Supporting Information

Fe-Catalyzed Oxidative C-H Functionalization / C-S Bond Formation

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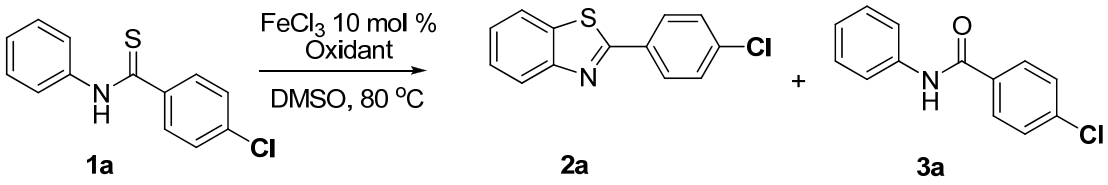
1. General Considerations

All manipulations were carried out using standard Schlenk techniques. All glassware was oven dried at 120 ^{o}C for more than 1 hour prior to use. Dimethyl sulfoxide (DMSO) was dried and distilled from calcium hydride. Anhydrous dioxane was purchased from Sigma-Aldrich (99.9+% in a SureSeal TM bottle). Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich (99.5% in a SureSealTM bottle). Toluene was dried and distilled from sodium/benzophenone immediately prior to use under argon atmosphere. Tetrahydrofuran (THF) was dried and distilled from sodium/benzophenone immediately prior to use under nitrogen atmosphere. Unless otherwise stated, analytical grade solvents and commercially available reagents were used as received. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 30-60 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the indicated solvent, which are listed below as volume/volume ratios.

All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer or a Varian Mercury 600 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (TMS, 0 ppm for ^{1}H) and $CDCl_3$ (77.16 ppm for ^{13}C) or [D_6]DMSO (39.52 ppm for ^{13}C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion (M^+). HPLC yields were recorded with a Dionex P680A LPG-4 high performance liquid chromatography instrument with a UV detector. For the *in situ* IR kinetic experiments, the reaction spectra were recorded using a React IR iC10 from Mettler-Toledo AutoChem fitted with a diamond-tipped probe.

2. Detailed results of Screening

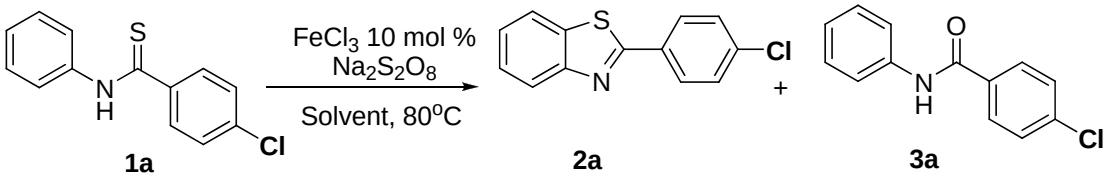
Table S1: **Oxidant Effect.**[a]



Entry	Oxidant	Conversion **1a**[%]	Yield[%] **2a**	**3a**
1	O_2	2	0	2
2	$K_2S_2O_8$	100	31	49
3	$2KHSO_5.KHSO_4.K_2SO_4$	100	2	98
4	ZnO_2	5	0	5
5	$NaBO_3.4H_2O$	42	0	23
6	$^tBuOO^tBu$	73	0	73
7	^tBuOOH	91	14	56
8	**$Na_2S_2O_8$**	**100**	**68**	**28**
9	$(NH_4)_2S_2O_8$	1	0	1

[a] Reaction conditions: **1a** (0.5 mmol), oxidant (0.5 mmol) and $FeCl_3$ (0.05 mmol) in 2 mL of DMSO at 80 °C for 4 h. Yields were determined by HPLC with internal standard.

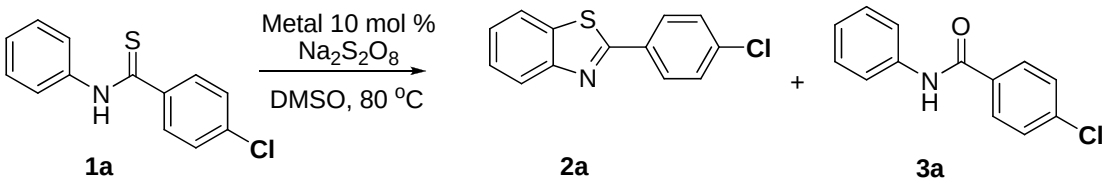
Table S2: **Solvent Effect.**[a]



Entry	Solvent	Conversion **1a**[%]	Yield[%] **2a**	**3a**
1	DMSO	100	63	29
2	DMF	38	10	26
3	Toluene	24	1	10
4	Dioxane	17	0	11
5[b]	**DMSO**	**100**	**68**	**28**

[a] Reaction conditions: **1a** (0.5 mmol), $Na_2S_2O_8$ (0.5 mmol) and $FeCl_3$ (0.05 mmol) in 2 mL dry solvent at 80 °C for 4 h. Yields were determined by HPLC with internal standard. [b] DMSO without distillation.

Table S3: **Catalyst Effect.**[a]



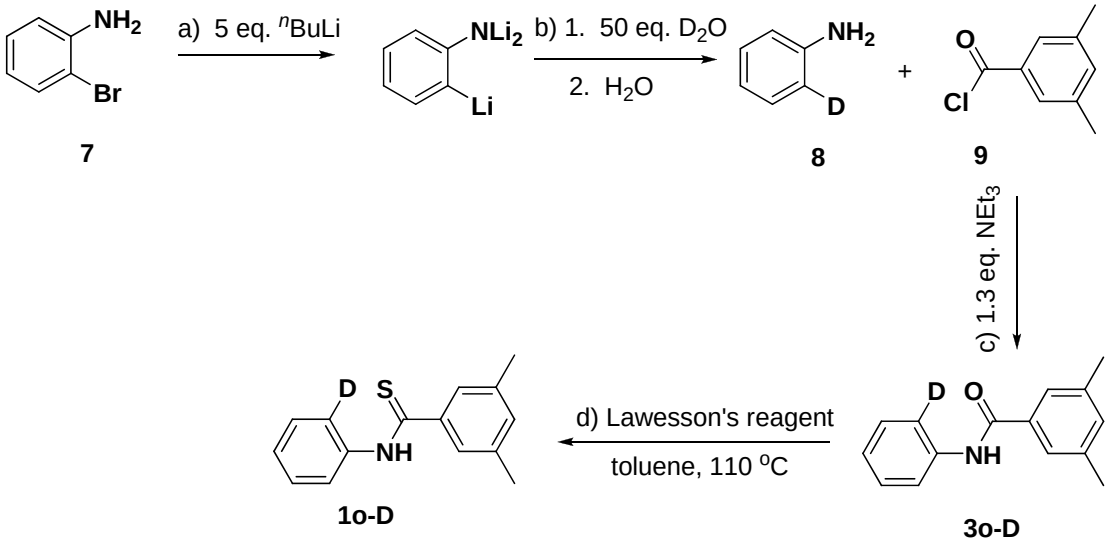
1a **2a** **3a**

Entry	Oxidant	Conversion **1a**[%]	Yield[%]	
			2a	**3a**
1	$PdCl_2(PPh_3)_2$	100	7	79
2	$NiCl_2(PPh_3)_2$	100	15	67
3	CuI	100	1	47
4	$CuCl_2$	100	13	66
5	$MnCl_2{\cdot}3H_2O$	100	21	70
6	$CoCl_2$	100	15	70
7	**$FeCl_3$**	**100**	**68**	**28**
8	no	100	16	81

[a] Reaction conditions: **1a** (0.5 mmol), $Na_2S_2O_8$ (0.5 mmol) and catalyst (0.05 mmol) in 2 mL DMSO 80 °C for 4 h. Yields were determined by HPLC with internal standard.

3. Isotope Effect Experiments

3.1. Preparation of **1o-D**



Scheme S1. Preparation of **1o-D**. a) added 5 equiv. nBuLi at -78 °C and stirred for 1h, then warmed to rt and stirred for 1h; b) added 50 equiv. D_2O at -78 °C, then warmed to rtstirred for 1h, qenched with water; c) added 1.1 equiv. **9** to the mixture of pure **8** and 1.3 equiv. NEt_3 at rt; d) 0.55 equiv. Lawesson's Reagent, refluxed in toluene for 3 h.

Preparation 2-deuterium aniline (**8**): A Schlenk flask equipped with a stir-bar was purged with nitrogen. 2-Bromoaniline (5.16 g, 30.0 mmol) and 30 mL of anhydrous THF was added to the reaction flask via a syringe and then ^{n}BuLi (62.5 mL, 150 mmol, 2.4 M) was added to the mixture at -78 °C. After stirring at -78 °C for 1 h, the mixture was warmed to rt and stirred for 1 h. Then D_2O (1.5 mol) was adding to the reaction mixture at -78 °C, which was warmed to rt and kept at rt for 1 h. Finally the reaction mixture was quenched with water and extracted with ethyl acetate (100 mL x 2). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph (ethyl acetate/ petroleum ether = 1 : 40) to obtain the compound **8** 0.62 g (yield 22%).

Preparation N-(2-deuterium phenyl)-3,5-dimethylbenzothiozamide (**1o-D**): To a 50 mL flask equipped with a stir-bar was added compound **8** (0.4744 g, 5.0 mmol), NEt_3 (0.6868 g, 6.5 mmol) and 10 mL of CH_2Cl_2. Then 3,5-dimethylbenzoyl chloride (0.9555 g, 5.5 mmol) was added slowly at rt. 3 h later, the reaction mixture was washed with water and extracted with CH_2Cl_2 (20 mL x 2). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to obtain the crude **3o-D**. A Schlenk flask equipped with a stir-bar was charged with **3o-D** (0.9012 g, 4.0 mmol) and Lawesson's reagent (0.8720 g, 2.1 mmol). After that, the reaction flask was purged with nitrogen. Then 5 mL of anhydrous toluene was added to the reaction tube via a syringe. The resulting mixture was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction mixture was directly purified by neutral alumina column chromatography (ethyl acetate/ petroleum ether = 1 : 4) to obtain the **1o-D** 0.8024 g (yield 83%). Comparing the ^{1}H NMR spectra of **1o-D** (**Figure S2**) and **1o (Figure S1), 76% deuterium** was contained.

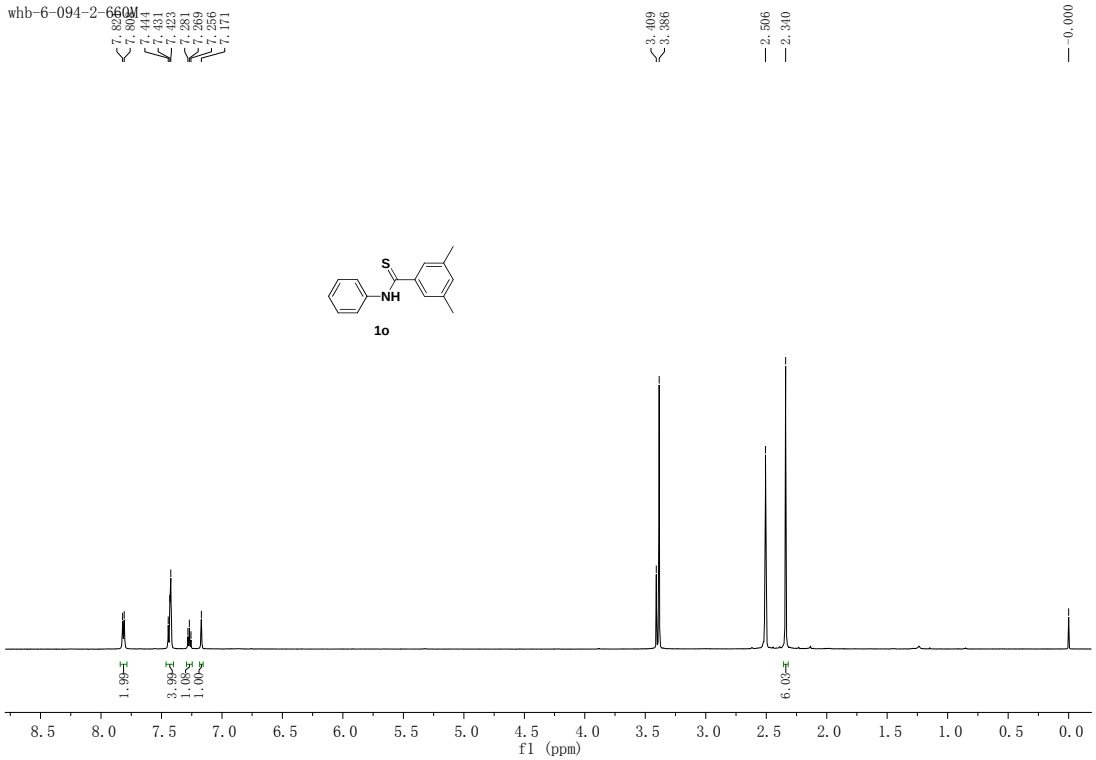


Figure S1. ^{1}H NMR spectrum of **1o**.

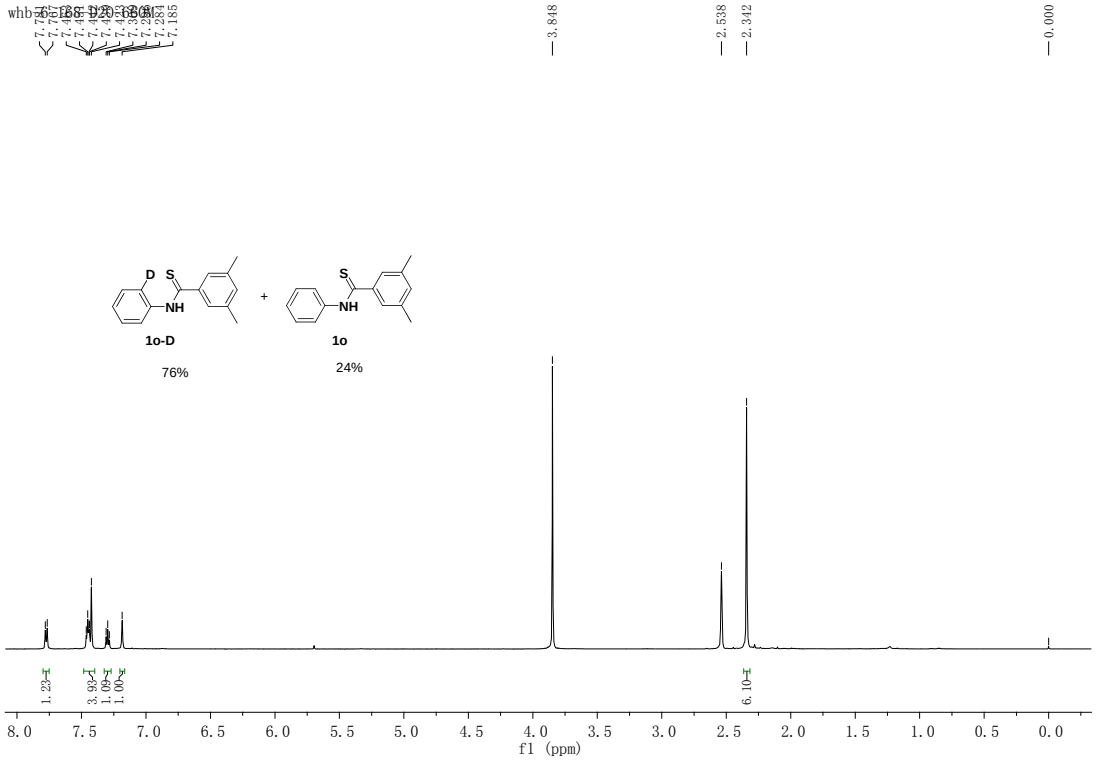


Figure S2. ^{1}H NMR spectrum of **1o-D and 1o**.

3.2. Kinetic Isotope Effect of 1o-D under the standard condition.

A Schlenk tube equipped with a stir-bar was charged with $FeCl_3$ (0.05 mmol), **1o-D** (120.9 mg, 0.50 mmol, **76% of deuterium**) and $Na_2S_2O_8$ (124.1 mg, 0.50 mmol). After that, the reaction tube was purged with nitrogen. Then pyridine (1.0 mmol) and 2 mL of DMSO was added to the reaction tube via a syringe. Finally, the Schlenk tube was warmed to 80 ^oC and stirred for 3 hours. Then the reaction mixture was quenched with water and extracted with ethyl acetate (20 mL x 2). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph (ethyl acetate/ petroleum ether = 1 : 20) to yield the desired product **2o-D** 111.4 mg (yield 93%). Comparing the ^1H NMR spectra of **2o-D** (**Figure S4**) and **2o (Figure S3),** we found the ratio of **2o-D** : **2o (only generate from 1o-D)** was 57 : 43. **So the KIE value was 1.3**.

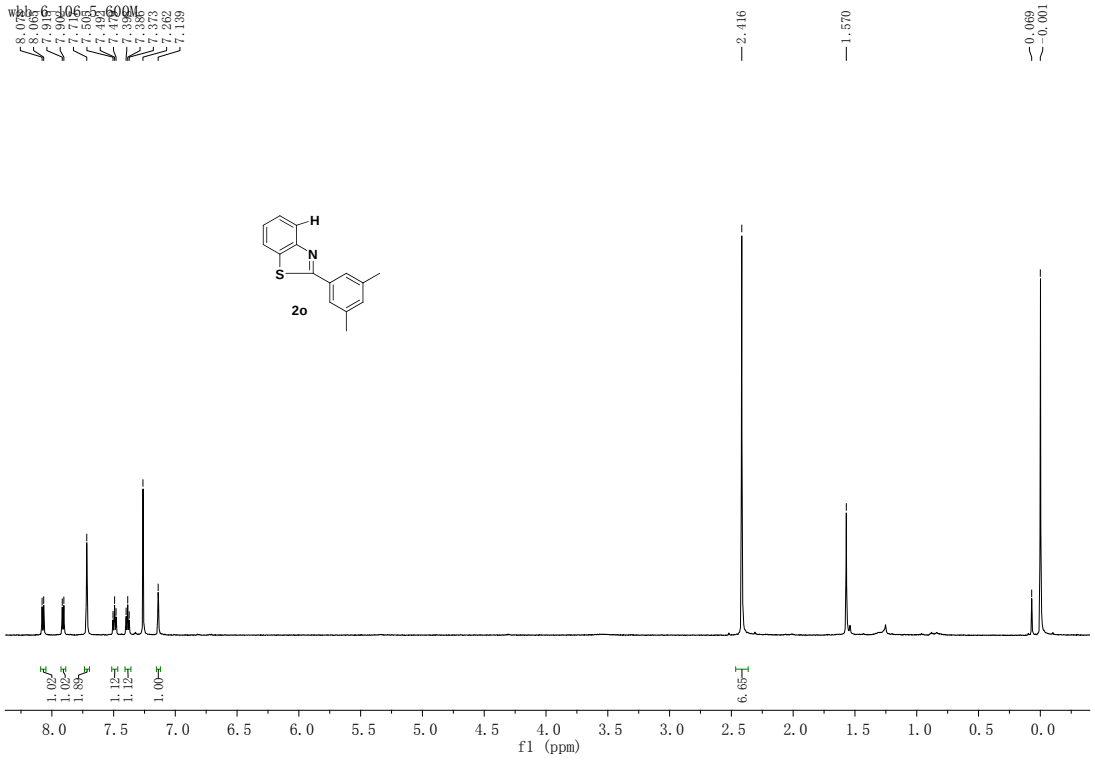


Figure S3. ^1H NMR spectrum of **2o**.

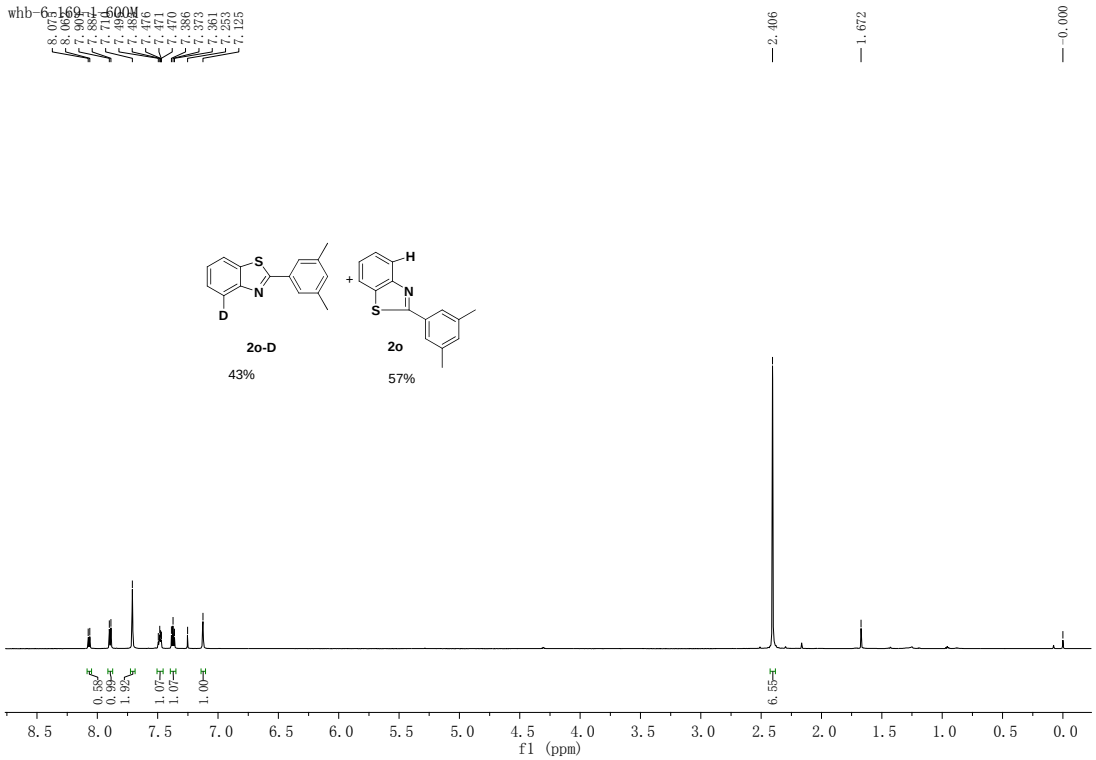


Figure S4. ^{1}H NMR spectrum of **2o and 2o-D**.

