Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Thiol substrate-promoted dehydrogenative cyclization of arylmethyl thiols with *ortho*-substituted amines: a universal approach to heteroaromatic compounds

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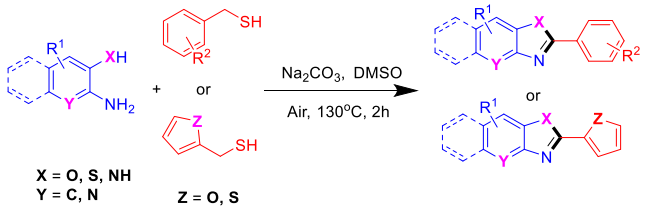
1. General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded in $CDCl_3$ or DMSO-d6 at room temperature on the Bruker DPX-400 spectrometer (400 MHz, 100 MHz and 377 MHz). The chemical-shifts scale is based on internal TMS. For spectra, chemical shifts were reported in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature.

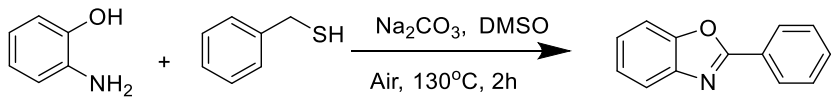
All reactions were monitored and post-processing by TLC with Qingdao GF_{254} silica gel coated plates. Most reagents were obtained from commercial suppliers such as J&K Scientific and used without further purification unless otherwise noted.

2. General procedure for product synthesis



To a solution of *o*-substituted aniline (0. 25 mmol) in dimethyl sulfoxide (1.0 mL) was added arylmethylmercaptan (0.50 mmol), Na_2CO_3 (53 mg, 0.50 mmol) under air atmosphere in a screw-cap Schlenk test tube. The reaction mixture was stirred at 130 ℃ for 2 h. After the reaction was finished, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with dichloromethane (3.0 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding products（Petroleum ether / dichloromethane = 3:1-2:1）.

3. General experimental procedure for the scale-up reaction.

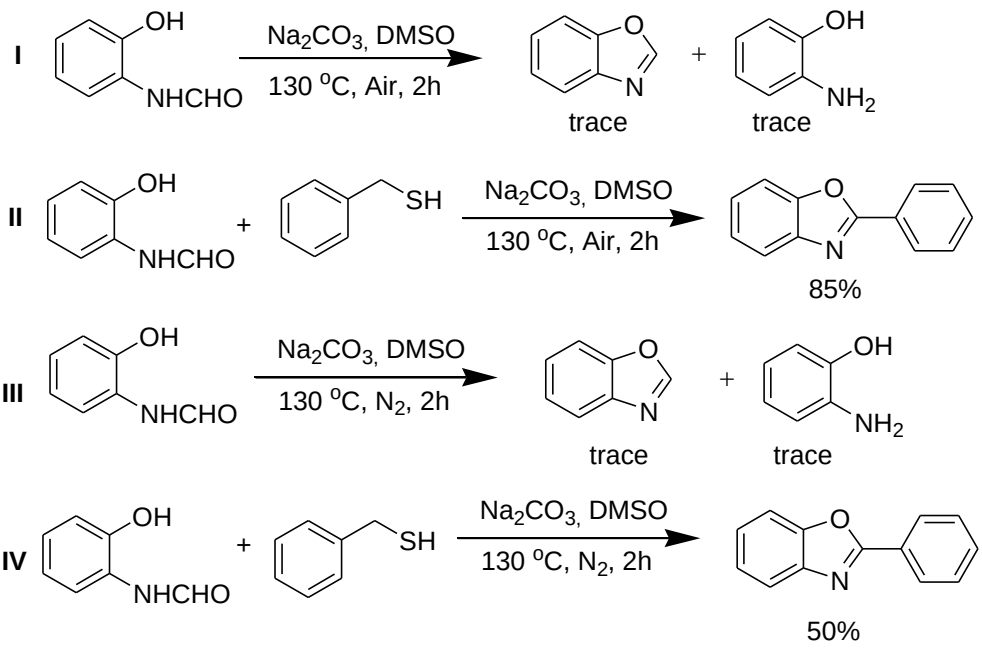


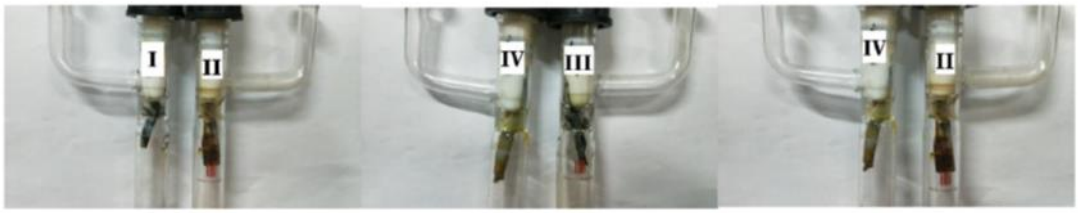
1a **2a** **3aa**

To a solution of *o*-hydroxyaniline (**1a**, 109 mg, 1 mmol) in dimethyl sulfoxide (4.0 mL) was added Benzyl mercaptan (**2a**, 234 uL, 2 mmol), Na_2CO_3 (212 mg, 2 mmol) under air atmosphere in a round-bottomed flask. The mixture was refluxed at 130 ℃ for 2 h. After the reaction was finished, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with dichloromethane (12.0 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the **3aa** products（Petroleum ether / dichloromethane = 3:1, 128.7 mg, 66%）.

4. Decarbonylation experiment results of Scheme 3 eqn(4)

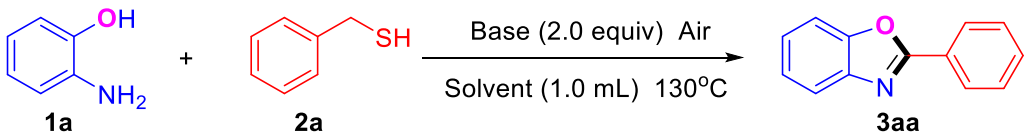
In order to explain the transfer of N-formylaniline to amine, the following reactions were conducted to determine the extrusion of CO.





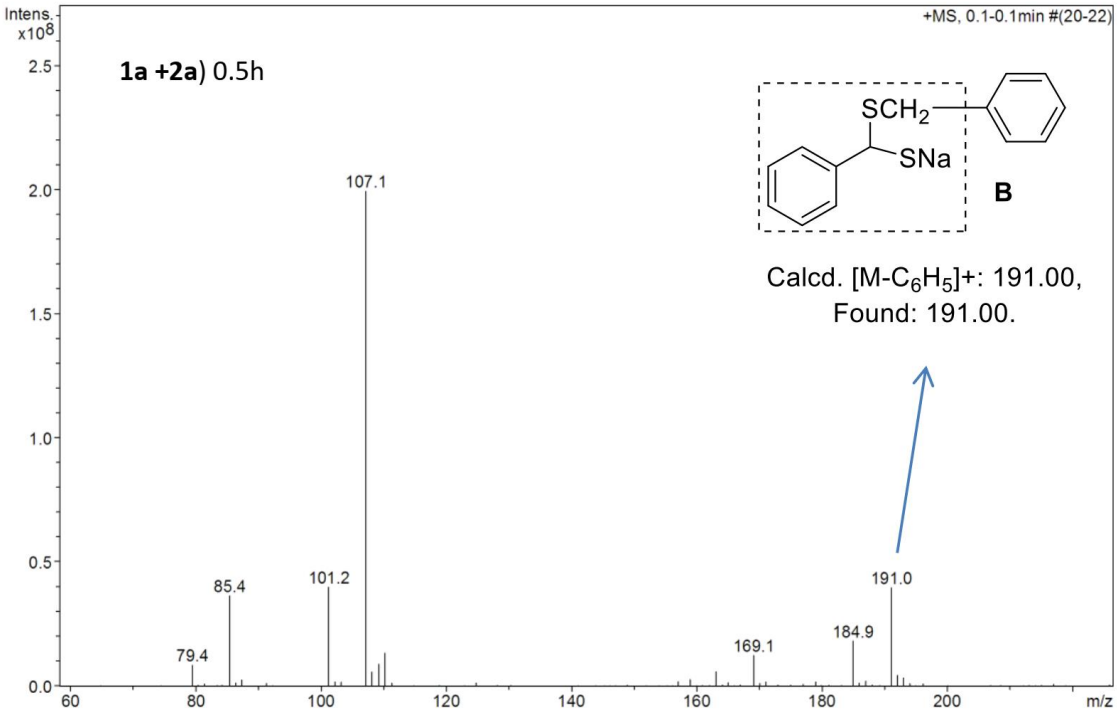
According to the literature, a piece of test strip containing $PdCl_2$ and PMA (phosphomolybdic acid) was put into the reaction tube and sealed for 5 min to determine the extrusion of CO after the completion of the reaction. To our delight, all the test papers in the four tubes that were conducted under the standard procedure turned to dark blue. The results indicated that the extrusion of CO was occurred when N-formylaniline was applied to the optimal conditions in air or N_2 atmosphere.

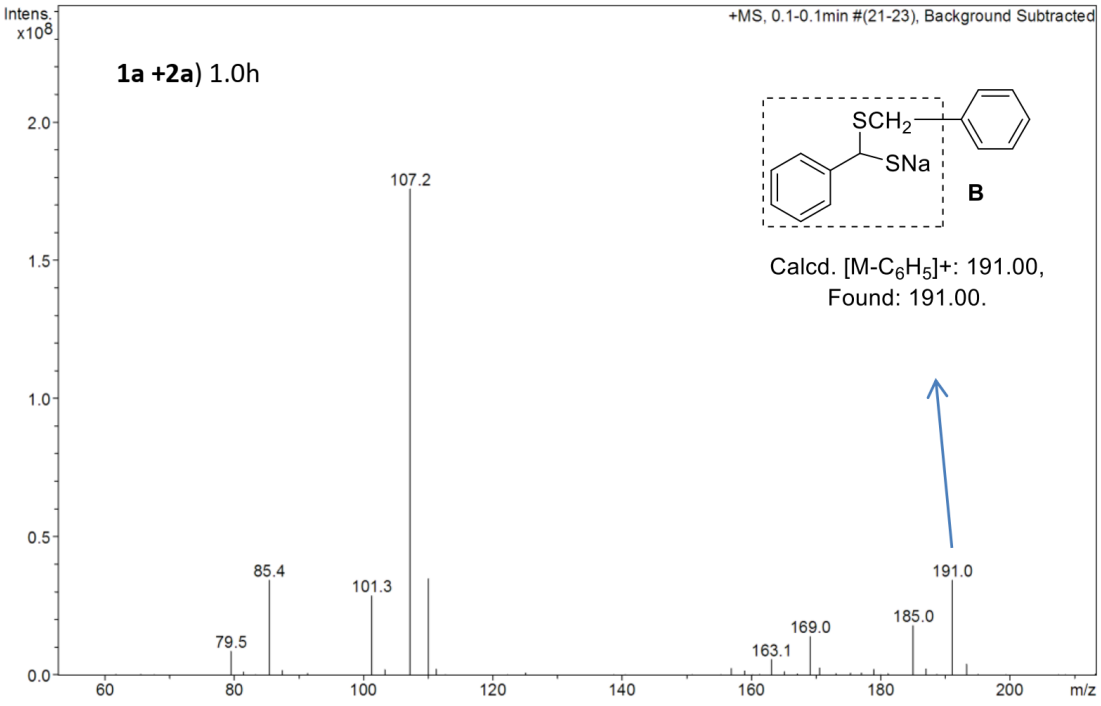
5. Mass spectrometry and nuclear magnetic experiment results of template reaction

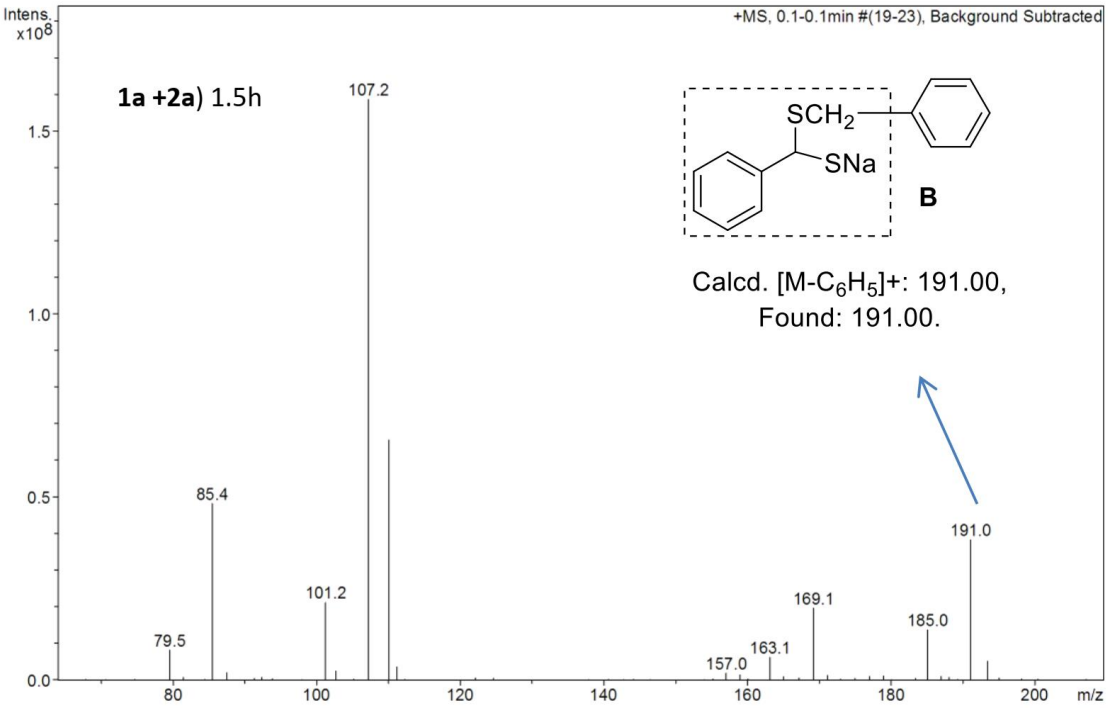


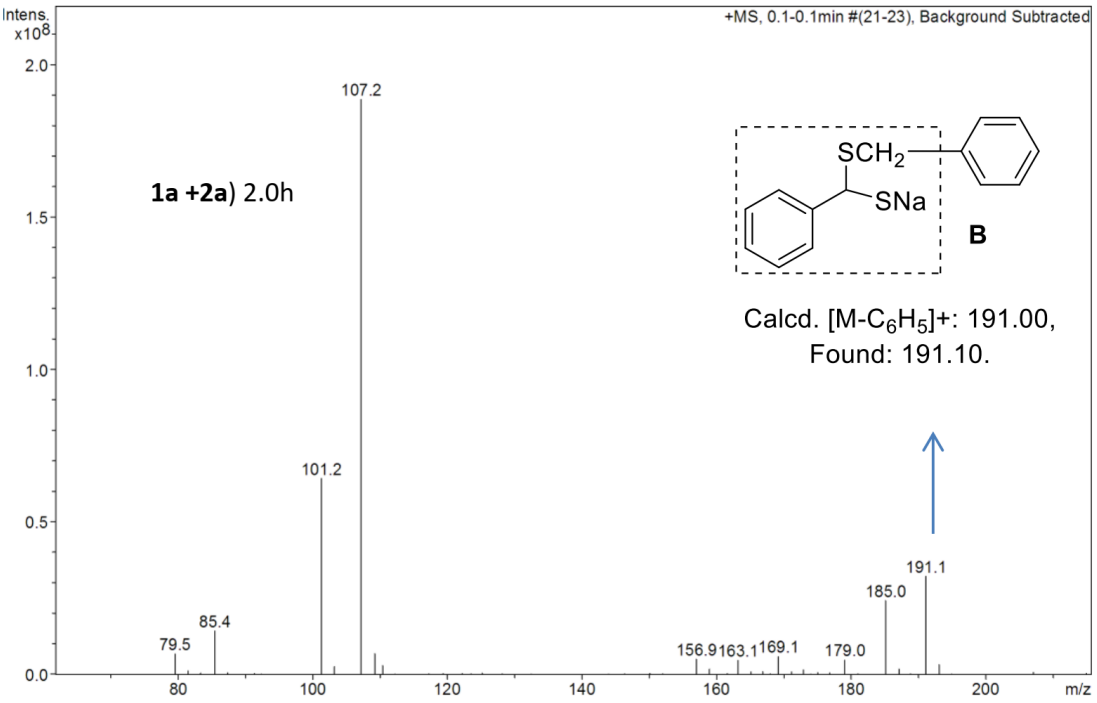
To a solution of 2-hydroxyaniline (27 mg, 0. 25 mmol) in dimethyl sulfoxide (1.0 mL) was added benzyl mercaptan (58 uL, 0.50 mmol), Na_2CO_3 (53 mg, 0.50 mmol) under air atmosphere in a screw-cap Schlenk test tube. The reaction mixture was stirred at 130 ℃ for 2h. After the reaction was finished, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with

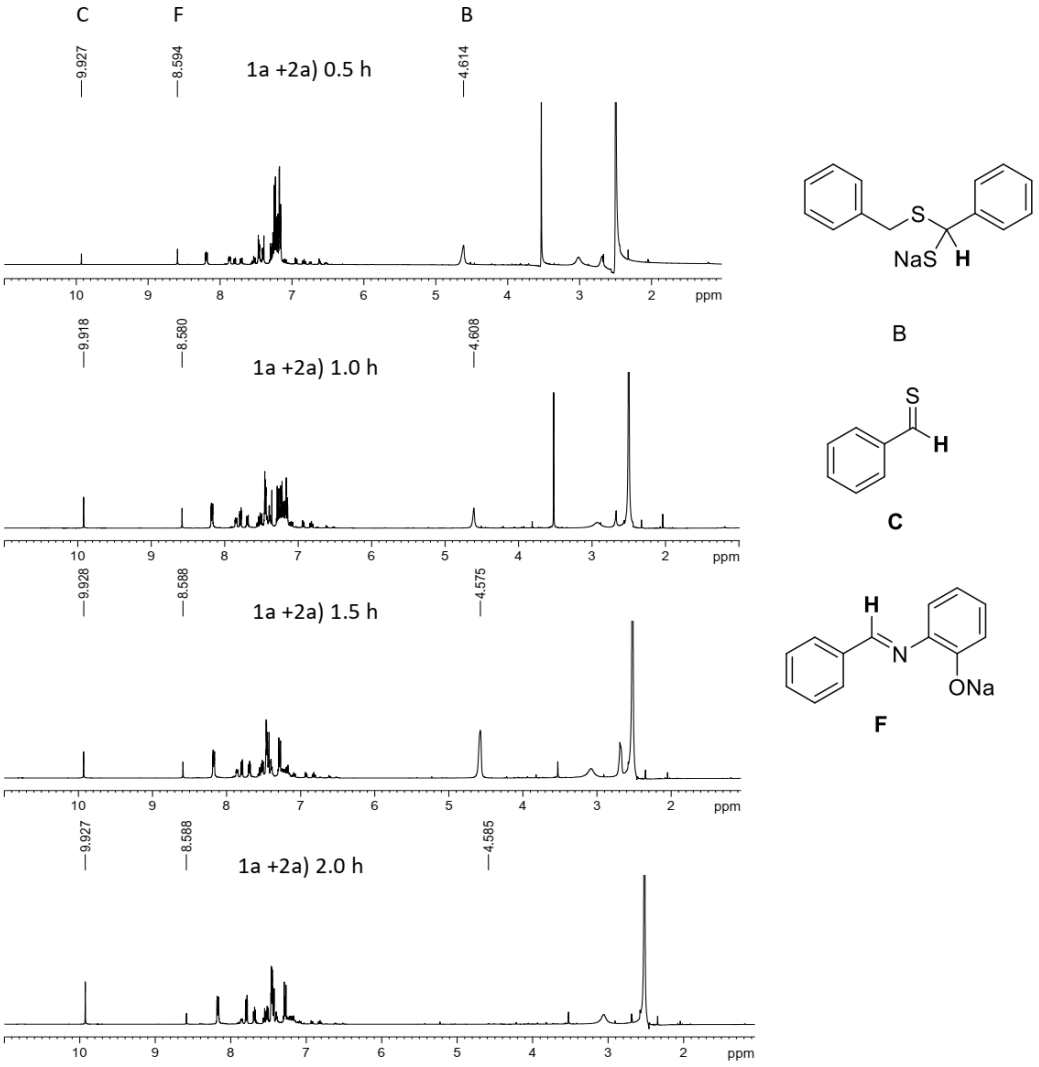
dichloromethane (3.0 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The processed samples were separately passed through mass spectrometry and nuclear magnetic detection. The test results are as follows.





