Supporting Information

For

Synthesis of 2-substituted benzo[*b*]thiophene by Pd-catalyzed coupling of 2-iodothiophenol with phenylacetylene

Jingwen Chen,[a] Haifeng Xiang,[a]* Li Yang,[a,b] Xiangge Zhou[a]*

[a] Institute of Homogeneous Catalysis, College of Chemistry, Sichuan University, Chengdu 610064, China.
[b] College of Chemistry and Chemical Engineering, Yibin University, Yinbin 644000, China

Email: zhouxiangge@scu.edu.cn, Fax: +86-28-85412904.

Contents

1. General methods

Analytical thin layer chromatography (TLC) was performed using silica gel GF254 plates. Column chromatography was performed using silica gel (300-400mesh) eluting with petroleum ether/ethyl acetate. NMR and GCMS characterized all products. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker DPX) with $CDCl_3$ as solvent. Chemical shifts are reported in ppm using TMS as internal standard. GCMS was recorded on a commercial apparatus (EI Source, TOF). UV/vis absorption spectra were recorded using a UV 765 spectrophotometer with quartz cuvettes of 1 cm path length. Fluorescence spectra were obtained using an F-7000 fluorescence spectrophotometer (Hitachi) at room temperature. The slit width was 5.0 nm for both excitation and emission. The photon multiplier voltage was 400 V. Samples in solution and powder were contained in volumetric flask (100 ml) and round-bottom flask (50 ml). HRMS was recorded on a commercial apparatus (ESI Source, TOF). Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification.

2. General experiment procedure

2.1 General synthesis of the 2-substituted Benzo[*b*]thiophenes

2-iodothiophenol (0.5 mmol), phenylacetylene (4 equiv.), $Pd(OAc)_2$ (15 mol%), tetramethylethylenediamine (20 mol%), $AgCOOCF_3$ (1.1 equiv.) were combined in DMF in a 10 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred in 110 °C oil bath for 24 hours with nitrogen gas atmosphere. After cooled to room temperature, the mixture was extracted with ethyl acetate (3 x 10 mL). The residue was purified by silica-gel column chromatography to afford the corresponding product.

2.2 Measurement of Fluorescence Quantum Yield (Φ)

Φ was measured by the optical dilute method of Demas and Crosby1 with a standard of quinine sulfate ($\Phi_r = 0.55$, quinine in 5.0×10^{-5} mol/L sulfuric acid) calculated by $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2 - (D_s/D_r)$, where the subscripts s and r refer to the sample and reference standard solution, respectively; n is the refractive index of the solvents; and D is the integrated intensity. The excitation intensity B is calculated by $B = 1-10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length (L = 1 cm in all cases). The refractive indices of the solvents at room temperature are taken from a standard source. Errors for Φ values (±10%) are estimated.

2.3 Screening of solvent and time

Entry	Catalyst (mol %)	Ligand	Additive	T/℃	Solvent	Time/h	Yields (%)[b]
1	$Pd(OAc)_2$	TMEDA	AgTFA	100	DMSO	24	78
2	$Pd(OAc)_2$	TMEDA	AgTFA	100	*p*-xylene	24	74
3	$Pd(OAc)_2$	TMEDA	AgTFA	100	*0*-xylene	24	71
4	$Pd(OAc)_2$	TMEDA	AgTFA	100	*m*-xylene	24	72
5	$Pd(OAc)_2$	TMEDA	AgTFA	100	toluene	24	80
6	$Pd(OAc)_2$	TMEDA	AgTFA	110	DMF	12	63
7	$Pd(OAc)_2$	TMEDA	AgTFA	110	DMF	36	81
8	$Pd(OAc)_2$	TMEDA	AgTFA	110	DMF	72	82

[a]Reaction condition: 2-iodophenol (0.5 mmol), phenylacetylene (4 equiv.), TMEDA (20 mol%) and AgTFA (1.1 equiv.) in solvent (2 mL) under N_2 . [b]Isolated yields.

2.4 synthesis of 2-(4-(*tert*-butyl)phenyl)benzo[*b*]thiophene 1,1-dioxide 4

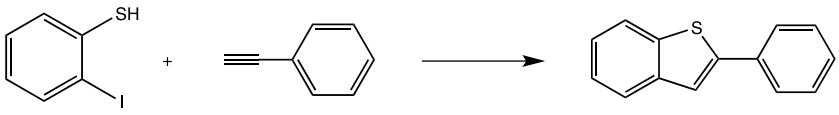
To a magnetic stirred solution of 2-(4-tert-butylphenyl)benzo[*b*]thiophene (133mg 0.5 mmol), formic acid (1 mL) and H_2O_2 (30% of the concentration 0.5mL) in dichloromethane (10 mL) was stirred at room temperature for 4h. Later, reaction was extracted with ethyl acetate (3x 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. Solvent was removed by rotary evaporation under reduce pressure and the residue was purified by thin layer chromatography with ethyl acetate and petroleum ether .

2.5 Synthesis of (4-methoxyphenyl)(2-(4-methoxyphenyl)benzo[*b*]thiophen-3-yl)methanone

To a magnetic stirred solution under anaerobic conditions (N_2) of 4-methoxybenzoyl chloride (0,1 mL. 0.8 mmol) and tin (IV) chloride (0.1 mL 1.0 mmol) in 1,2-dichloroethane (50 mL) was added dropwise the corresponding 2-(4-methoxyphenyl)benzo[*b*]thiophene 22 (94.2 mg 0.30 mmol) dissolved in 1,2-dichloroethane (10 mL). The mixture was stirred at room temperature under anaerobic conditions (N_2) for 6h. Later, reaction was poured into a cold aqueous solution of $NaHCO_3$ (1 M) and transferred to a 250 mL. Then the mixture was extracted with ethyl acetate (3x 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. Solvent was removed by rotary evaporation under reduce pressure and the residue was purified by thin layer chromatography with CH_2Cl_2 .

3. Mechanistic investigation

3.1 Radical/electron trapping experiment[a]

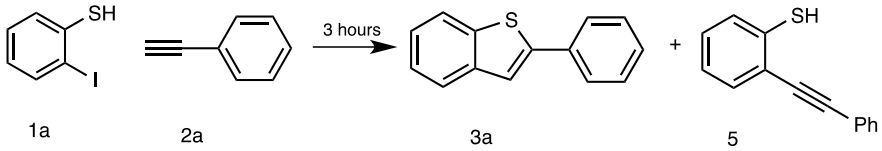


1a 2a 3a

Entry	Scavenger	Yield[%][b]
1	none	81
2	TEMPO(1 equiv)	80

[a]Reaction conditions: 2-iodothiophenols 0.5 mmol, alkynes 4 equiv., DMF 2 mL, $Pd(OAc)_2$ 10 mol%, Ag_2CO_3 1.1 equiv., TMEDA 20 mol% [b]Isolated yield.

3.2 GC/MS data

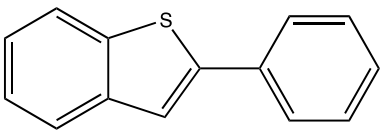


1a 2a 3a 5

The intermediate 8 was detected by using GCMS in the reaction mixture of 2-iodothiophenol with phenylacetylene after 3 hours at 7.216min, and the product 3a was detected by using GC/MS at 7.740min.

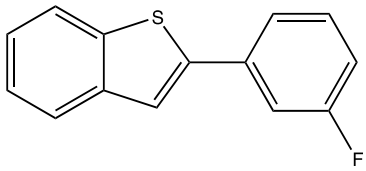
4 Characterization data

3a. 2-phenylbenzo[*b*]thiophene[2]



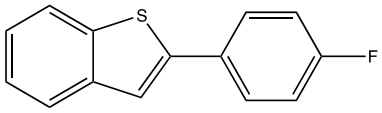
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.87 – 7.81 (m, 1H), 7.80 – 7.70 (m, 3H), 7.55 (d, *J* = 0.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.38 – 7.29 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.26, 140.71, 139.52, 134.31, 132.54, 129.25, 128.48, 126.52, 124.54, 122.31, 119.48. MS (EI,70eV) *m/z* 210. Anal. Calcd. (Found): C, 79.96 (79.95); H, 4.79 (4.81); S, 15.25 (15.27). Mp:166-168℃

3b. 2-(3-fluorophenyl)-benzo[*b*]thiophene[3]



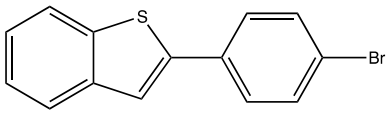
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.87 – 7.76 (m, 2H), 7.56 (d, *J* = 0.9 Hz, 1H), 7.50 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 7.45 – 7.30 (m, 4H), 7.04 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 130.53, 130.44, 124.71, 124.69, 123.79, 122.31, 122.21, 120.31, 115.15, 114.93, 113.44, 113.21. MS (EI,70eV) *m/z* 228. Anal. Calcd. (Found): C, 73.66 (73.66); H, 3.97 (3.99); S, 14.05 (14.10). Mp:124-126℃

3c. 2-(4-fluorophenyl) benzo[*b*]thiophene [4]



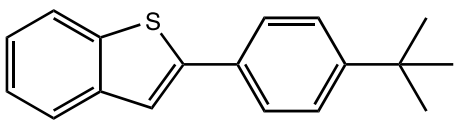
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.86 – 7.73 (m, 1H), 7.73 – 7.64 (m, 1H), 7.55 – 7.44 (m, 3H), 7.24 (dd, *J* = 5.8, 3.3 Hz, 3H), 7.18 – 7.07 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ135.56，128.73, 128.23, 128.15, 127.68, 124.62, 124.39, 123.55, 122.26, 119.45, 116.07, 115.86. MS (EI,70eV) *m/z* 228. Anal. Calcd. (Found): C, 73.66 (73.63); H, 3.97 (3.98); S, 14.05 (14.09). Mp:162-164℃

3d. 2-(4-bromophenyl)-benzo[*b*]thiophene[5]



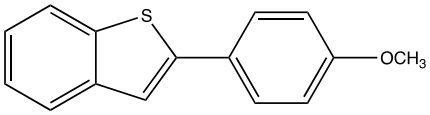
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.86 – 7.74 (m, 1H), 7.73-7.65(m, 1H), 7.62 – 7.44 (m, 5H), 7.41 – 7.27 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 140.57, 133.28, 132.08, 131.83, 127.93, 124.69, 124.63, 123.69, 122.31, 122.23, 119.93. MS (EI,70eV) *m/z* 288. Anal. Calcd. (Found): C, 58.15 (58.18); H, 3.14 (3.10); S, 11.09 (11.05).Mp:204-206℃

3e. 2-(4-tert-butylphenyl)benzo[*b*]thiophene[6]



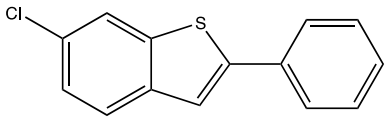
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.97 – 7.89 (m, 1H), 7.84 – 7.73 (m, 1H), 7.69 – 7.62 (m, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.45 (m, 2H), 7.38 – 7.36 (m, 2H), 1.31 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.57, 144.33, 140.69, 139.40, 138.03, 132.26, 125.48, 124.33, 123.43, 123.03, 122.90, 118.83, 34.93, 31.28. MS (EI,70eV) *m/z* 266. Anal. Calcd. (Found): C, 81.15 (81.11); H, 6.81 (6.82); S, 12.04 (12.07).Mp:165-167℃

3f. 2-(4-methoxyphenyl)benzo[*b*]thiophene



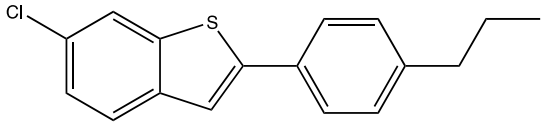
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.87 – 7.78 (m, 1H), 7.51 – 7.40 (m, 1H), 7.37 – 7.26 (m, 1H), 7.17 (s, 0H), 7.03 – 6.90 (m, 1H), 3.80 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 139.59, 137.04, 136.66, 128.76, 127.47, 126.70, 123.28, 121.87, 121.52, 117.15, 113.11, 54.32. MS (EI,70eV) *m/z* 240. Anal. Calcd. (Found): C, 74.97(74.93); H, 5.03(5.00); S, 13.34(13.33). Mp: 193-194 °C

3g. 6-chloro-2-phenylbenzo[*b*]thiophene[4]



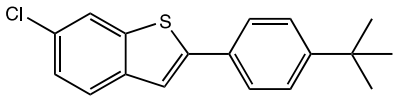
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.80 (d, *J* = 1.9 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.51 – 7.48 (m, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.88, 140.47, 139.11, 133.86, 132.52, 130.29, 129.04, 128.54, 128.46, 126.46, 125.38, 124.32, 121.86, 118.91. MS (EI,70eV) *m/z* 244. Anal. Calcd. (Found): C, 68.71 (68.67); H, 3.71 (3.73); S, 13.10 (13.14). Mp:192-194℃

3h. 6-chloro-2-(4-propylphenyl)benzo[*b*]thiophene



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.89 – 7.76 (m, 1H), 7.67 – 7.56 (m, 1H), 7.50 – 7.40 (m, 2H), 7.38 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 2.63 (dt, *J* = 15.4, 7.6 Hz, 2H), 1.68 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.98 (dt, *J* = 12.3, 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$)δ 144.26, 143.44, 140.32, 139.22, 132.41, 128.64, 126.34, 124.16, 121.81 119.01, 118.30, 38.06, 24.50, 13.86. MS (EI,70eV) *m/z* 286. Anal. Calcd. (Found): C, 71.19(71.22); H, 5.27(5.31); S, 11.18(11.15). Mp:94-96℃

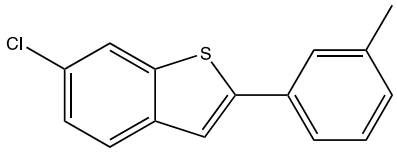
3i. 2-(4-(tert-butyl)phenyl)-6-chlorobenzo[*b*]thiophene



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.79 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.38 – 7.34 (m, 2H), 1.36 (s, 9H).

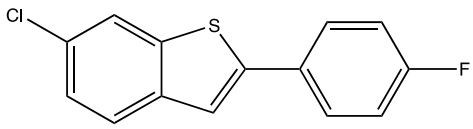
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.57, 132.25, 132.25, 126.20, 125.97, 125.47, 125.28, 124.16, 121.81, 119.30, 118.82, 118.36, 34.92, 31.25. MS (EI,70eV) *m/z* 300. Anal. Calcd. (Found): C, 71.86(71.88); H, 5.70(5.72); S, 10.66(10.64). Mp:88-90℃

3j. 6-chloro-2-(m-tolyl)benzo[*b*]thiophene



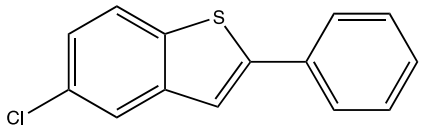
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.84 – 7.75 (m, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.45 (d, *J* = 0.8 Hz, 1H), 7.35 – 7.19 (m, 4H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04, 140.29, 139.20, 138.62, 131.05, 129.72, 129.54, 126.34, 125.30, 124.16, 121.81, 118.29, 21.31. MS (EI,70eV) *m/z* 258. Anal. Calcd. (Found): C, 69.62(69.60); H, 4.28(4.24); S, 12.39(12.42) Mp:92-94℃

3k. 6-chloro-2-(4-fluorophenyl)benzo[*b*]thiophene



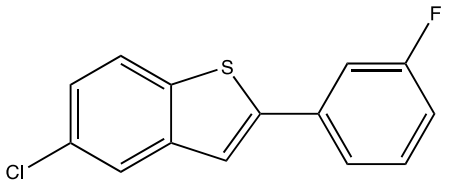
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.72 – 7.62 (m, 1H), 7.57 – 7.46 (m, 3H), 7.13 (t, *J* = 8.6 Hz, 1H), 7.04 (t, *J* = 8.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.59, 134.50, 128.23, 128.15, 125.48, 124.30, 121.84, 117.82, 116.19, 116.04, 115.97, 115.82. MS (EI,70eV) *m/z* 262. Anal. Calcd. (Found): C, 64.00 (64.02); H, 3.07 (3.05); S, 12.20 (12.18).Mp:140-142℃

3l. 5-chloro-2-phenyl-benzo[*b*]thiophene[4]



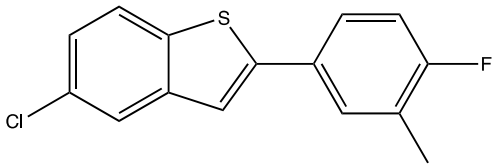
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.80 – 7.66 (m, 3H), 7.48 – 7.40 (m, 3H), 7.39 – 7.33 (m, 2H), 7.29 – 7.24 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.37, 141.78, 137.56, 133.83, 132.52, 130.72, 129.22, 129.05, 128.68, 126.56, 124.71, 123.28, 123.02, 118.66. MS (EI,70eV) *m/z* 244. Anal. Calcd. (Found): C, 68.71(68.69); H, 3.71(3.74); S, 13.10(13.14). Mp:190-192℃

3m. 5-chloro-2-(3-fluorophenyl)benzo[*b*]thiophene



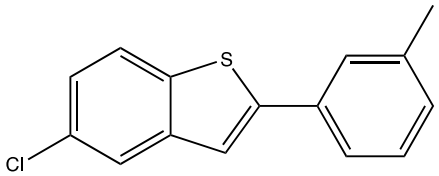
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.77 – 7.72 (m, 1H), 7.53 – 7.45 (m, 1H), 7.44 – 7.32 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.17 (m, 1H). 7.16 – 7.00 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.53, 137.60, 130.91, 130.65, 130.57, 130.20, 130.12, 128.51, 128.47, 125.13, 123.33, 123.23, 122.28, 122.25, 119.50, 119.36, 119.13, 117.05, 116.83, 115.58, 115.37, 113.53, 113.30. MS (EI,70eV) *m/z* 262. Anal. Calcd. (Found): C, 64.00(64.02); H, 3.07(3.05); S, 12.20(12.17). Mp:96-98℃

3n. 5-chloro-2-(4-fluoro-3-methylphenyl)benzo[*b*]thiophene



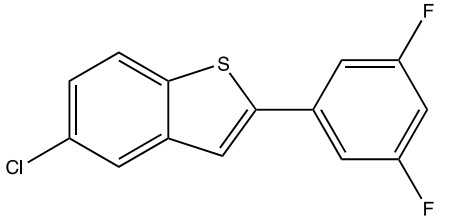
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.72 – 7.70 (m, 1H), 7.53 – 7.48 (m, 1H), 7.38 – 7.34 (m, 2H), 7.29 – 7.24 (m, 1H), 7.06 (t, *J* = 8.8 Hz, 1H), 6.96 (t, *J* = 8.9 Hz, 1H), 2.34 (d, *J* = 1.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.00, 162.84, 145.47, 141.79, 137.46, 135.72, 135.66, 131.91, 131.83, 130.77, 129.72, 129.67, 125.74, 125.63, 125.55, 125.45, 124.65, 123.22, 122.93, 118.43, 117.49, 115.77, 115.57, 115.54, 115.34, 14.66. MS (EI,70eV) *m/z* 276. Anal. Calcd. (Found): C, 65.10(65.09); H, 3.64(3.67); S, 11.59(11.56).

3o. 5-chloro-2-(m-tolyl)benzo[*b*]thiophene



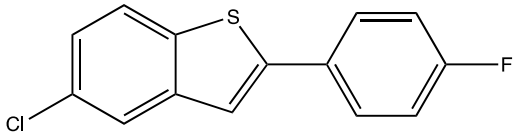
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.75 – 7.71 (m, 2H), 7.52 – 7.45 (m, 2H), 7.36 – 7.30 (m, 1H), 7.29 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.57, 141.80, 138.75, 137.53, 129.48, 128.93, 127.24, 124.61, 123.71, 123.25, 122.95, 118.53, 21.45. MS (EI,70eV) *m/z* 258. Anal. Calcd. (Found): C, 69.62(69.64); H, 4.28(4.26); S, 12.39(13.44). Mp:72-74℃

3p. 5-chloro-2-(3,5-difluorophenyl)benzo[*b*]thiophene



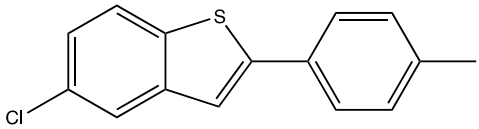
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.82 – 7.64 (m, 2H), 7.55 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.40 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.60, 164.47, 162.13, 162.00, 144.56, 143.52, 141.51, 141.28, 137.64, 137.62, 136.91, 135.58, 134.99, 131.10, 130.92, 130.27, 128.57, 126.49, 125.55, 125.15, 124.68, 123.44, 123.37, 123.33, 123.23, 120.27, 119.53, 109.58, 109.51, 109.39, 109.32, 104.06, 103.81, 103.56. MS (EI,70eV) *m/z* 280. Anal. Calcd. (Found): C, 59.90(59.94); H, 2.51(2.47); S, 11.42(11.44). Mp:146-148℃

3q. 5-chloro-2-(4-fluorophenyl)benzo[*b*]thiophene



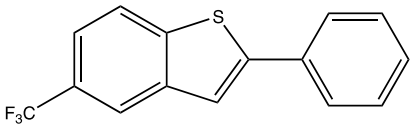
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.76 – 7.62 (m, 1H), 7.51 (ddd, *J* = 8.4, 5.4, 2.5 Hz, 3H), 7.26 (s, 1H), 7.04 (td, *J* = 8.7, 2.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.50, 128.33, 128.25, 124.78, 123.26, 123.01, 118.65, 117.82, 117.79, 116.19, 116.03, 115.97. MS (EI,70eV) *m/z* 262. Anal. Calcd. (Found): C, 64.00(63.98); H, 3.07(3.11); S, 12.20(12.18). Mp:152-154℃

3r. 5-chloro-2-(p-tolyl)benzo[*b*]thiophene



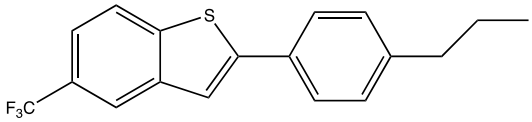
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.75 – 7.67 (m, 1H), 7.63 – 7.54 (m, 1H), 7.44 – 7.40 (m, 2H), 7.29 – 7.20 (m, 2H), 7.18 – 7.09 (m, 2H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.88, 139.51, 138.78, 132.40, 129.72, 129.23, 126.43, 124.49, 123.23, 122.86, 118.78, 118.05, 21.66. MS (EI,70eV) *m/z* 258. Anal. Calcd. (Found): C, 69.62(69.95); H, 4.28(4.31); S, 12.39(12.35). Mp:108-110℃

3s. 2-phenyl-5-(trifluoromethyl)benzo[*b*]thiophene[5]



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 8.07 – 8.02 (m, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.61 (s, 1H), 7.53 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.42 – 7.34 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.56, 140.23, 133.61, 129.12, 128.87, 126.63, 122.78, 120.62, 120.58, 120.53, 119.34. MS (EI,70eV) *m/z* 278. Anal. Calcd. (Found): C, 64.74(64.77); H, 3.26(3.26); S, 11.52(11.51). Mp:175-177℃

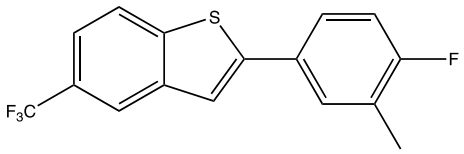
3t. 2-(4-propylphenyl)-5-(trifluoromethyl)benzo[*b*]thiophene



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 8.02 – 7.94 (m, 1H), 7.91 – 7.84 (m, 1H), 7.66 – 7.59 (m, 2H), 7.53 – 7.43 (m, 2H), 7.36 – 7.18 (m, 2H), 2.77 – 2.60 (m, 2H), 1.84 – 1.64 (m, 2H), 0.99 (dt, *J* = 14.7, 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.77, 143.80, 140.35, 138.53, 131.06, 129.20, 129.09, 128.50 126.50, 122.70, 120.44, 120.39, 120.31, 120.27, 118.71, 37.79, 24.45, 13.81. MS (EI,70eV) *m/z* 320. Anal. Calcd. (Found): C, 67.48(67.45); H, 4.72(4.71); S, 10.01(10.02). Mp:90-92℃

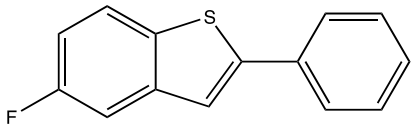
3u. 2-(4-fluoro-3-methylphenyl)-5-(trifluoromethyl)benzo[*b*]thiophene



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 8.10 – 7.84 (m, 1H), 7.63 – 7.49 (m, 1H), 7.46 – 7.40 (m, 1H), 7.32 (ddt, *J* = 3.6, 2.7, 1.1 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.15 – 7.09 (m, 1H), 1.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.04, 130.10, 128.49, 128.46, 123.43, 122.84, 122.37, 120.20, 119.35, 119.12, 117.03, 116.81, 115.56, 113.63, 113.40, 29.52. MS (EI,70eV) *m/z* 310. Anal. Calcd. (Found): C, 61.93(61.94); H, 3.25(3.27); S, 10.33(10.30). Mp:76-78℃

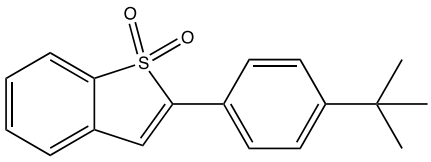
3v. 5-fluoro-2-phenylbenzo[*b*]thiophene



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.78 – 7.67 (m, 3H), 7.50 – 7.40 (m, 4H), 7.39 – 7.32 (m, 1H), 7.07 (td, *J* = 8.8, 2.5 Hz, 1H).

