Supporting Infomation

One-Pot Catalytic Oxidation for the Synthesis of 2-Biphenylbenzoxazoles, Benzothiazoles and 1-Substituted Benzimidazoles: A Convenient and Efficient Strategy

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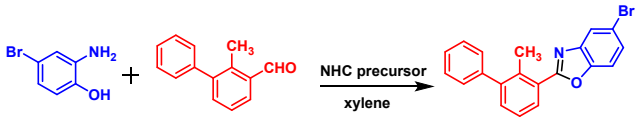
1. Supplementary reaction conditions [a]



1a 2a 3a

Entry	Oxidant (equiv)[b]	T (°C)	D (equiv)	Oxidant	Time (h)[c]	Yield (%)[d]
1	0	120	0.075	-	10	30
2	0	120	0.05	-	10	25
3	3	120	0.1	MnO_2	10	68
4	-	120	0.1	O_2	10	73[e]
5	3	120	0.1	DMP[f]	10	52

[a] Reaction conditions: 1a (0.3 mmol, 1 equiv.), 2a (0.36 mmol, 1.2 equiv.), NHC precursor (D) and Oxidant in 3 ml xylene. [b] After 1 h of reaction, Oxidant was added. [c] Total reaction time. [d] Isolated yield. [e] Continuous supply of O_2. [f] Dess-Martin periodinane.

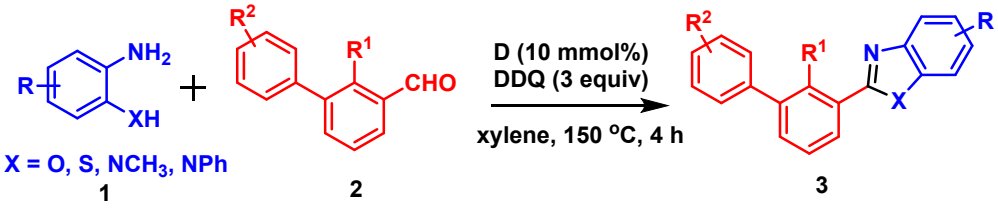
In the reaction, 1.2 eq aldehyde were employed to ensure complete conversion. Notably, no significant benzoin condensation byproducts were detected, primarily because the aldehyde was oxidized to the corresponding acid by the oxidant and could be readily removed during the workup procedure.

2. General Information

All of the chemical reagents and solvents were obtained from commercial sources and used directly without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 or 600 MHz spectrometer. Chemical shifts (δ) are given in relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$. Coupling constants, *J*, were reported in hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on a Q-STAR Elite ESI-LC-MS/MS Spectrometer. Chemical names were generated using Cambridge Soft. ChemDraw Ultra 16.0.

3. Experimental Details and Characterization Data

General Procedure for the synthesis of 3:



NHC precursor D (10 mmol%) was added to a solution of Compound **1** (0.3 mmol) and compound **2** (0.36 mmol) in 3 ml of xylene under air at 150 °C. After stirring for 1 h, DDQ (0.9 mmol) was added, and the reaction was continued under reflux for an additional 3 h. After the reaction was completed, the mixture was extracted with ethyl acetate (10ml x 3). The organic layer was washed with saturated saline and dried over anhydrous sodium sulfate. After removing the solvent in a vacuum, the resulting residue was purified by column chromatography on silica gel to give the desired products **3**.

5-bromo-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3a). The title compound was

isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (100.2 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.95 (t, *J* = 1.2 Hz, 1H), 7.54-7.31 (m, 9H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 149.4, 144.1, 143.7, 141.5, 136.5, 133.0, 129.5, 129.4, 128.3, 128.1, 127.2, 126.8, 125.7, 123.2, 117.1, 111.8, 19.2. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0335.

5-methyl-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3b). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (81.6 mg, 91% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.68-7.60 (m, 1H), 7.53-7.37 (m, 8H), 7.22 (dd, *J* = 8.3, 1.7 Hz, 1H), 2.65 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 148.7, 144.0, 142.3, 141.7, 136.2, 134.2, 132.5, 129.4, 129.4, 128.2, 127.6, 127.1, 126.2, 125.6, 120.1, 109.9, 21.6, 19.2. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{18}NO^+$ 300.1383, found 300.1380.

5-methoxy-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3c). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (86.9 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.52-7.33 (m, 9H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.91 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 157.3, 145.1, 144.0, 142.9, 141.7, 136.2, 132.6, 129.4, 129.4, 128.2, 127.5, 127.1, 125.7, 113.9, 110.7, 102.9, 56.0, 19.2. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{18}NO_2^+$ 316.1332, found 316.1330.

5-fluoro-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3d). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (85.4 mg, 94% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.59-7.36 (m, 9H), 7.14 (m,1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 160.1 (d, *J* = 241 Hz), 146.7, 144.1, 142.9 (d, *J* = 13 Hz), 141.5, 136.4, 132.9, 129.5, 129.4, 128.3, 127.2, 127.1, 125.7, 112.8 (d, *J* = 26 Hz), 110.8 (d, *J* = 10 Hz), 106.6 (d, *J* = 25 Hz), 19.3. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{15}FNO^+$ 304.1132, found 304.1132.

5-chloro-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3e). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (91.9 mg, 96% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.1, 2.3 Hz, 1H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.57-7.35 (m, 9H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 149.0, 144.1, 143.2, 141.5, 136.5, 133.0, 129.9, 129.5, 129.4, 128.3, 127.2, 126.9, 125.7, 125.4, 120.2, 111.3, 19.3. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{15}ClNO^+$ 320.0837, found 320.0838.

2-(2-methyl-[1,1'-biphenyl]-3-yl)-5-(trifluoromethyl)benzo[*d*]oxazole (3f). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (98.5 mg, 93% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.24-8.05 (m, 2H), 7.78-7.64 (m, 2H), 7.53-7.34 (m, 7H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.3, 152.1, 144.2, 142.2, 141.4, 136.7, 133.2, 129.5, 129.4, 128.3, 127.3, 127.2 (q, *J* = 32 Hz), 126.6, 125.8, 124.3 (q, *J* = 270 Hz), 122.4 (q, *J* = 4 Hz), 117.9 (q, *J* = 4 Hz), 111.0, 19.3. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{15}F_3NO^+$ 354.1100, found 354.1104.

2-(2-methyl-[1,1'-biphenyl]-3-yl)-5-nitrobenzo[*d*]oxazole (3g). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a yellow solid (93.1 mg, 94% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 8.9, 2.3 Hz, 1H), 8.17 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.52-7.36 (m, 7H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 153.9, 145.3, 144.4, 142.5, 141.3, 137.1, 133.6,

129.6, 129.3, 128.3, 127.3, 126.0, 125.9, 121.2, 116.6, 110.7, 19.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}N_2O_3^+$ 331.1077, found 331.1078.

4-bromo-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3h). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (95.8 mg, 88% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.58 (m, 2H), 7.51-7.34 (m, 7H), 7.28 (t, *J* = 8.0 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 150.6, 144.0, 141.5, 141.5, 136.6, 133.0, 129.7, 129.4, 128.3, 127.7, 127.2, 126.9, 125.9, 125.7, 112.9, 109.7, 19.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0334.

6-bromo-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3i). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (103.5 mg, 95% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.54-7.36 (m, 8H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.2, 150.9, 144.1, 141.5, 141.3, 136.5, 132.9, 129.5, 129.4, 128.3, 127.9, 127.2, 126.8, 125.7, 121.2, 118.0, 114.1, 19.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0334.

7-bromo-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3j). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (94.7 mg, 87% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.50-7.37 (m, 7H), 7.28 (d, *J* = 7.9 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.9, 148.7, 144.1, 142.7, 141.5, 136.6, 133.1, 129.7, 129.4, 128.2, 128.3, 127.2, 126.7, 125.8, 125.6, 119.2, 102.5, 19.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0333.

7-chloro-2-(2-methyl-[1,1'-biphenyl]-3-yl)-5-nitrobenzo[*d*]oxazole (3k). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a grey solid (104.8 mg, 96% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 2.1 Hz, 1H), 8.38 (d, *J* = 2.1 Hz, 1H), 8.22 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.52-7.36 (m, 7H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 150.7, 145.4, 144.4, 143.1, 141.1, 137.3, 134.0, 129.8, 129.3, 128.3, 127.4, 126.0, 125.4, 121.4, 116.6, 115.0, 19.4. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{14}ClN_2O_3^+$ 365.0687, found 365.0688.

2-([1,1'-biphenyl]-3-yl)-5-bromobenzo[*d*]oxazole (3l). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (94.2 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 (t, *J* = 1.8 Hz, 1H), 8.25-8.21 (m, 1H), 7.95 (d, *J* = 1.3 Hz, 1H), 7.83-7.79 (m, 1H), 7.74-7.69 (m, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.54-7.49 (m, 4H), 7.46-7.41 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.1, 149.8, 143.7, 142.1, 139.9, 130.6, 129.5, 129.0, 128.2, 127.9, 127.2, 127.2, 126.5, 126.4, 123.0, 117.4, 111.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{13}BrNO^+$ 350.0175, found 350.0174.

2-(2-fluoro-[1,1'-biphenyl]-3-yl)-5-methylbenzo[*d*]oxazole (3m). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (82.7 mg, 91% yield). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.22 (ddd, *J* = 8.4, 6.6, 1.8 Hz, 1H), 7.68-7.60 (m, 4H), 7.54-7.48 (m, 3H), 7.47-7.42 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.7 (d, *J* = 5 Hz), 157.7 (d, *J* = 260 Hz), 148.8, 142.0, 135.0, 134.6, 133.8 (d, *J* = 5 Hz), 130.8 (d, *J* = 15 Hz), 129.6, 129.2 (d, *J* = 5

Hz), 128.5, 128.1, 126.7, 124.5 (d, *J* = 5 Hz), 120.3, 116.3 (d, *J* = 12 Hz), 110.1, 21.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}FNO^+$ 304.1132, found 304.1128.

5-bromo-2-(4'-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3n). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (96.9 mg, 89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (t, *J* = 1.8 Hz, 1H), 8.25-8.17 (m, 1H), 7.95-7.94 (m, 1H), 7.81-7.78 (m, 1H), 7.63-7.58 (m, 3H), 7.50-7.49 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 149.8, 143.7, 142.0, 137.8, 137.0, 130.4, 129.7, 129.4, 128.2, 127.1, 127.0, 126.3, 126.2, 123.0, 117.4, 111.9, 21.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0333.

5-bromo-2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3o). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (111.1 mg, 89% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (d, *J* = 1.8 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.94 (s, 1H), 7.83-7.75 (m, 5H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.51 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.7, 149.8, 143.6, 143.4, 140.6, 130.7, 130.0 (q, *J* = 33 Hz), 129.7, 128.4, 127.5, 127.4, 127.3, 126.5, 125.9 (q, *J* = 4 Hz), 124.2 (q, *J* = 270 Hz), 123.1, 117.5, 111.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{12}BrF_3NO^+$ 418.0049, found 418.0050.

5-bromo-2-(3'-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazole (3p). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (98.0 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (t, *J* = 1.8 Hz, 1H), 8.24-8.20 (m, 1H), 7.95 (t, *J* = 1.2 Hz, 1H), 7.82-7.78 (m, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56-7.47 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29-7.24 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 149.8, 143.7, 142.2, 139.9, 138.6, 130.7, 129.4, 128.9, 128.7, 128.2, 128.0, 127.1, 126.4, 126.4, 124.3, 123.0, 117.4, 111.9, 21.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNO^+$ 364.0332, found 364.0332.

5-bromo-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]thiazole (3q). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (110.3 mg, 97% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.69-7.63 (m, 2H), 7.50-7.45 (m, 2H), 7.43-7.36 (m, 5H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 169.0, 152.6, 143.9, 141.6, 137.5, 134.8, 133.7, 132.0, 129.8, 129.7, 129.3, 128.3, 127.2, 125.8, 124.5, 124.0, 118.8, 18.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}BrNS^+$ 380.0103, found 380.0105.

5-chloro-2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)benzo[*d*]thiazole (3r). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (114.4 mg, 98% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 (t, *J* = 1.9 Hz, 1H), 8.10-8.08 (m, 2H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.84-7.72 (m, 5H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 169.4, 154.9, 143.6, 140.8, 134.0, 133.3, 132.5, 130.0 (q, *J* = 30 Hz), 129.8, 127.6, 127.4, 126.3, 125.9, 125.9 (q, *J* = 12 Hz), 125.9, 124.2 (q, *J* = 270 Hz), 123.1, 122.4. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{12}ClF_3NS^+$ 390.0326, found 390.0327.

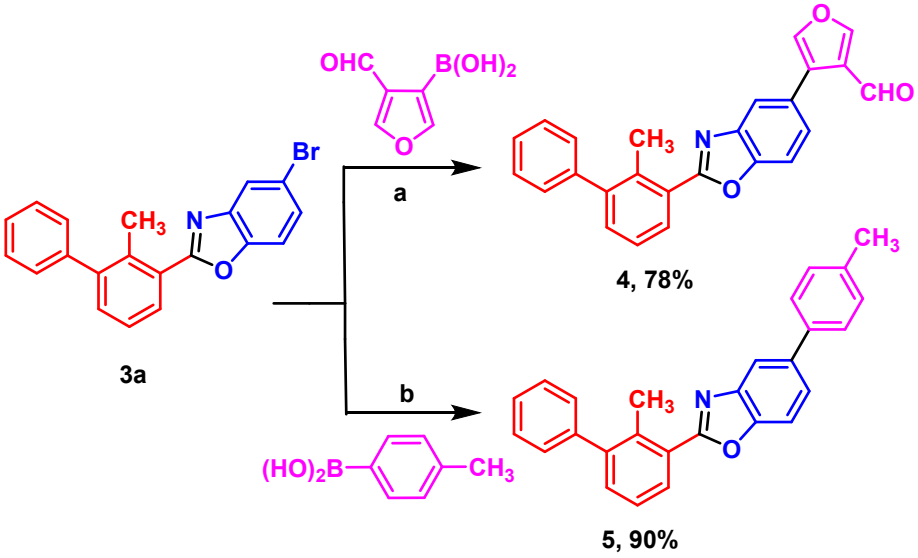
5-chloro-2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]thiazole (3s). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (97.5 mg, 97% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.68 (dd, *J* = 6.3, 2.8 Hz, 1H), 7.50-7.37 (m, 8H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 154.5, 143.9, 141.6, 134.8, 134.1, 133.7, 132.2, 132.0, 129.8, 129.3, 128.3,

127.2, 125.8, 125.7, 123.2, 122.2, 18.7. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{15}ClNS^+$ 336.0608, found 336.0608.

1-methyl-2-(2-methyl-[1,1'-biphenyl]-3-yl)-1H-benzo[*d*]imidazole (3t). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (79.5 mg, 89% yield). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.49-7.41 (m, 3H), 7.45-7.38 (m, 3H), 7.41-7.33 (m, 5H), 3.71 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 154.1, 143.2, 143.0, 141.5, 135.6, 135.5, 131.4, 130.8, 129.4, 129.3, 128.2, 127.1, 125.6, 122.7, 122.3, 119.9, 109.5, 30.7, 18.0. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{19}N_2^+$ 299.1543, found 299.1545.

2-(2-methyl-[1,1'-biphenyl]-3-yl)-1-phenyl-1H-benzo[*d*]imidazole (3u). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 10 : 1) as a white solid (91.8 mg, 85% yield). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.47-7.42 (m, 3H), 7.42 -7.36 (m, 5H), 7.36-7.32 (m, 2H), 7.28-7.22 (m, 4H), 7.21-7.18 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 153.3, 142.9, 141.6, 136.4, 135.6, 135.3, 131.1, 130.1, 129.4, 129.2, 128.1, 127.9, 127.0, 126.5, 125.3, 123.3, 122.9, 120.1, 116.2, 115.2, 110.5, 18.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{26}H_{21}N_2^+$ 361.1699, found 361.1697.

4. Synthetic Transformations



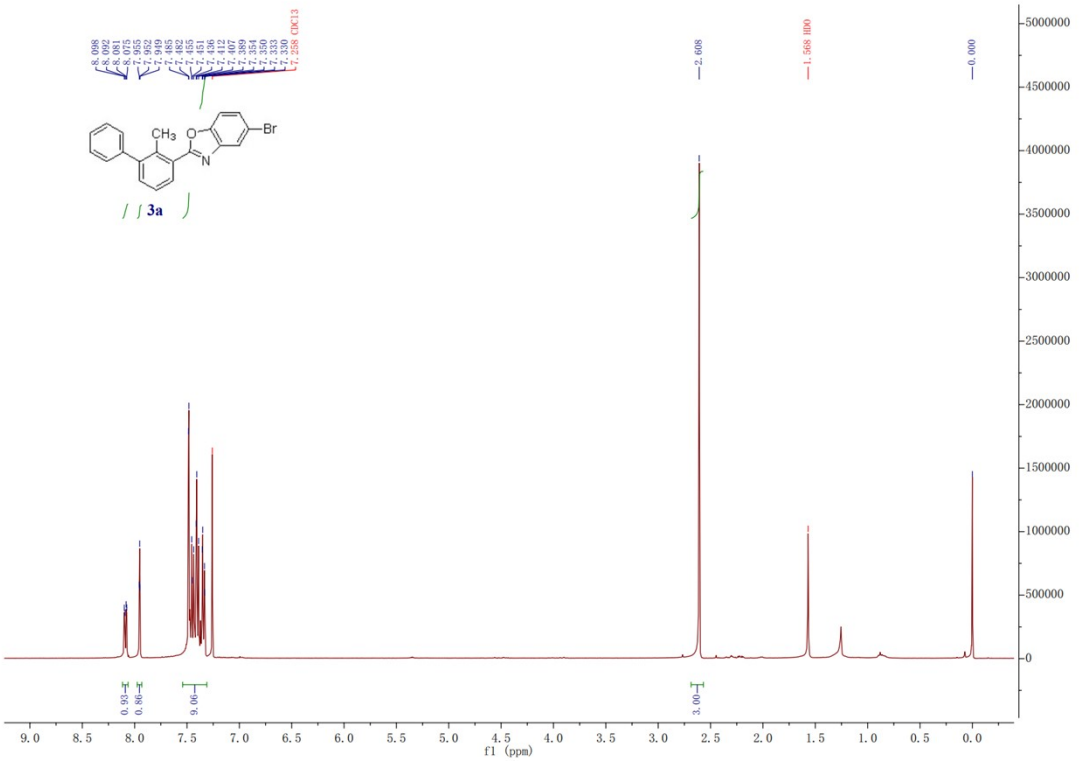
The compound **3a** (1 mmol), substituted arylboronic acids (1.5 mmol), $(PPh_3)_4Pd$ (0.02 mmol), and Cs_2CO_3 (2 mmol) in DMF/H_2O (3:1, 20 mL) were heated at 80 °C under argon overnight. After the reaction was completed, the mixture was extracted with ethyl acetate (30ml x 3). The organic layer was washed with saturated saline and dried over anhydrous sodium sulfate. After removing the solvent in a vacuum, the resulting residue was purified by column chromatography on silica gel to give the desired products **4** and **5**.

4-(2-(2-methyl-[1,1'-biphenyl]-3-yl)benzo[*d*]oxazol-5-yl)furan-3-carbaldehyde (4). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 6 : 1) as a white solid (295.6 mg, 78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 8.34-8.25 (m, 1H), 8.15 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.93 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.70 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.51-7.36 (m, 8H), 6.92 (d, *J* = 3.7 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3,164.9, 152.1, 151.2, 144.2, 142.9, 141.5, 136.6, 133.0, 129.5, 129.4, 128.3, 127.2, 126.8,

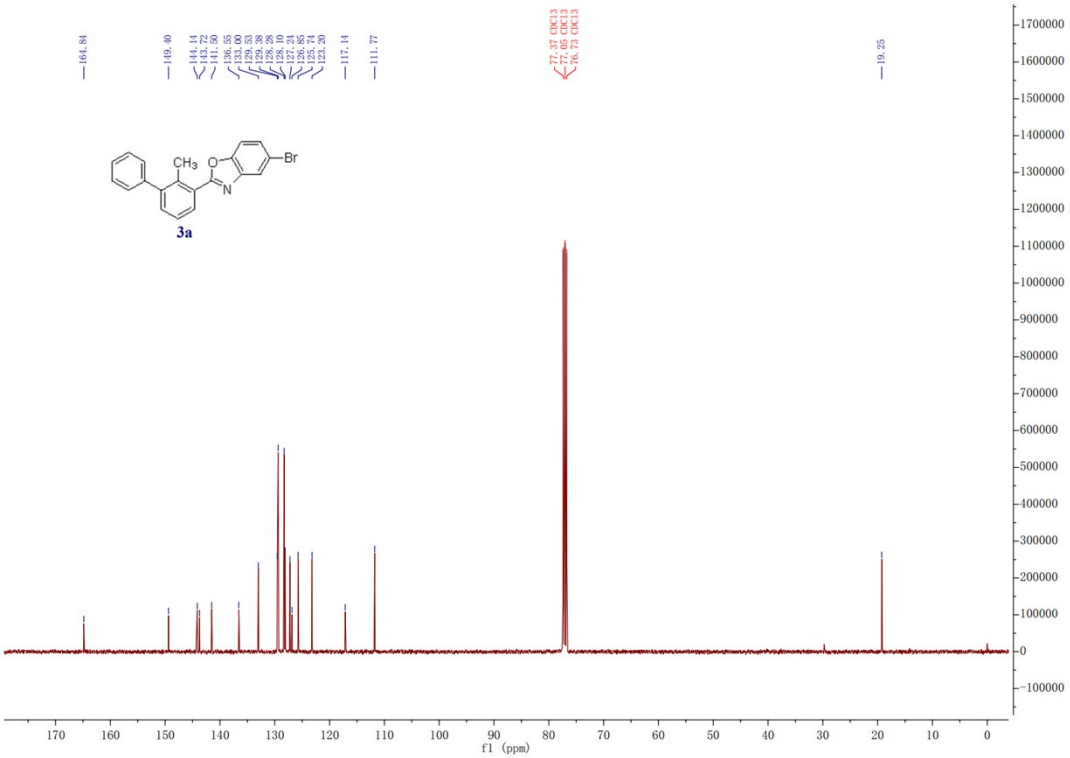
125.9, 125.7, 122.8, 117.2, 111.2, 107.6, 19.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{18}NO_3^+$ 380.1281, found 380.1285.