4. Experiments Monitor by *in-situ* IR

4.1. Stoichiometric reactions monitor by *in-situ* IR.

General Procedure for Stoichiometric reactions of Fe-Catalyzed Oxidative C-H Functionalization / C-S Bond Formation with 4-chloro-N-phenylbenzothioamide (1a) (1.0 mmol scale) monitored by *in-situ* IR: A three-necked tube equipped with a stir-bar was fixed on the *in situ* IR and purged with nitrogen gas. At 40 ^{o}C, 5 mL of DMSO was added to the reaction tube via a syringe, and then pyridine, 4-chloro-N-phenylbenzothioamide **(1a),** $FeCl_3$ were added to the tube in differrent sequences. 2h later, the reaction was then cooled to room temperature and the yield was determined by HPLC.

Stoichiometric reactions with $Na_2S_2O_8$ (1.0 mmol), pyriding (20 mmol,), $FeCl_3$ (1.0 mmol) and 1a (1.0 mmol) added in sequence: kinetic profiles of the stoichiometric reaction were shown in Figure S6 and Figure S7.

As shown in Figure S6, observing the peak 1269 cm^{-1} (assigned as the oxidant $Na_2S_2O_8$ by comparing with authentic sample in DMSO, which was showed in Figure S5), we could known that dissolving of $Na_2S_2O_8$ in DMSO required ca. 5 minutes, no change was observed when pyridine and $FeCl_3$ were added. However, it was interesting to note that the peak was rapidly decreased only as soon as the substrate **1a** was introduced. Figure S7 further revealed the interaction between the oxidant, Fe-catalyst and substrate **1a** more clearly. The profiles of ConcIRT vs time shown in the figure S7 represented the relative concentrations vs time for individual species. It was clear that no reaction occurred when $Na_2S_2O_8$, pyridine and $FeCl_3$ were mixed together. However, as soon as **1a** was added, $Na_2S_2O_8$ and **1a** were consumed rapidly, and the desired product **2a** was formed correspondingly. We also examined others stoichoimetric reactions by varying the addition sequences of these species (Figure S8 and Figure S9), and concluded that **the C-H activation and C-S bond formation only occurred when $Na_2S_2O_8$, $FeCl_3$ and 1a were mixed together.**

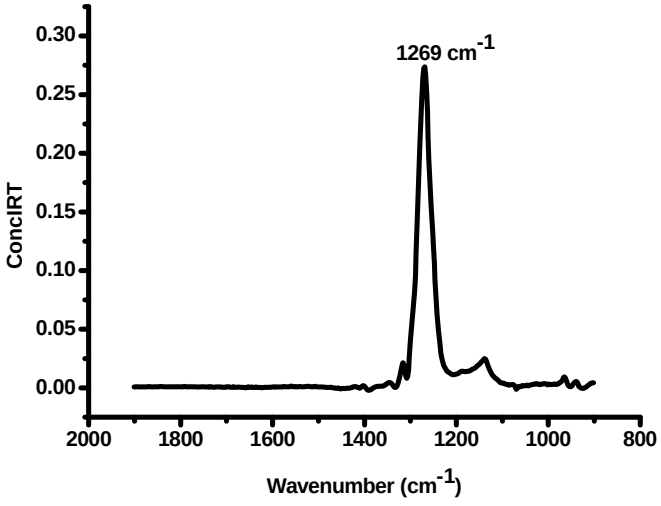


Figure S5. The IR spectrum of the $Na_2S_2O_8$ mornitored by in situ IR.

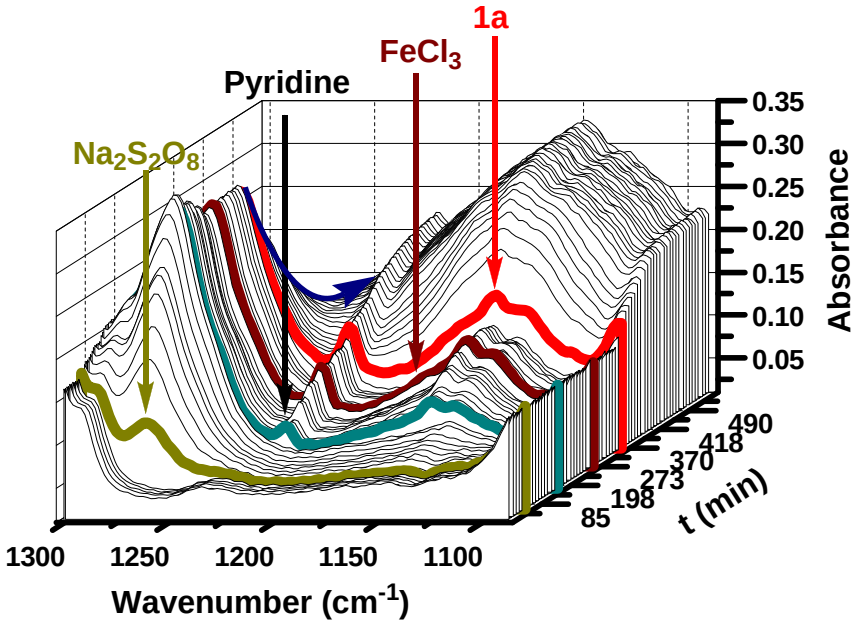


Figure S6. The 3D-kinetic profiles of the stoichiometric reaction in the sequence of $Na_2S_2O_8$ (1.0 mmol), pyridine (20 mmol,), $FeCl_3$ (1.0 mmol) and **1a** (1.0 mmol) was monitored by in situ IR

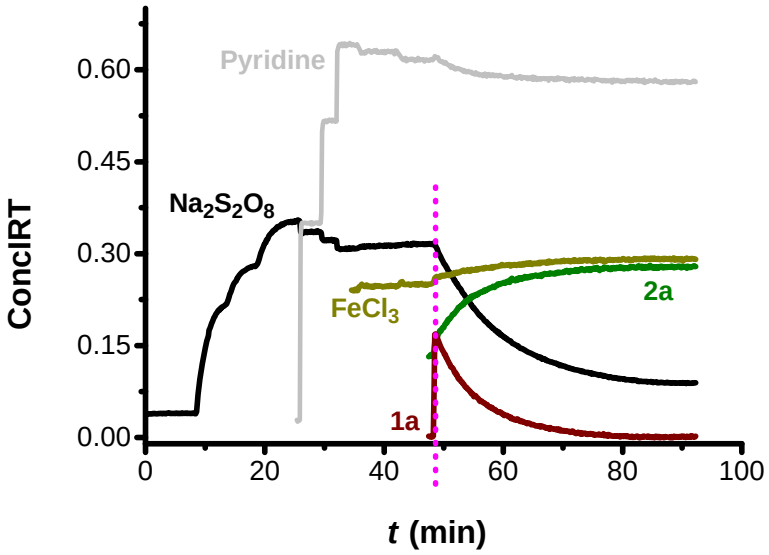


Figure S7. The 2D-kinetic profiles of the stoichiometric reaction in the adding sequence of $Na_2S_2O_8$ (1.0 mmol), pyridine (20 mmol,), $FeCl_3$ (1.0 mmol) and **1a** (1.0 mmol) was mornitored by in situ IR.

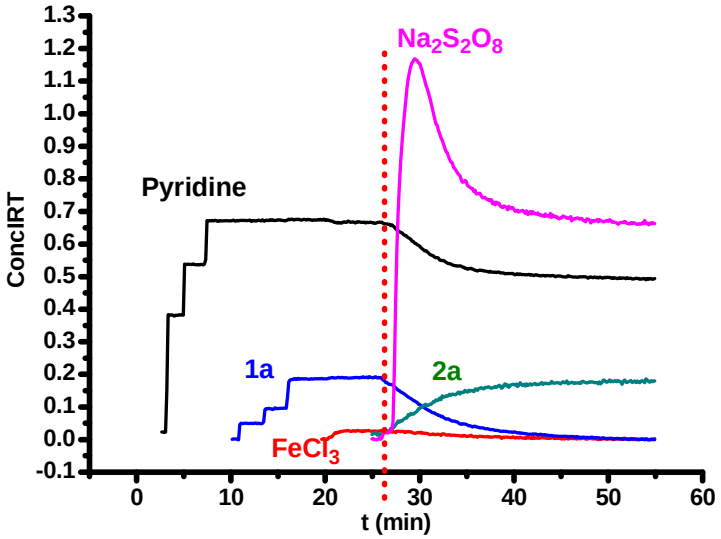


Figure S8. The 2D-kinetic profiles of the stoichiometric reaction in the adding sequence of pyridine (20 mmol), **1a** (1.0 mmol), $FeCl_3$ (1.0 mmol), and $Na_2S_2O_8$ (1.0 mmol) was monitored by in situ IR.

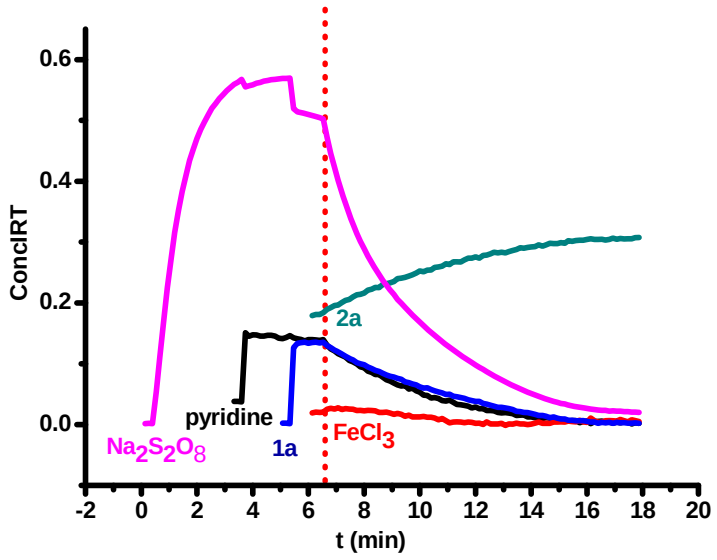


Figure S9. The 2D-kinetic profiles of the stoichiometric reaction in the adding sequence of $Na_2S_2O_8$ (1.0 mmol), pyridine (2.0 mmol), **1a** (1.0 mmol), and $FeCl_3$ (0.1 mmol) was monitored by in situ IR.

4.2. Kinetic order investigation by *in-situ* IR. (Results see Table S4 , Figure S10 - S17)

General Procedure for the investigation of Fe-Catalyzed Oxidative C-H Functionalization / C-S Bond Formation with 4-chloro-N-phenylbenzothioamide (1a) (1.0 mmol) monitored by *in-situ* IR: A three-neck tube equipped with a stir-bar and $Na_2S_2O_8$ was fixed on the *in situ* IR and purged with nitrogen gas At 40 ^oC, 4 mL of DMSO was added to the reaction tube via a syringe, and then the reactants and catalyst in DMSO were added to the tube in the sequence of pyridine (2.0 mmol), 4-chloro-N-phenylbenzothioamide **(1a),** $FeCl_3$ (0.10 mmol). 2 h later, the reaction was then cooled to room temperature and the yield was determined by HPLC.

Table S4, entry 1-4, Figure S10-A and Figure S11-S14 indicated clearly that the reaction was first order in [**1a**], and Table S4, entry 3, 5-7, Figure S10-B and Figure S13, S15-S17 revealed that zero order in [$Na_2S_2O_8$].

Table S4 Reaction rates in different concentrations of **1a** and $Na_2S_2O_8$

Entry	[**1a**](mol*L^{-1})	[$Na_2S_2O_8$](mol*L^{-1})	rate(mol*L^{-1}*min^{-1})
1	0.20	0.20	$1.56*10^{-2}$
2	0.15	0.20	$1.22*10^{-2}$
3	0.10	0.20	$9.25*10^{-3}$
4	0.06	0.20	$5.23*10^{-3}$
5	0.10	0.25	$8.45*10^{-3}$
6	0.10	0.15	$8.66*10^{-3}$
7	0.10	0.10	$8.32*10^{-3}$

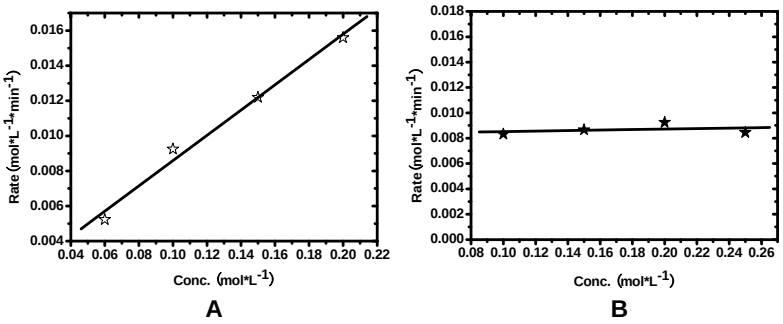


Figure S10. Order kinetic experiment dependence on [**1a**] and [$Na_2S_2O_8$]; **A:** first order kinetic dependence on [**1a**]; **B:** zero order kinetic dependence on [$Na_2S_2O_8$].

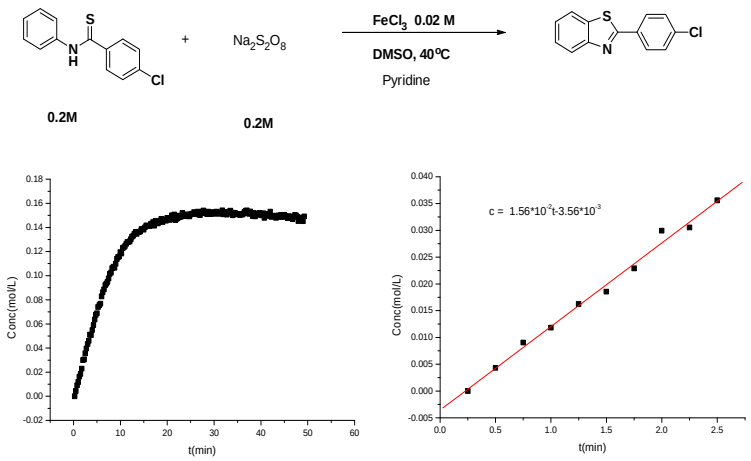


Figure S11. Order kinetic experiment with **0.20 M 1a,** 0.20 M $Na_2S_2O_8$, 0.40 M pyridine, 0.02 M $FeCl_3$.

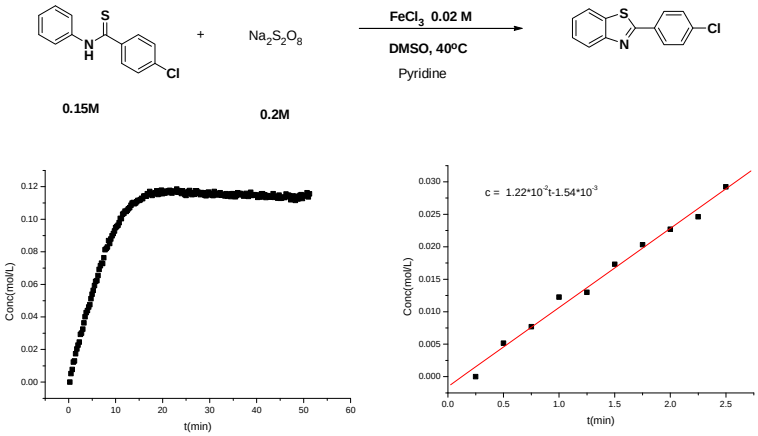


Figure S12. Order kinetic experiment with **0.15 M 1a,** 0.20 M $Na_2S_2O_8$, 0.40 M pyridine, 0.02 M $FeCl_3$.

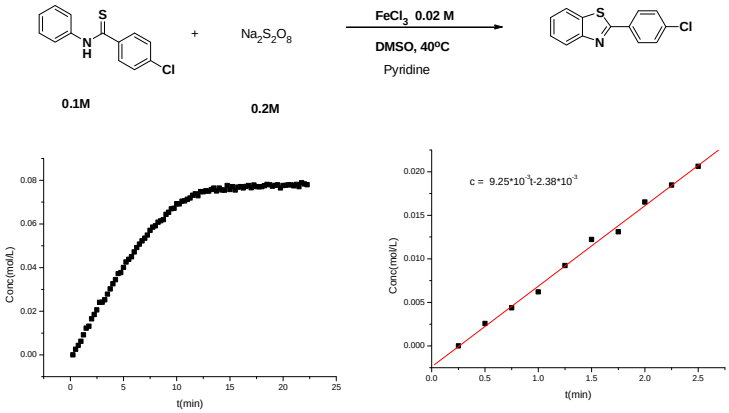


Figure S13. Order kinetic experiment with **0.10 M 1a, 0.20 M $Na_2S_2O_8$**, 0.40 M pyridine, 0.02 M $FeCl_3$.

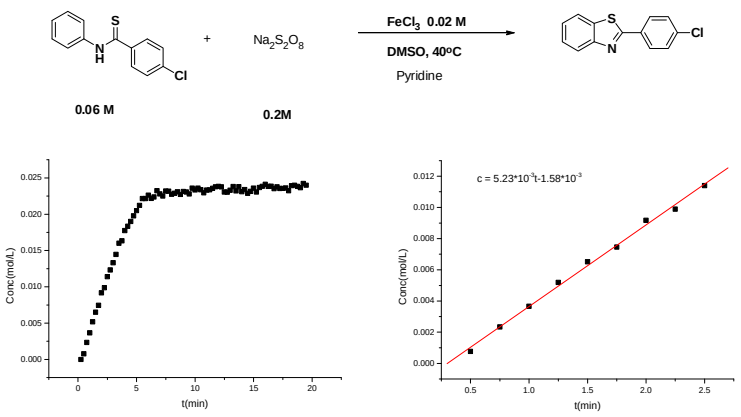


Figure S14. Order kinetic experiment with **0.06 M 1a,** 0.20 M $Na_2S_2O_8$, 0.40 M pyridine, 0.02 M $FeCl_3$.

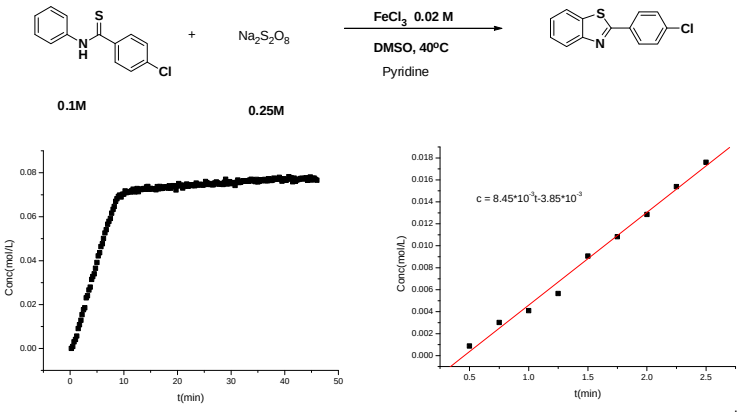


Figure S15. Order kinetic experiment with 0.10 M **1a**, **0.25 M $Na_2S_2O_8$**, 0.40 M pyridine, 0.02 M $FeCl_3$.

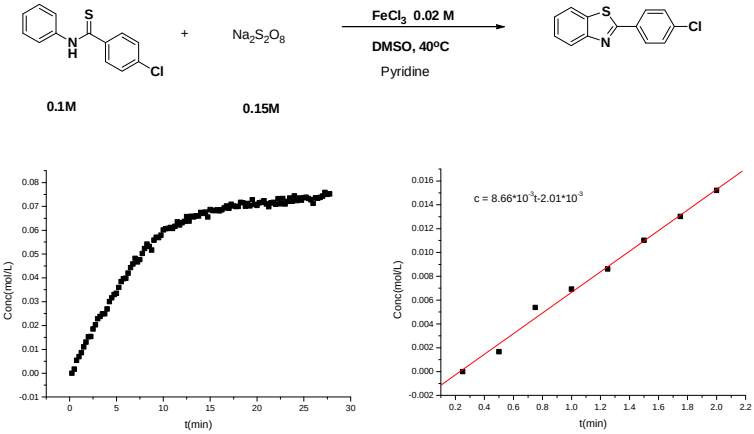


Figure S16. Order kinetic experiment with 0.10 M **1a**, **0.15 M $Na_2S_2O_8$**, 0.40 M pyridine, 0.02 M $FeCl_3$.

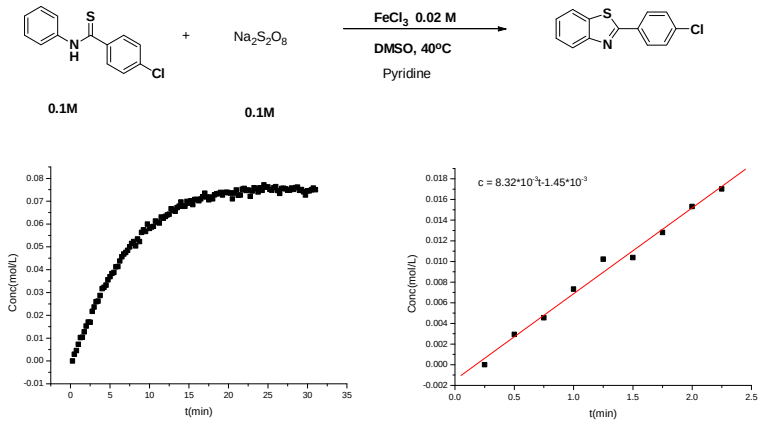


Figure S17. Order kinetic experiment with 0.10 M **1a**, **0.10 M $Na_2S_2O_8$**, 0.40 M pyridine, 0.02 M $FeCl_3$.

