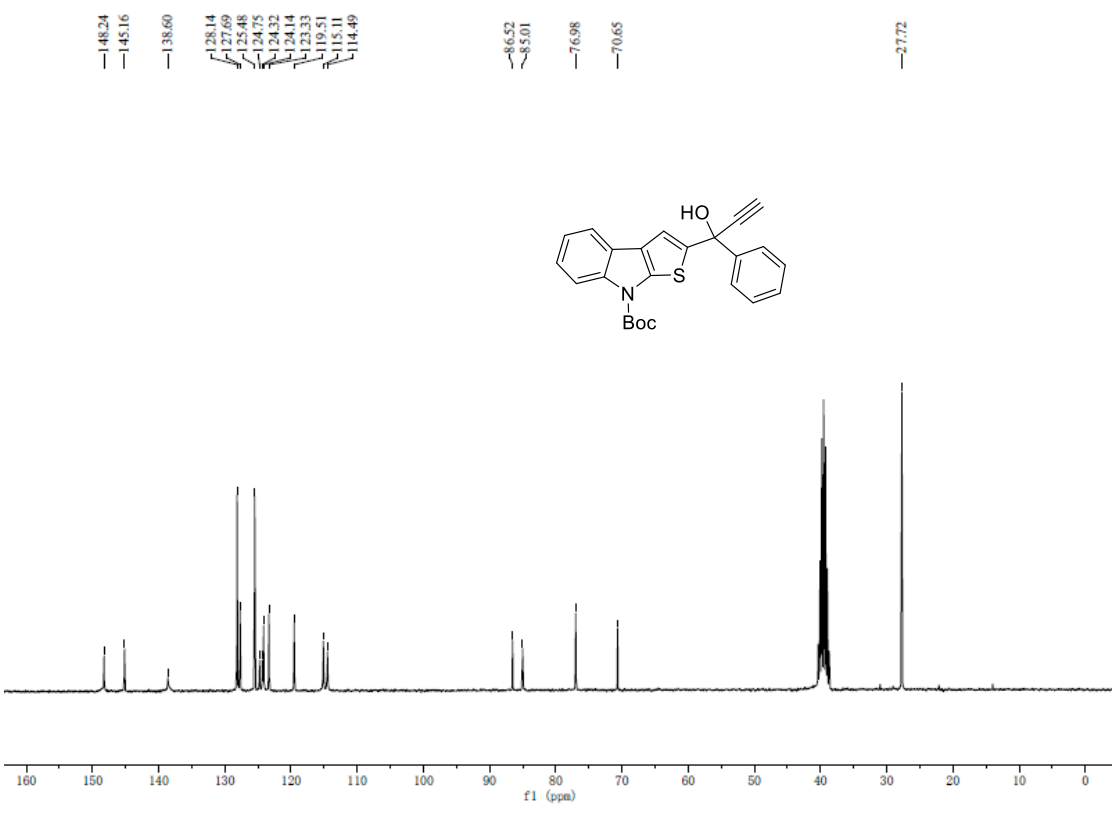




^{1}H and ^{13}C NMR of **8**

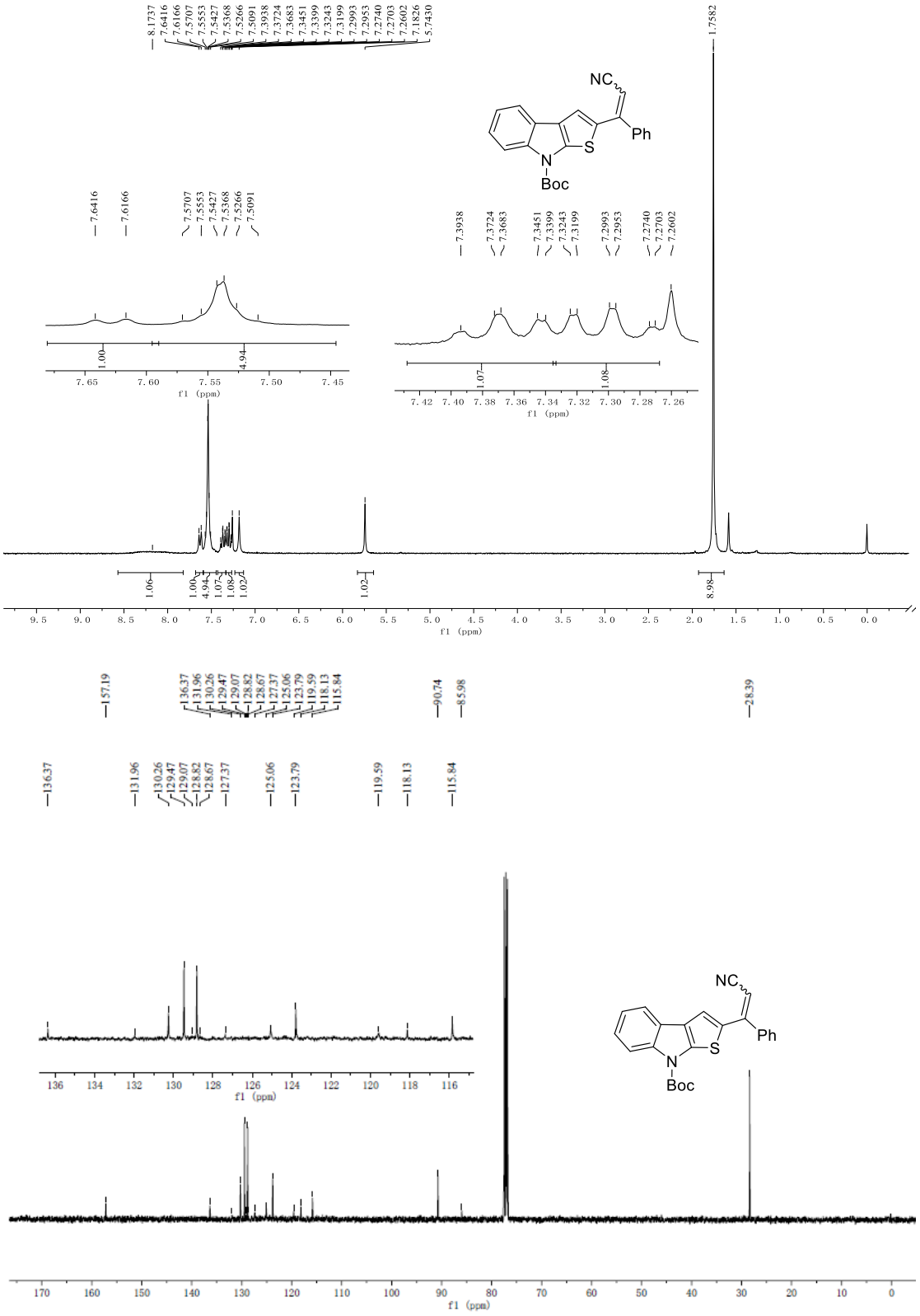
^{1}H NMR (300 MHz, DMSO-d_6), ^{13}C NMR (75 MHz, DMSO-d_6)





