Electronic Supplementary Information

The decarboxylative C-H heteroarylation of azoles catalyzed by nickel catalysts to access unsymmetrical biheteroaryls

Ke Yang,* Mengjie Song, Zhiyan Ma, Yi Li, Zhengyi Li,* Xiaoqiang Sun*

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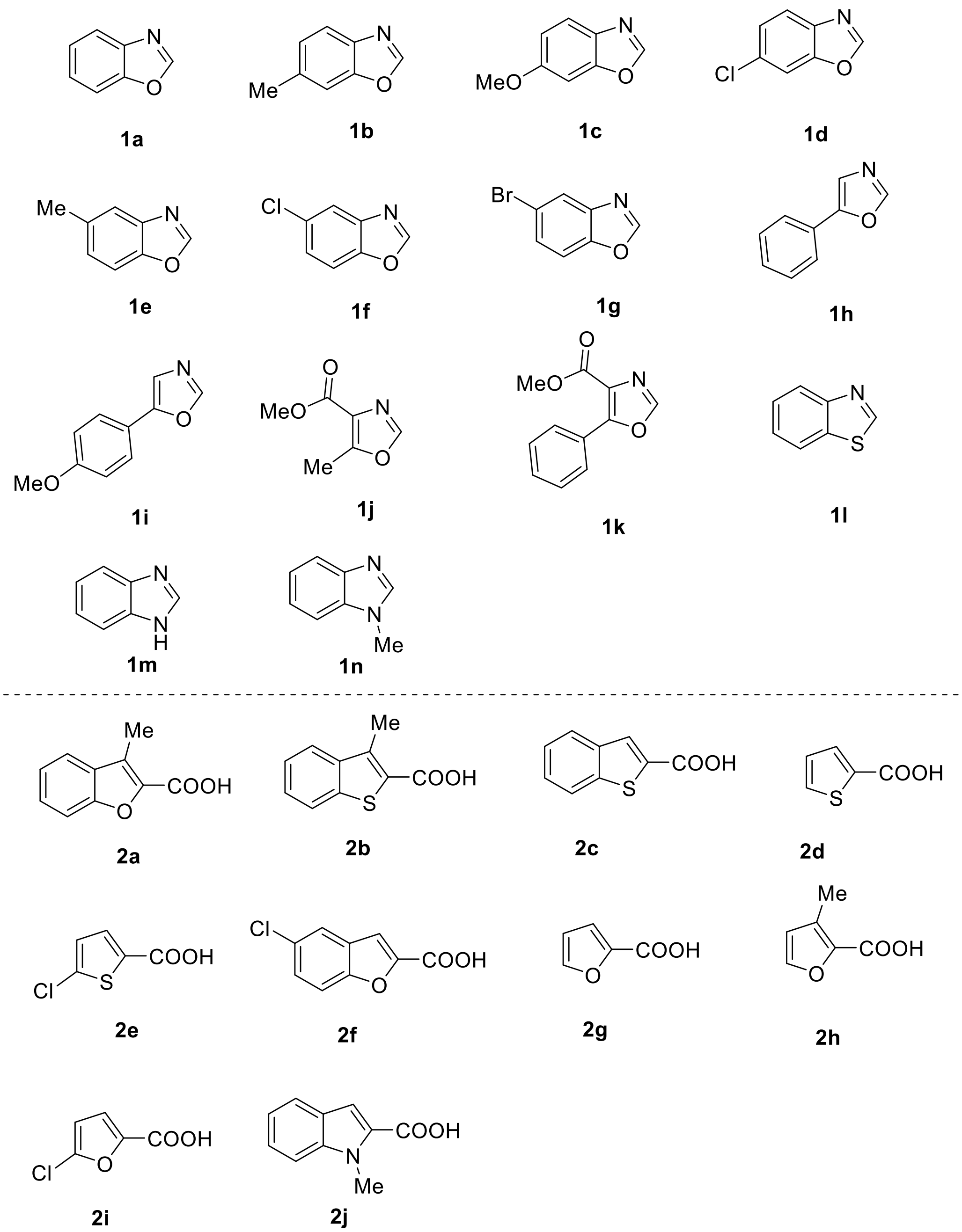
I. General Information

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. Melting points were measured by an X4-A microscopic melting point apparatus. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III–500, 400 or 300 spectrometers. ^{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). Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI).

II. Experimental Section

Starting materials:



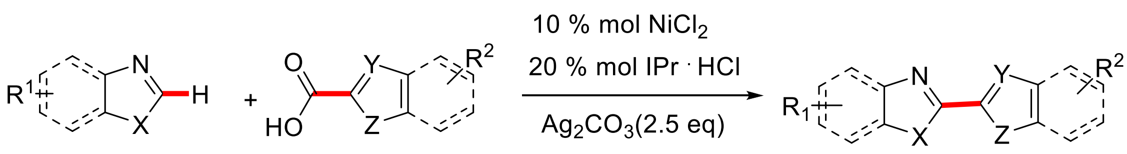
Azoles (**1a-l**), imidazole **(1m-1n)** and heteroaryl carboxylic acids (**2**)

Azoles (**1a-1b**, **1d-1h**, **1l)** and benzoic acids (**2**) were purchased from Adamas-beta, TCI, Alfa Aesar and J&K[@]. Imidazole (**1m-1n)** were purchased from Adamas-beta. Azoles (**1c**) was prepared from condensation of the corresponding 2-aminophenols and triethyl orthoformate according to the reported procedure.[1] Azoles (**1i**) was prepared from *p*-toluenesulfonylmethylisocyanide and the corresponding benzaldehyde in methanol according to the reported procedure.[2] Azoles (**1j** and **1k**) were prepared from methyl 2-isocyanoacetate and the corresponding anhydrides in THF according to the reported procedure.[3]

Optimization of the reaction conditions for the decarboxylative arylation

A 35 mL oven-dried pressure tube was charged with benzoxazole (**1a**, 0.2 mmol), 3-methylbenzofuran-2-carboxylic acid (0.6 mmol), Ni source (0.02 mmol), ligand (0.04 mmol), Ag_2CO_3 (0.5 mmol) and solvent (1.5 mL). The tube was then sealed and stirred vigorously at 160 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with DCM (15 mL), filtered through a pad of Celite. The filtrate was concentrated in vacuo, and the crude product was analyzed by ^1H NMR in $CDCl_3$. Yields and conversions are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard. And the residue was purified by flash chromatography on silica gel (gradient eluent of 10% DCM in petroleum ether, v/v) to yield the product **3a**.

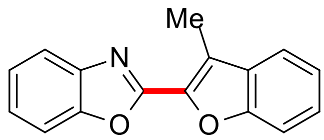
General procedure for the scope study



1 **2** **3**

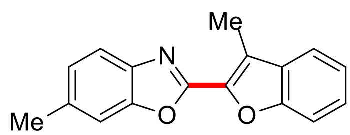
A 35 mL oven-dried pressure tube was charged with azoles (**1**, 0.2 mmol), heteroaryl carboxylic acids (**2**, 0.6 mmol), $NiCl_2$ (2.6 mg, 0.02 mmol), IPr·HCl (17 mg, 0.04 mmol), Ag_2CO_3 (138 mg, 0.5 mmol) and $PhCF_3$ (1.5 mL). The tube was then sealed and stirred vigorously at 165 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with DCM (15 mL), filtered through a pad of Celite, and then the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel (gradient eluent of 10% DCM in petroleum ether, v/v) to give the desired product **3**.

Data of compounds



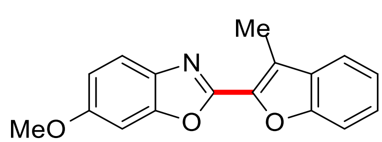
3a

White solid, 34.9 mg, yield: 70%, m.p. 97-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 1H), 7.59 – 7.52 (m, 3H), 7.38 – 7.24 (m, 4H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.18, 154.84, 150.04, 141.55, 139.29, 129.42, 126.94, 125.33, 124.86, 123.22, 121.64, 120.47, 120.18, 111.80, 110.59, 9.13. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{12}NO_2$ $[M+H]^+$: 250.0863, found: 250.0862.



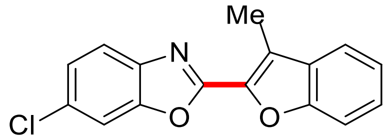
3b

White solid, 35.2 mg, yield: 67% (known compound[4]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 3H), 7.46 - 7.41 (m, 2H), 7.36 - 7.31 (m, 1H), 7.23 – 7.19 (m, 1H), 2.73 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.92, 154.98, 150.55, 139.67, 139.54, 136.09, 129.68, 126.96, 126.30, 123.35, 121.27, 120.59, 119.69, 111.97, 110.91, 21.97, 9.26.



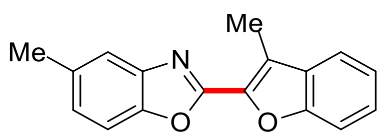
3c

White solid, 27.9 mg, yield: 50%, m.p. 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 17.4, 8.0 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 - 7.18 (m, 2H), 7.69 - 6.87 (m, 1H), 3.80 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.77, 157.11, 155.00, 144.90, 142.64, 139.59, 129.66, 127.07, 123.40, 121.55, 120.64, 114.24, 111.99, 110.90, 103.04, 56.06, 9.29. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{14}NO_3$ $[M+H]^+$: 280.0968, found: 280.0972.



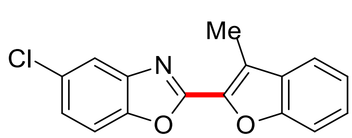
3d

White solid, 35.7 mg, yield: 63%, m.p. 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.66 - 7.58 (m, 3H), 7.46 - 7.42 (m, 1H), 7.37 - 7.31 (m, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 155.14, 150.44, 140.59, 139.07, 131.12, 129.54, 127.42, 125.82, 123.55, 122.53, 120.79, 120.78, 112.07, 111.44, 9.35. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{11}ClNO_2$ $[M+H]^+$: 284.0473, found: 284.0469.



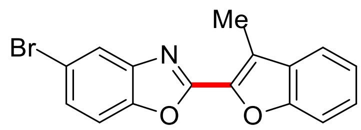
3e

White solid, 39.5 mg, yield: 75%, m.p. 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.59 (m, 3H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 2.75 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.51, 155.04, 148.55, 141.92, 139.69, 134.96, 129.69, 127.06, 126.70, 123.40, 121.53, 120.65, 120.27, 112.02, 110.13, 21.66, 9.30. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{14}NO_2$ $[M+H]^+$: 264.1019, found: 264.1018.



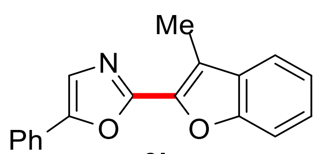
3f

White solid, 34.5 mg, yield: 61%, m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.60 (dd, J = 17.3, 8.0 Hz, 2H), 7.50 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.31 (t, J = 7.7 Hz, 2H), 2.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.49, 154.01, 147.70, 141.76, 137.89, 129.42, 128.36, 126.33, 124.62, 122.41, 121.64, 119.66, 119.10, 110.92, 110.32, 8.20. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{11}ClNO_2$ $[M+H]^+$: 284.0473, found: 284.0472.



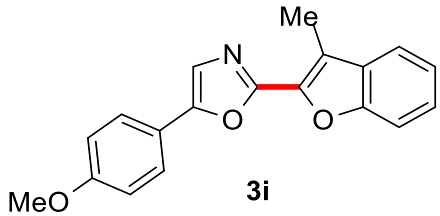
3g

Yellow solid, 39.2 mg, yield: 60%, m.p. 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.61 (dd, J = 19.7, 8.0 Hz, 2H), 7.47 - 7.42 (m, 3H), 7.32 (t, J = 12.4 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 155.14, 149.24, 143.35, 138.96, 129.48, 128.47, 127.47, 123.54, 123.24, 122.83, 120.79, 117.83, 112.05, 111.94, 9.34. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{11}BrNO_2$ $[M+H]^+$: 327.9968, found: 327.9973.



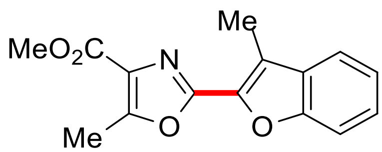
3h

White solid, 31.9 mg, yield: 58%, m.p. 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 - 7.75 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.53 (s, 1H), 7.49 - 7.45 (m, 2H), 7.42 - 7.29 (m, 3H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.90, 154.69, 151.29, 139.97, 129.81, 129.15, 128.81, 127.78, 126.44, 124.46, 123.61, 123.26, 120.37, 118.58, 111.88, 9.07. Ms (ESI): m/z = 276.1 $[M + H^+]$. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1091, found: 276.1090.



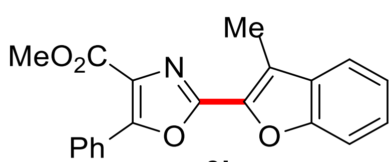
3i

White solid, 36.6 mg, yield: 60%, m.p. 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.40 - 7.28 (m, 3H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.13, 154.63, 154.31, 151.37, 140.08, 129.86, 126.28, 126.03, 123.21, 122.09, 120.62, 120.29, 118.09, 114.61, 111.82, 55.52, 9.03. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1125, found: 306.1120.



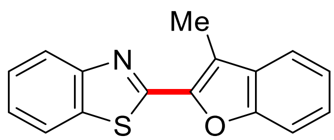
3j

White solid, 34.1 mg, yield: 63%, m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H), 2.76 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80, 156.26, 154.69, 153.32, 139.02, 129.60, 128.73, 126.72, 123.34, 120.53, 119.54, 111.91, 52.17, 29.84, 12.27, 9.08. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{14}NO_4$ $[M+H]^+$: 272.0917, found: 272.0921.



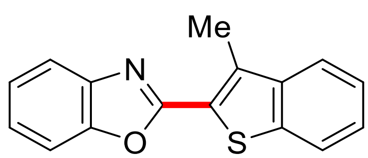
3k

White solid, 46.6 mg, yield: 70%, m.p. 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.1 Hz, 2H), 7.63 − 7.50 (m, 5H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 3.99 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.68, 155.04, 154.87, 153.42, 138.88, 130.66, 129.52, 128.69, 128.49, 126.91, 126.76, 123.37, 120.54, 120.17, 111.99, 52.49, 9.13. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{16}NO_4$ $[M+H]^+$: 334.1074, found: 334.1070.



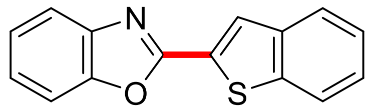
3l

Yellow solid, 29.0 mg, yield: 55% (known compound[4]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.45 − 7.41 (m, 1H), 7.34 − 7.30 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.35, 154.66, 154.08, 145.40, 134.47, 130.37, 126.63, 126.56, 125.33, 123.48, 123.29, 121.61, 120.58, 118.80, 111.78, 9.54.



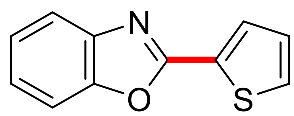
3m

Yellow solid, 35.0 mg, yield: 66% (known compound[4]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.80 (m, 3H), 7.62 - 7.59 (m, 1H), 7.47 - 7.43 (m, 2H), 7.40 - 7.36 (m, 2H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.95, 150.46, 142.01, 140.72, 140.29, 136.92, 126.67, 125.35, 124.92, 124.78, 123.58, 123.34, 122.69, 120.17, 110.67, 13.66.



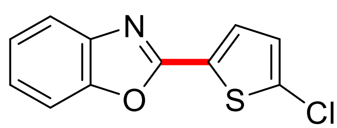
3n

Yellow solid, 26.1 mg, yield: 52% (known compound[5]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.98 – 7.87 (m, 2H), 7.85 – 7.77 (m, 1H), 7.64 – 7.56 (m, 1H), 7.49 – 7.35 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.01, 150.71, 142.01, 141.25, 139.38, 129.31, 126.81, 126.45, 125.54, 125.10, 124.97, 124.89, 122.64, 120.15, 110.57.



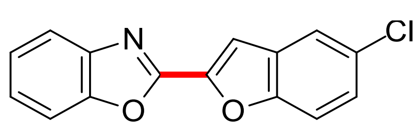
3o

White solid, 28.5 mg, yield: 71% (known compound[6]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.75 - 7.73 (m, 1H), 7.57 - 7.54 (m, 2H), 7.37 - 7.32 (m, 2H), 7.21 (dd, *J* = 4.8, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.19, 150.57, 142.13, 130.40, 130.09, 129.79, 128.40, 125.22, 124.86, 119.94, 110.57.



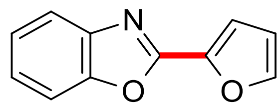
3p

Yellow solid, 29.2 mg, yield: 62% (known compound[7]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.70 (m, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.37 - 7.32 (m, 2H), 7.00 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.94, 150.48, 141.92, 135.41, 129.34, 128.21, 127.69, 125.46, 125.02, 120.00, 110.59.



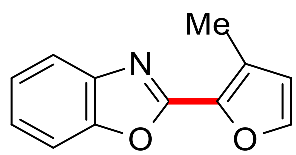
3q

White solid, 32.3 mg, yield: 60% (known compound[8]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.81 (m, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.62 - 7.60 (m, 1H), 7.57 - 7.54 (m, 2H), 7.42 - 7.37 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.96, 154.29, 150.60, 145.15, 141.65, 129.76, 128.99, 127.36, 126.26, 125.36, 121.84, 120.76, 113.23, 110.93, 109.61.



