Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iron-catalyzed one-pot cyclization and amination of 2-alkynylthioanisoles using nitrosobenzenes as amine source

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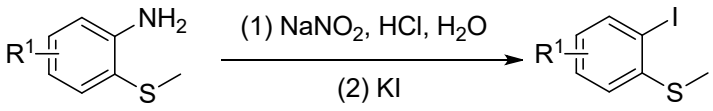
General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400M and Mercury 600M in $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of ^{1}H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reactions were carried out under argon atmosphere in oven-dried glassware, unless otherwise noted. All reagents were purchased commercially and used as received, unless otherwise noted.

Experimental section

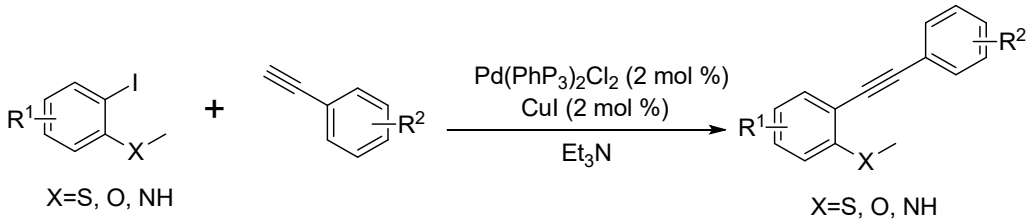
General Procedure for the Synthesis of S-1 [1]



S-1

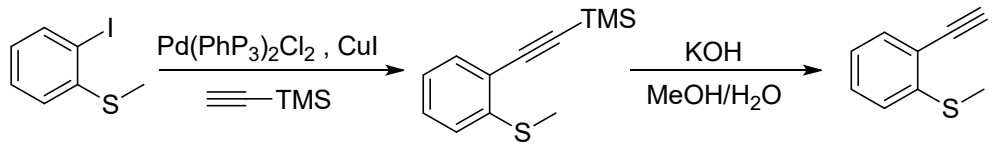
A mixture of 2-(methylthio)aniline (149 mg, 1.5 mmol), aqueous HCl (37%, 0.3 mL) and water (1.3 mL) was cooled to 0 °C. A solution of $NaNO_2$ (113 mg, 1.6 mmol) in water (0.3 mL) was added dropwise and stirred for 10 min. The resulting diazonium salt was treated with a solution of KI (285 mg, 1.7 mmol) in water (0.3 mL). The resulting brown foamy mixture was stirred for 30 min at room temperature and heated at reflux for 15 min. After cooling to ambient temperature, the reaction was diluted with water (10 mL) and neutralized by slow addition of aquesou $Na_2S_2O_3$. The mixture was extracted with dichloromethane (10 mL × 2). The combined organic layer was dried over $NaSO_4$, filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography to afford (2-iodophenyl)(methyl)sulfane as colorless oil (260 mg, 81%).

General Procedure for the Synthesis of 1a-1r, 1t-1u [2]



To a solution of (2-iodophenyl)(methyl)sulfane (5 mmol), CuI (2 mol%), and $Pd(Ph_3P)_2Cl_2$ (2 mol %) in Et_3N (100 mL) was added drop-wise an alkyne (6 mmol) under N_2. The reaction mixture was stirred for 5-10 h at room temperature. Upon completion, the mixture was diluted with diethyl ether and then washed with water and brine successively. The organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified through silica gel flash chromatography to give the desired product in mostly > 90% yield.

General Procedure for the Synthesis of 1s [2][3]

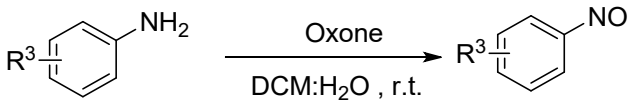


S-3

S-3 was synthesized using a literature procedure in 98% yield.

A solution of KOH (0.45 g, 8.0 mmol, 2 equiv) in 2 mL of water was added dropwise to *o*-(trimethylsilylethynyl)thioanisole (0.88 g, 4.0 mmol) in 20 mL of CH_3OH under an argon atmosphere at 25 °C. The mixture was stirred for another 0.5 h at 25 °C, and the CH_3OH was removed under vacuum. The residue was added to 20 mL of brine, and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na_2SO_4), filtered, and the solvent removed under vacuum. Purification by flash chromatography afforded the **1s** (yield = 86%) as a yellow oil.

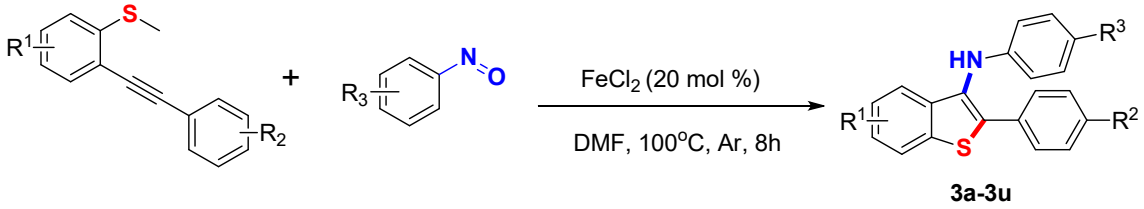
Preparation of Substituted Phenyl Nitroso [4]



A solution of Oxone (2-4 equiv) in (8-154 mL) water was added to a solution of

aniline derivatives (1 equiv) in dichloromethane with vigorous stirring. The reaction mixture was stirred at room temperature under argon atmosphere for 30 min to 24 h. After disappearance of starting materials (indicated by TLC), the reaction was quenched by addition of saturated sodium bicarbonate solution (30-60 mL). The mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with 1M HCl (20-40 mL) then with brine solution (30-60 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was subjected to column chromatography (silica gel) to afford the analytically pure products.

General Procedure for the Synthesis of *N*,2-Diphenylbenzo[*b*]thiophen-3-amine



To a flame dried transparent Schlenk tube equipped with a stirring bar was added methyl(2-(phenylethynyl)phenyl)sulfane (0.3 mmol), DMF (2 mL), $FeCl_2$ (20 mol %), nitrosobenzene (0.45 mmol, 1.5 equiv). The reaction mixture was stirred under argon atmosphere at 100 °C for 8h. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silicagel column chromatography using a petroleum ether to afford the corresponding products.

The X-ray data of 3o (CCDC 2117253)

Crystal **3o** growth with the volatilization method: an amount of 24 mg **3o** was dissolved in dichloromethane on the brown small reagent bottle (5 mL), which acted as good solvent, and a layer of petroleum ether was injected on the surface of dichloromethane, and the cap is covered with a thin film, transparent crystals will be presented after seven days.

Crystals of $C_{20}H_{14}FNS$ (**3o**) was determinated. A suitable crystal was selected and determinated on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2 [5], the structure was solved with the ShelXT [6] structure solution program using Intrinsic Phasing and refined with the ShelXL [7] refinement package using Least Squares minimisation.

All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculations. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: 2117253.

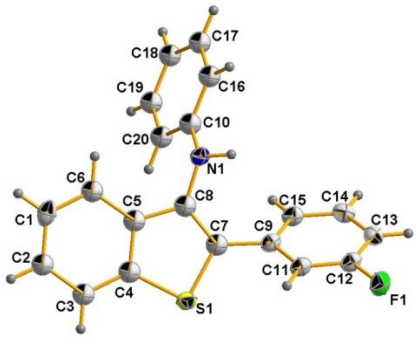


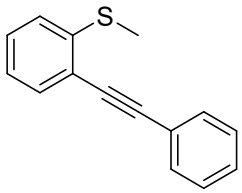
Figure S1 X-ray crystal structure of compound **3o**

Table S1 Crystal data and structure refinement for 3o.

Identification code	3o
Empirical formula	$C_{40}H_{28}F_2N_2S_2$
Formula weight	638.76
Temperature/K	149.99(10)

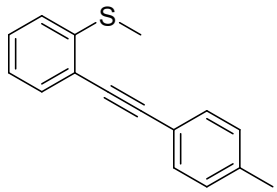
Crystal system	triclinic
Space group	P-1
a/Å	9.4119(3)
b/Å	9.9546(3)
c/Å	16.8497(5)
α /°	78.350(2)
β /°	89.392(2)
γ /°	82.699(2)
Volume/Å^3	1533.44(8)
Z	2
ρ_{calc}g/cm^3	1.383
μ /mm^{-1}	1.943
F(000)	664.0
Crystal size/mm^3	0.1 × 0.07 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.356 to 154.736
Index ranges	-11 ⩽ h ⩽ 10, -12 ⩽ k ⩽ 12, -15 ⩽ l ⩽ 21
Reflections collected	18124
Independent reflections	6162 [R_{int} = 0.0552, R_{sigma} = 0.0590]
Data/restraints/parameters	6162/0/415
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1303
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1344
Largest diff. peak/hole / e Å^{-3}	0.51/-0.44

Characterization Data for the Products



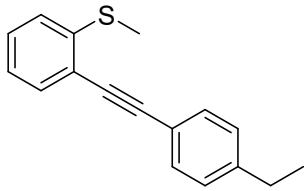
methyl(2-(phenylethynyl)phenyl)sulfane (1a) [8]

Yellow oil (0.84 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.58 (m, 2 H), 7.48 (s, 1 H), 7.27-7.36 (m, 5 H), 7.0 (m, 1 H), 2.51 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.7, 132.2, 131.5, 128.7, 128.3, 128.2, 124.2, 124.1, 123.1, 121.3, 95.8, 86.9, 15.0.



methyl(2-(*p*-tolylethynyl)phenyl)sulfane (1b) [8]

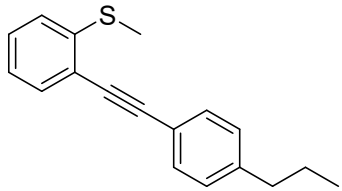
Yellow solid (0.96 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49 (d, *J* = 8 Hz, 3 H), 7.31-7.27 (m, 1 H), 7.17 (d, *J* = 8 Hz, 3 H), 7.13-7.09 (m, 1 H), 2.51 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.5, 138.5, 132.1, 131.5, 129.1, 128.6, 124.2, 124.0, 121.5, 120.1, 96.1, 86.2, 21.5, 15.1.



(2-((4-ethylphenyl)ethynyl)phenyl)(methyl)sulfane (1c) [8]

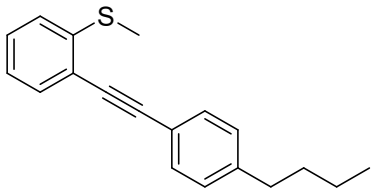
Yellow oil (1.059 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50-7.45 (m, 3 H), 7.28-7.24 (m, 1 H), 7.17-7.13 (m, 3 H), 7.10-7.06 (m, 1 H), 2.67-2.61 (m, 2 H), 2.47 (s, 3 H), 1.24-1.20 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.8,

141.5, 132.0, 131.5, 128.5, 127.8, 124.1, 123.9, 121.4, 120.3, 96.1, 86.2, 28.8, 15.3, 15.0.



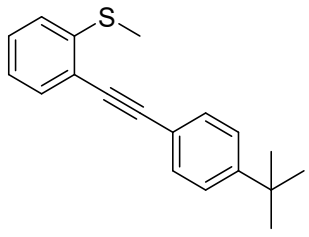
methyl(2-((4-propylphenyl)ethynyl)phenyl)sulfane (1d) [8]

Yellow solid (1.13 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-7.45 (m, 3 H), 7.29-7.24 (m, 1 H), 7.15 (d, *J* = 8 Hz, 3 H), 7.10-7.06 (m, 1 H), 2.60-2.56 (m, 2 H), 2.48 (s, 3 H), 1.68-1.58 (m, 2 H), 0.95-0.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.3, 141.5, 132.1, 131.4, 128.5, 128.5, 124.2, 124.0, 121.5, 120.3, 96.1, 86.2, 37.9, 24.3, 15.0, 13.7.



(2-((4-butylphenyl)ethynyl)phenyl)(methyl)sulfane (1e) [8]

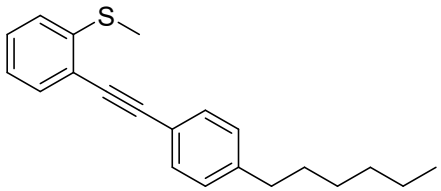
yellow oil (0.98 g, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.50-7.46 (m, 3 H), 7.29-7.26 (m, 1 H), 7.17-7.15 (m, 3 H), 7.11-7.08 (m, 1 H), 2.63-2.60 (m, *J* = 8.4 Hz, 2 H), 2.49 (s, 3 H), 1.62-1.57 (m, 2 H), 1.37-1.33 (m, 2 H), 0.94-0.92 (m, 3 H); ^{13}C NMR (150 MHz, CDCl3, ppm): δ = 143.7, 141.7, 132.2 131.6, 128.7, 128.6, 124.3, 124.2, 121.7, 120.4, 96.3, 86.4, 35.8, 33.6, 22.4, 15.2, 14.0.



(2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)(methyl)sulfane (1f) [8]

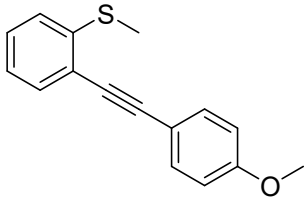
Yellow solid (1.01 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.46 (m, 3 H), 7.38-7.27 (m, 2 H), 7.25-7.23 (m, 1 H), 7.17-7.01 (m, 2 H), 2.49 (d, *J* = 2.8 Hz, 3 H), 1.32 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.7, 141.7, 132.2,

131.6, 128.7, 128.6, 124.3, 124.2, 121.7, 120.4, 96.2, 86.3, 35.7, 33.5, 22.4, 17.1, 15.2, 14.1.



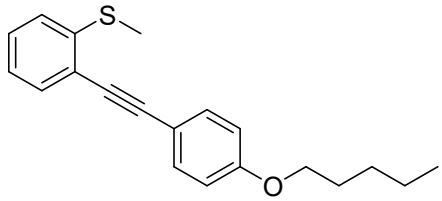
(2-((4-hexylphenyl)ethynyl)phenyl)(methyl)sulfane (1g) [8]

yellow oil (1.12 g,76% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.50-7.46 (m, 3 H), 7.27 (t, *J* = 7.8 Hz, 1 H), 7.15 (d, *J* = 7.8 Hz, 3 H), 7.09 (t, *J* = 7.8 Hz, 1 H), 2.60 (t, *J* = 8.4 Hz, 2 H), 2.49 (s, 3 H), 1.63-1.58 (m, 2 H), 1.35-1.29 (m, 4 H), 0.90-0.87 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 143.7, 141.7, 132.2 131.6, 128.7, 128.6, 124.3, 124.2, 121.7, 120.4, 96.2, 86.4, 36.0, 31.5, 31.0, 22.6, 15.2, 14.2.



(2-((4-methoxyphenyl)ethynyl)phenyl)(methyl)sulfane (1h) [8]

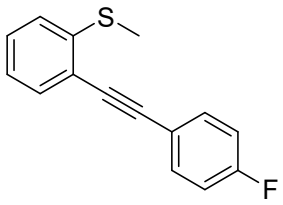
Yellow solid (0.91 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.28-7.23 (m, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.10-7.06 (m, 1 H), 6.87-6.81 (m, 2 H), 3.79 (s, 3 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.9, 141.5, 134.1, 133.1, 132.1, 128.5, 124.2, 121.8, 115.4, 114.1, 96.0, 85.8, 55.4, 15.1.



methyl(2-((4-(pentyloxy)phenyl)ethynyl)phenyl)sulfane (1i) [8]

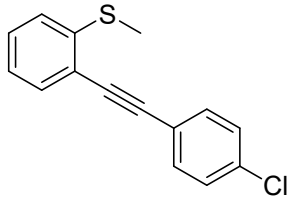
Yellow solid (1.24 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50-7.42 (m, 3 H), 7.28-7.24 (m, 1 H), 7.16-7.07 (m, 2 H), 6.87-6.81 (m, 2 H), 3.96-3.92 (m, 2 H), 2.49 (s, 3 H), 1.81-1.75 (m, 2 H), 1.47-1.35 (m, 4 H), 0.95-0.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.3, 141.3, 133.9, 133.0, 131.9, 128.3, 124.1,

123.9, 121.6, 114.4, 96.0, 85.5, 68.0, 28.8, 28.1, 22.4, 15.0, 14.0.



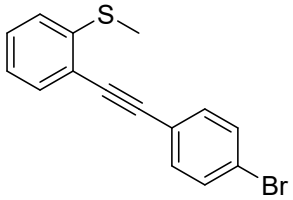
(2-((4-fluorophenyl)ethynyl)phenyl)(methyl)sulfane (1j) [8]

Yellow solid (0.97 g, 80% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-7.46 (m, 2 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.24-7.20 (m, 1 H), 7.10 (d, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.6 Hz, 1 H), 6.99-6.94 (m, 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.0, 161.5, 141.8, 133.6 (d, *J* = 9 Hz, 1 C), 132.3, 129.0, 124.3 (d, *J* = 14 Hz, 1 C), 121.3, 119.4 (d, *J* = 4 Hz, 1 C), 115.7 (d, *J* = 22 Hz, 1 C), 94.9, 86.7, 15.2.



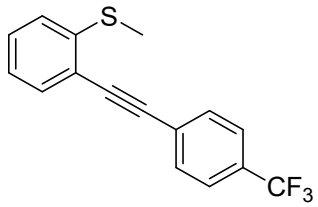
(2-((4-chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1k) [8]

Yellow solid (1.09 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50-7.45 (m, 3 H), 7.32-7.27 (m, 3 H), 7.16 (d, *J* = 8 Hz, 1 H), 7.12-7.08 (m, 1 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.7, 134.3, 132.7, 132.2, 128.9, 128.6, 124.2, 123.9, 121.6, 120.8, 94.6, 87.8, 15.0.



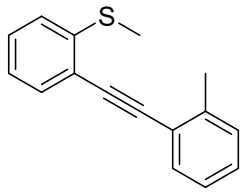
(2-((4-bromophenyl)ethynyl)phenyl)(methyl)sulfane (1l) [8]

yellow oil (1.18 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-7.45 (m, 3 H), 7.43-7.41 (m, 2 H), 7.33-7.29 (m, 1 H), 7.17 (d, J = 7.6 Hz, 1 H), 7.12-7.09 (m, 1 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, CDCl3, ppm): δ = 141.8, 133.0, 132.2 131.6, 129.0, 124.2, 124.0, 122.6, 122.1, 120.9, 94.7, 88.0, 15.0.



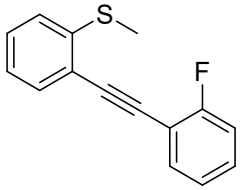
(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)(methyl)sulfane (1m) [8]

Yellow oil (1.20 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.68 (d, *J* = 8 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.52-7.49 (m, 1 H), 7.36-7.31 (m, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.15-7.11 (m, 1 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 142.3, 132.5, 131.9, 130.3, 129.9, 129.4, 127.2, 125.4-125.3 (m, 1C), 124.4, 124.3, 122.7, 120.7, 94.4, 89.4, 15.1.



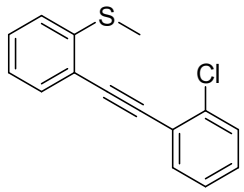
methyl(2-(*o*-tolylethynyl)phenyl)sulfane (1n) [8]

Yellow oil (0.86 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.62-7.60 (m, 1 H), 7.54-7.51 (m, 2 H), 7.45-7.39 (m, 1 H), 7.36 (d, *J* = 8 Hz, 1 H), 7.31-7.22 (m, 3 H), 2.64 (s, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.6, 138.0, 132.1, 132.1, 129.3, 128.6, 128.2, 124.2, 124.0, 122.9, 121.3, 96.0, 86.5, 21.2, 15.0.



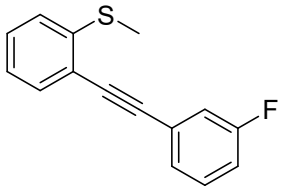
(2-((2-fluorophenyl)ethynyl)phenyl)(methyl)sulfane (1o) [8]

Colorless oil (0.97 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-7.46 (m, 1 H), 7.36-7.28 (m, 4 H), 7.17 (d, *J* = 8 Hz, 1 H), 7.13-7.09 (m, 1 H), 7.06-7.01 (m, 1 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.7, 161.3, 142.1, 132.4, 130.0 (d, *J* = 8 Hz, 1 C), 129.2, 127.6 (d, *J* = 3 Hz, 1 C), 125.2 (d, *J* = 10 Hz, 1 C), 124.3 (d, *J* = 15 Hz, 1 C), 120.9, 118.4 (d, *J* = 23 Hz, 1 C), 115.8 (d, *J* = 21 Hz, 1 C), 94.6 (d, *J* = 3 Hz, 1 C), 87.9, 15.2.



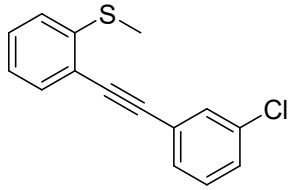
(2-((2-chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1p) [8]

Yellow solid (1.09 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.52 (m, 1 H), 7.46-7.44 (m, 1 H), 7.35-7.33 (m, 1 H), 7.25-7.21 (m, 1 H), 7.18-7.15 (m, 2 H), 7.11 (d, *J* = 8 Hz, 1 H),7.06-7.02 (m, 1 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 142.0, 135.9, 133.6, 132.8, 129.5, 129.4, 129.2, 126.5, 124.5, 124.4, 123.3, 121.2, 92.6, 92.1, 15.3.



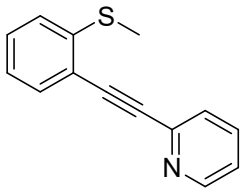
(2-((3-fluorophenyl)ethynyl)phenyl)(methyl)sulfane (1q) [8]

Brown oil (0.87 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48-7.46 (m, 1 H), 7.36-7.26 (m, 4 H), 7.17 (d, *J* = 8 Hz, 1 H), 7.12-7.08 (m, 1 H), 7.06-7.03 (m, 1 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.7, 161.3, 142.1, 132.4, 130.0 (d, *J* = 8 Hz, 1 C), 129.2, 127.6 (d, *J* = 3 Hz, 1 C), 125.2 (d, *J* = 10 Hz, 1 C), 124.3 (d, *J* = 16 Hz, 1 C), 120.9, 118.4 (d, *J* = 23 Hz, 1 C), 115.8 (d, *J* = 21 Hz, 1 C), 94.6 (d, *J* = 3 Hz, 1 C), 87.9, 15.2.



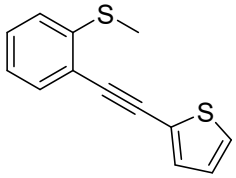
(2-((3-chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1r) [8]

Yellow solid (1.03 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.55 (m, 1 H), 7.47-7.42 (m, 2 H), 7.32-7.27 (m, 2 H), 7.24 (d, *J* = 8 Hz, 1 H), 7.16 (d, *J* = 8 Hz, 1 H), 7.12-7.08 (m, 1 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.9, 134.1, 132.2, 131.3, 129.6, 129.5, 129.1, 128.6, 124.8, 124.2, 124.0, 120.7, 94.2, 88.0, 15.0.



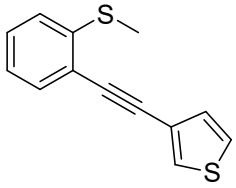
2-((2-(methylthio)phenyl)ethynyl)pyridine (1s) [8]

Yellow oil (0.889 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.60 (t, *J* = 5 Hz, 1 H), 7.71-7.64 (m, 1 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.36-7.29 (m, 2 H), 7.18 (d, *J* = 8 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 2.51 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.9, 143.2, 142.4, 136.4, 132.8, 129.6, 127.5, 124.3, 124.2, 123.6, 123.0, 94.6, 87.0, 15.1.



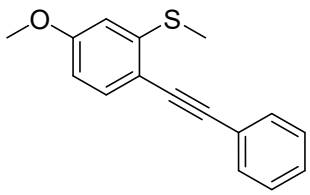
2-((2-(methylthio)phenyl)ethynyl)thiophene (1t) [8]

Yellow oil (1.04 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.44 (d, *J* = 7.6 Hz, 1 H), 7.30-7.25 (m, 3 H), 7.15 (d, *J* = 8 Hz, 1 H), 7.08 (t, *J* = 7.2 Hz, 1 H), 6.98 (t, *J* = 4.8 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.7, 132.2, 132.1, 129.0, 127.6, 127.2, 124.3, 123.1, 121.1, 90.6, 89.0, 15.2.



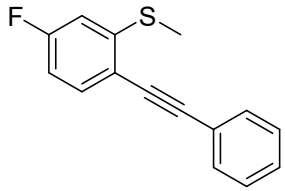
3-((2-(methylthio)phenyl)ethynyl)thiophene (1u) [8]

Yellow oil (0.94 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.55-7.53 (m, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.28-7.24 (m, 2 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.10-7.06 (m, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.6, 132.2, 129.9, 128.8, 128.7, 125.4, 124.3, 124.2, 122.2, 121.3, 91.0, 86.5, 15.1.



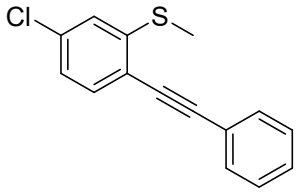
(5-methoxy-2-(phenylethynyl)phenyl)(methyl)sulfane (1v) [8]

Yellow oil (0.79 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.53 (m, 2 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 7.34-7.28 (m, 3 H), 6.69 (s, 1 H), 6.63-6.60 (m, 1 H), 3.79 (s, 3 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 160.2, 143.5, 133.6, 131.5, 128.4, 128.1, 123.6, 113.8, 110.8, 109.4, 94.4, 87.0, 55.4, 15.1.



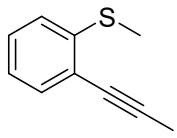
(5-fluoro-2-(phenylethynyl)phenyl)(methyl)sulfane (1w) [8]

Yellow oil (0.80 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.55 (m, 2 H), 7.46-7.42 (m, 1 H), 7.36-7.34 (m, 3 H), 6.87-6.84 (m, 1 H), 6.82-6.78 (m, 1 H), 3.63 (s, 1 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.0 (d, *J* = 249 Hz, 1 C), 144.9 (d, *J* = 8 Hz, 1 C), 133.8 (d, *J* = 9 Hz, 1 C), 131.7, 128.5 (d, *J* = 10 Hz, 1 C), 123.1, 117.0, 111.5, 111.2, 111.1, 111.0, 95.7, 85.9, 15.1.



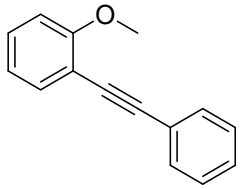
(5-chloro-2-(phenylethynyl)phenyl)(methyl)sulfane (1x) [8]

Yellow oil (0.72 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.54 (m, 2 H), 7.35-7.31 (m, 4 H), 7.07-7.02 (m, 2 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.0, 134.9, 133.0, 131.6, 128.7, 128.4, 124.4, 123.6, 122.9, 119.5, 96.8, 86.0, 15.0.



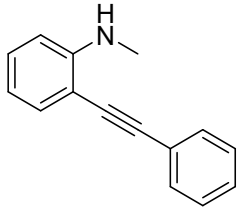
methyl(2-(prop-1-yn-1-yl)phenyl)sulfane (1aa) [8]

Yellow oil (0.61 g, 75% yield). $_1$H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.36-6.35 (d, *J* = 7.6 Hz, 1 H), 7.26-7.22 (m, 1 H), 7.13-7.11 (d, *J* = 8.0 Hz, 1 H), 7.07-7.03 (m, 1 H), 2.48-2.47 (d, *J* = 2.4 Hz, 3 H), 2.14-2.13 (d, *J* = 1.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 140.9, 132.1, 127.9, 123.9, 123.6, 121.6, 92.5, 77.1, 14.8, 4.4.



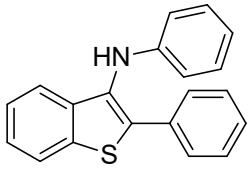
1-methoxy-2-(phenylethynyl)benzene (1ab) [8]

Yellow oil (0.95 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.55 (m, 2 H), 7.51-7.49 (m, 1 H), 7.35-7.27 (m, 4 H), 6.95-6.87 (m, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.8, 135.5, 131.6, 129.7, 128.2, 128.1, 123.5, 120.4, 112.3, 110.6, 93.4, 85.7, 55.8.



***N*-methyl-2-(phenylethynyl)aniline (1ac)** [8]

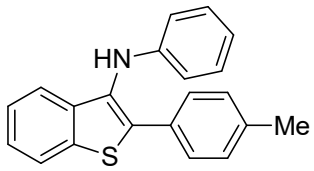
Yellow oil (0.95 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.55 (m, 2 H), 7.51-7.49 (m, 1 H), 7.35-7.27 (m, 4 H), 6.95-6.87 (m, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 195.8, 135.5, 131.6, 129.7, 128.2, 128.1, 123.5, 120.4, 112.3, 110.6, 93.4, 85.7, 55.8.



***N*,2-diphenylbenzo[*b*]thiophen-3-amine (3a)**

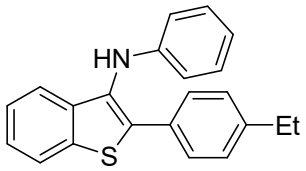
White solid (68.65 mg, 76% yield). melting point: 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.52 (d, *J* = 7.2

Hz, 1 H), 7.39-7.28 (m, 5 H), 7.20-7.16 (m, 2 H), 6.83 (t, *J* = 7.2 Hz, 1 H), 6.71 (d, *J* = 7.6 Hz, 2 H), 5.51 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.4, 137.3, 137.1, 134.3, 133.4, 129.5, 129.4，129.1, 128.7, 128.4, 125.0, 124.4, 122.8, 122.7, 119.4, 114.9; HRMS calcd for $C_{20}H_{16}NS$ $[M+H]^+$ 302.0998; found: 302.0999.



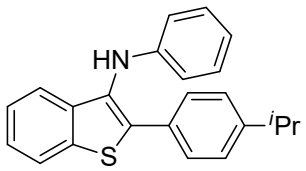
***N*-phenyl-2-(*p*-tolyl)benzo[*b*]thiophen-3-amine (3b)**

Yellow oil (52.94 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 3 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 7.18 (t, *J* = 7.2 Hz, 4 H), 6.82 (t, *J* = 7.2 Hz, 1 H), 6.70 (d, *J* = 7.8 Hz, 2 H), 5.48 (s, 1 H), 2.35 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 146.6, 138.4, 137.5, 137.0, 134.7, 130.5, 129.8, 129.5, 129.2, 128.6, 124.8, 124.4, 122.7, 122.6, 119.3, 114.8, 21.4; HRMS calcd for $C_{21}H_{18}NS$ $[M+H]^+$ 316.1155; found: 316.1165.



