Supplementary Information

Regiospecific alkyl addition of (hetero)arene-fused thiophenes enabled by a visible-light-mediated photocatalytic desulfuration approach

Jiamei Di,† Huan He,† Falu Wang, Fei Xue, Xiao-Yu Liu* and Yong Qin*

Sichuan Engineering Laboratory for Plant-Sourced Drug and Research Center for Drug Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu 610041, China. E-mail: xyliu@scu.edu.cn, yongqin@scu.edu.cn

Table of Contents

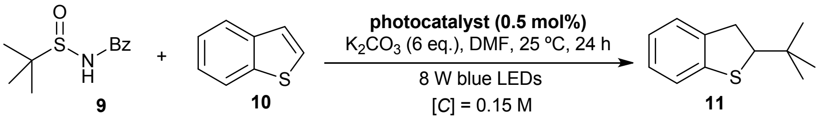
1. General information

The solvents used for radical reactions were degassed in flame-dried glassware via syringe needle under Argon for 30 min. All reactions that require anhydrous conditions were performed in flame-dried glassware under Ar atmosphere and all reagents were purchased from commercial suppliers (the photocatalyst $Ir(dtbbpy)(ppy)_2PF_6$ was purchased from J&K) without further purification. Solvent purification was conducted according to *Purification of Laboratory Chemicals* 2nd edn (Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., Pergamon Press: Oxford, 1980). The products were purified by flash column chromatography on silica gel (200 – 300 meshes) from the Anhui Liangchen Silicon Material Company (China). Reactions were monitored by thin layer chromatography (TLC, 0.2 mm, HSGF254) supplied by Yantai Chemicals (China). Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of phosphomolybdic acid or basic solution of $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on Varian INOVA-400/54 and Agilent DD2-600/54 and calibrated by using residual undeuterated chloroform (δ, ^1H NMR = 7.260, ^{13}C NMR = 77.00). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS or Agilent LC-MSD TOF ESI mass spectrometers.

2. Optimization of the reaction conditions

General procedure for condition optimization: Under Argon, to a 10 mL vial equipped with a rubber septum and magnetic stir bar was charged with benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), *N*-benzoyl *tert*-butyl-sulfinamide (1.5–3.0 equiv), photocatalyst (0.005 equiv), base (3.0–6.0 equiv), and degassed solvent. The reaction mixture was stirred under irradiation of 8 W blue LEDs at indicated temperature for 24 h. Then the reaction was quenched with H_2O, and extracted into EtOAc (3 x 10 mL) and washed with brine (10 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated to yield the crude product. Purification of the residue by flash chromatography on silica gel using petroleum ether afforded the corresponding products. The reaction conversion was determined by ^1H NMR analysis of the crude product. Yield was calculated according to the isolated mixtures containing product and unconverted starting material and their ratio in ^1H NMR.

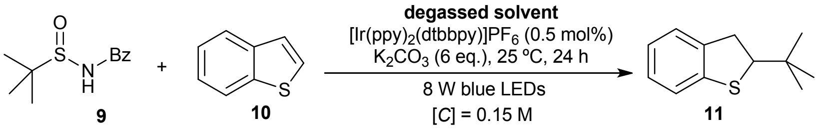
2.1 The effect of photocatalyst



Entry	Photocatalyst	Conversion	Yield
1	$[Ir(dtbbpy)(ppy)_2]PF_6$	20%	16%
2	$[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$	7%	6%
3	$Ir(ppy)_3$	0%	0%

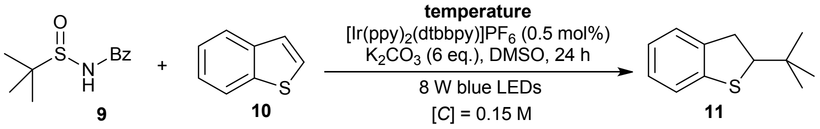
4	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	0%	0%

2.2 The effect of solvent



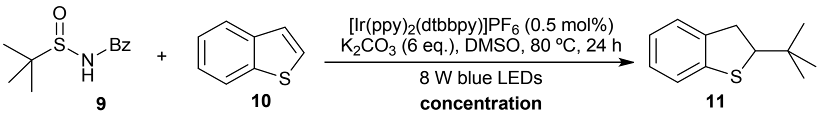
Entry	Solvent	Conversion	Yield
1	1,4-dioxane	trace	—
2	PhMe	trace	—
3	MeCN	11%	10%
4	THF	6%	4%
5	DCE	trace	—
6	DMF	20%	16%
7	DMA	trace	—
8	EtOAc	trace	—
9	DMSO	46%	33%
10	MeOH	trace	—
11	DMSO/H_2O (3: 1)	trace	—

2.3 The effect of temperature



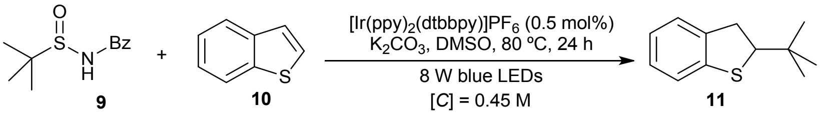
Entry	Temperature	Conversion	Yield
1	25 ºC	46%	33%
2	50 ºC	67%	54%
3	80 ºC	80%	75%

2.4 The effect of reaction concentration



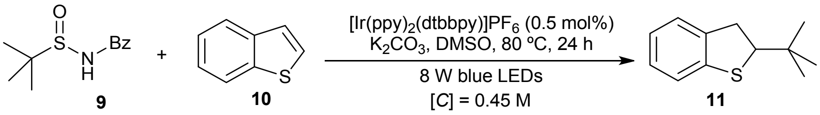
Entry	Concentration	Conversion	Yield
1	0.15 M	80%	75%
2	0.30 M	88%	80%
3	0.45 M	100%	92%
4	0.60 M	77%	62%

2.5 The effect of ratio of 9/10



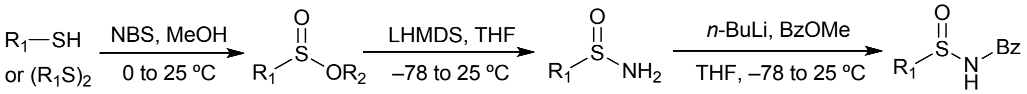
Entry	**9** : **10** ratio	Equiv of K_2CO_3	Conversion	Yield
1	3.0 : 1	6.0	100%	92%
2	2.2 : 1	4.4	92%	88%
3	1.5 : 1	3.0	82%	66%

2.6 Control experiments



Entry	Variation from standard conditions	Yield
1	none	92%
2	no light	0%
3	no base	0%
4	no photocatalyst	0%

3. Preparation of *N*-benzoyl alkyl-sulfinamides



S1 R_1 = *n*-Bu, R_2 = Me
S2 R_1 = *i*-Pr, R_2 = *i*-Pr
S3 R_1 = cyclopentyl, R_2 = Me
S4 R_1 = cyclohexyl, R_2 = Me

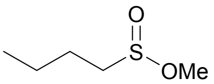
S5 R_1 = *n*-Bu
S6 R_1 = *i*-Pr
S7 R_1 = cyclopentyl
S8 R_1 = cyclohexyl

S9 R_1 = *n*-Bu
S10 R_1 = *i*-Pr
S11 R_1 = cyclopentyl
S12 R_1 = cyclohexyl
9 R_1 = *t*-Bu

General procedure for the preparation of methyl sufinates S1–S4: Solid *N*-bromosuccinimide powder (3.0 equiv) was added in portions to a solution of thiol or disulfide (1.0 equiv) in methanol at 0 °C. The cold bath was removed and the mixture was stirred at room temperature overnight. The mixture was poured into ice water, followed by the addition of saturated $NaHCO_3$ solution. The biphasic mixture was transferred to a separation funnel and shaken until discoloration. The phases were separated and the aqueous layer was extracted with dichloromethane (x 3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford a yellowish crude sulfinate. Purification of the crude product by flash chromatography on silica gel afforded corresponding methyl sulfinate.

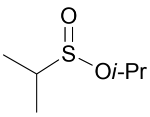
General procedure for the synthesis of sufinamides S5–S8: To a stirred solution of the methyl sulfinate (1.0 equiv) in THF at –78 ºC under argon, lithium hexamethyldisilazide (LHMDS, 1.5 or 3.0 equiv, 1 M in THF) was added via cannula. Then the mixture was warmed to room temperature and was monitored by TLC. Upon completion (about 0.5 h), saturated NH_4Cl aqueous was added and the mixture was stirred overnight. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum. The crude was recrystallized in dichloromethane and washed with pentane to afford pure sulfinamide.

General procedure for the synthesis of *N*-benzoyl alkyl-sulfinamides S9–S12 and 9: To a round bottom flask was added sulfinamide (1.0 equiv) and THF. At –78 ºC, *n*-BuLi (3.0 equiv, 2.5 M in THF) was added over 20 min followed by addition of methyl benzoate (3.0 equiv). The resulting mixture was stirred at room temperature overnight. Upon completion, saturated aqueous NH_4Cl and H_2O were added, and the complex was extracted with EtOAc for 3 times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The crude was recrystallized in THF and washed with pentane to afford pure *N*-benzoyl alkyl-sulfinamides.



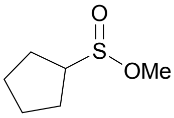
S1

Following the general procedure, the reaction of 1,2-dibutyldisulfane (16.0 mL, 84 mmol, 1.0 equiv) and NBS (44.9 g, 252 mmol, 3.0 equiv) proceeded for 4 h to afford product **S1** (17.2 g, 75%) as a colorless oil after purification by silica gel flash chromatography (petroleum ether:EtOAc = 5:1). IR (neat): $v_{\max}$ = 2961, 2874, 1709, 1463, 1035, 985, 717, 597 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 2.81 – 2.65 (m, 2H), 1.71 – 1.64 (m, 2H), 1.49 – 1.40 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.4, 54.2, 23.1, 21.8, 13.5; HRMS (*m/z*): [M + Na]$^+$ calcd. for $C_5H_{12}NaO_2S$, 159.0450; found 159.0448.



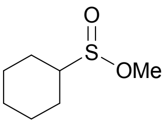
S2

Because of the volatility of methyl propane-2-sulfinate, the isopropyl ester **S2** was prepared according to the literature.[1]. Following the general procedure, except for using isopropanol instead of methanol, the reaction of propane-2-thiol (6.9 mL, 81.4 mmol, 1.0 equiv) and NBS (43.5 g, 244 mol, 3.0 equiv) proceeded for 12 h to afford the product **S2** (7.3 g, 60%) as colorless oil after purification by silica gel flash chromatography (petroleum ether:EtOAc = 10:1). The spectroscopic data were in good agreement with those reported in literature.[1]



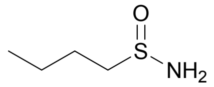
S3

Following the general procedure, the reaction of cyclopentanethiol (32 mL, 0.30 mol, 1.0 equiv) and NBS (160.0 g, 0.90 mol, 3.0 equiv) proceeded for 12 h to afford the product **S3** (36.9 g, 83%) as colorless oil after purification by silica gel flash chromatography (petroleum ether:EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.16 – 3.09 (m, 1H), 2.03 – 1.99 (m, 1H), 1.96 – 1.80 (m, 4H), 1.67 – 1.65 (m, 3H); ^{13}C NMR (600 MHz, $CDCl_3$): δ 64.2, 54.6, 25.9, 25.9, 25.9, 24.9; IR (neat): $v_{\max}$ = 2949, 2868, 1738, 1449, 1127, 1106, 986 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_6H_{13}O_2S$, 149.0631; found, 149.0631.



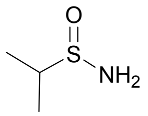
S4

Following the general procedure, the reaction of cyclohexanethiol (25 mL, 0.20 mol, 1.0 equiv) and NBS (106.0 g, 0.60 mol, 3.0 equiv) proceeded for 12 h to afford the product **S4** (28.0 g, 86%) as colorless oil after purification by silica gel flash chromatography (petroleum ether:EtOAc = 20:1). The spectroscopic data were in good agreement with those reported in literature.[2]

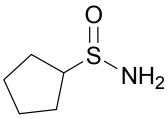


S5

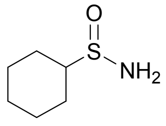
Following the general procedure, aminolysis of **S1** (19.3 g, 141 mmol, 1.0 equiv) by LHMDS (1 M in THF, 208 mL, 1.5 equiv) in THF (470 mL) proceeded in 2 h to provide the product **S5** (10.4 g, 62%) as a white solid after purification by silica gel flash chromatography (petroleum ether:acetone = 1:1). M.p. = 56 – 58 °C; IR (neat): ν_{max} = 3225, 2958, 2930, 2871, 1577, 1464, 1026, 881, 656 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.59 (s, 2H), 2.79 – 2.66 (m, 2H), 1.67 – 1.57 (m, 2H), 1.47 – 1.34 (m, 2H), 0.89 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.8, 24.9, 21.7, 13.6; HRMS (*m/z*) : [M + Na]$^+$ calcd. for $C_4H_{11}NNaOS$, 144.0454; found 144.0451.


S6

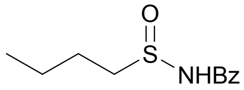
Following the general procedure, the aminolysis of of isopropyl propane-2-sulfinate **S2** (6.6 g, 43.9 mmol, 1.0 equiv) with LHMDS (1 M in THF, 132 mL, 132 mmol, 3.0 equiv) in THF (100 mL) proceeded for 1 h to provide the product **S6** (3.8 g, 81%) as colorless oil after purification by silica gel flash chromatography (petroleum ether:EtOAc = 1:1) The spectroscopic data were in good agreement with those reported in literature.[3]


S7

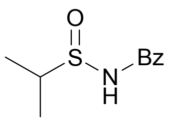
Following the general procedure, the aminolysis of **S3** (15.0 g, 101 mmol, 1.0 equiv) with LHMDS (1 M in THF, 152 mL, 152 mmol, 1.5 equiv) in THF (200 mL) proceeded for 1 h to provide the product **S7** (9.4 g, 70%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 1:1). M.p. = 82 – 83 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.87 (s, 2H), δ 3.09 – 3.01 (m, 1H), 2.10 – 1.99 (m, 1H), 1.98 – 1.89 (m, 2H), 1.83 – 1.65 (5H); ^{13}C NMR (600 MHz, CDCl$_3$) δ 65.0, 27.5, 25.9, 25.8, 25.4; IR (neat): ν_{max} = 2949, 2868, 1738, 1449, 1127, 1106, 986 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_5H_{12}NOS$, 134.0634; found, 134.0633.


S8

Following the general procedure, the aminolysis of methyl cyclohexanesulfinate **S4** (17.5 g, 108 mmol, 1.0 equiv) with LHMDS (1 M in THF, 162 mmol, 162 mL, 1.5 equiv) in THF (200 mL) proceeded for 1 h to provide the product **S8** (13.5 g, 85%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 1:1). M.p. = 95 – 98 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.05 – 3.94 (m, 2H), 2.51 – 2.43 (m, 1H), 2.04 (d, J = 11.6 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.68 (d, J = 12.4 Hz, 1H), 1.49 – 1.18 (m, 5H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 63.5, 25.7, 25.5, 25.3, 25.1, 25.1; IR (neat): ν_{max} = 3266, 3184, 3092, 2928, 2851, 1452, 1016 cm^{-1};IR (neat): ν_{max} = 3266, 3184, 3092, 2928, 2851, 1452, 1016 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_6H_{14}NOS$, 148.0796; found, 148.0791.

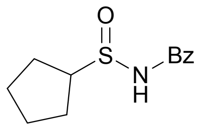

S9

Prepared according to the general procedure from **S5** (11.6 g, 95.7 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 115 mL, 287 mmol, 3.0 equiv), methyl benzoate (35.8 mL 287 mmmol, 3.0 equiv) and anhydrous THF (210 mL) for 20 h to provide product **S9** (11.0 g, 51%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 2:1). M.p. = 83 – 85 °C. IR (neat): ν_{max} = 3167, 2959, 2931, 2871, 1677, 1451, 1250, 1080, 1047, 782, 707 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.16 (br.s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.45 –7.40 (m, 2H), 3.15 – 3.02 (m, 2H), 1.60 – 1.54 (m, 2H), 1.44 – 1.33 (m, 2H), 0.86 – 0.82 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.4, 133.1, 131.4, 128.6, 128.2, 54.2, 24.7, 21.7, 13.6; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{11}H_{16}NO_2S$, 226.0896; found 226.0893.



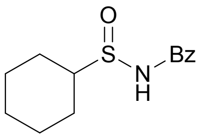
S10

Prepared according to the general procedure from **S6** (10.0 g, 94.2 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 113 mL, 283 mmol, 3.0 equiv), methyl benzoate (35 mL, 283 mmol, 3.0 equiv) and anhydrous THF (300 mL) for 15 h to provide product **S10** (17.1 g, 86%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 1:1). M.p. = 135 – 138 ^{o}C;. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.89 - 7.81 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.33 – 3.27 (m, 1H), 1.29 (d, J = 7.2Hz, 3H), 1.26 (d, J = 7.2Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.6, 133.1, 131.6, 128.7, 128.7, 128.1, 128.1, 54.1, 15.5, 15.1; IR (neat): ν_{max} = 3170, 2984, 1680, 1451, 1419, 1237, 1048, 1066, 1025 cm^{-1}; HRMS (m/z): $[M + H]^+$ calcd. for $C_{10}H_{14}NO_2S$, 212.0745; found, 212.0741.



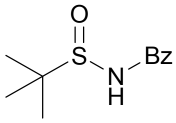
S11

Prepared according to the general procedure from **S7** (15.6 g, 117 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 140 mL, 351 mmol, 3.0 equiv), methyl benzoate (43.8 mL 351 mmol, 3.0 equiv) and anhydrous THF (390 mL) for 15 h to provide product **S11** (19.1 g, 69%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 3:1). M.p. = 131 – 136 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.89 – 7.87 (m, 2H), 7.56 (t, J= 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.73 – 3.66 (m, 1H), 2.02 – 1.80 (m, 2H), 1.78 – 1.50 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.5, 133.1, 131.6, 128.7, 128.7, 128.1, 128.1, 63.1, 26.8 , 26.7 , 26.0 , 25.9; IR (neat): ν_{max} = 3163, 2957, 2867, 1677, 1451, 1419, 1245, 1055 cm^{-1}; HRMS (m/z): $[M + H]^+$ calcd. for $C_{12}H_{16}NO_2S$, 238.0896; found, 238.0898.



S12

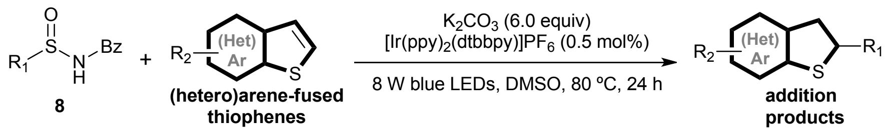
Prepared according to the general procedure from **S8** (11.2 g, 76.1 mmol, 1.0 equiv), *n*-BuLi (2.5 M in THF, 91.2 mL, 228 mmol, 3.0 equiv), methyl benzoate (28.5 mL, 228 mmol, 3.0 equiv) and anhydrous THF (280 mL) for 15 h to provide product **S12** (14.1 g, 74%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 2:1). M.p. = 120 – 126 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.12 – 3.04 (m, 1H), 2.00 – 1.94 (m, 2H), 1.86 – 1.74 (m, 2H), 1.67 – 1.57 (m, 1H), 1.50 – 1.13 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.0, 133.0, 132.0, 128.7, 128.7, 128.1, 128.1, 62.0, 25.8 , 25.5, 25.3, 25.0, 24.9; IR (neat): ν_{max} = 3164, 2930, 2853, 1678, 1413, 1450, 1243, 1025, 1043, 1057 cm^{-1}; HRMS (m/z): $[M + H]^+$ calcd. for $C_{13}H_{18}NO_2S$, 252.1058; found, 252.1054.



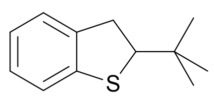
9

Prepared according to the general procedure from *tert*-butyl sulfonamide (15.5 g, 128 mmol, 1.0 equiv), *n*-BuLi (2.5 M in THF, 154 mL, 384 mmol, 3.0 equiv), methyl benzoate (48.0 mL, 384 mmol, 3.0 equiv) and anhydrous THF (400 mL) for 15 h to provide product **9** (21.6 g, 75%) as white solid after purification by silica gel flash chromatography (petroleum ether:EtOAc = 3:1). M.p. = 137 – 142 ^{o}C. The spectroscopic data were in good agreement with those reported in literature.[4]

4. Photocatalytic alkyl addition of (hetero)arene-fused thiophenes

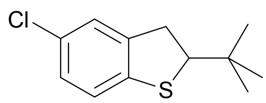


General procedure: Under argon, to a 10 mL vial equipped with a rubber septum and magnetic stir bar was charged with (hetero)arene-fused thiophene (0.4 mmol, 1.0 equiv), *N*-benzoyl alkyl-sulfinamide (3.0 equiv), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (0.005 equiv), K_2CO_3 (6.0 equiv), and degassed DMSO. The reaction mixture was stirred under irradiation of 8 W blue LEDs at 80 ºC, which gradually became a solution. After 24 h, the reaction was quenched with H_2O, and extracted into EtOAc (3 x 10 mL) and washed with brine (10 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated to yield the crude product. Purification of the residue by flash chromatography on silica gel using the indicated solvent system afforded the corresponding products.



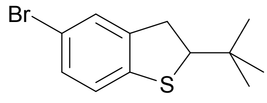
11

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **11** was isolated by flash chromatography with petroleum as a slightly yellow oil (70.6 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (m, 3H), 6.96 (m, 1H), 3.92 (t, J = 8.8 Hz, 1H), 3.29 – 3.06 (m, 2H), 1.02 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.3, 140.1, 127.1, 124.1, 123.8, 121.6, 62.8, 37.5, 34.2, 27.5, 27.5, 27.5; IR (neat): $v_{\max}$ = 2959, 2917, 2850, 1732, 1463, 1364, 1260, 1087, 1018 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{16}S$, 192.0963; found, 192.0967.



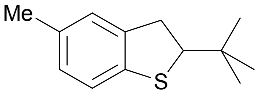
12

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 5-chlorobenzothiophene (67.2 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **12** was isolated by flash chromatography with petroleum as a colorless oil (84.9 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 13.6 Hz, 3H), 3.93 (t, J = 8.6 Hz, 1H), 3.24 – 3.12 (m, 2H), 1.01 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 142.0, 140.0, 129.3, 127.1, 124.3, 122.4, 63.2, 37.3, 34.3, 27.3, 27.3, 27.3; IR (neat): $v_{\max}$ = 2954, 2917, 2850, 1736, 1463, 1377, 1260, 1086, 1020 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{15}ClS$, 226.0573; found, 226.0577.

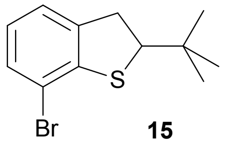


13

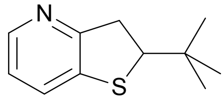
According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 5-bromobenzothiophene (84.8 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **13** was isolated by flash chromatography with petroleum as a colorless oil (91.8 mg, 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.12 (m, 2H), 6.99 (d, J = 8.2 Hz, 1H), 3.91 (t, J = 8.6 Hz, 1H), 3.16 (m, 2H), 1.00 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 142.4, 140.7, 130.0, 127.1, 122.9, 116.9, 63.2, 37.3, 34.3, 27.3, 27.3, 27.3; IR (neat): $v_{\max}$ = 2920, 1735, 1460, 1260, 1021, 750 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{12}H_{15}BrS$, 270.0078; found, 270.0071.


14

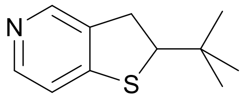
According to the general procedure, $Ir(dtbbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 5-methylbenzothiophene (59.2 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **14** and starting material (71.3 mg, 82% conversion, 71% yield, 91% yield of **14** brsm). Pure **14** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 3.90 (t, J = 8.8 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.26 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 140.2, 137.8, 133.5, 127.9,125.0, 121.3, 63.0, 37.4, 34.2, 27.5, 27.5, 27.5, 20.9; IR (neat): $v_{\max}$ = 2955, 2921, 2851, 1463, 1377, 1275, 1023 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{13}H_{18}S$, 206.1129; found, 206.1124.


15

According to the general procedure, $Ir(dtbbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 7-bromobenzothiophene (84.8 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **15** was isolated by flash chromatography with petroleum as a colorless oil (91.8 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 3.95 (t, J = 9.2 Hz, 1H), 3.39 – 2.26 (m, 2H), 1.03 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.6, 141.5, 130.2, 125.3, 122.7, 115.7, 61.9, 38.8, 34.1, 27.4, 27.4, 27.4; IR (neat): $v_{\max}$ = 2958, 2867, 1557, 1416, 1364, 1091, 1044, 759 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{12}H_{15}BrS$, 270.0078; found, 270.0073.

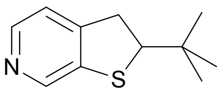

16

According to the general procedure, $Ir(dtbbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[3,2-*b*]pyridine (54.0 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **16** was isolated by flash chromatography with petroleum ether:EtOAc (10:1 v/v) as a slightly yellow oli (64.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 4.4 Hz , 1H), 7.30 (d, J = 7.6 Hz, 1H), 6.87 – 6.84 (m, 1H), 3.92 (t, J = 8.4 Hz, 1H), 3.26 – 3.12 (m, 2H), 1.03 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.8, 148.0, 134.3, 130.7, 118.6, 60.3, 35.1, 34.3, 27.1, 27.1, 27.1; IR (neat): $v_{\max}$ = 2961, 2924, 1462, 1365, 1258, 1103, 747 cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{11}H_{16}NS$, 194.1003; found, 194.0998.

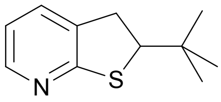

17

According to the general procedure, $Ir(dtbbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[3,2-*c*]pyridine (54.0 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Purification of the crude product by flash chromatography eluting with petroleum ether:EtOAc (10:1 v/v) gave compound **17** as a slightly yellow oli (60.2 mg, 75%), with 9.7 mg of starting material recovered (conversion: 82%, 95% yield of **17** brsm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.22 (d, J = 5.2 Hz, 1H), 7.11 (d, J = 5.2 Hz, 1H), 3.95 (t, J = 8.8 Hz, 1H), 3.30 –

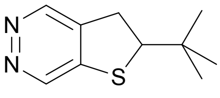
3.15 (m, 2H), 1.02 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 153.5, 147.6, 143.9, 136.3, 117.0, 63.2, 34.6, 34.4, 27.3, 27.3, 27.3; IR (neat): $v_{\max}$ = 2960, 1709, 1575, 1464, 1366, 1245, 1098 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{11}H_{16}NS$, 194.1003; found, 194.0998.


18

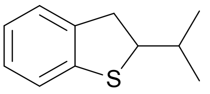
According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[2,3-*c*]pyridine (54.0 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **18** was isolated by flash chromatography with petroleum ether:EtOAc (10:1 v/v) as a slightly yellow solid (68.7 mg, 89%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 8.20 (d, *J* = 4.8 Hz, 1H), 7.05 (d, *J* = 4.4 Hz, 1H), 3.93 (t, *J* = 8.4 Hz, 1H), 3.26 – 3.13 (m, 2H), 1.01 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 149.2, 145.0, 142.4, 139.2, 119.3, 62.7, 37.2, 34.4, 27.3, 27.3, 27.3; IR (neat): $v_{\max}$ = 2917, 2850, 1735, 1464, 1023, 797 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{11}H_{14}NS$, 194.0847; found, 194.0840.


19

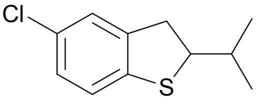
According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[3,2-*b*]pyridine (54.1 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **19** was isolated by flash chromatography with petroleum ether:EtOAc (10:1 v/v) as a slightly yellow oli (73.3 mg, 95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, *J* = 5.2 Hz , 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.83 (m, 1H), 3.92 (t, *J* = 8.6 Hz, 1H), 3.26 – 3.12 (m, 2H), 1.03 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 165.8, 148.0, 134.3, 130.8, 118.6, 60.3, 35.1, 34.3, 27.2, 27.2, 27.2; IR (neat): $v_{\max}$ = 2959, 2868, 1563, 1583, 1466, 1394, 1188, 1129, 1087, 779 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{11}H_{16}NS$, 194.1003; found, 194.0996.


20

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[3,2-*b*]pyridine (54.4 mg, 0.4 mmol, 1.0 equiv), **9** (270 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. The product **20** was isolated by flash chromatography with petroleum ether:EtOAc (5:1 v/v) as a white solid (57.4 mg, 74%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.01 (s, 1H), 8.83 (s, 1H), 4.01 (t, *J* = 8.8 Hz, 1H), 3.27 (dd, *J* = 18.0, 8.7 Hz, 2H), 1.02 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 146.5, 146.3, 145.6, 139.5, 63.1, 34.9, 32.3, 27.2, 27.2, 27.2; IR (neat): $v_{\max}$ = 3358, 2960, 2923, 1670, 1488, 1365, 1248, 1038, 960 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{10}H_{14}N_2S$, 195.0878; found, 195.0878.

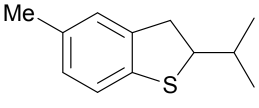

21

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), **S10** (253 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **21** and starting material (54.2 mg, 63% conversion, 48% yield, 76% yield of **21** brsm). Pure **21** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.04 (d, *J* = 8.0, 2H), 6.95 – 6.89 (m, 2H), 3.78 (q, *J* = 7.6 Hz, 1H), 3.35 – 3.29 (m, 1H), 3.09 – 3.03 (m, 1H), 1.98 – 1.93 (m, 1H), 1.02 – 0.99 (m, 6H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 141.3, 140.1, 127.1, 124.2, 123.9, 121.8, 58.8, 40.4, 33.9, 21.1, 20.7; IR (neat): $v_{\max}$ = 2954, 2922, 2852, 1736, 1461, 1377, 1260, 750 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{11}H_{14}S$, 178.0816; found, 178.0811.



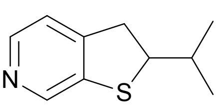
22

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 5-chlorobenzothiophene (67.2 mg, 0.4 mmol, 1.0 equiv), **S10** (253 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **22** and starting material (65.1 mg, 56% conversion, 43% yield, 75% yield of **22** brsm). Pure **22** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 – 7.05 (m, 3H), 3.83 (q, J = 8.0, 1H), 3.30 (dd, J = 15.6, 7.6 Hz, 1H), 3.04 (dd, J = 16.0, 8.8 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.01 – 0.99 (m, 6H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 142.0, 140.0, 129.4, 127.2, 124.4, 122.6, 59.2, 40.2, 33.8, 20.8, 20.6; IR (neat): $\nu_{\max}$ = 2962, 2869, 1456, 1403, 1365, 1232, 1082, 816 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{11}H_{13}ClS$, 212.0420; found, 212.0419.