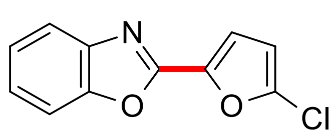
3r

Yellow solid, 24.0 mg, yield: 65% (known compound[9]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.74 (m, 1H), 7.67 (s, 1H), 7.58 - 7.55 (m, 1H), 7.38 - 7.33 (m, 2H), 7.28 (d, J = 3.5 Hz, 1H), 6.62 (dd, J = 3.6, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.44, 150.28, 145.88, 142.75, 141.77, 125.43, 124.99, 120.28, 114.42, 112.41, 110.71.



3s

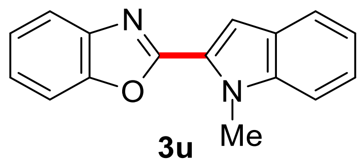
White solid, 27.9 mg, yield: 70%, m.p. 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 - 7.43 (m, 1H), 7.57 - 7.54 (m, 2H), 7.36 - 7.31 (m, 2H), 6.46 (d, J = 1.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.27, 149.96, 144.82, 141.80, 138.68, 127.08, 124.96, 124.80, 120.05, 115.44, 110.58, 11.40. HRMS (ESI, m/z): calcd. for $C_{12}H_{10}NO_2$ $[M+H]^+$: 200.0706, found: 200.0705.



3t

White solid, 26.7 mg, yield: 61%, m.p. 93-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 - 7.74 (m, 1H), 7.56 - 7.52 (m, 1H), 7.37 - 7.35 (m, 2H), 7.24 (d, J = 3.6 Hz, 1H), 6.40 (d,

J = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.30, 150.21, 142.05, 141.61, 140.71, 125.65, 125.14, 120.34, 116.20, 110.75, 109.31. HRMS (ESI, *m/z*): calcd. for $C_{11}H_7ClNO_2$ $[M+H]^+$: 220.0160, found: 220.0160.



3u

White solid, 24.8 mg, yield: 50% (known compound[10]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.76 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.59 - 7.57 (m, 1H), 7.44 - 7.42 (m, 2H), 7.37 - 7.34 (m, 3H), 7.18 (t, J = 7.2 Hz, 1H), 4.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.83, 149.96, 142.17, 139.91, 127.02, 126.34, 125.29, 124.70, 124.54, 122.11, 120.75, 120.00, 110.51, 110.22, 107.64, 32.28.

III. References and notes:

(1) S. Wertz, S. Kodama, A. Studer, *Angew*. *Chem*., *Int*. *Ed*. **2011**, *50*, 11511.

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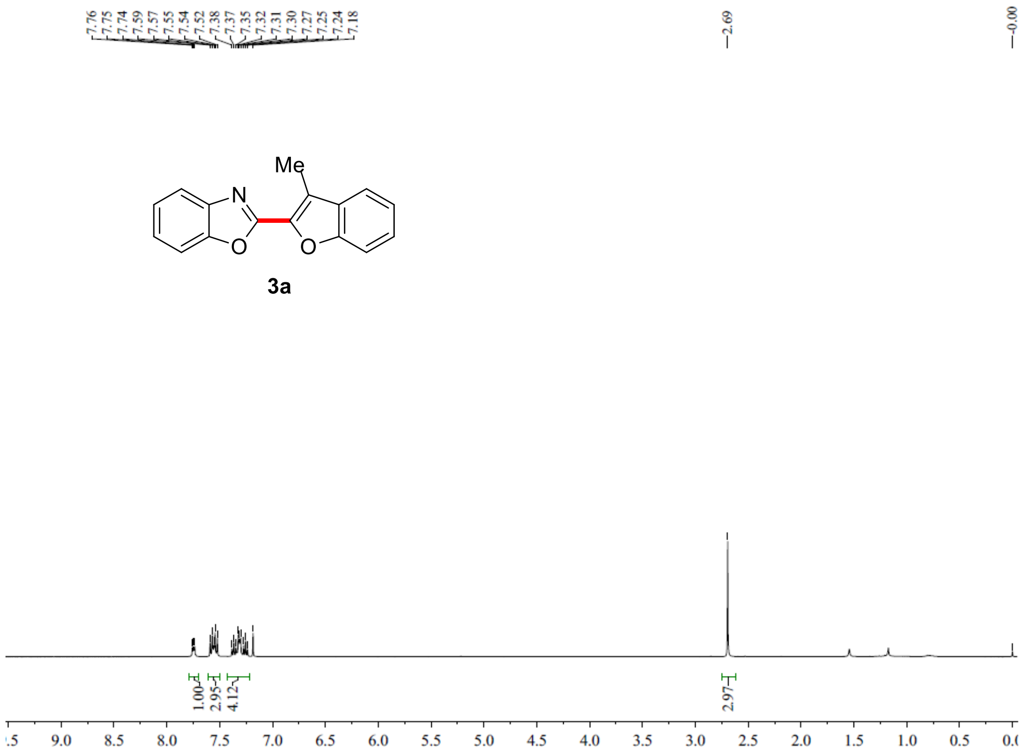
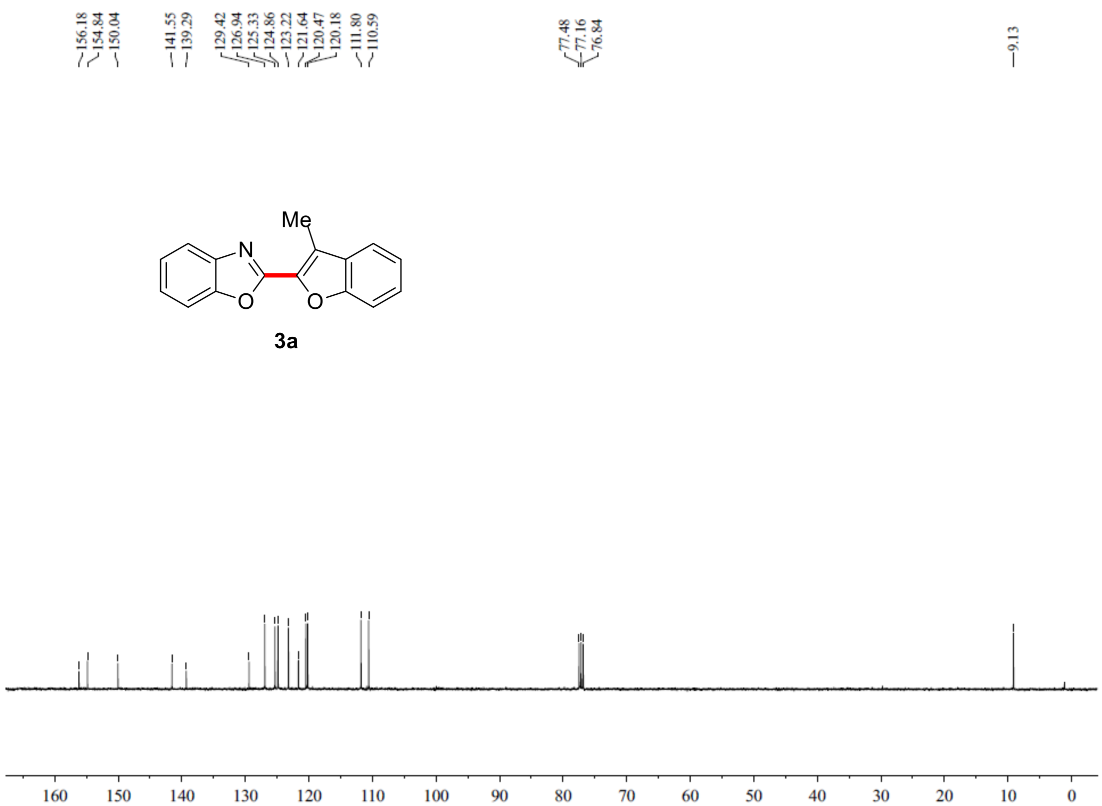
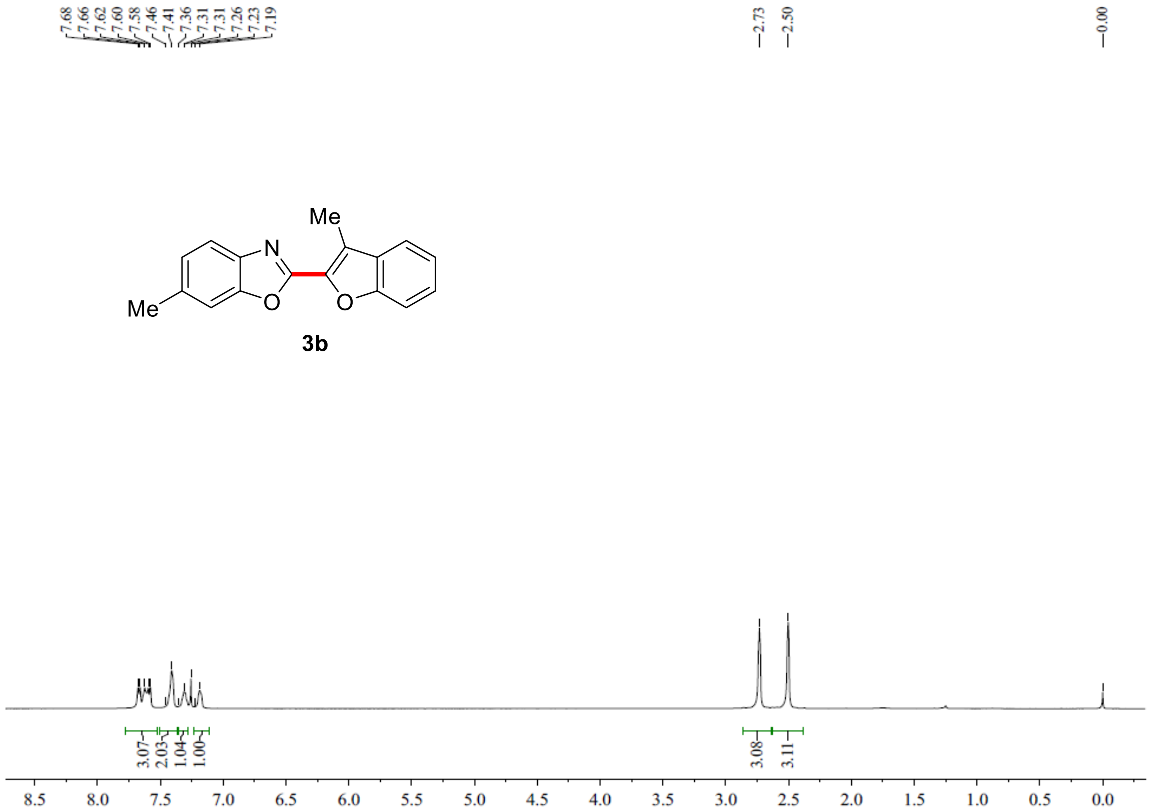
IV. ^{1}H and ^{13}C NMR Spectra



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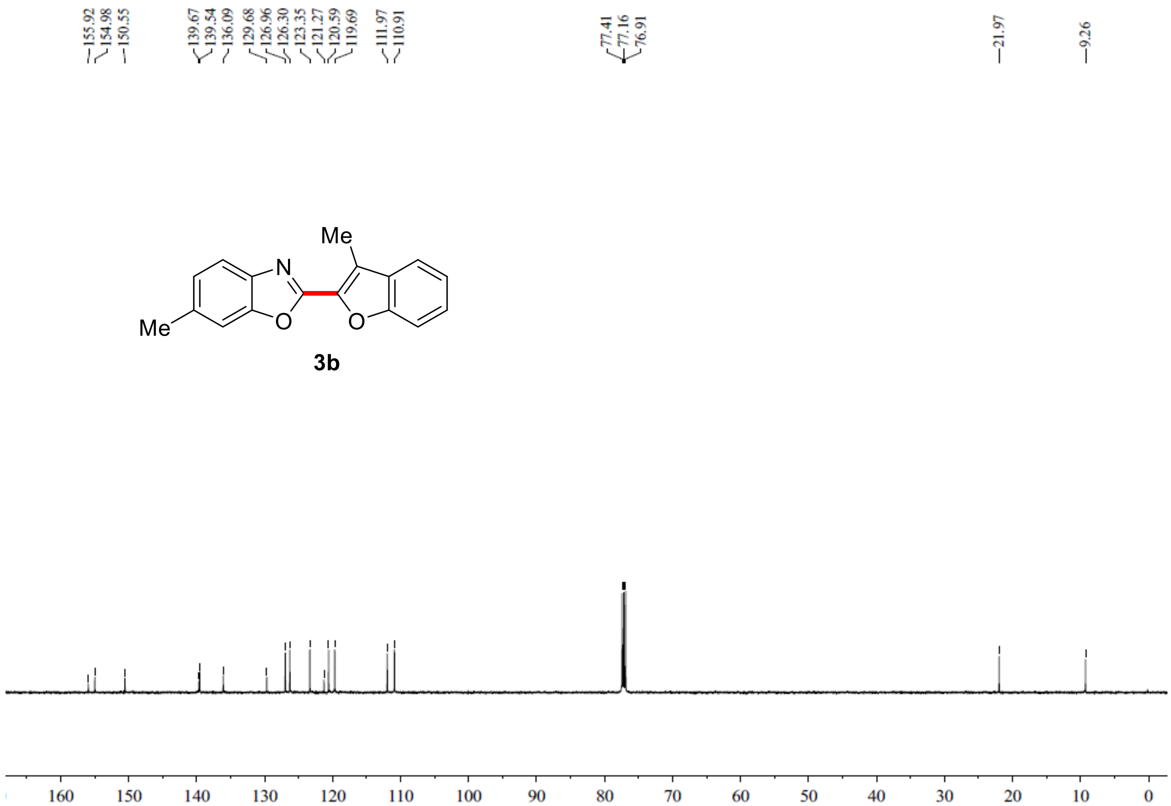
7.62
7.60
7.58
7.46
7.41
7.36
7.31
7.31
7.26
7.23
7.19
2.73
2.50
0.00
Me
N
O
Me
O
3b
3.07
2.03
1.04
1.00
3.08
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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154.98
150.55
139.67
139.54
136.09
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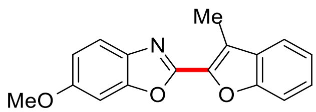
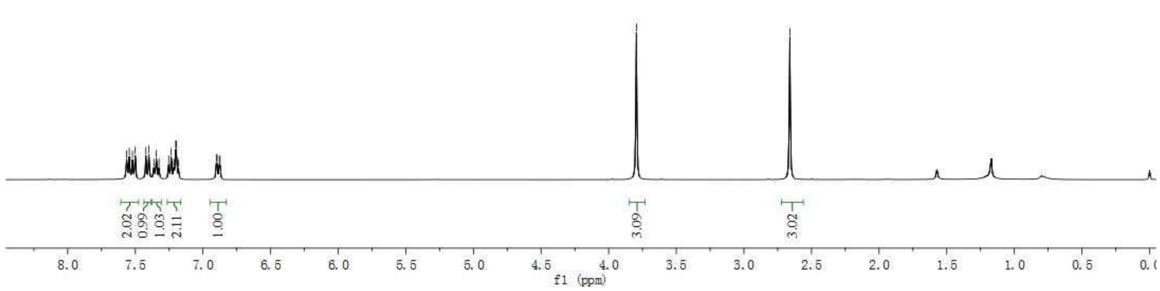
126.96
126.30
123.35
121.27
120.59
119.69
111.97
110.91
77.41
77.16
76.91
21.97
9.26
Me
N
O
Me
O
3b
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Me
N
MeO
O
O

3c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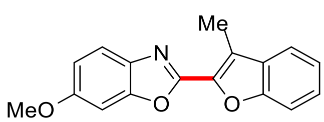
7.545
7.521
7.501
7.422
7.400
7.345
7.254
7.235
7.216
7.202
7.197
6.901
6.896
6.878
6.874
3.795
2.660
2.02
0.99
1.03
2.11
1.00
3.09
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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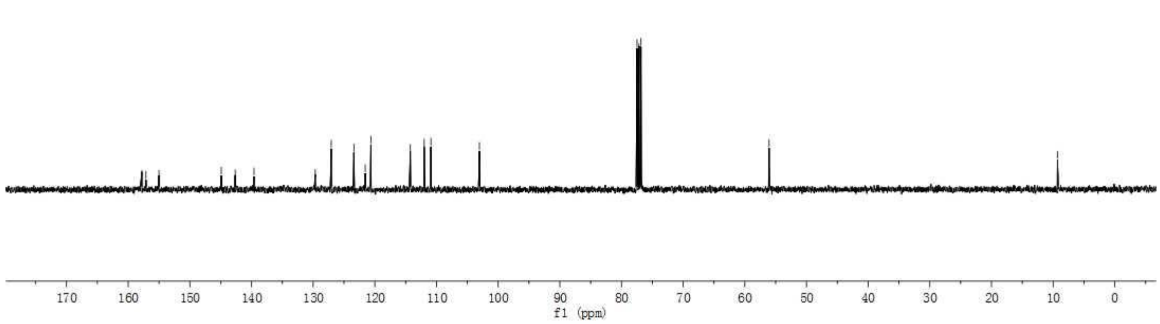
N
MeO
O
O

