Supporting Information

Transition-metal-free Arylation of Benzoxazoles with Aryl Nitriles

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1. General

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Cs_2CO_3 (99.9%) was obtained from Aladdin (Shanghai, China) and anhydrous DMF was obtained from Innochem (Beijing, China). [1,1'-biphenyl]-4-carbonitrile was prepared according to the procedures reported in the literature.[1] 5-Methylbenzo[*d*]oxazole, 5-(*tert*-butyl)benzo[*d*]oxazole and 5-phenylbenzo[*d*]oxazole were prepared according to the procedures reported in the literature.[2] Benzonitrile ^{13}C was prepared according to the procedures reported in the literature.[3] 6-phenylbenzo[d]thiazole, 5-(4-fluorophenyl)benzo[d]oxazole and 5-(4-(trifluoromethyl)phenyl)benzo[d]oxazole were prepared according to the procedures reported in the literature.[4] 4-methylbenzo[d]thiazole and 6-bromobenzo[d]thiazole were prepared according to the procedures reported in the literature.[5] Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas in dried glassware using standard vacuum-line techniques. All reactions were performed in a 25-mL Schlenk tube and heated in a heating module (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200–300 mesh). Preparative thin-layer chromatography (PTLC) was performed using QingDao Haiyang chemical Plant GF254 silica coated plates (0.75 mm) prepared in our laboratory. Gas chromatography (GC) analysis was conducted on a Aglient 7024A instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) with biphenyl as an internal standard. GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). The high-resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. ^1H and ^{13}C NMR data were recorded with Bruker Advanced II (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual peak of $CDCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, td = triplet of doublets, q = quartet, m = multiplet, v = virtual coupling, br = broad signal), coupling constant (Hz), and integration.

[1] Liu, L. F.; Zhang, Y. H.; Xin, B. W. *J. Org. Chem.* **2006**, *71*, 3994.
[2] Gao, F.; Kim, B.-S.; Walsh, P. J. *Chem. Commun.* **2014**, *50*, 10661.
[3] Xi, Z. F.; Sato, K.; Gao, Y.; Lu, J. M.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125,* 9568.
[4] Verma, A. K.; Danodia, A. K.; Saunthwal, R. K.; Patel, M.; Choudhary, D. *Org. Lett*. **2015**, *17*, 3658.
[5] Katritzky, A. R.; Rogovoy, B. V.; Chassaing, C.; Vvedensky, V.; Forood, B.; Flatt, B.; Nakai, H. *J. Heterocylic Chem*. **2000**, *37*, 1655.

High resolution massspectra (HRMS) was measured with a 6545 Q-TOF LCMS instrument and accurate masses were reported for the molecular ion $[M+H]^+$.

2. Transition-metal-free Arylation of Benzoxazoles with Aryl Nitriles

General Procedure: A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding aryl nitrile (0.2 mmol), the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (130.3 mg, 0.4 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, benzoxazole (0.6 mmol) and DMF (1.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the organic phase was washed by saturated NaCl (aq), dried over Na_2SO_4, concentrated and directly purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ethyl acetate as the eluent) to afford the product.

Note: The reaction of **3h** and **3i** were conducted with K_3PO_4 (84.9 mg，0.4 mmol) and DMSO (1.0 mL). The reaction of **3j**, **3k**, **3l**, **3m** and **3n** were conducted with K_3PO_4 (84.9 mg, 0.4 mmol) and ^{n}hexane (1.0 mL).

3. Large-scale Experiment

General Procedure: A 100-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding 2-naphthonitrile (1.53 g, 10.0 mmol), the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (6.52 g, 20 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, benzoxazole (3.57 g, 30.0 mmol) and DMF (25.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in an oil bath with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq) (25.0 mL). After exacted with ethyl acetate (25.0 mL × 3) three times, the combined organic phase was washed by saturated NaCl (aq), dried over Na_2SO_4, filtered and evaporated in vacuo. Then was purified by column chromatography on silica gel (Petroleum ether / ethyl acetate = 400 / 1) to afford the product as a white solid (2.00 g, 82%).

4. Methylation of Azoles

General Procedure: A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. Then the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, KOH (0.4 mmol, 22.4 mg)/LiO^{t}Bu (0.3 mmol, 24.0 mg) was added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, 5-*tert*-butyl benzoxazole (0.2 mmol)/benzothiazole (0.2 mmol), MeCN (0.7 mL)/ MeCN (0.5 mL) and DMF (0.3 mL)/DMF (0.5 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the organic phase was washed by saturated NaCl (aq), dried over Na_2SO_4, concentrated and directly purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ethyl acetate as the eluent) to afford the product.

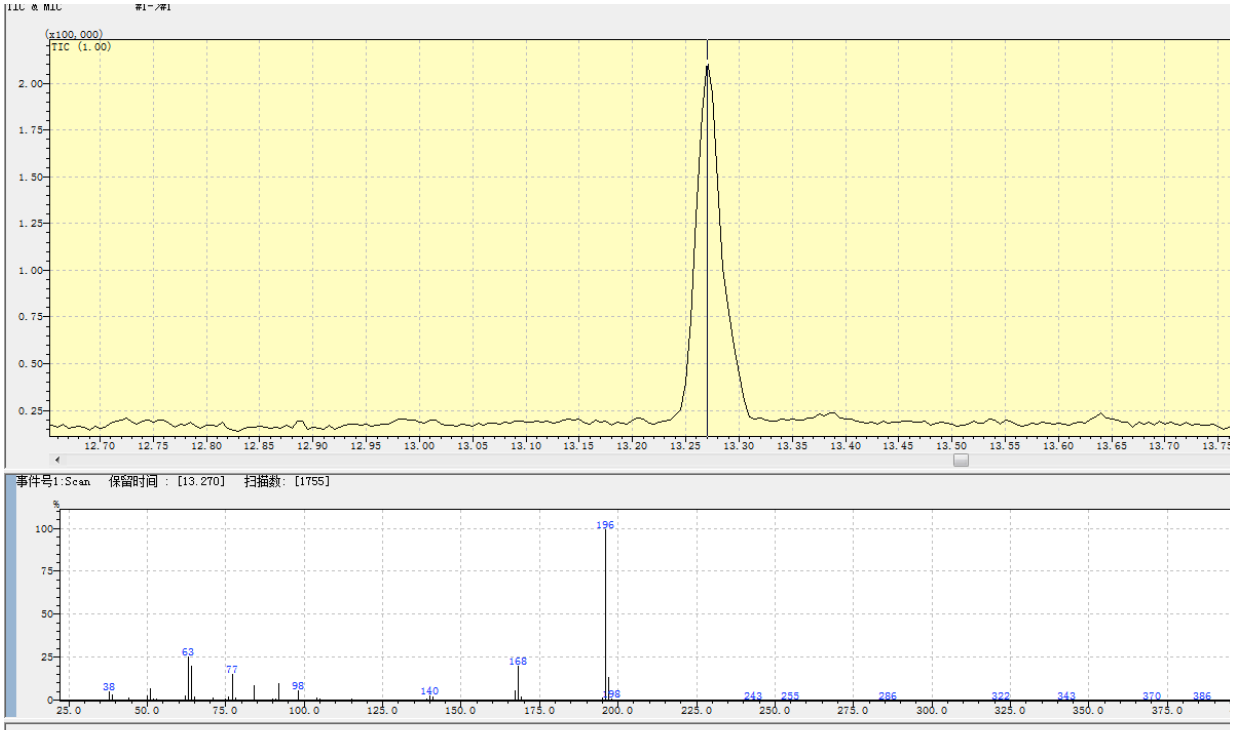
Note: For methylation of benzothiazole, when the reaction mixture was cooled to room temperature, the reaction mixture was concentrated and directly purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ethyl acetate as the eluent) to afford the product.

5. Radical Trapping Experiment

General Procedure: A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding 2-naphthonitrile (30.6 mg, 0.2 mmol), the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (130.3 mg, 0.4 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, benzoxazole (71.5 mg, 0.6 mmol), radical scavenger (0.2 mmol) and DMF (1.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the organic phase was washed by saturated NaCl (aq), dried over Na_2SO_4, concentrated and directly purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ethyl acetate as the eluent) to afford the product.

6. Control Experiments

General Procedure: For eq. 1, A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. Then the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (130.3 mg, 0.4 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, benzonitrile ^{13}C (20.8 mg, 0.2mmol) and benzoxazole (71.5 mg, 0.6 mmol) and DMF (1.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the organic phase was monitored by GC-MS and TLC.



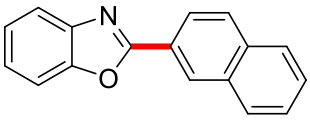
For eq. 2, A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. Then the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (130.3 mg, 0.4 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, benzoxazole (71.5 mg, 0.6 mmol) and DMF (1.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the result was determined by GC, calibrated using biphenyl as internal standard.

For eq. 3, A 25-mL sealed tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding 2-naphthonitrile (30.6 mg, 0.2 mmol), and 2-aminophenolthe (65.5 mg, 0.6 mmol), the tube was

introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Cs_2CO_3 (130.3 mg, 0.4 mmol) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, DMF (1.0 mL) were added to the vessel under nitrogen atmosphere. The vessel was then heated at 160 ^{o}C for 20 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature and quenched with saturated NaCl (aq). After exacted with ethyl acetate, the yield was determined by GC, calibrated using biphenyl as internal standard.

7. Analytical Data of Products

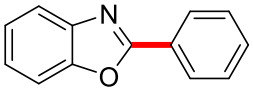
2-(naphthalen-2-yl)benzo[d]oxazole(3a)[6]



3a

White solid (40.2 mg, 82%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.32 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.98-7.96 (m, 2H), 7.90-7.88 (m, 1H), 7.84-7.80 (m, 1H), 7.64-7.59 (m, 1H), 7.58-7.53 (m, 2H), 7.40-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 151.0, 142.3, 134.8, 133.1, 129.1, 128.9, 128.3, 128.0, 127.9, 127.0, 125.3, 124.8, 124.5, 124.0, 120.1, 110.7.

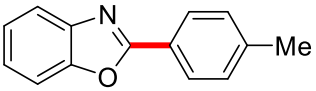
2-phenylbenzo[d]oxazole (3b)[6]



3b

White solid (27.7 mg, 71%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 7.80-7.77 (m, 1H), 7.58-7.55 (m, 1H), 7.52-7.50 (m, 3H), 7.36-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.9, 142.2, 131.7, 129.0, 127.7, 127.3, 125.2, 124.7, 120.1, 110.7.

2-(p-tolyl)benzo[d]oxazole(3c)[7]

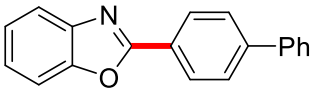


3c

White solid (21.8 mg, 52%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8 Hz, 2H), 7.79-7.74 (m, 1H), 7.59-7.55 (m, 1H), 7.37-7.32 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 150.8, 142.3, 142.2, 129.8, 127.7, 125.0, 124.6, 124.5, 120.0, 110.6, 21.8.

2-([1,1'-biphenyl]-4-yl)benzo[d]oxazole (3d)[7]

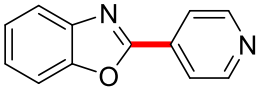
[6] Ueda, S.; Nagasawa, H. *Angew. Chem. Int. Ed*. **2008**, *47,* 6411.
[7] Zhang, M.; Zhang, S.; Liu, S.; Cheng, J. *Chem. Commun*. **2011***, 47,* 11522.



3d

White solid (36.9 mg, 68%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 80 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 6.8 Hz, 2H), 7.80-7.75 (m, 3H), 7.67 (d, *J* = 4.8 Hz, 2H), 7.60-7.48 (m, 3H), 7.42-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 151.0, 144.4, 142.4, 140.2, 129.1, 128.2, 128.2, 127.7, 127.3, 126.1, 125.3, 124.8, 120.1, 110.7.

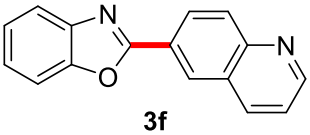
2-(pyridin-4-yl)benzo[d]oxazole(3e)[8]



3e

Yellow solid (20.4 mg, 52%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 20 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.2 Hz, 2H), 7.98 (d, *J* = 4.8 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 6.8 Hz, 1H), 7.36-7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 151.0, 150.7, 141.9, 134.6, 126.5, 125.3, 121.2, 120.8, 111.1.

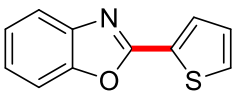
2-(quinolin-6-yl)benzo[d]oxazole (3f)[9]



3f

Yellow solid (37.4 mg, 76%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 5 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90-8.89 (m, 1H), 8.59 (d, *J* = 1.2 Hz, 1H), 8.44 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 8.16-8.14 (m, 2H), 7.74-7.72 (m, 1H), 7.53-7.51 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.1, 151.1, 149.6, 142.3, 137.1, 130.6, 128.2, 128.1, 127.9, 125.7, 125.4, 125.0, 122.3, 120.4, 110.9.

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

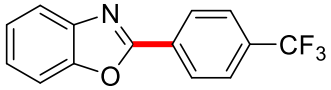


3g

[8] Ranjit, S.; Liu, X. *Chem. Eur. J.* **2011**, *17,* 1105.
[9] Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc*. **2012**, *134,* 169.

White solid (25.8 mg, 64%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 50 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 2.4 Hz, 1H), 7.73-7.71 (m, 1H), 7.52-7.51 (m, 2H), 7.32-7.30 (m, 2H), 7.15-7.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 150.5, 142.1, 130.4, 130.0, 129.7, 128.4, 125.2, 124.8, 119.9, 110.5.

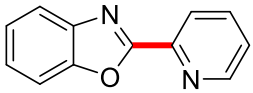
Phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (3h)[7]



3h

White solid (27.4 mg, 52%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.0 Hz, 2H), 7.82-7.78 (m, 3H), 7.62-7.60 (m, 1H), 7.42-7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 151.1, 142.2, 133.2 (q, J = 33.0 Hz), 130.7, 128.1, 126.2 (q, J = 4.0 Hz), 126.1, 125.2, 124.0 (q, J = 271.0 Hz), 120.7, 111.0.

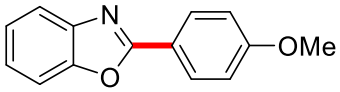
2-(pyridin-2-yl)benzo[d]oxazole (3i)[10]



3i

Yellow solid (32.2 mg, 82%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 20 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73-8.72 (m, 1H), 8.29-8.25 (m, 1H), 7.82-7.74 (m, 2H), 7.58-7.57 (m, 1H), 7.35-7.28 (m, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 151.1, 150.4, 146.1, 141.8, 137.2, 126.2, 125.7, 125.0, 123.5, 120.7, 111.3.

2-(4-methoxyphenyl)benzo[d]oxazole (3j)[6]

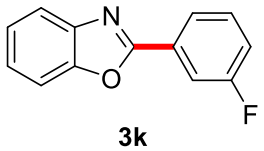


3j

White solid (22.1 mg, 49%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.76-7.71 (m, 1H), 7.59-7.52 (m, 1H), 7.35-7.30 (m, 2H), 7.03 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.4, 150.8, 142.4, 129.5, 124.7, 124.6, 119.8, 119.7, 114.5, 110.5, 55.6.

[10] Do, H.; Daugulis, O. *J. Am. Chem. Soc.* **2007**, *129,* 12404.

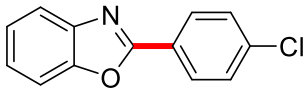
2-(3-fluorophenyl)benzo[d]oxazole (3k)[11]



3k

White solid (27.3 mg, 64%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.82-7.80 (m, 1H), 7.62-7.60 (m, 1H), 7.54-7.49 (m, 1H), 7.41-7.29 (m, 2H), 7.29-7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J*= 240.0 Hz), 161.9 (d, *J* = 4.0 Hz), 150.9, 142.0, 130.7 (d, *J*= 8.0 Hz), 129.3 (d, *J* = 8.0 Hz) , 125.6, 124.9, 123.4 (d, *J* = 4.0 Hz), 120.3, 118.6 (d, *J*= 21.0 Hz), 114.7 (d, *J* =24.0 Hz), 110.8.

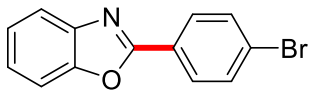
2-(4-chlorophenyl)benzo[d]oxazole (3l)[6]



3l

White solid (22.5 mg, 49%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.76-7.74 (m, 1H), 7.54-7.52 (m, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.34-7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 150.9, 142.1, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.2, 110.8.

2-(4-bromophenyl)benzo[d]oxazole (3m)[6]

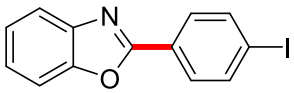


3m

White solid (21.9 mg, 40%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.78-7.76 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.58-7.56 (m, 1H), 7.37-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 150.9, 142.1, 132.4, 129.1, 126.4, 126.2, 125.5, 124.9, 120.2, 110.8.

2-(4-iodophenyl)benzo[d]oxazole (3n)[6]

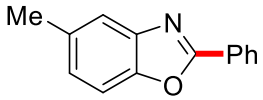
[11] Johnson, S. M.; Connelly, S.; Wilson, I. A.; Kelly, J. W. *J. Med. Chem.* **2008,** *51,* 260.



3n

White solid (34.0 mg, 53%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.78-7.75 (m, 1H), 7.58-7.56 (m, 1H), 7.37-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 150.8, 142.1, 138.3, 129.1, 126.7, 125.5, 124.9, 120.2, 110.8, 98.6.

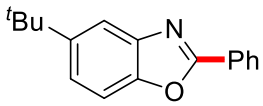
5-methyl-2-phenylbenzo[d]oxazole (30)[6]



3o

White solid (34.3 mg, 82%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 2H), 7.56 (s, 1H), 7.53-7.51 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 149.1, 142.4, 134.5, 131.5, 129.0, 127.7, 127.4, 126.3, 120.0, 110.6, 21.7.

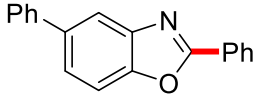
5-(tert-butyl)-2-phenylbenzo[d]oxazole (3p)[7]



3p

White solid (38.7 mg, 77%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.24 (m, 2H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.53-7.49 (m, 4H), 7.42 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 148.9, 148.2, 142.1, 131.5, 129.0, 127.6, 127.5, 123.0, 116.6, 109.8, 35.0, 31.9.

2,5-diphenylbenzo[d]oxazole (3q)[12]

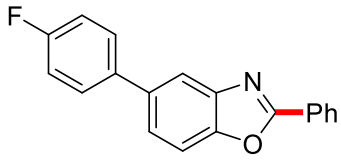


3q

[12] Wang, Y.; Sarris, K.; Sauer, D. R.; Djuric, S. W. *Tetrahedron Lett.* **2006**, *47,* 4823.

White solid (33.6 mg, 62%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.28 (m, 2H), 7.99 (s, 1H), 7.66-7.62 (m, 3H), 7.60-7.54 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 2H*),* 7.39 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 150.3, 142.8, 141.1, 138.5, 131.7, 129.0, 128.9, 127.7, 127.5, 127.3, 127.1, 124.8, 118.5, 110.6.

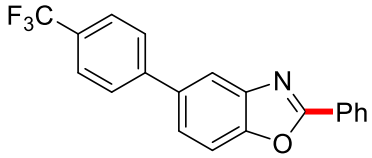
5-(4-fluorophenyl)-2-phenylbenzo[d]oxazole(3r)



3r

White solid (31.8 mg, 55%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 300 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.26 (m, 2H), 7.90 (s, 1H), 7.61-7.57 (m, 3H), 7.55-7.49 (m, 4H), 7.17-7.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, *J* = 5.0 Hz), 161.4, 150.4, 142.9, 137.6, 137.3 (d, *J* = 3.0 Hz), 131.8, 129.1, 129.0, 127.8, 127.2, 124.7, 118.4, 115.8 (d, *J* = 22.0 Hz), 110.7. HRMS (APCl) *m/z* calcd for $C_{19}H_{12}FNO$ $[M+H]^+$: 290.0976 found 290.0969.

2-phenyl-5-(4-(trifluoromethyl)phenyl)benzo[d]oxazole(3s)[13]

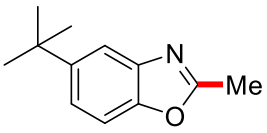


3s

White solid (16.3 mg, 24%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 300 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.27 (m, 2H), 7.97 (s, 1H), 7.73 (m, 4H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.58-7.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 151.0, 144.7, 143.0, 137.0, 131.9, 129.5 (q, *J* = 33.0 Hz), 129.1, 127.9, 127.8, 127.1, 125.9 (q, *J* = 4.0 Hz), 124.8, 124.4 (q, *J* = 270.0 Hz), 118.8, 111.0.

6-(tert-butyl)-2-methylbenzo[d]oxazole(5)[14]

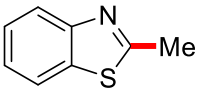
[13] Liu, D.; Liu, B.; Cheng, J. *RSC Adv.* **2013**, *3*, 9193.
[14] Dulong, F.; Thuery, P.; Thuery, M.; Cantat, T. *Organometallics*. **2013**, *32,* 1328.



5

Yellow oil (30.7 mg, 81%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.2 Hz, 1H), 7.38-7.32 (m, 2H), 2.61 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 149.1, 147.7, 141.6, 122.1, 116.1, 109.4, 35.0, 31.9, 14.6.

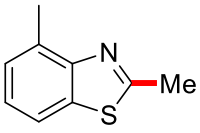
2-methylbenzo[d]thiazole(7a)[15]



7a

Yellow oil (19.7 mg, 66%); Preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.30-7.25 (m, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 153.4, 135.6, 125.9, 124.7, 122.4, 121.4, 20.1.

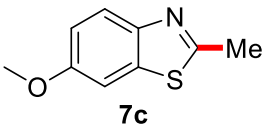
2,4-dimethylbenzo[d]thiazole(7b)[16]



7b

Oil (20.2 mg, 62%); Flash chromatography (petroleum ether/ethyl acetate = 500 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64(m, 1H), 7.24-7.23(m, 2H), 2.84 (s, 3H), 2.74(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 152.6, 135.4, 132.1, 126.4, 124.4, 118.6, 20.0, 18.4.

6-methoxy-2-methylbenzo[d]thiazole(7c)[17]

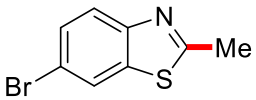


7c

[15] Mase, T.; Itoh, T. *Org. Lett*. **2007**, *9*, 3687.
[16] Hang, X.; Tang, J. *Tetrahedron*. **2003**, *59*, 4851.
[17] Ma, D.; Xie, S. W.; Xue, P.; Zhang, X, J.; Dong, J. H.; Jiang, Y. W. *Angew. Chem. Int. Ed*. **2009**, *121*, 4286.

Oil (14.3 mg, 40%); Flash chromatography (petroleum ether/ethyl acetate = 300 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 9.2 Hz, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 157.4, 147.9, 136.9, 122.8, 115.0, 104.3, 55.8, 20.0.

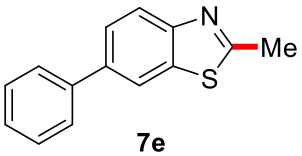
6-bromo-2-methylbenzo[d]thiazole(7d)[17][18]



7d

White solid (33.3 mg, 73%); Flash chromatography (petroleum ether/ethyl acetate = 300 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 1H), 7.75-7.73 (m, 1H), 7.49-7.47 (m, 1H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 152.5, 137.5, 129.6, 124.1, 123.7, 118.4, 20.3.