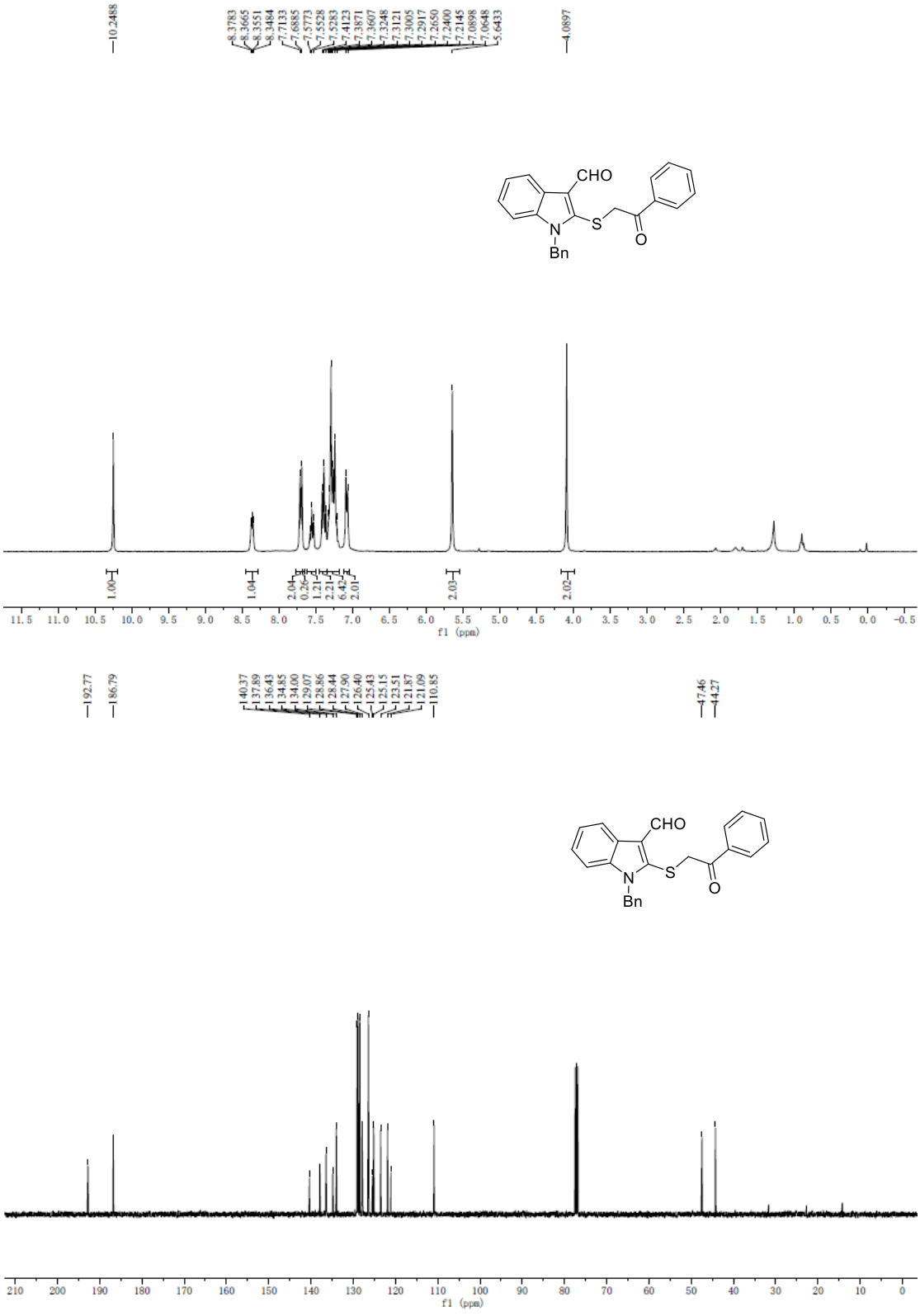
^{1}H and ^{13}C NMR of **9**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



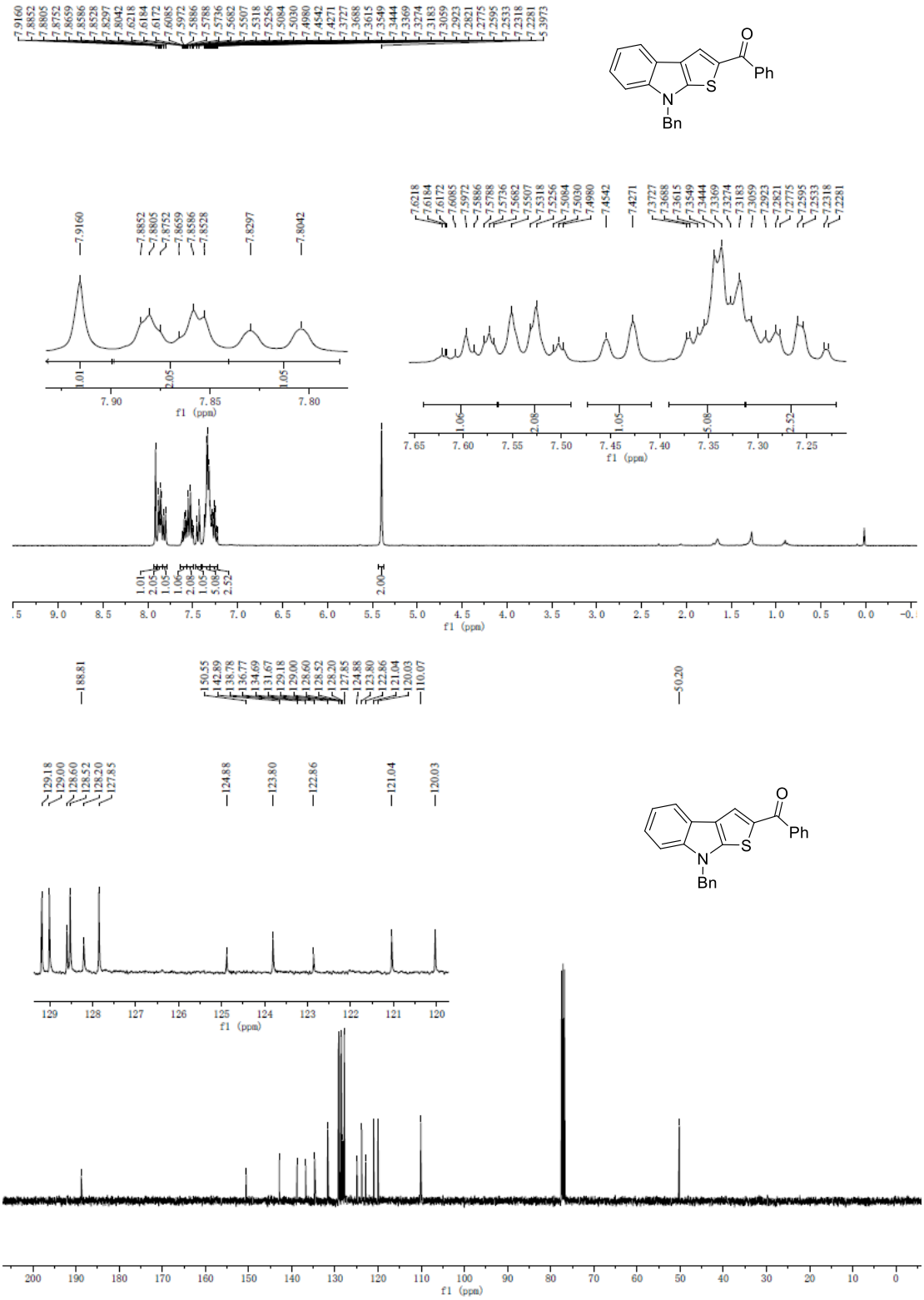