3c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111.992
110.904
103.037
77.479
77.161
76.844
56.066
9.294
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150
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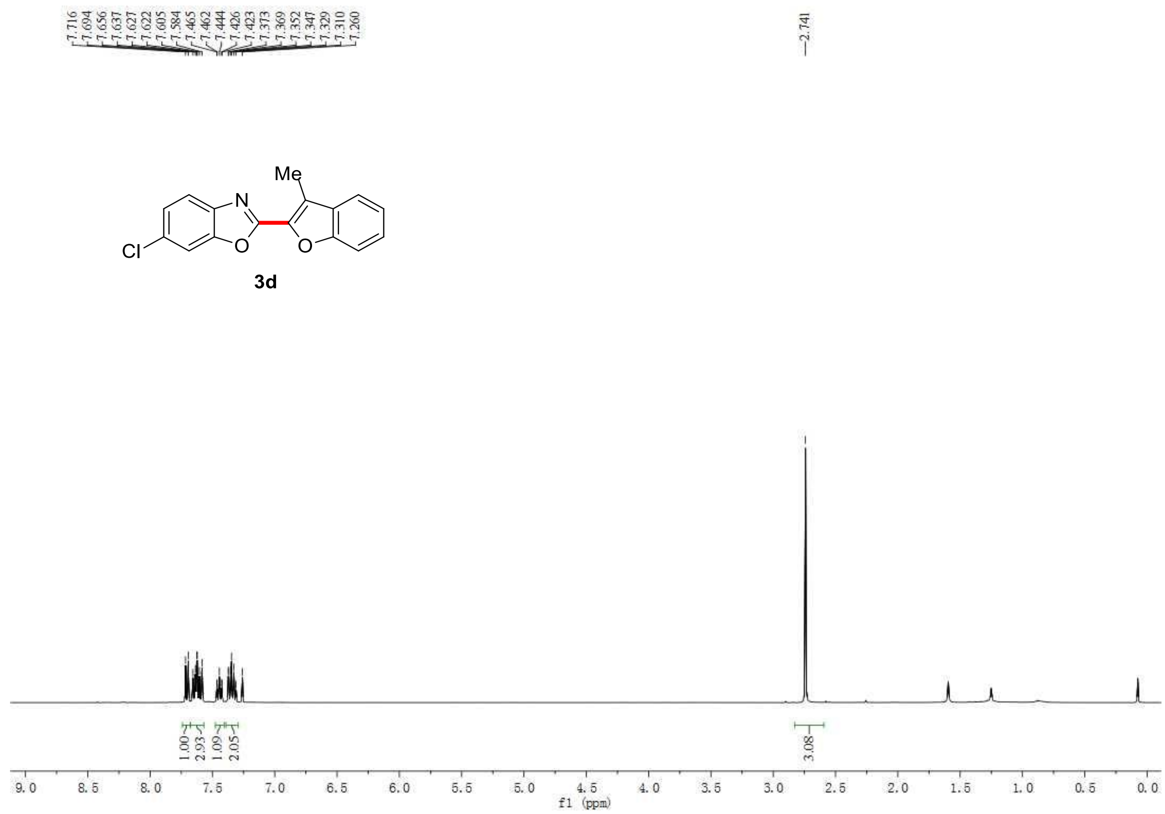
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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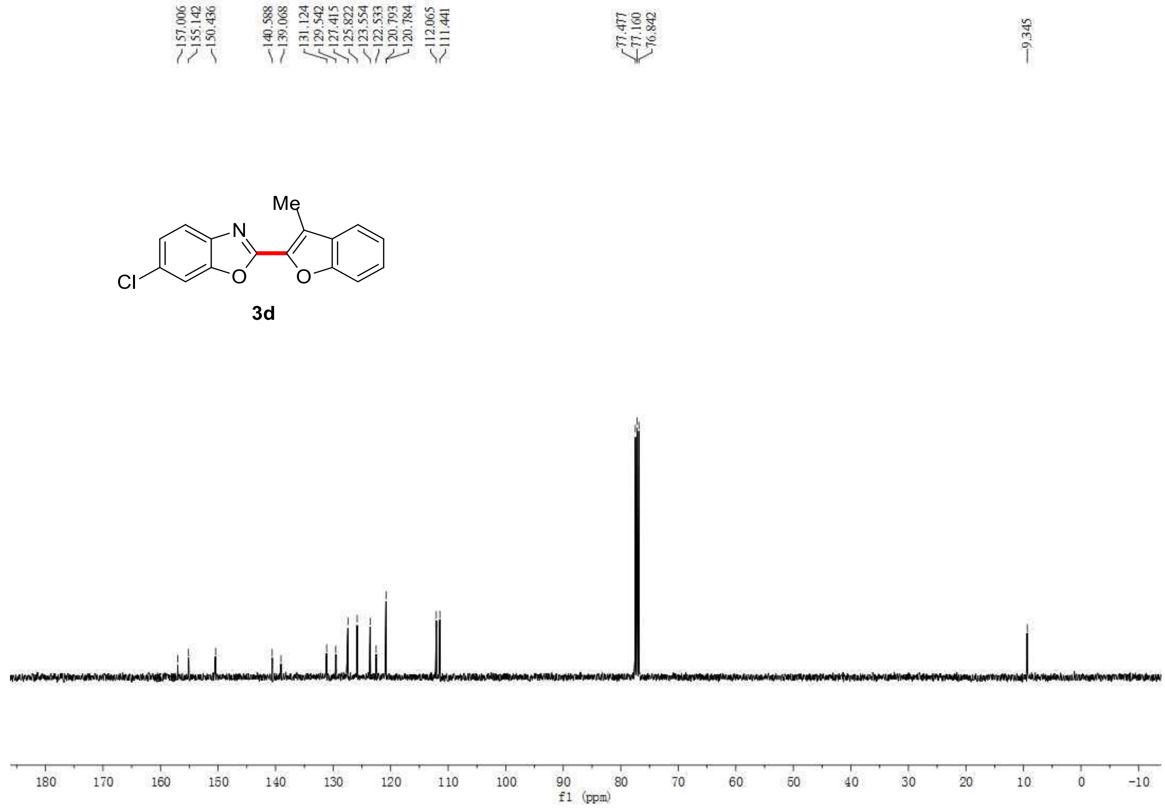
2.741
Me
N
O
Cl
3d
1.00 2.93 1.09 2.05
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.588 139.068 131.124 129.542 127.415 125.822 123.554 122.533 120.793 120.784 112.065 111.441
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O
Cl
3d
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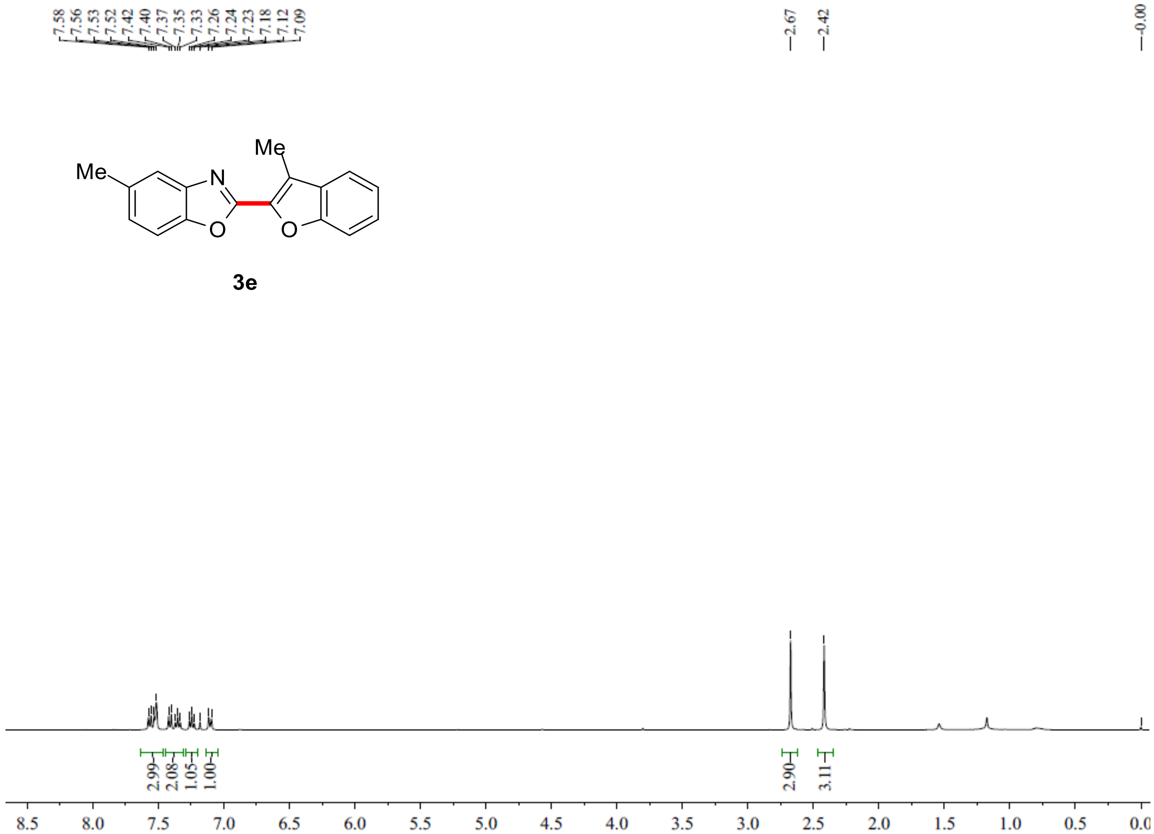
f1 (ppm)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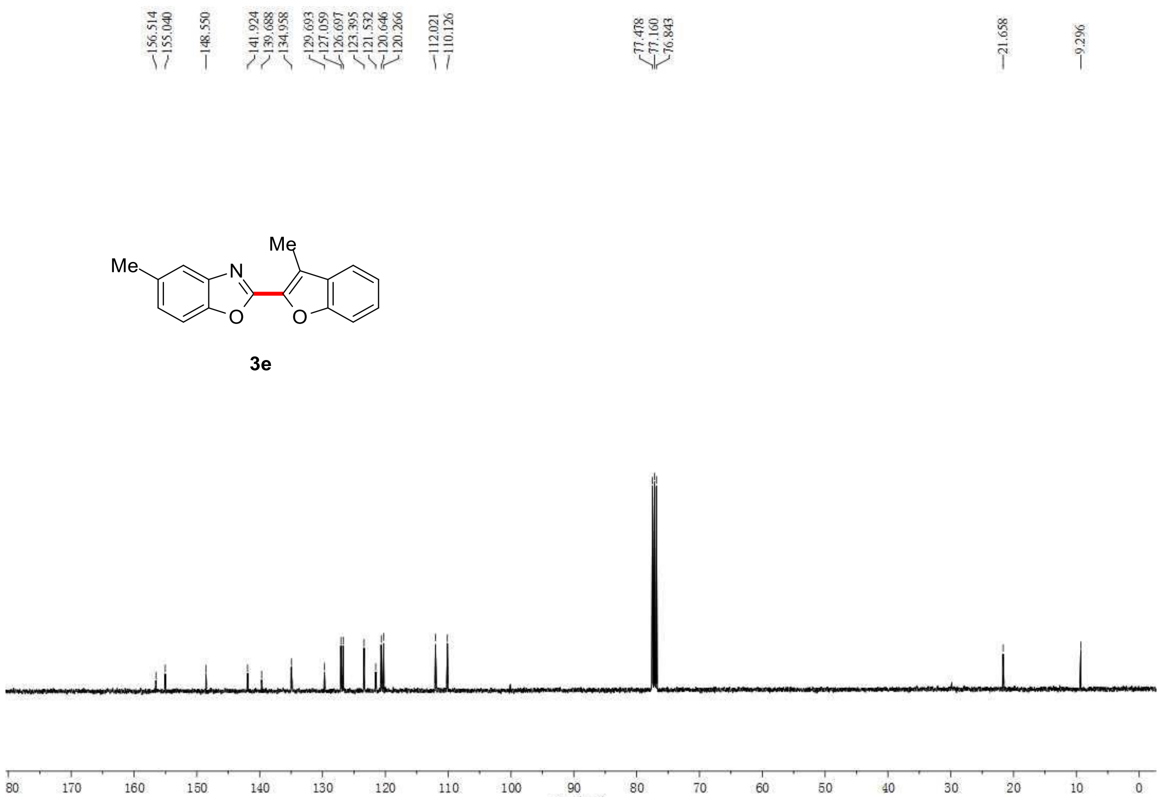
7.35
7.33
7.26
7.24
7.23
7.18
7.12
7.09
2.67
2.42
0.00
Me
N
O
Me
O
2.99
2.08
1.05
1.00
2.90
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3e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120.266
112.021
110.126
77.478
77.160
76.843
21.658
9.296
Me
N
O
Me
O
180
170
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150
140
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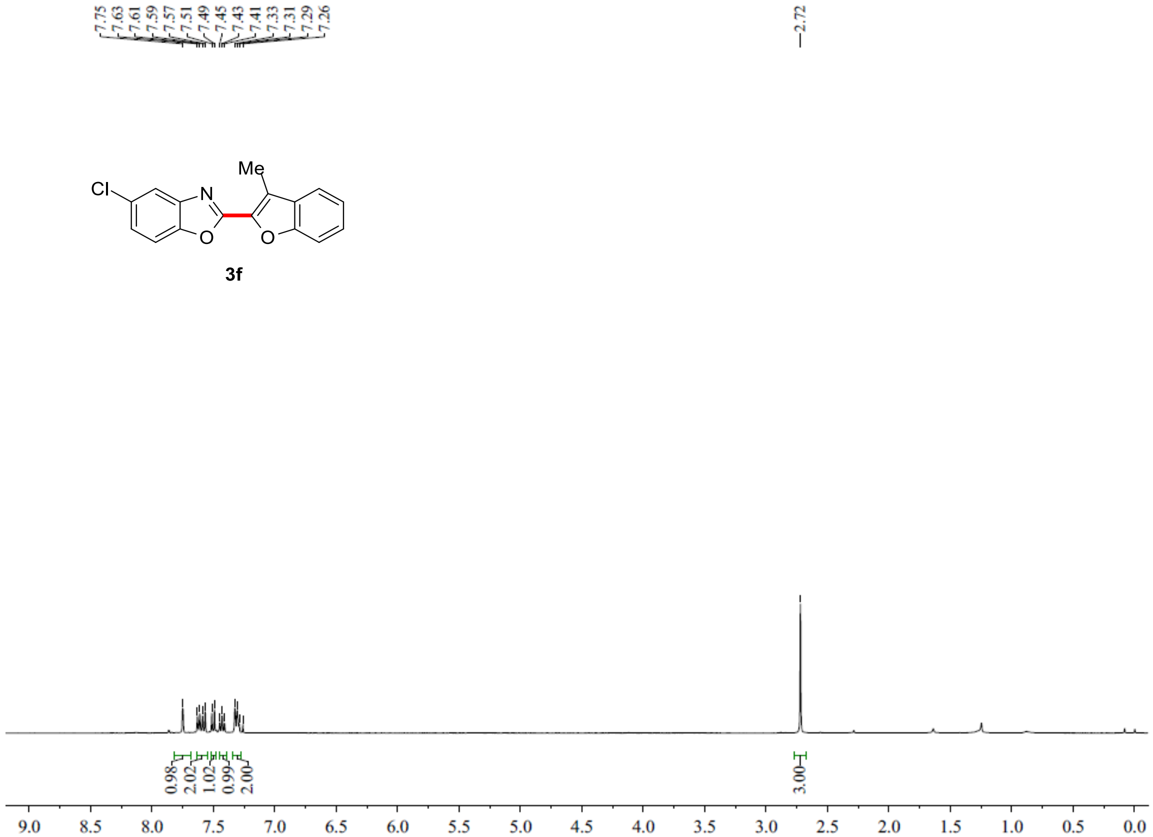
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3e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7.41
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7.29
7.26
2.72
Me
Cl
N
O
O
3f
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2.02
1.02
0.99
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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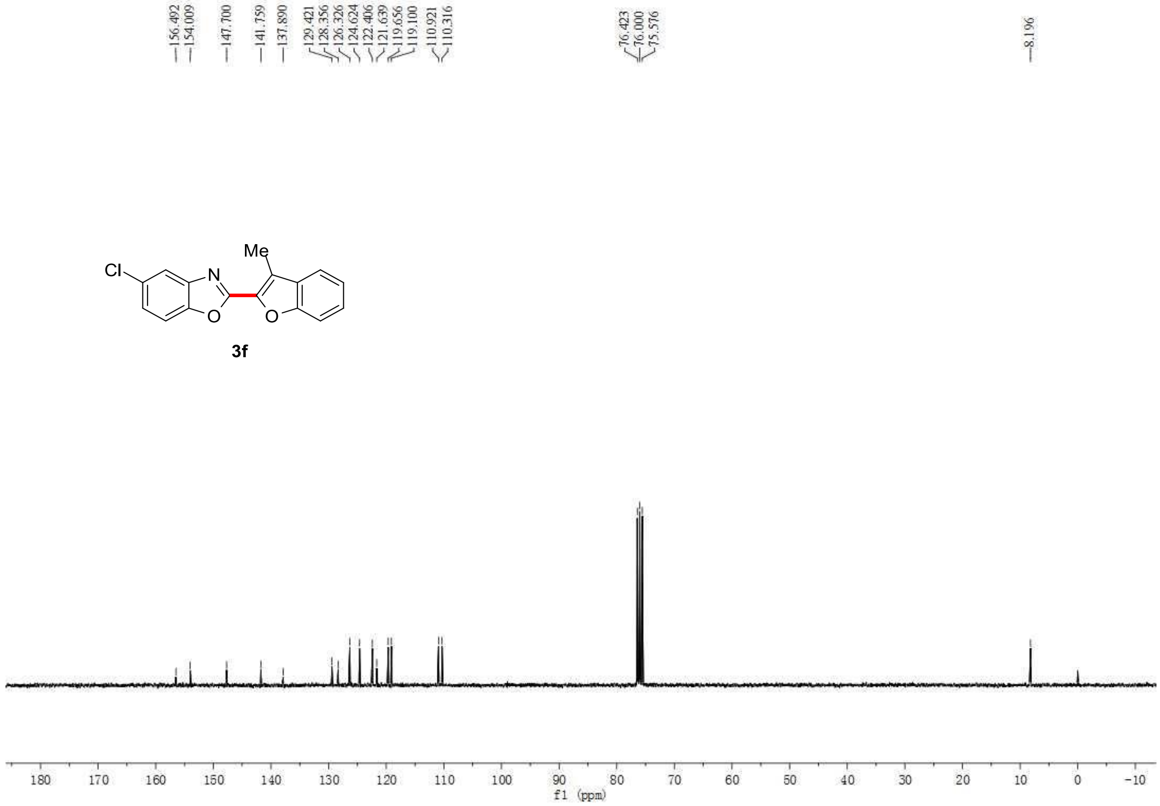
0.0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110.921
110.316
76.423
76.000
75.576
8.196
Me
Cl
N
O
O
3f
180
170
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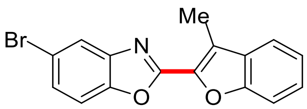
f1 (ppm)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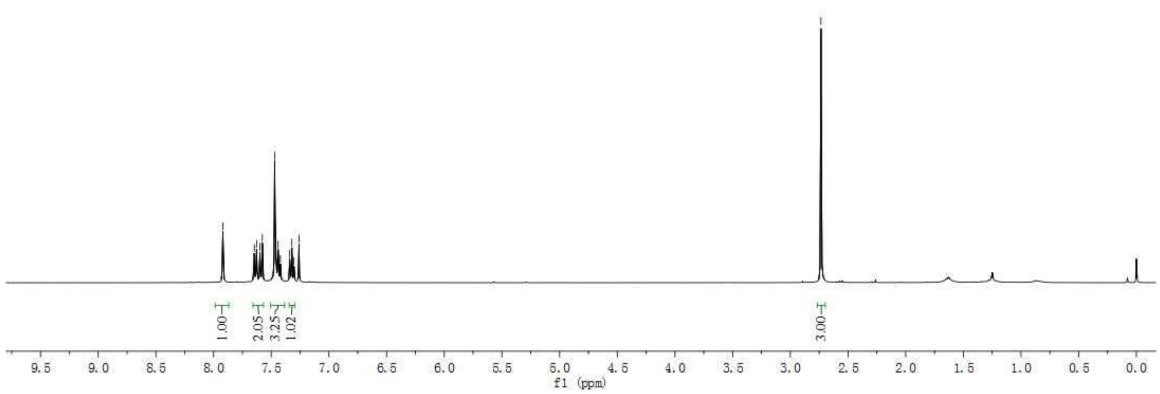
Br
N
O
O

