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Electronic Supplementary Information

Co-containing mesoporous zeolite ETS-10 catalyzed direct 2-alkylation of azoles with ethers

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1. General information

All the solvents and commercially available reagents were purchased from commercial sources and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE Ⅲ–300 or 400 MHz spectrometer. ^{1}H NMR data were reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift (*δ* ppm), multiplicity, and coupling constant (Hz). Infrared (IR) spectra were recorded on a Bruker TENSOR 27 spectrophotometer and are reported as wave number (cm^{-1}). Mass (MS) analysis was obtained Agilent 1100 series LC/MSD system with Electrospray Ionization (ESI).

2. Preparation and characterization of Co/METS-10 catalyst

(1) Catalyst preparation

Mesoporous zeolite ETS-10 (METS-10) and mesoporous zeolite ZSM-5 (MZSM-5) were prepared according to our reported procedure.[3,4] The Co/MEST-10 catalyst was prepared by the incipient wetness impregnation method by use of the $Co(NO_3)_2$ solution. The Co loading was 3.0 wt.%. After impregnation, the sample was dried in air at ambient temperature for 24 h, and subsequently dried in an oven at 100 °C for 12 h, and finally calcined at 450 °C for 4h. Other catalysts Co/MZSM-5, Cu/MEST-10, Fe/MEST-10, Ni/MEST-10 were prepared with the similar method.

(2) Characterization of Co/MEST-10 catalyst by XPS and TEM

To study the state of Cu species in the Co/MEST-10 catalyst, the X-ray photoelectron spectroscopy (XPS) analysis was performed on a ESCALAB MK II system, and the result is shown in Figure S1. To investigate the position and the dispersion of the Co species in the Co/METS-10 catalyst, the transmission electron microscopy (TEM) and element mapping (EDS) analysis of the thin-sectioned Co/MEST-10 sample were carried out on a on a FEI Tecnai G2 F30 instrument, operating at 300 kV, and the results are shown in Figure S2 and Figure S3.

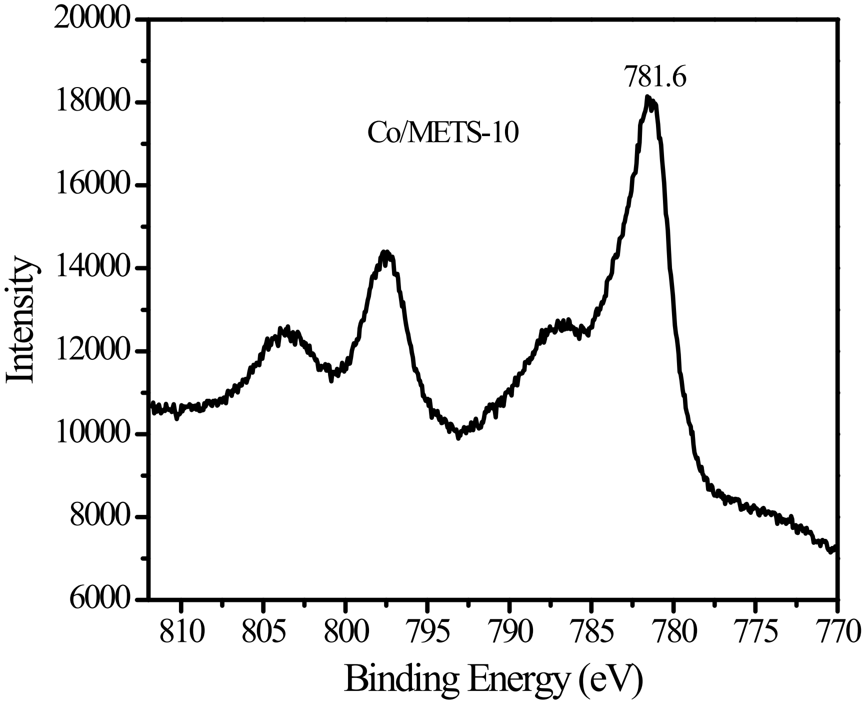


Figure S1 XPS spectrum of the Co/METS-10 catalyst.

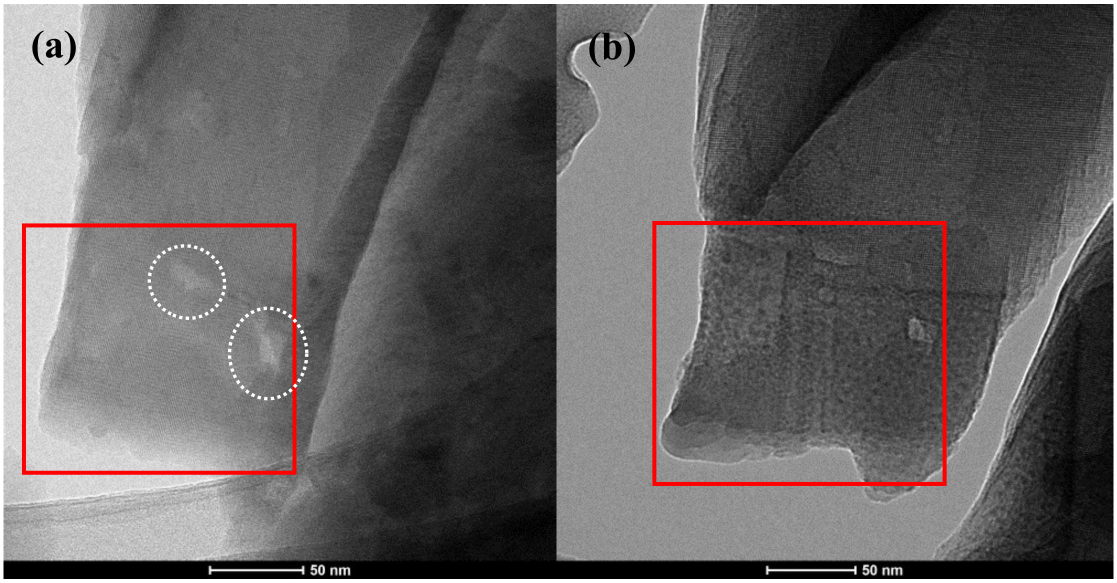


Figure S2. (a) TEM image of Co/METS-10 catalyst (b) TEM image of after the mapped Co/METS-10 catalyst (The selected zone is analyzed by element mapping, as shown in Figure S3).

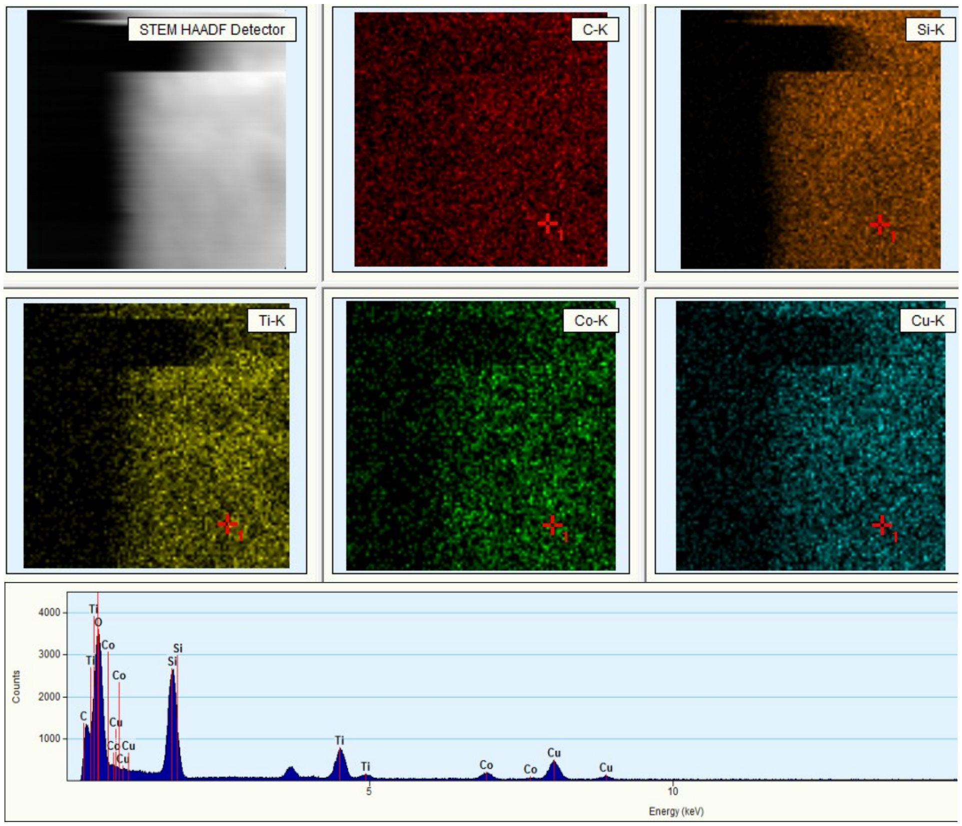


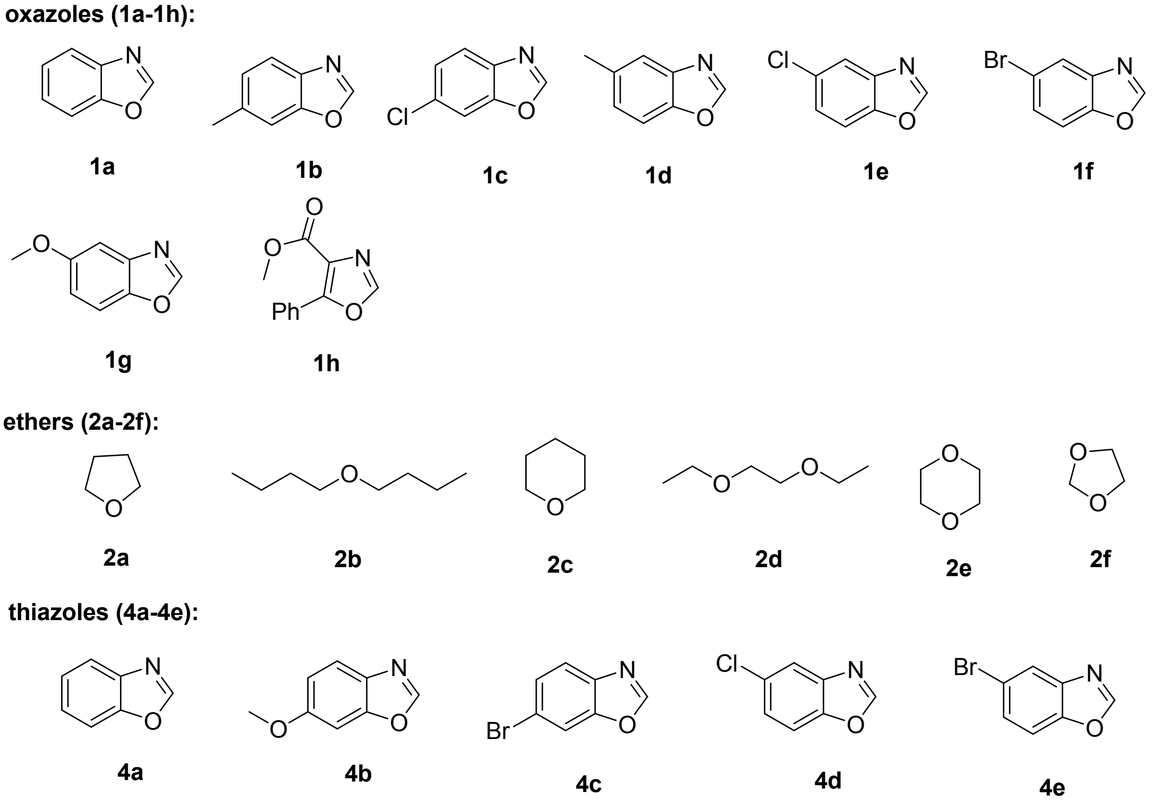
Figure S3. The element mapping and EDS analysis of O, Ti, Si, and Co in the selected area marked in Figure S2

Discussion:

From Figure S1, the binding energy of Co2p3/2 is 781.6 eV for the Co/METS-10 catalyst, which is assigned to the characteristics of the Co^{II} species. From Figure S2, it is clearly showed that the mesopores are existed in the Co/METS-10 catalyst (light areas, marked by white circle). Although there are no Co particles in the selected zone (Figure S2), the EDS element mapping indicates the presence of Co element is in the selected area (Figure S3). Therefore, it is suggested that the Co^{II} species should be highly dispersed in the micropores and mesopores of zeolite METS-10, and the percentage of the Co is 2.92 wt.% by element analysis.

3. Experimental section

(1) Starting materials



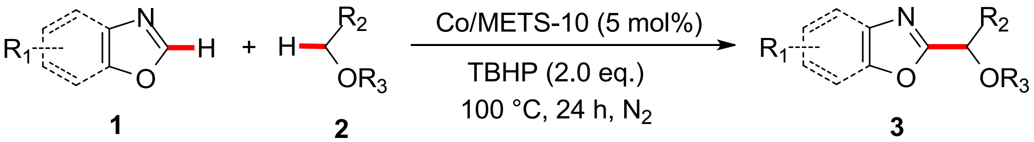
Oxazoles (1), ethers (2) and thiazoles (4)

Oxazoles (**1a-1f)**, ethers (**2**) and thiazoles (**4**) were purchased from Adamas-beta®, TCI, J&K$^{@}$ or Macklin. Oxazole (**1g**) was prepared from condensation of 2-amino-4-methoxyphenol and triethyl orthoformate according to the reported procedure.[1] Oxazole (**1h**) was prepared from methyl 2-isocyanoacetate and the corresponding benzoic anhydride in THF according to the reported procedure.[2]

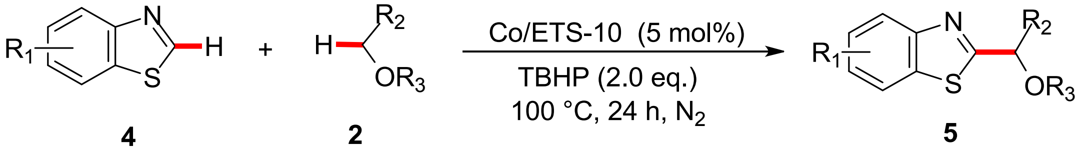
(2) Optimization of the reaction conditions

A 10 mL Schlenk tube was charged with benzoxazole **1a** (23.8 mg, 0.2 mmol) and catalyst (5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and additives (0.40 mmol) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times. The combined liquid phase was then concentrated in vacuo, and the crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are based on **1a**, determined by crude ^{1}H NMR using dibromomethane as the internal standard. And the residue was purified by flash chromatography on silica gel to yield the product **3a**.

(3) General procedure for the scope study

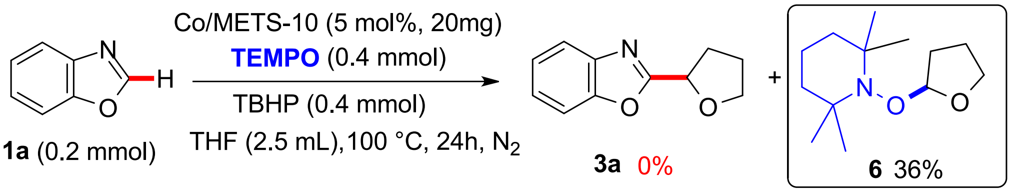


A 10 mL Schlenk tube was charged with oxazole **1** (0.2 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, **2** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. The cobalt catalyst was washed with DCM (15 mL) in three times. Then the combined liquid phase was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel to yield the desired products **3**.

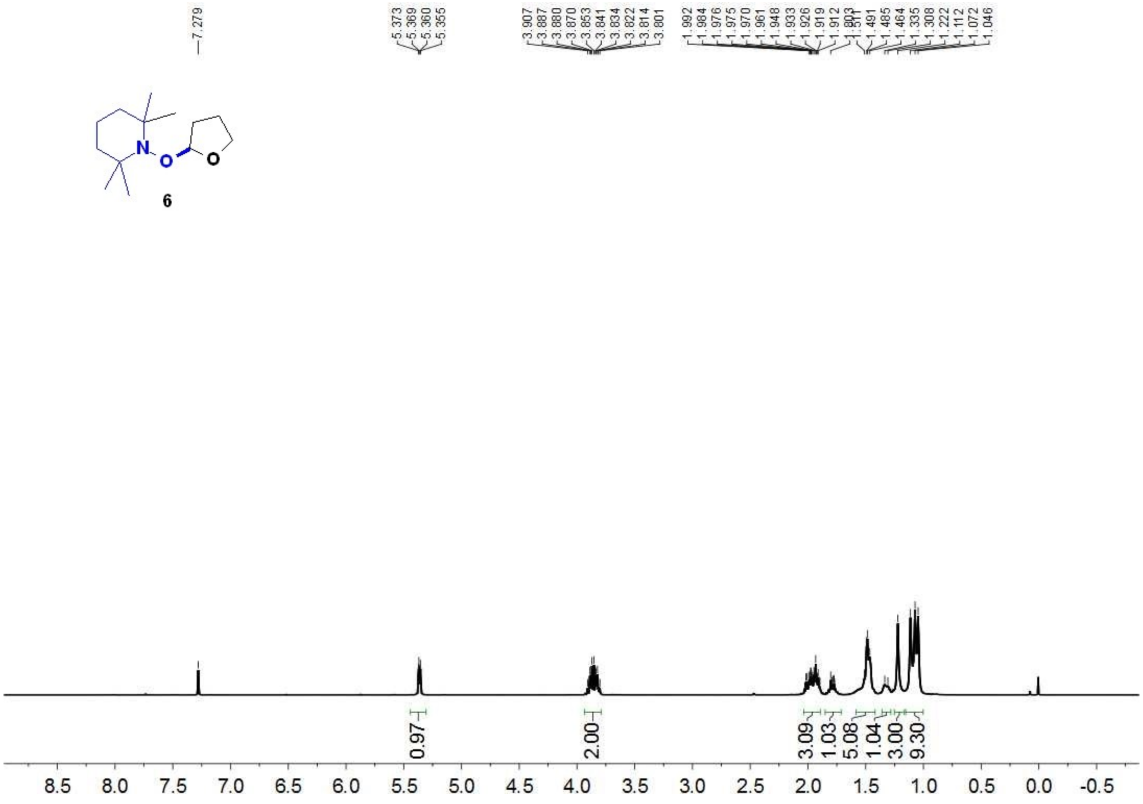


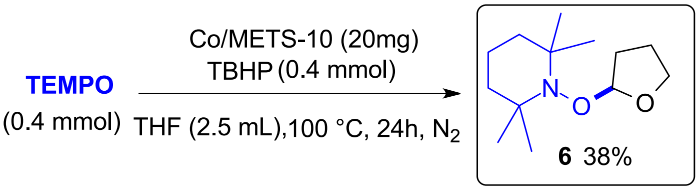
A 10 mL Schlenk tube was charged with thiazole **4** (0.2 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, **2** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. The cobalt catalyst was washed with DCM (15 mL) in three times. Then the combined liquid phase was concentrated in vacuo, the residue was purified by flash chromatography on silica gel to yield the desired products **5**.

(4) Radical trapping experiment



A 10 mL Schlenk tube was charged with oxazole **1a** (23.8 mg, 0.2 mmol), TEMPO (62.4 mg, 0.4 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times. The combined liquid phase was then concentrated in vacuo, and the residue was analyzed by crude ^{1}H NMR in $CDCl_3$, no desired product **3a** was observed. Next, the yield of product **6** (36% yield based on TEMPO) was analyzed by crude ^{1}H NMR in $CDCl_3$. The residue was purified by flash chromatography on silica gel to yield the desired products **6** (known compound[5]). 1H NMR (400 MHz, CDCl3) δ 5.36 (dd, J = 5.6, 2.0 Hz, 1H), 3.91 – 3.80 (m, 2H), 1.99 – 1.91 (m, 3H), 1.80 – 1.77 (m, 1H), 1.51 – 1.46 (m, 5H), 1.34 – 1.31 (m, 1H), 1.22 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H), 1.04 (s, 3H).





6 38%

A 10 mL Schlenk tube was charged with TEMPO (62.4 mg, 0.4 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times, and the combined liquid phase was then concentrated in vacuo. The yield of product **6** (38% yield based on TEMPO) was analyzed by crude ^{1}H NMR in $CDCl_3$,

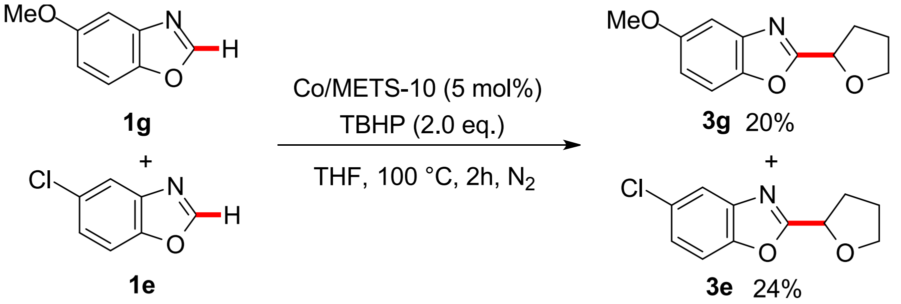
$$\underset{(0.4\ \text{mmol})}{\textbf{TEMPO}} \xrightarrow[\text{THF (2.5 mL),100 °C, 24h, } N_2]{\text{Co/METS-10 (20mg)} \atop \text{TBHP (0.8 mmol)}} \textbf{6}\ \ (89\%)$$

A 10 mL Schlenk tube was charged with TEMPO (62.4 mg, 0.4 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.80 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times, and the combined liquid phase was then concentrated in vacuo. The yield of product **6** (89% yield based on TEMPO) was analyzed by crude ^{1}H NMR in $CDCl_3$.

$$\underset{(0.4\ \text{mmol})}{\textbf{TEMPO}} \xrightarrow[\text{THF (2.5 mL),100 °C, 24h, } N_2]{\textbf{without Co/METS-10} \atop \text{TBHP (0.4 mmol)}} \textbf{6}\ \ (<5\%)$$

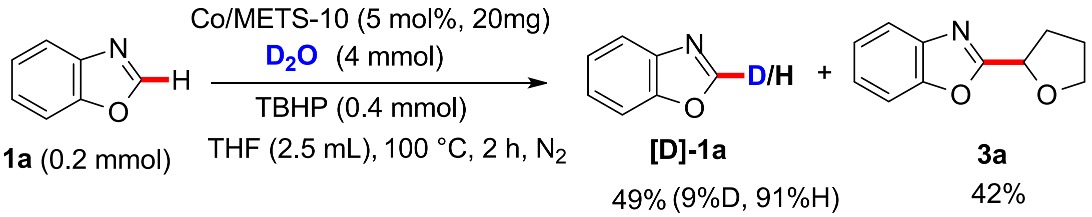
A 10 mL Schlenk tube was charged with TEMPO (62.4 mg, 0.4 mmol). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. The yield of product **6** (<5% yield based on TEMPO) was analyzed by crude ^{1}H NMR in $CDCl_3$.