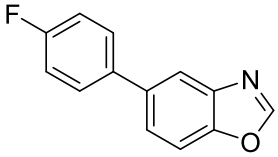
2-methyl-6-phenylbenzo[d]thiazole(7e)[4]



7e

Yellow solid (35.1 mg, 78%); Flash chromatography (petroleum ether/ethyl acetate = 200 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.38-7.34 (m, 1H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 152.8, 140.7, 138.2, 136.5, 128.9, 127.4, 127.4, 125.6, 122.5, 119.7, 20.2.

5-(4-fluorophenyl)benzo[d]oxazole(1r)



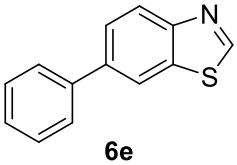
1r

White solid (1.59 g, 75%); Flash chromatography (petroleum ether/ethyl acetate = 200 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (s, 1H), 7.63-7.54 (m, 4H), 7.16-7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 245.0 Hz), 153.3, 149.6, 140.9, 137.7, 137.1 (d, *J* = 3.0 Hz), 129.1 (d, *J*

[18] Sawhney, S. N.; Boykin, D. W. J . Org. Chem., 1979, 44 , 1136.

= 8.0 Hz), 125.2, 119.1, 115.9 (d, *J* = 21.0 Hz), 111.1. HRMS (APCl) *m*/*z* calcd for $C_{13}H_8FNO$ $[M+H]^+$: 214.0663 found 214.0663.

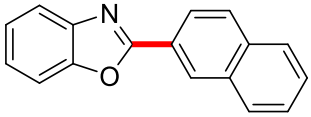
6-phenylbenzo[d]thiazole(6e)



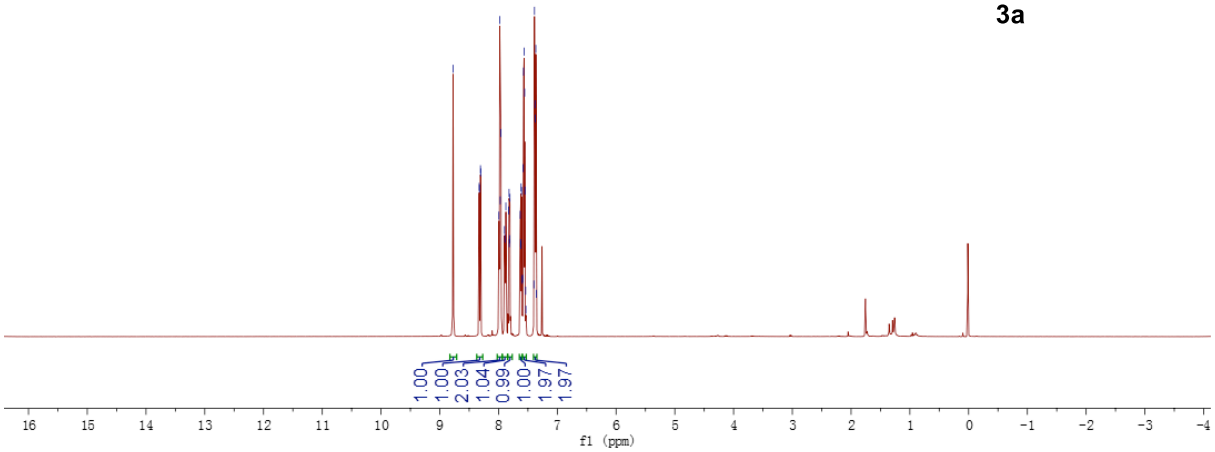
6e

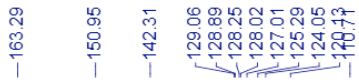
White solid (0.59g, 70%); Flash chromatography (petroleum ether/ethyl acetate = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.21-8.16 (m, 2H), 7.76 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 151.7, 139.7, 138.3, 133.6, 128.1, 126.8, 126.6, 125.1, 122.8, 119.3. HRMS (APCl) *m*/*z* calcd for $C_{13}H_9NS$ $[M+H]^+$: 212.0528 found 212.0530.

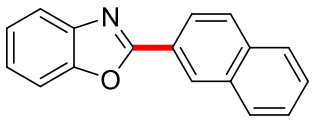
8. NMR Spectra of Products



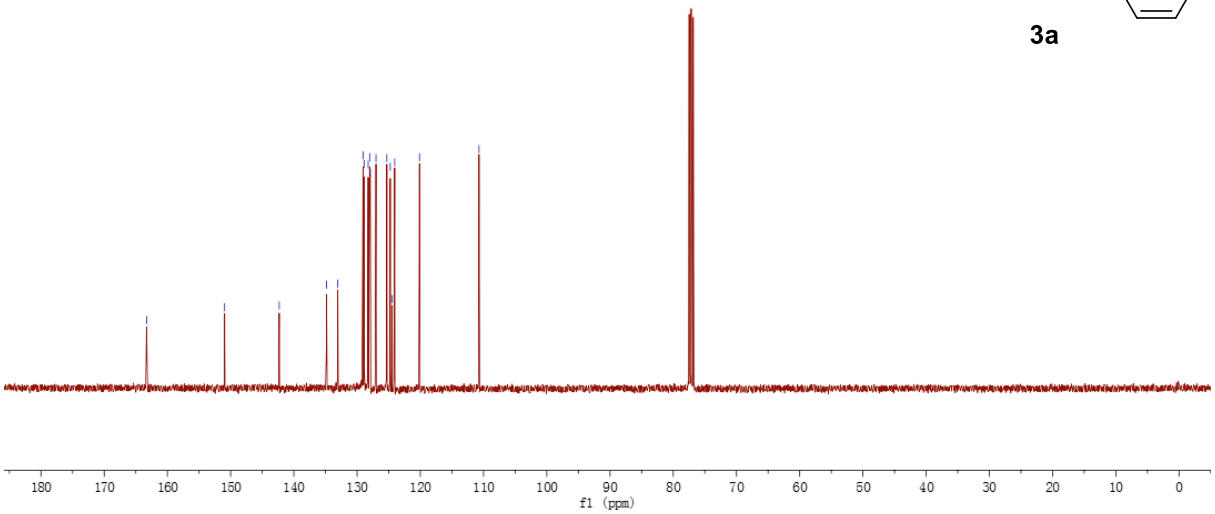
3a







3a




8.270
8.265
8.255
8.246
7.796
7.789
7.786
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7.575
7.571
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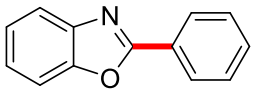
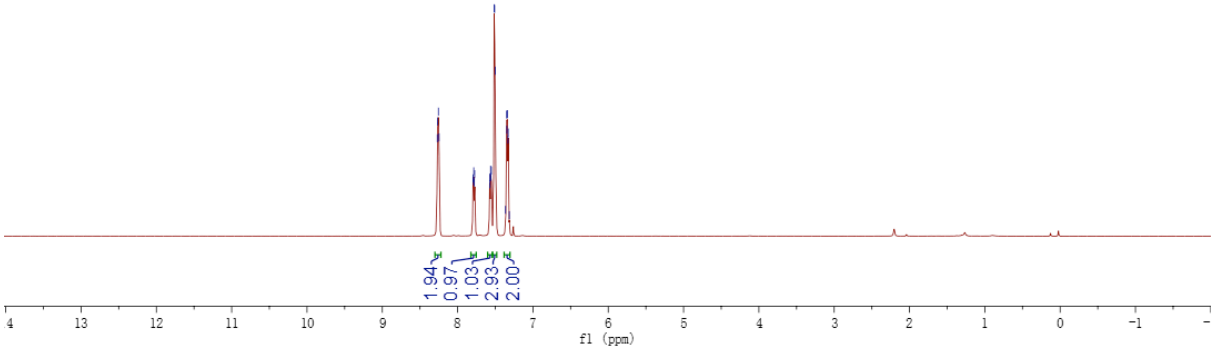
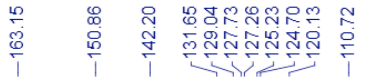
7.346
7.339
7.331
7.329
7.314


N
O

3b


1.94
0.97
1.03
2.93
2.00
f1 (ppm)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150.86
142.20
131.65
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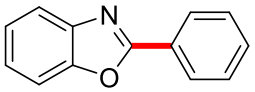
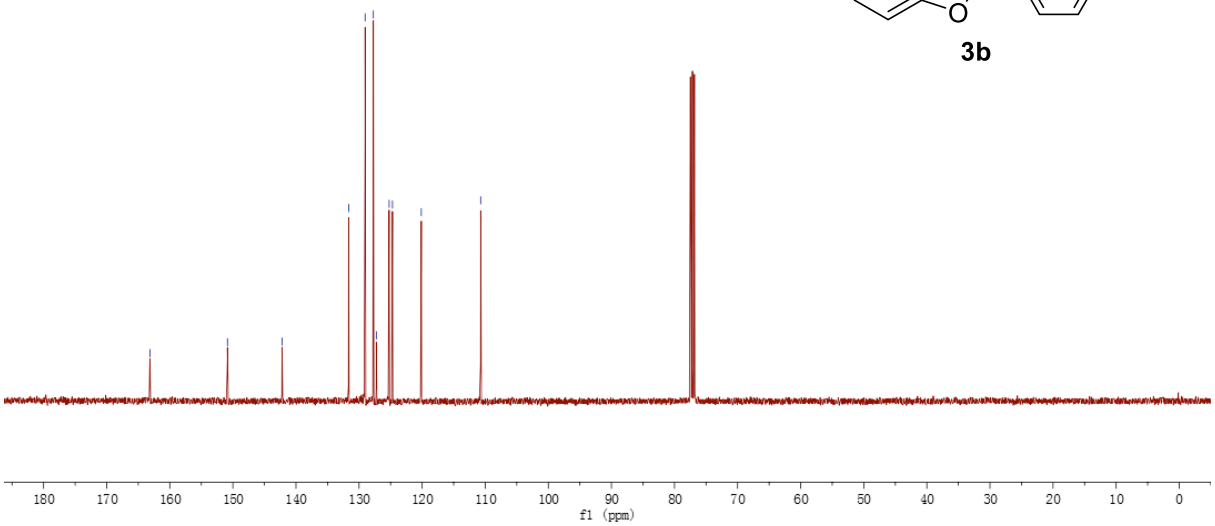
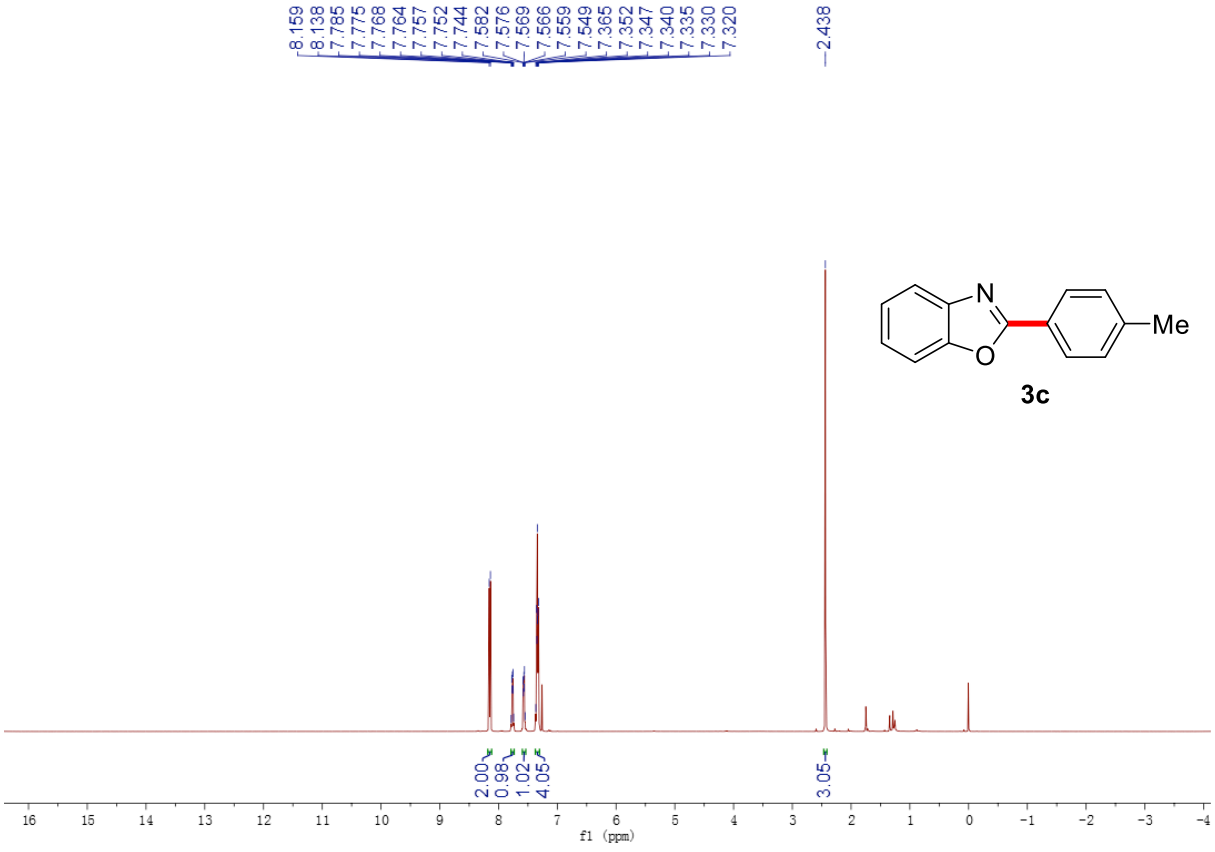
127.73
127.26
125.23
124.70
120.13
110.72


N
O

3b


f1 (ppm)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7.768
7.764
7.757
7.752
7.744
7.582
7.576
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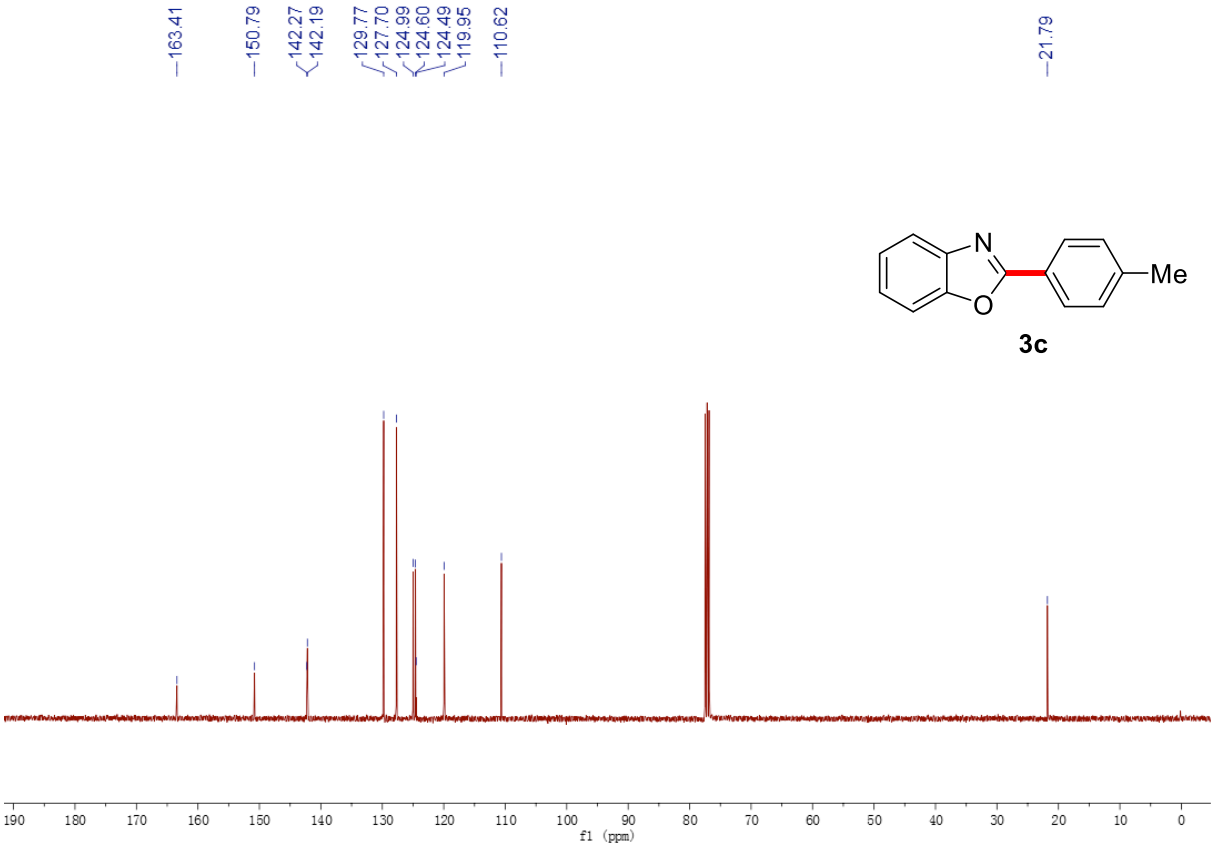
7.566
7.559
7.549
7.365
7.352
7.347
7.340
7.335
7.330
7.320
2.438
N
O
Me
3c
2.00
0.98
1.02
4.05
3.05
f1 (ppm)


163.41
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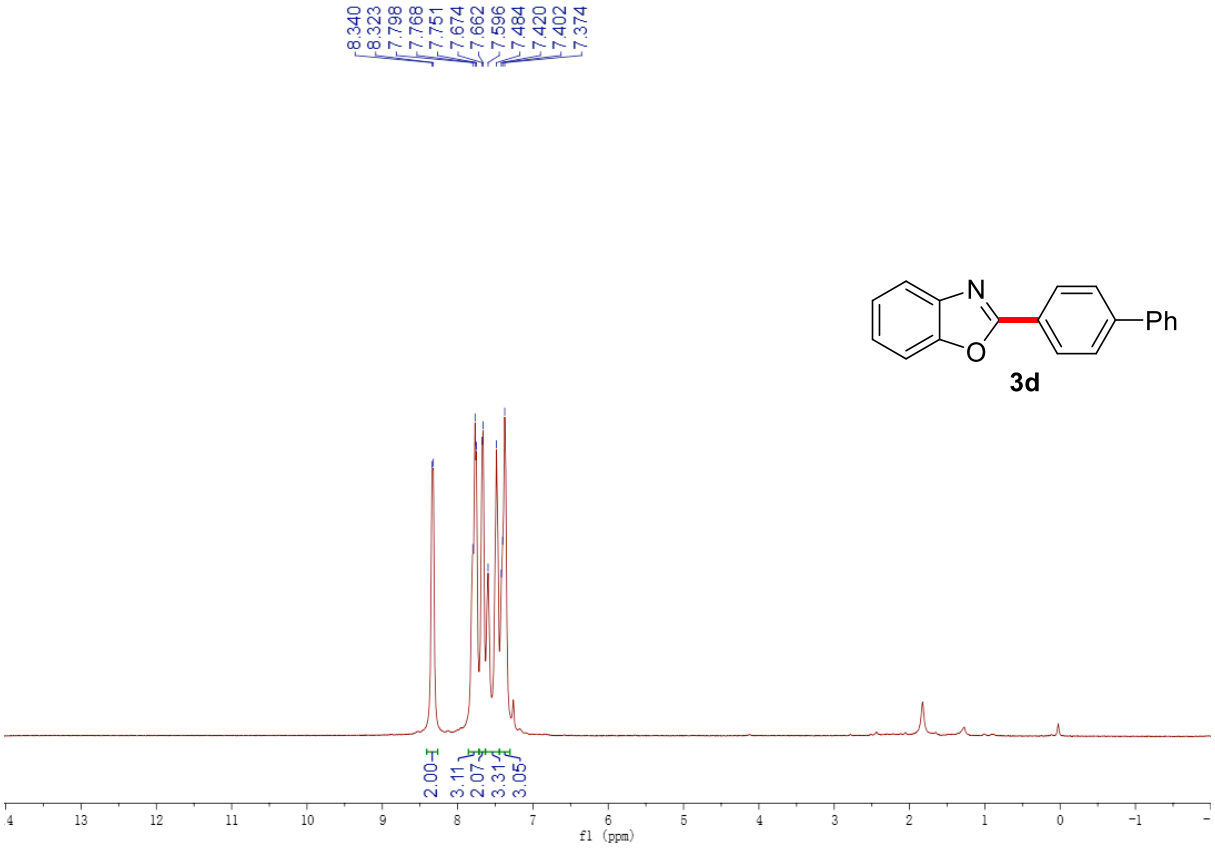
110.62
21.79
N
O
Me
3c
f1 (ppm)