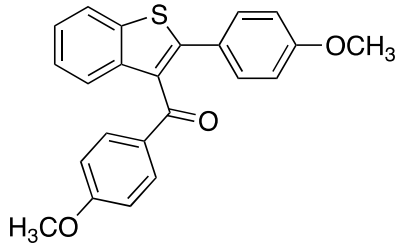
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.19, 159.79, 146.84, 141.58, 133.98, 129.03, 128.61, 126.52, 123.43, 119.14, 113.20, 109.09. MS (EI,70eV) *m/z* 228. Anal. Calcd. (Found): C, 73.66(73.66); H, 3.97(3.94); S, 14.05(14.02). Mp:89-91℃

4. 2-(4-(tert-butyl)phenyl)benzo[*b*]thiophene 1,1-dioxide



^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.81 – 7.73 (m, 3H), 7.60 – 7.45 (m, 4H), 7.40 (dt, *J* = 7.5, 0.8 Hz, 1H), 7.26 – 7.24 (m, 1H), 1.34 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.89, 142.70, 137.07, 133.72, 131.41, 129.69, 126.35, 126.28, 124.88, 124.27, 122.66, 121.49, 34.96, 31.13. MS (EI,70eV) *m/z* 298. Anal. Calcd. (Found): C, 72.45(72.41); H, 6.08(6.10); S, 10.75(10.73). Mp:158-160℃

5. (4-methoxyphenyl)(2-(4-methoxyphenyl)benzo[*b*]thiophen-3-yl)methanone

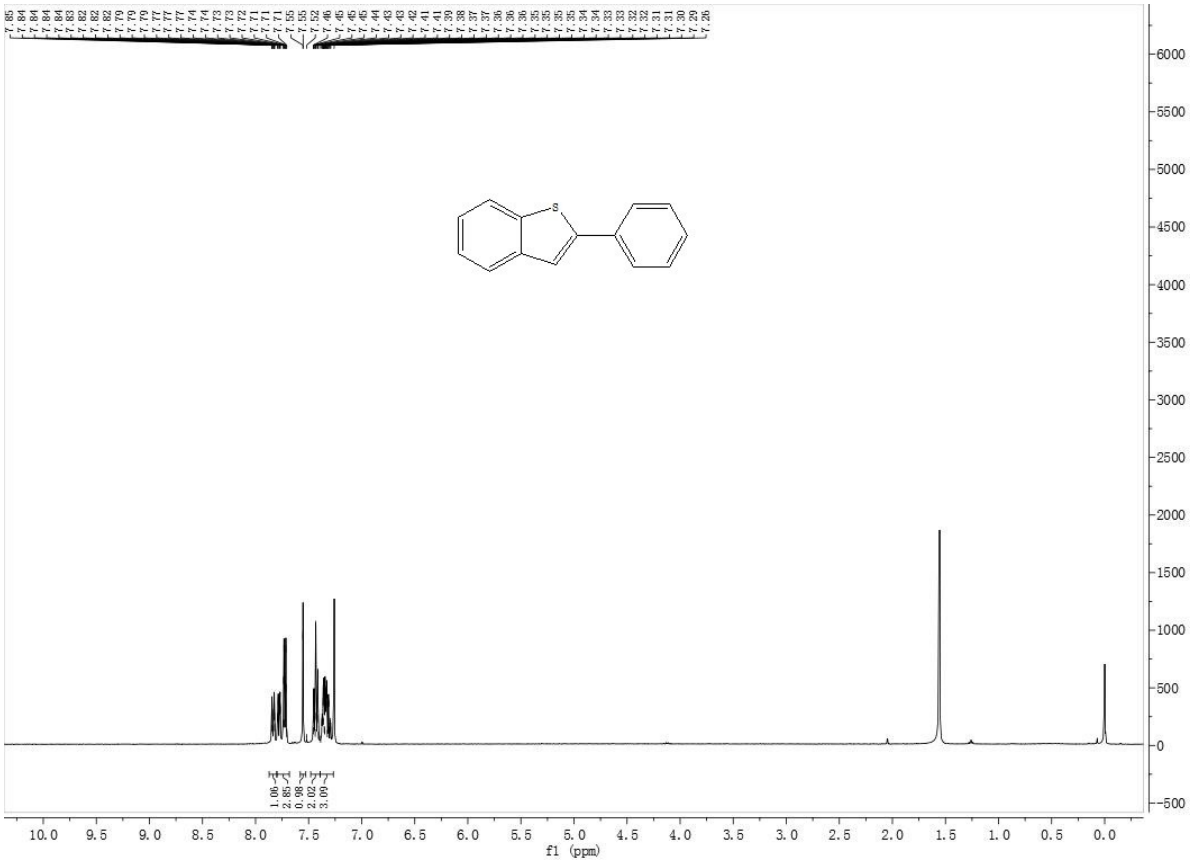


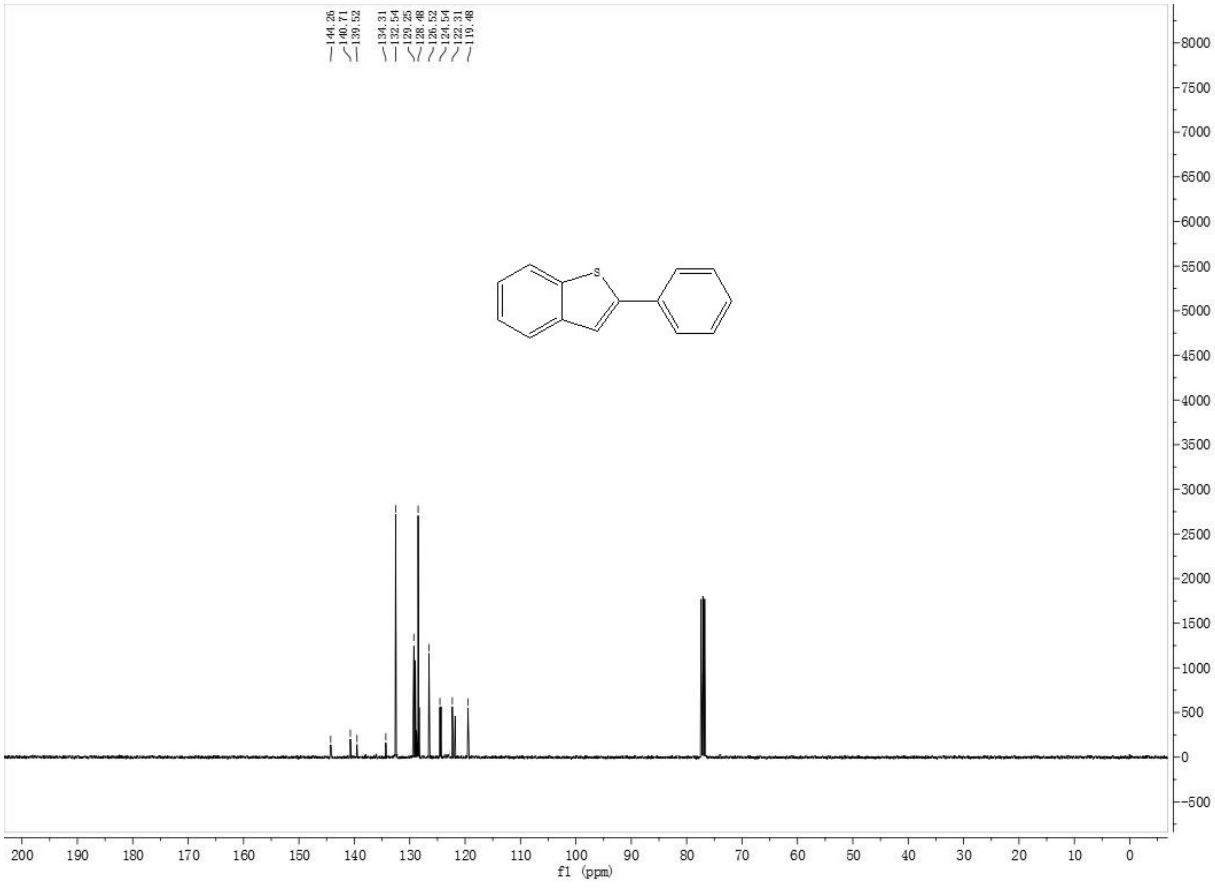
^{1}H NMR (400 MHz, Chloroform-*d*) white solid δ 7.88 – 7.83 (m, 1H), 7.81 – 7.75 (m, 2H), 7.65 – 7.62 (m, 1H), 7.43 – 7.29 (m, 4H), 6.83 – 6.72 (m, 4H), 3.77 (d, *J* = 16.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.26, 163.77, 159.97, 144.92, 139.90, 138.64, 132.37, 130.98, 130.41, 130.39, 125.84, 124.96, 124.73, 123.32, 121.90, 114.12, 113.69, 55.44, 55.28. HRMS(ESI) calculated $[C_{23}H_{18}O_3S]^+$ 374.0977 found 374.0972 Mp: 47-49℃

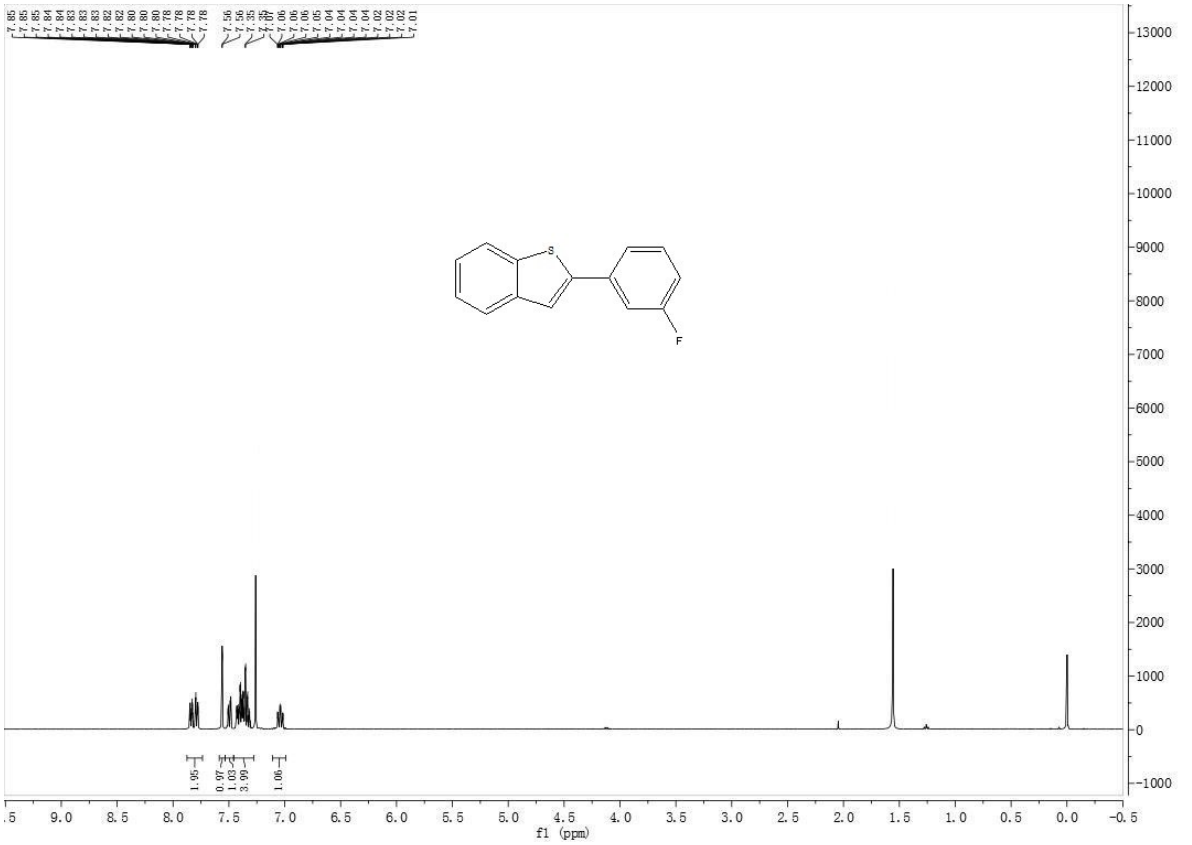
References

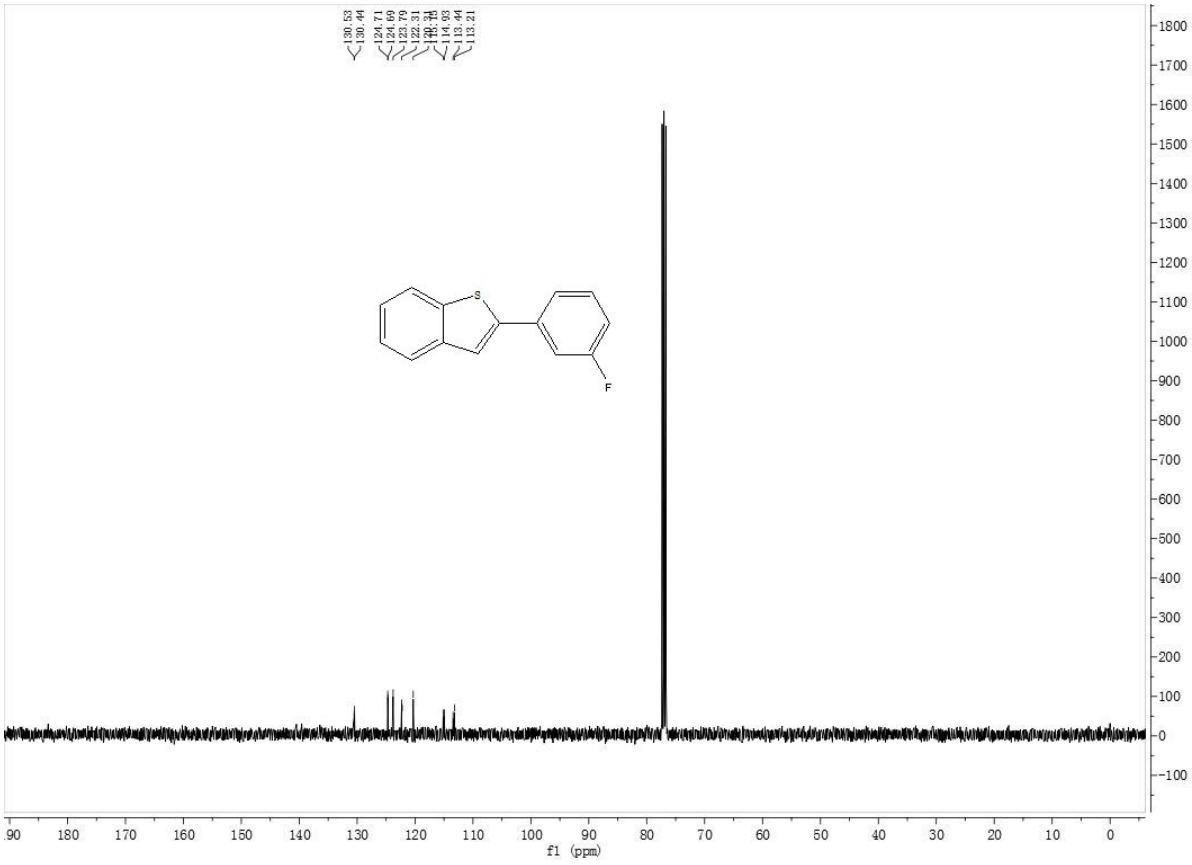
[1] J. N. Demas, G. A. Crosby, Measurement of Photoluminescence Quantum Yields. Review. *J. Phys. Chem*. 1971, **75**, 991−1024.
[2] T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, *Org. Lett.,* 2009, **11**, 2473.
[3] G, Veronica, F. Manuel, G. Patricia, H. Elsa, S. Roberto, *Org. Lett*, 2011, **13**, 5100.
[4] D. P. Hari, T. Hering, B. König, *Org. Lett.*, 2012, **14,** 5334.
[5] P. Jiang, X. Che, Y. Liao, H. Huang, G. Deng, *RSC Adv.,* 2016, **6**, 41751.
[6] Z. Duan, S. Ranjit and X. Liu, *Org. Lett.*, 2010, **12**, 2430.
[7] Y. Luo, X. Pan, C. Chen, L. Yao and J. Wu, *Chem. Commun*., 2015, **51**, 180.

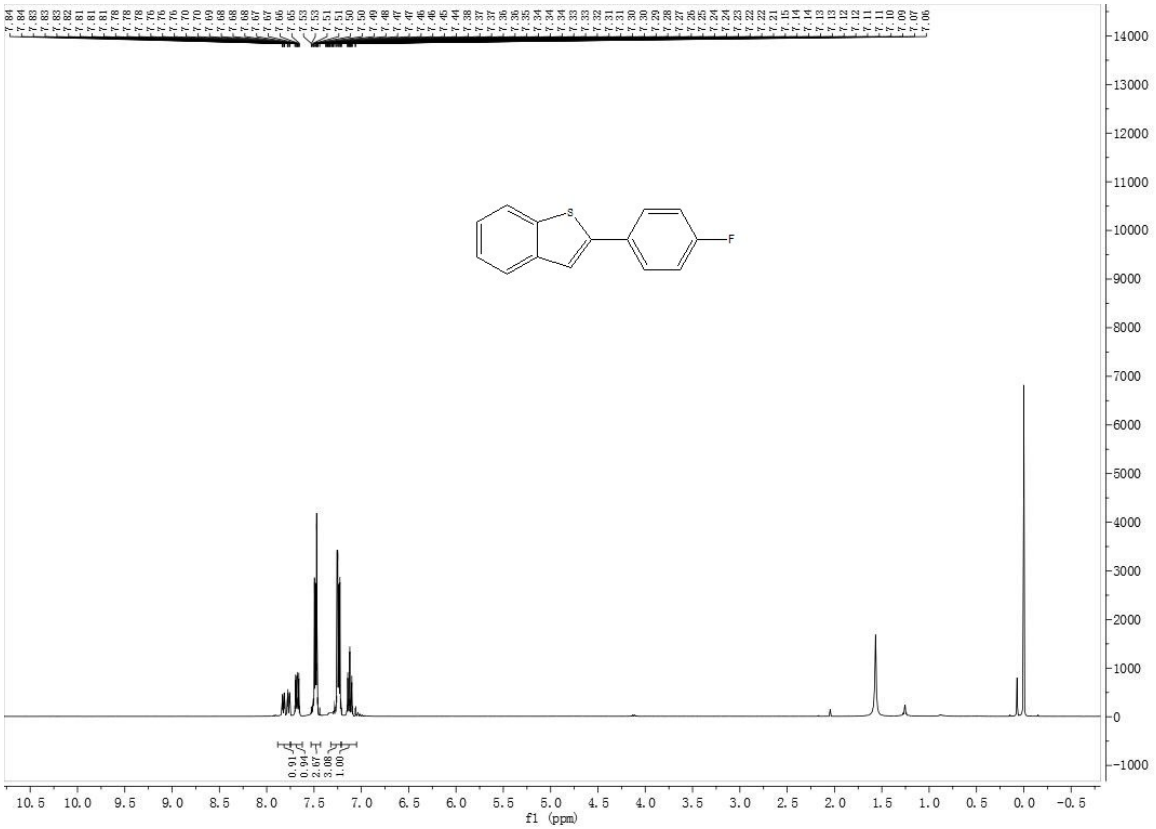
5.NMR spectra

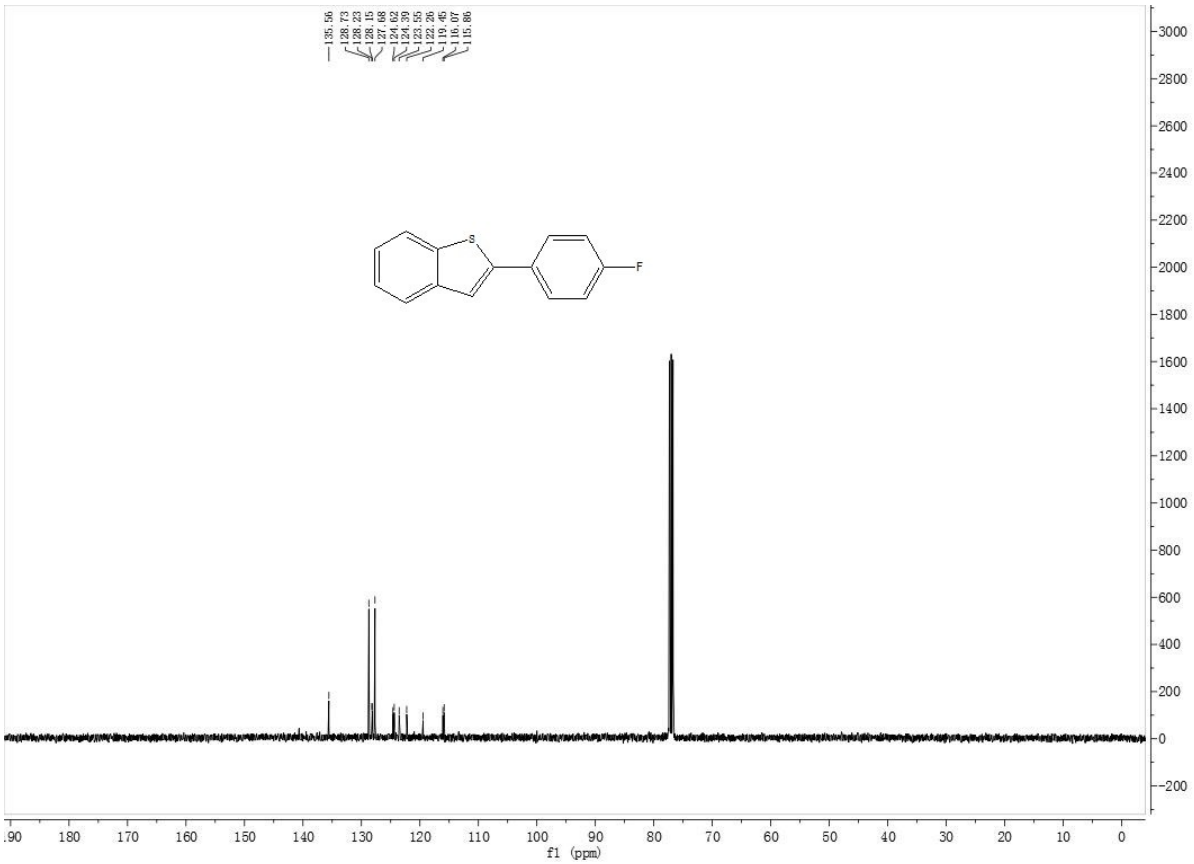

S
1.06
2.85
0.98
2.02
3.09
f1 (ppm)