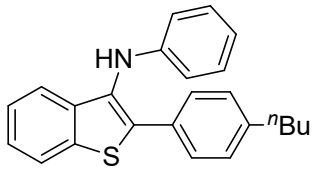
2-(4-ethylphenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3c)

Grey solid (48.38 mg, 49% yield). melting point: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.54-7.50 (m, 3 H), 7.35-7.28 (m, 2 H), 7.22-7.17 (m, 4 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.71 (d, *J* = 7.6 Hz, 2 H), 5.50 (s, 1 H), 2.68-2.62 (m, 2 H), 1.24 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.6, 144.7, 137.4, 137.0, 134.7, 130.6, 129.5, 129.2, 128.7, 128.6, 124.8, 124.4, 122.7, 122.6, 119.2, 114.8, 28.8, 15.5; HRMS calcd for $C_{22}H_{20}NS$ $[M+H]^+$ 330.1311; found: 330.1312.



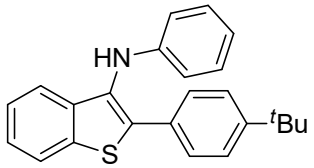
***N*-phenyl-2-(4-propylphenyl)benzo[*b*]thiophen-3-amine (3d)**

White solid (42.21 mg, 41% yield). melting point: 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.79 (d, *J* = 7.6 Hz, 1 H), 7.53-7.50 (m, 3 H), 7.34-7.25 (m, 2 H), 7.20-7.16 (m, 4 H), 6.82 (t, *J* = 7.2 Hz, 1 H), 6.71 (d, *J* = 7.6 Hz, 2 H), 2.58 (t, *J* = 7.2 Hz, 2 H), 1.68-1.59 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.6, 143.2, 137.4, 137.0, 134.6, 130.7, 129.5, 129.2, 129.1, 128.5, 124.8, 124.4, 122.7, 122.6, 119.2, 114.8, 37.9, 24.5, 14.0; HRMS calcd for $C_{23}H_{22}NS$ $[M+H]^+$ 344.1468; found: 344.1468.



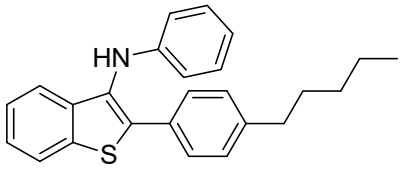
2-(4-butylphenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3e)

Yellow solid (62.14 mg, 58% yield). melting point: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.72 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 3 H), 7.27-7.18 (m, 2 H), 7.13-7.09 (m, 4 H), 6.75 (t, *J* = 7.6 Hz, 1 H), 6.63 (d, *J* = 7.6 Hz, 2 H), 2.53 (t, *J* = 7.6 Hz, 2 H), 1.56-1.48 (m, 2 H), 1.33-1.24 (m, 2 H), 0.85 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.6, 143.4, 137.4, 137.0, 134.6, 130.6, 129.5, 129.2, 128.6, 124.8, 124.4, 122.7, 122.6, 119.2, 114.8, 35.5, 33.6, 22.5, 14.1; HRMS calcd for $C_{24}H_{24}NS$ $[M+H]^+$ 358.1624; found: 358.1624.



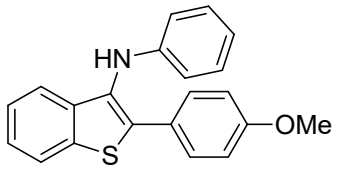
2-(4-(*tert*-butyl)phenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3f)

Yellow solid (53.57 mg, 50% yield). melting point: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.35-7.26 (m, 2 H), 7.19 (t, *J* = 7.6 Hz, 2 H), 6.83 (t, *J* = 7.6 Hz, 1 H), 6.72 (d, *J* = 7.6 Hz, 2 H), 5.52(s, 1 H), 1.32 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 151.5, 146.7, 137.5, 137.0, 134.7, 130.4, 129.5, 129.2, 128.4, 126.1, 124.8, 124.4, 122.7, 119.3, 114.8, 34.8, 31.4; HRMS calcd for $C_{24}H_{24}NS$ $[M+H]^+$ 358.1624; found: 358.1627.



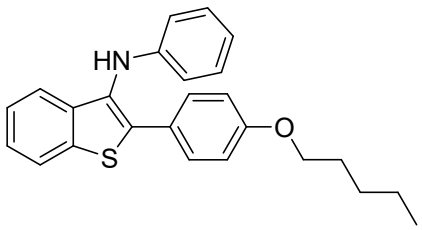
2-(4-pentylphenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3g)

White solid (43.43 mg, 39% yield). melting point: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.72 (d, *J* = 7.6 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 3 H), 7.27-7.18 (m, 2 H), 7.12-7.08 (m, 4 H), 6.74 (t, *J* = 7.6 Hz, 1 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 2.52 (t, *J* = 7.6 Hz, 2 H), 1.53 (t, *J* = 7.6 Hz, 2 H), 1.26-1.23 (m, 4 H), 0.81 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.6, 143.4, 137.5, 137.0, 134.7, 130.6, 129.5, 129.2, 128.6, 124.8, 124.4, 122.7, 122.6, 119.2, 114.8, 35.8, 31.6, 31.1, 22.7, 14.2; HRMS calcd for $C_{25}H_{26}NS$ $[M+H]^+$ 372.1781; found: 372.1782.



2-(4-methoxyphenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3h)

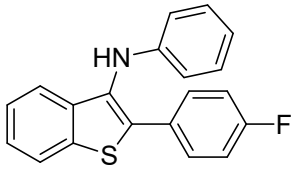
Yellow solid (66.55 mg, 67% yield). melting point: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.78 (d, *J* = 8.0 Hz, 1 H), 7.55-7.53 (m, 2 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.34-7.25 (m, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 6.91-6.88 (m, 2 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.44 (s, 1 H), 3.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.8, 146.6, 137.6, 136.8, 134.7, 130.0, 129.5, 128.7, 125.8, 124.7, 124.4, 122.7, 122.5, 119.2, 114.7, 114.5, 55.5; HRMS calcd for $C_{21}H_{18}NOS$ $[M+H]^+$ 332.1104; found: 332.1104.



2-(4-(pentyloxy)phenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3i)

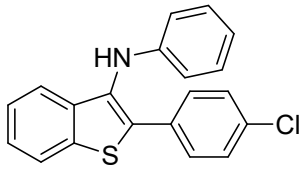
Yellow solid (59.24 mg, 51% yield). melting point: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.77 (d, *J* = 8.0 Hz, 1 H), 7.52-7.48 (m, 3 H), 7.32-7.24 (m, 2 H),

7.17 (t, *J* = 7.6 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.82-6.79 (m, 1 H), 6.68 (d, *J* = 8.0 Hz, 2 H), 5.42 (s, 1 H), 3.93 (t, *J* = 6.8 Hz, 2 H), 1.80-1.73 (m, 2 H), 1.46-1.32 (m, 4 H), 0.94-0.91 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.4, 146.6, 137.6, 136.7, 134.8, 129.9, 129.5, 128.5, 125.4, 124.6, 124.4, 122.6, 122.5, 119.1, 115.0, 114.6, 68.2, 29.0, 28.3, 22.6, 14.2; HRMS calcd for $C_{25}H_{26}NOS$ $[M+H]^+$ 388.1730; found: 388.1737.



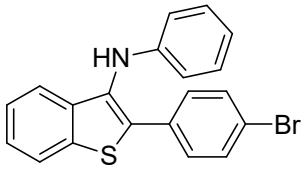
2-(4-fluorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3j)

Yellow solid (61.26 mg, 64% yield). melting point: 122-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.8 Hz, 1 H), 7.58-7.55 (m, 2 H), 7.51 (d, *J* = 7.8 Hz, 1 H), 7.35-7.33 (m, 1 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 2 H), 7.06-7.03 (m, 2 H), 6.82 (t, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 7.8 Hz, 2 H), 5.42 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 163.5, 161.9, 146.3, 137.3, 136.9, 133.5, 130.4 (d, *J* = 7.5 Hz, 1 C), 129.5, 129.4 (d, *J* = 7.5 Hz, 1 C), 125.1, 124.5, 122.7 (d, *J* = 10.5 Hz, 1 C), 119.4, 116.1, 116.0, 114.7; HRMS calcd for $C_{20}H_{15}FNS$ $[M+H]^+$ 320.0904; found:320.0899.



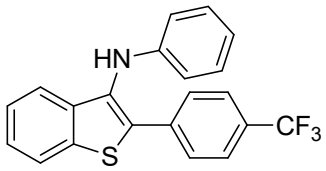
2-(4-chlorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3k)

White solid (78.40 mg, 78% yield). melting point: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.79 (d, *J* = 8.0 Hz, 1 H), 7.54-7.50 (m, 3 H), 7.36-7.26 (m, 4 H), 7.19-7.15 (m, 2 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 2 H), 5.42 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.1, 137.3, 137.0, 134.3, 133.2, 131.8, 129.8, 129.6, 129.2, 125.2, 124.6, 122.8, 122.7, 119.5, 114.7; HRMS calcd for $C_{20}H_{15}ClNS$ $[M+H]^+$ 336.0608; found: 336.0605.



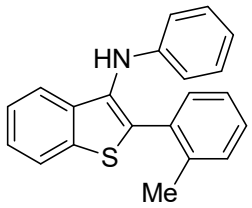
2-(4-bromophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3l)

White solid (70.49 mg, 62% yield). melting point: 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 8.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.48 (s, 4 H), 7.37-7.27 (m, 2 H), 7.18 (t, *J* = 8.0 Hz, 2 H), 6.83 (t, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.44 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.1, 137.3, 137.0, 133.2, 132.2, 130.1, 129.9, 129.6, 125.2, 124.6, 122.8, 122.7, 122.5, 119.5, 114.7; HRMS calcd for $C_{20}H_{15}BrNS$ $[M+H]^+$ 380.0103; found: 380.0106.



2-([1,1'-biphenyl]-4-yl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3m)

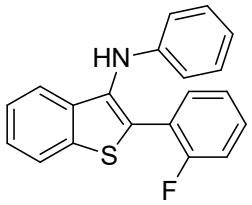
Grey solid (73.08 mg, 66% yield). melting point: 137-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.39-7.28 (m, 2 H), 7.20-7.16 (m, 2 H), 6.84 (d, *J* = 7.2 Hz, 1 H), 6.70-6.68 (m, 2 H), 5.46 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 145.9, 137.3, 137.2, 137.0, 132.6, 130.7, 129.6, 128.8, 126.0 (q, *J* = 4.0 Hz, 1 C), 125.6, 124.7, 122.9 (d, *J* = 6.0 Hz, 1 C), 119.7, 114.8; HRMS calcd for $C_{21}H_{15}F_3NS$ $[M+H]^+$ 370.0872; found: 370.0864.



***N*-phenyl-2-(*o*-tolyl)benzo[*b*]thiophen-3-amine (3n)**

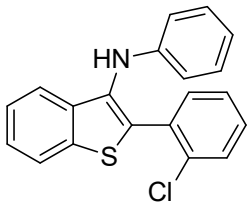
Yellow soild (57.66 mg, 61% yield). melting point: 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H), 7.37-7.18 (m, 6 H), 7.13 (t, *J* = 8.0 Hz, 2 H), 6.80 (d, *J* = 7.6 Hz, 1 H), 6.68 (d, *J* = 8.0 Hz, 2 H), 5.42

(s, 1 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 145.5, 138.3, 138.0, 135.7, 132.2, 131.4, 131.2, 131.1, 130.7, 129.2, 128.9, 126.1, 124.7, 124.1, 123.1, 122.7, 119.5, 115.6, 20.6; HRMS calcd for $C_{21}H_{18}NS$ $[M+H]^+$ 316.1155; found: 316.1164.



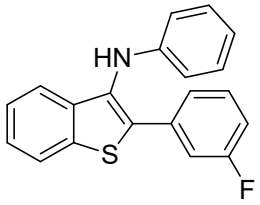
2-(2-fluorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3o)

Yellow soild (64.14 mg, 67% yield). melting point: 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.41-7.27 (m, 5 H), 7.18 (t, *J* = 8.0 Hz, 2 H), 7.02-6.98 (m, 1 H), 6.83 (t, *J* = 7.2 Hz, 1 H), 6.70 (d, *J* = 7.6 Hz, 2 H), 5.49 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.3, 161.9, 146.0, 137.2 (d, *J* = 11.0 Hz, 1 C), 135.4 (d, *J* = 8.0 Hz, 1 C), 130.5 (d, *J* = 8.0 Hz, 1 C), 130.3, 129.6, 125.3, 124.6, 124.3 (d, *J* = 3.0 Hz, 1 C), 122.8 (d, *J* = 5.0 Hz, 1 C), 119.6, 115.6, 115.3 (d, *J* = 10.0 Hz, 1 C), 115.1, 114.9, 100.1; HRMS calcd for $C_{20}H_{15}FNS$ $[M+H]^+$ 320.0904; found: 320.0904.



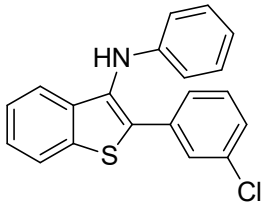
2-(2-chlorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3p)

Yellow soild (63.32 mg, 63% yield). melting point: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.83 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.48-7.42 (m, 2 H), 7.39-7.35 (m, 1 H), 7.32-7.25 (m, 3 H), 7.11 (t, *J* = 8.0 Hz, 2 H), 6.77 (t, *J* = 7.6 Hz, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 5.59 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 145.5, 138.2, 135.7, 134.5, 132.9, 132.0, 130.1, 129.2, 129.1, 127.0, 125.1, 124.2, 123.3, 122.7, 119.3, 115.4; HRMS calcd for $C_{20}H_{15}ClNS$ $[M+H]^+$ 336.0608; found: 336.0605.



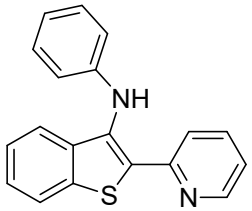
2-(3-fluorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3q)

Yellow solid (45.95 mg, 48% yield). melting point: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.41-7.27 (m, 5 H), 7.20-7.16 (m, 2 H), 7.02-6.98 (m, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.71-6.69 (m, 2 H), 5.49 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.3, 161.8, 146.0, 137.2 (d, *J* = 11.0 Hz, 1 C), 135.4 (d, *J* = 9.0 Hz, 1 C), 132.7, 130.5 (d, *J* = 8.0 Hz, 1 C), 130.2, 129.5, 125.3, 124.6, 124.3 (d, *J* = 3.0 Hz, 1 C), 122.8 (d, *J* = 5.0 Hz, 1 C), 119.6, 115.6, 115.3 (d, *J* = 9.0 Hz, 1 C), 115.1, 114.8; HRMS calcd for $C_{20}H_{15}FNS$ $[M+H]^+$ 320.0904; found: 320.0904.



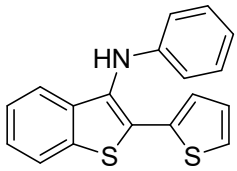
2-(3-chlorophenyl)-*N*-phenylbenzo[*b*]thiophen-3-amine (3r)

Yellow solid (48.25 mg, 48% yield). melting point: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 8.0 Hz, 1 H), 7.59 (s, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.50-7.47 (m, 1 H), 7.37-7.25 (m, 4 H), 7.17 (t, *J* = 8.0 Hz, 2 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.68 (d, *J* = 7.6 Hz, 2 H), 5.46 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.0, 137.2, 137.1, 135.1, 134.9, 132.5, 130.3, 130.2, 129.5, 128.6, 128.3, 126.6, 125.3, 124.6, 122.9, 122.8, 119.6, 114.8; HRMS calcd for $C_{20}H_{15}ClNS$ $[M+H]^+$ 336.0608; found: 336.0608.



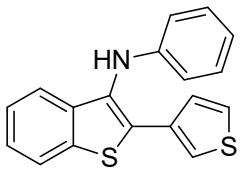
***N*-phenyl-2-(pyridin-2-yl)benzo[*b*]thiophen-3-amine (3s)**

Yellow solid (60.72mg, 67% yield). melting point: 150-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.68 (s, 1 H), 8.56 (d, *J* = 4.0 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.70-7.65 (m, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.36-7.32 (m, 1 H), 7.24-7.20 (m, 3 H), 7.11-7.08 (m, 1 H), 6.97-6.90 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.4, 148.6, 144.6, 137.5, 137.1, 136.9, 135.5, 129.1, 125.7, 124.6, 123.8, 122.9, 121.9, 121.6, 121.1, 121.0, 118.9; HRMS calcd for $C_{19}H_{15}N_2S$ [M+H]+ 303.0951; found: 303.0954



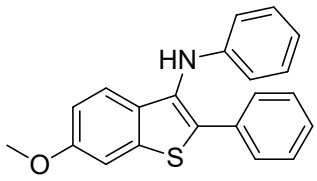
***N*-phenyl-2-(thiophen-2-yl)benzo[*b*]thiophen-3-amine (3t)**

Yellow solid (47.90 mg, 52% yield). melting point: 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.76 (d, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.36-7.25 (m, 4 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.05-7.03 (m, 1 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.39 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 145.7, 137.5, 136.3, 134.7, 130.8, 129.5, 128.9, 127.2, 126.9, 126.1, 125.3, 124.7, 122.7, 122.3, 119.3, 114.4; HRMS calcd for $C_{18}H_{14}NS_2$ [M+H]+ 308.0562; found: 308.0565.



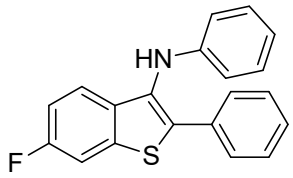
***N*-phenyl-2-(thiophen-3-yl)benzo[*b*]thiophen-3-amine (3u)**

White solid (37.77 mg, 41% yield). melting point: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.78 (d, *J* = 7.6 Hz, 1 H), 7.55-7.52 (m, 2 H), 7.40-7.38 (m, 1 H), 7.35-7.27 (m, 3 H), 7.20-7.16 (m, 2 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.42 (s, 1 H); ^{13}C NMR (100 MHz, CDCl3, ppm): δ = 146.3, 137.6, 136.6, 133.6, 130.9, 129.6, 129.0, 127.4, 126.4, 125.0, 124.6, 123.4, 122.7, 122.3, 119.3, 114.4; HRMS calcd for $C_{18}H_{14}NS_2$ [M+H]+ 308.0562; found: 308.0564.



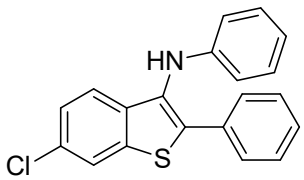
6-methoxy-*N*,2-diphenylbenzo[*b*]thiophen-3-amine (3v)

Brown oil (57.61 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.59-7.57 (m, 2 H), 7.41-7.34 (m, 3 H), 7.31-7.27 (m, 2 H), 7.21-7.17 (m, 2 H), 6.93-6.90 (m, 1 H), 6.83 (t, *J* = 7.2 Hz, 1 H), 6.72 (d, *J* = 7.6 Hz, 2 H), 5.50 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.0, 146.4, 138.5, 133.5, 129.5, 129.1, 128.5, 123.5, 119.3, 114.9, 114.4, 105.3, 55.8; HRMS calcd for $C_{21}H_{18}NOS$ [M+H]+ 332.1104; found: 332.1106.



6-fluoro-*N*,2-diphenylbenzo[*b*]thiophen-3-amine (3w)

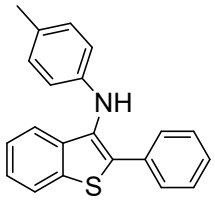
White solid (63.18 mg, 66% yield). melting point: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.55 (m, 2 H), 7.50-7.43 (m, 2 H), 7.39-7.31 (m, 3 H), 7.21-7.17 (m, 2 H), 7.05-7.00 (m, 1 H), 6.84 (t, *J* = 7.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.49 (s, 1 H); ^{13}C NMR (100 MHz, CDCl3, ppm): δ = 160.9 (d, *J* = 244 Hz, 1 C), 146.2, 138.0 (d, *J* = 10.0 Hz, 1 C), 133.7, 133.1, 129.6, 129.2, 128.6, 128.4, 124.0 (d, *J* = 9.0 Hz, 1 C), 119.6, 114.9, 113.4 (d, *J* = 24.0 Hz, 1 C), 108.9 (d, *J* = 25.0 Hz, 1 C); HRMS calcd for $C_{20}H_{15}FNS$ [M+H]+ 320.0904; found: 320.0908.



6-chloro-*N*,2-diphenylbenzo[*b*]thiophen-3-amine (3x)

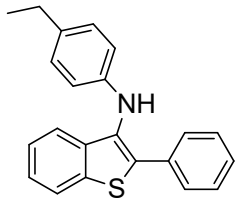
Yellow solid (71.37 mg, 71% yield). melting point: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.78 (s, 1 H), 7.57(d, *J* = 7.2 Hz,, 2 H), 7.42-7.32 (m, 4 H), 7.25-7.17 (m, 3 H), 6.84 (t, *J* = 7.2 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 5.48 (s, 1 H); ^{13}C

NMR (100 MHz, CDCl3, ppm): δ = 146.1, 138.1, 135.8, 134.5, 132.9, 131.0, 129.6, 129.2, 128.6, 128.5, 127.7, 125.3, 123.7, 122.3, 119.6, 114.9; HRMS calcd for $C_{20}H_{15}ClNS$ [M+H]+ 336.0608; found: 336.0610.



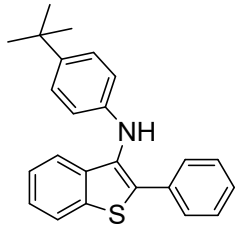
2-phenyl-*N*-(*p*-tolyl)benzo[*b*]thiophen-3-amine (4a)

Yellow solid (50.10 mg, 53% yield). melting point: 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 6.8 Hz, 2 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.40-7.26 (m, 5 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 8.4 Hz, 2 H), 5.46 (s, 1 H), 2.27 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.0, 137.3, 137.2, 133.5, 130.1, 130.0, 129.1, 128.7, 128.3, 124.9, 124.3, 122.9, 122.7, 115.1, 20.7; HRMS calcd for $C_{21}H_{18}NS$ $[M+H]^+$ 316.1155; found: 316.1156.



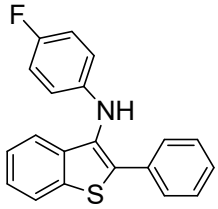
***N*-(4-ethylphenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4b)**

Yellow solid (45.42 mg, 46% yield). melting point: 106-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.79 (d, *J* = 7.8 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.37-7.26 (m, 5 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 7.8 Hz, 2 H), 5.45 (s,1 H), 2.59-2.55 (m, 2 H), 1.20 (t, *J* = 7.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 144.2, 137.3, 137.1, 135.2, 133.5, 133.4, 130.1, 129.1, 128.8, 128.7, 128.2, 124.9, 124.3, 122.9, 122.7, 115.1, 28.1, 15.8; HRMS calcd for $C_{22}H_{20}NS$ $[M+H]^+$ 330.1311; found: 330.1312.



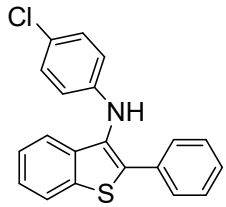
***N*-(4-(*tert*-butyl)phenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4c)**

Grey solid (46.07 mg, 43% yield). melting point: 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 6.8 Hz, 2 H), 7.53 (d, *J* = 7.2 Hz, 1 H), 7.39-7.26 (m, 5 H), 7.19 (d, *J* = 8.8 Hz, 2 H), 6.68-6.64 (m, 2 H), 5.48 (s, 1 H), 1.28 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.8, 142.2, 137.3, 137.1, 133.5, 133.2, 130.2, 129.1, 128.7, 128.2, 126.2, 124.9, 124.3, 123.0, 122.7, 114.8. 34.1, 31.7; HRMS calcd for $C_{24}H_{24}NS$ $[M+H]^+$ 358.1624; found: 358.1625.



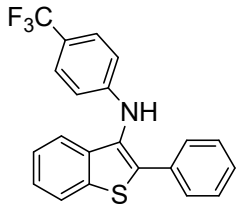
***N*-(4-fluorophenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4d)**

Grey solid (65.09 mg, 68% yield). melting point: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.57 (d, *J* = 7.2 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 1 H), 7.40-7.29 (m, 5 H), 6.91-6.85 (m, 2 H), 6.67-6.62 (m, 2 H), 5.45 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.2, 155.8, 142.5, 137.1 (d, *J* = 17.0 Hz, 1 C), 133.8, 133.3, 129.8, 129.1, 128.6, 128.4, 125.0, 124.5, 122.7 (d, *J* = 25.0 Hz, 1 C), 116.1, 116.0, 115.9 (d, *J* = 3.0 Hz, 1 C); HRMS calcd for $C_{20}H_{15}FNS$ $[M+H]^+$ 320.0904; found: 320.0905.



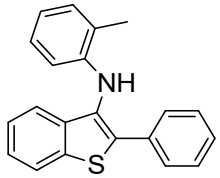
***N*-(4-chlorophenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4e)**

White solid (62.32 mg, 62% yield). melting point: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 7.6 Hz, 1 H), 7.57 (d, *J* = 6.8 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 1 H), 7.40-7.30 (m, 5 H), 7.14-7.10 (m, 2 H), 6.64-6.60 (m, 2 H), 5.49 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 145.1, 137.2, 137.1, 134.9, 133.1, 129.4, 129.1, 128.9, 128.7, 128.5, 125.1, 124.6, 124.0, 122.8, 122.5, 115.8; HRMS calcd for $C_{20}H_{15}ClNS$ $[M+H]^+$ 336.0608; found: 336.0608.



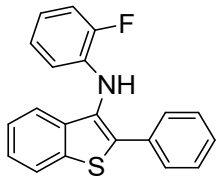
2-phenyl-*N*-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophen-3-amine (4f)

White solid (81.94 mg, 74% yield). melting point: 146-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 6.8 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.42-7.31 (m, 7 H), 6.70 (d, *J* = 8.4 Hz, 2 H), 5.69 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.3, 137.0 (d, *J* = 13.0 Hz, 1 C), 136.4, 132.9, 129.2, 128.7, 127.9, 126.9 (q, 1 C), 126.3, 125.2, 124.7, 123.6, 122.9, 122.4, 121.0, 120.7, 113.8; HRMS calcd for $C_{21}H_{15}F_3NS$ $[M+H]^+$ 370.0872; found: 370.0877.



2-phenyl-*N*-(*o*-tolyl)benzo[*b*]thiophen-3-amine (4g)

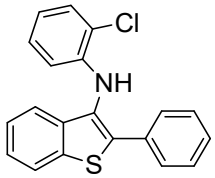
Brown oil (48.21 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 7.6 Hz, 1 H), 7.58 (d, *J* = 7.2 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.39-7.28 (m, 5 H), 7.18 (d, *J* = 7.2 Hz, 1 H), 7.01-6.97 (m, 1 H), 6.79 (d, *J* = 7.6 Hz, 1 H), 6.55 (d, *J* = 8.0 Hz, 1 H), 5.35 (s, 1 H), 2.30 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.3, 137.3, 137.1, 133.6, 133.4, 130.5, 130.0, 129.2, 128.5, 128.3, 127.2, 125.0, 124.4, 123.4, 122.8, 122.7, 119.4, 114.0, 17.9; HRMS calcd for $C_{21}H_{18}NS$ $[M+H]^+$ 316.1155; found: 316.1156.



***N*-(2-fluorophenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4h)**

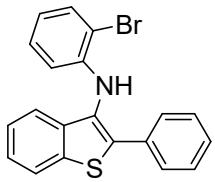
Yellow oil (58.39 mg, 61% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 7.8 Hz, 1 H), 7.61 (d, *J* = 7.8 Hz, 2 H), 7.53 (d, *J* = 7.8 Hz, 1 H) 7.39-7.30 (m, 5 H), 7.10-7.07 (m, 1 H), 6.84 (t, *J* = 7.8 Hz, 1 H), 6.72 (d, *J* = 4.8 Hz, 1 H), 6.55 (t, *J* = 8.4

Hz, 1 H), 5.69 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 152.6, 151.0, 137.4, 137.2, 135.7, 134.6 (d, *J* = 10.5 Hz, 1 C), 133.1, 131.8, 129.1, 128.5 (d, *J* = 10.5 Hz, 1 C), 125.1, 124.7 (d, *J* = 3.0 Hz, 1 C), 124.6, 122.8, 122.4, 118.8 (d, *J* = 7.5 Hz, 1 C), 115.1 (d, *J* = 6.0 Hz, 1 C), 115.0; HRMS calcd for $C_{20}H_{15}FNS$ $[M+H]^+$ 320.0904; found: 320.0915.



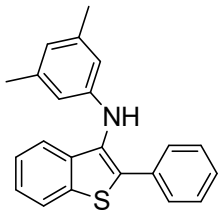
***N*-(2-chlorophenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4i)**

Yellow oil (67.34 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 7.6 Hz, 1 H), 7.63-7.61 (m, 2 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.39-7.29 (m, 6 H), 6.99-6.95 (m, 1 H), 6.74-6.70 (m, 1 H), 6.54-6.51 (m, 1 H), 6.03 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 142.4, 137.4, 137.0, 136.3, 133.0, 129.5, 129.1, 128.5, 128.4, 128.2, 127.9, 125.2, 124.6, 122.8, 122.3, 119.7, 119.3, 114.4; HRMS calcd for $C_{20}H_{15}NSCl$ $[M+H]^+$ 336.0608; found: 336.0616.



***N*-(2-bromophenyl)-2-phenylbenzo[*b*]thiophen-3-amine (4j)**

Yellow oil (65.95 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 7.6 Hz, 1 H), 7.64-7.61 (m, 2 H), 7.53-7.48 (m, 2 H), 7.40-7.29 (m, 5 H), 7.03-6.98 (m, 1 H), 6.68-6.64 (m, 1 H), 6.52-6.50 (m, 1 H), 6.04 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.3, 137.4, 137.0, 136.3, 133.0, 132.7, 129.1, 128.6, 128.5, 128.4, 128.3, 125.2, 124.7, 122.8, 122.4, 119.8, 114.5, 109.9; HRMS calcd for $C_{20}H_{15}BrNS$ $[M+H]^+$ 380.0103; found: 380.0104.



_N_-(3,5-dimethylphenyl)-2-phenylbenzo[_b_]thiophen-3-amine (4k)

Brown oil (51.34 mg, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 7.8 Hz, 1 H), 7.61 (d, *J* = 7.8 Hz, 2 H), 7.53 (d, *J* = 7.8 Hz, 1 H), 7.39-7.27 (m, 5 H), 6.49 (s, 1 H), 6.35 (s, 2 H), 5.41 (s, 1 H), 2.20 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 146.4, 139.2, 137.5, 137.0, 133.9, 133.4, 129.8, 129.1, 128.7, 128.3, 124.9, 124.4, 122.9, 122.7, 121.4, 112.8, 21.6; HRMS calcd for $C_{22}H_{20}NS$ $[M+H]^+$ 330.1311; found: 330.1312.