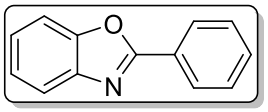

Intens.
x10^8
+MS, 0.1-0.1min #(19-23), Background Subtracted
1a +2a) 1.5h
107.2
SCH2
SNa
B
Calcd. [M-C6H5]+: 191.00,
Found: 191.00.
85.4
191.0
101.2
169.1
185.0
79.5
163.1
157.0
m/z


Intens.
x10^8
+MS, 0.1-0.1min #(21-23), Background Subtracted
1a +2a) 2.0h
107.2
SCH2
SNa
B
Calcd. [M-C6H5]+: 191.00,
Found: 191.10.
101.2
191.1
185.0
85.4
79.5
156.9
163.1
169.1
179.0
m/z



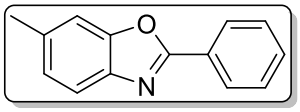
6. Characterization data of products

2-phenylbenzo[d]oxazole(3aa):[1]



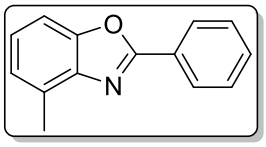
Prepared according to the general procedure to afford a white solid in 97% yield (47.29 mg), mp 103-104 ℃ (lit. mp 102-104 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.22 (m, 2H), 7.81-7.75 (m, 1H), 7.56-7.52 (m, 1H), 7.51-7.46 (m, 3H), 7.35-7.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.81, 150.54, 141.93, 131.30, 128.70, 127.42, 126.95, 124.91, 124.38, 119.83, 110.41.

6-methyl-2-phenylbenzo[d]oxazole(3ba):[2]



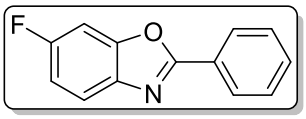
Prepared according to the general procedure to afford a white solid in 85% yield (44.41 mg), mp 94-95 ℃ (lit. mp 94-94.5 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.53-7.49 (m, 3H), 7.38 (s, 1H), 7.18-7.15 (m, 1H), 2.50 (s, 3H); ^{13C} NMR (101 MHz, $CDCl_3$) δ 162.51, 150.99, 139.84, 135.53, 131.24, 128.83, 127.41, 127.28, 125.77, 119.28, 110.72, 21.78.

4-methyl-2-phenylbenzo[d]oxazole(3ca):[3]



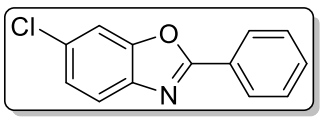
Prepared according to the general procedure to afford a white solid in 87% yield (45.46 mg), mp 91-92 ℃ (lit. mp 92-93 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.26 (m, 2H), 7.54-7.50 (m, 3H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.22, 150.48, 141.38, 131.22, 130.54, 128.78, 127.54, 127.38, 124.99, 124.69, 107.80, 16.55.

6-fluoro-2-phenylbenzo[d]oxazole(3da):[4]



Prepared according to the general procedure to afford a white solid in 81% yield (43.13 mg), mp 110-111 ℃ (lit. mp 109-110 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.14 (m, 2H), 7.68 (dd, *J* = 8.7, 4.9 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.28 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.09 (td, *J* = 9.5, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.65 (d, *J* = 4.04 Hz), 161.62 (d, J = 245.43 Hz), 150.65 (d, J = 15.15 Hz), 138.36 (d, J = 1.01 Hz), 131.56, 128.90, 127.42, 126.82, 120.19 (d, J = 10.10 Hz), 112.50 (d, J = 25.25 Hz), 98.63 (d, J = 28.28 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.05.

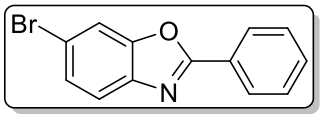
6-chloro-2-phenylbenzo[d]oxazole(3ea):[1]



Prepared according to the general procedure to afford a white solid in 81% yield (46.37 mg), mp 118-119 ℃ (lit. mp 117-108 ℃); ^{1}H NMR (400 MHz, CDCl3) δ 8.22 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63,

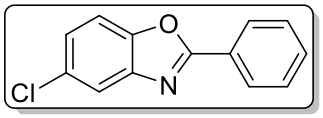
150.84, 140.81, 131.76, 130.61, 128.92, 127.59, 126.62, 125.23, 120.40, 111.19.

6-bromo-2-phenylbenzo[d]oxazole(3fa):[5]



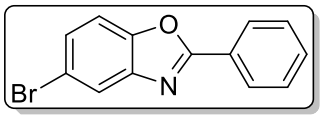
Prepared according to the general procedure to afford a white solid in 83% yield (56.65 mg), mp 103-105 ℃ (lit. mp 104-105 ℃); ^{1}H NMR (400 MHz, CDCl3) δ 8.21 (dd, J = 7.8, 1.7 Hz, 2H), 7.73 (d, J = 1.7 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.46 (dd, J = 8.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 151.15, 141.26, 131.82, 128.95, 127.99, 127.65, 126.60, 120.90, 117.92, 114.08.

5-chloro-2-phenylbenzo[d]oxazole(3ga):[2]



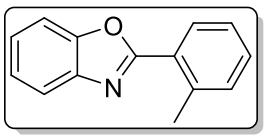
Prepared according to the general procedure to afford a white solid in 77% yield (44.08 mg), mp 104-105 ℃ (lit. mp 103-105 ℃); ^{1}H NMR (400 MHz, CDCl3) δ 8.22 (dd, J = 7.6, 1.5 Hz, 2H), 7.73 (d, J = 1.8 Hz, 1H), 7.51 (dt, J = 13.1, 7.3 Hz, 4H), 7.31 (dd, J = 8.6, 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.30, 149.27, 143.19, 131.88, 129.98, 128.94, 127.70, 126.62, 125.31, 119.91, 111.25.

5-bromo-2-phenylbenzo[d]oxazole(3ha):[6]



Prepared according to the general procedure to afford a white solid in 37% yield (25.25 mg), mp 111-112 ℃ (lit. mp 110-111 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 -8.20 (m, 2H), 7.91-7.88 (m, 1H), 7.55-7.50 (m, 3H), 7.44 (d, *J* = 1.4 Hz, 2H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10, 149.69, 143.67, 131.89, 128.93, 128.03, 127.72, 126.58, 122.93, 117.26, 111.75.

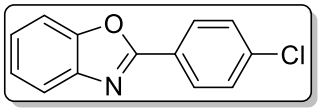
2-(o-tolyl)benzo[d]oxazole(3ab):[7]



Prepared according to the general procedure to afford a white solid in 66% yield (34.49 mg), mp 164-165 ℃ (lit. mp 163-166 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 6.7, 2.4 Hz, 1H), 7.85-7.77 (m, 1H), 7.63-7.56 (m, 1H), 7.44-7.40 (m, 1H),

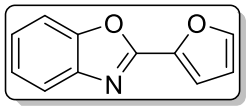
7.39-7.32 (m, 4H), 2.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 150.27, 142.09, 138.82, 131.77, 130.88, 129.92, 126.20, 126.04, 124.99, 124.34, 120.11, 110.46, 22.19.

3-(4-chlorophenyl)benzo[d]oxazole(3ac):[1]



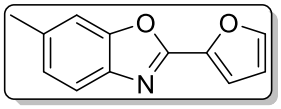
Prepared according to the general procedure to afford a white solid in 33% yield (18.89 mg), mp 149-150 ℃ (lit. mp 150 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.12 (m, 2H), 7.79-7.73 (m, 1H), 7.59-7.54 (m, 1H), 7.51-7.46 (m, 2H), 7.39-7.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.00, 150.68, 141.94, 137.71, 129.22, 128.79, 125.58, 125.31, 124.70, 120.04, 110.58.

2-(furan-2-yl)benzo[d]oxazole(3ad):[4]



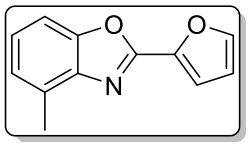
Prepared according to the general procedure to afford a white solid in 64% yield (29.60 mg), mp 84-85 ℃ (lit. mp 83-85 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 1H), 7.67-7.64 (m, 1H), 7.54 (dt, *J* = 6.9, 3.2 Hz, 1H), 7.33 (ddd, *J* = 7.4, 4.7, 2.1 Hz, 2H), 7.27-7.26 (m, 1H), 6.60 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.22, 150.07, 145.68, 142.54, 141.57, 125.22, 124.79, 120.07, 114.21, 112.21, 110.50.

2-(furan-2-yl)-6-methylbenzo[d]oxazole(3bd):[2]



Prepared according to the general procedure to afford a white solid in 52% yield (25.87 mg) , mp 52-53 ℃ (lit. mp 52-53 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.23 (dd, *J* = 3.5, 0.5 Hz, 1H), 7.16 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.60 (dd, *J* = 3.5, 1.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.82, 150.39, 145.45, 142.72, 139.39, 135.78, 126.04, 119.42, 113.75, 112.16, 110.68, 21.78.

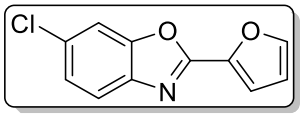
2-(furan-2-yl)-4-methylbenzo[d]oxazole(3cd)



Prepared according to the general procedure to afford a white solid in 78% yield (38.81 mg)，mp 82-83 ℃ ;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.7, 0.7 Hz,

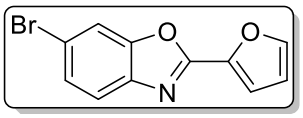
1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.32-7.27 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.54, 149.84, 145.51, 142.74, 140.82, 130.73, 125.32, 124.96, 113.88, 112.15, 107.78, 16.57. HR-MS(ESI$^+$): Calcd. For $C_{12}H_9NO_2$ $[M+H]^+$:200.0706, Found: 200.0707.

6-chloro-2-(furan-2-yl)benzo[d]oxazole(3ed):[8]



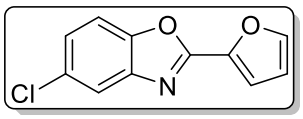
Prepared according to the general procedure to afford a white solid in 63% yield (34.49 mg), mp 116-118 ℃ (lit. mp 119 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.27 (dd, *J* = 3.5, 0.6 Hz, 1H), 6.62 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.80, 150.27, 146.02, 142.09, 140.42, 130.80, 125.54, 120.52, 114.77, 112.35, 111.18.

6-bromo-2-(furan-2-yl)benzo[d]oxazole(3fd)



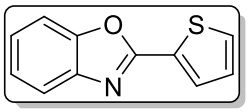
Prepared according to the general procedure to afford a white solid in 56% yield (36.83 mg) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.6 Hz, 1H), 7.68 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.47 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.28 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.62 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63, 150.55, 146.07, 142.05, 140.86, 128.29, 121.00, 118.06, 114.87, 114.04, 112.37.

5-chloro-2-(furan-2-yl)benzo[d]oxazole(3gd):[9]



Prepared according to the general procedure to afford a white solid in 46% yield (25.19 mg), mp 84-85 ℃ (lit. mp 83-85 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.68 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.30 (ddd, *J* = 6.1, 4.1, 1.3 Hz, 2H), 6.62 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 148.69, 146.12, 142.77, 142.09, 130.31, 125.50, 120.00, 114.98, 112.38, 111.23.

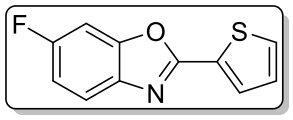
2-(thiophen-2-yl)benzo[d]oxazole(3ae):[6]



Prepared according to the general procedure to afford a white solid in 91% yield (45.73 mg), mp 103-105 ℃ (lit. mp 104-105 ℃); ^{1}H NMR (400

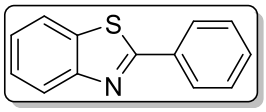
MHz, $CDCl_3$) δ 7.90 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.76-7.70 (m, 1H), 7.56-7.50 (m, 2H), 7.35-7.30 (m, 2H), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 150.33, 141.90, 130.18, 129.87, 129.55, 128.18, 125.00, 124.64, 119.71, 110.35.

6-fluoro-2-(thiophen-2-yl)benzo[d]oxazole(3de):[10]



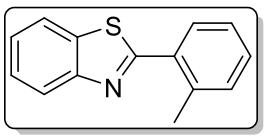
Prepared according to the general procedure to afford a white solid in 56% yield (30.66 mg), mp 112-113 ℃ (lit. mp 113-114 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.64 (dd, *J* = 8.7, 4.9 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.11-7.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.64 (d, J = 3.03 Hz), 160.58 (d, J = 245.58 Hz), 150.34 (d, J = 15.15 Hz), 138.26, 130.32, 129.93, 129.21, 128.27, 119.97 (d, J = 10.10 Hz), 112.61 (d, J = 25.25 Hz), 98.57 (d, J = 28.28 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.98.

2-phenylbenzo[d]thiazole(4ia):[1]



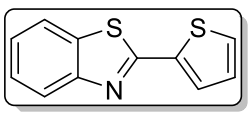
Prepared according to the general procedure to afford a white solid in 99% yield (52.22 mg), mp 115-116 ℃ (lit. mp 115 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13-8.07 (m, 3H), 7.90 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.53-7.47 (m, 4H), 7.41-7.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.02, 154.05, 134.98, 133.52, 130.92, 128.96, 127.49, 126.26, 125.13, 123.16, 121.57.

2-(o-tolyl)benzo[d]thiazole(4ib):[2]



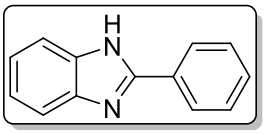
Prepared according to the general procedure to afford a white solid in 95% yield (53.44 mg), mp 59-60 ℃ (lit. mp 59 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.81-7.73 (m, 1H), 7.55-7.49 (m, 1H), 7.44-7.30 (m, 4H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.95, 153.73, 137.20, 135.54, 133.03, 131.49, 130.49, 129.96, 126.08, 126.06, 125.04, 123.32, 121.32, 21.31.

2-(thiophen-2-yl)benzo[d]thiazole(4ie):[2]



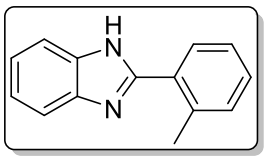
Prepared according to the general procedure to afford a white solid in 99% yield (53.71 mg), mp 99-100 ℃ (lit. mp 99.5 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.45 (dd, *J* = 11.4, 3.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.11-7.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.22, 153.49, 137.13, 134.52, 129.14, 128.47, 127.89, 126.26, 125.06, 122.77, 121.30.

2-phenyl-1H-benzo[d]imidazole(5ja):[1]



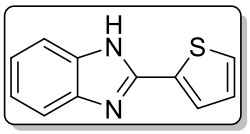
Prepared according to the general procedure to afford a white solid in 98% yield (47.53 mg), mp 293-295 ℃ (lit. mp 293 ℃); ^{1}H NMR (400 MHz, DMSO) δ 12.95 (s, 1H), 8.24 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.70-7.61 (m, 2H), 7.62-7.56 (m, 2H), 7.55-7.50 (m, 1H), 7.32-7.21 (m, 2H); ^{13}C NMR (101 MHz, DMSO) δ 151.70, 130.63, 130.32, 129.43, 126.91, 122.59.

2-(o-tolyl)-1H-benzo[d]imidazole(5jb):[11]



Prepared according to the general procedure to afford a white solid in 99% yield (51.48 mg), mp 111-113 ℃ (lit. mp 111-112 ℃); ^{1}H NMR (400 MHz, DMSO) δ 12.67 (s, 1H), 7.79-7.75 (m, 1H), 7.63 (s, 2H), 7.41-7.36 (m, 3H), 7.24-7.20 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 152.43, 137.49, 131.73, 130.56, 129.92, 129.78, 126.42, 122.36, 21.52.

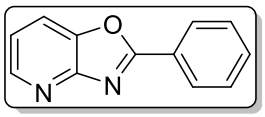
2-(thiophen-2-yl)-1H-benzo[d]imidazole(5je):[12]



Prepared according to the general procedure to afford a White solid in 84% yield (42.01 mg), mp 279-281 ℃ (lit. mp 280 ℃); ^{1}H NMR (400 MHz, DMSO) δ 12.98 (s, 1H), 7.87 (d, *J* = 2.8 Hz, 1H), 7.78-7.75 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.25 (ddd, *J* = 17.6, 6.9, 2.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 147.50, 144.08, 135.16, 134.19, 129.21, 128.75, 127.15, 123.09, 122.21, 119.01,

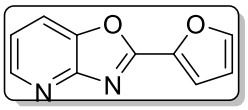
111.57.

2-phenyloxazolo[4,5-b]pyridine(6ka):[13]



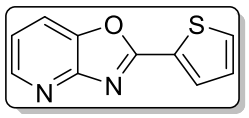
Prepared according to the general procedure to afford a white solid in 88% yield (43.12 mg), mp 127-128 ℃ (lit. mp 127-127.5 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.9, 1.3 Hz, 1H), 8.27 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.55-7.47 (m, 3H), 7.24 (dd, *J* = 8.1, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.62, 156.34, 146.68, 143.07, 132.41, 128.98, 128.09, 126.43, 120.03, 118.11.

2-(furan-2-yl)oxazolo[4,5-b]pyridine(6kd):[14]



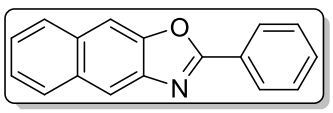
Prepared according to the general procedure to afford a white solid in 48% yield (22.33 mg), mp 88-89 ℃ (lit. mp 87-88 ℃) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.72 (d, *J* = 1.0 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 7.29 (dd, *J* = 8.1, 4.9 Hz, 1H), 6.65 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.56, 155.86, 146.97, 146.64, 142.44, 141.94, 120.10, 118.12, 116.25, 112.61.

2-(thiophen-2-yl)oxazolo[4,5-b]pyridine(6ke):[15]



Prepared according to the general procedure to afford a white solid in 79% yield (29.90 mg) , mp 142-144 ℃ (lit. mp 143-144 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.9, 1.4 Hz, 1H), 8.01 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.82 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.30 -7.26 (m, 1H), 7.22 (dd, *J* = 5.0, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55, 156.22, 146.71, 142.74, 131.81, 131.28, 128.81, 128.44, 119.90, 117.85.

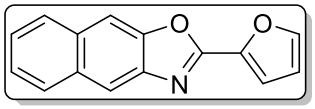
2-phenylnaphtho[2,3-d]oxazole(7la):[16]



Prepared according to the general procedure to afford a white solid in 73% yield (44.71 mg), mp 204-205 ℃ (lit. mp 203-205 ℃); 1H NMR (400 MHz, CDCl3) δ 8.38 -8.31 (m, 2H), 8.21 (s, 1H), 8.04-8.00 (m, 1H), 7.96 (d, *J* = 4.6 Hz, 2H), 7.57 (d, *J* =

6.8 Hz, 3H), 7.53-7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06 , 149.75, 142.08, 132.12, 131.78, 131.57, 129.00, 128.55, 128.16, 127.93, 126.97, 125.49, 124.71, 117.35, 106.38.

2-(furan-2-yl)naphtho[2,3-d]oxazole(7ld)



Prepared according to the general procedure to afford a white solid in 24% yield (14.14 mg)，mp 83-84 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.00 (dd, *J* = 6.1, 3.1 Hz, 1H), 7.97-7.91 (m, 2H), 7.73 (d, *J* = 1.0 Hz, 1H), 7.52-7.46 (m, 2H), 7.40-7.36 (m, 1H), 6.66 (dd, *J* = 3.5, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.97, 149.07, 146.35, 142.43, 141.47, 131.76, 131.63, 128.47, 127.89, 125.55, 124.82, 117.45, 115.57, 112.47, 106.36; HR-MS(ESI^{+}): Calcd. For $C_{15}H_9NO_2$ $[M+H]^{+}$:236.0706, Found: 236.0707.