4.3. Kinetic profiles of the comparison reaction was monitored by *in situ* IR

General procedure: A three-necked tube equipped with a stir-bar was charged with $FeCl_3$ (0.05 mmol), **1a** (0.50 mmol) and $Na_2S_2O_8$ (0.50 mmol). The tube was then fixed on the *in situ* IR and purged with nitrogen gas. At 40 ^oC, 5 mL of DMSO was then added to the reaction tube via a syringe. 4h later, the reaction was then cooled to room temperature and the yield was determined by HPLC. Figure S18 indicated that at the first stage, the C-H activation product **2a** was gained in high selectivity (red line of Figure S18). 30 minutes later, **3a** was produced mainly**.** Finally, we obtained 40% C-H activation /C-S bond forming product **2a** and 56% of 4-chloro-N-phenylbenzamide (**3a**).

In order to reveal the role of $FeCl_3$ and pyridine in the reaction more clearly, we carried out comparison experiments monitored by *in situ* IR.. Figure S18 showed the reaction profile of **1a**, $Na_2S_2O_8$ and pyridine with and without $FeCl_3$ catalyst. Almost no reaction took place without catalyst $FeCl_3$ (Figure S18, black line).

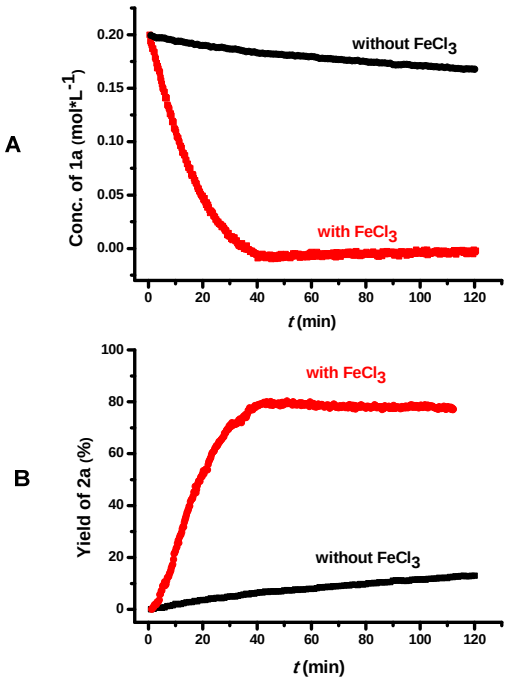


Figure S18. The reactions with $FeCl_3$ (0.2 mmol) or without catalyst between **1a** (2.0 mmol), pyridine (4.0 mmol) and $Na_2S_2O_8$ (2.0 mmol) in 10 mL DMSO at 40 ^oC monitored by *in situ* IR. **A:** the concentration of **1a** *vs* time (red

line is with $FeCl_3$ and black line is without $FeCl_3$); **B:** the yield of product **2a** *vs* time (red line is with $FeCl_3$ and black line is without $FeCl_3$).

Furthermore, we also compared the reaction of **1a**, $Na_2S_2O_8$, $FeCl_3$ with pyridine and without pyridine. As shown in Figure S19, the reaction without pyridine (Figure S19, black line) has slower rate and lower yield(40%, and 56% byproduct 4-chloro-*N*-phenylbenzamide (**3a**) as well).

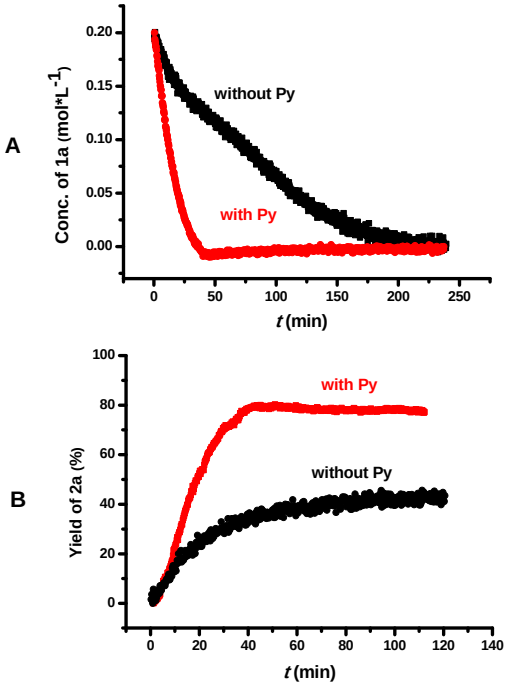


Figure S19. The reactions with or without pyridine between **1a** (2.0 mmol), $FeCl_3$ (0.2 mmol) and $Na_2S_2O_8$ (2.0 mmol) in 10 mL DMSO at 40 ^oC monitored by *in situ* IR. **A:** the concentration of **1a** *vs* time (red line is with pyridine and black line is without pyridine); **B:** the yield of product **2a** *vs* time (red line is with pyridine and black line is without pyridine).

In addition, we found the distribution of products were also interesting. In the first stage of the reaction, the C-H activation product was gained with high selectivity (red line of Figure S20). After around 30 minutes, the reaction turned to mainly produce **3a**. We could conclude that pyridine is critical to the high yields and high selectivities of C-H activation/C-S bond formation, but so far we have no enough data to rationalize the phenomena in the Figure S20.

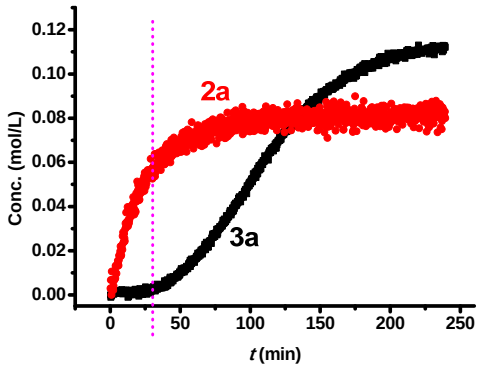
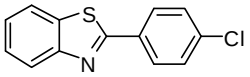


Figure S20. The kinetic profiles of the reaction between $Na_2S_2O_8$ (0.2 M), $FeCl_3$ (0.02 M) and **1a** (0.2 M) without pyridine was mornitored by in situ IR.

5. Analytical Data of Benzothiazoles

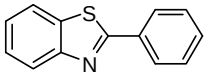
General procedure for Fe-Catalyzed Oxidative C-H Functionalization/C-S Bond Formation (Table 2, entry 1): A Schlenk tube equipped with a stir-bar was charged with $FeCl_3$ (8.3 mg, 0.01 mmol), **1b** (107.4mg, 0.50 mmol) and $Na_2S_2O_8$ (122.5 mg, 1.0 mmol). The reaction tube was purged with nitrogen. Then pyridine (79.0 mg, 1.0 mmol) and 2 mL of DMSO was added to the reaction tube via a syringe. The mixture was stirred at 80 ^oC for 3h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (20 mL x 2). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph (ethyl acetate/ petroleum ether = 1: 20) to yield the desired product **2b** (95.1 mg, 89%).

2-(4-chlorophenyl)benzothiazole[1] (2a)



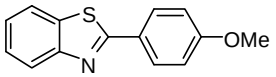
^1H NMR (300 MHz, $CDCl_3$) δ = 8.12 – 8.01 (m, 3H), 7.92 (d, J = 7.8 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.41 ppm (t, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.64, 154.12, 137.07, 135.14, 132.11, 129.32, 128.75, 126.58, 125.51, 123.40, 121.76 ppm.

2-phenylbenzothiazole[1] (2b)



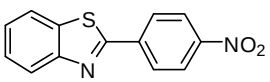
^1H NMR (300 MHz, $CDCl_3$) δ = 8.18 – 8.00 (m, 3H), 7.91 (d, J = 8.1 Hz, 1H), 7.60 – 7.44 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.95, 154.06, 134.99, 133.50 130.89, 128.94, 127.47, 126.25, 125.11, 123.16, 121.56 ppm.

2-(4-methoxyphenyl)benzothiazole[1] (2c)



^1H NMR (300 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.7 Hz, 3H), 7.88 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 3.89 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.79, 161.81, 154.16, 134.81, 130.89, 129.03, 126.15, 124.73, 122.75, 121.47, 114.26, 55.33 ppm.

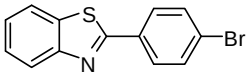
2-(4-nitrophenyl)benzothiazole (2d)



^1H NMR (300 MHz, $CDCl_3$) δ = 8.35 (d, J = 8.4 Hz, 2H), 8.26 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 ppm (t, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.97, 154.25, 149.17, 139.32, 135.63, 128.38, 127.07, 126.37, 124.46, 124.09, 121.98 ppm; HRMS (APCI) calcd for $C_{13}H_8N_2O_2S$ $[M]^+$: 256.0307; found

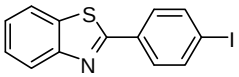
256.0304.

2-(4-bromophenyl)benzothiazole[2] (2e)



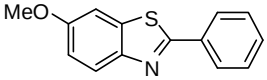
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.7 Hz, 1H), 7.41 ppm (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.59, 153.98, 134.98, 132.40, 132.14, 128.81, 126.47, 125.41, 123.28, 121.64 ppm.

2-(4-iodophenyl)benzothiazole[3] (2f)



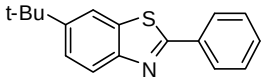
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.88 – 7.80 (m, 4H), 7.51 (t, J = 7.2 Hz, 1H), 7.41 ppm (t, J = 7.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.89, 154.05, 138.19, 135.00, 133.05, 128.94, 126.56, 125.52, 123.35, 121.74, 97.64 ppm.

6-methoxy-2-phenylbenzothiazole[1] (2g)



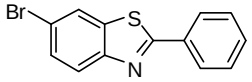
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.09 – 8.02 (m, 2H), 7.96 (d, J = 9.0 Hz, 1H), 7.57 – 7.43 (m, 3H), 7.37 (d, J = 2.1 Hz, 1H), 7.10 (dd, J = 8.9, 2.3 Hz, 1H), 3.90 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.96, 153.20, 144.13, 131.91, 129.20, 126.01, 124.45, 122.68, 119.18, 111.15, 99.51, 51.18 ppm.

6-tert-butyl-2-phenylbenzothiazole (2h)



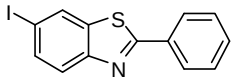
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96 – 7.89 (m, 2H), 7.86 (d, J = 8.7 Hz, 1H), 7.71 (s, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.31 – 7.23 (m, 3H), 1.22 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.35, 152.11, 148.60, 135.10, 133.75, 130.70, 128.93, 127.41, 124.49, 122.55, 117.67, 35.02, 31.54 ppm; HRMS (APCI) calcd for $C_{17}H_{17}NS$ $[M+H]^+$: 268.1160; found 268.1157.

6-bromo-2-phenylbenzothiazole[1] (2i)



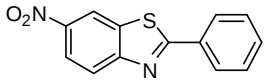
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11 – 8.02 (m, 3H), 7.92 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.51 ppm (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.47, 152.93, 136.62, 133.09, 131.25, 129.77, 129.07, 127.51, 124.26, 124.11, 118.74 ppm.

6-iodo-2-phenylbenzothiazole[1] (2j)



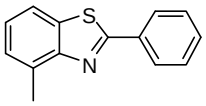
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 8.10 – 8.03 (m, 2H), 7.82 – 7.76 (m, 2H), 7.55 – 7.47 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.61, 153.57, 137.20, 135.53, 133.16, 131.44, 130.19, 129.21, 127.69, 124.77, 89.60 ppm.

6-nitro-2-phenylbenzothiazole[1] (2k)



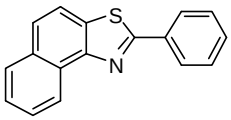
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.85 (s, 1H), 8.38 (d, J = 8.7 Hz, 1H), 8.21 – 8.06 (m, 3H), 7.63 – 7.47 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 173.92, 157.96, 144.99, 135.44, 132.81, 132.38, 129.43, 128.05, 123.45, 122.04, 118.37 ppm.

4-methyl-2-phenylbenzothiazole[4] (2l)



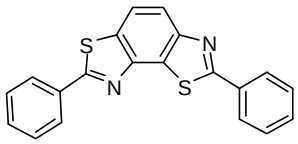
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.15 – 8.09 (m, 2H), 7.78 – 7.69 (m, 1H), 7.53 – 7.46 (m, 3H), 7.32 – 7.24 (m, 2H), 2.81 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.84, 153.95, 135.39, 134.32, 133.65, 131.02, 129.27, 127.91, 127.16, 125.45, 119.36, 18.94 ppm.

2-phenylnaphtho[1,2-d]thiazole (2m)



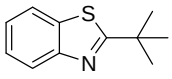
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.93 (d, J = 8.1 Hz, 1H), 8.21 (d, J = 6.3 Hz, 2H), 7.95 (t, J = 9.0 Hz, 2H), 7.82 (d, J = 8.7 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.63 – 7.48 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.88, 150.33, 133.87, 131.96, 131.61, 130.46, 128.91, 128.03, 127.21, 126.84, 126.02, 125.77, 124.02, 118.84 ppm; HRMS (APCI) calcd for $C_{17}H_{11}NS$ $[M]^+$: 261.0612; found 261.0619.

[5] (2n)



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 – 8.14 (m, 4H), 8.09 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.56 – 7.50 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.80, 168.08, 154.00, 147.87, 133.66, 133.49, 131.76, 131.28, 131.09, 129.22, 128.87, 127.63, 120.51, 119.46 ppm; HRMS (APCI) calcd for $C_{20}H_{12}N_2S_2$ $[M+H]^+$: 345.0520; found 345.0519.

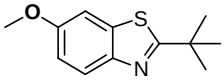
2-tert-butylbenzothiazole (5a)[6]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (d, J =6.9 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz,

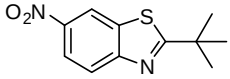
1H), 7.33 (t, *J* = 7.5 Hz, 1H), 1.52 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 181.39, 153.12, 134.80, 125.56, 124.34, 122.53, 121.26, 38.09, 30.57 ppm.

2-tert-butyl-6-methoxybenzothiazole (5b)



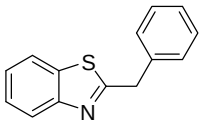
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 6.95 (dd, *J* = 9.0, 2.2 Hz, 1H), 3.76 (s, 3H), 1.41 ppm (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 179.47, 157.41, 147.87, 136.40, 123.30, 115.06, 104.35, 55.96,38.37,30.96ppm; HRMS (APCI) calcd for $C_{12}H_{15}NOS$ [M]+: 221.0874; found 221.0875.

2-tert-butyl-6-nitrobenzothiazole (5c)



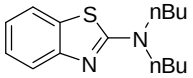
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.72 (s, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 1.48 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 188.56, 157.31, 144.76, 135.57, 123.09, 121.54, 118.30, 39.27, 30.78 ppm; HRMS (APCI) calcd for $C_{11}H_{12}N_2O_2S$ [M]+: 236.0619; found 236.0616.

2-benzylbenzothiazole (5d)[7]



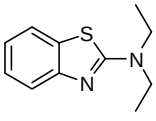
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.29 (m, 6H), 4.44 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.29, 153.36, 137.29, 135.76, 129.26, 128.97, 127.44, 126.07, 124.91, 122.87, 121.62, 40.72 ppm.

N,N-dibutylbenzothiazol-2-amine (5f)[8]



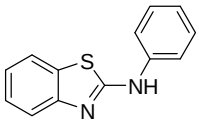
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.50 (t, *J* = 7.5 Hz, 4H), 1.77 – 1.57 (m, 4H), 1.48 – 1.31 (m, 4H), 0.97 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.67, 153.26, 130.61, 125.61, 120.49, 120.31, 118.43, 50.84, 29.53, 20.13, 13.85 ppm.

N,N-diethylbenzothiazol-2-amine (5g)[9]



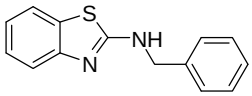
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63 – 7.46 (m, 2H), 7.33 – 7.22 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 3.58 (q, *J* = 7.2 Hz, 4H), 1.29 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.26, 153.19, 130.52, 125.76, 120.65, 120.47, 118.44, 45.32, 12.82 ppm.

N-phenylbenzothiazol-2-amine (5h)[10]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.94 (br.s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 6.9 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.22 – 7.10 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.98, 151.16, 140.15, 129.66, 126.20, 124.67, 122.29, 120.92, 119.04 ppm.

N-benzylbenzothiazol-2-amine (5i)[10]

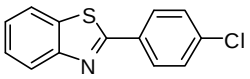


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.43 – 7.23 (m, 6H), 7.09 (t, J = 7.5 Hz, 1H), 6.06 (br.s, 1H), 4.64 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.99, 152.33, 137.59, 130.44, 128.93, 127.95, 127.76, 126.08, 121.64, 120.95, 118.88, 49.56 ppm.

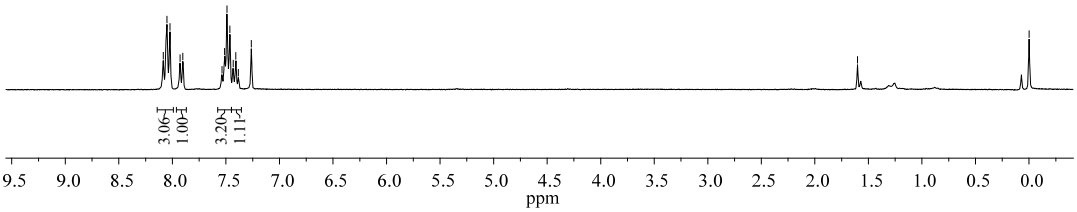
Reference

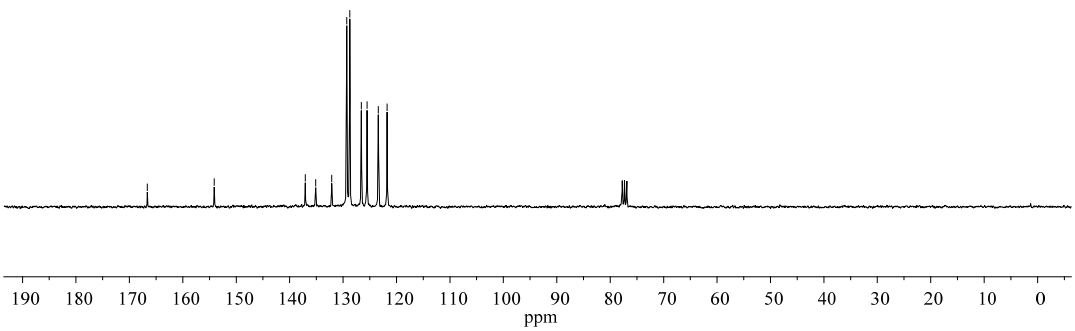
1. K. Inamoto, C. Hasegawa, K. Hiroya and T. Doi, *Org. Lett.*, 2008, **10**, 5147.
2. S. Billeau, F. Chatel, M. Robin, R. Faure and J. P. Galy, *Magn. Reson. Chem.*, 2006, **44**, 102.
3. L. Chen, C. Yang, S. Li and J. Qin, *Spectrochim Acta A Mol Biomol Spectrosc*, 2007, **68**, 317.
4. J. Perregaard and S. O. Lawesson, *Acta Chem. Scand., Ser. B*, 1977, **31**, 203.
5. G. Grandolini, A. Ricci, A. Martani and F. D. Monache, *J. Heterocycl. Chem.*, 1966, **3**, 302.
6. H. M. Walborsky and P. Ronman, *J. Org. Chem.*, 1978, **43**, 731.
7. H. Sharghi and O. Asemani, *Synth. Commun.*, 2009, **39**, 860.
8. M. W. Hooper, M. Utsunomiya and J. F. Hartwig, *J. Org. Chem.*, 2003, **68**, 2861.
9. E. Feng, H. Huang, Y. Zhou, D. Ye, H. Jiang and H. Liu, *J. Comb. Chem.*, 2010, **12**, 422.
10. J.-W. Qiu, X.-G. Zhang, R.-Y. Tang, P. Zhong and J.-H. Li, *Adv. Synth. Catal.*, 2009, **351**, 2319.

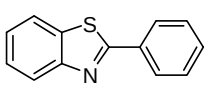
NMR Spectra of Products



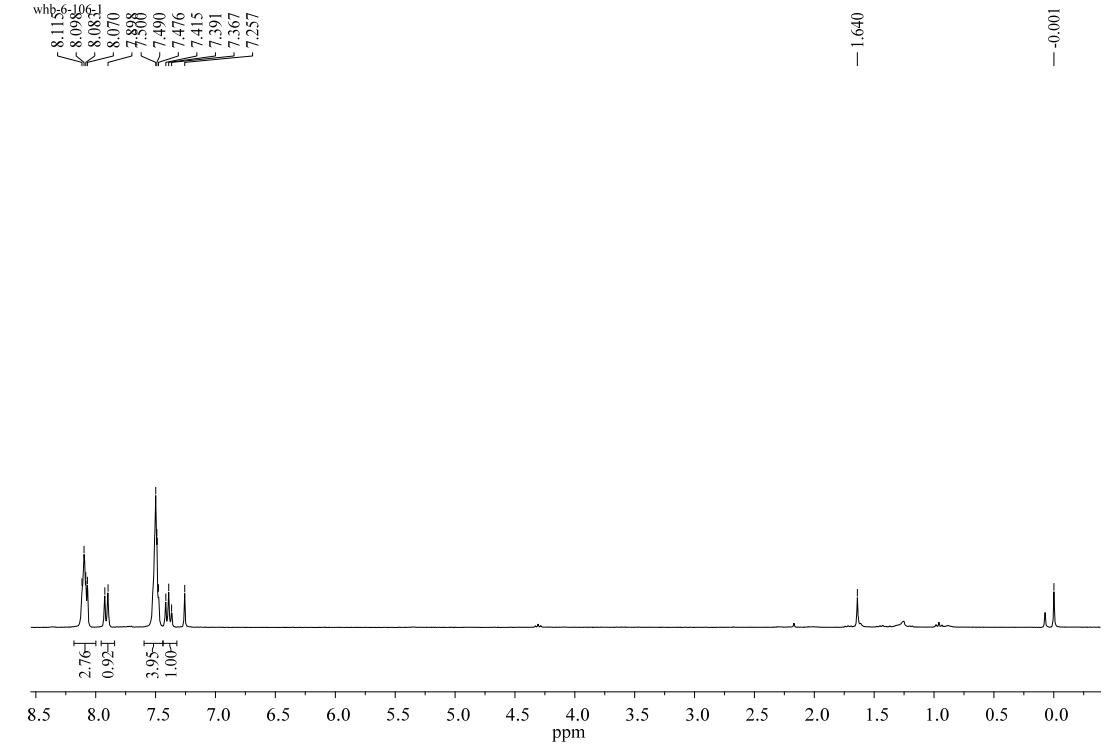
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.12 – 8.01 (m, 3H), 7.92 (d, J = 7.8 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.41 ppm (t, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.64, 154.12, 137.07, 135.14, 132.11, 129.32, 128.75, 126.58, 125.51, 123.40, 121.76 ppm.