Reference:

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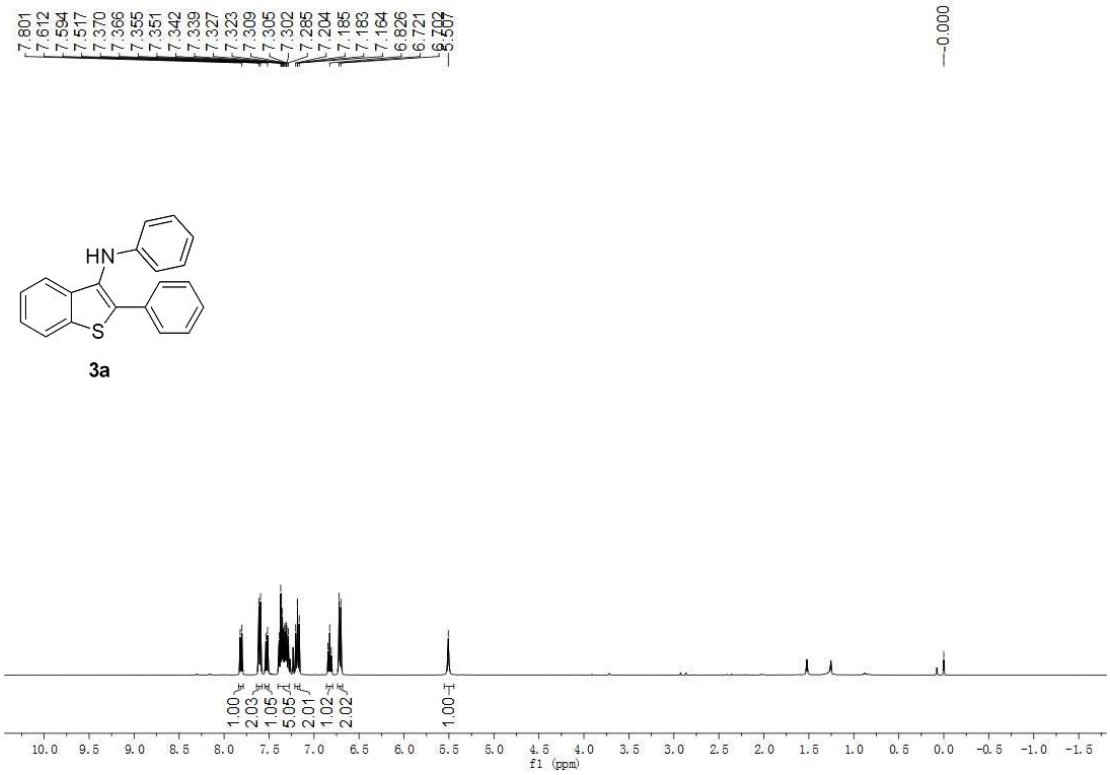
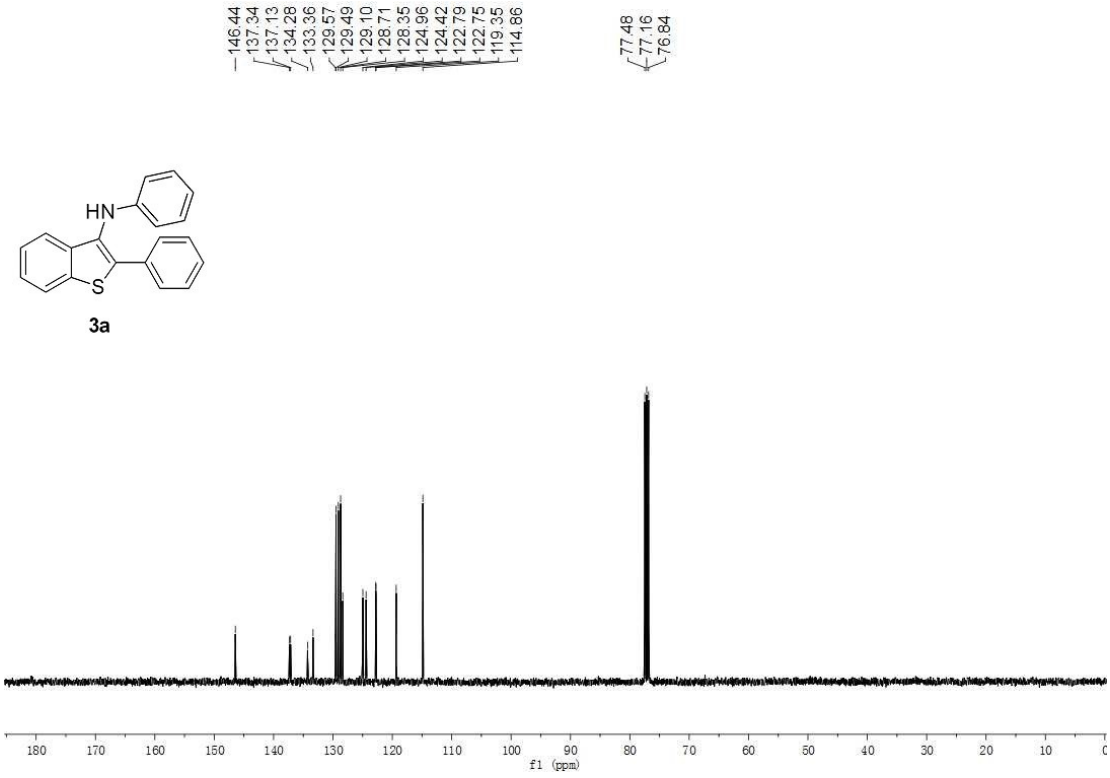
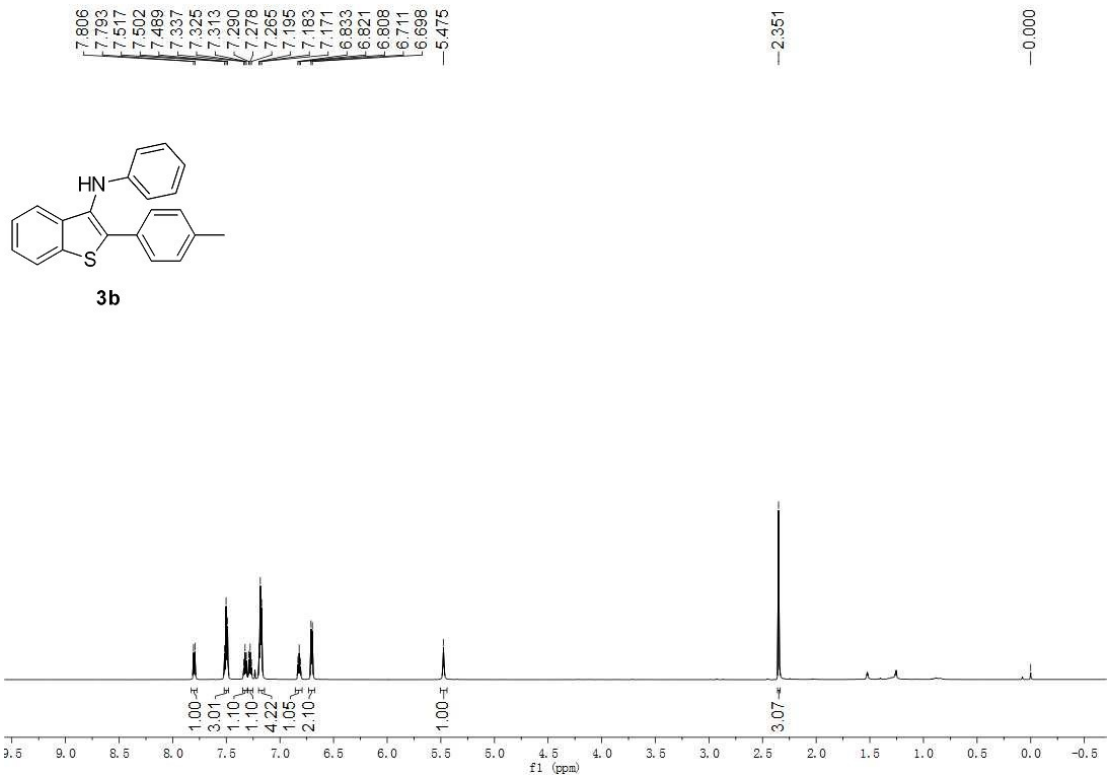
Copies of NMR spectra



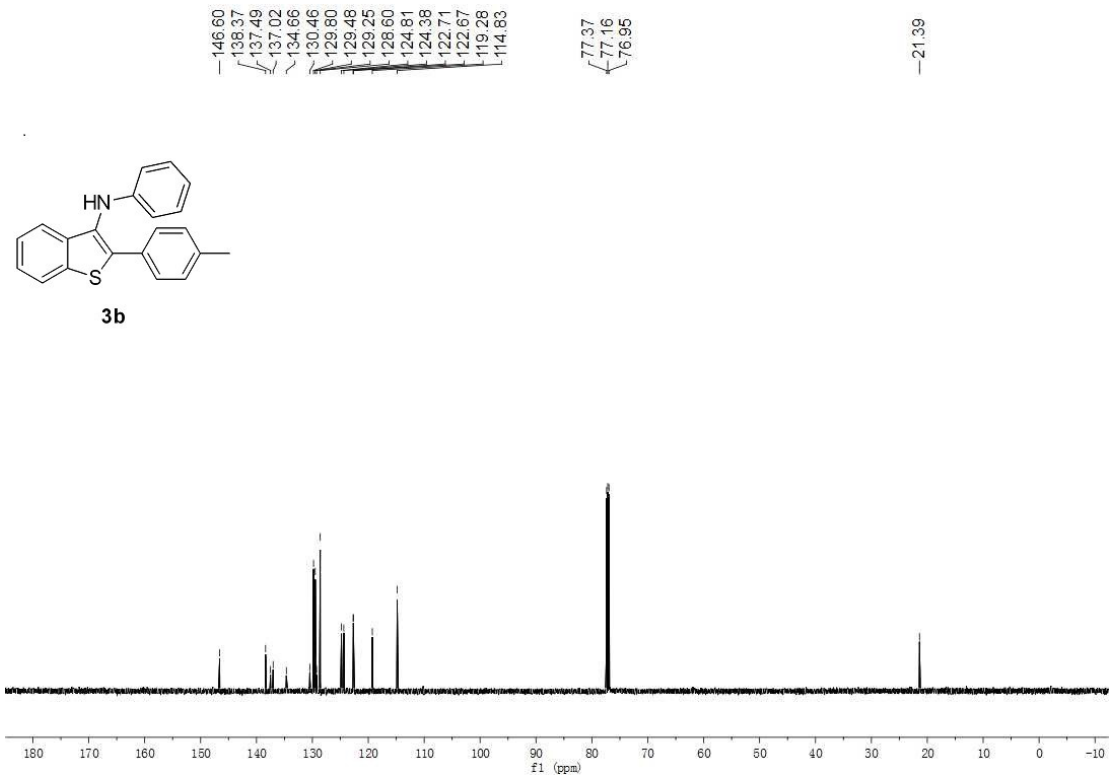
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



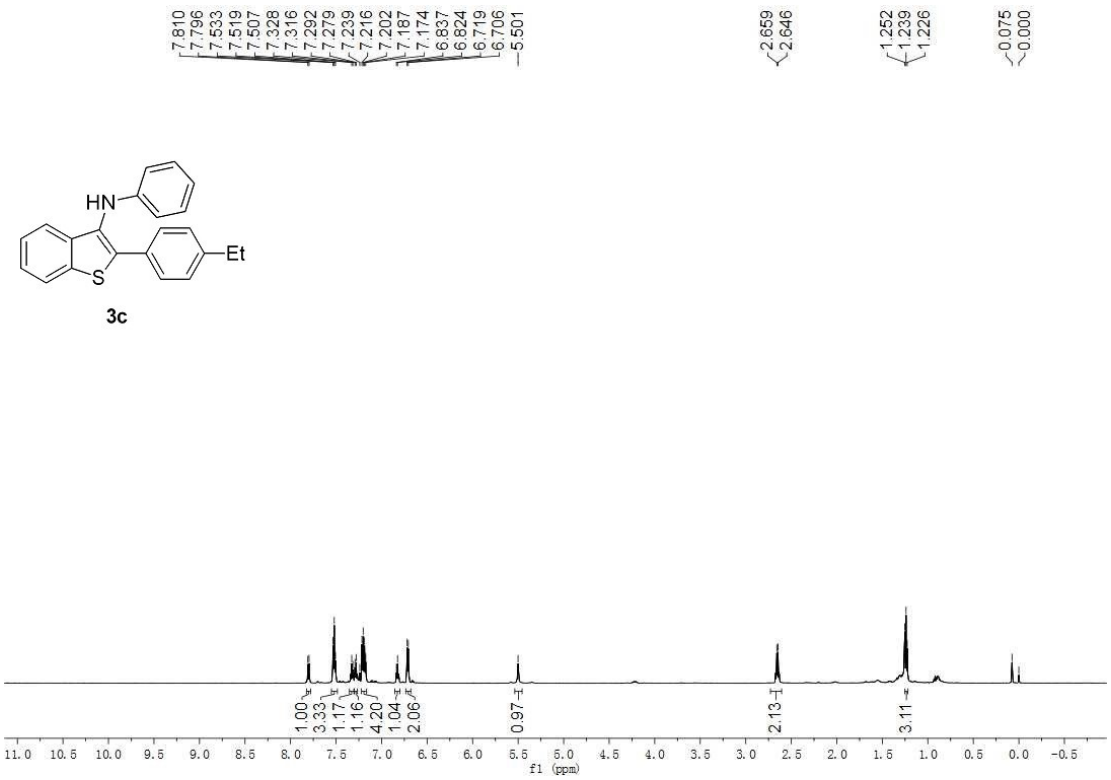
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



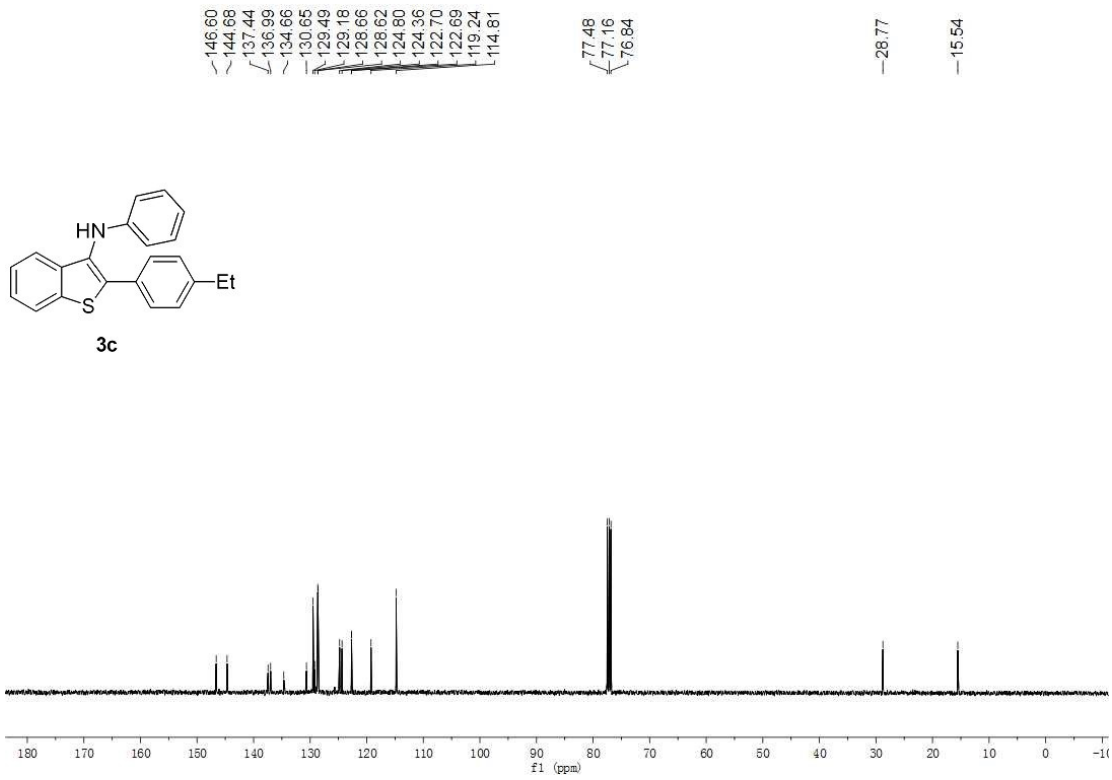
^{1}H NMR spectrum of **3b** (600 MHz, $CDCl_3$)



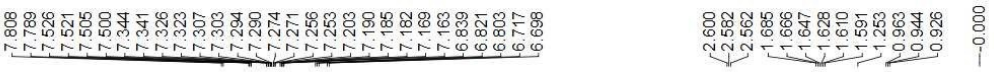
^{13}C NMR spectrum of **3b** (150 MHz, $CDCl_3$)

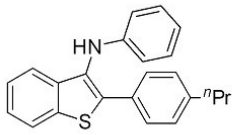


^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

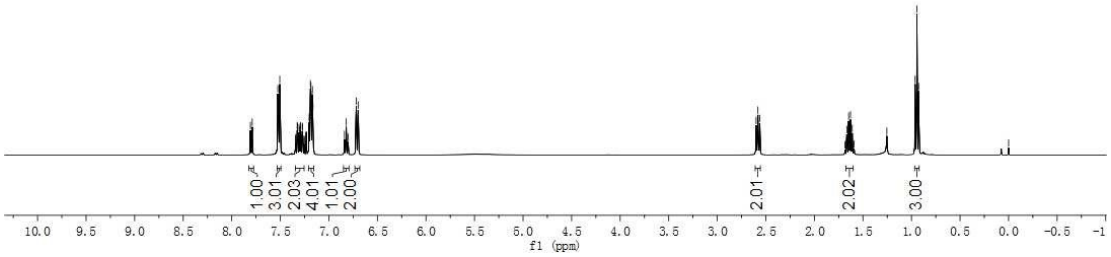


^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)





3d



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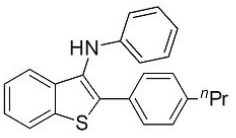
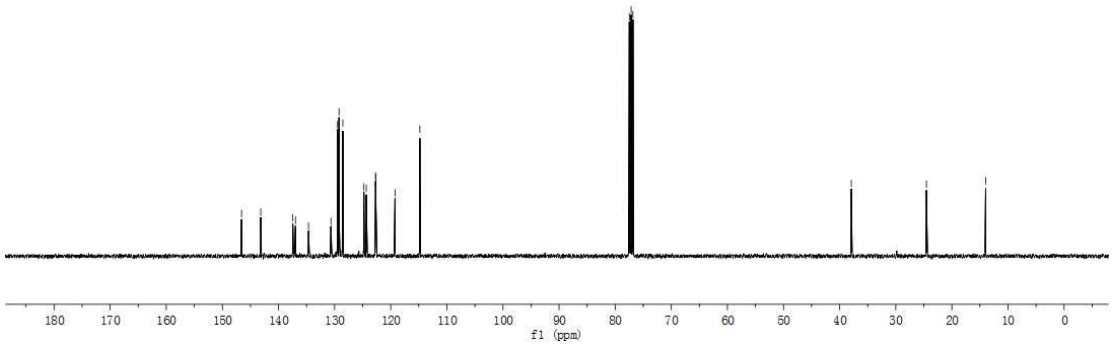
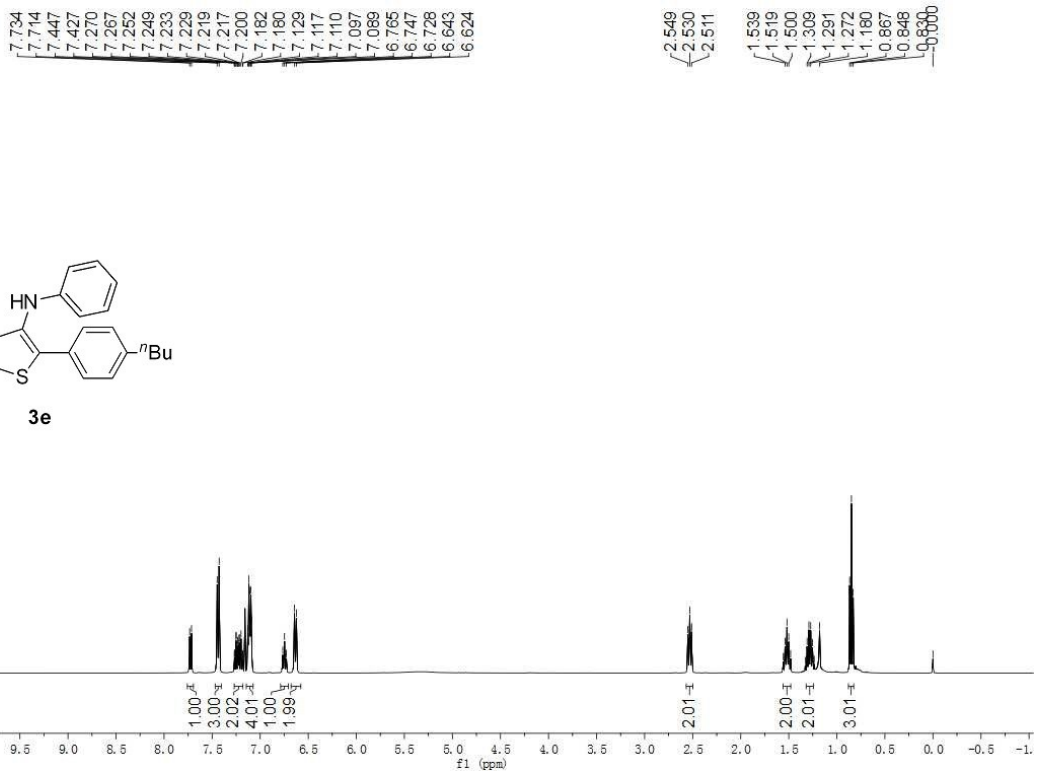


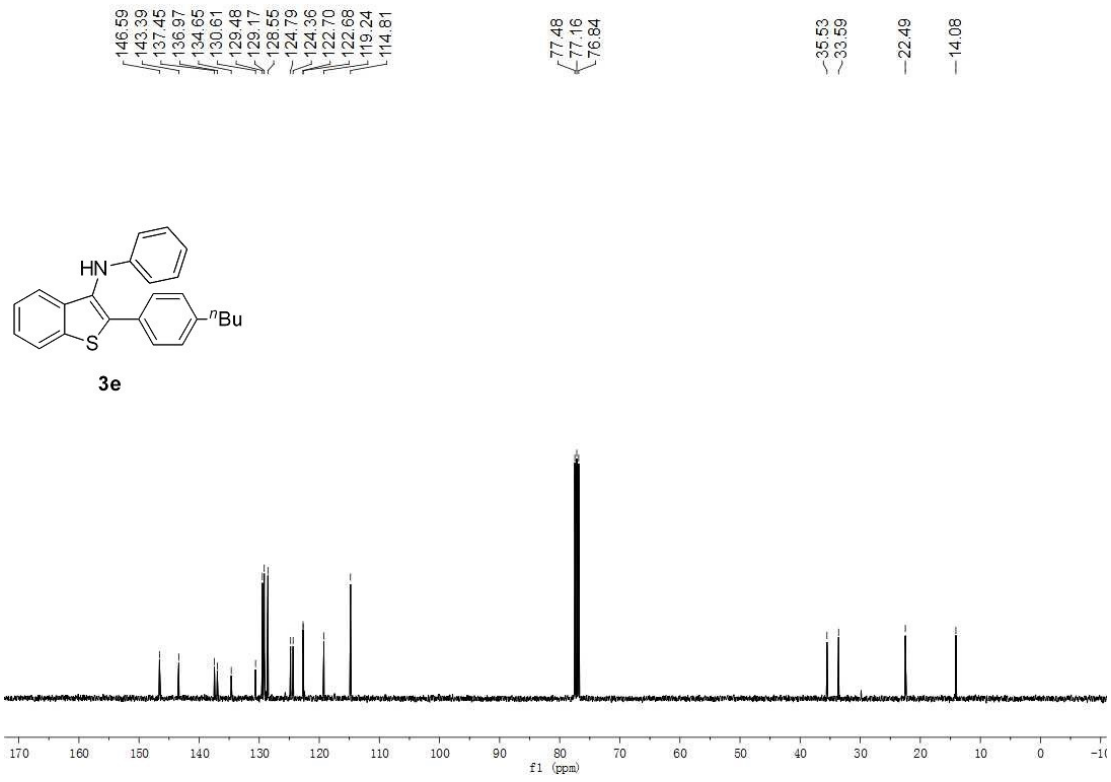
3d



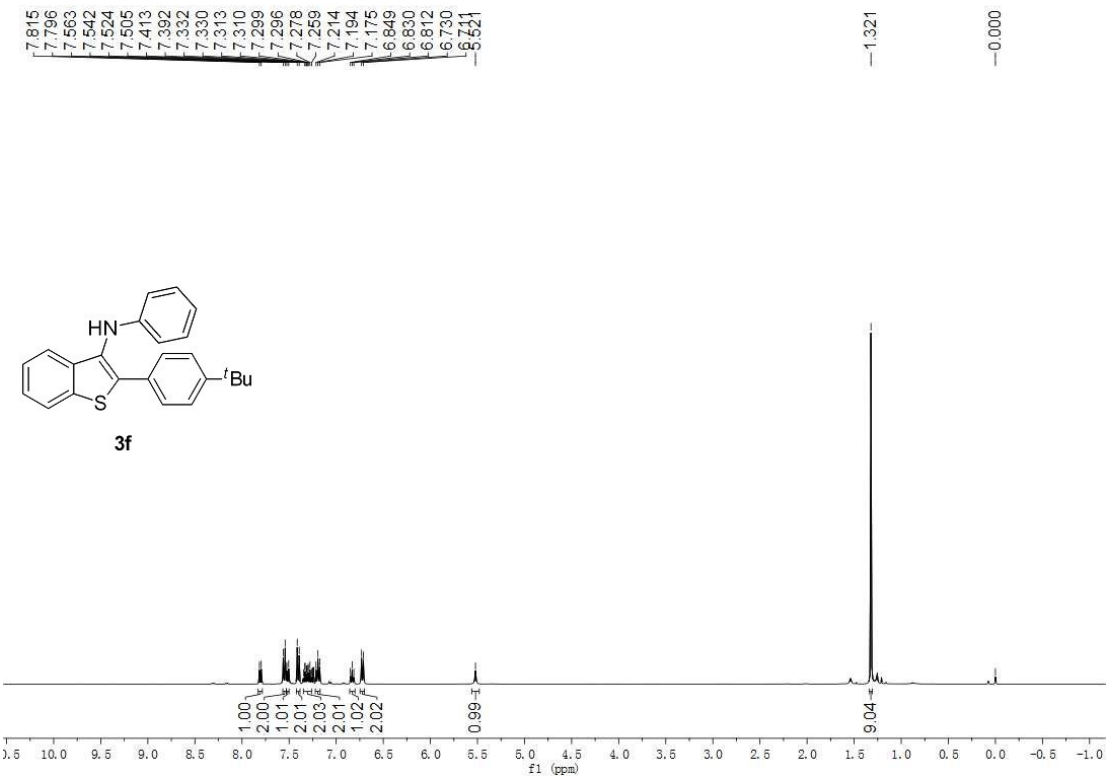
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



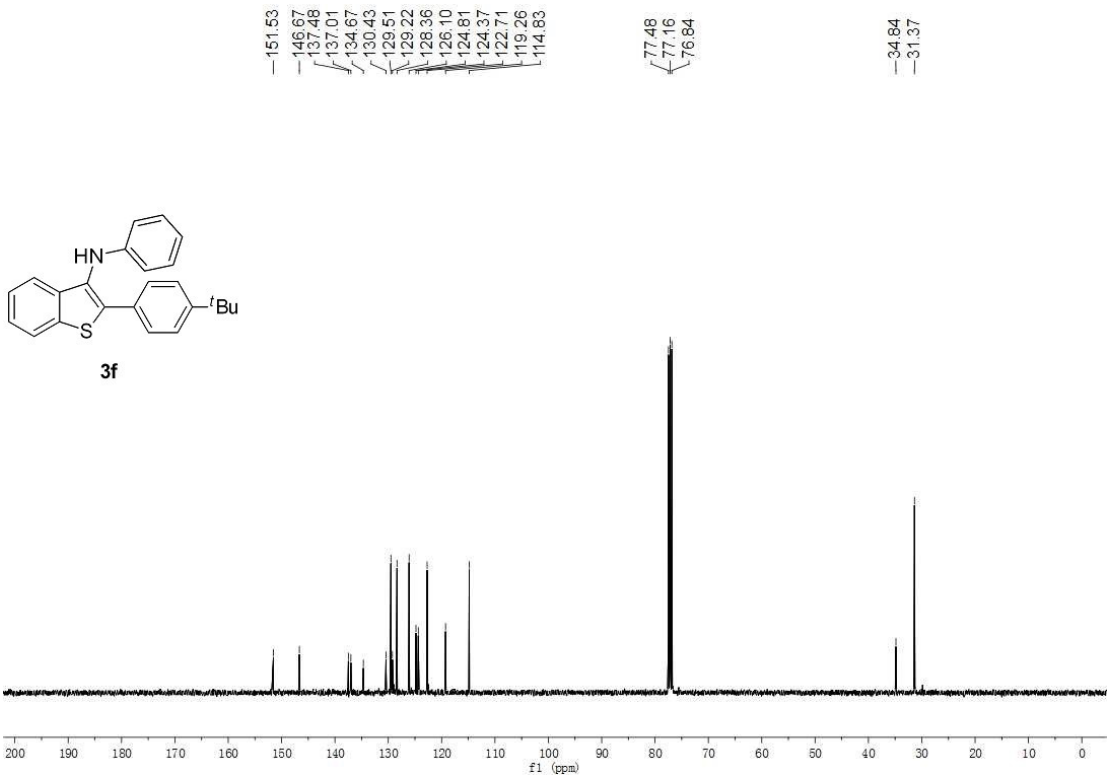
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



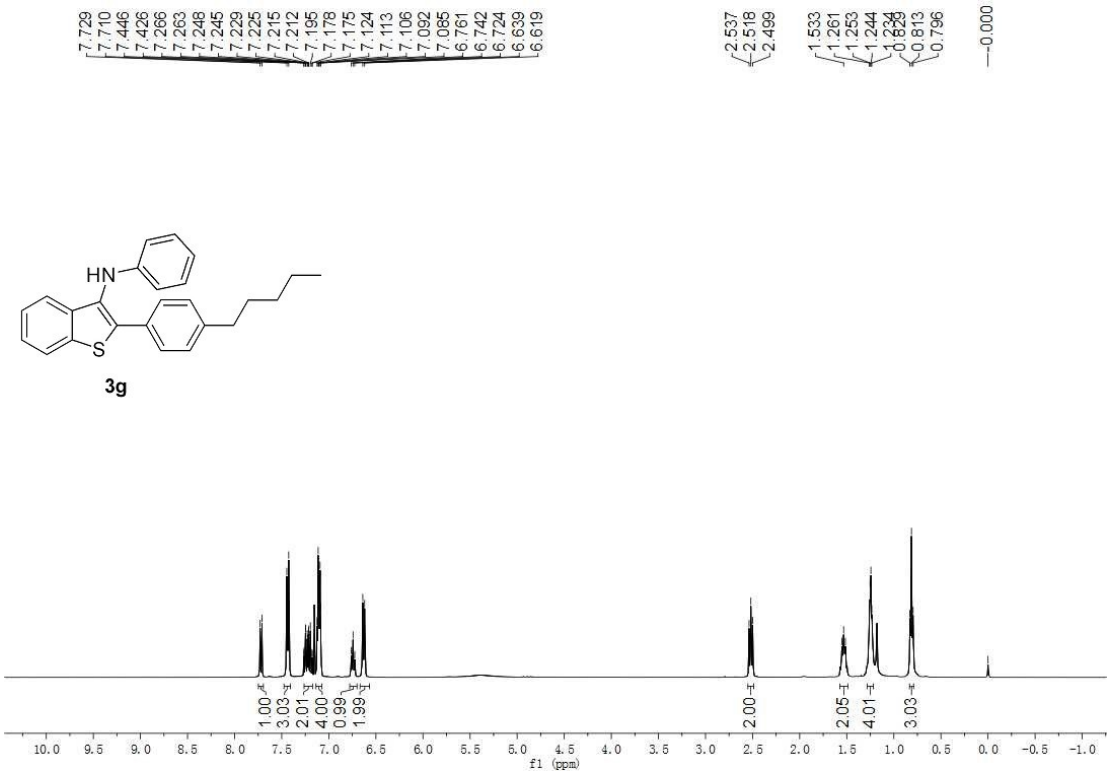
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



