External Oxidant-Free Oxidative Cross-Coupling: A Photoredox Cobalt-Catalyzed Aromatic C-H Thiolation for Constructing C-S Bonds

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Supporting Information

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General Considerations

All manipulations were carried out by using standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. 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. 60−90 ℃). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All Co-complexes were prepared following literature procedures.[1] 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 Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 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 + Hydrogen (M+H). Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, argon as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector).

Experimental Procedures

1. Preparation of Thiobenzamides[2]:

A mixture of the aniline (1.0 g), NEt_3 (1.3 mol equiv) and CH_2Cl_2 (10 mL) was added into a 50 mL flask equipped with a stir-bar. Then benzoyl chloride (1.1 mol equiv) was added slowly at room temperature for 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 pure benzamide. A mixture of the benzamide (1.0 g) and Lawesson's reagent (0.6 mol equiv) in dry toluene (40 mL) was heated at reflux under an atmosphere of nitrogen for 2 h, after which it was concentrated, purified by column chromatography (EtOAc/hexanes 1:4) and recrystallized from hexane /ethyl acetate.

2. Preparation of $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$[1]:

A 500mg (1.48 mmol) sample of $[Co(dmgH)_2Cl_2]$ was suspended in 50 mL of methanol. 4-(dimethylamino)pyridine (361 mg, 2.96 mmol, 2 equiv) was then added to the flask, after which the complex dissolved within 1 h, changing from a green suspension to a brown precipitate. The suspension was filtered and the precipitate washed with water (10 mL), ethanol (10 mL), and diethyl ether (10 mL) to give $[Co(dmgH)_2(4\text{-}NMe_2Py)Cl]$.

3. General Procedure for Benzothiazoles Synthesis:

Condition A: A mixture of *N*-phenylbenzothioamide **1a** (0.2 mmol), sodium glycinate (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.006 mmol, 3 mol %), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (0.016 mmol, 8 mol %) and DMAP (4-dimethylaminopyridine) (0.08 mmol, 40 mol %) in degased dry CH_3CN (2 mL) was stirred under an argon atmosphere and irradiation of a commercially available blue LED for 12 h. After completion of the reaction, the solid was filtered off and washed with ethyl acetate. After removal of the solvent of the filtrate, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford **2a** in 99% yield.

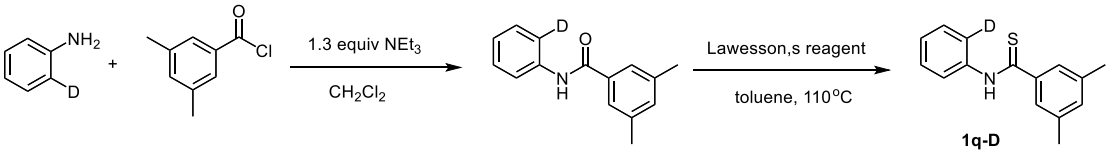
Condition B: A mixture of thioamides **1** (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.006 mmol, 3 mol %), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (0.016 mmol, 8 mol %) and TBAOH (1 M solution in MeOH) (0.02 mmol, 10 mol %) in degased dry CH_3CN (2 mL) was stirred under an argon atmosphere and irradiation of a commercially available blue LED for 12 h. After removal of the solvent, the pure

product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford corresponding benzothioazoles.

4. Preparation of *N*-(phenyl-d_5)Benzothioamide:

A mixture of the benzen-2,3,4,5,6-d_5-amine-d_2 (1mL) and triethylamine (2.08 mL) was added in dichloromethane (20 mL), and benzoyl chloride was slowly added in the reaction. Then the mixture was heated at reflux for 2 h then poured into water (100 mL) and extracted with dichloromethane. The organic layer was dried (Na_2SO_4), and concentrated in vacuo to obtain pure benzamide. A mixture of the benzamide (1.0 g) and Lawesson's reagent (0.6 mol equiv) in dry toluene (40 mL) was heated at reflux under an atmosphere of nitrogen for 2 h, after which it was concentrated, purified by column chromatography (EtOAc/hexanes 1:4) and recrystallized from hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.05 (s, 1H), 7.84 – 7.74 (m, 2H), 7.59 – 7.32 (m, 3H). HRMS (ESI) calcd for $C_{13}H_7D_5NS^+$, $[M+H]^+$ 219.0999, found 219.0992.

5. Preparation of 1q-D



To a 50 mL flask equipped with a stir-bar was added deuterated aniline (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. After 12 h, 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 benzamide. A Schlenk flask equipped with a stir-bar was charged with benzamide (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 120 ℃ 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 **1q-D** 0.8024 g (yield 83%). Comparing the ^{1}H NMR spectra of **1q-D** (Figure S1) and **1q**, **70% deuterium was contained**.

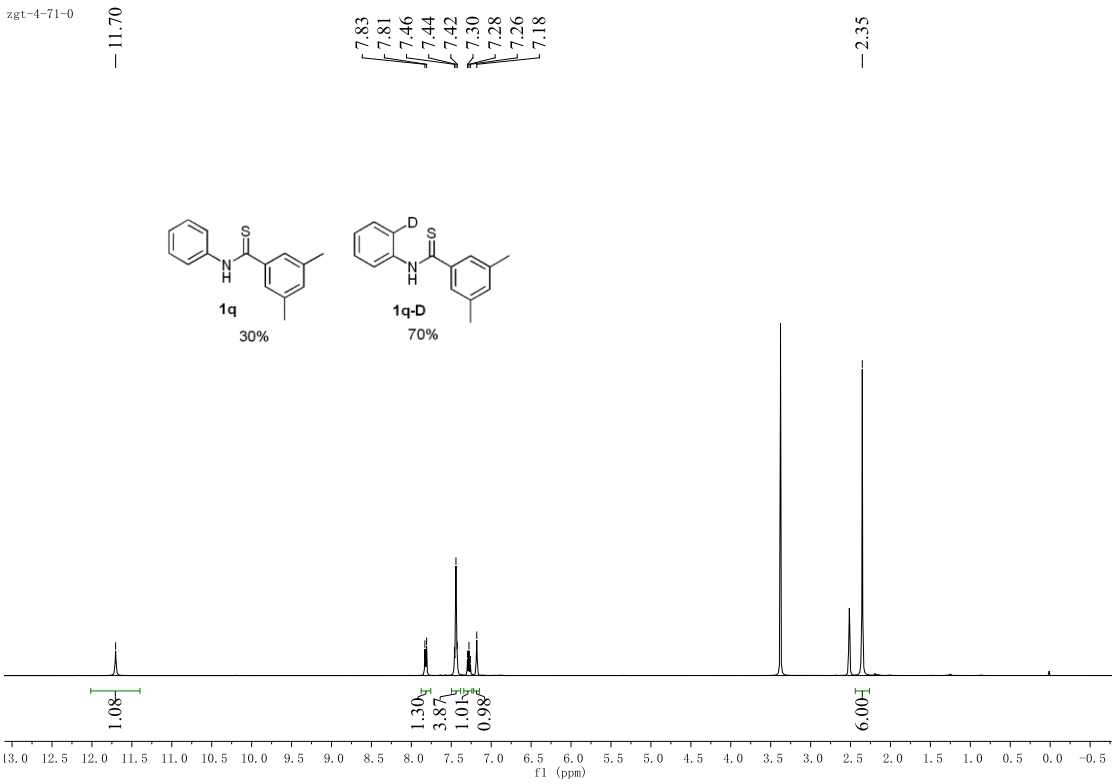
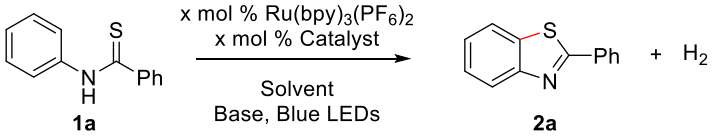


Figure S1. ^{1}H NMR (400M, d_6-DMSO) spectrum of **1q-D**.

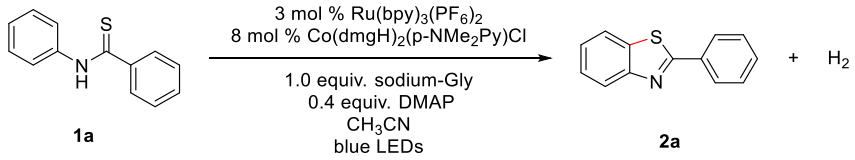
6. Table S1. Optimizing the Reaction Conditions[a]



Entry	Solvent	Photocatalyst (x mol%)	Catalyst (x mol%)	Base	Yield [b]	H_2 [c]
1	CH_3CN	$Ru(bpy)_3(PF_6)_2$(1)	$Co(dmgH)_2PyCl$(8)	Na_2CO_3(1.2 eq)	69%	20%
2	CH_3CN	$Ru(bpy)_3(PF_6)_2$(2)	$Co(dmgH)_2PyCl$(8)	Na_2CO_3(1.2 eq)	73%	12%
3	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2PyCl$(8)	Na_2CO_3(1.2 eq)	75%	25%
4	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2PyCl$(6)	Na_2CO_3(1.2 eq)	72%	18%
5	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2PyCl$(10)	Na_2CO_3(1.2 eq)	74%	17%
6	CH_3CN	$Ru(bpy)_3Cl_2$(3)	$Co(dmgH)_2PyCl$(10)	Na_2CO_3(1.2 eq)	58%	7%
7	CH_3CN	$Ir(ppy)_3$(3)	$Co(dmgH)_2PyCl$(8)	Na_2CO_3(1.2 eq)	0%	0%
8	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2(p\text{-}NMe_2Py)Cl$(8)	Na_2CO_3(1eq.)	99%	70%
9	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2(p\text{-}NMe_2Py)Cl$(8)	Na_2CO_3(0.8eq)	90%	43%
10	CH_3CN	$Ru(bpy)_3(PF_6)_2$(3)	$Co(dmgH)_2(p\text{-}NMe_2Py)Cl$(8)	Na_2CO_3(0.6eq)	89%	47%

[a] Conditions: **1a** (0.20 mmol), photocatalyst (x mmol), Catalyst (x mmol) and base (1.2 eq.) in solvent (2 mL) under an argon atmosphere and irradiation of 3W blue LEDs, RT, 12h; [b] isolated yields; [c] GC yields using pure methane as an internal standard.

7. Table S2. Control Experiments[a]



entry	visible Light	PS	PRC	base	yield[b]	H_2[c]
1	–	+	+	+	0%	0%
2	+	–	+	+	trace	0%
3	+	+	–	+	0%	0%
4	+	+	+	–	0%	0%
5	+	+	+	+	99%	99%
6[d]	+	+	+	+	0%	0%

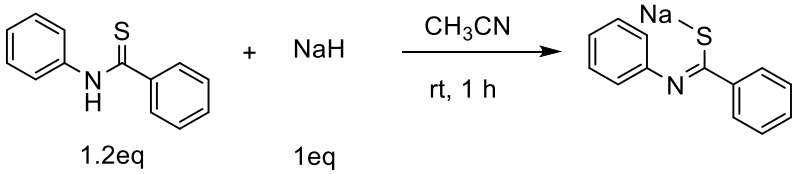
[a] Conditions: **1a** (0.20 mmol), $Ru(bpy)_3(PF_6)_2$ (3 mol%), $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$ (8 mol%) , sodium-Gly (1.0 equiv) and DMAP (0.4 equiv) in CH_3CN (2 mL) under an argon atmosphere, irradiation of 3W blue LED for 12 h at rt. [b] Isolated yields. [c] GC yields using pure methane as an internal standard. [d] without **1a**; PS: photosensitizer, PRC: proton reducing catalyst.

Mechanism Studys

1. Cyclic Voltammetry (CV) Experiments:

1.1 Preparation of Sodium *N*-phenylbenzimidothioate

A mixture of *N*-phenylbenzothioamide **1a** (0.1 mmol) and sodium hydride (0.83 mmol) was added in CH_3CN (1 mL). Then the mixture was stirred for 1 h.



1.2 CV experiments

The cyclic voltammetry (CV) was used to study the oxidation potential of substrate *N*-phenylbenzothioamide. As shown in the Figure S2, an obvious oxidative peak was detected with E_{pa}= 0.90 V (vs Ag/AgCl). This means *N*-phenylbenzothioamide **1a** first experienced an electron transfer to form a radical cation. Through the conversion of standard electrode potential, we obtained the potential of this oxidative peak is 0.94V vs SCE. Therefore it is difficult to be oxidized by $*Ru(bpy)_3^{2+}$ ($E_{1/2\ red}$ [$*Ru(bpy)_3^{2+}$/ $Ru(bpy)_3^{+}$] = +0.77 V vs SCE). Then in the presence of sodium *N*-phenylbenzimidothioate (sodium **1a**) in MeCN (Figure S3), a new oxidative peak was detected (E_{pa1}=0.49 V (vs Ag/AgCl)), Figure S3), we proposed that this peak can be ascribed to an electron transfer of the anion of **1a** to form the S-radical. Through the conversion of standard electrode potential, we obtained the potential of this oxidative peak is 0.53V vs SCE. Therefore, we can obtain that the anion intermediate of thioamide is much easier to be oxidized. Then the same oxidative peak at E_{pa2} = 0.90 V would be found, we proposed this peak can be ascribed to an electron transfer of excess *N*-phenylbenzothioamide **1a** experienced an electron transfer to form a radical cation.

General condition: solvent CH_3CN 4 mL, supporting electrolyte NBu_4BF_4 0.1 M, under N_2.

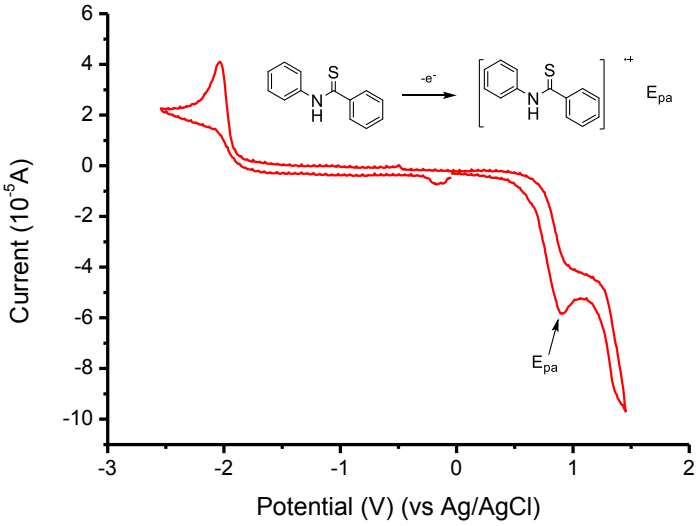


Figure S2. CV spectra in 0.1 M NBu_4PF_6 under N_2. 0.1 mM **1a** in degased CH_3CN at a steady glassy carbon disk electrode, d = 5 mm, scan rate 100 mV/s, range from -3.0V to 2V.

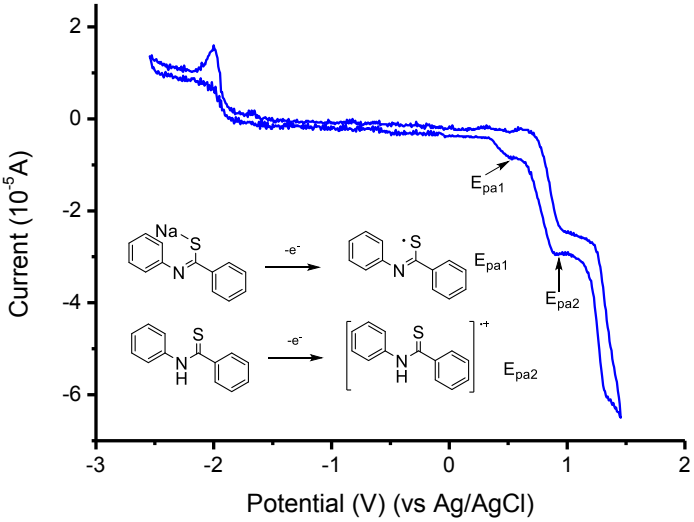
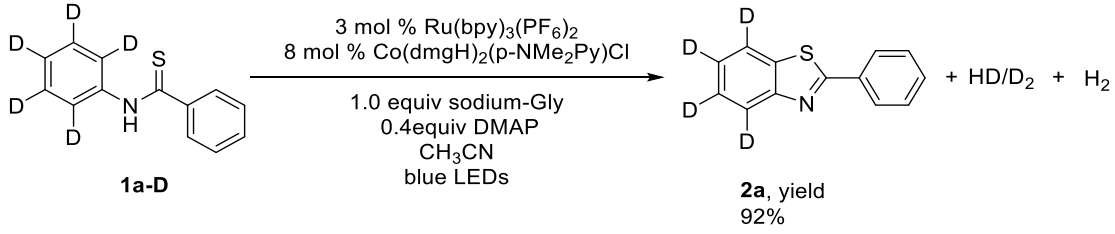


Figure S3. CV spectra in 0.1 M NBu_4PF_6 under N_2. 0.1 mM sodium *N*-phenylbenzimidothioate in degased CH_3CN at a steady glassy carbon disk electrode, d = 5 mm, scan rate 20 mV/s, range from -3.0V to 2V.

2. Deuterium Experiments for Reaction



1a-D

2a, yield 92%

A mixture of *N*-(phenyl-d_5)benzothioamide **1a-D** (0.2 mmol), sodium glycinate (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.006 mmol), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (0.016 mmol) and DMAP (0.08 mmol) in degased CH_3CN (2 mL) was stirred under an argon atmosphere and irradiation of blue LED for 12 h. After completion of the reaction, D_2 or HD was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, helium as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector, oven temp. 90 ℃, TCD temp. 100 ℃, injection temp. 100 ℃, CURR: 70). Under this condition, a negative peak would be found, it was belong to HD or D_2 while H_2 was shown as a positive peak. However, the ratio of H_2: HD: D_2 could not be get through this method. Then the solid was filtered off and washed with ethyl acetate. After removal of the solvent of the filtrate, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford **2a-D** in 92% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.10 – 8.07 (m, 2H), 7.50 – 7.47 (m, 3H).

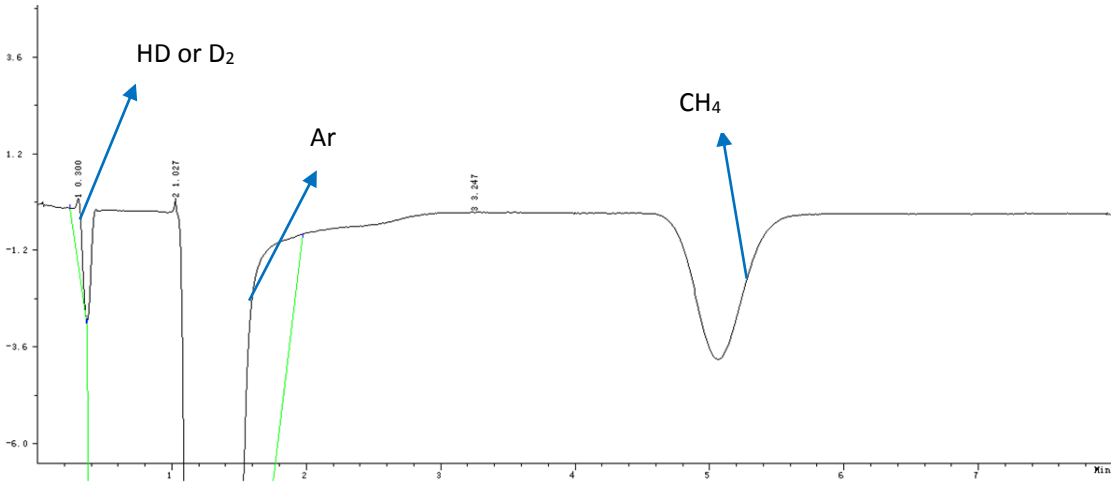
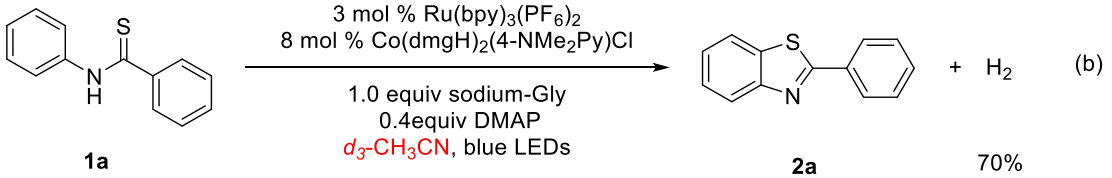


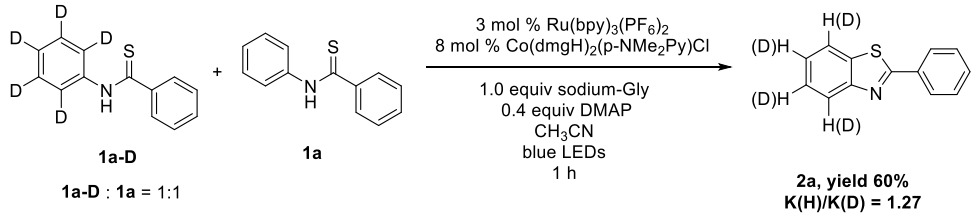
Figure S4. GC data of deuterium experiments.



A mixture of *N*-(phenyl-d_5)benzothioamide **1a-D** (0.2 mmol), sodium glycinate (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.006 mmol), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (0.016 mmol) and DMAP (0.08 mmol) in degased CH_3CN-d_3 (2 mL) was stirred under an argon atmosphere and irradiation of blue LED for 12 h. After completion of the reaction, D_2 or HD was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, helium as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector, oven temp. 90 ℃, TCD temp. 100 ℃, injection temp. 100 ℃, CURR: 70).

3. Kinetics of Isotopic Effect Experiments

3.1 Intermolecular KIE Experiment



A Schlenk tube equipped with a stir-bar was charged with $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 0.01 mmol), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (7.2 mg, 0.016 mmol), **1a-D** (21.8 mg, 0.10 mmol) and **1a** (21.3 mg, 0.1 mmol), sodium-Gly (19.4 mg, 0.20 mmol) and DMAP (9.8 mg, 0.08mmol). After that, the reaction tube was purged with argon. Then 2 mL of CH_3CN was added to the reaction tube via a syringe. Finally, the Schlenk tube was under irradiation of blue LED and stirred for 15 min. Then the solid was filtered off and washed with ethyl acetate. After removal of the solvent of the filtrate, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford a mixture of the products deuterium-**2a** (**2a-D**) and **2a** in 40% combined yields. Comparing the ^{1}H NMR spectra of **2a-D** and **2a** (Figure S5), we found the ratio of 2o-D : 2o was 3 : (6.29-4) or 2 : (4.53-3). So **the intermolecular KIE value was 1.31** (Figure S6).

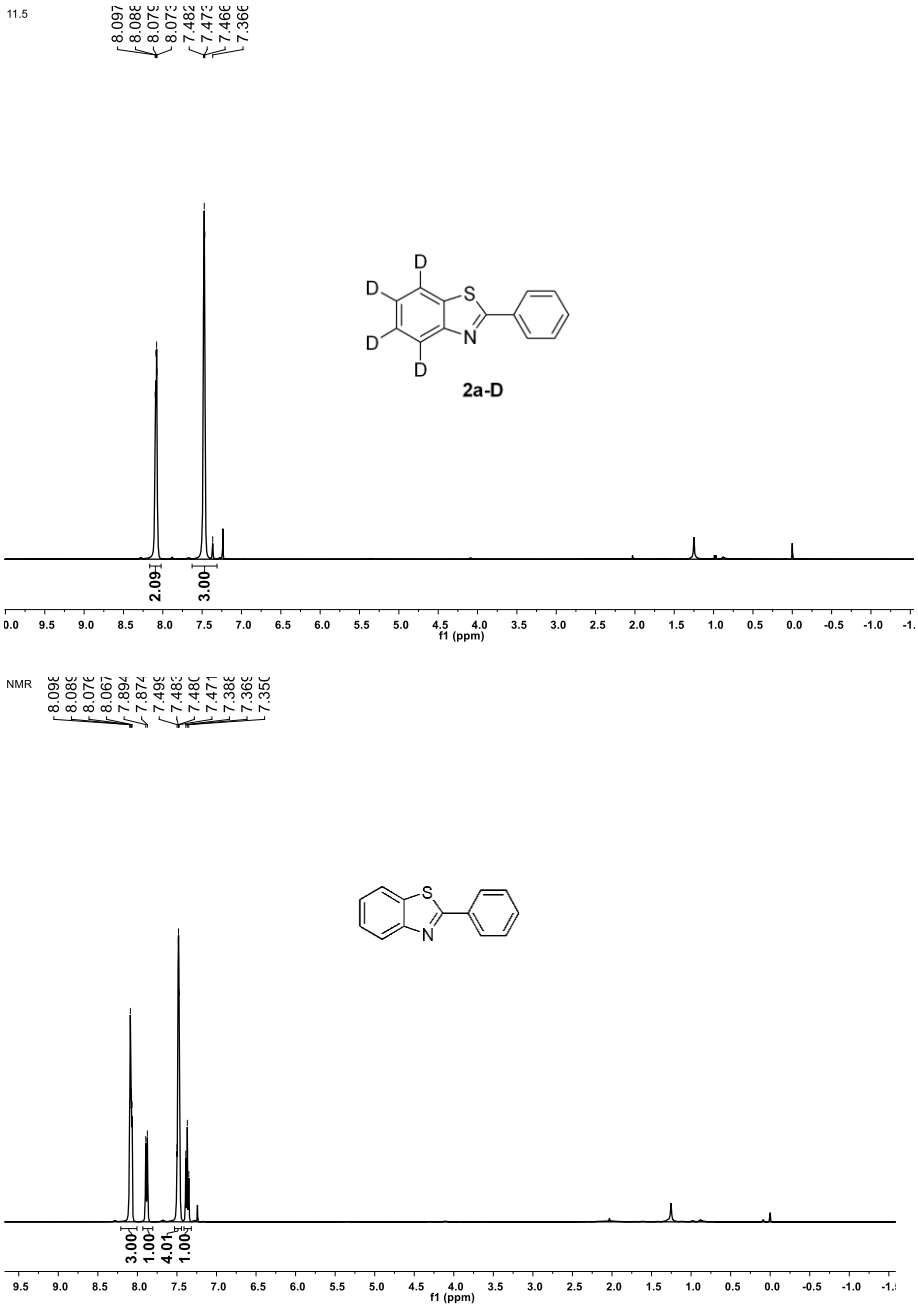


Figure S5. Comparison of the ^{1}H NMR of **2a-D** and **2a**.

