Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Visible-Light-Induced C–H Sulfenylation Using Sulfinic Acids

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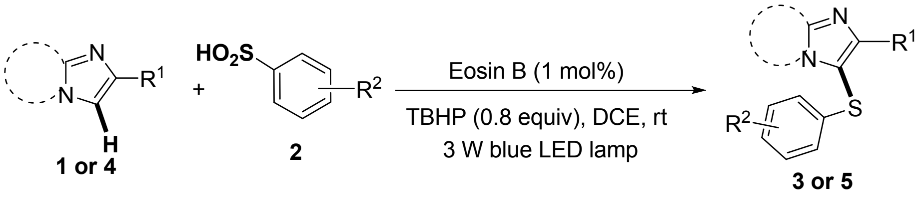
General experimental procedures

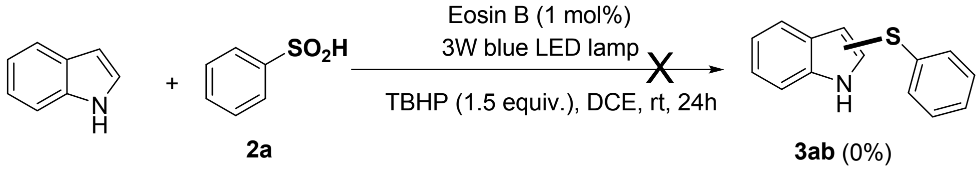
All reagents and solvents were obtained from commercial suppliers and used without further purification. TBHP= t*ert*-butyl hydroperoxide solution 5.5M in decane. Organic dyes were purchased from Sigma Aldrich. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ^{1}H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. (Note: ^{1}H and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer for 3y, 3z, and 3aa). Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in DMSO-d_6 or in $CDCl_3$. Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer. UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The fluorescenceemission intensity of reaction solution was recorded on a Fluoromax- 4 spectrofluorimeter.

General procedure for synthesis of C-3 sulfenylation of imidazoheterocycles 3 and 5



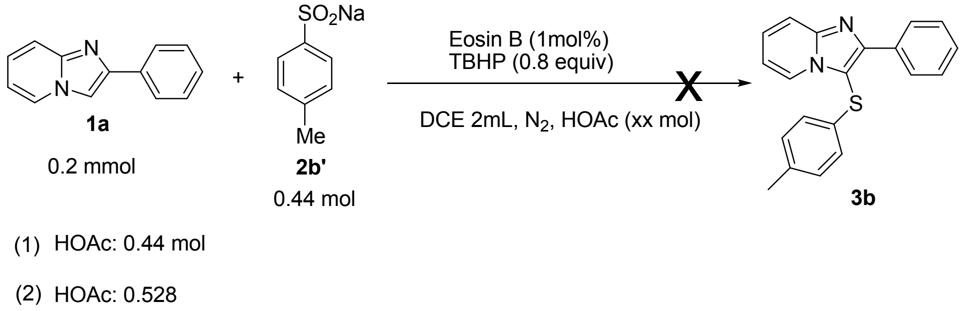
A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with imidazoheterocycles (0.2 mmol), sulfinic acids (0.44 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. After completion of the reaction (TLC), the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum (gradient eluent of ether/ethyl acetate: 1/20 to 1/3) as eluent to provide the desired product **3** and **5**.

Experiment procedure for the coupling of indole with benzenesulfinic acid under the standard conditions



A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with indole (0.2 mmol), benzenesulfinic (0.44 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. No desired product was observed by TLC.

The experiment procedure of visible-light-induced sulfenylation of 2-phenylimidazo[1,2-*a*]pyridine with sodium 4-methylbenzenesulfinate under acidic reaction conditions

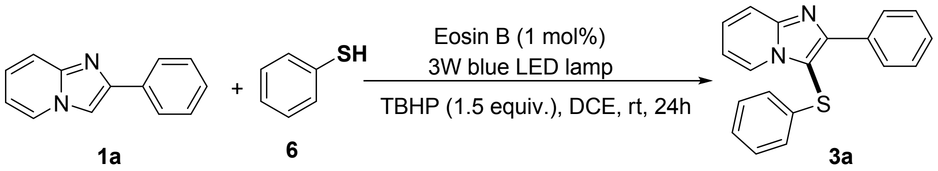


(1) HOAc: 0.44 mol

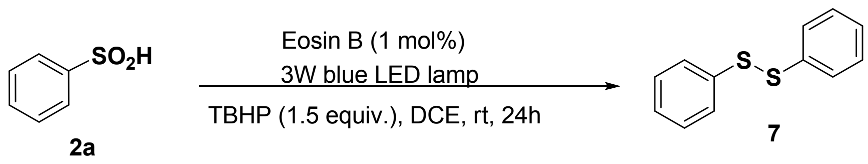
(2) HOAc: 0.528

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-*a*]pyridine **1a** (0.2 mmol), sodium 4-methylbenzenesulfinate **2b'** (0.44 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). Subsequently, HOAc (0.44, 0.58, respectively) and TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere in sequence. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. No desired product was observed by TLC.

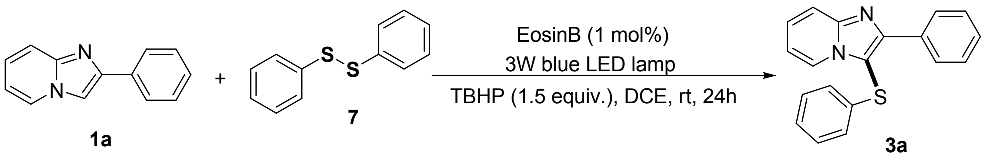
Experiments of investigations on the mechanism



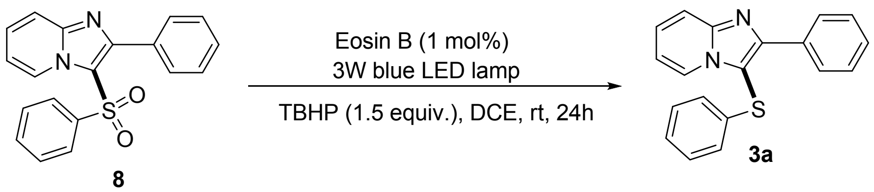
A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-*a*]pyridine (0.2 mmol), benzenethiol (0.44 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. After completion of the reaction(TLC), the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate(1/6) as eluent to provide the desired product **3a** in 32% yield as a white solid.



A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with benzenesulfinic acid (0.2 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. The reaction progress was monitored by TLC. After completion of the reaction (TLC), the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate（1/400） as eluent to provide the desired product **7** in 45% yield as a white solid.



A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 2-phenylimidazo[1,2-a]pyridine (0.2 mmol), 1,2-diphenyldisulfane (0.22 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. After completion of the reaction (TLC), and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product **3a** in 25% yield as a white solid.



A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (0.2 mmol), Eosin B (1.3 mg, 1 mol%). The tube was evacuated and backfilled with nitrogen (three times). TBHP (0.16 mmol, 0.8 equiv) in 2 mL of DCE were added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of a 3 W blue LED lamp for 24 h. The reaction progress was monitored by TLC, the reaction was completely unhappened.

Fluorescence quenching experiments

The fluorescence emission intensities were recorded on a Fluoromax-4spectrofluorimeter. The excitation wavelength was fixed at 323 nm, and the emission wavelength was measured at 372 nm (emission maximum). The samples were prepared by mixing Eosin B (1.0×10^{-8}mol/L) and different amount of TBHP in ethanol (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of TBHP stock solution is 1.0×10^{-7}mol/L in ethanol. For each quenching experiment, 0.1mL of TBHP stock solution was titrated to a mixed solution of Eosin B (0.1mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S1.

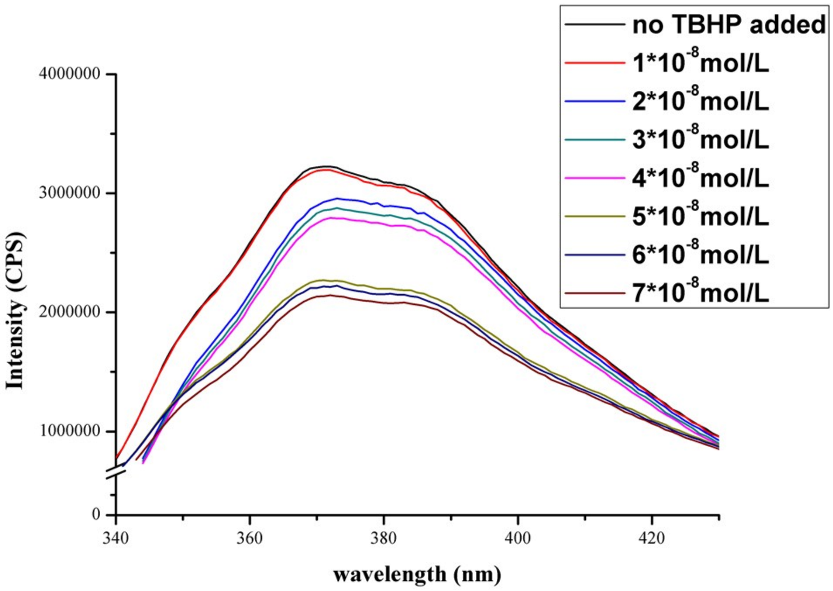


Figure S1 Quenching of Eosin B fluorescence emission in the presence of TBHP.

An indeed fluorescence quenching phenomenon of Eosin B under various concentrations of TBHP was demonstrated in a curve of [I_0/I] vs $C_{[TBHP]}$, as shown in Figure 2 (Stern-Volmer plots). For example, when $C_{[TBHP]}$ is 2×10^{-8}mol/L, the non-liner Stern-Volmer plots indicated energy transfer event operating between Eosin B's excited state and TBHP.

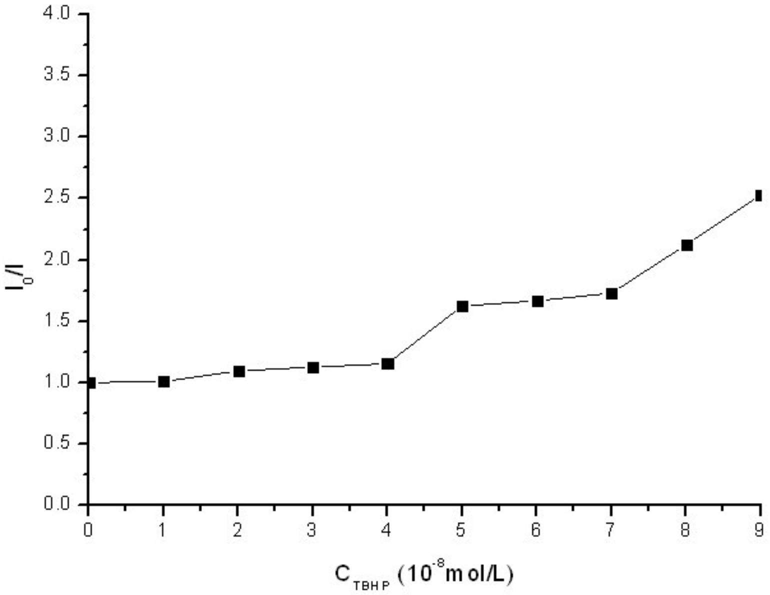


Figure S2 Stern-Volmer plots.

We also investigate fluorescence quenching experiments with respect to benzenesulfinic acid. The samples were prepared by mixing Eosin B (1×10^{-8}mol/L) and different amount of benzenesulfinic acid in ethanol (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of benzenesulfinic acid stock solution is 1×10^{-7}mol/L in ethanol. For each quenching experiment, 0.1 mL of benzenesulfinic acid stock solution was titrated to a mixed solution of Eosin B (0.1 mL, in a total volume = 1.0 mL). The emission intensity was collected and the results were presented in Figure S3.

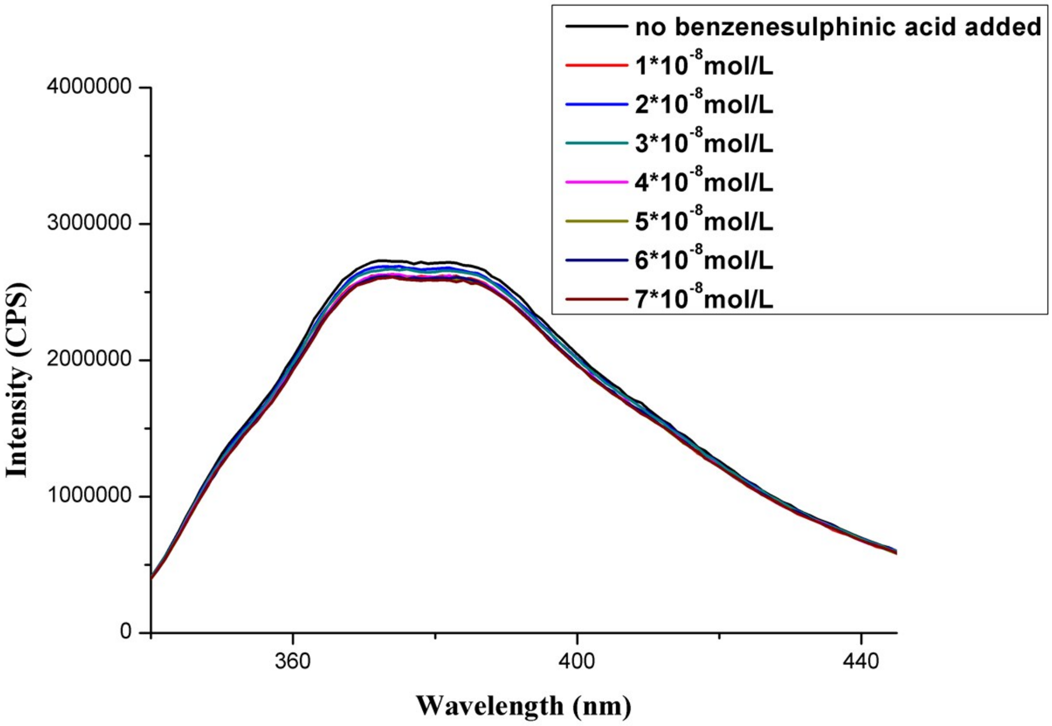


Figure S3 Quenching of Eosin Y fluorescence emission in the presence of benzenesulfinic acid.

Effect of Visible Light Irradiation

The reaction between 7-methyl-2-phenylimidazo[1,2-*a*]pyridine **1b** and 4-methylbenzenesulfinic acid **2b** was conducted under the standard conditions on a 0.3 mmol scale containing the internal reference 1,3,5-trimethoxybenzene (0.1 mmol). The mixture was subjected to sequential periods of stirring under visible light irradiation (3 W blue LED lamp) followed by stirring in the absence of light. At each time point, an aliquot (100μl) was taken under argon, which was then concentrated under reduced pressure. The crude material diluted with a $CDCl_3$ solution. The yields of tetrahydrofuran **3g**, measured by ^{1}H NMR.

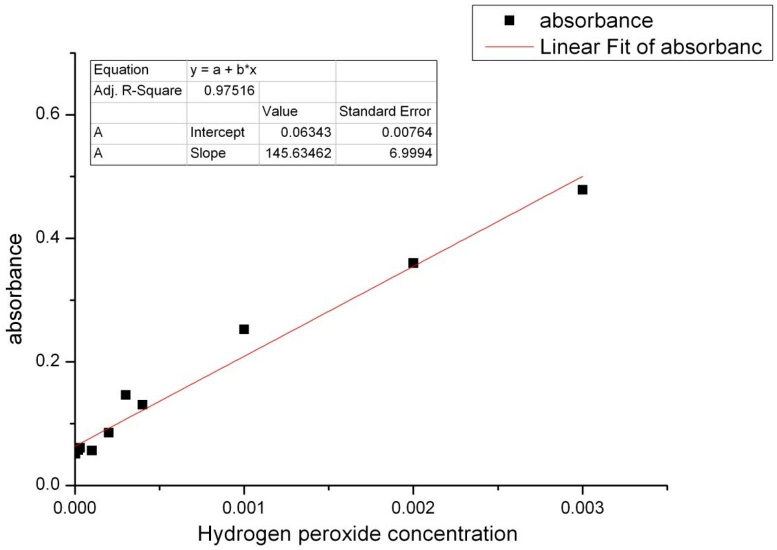
H_2O_2 Detectetion Experiment

According to the mechanism of enzyme catalyzed hydrogen peroxide using colorimetric determination in the previous reports, the present sulfenylation reaction might generate hydrogen peroxide. The classic method for detection hydrogen peroxide using the HRP catalyzed oxidation of H_2O_2-TMB occurrence coloration have reported everywhere.[1] According to the previous reports, HRP and TMB were added into the reaction solution in order to demonstrate whether hydrogen peroxide was generated or not in the present transformation.

The colorimetric assays for the conventions investigation of peroxidase-like activities were conducted by using the TMB-H_2O_2 chromogenic reactions. Typically, an aliquot of certain concentration of three reaction solutions (three reation solutions including the solution before the reaction of phenylimidazo[1,2-*a*]pyridine **1a** and benzene sulfinic acid **2a**, the solution after reaction of them, and the solution of phenylimidazo[1,2-*a*]pyridine **1a** only under the standard condition) were introduced into the TMB-H_2O_2 separately, of which the reaction products were monitored by UV-visible absorbance at 652 nm using 96-well plates and a microplate reader.[2]

The buffer solution of citric acid was prepared according to a classical method, of which citric acid (1.02 g) and $Na_2HPO_4 \cdot 12H_2O$ (3.68 g) were dissolved in 100 mL water, then storing at 4 °C for future usage. Subsequently, DMSO (10 mL) was mixed with TMB (5.0 mg), then keeping it at 4 °C for future usage. Also, HRP (12.5 mg) was dissolved in 10 L water, then storing at 4 °C for future usage. We have carefully made some corresponding experiments to investigate whether hydrogen peroxide was produced or not. Firstly, TMB (5.0 mg mL^{-1}, 20 μL), citric acid buffer (887 μL) and a series of different concentrations of hydrogen peroxide (30 %) were mixed to form the TMB-H_2O_2 substrate chromogenic solution, which the final concentration of TMB was 1.0 mg mL^{-1}. Subsequently, HRP (0.00125 mg mL^{-1}, 10 μL) was added into TMB-H_2O_2 substrate chromogenic solution to catalyze the color reaction, then measuring the absorbance after 10-20 minutes by microplate reader, with the corresponding hydrogen peroxide correction curve showing in Figure S4. As mentioned above, TMB (20 μL) and citric acid buffer (9.88 mL) were mixed with 100 μL of three reaction solution (three reation solutions including the solution before the reaction of phenylimidazo[1,2-*a*]pyridine **1a** and benzene sulfinic acid **2a**, the solution after reaction of them, and the solution of phenylimidazo[1,2-*a*]pyridine **1a** under the standard conditions) separately, which indeed the final concentration of

TMB was consistent. Additionally, the absorbance of reaction product was measured at 652 nm by microplate reader, indicating in Figure S5.



Equation	y = a + b*x		
Adj. R-Square	0.97516		
		Value	Standard Error
A	Intercept	0.06343	0.00764
A	Slope	145.63462	6.9994

Figure S4 The linear curve eatablished the concentration of H_2O_2 by Microplate reader.

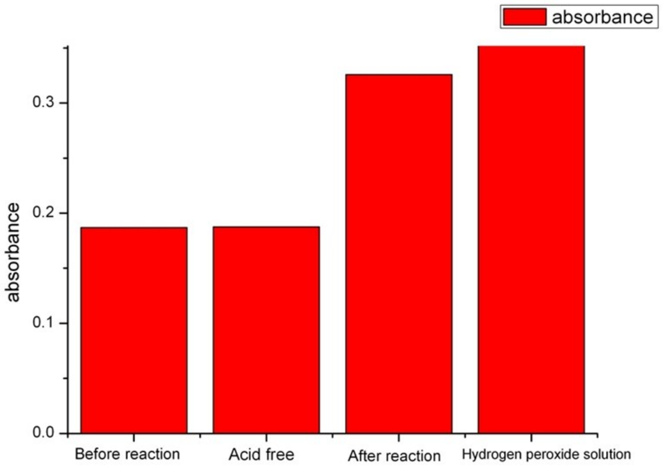
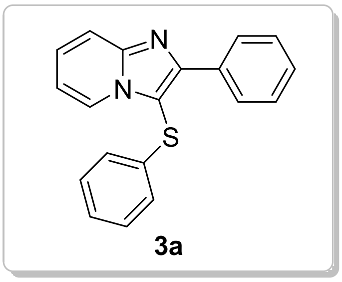


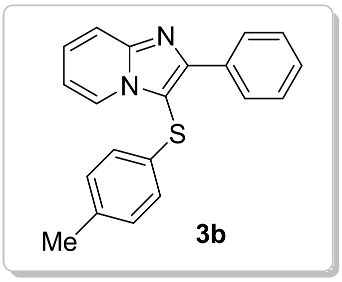
Figure S5 Absorbance of various reactive liquids of the same concentration.

Absorbance response based on H_2O_2 that was generated from oxidation of H_2O_2-TMB using HRP as catalyst, a classic assay for detection of hydrogen peroxide has been used. Therefore, by Figure S2, we can discover that the absorbance of the solution before the reaction of phenylimidazo[1,2-*a*]pyridine **1a** and benzene sulfinic acid **2a** is almost the same as the solution of phenylimidazo[1,2-*a*]pyridine **1a** under the standard conditions. We inferred that the reaction could not produce hydrogen peroxide without benzene sulfonic acid **2a** added. Furthermore, the absorbance of the solution before the reaction of phenylimidazo[1,2-a]pyridines with benzene sulfinic acid **2a**, the solution after reaction of them are different, and on this basis we speculated that hydrogen peroxide might be produced. Finally, through the correction curve of hydrogen peroxide, we could pretty calculate the yield of hydrogen peroxide. The different absorbance between after reaction and before reaction is the absorbance of the hydrogen peroxide. Substituting the data in a linear equation ($y = 145.6346x + 0.06343$), hydrogen peroxide can be successful obtained, maybe producing 0.096 mmol hydrogen peroxide.[3]



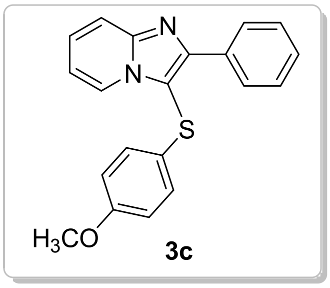
3a

2-Phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3a).[4] Eluent petroleum ether/ethyl acetate (3:1). 50 mg, 82 % yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.35 (d, 1H, J = 7.0 Hz), 8.18 (d, 2H, J = 7.5 Hz), 7.73 (d, 1H, J = 9.0 Hz), 7.41 (dd, 2H, J = 7.0 Hz, J = 8.0 Hz), 7.34 (t, 1H, J = 7.0 Hz), 7.31 (t, 1H, J = 6.5 Hz), 7.19-7.16 (m, 3H), 7.11-7.09 (m, 2H), 8.86 (t, 1H, J = 6.5 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 151.5, 147.2, 135.2, 133.4, 129.5, 128.8, 128.5, 128.4, 126.7, 126.1, 125.6, 124.5, 117.9, 113.1, 106.3. HRMS calc. for $C_{19}H_{15}N_2S$ (M+H)$^+$ 303.0950; found 303.0958.



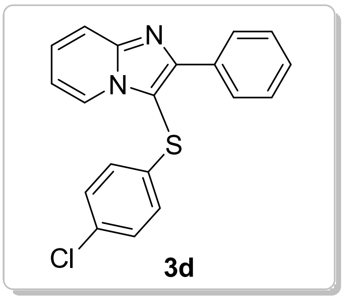
3b

2-Phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3b).[5] Eluent petroleum ether/ethyl acetate (3:1). 54 mg, 85% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.26-8.22 (m, 3H), 7.70 (d, 1H, J = 9.0 Hz), 7.42 (t, 2H, J = 7.5 Hz), 7.35 (t, 1H, J = 7.5 Hz), 7.28 (t, 1H, J = 6.5 Hz), 7.00 (d, 2H, J = 8.0 Hz), 6.89 (d, 2H, J = 8.0 Hz), 6.81 (t, 1H, J = 7.0 Hz), 2.23 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 151.2, 147.1, 136.1, 133.5, 131.5, 130.2, 128.6, 128.5, 128.4, 126.6, 125.9, 124.5, 117.6, 113.0, 106.9, 20.9. HRMS calc. for $C_{20}H_{17}N_2S$ (M+H)$^+$ 317.1107; found 317.1109.



3c

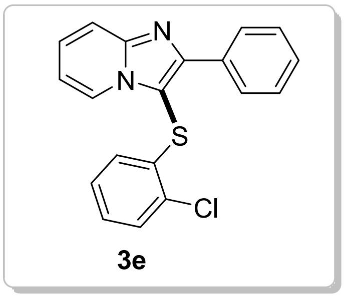
3-(4-Methoxyphenylthio)-2-phenylimidazo[1,2-*a*]pyridine (3c).[6] Eluent petroleum ether/ethyl acetate (4:1). 55 mg, 83% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.23 (d, 1H, J = 6.8 Hz), 8.15 (d, 2H, J = 7.4 Hz), 7.62 (d, 1H, J = 8.9 Hz), 7.36 (t, 2H, J = 7.5 Hz), 7.28 (t, 1H, J = 7.3 Hz), 7.23 (t, 1H, J = 7.5 Hz), 6.91 (d, 2H, J = 9.0 Hz), 6.79 (t, 1H, J = 6.5 Hz), 6.67 (d, 2H, J = 9.0 Hz), 3.63 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 158.8, 150.9, 147.0, 133.5, 130.0, 128.8, 128.6, 128.2, 126.8, 125.6, 124.7, 117.7, 115.3, 113.2, 108.1, 55.5. HRMS calc. for $C_{20}H_{17}N_2OS$ $(M+H)^+$ 333.1056; found 333.1051.



3d

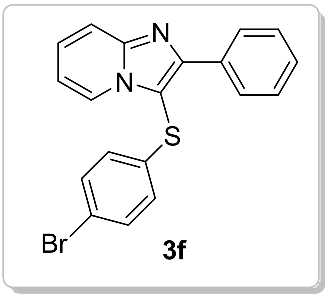
3-(4-Chlorophenylthio)-2-phenylimidazo[1,2-*a*]pyridine (3d).[7] Eluent petroleum ether/ethyl acetate (3:1). 48 mg, 72% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.22 (d, 1H, J = 7.0 Hz), 8.18 (d, 2H, J = 7.0 Hz), 7.72 (d, 1H, J = 9.0 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.37-7.31 (m, 2H), 7.15 (d, 2H, J = 8.5 Hz), 6.90 (d, 2H, J = 8.5 Hz), 6.86 (t, 1H, J = 6.5 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 151.7, 147.2, 133.8, 133.2, 132.1, 129.6, 128.8, 128.5, 128.4, 126.9, 124.4, 117.8, 113.3, 105.7. HRMS calc. for

$C_{19}H_{14}ClN_2S(M+H)^+$ 337.0561; found 337.0562.