2-(2-methyl-[1,1'-biphenyl]-3-yl)-5-(p-tolyl)benzo[*d*]oxazole (5). The title compound was isolated by silica gel flash column chromatography (n-hexane/EA = 6 : 1) as a white solid (337.5 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 6.0, 3.2 Hz, 1H), 8.05 (d, *J* = 1.6 Hz, 1H), 7.73-7.56 (m, 4H), 7.52-7.39 (m, 7H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.69 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 149.8, 144.0, 142.7, 141.6, 138.3, 137.1, 136.4, 132.7, 129.6, 129.5, 129.4, 128.3, 127.4, 127.3, 127.2, 125.7, 124.6, 124.4, 118.4, 110.5, 21.1, 19.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{22}NO^+$ 376.1696, found 376.1698.

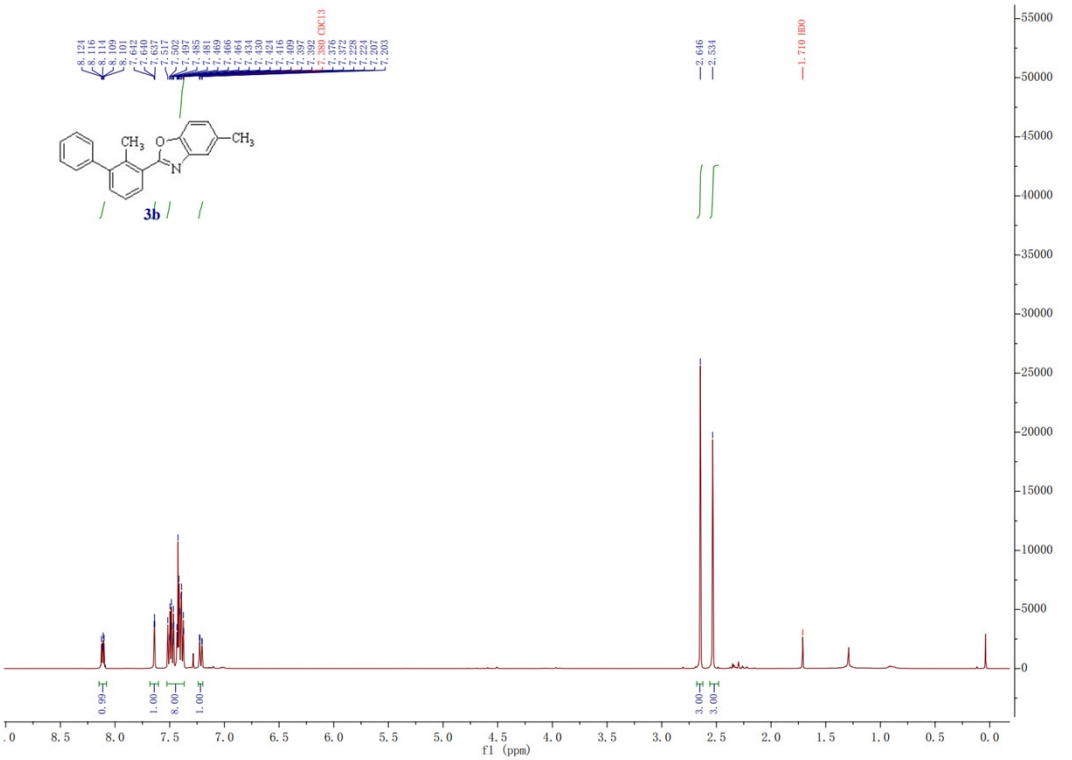
5. NMR Spectra



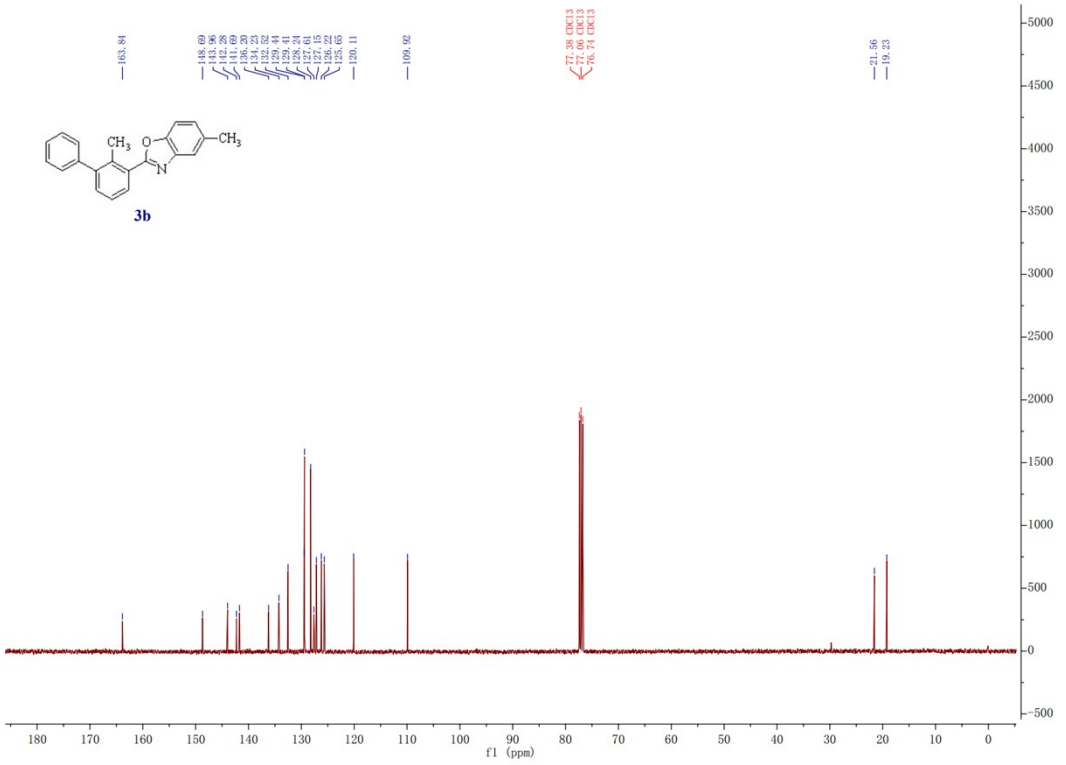
^{1}H NMR Spectrum of **3a**