3g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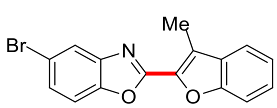
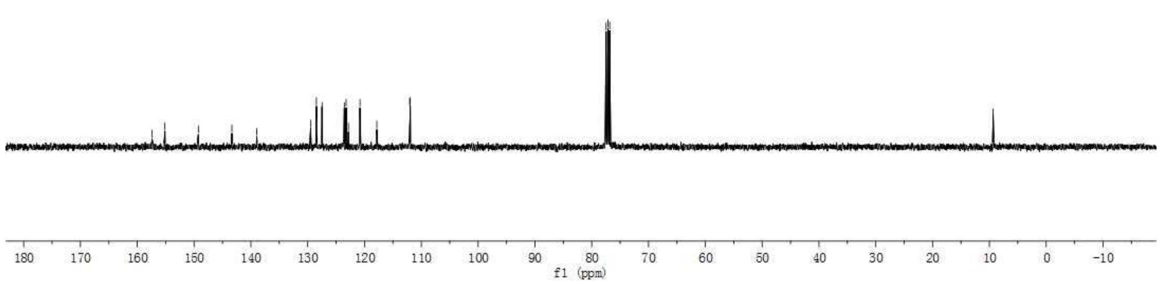
7.470
7.440
7.421
7.340
7.321
7.303
7.260
2.734
1.00
2.05
3.25
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
Br
N
O
O

