

S1

Supporting Information

The Palladium-Catalyzed Tandem Decarboxylation, Carbon-Carbon Triple Bond Oxidation and Decarbonylative Arylation of Benzoxazole C-H Bond

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S2

1).General methods:

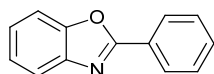
Chemicals were either purchased or purified by standard techniques without special instructions. ^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^1H 500 MHz, ^{13}C 125 MHz), using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz.

2). Optimization of the reaction of benzoxazole with 3-phenylpropionic acid:

The mixture of benzoxazole (22 μL , 0.2 mmol), 3-phenylpropionic acid (43 mg, 0.3 mmol)/phenylacetylene (30.6 mg, 0.3mmol), $\text{Pd}(\text{dba})_2$ (5.7 mg, 5 mol %), Cs_2CO_3 (130 mg, 0.4 mmol) and Ag_2CO_3 (54 mg, 0.2 mmol) in DMF (2 mL) and DMSO (100 μL) was stirred at 140 °C under Oxygen atmosphere for 11 h. After the completion of the reaction, as monitored by TLC, the solvent was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (300-400 mesh) with petroleum ether-EtOAc as eluent to give the desired product.

3) Spectral data for the products

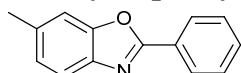
2-phenylbenzo[d]oxazole (3aa)¹



¹H NMR (CDCl₃, 500 MHz): δ 8.27-8.26 (m, 2H), 7.80-7.77 (m, 1H), 7.60-7.51 (m, 4H), 7.37-7.34 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): δ 163.1, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6.

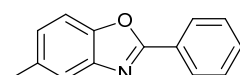
6-Methyl-2-phenylbenzo[d]oxazole (3ba)¹



¹H NMR (CDCl₃, 500 MHz): δ 8.24-8.23 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52-7.51 (m, 3H), 7.38 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 162.6, 151.1, 140.0, 135.5, 131.2, 128.8, 127.4, 127.4, 125.8, 119.3, 110.7, 21.8.

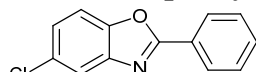
5-methyl-2-phenylbenzo[d]oxazole (3ca)¹



¹H NMR (CDCl₃, 500 MHz): δ 8.25-8.23 (m, 2H), 7.56-7.50 (m, 4H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 163.1, 149.0, 142.3, 134.4, 131.4, 128.8, 127.5, 127.3, 126.2, 120.0, 110.0, 21.5.

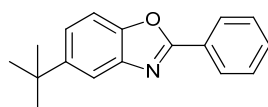
5-Chloro-2-phenylbenzo[d]oxazole (3da)²



¹H NMR (CDCl₃, 500 MHz): δ 8.23 (d, *J* = 7.0 Hz, 2H), 7.75 (s, 1H), 7.56-7.48 (m, 4H), 7.32 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 164.4, 149.4, 143.3, 131.9, 130.0, 129.0, 127.8, 126.7, 125.3, 120.0, 111.3.

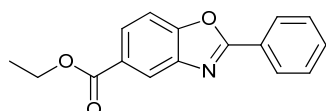
5-tert-butyl-2-phenylbenzo[d]oxazole (3ea)³



¹H NMR (CDCl₃, 500 MHz): δ 8.27-8.25 (m, 2H), 7.81 (d, *J* = 1.5 Hz, 1H), 7.53-7.49 (m, 4H), 7.42 (m, 1H), 1.41 (s, 9H).

¹³C NMR (CDCl₃, 125 MHz): δ 163.2, 148.8, 148.1, 142.0, 131.3, 128.9, 127.5, 127.4, 122.8, 116.5, 109.7, 34.9, 31.7.

Ethyl 5-carboxylate-2-phenylbenzo[d]oxazole (3fa)²

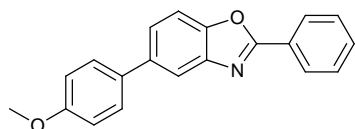


¹H NMR (CDCl₃, 500 MHz): δ 8.48 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.62-7.53 (m, 4H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H).

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^{13}C NMR (CDCl_3 , 125 MHz): δ 166.2, 153.6, 142.2, 131.9, 129.0, 127.8, 127.4, 127.0, 126.7, 122.0, 110.3, 61.2, 29.7, 14.3.

5-(4-methoxyphenyl)-2-phenylbenzo[d]oxazole (3ga)



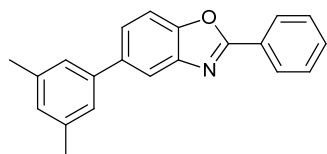
^1H NMR (CDCl_3 , 500 MHz): δ 8.30-8.27 (m, 2H), 7.92 (d, $J = 2.0\text{ Hz}$, 1H), 7.62-7.52 (m, 7H), 7.03-7.00 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 159.2, 150.0, 142.7, 138.1, 133.6, 131.5, 128.9, 128.4, 127.6, 127.2, 124.4, 117.9, 114.3, 110.5, 55.4.

IR (prism, cm^{-1}): 1712, 1223, 1108, 807, 744, 703.

HRMS exact mass calc'd for $\text{C}_{20}\text{H}_{16}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 302.1176; found m/z : 302.1188.

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



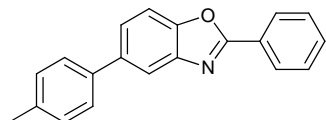
^1H NMR (CDCl_3 , 500 MHz): δ 8.20-8.18 (m, 2H), 7.86 (d, $J = 1.5\text{ Hz}$, 1H), 7.53-7.44 (m, 5H), 7.17 (s, 2H), 6.94 (s, 1H), 2.32 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.5, 150.2, 142.7, 141.1, 138.7, 138.4, 131.5, 129.0, 128.9, 127.6, 127.2, 125.4, 124.8, 118.4, 110.4, 21.4.

IR (prism, cm^{-1}): 1716, 1222, 1019, 845, 805, 668.

HRMS exact mass calc'd for $\text{C}_{21}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$): 300.1383; found m/z : 300.1384.

2-phenyl-5-(*p*-tolyl)benzo[d]oxazole(3ia)



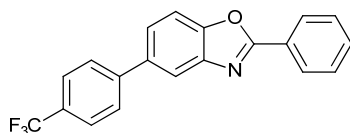
^1H NMR (CDCl_3 , 500 MHz): δ 8.30-8.27 (m, 2H), 7.96 (d, $J = 1.5\text{ Hz}$, 1H), 7.62 (d, $J = 8.5\text{ Hz}$, 1H), 7.58-7.53 (m, 6H), 7.29 (d, $J = 8.0\text{ Hz}$, 2H), 2.42 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 150.1, 142.7, 138.4, 138.2, 137.0, 131.5, 129.6, 128.9, 127.6, 127.3, 127.2, 124.6, 118.2, 110.50, 21.1.

IR (prism, cm^{-1}): 1550, 1285, 1033, 804, 770, 687.

HRMS exact mass calc'd for $\text{C}_{20}\text{H}_{16}\text{NO}$ ($[\text{M}+\text{H}]^+$): 286.1226; found m/z : 286.1231.

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



^1H NMR (CDCl_3 , 500 MHz): δ 8.29-8.27 (m, 2H), 7.97 (d, $J = 1.5\text{ Hz}$, 1H), 7.73 (t, $J = 9.5\text{ Hz}$, 4H), 7.66 (d, $J = 8.5\text{ Hz}$, 1H), 7.59-7.54 (m, 4H).

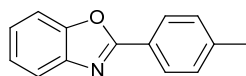
^{13}C NMR (CDCl_3 , 125 MHz): δ 164.0, 150.8, 144.5, 142.9, 136.9, 131.8, 129.3 (q, $J = 32.5\text{ Hz}$), 129.0, 127.7, 124.7 (q, $J = 270.2\text{ Hz}$), 126.9, 125.8 (q, $J = 3.8\text{ Hz}$), 125.4, 124.7, 118.7, 110.9.

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IR (prism, cm^{-1}): 1671, 1590, 1469, 1105, 821.

HRMS exact mass calc'd for $\text{C}_{20}\text{H}_{13}\text{NO}$ ($[\text{M}+\text{H}]^+$): 340.0944; found m/z : 340.0943.

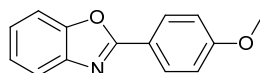
2-*p*-tolylbenzo[*d*]oxazole(3ab)²



¹H NMR (CDCl_3 , 500 MHz): δ 8.15 (d, $J = 8.5$ Hz, 2H), 7.78-7.75 (m, 1H), 7.58-7.55 (m, 1H), 7.36-7.32 (m, 4H), 2.44 (s, 3H).

¹³C NMR (CDCl_3 , 125 MHz): δ 163.3, 150.7, 142.2, 142.0, 129.6, 127.6, 124.8, 124.5, 124.4, 119.8, 110.5, 21.6.

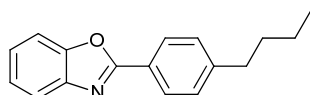
2-(4-methoxyphenyl)benzo[*d*]oxazole(3ac)²



¹H NMR (CDCl_3 , 500 MHz): δ 8.20 (d, $J = 8.5$ Hz, 2H), 7.75-7.73 (m, 1H), 7.56-7.54 (m, 1H), 7.35-7.30 (m, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 3.89 (s, 3H).

¹³C NMR (CDCl_3 , 125 MHz): δ 163.2, 162.3, 150.7, 142.3, 129.4, 124.6, 124.4, 119.7, 119.6, 114.4, 110.4, 55.4.

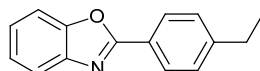
2-(4-butylphenyl)benzo[*d*]oxazole (3ad)⁴



¹H NMR (CDCl_3 , 500 MHz): δ 8.17 (d, $J = 8.5$ Hz, 2H), 7.78-7.76 (m, 1H), 7.58-7.56 (m, 1H), 7.36-7.32 (m, 4H), 2.70 (t, $J = 7.5$ Hz, 2H), 1.69-1.62 (m, 2H), 1.42-1.34 (m, 2H), 0.95 (t, $J = 7.5$ Hz, 3H).

¹³C NMR (CDCl_3 , 125 MHz): δ 163.3, 150.7, 147.0, 142.2, 129.0, 127.6, 124.8, 124.6, 124.4, 119.8, 110.5, 35.7, 33.3, 22.3, 13.9.

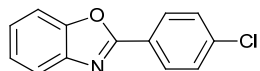
2-(4-Ethylphenyl)benzo[*d*]oxazole(3ae)¹



¹H NMR (CDCl_3 , 500 MHz): δ 8.18 (d, $J = 8.5$ Hz, 2H), 7.78-7.76 (m, 1H), 7.58-7.57 (m, 1H), 7.37-7.33 (m, 4H), 2.74 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.5$ Hz, 3H).

¹³C NMR (CDCl_3 , 125 MHz): δ 163.3, 150.7, 148.2, 142.2, 128.5, 127.7, 124.8, 124.6, 124.5, 119.8, 110.5, 28.9, 15.2.

2-(4-chlorophenyl)benzo[*d*]oxazole(3af)²



¹H NMR (CDCl_3 , 500 MHz): δ 8.19 (d, $J = 8.5$ Hz, 2H), 7.78-7.76 (m, 1H), 7.59-7.58 (m, 1H), 7.50 (d, $J = 9.0$ Hz, 2H), 7.38-7.36 (m, 2H).

¹³C NMR (CDCl_3 , 125 MHz): δ 162.1, 150.8, 142.0, 137.8, 129.3, 128.9, 125.7, 125.4, 124.7, 120.1, 110.6.