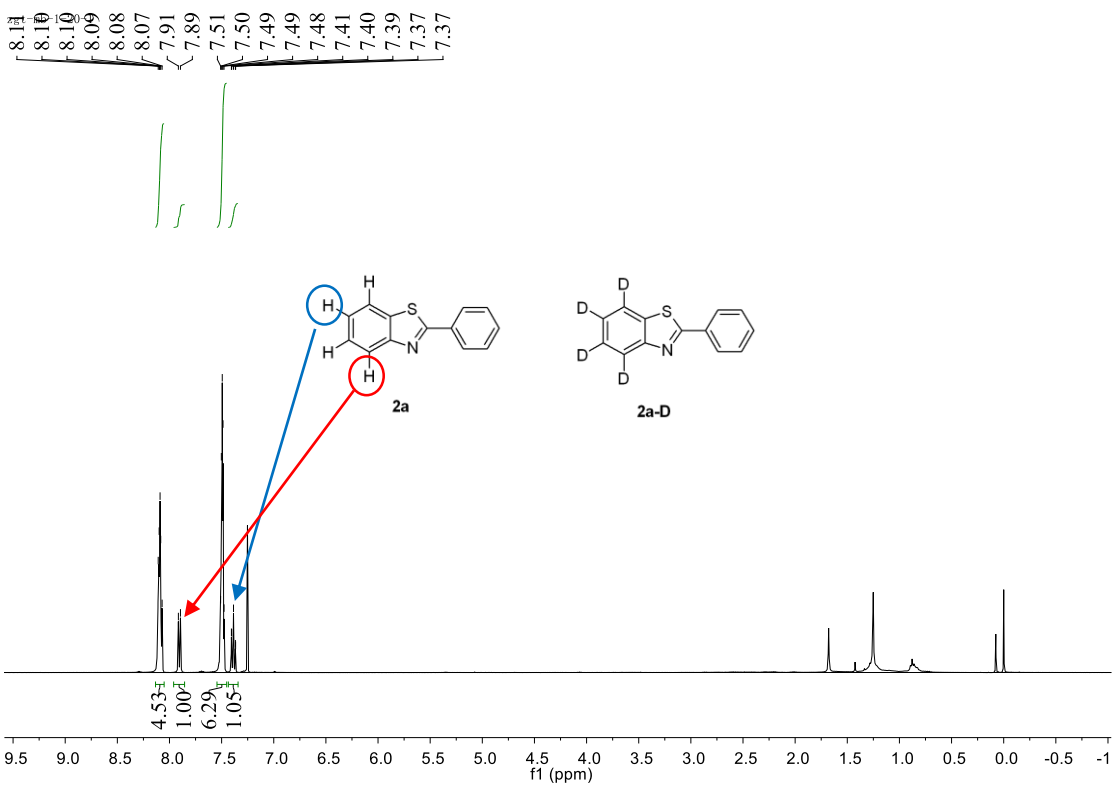


Figure S6. ^{1}H NMR of a mixture of the products deuterium-**2a** (**2a-D**) and **2a**.

3.2 Intramolecular KIE Experiment

A mixture of *N*-phenylbenzothioamide **1q-D** (0.2 mmol), sodium glycinate (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.006 mmol, 3 mol %), $Co^{III}(dmgH)_2(4\text{-}NMe_2Py)Cl$ (0.016 mmol, 8 mol %) and DMAP (4-dimethylaminopyridine) (0.08 mmol, 40 mol %) in degased dry CH_3CN (2 mL) was stirred under an argon atmosphere and irradiation of a commercially available blue LEDs for 12 h. After completion of the reaction, the solid was filtered off and washed with ethyl acetate. After removal of the solvent of the filtrate, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford a mixture of the products deuterium-**2q** (**2q-D**) and **2q** in 99% yield. As Shown in the ^{1}H NMR spectra (Figure S7), we found the ratio of **2q** : **2q-D** was 66 : 34. Because the **70% deuterated** substrate **1q-D** was used, the real ratio of **2q** : **2q-D** (only generate from **1q-D**) was 36:34. **Therefore, the intramolecular KIE value was 1.06.**

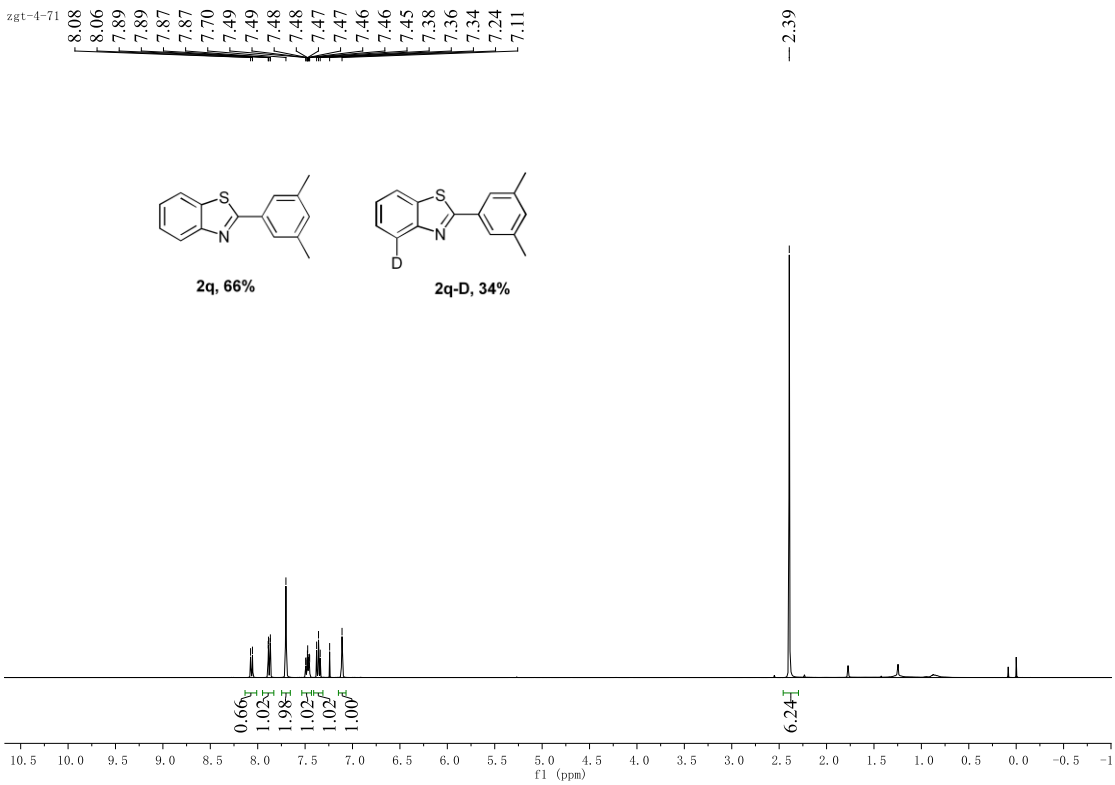


Figure S7. ^{1}H NMR of a mixture of the products deuterium-**2q** (**2q-D**) and **2q**

4. Emission Quenching Experiments For $Ru(bpy)_3(PF_6)_2$

Emission intensities were recorded using a HITACHI F-4500 Fluorescence Spectrometer. All $Ru(bpy)_3(PF_6)_2$ solutions were excited at 450 nm and the emission intensity at 615 nm was observed. CH_3CN was degassed with a stream of N_2 for 30 min and then moved to glove box. All the solutions were prepared in the glove box. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of $Ru(bpy)_3(PF_6)_2$ in CH_3CN was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

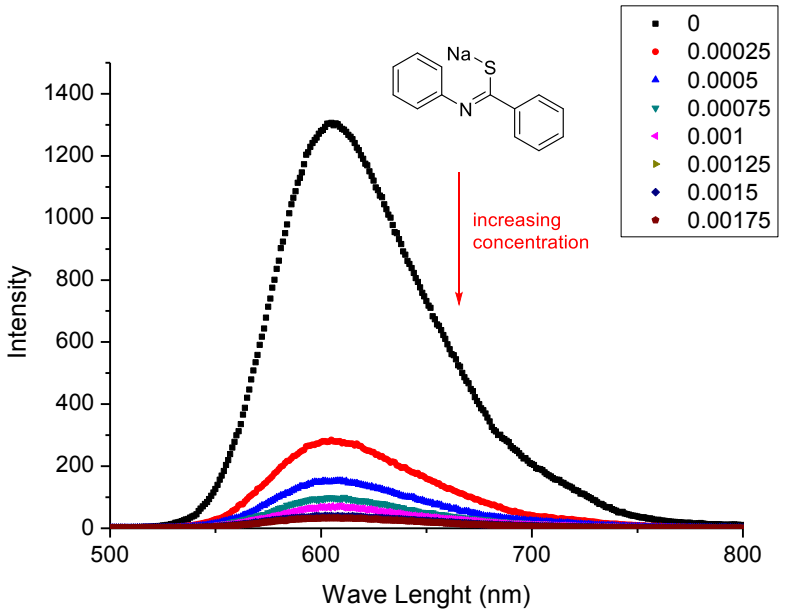


Figure S8: $Ru(bpy)_3(PF_6)_2$ Emission Quenching by $Co(dmgH)_2$(*p*-NMe_2Py)Cl

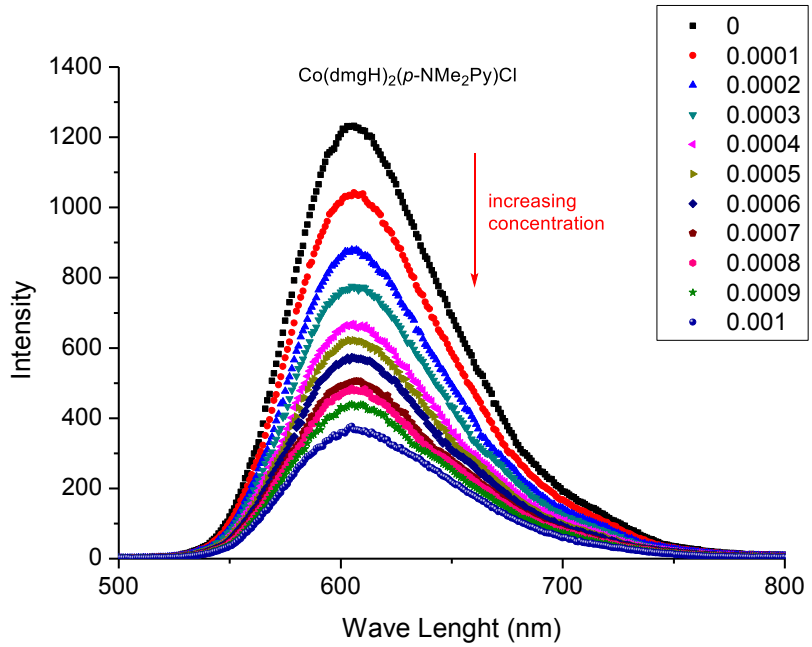


Figure S9: $Ru(bpy)_3(PF_6)_2$ Emission Quenching by DMAP

5. Monitoring the Reaction Using Condition A

The reaction was detected during different time to monitor the kinetic profile of **1a** under the condition A. A mixture of **1a** (0.20 mmol), $Ru(bpy)_3(PF_6)_2$ (3 mol%), $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$ (8 mol%), sodium-Gly (1.0 equiv) and DMAP (0.4 equiv) in CH_3CN (2 mL) under an argon atmosphere was irradiated by 3W blue LEDs, the isolated yield was shown. As shown in Figure 10, under the irradiation of blue LED, **1a** was converted completely only in 1-2 hours. And in the meantime, corresponding benzothiazole **2a** and H_2 was detected.

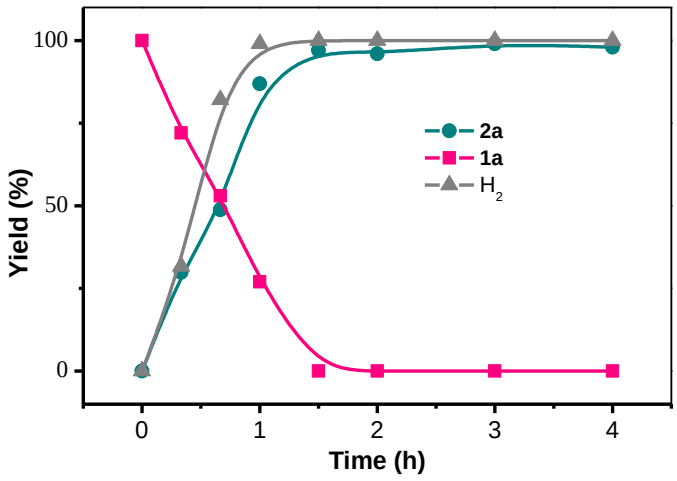


Figure S10. The kinetic profile of the reaction over time; isolated yields were shown.

6. Kinetic order investigation by *in-situ* IR.

General Procedure for the investigation of kinetics monitored by *in-situ* IR: A three-neck tube equipped with a stir-bar, $Ru(bpy)_3(PF_6)_2$, $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$ and **1a** was fixed on the *in situ* IR and purged with nitrogen gas. At 30 ℃, 10 mol% TBAOH (1M solution in MeOH) and 5 mL of degassed CH_3CN was added to the reaction tube via a syringe, and then the tube was irradiated by blue LED. 1 h later, the reaction was then cooled to room temperature and the yield was determined by GC.

Order in Substrate. The order in a substrate **1a** was determined by studying the initial rate of reaction with different concentration of **1a**. Using the above mentioned general procedure, 1a (0.3 ~ 0.5 mmol), $Ru(bpy)_3(PF_6)_2$ (10.4 mg, 0.012 mmol), $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$ (14.4 mg, 0.032 mmol) was added. Product yield from the corresponding reaction was monitored by GC-FID using an internal standard (diphenyl). Finally, the profiles of relative concentrations vs time for product **2a** could be obtained to analyse the initial rate of reaction. As shown in Figure S11, the reaction rate was unvaried when using different concentrations of the substrate **1a**. Therefore, these result indicated a zero order reaction dependence on [**1a**].

Order in $Ru(bpy)_3(PF_6)_2$. The order in photosensitizer $Ru(bpy)_3(PF_6)_2$ was also determined by the same method. Using the above mentioned general procedure, **1a** (85.2 mg, 0.4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.008 ~ 0.02 mmol), $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$ (14.4 mg, 0.032 mmol) was added. Product yield from the corresponding reaction was monitored by GC-FID using an internal standard (diphenyl). From Figure S12, the initial rate of reaction was changeless when using different concentrations of the photosensitizer. Therefore, these result indicated a zero order reaction dependence on [$Ru(bpy)_3(PF_6)_2$].

Order in Co(dmgH)$_2$(4-NMe$_2$Py)Cl. The order in Co(dmgH)$_2$(4-NMe$_2$py)Cl was determined by studying the initial rate of reaction with different concentration of cobalt catalyst. Using the above mentioned general procedure, **1a** (0.4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (10.4 mg, 0.012 mmol), Co(dmgH)$_2$(4-NMe$_2$Py)Cl (0.008 ~ 0.0032 mmol) was added. Product yield from the corresponding reaction was monitored by GC-FID using an internal standard (diphenyl). Finally, the profiles of relative concentrations vs time for product **2a** could be obtained to analyse the initial rate of reaction (Figure S13). A log plot of initial rate (Δ[**2a**]/Δt) versus [Co(dmgH)$_2$(4-NMe$_2$py)Cl] gave a straight line (R^2 = 0.96846), indicative of a 1st order dependence on [Co(dmgH)$_2$(4-NMe$_2$py)Cl]. k_{obs} = 0.29165 min^{-1}.

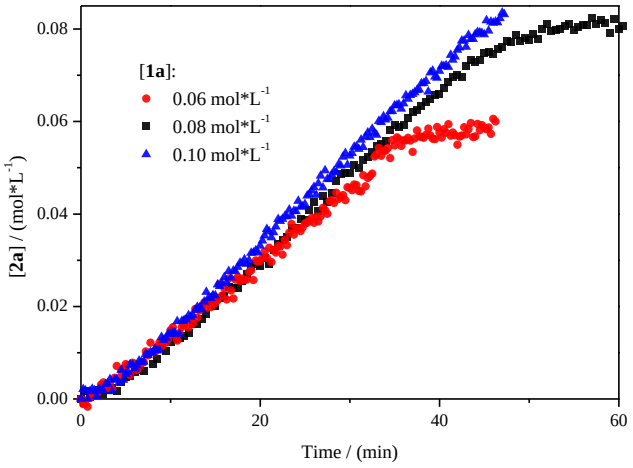


Figure S11, the profiles of relative concentrations of **2a** vs time in different [**1a**].

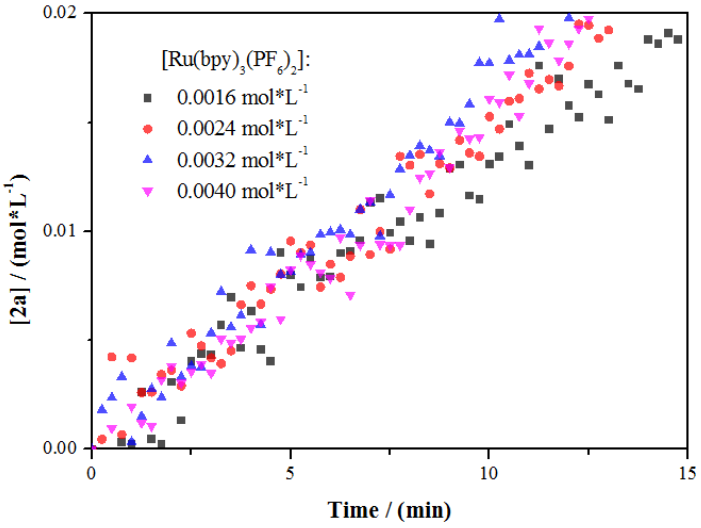


Figure S12. The profiles of relative concentrations of **2a** vs time in different [Ru(bpy)$_3$(PF$_6$)$_2$].

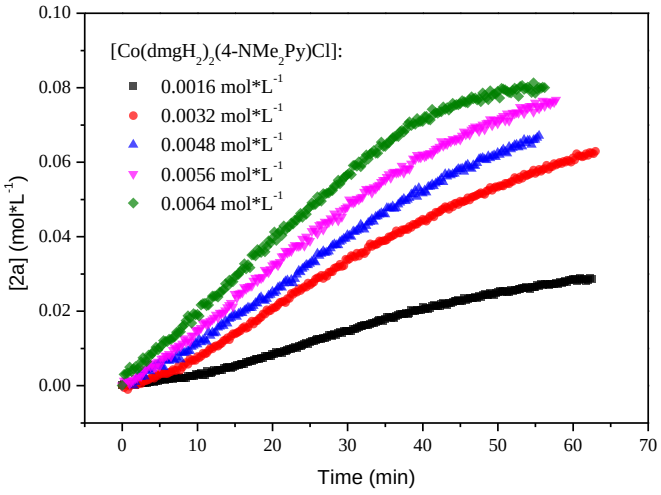


Figure S13. The profiles of relative concentrations of **2a** vs time in different [Co(dmgH)$_2$(4-NMe$_2$py)Cl].

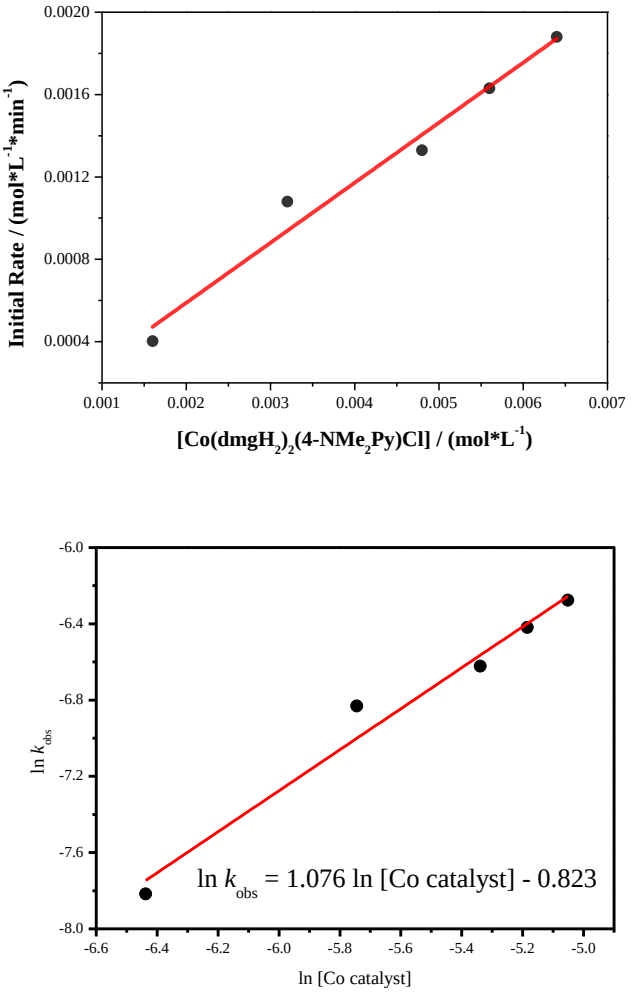


Figure S14. First order kinetic experiment dependence on [Co(dmgH)$_2$(4-NMe$_2$py)Cl].

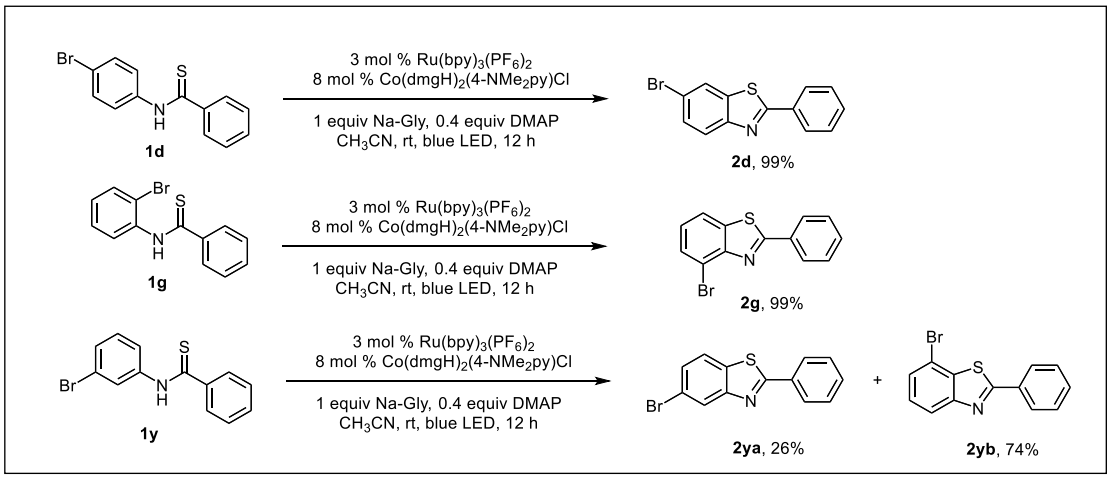
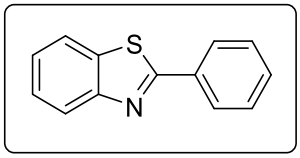
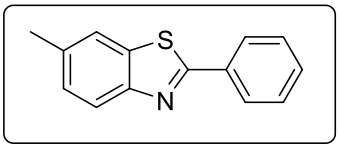


Figure S15. The limitation of the *meta*- substitution on the *N*-aryl ring of substrates.

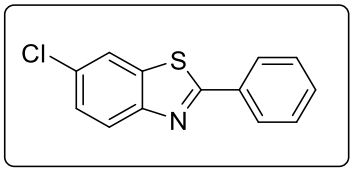
Characterization of Products



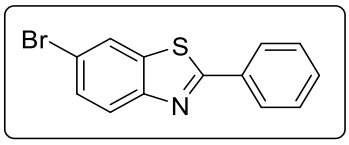
2-phenylbenzothiazole (**2a**);[2] condition A: 41.6 mg (yield: 99%, 0.2 mmol scale), condition B: 95%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 – 8.07 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.47 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.09, 154.18, 135.11, 133.67, 130.99, 129.05, 127.60, 126.35, 125.22, 123.28, 121.65.



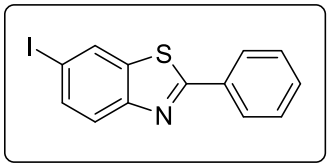
6-methyl-2-phenylbenzothiazole (**2b**);[2] 43.2 mg (yield: 96%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 – 8.05 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.65 (s, 1H), 7.46 – 7.45 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.03, 152.28, 135.38, 135.25, 133.78, 130.78, 129.00, 127.95, 127.46, 122.75, 121.39, 21.57.



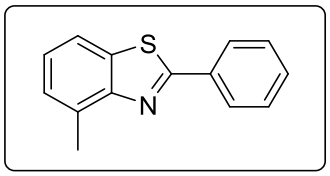
6-chloro-2-phenylbenzothiazole (**2c**);[3] 49.2 mg (yield: 99%, 0.2 mmol scale), condition B: 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 8.02 (m, 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 2 Hz, 1H), 7.48 – 7.47 (m, 3H), 7.42 (dd, *J* = 8.7, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.54, 152.69, 136.23, 133.23, 131.26, 131.10, 129.10, 127.56, 127.14, 123.95, 121.23.



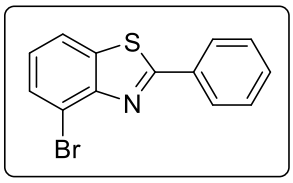
6-bromo-2-phenylbenzothiazole (**2d**);[2] 57.7 mg (yield: 99%, 0.2 mmol scale), condition B: 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 8.04 (m, 2H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.45 – 7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.58, 153.00, 136.68, 133.16, 131.32, 129.85, 129.13, 127.57, 124.31, 124.17, 118.76.



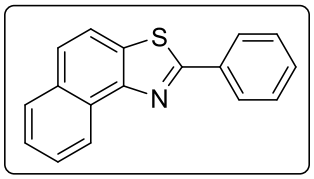
6-iodo-2-phenylbenzothiazole (**2e**);[2] 65.9 mg (yield: 98%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 8.07– 8.05 (m, 2H), 7.77 (q, J = 8.5 Hz, 2H), 7.49 (d, J = 4.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.48, 152.45, 136.08, 134.42, 132.06, 130.30, 129.07, 128.07, 126.58, 123.64, 88.43.



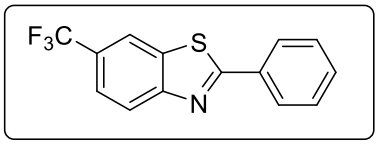
4-methyl-2-phenylbenzothiazole (**2f**);[2] 45.0 mg (yield: 99%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 – 8.09 (m, 2H), 7.72 – 7.70 (m, 1H), 7.49 – 7.46 (m, 3H), 7.26 – 7.23 (m, 2H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.62, 153.55, 135.03, 134.00, 133.40, 130.74, 128.98, 127.57, 126.82, 125.11, 119.00, 18.44.



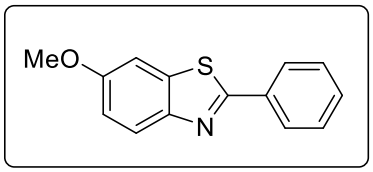
4-bromo-2-phenylbenzothiazole (**2g**);[3] 58.0 mg (yield: 99%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 – 8.12 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.43 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.60, 152.33, 135.91, 133.27, 131.36, 129.80, 129.03, 127.80, 125.96, 120.79, 116.94.



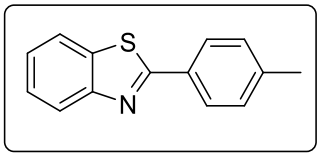
2-phenylnaphthothiazole (**2h**);[2] 51.8 mg (yield: 99%, 0.2 mmol scale), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.13, 150.39, 133.97, 132.11, 131.67, 130.65, 129.06, 128.79, 128.09, 127.39, 126.99, 126.18, 125.97, 124.09, 118.97.



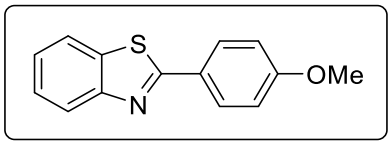
2-phenyl-6-(trifluoromethyl)benzothiazole (**2i**);[4] 50.7 mg (yield: 91%, 0.2 mmol scale), condition B: 91%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.02 (m, 4H), 7.73 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.58 – 7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.13, 156.03, 135.08, 132.99, 131.69, 129.17, 127.75, 127.24 (q, *J* = 201 Hz), 123.48, 123.32 (q, *J* = 3.4 Hz), 122.82, 119.31 (q, *J* = 4.2 Hz).



