Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Carbene-Catalyzed LUMO Activation of Alkyne Esters for Access to Functional Pyridines

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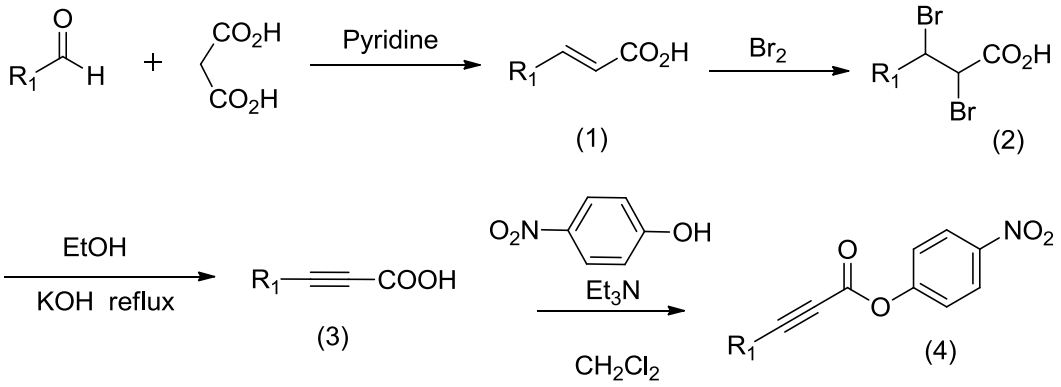
Table of Contents

Part 1. General Information

Commercially available materials purchased from Innochem and J&K were used as received. THF was distilled from Na and used directly. Unless otherwise specified, all reactions were carried out under an atmosphere of argon in 10 mL Schlenk tube. NMR spectra were measured either on a Bruker ASCEND 400 (400 MHz) or on a JEOL-ECX-500 (500 MHz) spectrometer. The chemical shift δ values were corrected to 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR) for $CHCl_3$. ^{1}H NMR splitting patterns are designated as singlet (s), double (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the base of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). High resolution mass spectrometer analysis (HRMS) was performed on Thermo Fisher Q Exactive mass spectrometer. Analytical thin-layer chromatography (TLC) was carried out on pre-coated silica gel plate (0.2 mm thickness). Melting Point (MP): Melting points were measured on a Beijing Tech XT-4 micro melting point apparatus and are uncorrected. Visualization was performed with short wave UV light.

Part 2. Experimental Section

I : General procedure for the preparation of alkyne acid ester: The alkyne acid ester substrates were prepared and characterized according to a known procedure, [1] as briefed below:



Step 1: Aldehydes (50 mmol), malonic acid (50 mmol), pyridine (150 mmol), and a few drops of piperidine were added in a 50 mL three-neck flask equipped with a reflux condenser. The reaction mixture was stirred at 100 ℃ for 8 h and then 120 ℃ for 2 h. After that the reaction mixture was transferred to a beaker containing 10 mL concentrated hydrochloric acid and 30 mL ice water. After the mixture was cooled, the resultant precipitate was filtered, washed three times with ice water, and recrystallized with ethanol to give pure propenoic acids.

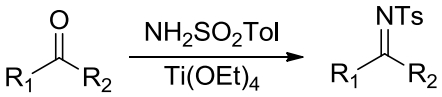
Step 2: To an ice-bath cooled mixture of propenoic acids (85 mmol) and chloroform (50 mL) was added bromine (5.3 mL, 102mmol) dropwisely and the resulting solution was stirred at this temperature for 20 min. The solution was stored in refrigerator overnight, filtered and washed twice with cold chloroform to give the crude product 2,3-dibromopropanoic acid derivatives which was used in the next step without further purification.

Step 3: To a suspension of 7.1 g of KOH in methanol (100 ml), 10.2 g (33.1 mmol) of 2, 3-dibromo-3-phenylpropanoic acid was added in portions over a period of 30 min. The mixture was then heated under reflux over a period of 2 h. After removing the solvent in vacuum, the residue was taken up in 10 % hydrovhloric acid. The solution was washed with EA and then set to pH > 10 with a 6 N aq. NaOH solution. The mixture was extracted with EA and the organic phase was dried over $MgSO_4$. Following filtration and the removal of solvent in vacuum, 5.7 g (39.0 mmol, 85%) of 3-phenylpropiolic acid was obtained.

Step 4: A solution of the corresponding carboxylic acid (15 mmol) in 10 mL of thionyl chloride was heated to reflux for 2 h. Thionyl chloride was then removed under vacuum. The remaining residue was diluted with 20 mL CH_2Cl_2, followed by a dropwise addition of a

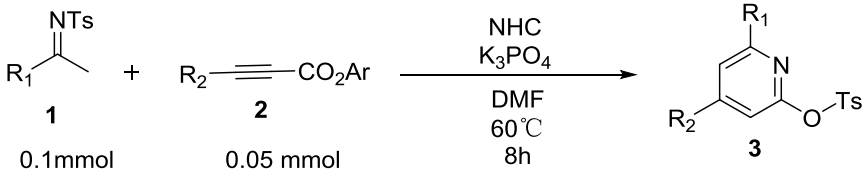
solution of Et_3N (45 mmol) and 4-nitrophenol (22.5 mmol) in 10 mL of CH_2Cl_2 at 0 ^oC. The mixture was allowed to warm to rt and stirred overnight. When the reaction was completed as indicated by TLC analysis, the mixture was washed with saturated aqueous $NaHCO_3$, The aqueous layers were extracted with CH_2Cl_2 (20 mL ×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was subjected to SiO_2 flash column chromatography to obtain the ester products.

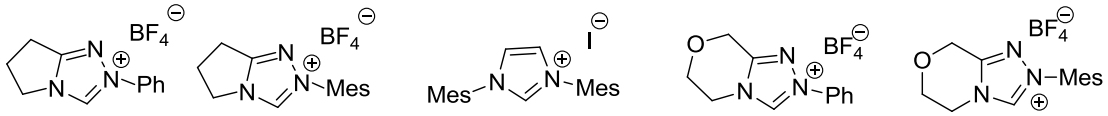
II: General procedure for the preparation of imine substrates: The imine substrates were prepared and characterized according to a known procedure, [2] as briefed below:



In a 50 mL two-neck round-bottomed flask fitted with a condenser, septum, argon inlet, and magnetic stirring bar was charged with racemic *t*-Butylsulfonamide (**3**) 200 mg (1.30 mmol), the corresponding aldehyde (1.30 mmol) or ketone (1.4 mmol) in of CH_2Cl_2 (20 mL), and finally $Ti(OEt)_4$ (2.6 mmol) was added. The solution was heated under reflux and monitored by TLC. When the reaction was finished 5 mL of MeOH and some drops of $NaHCO_3$ were added, until precipitation of the titanium salts. Then it was filtered through a short pad of anhydrous Na_2SO_4, washed with EtOAc, and the organic layer concentrated. The crude product was then purified by column chromatography using EtOAc and hexanes as the eluent.

III General procedures for the NHC catalytic addition of imine to alkyne acid ester





To a dry Schlenk tube equipped with a magnetic stir bar, was added imine **1** (0.1 mmol), alkyne ester **2** (0.05 mmol), NHC-B and K_3PO_4 (0.05 mmol). Anhydrous DMF (0.5 mL) was added, and the reaction mixture was stirred at room temperature till alkyne ester was completely consumed (for 2h, then heated 60℃ for 8h, monitored by TLC). The reaction mixture was concentrated under reduced pressure. The resulting crude residue was purified via column

chromatography on silica gel (hexane/EtOAc) to afford the desired pyridine product **3**.

IV Condition optimization for the synthesis of pyridine 3a.

Table S1. The effects of catalysts and bases [a]

Entry	Cat.	Base	Yield(%)[b]
1	A	$NaHCO_3$	25
2	A	Et_3N	15
3	A	K_3PO_4	38
4	B	$NaHCO_3$	30
5	B	Et_3N	19
6	B	K_3PO_4	40
7	C	$NaHCO_3$	20
8	C	Et_3N	18
9	C	K_3PO_4	22
10	D	$NaHCO_3$	20
11	D	Et_3N	12
12	D	K_3PO_4	24
13	E	$NaHCO_3$	NR
14	E	Et_3N	28
15	E	K_3PO_4	21

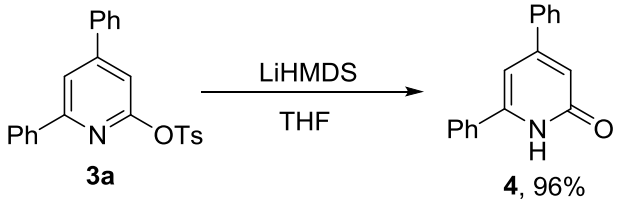
[a] Reaction conditions: **1a** (0.1 mmol, 2.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.**)**, NHC (20 mol%), in 0.5 mL THF at at 25 ℃. [b] Isolated yield based on **2a**;

Table S2 The effect of the Solvent[a]

Entry	Solvent	Yield(%)[b]
1	Toluene	Trace
2	DCM	Trace
3	DMF	83
4	EtOAc	22
5	$CHCl_3$	NR
6	THF	38
7	CH_3CN	39
8	Acetone	34
9	DMSO	25

[a] General condition: **1a** (0.1 mmol, 2.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.**)**, NHC (20 mol%), K_3PO_4 (100 mol%), at 25 ℃. [b] Isolated yield based on **2a**;

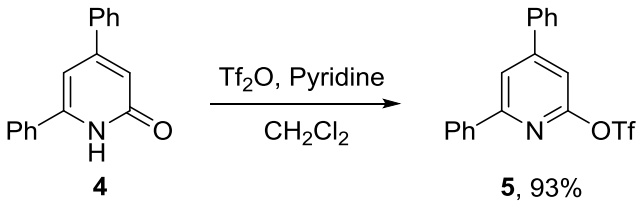
General procedure for the preparation of 4: The product **4** was prepared and characterized according to known procedures,[3] as briefed below:



3a **4**, 96%

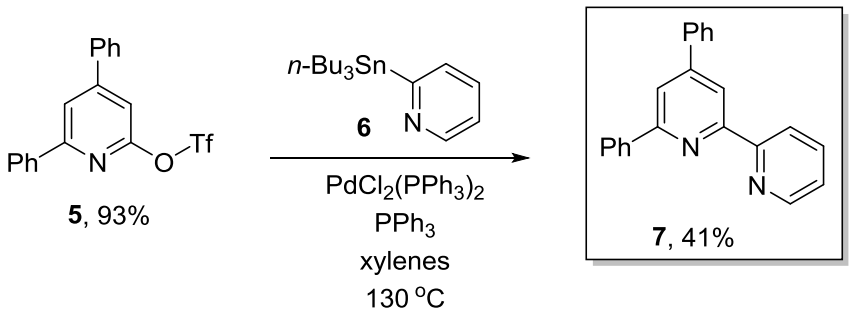
To an oven-dried 25ml round-bottom flask was charged with **3a** (120 mg, 0.3 mmol) and anhydrous THF (3 mL). Then LiHMDS (1 M in THF, 0.9 mL, 0.9 mmol) was added to the flask and the resulting mixture was stirred at rt for 3 h. The reaction was quenched with water (10 mL) and the resulting mixture was extracted with EtOAc (15 mL×3). The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to using hexane/EtOAc (5:1) as the eluent.

General procedure for the preparation of 5: The product **5** was prepared and characterized according to known procedures,[4] as briefed below:



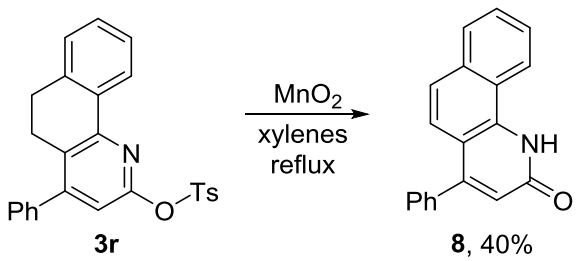
To a dry Schlenk tube equipped with a magnetic stir bar, and **4** was dissolved in anhydrous CH_2Cl_2 (5 mL) and cooled to 0 ℃ via an ice bath. Pyridine (1.5 equiv, 1.5 mmol) was added followed by triflic anhydride (1.2 equiv, 1.2 mmol). The ice bath was removed after 5 min, and the solution was stirred at rt for an additional 2 h. The solvent was concentrated, and the crude product was purified by chromatography on silica gel using EtOAc/heptane = 1:9 to give expected product **5**.

General procedure for the preparation of 7: The product **7** was prepared and characterized according to a known procedure,[5] as briefed below:



In a dry Schlenk tube equipped with magnetic stir bar, septum, argon inlet, **5** was dissolved in xylenen, **6** (1.5 equiv) was added followed by bis(triphenylphosphine)palladium(II) chloride (0.1 equiv). Triphenylphosphine (0.1 equiv). The solution was heated at reflux for 8 h. The solvent was concentrated, and the crude product was purified by column chromatography on silica gel using EtOAc/hexane = 1:3 as eluent.

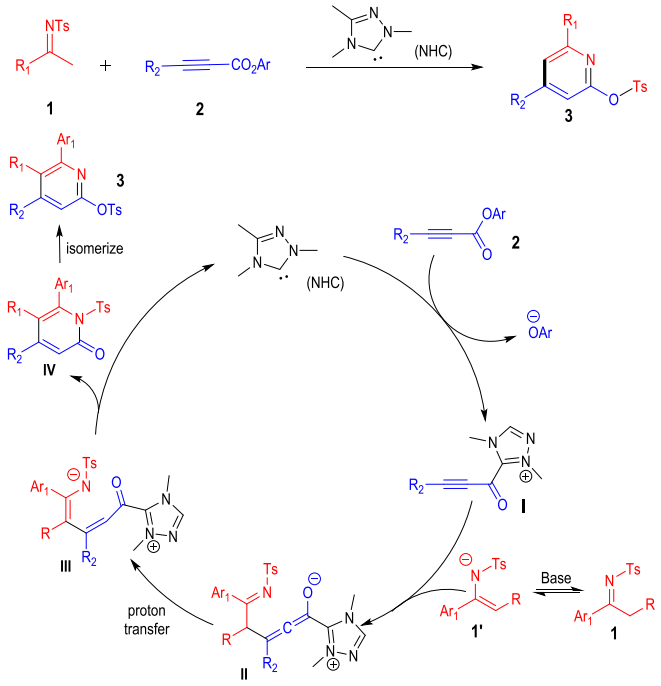
General procedure for the preparation of 8: The pruduct **8** was prepared and characterized according to known procedures,[6] as briefed below:



3r **8**, 40%

To an oven-dried 10 ml round-bottom flask equipped with a magnetic stir bar, was added **3r** (0.1 mmol), MnO_2 (1 mmol), xylenes (2 ml), the reaction mixture was stirred at reflux for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (hexane/EtOAc) to afford the desired product **8**.

V. Postulated reaction mechanism:



The addition of an NHC catalyst to the unsaturated ester **2** gives azolium ester intermediate **I** that is then reacted with enimide intermediate **1'** under basic conditions to afford intermediate **II**. Intermeidate **II** undergoes an proton transfer process to generate azolium ester intermediate **III**. Lactam **IV** could be afforded through an intromolecular amide formation process, which is then completely isomerized to the final hydroxyl pyridine product **3** after heating at 60 ^{o}C for 6 h.

References

[1] a) A. R. Katritzky, S. Ozcana, E. odadze, *Org. Biomol. Chem.* **2010**, *8*, 1296; b) U. Ugo Azzena, G. Dettori, L. Pisano, M. Pittalis, *Tetrahedron* **2011**, *67*, 3470; c) L. Hao, Y. Du, H. Lv, X. Chen, H. Jiang, Y. Shao, Y. R. Chi, *Org. Lett*. **2012**, *14*, 2154; d) J.-G. Mao, W.-L. Bao, *Org. Lett*. **2014**, *16*, 2646.

[2] J. Luis, G. Ruano, J. Alemán, M. B. Cid, A. Parra, *Org. Lett.* **2005**, *7*, 179.

[3] L. Wang, G.-Y. Zhu, W.-F. Tang, T. Lu, D. Du, *Tetrahedron* **2016**, *72*, 6510.

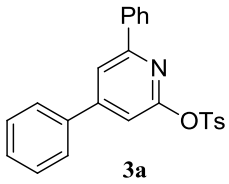
[4] C. Doebelin, P. Wagner, F. Bihel, N. Humbert, C. A. Kenfack, Y. Mely, J.-J. Bourguignon, M. Schmitt, *J. Org. Chem*. **2014**, *79*, 908.

[5] A. Godard, J-C. Rovera, F. Marsais, N. Pld, G. Queguiner, *Tetrahedron* **1992**, *20*, 4123.

[6] J. Míšek, F. Teplý, I. G. Stará, M. Tichý, D. Šaman, I. Císařovár, P. Vojtíšek, I. Starý, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3188.