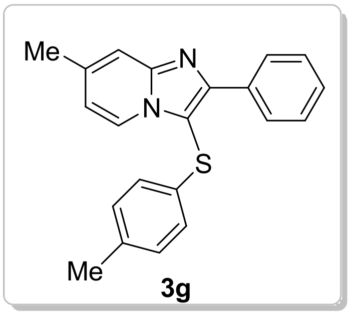
3e

3-(2-Chlorophenylthio)-2-phenylimidazo[1,2-*a*]pyridine (3e). Eluent petroleum ether/ethyl acetate (3:1). 43 mg, 65% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.20 (d, 1H, J = 6.0 Hz), 8.16 (d, 2H, J = 7.5 Hz), 7.75 (d, 1H, J = 9.0 Hz), 7.44-7.33 (m, 5H), 7.05 (t, 1H, J = 6.5 Hz), 6.94 (t, 1H, J = 6.5 Hz), 6.85 (t, 1H, J = 6.5 Hz), 6.37 (d, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 152.2, 147.6, 134.4, 133.2, 131.2, 130.2, 128.9, 128.7, 128.5, 127.8, 127.1, 127.0, 125.7, 124.6, 117.9, 113.5, 104.8. HRMS calc. for $C_{19}H_{14}ClN_2S(M+H)^+$ 337.0561; found 337.0562.



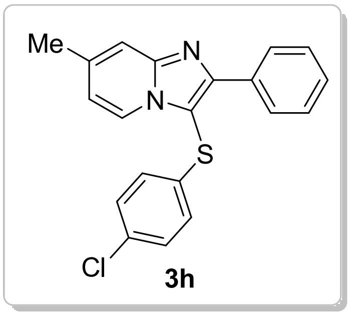
3f

3-(4-Bromophenylthio)-2-phenylimidazo[1,2-*a*]pyridine (3f).[5] Eluent petroleum ether/ethyl acetate (3:1). 57 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.23 (d, 1H, J = 6.5 Hz), 8.18 (d, 2H, J = 7.0 Hz), 7.74 (d, 1H, J = 9.0 Hz), 7.45 (t, 2H, J = 7.0 Hz), 7.40-7.31 (m, 3H), 6.89-6.85 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.8, 147.4, 134.6, 133.3, 132.6, 128.9, 128.6, 128.5, 127.2, 127.0, 124.5, 120.0, 117.9, 113.4, 105.7. HRMS calc. for $C_{19}H_{14}BrN_2S$ $(M+H)^+$ 381.0056; found, 381.0059, 383.0052.



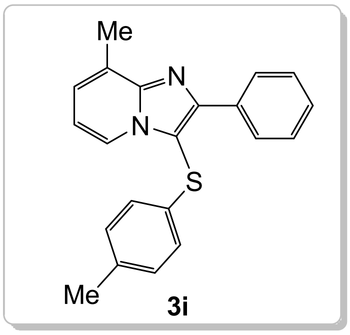
3g

7-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3g).[4] Eluent petroleum ether/ethyl acetate (3:1). 54 mg, 82% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.23 (d, 2H, J = 7.5 Hz), 8.13 (d, 1H, J = 7.0 Hz), 7.49 (s, 1H), 7.44 (t, 2H, J = 7.5 Hz), 7.36 (t, 1H, J = 7.0 Hz), 7.01 (d, 2H, J = 8.0 Hz), 6.91 (d, 2H, J = 8.0 Hz), 6.67 (d, 1H, J = 7.0 Hz), 2.42 (s, 3H), 2.26(s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 151.2, 147.5, 137.9, 136.0, 133.7, 132.0, 130.3, 128.6, 128.5, 128.4, 125.8, 123.8, 116.3, 115.7, 106.1, 21.5, 21.0. HRMS calc. for $C_{21}H_{19}N_2S$ (M+H)$^+$ 331.1263; found 331.1269.



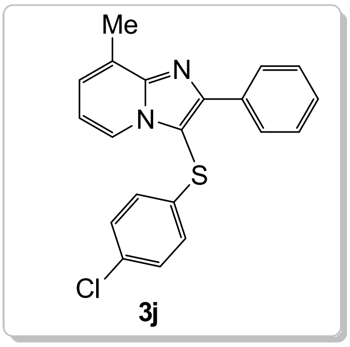
3h

3-(4-Chlorophenylthio)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (3h). Eluent petroleum ether/ethyl acetate (3:1). 52 mg, 69% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.16 (d, 2H, J = 8.5 Hz), 8.07 (d, 1H, J = 6.5 Hz), 7.49 (s, 1H), 7.48 (s, 1H), 7.41 (dd, 1H, J = 7.0 Hz, J = 8.0 Hz), 7.36 (t, 1H, J = 7.5 Hz), 7.14 (d, 2H, J = 7.0 Hz), 6.90 (d, 2H, J = 7.0 Hz), 6.68 (d, 2H, J = 7.0 Hz), 2.41 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 151.5, 147.6, 138.1, 134.1, 133.4, 131.9, 129.5, 128.6, 128.5, 128.3, 126.8, 123.5, 116.3, 115.9, 104.9, 21.4. HRMS calc. for $C_{20}H_{16}ClN_2S$ $(M+H)^+$ 351.0717; found 351.0721.



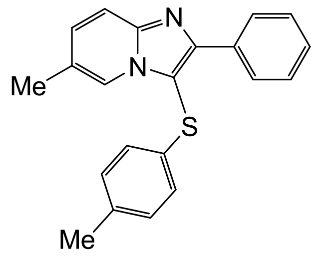
3i

8-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3i).[8] Eluent petroleum ether/ethyl acetate (3:1). 57 mg, 86% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.25 (d, 2H, *J* = 7.0 Hz), 8.16 (d, 1H, *J* = 6.5 Hz), 7.46 (t, 1H, *J* = 7.5 Hz), 7.38 (t, 1H, *J* = 6.5 Hz), 7.11 (d, 1H, *J* = 5.5 Hz), 7.03 (d, 2H, *J* = 8.5 Hz), 6.93 (d, 2H, *J* = 8.5 Hz), 6.77 (t, 1H, *J* = 6.5 Hz), 2.74 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.0, 147.5, 136.1, 133.9, 132.0, 130.3, 128.7, 128.5, 127.8, 125.9, 125.5, 122.5, 113.1, 107.2, 29.9, 21.0. HRMS calc. for $C_{21}H_{19}N_2S$ $(M+H)^+$ 331.1263; found 331.1269.



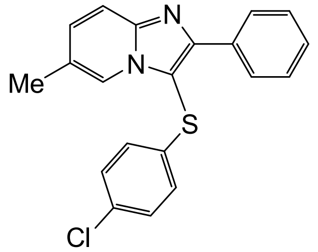
3j

3-(4-Chlorophenylthio)-8-methyl-2-phenylimidazo[1,2-a]pyridine (3j). Eluent petroleum ether/ethyl acetate (3:1). 51mg, 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.09 (dd, 2H, *J* = 7.0 Hz), 7.97 (dd, 1H, *J* = 7.0 Hz), 7.32-7.29 (m, 2H), 7.26-7.22 (m, 1H), 7.02 (d, 1H, *J* = 8.5 Hz), 6.96 (dd, 1H, *J* = 6.5 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 6.79-6.76 (m, 2H), 6.61 (dt, 1H, *J* = 7.0 Hz), 2.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.3, 147.4, 135.9, 134.2, 130.2, 129.6, 128.6, 128.5, 128.4, 126.9, 125.9, 125.8, 122.4, 113.0, 106.0, 20.9. HRMS calc. for $C_{20}H_{16}ClN_2S$ $(M+H)^+$ 351.0717; found 351.0721.



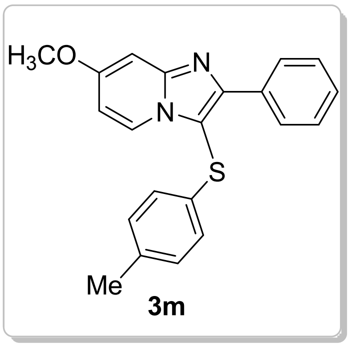
3k

6-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3k).[9] Eluent petroleum ether/ethyl acetate (3:1). 56 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.23 (d, 2H, *J* = 7.5 Hz), 8.10 (s, 1H), 7.64 (d, 1H, *J* = 8.0 Hz), 7.41 (t, 1H, *J* = 7.5 Hz), 7.38 (t, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 9.0 Hz), 7.03 (d, 2H, *J* = 9.0 Hz), 6.93 (d, 2H, *J* = 9.0 Hz), 2.31 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.1, 146.1, 135.9, 133.6, 131.9, 130.2, 129.7, 128.42, 128.38, 128.30, 125.7, 122.8, 122.2, 117.0, 106.3, 20.7. HRMS calc. for $C_{21}H_{19}N_2S$ $(M+H)^+$ 331.1263; found 331.1269.



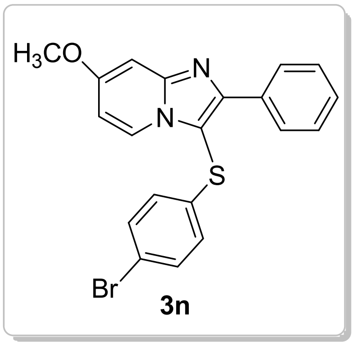
3l

3-(4-Chlorophenylthio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3l). Eluent petroleum ether/ethyl acetate (3:1). 49 mg, 70% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.17 (d, 2H, $J = 7.5$ Hz), 8.10 (d, 1H, $J = 6.0$ Hz), 7.50 (s, 1H), 7.44 (t, 1H, $J = 7.5$ Hz), 7.37 (t, 1H, $J = 7.5$ Hz), 7.17 (d, 2H, $J = 9.0$ Hz), 6.91 (d, 2H, $J = 9.0$ Hz), 6.71 (d, 1H, $J = 6.5$ Hz), 2.44 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 150.5, 146.6, 137.1, 133.1, 132.3, 130.9, 128.5, 128.3, 127.6, 127.4, 127.2, 125.7, 122.4, 115.3, 114.8, 103.8, 20.4. HRMS calc. for $C_{20}H_{16}ClN_2S$ (M+H)$^+$ 351.0717; found 351.0721.



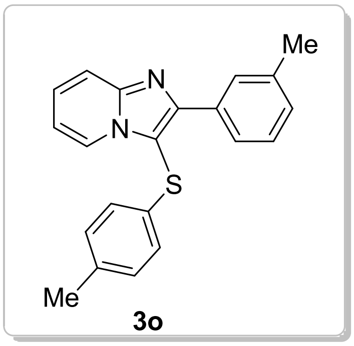
3m

7-Methoxy-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3m). Eluent petroleum ether/ethyl acetate (3:1). 52 mg, 75% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.24 (d, 2H, $J = 8.0$ Hz), 8.01 (d, 1H, $J = 7.5$ Hz), 7.43 (dd, 2H, $J = 7.5$ Hz, $J = 8.0$ Hz), 7.34 (dd, 1H, $J = 6.0$ Hz, $J = 7.5$ Hz), 7.01-6.99 (m, 3H), 6.92 (d, 2H, $J = 8.5$ Hz), 6.52 (d, 1H, $J = 7.5$ Hz), 3.83 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 159.4, 151.0, 148.5, 135.9, 133.6, 132.0, 130.2, 128.4, 128.2, 125.7, 124.9, 107.7, 105.3, 95.2, 55.8, 20.8. HRMS calc. for $C_{21}H_{19}N_2OS$ (M+H)$^+$ 347.1213; found 347.1215.



3n

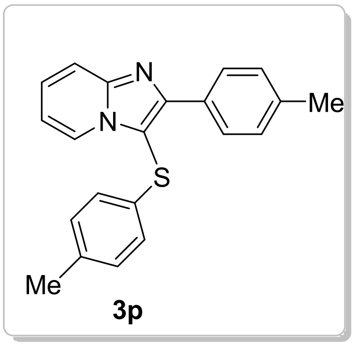
3-(4-Bromophenylthio)-7-methoxy-2-phenylimidazo[1,2-*a*]pyridine (3n). Eluent petroleum ether/ethyl acetate (3:1). 52 mg, 64% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.15 (d, 2H, *J* = 6.0 Hz), 8.02 (d, 1H, *J* = 7.5 Hz), 7.42 (dd, 2H, *J* = 7.0 Hz, *J* = 8.0 Hz), 7.35 (dd, 1H, *J* = 6.5 Hz, *J* = 6.0 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 7.01 (s, 1H), 6.91 (d, 2H, *J* = 8.5 Hz), 6.57 (d, 1H, *J* = 7.5 Hz), 3.88 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 159.8, 151.6, 148.9, 134.4, 133.4, 132.1, 129.7, 128.7, 128.6, 128.2, 126.9, 124.8, 108.2, 104.3, 95.4, 55.9. HRMS calc. for $C_{20}H_{16}BrN_2OS$ (M+Na)$^+$ 411.0161; found 411.0162, 413.0169.



3o

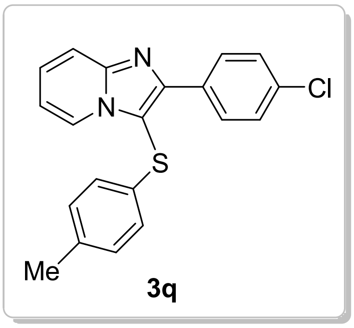
2-*m*-Tolyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3o). Eluent petroleum ether/ethyl acetate (3:1). 51 mg, 78% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.83 (s, 1H), 8.49 (d, 1H, *J* = 7.5 Hz), 8.20 (d, 1H, *J* = 7.0 Hz), 7.95 (dd, 2H, *J* = 7.5 Hz, *J* = 8.5 Hz), 7.51 (dd, 2H, *J* = 8.5 Hz), 7.04 (d, 2H, *J* = 8.5 Hz), 7.00 (d, 2H, *J* = 8.5 Hz), 6.75 (t, 1H, *J* = 6.5 Hz), 2.80 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ

150.7, 147.5, 136.1, 133.5, 133.4, 130.3, 128.8, 128.0, 127.9, 127.7, 126.3, 126.2, 126.1, 126.0, 122.4, 113.1, 107.7, 20.9, 16.9. HRMS calc. for $C_{21}H_{19}N_2S$ $(M+H)^+$ 331.1263; found 331.1269.



3p

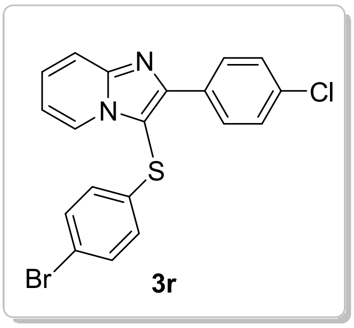
2-*p*-Tolyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3p).[6] Eluent petroleum ether/ethyl acetate (3:1). 48 mg, 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.15 (d, 1H, J = 7.0 Hz), 8.03 (d, 2H, J = 8.5 Hz), 7.60 (d, 1H, J = 9.0 Hz), 7.20-7.14 (m, 3H), 6.90 (d, 2H, J = 8.0 Hz), 6.80 (d, 2H, J = 8.0 Hz), 6.75 (t, 1H, J = 6.5 Hz), 2.28 (s, 3H), 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.3, 147.0, 138.5, 136.0, 131.6, 130.6, 130.2, 129.2, 128.3, 126.5, 125.8, 124.5, 117.5, 112.9, 106.5, 21.4, 20.9. HRMS calc. for $C_{21}H_{19}N_2S$ $(M+H)^+$ 331.1263; found 331.1269.



3q

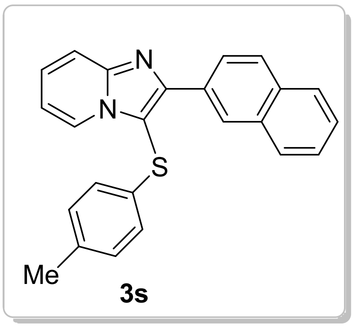
2-(4-Chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3q).[8] Eluent petroleum ether/ethyl acetate (3:1). 52 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.25 (d, 1H, J = 6.5 Hz), 8.18 (d, 2H, J = 6.5 Hz), 7.75 (d, 1H, J = 9.0 Hz), 7.38 (d, 2H, J =

8.5 Hz), 7.30 (t, 1H, *J* = 6.0 Hz), 7.00 (d, 2H, *J* = 8.0 Hz), 6.88 (d, 2H, *J* = 8.0 Hz), 6.83 (t, 1H, *J* = 6.0 Hz), 2.24 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 150.0, 147.1, 136.4, 134.7, 132.1, 131.3, 130.4, 129.7, 128.8, 126.9, 126.0, 124.7, 117.8, 113.3, 107.2, 21.0. HRMS calc. for $C_{20}H_{16}ClN_2S$ (M+H)$^+$ 351.0717; found 351.0721.



3r

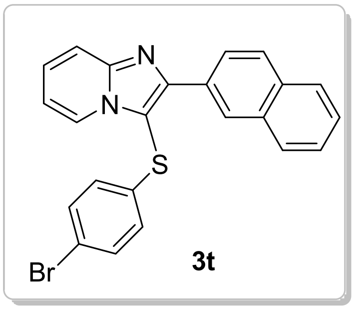
3-(4-Bromophenylthio)-2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (3r). Eluent petroleum ether/ethyl acetate (3:1). 56 mg, 68% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.23 (d, 1H, *J* = 6.5 Hz), 8.14 (d, 2H, *J* = 6.5 Hz), 7.72 (d, 1H, *J* = 8.5 Hz), 7.40 (d, 2H, *J* = 9.0 Hz), 7.36 (t, 1H, *J* = 8.5 Hz), 7.17 (d, 2H, *J* = 7.0 Hz), 6.91-6.89 (m, 3H), 2.24 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 150.6, 147.4, 134.9, 133.6, 132.4, 131.9, 129.8, 129.7, 128.9, 127.3, 127.1, 124.5, 118.0, 113.6, 106.1. HRMS calc. for $C_{19}H_{13}BrClN_2S$ (M+Na)$^+$ 414.9666; found 414.9669, 416.9658.



3s

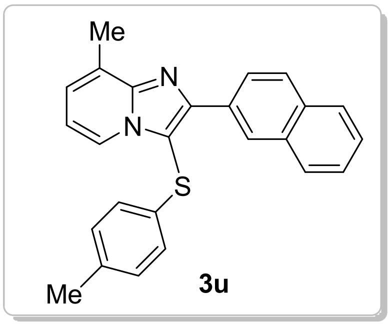
2-(Naphthalen-2-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3s).[10] Eluent petroleum ether/ethyl acetate (5:1). 63 mg, 87% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.77

(s, 1H), 8.43 (d, 1H, *J* = 8.5 Hz), 8.33 (d, 1H, *J* = 7.0 Hz), 7.90 (d, 2H, *J* = 8.0 Hz), 7.85 (d, 1H, *J* = 5.5 Hz), 7.78 (d, 1H, *J* = 8.5 Hz), 7.48 (d, 2H, *J* = 5.5 Hz), 7.34 (t, 1H, *J* = 7.5 Hz), 7.03 (d, 2H, *J* = 8.5 Hz), 6.98 (d, 2H, *J* = 8.5 Hz), 6.87 (t, 1H, *J* = 8.0 Hz), 2.26 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 149.8, 145.9, 135.1, 132.3, 132.2, 130.4, 129.8, 129.2, 127.6, 126.9, 126.8, 126.6, 125.7, 125.3, 125.1, 125.0, 124.9, 123.5, 116.5, 112.0, 106.4, 19.8. HRMS calc. for $C_{24}H_{19}N_2S$ (M+H)$^+$ 367.1263; found 367.1265.



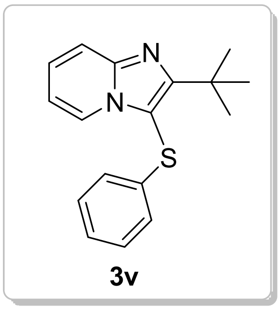
3t

3-(4-Bromophenylthio)-2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (3t). Eluent petroleum ether/ethyl acetate (5:1). 72 mg, 84% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.59 (s, 1H), 8.25 (d, 1H, *J* = 8.5 Hz), 8.15 (d, 1H, *J* = 7.0 Hz), 7.79 (d, 2H, *J* = 8.0 Hz), 7.72 (d, 1H, *J* = 5.5 Hz), 7.68 (d, 1H, *J* = 8.5 Hz), 7.37 (d, 2H, *J* = 5.5 Hz), 7.23-7.20 (m, 3H), 6.80-6.76 (m, 3H), 7.03 (d, 2H, *J* = 8.5 Hz), 6.98 (d, 2H, *J* = 8.5 Hz), 6.87 (t, 1H, *J* = 8.0 Hz), 2.26 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 150.4, 146.2, 133.4, 132.3, 132.2, 131.4, 129.5, 127.6, 127.0, 126.8, 126.6, 126.2, 125.9, 125.4, 125.1, 124.7, 123.3, 118.9, 116.7, 112.3, 104.9. HRMS calc. for $C_{23}H_{16}BrN_2S$ (M+H)$^+$ 431.0212; found 431.0216, 433.0203.



3u

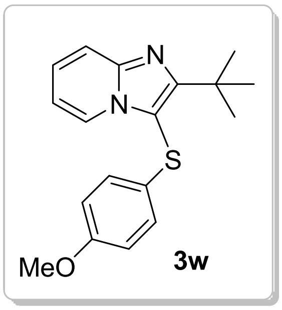
8-Methyl-2-(naphthalen-2-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3u). Eluent petroleum ether/ethyl acetate (4:1). 67 mg, 89% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.13-8.10 (m, 4H), 7.54 (s, 1H), 7.42-7.39 (m, 5H), 7.33 (t, 1H, J = 7.5 Hz), 7.07 (t, 3H, J = 8.0 Hz), 7.01-6.98 (m, 4H), 6.83 (d, 1H, J = 9.5 Hz), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 153.6, 152.3, 151.7, 151.2, 136.4, 136.2, 133.6, 132.1, 130.3, 130.2, 128.5, 128.4, 128.1, 127.5, 127.4, 126.2, 126.1, 123.9, 118.1, 112.9, 108.6, 108.4, 20.94, 34.1, 20.93. HRMS calc. for $C_{25}H_{21}N_2S$ $(M+H)^+$ 381.1420; found 381.1430.



3v

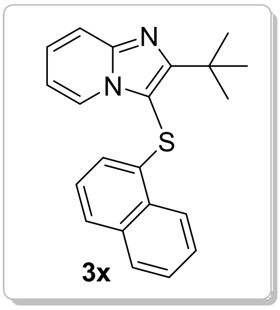
2-*tert*-Butyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3v).[7] Eluent petroleum ether/ethyl acetate (2:1). 40 mg, 71% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.14 (d, 1H, J = 7.0 Hz), 7.68 (s, 1H, J = 9.0 Hz), 7.28-7.24 (m, 1H), 7.18 (t, 2H, J = 7.5 Hz), 7.09 (t, 1H, J = 7.5 Hz), 6.85 (d, 2H, J = 8.5 Hz), 6.79 (t, 1H, J = 7.0 Hz), 1.54 (s, 9H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 152.4, 145.8, 135.9, 129.3, 125.8, 125.5, 125.5, 124.9, 123.8, 117.4, 112.7, 104.7, 30.5. HRMS calc. for $C_{17}H_{19}N_2S$ $(M+Na)^+$

282.1263; found 283.1268.



3w

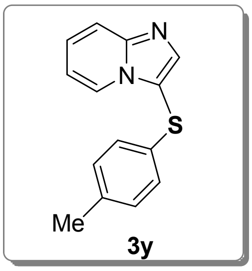
2-*tert*-Butyl-3-(4-methoxyphenylthio)imidazo[1,2-*a*]pyridine (3w). Eluent petroleum ether/ethyl acetate (2:1). 46 mg, 74% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.07 (d, 1H, J = 7.0 Hz), 7.59 (d, 1H, J = 9.0 Hz), 6.75-6.65 (m, 1H), 3.63 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 161.9, 158.2, 145.7, 126.9, 126.5, 125.9, 124.0, 117.4, 115.2, 112.8, 106.0, 55.5, 31.4, 30.7. HRMS calc. for $C_{18}H_{21}N_2OS$ (M+H)$^+$ 313.1369; found 313.1375.



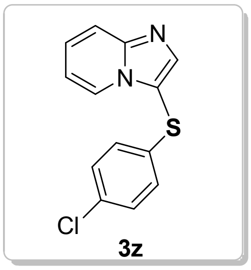
3x

2-*tert*-Butyl-3-(naphthalen-1-ylthio)imidazo[1,2-*a*]pyridine (3x). Eluent petroleum ether/ethyl acetate (2:1). 50 mg, 76% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.10 (d, 1H, J = 6.5 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.61 (d, 1H, J = 8.5 Hz), 7.47 (d, 1H, J = 7.5 Hz), 7.33-7.30 (m, 2H), 7.21 (t, 1H, J = 8.5 Hz), 7.10 (s, 1H), 6.98 (d, 1H, J = 8.5 Hz), 6.71 (t, 1H, J = 6.5 Hz), 1.49 (s, 9H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 161.4, 144.7, 132.8, 132.3, 130.6, 128.0, 126.7, 125.9, 125.7, 125.0, 124.5, 122.9, 122.3, 121.6, 116.3, 111.9, 103.6, 33.0, 29.5. HRMS calc. for $C_{21}H_{21}N_2S$ (M+H)$^+$ 333.1420;

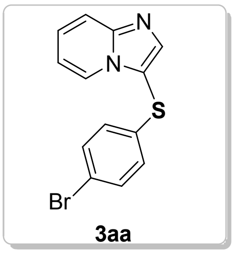
found 333.1421.


3y

3-(*p*-Tolylthio)imidazo[1,2-*a*]pyridine (3y). Eluent petroleum ether/ethyl acetate (3:1). 39 mg, 82% yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ 7.99 (d, 1H, J = 6.8 Hz), 7.94 (d, 2H, J = 8.4 Hz), 7.77 (s, 1H), 7.45-7.41 (m, 3H), 7.30 (t, 1H, J = 7.2 Hz), 6.61 (d, 1H, J = 6.8 Hz), 2.40 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) δ 146.0, 145.2, 136.0, 133.6, 128.7, 127.9, 126.0, 124.8, 115.8, 115.3, 107.6, 21.4. HRMS calc. for $C_{14}H_{13}N_2S$ (M+H)$^+$ 241.0794; found 241.0787.