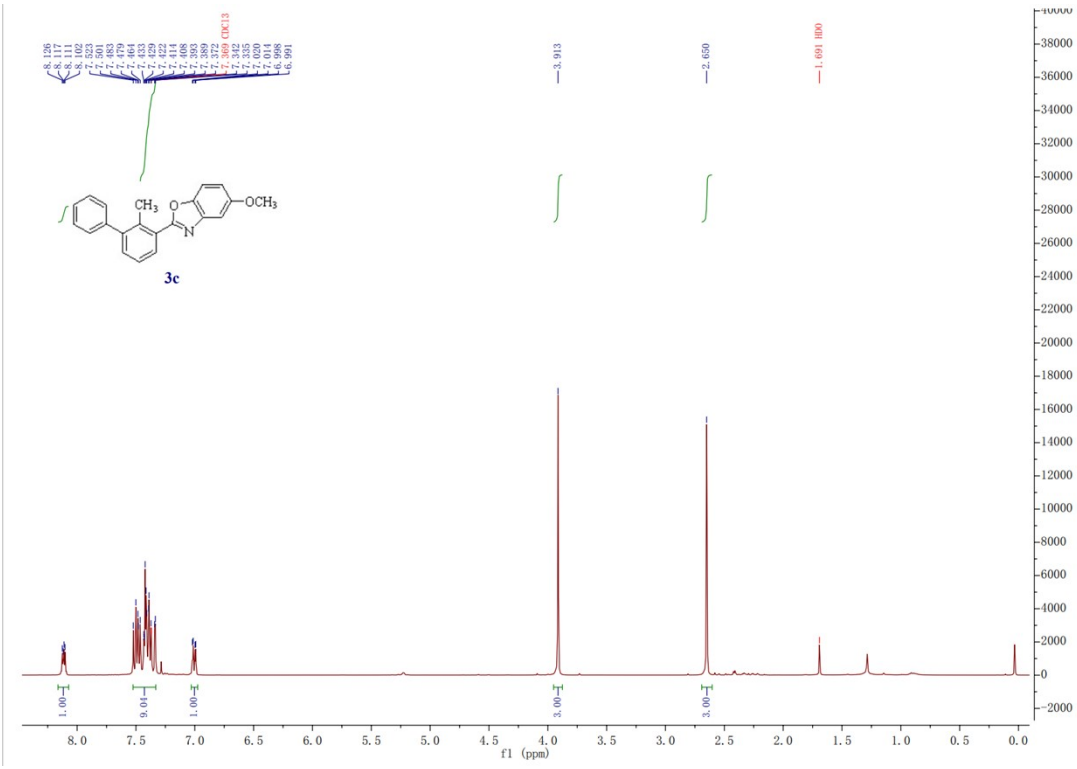
^{13}C NMR Spectrum of **3a**



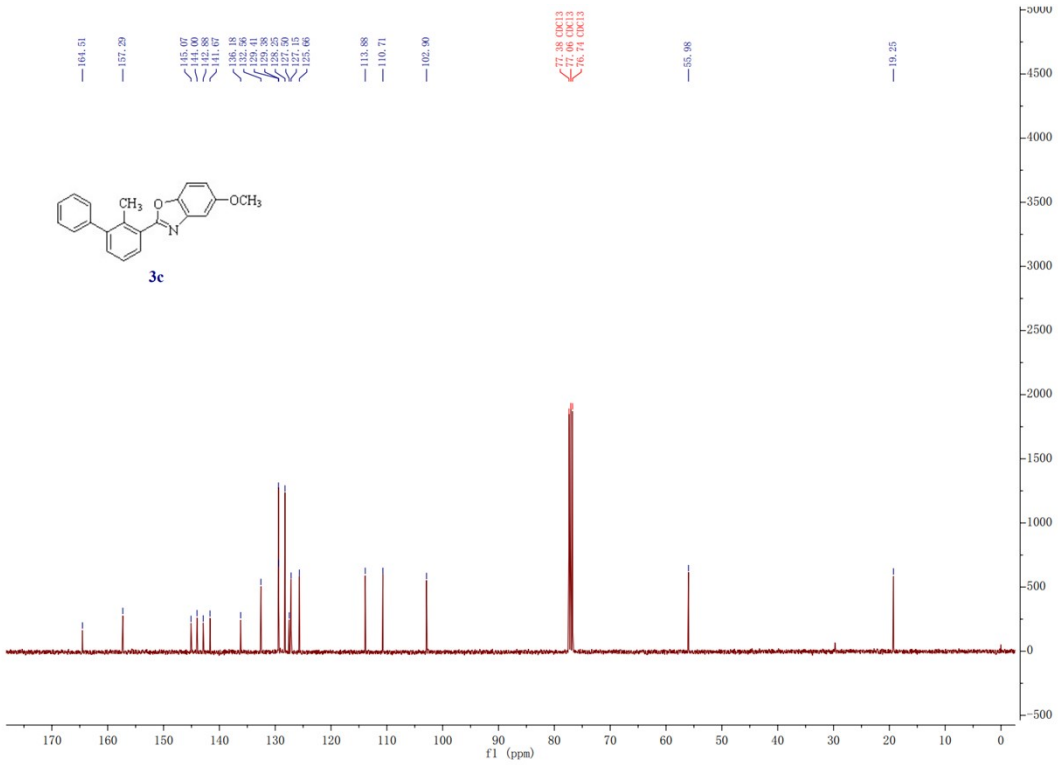
^{1}H NMR Spectrum of **3b**



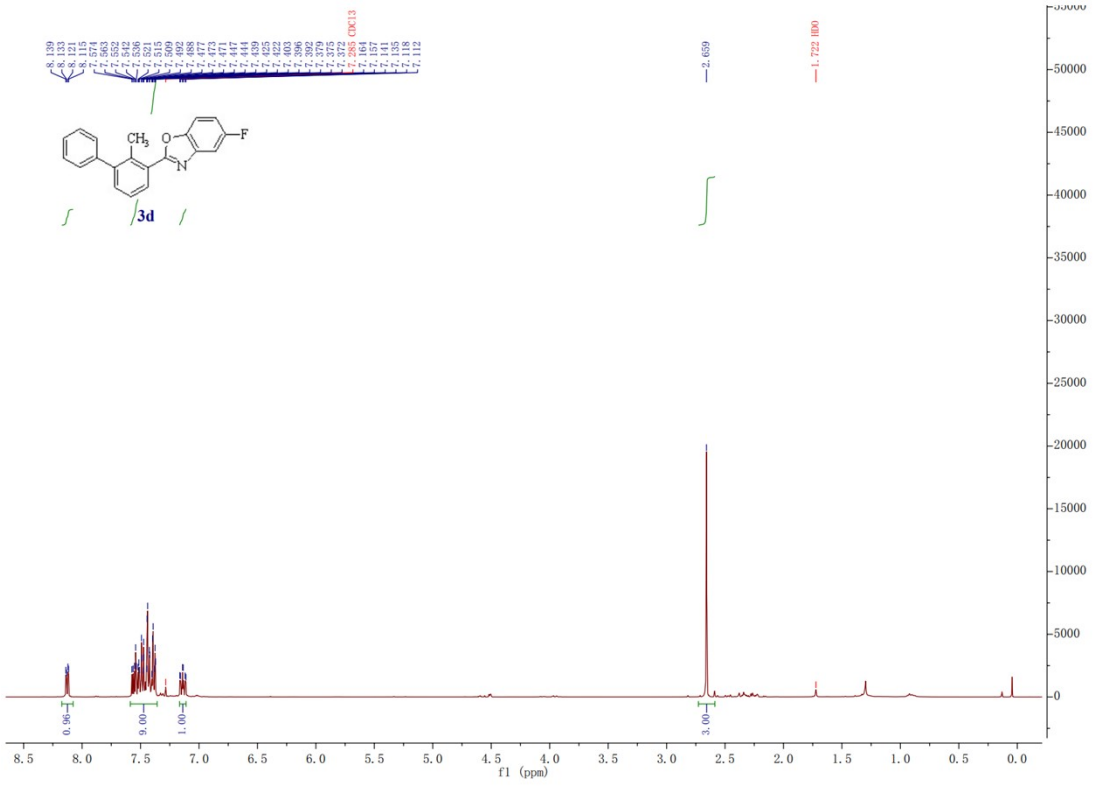
^{13}C NMR Spectrum of **3b**



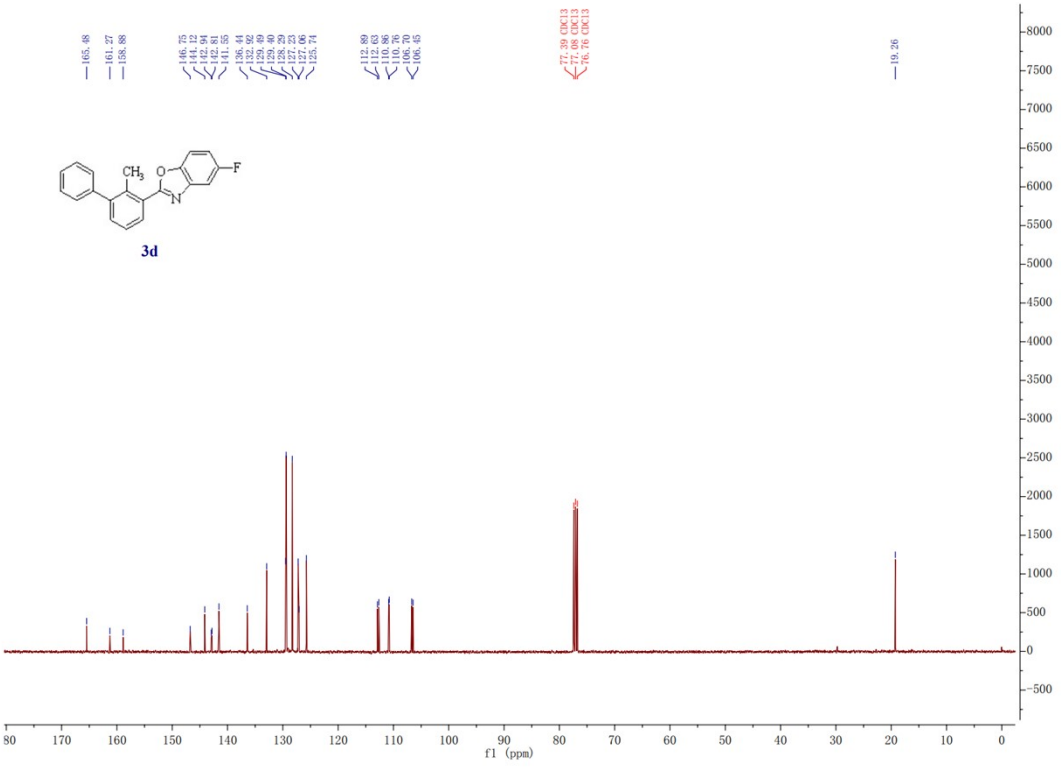
^{1}H NMR Spectrum of **3c**



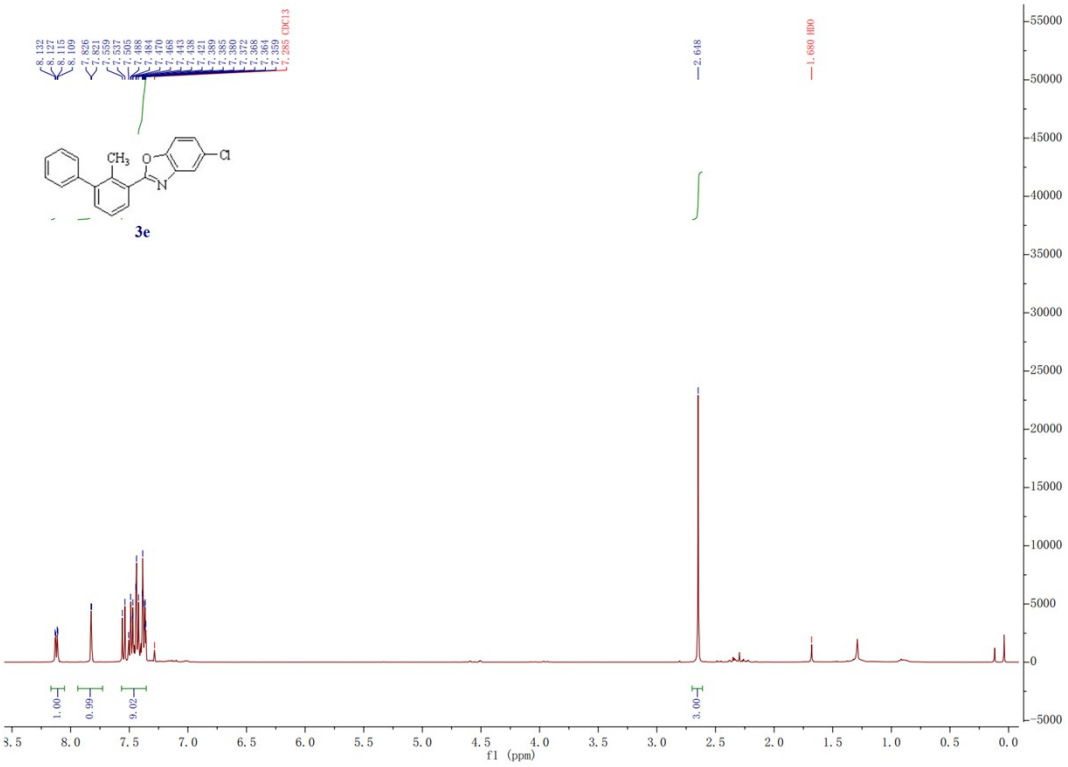
^{13}C NMR Spectrum of **3c**



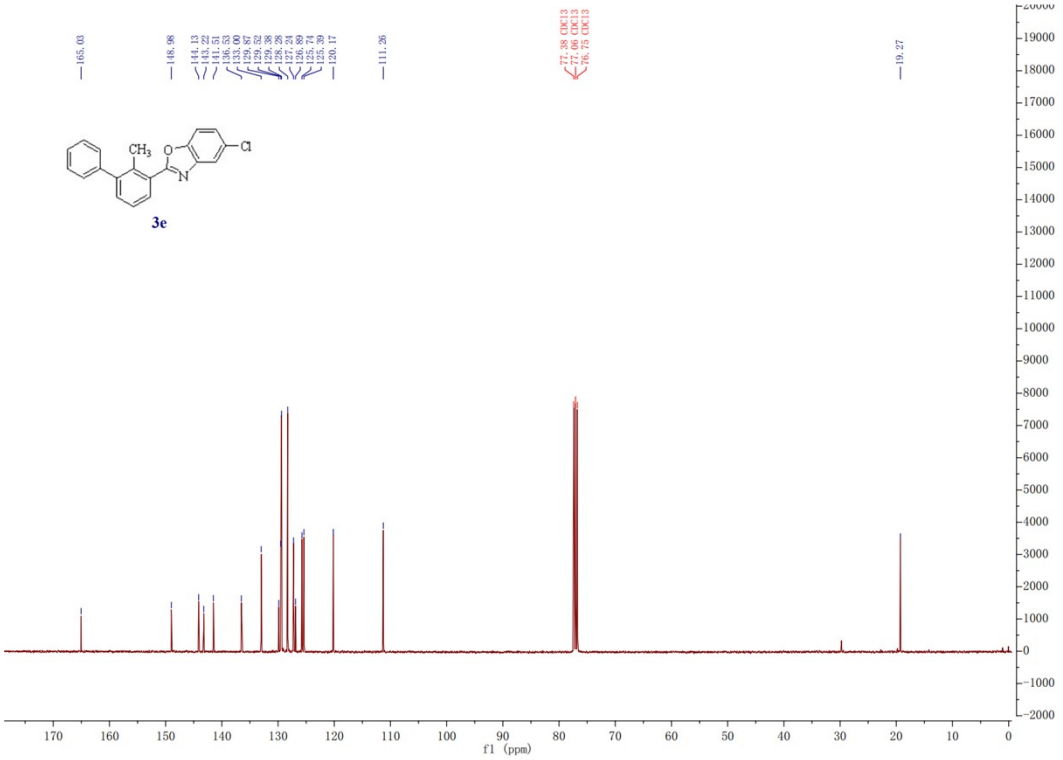
^{1}H NMR Spectrum of **3d**



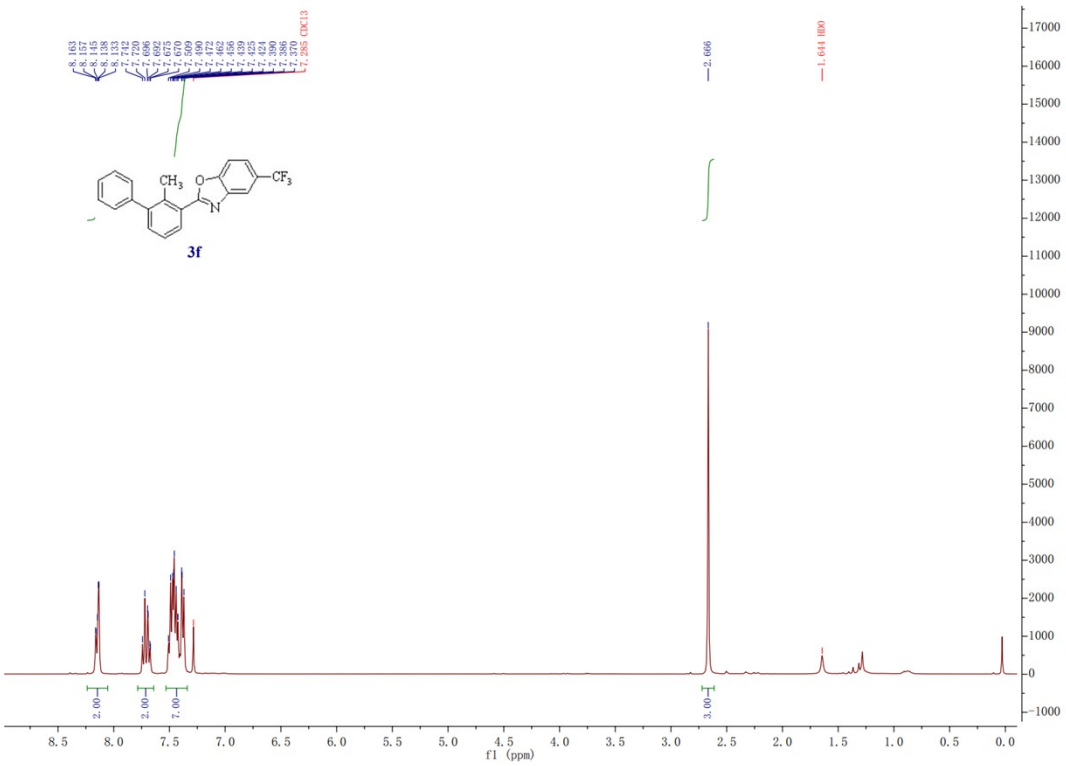
^{13}C NMR Spectrum of **3d**



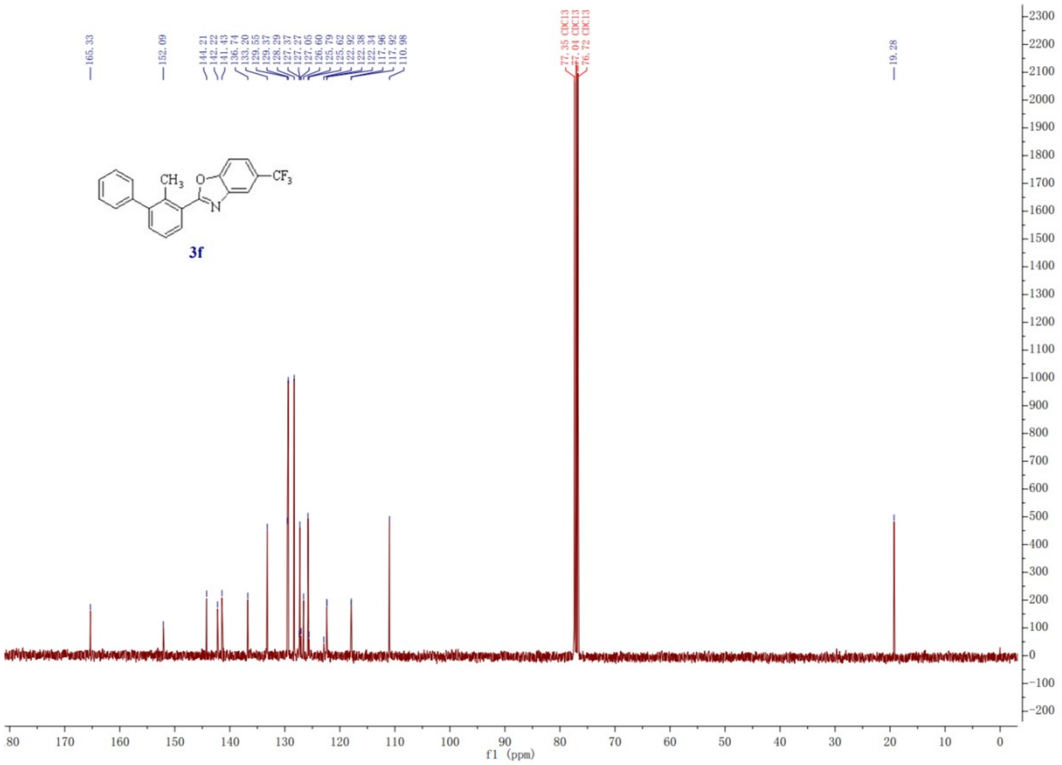
^{1}H NMR Spectrum of **3e**



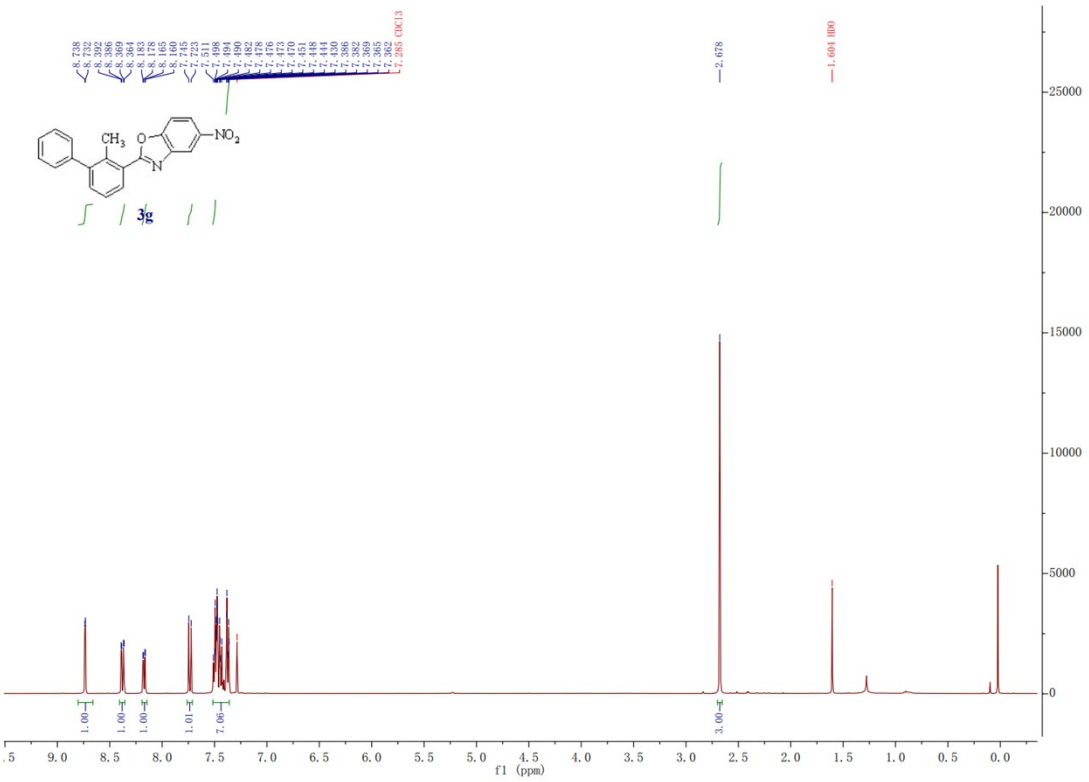
^{13}C NMR Spectrum of **3e**



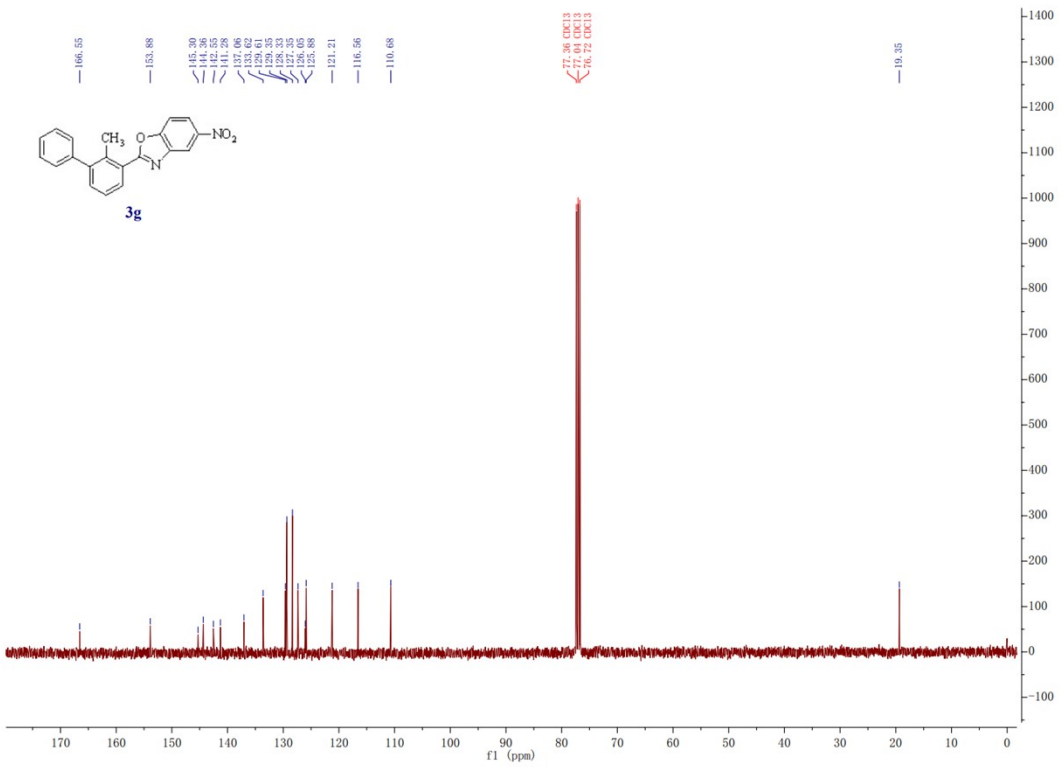
^{1}H NMR Spectrum of **3f**



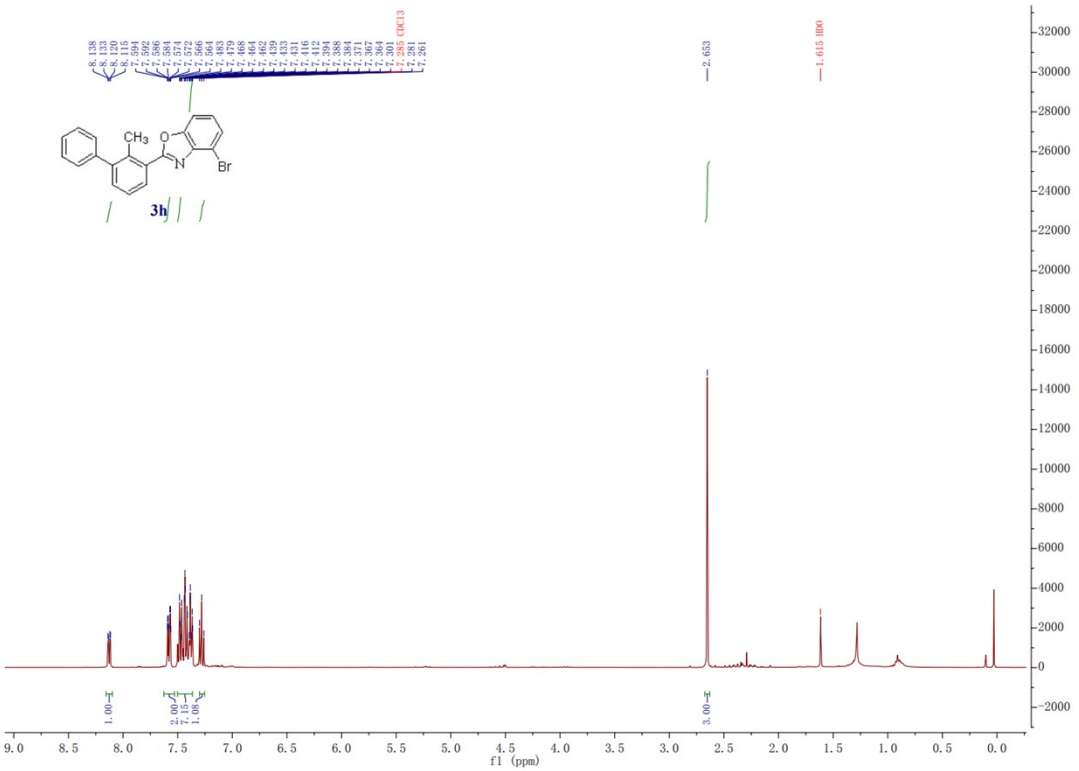