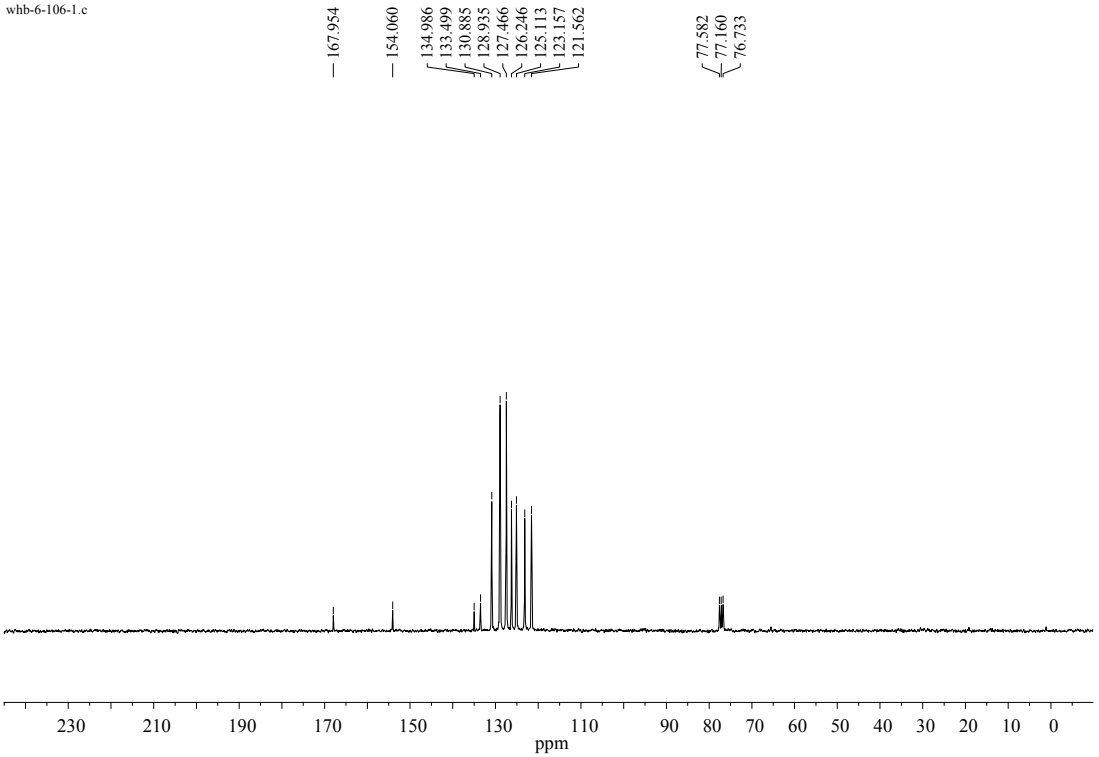


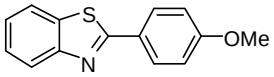




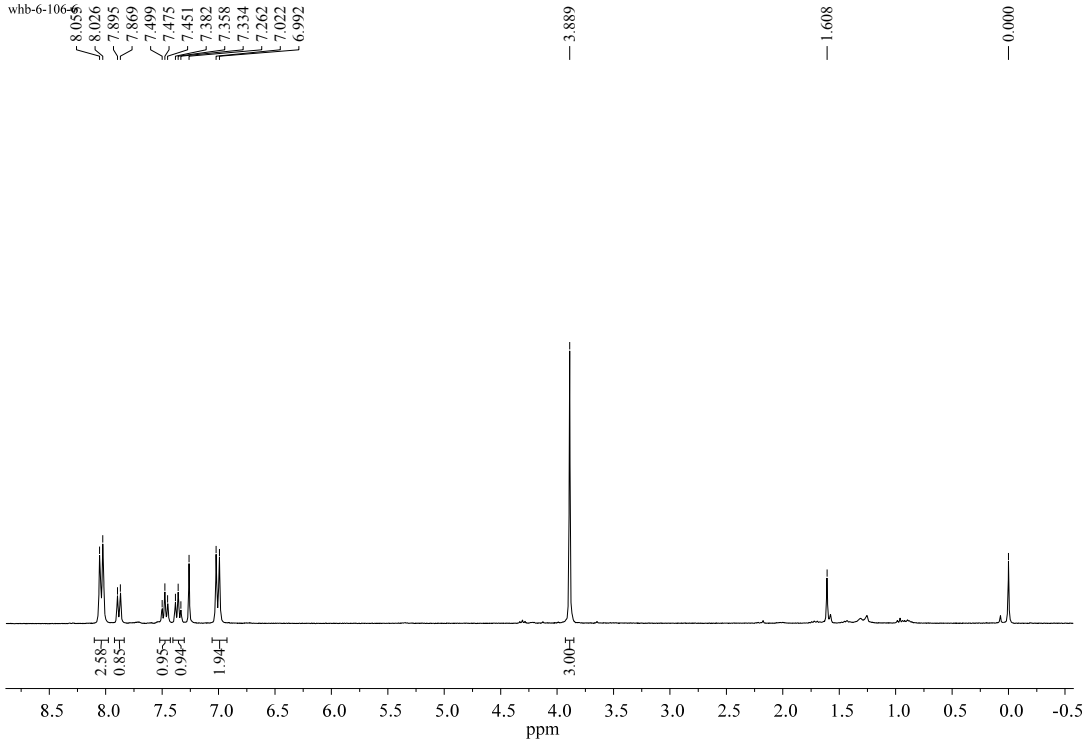
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 – 8.00 (m, 3H), 7.91 (d, J = 8.1 Hz, 1H), 7.60 – 7.44 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.95, 154.06, 134.99, 133.50 130.89, 128.94, 127.47, 126.25, 125.11, 123.16, 121.56 ppm.

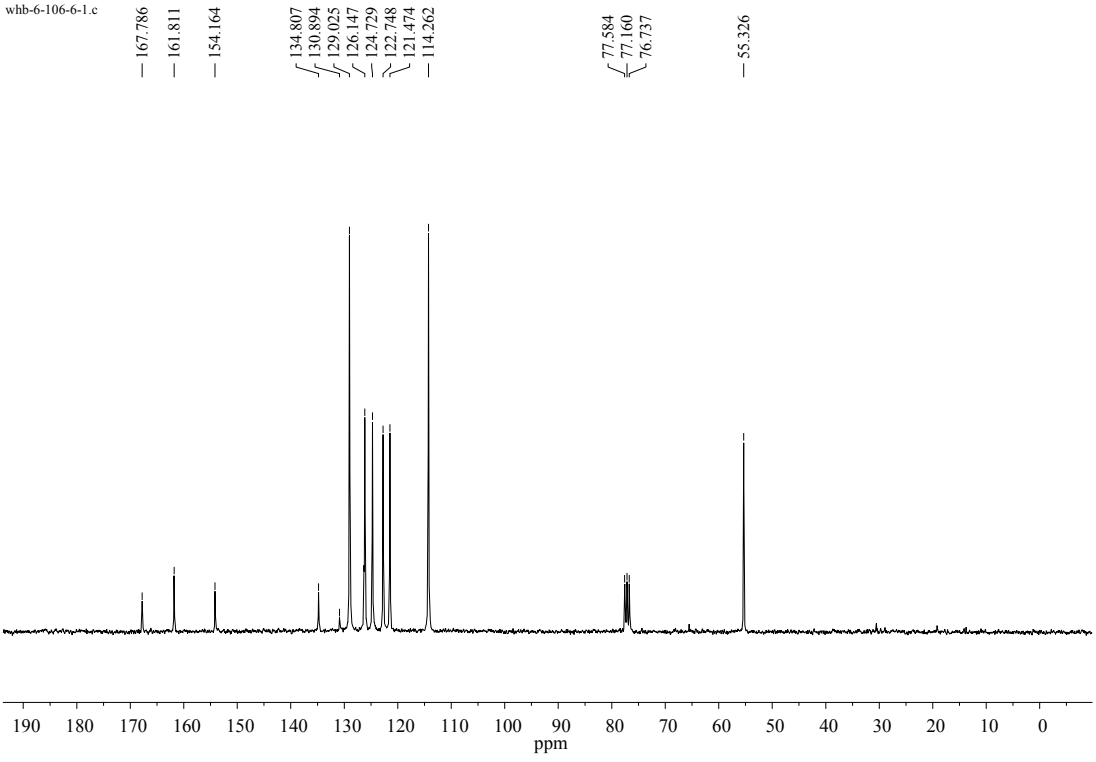


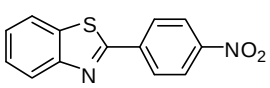




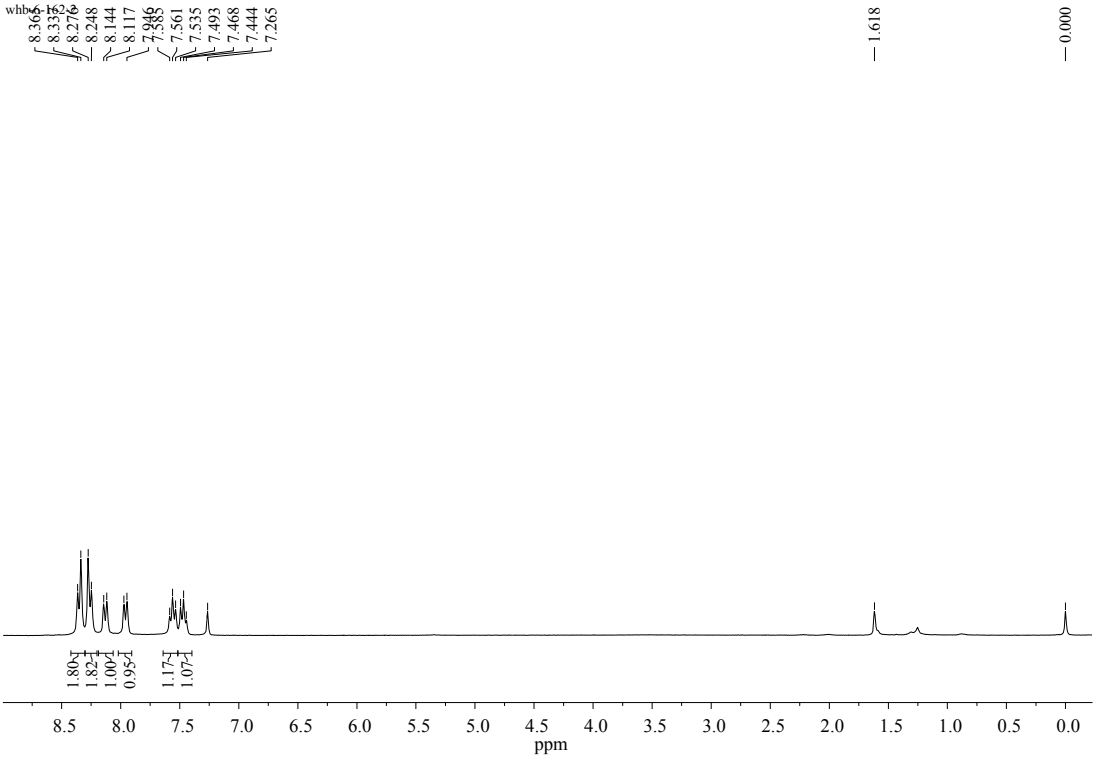
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.7 Hz, 3H), 7.88 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 3.89 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.79, 161.81, 154.16, 134.81, 130.89, 129.03, 126.15, 124.73, 122.75, 121.47, 114.26, 55.33 ppm.

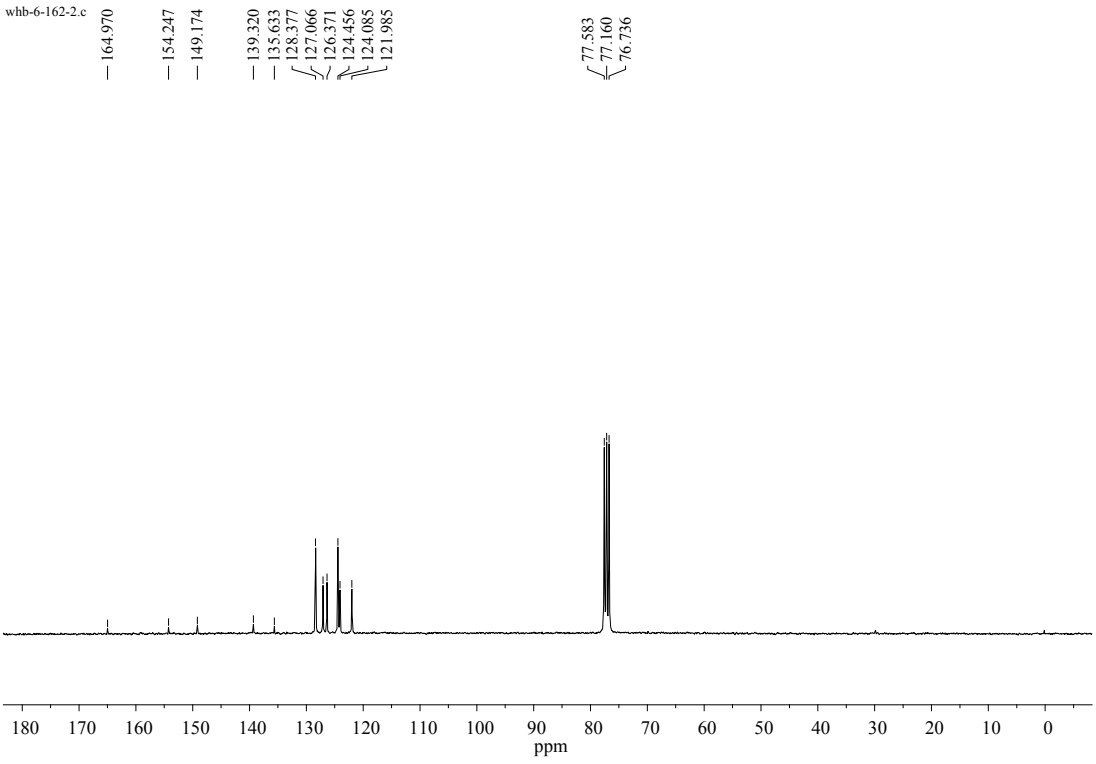


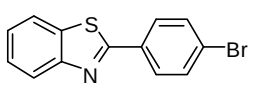




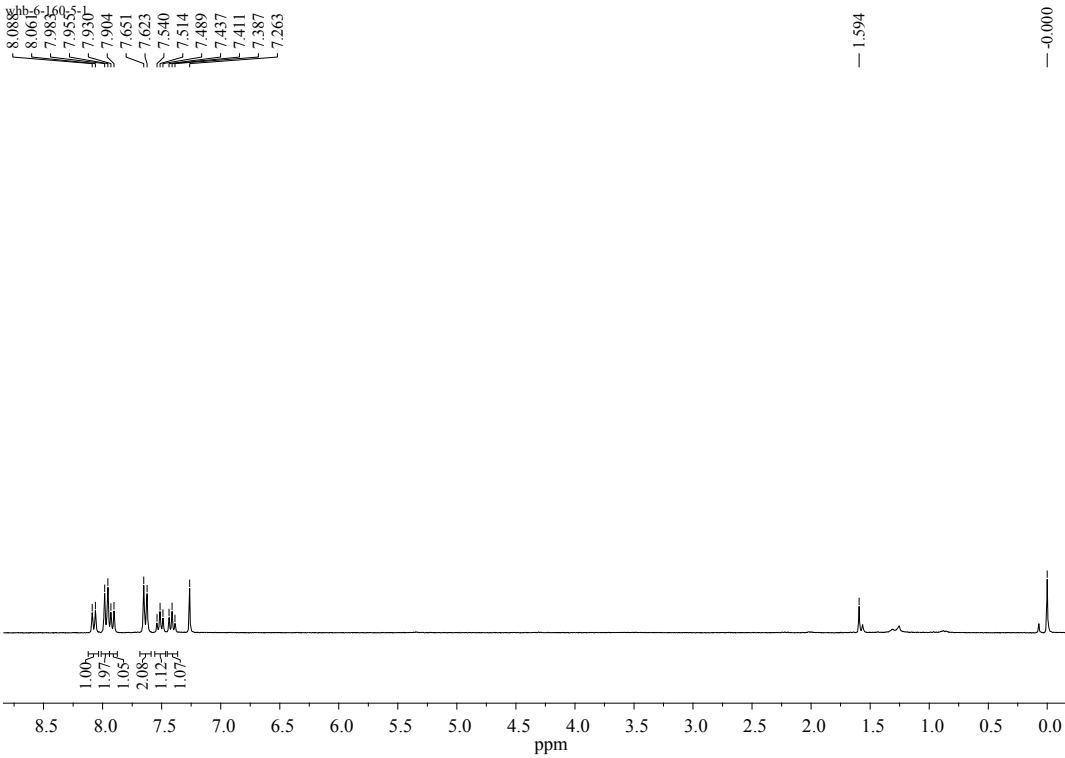
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.35 (d, J = 8.4 Hz, 2H), 8.26 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 ppm (t, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.97, 154.25, 149.17, 139.32, 135.63, 128.38, 127.07, 126.37, 124.46, 124.09, 121.98 ppm.

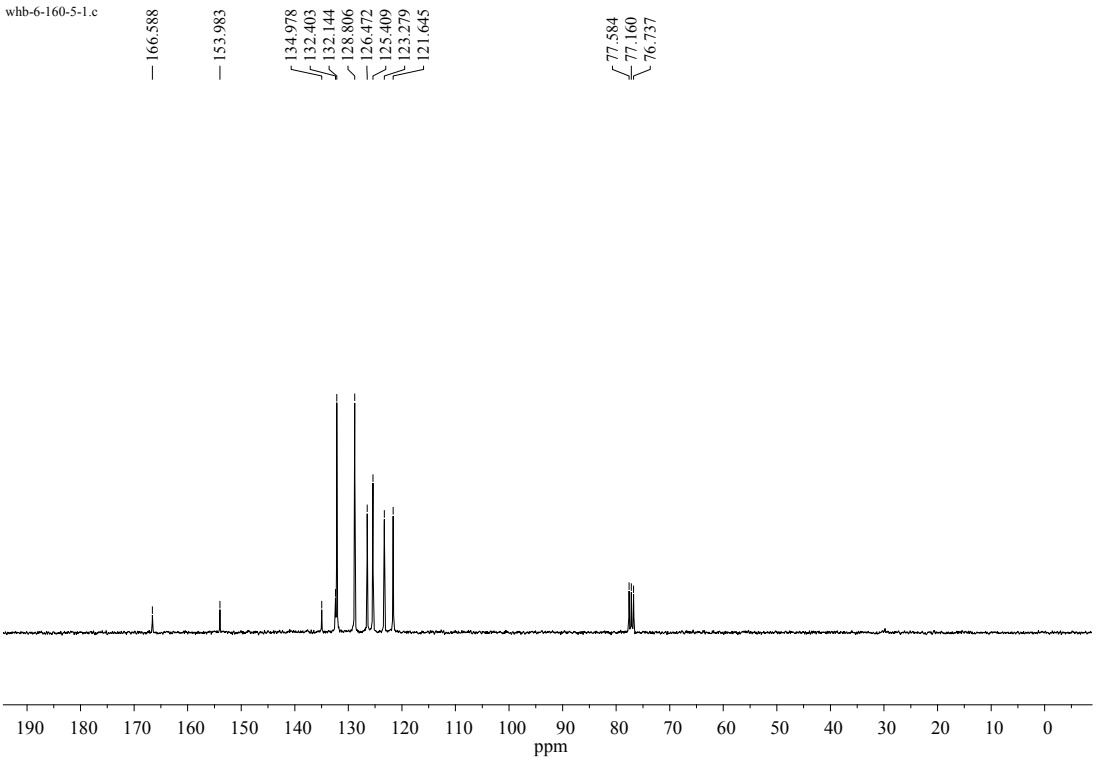


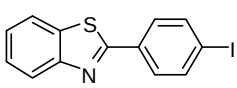




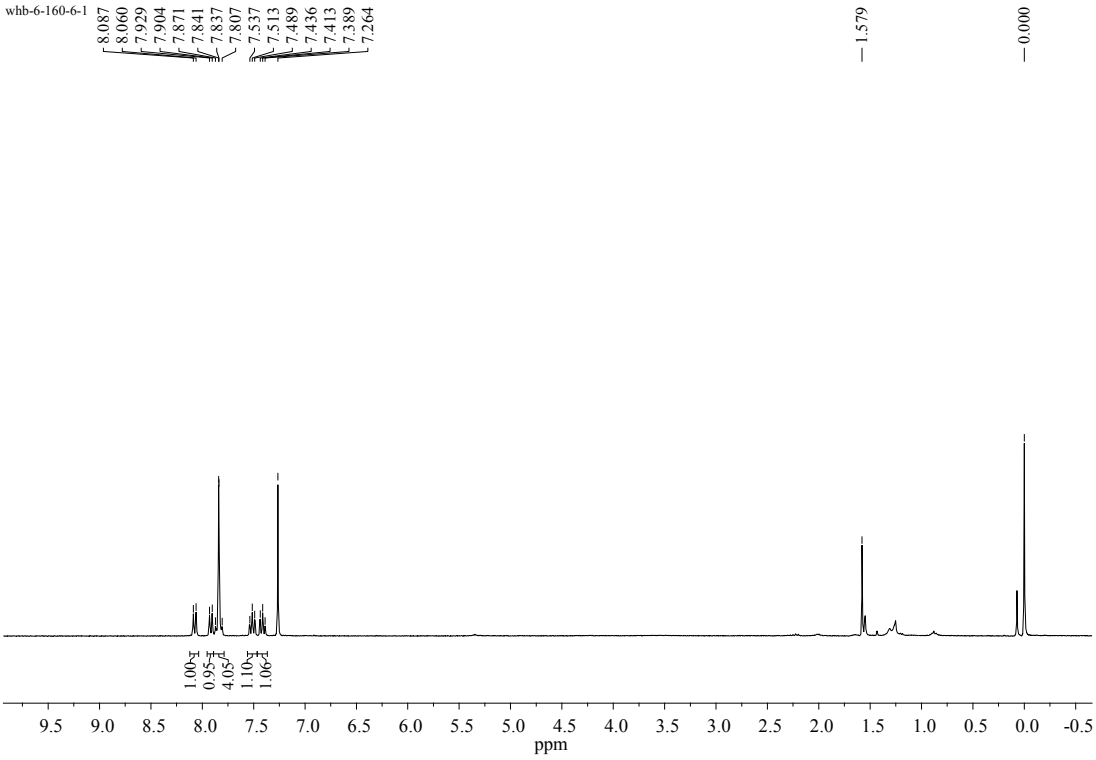
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.7 Hz, 1H), 7.41 ppm (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.59, 153.98, 134.98, 132.40, 132.14, 128.81, 126.47, 125.41, 123.28, 121.64 ppm.