Part 3. Characterization of Products

4,6-diphenylpyridin-2-yl 4-methylbenzenesulfonate (**3a**)**:**



3a

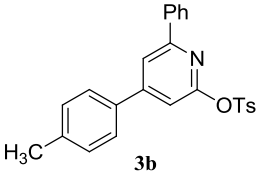
was obtained 83% yield as white solid. mp：96-98℃.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.77-7.75 (m, 2H) , 7.66 (dd, J_1 = 2.0 Hz, J_2 = 1.8 Hz, 2H), 7.54-7.46 (m, 3H), 7.42-7.36 (m, 5H), 7.25 (s, 1H), 2.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 156.6, 153.9, 145.1, 137.7, 137.5, 134.5, 134.4, 129.8, 129.7, 129.3, 128.9, 128.7, 127.3, 127.1, 117.1, 111.8, 21.3;

HRMS (ESI) calcd for $C_{24}H_{20}NO_3S^+$: 402.1158, Found: 402.1165

6-phenyl-4-(p-tolyl)pyridin-2-yl 4-methylbenzenesulfonate (3b):



3b

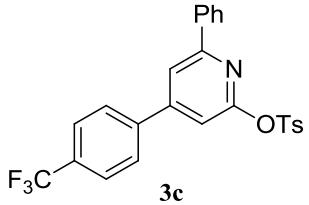
was obtained in 65% yield as white solid. mp：135-137℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J_1 = 3.9 Hz, J_2 = 4.2 Hz, 2H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.76-7.73 (m, 2H), 7.57 (dt, J_1 = 4.1 Hz, J_2 = 4.2 Hz, 2H), 7.42-7.39 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32-7.30 (d, *J* = 7.9 Hz, 2H) , 7.24 (d, *J* = 1.3 Hz, 1H), 2.48 (s, 3H) , 2.43 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 156.6, 153.8, 145.0, 140.0, 137.7, 134.5, 130.0, 129.7, 129.6, 128.9, 128.7, 127.1, 116.9, 111.5, 21.8, 21.4;

HRMS (ESI) calcd for $C_{25}H_{22}NO_3S^+$: 416.1315, Found: 416.1319

6-phenyl-4-(4-(trifluoromethyl) phenyl) pyridin-2-yl 4-methylbenzenesulfonate (3c)



3c

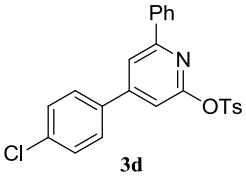
was obtained in 84% yield as white solid. mp：120-121℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 1.0 Hz, 1H), 7.79-7.75 (m, 7H) , 7.43-7.40 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 156.9, 156.6, 152.6, 145.2, 137.5, 137.1, 136.1, 135.9, 135.8, 135.7, 134.5, 129.8, 129.7, 129.6, 128.9, 128.8, 128.5, 127.1, 116.8, 111.6, 21.9;

HRMS (ESI) calcd for $C_{25}H_{19}F_3NO_3S^+$: 470.1032, Found: 470.1029

4-(4-chlorophenyl)-6-phenylpyridin-2-yl 4-methylbenzenesulfonate (3d):



3d

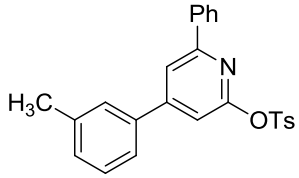
was obtained in 84% yield as white solid. mp：148-150℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.3 Hz, 2H), 7.83 (t, *J* = 3.1 Hz, 1H), 7.78-7.76 (m, 7H) , 7.43-7.38 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 156.9, 152.4, 145.3, 141.0, 137.3, 134.4, 129.9, 129.8, ,129.7, 128.9, ,128.8, 127.5, 127.1, 126.3, 126.2, 117.9, 21.9;

HRMS (ESI) calcd for $C_{24}H_{19}ClNO_3S^+$: 435.0690, Found: 435.0698

6-phenyl-4-(m-tolyl)pyridin-2-yl 4-methylbenzenesulfonate (**3e**)



3e

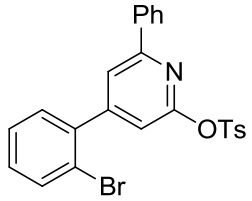
was obtained in 81% yield as white solid. mp：82-84℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 1.4 Hz, 1H), 7.77-7.75 (m, 2H) , 7.46-7.36 (m, 8H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 1.5 Hz, 1H) , 2.48 (s, 3H) , 2.45 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 156.6, 154.1, 145.1, 139.1, 137.7, 137.5, 134.5, 130.5, 129.7, 129.6, 129.2, 128.9, 128.7, 127.9, 127.1, 124.4, 117.2, 111.8, 21.8, 21.6;

HRMS (ESI) calcd for $C_{25}H_{22}NO_3S^+$: 416.1315, Found: 416.1311.

4-(2-bromophenyl)-6-phenylpyridin-2-yl-4-methylbenzenesulfonate (3f)



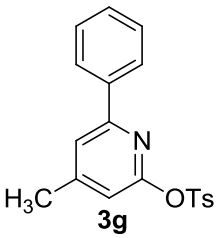
3f

was obtained in 48%% yield as white solid. mp：109-111℃;

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H) 7.89 (dt, J_1 = 4.3 Hz, J_2 = 4.0 Hz, 2H), 7.4-7.52 (m, 3H) , 7.44-7.38 (m, 5H), 7.29 (d, *J* = 7.9 Hz, 2H) , 7.06 (s, 1H), 2.42 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 156.0, 153.7, 145.1, 139.1, 137.5, 134.5, 133.7, 130.8, 130.4, 129.8, 129.7, 129.6, 128.9, 128.7, 127.9, 127.1, 126.6, 121.8, 119.8, 114.3, 21.8.

HRMS (ESI) calcd for $C_{24}H_{19}BrNO_3S^+$: 480.0264, Found: 480.0277.



3g

4-methyl-6-phenylpyridin-2-yl 4-methylbenzenesulfonate (3g)

was obtained in 67% yield as white solid. mp：128-130℃.

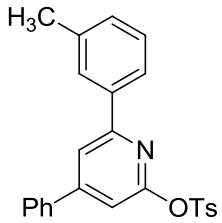
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.45 (s, 1H), 7.36 (t, *J* = 16.2 Hz, 5H) , 6.89 (s, 1H), 2.47 (s, 3H), 2.43

(s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 155.8, 152.7, 145.0, 137.6, 134.6, 129.6, 129.5, 128.9, 128.6, 126.9, 119.9, 114.5, 21.8, 21.4;

HRMS (ESI) calcd for $C_{19}H_{18}NO_3S^+$: 339.0924, Found: 339.0921.

4-phenyl-6-(m-tolyl)pyridin-2-yl 4-methylbenzenesulfonate (3h)



3h

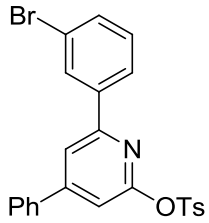
was obtained in 84% yield as white solid. mp：99-100℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.83 (t, *J* = 1.5 Hz, 1H), 7.66 (t, *J* = 9.6 Hz, 2H), 7.57-7.48 (m, 5H) , 7.38 (d, *J* = 8.3 Hz, 2H) , 7.31 (t, *J* = 15.3 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H) ;

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 156.8, 153.9, 145.1, 138.4, 137.6, 137.5, 134.6, 130.5, 129.7, 129.6, 129.3, 129.2,129.1, 128.9, 128.7, 128.6, 127.7, 127.3, 127.2, 124.2, 120.0, 117.2, 111.8, 21.9, 21.6;

HRMS (ESI) calcd for $C_{25}H_{22}NO_3S^+$: 416.1315, Found: 416.1319.

6-(3-bromophenyl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3i)



3i

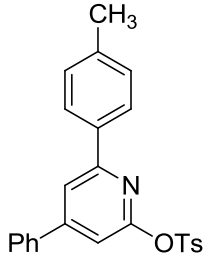
was obtained in 60% yield as white solid. mp：118-120℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.81-7.79 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 (dd, J_1 = 2.3 Hz, J_2 = 1.9 Hz, 2H), 7.54-7.49 (m, 4H) , 7.43 (d, *J* = 8.2 Hz, 2H) , 7.30-7.28 (m, 2H), 2.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 154.9, 154.2, 145.3, 139.6, 137.1, 134.5, 132.5, 130.2,130.1, 129.9, 129.8, 129.3, 128.8, 127.2, 125.3, 123.0, 117.2, 112.5, 21.9;

HRMS (ESI) calcd for $C_{24}H_{19}BrNO_3S^+$: 480.0264, Found: 480.0270.

4-phenyl-6-(p-tolyl)pyridin-2-yl 4-methylbenzenesulfonate (3j):



3j

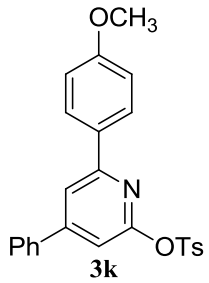
was obtained in 87% yield as white solid.， mp：121-123℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.99 (dt, J_1 = 4.0 Hz, J_2 = 3.9 Hz, 2H), 7.81 (d, *J* = 1.2 Hz, 1H), 7.67-7.64 (m, 4H), 7.53-7.47 (m, 3H) , 7.37 (dd, J_1 = 0.7 Hz, J_2 = 0.7 Hz, 2H) , 7.22-7.20 (m, 3H), 2.49 (s, 3H), 2.40 (s, 3H) ;

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 156.6, 153.8, 145.0, 139.8, 137.5, 134.8, 134.5, 129.6, 129.4, 129.2, 128.9, 127.2, 126.9, 116.7, 111.3, 21.8, 21.4;

HRMS (ESI) calcd for $C_{25}H_{22}NO_3S^+$: 416.1315, Found: 416.1320.

6-(4-methoxyphenyl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3k):



3k

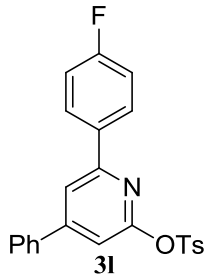
was obtained in 85% yield as white solid. mp：107-109℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.97 (d, *J* = 8.6 Hz, 2H) , 7.76 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.52-7.48 (m, 3H) , 7.37 (d, *J* = 10.5 Hz, 2H), 7.18 (s, 1H), 6.92 (d, *J* = 10.5 Hz, 2H), 3.87 (s, 3H), 2.48 (s, 3H) ;

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 157.7, 156.4, 153.8, 145.1, 137.7, 130.3, 129.7, 129.8, 128.9 ,128.5, 127.2, 116.3, 114.0, 110.9, 55.1, 21.9;

HRMS (ESI) calcd for $C_{25}H_{22}NO_4S^+$: 432.1264, Found: 432.1268.

6-(4-fluorophenyl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3l):



3l

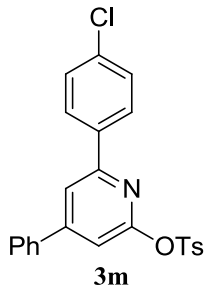
was obtained in 81% yield as white solid. mp: 105-107℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, J_1 = 3.9 Hz, J_2 = 3.8 Hz, 2H), 7.78-7.73 (m, 3H), 7.66-7.63(m, 2H), 7.54-7.46 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.12-7.06 (m, 2H), 2.49 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 162.6, 157.7, 155.5, 154.0, 145.1, 129.6, 129.3, 128.9, 128.8, 128.7, 127.2, 116.7, 115.7, 115.5, 111.6, 21.8;

HRMS (ESI) calcd for $C_{24}H_{19}FNO_3S^+$: 420.1064, Found: 420.1069

6-(4-chlorophenyl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3m):



3m

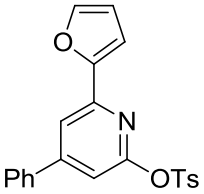
was obtained in 78 % yield as white solid. mp: 106-108℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.8 (d, *J* = 0.8 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.65 (dd, J_1 = 2.2 Hz, J_2 = 1.7 Hz, 2H), 7.54-7.49 (m, 3H) , 7.37 (d, *J* = 8.7 Hz, 5H), 2.49 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 154.2, 145.2, 137.3, 136.1, 135.8, 134.5, 129.9, 129.7, 129.4, 128.9, 128.3, 127.2,116.9, 112.0, 21.9;

HRMS (ESI) calcd for $C_{24}H_{19}ClNO_3S^+$: 436.0769, Found: 436.0773.

6-(furan-2-yl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3n):



3n

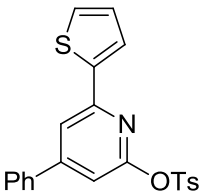
was obtained in 73% yield as white solid. m.p 137-138℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.8 (d, *J* = 1.2 Hz, 1H), 7.66 (dd, J_1 = 1.7 Hz, J_2 = 1.4 Hz, 2H), 7.52-7.47 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.2 (d, *J* = 1.2 Hz, 1H), 6.8 (d, *J* = 3.4 Hz, 1H), 6.51 (m, 1H), 2.48 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 153.8, 152.6, 148.4, 145.2, 143.8, 137.2, 134.4, 129.8, 129.6, 129.3, 129.0, 127.2, 114.9, 112.3, 111.2, 110.1, 21.6;

HRMS (ESI) calcd for $C_{22}H_{18}NO_4S^+$: 392.0951, Found: 392.0955

4-phenyl-6-(thiophen-2-yl)pyridin-2-yl 4-methylbenzenesulfonate (3o):



3o

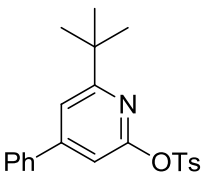
was obtained in 59% yield as white solid. mp: 133-135℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.8 (d, *J* = 1.3 Hz, 1H), 7.66 (dd, J_1 = 2.2 Hz, J_2 = 1.9 Hz, 2H), 7.52-7.46 (m, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 3.7 Hz, 1H), 6.51 (m, 1H), 2.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 153.4, 151.1, 145.5, 142.5, 137.5, 134.6, 129.8, 129.7, 129.3, 128.9, 128.4, 128.1, 127.2, 125.8, 114.9, 110.7, 21.6;

HRMS (ESI) calcd for $C_{22}H_{18}NO_3S_2^+$: 408.0723, Found: 408.0723.

6-(tert-butyl)-4-phenylpyridin-2-yl 4-methylbenzenesulfonate (3p):

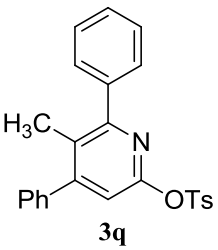


3p

was obtained in 75% yield as white solid. 89-91℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.59 (dt, J_1 = 3.9 Hz, J_2 = 3.3 Hz , 1H), 7.51-7.43 (m, 3H), 7.38 (d, *J* = 1.4 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 1.2 Hz, 1H), 2.45 (s, 3H), 1.19 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 156.9, 153.2, 144.8, 137.9, 134.5, 129.5, 129.4, 129.1, 128.7, 127.2, 116.0, 110.5, 37.6, 29.8, 21.7;



3q

HRMS (ESI) calcd for $C_{22}H_{24}NO_3S^+$: 382.1471, Found: 382.1475.

5-methyl-4,6-diphenylpyridin-2-yl 4-methylbenzenesulfonate (3q):

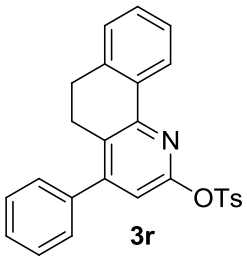
was obtained in 42% yield as white solid. mp： 80-82℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, J_1 = 3.6 Hz, J_2 = 3.5 Hz , 2H), 7.5-7.33 (m , 10 H), 7.32 (dd, J_1 = 0.8 Hz, J_2 = 0.8 Hz, 2H), 7.01 (s, 1H), 2.45 (s, 3H), 2.19 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 155.4, 154.3, 145.0, 139.4, 138.9, 134.1, 129.5, 129.4, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 114.6, 21.7, 17.9;

HRMS (ESI) calcd for $C_{25}H_{22}NO_3S^+$: 416.1315, Found: 416.1318.

4-phenyl-5,6-dihydrobenzo[h]quinolin-2-yl 4-methylbenzenesulfonate(3r):



3r

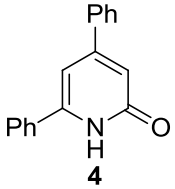
was obtained in 65% yield as white solid. mp：145-147℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.3 Hz , 2H), 7.70 (d , J = 7.9, 1H), 7.49-7.44 (m, 3H), 7.40-7.39 (d, J = 8.6, 2H), 7.33-7.23(m, 4H), 7.18 (d , J = 7.3, 1H), 6.96 (s, 1H), 2.83 (dq, J_1 =15.7, J_2 =14.2, 4H), 2.5(s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 153.1, 151.9, 145.0, 138.1, 137.9, 134.8, 133.8, 129.7, 129.6, 128.9, 128.7, 128.6, 128.6, 128.4, 127.6, 126.9, 125.9, 114.6, 27.9, 25.1, 21.8;

HRMS (ESI) calcd for $C_{26}H_{22}NO_3S^+$: 428.1315, Found: 428.1301.

4,6-diphenylpyridin-2(1H)-one(4):



4

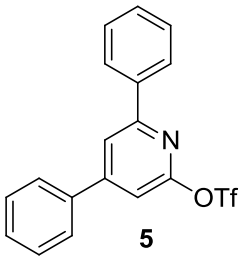
was obtained in 96% yield as white solid. mp：207-208℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.27(s, 1H), 7.76-7.74 (d, J = 7.8 Hz, 2H), 7.65 (dt , J_1 = 3.0, J_2 = 2.3 Hz ,1H), 7.55-7.45 (m,7H), 6.75 (dd, J_1 = 1.7 Hz, J_2 = 2.4 Hz , 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 153.9, 146.9, 138.2, 133.8, 130.2, 129.6, 129.3, 129.1, 127.0, 126.9, 115.3, 105.0;

HRMS (ESI) calcd for $C_{17}H_{14}NO^+$: 248.1070, Found: 248.1068.

4,6-diphenylpyridin-2-yl trifluoromethanesulfonate(5):



5

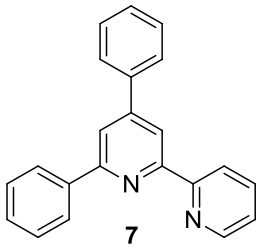
was obtained in 93% yield as light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, J_1 = 1.6 Hz, J_2 = 1.3 Hz , 2H), 8.0 (d , J = 1.1, 1H), 7.69 (dd, J_1 = 1.8 Hz, J_2 = 1.2 Hz , 2H), 7.57-7.48 (m, 6H), 7.27 (d , J = 1.2, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 156.6, 154.9, 136.9, 130.2, 130.1, 129.4, 129.0, 127.2, 127.1, 123.6, 120.4, 118.4, 117.2, 114.0, 110.8;

HRMS (ESI) calcd for $C_{18}H_{13}F_3NO_3S^+$: 380.0563, Found: 380.0552.

4,6-diphenyl-2,2'-bipyridine(7):



7

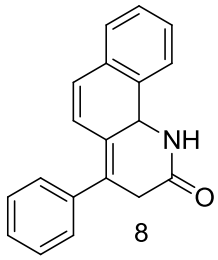
was obtained in 41% yield as white solid. mp：136-137℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dq, J_1 = 2.7 Hz, J_2 = 2.7 Hz , 2H), 8.66 (d , J = 1.6, 1H), 8.22 (dt, J_1 = 3.3 Hz, J_2 = 2.4 Hz, 2H), 8.0 (d, J = 1.4, 1H), 7.87 (td , J_1 = 2.1, J_2 = 1.9, J_3 = 2.0, 1H), 7.83 (dt, J_1 = 3.4 Hz, J_2 = 2.9 Hz, 2H), 7.55-7.51(m, 4H), 7.49-7.45(m, 2H), 7.36-7.33(m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 156.5, 156.4, 150.4, 149.2, 139.6, 138.9, 136.9, 129.2, 129.1, 128.8, 127.4, 127.2, 123.9, 121.6, 118.6, 117.6 ;

HRMS (ESI) calcd for $C_{22}H_{17}N_2$+: 309.1386, Found: 309.1379.