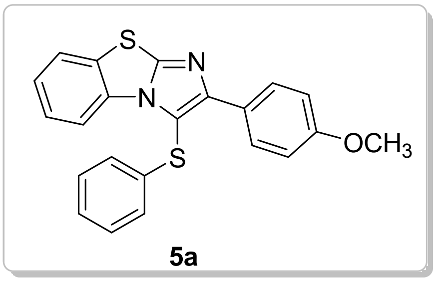

3z

3-(4-Chlorophenylthio)imidazo[1,2-*a*]pyridine (3y).[11] Eluent petroleum ether/ethyl acetate (4:1). 36 mg, 69% yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ 8.17 (d, 1H, J = 6.8 Hz), 7.99 (s, 1H), 7.72 (d, 1H, J = 9.2 Hz), 7.32 (t, 1H, J = 7.2 Hz), 7.17 (d, 2H, J = 6.8 Hz), 6.94-6.88 (m, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) δ 148.2, 142.6, 133.7, 132.2, 129.4, 127.5, 126.2, 124.1, 118.3, 113.4, 110.2. HRMS calc. for $C_{13}H_{10}ClN_2S$ (M+H)$^+$ 261.0248; found 261.0241.



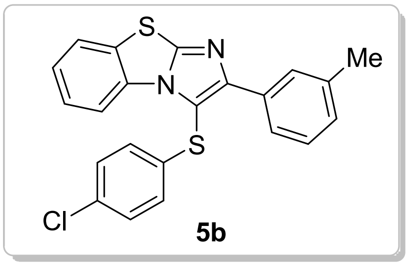
3aa

3-(4-Bromophenylthio)imidazo[1,2-*a*]pyridine (3aa). Eluent petroleum ether/ethyl acetate (3:1). 43 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.16 (d, 1H, J = 6.8 Hz), 7.99 (s, 1H), 7.72 (d, 1H, J = 9.2 Hz), 7.34-7.28 (m, 3H), 6.91-6.83 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 148.2, 142.6, 134.5, 132.3, 127.7, 126.2, 124.1, 120.0, 118.3, 113.4, 110.0. HRMS calc. for $C_{13}H_{10}BrN_2S$ $(M+H)^+$ 304.9743; found 304.9736, 306.9727.



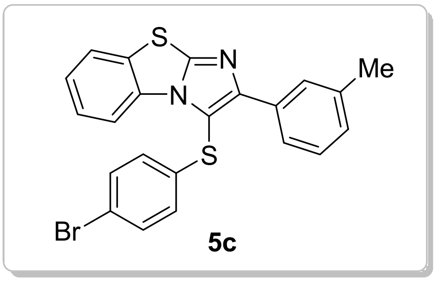
5a

2-(4-**Methoxybenzene)-3-(phenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5a)**. Eluent petroleum ether/ethyl acetate (15:1). 60 mg, 77% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.31 (d, 1H, J = 6.5 Hz), 8.23 (d, 2H, J = 6.5 Hz), 7.71 (d, 1H, J = 9.0 Hz), 7.45 (t, 2H, J = 7.0 Hz), 7.38 (dd, 1H, J = 7.5 Hz), 7.31 (t, 1H, J = 7.5 Hz), 6.90 (d, 2H, J = 9.0 Hz), 6.88 (t, 1H, J = 6.5 Hz), 6.75 (d, 2H, J = 9.0 Hz), 3.71 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ157.5, 149.7, 145.8, 132.3, 128.8, 127.9, 127.8, 127.5, 127.4, 127.0, 125.6, 124.4, 123.5, 116.5, 116.4, 114.3, 114.1, 112.0, 106.9, 54.3. HRMS calc. for $C_{22}H_{17}N_2OS_2$ $(M+H)^+$ 389.0777; found 389.0786.



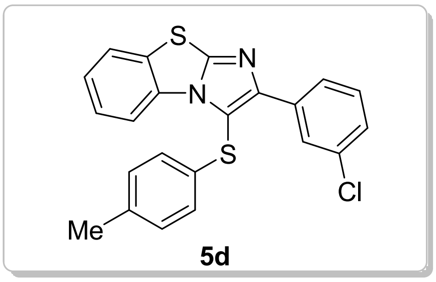
5b

2-(3-**Methylbenzene)-3-(4-chlorophenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5b)**. Eluent petroleum ether/ethyl acetate (15:1). 60 mg, 74% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.25 (d, 1H, J = 7.5 Hz), 8.05-8.00 (m, 3H), 7.45-7.37 (m, 4H), 7.09 (d, 2H, J = 8.0 Hz), 7.03 (d, 2H, J = 8.0 Hz), 2.13 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 150.94, 150.6, 136.5, 135.3, 133.6, 133.0, 132.2, 131.0, 130.8, 130.0, 128.5, 127.2, 127.1, 126.0, 125.9, 125.5, 114.2, 111.1, 20.8. HRMS calc. for $C_{22}H_{16}ClN_2S_2$ (M+H)$^+$ 407.0438; found 407.0431.



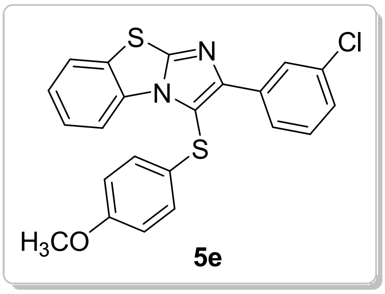
5c

2-(3-**Methylbenzene)-3-(4-bromophenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5c)**. Eluent petroleum ether/ethyl acetate (15:1). 63 mg, 70% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.38 (d, 1H, J = 7.5 Hz), 8.17 (s, 1H), 8.04 (d, 2H, J = 7.5 Hz), 7.70 (d, 1H, J = 7.5 Hz), 7.37-7.30 (m, 4H), 7.06 (m, 4H), 2.27 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 151.8, 150.9, 136.5, 135.2, 134.5, 133.5, 132.5, 130.6, 130.4, 129.8, 128.4, 128.0, 126.6, 126.2, 125.9, 125.3, 124.2, 114.7, 111.6, 21.1. HRMS calc. for $C_{22}H_{16}BrN_2S_2$ (M+H)$^+$ 450.9933; found 450.9936, 452.9924.



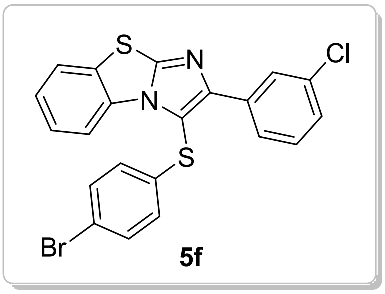
5d

2-(3-Chlorobenzene)-3-(4-methylphenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5d). Eluent petroleum ether/ethyl acetate (15:1). 59 mg, 73% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.25 (d, 1H, J = 8.0 Hz), 8.06-8.01 (m, 3H), 7.46-7.39 (m, 4H), 7.09 (d, 2H, J = 8.0 Hz), 7.05 (d, 2H, J = 8.0 Hz), 2.17 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 150.5, 150.1, 136.0, 134.9, 133.2, 132.5, 131.7, 130.5, 130.3, 129.6, 128.0, 126.7, 126.6, 125.6, 125.5, 125.4, 125.1, 113.7, 110.6, 20.4. HRMS calc. for $C_{22}H_{16}ClN_2S_2$ (M+H)$^+$ 407.0438; found 407.0431.



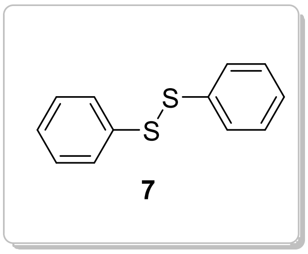
5e

2-(3-Chlorobenzene)-3-(4-methylphenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5e). Eluent petroleum ether/ethyl acetate (20:1). 71 mg, 80% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.35 (d, 1H, J = 7.5 Hz), 8.12 (s, 1H), 8.08 (d, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.0 Hz), 7.49-7.41 (m, 4H), 7.14 (d, 2H, J = 7.0 Hz), 6.88 (d, 2H, J = 7.0 Hz), 3.66 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 158.3, 150.3, 149.8, 134.9, 133.2, 132.6, 130.4, 129.6, 128.0, 127.9, 127.7, 126.7, 125.6, 125.4, 125.1, 115.6, 113.8, 111.7, 55.1. HRMS calc. for $C_{22}H_{16}ClN_2OS_2$ (M+H)$^+$ 443.0387; found 443.0389.



5f

2-(3-**Chlorobenzene)-3-(4-bromophenylthio)benzo[*d*]imidazo[2,1-*b*]thiazole (5f)**. Eluent petroleum ether/ethyl acetate (20:1). 58 mg, 62% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 8.24 (d, 1H, J = 8.0 Hz), 8.09 (d, 1H, J = 7.5 Hz), 8.04 (s, 1H), 8.00 (d, 1H, J = 7.5 Hz), 7.48-7.44 (m, 4H), 7.37 (d, 2H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.0 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm) δ 150.9, 150.6, 135.1, 134.7, 133.2, 132.7, 132.5, 130.5, 129.7, 128.2, 127.4, 126.9, 126.8, 125.6, 125.2, 119.5, 113.6, 109.4, 99.5. HRMS calc. for $C_{21}H_{13}BrClN_2S_2$ (M+H)$^+$ 470.9387; found 470.9395, 472.9381.



7

1,2-Diphenyldisulfane (7).[12] Eluent petroleum ether/ethyl acetate (400:1). 19 mg, 45% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 7.48 (d, 2H, J = 7.5 Hz), 7.28 (t, 2H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.0 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm) δ 137.1, 129.1, 127.6, 127.2. HRMS calc. for $C_{12}H_{11}S_2$ (M+H)$^+$ 219.0297; found 219.0302.

References

(1) H.-Y. Song, J.-Z. Liu, L.-P. Weng, L.-N. Ji. *Journal of Molecular Catalysis B: Enzymatic.,* 2009, **57**, 48-54.

(2) L. Zhang, S Lia, M Dong, Y. Jiang, R. Lia, S. Zhang, X. Lv, L. Chen, H. Wang, *Biosens. Bioelectron.,* 2017 , **87**, 1036-1043.

(3) Y. Wang, S. Li, L. Feng, C. Nie, L. Liu, F. Lv, S. Wang. *ACS Appl. Mater. Interfaces,* 2015, **7**, 24110-24118.

(4) J. Rafique, S. Saba, A. R. Rosário and A. L. Braga, *Chem. Eur.J.,* 2016, **22**, 11854–11862.

(5) X. Huang, S. Wang, B. Li, X. Wang, Z. Ge and R. Li, *RSC Adv.,* 2015, **5**, 22654–22657.

(6) C. Ravi, N. N. K. Reddy, V. Pappula, S. Samanta and S. Adimurthy, *J. Org. Chem.,* 2016, **81**, 9964–9972.

(7) C. Ravi, D. C. Mohan and S. Adimurthy, *Org. Lett.,* 2014, **16**, 2978–2981;

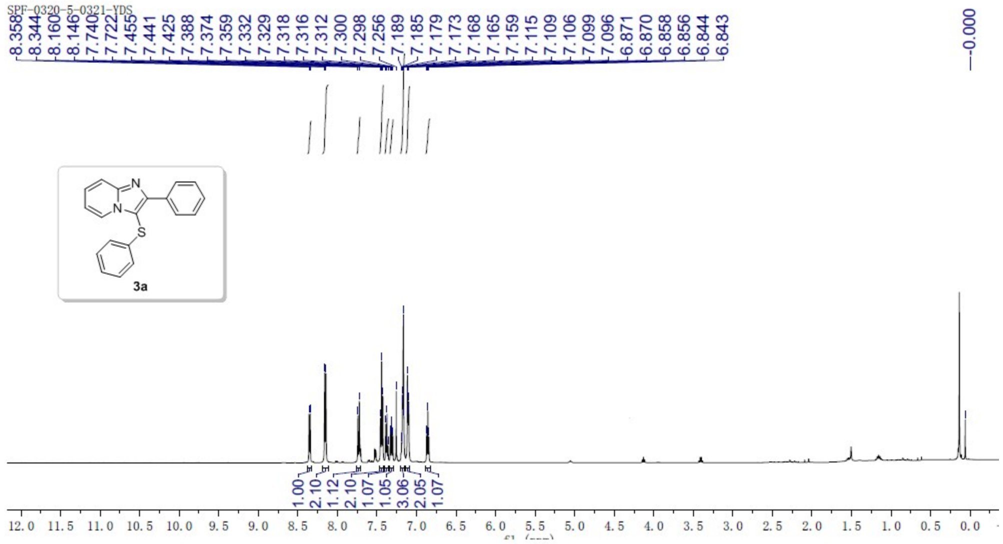
(8) C. Ravi, D. C. Mohan and S. Adimurthy, *Org. Biomol. Chem.,* 2016, **14**, 2282–2290;

(9) M. A. Hiebel and S. Berteina-Raboin, *Green Chem.,* 2015, **17**, 937–944;

(10) S. Kundu and B. Basu, *RSC Adv.,* 2015, **5**, 50178–50185.

(11) Z. Zheng, D. Qi and L. Shi, *Catal. Commun.,* 2015, **66**, 83–86.