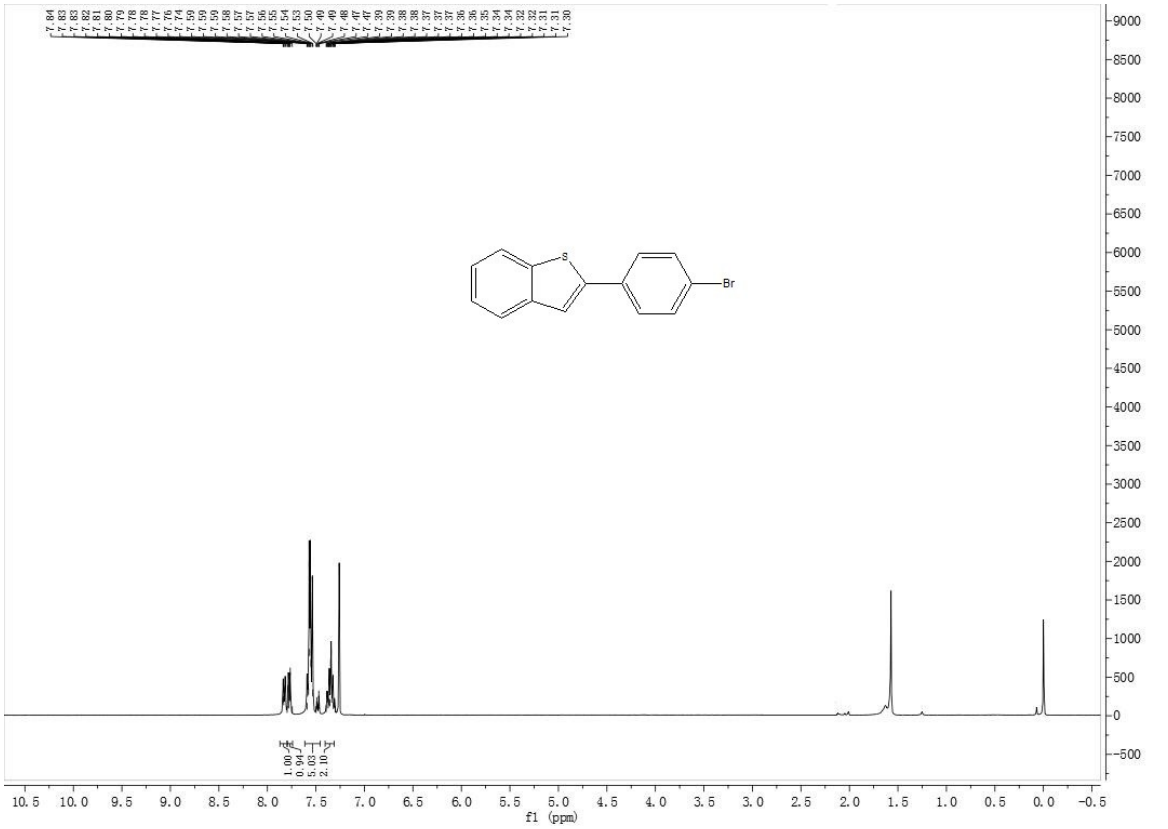

144.26
140.71
139.52
134.31
132.54
129.25
128.48
126.52
124.54
122.31
119.48
S
f1 (ppm)

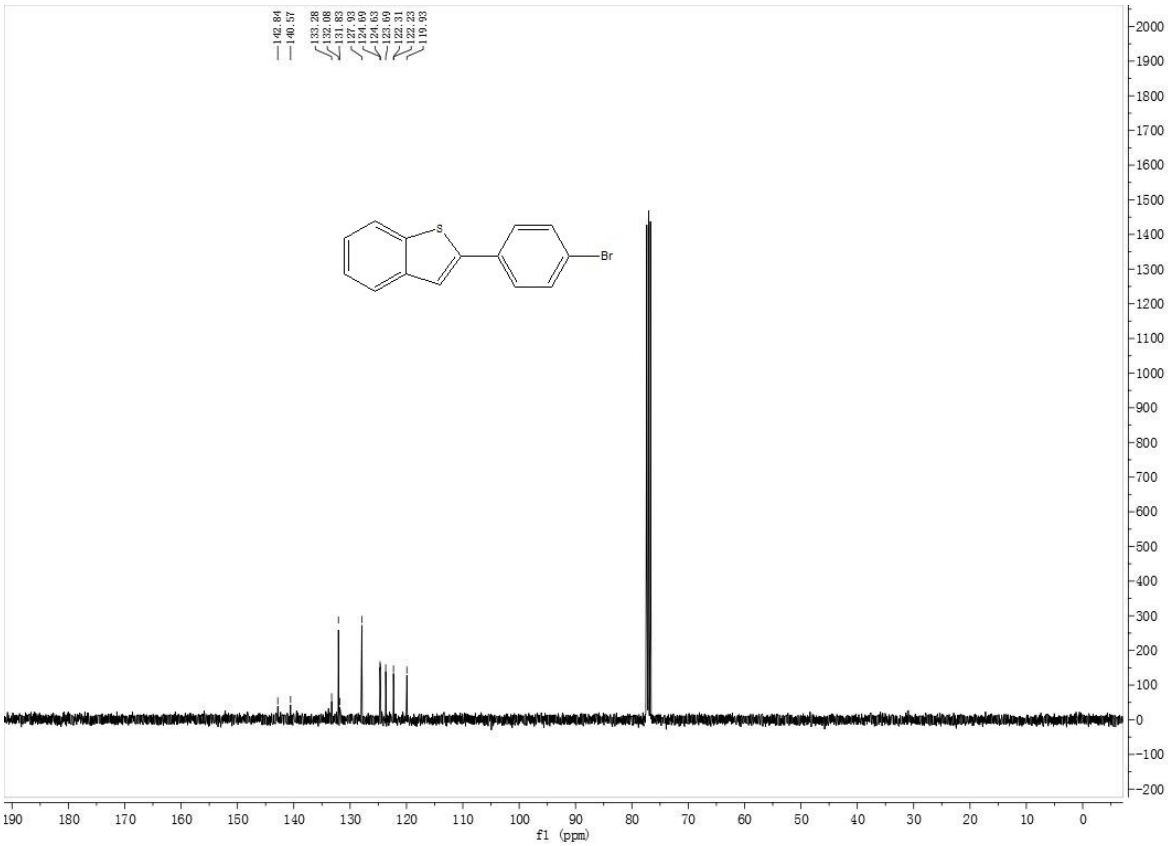

S
F
1.95
0.97
1.03
3.99
1.06
f1 (ppm)

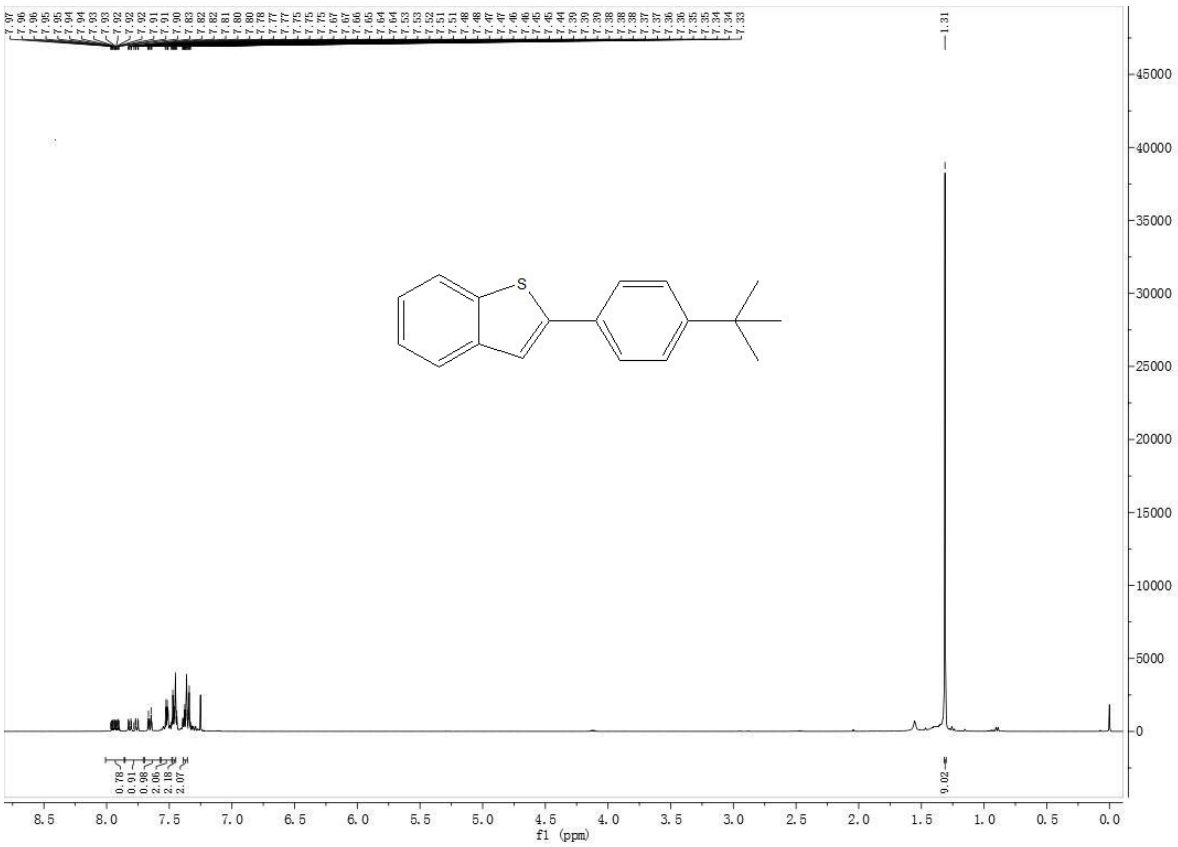

130.53
130.44
124.71
124.69
123.79
122.31
114.93
113.44
113.21
S
F
f1 (ppm)

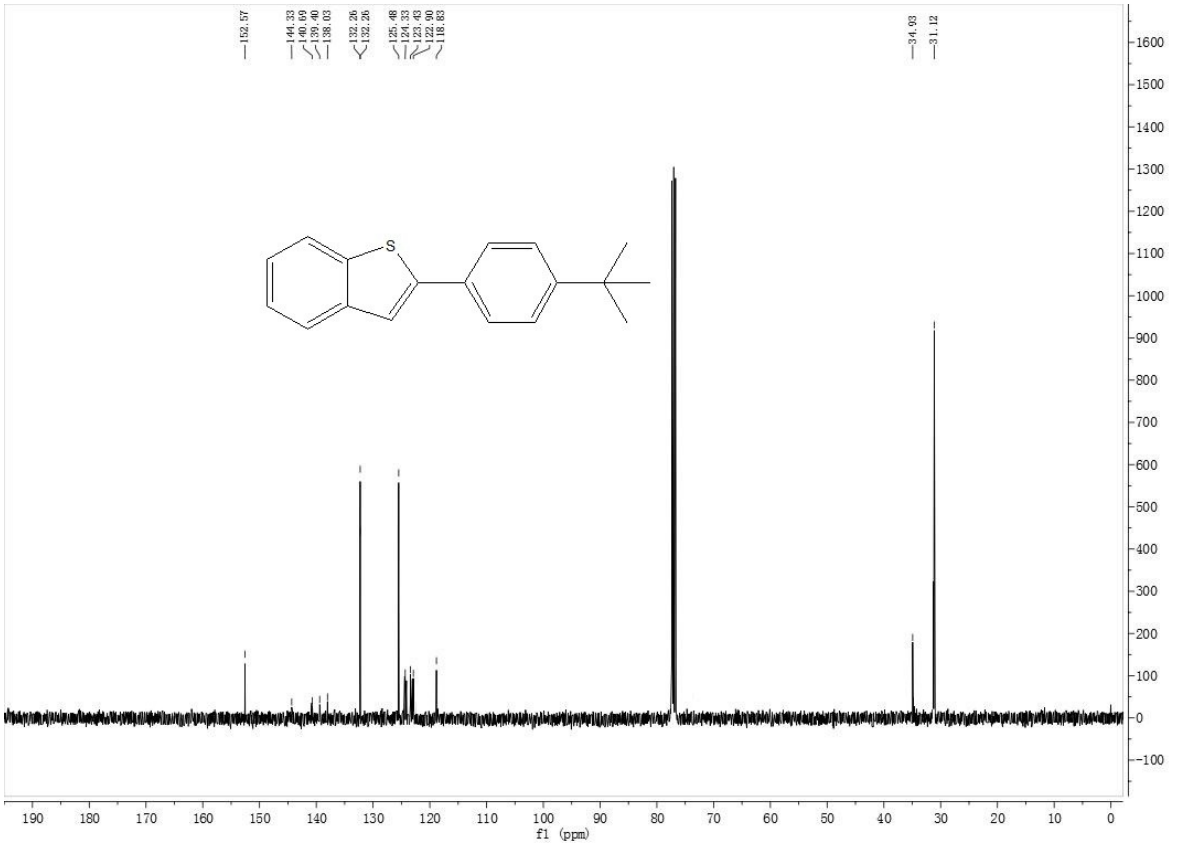

S
F
0.91
0.94
2.67
3.08
1.00
f1 (ppm)

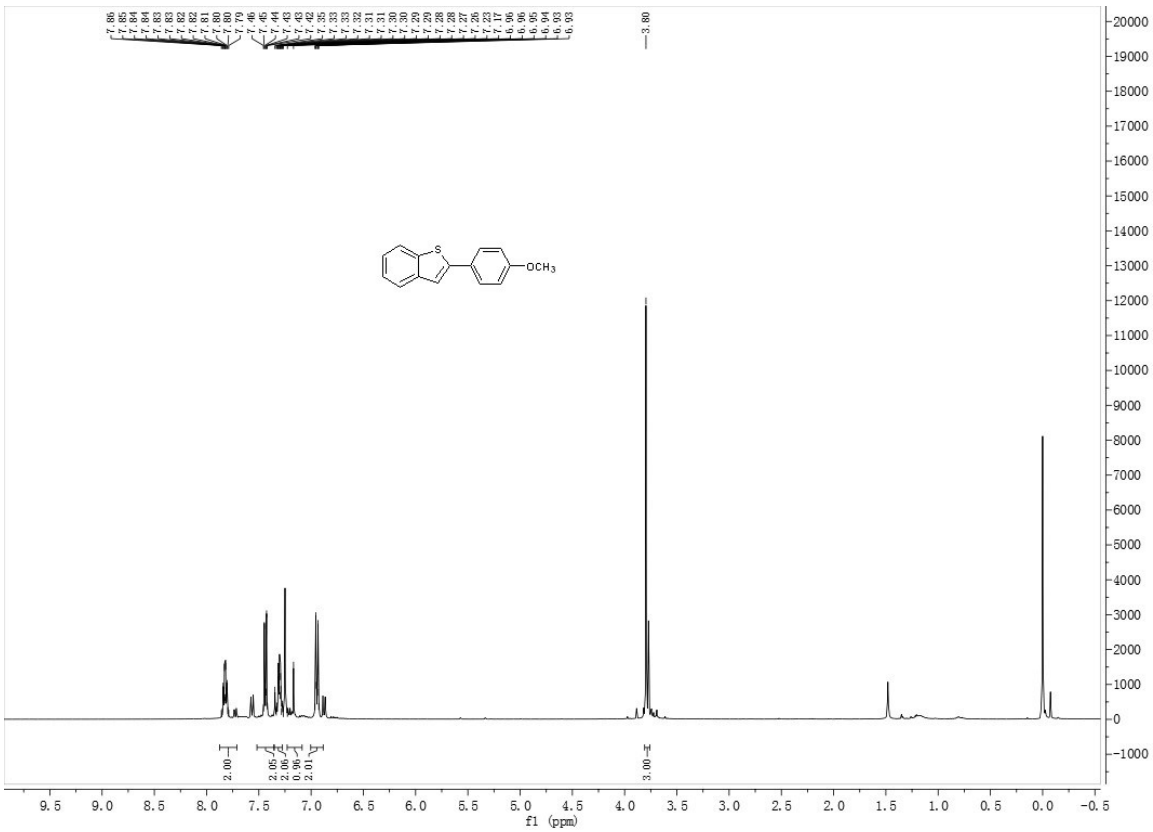

135.56
128.73
128.23
128.15
127.68
124.52
124.39
123.55
122.26
119.45
116.07
115.86
S
F
f1 (ppm)

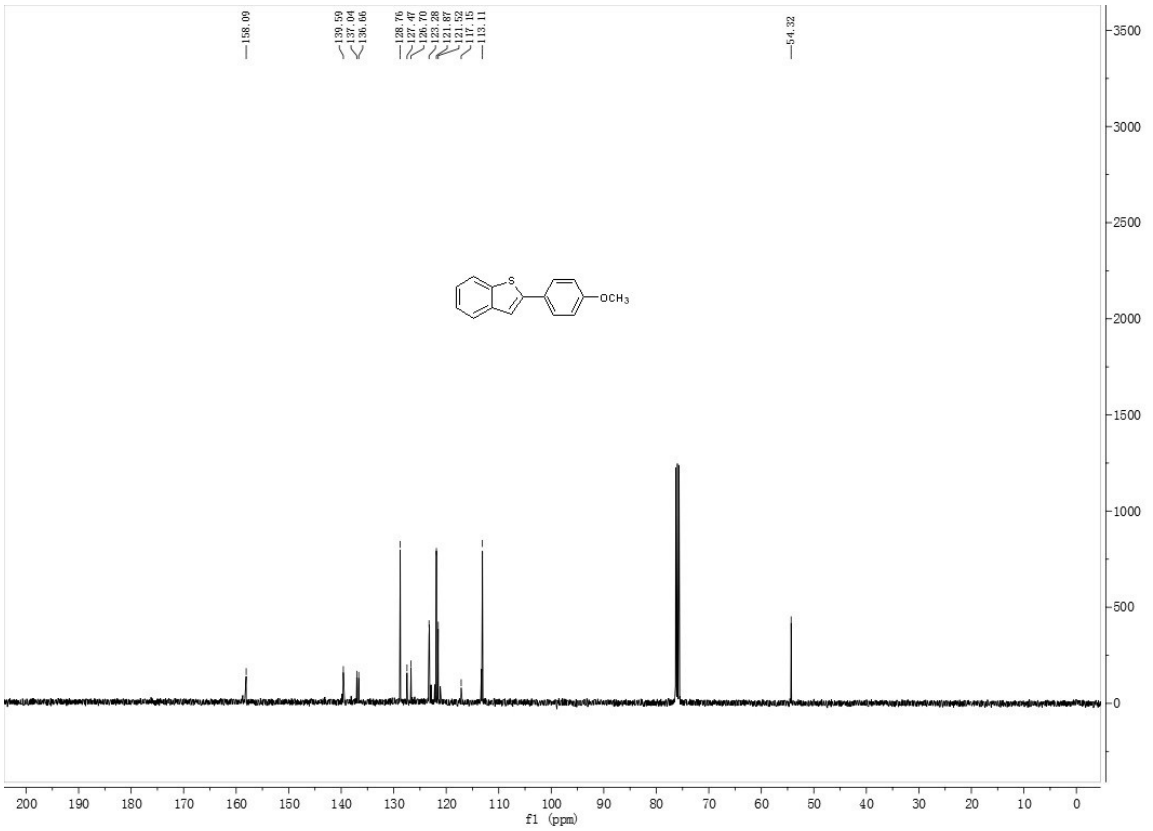

S
Br
f1 (ppm)

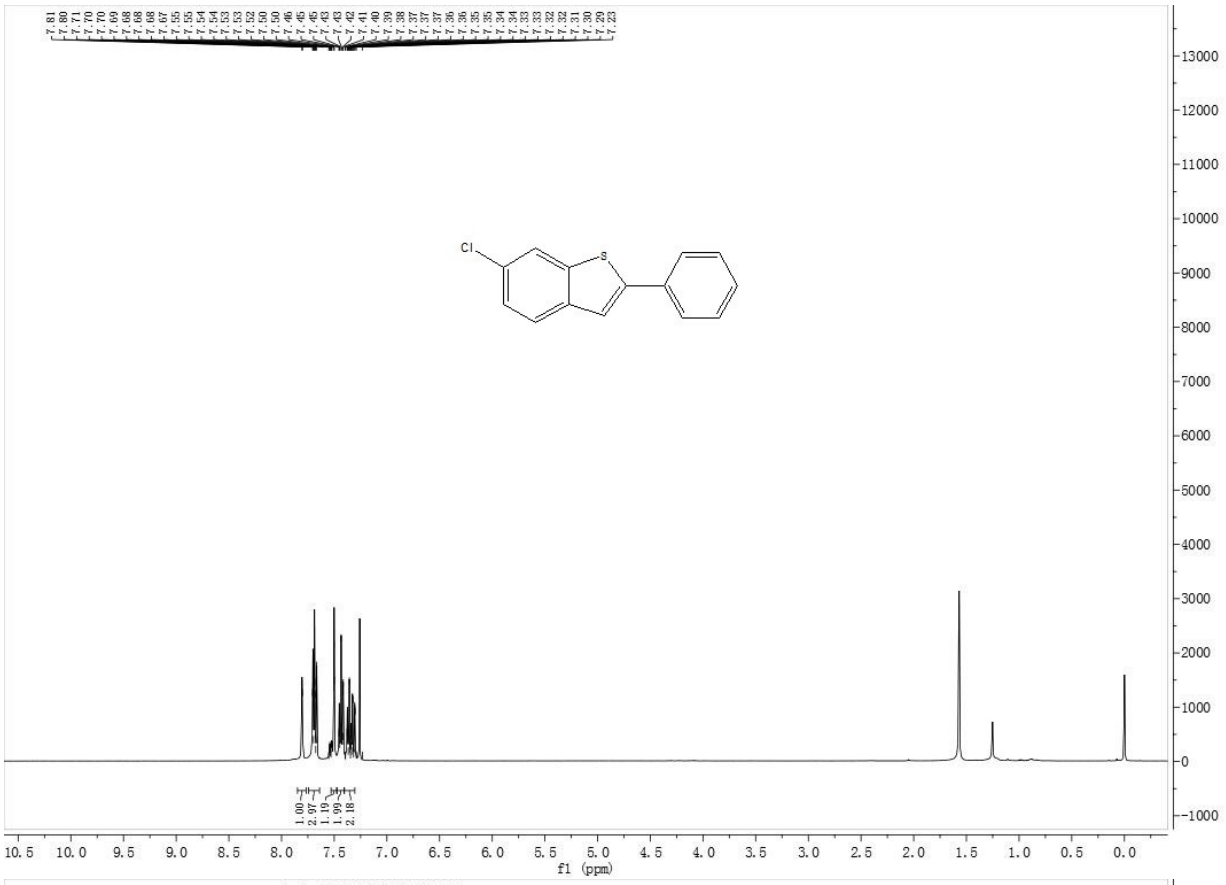

S
Br
f1 (ppm)

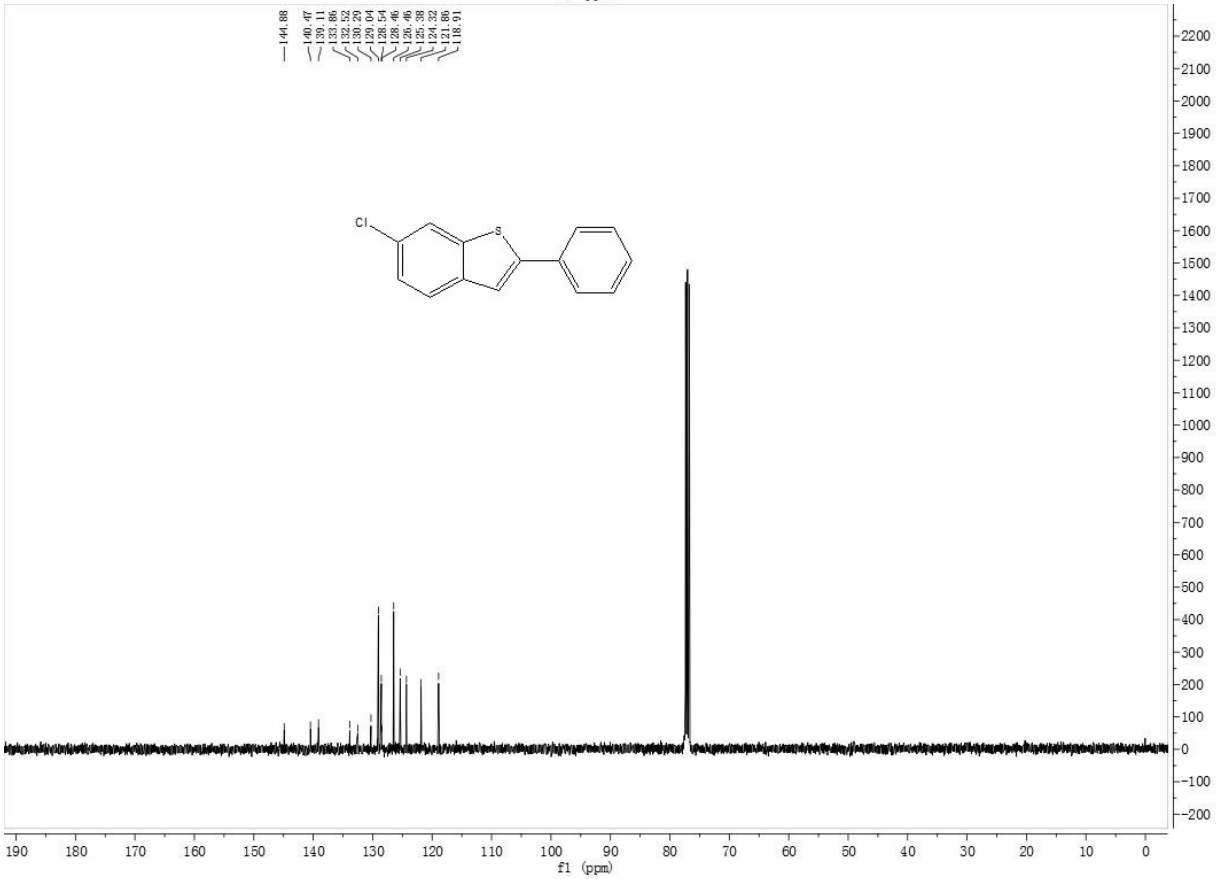

S
1.31
9.02
f1 (ppm)