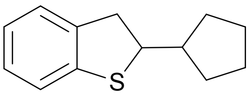
23

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), 5-methylbenzothiophene (59.2 mg, 0.4 mmol, 1.0 equiv), **S10** (253 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **23** and starting material (54.0 mg, 64% conversion, 45% yield, 67% yield of **23** brsm). Pure **23** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.04 (d, J = 8.0 Hz, 2H), 6.95 – 6.89 (m, 2H), 3.78 (q, J = 7.6 Hz, 1H), 3.28 (dd, J = 15.6, 7.6 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.26 (s, 3H), 1.01 – 0.99 (m, 6H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 140.3, 137.8, 133.5, 127.9, 125.1, 121.5, 58.9, 40.3, 33.9, 21.0, 20.9, 20.6; IR (neat): $\nu_{\max}$ = 2954, 2922, 2852, 1736, 1461, 1377, 1260, 750 cm^{-1}; HRMS (*m/z*): $[M]^+$ calcd. for $C_{11}H_{16}S$, 192.0970; found, 192.0967.



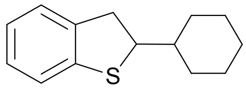
24

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), thieno[2,3-*c*]pyridine (54.0 mg, 0.4 mmol, 1.0 equiv), **S10** (253 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Purification of the crude product by flash chromatography eluting with petroleum ether:EtOAc (10:1 v/v) gave compound **24** as a colorless oli (25.8 mg, 36%), with 17.8 mg of starting material recovered (conversion: 67%, 54% yield of **24** brsm). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1H), 8.22 (d, J = 4.8 Hz, 1H), 7.06 (d, J = 4.8 Hz, 1H), 3.82 (q, J = 8.0 Hz, 1H), 3.33 (dd, J = 16.4, 8.0 Hz, 1H), 3.07 (dd, J = 16.4, 8.4 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.02 – 0.99 (m, 6H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 149.4, 145.1, 142.4, 139.4, 119.5, 58.5, 39.9, 33.9, 20.7, 20.5; IR (neat): $\nu_{\max}$ = 2955, 2920, 2349, 1736, 1462, 1377, 1260, 1024, 749 cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{10}H_{14}NS$, 180.0847; found, 180.0840.



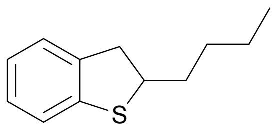
25

According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 μmol, 0.005 equiv), K_2CO_3 (331 mg, 2.4 mmol, 6.0 equiv), benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), **S11** (284 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **25** and starting material (65.3 mg, 70% conversion, 56% yield, 88% yield of **25** brsm). Pure **25** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 – 7.07 (m, 3H), δ 6.98 (t, J = 7.2 Hz, 1H), δ 3.80 (q, J = 8.4 Hz, 1H), δ 3.33 (dd, J = 15.6, 7.6 Hz, 1H), δ 3.06 (dd, J = 15.6, 8.0 Hz, 1H), δ 2.23 – 2.12 (m, 1H), 1.86 – 1.83 (m, 2H), 1.68 – 1.56 (m, 4H), 1.33 – 1.21 (m, 2H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 141.4, 139.9, 127.2, 124.3, 123.9, 121.9, 57.0, 45.6, 41.7, 31.9, 31.4, 25.5, 25.3; IR (neat): $\nu_{\max}$ = 2954, 2920, 2851, 1735, 1459, 1376, 1260, 1089, 800, 750 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{13}H_{16}S$, 204.0970; found, 204.0968.



26

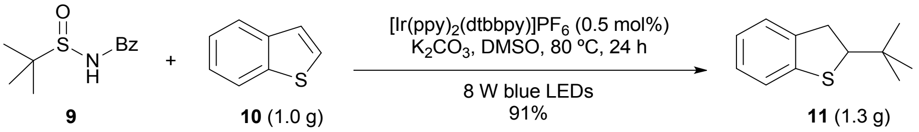
According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K$_2$CO$_3$ (331 mg, 2.4 mmol, 6.0 equiv), benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), **S12** (301 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **26** and starting material (65.0 mg, 63% conversion, 47% yield, 85% yield of **26** brsm). Pure **26** could be obtained through preparative thin layer chromatography (petroleum). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 6.95 (m, 4H), 3.79 – 3.74 (m, 1H), δ 3.39 – 3.28 (m, 1H), 3.09 – 3.03 (m, 1H), 1.85 – 1.55 (m, 6H), 1.25 – 1.02 (m, 5H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 141.2, 140.1, 127.2, 124.2, 123.9, 121.8, 57.9, 43.4, 40.1, 31.9, 31.2, 29.7, 26.2, 26.1; IR (neat): $\nu_{\max}$ = 2921, 2850, 1736, 1461, 1264, 732, 702 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{14}H_{18}S$, 218.1129; found, 218.1124.



27

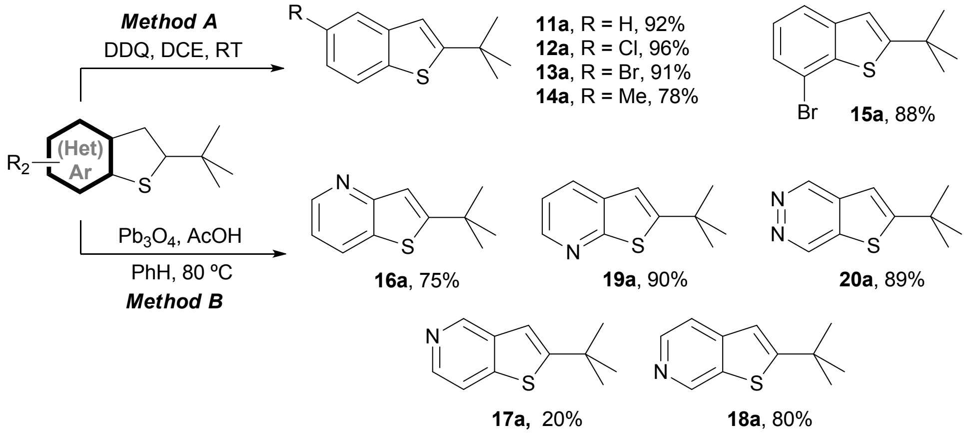
According to the general procedure, Ir(dtbbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 µmol, 0.005 equiv), K$_2$CO$_3$ (331 mg, 2.4 mmol, 6.0 equiv), benzothiophene (53.6 mg, 0.4 mmol, 1.0 equiv), **S9** (301 mg, 1.2 mmol, 3.0 equiv) and degassed DMSO (0.90 mL) were used. Flash chromatography of the crude product on silica gel eluting with petroleum yielded a colorless oil containing product **27** and starting material (53.6 mg, 14% conversion, 10% yield, 85% yield of **27** brsm).

Gram scale reaction



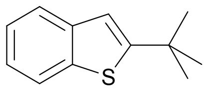
According to the general procedure, benzothiophene (1.0 g, 7.5 mmol, 1.0 equiv), *N*-benzoyl *tert*-butyl-sulfinamide **9** (5.0 g, 22.4 mmol, 3.0 equiv.), Ir(dtbbpy)(ppy)$_2$PF$_6$ (34 mg, 0.04 mmol, 0.005 equiv), K$_2$CO$_3$ (6.2 g, 44.5 mmol, 6.0 equiv), and degassed DMSO (16 mL) were used. After 24 h, the product (**11**, 1.3 g, 91%) was isolated by flash chromatography eluting with petroleum.

5. Oxidation



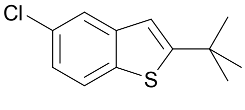
General procedure for method A: 2,3-Dichloro-5,6-dicyanobenzoquinone (1.2 – 2.0 equiv) was added to a stirred solution of the above-mentioned addition product (1.0 equiv) in 1,2-dichloroethane. Then the mixture was stirred at room temperature and was monitored by TLC. Upon completion (about 12 h), the mixture was then concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel with petroleum ether afforded pure product.

General procedure for method B: To a solution of the above-mentioned addition product (1.0 equiv) and acetic acid (10.0 equiv) in benzene was added lead oxide (1.3 equiv). The mixture was heated to 80 ºC and stirred for overnight. After being cooled to room temperature, the mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel afforded pure product.



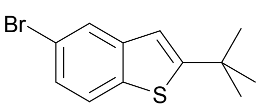
11a

Following the general procedure (*method A*), the reaction of **11** (24.9 mg, 0.13 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyanobenzoquinone (42.0 mg, 0.16 mmol, 1.2 equiv) in 1,2-dichloroethane (1.5 mL) proceeded for 12 h to afford the product **11a** (23.1 mg, 92%) after purification by silica gel flash chromatography (petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.03 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 158.2, 140.0, 138.9, 124.0, 123.3, 122.8, 122.0, 117.6, 34.9, 32.1, 32.1, 32.1; IR (neat): $\nu_{\max}$ = 2954, 2922, 2851, 1737, 1459, 1377, 1260, 764 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{14}S$, 190.0816; found, 190.0812.



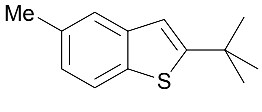
12a

Following the general procedure (*method A*), the reaction of **12** (18.1 mg, 0.08 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyanobenzoquinone (22.0 mg, 0.10 mmol, 1.2 equiv) in 1,2-dichloroethane (1.0 mL) proceeded for 12 h to afford the product **12a** (17.3 mg, 96%) after purification by silica gel flash chromatography (petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 – 7.62 (m, 2H), 7.20 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 160.5, 141.2, 137.0, 130.1, 123.8, 123.1, 122.4, 117.1, 35.1, 32.1, 32.1, 32.1; IR (neat): $\nu_{\max}$ = 2960, 2924, 1462, 1434, 1364, 1241, 1076, 796 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{13}ClS$, 224.0416; found, 224.0412.



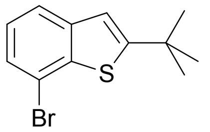
13a

Following the general procedure (*method A*), the reaction of **13** (15.2 mg, 0.06 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyanobenzoquinone (20.0 mg, 0.09 mmol, 1.5 equiv) in 1,2-dichloroethane (1.0 mL) proceeded for 12 h to afford the product **13a** (12.9 mg, 91%) after purification by silica gel flash chromatography (petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.61(d, J = 8.4 Hz, 1H), 7.33 (d, J = 10.4 Hz, 1H), 6.95 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 160.3, 141.6, 137.4, 126.2, 125.4, 123.3, 117.8, 116.9, 35.0, 32.0, 32.0, 32.0; IR (neat): $\nu_{\max}$ = 2963, 1577, 1472, 1432, 1367, 1242, 1179, 1072, 883 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{13}BrS$, 267.9920; found, 267.9916.



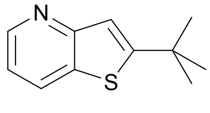
14a

Following the general procedure (*method A*), the reaction of **14** (8.2 mg, 0.04 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyanobenzoquinone (18.0 mg, 0.08 mmol, 2.0 equiv) in 1,2-dichloroethane (0.8 mL) proceeded for 12 h to afford the product **14a** (6.0 mg, 78%) after purification by silica gel flash chromatography (petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 8.0 Hz, 1H), 7.46(s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.95 (s, 1H), 2.44 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 158.4, 140.4, 136.0, 133.6, 125.1, 122.9, 121.7, 117.4, 34.9, 32.2, 32.2, 32.2, 21.4; IR (neat): $\nu_{\max}$ = 2953, 2918, 2850, 1737, 1461, 1377, 1259, 1155, 1095, 1023, 801 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{13}H_{16}S$, 204.0813; found, 204.0812.



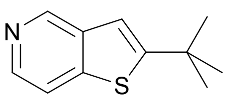
15a

Following the general procedure (*method A*), the reaction of **15** (7.9 mg, 0.03 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyanobenzoquinone (10.0 mg, 0.04 mmol, 1.5 equiv) in 1,2-dichloroethane (0.8 mL) proceeded for 12 h to afford the product **15a** (7.1 mg, 91%) after purification by silica gel flash chromatography (petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 1.46 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 159.3, 141.0, 140.5, 126.2, 125.4, 121.8, 118.7, 115.5, 35.1, 32.1, 32.1, 32.1; IR (neat): $\nu_{\max}$ = 2921, 2851, 1736, 1463, 1365, 1260, 1095, 1024, 802 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{12}H_{15}BrS$, 267.9920; found, 267.9915.



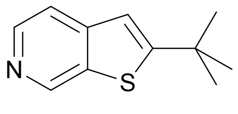
16a

Following the general procedure (*method B*), the reaction of **16** (10.3 mg, 0.05 mmol, 1.0 equiv), lead oxide (44.5 mg, 0.07mmol, 1.3 equiv) and AcOH (0.09 mL, 0.5 mmol, 10.0 equiv) in PhH (0.3 mL) proceeded for 12 h at 80 ºC to afford the product **16a** (7.5 mg, 75%) after purification by silica gel flash chromatography (petroleum ether:EtOAc = 10:1 v/v). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.46 (s, 1H), 7.90 (d, J = 5.2 Hz, 1H), 7.22 (d, J = 3.2 Hz, 1H), 6.95 (s, 1H), 1.46 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 161.2, 158.6, 145.5, 133.5, 130.0, 119.3, 115.0, 35.2, 31.9, 31.9, 31.9; IR (neat): $\nu_{\max}$ = 2962, 2927, 2866, 1730, 1562, 1521, 1380, 1232, 1103, 831 cm^{-1}; HRMS (*m/z*): [M + H]$^+$ calcd. for $C_{11}H_{14}NS$, 192.0839; found, 192.0840.



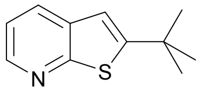
17a

Following the general procedure (*method B*), the reaction of **17** (20.0 mg, 0.10 mmol, 1.0 equiv), lead oxide (100 mg, 0.14 mmol, 1.3 equiv) and AcOH (0.18 mL, 1.0 mmol, 10.0 equiv) in PhH (0.6 mL) proceeded for 12 h at 80 ºC to afford the product **17a** (4.3 mg, 20%) after purification by silica gel flash chromatography (petroleum ether:EtOAc = 10:1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.37 (d, J = 6.0 Hz, 1H), 7.70 (d, J = 5.4 Hz, 1H), 7.12 (s, 1H), 1.47 (s, 9H); ^{13}C NMR (600 MHz, $CDCl_3$) δ 159.7, 146.4, 144.8, 141.9, 136.5, 116.9, 115.9, 35.1, 32.1, 32.1, 32.1; IR (neat): ν_{max} = 2923, 2853, 1725, 1465, 1365, 1260, 1024, 804 cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{11}H_{14}NS$, 192.0841; found, 192.0841.



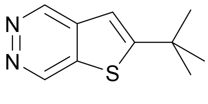
18a

Following the general procedure (*method B*), the reaction of **18** (9.9 mg, 0.05 mmol, 1.0 equiv), lead oxide (46.1 mg, 0.07 mmol, 1.3 equiv) and AcOH (0.09 mL, 0.5 mmol, 10 equiv) in PhH (0.3 mL) proceeded for 12 h at 80 ºC to afford the product **18a** (7.9 mg, 80%) after purification by silica gel flash chromatography (petroleum ether:EtOAc = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.44 (d, J = 5.2 Hz, 1H), 7.55 (d, J = 5.6 Hz, 1H), 7.07 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 164.9, 145.4, 144.0, 143.0, 117.1, 117.0, 35.4, 32.1, 32.1, 32.1; IR (neat): ν_{max} = 3055, 2967, 2869, 1577, 1406, 1251, 1185, 846 cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{11}H_{14}NS$, 192.0839; found, 192.0840



19a

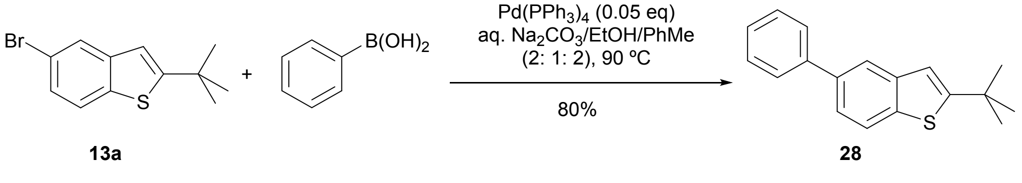
Following the general procedure (*method B*), the reaction of **19** (13.8 mg, 0.07 mmol, 1.0 equiv), lead oxide (64.0 mg, 0.09 mmol, 1.3 equiv) and AcOH (0.12 mL, 0.7 mmol, 10 equiv) in PhH (0.4 mL) proceeded for 12 h at 80 ºC to afford the product **19a** (12.1 mg, 90%) after purification by silica gel flash chromatography (petroleum ether:EtOAc = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 4.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.95 (s, 1H), 1.46 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.2, 158.6, 145.5, 133.5, 130.0, 119.3, 115.0, 35.2, 31.9, 31.9, 31.9; IR (neat): ν_{max} = 2961, 2866, 1562, 1520, 1380, 1364, 1232, 1103, 830 cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{11}H_{16}NS$, 192.0839; found, 192.0840.



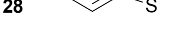
20a

Following the general procedure (*method B*), the reaction of **20** (8.6 mg, 0.04 mmol, 1.0 equiv), lead oxide (32.0 mg, 0.05 mmol, 1.3 equiv) and AcOH (0.07 mL, 0.4 mmol, 10 equiv) in PhH (0.2 mL) proceeded for 12 h at 80 ºC to afford the product **20a** (7.5 mg, 89%) after purification by silica gel flash chromatography (petroleum ether:EtOAc = 5:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 9.42 (s, 1H), 7.20 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.6, 145.9, 145.7, 138.3, 136.8, 128.6, 127.3, 115.9, 35.6, 32.2, 32.2, 32.2; IR (neat): ν_{max} = 2961, 1491, 1366, 1268, 1247, 1209, 1109, 1040, 961cm^{-1}; HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{10}H_{13}N_2S$, 193.0791; found, 193.0793.

6. Suzuki coupling



13a **28**



28

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, **13a** (20.2 mg, 0.07 mmol, 1.0 equiv), and tetrakis(triphenylphosphine)palladium (4.3 mg, 3.8 μmol, 0.05 equiv) were mixed in toluene (0.8 mL) and stirred for 5 mins. Under argon, to the solution was added a solution of phenylboronic acid (11 mg, 0.09 mmol, 1.2 equiv) in EtOH (0.4 mL) and 2M of Na_2CO_3 aq. (0.8 mL) by syringe. The mixture was allowed to stir at 90 ºC for 12 h, and then quenched with H_2O, diluted with EtOAc. The aqueous layer was extracted with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, and concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel with petroleum ether afforded **28** as a white solid (16.2 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 9.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.08 (s, 1H), 1.47 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.7, 141.5, 140.5, 137.9, 137.4, 128.7, 128.7, 127.3, 127.2, 126.8, 123.0, 122.2, 121.2, 117.8, 34.9, 32.1, 32.1, 32.1; IR (neat): ν_{max} = 2964, 2347, 1580, 1433, 1263, 1072, 893 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{18}H_{18}S$, 266.1129; found, 266.1123. IR (neat): ν_{max} = 2964, 2347, 1580, 1433, 1263, 1072, 893 cm^{-1}; HRMS (*m/z*): [M]$^+$ calcd. for $C_{18}H_{18}S$, 266.1129; found, 266.1123.

7. References

1. P. Brownbridge and I. C. Jowett, *Synthesis*, 1988, **3**, 252.
2. J. A. Lujan-Montelongo, A. O. Estevez and F. F. Fleming, *Eur. J. Org. Chem*., 2015, **7**, 1602.
3. H. H. Jung, A. W. Buesking and J. A. Ellman, *J. Org. Chem.*, 2012, **77**, 9593.
4. A. K. Belfrage, P. Wakchaure, M. Larhed and A. Sandström, *Eur. J. Org. Chem.*, 2015, **2015**, 7069.