(12) D. Yang, P. Sun, W. Wei, L. Meng, L. He and B. Fang*, Org. Chem. Front.,* 2016, **3**, 1457–1461;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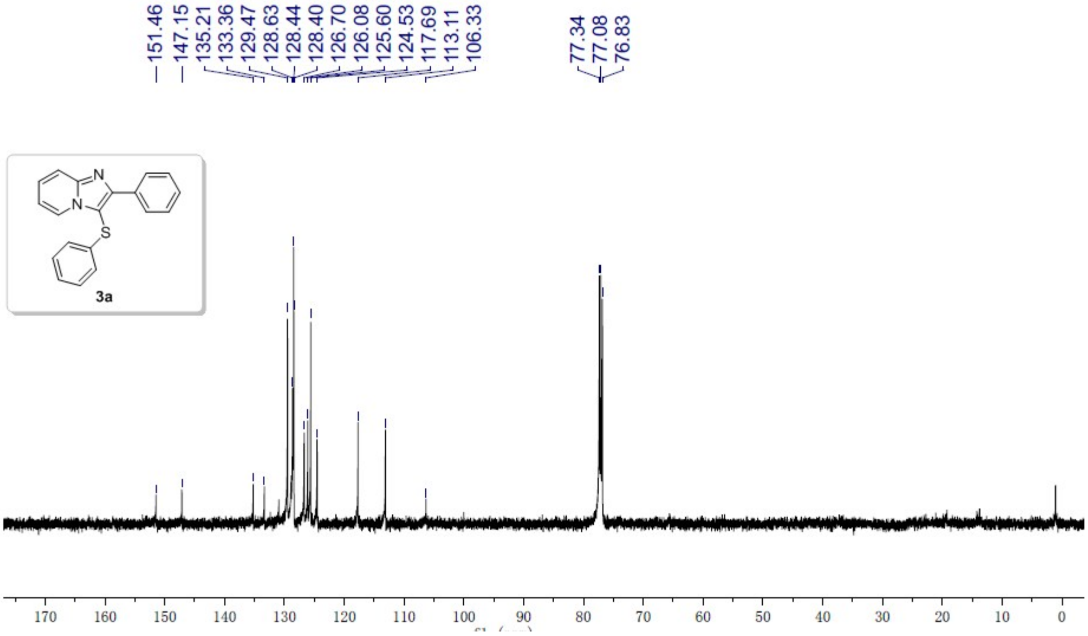
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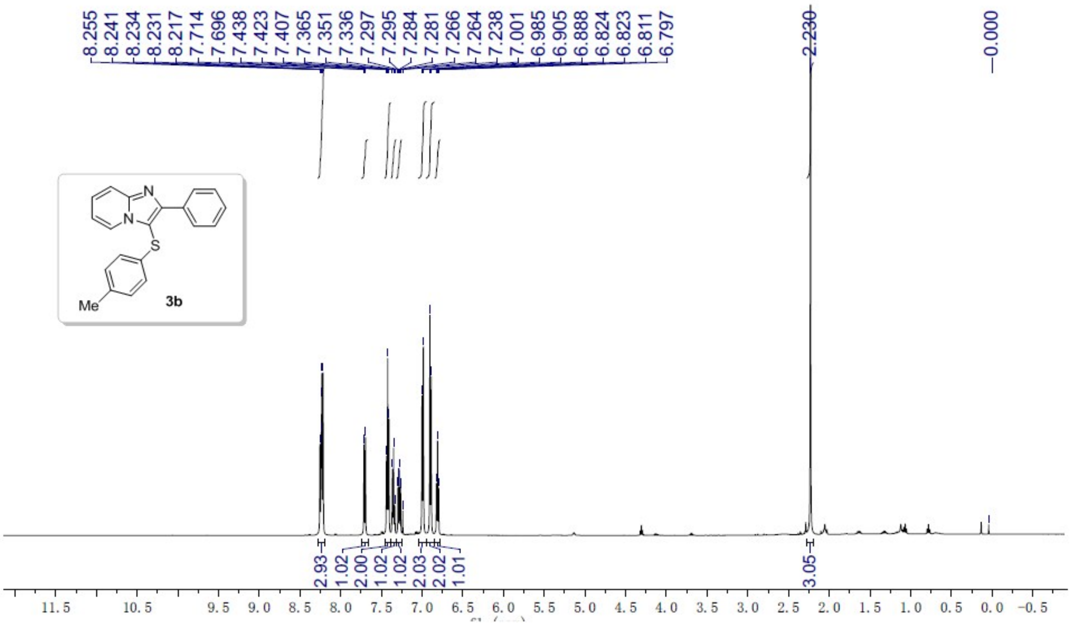
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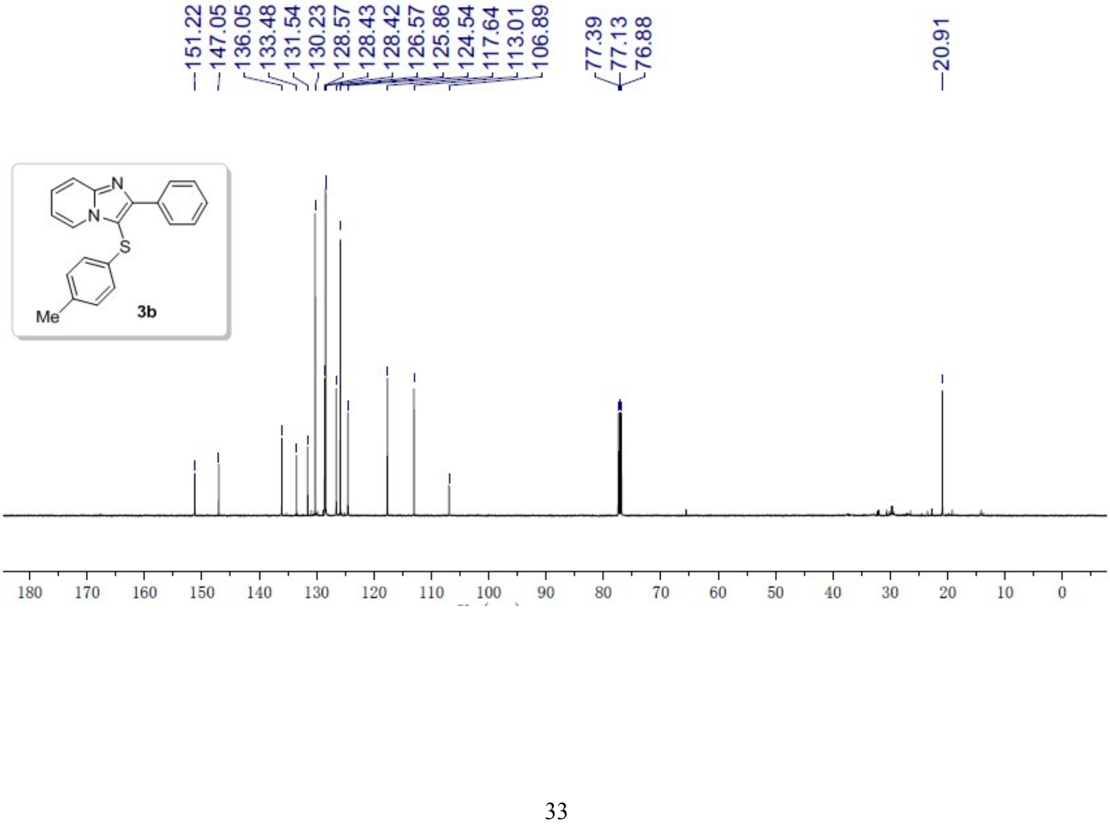
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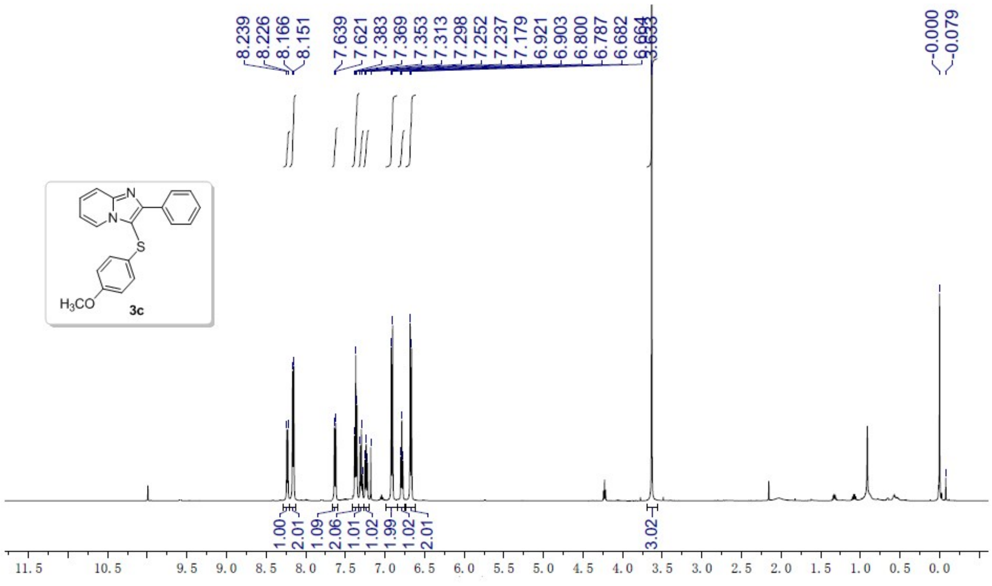
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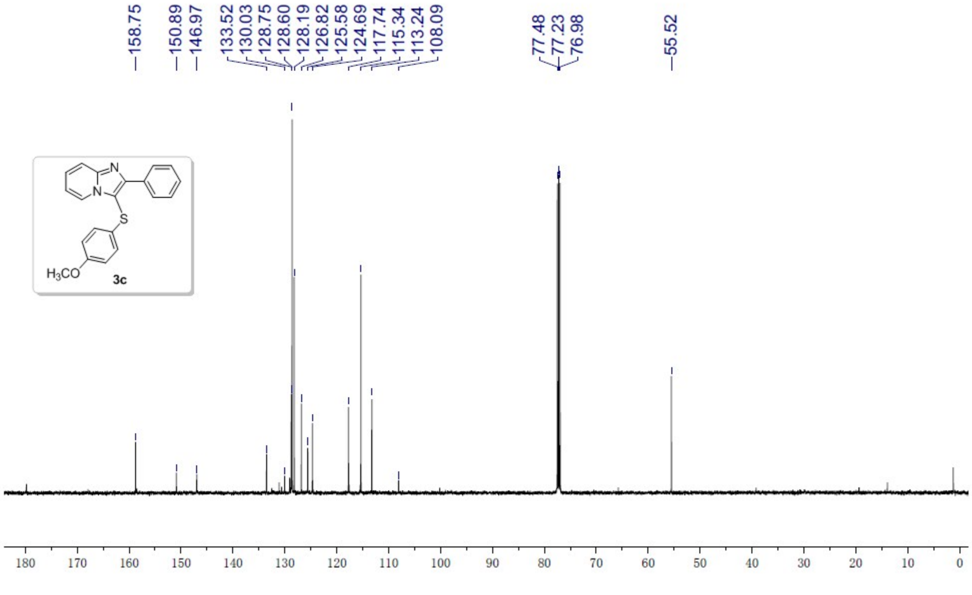
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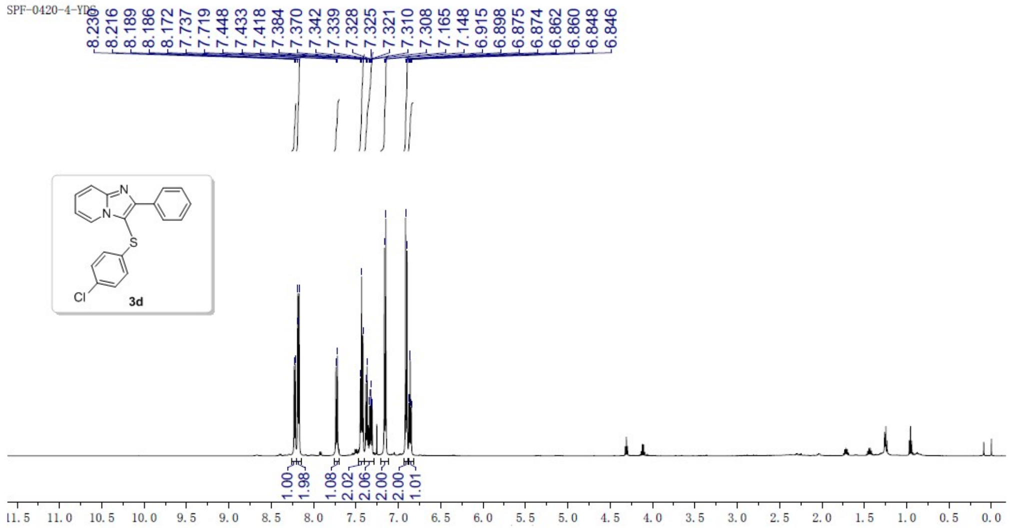
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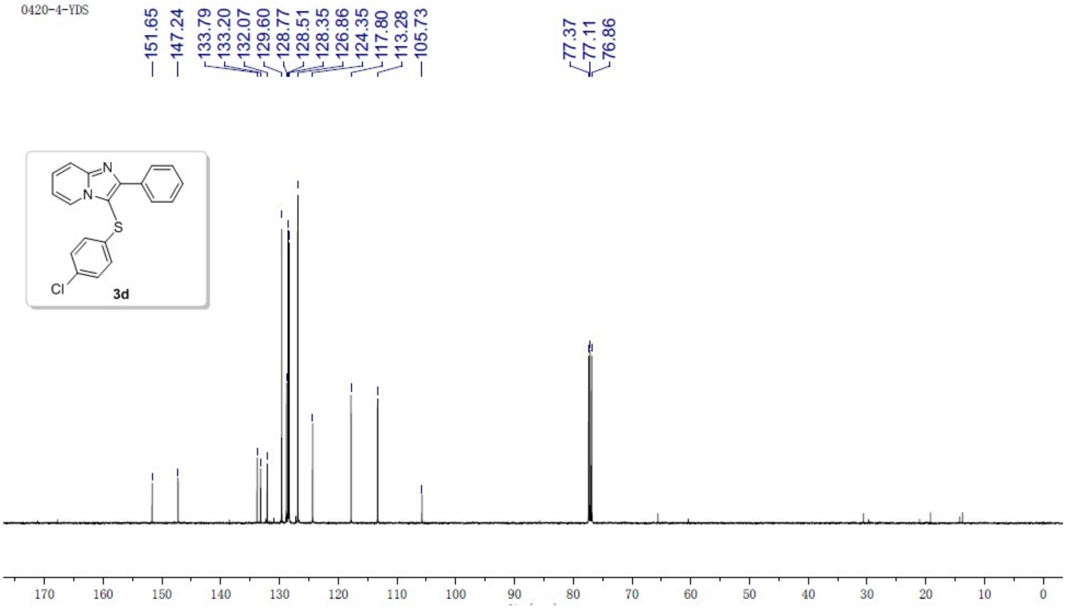
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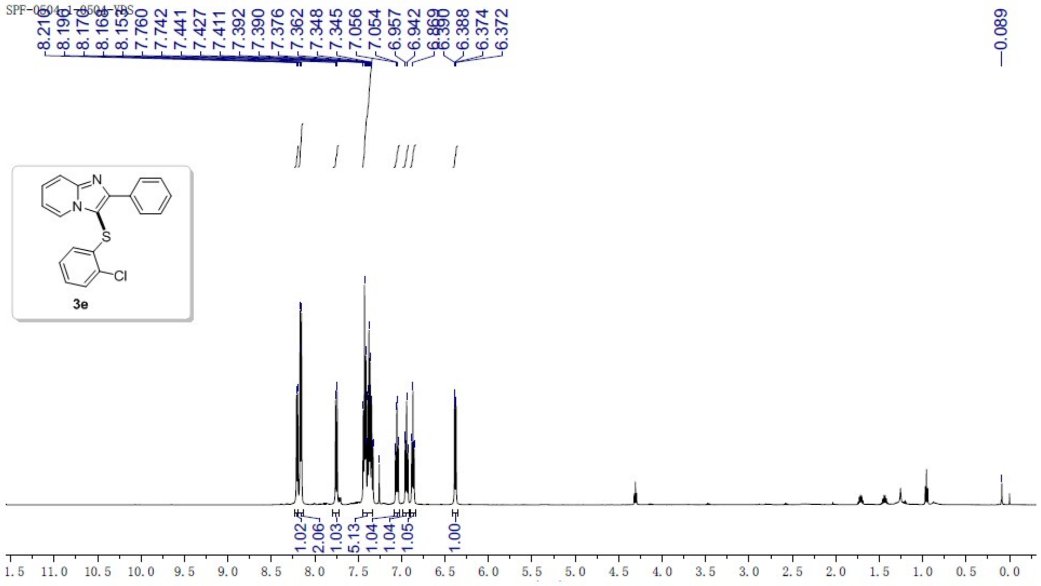
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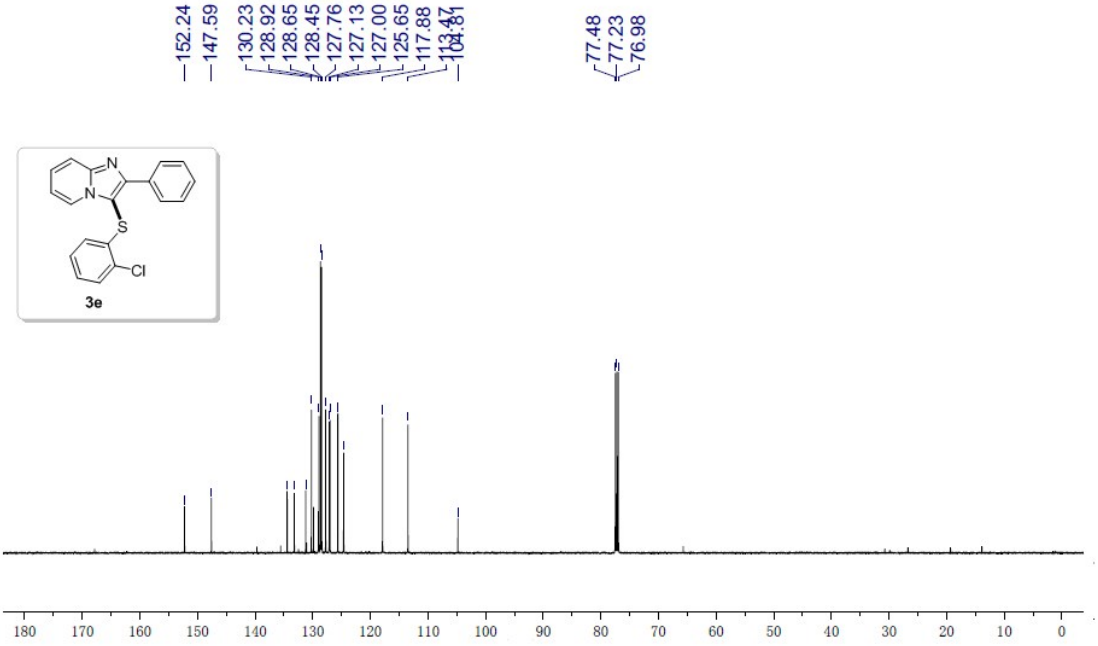
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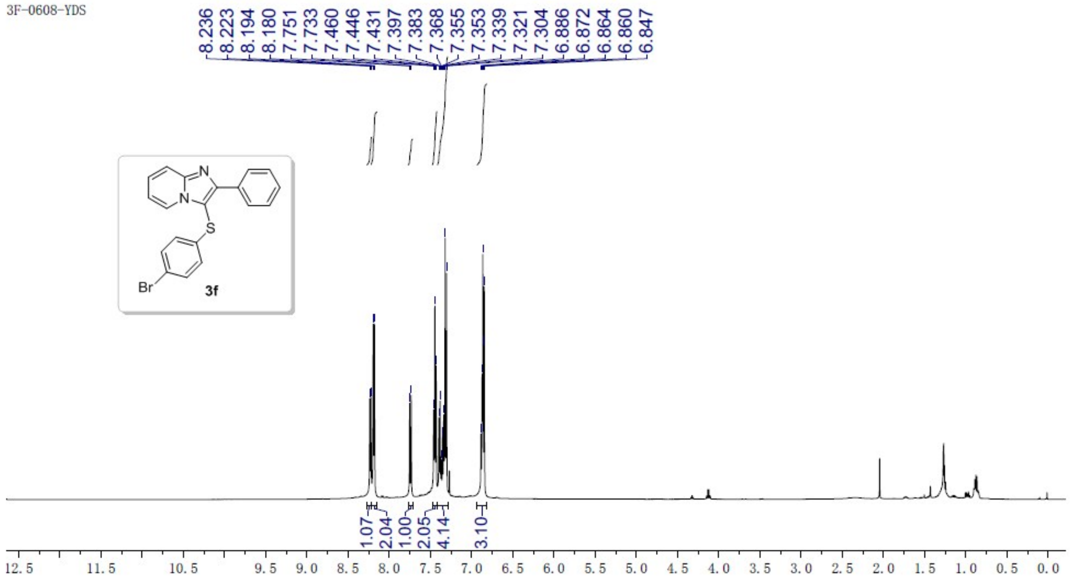
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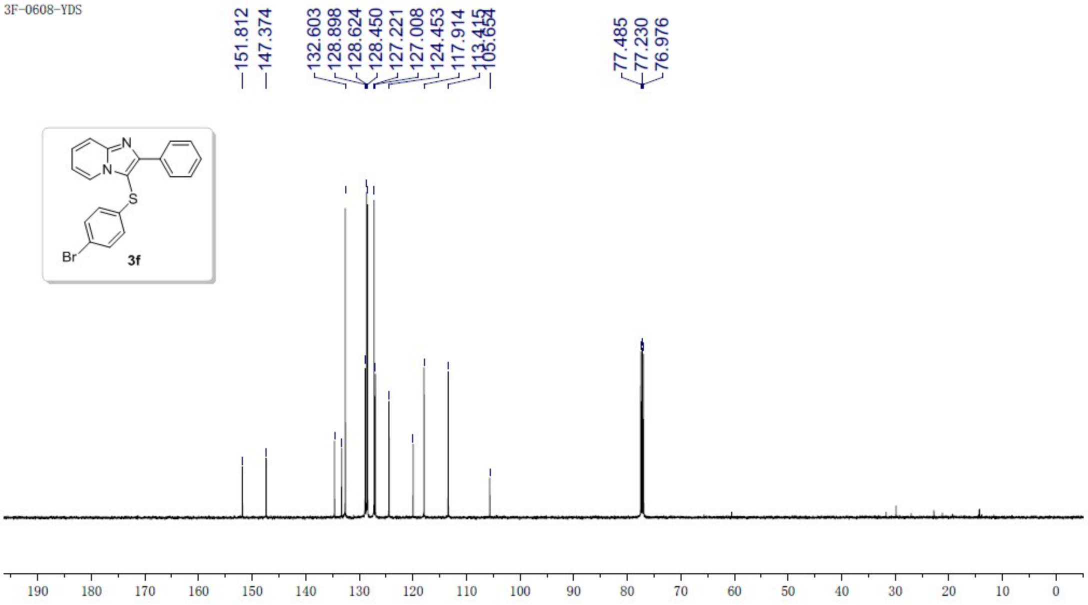
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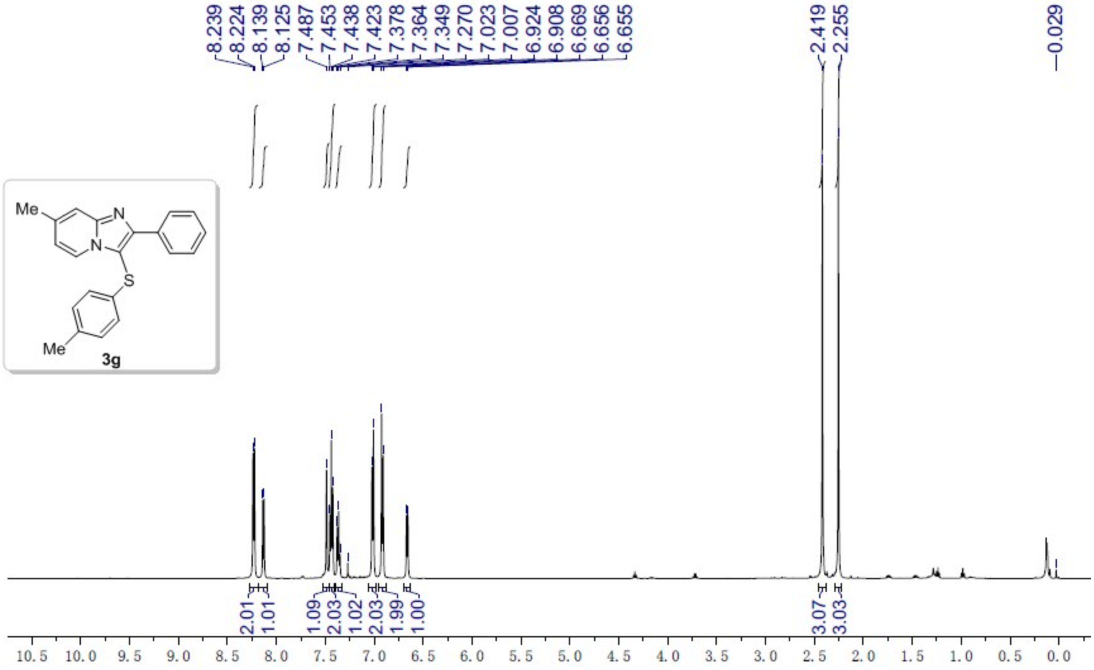
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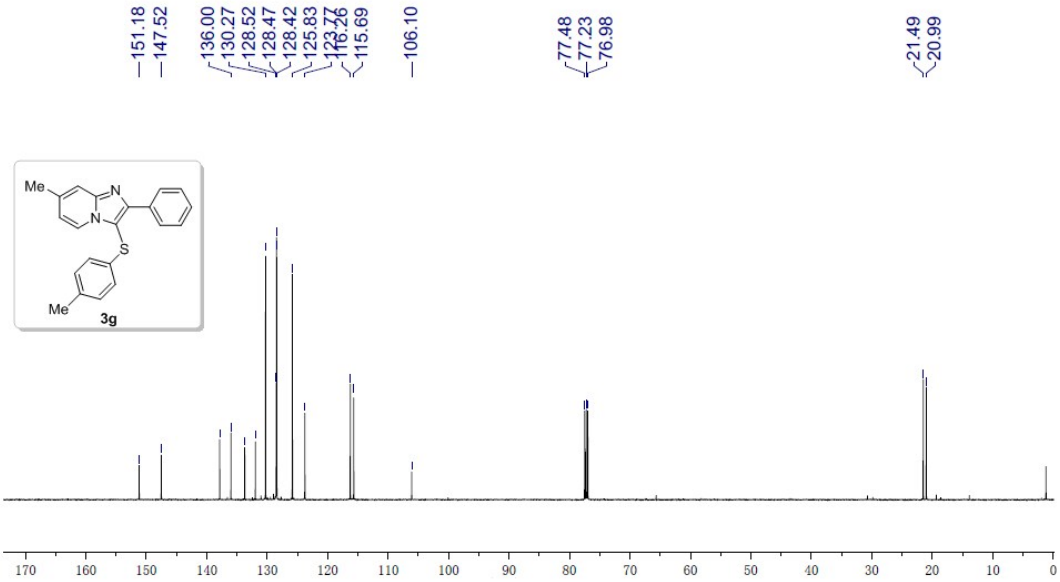
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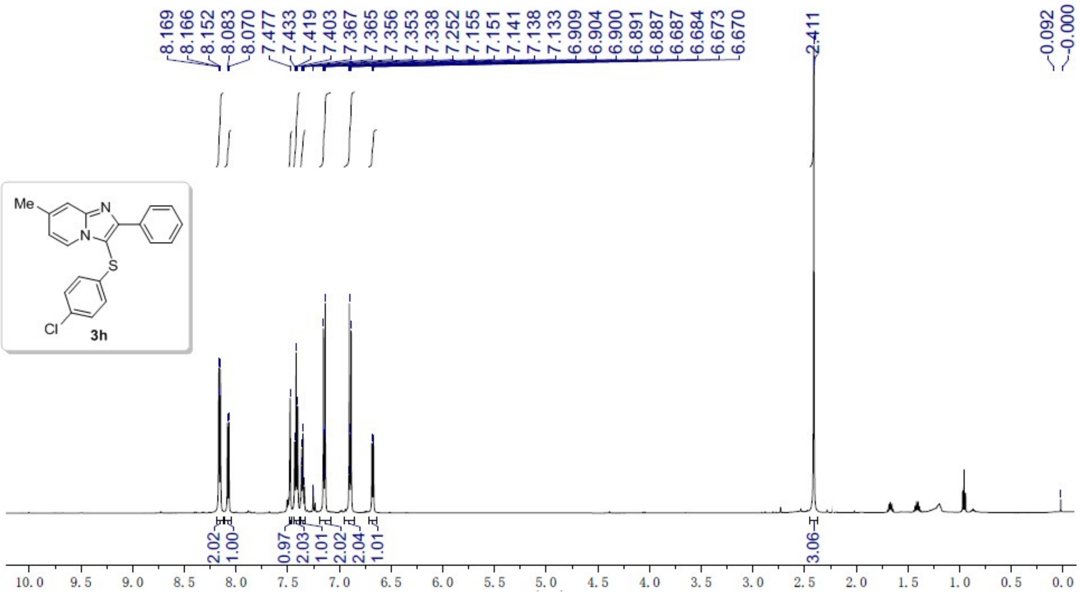
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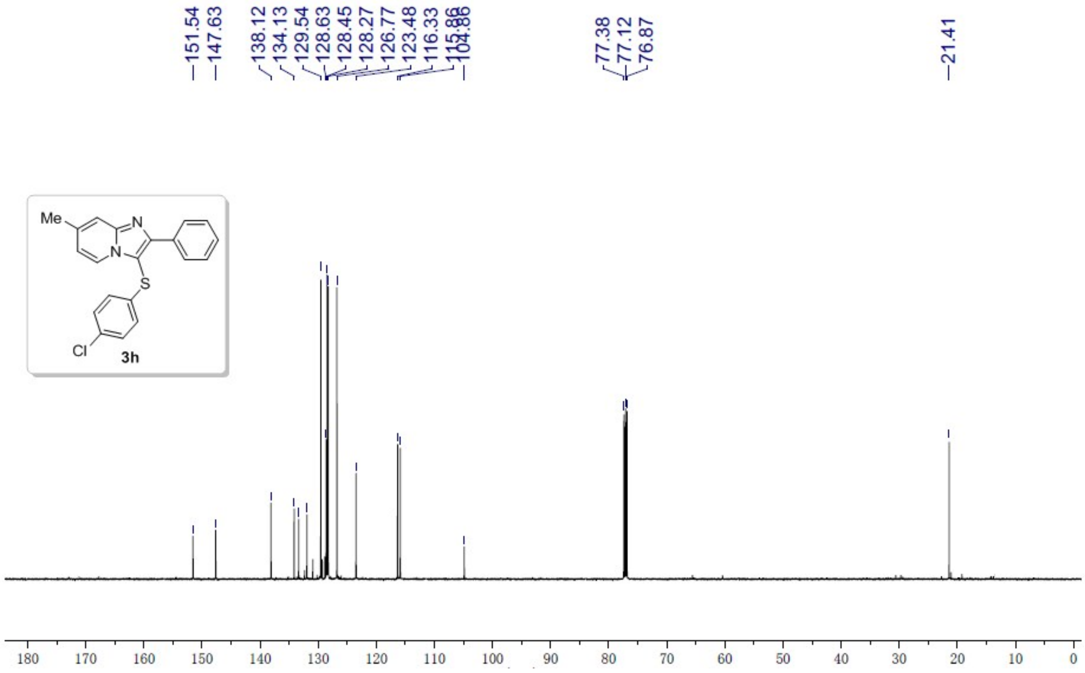
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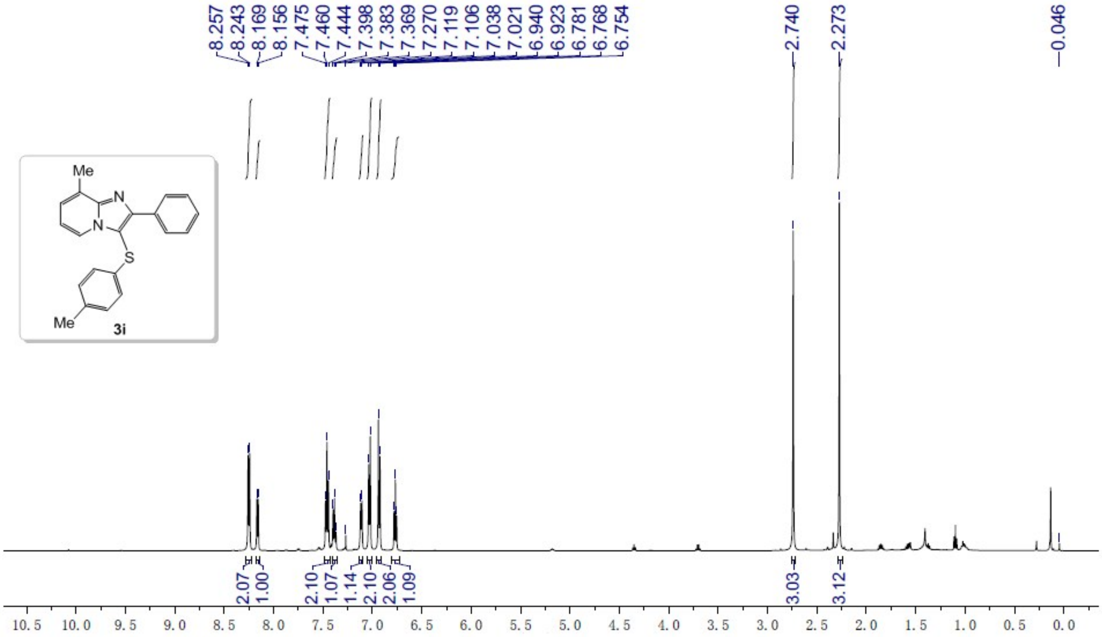
