SUPPORTING INFORMATION

ReigoselectiveArylation of Thiazole Derivatives at 5-Position via Pd Catalysis under a Ligand-Free Condition

Xiang-Wei Liu[1], Jiang-Ling Shi[2], Jia-Xuan Yan[1], Jiang-Bo Wei[1], Kun Peng[3], Le Dai[3], Chen-Guang Li[3], Bi-Qin Wang[2] and Zhang-Jie Shi[1]*

[1]*Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871 and State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China* [2] *College of Chemistry and Material Chemistry, Sichuan Normal University, Sichuan 610066, China and* [3] *DSM nutritional products, DSM nutrition center, DSM (China) limited, No. 476 Li Bing Road, Zhangjiang Hi-tech Park, Pudong new area, Shanghai, 201203, China.*

zshi@pku.edu.cn

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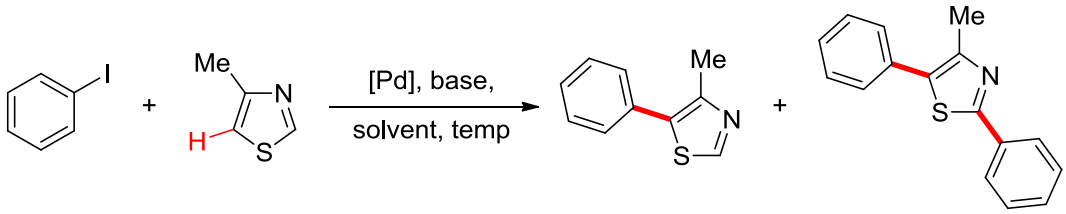
1. General Information:

Unless otherwise noted, all reactions were run under N_2 atmosphere. Prior to starting experiments, the hot plate was turned on, and the oil bath was allowed to equilibrate to the desired temperature over 30 minutes. All starting materials were commercially available and were used as received. All reagents were handled in air. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV (400 MHz or 500 MHz and 125 MHz or 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet and m = multiplet. High resolution mass spectra (HRMS-ESI) were recorded at the Center for Mass Spectrometry, Peking University.

2. Experimental:

Table S1: Screening of reaction conditions

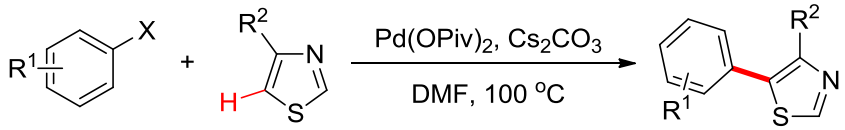


1a **2a** **3aa** **4aa**

entry	[Pd] (mol%)	base (equiv)	solvent (mL)	A/B ratio	temp (^{o}C)	yield (%)[b]	
						3aa	**4aa**
1	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	80	3
2	$Pd(OAc)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	54	5
3	$Pd(OTFA)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	43	7
4	$PdCl_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	10	2
5	$[Pd(allyl)Cl]_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	31	3
6	$Pd[(CH_3CN)_4](BF_4)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	30	11
7	$Pd[(CH_3CN)_4](OTs)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	27	7
8	$Pd(CH_3CN_2Cl_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	24	4
9	$Pd(OPiv)_2$ (10)	Na_2CO_3 (1.0)	DMF (2.0)	2/1	140	57	3
10	$Pd(OPiv)_2$ (10)	K_2CO_3 (1.0)	DMF (2.0)	2/1	140	75	5
11	$Pd(OPiv)_2$ (10)	Rb_2CO_3 (1.0)	DMF (2.0)	2/1	140	67	3
12	$Pd(OPiv)_2$ (10)	K_3PO_3 (1.0)	DMF (2.0)	2/1	140	65	4
13	$Pd(OPiv)_2$ (10)	CsOAc (1.0)	DMF (2.0)	2/1	140	65	4
14	$Pd(OPiv)_2$ (10)	CsF (1.0)	DMF (2.0)	2/1	140	38	2
15	$Pd(OPiv)_2$ (10)	CsOPiv (1.0)	DMF (2.0)	2/1	140	66	3
16	$Pd(OPiv)_2$ (10)	NaOPiv (1.0)	DMF (2.0)	2/1	140	53	4
17	$Pd(OPiv)_2$ (10)	KOPiv (1.0)	DMF (2.0)	2/1	140	56	2
18	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (0)	DMF (2.0)	2/1	140	5	1
19	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (0.5)	DMF (2.0)	2/1	140	64	3
20	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.5)	DMF (2.0)	2/1	140	58	2
21	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (2.0)	DMF (2.0)	2/1	140	53	2
22	$Pd(OAc)_2$ (10) + PivOH (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	42	2
23	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMAc (2.0)	2/1	140	64	2
24	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	NMP (2.0)	2/1	140	44	3
25	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	*o*-Xylene (2.0)	2/1	140	67	4
26	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	Mesitylene (2.0)	2/1	140	53	5
27	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	$^{n}Bu_2O$ (2.0)	2/1	140	44	4
28	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	CH_3NO_2 (2.0)	2/1	140	NR	NR
29	$Pd(OPiv)_2$ (0)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	NR	NR
30	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	1.5/1	140	61	3
31	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	1/1	140	52	4
32	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	1/1.5	140	60	7
33	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	1/2	140	55	6
34	$Pd(OPiv)_2$ (5)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	(49)[c]	---
35	$Pd(OPiv)_2$ (2)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	(35)[c]	---
36	$Pd(OPiv)_2$ (1)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	(13)[c]	---
37	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (1.0)	2/1	140	77	3
38	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (3.0)	2/1	140	77	3
39[d]	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	72	2
40[e]	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	140	69	3
41	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	120	81	2
42	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	**100**	**84 (75)**[c]	**3**
43	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	80	53	1
44	$Pd(OPiv)_2$ (10)	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	60	3	---
45	$Pd_2(dba)_3$	Cs_2CO_3 (1.0)	DMF (2.0)	2/1	100	3	---

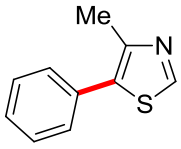
[a] All the reactions were carried out in 0.2 mmol scale in 2 mL of solvent.
[b] NMR yields with methylene bromide as an internal standard.
[c] Isolated yield in the parenthesis.
[d] The reacton was performed for 12 h.
[e] The reacton was performed for 6 h.

General Procedure for Regioselective 5-Arylation of 4-Methylthiazole/Thiazole

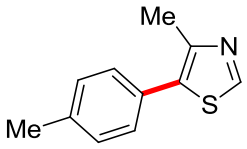


X = I, Br R = Me, H

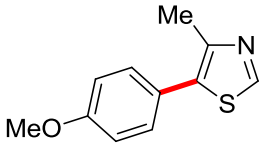
To a flame-dried 25 mL Schlenk tube, were added $Pd(OPiv)_2$ (6.2 mg, 0.02 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol), aryl halide (0.2 mmol), thiazole derivative (0.4 mmol), and DMF (2 mL). The tube was capped, the system was excavated and backfilled with N_2 for three times, and then was stirred at 100 ℃ on a preheated parallel reactor for 24 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through a short pad of Celite, washed with EtOAc, and concentrated in vacuo. The resulting residue was purified by column chromatography using hexanes:EtOAc (20:1 to 10:1, depending on different substrates) as the eluent.



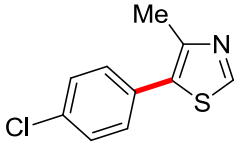
4-methyl-5-phenylthiazole (**3aa**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.48 – 7.39 (m, 4H), 7.39 – 7.32 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 148.5, 132.0, 131.9, 129.3, 128.7, 127.9, 16.1.



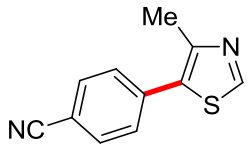
4-methyl-5-(p-tolyl)thiazole (**3ba**)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.53 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.2, 137.9, 132.0, 129.4, 129.2, 129.0, 21.2, 16.1.



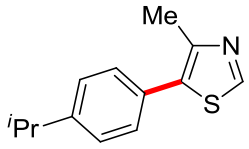
5-(4-methoxyphenyl)-4-methylthiazole (**3ca**)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 149.7, 148.0, 131.7, 130.6, 124.2, 114.2, 55.4, 16.0.



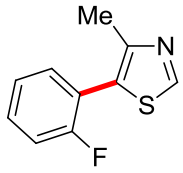
5-(4-chlorophenyl)-4-methylthiazole (**3da**)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.45 – 7.34 (m, 4H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.9, 134.0, 130.7, 130.5, 130.5, 129.0, 16.0.



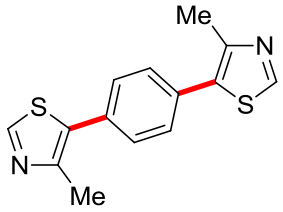
4-(4-methylthiazol-5-yl)benzonitrile (**3ea**)[3]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 150.1, 136.9, 132.5, 130.1, 129.7, 118.4, 111.5, 16.3.



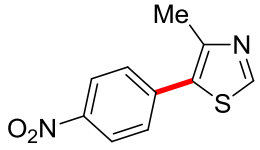
5-(4-isopropylphenyl)-4-methylthiazole (**3fa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 2.54 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.8, 148.2, 132.0, 129.4, 129.3, 126.8, 33.9, 23.9, 16.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}NS^+$: 218.0998 found 218.09925.



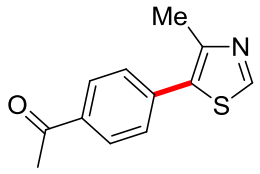
5-(2-fluorophenyl)-4-methylthiazole (**3ga**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.40 - 7.36 (m, 2H), 7.24 - 7.13 (m, 2H), 2.44 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, *J* = 2.8 Hz), 151.7, 151.0, 132.2 (d, *J* = 2.5 Hz), 130.3 (d, *J* = 8.1 Hz), 124.5, 124.2 (d, *J* = 3.7 Hz), 119.6 (d, *J* = 15.2 Hz), 116.1 (d, *J* = 22.0 Hz), 16.0 (d, *J* = 2.8 Hz). HRMS: m/z: $[M + H]^+$ calculated for $C_{10}H_9FNS^+$: 194.0434 found 194.04353.



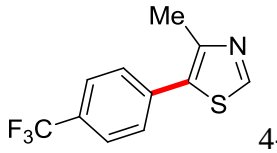
1,4-bis(4-methylthiazol-5-yl)benzene (**3ha**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.52 (s, 4H), 2.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.9, 131.6, 131.2, 129.5, 16.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{13}N_2S_2^+$: 273.0515 found 273.05111.



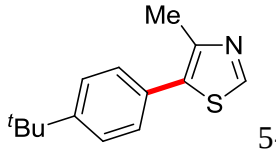
4-methyl-5-(4-nitrophenyl)thiazole (**3ia**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 150.4, 147.1, 138.8, 129.8, 129.7, 124.0, 16.4. HRMS: m/z: $[M + H]^+$ calculated for $C_{10}H_9N_2O_2S^+$: 221.0379 found 221.03795.



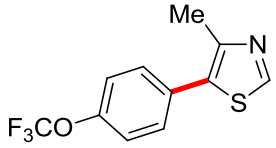
1-(4-(4-methylthiazol-5-yl)phenyl)ethanone (**3ja**)[3a, b]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 2.64 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 151.1, 149.6, 136.9, 136.2, 130.9, 129.3, 128.8, 26.6, 16.4.



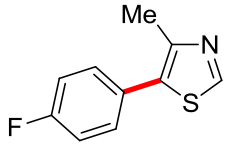
4-methyl-5-(4-(trifluoromethyl)phenyl)thiazole (**3ka**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 149.6, 135.7, 130.4, 129.9 (d, *J* = 32.5 Hz), 129.5, 124.0 (d, *J* = 270.5 Hz), 125.7 (d, *J* = 3.7 Hz), 16.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_9F_3NS^+$: 244.0402 found 244.03971.



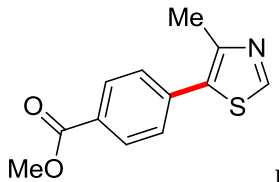
5-(4-(tert-butyl)phenyl)-4-methylthiazole (**3la**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 2.55 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.02 (s), 150.0, 148.3, 131.9, 129.0, 129.0, 125.7, 34.7, 31.3, 16.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{18}NS^+$: 232.1154 found 232.11549.



4-methyl-5-(4-(trifluoromethoxy)phenyl)thiazole (**3ma**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.1, 148.8 (q, *J* = 1.7 Hz), 130.7, 130.7, 130.4, 121.2, 120.5(q, *J* = 256.1 Hz), 16.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_9F_3NOS^+$: 260.0351 found 260.03469.

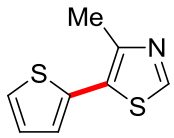


5-(4-fluorophenyl)-4-methylthiazole (**3na**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.41 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.8 Hz), 150.3, 148.7, 131.1 (d, *J* = 8.1 Hz), 130.8, 128.0 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 21.6 Hz), 15.9.

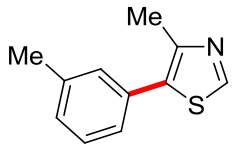


methyl 4-(4-methylthiazol-5-yl)benzoate (**3oa**)[4]: ^{1}H NMR (400

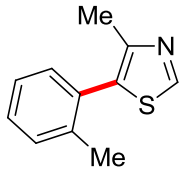
MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 3.95 (s, 3H), 2.57 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 151.0, 149.5, 136.7, 130.9, 130.0, 129.4, 129.1, 52.2, 16.3.



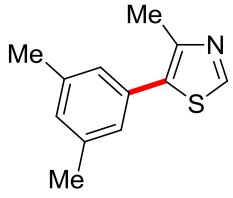
4-methyl-5-(thiophen-2-yl)thiazole (**3pa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.36 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.1, 133.2, 127.6, 127.2, 126.2, 125.5, 16.5. HRMS: m/z: $[M + H]^+$ calculated for $C_8H_8NS_2^+$: 182.0093 found 182.00956.



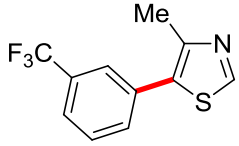
4-methyl-5-(m-tolyl)thiazole (**3qa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.25 (s, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 2.54 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 148.4, 138.4, 132.0, 131.9, 130.0, 128.7, 128.6, 126.4, 21.4, 16.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_{12}NS^+$: 190.0685 found 190.06863.



4-methyl-5-(o-tolyl)thiazole (**3ra**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.19 (m, 2H), 2.28 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 149.8, 137.9, 131.3, 130.9, 130.3, 130.3, 128.8, 125.8, 20.1, 15.4. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_{12}NS^+$: 190.0685 found 190.06866.

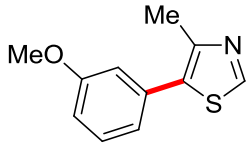


5-(3,5-dimethylphenyl)-4-methylthiazole (**3sa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.06 (s, 2H), 7.00 (s, 1H), 2.53 (s, 3H), 2.36 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 148.3, 138.3, 132.2, 131.78, 129.6, 127.1, 21.3, 16.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{14}NS^+$: 204.0841 found 204.08421.

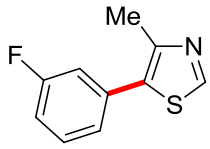


4-methyl-5-(3-(trifluoromethyl)phenyl)thiazole (**3ta**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.70 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.53 (m, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 149.5, 132.9, 132.5 (q, *J* = 1.0 Hz), 131.3 (q, *J* = 32.4 Hz), 130.3, 129.3, 126.0 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.8 Hz), 16.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_9F_3NS^+$:

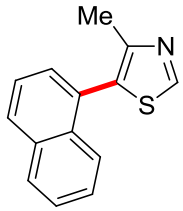
244.0402 found 244.03981.



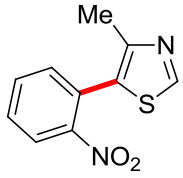
5-(3-methoxyphenyl)-4-methylthiazole (**3ua**)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.84 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 150.3, 148.6, 133.3, 131.8, 129.7, 121.8, 115.1, 113.4, 55.3, 16.2.



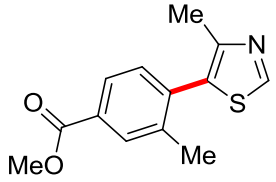
5-(3-fluorophenyl)-4-methylthiazole (**3va**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.39 (td, *J* = 8.0, 6.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 (dt, *J* = 9.7, 1.9 Hz, 1H), 7.06 (td, *J* = 8.4, 2.3 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 245.6 Hz), 150.7, 149.1, 134.1 (d, *J* = 8.3 Hz), 130.6 (d, *J* = 2.4 Hz), 130.3 (d, *J* = 8.6 Hz), 125.1 (d, *J* = 3.0 Hz), 116.2 (d, *J* = 22.3 Hz), 114.9 (d, *J* = 20.9 Hz), 16.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{10}H_9FNS^+$: 194.0434 found 194.04355.



4-methyl-5-(naphthalen-1-yl)thiazole (**3wa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.44 (m, 4H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 150.9, 133.7, 132.5, 129.14, 129.2, 129.1, 128.9, 128.5, 126.7, 126.2, 125.6, 125.2, 15.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NS^+$: 226.0685 found 226.06864.



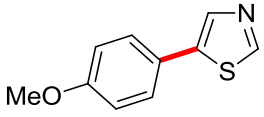
4-methyl-5-(2-nitrophenyl)thiazole (**3xa**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.66 (td, *J* = 7.5, 1.3 Hz, 1H), 7.59 (td, *J* = 7.8, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.4 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 151.1, 150.0, 133.7, 132.6, 129.8, 126.4, 125.6, 124.6, 15.4. HRMS: m/z: $[M + H]^+$ calculated for $C_{10}H_9N_2O_2S^+$: 221.0379 found 221.03798.



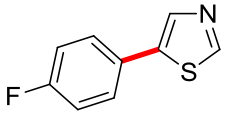
methyl 3-methyl-4-(4-methylthiazol-5-yl)benzoate (**3ya**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.98 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.32 (d,

J = 7.9 Hz, 1H), 3.94 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 151.5, 150.1, 138.2, 135.9, 131.4, 131.4, 130.4, 129.2, 126.9, 52.2, 20.1, 15.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}NO_2S^+$: 248.0740 found 248.07413.

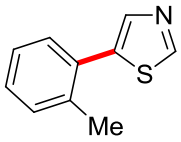
5-phenylthiazole (**3ab**)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.08 (s, 1H), 7.59 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.42 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.38 – 7.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 139.4, 139.0, 131.1, 129.1, 128.5, 127.0.



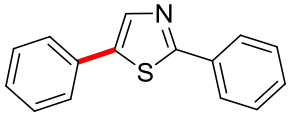
5-(4-methoxyphenyl)thiazole (**3cb**)[5c]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.97 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 151.2, 139.2, 138.1, 128.3, 123.7, 114. 6, 55.4.



5-(4-fluorophenyl)thiazole (**3nb**)[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.01 (s, 1H), 7.59 – 7.50 (m, 2H), 7.16 – 7.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.3 Hz), 152.1, 139.0, 138.3, 128.8 (d, *J* = 8.2 Hz), 127.3 (d, *J* = 3.5 Hz), 116.2 (d, *J* = 21.8 Hz),.



5-(*o*-tolyl)thiazole (**3rb**)[7]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.85 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.27 – 7.20 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 141.7, 136.6, 130.8, 130.8, 130.3, 128.7, 126.1, 21.0.



2,5-diphenylthiazole (**7**)[8]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.99 - 7.96 (m, 2H), 7.63 – 7.61 (m, 2H), 7.46 – 7.33 (m, 6H).