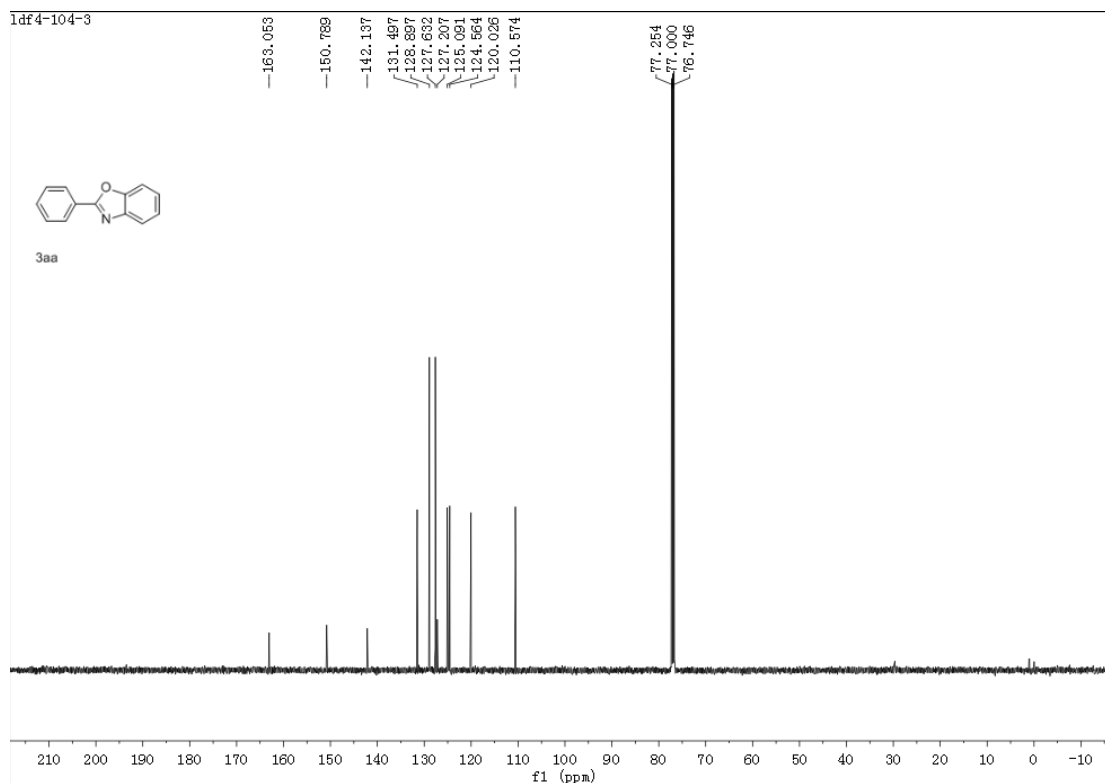
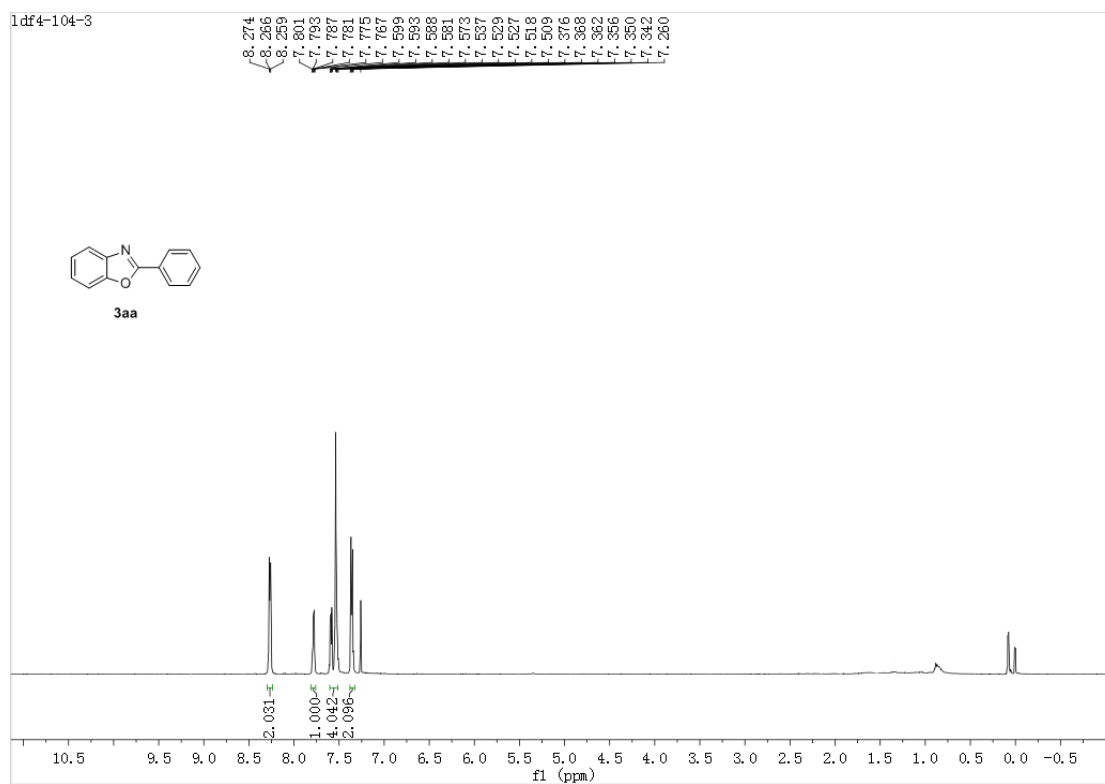
S6

4) References

- (1) A. Ghodbane, P. Jolinat and S. Fery-Forgues, *Langmuir*, 2012, **28**, 855.
- (2) W. Yoo, H. Yuan, H. Miyamura and S. Kobayashi, *Adv. Synth. Catal.*, 2011, **17**, 3085.
- (3) M. Zhang, S. Zhang, M. Liu and J. Cheng, *Chem. Commun.*, 2011, **47**, 11522.
- (4) S. Ueda and H. Nagasawa, *Angew. Chem. Int. Ed.*, 2008, **47**, 6411.

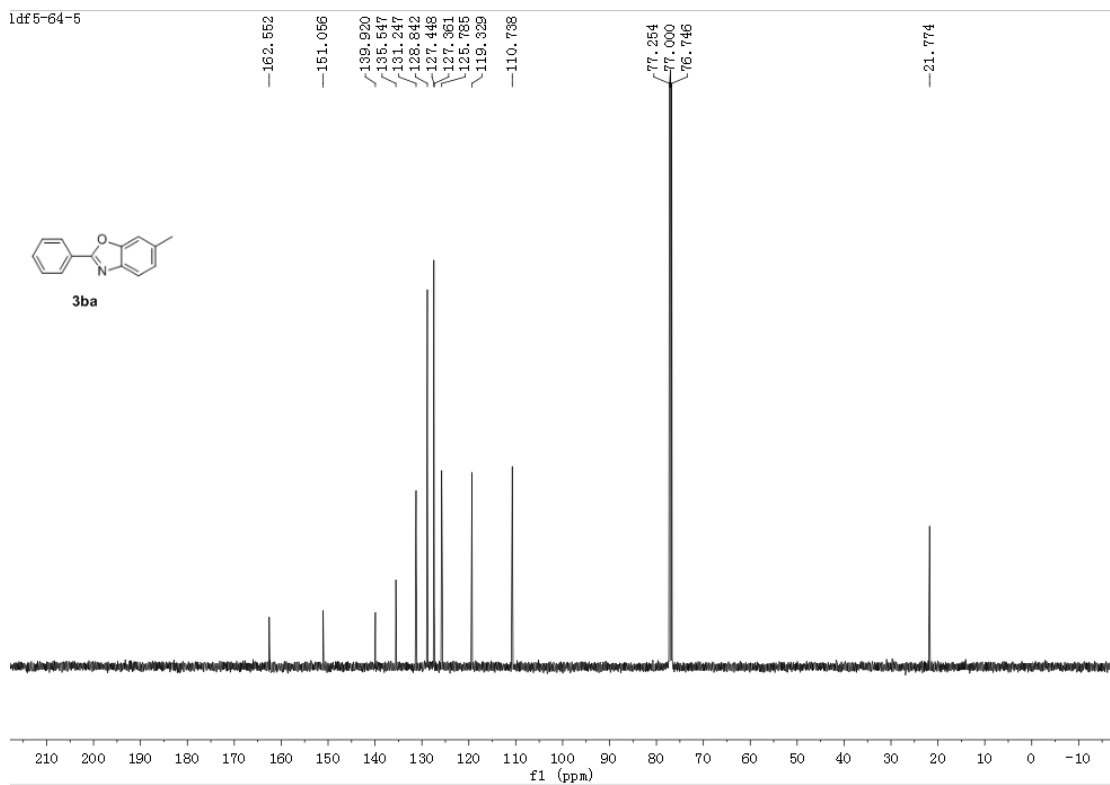
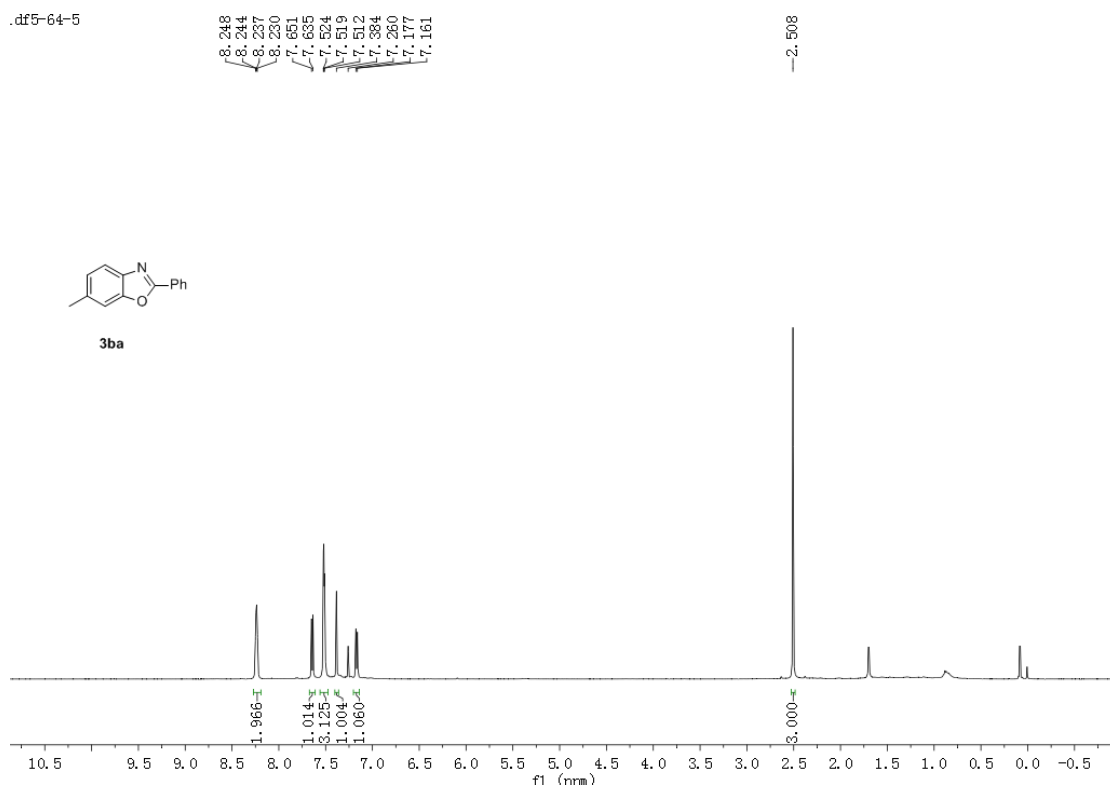
S7

5) Copies of the Products ^1H NMR and ^{13}C NMR :