8.340
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7.596
7.484
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O
Ph
3d
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3.11
2.07
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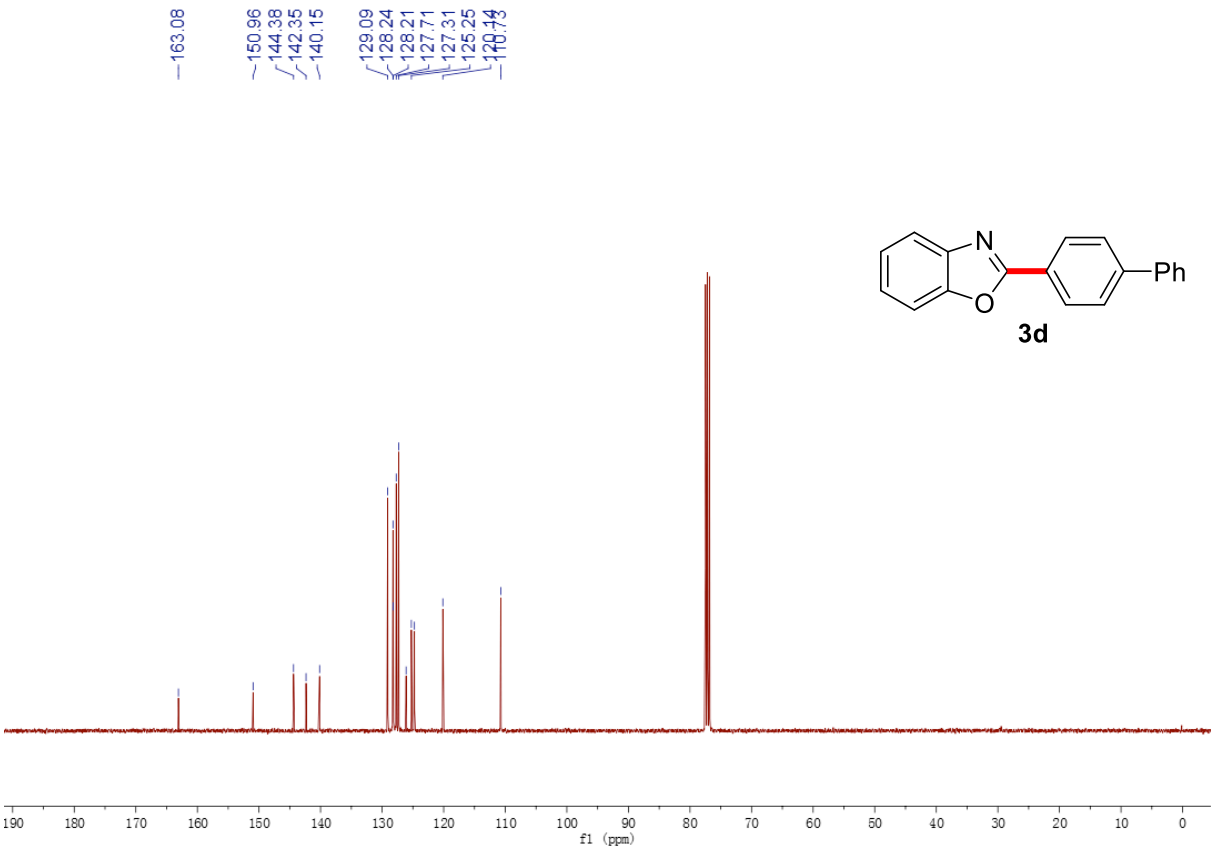
3.05
f1 (ppm)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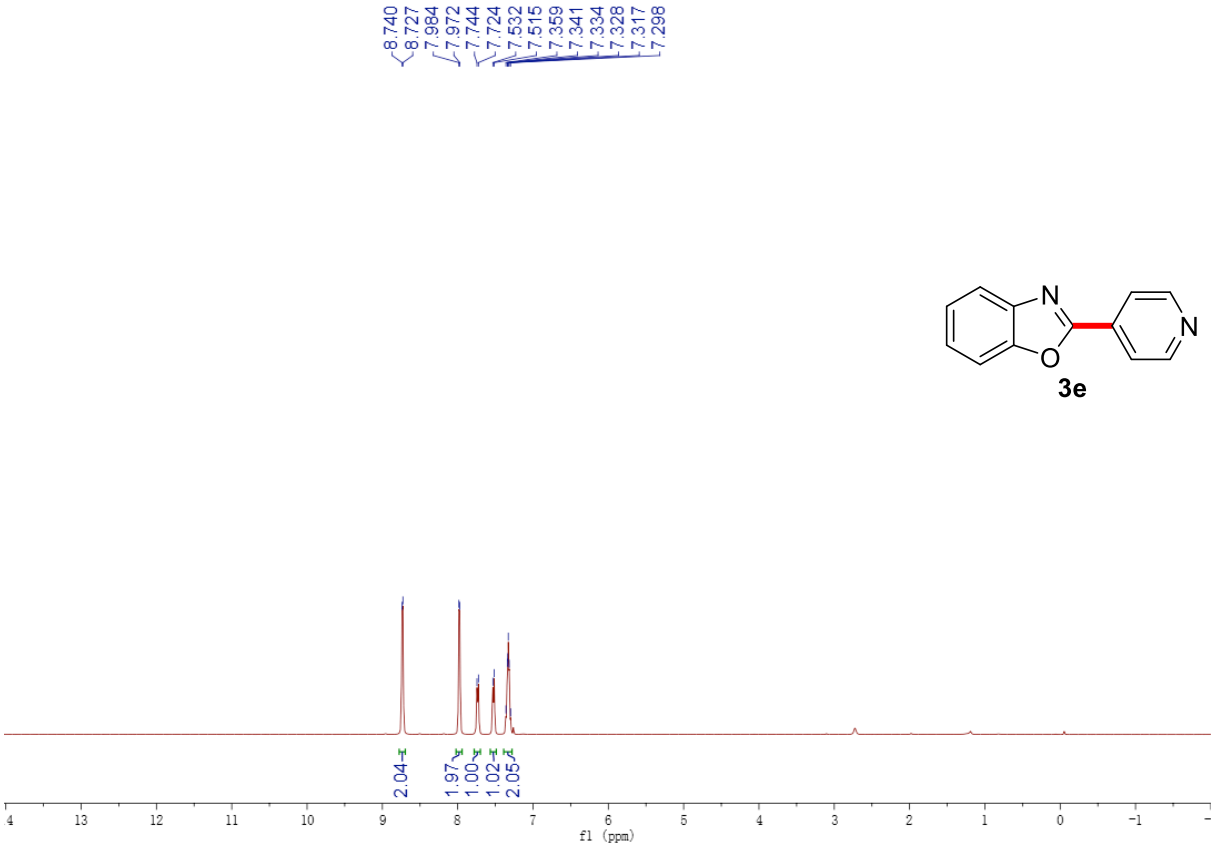
O
Ph
3d
f1 (ppm)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7.724
7.532
7.515
7.359
7.341
7.334
7.328
7.317
7.298
N
O
N
3e
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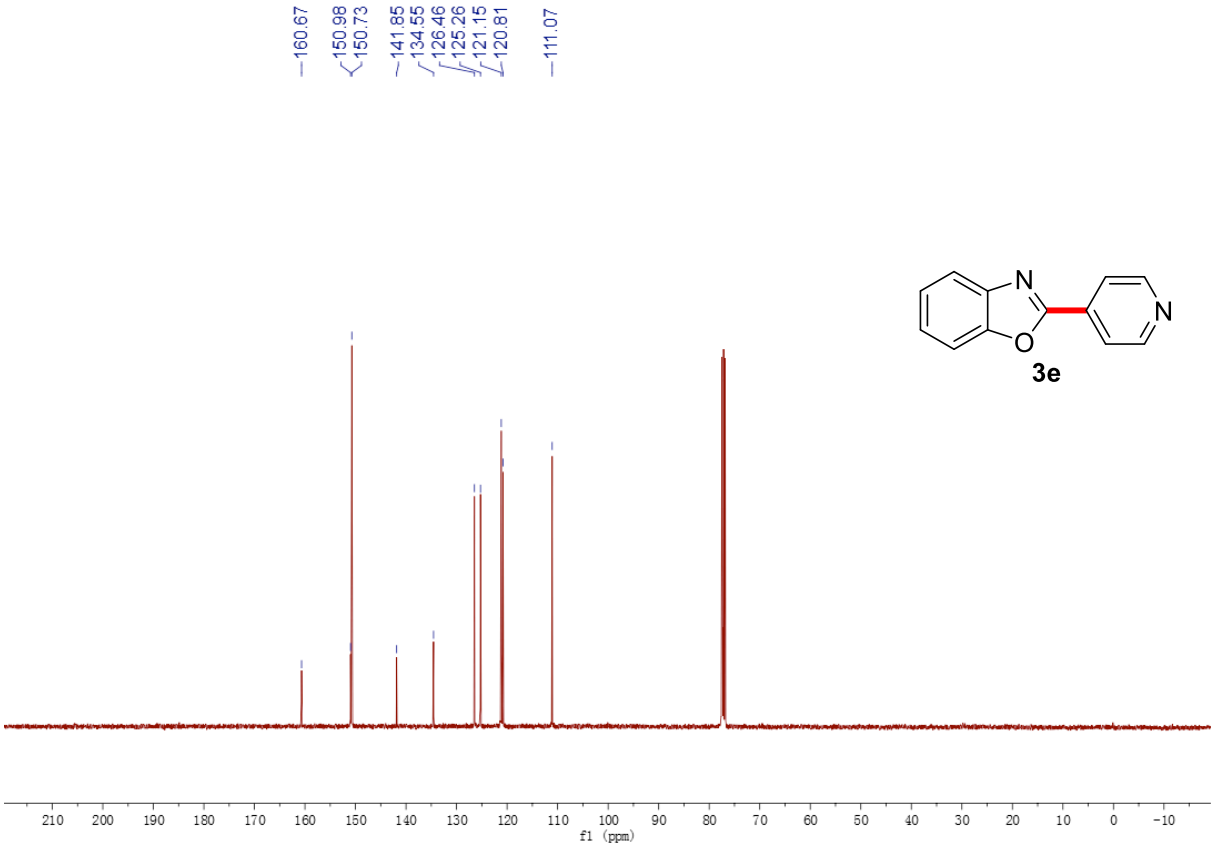
1.97
1.00
1.02
2.05
f1 (ppm)


160.67
150.98
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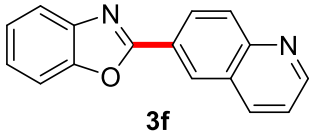
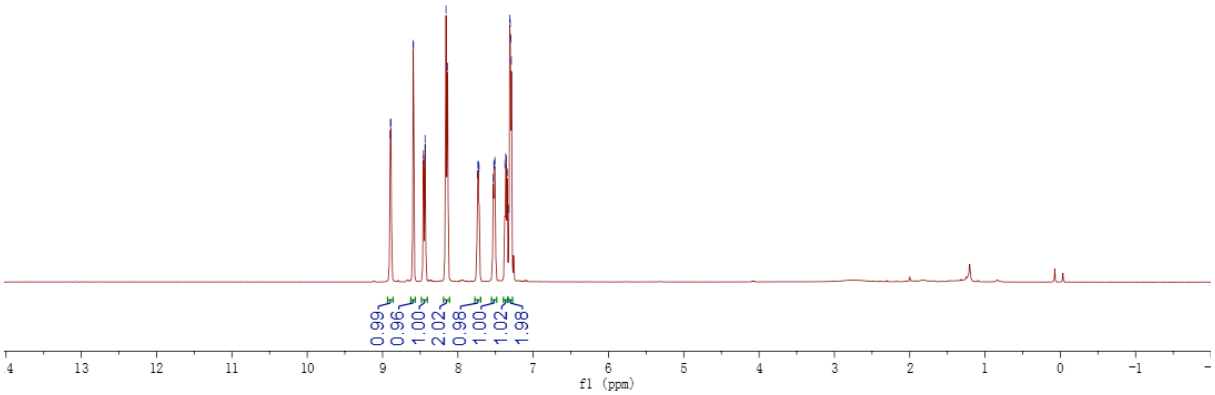
141.85
134.55
126.46
125.26
121.15
120.81
111.07
N
O
N
3e
f1 (ppm)

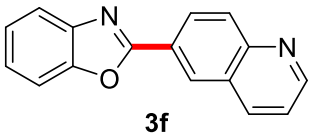

8.899
8.895
8.889
8.592
8.589
8.457
8.453
8.435
8.431
8.157
8.135
7.741
7.733
7.727
7.719
7.530
7.522
7.515
7.507
7.375
7.364
7.354
7.344
7.322
7.312
7.304
7.297
7.289


N
O
N

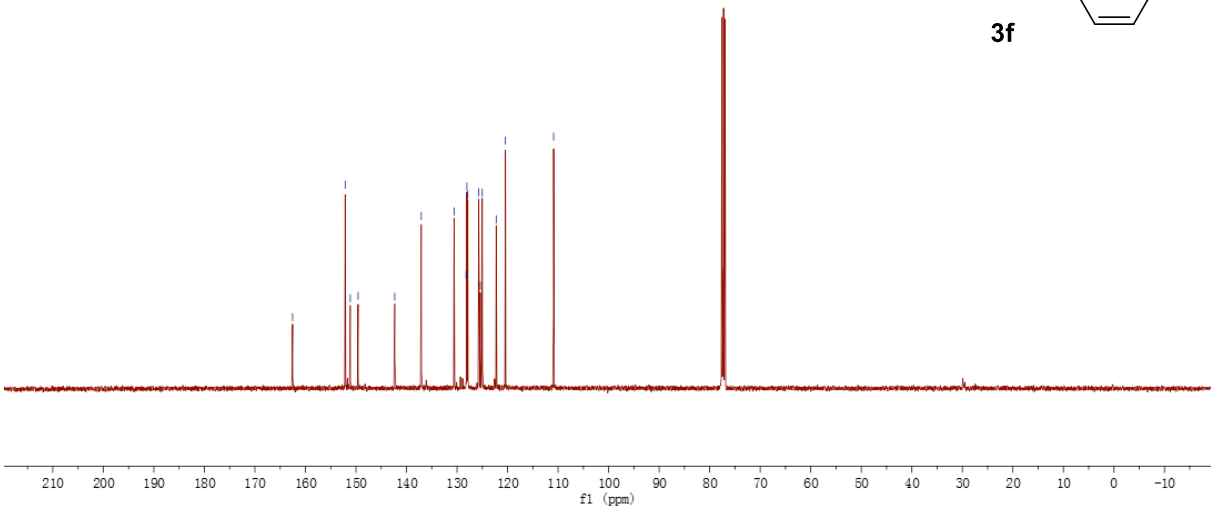
3f

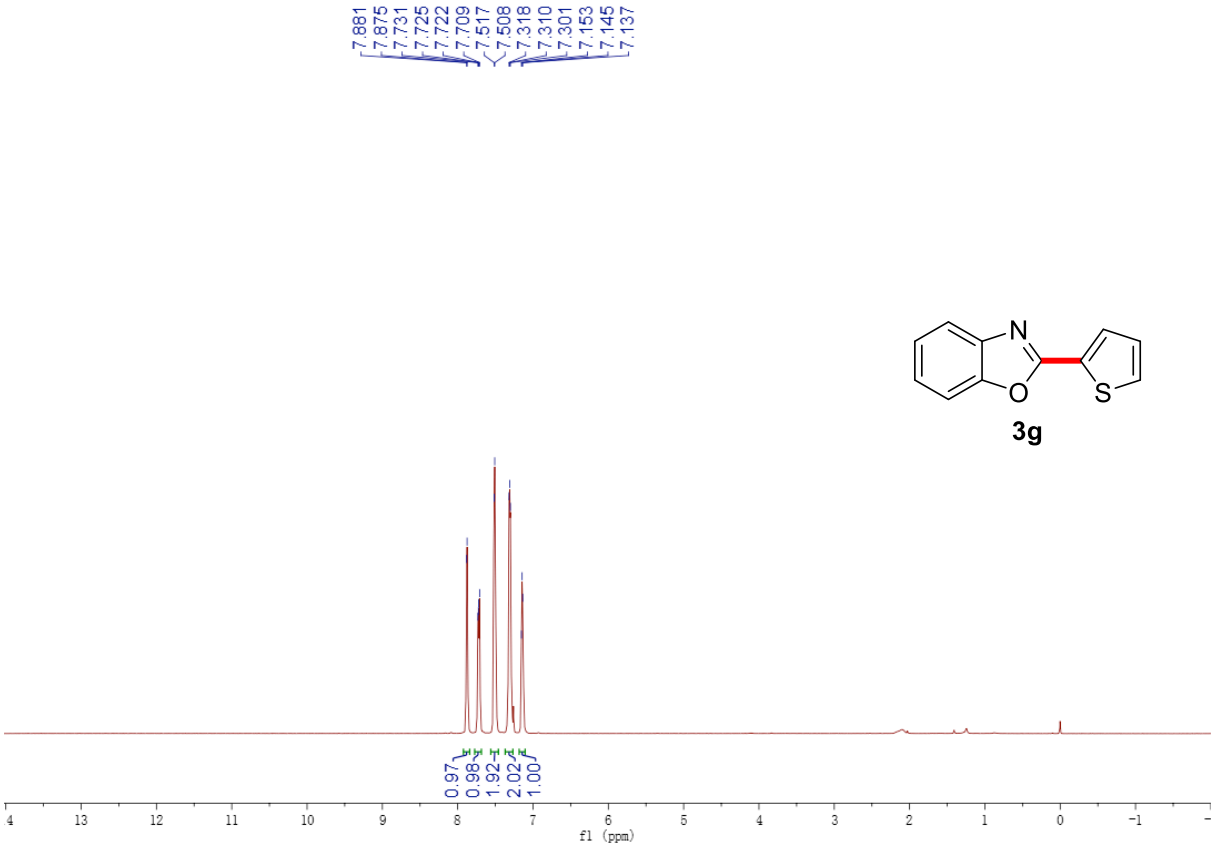

0.99
0.96
1.00
2.02
0.98
1.00
1.02
1.98
f1 (ppm)

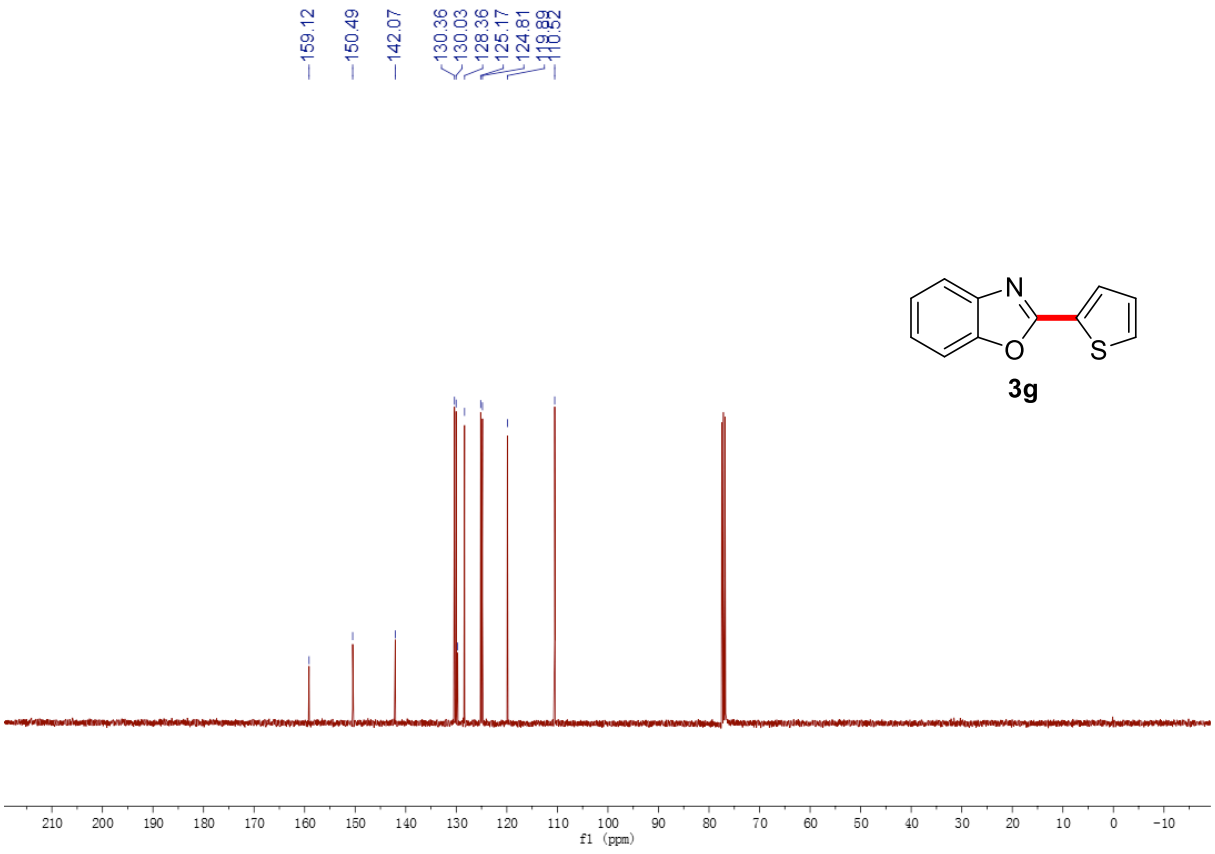

162.54
152.13
137.08
130.58
128.21
128.05
127.88
125.70
125.41
125.01
122.25
120.42
110.89