8. NMR spectra

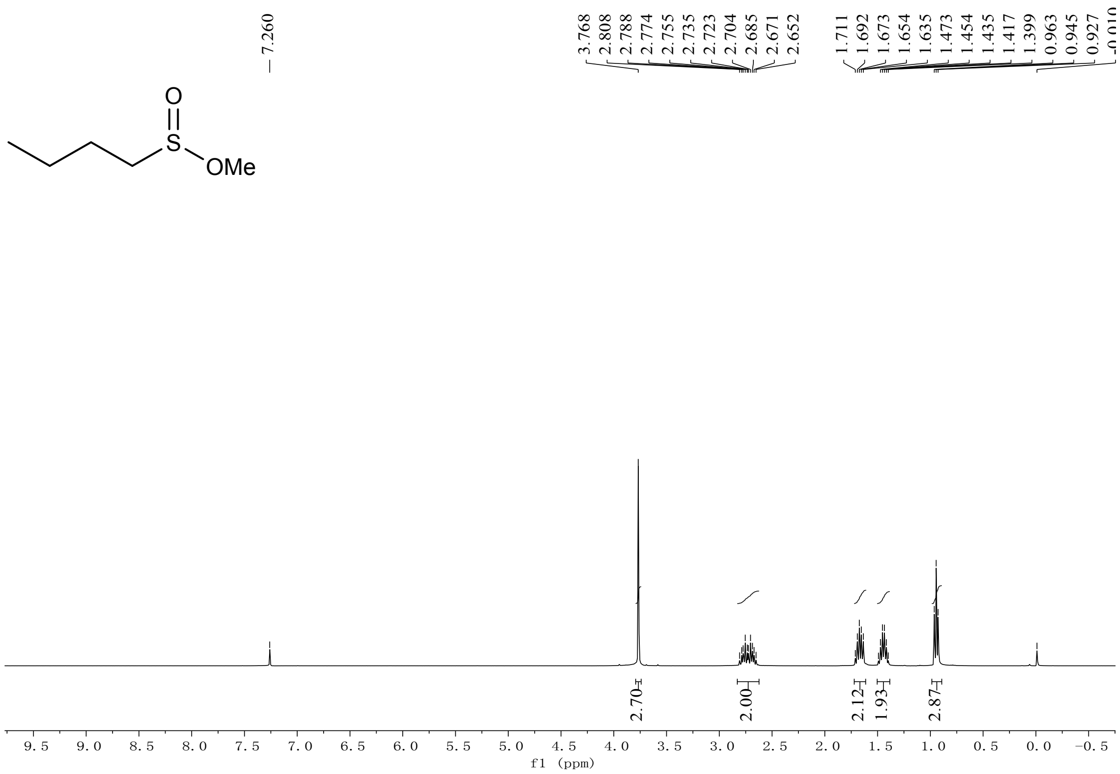


Figure S1 ^{1}H NMR spectrum of compound **S1**

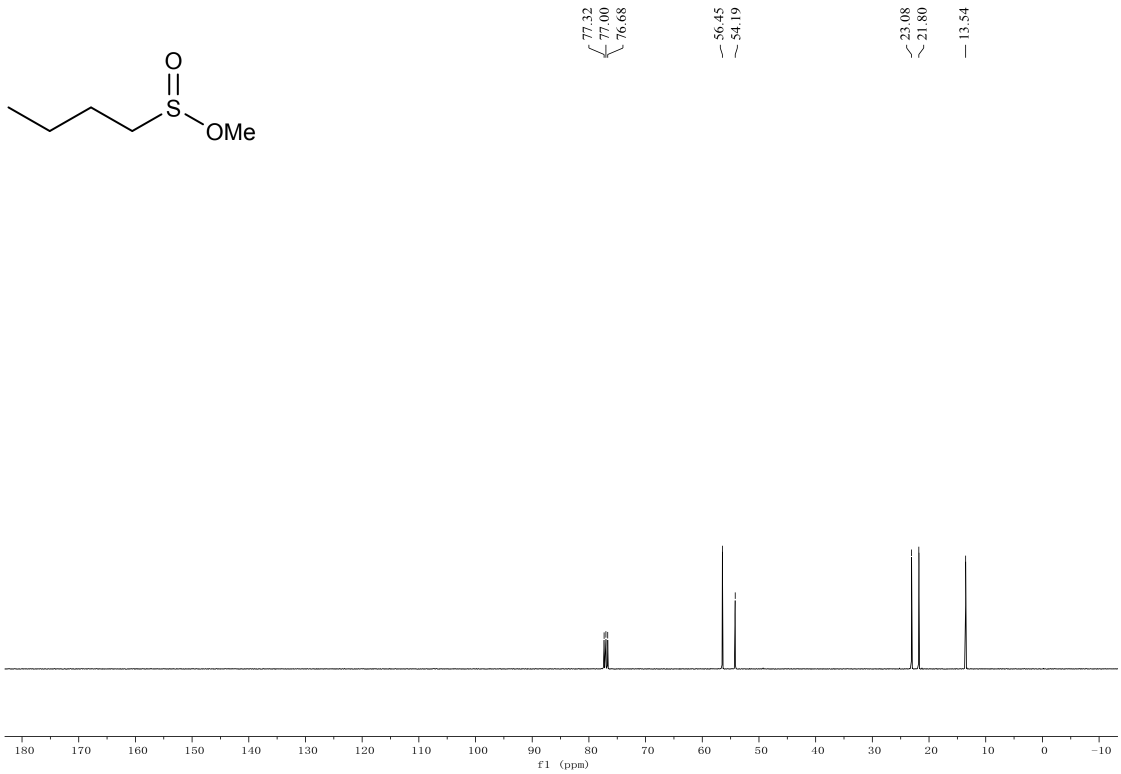


Figure S2 ^{13}C NMR spectrum of compound **S1**

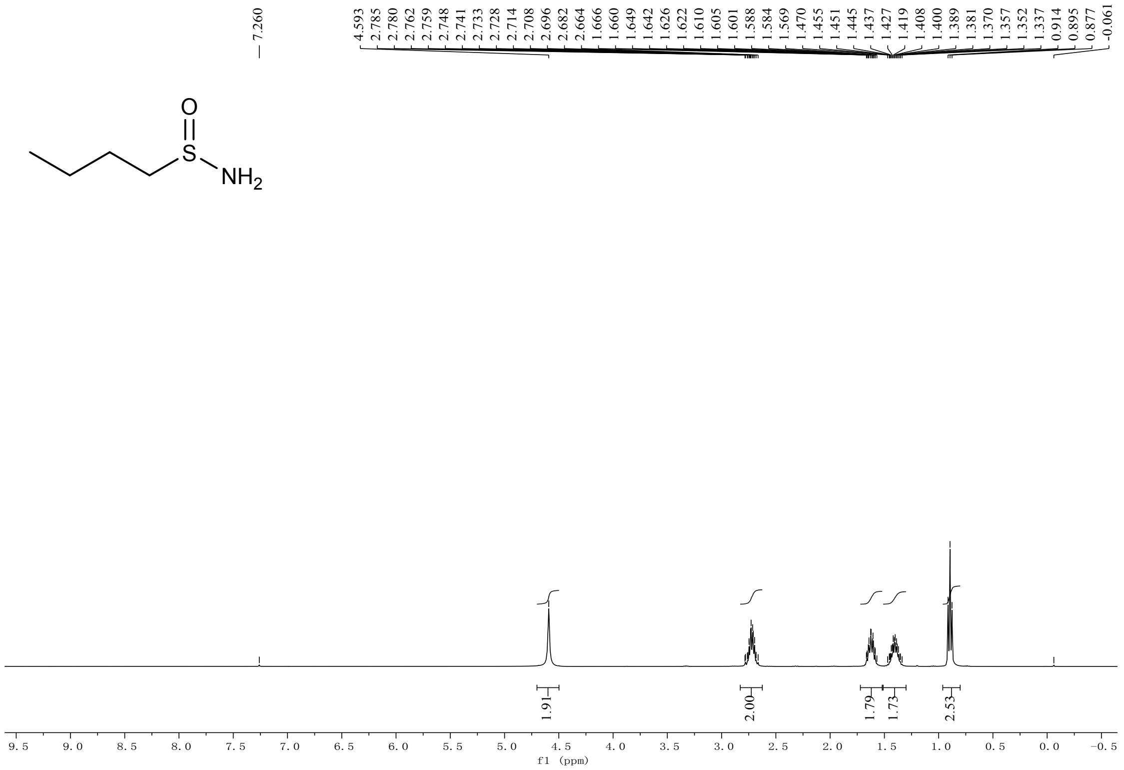


Figure S3 ^{1}H NMR spectrum of compound **S5**

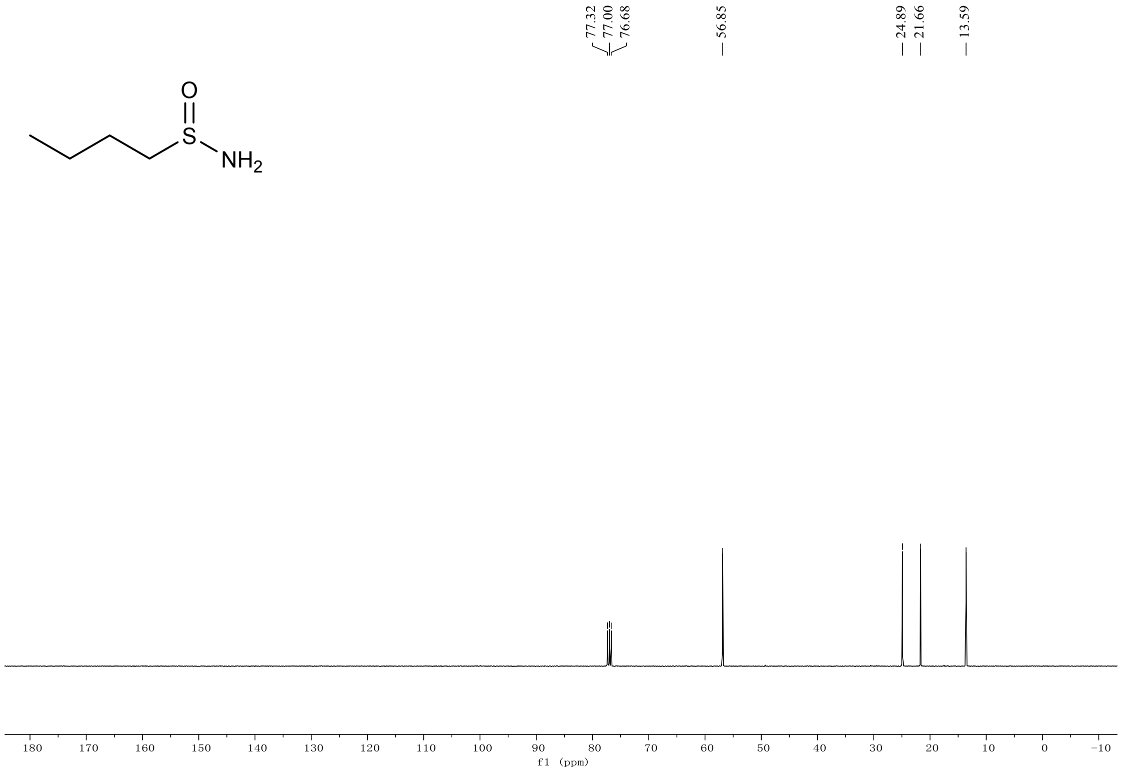


Figure S4 ^{13}C NMR spectrum of compound **S5**

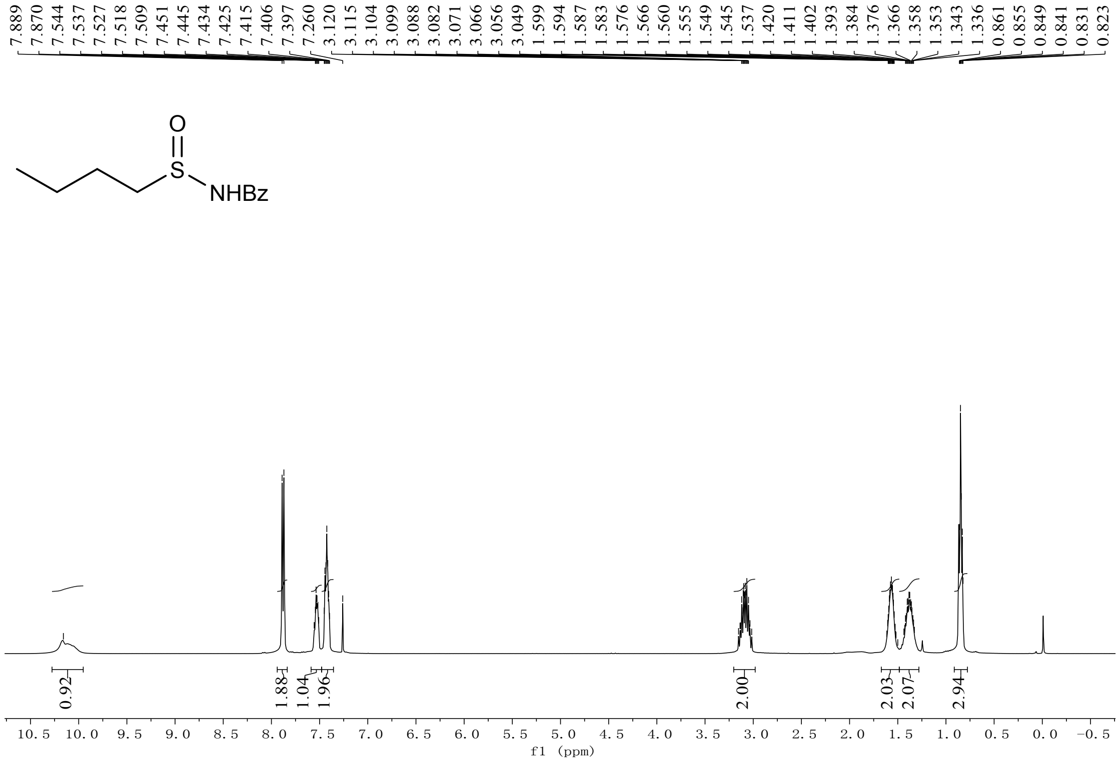


Figure S5 ^{1}H NMR spectrum of compound **S9**

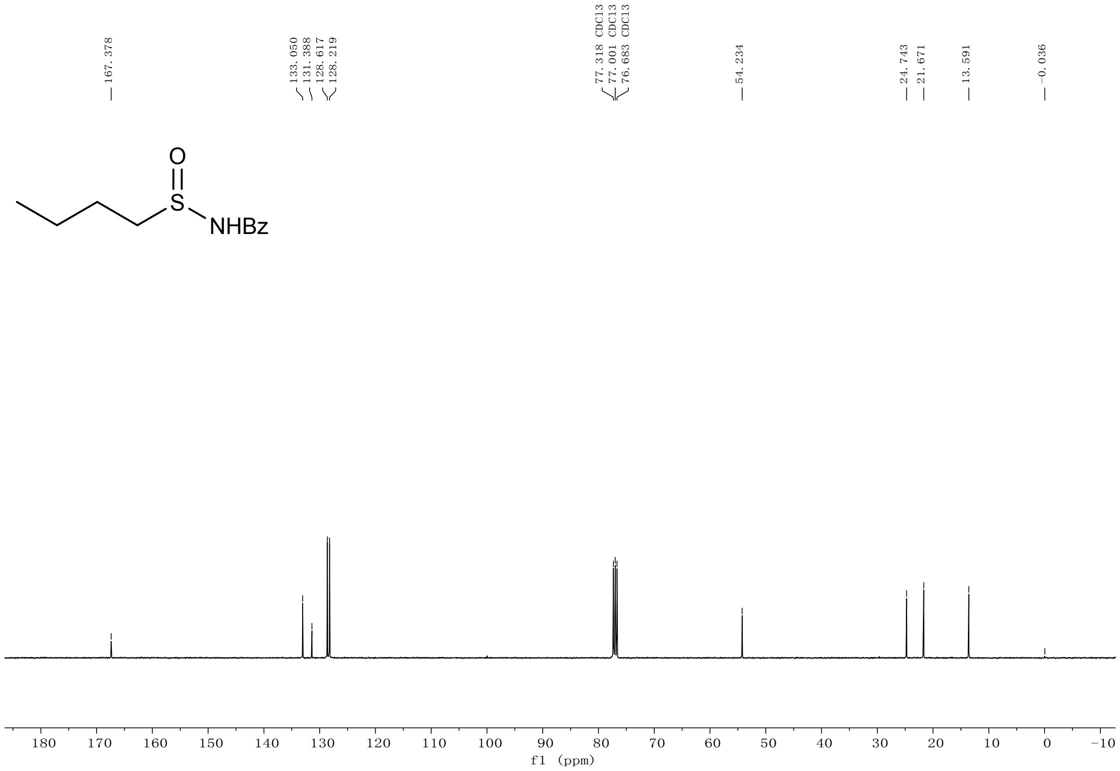


Figure S6 ^{13}C NMR spectrum of compound **S9**

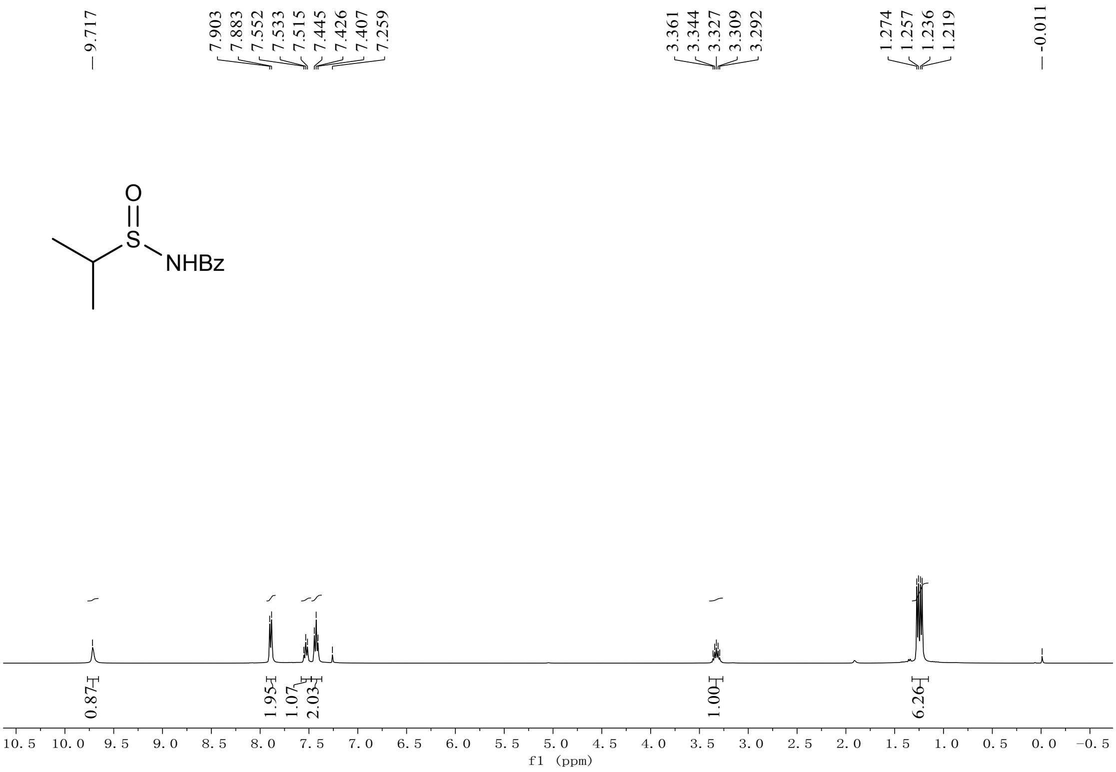


Figure S7 ^{1}H NMR spectrum of compound **S10**

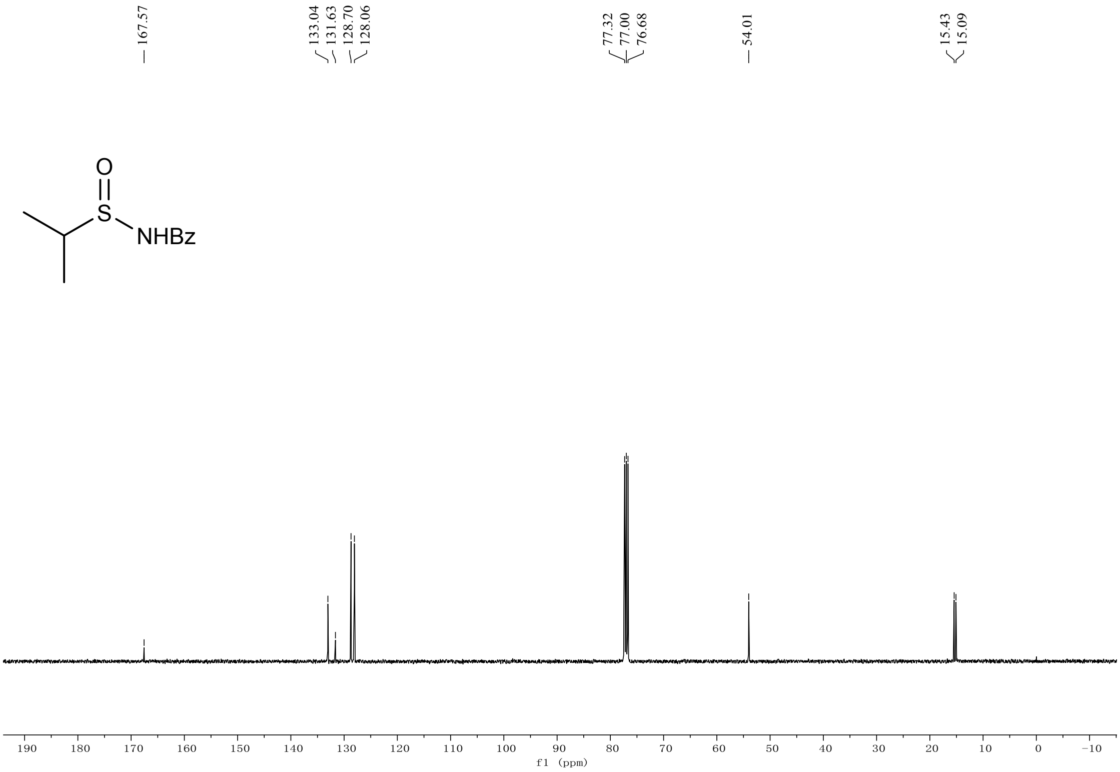


Figure S8 ^{13}C NMR spectrum of compound **S10**

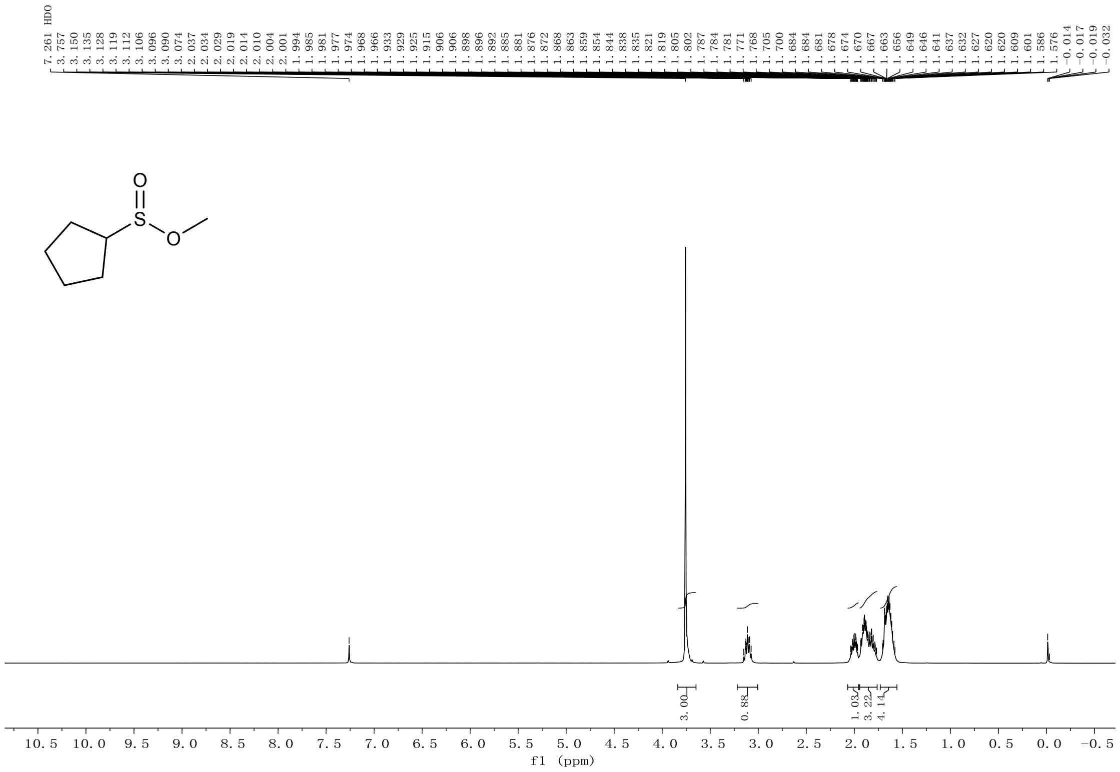


Figure S9 ^{1}H NMR spectrum of compound **S3**

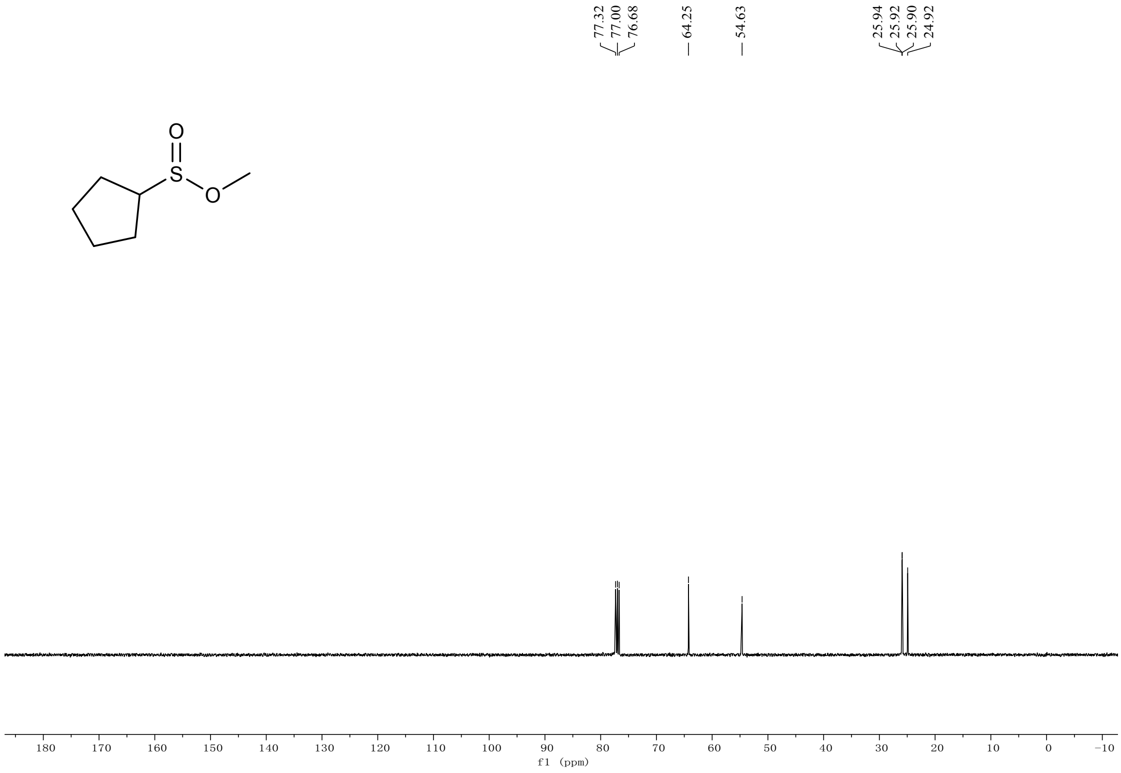


Figure S10 ^{13}C NMR spectrum of compound **S3**

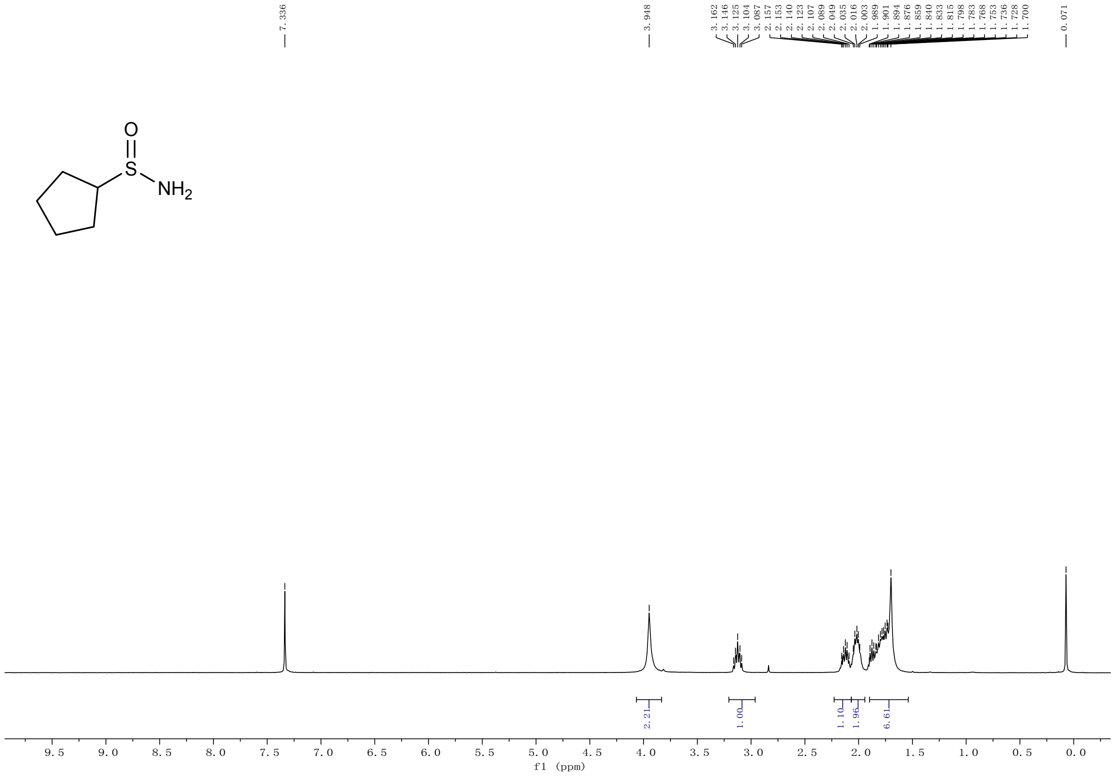


Figure S11 ^{1}H NMR spectrum of compound **S7**

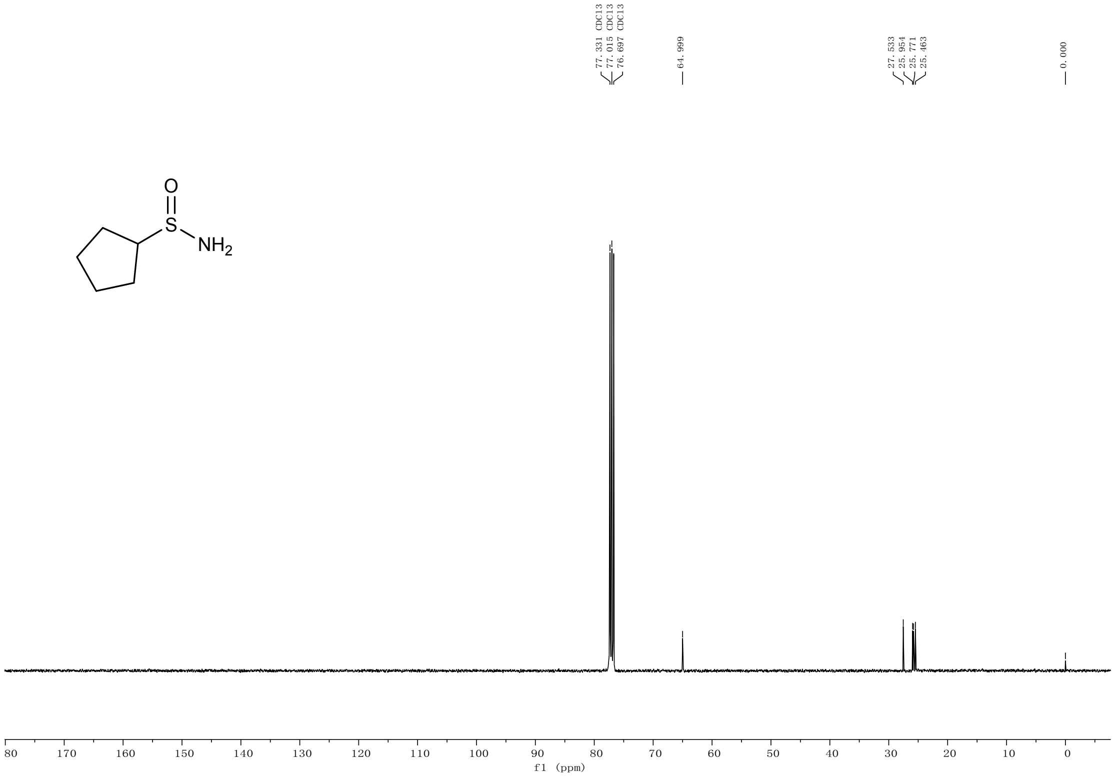


Figure S12 ^{13}C NMR spectrum of compound **S7**