(5) Intermolecular competition experiment



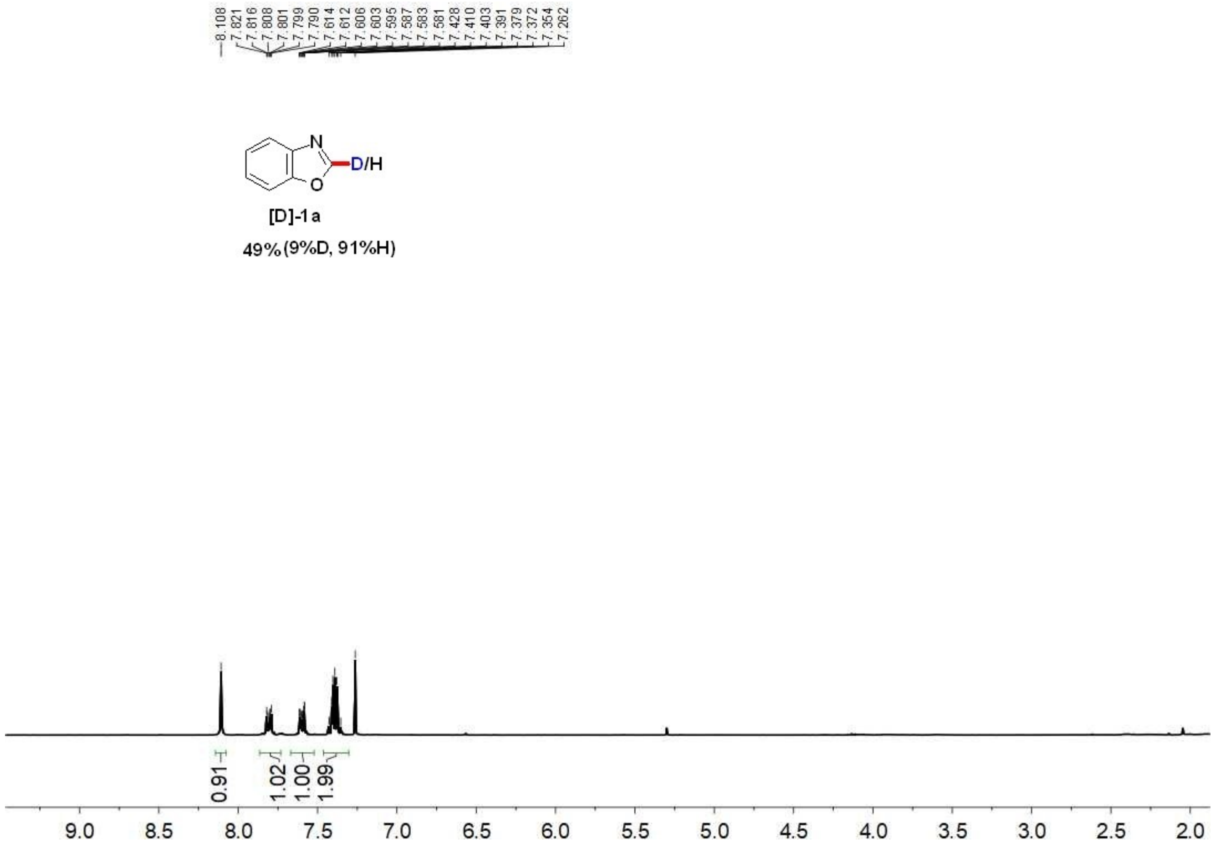
A 10 mL Schlenk tube was charged with oxazole **1g** (0.1 mmol), **1e** (0.1 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, **2a** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times, and the combined liquid phase was then concentrated in vacuo. The crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are based on **1g** and **1e**, determined by crude ^{1}H NMR using dibromomethane as the internal standard, the desired product **3g** (20%) and **3e** (24%) were analyzed by crude ^{1}H NMR.

(6) The intermolecular H/D exchange experiment

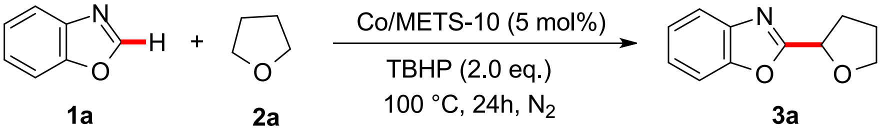


Scheme S1 The intermolecular H/D exchange experiment

A 10 mL Schlenk tube was charged with oxazole **1a** (23.8 mg, 0.2 mmol), D_2O (4 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 2 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and filtered to obtain the liquid phase. After that, the catalyst was washed with DCM (15 mL) in three times. The combined liquid phase was then concentrated in vacuo, and the residue was analyzed by crude ^{1}H NMR in $CDCl_3$, the desired product **3a** was observed in 42% yield and **[D]-1a** was 49% yield. The residue was purified by flash chromatography on silica gel to yield the product of **[D]-1a** (9%D, 91%H).



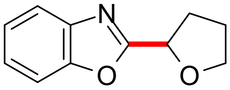
(7) Co/METS-10 catalyst recyclability experiments



Cycle	1st	2nd	3rd	4th	5th
NMR yield	82%	80%	80%	78%	75%

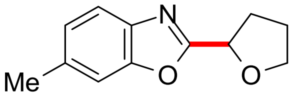
A 10 mL Schlenk tube was charged with oxazole **1a** (0.2 mmol) and Co/METS-10 (20 mg, 5 mol% metal loading). The tube was evacuated and filled with N_2 three times. Next, THF **2a** (2.5 mL) and TBHP (0.08 mL, 0.40 mmol, 5.0-6.0 M in *n*-decane) were added into the tube quickly. The tube was then sealed and stirred vigorously at 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was transferred to centrifugal tube carefully, and the catalyst was separated by centrifugation and washed with THF (15 mL) in three times. The combined liquid phase was then concentrated in vacuo, and the residue was analyzed by crude ^{1}H NMR in $CDCl_3$. The recovered catalyst was used for next round experiment.

(7) Product data



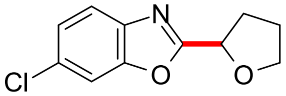
3a

Colorless oil, 30.3 mg, yield: 80% (known compound[6]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 1H), 7.53 – 7.51 (m, 1H), 7.35 – 7.30 (m, 2H), 5.20 (t, *J* = 6.8 Hz, 1H), 4.15 – 4.09 (m, 1H), 4.03 – 3.98 (m, 1H), 2.43 – 2.37 (m, 2H), 2.22 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.36, 150.97, 140.94, 125.26, 124.49, 120.28, 110.88, 74.04, 69.47, 30.88, 25.93.



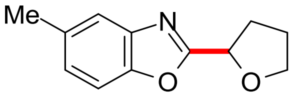
3b

Colorless oil, 29.7 mg, yield: 73% (known compound[7]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.17 (t, *J* = 6.4 Hz, 1H), 4.13 – 4.07 (m, 1H), 4.02 – 3.96 (m, 1H), 2.46 (s, 3H), 2.41 – 2.35 (m, 2H), 2.19 – 2.12 (m, 1H), 2.08 – 2.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.75, 151.27, 138.70, 135.66, 125.69, 119.56, 110.99, 74.03, 69.39, 30.79, 25.91, 21.83.



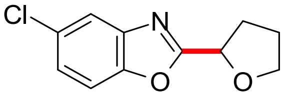
3c

White solid, 31.3 mg, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.17 (dd, *J* = 7.6, 6.4 Hz, 1H), 4.12 – 4.07 (m, 1H), 4.02 – 3.97 (m, 1H), 2.43 – 2.33 (m, 2H), 2.18 – 2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 151.05, 139.63, 130.83, 125.14, 120.70, 111.43, 73.80, 69.44, 30.77, 25.82. IR (KBr) ν 2979, 2954, 2875, 1613, 1569, 1461, 1428, 1328, 1260, 1227, 1050, 961, 916, 815, 703 cm^{-1}. Ms (ESI): m/z = 246.10 $[M+Na]^+$.



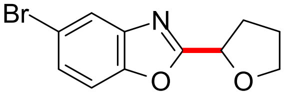
3d

Yellow oil, 30.5 mg, yield: 75% (known compound[8]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.17 (t, *J* = 6.8 Hz, 1H), 4.13 – 4.08 (m, 1H), 4.02 – 3.96 (m, 1H), 2.44 (s, 3H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.19 – 2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.32, 149.11, 141.02, 134.22, 126.25, 120.06, 110.12, 73.99, 69.35, 30.78, 25.83, 21.47.



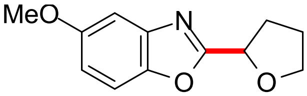
3e

White solid, 32.2 mg, yield: 72% (known compound[8]).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.20 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.15 – 3.99 (m, 2H), 2.40 – 2.35 (m, 2H), 2.21 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.75, 149.46, 141.99, 129.89, 125.53, 120.21, 111.53, 73.85, 69.48, 30.83, 25.83.



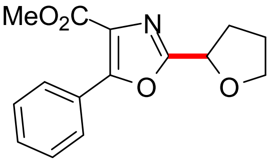
3f

White solid, 45.6 mg, yield: 85%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 1.2 Hz, 1H), 7.46 – 7.38 (m, 2H), 5.19 (t, *J* = 7.2 Hz, 1H), 4.14 – 3.98 (m, 2H), 2.44 – 2.34 (m, 2H), 2.20 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.56, 149.87, 142.46, 128.24, 123.21, 117.13, 112.04, 73.81, 69.48, 30.84, 25.83.IR (KBr) ν 2982, 2958, 2876, 1637, 1564, 1448, 1258, 1156, 1060, 912, 802, 748, 681 cm^{-1}. Ms (ESI): m/z = 268.00 [M+H]$^+$.



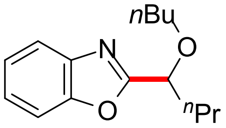
3g

White solid, 30.7 mg, yield: 70% (known compound[9]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, *J* = 9.2 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.18 (t, *J* = 6.8 Hz, 1H), 4.15 – 3.98 (m, 2H), 3.84 (s, 3H), 2.43 – 2.37 (m, 2H), 2.21 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.06, 157.22, 145.51, 141.67, 113.72, 110.90, 103.09, 73.97, 69.34, 55.94, 30.77, 25.83.



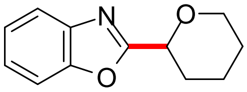
3h

Colorless oil, 27.9 mg, yield: 51% (known compound[7]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.07 (m, 2H), 7.49 – 7.48 (m, 3H), 5.13 (t, *J* = 6.8 Hz, 1H), 4.13 – 3.95 (m, 5H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.23 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.56, 156.00, 130.46, 128.47, 128.44, 126.82, 126.47, 73.35, 69.33, 52.35, 30.71, 25.99.



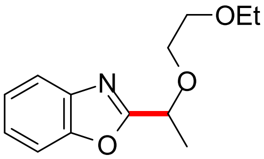
3i

Colorless oil, 24.7 mg, yield: 50%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.73 (m, 1H), 7.58 – 7.55 (m, 1H), 7.37 – 7.35 (m, 2H), 4.61 – 4.57 (m, 1H), 3.57 – 3.44 (m, 2H), 2.06 – 1.90 (m, 2H), 1.61 – 1.35 (m, 6H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.17, 150.81, 140.75, 125.15, 124.37, 120.19, 110.89, 75.60, 70.05, 36.09, 31.73, 19.22, 18.62, 13.84, 13.78. IR (KBr) ν 2960, 2934, 2873, 1637, 1455, 1241, 1094, 747 cm^{-1}. Ms (ESI): m/z = 248.20 [M+H]$^{+}$.



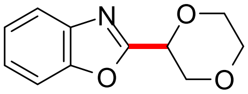
3j

Yellow oil, 24.4 mg, yield: 60% (known compound[9]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.71 (m, 1H), 7.54 – 7.52 (m, 1H), 7.33 – 7.28 (m, 2H), 4.73 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.18 – 4.15 (m, 1H), 3.71 – 3.65 (m, 1H), 2.13 – 1.94 (m, 3H), 1.78 – 1.61 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.08, 150.61, 140.77, 125.17, 124.41, 120.25, 110.80, 73.35, 68.84, 29.75, 25.45, 22.64.



3k

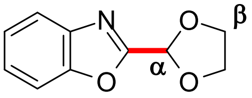
Colorless oil, 28.7 mg, yield: 61% (known compound[7]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.71 (m, 1H), 7.55 – 7.53 (m, 1H), 7.37 – 7.31 (m, 2H), 4.84 (q, *J* = 6.8 Hz, 1H), 3.71 (t, *J* = 4.8 Hz, 2H), 3.61 – 3.60 (m, 2H), 3.52 – 3.47 (m, 2H), 1.69 (d, *J* = 6.8 Hz, 3H), 1.17 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.05, 150.78, 140.72, 125.26, 124.41, 120.23, 110.87, 71.94, 69.68, 69.17, 66.68, 19.56, 15.09.



3l

Colorless oil, 25.9 mg, yield: 63% (known compound[7]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.72 (m, 1H), 7.56 – 7.53 (m, 1H), 7.39 – 7.32 (m, 2H), 4.97 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.20 (dd, *J* = 11.6, 3.2 Hz, 1H), 4.05 – 3.91

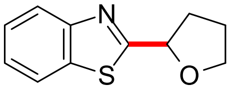
(m, 3H), 3.88 – 3.77 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.72, 150.56, 140.58, 125.57, 124.69, 120.43, 110.88, 71.09, 68.52, 66.58, 66.43.



(α : β = 3.3 : 1)

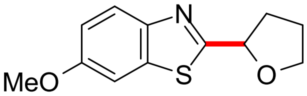
3m

Colorless oil, mixture, 25.6 mg, yield: 67% (known compound[7]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 1H), 7.58 – 7.56 (m, 1H), 7.41 – 7.36 (m, 2H), 6.21 (s, 0.77 H), 5.34 – 5.31 (m, 0.23 H), 5.27 (s, 0.23 H), 5.18 (s, 0.23 H), 4.38 – 4.28 (m, 2H), 4.20 – 4.14 (m, 1.54 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 161.91, 150.95, 150.71, 140.63, 140.40, 125.94, 125.68, 124.75, 124.73, 120.80, 120.44, 111.11, 110.95, 97.16, 96.42, 70.55, 68.70, 65.76.



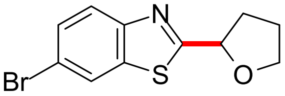
5a

Colorless oil, 34.9 mg, yield: 85% (known compound[6]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 1H), 5.35 (dd, J = 8.0, 5.6 Hz, 1H), 4.19 – 4.13 (m, 1H), 4.03 – 4.98 (m, 1H), 2.55 – 2.48 (m, 1H), 2.30 – 2.23 (m, 1H), 2.07 – 2.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.42, 153.67, 134.73, 125.95, 124.79, 122.79, 121.79, 78.76, 69.47, 33.40, 25.72.



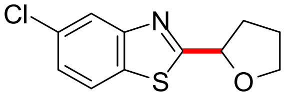
5b

White solid, 35.3 mg, yield: 75% (known compound[8]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.05 (dd, J = 8.8, 2.4 Hz, 1H), 5.30 (dd, J = 7.6, 5.2 Hz, 1H), 4.16 – 4.11 (m, 1H), 4.01 – 3.96 (m, 1H), 3.86 (s, 3H), 2.51 – 2.41 (m, 1H), 2.30 – 2.22 (m, 1H), 2.06 – 1.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 157.41, 148.12, 136.08, 123.25, 115.27, 104.25, 78.68, 69.38, 55.79, 33.30, 25.73.



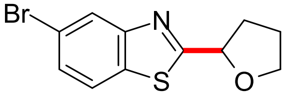
5c

White solid, 47.1 mg, yield: 83% (known compound[10]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J* = 1.6 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 8.8, 1.6 Hz, 1H), 5.33 – 5.29 (m, 1H), 4.17 – 4.12 (m, 1H), 4.03 – 3.97 (m, 1H), 2.56 – 2.47 (m, 1H), 2.29 – 2.21 (m, 1H), 2.07 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.15, 152.61, 136.49, 129.42, 124.34, 123.93, 118.36, 78.61, 69.54, 33.34, 25.74.



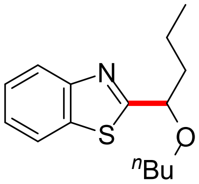
5d

White solid, 33.6 mg, yield: 70%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.33 (dd, *J* = 7.6, 5.2 Hz, 1H), 4.18 – 4.13 (m, 1H), 4.04 – 3.98 (m, 1H), 2.55 – 2.50 (m, 1H), 2.28 – 2.23 (m, 1H), 2.08 – 2.02 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.62, 154.61, 133.07, 131.93, 125.29, 122.66, 122.52, 78.68, 69.56, 33.38, 25.72. IR (KBr) ν 2978, 2951, 2874, 1589, 1546, 1437, 1323, 1144, 1068, 922, 801 cm^{-1}. Ms (ESI): m/z = 240.10 [M+H]$^+$.



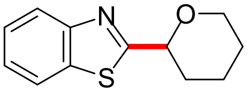
5e

White solid, 46.0 mg, yield: 81% (known compound[8]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.33 (dd, *J* = 8.0, 5.2 Hz, 1H), 4.18 – 4.13 (m, 1H), 4.03 – 3.98 (m, 1H), 2.57 – 2.48 (m, 1H), 2.28 – 2.23 (m, 1H), 2.09 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.43, 154.93, 133.60, 127.91, 125.72, 122.87, 119.51, 78.65, 69.57, 33.38, 25.72.



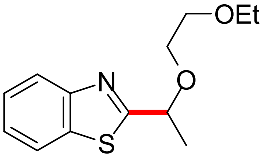
5f

Colorless oil, 27.9 mg, yield: 53% (known compound[6]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.37 (m, 2H), 4.69 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.62 – 3.48 (m, 2H), 1.97 – 1.86 (m, 2H), 1.65 – 1.40 (m, 6H), 0.99 – 0.91 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 176.61, 153.13, 134.95, 125.88, 124.95, 122.89, 121.91, 80.25, 70.38, 39.40, 31.95, 19.35, 18.73, 13.94, 13.86.



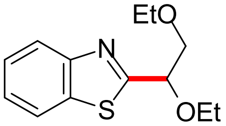
5g

Colorless oil, 28.5 mg, yield: 65%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.39 – 7.35 (m, 1H), 4.81 – 4.78 (m, 1H), 4.22 – 4.18 (m, 1H), 3.73 – 3.67 (m, 1H), 2.29 – 2.27 (m, 1H), 2.00 – 1.97 (m, 1H), 1.78 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.92, 153.07, 134.69, 125.89, 124.81, 122.92, 121.79, 77.91, 69.01, 32.50, 25.62, 23.02. IR (KBr) ν 2939, 2851, 1524, 1438, 1334, 1262, 1205, 1091, 1046, 989, 904, 883, 760, 730 cm^{-1}. Ms (ESI): m/z = 220.00 [M+H]$^+$.



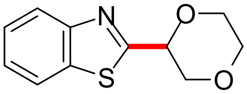
5ha

Colorless oil, 22.6 mg, yield: 45%.^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 1H), 4.93 (q, *J* = 6.4 Hz, 1H), 3.74 – 3.71 (m, 2H), 3.64 – 3.62 (m, 2H), 3.57 – 3.51 (m, 2H), 1.67 (d, *J* = 6.4 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 176.14, 153.07, 134.97, 125.92, 125.01, 122.92, 121.88, 76.78, 69.75, 69.29, 66.70, 22.56, 15.17. IR (KBr) ν 2977, 2929, 2869, 1520, 1440, 1312, 1108, 761, 731 cm^{-1}. Ms (ESI): m/z =252.15 [M+H]$^+$.



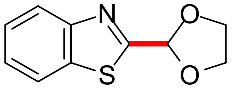
5hb

Colorless oil, 10.6 mg, yield: 21%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.94 (dd, *J* = 6.8, 3.6 Hz, 1H), 3.90 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.82 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.79, 153.20, 135.10, 125.95, 125.07, 123.02, 121.83, 79.59, 73.58, 67.15, 66.51, 15.34, 15.08. IR (KBr) ν 2976, 2929, 2871, 1518, 1439, 1323, 1110, 867, 761, 731 cm^{-1}. Ms (ESI): m/z =274.10 [M+Na]$^+$.



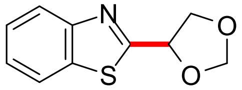
5i

Colorless oil, 37.2 mg, yield: 84% (known compound[6]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.42 – 7.38 (m, 1H), 5.07 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.32 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.05 – 3.96 (m, 2H), 3.87 – 3.69 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.03, 153.03, 134.57, 126.16, 125.17, 123.14, 121.83, 75.45, 70.52, 67.01, 66.42.



5ja

Colorless oil, 17.8 mg, yield: 43% (known compound[8]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.26 (s, 1H), 4.23 – 4.11 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.23, 153.27, 134.96, 126.26, 125.73, 123.81, 121.95, 100.54, 65.76.



5jb

Colorless oil, 11.2 mg, yield: 27% (known compound[8]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 5.48 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.32 (s, 1H), 5.13 (s, 1H), 4.41 – 4.38 (m, 1H), 4.23 (dd, *J* = 8.8, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 172.49, 153.43, 134.70, 126.24, 125.26, 123.03, 121.90, 96.37, 75.15, 71.06.

4. References and notes

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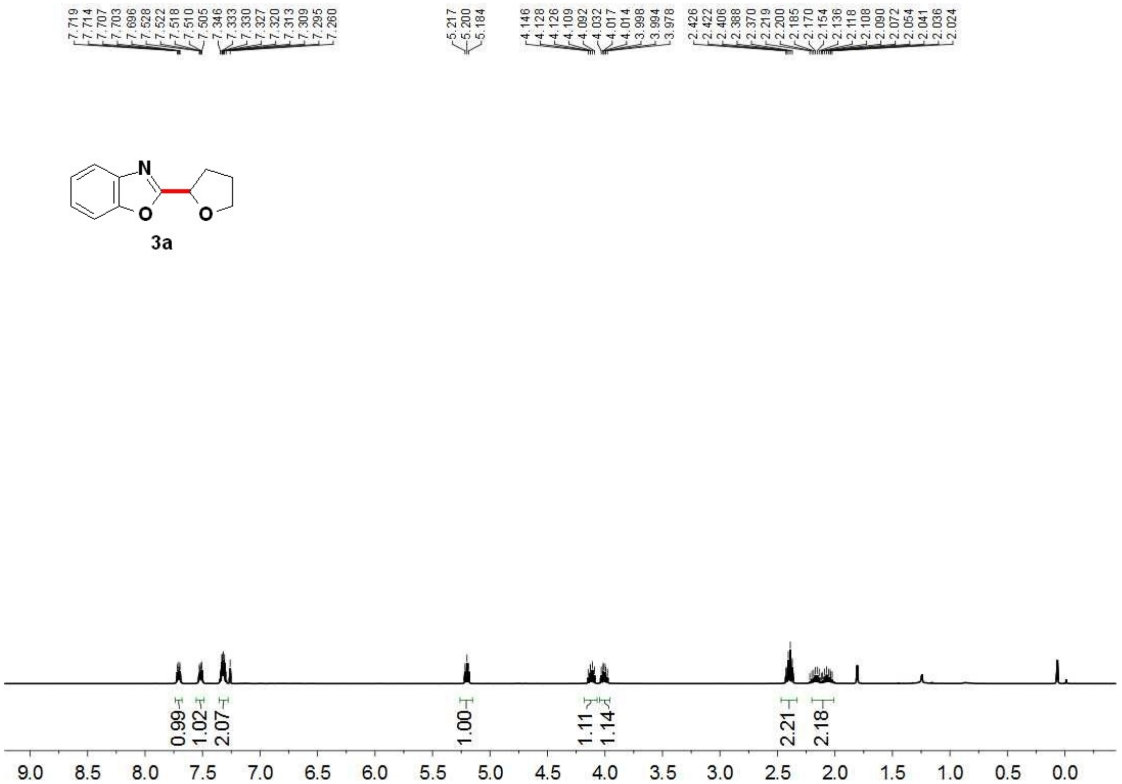
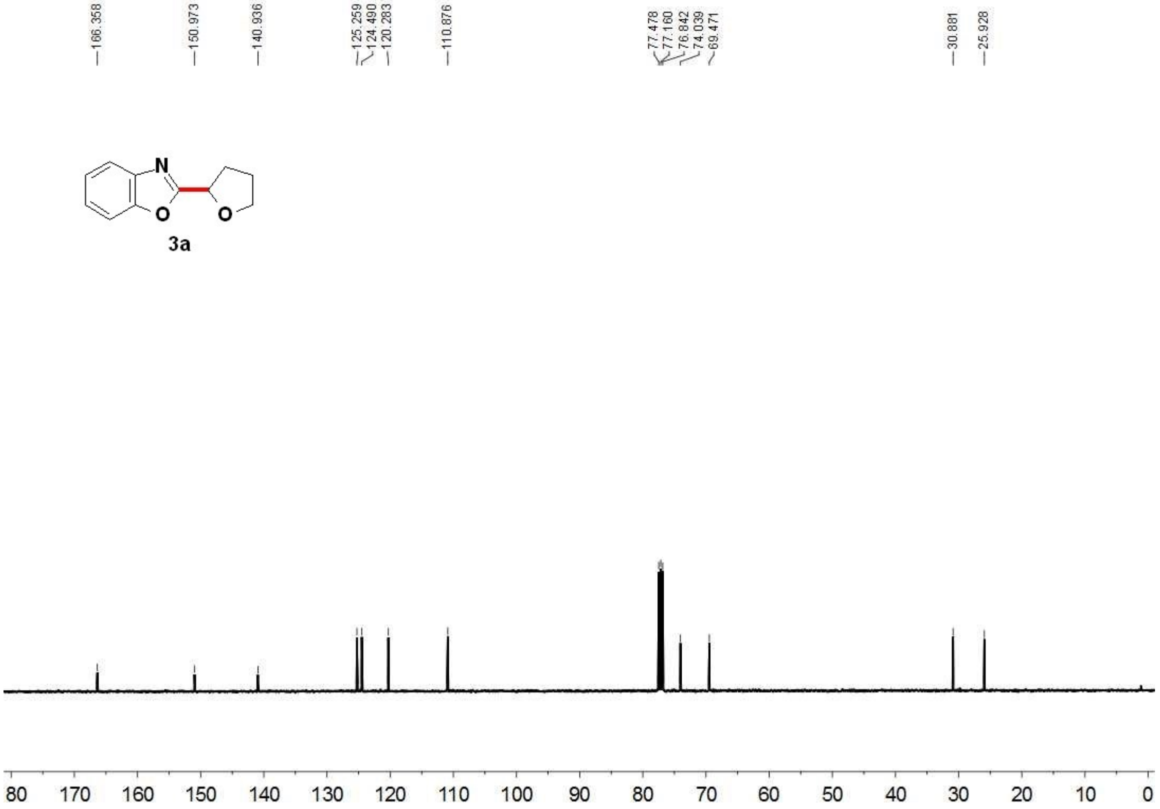
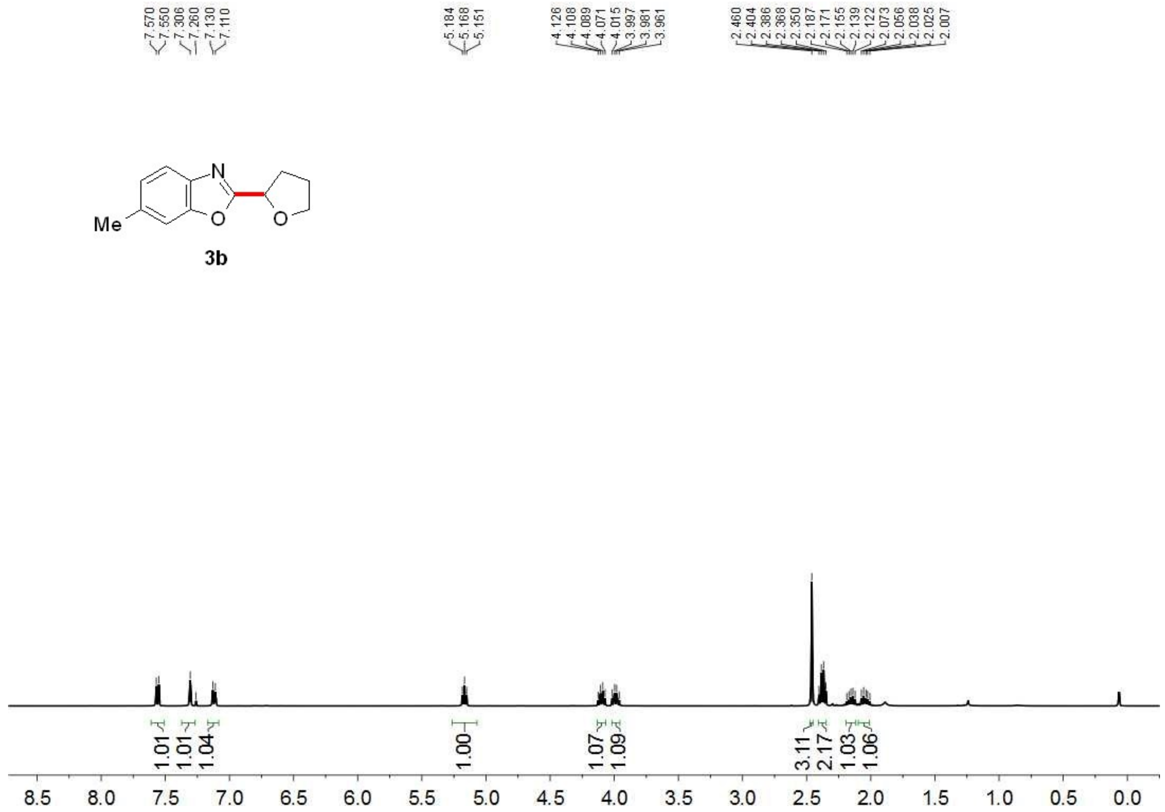
5. ^{1}H and ^{13}C NMR spectra