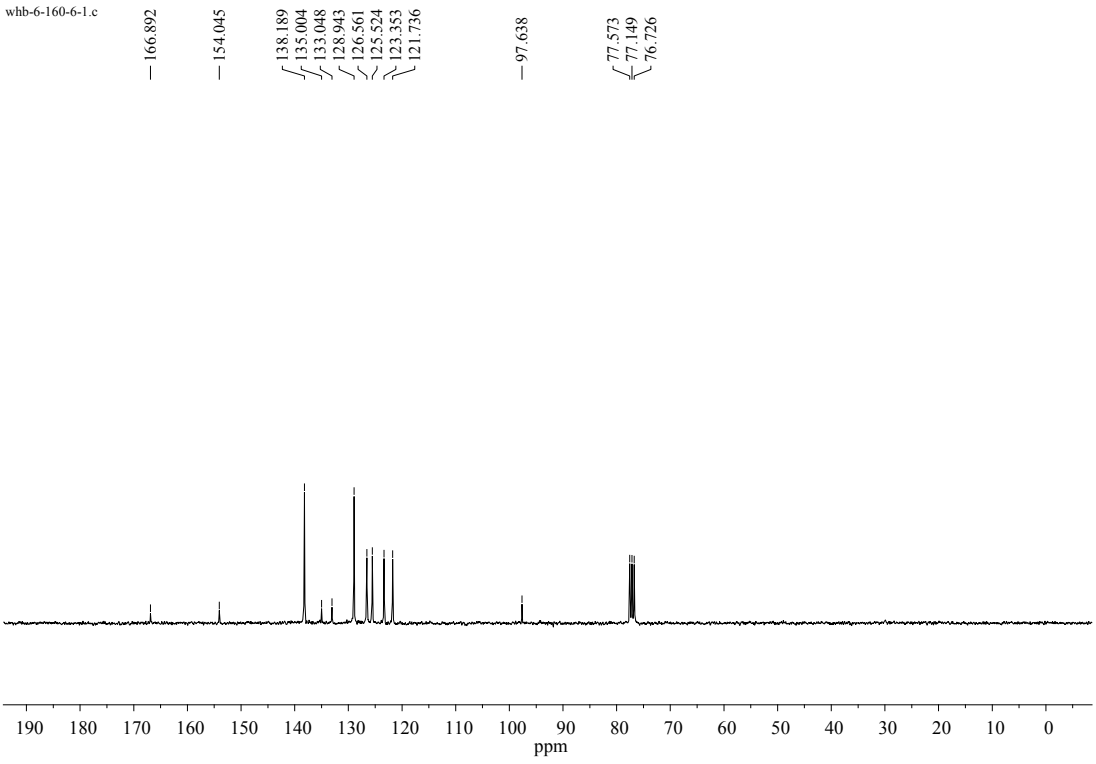


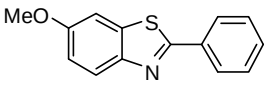




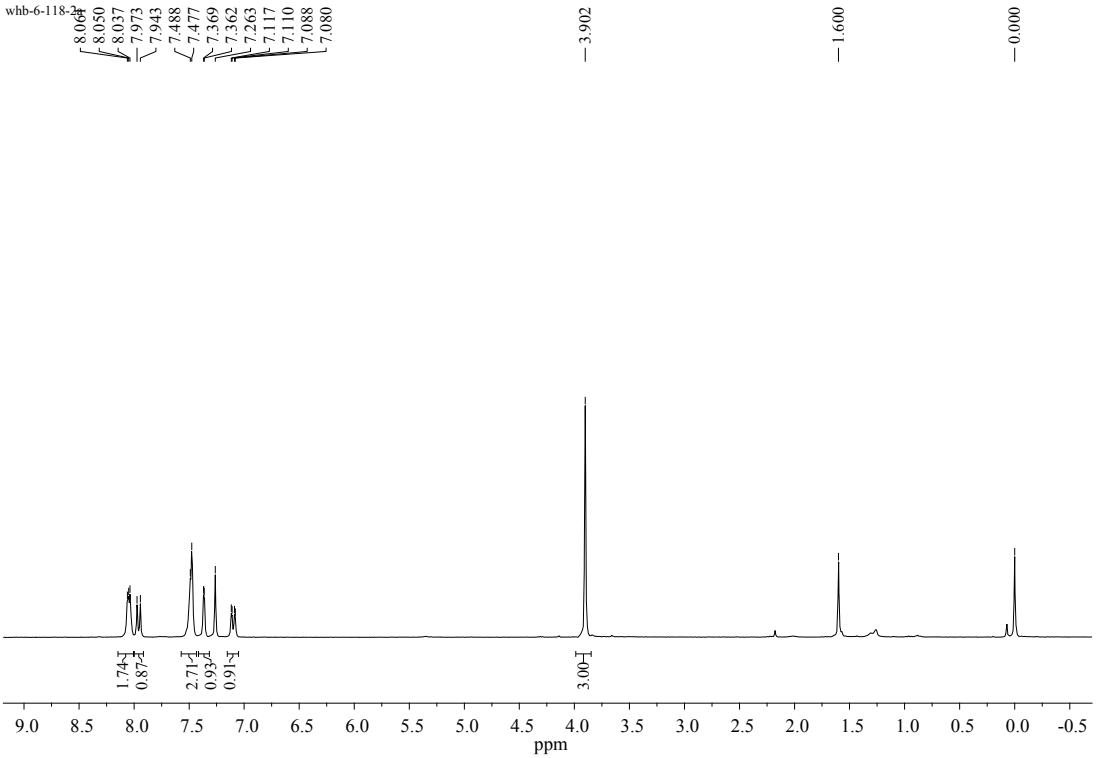
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.88 – 7.80 (m, 4H), 7.51 (t, J = 7.2 Hz, 1H), 7.41 ppm (t, J = 7.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.89, 154.05, 138.19, 135.00, 133.05, 128.94, 126.56, 125.52, 123.35, 121.74, 97.64 ppm.

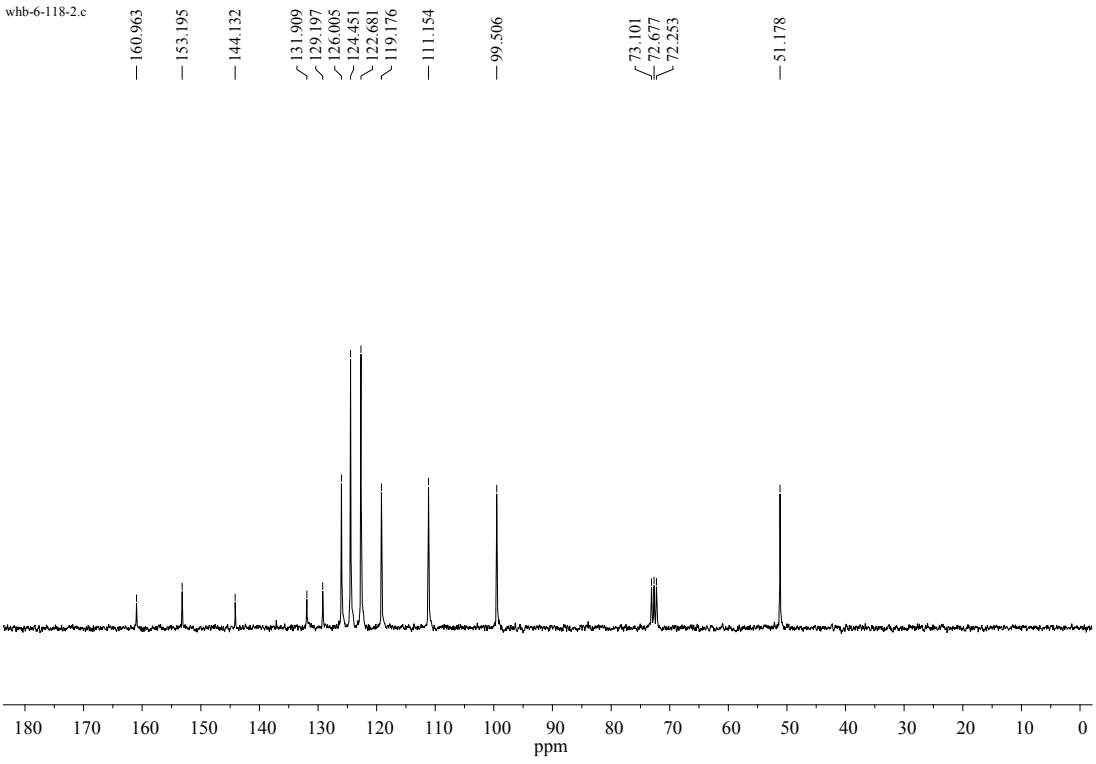


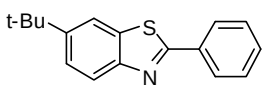




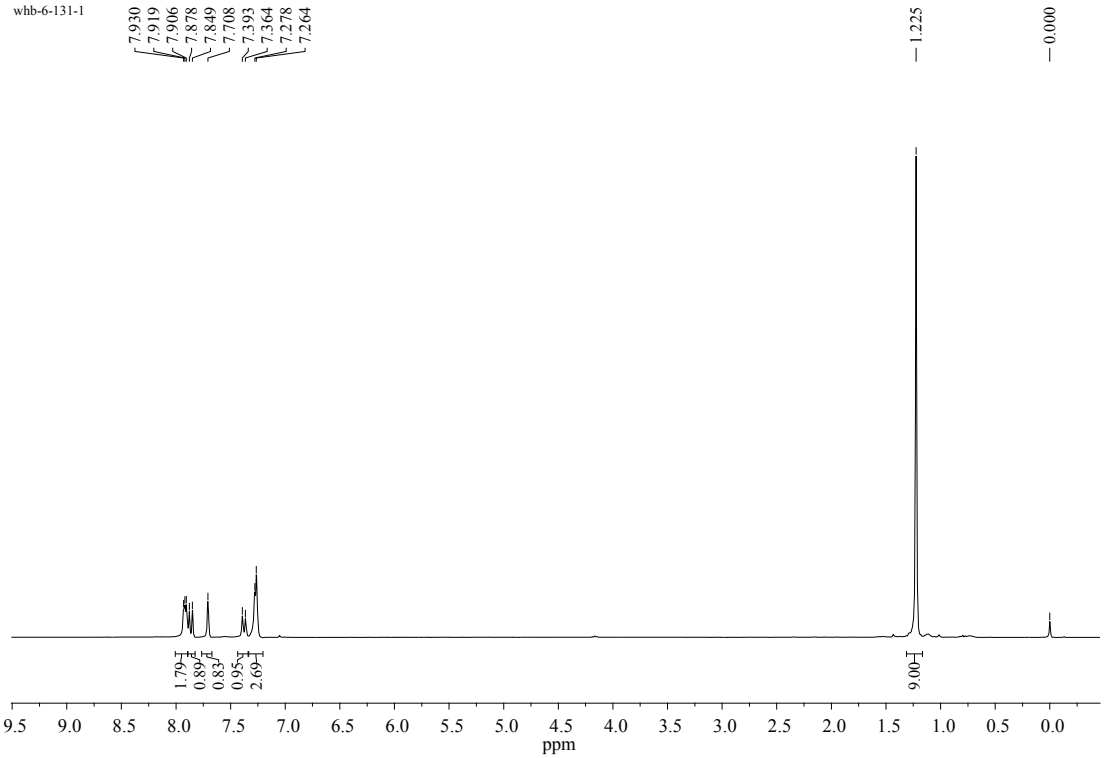
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.09 – 8.02 (m, 2H), 7.96 (d, J = 9.0 Hz, 1H), 7.57 – 7.43 (m, 3H), 7.37 (d, J = 2.1 Hz, 1H), 7.10 (dd, J = 8.9, 2.3 Hz, 1H), 3.90 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.96, 153.20, 144.13, 131.91, 129.20, 126.01, 124.45, 122.68, 119.18, 111.15, 99.51, 51.18 ppm.

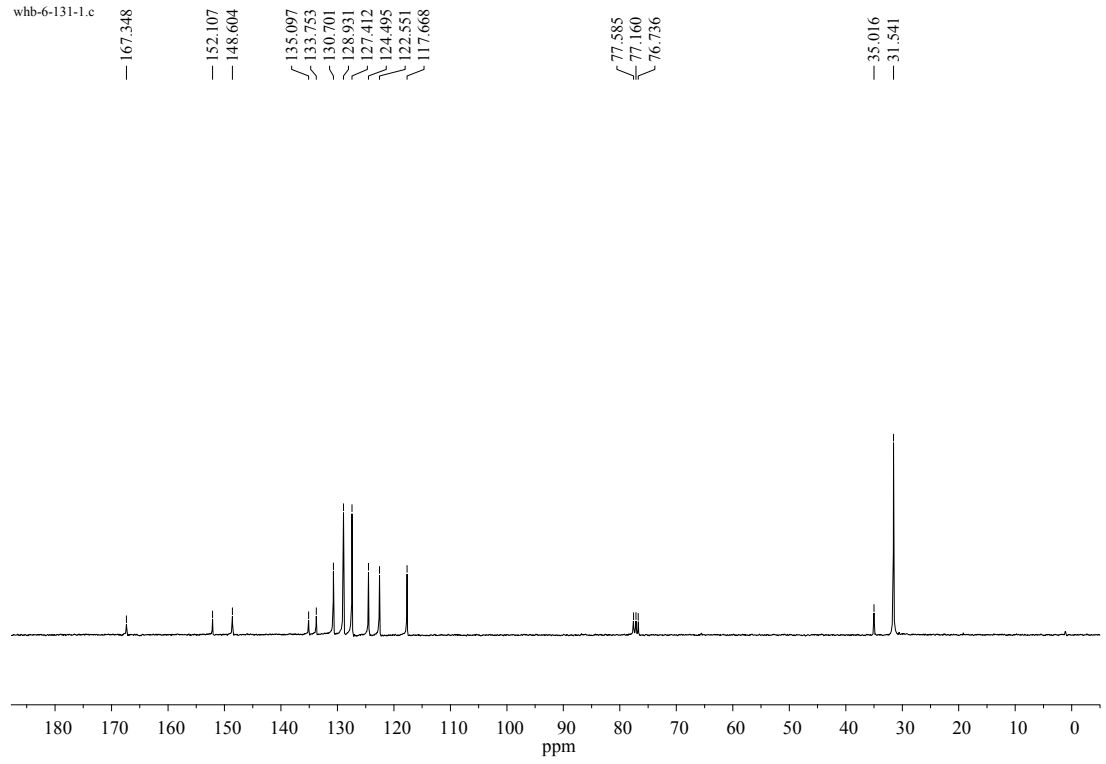


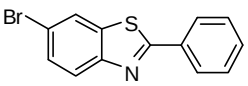




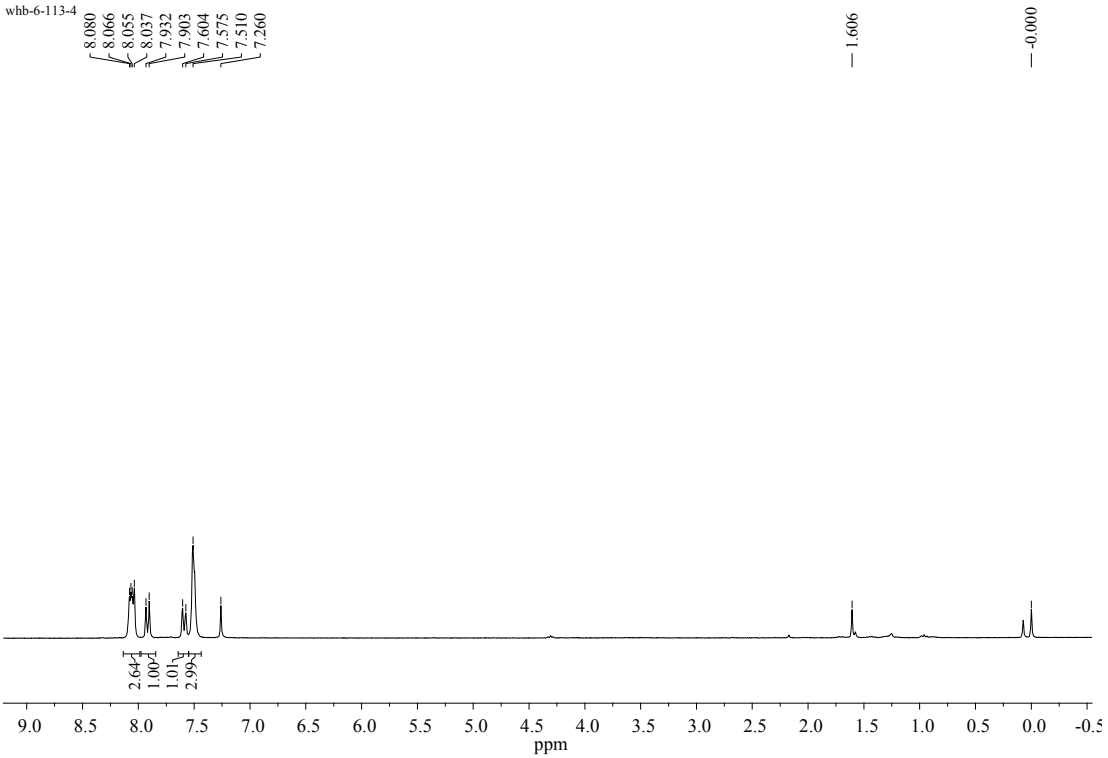
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96 – 7.89 (m, 2H), 7.86 (d, J = 8.7 Hz, 1H), 7.71 (s, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.31 – 7.23 (m, 3H), 1.22 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.35, 152.11, 148.60, 135.10, 133.75, 130.70, 128.93, 127.41, 124.49, 122.55, 117.67, 35.02, 31.54 ppm.