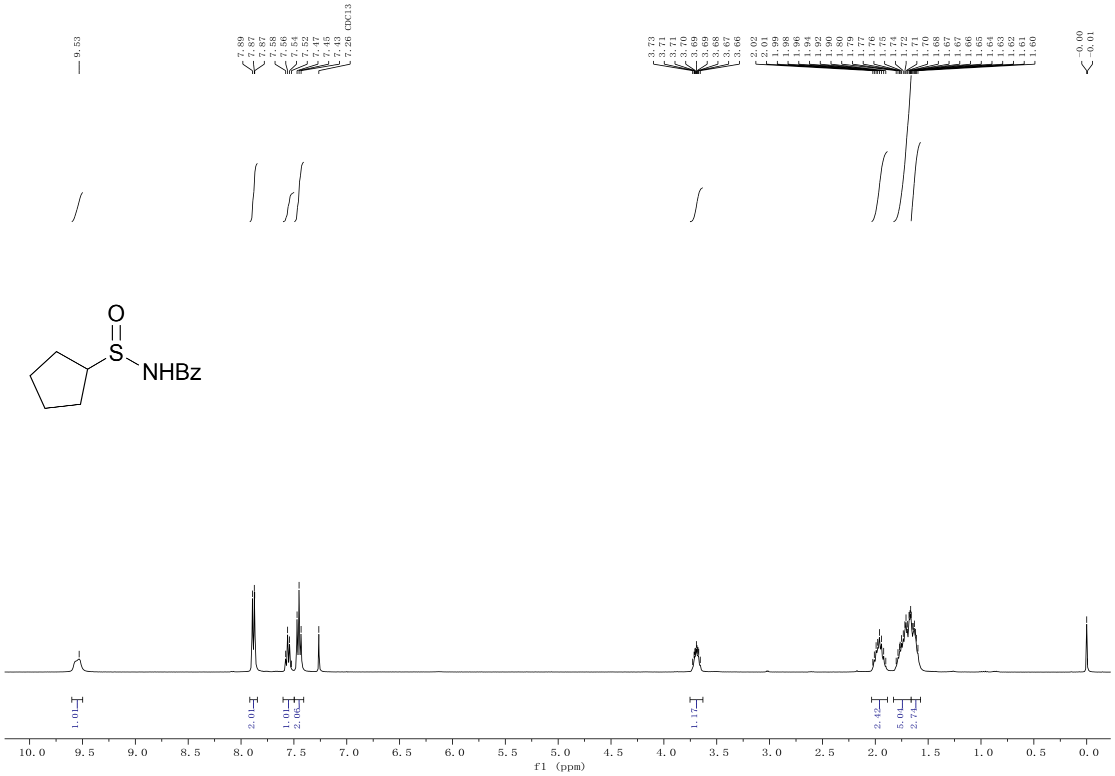


Figure S13 ^{1}H NMR spectrum of compound **S11**

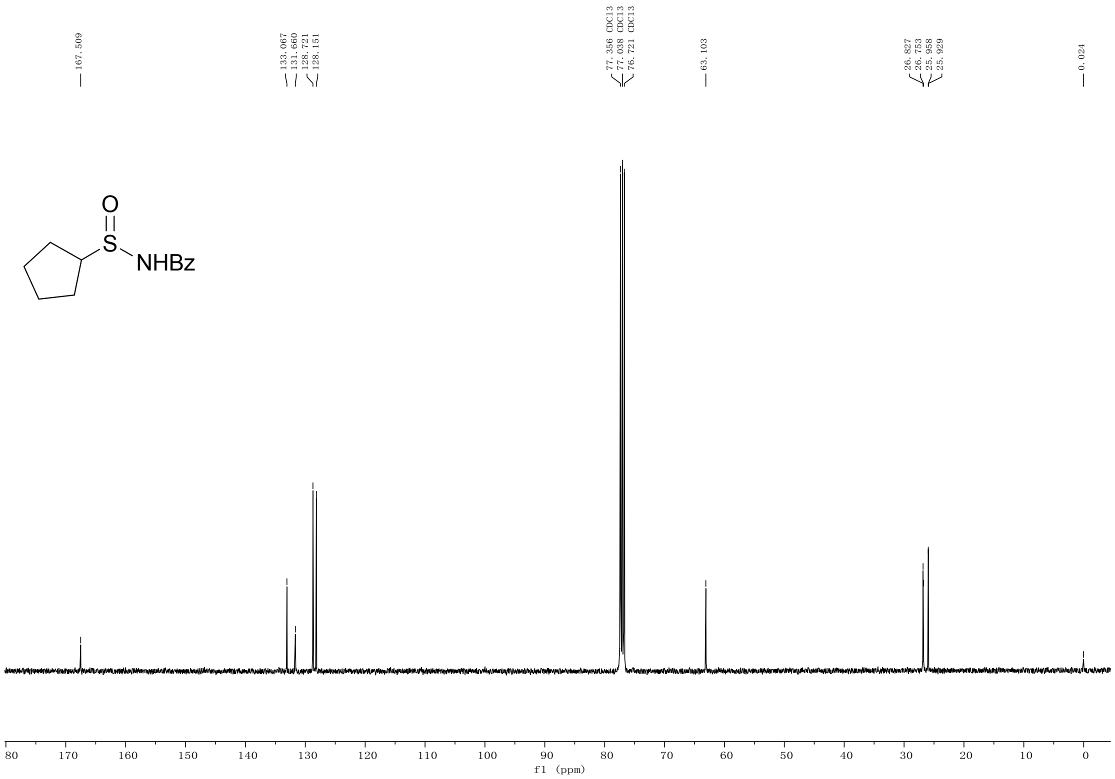


Figure S14 ^{13}C NMR spectrum of compound **S11**

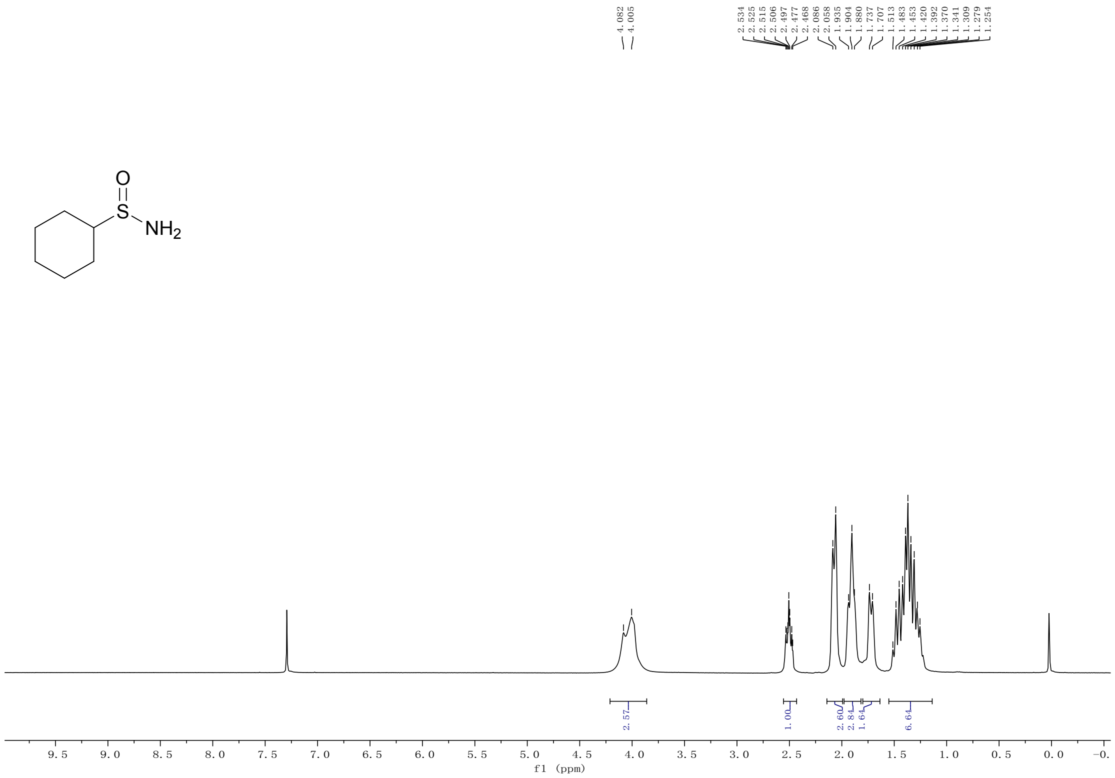


Figure S15 ^{1}H NMR spectrum of compound **S8**

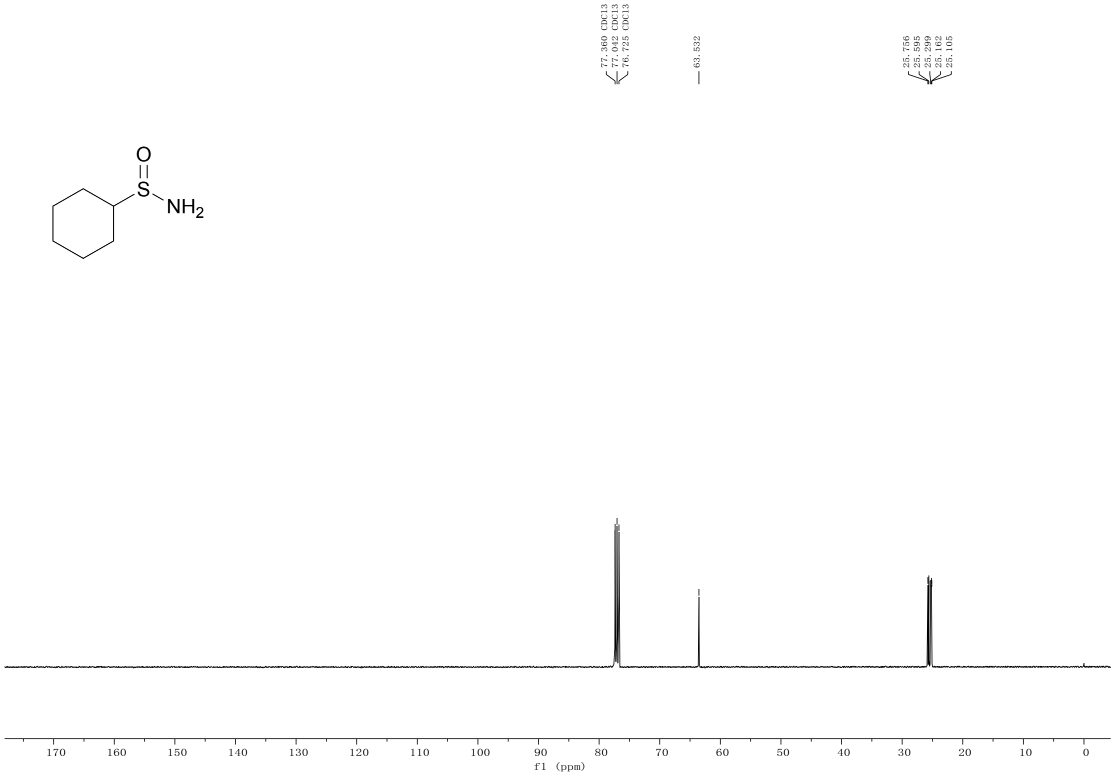


Figure S16 ^{13}C NMR spectrum of compound **S8**

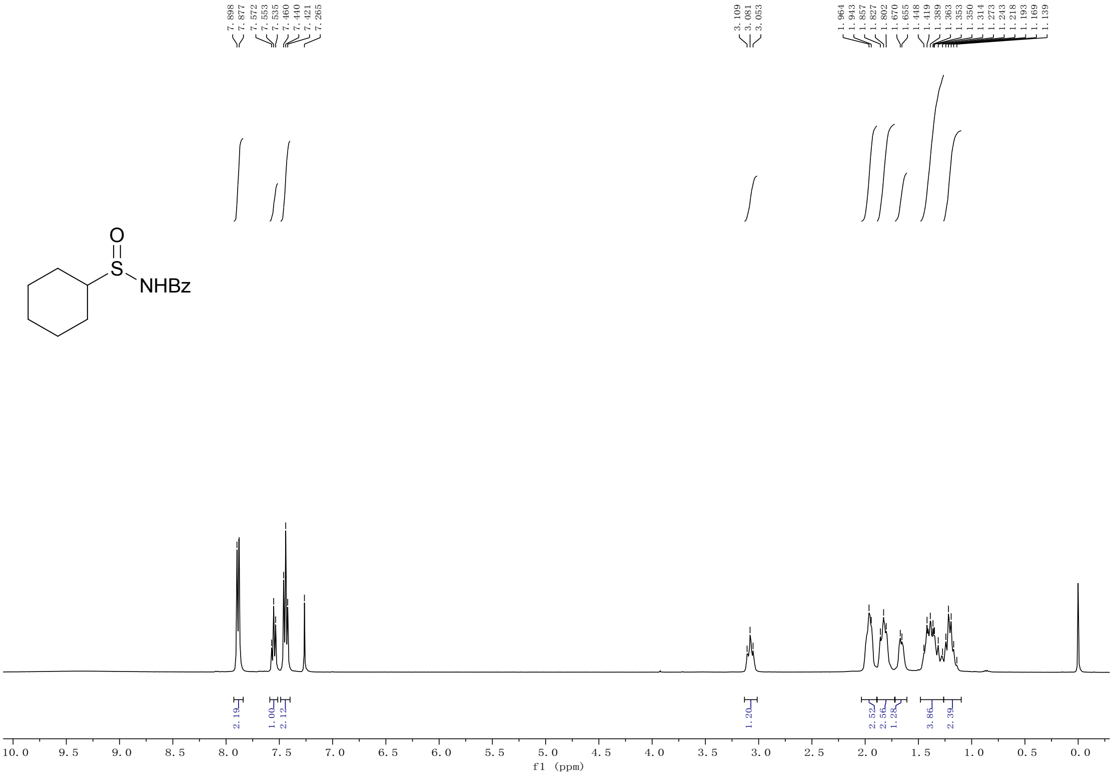


Figure S17 ^{1}H NMR spectrum of compound **S12**

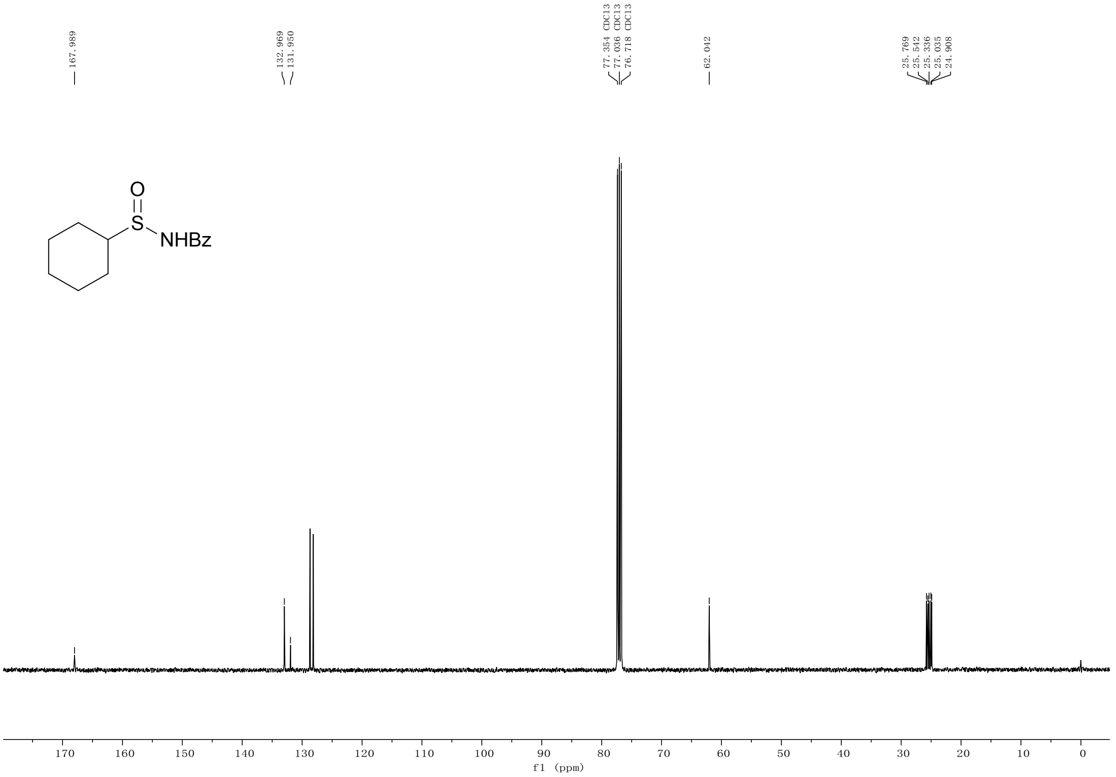


Figure S18 ^{13}C NMR spectrum of compound **S12**

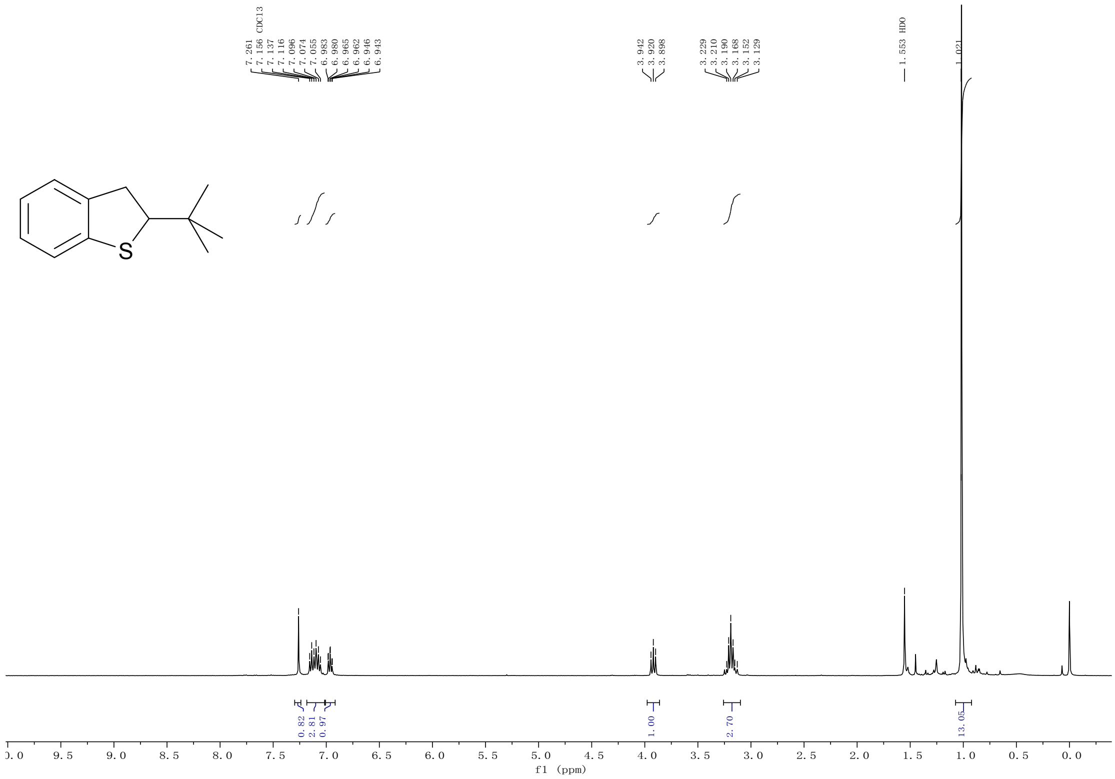


Figure S19 ^{1}H NMR spectrum of compound **11**

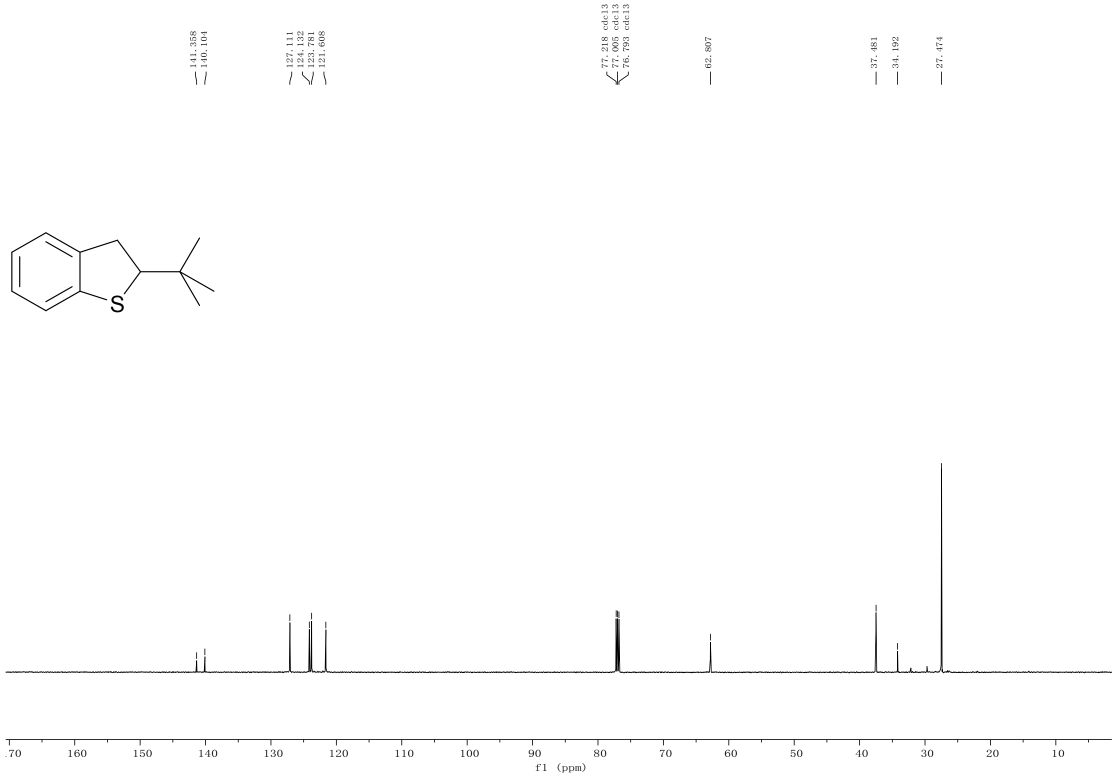


Figure S20 ^{13}C NMR spectrum of compound **11**

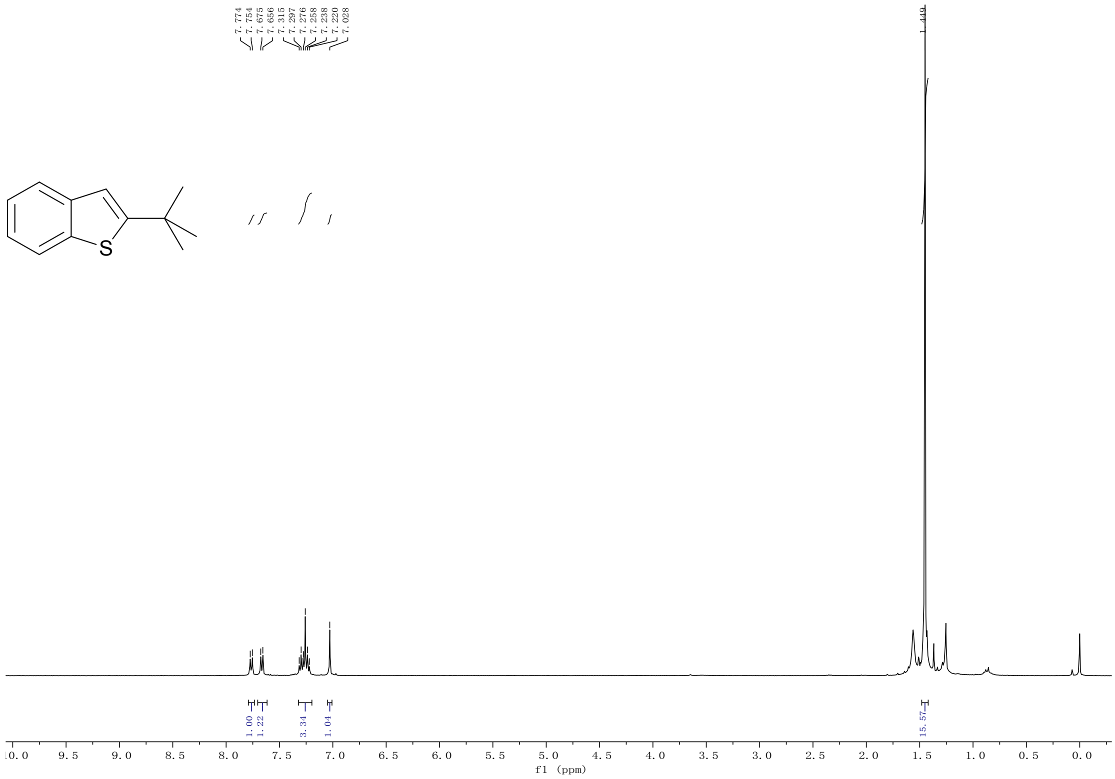


Figure S21 ^{1}H NMR spectrum of compound **11a**

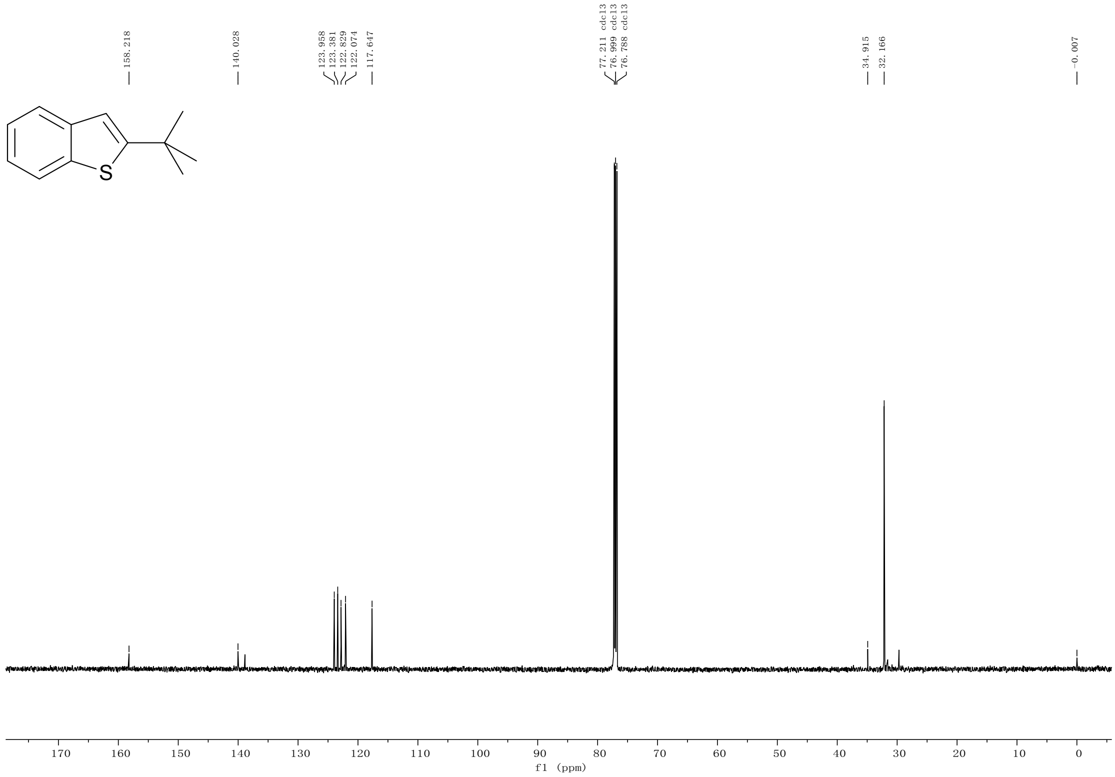


Figure S22 ^{13}C NMR spectrum of compound **11a**

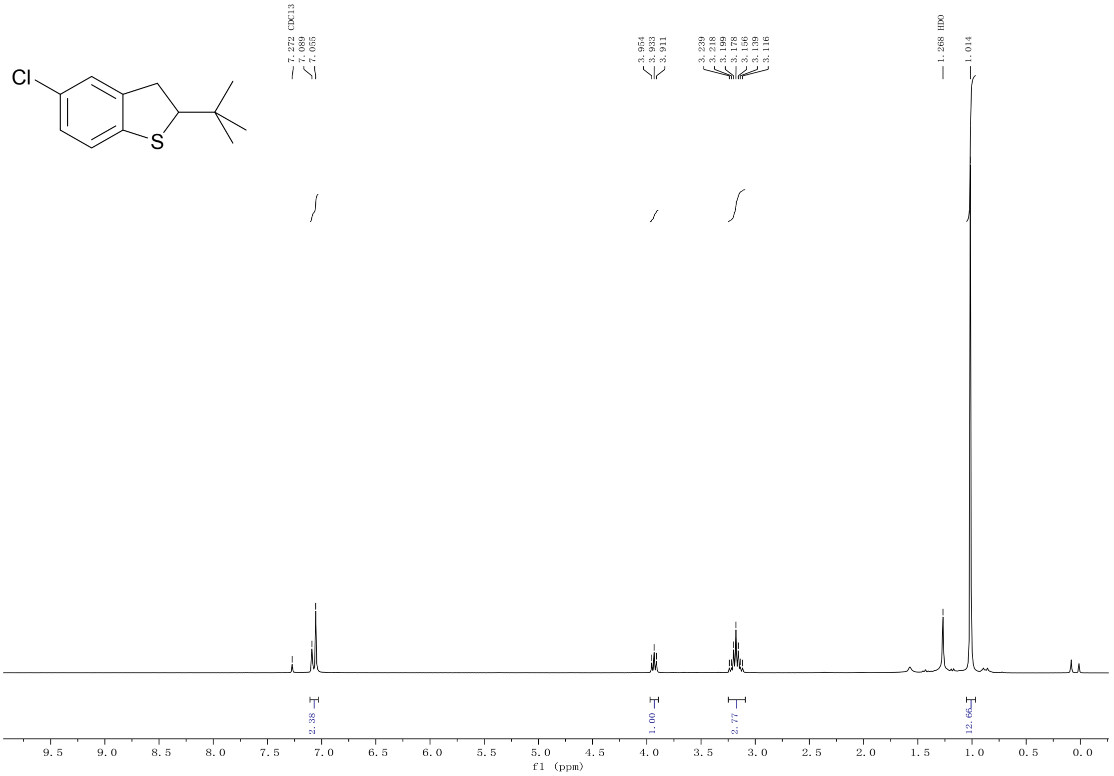


Figure S23 ^{1}H NMR spectrum of compound **12**

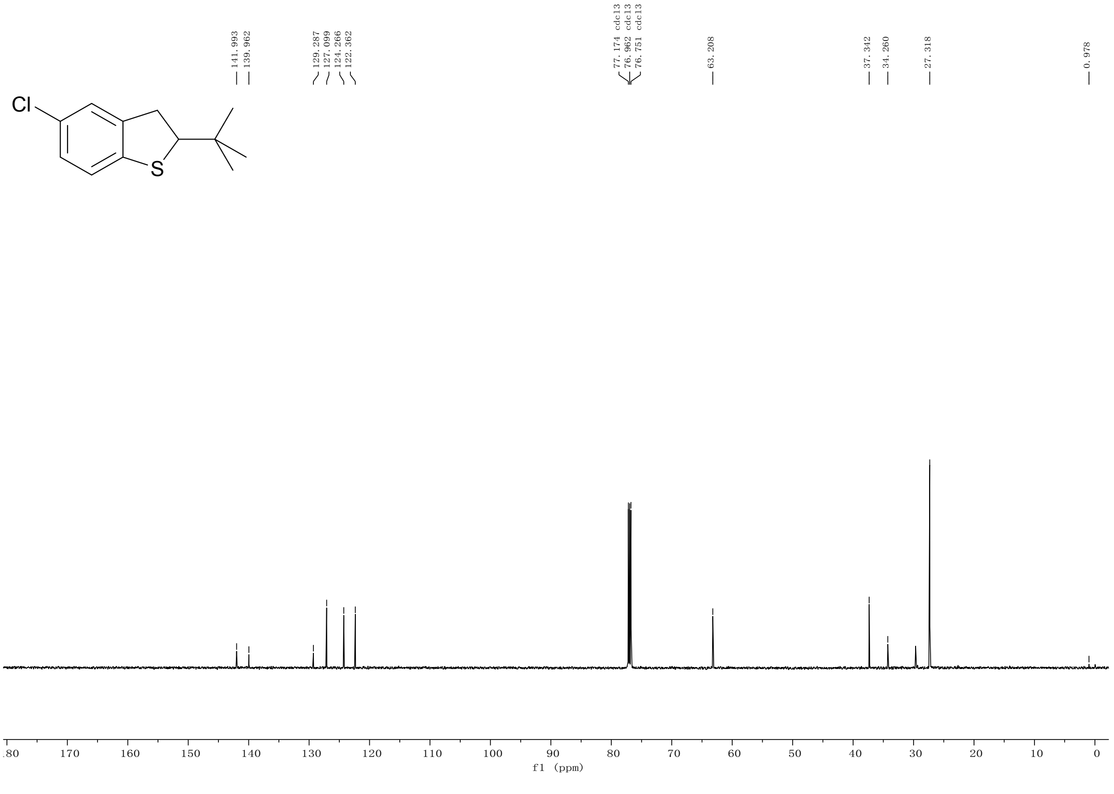


Figure S24 ^{13}C NMR spectrum of compound **12**