3. Reference:

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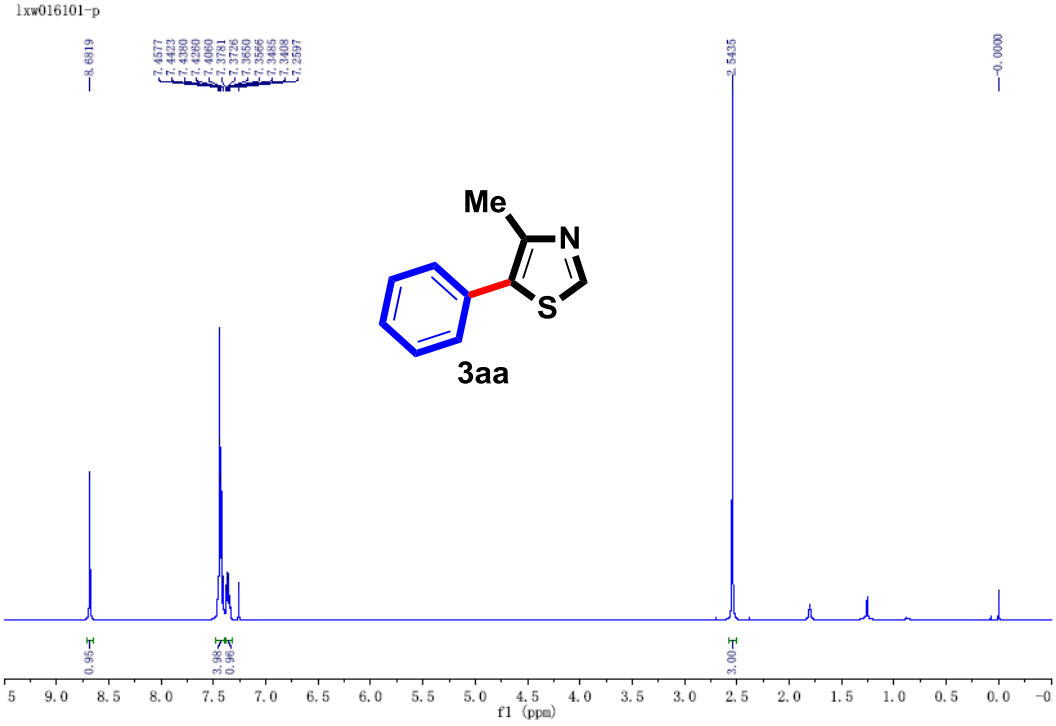
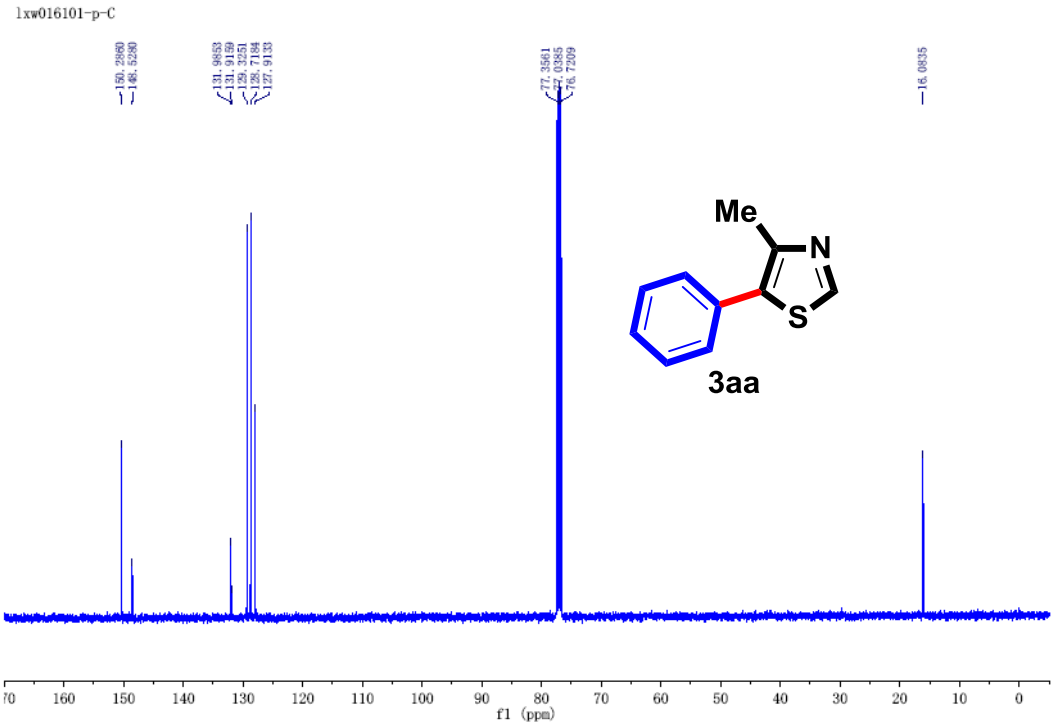
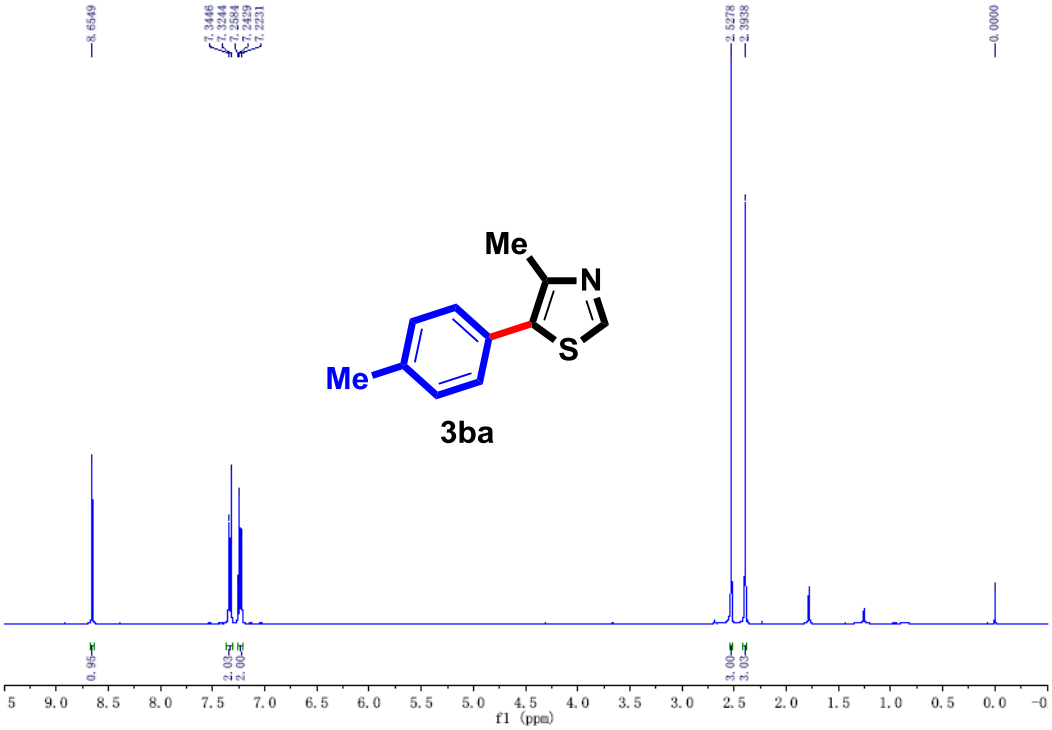
4. ^{1}H and ^{13}C NMR spectral scopies obtained in this study.

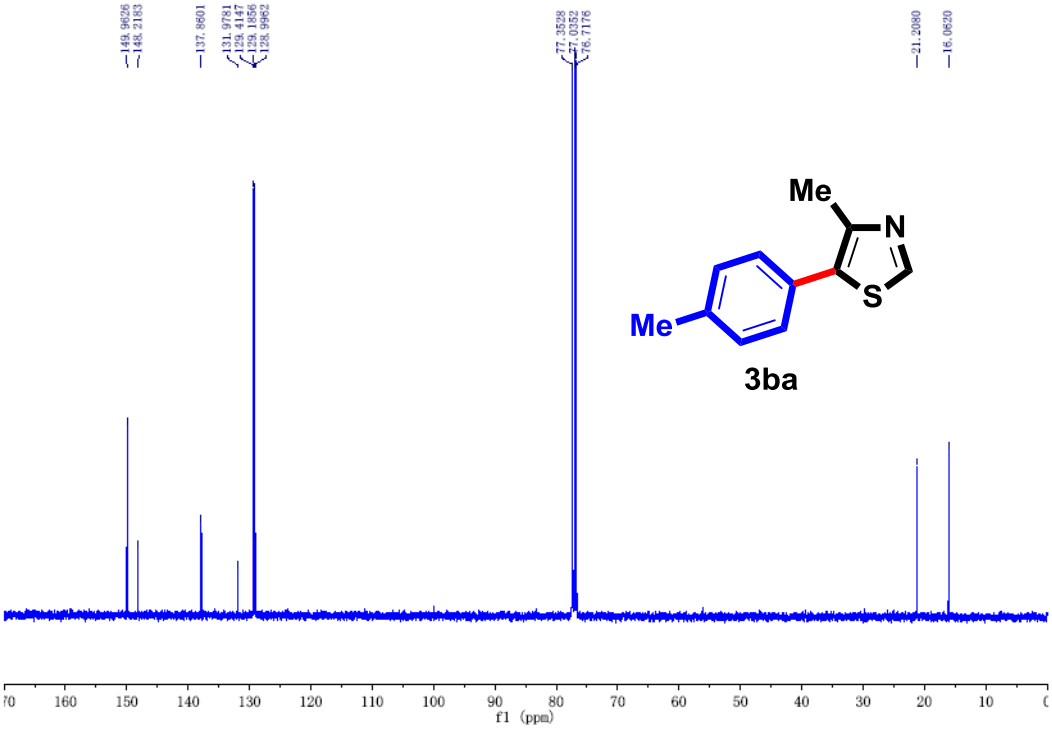
Spectra of **3aa**



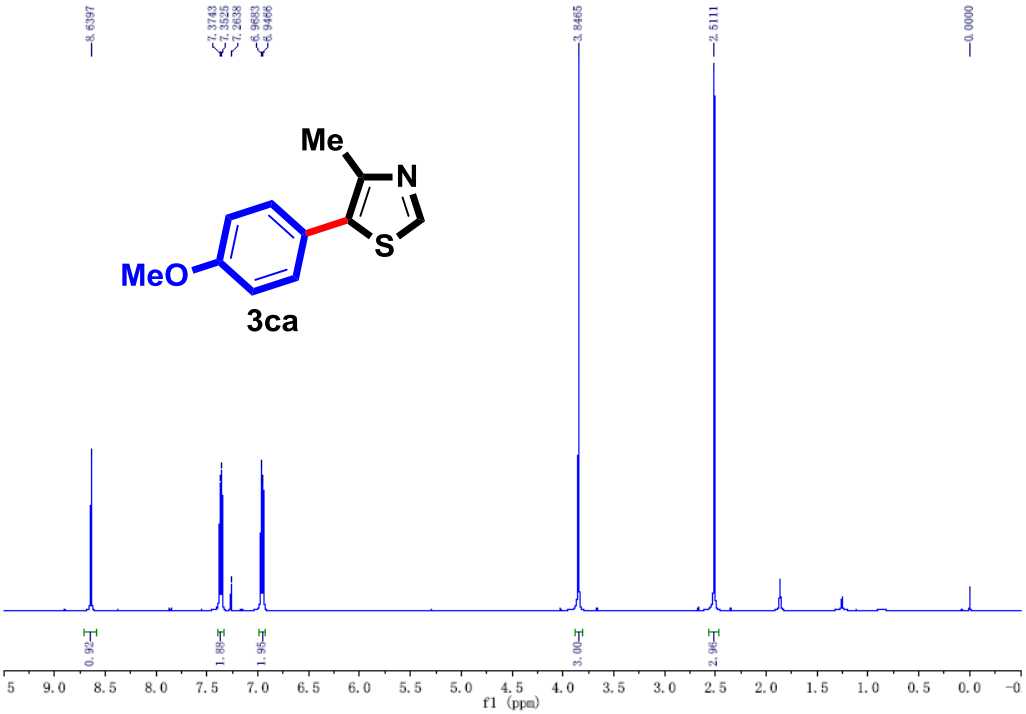


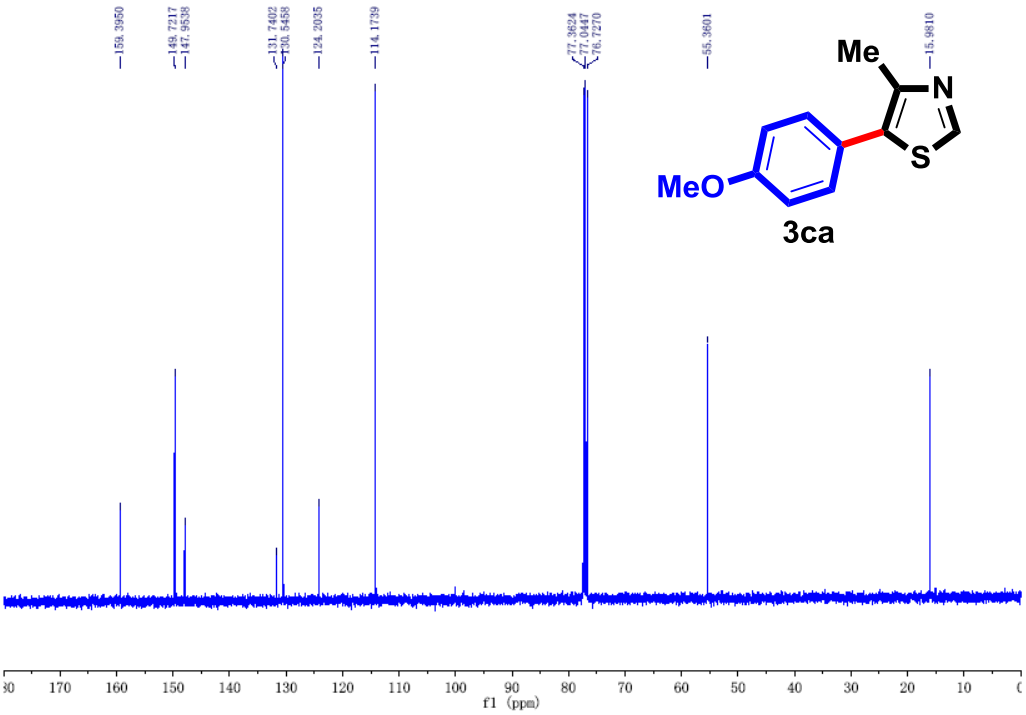
Spectra of **3ba**





Spectra of **3ca**





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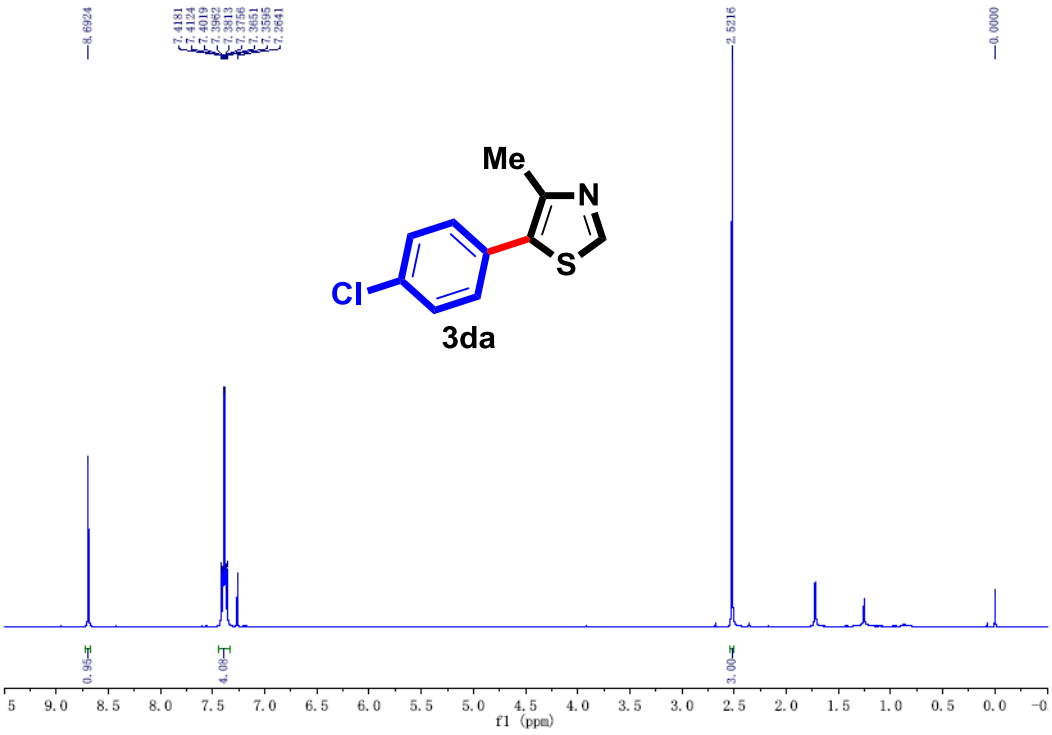
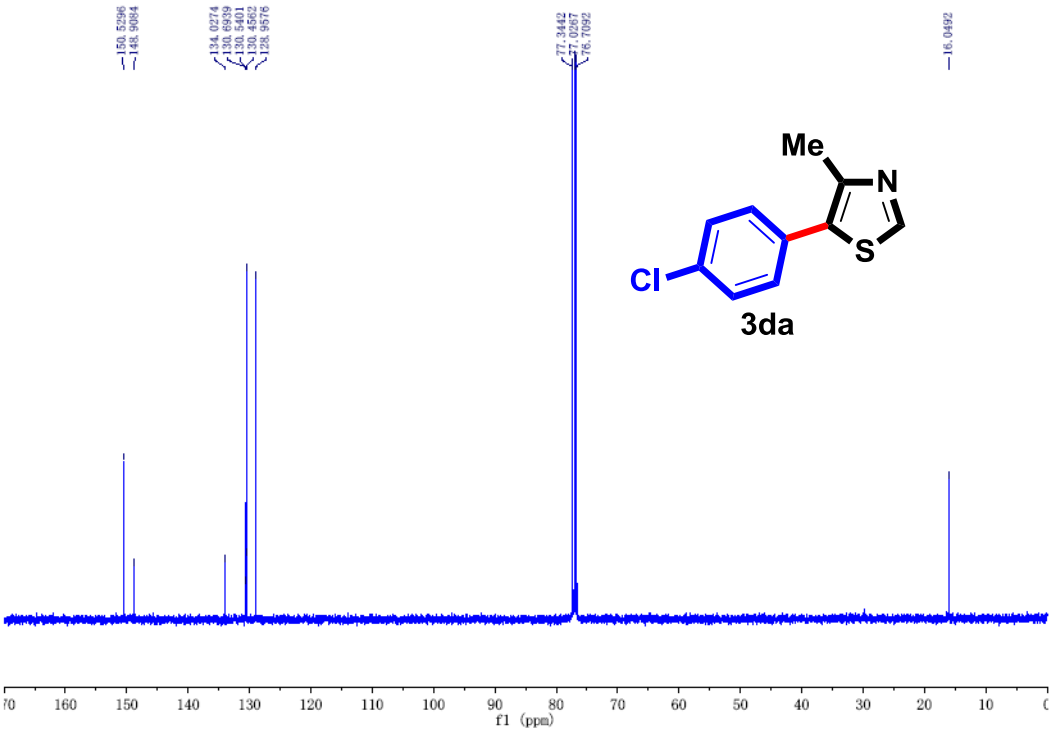
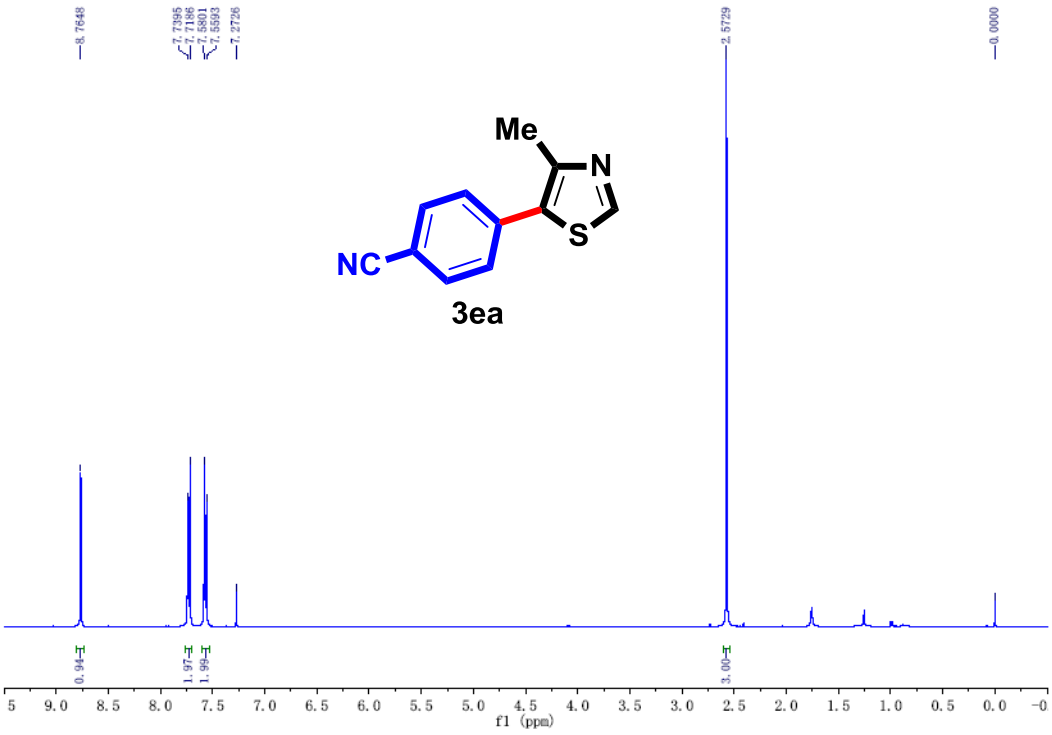
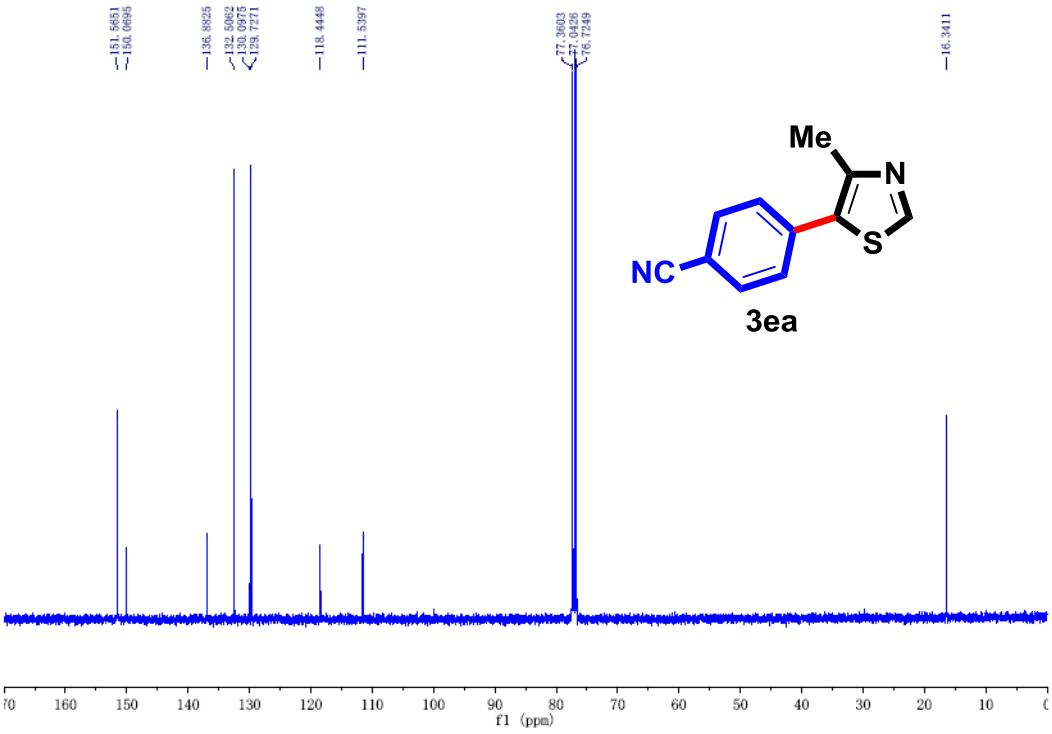