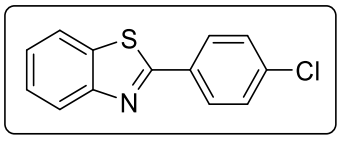
6-methoxy-2-phenylbenzothiazole (**2j**);[2] 21.0 mg (yield: 45%, 0.2 mmol scale), condition B: 76%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 8.03 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.49 – 7.46 (m, 3H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.57, 157.80, 148.69, 136.43, 133.76, 130.56, 128.99, 127.26, 123.73, 115.66, 104.19, 55.81.



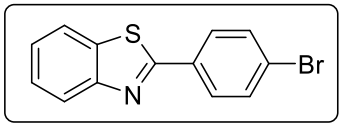
2-(p-tolyl)benzothiazole (**2k**);[5] 43.3 mg (yield: 96%, 0.2 mmol scale),white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.26, 154.19, 141.44, 134.98, 130.99, 129.74, 127.52, 126.26, 125.02, 123.07, 121.58, 21.53.



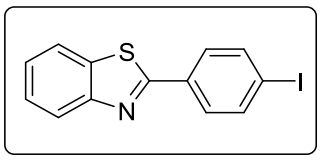
2-(4-methoxyphenyl)benzothiazole (**2l**);[2] 47.2 mg (yield: 98%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 – 8.00 (m, 3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.88, 161.96, 154.25, 134.89, 129.14, 126.46, 126.22, 124.81, 122.84, 121.53, 114.39, 55.46.



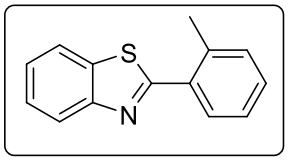
2-(4-chlorophenyl)benzothiazole (**2m**);[2] 49.0 mg (yield: 99%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.65, 154.05, 137.08, 135.06, 132.12, 129.30, 128.74, 126.51, 125.44, 123.32, 121.67.



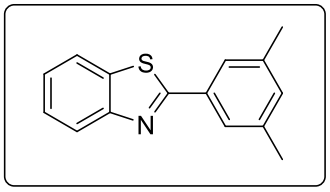
2-(4-bromophenyl)benzothiazole (**2n**);[2] 58.0 mg (yield: 99%, 0.2 mmol scale), condition B: 98%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.78, 153.94, 134.98, 132.47, 132.28, 128.96, 126.57, 125.52, 123.31, 121.69.



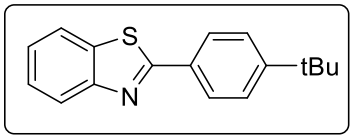
2-(4-iodophenyl)benzothiazole (**2o**);[2] 53.8 mg (yield: 80%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.76 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.84, 154.05, 138.18, 135.00, 133.08, 128.93, 126.51, 125.48, 123.35, 121.68, 97.53.



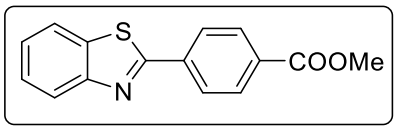
2-(o-tolyl)benzothiazole (**2p**);[6] 45.2 mg (yield: 99%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.27 (m, 4H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.02, 153.85, 137.30, 135.64, 133.14, 131.58, 130.58, 130.03, 126.16, 126.14, 125.12, 123.42, 121.39, 21.39.



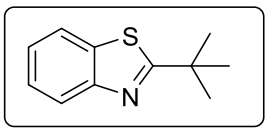
2-(3,5-dimethylphenyl)benzothiazole (**2q**);[7] 47.7 mg (yield: 99%, 0.2 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 2H), 7.48 – 7.41 (m, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.10 (s, 1H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.59, 154.14, 138.74, 135.03, 133.47, 132.79, 126.27, 125.38, 125.07, 123.14, 121.60, 21.26.



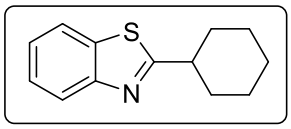
2-(4-(tert-butyl)phenyl)benzothiazole (**2r**);[8] 53.4 mg (yield: 99%, 0.2 mmol scale), condition B: 96%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 154.58, 154.20, 134.99, 130.91, 127.39, 126.25, 126.01, 125.02, 123.10, 121.59, 35.01, 31.21.



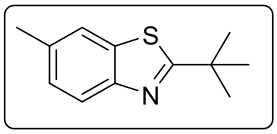
methyl 4-(benzothiazol-2-yl)benzoate (**2t**);[9] 45.2 mg (yield: 84%, 0.2 mmol scale), white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 4H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.01, 165.83, 153.64, 136.98, 134.80, 131.59, 129.70, 126.91, 126.03, 125.14, 123.10, 121.15, 51.72.



2-(tert-butyl)benzothiazole (**2u**);[2] 37.5 mg (yield: 99%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 181.91, 153.23, 134.96, 125.76, 124.53, 122.66, 121.47, 38.33, 30.77.

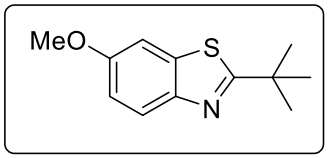


2-cyclohexylbenzothiazole (**2v**);[2] 28.0 mg (yield: 65%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.38 – 7.30 (m, 1H), 3.14 – 3.07 (m, 1H), 2.23 – 2.19 (m, 2H), 1.93 – 1.85 (m, 2H), 1.79 – 1.75 (m, 1H), 1.66 – 1.59 (m, 2H), 1.51 – 1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.69, 153.08, 134.53, 125.82, 124.52, 122.55, 121.58, 43.46, 33.46, 26.09, 25.80.

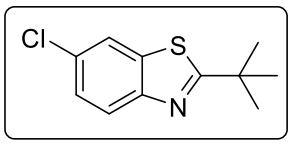


2-(tert-butyl)-6-methylbenzothiazole (**2ua**);[2] 28.5 mg (yield: 70%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.4 Hz, 1H), 7.63 (s, 1H), 7.28 – 7.22 (m, 1H), 2.47 (s,

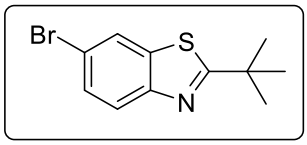
3H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.81, 151.28, 135.09, 134.52, 127.29, 122.12, 121.23, 38.23, 30.77, 21.49.



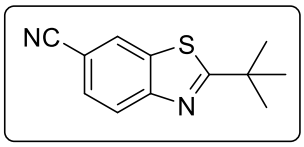
2-(*tert*-butyl)-6-methoxybenzothiazole (**2ub**);[2] 26.0 mg (yield: 59%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.86 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.34, 157.19, 147.66, 136.19, 123.09, 114.85, 104.16, 55.80, 38.18, 30.76.



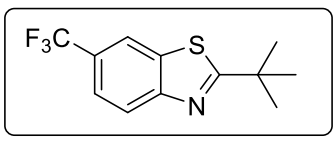
2-(*tert*-butyl)-6-chlorobenzothiazole (**2uc**);[10] 42.3 mg (yield: 94%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.41 – 7.38 (m, *J* = 8.7, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 182.46, 151.79, 136.20, 130.36, 126.52, 123.42, 121.07, 38.43, 30.68.



6-bromo-2-(tert-butyl)benzothiazole (**2ud**);[10] 44.6 mg (yield: 83%, 0.2 mmol scale), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 1.6 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.55 (m, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 182.51, 152.13, 136.70, 129.22, 124.00, 123.81, 118.01, 38.43, 30.68.

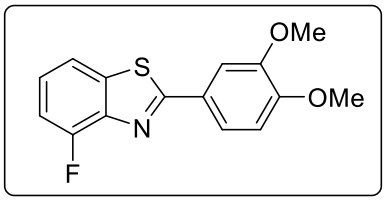


2-(*tert*-butyl)benzothiazole-6-carbonitrile (**2ue**), 38.9 mg (yield: 90%, 0.2 mmol scale), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.6 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.66, 155.72, 135.55, 129.05, 126.34, 123.45, 118.92, 107.97, 38.84, 30.62; HRMS: (ESI+) m/z calcd. for $C_{12}H_{13}N_2S^+$ $[M+H]^+$: 217.0794, found: 217.0791.



2-(*tert*-butyl)-6-(trifluoromethyl)benzothiazole (**2uf**), 44.5 mg (yield: 86%, 0.2 mmol scale), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* =

8.6, 1.5 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.29, 155.27, 135.10, 126.74 (q, *J* = 32.0 Hz), 125.64, 122.99, 122.78 (q, *J* = 3.5 Hz), 119.17 (q, *J* = 4.3 Hz), 38.68, 30.66; ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.28; HRMS: (ESI+) m/z calcd. for $C_{12}H_{13}F_3NS^+$ $[M+H]^+$: 260.0715, found: 260.0711.



2-(3,4-dimethoxyphenyl)-4-fluorobenzothiazole (**2w**),[11] white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.11 – 7.91 (m, 1H), 7,65 – 7,59 (m, 2H), 7.55 – 7.35 (m, 2H), 7.12 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), ^{19}F NMR (377 MHz, DMSO-d_6) δ -122.70.

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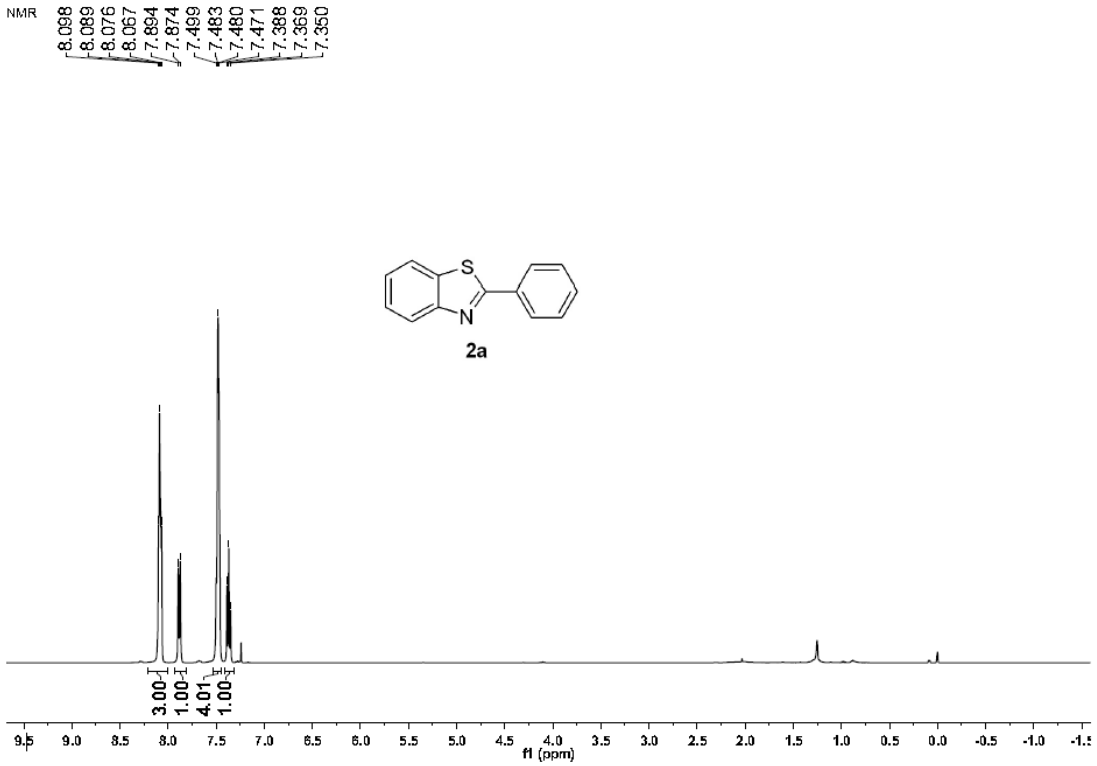
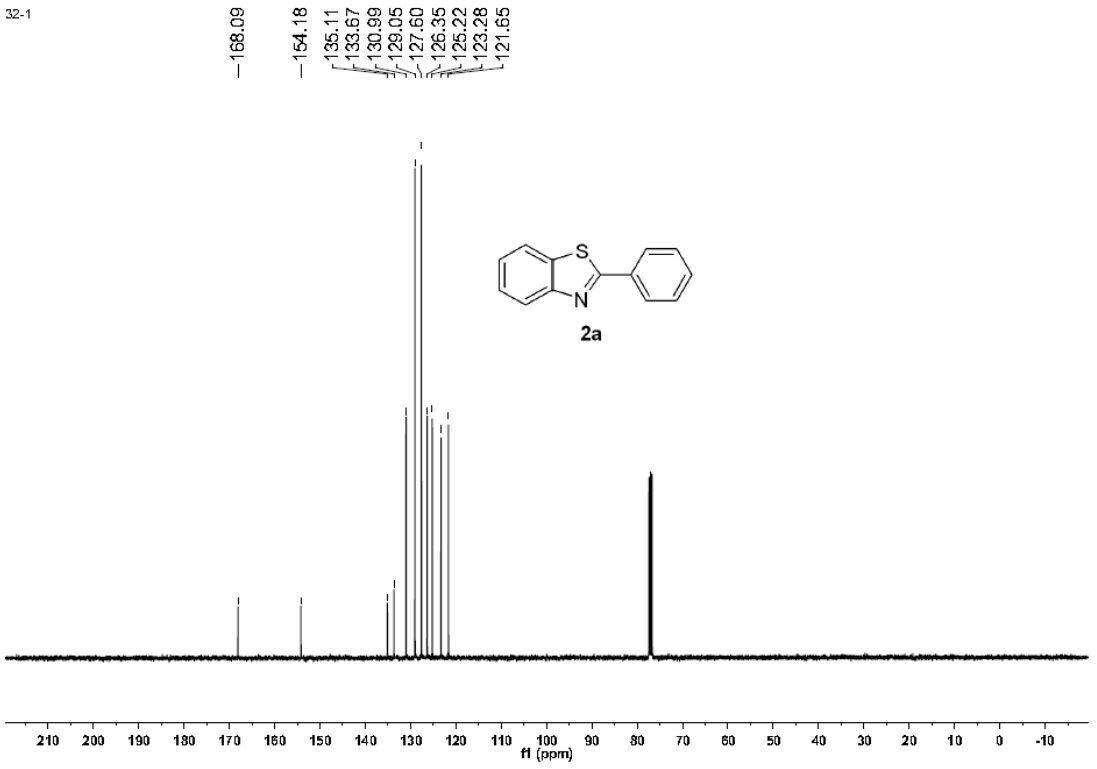
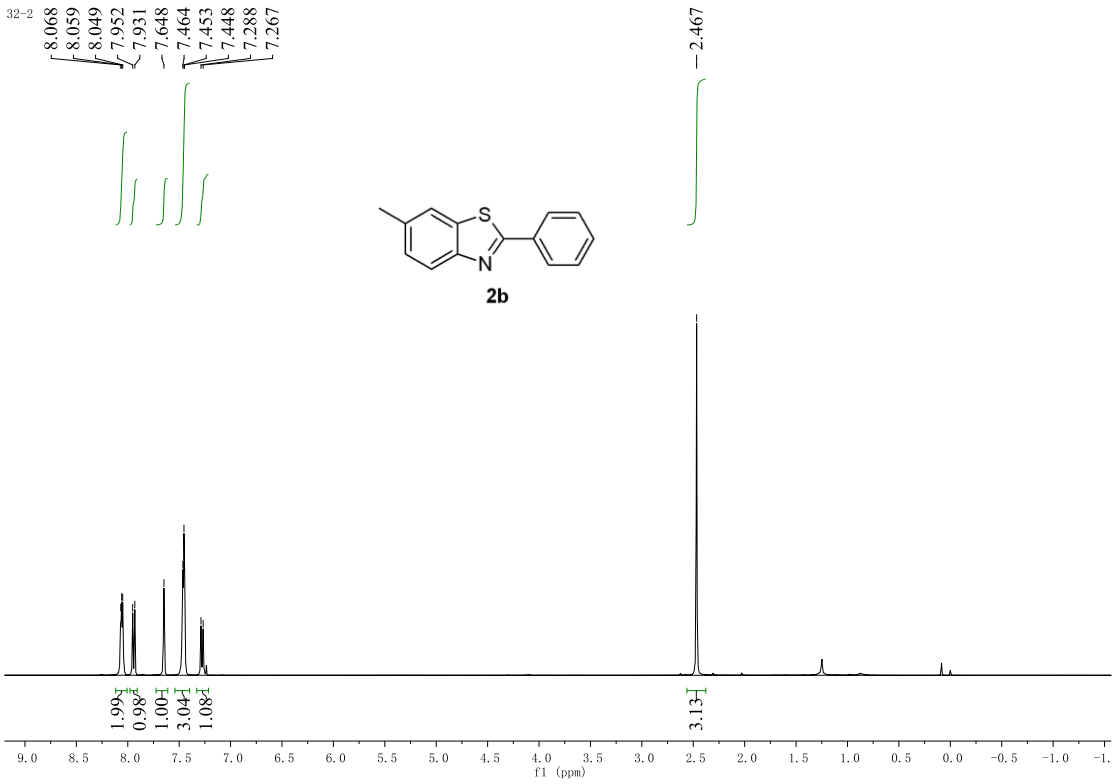
NMR Spectra of Products



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8.049
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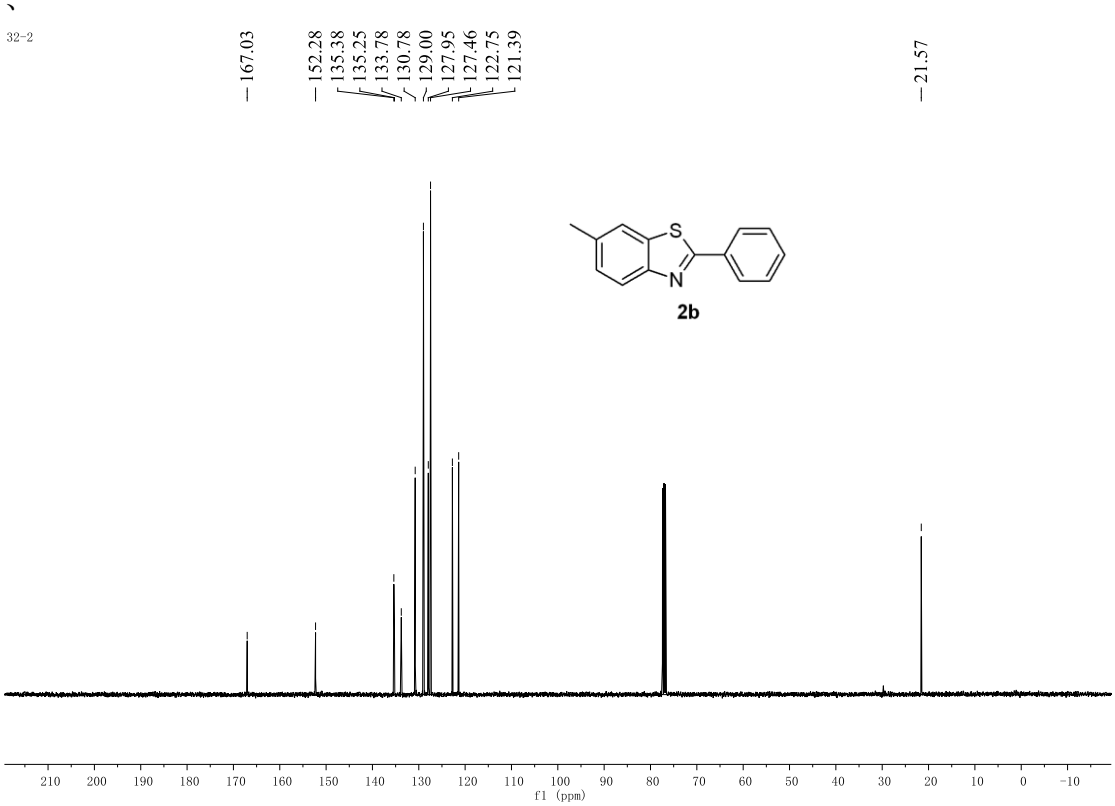
7.931
7.648
7.464
7.453
7.448
7.288
7.267
2.467
S
N
2b
1.99
0.98
1.00
3.04
1.08
3.13
f1 (ppm)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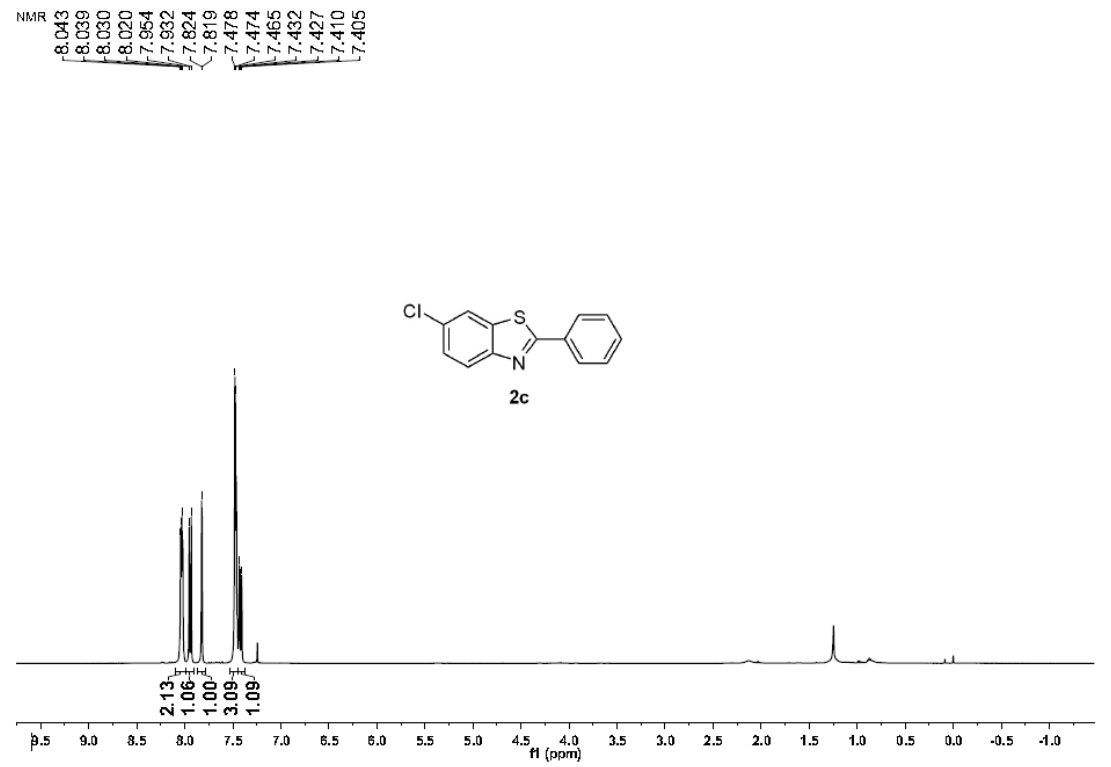
152.28
135.38
135.25
133.78
130.78
129.00
127.95
127.46
122.75
121.39
21.57
S
N
2b
f1 (ppm)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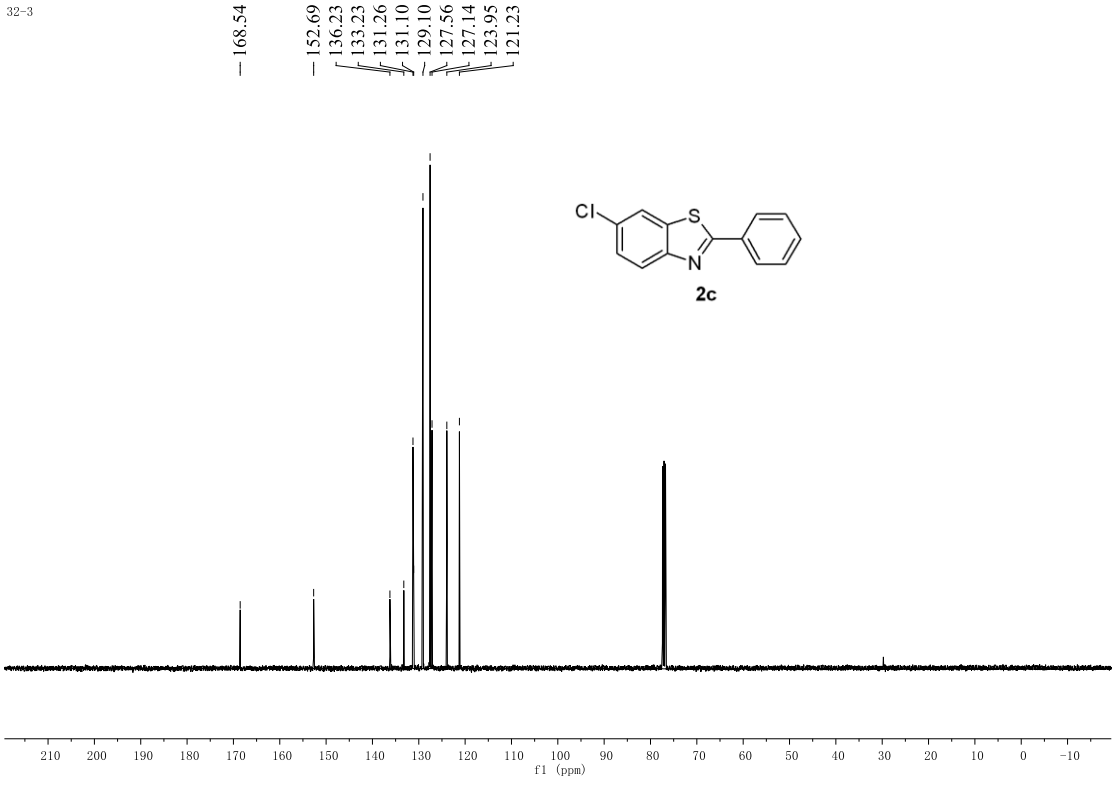
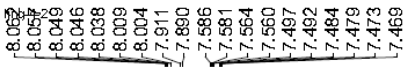
8.030
8.020
7.954
7.932
7.824
7.819
7.478
7.474
7.465
7.432
7.427
7.410
7.405
Cl
S
N
2c
2.13
1.06
1.00
3.09
1.09
f1 (ppm)


32-3
168.54
152.69
136.23
133.23
131.26
131.10
129.10
127.56
127.14
123.95
121.23
Cl
S
N
2c
f1 (ppm)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8.038
8.009
8.004
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7.586
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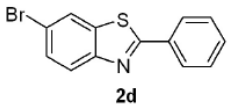
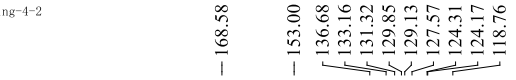
7.564
7.560
7.497
7.492
7.484
7.479
7.473
7.469


Br
S
N

2d

2.00
0.94
1.00
1.00
3.01
f1 (ppm)

ling-4-2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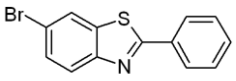
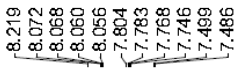
124.17
118.76


Br
S
N

2d

f1 (ppm)

NMR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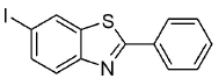
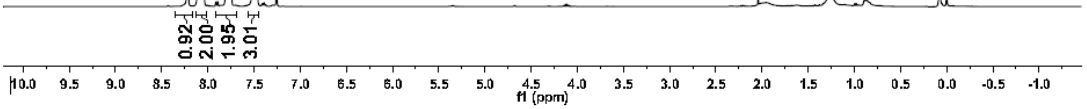
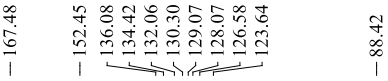
8.068
8.060
8.056
7.804
7.783
7.768
7.746
7.499
7.486


