Regioselective Synthesis of Oxazole Derivatives *via* Palladium-Catalyzed and Copper-Mediated Cascade Oxidative Cyclization

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Supporting Information

A. General methods

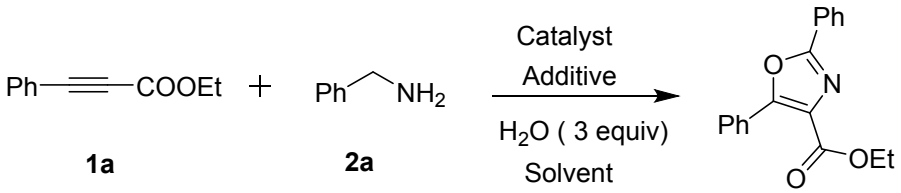
^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer.

B. General procedure for the synthesis of oxazole derivatives

Propargyl ester (0.5 mmol), benzylamine (0.75 mmol), H_2O (1.5 mmol) were added to 1.5 mL DMSO. Then $Pd(CH_3CN)_2Cl_2$ (5 mol%) and $CuBr_2$ (2 equiv) were added and the mixture was stirred under air at 100 ^{o}C for 8 h. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was eventually purified by flash column chromatography (EtOAc: Petroleum=1:15) on a silica gel to afford the product.

C. Screening reaction conditions

Table 1. Survey of reaction conditions for reaction [a]



1a **2a** **3aa**

entry	catalyst	additive	solvent	yields[b]
1	$Pd(OAc)_2$	-	DMF	N.D.
2	$Pd(OAc)_2$	-	DMSO	3%
3	$Pd(OAc)_2$	$CuCl_2$	DMSO	18%
4	-	$CuCl_2$	DMSO	Trace
5	$Pd(OAc)_2$	K_2CO_3	DMSO	N.D.
6[c]	$Pd(OAc)_2$	DABCO	DMSO	N.D.
7[c]	$Pd(OAc)_2$	HOAc	DMSO	N.D.
8	$Pd(OAc)_2$	$ZnCl_2$	DMSO	N.D.
9	$Pd(OAc)_2$	$FeCl_3$	DMSO	N.D.
10	$Pd(OAc)_2$	$LiCl_2$	DMSO	N.D.
11	$Pd(OAc)_2$	$CuCl_2$	CH_3CN	N.D.
12	$Pd(OAc)_2$	$CuCl_2$	1,4-Dioxane	N.R.
13	$Pd(OAc)_2$	$CuCl_2$	THF	N.R.
14	$Pd(OAc)_2$	$CuCl_2$	DCE	N.R.
15	$Pd(OAc)_2$	$CuCl_2$	Toluene	N.D.
16	$Pd(OAc)_2$	$CuBr_2$	DMSO	30%
17	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO	N.D.
18	$Pd(OAc)_2$	$Cu(OTf)_2$	DMSO	N.D.

19	$Pd(OAc)_2$	CuF_2	DMSO	N.D.
20	$PdCl_2$	$CuBr_2$	DMSO	52%
21	$PdBr_2$	$CuBr_2$	DMSO	50%
22	$Pd(TFA)_2$	$CuBr_2$	DMSO	23%
23	$Pd(dba)_2$	$CuBr_2$	DMSO	11%
24	$Pd(PPh_3)_2Cl_2$	$CuBr_2$	DMSO	58%
25	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	63%
26[c]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	72%
27[d]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	56%
28[c, e]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	81% (75%)[f]
29[c, e, g]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	80%
30[c, e, h]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	N.P.
31[c, e, i]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	78%
32[c, e, j]	$Pd(CH_3CN)_2Cl_2$	$CuBr_2$	DMSO	39%

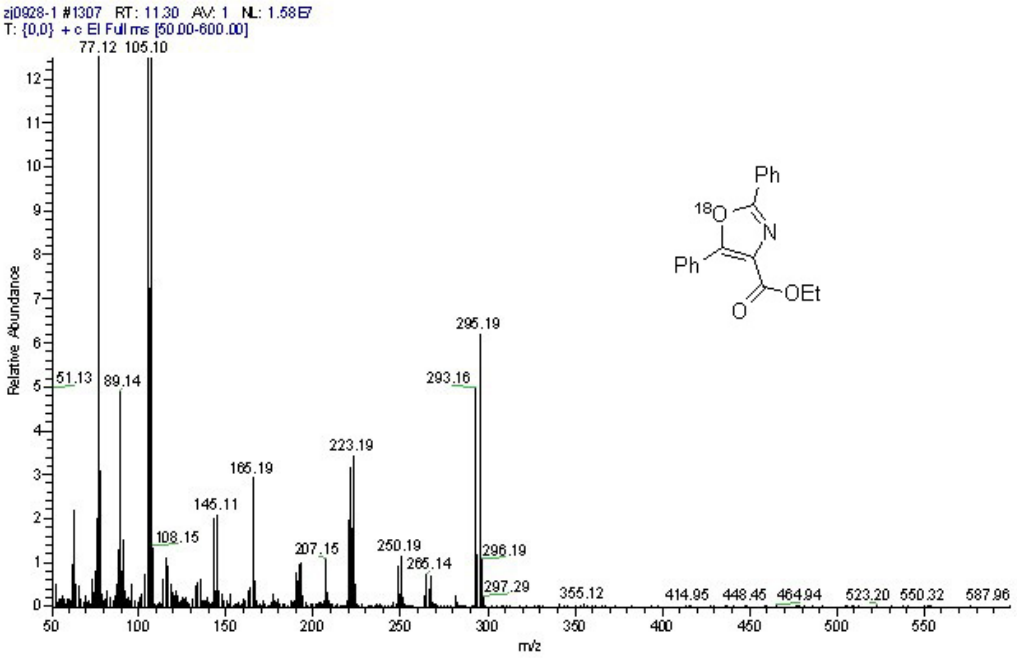
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), H_2O (1.5 mmol), catalyst (10 mol%) and additive (1equiv) in 1.5 mL of solvent under O_2 (1 atm) at 100 °C for 8 h. [b] Determined by GC. [c] 5 mol% of catalyst. [d] 2 mol% of catalyst. [e] 2 equiv of additive. [f] Isolated yield. [g] Under an air atmosphere. [h] at 50°C. [i] at 120°C. [j] Under an N_2 atmosphere.

We began our studies with the model reaction of ethyl phenylpropiolate (**1a**) and benzylamine (**2a**). With $Pd(OAc)_2$ as the catalyst under oxygen atmosphere (1 atm), no desired product was obtained in DMF while 3% yield of **3aa** in DMSO (Table 1, entries 1, 2). In other to optimize the conditions, different additives were tested and the yield of **3aa** was increased to 18% and 30% when $CuCl_2$ and $CuBr_2$ was used respectively (Table 1, entries 3 and 16). Palladium catalyst was crucial because we only got trace amount of product in the absence of palladium (Table 1, entry 4). Other additives showed no efficiency to this reaction (Table 1, entries 4-10, 17-19). Further investigation revealed that among the solvents we chose, this transformation could only go smoothly in DMSO (Table 1, entries 11-15). Subsequently, the effect of different palladium catalysts was surveyed (Table 1, entries 20-25). $Pd(CH_3CN)_2Cl_2$ turned to be an efficient catalyst and 63% yield of the product was achieved (Table 1, entry 25). When the mount of catalyst and additive switched to 5% and 2 equiv, 75% isolated yield the corresponding product **3aa** could be obtained (Table 1, entries 26-28). Then we found it worked equally well when performed under air (Table 1, entry 29). However, oxygen also promoted this reaction since the yield decreased to 39% under argon atmosphere (Table 1, entry 32).

D. Control Experiments

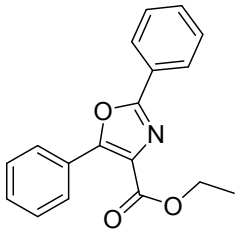
Procedure for ^{18}O-labeling experiment

Ethyl phenylpropiolate **1a** (0.5 mmol), benzylamine **2a** (0.75 mmol), $H_2{}^{18}O$ (1.5 mmol) were added to 1.5 mL DMSO. Then $Pd(CH_3CN)_2Cl_2$ (5 mol%) and $CuBr_2$ (2 equiv) were added and the mixture was stirred under air at 100 ^oC for 8 h. Then, water was added to the mixture and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was eventually purified by flash column chromatography (EtOAc: Petroleum=1:15) on a silica gel to afford the product.



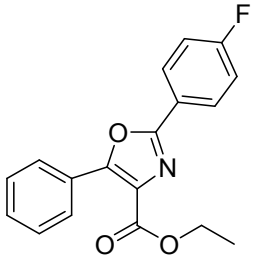
E. Analytical data for 3aa-3oa

ethyl 2,5-diphenyloxazole-4-carboxylate (3aa)[1]



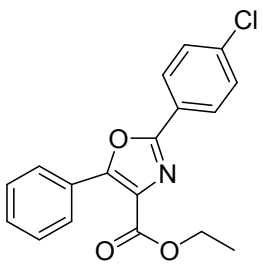
Yellow solid. M.p.: 70-71 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 6.7, 2.9 Hz, 2H), 8.03 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.50-7.32 (m, 6H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.31, 159.84, 155.07, 131.06, 130.27, 128.81, 128.57, 128.40, 128.35, 127.18, 126.89, 126.44, 61.47, 14.29. ppm; MS (EI, 70 eV) *m/z*: 77, 105, 221, 293. IR (KBr): 3062, 2982, 1720, 1562, 1488, 1215, 1098, 1448, 1243, 1056, 928, 765, 710, 688.

ethyl 2-(4-fluorophenyl)-5-phenyloxazole-4-carboxylate (3ab)



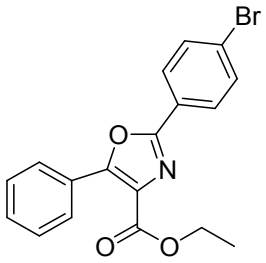
Yellow solid. M.p.: 115-117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.04 (m, 2H), 8.01 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.47 -7.38 (m, 3H), 7.10 (t, *J* = 8.7 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5(d, *J* = 250 Hz), 162.2, 159.0, 155.1, 130.0, 129.1, 129.0, 128.4(d, *J* = 20 Hz), 128.3, 127.6, 122.8(d, *J* = 3 Hz), 116.1(d, *J* = 22 Hz), 61.5, 14.3ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -108.1 (m, 1F) ppm. MS (EI, 70 eV) *m/z*: 77, 105, 123, 239, 311. HRMS (ESI) m/z: calcd for $C_{18}H_{14}FNNaO_3$ $[M+Na]^+$, 334.0850; found,334.0863. IR (KBr): 3070, 2983, 1720, 1609, 1563, 1497, 1218, 1097, 824, 760, 692.

ethyl 2-(4-chlorophenyl)-5-phenyloxazole-4-carboxylate (3ac)[2]



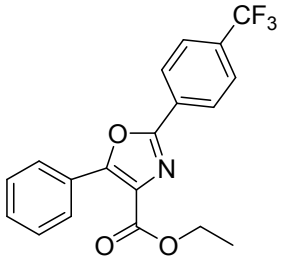
White solid. M.p.: 100-102 ºC.[1]H NMR (400 MHz, $CDCl_3$) δ 8.19-7.99 (m, 4H), 7.53-7.41 (m, 5H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ =162.1, 158.8, 155.2, 137.3, 130.4, 129.2, 128.5, 128.4, 128.3, 128.1, 126.9, 124.9, 61.5, 14.3 ppm; MS (EI, 70 eV) *m/z*: 77, 105, 139, 255, 327. IR (KBr): 2983, 1719, 1495, 1269, 1213, 1092, 757.

ethyl 2-(4-bromophenyl)-5-phenyloxazole-4-carboxylate (3ad)



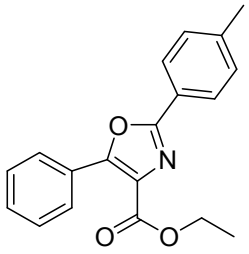
White solid. M.p.: 97-98 ºC. [1]H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.9 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.53-7.43 (m, 3H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ = 162.1, 158.9, 155.3, 132.1, 130.4, 128.6, 128.4, 128.2, 126.9, 125.7, 125.3, 61.5, 14.2ppm; MS (EI, 70 eV) *m/z*: 77, 105, 182, 301, 371. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ $[M+Na]^+$, 394.0049; found,394.0026. IR (KBr): 2923, 1720, 1604, 1560, 1484, 1214, 1097, 1013, 822, 757, 692.

ethyl 2-(4-(trifluoromethyl)phenyl)-5-phenyloxazole-4-carboxylate(3ae)



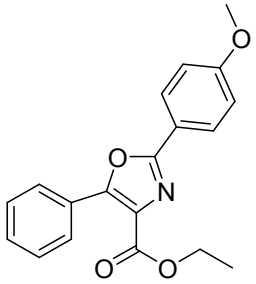
White solid. M.p.: 101-103 ºC.[1]H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 2H), 8.06-7.95 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.46- 7.32 (m, 3H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).[13]C NMR (100 MHz, $CDCl_3$) δ = 162.0, 158.3, 155.7, 132.5 (q, *J* = 33 Hz), 130.6, 129.6, 128.6, 128.5, 127.0, 126.8, 125.8 (q, *J* = 3.7 Hz,), 125.1, 122.4, 61.6, 14.2ppm. [19]F NMR (376 MHz, $CDCl_3$) δ: -62.9 (s, 3F) ppm. MS (EI, 70 eV) *m/z*:77, 105, 145, 173, 361. HRMS (ESI) m/z: calcd for $C_{19}H_{14}F_3NNaO_3$ $[M+Na]^+$, 384.0818; found,384.0823. IR (KBr): 2965, 1722, 1619, 1563, 1495, 1322, 1127, 847, 756, 709.

ethyl 5-phenyl-2-p-tolyloxazole-4-carboxylate (3af)[3]



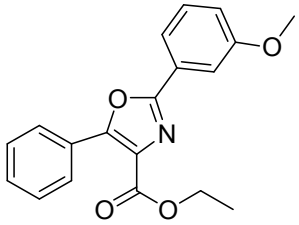
White solid. M.p.: 84-86 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.07 (m, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.54-7.40 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 160.1, 154.8, 141.5, 130.2, 129.5, 128.5, 128.4, 128.2, 127.2, 126.8, 123.7, 61.4, 21.6, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 91, 119, 235, 307. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_3$ $[M+Na]^+$, 330.1101; found,330.1102. IR (KBr): 2981, 2925, 1718, 1613, 1588, 1497, 1213, 1098, 1025, 760, 692.

ethyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3ag)[3]



Yellow solid. M.p.: 77-78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.00 (m, 4H), 7.52 - 7.43 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4 161.9, 133.5, 130.1, 128.6, 128.5, 128.4, 128.3, 128.1, 127.3, 119.1, 114.3, 61.4, 55.4, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 135, 207, 323. IR (KBr): 2983, 1718, 1613, 1499, 1256, 1096, 756.