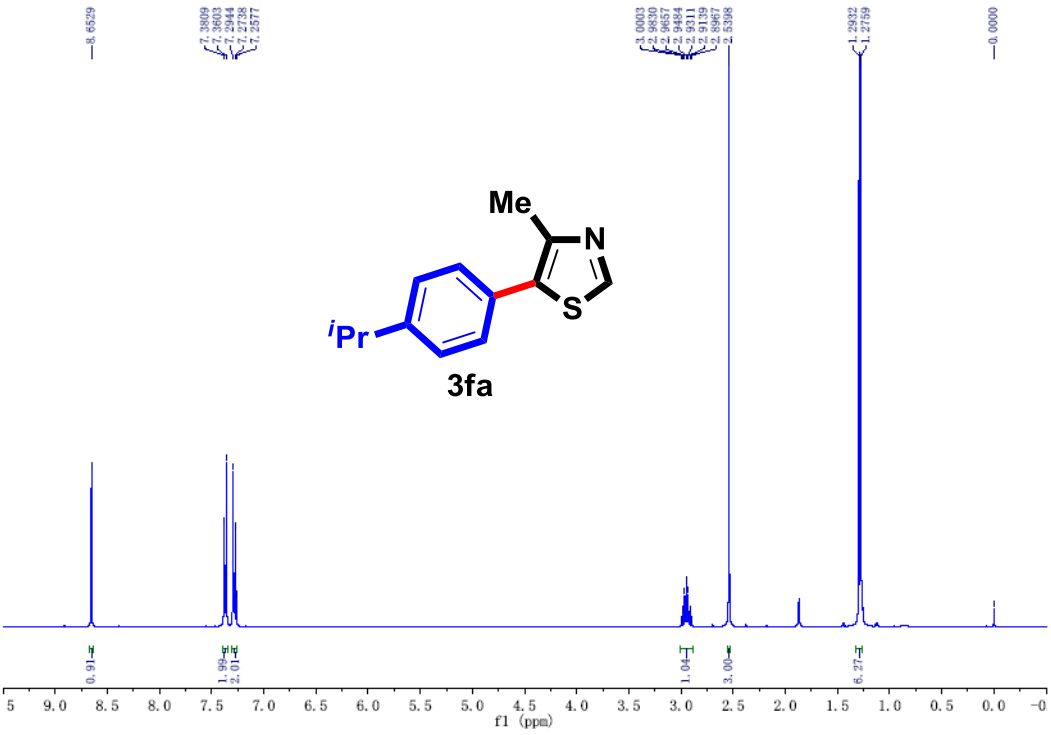


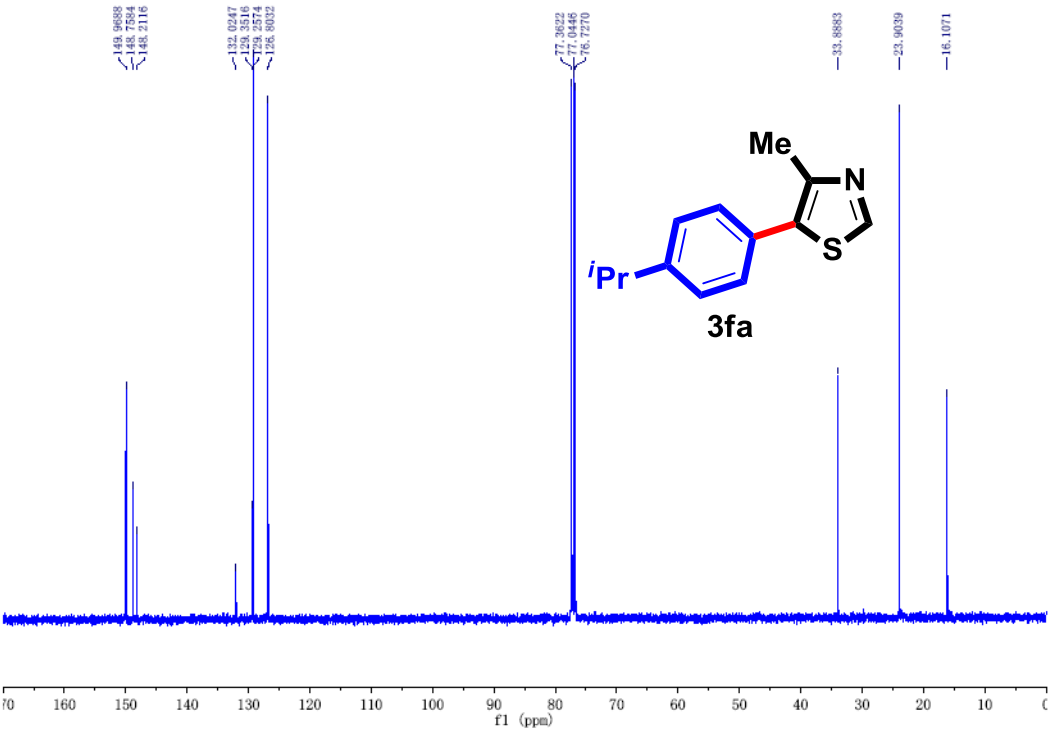
Spectra of **3ea**



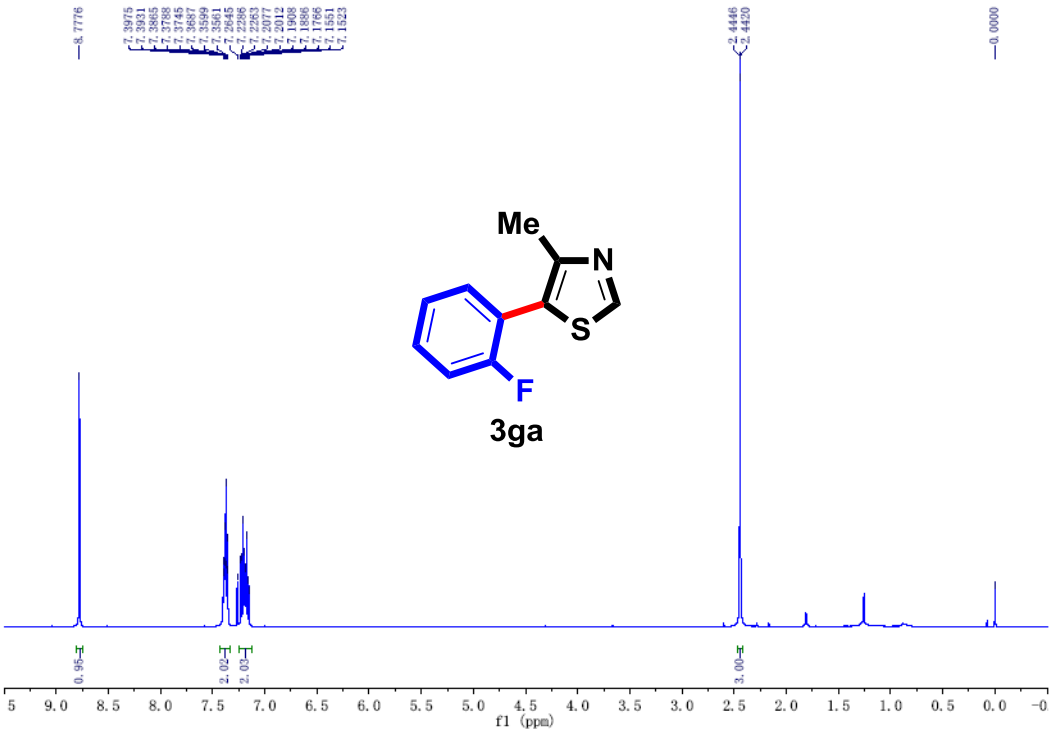


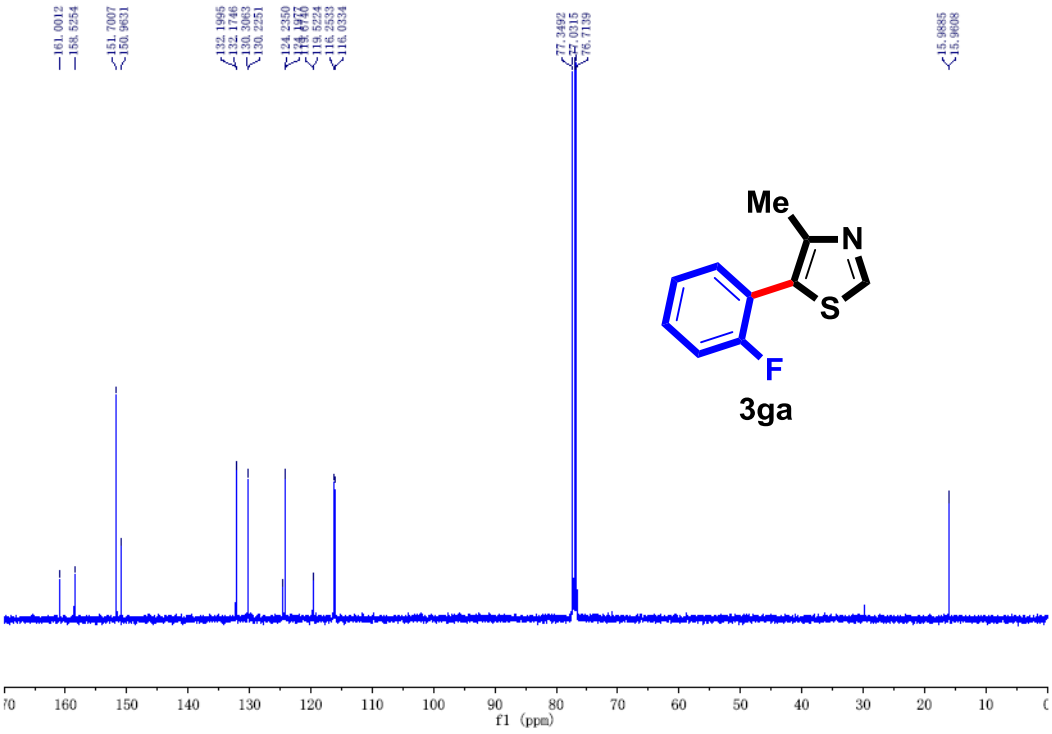
Spectra of **3fa**



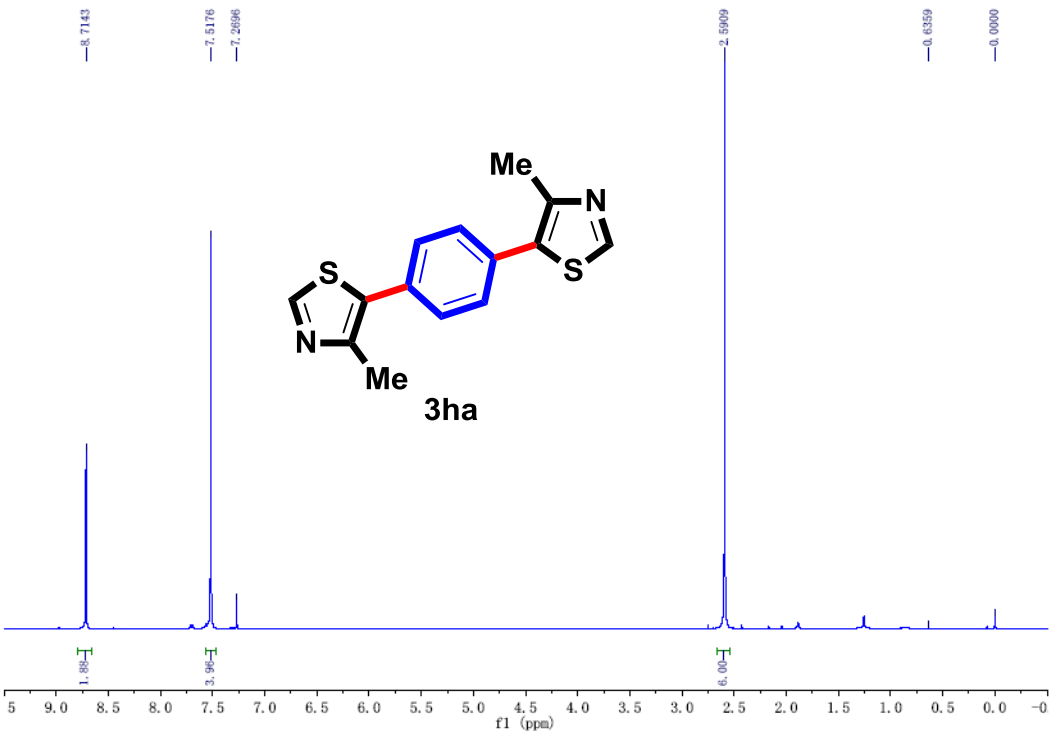


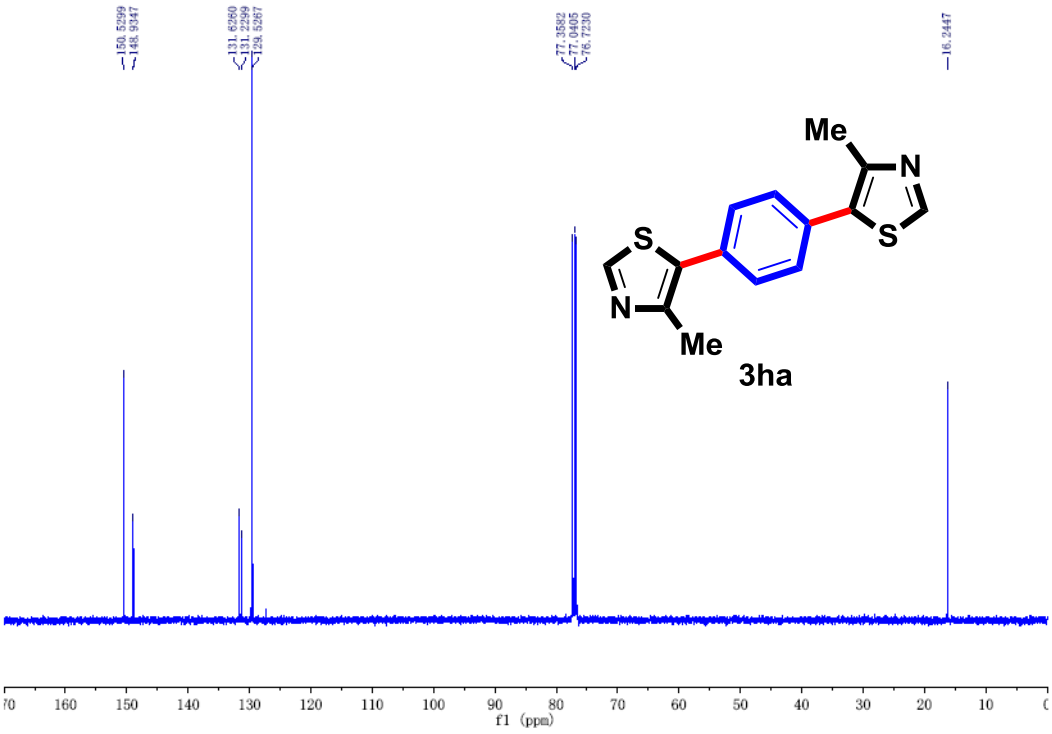
Spectra of **3ga**



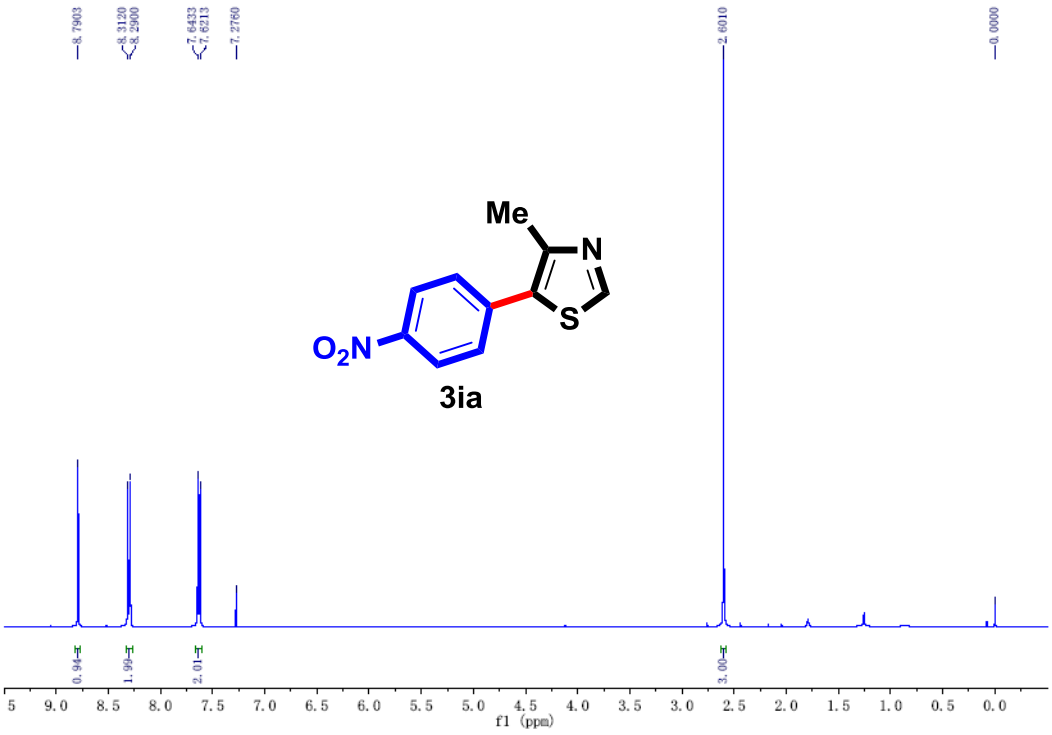


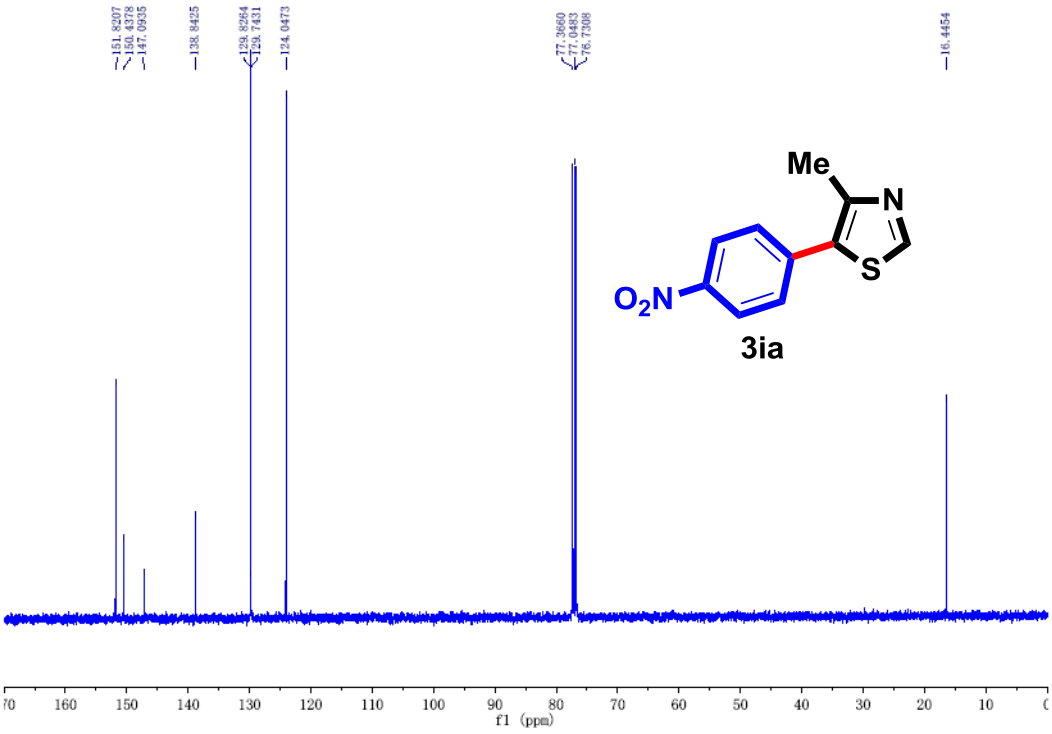
Spectra of **3ha**





Spectra of **3ia**