I
S
N

2e


0.92
2.00
1.95
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

32-4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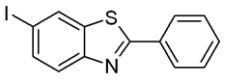
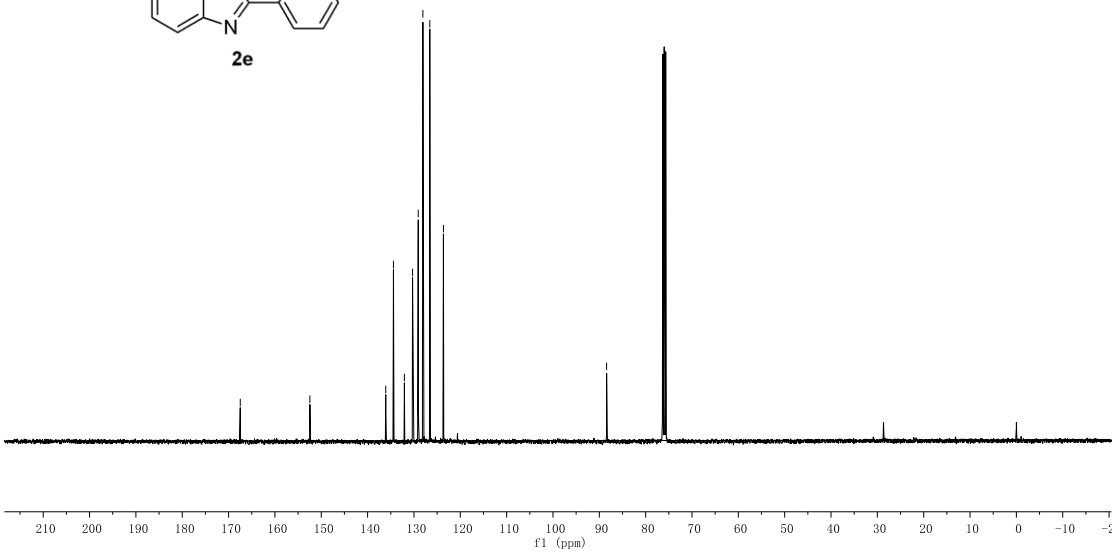
129.07
128.07
126.58
123.64
88.42


I
S
N

2e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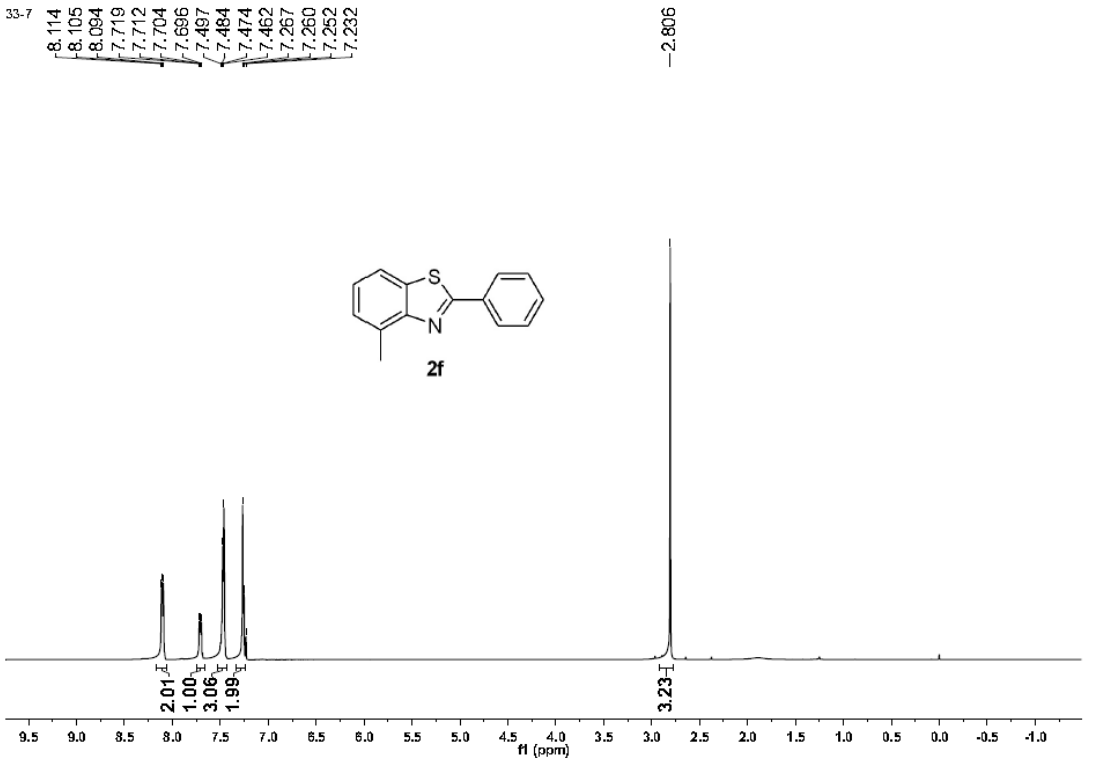
f1 (ppm)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8.094
7.719
7.712
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7.696
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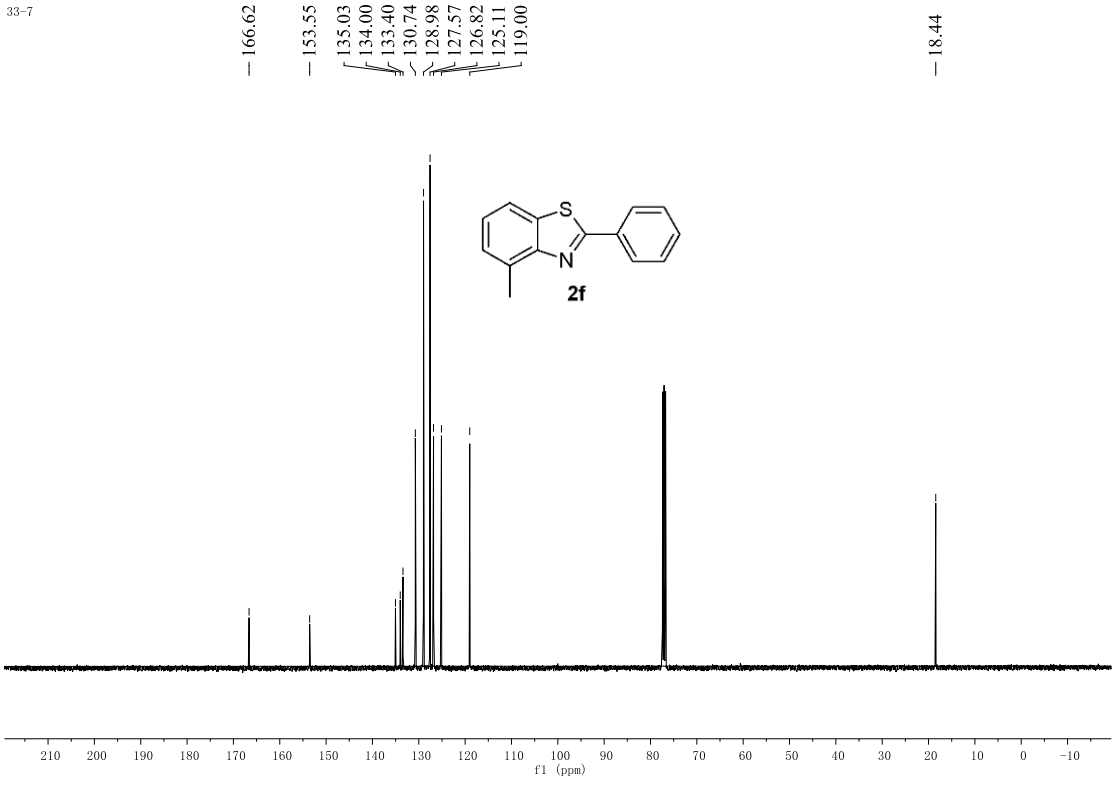
7.484
7.474
7.462
7.267
7.260
7.252
7.232
2.806
2f
2.01
1.00
3.06
1.99
3.23
f1 (ppm)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119.00
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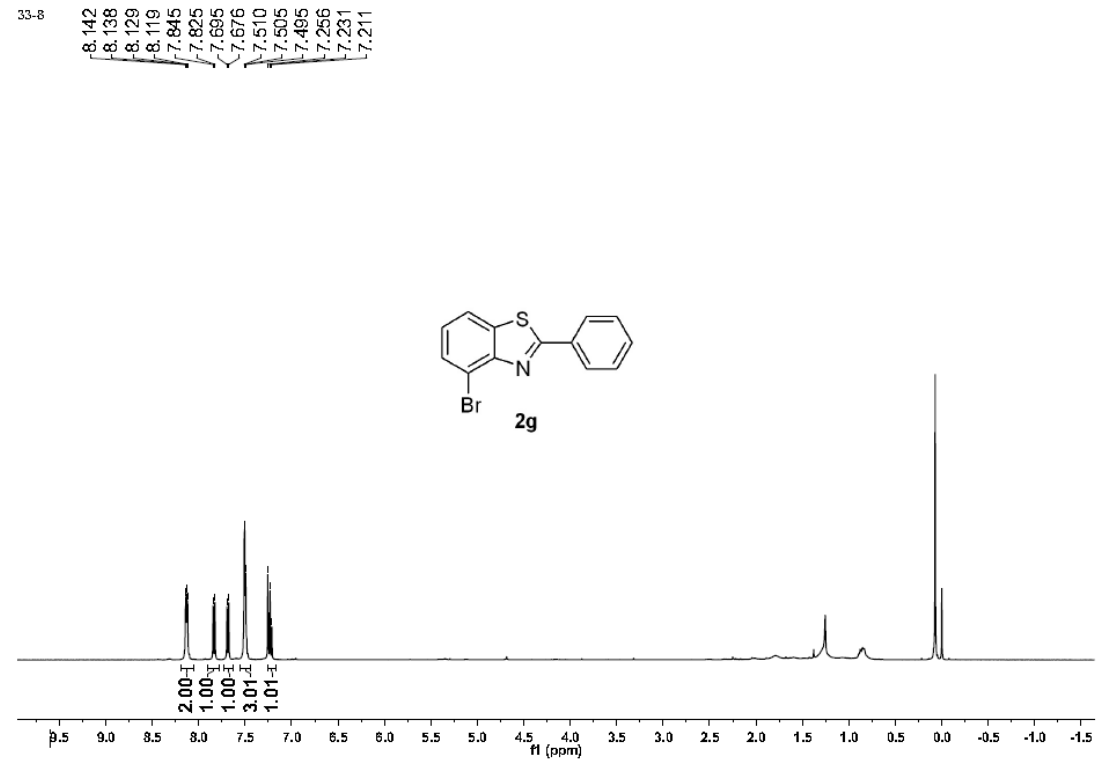
2f
f1 (ppm)


33-8
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8.138
8.129
8.119
7.845
7.825
7.695
7.676
7.510
7.505
7.495
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7.211
S
N
Br
2g
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1.00
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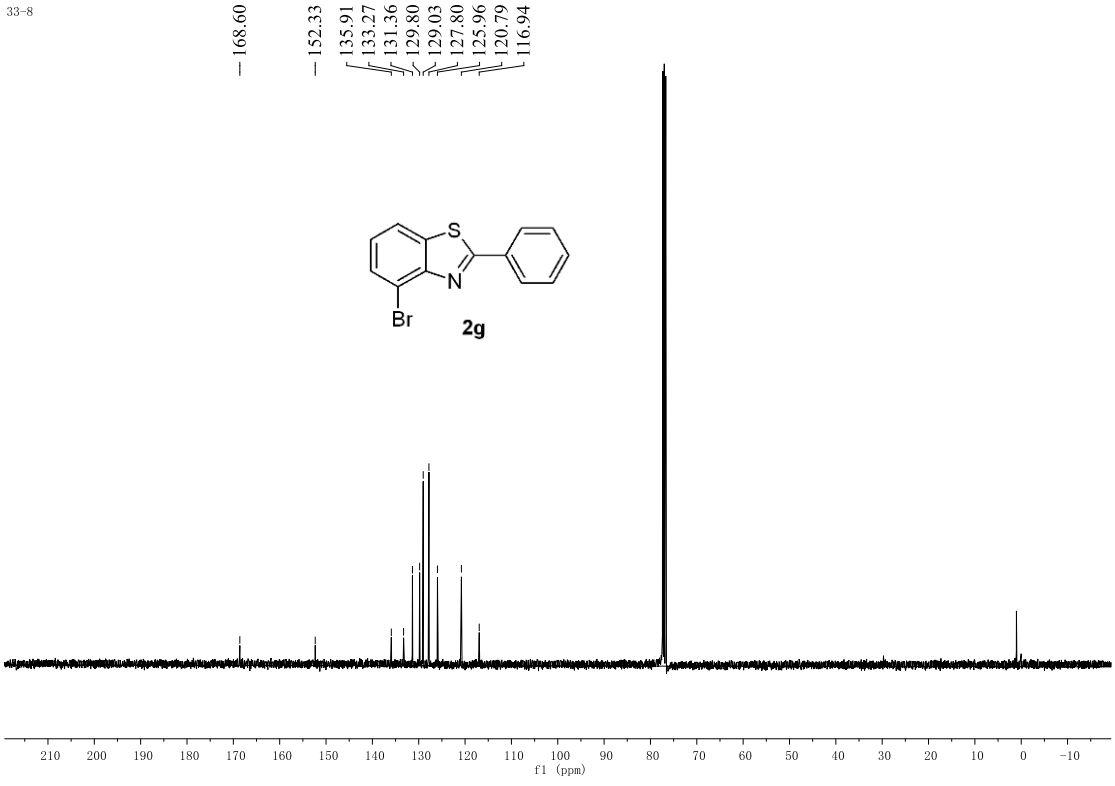
1.01
f1 (ppm)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133.27
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125.96
120.79
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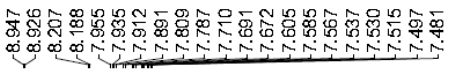
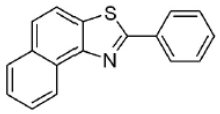
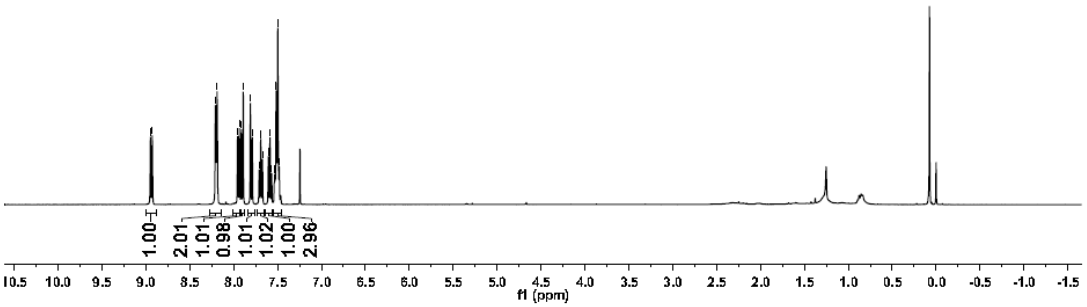
S
N
Br
2g
f1 (ppm)

34-3


8.947
8.926
8.207
8.188
7.955
7.935
7.912
7.891
7.809
7.787
7.710
7.691
7.672
7.605
7.585
7.567
7.537
7.530
7.515
7.497
7.481

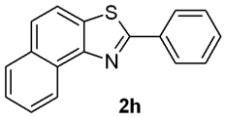


2h

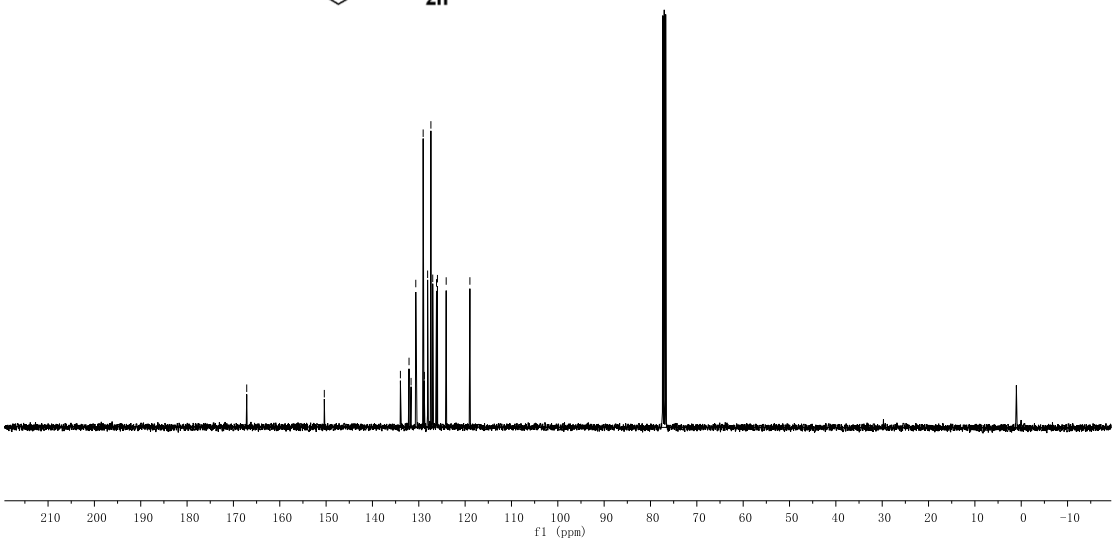

1.00
2.01
1.01
0.98
1.01
1.02
1.00
2.96
f1 (ppm)

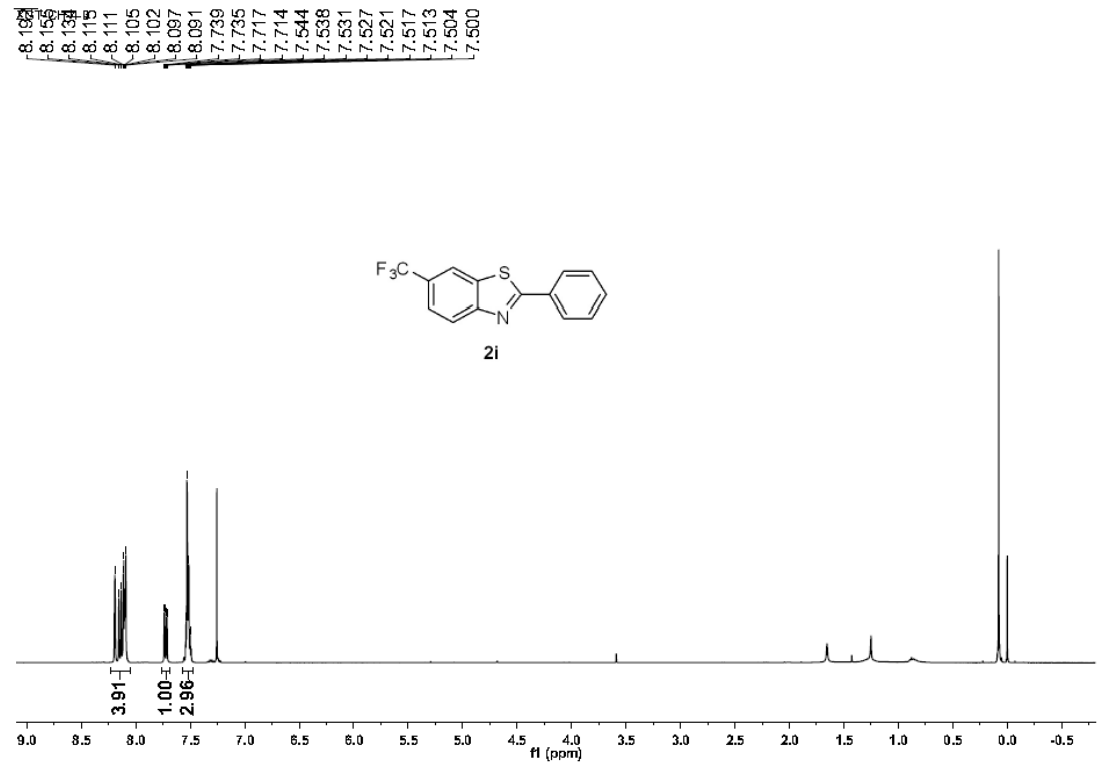
34-3

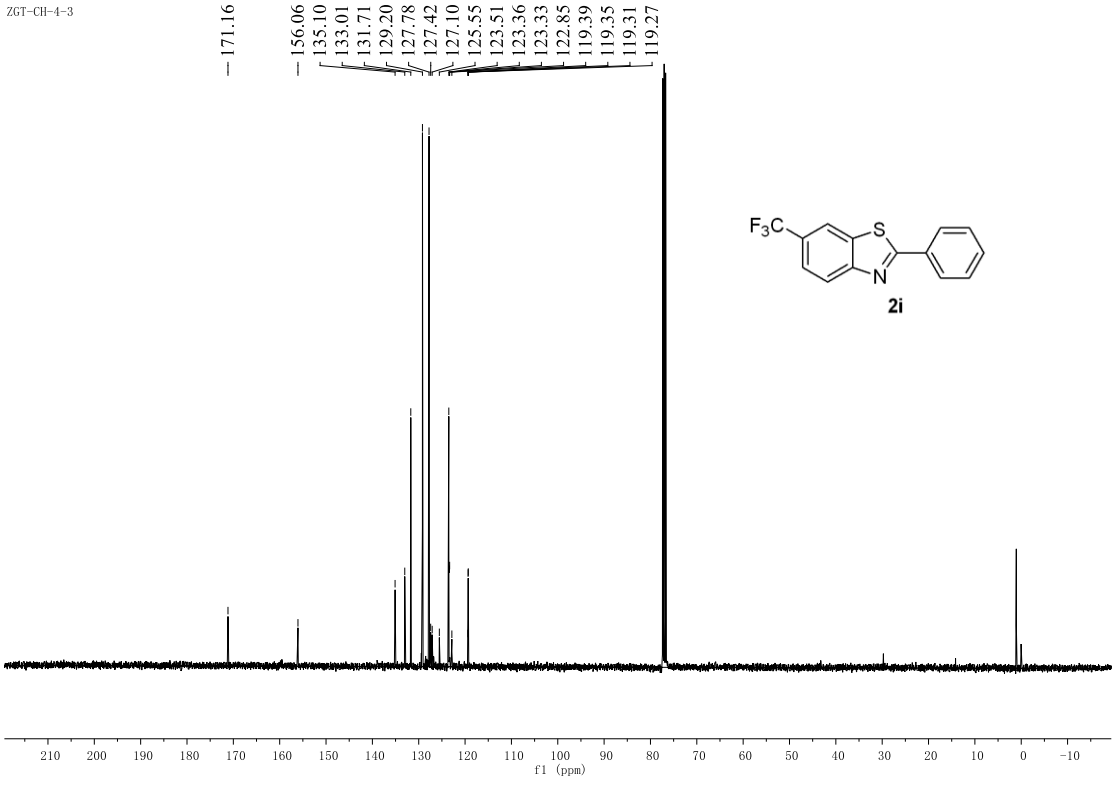

167.13
150.39
133.97
132.11
131.67
130.65
129.06
128.79
128.09
127.39
126.99
126.18
125.97
124.09
118.97

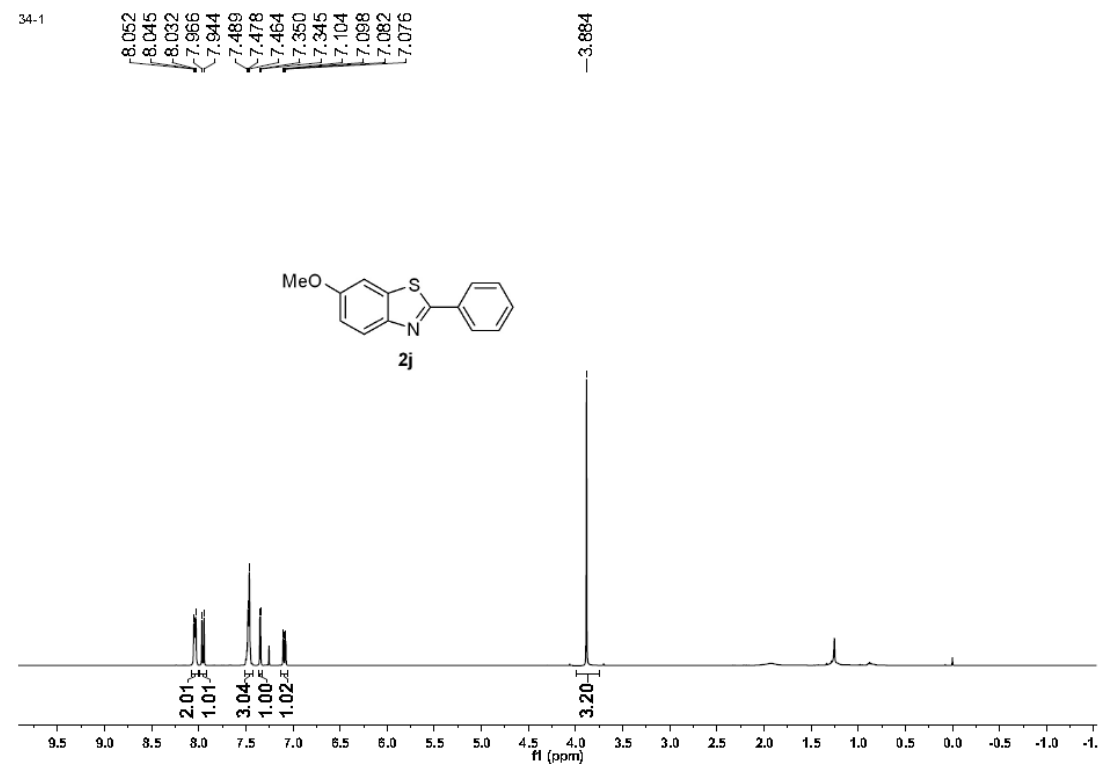


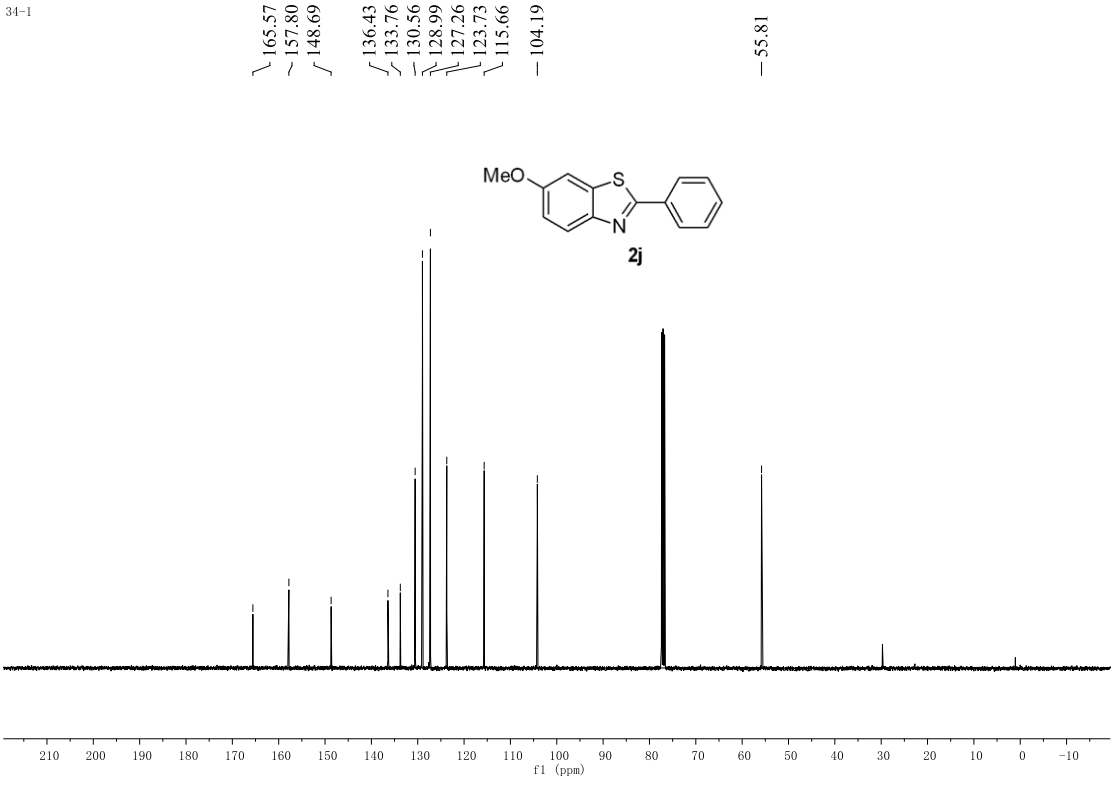
2h

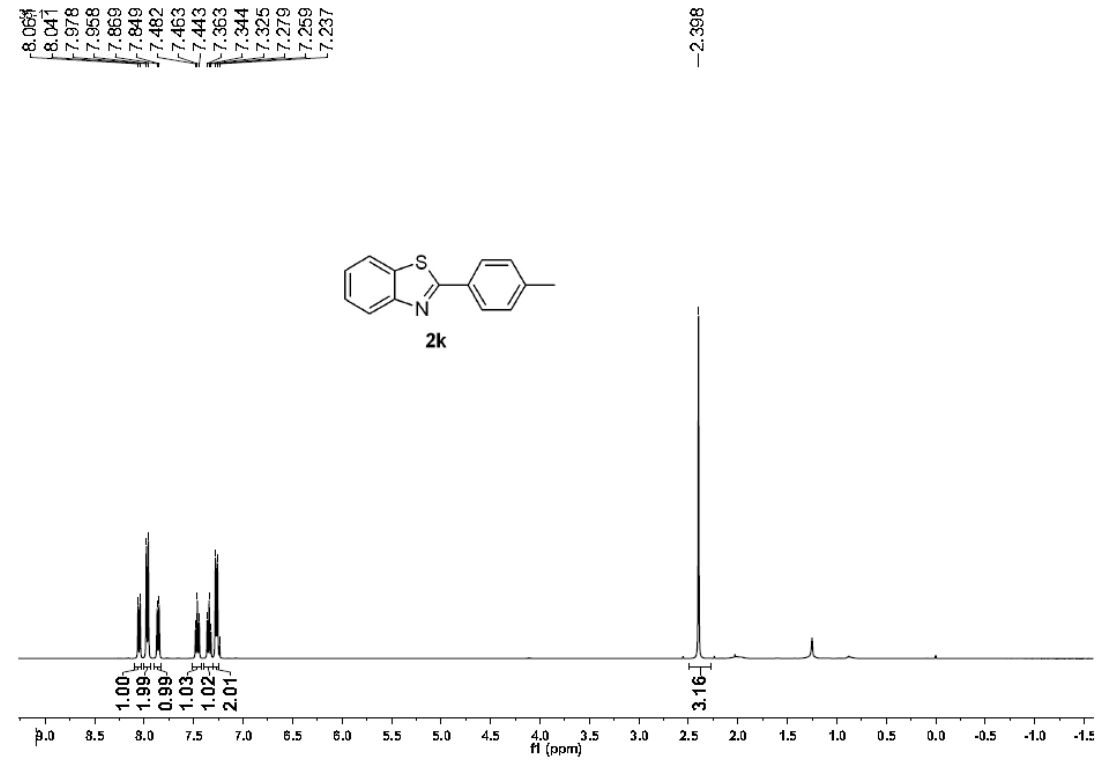

f1 (ppm)