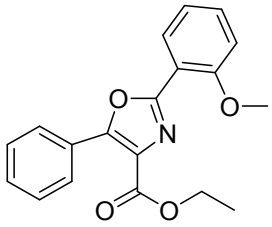
ethyl 2-(3-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3ah)



Orange solid. M.p.: 87-89 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.06 (m, 2H), 7.76-7.70 (m, 1H), 7.68 (dd, *J* = 2.3, 1.6 Hz, 1H), 7.54-7.45 (m, 3H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.08-7.02 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 159.9, 159.8, 155.1, 130.3, 129.9, 128.6, 128.4, 128.3, 127.6, 127.1, 119.3, 117.7, 111.5, 61.5, 55.5, 14.3 ppm; MS (EI, 70 eV)

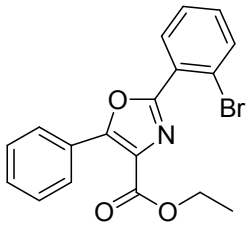
m/z: 77, 105, 135, 207, 323. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_4$ $[M+Na]^+$, 346.1050; found,346.1046. IR (KBr): 2924, 1719, 1596, 1564, 1098, 1037, 757.

ethyl 2-(2-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3ai)



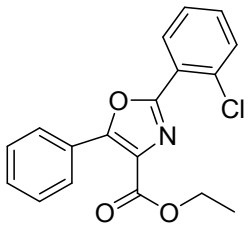
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.14 (m, 2H), 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54-7.42 (m, 4H), 7.06 (dd, *J* = 14.3, 7.8 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 1.0 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ162.5, 158.6, 158.0, 154.7, 132.4, 130.7, 130.1, 128.5, 128.4, 128.0, 127.4, 120.6, 115.6, 111.9, 61.3, 56.0, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 135, 249, 323. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_4$ $[M+Na]^+$, 346.1050; found,346.1063. IR (KBr): 2960, 1719, 1590, 1563, 1488, 1215, 1101, 1023, 913, 746, 694.

ethyl 2-(2-bromophenyl)-5-phenyloxazole-4-carboxylate (3aj)



Yellow solid. M.p.: 64-65 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.12 (m, 2H), 8.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.52-7.38 (m, 4H), 7.32 (td, *J* = 7.9, 1.7 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.2, 158.5, 155.7, 134.4, 132.0, 131.9, 130.4, 128.6, 128.5, 128.0, 127.6, 127.4, 127.0, 121.3, 61.5, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 185, 373. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ $[M+Na]^+$, 394.0049; found,394.0053. IR (KBr): 3064, 2982, 1720, 1565, 1491, 1464, 1217, 1101, 1025, 767, 731, 690

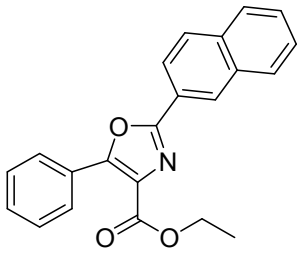
ethyl 2-(2-chlorophenyl)-5-phenyloxazole-4-carboxylate (3ak)



Yellow solid. M.p.: 74-75 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.05 (m, 2H), 8.03 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.35-7.25 (m, 2H), 4.37 (q, *J* = 7.1 Hz,

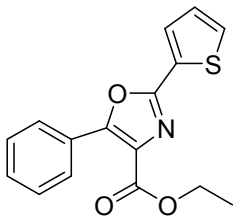
2H), 1.34 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.2, 158.0, 155.7, 132.8, 131.7, 131.6, 131.1, 130.4, 128.6, 128.4, 128.0, 127.0, 126.9, 125.6, 61.5, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 139, 206, 327. HRMS (ESI) m/z: calcd for $C_{18}H_{14}ClNNaO_3$ $[M+Na]^+$, 350.0554; found,350.0566. IR (KBr): 2982, 1719, 1564, 1489, 1268, 1015, 1099,756.

ethyl 2-(naphthalen-2-yl)-5-phenyloxazole-4-carboxylate (3al)



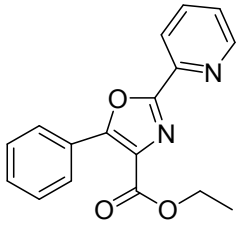
White solid. M.p.: 131-122 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 7.1 Hz, 1H), 8.20-8.11 (m, 2H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.60 – 7.41 (m, 5H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 159.8, 154.8, 133.9, 131.9, 130.3, 130.2, 128.6, 128.5, 128.4, 128.3, 127.9, 127.2, 126.5, 126.0, 124.9, 123.0, 61.4, 14.4ppm; MS (EI, 70 eV) *m/z*: 77, 105, 127, 155, 343. HRMS (ESI) m/z: calcd for $C_{22}H_{17}NNaO_3$ $[M+Na]^+$, 366.1101; found,366.1094. IR (KBr): 2983, 1717, 1551, 1490, 1265, 1222, 1097, 756.

ethyl 5-phenyl-2-(thiophen-2-yl)oxazole-4-carboxylate (3am)



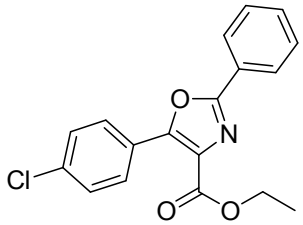
Yellow solid. M.p.: 72-74 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.82 (s, 1H), 7.54-7.42 (m, 4H), 7.14 (dd, *J* = 4.8, 3.7 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 156.1, 154.5, 130.2, 129.4, 129.1, 128.7, 128.5, 128.4, 128.2, 128.0, 126.9, 61.5, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 111, 226, 299. HRMS (ESI) m/z: calcd for $C_{16}H_{13}NNaO_3$ $[M+Na]^+$, 322.0508; found,322.0522. IR (KBr): 3079, 2982, 1720, 1594, 1492, 1209, 1093, 758, 722.

ethyl 5-phenyl-2-(pyridin-2-yl)oxazole-4-carboxylate (3an)



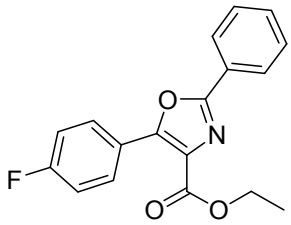
Yellow solid. M.p.: 126-128 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.5 Hz, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 8.19 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.89 (td, *J* = 7.8, 1.2 Hz, 1H), 7.54-7.48 (m, 3H), 7.45 (dd, *J* = 7.2, 5.1 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 158.4, 156.3, 150.0, 145.2, 137.1, 130.6, 130.0, 128.9, 128.3, 126.8, 125.3, 122.9, 61.5, 14.3ppm; MS (EI, 70 eV) *m/z*: 79, 106, 207, 294. HRMS (ESI) m/z: calcd for $C_{17}H_{14}N_2NaO_3$ $[M+Na]^+$, 317.0897; found,317.0891. IR (KBr): 2982, 2924, 1720, 1585, 1563, 1490, 1217, 1095, 756.

ethyl 5-(4-chlorophenyl)-2-phenyloxazole-4-carboxylate (3ba)



White solid. M.p.: 110-111 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 8.12 -8.07 (m, 2H), 7.47 (ddt, *J* = 11.3, 9.2, 2.2 Hz, 5H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =162.2, 159.9, 153.9, 136.3, 131.2, 129.8, 128.8, 128.7, 128.6, 126.9, 126.2, 125.6, 61.6, 14.3 ppm; MS (EI, 70 eV) *m/z*: 77, 105, 139, 255, 327. HRMS (ESI) m/z: calcd for $C_{18}H_{14}ClNNaO_3$ $[M+Na]^+$, 350.0554; found, 350.0556. IR (KBr): 2983, 1718, 1486, 1215, 1092, 753, 712.

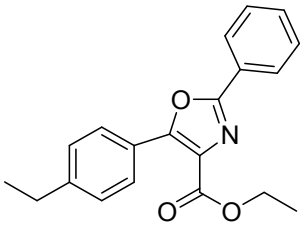
ethyl 5-(4-fluorophenyl)-2-phenyloxazole-4-carboxylate (3ca)



White solid. M.p.: 111-112 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.05 (m, 4H), 7.56 -7.41 (m, 3H), 7.18 (t, *J* = 8.7 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.0, 162.4(d, *J* = 190 Hz), 162.3, 159.7, 154.2, 131.1, 130.8(d, *J* = 9 Hz), 128.3, 128.1, 126.8, 126.3, 123.3(d, *J* = 3 Hz), 115.6(d, *J* = 22 Hz), 61.5, 14.3ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -109.1 (m, 1F) ppm. MS (EI, 70 eV) *m/z*: 77, 95, 105, 123, 239, 311. HRMS (ESI) m/z: calcd for

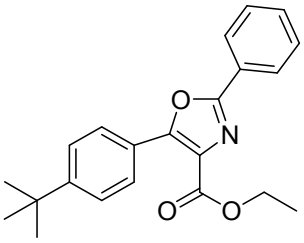
$C_{18}H_{14}FNNaO_3$ [M+Na]$^+$, 334.0850; found,334.0855. IR (KBr): 2983, 1712, 1600, 1501, 1451, 1229, 1090, 840, 705.

ethyl 5-(4-ethylphenyl)-2-phenyloxazole-4-carboxylate (3da)



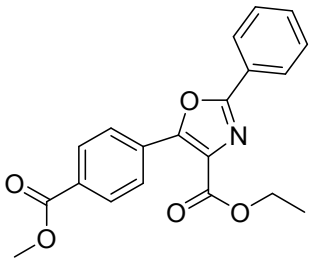
Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.6, 3.0 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.54-7.41 (m, 3H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 159.5, 155.4, 146.9, 130.9, 128.8, 128.6, 127.9, 127.8, 126.8, 126.5, 124.5, 61.4, 28.9, 15.3, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 133, 249, 321. HRMS (ESI) m/z: calcd for $C_{20}H_{19}NNaO_3$ [M+Na]$^+$, 344.1257; found, 344.1259. IR (KBr): 2967, 2932, 1721, 1569, 1503, 1452, 1215, 1094.

ethyl 5-(4-tert-butylphenyl)-2-phenyloxazole-4-carboxylate (3ea)



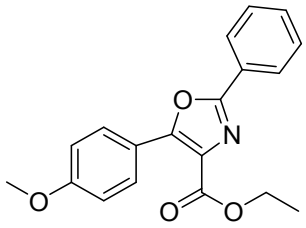
Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 3.6 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 5H), 7.50 – 7.46 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.37 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 155.4, 153.8, 146.9, 131.0, 128.8, 128.4, 127.9, 126.8, 126.5, 125.4, 124.3, 61.4, 43.9, 31.1, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 145, 334, 349. HRMS (ESI) m/z: calcd for $C_{22}H_{23}NNaO_3$ [M+Na]$^+$, 372.1570; found, 372.1576. IR (KBr): 2963, 1721, 1611, 1571, 1502, 1452, 1214, 1092, 710.

ethyl 5-(4-(methoxycarbonyl)phenyl)-2-phenyloxazole-4-carboxylate (3fa)



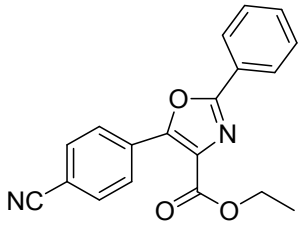
White solid. M.p.: 108-110 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 8.19 – 8.11 (m, 4H), 7.49 (d, *J* = 5.1 Hz, 3H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3, 162.0, 160.3, 153.5, 131.3, 131.2, 131.1, 129.6, 129.5, 128.8, 128.3, 126.9, 126.1, 61.7, 52.3, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 135, 163, 279, 351. HRMS (ESI) m/z: calcd for $C_{20}H_{17}NNaO_5$ $[M+Na]^+$, 374.0999; found, 374.998. IR (KBr): 2954, 1723, 1562, 1493, 1280, 1221, 1098, 1092, 711.

ethyl 5-(4-methoxyphenyl)-2-phenyloxazole-4-carboxylate (3ga) [4]



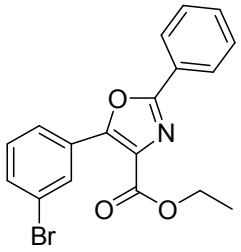
Yellow solid. M.p.: 128-130 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.6, 3.0 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 7.51-7.45 (m, 3H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 161.2, 159.2, 155.4, 130.9, 130.2, 131.1, 128.8, 127.1, 126.8, 126.5, 119.7, 113.9, 61.4, 55.4, 14.4ppm; MS (EI, 70 eV) *m/z*: 57, 77, 105, 135, 142, 207, 251, 323. IR (KBr): 2980, 2928, 1714, 1607, 1503, 1451, 1258, 1212, 1179, 1026, 747, 706.

ethyl 5-(4-cyanophenyl)-2-phenyloxazole-4-carboxylate (3ha)



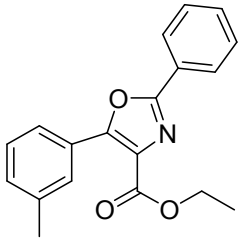
Yellow solid. M.p.: 113-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.26 (m, 2H), 8.16 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.81 -7.76 (m, 2H), 7.55-7.48 (m, 3H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.0, 160.8, 152.6, 132.2, 131.2, 130.4, 129.0, 128.8, 127.1, 125.9, 118.3, 113.4, 61.9, 14.3 ppm; MS (EI, 70 eV) *m/z*: 57, 77, 130, 207, 318. HRMS (ESI) m/z: calcd for $C_{19}H_{14}N_2NaO_3$ $[M+Na]^+$, 341.0897; found, 341.0897. IR (KBr): 2982, 2925, 2228, 1718, 1608, 1493, 1449, 1218, 1095, 709.

ethyl 5-(3-bromophenyl)-2-phenyloxazole-4-carboxylate (3ia)



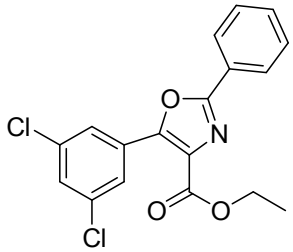
Yellow solid. M.p.: 82-84 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.19-8.11 (m, 2H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 3H), 7.36 (t, *J* = 8.0 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.0, 160.2, 153.1, 133.1, 131.3, 131.2, 129.9, 129.1, 129.0, 128.9, 127.1, 127.0, 126.1, 122.4, 61.7, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 105, 157, 183, 301, 373. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ $[M+Na]^+$, 394.0049; found, 394.0054. IR (KBr): 2985, 1721, 1562, 1477, 1221, 1108, 748.

ethyl 2-phenyl-5-*m*-tolyloxazole-4-carboxylate (3ja)



Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 6.2, 2.5 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.52-7.45 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.31-7.23 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H)..^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 159.8, 155.2, 138.1, 131.1, 131.0, 129.0, 128.8, 128.3, 128.2, 127.1, 126.9, 126.5, 125.8, 61.4, 21.5, 14.3ppm; MS (EI, 70 eV) *m/z*: 77, 91, 105, 119, 235, 307. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_3$ $[M+Na]^+$, 330.1011; found, 330.1012. IR (KBr): 2981, 2926, 1720, 1564, 1485, 1212, 1100, 711.

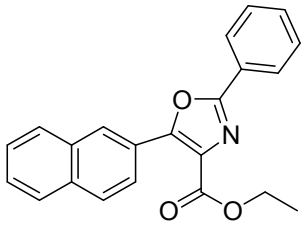
ethyl 5-(3,5-dichlorophenyl)-2-phenyloxazole-4-carboxylate (3ka)



Yellow solid. M.p.: 106-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.11 (m, 2H), 8.07 (d, *J* = 1.9 Hz, 2H), 7.56-7.45 (m, 3H), 7.43 (t, *J* = 1.8 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.8, 160.4, 151.7,

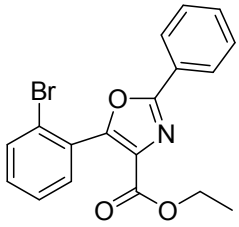
135.2, 131.5, 129.9, 129.8, 129.7, 128.9, 127.0, 126.6, 125.9, 61.9, 14.2ppm; MS (EI, 70 eV) *m/z*: 77, 105, 145, 173, 207, 361. HRMS (ESI) m/z: calcd for $C_{18}H_{13}Cl_2NNaO_3$ $[M+Na]^+$, 384.0165; found, 384.0162. IR (KBr): 2983, 2925, 1718, 1557, 1443, 1218, 1108, 798.

ethyl 5-(naphthalen-3-yl)-2-phenyloxazole-4-carboxylate (3la)



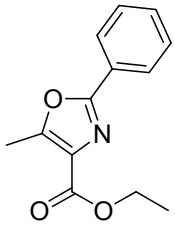
Grey solid. M.p.: 76-78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.23-8.16 (m, 2H), 8.13 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97-7.87 (m, 2H), 7.87-7.81 (m, 1H), 7.57-7.45 (m, 5H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.4, 159.9, 155.1, 133.9, 132.8, 131.1, 129.0, 128.9, 128.8, 128.6, 128.0, 127.7, 127.5, 126.9, 126.7, 126.5, 125.1, 124.5, 61.5, 14.4ppm; MS (EI, 70 eV) *m/z*: 77, 105, 127, 155, 343. HRMS (ESI) m/z: calcd for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$, 344.1257; found, 344.1271. IR (KBr): 3059, 2983, 2929, 1719, 1562, 1489, 1211, 1094, 751.

ethyl 5-(2-bromophenyl)-2-phenyloxazole-4-carboxylate (3ma)



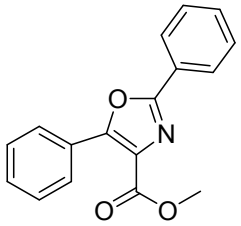
Yellow solid. M.p.: 100-102 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.12 (m, 2H), 7.72 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.52-7.33 (m, 5H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5, 161.1, 153.7, 133.1, 132.5, 131.6, 131.2, 130.8, 129.3, 128.8, 127.0, 126.9, 126.4, 123.9, 61.3, 14.0ppm; MS (EI, 70 eV) *m/z*: 77, 105, 142, 264, 292, 371. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ $[M+Na]^+$, 394.0049; found, 394.0056. IR (KBr): 2982, 2926, 1730, 1616, 1560, 1475, 1197, 1100, 757.

ethyl 5-methyl-2-phenyloxazole-4-carboxylate (3na) [5]



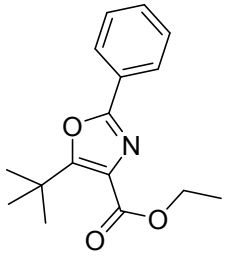
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 2H), 7.49-7.40 (m, 3H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 159.7, 156.1, 130.7, 128.8, 128.7, 126.7, 126.6, 61.0, 14.4, 12.2ppm; MS (EI, 70 eV) *m/z*: 77, 105, 185, 231. IR (KBr): 2984, 2924, 1720, 1615, 1563, 1486, 1102, 913, 744.

methyl 2,5-diphenyloxazole-4-carboxylate (3oa) [6]



White solid. M.p.: 71-73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.1, 1.4 Hz, 4H), 7.52-7.44 (m, 6H), 3.97 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 162.7, 123.6, 131.1, 130.4, 130.2, 128.9, 128.5, 128.0, 127.0, 126.8, 126.3, 52.4ppm; MS (EI, 70 eV) *m/z*: 77, 105, 165, 279. IR (KBr): 3063, 2950, 1723, 1564, 1489, 1443, 1223, 1102, 711, 689.

ethyl 5-(tert-butyl)-2-phenyloxazole-4-carboxylate (3pa) [1]



Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.94 (m, 2H), 7.41-7.35 (m, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.45 (s, 9H), 1.36 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5, 162.5, 157.8, 130.6, 128.7, 127.6, 126.7, 126.6, 61.2, 33.5, 28.2, 14.3ppm; MS (EI, 70 eV) *m/z*: 106, 212, 258, 273. IR (KBr): 2988, 1764, 1567, 1454, 1373, 1242.