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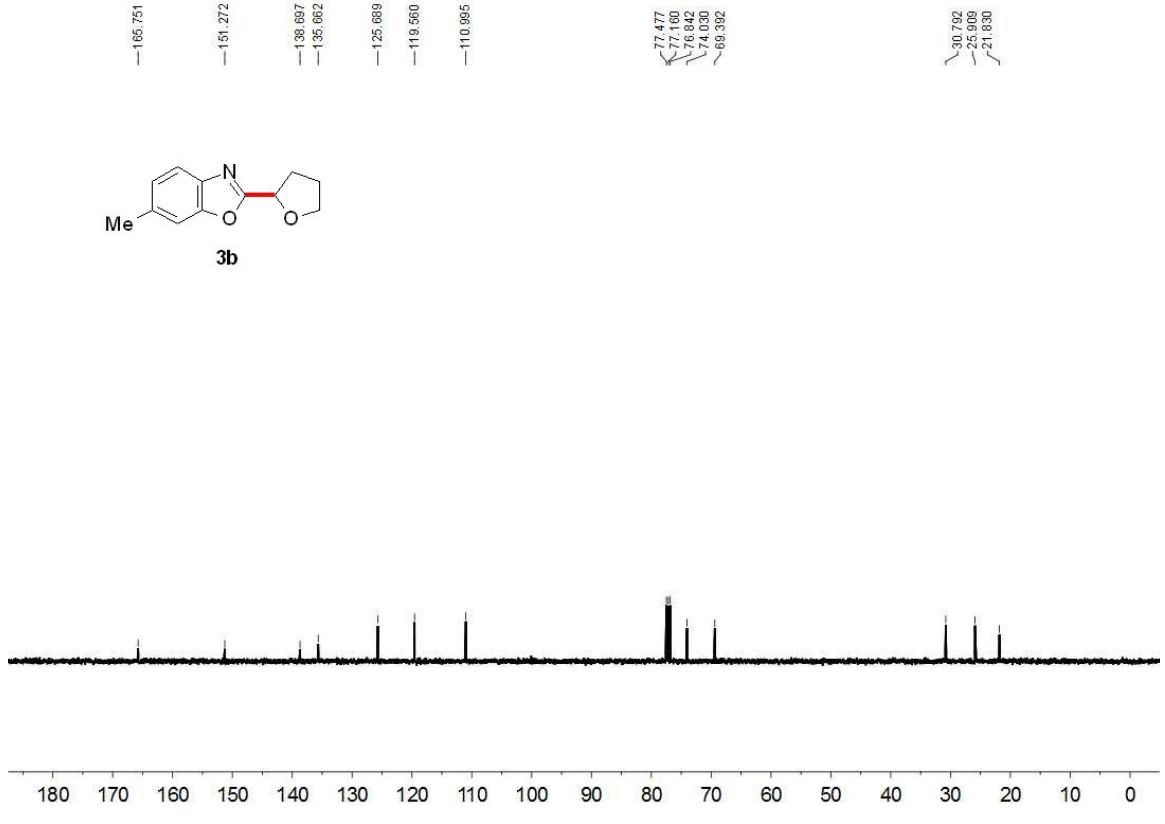
3b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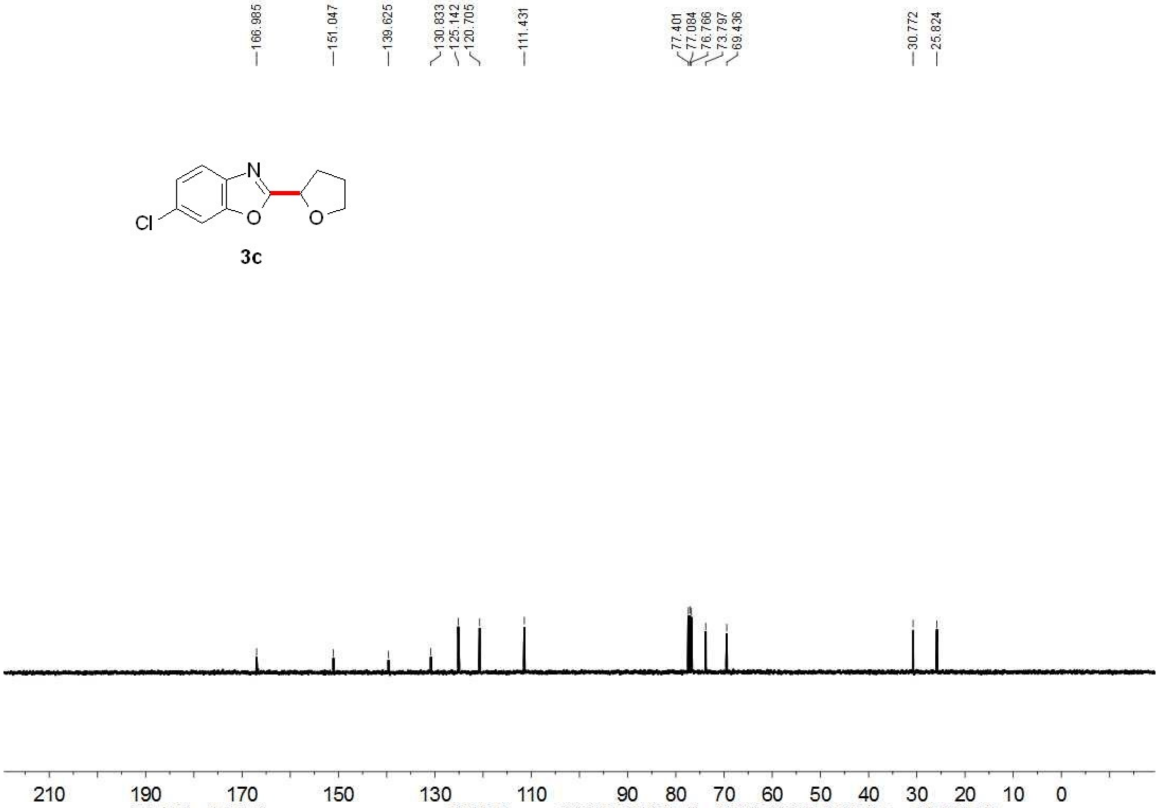
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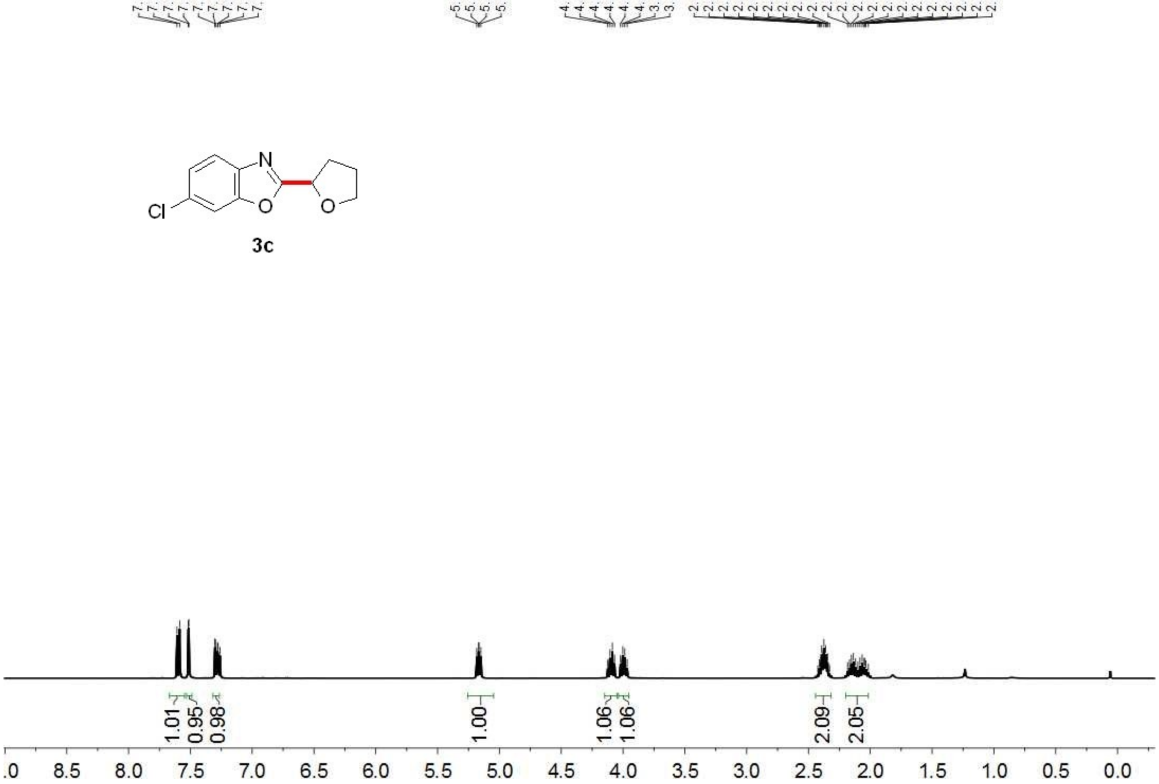
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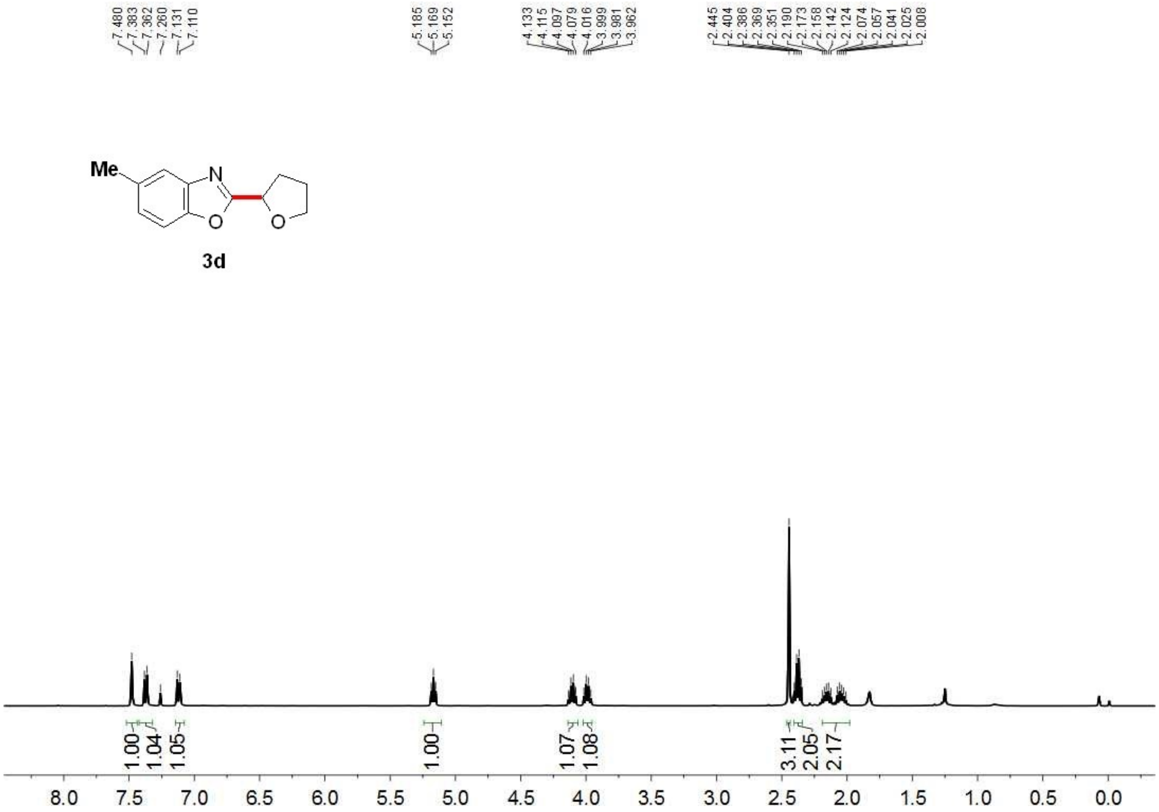
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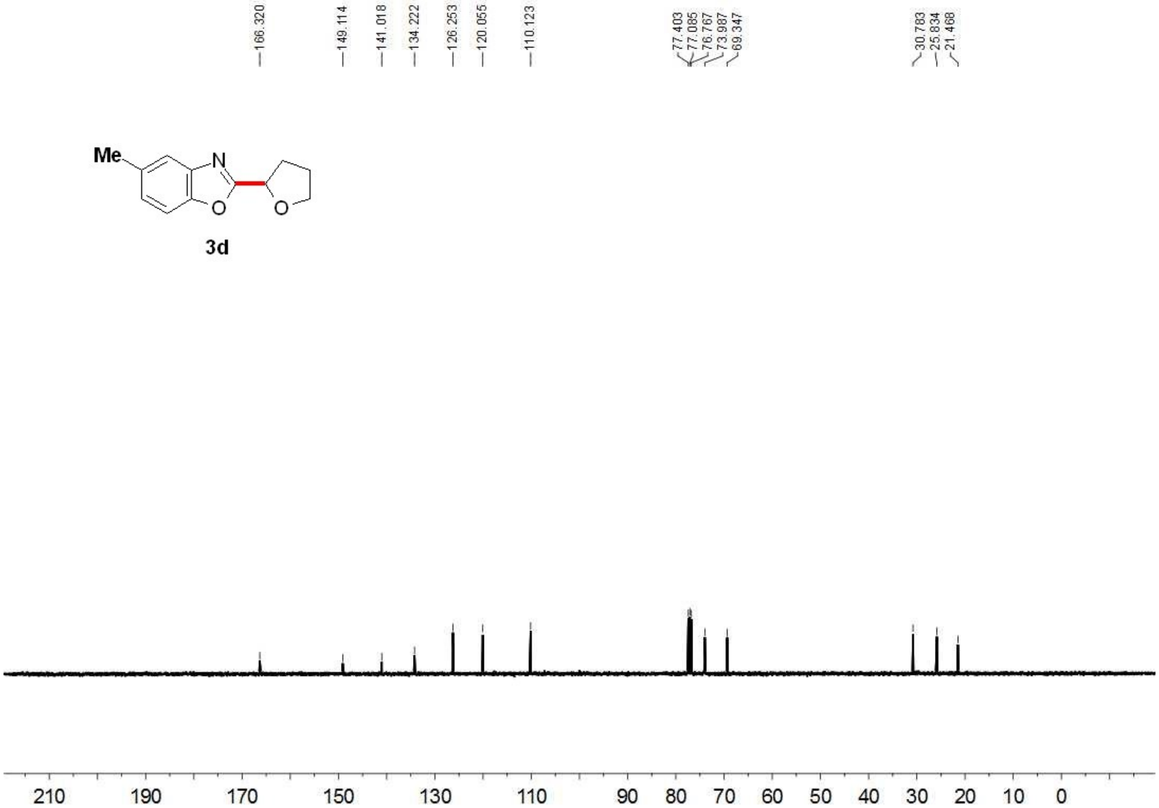
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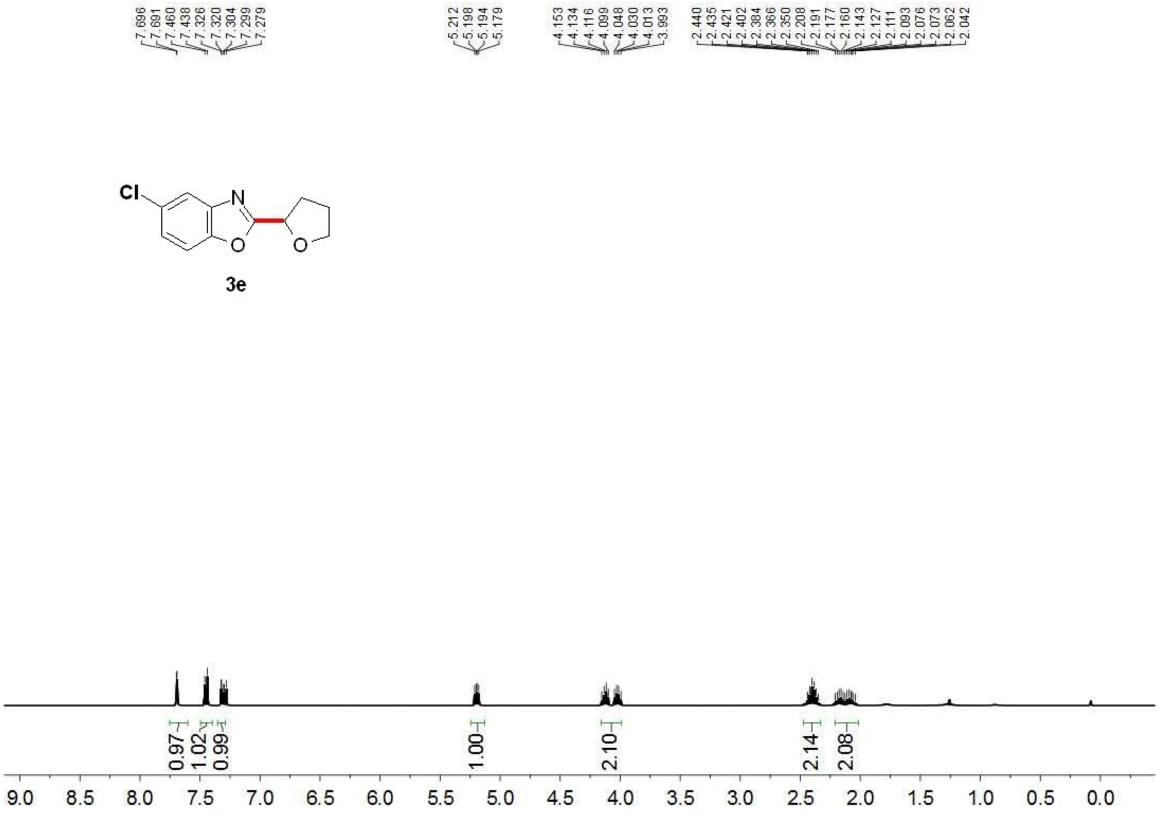
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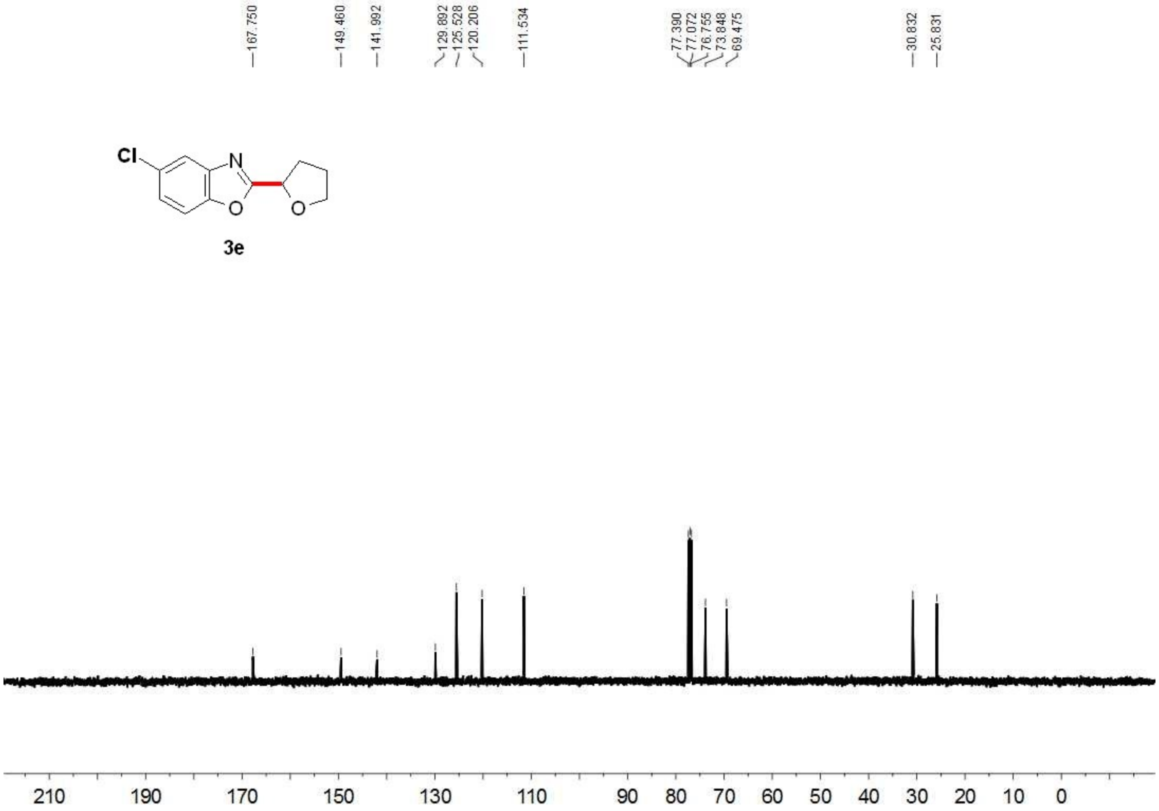
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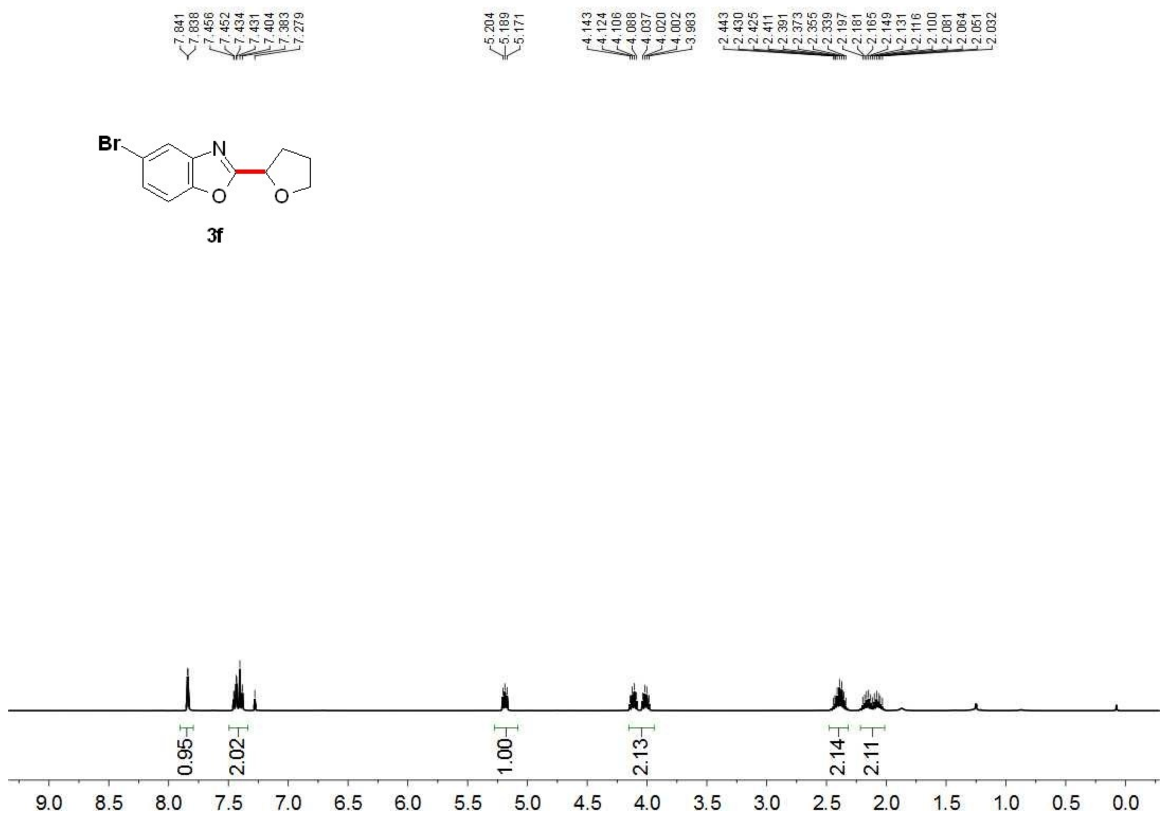
3e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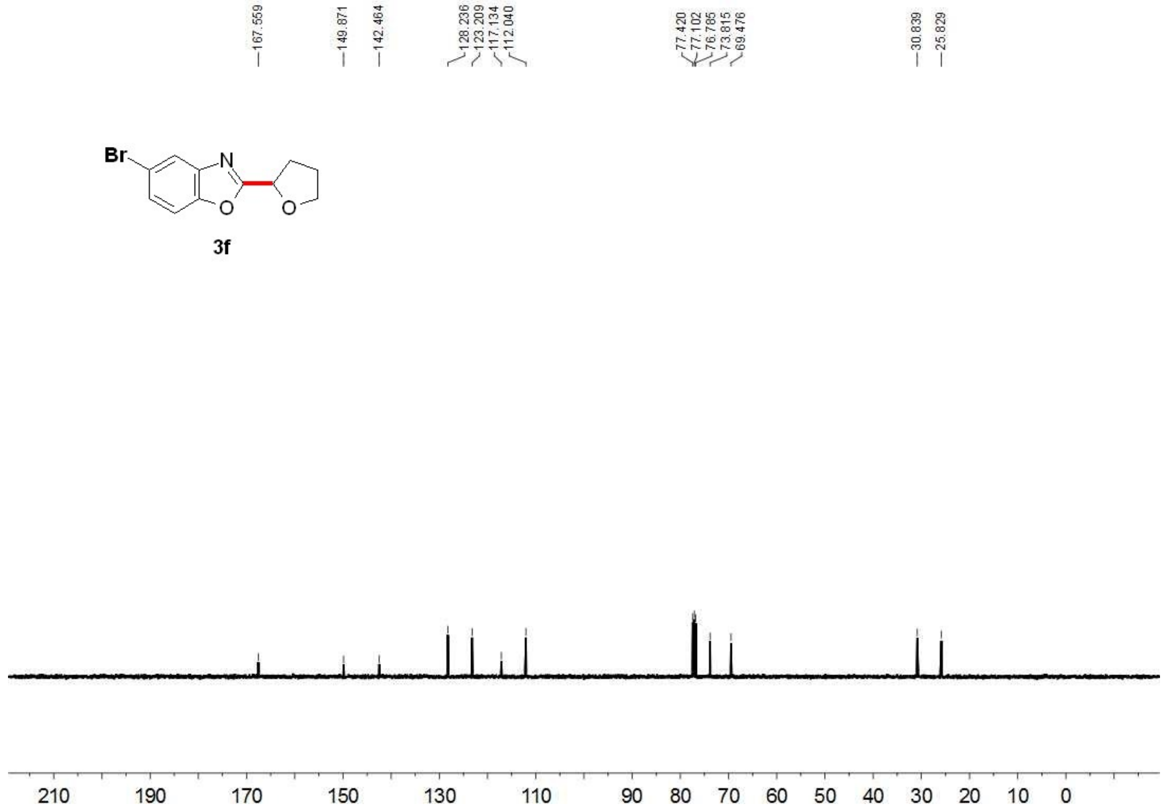
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Br
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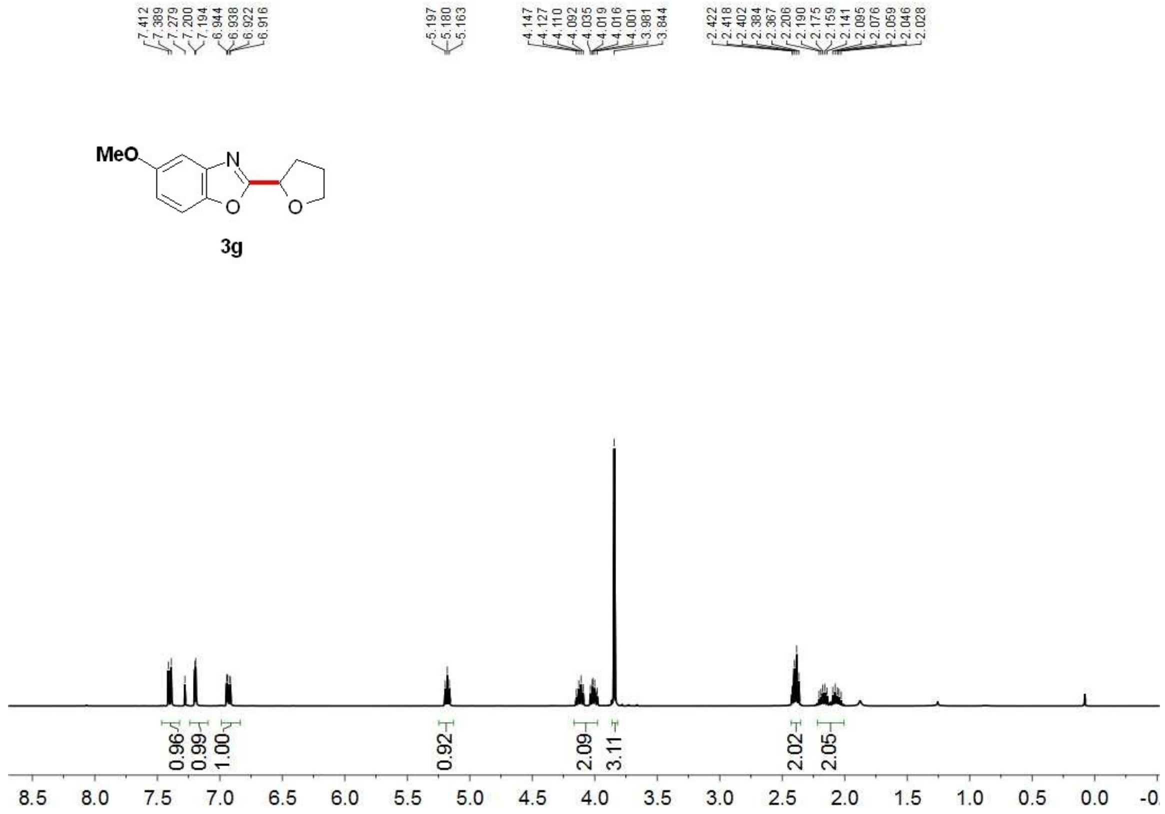
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4.035
4.019
4.016
4.001
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2.402
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2.367
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2.175
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2.046
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1.00
0.92
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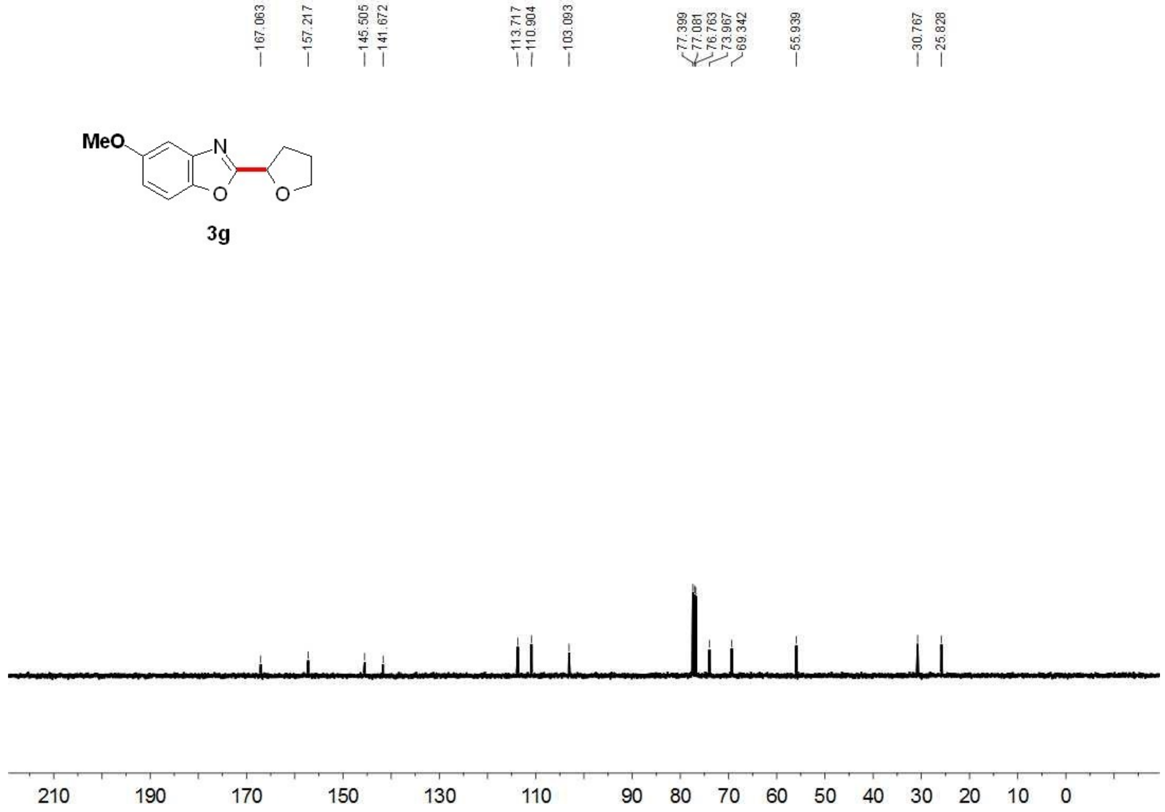
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55.939
30.767
25.828
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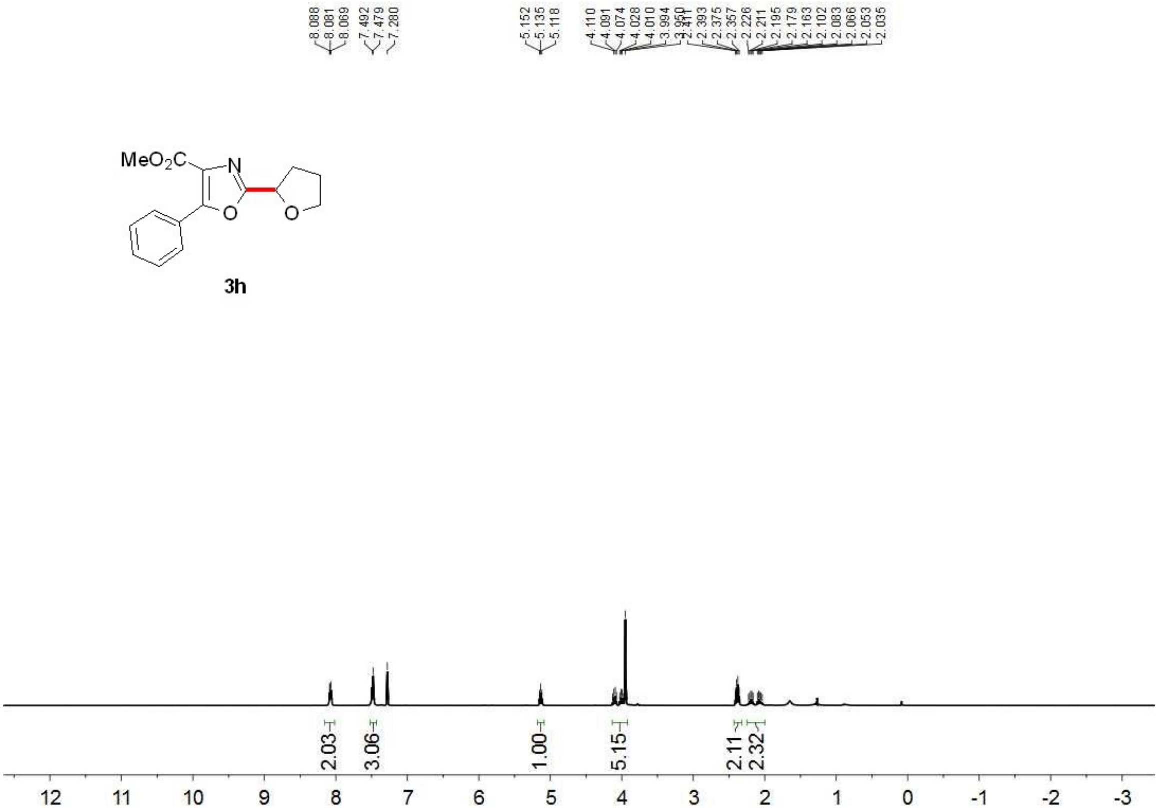