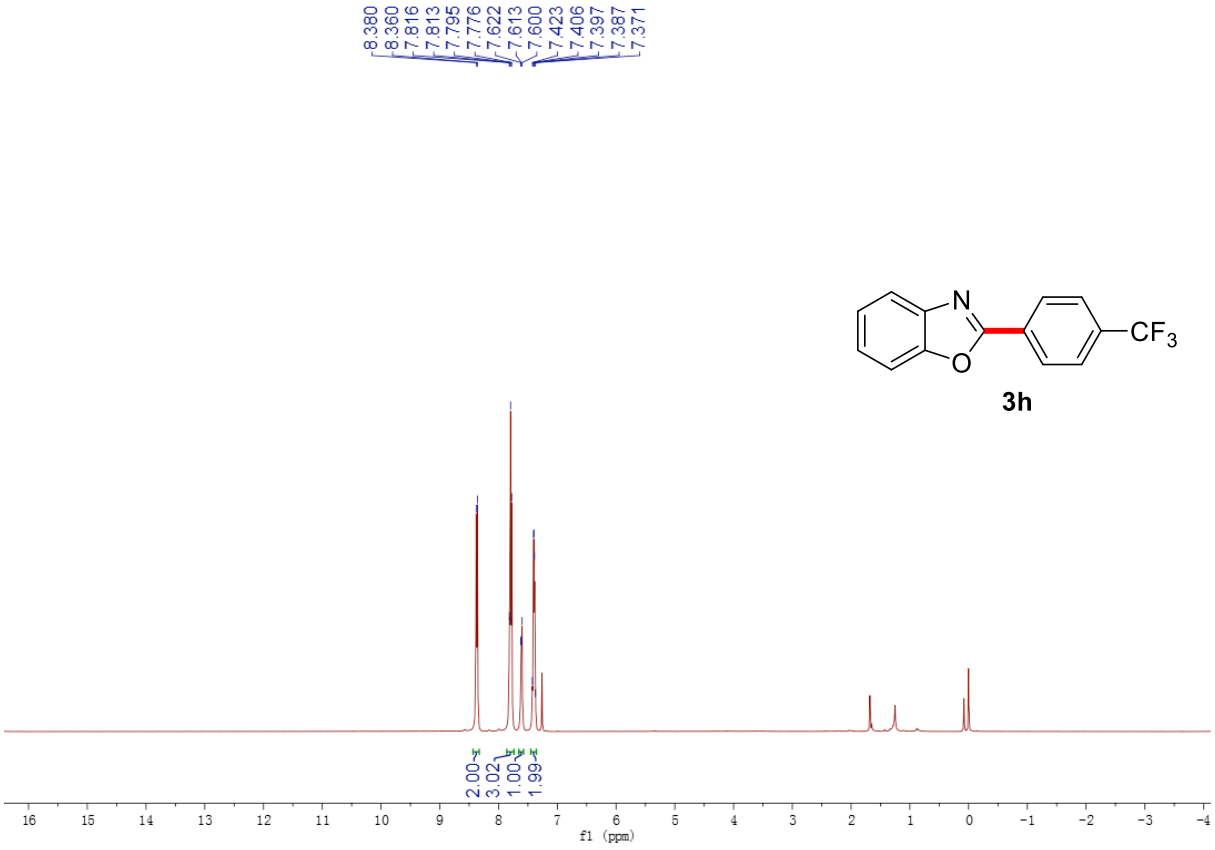

N
O
N

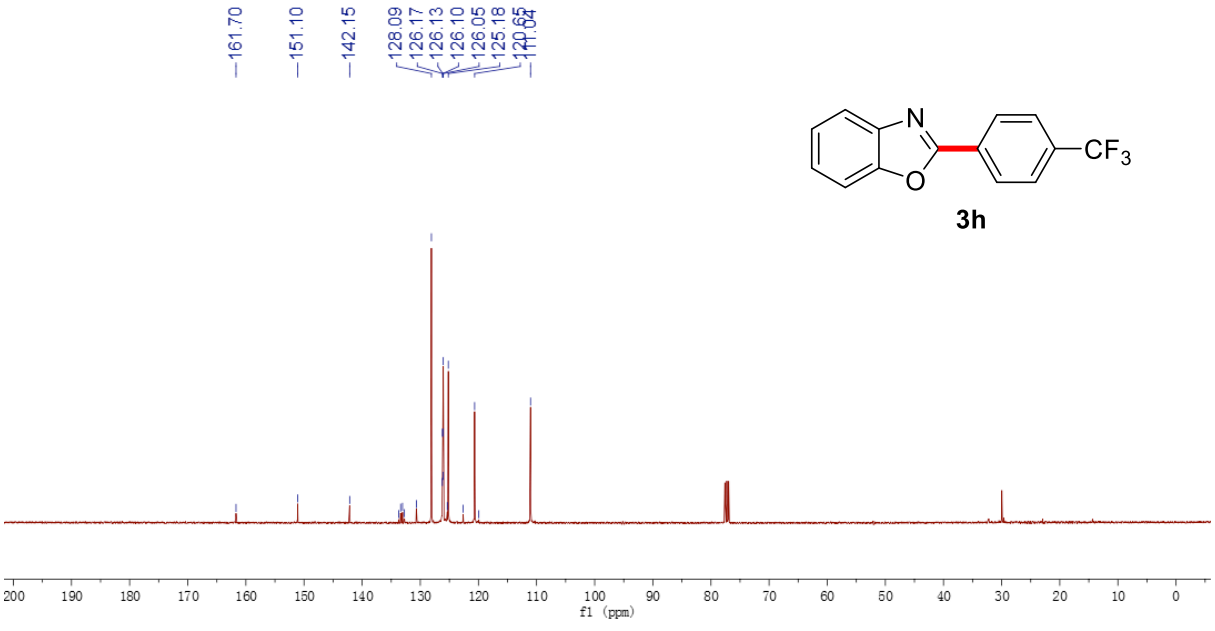
3f

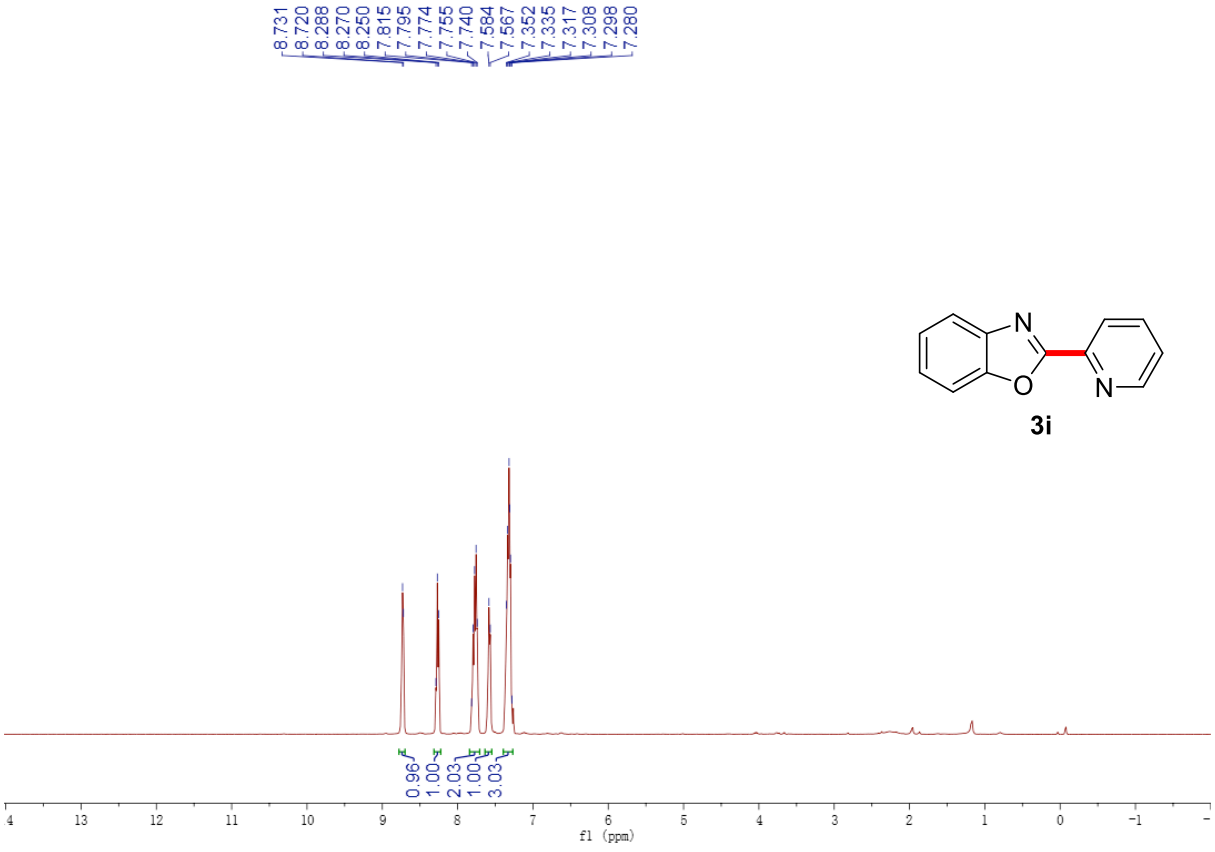

f1 (ppm)

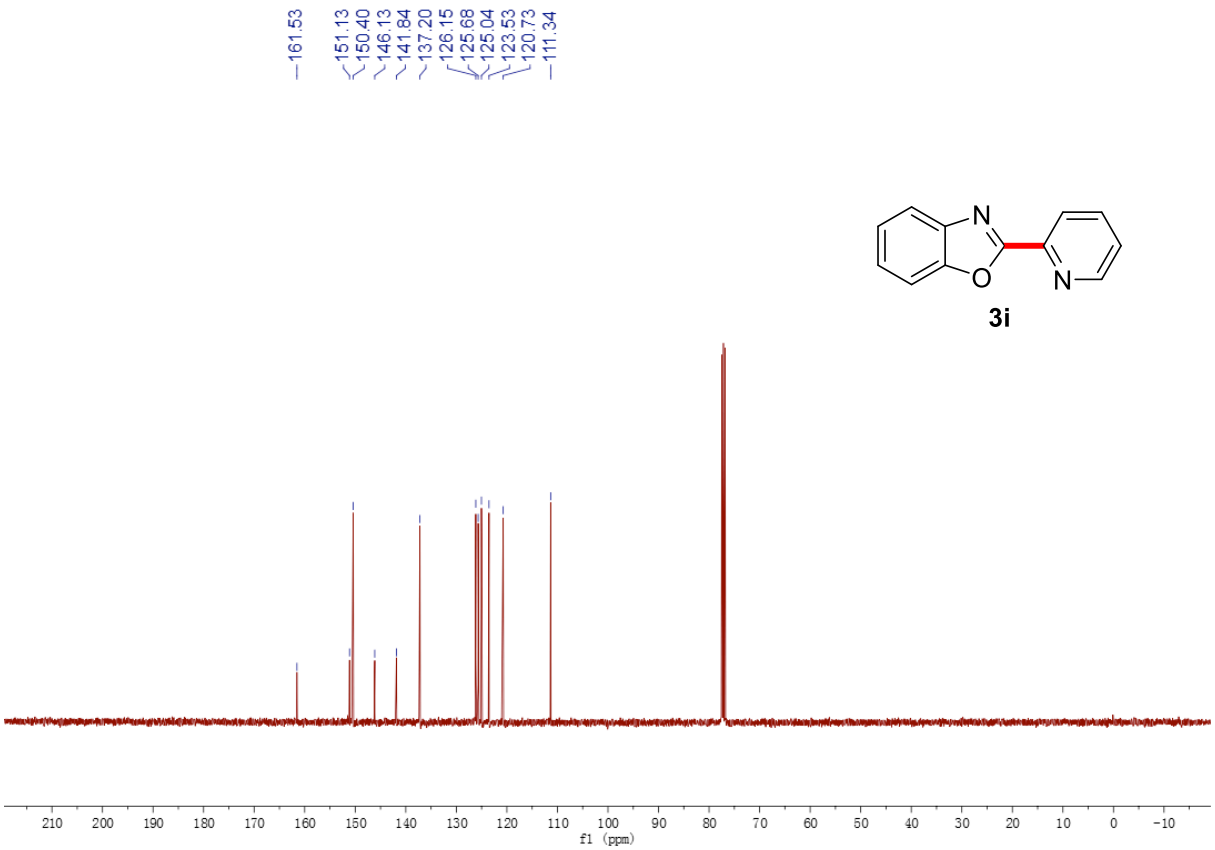

7.881
7.875
7.731
7.725
7.722
7.709
7.517
7.508
7.318
7.310
7.301
7.153
7.145
7.137
N
O
S
3g
0.97
0.98
1.92
2.02
1.00
f1 (ppm)

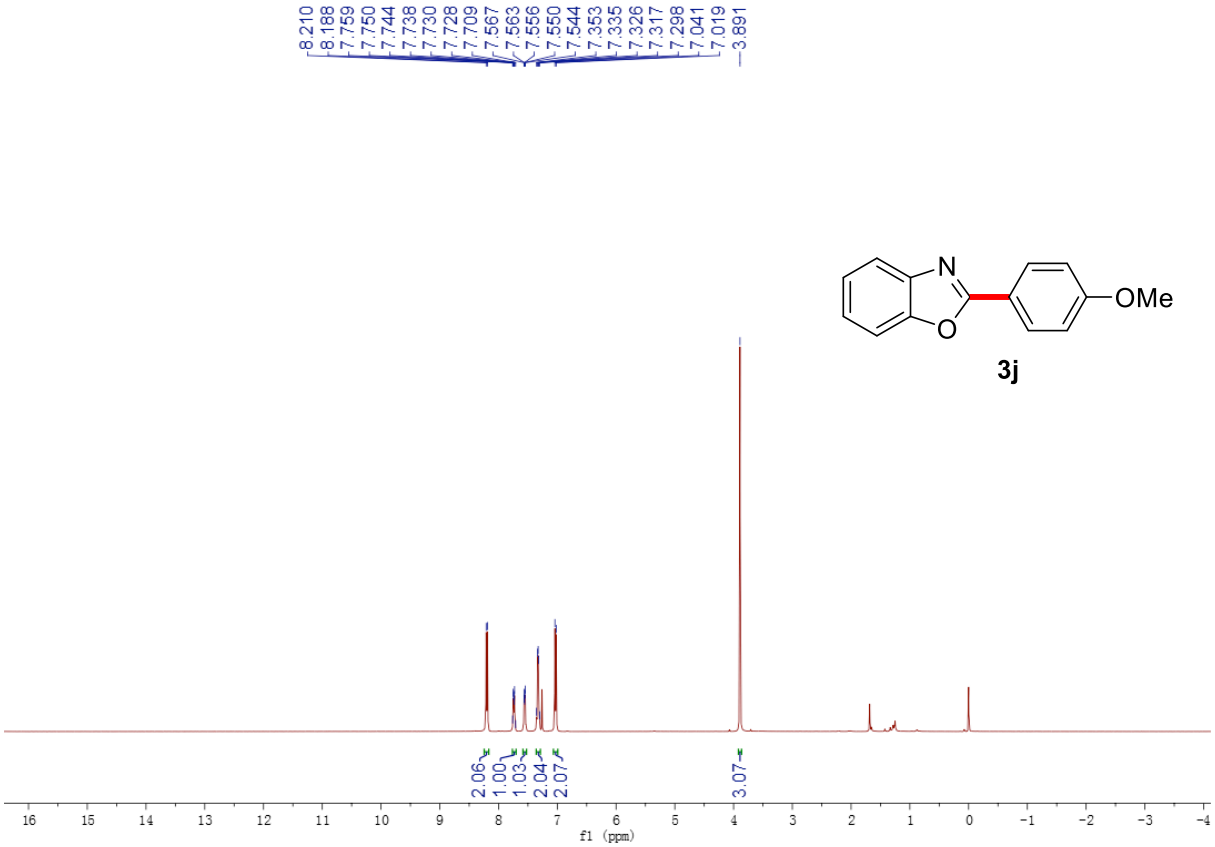

159.12
150.49
142.07
130.36
130.03
128.36
125.17
124.81
N
O
S
3g
f1 (ppm)

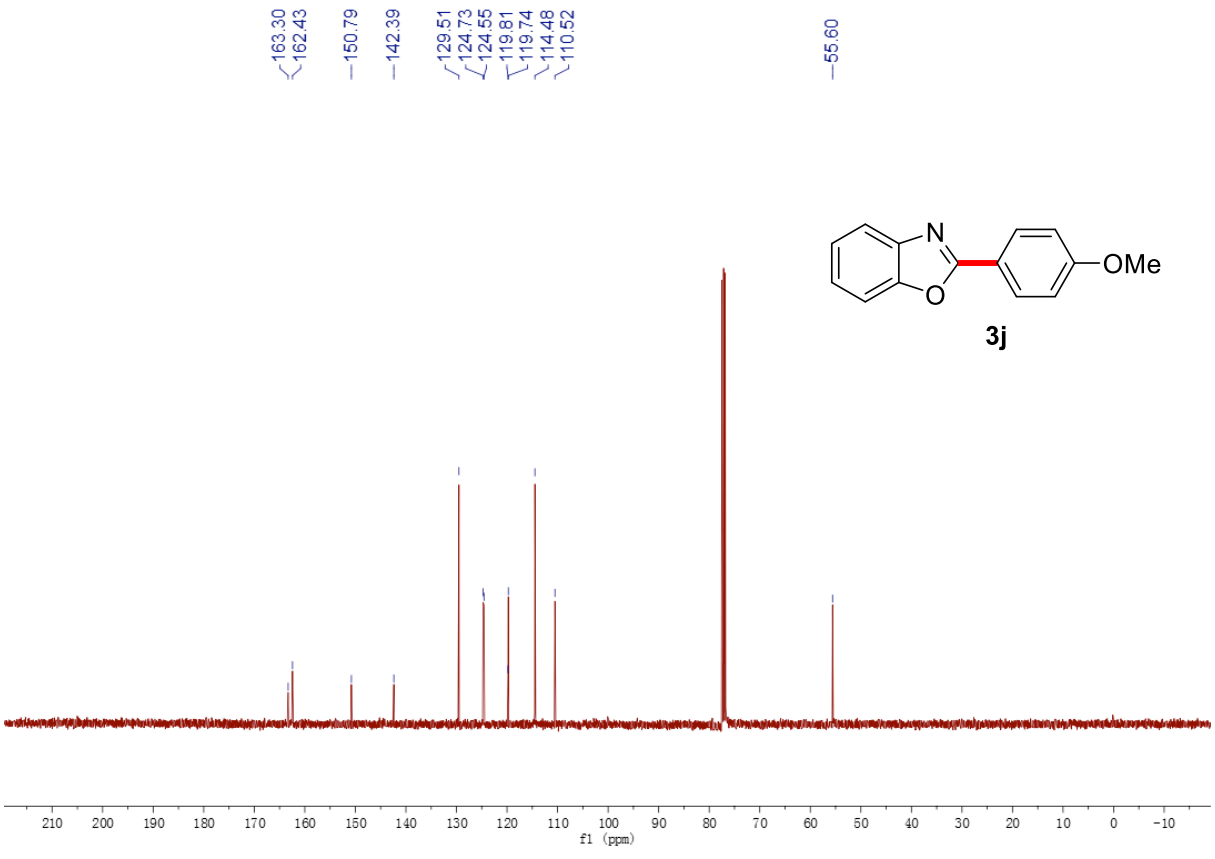

8.380
8.360
7.816
7.813
7.795
7.776
7.622
7.613
7.600
7.423
7.406
7.397
7.387
7.371
N
O
CF3
3h
2.00
3.02
1.00
1.99
f1 (ppm)

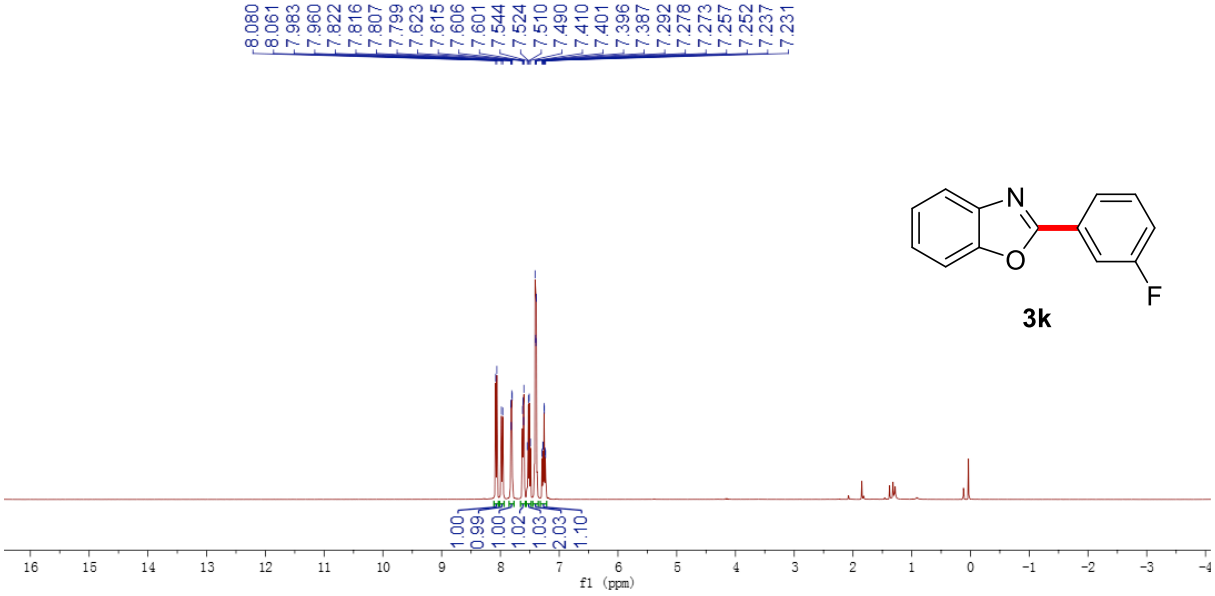

161.70
151.10
142.15
128.09
126.17
126.13
126.10
126.05
125.18
120.65
111.04
N
O
CF3
3h
f1 (ppm)

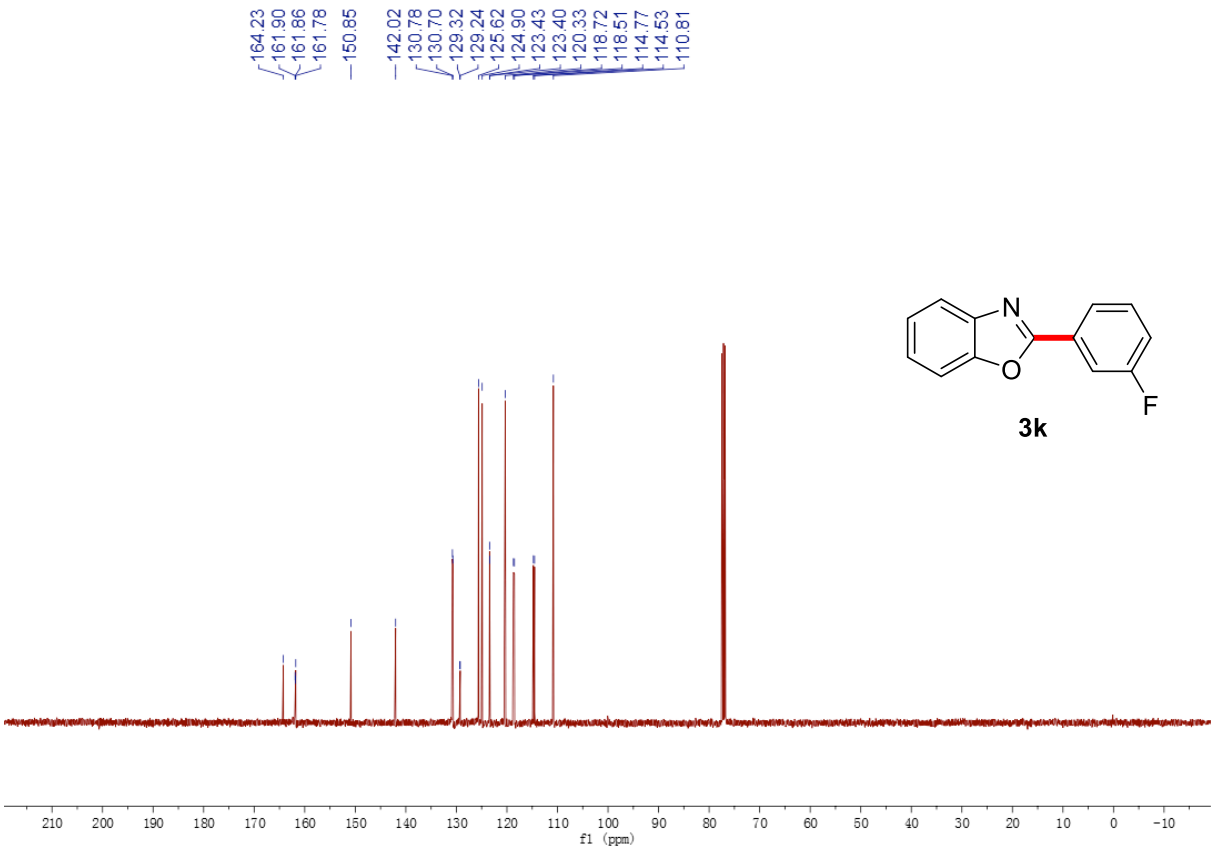

8.731
8.720
8.288
8.270
8.250
7.815
7.795
7.774
7.755
7.740
7.584
7.567
7.352
7.335
7.317
7.308
7.298
7.280
N
O
N
3i
0.96
1.00
2.03
1.00
3.03
f1 (ppm)


161.53
151.13
150.40
146.13
141.84
137.20
126.15
125.68
125.04
123.53
120.73
111.34
N
O
N
3i
f1 (ppm)

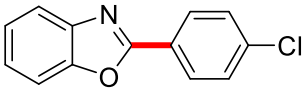

8.210
8.188
7.759
7.750
7.744
7.738
7.730
7.728
7.709
7.567
7.563
7.556
7.550
7.544
7.353
7.335
7.326
7.317
7.298
7.041
7.019
3.891
N
O
OMe
3j
2.06
1.00
1.03
2.04
2.07
3.07
f1 (ppm)


163.30
162.43
150.79
142.39
129.51
124.73
124.55
119.81
119.74
114.48
110.52
55.60
N
O
OMe
3j
f1 (ppm)

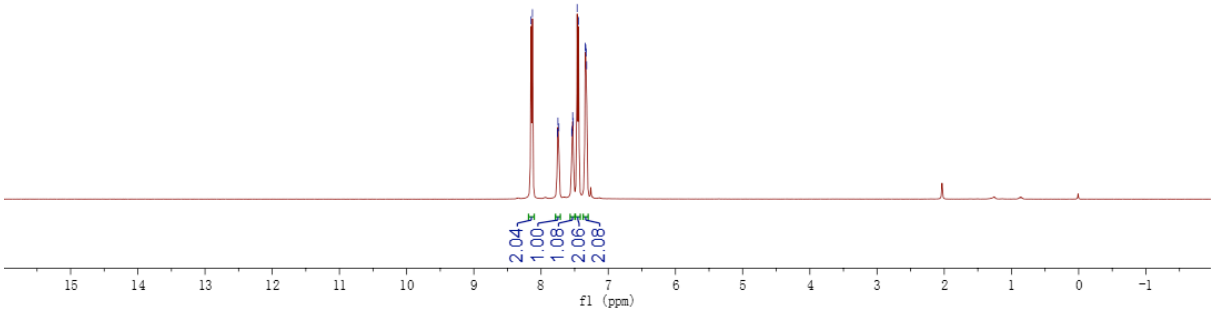

8.080
8.061
7.983
7.960
7.822
7.816
7.807
7.799
7.623
7.615
7.606
7.601
7.544
7.524
7.510
7.490
7.410
7.401
7.396
7.387
7.292
7.278
7.273
7.257
7.252
7.237
7.231
N
O
F
3k
1.00
0.99
1.00
1.02
1.03
2.03
1.10
f1 (ppm)

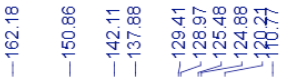

164.23
161.90
161.86
161.78
150.85
142.02
130.78
130.70
129.32
129.24
125.62
124.90
123.43
123.40
120.33
118.72
118.51
114.77
114.53
110.81
N
O
F
3k
f1 (ppm)

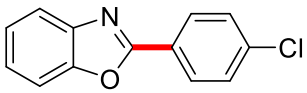

8.149
8.128
7.757
7.749
7.735
7.543
7.537
7.529
7.521
7.463
7.441
7.343
7.335
7.329
7.321