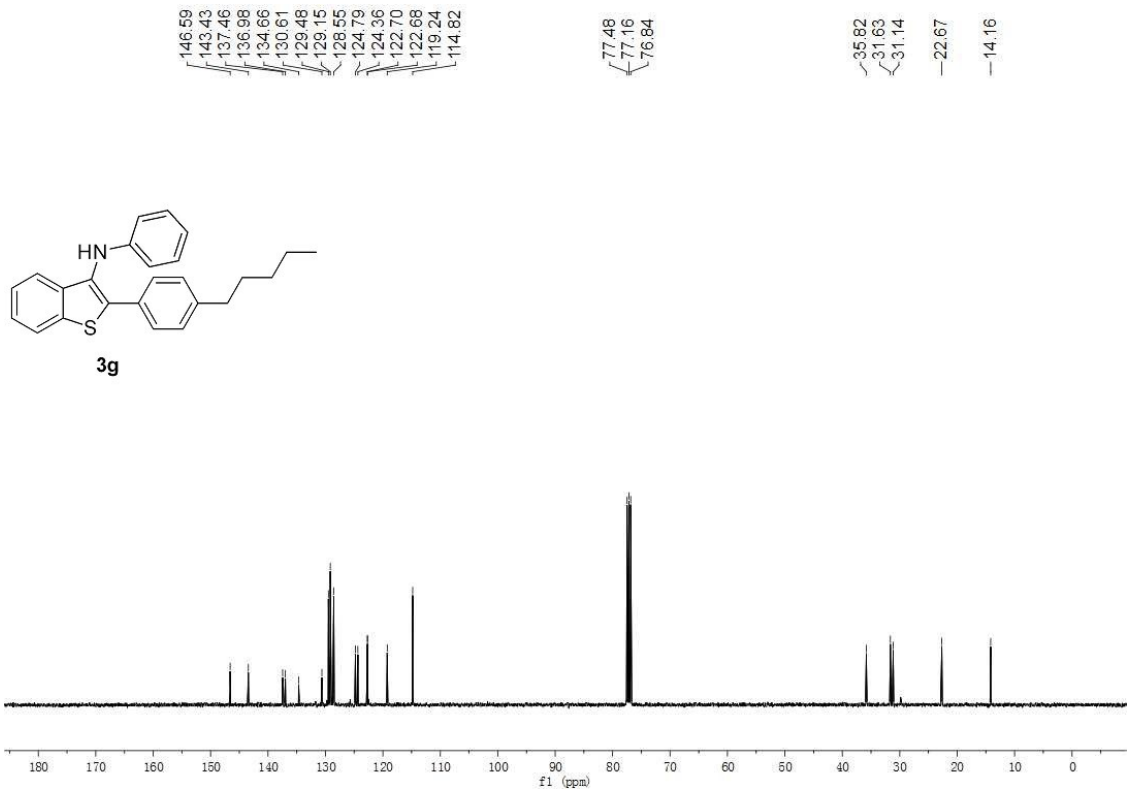
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



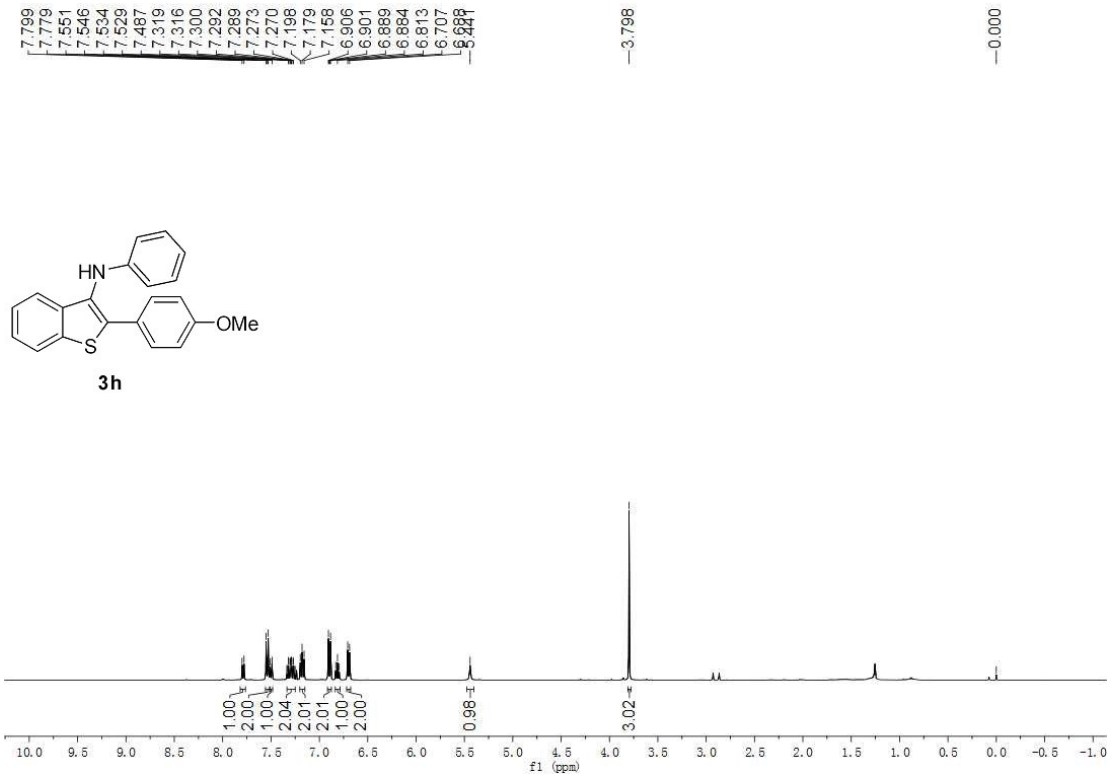
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



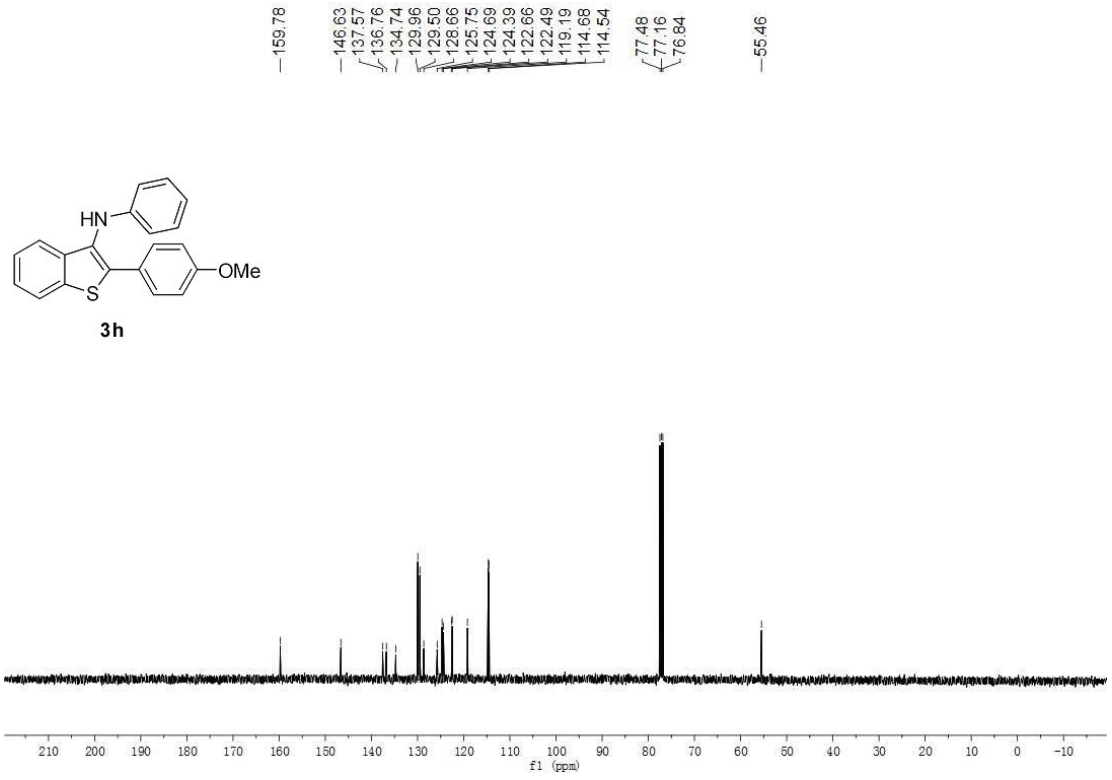
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



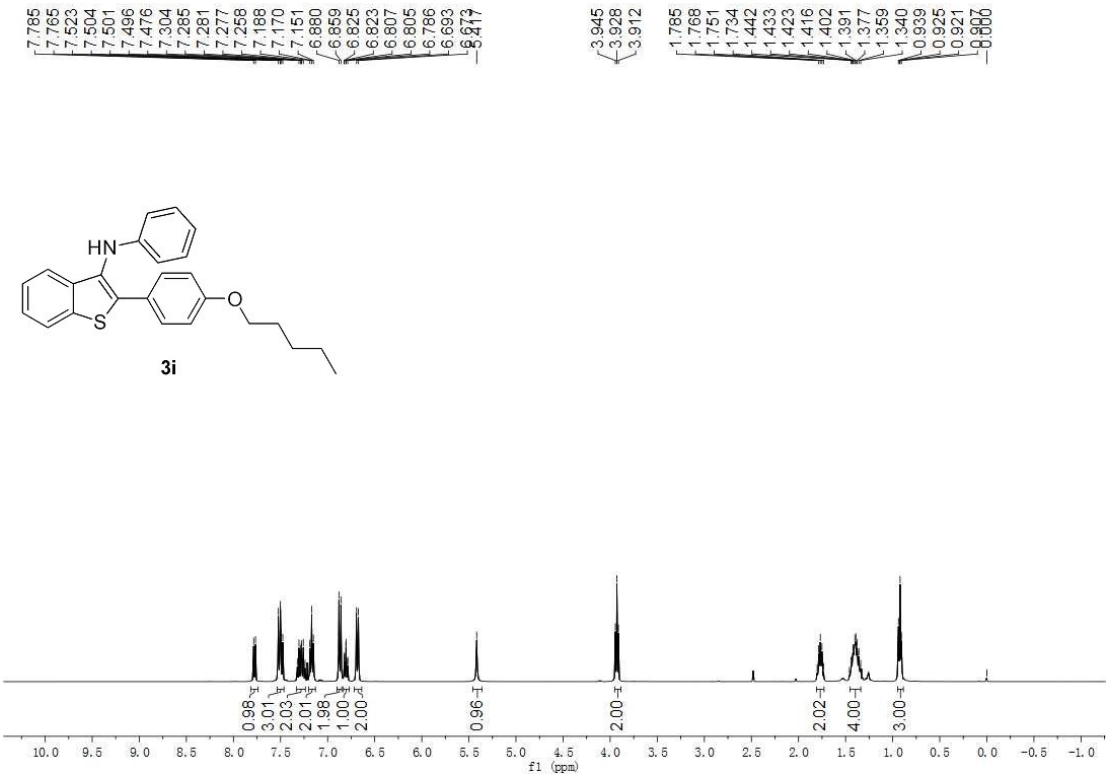
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



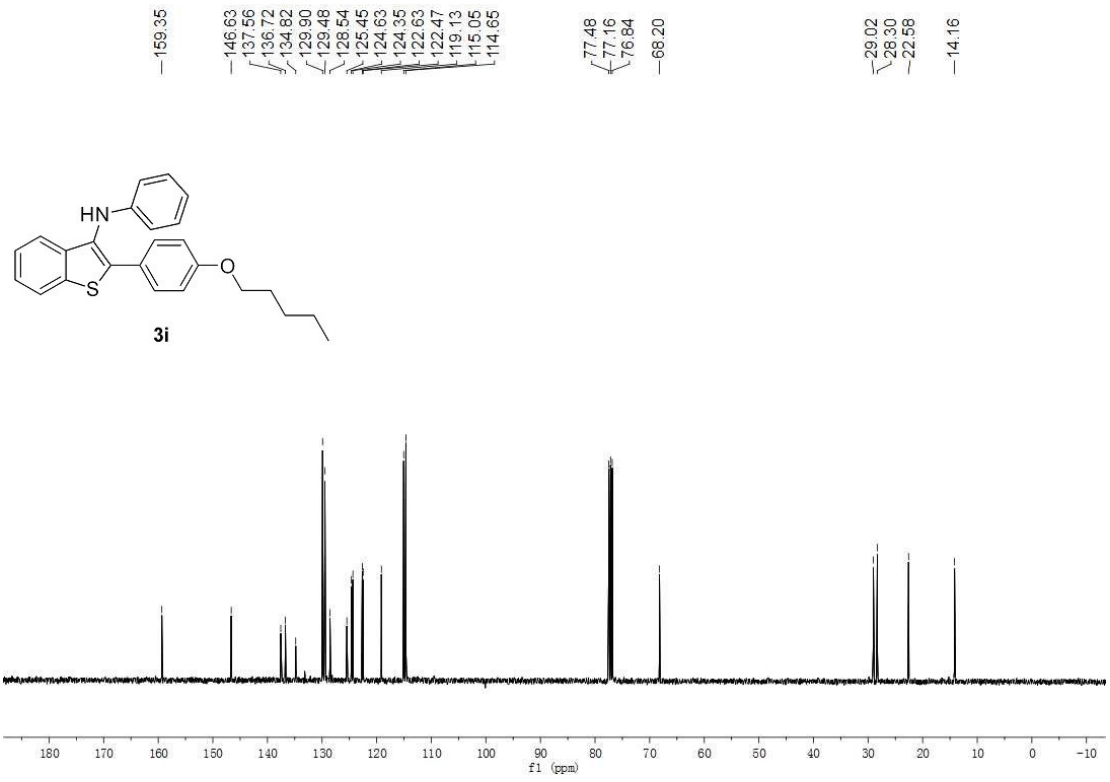
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



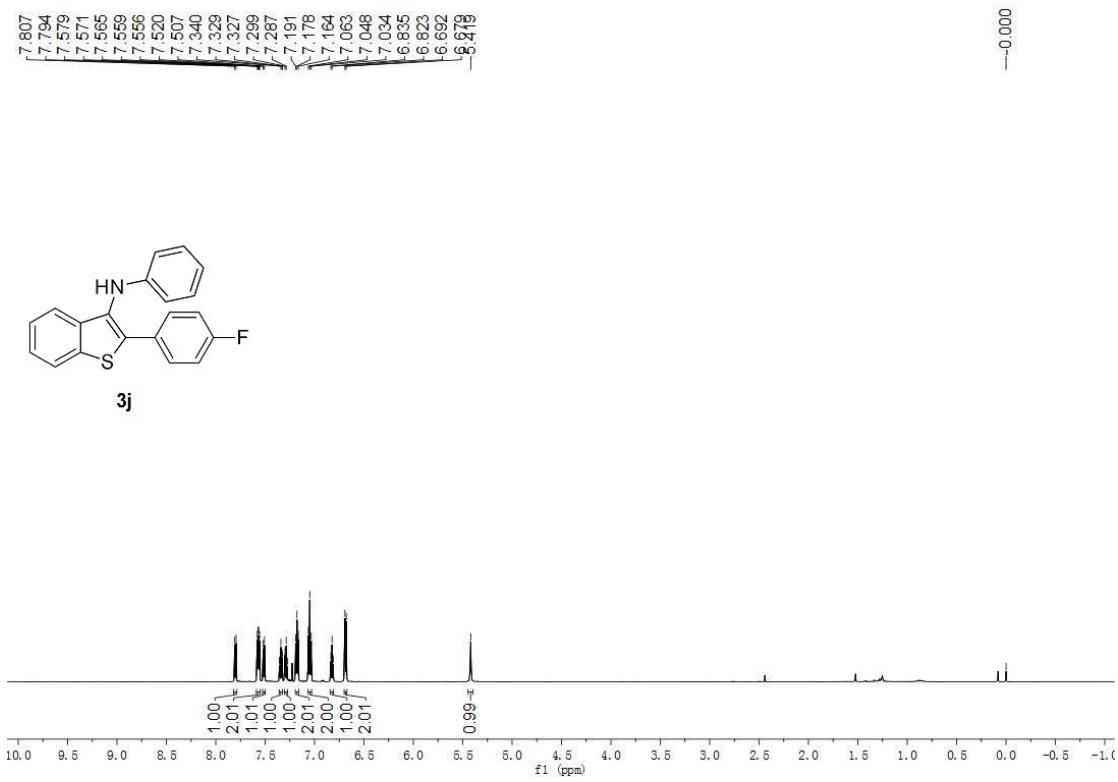
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



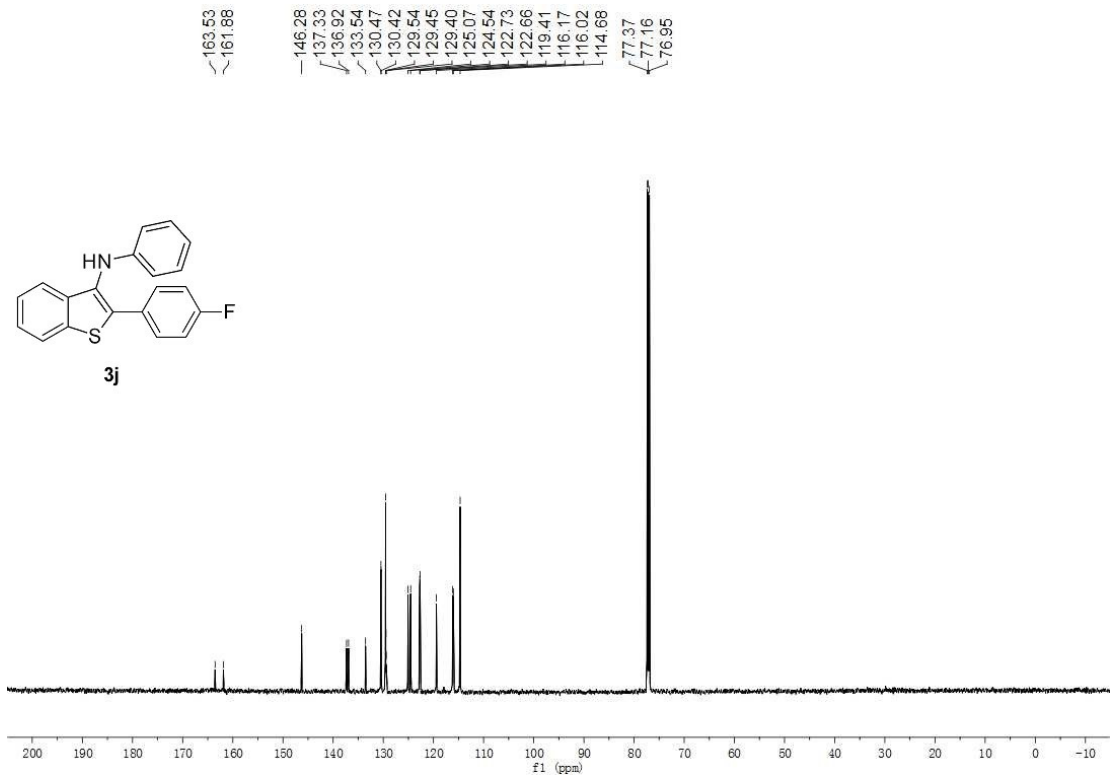
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



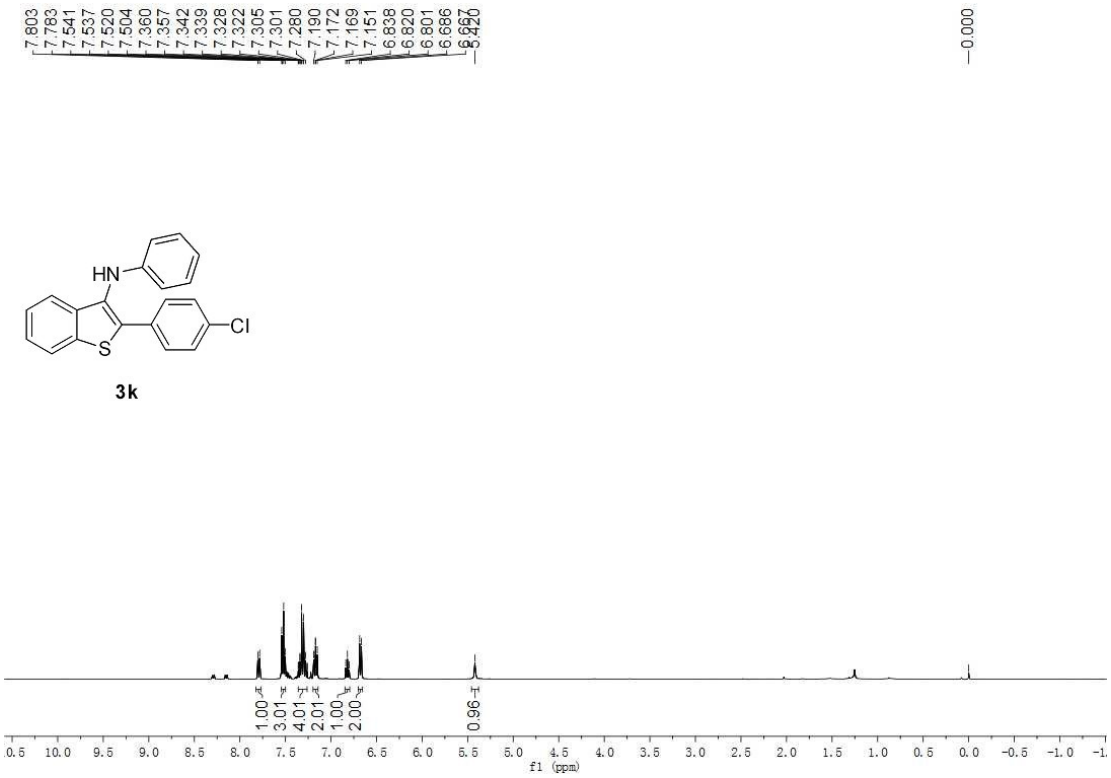
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



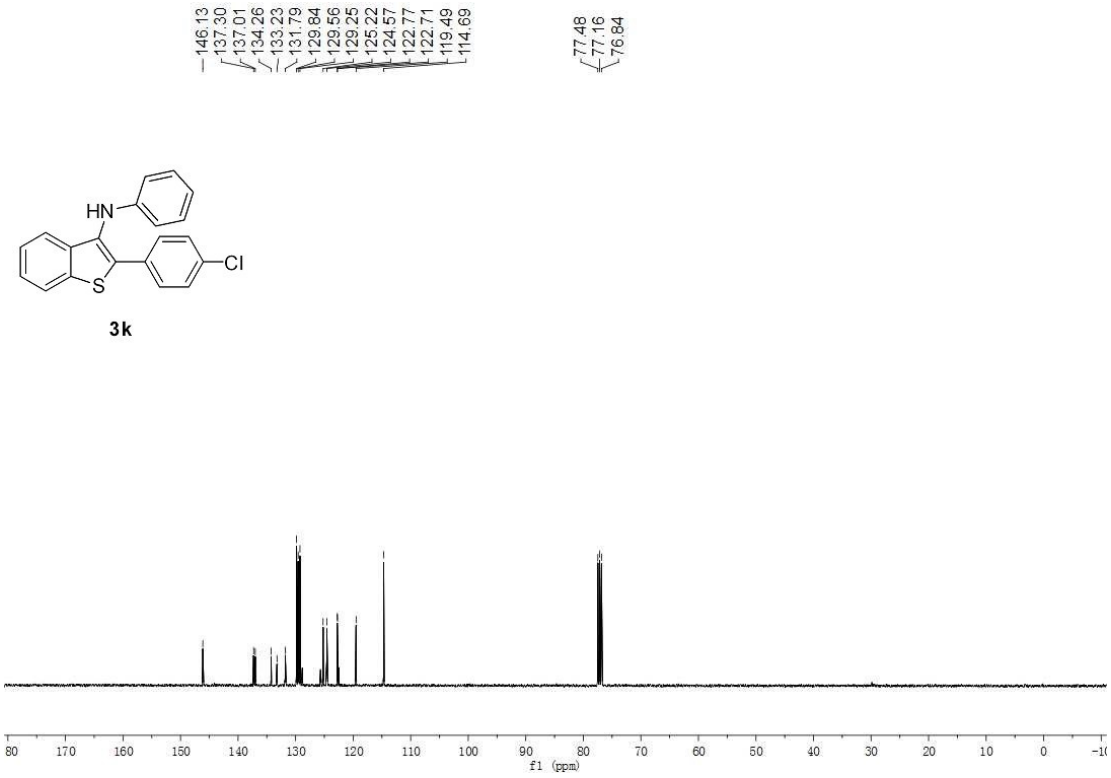
^{1}H NMR spectrum of **3j** (600 MHz, $CDCl_3$)



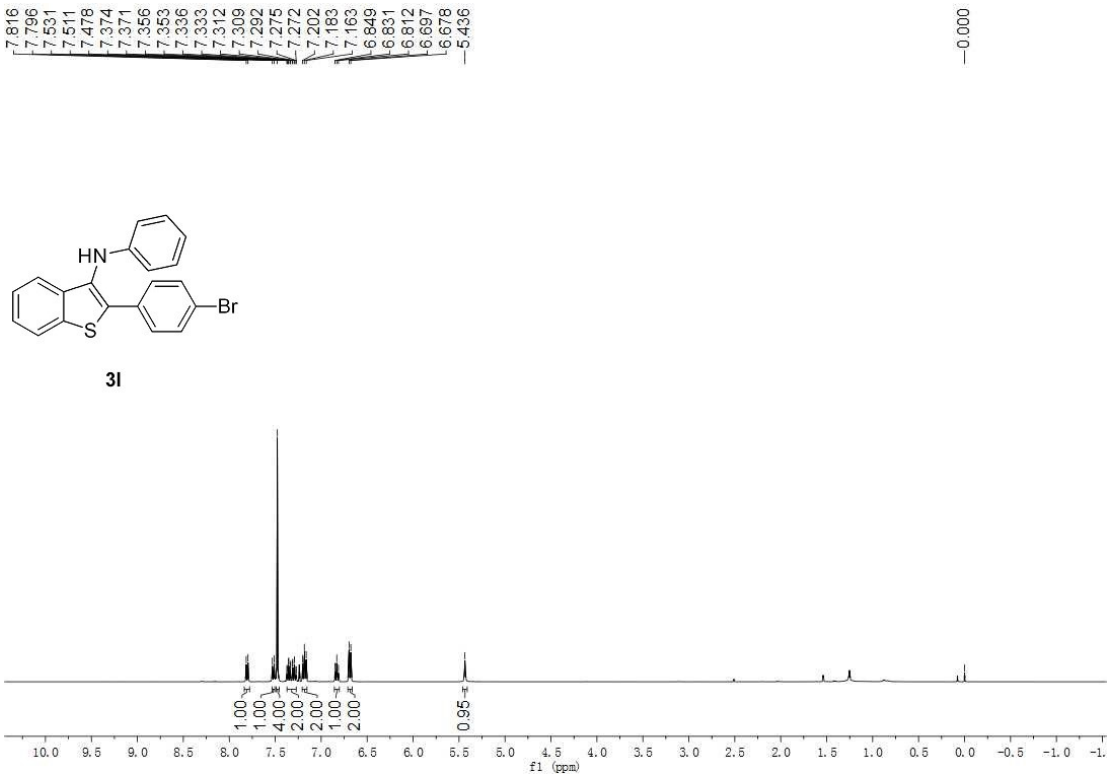
^{13}C NMR spectrum of **3j** (150 MHz, $CDCl_3$)



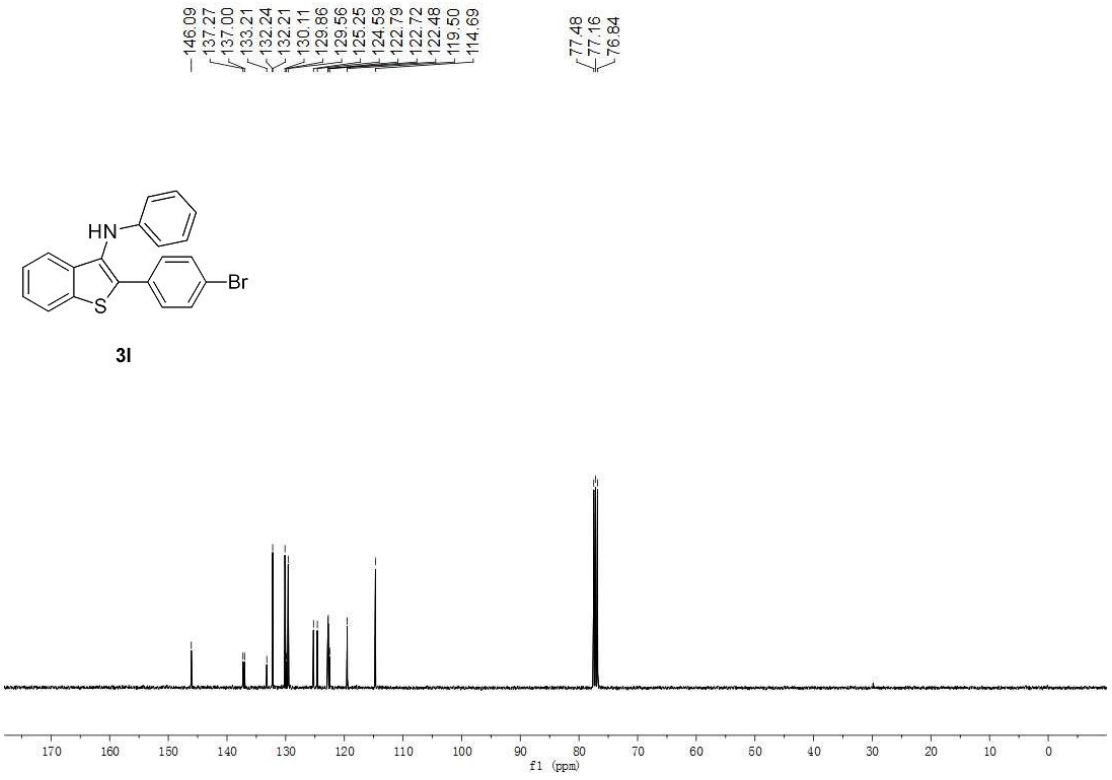
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