3g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2.211
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2.035
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3.06
1.00
5.15
2.11
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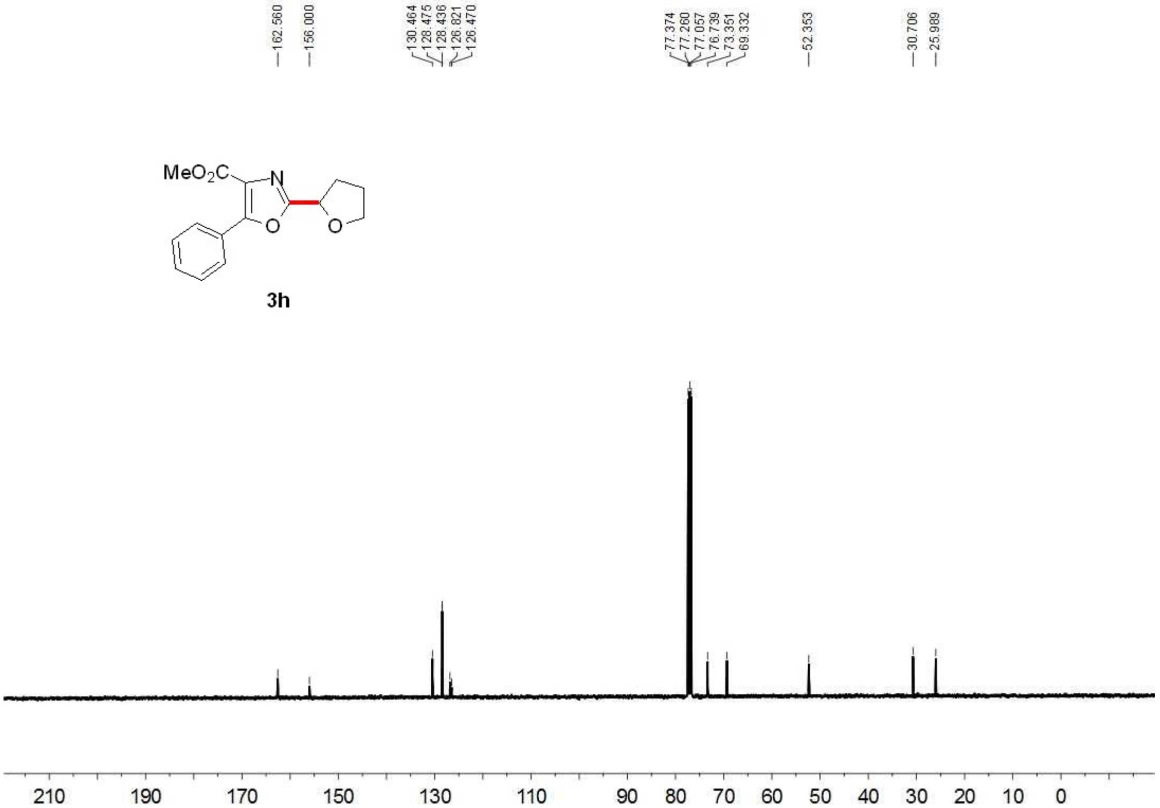
3h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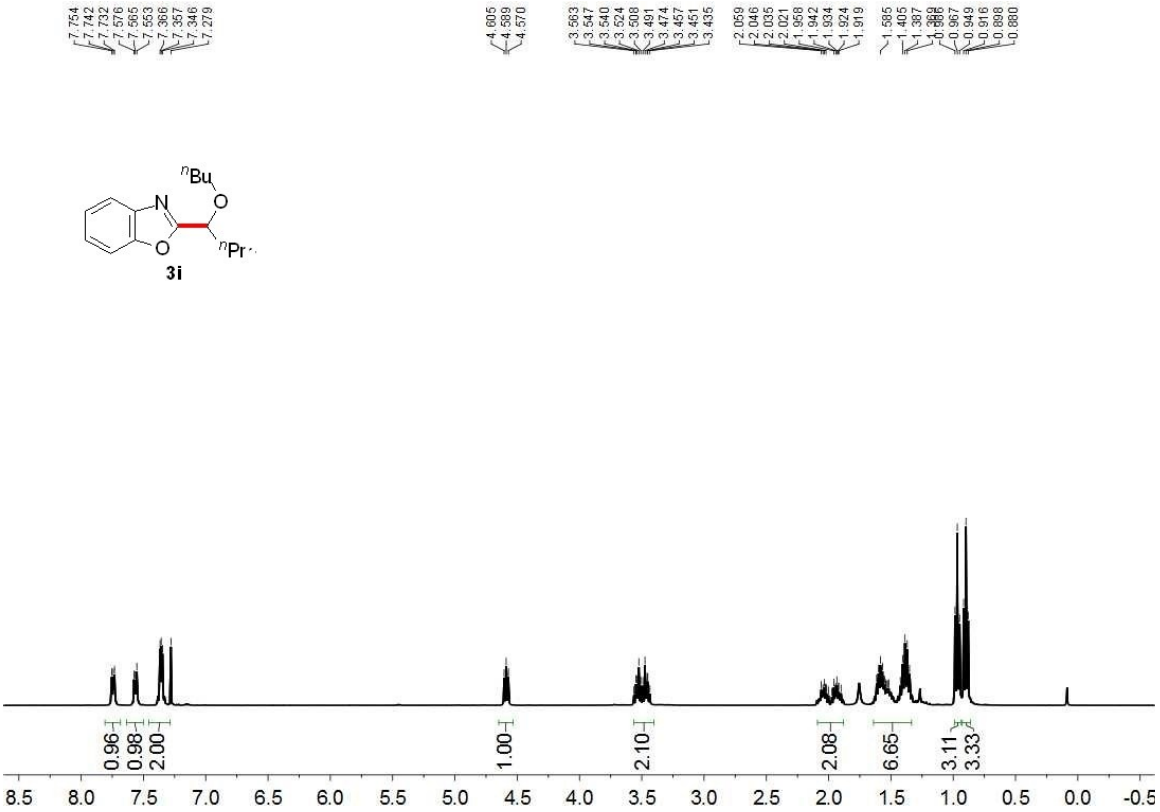
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O
N
O
^{n}Pr
3i
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1.00
2.10
2.08
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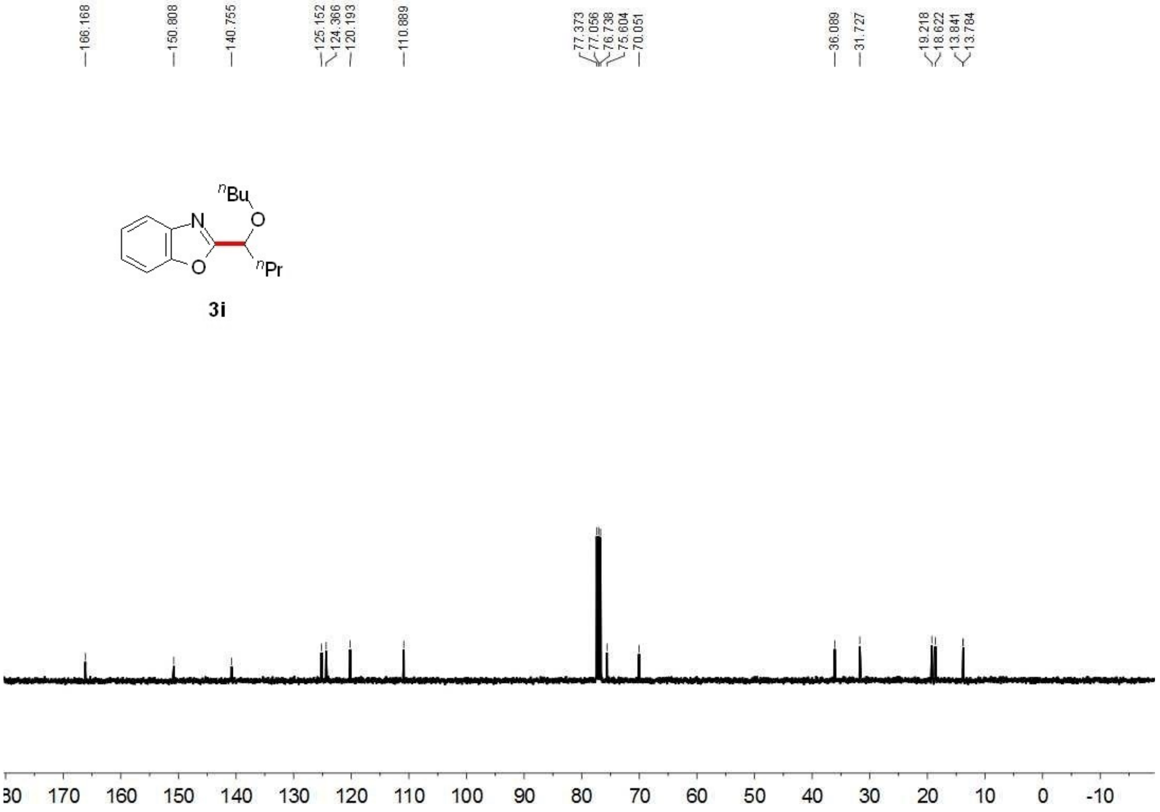
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^{n}Bu
O
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O
^{n}Pr
3i
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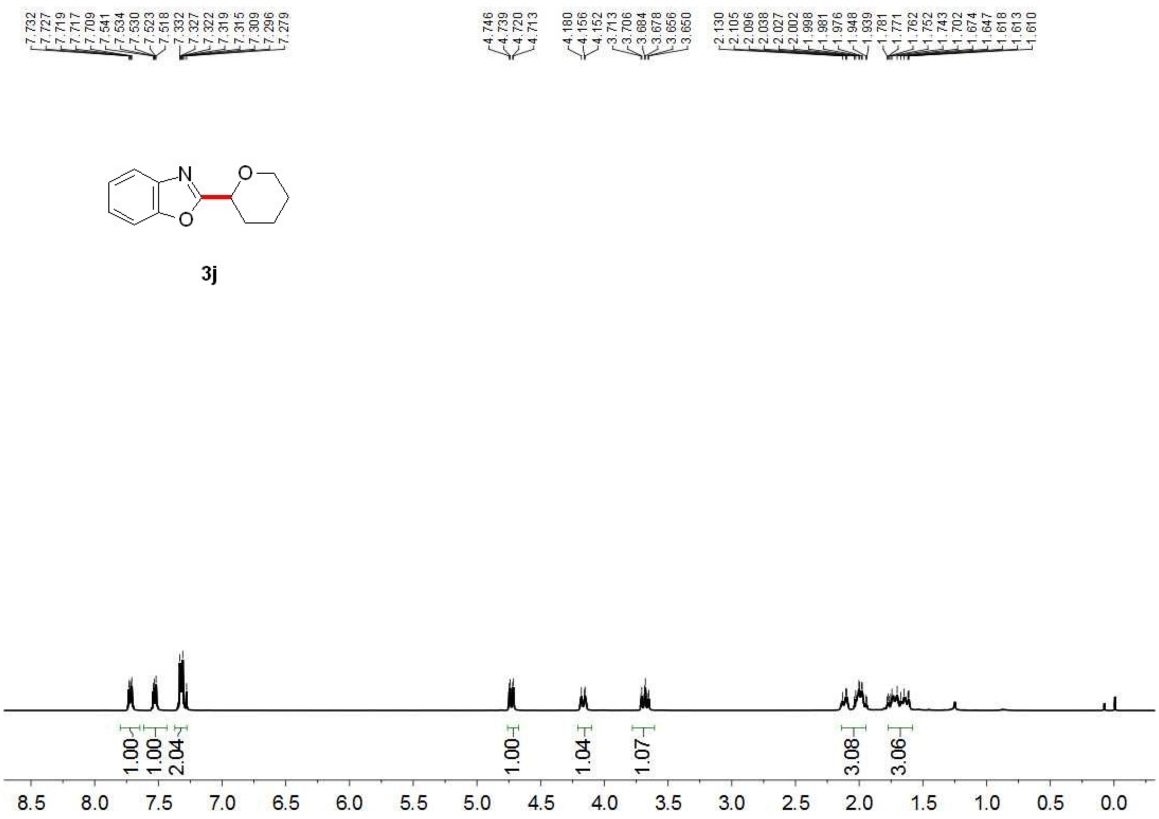
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1.00
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1.07
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3.06
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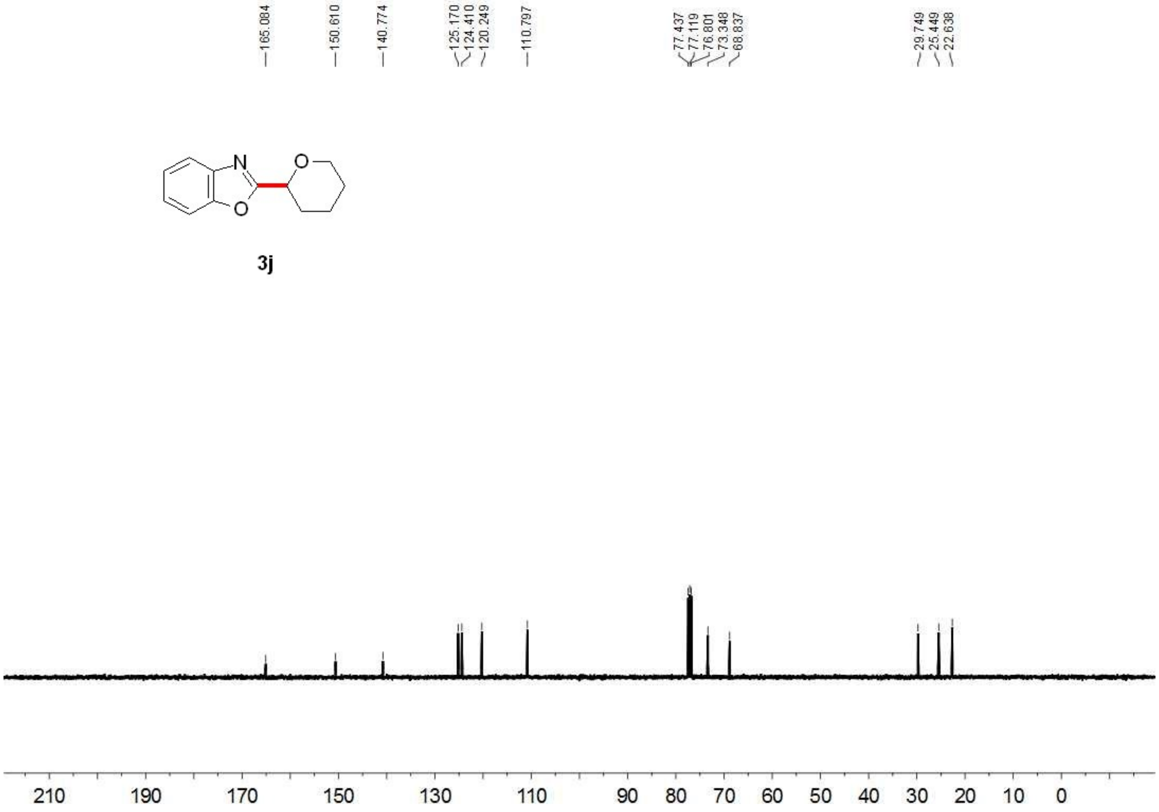
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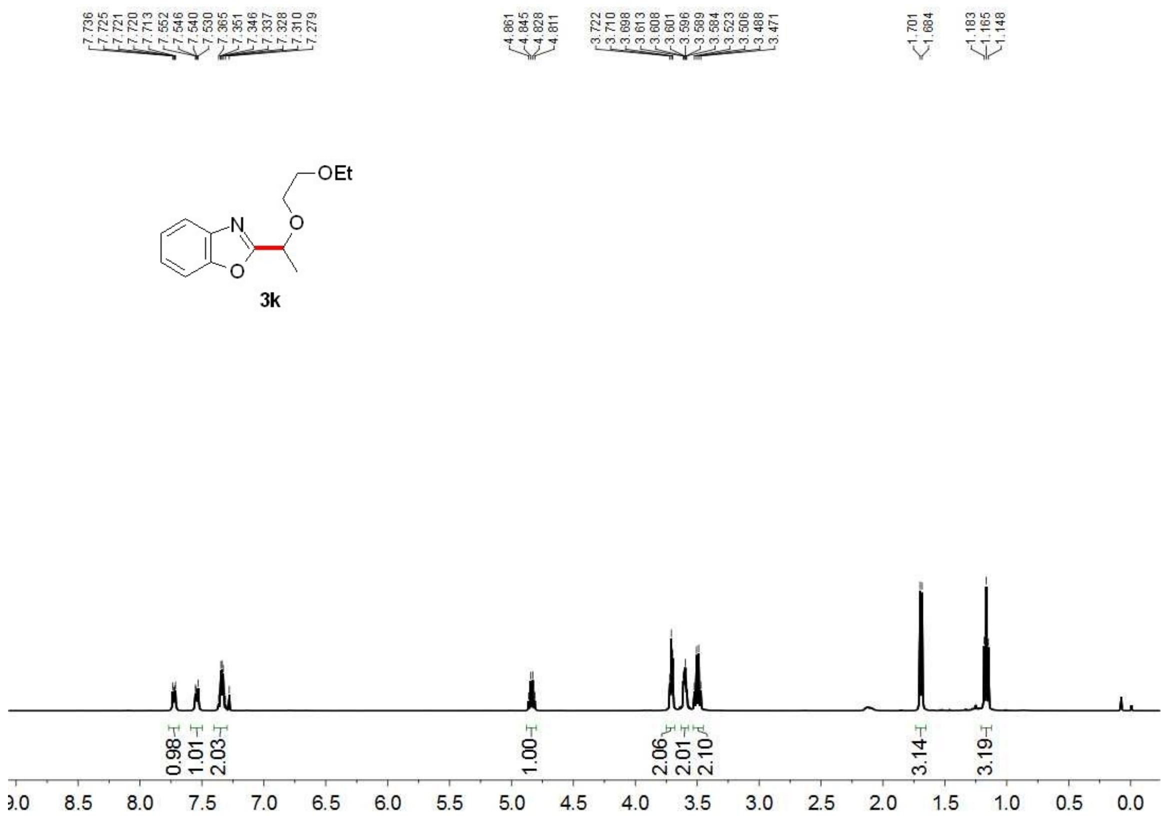
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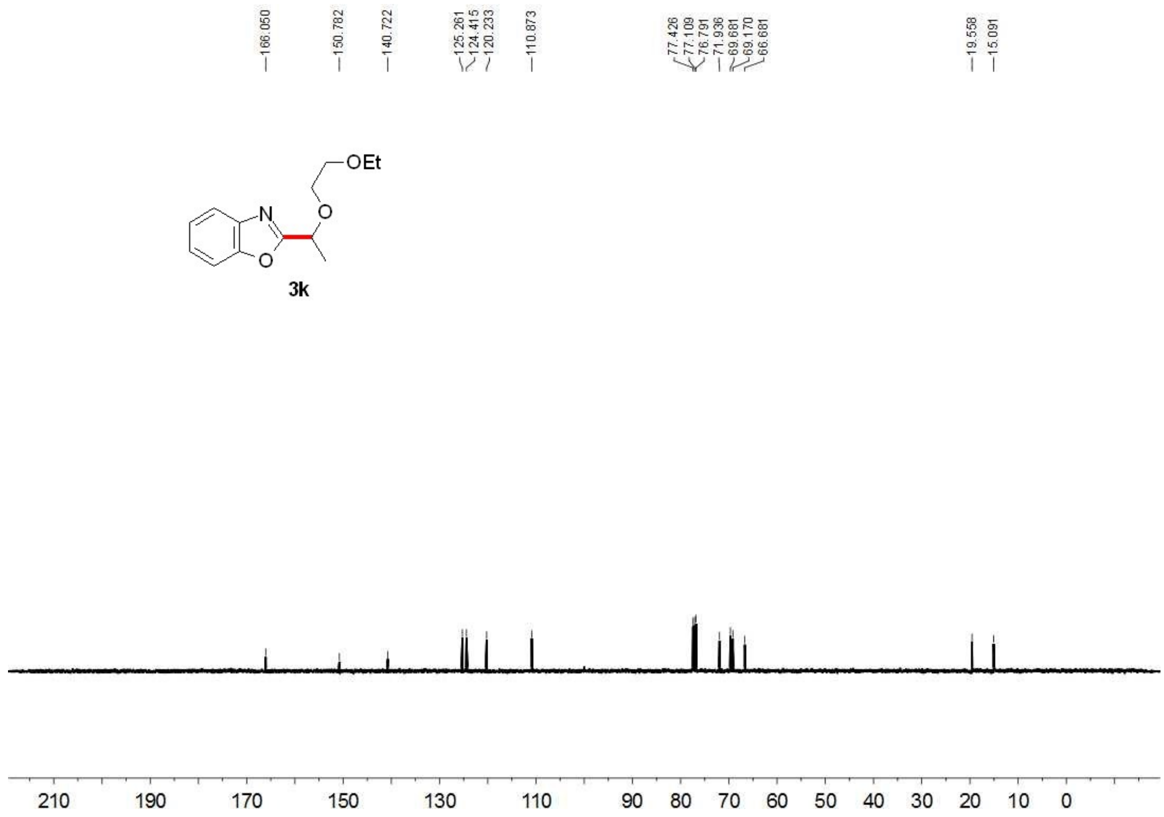
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66.681
19.558
15.091
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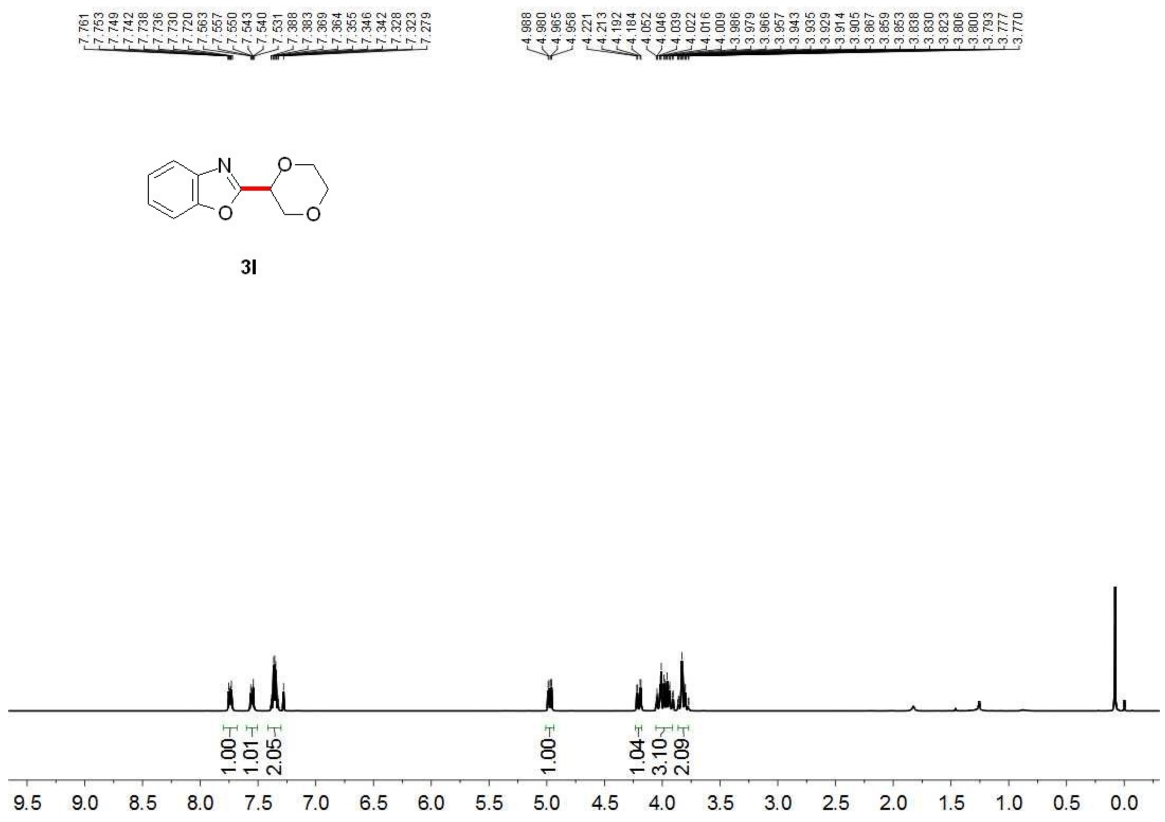
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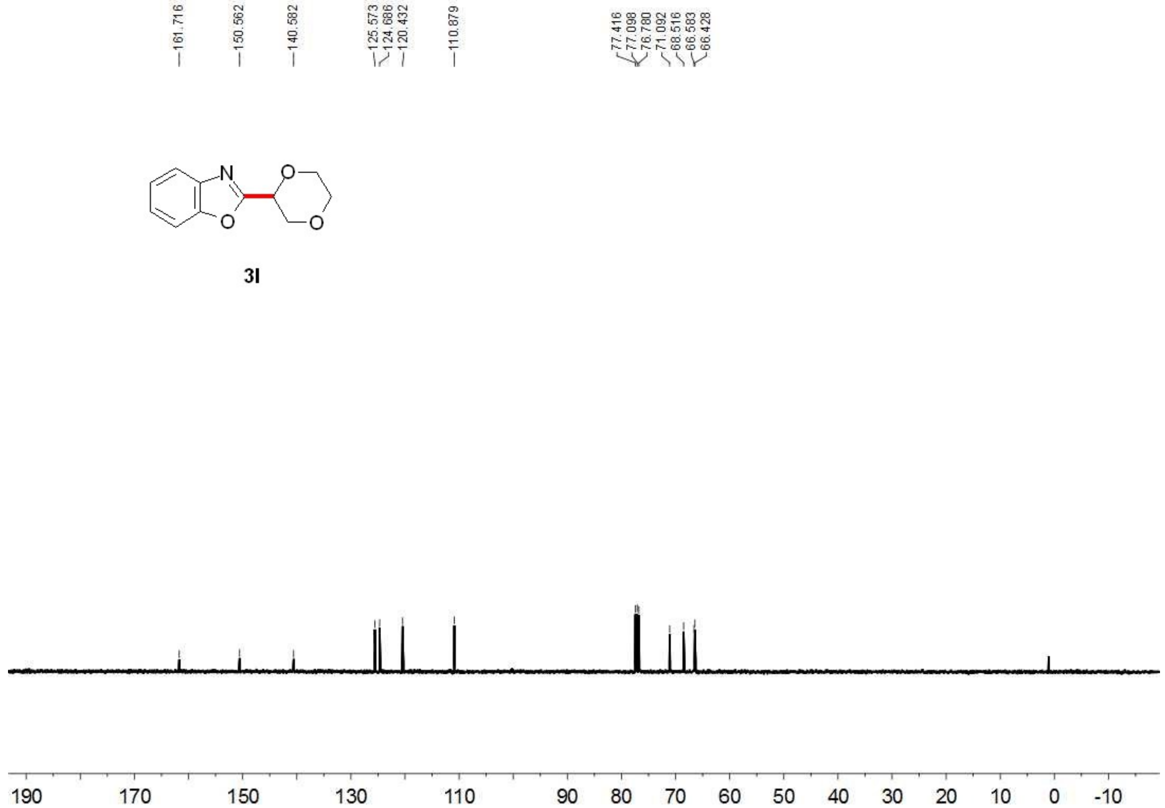
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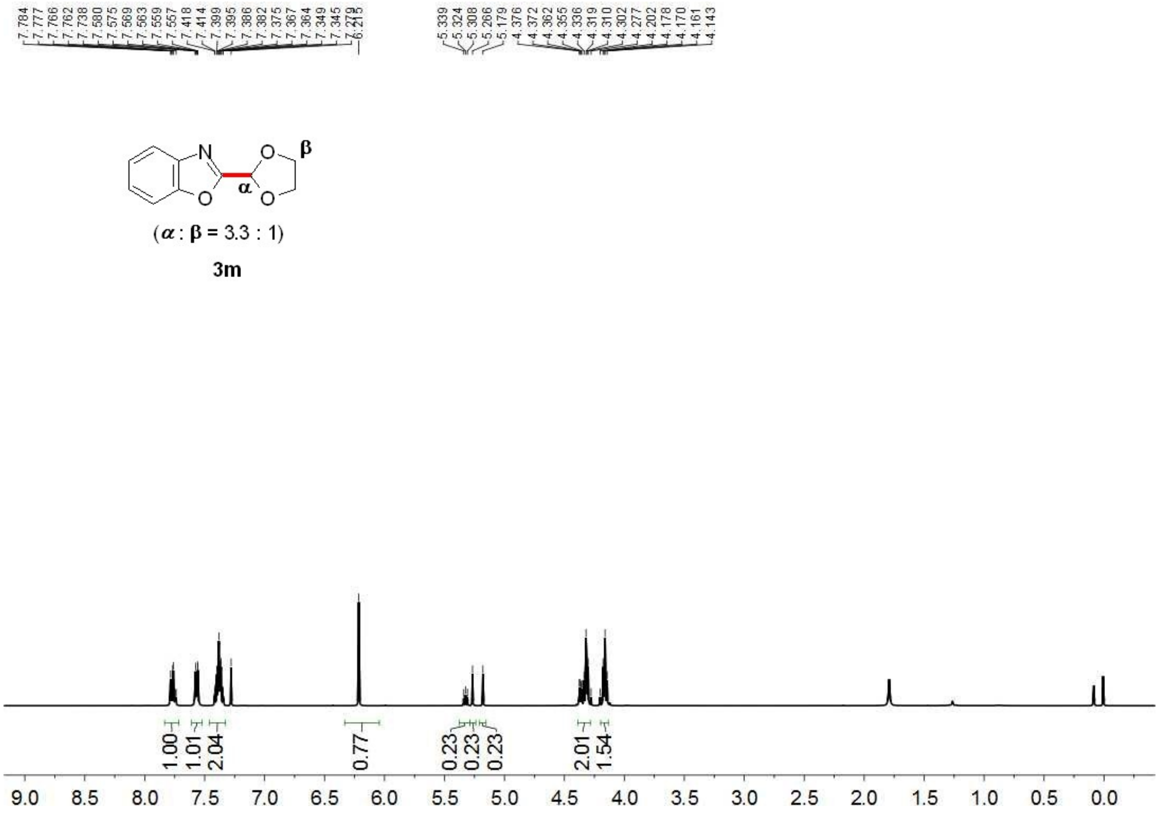
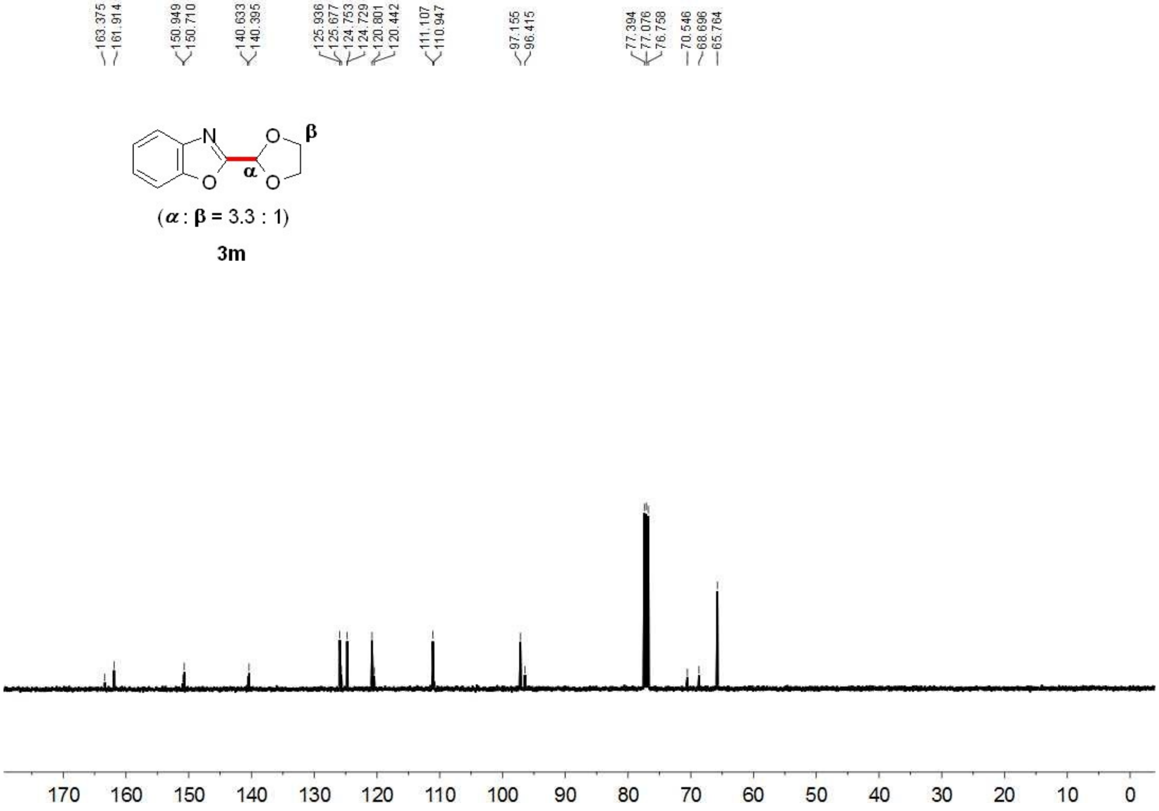