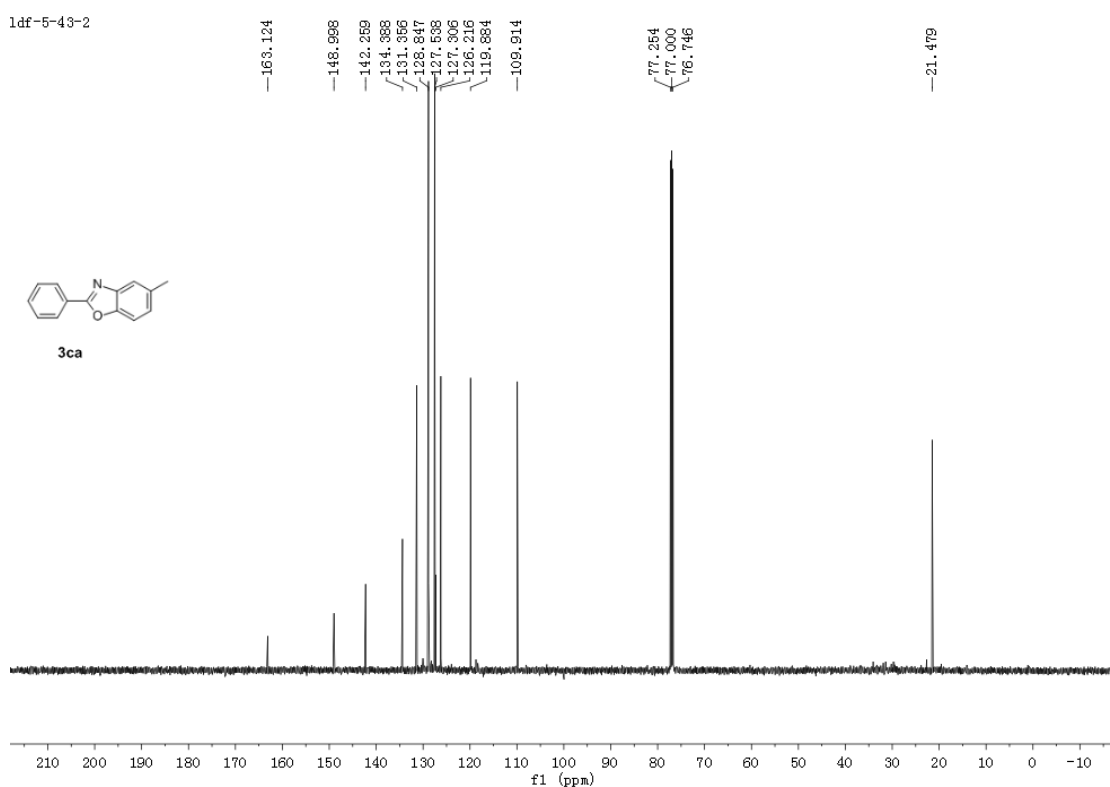
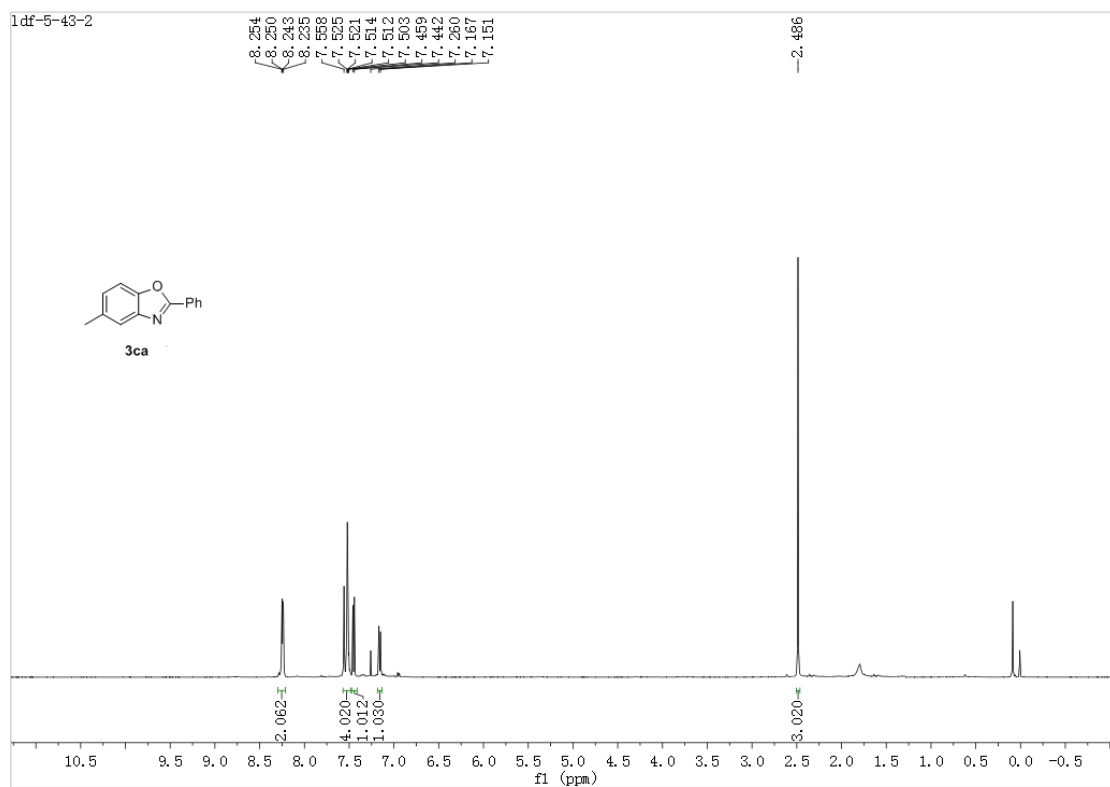
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S8

S9

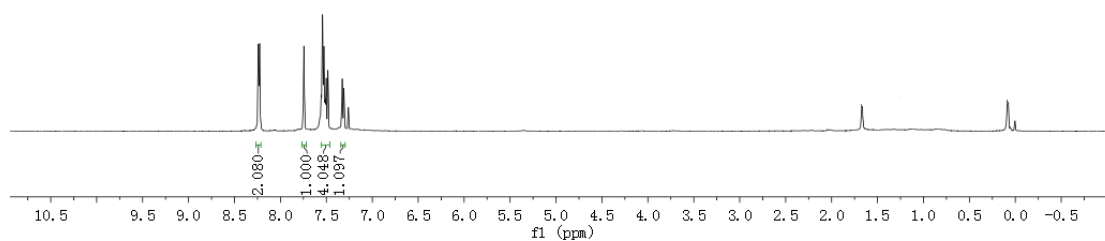
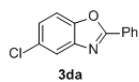


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S10

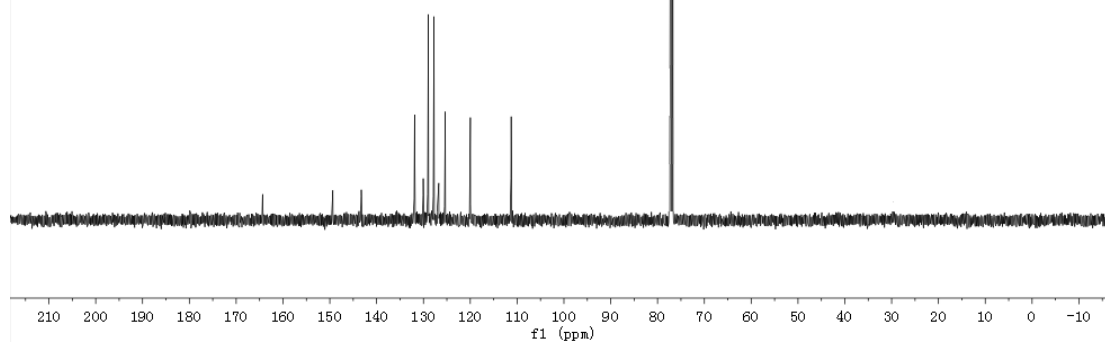
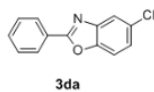
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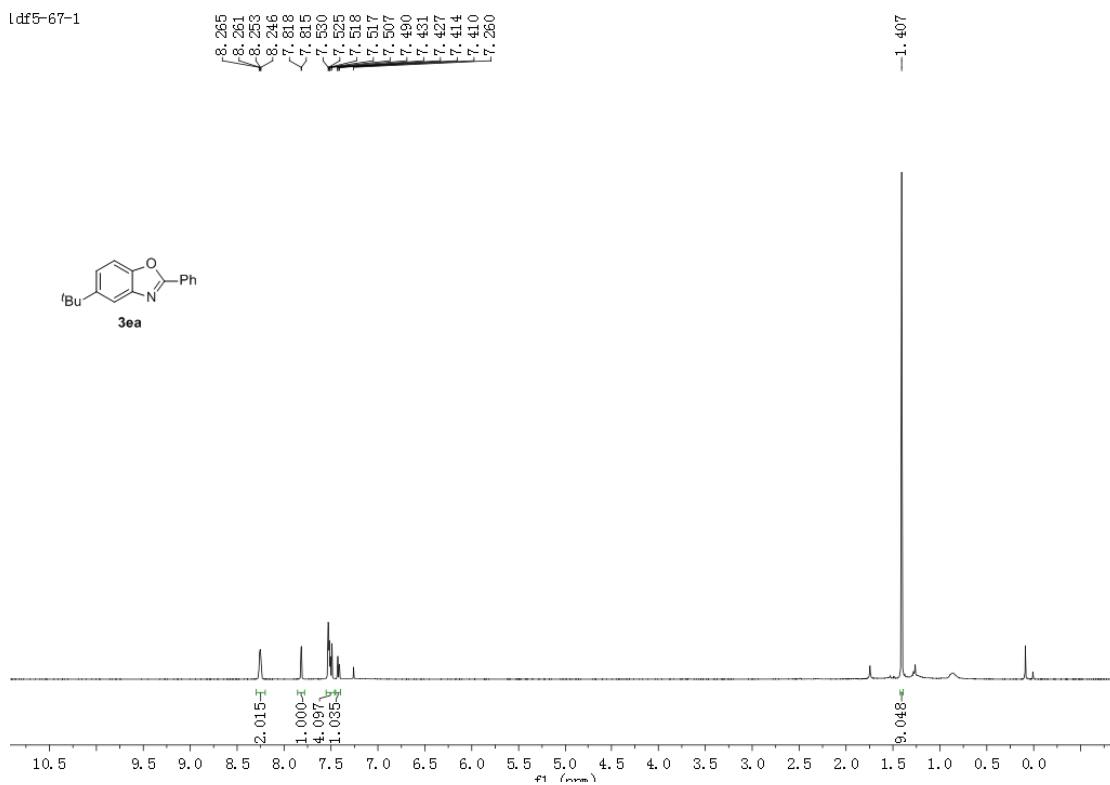
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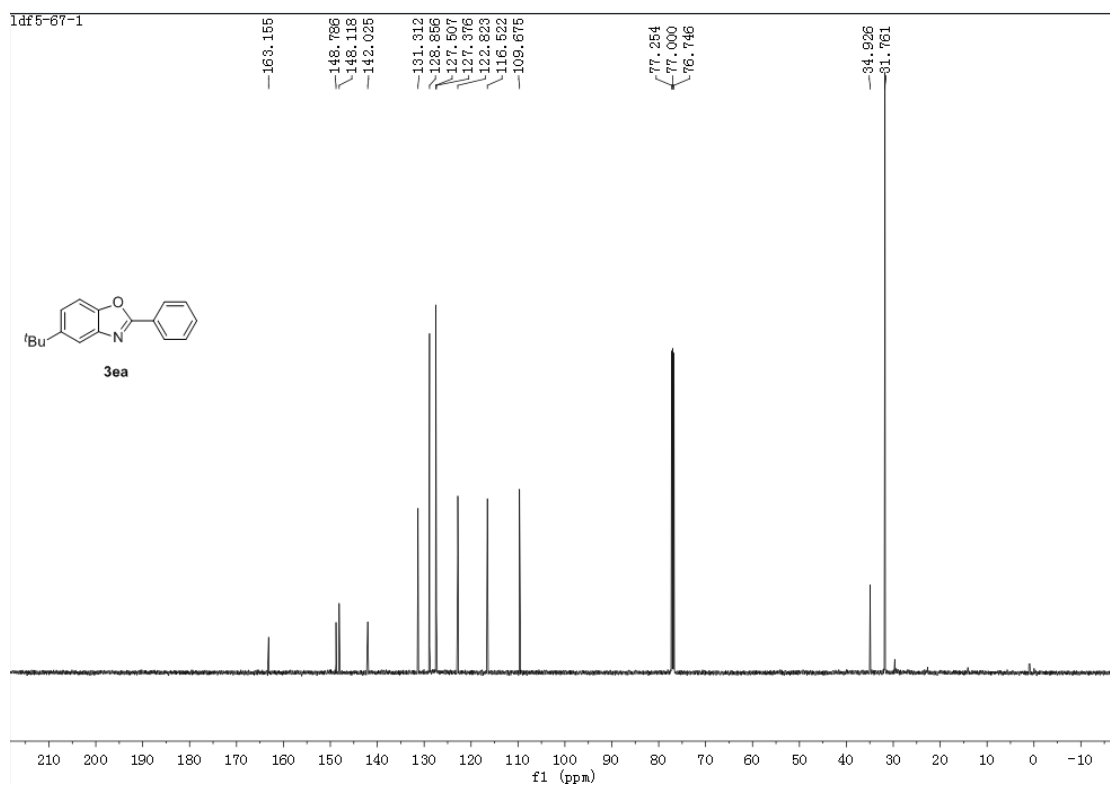


