Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Benzo[1,3]oxazines via Copper(I)-catalyzed Cascade Annulation of Nitriles, Aldehydes and Diaryliodonium Salts

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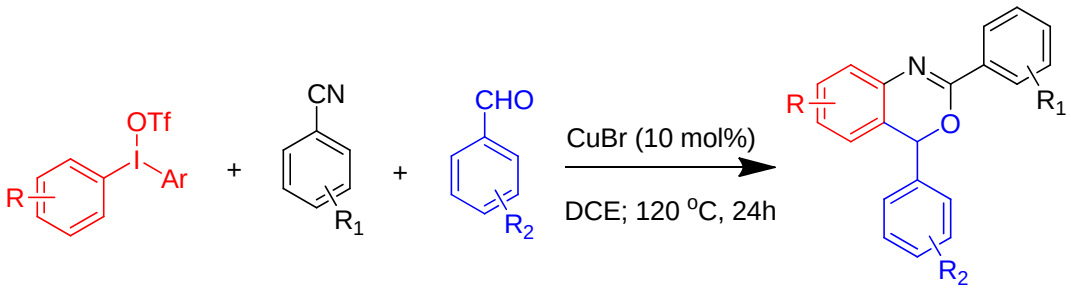
1. General Comments

All the reactions were carried out in pre-dried a screwcapped tube with a Teflon-lined septum under N_2 atmosphere. Diaryliodonium reagents were prepared according to the literatues[1]. All of the solvents were fresh distilled. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL-300MHz or AL-400MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, singlet. Mass spectra were obtained using Bruker Esquire ion trap mass spectrometer in positive mode. The reaction progress was monitored by GC-MS if applicable, using n-Dodecane as internal standard.

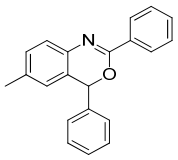
2 Experimental Sections

General procedure for the preparation of desired compound



1 2 3 4

A sealed tube was charged with the mixture of diaryliodonium triflates (0.5 mmol),nitrile (0.5 mmol), aldehyde(0.5 mmol), then stirred in dichloroethane (2.5 mL) at 120 ^{o}C under nitrogen atmosphere for indicated time. After completion, the crude product was diluted with water (5 mL) and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate: 50:1 to 20:1) to obtain the corresponding product.



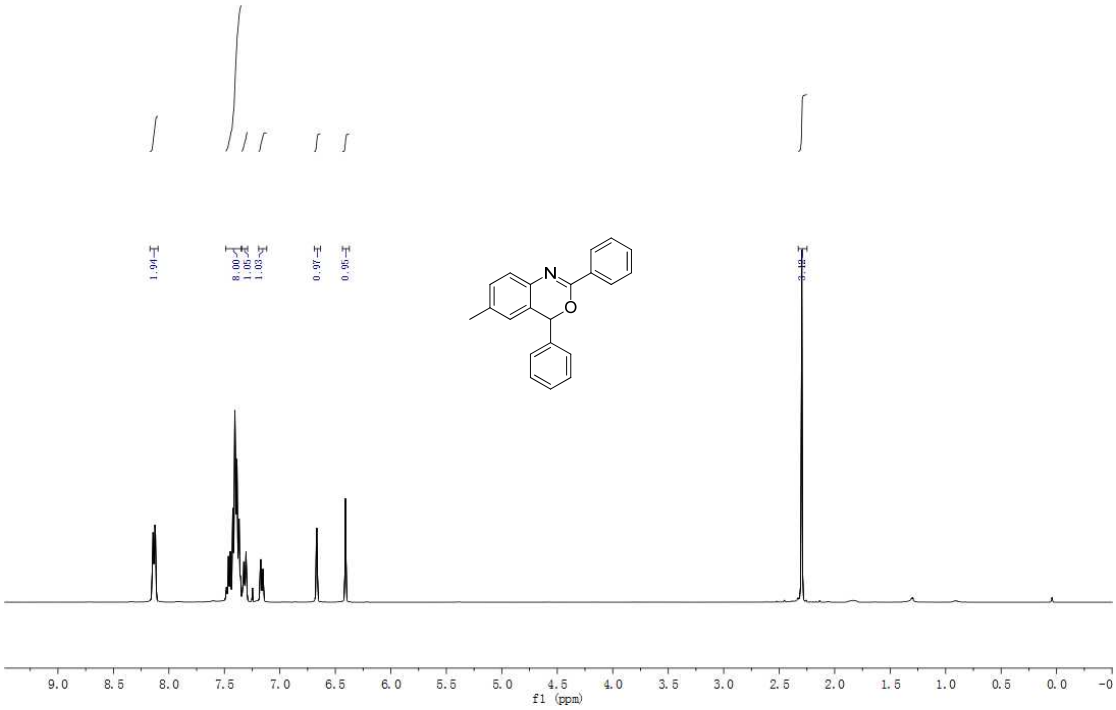
6-methyl-2,4-diphenyl-4H-benzo[d][1,3]oxazine (4aaa): white solid, 121 mg, yield: 81%, melt point: 154^{o}C.

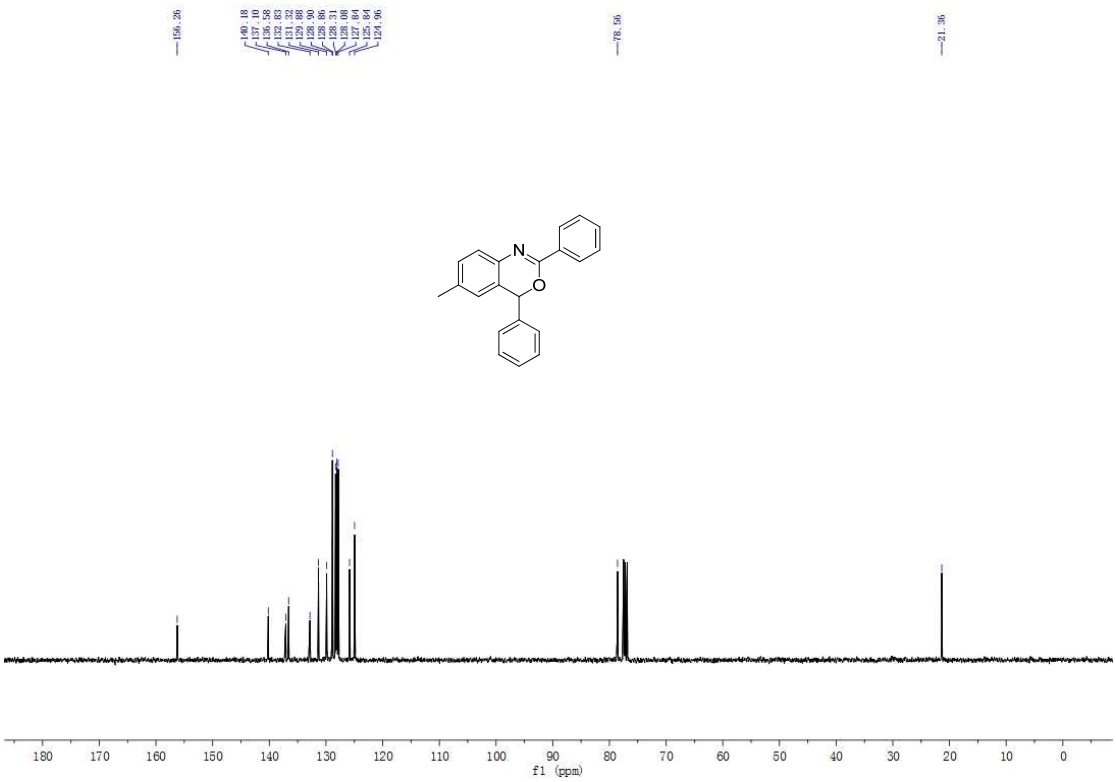
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.17 - 8.10 (m, 2H), 7.49 - 7.35 (m, 8H), 7.34 - 7.29 (m, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.67 (s, 1H), 6.41 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.3, 140.2, 137.1, 136.6, 132.8, 131.3, 129.9, 128.9, 128.9 (2×CH), 128.3(2×CH), 128.1(2×CH), 127.8(2×CH), 125.8, 125.0, 78.6, 21.4.

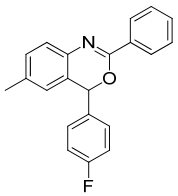
ESI-HRMS: m/z calcd for C21H17NO $[M+H]^{+}$:300.1310; found: 300.1313.

GC-MS：299





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



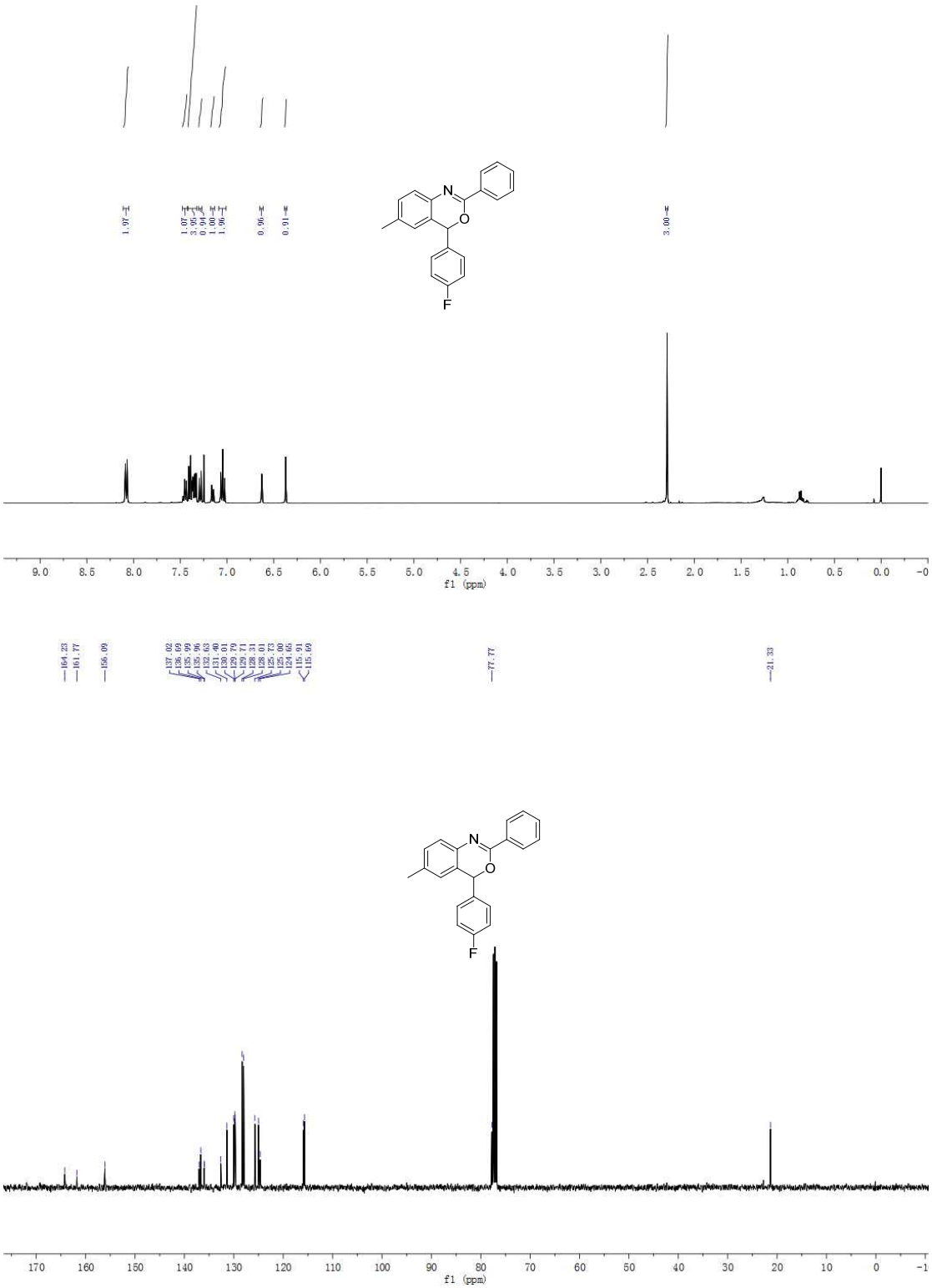
4-(4-fluorophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aab): colorless oil, 143 mg, yield: 90%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.08 (dt, J = 8.6, 1.9 Hz, 2H), 7.45 (ddd, J = 6.1, 3.6, 1.3 Hz, 1H), 7.42 - 7.32 (m, 4H), 7.29 (d, J = 7.9 Hz, 1H), 7.15 (dd, J = 7.9, 1.3 Hz, 1H), 7.09 - 7.01 (m, 2H), 6.63 (s, 1H), 6.37 (s, 1H), 2.29 (s, 3H).

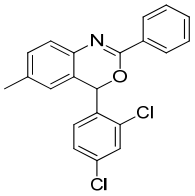
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.5 Hz), 156.1, 137.0, 136.7, 136.0 (d, J = 3.0 Hz), 132.6, 131.4, 130.0, 129.8 (d, J = 8.4 Hz, 2×CH), 128.3(2×CH), 128.0(2×CH), 125.7, 125.0, 124.6, 115.8 (d, J = 21.5 Hz, 2×CH), 77.8, 21.3.

ESI-HRMS: m/z calcd for C21H16FNO $[M+H]^{+}$:318.1216; found:318.1218.

GC-MS：317.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



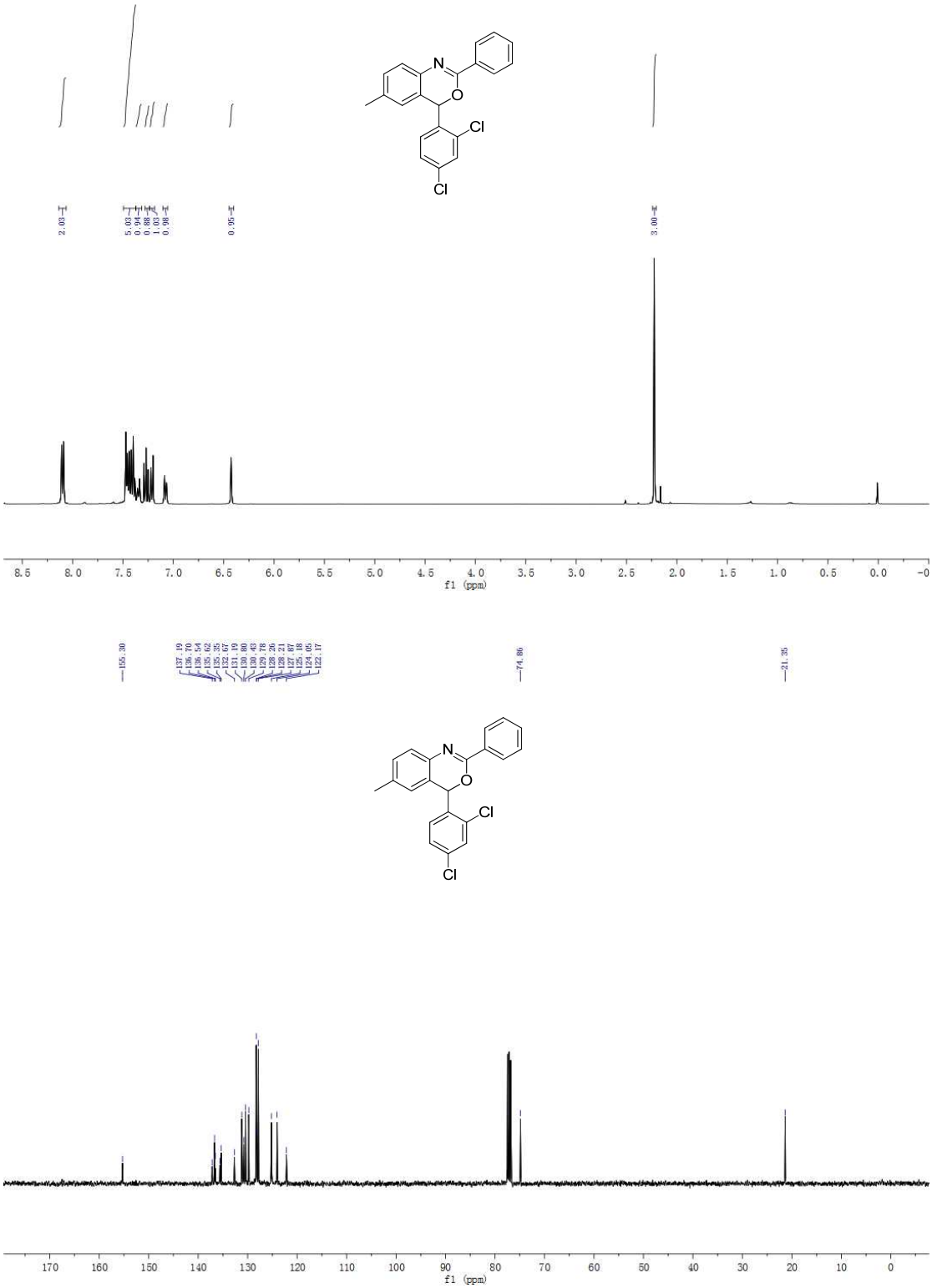
4-(2,4-dichlorophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine(4aac): white solid, 174 mg, yield: 95%, melt point:184 ^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.06 (m, 2H), 7.49 - 7.37 (m, 5H), 7.34 (d, J = 7.8 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.43 (s, 1H), 2.23 (s, 3H).

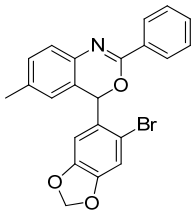
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 155.3, 137.2, 136.7, 136.5, 135.6, 135.4, 132.7, 131.2, 130.8, 130.4, 129.8, 128.3(2×CH), 128.2, 127.9 (2×CH), 125.2, 124.1, 122.2, 74.9, 21.4.

ESI-HRMS: m/z calcd for C21H15ClNO $[M+H]^{+}$:368.0531; found:368.0533.

GC-MS：367.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



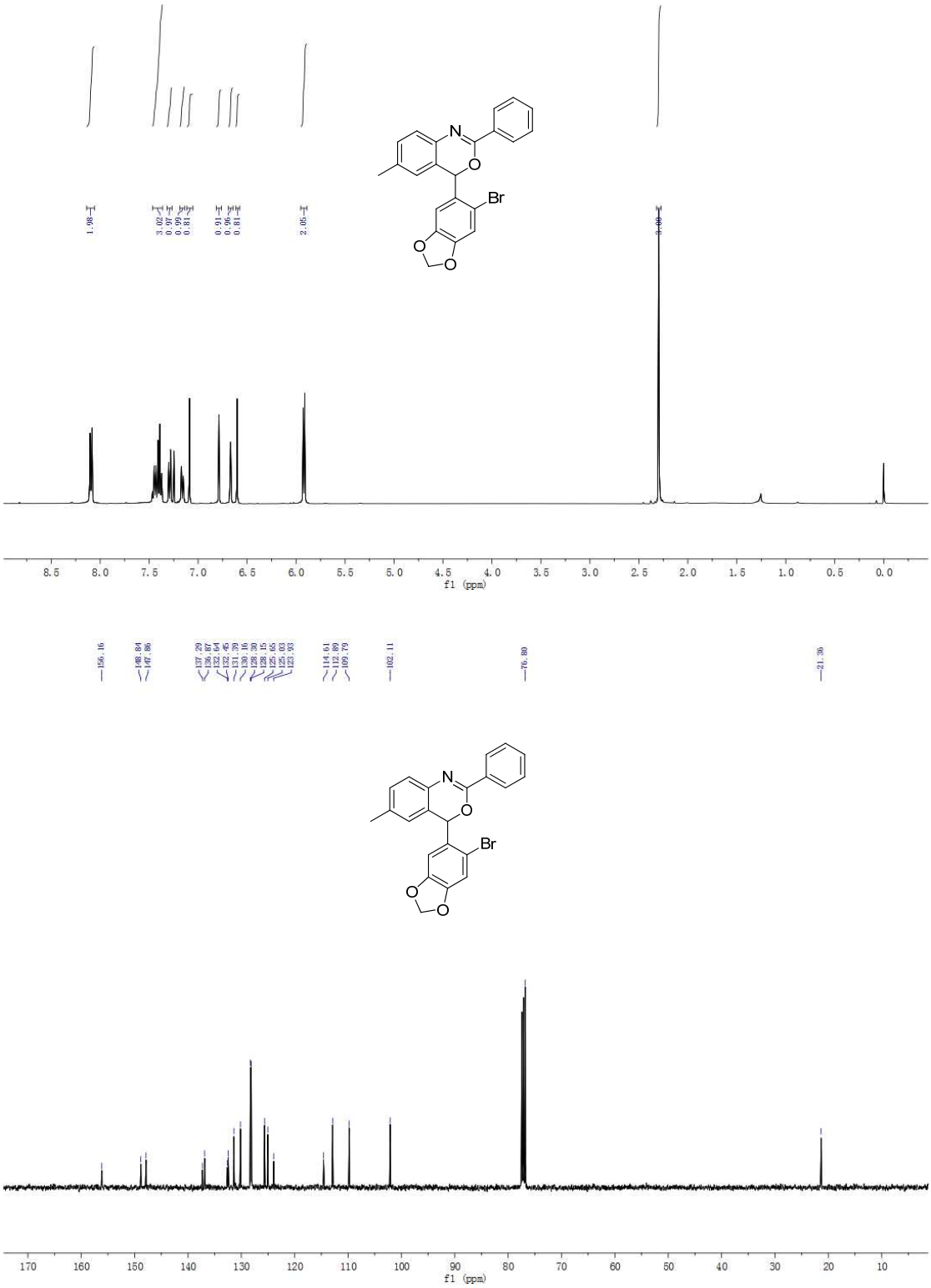
4-(6-bromobenzo[d][1,3]dioxol-5-yl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aad): white solid,160 mg, yield: 76%, melt point: 190^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.06 (m, 2H), 7.46 - 7.36 (m, 3H), 7.29 (d, J = 7.9 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.09 (s, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.67 (s, 1H), 6.60 (s, 1H), 5.95 - 5.89 (m, 2H), 2.30 (s, 3H).

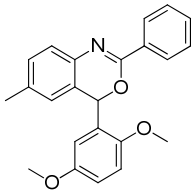
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.2, 148.8, 147.9, 137.3, 136.9, 132.6, 132.5, 131.4, 130.2, 128.3(2×CH), 128.2(2×CH), 125.7, 125.0, 123.9, 114.6, 112.9, 109.8, 102.1, 76.8, 21.4.

ESI-HRMS: m/z calcd for C22H16BrNO $[M+H]^{+}$:422.0314; found:422.0311.

GC-MS：421.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



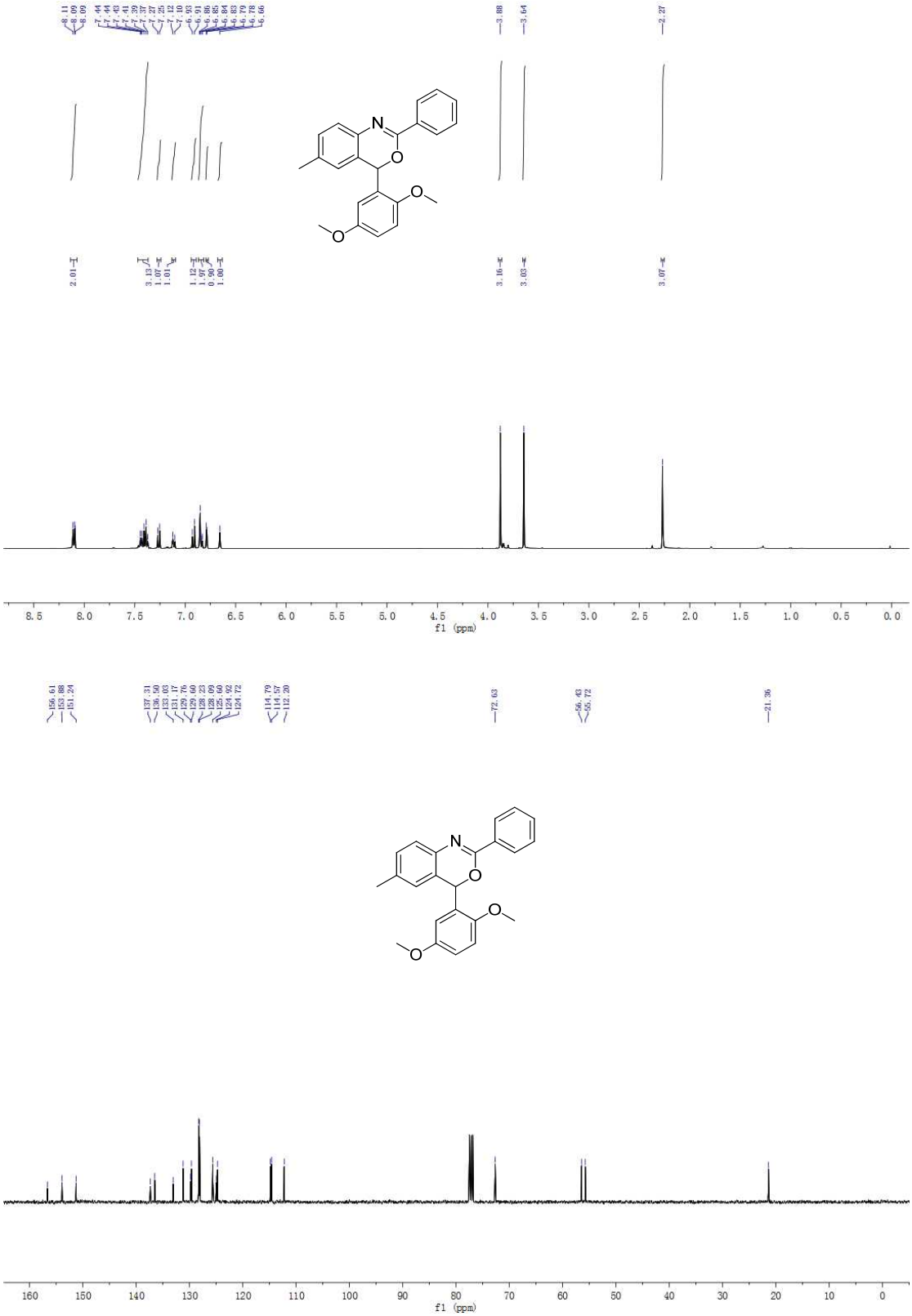
4-(2,5-dimethoxyphenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aae): colorless oil, 93 mg, yield: 54%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.07 (m, 2H), 7.47 - 7.37 (m, 3H), 7.26 (d, J = 7.9 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 6.84 (dd, J = 8.7, 3.1 Hz, 2H), 6.79 (d, J = 3.0 Hz, 1H), 6.66 (s, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 2.27 (s, 3H).