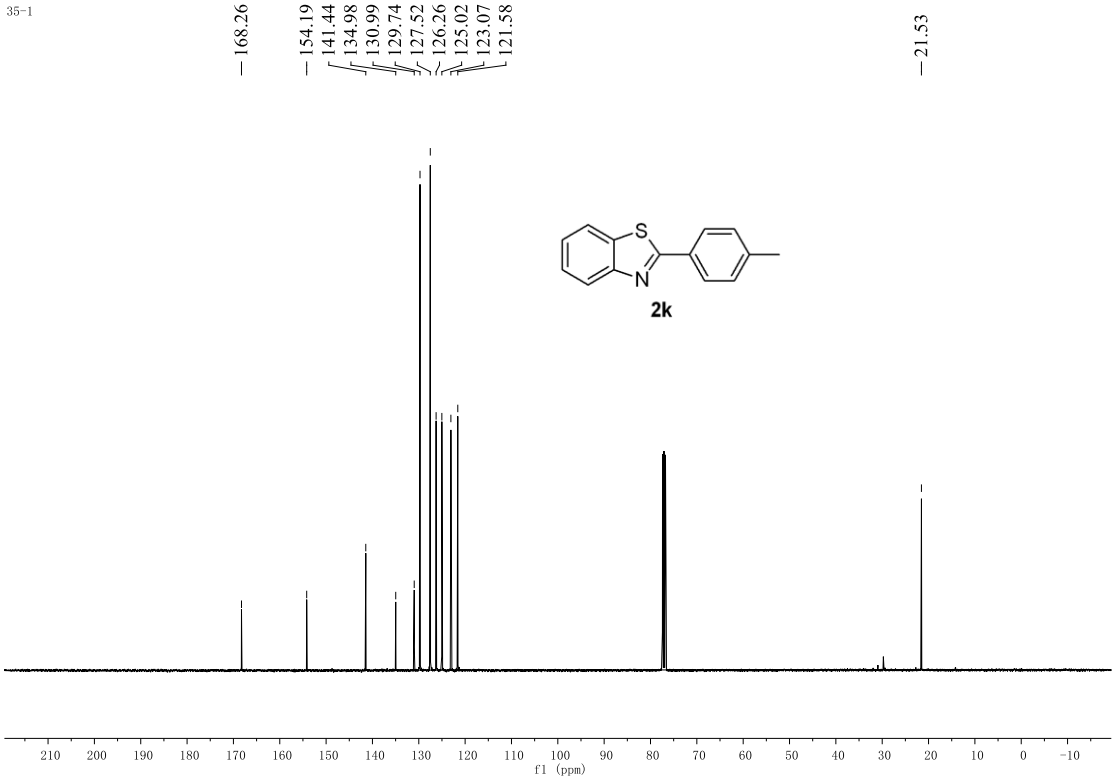

8.111
8.105
8.102
8.097
8.091
7.739
7.735
7.717
7.714
7.544
7.538
7.531
7.527
7.521
7.517
7.513
7.504
7.500
F3C
S
N
2i
3.91
1.00
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

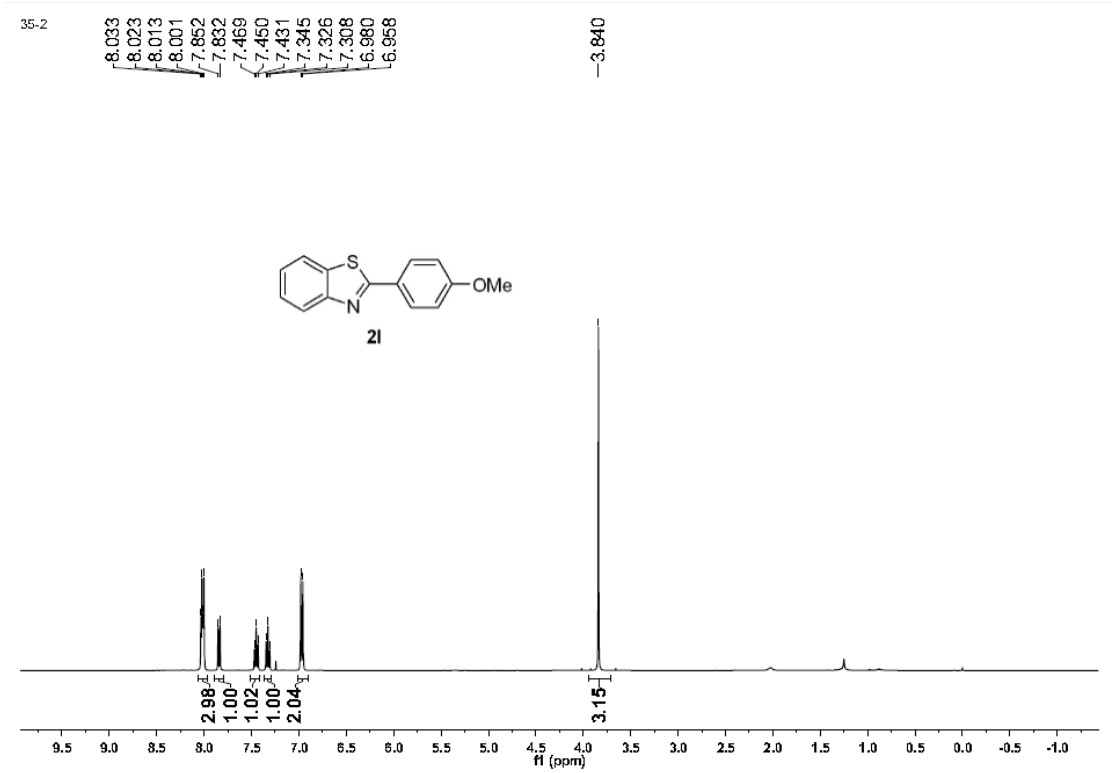

ZGT-CH-4-3
171.16
156.06
135.10
133.01
131.71
129.20
127.78
127.42
127.10
125.55
123.51
123.36
123.33
122.85
119.39
119.35
119.31
119.27
F3C
S
N
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

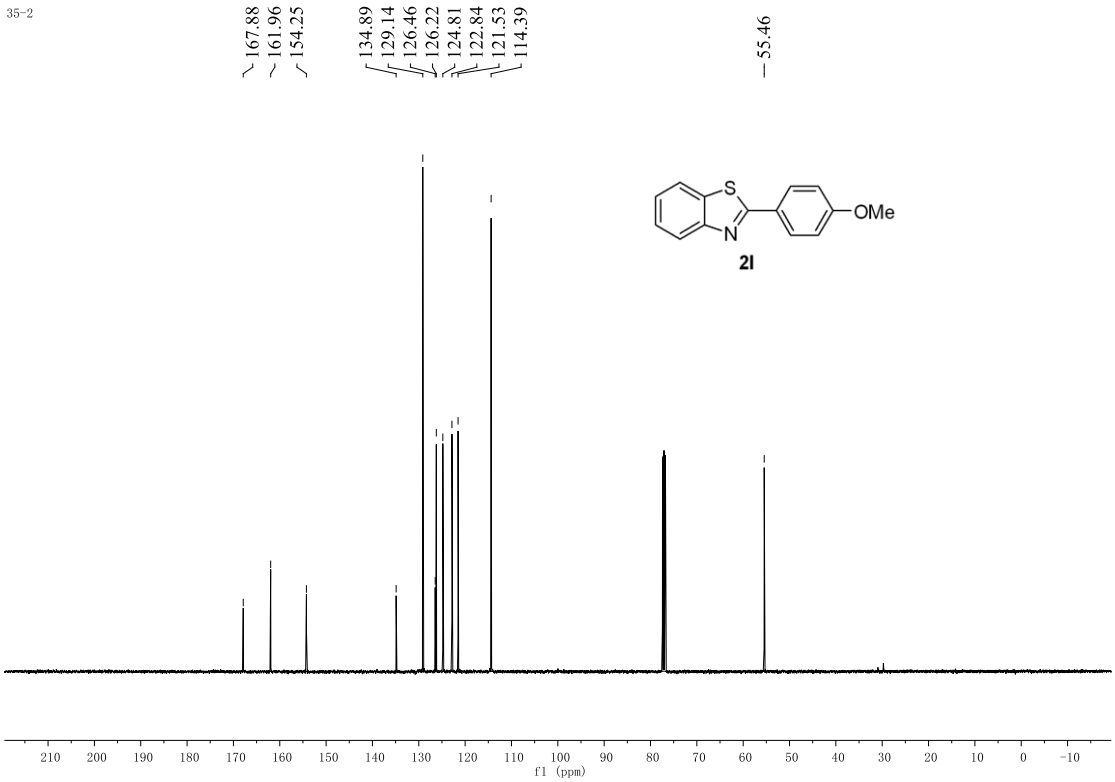

34-1
8.052
8.045
8.032
7.966
7.944
7.489
7.478
7.464
7.350
7.345
7.104
7.098
7.082
7.076
3.884
MeO
S
N
2j
2.01
1.01
3.04
1.00
1.02
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)

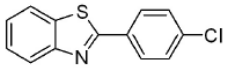

34-1
165.57
157.80
148.69
136.43
133.76
130.56
128.99
127.26
123.73
115.66
104.19
55.81
MeO
S
N
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.063
8.041
7.978
7.958
7.869
7.849
7.482
7.463
7.443
7.363
7.344
7.325
7.279
7.259
7.237
2.398
2k
1.00
1.99
0.99
1.03
1.02
2.01
3.16
f1 (ppm)

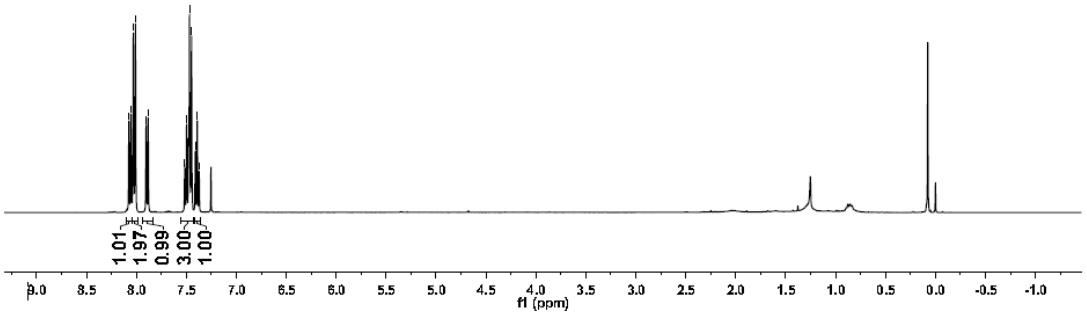

35-1
168.26
154.19
141.44
134.98
130.99
129.74
127.52
126.26
125.02
123.07
121.58
21.53
2k
f1 (ppm)


35-2
8.033
8.023
8.013
8.001
7.852
7.832
7.469
7.450
7.431
7.345
7.326
7.308
6.980
6.958
3.840
S
N
OMe
2l
2.98
1.00
1.02
1.00
2.04
3.15
f1 (ppm)


35-2
167.88
161.96
154.25
134.89
129.14
126.46
126.22
124.81
122.84
121.53
114.39
55.46
S
N
OMe
2l
f1 (ppm)

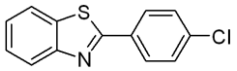


2m

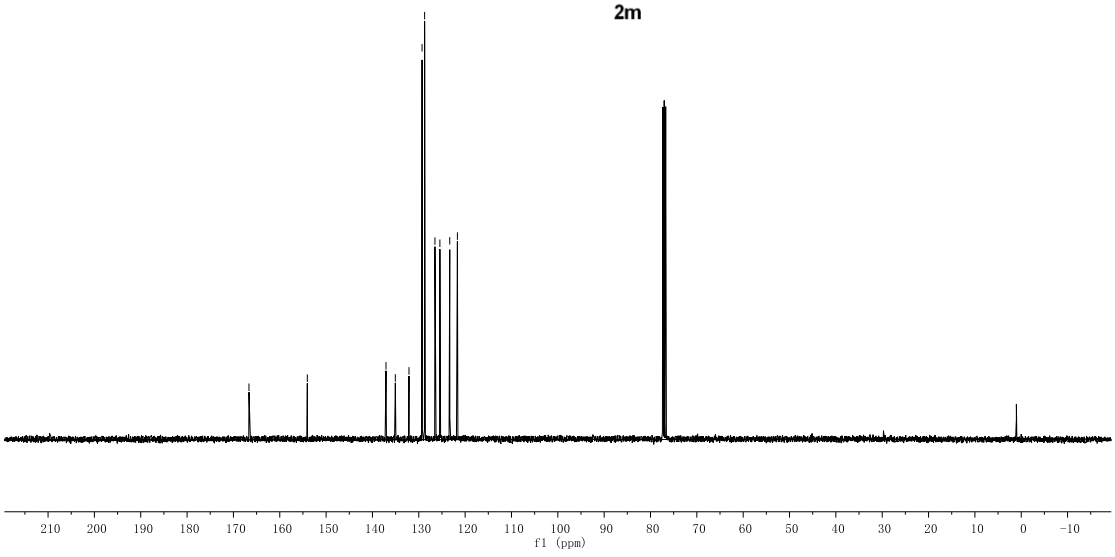


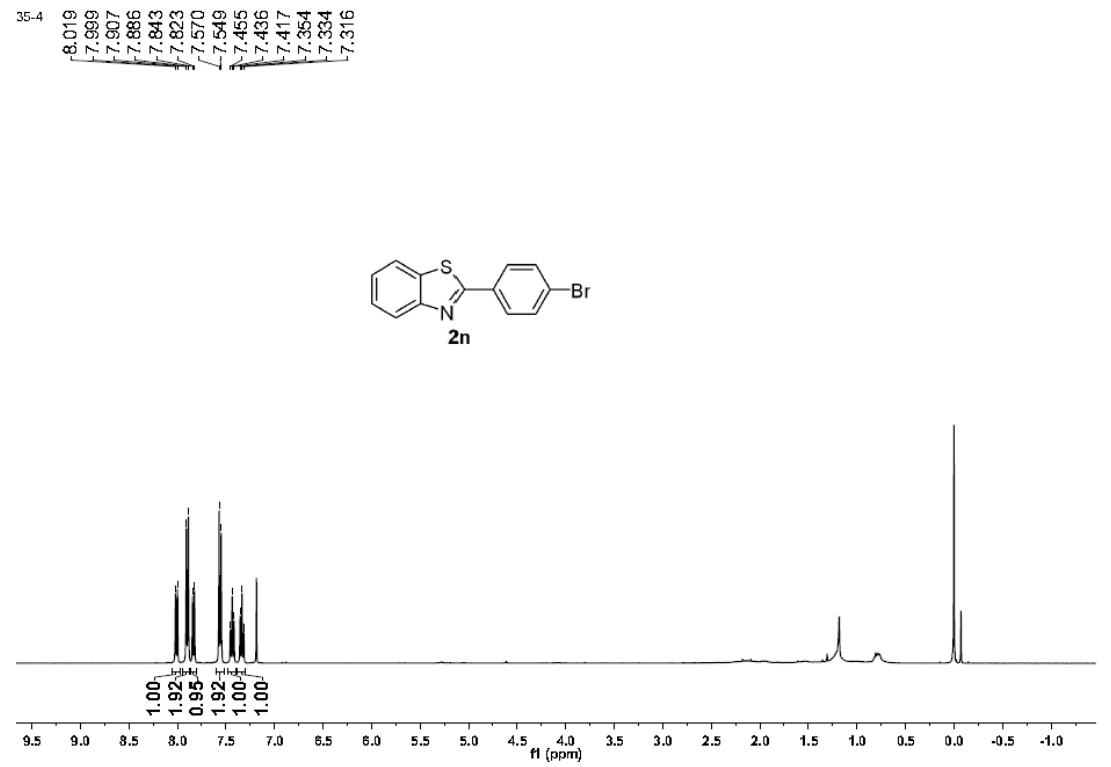
37-1

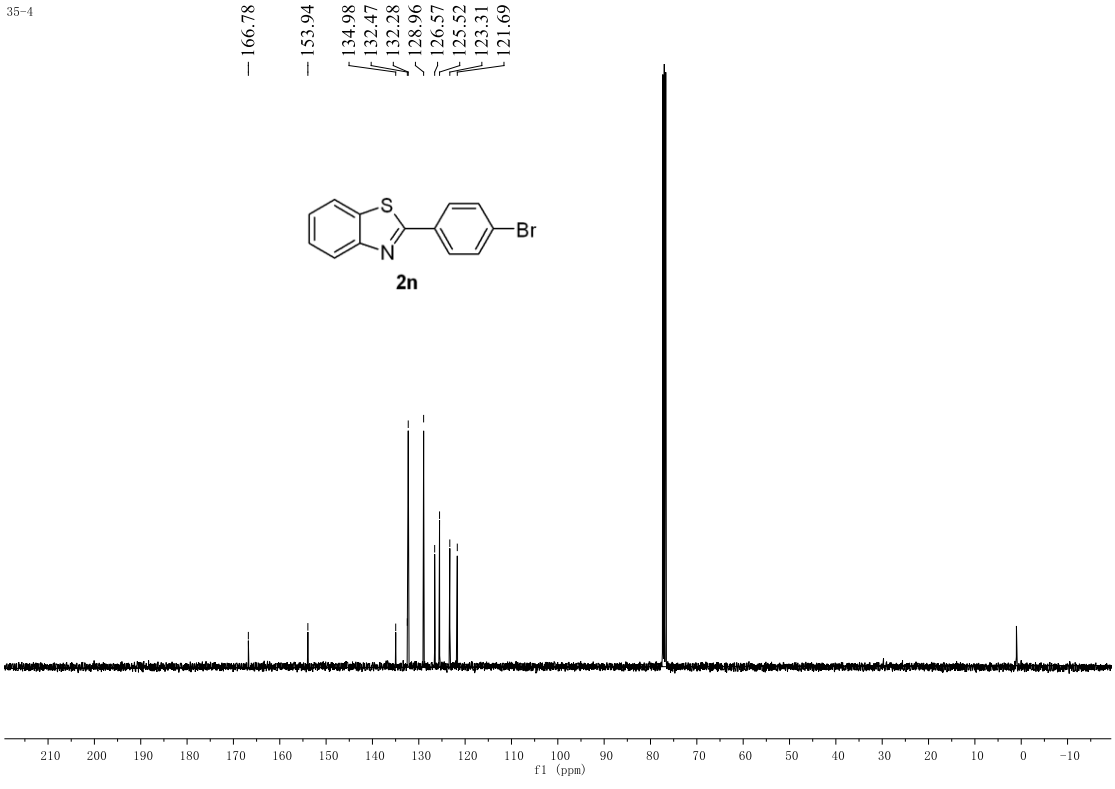
166.65
154.05
137.08
135.06
132.12
129.30
128.74
126.51
125.44
123.32
121.67