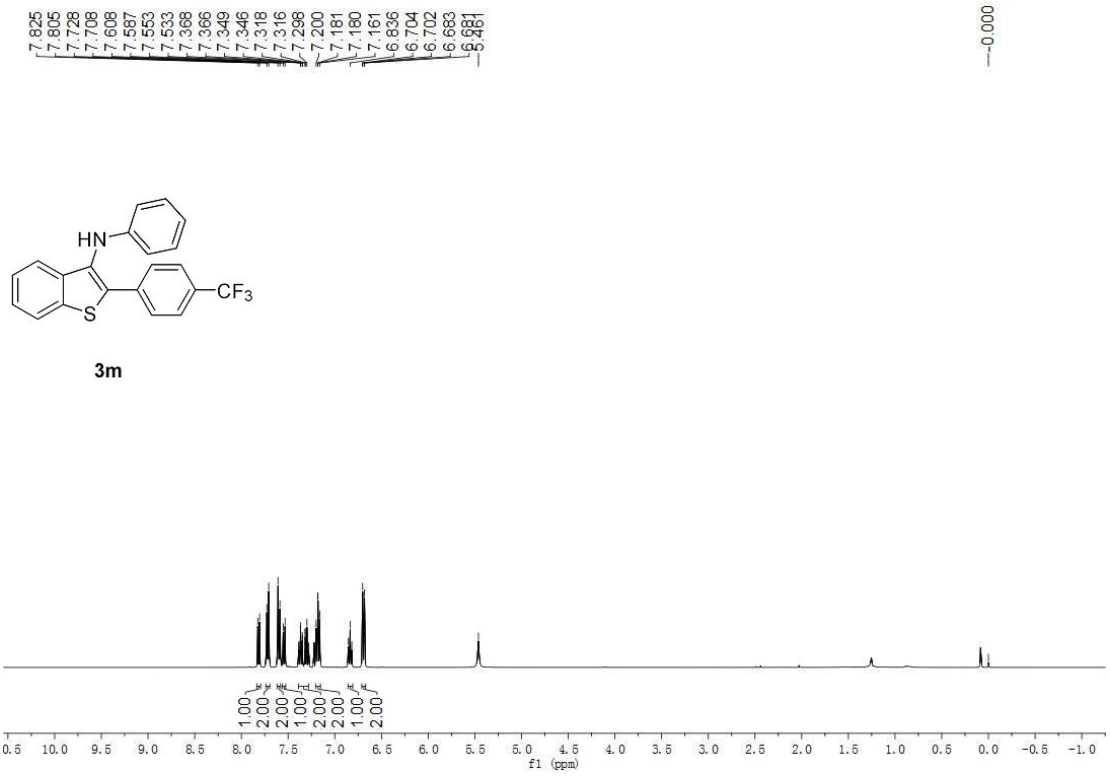
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



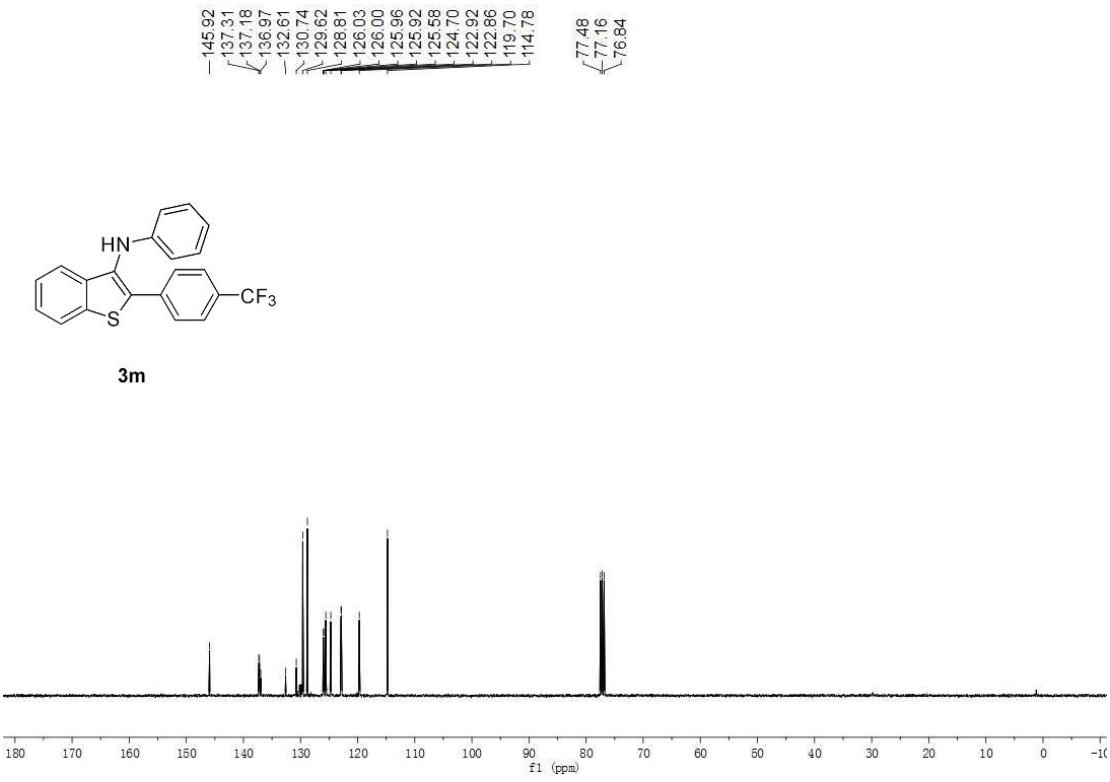
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



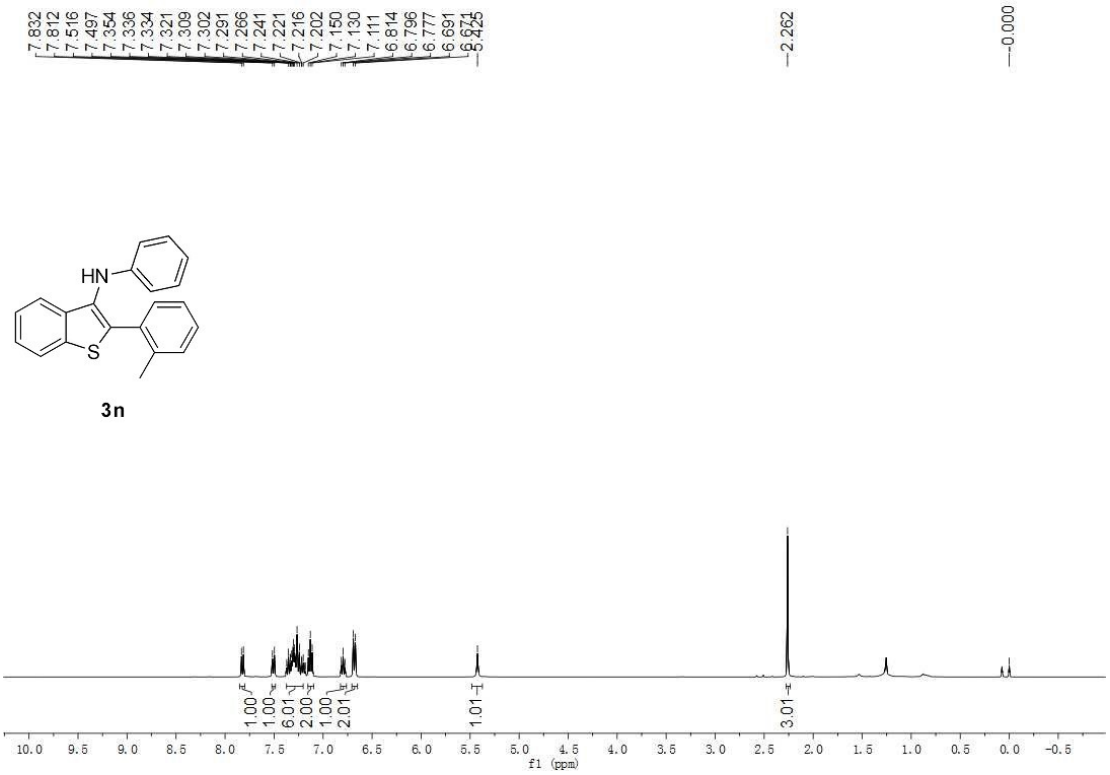
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



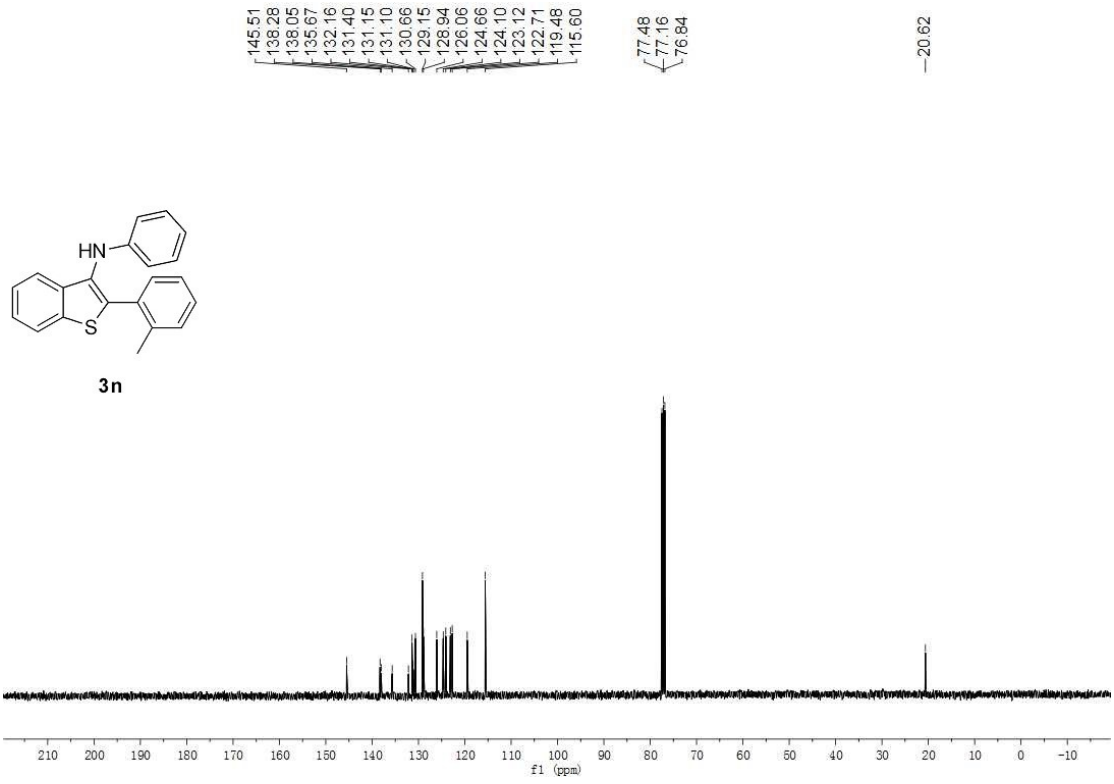
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



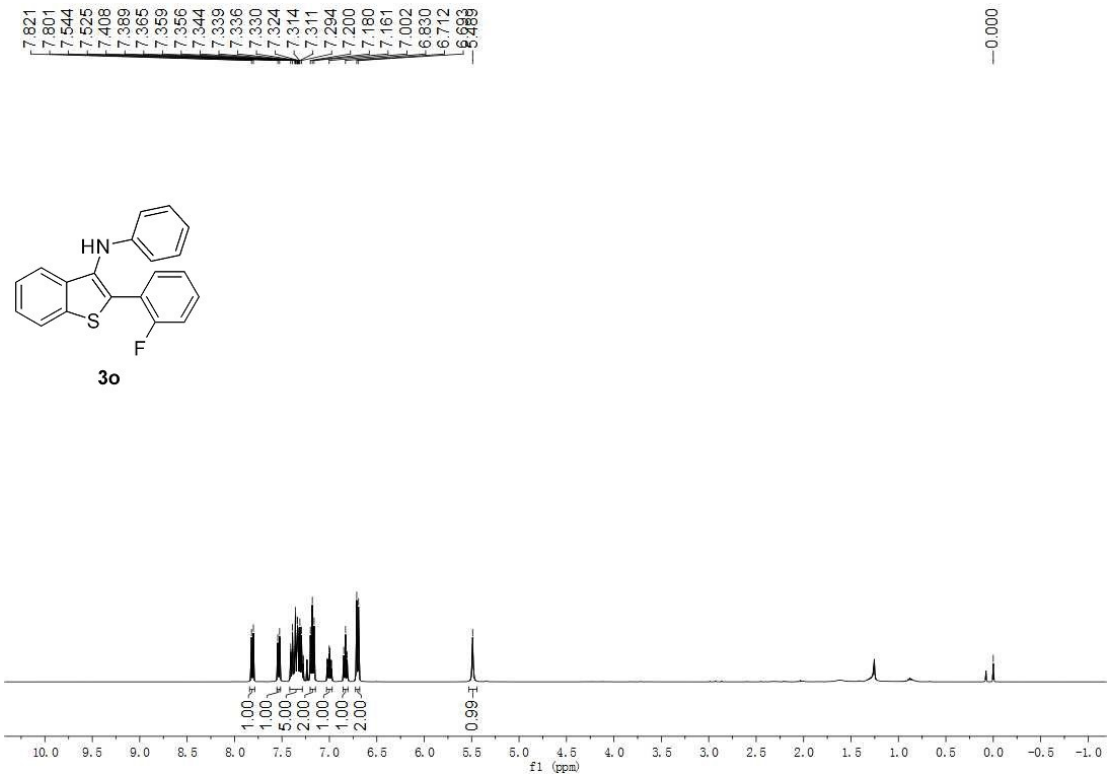
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



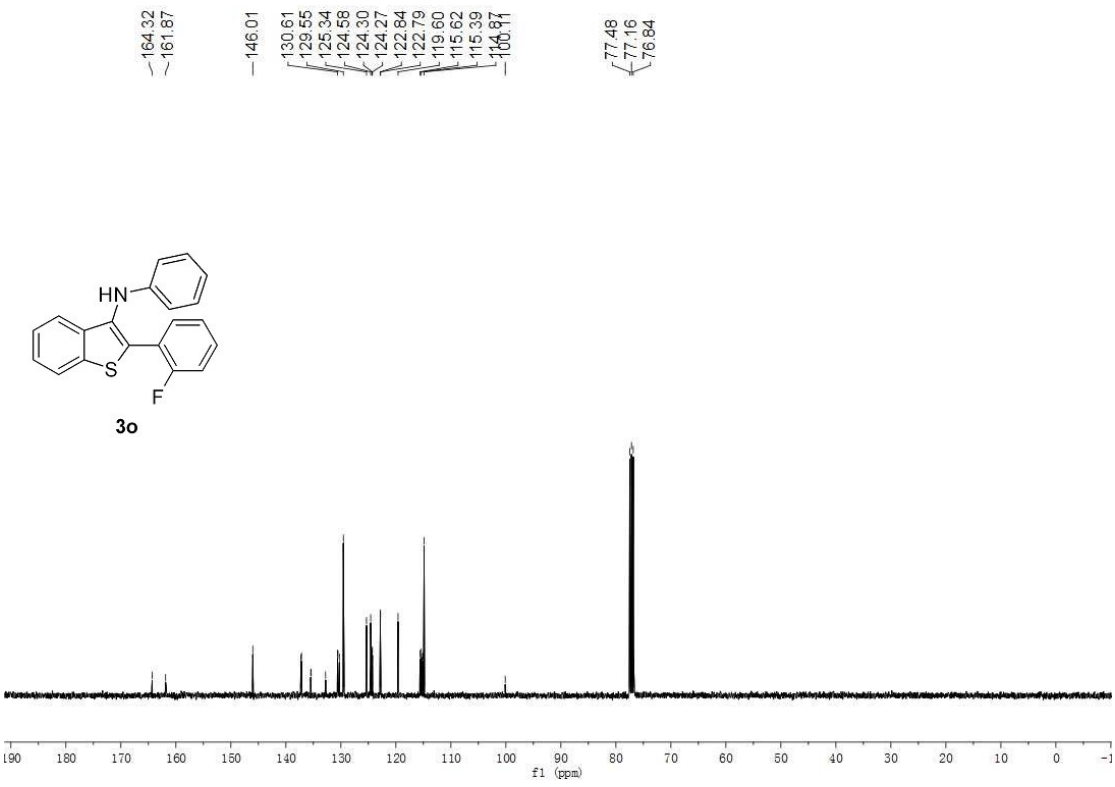
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



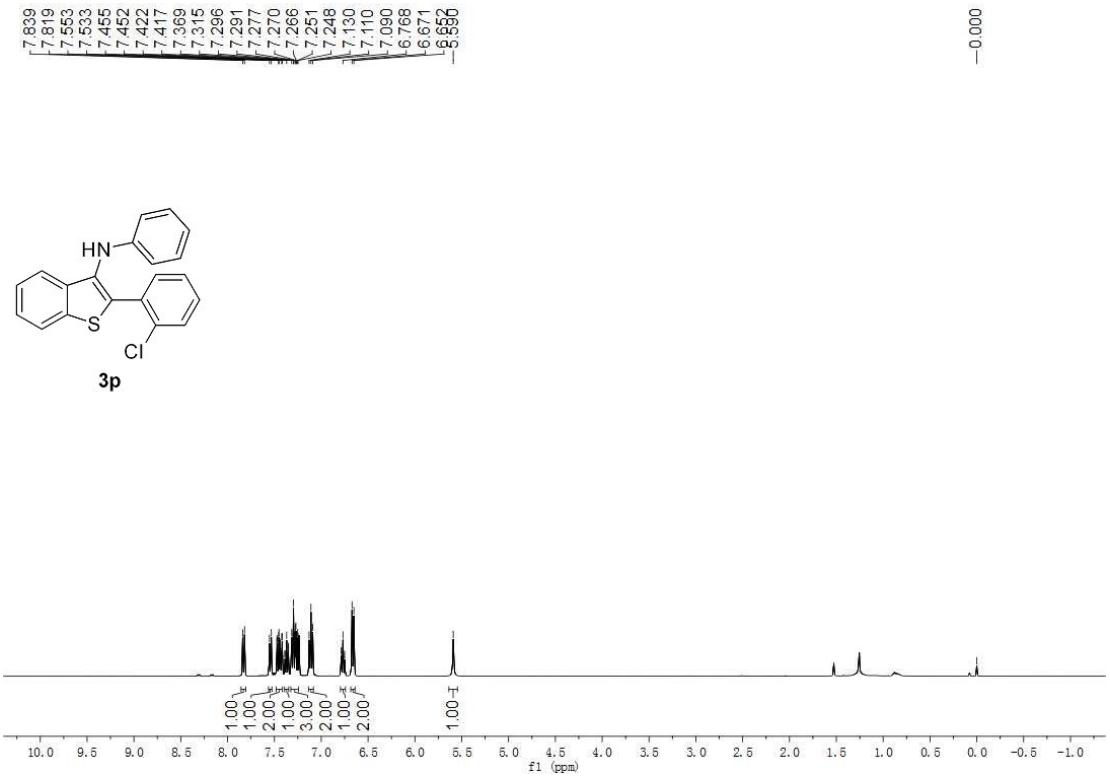
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



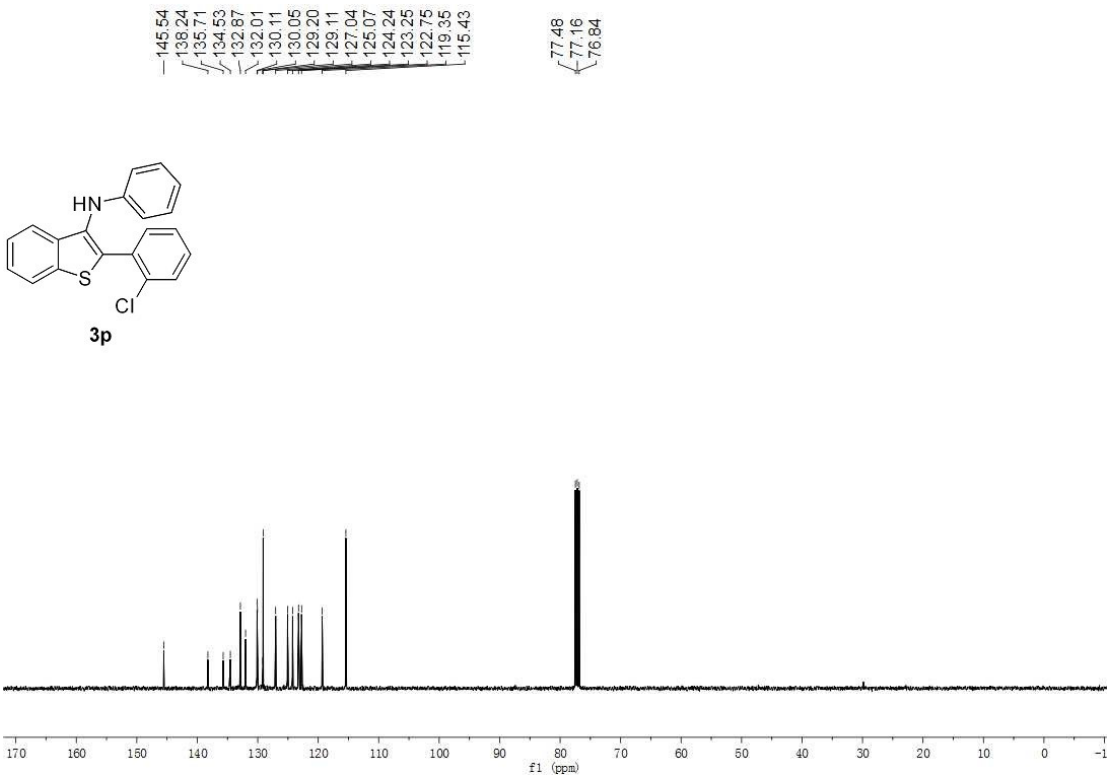
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



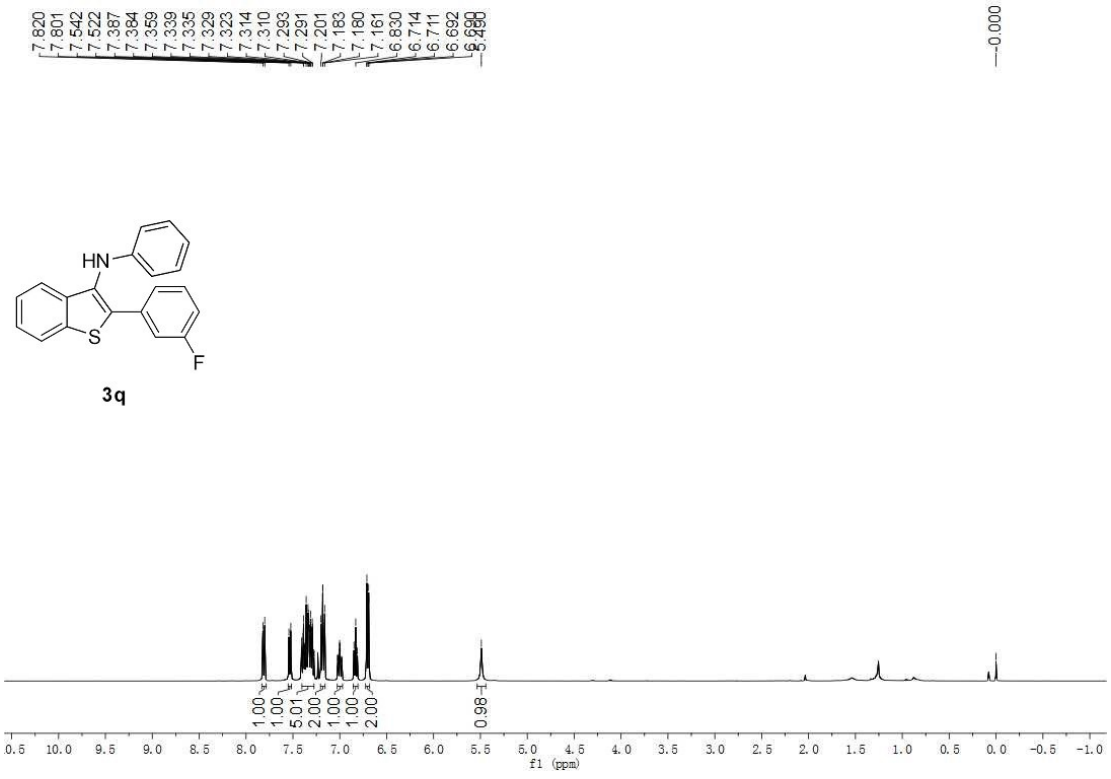
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



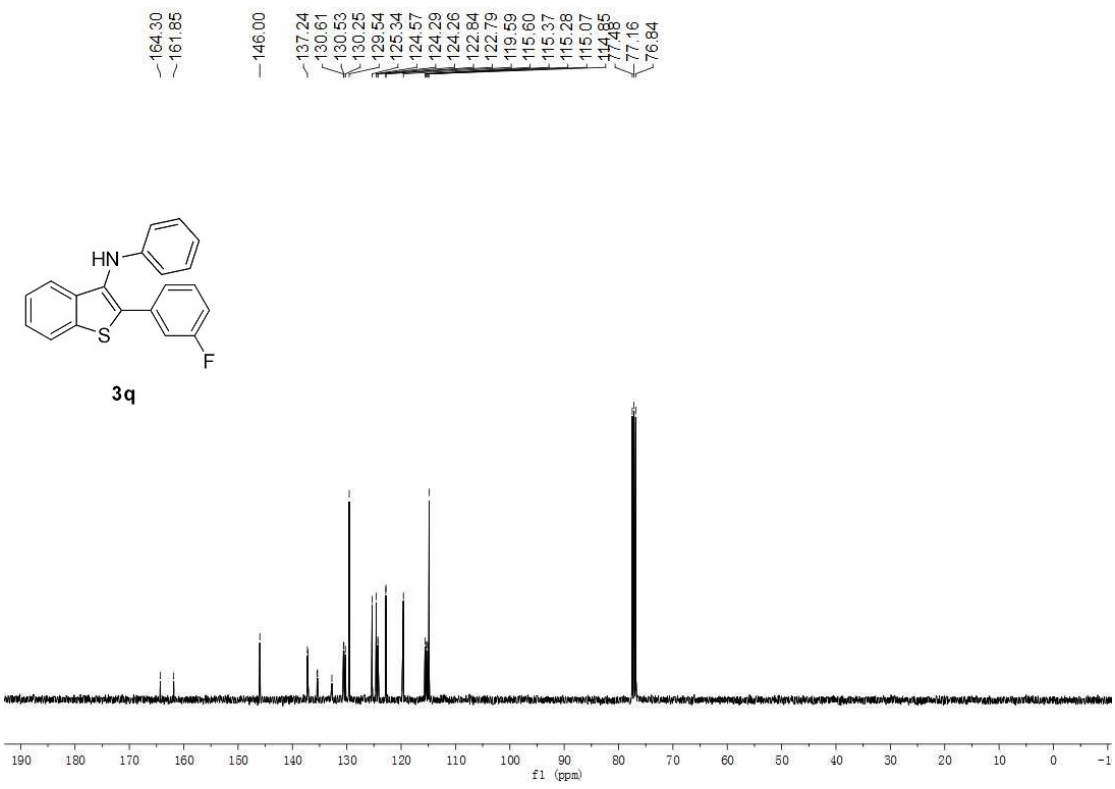
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



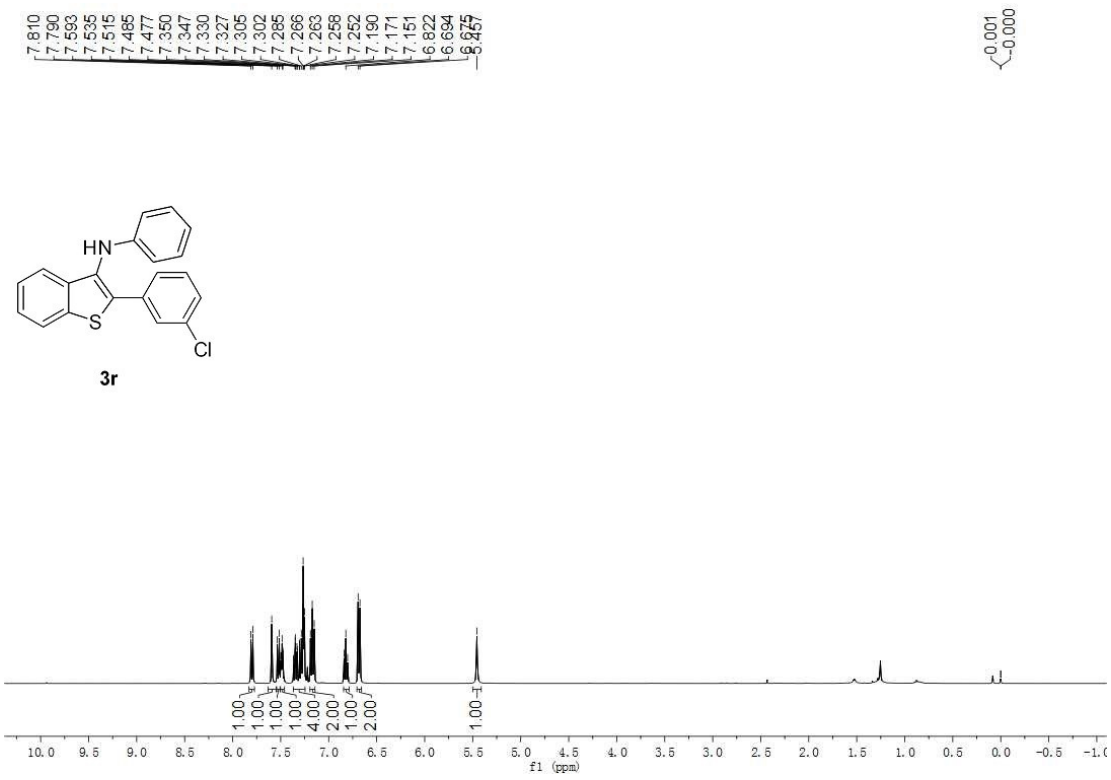
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$)