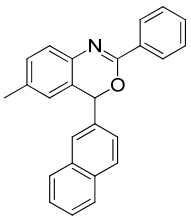
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.6, 153.9, 151.2, 137.3, 136.5, 133.0, 131.2, 129.8, 129.6, 128.2(2×CH), 128.1(2×CH), 125.6, 124.9, 124.7, 114.8, 114.6, 112.2, 72.6, 56.4, 55.7, 21.4.

ESI-HRMS: m/z calcd for C23H21NO3 $[M+H]^{+}$:360.1521; found:360.1522.

GC-MS：359.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



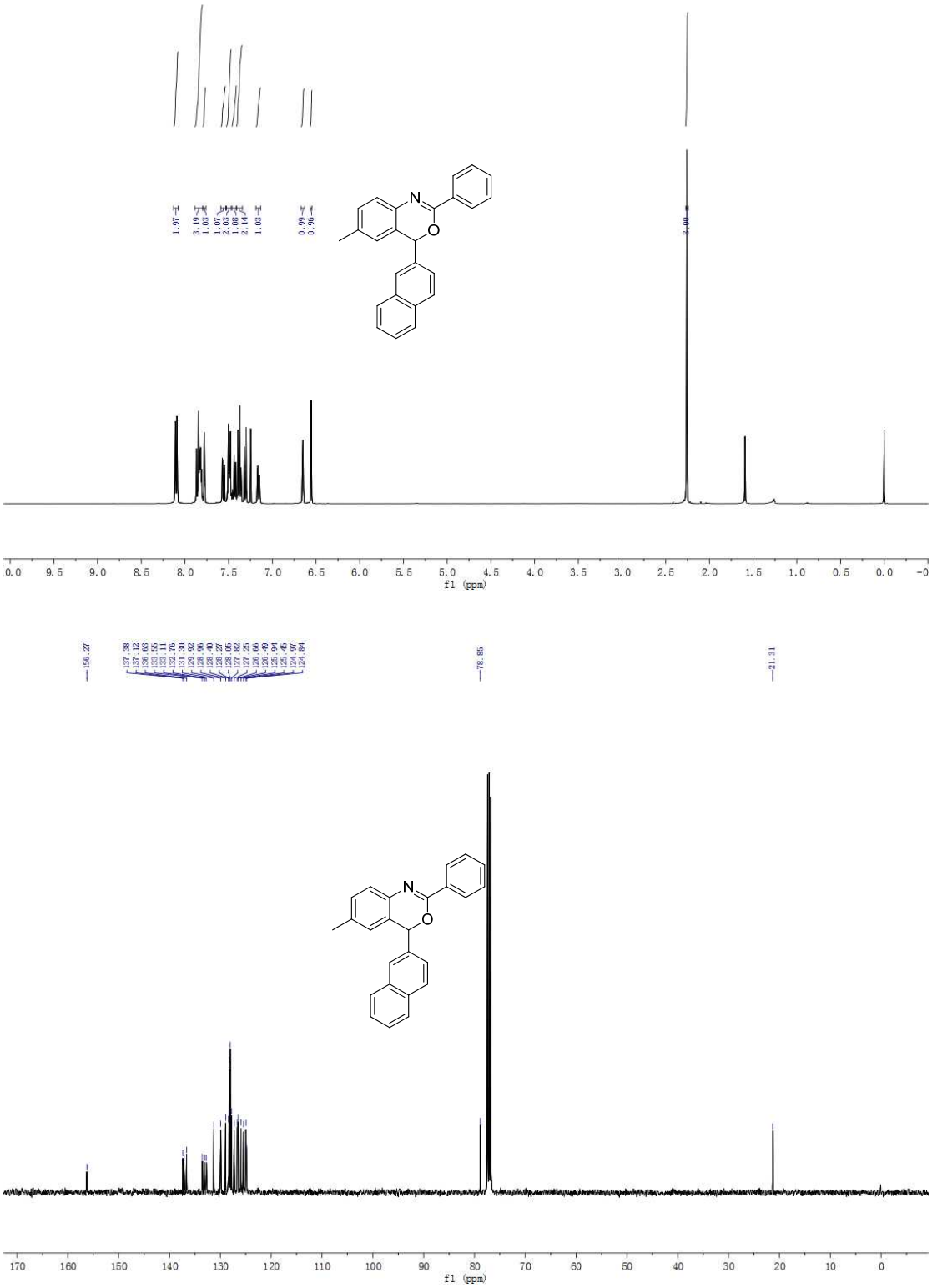
6-methyl-4-(naphthalen-2-yl)-2-phenyl-4H-benzo[d][1,3]oxazine (4aaf): white solid, 98 mg, yield: 56%, melt point:150 ^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.13 - 8.08 (m, 2H), 7.89 - 7.80 (m, 3H), 7.78 (s, 1H), 7.56 (dd, J = 8.5, 1.7 Hz, 1H), 7.53 - 7.47 (m, 2H), 7.46 - 7.41 (m, 1H), 7.38 (t, J = 7.4 Hz, 2H), 7.19 - 7.13 (m, 1H), 6.65 (d, J = 0.6 Hz, 1H), 6.55 (s, 1H), 2.26 (s, 3H).

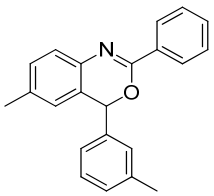
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.3, 137.4, 137.1, 136.6, 133.6, 133.1, 132.8, 131.3, 129.9, 129.0, 128.4, 128.3(2×CH), 128.1(2×CH), 127.8, 127.3, 126.7, 126.5, 125.9, 125.5, 125.0, 124.8, 78.9, 21.3.

ESI-HRMS: m/z calcd for C25H19NO $[M+H]^{+}$:350.1467; found:350.1467.

GC-MS：349.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



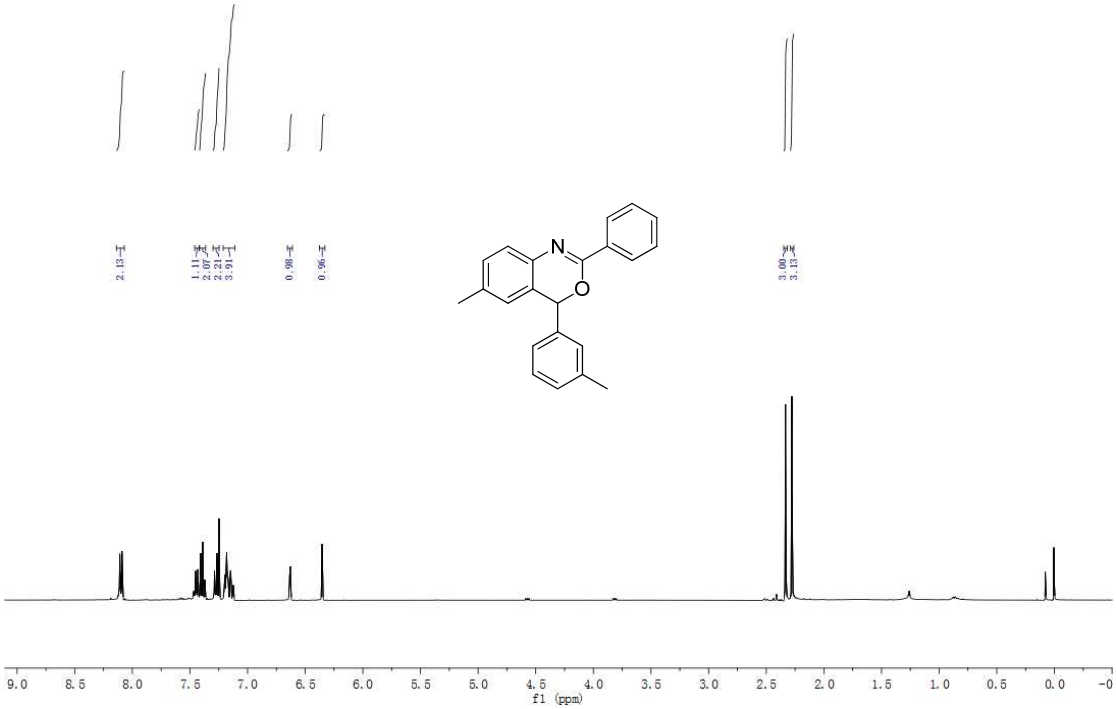
6-methyl-2-phenyl-4-(m-tolyl)-4H-benzo[d][1,3]oxazine (4aag): green oil, 89 mg, yield: 57%.

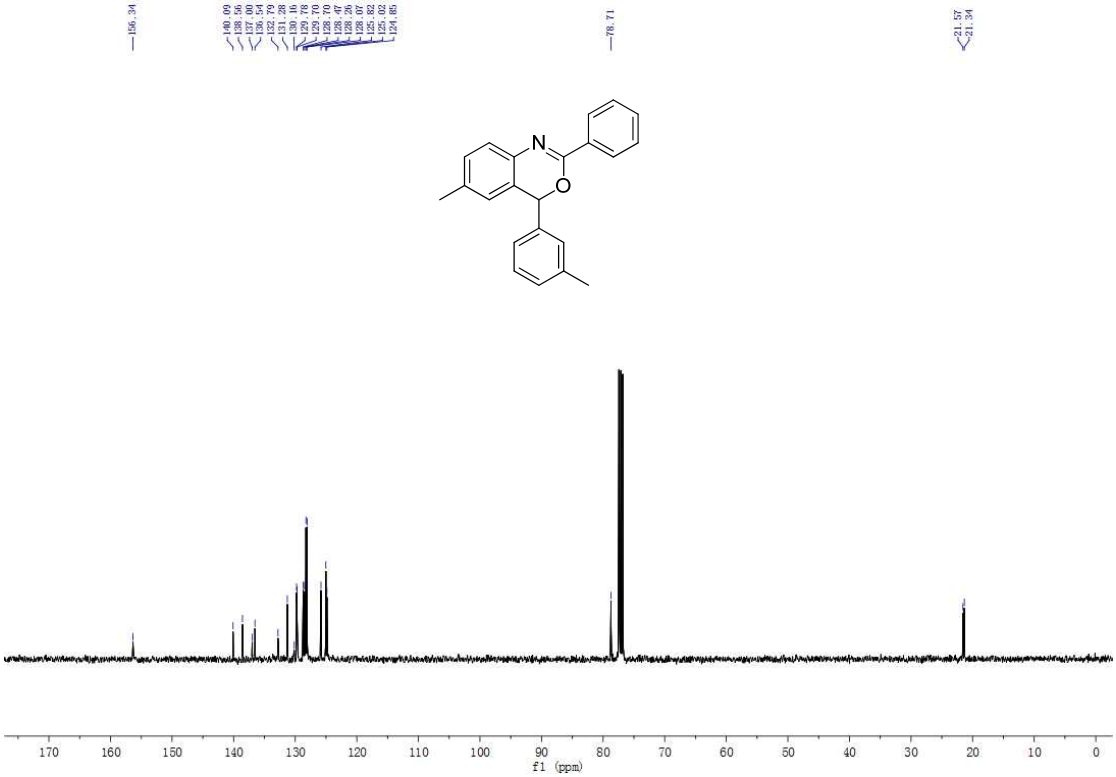
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.07 (m, 2H), 7.44 (dt, J = 2.7, 2.1 Hz, 1H), 7.42 - 7.36 (m, 2H), 7.30 - 7.25 (m, 2H), 7.16 (dt, J = 9.3, 3.8 Hz, 4H), 6.63 (d, J = 1.0 Hz, 1H), 6.35 (s, 1H), 2.33 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.3, 140.1, 138.6, 137.0, 136.5, 132.8, 131.3, 130.2, 129.8, 129.7, 128.7, 128.5, 128.3(2×CH), 128.1(2×CH), 125.8, 125.0, 124.9, 78.7, 21.6, 21.3.

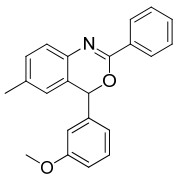
ESI-HRMS: m/z calcd for C22H19NO $[M+H]^{+}$:314.1467; found:314.1465.

GC-MS：313.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



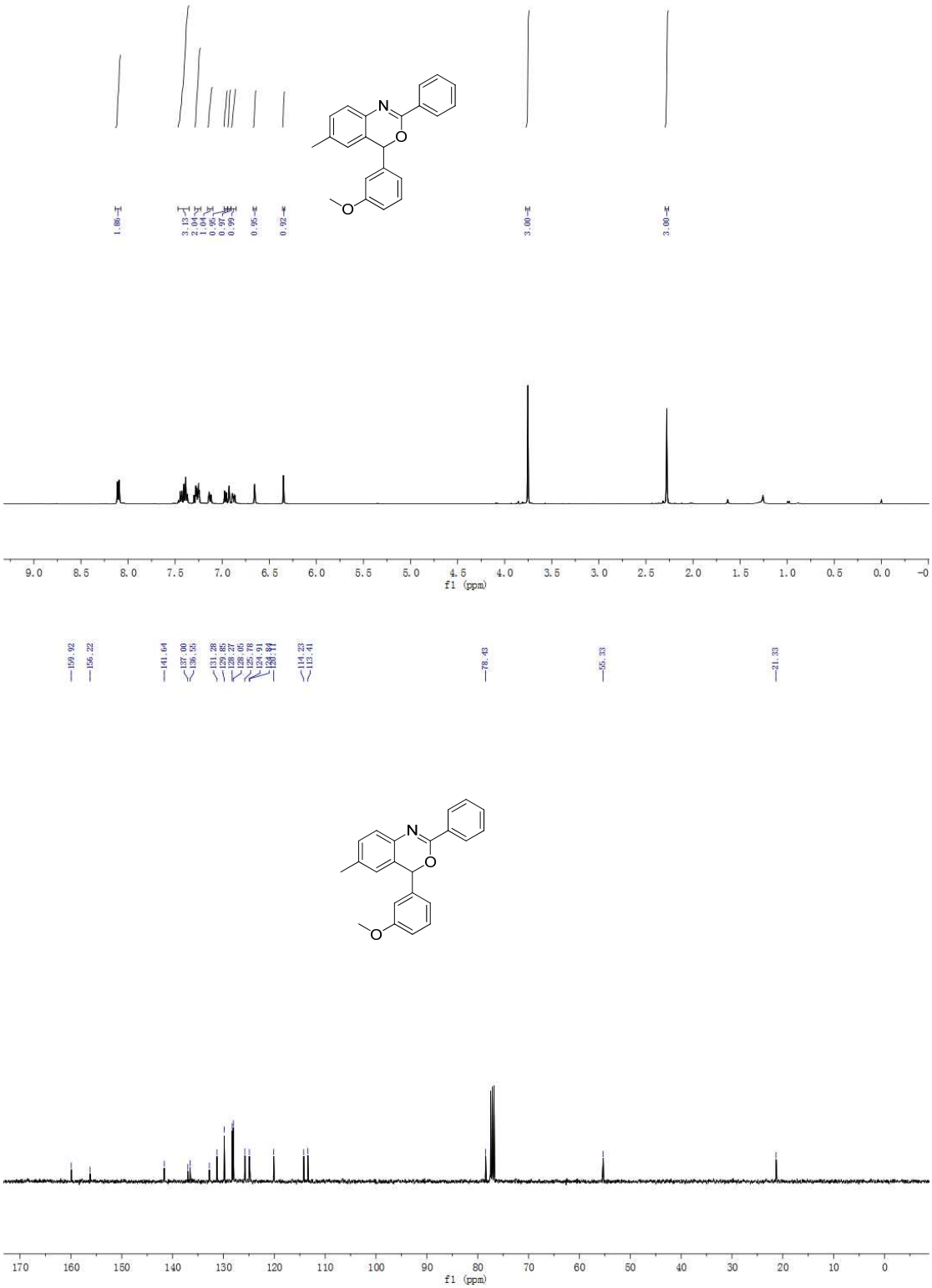
4-(3-methoxyphenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aah): colorless oil, 84 mg, yield: 51%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.10 (d, J = 7.1 Hz, 2H), 7.42 (ddd, J = 23.5, 10.8, 5.7 Hz, 3H), 7.29 - 7.23 (m, 2H), 7.13 (d, J = 7.5 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.93 (s, 1H), 6.88 (dd, J = 8.2, 2.5 Hz, 1H), 6.66 (s, 1H), 6.35 (s, 1H), 3.75 (s, 3H), 2.28 (s, 3H).

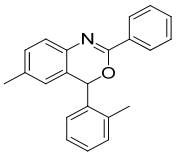
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.9, 156.2, 141.6, 137.0, 136.6, 132. 8, 131.3, 129.9(2×CH), 128.3(2×CH), 128.1(2×CH), 125.8, 124.9, 124.8, 120.1, 114.2, 113.4, 78.4, 55.3, 21.3.

ESI-HRMS: m/z calcd for C22H10NO2 $[M+H]^{+}$:330.1416; found:330.1418.

GC-MS：329.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



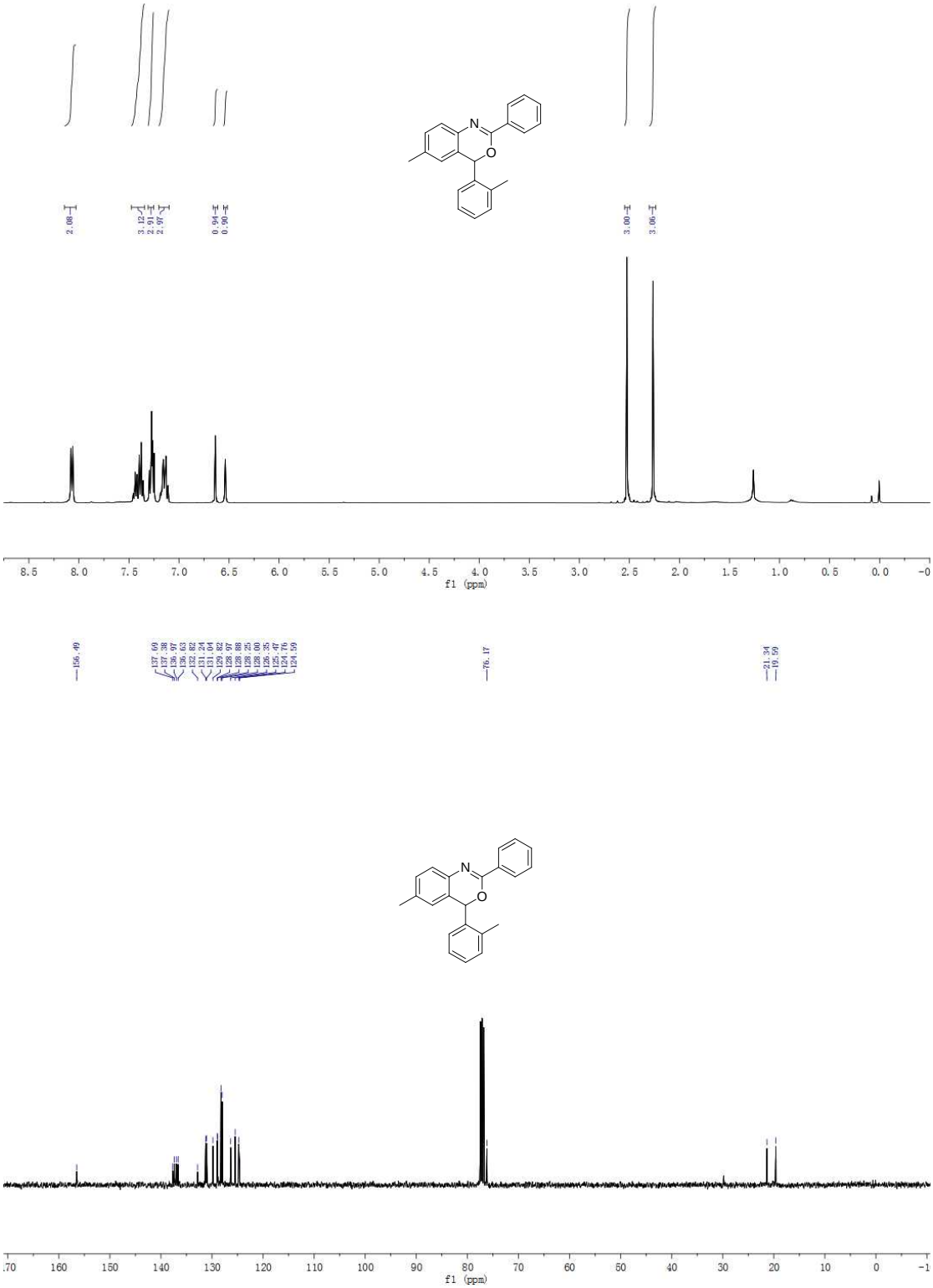
6-methyl-2-phenyl-4-(o-tolyl)-4H-benzo[d][1,3]oxazine (4aai): colorless oil, 94 mg, yield: 60%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.03 (m, 2H), 7.41 (dt, J = 14.8, 7.1 Hz, 3H), 7.28 (t, J = 6.6 Hz, 3H), 7.20 - 7.10 (m, 3H), 6.66 - 6.61 (m, 1H), 6.54 (s, 1H), 2.53 (s, 3H), 2.27 (s, 3H).

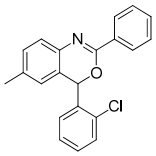
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.5, 137.7, 137.4, 137.0, 136.6, 132.8, 131.2, 131.0, 129.8, 129.0, 128.9, 128.3(2×CH), 128.0(2×CH), 126.4, 125.47, 124.7, 124.6, 76.2, 21.3, 19.6.

ESI-HRMS: m/z calcd for C22H19NO $[M+H]^{+}$:314.1467; found:314.1469.

GC-MS：313.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



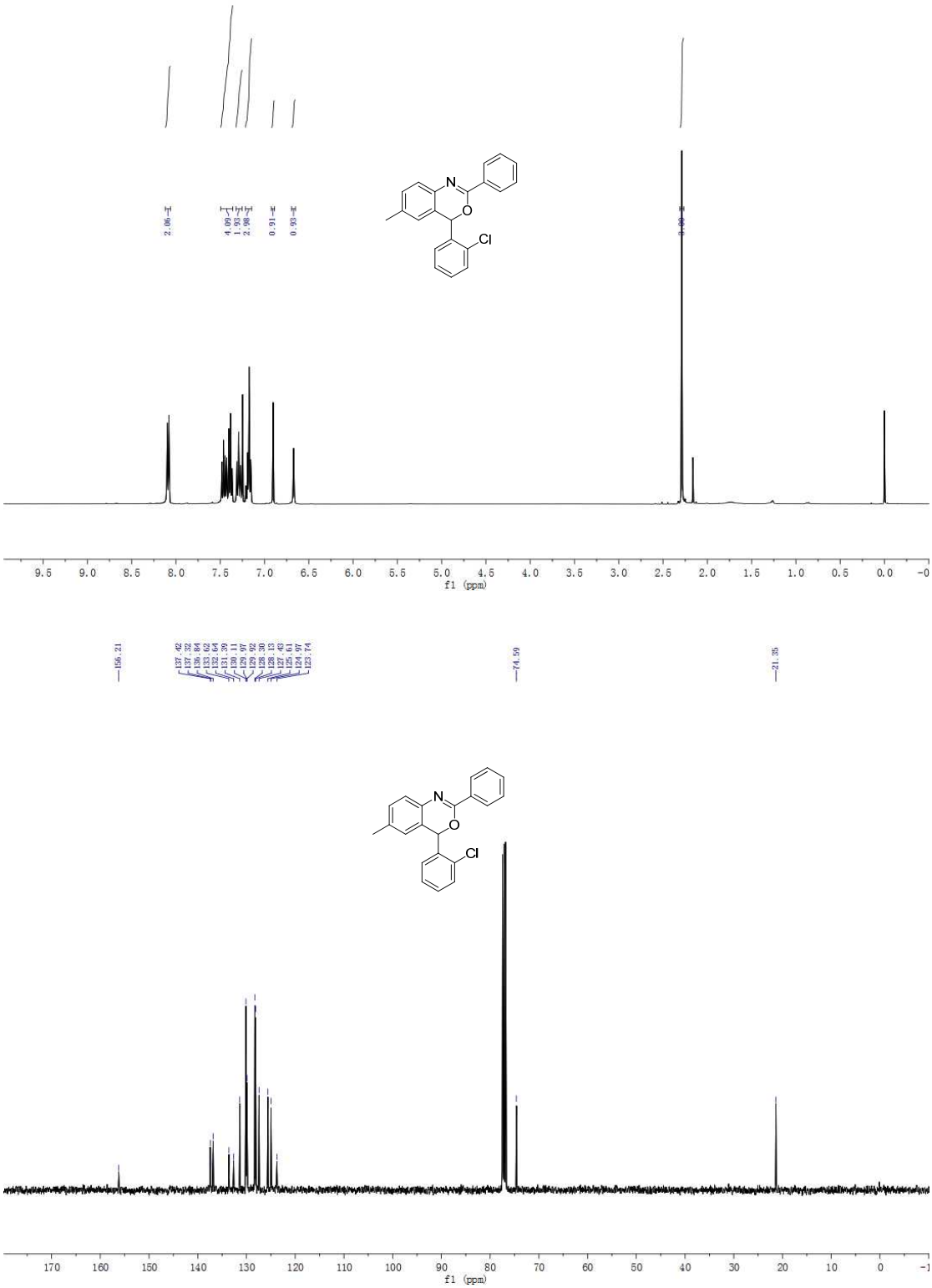
4-(2-chlorophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aaj): white solid, 135 mg, yield: 81%, melt point:123 ^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.12 - 8.06 (m, 2H), 7.50 - 7.36 (m, 4H), 7.32 - 7.25 (m, 2H), 7.22 - 7.15 (m, 3H), 6.90 (s, 1H), 6.67 (s, 1H), 2.29 (s, 3H).