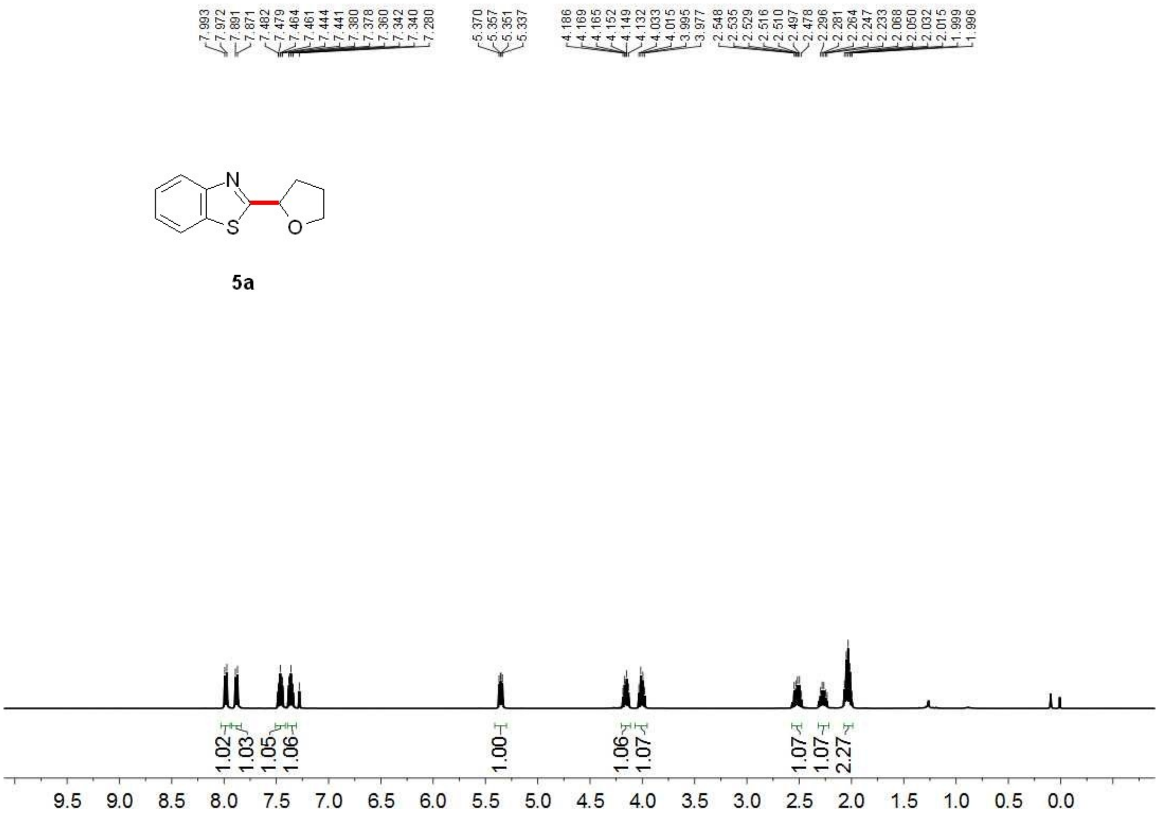
(α : β = 3.3 : 1)