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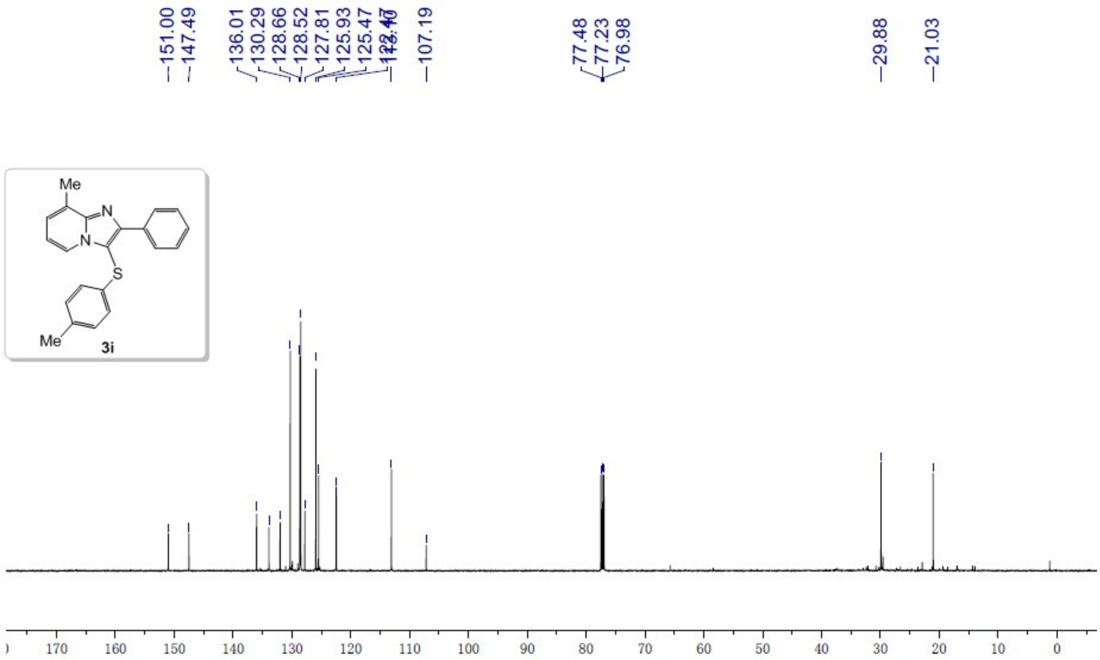
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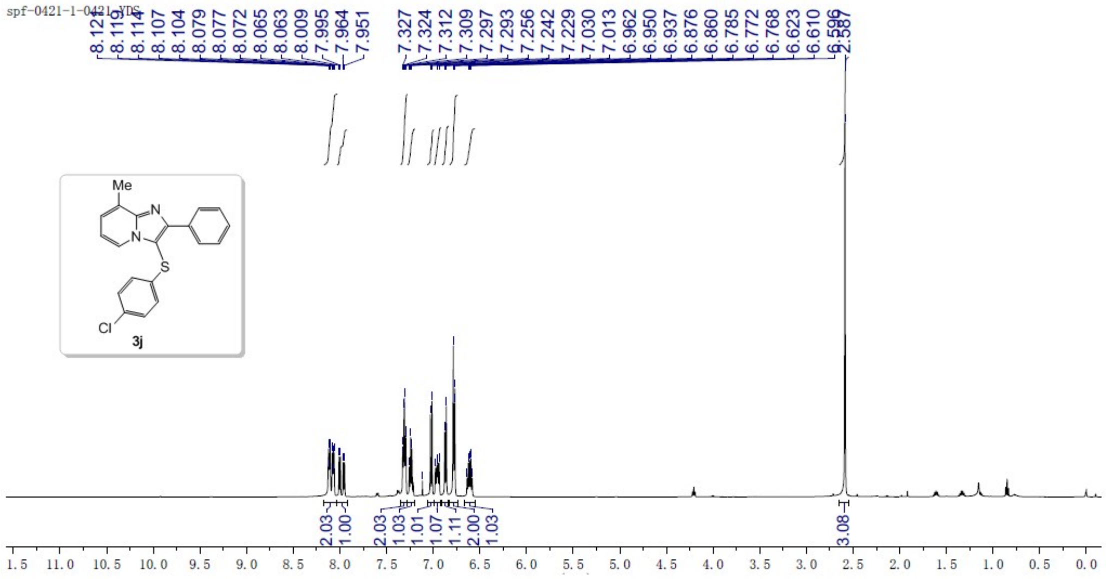
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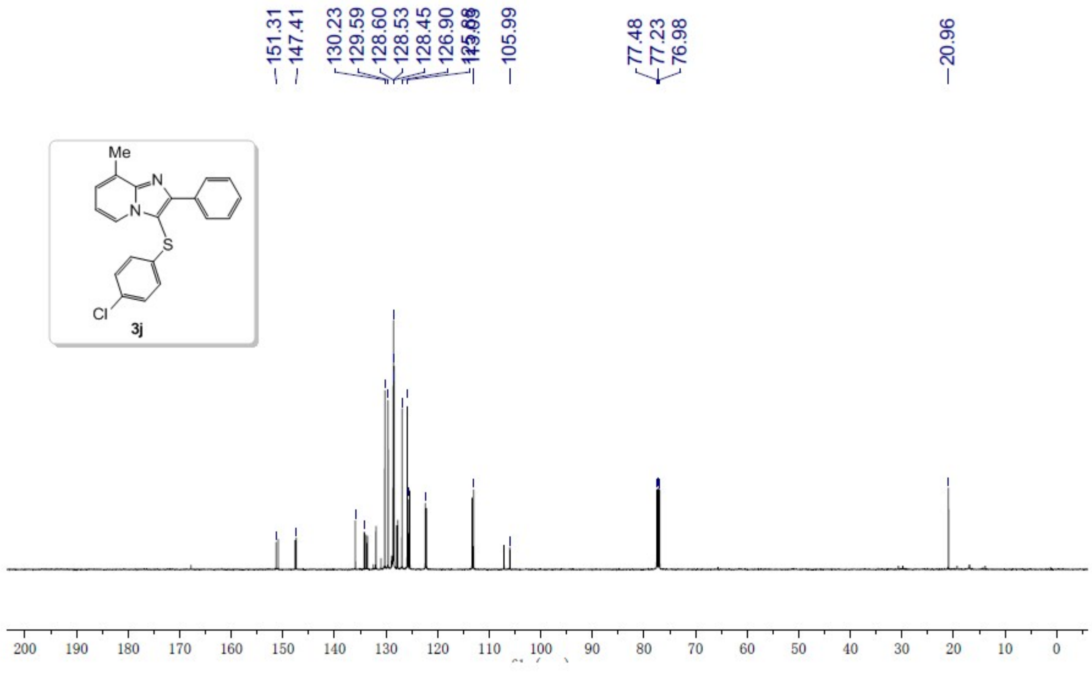
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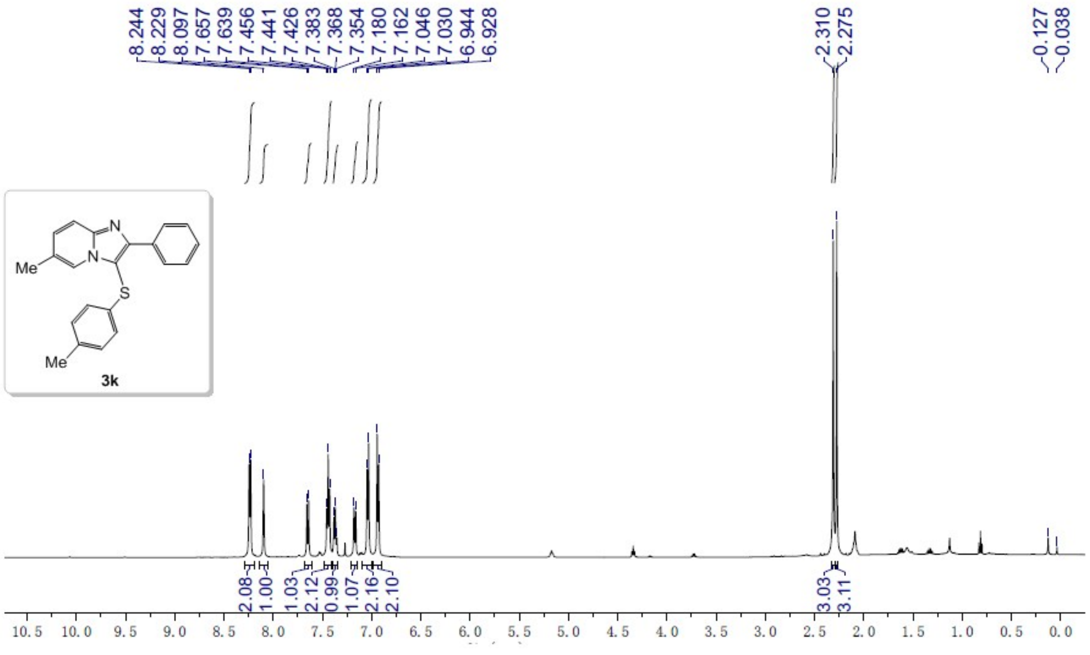
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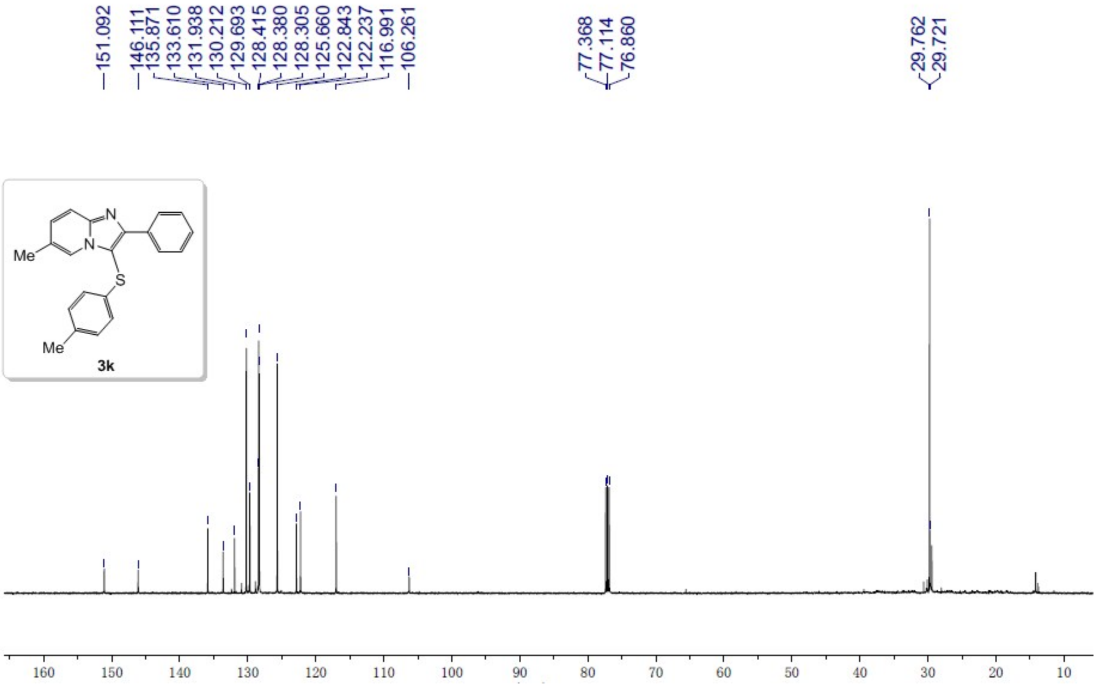
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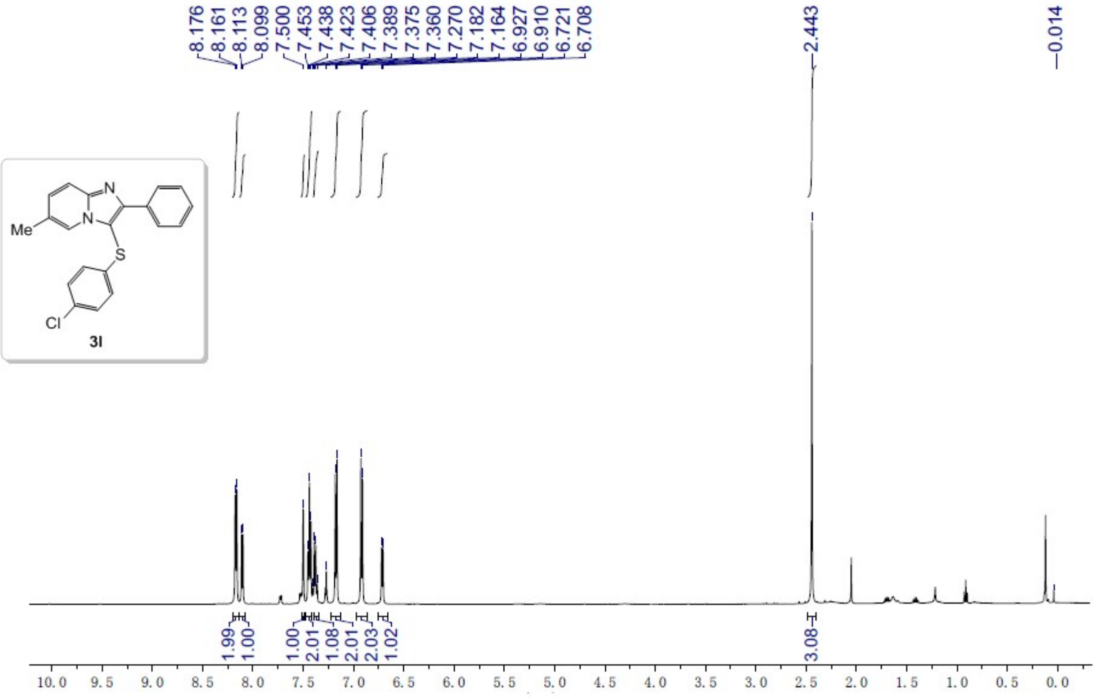
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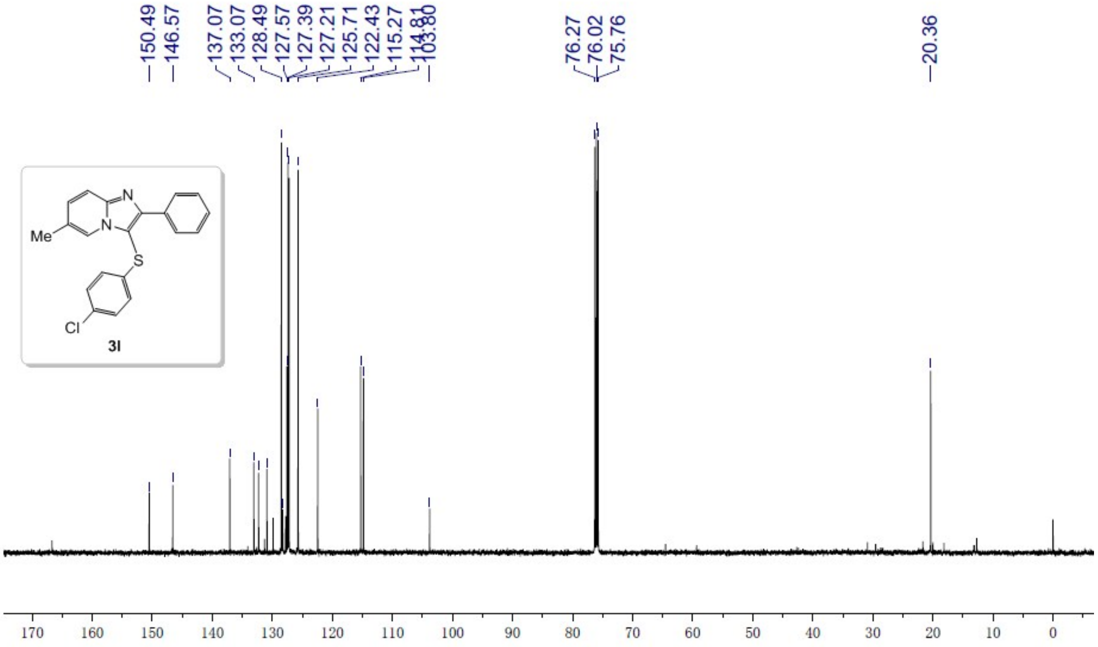
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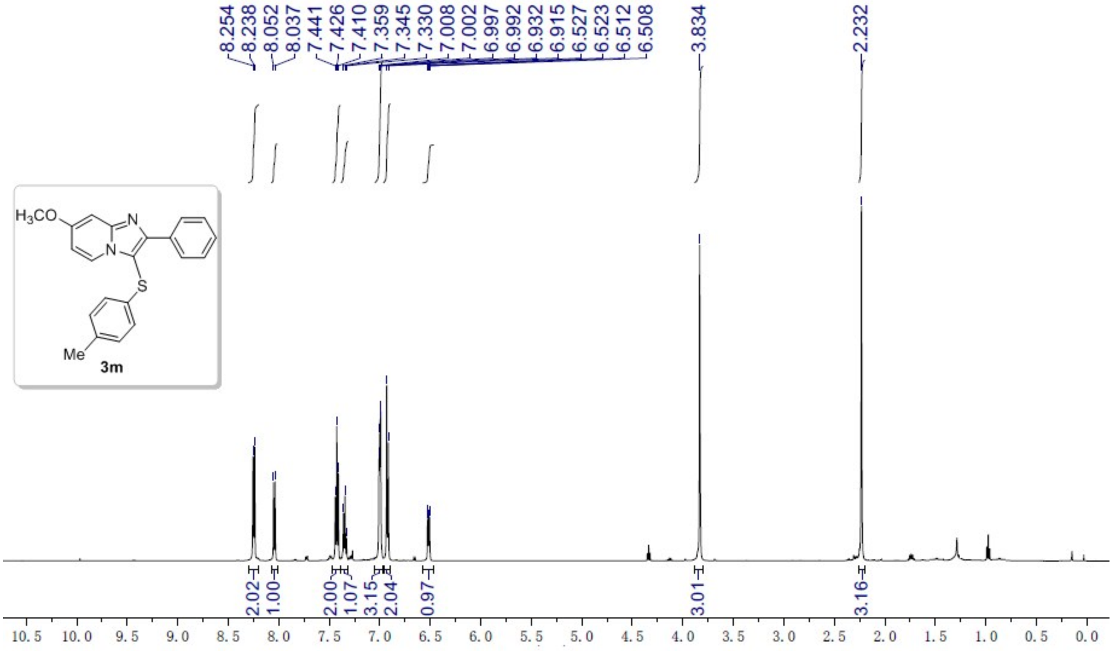
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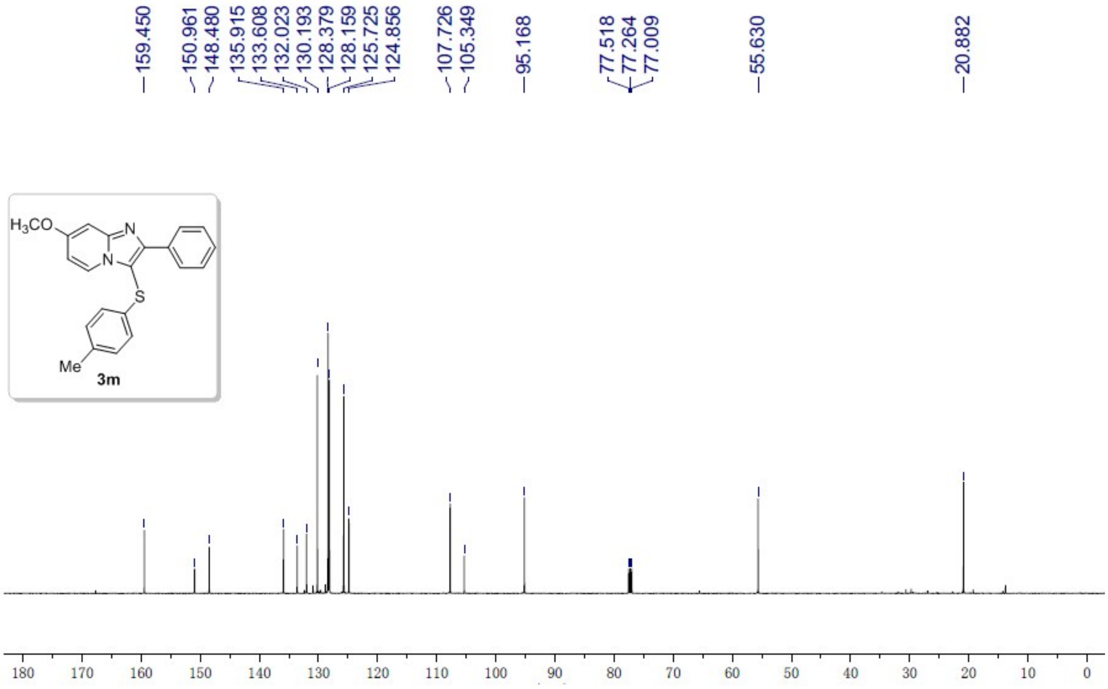
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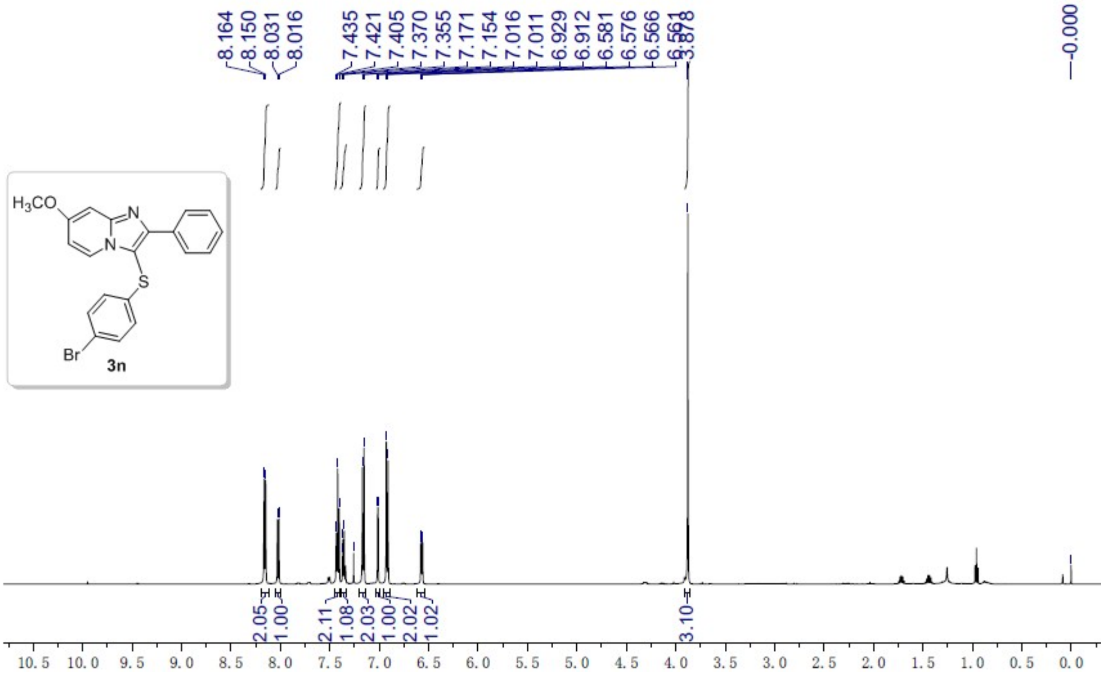
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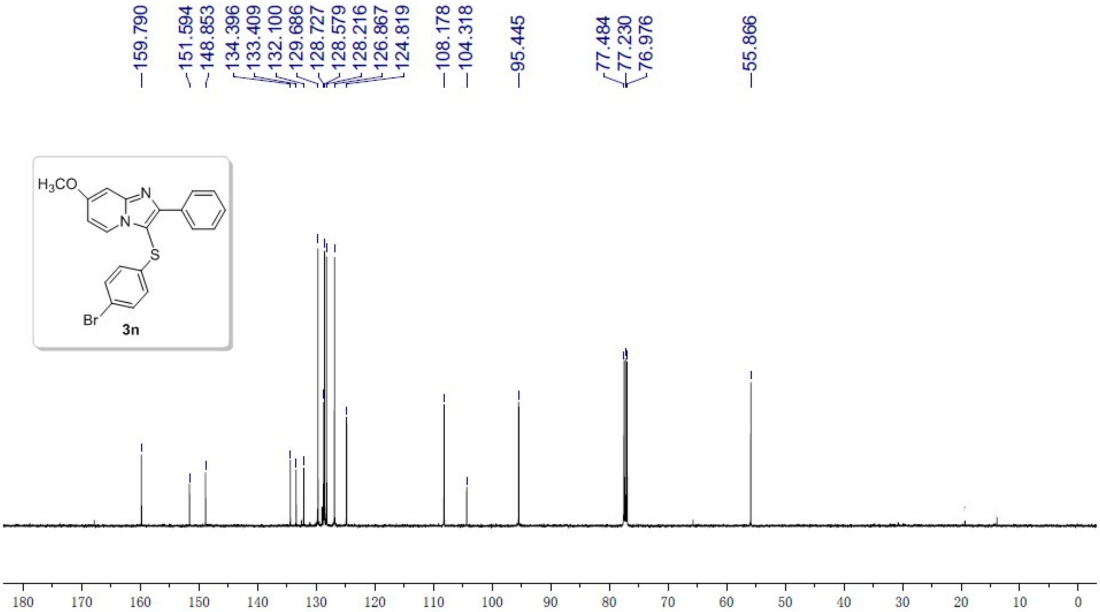
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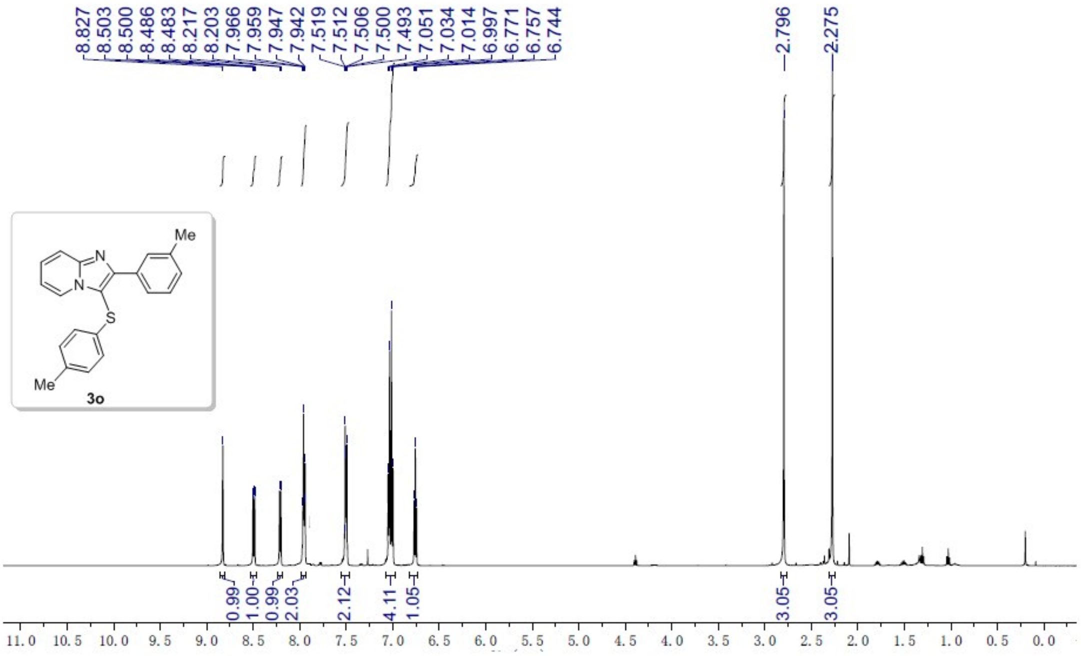
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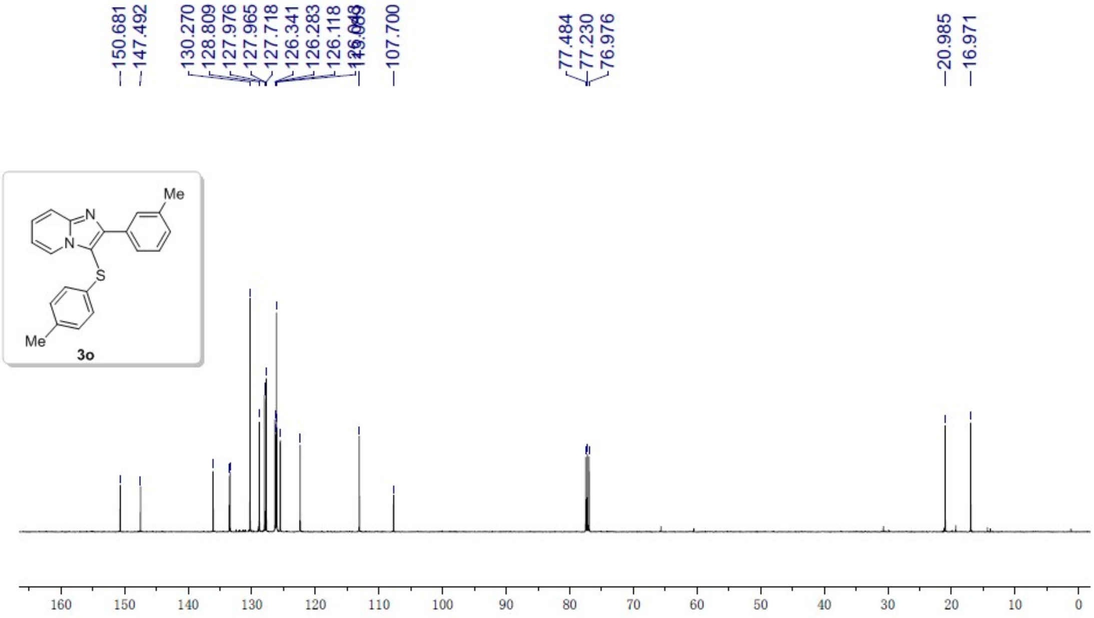
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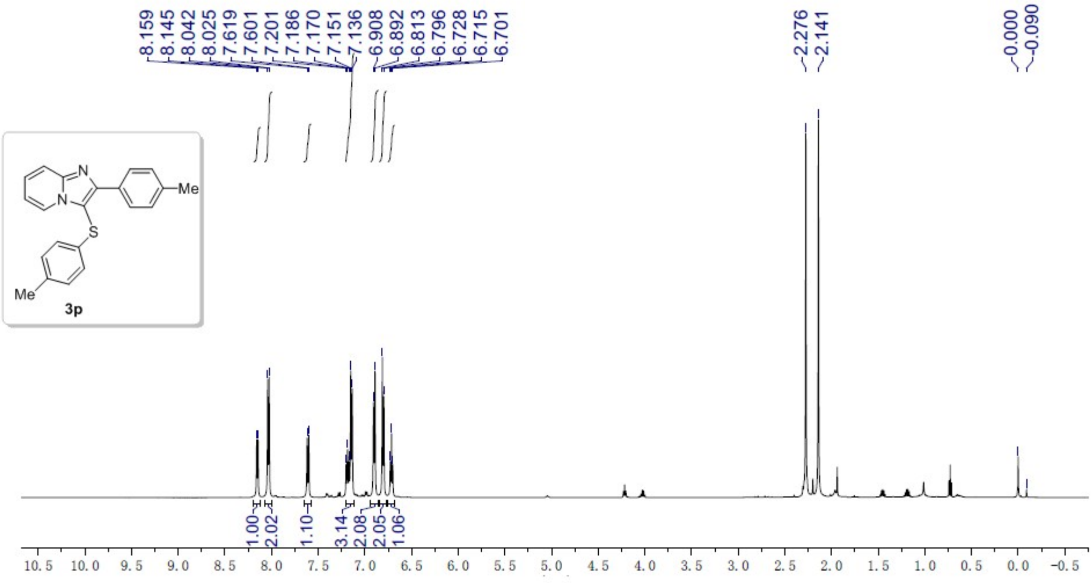
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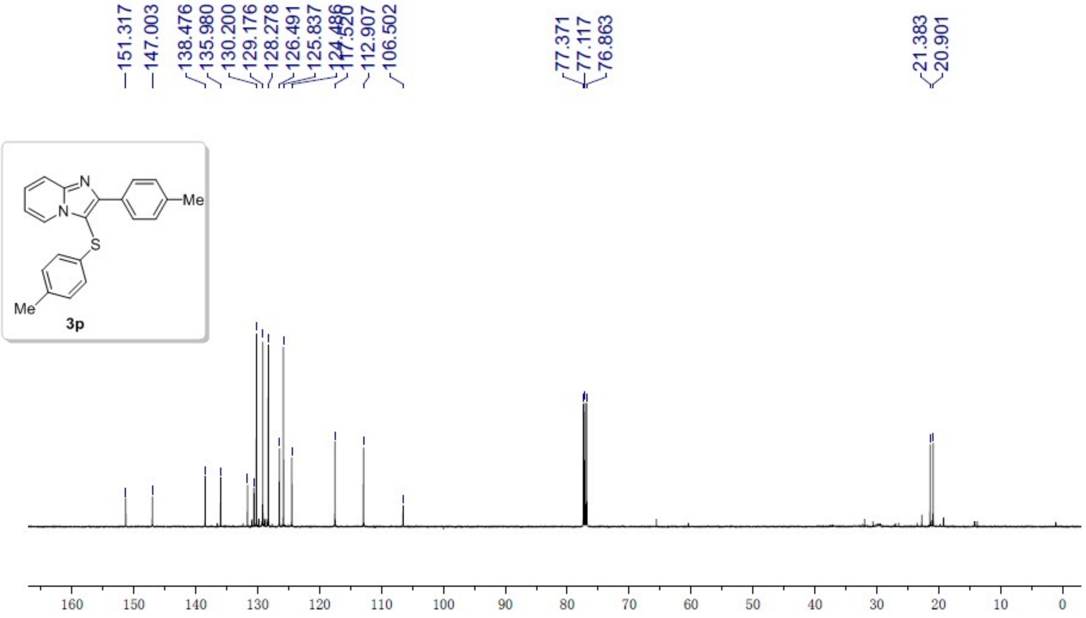
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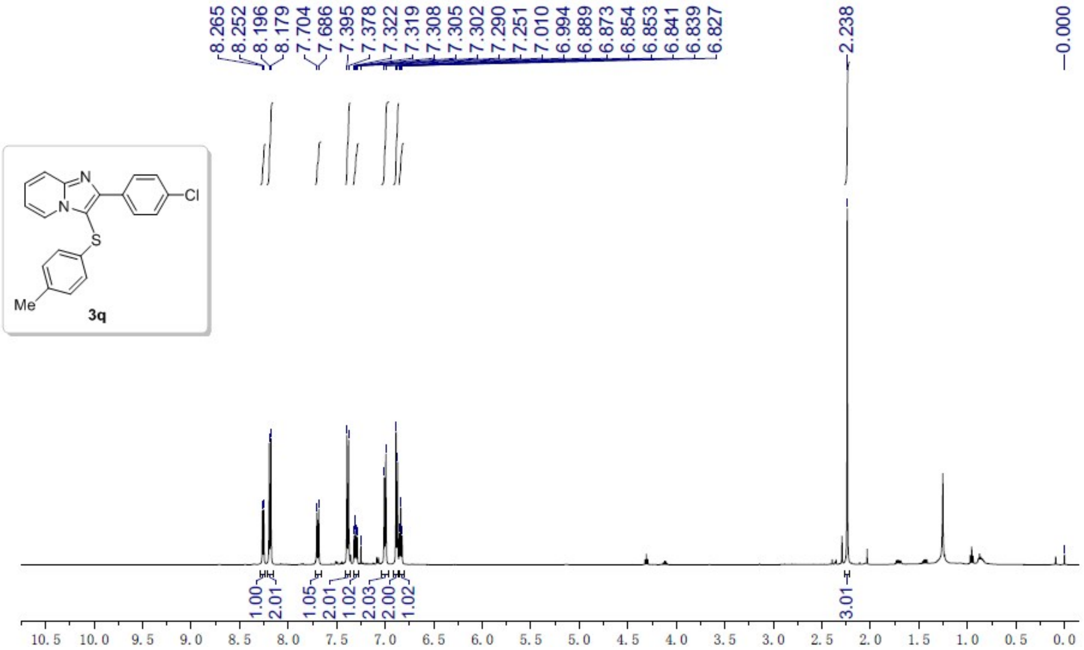
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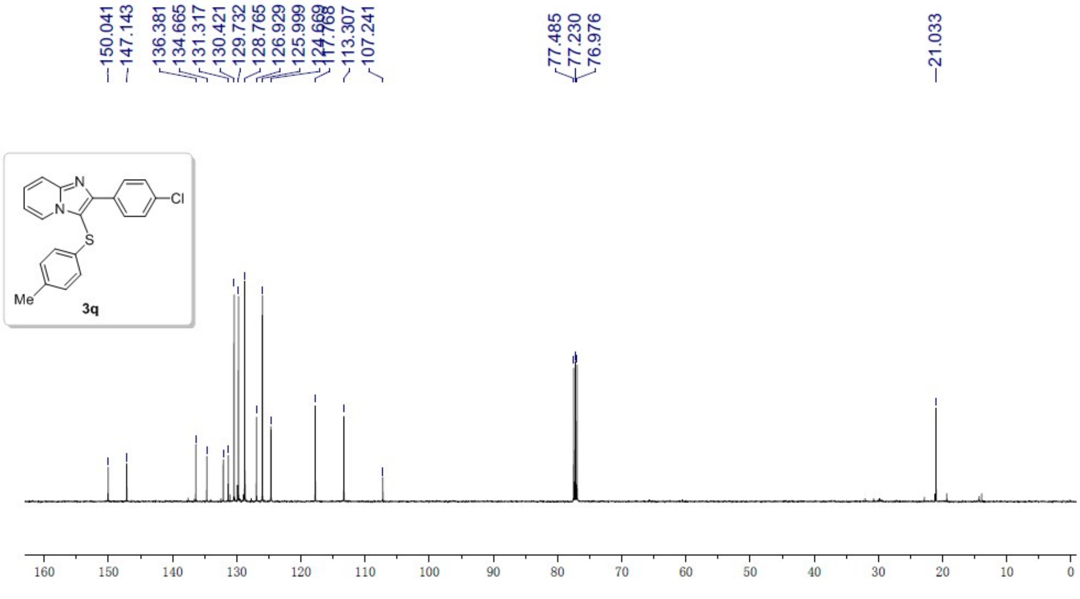
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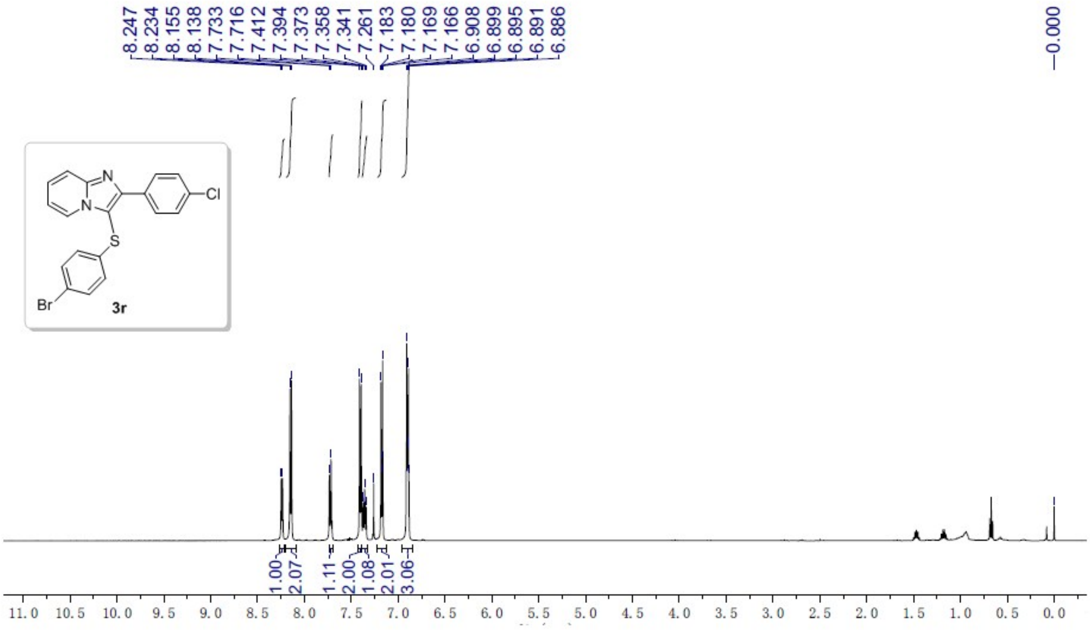