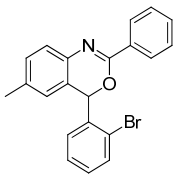
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.2, 137.4, 137.3, 136.8, 133.6, 132.6, 131.4, 130.1(2×CH), 130.0, 129.9, 128.3(2×CH), 128.1(2×CH), 127.4, 125.6, 125.0, 123.7, 74.6, 21.4.

ESI-HRMS: m/z calcd for C21H16ClNO $[M+H]^{+}$:334.0920; found:334.0919.

GC-MS：333.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



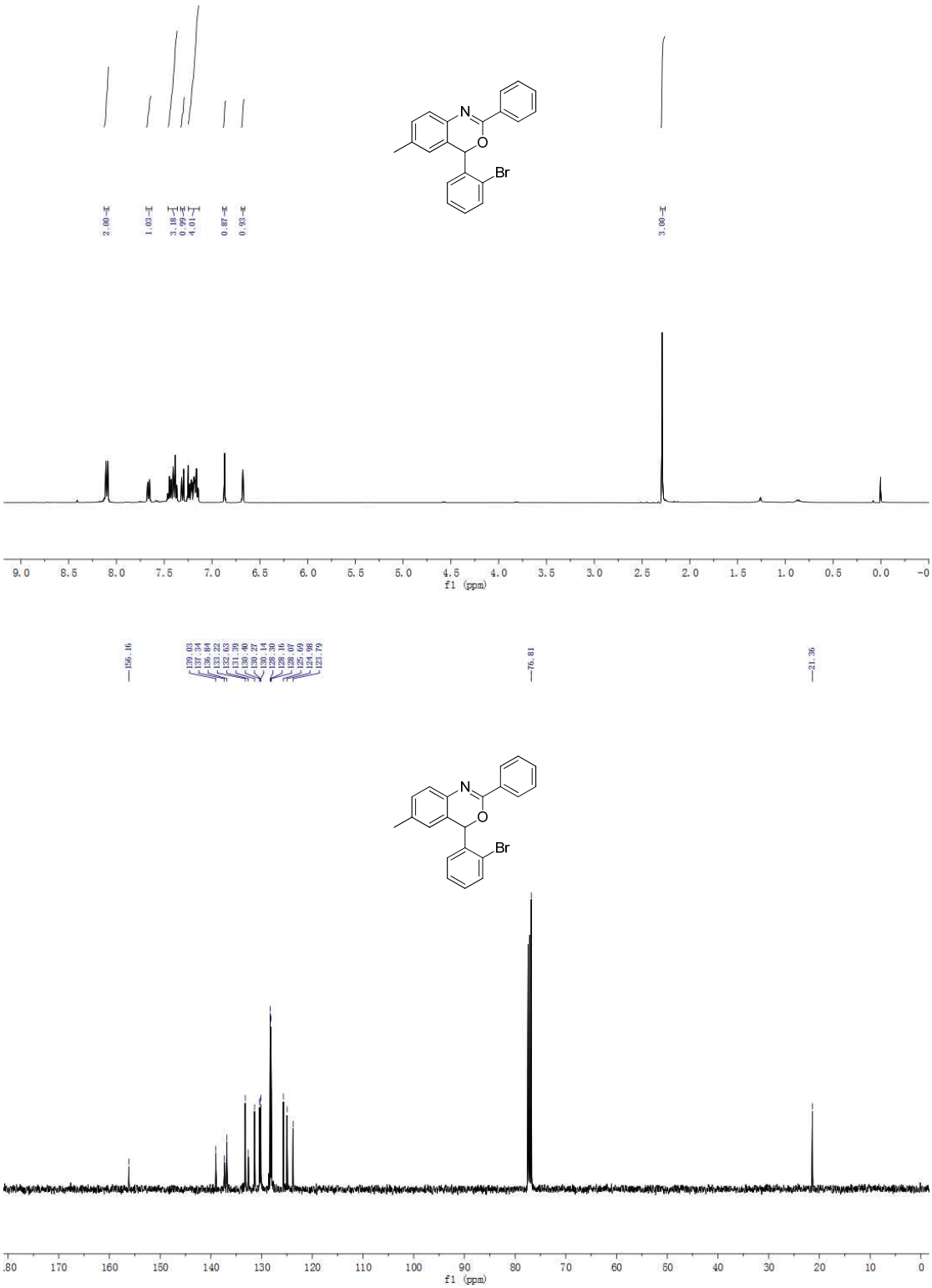
4-(2-bromophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aak): colorless oil, 114 mg, yield: 61%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.10 (dd, J = 11.3, 4.2 Hz, 2H), 7.69 - 7.63 (m, 1H), 7.46 - 7.36 (m, 3H), 7.31 (d, J = 8.0 Hz, 1H), 7.25 - 7.13 (m, 4H), 6.87 (s, 1H), 6.68 (s, 1H), 2.29 (s, 3H).

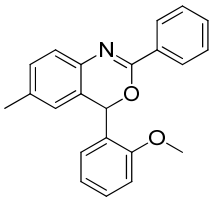
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.2, 139.0, 137.3, 136.8, 133.2, 132.6, 131.4, 130.4, 130.3, 130.1, 128.3(2×CH), 128.2(2×CH), 128.1, 125.7, 125.0, 123.8, 76.8, 21.4.

ESI-HRMS: m/z calcd for C21H16BrNO $[M+H]^{+}$:378.0415; found:378.0420.

GC-MS：377.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



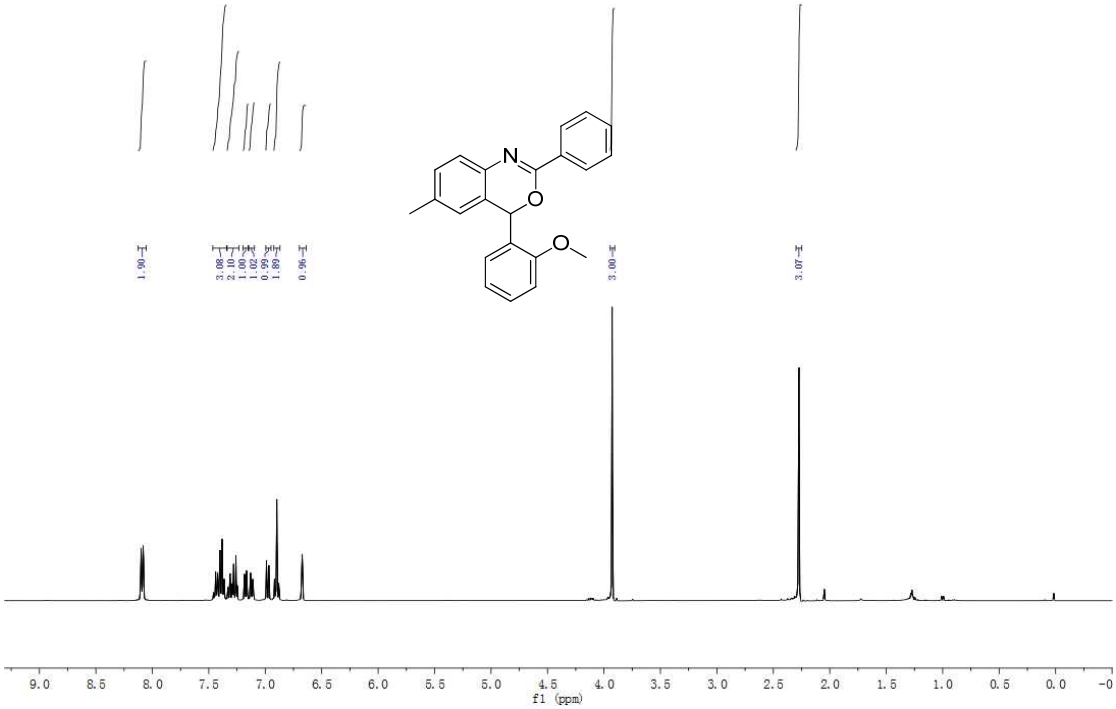
4-(2-methoxyphenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aal): colorless oil, 122 mg, yield: 74%.

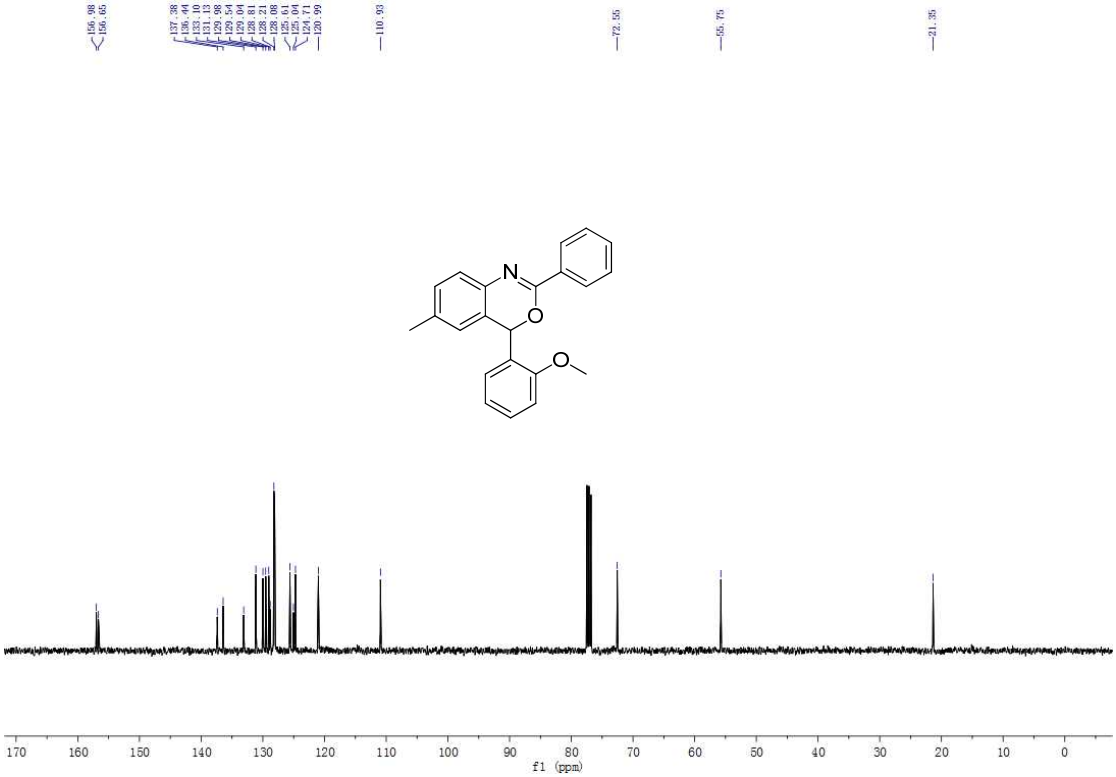
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.12 – 8.05 (m, 2H), 7.46 - 7.34 (m, 3H), 7.34 - 7.23 (m, 2H), 7.17 (dd, J = 7.6, 1.1 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.92 - 6.87 (m, 2H), 6.67 (s, 1H), 3.93 (s, 3H), 2.27 (s, 3H).

^{13}C (101 MHz, CHLOROFORM-D) δ 157.0, 156.7, 137.4, 136.4, 133.1, 131.1, 130.0, 129.5, 129.0, 128.8, 128.2(2×CH), 128.1(2×CH), 125.6, 125.0, 124.7, 121.0, 110.9, 72.6, 55.8, 21.4.

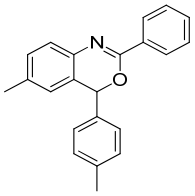
ESI-HRMS: m/z calcd for C22H19NO2 $[M+H]^{+}$:330.1416; found:330.1419.

GC-MS：329.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



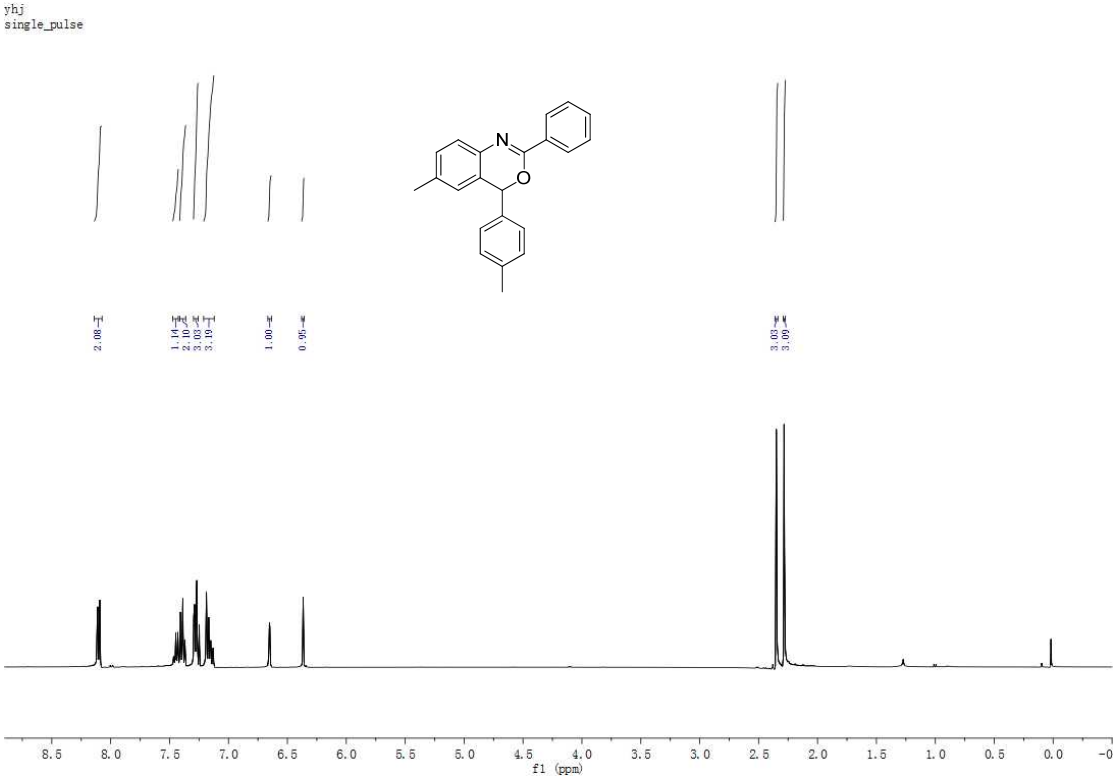
6-methyl-2-phenyl-4-(p-tolyl)-4H-benzo[d][1,3]oxazine (4aam): colorless oil, 95.5 mg, yield: 61%.

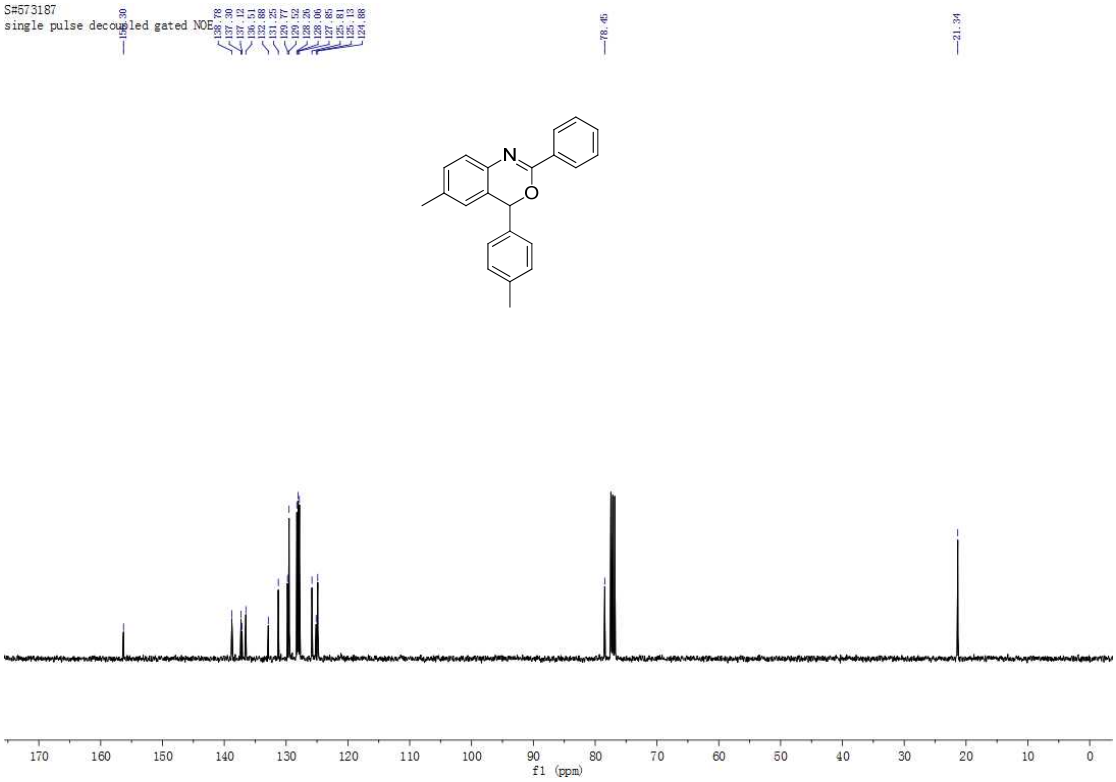
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.14 - 8.07 (m, 2H), 7.45 (ddd, J = 6.0, 3.5, 1.3 Hz, 1H), 7.41 - 7.36 (m, 2H), 7.28 (dd, J = 8.1, 2.5 Hz, 3H), 7.21 - 7.12 (m, 3H), 6.65 (s, 1H), 6.37 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.3, 138.8, 137.3, 137.1, 136.5, 132.9, 131.3, 129.8, 129.5 (2×CH), 128.3(2×CH), 128.1(2×CH), 127.9(2×CH), 125.8, 125.13, 124.9, 78.5, 21.3.

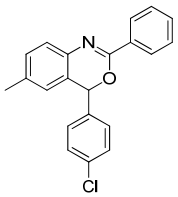
ESI-HRMS: m/z calcd for C22H19NO $[M+H]^{+}$:314.1467; found:314.1466.

GC-MS：313.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



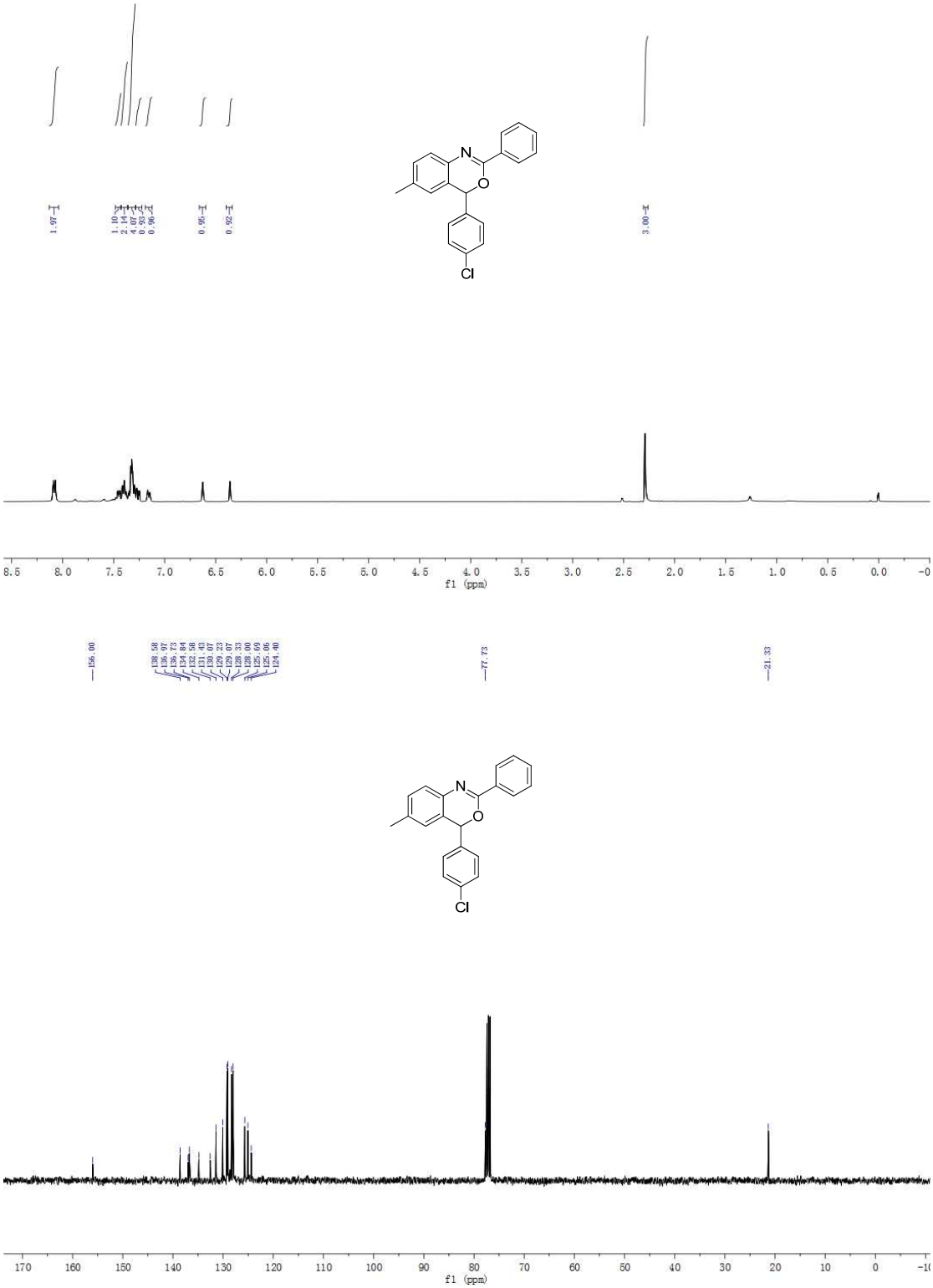
4-(4-chlorophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aan): yellow oil, 113 mg, yield: 68%.

^{1}H NMR(400 MHz, CHLOROFORM-D) δ 8.13 – 8.04 (m, 2H), 7.48 - 7.43 (m, 1H), 7.43 - 7.36 (m, 2H), 7.36 - 7.29 (m, 4H), 7.26 (dd, J = 9.3, 2.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.63 (s, 1H), 6.36 (d, J = 2.2 Hz, 1H), 2.29 (d, J = 2.4 Hz, 3H).

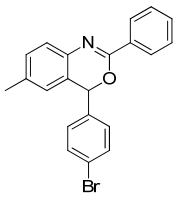
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.0, 138.6, 137.0, 136.7, 134.8, 132.6, 131.4, 130.1, 129.2(2×CH), 129.1(2×CH), 128.3(2×CH), 128.0(2×CH), 125.7, 125.1, 124.4, 77.7, 21.3.

ESI-HRMS: m/z calcd for C21H16ClNO $[M+H]^{+}$:334.0920; found:334.0921.