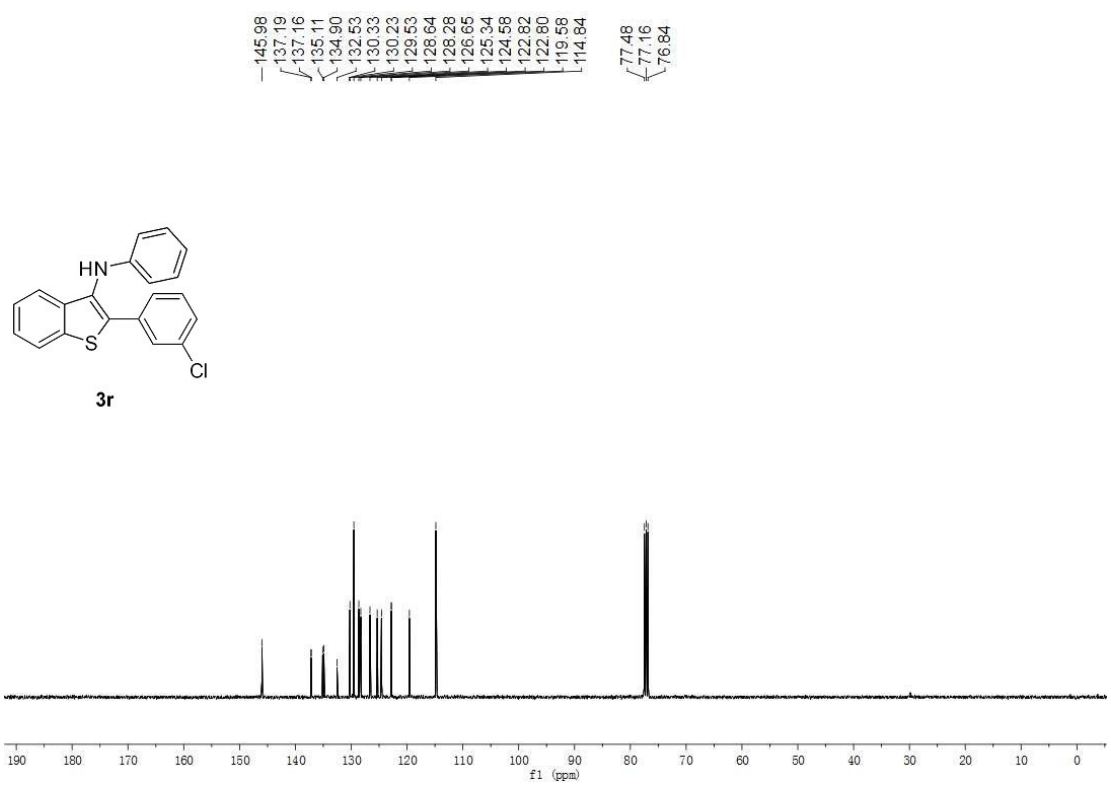
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



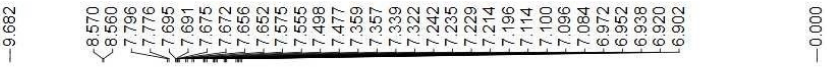
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)

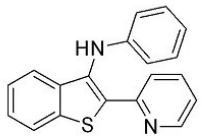


^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)

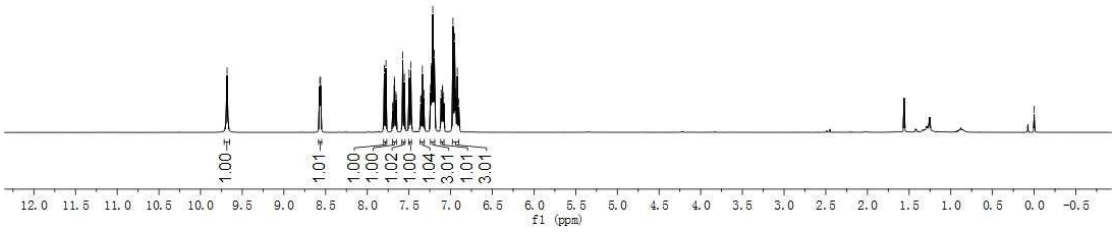


^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$)

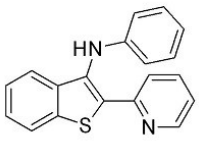




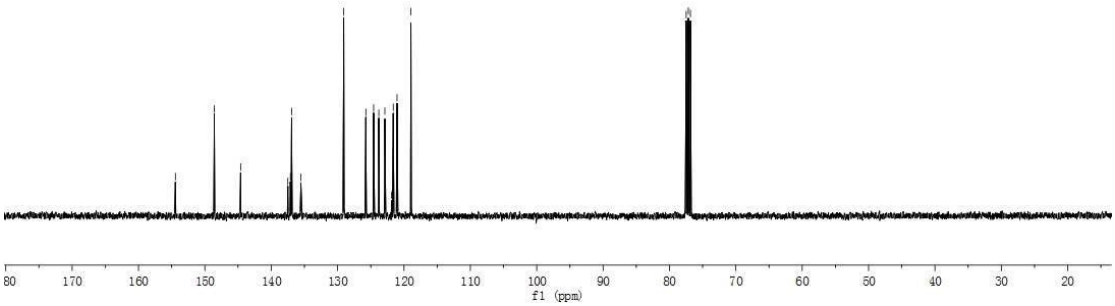
3s



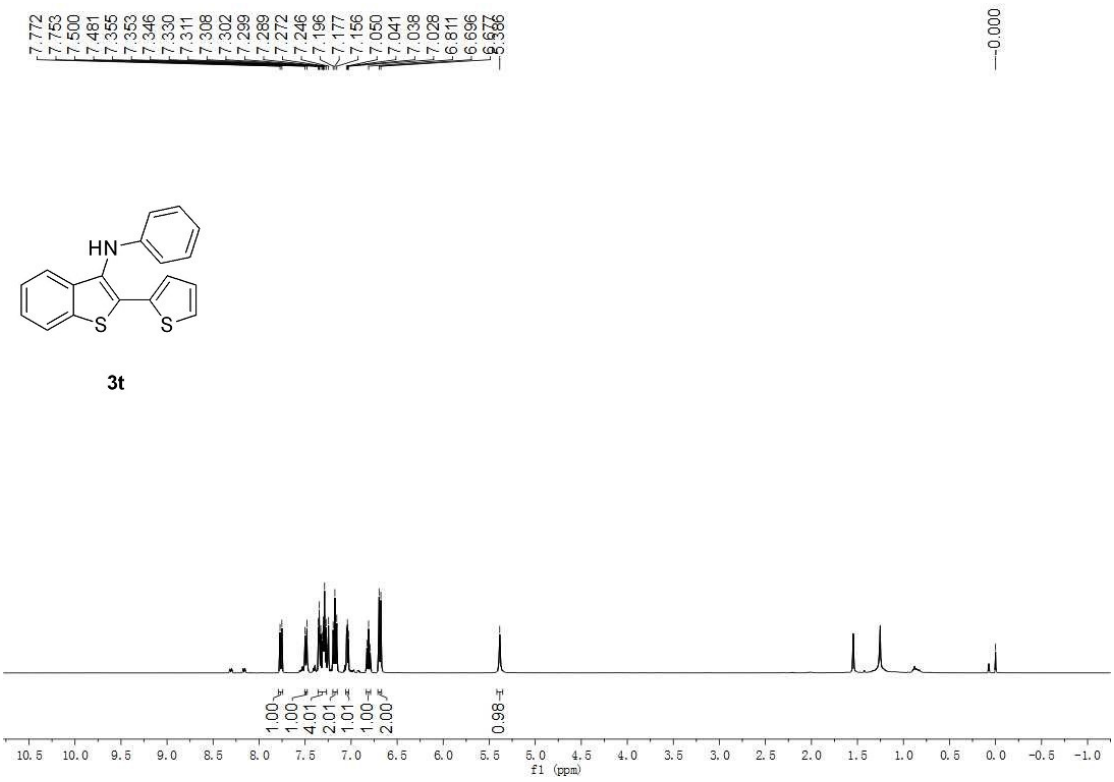
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



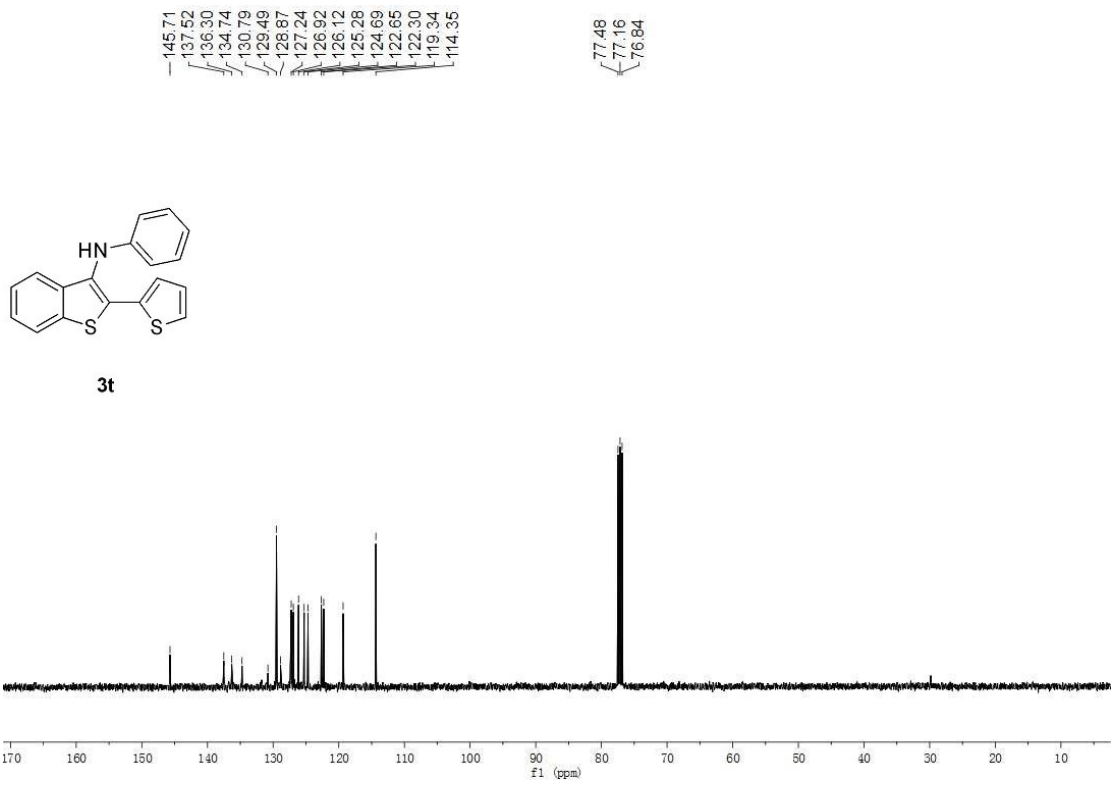
3s



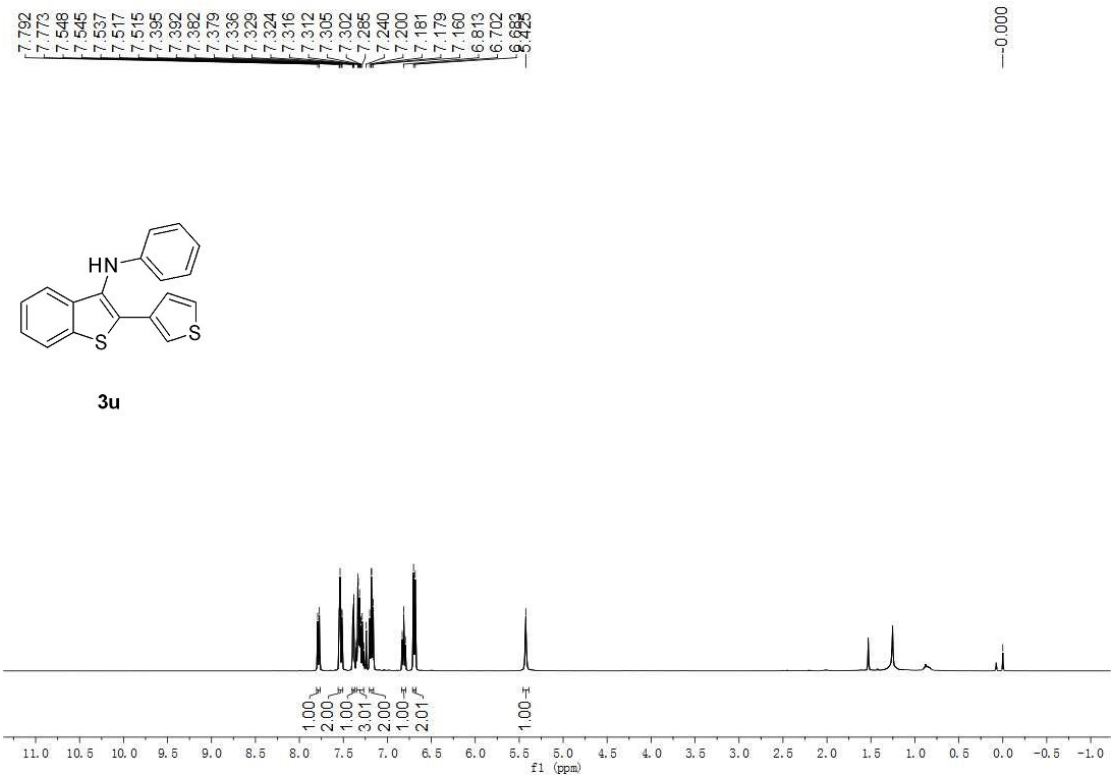
^{13}C NMR spectrum of **3s** (100 MHz, $CDCl_3$)



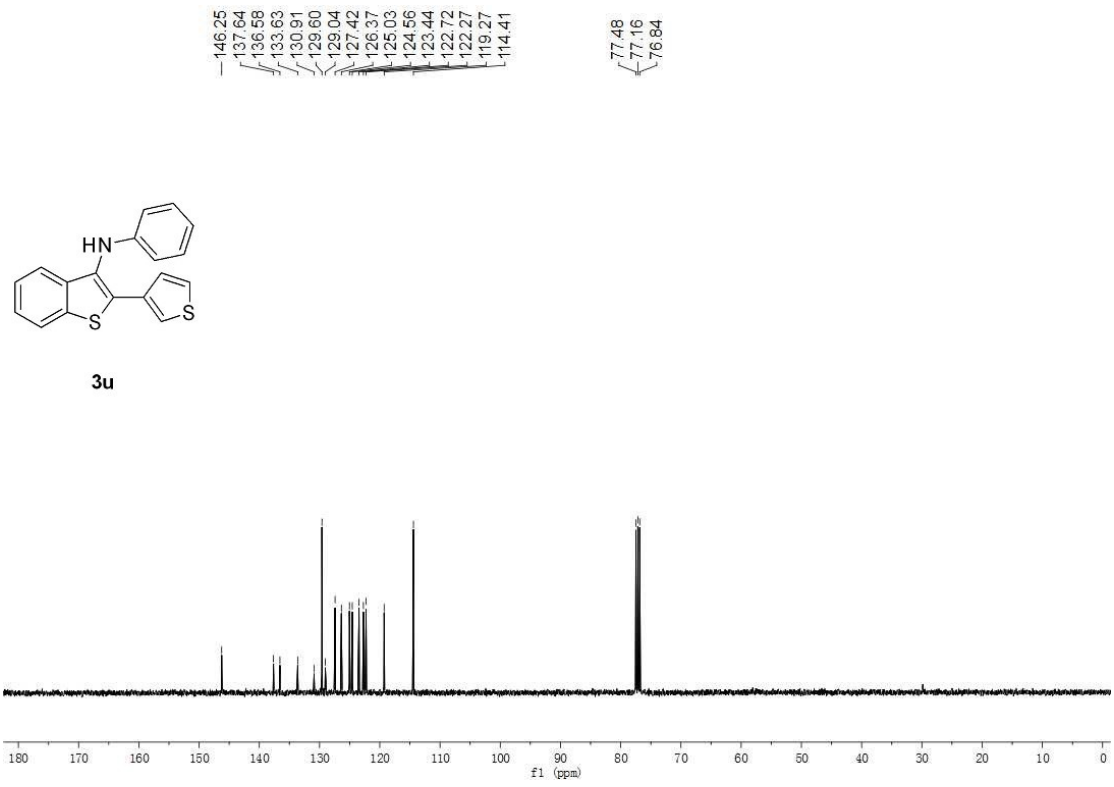
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



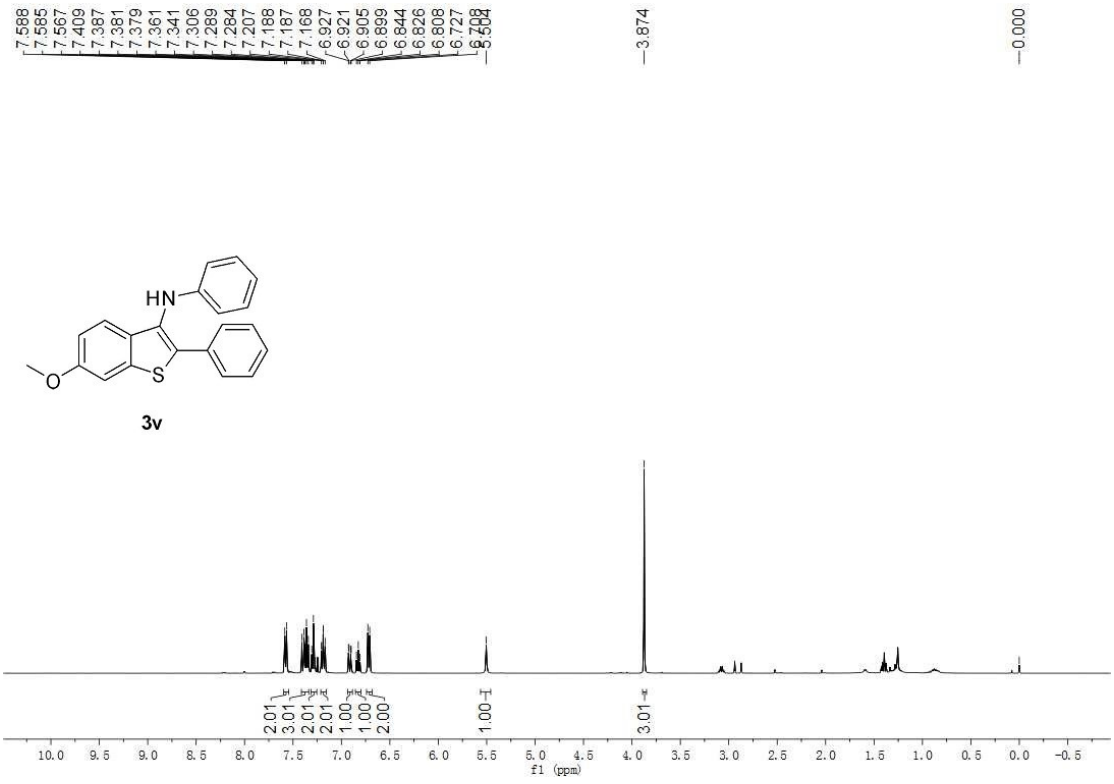
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$)



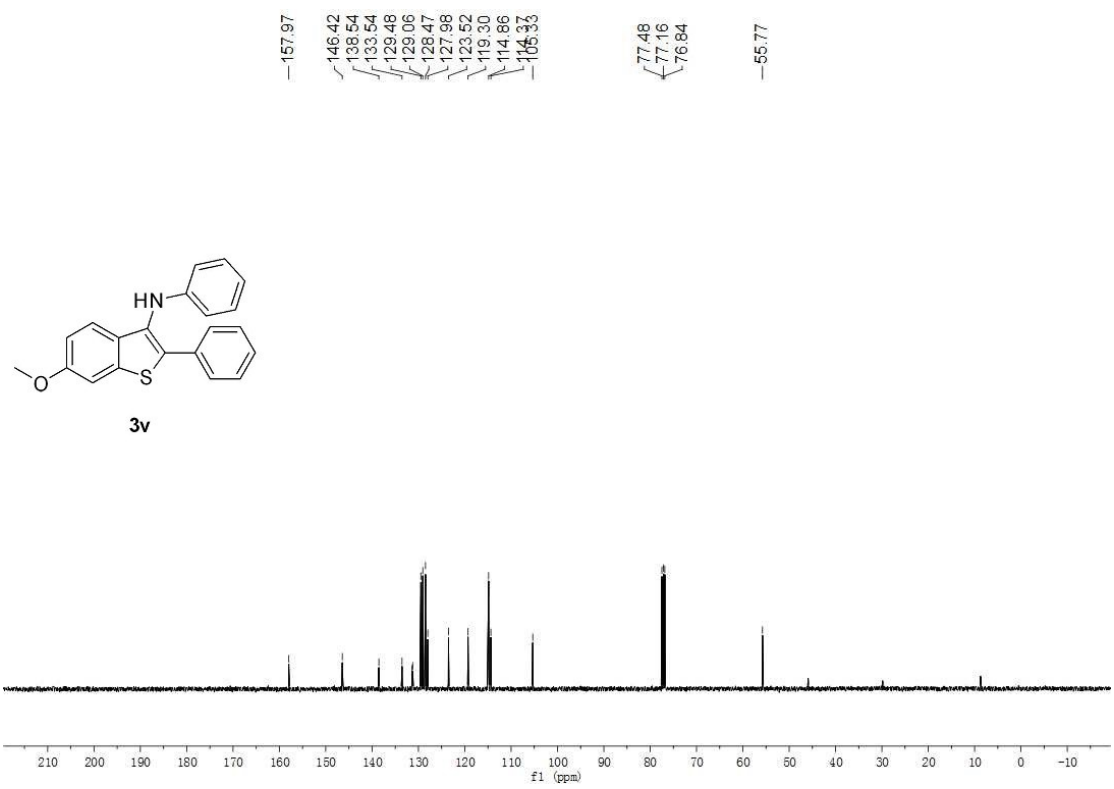
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



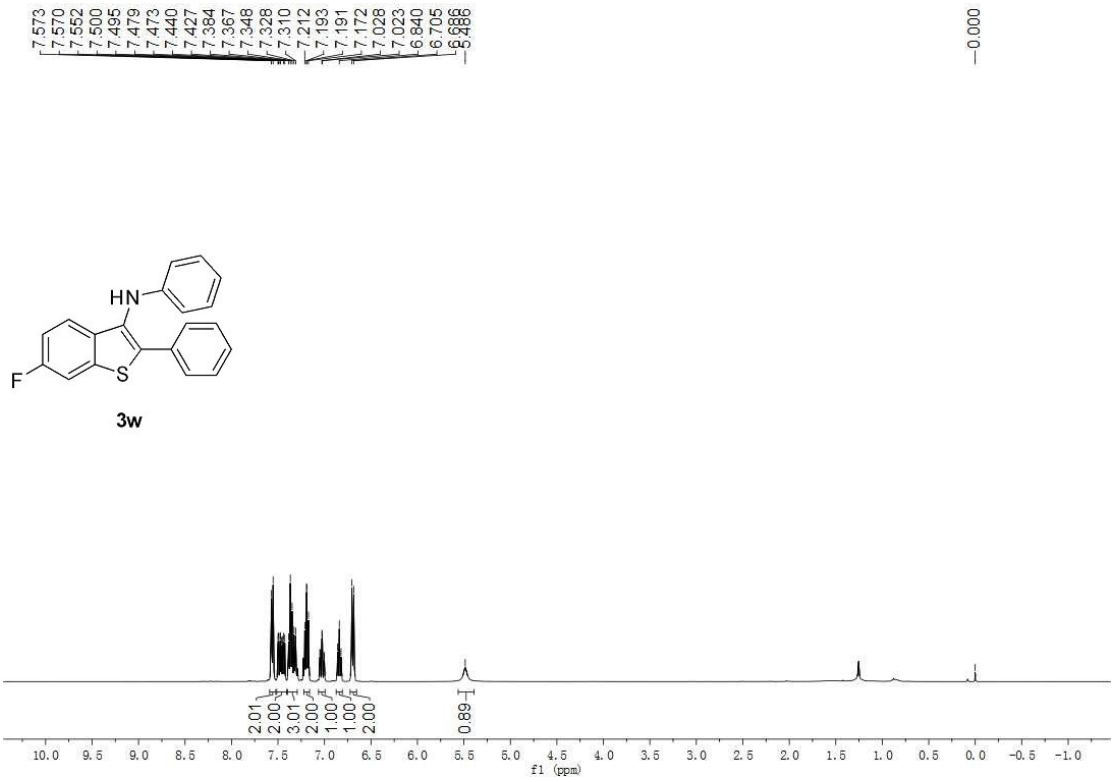
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$)



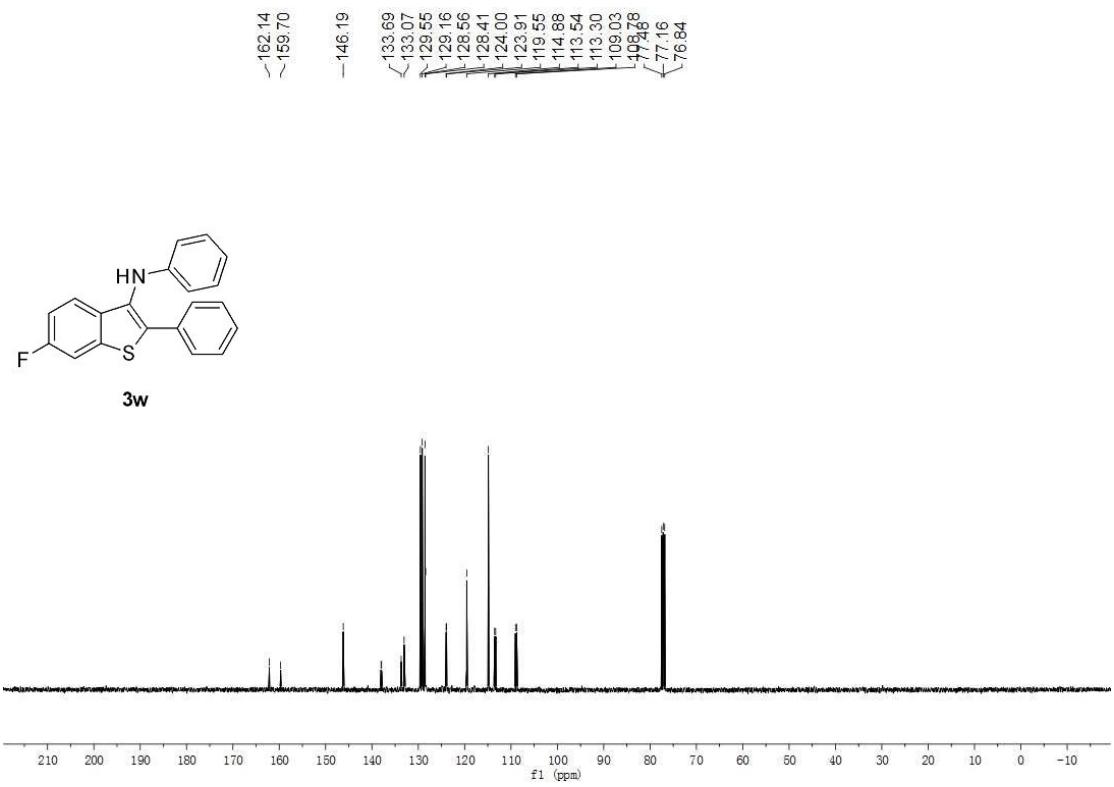
^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)



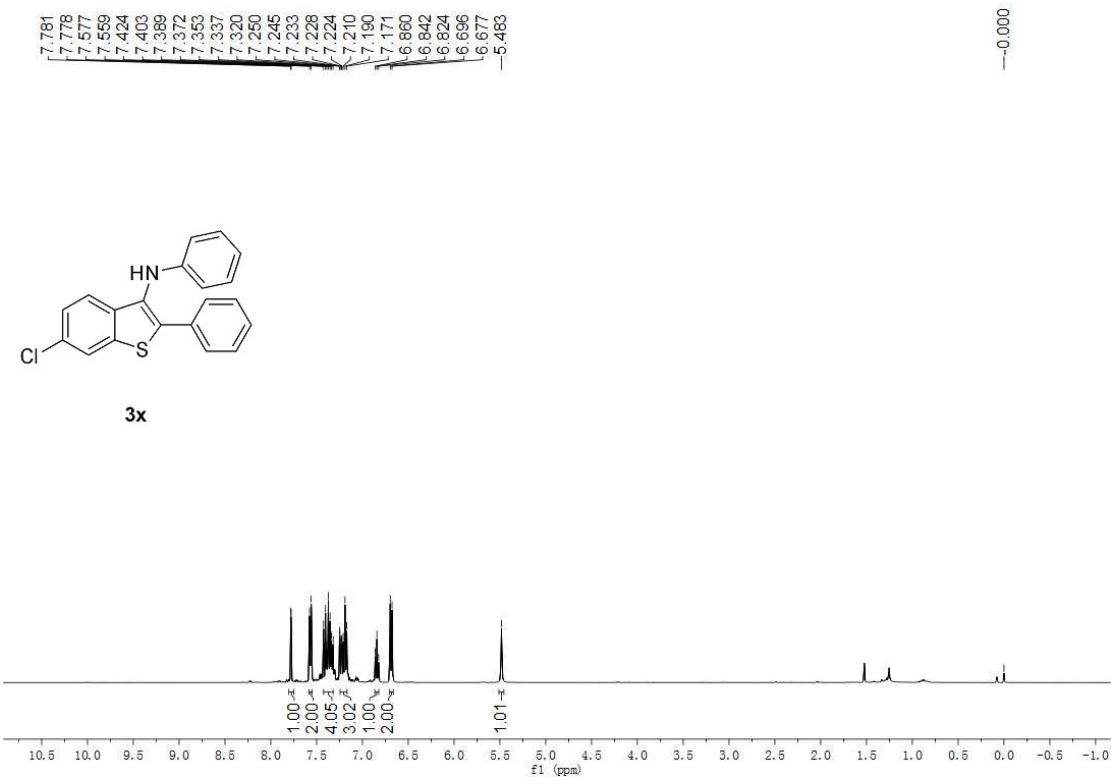
^{13}C NMR spectrum of **3v** (100 MHz, $CDCl_3$)