F. Reference

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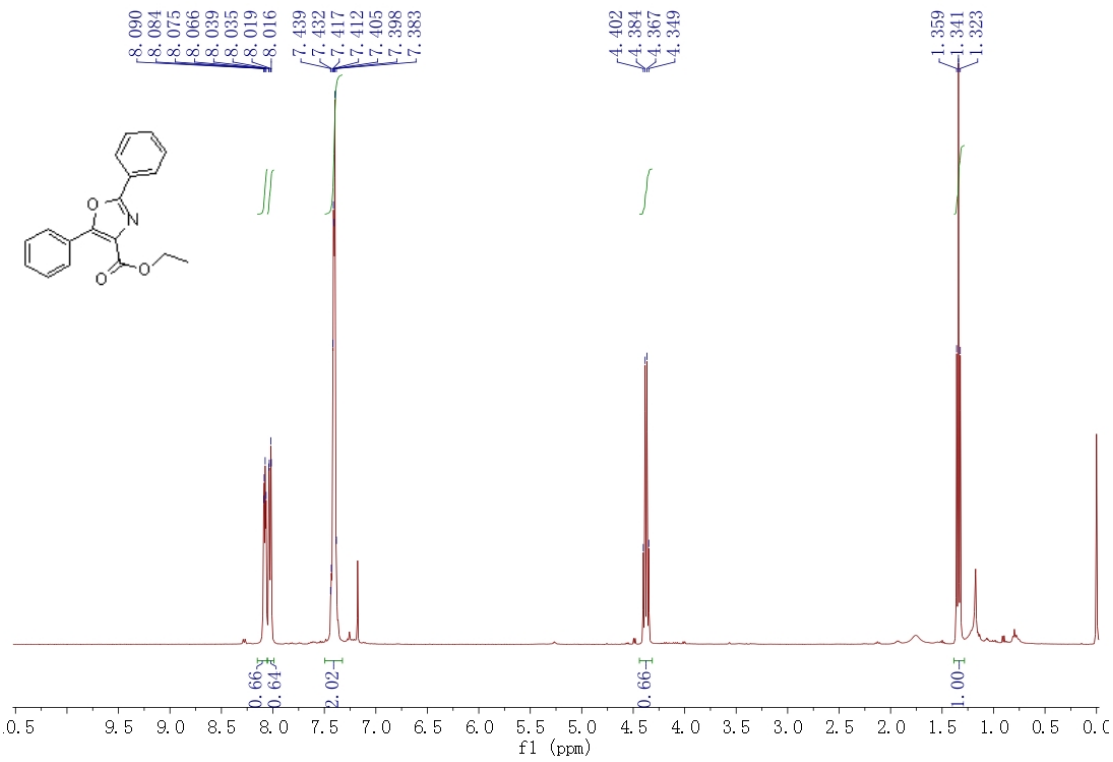
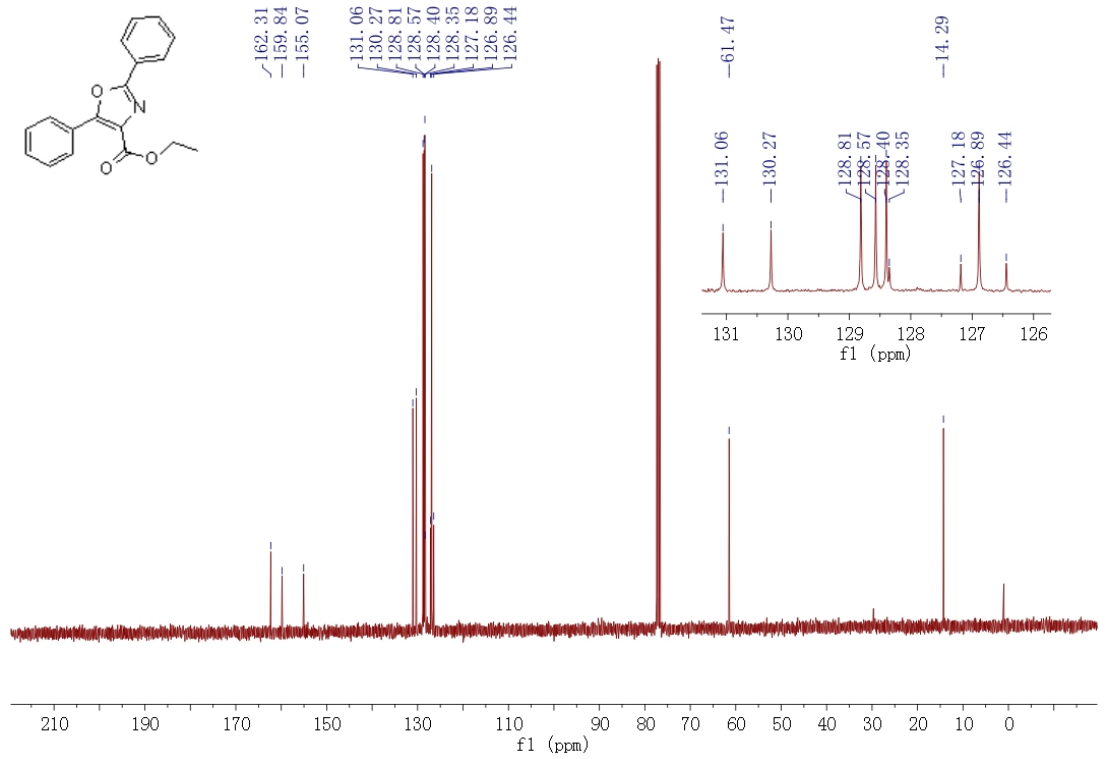
6. P. M. T. Ferreira, L. S. Monteiro and G. Pereira. *Eur. J. Org. Chem.*, 2008, 4676.

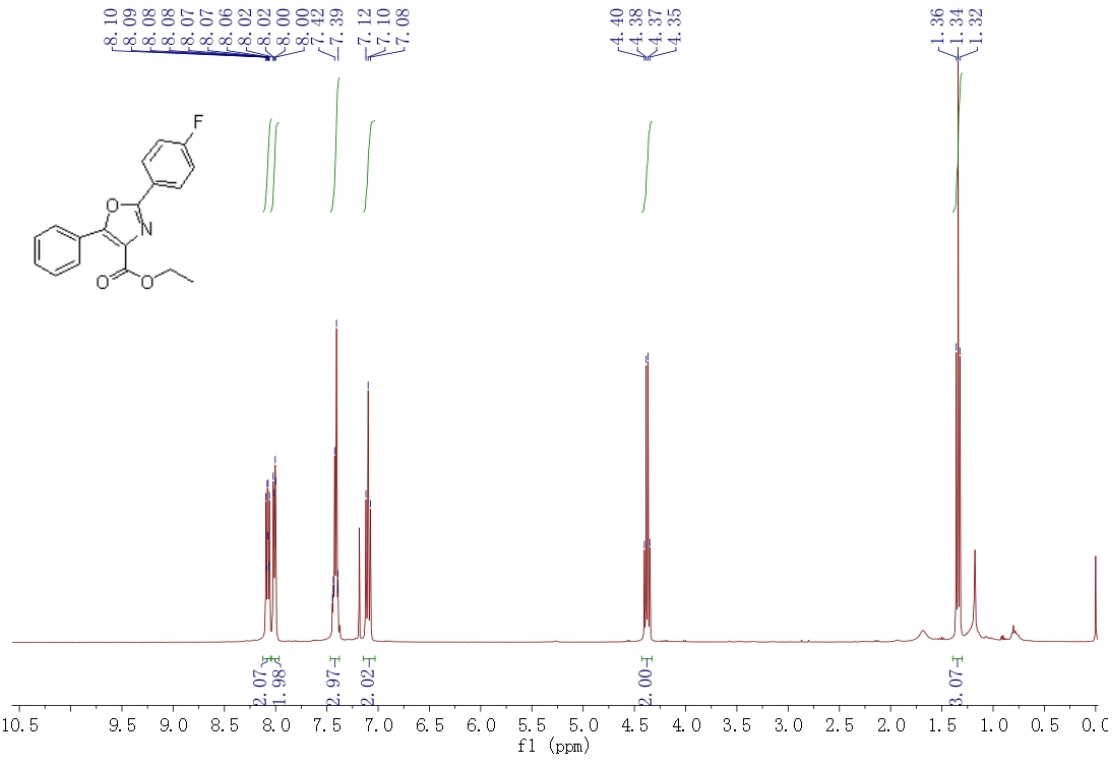
G. NMR Spectra



3aa-H



3aa-C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8.09
8.08
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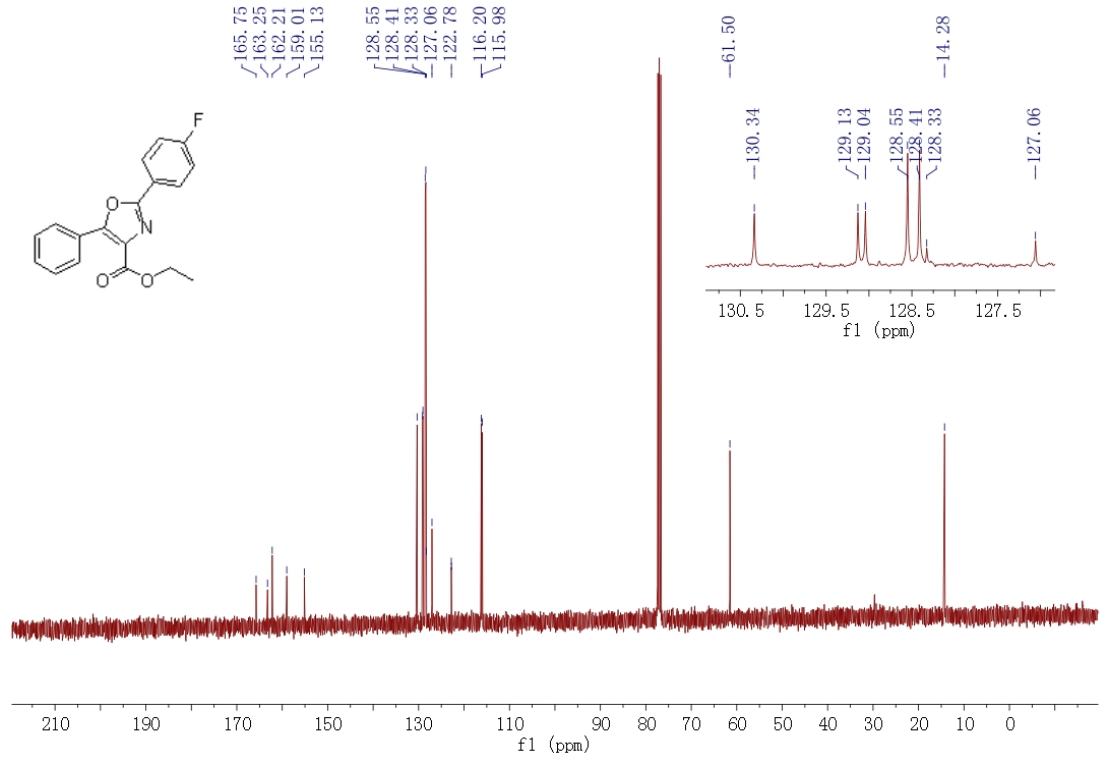
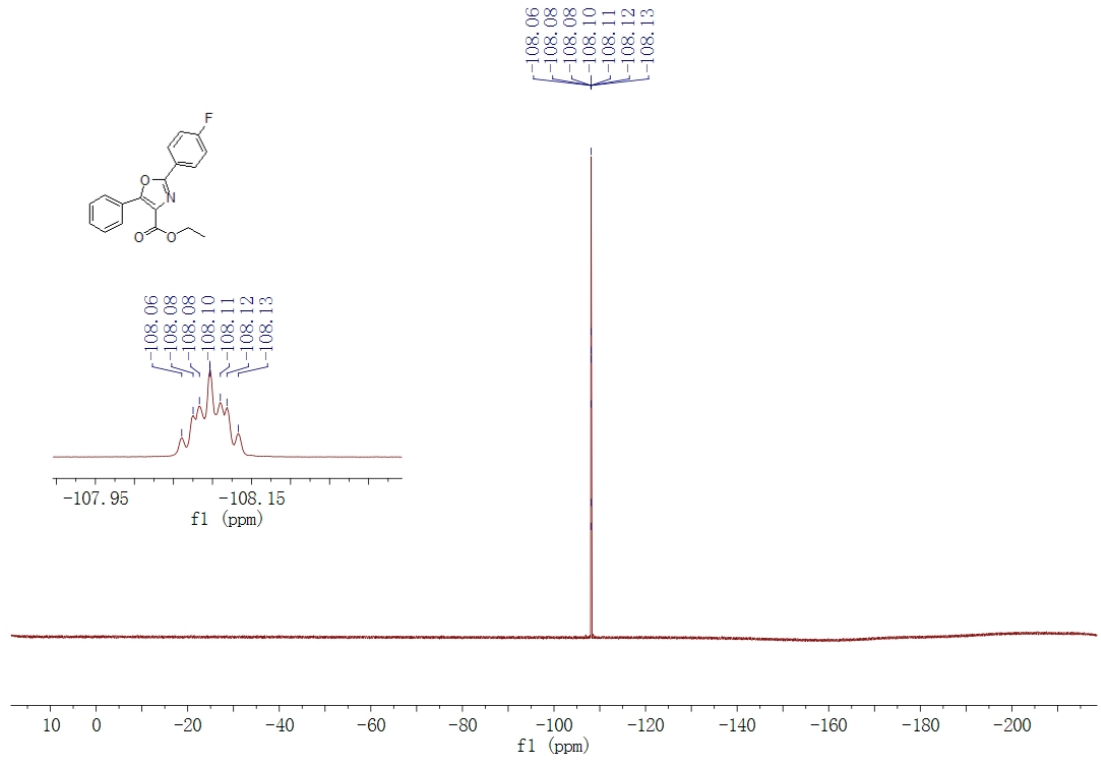
8.07
8.07
8.06
8.02
8.02
8.00
8.00
7.42
7.39
7.12
7.10
7.08
4.40
4.38
4.37
4.35
1.36
1.34
1.32
F
O
N
O
O
2.07
1.98
2.97
2.02
2.00
3.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