7. **References:**

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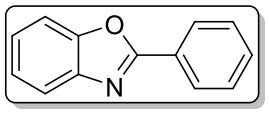
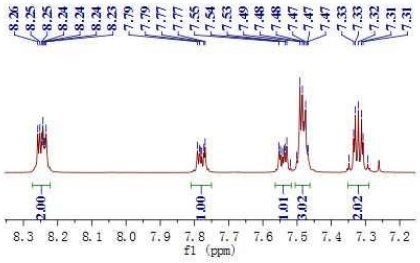
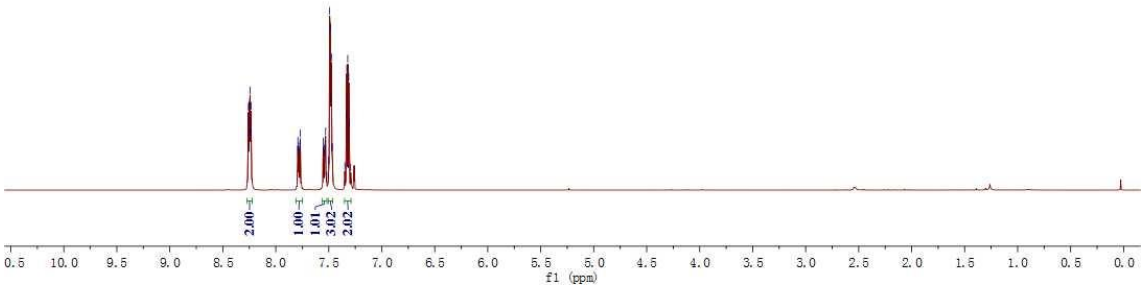
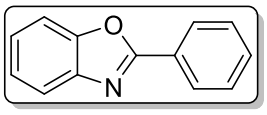
8. NMR spectra

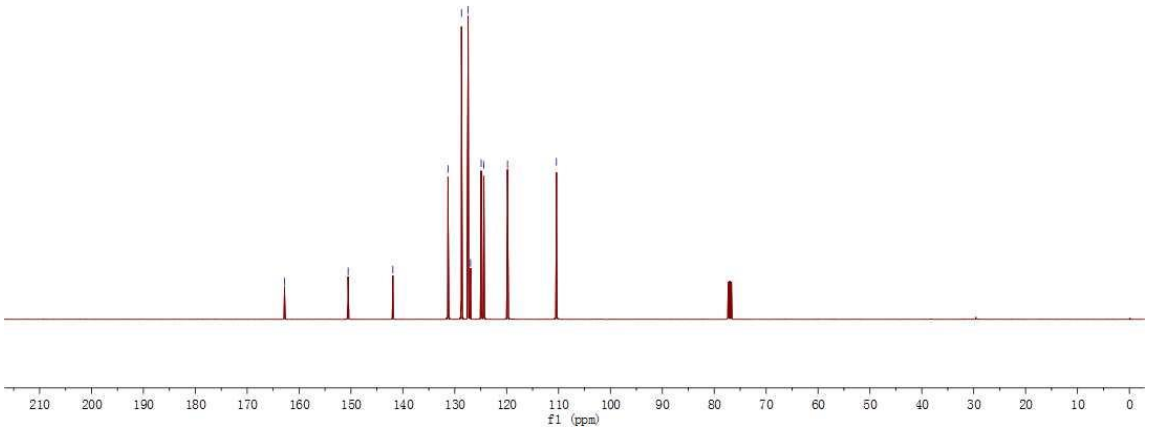
2-phenylbenzo[d]oxazole(3aa)



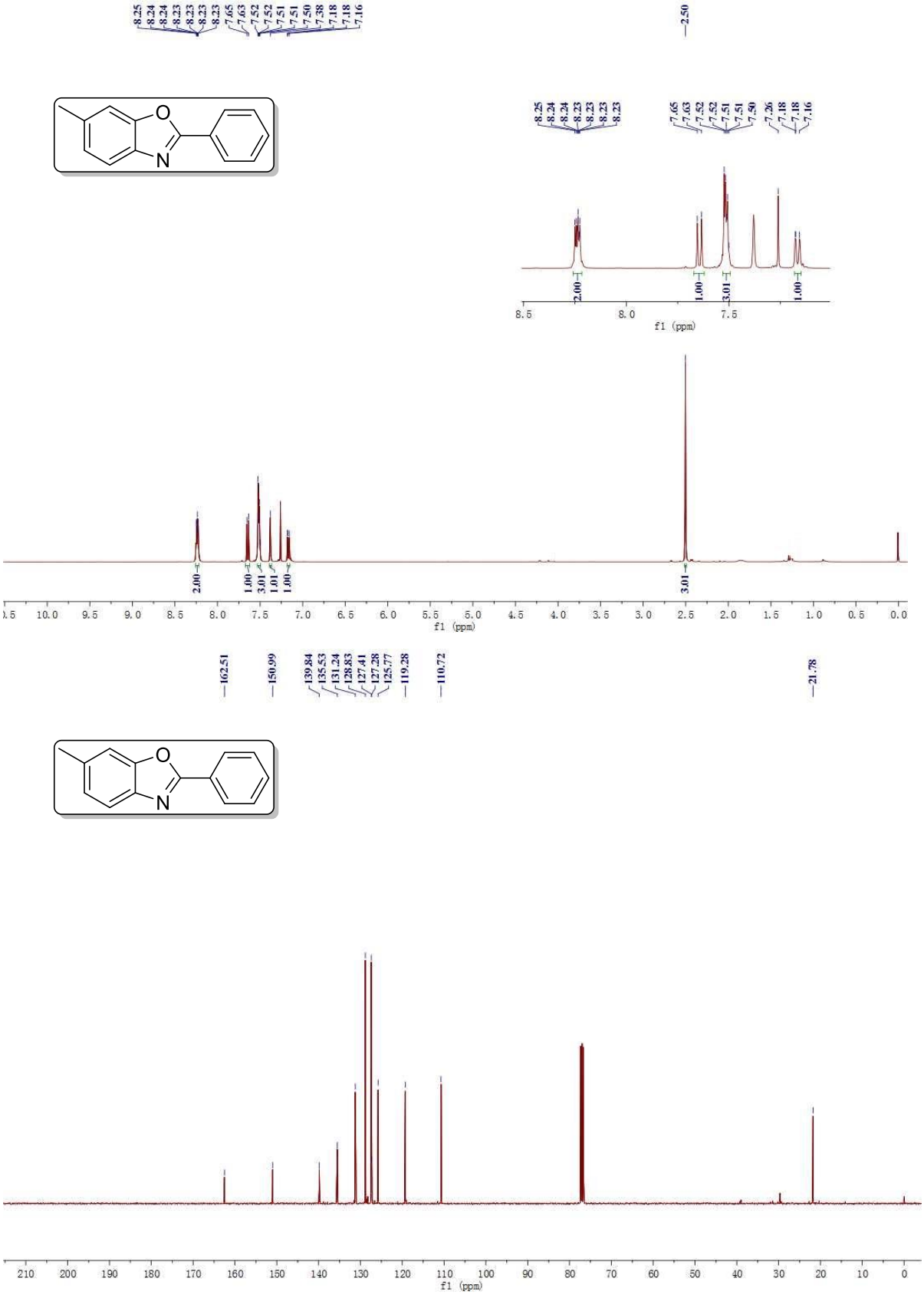




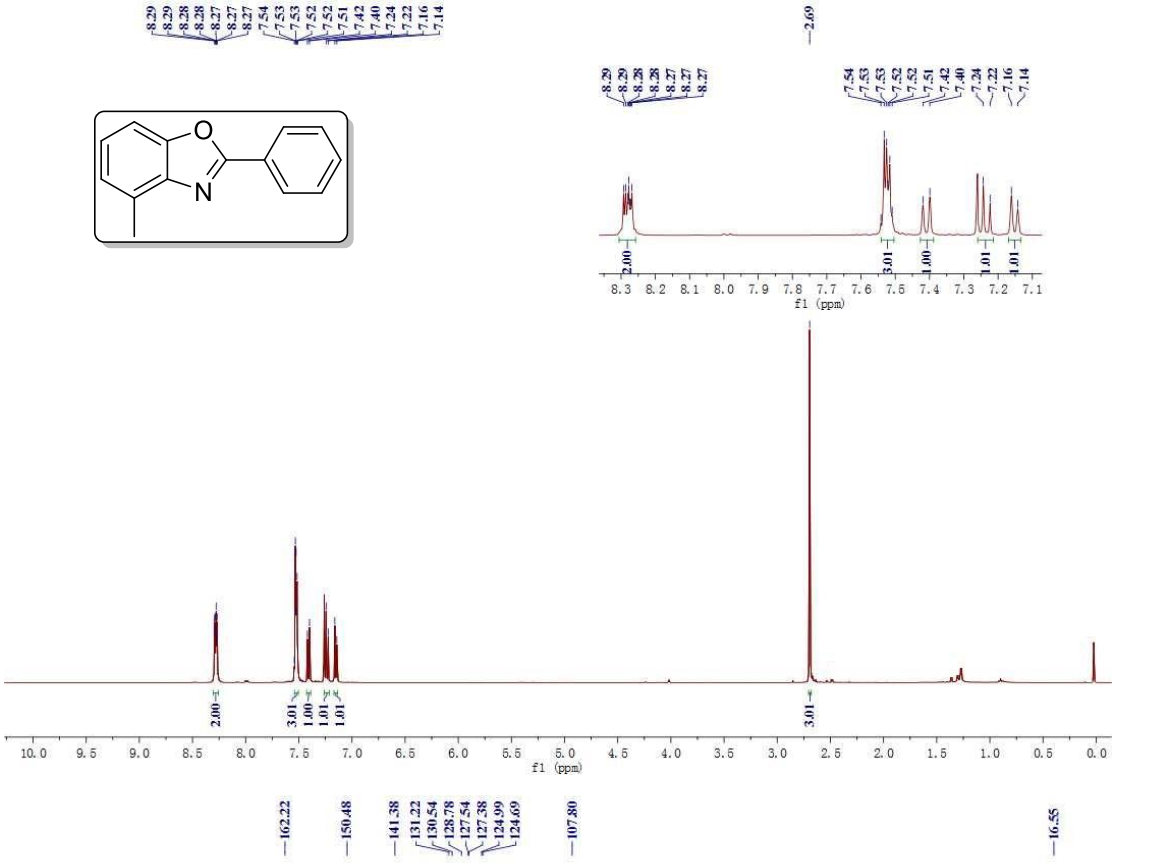


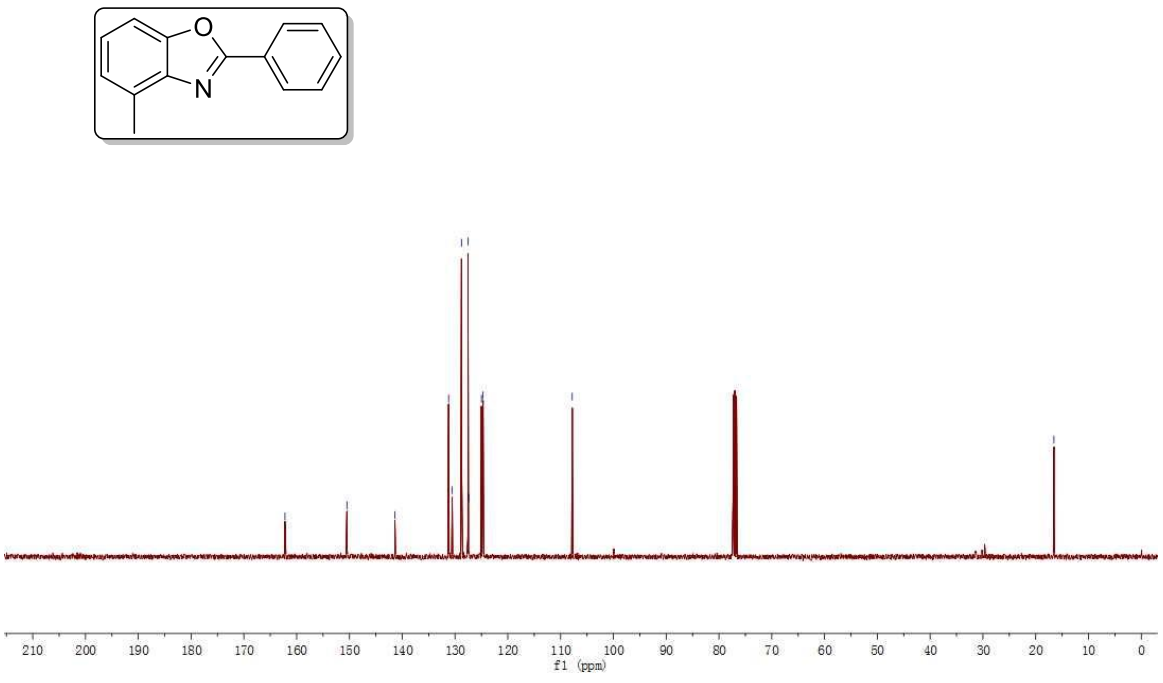


6-methyl-2-phenylbenzo[d]oxazole(3ba)

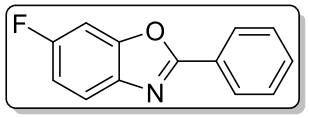


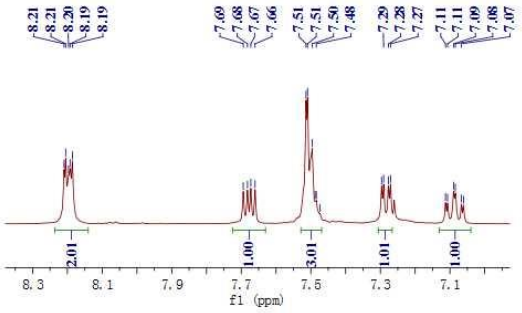
4-methyl-2-phenylbenzo[d]oxazole(3ca)

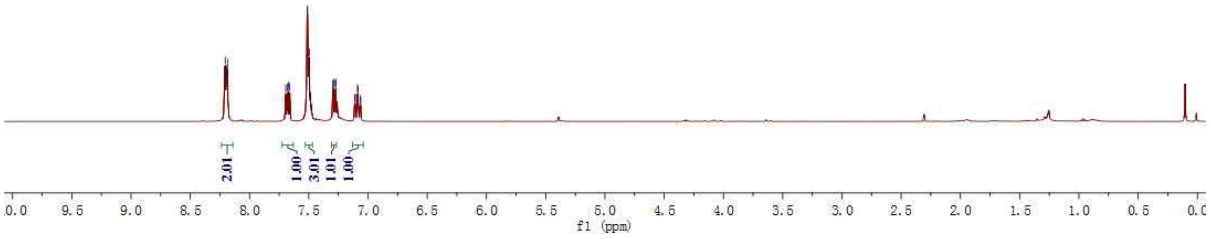


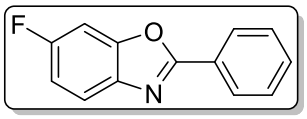


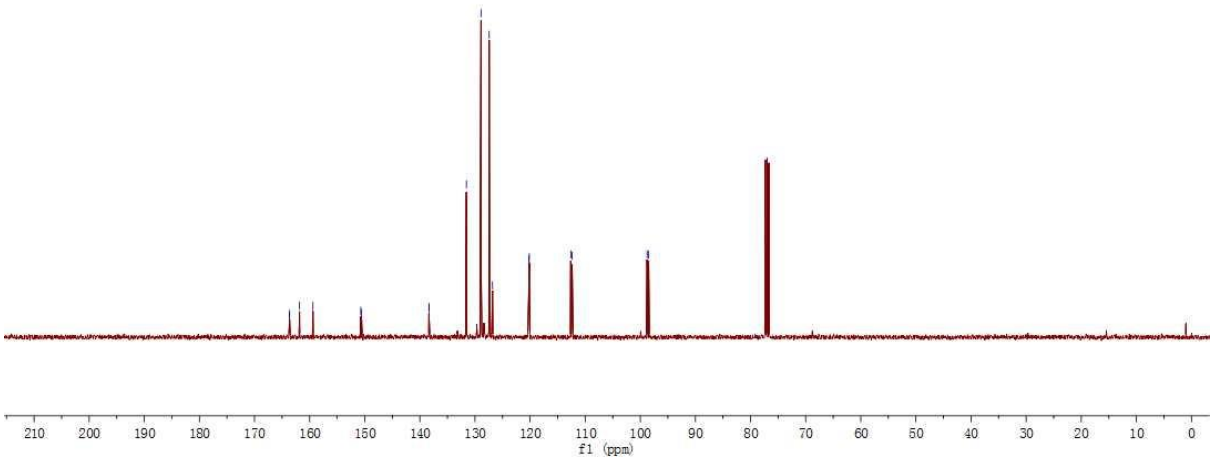
6-fluoro-2-phenylbenzo[d]oxazole(3da)

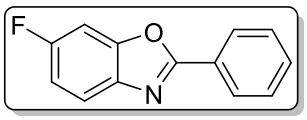




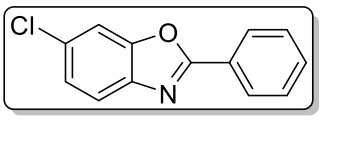


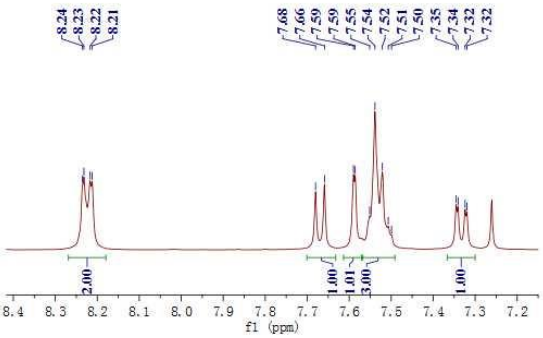


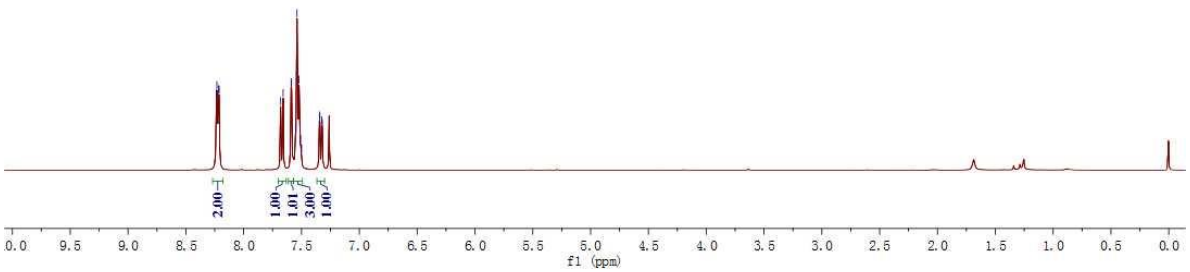


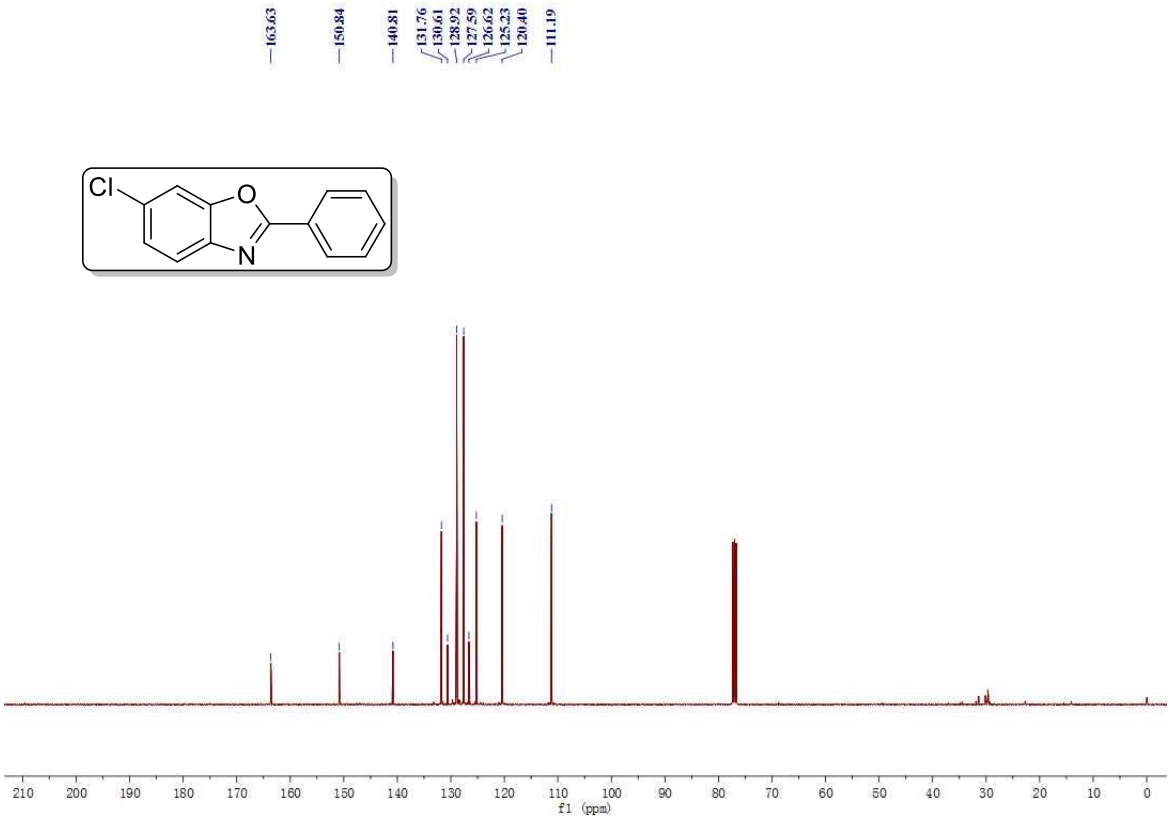


6-chloro-2-phenylbenzo[d]oxazole(3ea)