GC-MS：333.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



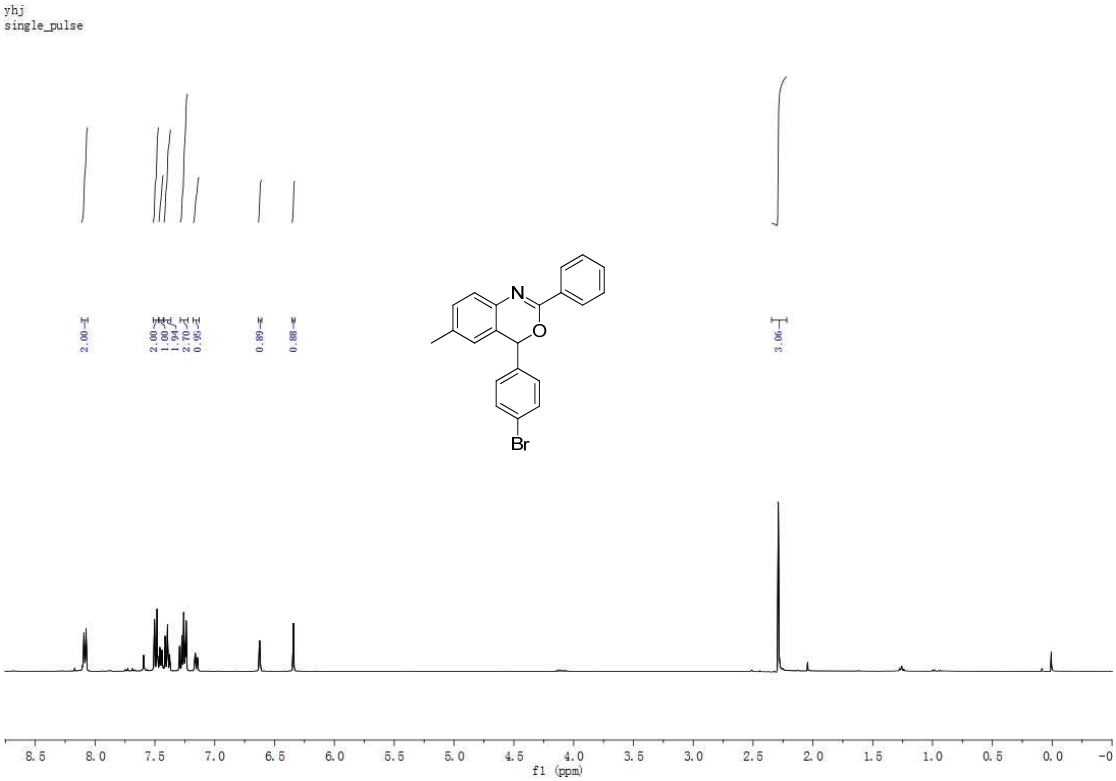
4-(4-bromophenyl)-6-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4aao): white solid, 117 mg, yield: 62%, melt point: 120^{o}C.

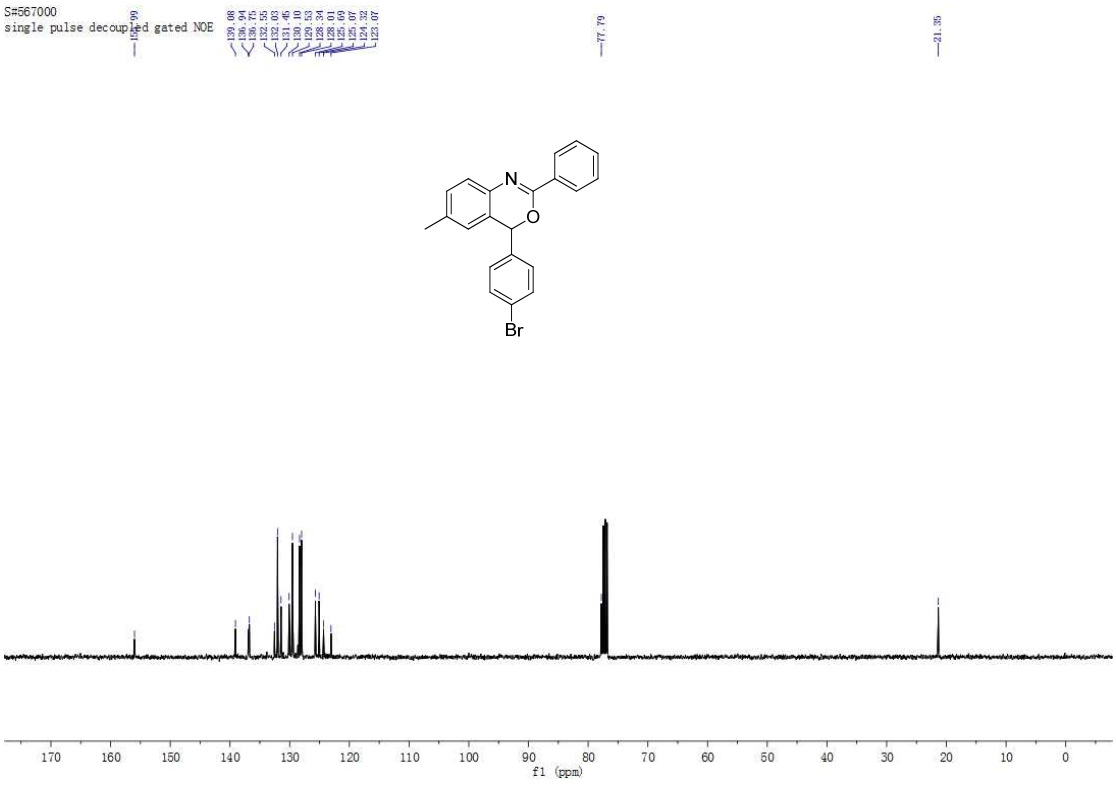
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.08 (dd, J = 5.3, 3.3 Hz, 2H), 7.51 - 7.47 (m, 2H), 7.47 - 7.43 (m, 1H), 7.39 (dd, J = 10.2, 4.6 Hz, 2H), 7.30 - 7.22 (m, 3H), 7.18 - 7.13 (m, 1H), 6.62 (s, 1H), 6.34 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.0, 139.1, 136.9, 136.8, 132.6, 132.0(2×CH), 131.5, 130.1, 129.5(2×CH), 128.3(2×CH), 128.0(2×CH), 125.7, 125.1, 124.3, 123.1, 77.8, 21.4.

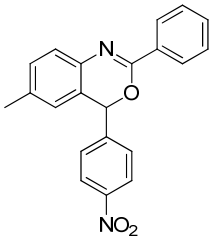
ESI-HRMS: m/z calcd for C21H16BrNO $[M+H]^{+}$:378.0415; found:378.0418.

GC-MS：377.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



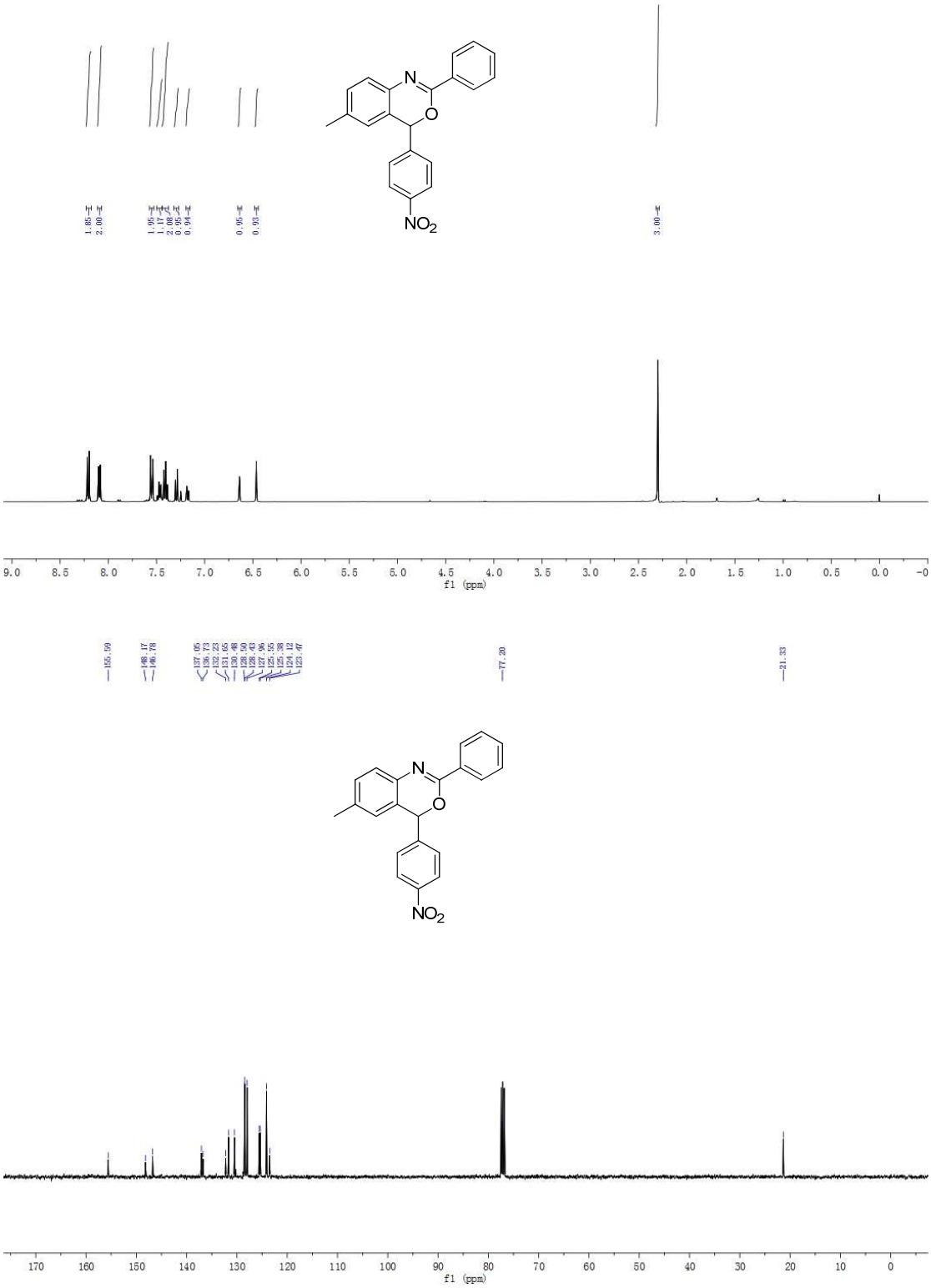
6-methyl-4-(4-nitrophenyl)-2-phenyl-4H-benzo[d][1,3]oxazine (4aap): yellow oil, 129 mg, yield: 75%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.23 - 8.18 (m, 2H), 8.11 - 8.07 (m, 2H), 7.55 (dd, J = 9.0, 1.8 Hz, 2H), 7.50 - 7.44 (m, 1H), 7.44 - 7.38 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.19 - 7.15 (m, 1H), 6.64 (s, 1H), 6.46 (s, 1H), 2.30 (s, 3H).

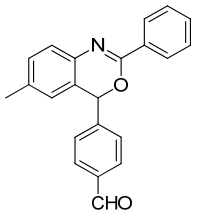
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 155.6, 148.2, 146.8, 137.1, 136.7, 132.2, 131.7, 130.5, 128.5(2×CH), 128.4(2×CH), 128.0(2×CH), 125.6, 125.4, 124.1(2×CH), 123.5, 77.2, 21.3.

ESI-HRMS: m/z calcd for C21H16N2O3 $[M+H]^{+}$:345.1161; found:345.1166.

GC-MS：344.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



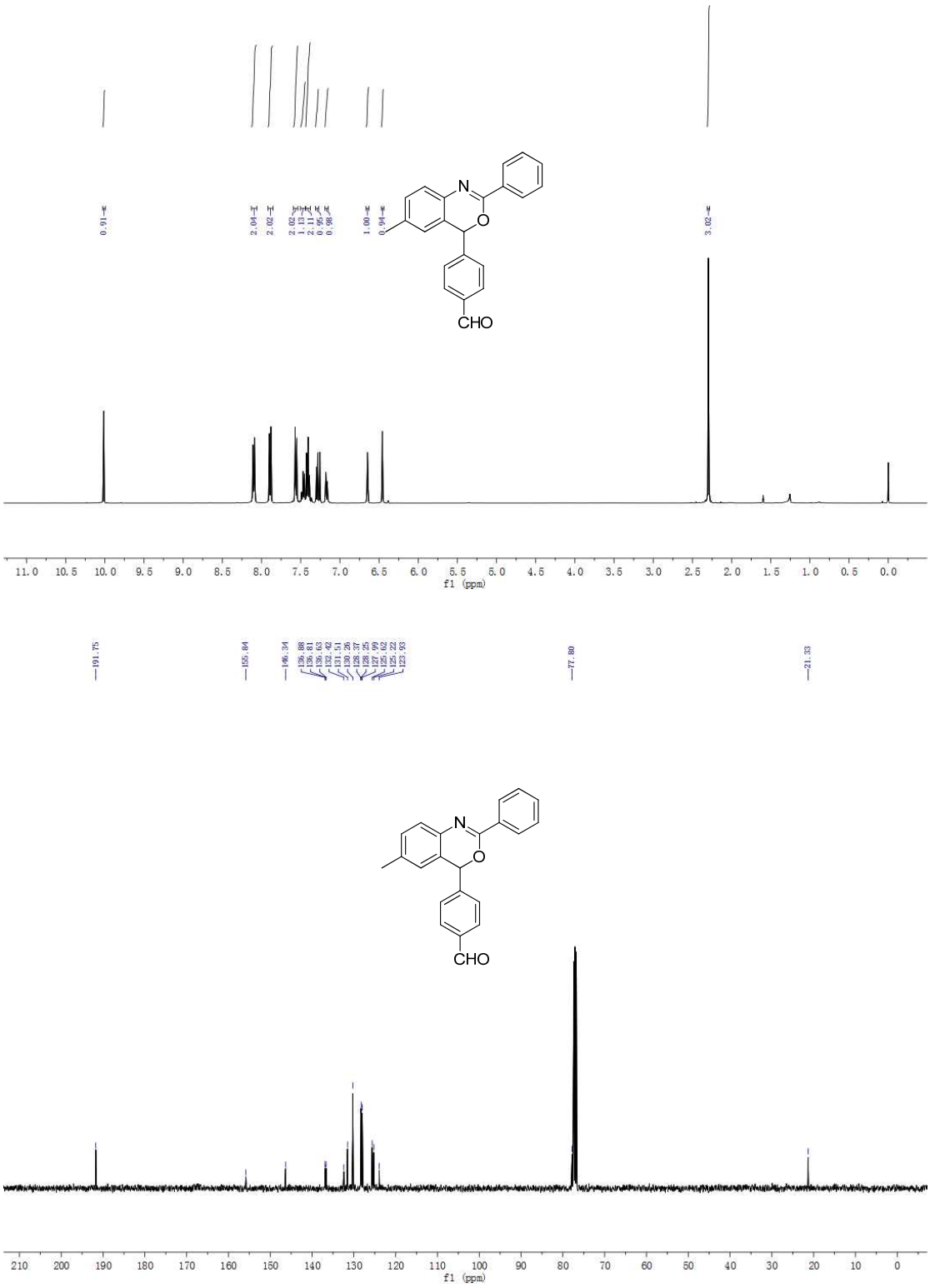
4-(6-methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)benzaldehyde (4aaq): colorless oil, 116 mg, yield: 71%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.01 (s, 1H), 8.10 (dd, J = 8.3, 1.0 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.47 (dd, J = 10.5, 4.1 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.9 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 6.65 (s, 1H), 6.46 (s, 1H), 2.30 (s, 3H).

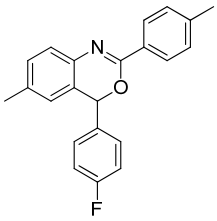
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 191.8, 155.8, 146.3, 136.9, 136.8, 136.6, 132.4, 131.5, 130.3 (3×CH), 128.4(2×CH), 128.3(2×CH), 128.0 (2×CH), 125.6, 125.2, 123.9, 77.8, 21.3.

ESI-HRMS: m/z calcd for C22H17NO2 $[M+H]^{+}$:328.1259; found:328.1260.

GC-MS：327.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



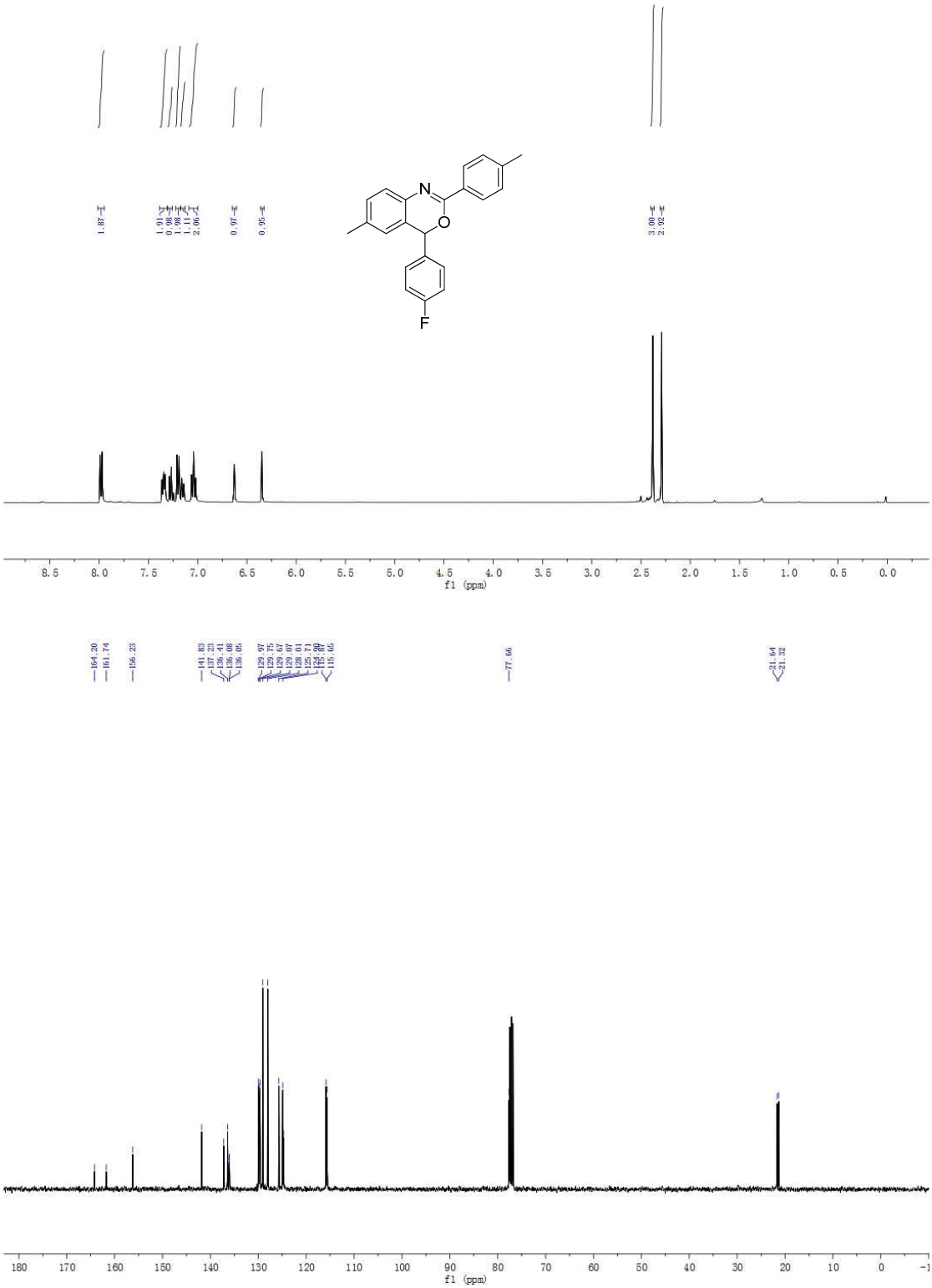
4-(4-fluorophenyl)-6-methyl-2-(p-tolyl)-4H-benzo[d][1,3]oxazine (4abb): white solid, 132 mg, yield: 80%, melt point: 118^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.98 (d, J = 8.1 Hz, 2H), 7.35 (dd, J = 8.4, 5.5 Hz, 2H), 7.28 (d, J = 7.9 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 1H), 7.04 (t, J = 8.6 Hz, 2H), 6.63 (s, 1H), 6.35 (s, 1H), 2.38 (s, 3H), 2.29 (s, 3H).

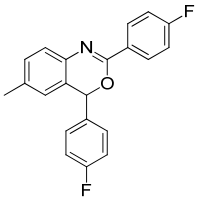
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.5 Hz), 156.2, 141.8, 137.2, 136.4, 136.1 (d, J = 3.1 Hz), 123.0, 129.9, 129.7 (d, J = 8.2 Hz, 2×CH), 129.1 (2×CH), 128.0(2×CH), 125.7, 124.9, 124.7, 115.8(d, J = 21.5 Hz, 2×CH), 77.7, 21.6, 21.3.

ESI-HRMS: m/z calcd for C22H18NO $[M+H]^{+}$:332.1372; found:332.1374.

GC-MS：331.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



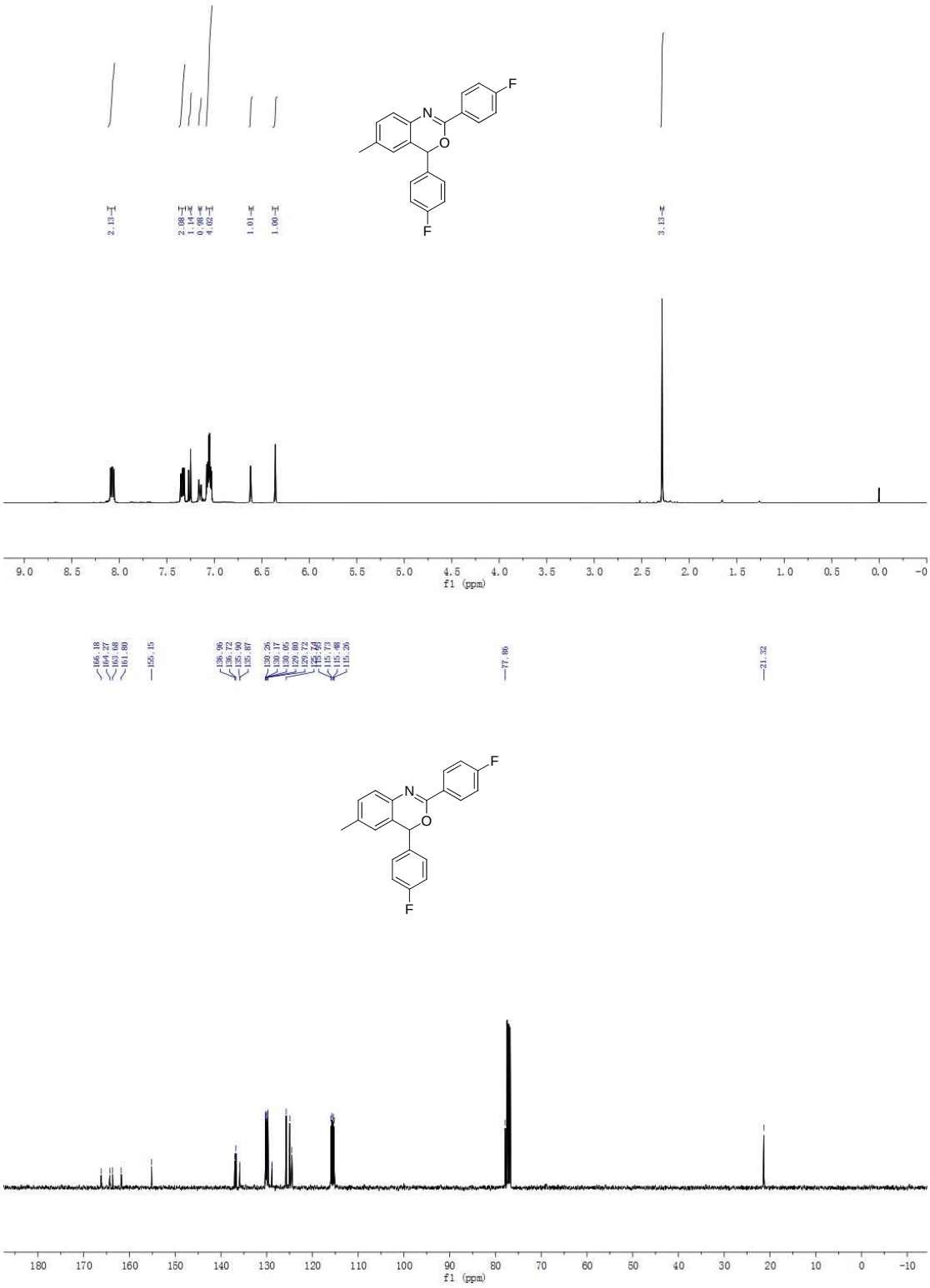
2,4-bis(4-fluorophenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4acb): colorless oil, 157.5 mg, yield: 94%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.12 - 8.04 (m, 2H), 7.37 - 7.30 (m, 2H), 7.26 (d, J = 8.1 Hz, 1H), 7.16 - 7.14 (m, 1H), 7.08 - 7.02 (m, 4H), 6.62 (s, 1H), 6.36 (s, 1H), 2.29 (s, 3H).

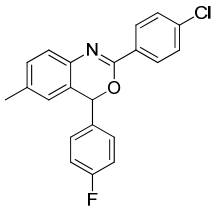
^{13}C NMR (101 MHz, CHLOROFORM-D) δ164.9 (d, J = 251.5 Hz), 163.0 (d, J = 248.0 Hz), 155.2, 137.0, 136.7, 135.9 (d, J = 2.9 Hz), 130.2 (d, J = 8.8 Hz, 2×CH), 130.1, 129. 8 (d, J = 8.5 Hz, 2×CH), 128.9, 128.8, 125.7, 124.9, 124.5, 115.8 (d, J = 21.6 Hz, 2×CH), 115.4 (d, J = 21.8 Hz, 2×CH), 77.9, 21.3.

ESI-HRMS: m/z calcd for C21H25F2NO $[M+H]^{+}$:336.1122; found:336.1123.