4-phenyl-1,10b-dihydrobenzo[h]quinolin-2(3H)-one(8):



8

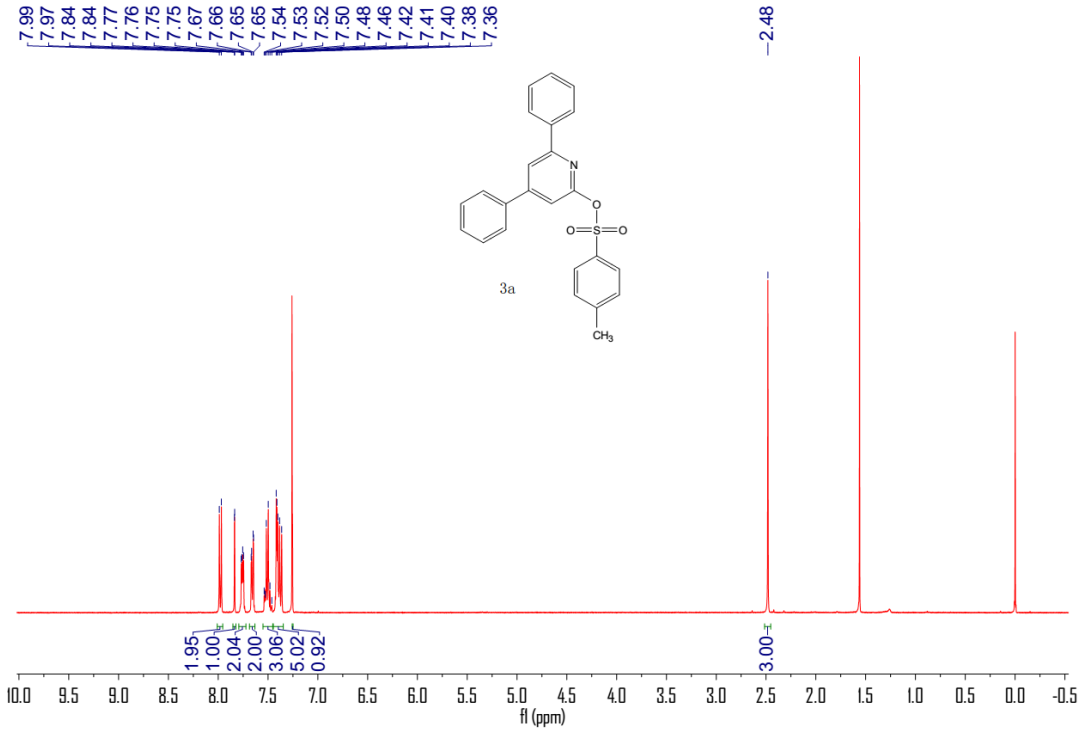
was obtained in 40% yield as white solid[6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.72 (dd, J = 8.7 Hz, 1H), 7.89 (dd, J_1 = 1.3 Hz, J_2 = 1.4 Hz, 1H), 7.75-7.72 (m, 1H), 7.68-7.65 (m, 1H), 7.57-7.50 (m, 7H), 6.83 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 154.2, 137.6, 135.9, 134.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.2, 123.4, 122.8, 122.2, 121.5, 120.8, 115.7.

HRMS (ESI) calcd for $C_{19}H_{16}NO^+$: 274.1226, Found: 274.1218.