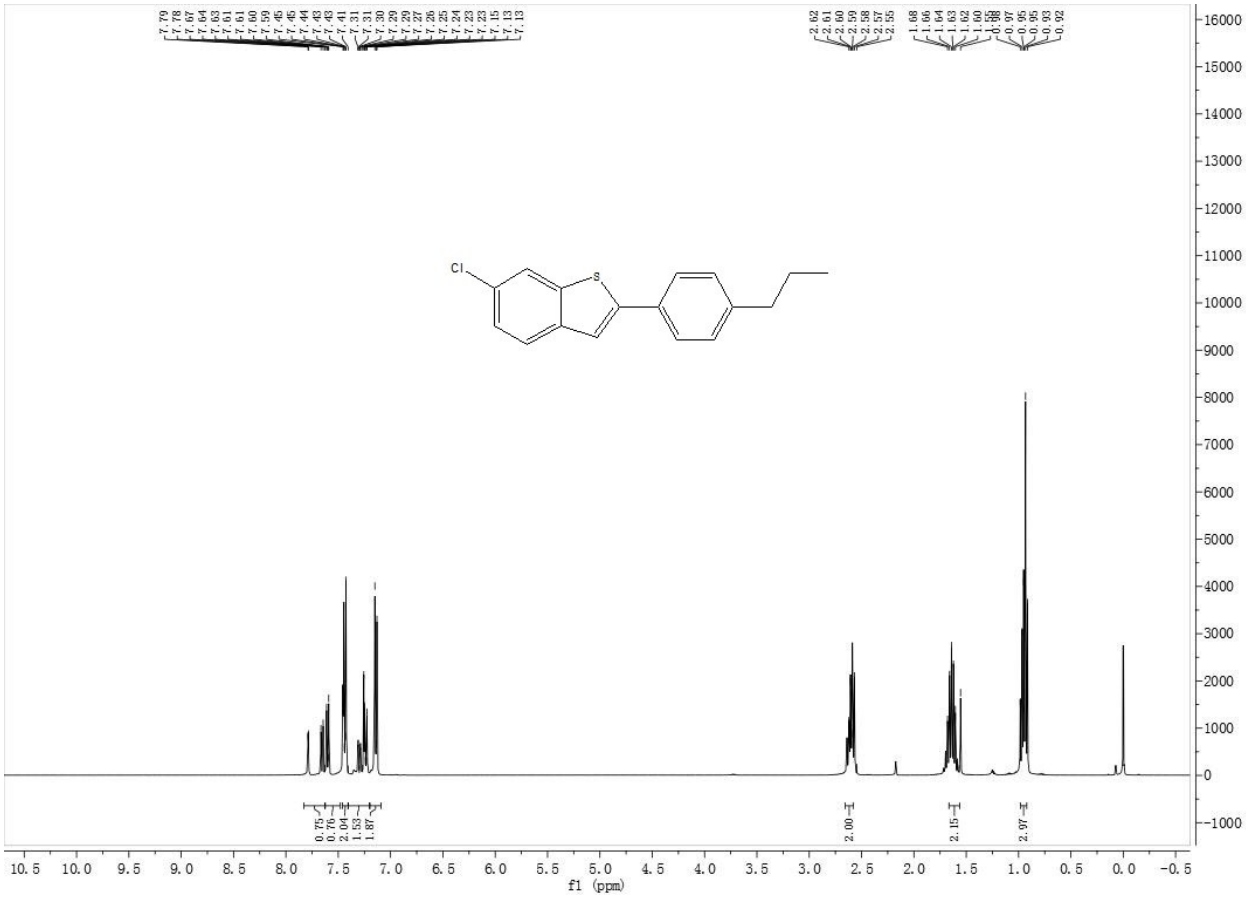

152.57
144.33
140.69
139.40
138.03
132.26
132.26
125.48
124.33
123.43
122.90
118.83
34.93
31.12
S
f1 (ppm)

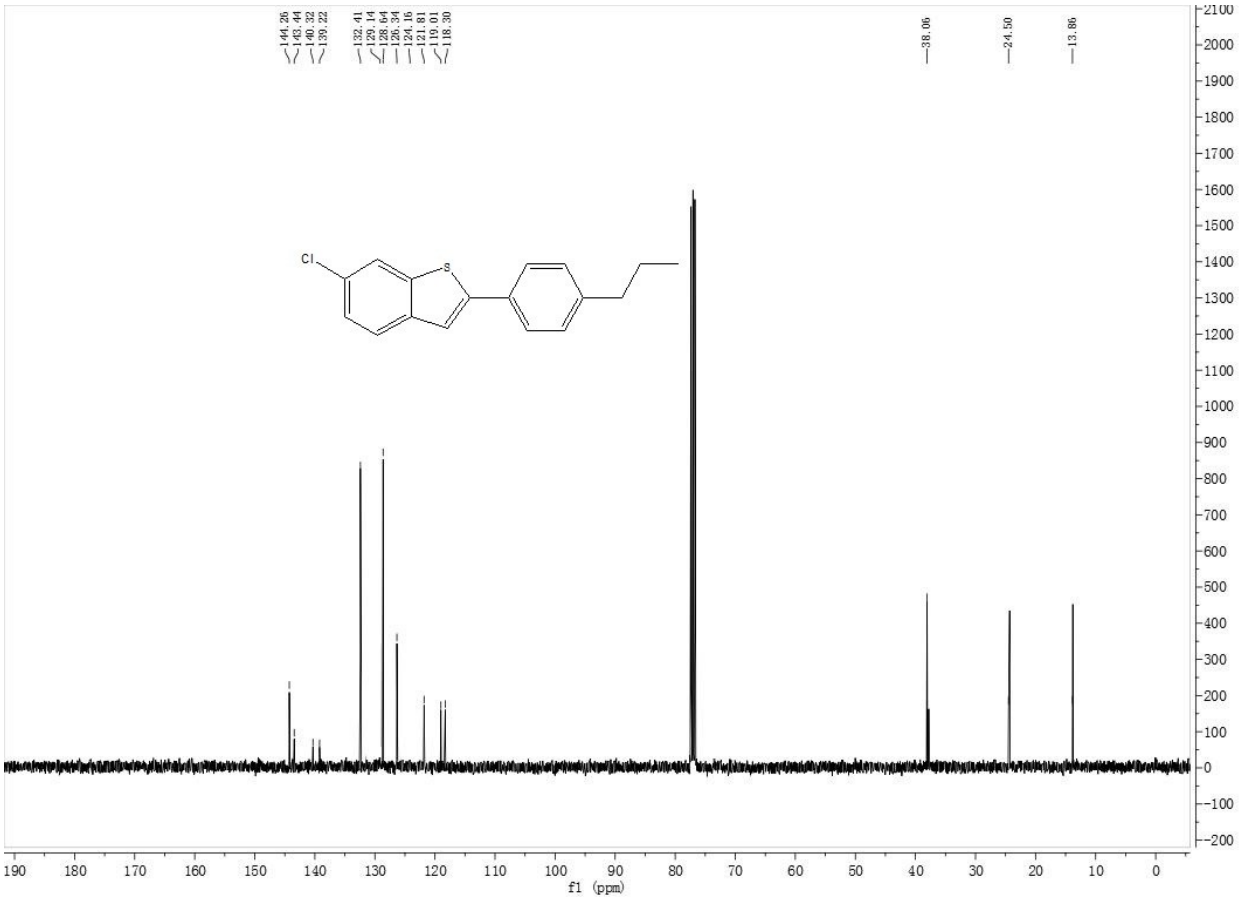

7.86 7.85 7.84 7.84 7.83 7.83 7.82 7.82 7.81 7.80 7.80 7.79 7.46 7.45 7.44 7.43 7.43 7.42 7.35 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.23 7.17 6.96 6.95 6.94 6.94 6.93
3.80
OCH3
2.00
2.05
2.06
0.96
2.01
3.00
f1 (ppm)

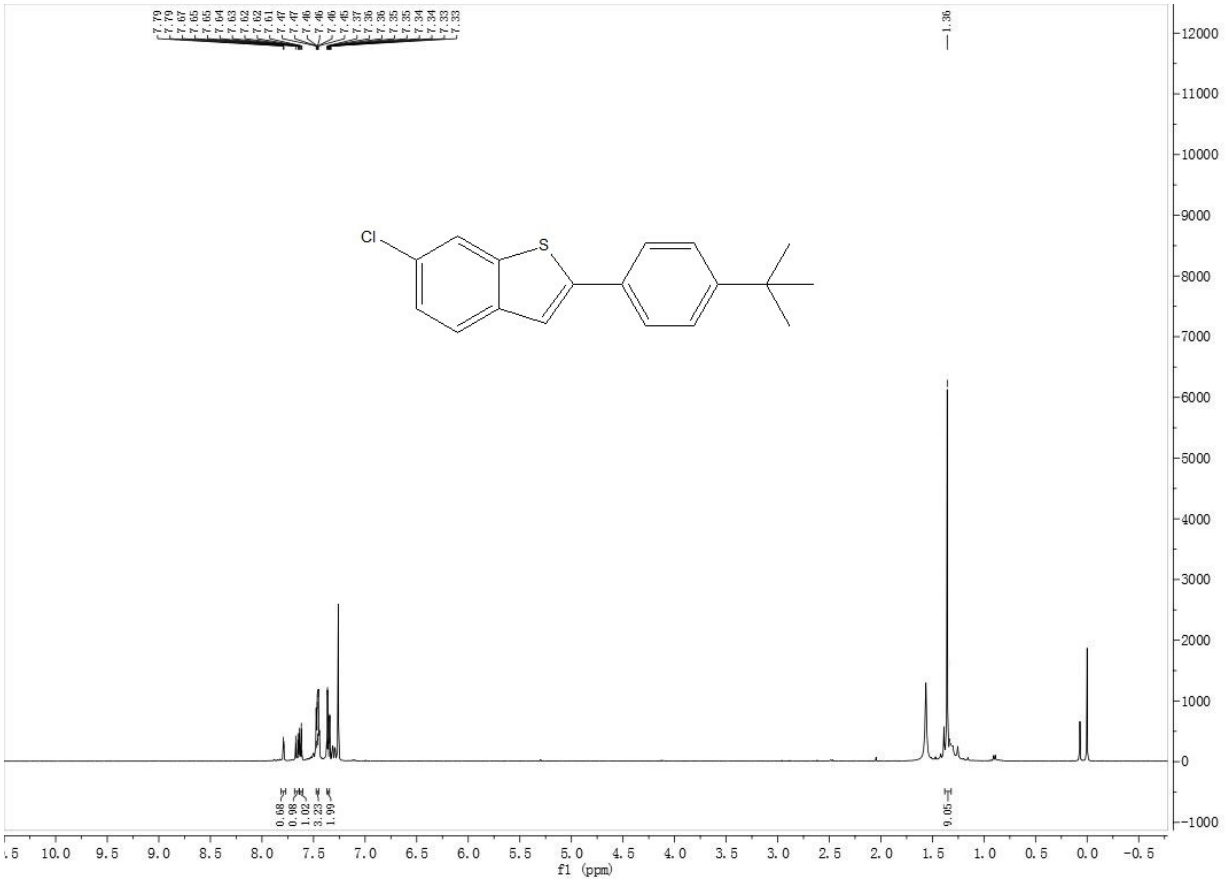

158.09
139.59
137.04
136.66
128.76
127.47
126.70
123.28
121.87
121.52
117.15
113.11
54.32
OCH3
f1 (ppm)

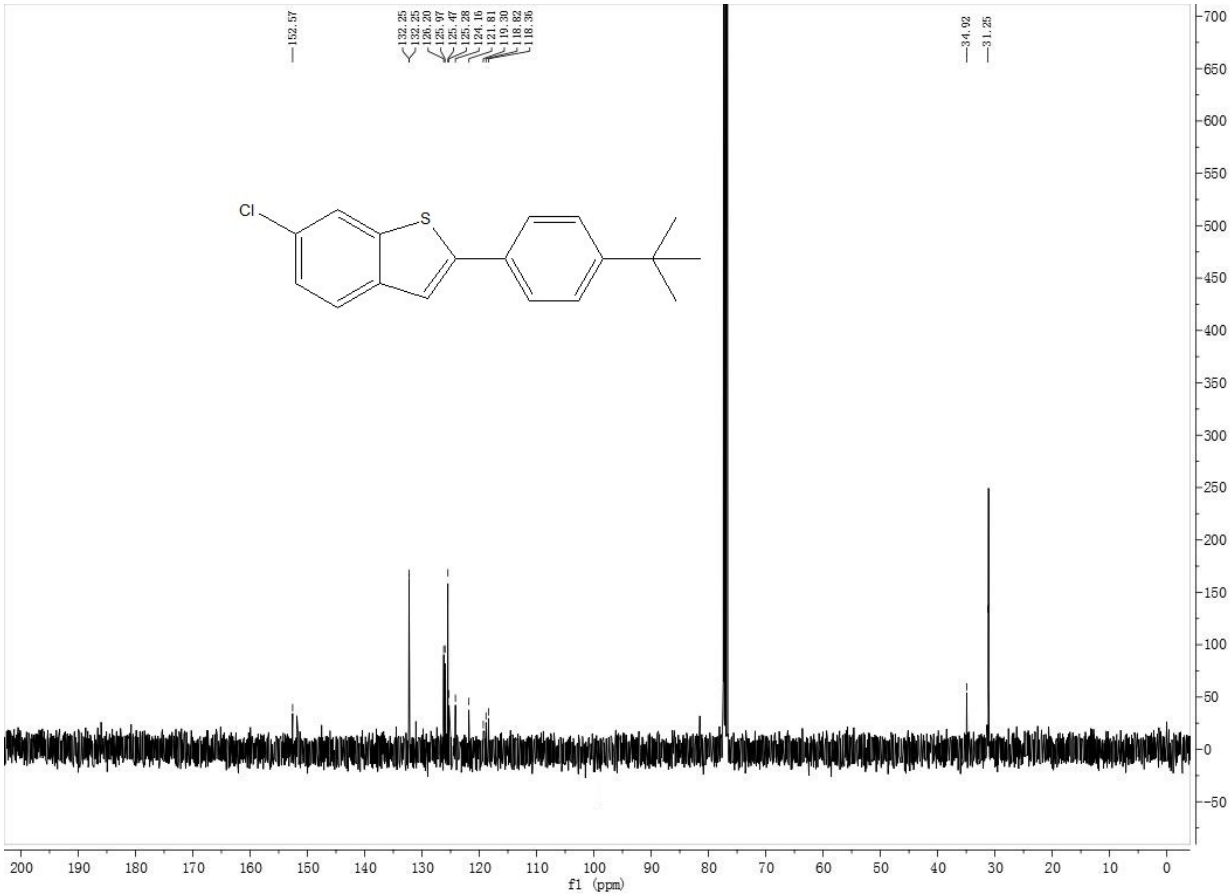

7.81 7.80 7.71 7.70 7.70 7.69 7.69 7.68 7.68 7.67 7.55 7.55 7.54 7.54 7.53 7.53 7.52 7.50 7.50 7.46 7.45 7.45 7.43 7.43 7.42 7.42 7.41 7.40 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.23
Cl
S
1.00 2.97 1.09 1.08 2.18
f1 (ppm)

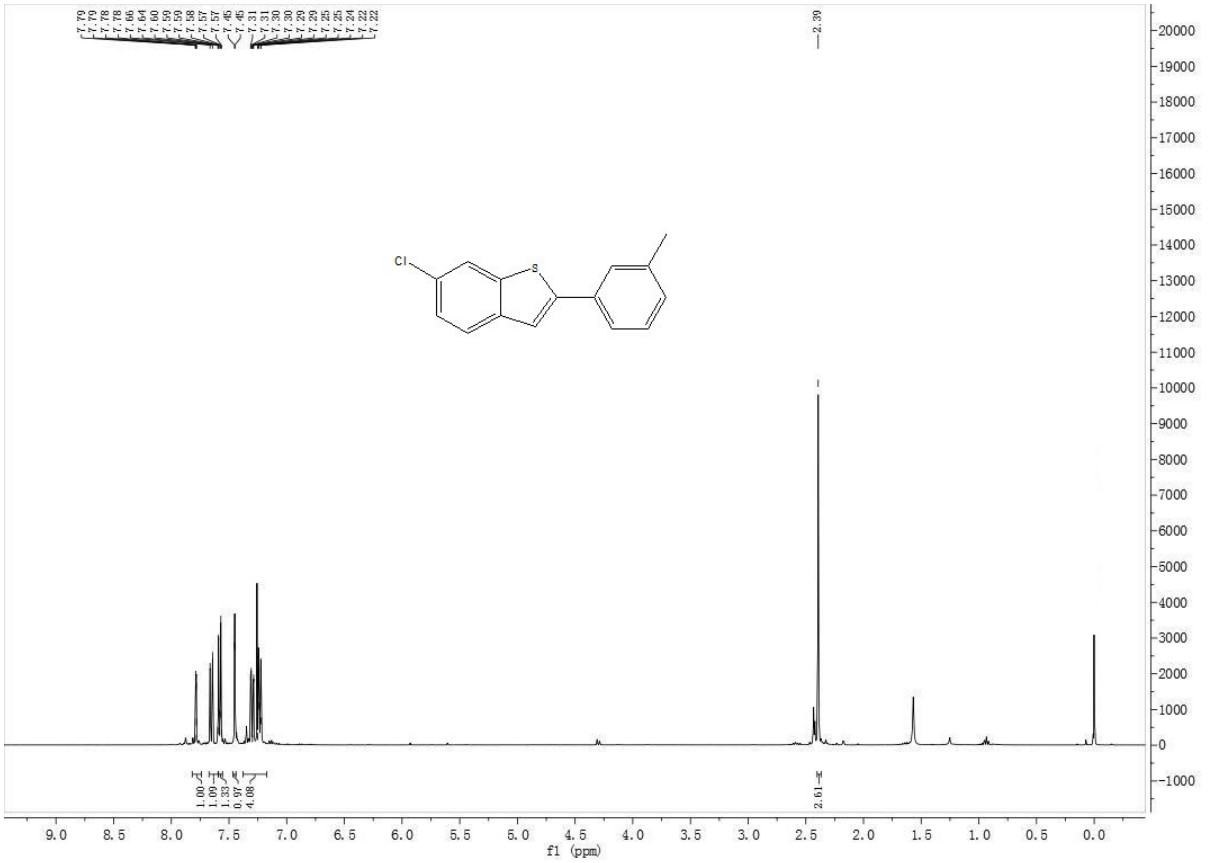

144.88 140.47 139.11 133.86 132.52 130.29 129.04 128.54 128.46 126.48 125.38 124.32 121.86 118.91
Cl
S
f1 (ppm)

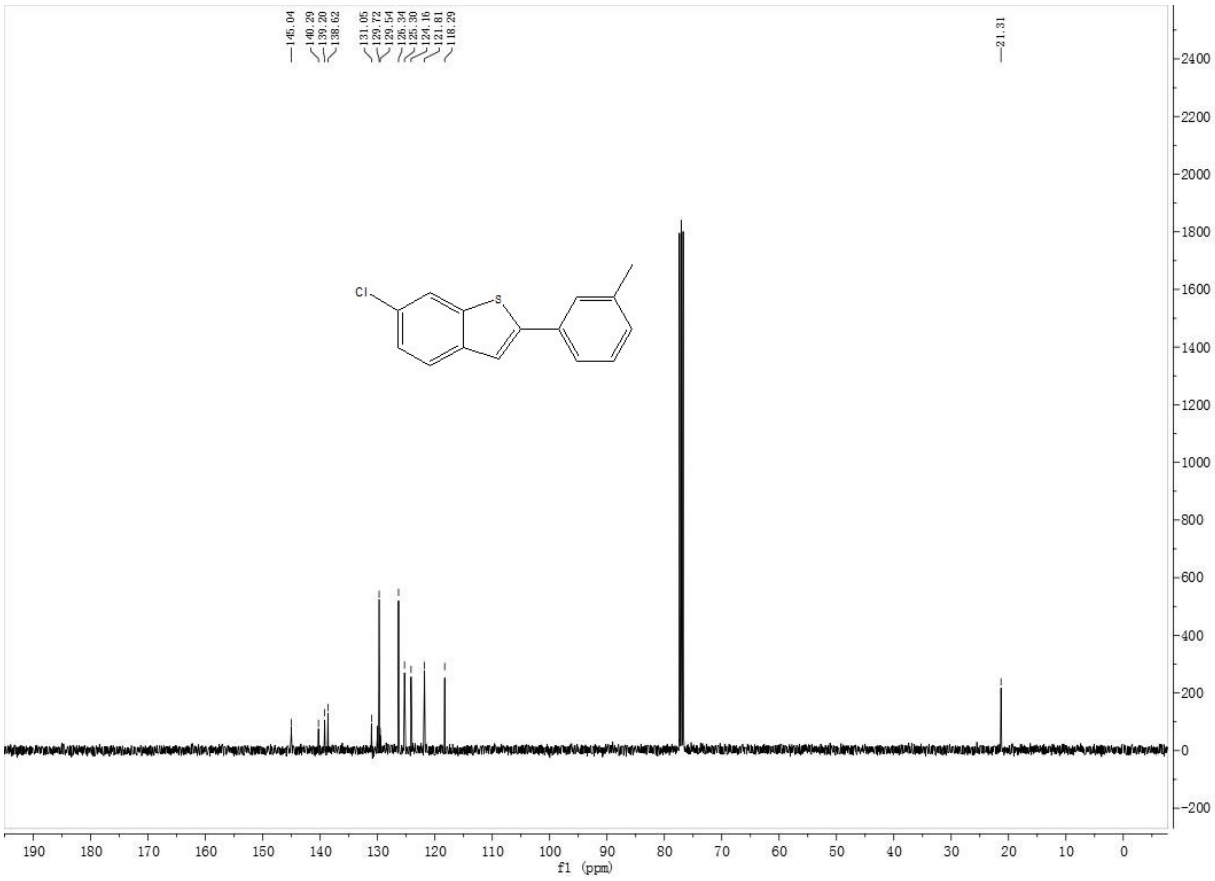

7.79
7.78
7.67
7.64
7.63
7.61
7.61
7.60
7.59
7.45
7.45
7.44
7.43
7.41
7.31
7.30
7.29
7.29
7.27
7.26
7.25
7.24
7.23
7.15
7.13
7.13
2.62
2.61
2.60
2.59
2.58
2.57
2.55
1.68
1.66
1.64
1.63
1.62
1.60
0.97
0.95
0.95
0.93
0.92
Cl
S
0.75
0.76
2.04
1.53
1.87
2.00
2.15
2.97
f1 (ppm)