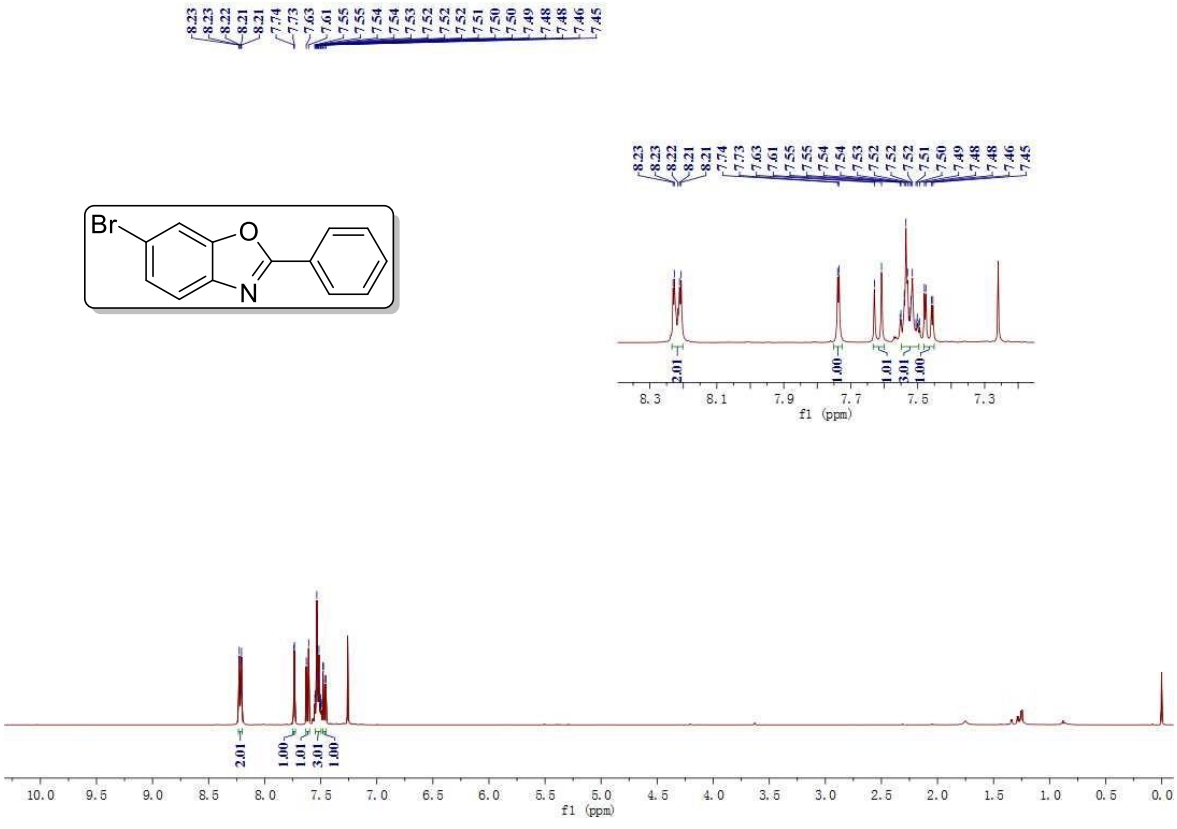


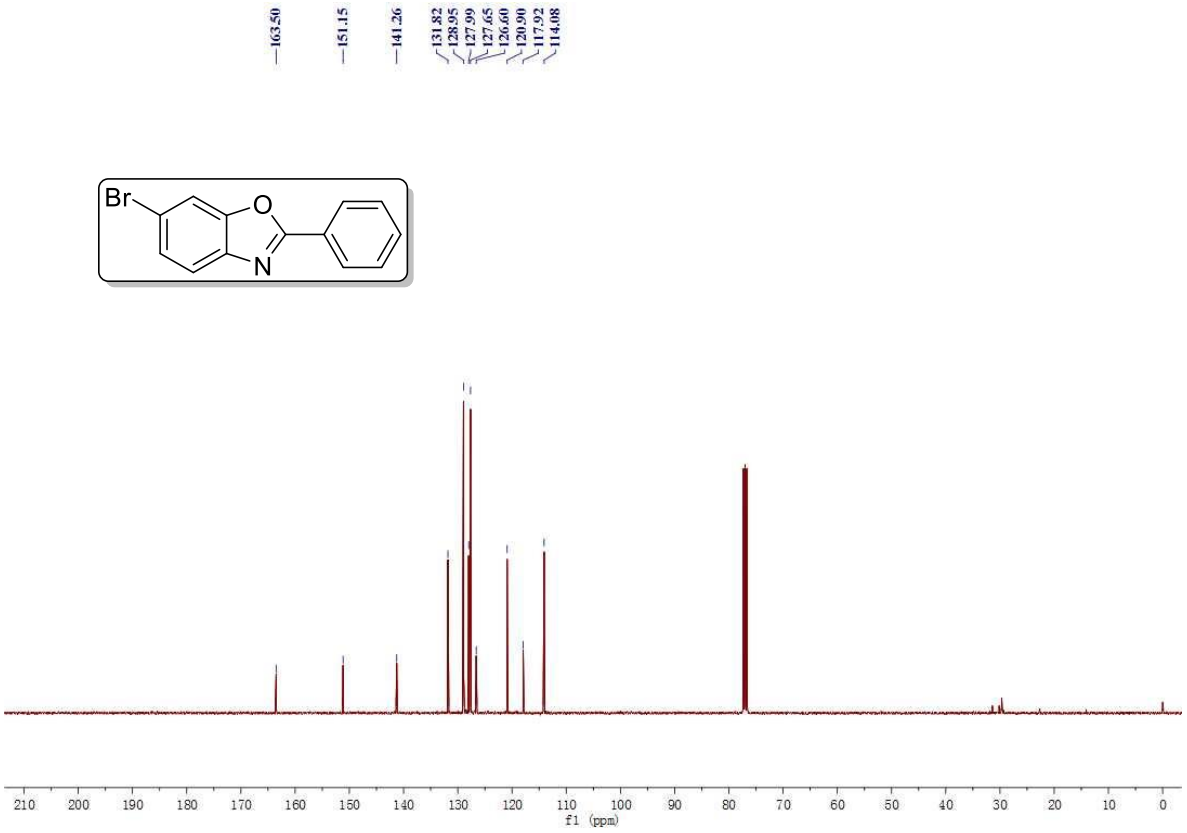




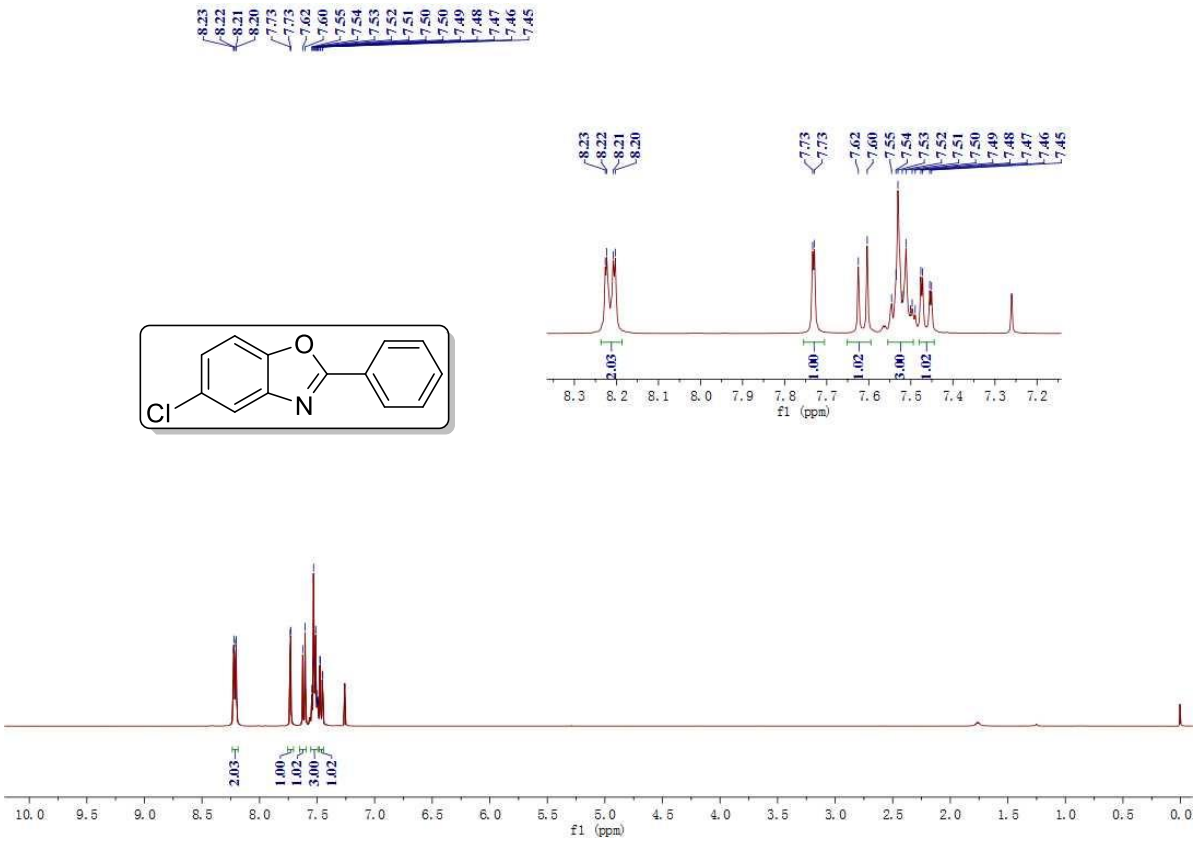


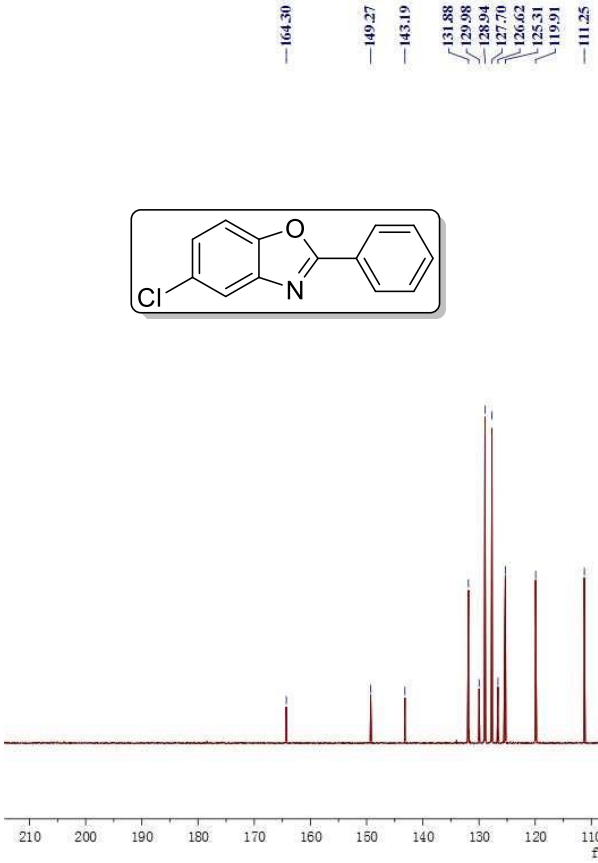
6-bromo-2-phenylbenzo[d]oxazole(3fa)



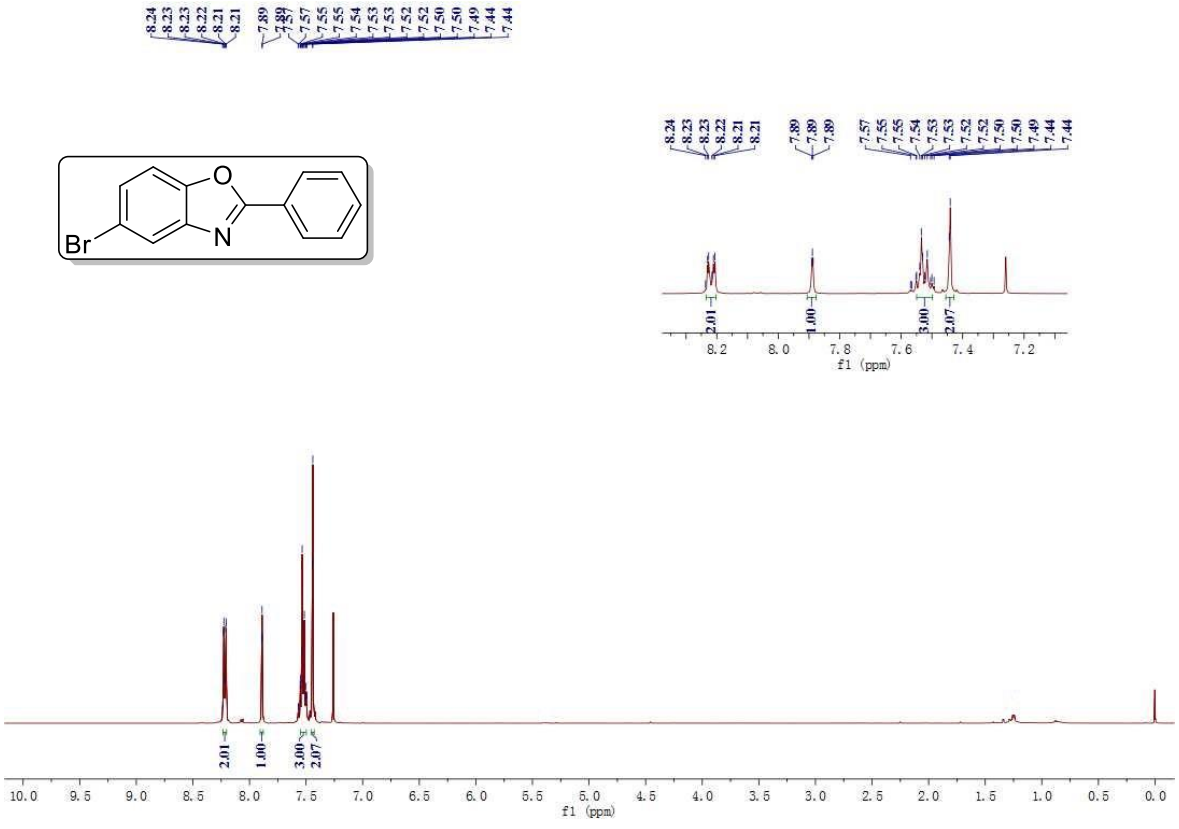


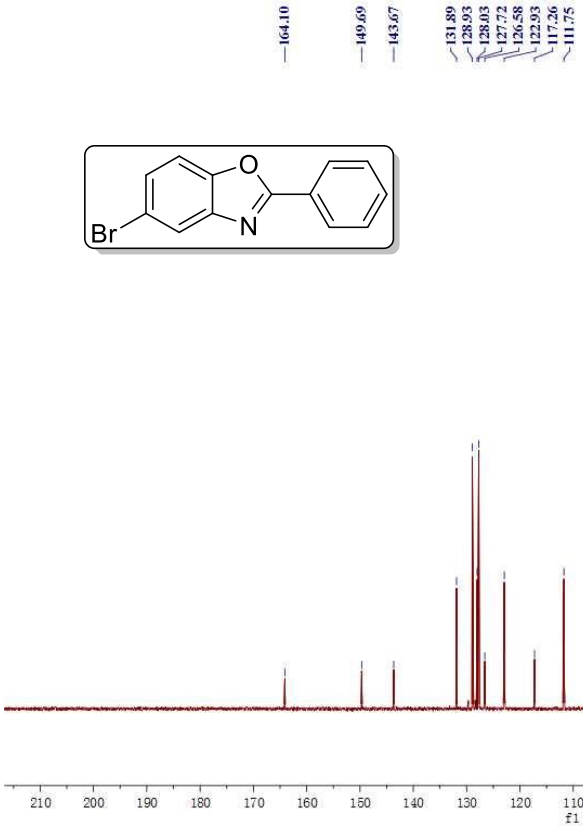
5-chloro-2-phenylbenzo[d]oxazole(3ga)



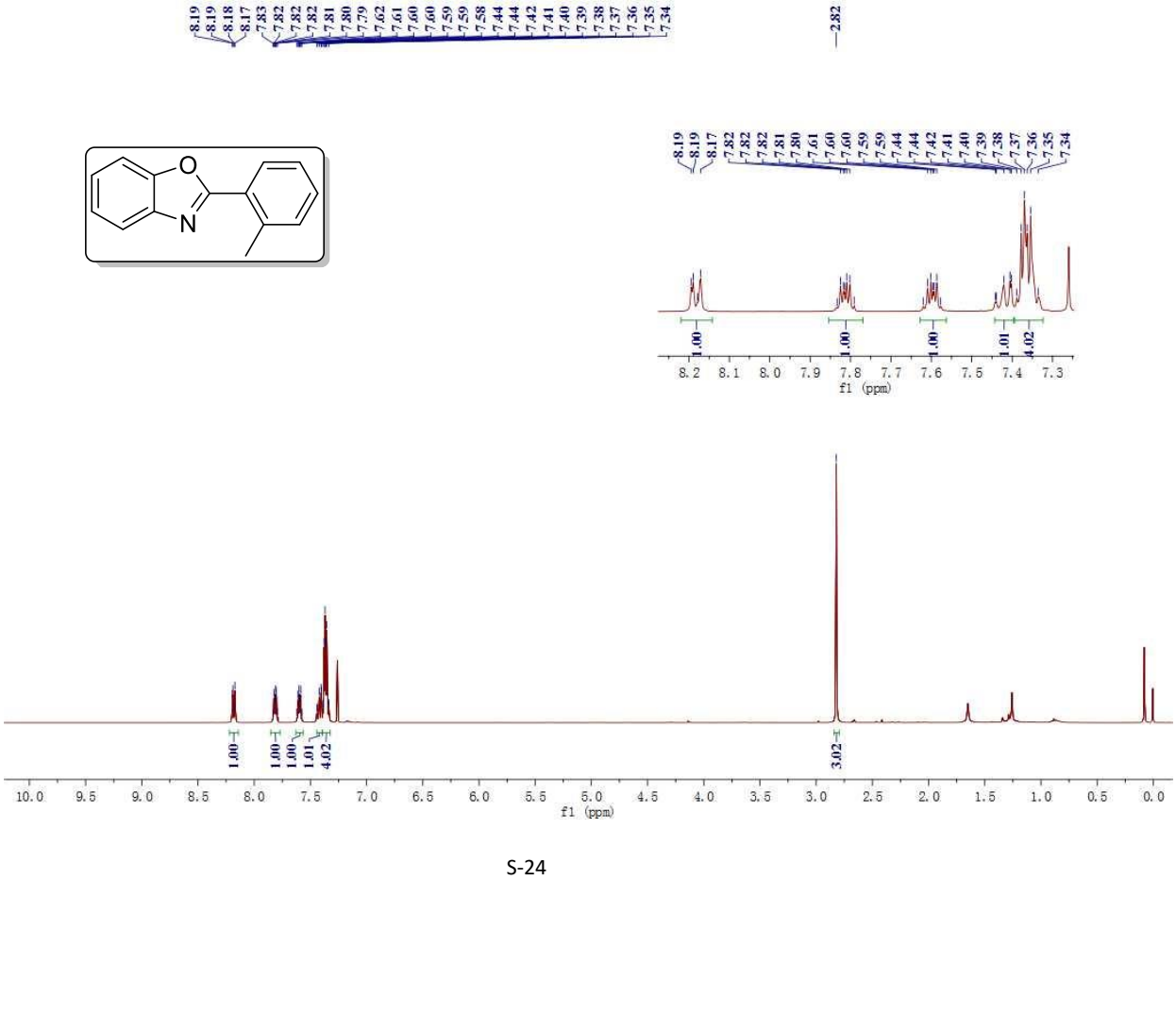


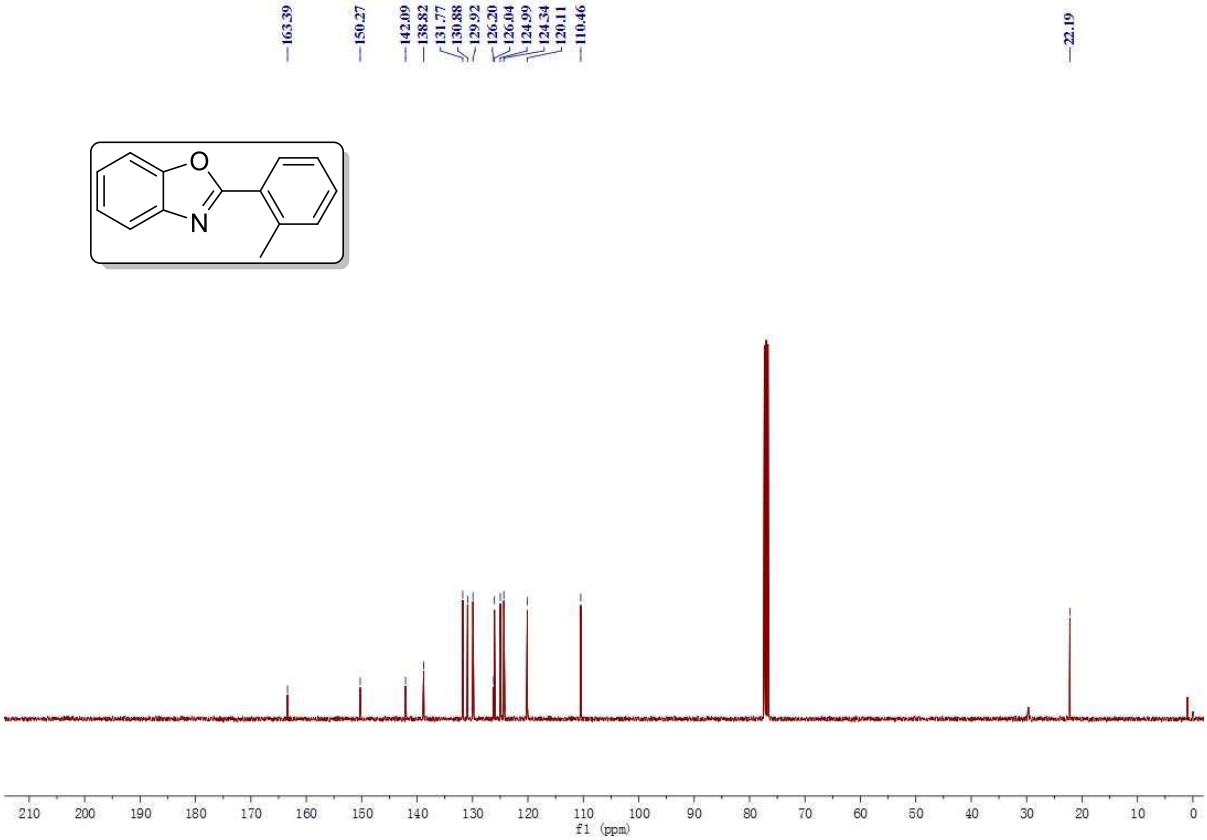
5-bromo-2-phenylbenzo[d]oxazole(3ha)