NMR spectra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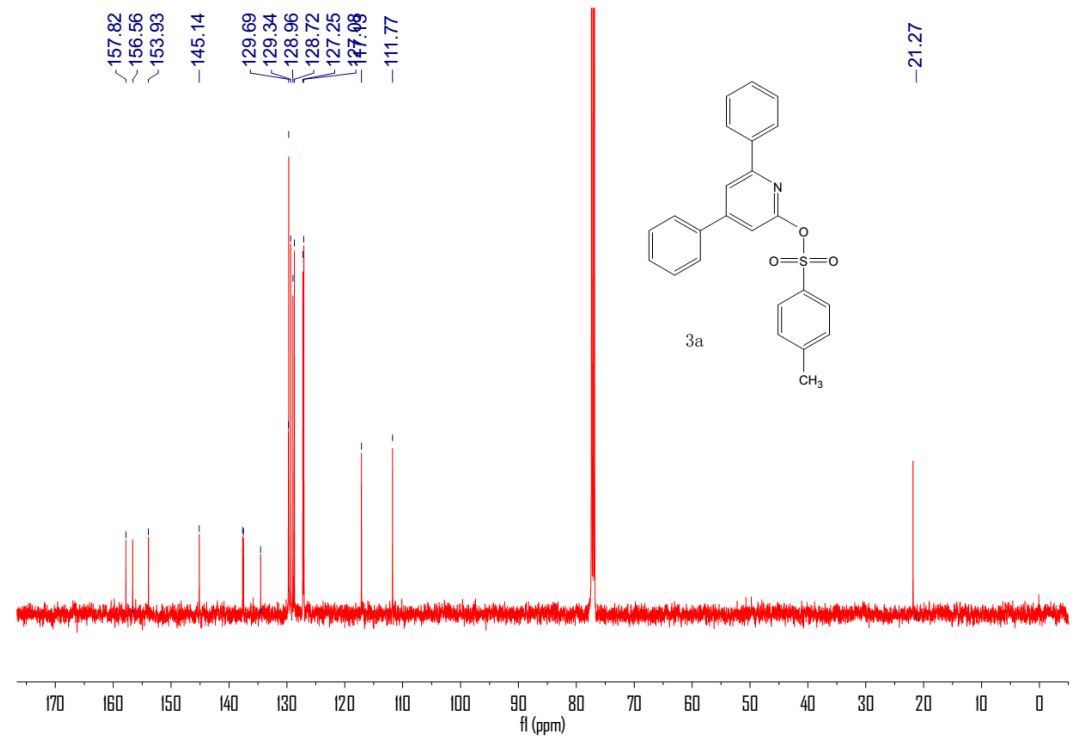
7.97
7.84
7.84
7.77
7.76
7.75
7.75
7.67
7.66
7.65
7.65
7.54
7.53
7.52
7.50
7.48
7.46
7.42
7.41
7.40
7.38
7.36
2.48
3a
CH3
1.95
1.00
2.04
2.00
3.06
5.02
0.92
3.00
f1 (ppm)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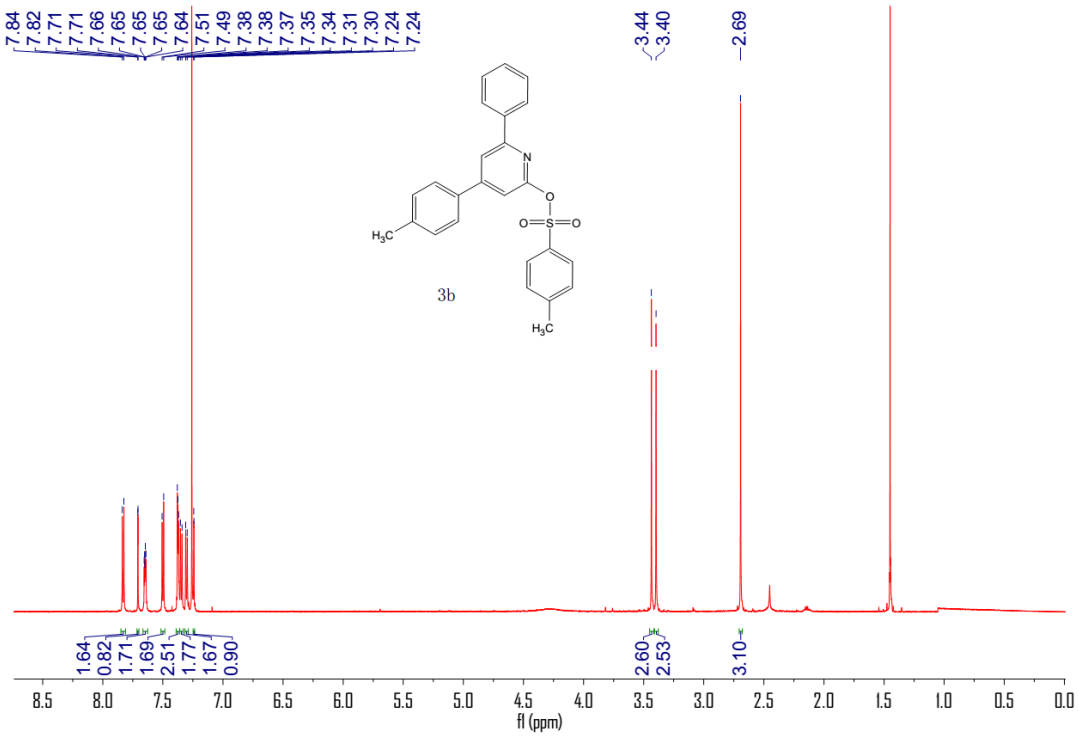
111.77
21.27
3a
CH3
f1 (ppm)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7.37
7.35
7.34
7.31
7.30
7.24
7.24
3.44
3.40
2.69
3b
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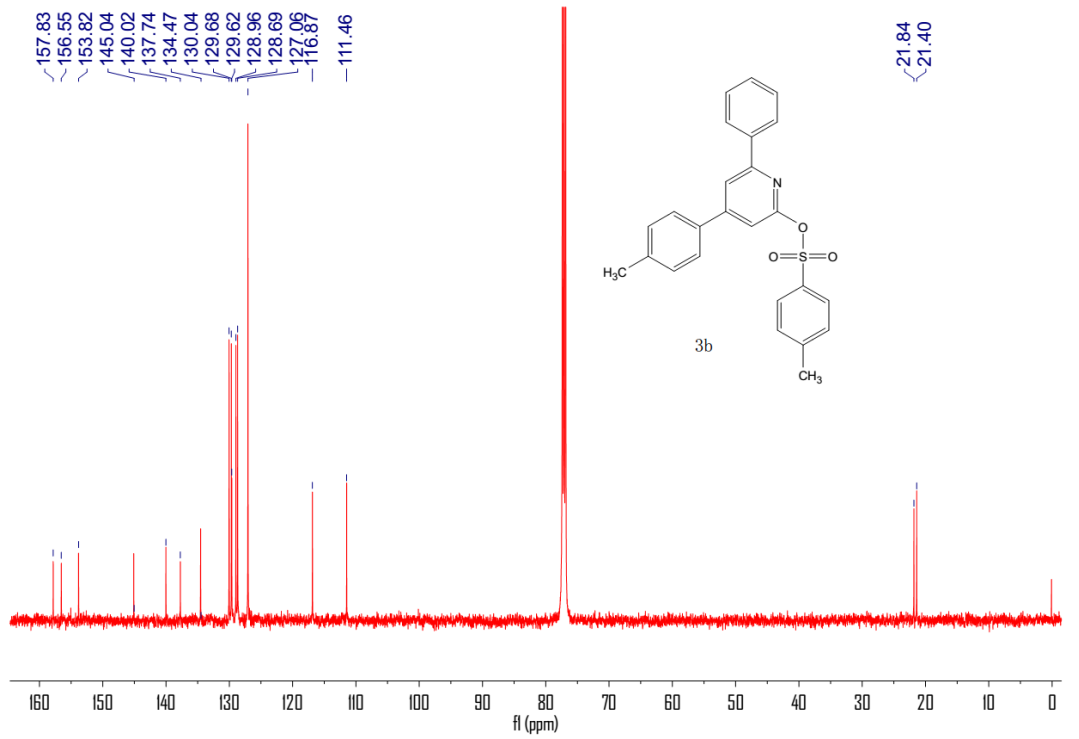
3.10
f1 (ppm)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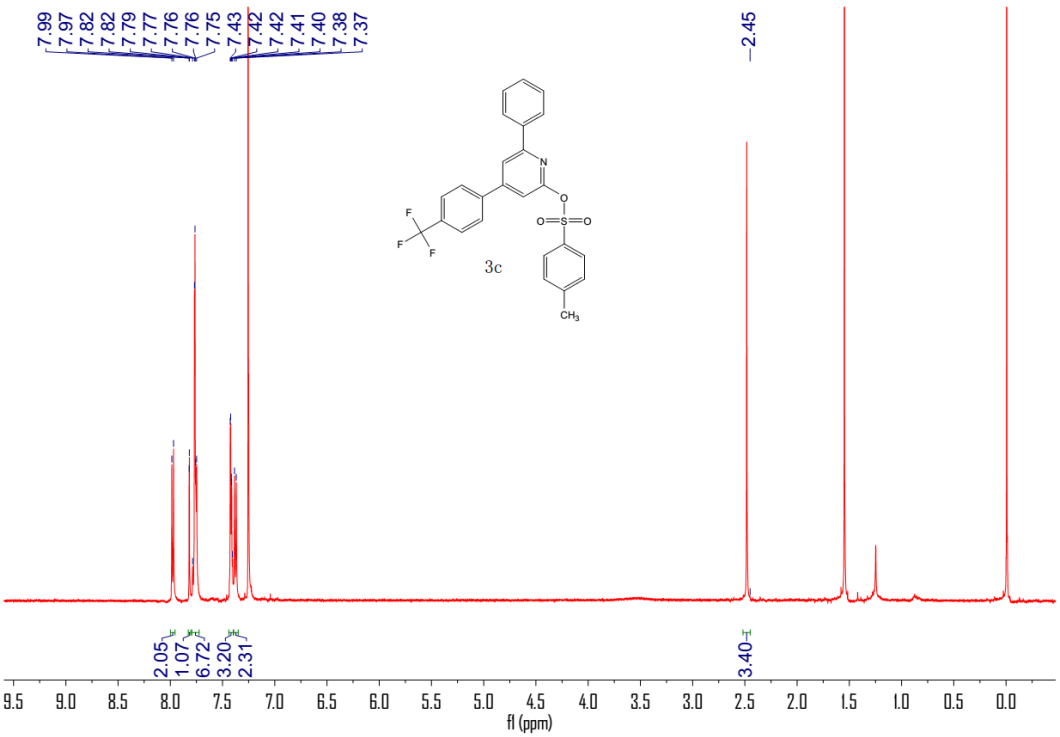
111.46
21.84
21.40
3b
f1 (ppm)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7.42
7.41
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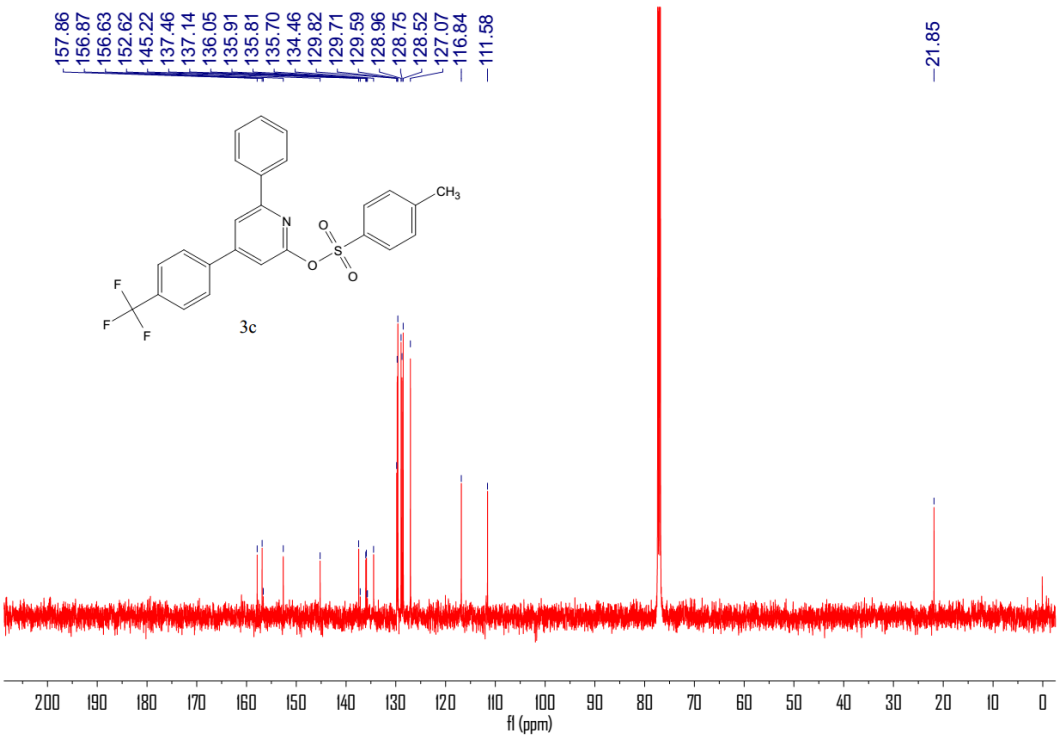
1.07
6.72
3.20
2.31
3.40
fl (ppm)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152.62
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135.70
134.46
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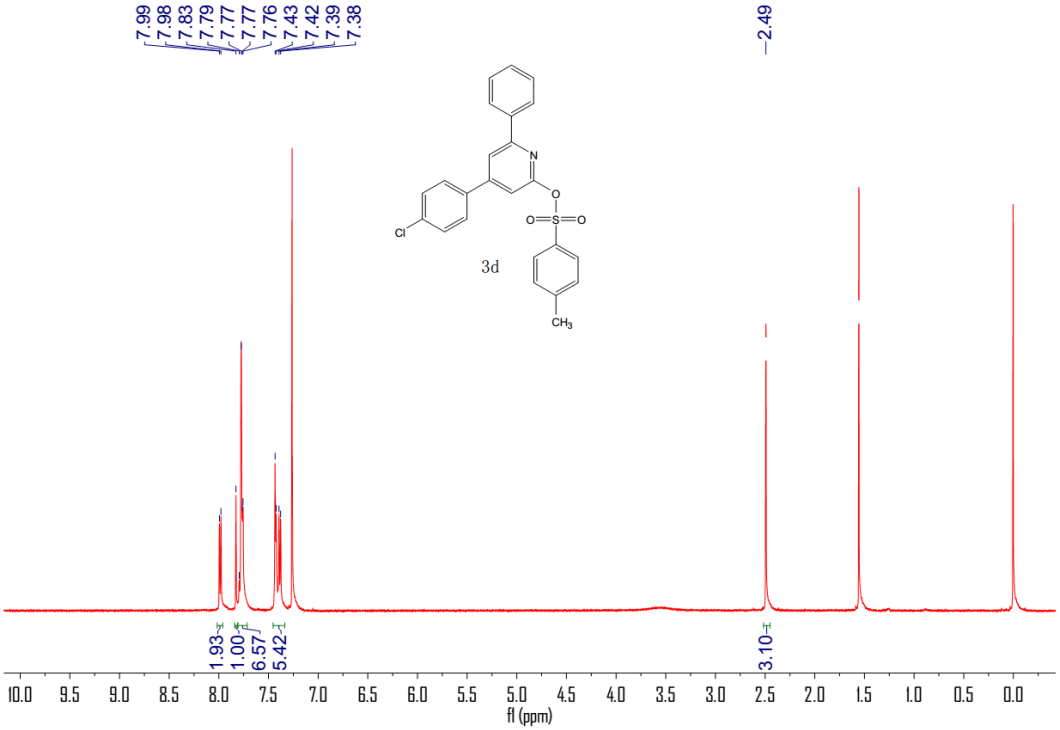
128.75
128.52
127.07
116.84
111.58
21.85
3c
fl (ppm)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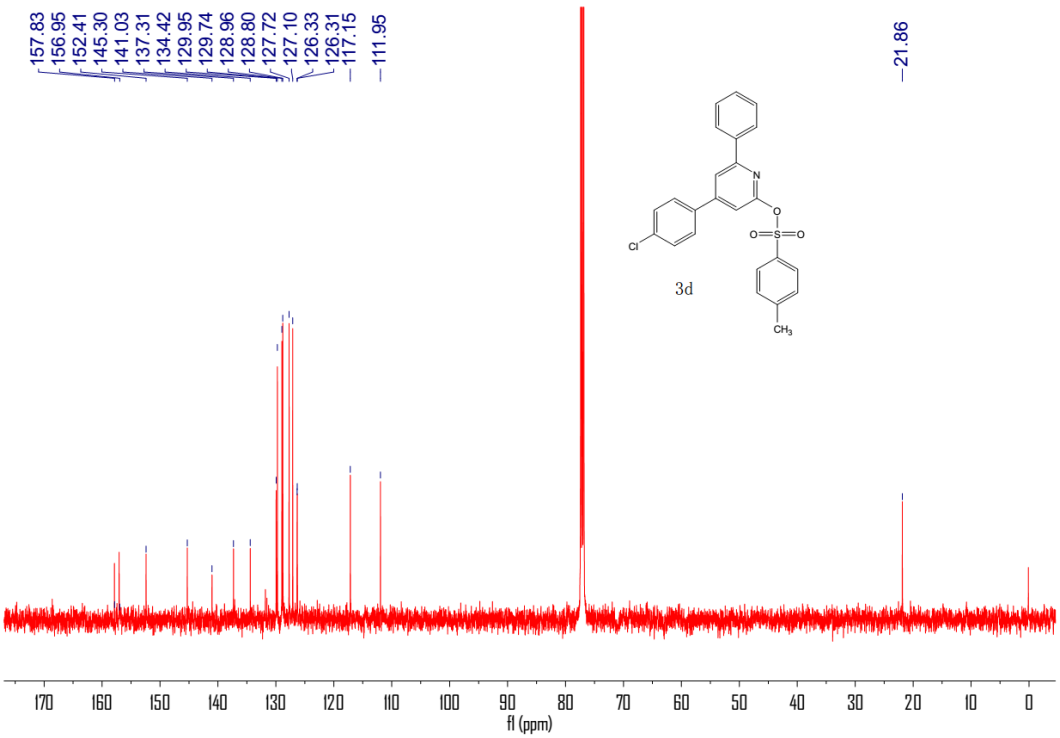
7.43
7.42
7.39
7.38
2.49
3d
1.93
1.00
6.57
5.42
3.10
fl (ppm)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137.31
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129.95
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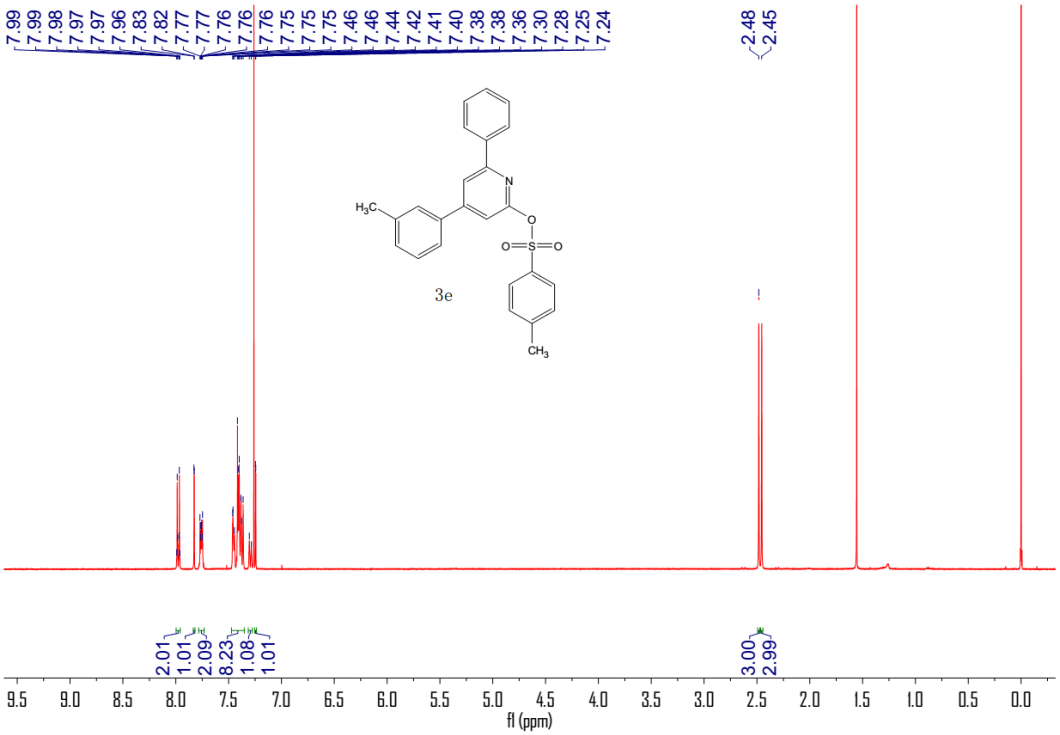
128.80
127.72
127.10
126.33
126.31
117.15
111.95
21.86
3d
fl (ppm)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7.76
7.75
7.75
7.75
7.46
7.46
7.44
7.42
7.41
7.40
7.38
7.38
7.36
7.30
7.28
7.25
7.24
2.48
2.45
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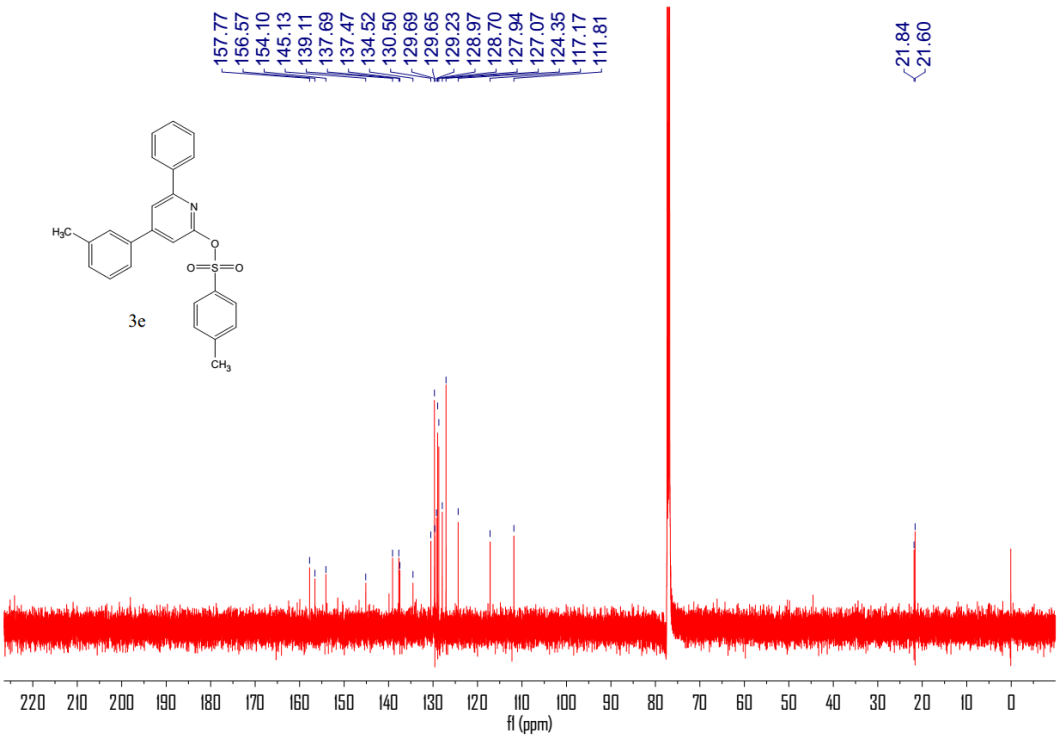
1.01
2.09
8.23
1.08
1.01
3.00
2.99
f1 (ppm)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129.65
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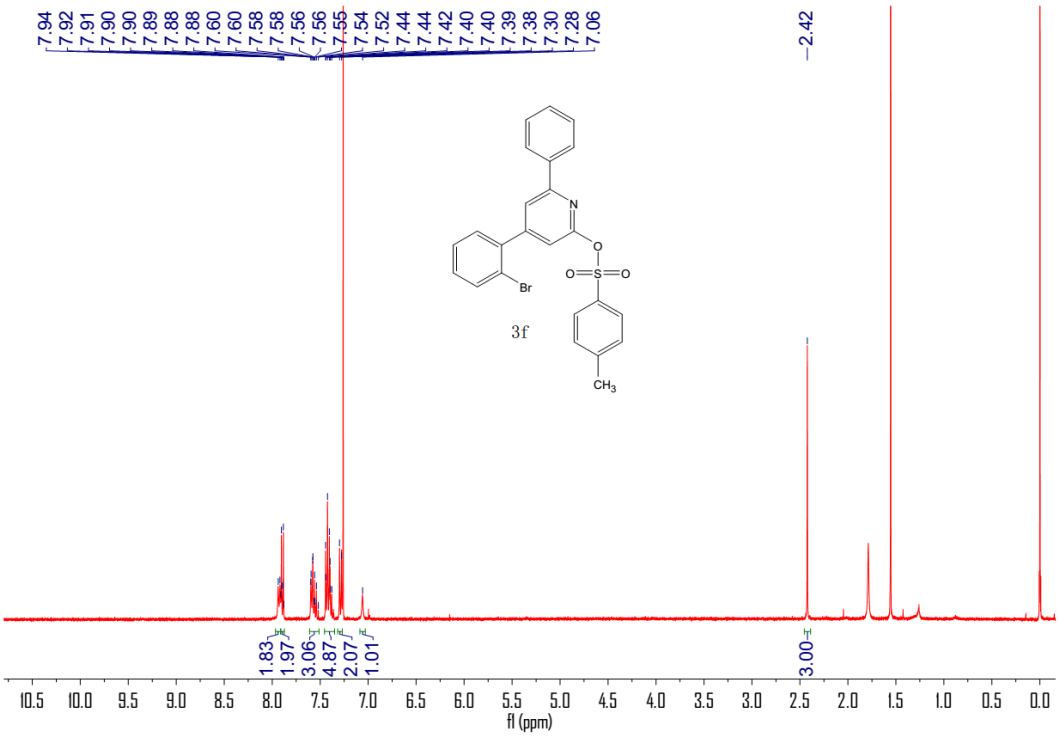
127.07
124.35
117.17