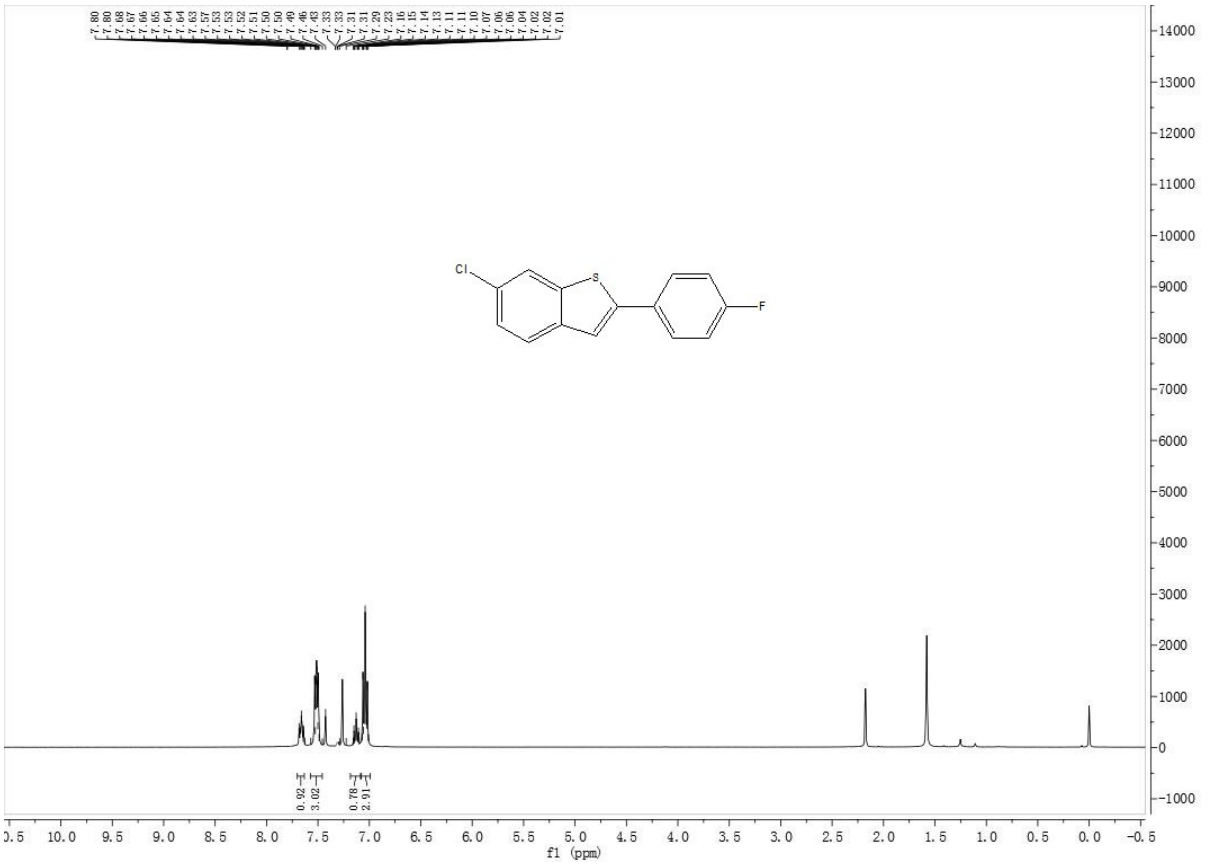

144.26
143.44
140.22
139.22
132.41
129.14
128.64
126.34
124.15
121.81
119.01
118.30
38.06
24.50
13.86
Cl
S
f1 (ppm)

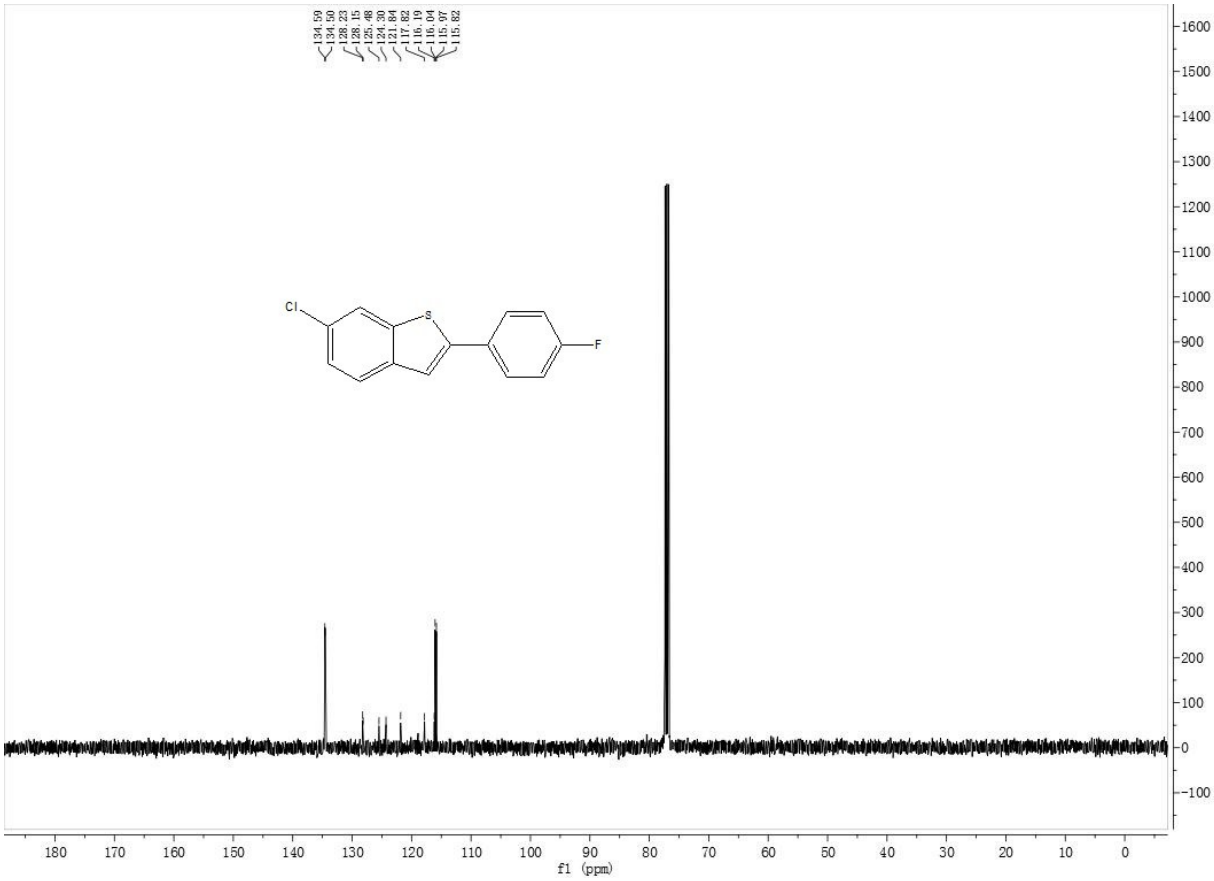

7.79
7.79
7.67
7.65
7.65
7.64
7.63
7.62
7.62
7.61
7.47
7.46
7.46
7.46
7.45
7.37
7.36
7.35
7.35
7.34
7.34
7.33
1.36
Cl
S
0.68
0.98
1.02
3.23
1.99
9.05
f1 (ppm)

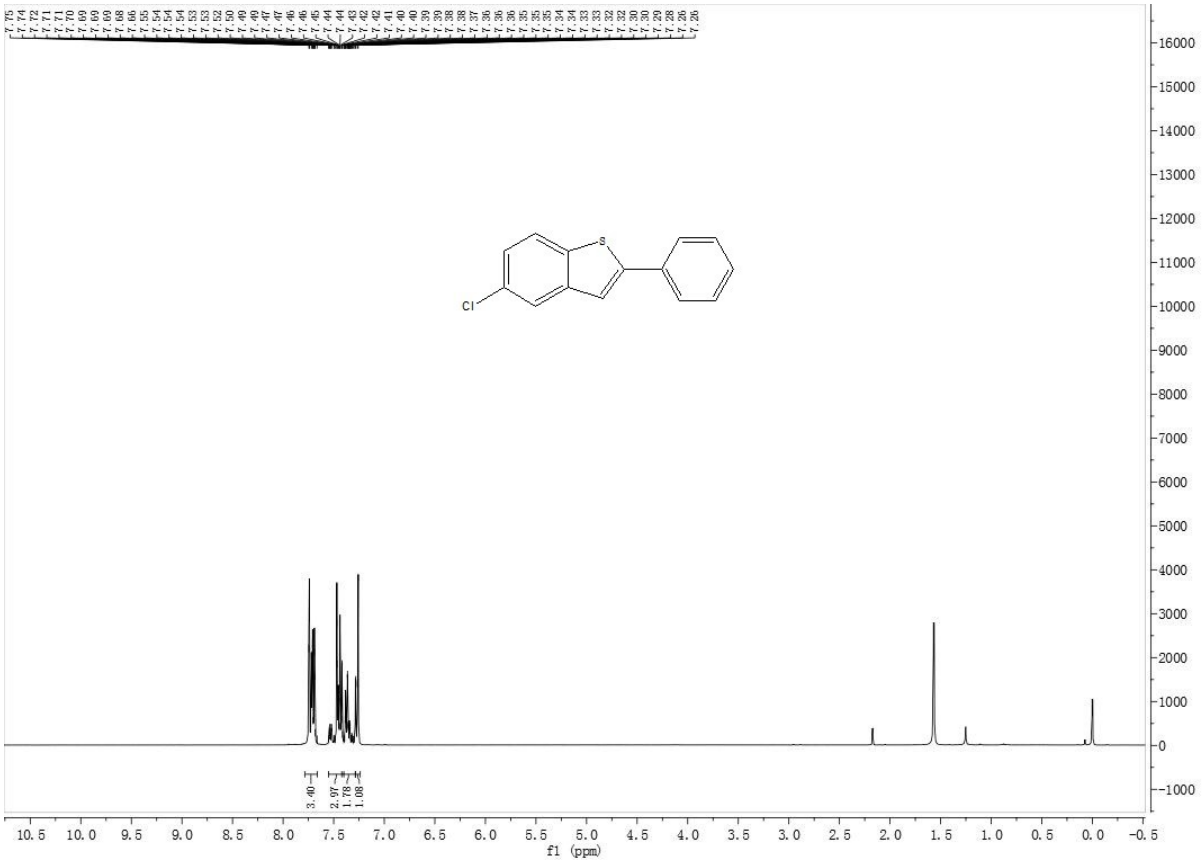

152.57
132.25
132.25
126.20
125.97
125.47
125.28
121.16
121.81
119.30
118.82
118.36
34.92
31.25
Cl
S
f1 (ppm)

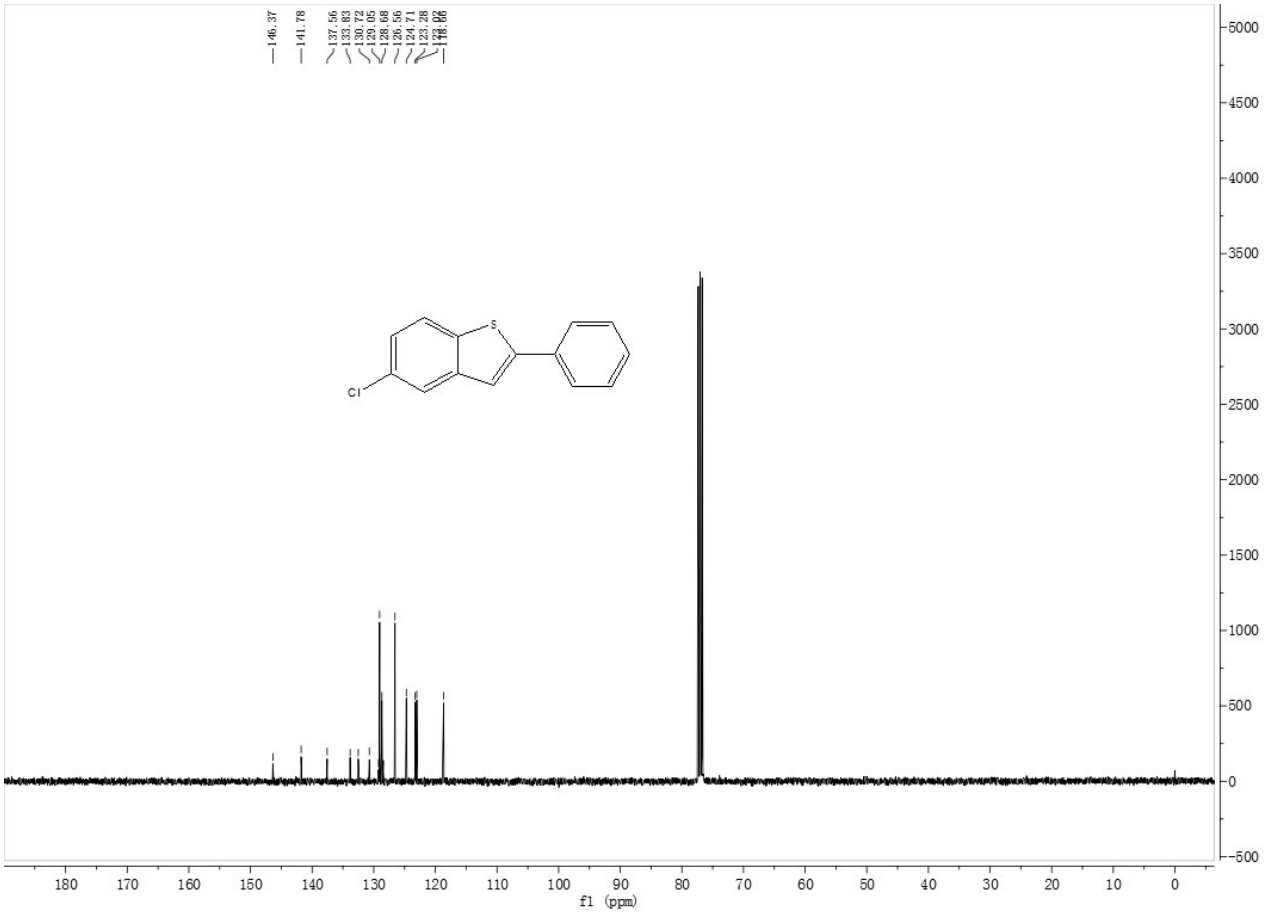

7.79
7.79
7.78
7.78
7.66
7.64
7.60
7.59
7.59
7.58
7.57
7.57
7.46
7.45
7.31
7.30
7.30
7.29
7.25
7.23
7.24
7.22
7.22
2.30
Cl
S
1.00
1.09
1.33
0.97
4.08
2.61
f1 (ppm)

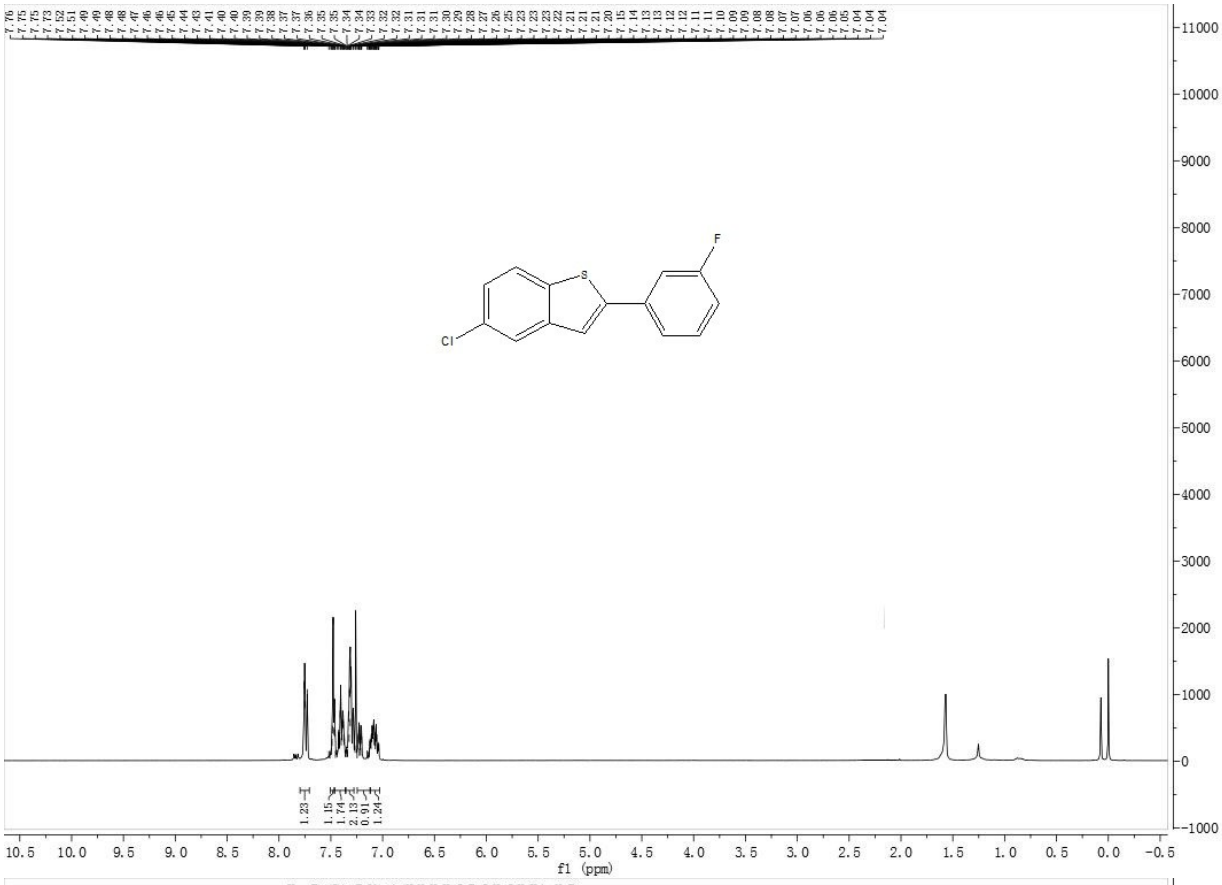

145.04
140.29
139.20
138.62
131.05
129.72
129.54
126.34
125.30
124.16
121.81
118.29
21.31
Cl
S
f1 (ppm)

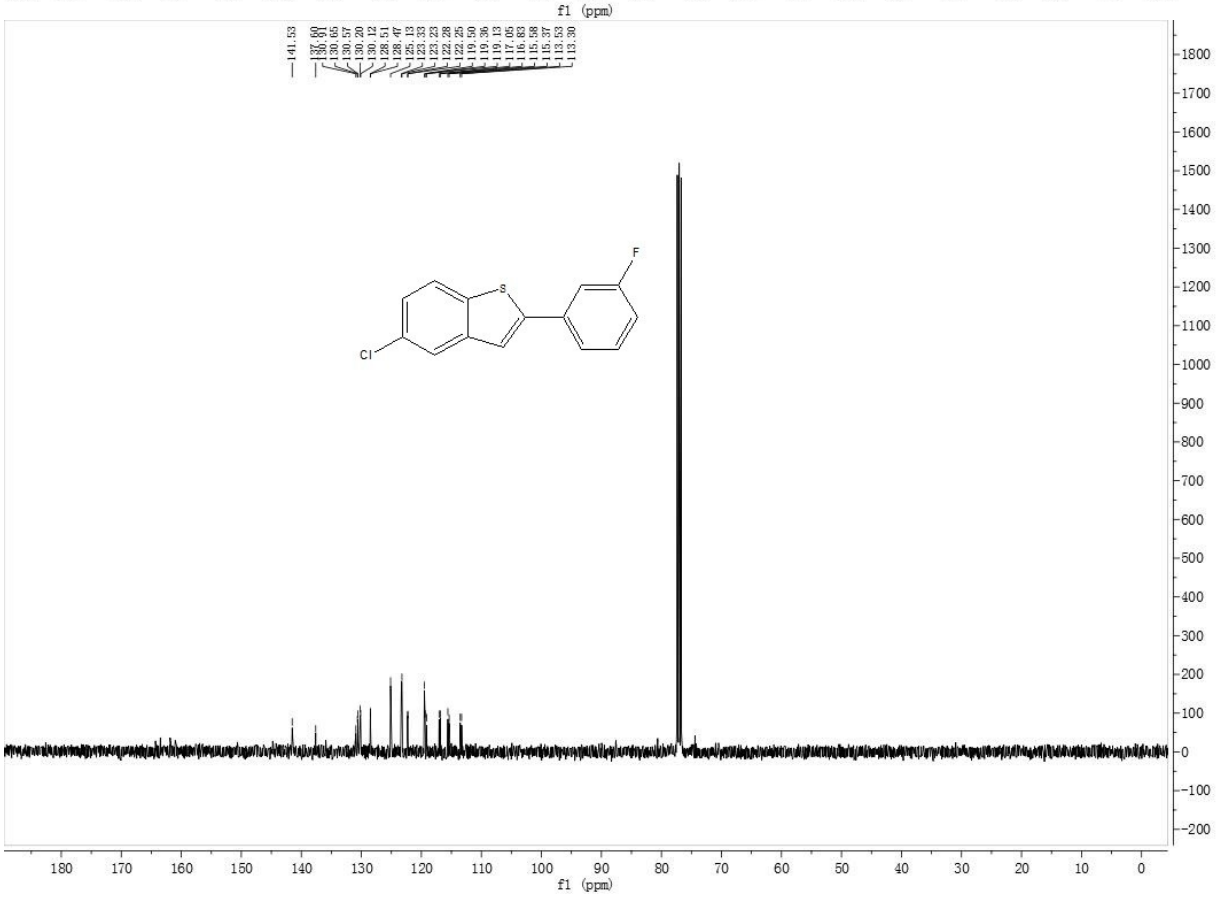

7.80
7.80
7.68
7.67
7.66
7.65
7.64
7.64
7.63
7.57
7.53
7.53
7.52
7.51
7.50
7.50
7.49
7.46
7.43
7.33
7.31
7.31
7.29
7.23
7.16
7.15
7.14
7.13
7.11
7.10
7.07
7.06
7.06
7.04
7.02
7.02
7.01
Cl
S
F
0.92
3.02
0.78
2.91
f1 (ppm)

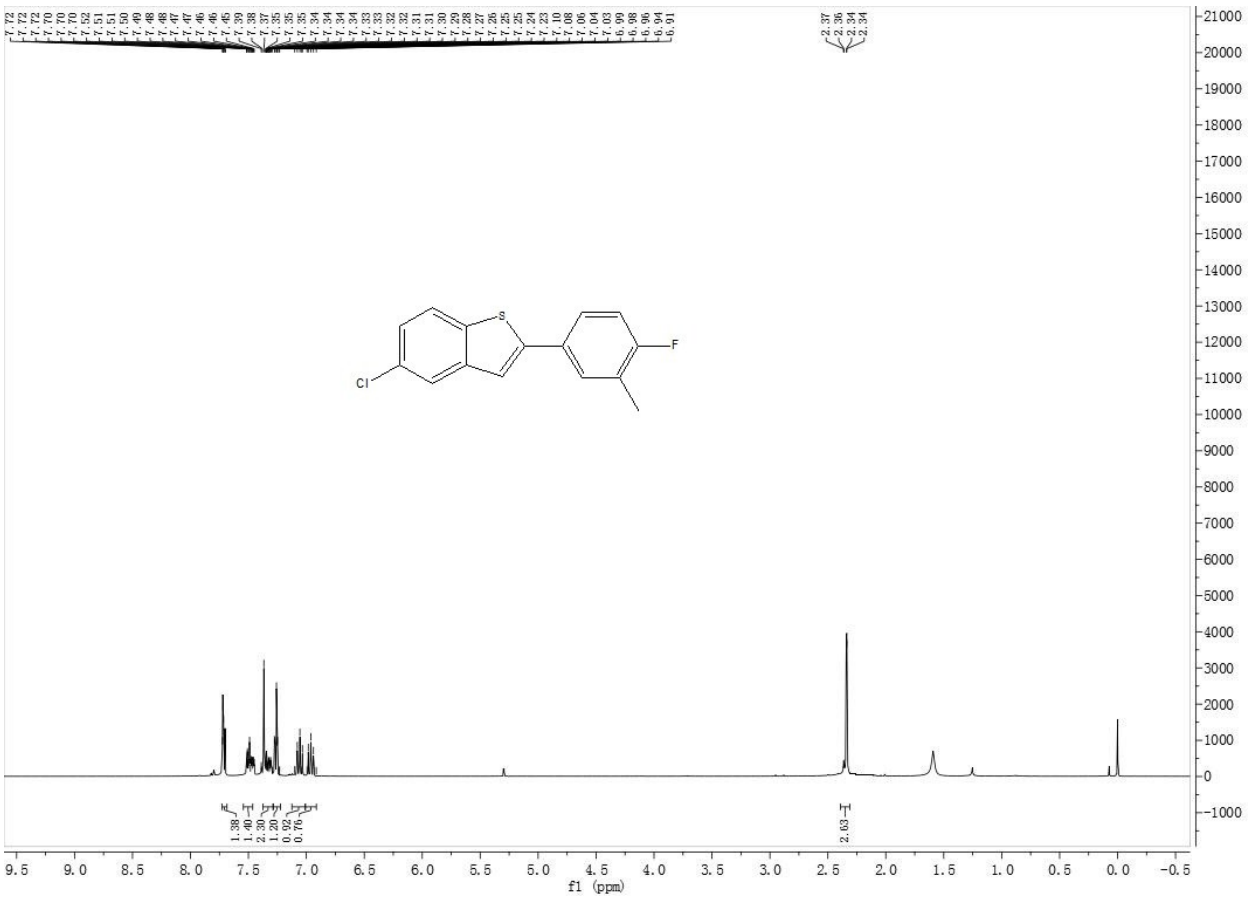

134.59
134.50
128.23
128.15
125.48
124.30
121.94
117.82
116.19
116.04
115.97
115.82
Cl
S
F
f1 (ppm)