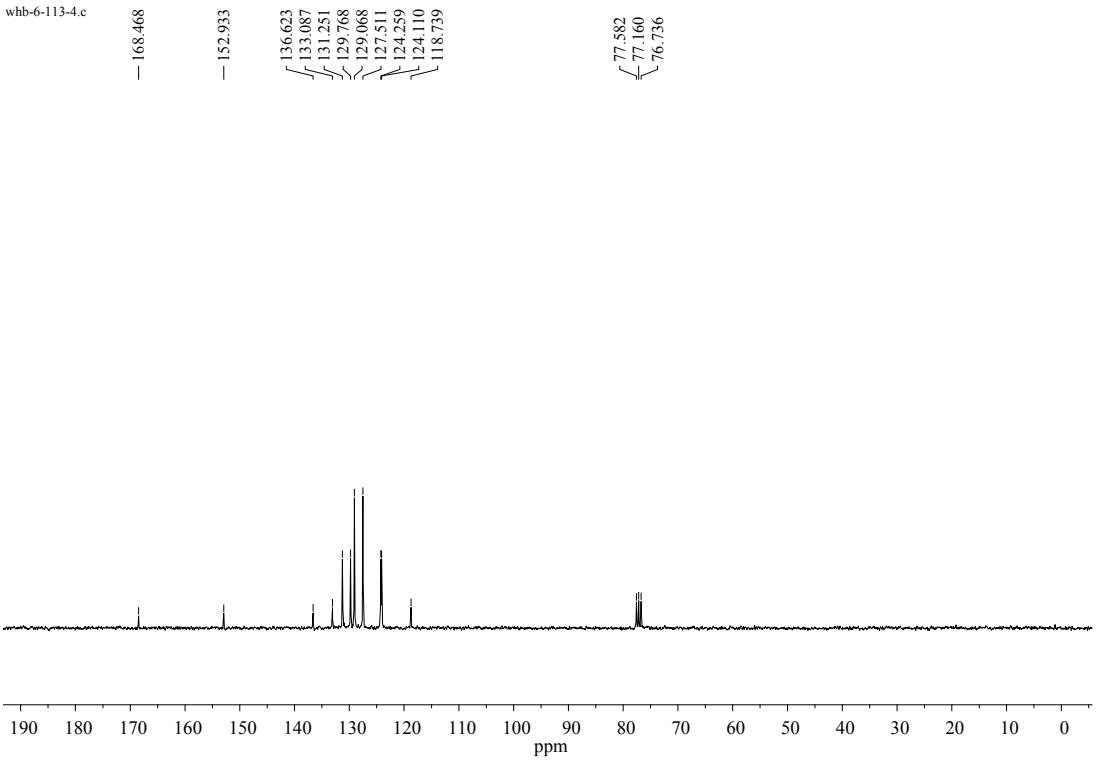


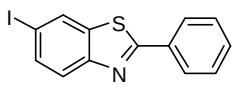




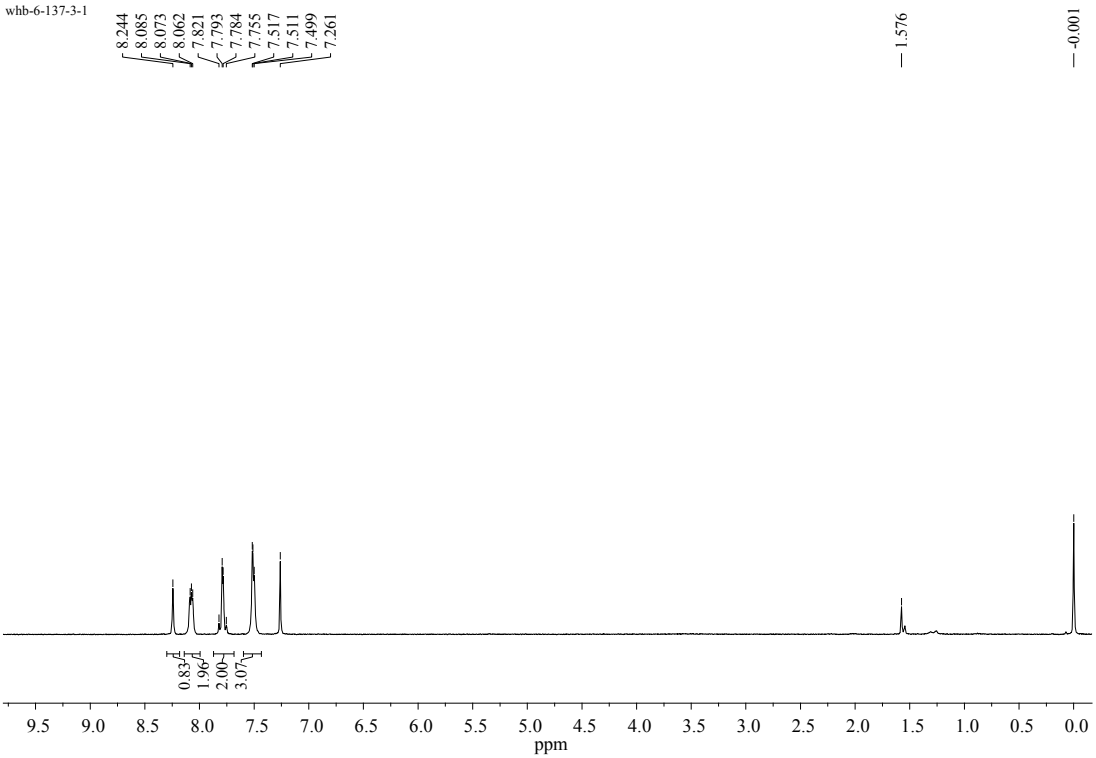
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11 – 8.02 (m, 3H), 7.92 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.51 ppm (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.47, 152.93, 136.62, 133.09, 131.25, 129.77, 129.07, 127.51, 124.26, 124.11, 118.74 ppm.

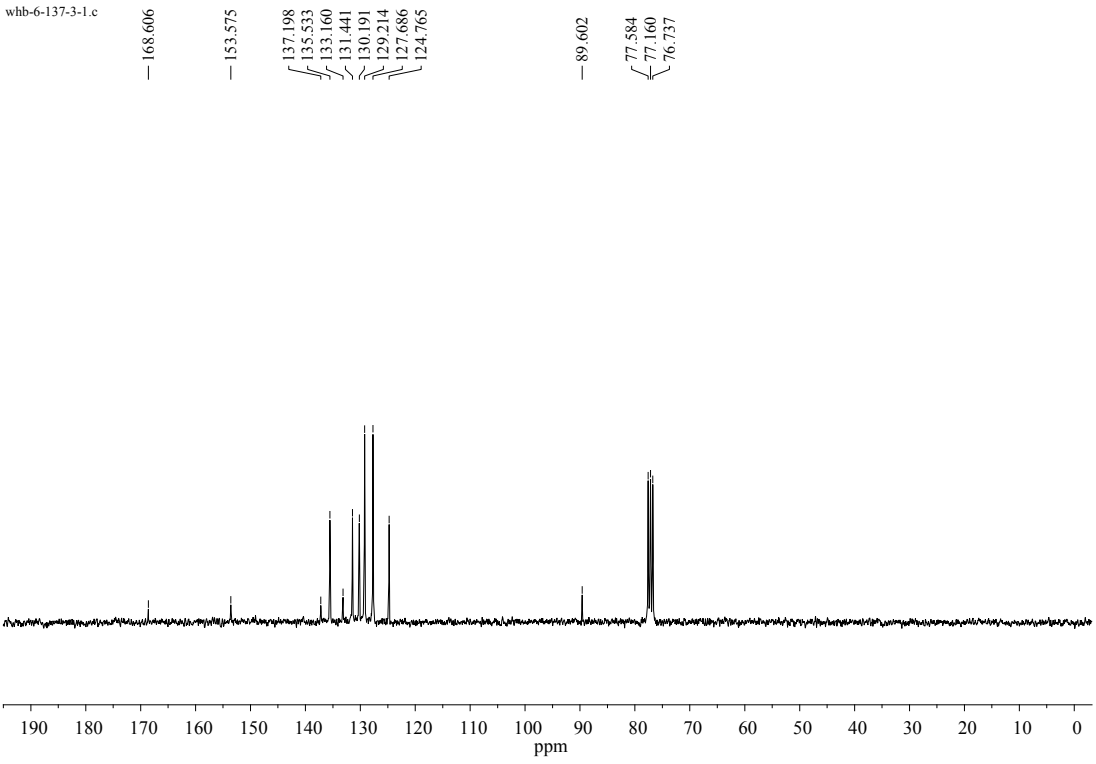


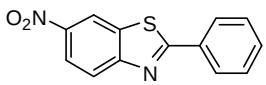




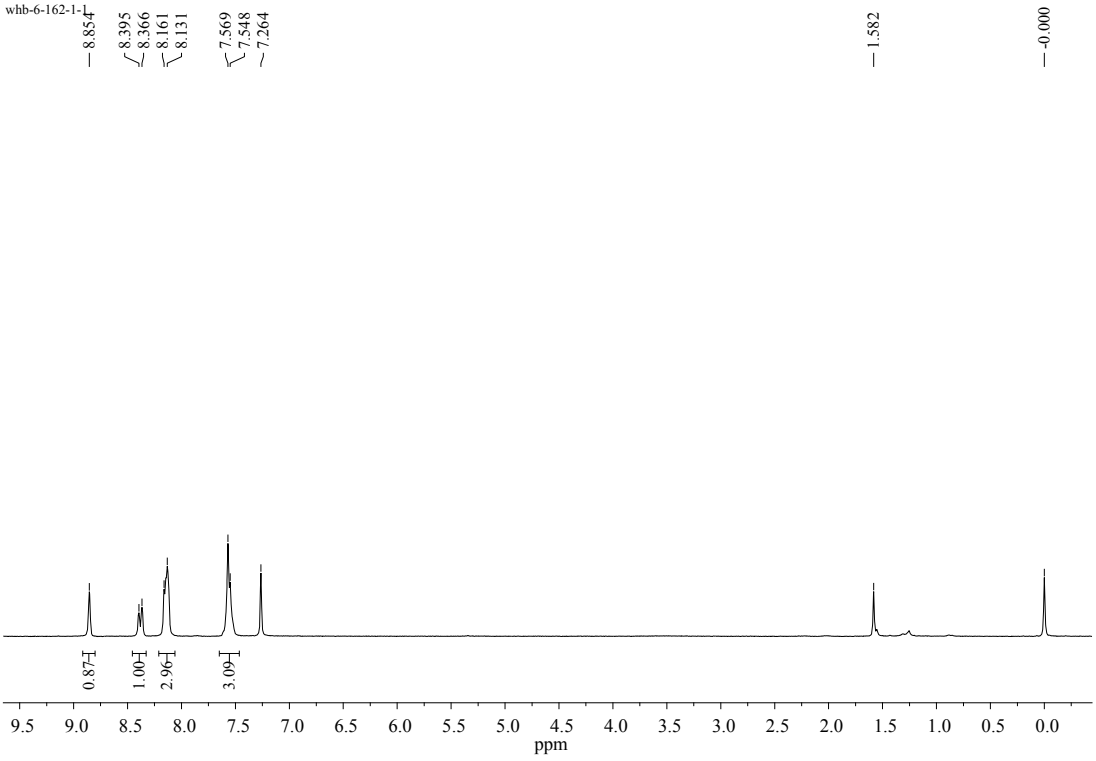
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 8.10 – 8.03 (m, 2H), 7.82 – 7.76 (m, 2H), 7.55 – 7.47 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.61, 153.57, 137.20, 135.53, 133.16, 131.44, 130.19, 129.21, 127.69, 124.77, 89.60 ppm.

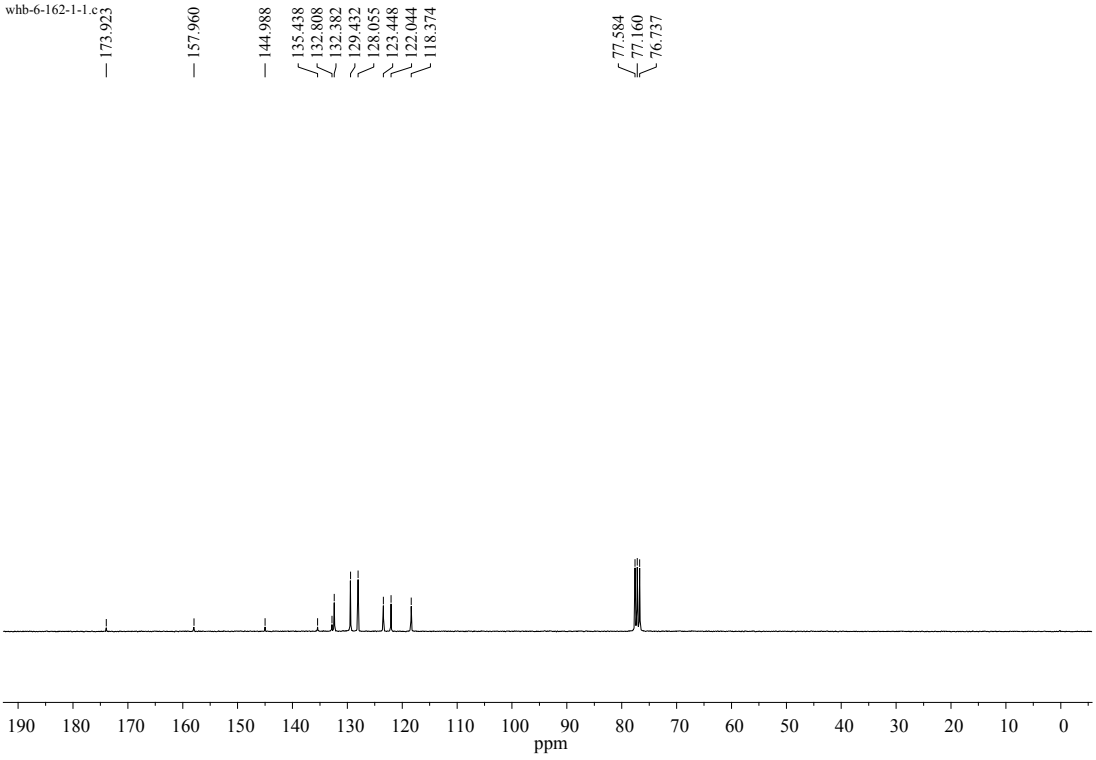


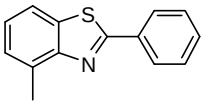




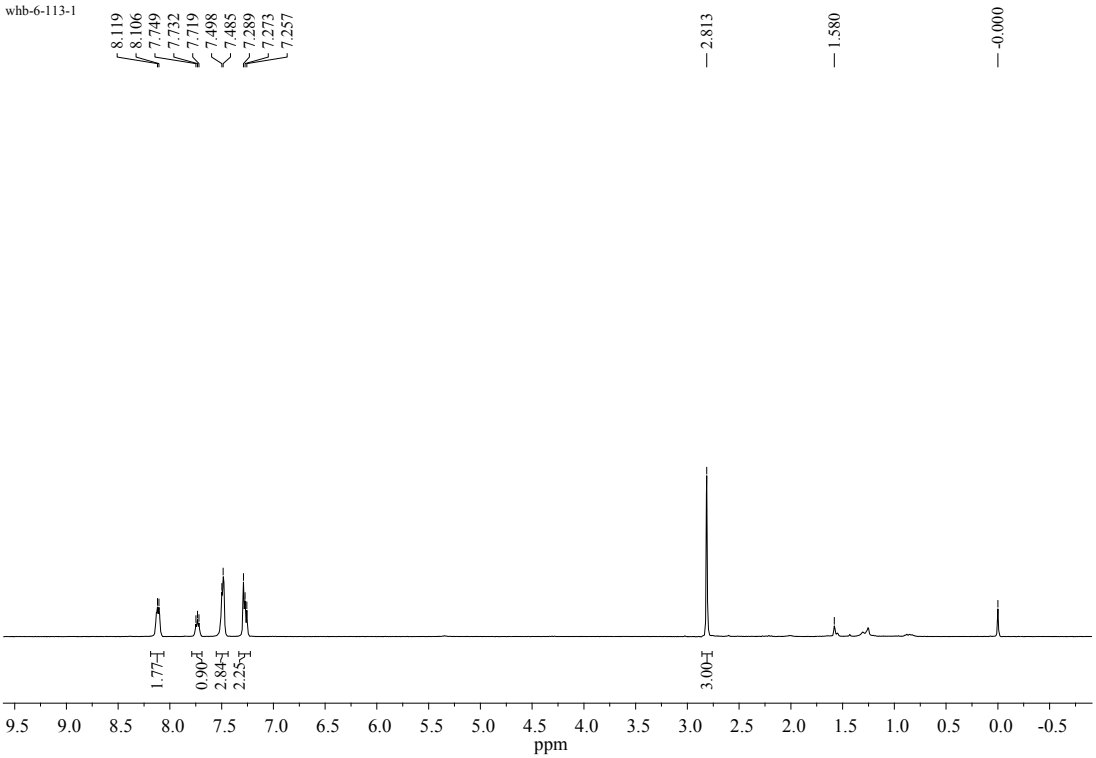
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.85 (s, 1H), 8.38 (d, J = 8.7 Hz, 1H), 8.21 – 8.06 (m, 3H), 7.63 – 7.47 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 173.92, 157.96, 144.99, 135.44, 132.81, 132.38, 129.43, 128.05, 123.45, 122.04, 118.37 ppm.

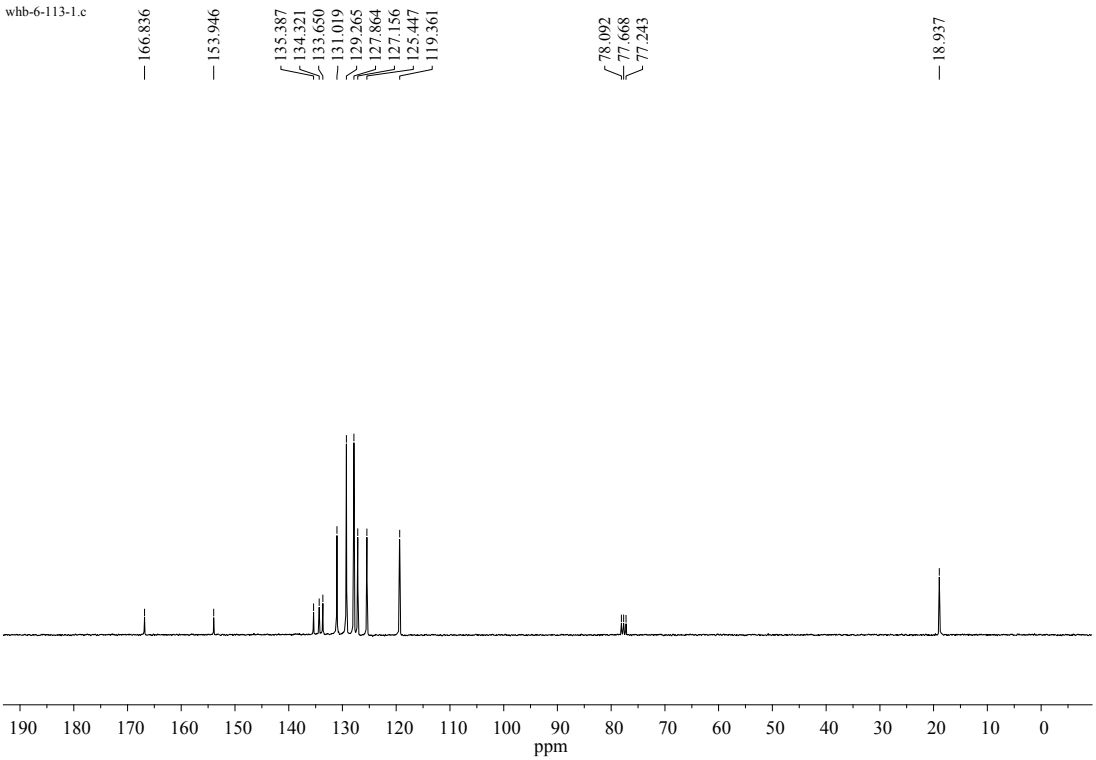


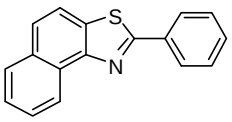




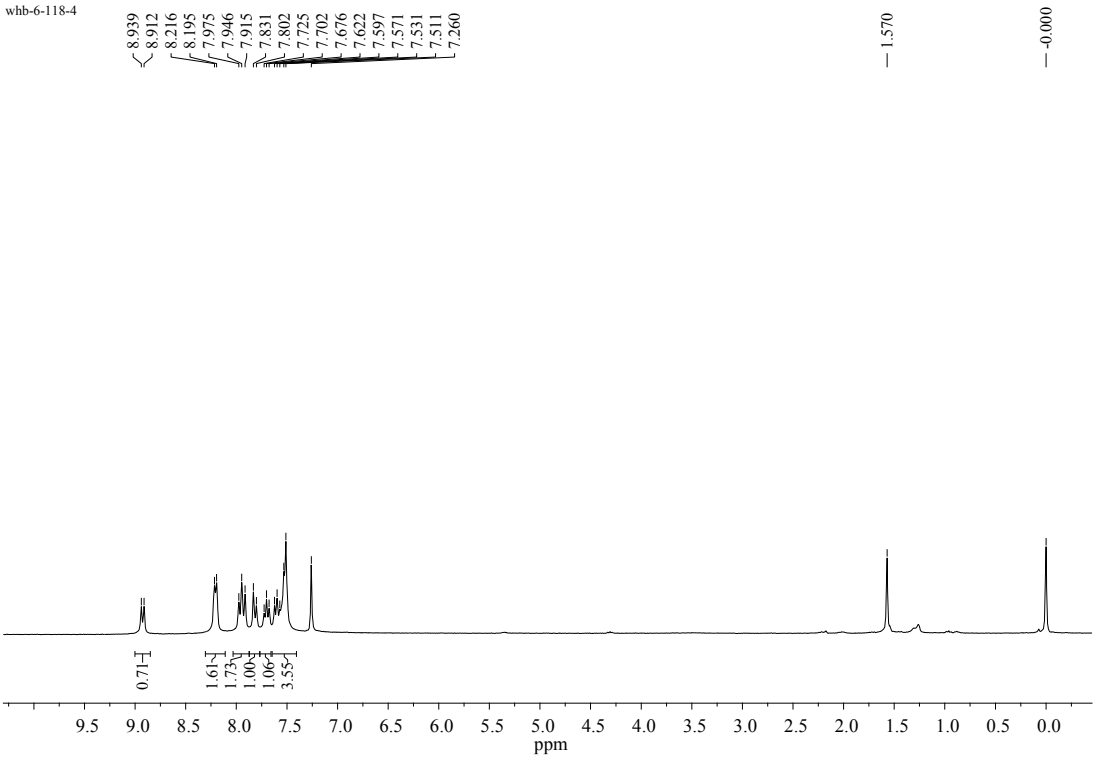
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.15 – 8.09 (m, 2H), 7.78 – 7.69 (m, 1H), 7.53 – 7.46 (m, 3H), 7.32 – 7.24 (m, 2H), 2.81 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.84, 153.95, 135.39, 134.32, 133.65, 131.02, 129.27, 127.91, 127.16, 125.45, 119.36, 18.94 ppm.