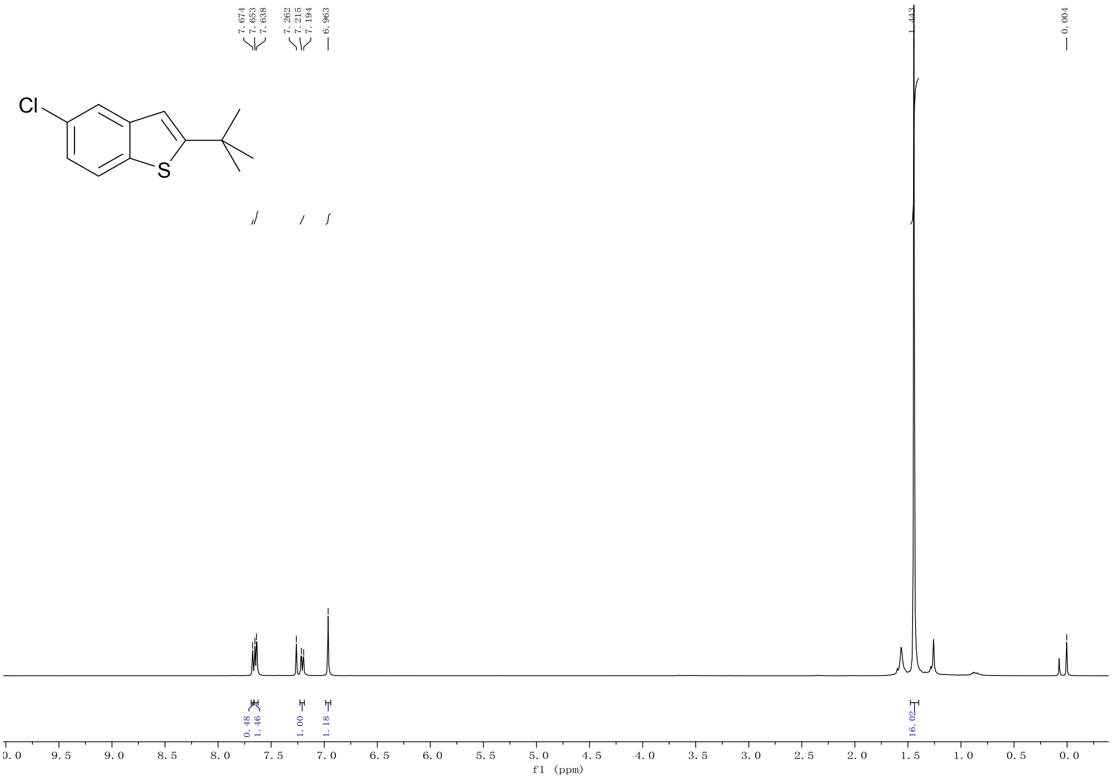


Figure S25 ^{1}H NMR spectrum of compound **12a**

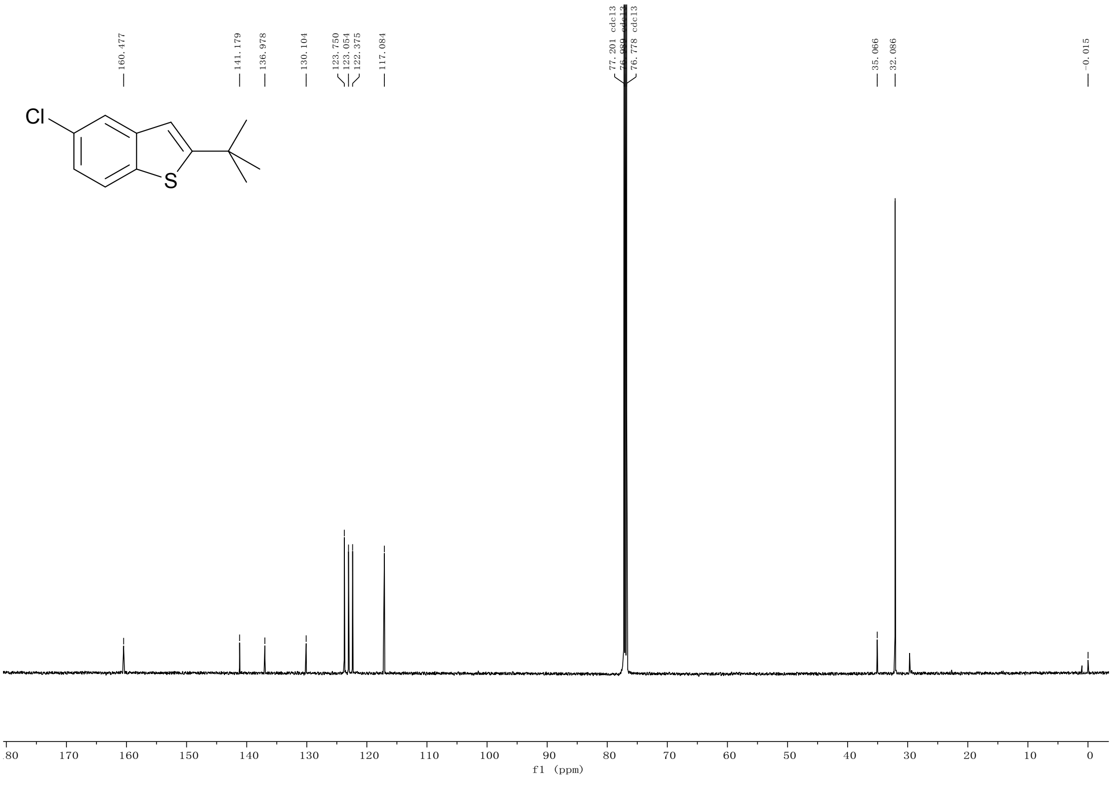


Figure S26 ^{13}C NMR spectrum of compound **12a**

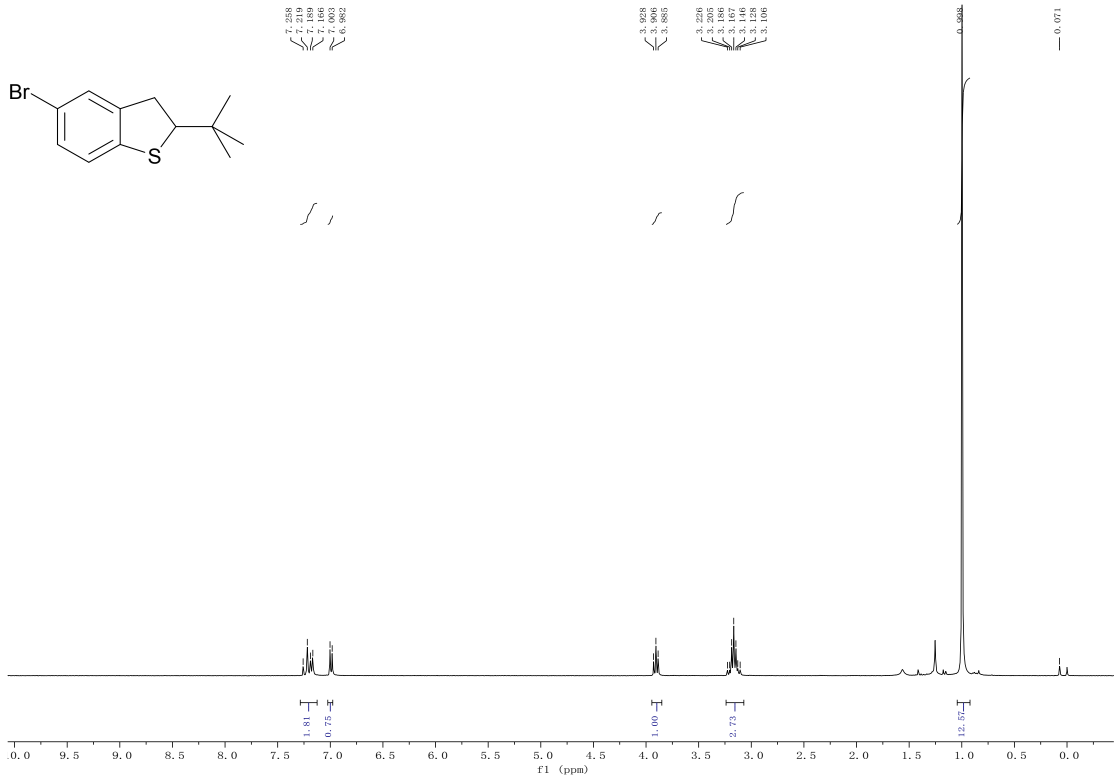


Figure S27 ^{1}H NMR spectrum of compound **13**

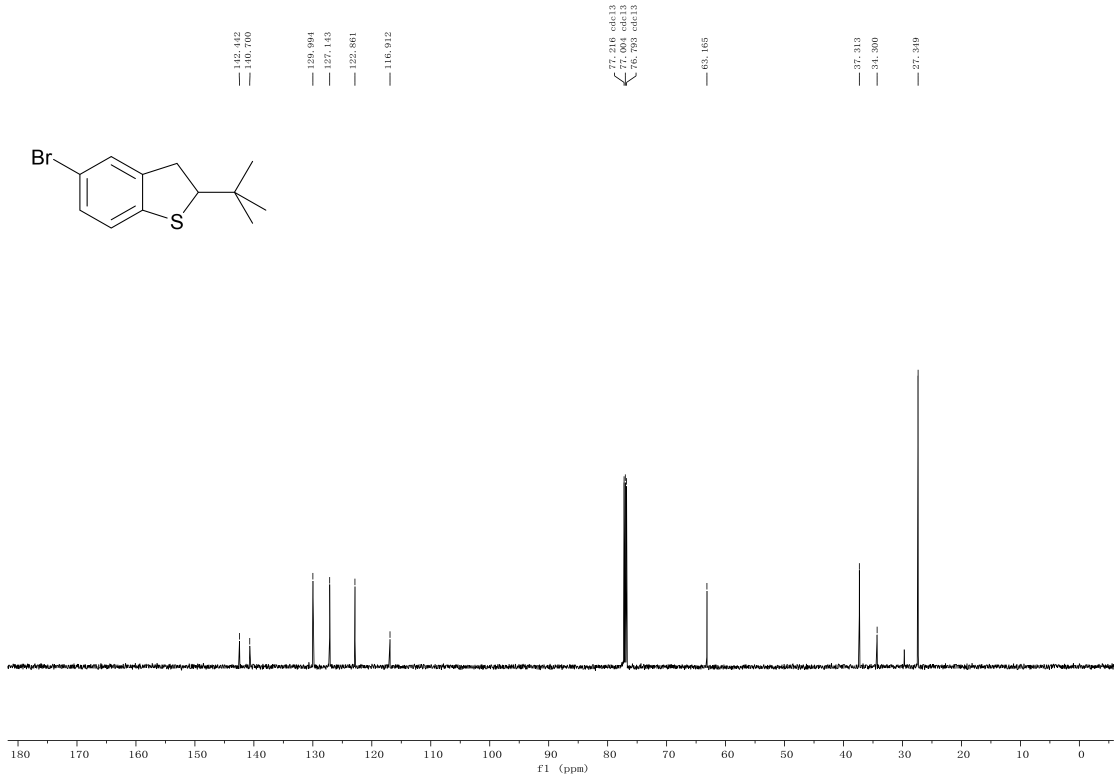


Figure S28 ^{13}C NMR spectrum of compound **13**

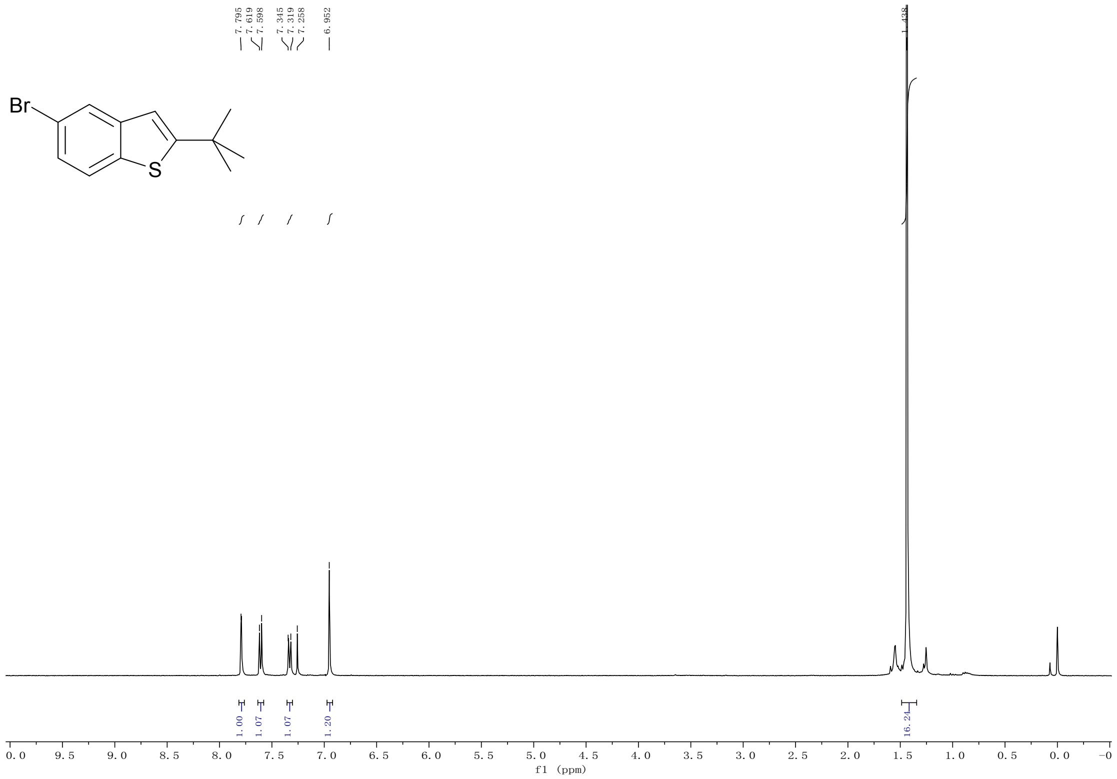


Figure S29 ^{1}H NMR spectrum of compound **13a**

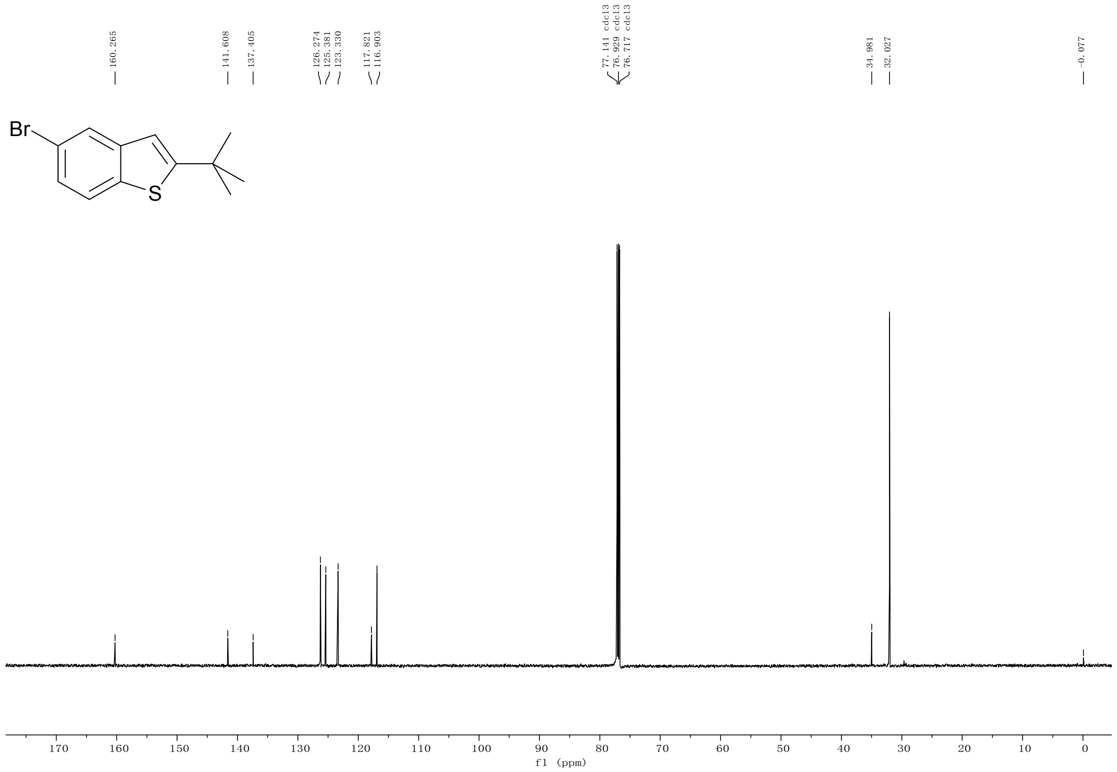


Figure S30 ^{13}C NMR spectrum of compound **13a**

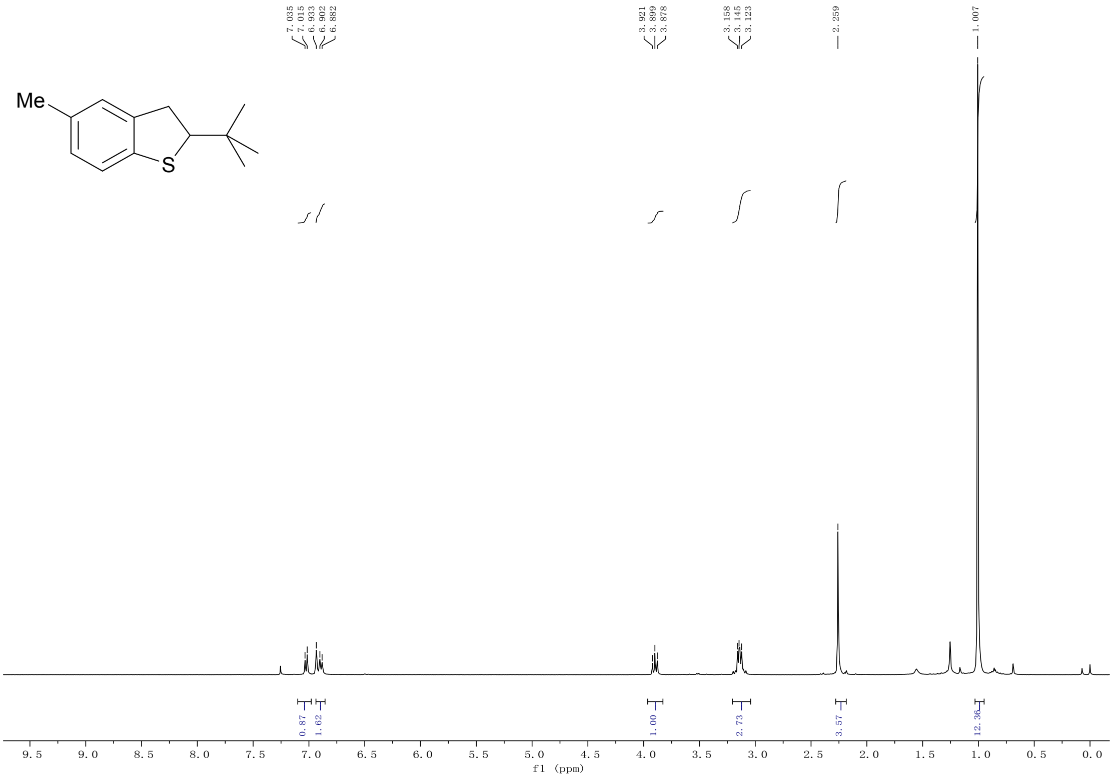


Figure S31 ^{1}H NMR spectrum of compound **14**

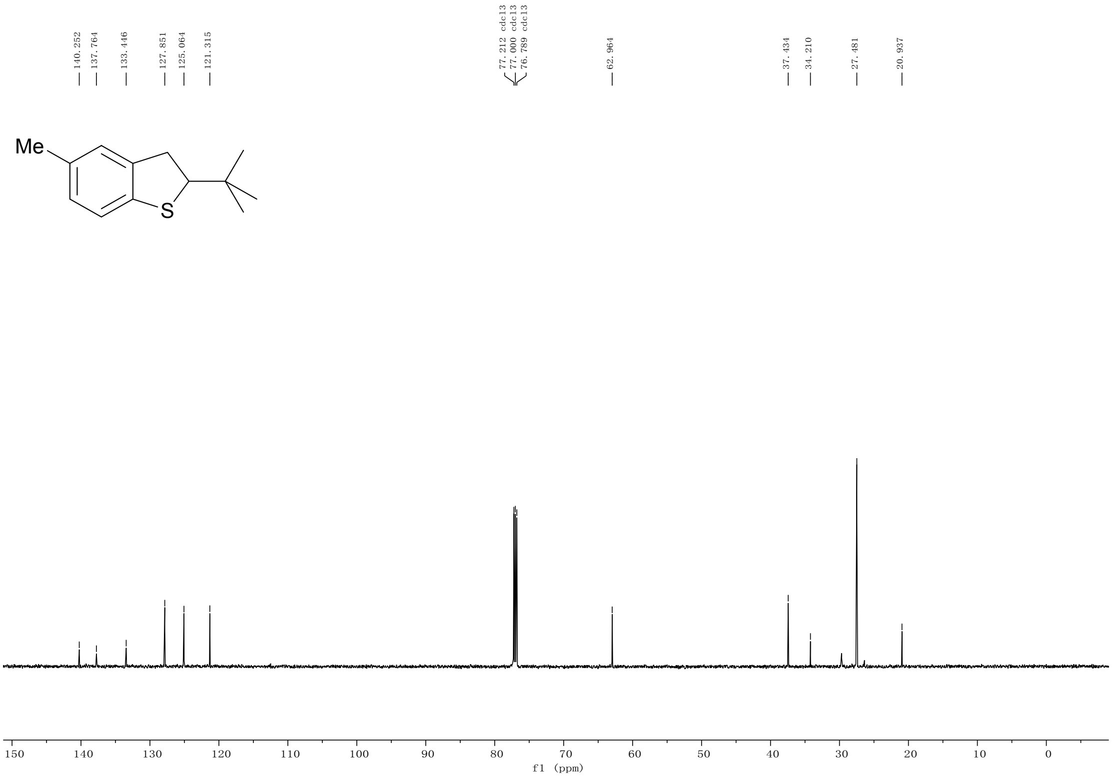


Figure S32 ^{13}C NMR spectrum of compound **14**

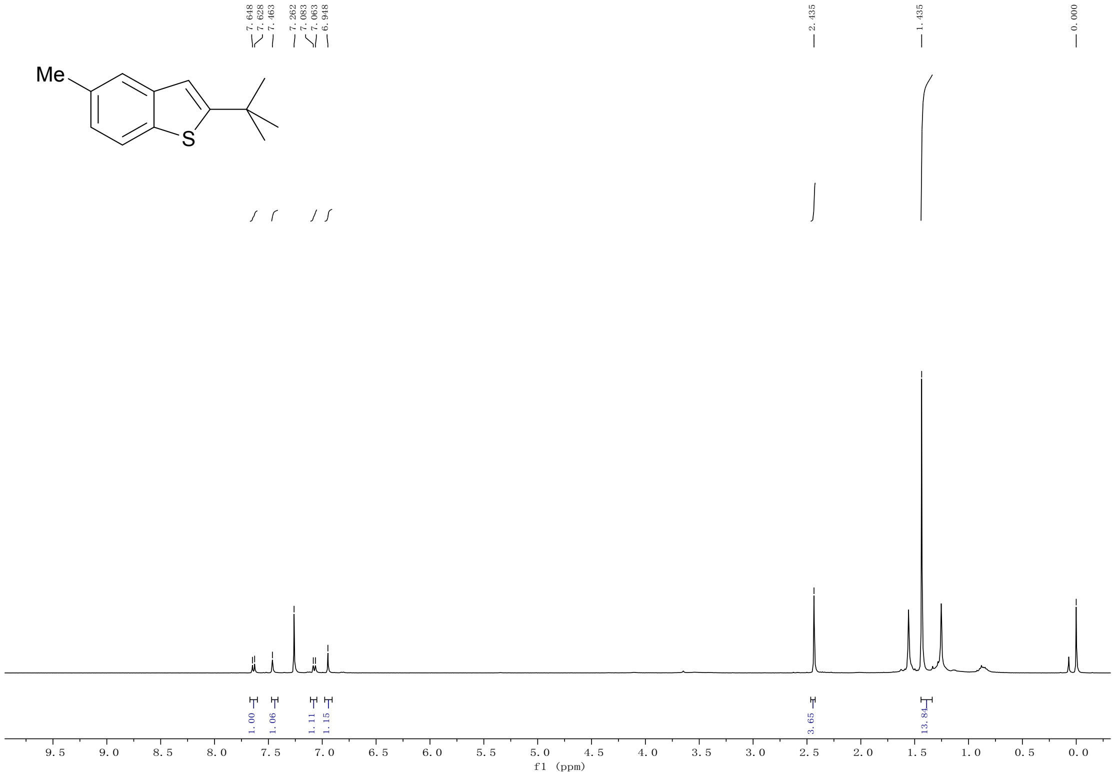


Figure S33 ^{1}H NMR spectrum of compound **14a**

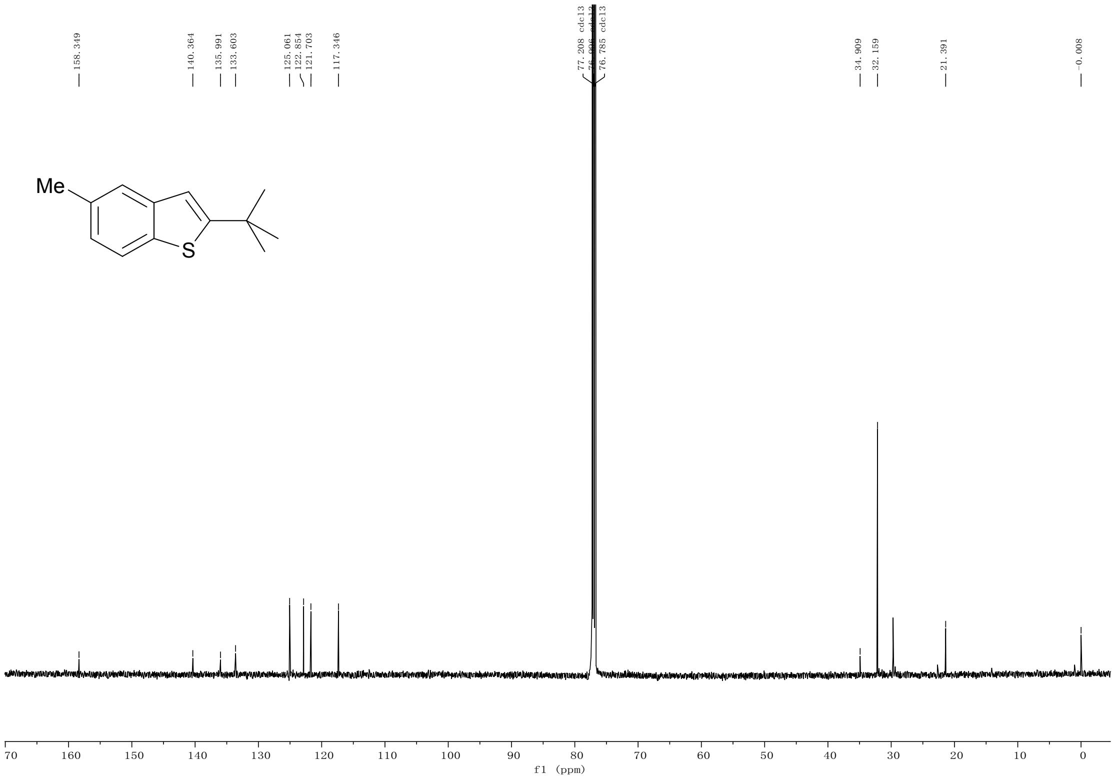


Figure S34 ^{13}C NMR spectrum of compound **14a**

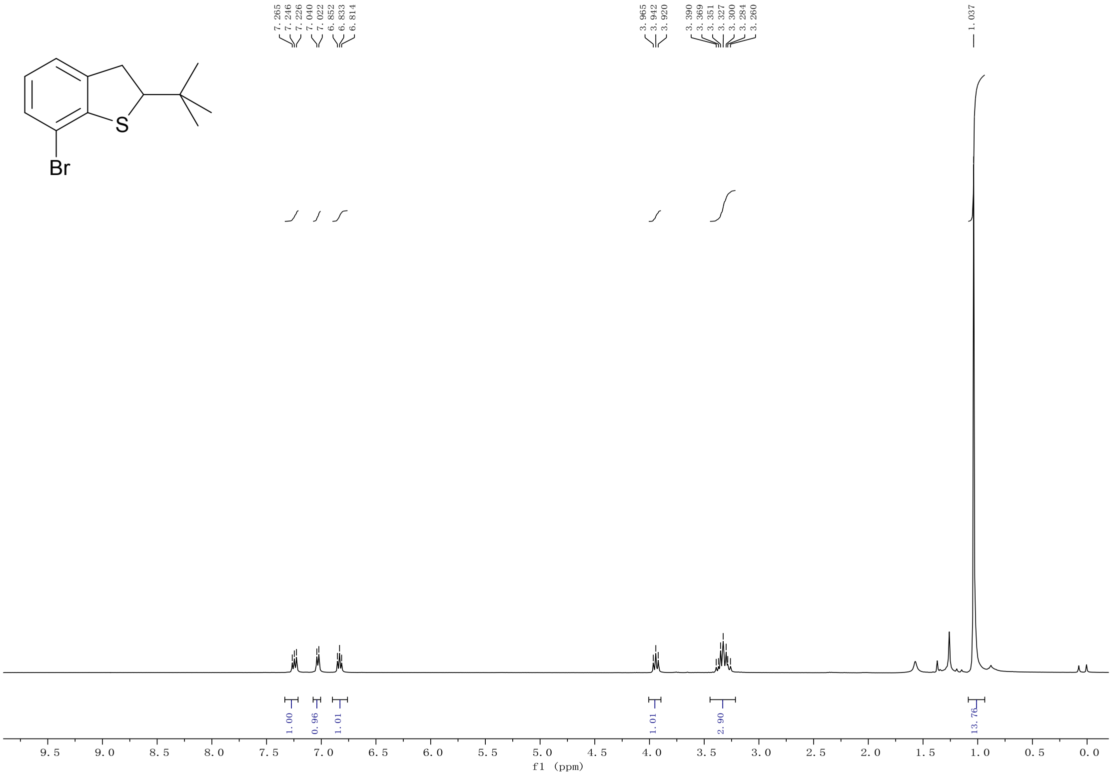


Figure S35 ^{1}H NMR spectrum of compound **15**

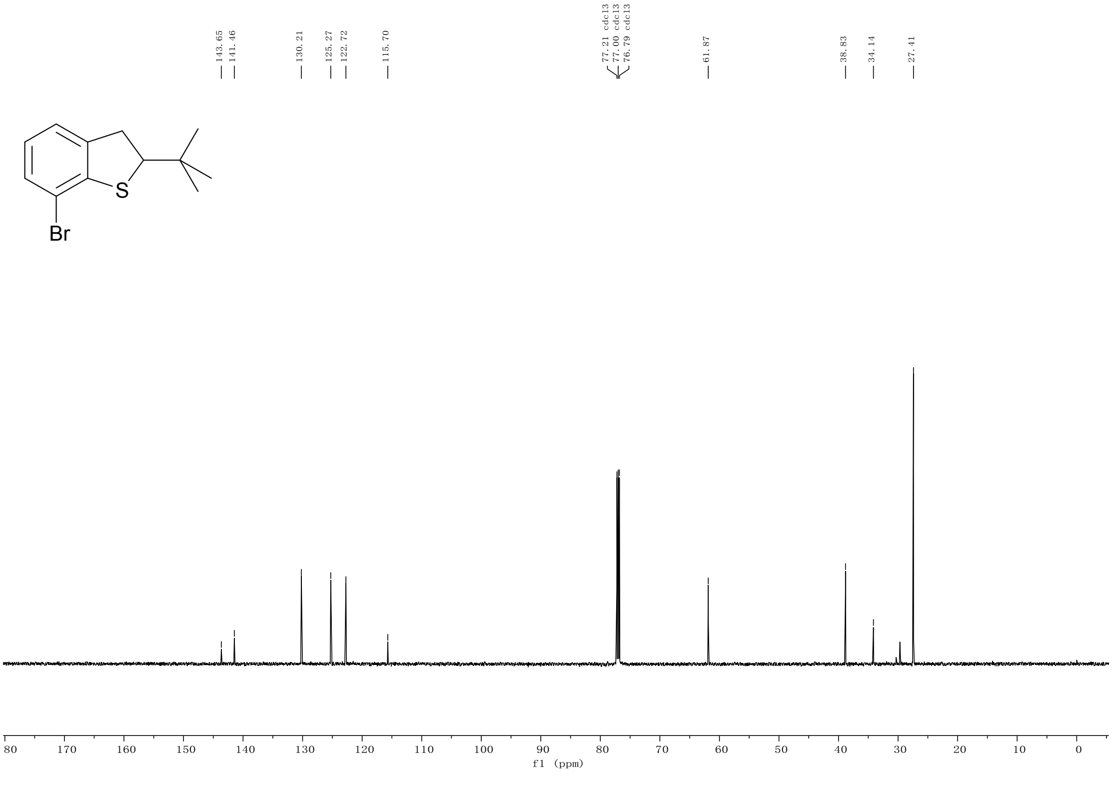


Figure S36 ^{13}C NMR spectrum of compound **15**