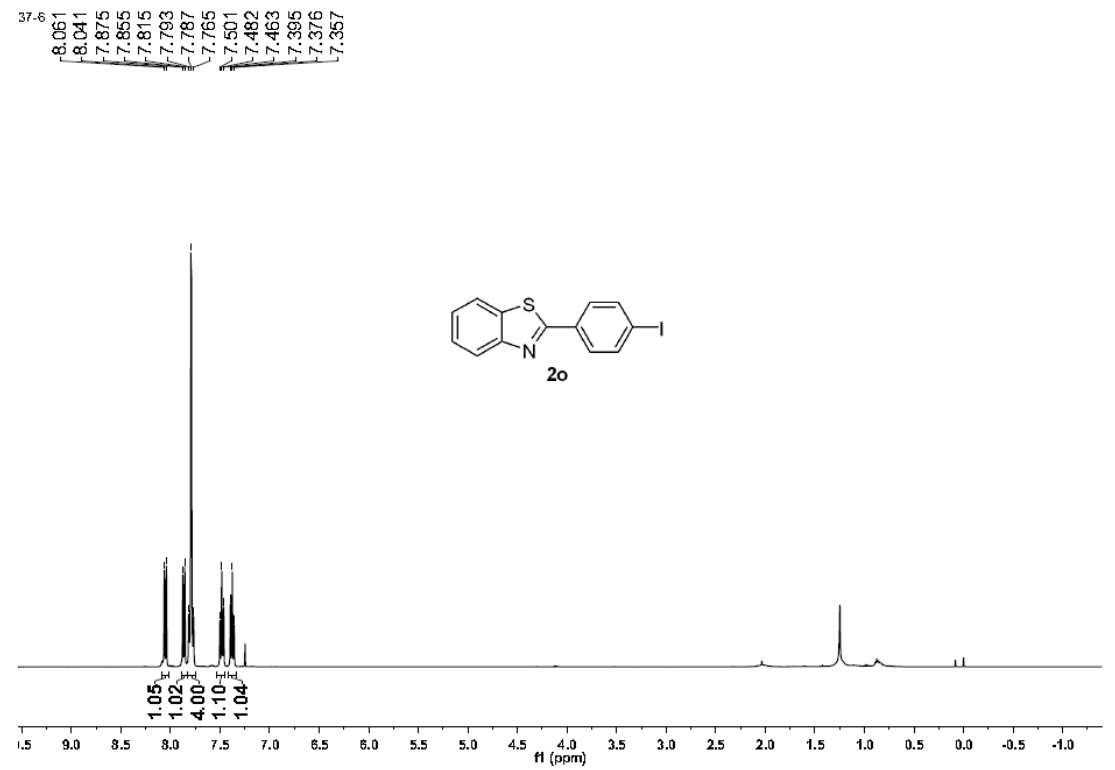


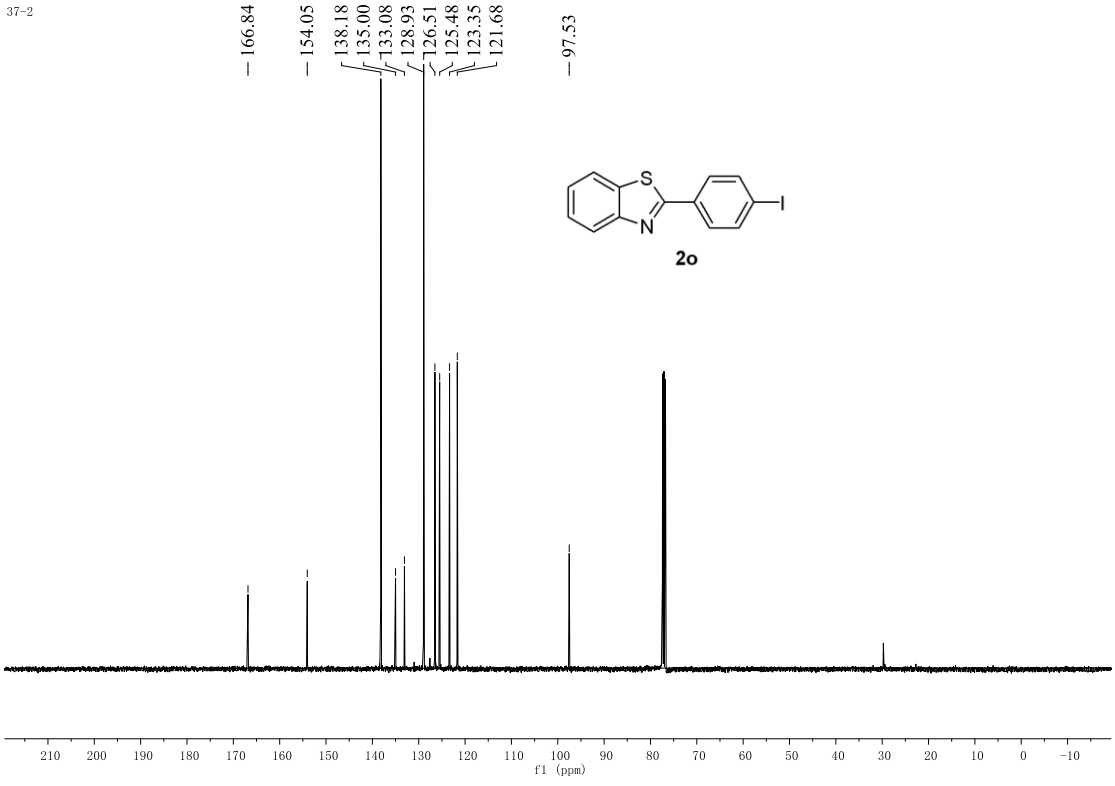
2m

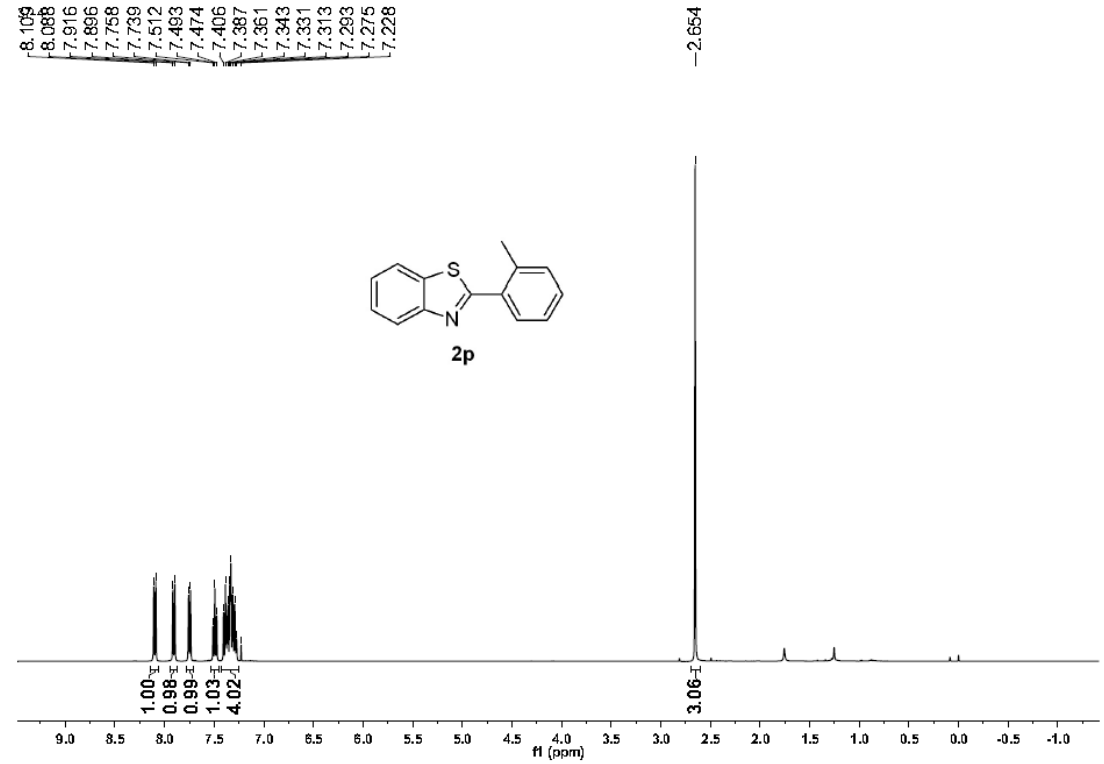


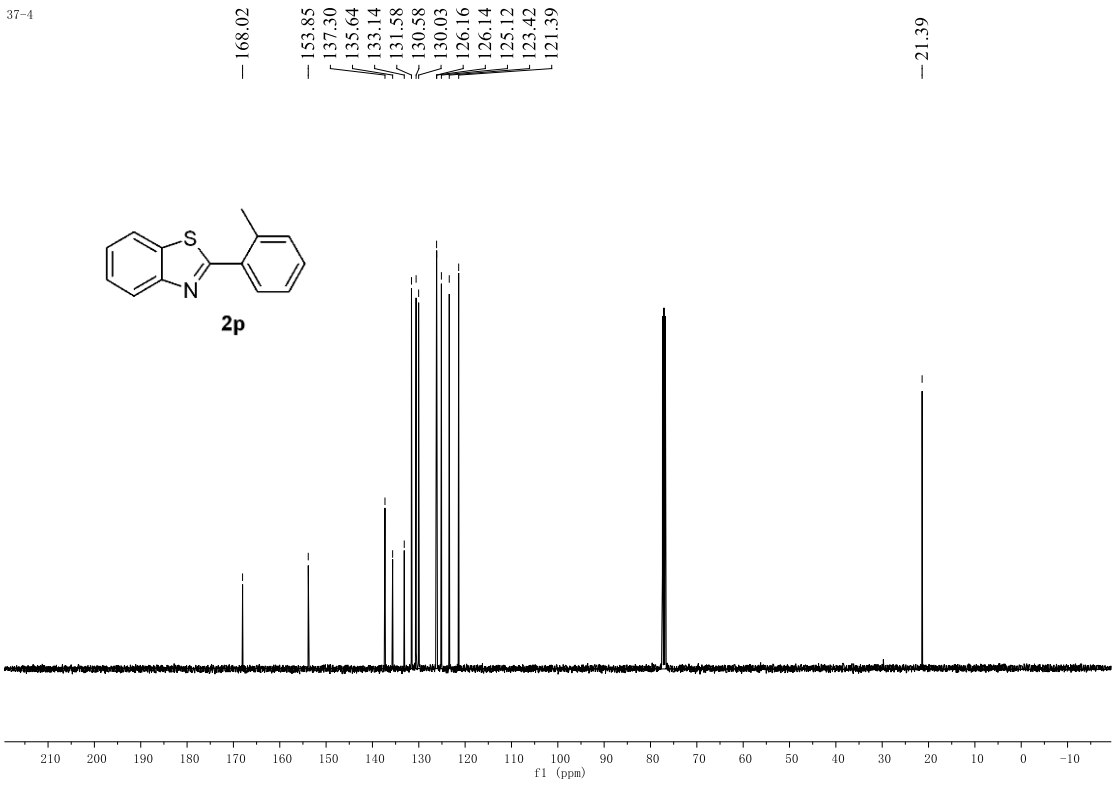

35-4
8.019
7.999
7.907
7.886
7.843
7.823
7.570
7.549
7.455
7.436
7.417
7.354
7.334
7.316
S
N
Br
2n
1.00
1.92
0.95
1.92
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

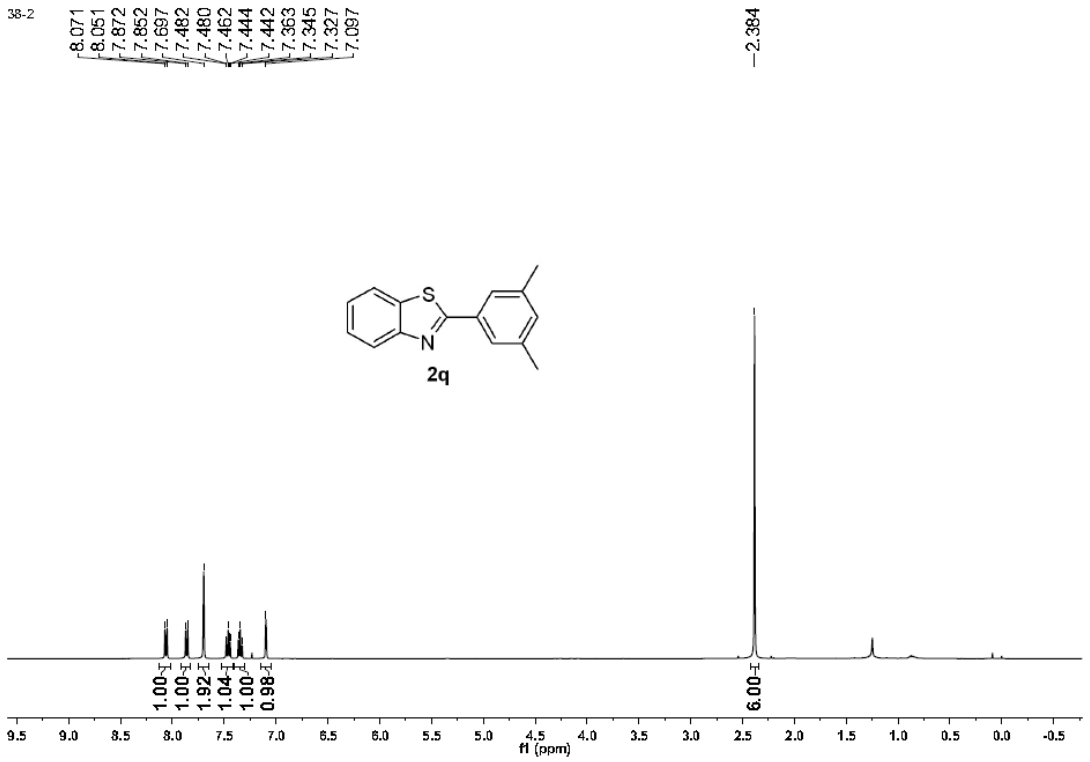

35-4
166.78
153.94
134.98
132.47
132.28
128.96
126.57
125.52
123.31
121.69
S
N
Br
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

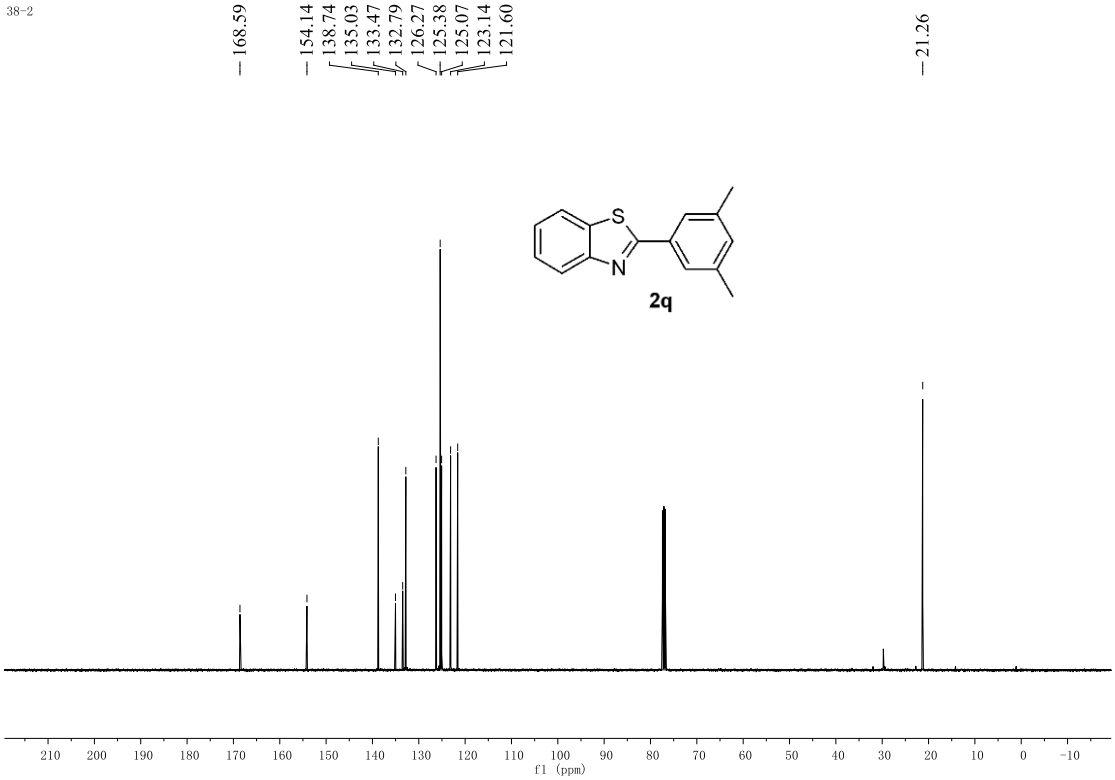

37-6
8.061
8.041
7.875
7.855
7.815
7.793
7.787
7.765
7.501
7.482
7.463
7.395
7.376
7.357
1.05
1.02
4.00
1.10
1.04
f1 (ppm)
2o

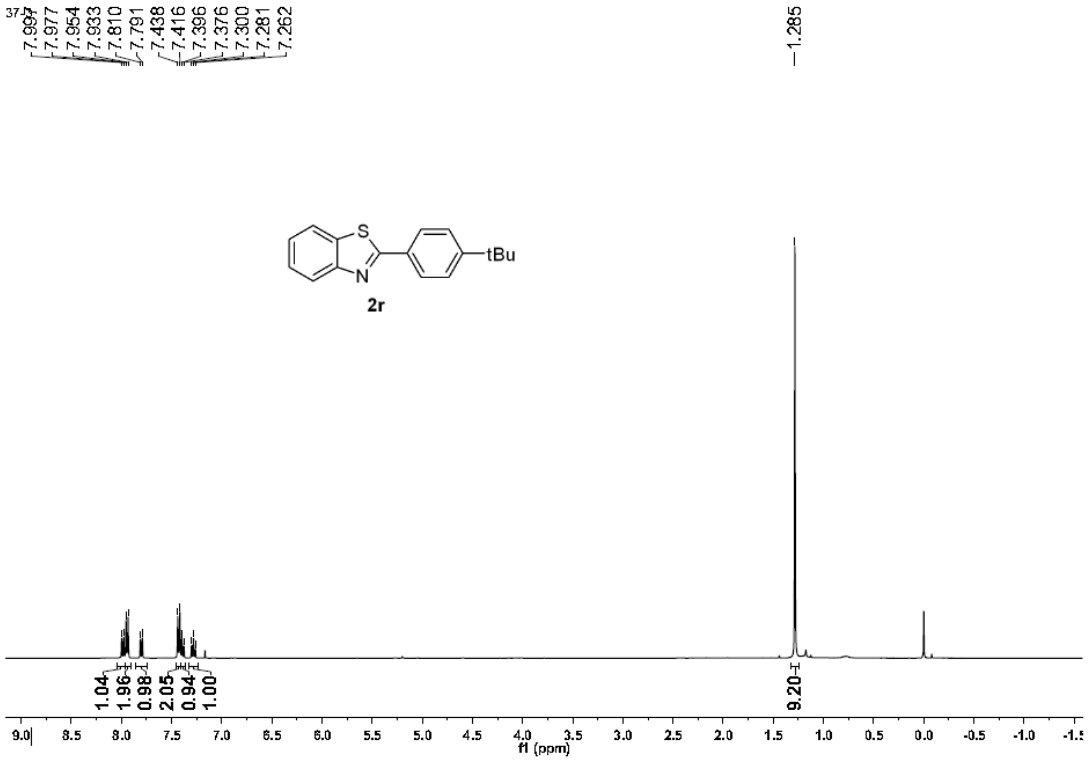

37-2
166.84
154.05
138.18
135.00
133.08
128.93
126.51
125.48
123.35
121.68
97.53
f1 (ppm)
2o

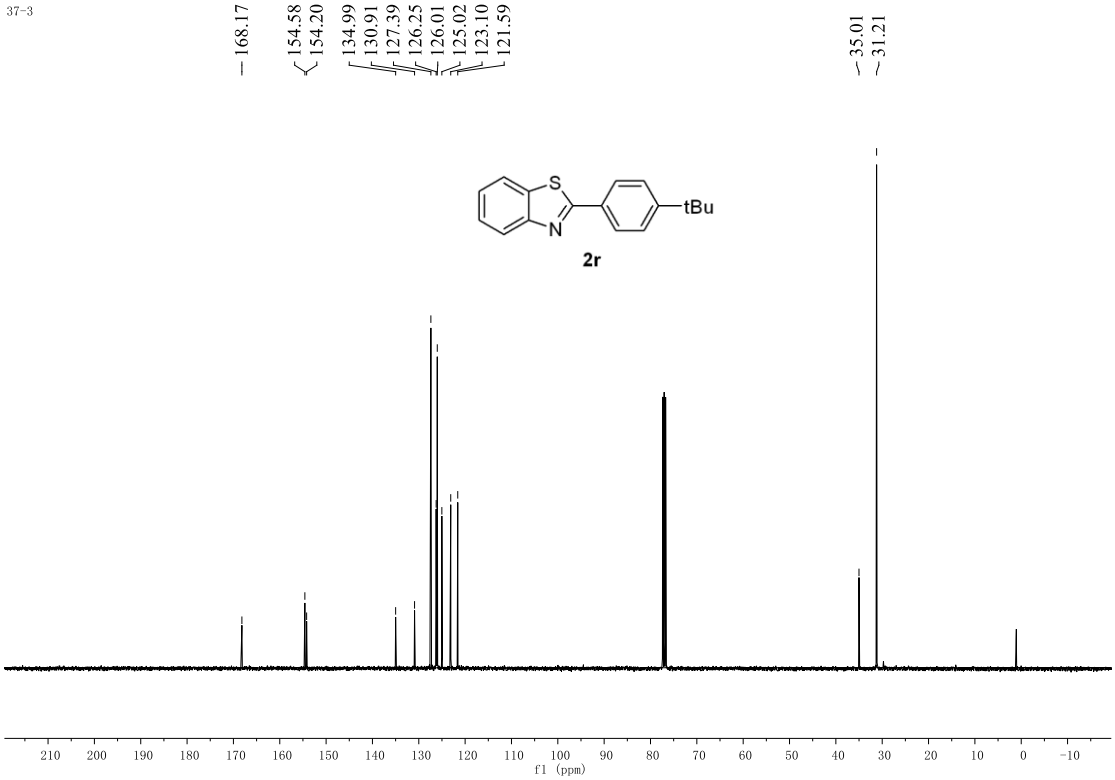

8.109
8.088
7.916
7.896
7.758
7.739
7.512
7.493
7.474
7.406
7.387
7.361
7.343
7.331
7.313
7.293
7.275
7.228
2.654
S
N
2p
1.00
0.98
0.99
1.03
4.02
3.06
f1 (ppm)

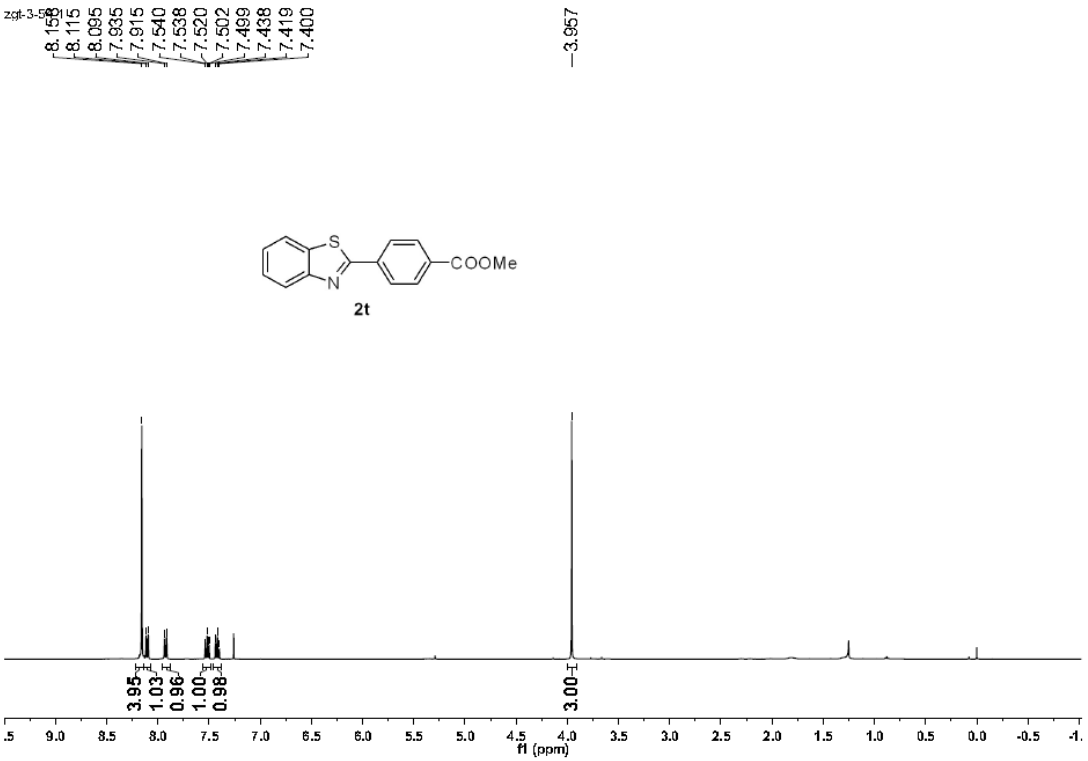

37-4
168.02
153.85
137.30
135.64
133.14
131.58
130.58
130.03
126.16
126.14
125.12
123.42
121.39
21.39
S
N
2p
f1 (ppm)

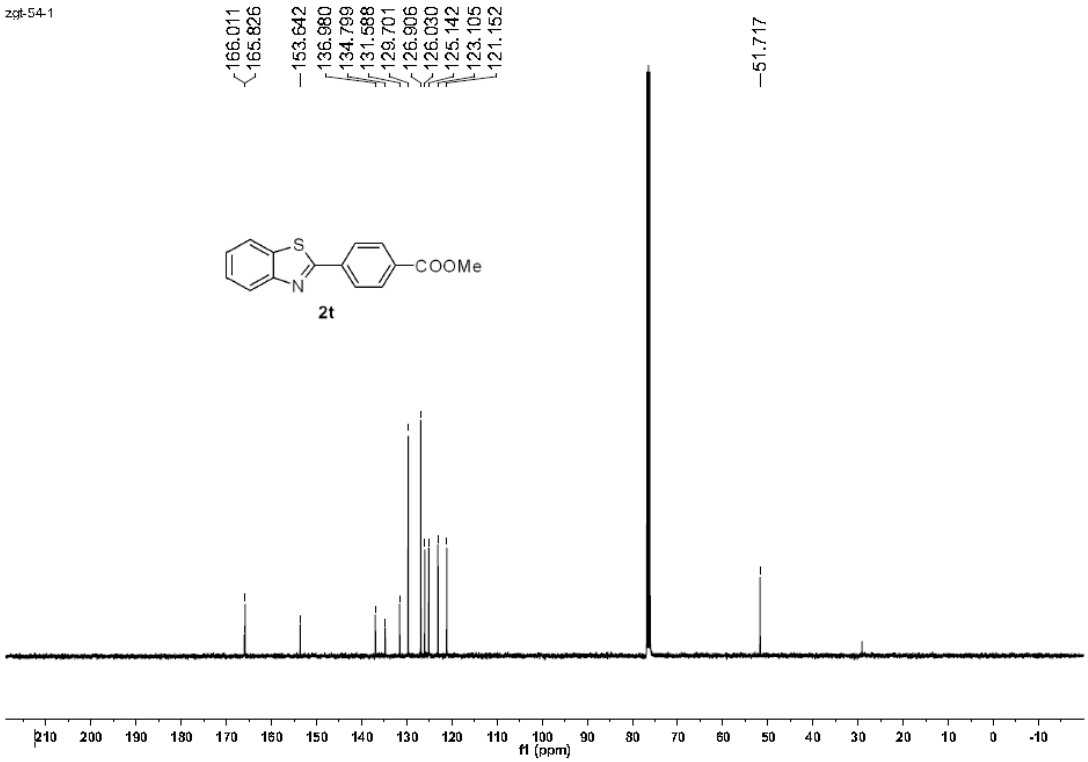

38-2
8.071
8.051
7.872
7.852
7.697
7.482
7.480
7.462
7.444
7.442
7.363
7.345
7.327
7.097
2.384
2q
1.00
1.00
1.92
1.04
1.00
0.98
6.00
f1 (ppm)

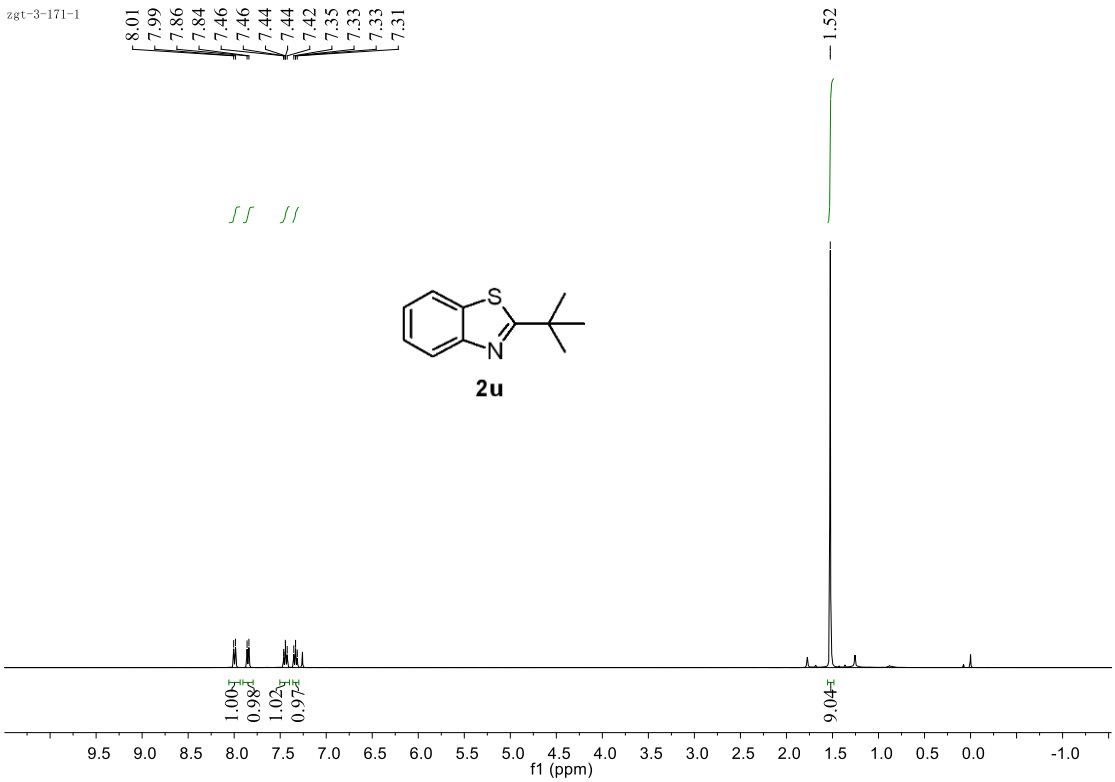

38-2
168.59
154.14
138.74
135.03
133.47
132.79
126.27
125.38
125.07
123.14
121.60
21.26
2q
f1 (ppm)


7.997
7.977
7.954
7.933
7.810
7.791
7.438
7.416
7.396
7.376
7.300
7.281
7.262
1.285
S
N
tBu
2r
1.04
1.96
0.98
2.05
0.94
1.00
9.20
f1 (ppm)