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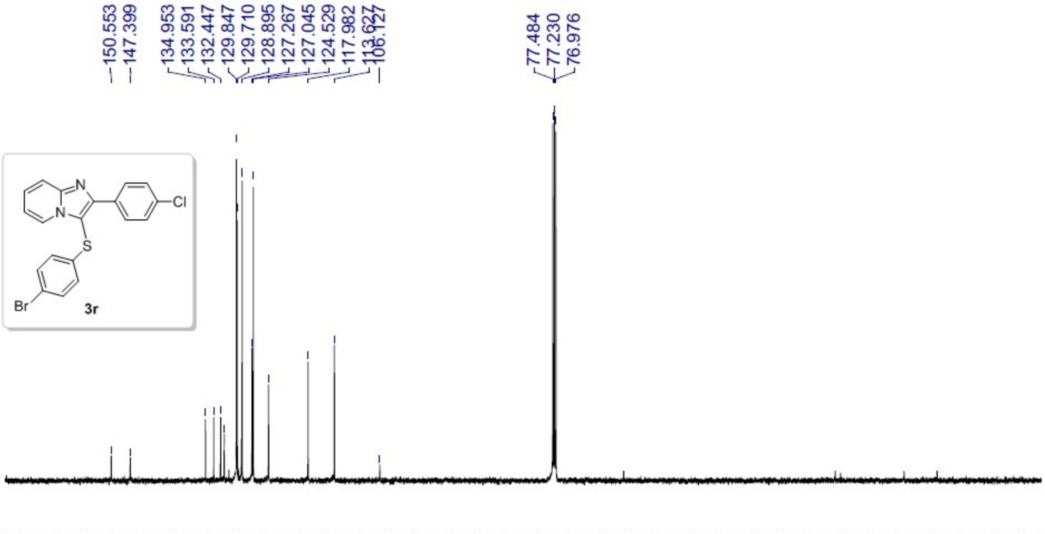