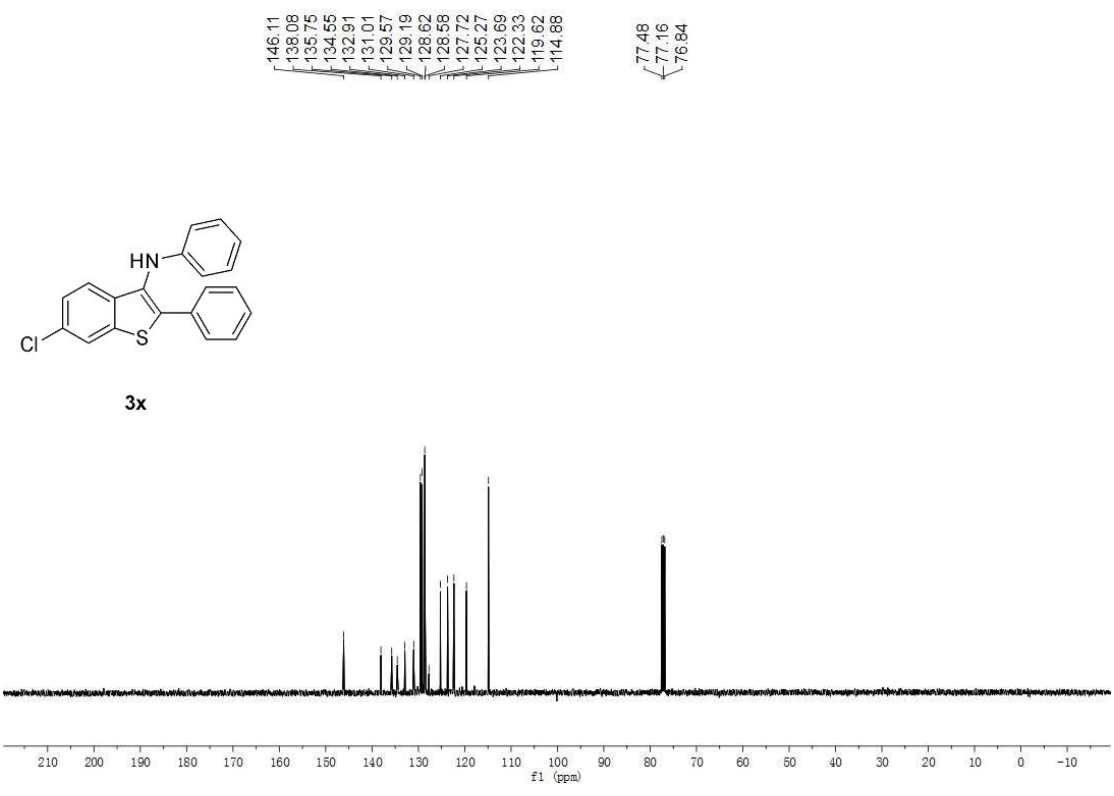
^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$)



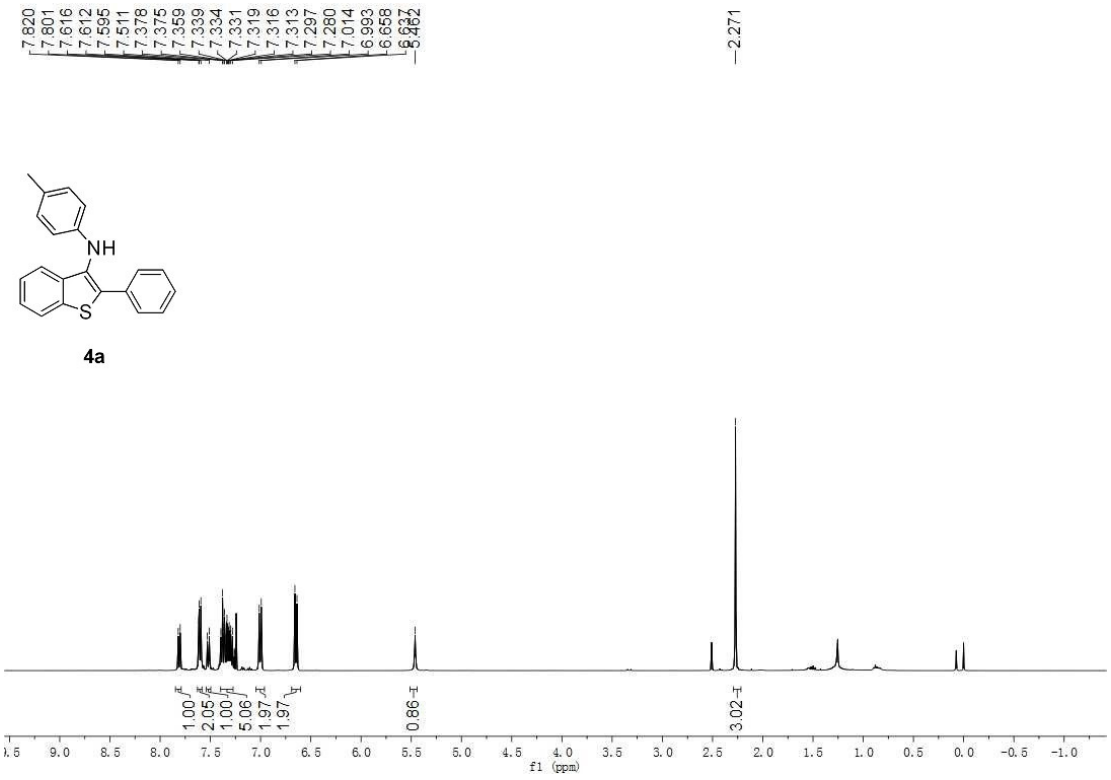
^{13}C NMR spectrum of **3w** (100 MHz, $CDCl_3$)



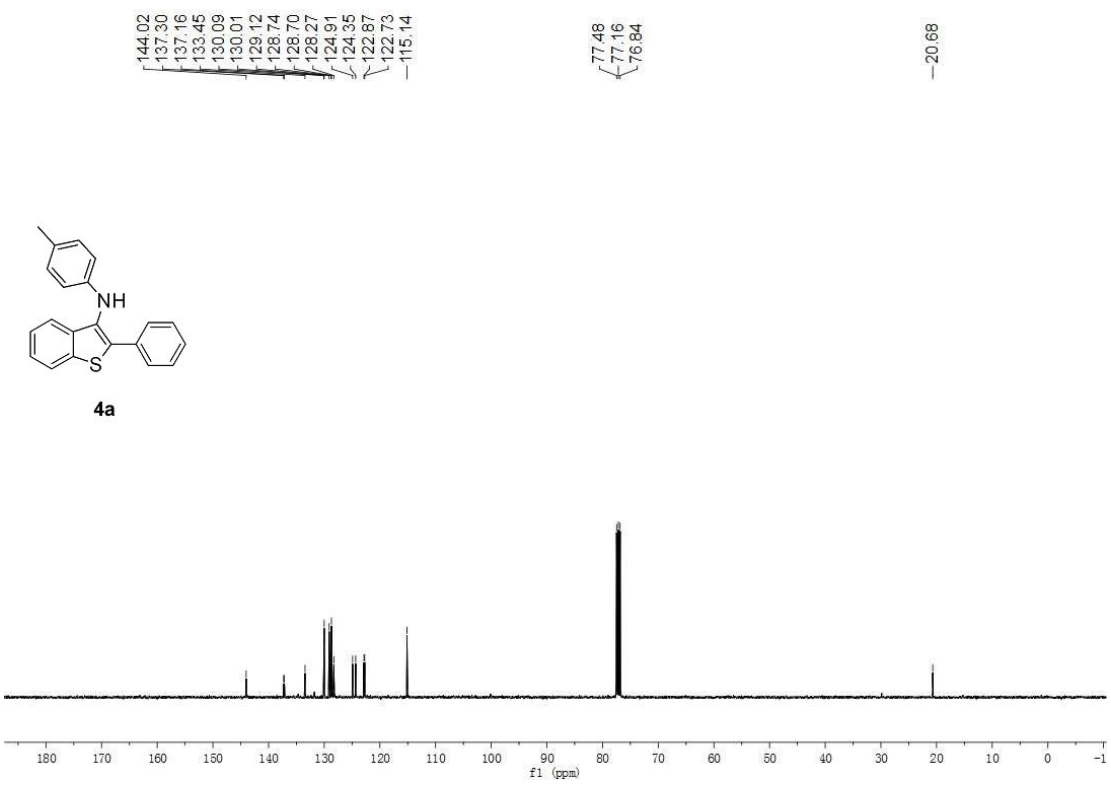
^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)



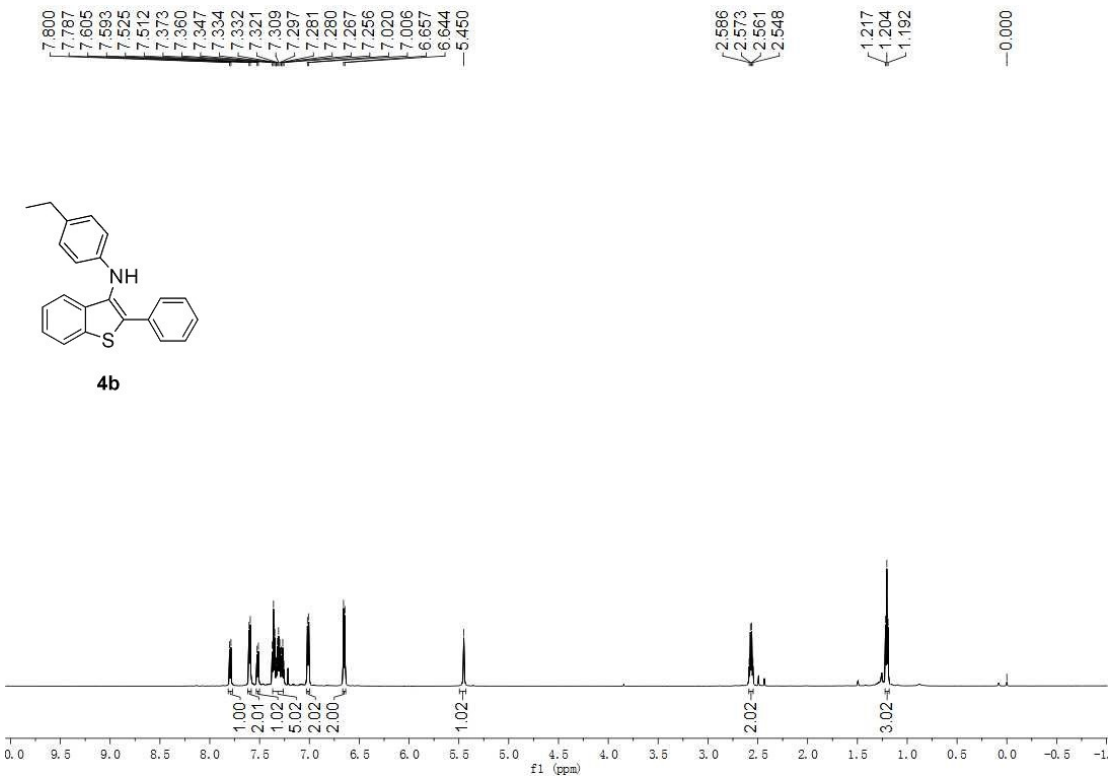
^{13}C NMR spectrum of **3x** (100 MHz, $CDCl_3$)



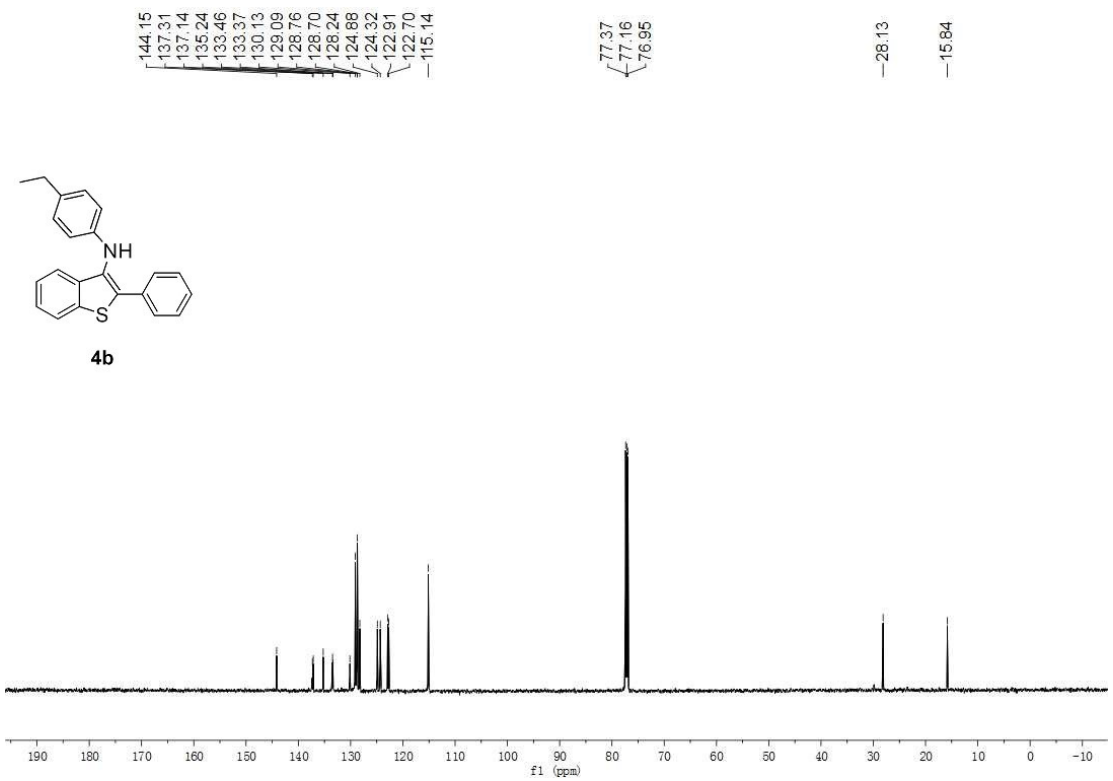
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



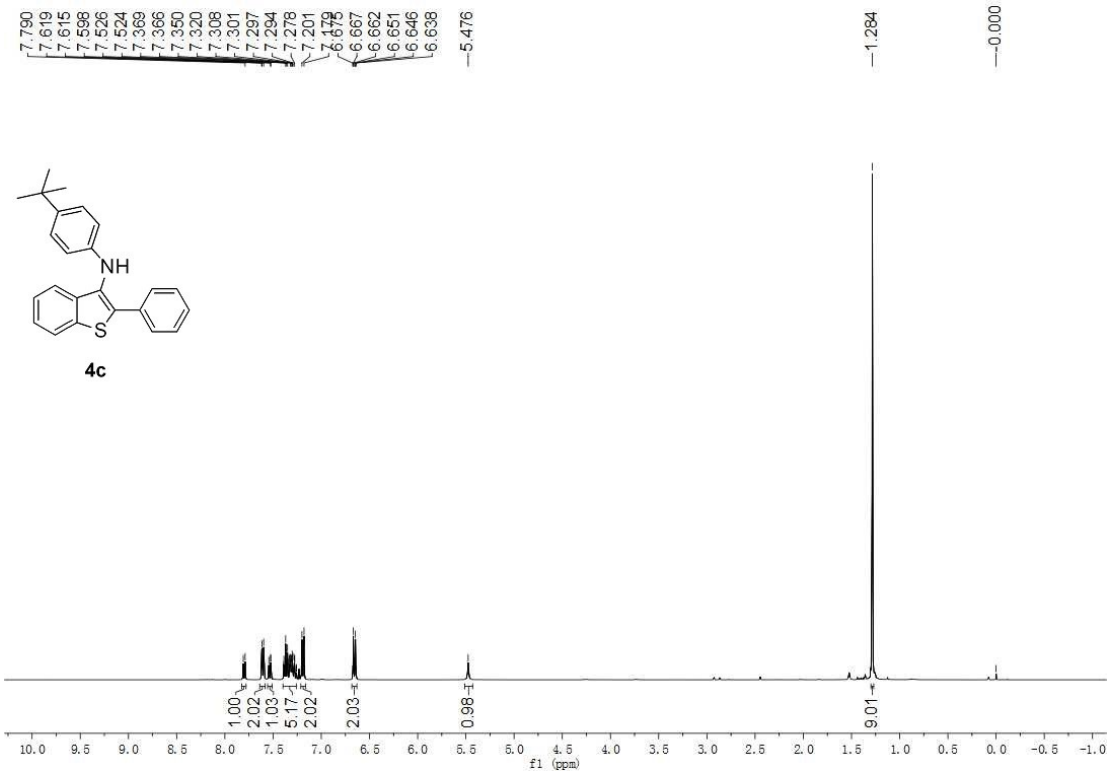
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



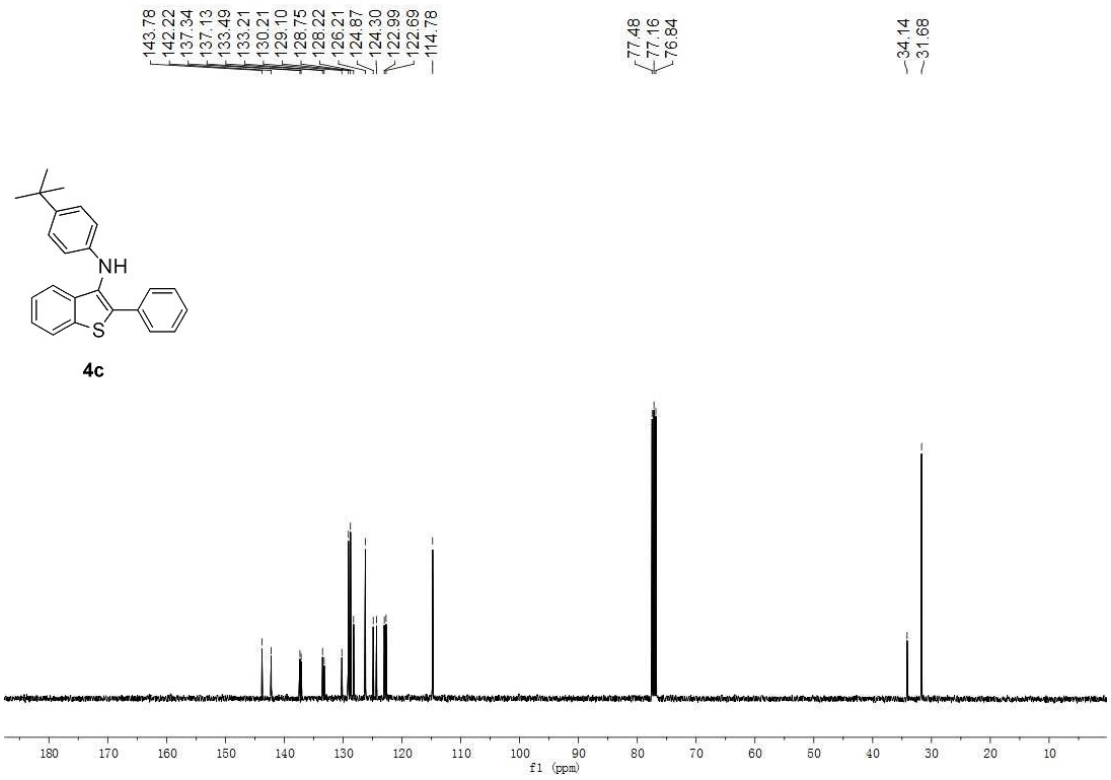
^{1}H NMR spectrum of **4b** (600 MHz, $CDCl_3$)



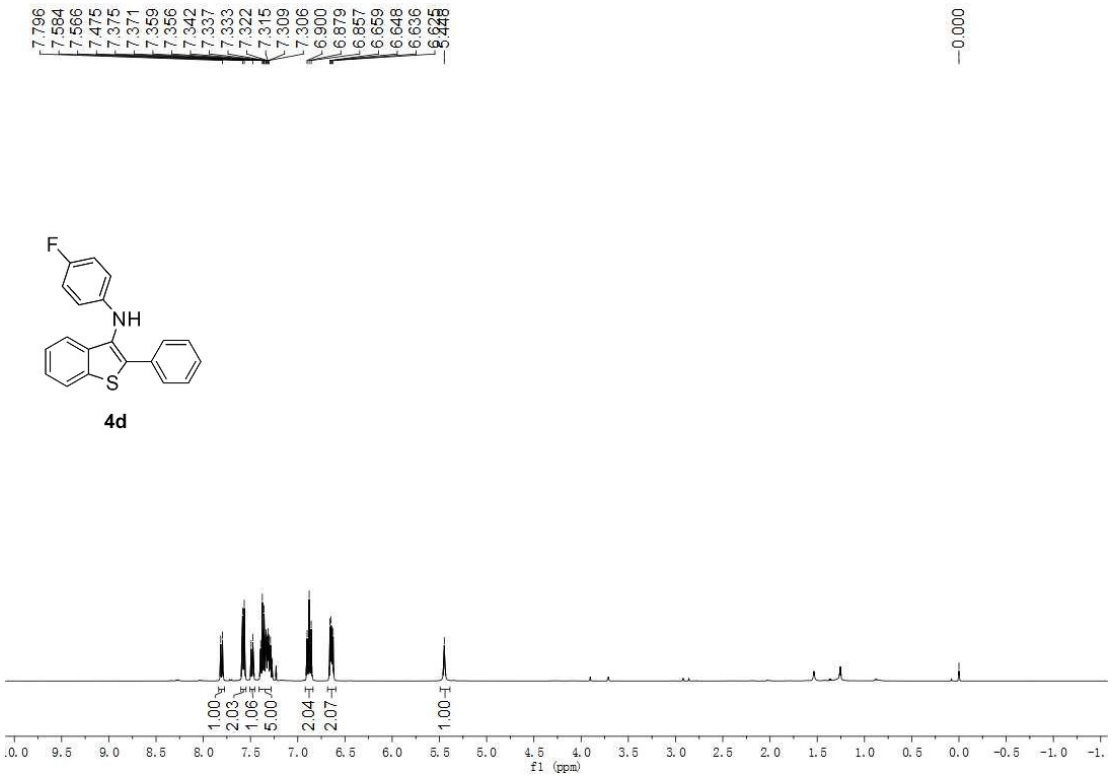
^{13}C NMR spectrum of **4b** (150 MHz, $CDCl_3$)



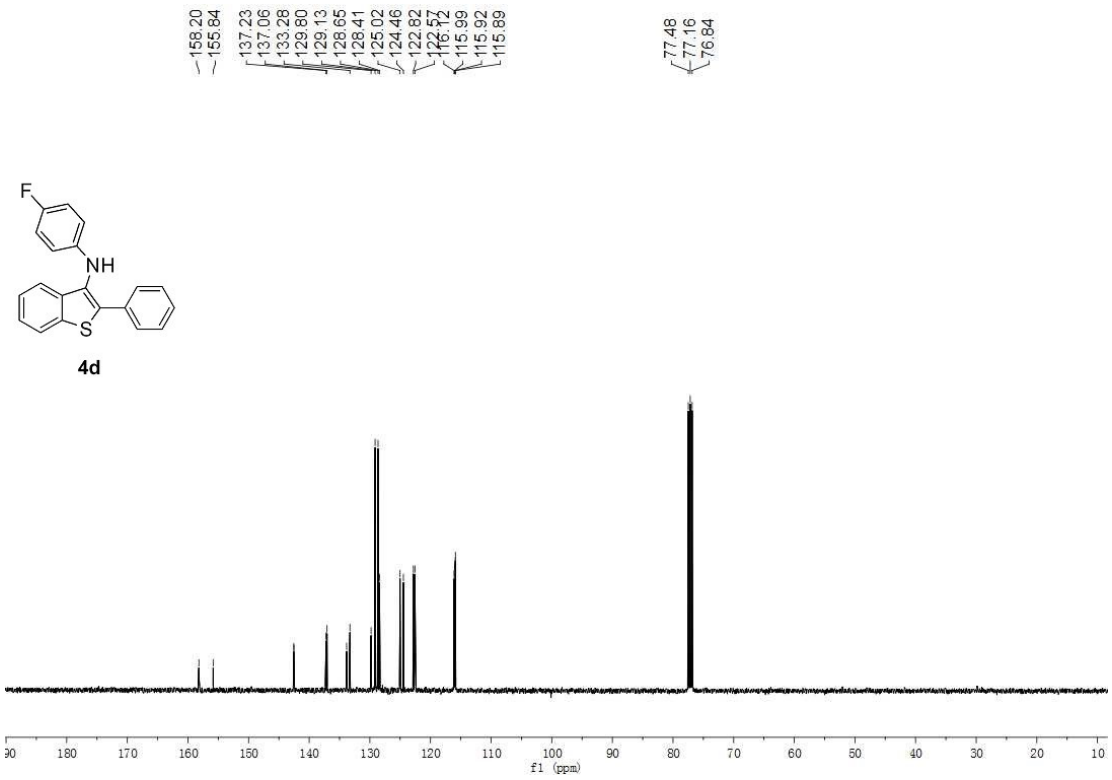
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



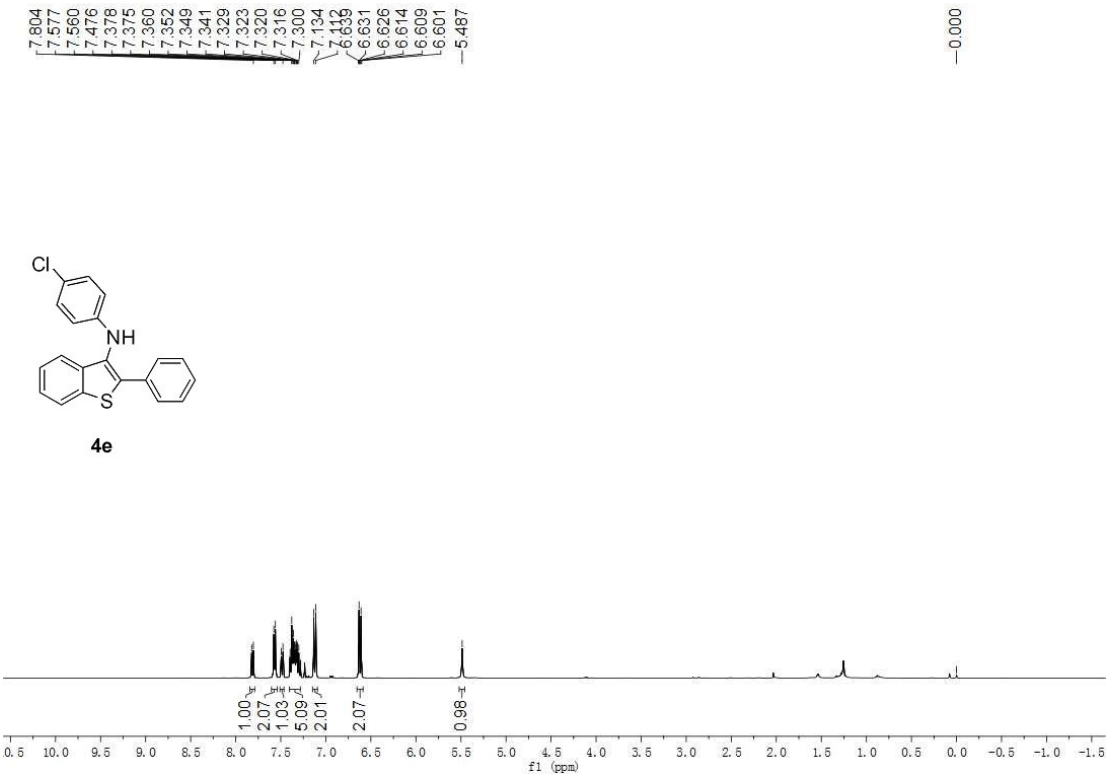
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



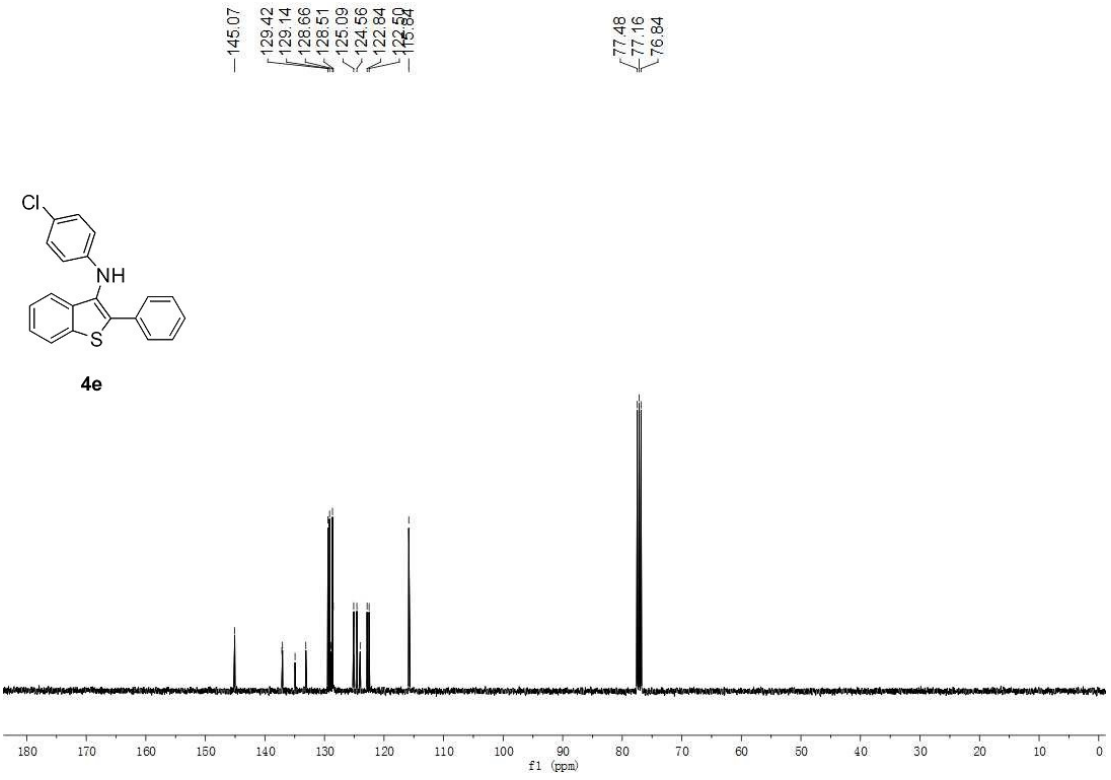
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



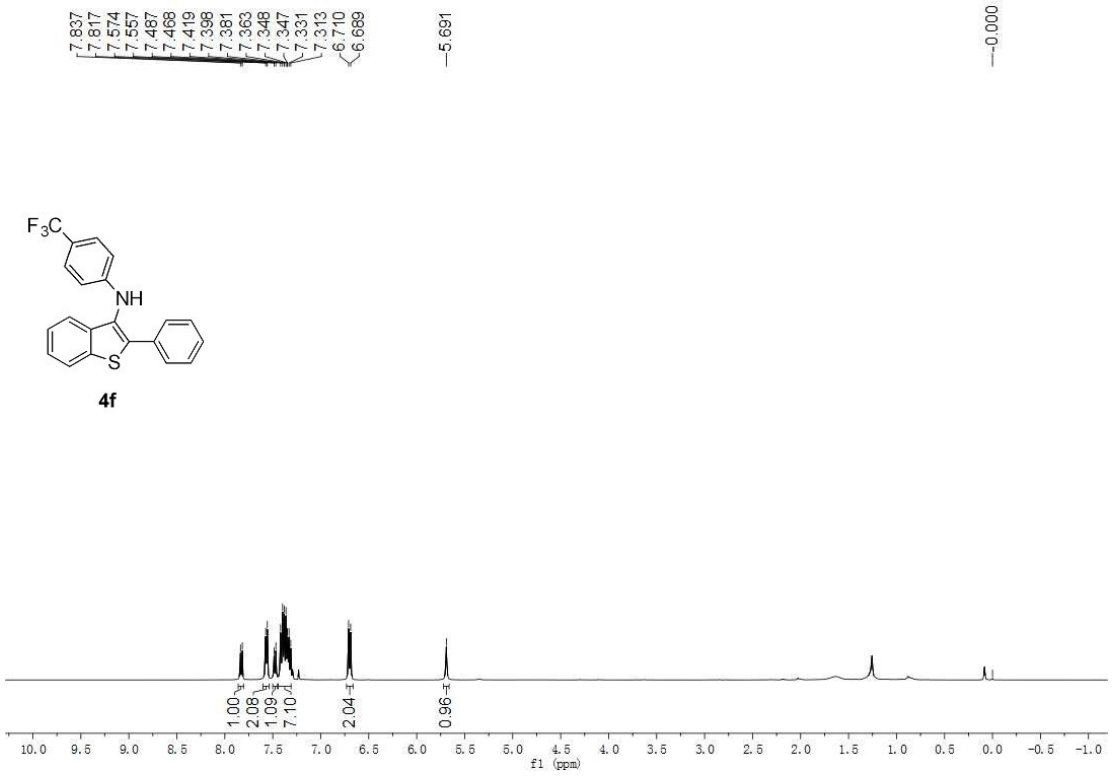
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