S11

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ldf5-67-1

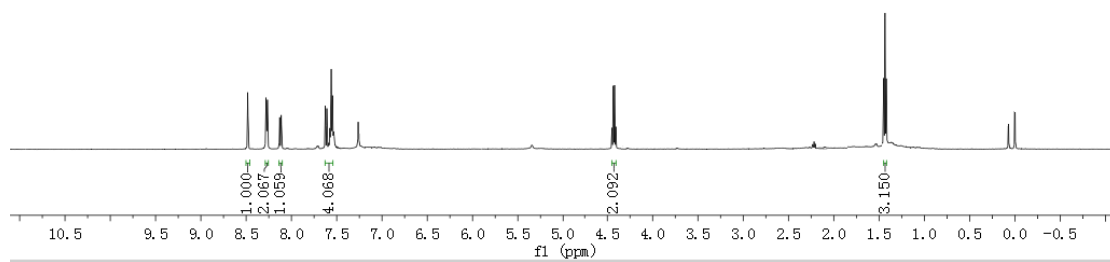
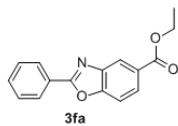


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S12

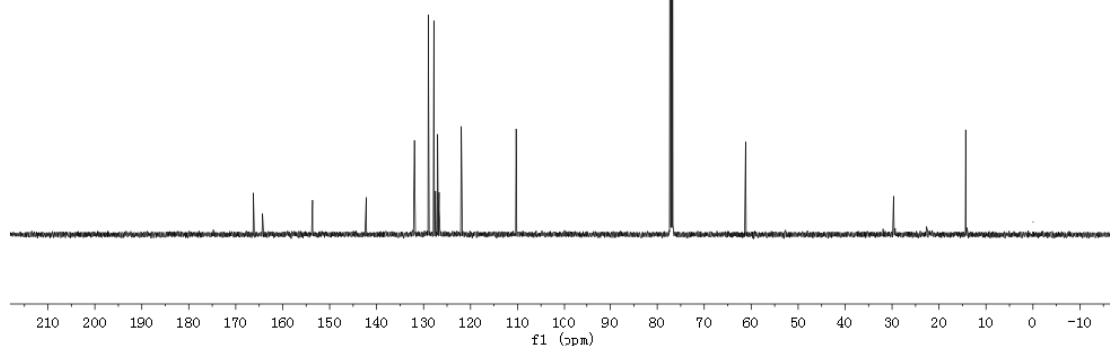
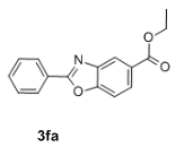
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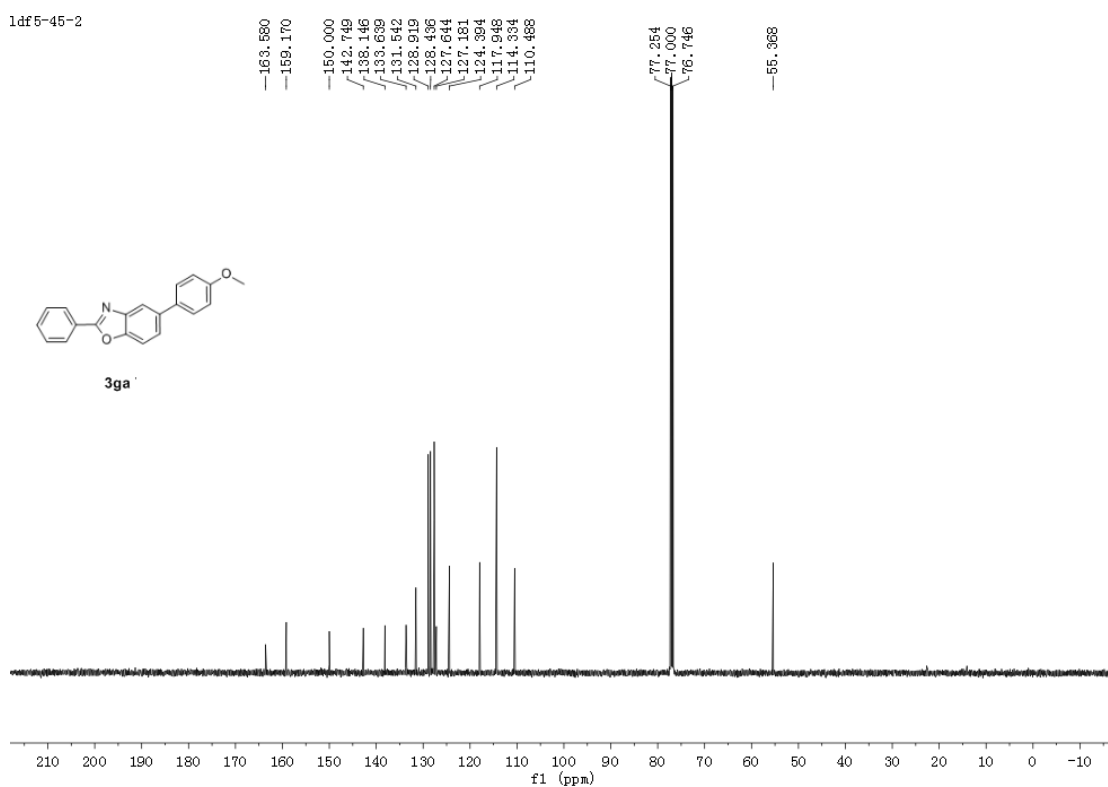
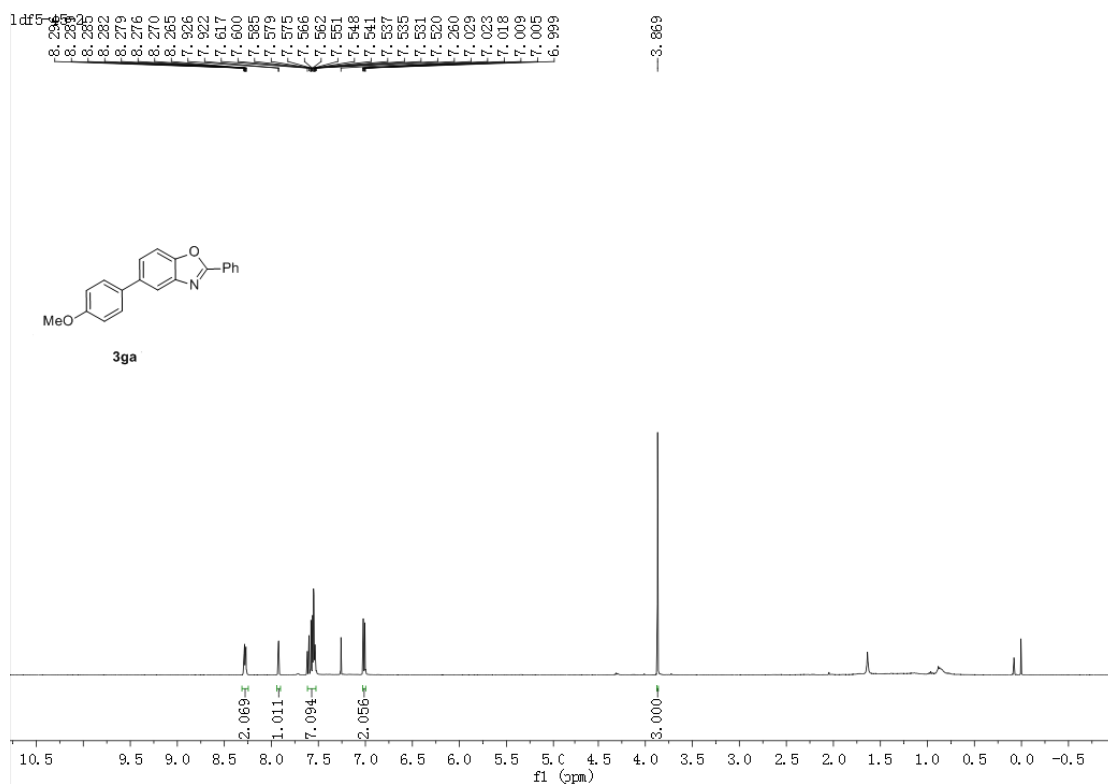