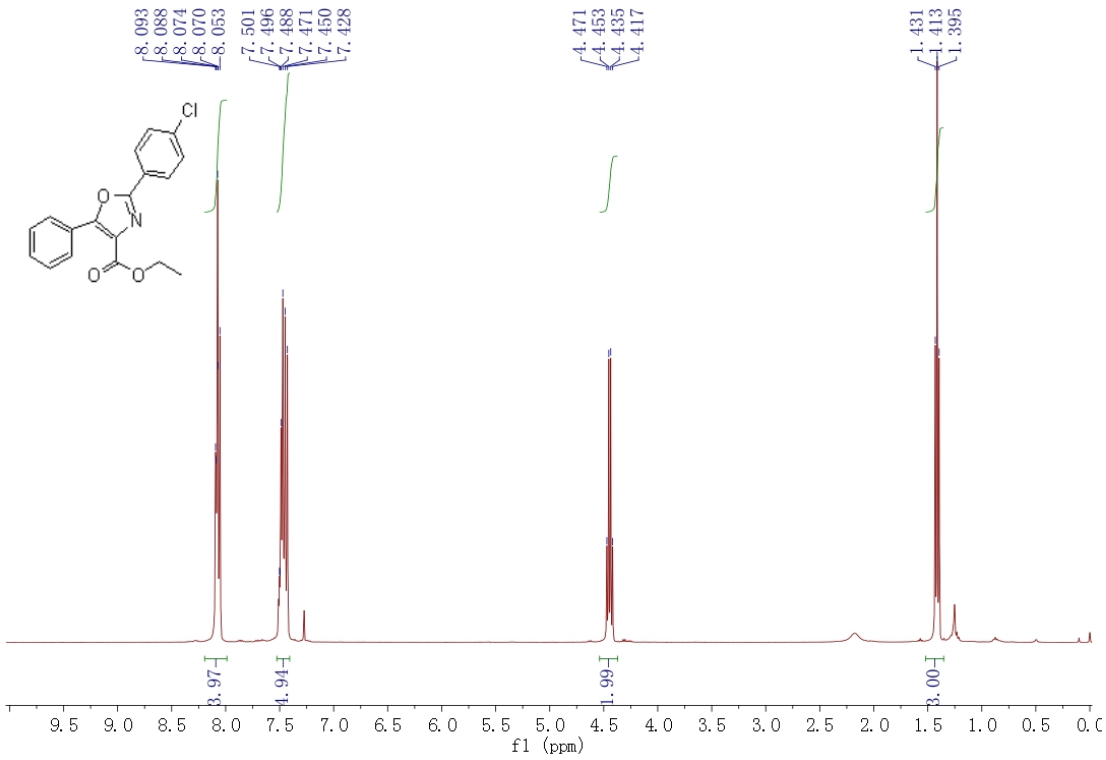
3ab-H


165.75
163.25
162.21
159.01
155.13
128.55
128.41
128.33
127.06
122.78
116.20
115.98
61.50
14.28
130.34
129.13
129.04
128.55
128.41
128.33
127.06
F
O
N
O
O
130.5
129.5
128.5
127.5
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ab-C


-108.06
-108.08
-108.08
-108.10
-108.11
-108.12
-108.13
F
O
N
O
O
-108.06
-108.08
-108.08
-108.10
-108.11
-108.12
-108.13
-107.95
-108.15
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

3ab-F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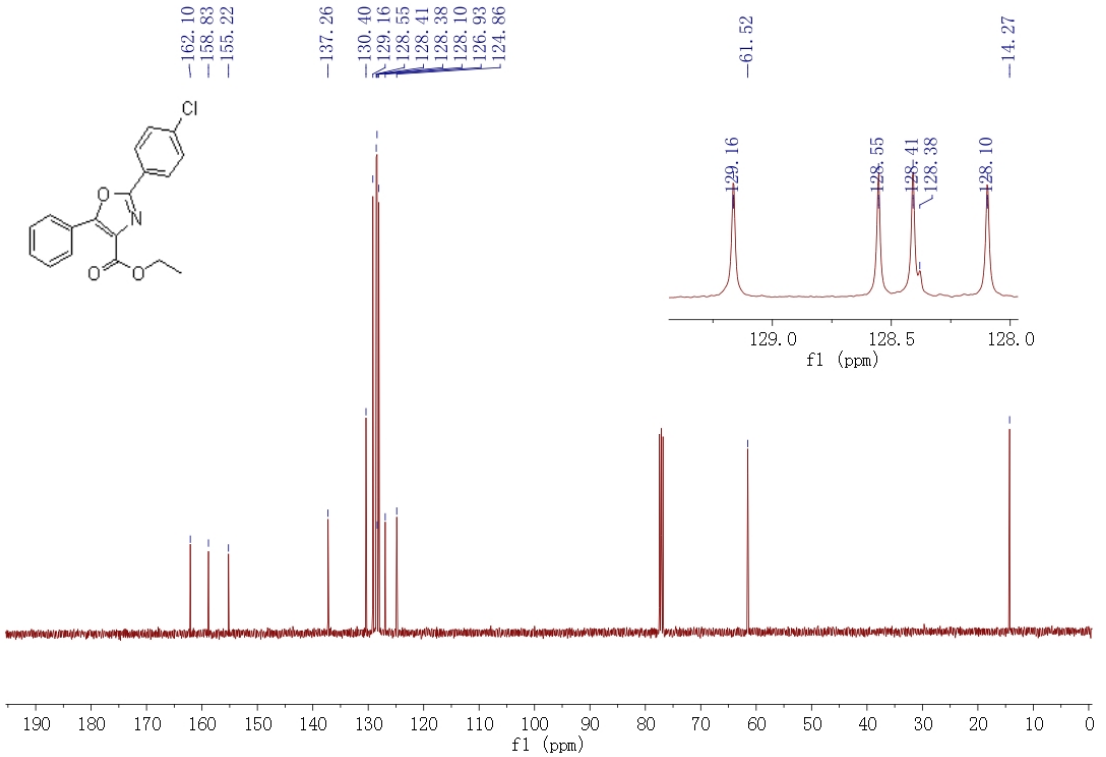
8.088
8.074
8.070
8.053
7.501
7.496
7.488
7.471
7.450
7.428
4.471
4.453
4.435
4.417
1.431
1.413
1.395
Cl
O
N
O
O
3.97
4.94
1.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ac-H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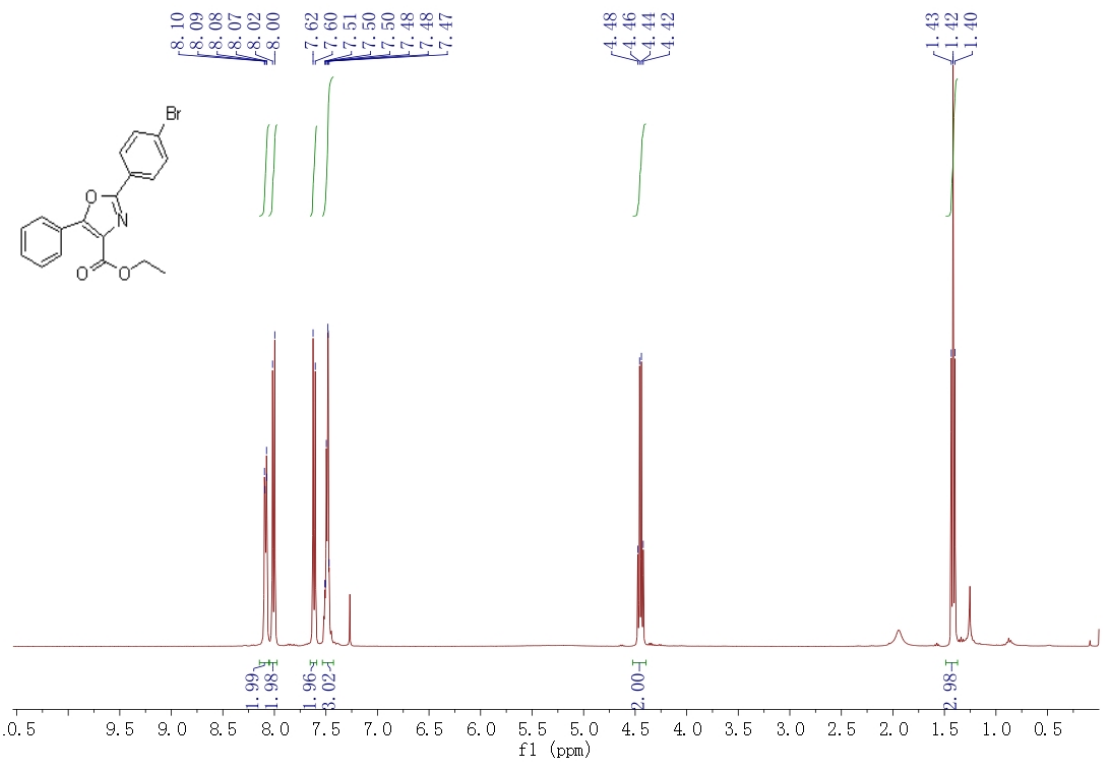
158.83
155.22
137.26
130.40
129.16
128.55
128.41
128.38
128.10
126.93
124.86
61.52
14.27
Cl
O
N
O
O
129.16
128.55
128.41
128.38
128.10
129.0
128.5
128.0
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ac-C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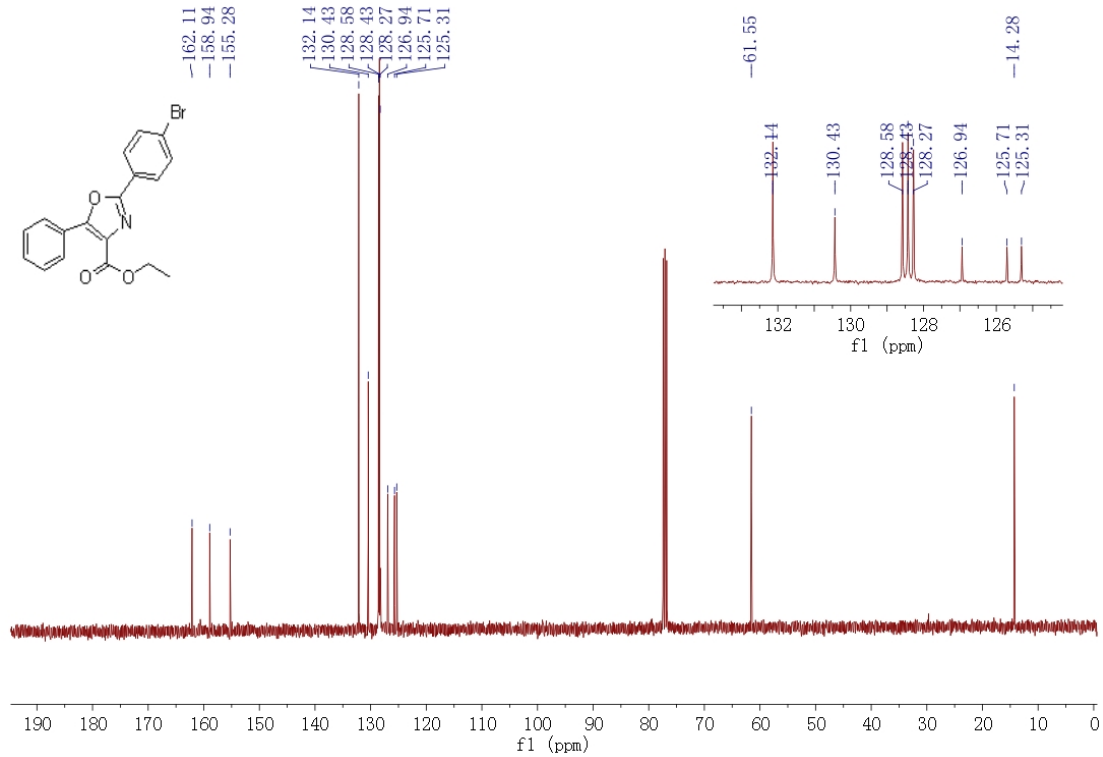
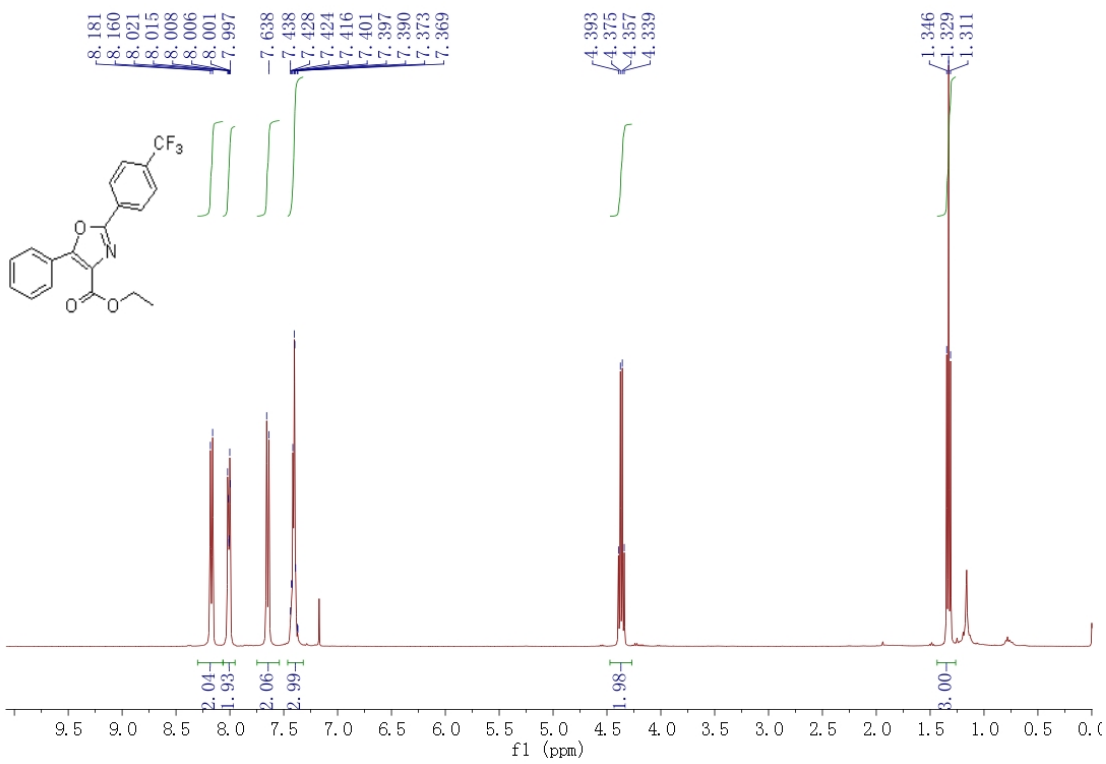
8.09
8.08
8.07
8.02
8.00
7.62
7.60
7.51
7.50
7.48
7.48
7.47
4.48
4.46
4.44
4.42
1.43
1.42
1.40
Br
O
N
O
O
1.99
1.98
1.96
3.02
2.00
2.98
f1 (ppm)

3ad-H


162.11
158.94
155.28
132.14
130.43
128.58
128.43
128.27
126.94
125.71
125.31
61.55
14.28
Br
O
N
O
O
f1 (ppm)
f1 (ppm)