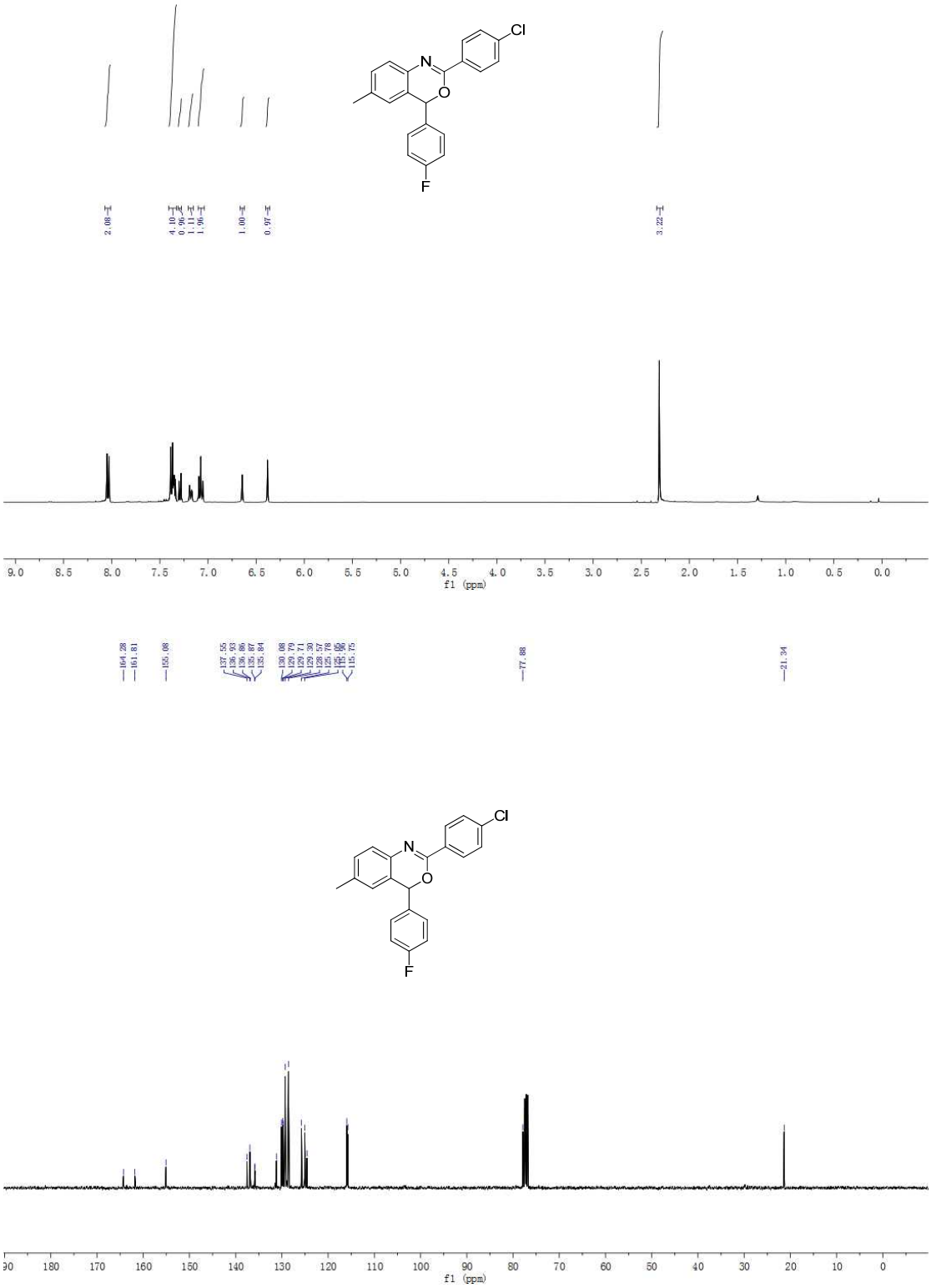
GC-MS：335.



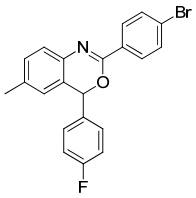
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



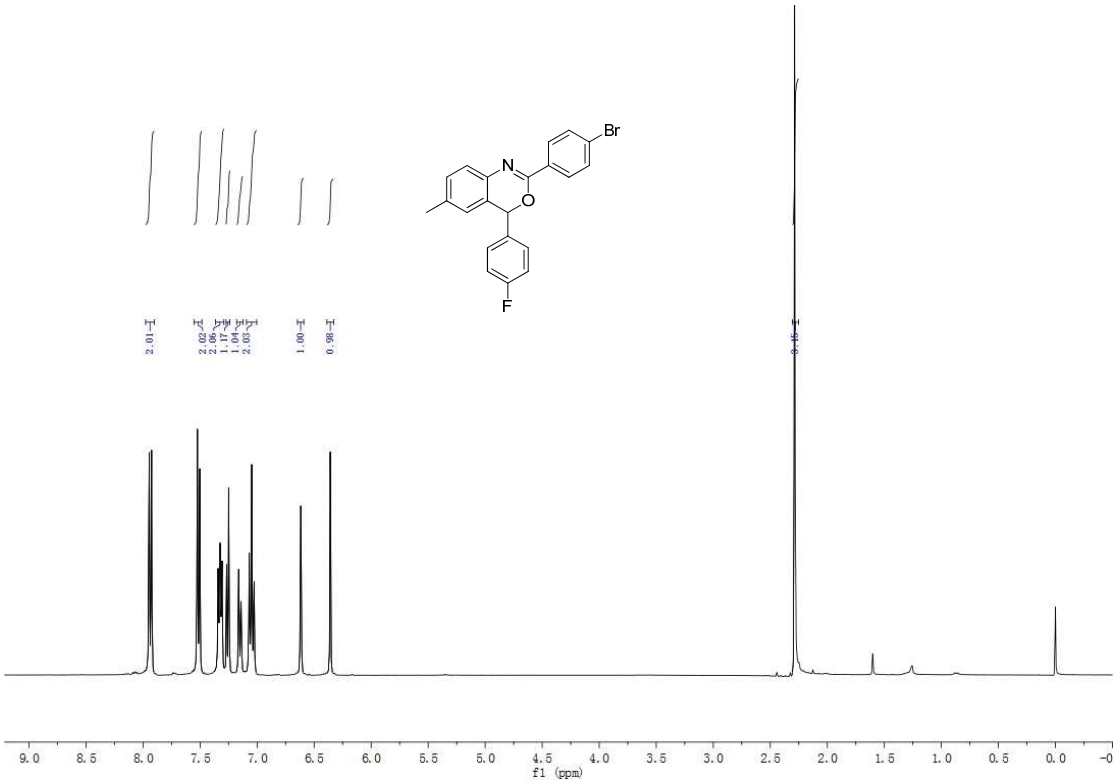
2-(4-chlorophenyl)-4-(4-fluorophenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4adb):
white solid, 160 mg, yield: 91%, melt point:128 ^{o}C.
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.07 - 8.01 (m, 2H), 7.41 - 7.33 (m, 4H), 7.29 (d, J = 7.9 Hz, 1H), 7.18 (dd, J = 10.6, 3.5 Hz, 1H), 7.10 - 7.04 (m, 2H), 6.64 (s, 1H), 6.38 (s, 1H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 248.1 Hz), 155.1, 137.6, 136.9, 136.9, 135.9 (d, J = 3.0 Hz), 131.2, 130.1, 129.8 (d, J = 8.4 Hz, 2×CH), 129.3(2×CH), 128.6(2×CH), 125.8, 125.1, 124.6, 115.9 (d, J = 21.6 Hz, 2×CH), 77.9, 21.3.
ESI-HRMS: m/z calcd for C21H15ClNO $[M+H]^{+}$:352.0826; found:352.0828.
GC-MS：351.

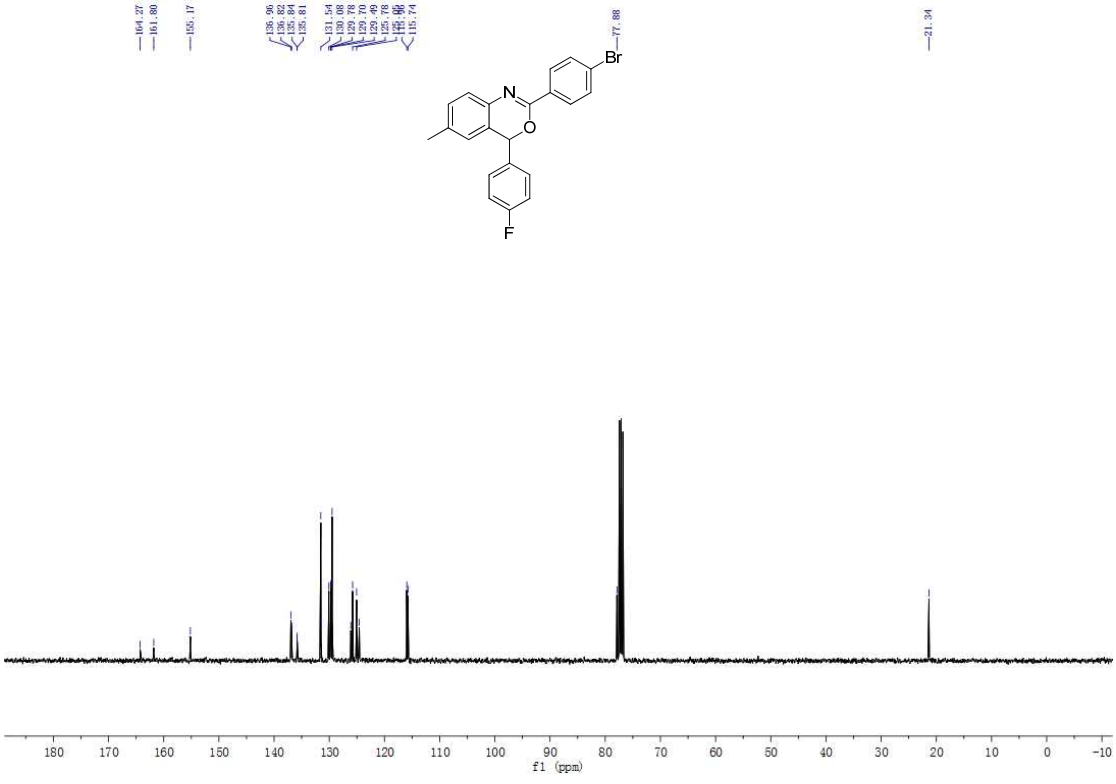


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

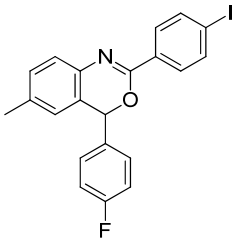


2-(4-bromophenyl)-4-(4-fluorophenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4aeb):
white solid, 182 mg, yield: 92%, melt point:153 ^{o}C.
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.94 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.33 (dd, J = 8.3, 5.5 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.05 (t, J = 8.6 Hz, 2H), 6.62 (s, 1H), 6.36 (s, 1H), 2.29 (s, 3H).
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 248.0 Hz), 155.2, 137.0, 136.8, 135.8 (d, J = 2.8 Hz), 131.6, 131.5, 130.1, 129.7 (d, J = 8.5 Hz,2×CH), 129.5, 126.1, 125.8, 125.1, 124.6, 115.9 (d, J = 21.7 Hz, 2×CH), 77.9, 21.3.
ESI-HRMS: m/z calcd for C21H15BrNO $[M+H]^{+}$:396.0321; found:396.0322.
GC-MS：395.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



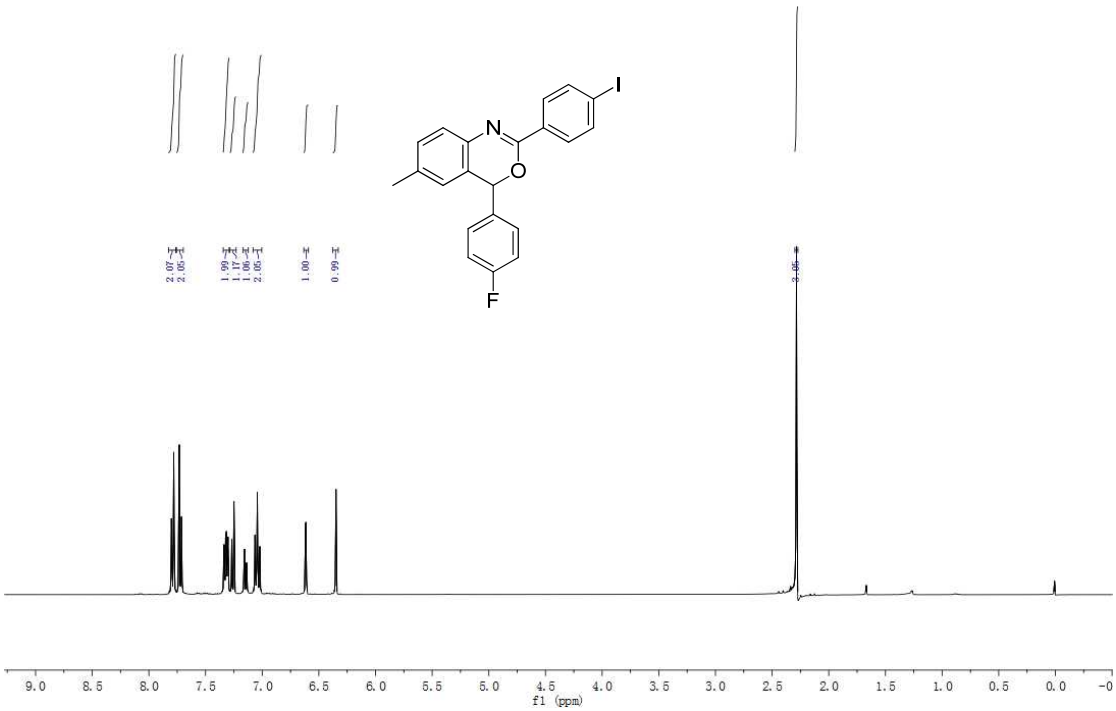
6-methyl-2-phenyl-4-(p-tolyl)-4H-benzo[d][1,3]oxazine (4afb): white solid, 195 mg, yield: 88%, melt point: 157^{o}C.

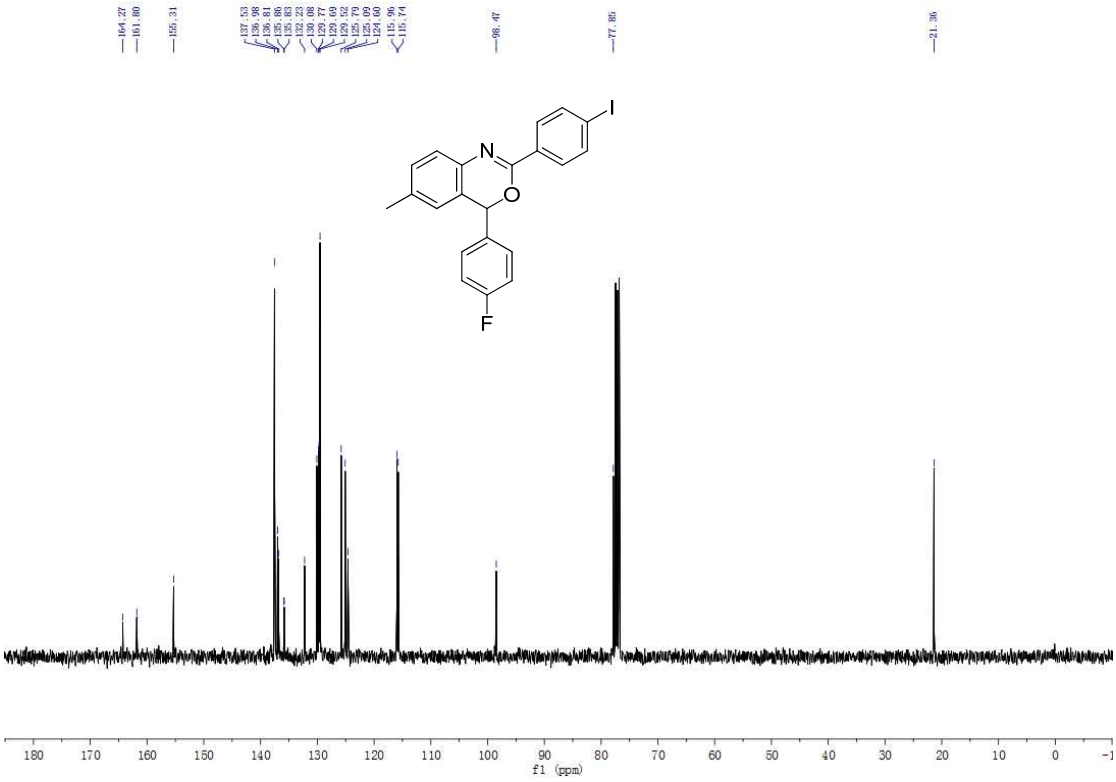
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.83 - 7.76 (m, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.32 (dd, J = 8.5, 5.5 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.08 - 7.00 (m, 2H), 6.62 (s, 1H), 6.35 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 248.2 Hz), 155.3, 137.5(2×CH), 137.0, 136.8, 135.9 (d, J = 3.3 Hz), 132.2, 130.1, 129.7 (d, J = 8.5 Hz，2×CH), 129.5(2×CH), 125.8, 125.1, 124.6, 115.9 (d, J = 21.7 Hz，2×CH), 98.5, 77.9, 21.4.

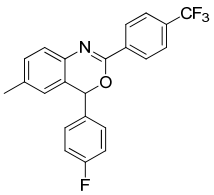
ESI-HRMS: m/z calcd for C21H15FINO $[M+H]^{+}$:444.0182; found:444.0182.

GC-MS：443.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



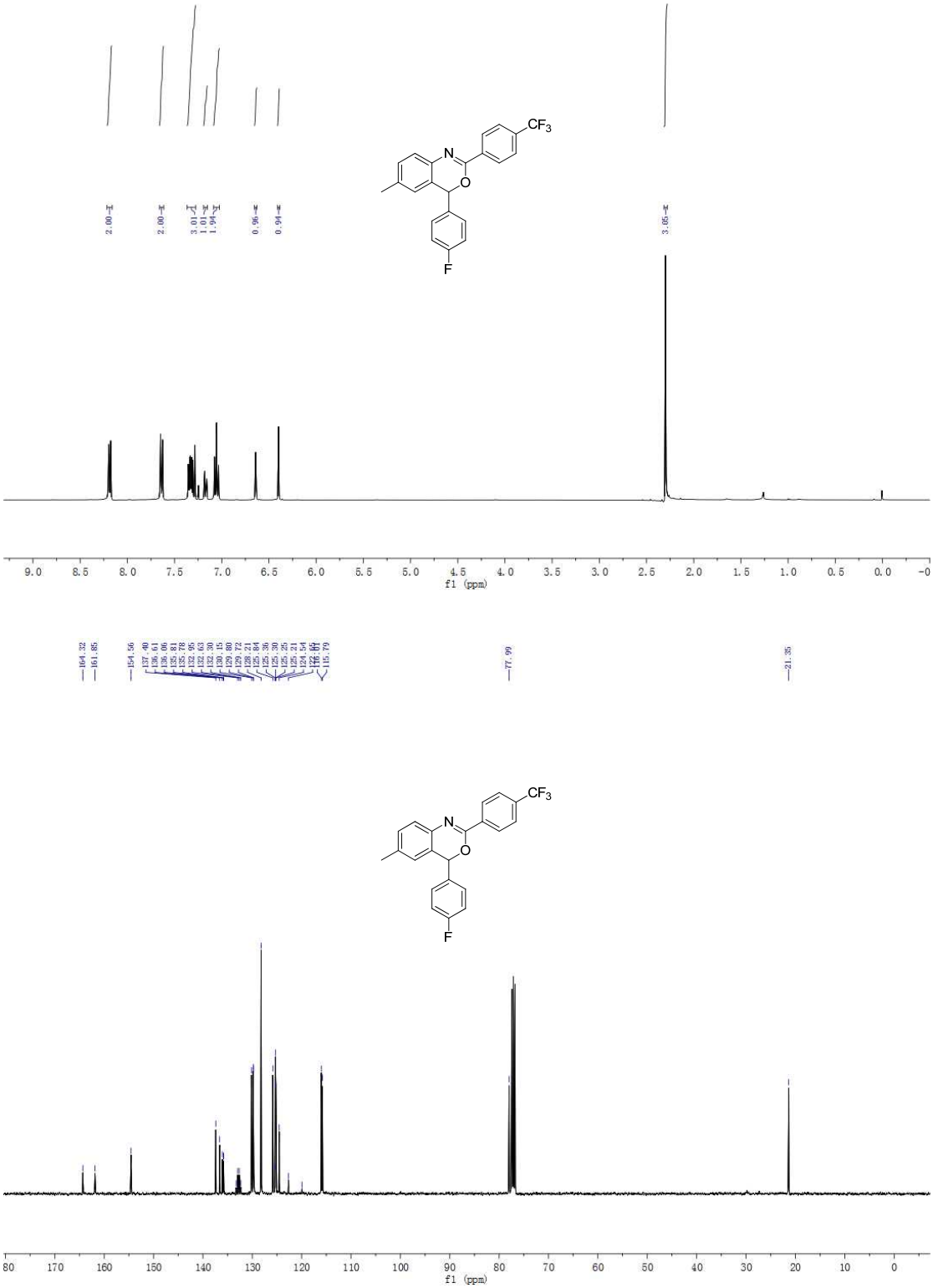
4-(4-fluorophenyl)-6-methyl-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazine (4agb): white solid, 177 mg, yield: 92%, melt point:123 ^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.19 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.33 (ddd, J = 15.1, 9.3, 4.9 Hz, 3H), 7.17 (d, J = 8.1 Hz, 1H), 7.09 - 7.02 (m, 2H), 6.64 (s, 1H), 6.40 (s, 1H), 2.30 (s, 3H).

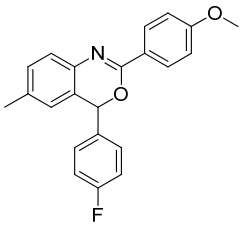
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.1 (d, J = 248.2 Hz), 154.6, 137.4, 136.6, 136.1, 135.8 (d, J = 3.1 Hz), 132.8 (q, J = 32.5 Hz), 130.15, 129.8 (d, J = 8.5 Hz，2×CH), 128.2(2×CH), 125.8, 125.4, 125.3, 125.2 (d, J = 3.7 Hz，2×CH), 124.5, 122.7, 119.9, 115.9 (d, J = 21.7 Hz，2×CH), 78.0, 21.4.

ESI-HRMS: m/z calcd for C22H15 F4NO $[M+H]^{+}$:386.1090; found:386.1094.

GC-MS：385.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



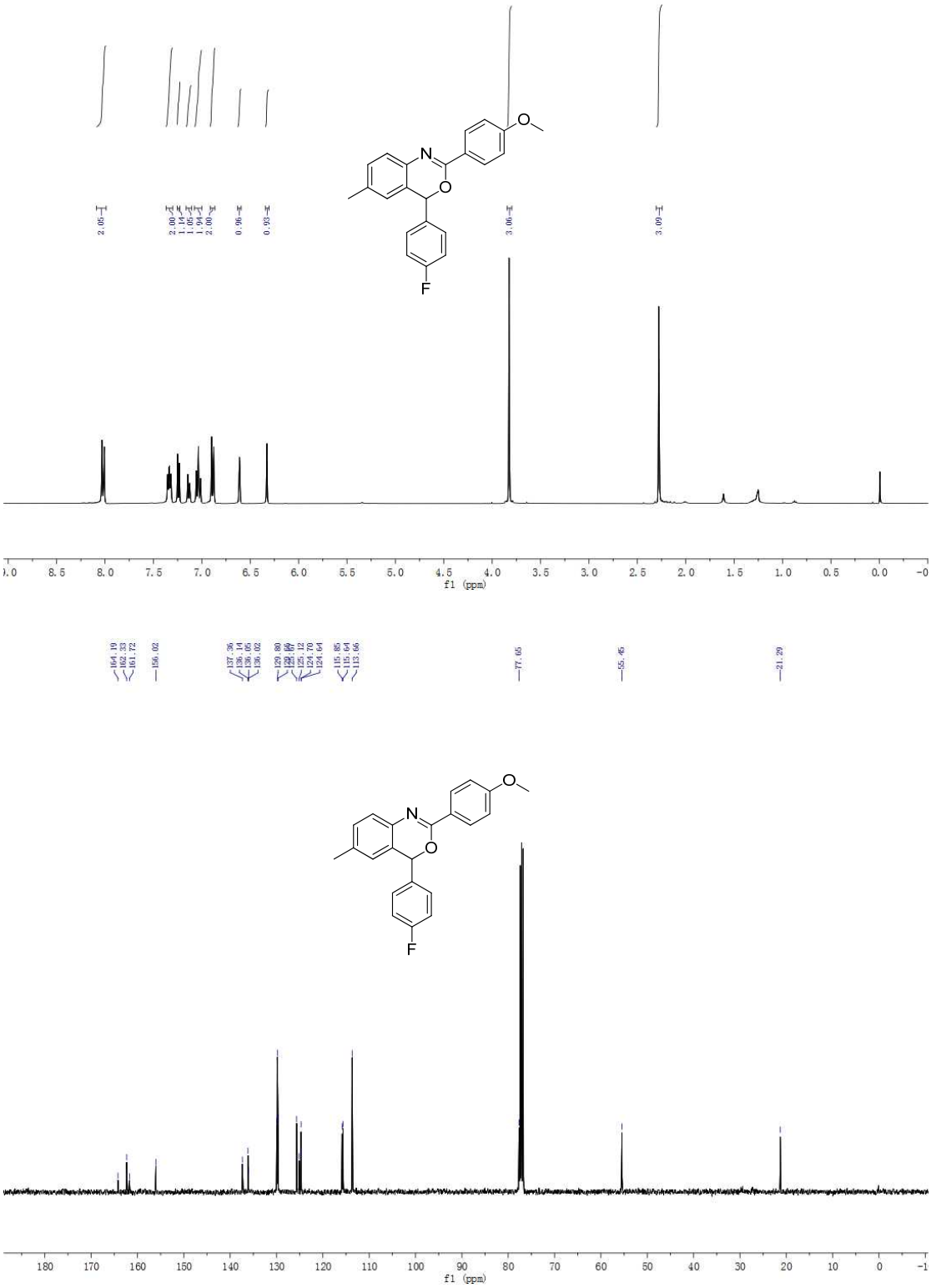
4-(4-fluorophenyl)-2-(4-methoxyphenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4ahb): colorless oil, 40 mg, yield: 23%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.09 - 7.99 (m, 2H), 7.34 (dd, J = 7.8, 5.5 Hz, 2H), 7.25 - 7.23 (m, 1H), 7.13 (d, J = 7.7 Hz, 1H), 7.08 - 7.00 (m, 2H), 6.91 - 6.86 (m, 2H), 6.61 (s, 1H), 6.33 (s, 1H), 3.83 (s, 3H), 2.28 (s, 3H).