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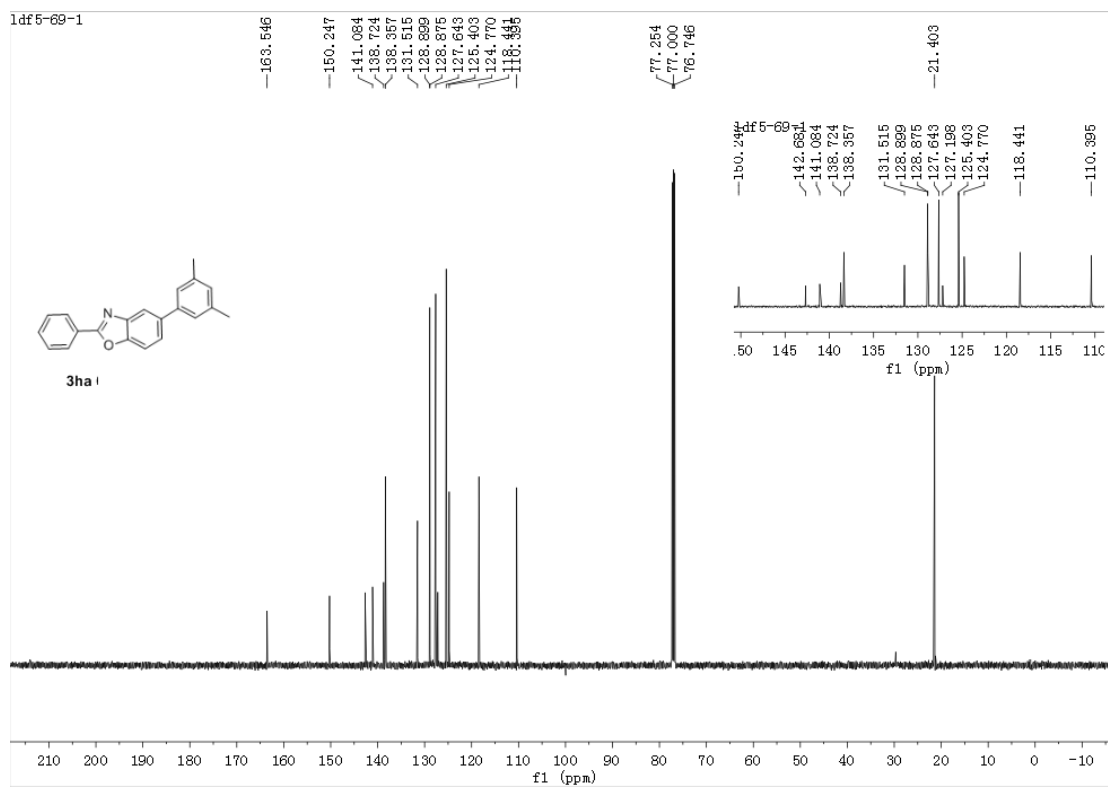
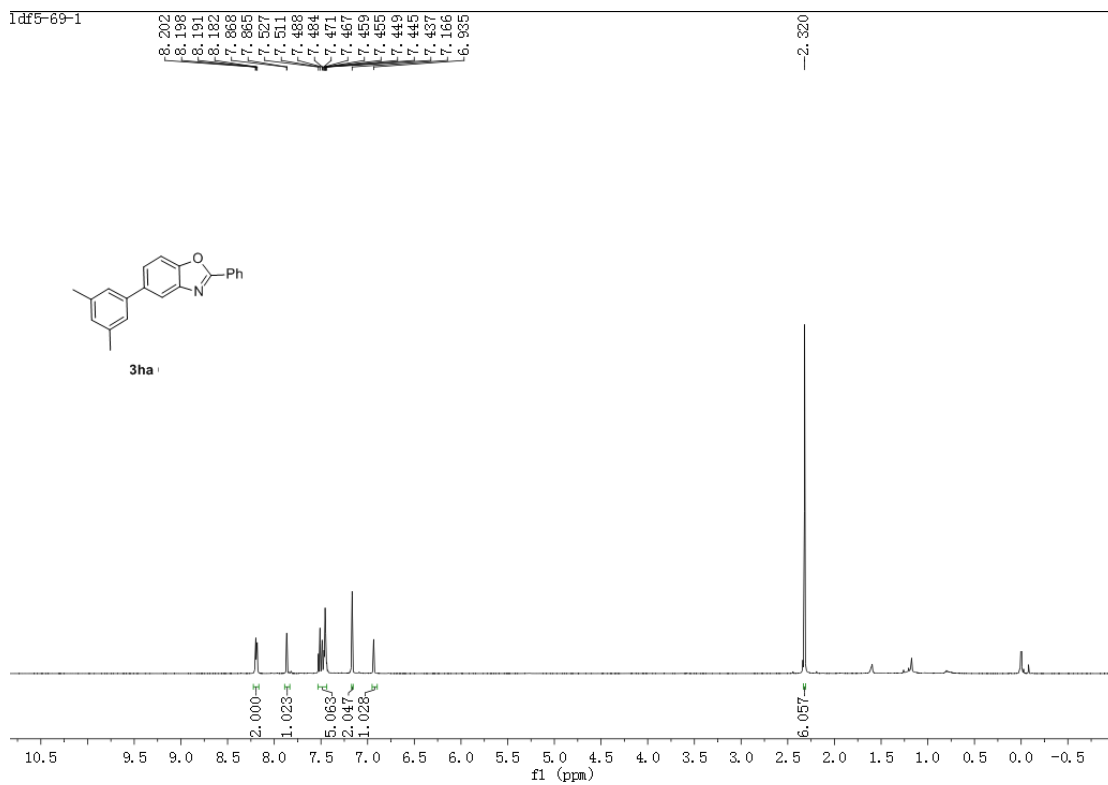


S13



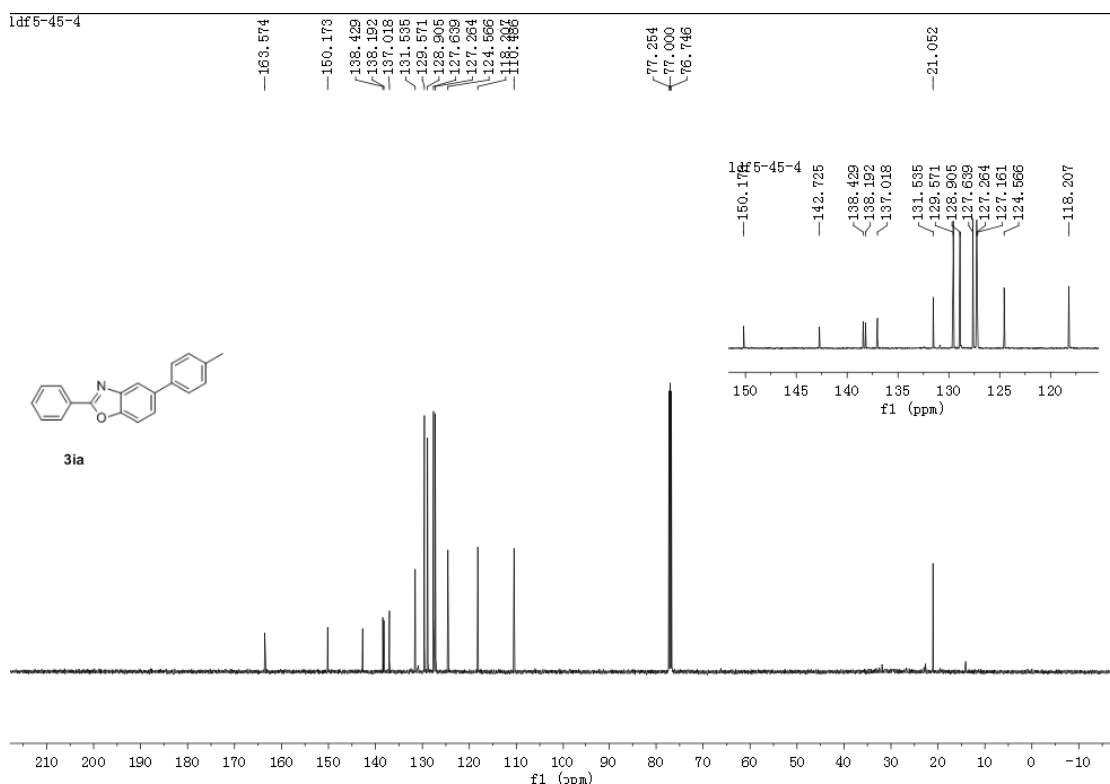
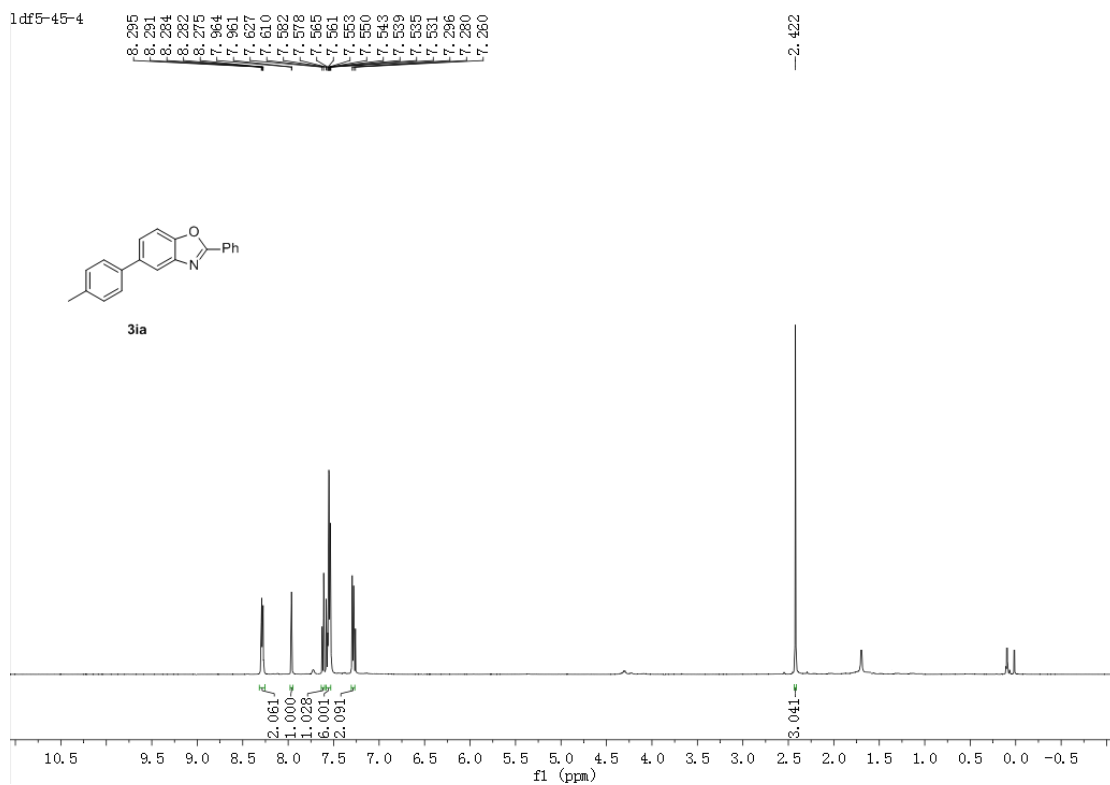
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S14