N
O
Cl

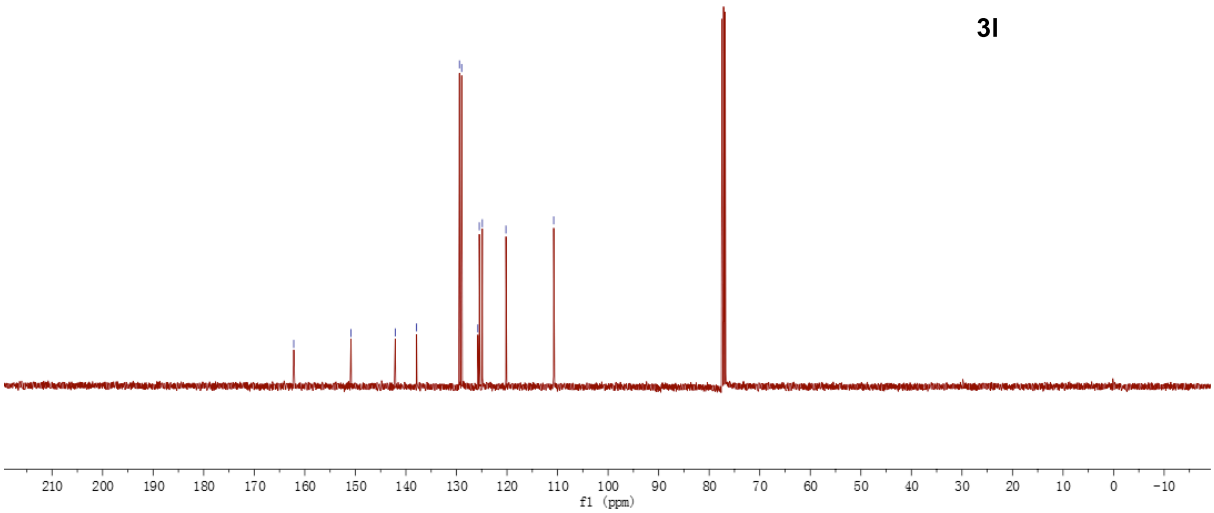
3l

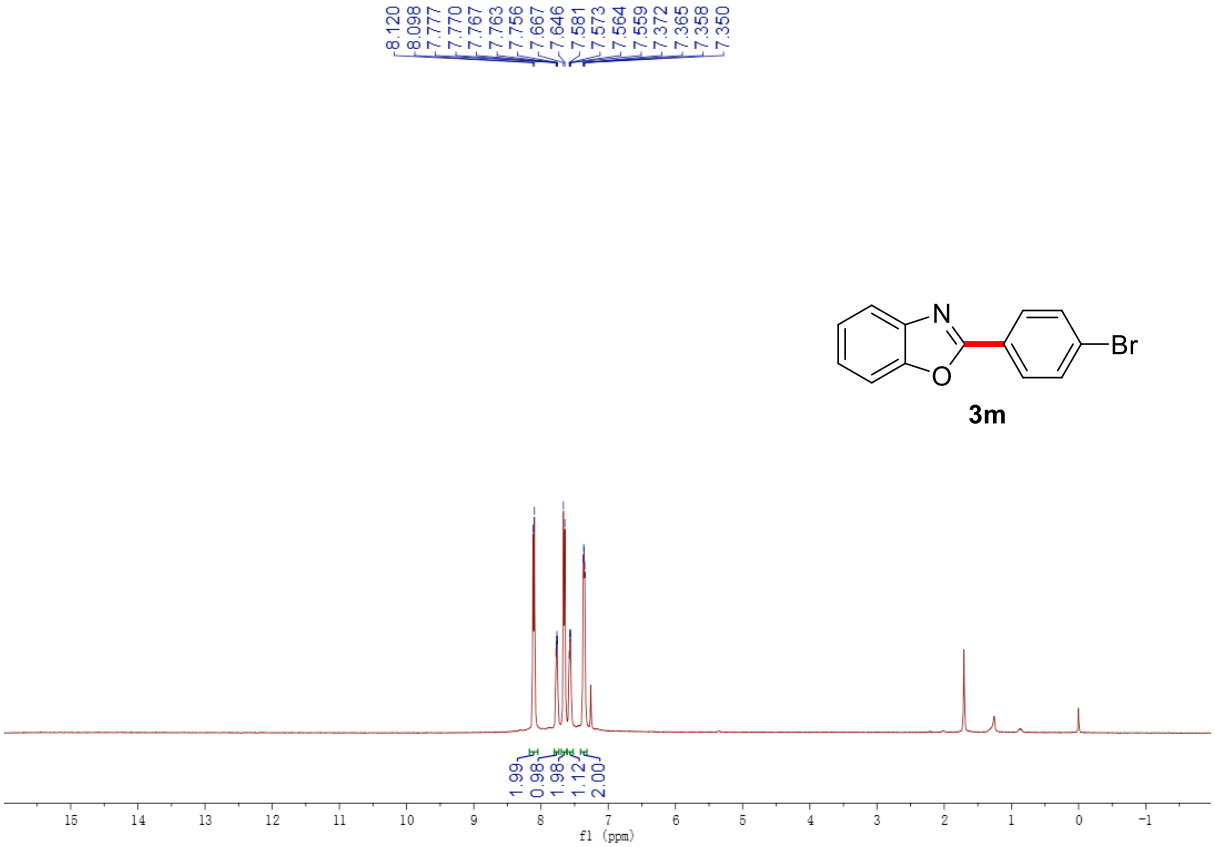

2.04
1.00
1.08
2.06
2.08
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

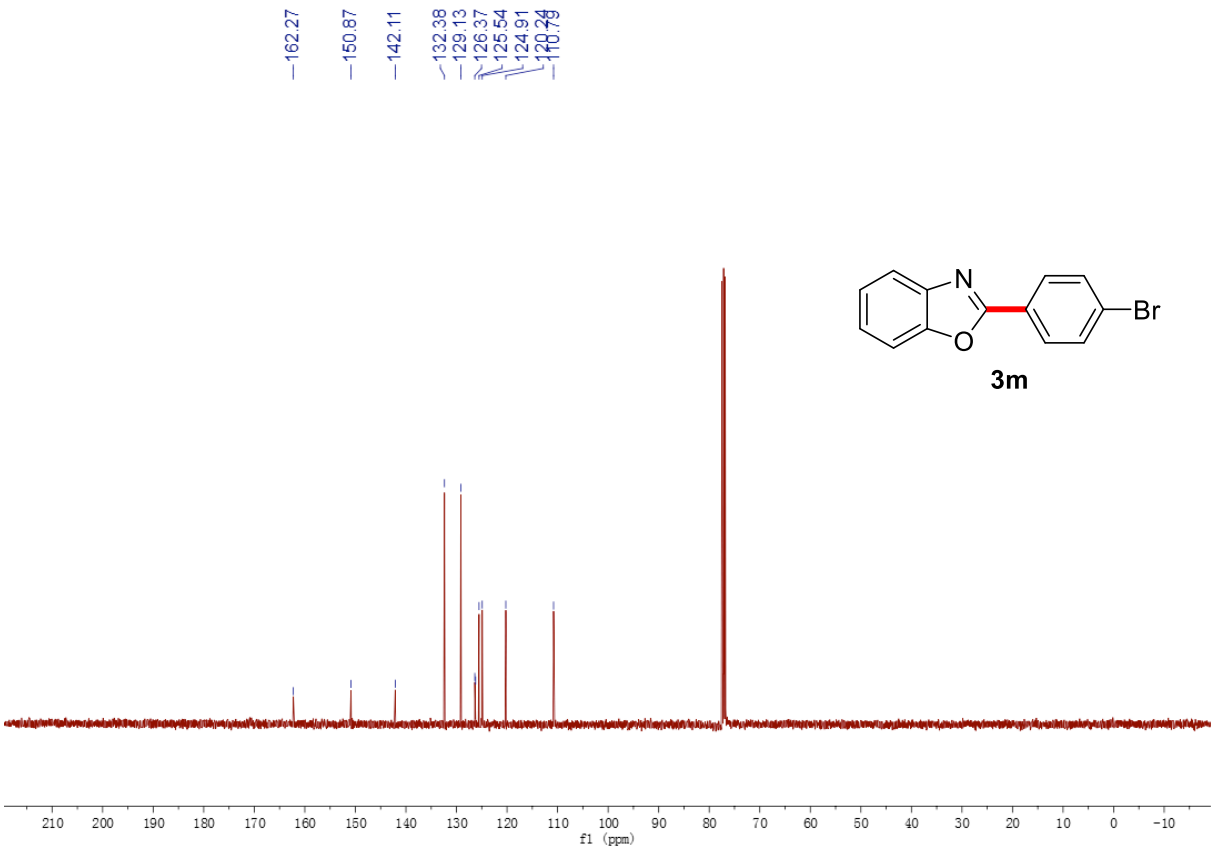

162.18
150.86
142.11
137.88
129.41
128.97
125.48
124.88
120.21
110.71


N
O
Cl

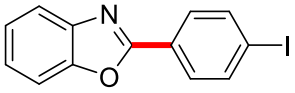
3l


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

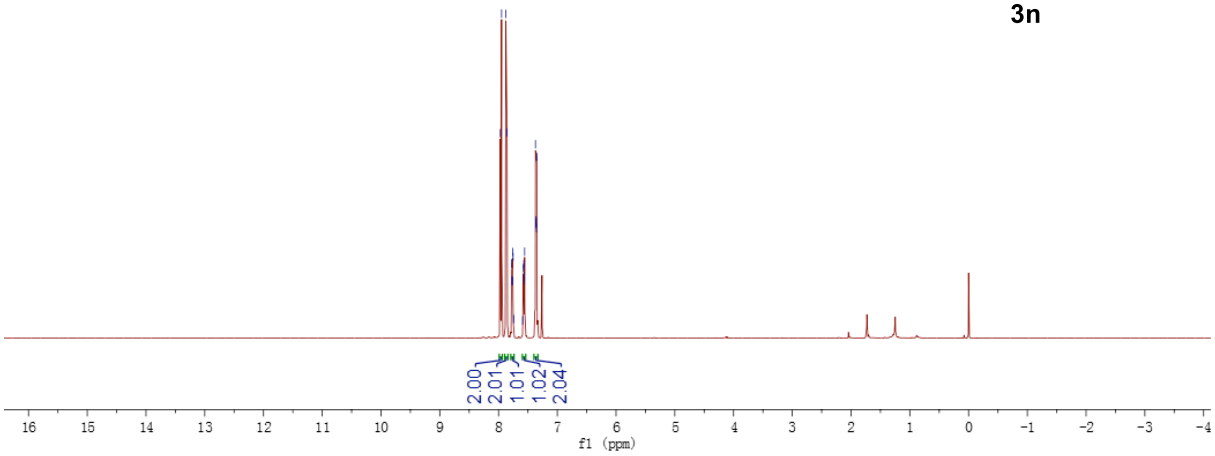

8.120
8.098
7.777
7.770
7.767
7.763
7.756
7.667
7.646
7.581
7.573
7.564
7.559
7.372
7.365
7.358
7.350
N
O
Br
3m
1.99
0.98
1.98
1.12
2.00
f1 (ppm)


162.27
150.87
142.11
132.38
129.13
126.37
125.54
124.91
120.24
110.79
N
O
Br
3m
f1 (ppm)

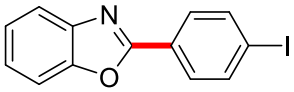

7.969
7.948
7.876
7.854
7.775
7.769
7.765
7.761
7.752
7.742
7.589
7.578
7.570
7.566
7.561
7.555
7.372
7.365
7.362
7.358
7.355
7.349


N
O
I

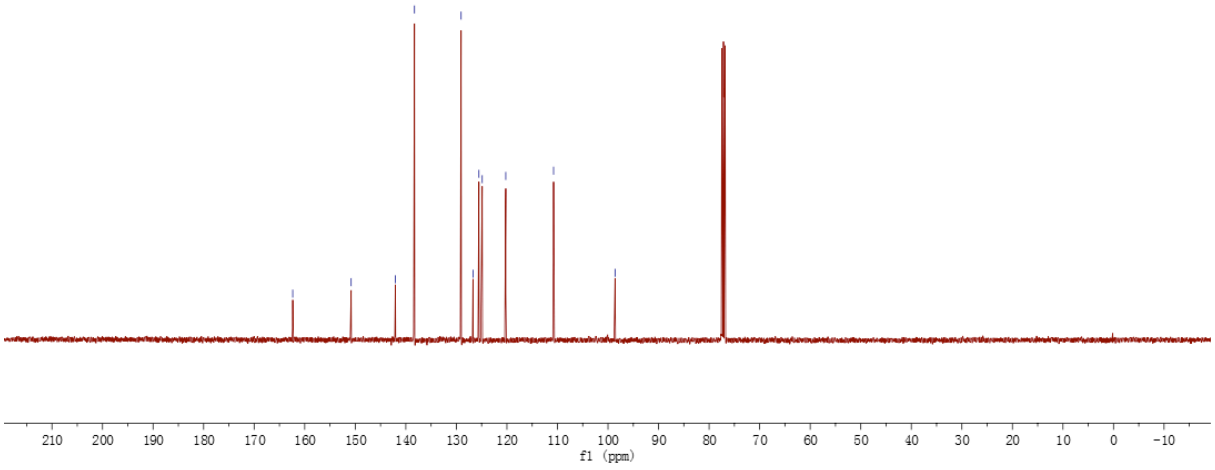
3n

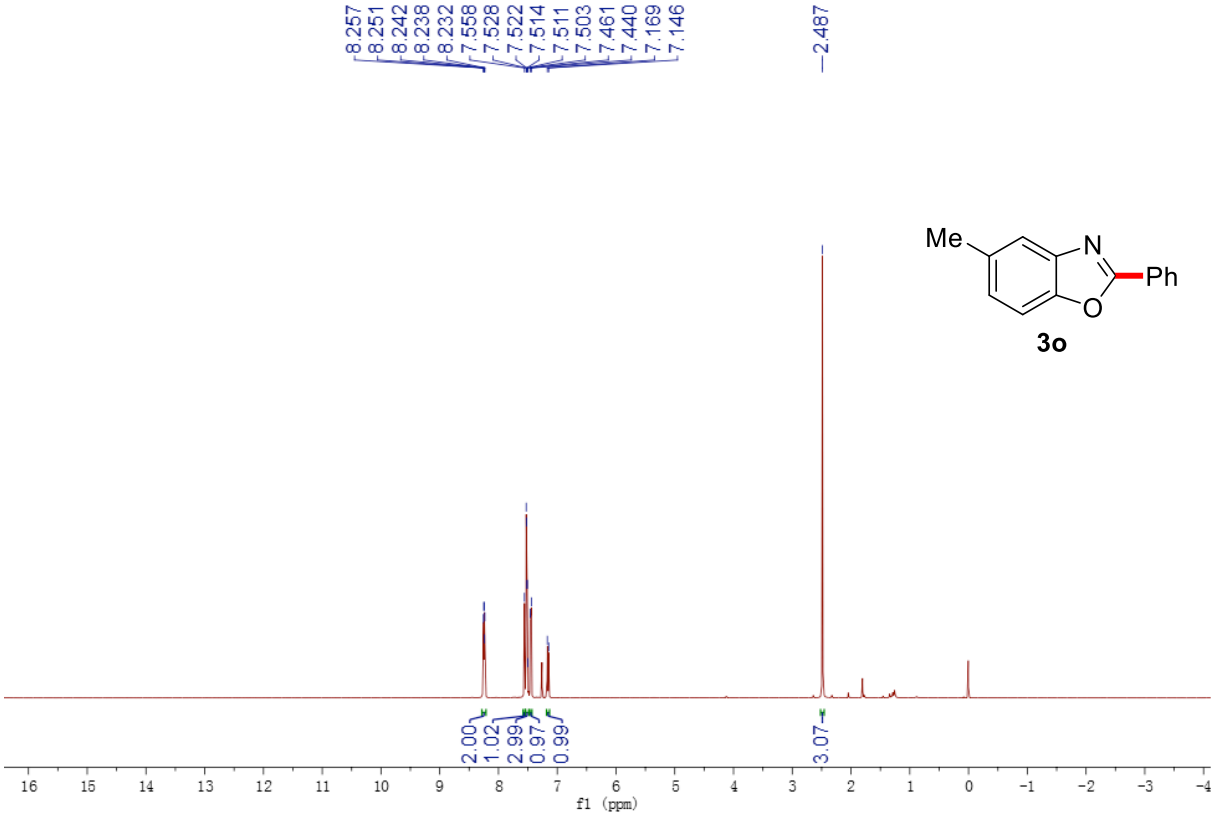

2.00
2.01
1.01
1.02
2.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

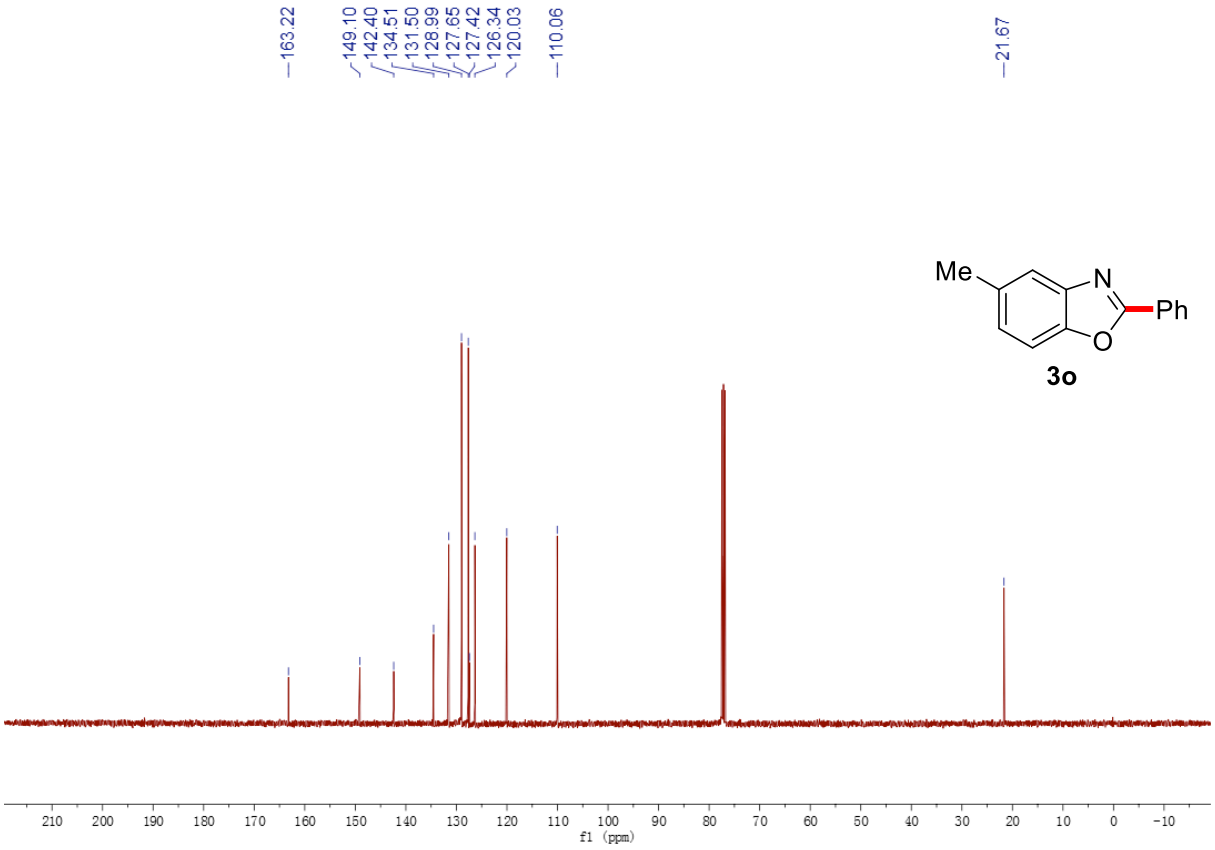

162.37
150.81
142.06
138.28
129.06
126.71
125.54
124.88
120.22
110.77
98.61

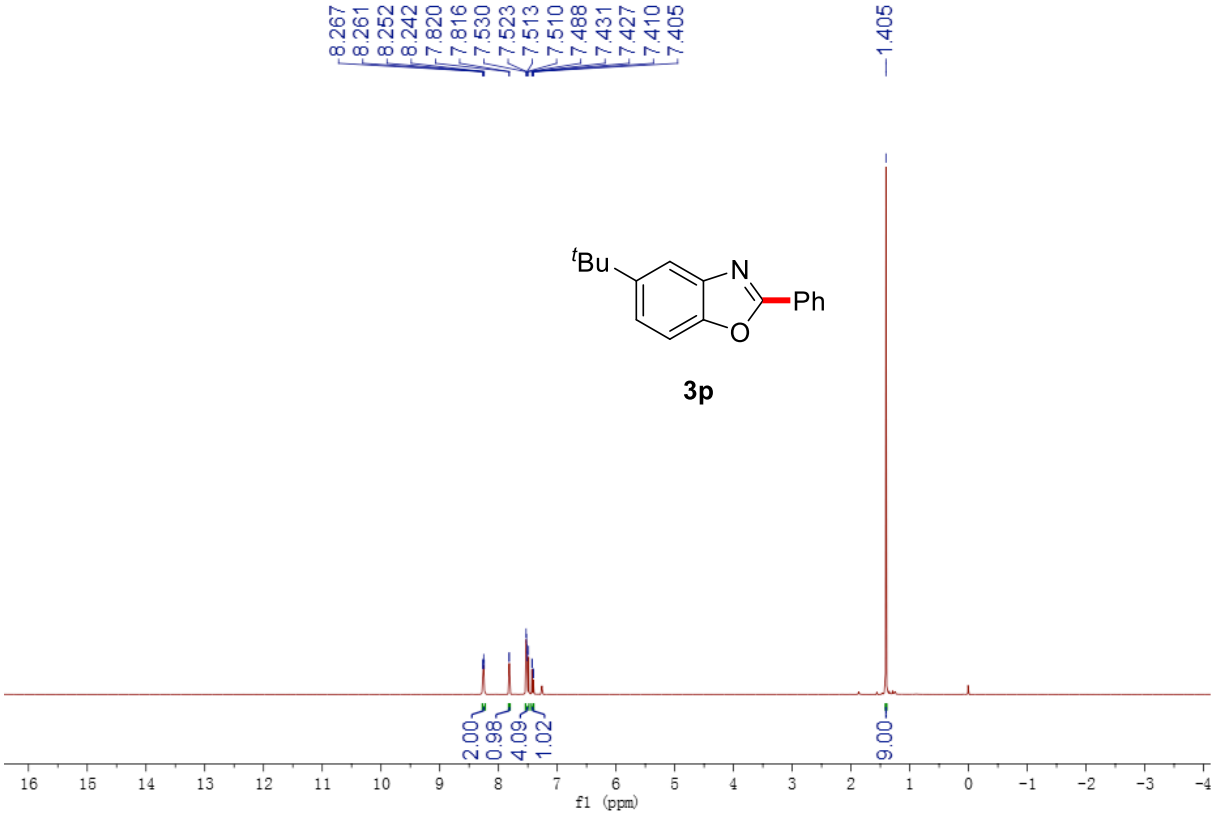

N
O
I

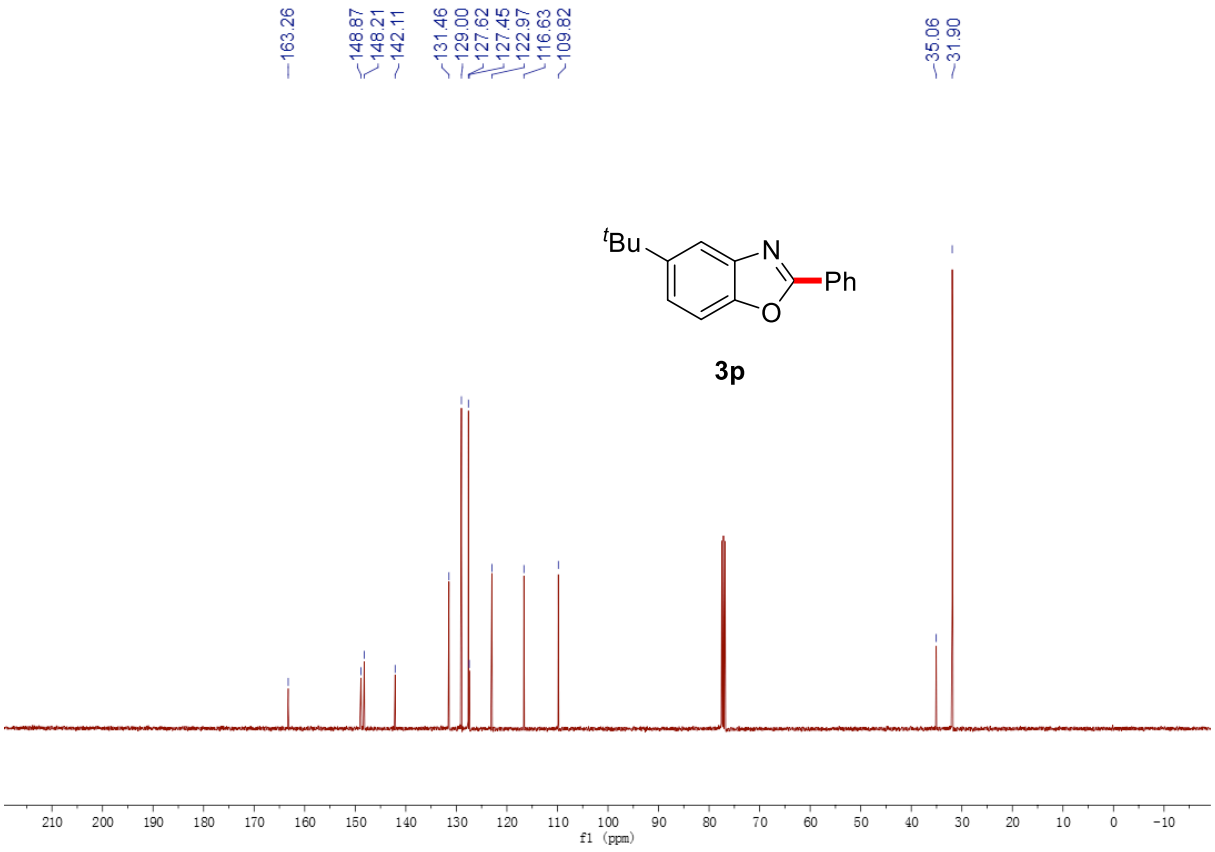
3n


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

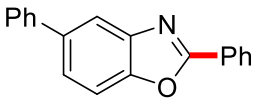

8.257
8.251
8.242
8.238
8.232
7.558
7.528
7.522
7.514
7.511
7.503
7.461
7.440
7.169
7.146
2.487
Me
N
Ph
O
3o
2.00
1.02
2.99
0.97
0.99
3.07
f1 (ppm)