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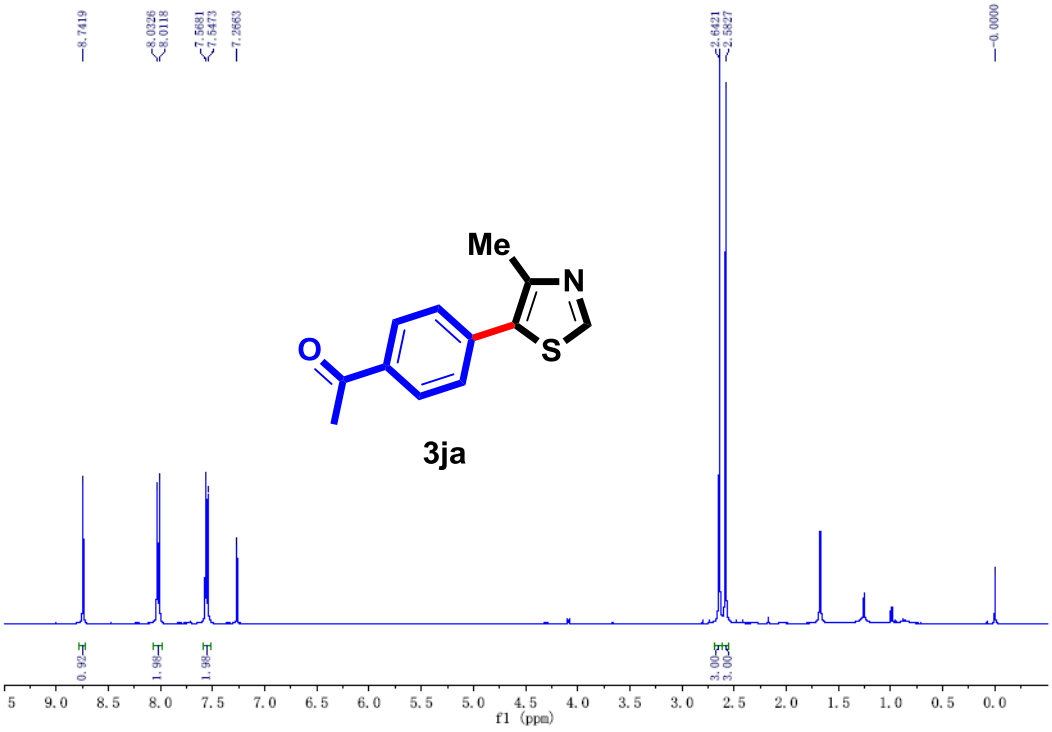

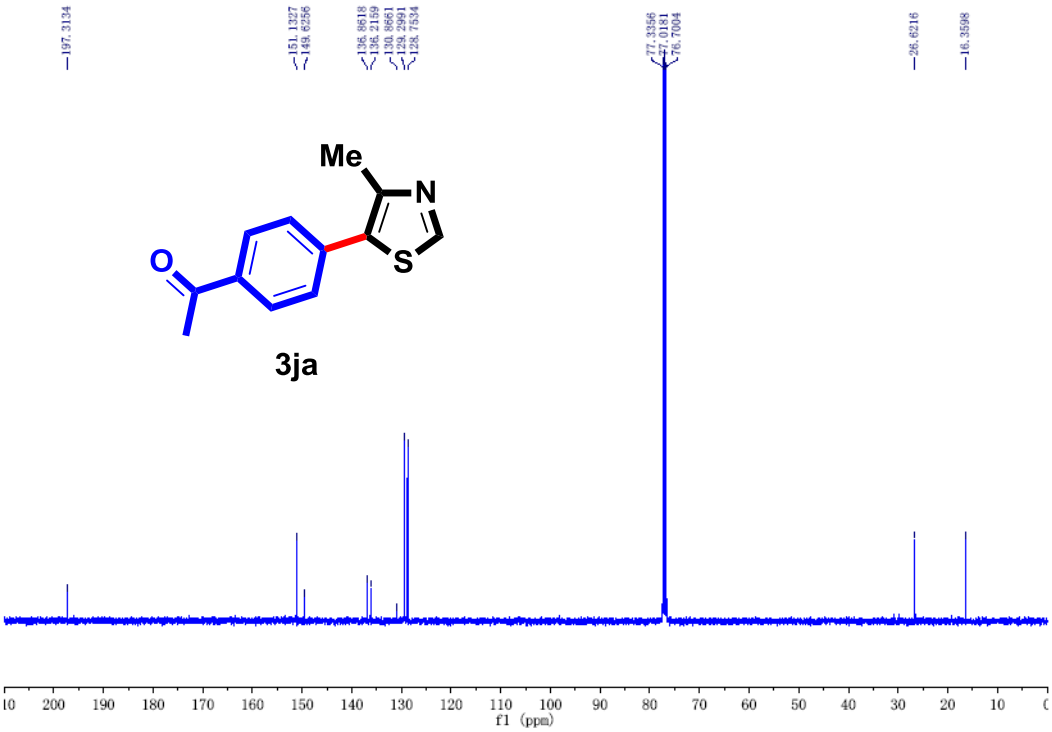

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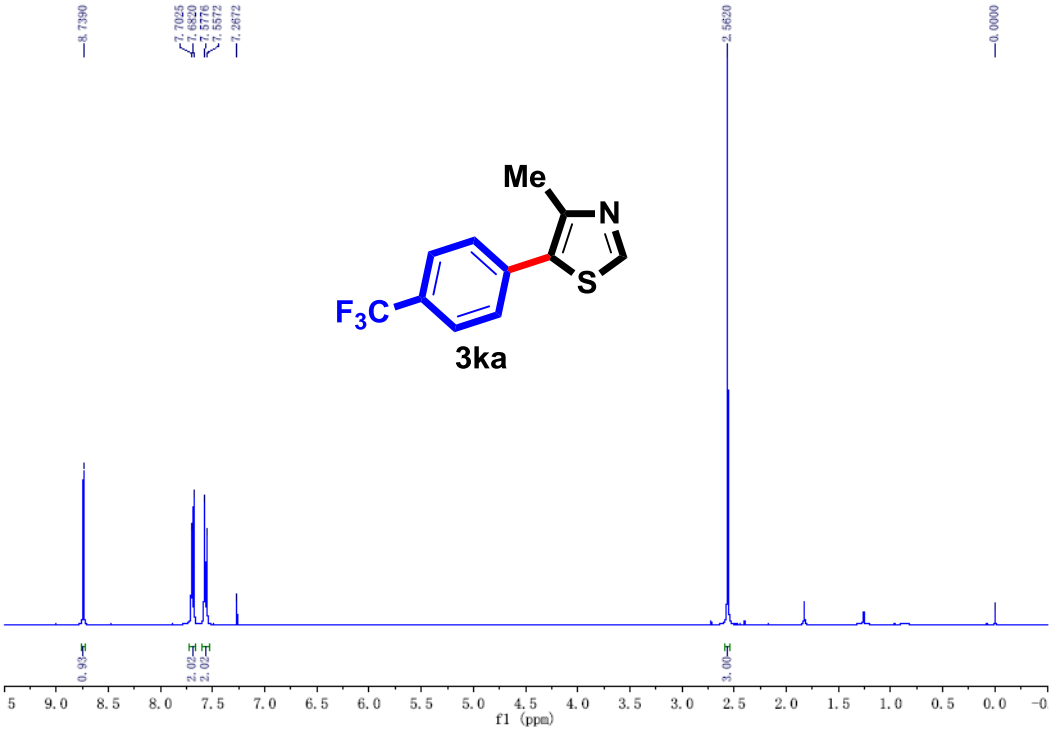

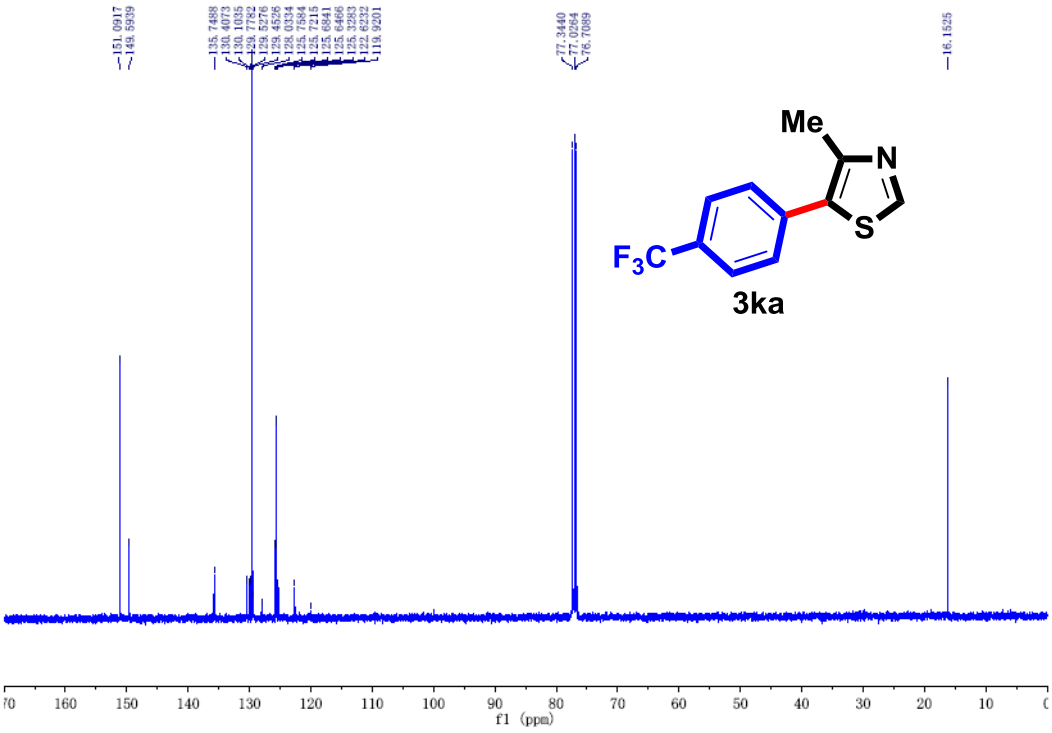

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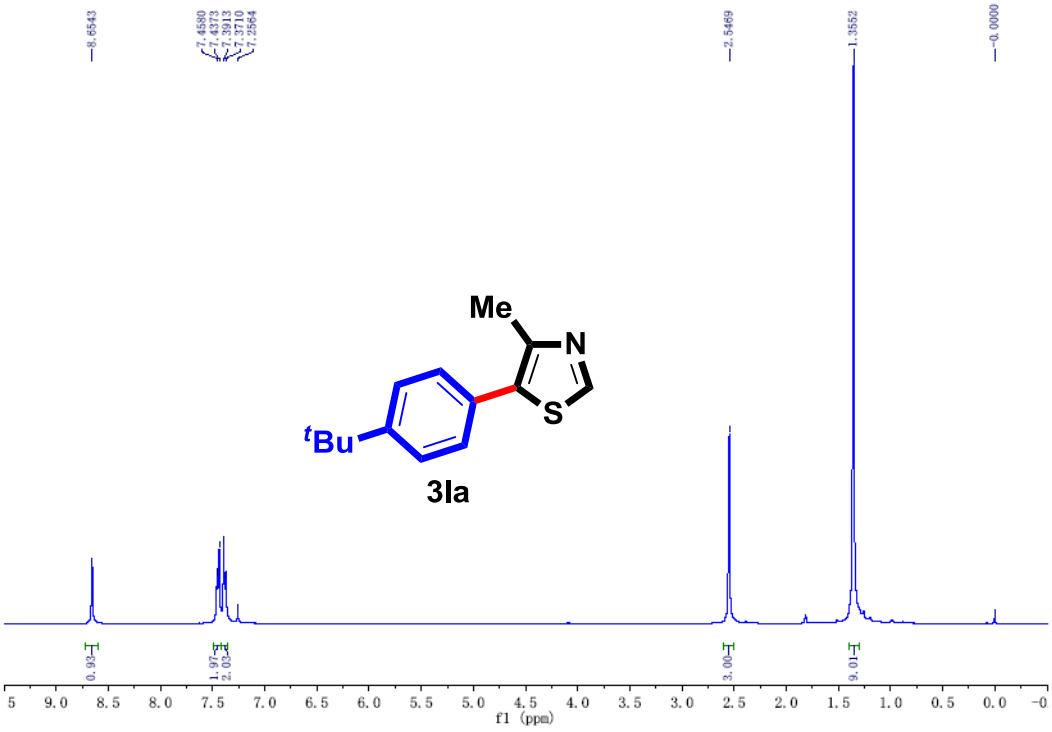

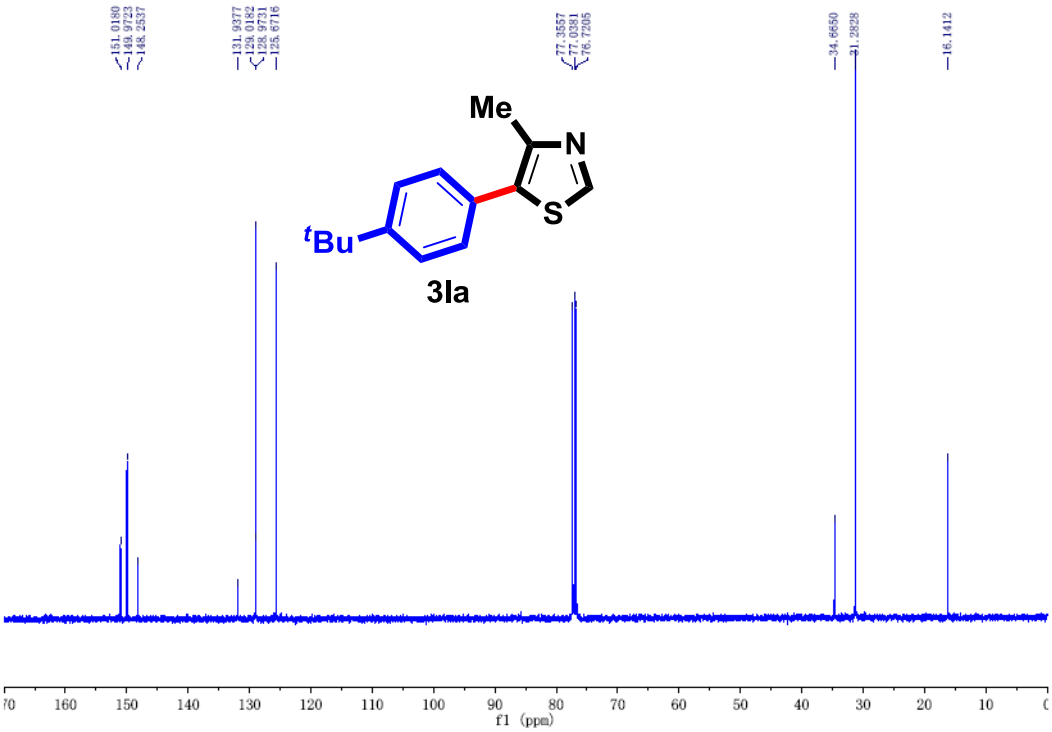

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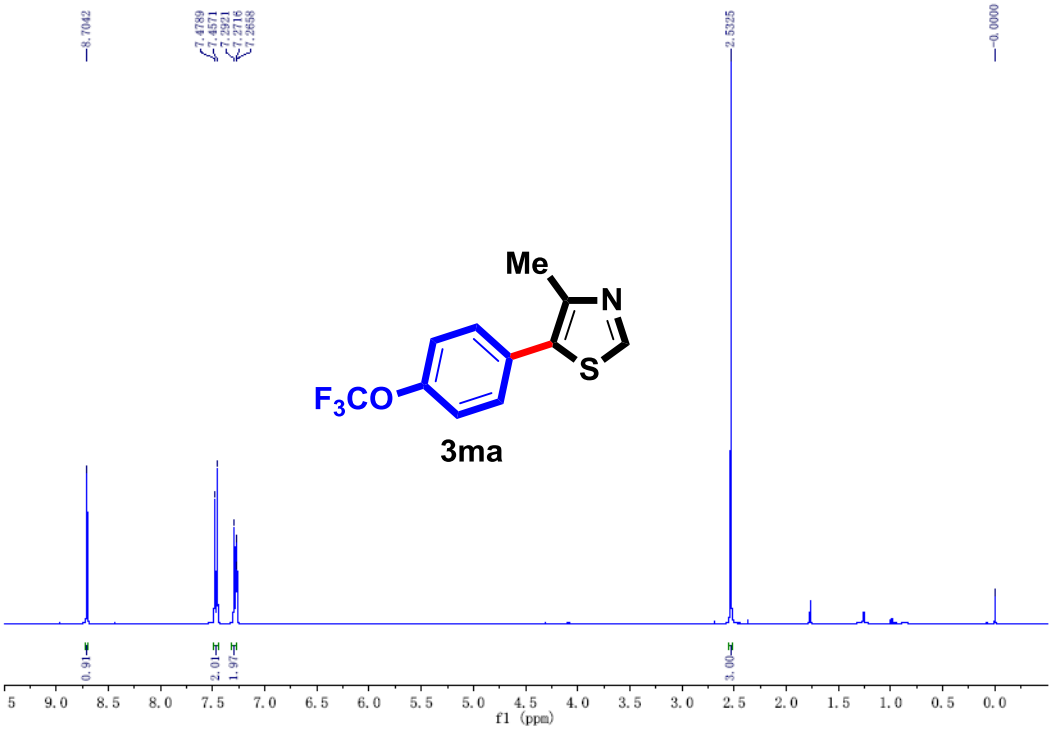