3m



(α : β = 3.3 : 1)

3m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2.032
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1.996
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S
O
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1.07
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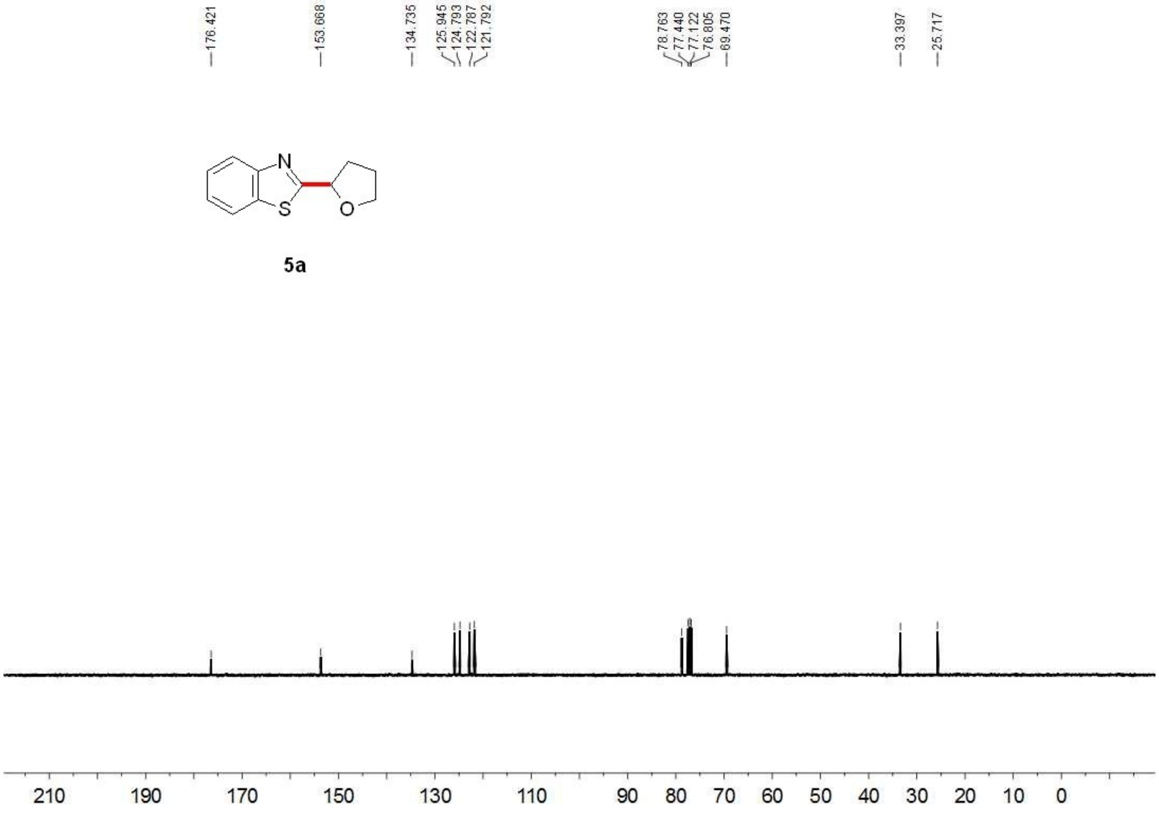
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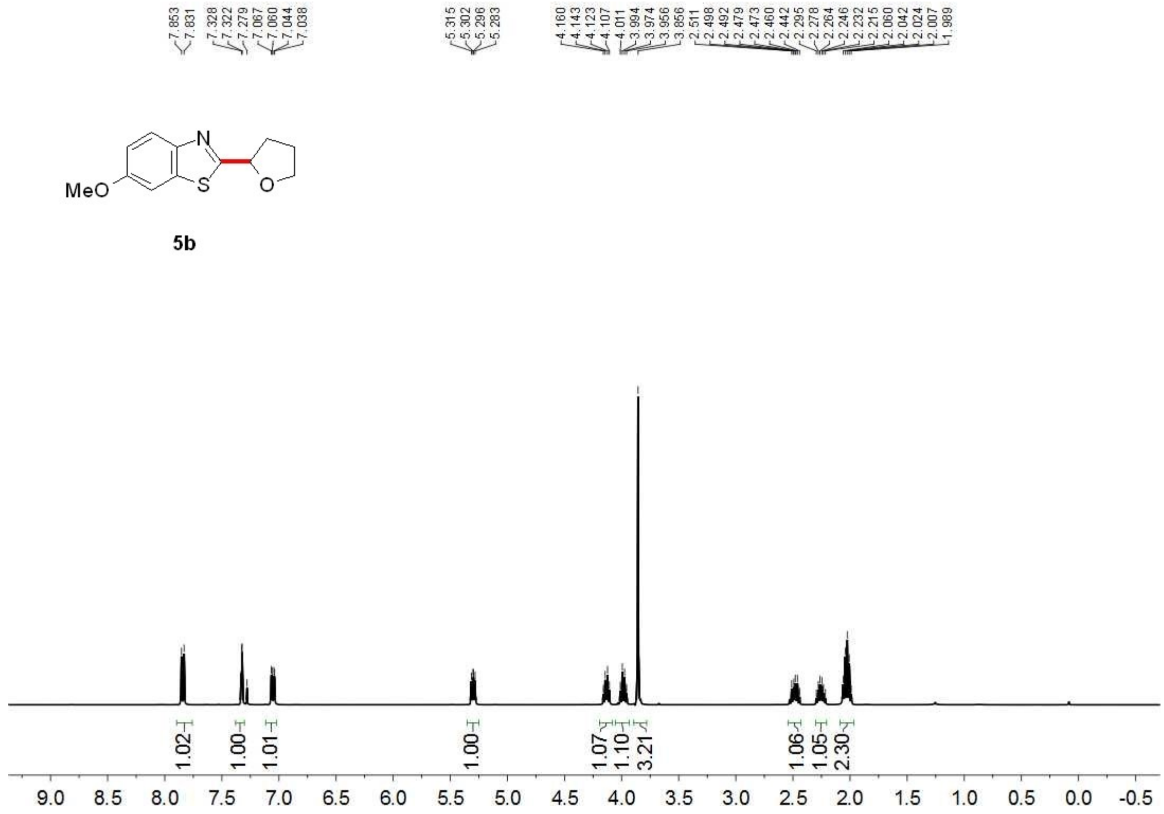
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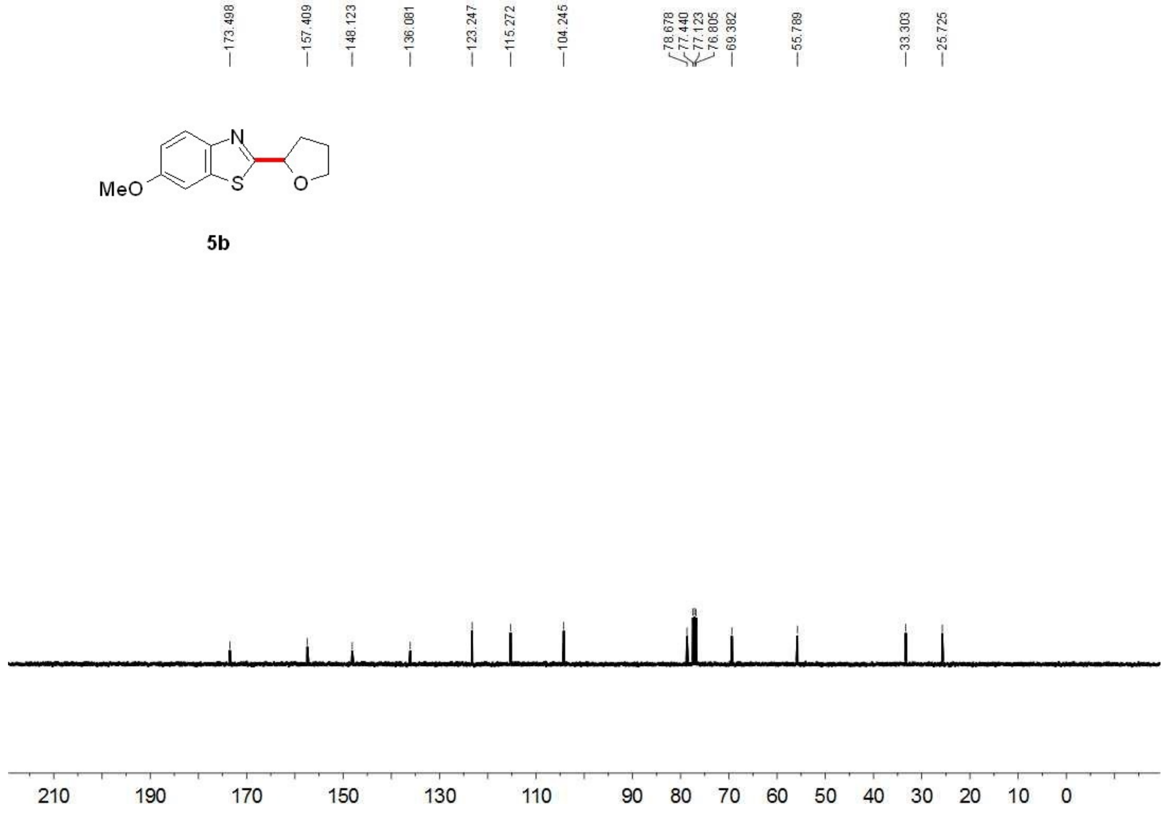
5b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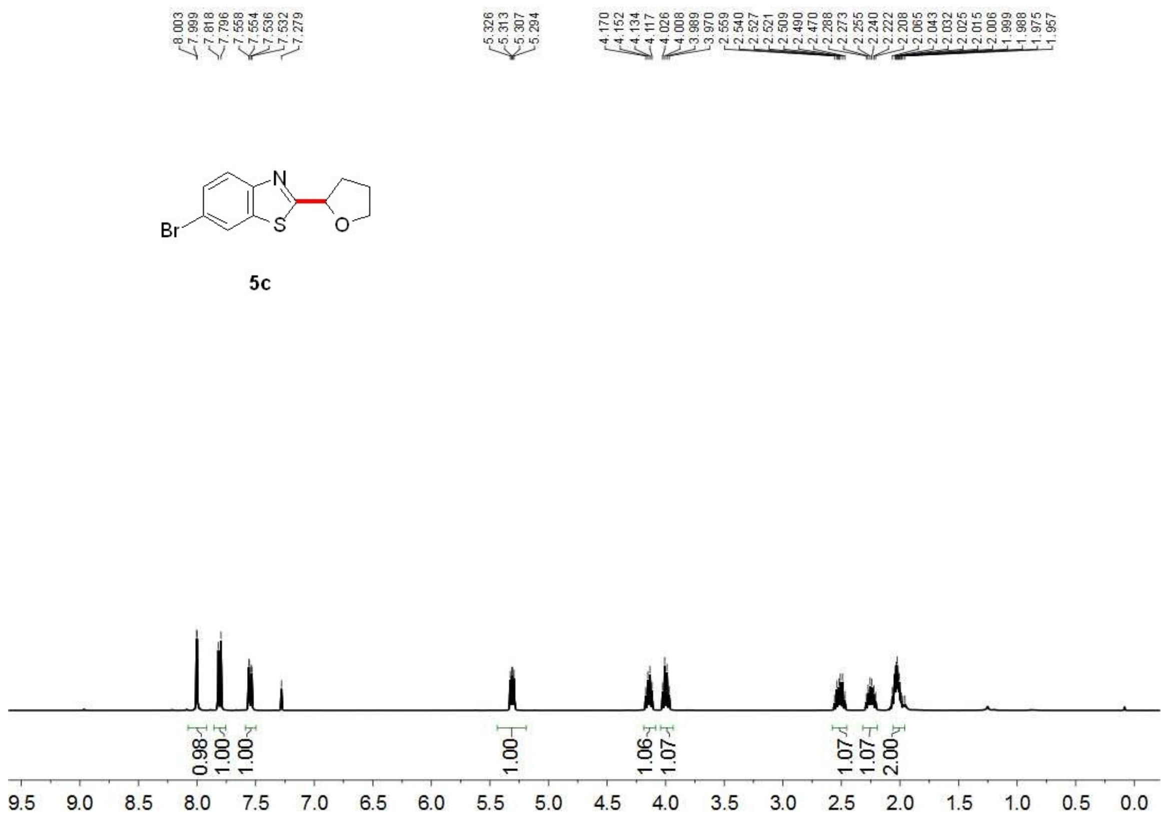
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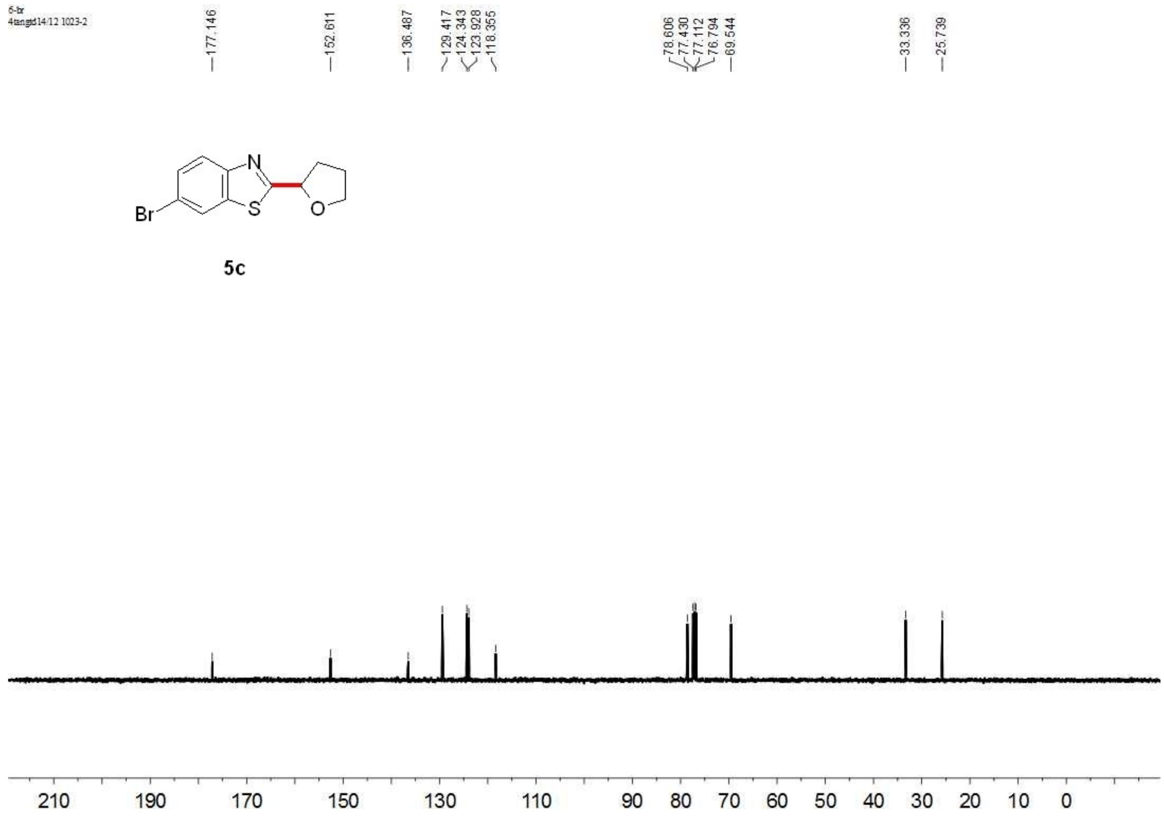
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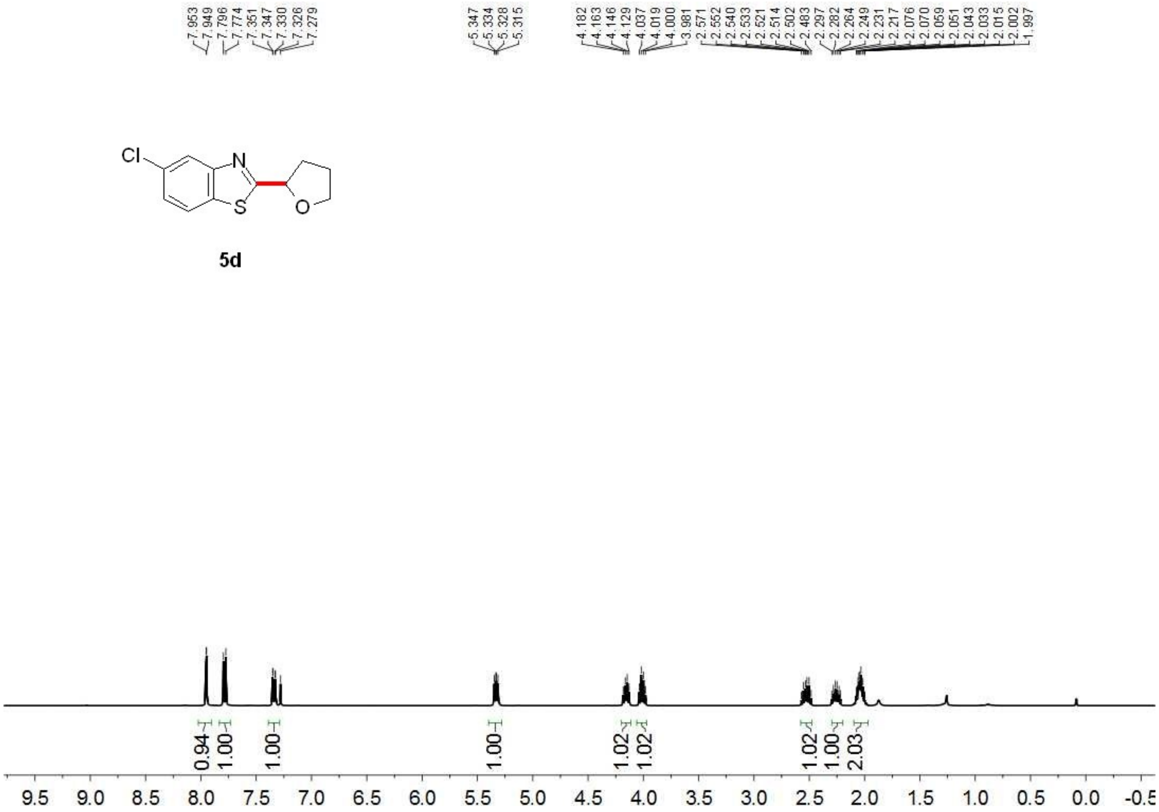
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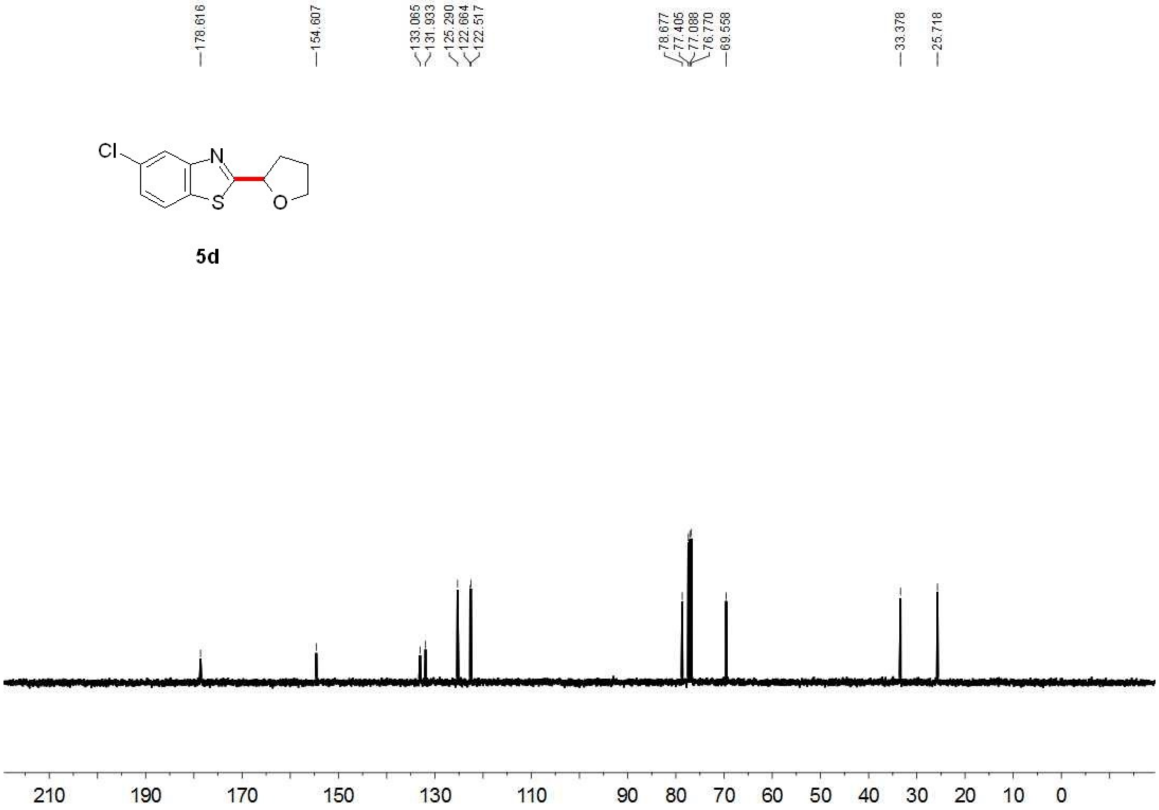
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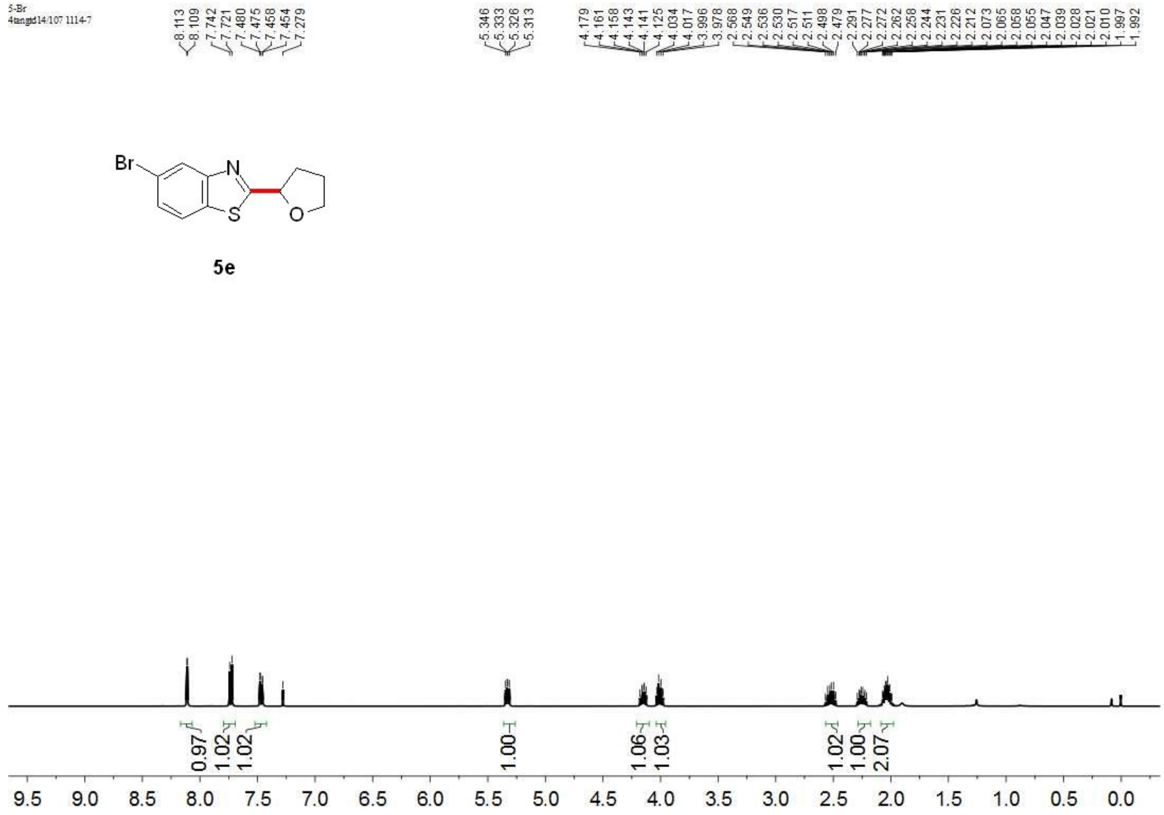