111.81
21.84
21.60
3e
f1 (ppm)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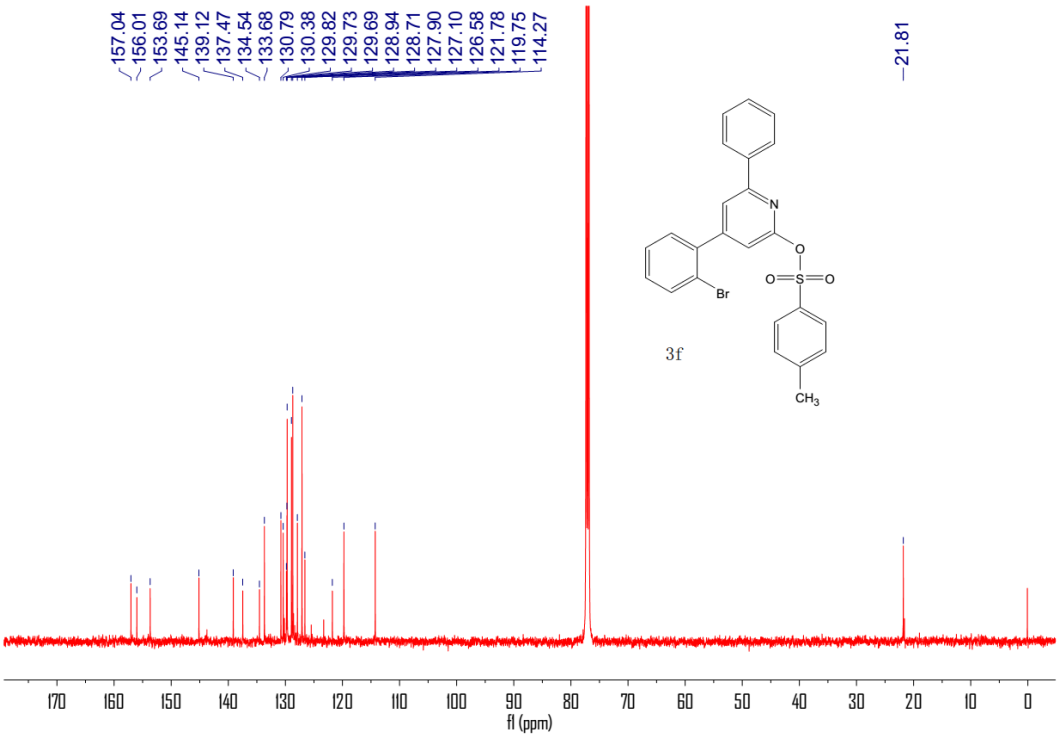
7.58
7.58
7.56
7.56
7.55
7.54
7.52
7.44
7.44
7.42
7.40
7.40
7.39
7.38
7.30
7.28
7.06
2.42
N
O
O=S=O
Br
3f
CH3
1.83
1.97
3.06
4.87
2.07
1.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.68
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130.38
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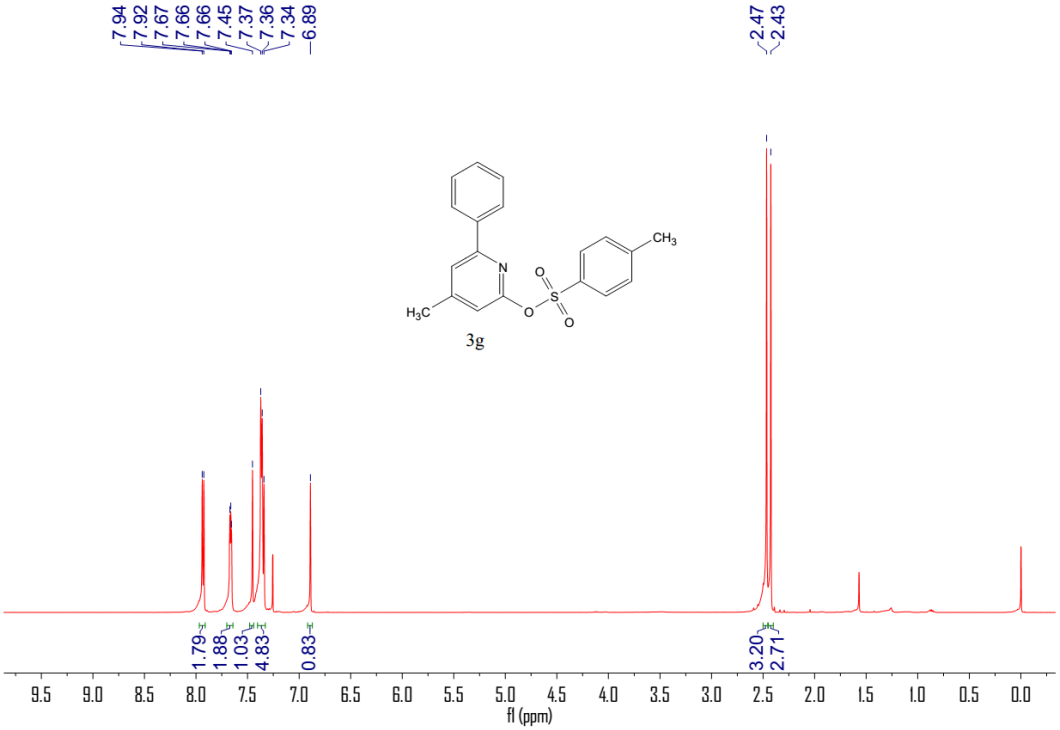
129.73
129.69
128.94
128.71
127.90
127.10
126.58
121.78
119.75
114.27
21.81
N
O
O=S=O
Br
3f
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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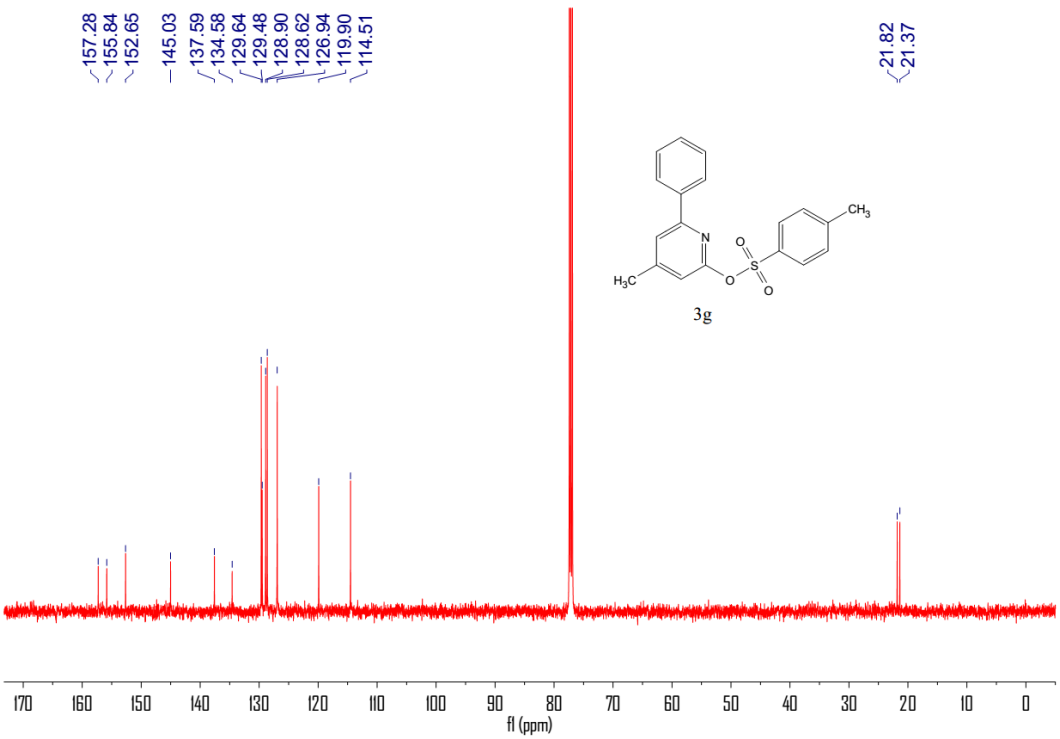
3g
1.79
1.88
1.03
4.83
0.83
3.20
2.71
f1 (ppm)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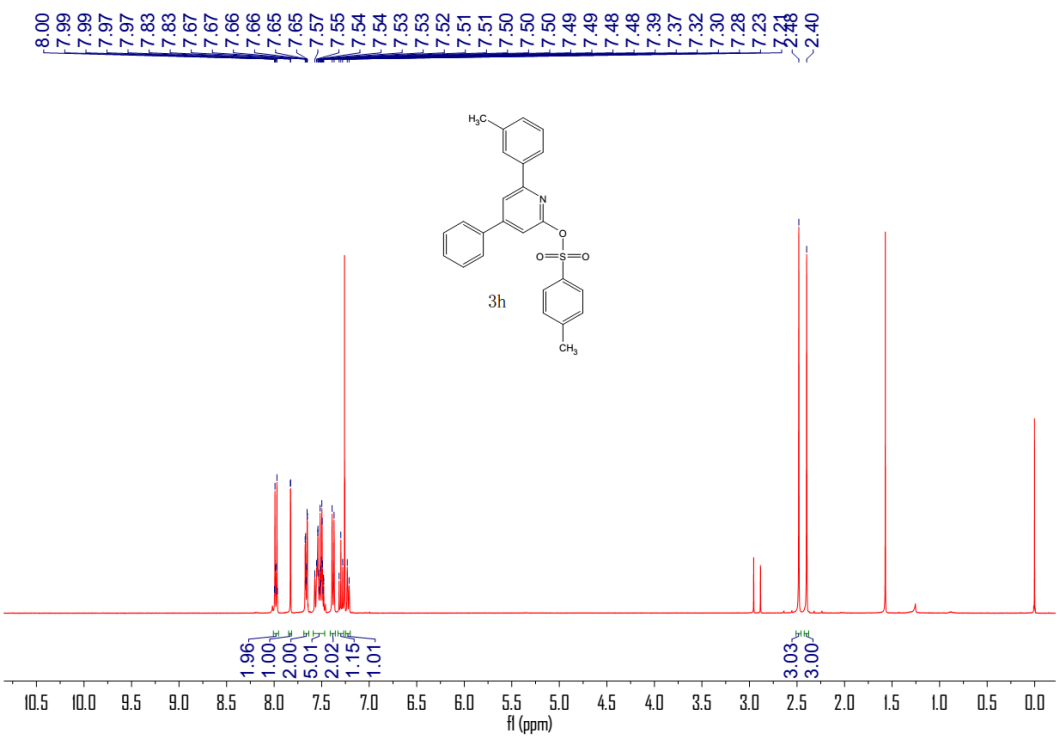
119.90
114.51
21.82
21.37
3g
f1 (ppm)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7.54
7.54
7.53
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7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.39
7.37
7.32
7.30
7.28
7.23
2.48
2.40
3h
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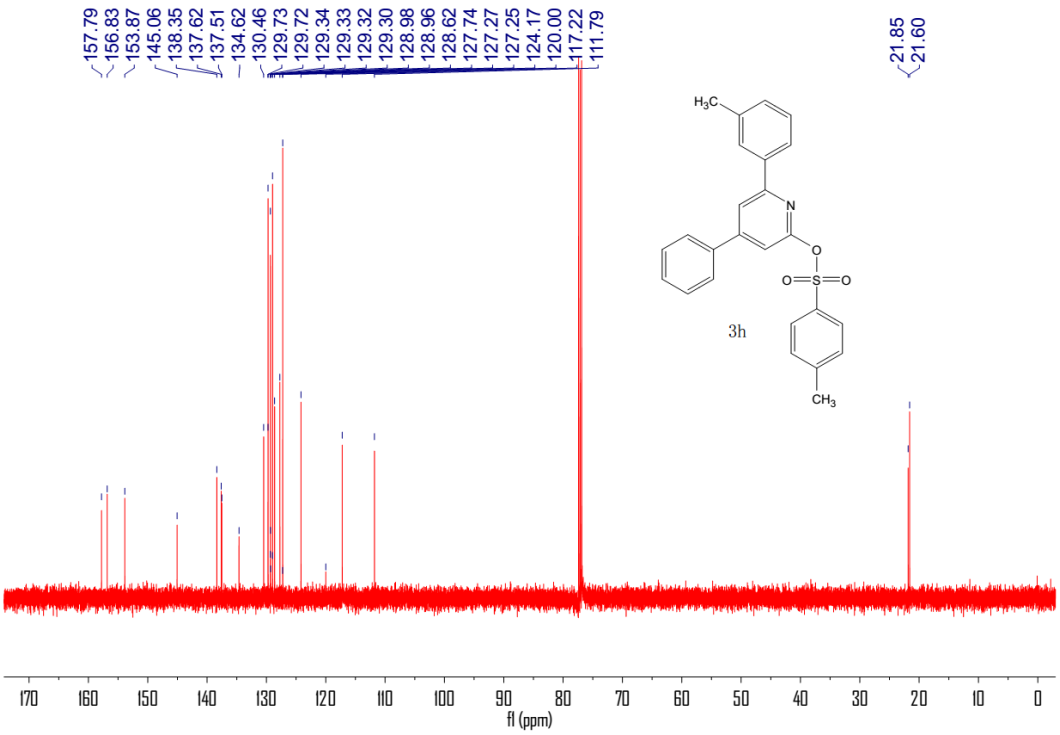
1.00
2.00
5.01
2.02
1.15
1.01
3.03
3.00
f1 (ppm)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134.62
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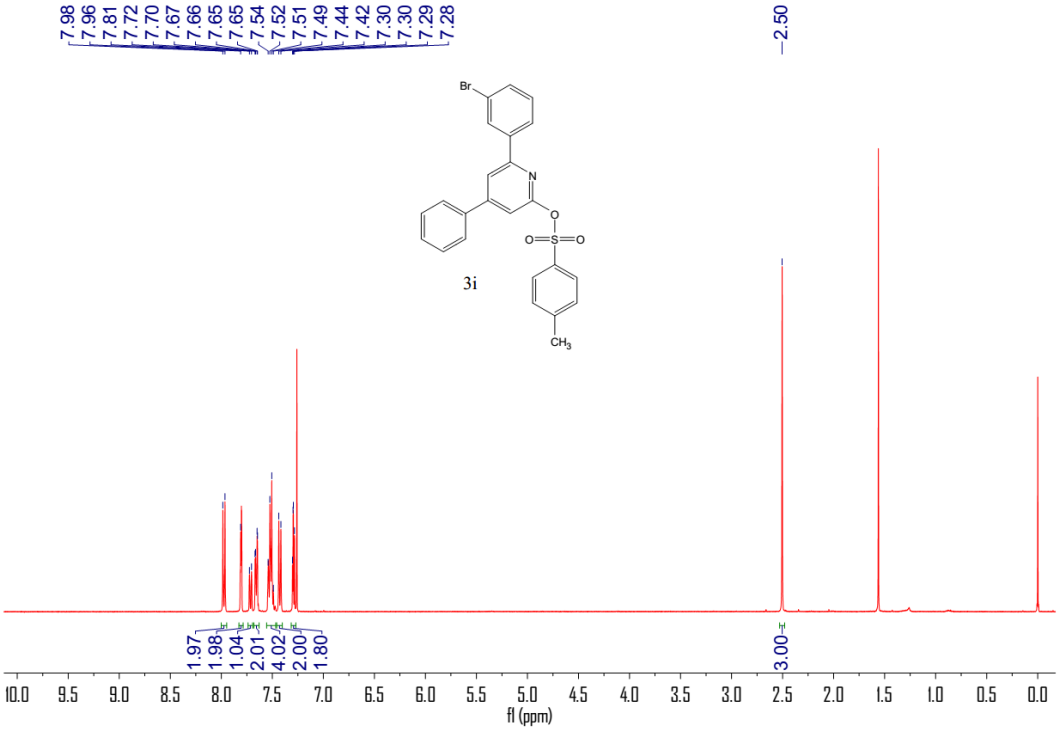
129.72
129.34
129.33
129.32
129.30
128.98
128.96
128.62
127.74
127.27
127.25
124.17
120.00
117.22
111.79
21.85
21.60
3h
f1 (ppm)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7.65
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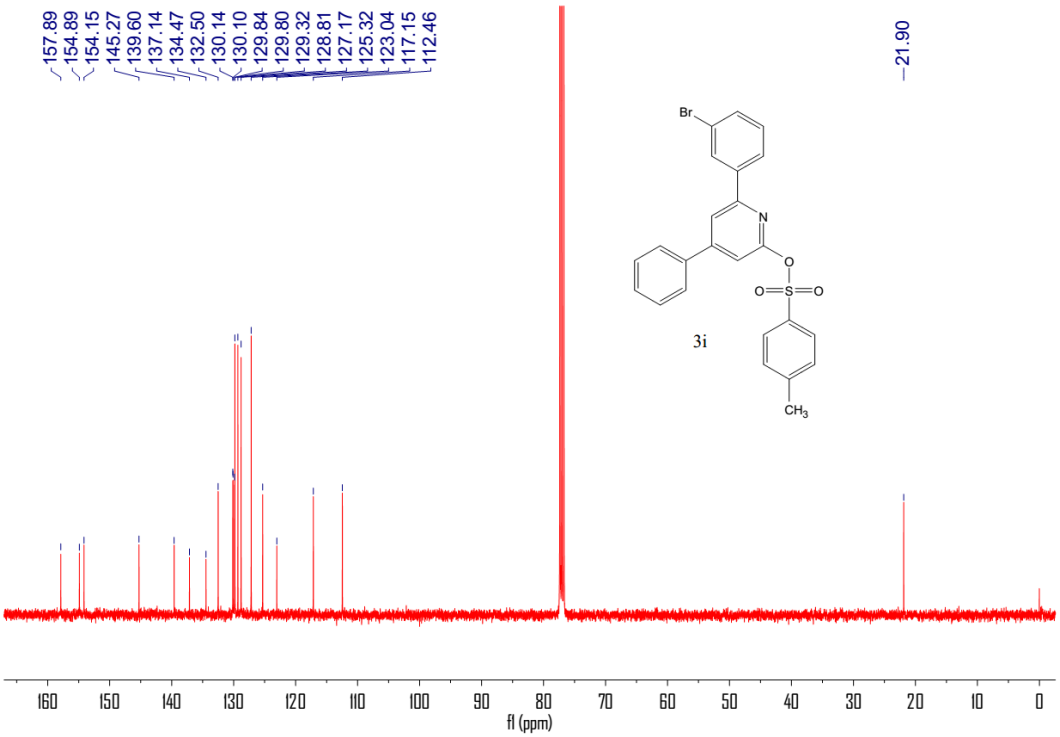
7.52
7.51
7.49
7.44
7.42
7.30
7.30
7.29
7.28
2.50
Br
N
O
O=S=O
CH3
3i
1.97
1.98
1.04
2.01
4.02
2.00
1.80
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.14
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132.50
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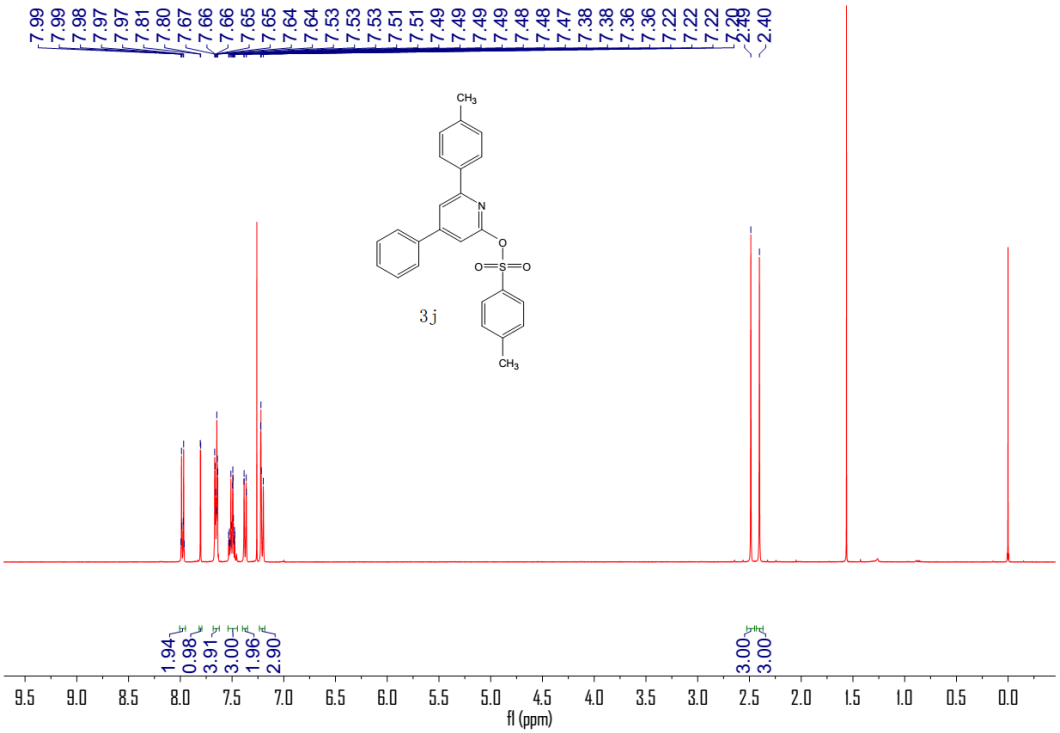
130.10
129.84
129.80
129.32
128.81
127.17
125.32
123.04
117.15
112.46
21.90
Br
N
O
O=S=O
CH3