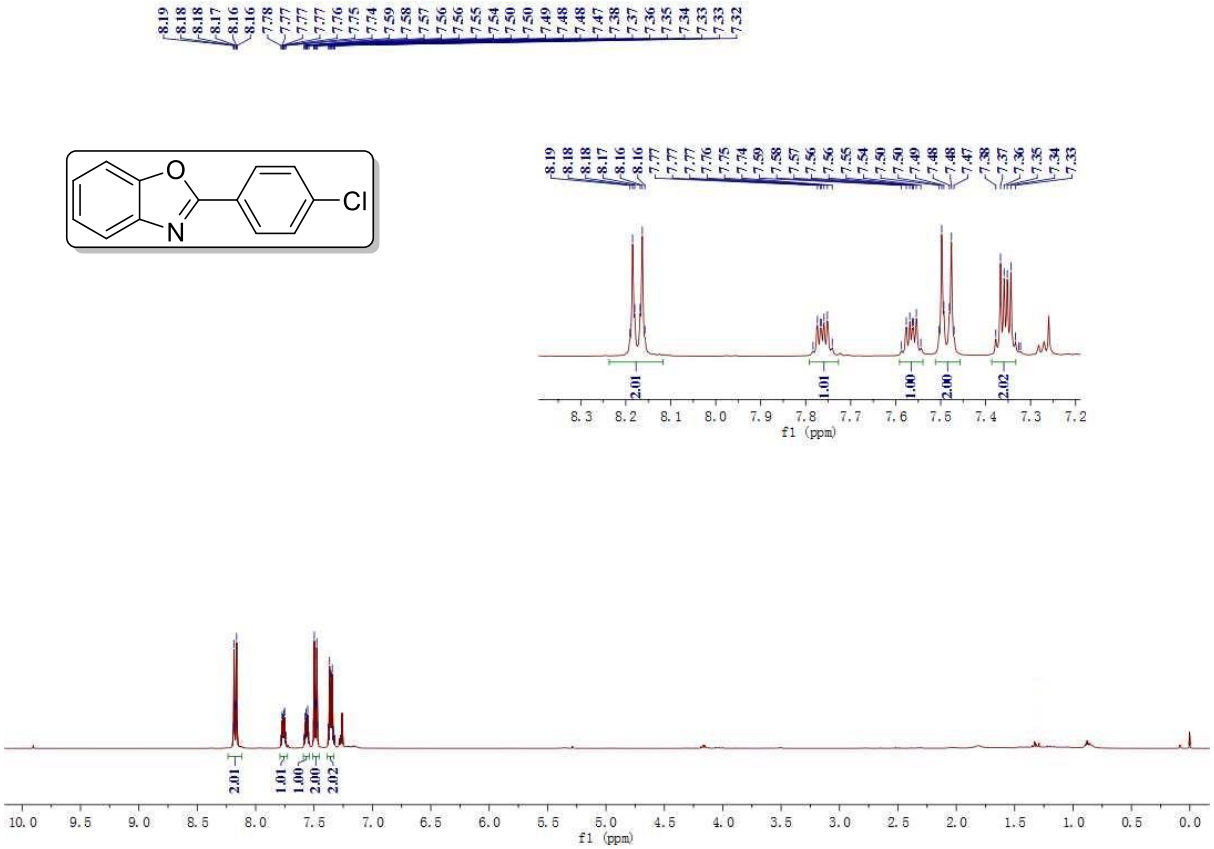


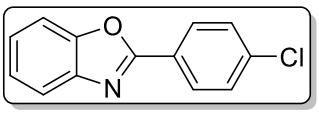
2-(o-tolyl)benzo[d]oxazole(3ab)

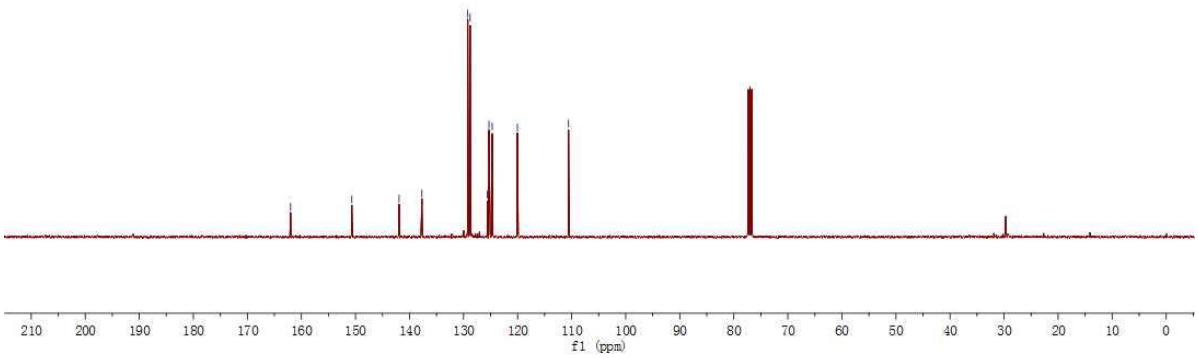




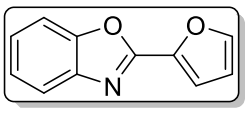
3-(4-chlorophenyl)benzo[d]oxazole(3ac)

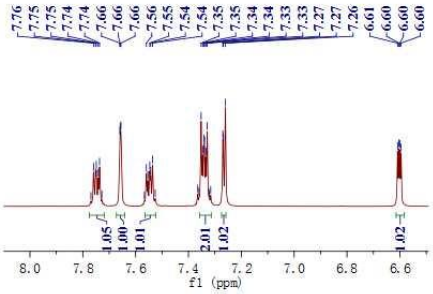


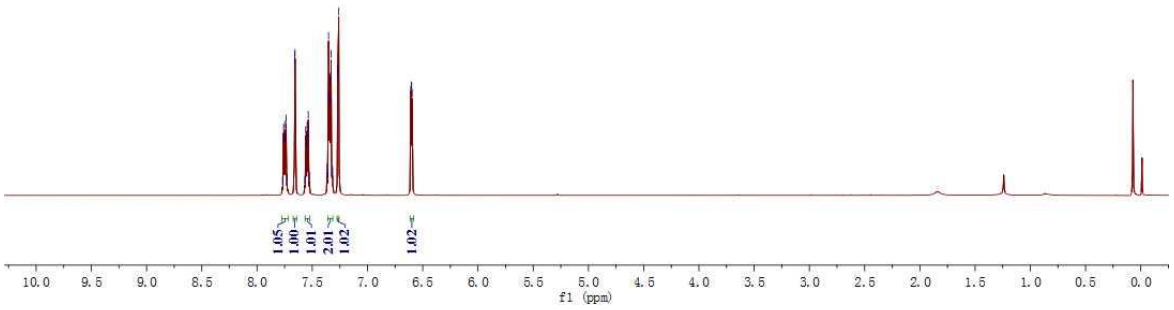


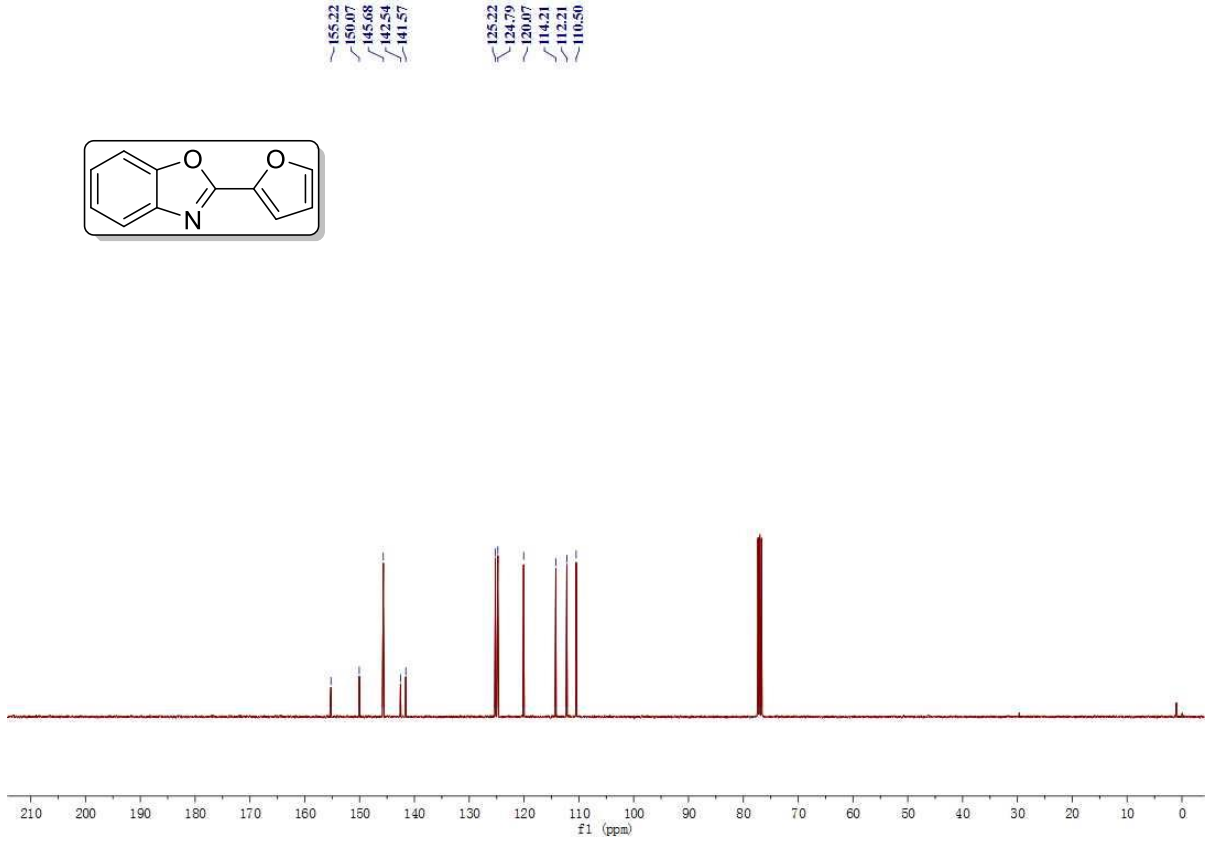


2-(furan-2-yl)benzo[d]oxazole(3ad)

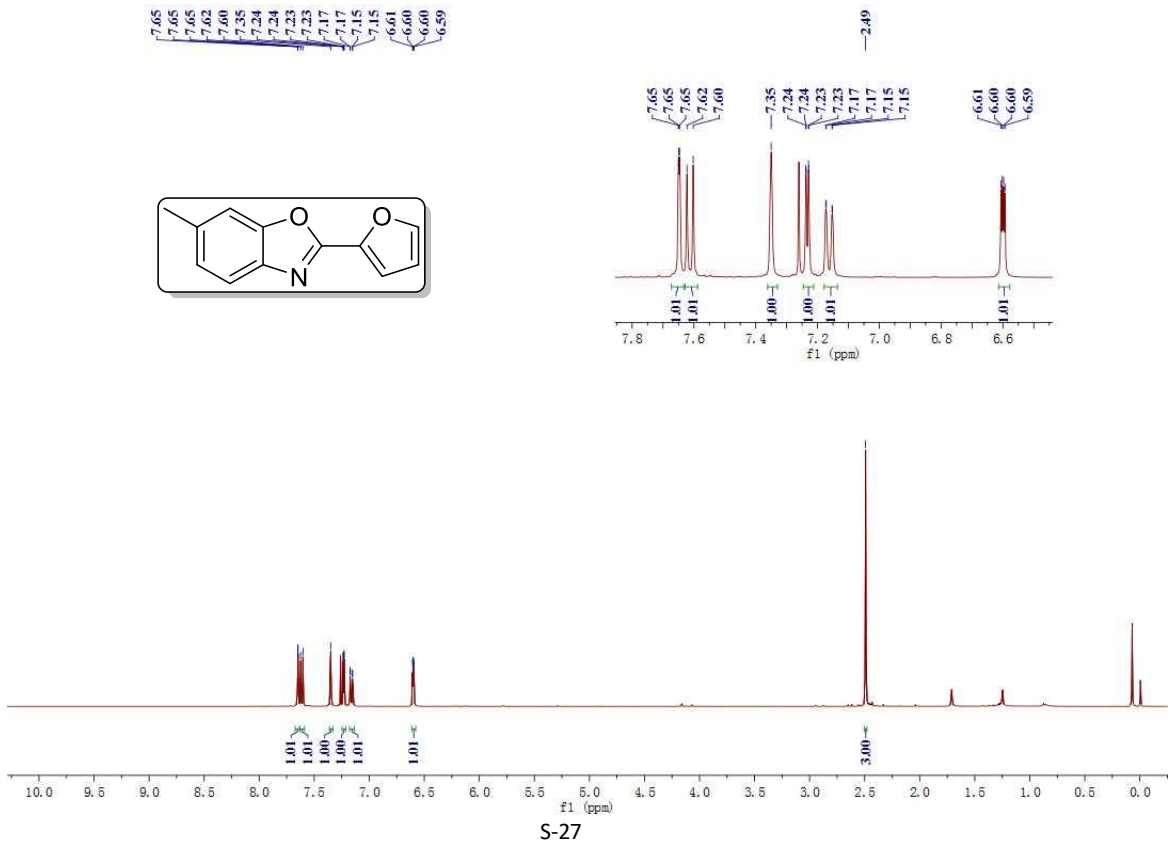


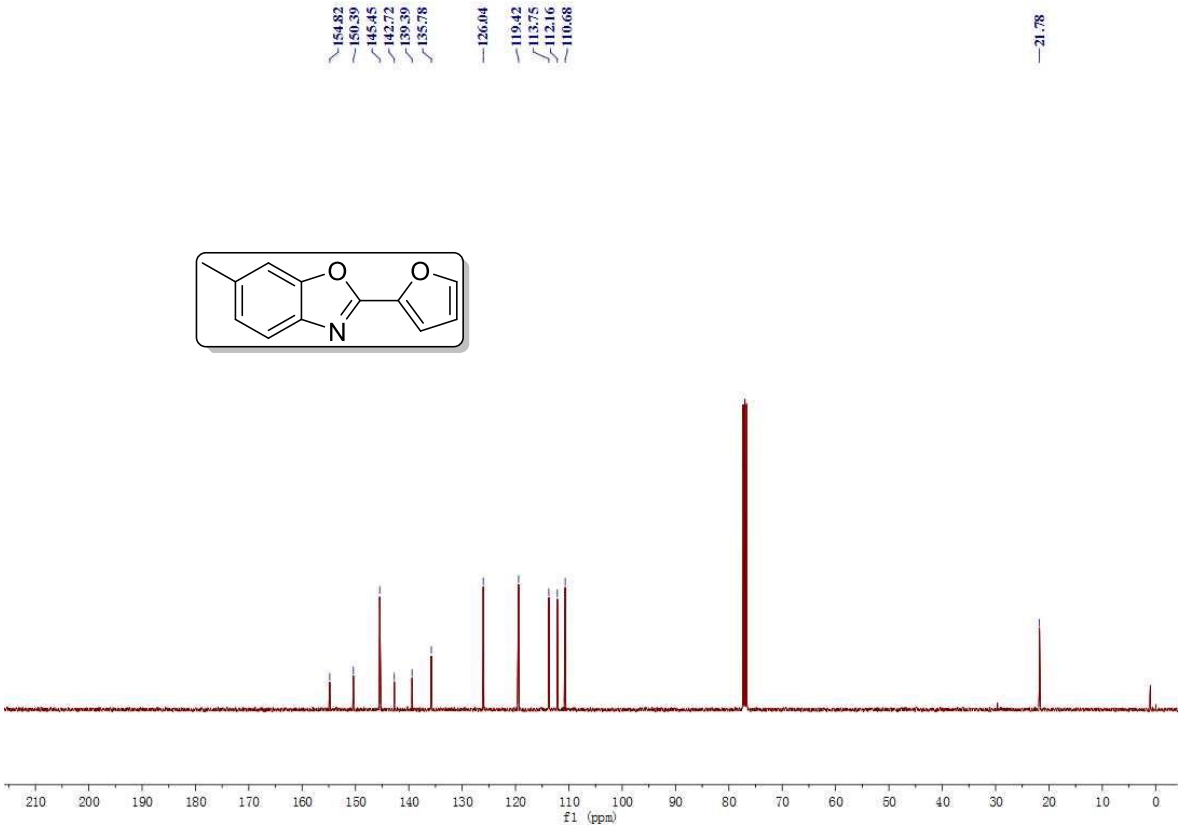




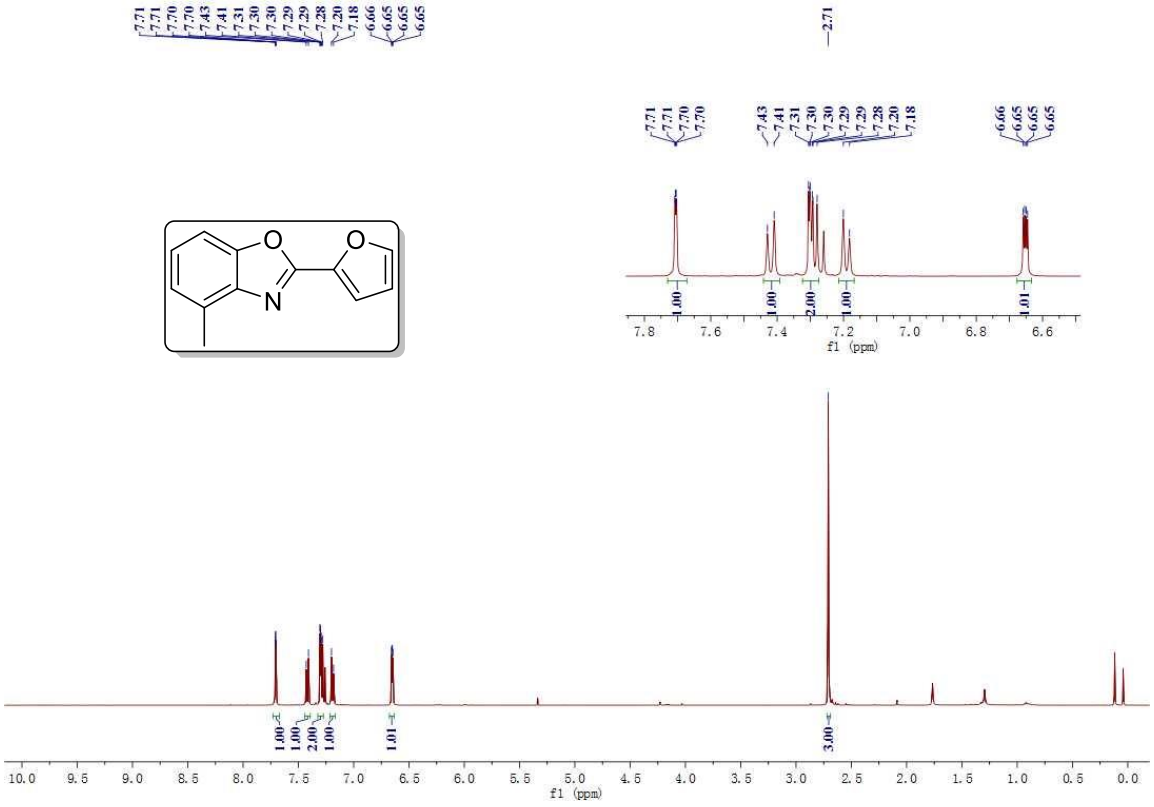


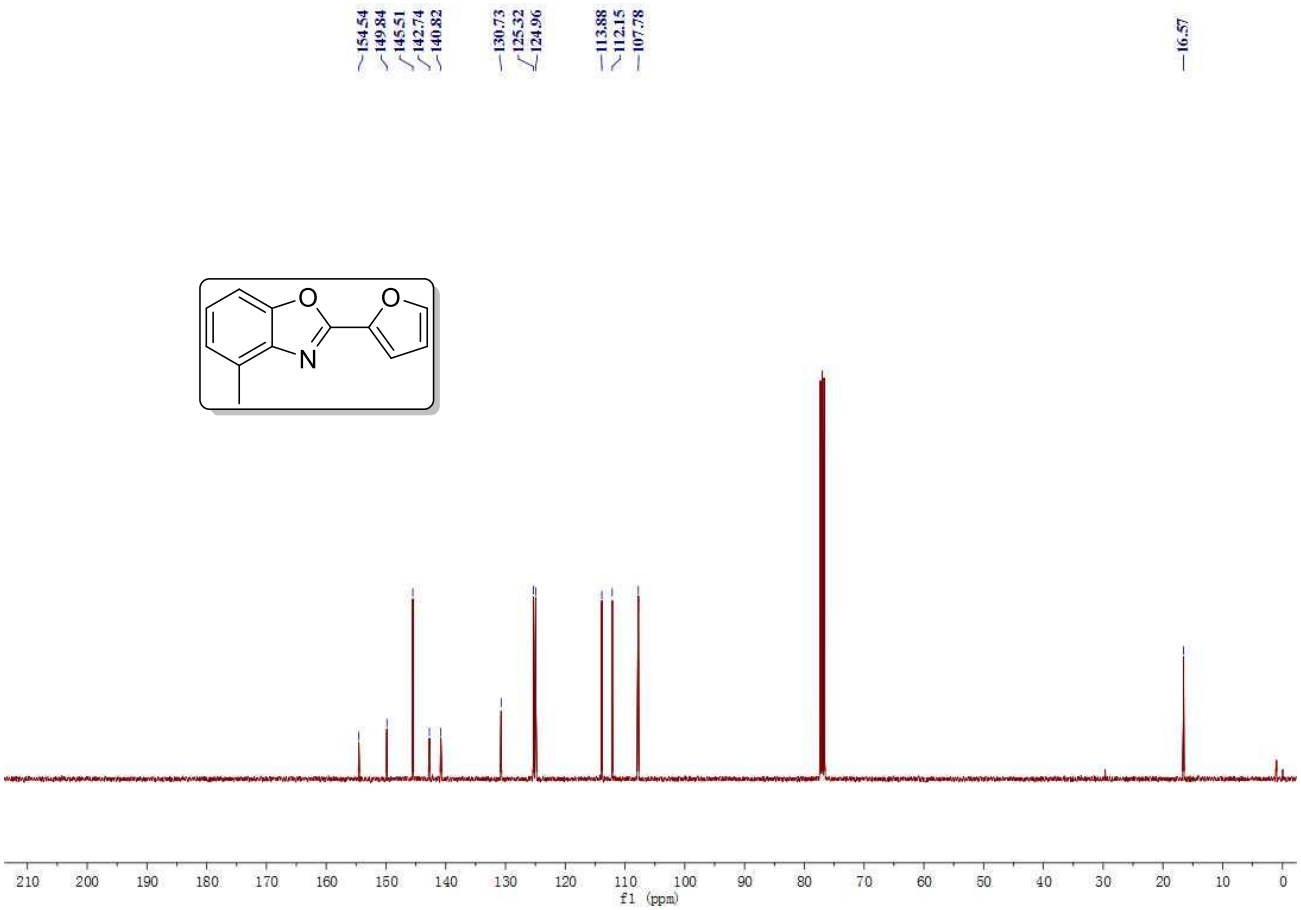
2-(furan-2-yl)-6-methylbenzo[d]oxazole(3bd)