3g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123.237
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120.791
117.828
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77.160
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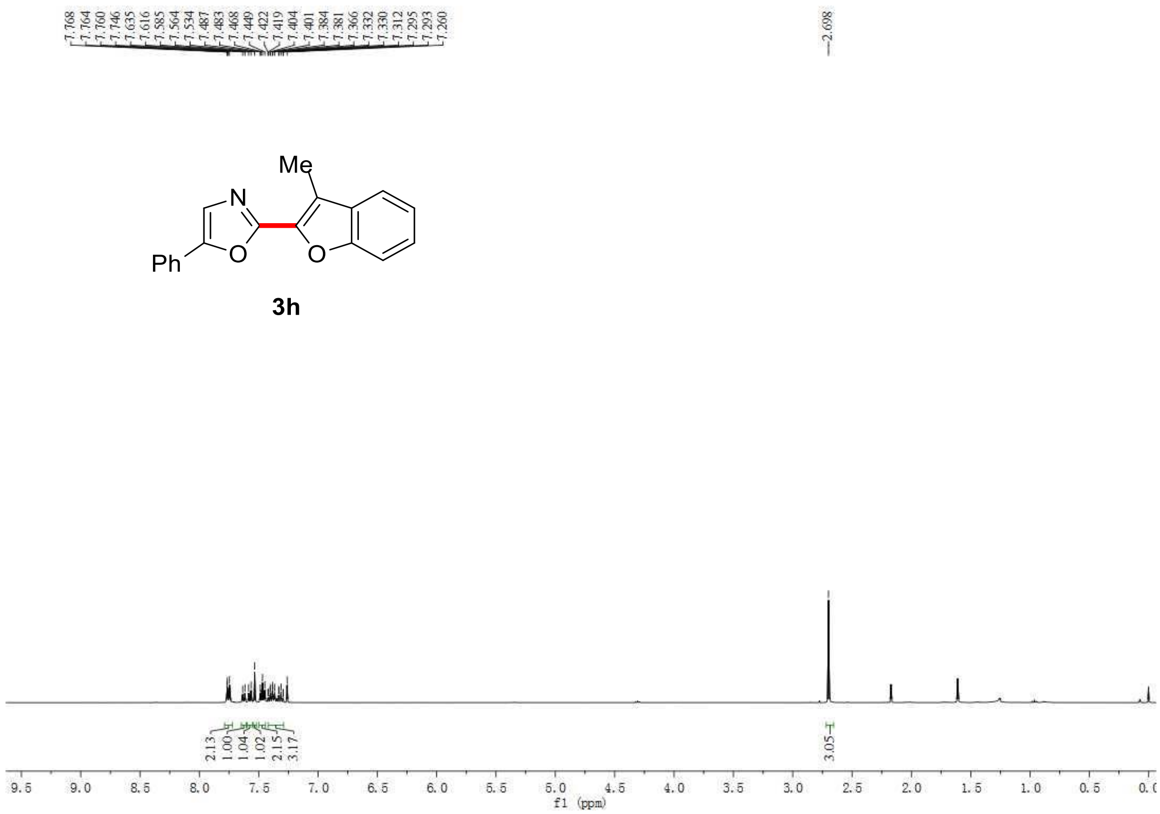
f1 (ppm)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7.449
7.422
7.419
7.404
7.401
7.384
7.381
7.366
7.332
7.330
7.312
7.295
7.293
7.260
2.698
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Ph
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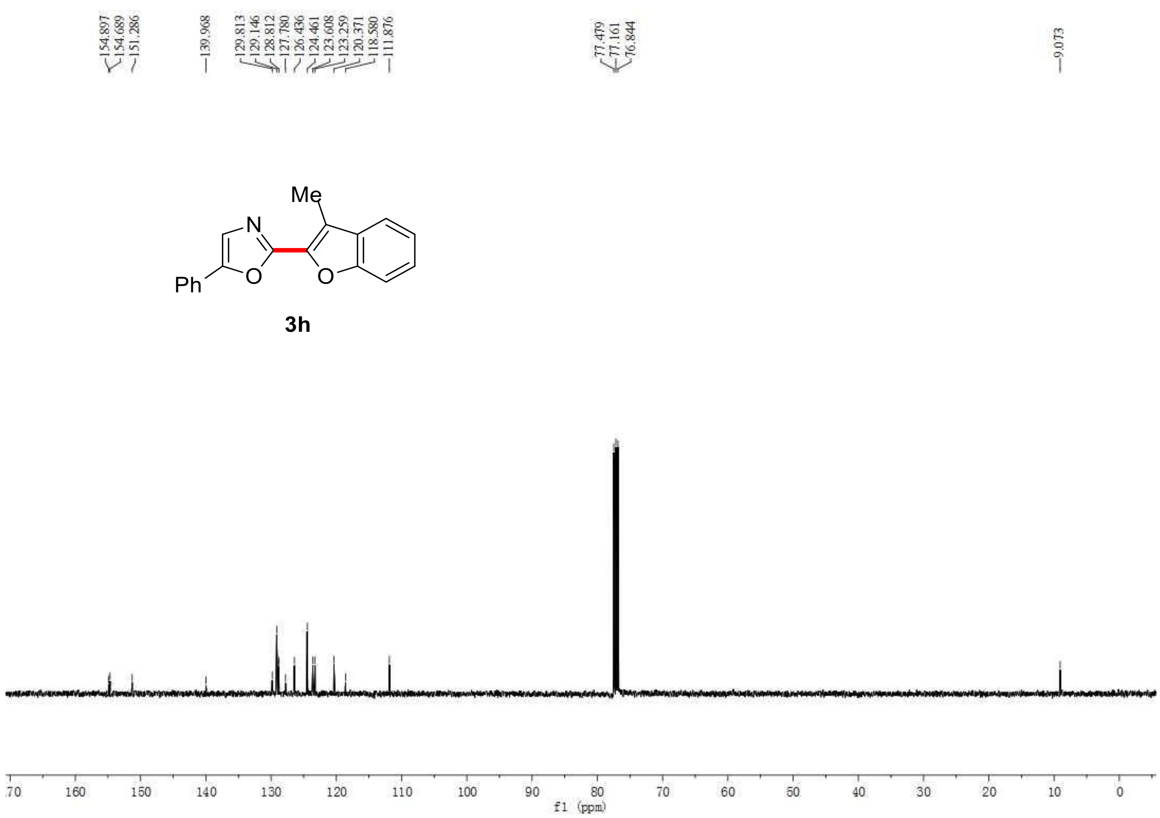
1.02
2.15
3.17
3.05
f1 (ppm)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77.479
77.161
76.844
9.073
Me
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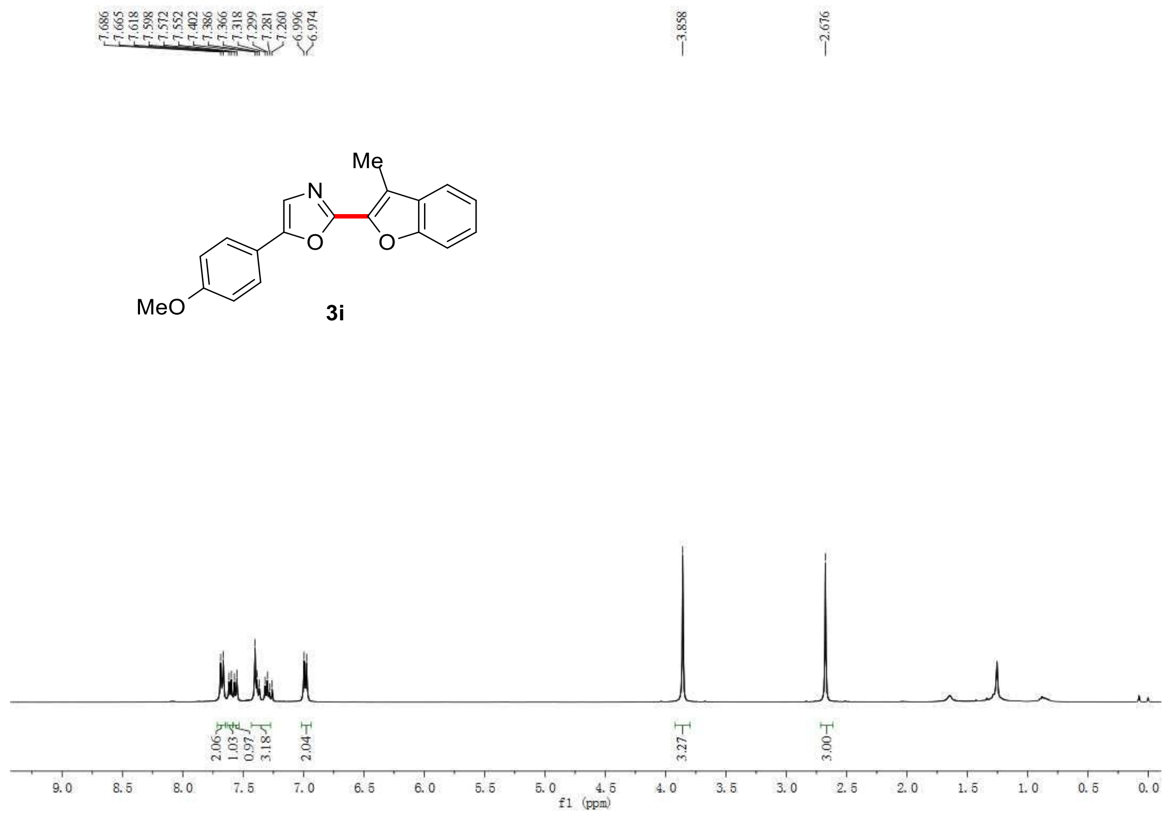
O
O
Ph
3h
f1 (ppm)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7.260
6.996
6.974
3.858
2.676
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MeO
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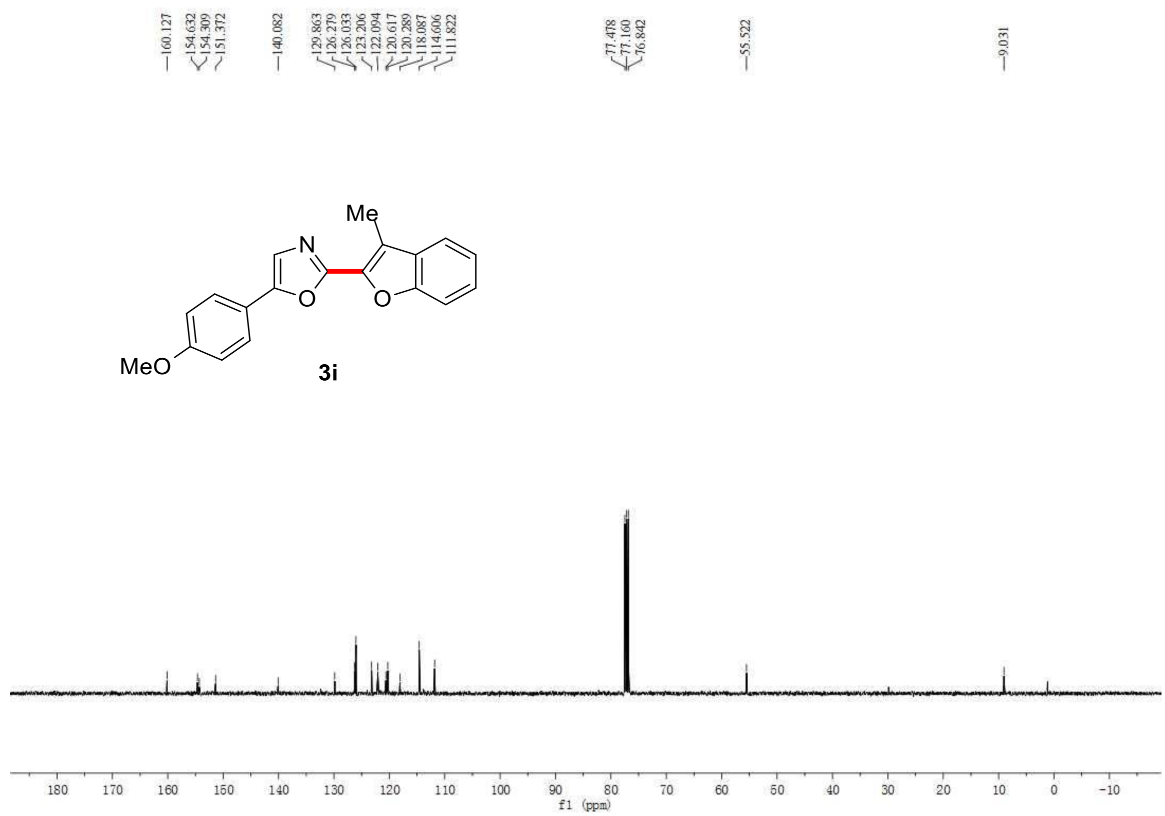
2.04
3.27
3.00
f1 (ppm)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118.087
114.606
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77.478
77.160
76.842
55.522
9.031
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N
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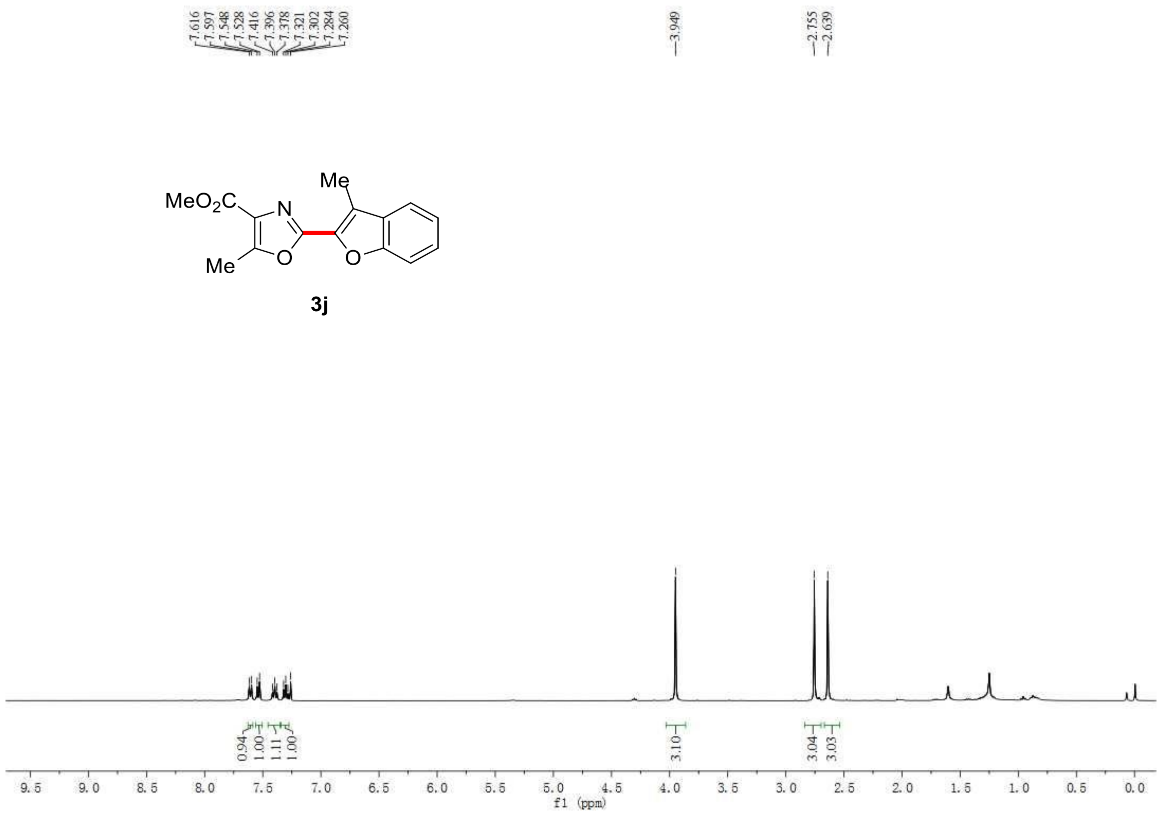
O
MeO
3i
f1 (ppm)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7.321
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7.260
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2.755
2.639
MeO2C
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Me
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O
O
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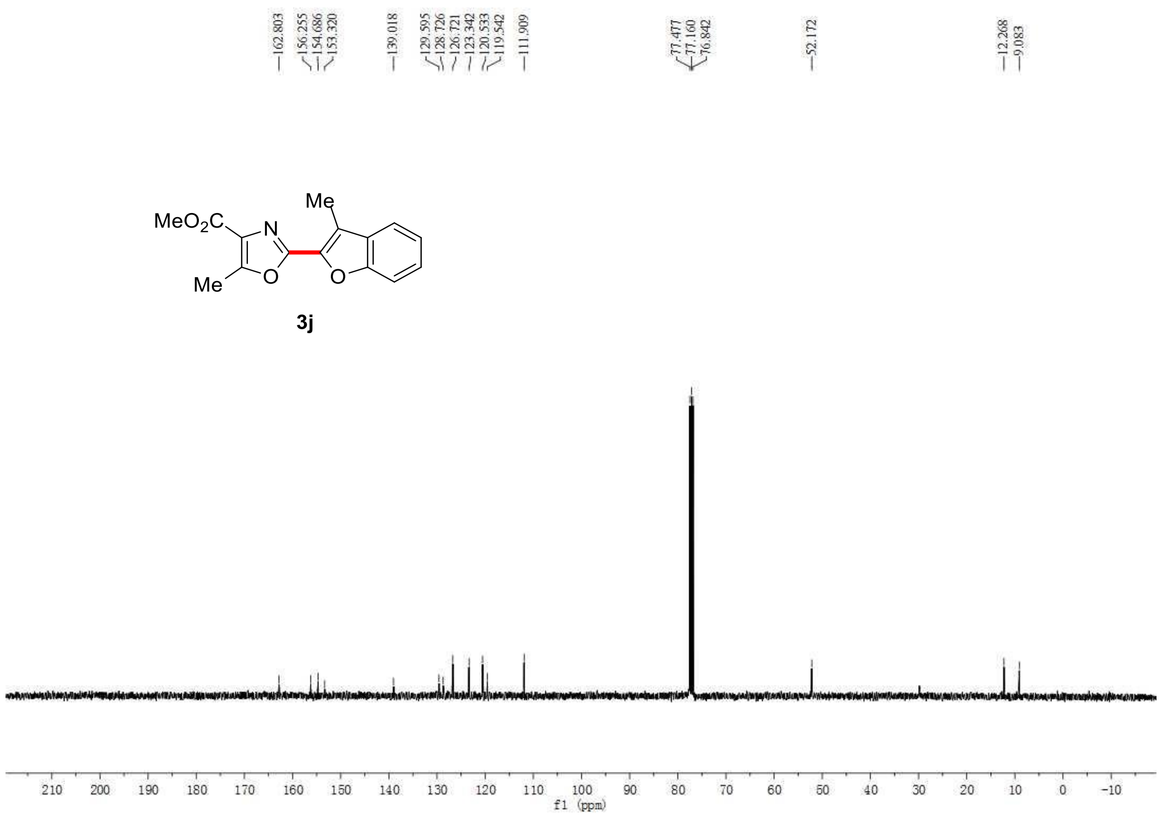
1.00
3.10
3.04
3.03
f1 (ppm)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Me
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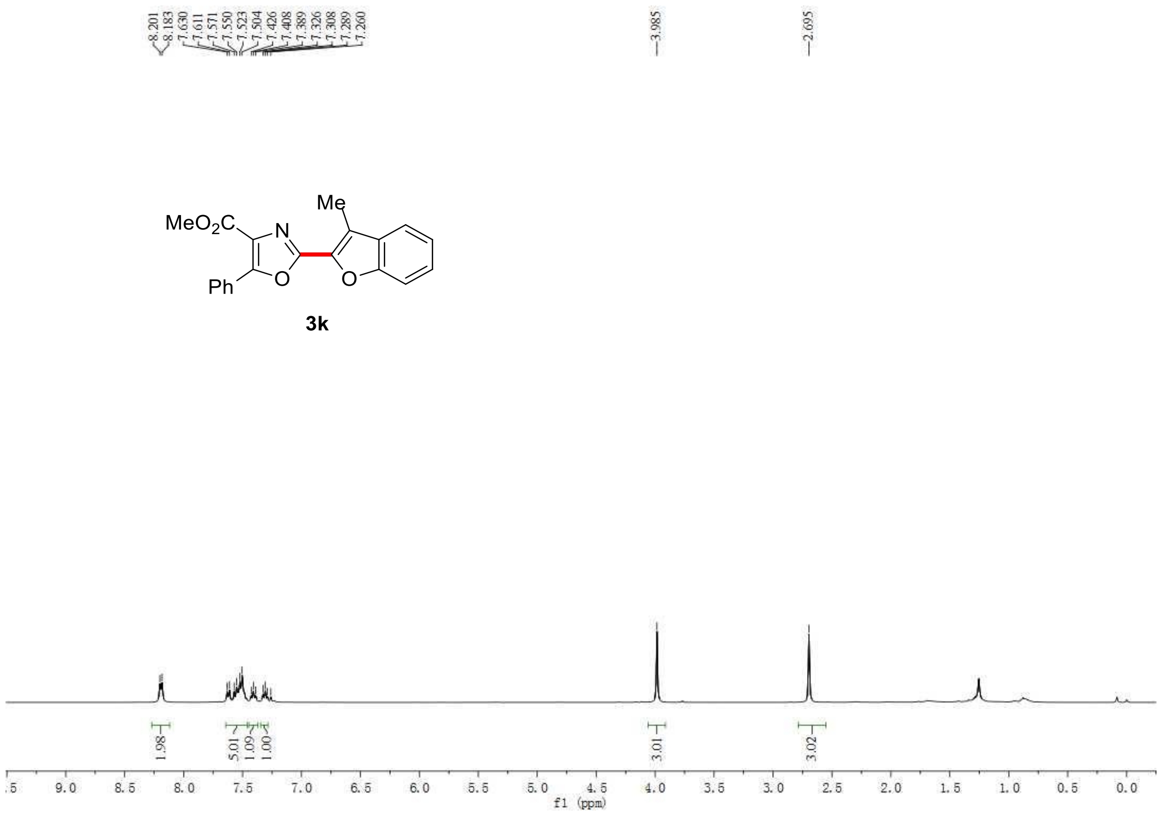
O
O
3j
f1 (ppm)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7.308
7.289
7.260
3.985
2.695
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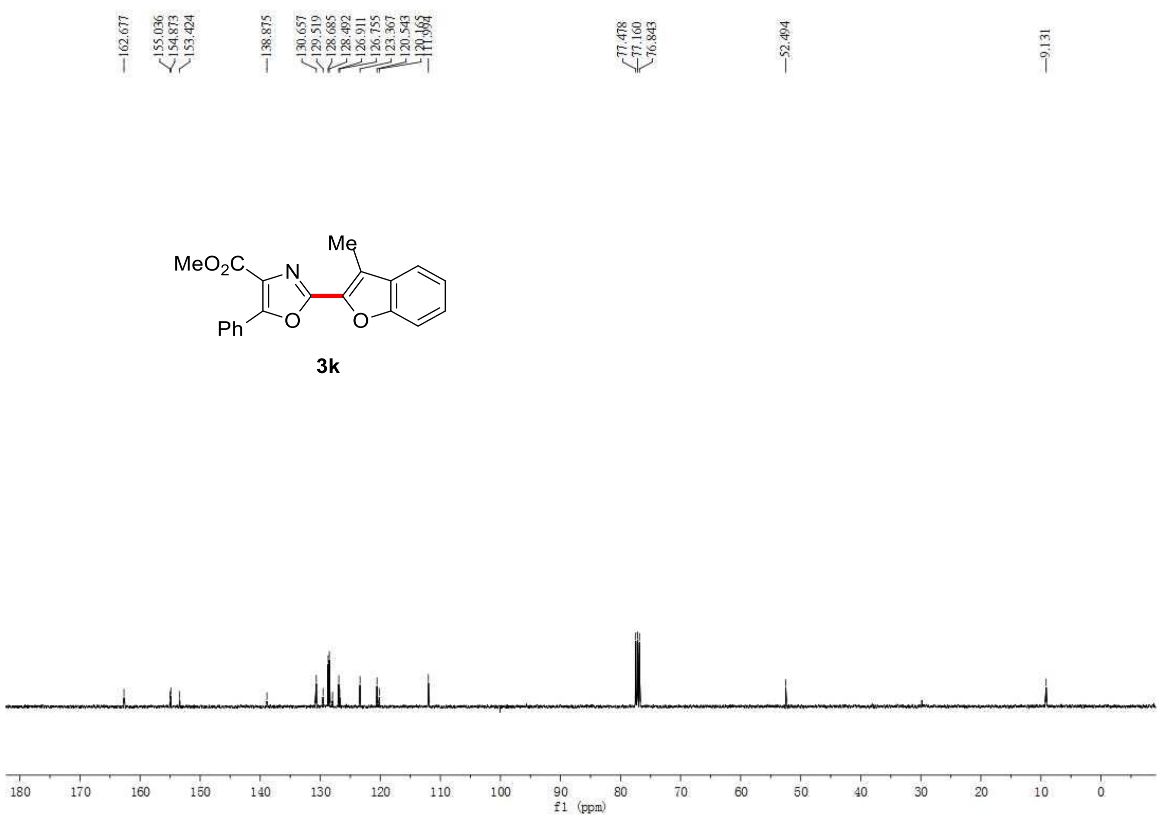
1.00
3.01
3.02
f1 (ppm)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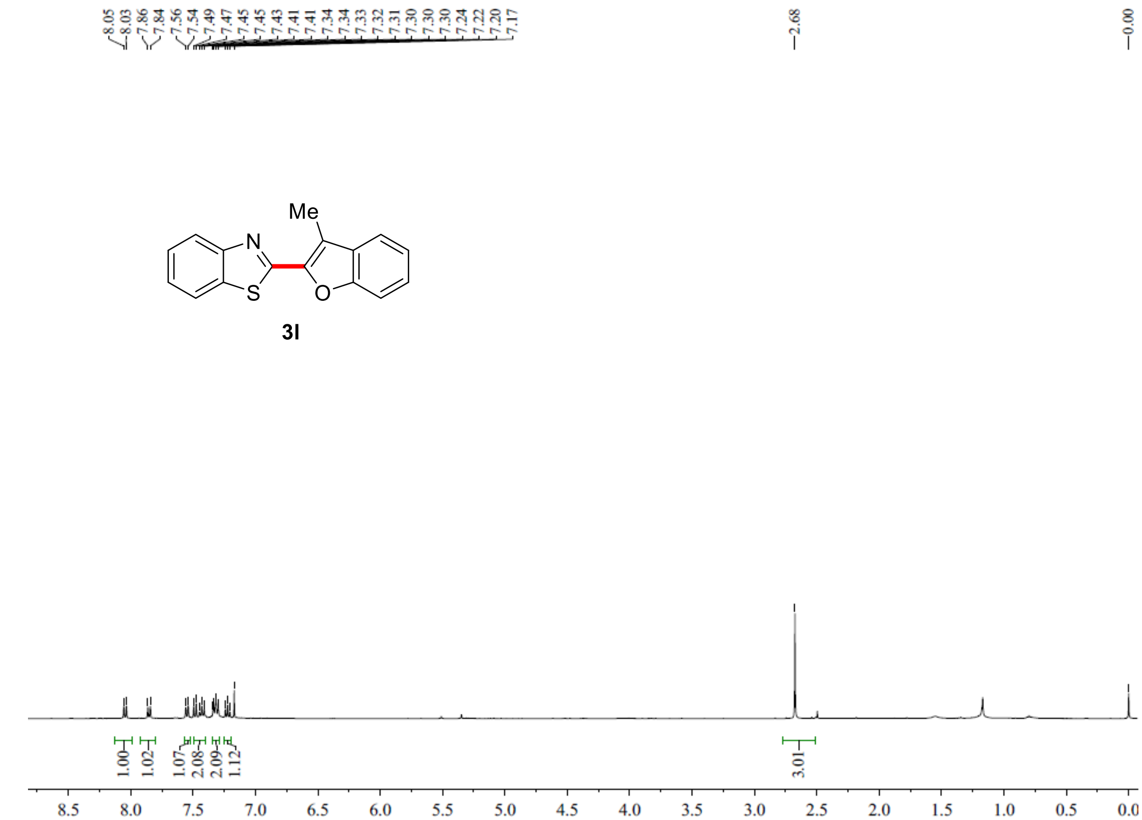
O
3k
f1 (ppm)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7.54
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7.47
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7.45
7.43
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7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.24
7.22
7.20
7.17
2.68
0.00
Me
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S
O
3l
1.00
1.02
1.07
2.08
2.09
1.12
3.01
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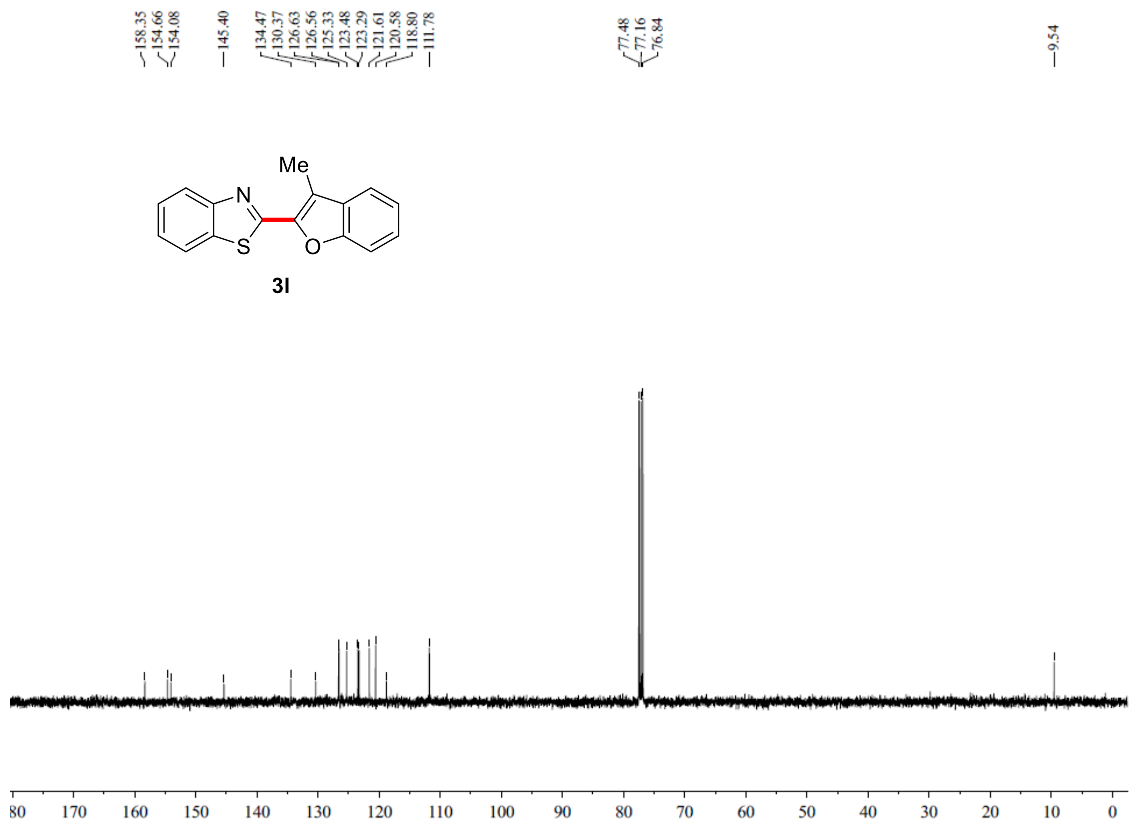
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123.29
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120.58
118.80
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76.84
9.54
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S
O
3l
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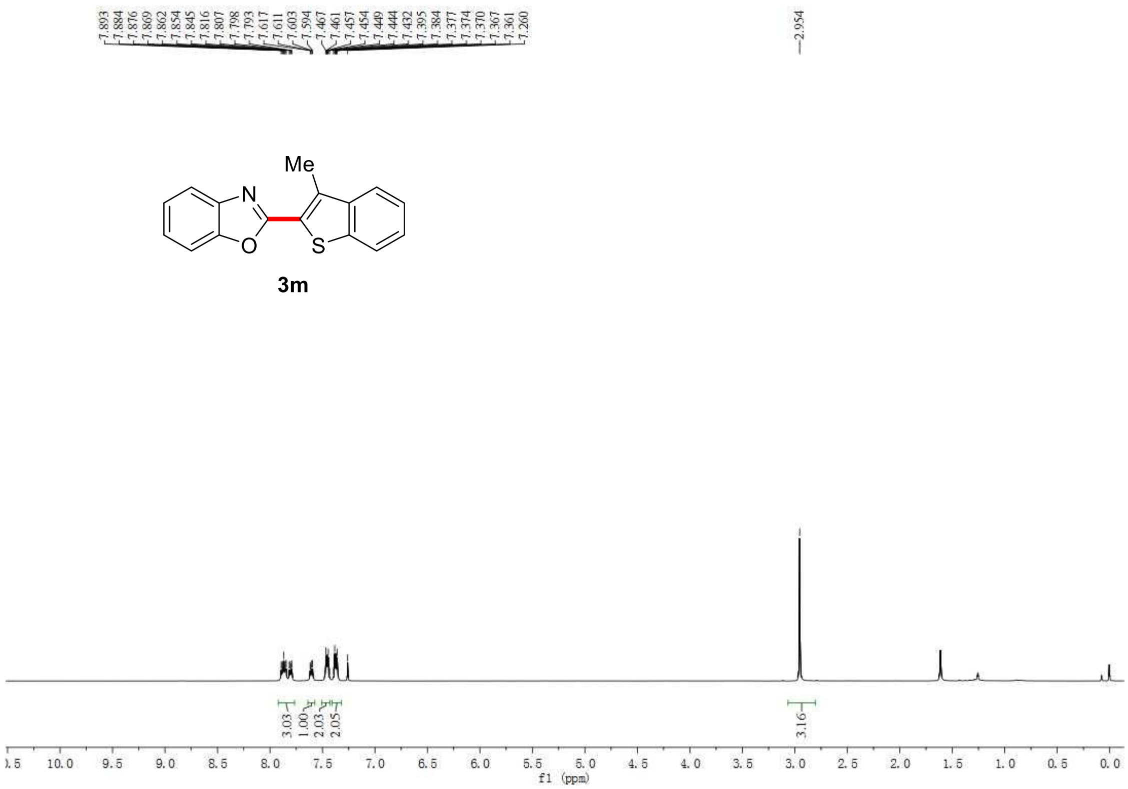