3i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.47
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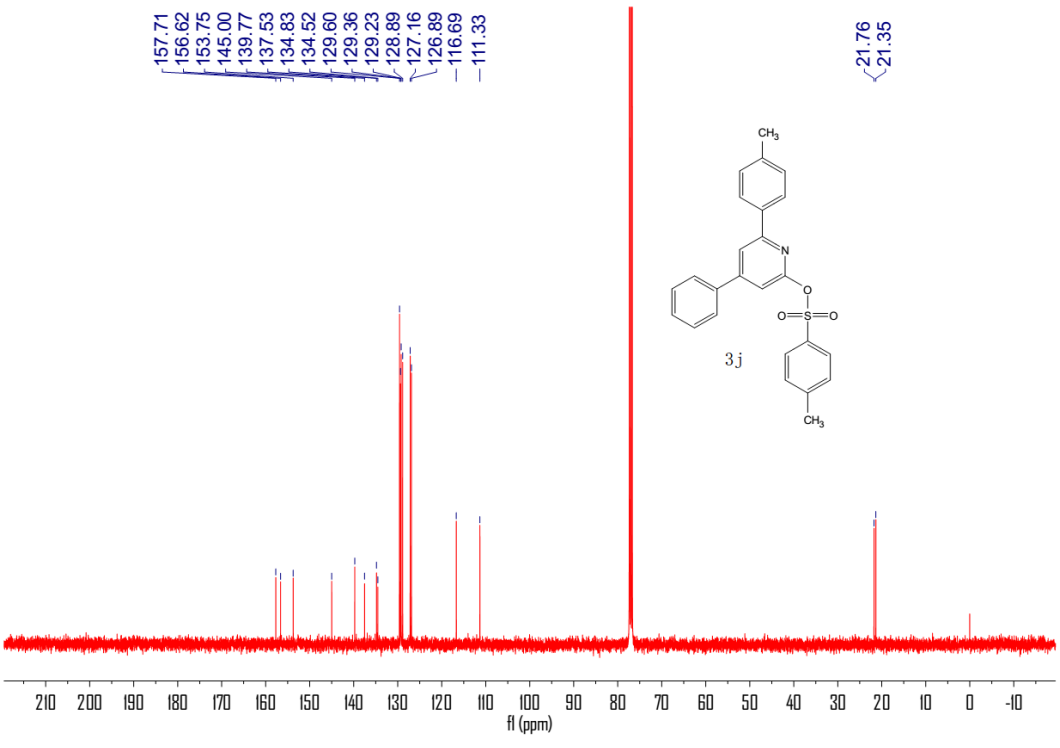
7.38
7.36
7.36
7.22
7.22
2.49
2.40
CH3
N
O
O=S=O
3j
CH3
1.94
0.98
3.91
3.00
1.96
2.90
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.36
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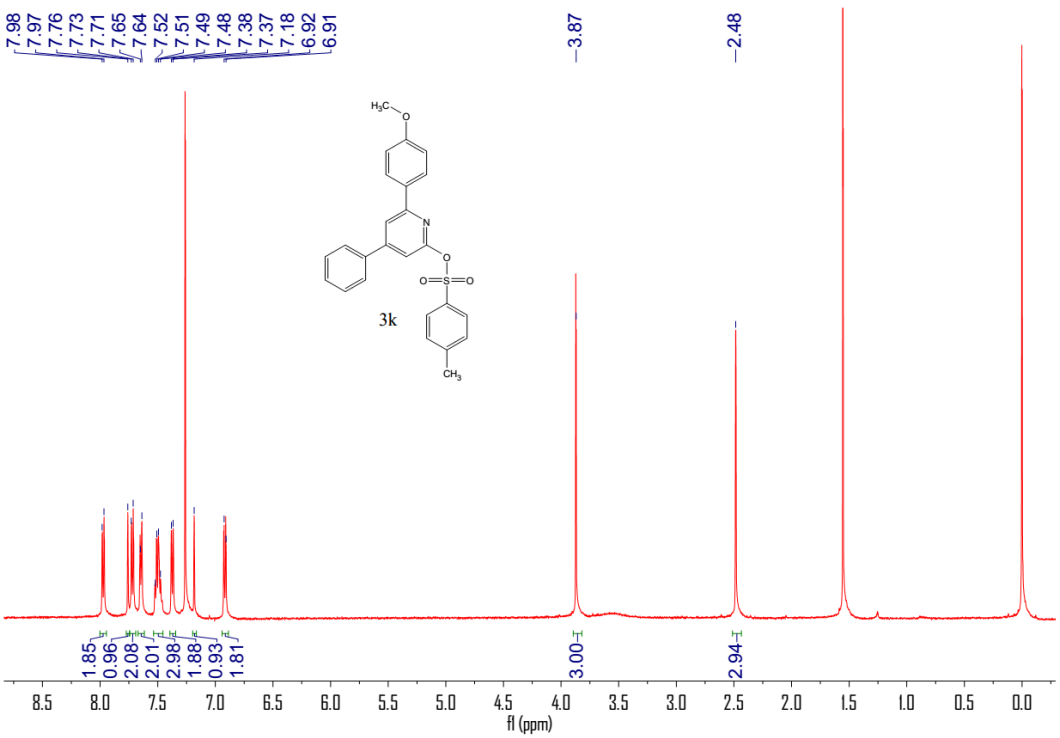
127.16
126.89
116.69
111.33
21.76
21.35
CH3
N
O
O=S=O
3j
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.64
7.52
7.51
7.49
7.48
7.38
7.37
7.18
6.92
6.91
3.87
2.48
3k
1.85
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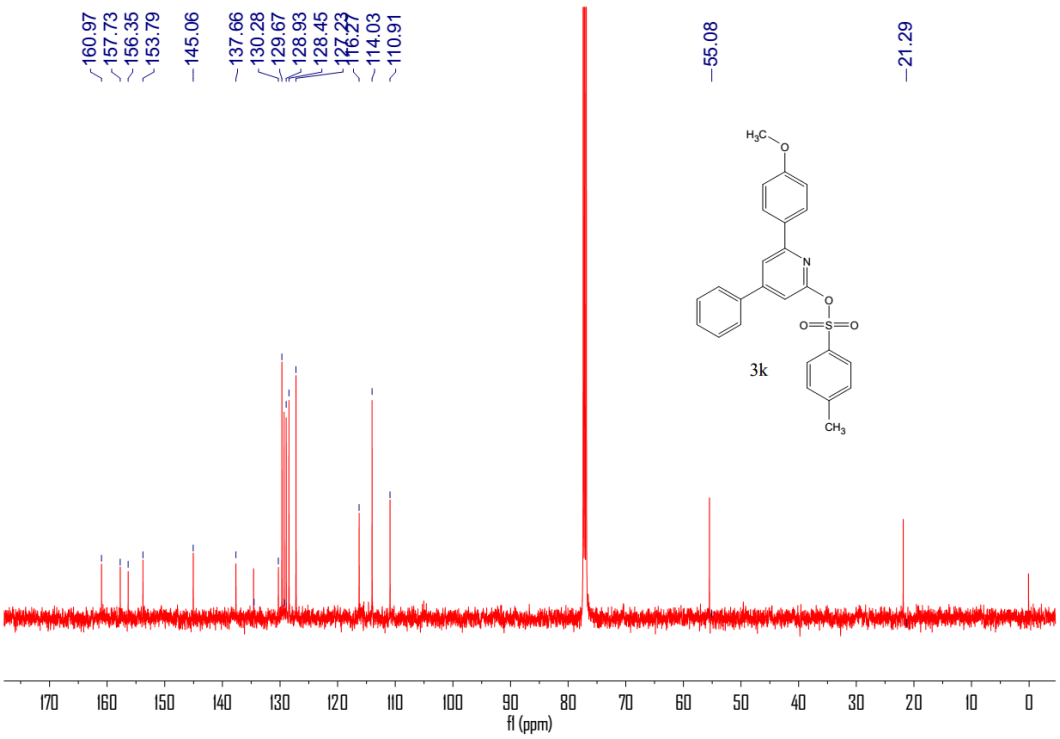
2.08
2.01
2.98
1.88
0.93
1.81
3.00
2.94
f1 (ppm)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129.67
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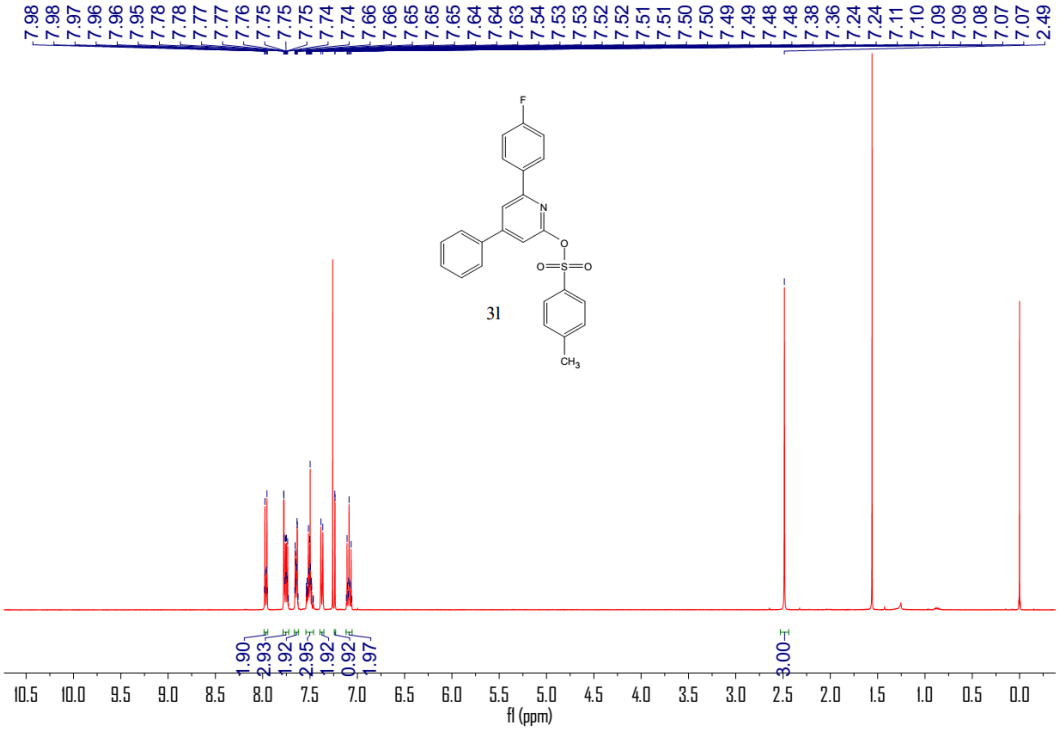
128.45
114.03
110.91
55.08
21.29
3k
f1 (ppm)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7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.38
7.36
7.24
7.24
7.11
7.10
7.09
7.09
7.08
7.07
7.07
2.49
F
N
O
O=S=O
CH3
31
1.90
2.93
1.92
2.95
1.92
0.92
1.97
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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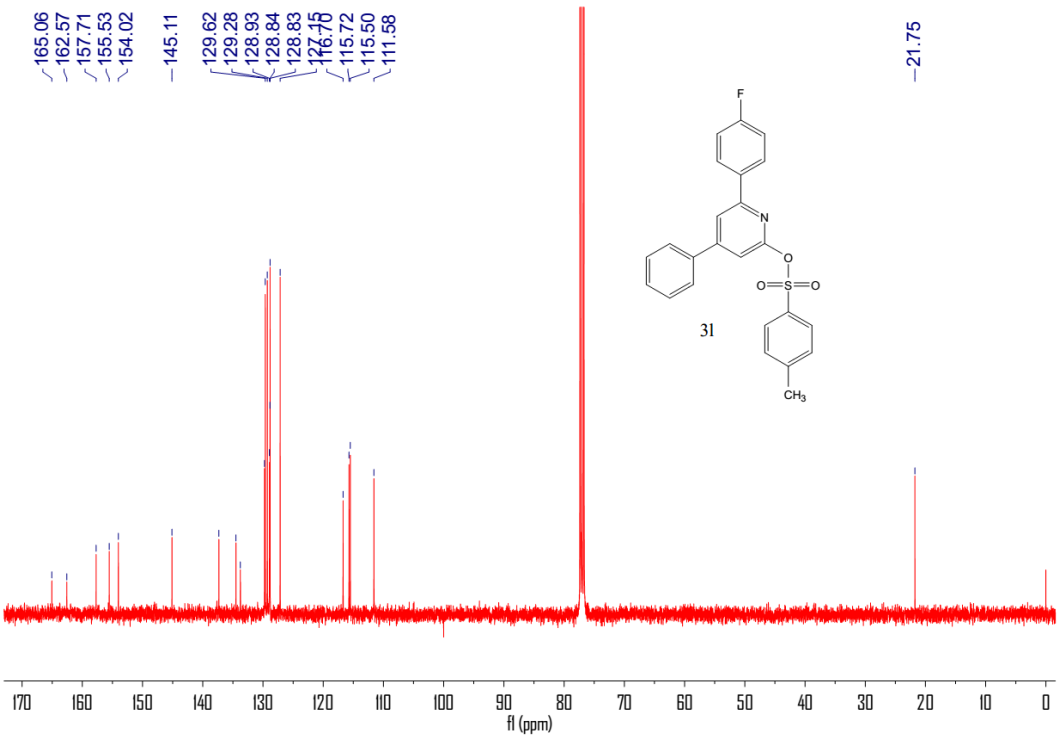
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.28
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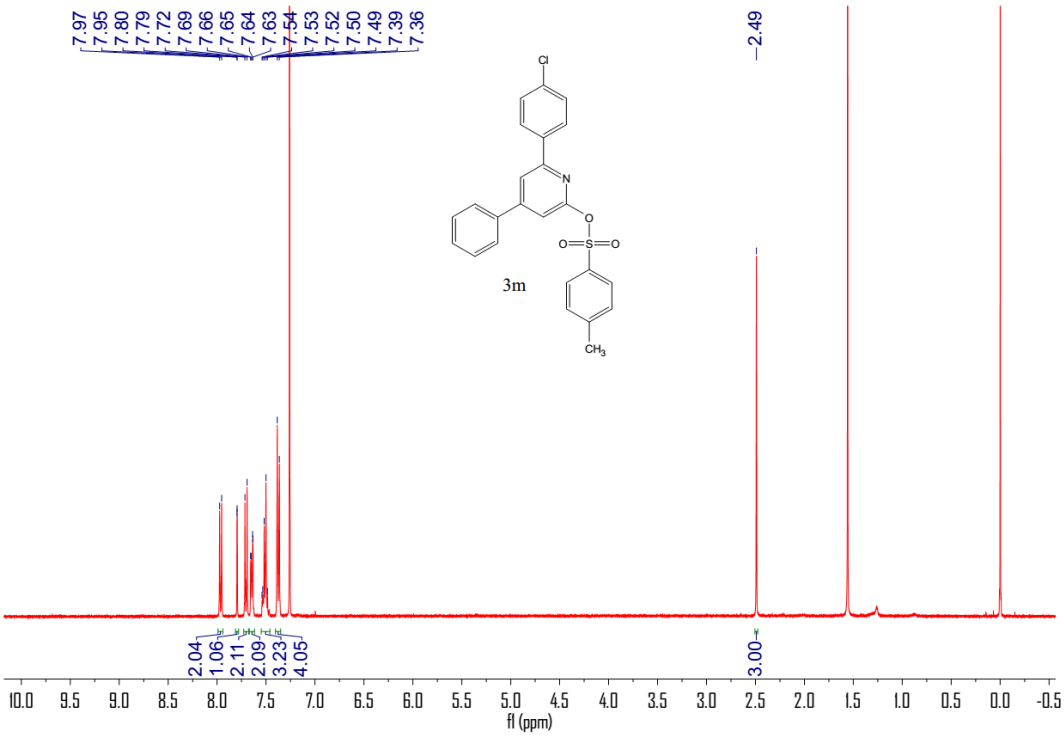
128.84
128.83
127.15
116.70
115.72
115.50
111.58
21.75
F
N
O
O=S=O
CH3
31
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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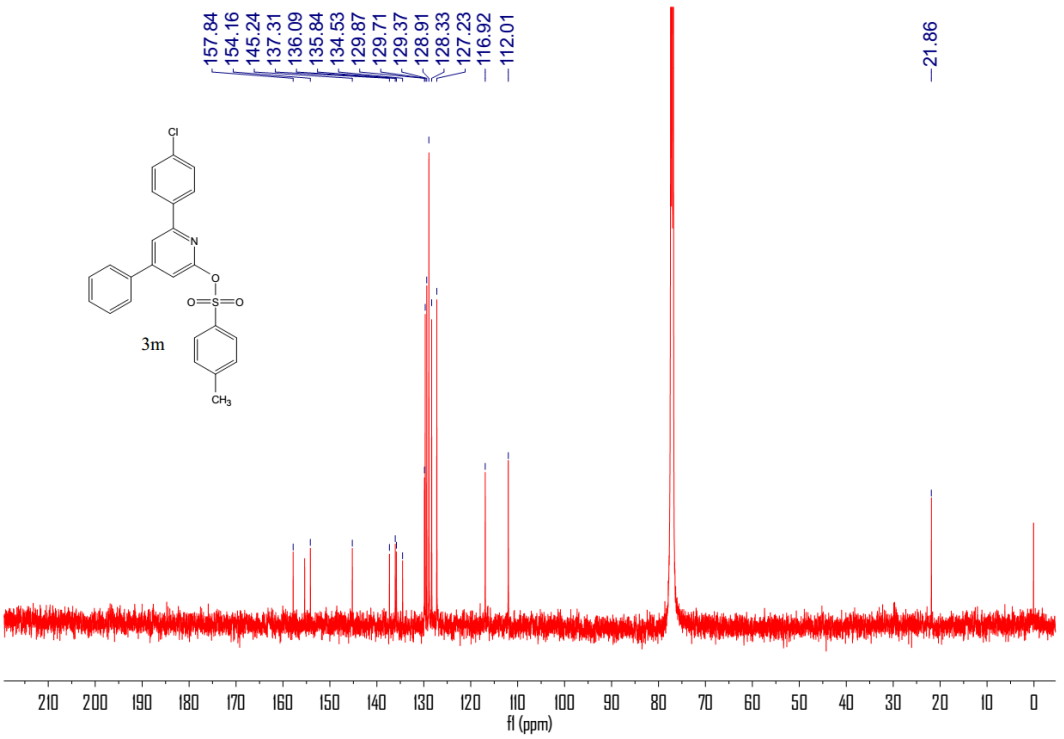
7.66
7.65
7.64
7.63
7.54
7.53
7.52
7.50
7.49
7.39
7.36
2.49
Cl
N
O
O=S=O
3m
CH3
2.04
1.06
2.11
2.09
3.23
4.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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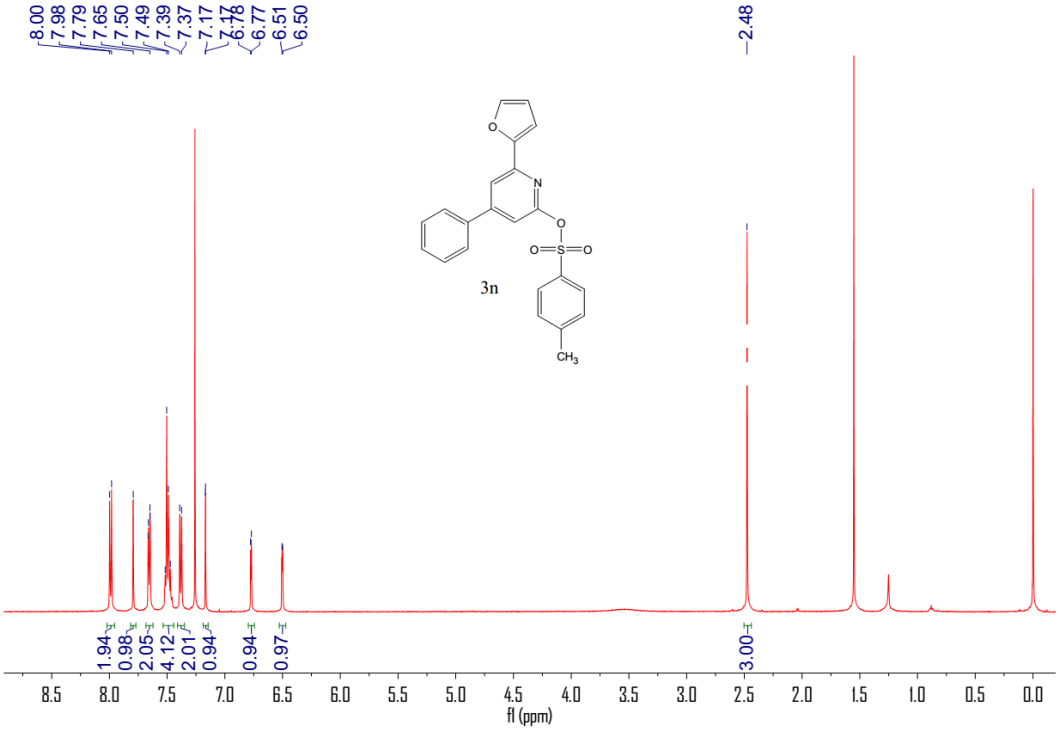
129.87
129.71
129.37
128.91
128.33
127.23
116.92
112.01
21.86
Cl
N
O
O=S=O
3m
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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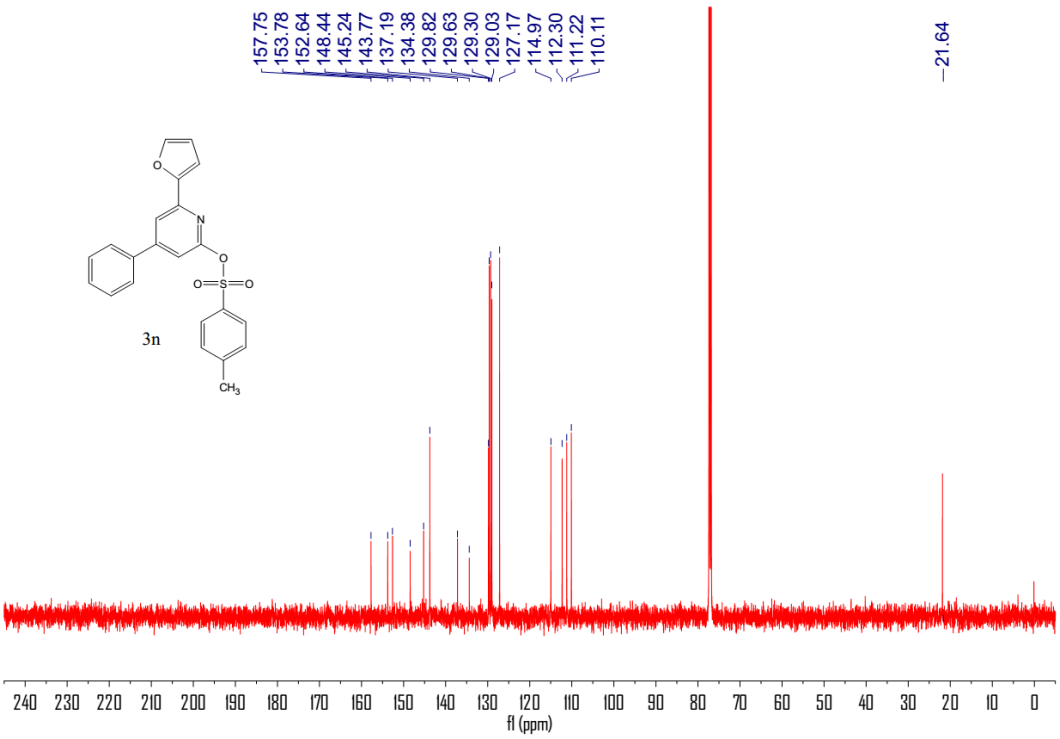