3ad-C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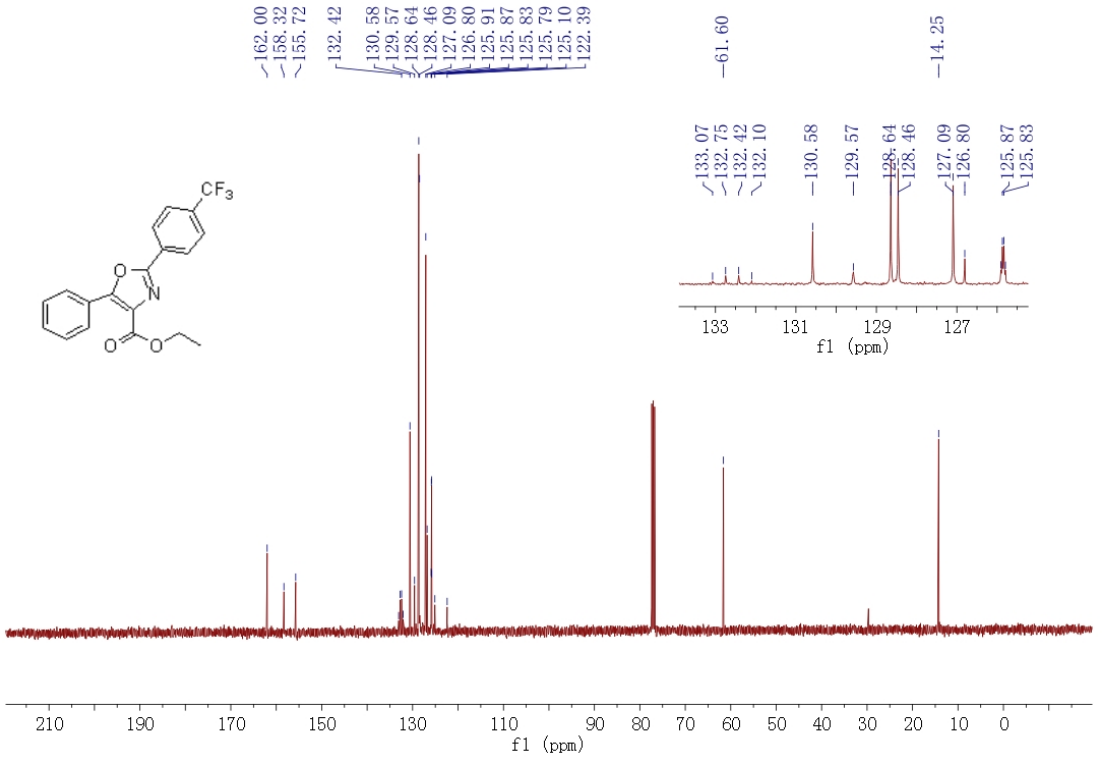
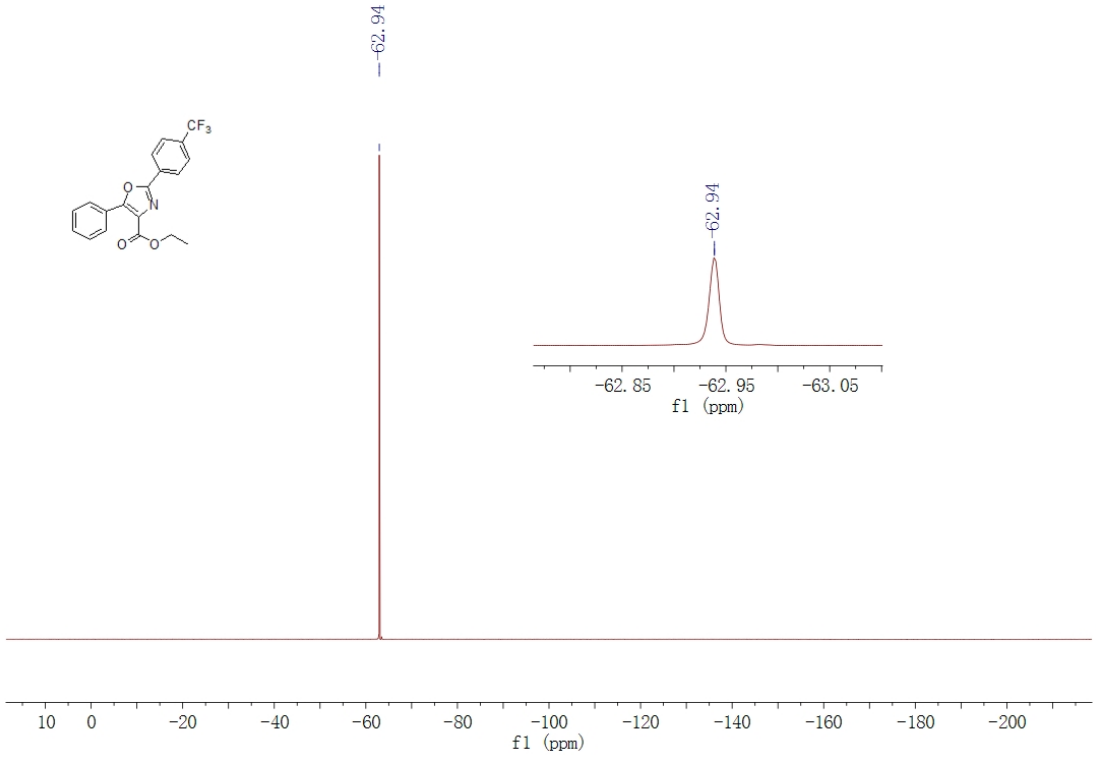
8.160
8.021
8.015
8.008
8.006
8.001
7.997
7.638
7.438
7.428
7.424
7.416
7.401
7.397
7.390
7.373
7.369
4.393
4.375
4.357
4.339
1.346
1.329
1.311
CF3
O
N
O
O
2.04
1.93
2.06
2.99
1.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

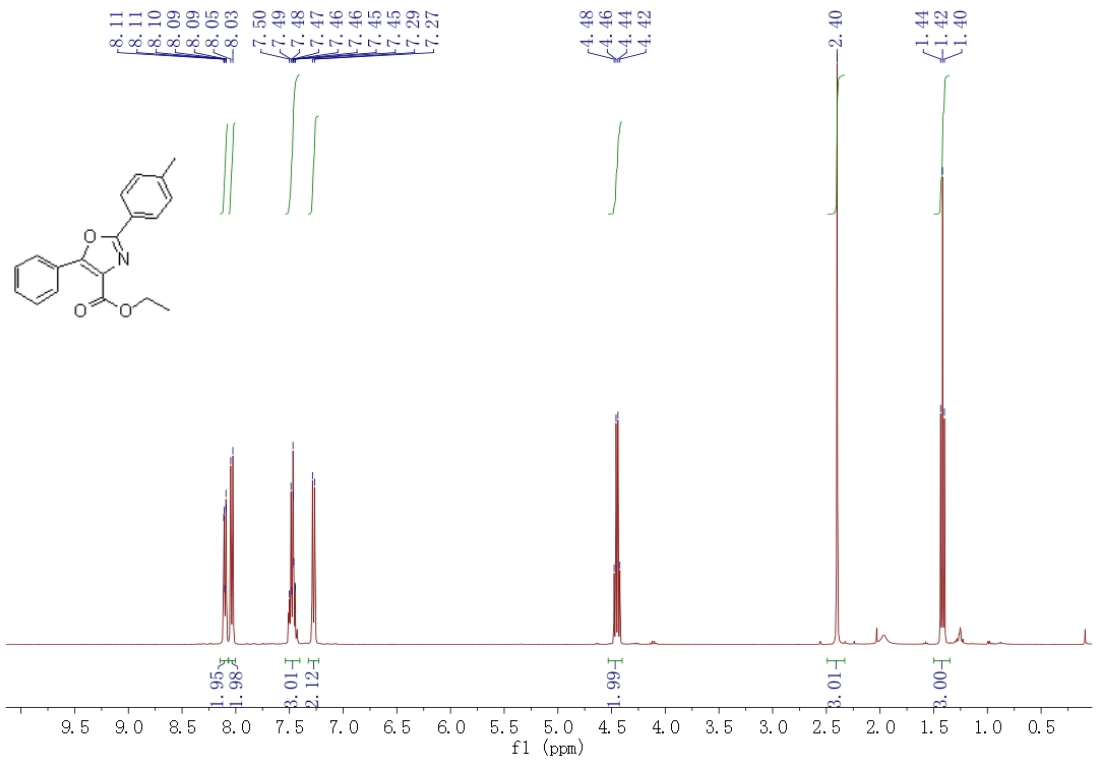
3ae-H


162.00
158.32
155.72
132.42
130.58
129.57
128.64
128.46
127.09
126.80
125.91
125.87
125.83
125.79
125.10
122.39
61.60
14.25
133.07
132.75
132.42
132.10
130.58
129.57
128.64
128.46
127.09
126.80
125.87
125.83
133
131
129
127
f1 (ppm)
CF3
O
N
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

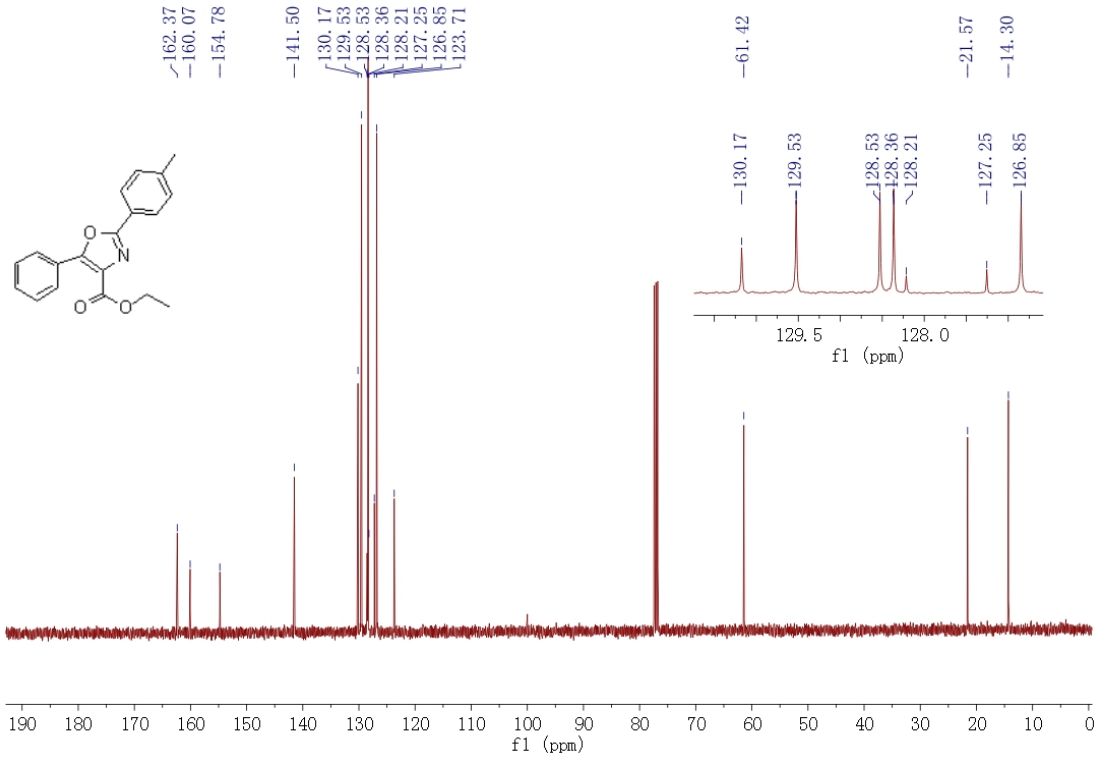
3ae-C


-62.94
CF3
O
N
O
O
-62.94
-62.85
-62.95
-63.05
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

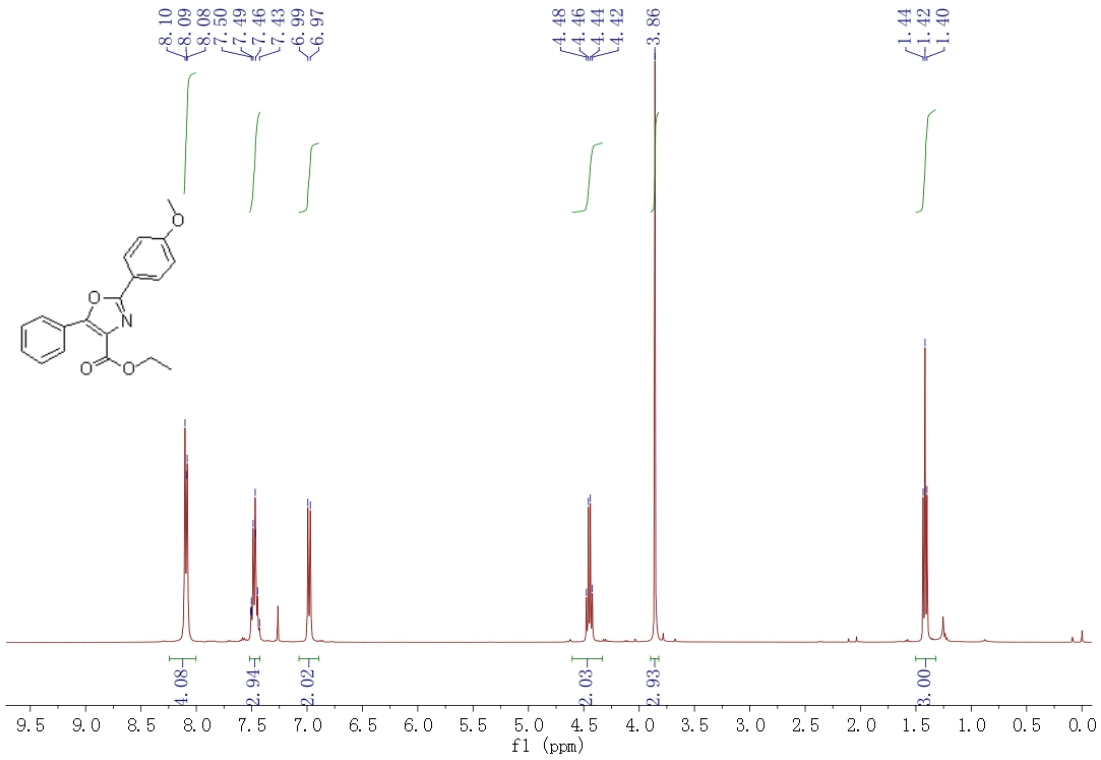
3ae-F


8.11
8.11
8.10
8.09
8.09
8.05
8.03
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.29
7.27
4.48
4.46
4.44
4.42
2.40
1.44
1.42
1.40
1.95
1.98
3.01
2.12
1.99
3.01
3.00
f1 (ppm)

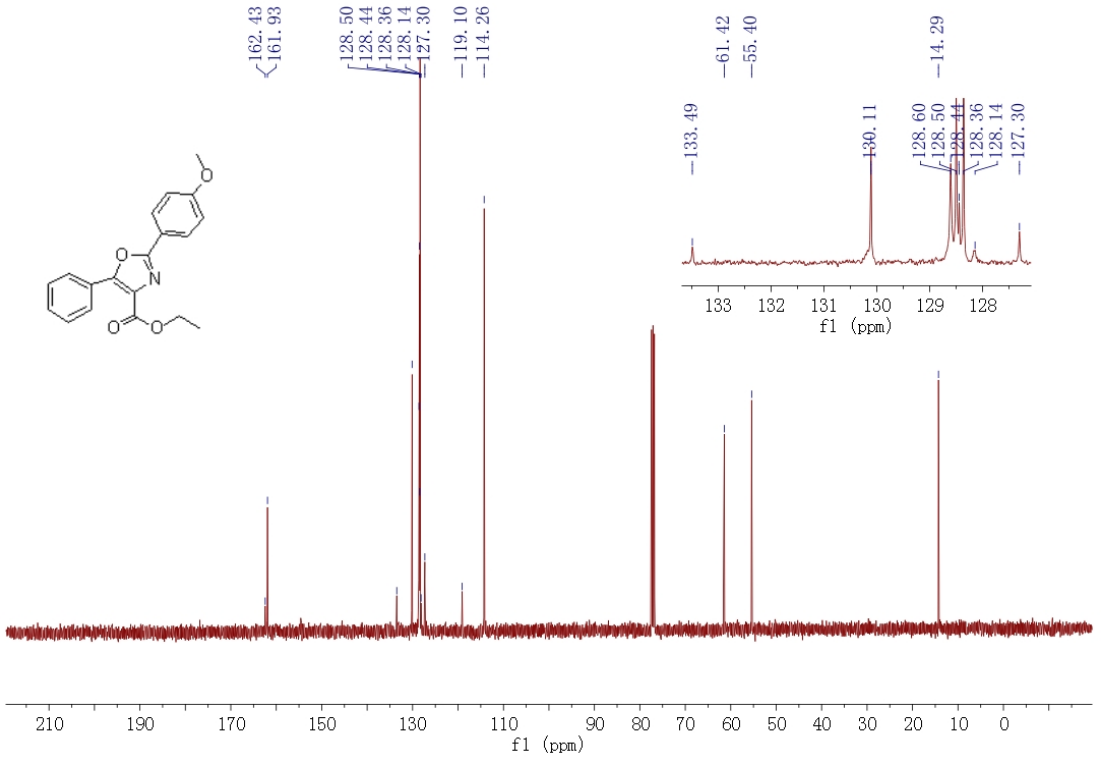
3af-H


162.37
160.07
154.78
141.50
130.17
129.53
128.53
128.36
128.21
127.25
126.85
123.71
61.42
21.57
14.30
130.17
129.53
128.53
128.36
128.21
127.25
126.85
129.5
128.0
f1 (ppm)
f1 (ppm)