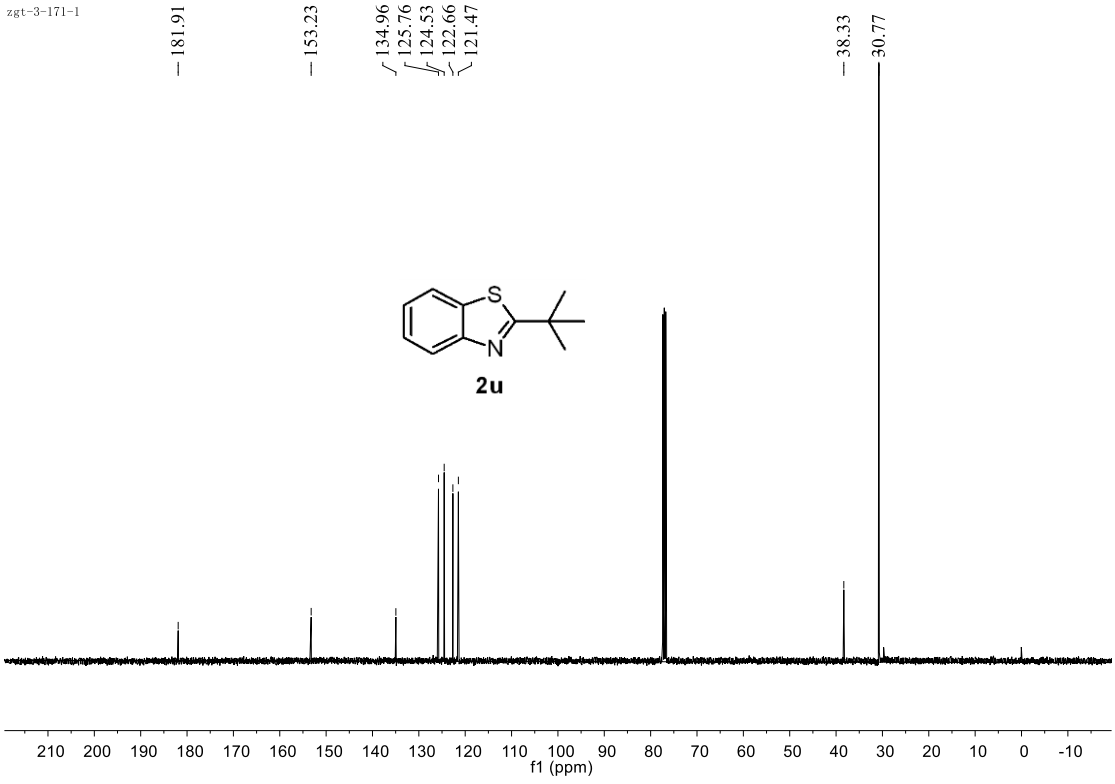

37-3
168.17
154.58
154.20
134.99
130.91
127.39
126.25
126.01
125.02
123.10
121.59
35.01
31.21
S
N
tBu
2r
f1 (ppm)


zgt-3-58
8.159
8.115
8.095
7.935
7.915
7.540
7.538
7.520
7.502
7.489
7.438
7.419
7.400
3.957
COOMe
2t
3.95
1.03
0.96
1.00
0.98
3.00
f1 (ppm)

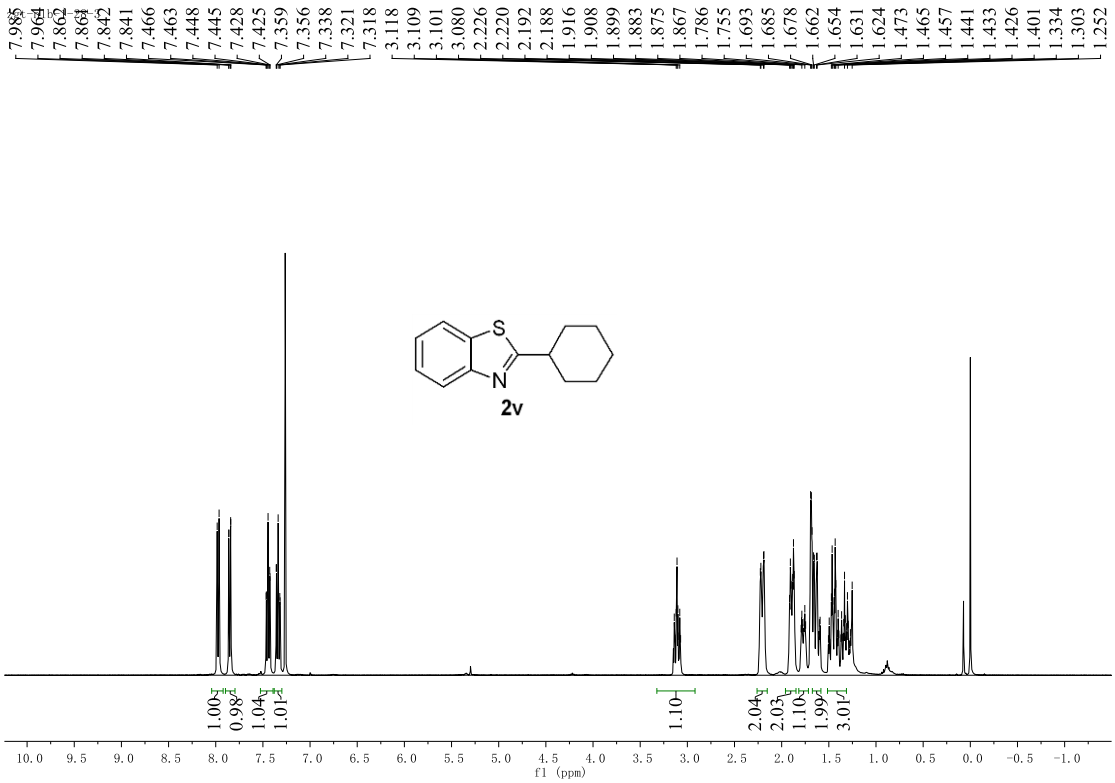

zgt-54-1
166.011
165.826
153.642
136.980
134.799
131.588
129.701
126.906
126.030
125.142
123.105
121.152
51.717
COOMe
2t
f1 (ppm)

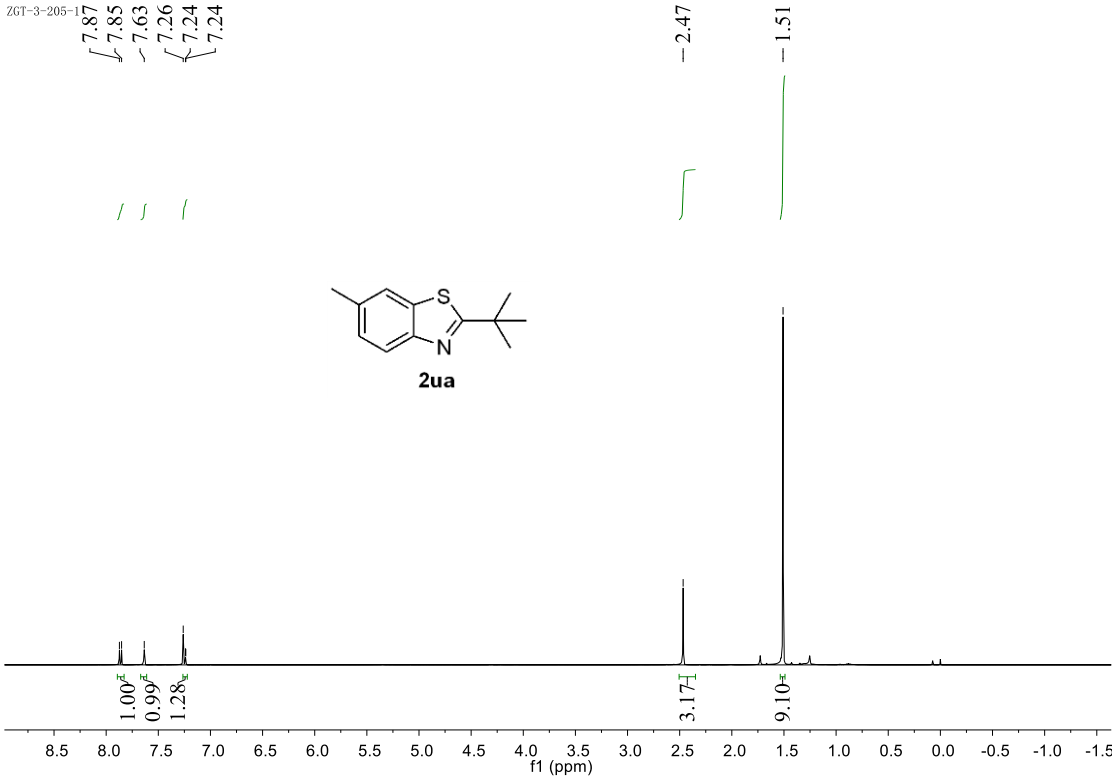

zgt-3-171-1
8.01
7.99
7.86
7.84
7.46
7.46
7.44
7.44
7.42
7.35
7.33
7.33
7.31
1.52
1.00
0.98
1.02
0.97
9.04
f1 (ppm)

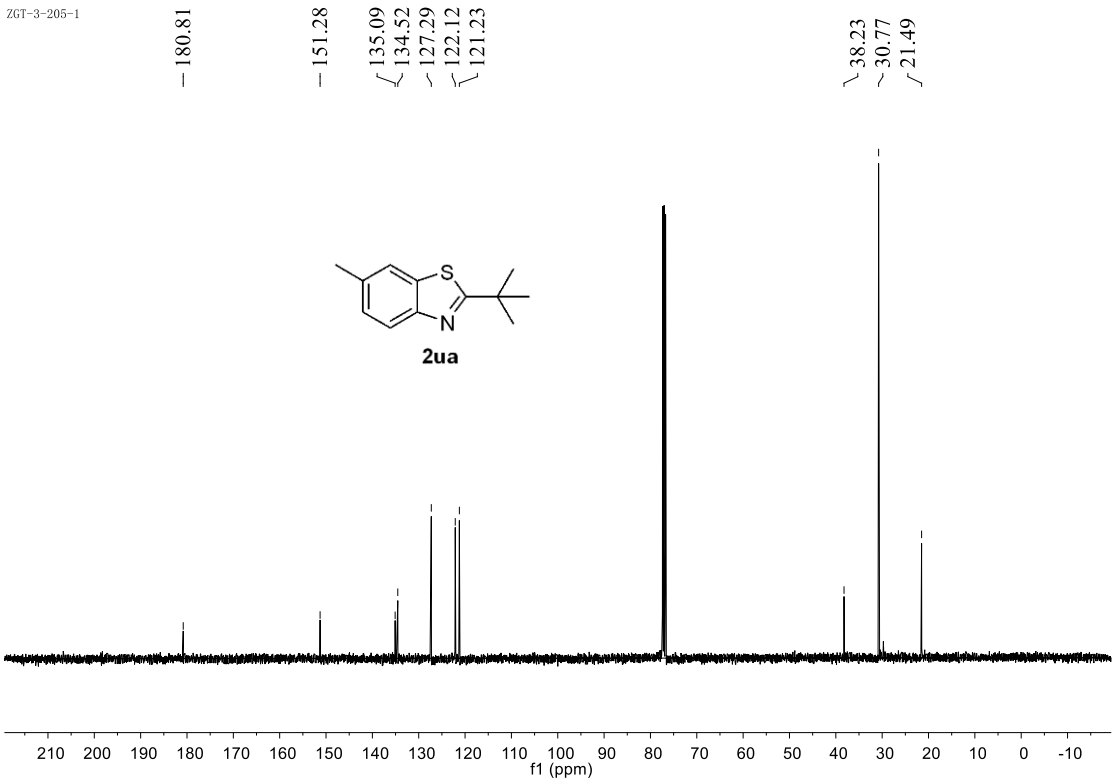
2u

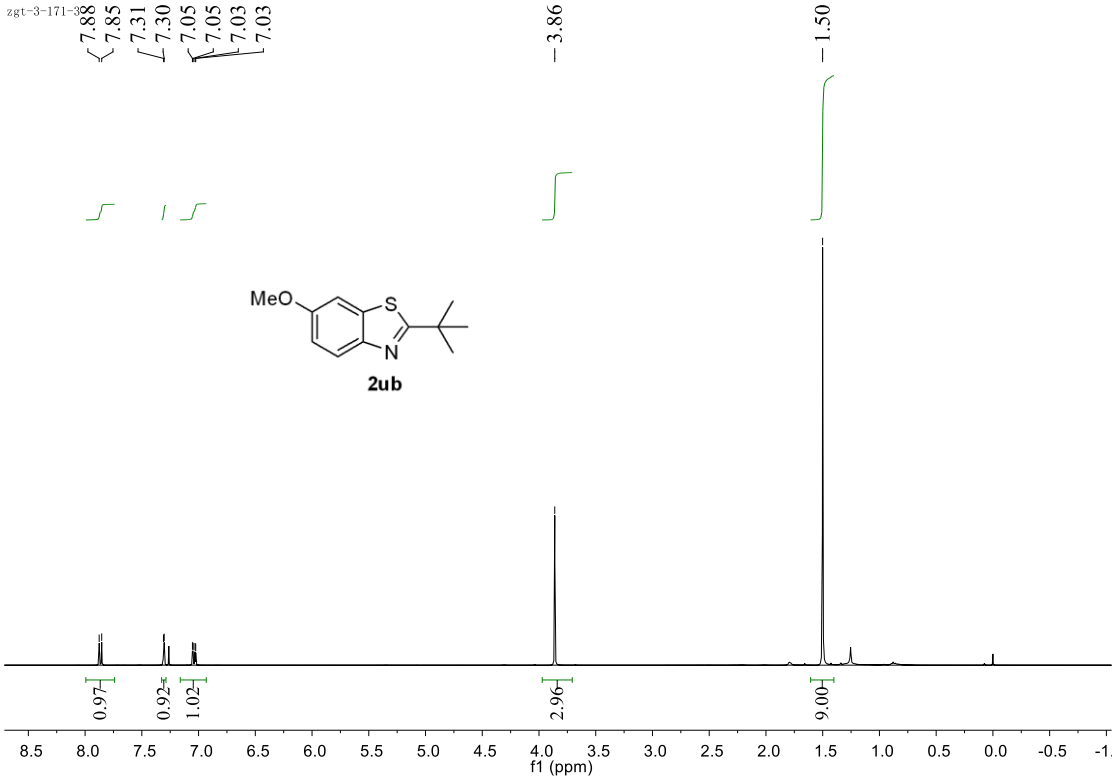

zgt-3-171-1
181.91
153.23
134.96
125.76
124.53
122.66
121.47
38.33
30.77
f1 (ppm)

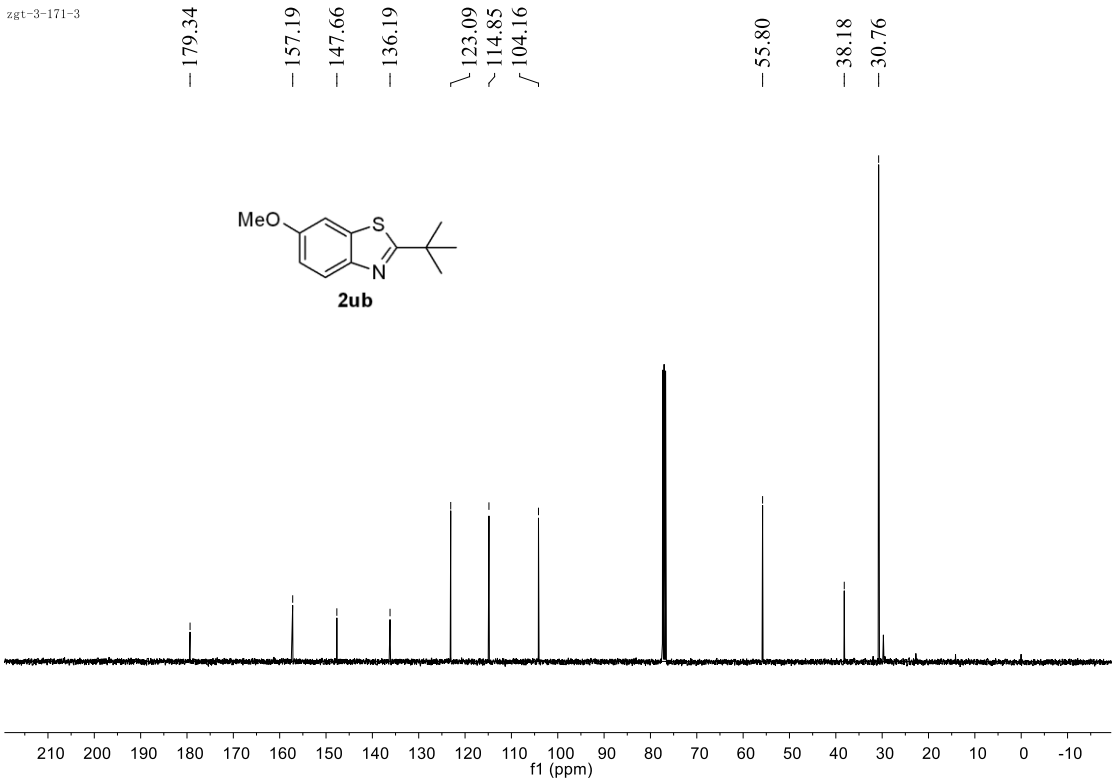
2u

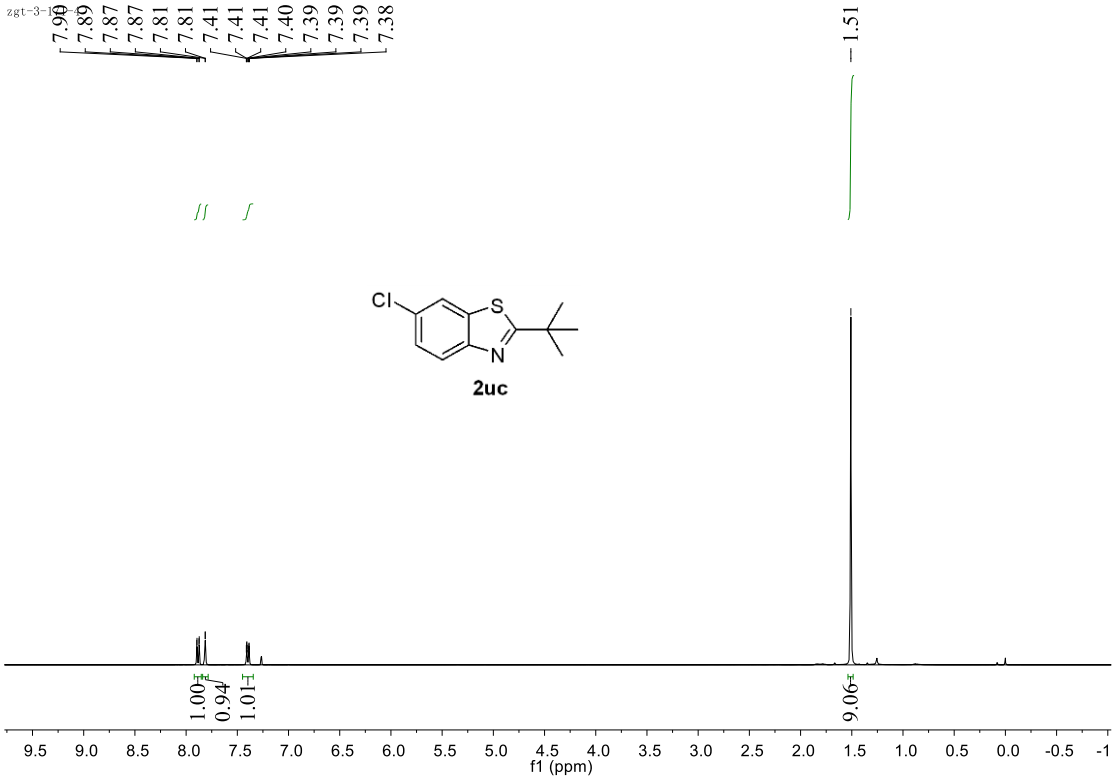

7.985
7.964
7.862
7.864
7.842
7.841
7.466
7.463
7.448
7.445
7.428
7.425
7.359
7.356
7.338
7.321
7.318
3.118
3.109
3.101
3.080
2.226
2.220
2.192
2.188
1.916
1.908
1.899
1.883
1.875
1.867
1.786
1.755
1.693
1.685
1.678
1.662
1.654
1.631
1.624
1.473
1.465
1.457
1.441
1.433
1.426
1.401
1.334
1.303
1.252
2v
1.00
0.98
1.04
1.01
1.10
2.04
2.03
1.10
1.99
3.01
f1 (ppm)

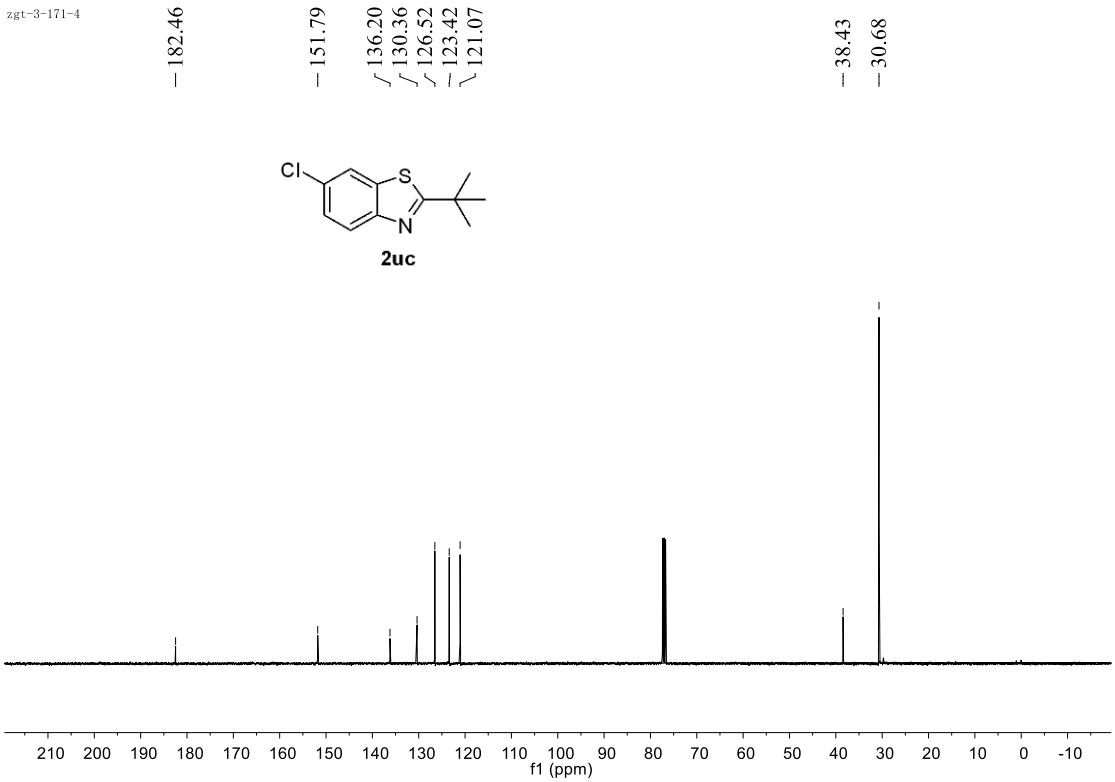

ZGT-3-205-1
7.87
7.85
7.63
7.26
7.24
7.24
2.47
1.51
2ua
1.00
0.99
1.28
3.17
9.10
f1 (ppm)

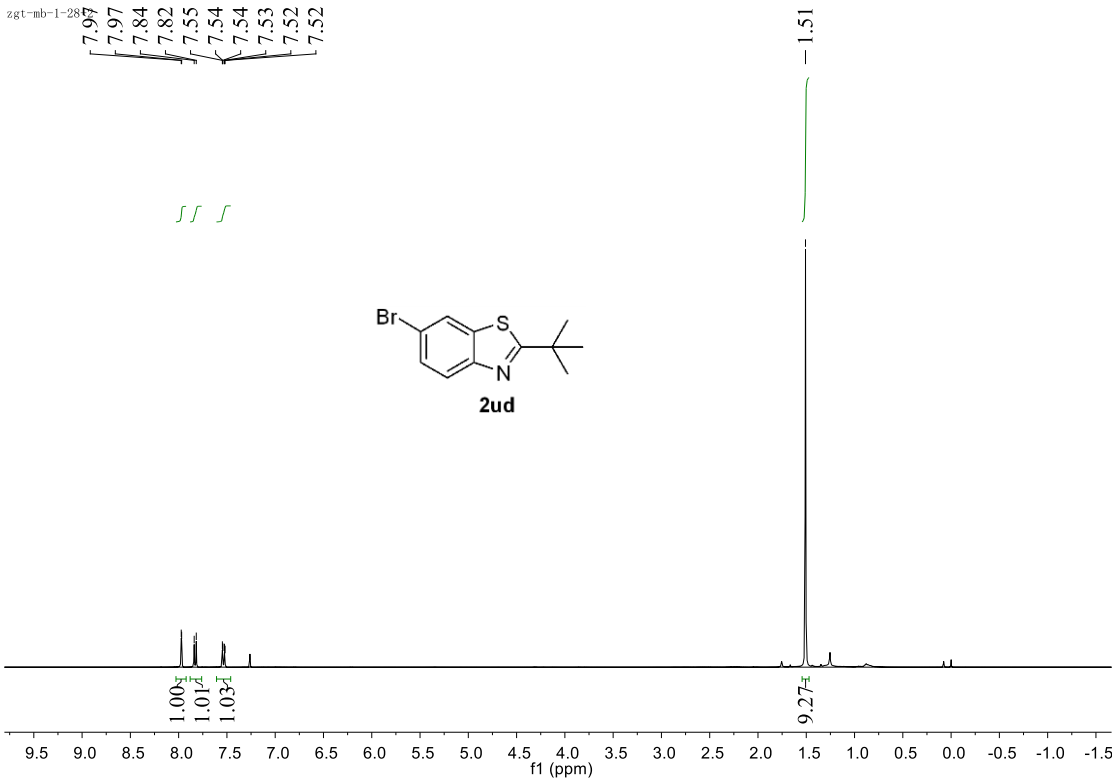

ZGT-3-205-1
180.81
151.28
135.09
134.52
127.29
122.12
121.23
38.23
30.77
21.49
S
N
2ua
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

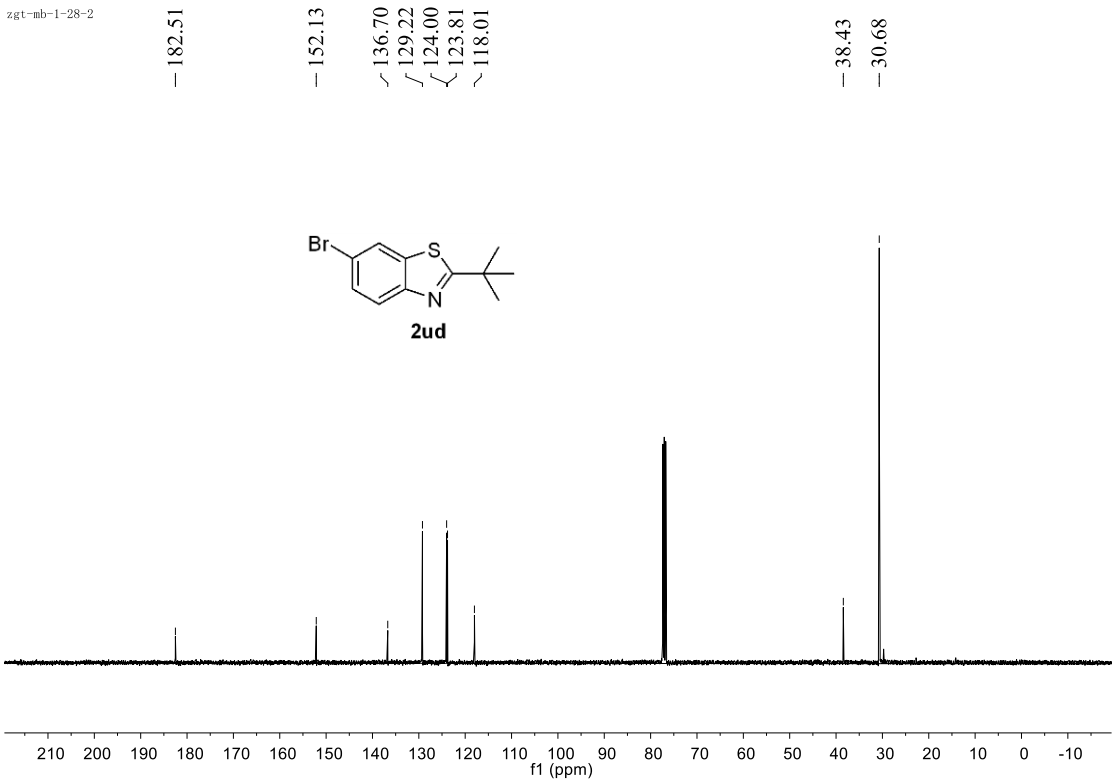

zgt-3-171-3
7.88
7.85
7.31
7.30
7.05
7.05
7.03
7.03
3.86
1.50
MeO
S
N
2ub
0.97
0.92
1.02
2.96
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