^{13}C NMR Spectrum of **3f**



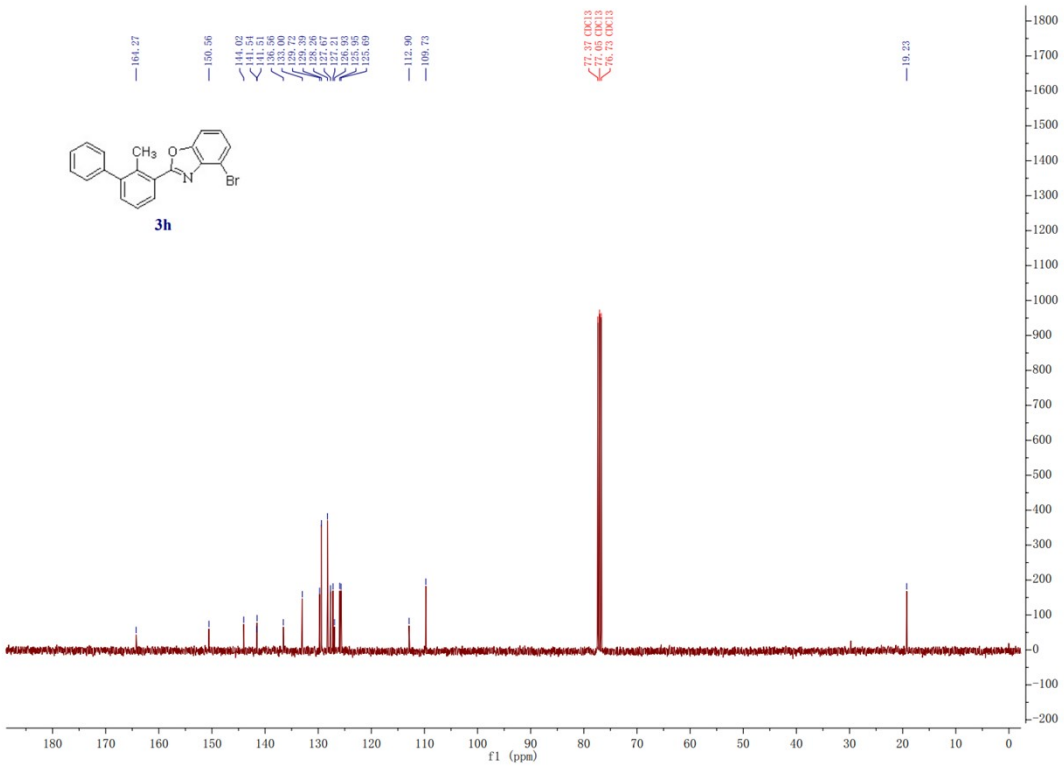
^{1}H NMR Spectrum of **3g**



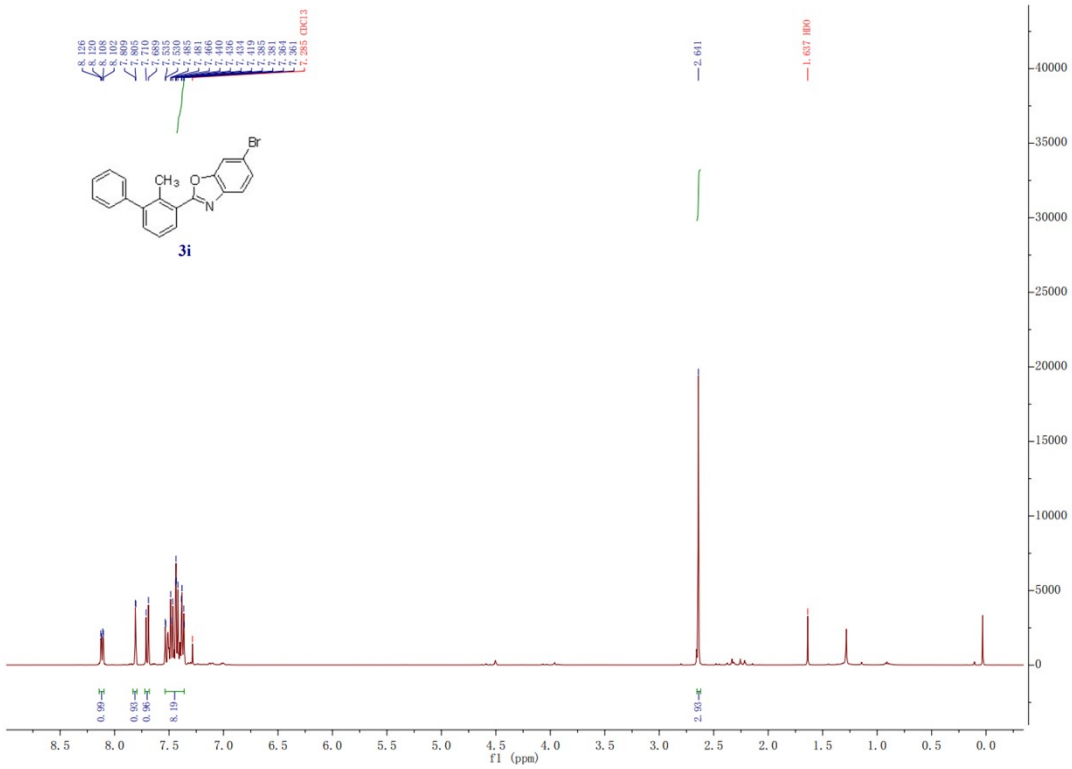
^{13}C NMR Spectrum of **3g**



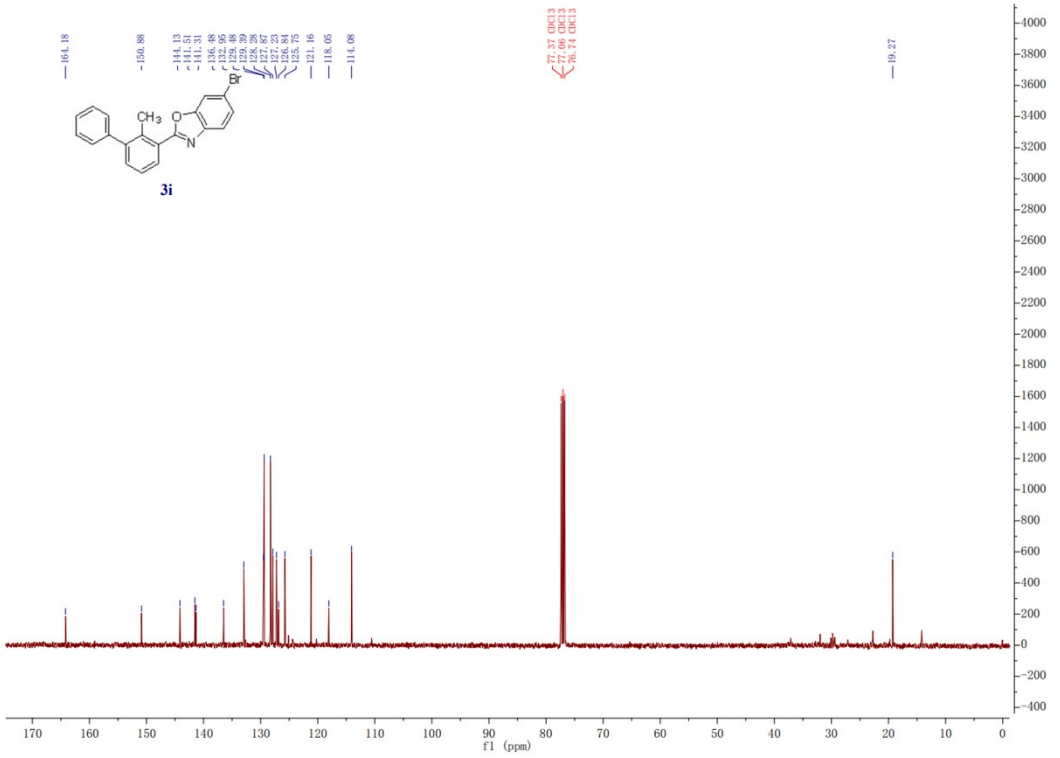
^{1}H NMR Spectrum of **3h**



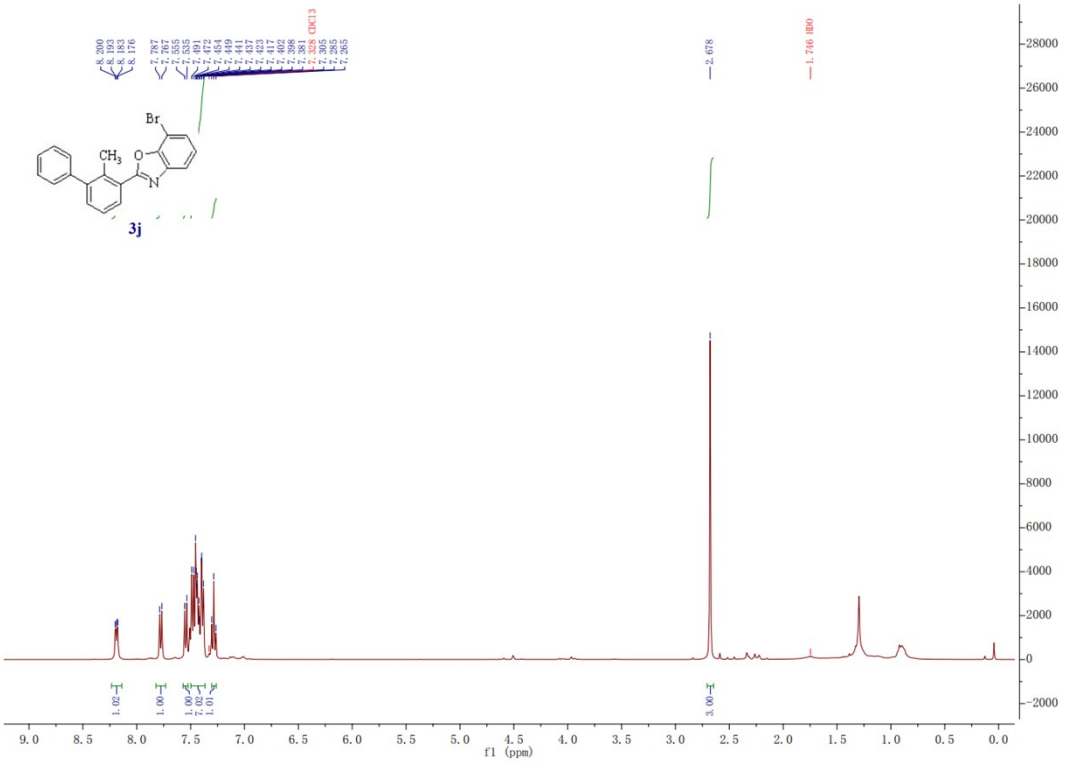
^{13}C NMR Spectrum of **3h**



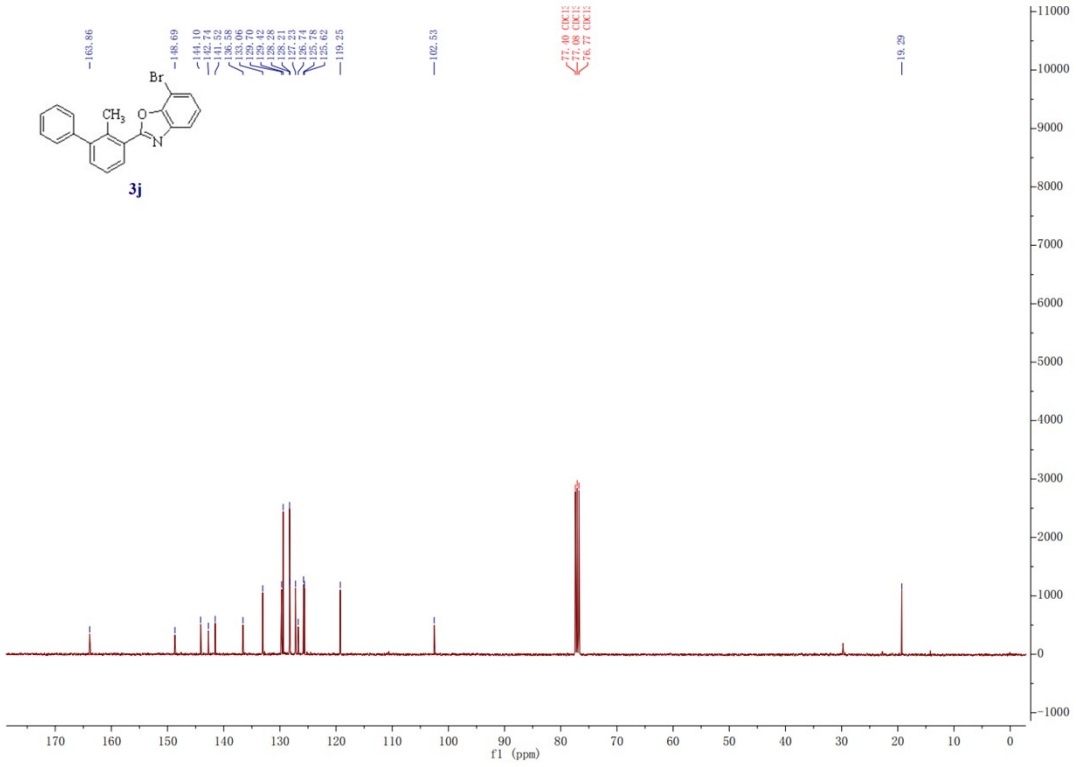
^{1}H NMR Spectrum of **3i**



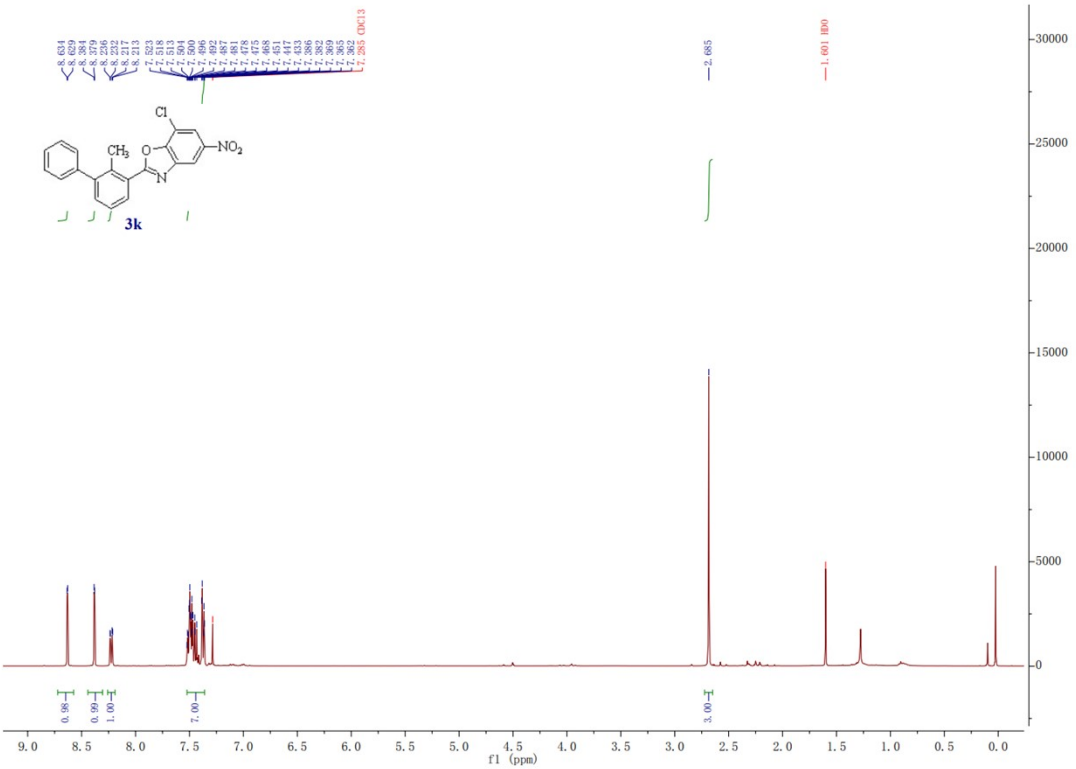
^{13}C NMR Spectrum of **3i**



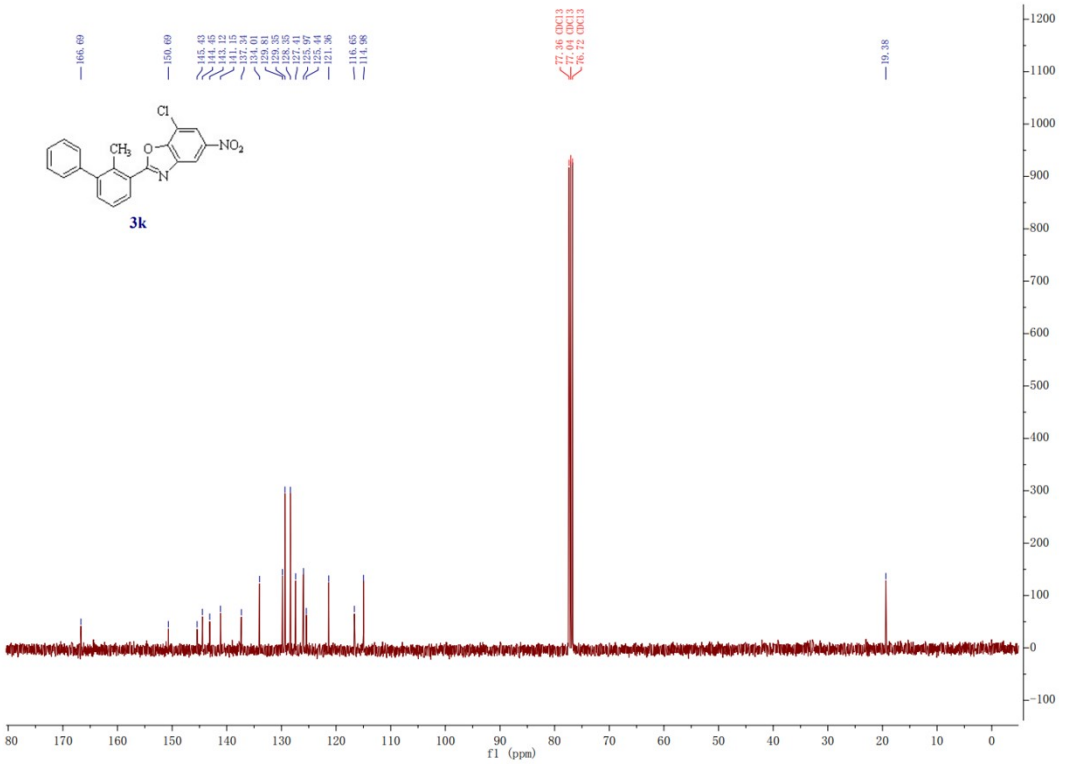
^{1}H NMR Spectrum of **3j**



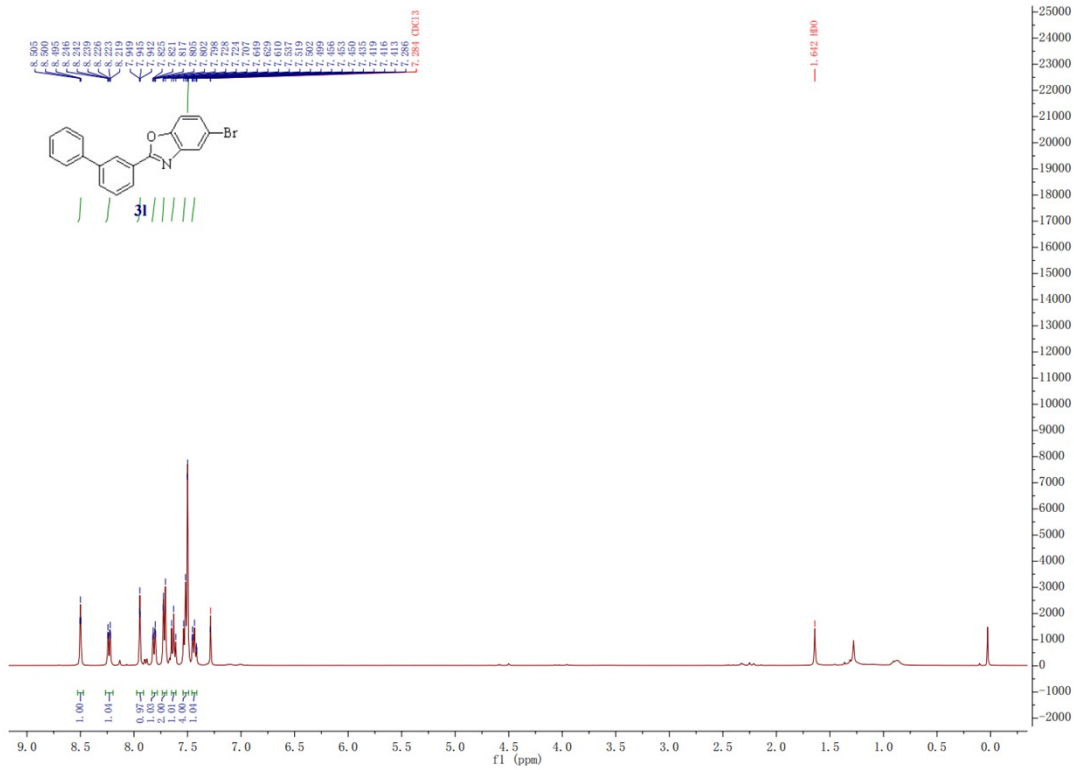
^{13}C NMR Spectrum of **3j**



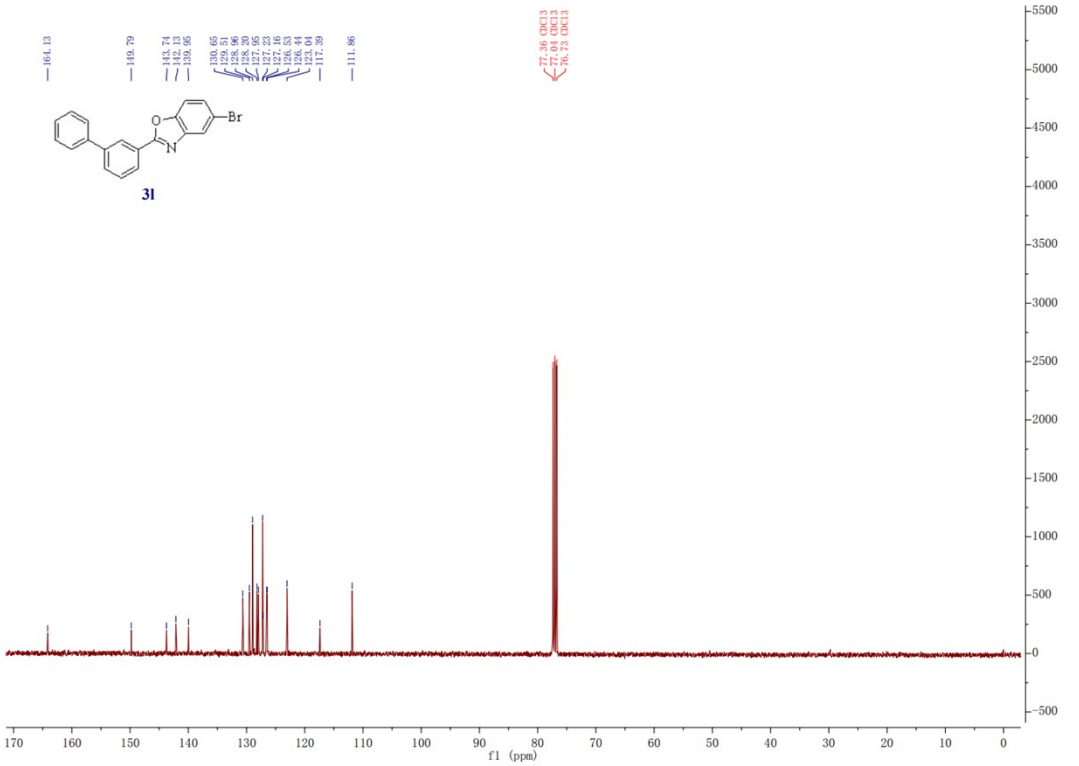
^{1}H NMR Spectrum of **3k**



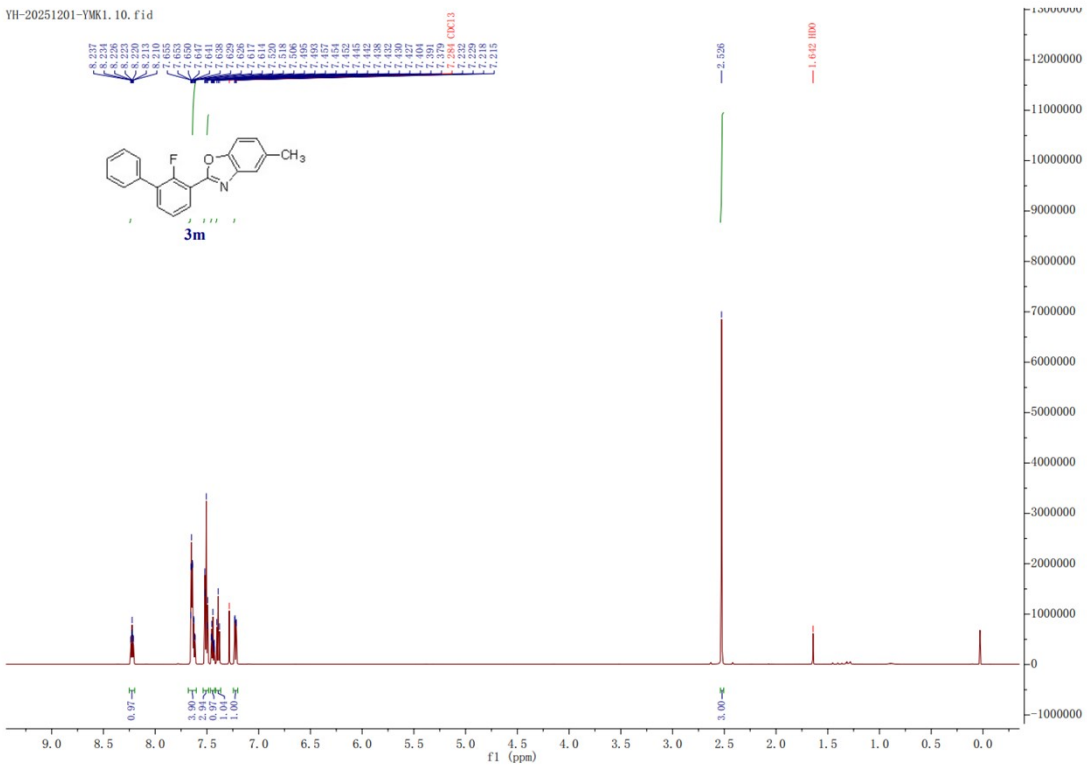
^{13}C NMR Spectrum of **3k**



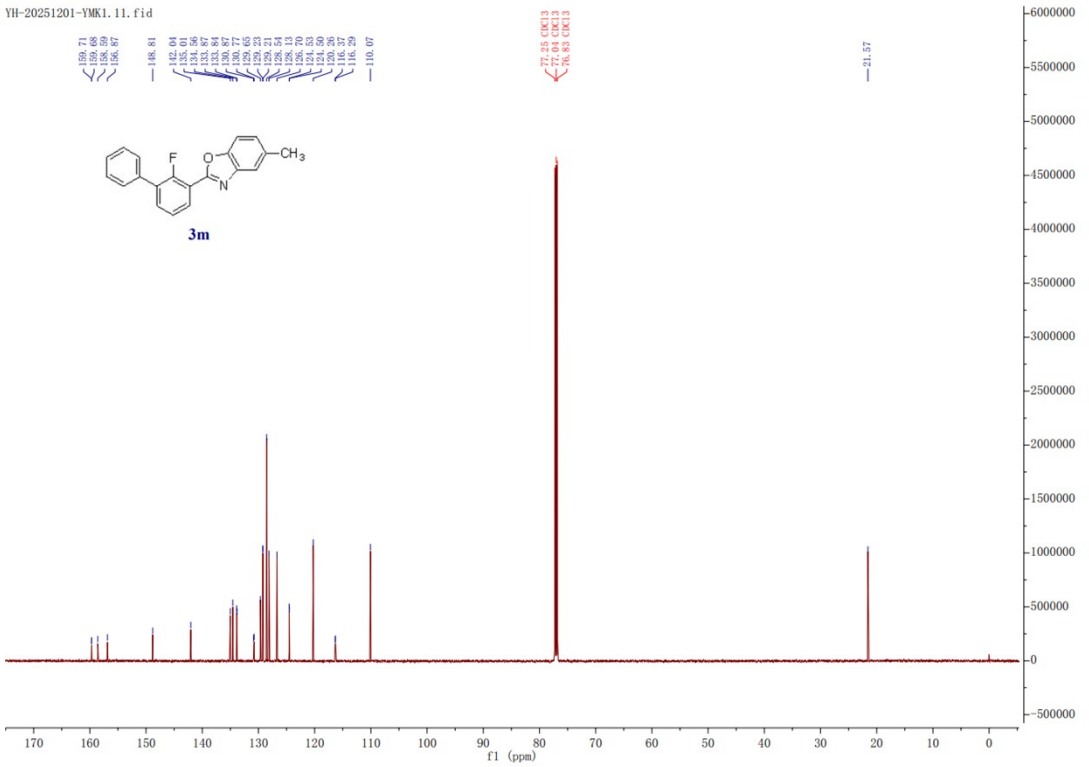