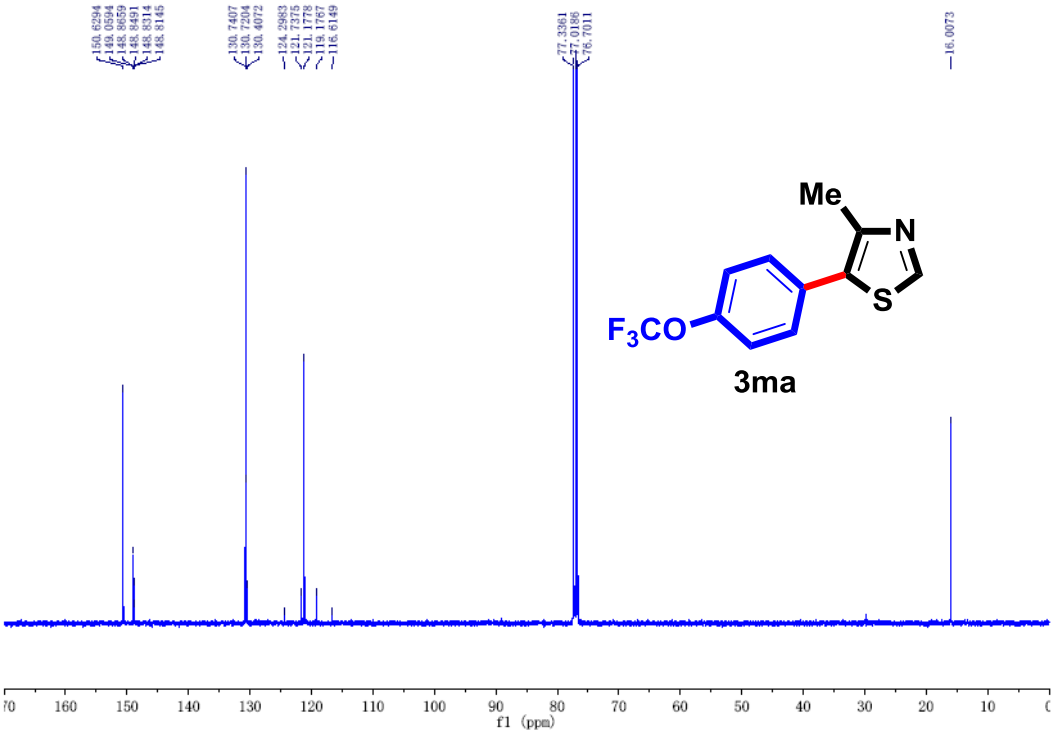

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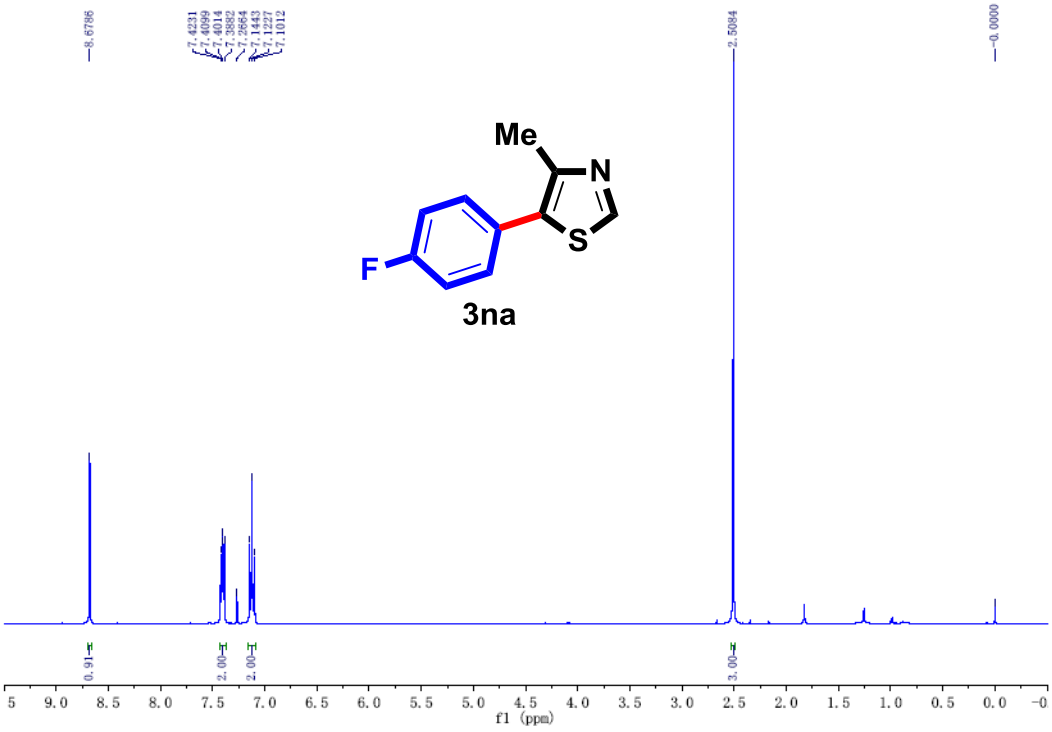

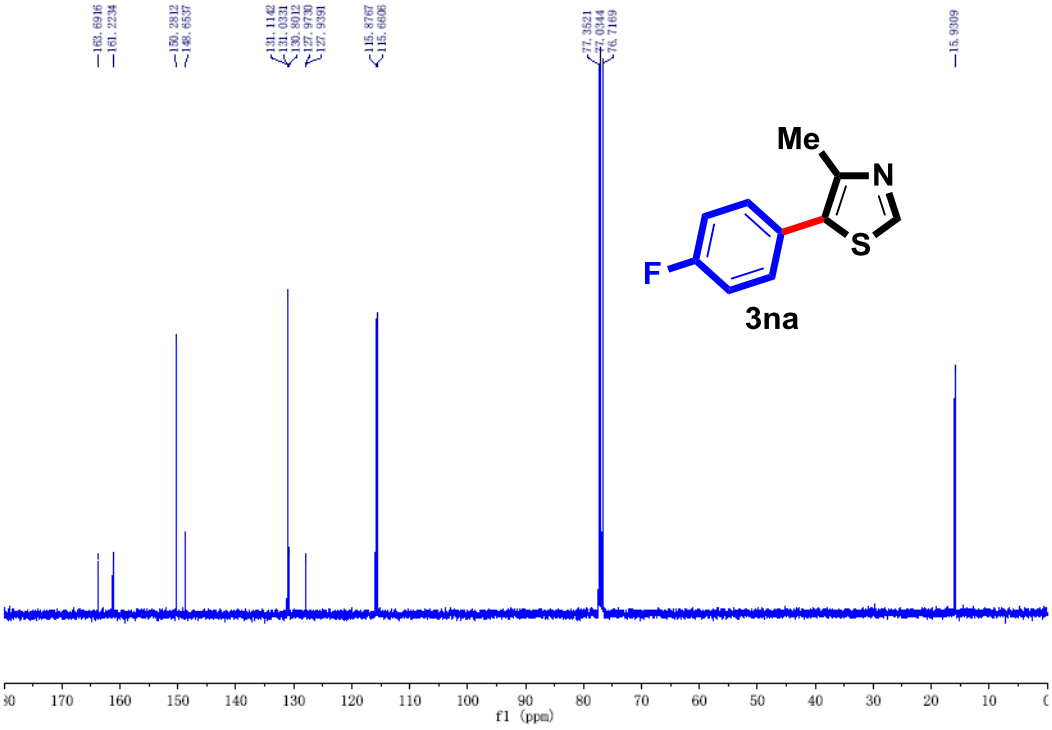

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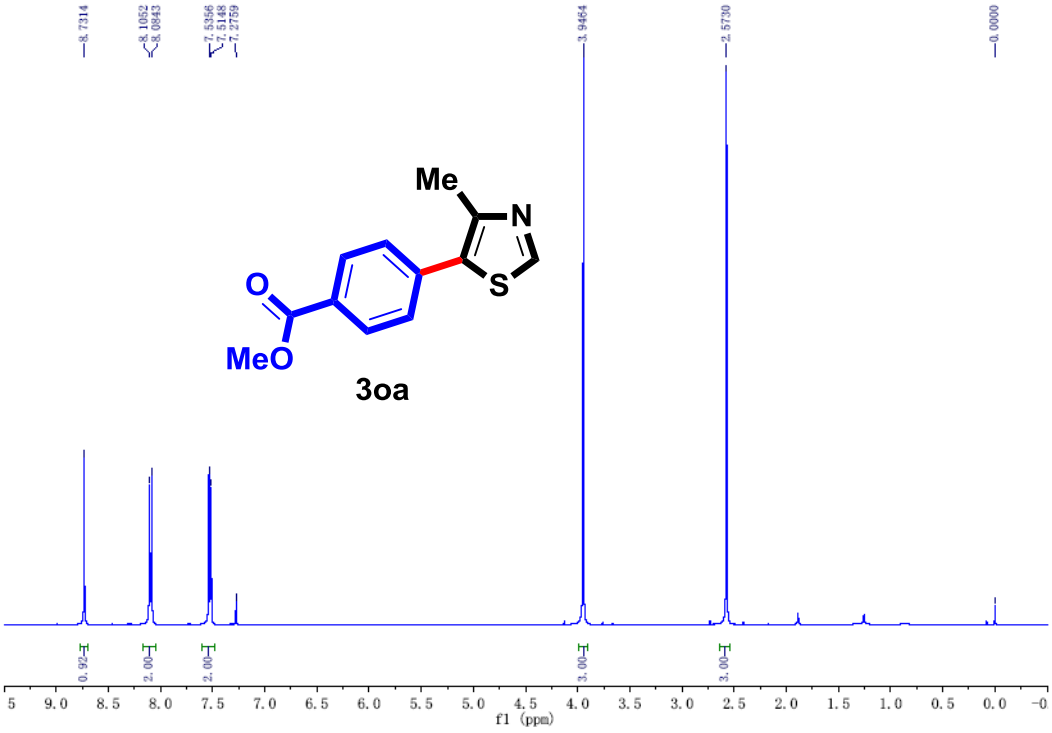

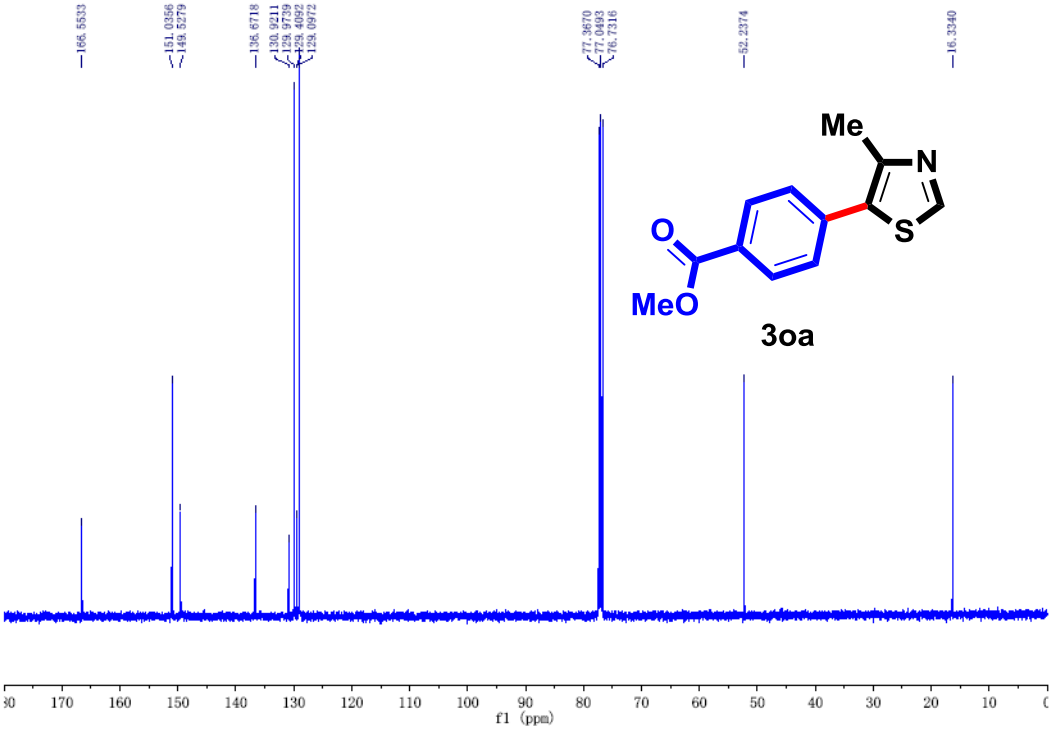

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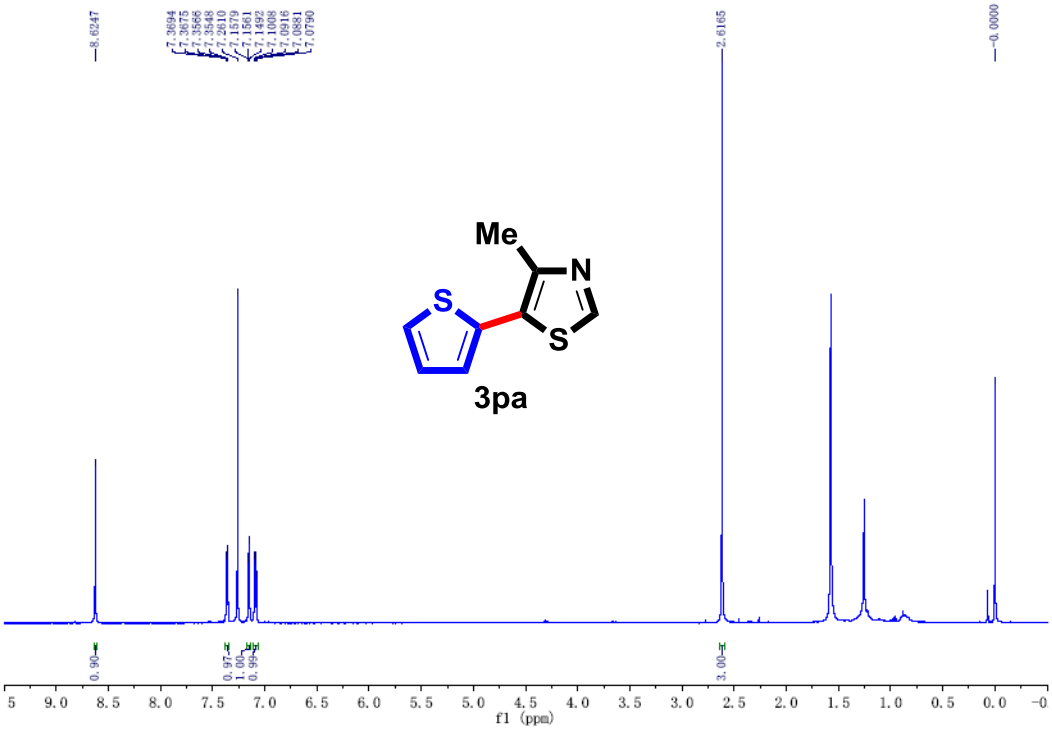

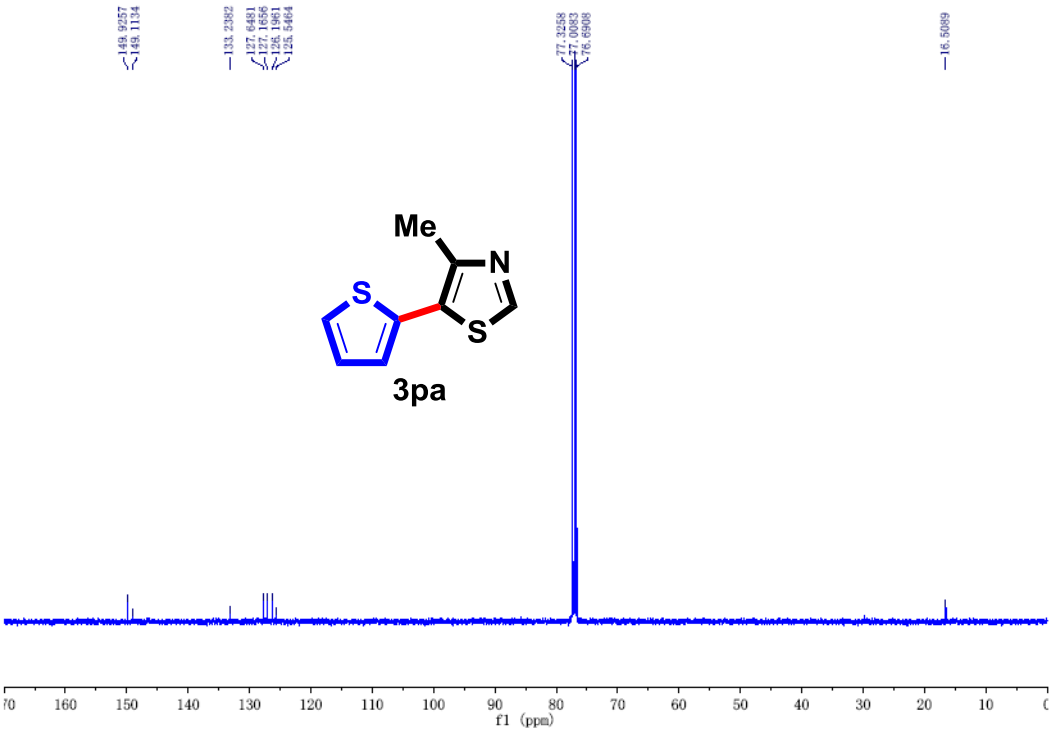

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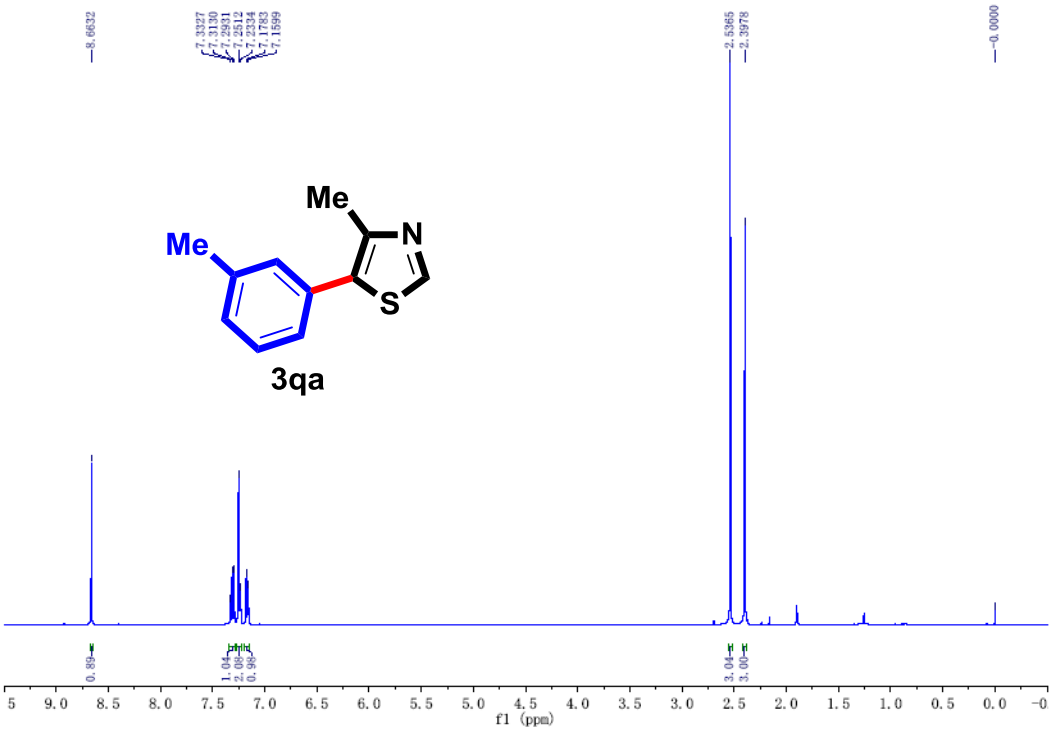