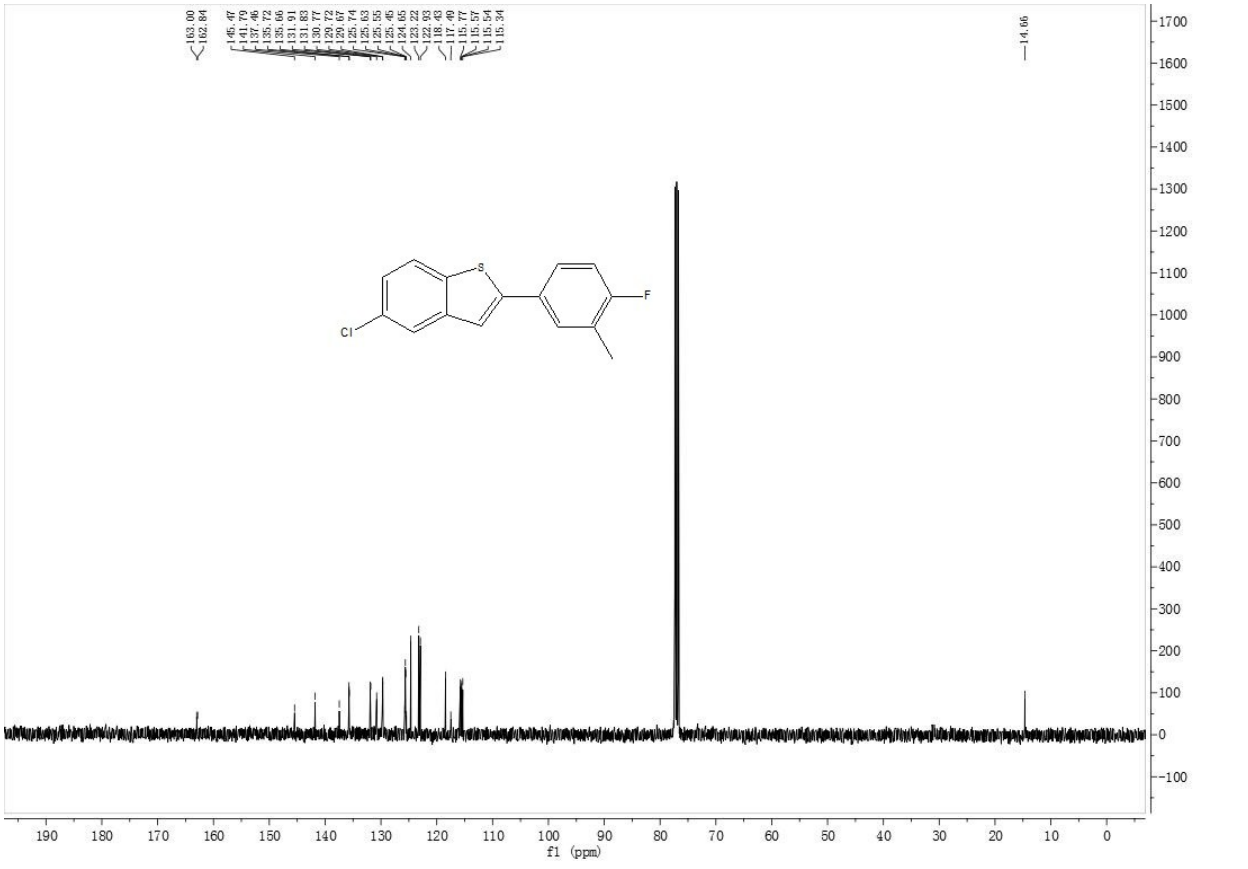

S
Cl
3.40
2.97
1.78
1.08
f1 (ppm)

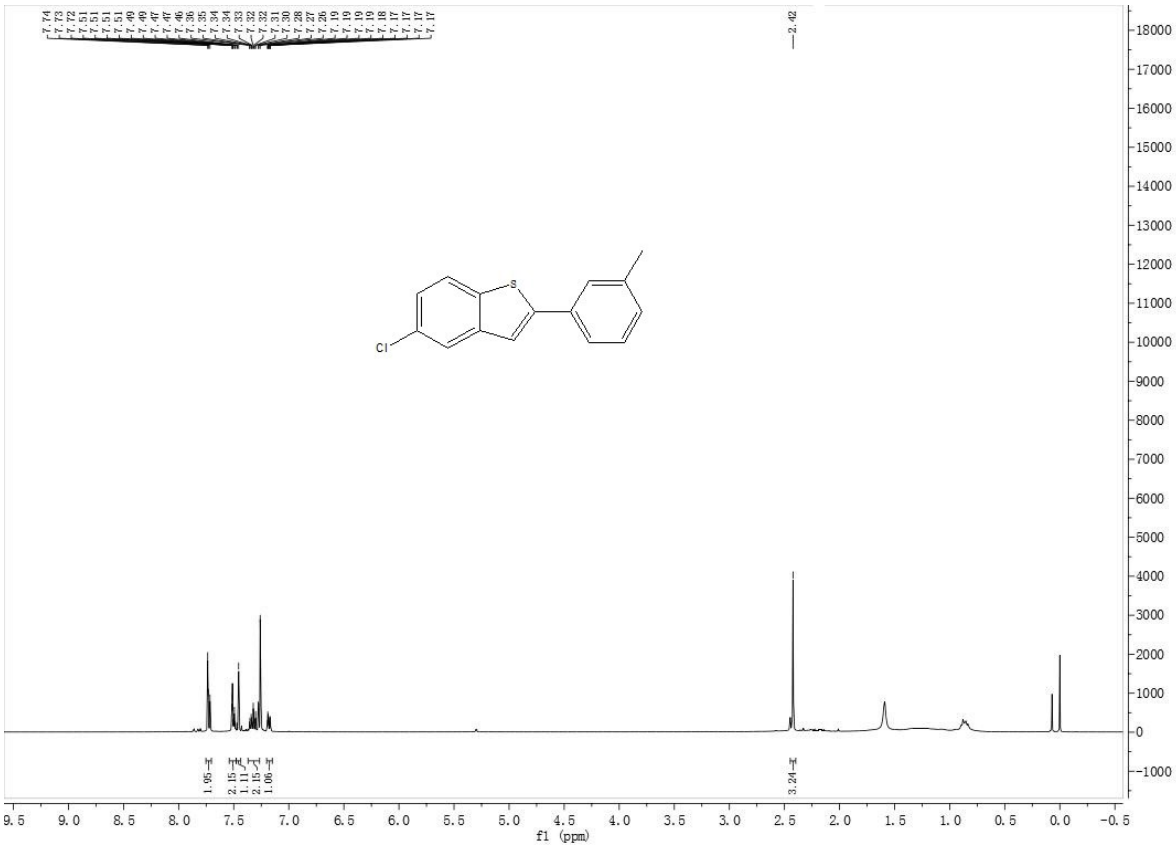

146.37
141.78
137.56
133.83
130.72
129.05
128.68
126.56
124.71
123.28
S
Cl
f1 (ppm)

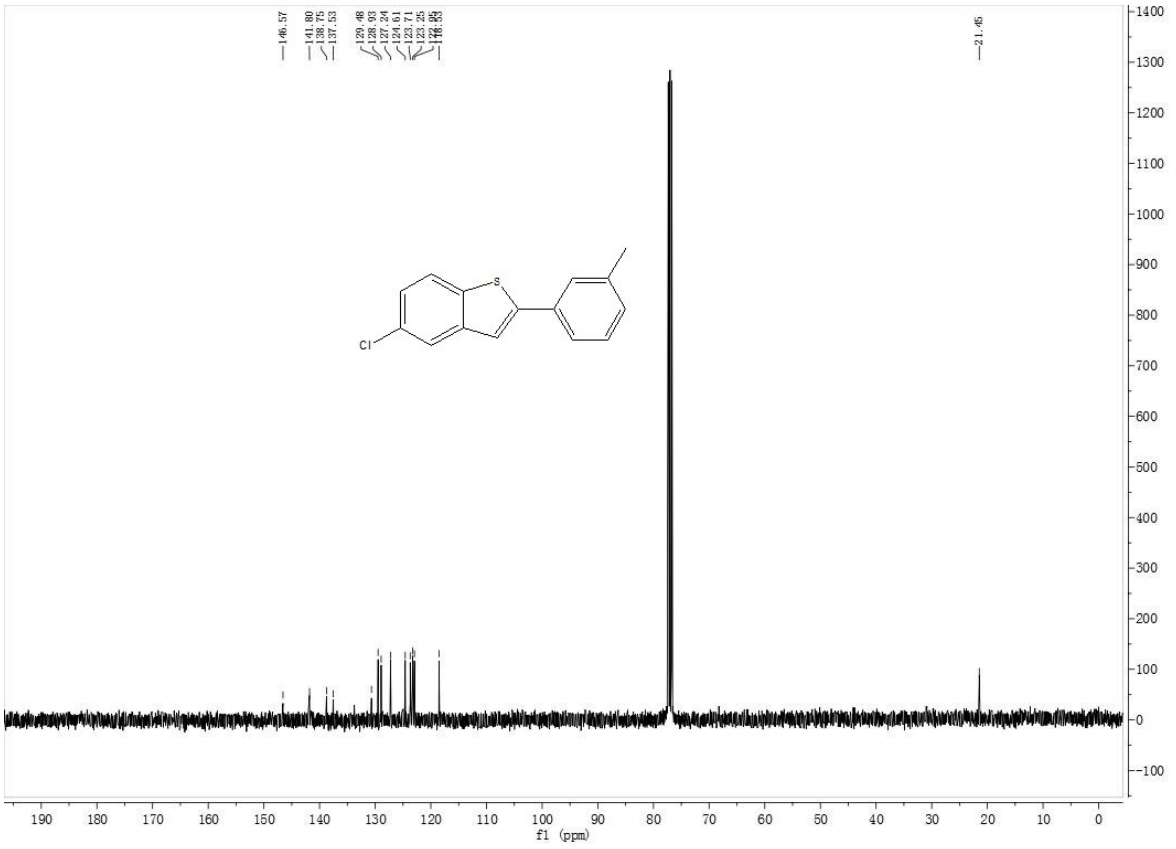

F
S
Cl
f1 (ppm)

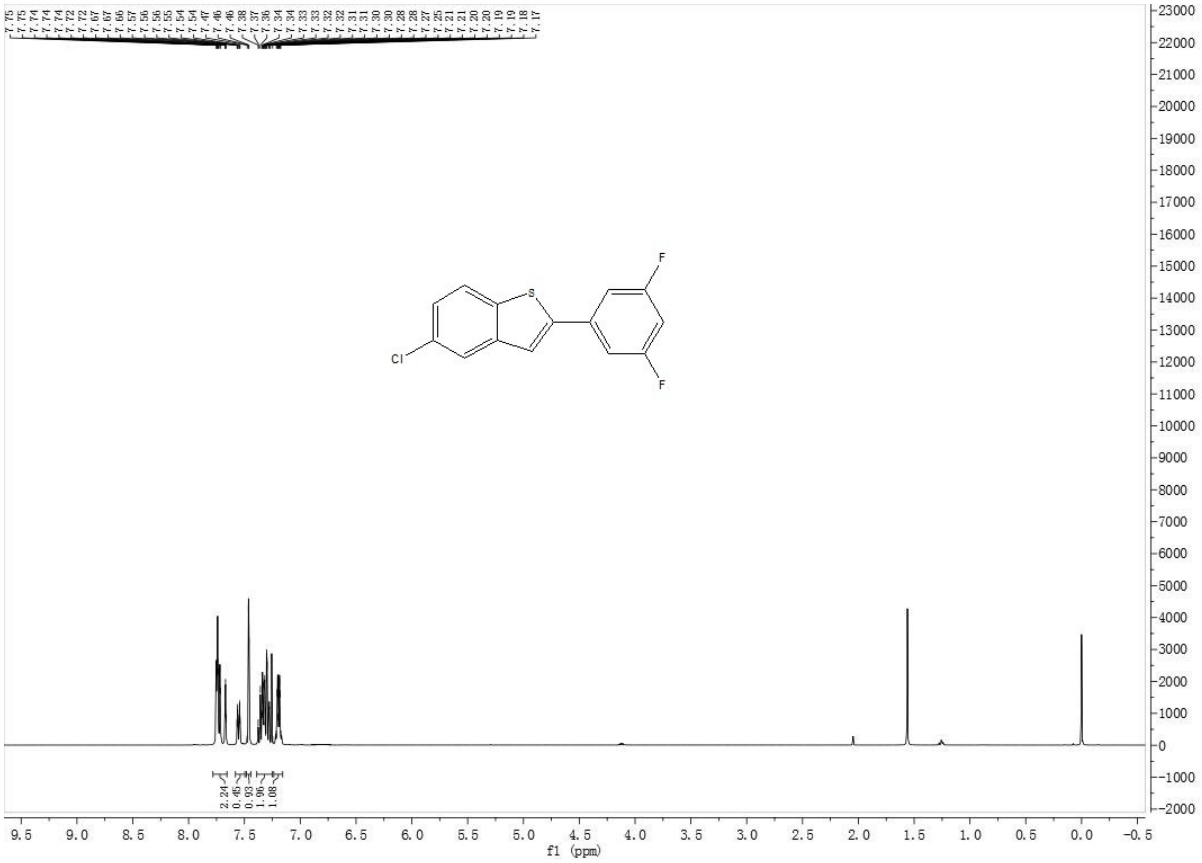

F
S
Cl
f1 (ppm)

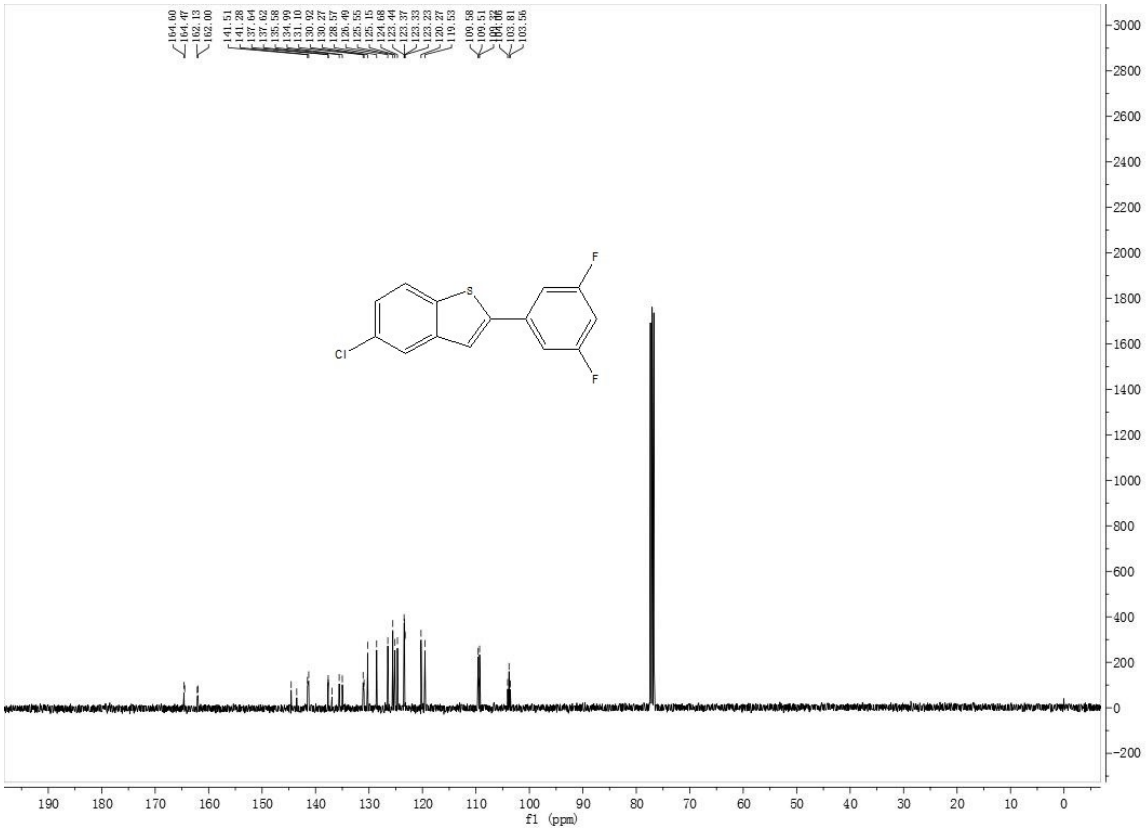

S
F
Cl
f1 (ppm)

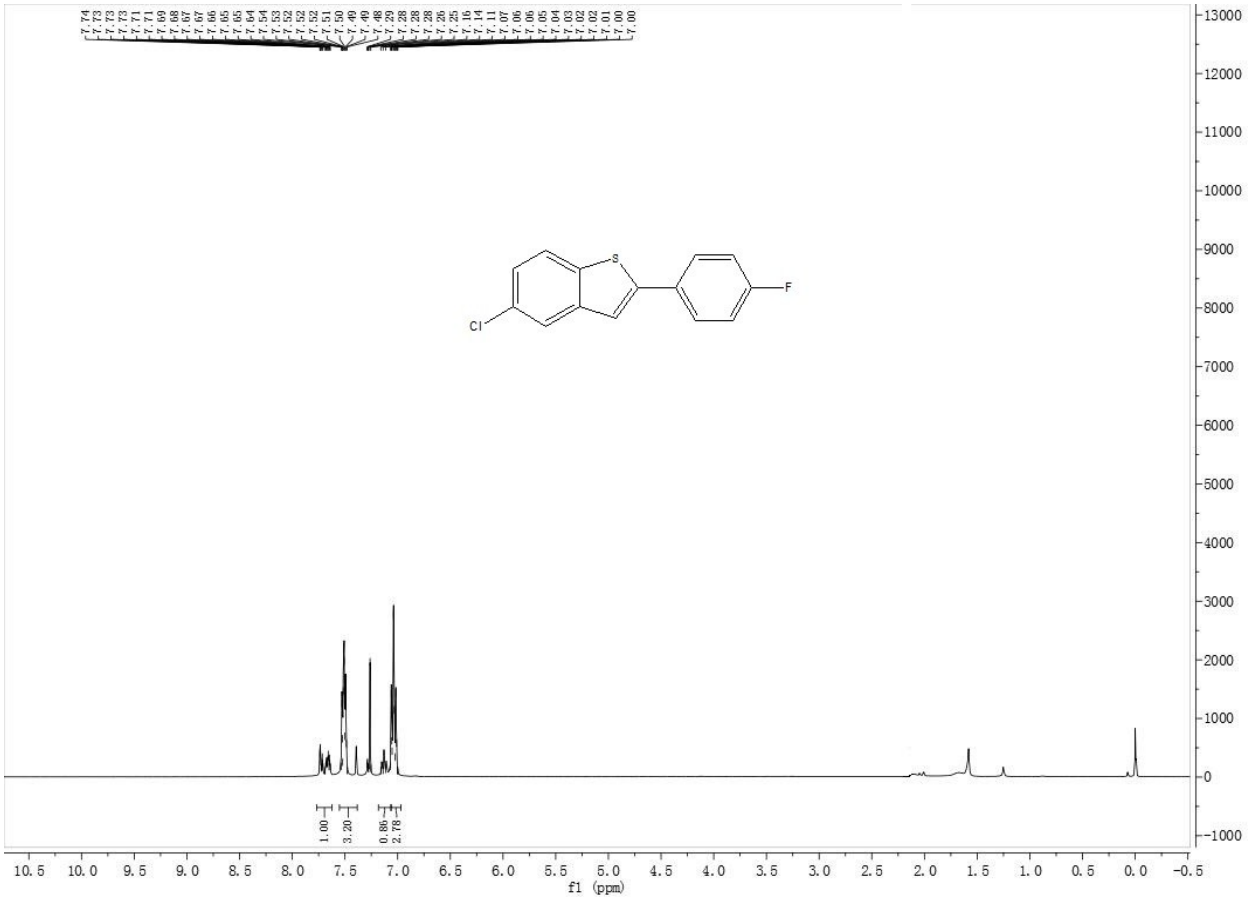

S
F
Cl
f1 (ppm)

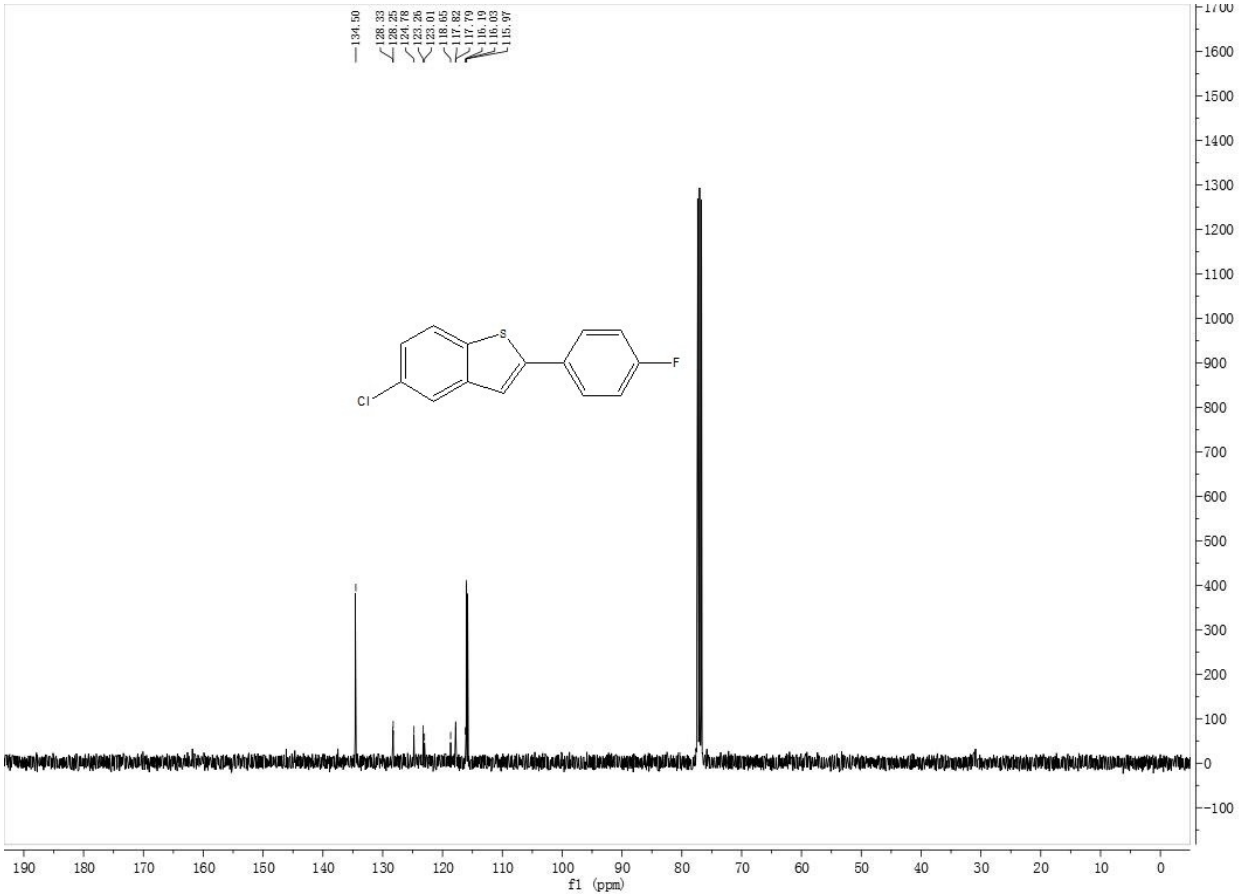

7.74
7.73
7.72
7.51
7.51
7.51
7.51
7.49
7.49
7.47
7.47
7.46
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.19
7.19
7.19
7.18
7.17
7.17
7.17
7.17
2.42
S
Cl
1.95
2.15
1.11
2.15
1.06
3.24
f1 (ppm)