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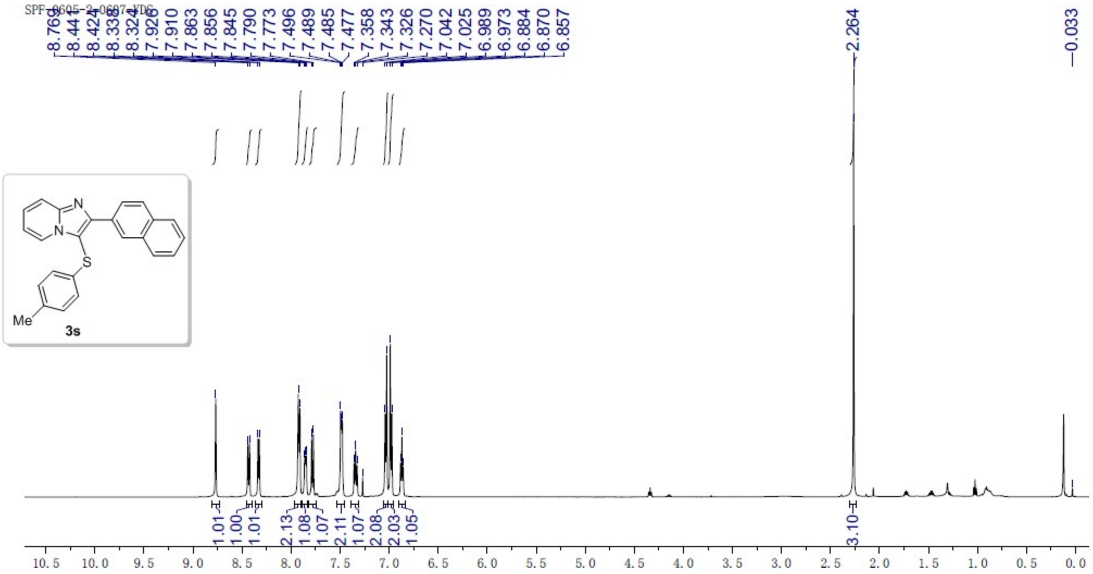
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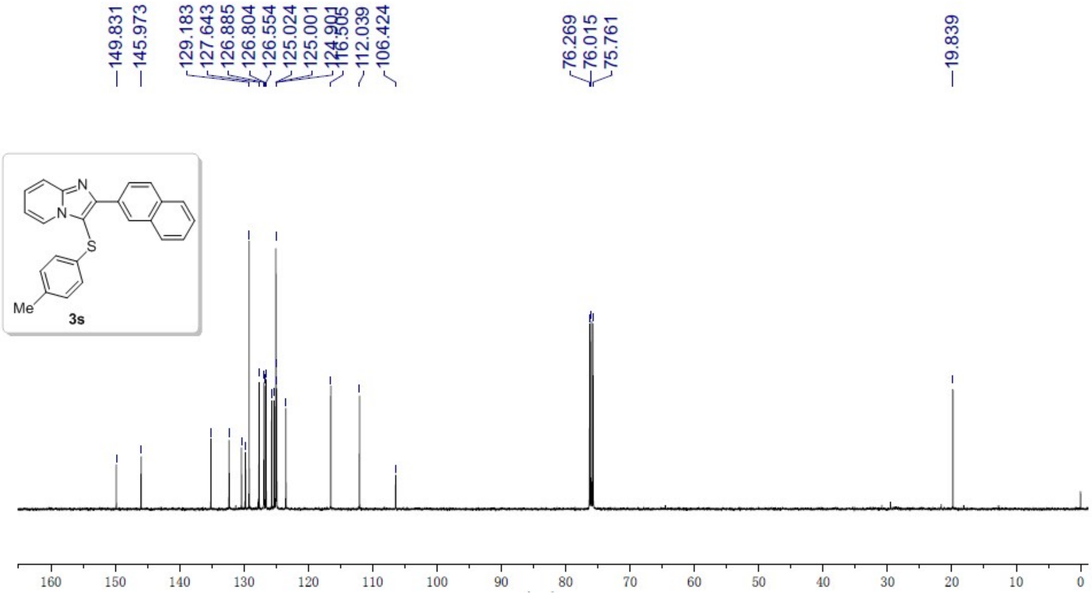
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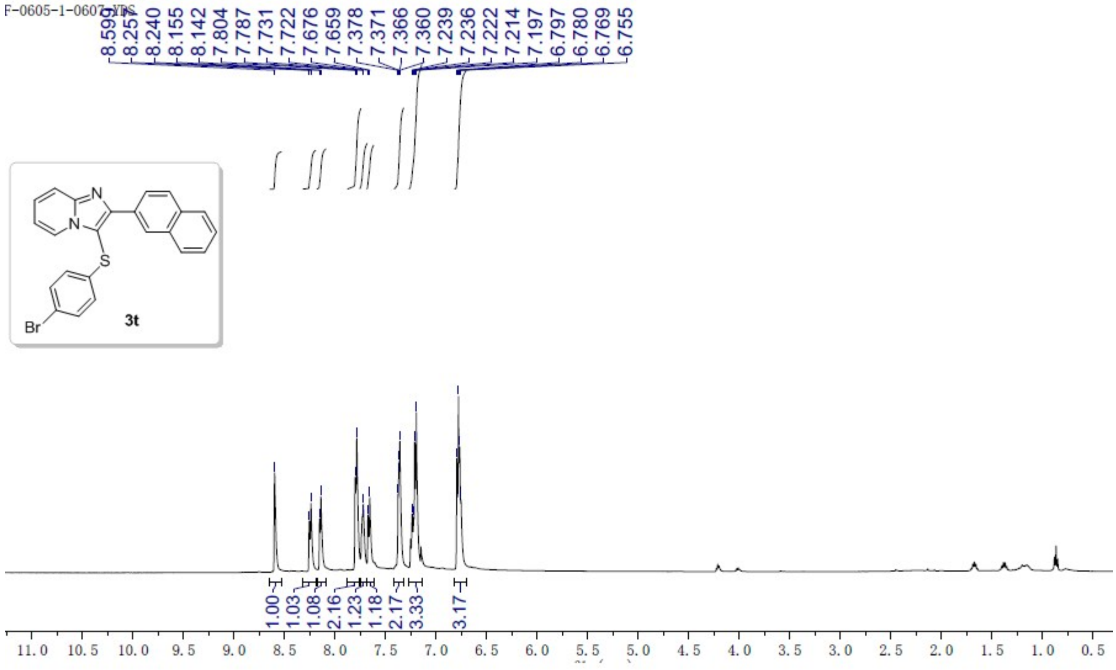
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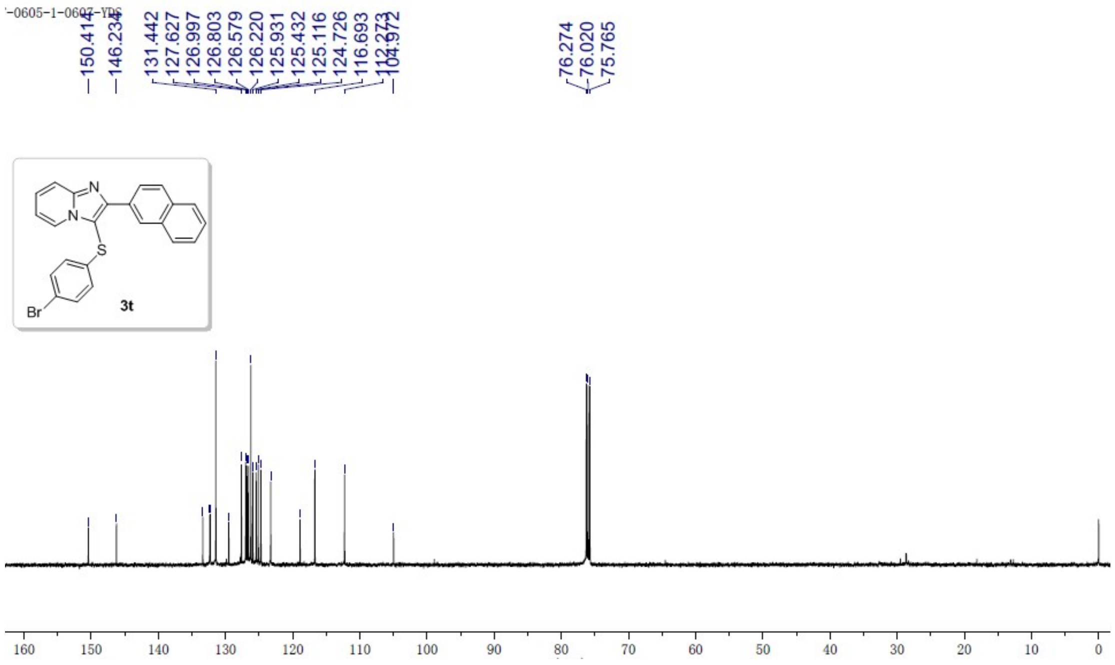
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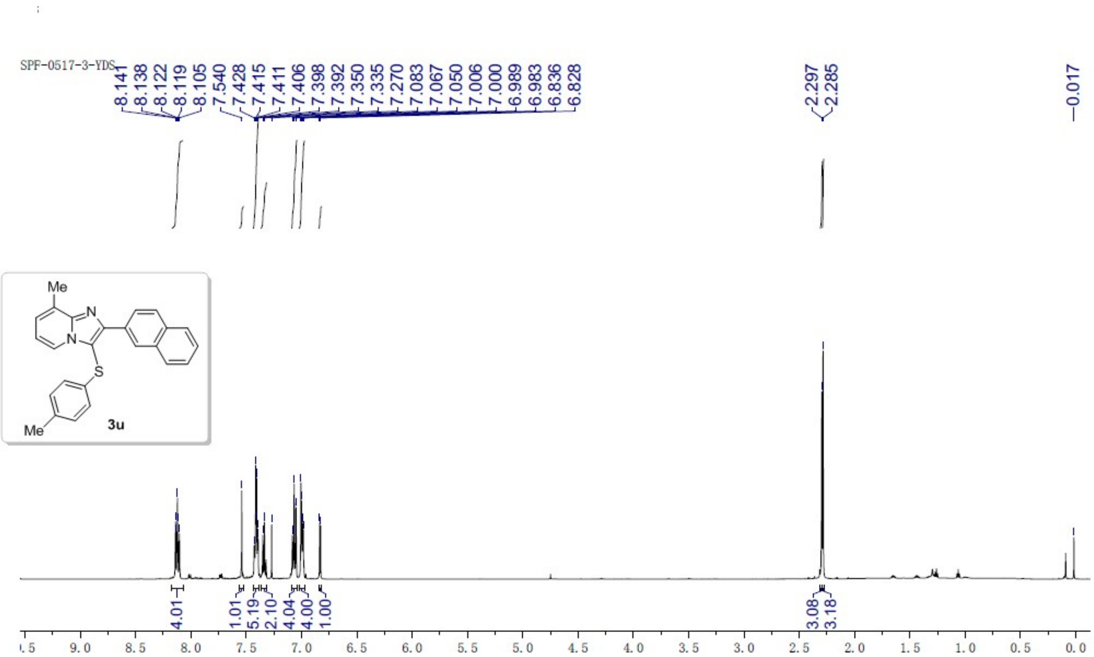
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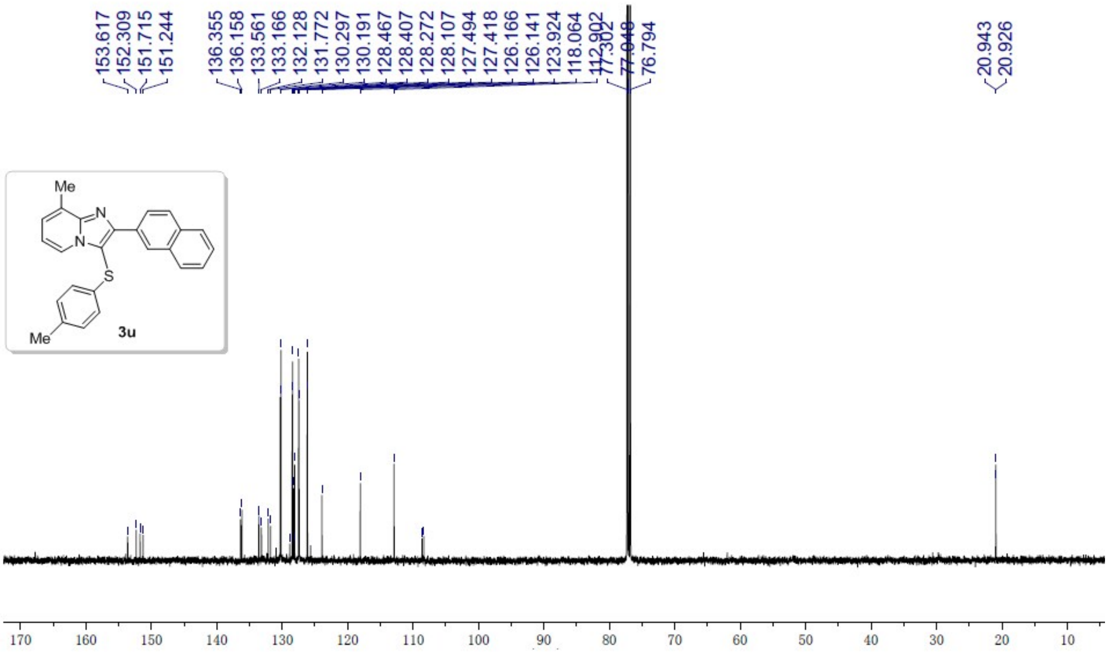
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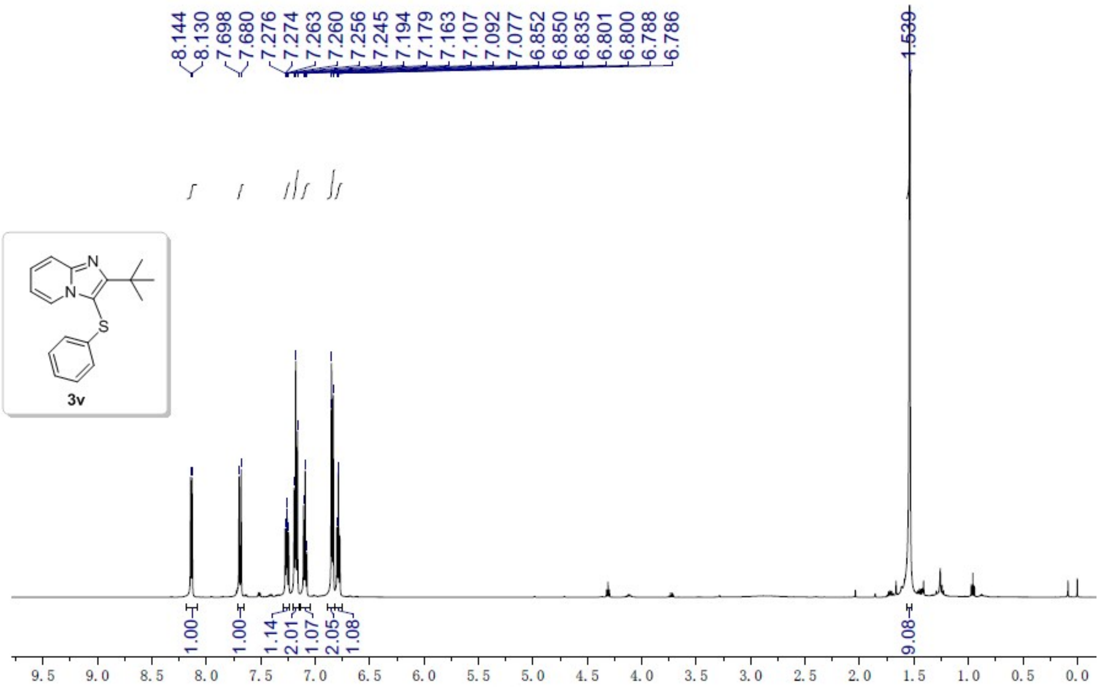
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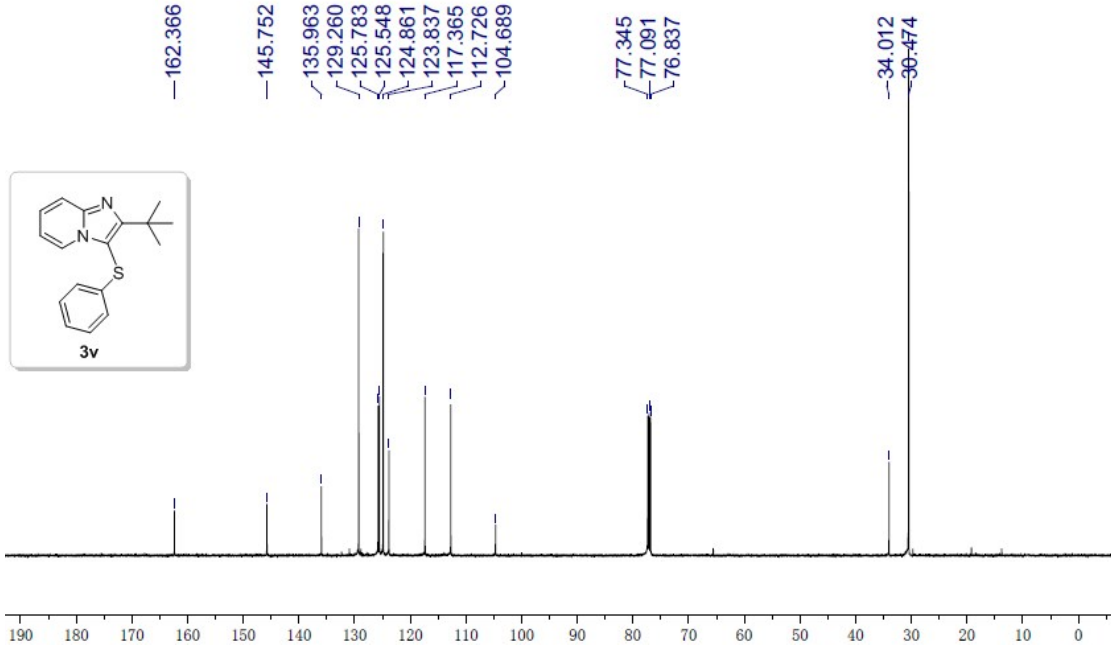
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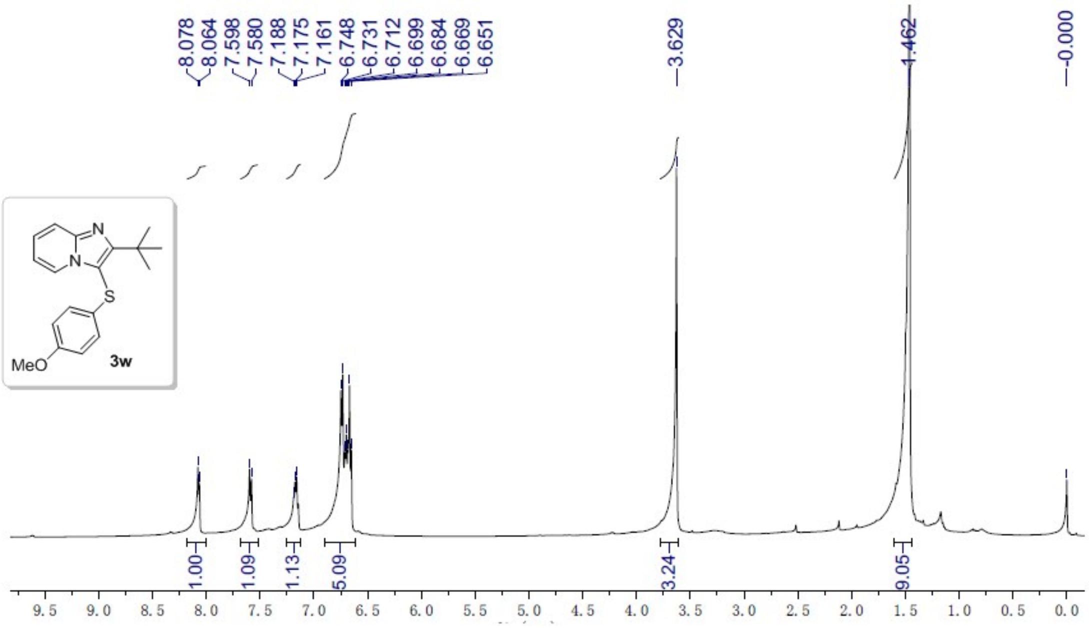
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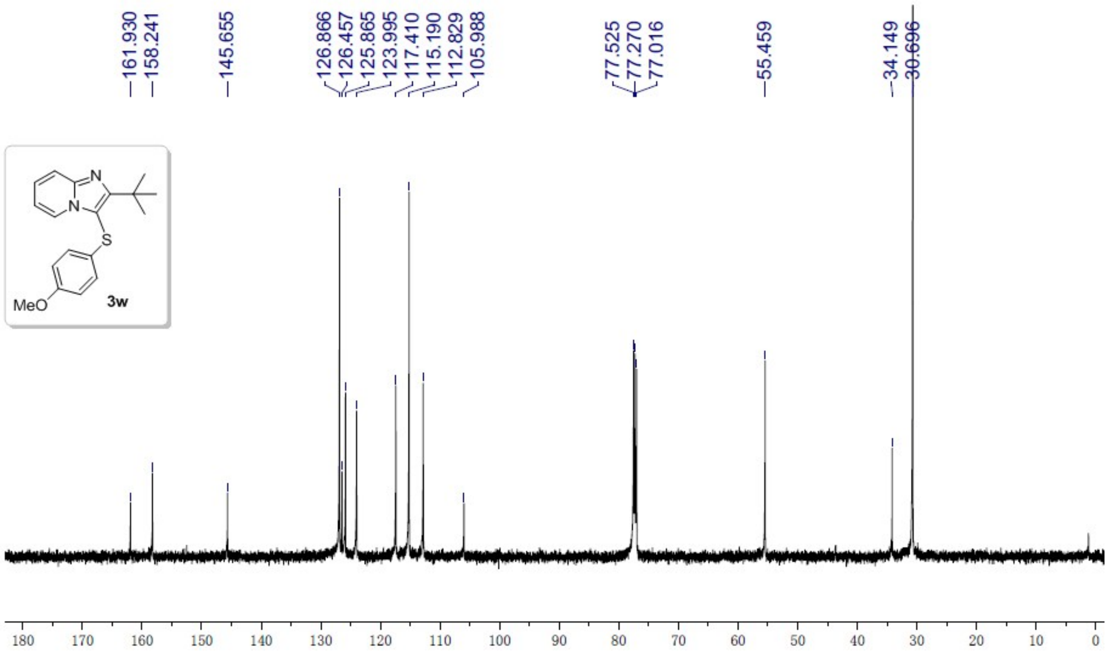
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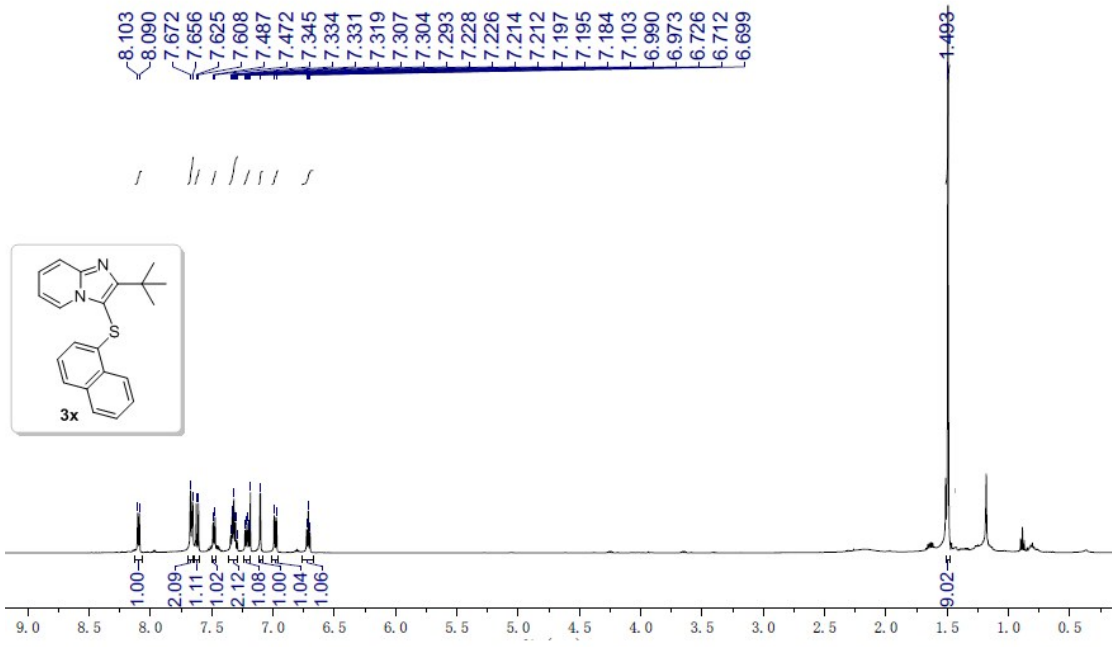
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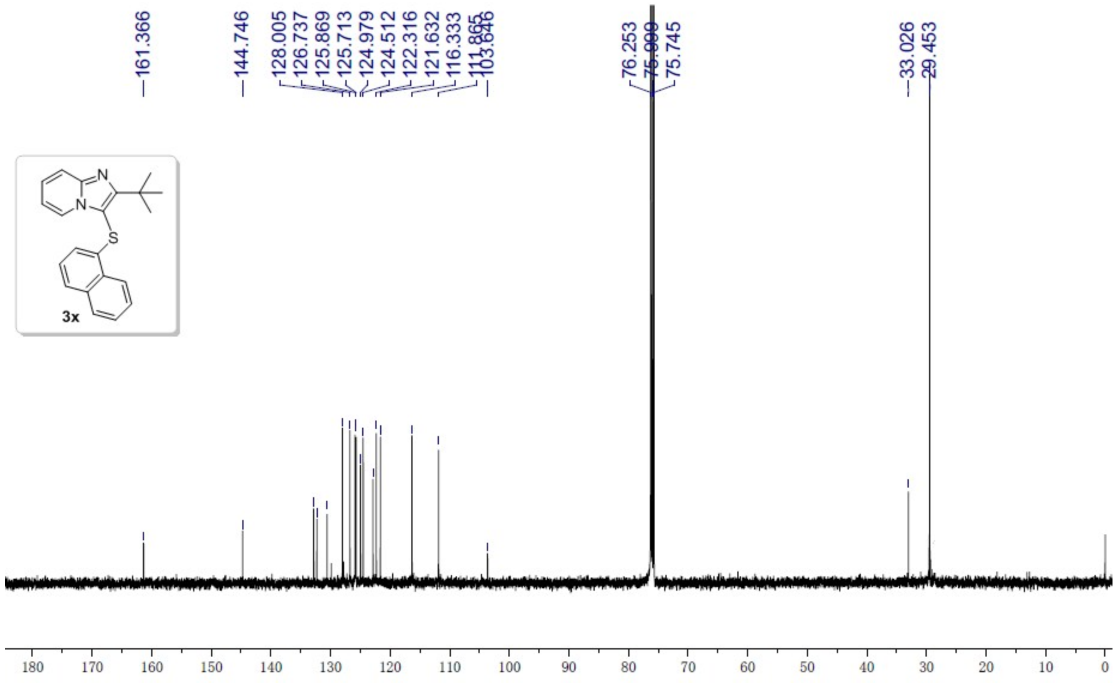
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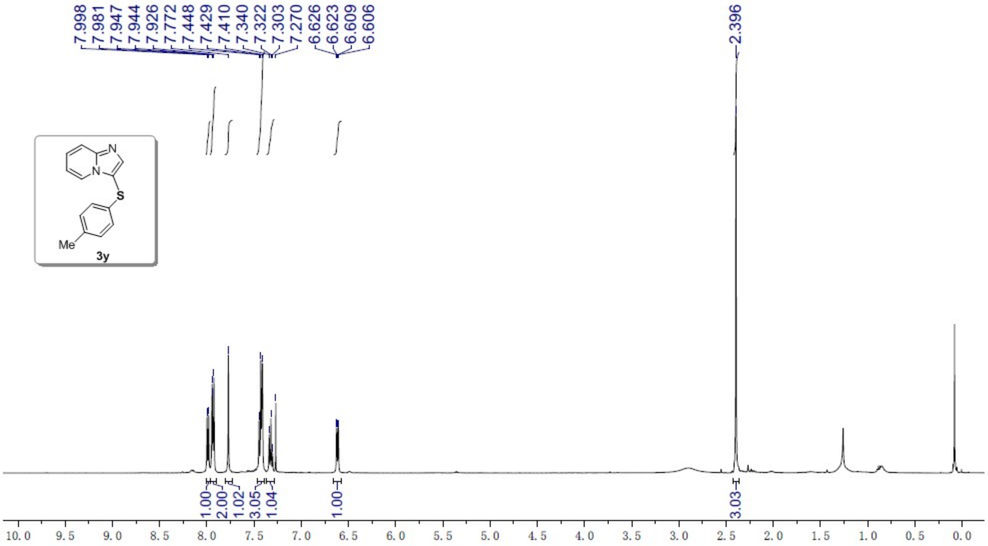
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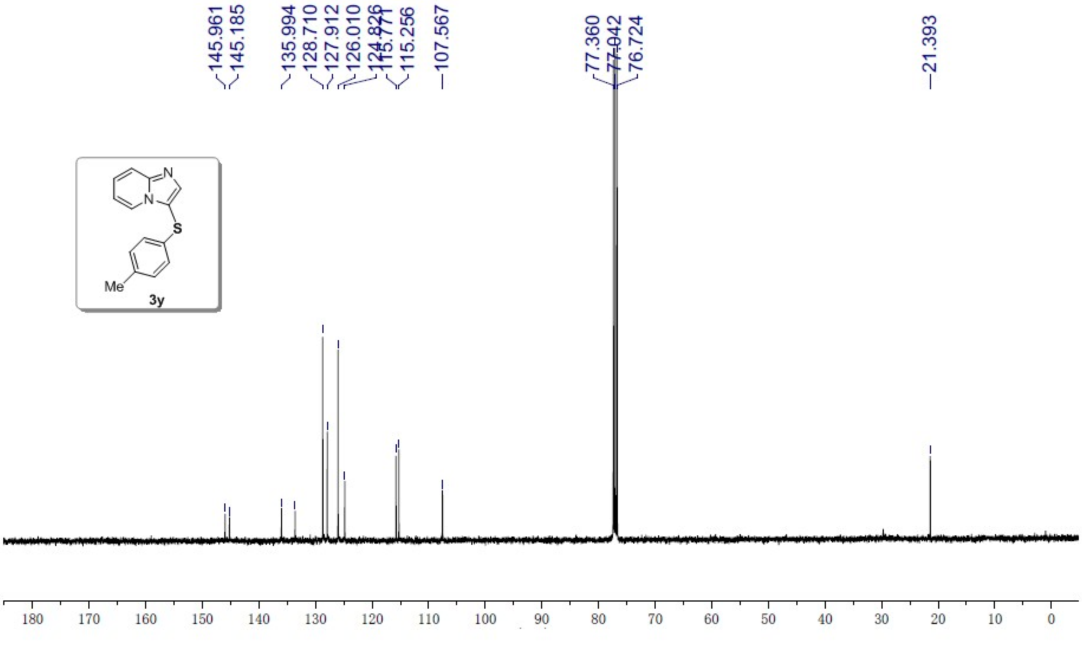
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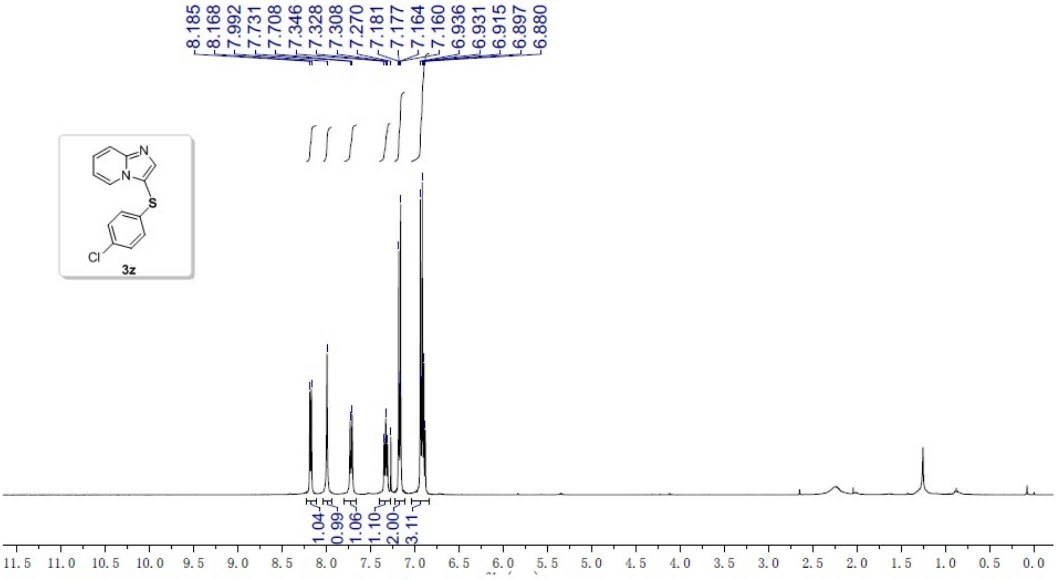
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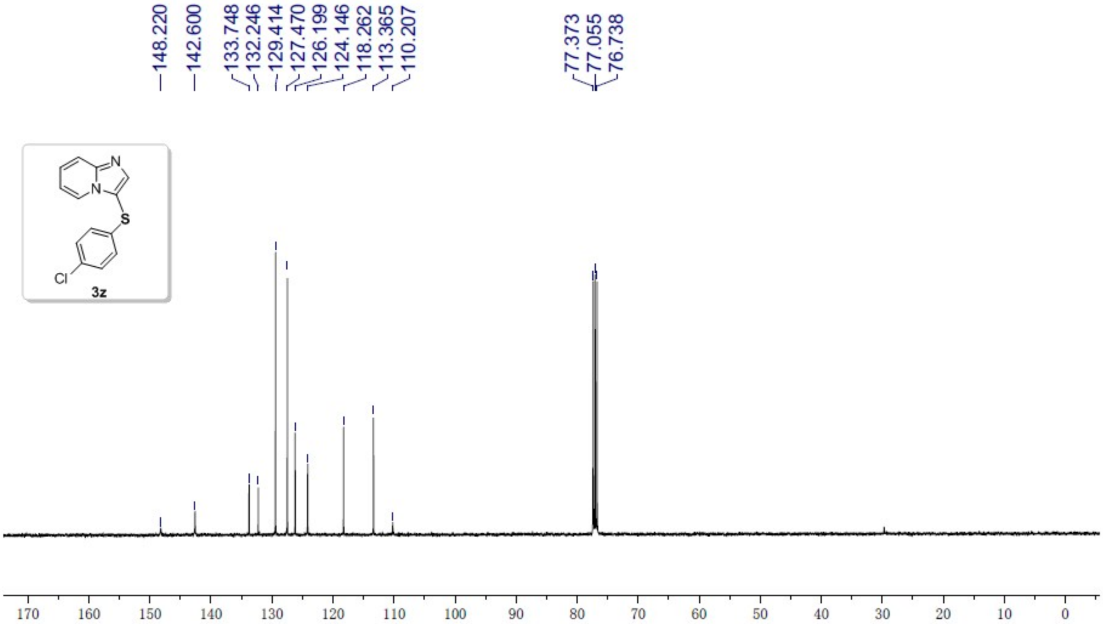