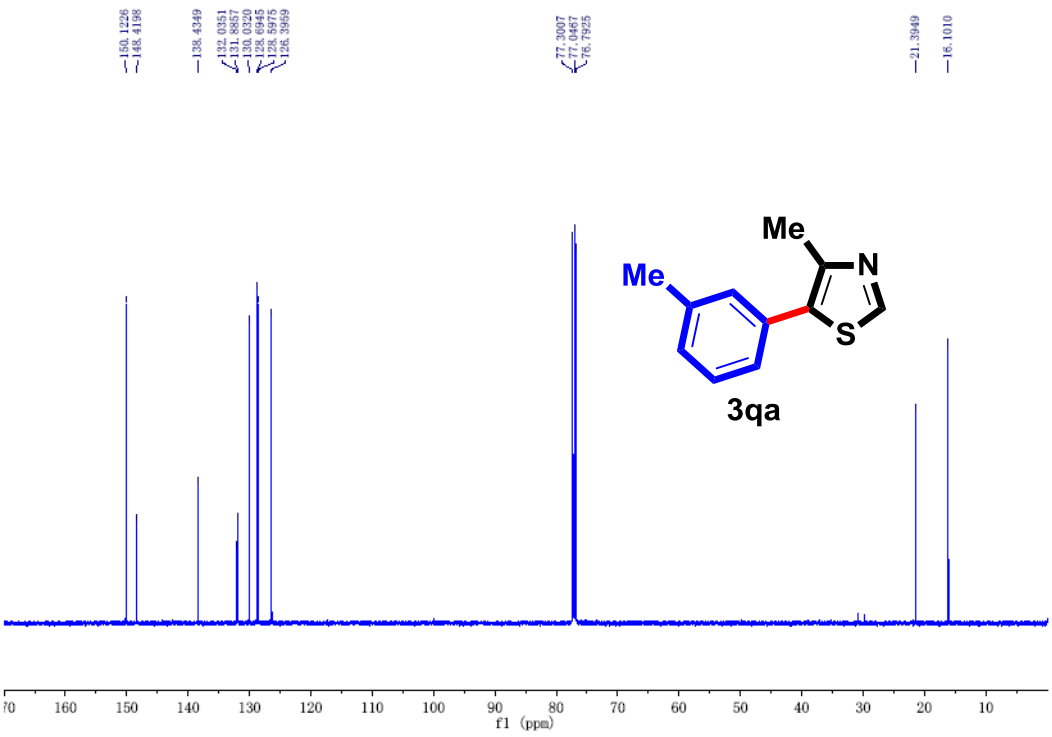

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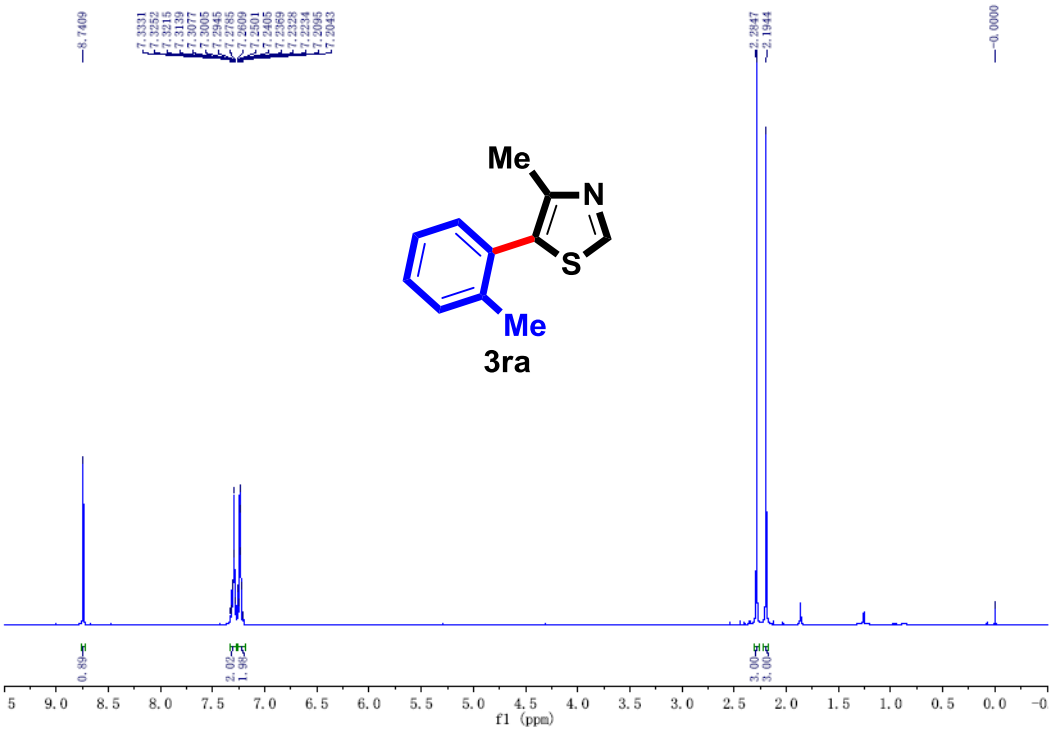

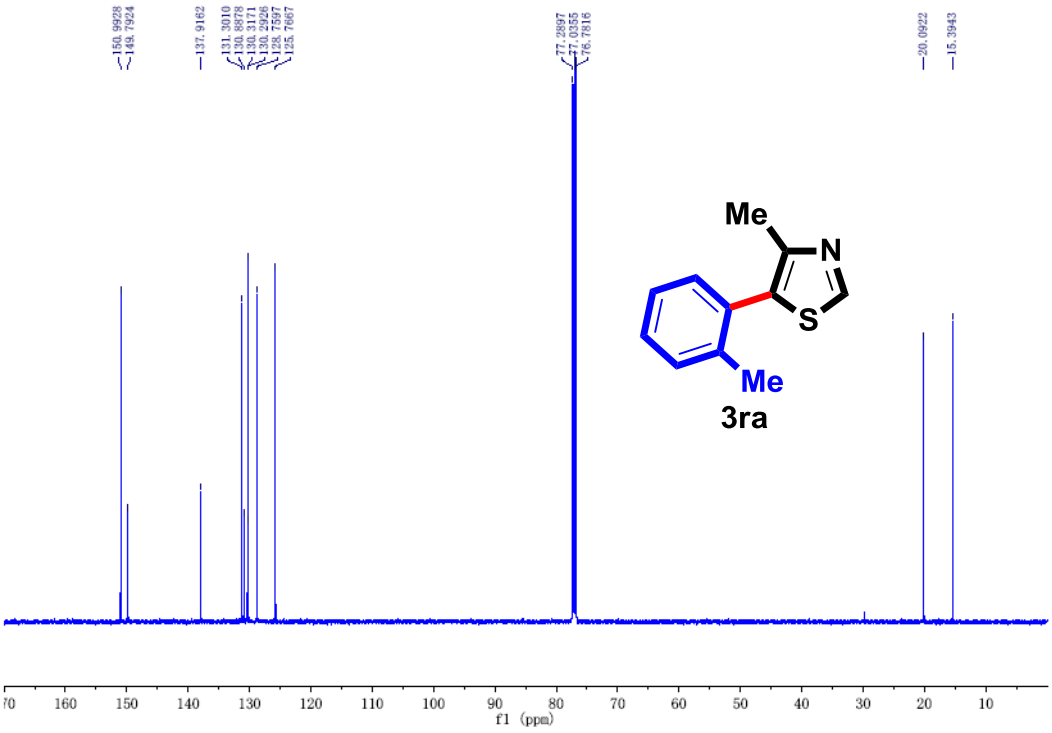

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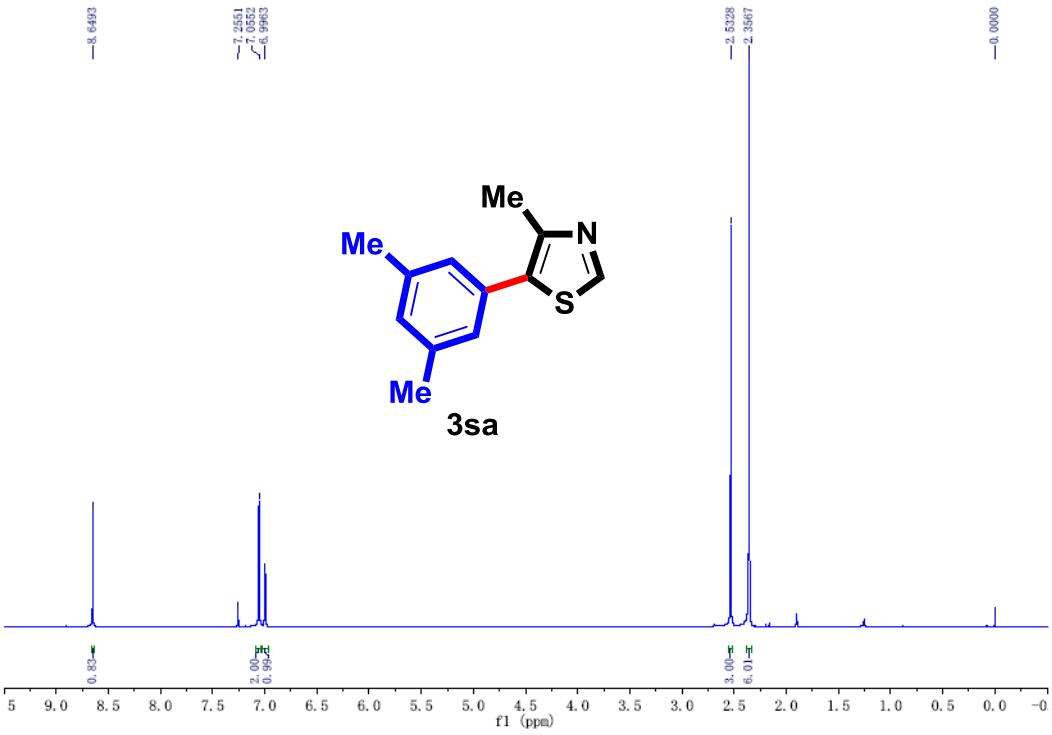

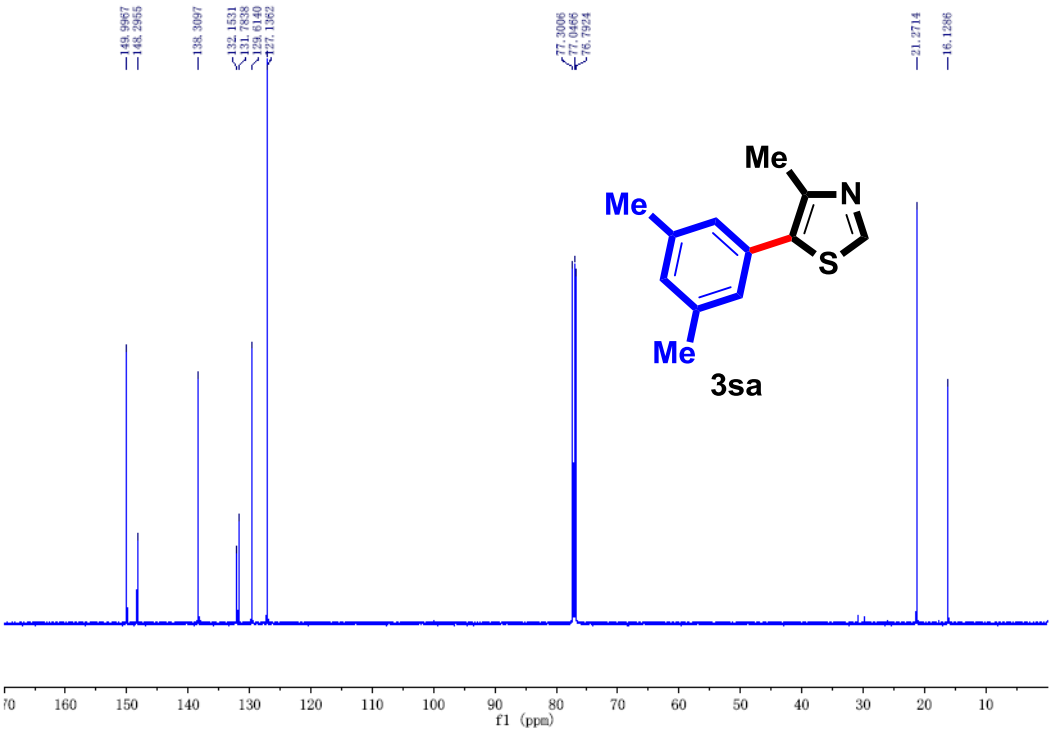

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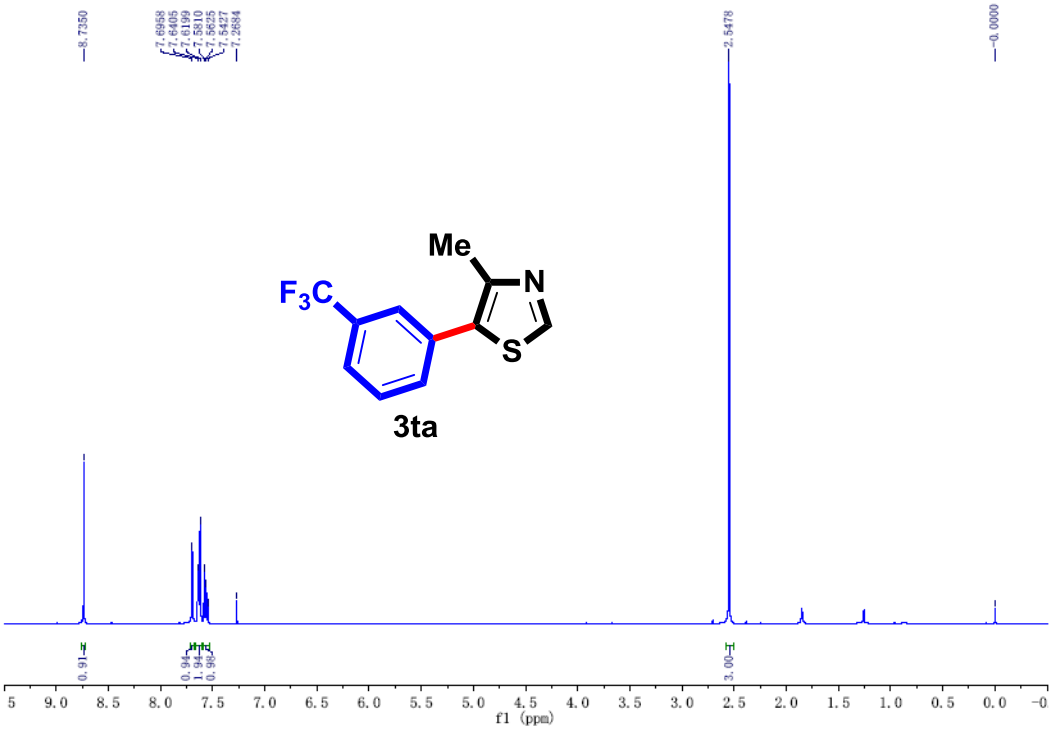

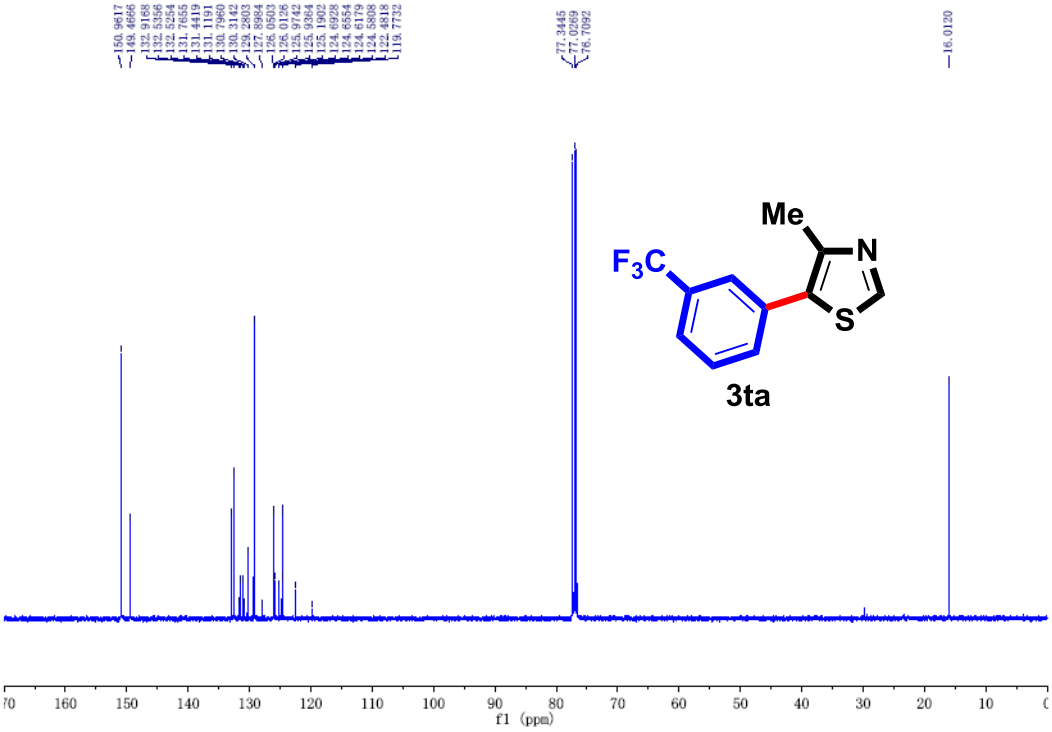

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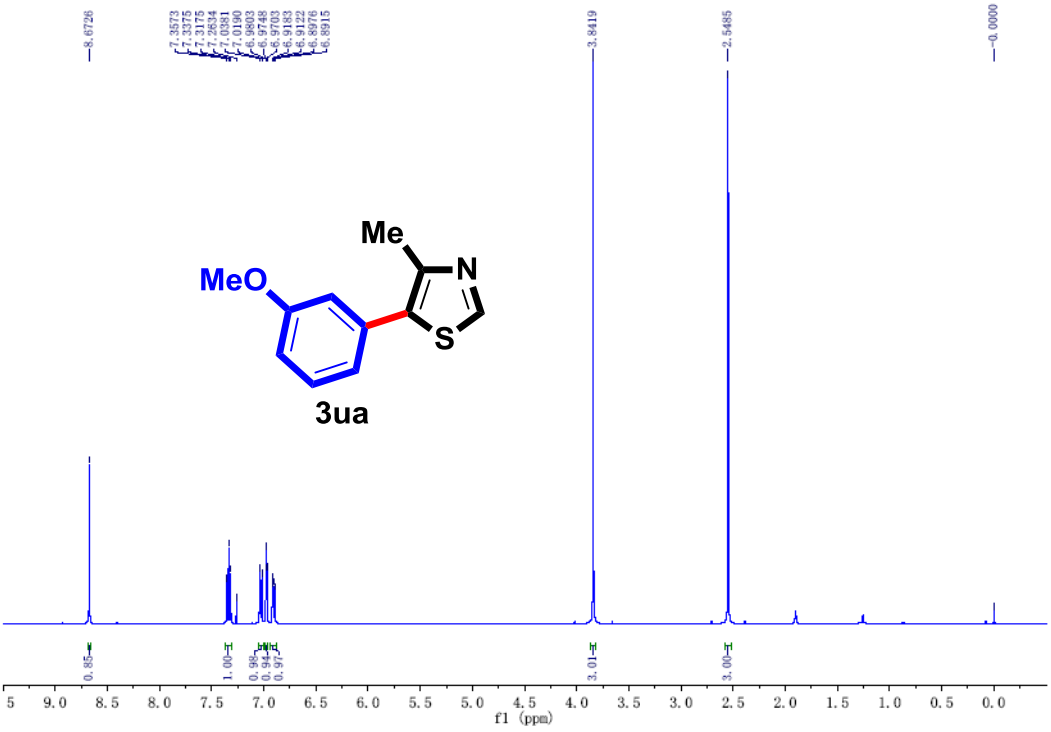