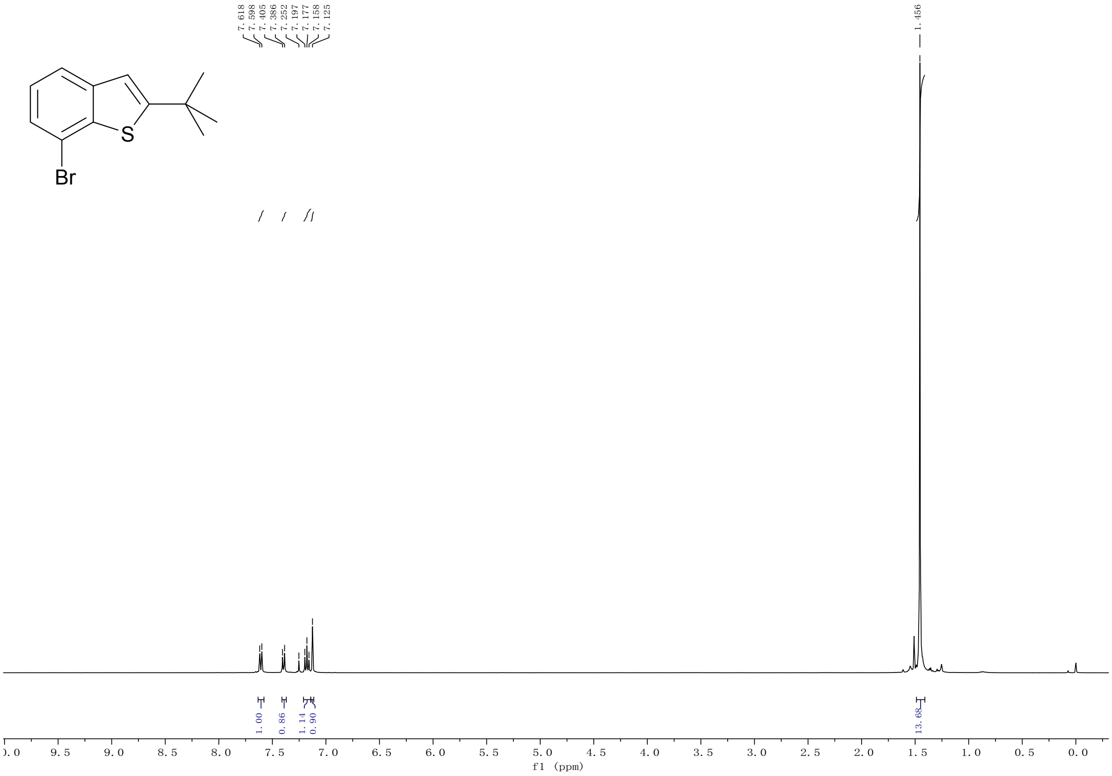


Figure S37 ^{1}H NMR spectrum of compound **15a**

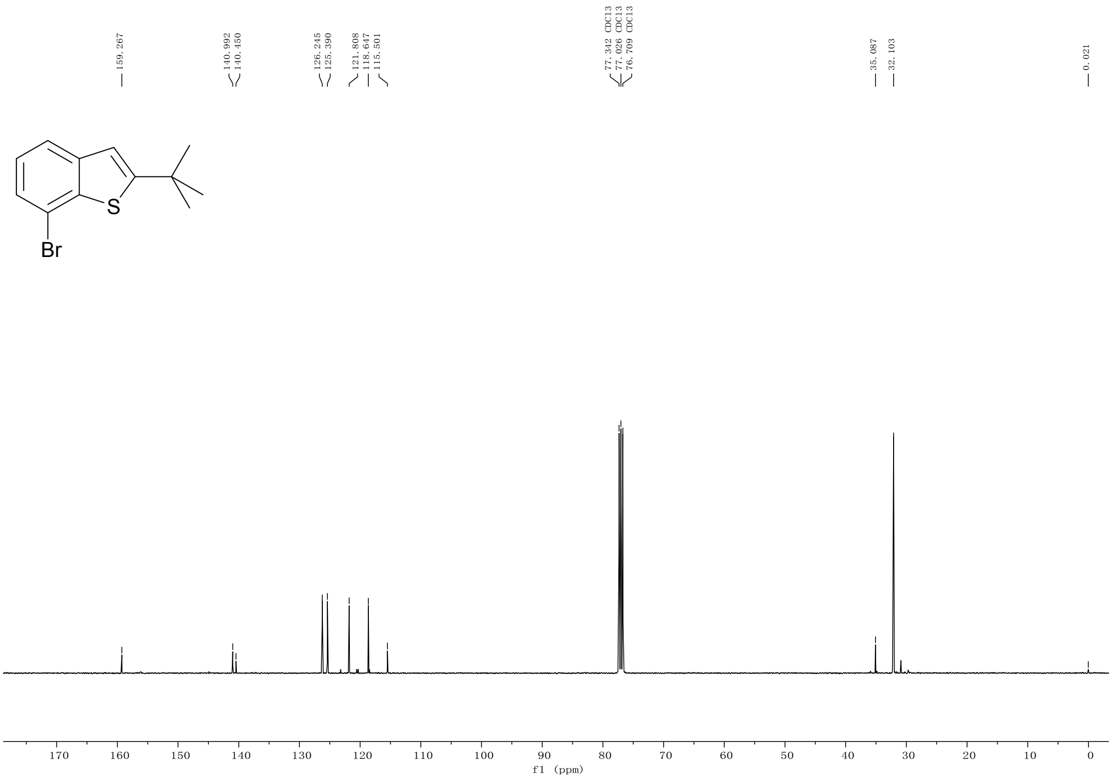


Figure S38 ^{13}C NMR spectrum of compound **15a**

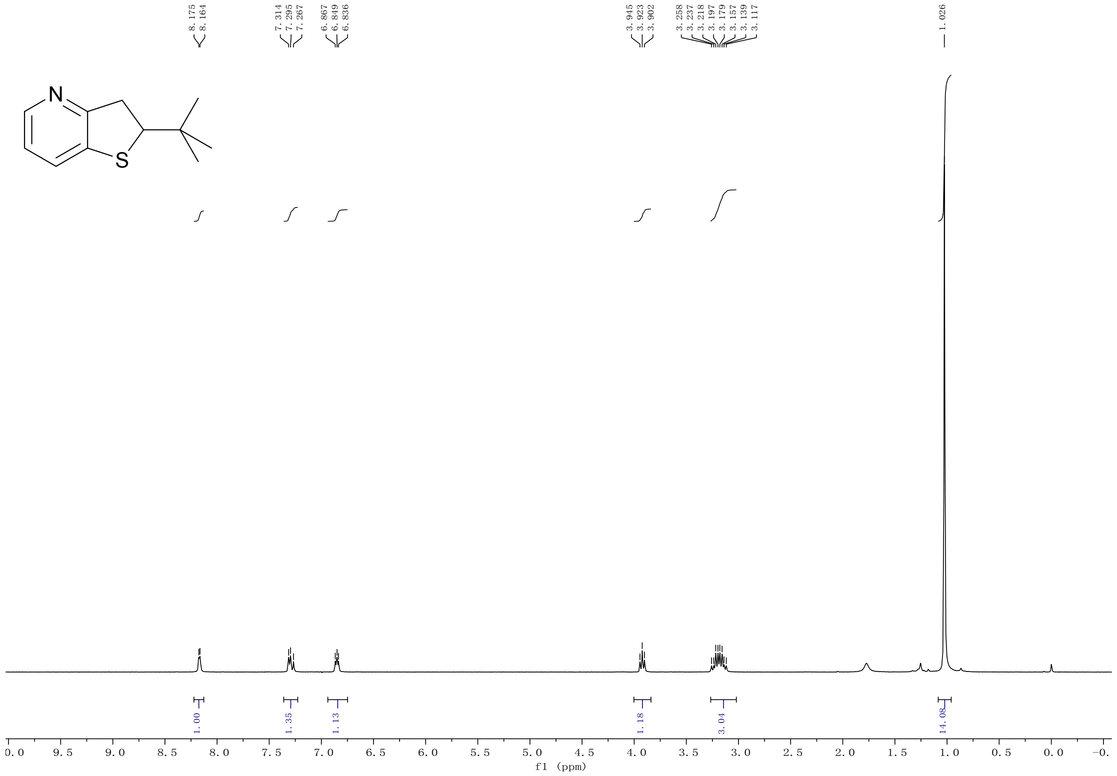


Figure S39 ^{1}H NMR spectrum of compound **16**

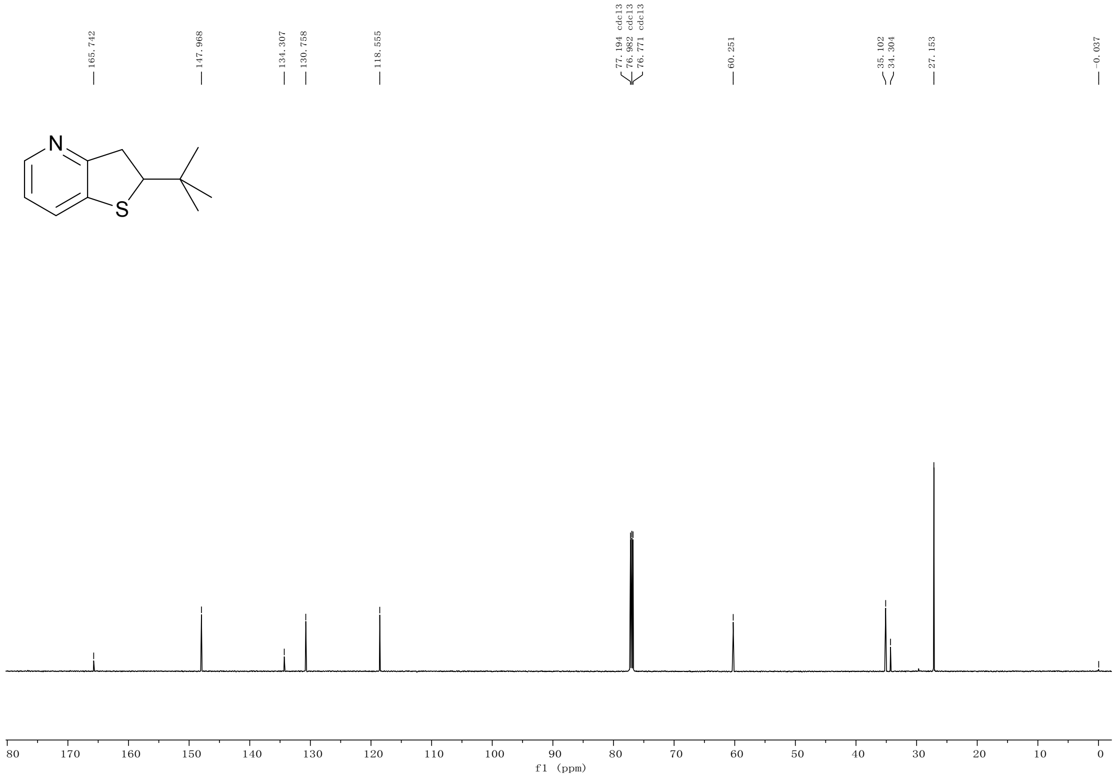


Figure S40 ^{13}C NMR spectrum of compound **16**

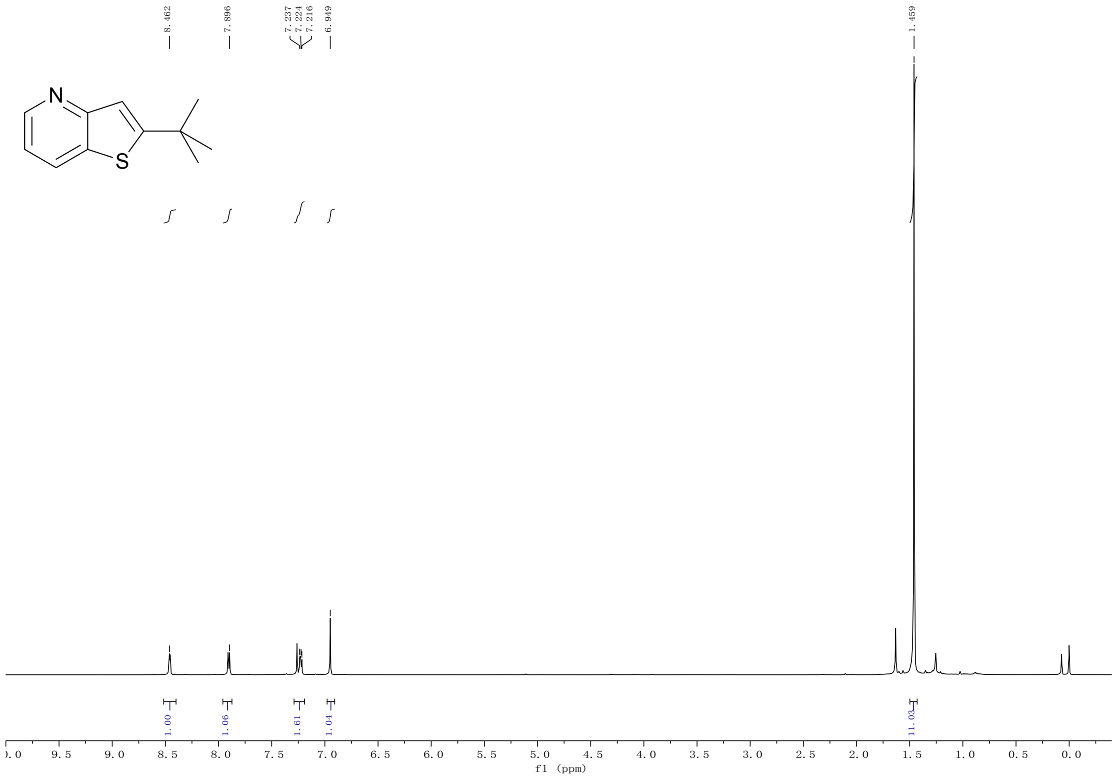


Figure S41 ^{1}H NMR spectrum of compound **16a**

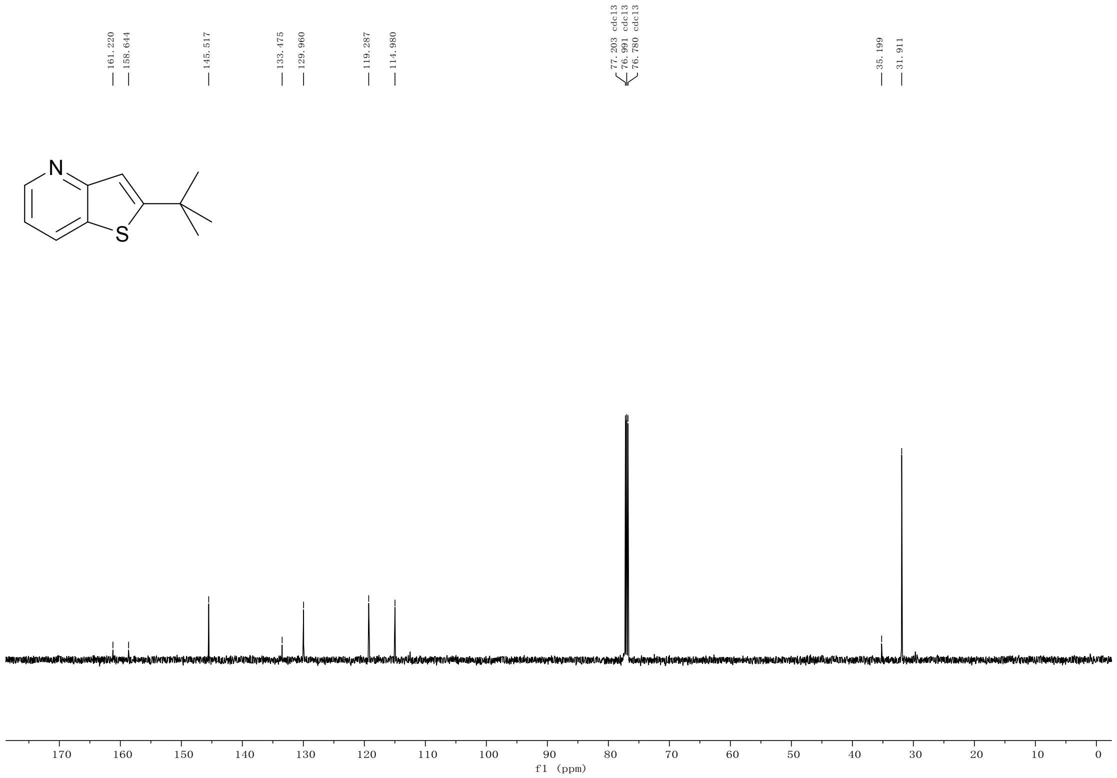


Figure S42 ^{13}C NMR spectrum of compound **16a**

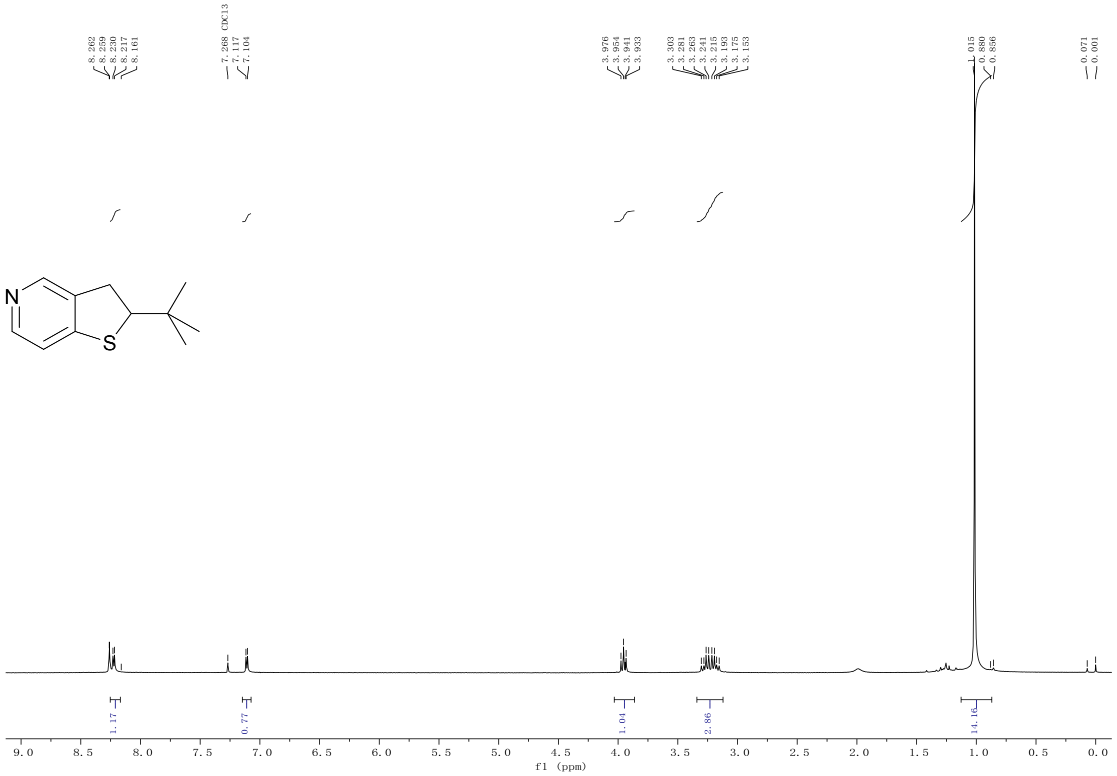


Figure S43 ^{1}H NMR spectrum of compound **17**

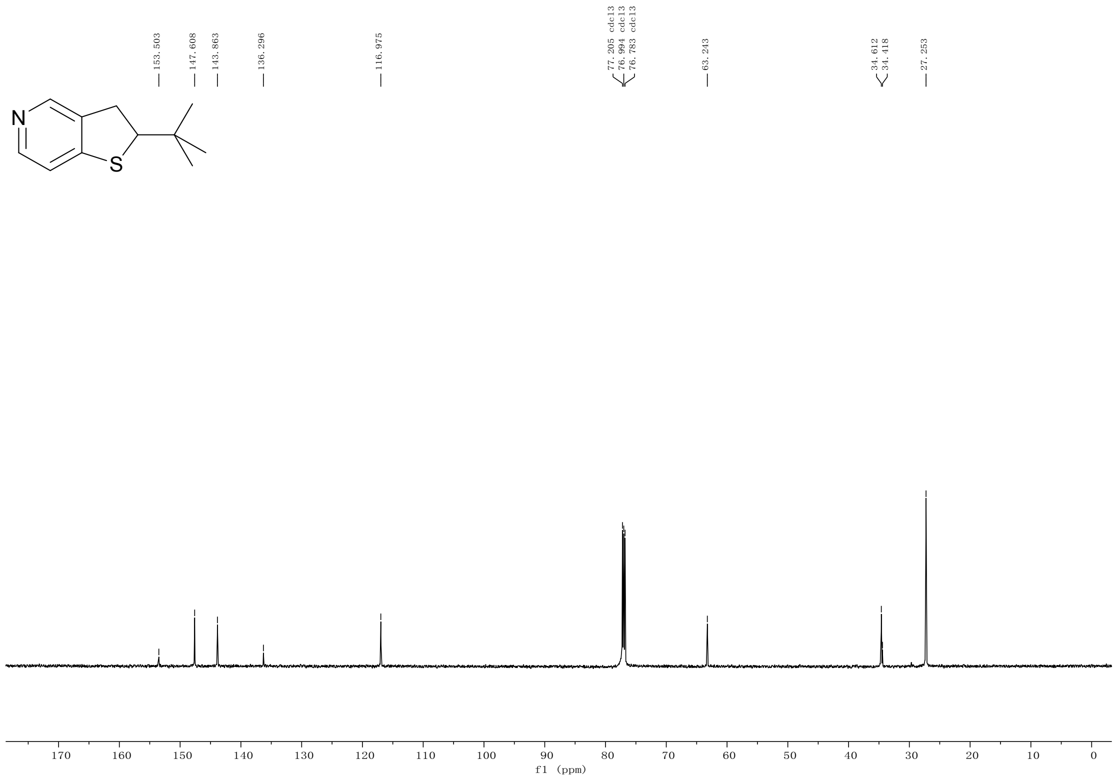


Figure S44 ^{13}C NMR spectrum of compound **17**

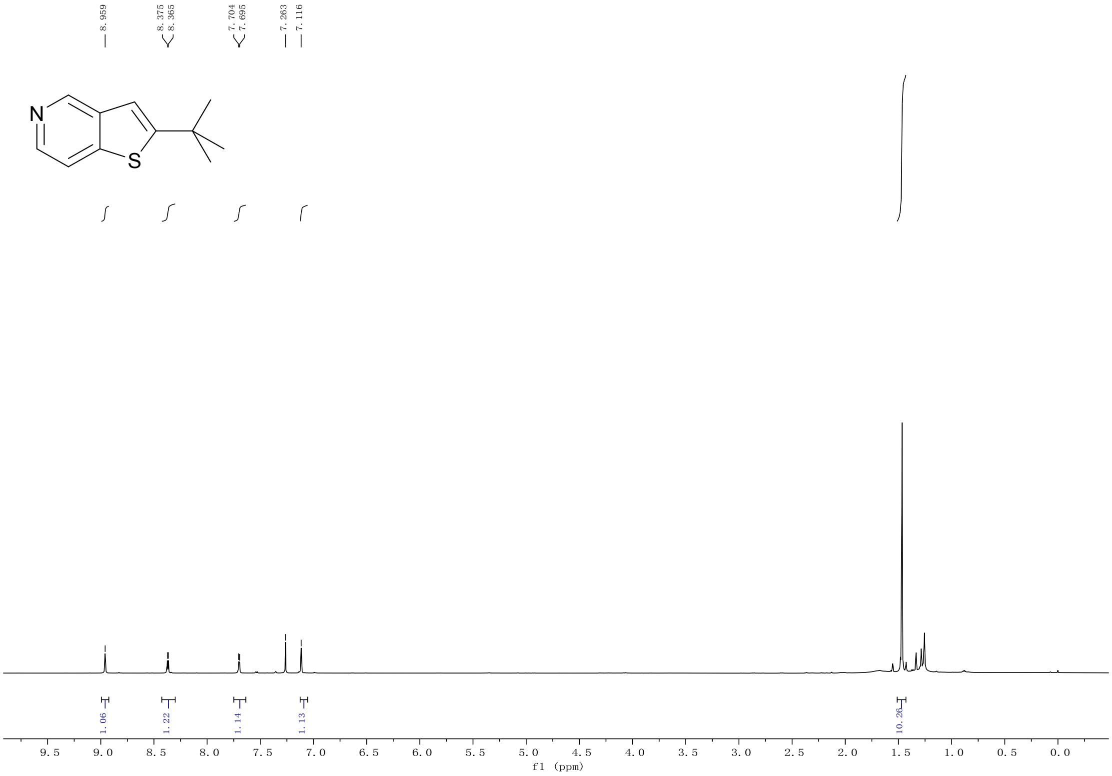


Figure S45 ^{1}H NMR spectrum of compound **17a**

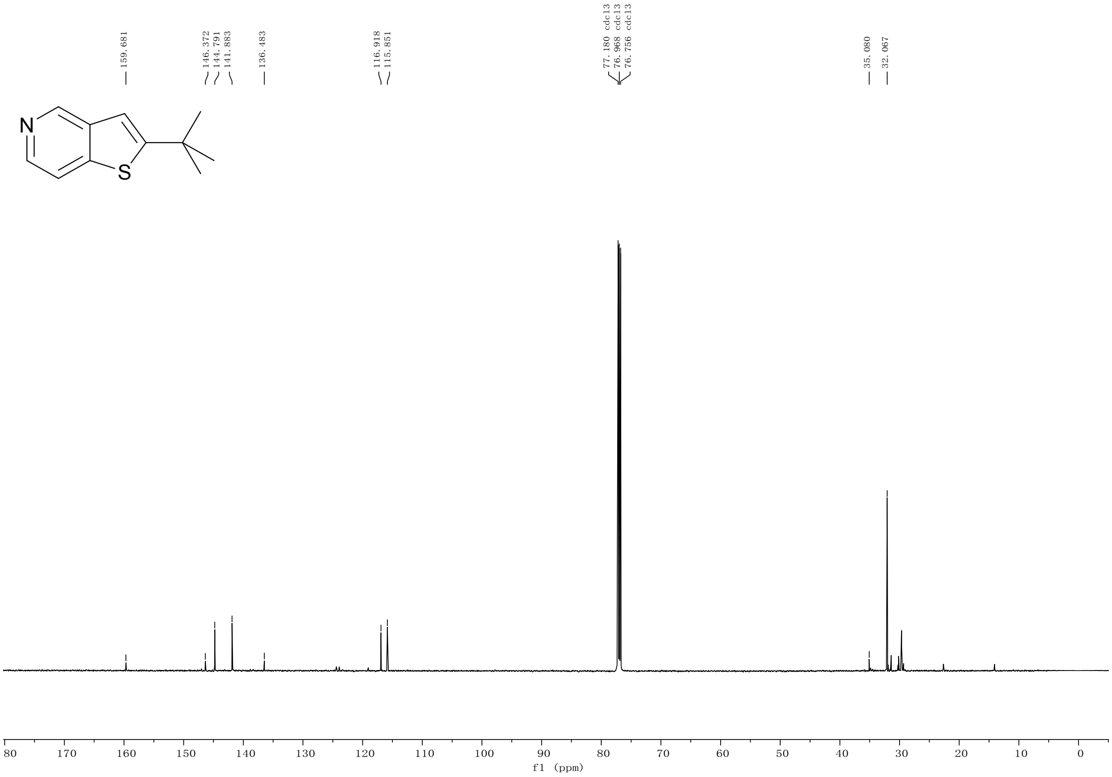


Figure S46 ^{13}C NMR spectrum of compound **17a**

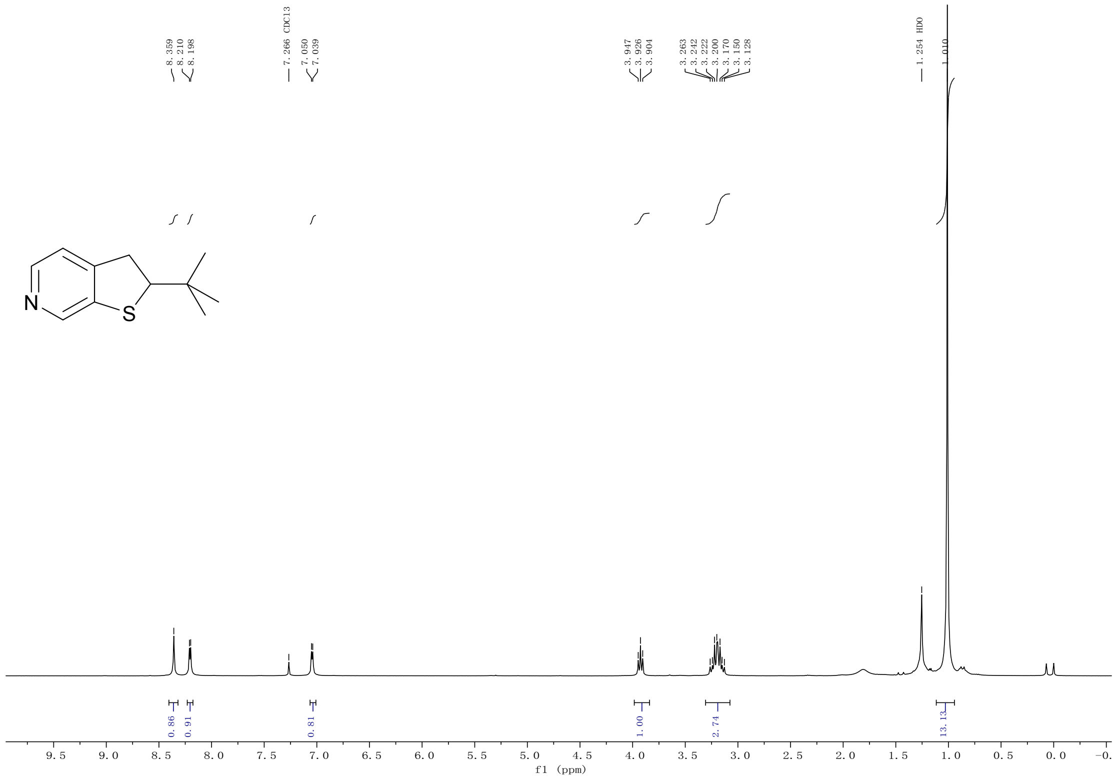


Figure S47 ^{1}H NMR spectrum of compound **18**

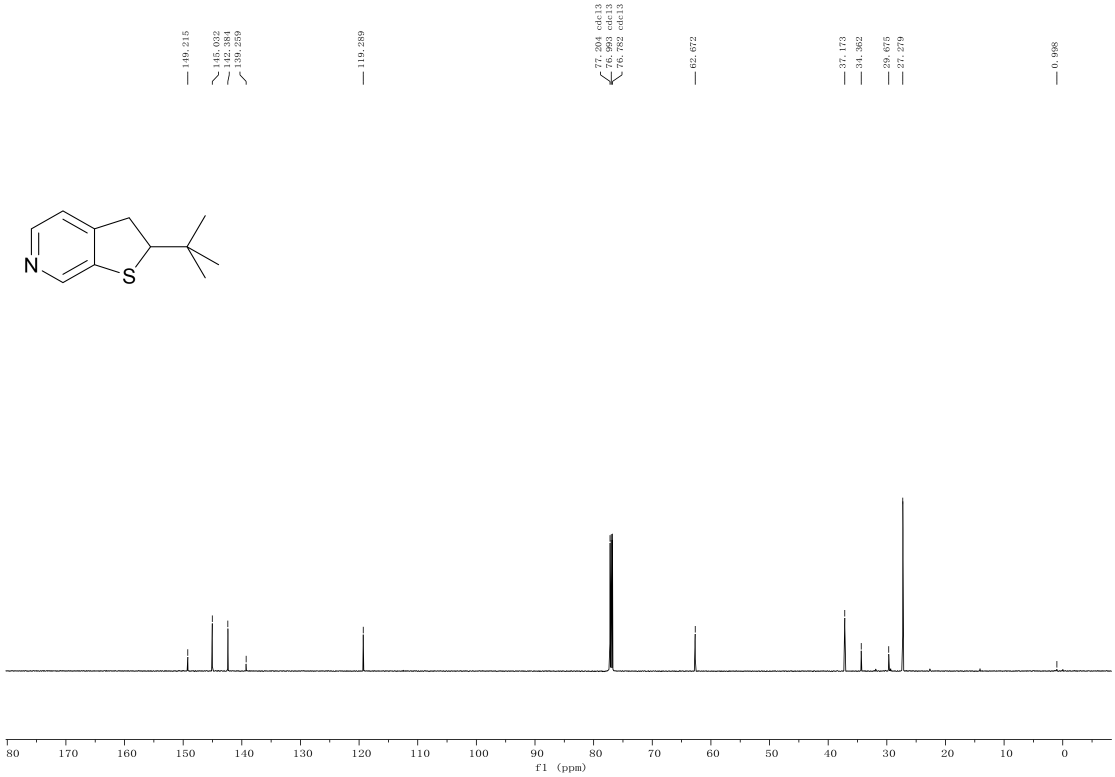


Figure S48 ^{13}C NMR spectrum of compound **18**