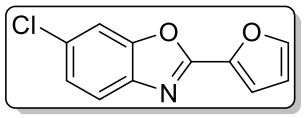


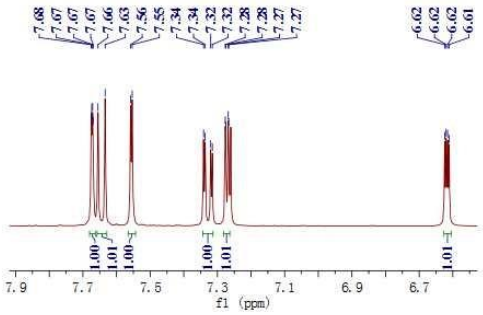
2-(furan-2-yl)-4-methylbenzo[d]oxazole(3cd)

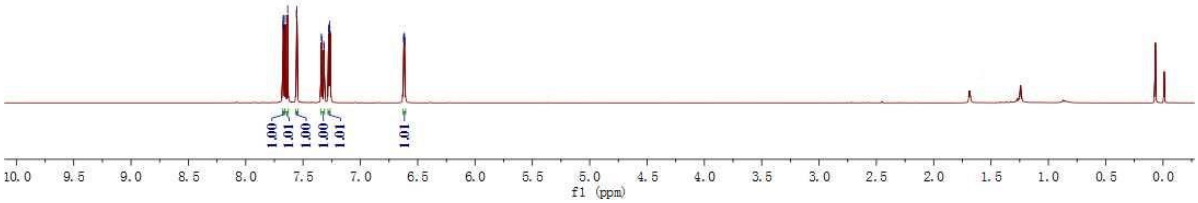


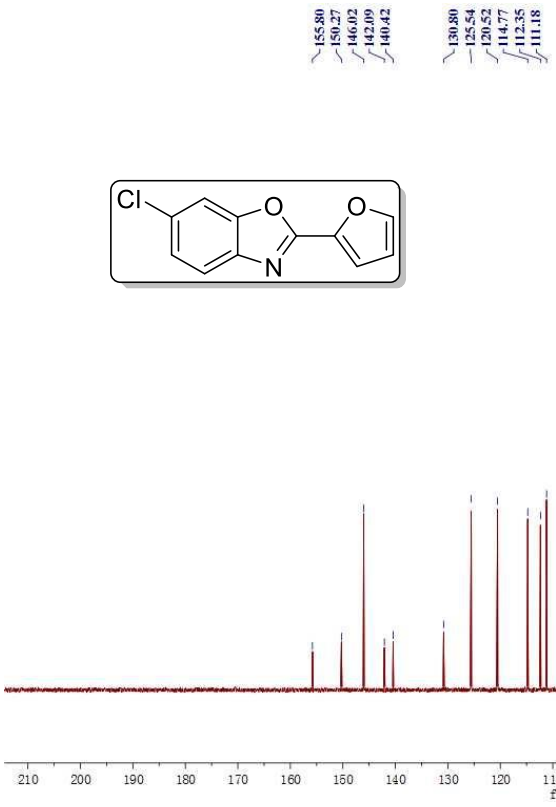


6-chloro-2-(furan-2-yl)benzo[d]oxazole(3ed)

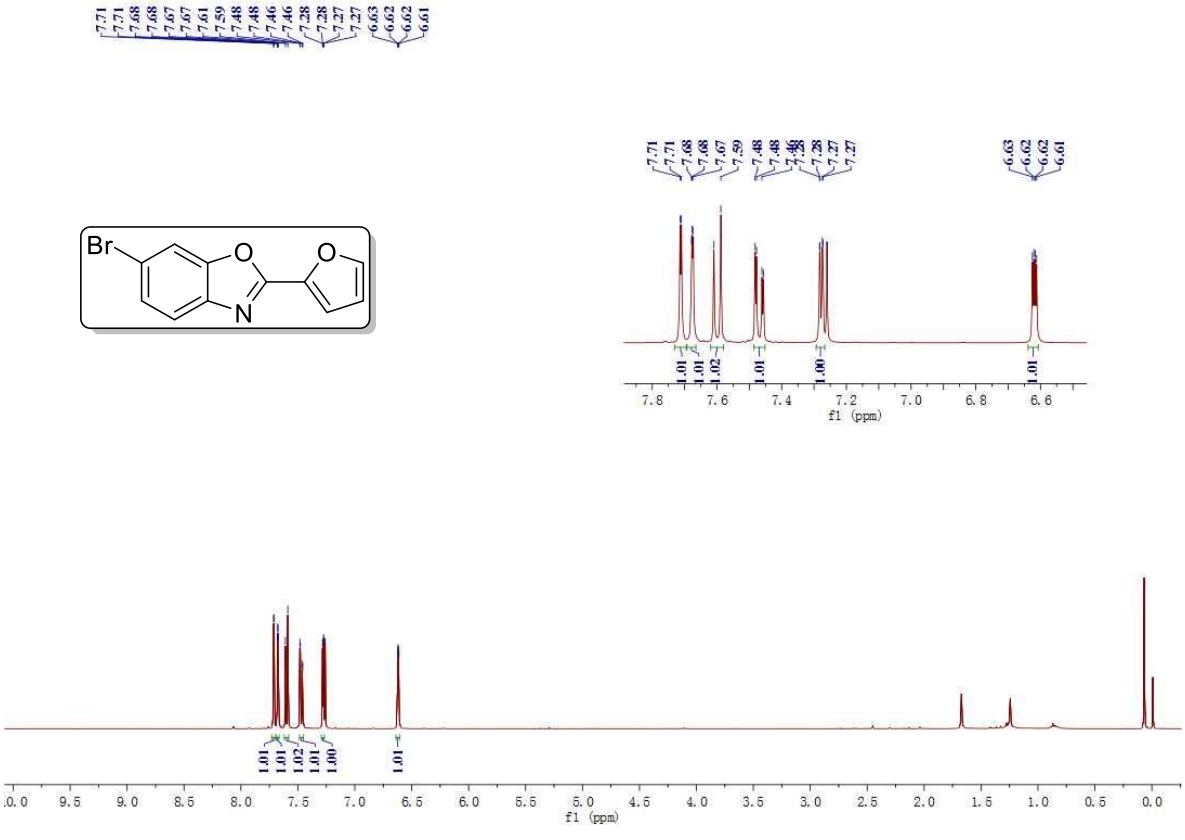


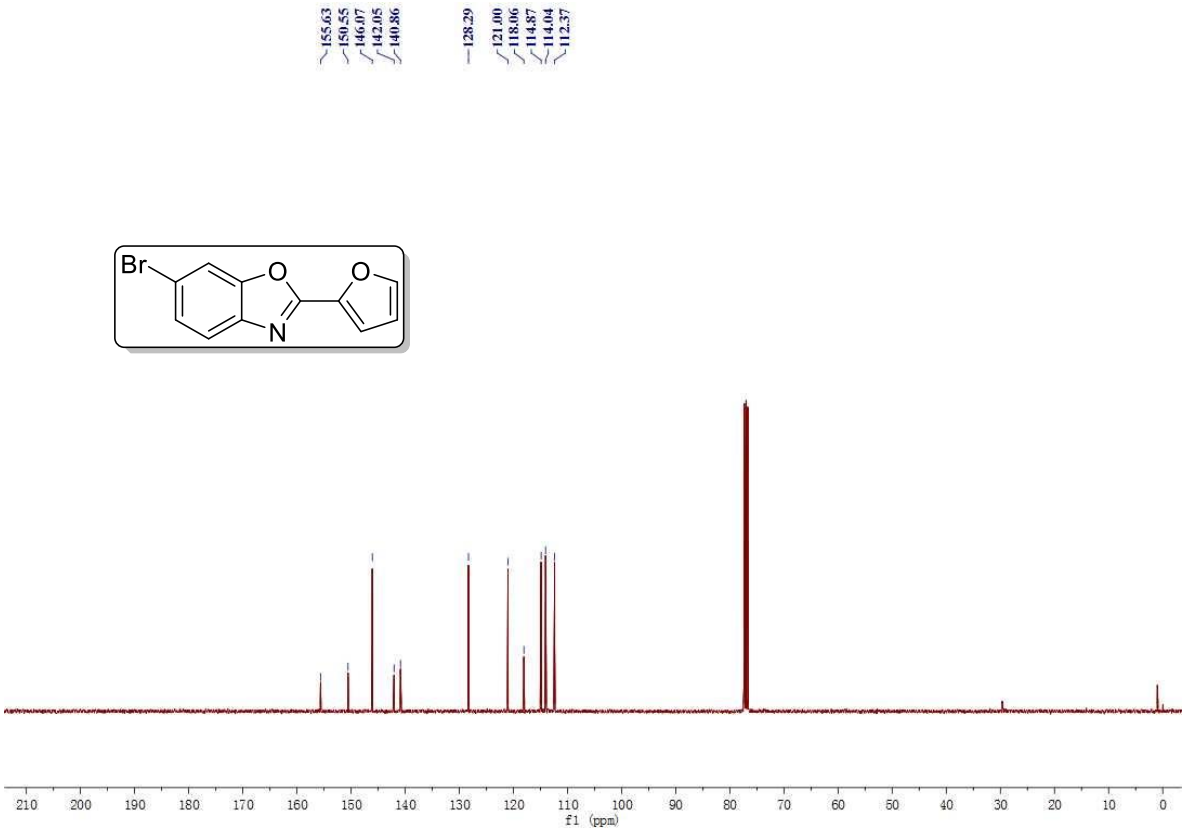




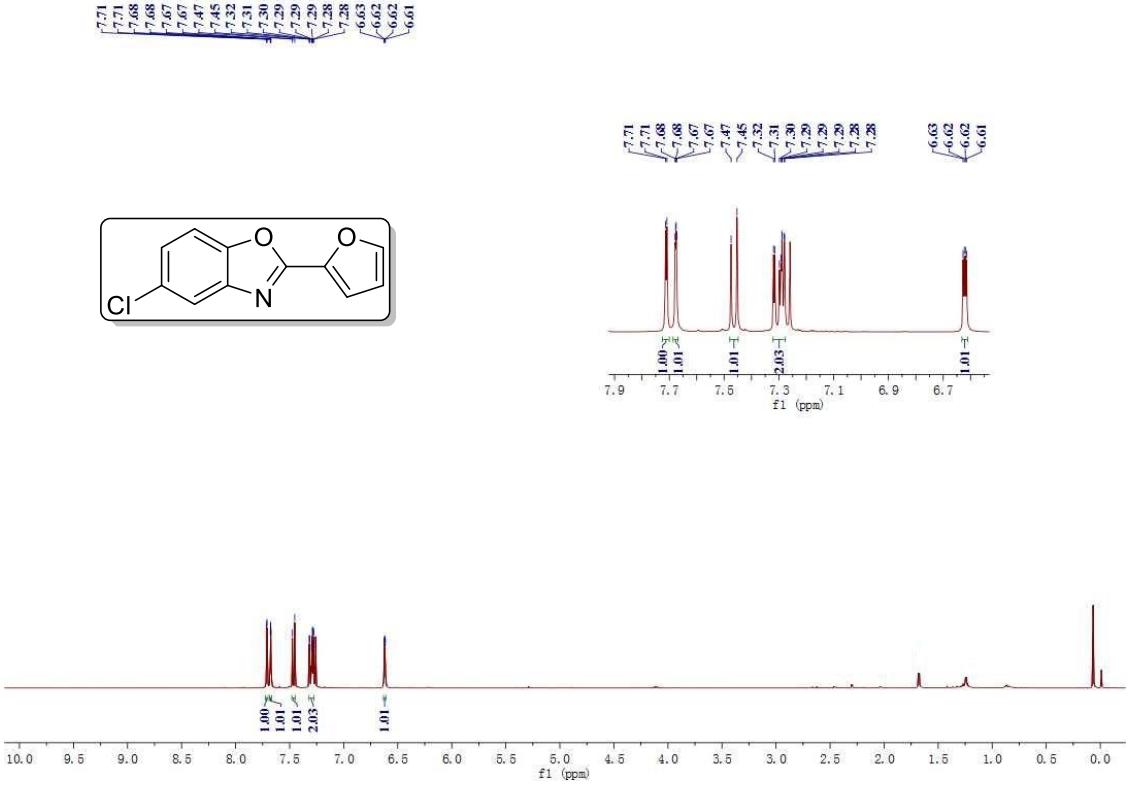


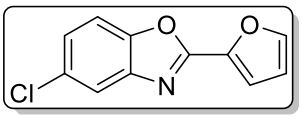
6-bromo-2-(furan-2-yl)benzo[d]oxazole(3fd)

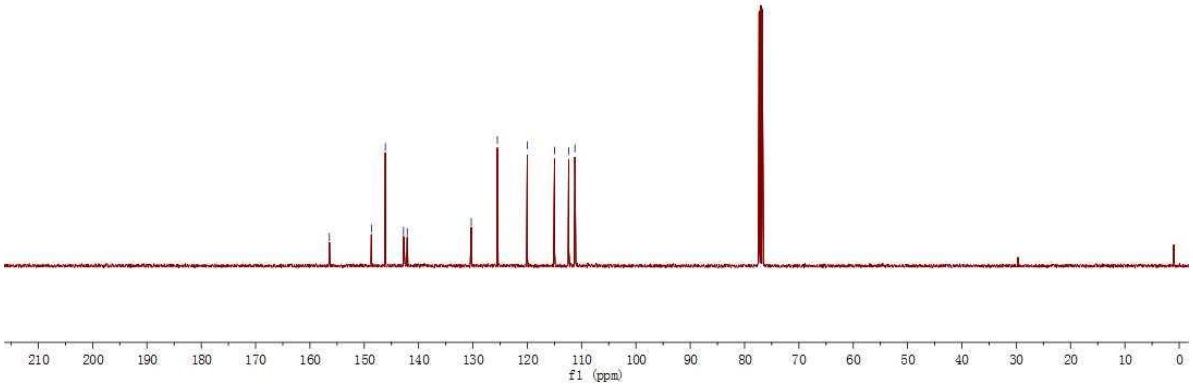




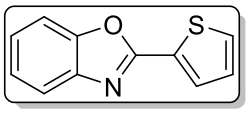
5-chloro-2-(furan-2-yl)benzo[d]oxazole(3gd)

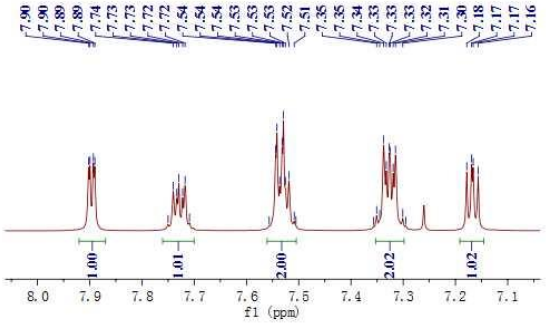


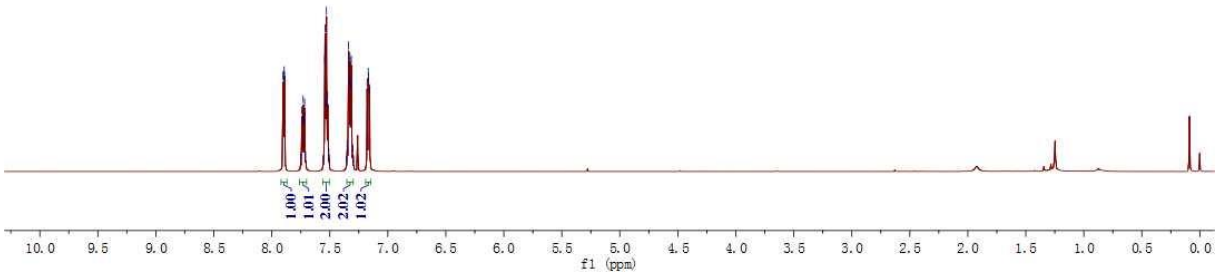


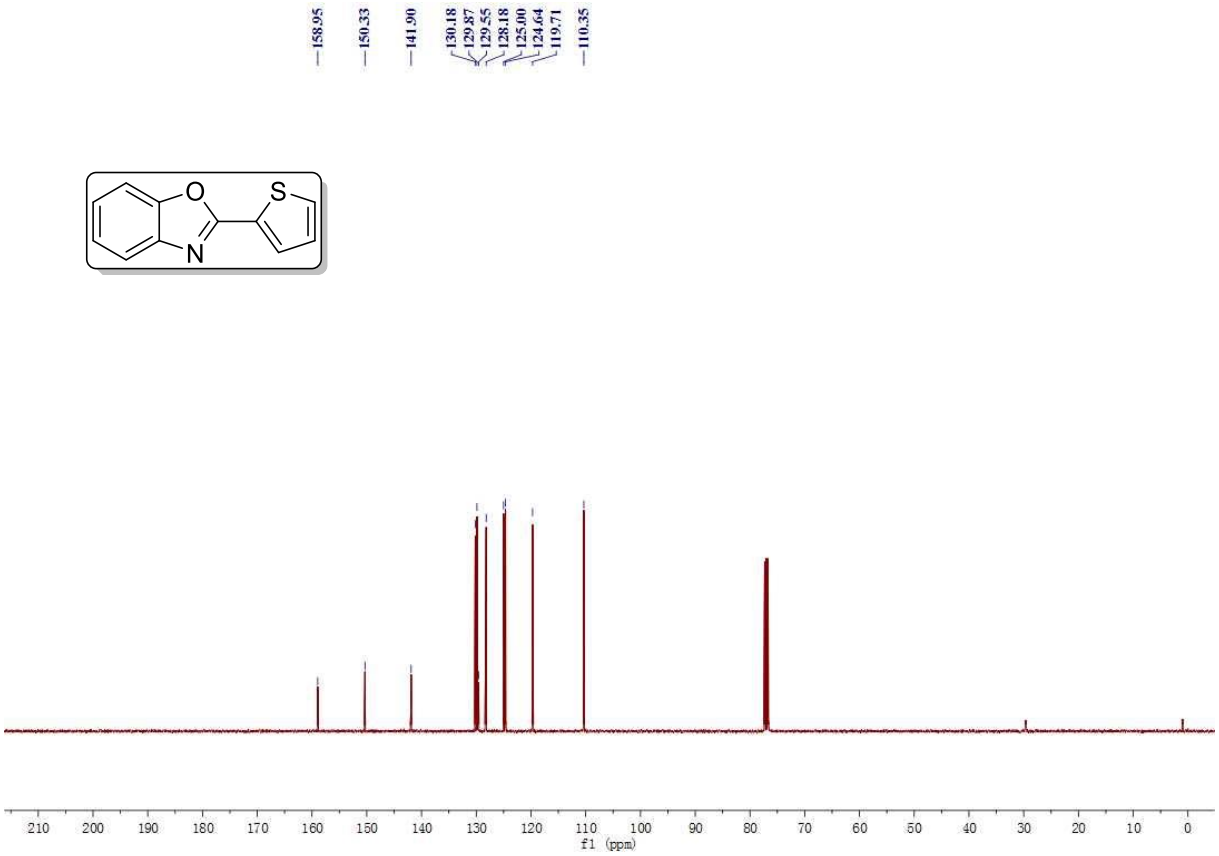


2-(thiophen-2-yl)benzo[d]oxazole(3ae)