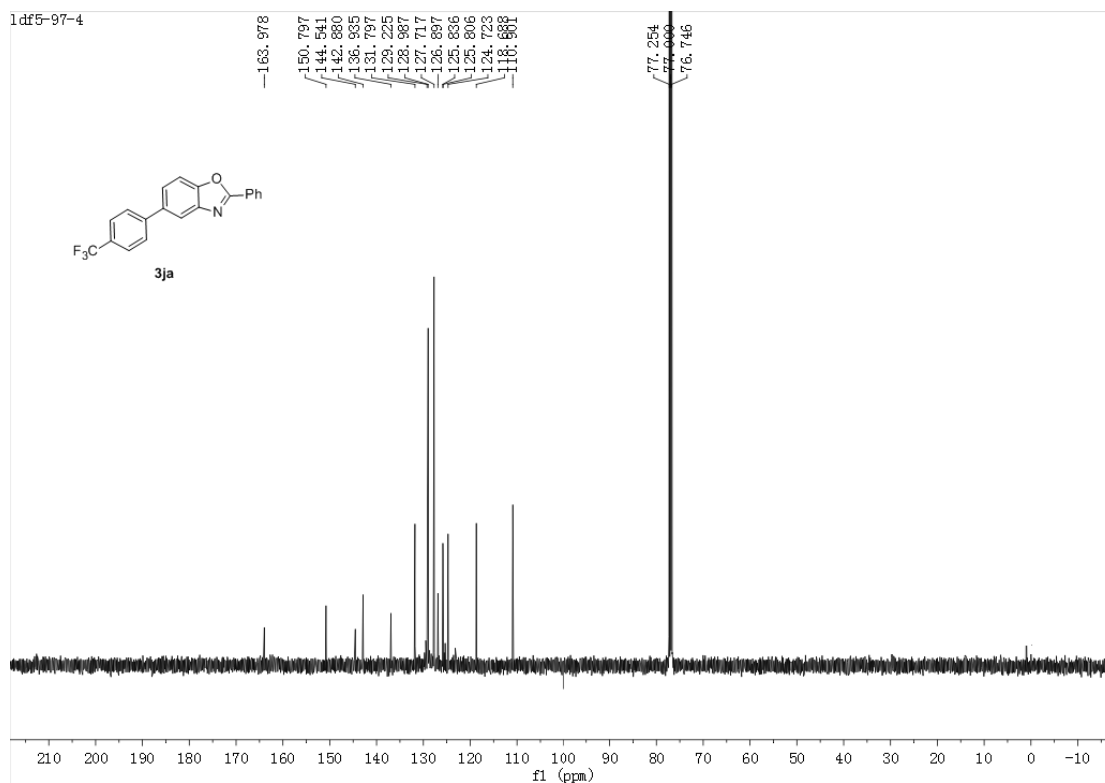
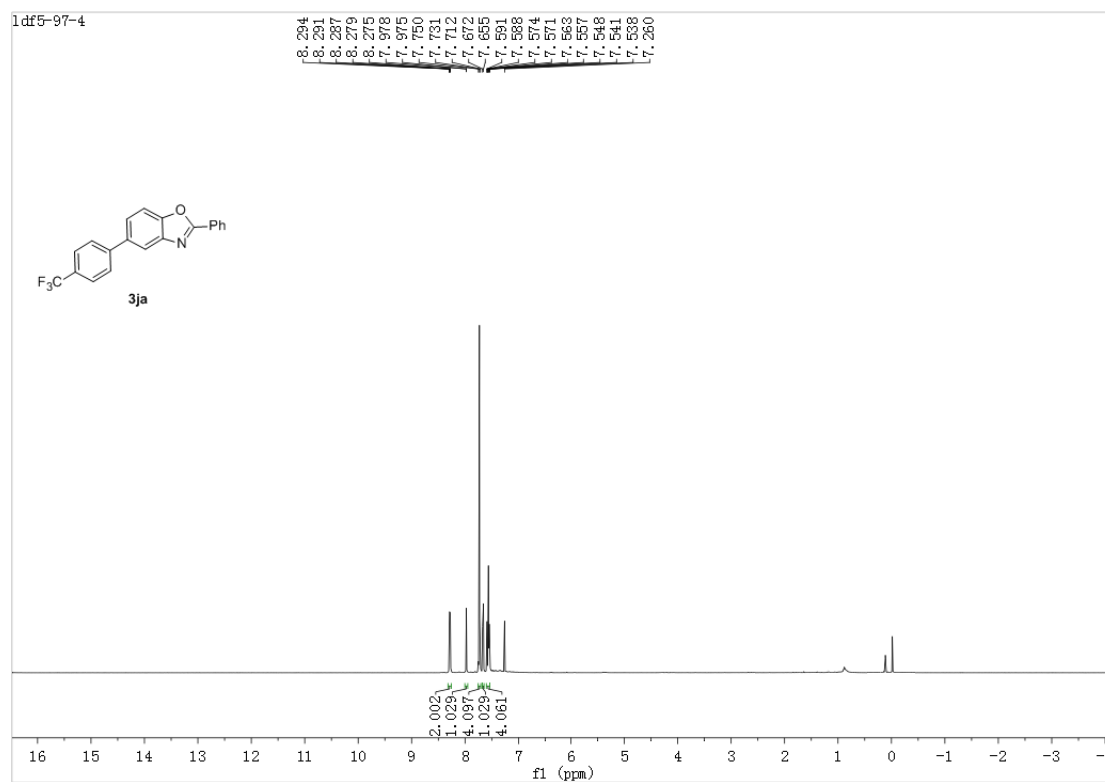
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S15



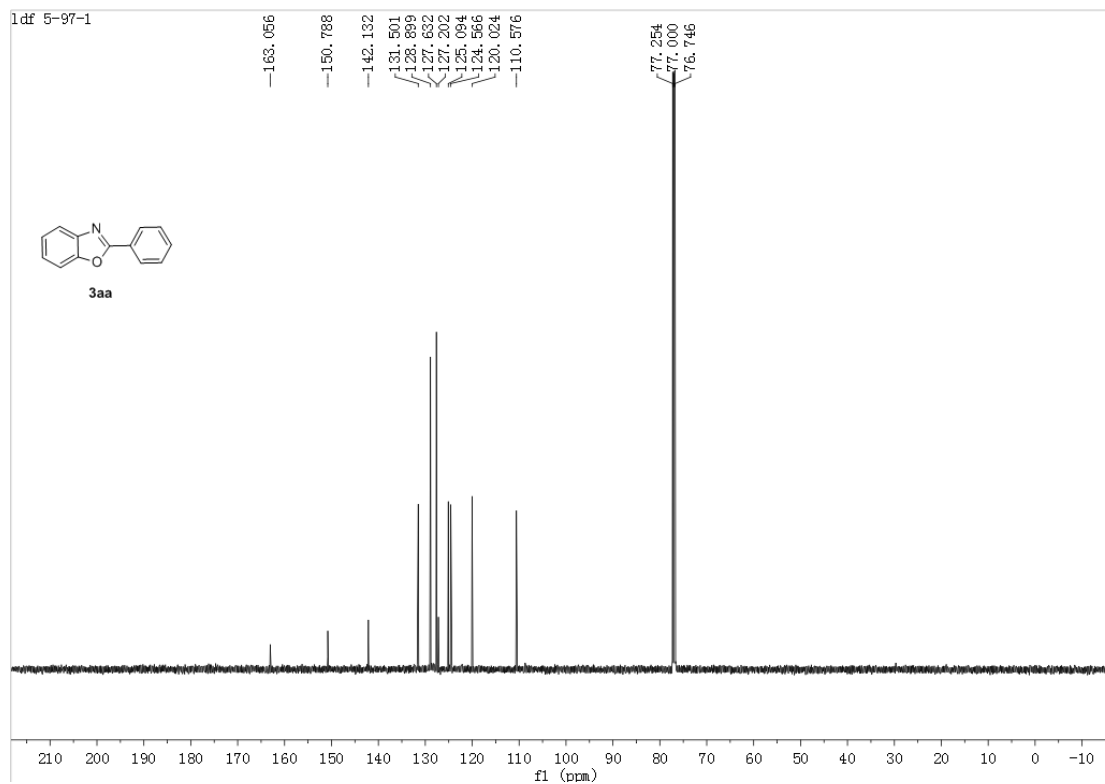
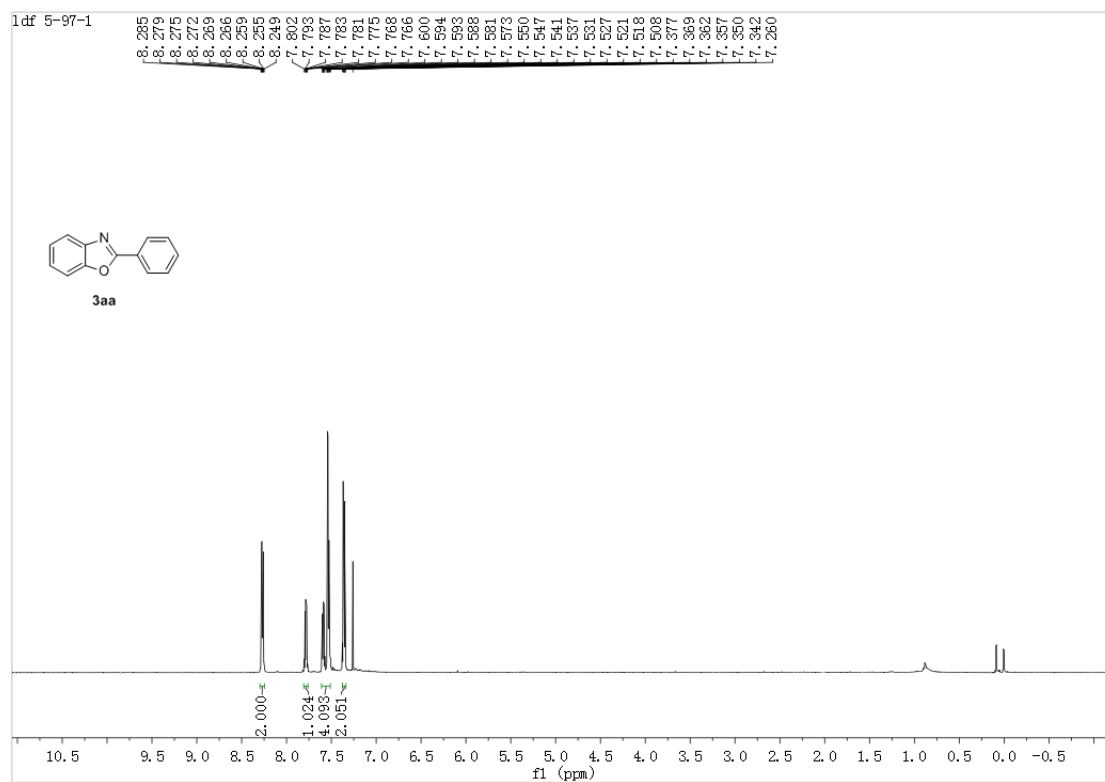
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S16