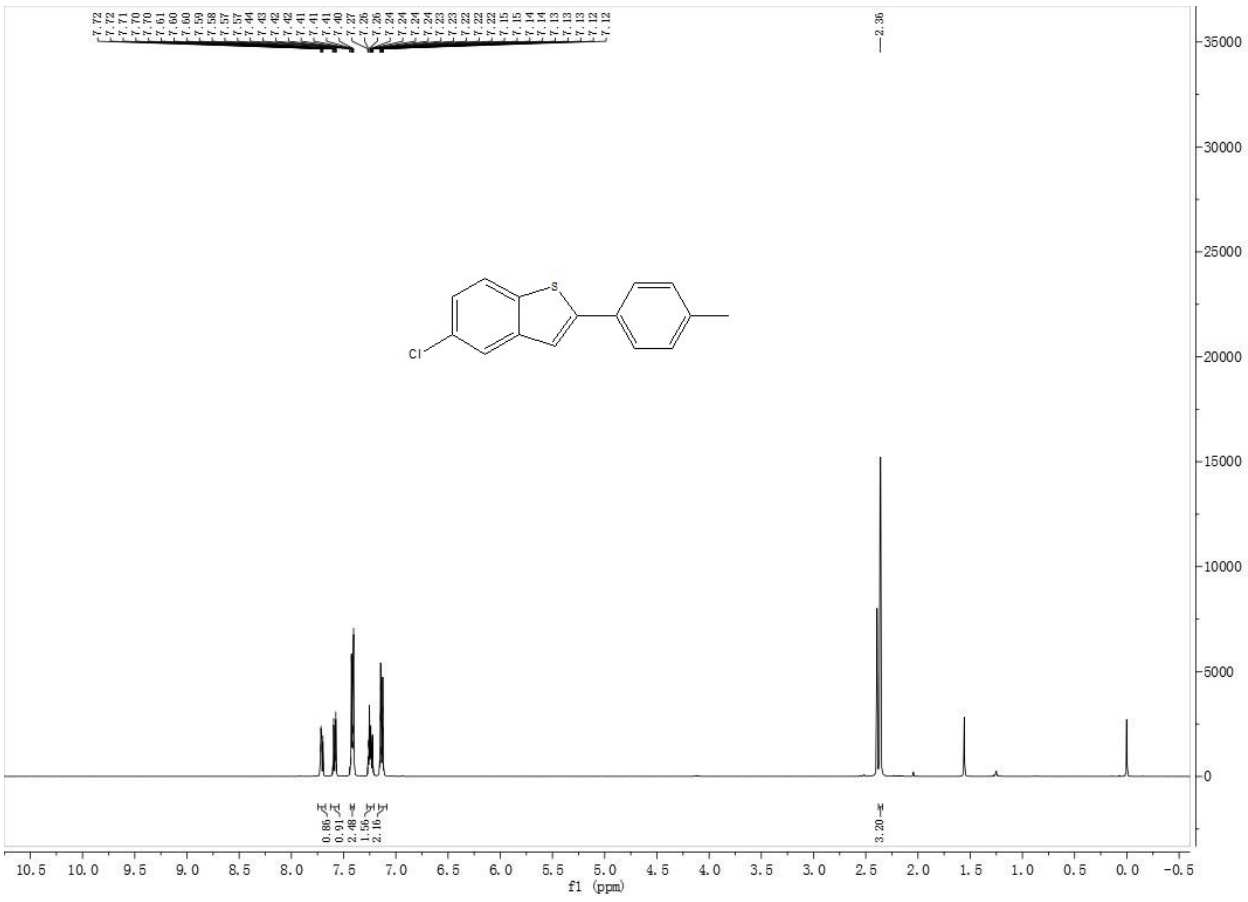

146.57
141.80
138.75
137.53
129.48
128.93
127.24
124.61
123.71
123.25
118.53
21.45
S
Cl
f1 (ppm)

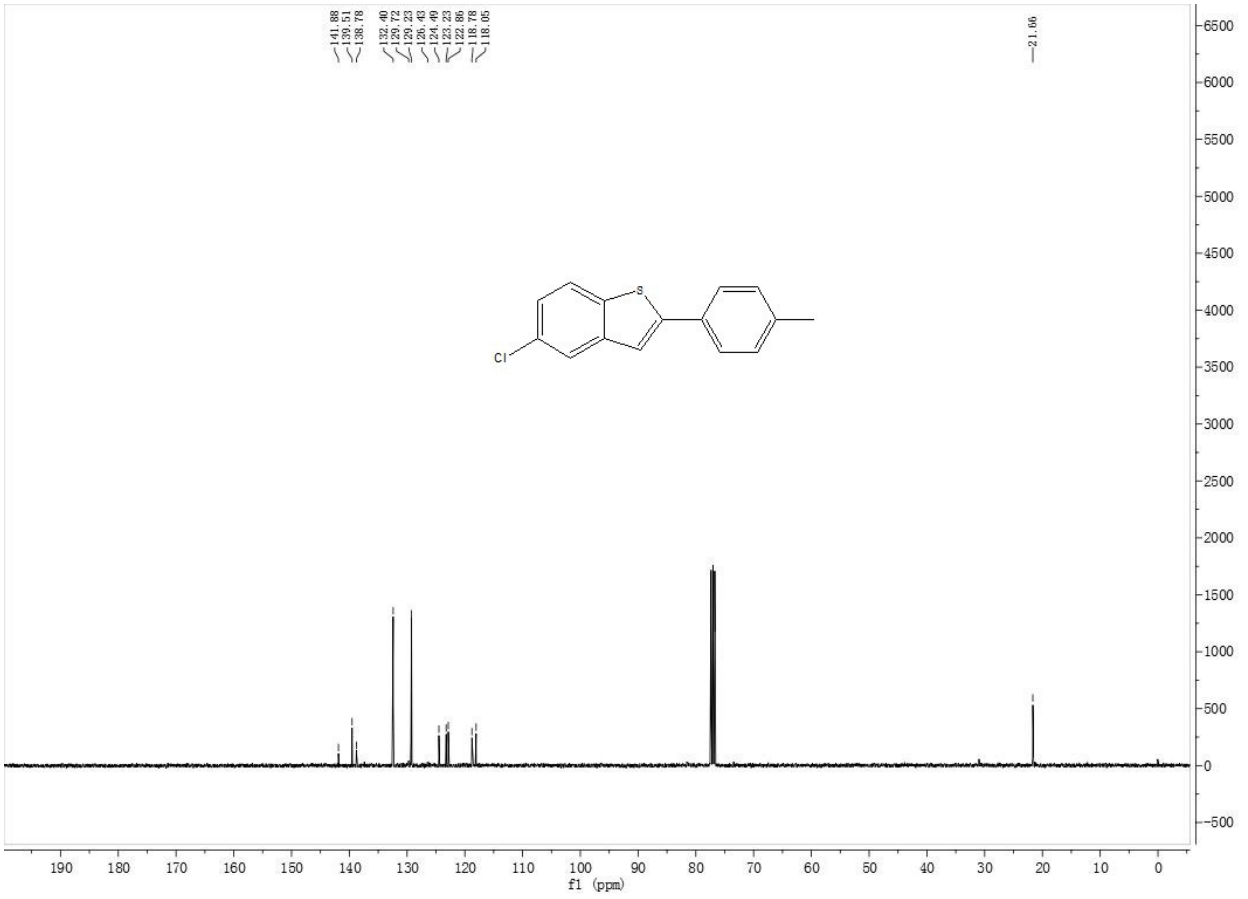

S
F
Cl
F
f1 (ppm)

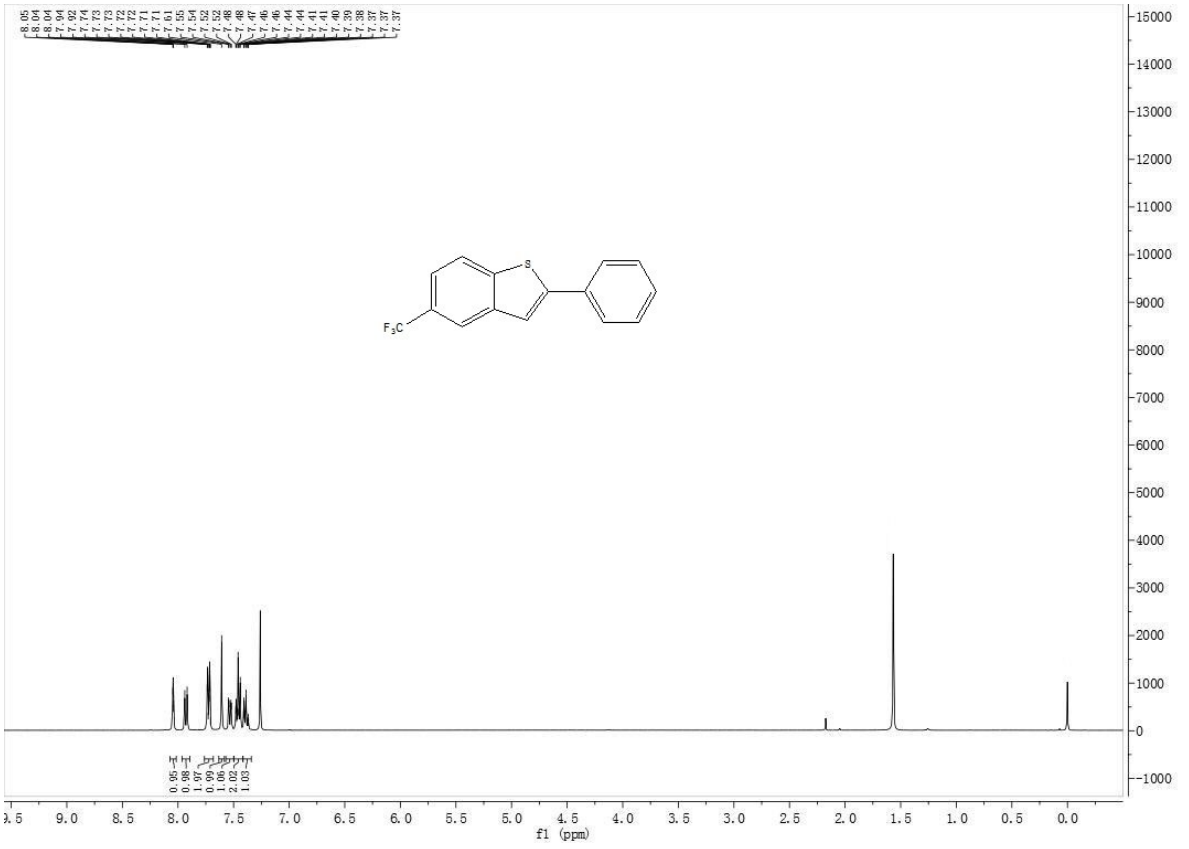

S
F
Cl
F
f1 (ppm)

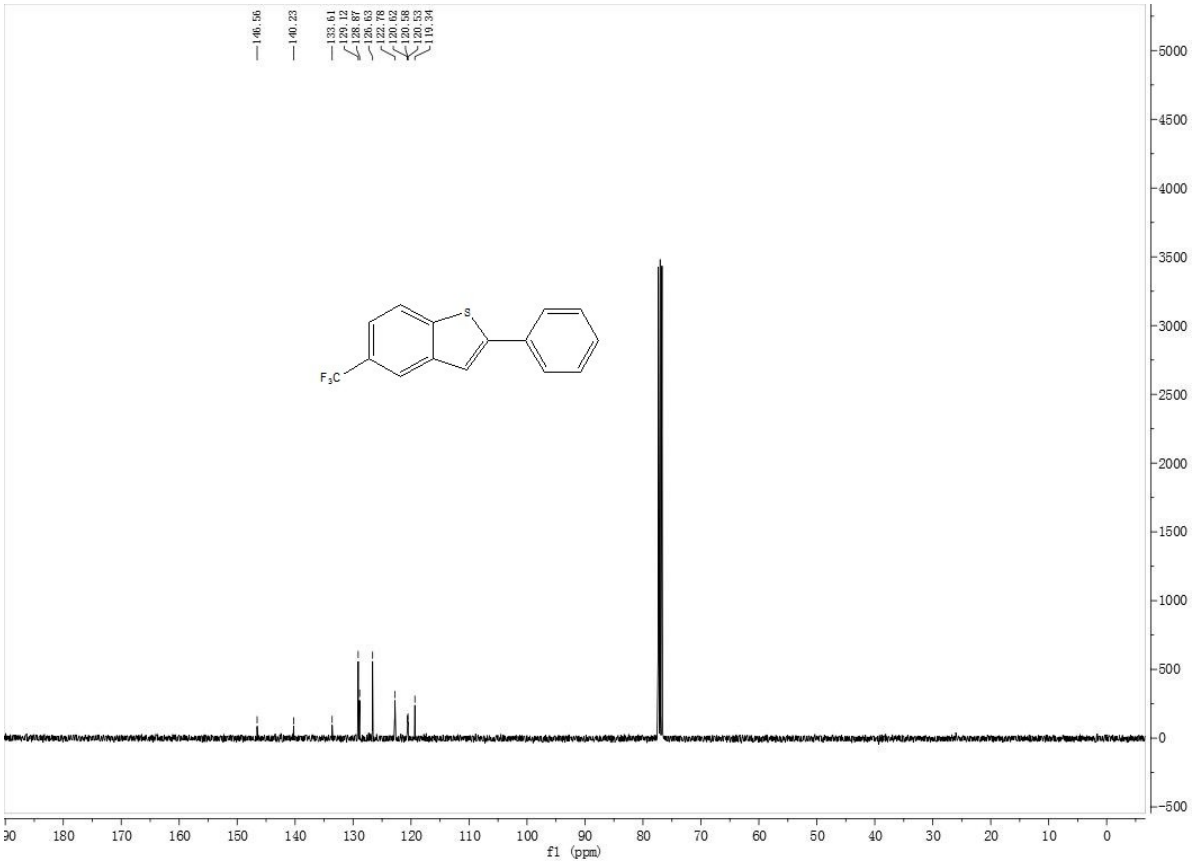

7.74
7.73
7.73
7.73
7.71
7.71
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.64
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.29
7.28
7.28
7.28
7.26
7.25
7.16
7.14
7.11
7.07
7.06
7.05
7.04
7.03
7.02
7.02
7.01
7.00
7.00
S
F
Cl
1.00
3.20
0.80
2.78
f1 (ppm)

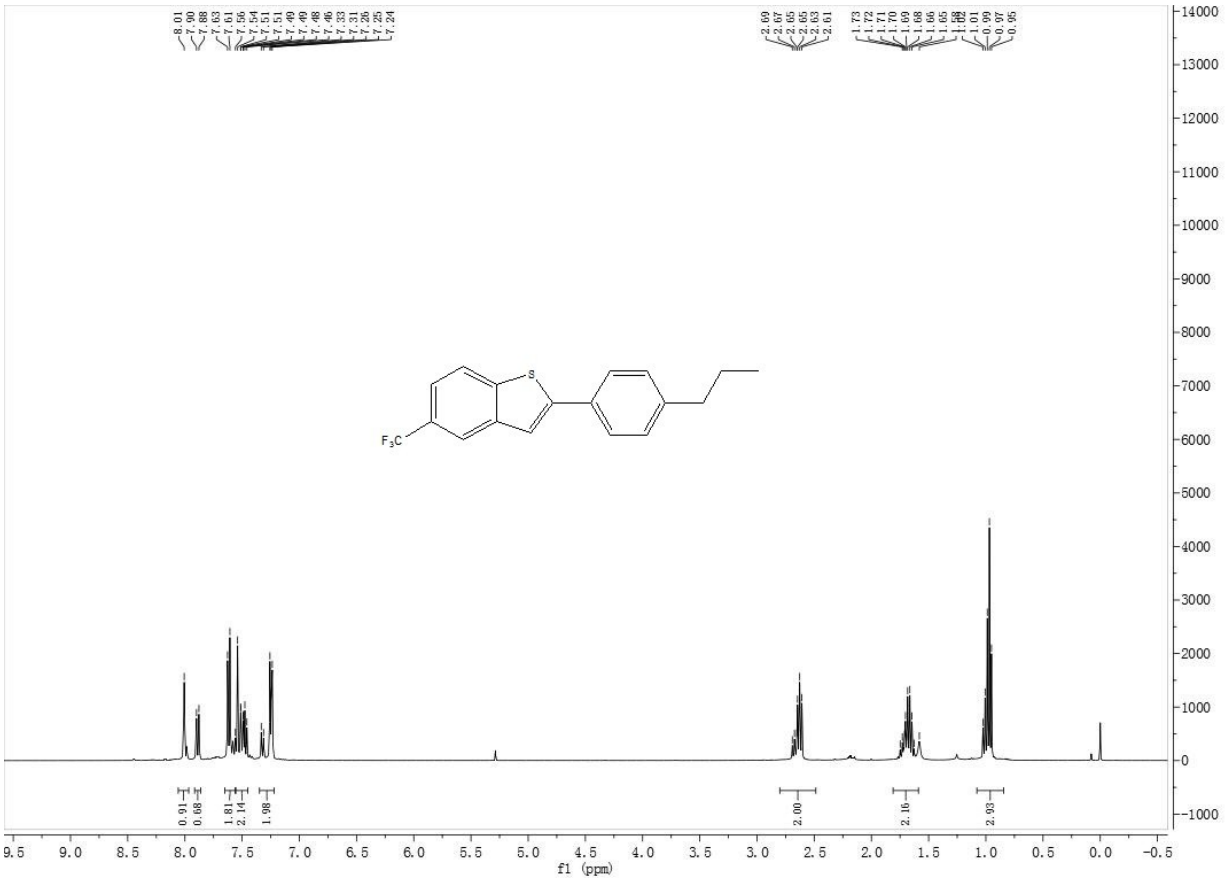

134.50
128.33
128.25
124.78
123.26
123.01
118.65
117.82
117.79
116.19
116.03
115.97
S
F
Cl
f1 (ppm)

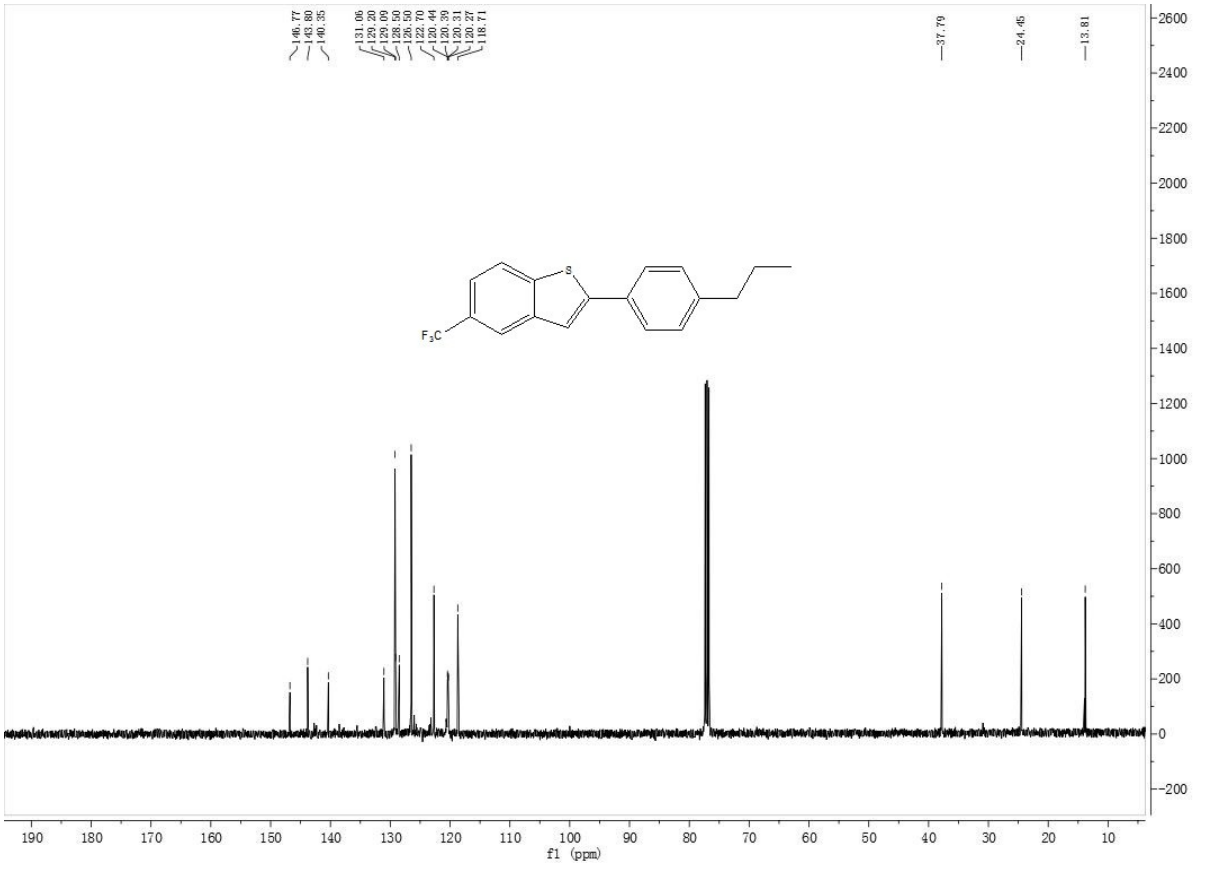

7.72
7.72
7.71
7.70
7.70
7.61
7.60
7.60
7.59
7.58
7.57
7.57
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.27
7.26
7.26
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.15
7.15
7.14
7.13
7.13
7.12
7.12
2.36
S
Cl
0.86
0.91
2.48
1.56
2.16
3.20
35000
30000
25000
20000
15000
10000
5000
0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

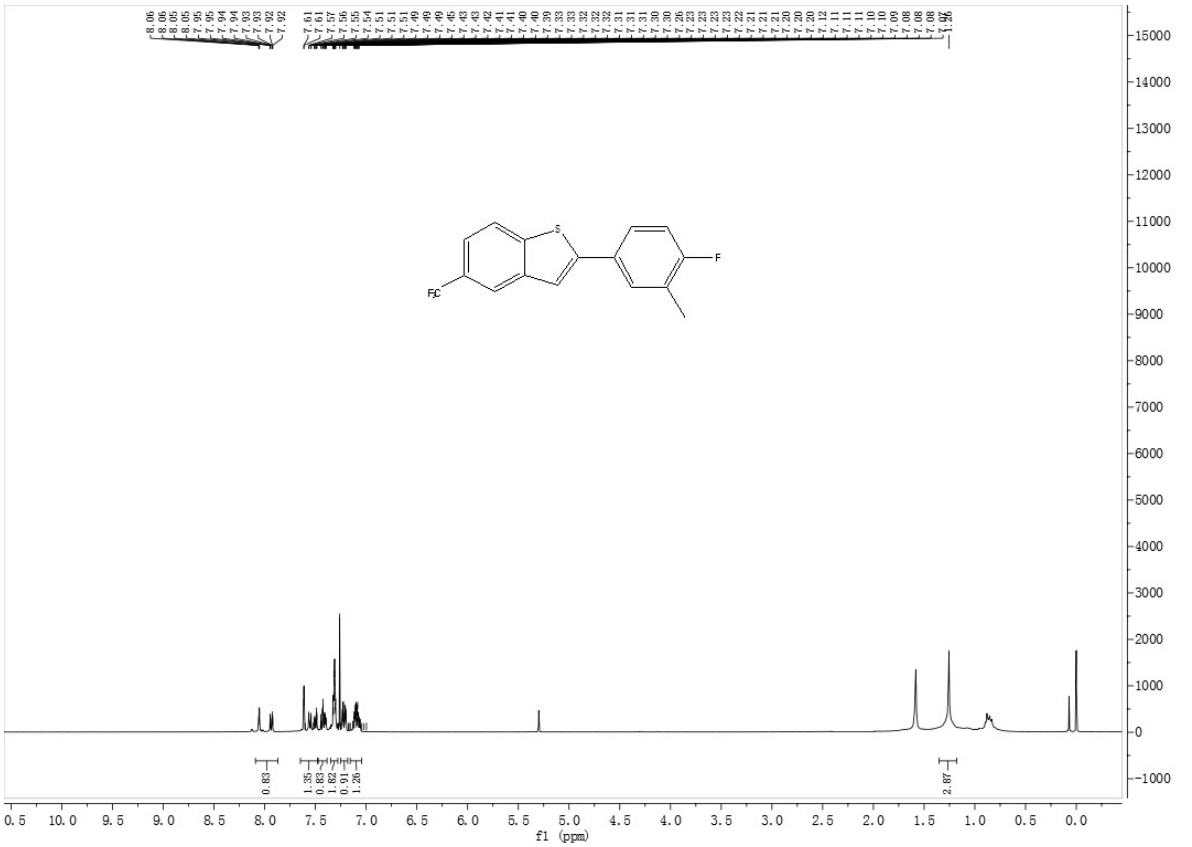

141.88
139.51
138.78
132.40
129.72
129.23
126.45
124.49
123.23
122.86
118.78
118.05
21.66
S
Cl
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