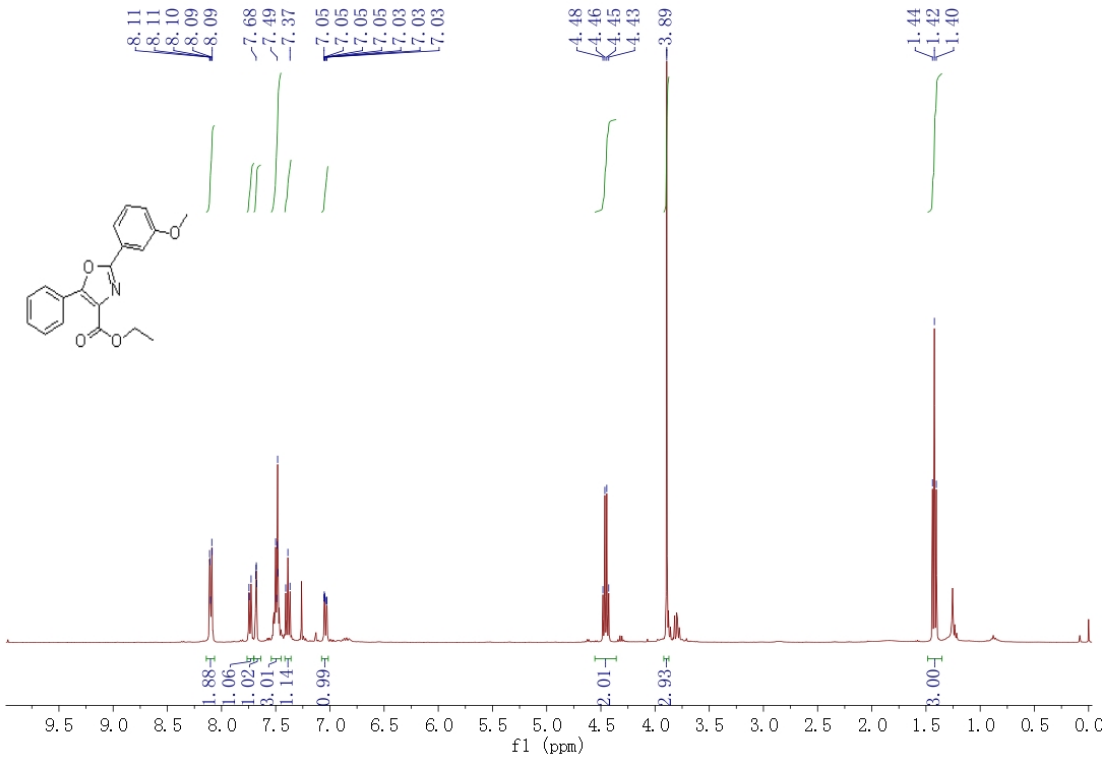
3af-C


8.10
8.09
8.08
7.50
7.49
7.46
7.43
6.99
6.97
4.48
4.46
4.44
4.42
3.86
1.44
1.42
1.40
4.08
2.94
2.02
2.03
2.93
3.00
f1 (ppm)

3ag-H


162.43
161.93
128.50
128.44
128.36
128.14
127.30
119.10
114.26
61.42
55.40
14.29
133.49
130.11
128.60
128.50
128.44
128.36
128.14
127.30
f1 (ppm)

3ag-C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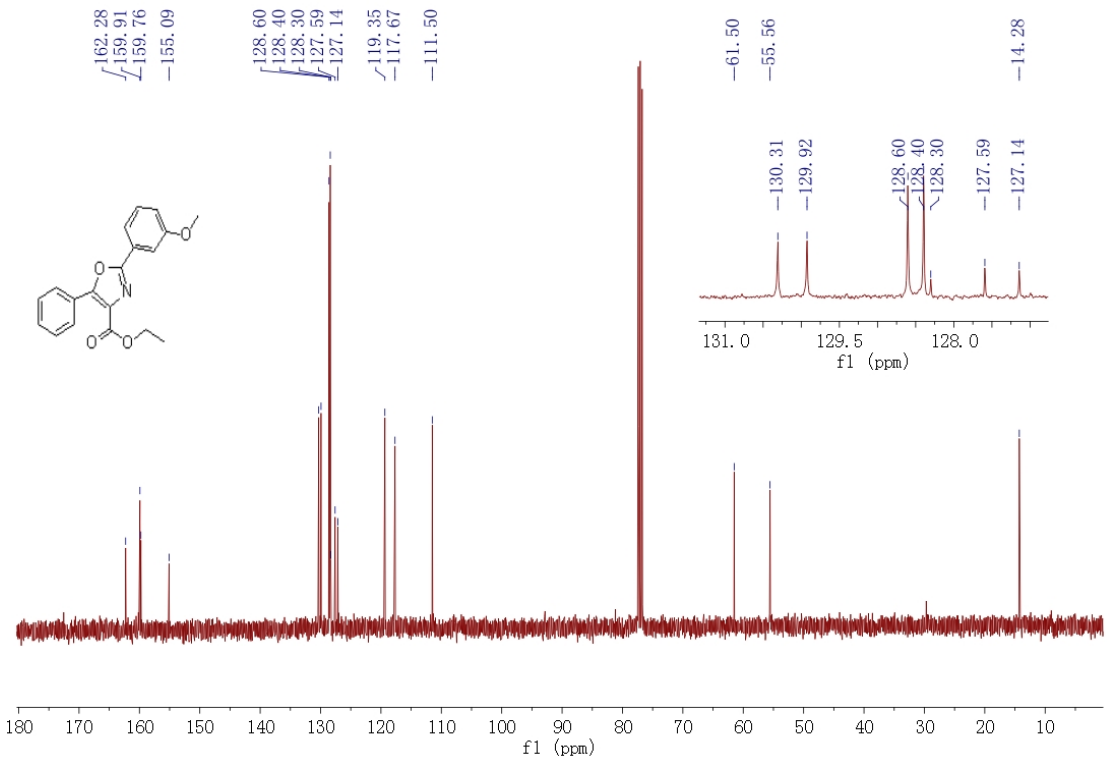
8.11
8.10
8.09
8.09
7.68
7.49
7.37
7.05
7.05
7.05
7.05
7.03
7.03
7.03
4.48
4.46
4.45
4.43
3.89
1.44
1.42
1.40
1.88
1.06
1.02
3.01
1.14
0.99
2.01
2.93
3.00
f1 (ppm)

3ah-H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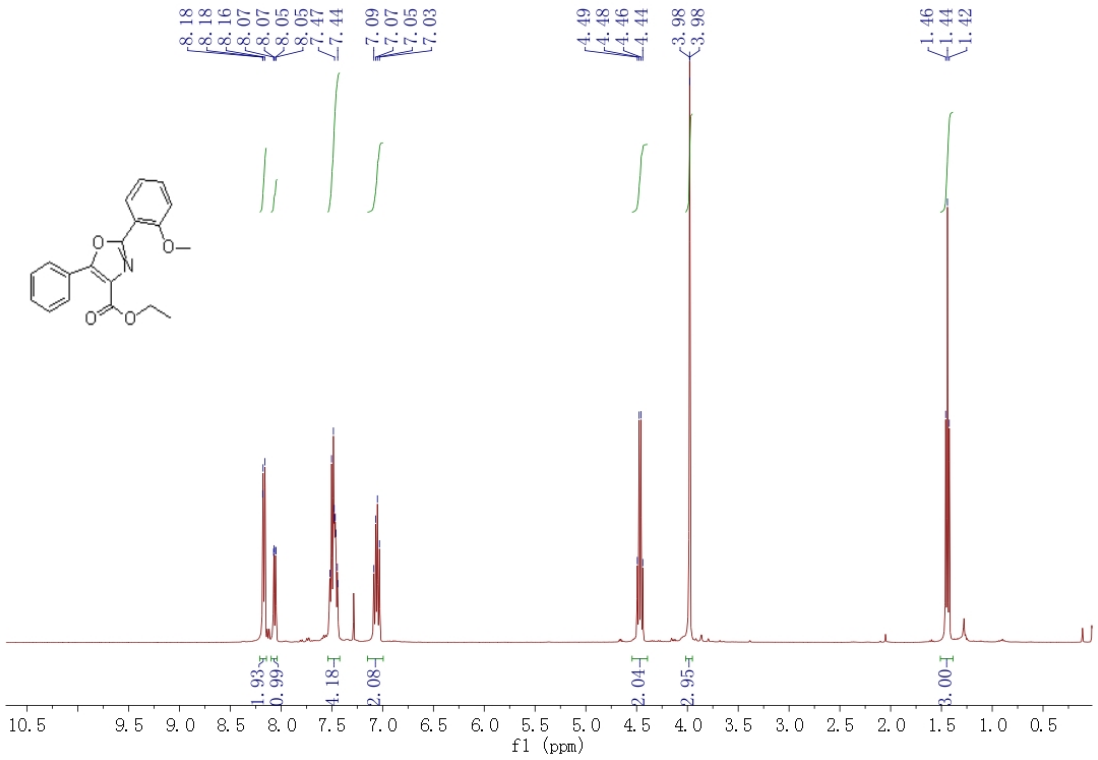
159.91
159.76
155.09
128.60
128.40
128.30
127.59
127.14
119.35
117.67
111.50
61.50
55.56
14.28
130.31
129.92
128.60
128.40
128.30
127.59
127.14
131.0
129.5
128.0
f1 (ppm)
f1 (ppm)

3ah-C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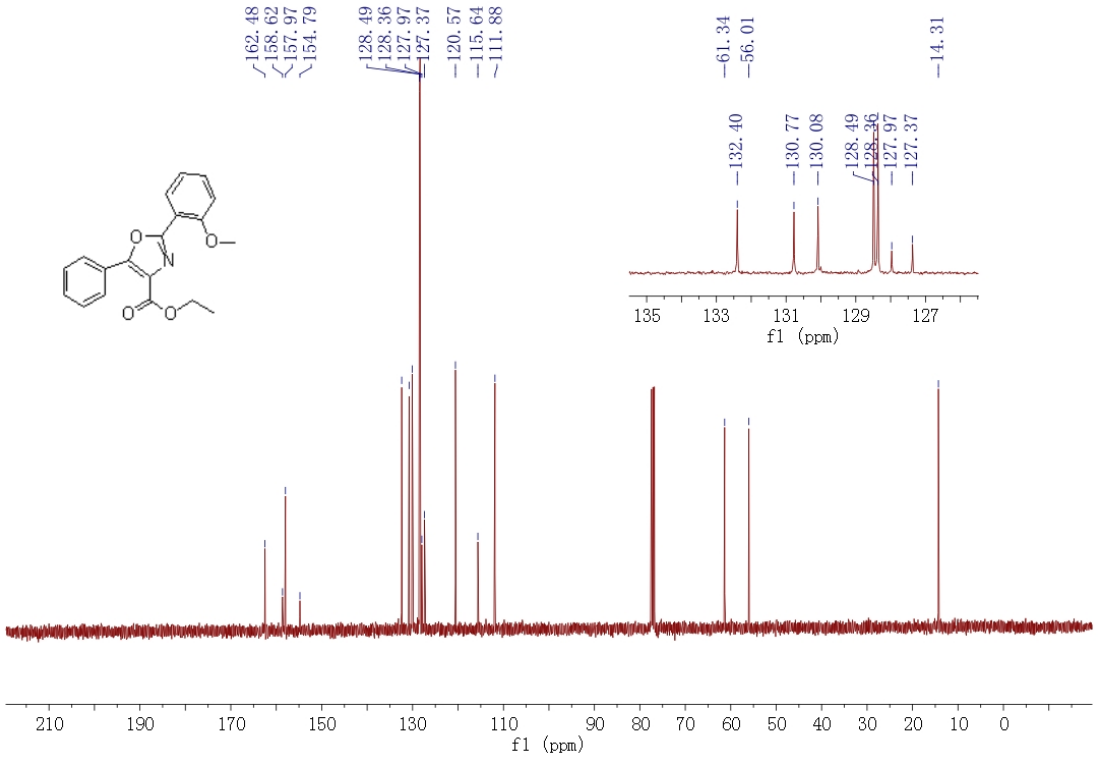
8.18
8.16
8.07
8.07
8.05
8.05
7.47
7.44
7.09
7.07
7.05
7.03
4.49
4.48
4.46
4.44
3.98
3.98
1.46
1.44
1.42
1.93
0.99
4.18
2.08
2.04
2.95
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

3ai-H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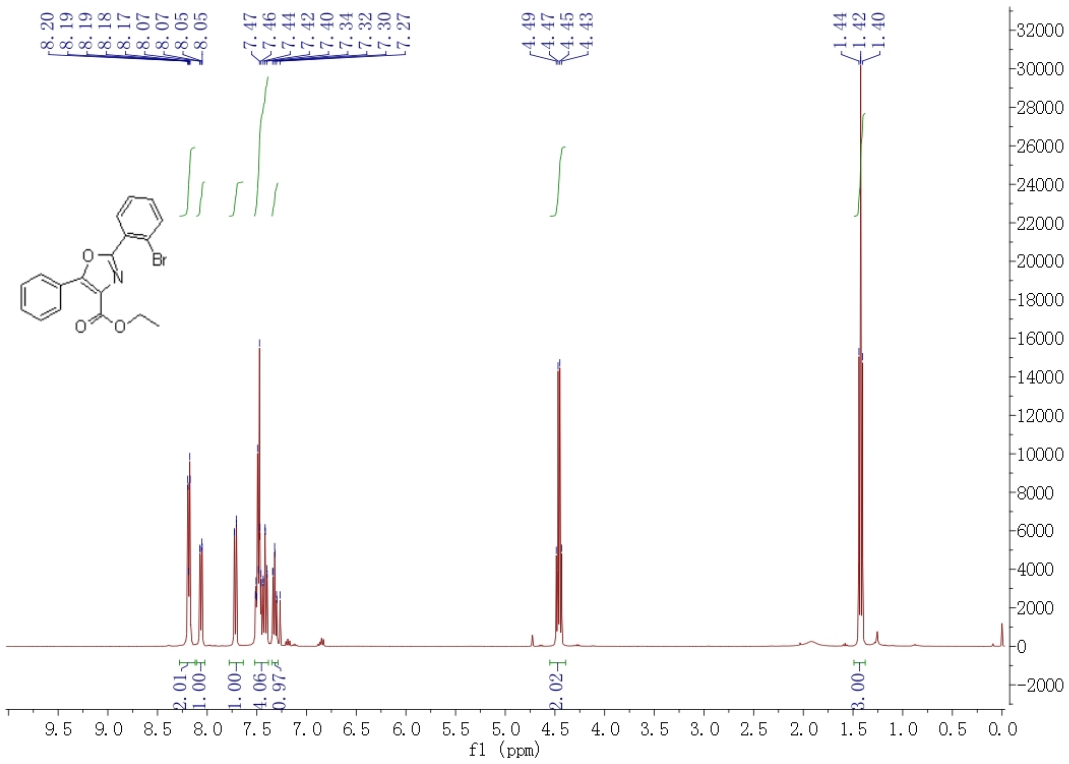
157.97
154.79
128.49
128.36
127.97
127.37
120.57
115.64
111.88
61.34
56.01
14.31
132.40
130.77
130.08
128.49
128.36
127.97
127.37
135 133 131 129 127
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ai-C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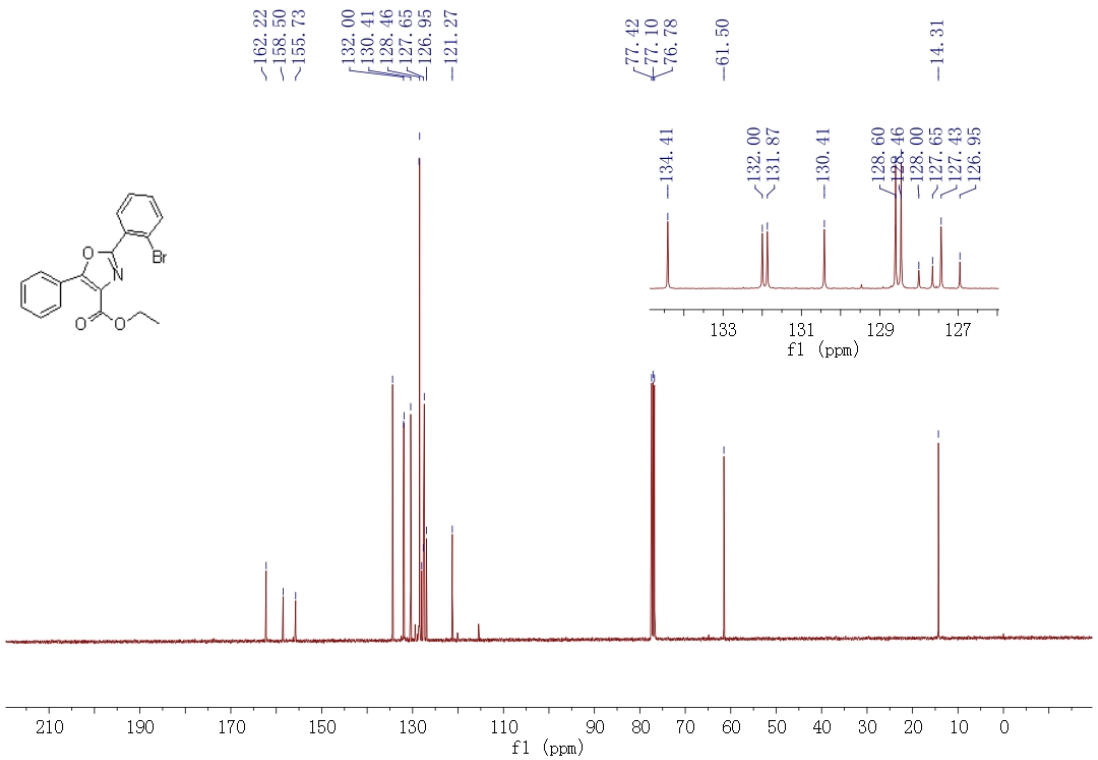
8.19
8.19
8.18
8.17
8.07
8.07
8.05
8.05
7.47
7.46
7.44
7.42
7.40
7.34
7.32
7.30
7.27
4.49
4.47
4.45
4.43
1.44
1.42
1.40
Br
O
N
O
O
2.01
1.00
1.00
4.06
0.97
2.02
3.00
f1 (ppm)