^{1}H NMR Spectrum of **3l**



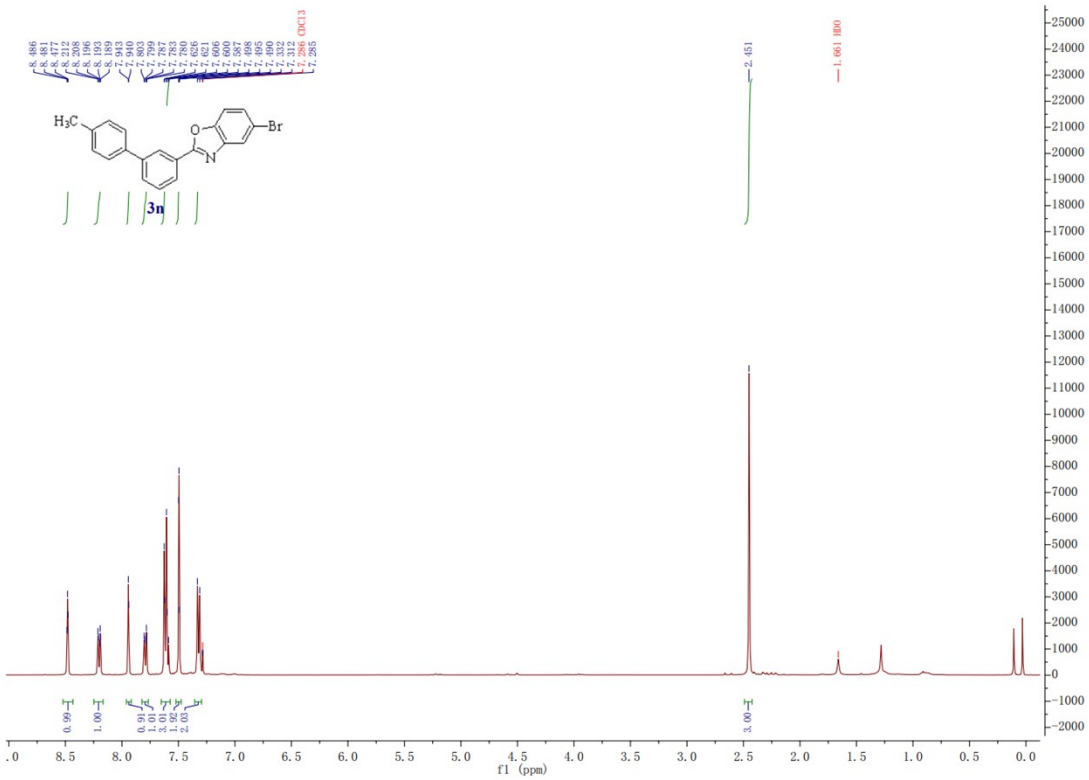
^{13}C NMR Spectrum of **3l**



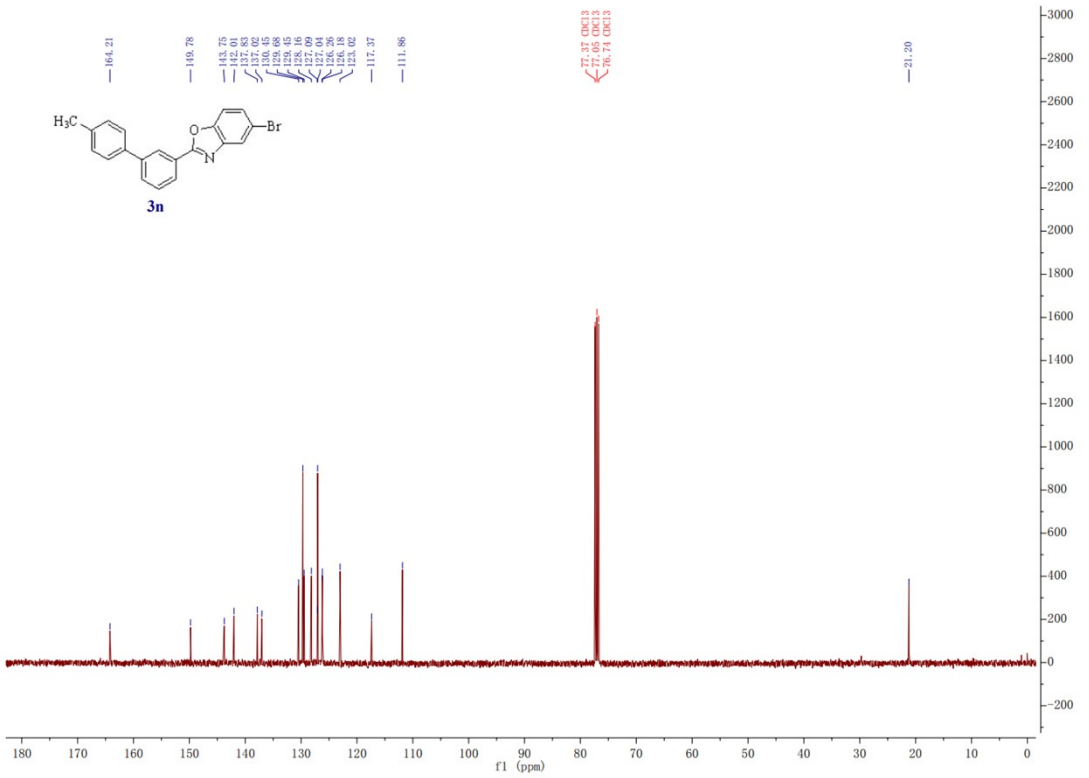
^{1}H NMR Spectrum of **3m**



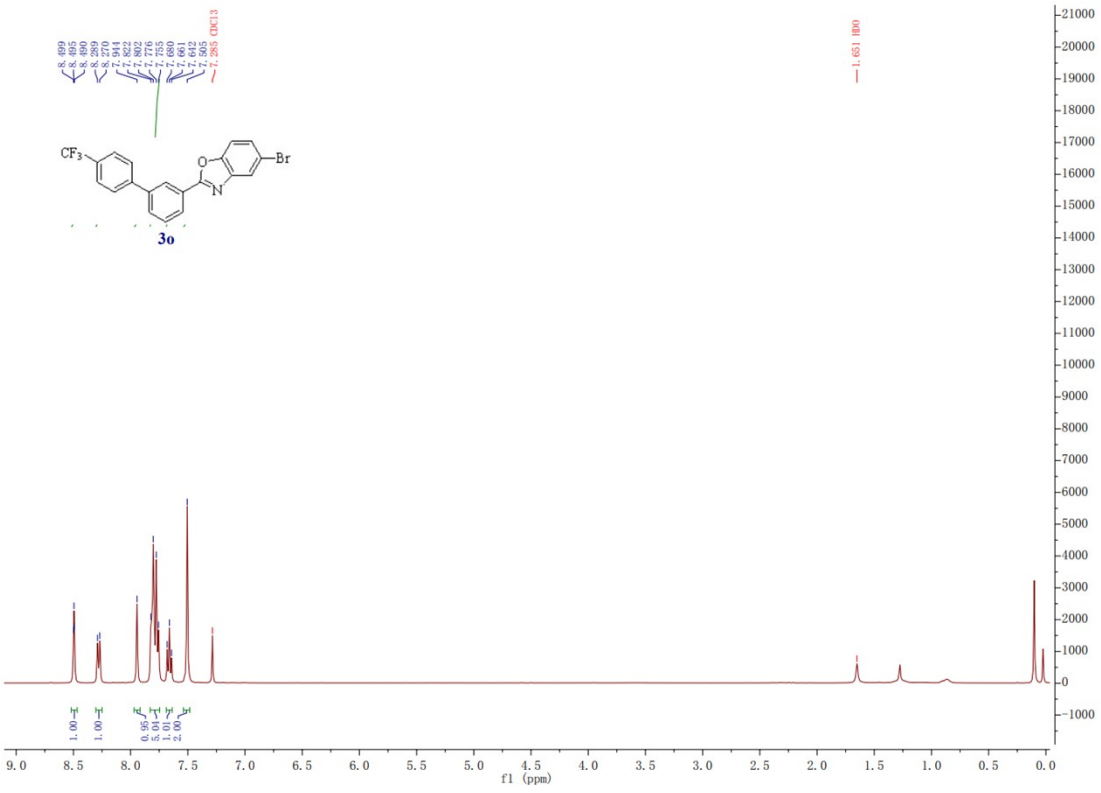
^{13}C NMR Spectrum of **3m**



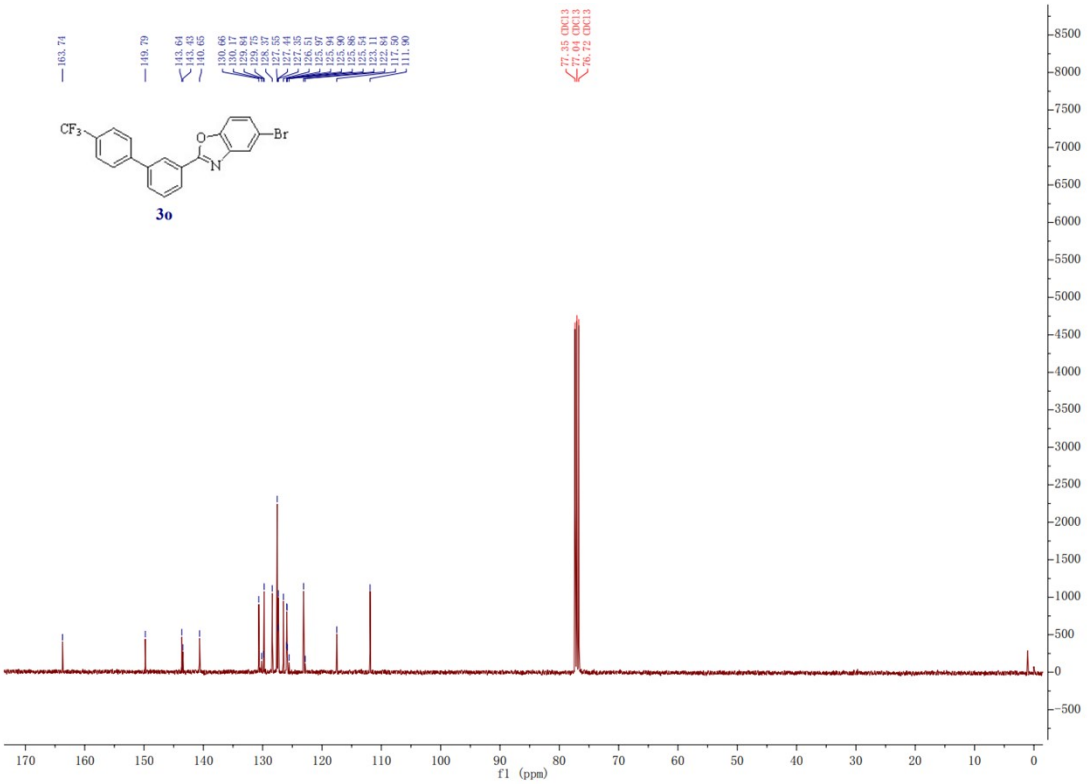
^{1}H NMR Spectrum of **3n**



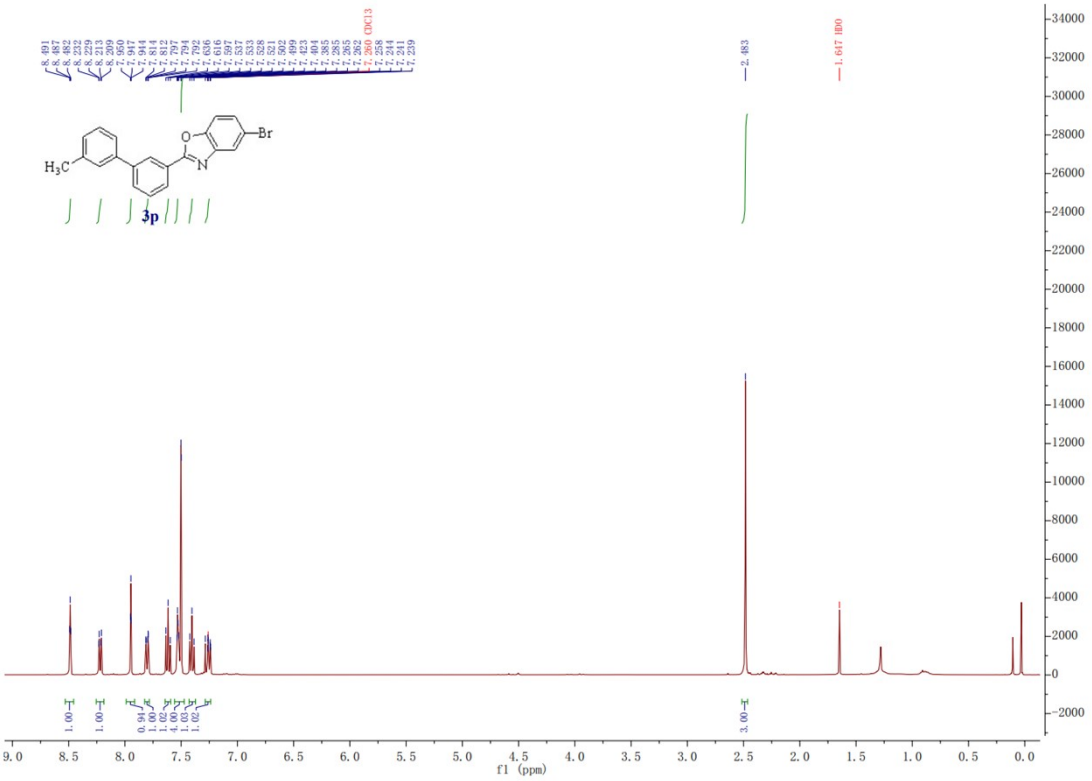
^{13}C NMR Spectrum of **3n**



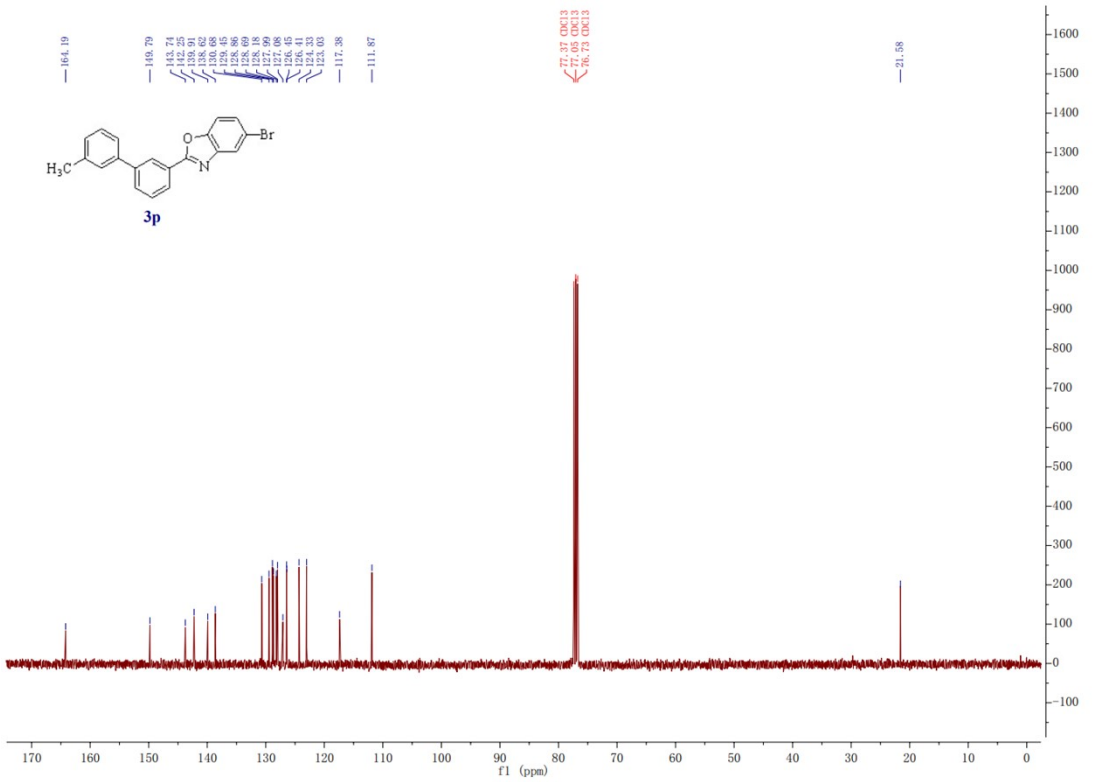
^{1}H NMR Spectrum of **3o**



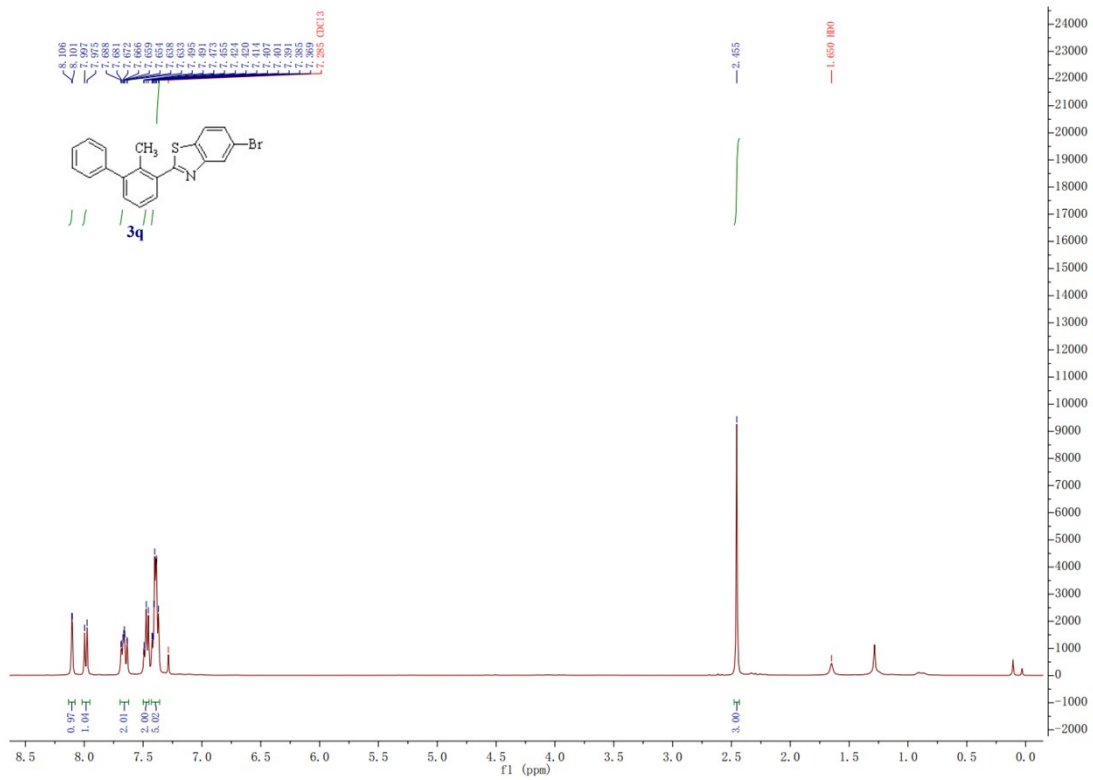
^{13}C NMR Spectrum of **3o**



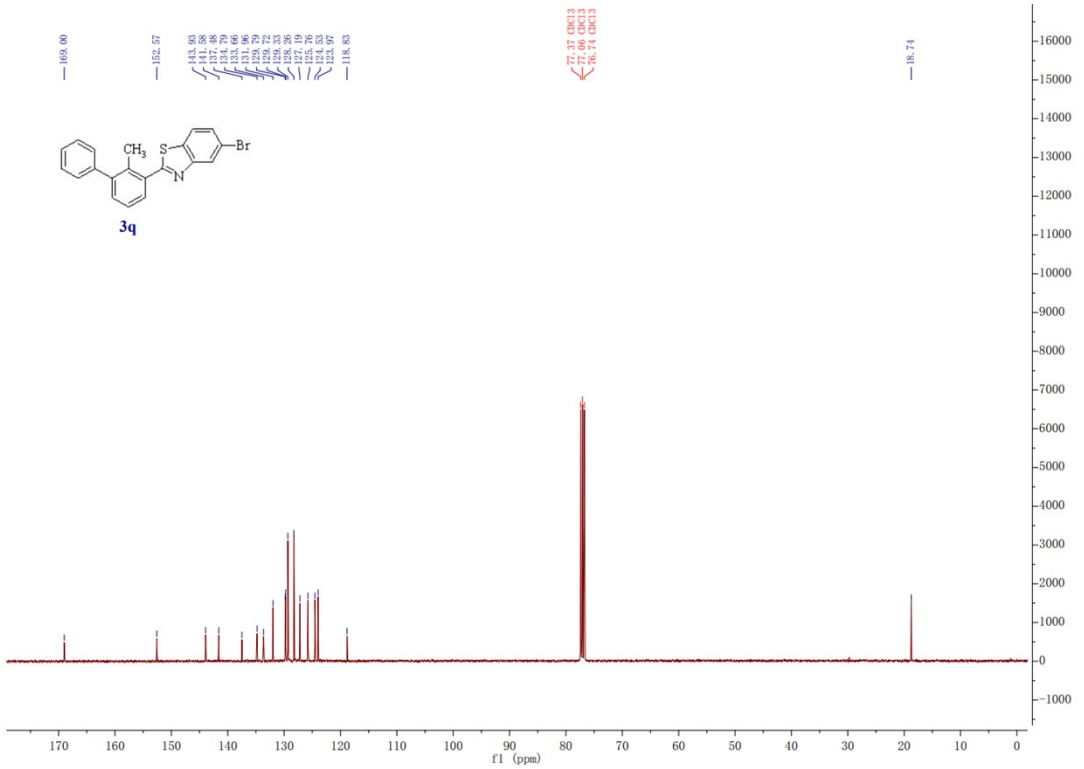
^{1}H NMR Spectrum of **3p**



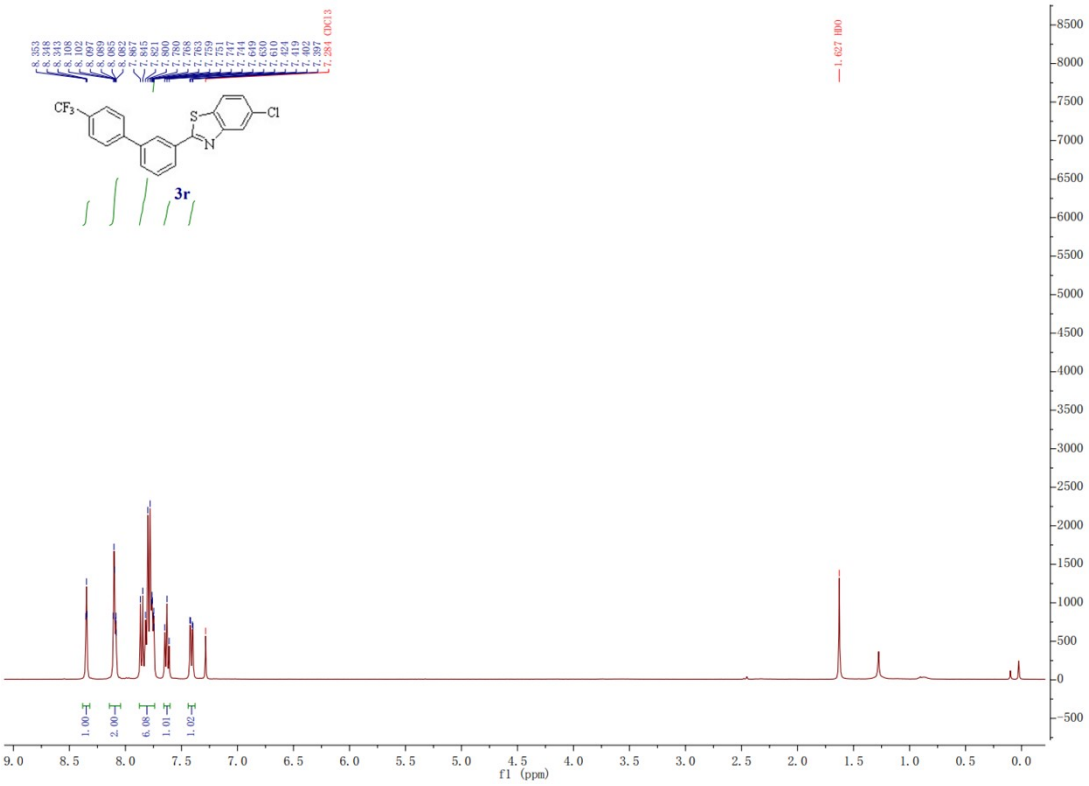
^{13}C NMR Spectrum of **3p**



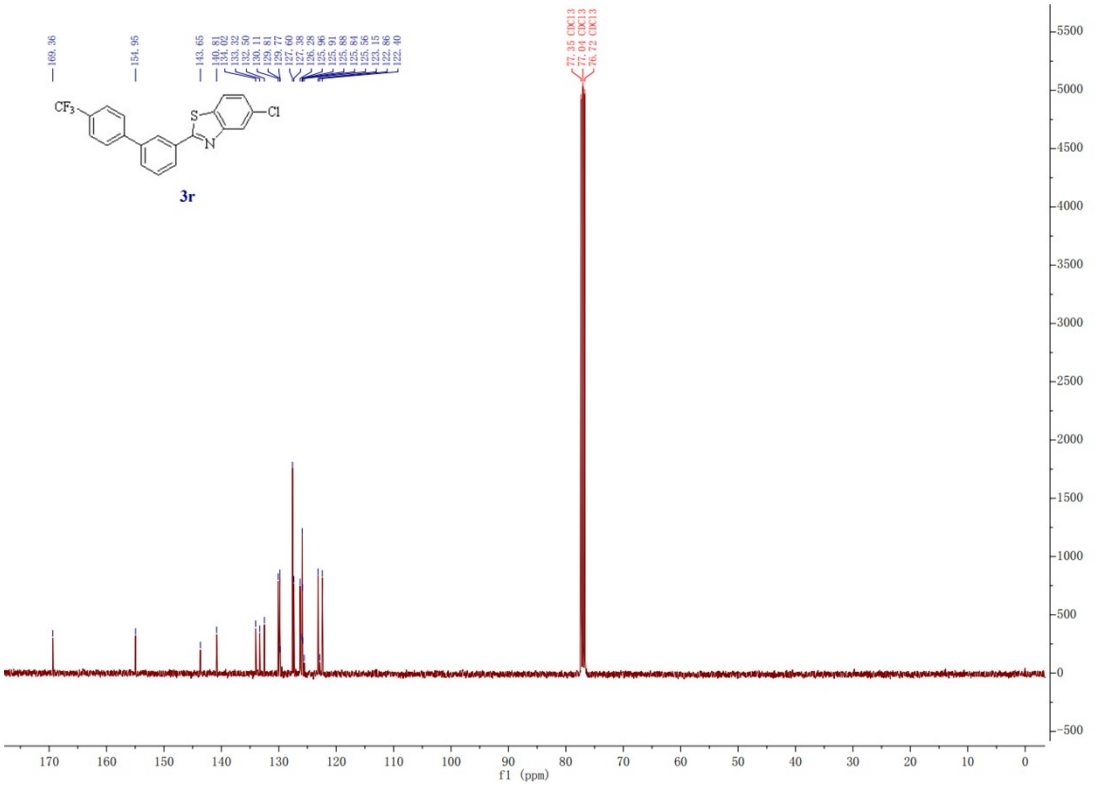
^{1}H NMR Spectrum of **3q**



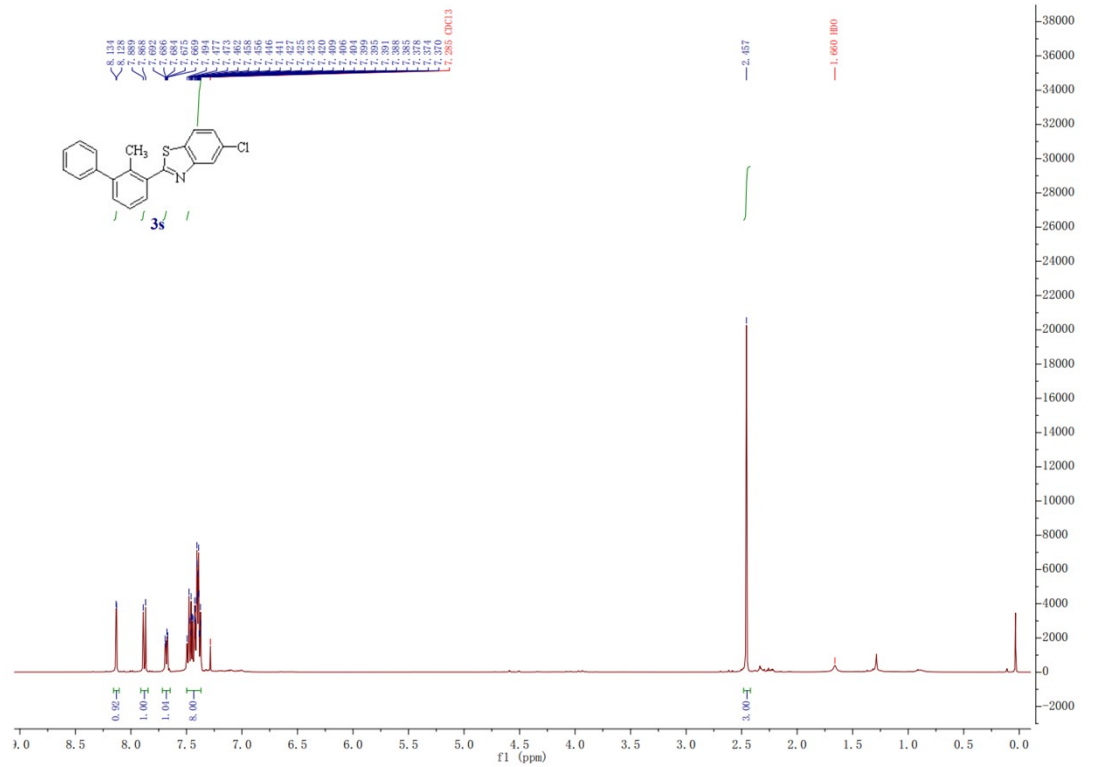