7.49
7.39
7.37
7.17
6.78
6.77
6.51
6.50
2.48
3n
1.94
0.98
2.05
4.12
2.01
0.94
0.94
0.97
3.00
f1 (ppm)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129.03
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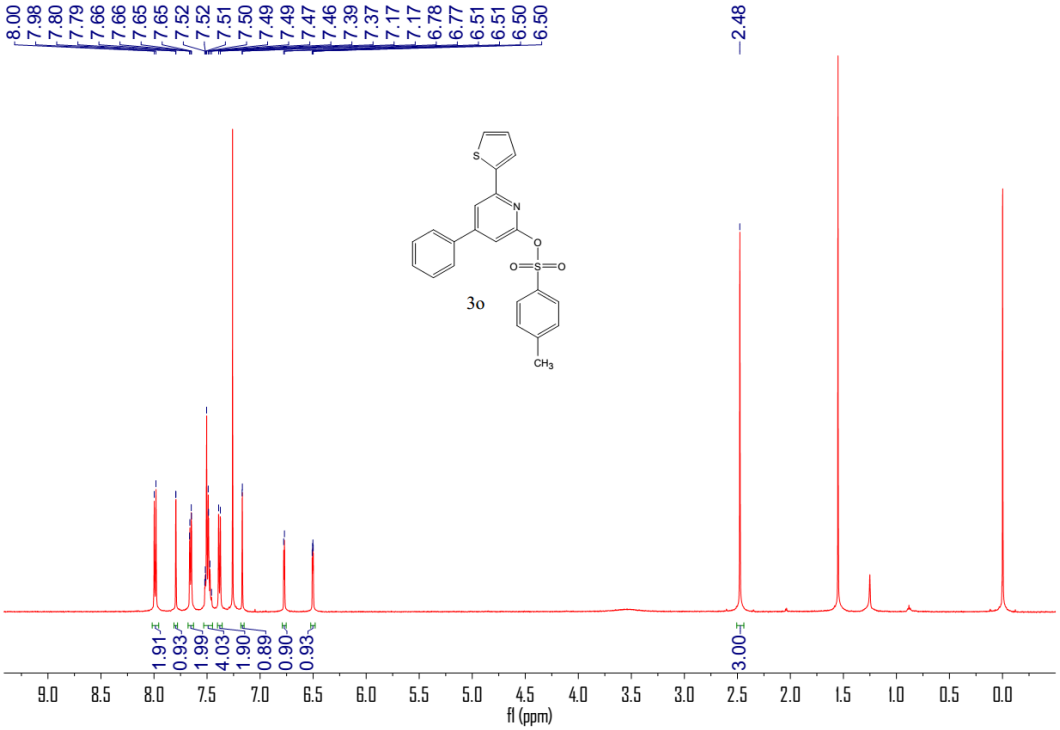
114.97
112.30
111.22
110.11
21.64
3n
f1 (ppm)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7.49
7.47
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6.51
6.51
6.50
6.50
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3o
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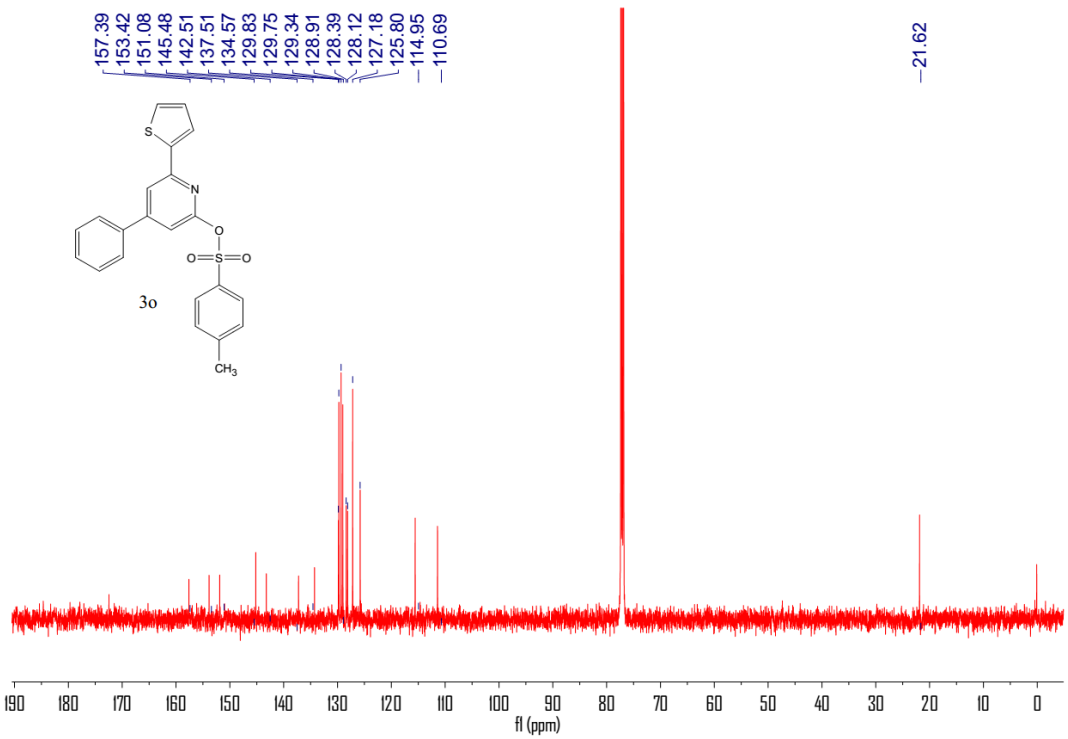
0.93
1.99
4.03
1.90
0.89
0.90
0.93
3.00
f1 (ppm)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129.83
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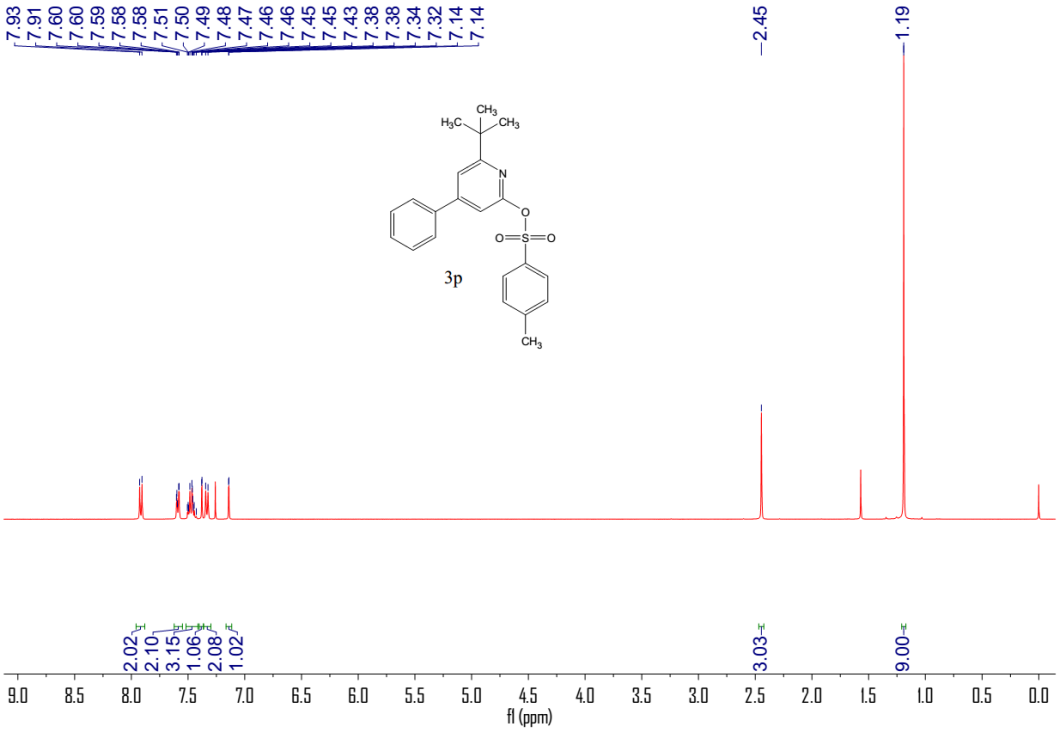
128.39
128.12
127.18
125.80
114.95
110.69
21.62
3o
f1 (ppm)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7.58
7.51
7.50
7.49
7.48
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7.45
7.45
7.43
7.38
7.38
7.34
7.32
7.14
7.14
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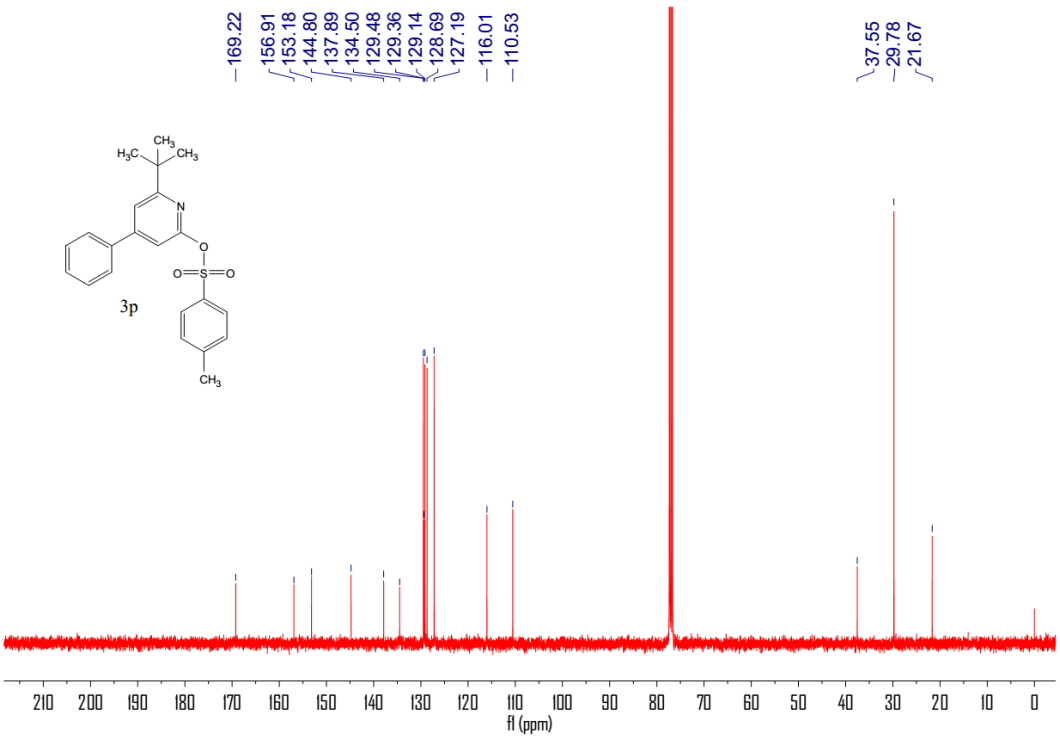
2.02
2.10
3.15
1.06
2.08
1.02
3.03
9.00
f1 (ppm)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116.01
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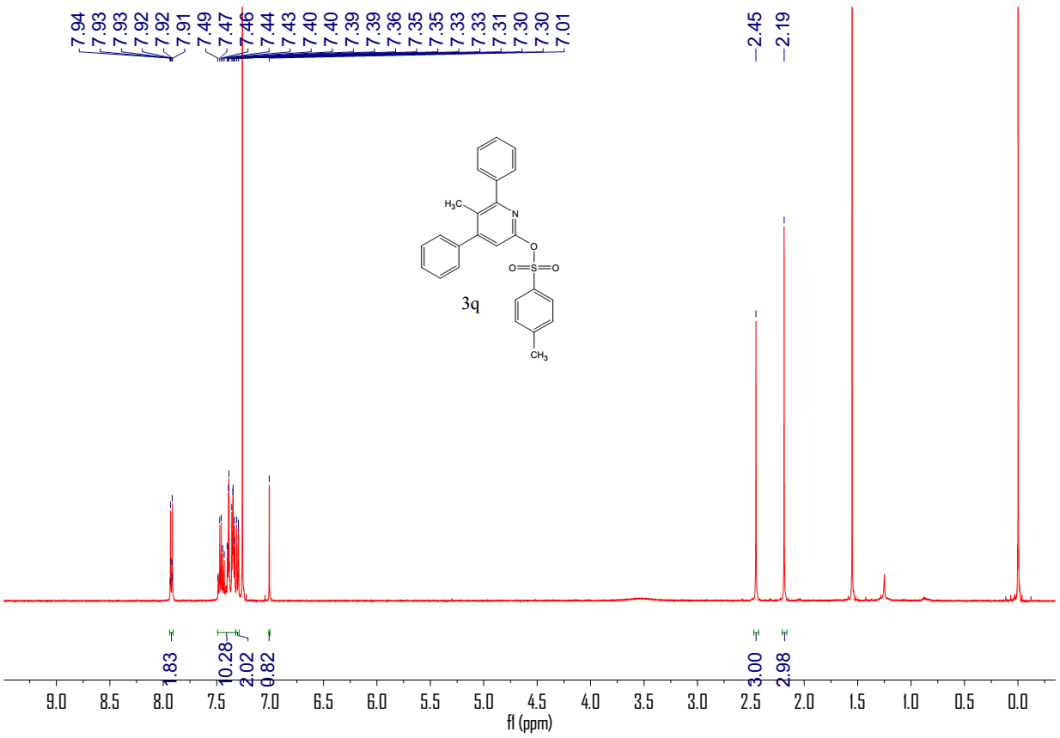
37.55
29.78
21.67
3p
f1 (ppm)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7.39
7.39
7.36
7.35
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7.33
7.33
7.31
7.30
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2.19
3q
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10.28
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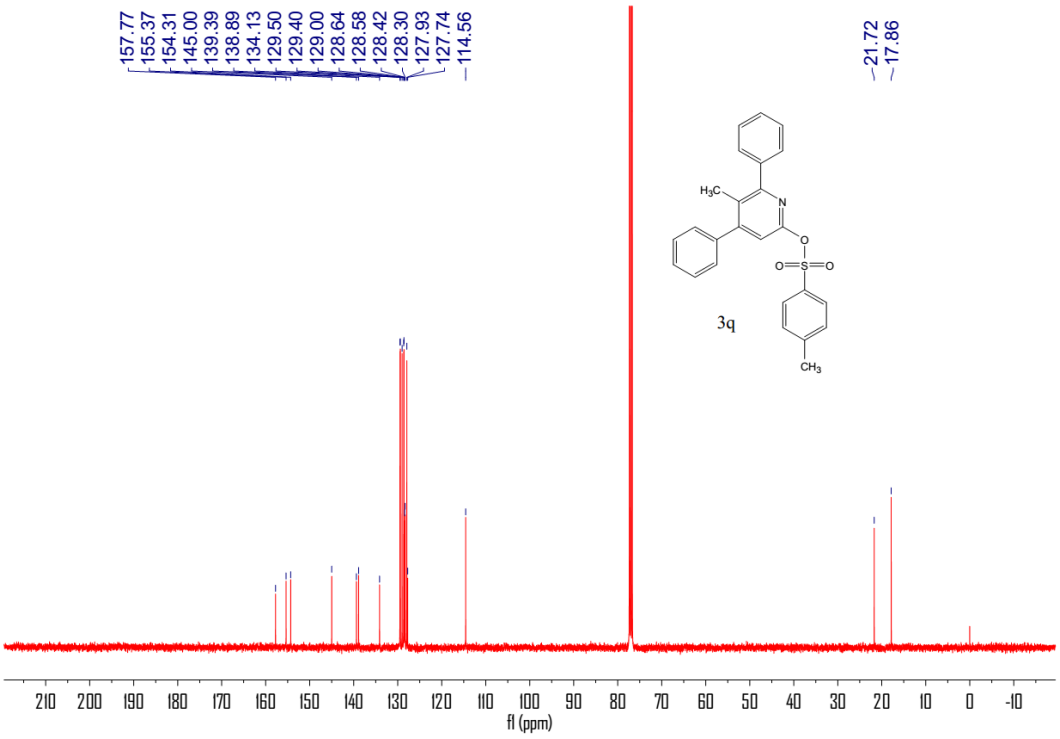
f1 (ppm)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129.00
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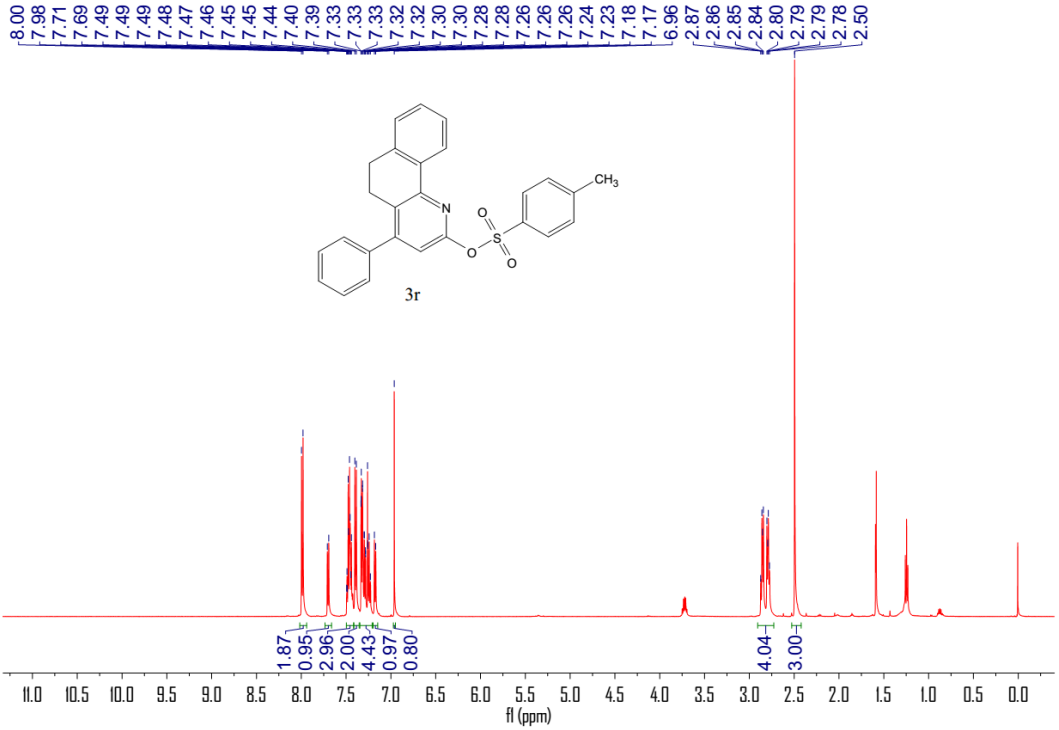
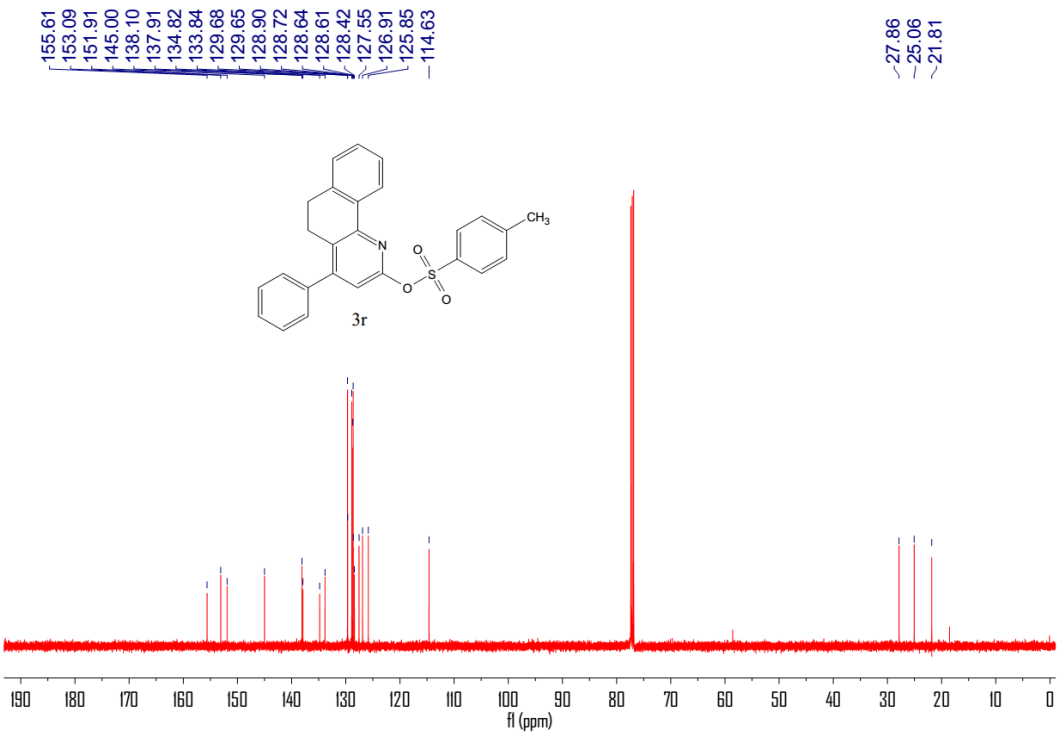
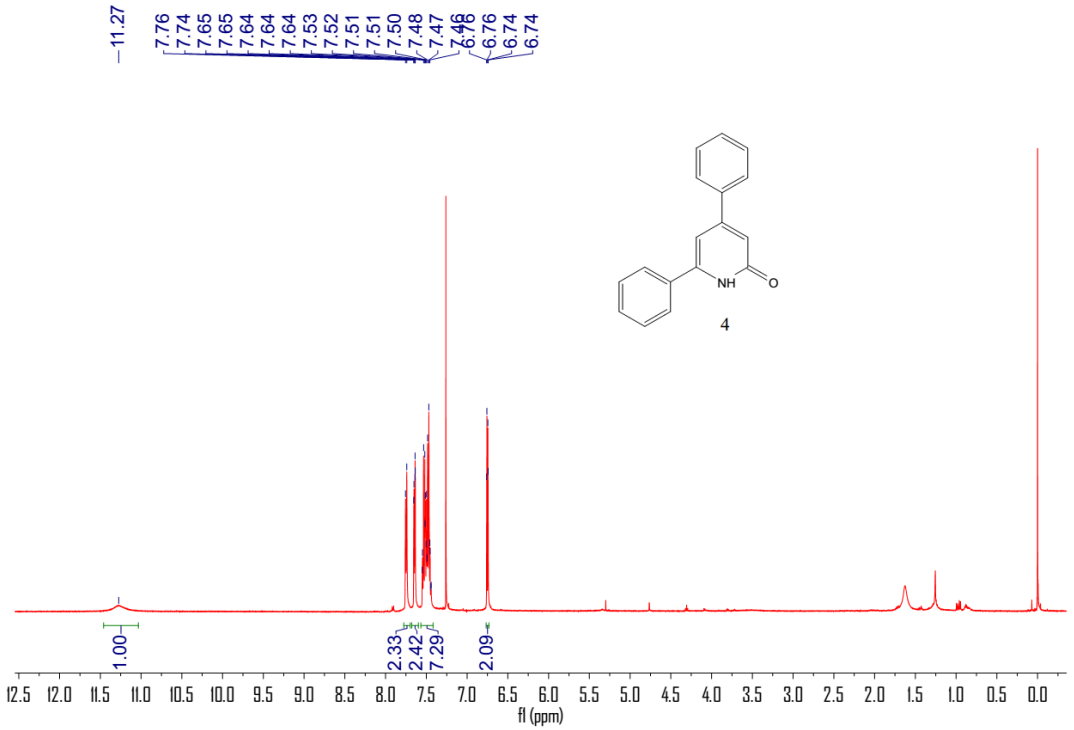
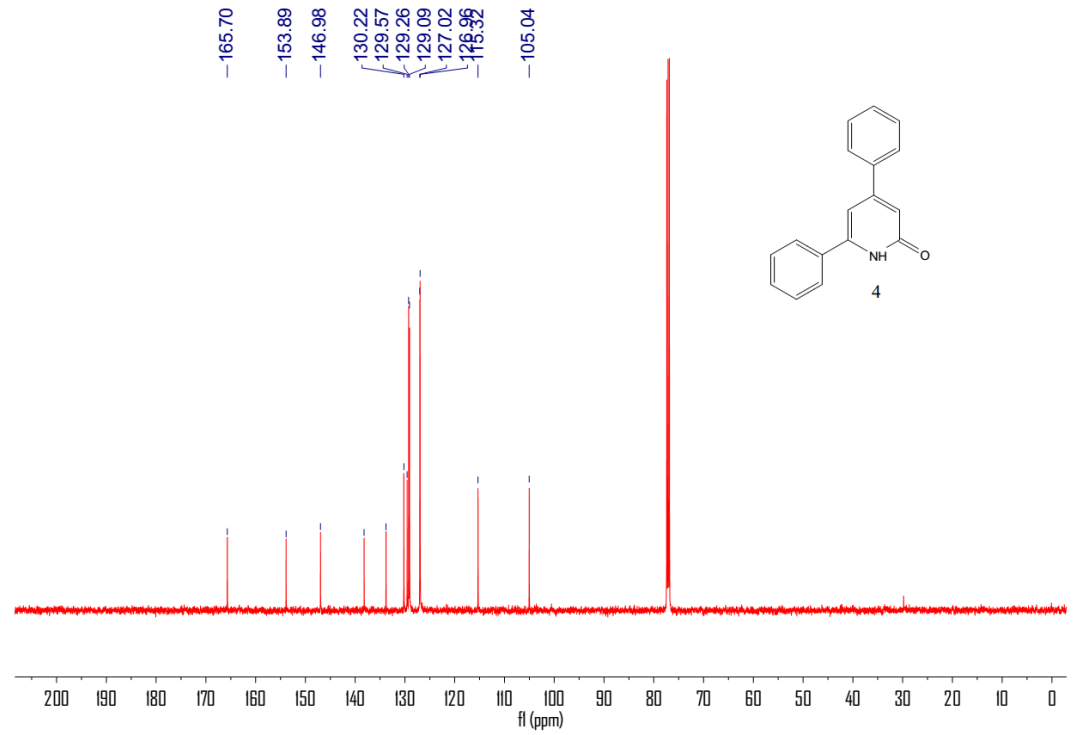
128.58
128.42
128.30
127.93
127.74
114.56
21.72
17.86
3q
f1 (ppm)