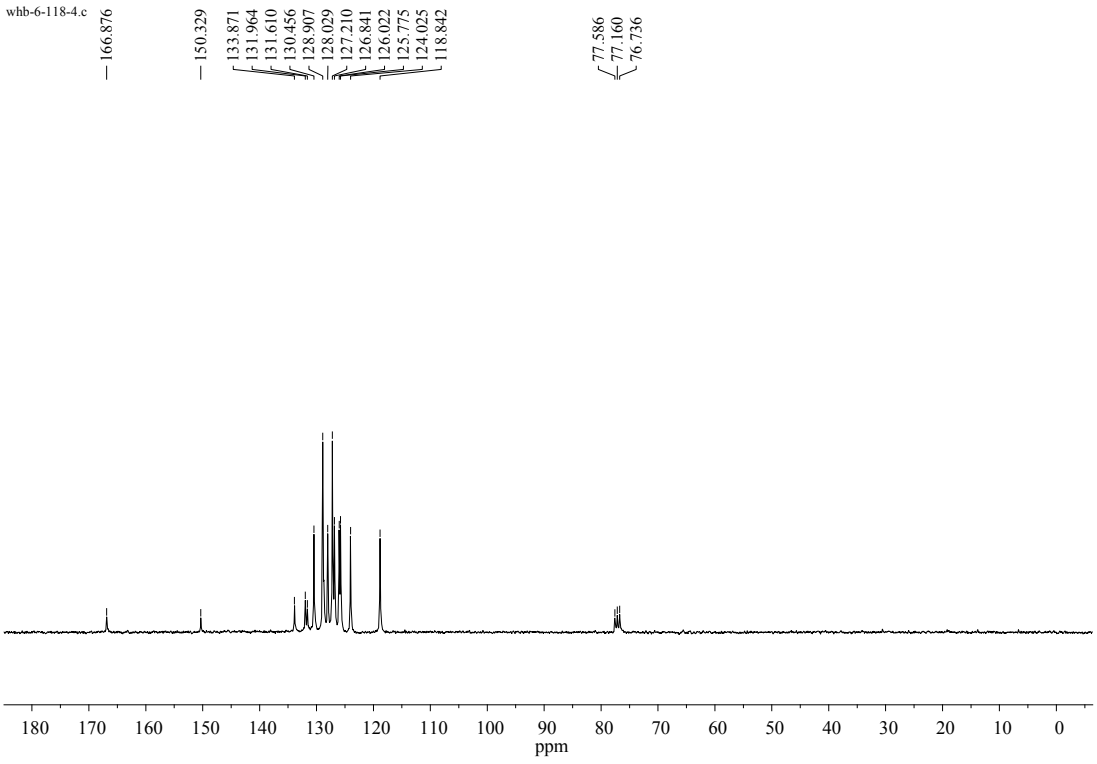


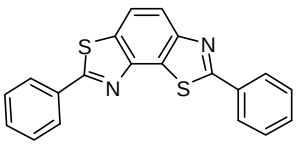




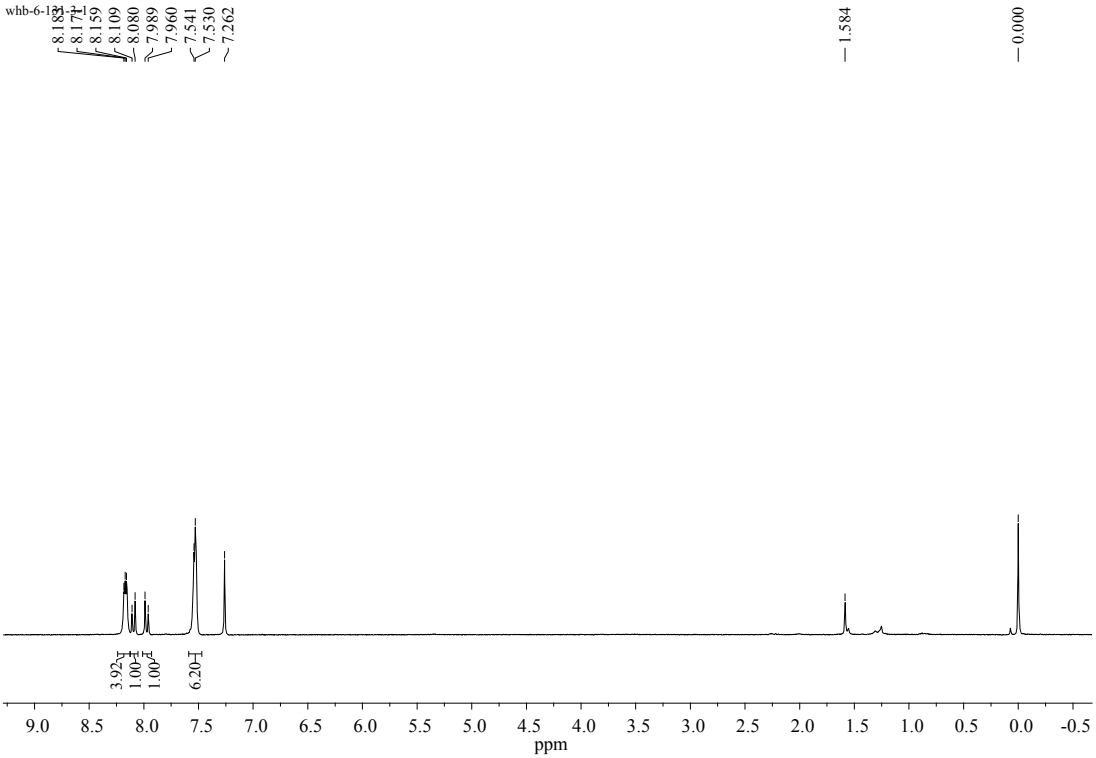
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.93 (d, J = 8.1 Hz, 1H), 8.21 (d, J = 6.3 Hz, 2H), 7.95 (t, J = 9.0 Hz, 2H), 7.82 (d, J = 8.7 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.63 – 7.48 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.88, 150.33, 133.87, 131.96, 131.61, 130.46, 128.91, 128.03, 127.21, 126.84, 126.02, 125.77, 124.02, 118.84 ppm.

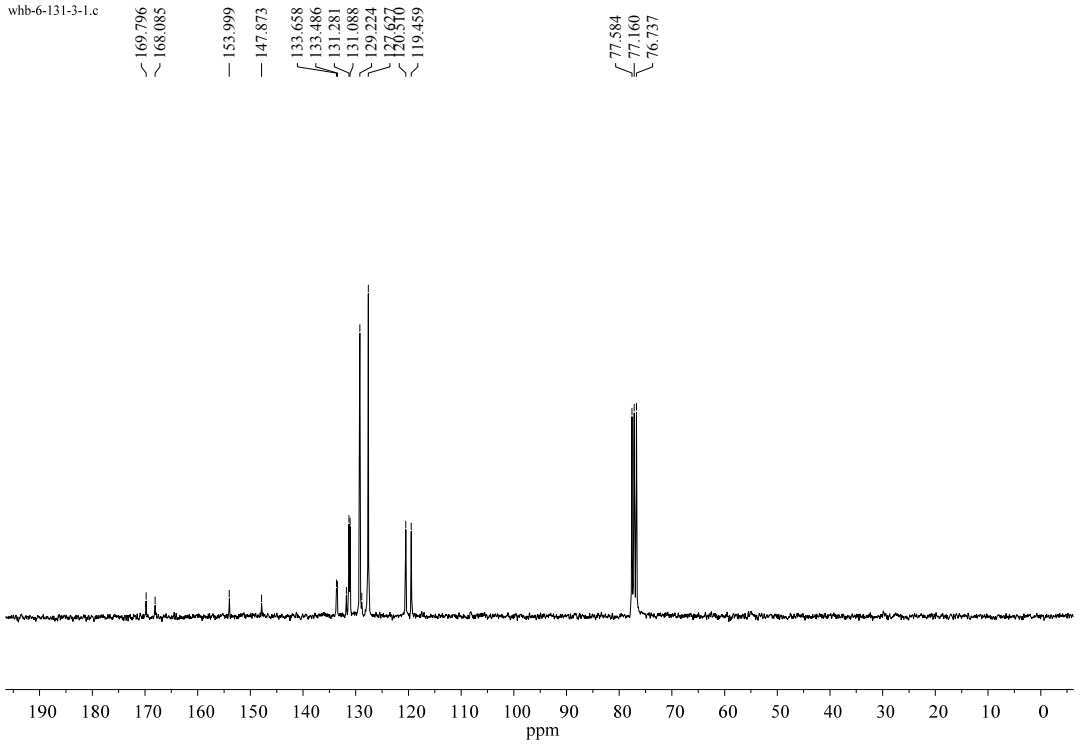


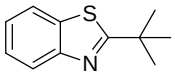




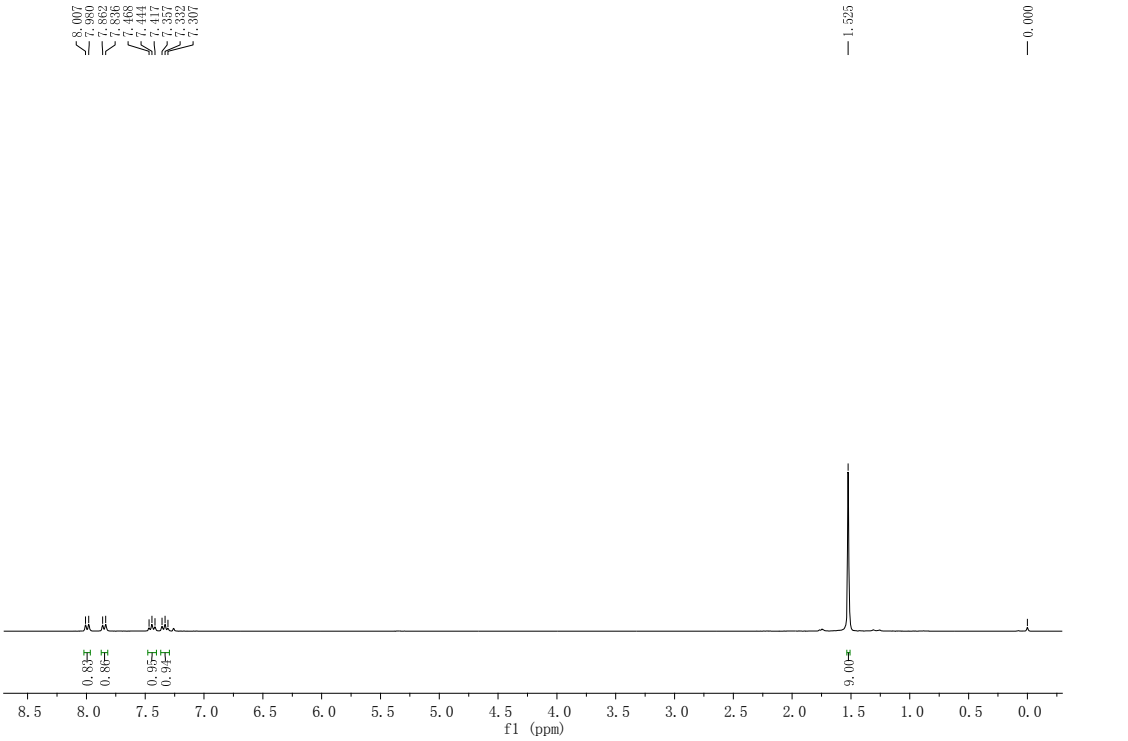
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 – 8.14 (m, 4H), 8.09 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.56 – 7.50 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.80, 168.08, 154.00, 147.87, 133.66, 133.49, 131.76, 131.28, 131.09, 129.22, 128.87, 127.63, 120.51, 119.46 ppm.

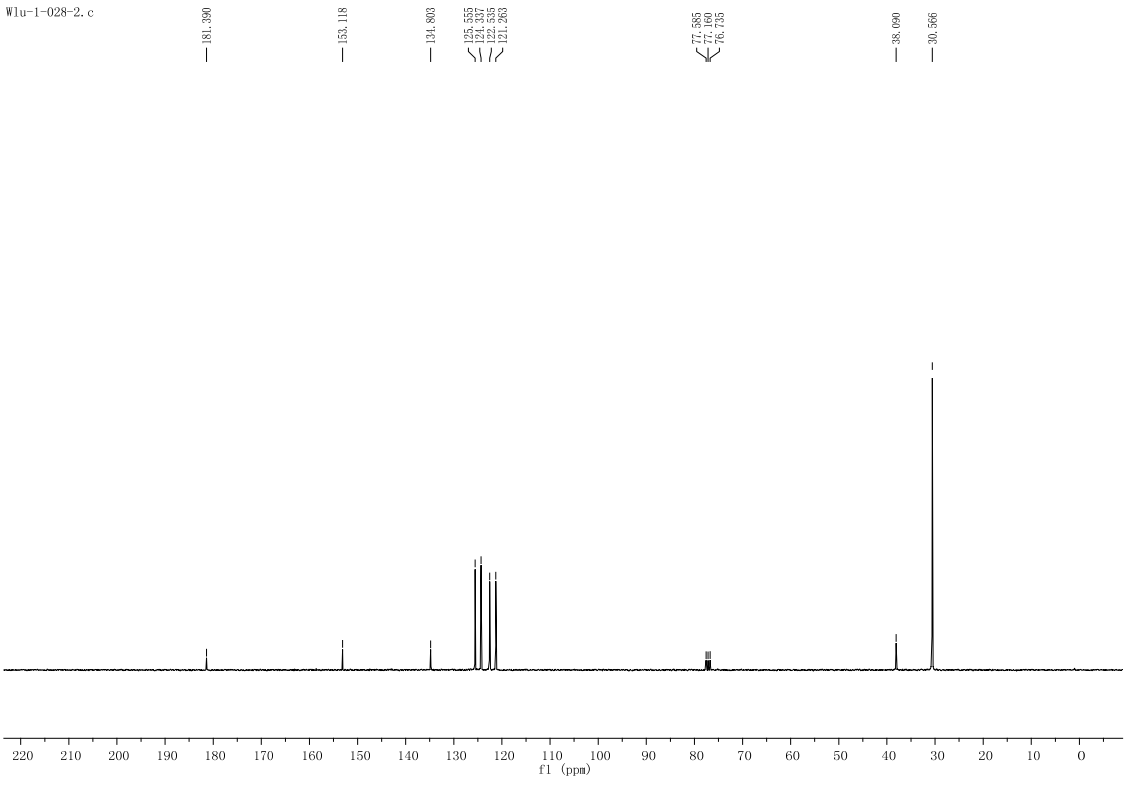


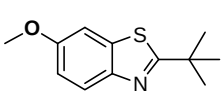




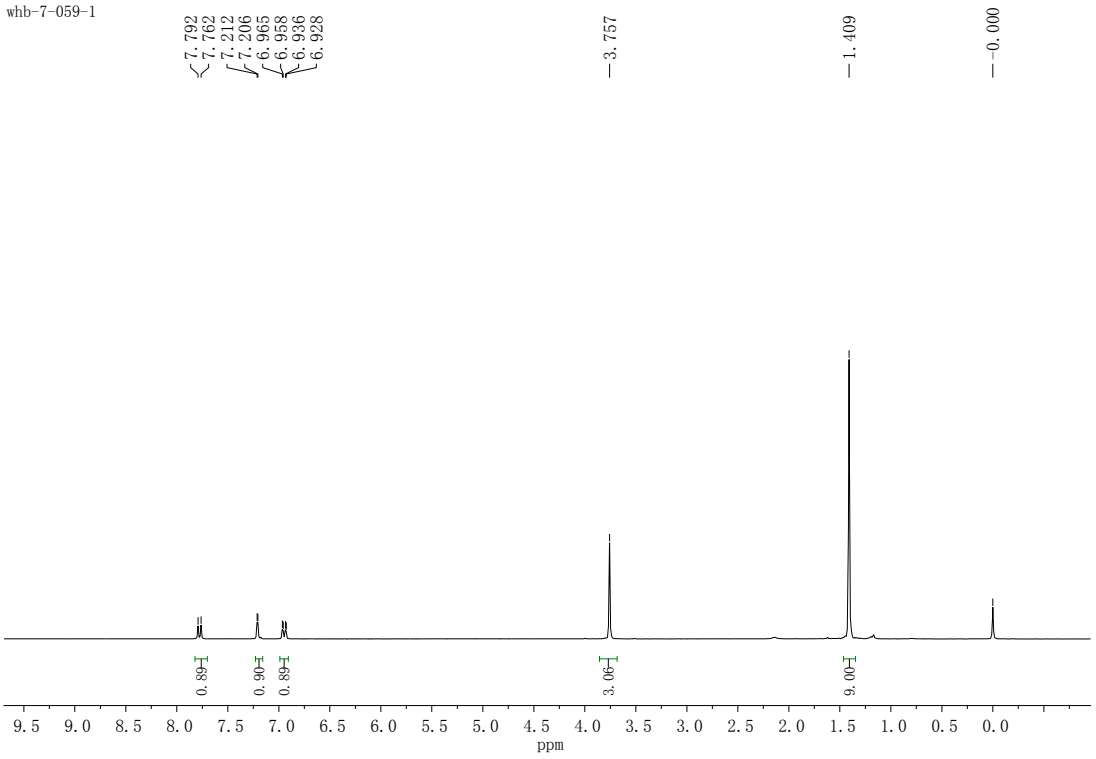
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (d, J =6.9 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 1.52 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 181.39, 153.12, 134.80, 125.56, 124.34, 122.53, 121.26, 38.09, 30.57 ppm.

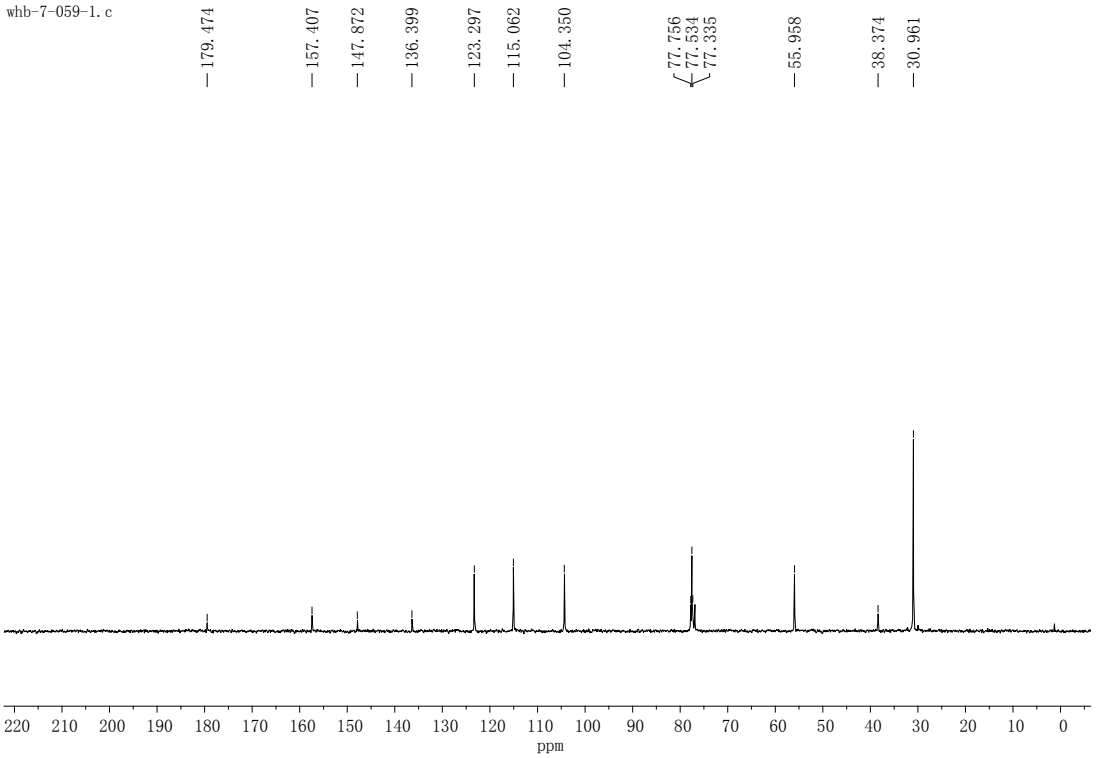


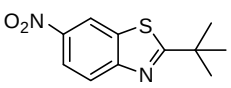




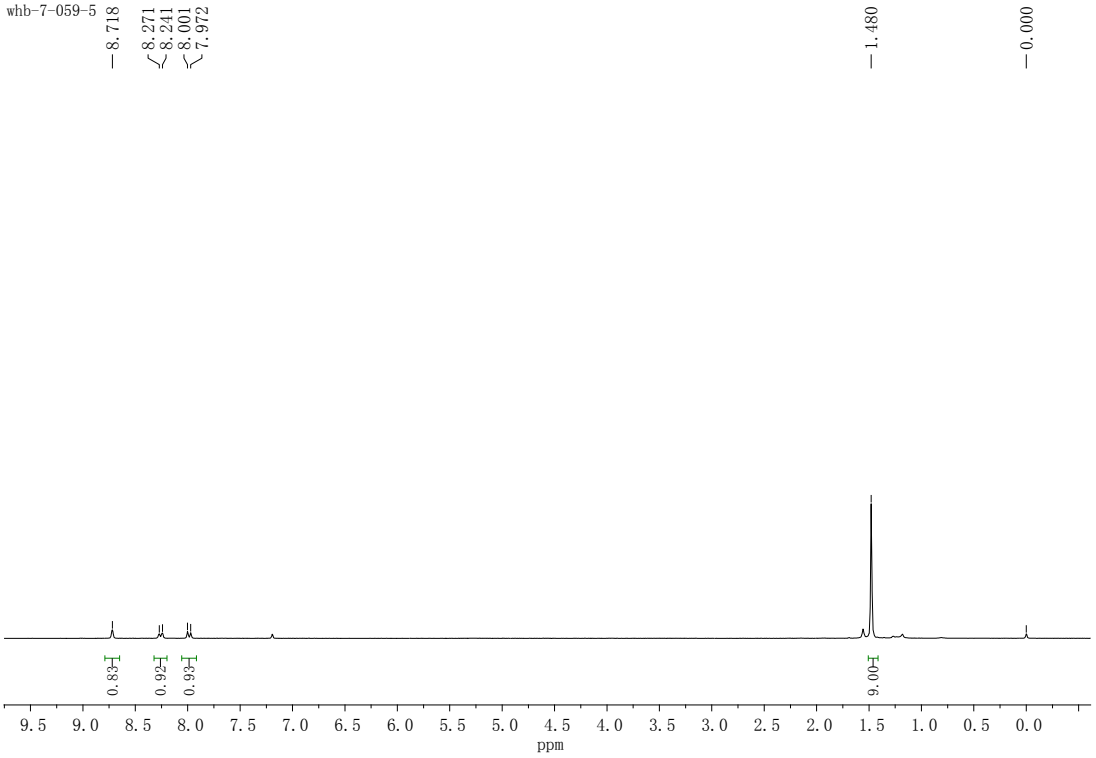
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 9.0 Hz, 1H), 7.21 (d, J = 1.8 Hz, 1H), 6.95 (dd, J = 9.0, 2.2 Hz, 1H), 3.76 (s, 3H), 1.41 ppm (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 179.47, 157.41, 147.87, 136.40, 123.30, 115.06, 104.35, 55.96,38.37,30.96ppm.