^{13}C NMR Spectrum of **3q**



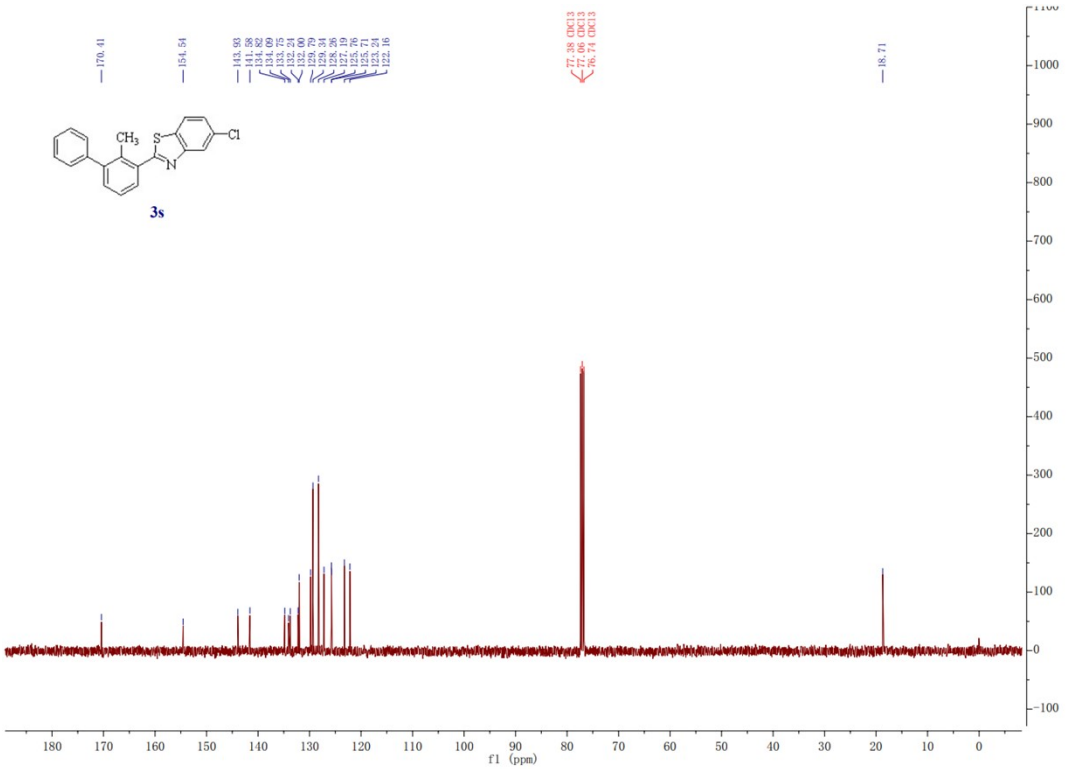
^{1}H NMR Spectrum of **3r**



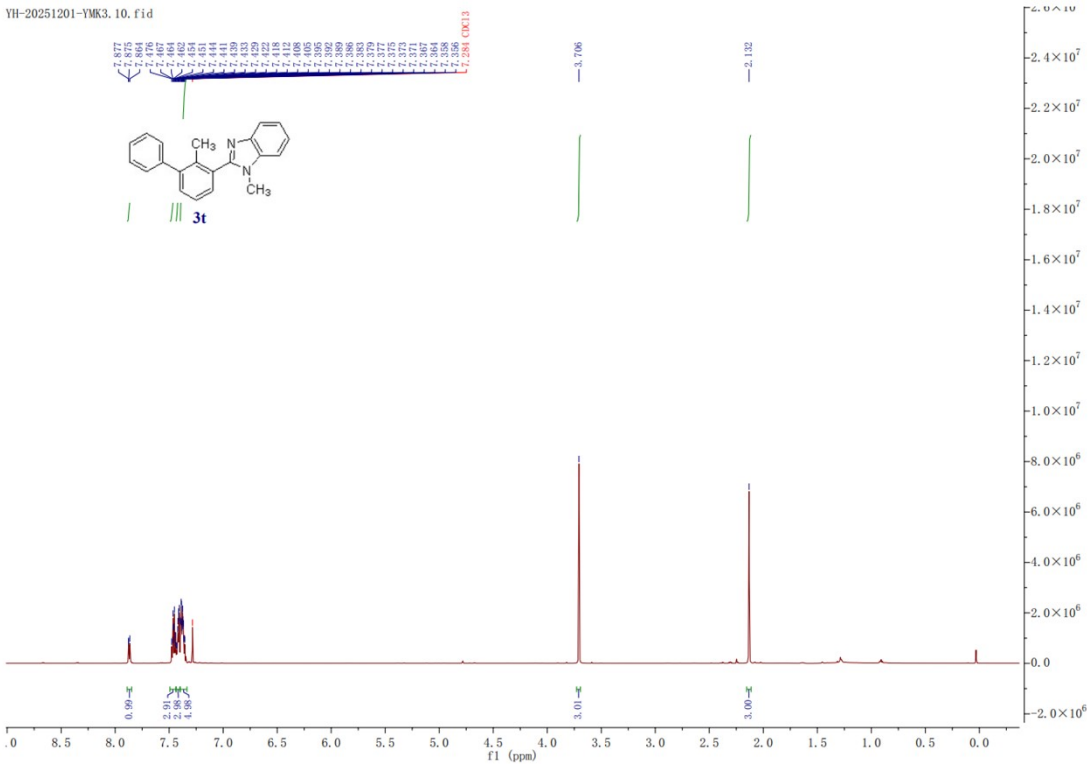
^{13}C NMR Spectrum of **3r**



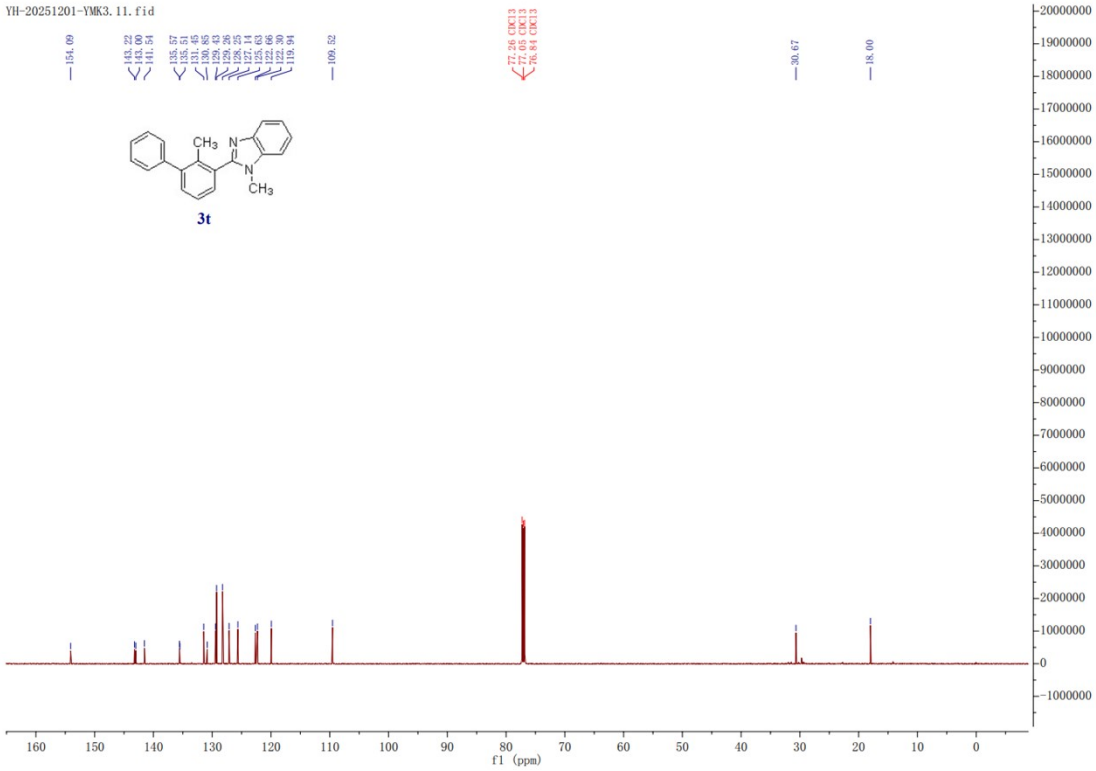
^{1}H NMR Spectrum of **3s**



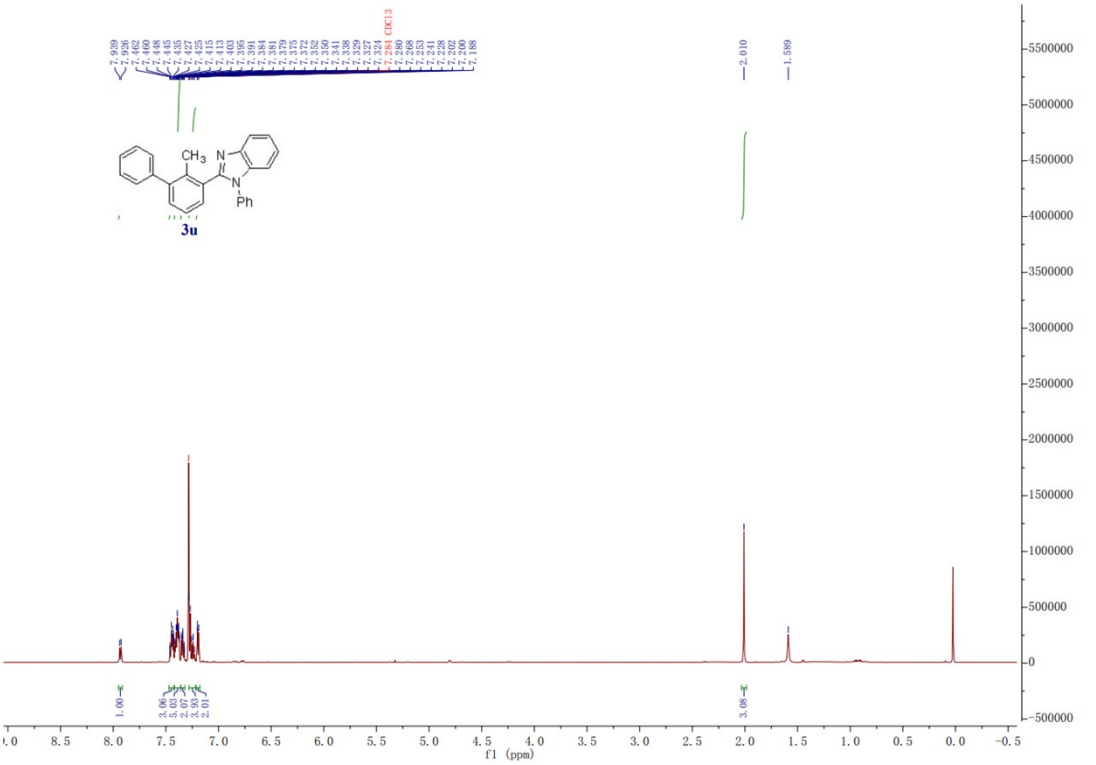
^{13}C NMR Spectrum of **3s**



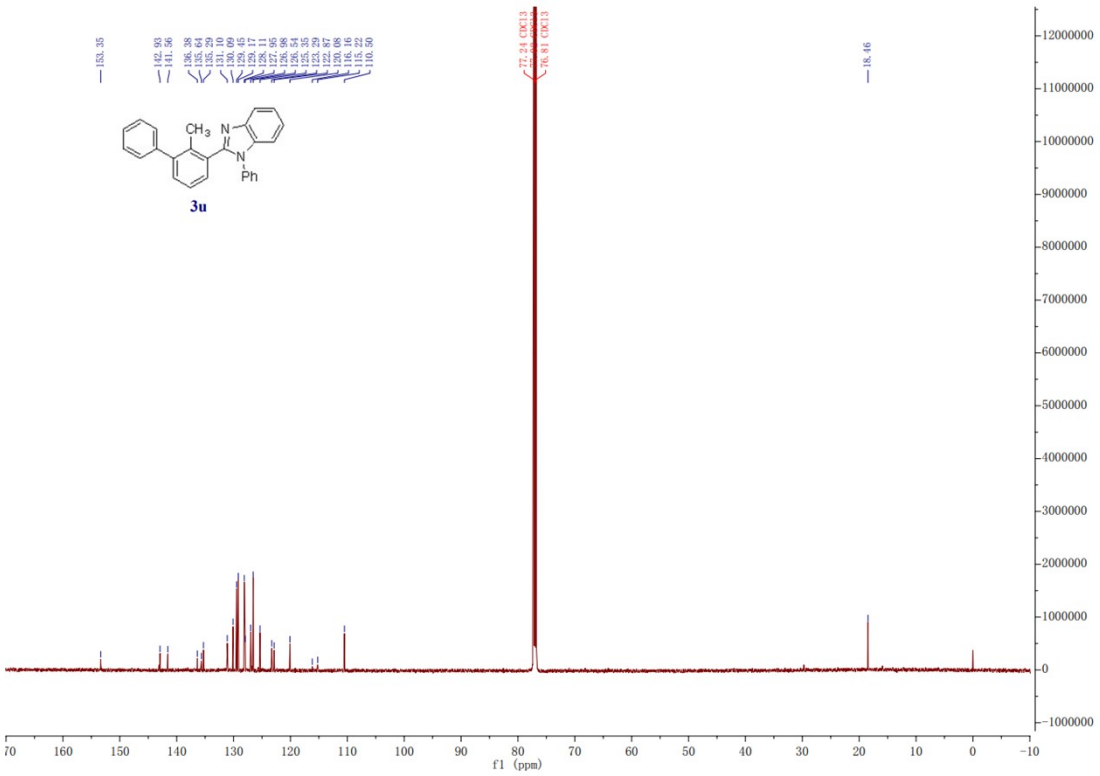
^{1}H NMR Spectrum of **3t**



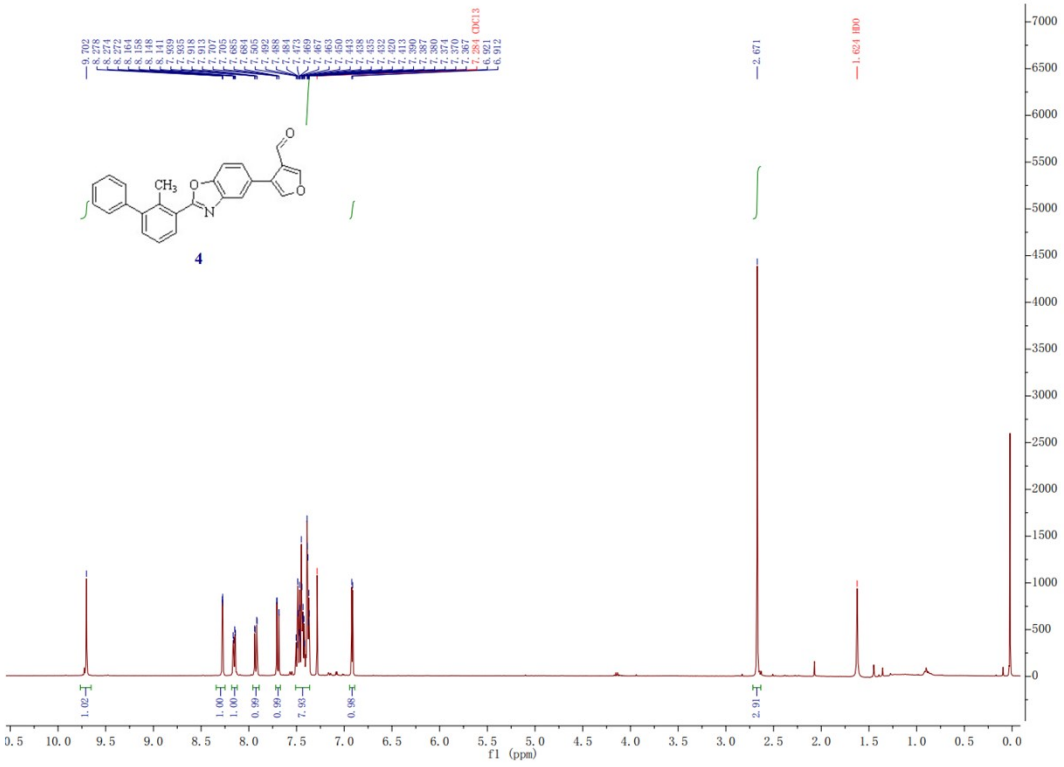
^{13}C NMR Spectrum of **3t**



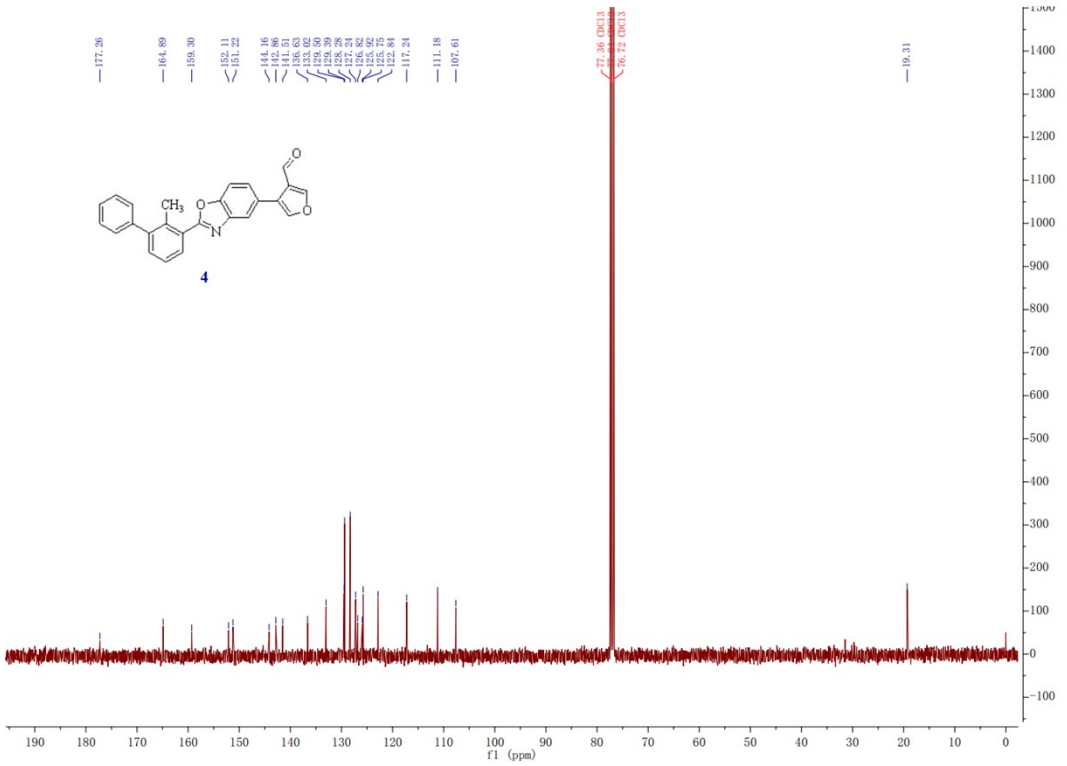
^{1}H NMR Spectrum of **3u**



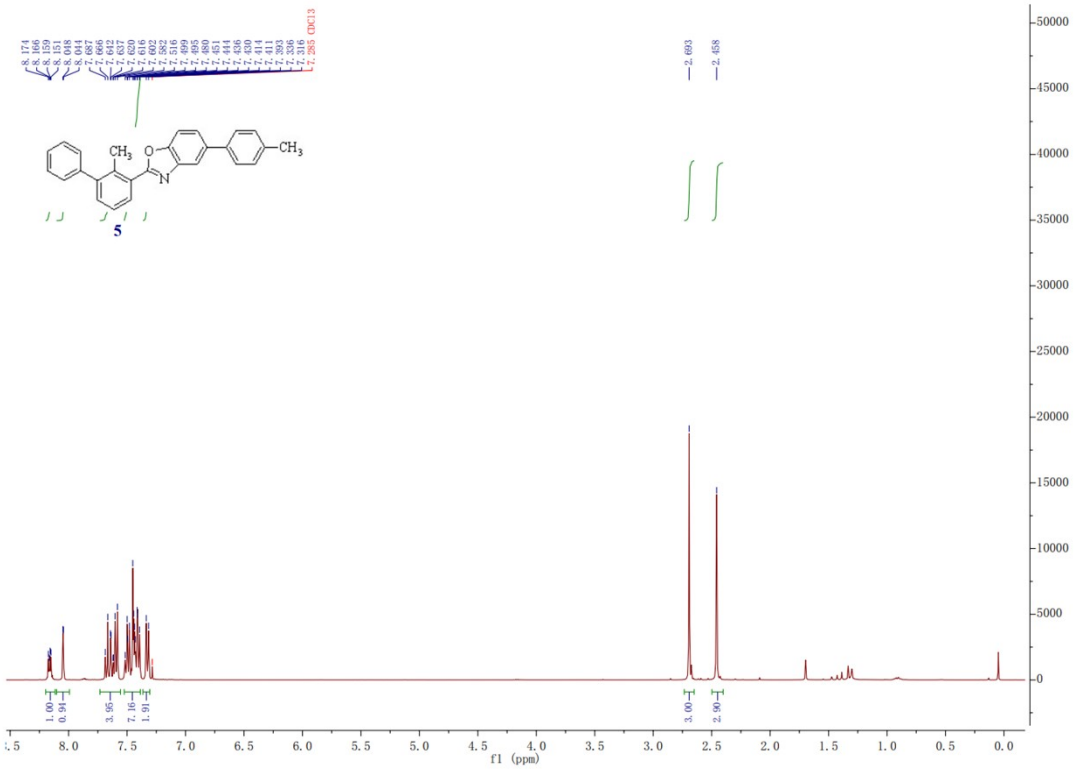
^{13}C NMR Spectrum of **3u**



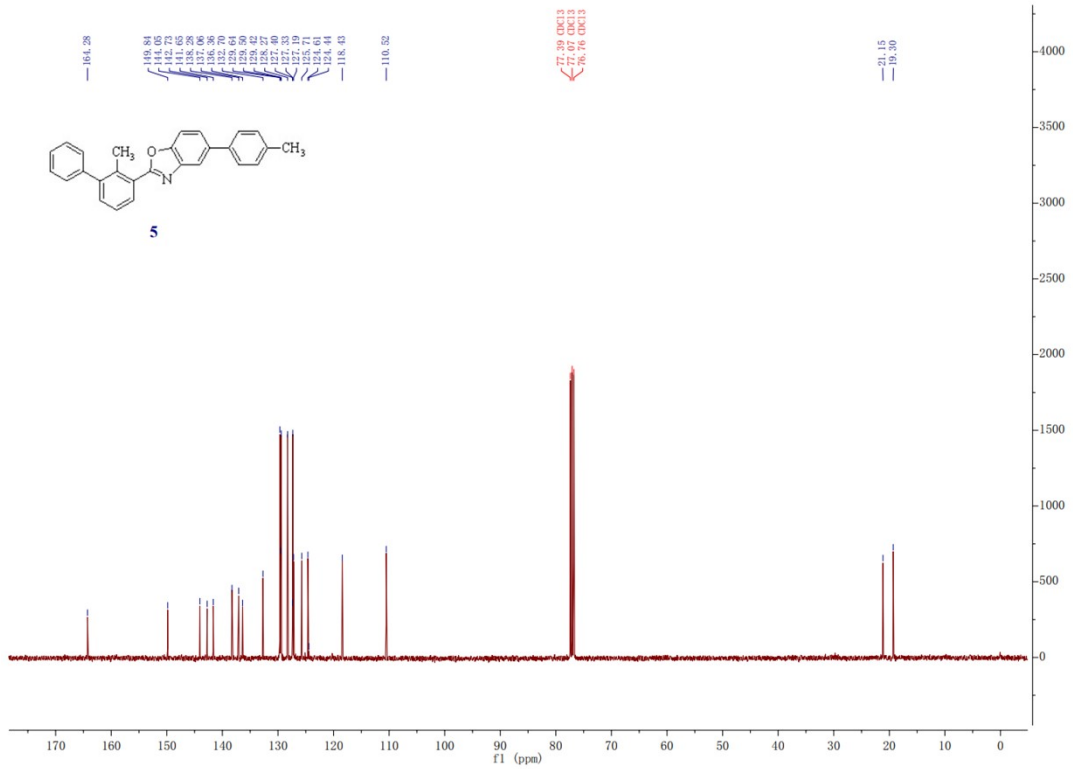
^{1}H NMR Spectrum of **4**



^{13}C NMR Spectrum of **4**

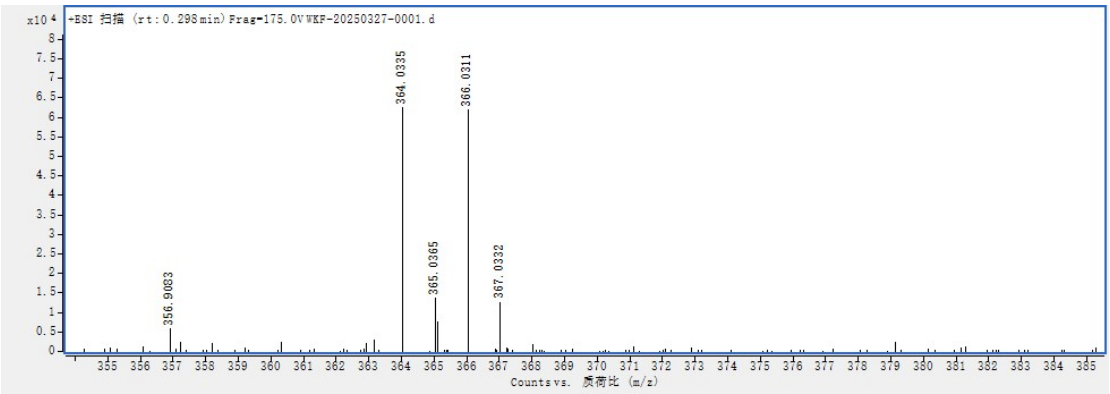