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7.854
7.845
7.816
7.807
7.798
7.793
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7.603
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7.457
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7.449
7.444
7.432
7.395
7.384
7.377
7.374
7.370
7.367
7.361
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Me
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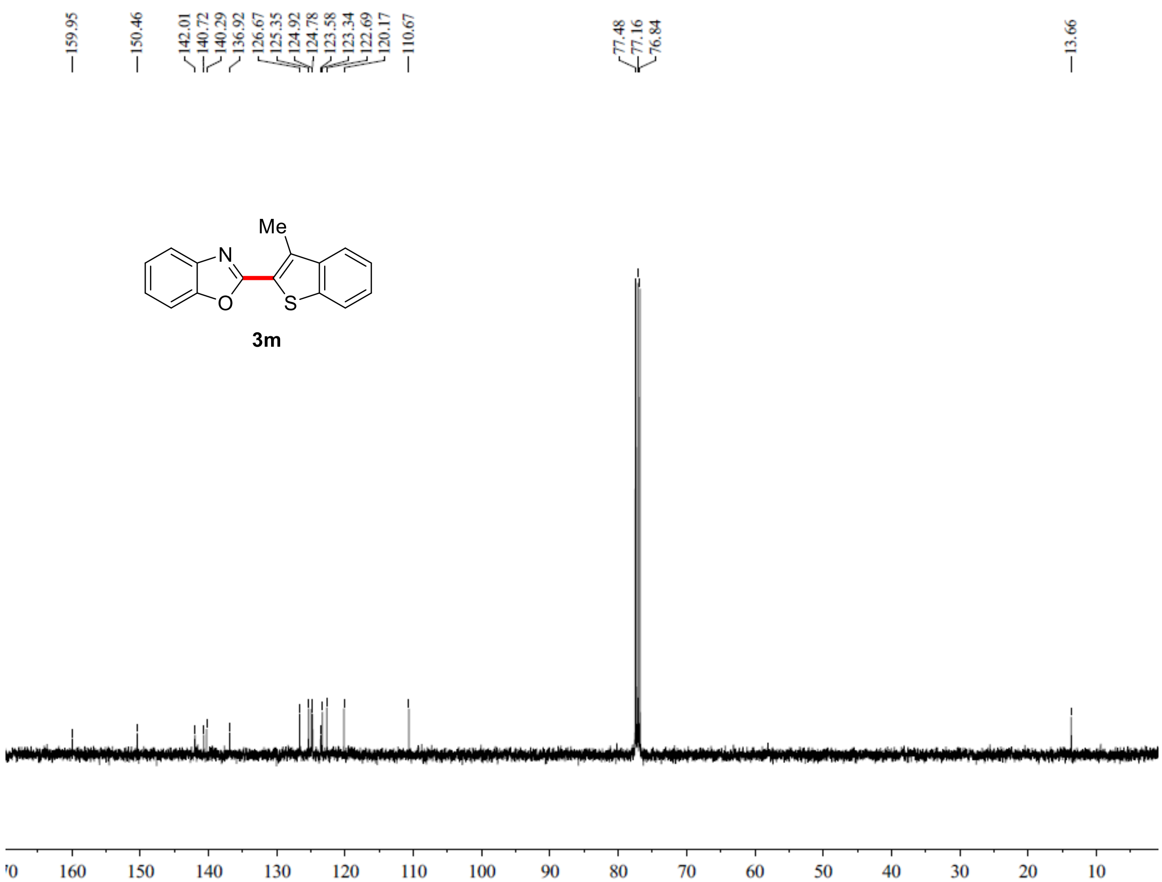
O
S
3m
3.03
1.00
2.03
2.05
3.16
f1 (ppm)



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140.29
136.92
126.67
125.35
124.92
124.78
123.58
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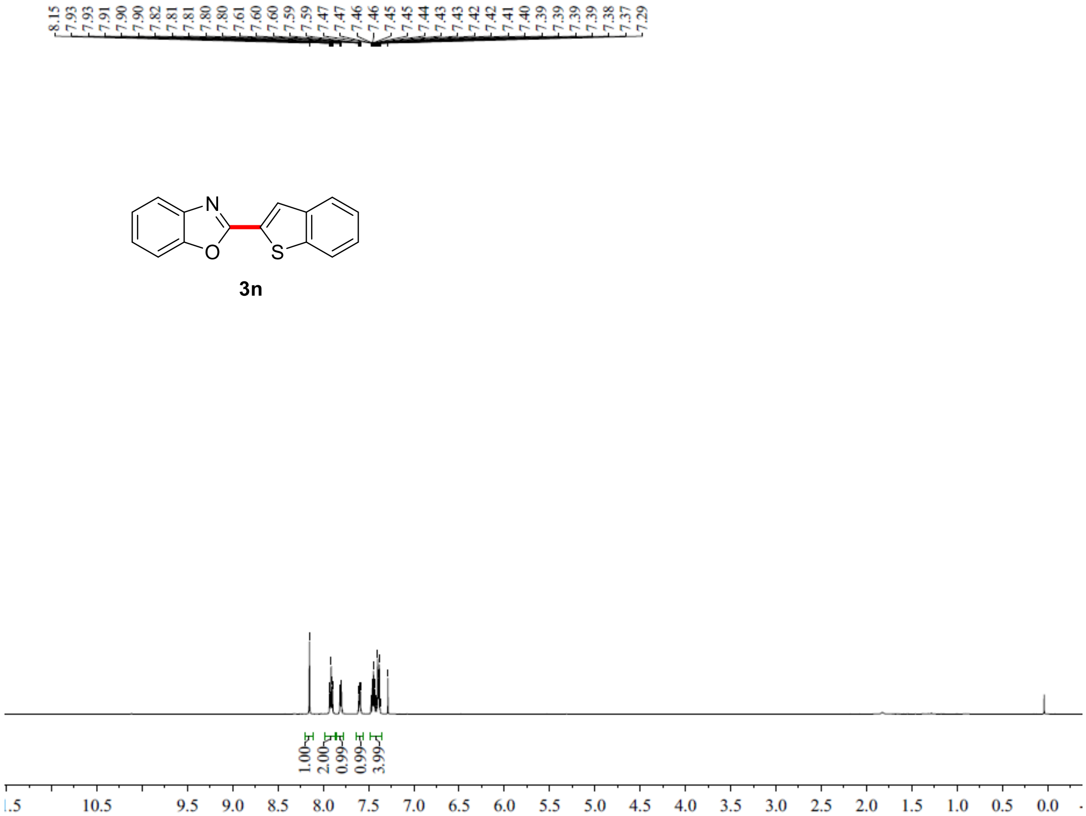
Me
N
O
S
3m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N
O
S
3n
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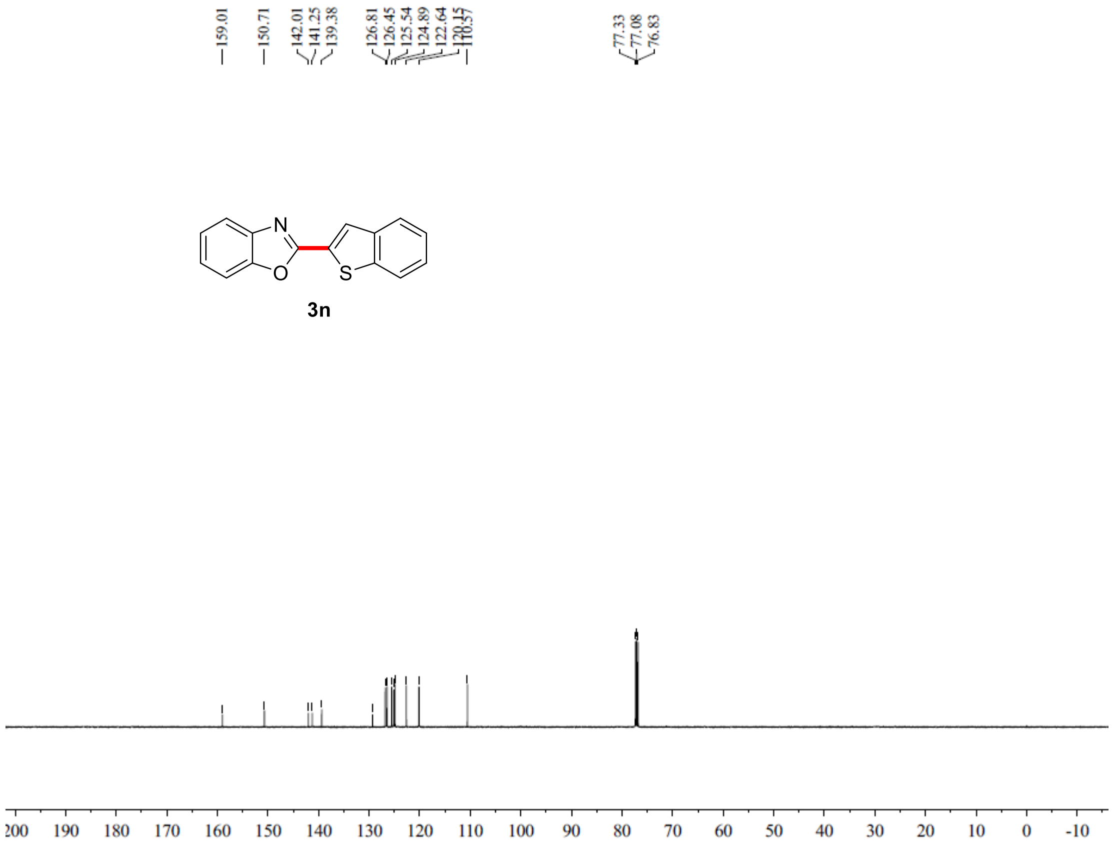
2.00
0.99
0.99
3.99
1.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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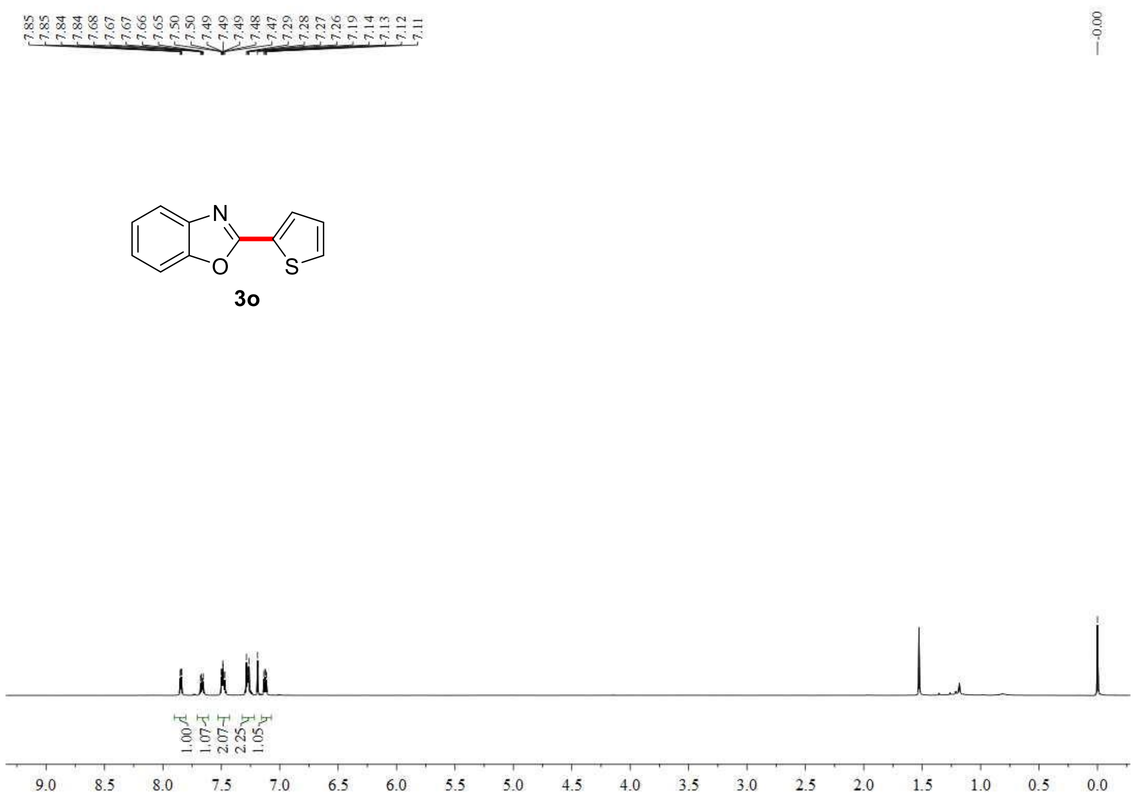
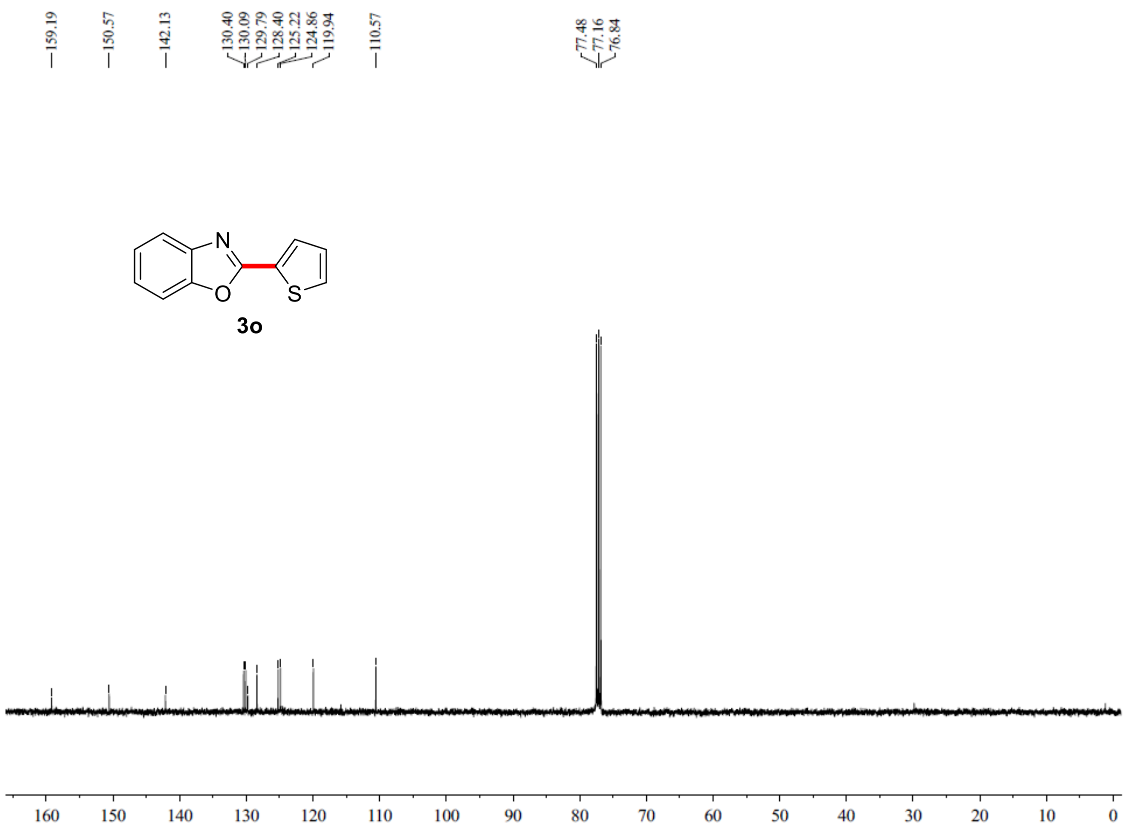
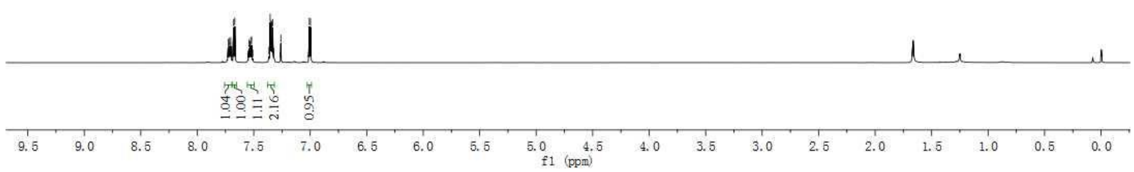