163.22
149.10
142.40
134.51
131.50
128.99
127.65
127.42
126.34
120.03
110.06
21.67
Me
N
Ph
O
3o
f1 (ppm)

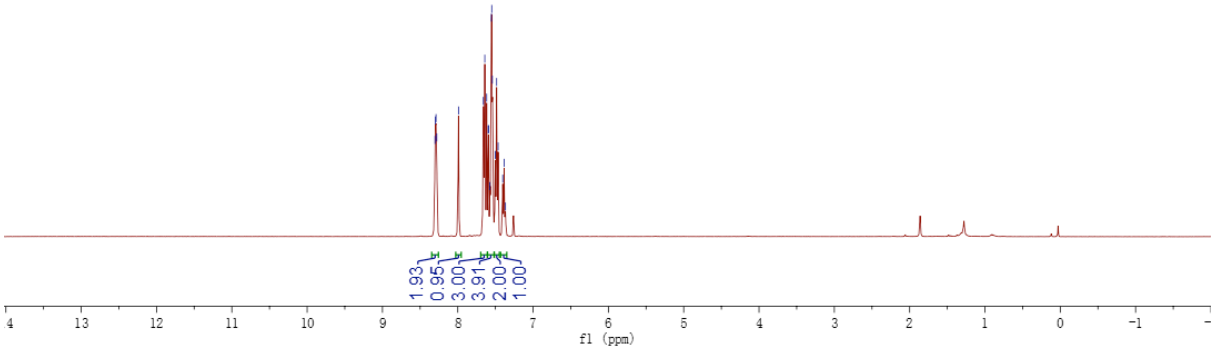

8.267
8.261
8.252
8.242
7.820
7.816
7.530
7.523
7.513
7.510
7.488
7.431
7.427
7.410
7.405
1.405
tBu
N
Ph
O
3p
2.00
0.98
4.09
1.02
9.00
f1 (ppm)


163.26
148.87
148.21
142.11
131.46
129.00
127.62
127.45
122.97
116.63
109.82
35.06
31.90
tBu
N
Ph
O
3p
f1 (ppm)

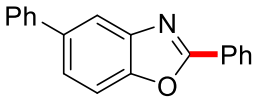

8.302
8.298
8.289
8.279
7.990
7.660
7.641
7.616
7.596
7.593
7.575
7.554
7.549
7.541
7.503
7.484
7.465
7.403
7.385
7.367


Ph
N
Ph
O

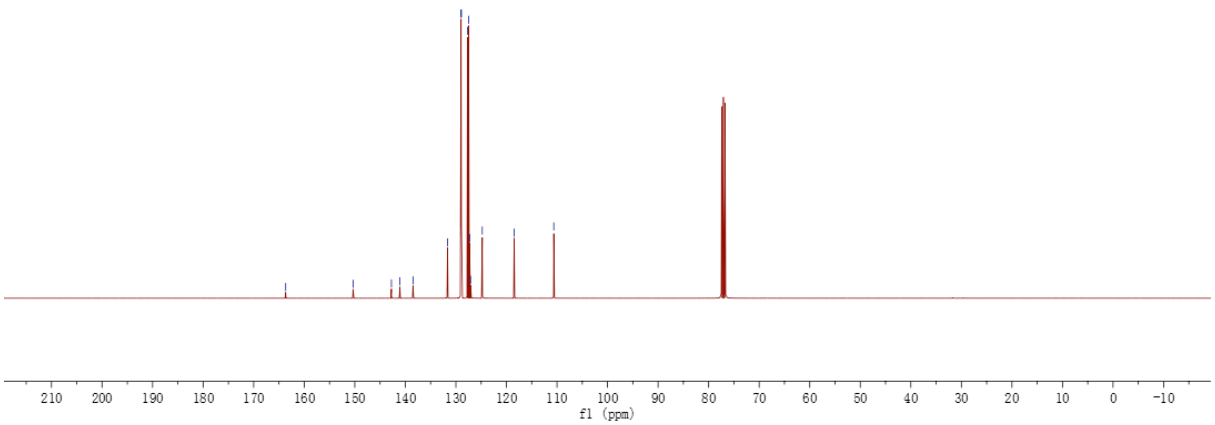
3q


1.93
0.95
3.00
3.91
2.00
1.00
f1 (ppm)

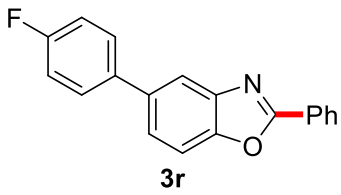

163.67
150.34
142.75
141.07
138.48
131.65
128.98
128.92
127.69
127.48
127.30
127.11
124.78
118.47
110.63


Ph
N
Ph
O

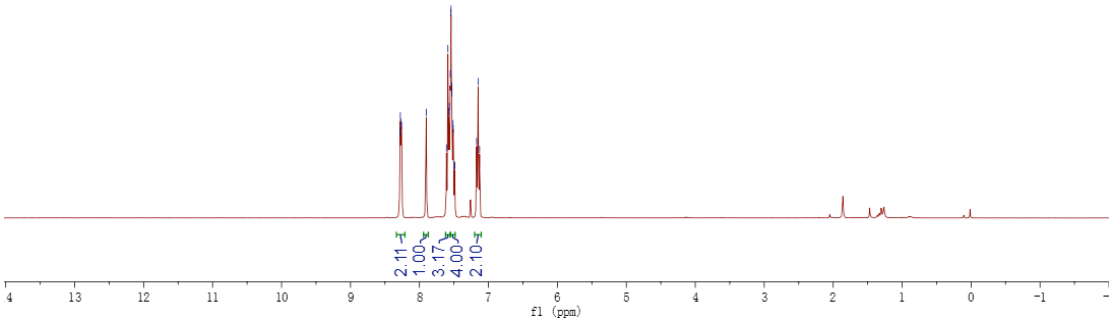
3q


f1 (ppm)

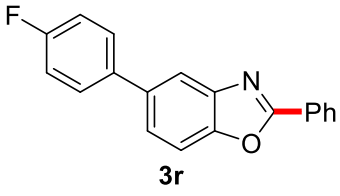

8.282
8.277
8.266
8.258
7.901
7.608
7.587
7.574
7.566
7.553
7.545
7.541
7.533
7.528
7.513
7.509
7.492
7.488
7.171
7.149
7.128


F
N
Ph
O

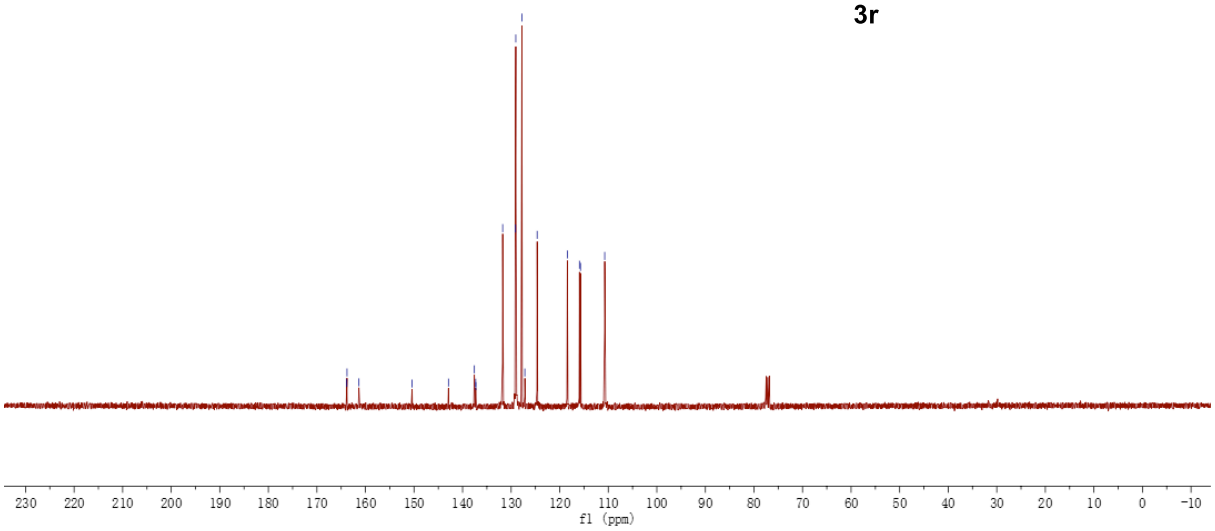
3r

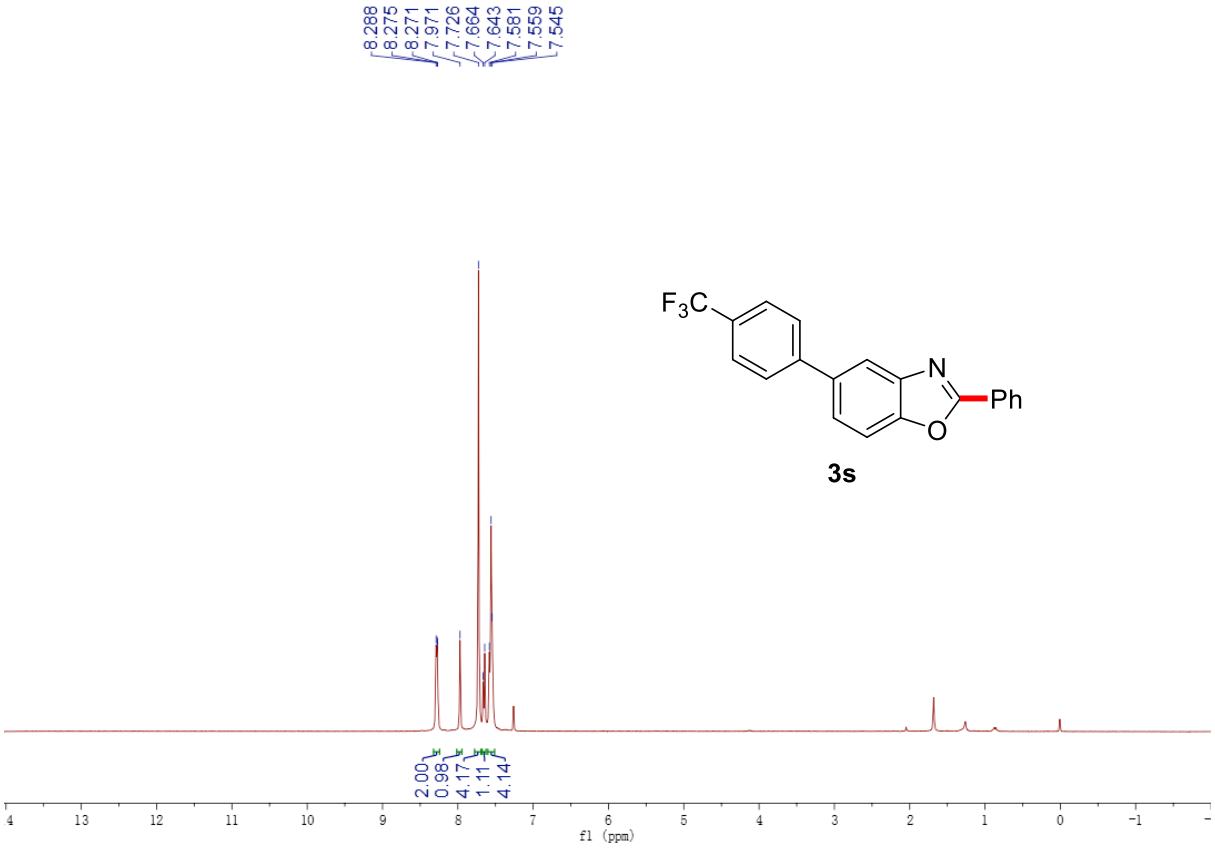

2.11
1.00
3.17
4.00
2.10
f1 (ppm)

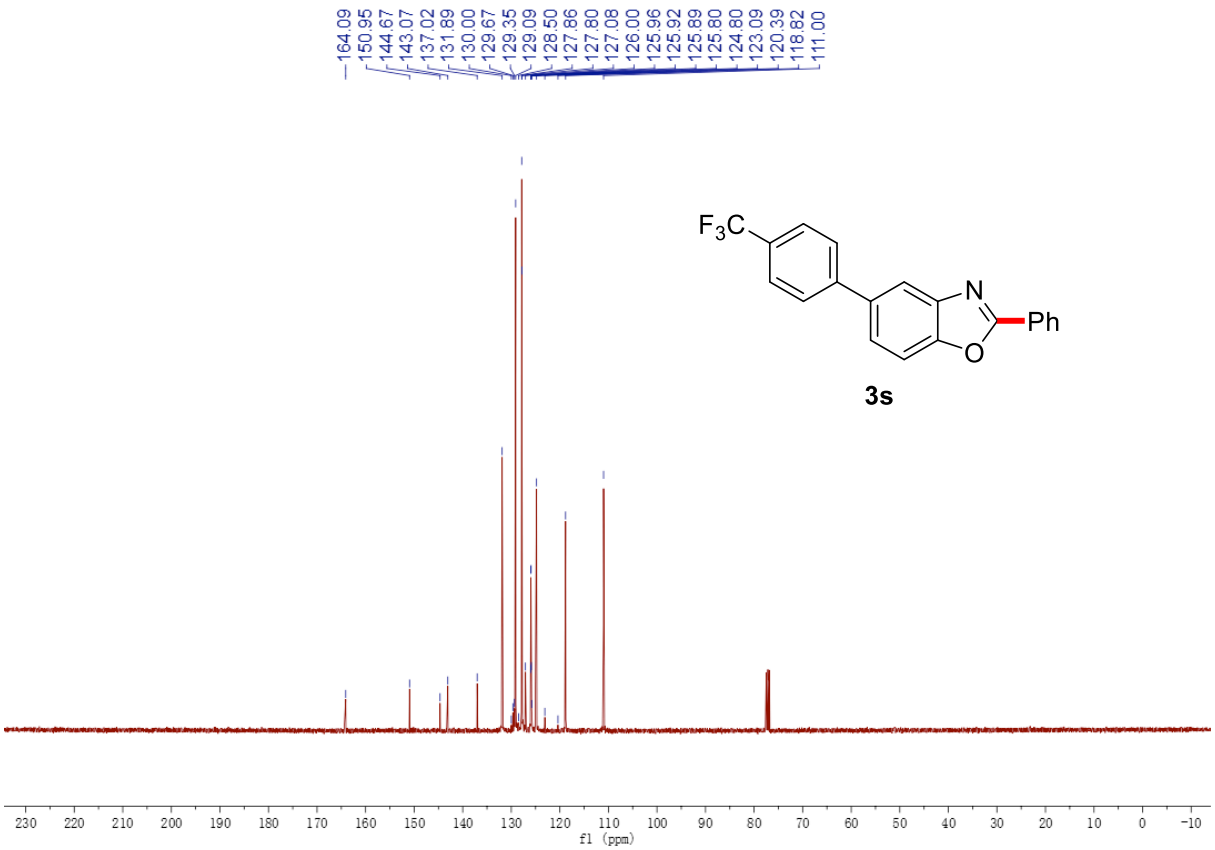

163.85
163.80
161.35
150.40
142.91
137.57
137.30
137.27
131.75
129.10
129.04
127.79
127.18
124.65
118.43
115.94
115.72
110.73

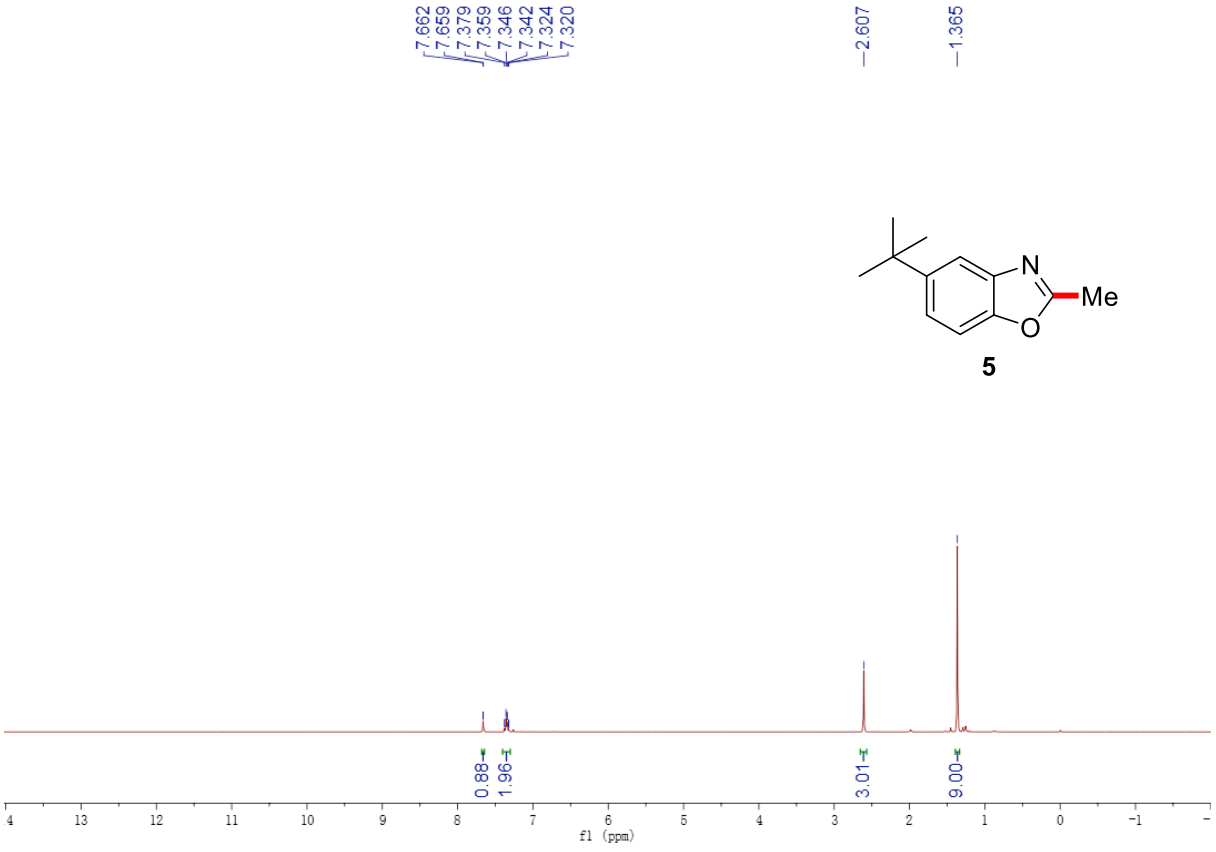

F
N
Ph
O

3r

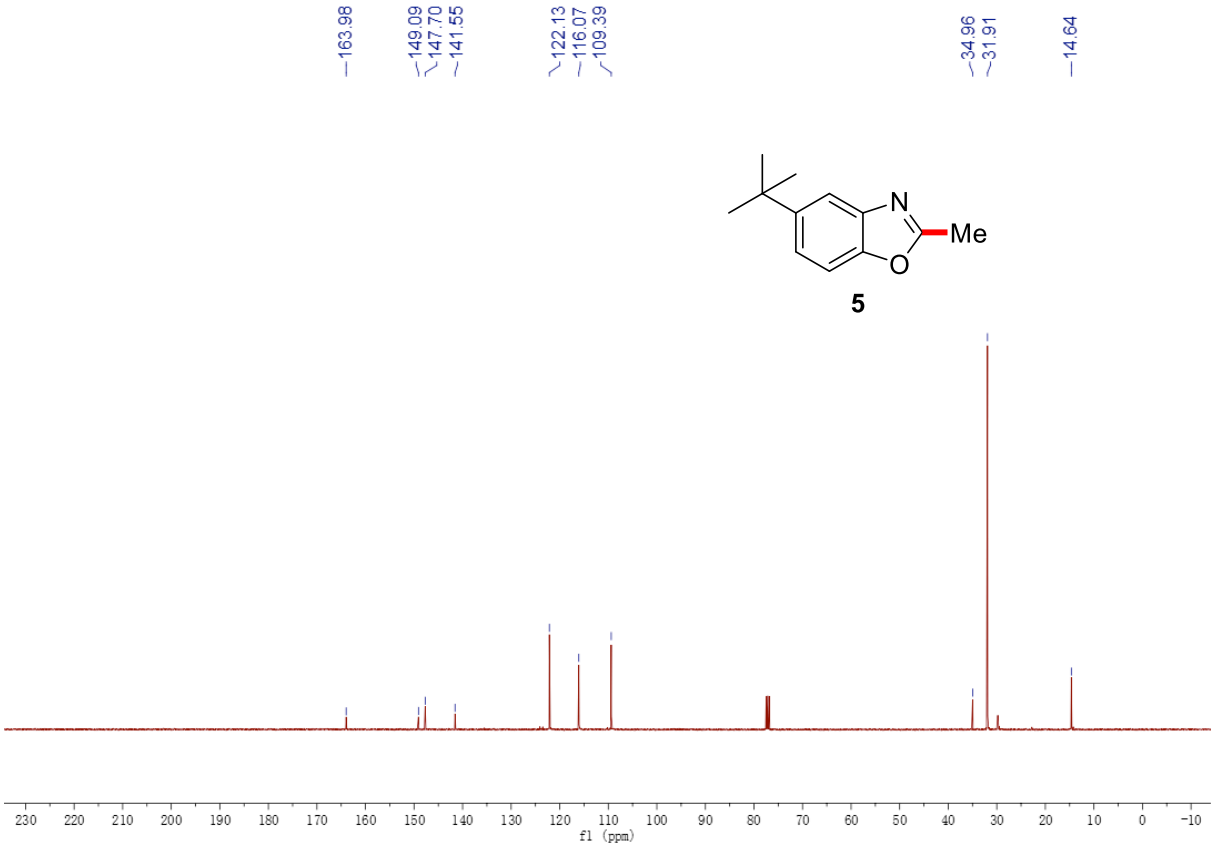

f1 (ppm)