3aj-H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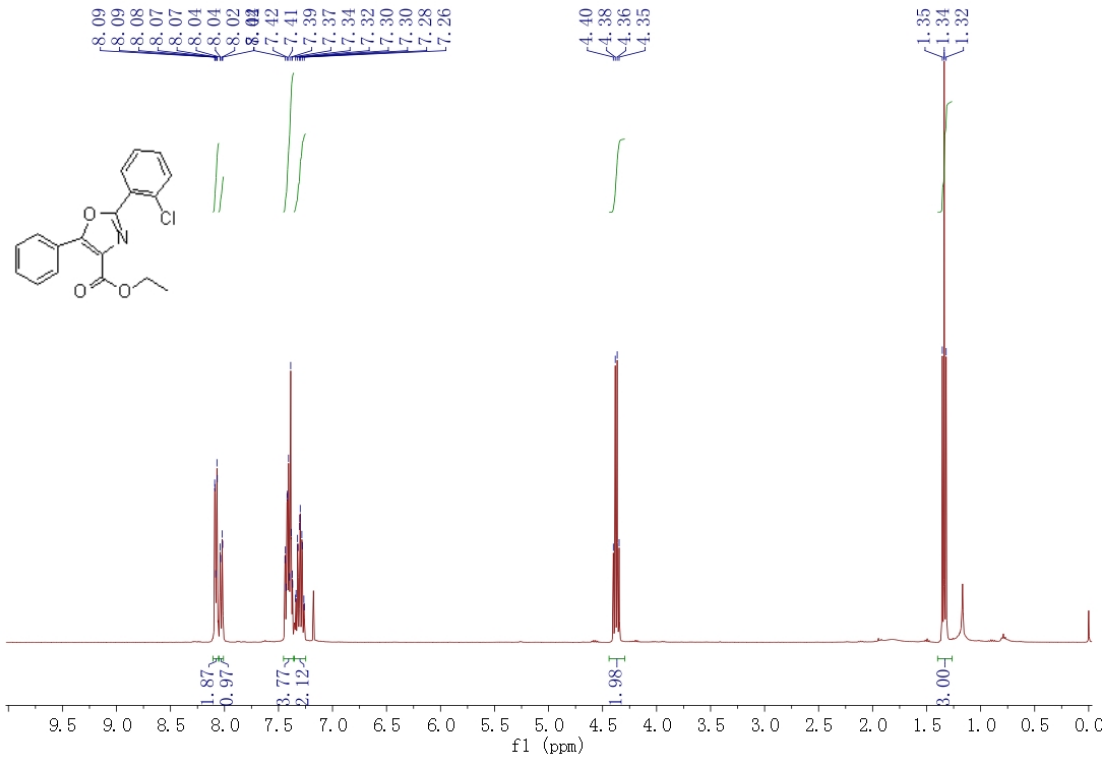
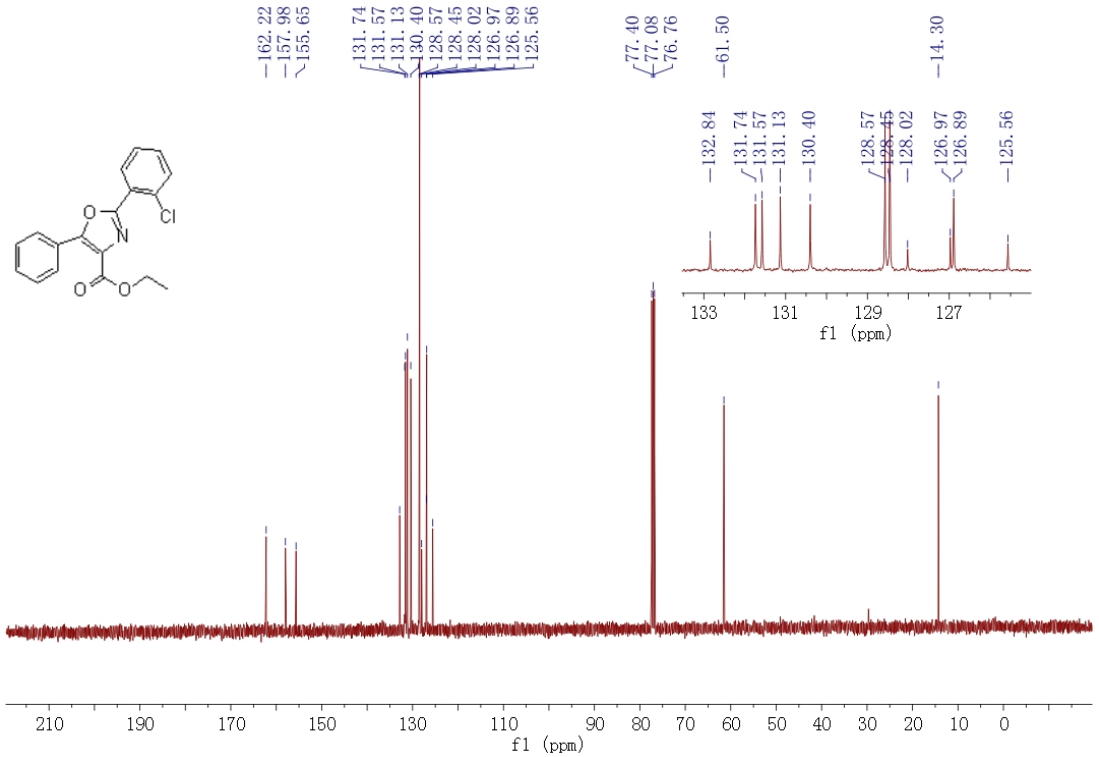
130.41
128.46
127.65
126.95
121.27
77.42
77.10
76.78
61.50
14.31
134.41
132.00
131.87
130.41
128.60
128.46
128.00
127.65
127.43
126.95
Br
O
N
O
O
f1 (ppm)
f1 (ppm)

3aj-C


8.09
8.09
8.08
8.07
8.07
8.04
8.04
8.02
7.42
7.41
7.39
7.37
7.34
7.32
7.30
7.30
7.28
7.26
4.40
4.38
4.36
4.35
1.35
1.34
1.32
Cl
O
N
O
O
1.87
0.97
3.77
2.12
1.98
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)

3ak-H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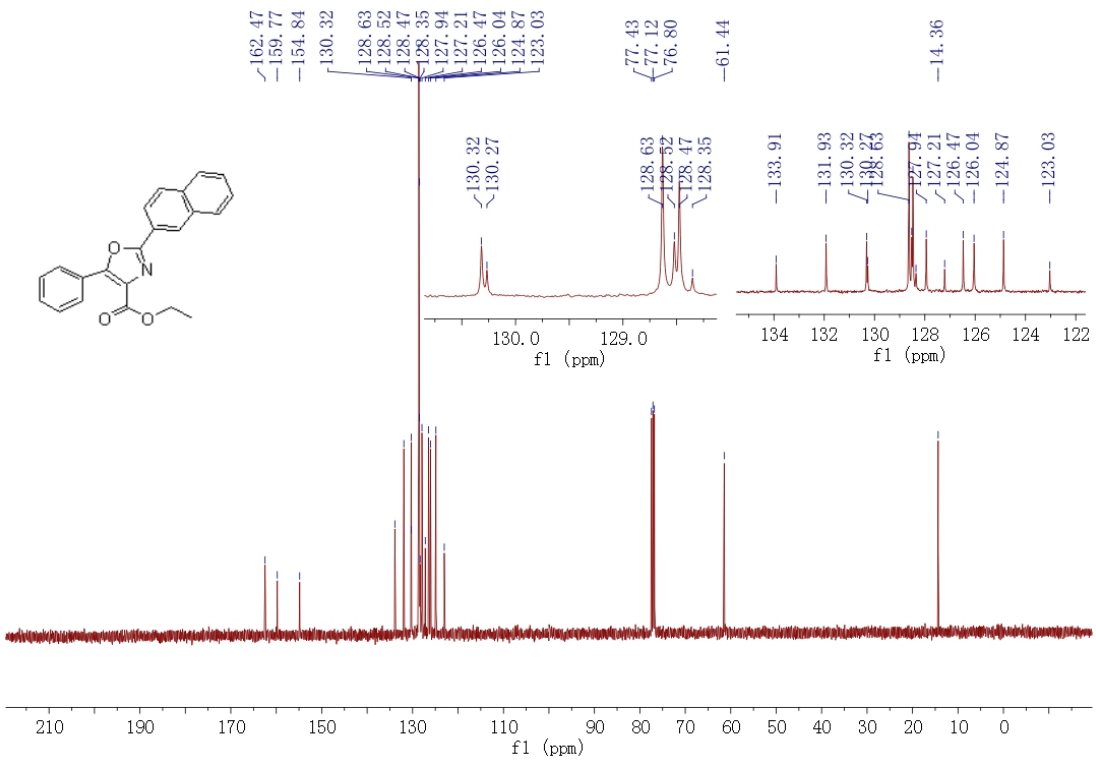
157.98
155.65
131.74
131.57
131.13
130.40
128.57
128.45
128.02
126.97
126.89
125.56
77.40
77.08
76.76
61.50
14.30
132.84
131.74
131.57
131.13
130.40
128.57
128.45
128.02
126.97
126.89
125.56
133
131
129
127
f1 (ppm)
Cl
O
N
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ak-C


162.47
159.77
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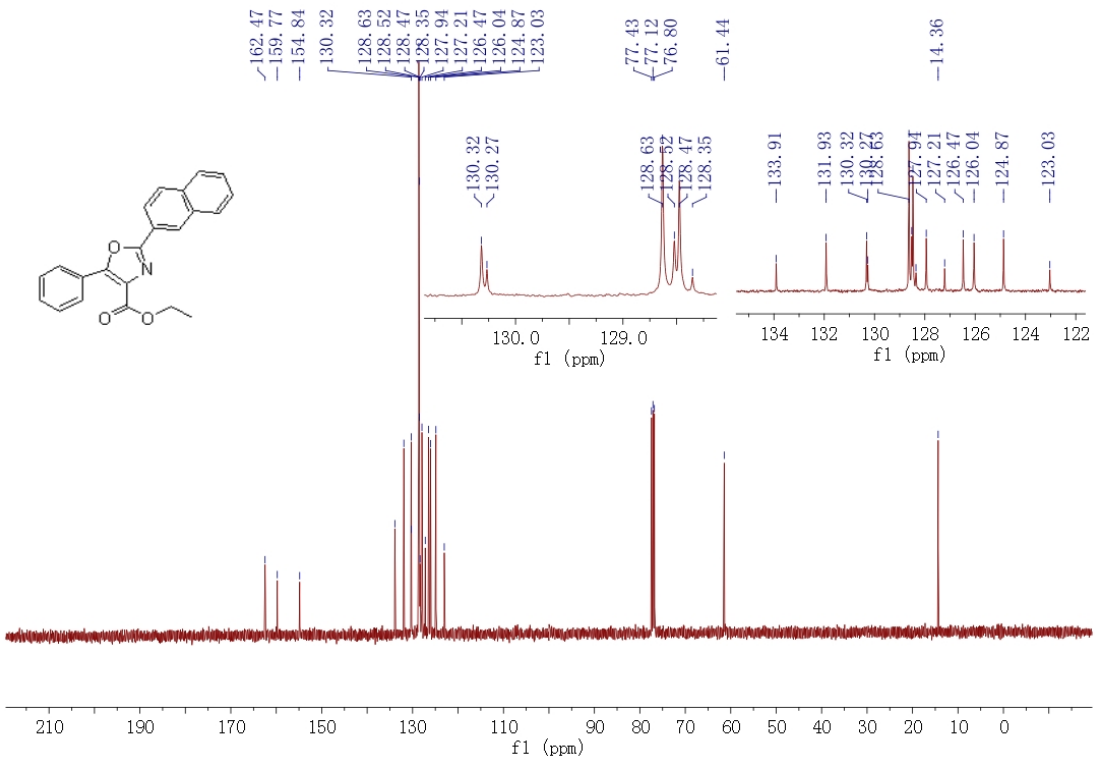
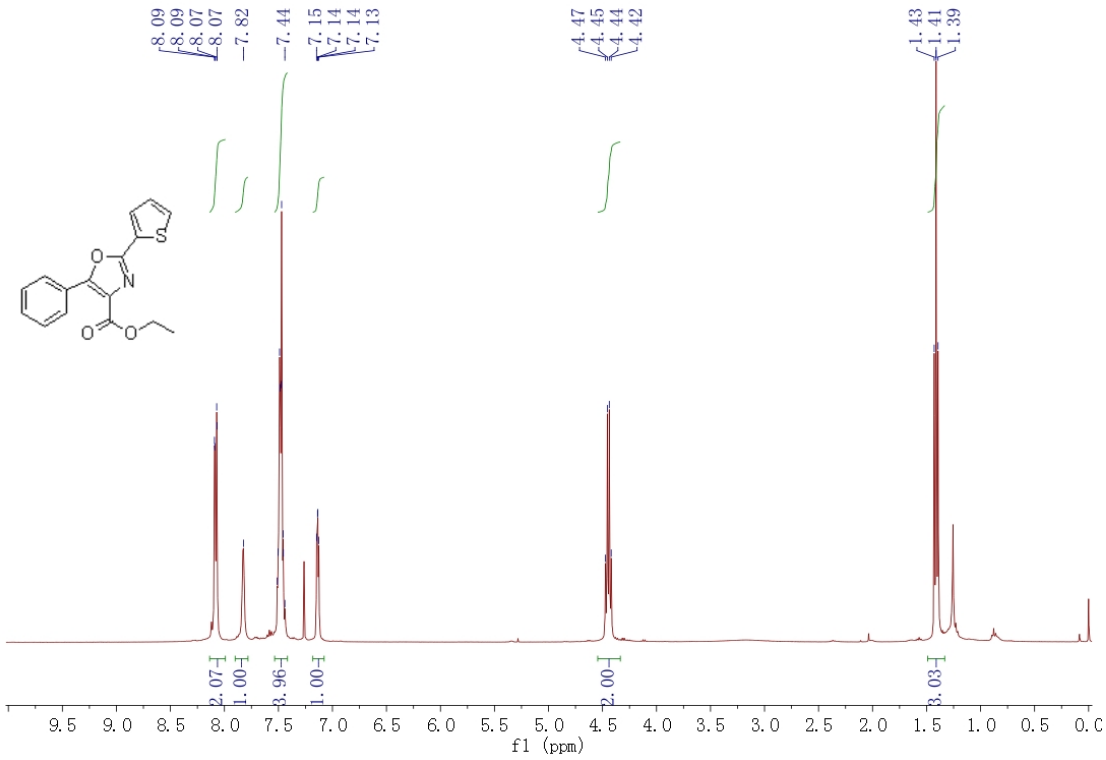
130.32
128.63
128.52
128.47
128.35
127.94
127.21
126.47
126.04
124.87
123.03
77.43
77.12
76.80
61.44
14.36
130.32
130.27
128.63
128.52
128.47
128.35
133.91
131.93
130.32
127.94
127.21
126.47
126.04
124.87
123.03
130.0
129.0
f1 (ppm)
134
132
130
128
126
124
122
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