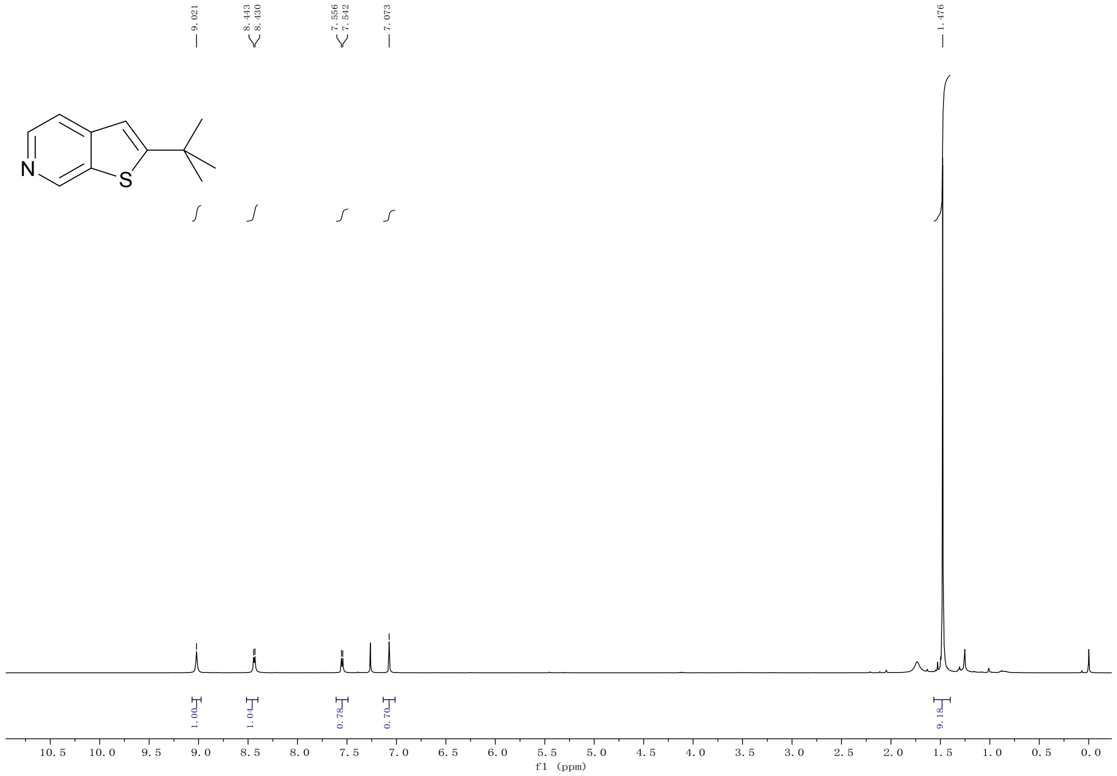


Figure S49 ^{1}H NMR spectrum of compound **18a**

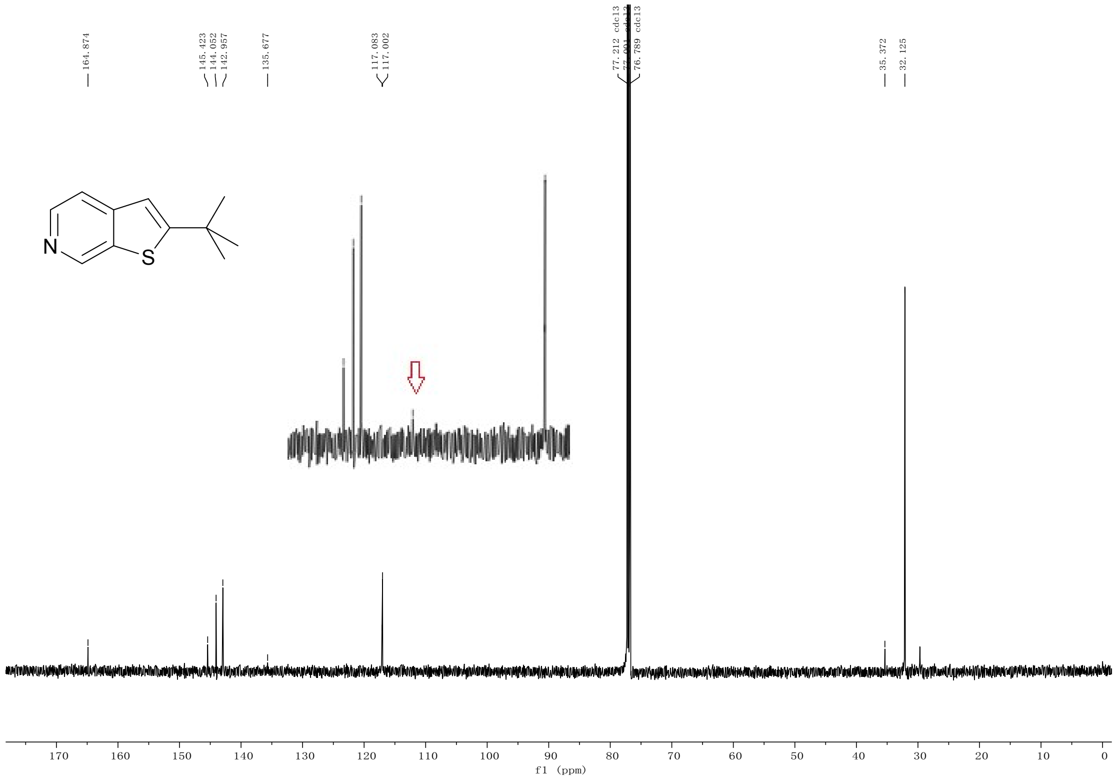


Figure S50 ^{13}C NMR spectrum of compound **18a**

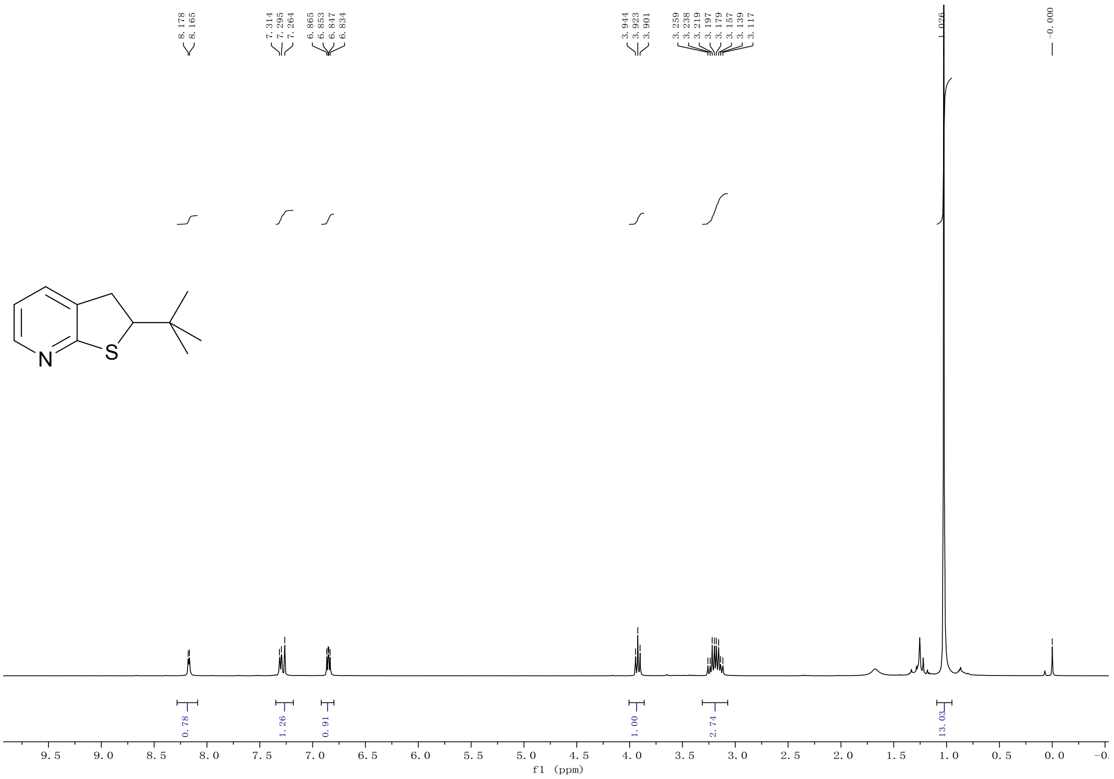


Figure S51 ^{1}H NMR spectrum of compound **19**

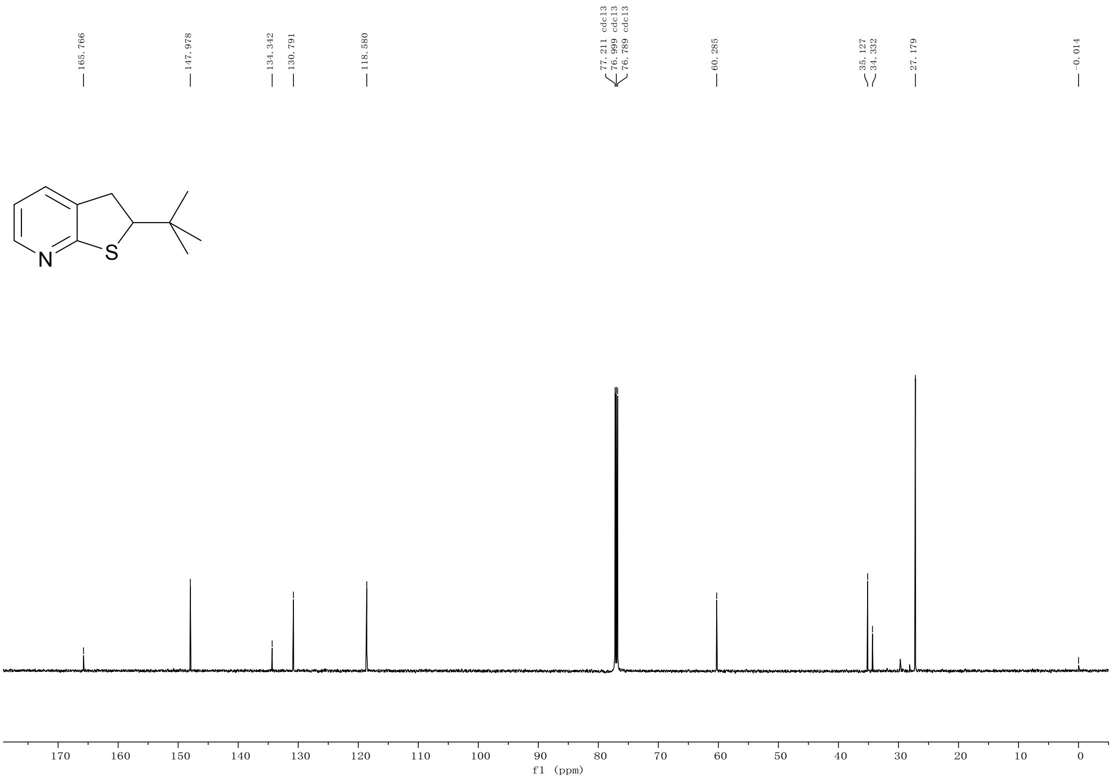


Figure S52 ^{13}C NMR spectrum of compound **19**

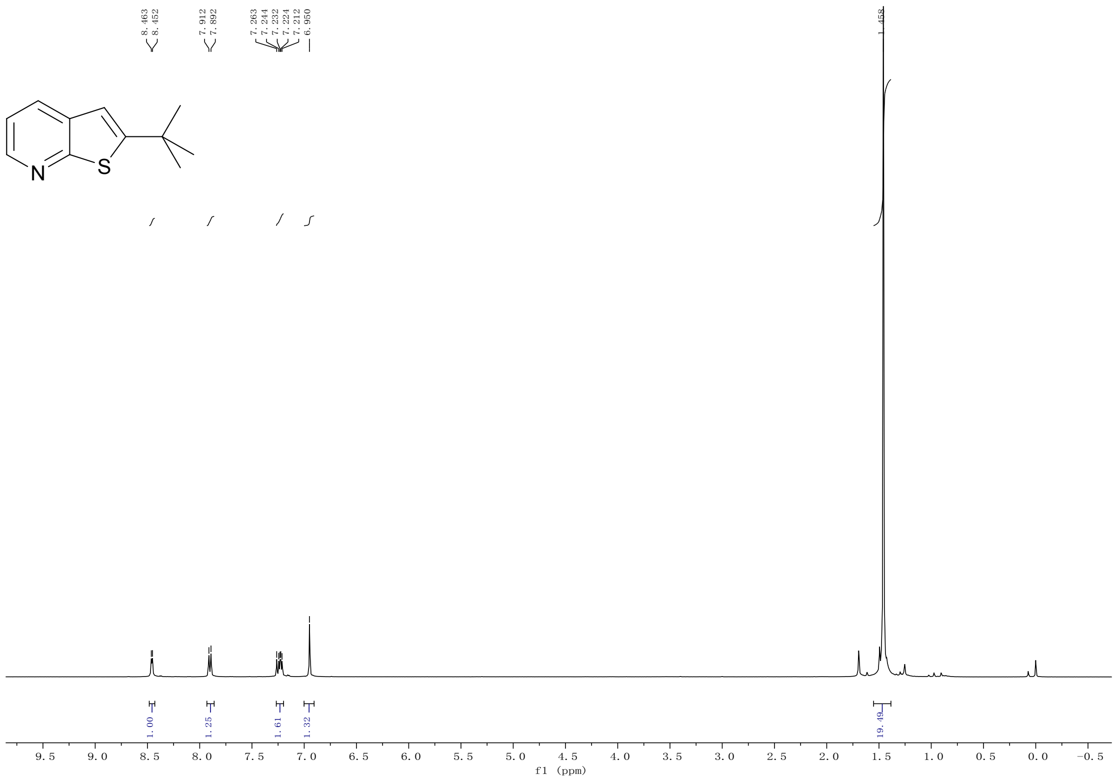


Figure S53 ^{1}H NMR spectrum of compound **19a**

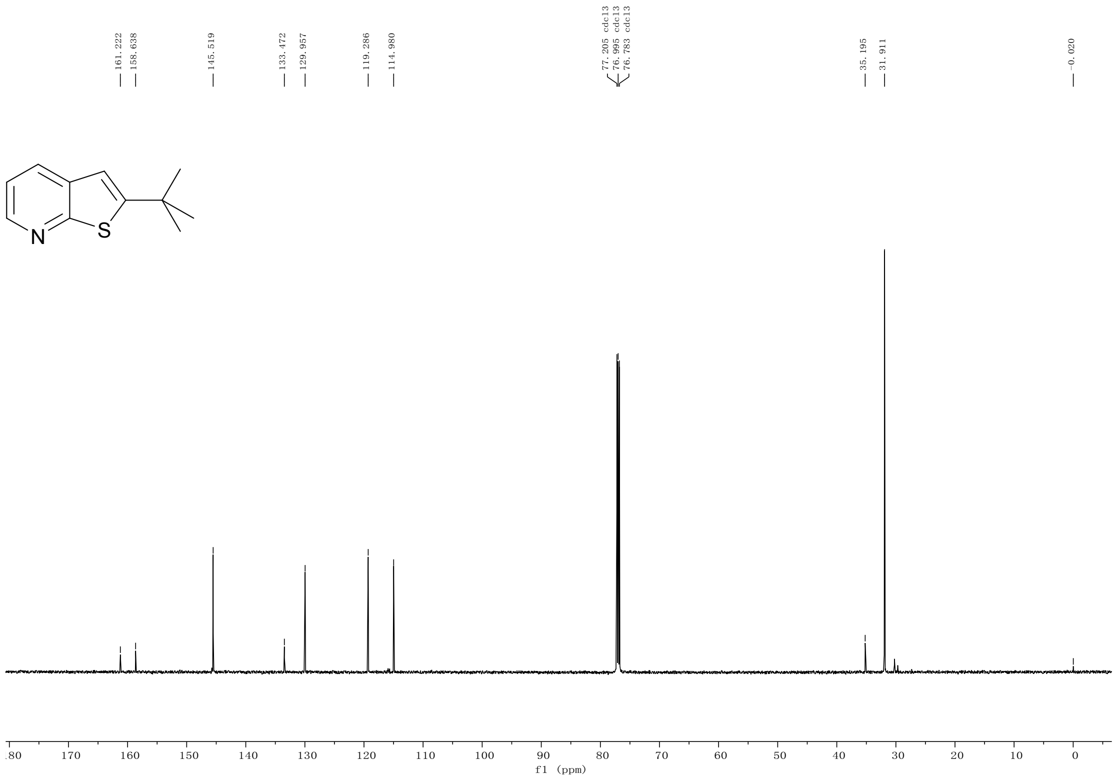


Figure S54 ^{13}C NMR spectrum of compound **19a**

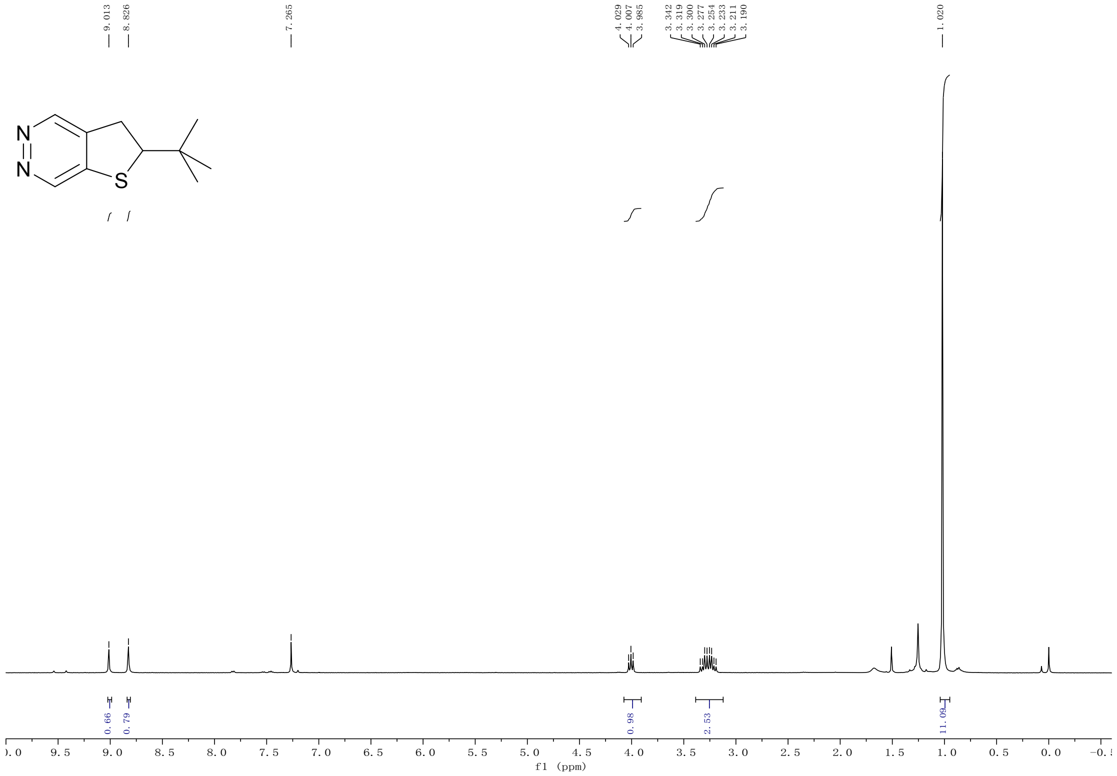


Figure S55 ^{1}H NMR spectrum of compound **20**

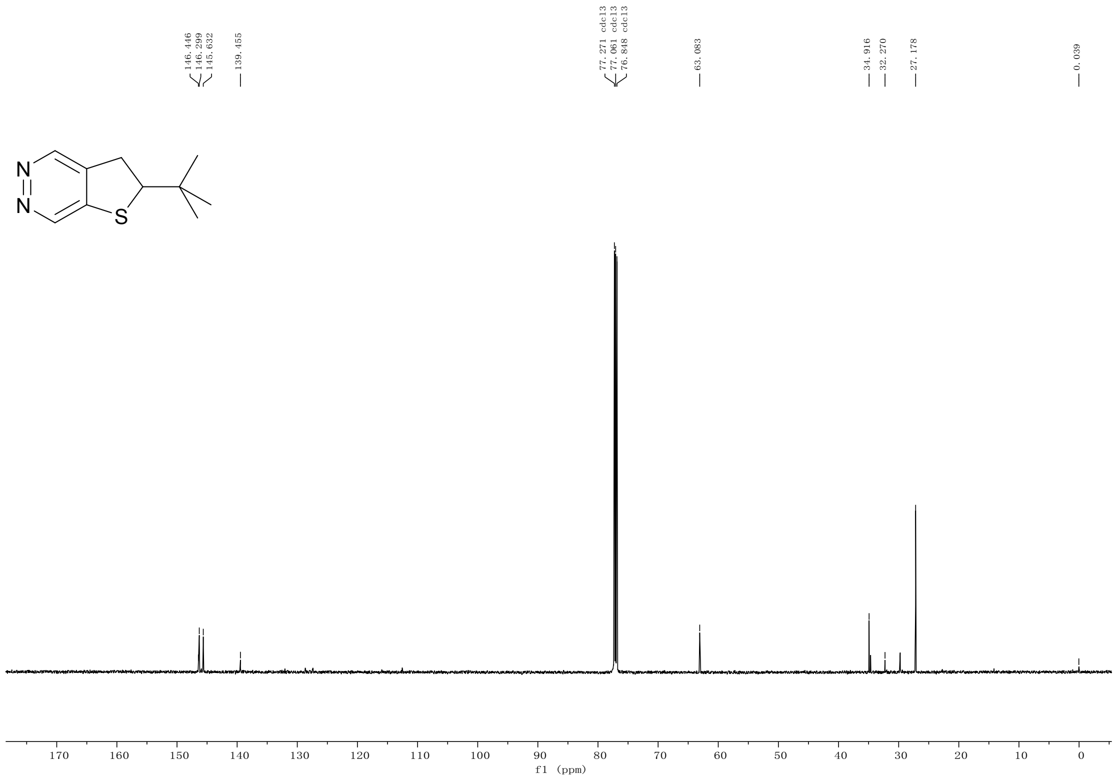


Figure S56 ^{13}C NMR spectrum of compound **20**

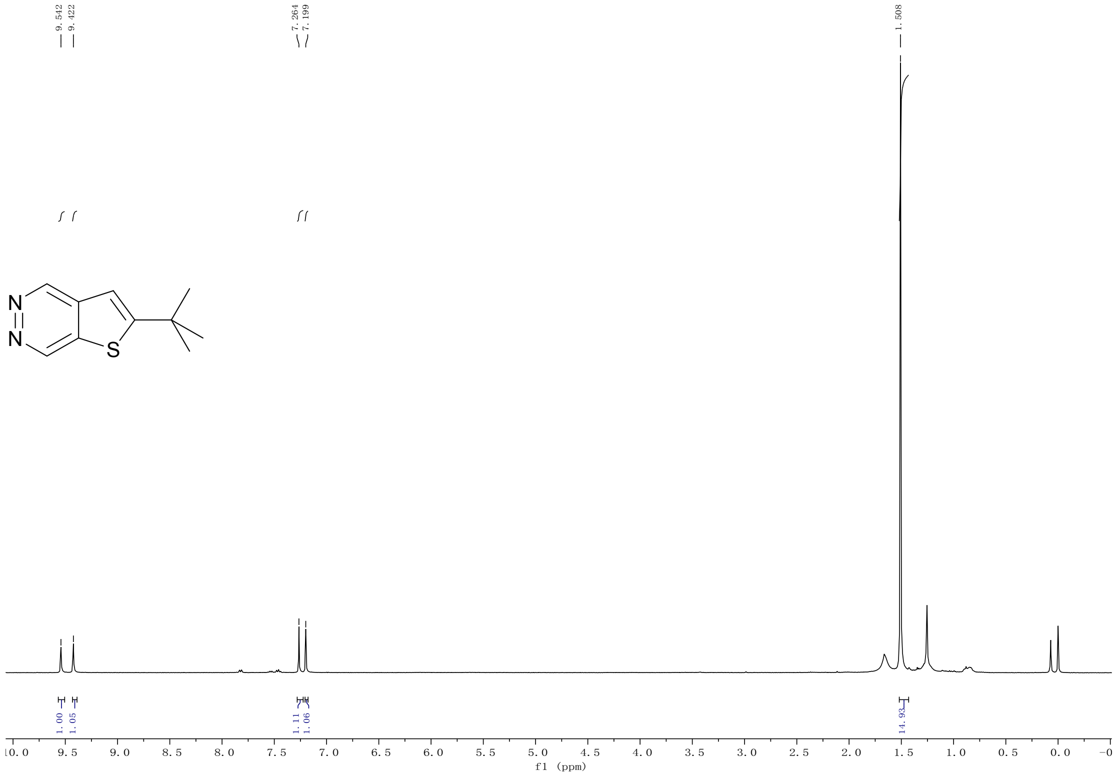


Figure S57 ^{1}H NMR spectrum of compound **20a**

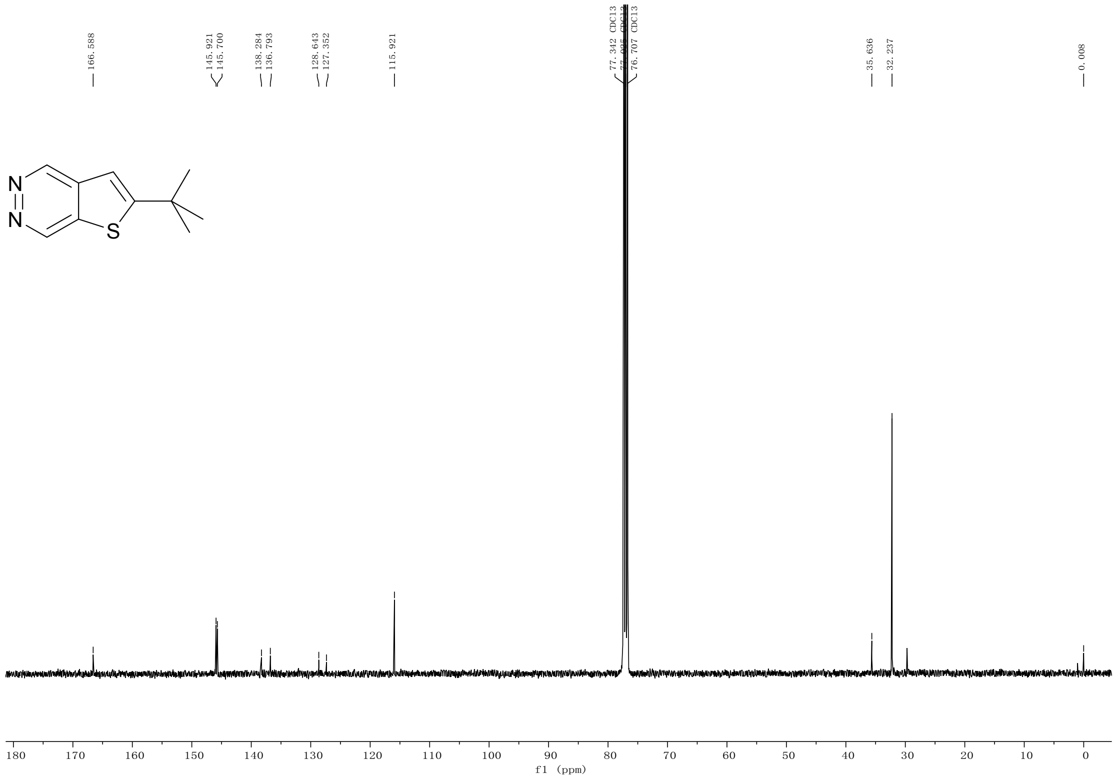


Figure S58 ^{13}C NMR spectrum of compound **20a**

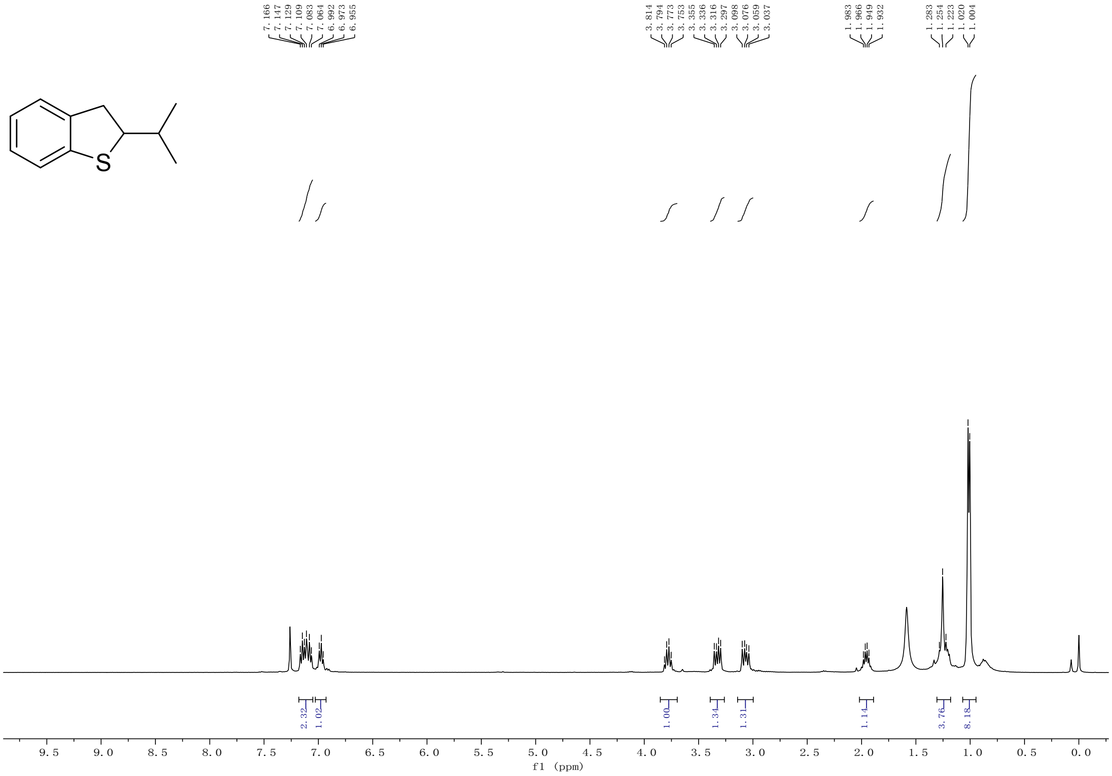


Figure S59 ^{1}H NMR spectrum of compound **21**

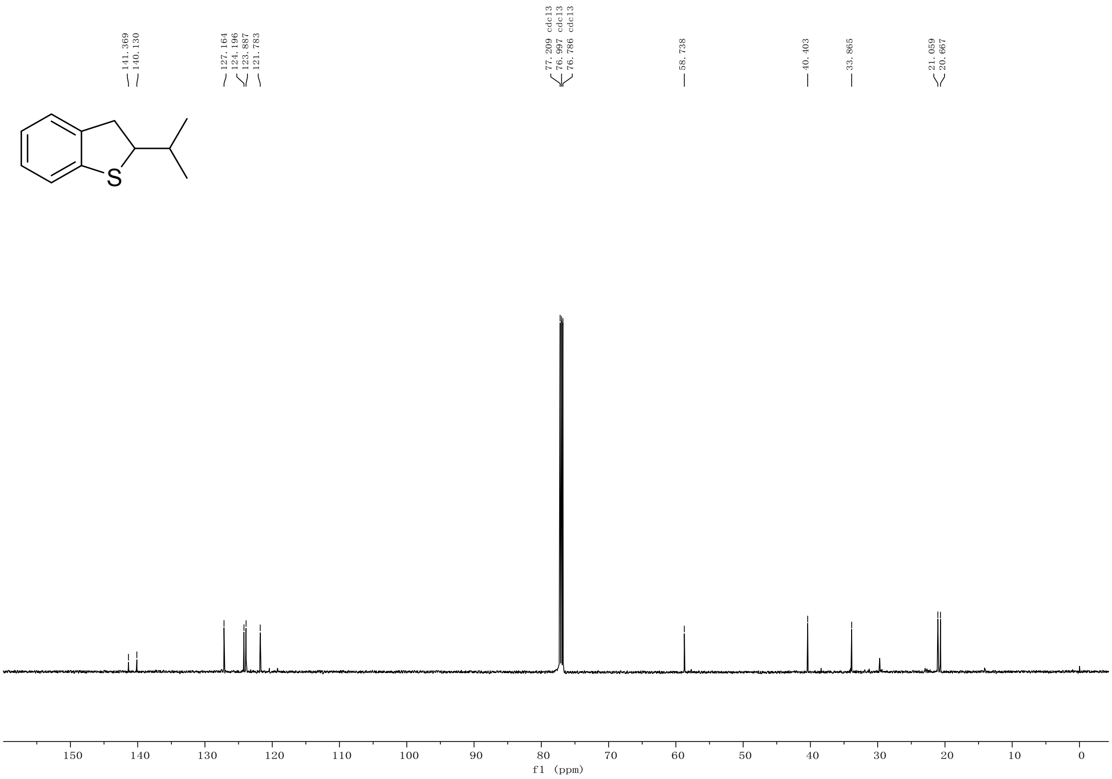


Figure S60 ^{13}C NMR spectrum of compound **21**