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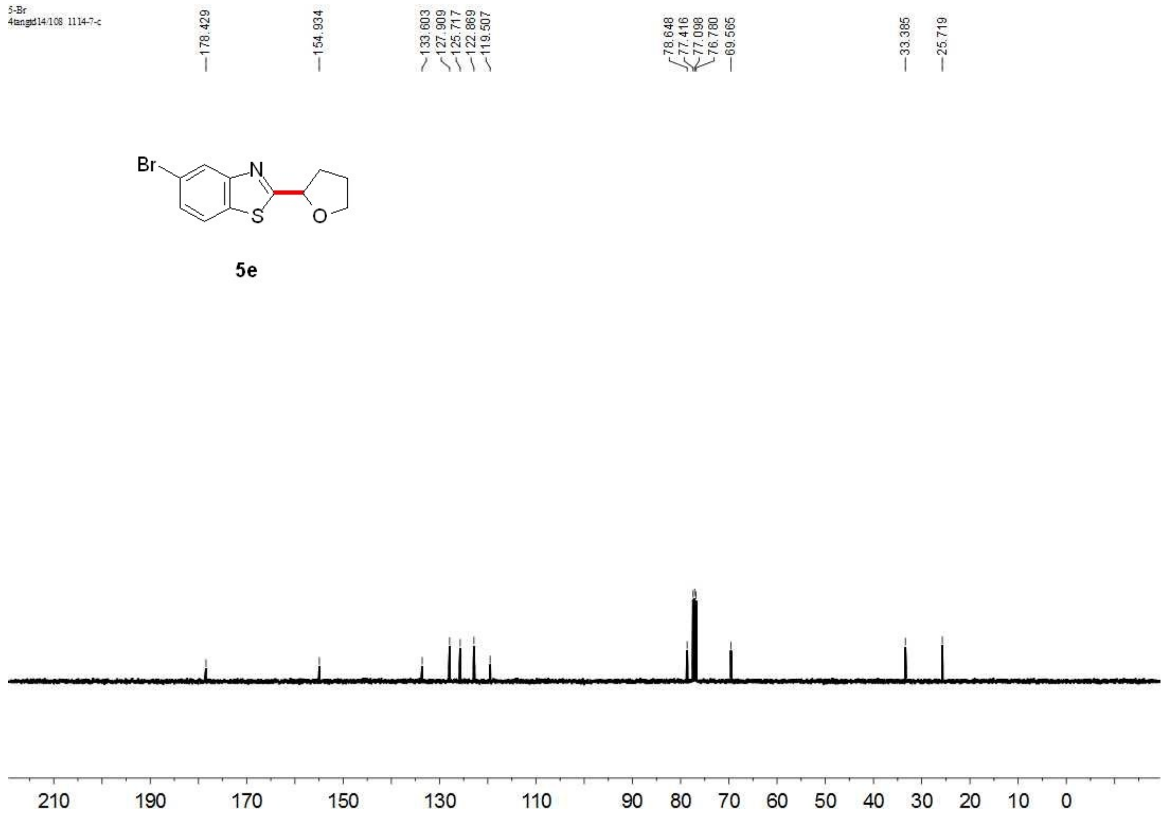
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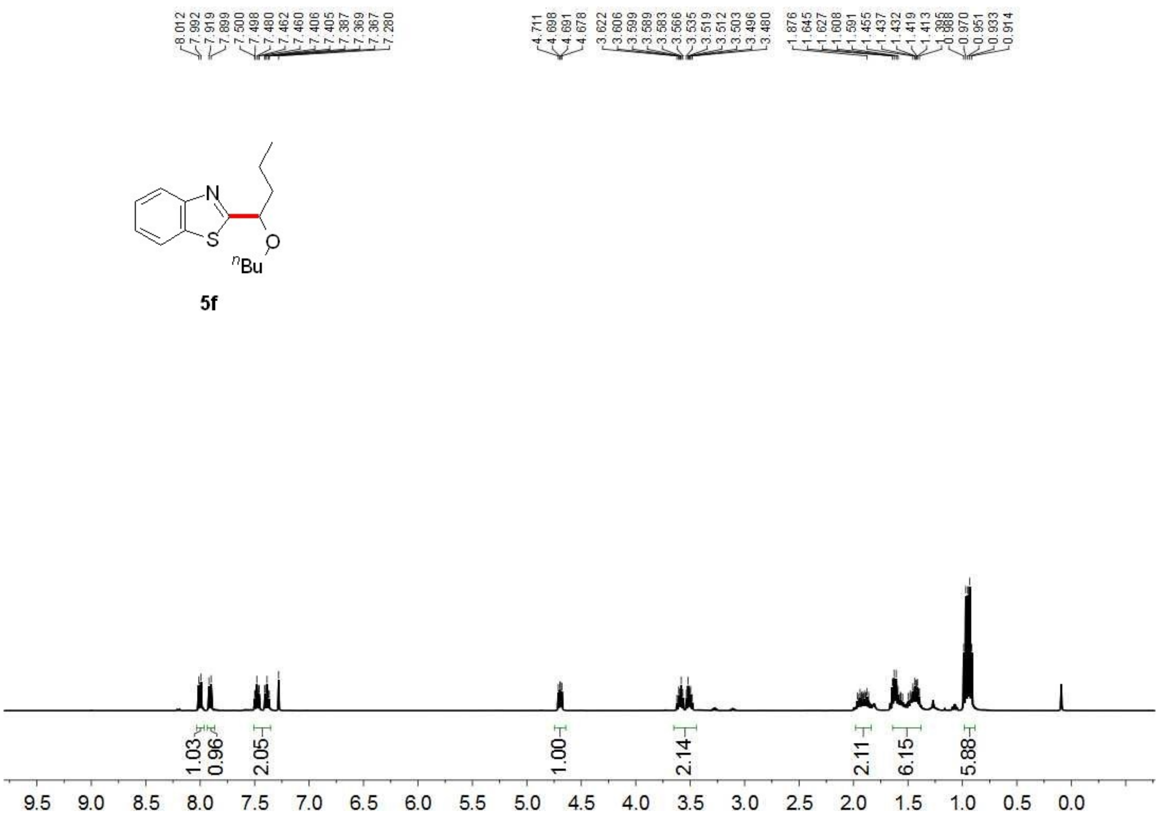
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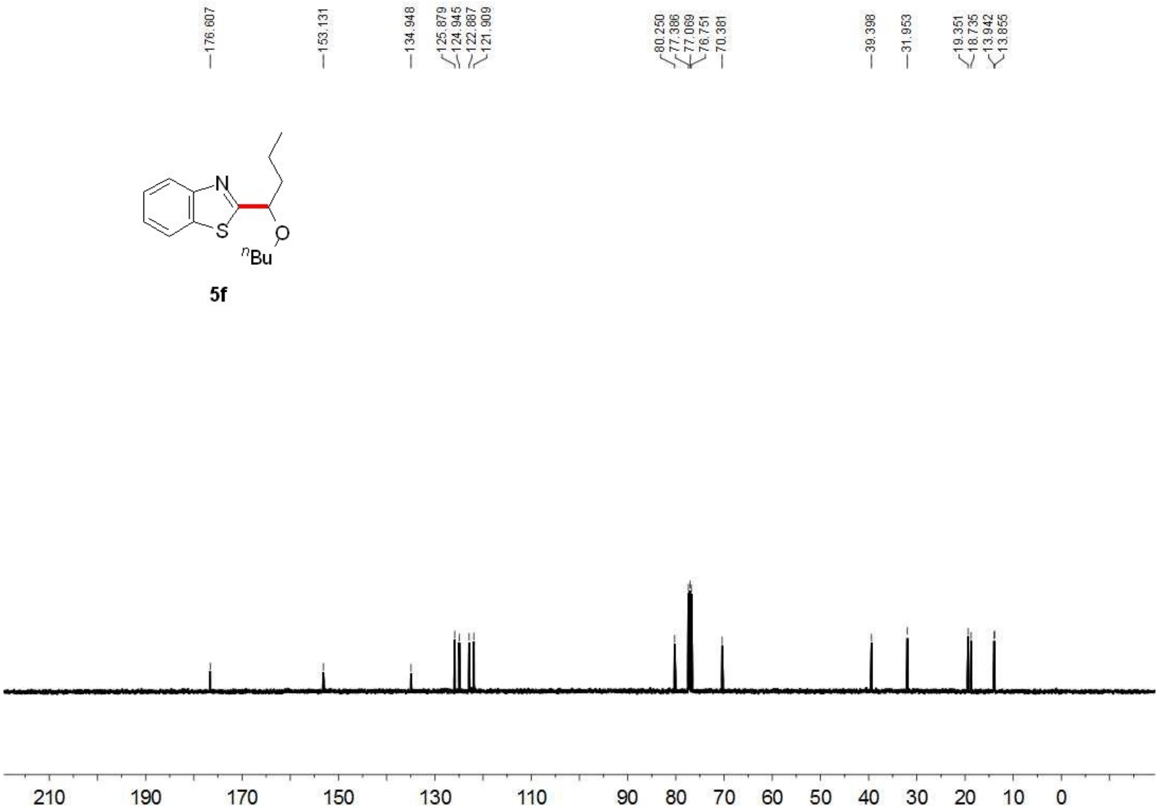
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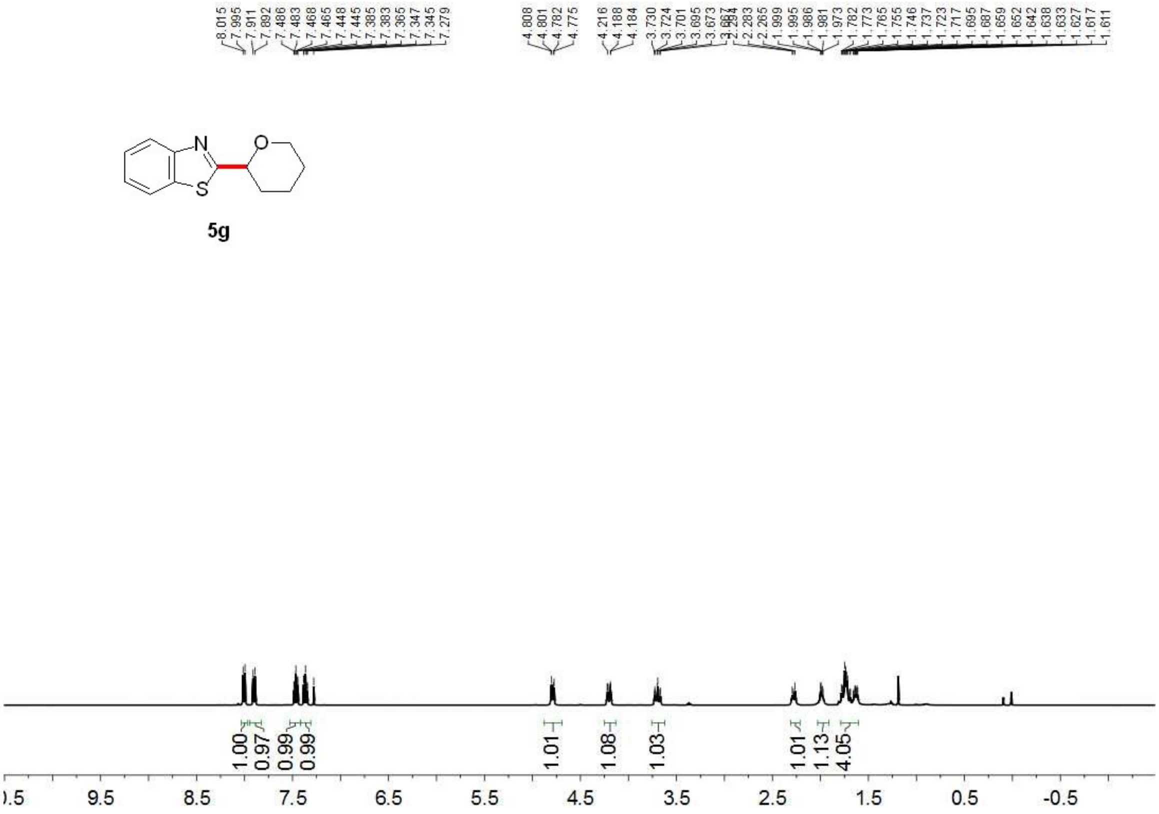
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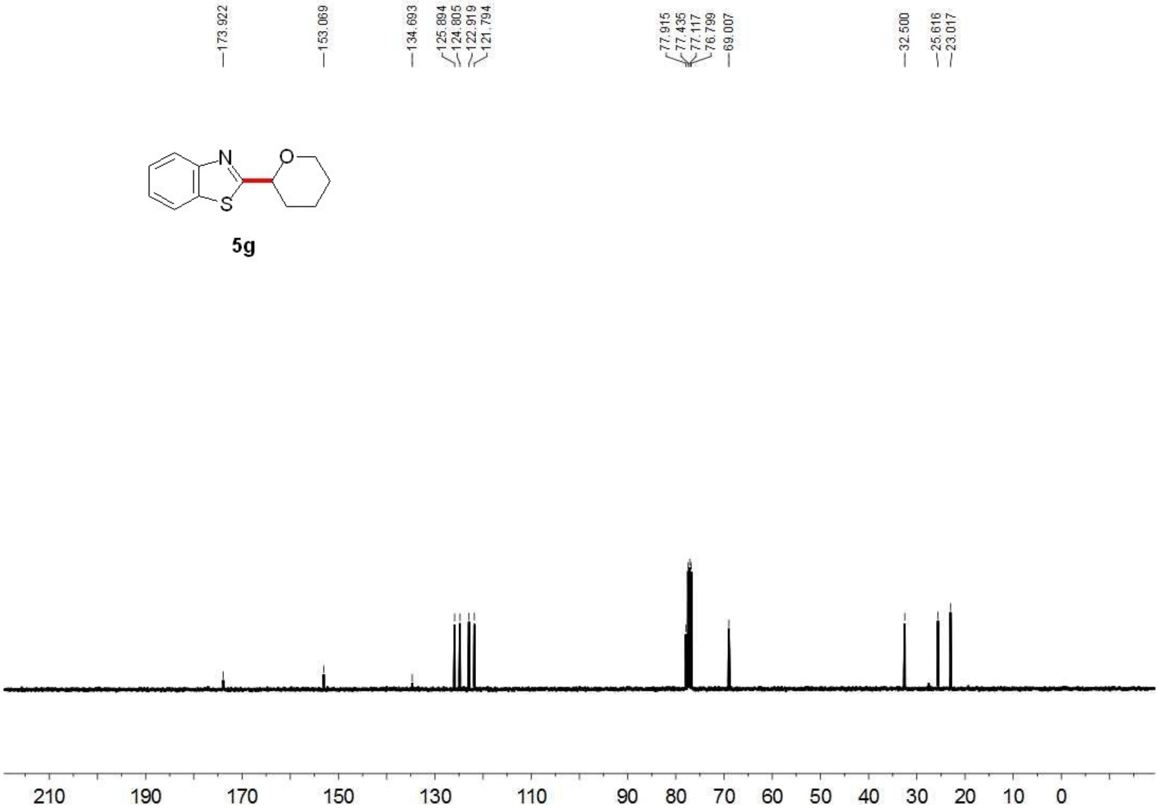
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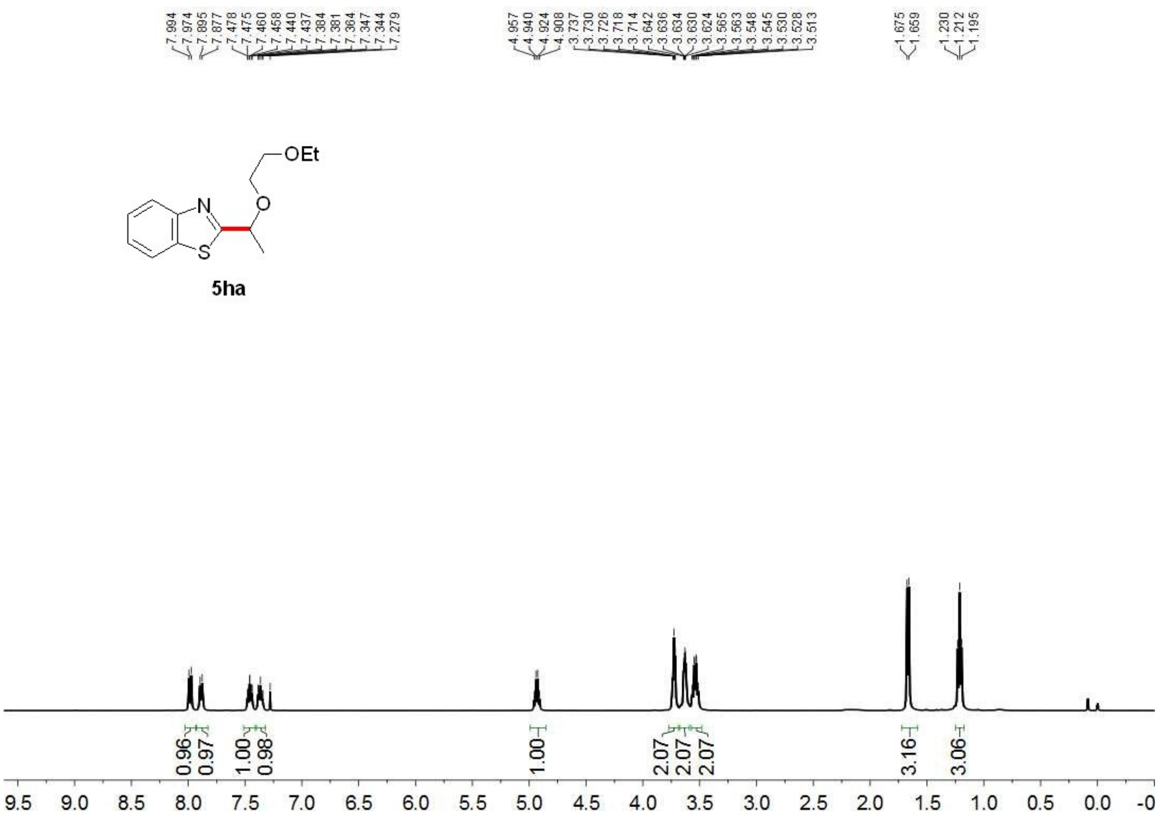
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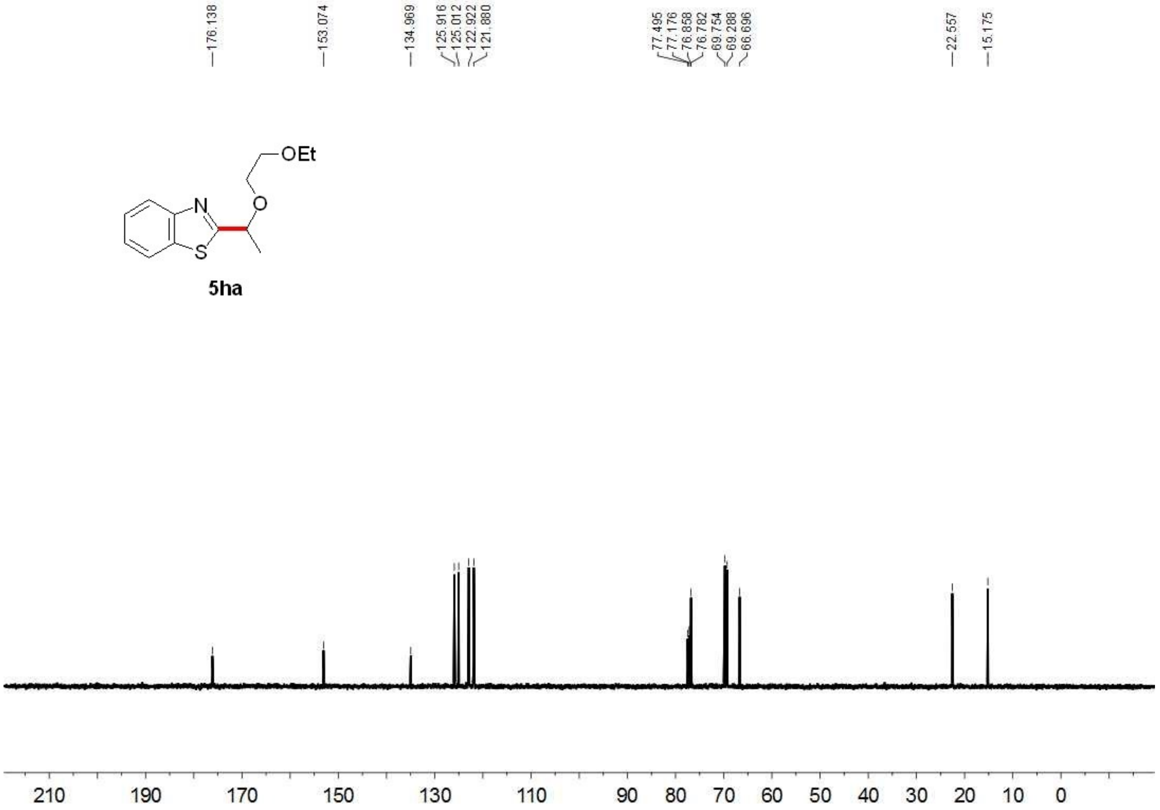
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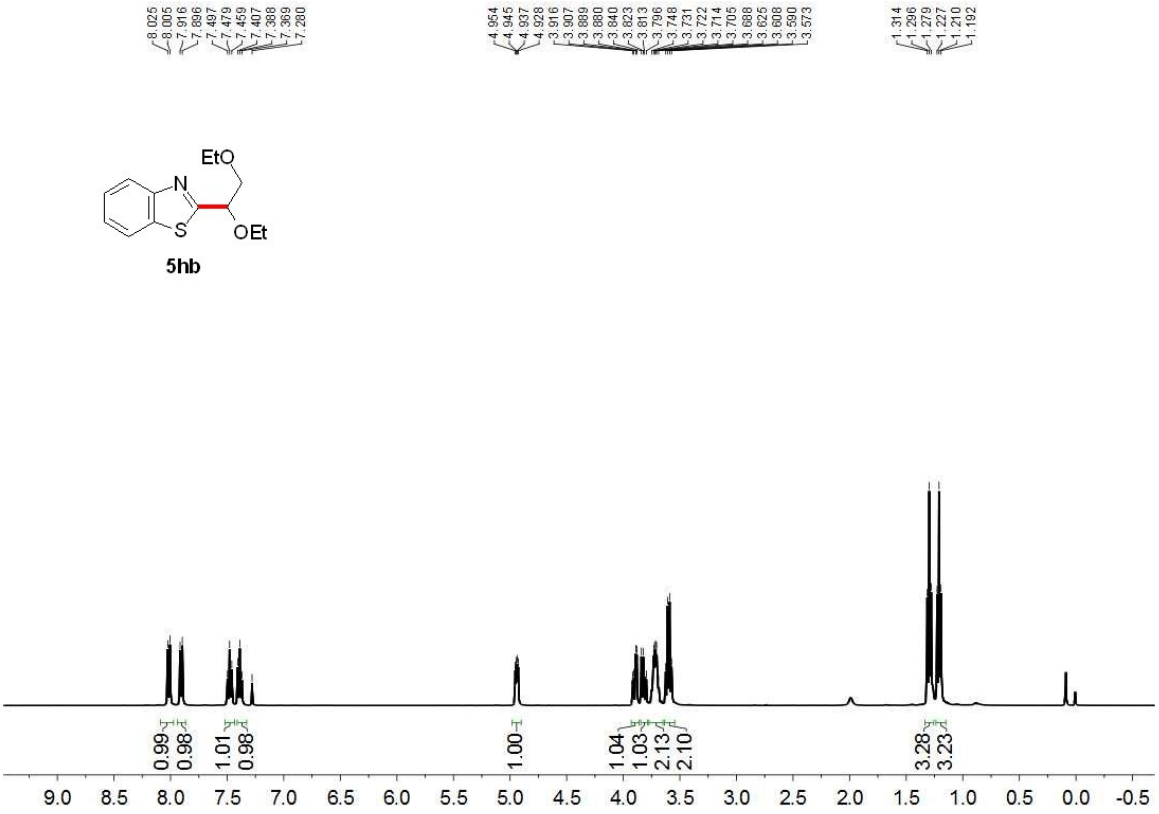
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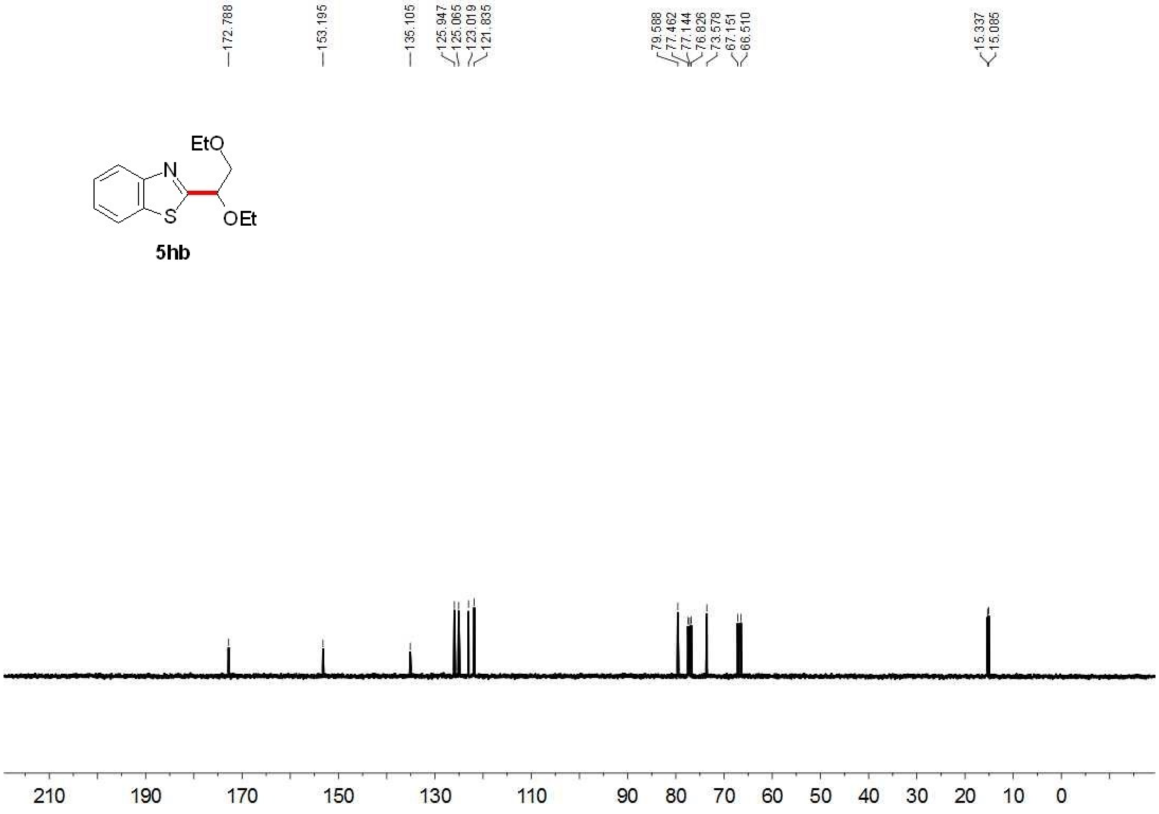
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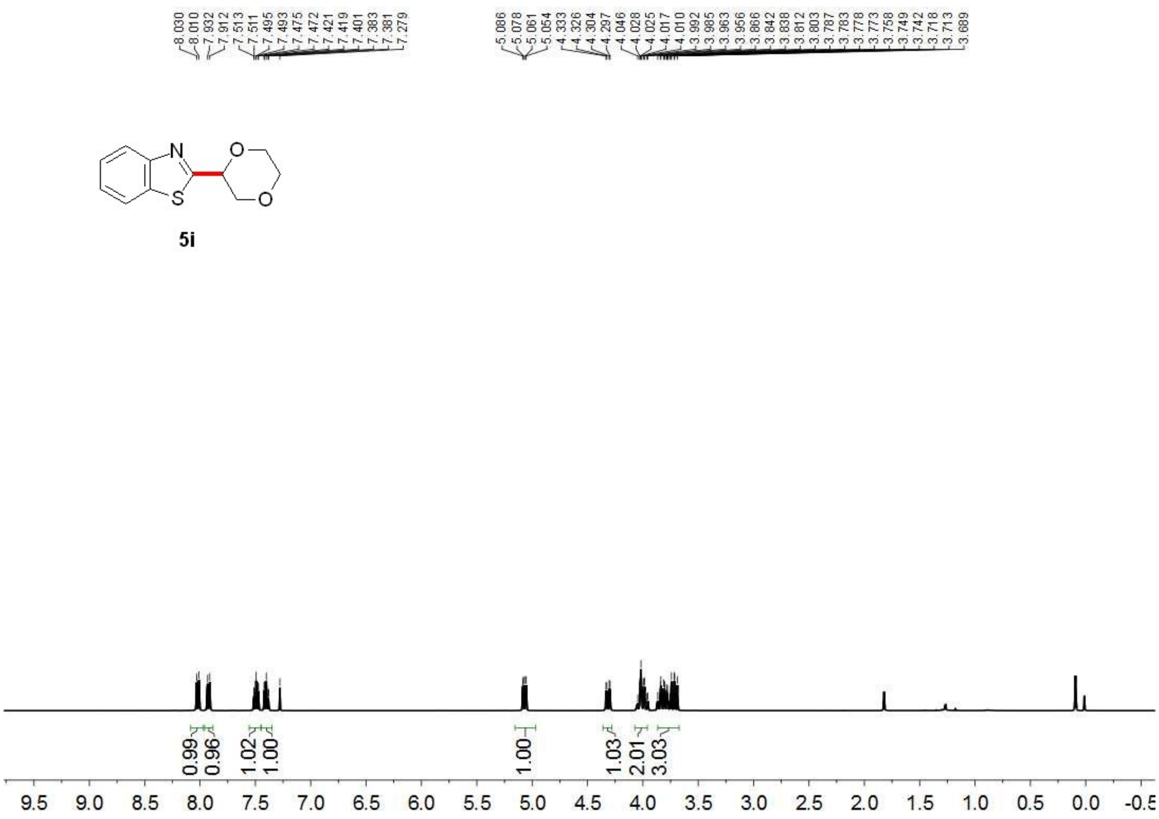