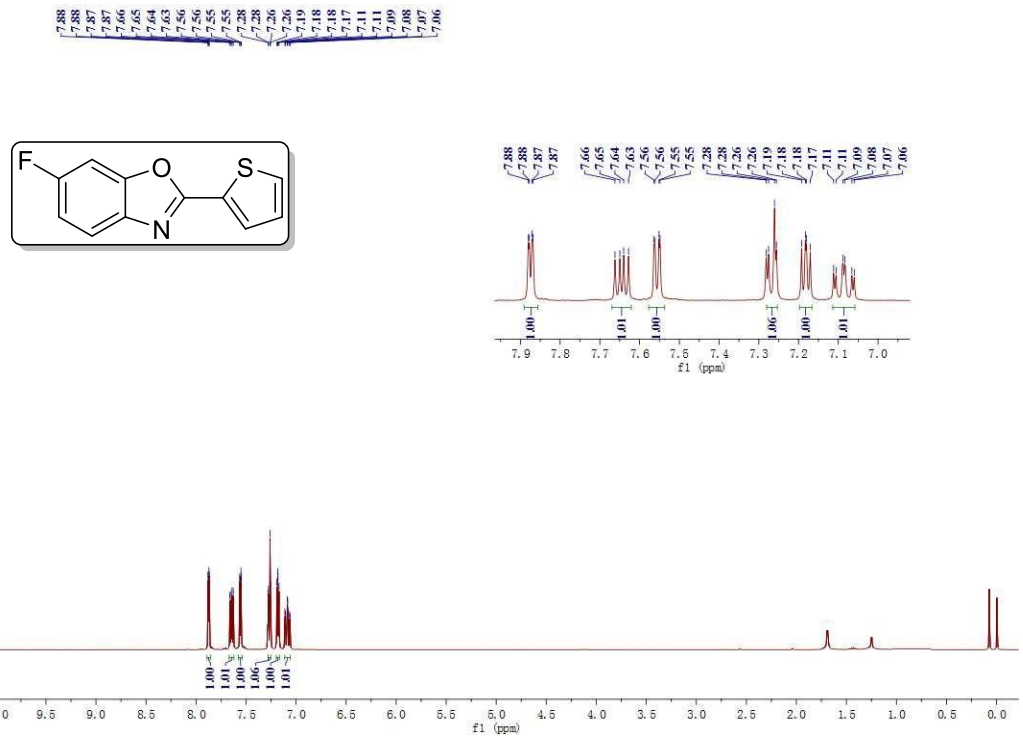


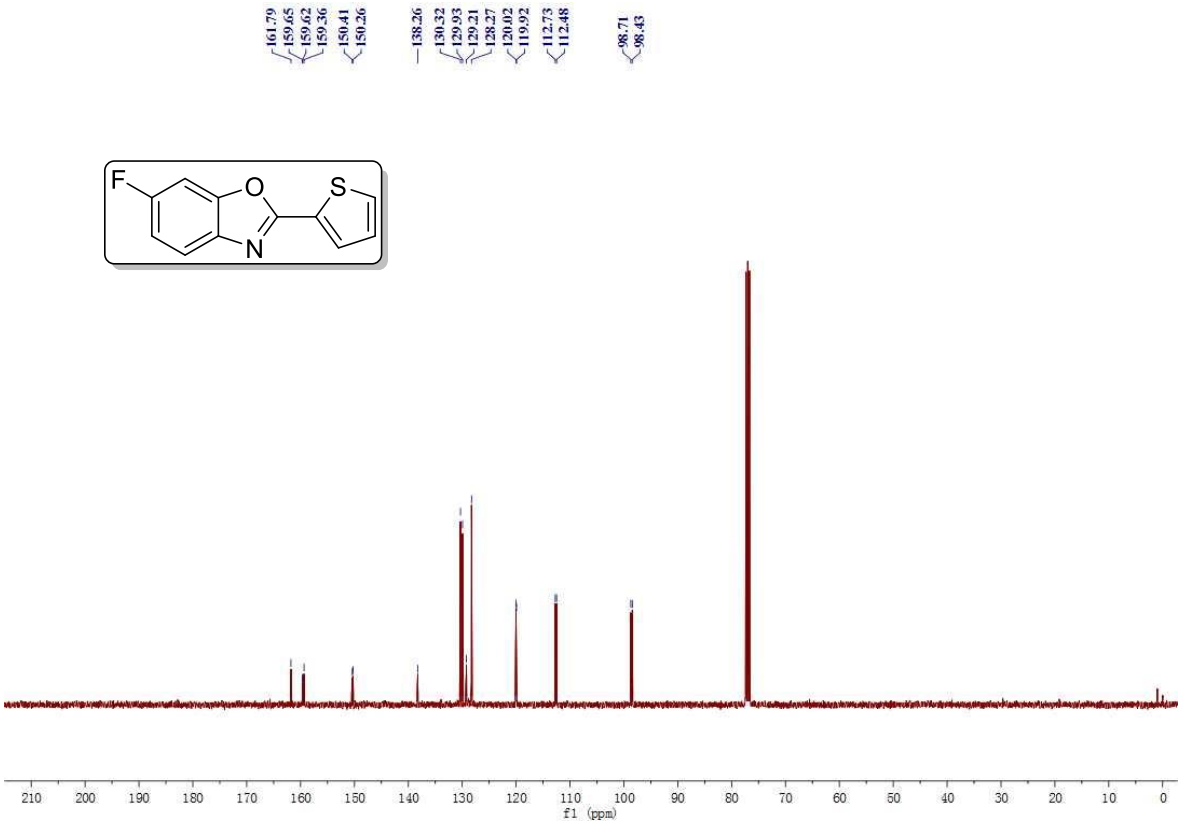


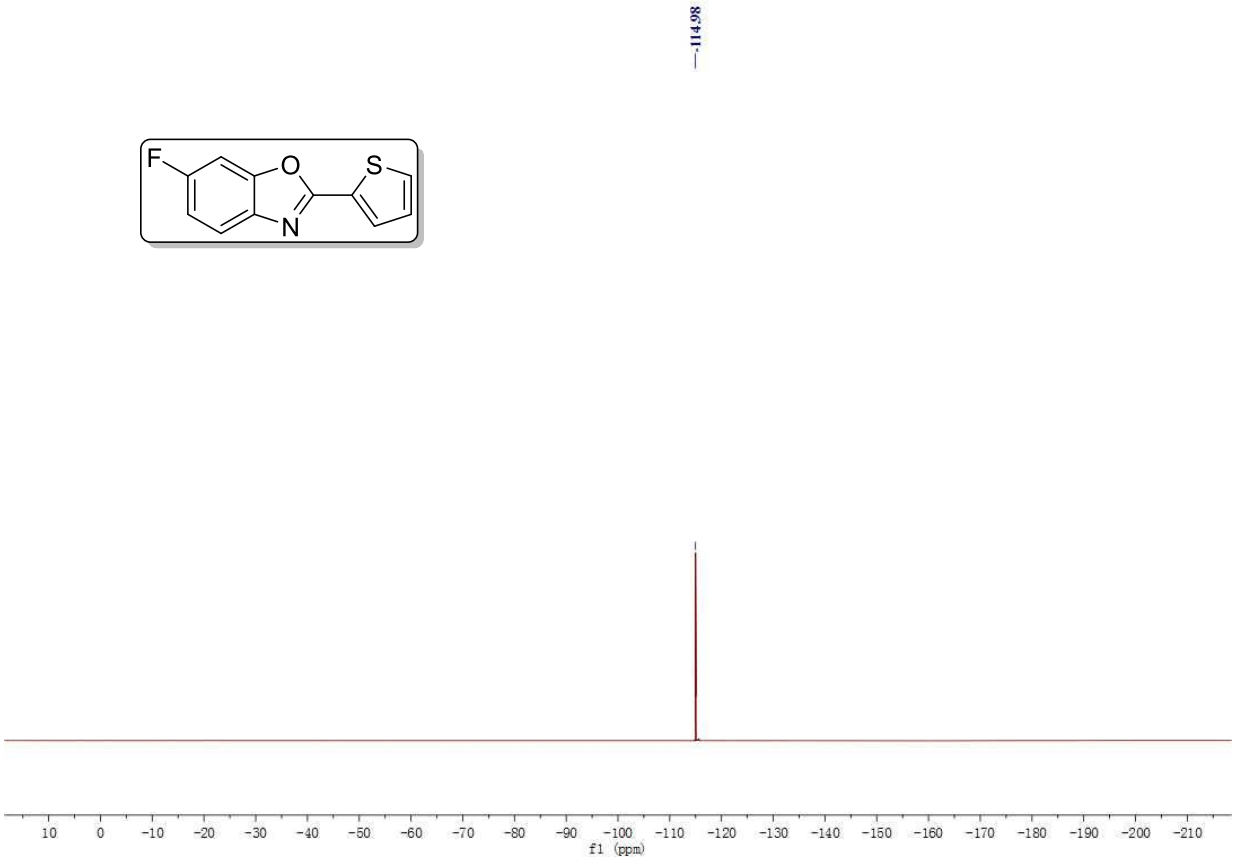




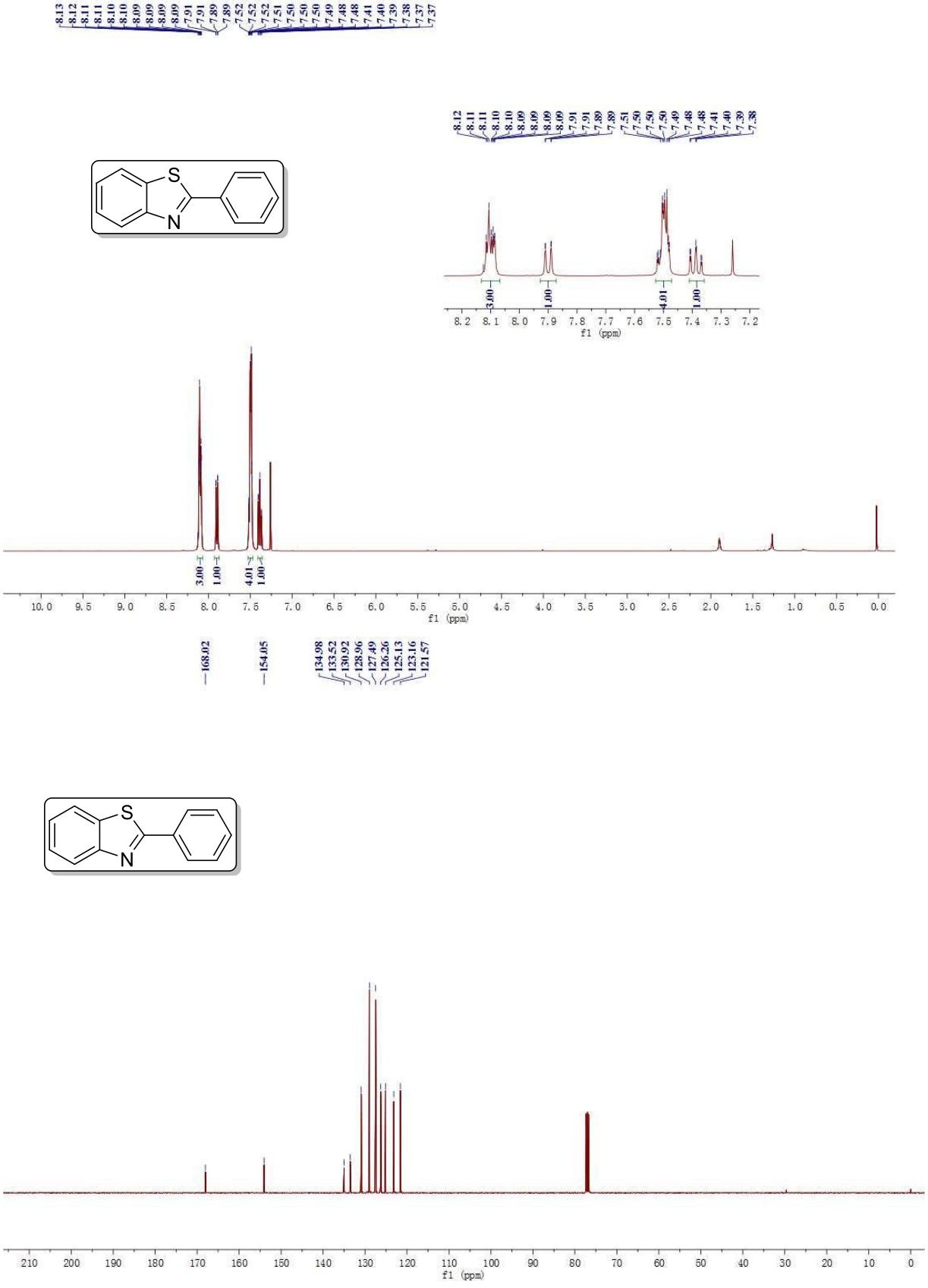
6-fluoro-2-(thiophen-2-yl)benzo[d]oxazole(3de)



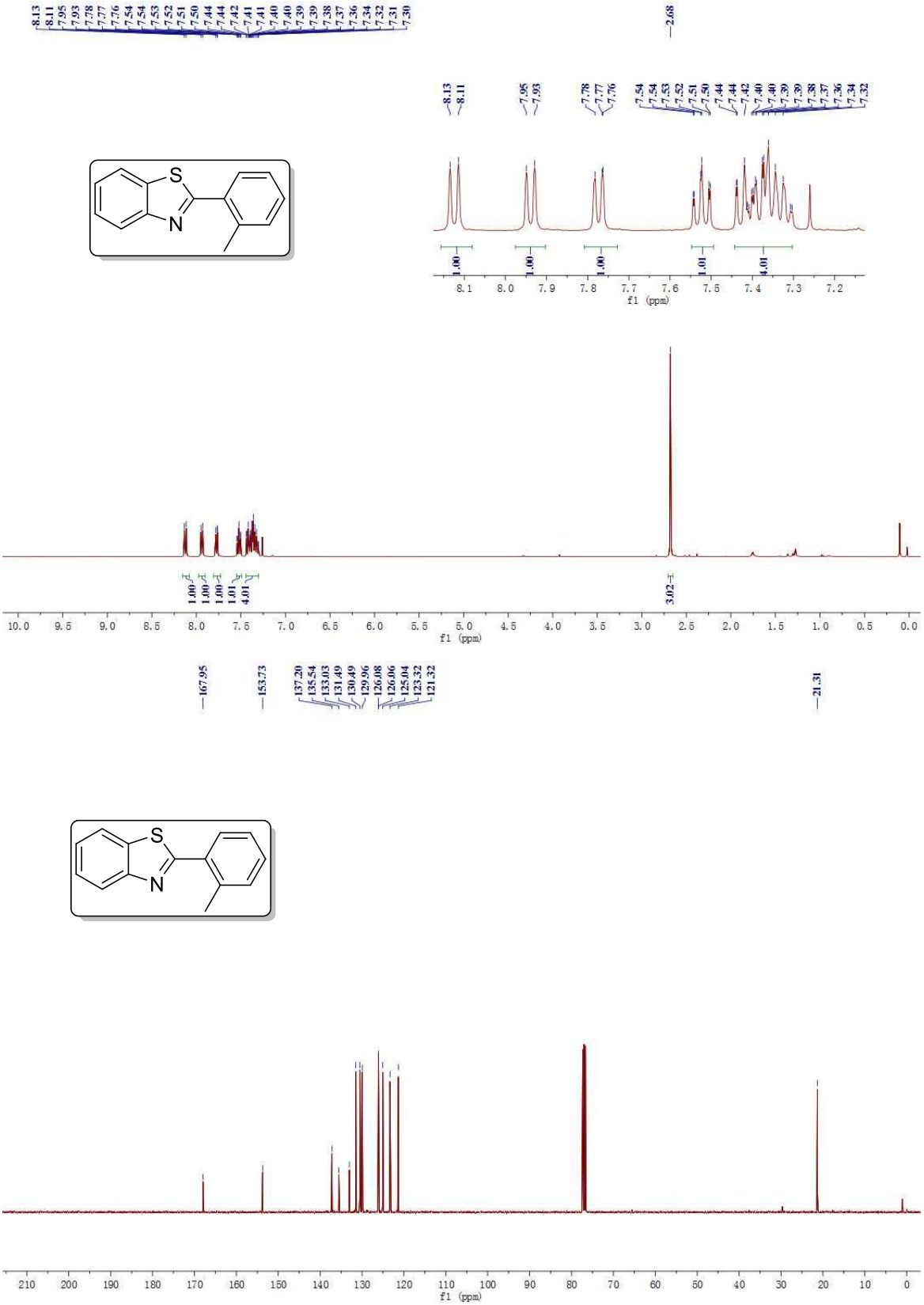

161.79
159.65
159.62
159.36
150.41
150.26
138.26
130.32
129.93
129.21
128.27
120.02
119.92
112.73
112.48
98.71
98.43
F
O
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.98
F
O
S
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

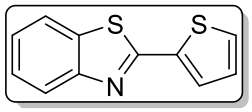
2-phenylbenzo[d]thiazole(4ia)

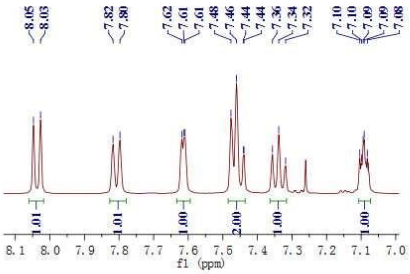


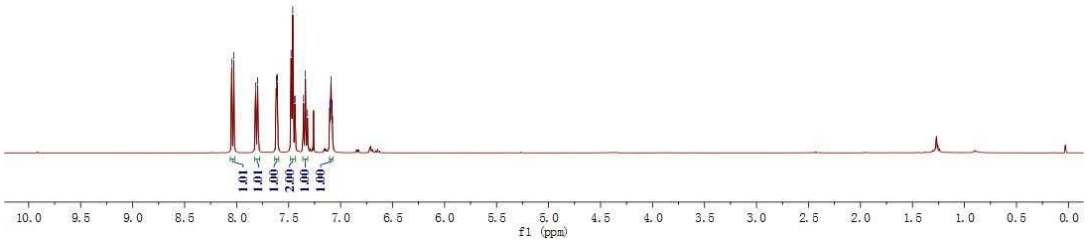
2-(o-tolyl)benzo[d]thiazole(4ib)

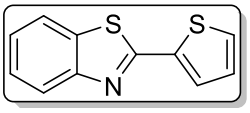


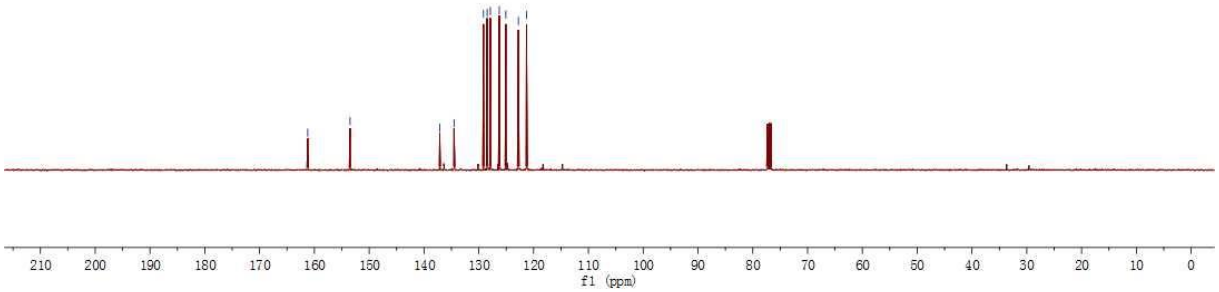
2-(thiophen-2-yl)benzo[d]thiazole(4ie)