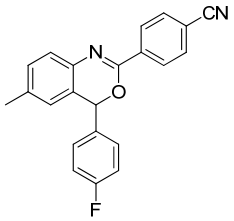
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.9 Hz), 162.3, 156.0, 137.4, 136.1, 136.0 (d, J = 2.9 Hz), 130.0, 129.8(2×CH), 129.7 (d, J = 8.4 Hz, 2×CH), 125.7, 125.1, 124.7, 124.6, 115.7 (d, J = 21.6 Hz, 2×CH), 113.7 (2×CH), 77.7, 55.5, 21.3.

ESI-HRMS: m/z calcd for C22H18FNO2 $[M+H]^{+}$:348.1322; found:348.1325.

GC-MS：347.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



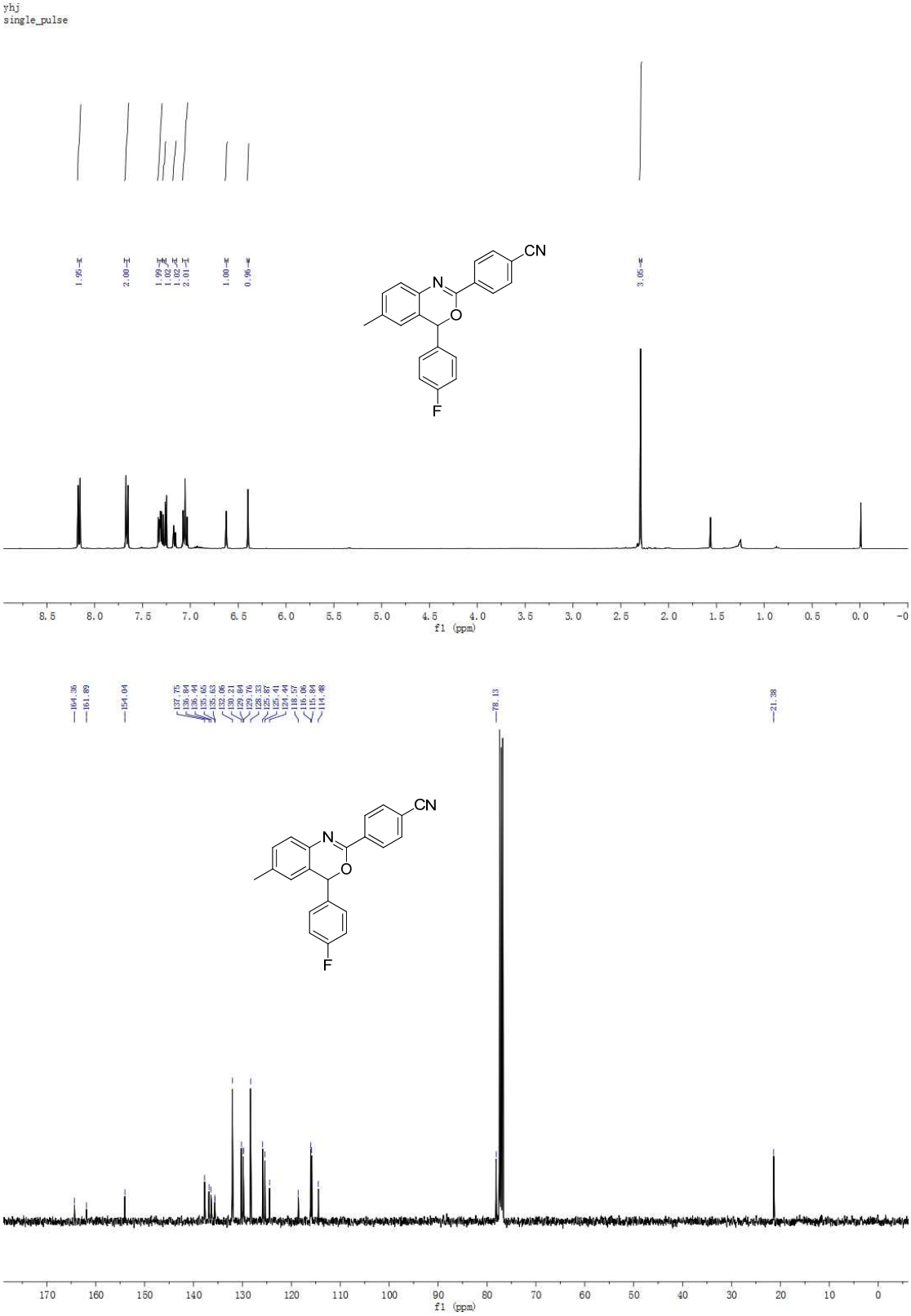
4-(4-(4-fluorophenyl)-6-methyl-4H-benzo[d][1,3]oxazin-2-yl)benzonitrile (4aib): white solid, 80 mg, yield: 47%, melt point:159 ^{o}C.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.18 – 8.14 (m, 2H), 7.69 - 7.64 (m, 2H), 7.34 - 7.29 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.2, 1.2 Hz, 1H), 7.08 - 7.02 (m, 2H), 6.63 (s, 1H), 6.40 (s, 1H), 2.29 (s, 3H).

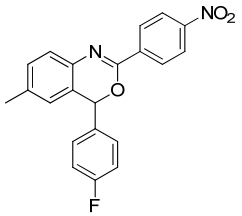
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.12 (d, J = 248.3 Hz), 154.0, 137.6, 136.8, 136.4, 135.6 (d, J = 2.8 Hz), 132.1(2×CH), 130.2, 129.8 (d, J = 8.2 Hz，2×CH), 128.3(2×CH), 125.9, 125.4, 124.4, 118.6, 116.0 (d, J = 21.8 Hz，2×CH), 114.5, 78.1, 21.4.

ESI-HRMS: m/z calcd for C22H15FN2O $[M+H]^{+}$:343.1186; found:343.1188.

GC-MS：342.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



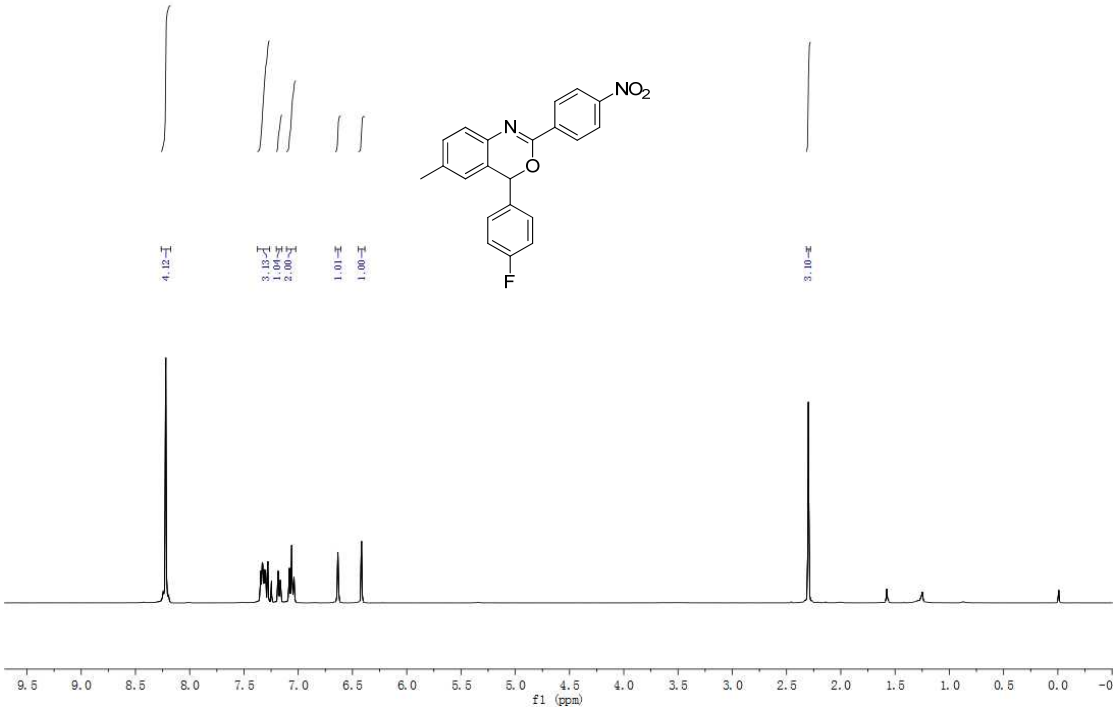
4-(4-fluorophenyl)-6-methyl-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (4ajb): yellow solid, 136 mg, yield: 75%, melt point:159 ^{o}C.

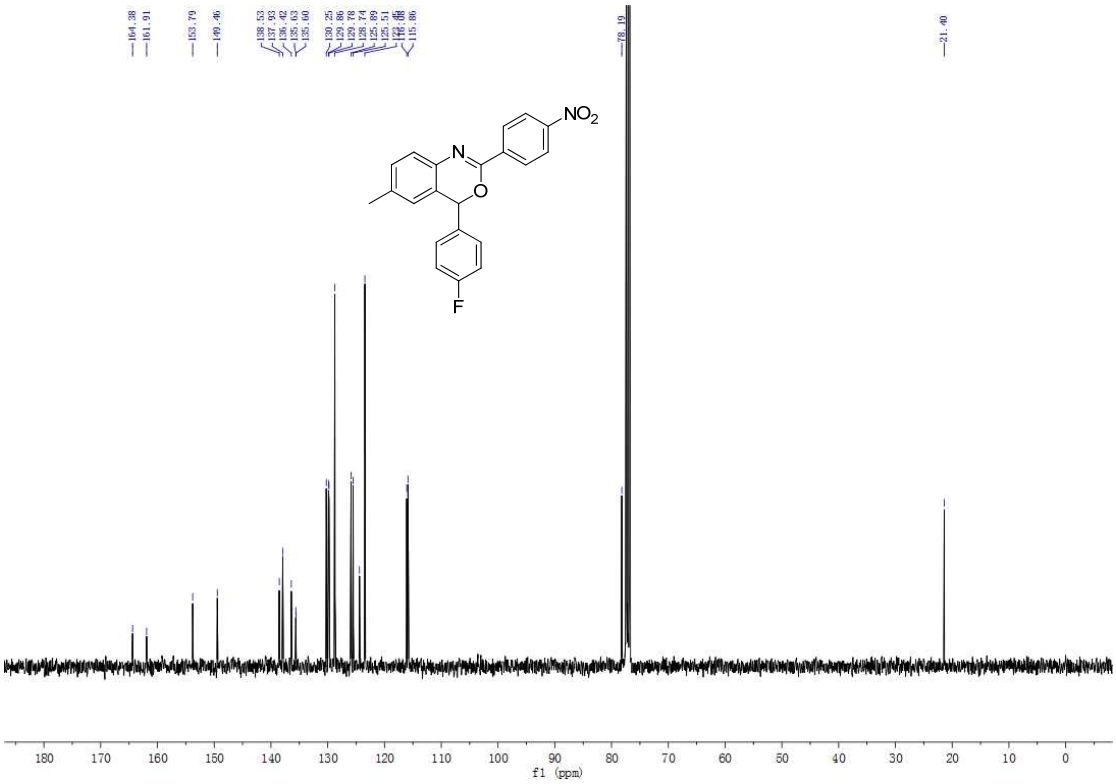
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.26 - 8.17 (m, 4H), 7.32 (ddd, J = 13.5, 9.6, 6.8 Hz, 3H), 7.18 (d, J = 7.9 Hz, 1H), 7.06 (dd, J = 12.2, 4.9 Hz, 2H), 6.63 (s, 1H), 6.42 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.1 (d, J = 248.3 Hz), 153.8, 149.5, 138.5, 137.9, 136.4, 135.6 (d, J = 2.9 Hz), 130.3, 129.8 (d, J = 8.4 Hz，2×CH), 128.7(2×CH), 125.9, 125.5, 124.4, 123.5(2×CH), 116.0 (d, J = 21.7 Hz，2×CH), 78.2, 21.4.

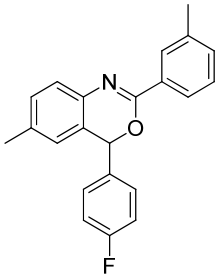
ESI-HRMS: m/z calcd for C21H15FN2O3 $[M+H]^{+}$:363.1067; found:363.1067.

GC-MS：362.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



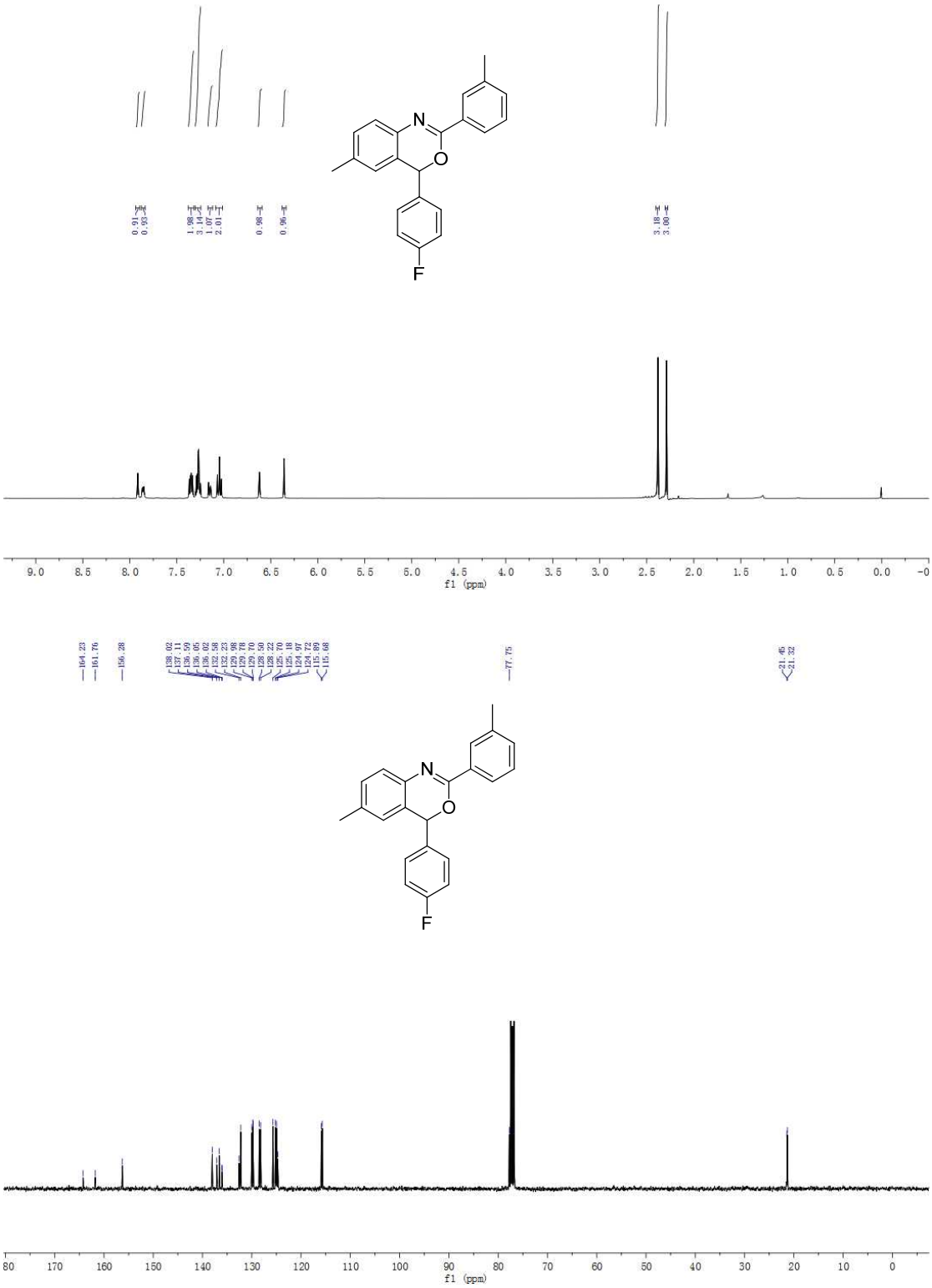
4-(4-fluorophenyl)-6-methyl-2-(m-tolyl)-4H-benzo[d][1,3]oxazine(4akb): colorless oil, 132 mg, yield: 80%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.91 (s, 1H), 7.88 - 7.83 (m, 1H), 7.38 - 7.32 (m, 2H), 7.30 - 7.24 (m, 3H), 7.15 (d, J = 8.8 Hz, 1H), 7.09 - 7.01 (m, 2H), 6.62 (s, 1H), 6.36 (s, 1H), 2.38 (s, 3H), 2.29 (s, 3H).

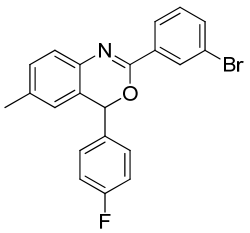
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.7 Hz), 156.3, 138.0, 137.1, 136.6, 136.0 (d, J = 3.0 Hz), 132.6, 132.2, 130.0, 129.7 (d, J = 8.4 Hz，2×CH), 128.5, 128.2, 125.7, 125.2, 125.0, 124.7, 115.8 (d, J = 21.7 Hz，2×CH), 77.8, 21.5, 21.3.

ESI-HRMS: m/z calcd for C22H18FNO $[M+H]^{+}$:332.1372; found:332.1374.

GC-MS：331.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



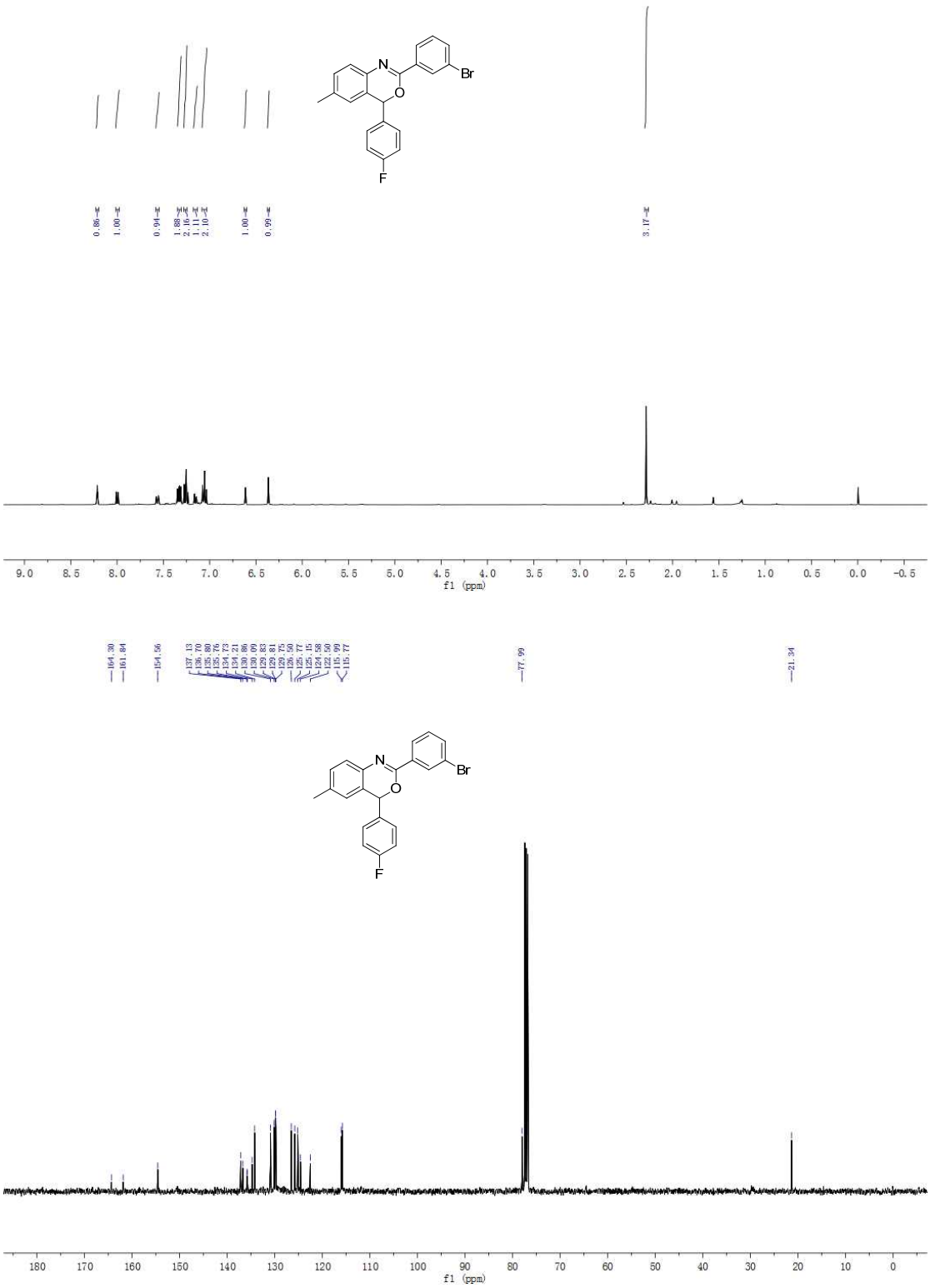
2-(3-bromophenyl)-4-(4-fluorophenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4alb): colorless oil, 160 mg, yield: 81%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.21 (t, J = 1.8 Hz, 1H), 8.00 (dt, J = 7.8, 1.1 Hz, 1H), 7.58 - 7.55 (m, 1H), 7.35 - 7.31 (m, 2H), 7.26 (t, J = 4.9 Hz, 2H), 7.18 - 7.13 (m, 1H), 7.08 - 7.03 (m, 2H), 6.61 (d, J = 0.6 Hz, 1H), 6.37 (s, 1H), 2.29 (s, 3H).

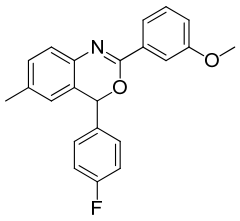
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.1 (d, J = 248.0 Hz), 154.6, 137.1, 136.7, 135.8 (d, J = 3.3 Hz), 134.7, 134.2, 130.9, 129.8, 129.8 (d, J = 8.2 Hz，2×CH), 129.8, 126.5, 125.8, 125.2, 124.6, 122.5, 115.9 (d, J = 21.7 Hz，2×CH), 78.0, 21.3.

ESI-HRMS: m/z calcd for C21H15BrFNO $[M+H]^{+}$:396.0321; found:396.0321.

GC-MS：395.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



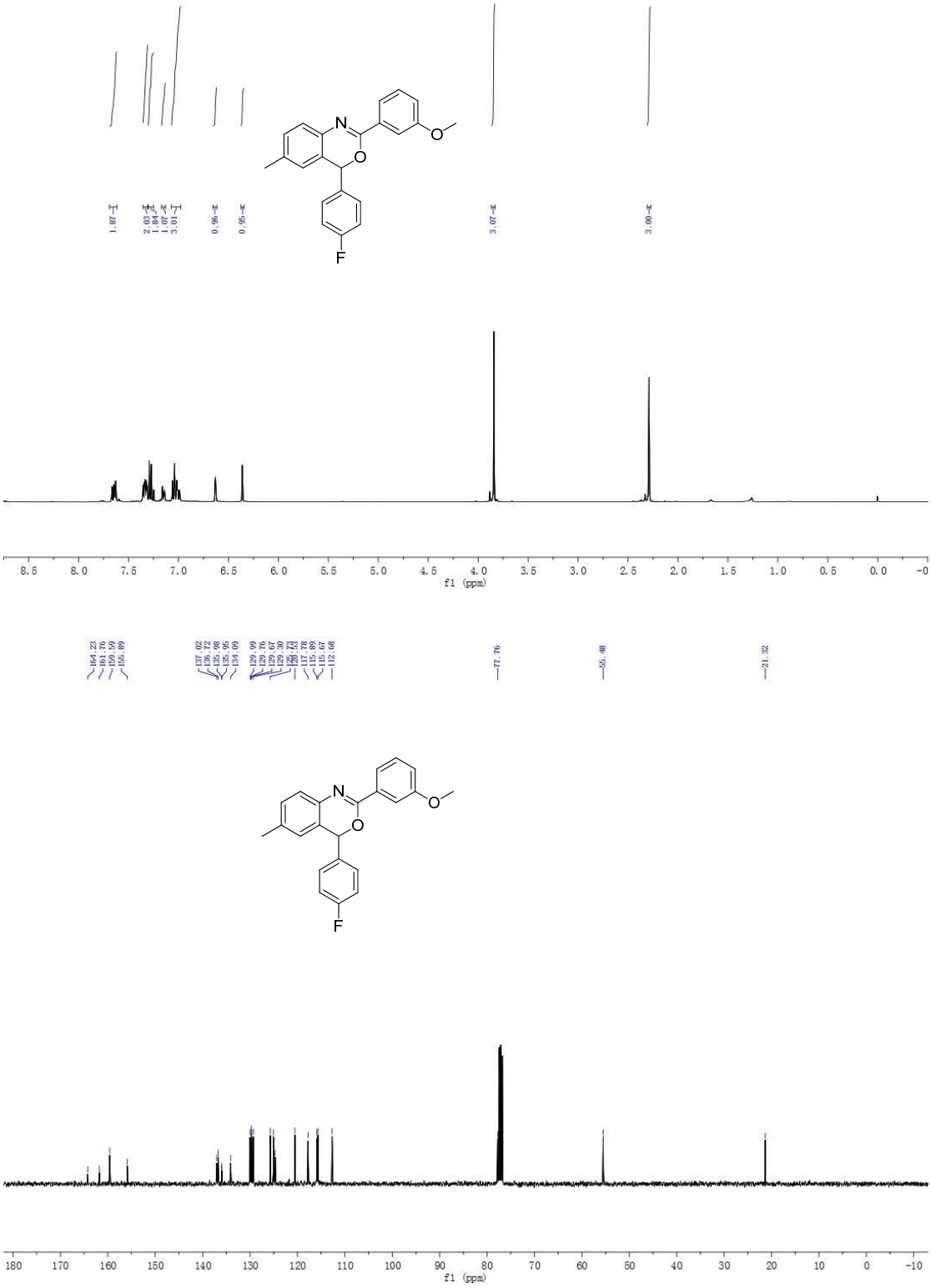
4-(4-fluorophenyl)-2-(3-methoxyphenyl)-6-methyl-4H-benzo[d][1,3]oxazine (4amb): colorless oil, 111 mg, yield: 64%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.69 - 7.62 (m, 2H), 7.33 (dd, J = 8.2, 2.8 Hz, 2H), 7.27 (t, J = 8.4 Hz, 2H), 7.15 (d, J = 7.8 Hz, 1H), 7.07 - 6.98 (m, 3H), 6.63 (s, 1H), 6.36 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H).