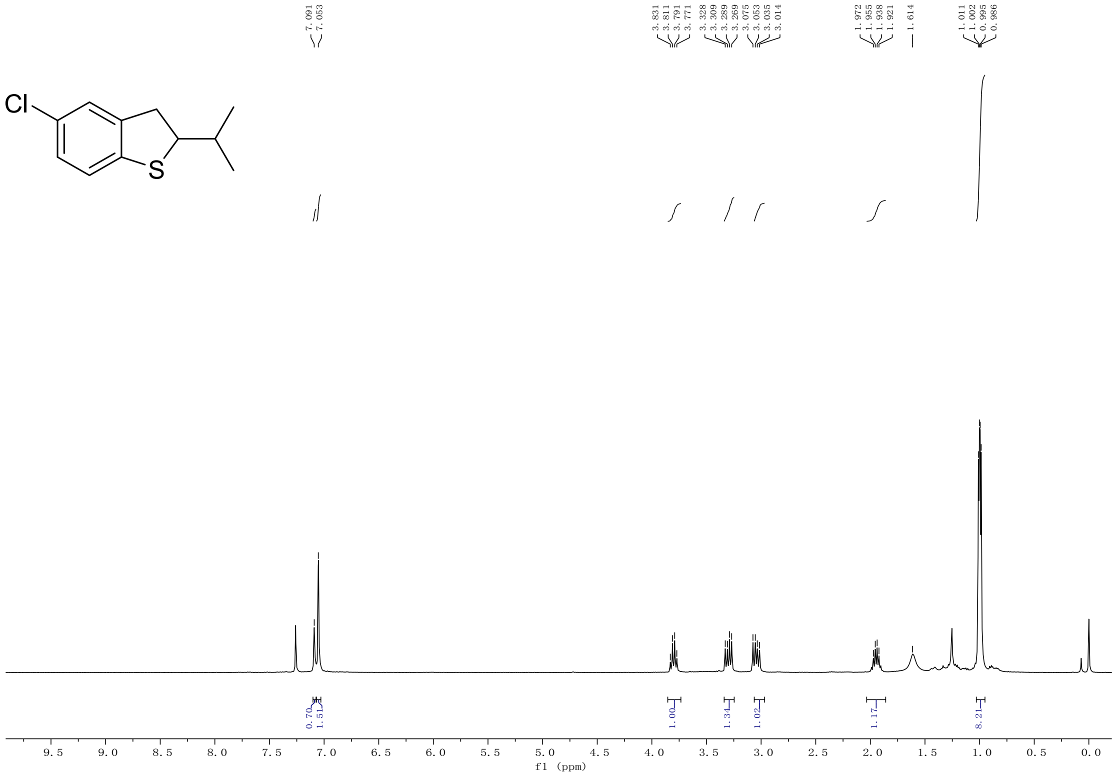


Figure S61 ^{1}H NMR spectrum of compound **22**

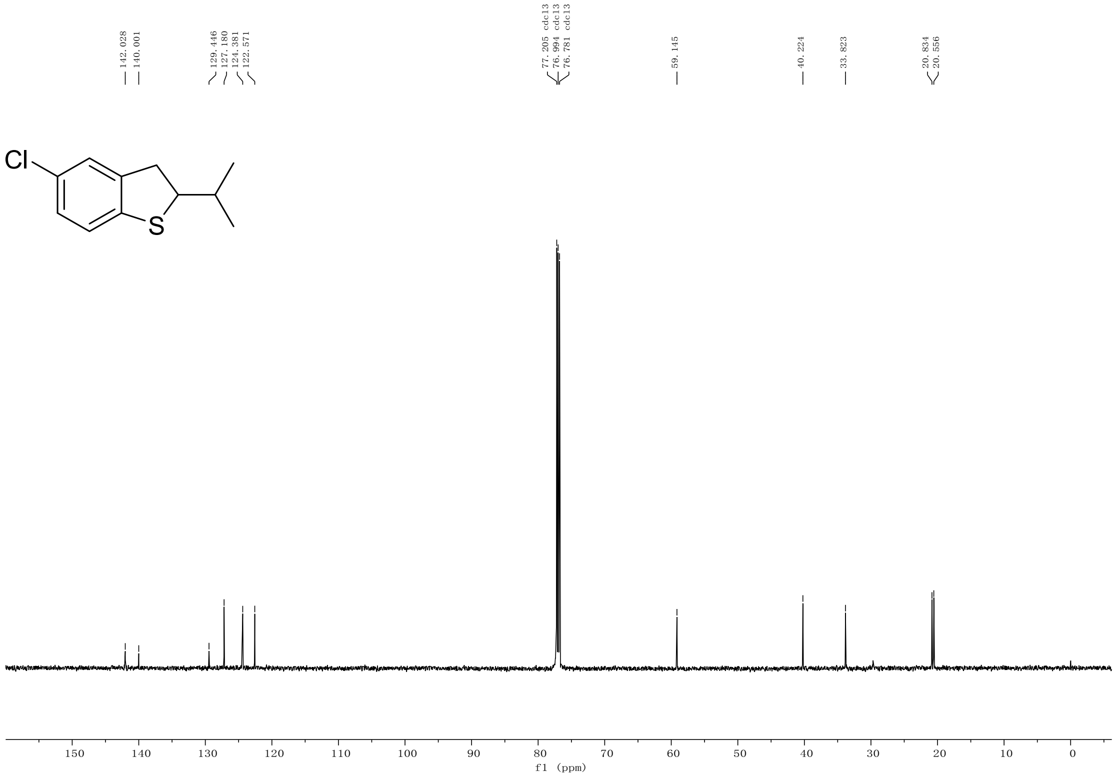


Figure S62 ^{13}C NMR spectrum of compound **22**

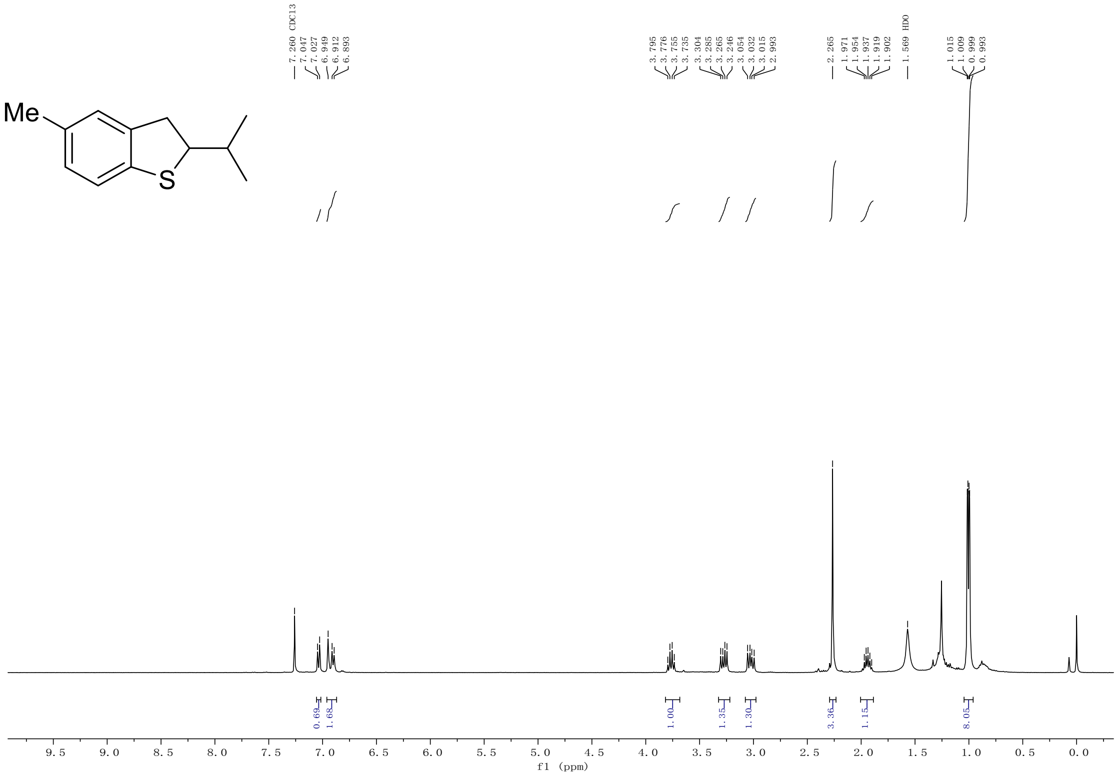


Figure S63 ^{1}H NMR spectrum of compound **23**

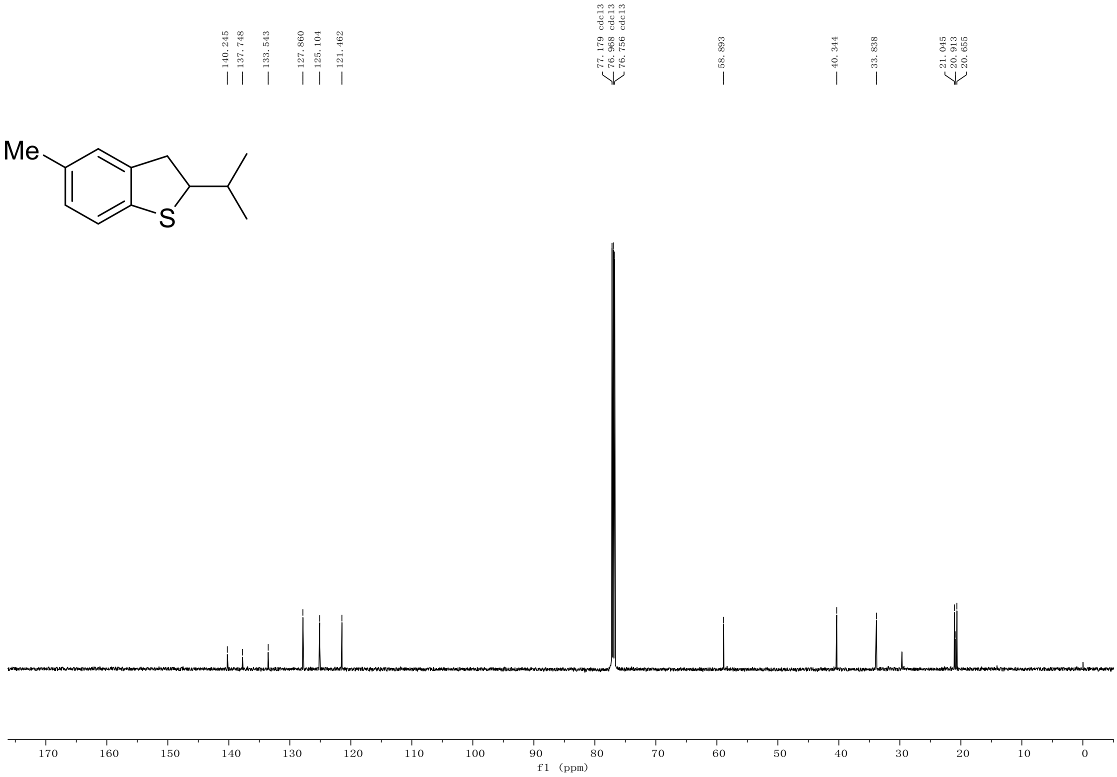


Figure S64 ^{13}C NMR spectrum of compound **23**

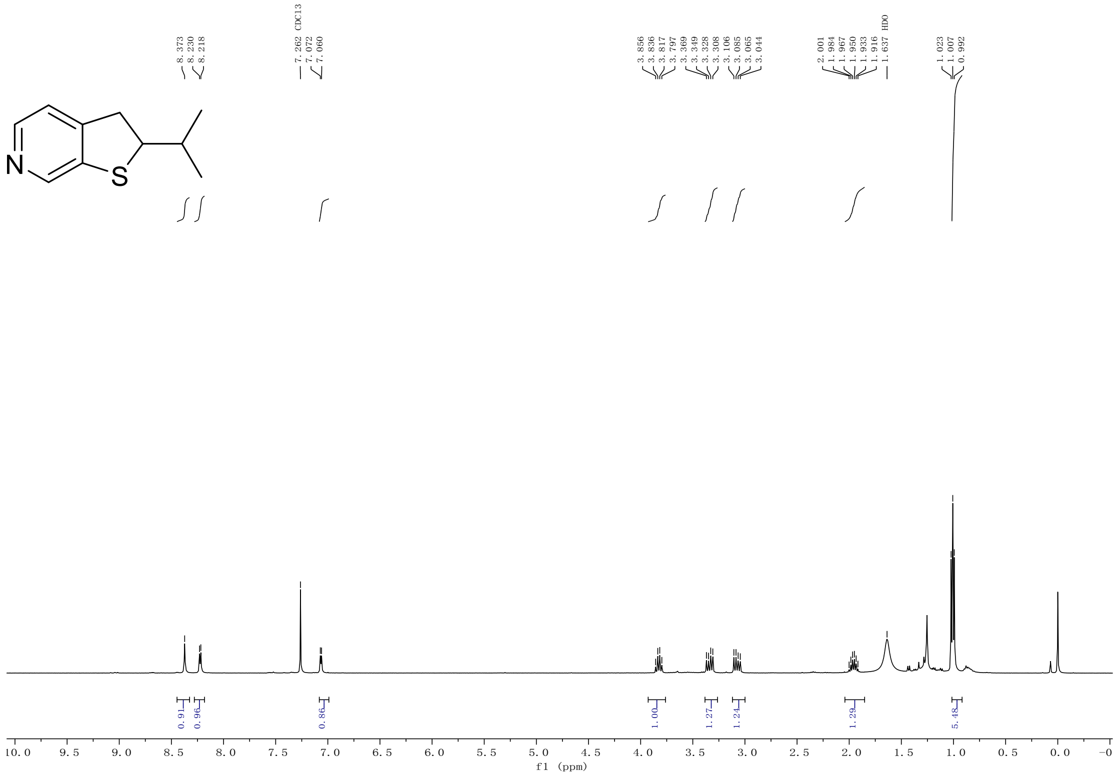


Figure S65 ^{1}H NMR spectrum of compound **24**

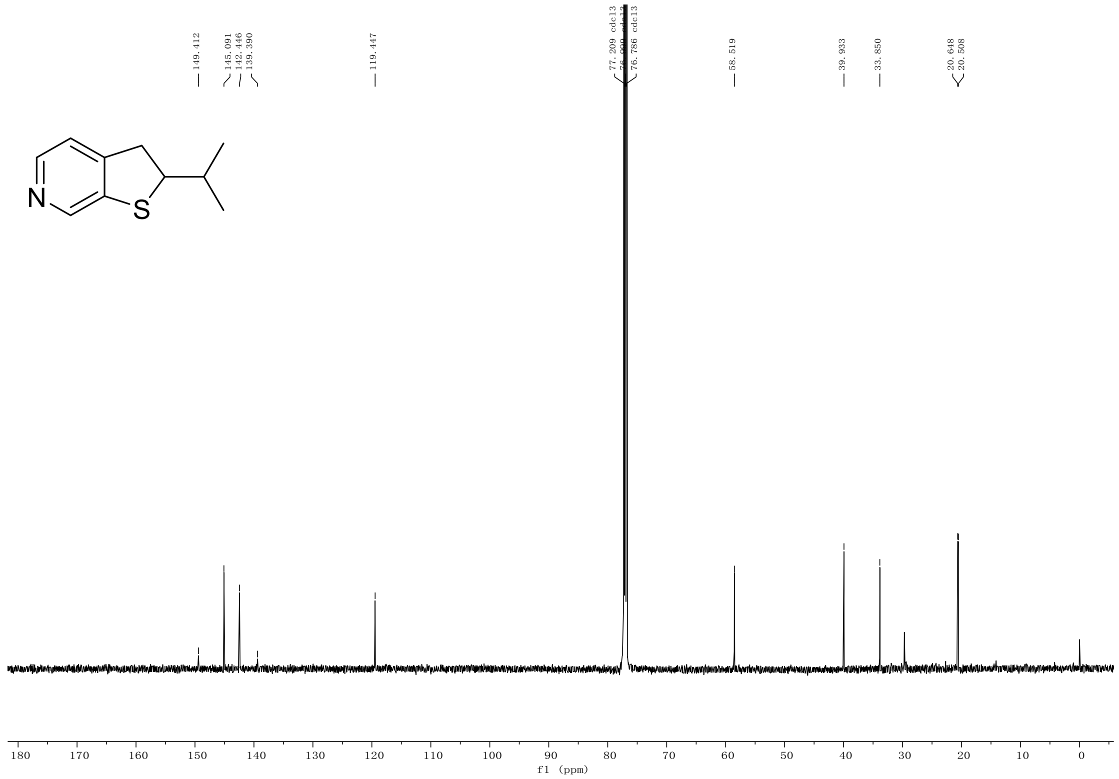


Figure S66 ^{13}C NMR spectrum of compound **24**

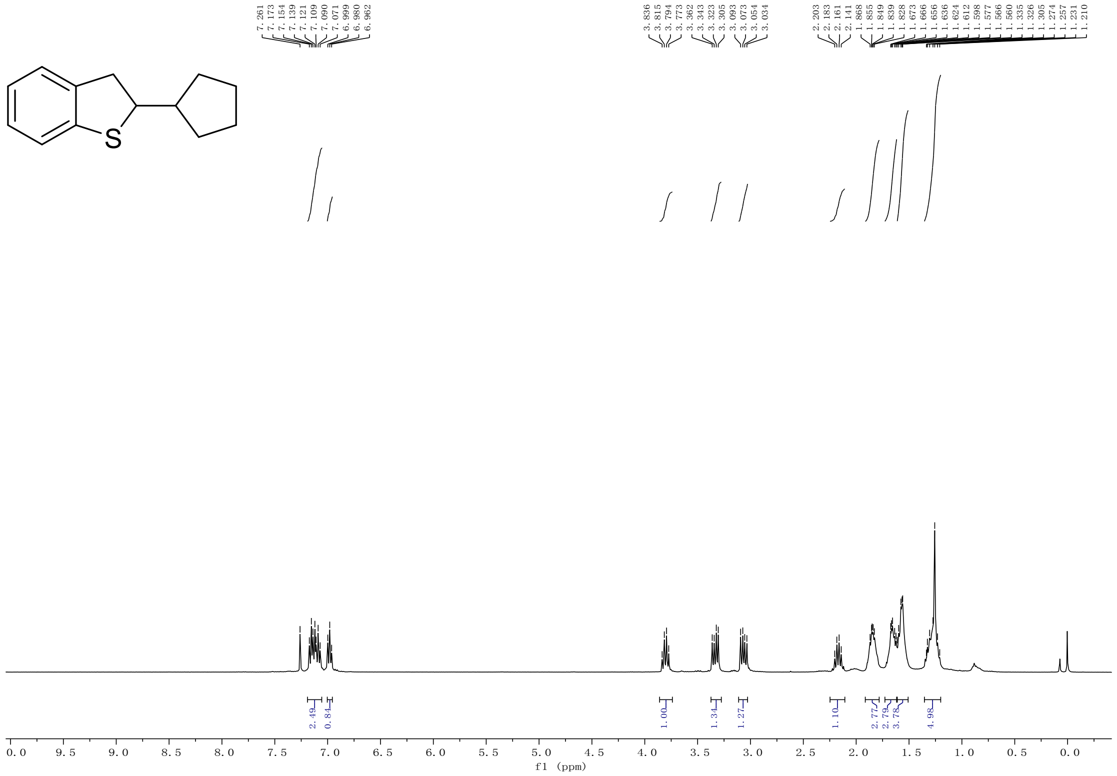


Figure S67 ^{1}H NMR spectrum of compound **25**

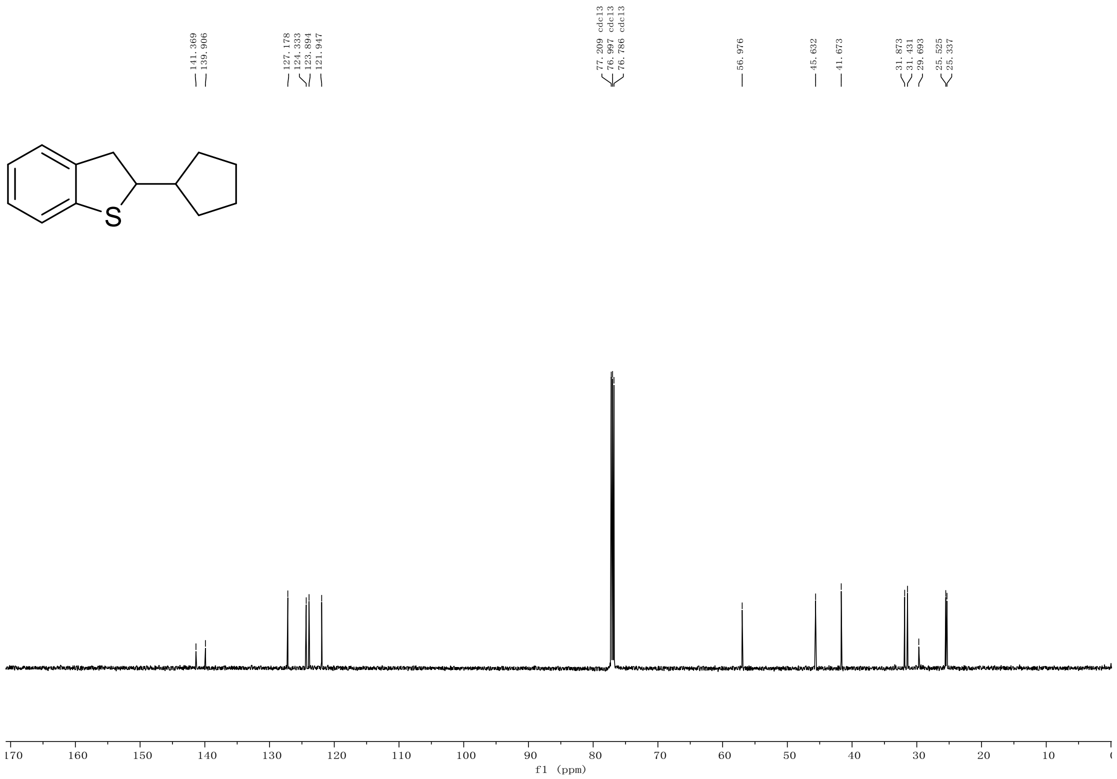


Figure S68 ^{13}C NMR spectrum of compound **25**

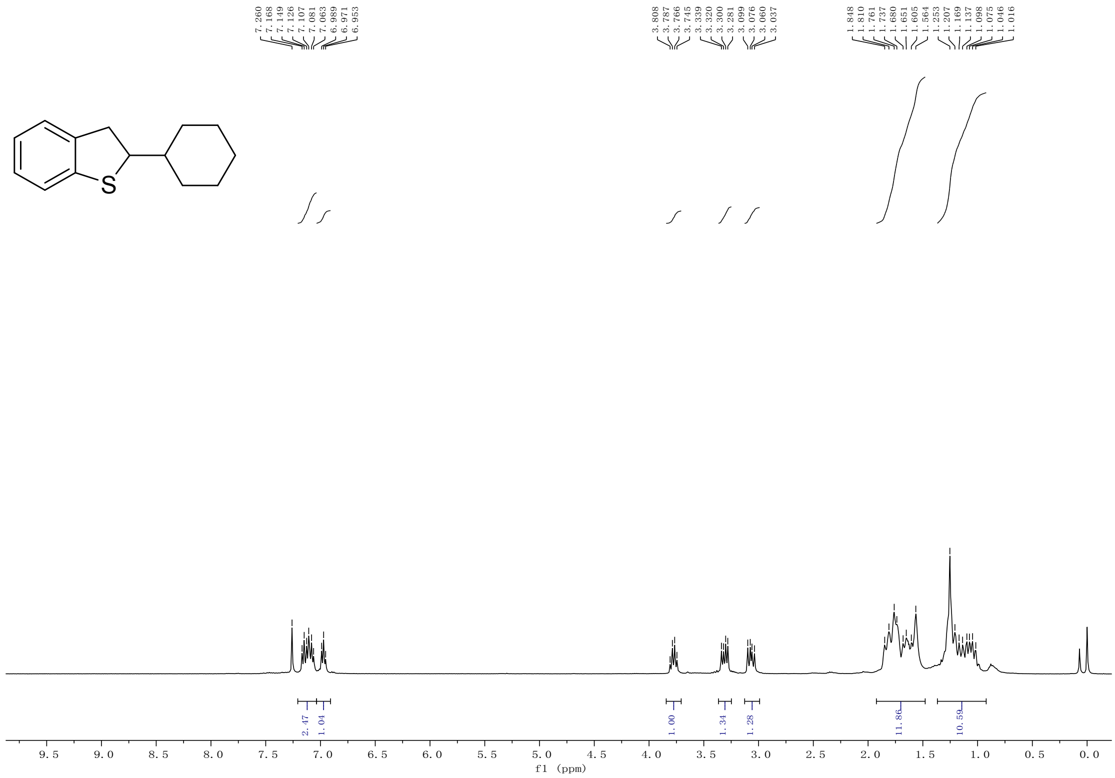


Figure S69 ^{1}H NMR spectrum of compound **26**

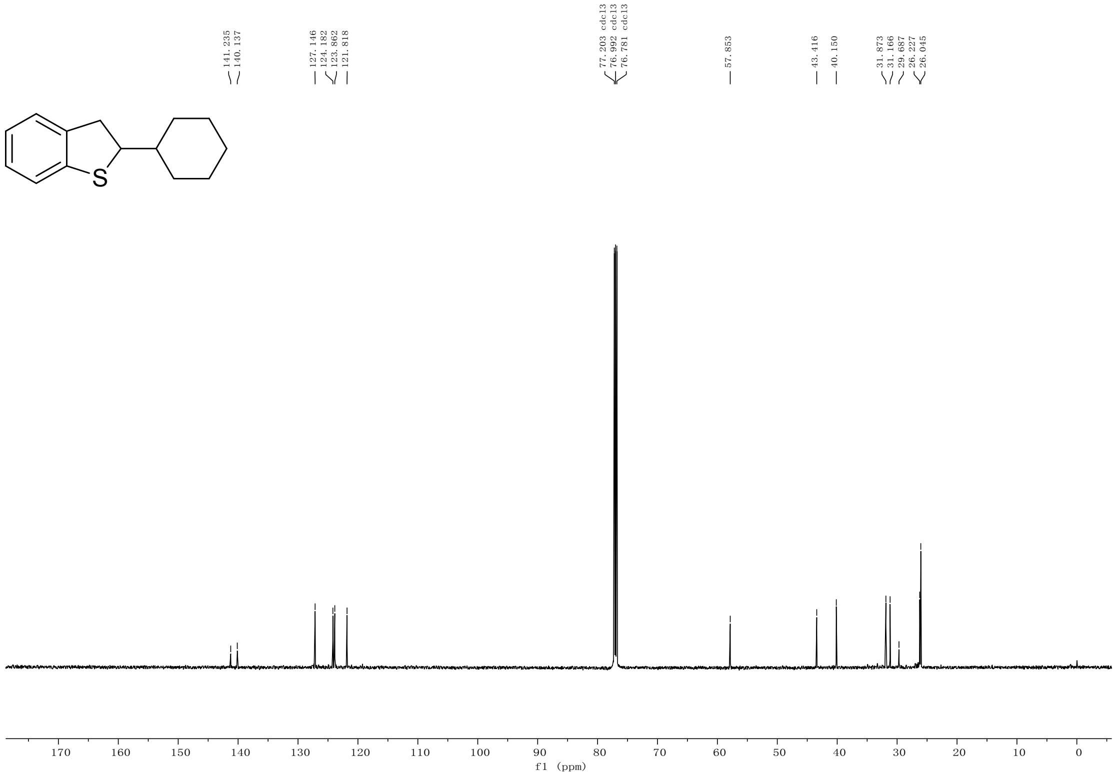


Figure S70 ^{13}C NMR spectrum of compound **26**

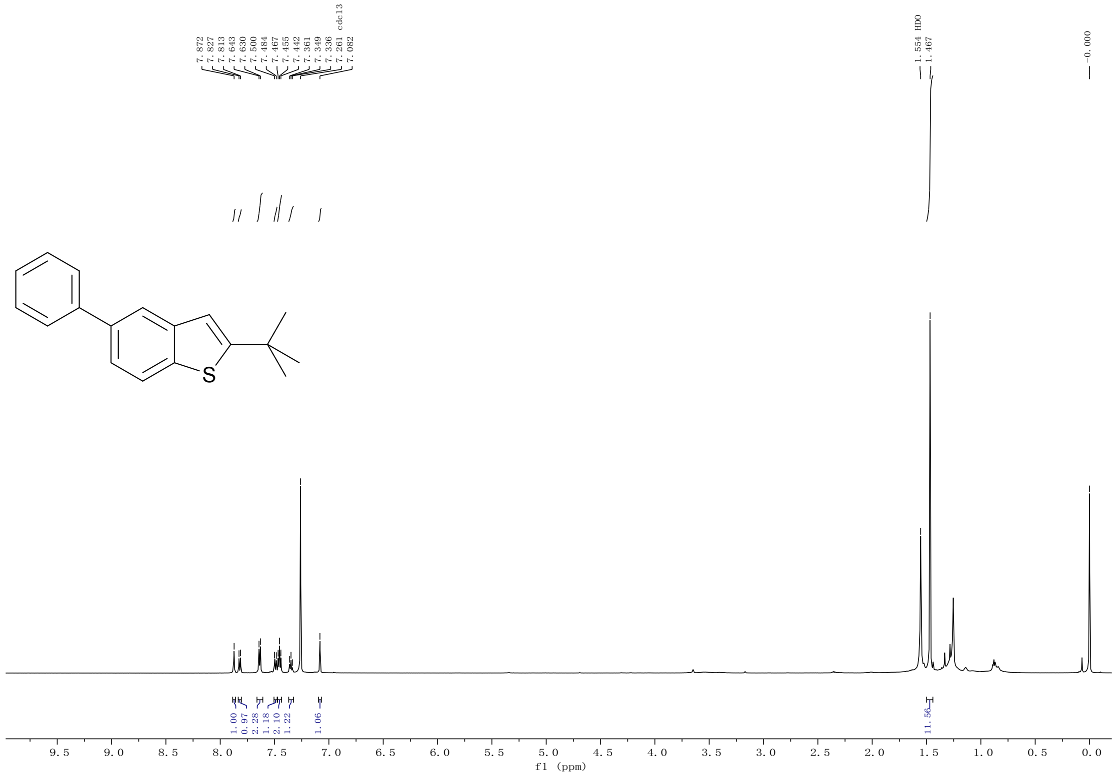


Figure S71 ^{1}H NMR spectrum of compound **28**

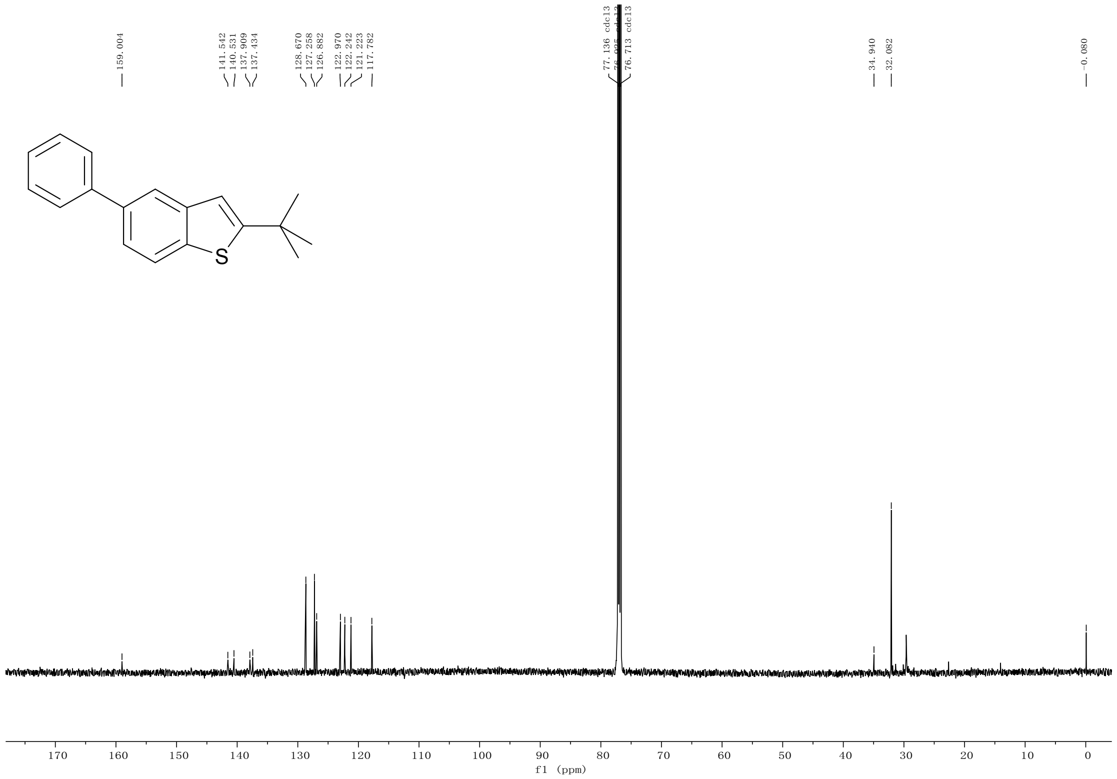


Figure S72 ^{13}C NMR spectrum of compound **28**