^{1}H NMR Spectrum of **5**

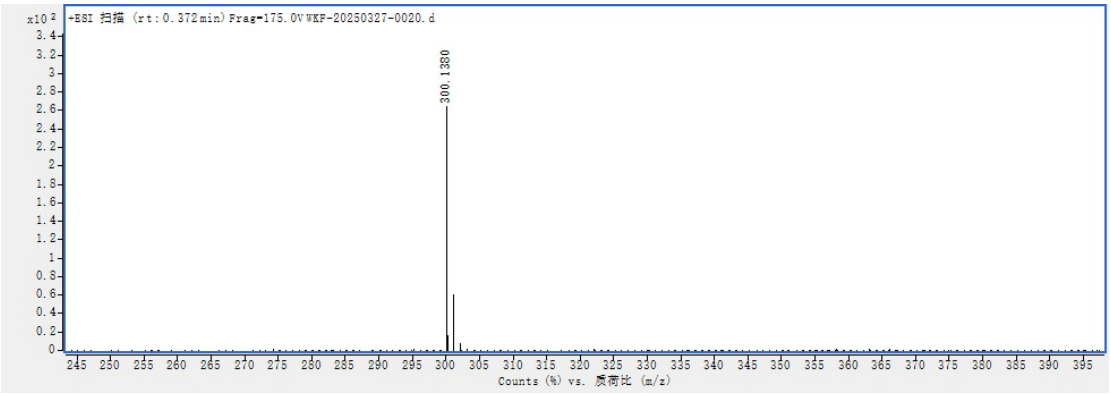


^{13}C NMR Spectrum of **5**

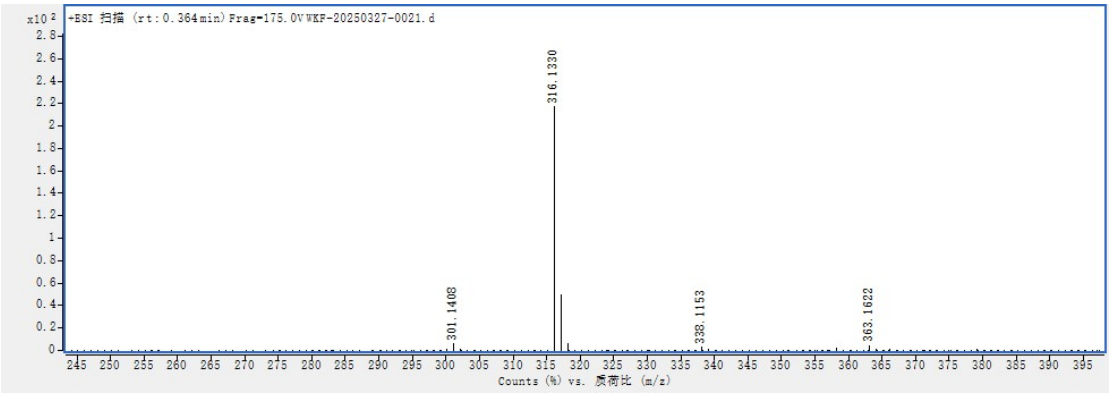
6. HRMS Spectra



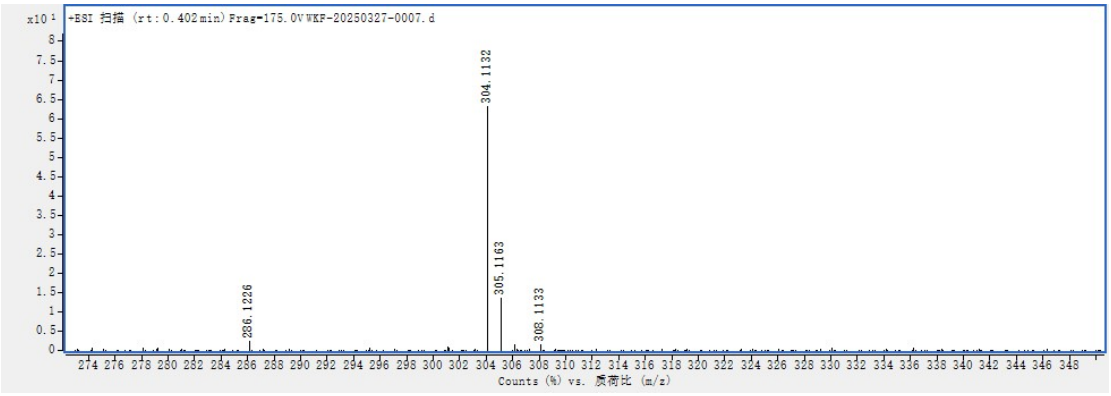
HRMS spectrum of **3a**



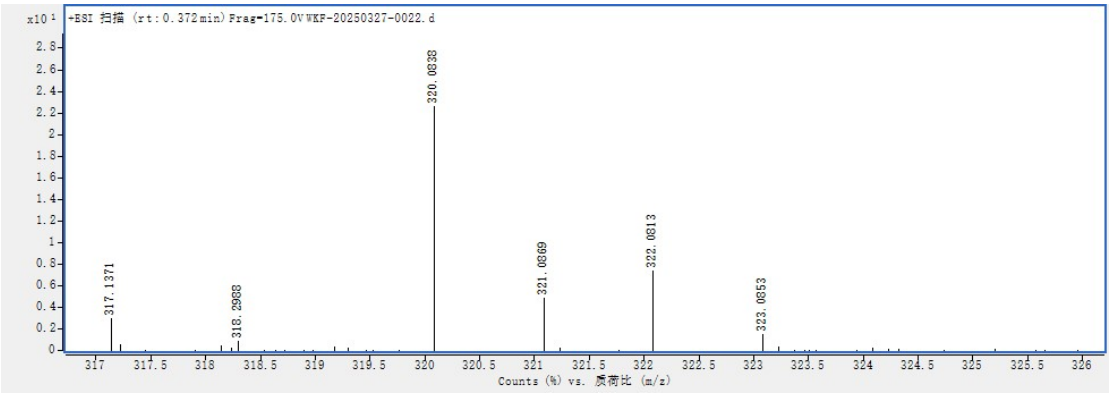
HRMS spectrum of **3b**



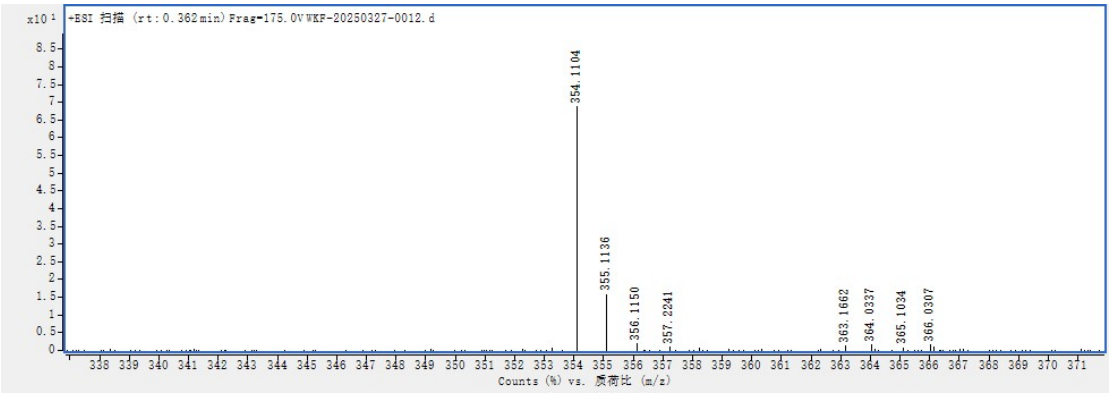
HRMS spectrum of **3c**



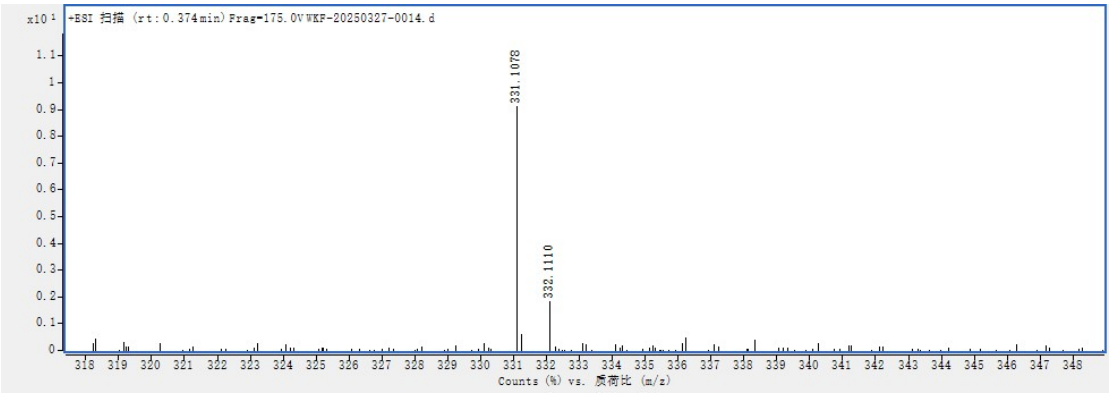
HRMS spectrum of **3d**



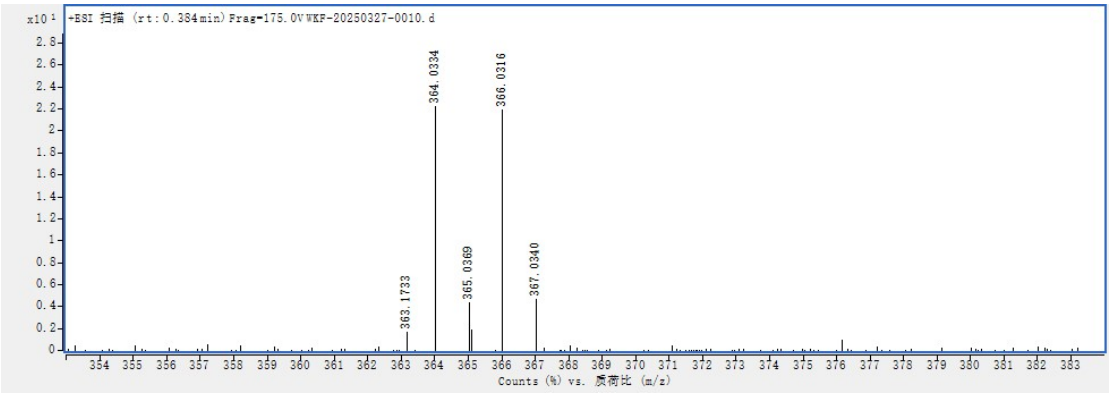
HRMS spectrum of **3e**



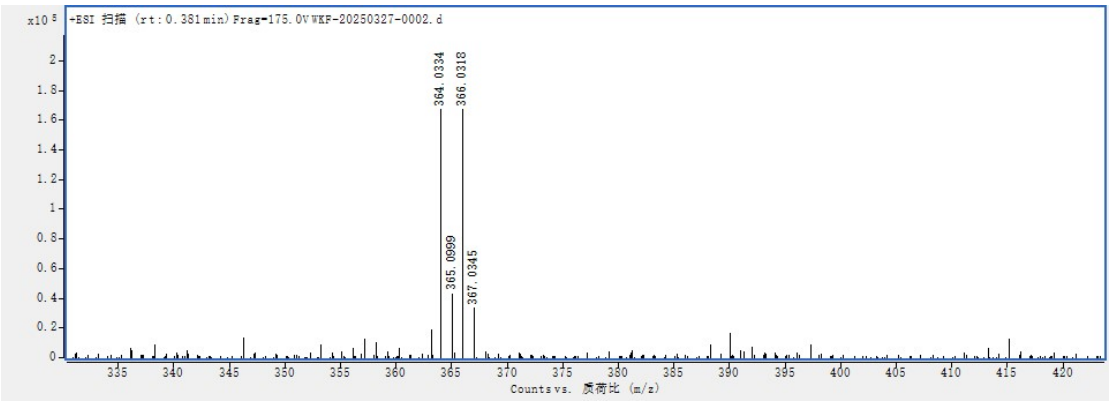
HRMS spectrum of **3f**



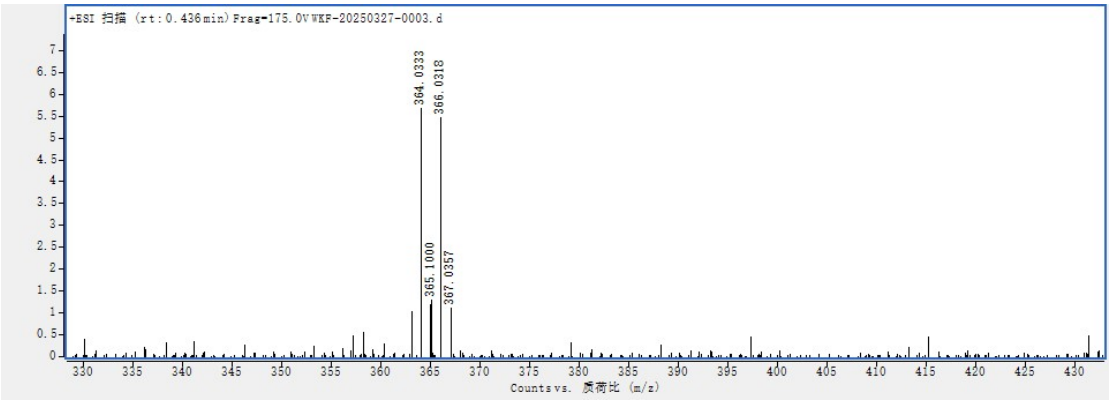
HRMS spectrum of **3g**



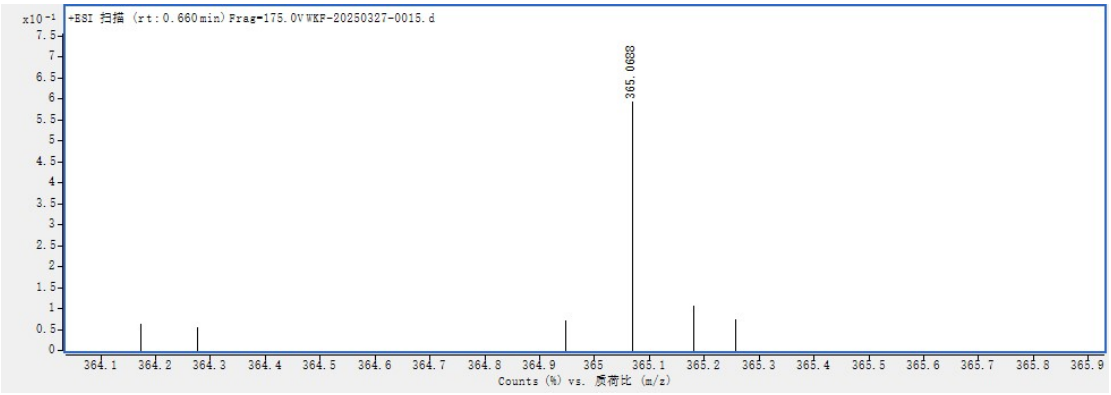
HRMS spectrum of **3h**



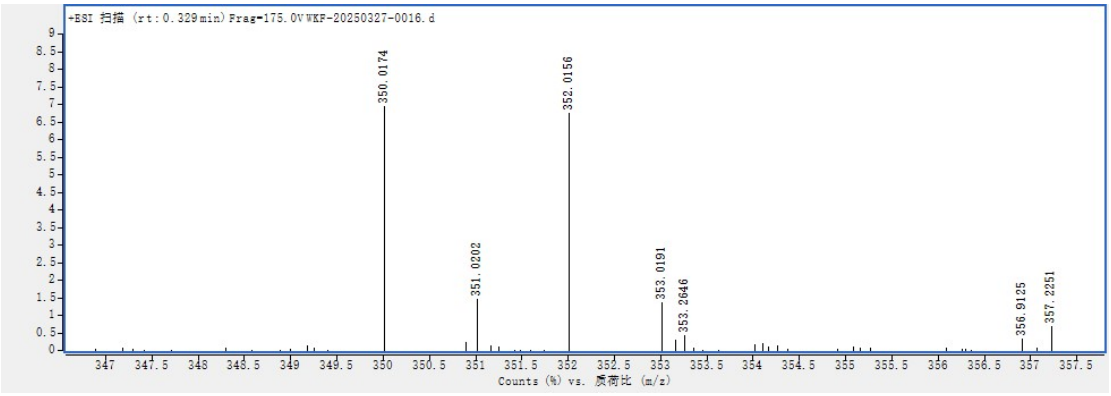
HRMS spectrum of **3i**



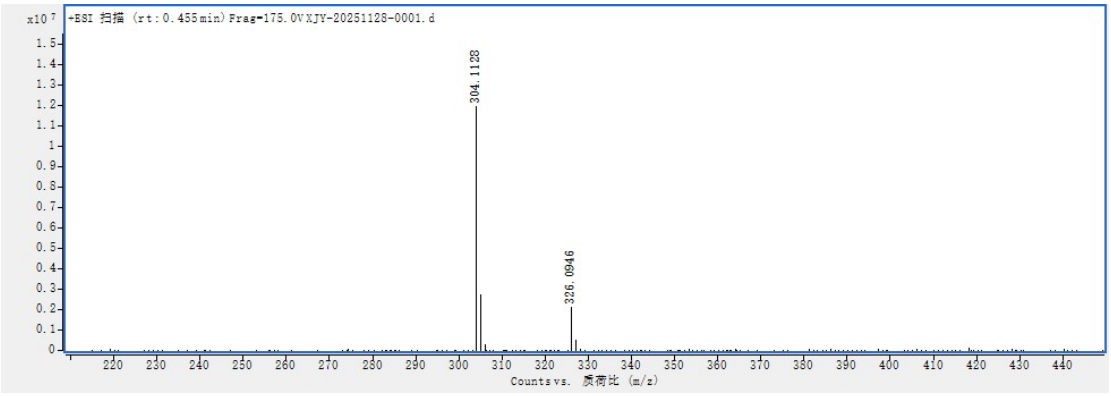