5i

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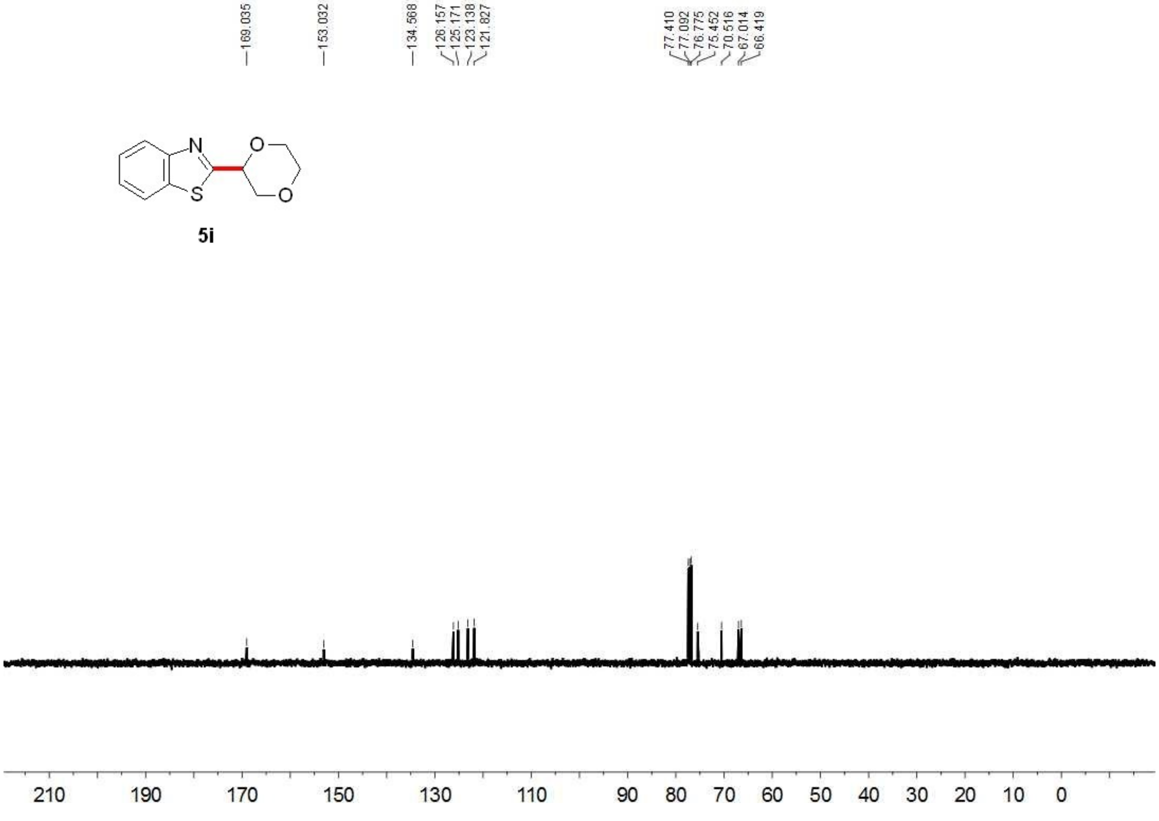

5i

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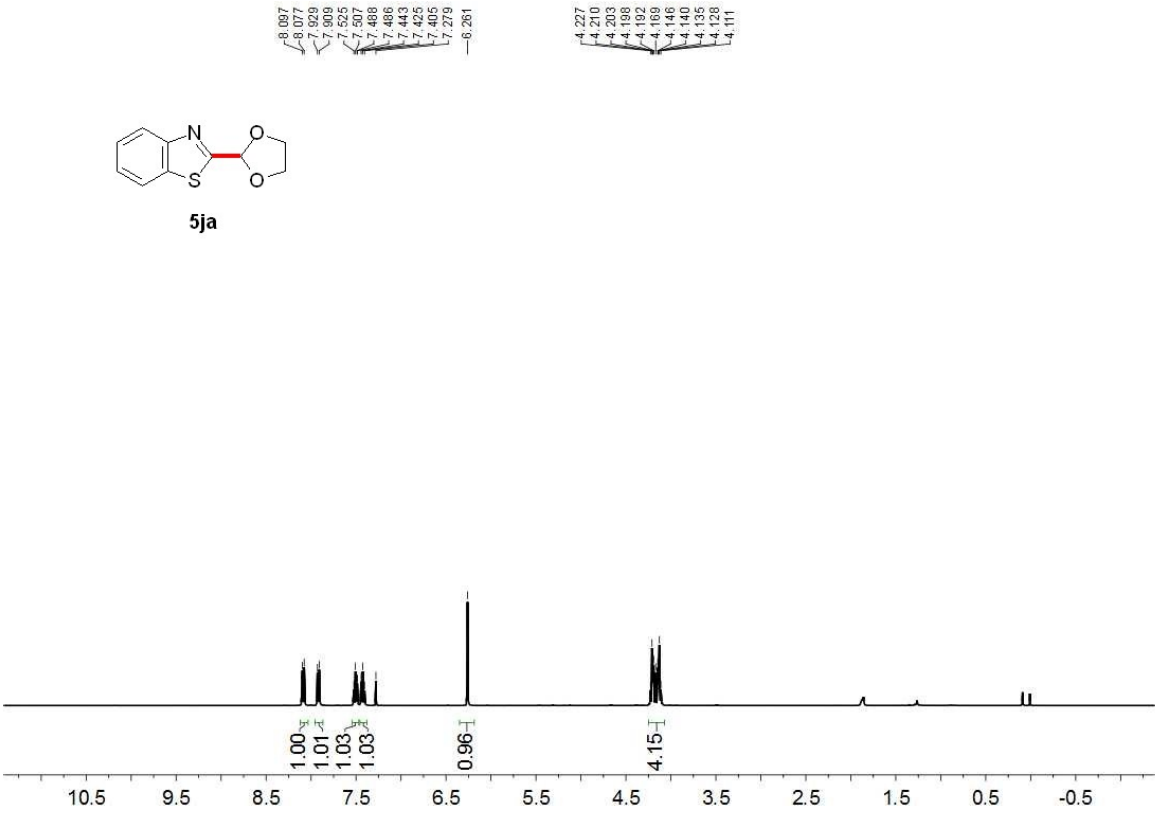
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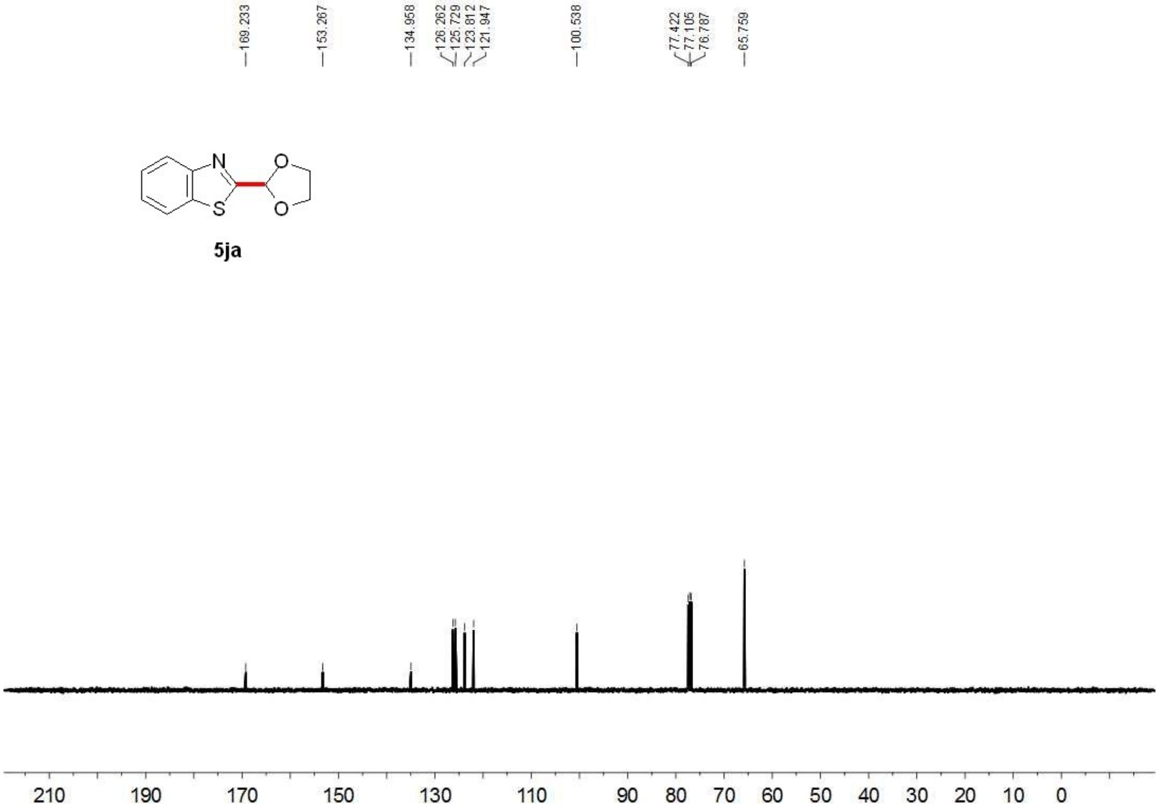
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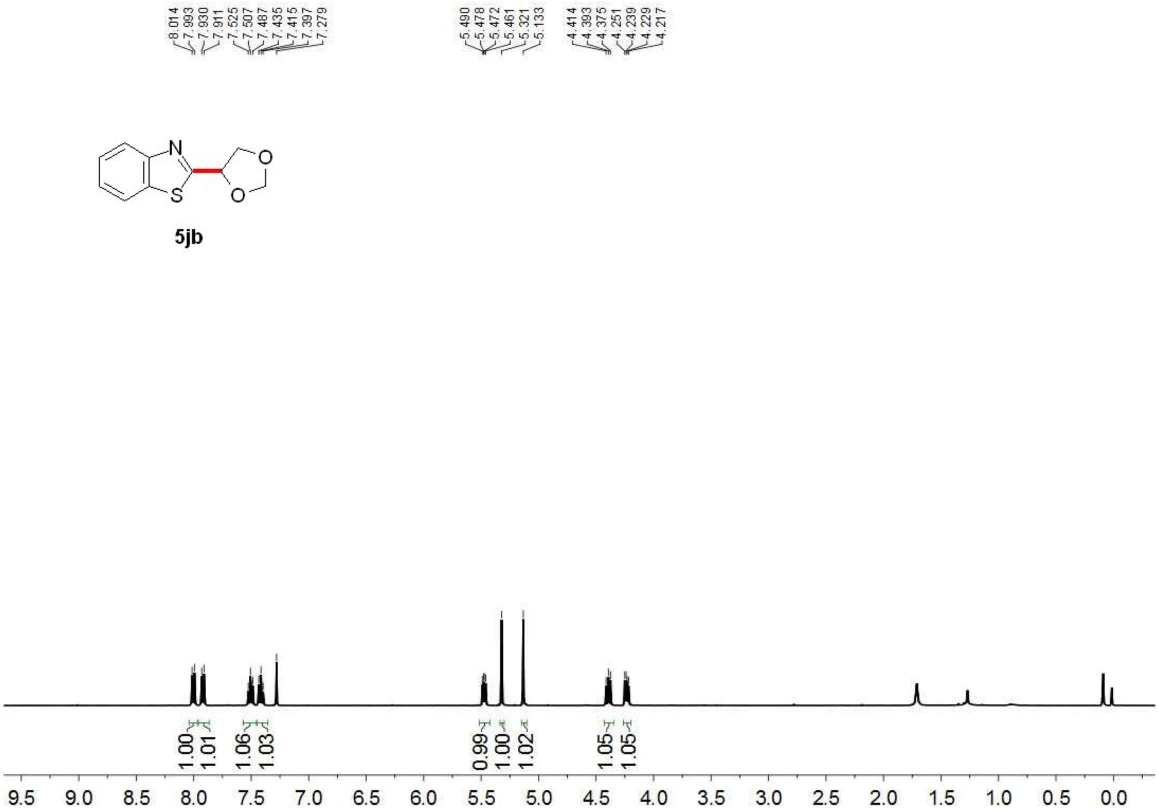
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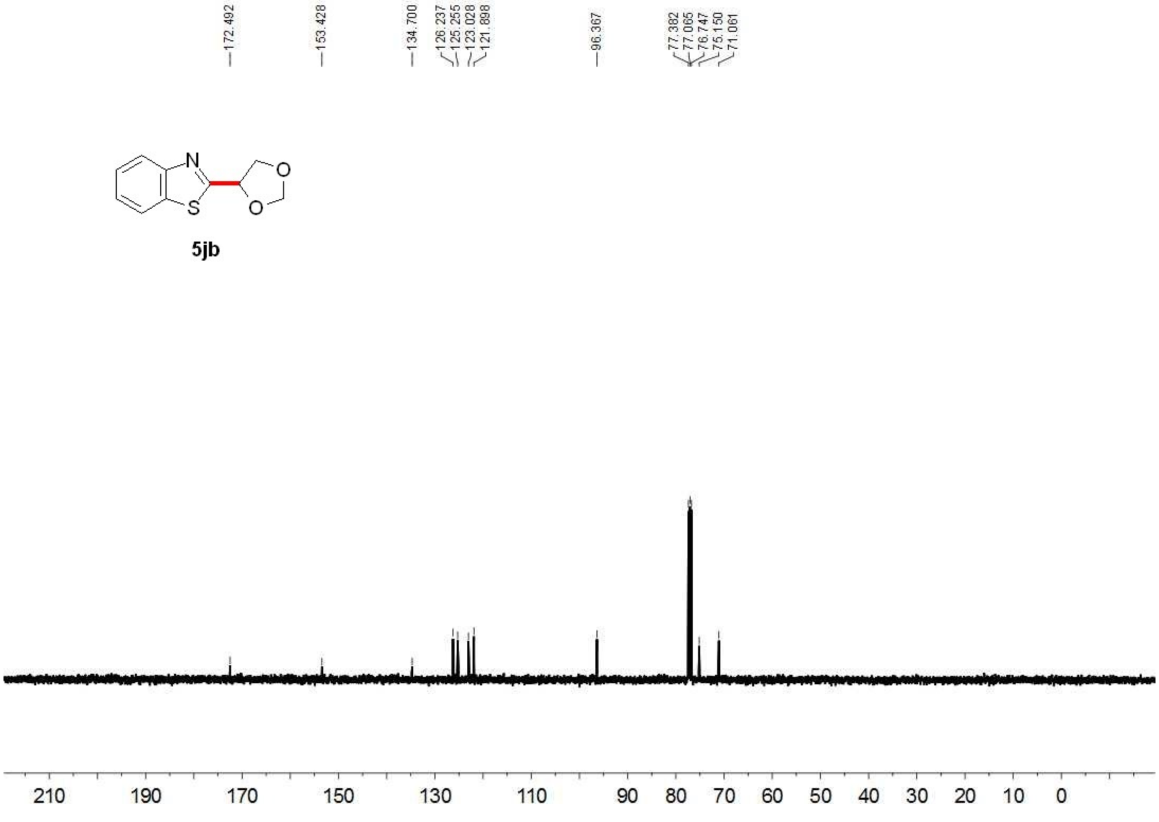
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