S16

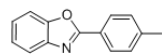
S17



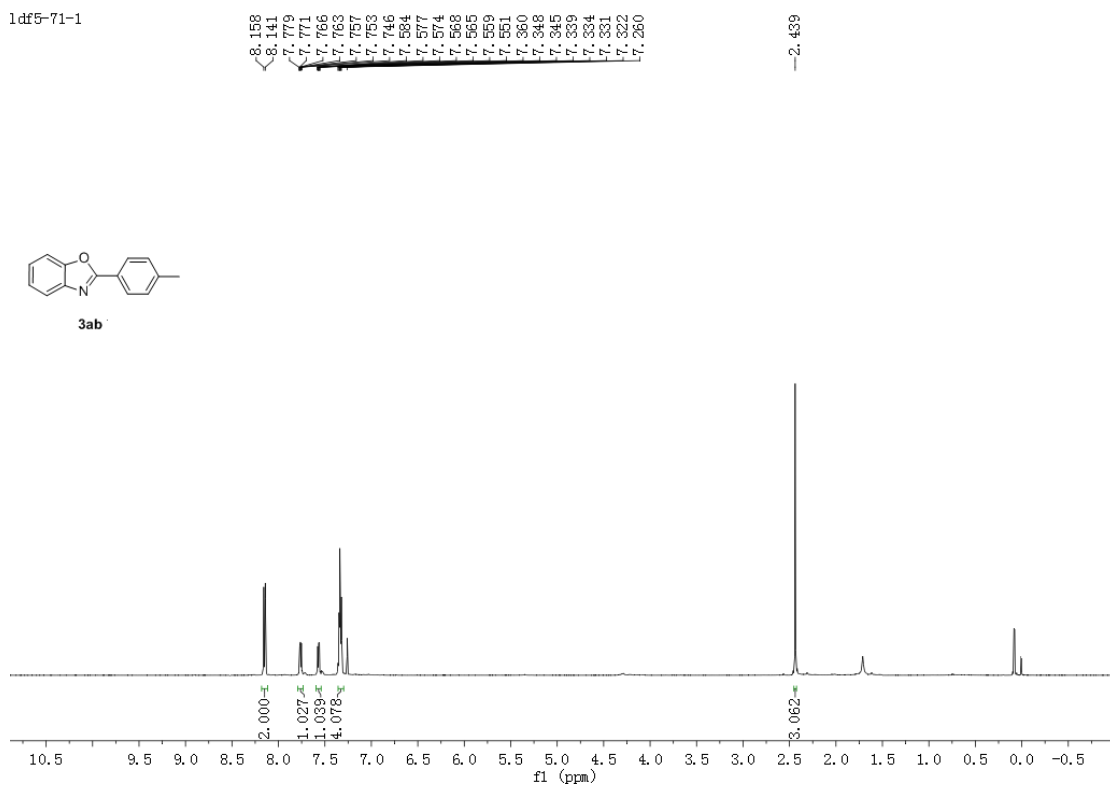
S17

S18

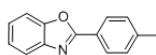
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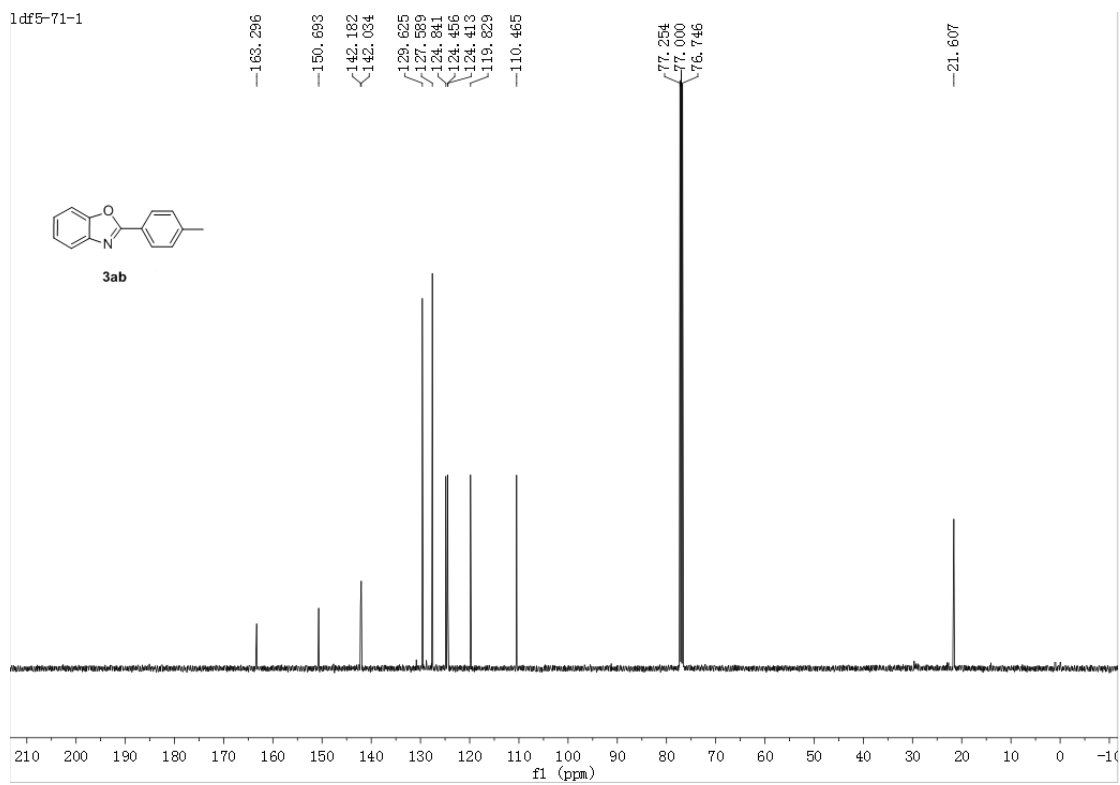
3ab



ldf5-71-1

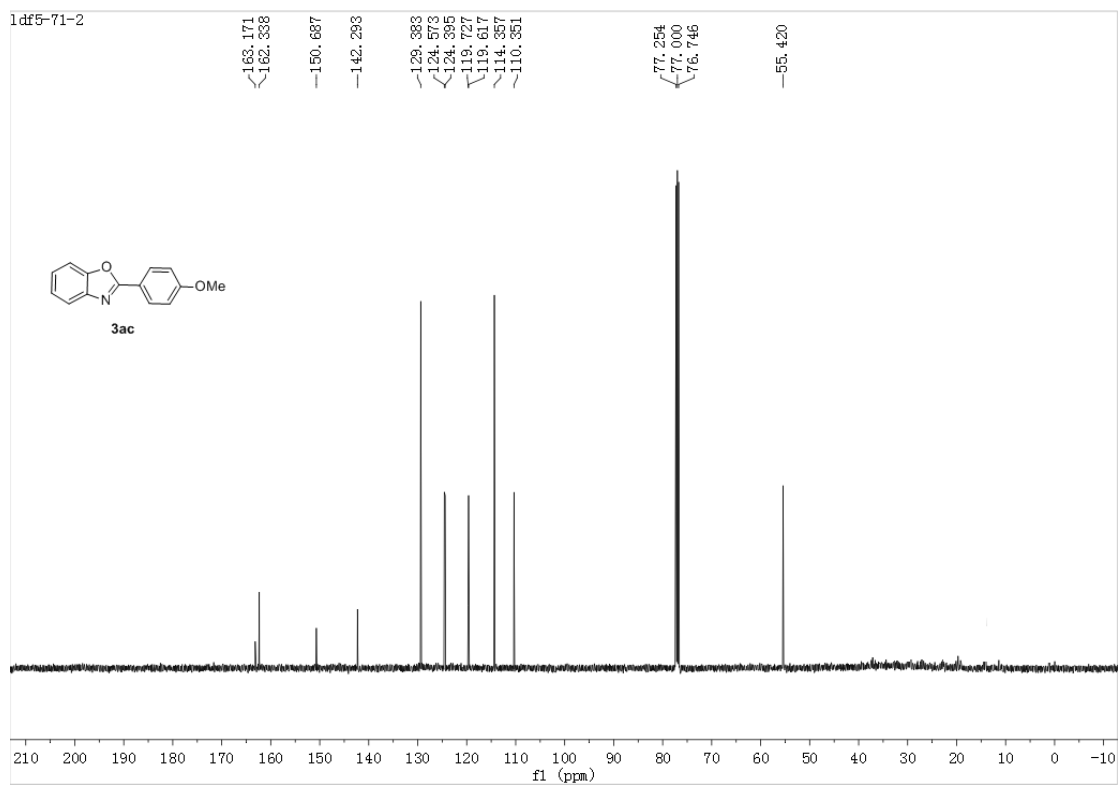
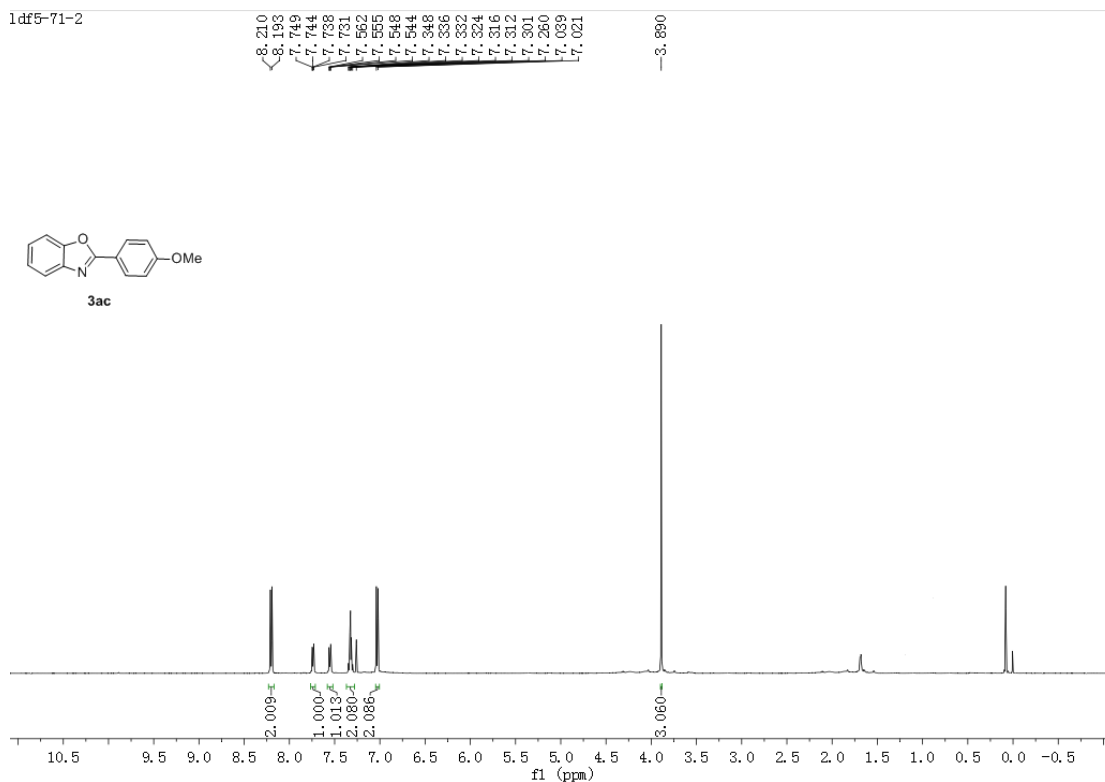


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S18

S19

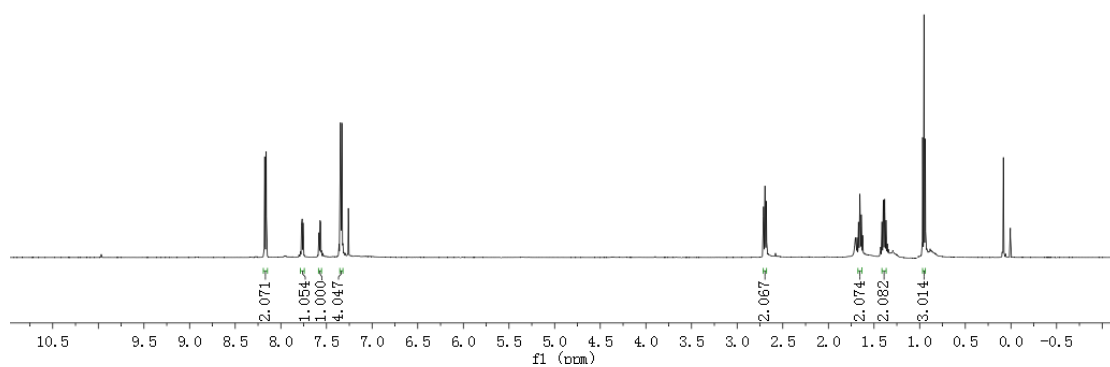
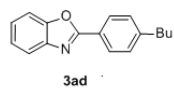


S20

1df5-72-2

8.177
8.160
7.783
7.774
7.769
7.766
7.760
7.756
7.581
7.573
7.572
7.568
7.563
7.555
7.361
7.346
7.342
7.335
7.331
7.321
7.260

2.711
2.695
2.680
1.655
1.640
1.413
1.398
1.383
1.369
1.353
1.338



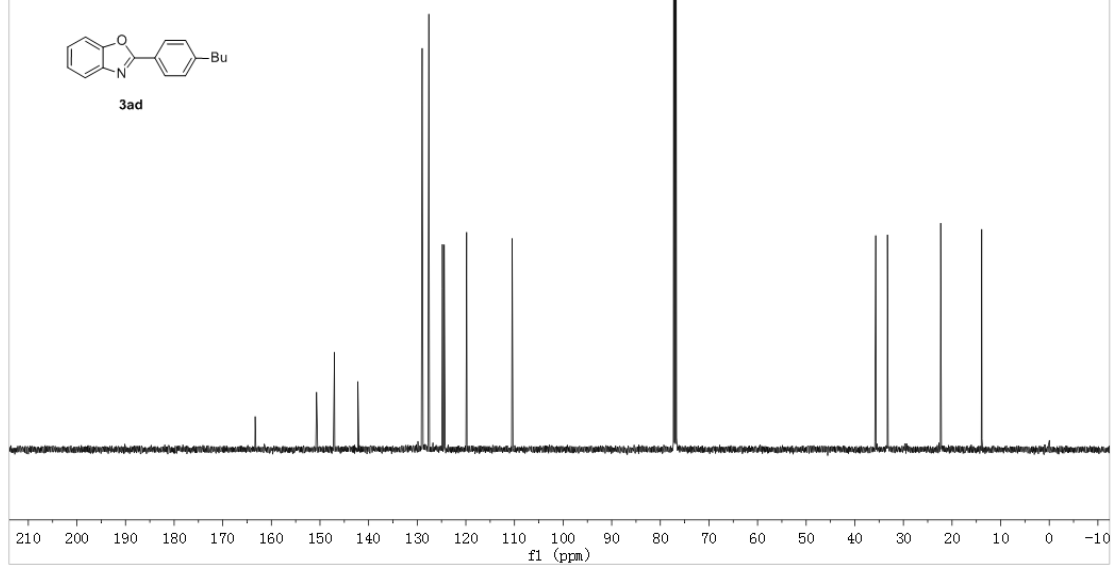
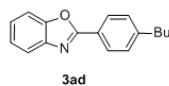
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163.331
150.709
147.023
142.206
128.965
127.617
124.827
124.582
124.447
119.836
110.468