^{1}H and ^{13}C NMR of **15**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



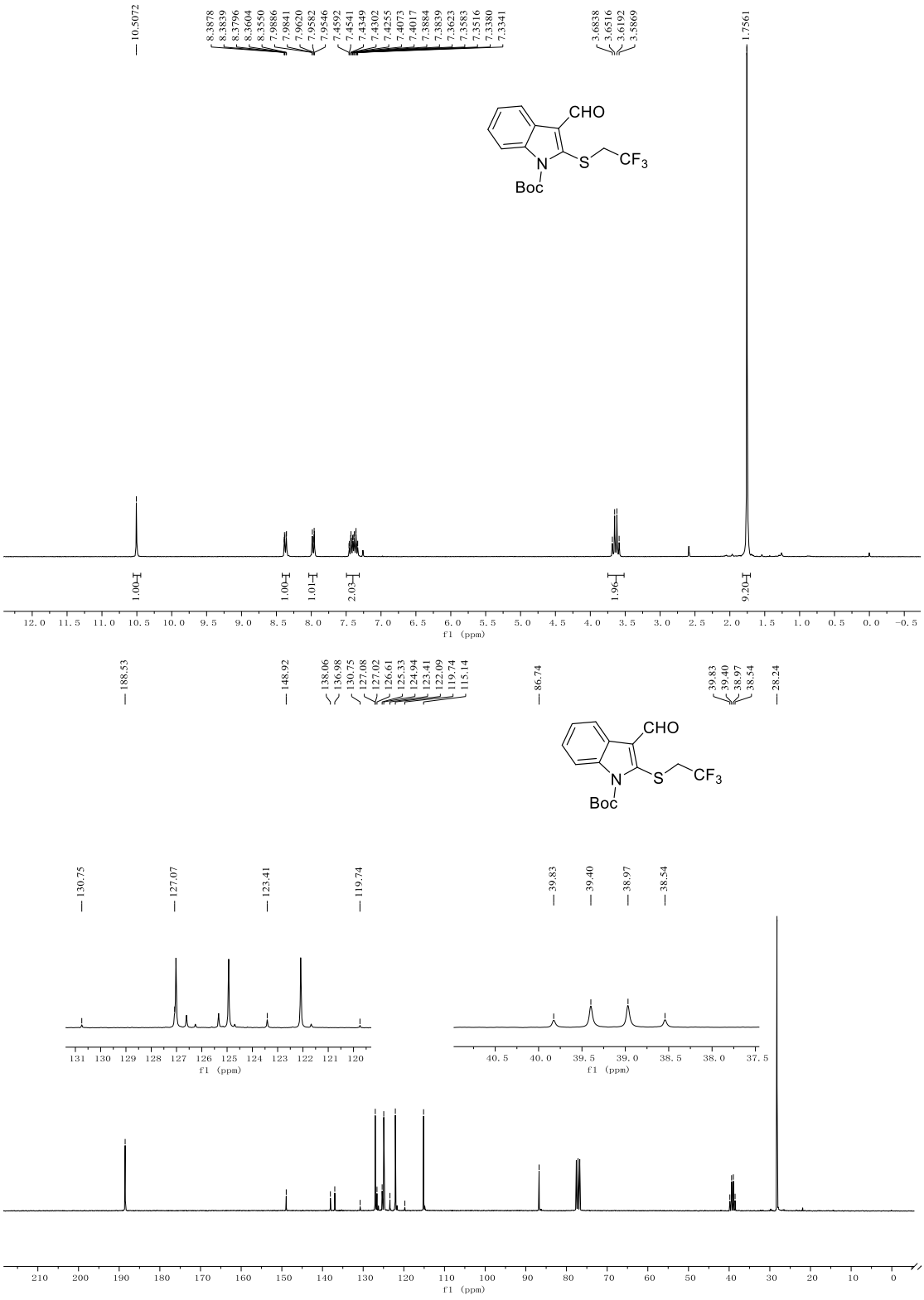
^{1}H and ^{13}C NMR of **16**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR of **18**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H and ^{13}C NMR of **20**

^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$)