8.288
8.275
8.271
7.971
7.726
7.664
7.643
7.581
7.559
7.545
F3C
N
Ph
O
3s
2.00
0.98
4.17
1.11
4.14
f1 (ppm)

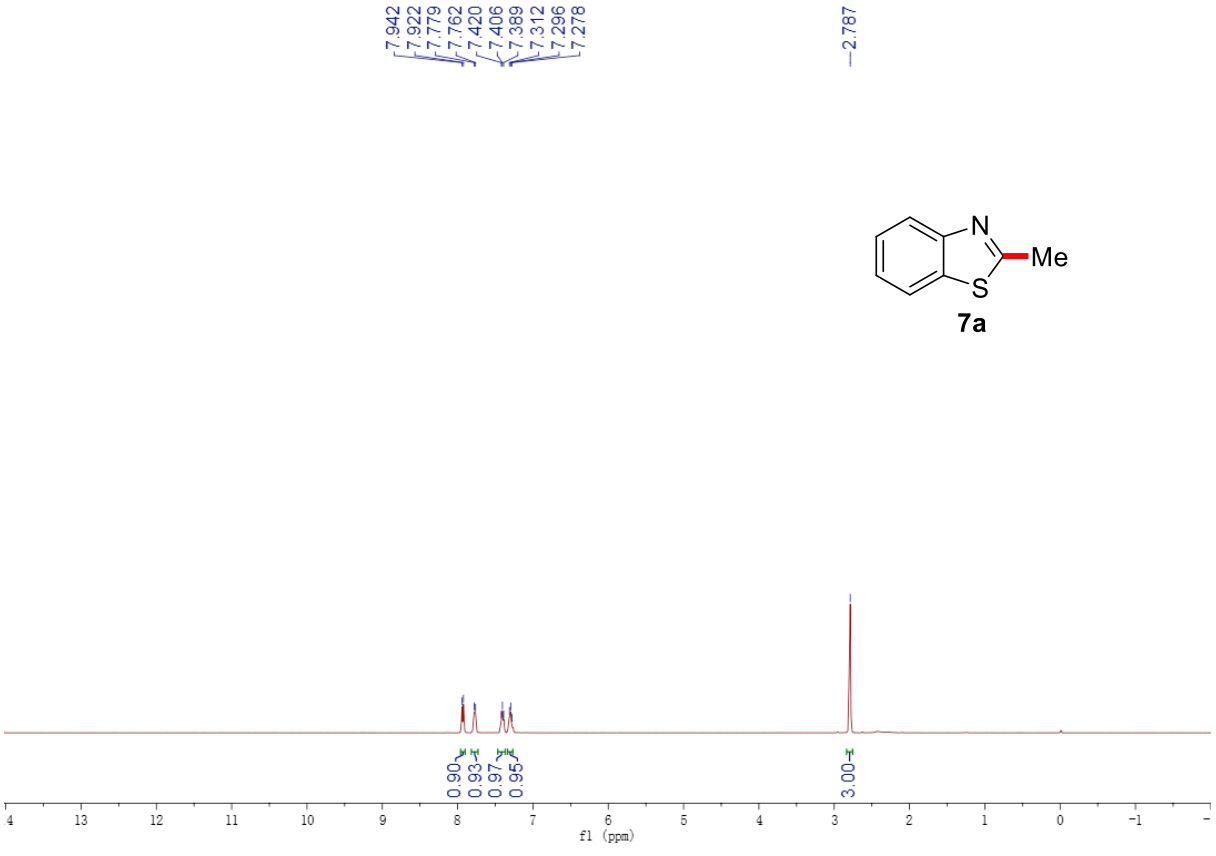

164.09
150.95
144.67
143.07
137.02
131.89
130.00
129.67
129.35
129.09
128.50
127.86
127.80
127.08
126.00
125.96
125.92
125.89
125.80
124.80
123.09
120.39
118.82
111.00
F3C
N
Ph
O
3s
f1 (ppm)

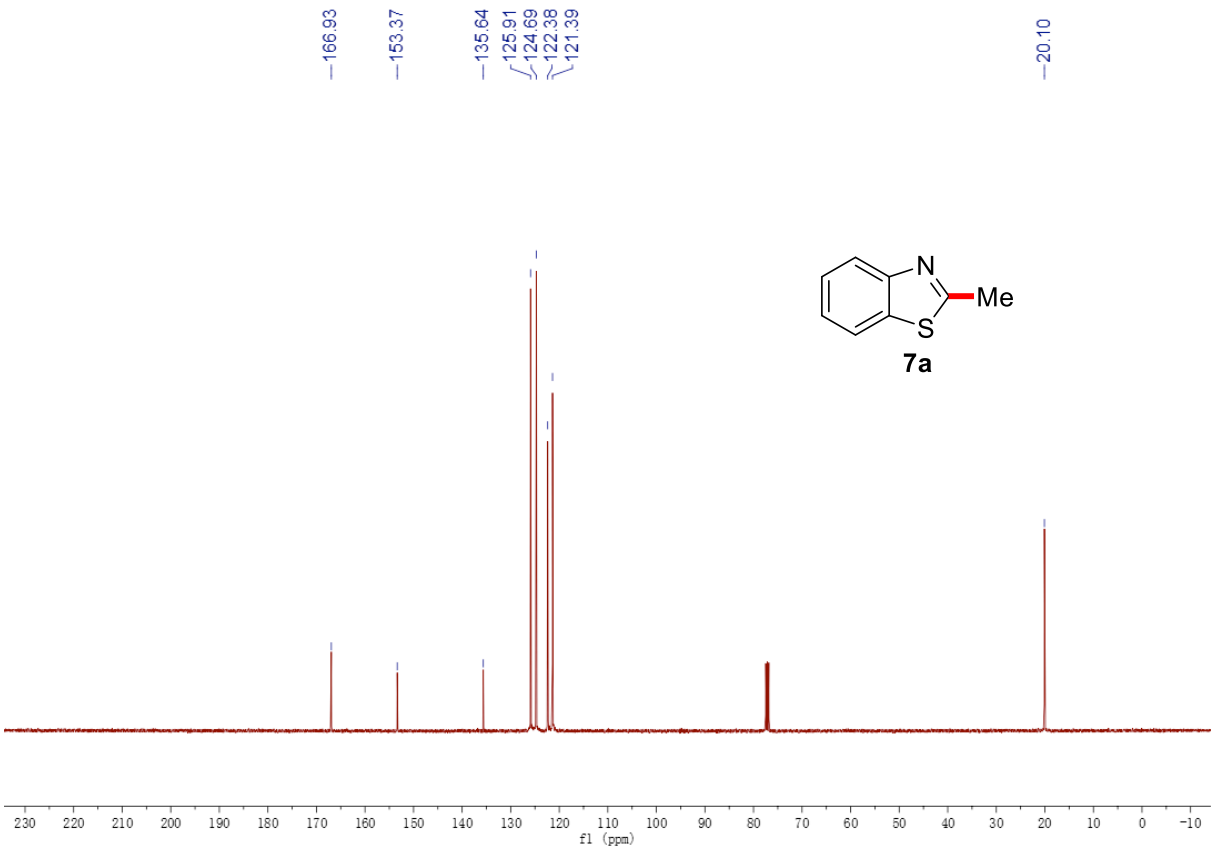

7.662
7.659
7.379
7.359
7.346
7.342
7.324
7.320
2.607
1.365
N
Me
O
0.88
1.96
3.01
9.00
f1 (ppm)

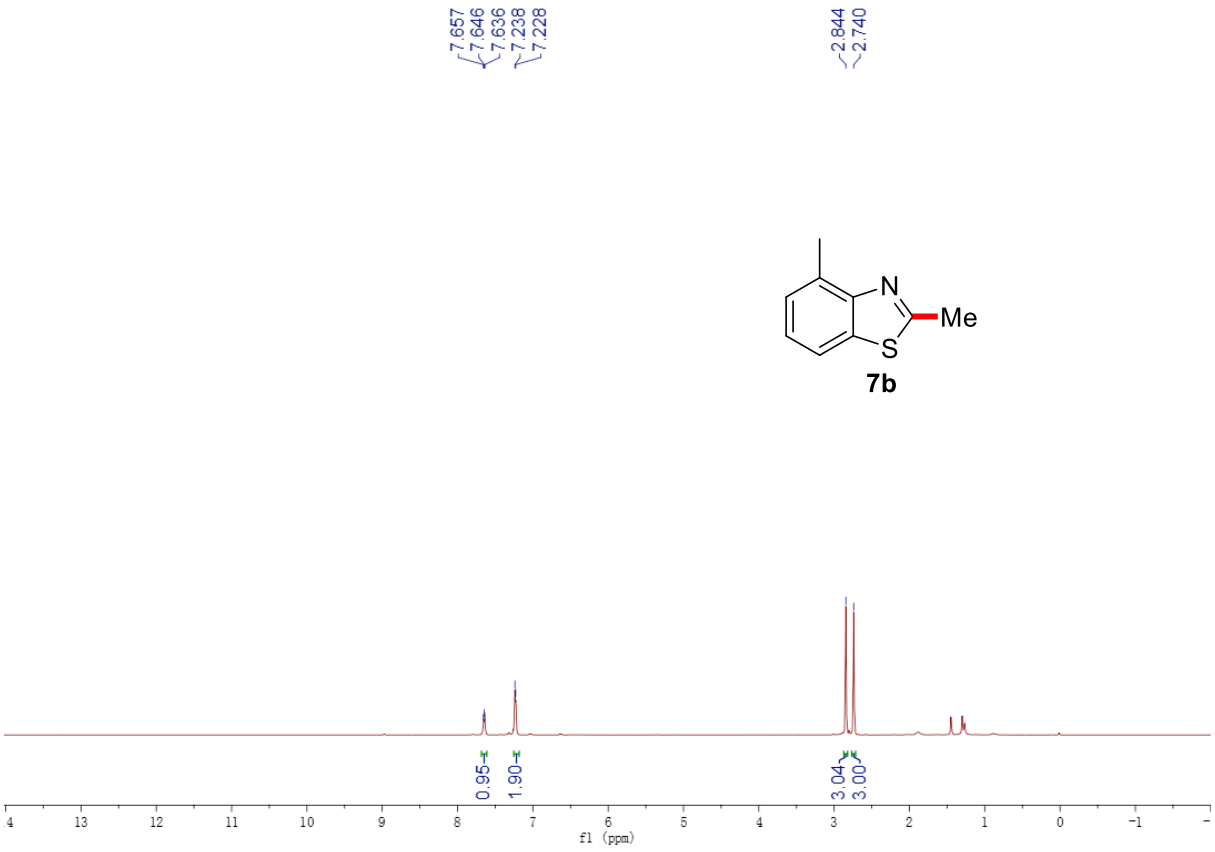
5

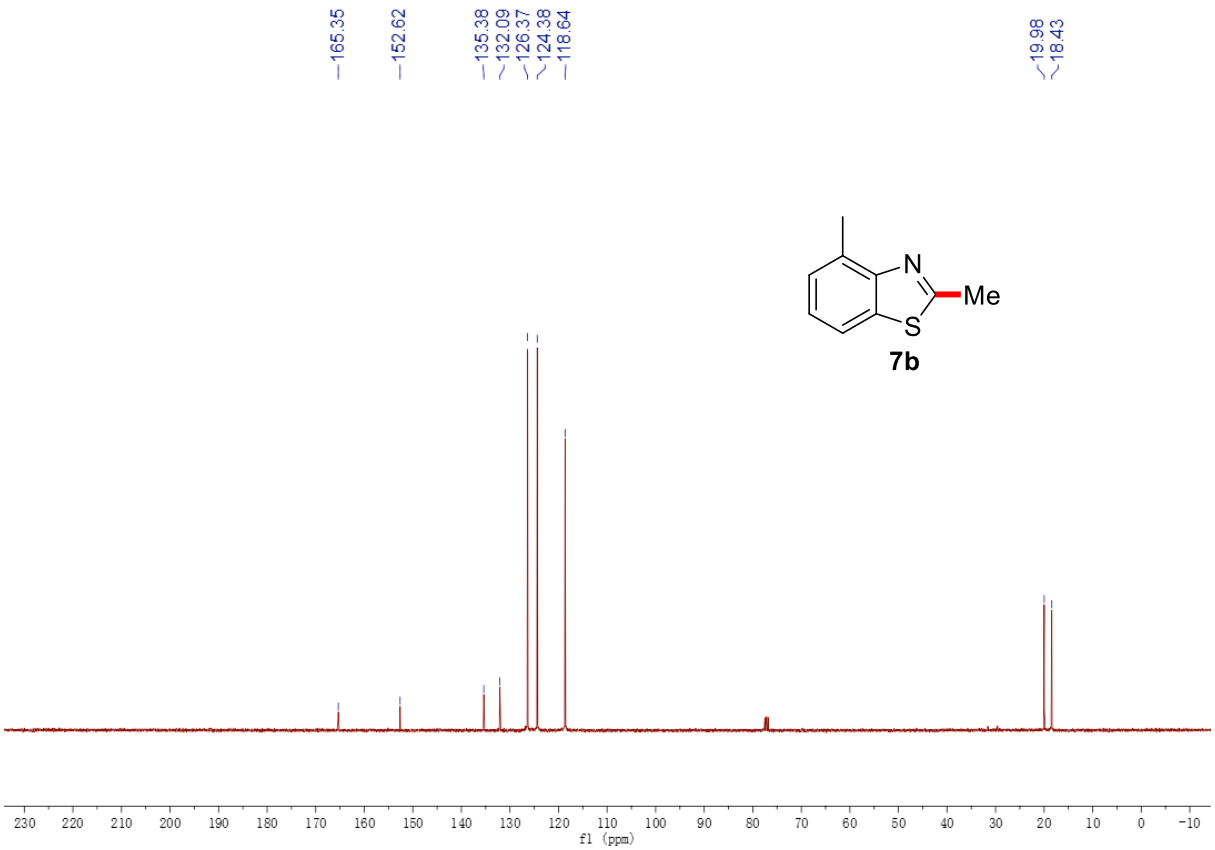

163.98
149.09
147.70
141.55
122.13
116.07
109.39
34.96
31.91
14.64
N
Me
O
f1 (ppm)

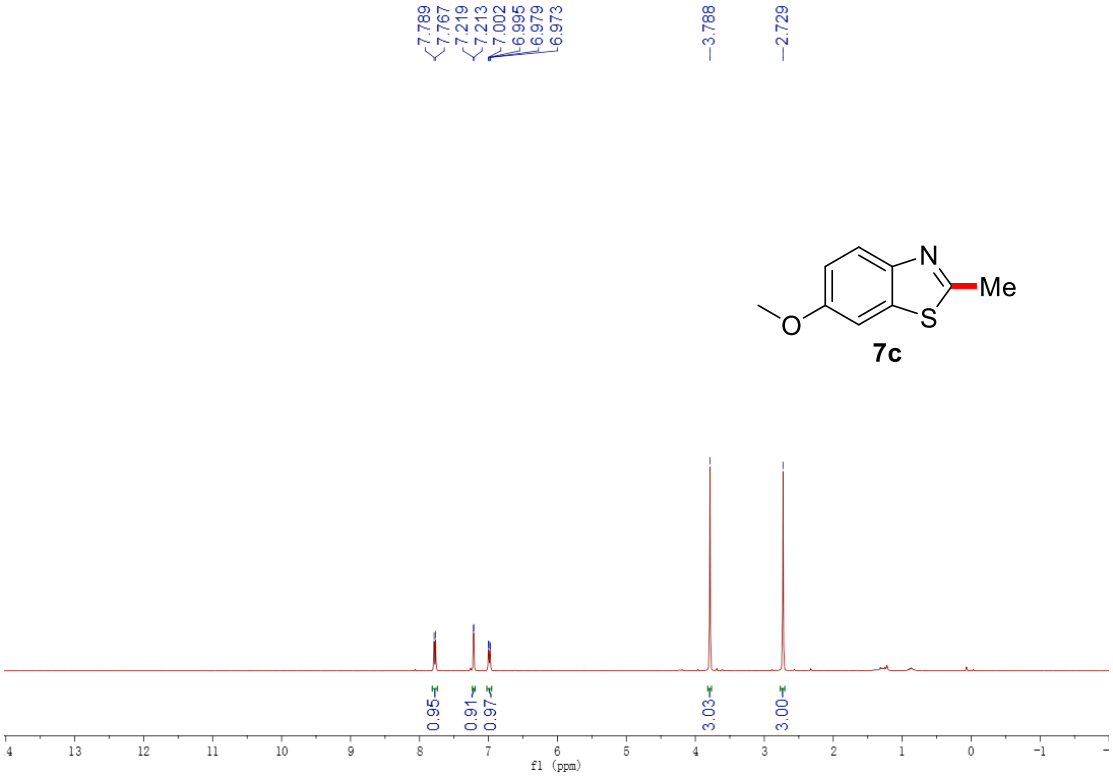
5

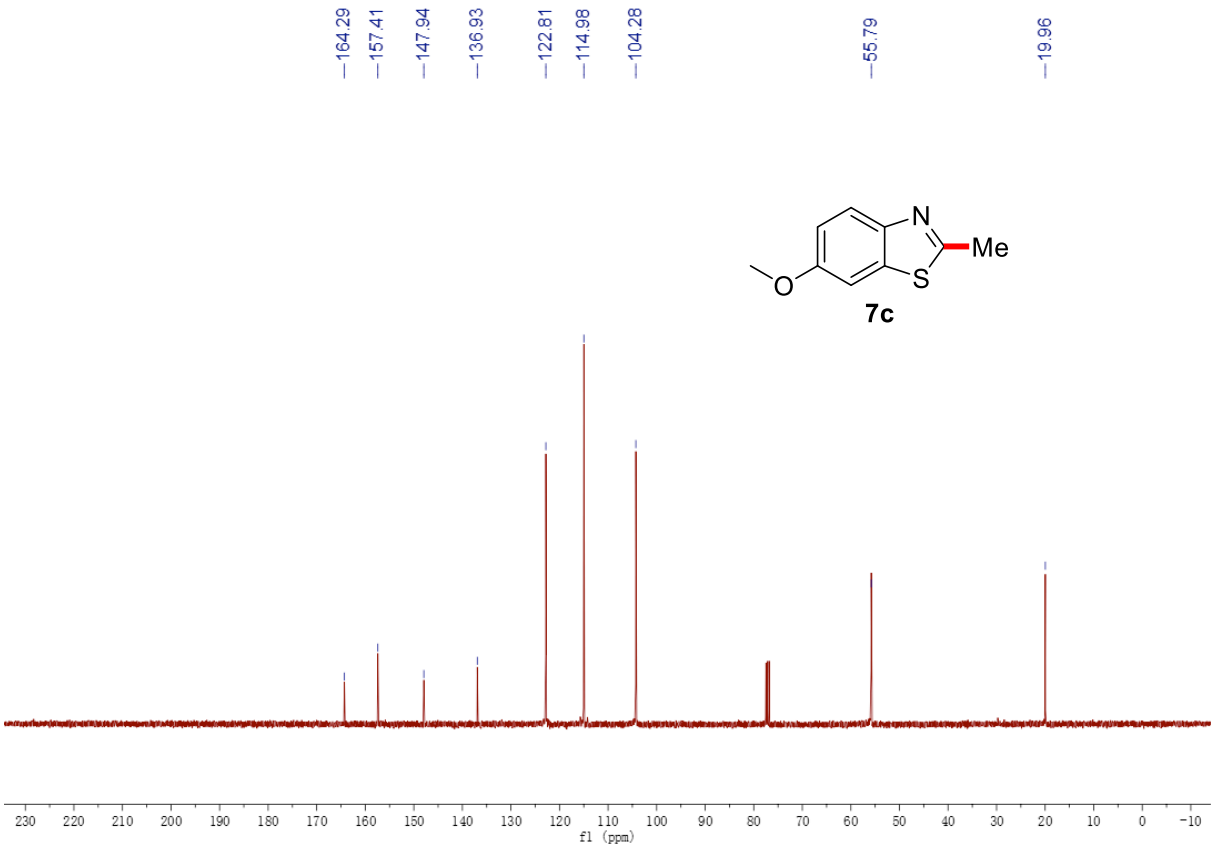

7.942
7.922
7.779
7.762
7.420
7.406
7.389
7.312
7.296
7.278
2.787
N
Me
S
7a
0.90
0.93
0.97
0.95
3.00
f1 (ppm)

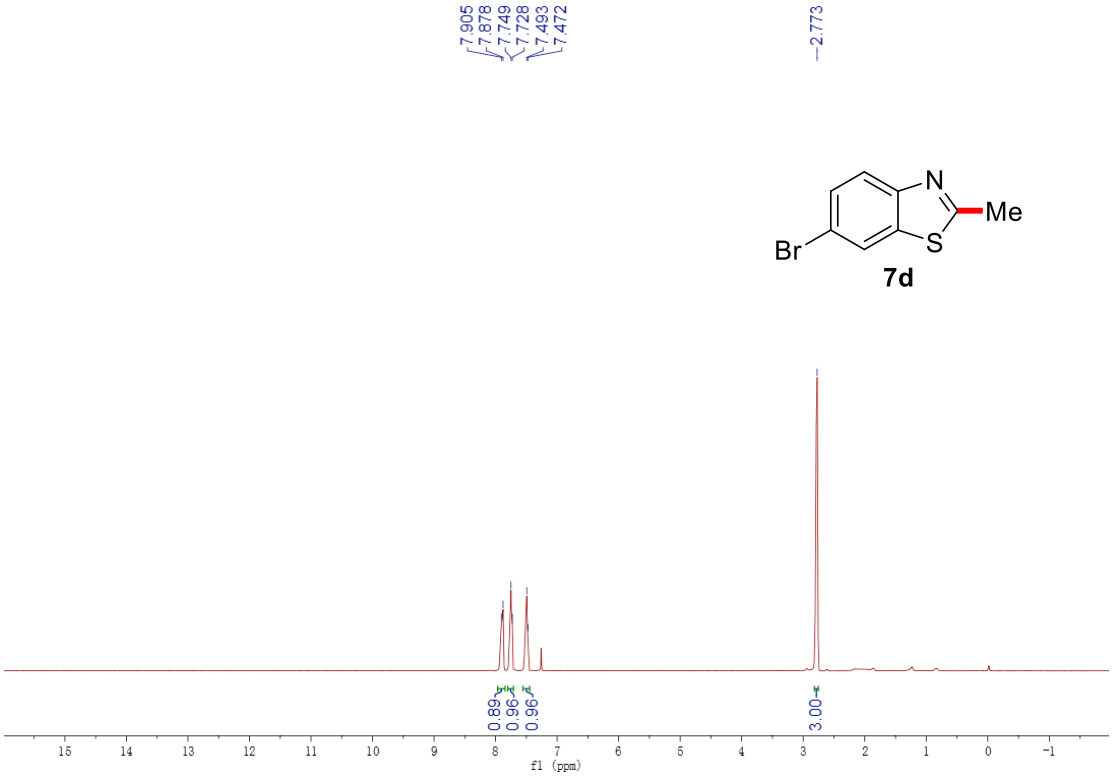

166.93
153.37
135.64
125.91
124.69
122.38
121.39
20.10
N
Me
S
7a
f1 (ppm)