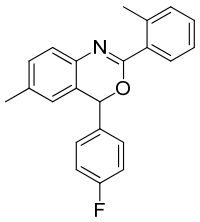
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.8 Hz), 159.6, 155.9, 137.0, 136.7, 136.0 (d, J = 3.0 Hz), 134.1, 130.0, 129.7 (d, J = 8.4 Hz，2×CH), 129.3, 125.7, 125.1, 124.7, 120.5, 117.8, 115.8 (d, J = 21.7 Hz，2×CH), 112.7, 77.8, 55.5, 21.3.

ESI-HRMS: m/z calcd for C22H18FNO2 $[M+H]^{+}$:348.1322; found:348.1323.

GC-MS：347.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



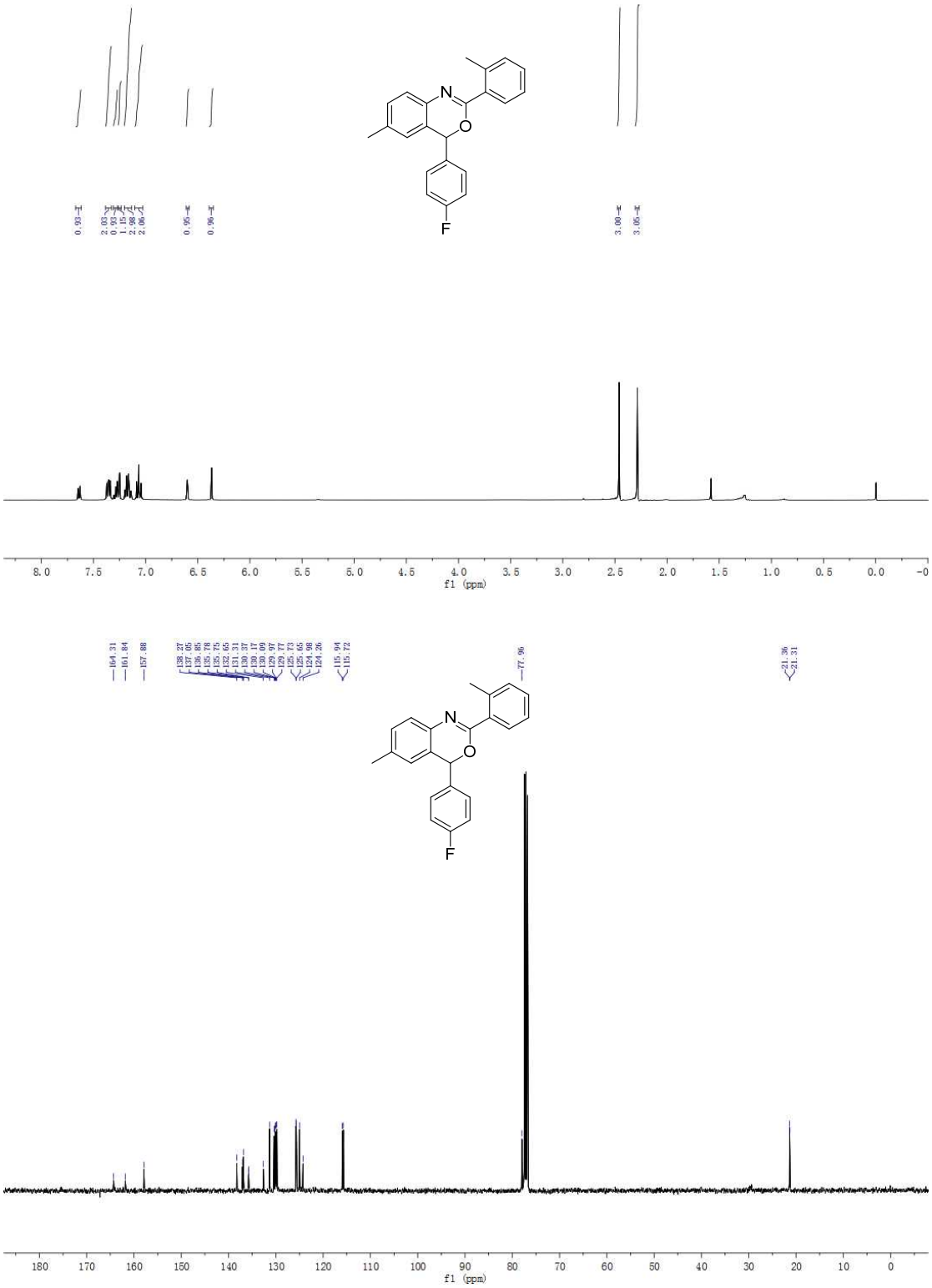
4-(4-fluorophenyl)-6-methyl-2-(o-tolyl)-4H-benzo[d][1,3]oxazine (4anb): colorless oil, 89 mg, yield: 54%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.64 (dd, J = 6.4, 2.4 Hz, 1H), 7.38 - 7.33 (m, 2H), 7.29 (dd, J = 9.7, 3.4 Hz, 1H), 7.25 (d, J = 1.9 Hz, 1H), 7.20 - 7.13 (m, 3H), 7.10 - 7.03 (m, 2H), 6.60 (s, 1H), 6.37 (s, 1H), 2.46 (s, 3H), 2.28 (s, 3H).

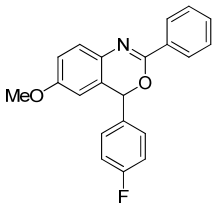
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.1 (d, J = 248.2 Hz), 157.9, 138.3, 137.1, 136.9, 135.8 (d, J = 3.2 Hz), 132.7, 131.3, 130.4, 130.2, 130.1, 130.0, 129.8, 125.7 (d, J = 8.3 Hz，2×CH), 125.0, 124.3, 115.8 (d, J = 21.7 Hz，2×CH), 78.0, 21.4, 21.3.

ESI-HRMS: m/z calcd for C22H18FNO $[M+H]^{+}$:332.1372; found:332.1375.

GC-MS：331.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



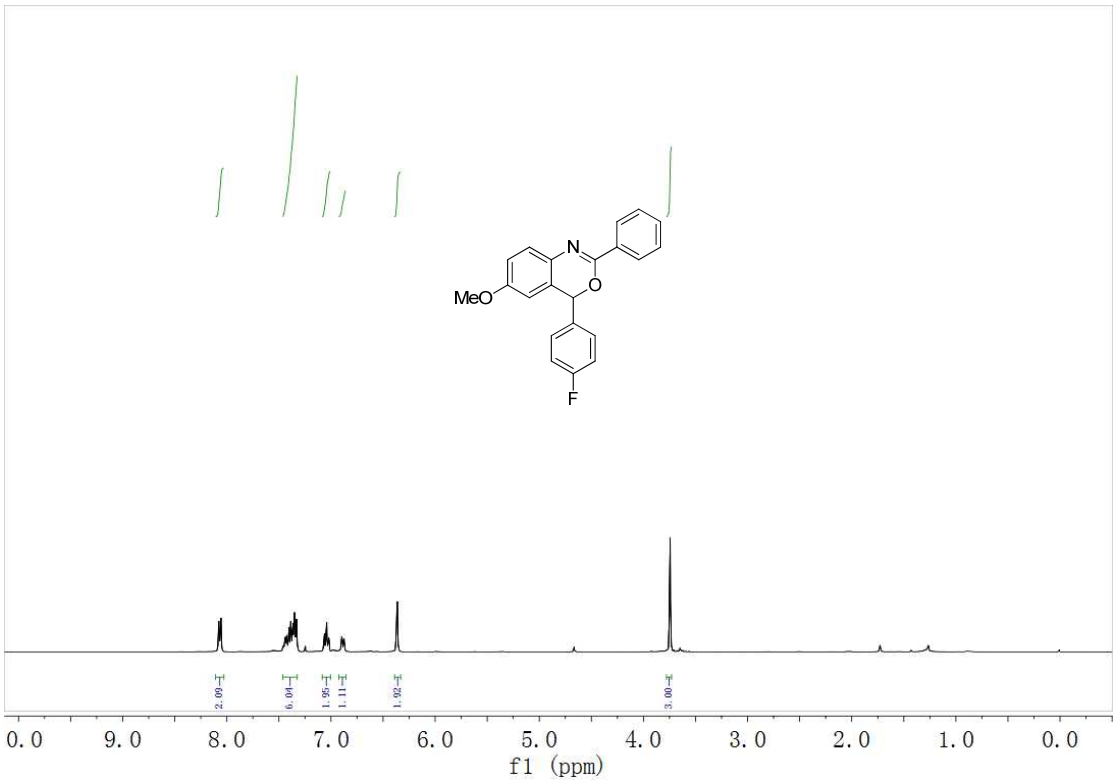
4-(4-fluorophenyl)-6-methoxy-2-phenyl-4H-benzo[d][1,3]oxazine (4bab): colorless oil, 128 mg, yield: 77%.

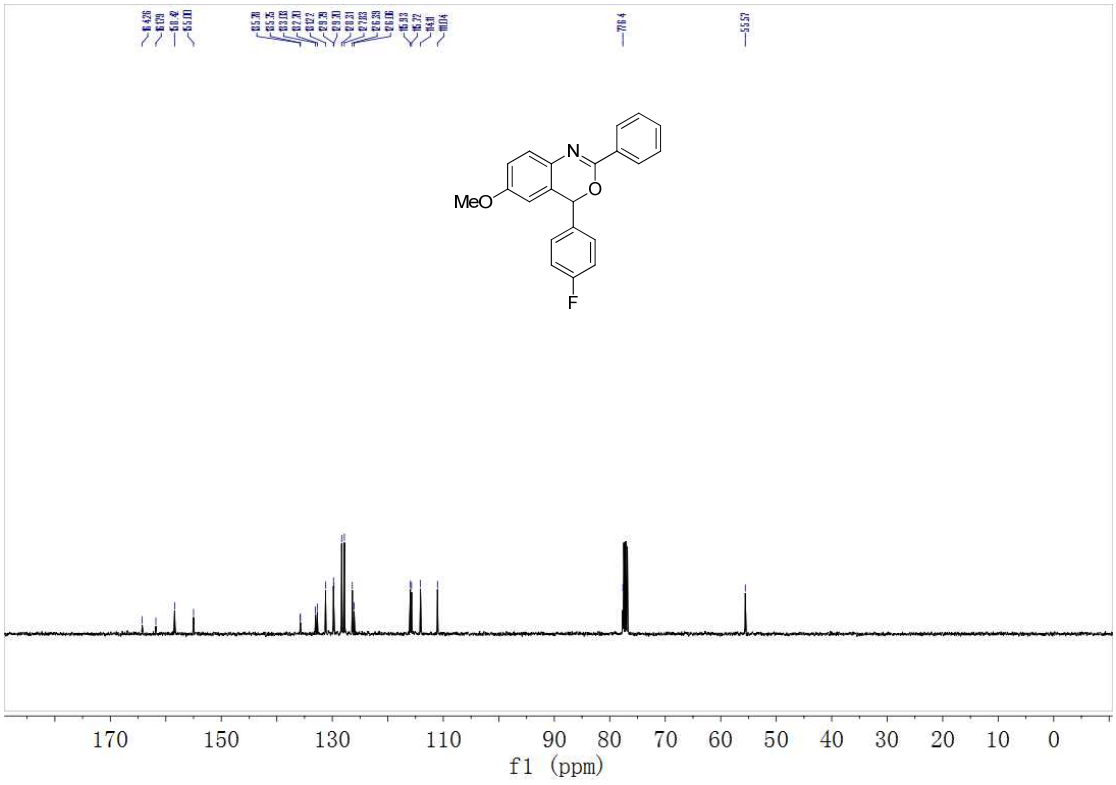
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.07 (d, J = 8.2 Hz, 2H), 7.39 (dddd, J = 13.9, 11.8, 7.1, 1.3 Hz, 6H), 7.04 (td, J = 8.6, 1.6 Hz, 2H), 6.88 (dd, J = 8.6, 2.2 Hz, 1H), 6.36 (d, J = 1.4 Hz, 2H), 3.74 (d, J = 1.5 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.8 Hz), 158.4, 155.0, 135.7 (d, J = 2.8 Hz), 133.0, 132.7, 131.2, 129.7 (d, J = 8.5 Hz, 2×CH), 128.3(2×CH), 127.8(2×CH), 126.4, 126.1, 115.8 (d, J = 21.6 Hz, 2×CH), 114.1, 111.0, 77.6, 55.6.

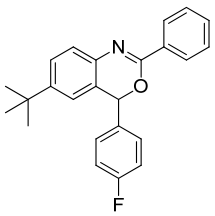
ESI-HRMS: m/z calcd for C21H16FNO2 $[M+H]^{+}$:334.1165; found:334.1168.

GC-MS：333.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



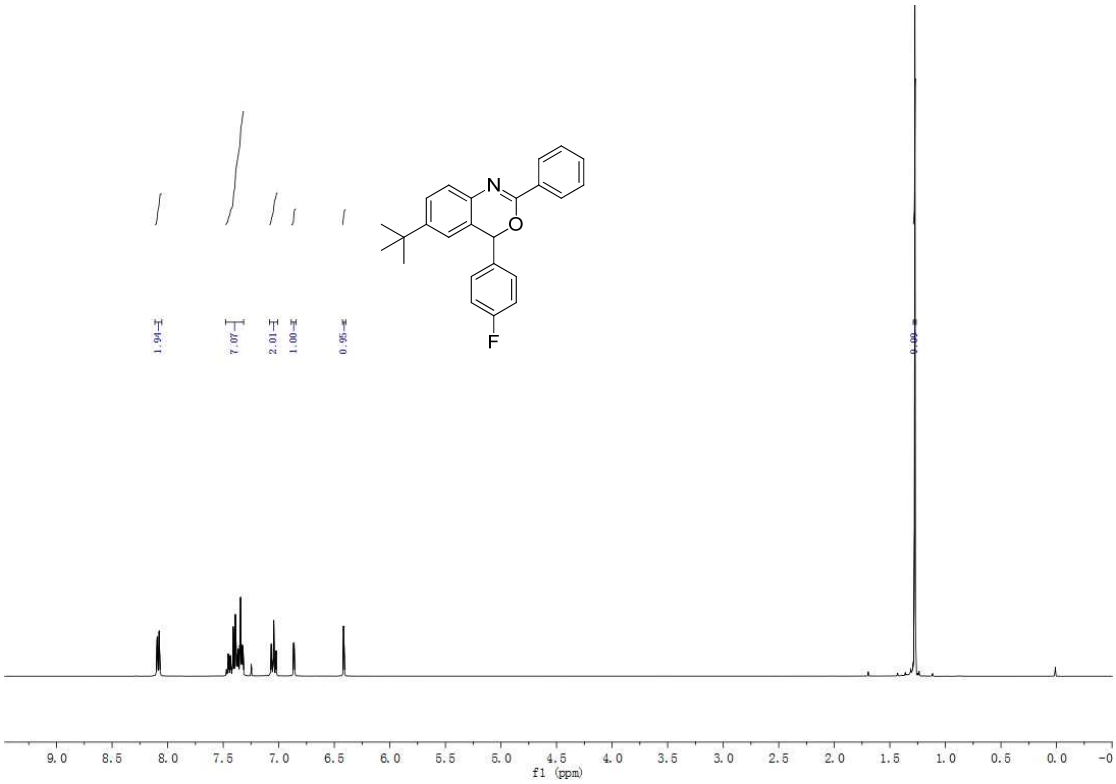
6-(tert-butyl)-4-(4-fluorophenyl)-2-phenyl-4H-benzo[d][1,3]oxazine (4cab): white solid, 165 mg, yield: 92%, melt point:170 ^{o}C.

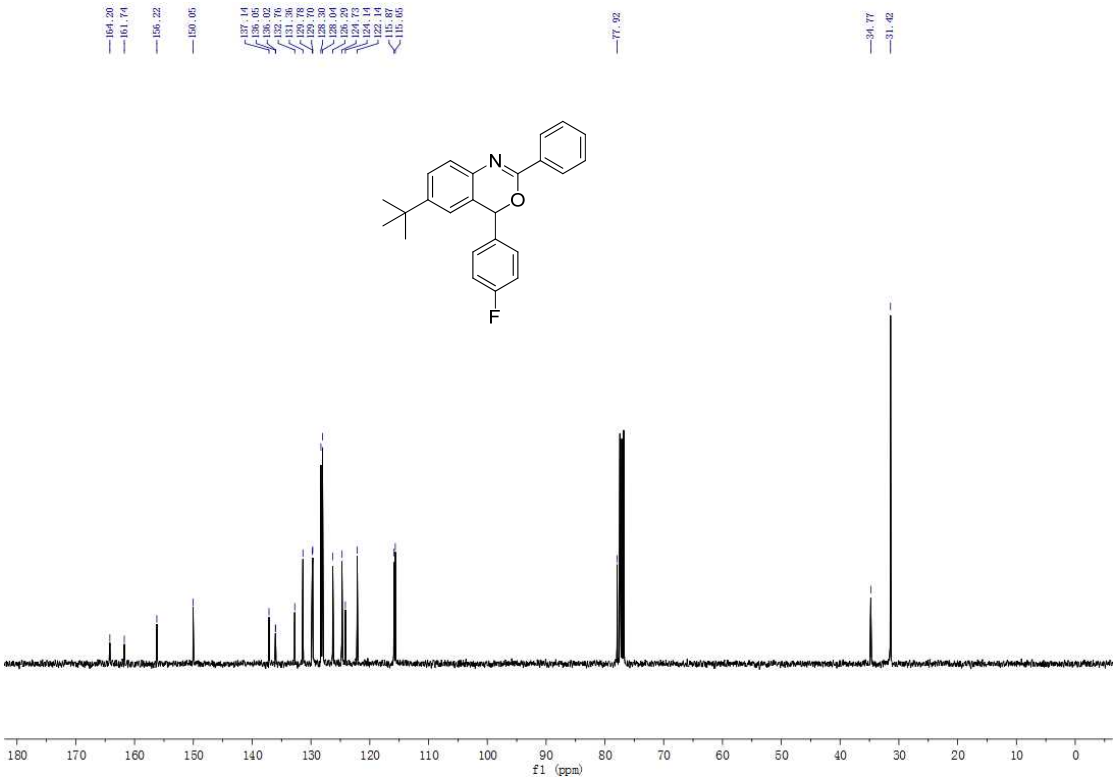
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.11 - 8.05 (m, 2H), 7.48 - 7.32 (m, 7H), 7.08 - 7.01 (m, 2H), 6.86 (d, J = 1.9 Hz, 1H), 6.42 (s, 1H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.5 Hz), 156.2, 150.1, 137.1, 136.0 (d, J = 2.9 Hz), 132.7, 131.4, 129.7 (d, J = 8.2 Hz, 2×CH), 128.3(2×CH), 128.0(2×CH), 126.3, 124.7, 124.1, 122.1, 115.8 (d, J = 21.6 Hz, 2×CH), 77.9, 34.8, 31.4.

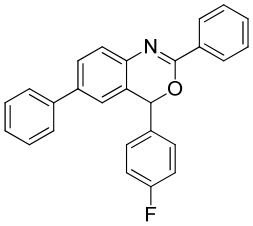
ESI-HRMS: m/z calcd for C24H22FNO $[M+H]^{+}$:360.1685; found:360.1688.

GC-MS：359.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



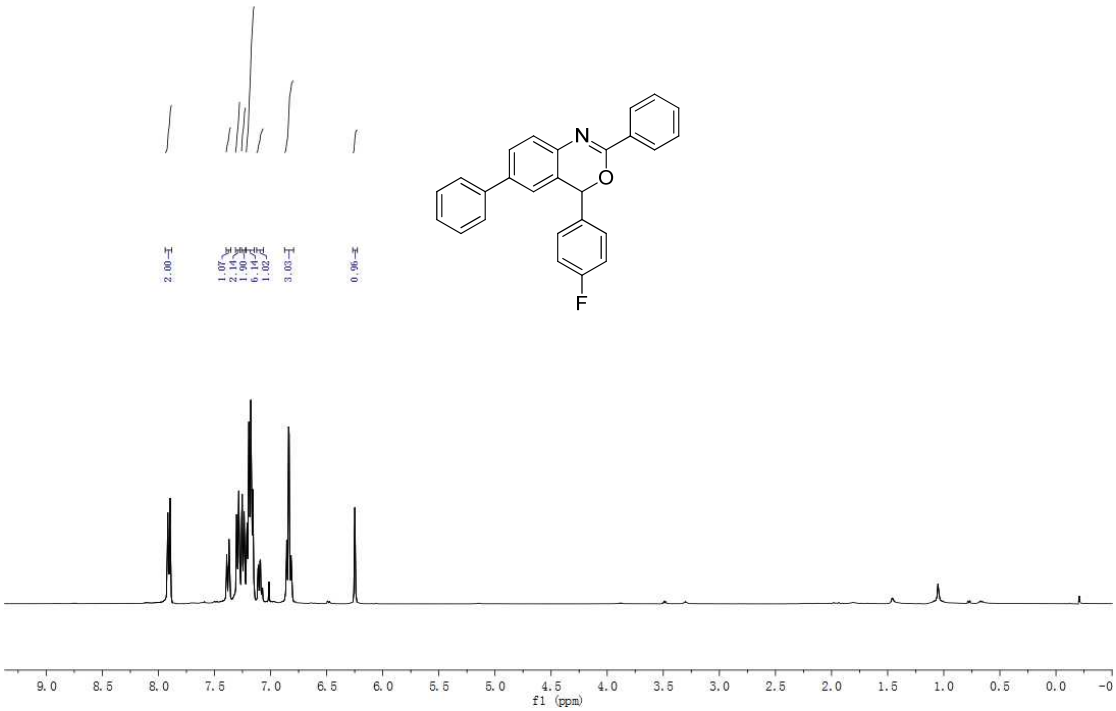
4-(4-fluorophenyl)-2,6-diphenyl-4H-benzo[d][1,3]oxazine (4dab): colorless oil, 85 mg, yield: 45%.

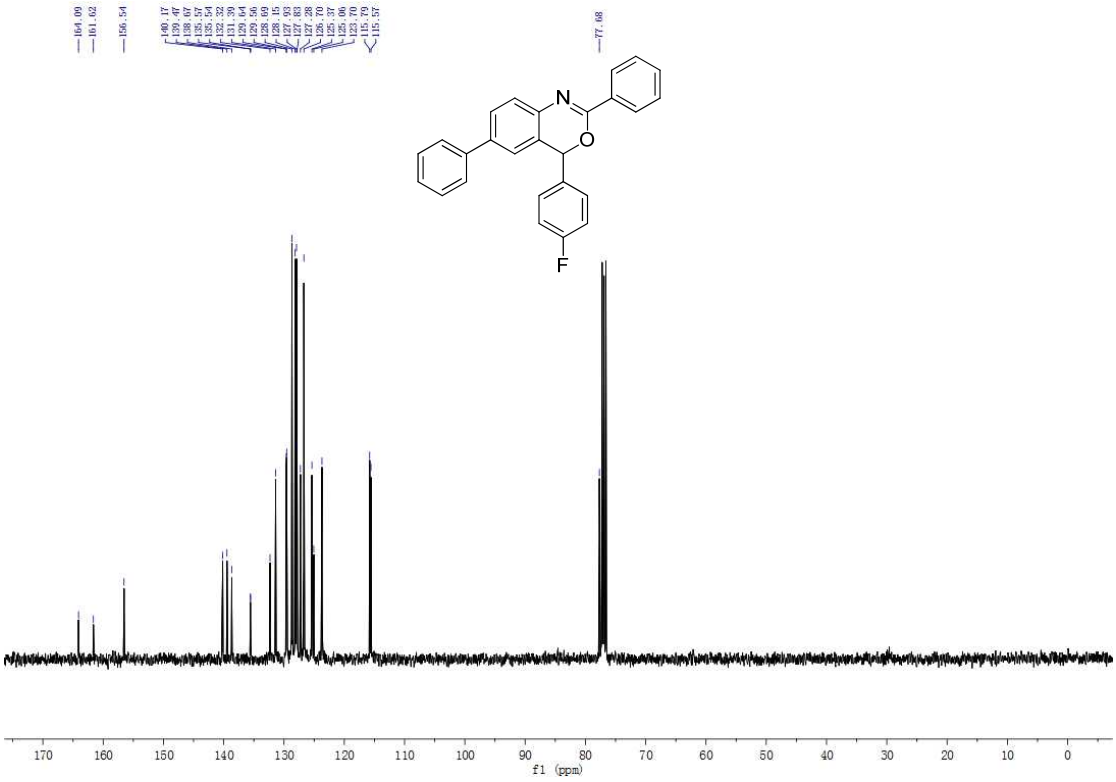
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.94 - 7.88 (m, 2H), 7.40 - 7.35 (m, 1H), 7.29 (dd, J = 7.2, 1.1 Hz, 2H), 7.26 - 7.22 (m, 2H), 7.19 (tdd, J = 6.6, 4.1, 2.4 Hz, 6H), 7.12 - 7.06 (m, 1H), 6.88 – 6.79 (m, 3H), 6.25 (s, 1H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ162.9 (d, J = 248.0 Hz), 156.5, 140.2, 139.5, 138.7, 135.6 (d, J = 2.9 Hz), 132.3, 131.4, 129.6 (d, J = 8.4 Hz, 2×CH), 128.7(2×CH), 128.2(2×CH), 127.9(2×CH), 127.8, 127.3, 126.7(2×CH), 125.4(2×CH), 125.1, 123.7, 115.7 (d, J = 21.7 Hz, 2×CH), 77.7.