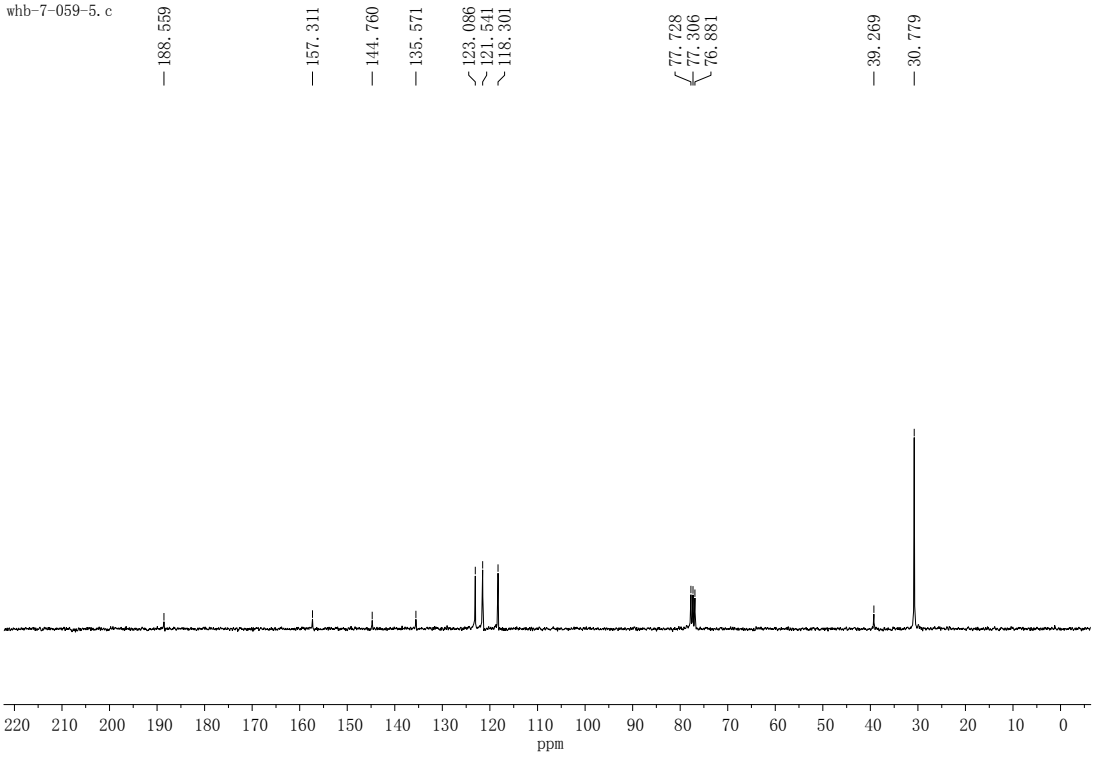


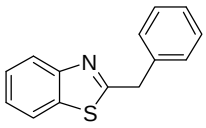




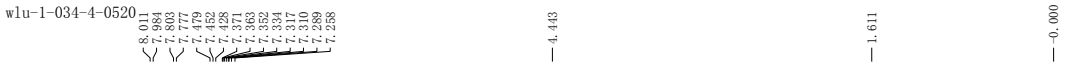
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.72 (s, 1H), 8.26 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 1.48 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 188.56, 157.31, 144.76, 135.57, 123.09, 121.54, 118.30, 39.27, 30.78 ppm.

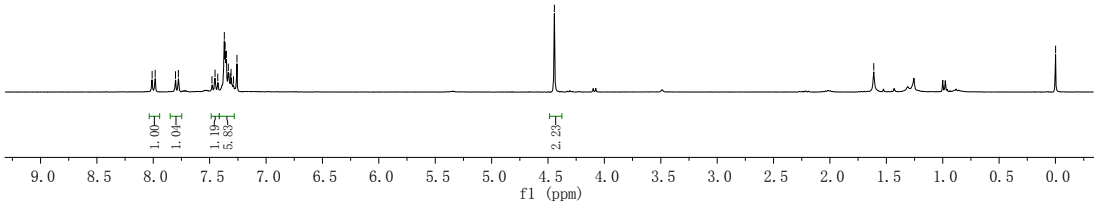


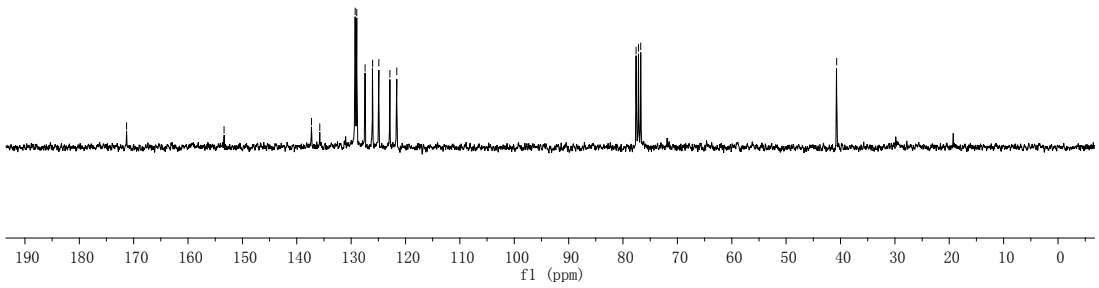


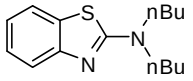


^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.38 – 7.29 (m, 6H), 4.44 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.29, 153.36, 137.29, 135.76, 129.26, 128.97, 127.44, 126.07, 124.91, 122.87, 121.62, 40.72 ppm.

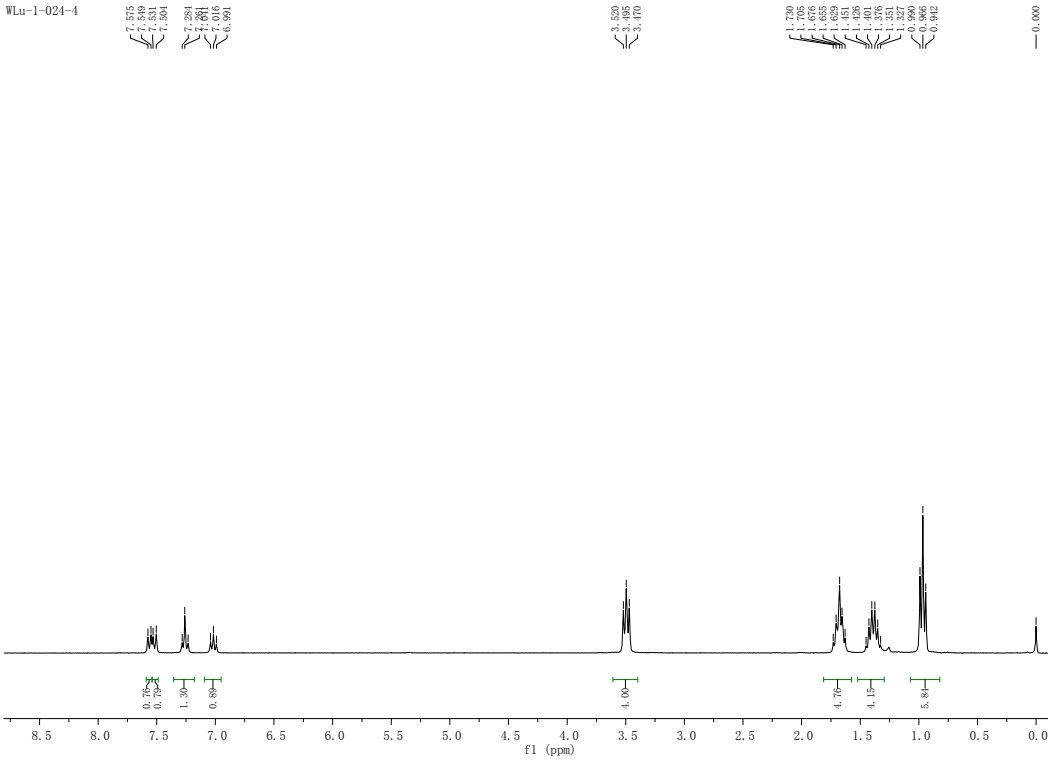


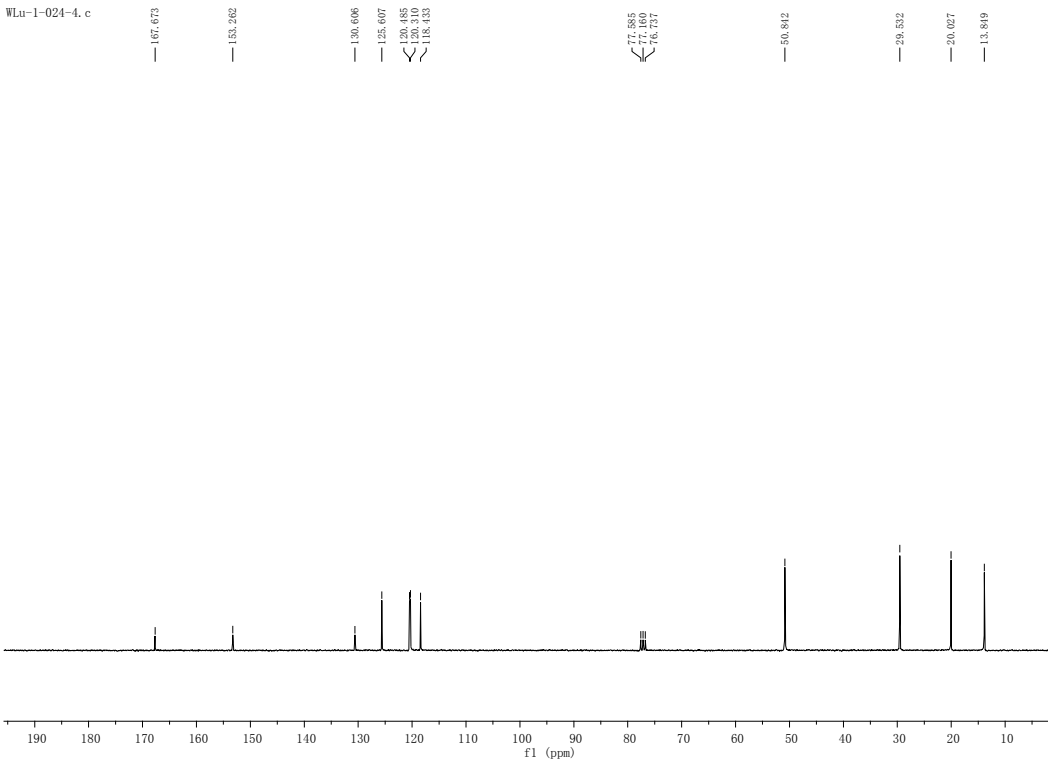


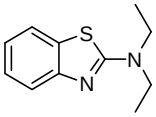




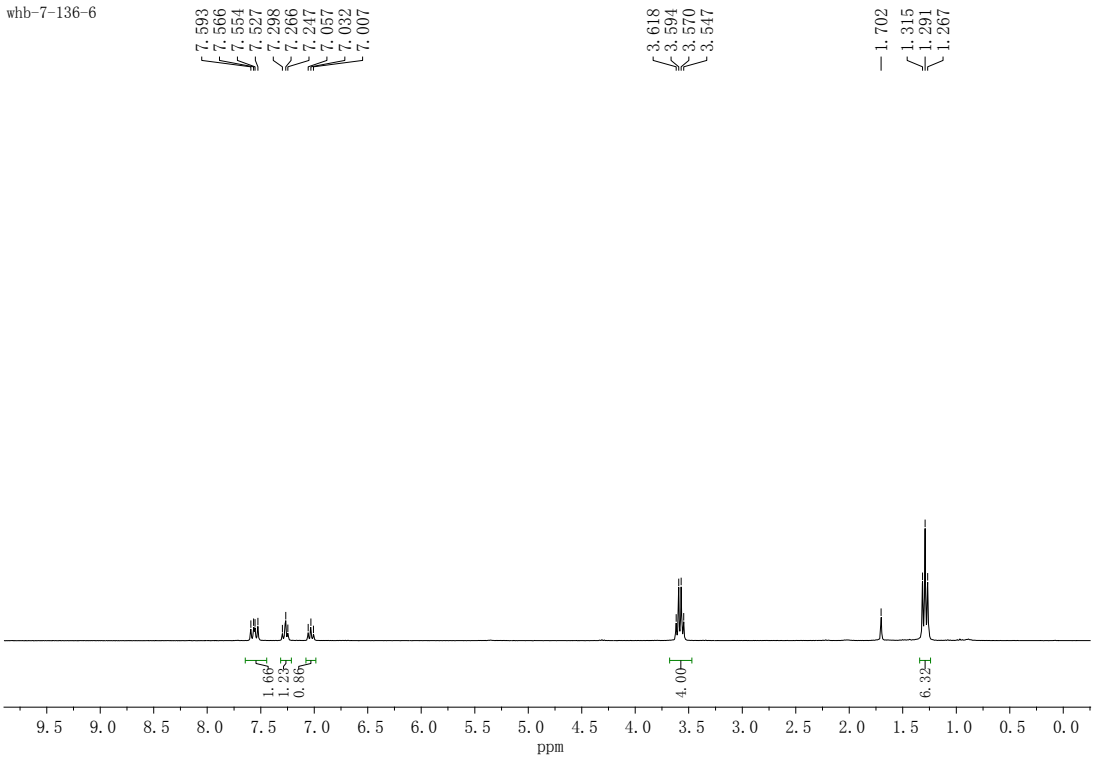
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 3.50 (t, J = 7.5 Hz, 4H), 1.77 – 1.57 (m, 4H), 1.48 – 1.31 (m, 4H), 0.97 ppm (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.67, 153.26, 130.61, 125.61, 120.49, 120.31, 118.43, 50.84, 29.53, 20.13, 13.85 ppm.

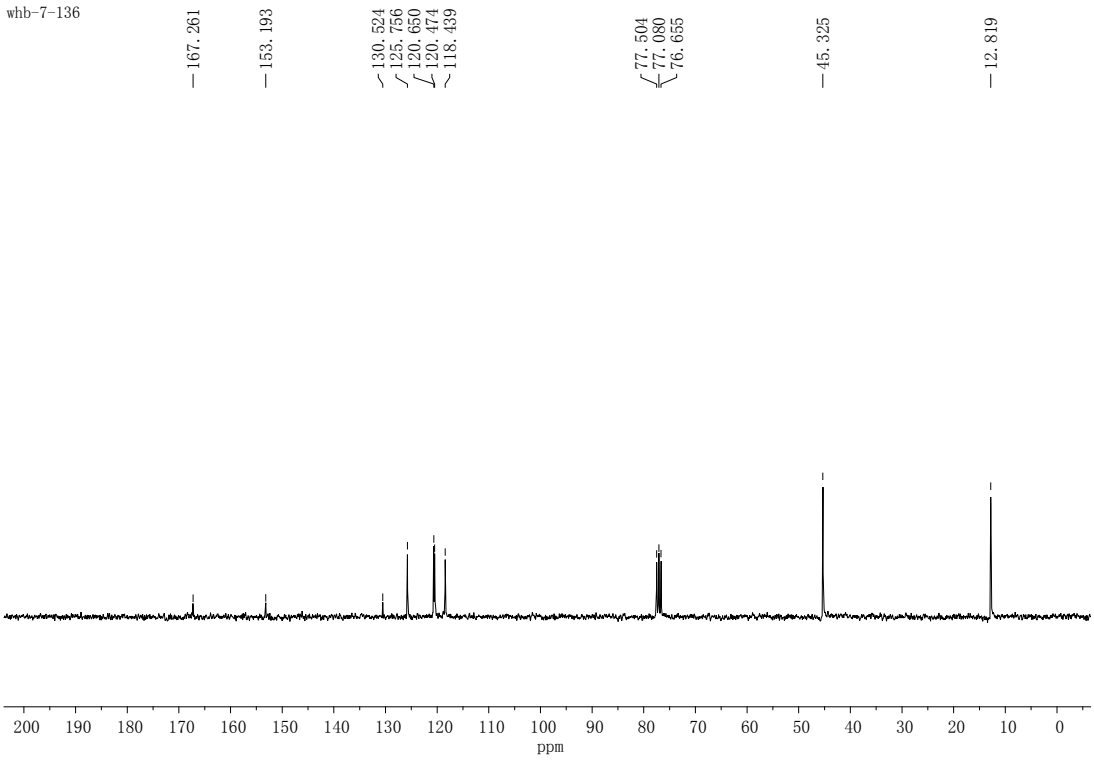


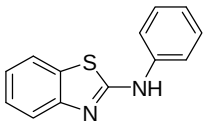




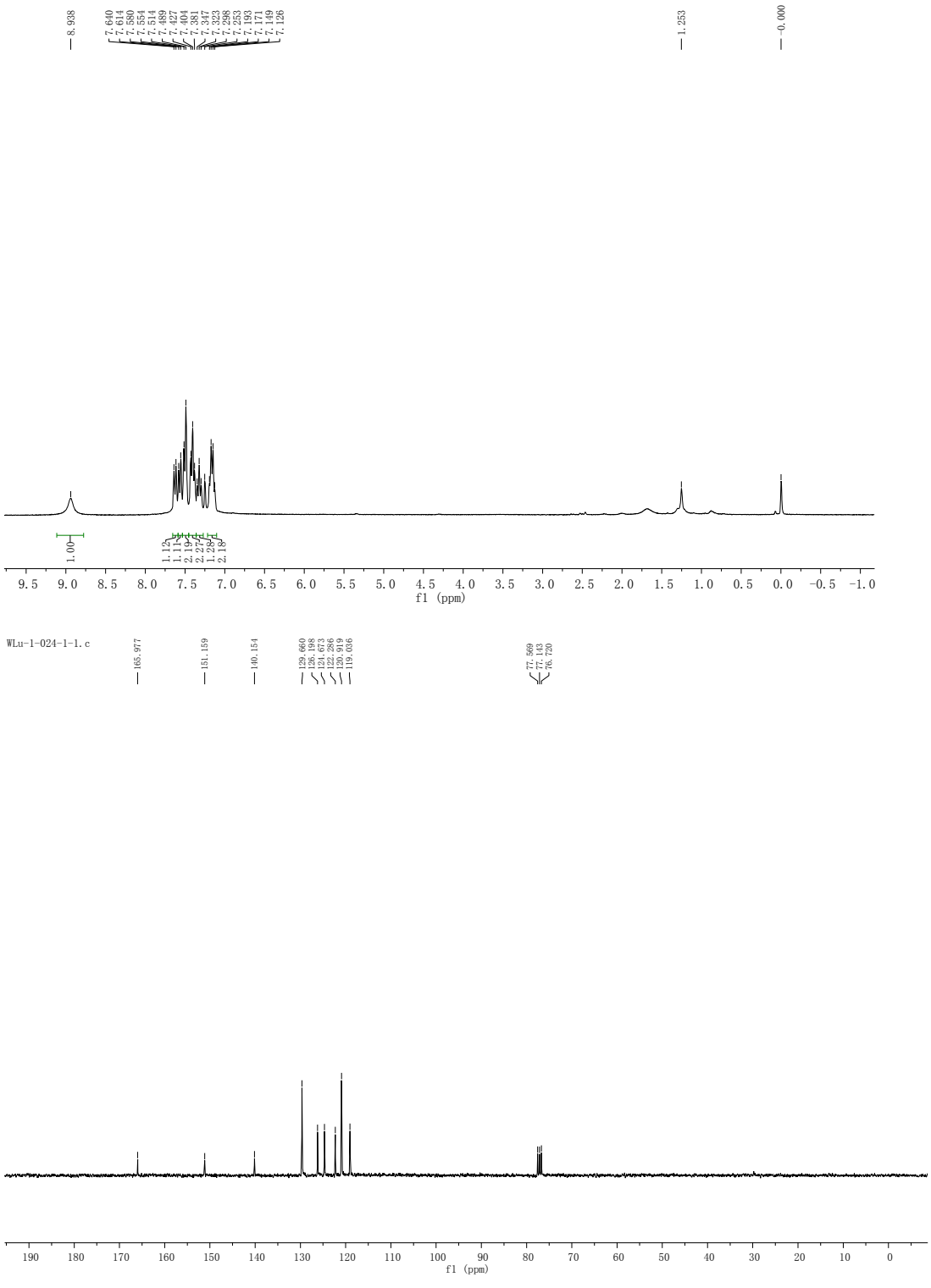
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63 – 7.46 (m, 2H), 7.33 – 7.22 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 3.58 (q, J = 7.2 Hz, 4H), 1.29 ppm (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.26, 153.19, 130.52, 125.76, 120.65, 120.47, 118.44, 45.32, 12.82 ppm.

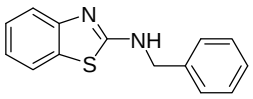






^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.94 (br.s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 6.9 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.22 – 7.10 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.98, 151.16, 140.15, 129.66, 126.20, 124.67, 122.29, 120.92, 119.04 ppm.





^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.43 – 7.23 (m, 6H), 7.09 (t, J = 7.5 Hz, 1H), 6.06 (br.s, 1H), 4.64 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.99, 152.33, 137.59, 130.44, 128.93, 127.95, 127.76, 126.08, 121.64, 120.95, 118.88, 49.56 ppm.