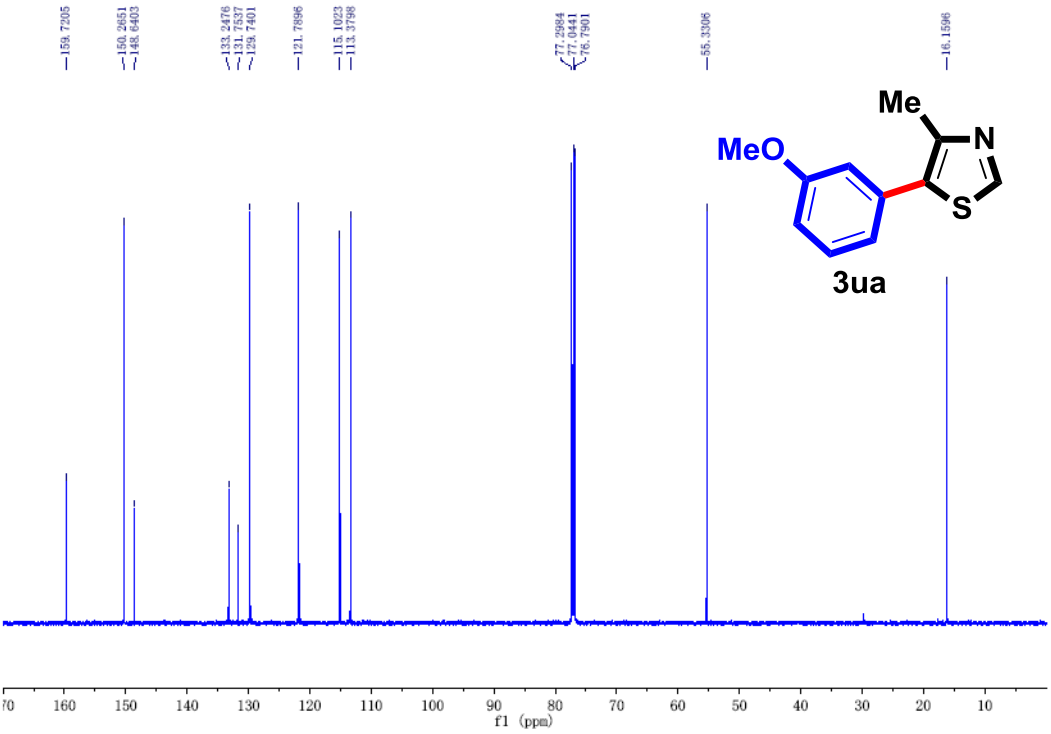

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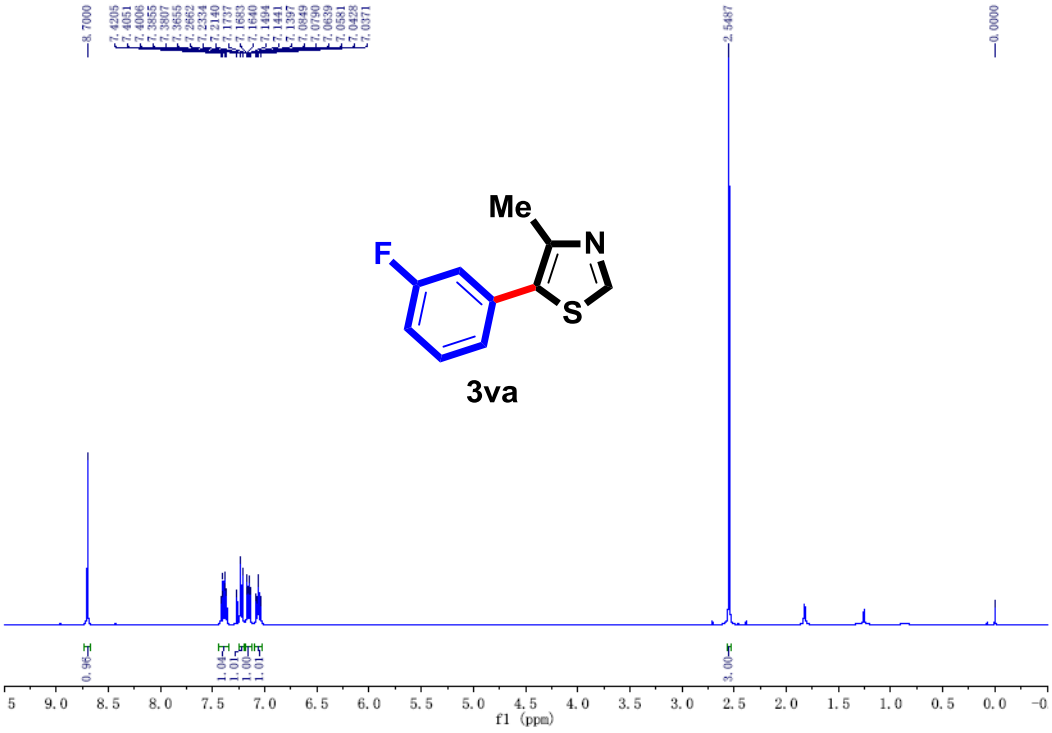

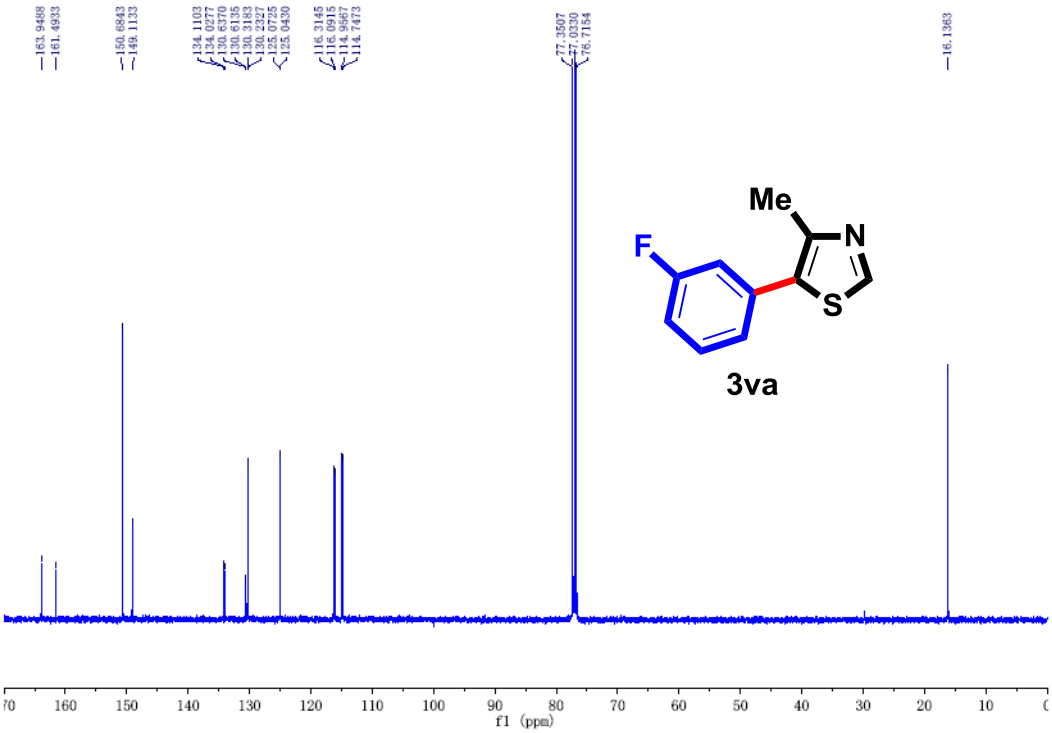

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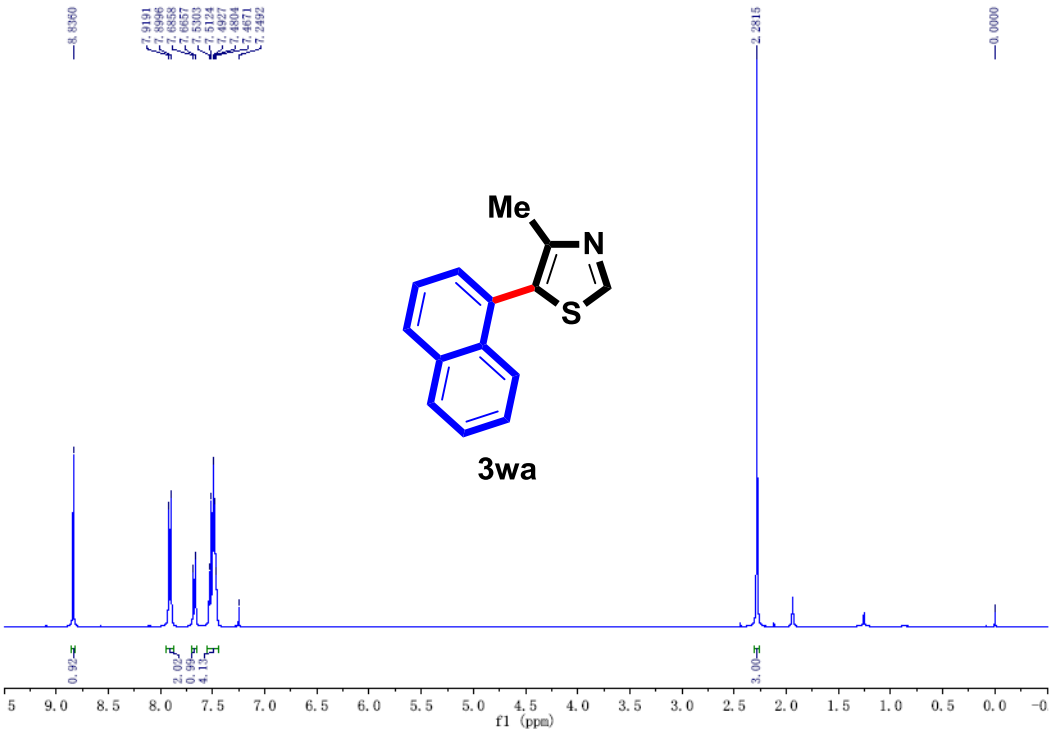

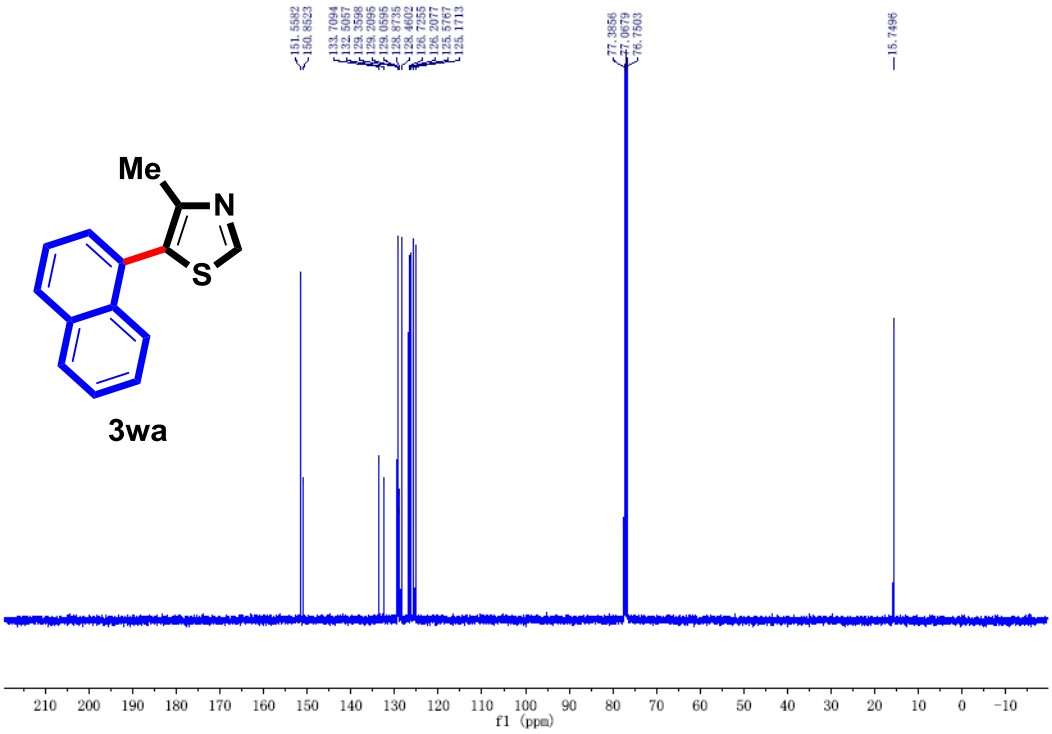

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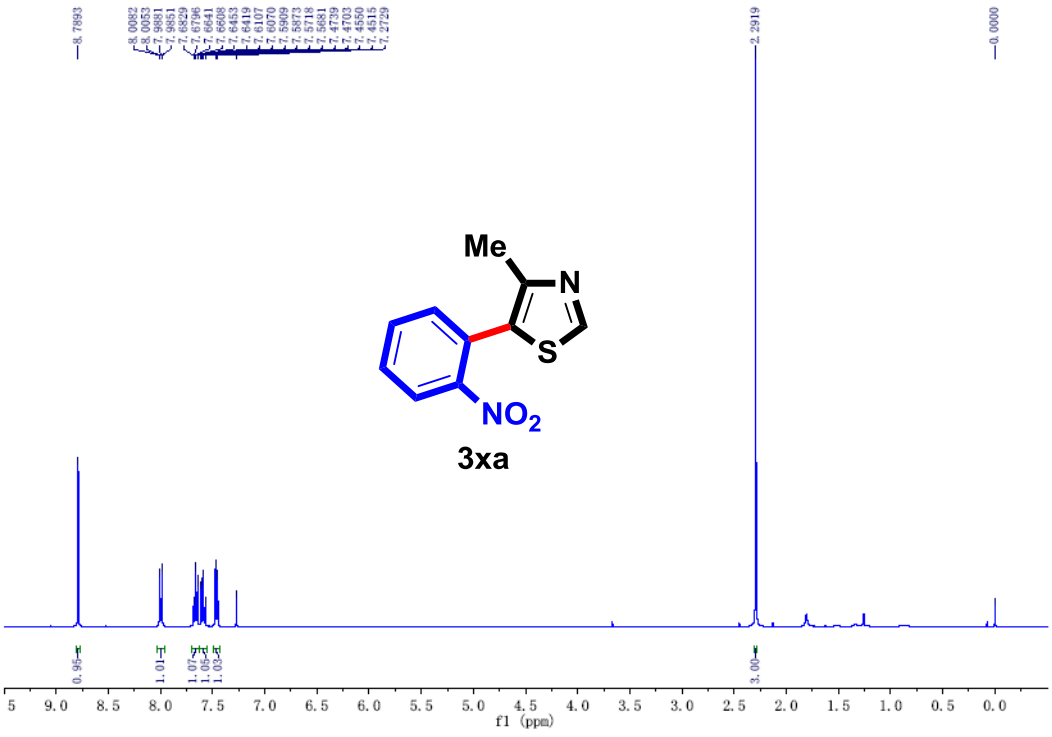

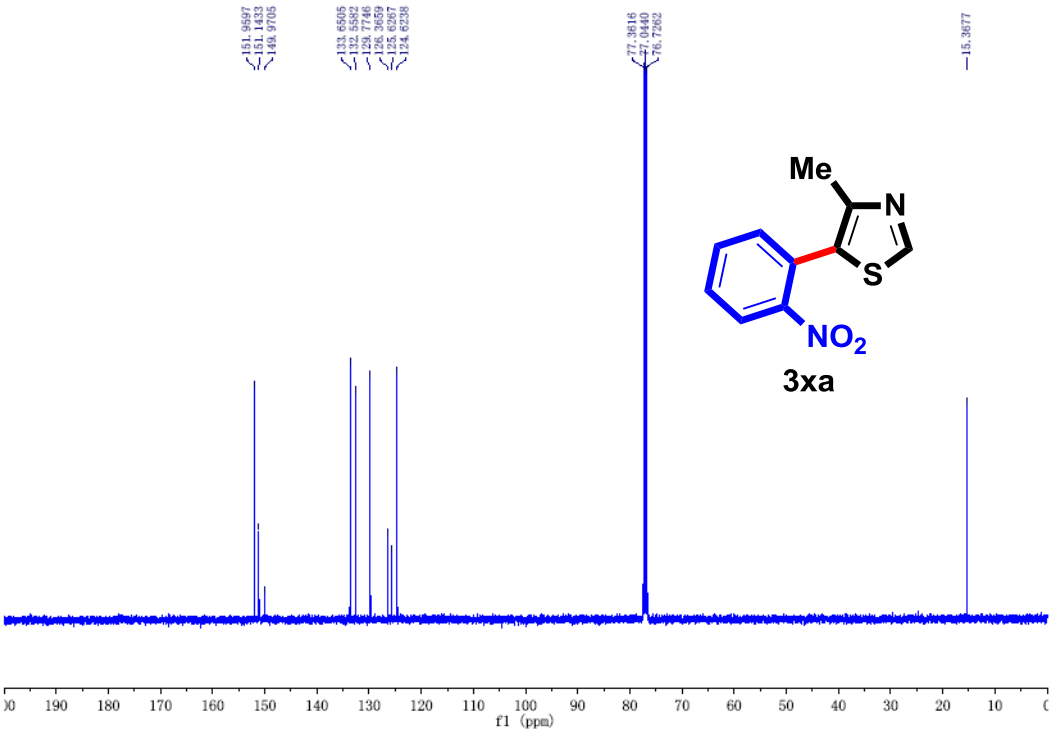

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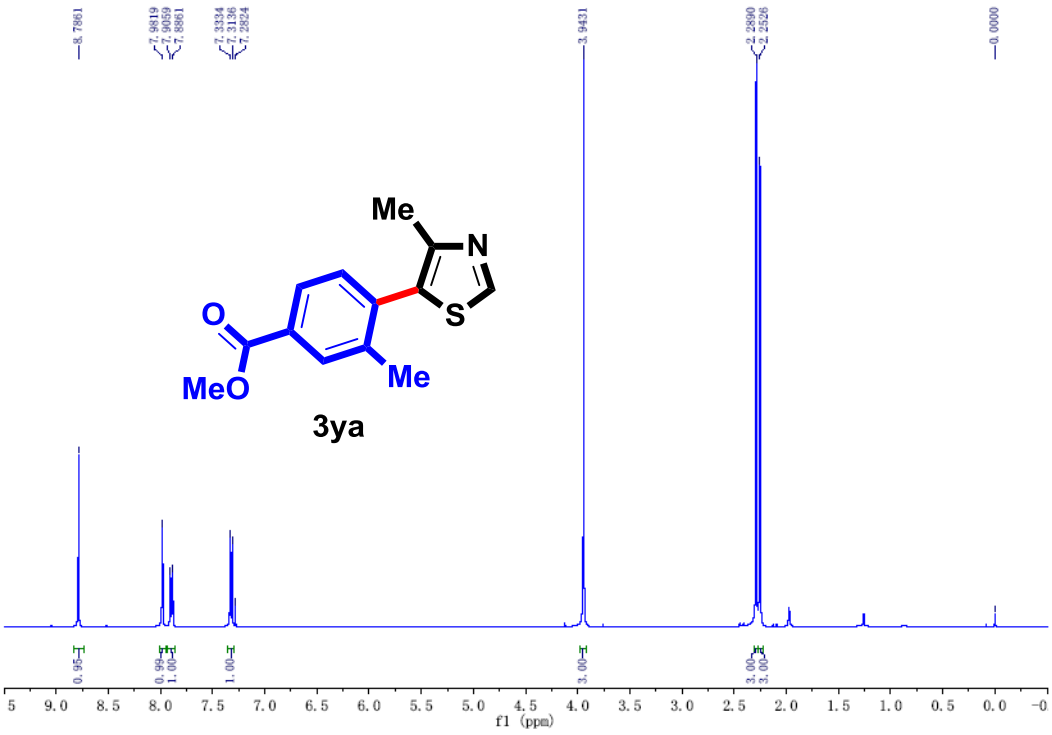