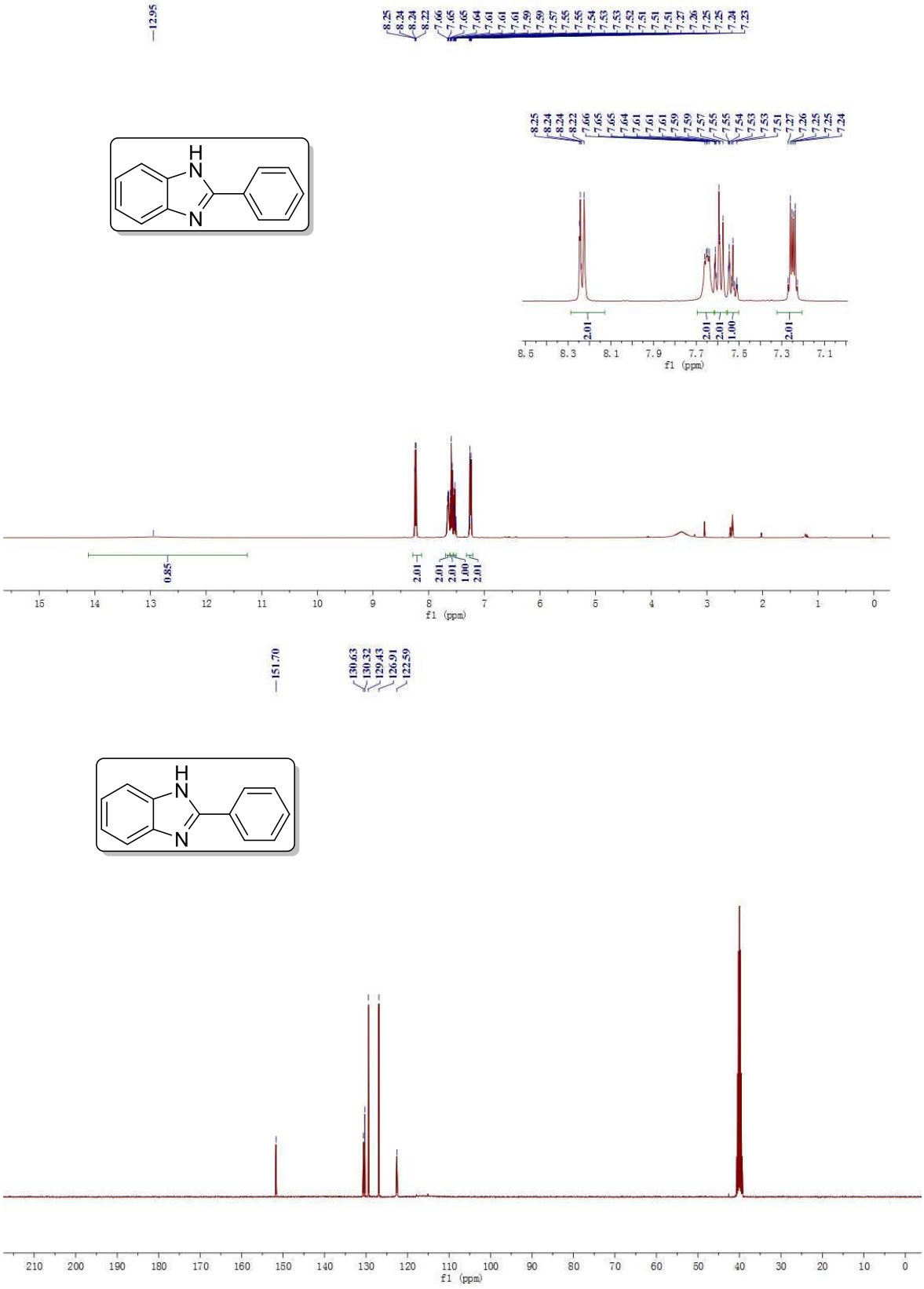




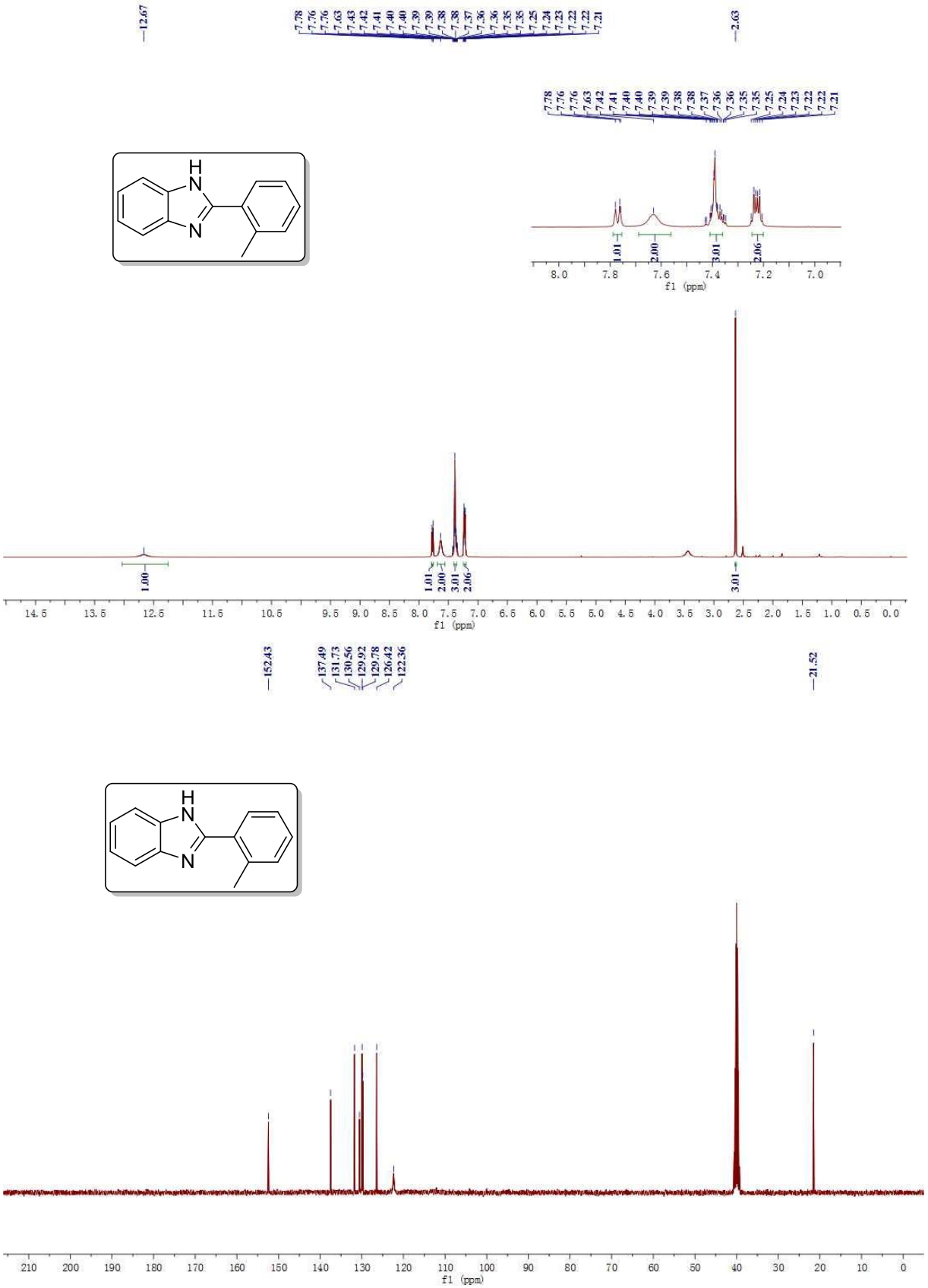




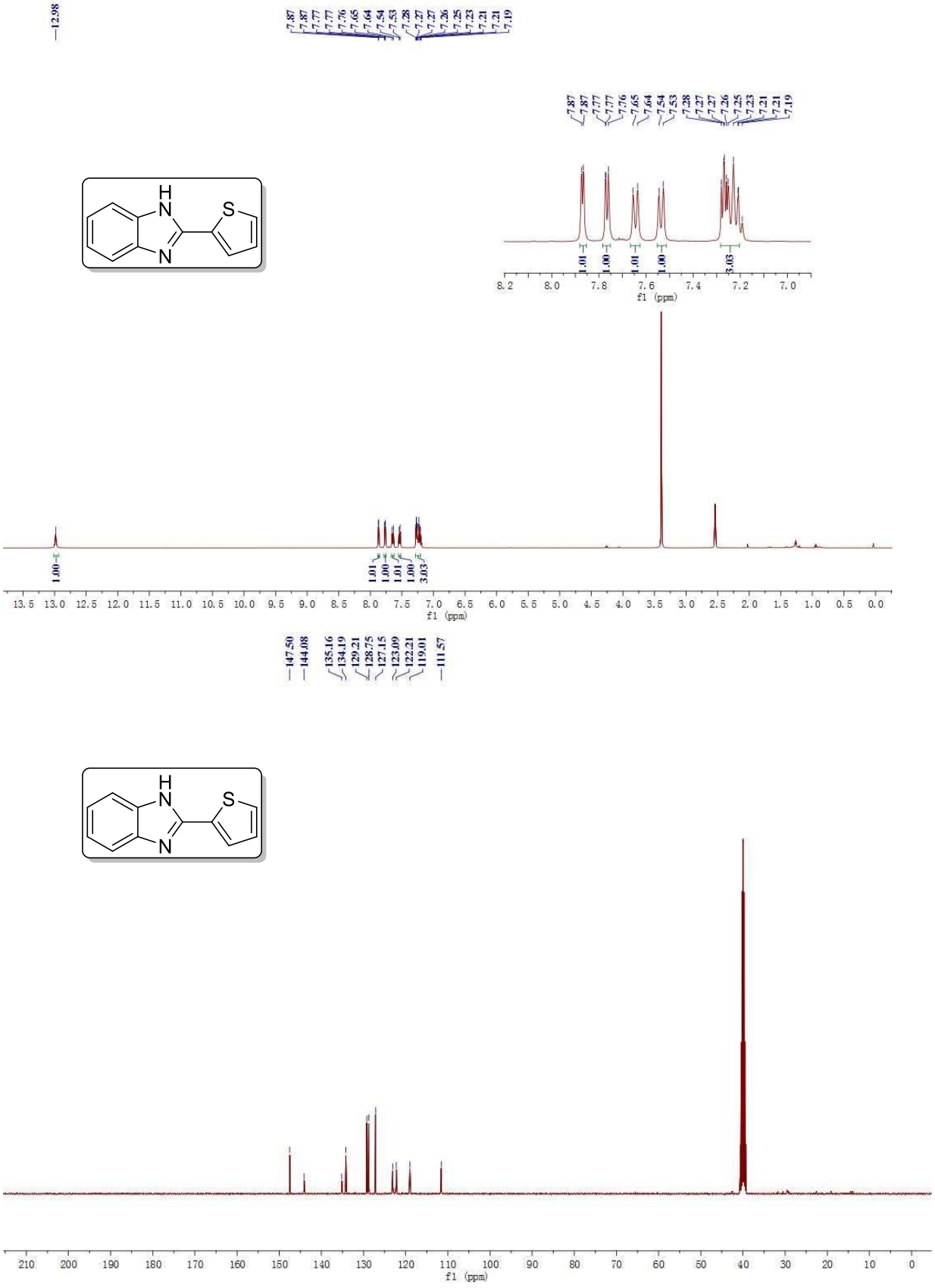
2-phenyl-1H-benzo[d]imidazole(5ja)



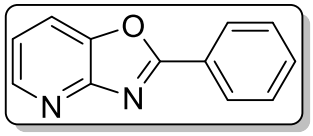
2-(o-tolyl)-1H-benzo[d]imidazole(5jb)

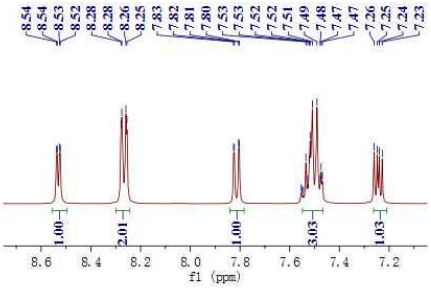


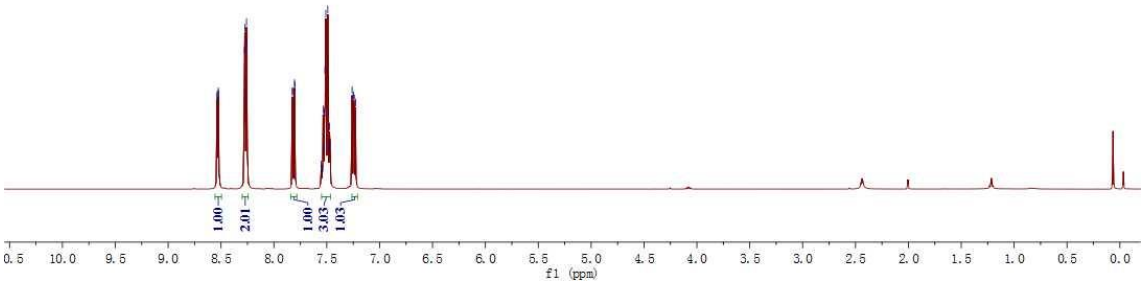
2-(thiophen-2-yl)-1H-benzo[d]imidazole(5je)

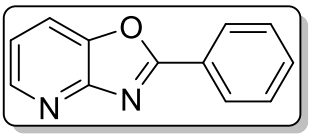


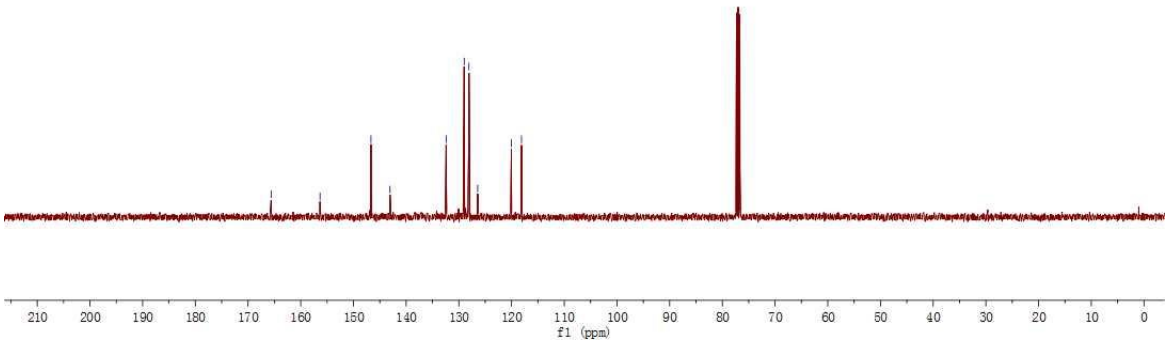
2-phenyloxazolo[4,5-b]pyridine(6ka)



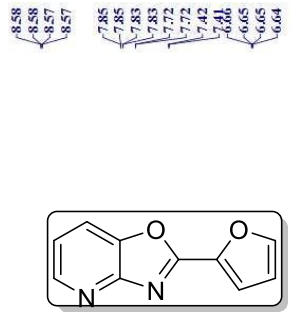


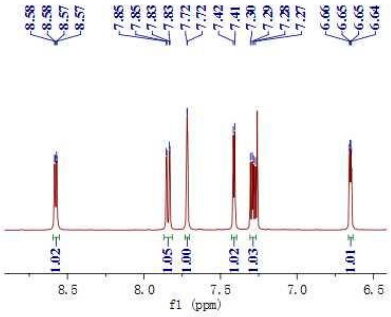


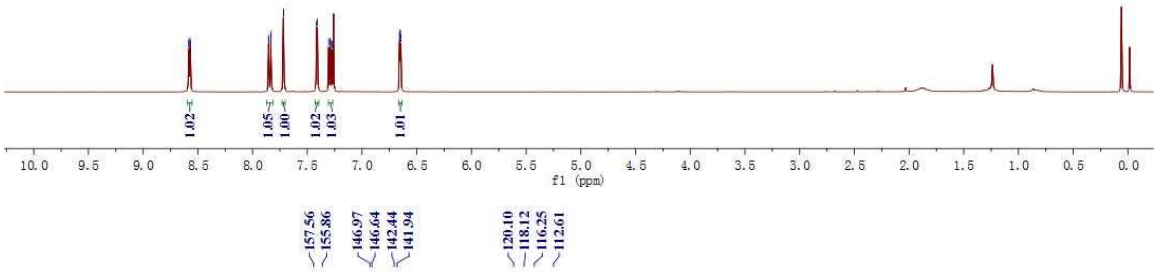


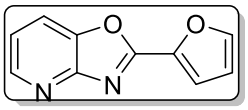


2-(furan-2-yl)oxazolo[4,5-b]pyridine(6kd)

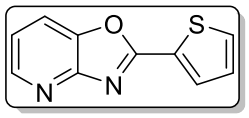


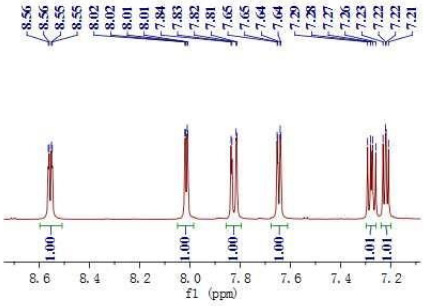


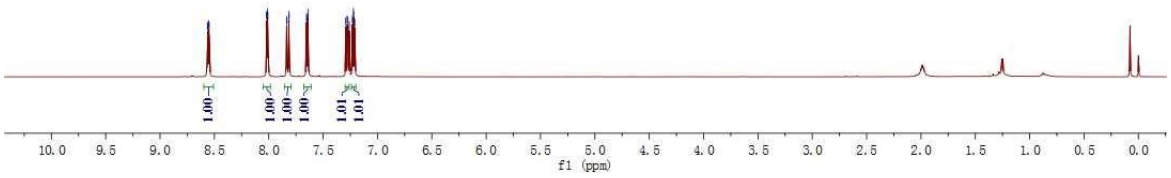


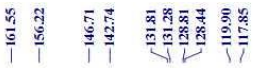


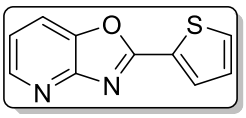
2-(thiophen-2-yl)oxazolo[4,5-b]pyridine(6ke)

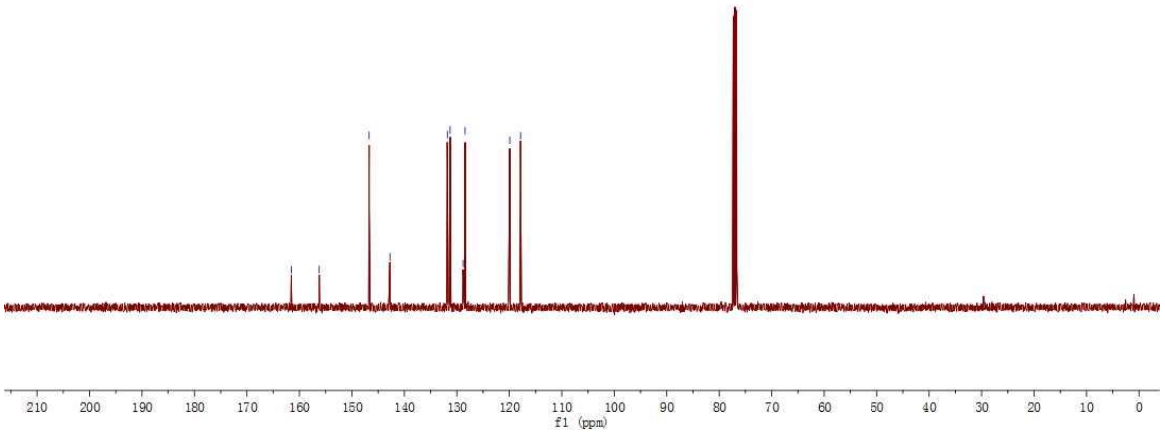




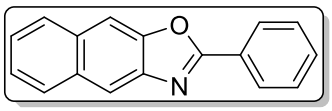


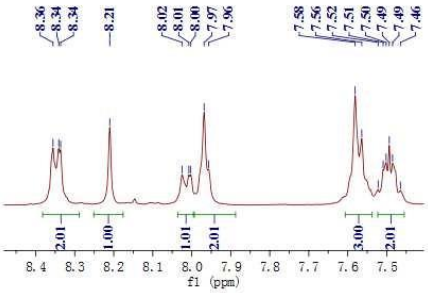


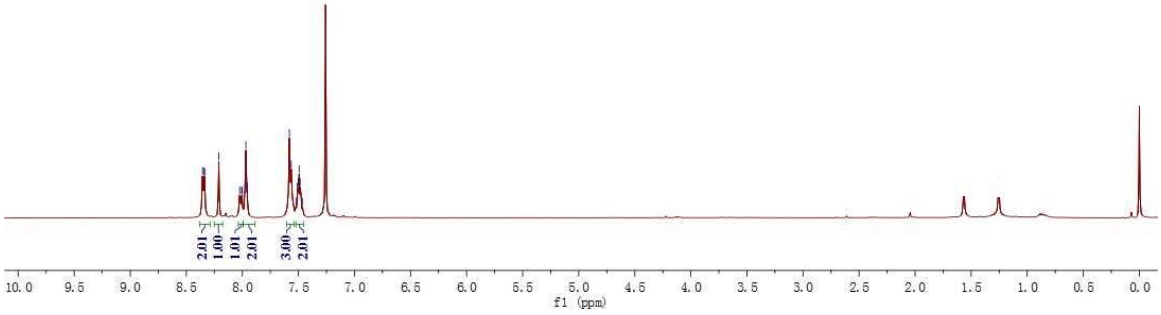


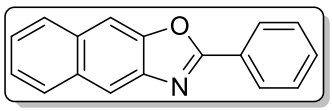


2-phenylnaphtho[2,3-d]oxazole(7la)









2-(furan-2-yl)naphtho[2,3-d]oxazole(7ld)