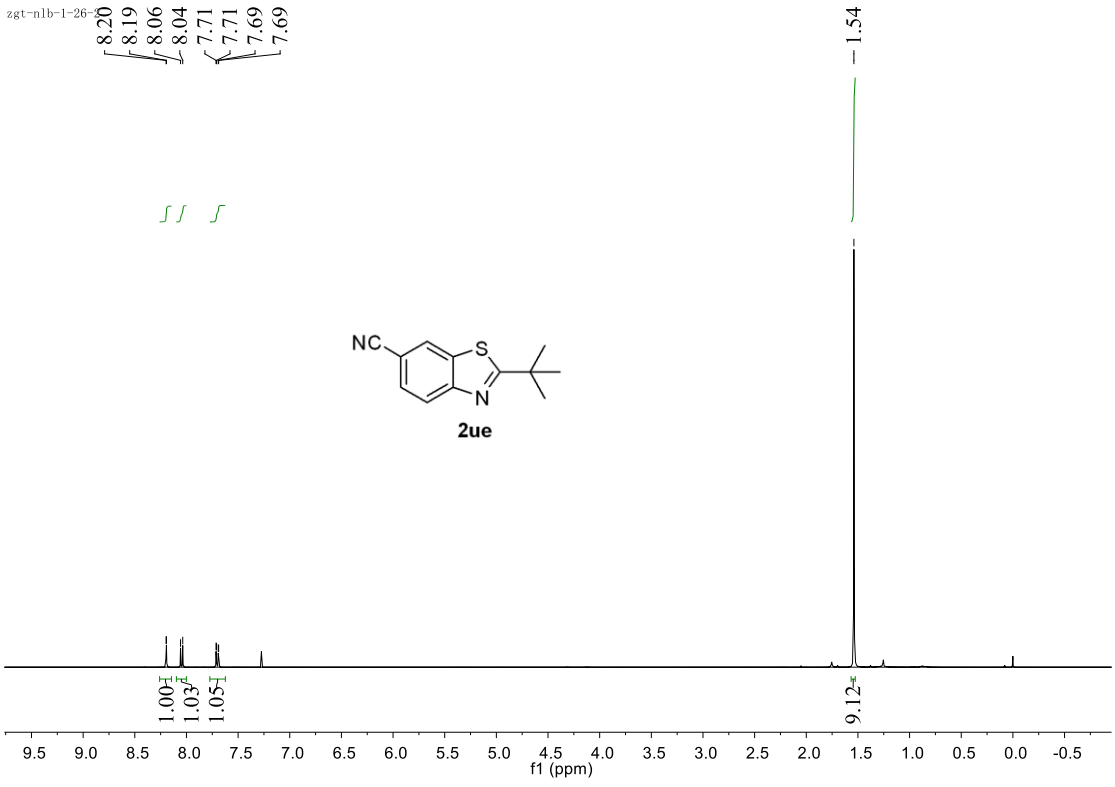

zgt-3-171-3
179.34
157.19
147.66
136.19
123.09
114.85
104.16
55.80
38.18
30.76
MeO
S
N
2ub
f1 (ppm)

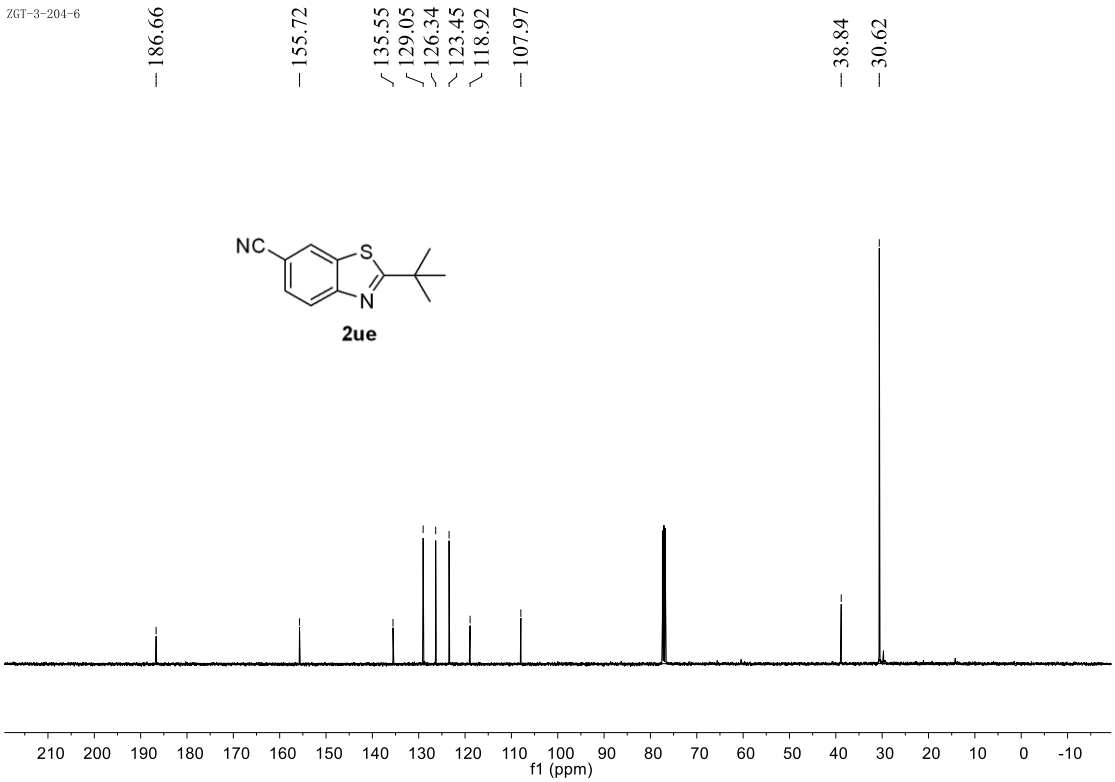

7.90
7.89
7.87
7.87
7.81
7.81
7.41
7.41
7.41
7.40
7.39
7.39
7.39
7.38
1.51
Cl
S
N
2uc
1.00
0.94
1.01
9.06
f1 (ppm)

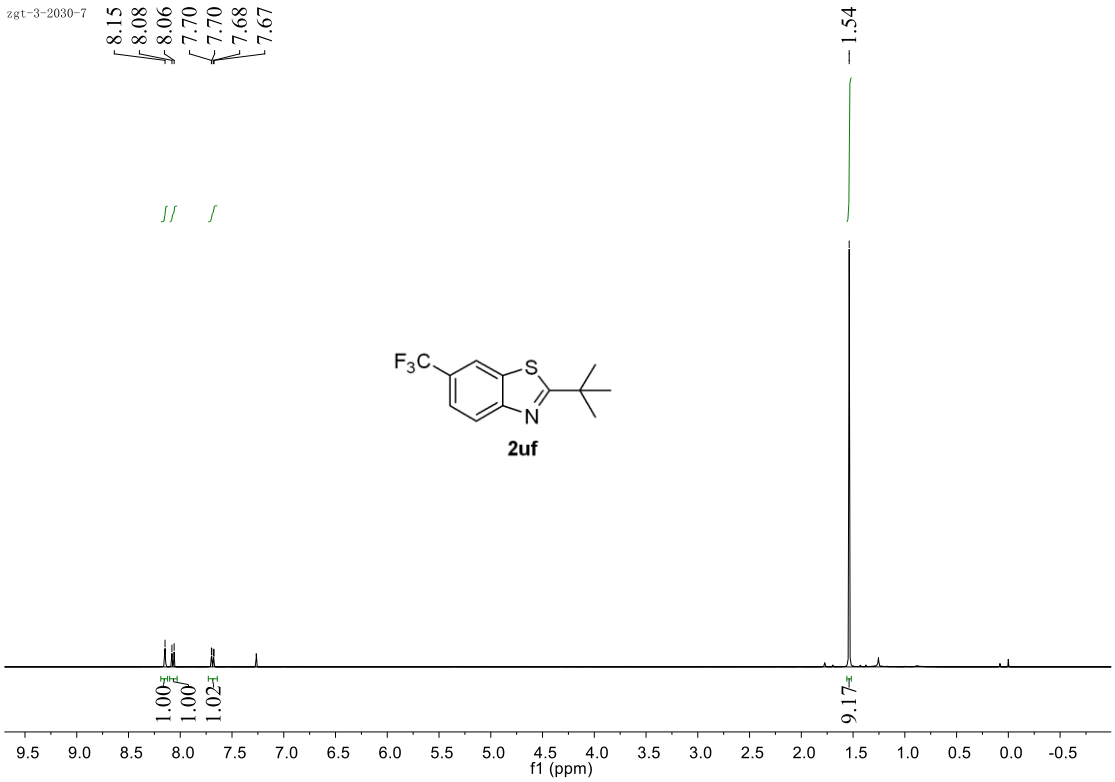

zgt-3-171-4
182.46
151.79
136.20
130.36
126.52
123.42
121.07
38.43
30.68
Cl
S
N
2uc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

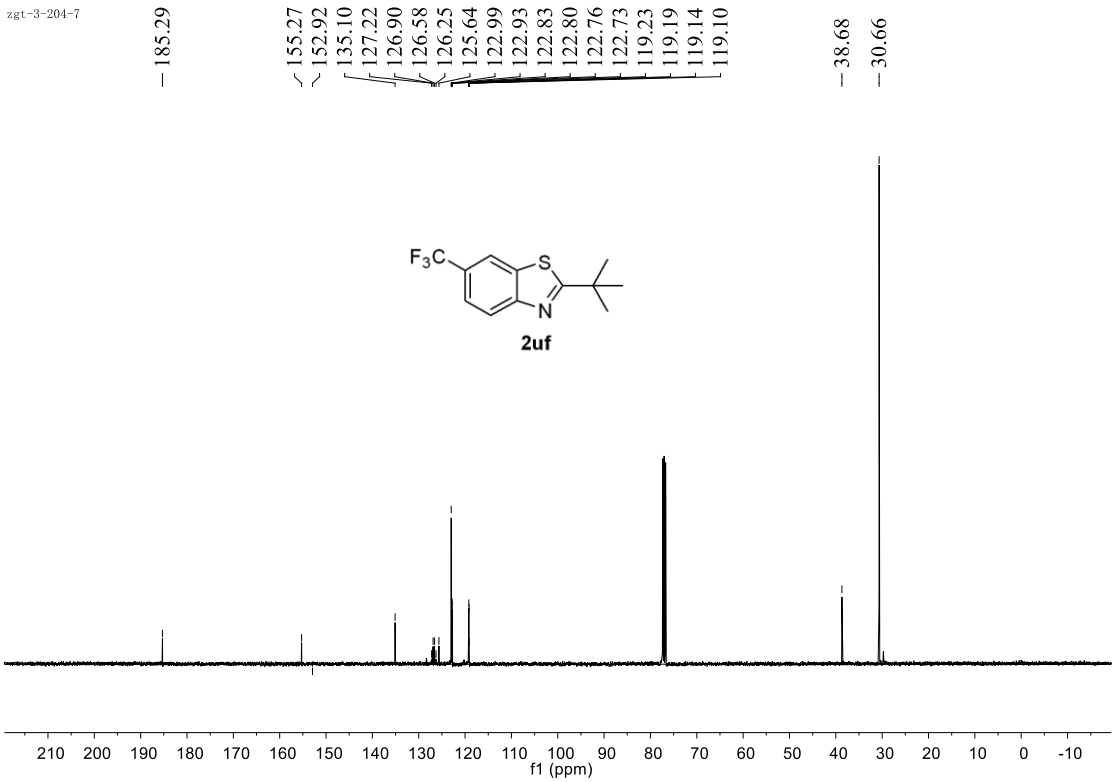

zgt-mb-1-288
7.97
7.97
7.84
7.82
7.55
7.54
7.54
7.53
7.52
7.52
1.51
Br
S
N
2ud
1.00
1.01
1.03
9.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

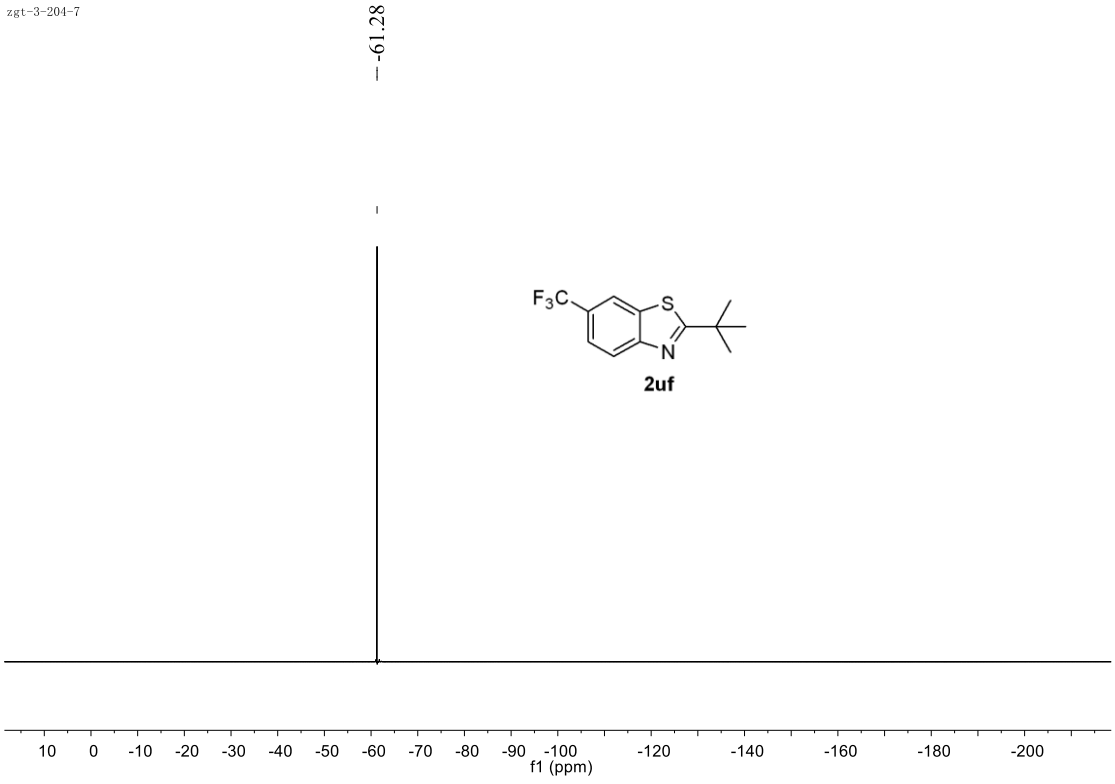

zgt-mb-1-28-2
182.51
152.13
136.70
129.22
124.00
123.81
118.01
38.43
30.68
Br
S
N
2ud
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

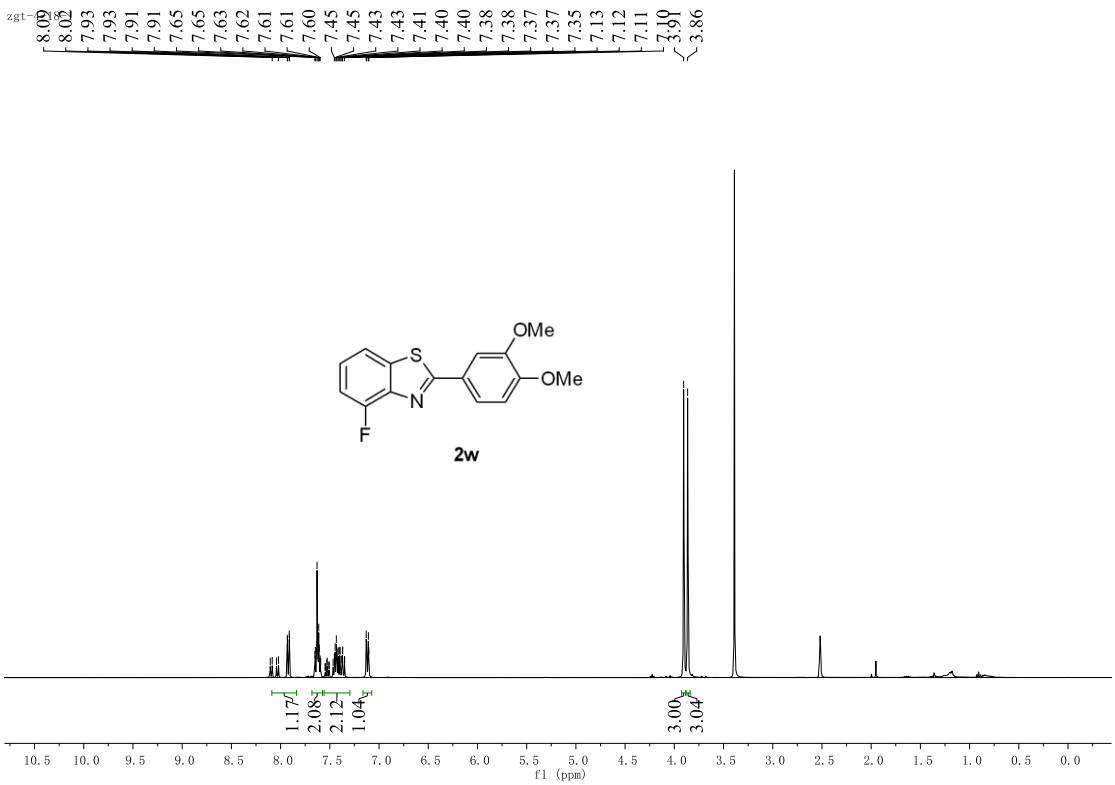

zgt-nlb-1-26-2
8.20
8.19
8.06
8.04
7.71
7.71
7.69
7.69
1.54
NC
S
N
2ue
1.00
1.03
1.05
9.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

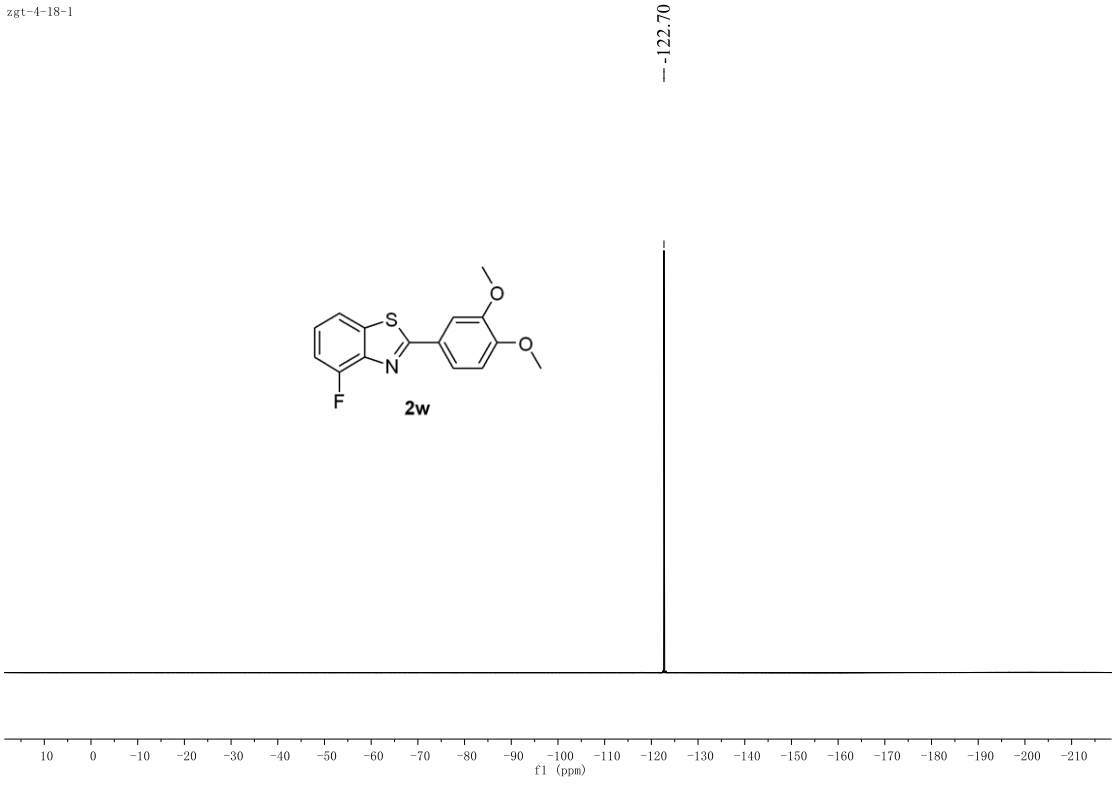

ZGT-3-204-6
186.66
155.72
135.55
129.05
126.34
123.45
118.92
107.97
38.84
30.62
NC
S
N
2ue
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

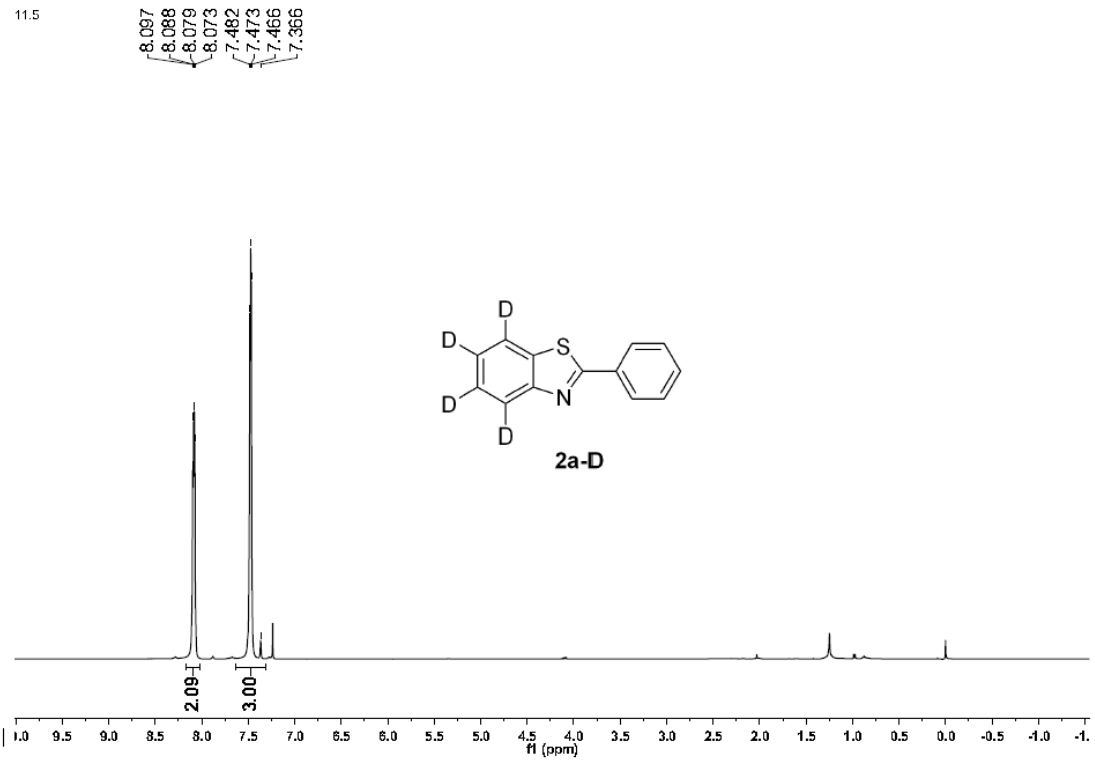

zgt-3-2030-7
8.15
8.08
8.06
7.70
7.70
7.68
7.67
1.54
F3C
S
N
2uf
1.00
1.00
1.02
9.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

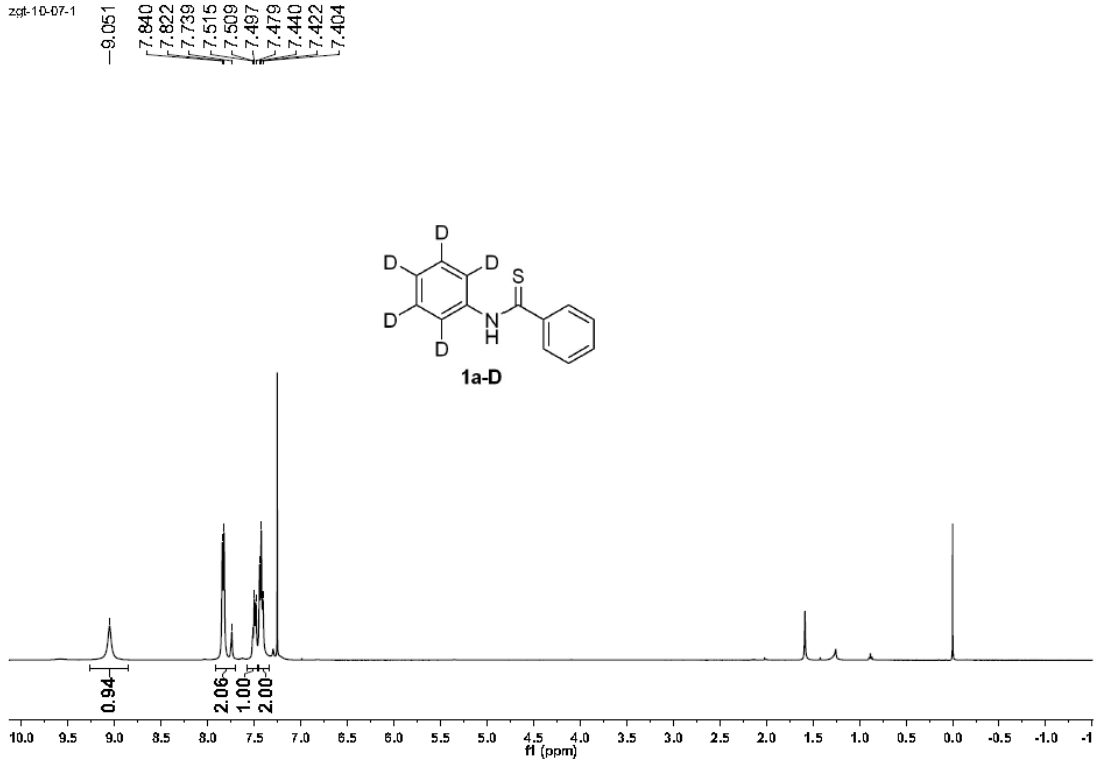

zgt-3-204-7
185.29
155.27
152.92
135.10
127.22
126.90
126.58
126.25
125.64
122.99
122.93
122.83
122.80
122.76
122.73
119.23
119.19
119.14
119.10
38.68
30.66
F3C
S
N
2uf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


zgt-3-204-7
-61.28
F3C
S
N
2uf
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


zgt-
8.02
8.02
7.93
7.93
7.91
7.91
7.65
7.65
7.63
7.62
7.61
7.61
7.60
7.45
7.45
7.43
7.43
7.41
7.40
7.40
7.38
7.38
7.37
7.37
7.35
7.13
7.12
7.11
7.10
3.91
3.86
OMe
OMe
S
N
F
2w
1.17
2.08
2.12
1.04
3.00
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


zgt-4-18-1
-122.70
O
O
S
N
F
2w
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


11.5
8.097
8.088
8.079
8.073
7.482
7.473
7.466
7.366
D
D
D
D
S
N
2a-D
2.09
3.00
f1 (ppm)


zgt-10-07-1
9.051
7.840
7.822
7.739
7.515
7.509
7.497
7.479
7.440
7.422
7.404
D
D
D
D
D
S
N
H
1a-D
0.94
2.06
1.00
2.00
f1 (ppm)