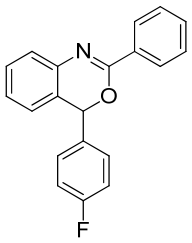
ESI-HRMS: m/z calcd for C26H18FNO $[M+H]^{+}$:380.1372; found:380.1371.

GC-MS：379.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



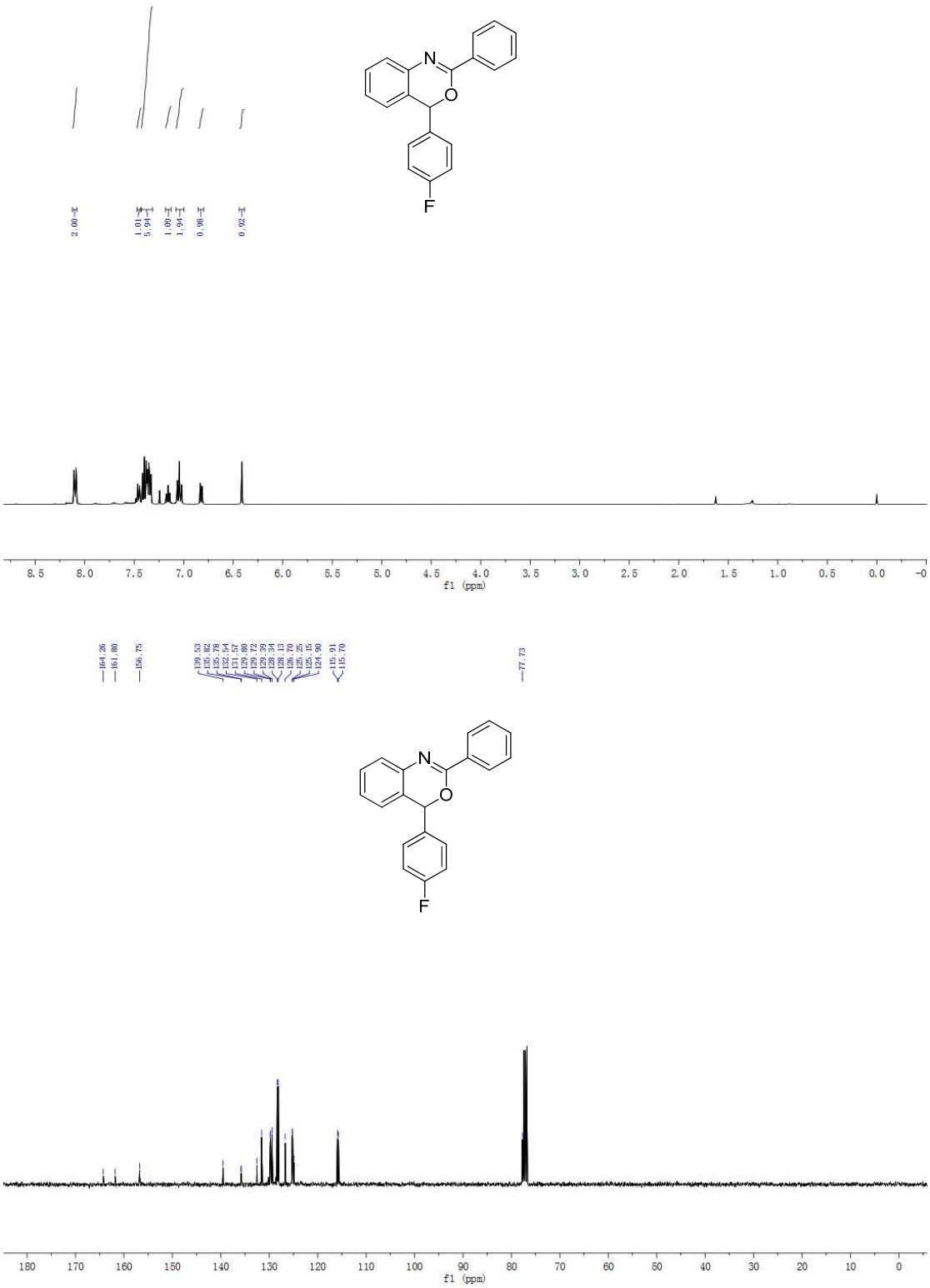
4-(4-fluorophenyl)-2-phenyl-4H-benzo[d][1,3]oxazine (4eab): colorless oil, 97 mg, yield: 64%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.13 - 8.08 (m, 2H), 7.45 (t, J = 6.9 Hz, 1H), 7.43 - 7.31 (m, 6H), 7.16 (dd, J = 10.3, 4.4 Hz, 1H), 7.04 (t, J = 8.6 Hz, 2H), 6.82 (d, J = 7.7 Hz, 1H), 6.41 (s, 1H).

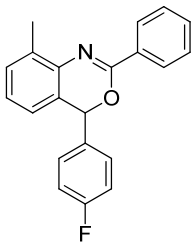
^{13}C NMR (101 MHz, CHLOROFORM-D) δ163.0 (d, J = 247.9 Hz), 156.8, 139.5, 135.8 (d, J = 3.3 Hz), 132.5, 131.6, 129.8 (d, J = 8.3 Hz，2×CH), 129.4, 128.3(2×CH), 128.1 (2×CH), 126.7, 125.3, 125.2, 124.9, 115.8 (d, J = 21.5 Hz，2×CH), 77.7.

ESI-HRMS: m/z calcd for C20H14NO $[M+H]^{+}$:304.1059; found:304.1062.

GC-MS：303.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



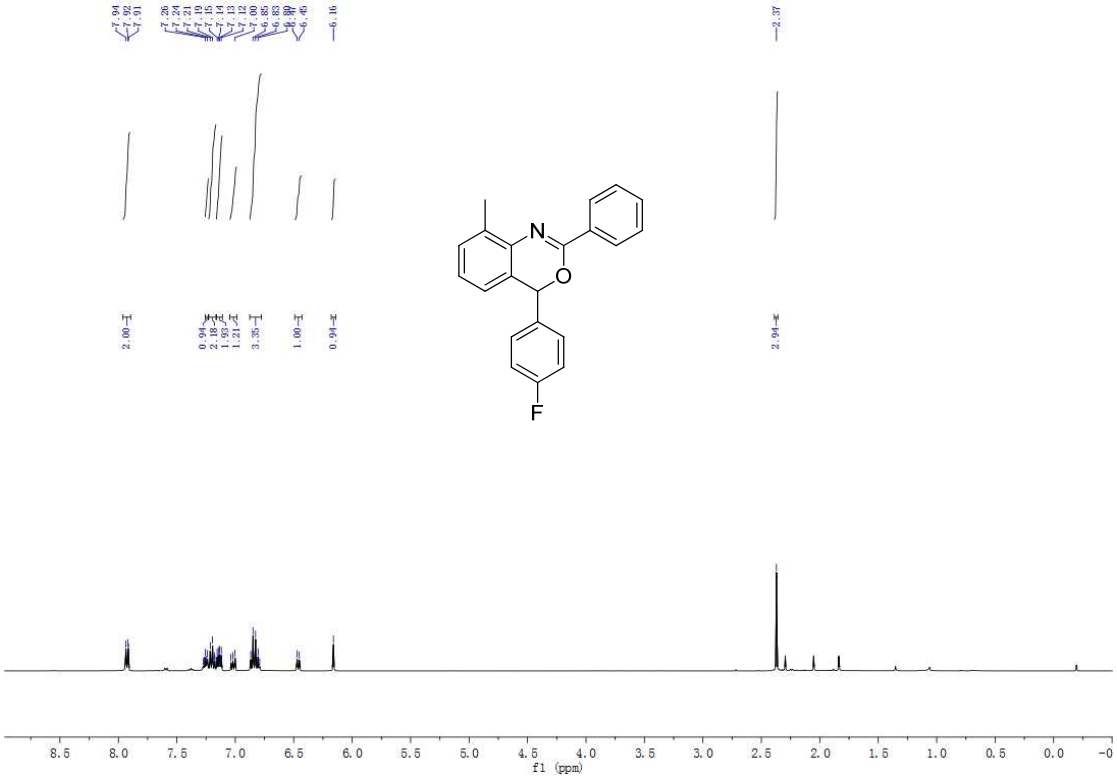
4-(4-fluorophenyl)-8-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (4fab): colorless oil, 84 mg, yield: 53%.

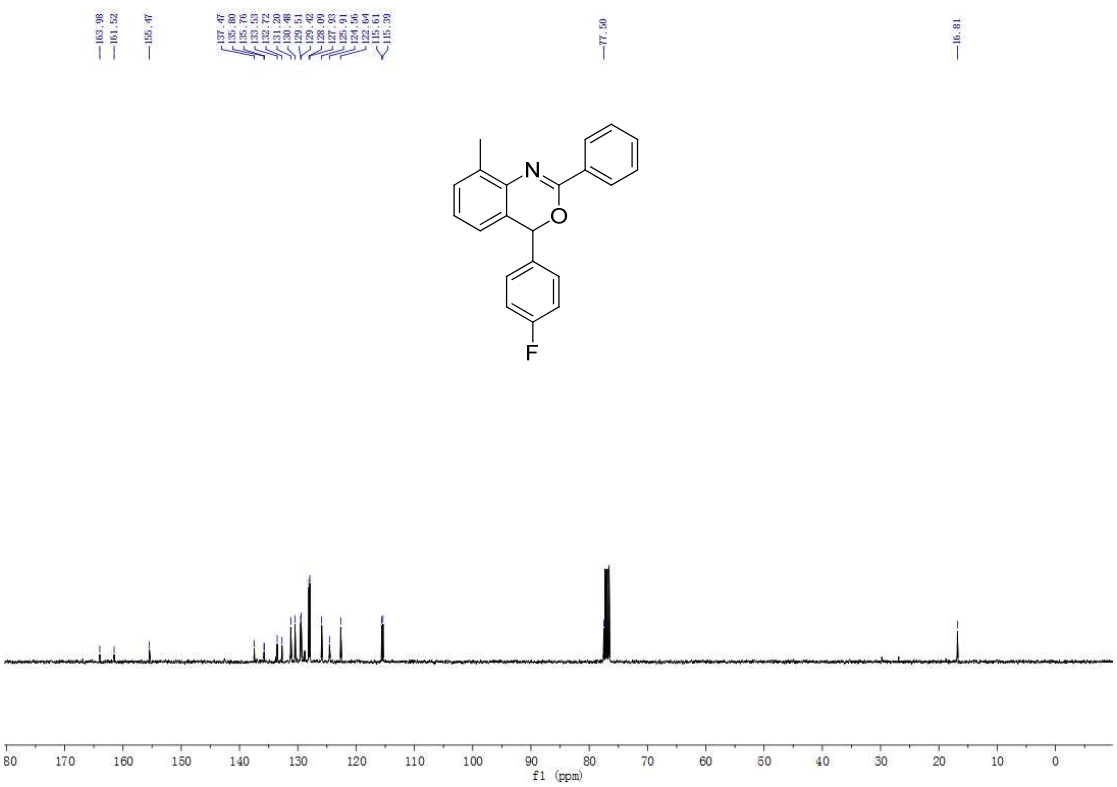
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.96 - 7.90 (m, 2H), 7.26 - 7.23 (m, 1H), 7.19 (dd, J = 11.6, 4.6 Hz, 2H), 7.16 - 7.11 (m, 2H), 7.05 - 6.99 (m, 1H), 6.82 (dt, J = 7.0, 6.5 Hz, 3H), 6.46 (d, J = 7.3 Hz, 1H), 6.16 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ162.8 (d, J = 247.6 Hz), 155.5, 137.5, 135.8 (d, J = 3.2 Hz), 133.5, 132.7, 131.2, 130.5, 129.5 (d, J = 8.5 Hz, 2×CH), 128.1(2×CH), 127.9(2×CH), 125.9, 124.6, 122.6, 115.5 (d, J = 21.8 Hz, 2×CH), 77.5, 16.8.

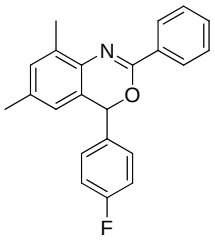
ESI-HRMS: m/z calcd for C21H16FNO $[M+H]^{+}$:318.1216; found:318.1218.

GC-MS：317.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



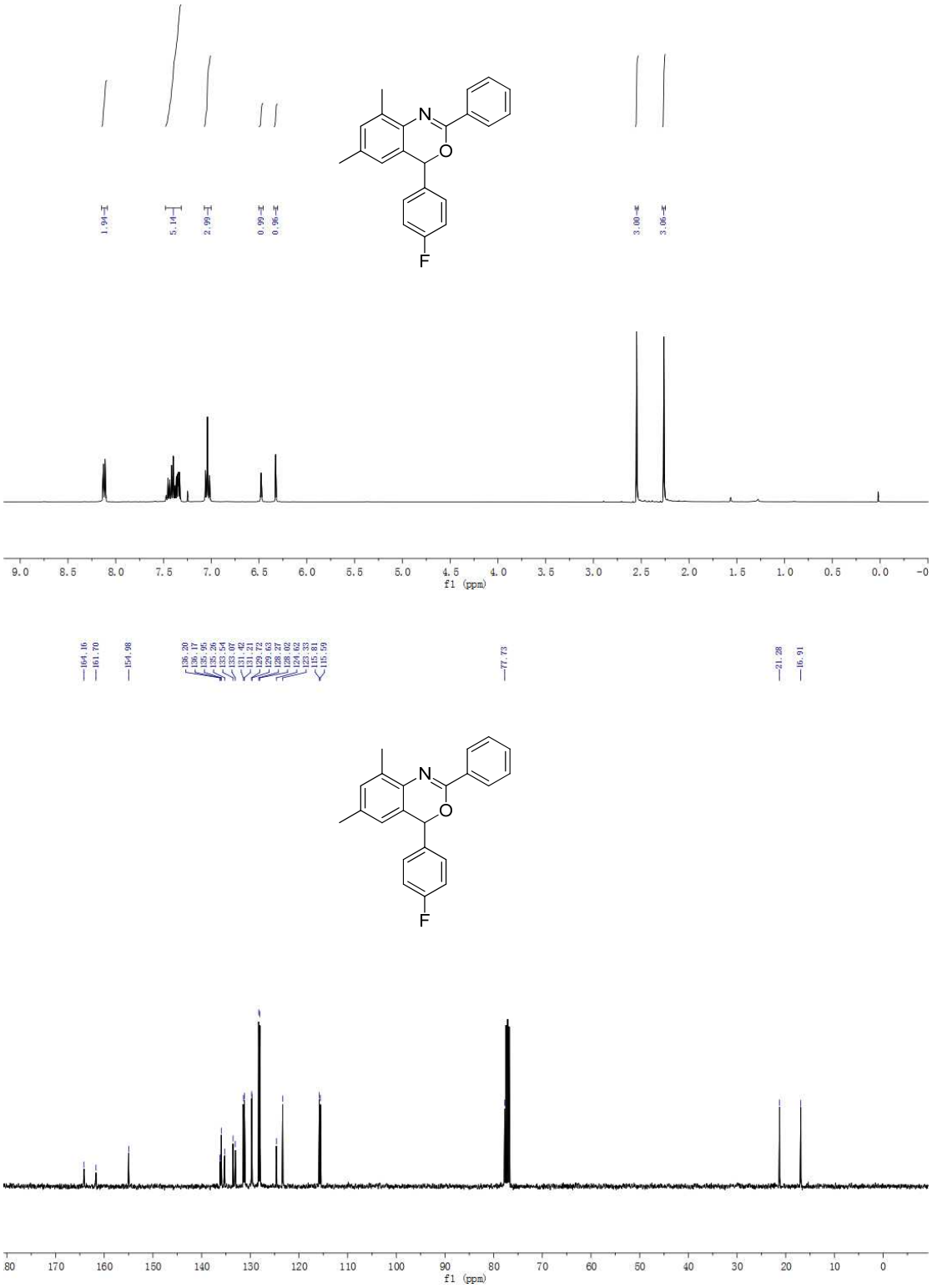
4-(4-fluorophenyl)-6,8-dimethyl-2-phenyl-4H-benzo[d][1,3]oxazine (4gab): colorless oil, 146 mg, yield: 88%.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.12 (dt, J = 8.5, 1.9 Hz, 2H), 7.48 - 7.31 (m, 5H), 7.07 - 7.00 (m, 3H), 6.48 (s, 1H), 6.33 (s, 1H), 2.55 (s, 3H), 2.26 (s, 3H).

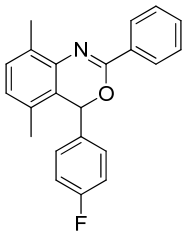
^{13}C NMR (101 MHz, CHLOROFORM-D) δ162.9 (d, J = 247.6 Hz), 155.0, 136.2 (d, J = 2.9 Hz), 136.0, 135.3, 133.5, 133.1, 131.4, 131.2, 129.7 (d, J = 8.4 Hz，2×CH), 128.3(2×CH), 128.0 (2×CH), 124.6, 123.3, 115.7 (d, J = 21.7 Hz，2×CH), 77.7, 21.3, 16.9.

ESI-HRMS: m/z calcd for C22H18FNO $[M+H]^{+}$:332.1372; found:332.1374.

GC-MS：331.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



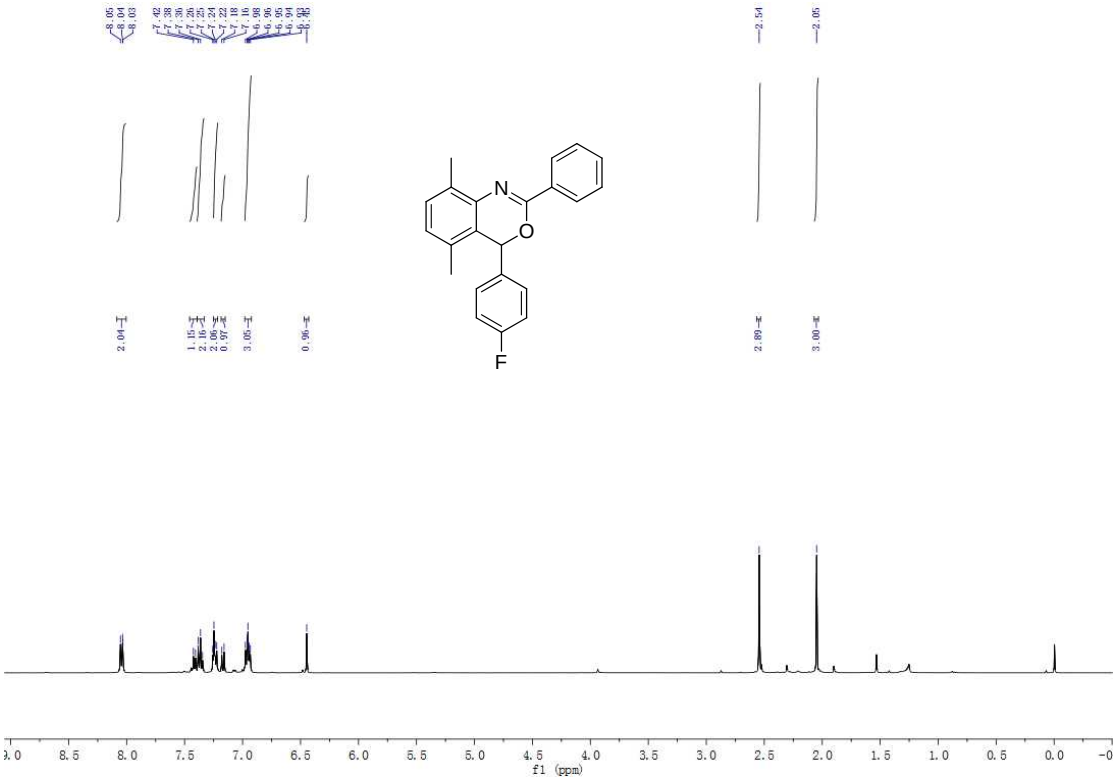
4-(4-fluorophenyl)-5,8-dimethyl-2-phenyl-4H-benzo[d][1,3]oxazine (4hab): colorless oil, 66 mg, yield: 40%.

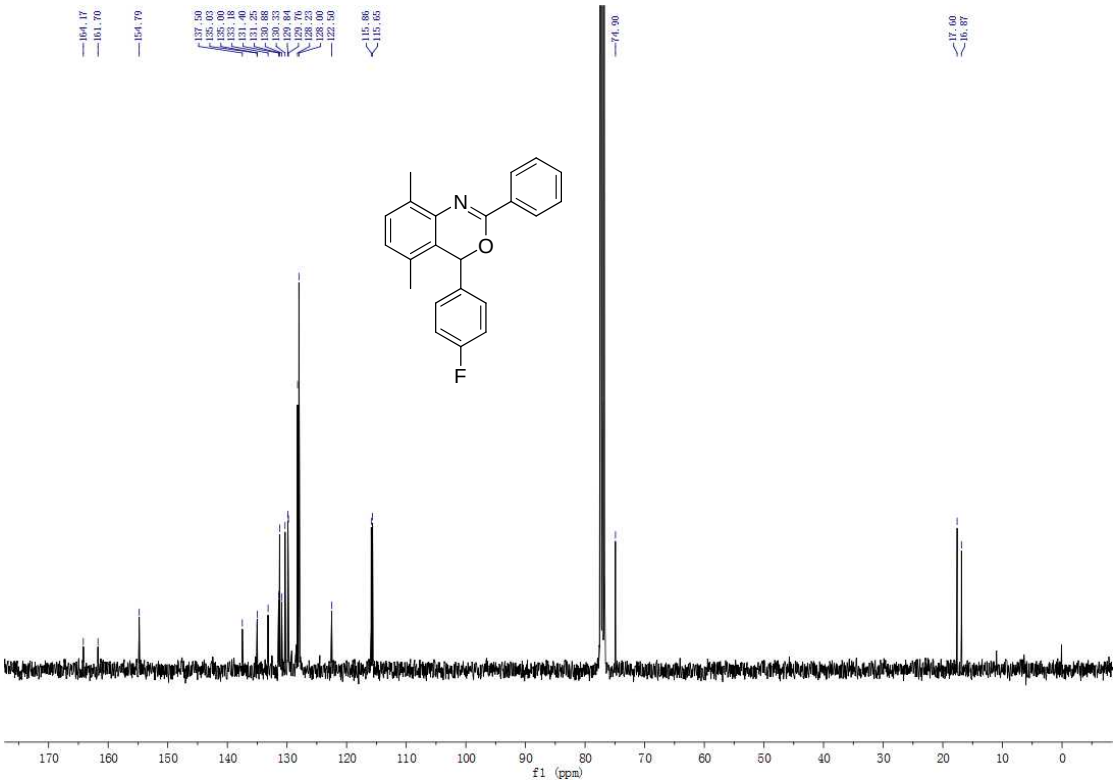
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.08 - 8.00 (m, 2H), 7.42 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.25 - 7.21 (m, 2H), 7.17 (d, J = 7.7 Hz, 1H), 6.98 - 6.92 (m, 3H), 6.45 (s, 1H), 2.54 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ162.9 (d, J = 247.5 Hz), 154.8, 137.5, 135.0 (d, J = 3.0 Hz), 133.2, 131.4, 131.3, 130.9, 130.3, 129.8 (d, J = 8.5 Hz，2×CH), 128.2(2×CH), 128.0(3×CH), 122.5, 115.8 (d, J = 21.8 Hz，2×CH), 74.9, 17.6, 16.87.

ESI-HRMS: m/z calcd for C22H18FNO $[M+H]^{+}$:332.1372; found:332.1371.

GC-MS：331.





^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

Reference:

1 (a) E. Skucas and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2012, **134**, 9090; (b) M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal.*, 2007, **349**, 2610; (c) M. Bielawski and B. Olofsson, *Chem. Commun.*, 2007, 2521; (d) Bielawski and B. Olofsson, *Org. Synth.*, 2009, **86**, 308.