77.254
77.000
76.746

35.695
33.279

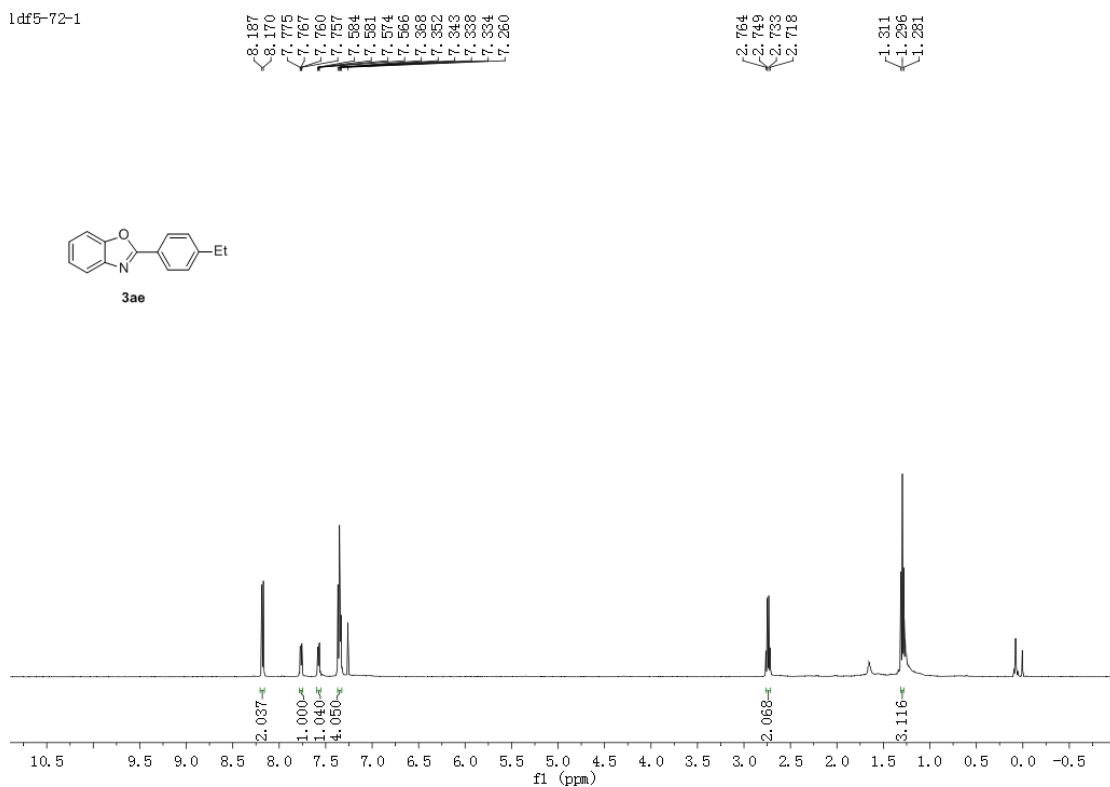
22.330
13.831



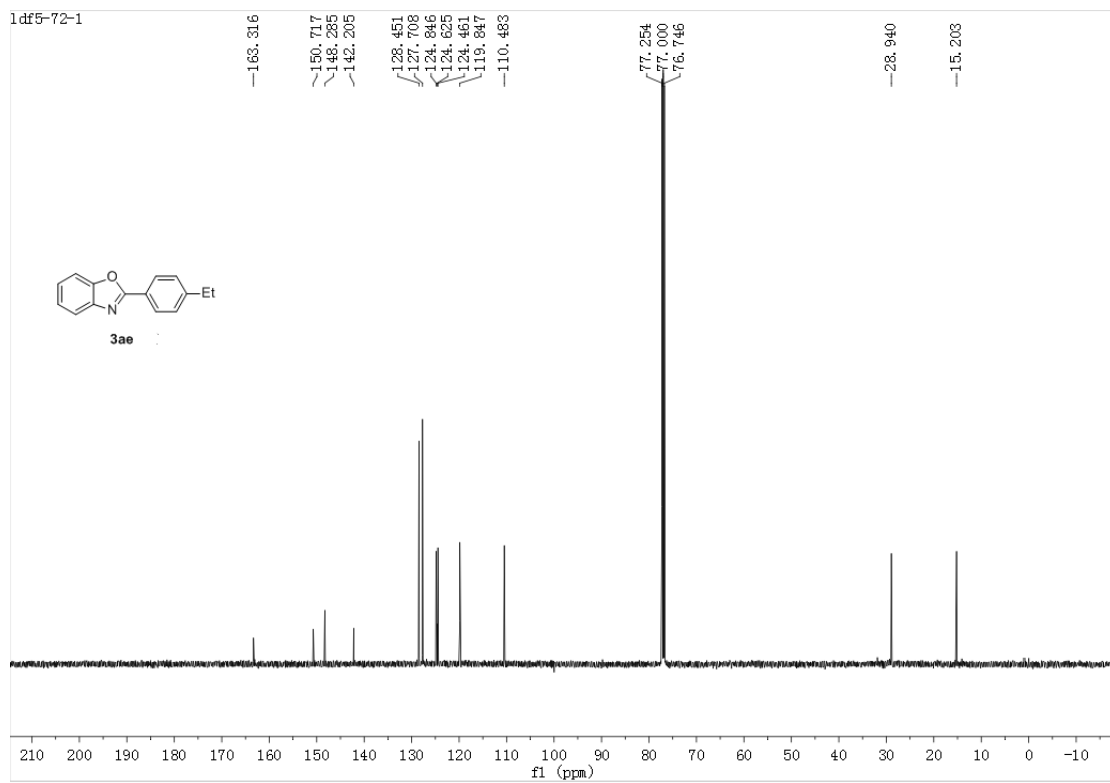
S20

S21

ldf5-72-1

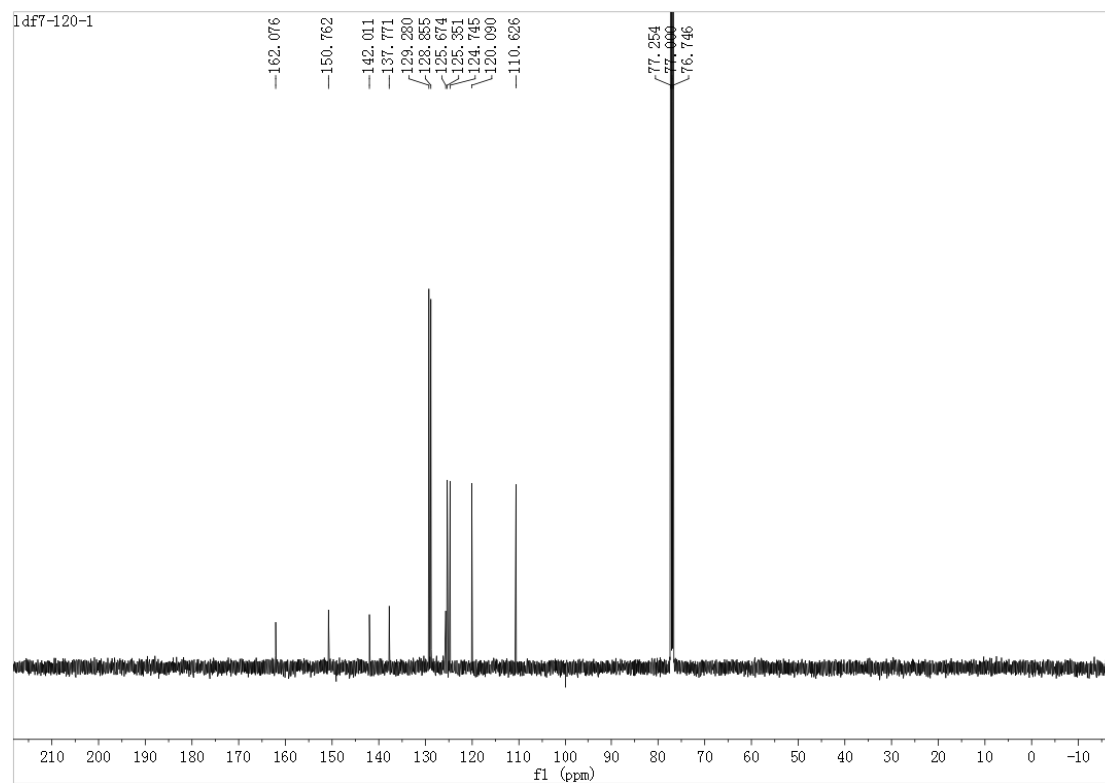
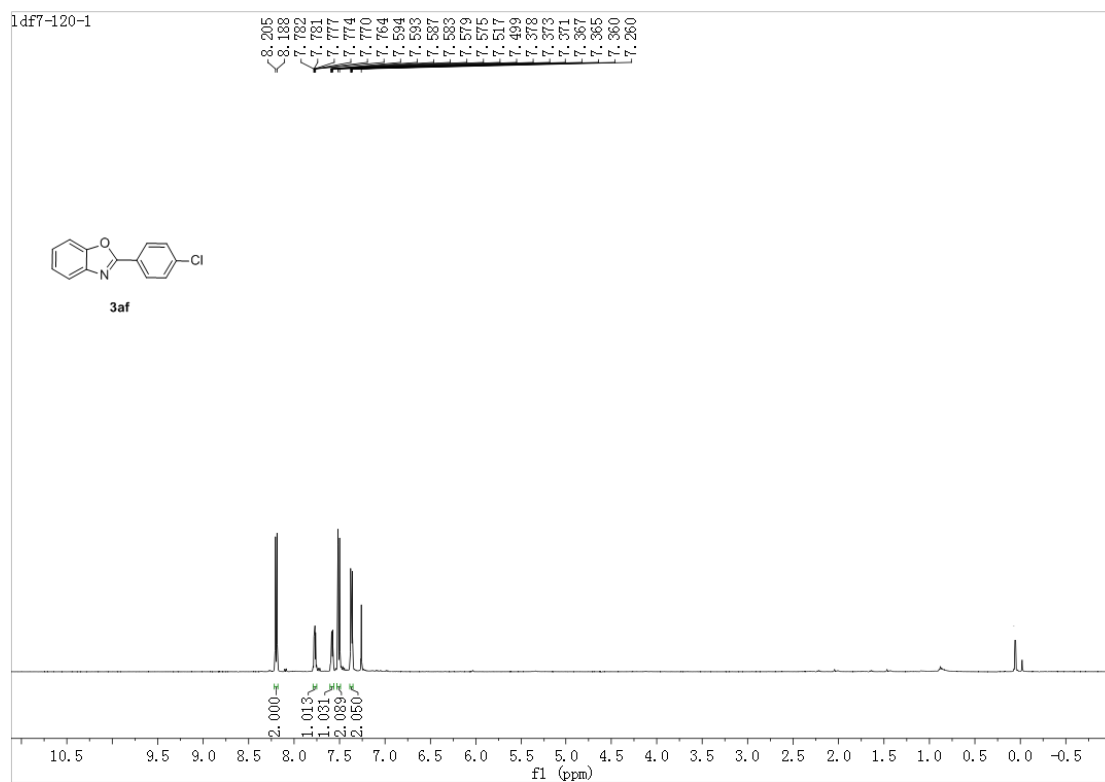


ldf5-72-1



S21

S22



S22