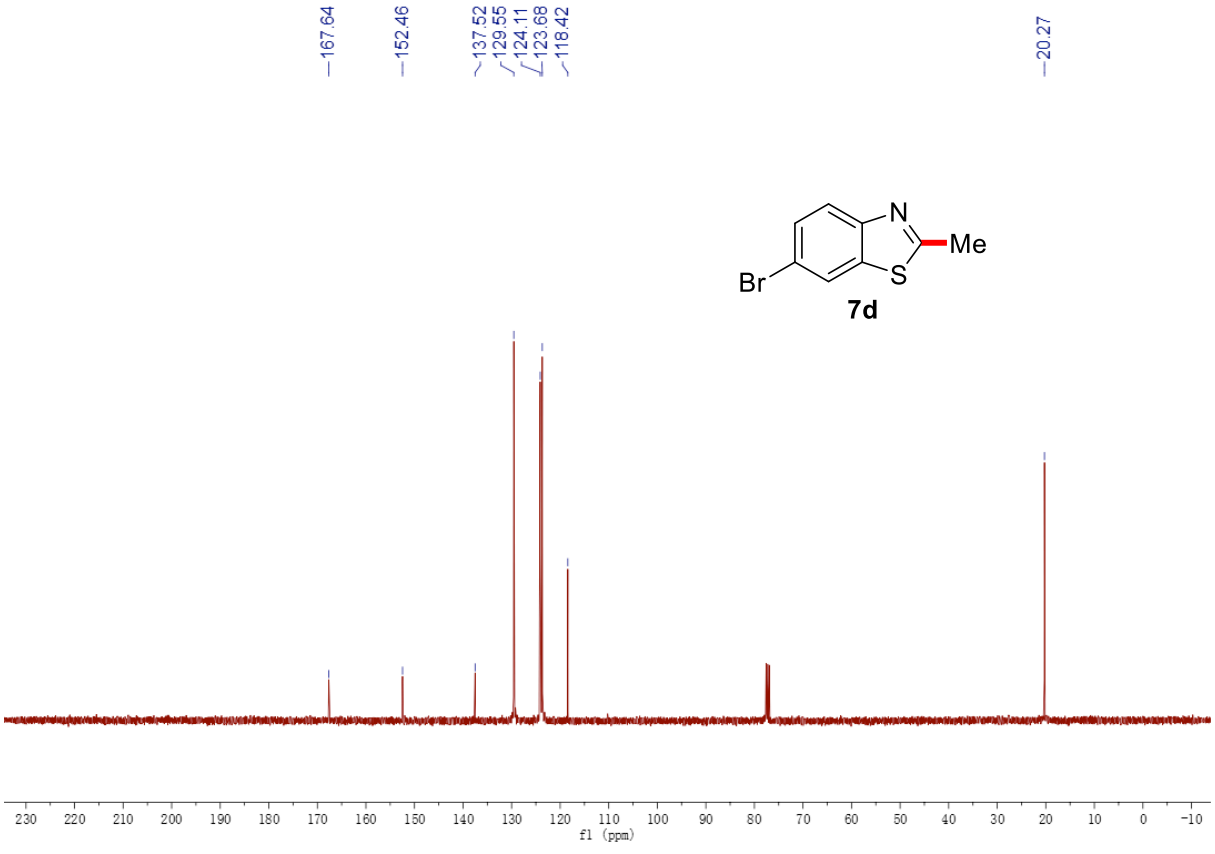

7.657
7.646
7.636
7.238
7.228
2.844
2.740
N
Me
S
7b
0.95
1.90
3.04
3.00
f1 (ppm)

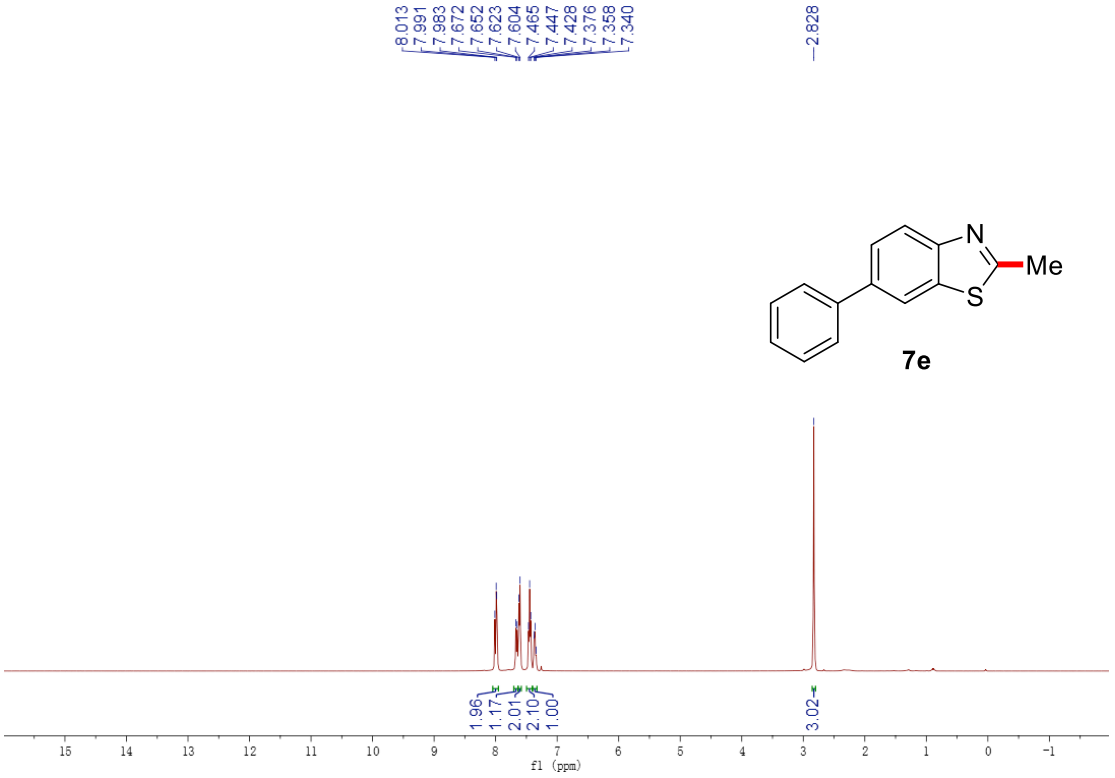

165.35
152.62
135.38
132.09
126.37
124.38
118.64
19.98
18.43
N
Me
S
7b
f1 (ppm)

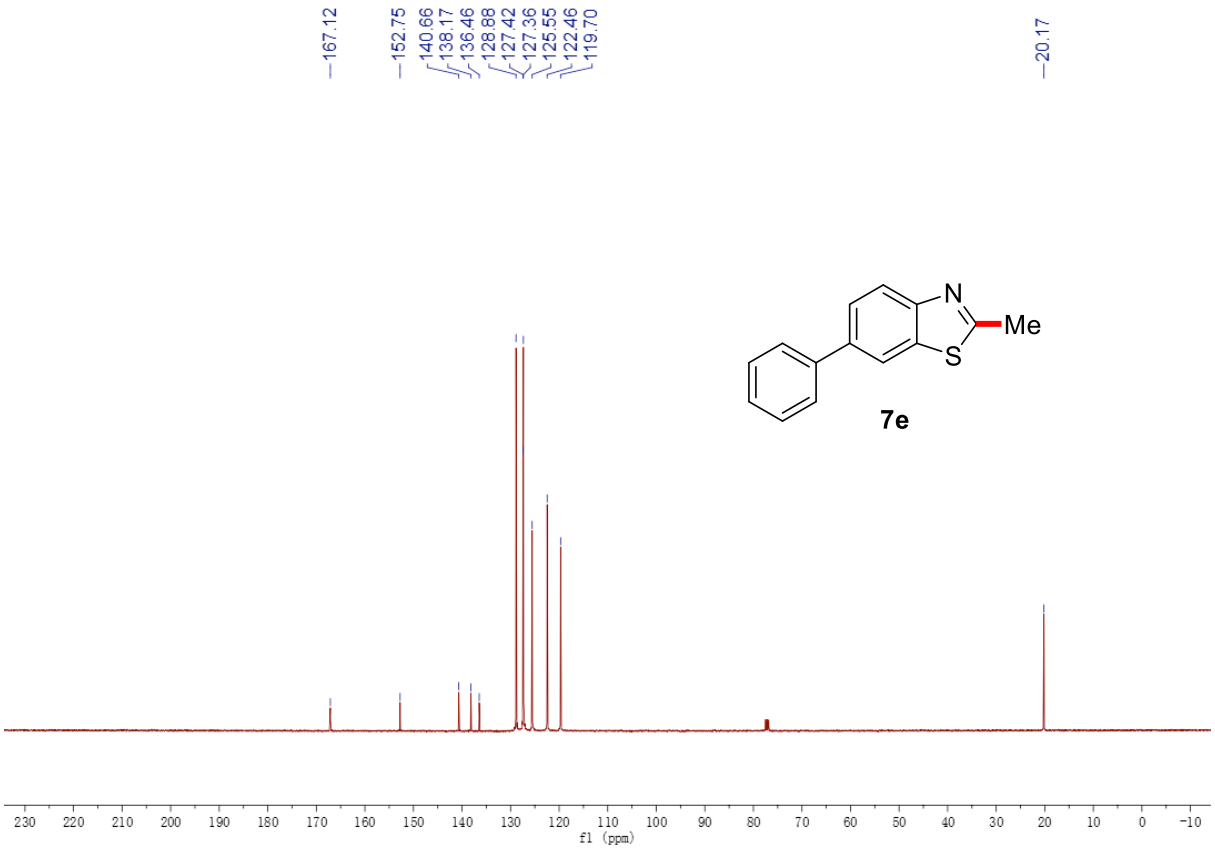

7.789
7.767
7.219
7.213
7.002
6.995
6.979
6.973
3.788
2.729
N
Me
O
S
7c
0.95
0.91
0.97
3.03
3.00
f1 (ppm)

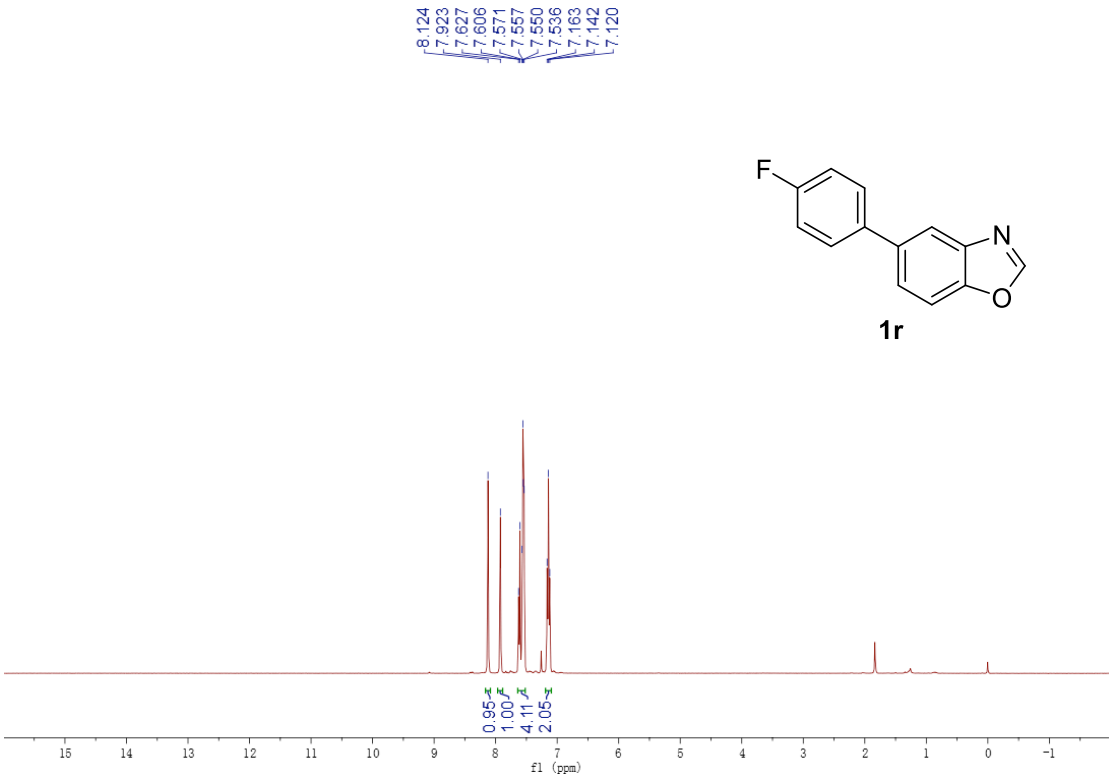

164.29
157.41
147.94
136.93
122.81
114.98
104.28
55.79
19.96
N
Me
O
S
7c
f1 (ppm)

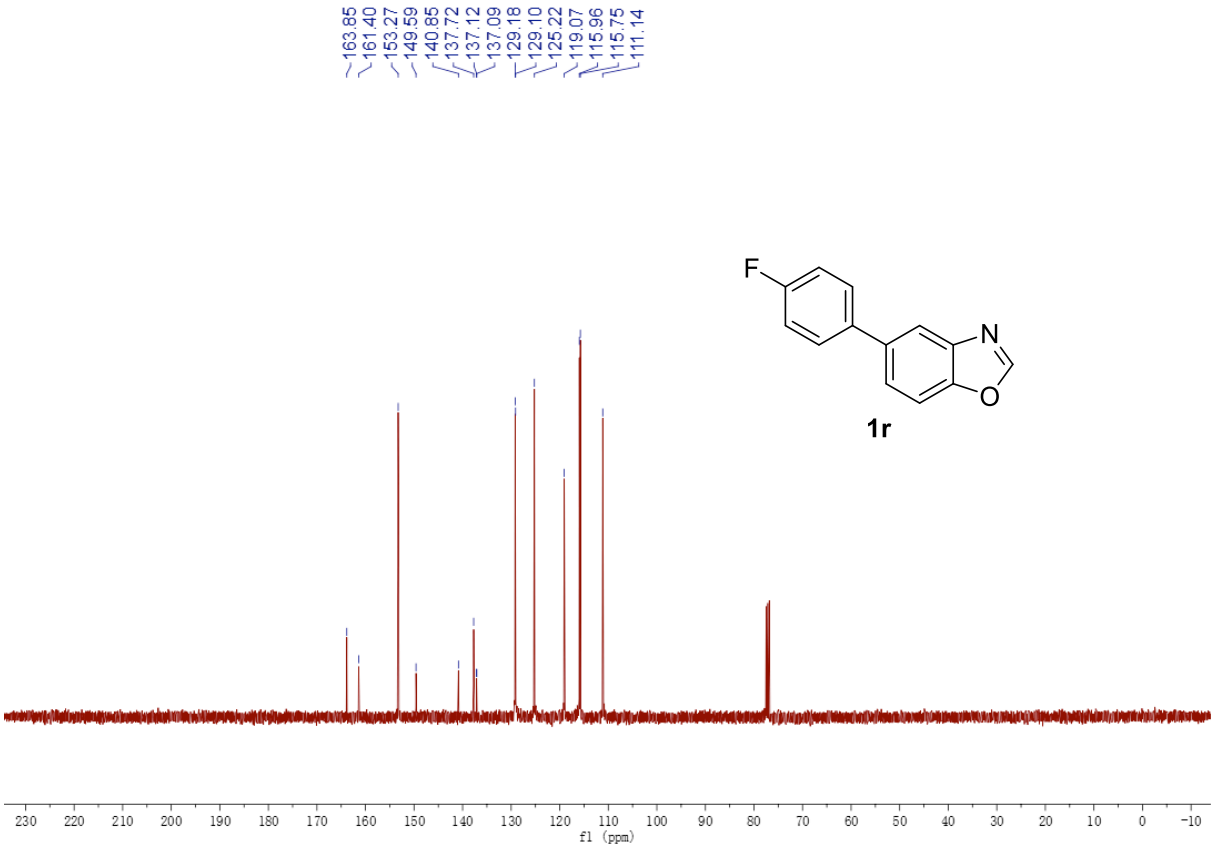

7.905
7.878
7.749
7.728
7.493
7.472
2.773
N
Me
Br
S
7d
0.89
0.96
0.96
3.00
f1 (ppm)

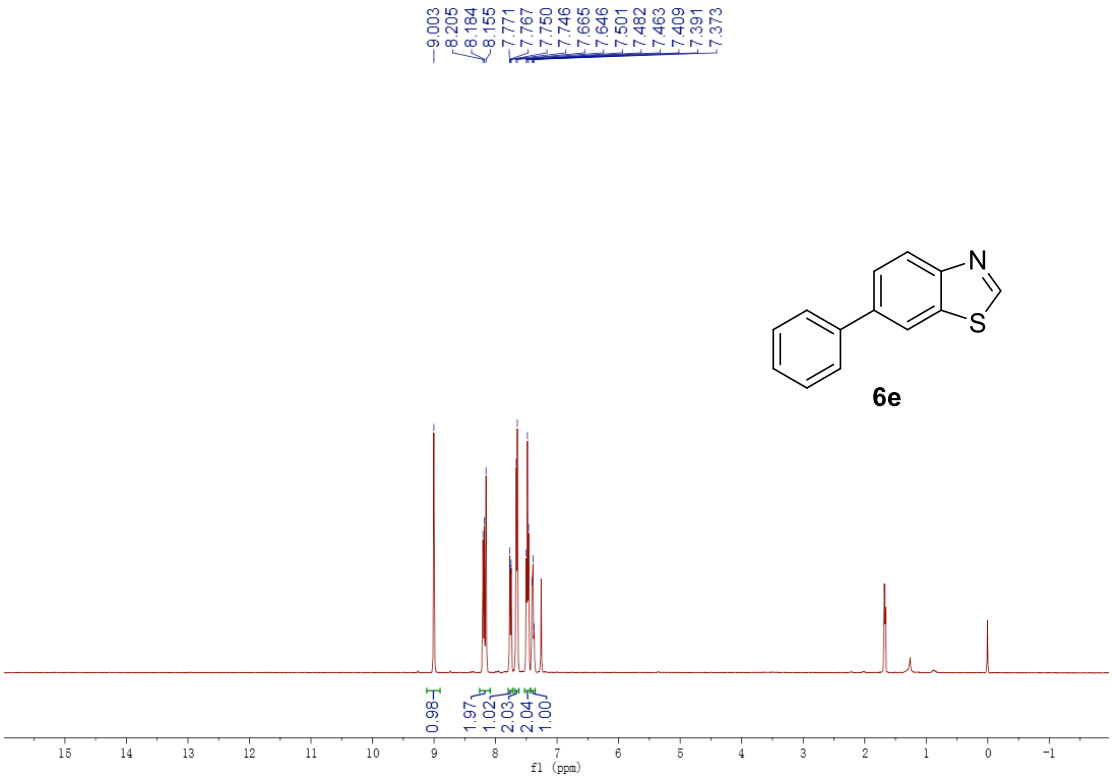

167.64
152.46
137.52
129.55
124.11
123.68
118.42
20.27
N
Me
Br
S
7d
f1 (ppm)

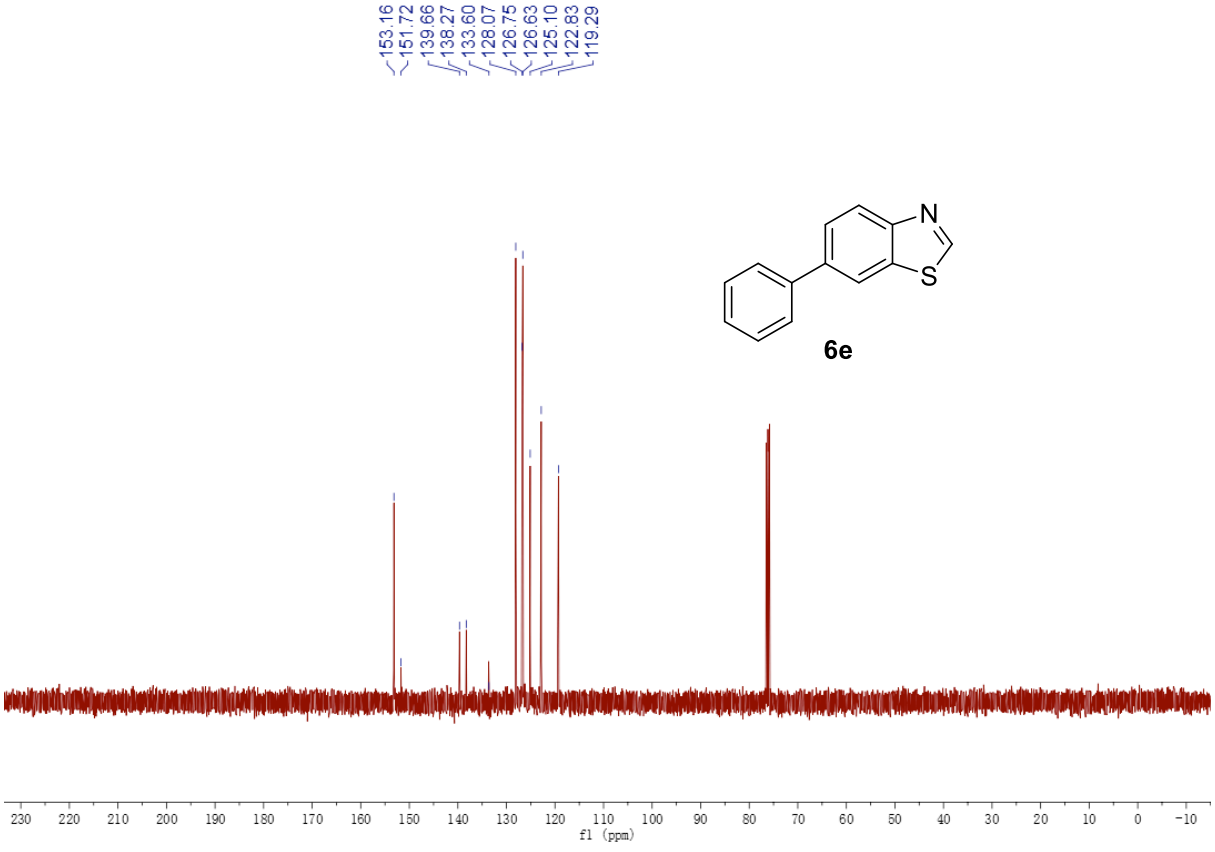

8.013
7.991
7.983
7.672
7.652
7.623
7.604
7.465
7.447
7.428
7.376
7.358
7.340
2.828
N
Me
S
7e
1.96
1.17
2.01
2.10
1.00
3.02
f1 (ppm)


167.12
152.75
140.66
138.17
136.46
128.88
127.42
127.36
125.55
122.46
119.70
20.17
N
Me
S
7e
f1 (ppm)


8.124
7.923
7.627
7.606
7.571
7.557
7.550
7.536
7.163
7.142
7.120
F
N
O
1r
0.95
1.00
4.11
2.05
f1 (ppm)


163.85
161.40
153.27
149.59
140.85
137.72
137.12
137.09
129.18
129.10
125.22
119.07
115.96
115.75
111.14
F
N
O
1r
f1 (ppm)


9.003
8.205
8.184
8.155
7.771
7.767
7.750
7.746
7.665
7.646
7.501
7.482
7.463
7.409
7.391
7.373
N
S
6e
0.98
1.97
1.02
2.03
2.04
1.00
f1 (ppm)


153.16
151.72
139.66
138.27
133.60
128.07
126.75
126.63
125.10
122.83
119.29
N
S
6e
f1 (ppm)