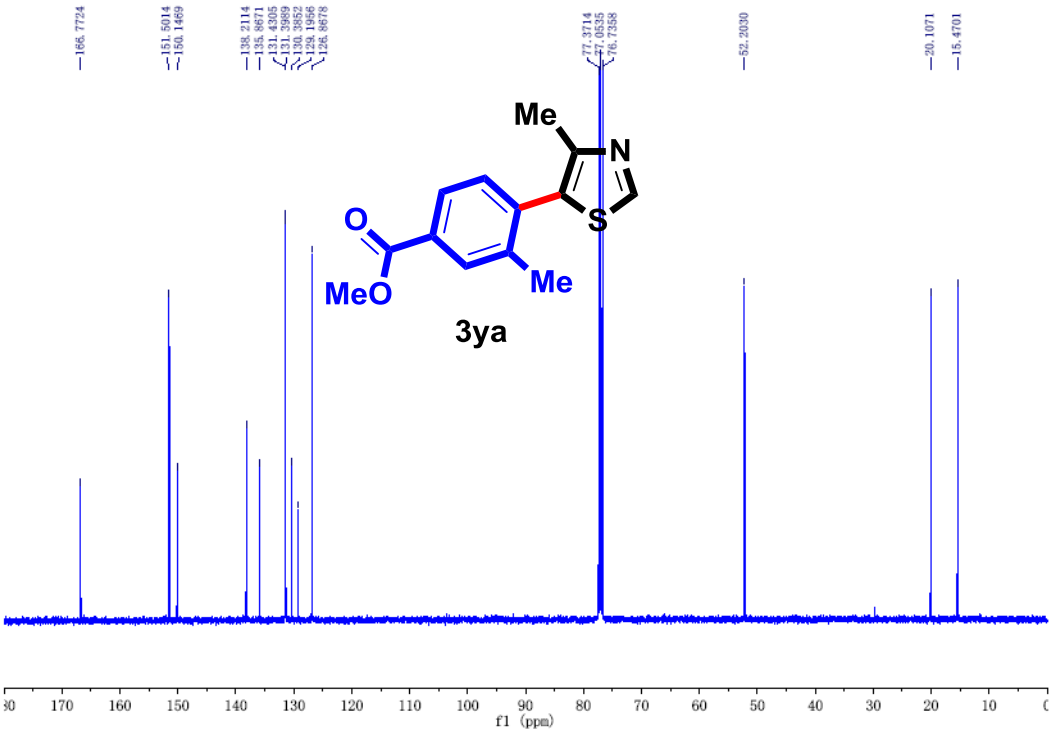

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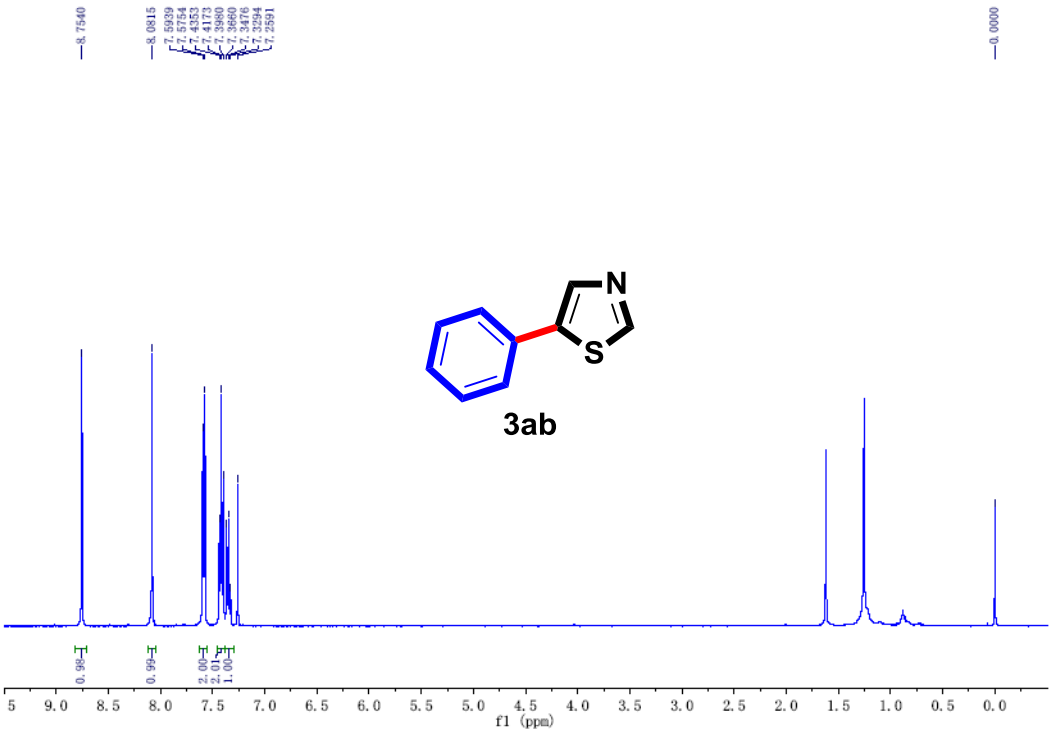

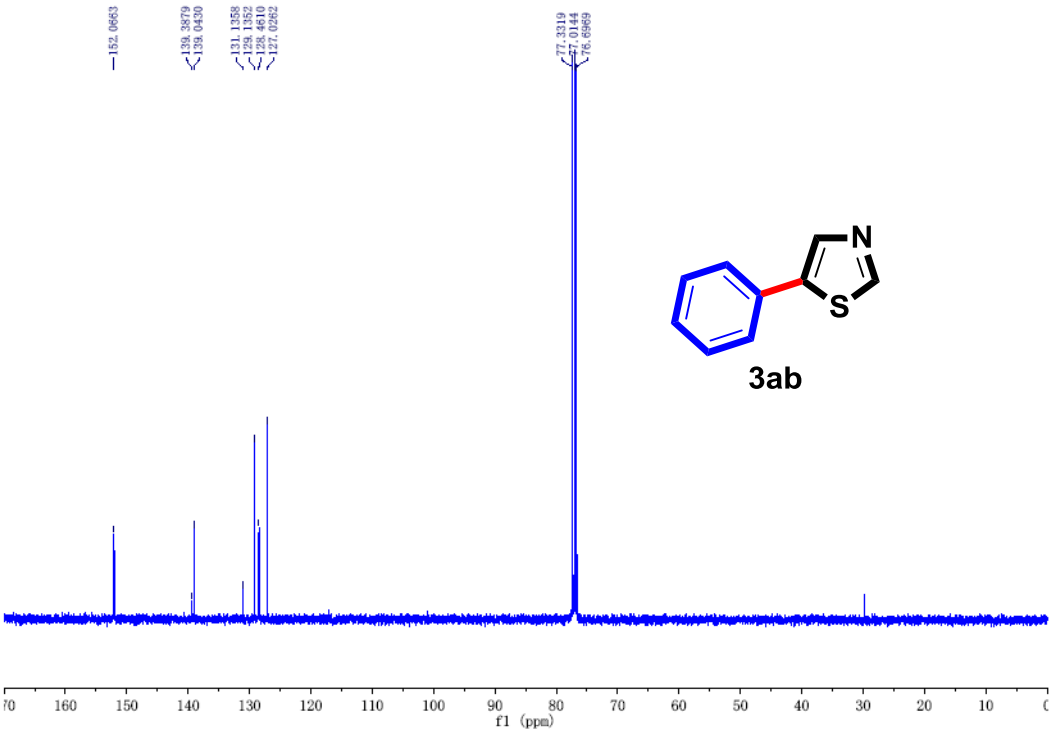

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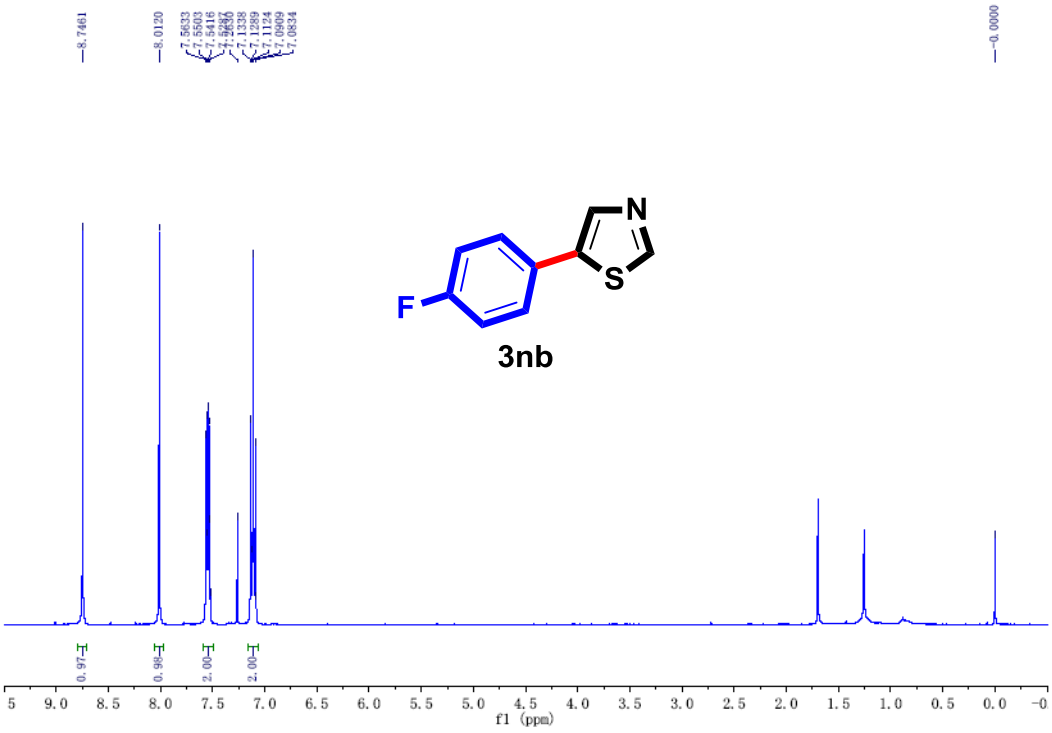

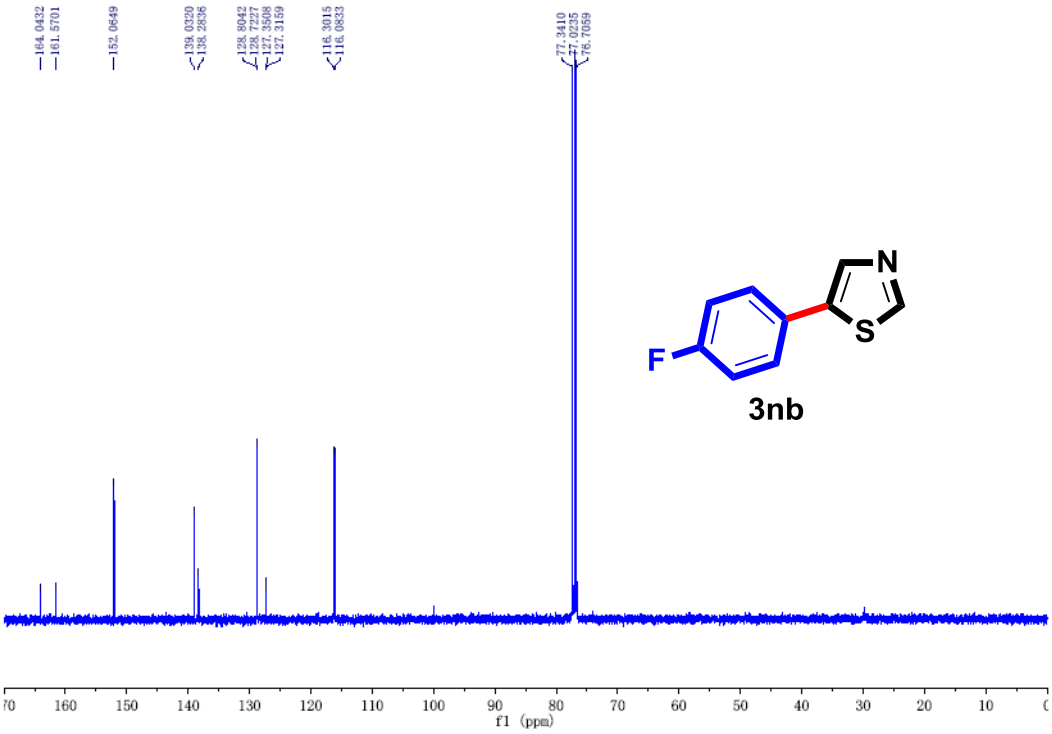

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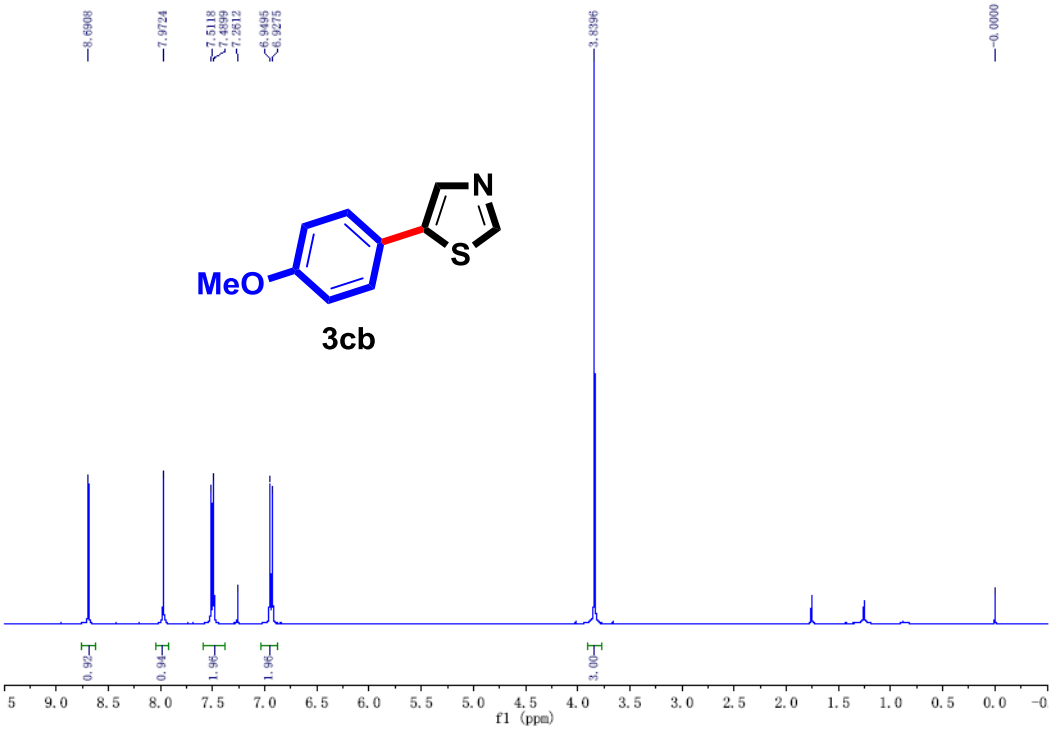

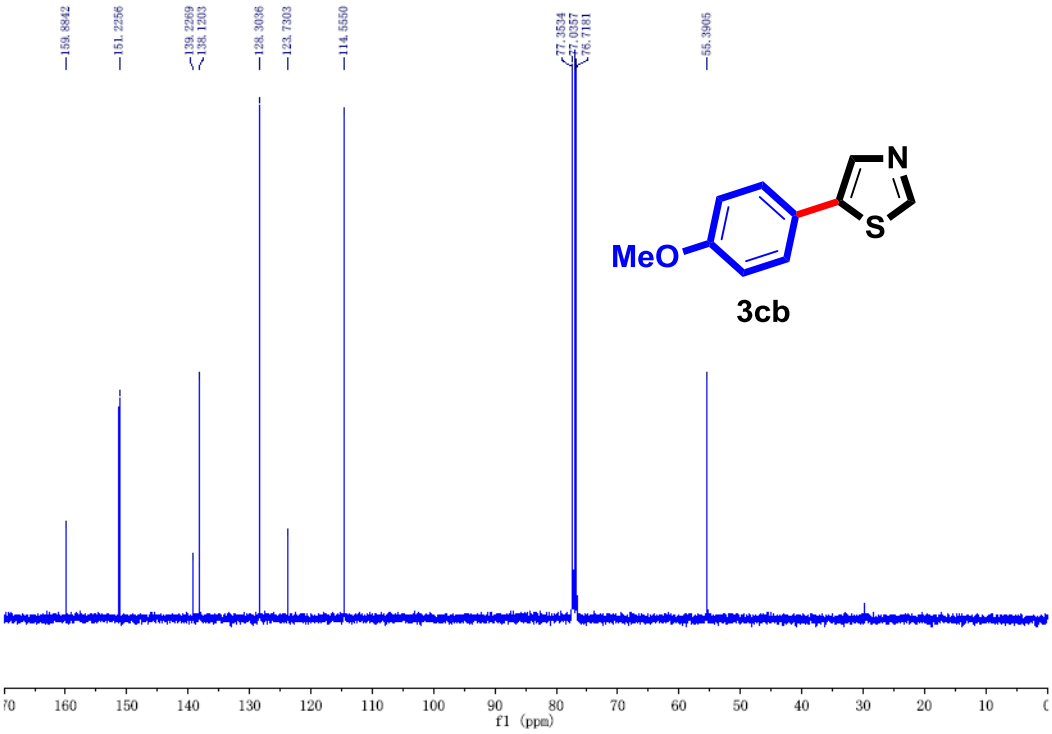

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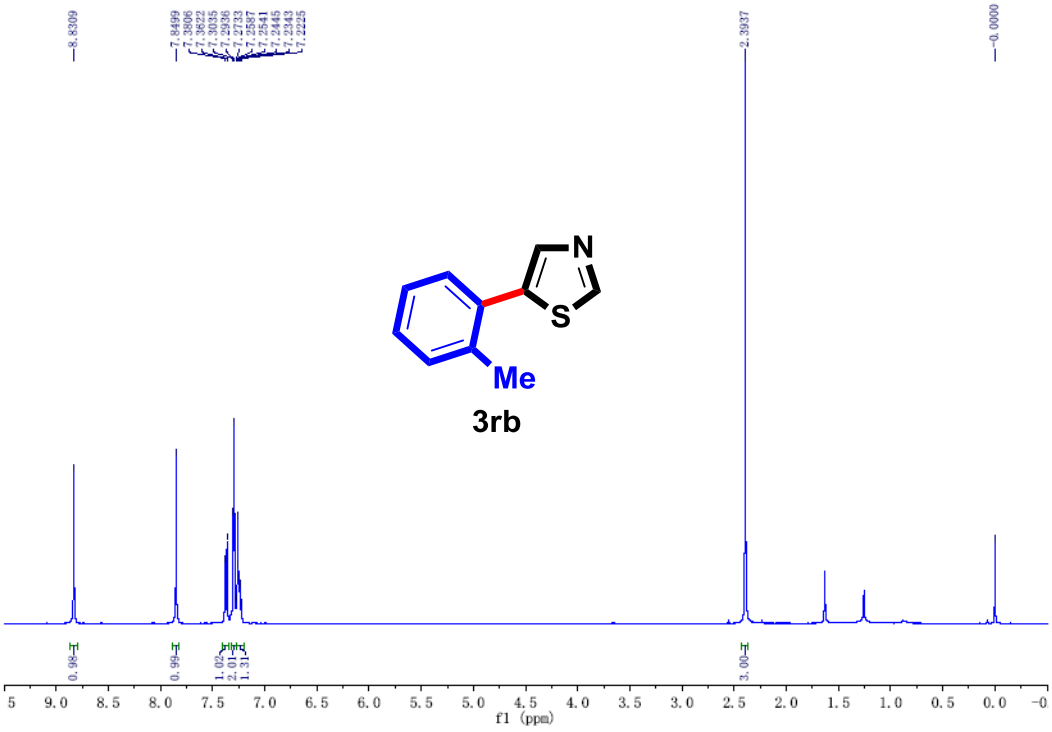

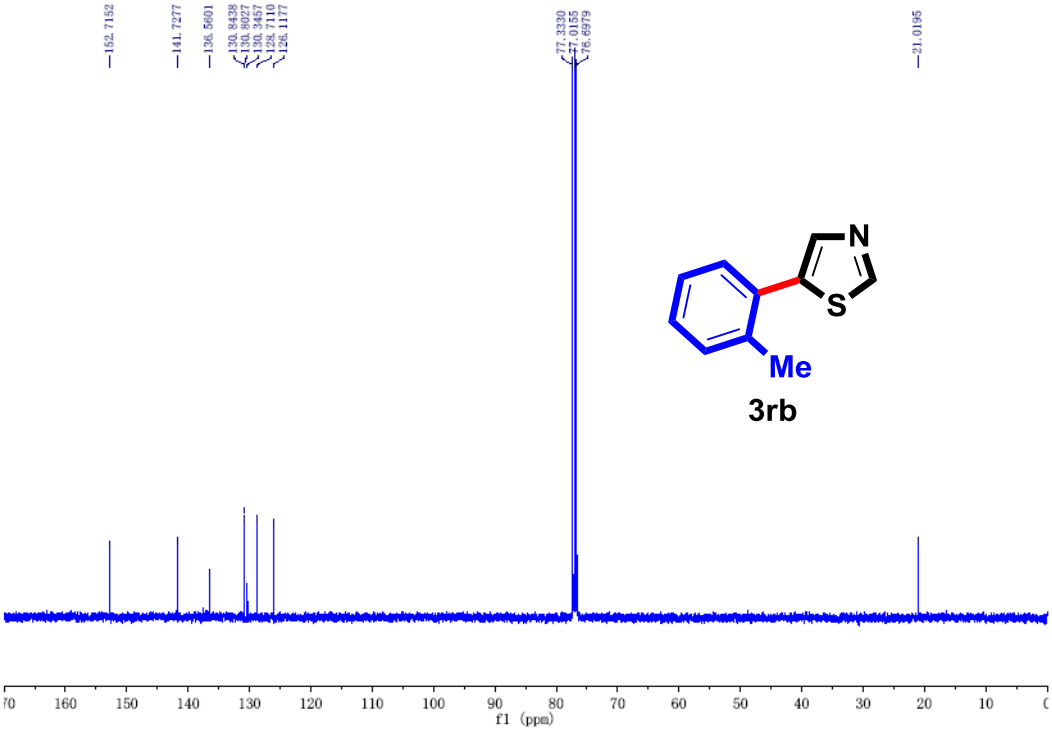

Spectra of **7**