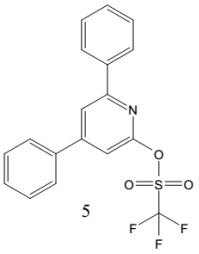

8.00
7.98
7.71
7.69
7.49
7.49
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.40
7.39
7.33
7.33
7.33
7.32
7.32
7.30
7.30
7.28
7.28
7.26
7.26
7.24
7.23
7.18
7.17
6.96
2.87
2.86
2.85
2.84
2.80
2.79
2.79
2.78
2.50
CH3
N
O
S
O
O
O
3r
1.87
0.95
2.96
2.00
4.43
0.97
0.80
4.04
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.61
153.09
151.91
145.00
138.10
137.91
134.82
133.84
129.68
129.65
128.90
128.72
128.64
128.61
128.42
127.55
126.91
125.85
114.63
27.86
25.06
21.81
CH3
N
O
S
O
O
O
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

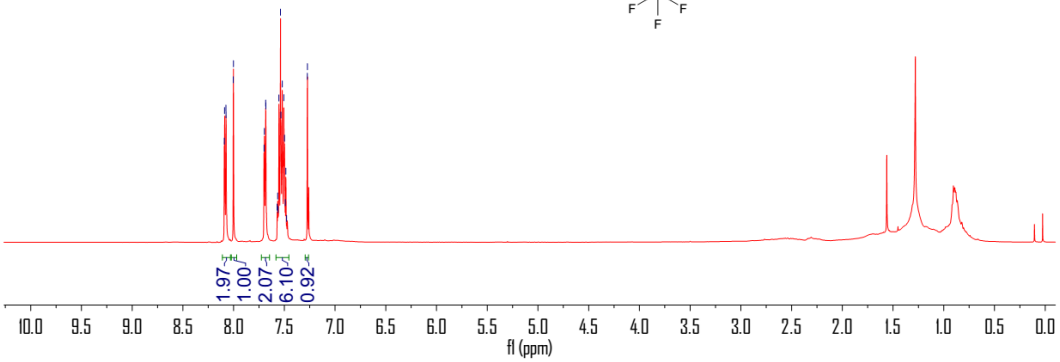

11.27
7.76
7.74
7.65
7.64
7.64
7.64
7.53
7.52
7.51
7.51
7.50
7.48
7.47
6.76
6.74
6.74
NH
O
4
1.00
2.33
2.42
7.29
2.09
f1 (ppm)


165.70
153.89
146.98
130.22
129.57
129.26
129.09
127.02
105.04
NH
O
4
f1 (ppm)

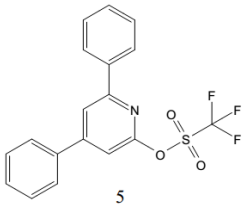

8.09
8.09
8.08
8.07
8.00
8.00
7.70
7.70
7.68
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.48
7.48
7.27
7.27


N
O
O=S=O
F
F
F

5

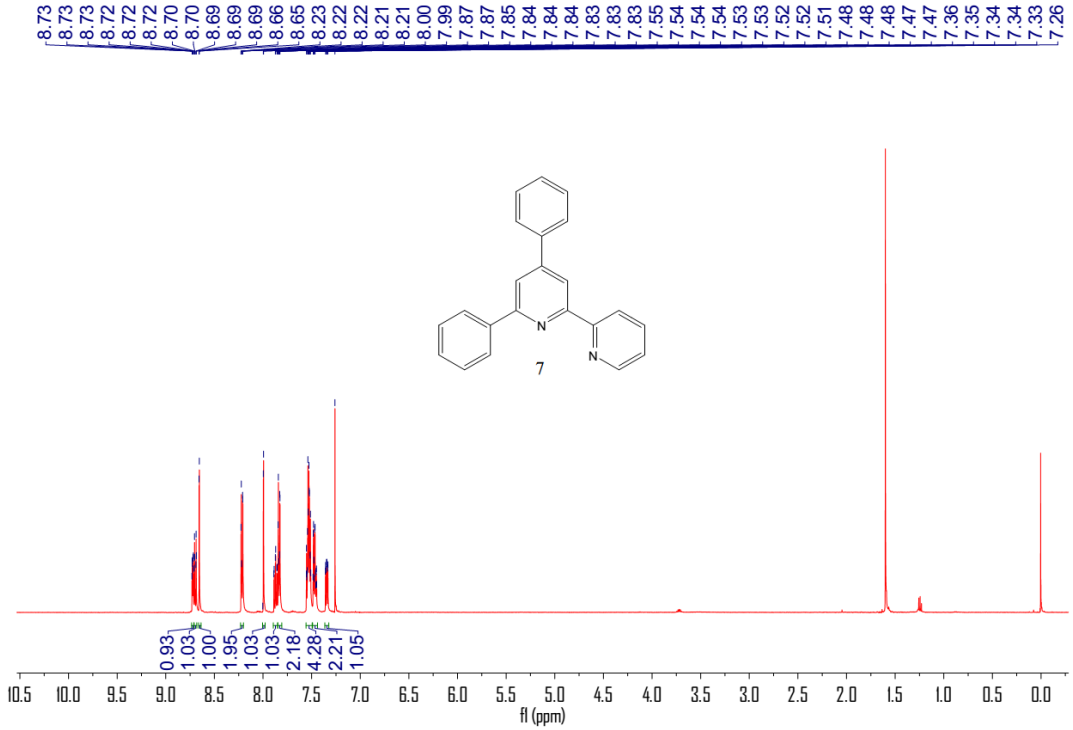

1.97
1.00
2.07
6.10
0.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

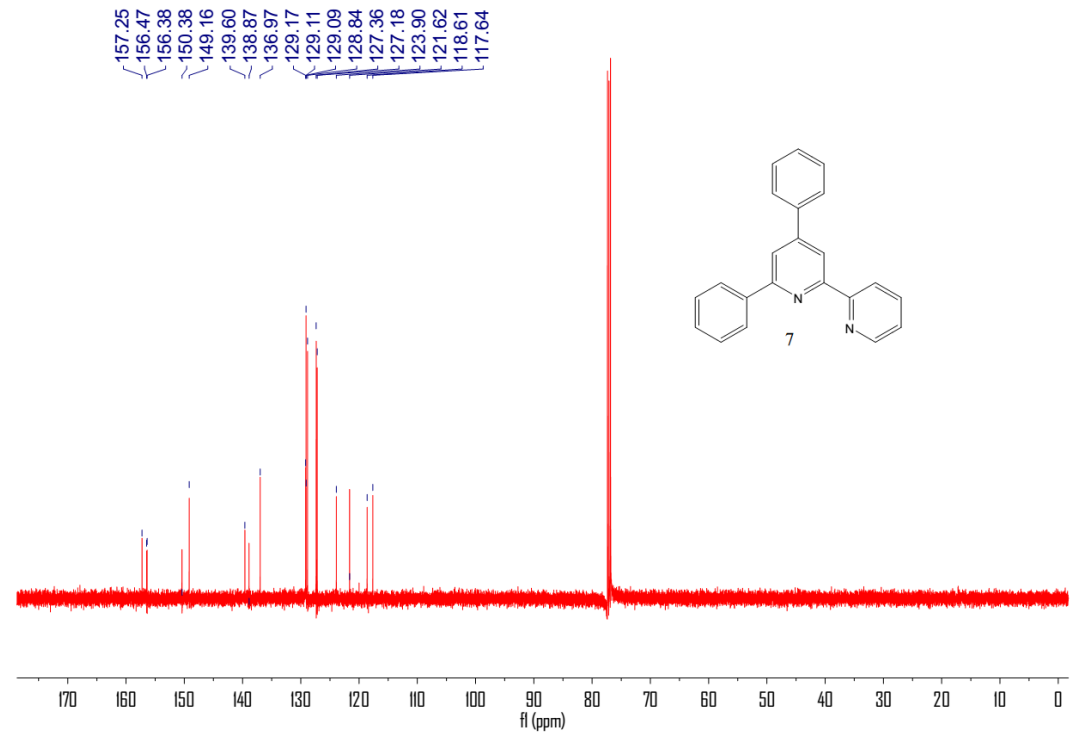

157.38
156.61
154.91
136.90
130.20
130.08
129.41
128.98
127.21
127.11
123.63
120.41
118.43
117.22
114.03
110.77

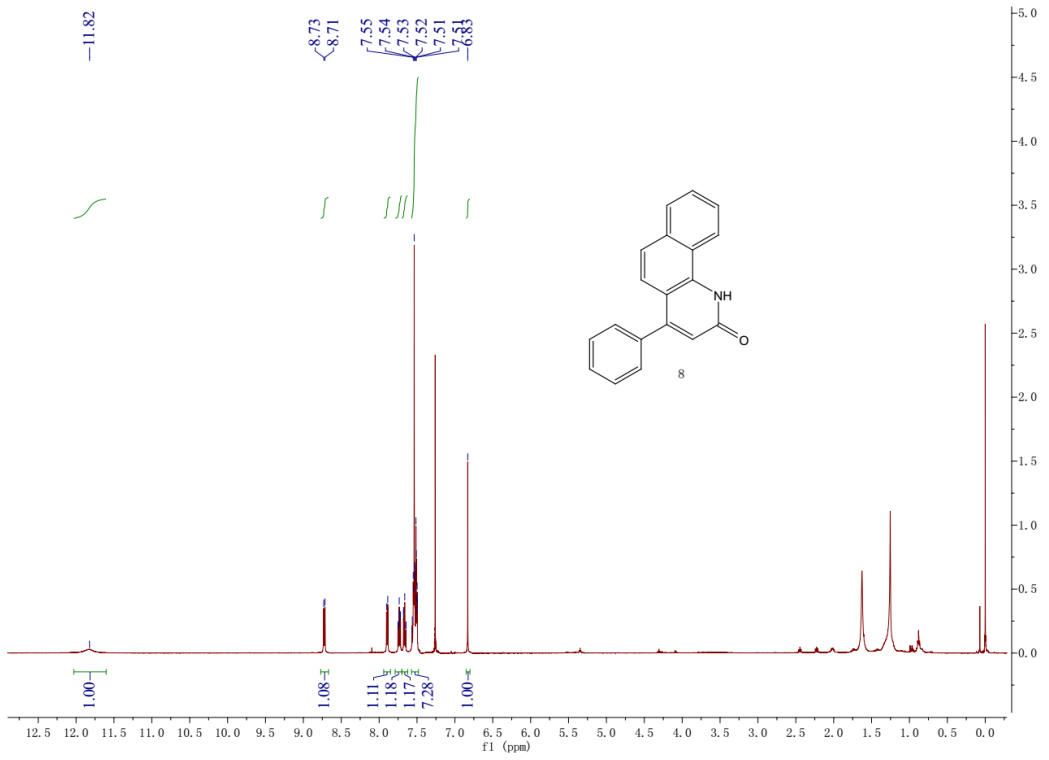

N
O
O
S
O
F
F
F

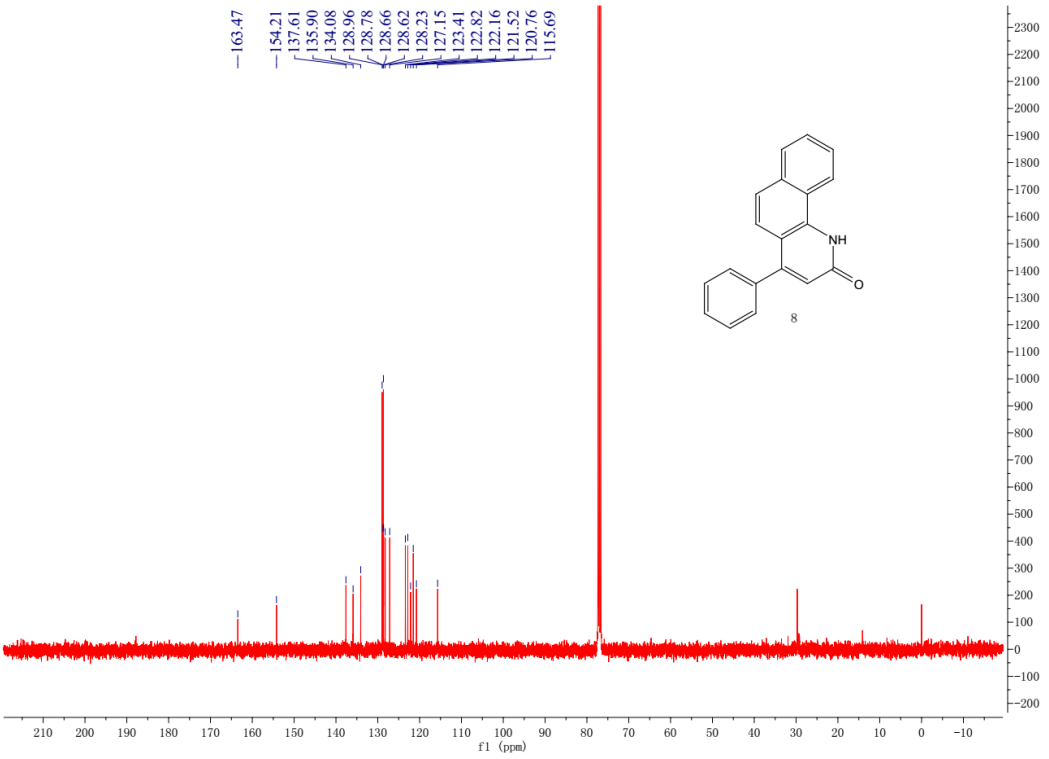
5

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.73
8.73
8.73
8.72
8.72
8.72
8.70
8.70
8.69
8.69
8.69
8.66
8.65
8.23
8.22
8.22
8.21
8.21
8.00
7.99
7.87
7.87
7.85
7.84
7.84
7.84
7.83
7.83
7.83
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.48
7.48
7.47
7.47
7.36
7.35
7.34
7.34
7.33
7.26
N
N
7
0.93
1.03
1.00
1.95
1.03
1.03
2.18
4.28
2.21
1.05
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)


157.25
156.47
156.38
150.38
149.16
139.60
138.87
136.97
129.17
129.11
129.09
128.84
127.36
127.18
123.90
121.62
118.61
117.64
N
N
7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.82
8.73
8.71
7.55
7.54
7.53
7.52
7.51
7.51
6.83
NH
O
8
1.00
1.08
1.11
1.18
1.17
7.28
1.00
f1 (ppm)


163.47
154.21
137.61
135.90
134.08
128.96
128.78
128.66
128.62
128.23
127.15
123.41
122.82
122.16
121.52
120.76
115.69
NH
O
8
f1 (ppm)