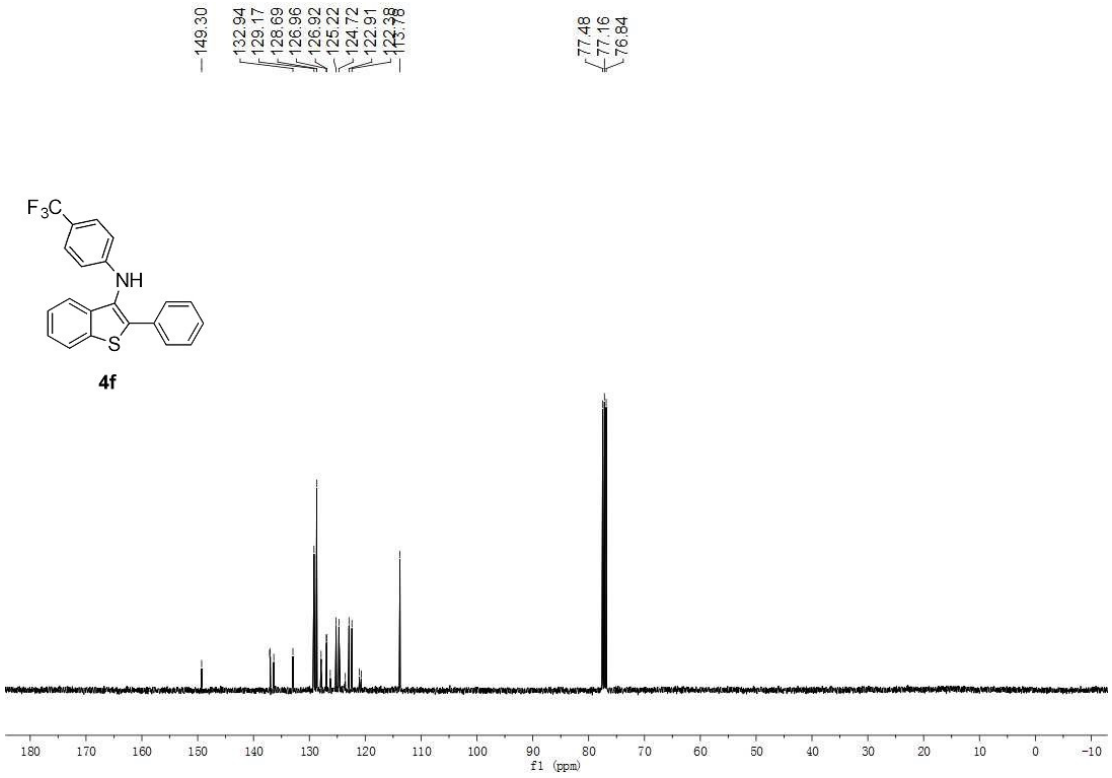
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



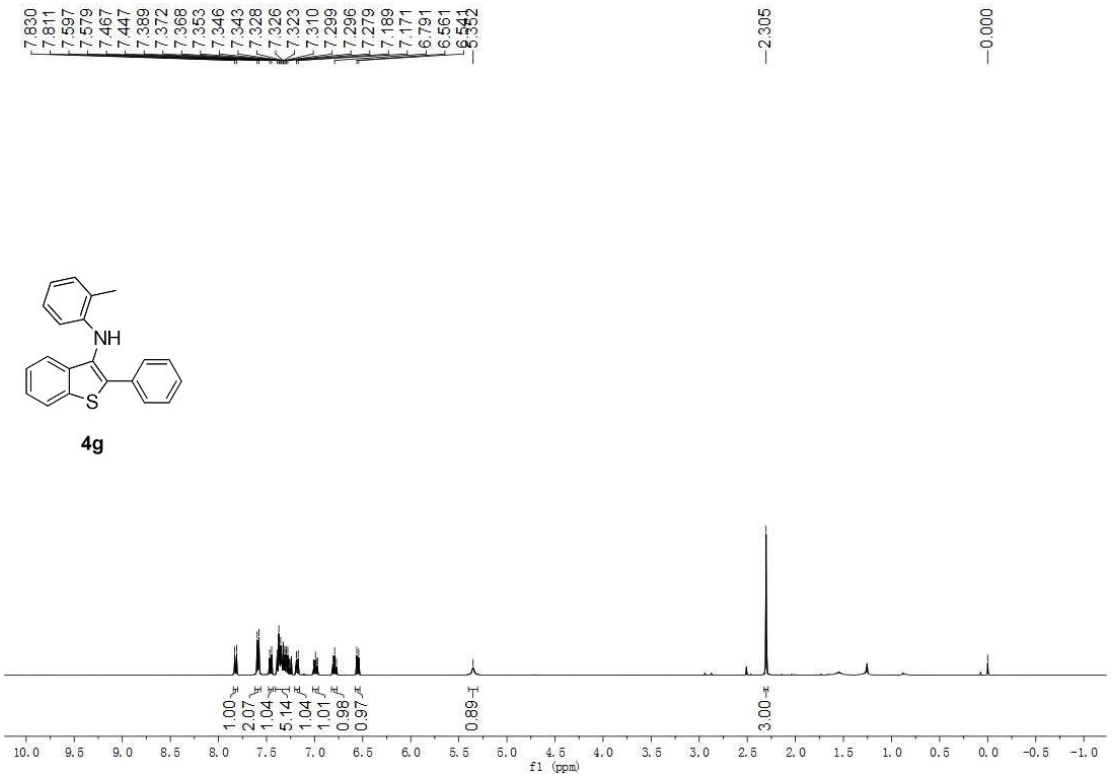
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



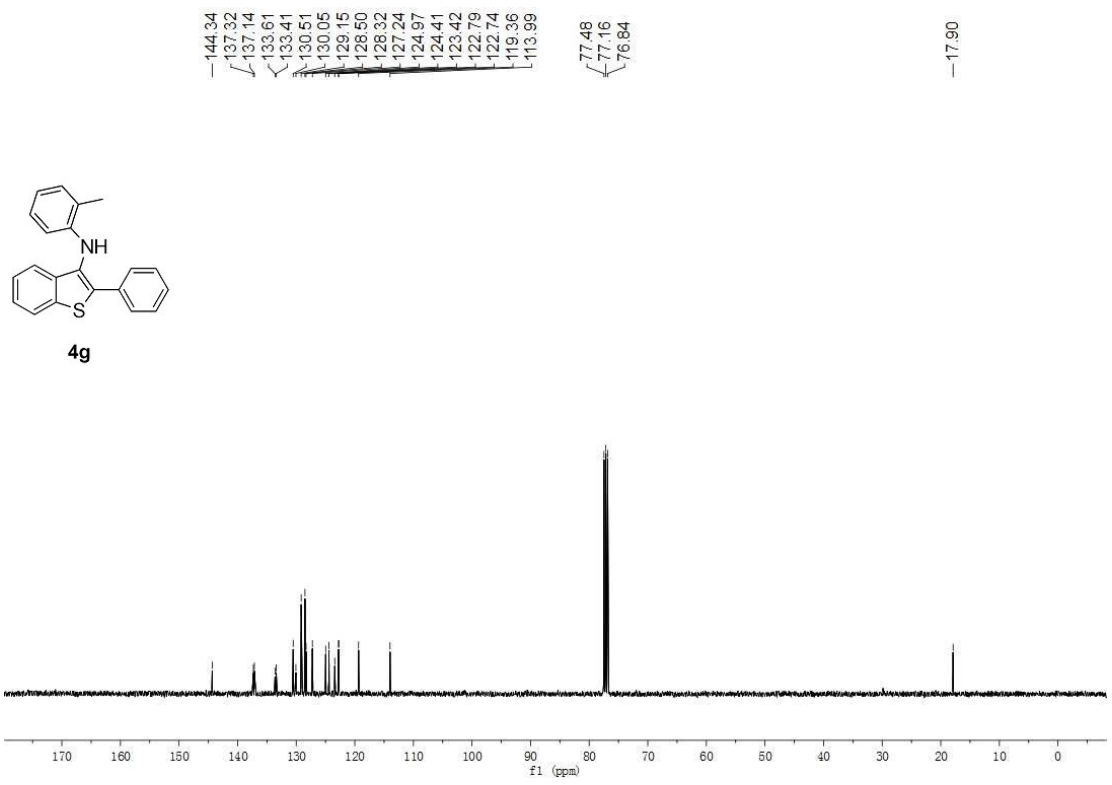
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



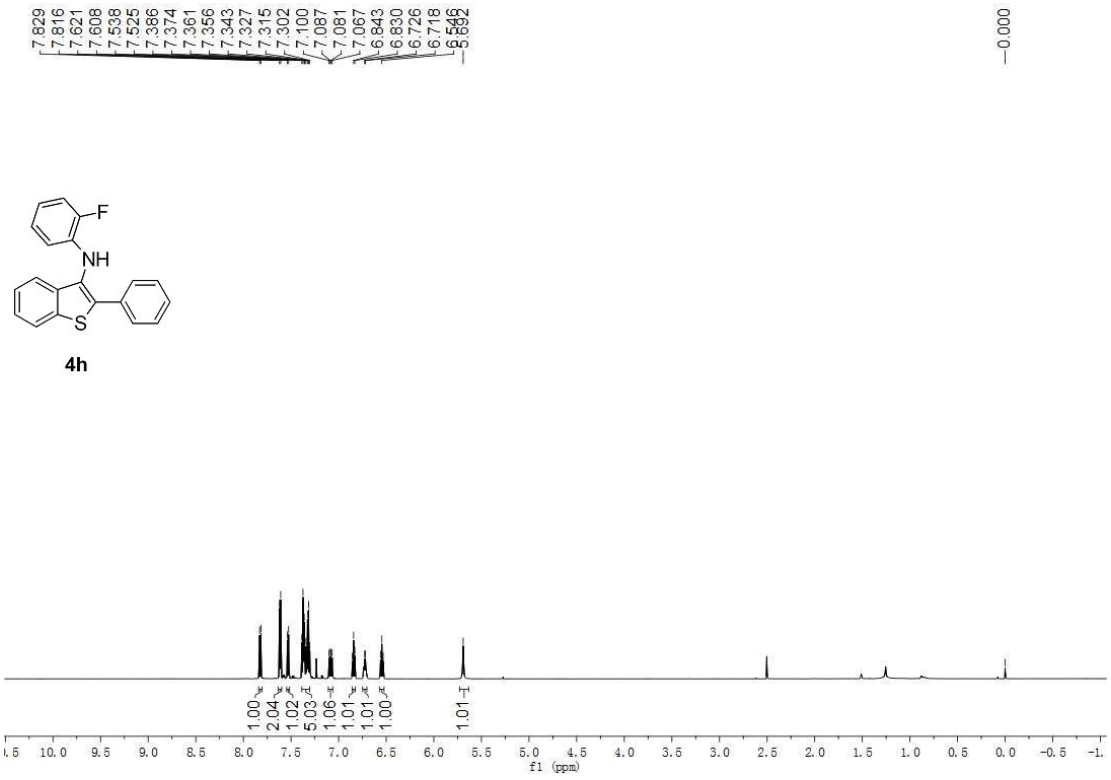
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



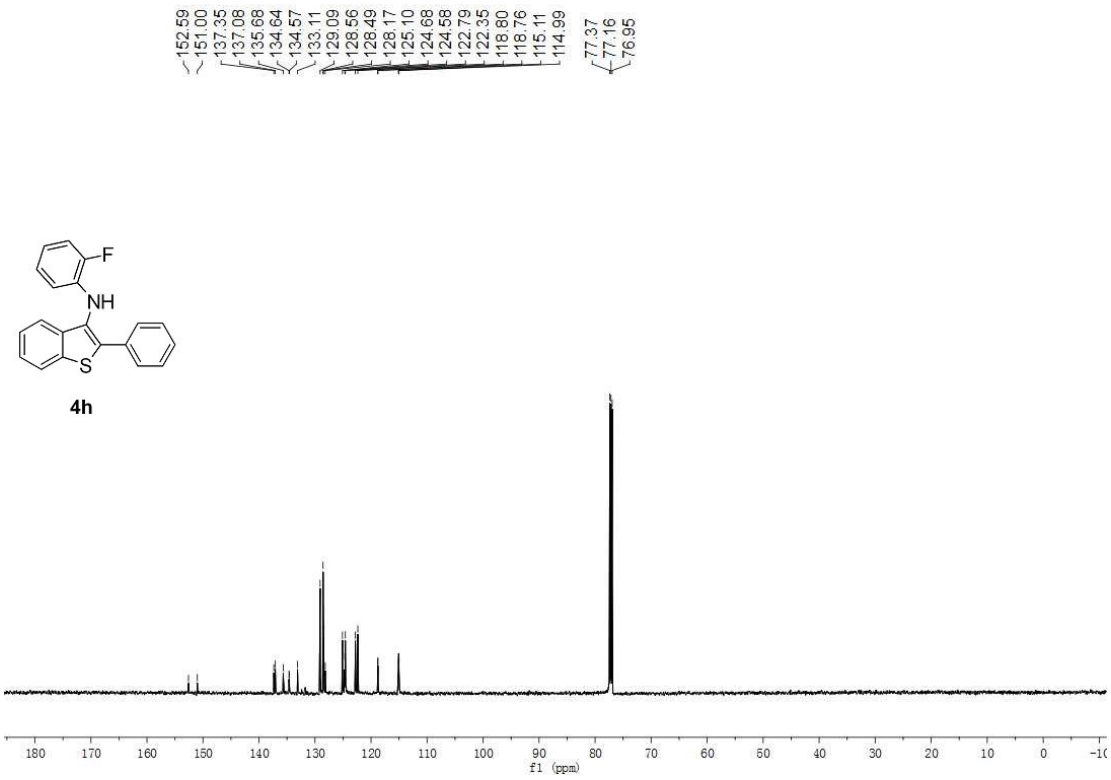
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



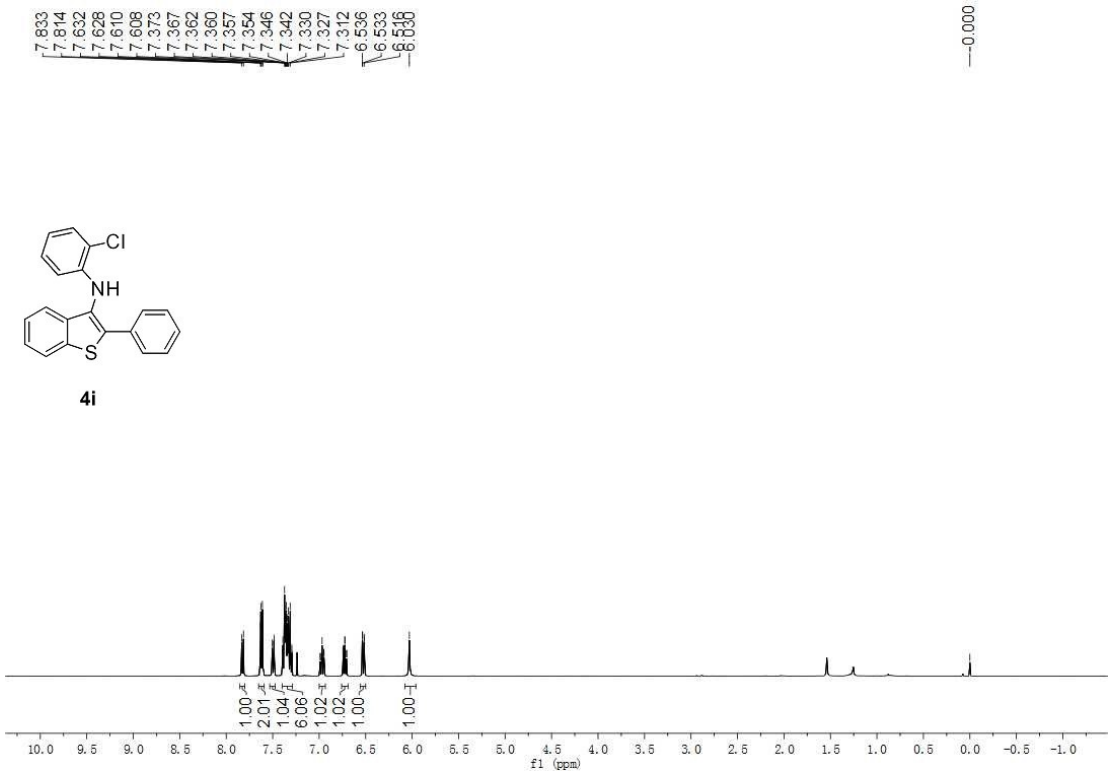
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



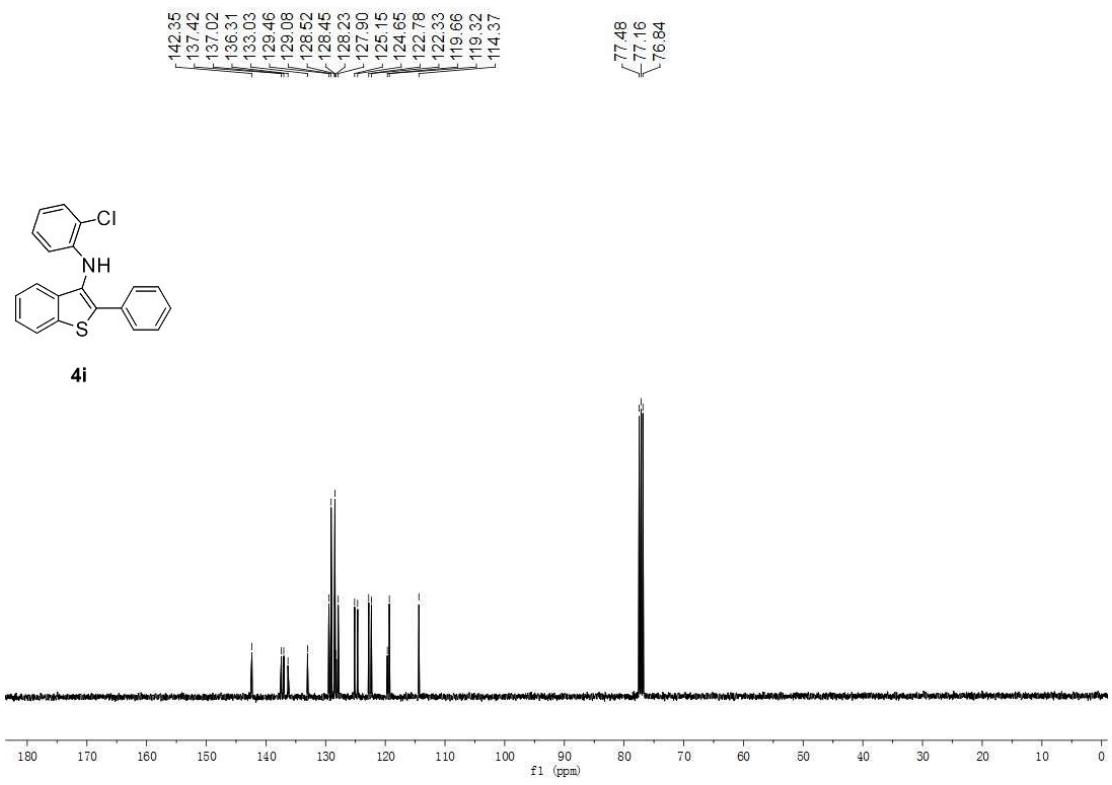
^{1}H NMR spectrum of **4h** (600 MHz, $CDCl_3$)



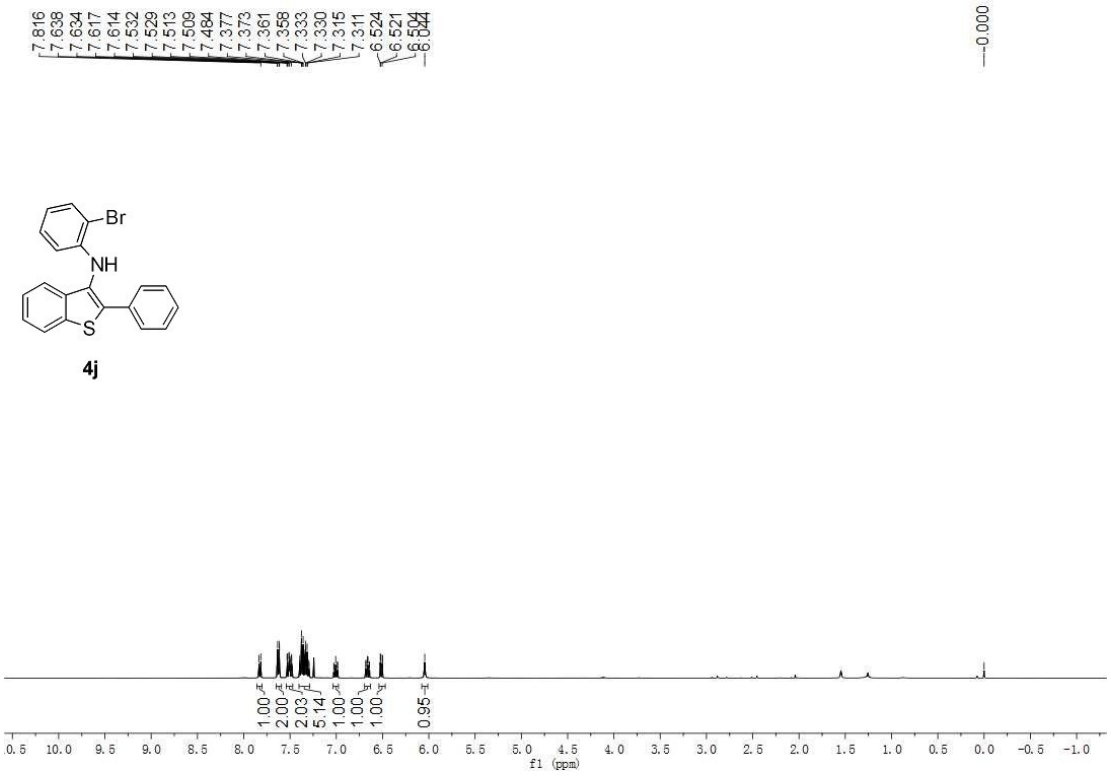
^{13}C NMR spectrum of **4h** (150 MHz, $CDCl_3$)



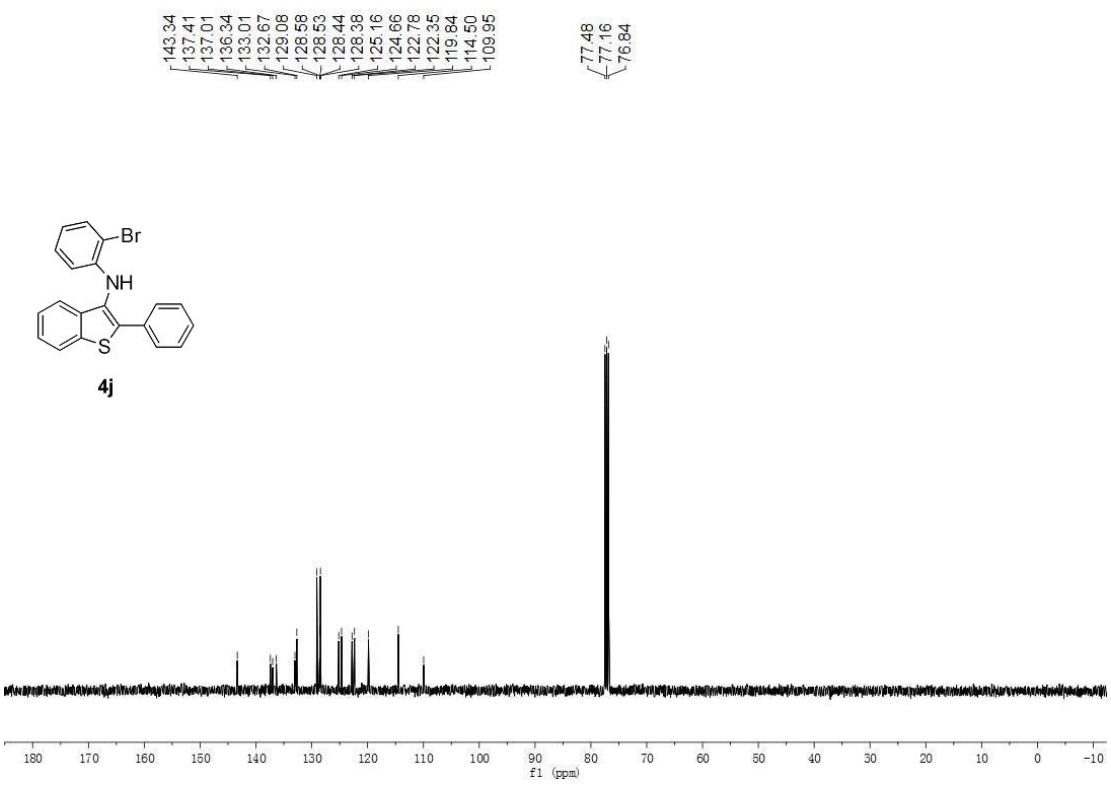
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



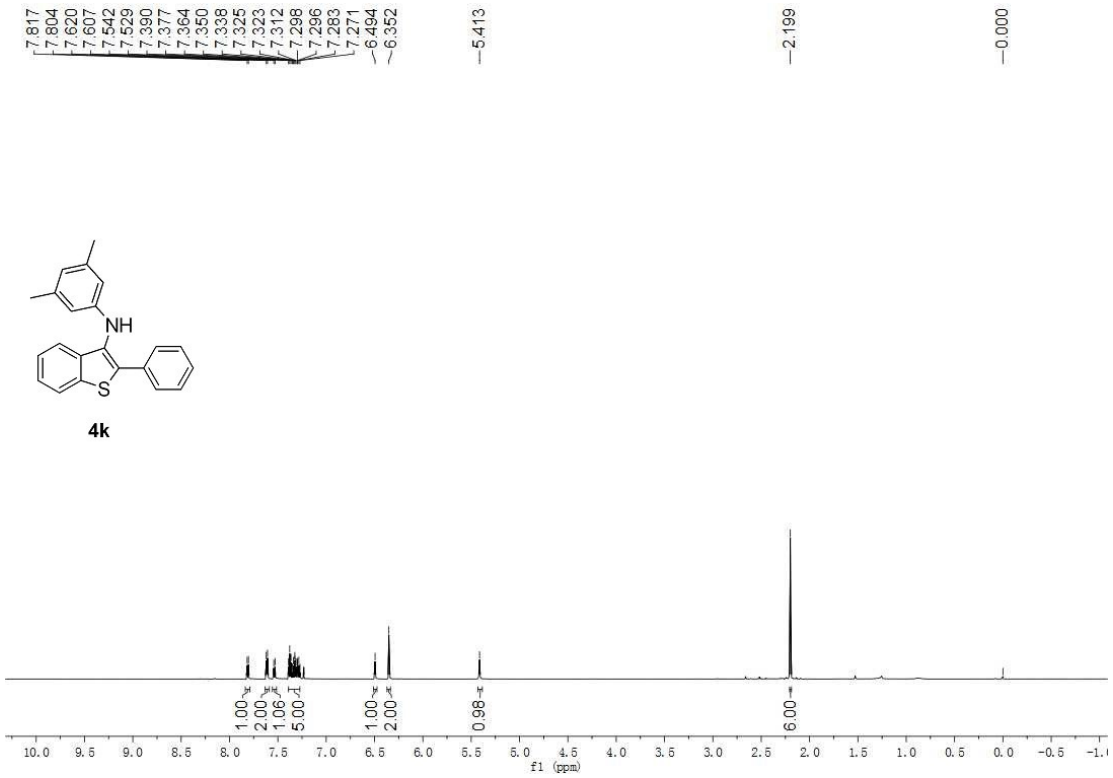
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



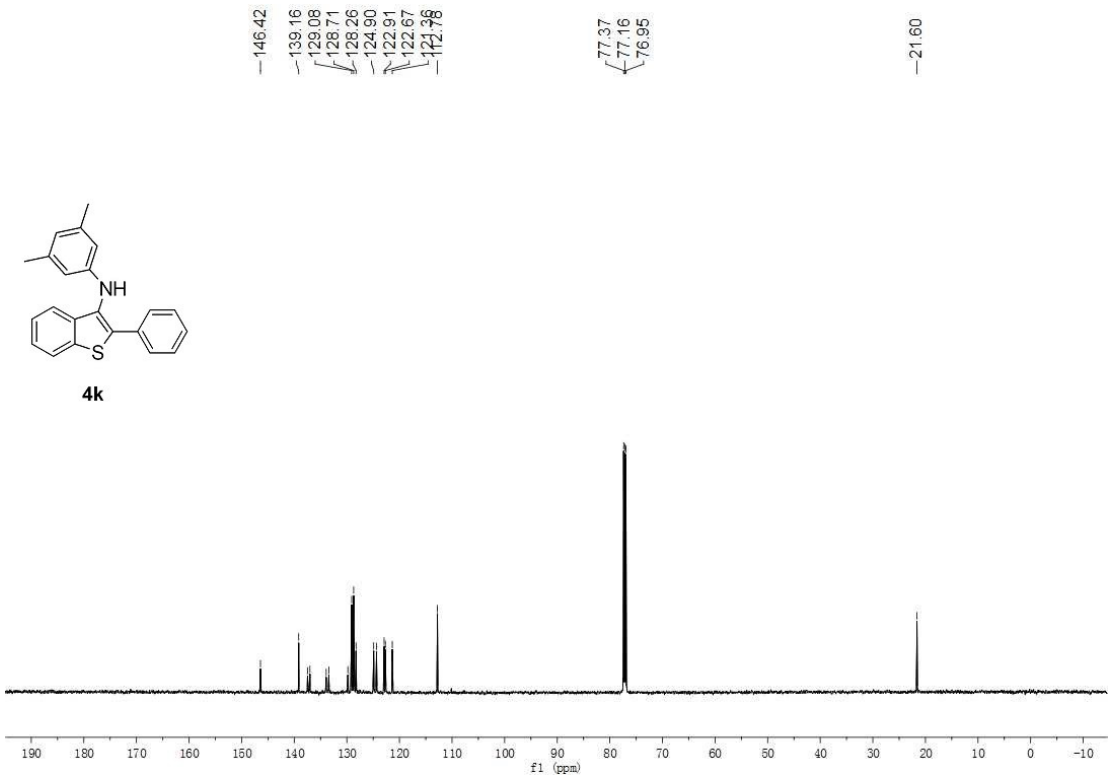
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4k** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4k** (150 MHz, $CDCl_3$)