7.85 7.85 7.84 7.84 7.68 7.67 7.67 7.66 7.65 7.50 7.50 7.49 7.49 7.49 7.48 7.47 7.29 7.28 7.27 7.26 7.19 7.14 7.13 7.12 7.11
-0.00
N
O
S
3o
1.00 1.07 2.07 2.25 1.05


159.19
150.57
142.13
130.40 130.09 129.79 128.40 125.22 124.86 119.94
110.57
77.48 77.16 76.84
N
O
S
3o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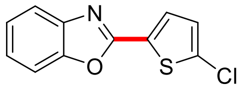
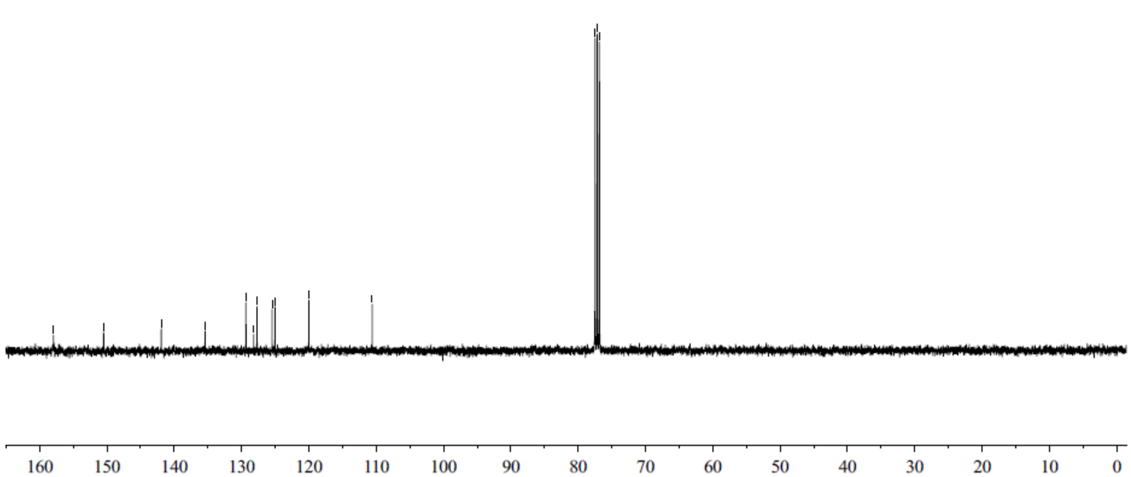
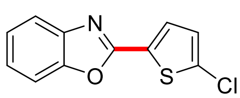
7.718
7.711
7.703
7.678
7.668
7.551
7.542
7.534
7.527
7.519
7.508
7.365
7.355
7.347
7.340
7.332
7.321
7.260
7.008
6.998
1.04
1.00
1.11
2.16
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

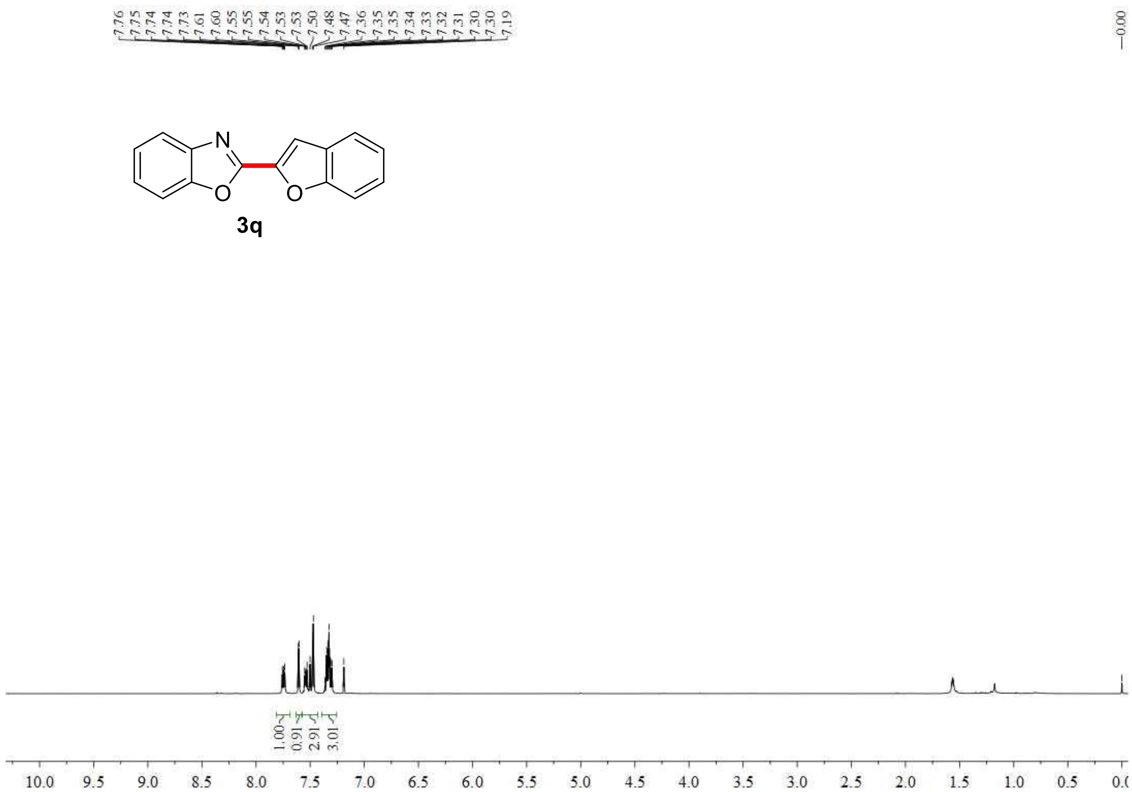

N
O
S
Cl

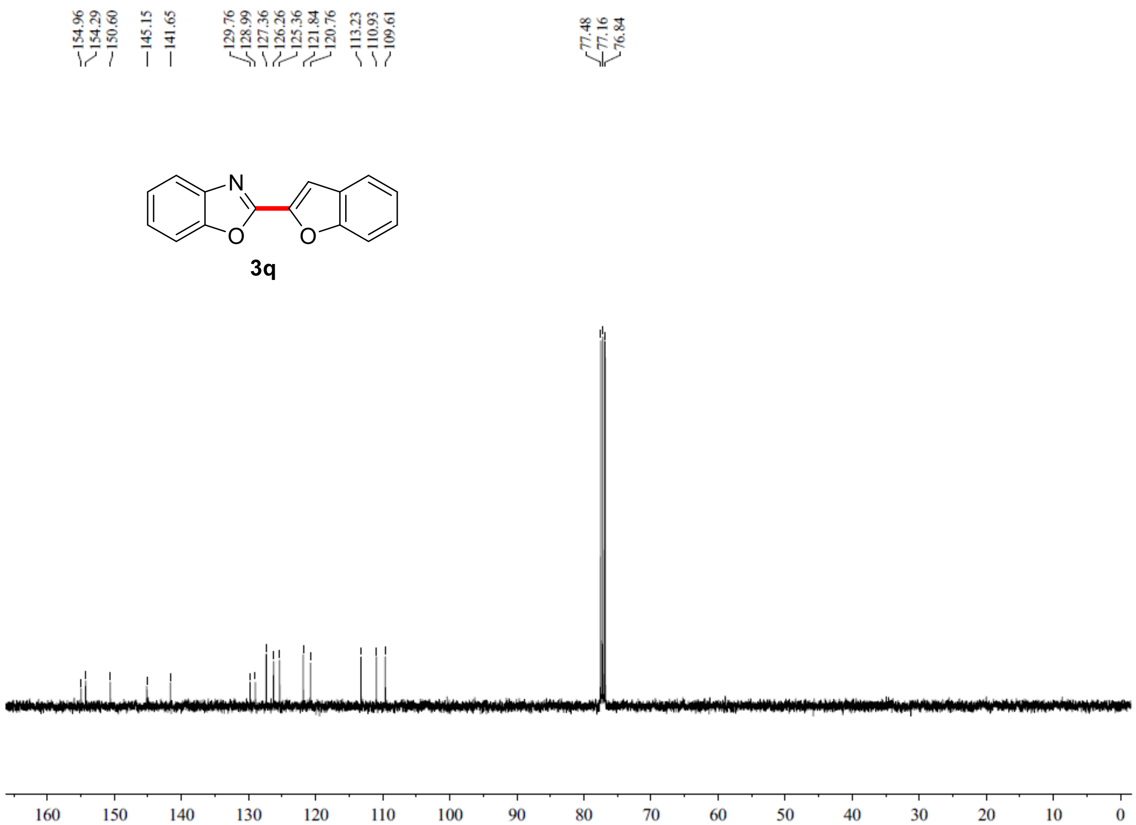
3p

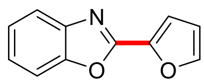

157.94
150.48
141.92
135.41
129.34
128.21
127.69
125.46
125.02
120.00
110.59
77.48
77.16
76.84
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


N
O
S
Cl

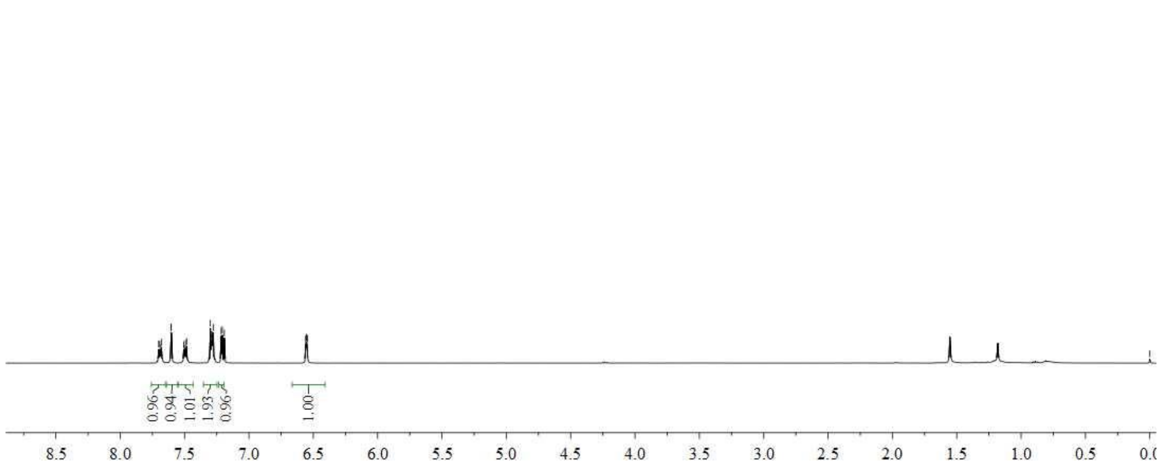
3p


7.76
7.75
7.74
7.74
7.73
7.61
7.60
7.55
7.55
7.54
7.53
7.53
7.50
7.48
7.47
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.19
0.00
N
O
O
3q
1.00
0.91
2.91
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

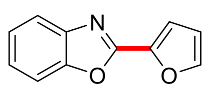

154.96
154.29
150.60
145.15
141.65
129.76
128.99
127.36
126.26
125.36
121.84
120.76
113.23
110.93
109.61
77.48
77.16
76.84
N
O
O
3q
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



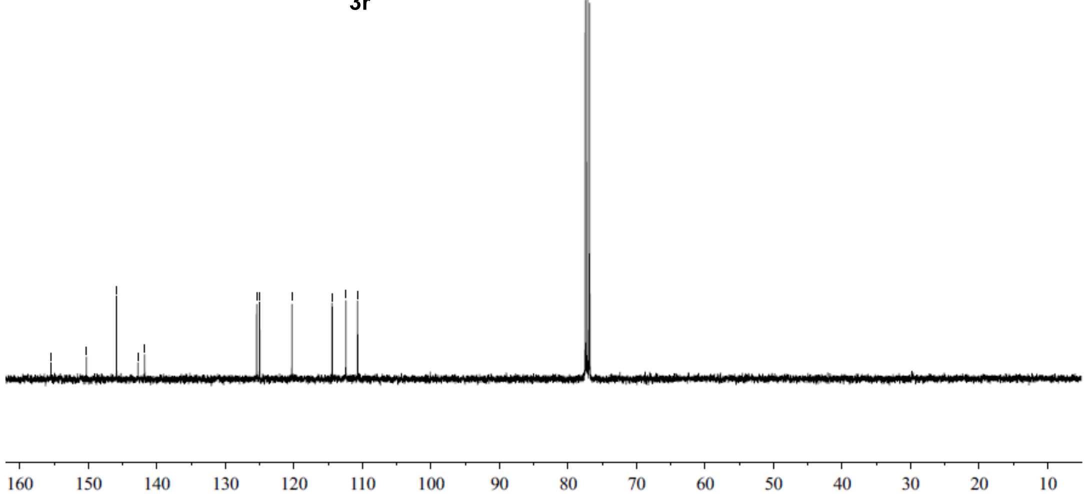
3r



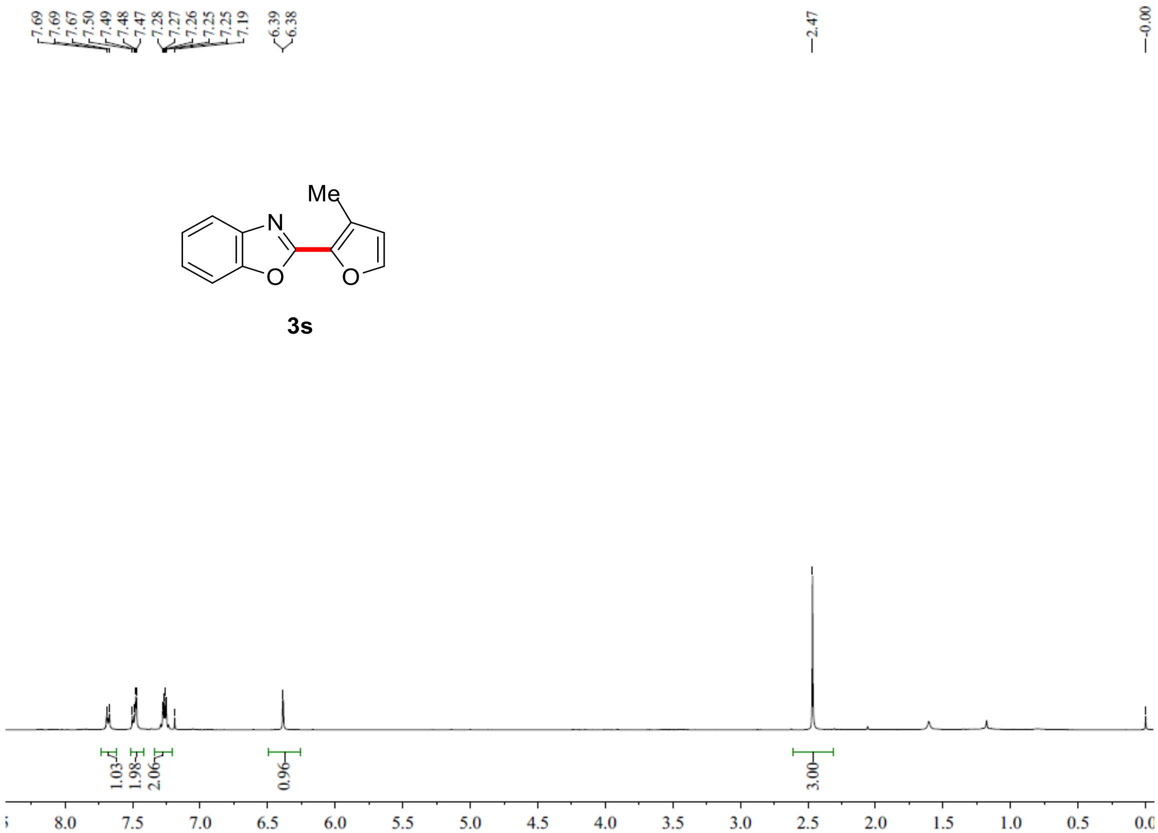
7.70
7.69
7.68
7.61
7.60
7.51
7.49
7.48
7.30
7.29
7.29
7.28
7.28
7.22
7.21
7.19
6.56
6.55
6.55
6.55
0.00
0.96
0.94
1.01
1.93
0.96
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