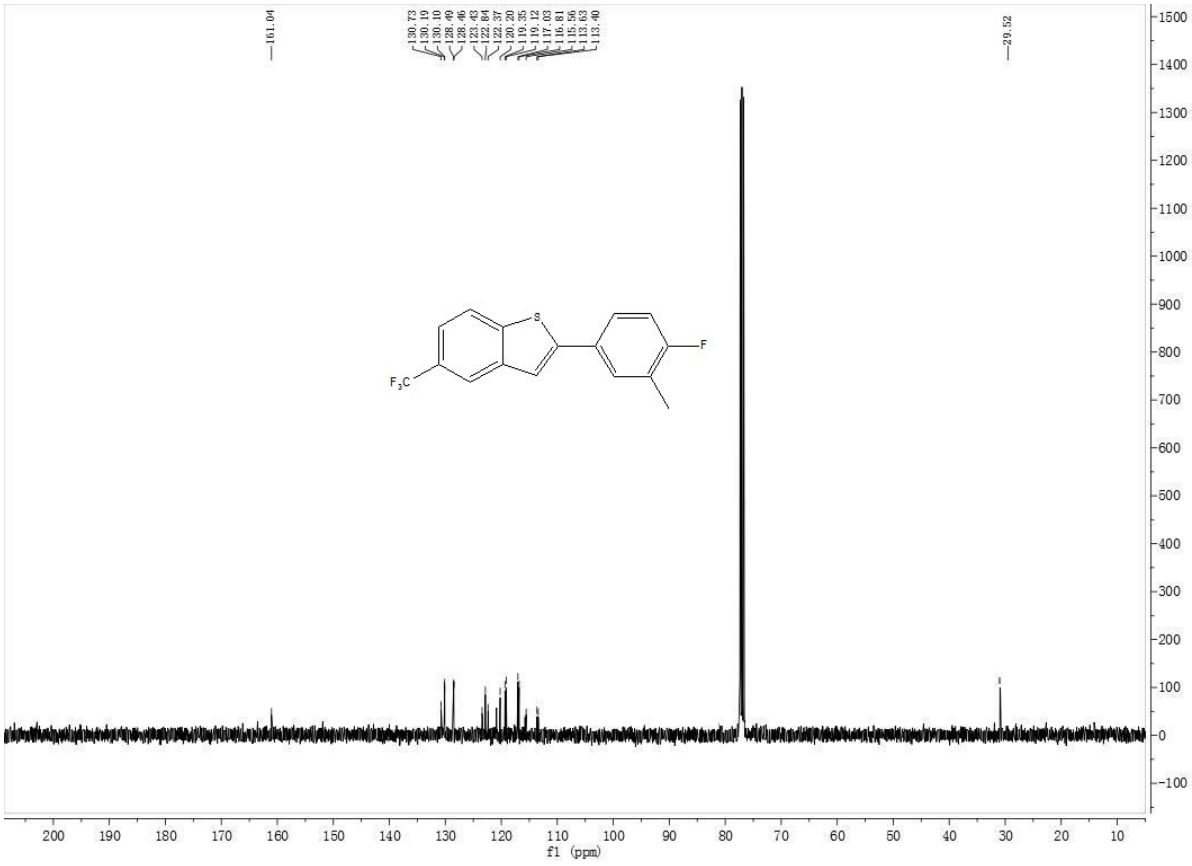

8.05
8.04
8.04
7.94
7.92
7.74
7.73
7.73
7.72
7.72
7.71
7.71
7.61
7.61
7.55
7.54
7.52
7.48
7.46
7.47
7.46
7.44
7.44
7.41
7.41
7.40
7.39
7.38
7.37
7.37
7.37
S
F3C
0.95
0.98
1.00
0.97
0.99
1.06
2.02
1.03
f1 (ppm)

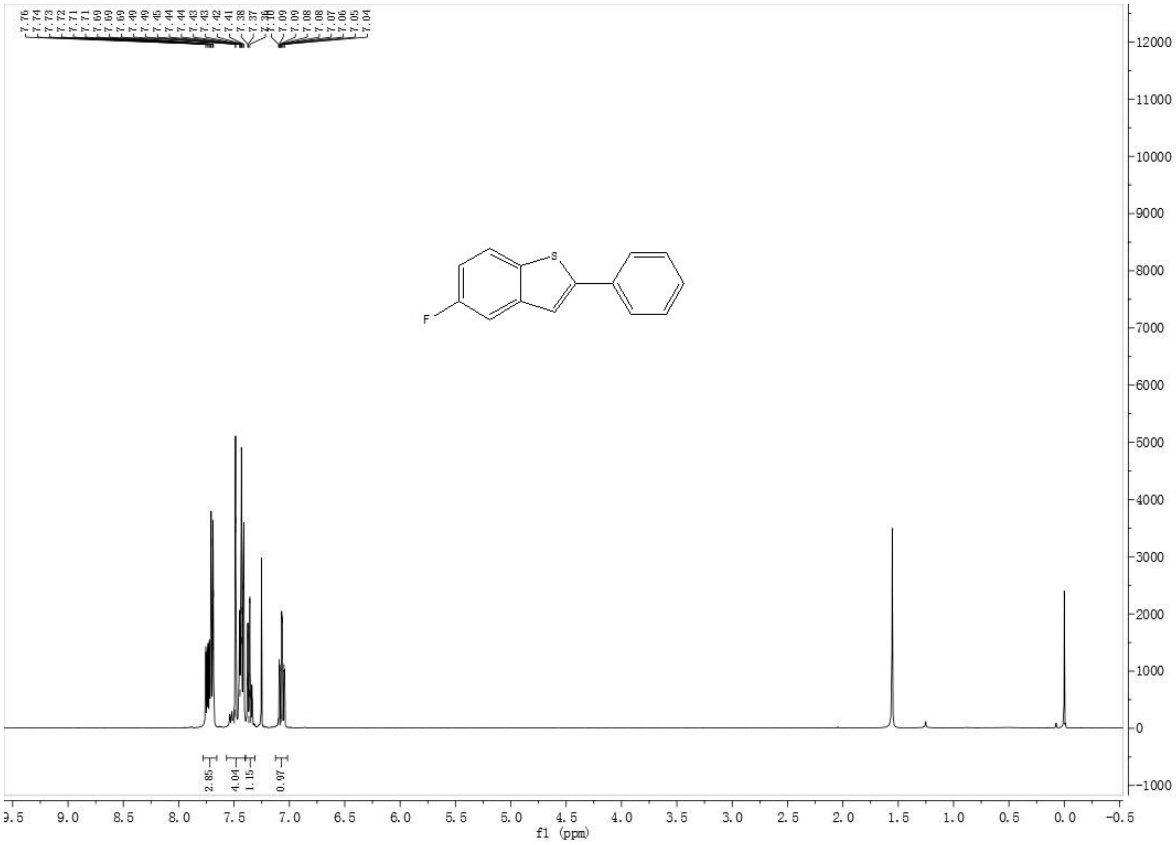

146.56
140.23
133.61
129.12
128.87
126.63
122.78
120.62
120.58
120.53
119.34
S
F3C
f1 (ppm)

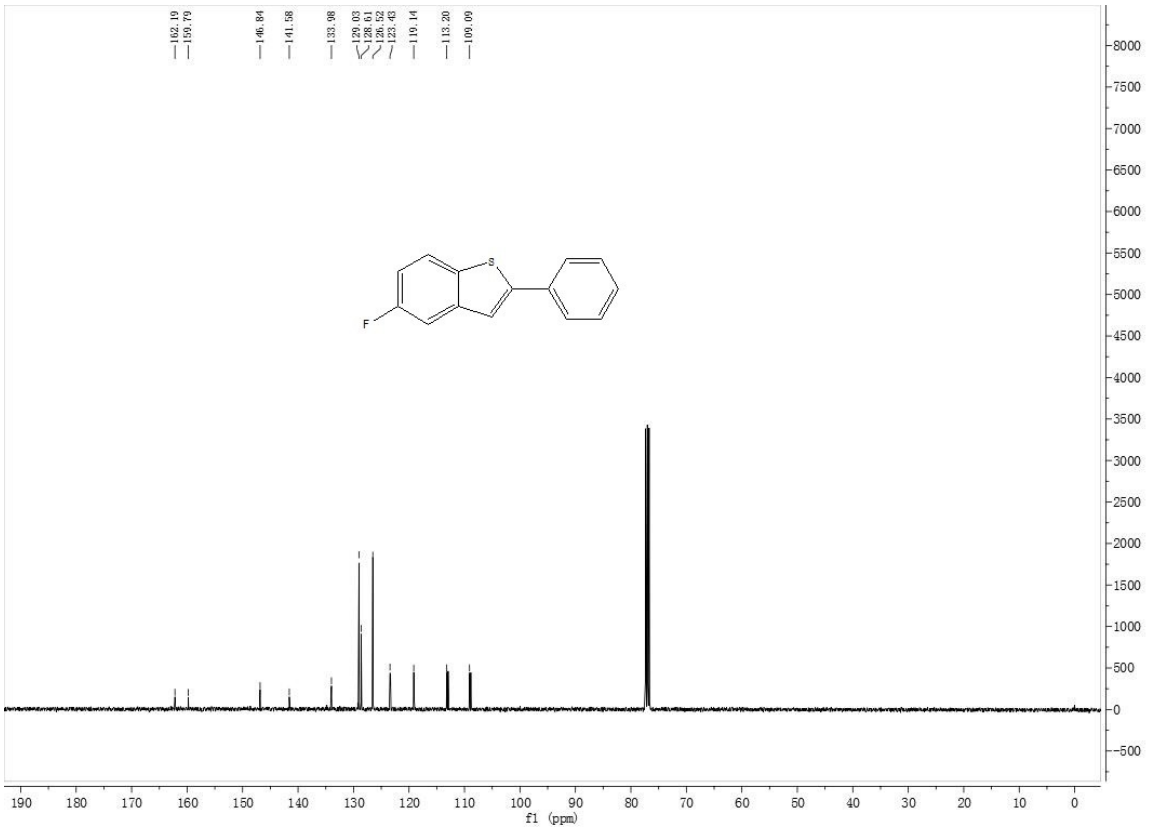

8.01
7.90
7.88
7.63
7.61
7.56
7.54
7.51
7.51
7.49
7.49
7.48
7.46
7.33
7.31
7.26
7.25
7.24
2.69
2.67
2.65
2.65
2.63
2.61
1.73
1.72
1.71
1.70
1.69
1.68
1.66
1.65
1.01
0.99
0.97
0.95
S
F3C
0.91
0.68
1.81
2.14
1.98
2.00
2.16
2.93
f1 (ppm)

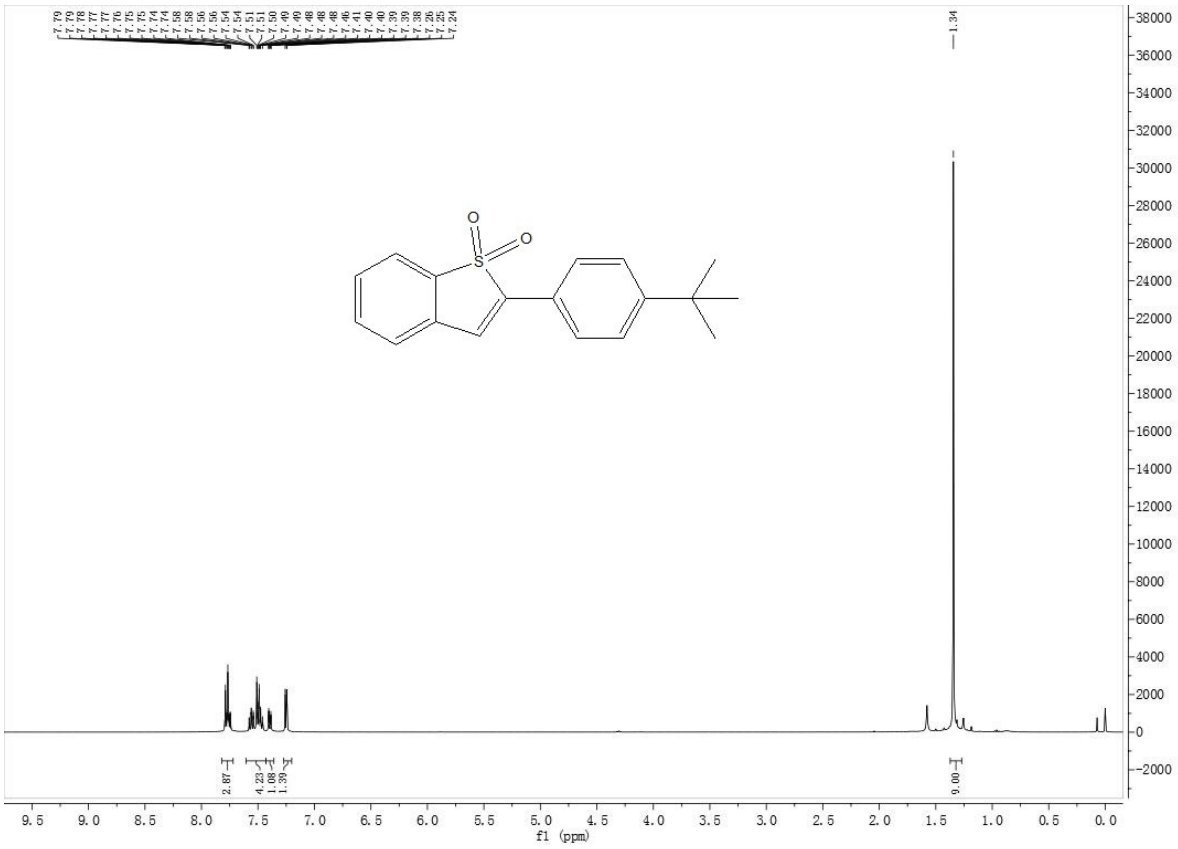

146.77
143.80
140.35
131.06
129.20
129.09
128.90
126.59
122.70
120.44
120.39
120.31
120.27
118.71
37.79
24.45
13.81
S
F3C
f1 (ppm)

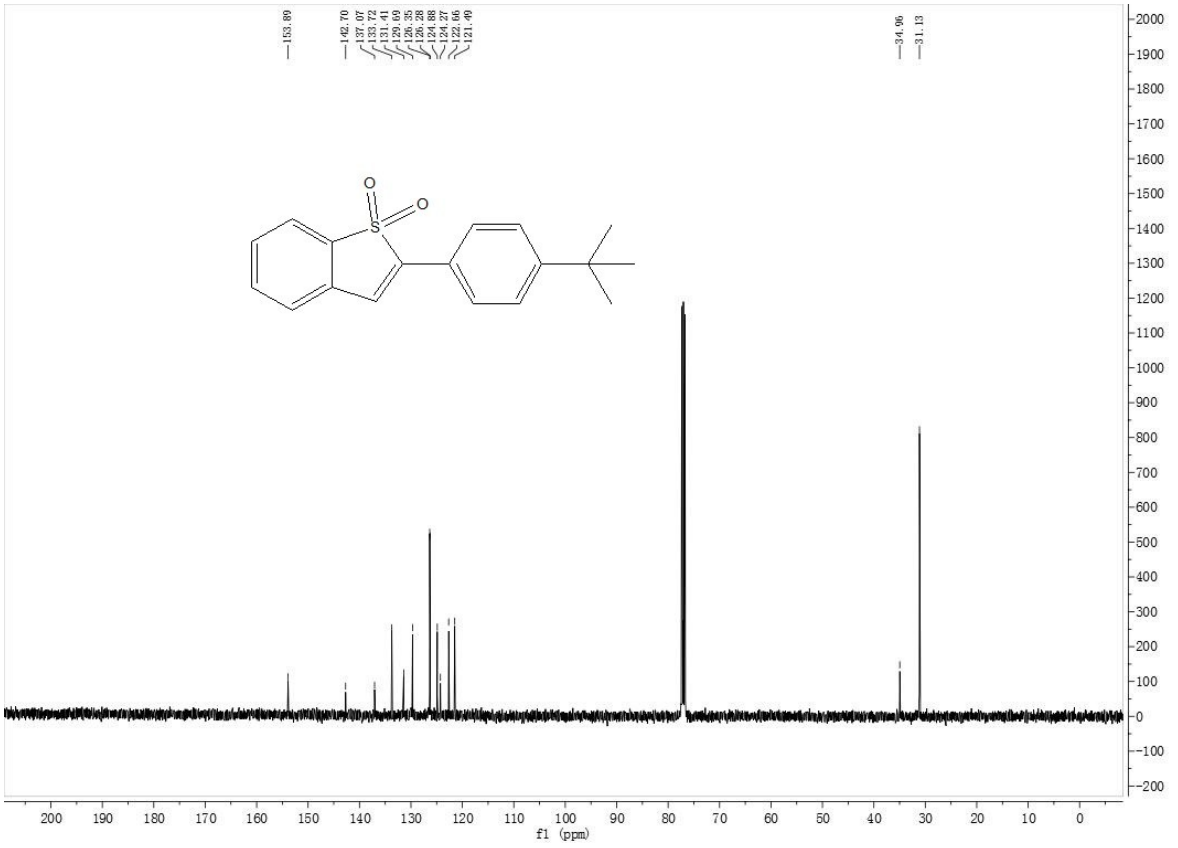

S
F
F3C
0.83
1.35
0.83
1.82
0.91
1.26
2.87
f1 (ppm)

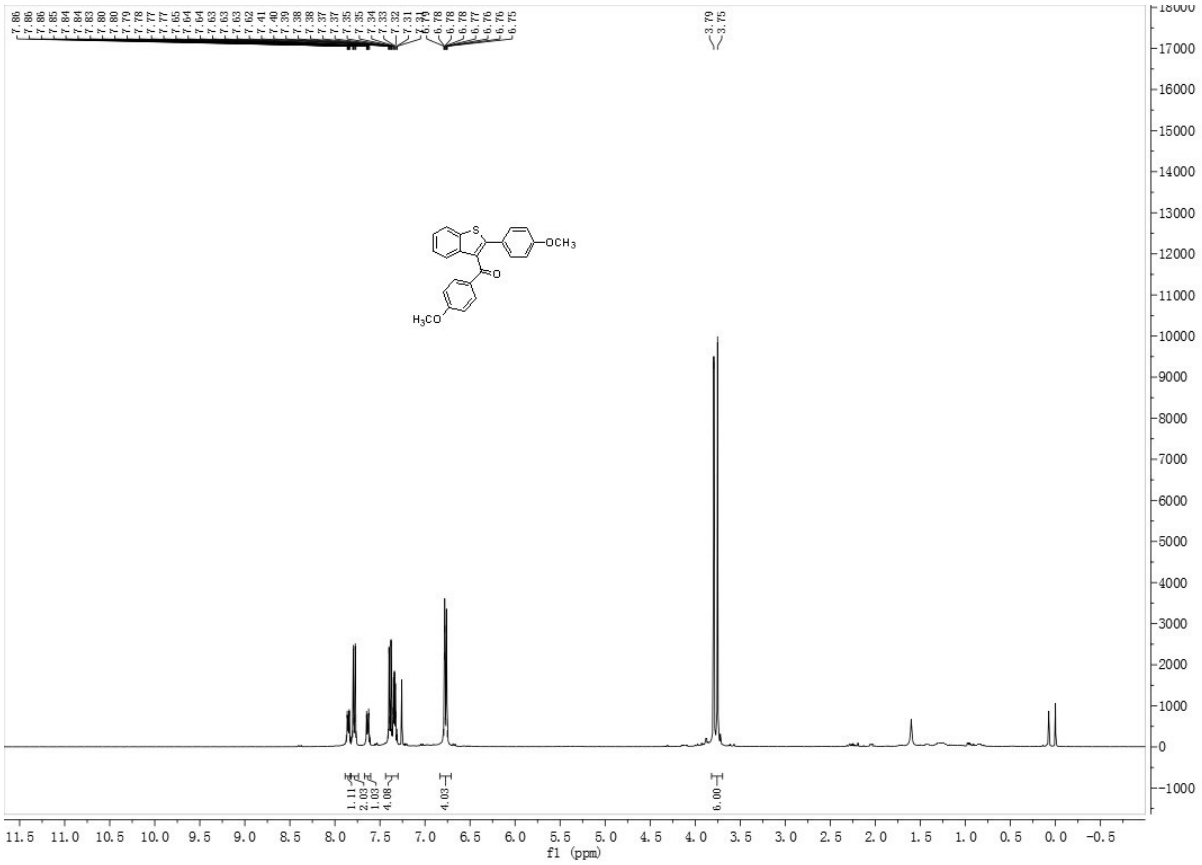

161.04
130.73
130.19
130.10
128.49
128.46
123.43
122.84
122.37
120.20
119.35
119.12
117.03
116.81
115.56
113.63
113.40
29.52
S
F
F3C
f1 (ppm)

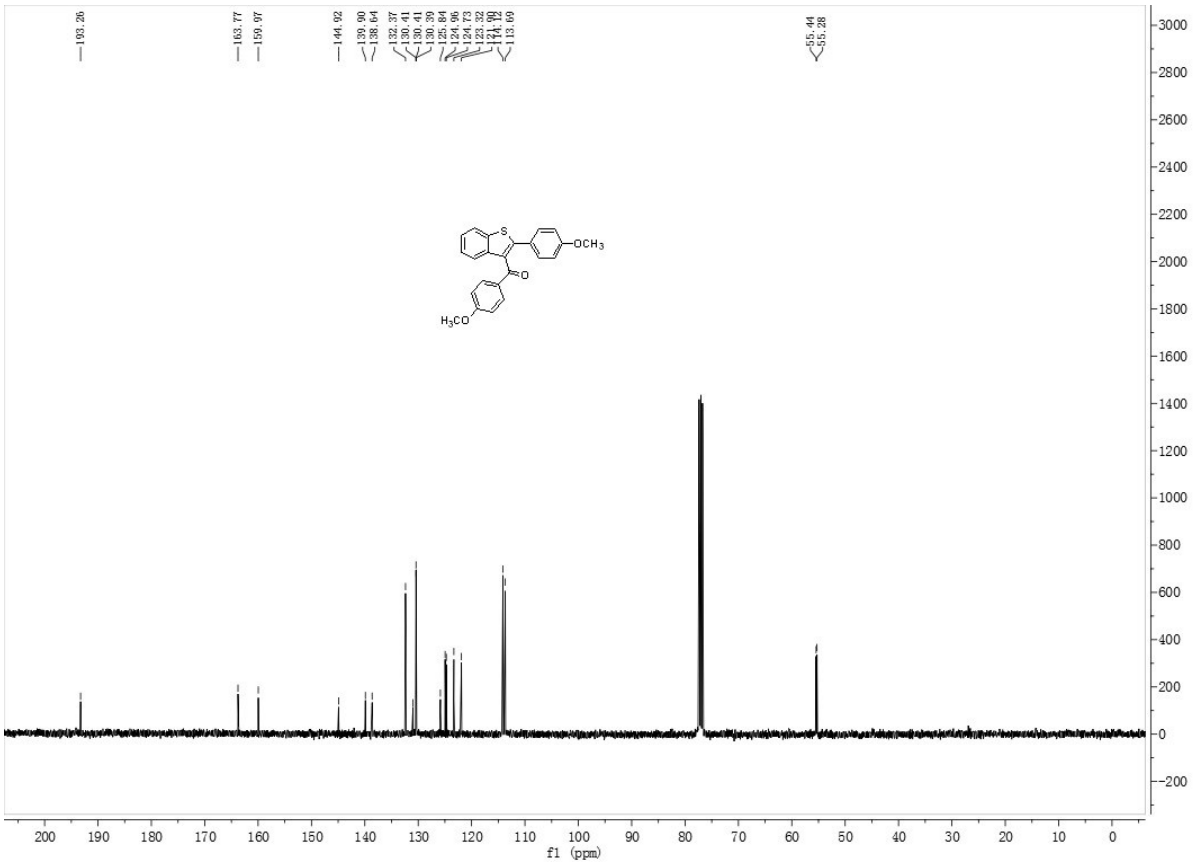

7.76
7.74
7.73
7.72
7.71
7.71
7.69
7.69
7.69
7.49
7.49
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.38
7.37
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.05
7.04
S
F
2.85
4.04
1.15
0.97
f1 (ppm)


162.19
159.79
146.84
141.58
133.98
129.03
128.61
126.52
123.45
119.14
113.20
109.09
S
F
f1 (ppm)


7.79
7.78
7.77
7.76
7.75
7.74
7.58
7.56
7.54
7.51
7.50
7.49
7.48
7.46
7.41
7.40
7.39
7.38
7.26
7.24
1.34
O
O
S
2.87
4.23
1.08
1.39
9.00
f1 (ppm)


153.80
142.70
137.07
133.72
131.41
129.69
126.33
126.28
124.88
124.27
122.66
121.49
34.96
31.13
O
O
S
f1 (ppm)


7.86
7.86
7.86
7.85
7.84
7.84
7.83
7.80
7.80
7.79
7.78
7.77
7.77
7.65
7.64
7.64
7.63
7.63
7.62
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.34
7.33
7.32
7.31
6.78
6.78
6.78
6.77
6.76
6.76
6.75
3.79
3.75
OCH3
O
H3CO
1.11
2.03
1.03
4.08
4.03
6.00
f1 (ppm)


193.26
163.77
159.97
144.92
139.90
138.64
132.37
130.41
130.41
130.39
125.84
124.96
124.73
123.32
114.19
114.12
113.69
55.44
55.28
OCH3
O
H3CO
f1 (ppm)