HRMS spectrum of **3j**



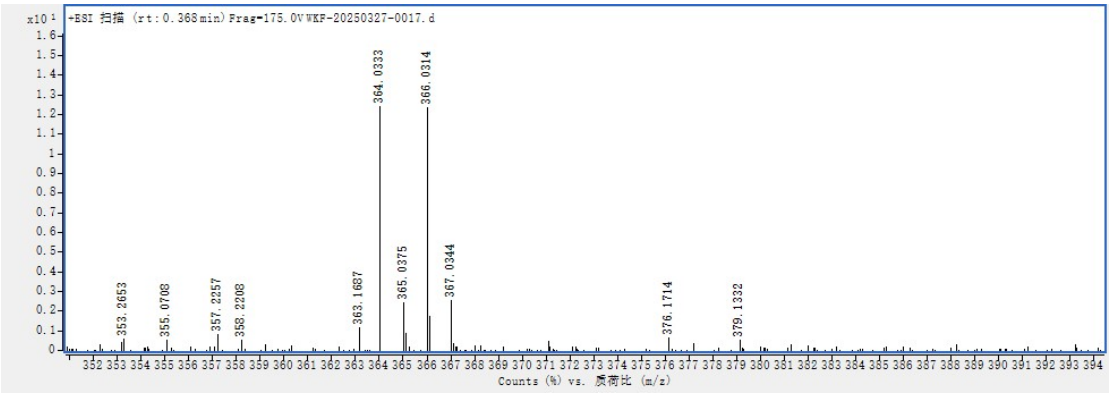
HRMS spectrum of **3k**



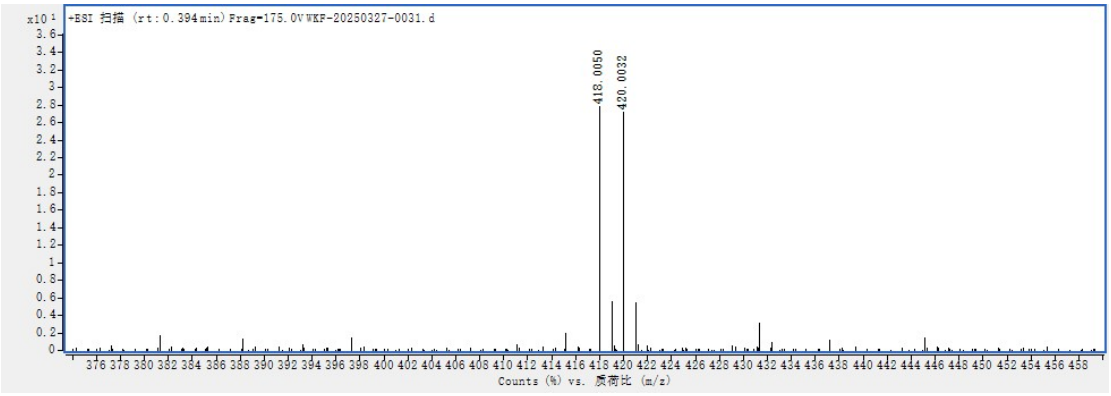
HRMS spectrum of **3l**



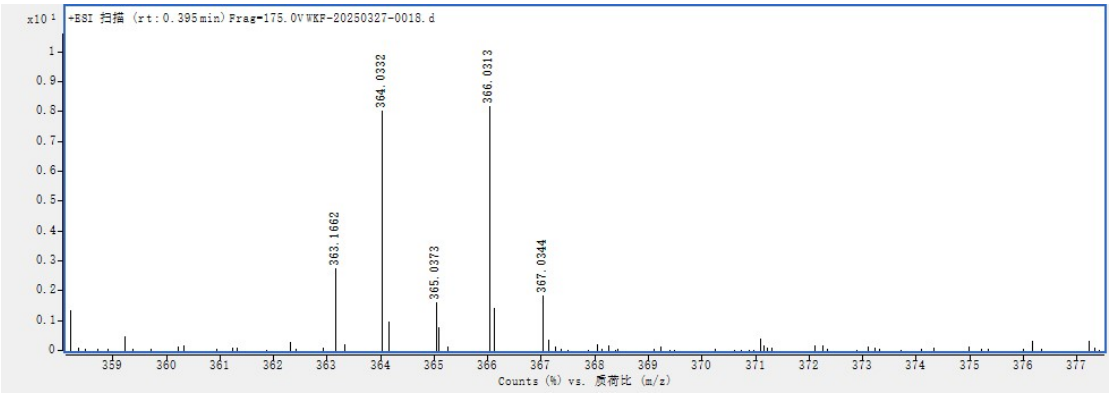
HRMS spectrum of **3m**



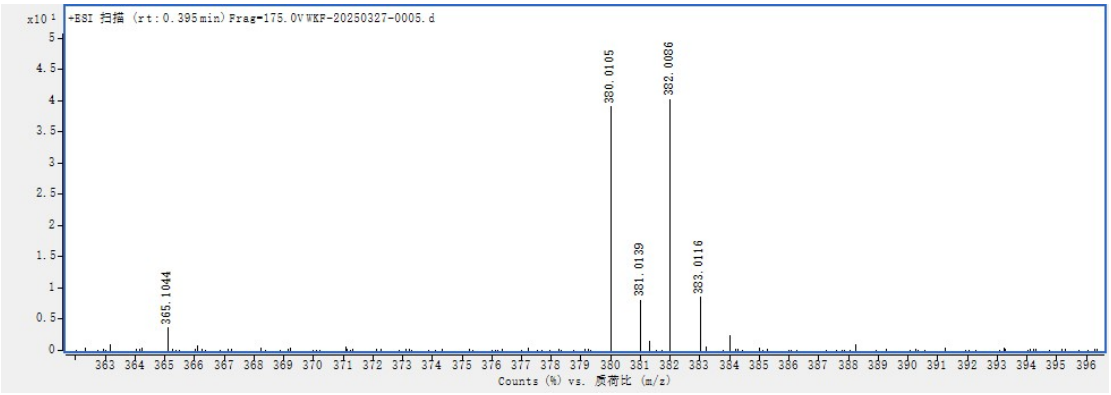
HRMS spectrum of **3n**



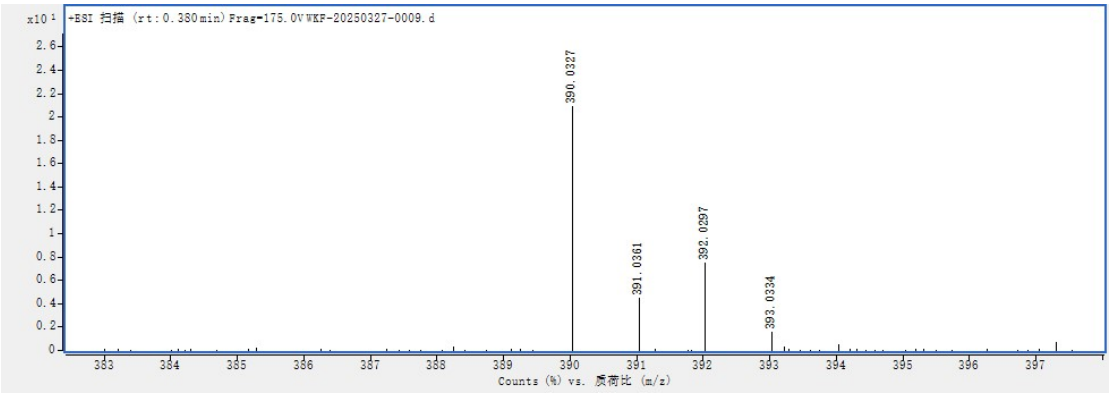
HRMS spectrum of **3o**



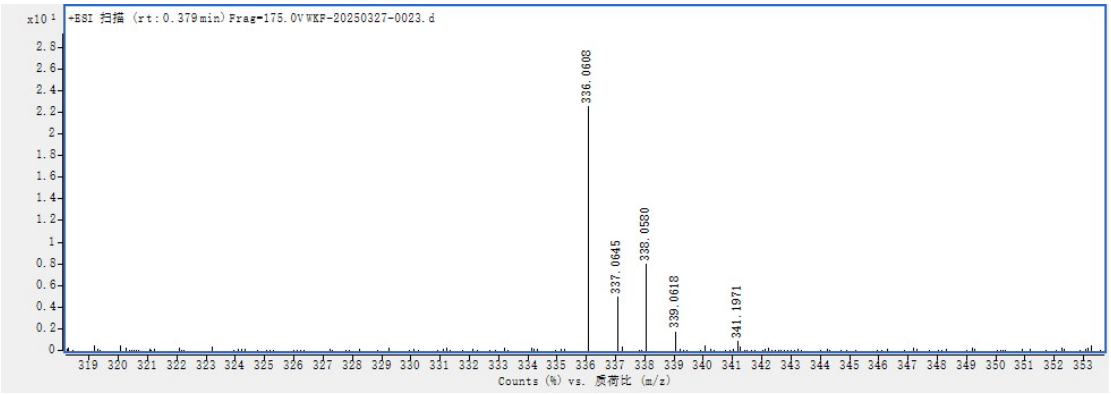
HRMS spectrum of **3p**



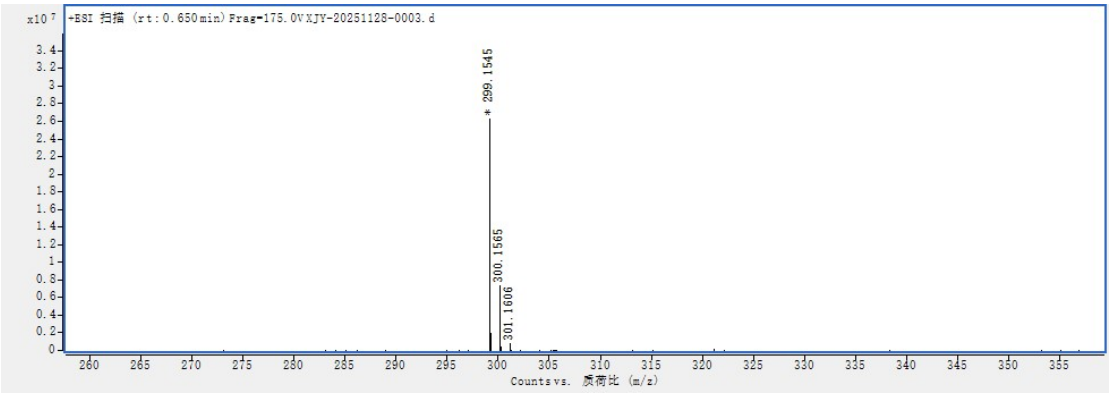
HRMS spectrum of **3q**



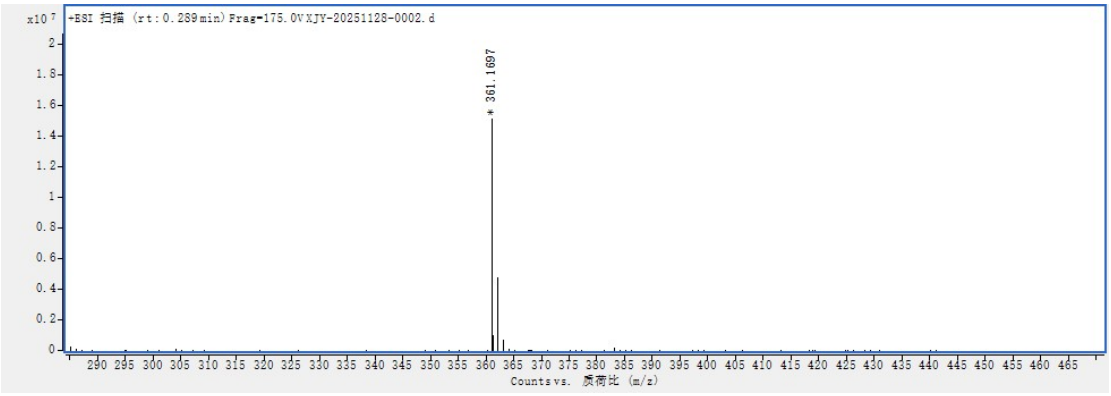
HRMS spectrum of **3r**



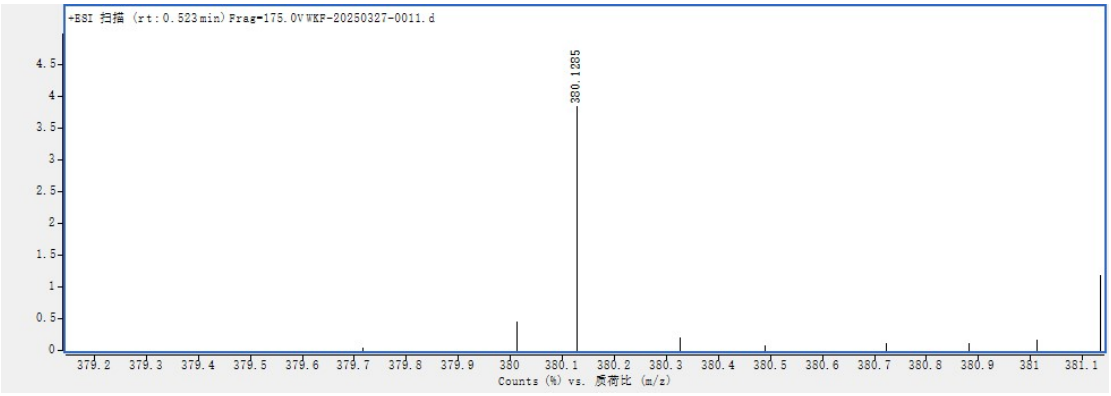
HRMS spectrum of **3s**



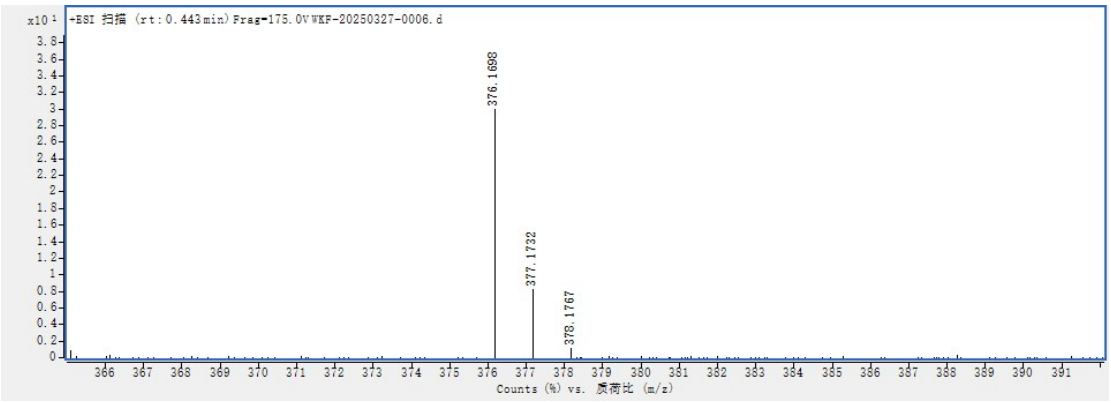
HRMS spectrum of **3t**



HRMS spectrum of **3u**



HRMS spectrum of **4**



HRMS spectrum of **5**