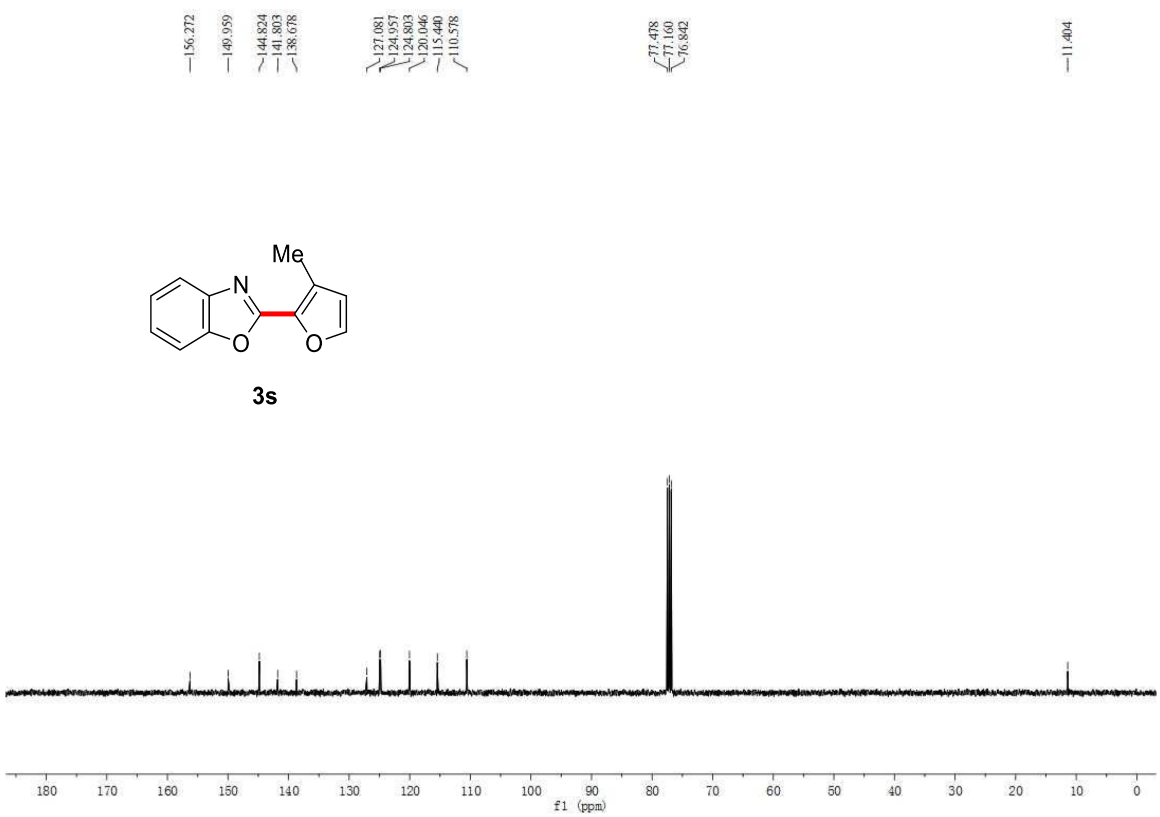


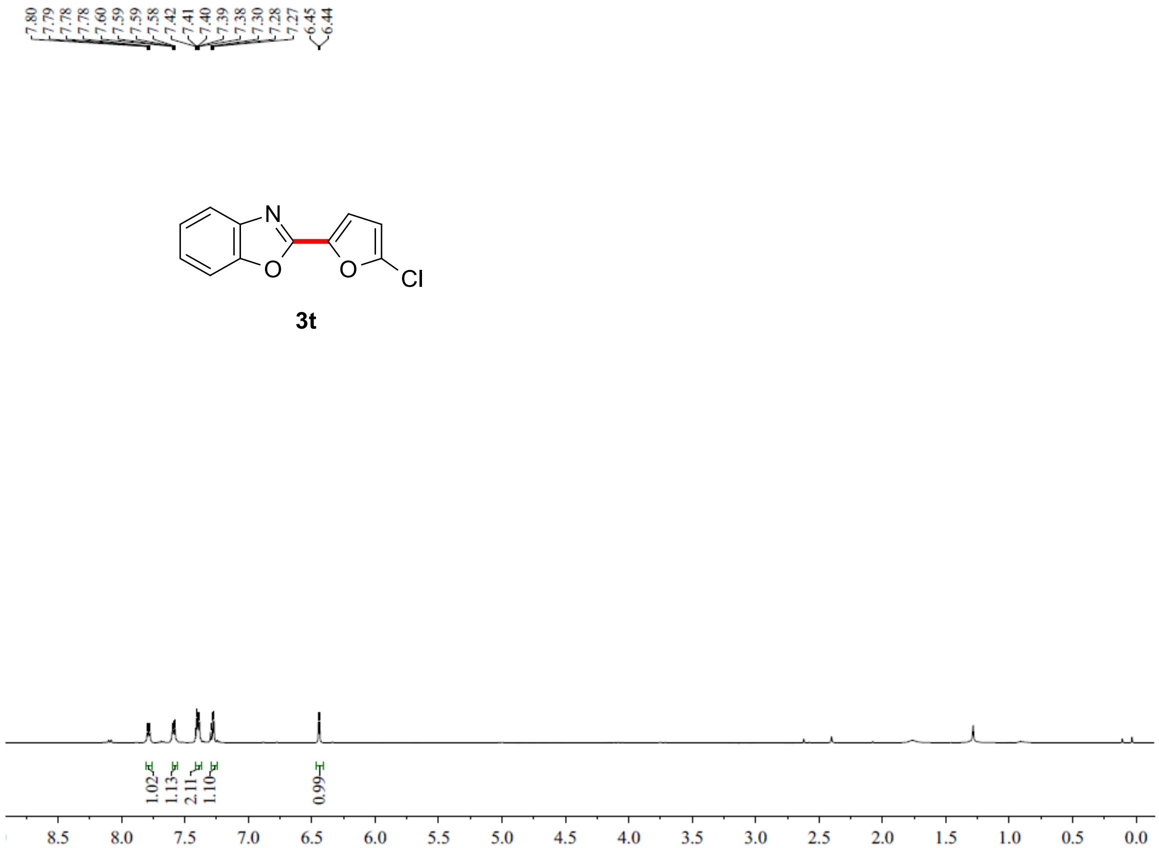
3r

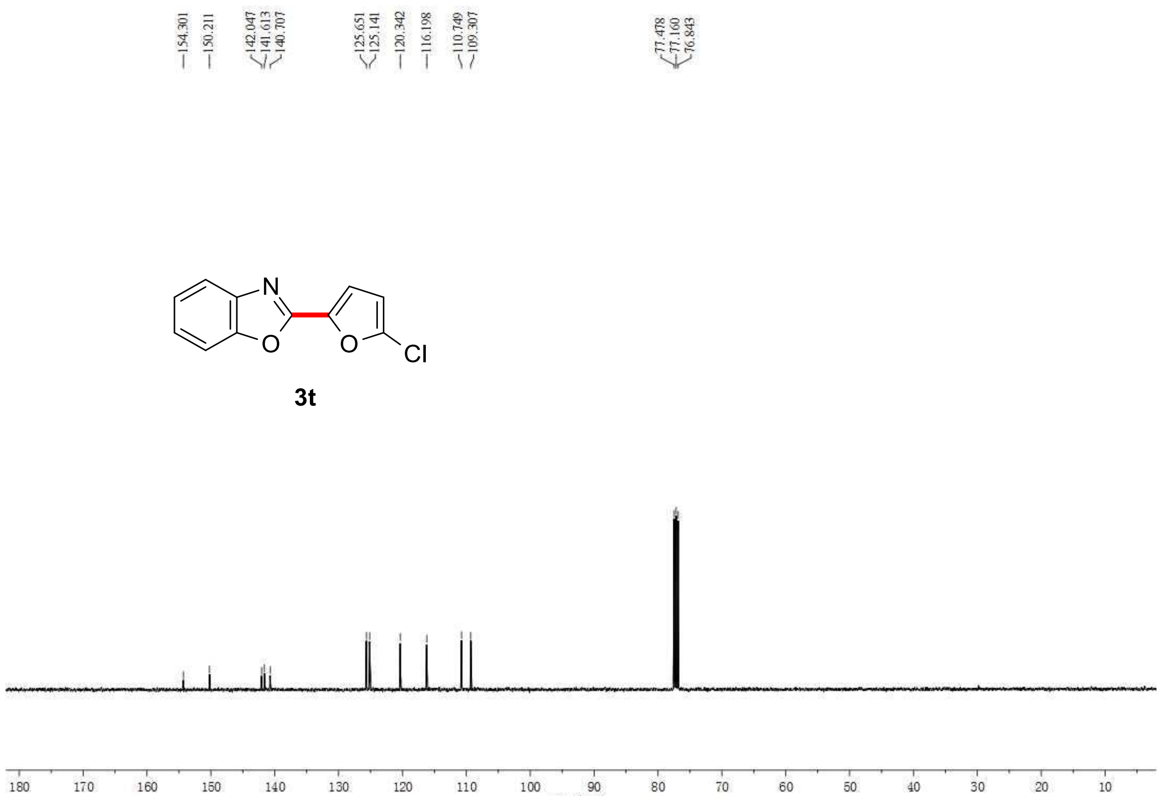


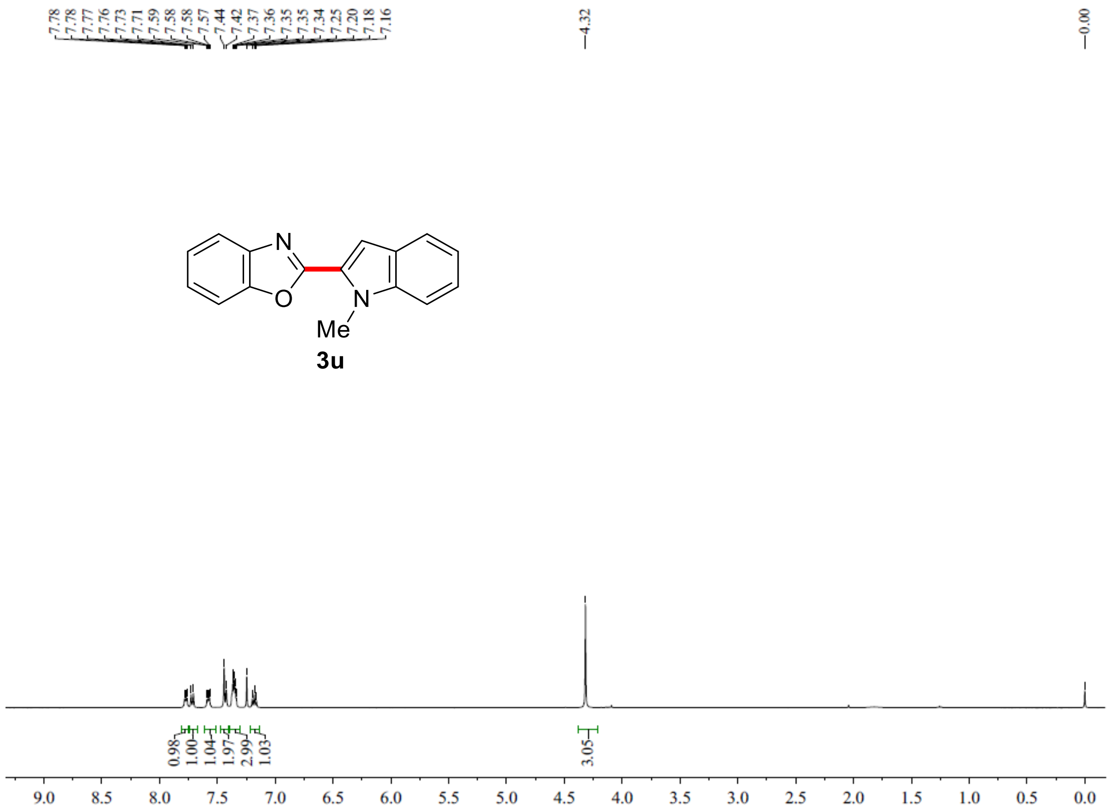
155.44
150.28
145.88
142.75
141.77
125.43
124.99
120.28
114.42
112.41
110.71
77.48
77.16
76.84
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

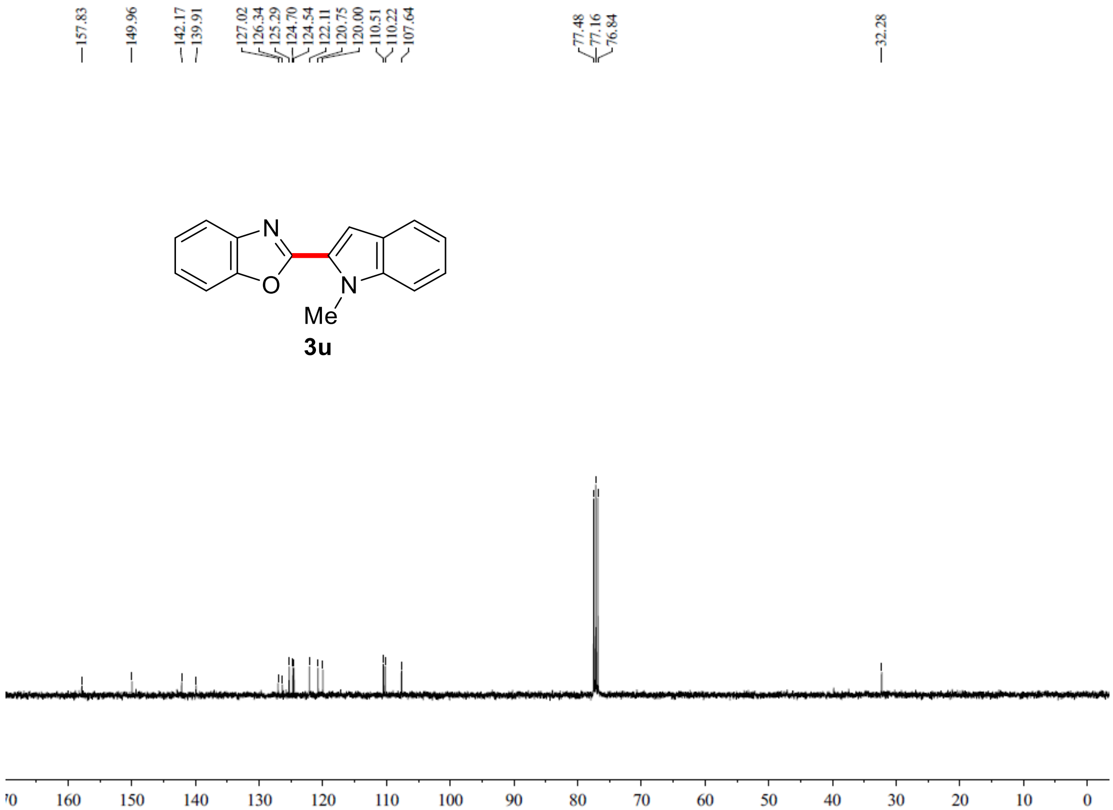

7.69
7.69
7.67
7.50
7.49
7.48
7.47
7.28
7.27
7.26
7.25
7.25
7.19
6.39
6.38
2.47
0.00
Me
N
O
O
3s
1.03
1.98
2.06
0.96
3.00


156.272
149.959
144.824
141.803
138.678
127.081
124.957
124.803
120.046
115.440
110.578
77.478
77.160
76.842
11.404
Me
N
O
O
3s
f1 (ppm)


7.80
7.79
7.78
7.78
7.60
7.59
7.59
7.58
7.42
7.41
7.40
7.39
7.38
7.30
7.28
7.27
6.45
6.44
N
O
O
Cl
3t
1.02
1.13
2.11
1.10
0.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


154.301
150.211
142.047
141.613
140.707
125.651
125.141
120.342
116.198
110.749
109.307
77.478
77.160
76.843
N
O
O
Cl
3t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.78
7.78
7.77
7.76
7.73
7.71
7.59
7.58
7.58
7.57
7.44
7.42
7.37
7.36
7.35
7.35
7.34
7.25
7.20
7.18
7.16
4.32
0.00
N
O
N
Me
3u
0.98
1.00
1.04
1.97
2.99
1.03
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


157.83
149.96
142.17
139.91
127.02
126.34
125.29
124.70
124.54
122.11
120.75
120.00
110.51
110.22
107.64
77.48
77.16
76.84
32.28
N
O
N
Me
3u
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0