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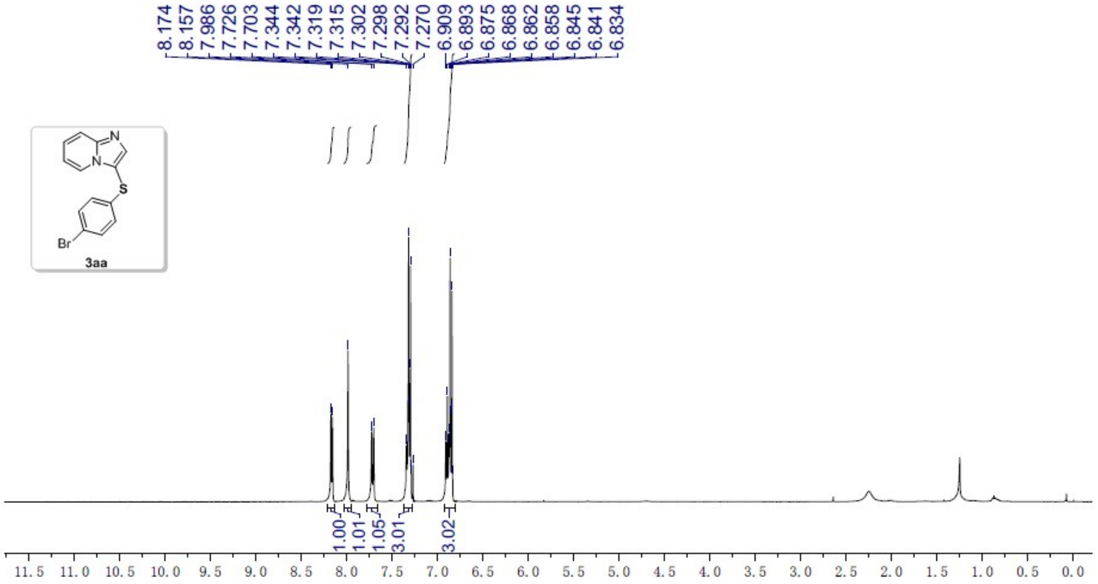
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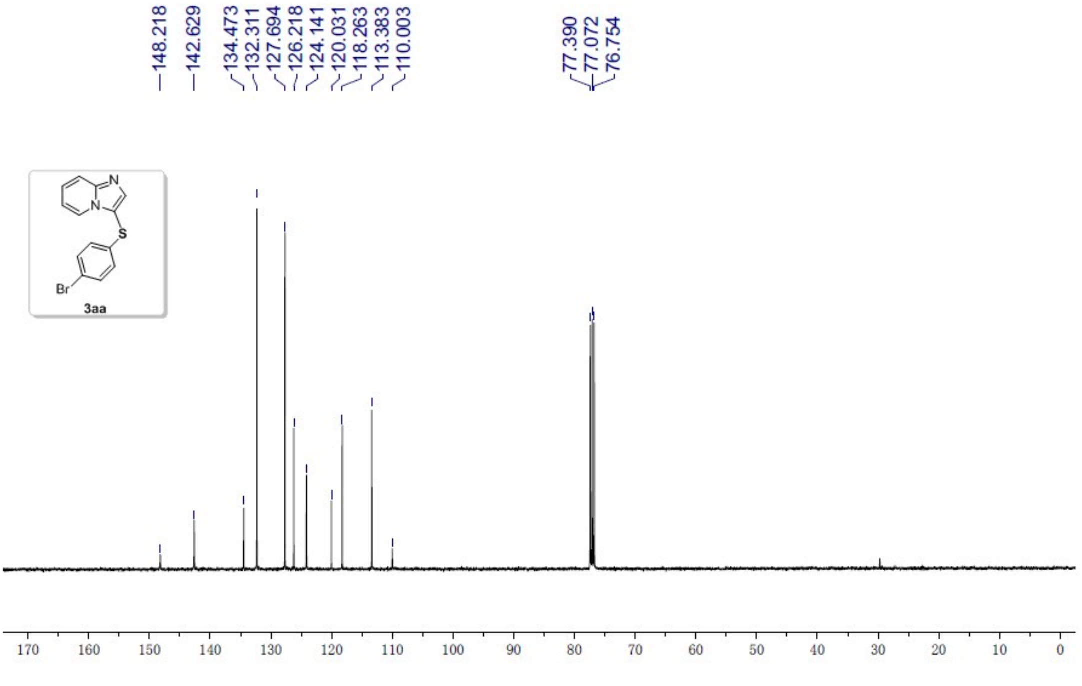
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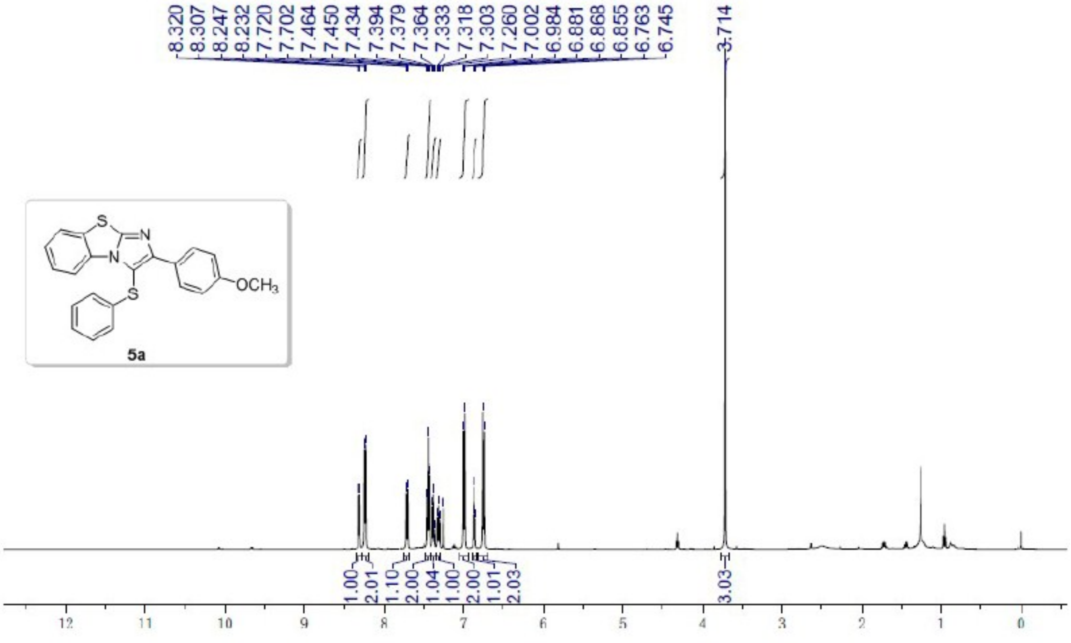
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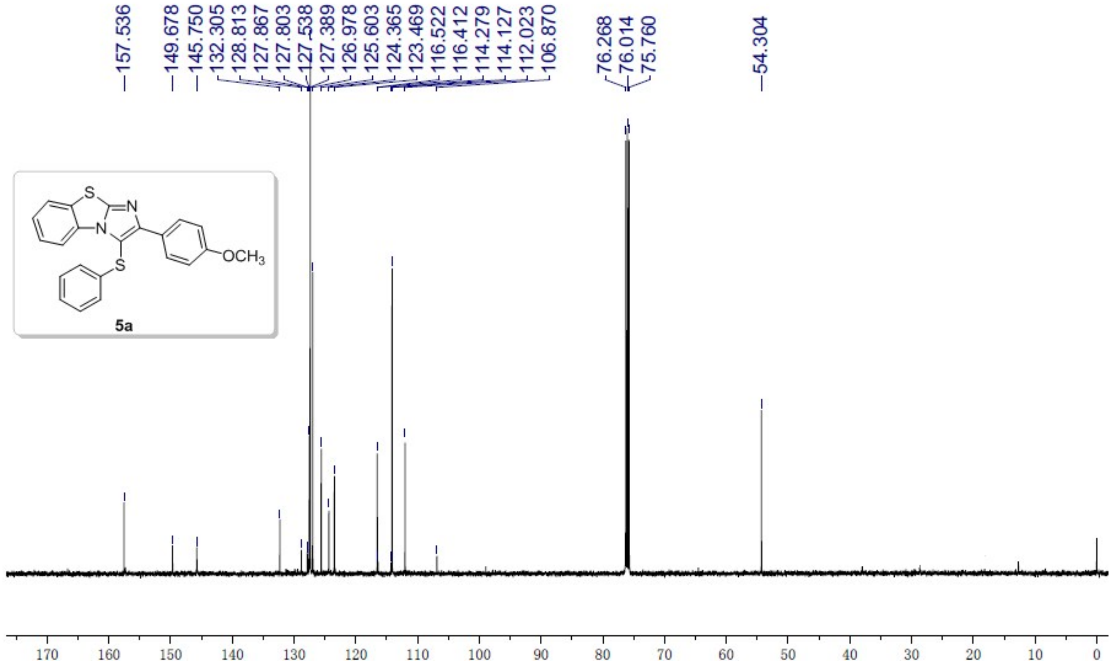
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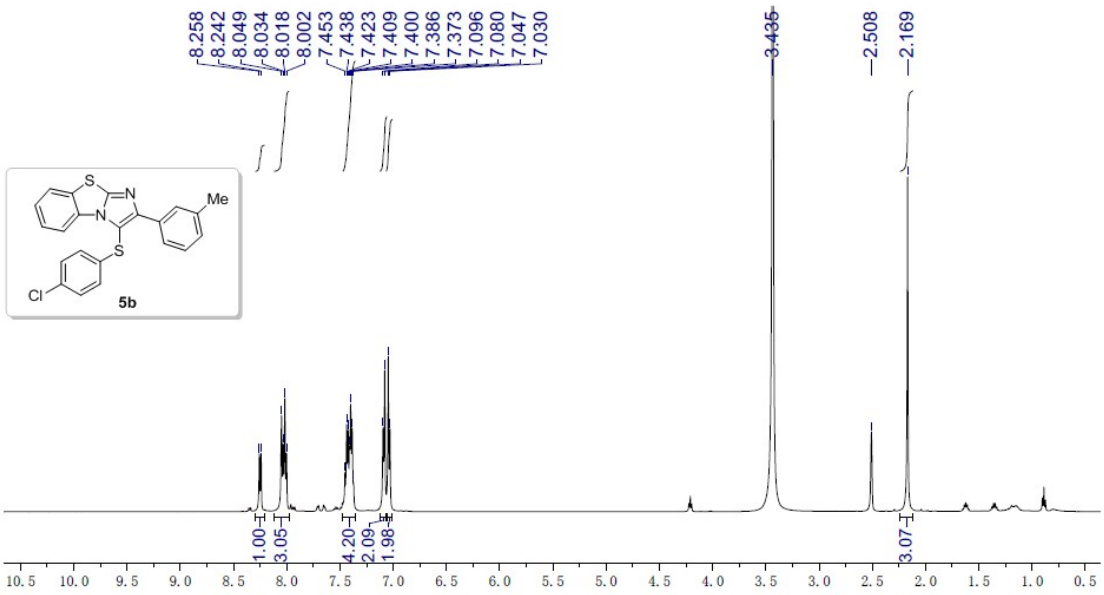
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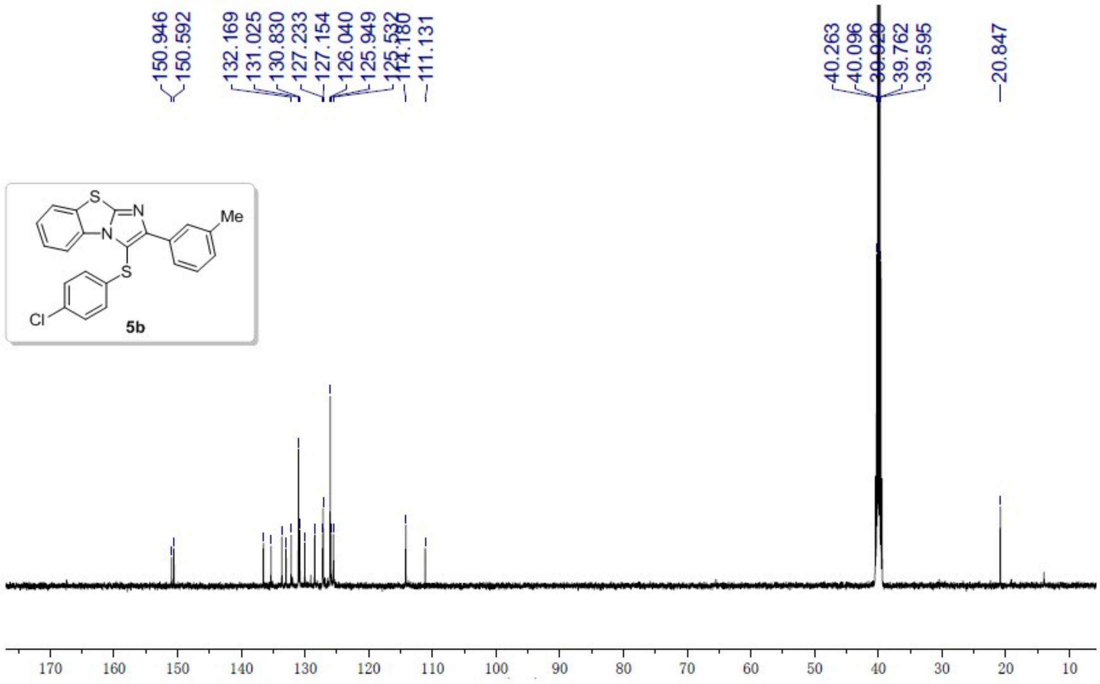
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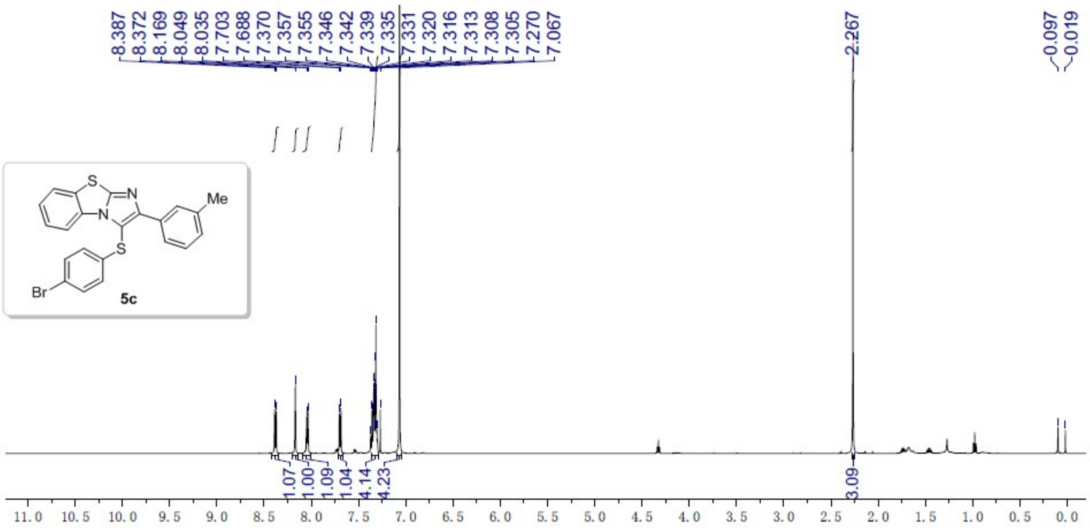
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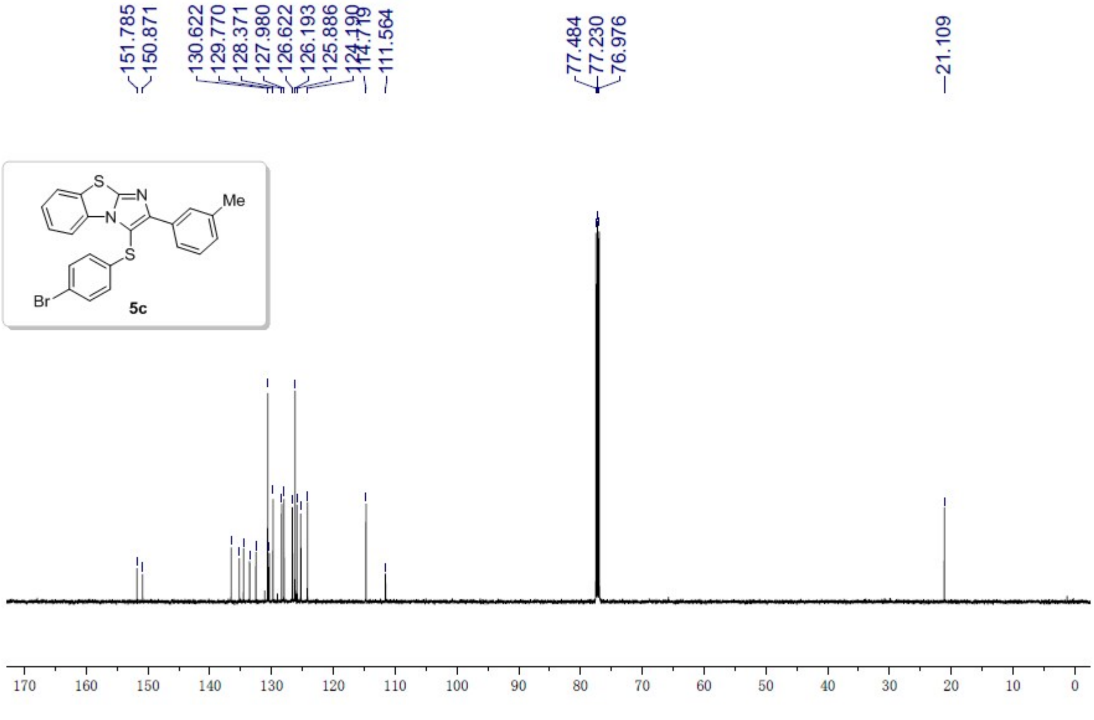
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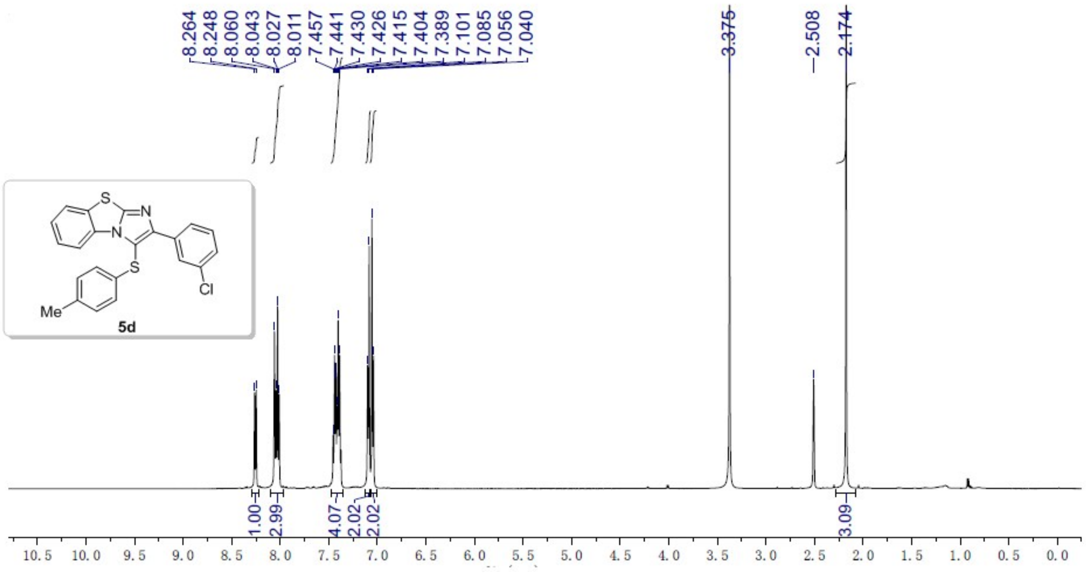
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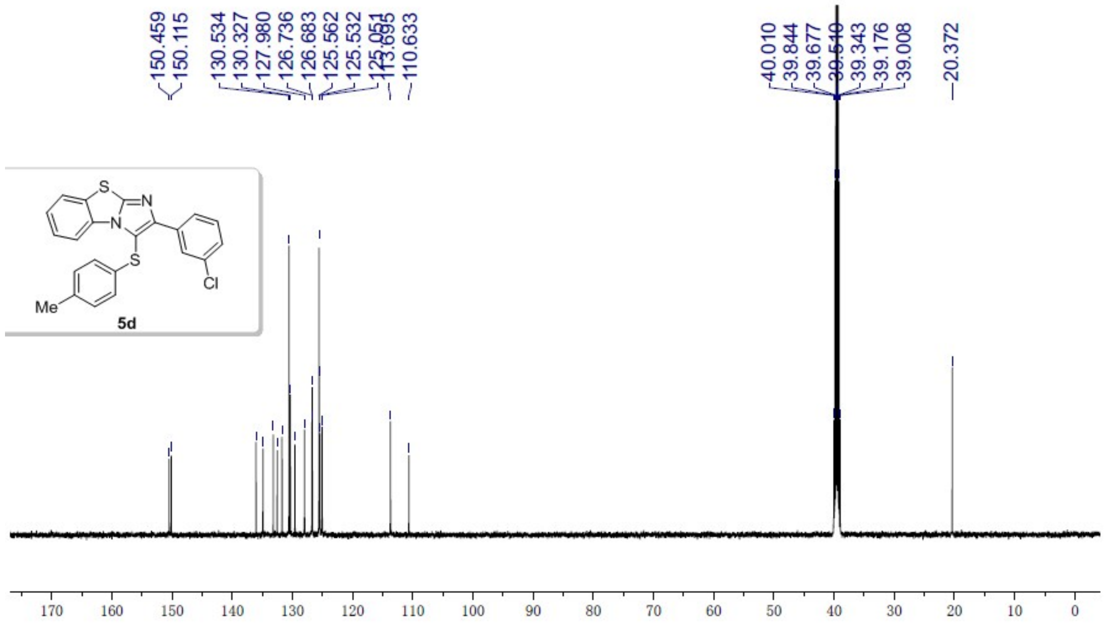
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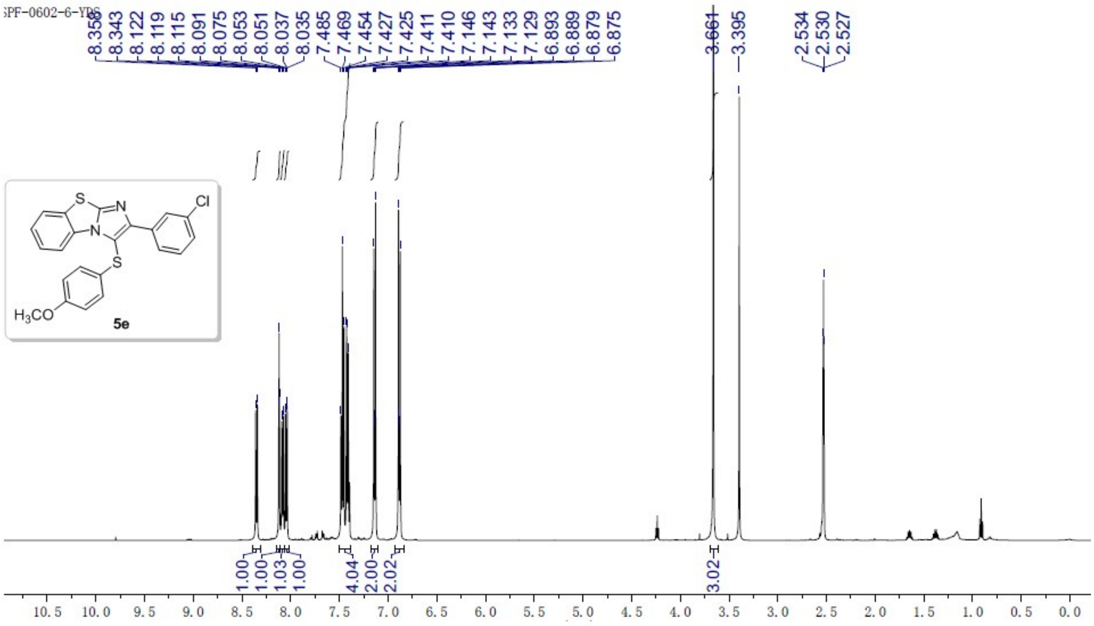
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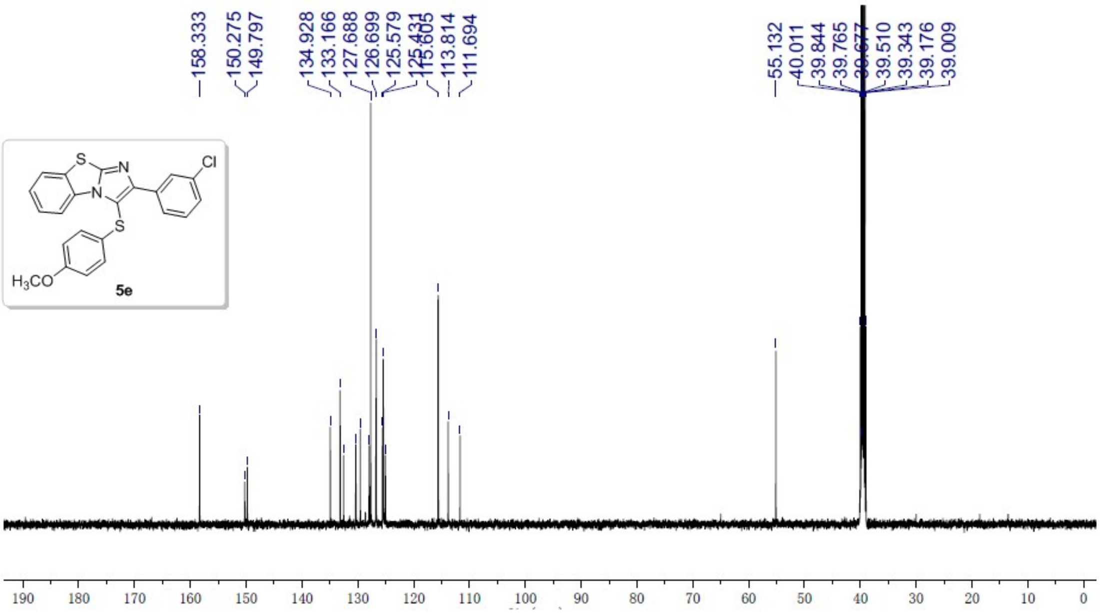
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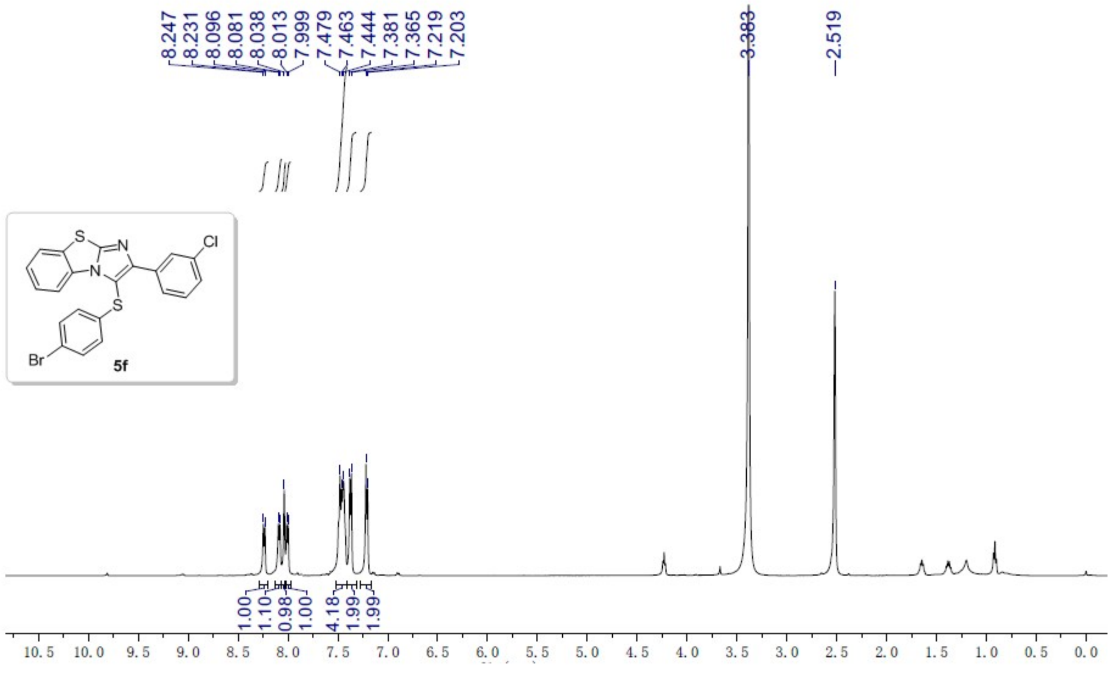
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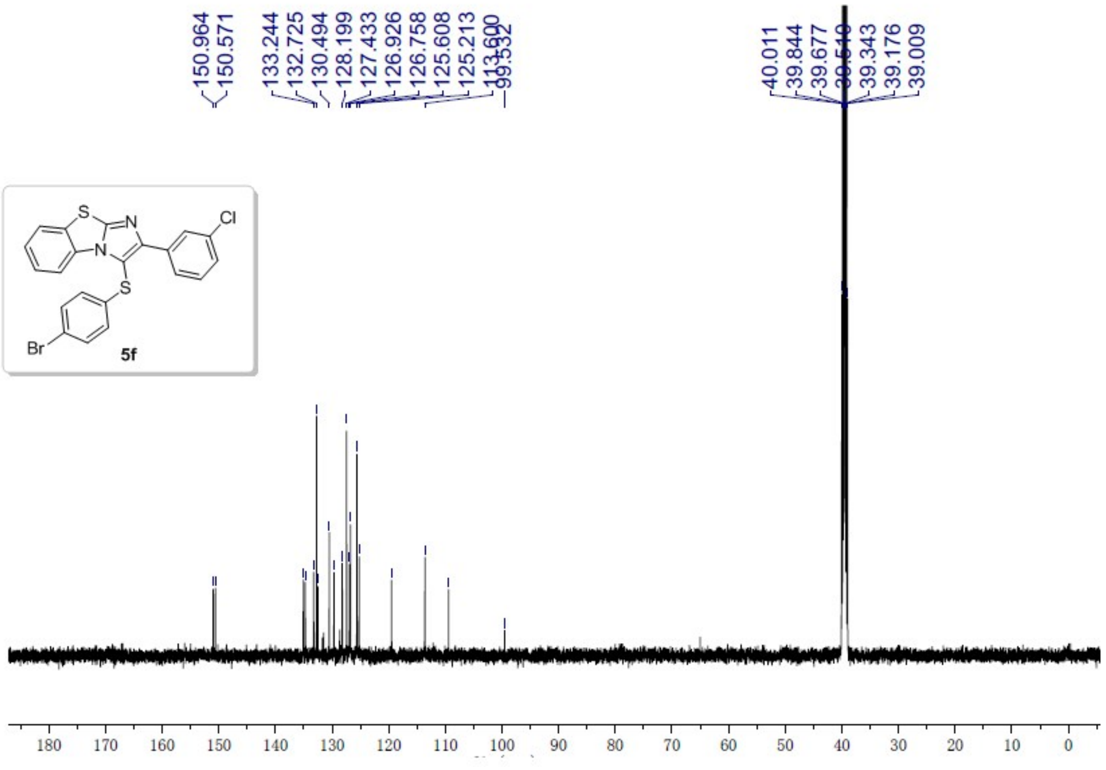
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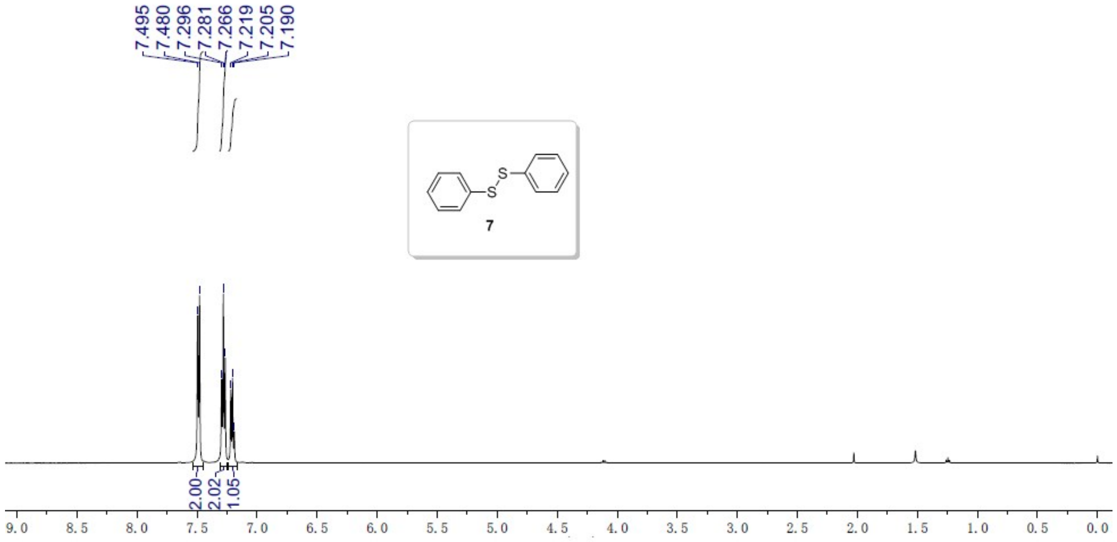
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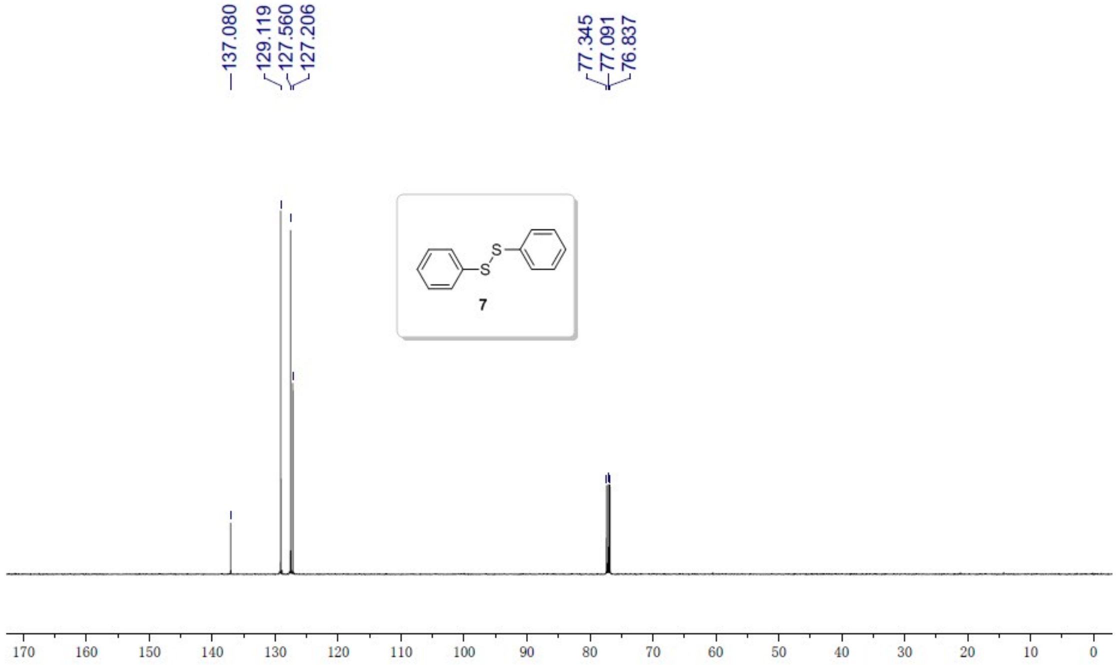
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