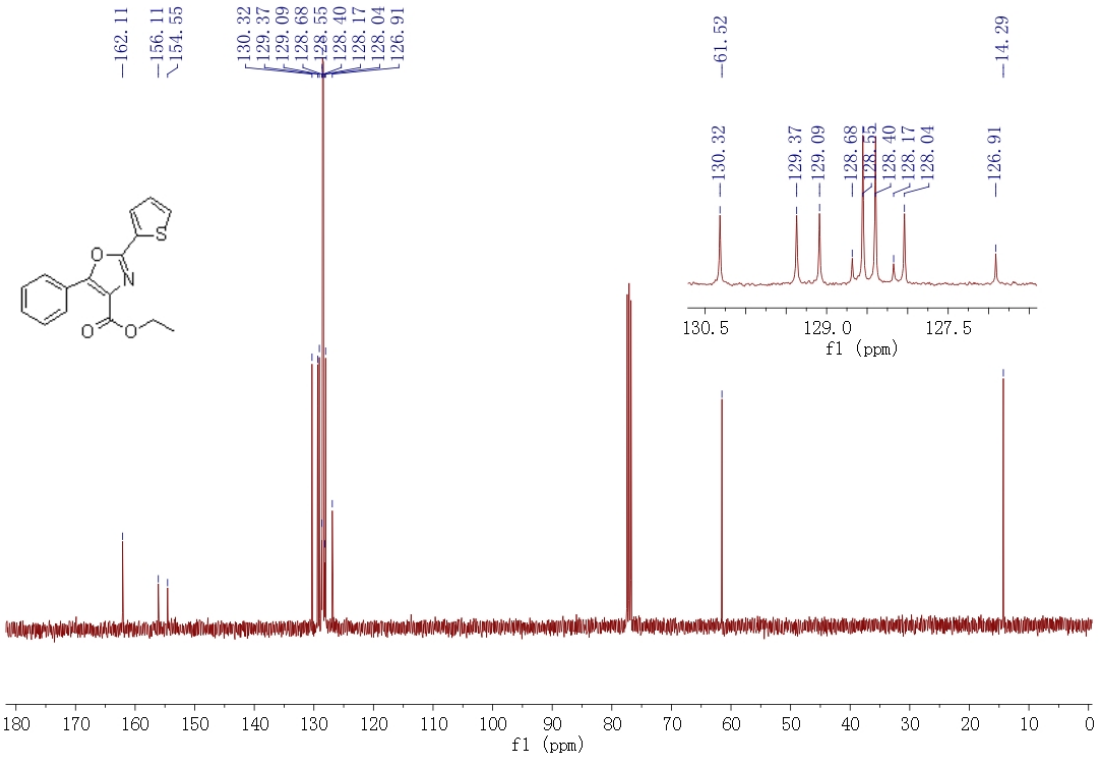
3al-H


162.47
159.77
154.84
130.32
128.63
128.52
128.47
128.35
127.94
127.21
126.47
126.04
124.87
123.03
77.43
77.12
76.80
61.44
14.36
130.32
130.27
128.63
128.52
128.47
128.35
133.91
131.93
130.32
127.94
127.21
126.47
126.04
124.87
123.03
130.0
129.0
f1 (ppm)
134
132
130
128
126
124
122
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

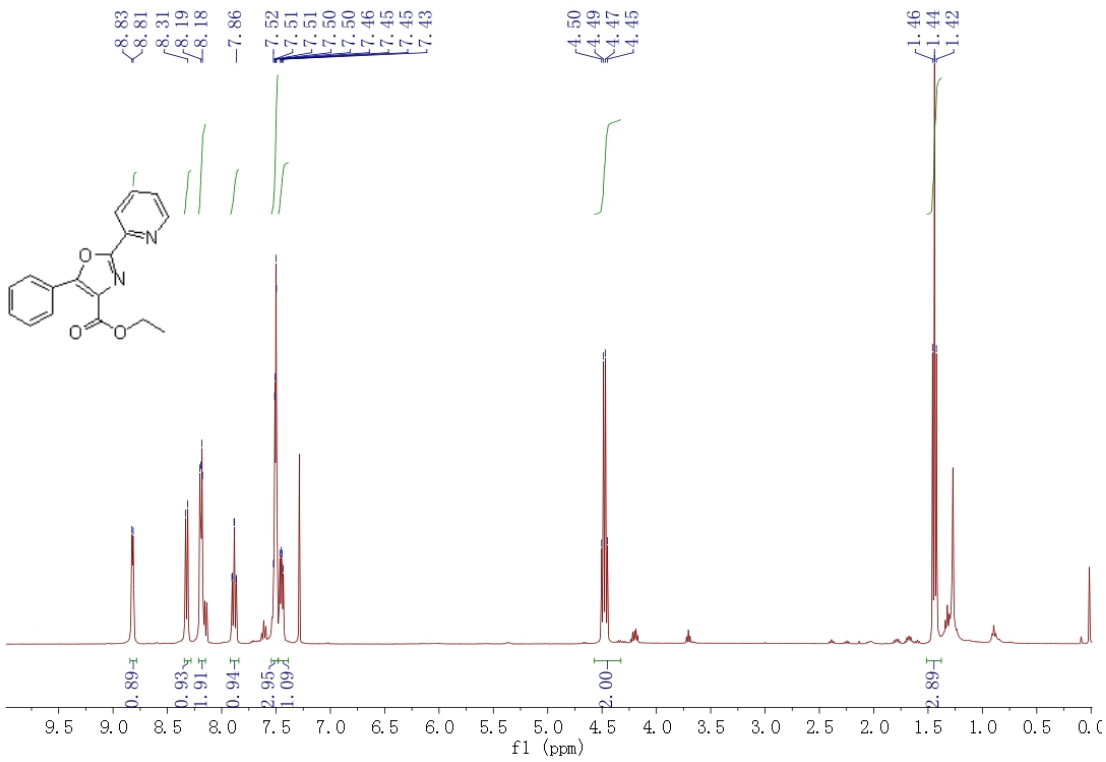
3al-C


8.09
8.09
8.07
8.07
7.82
7.44
7.15
7.14
7.14
7.13
4.47
4.45
4.44
4.42
1.43
1.41
1.39
2.07
1.00
3.96
1.00
2.00
3.03
f1 (ppm)

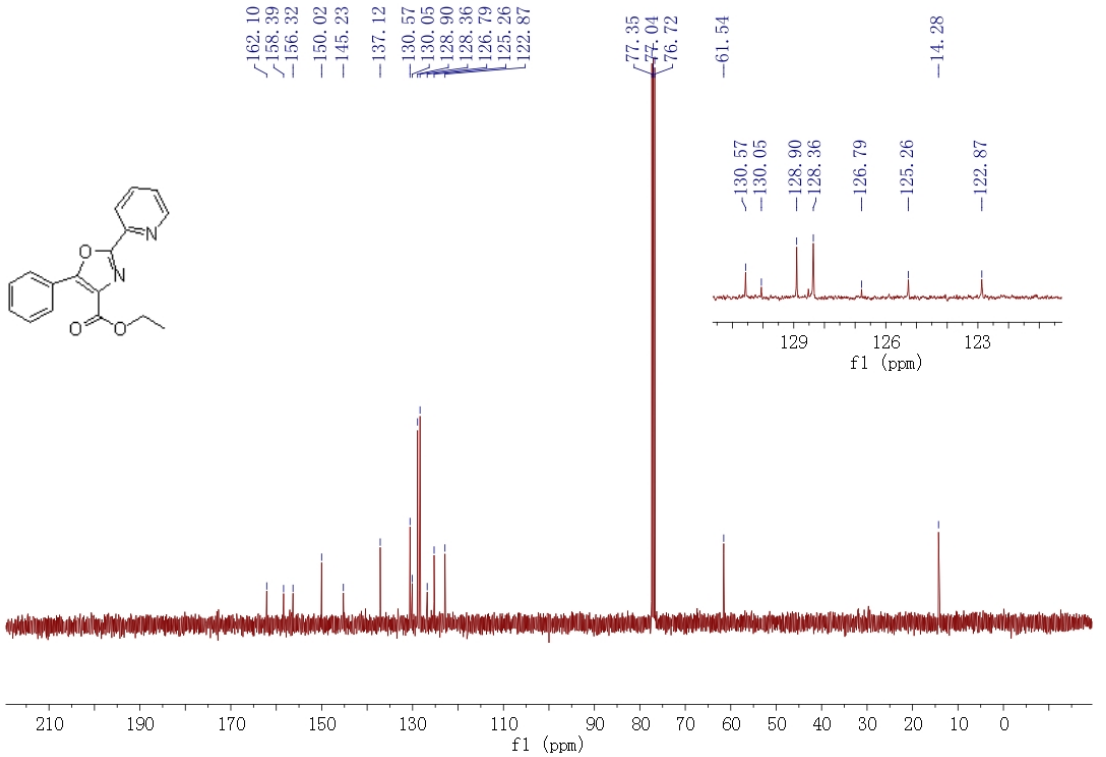
3am-H


162.11
156.11
154.55
130.32
129.37
129.09
128.68
128.55
128.40
128.17
128.04
126.91
61.52
14.29
f1 (ppm)

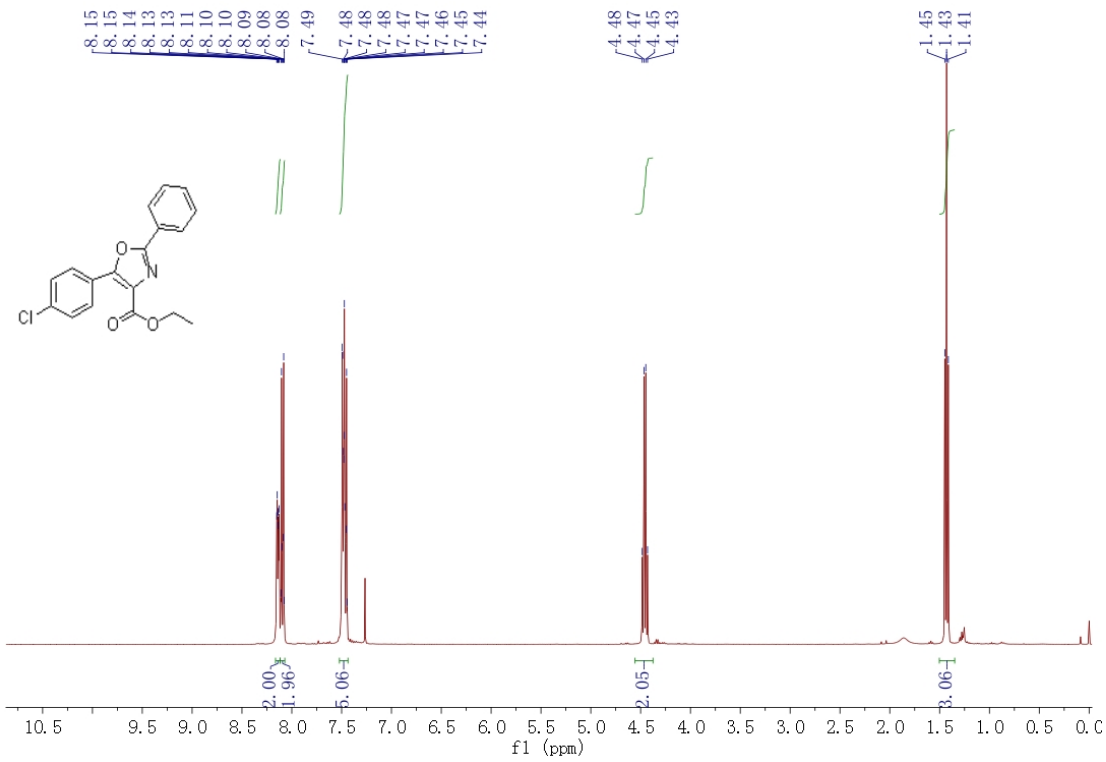
3am-C


8.83
8.81
8.31
8.19
8.18
7.86
7.52
7.51
7.51
7.50
7.50
7.46
7.45
7.45
7.43
4.50
4.49
4.47
4.45
1.46
1.44
1.42
0.89
0.93
1.91
0.94
2.95
1.09
2.00
2.89
f1 (ppm)

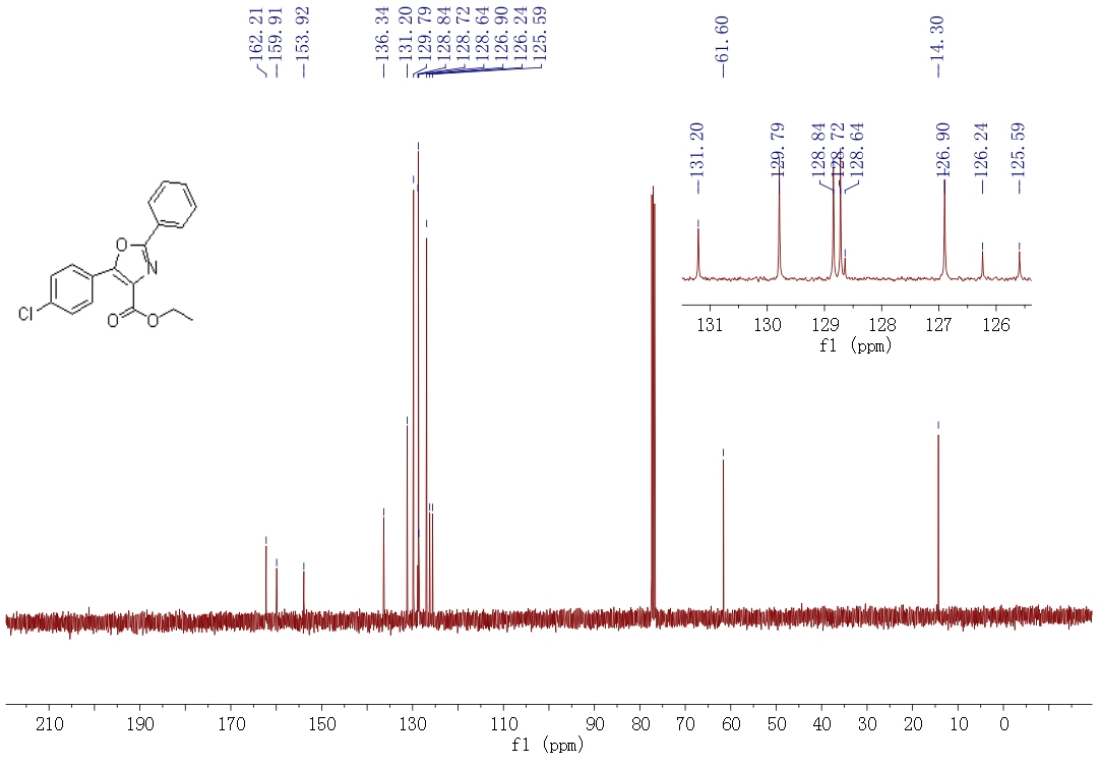
3an-H


162.10
158.39
156.32
150.02
145.23
137.12
130.57
130.05
128.90
128.36
126.79
125.26
122.87
77.35
77.04
76.72
61.54
14.28
f1 (ppm)

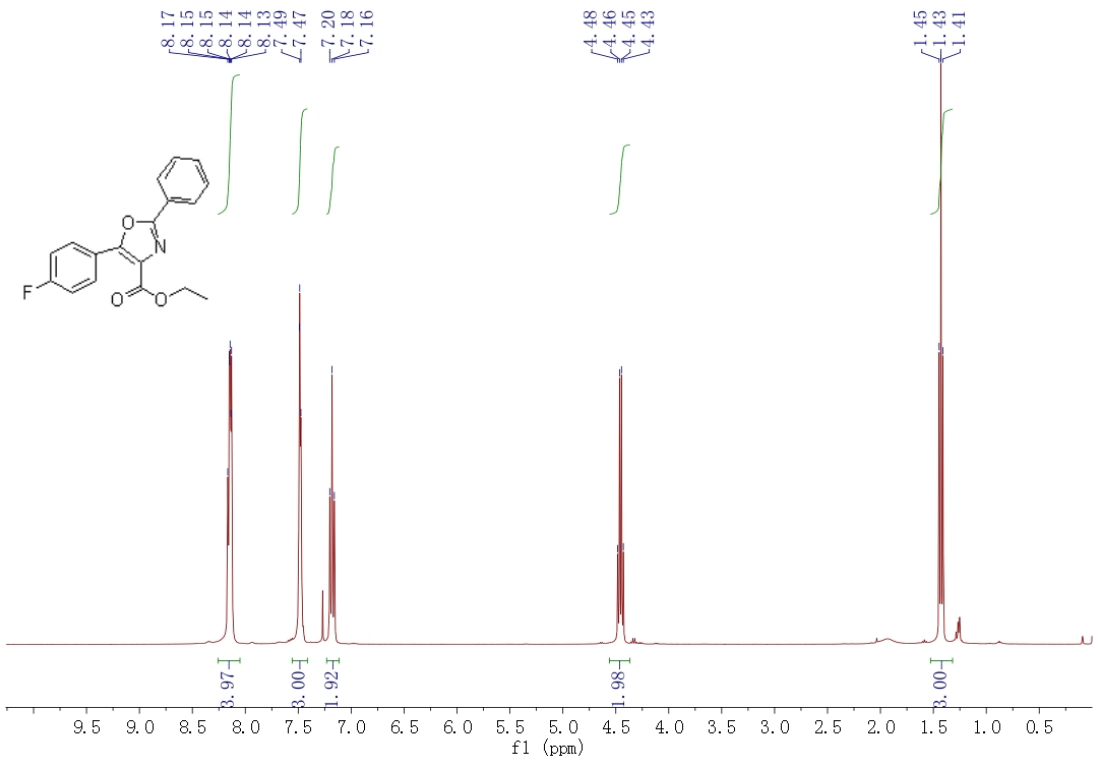
3an-C


8.15
8.15
8.14
8.13
8.13
8.11
8.10
8.10
8.09
8.08
8.08
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.45
7.44
4.48
4.47
4.45
4.43
1.45
1.43
1.41
Cl
O
N
O
O
2.00
1.96
5.06
2.05
3.06
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
f1 (ppm)

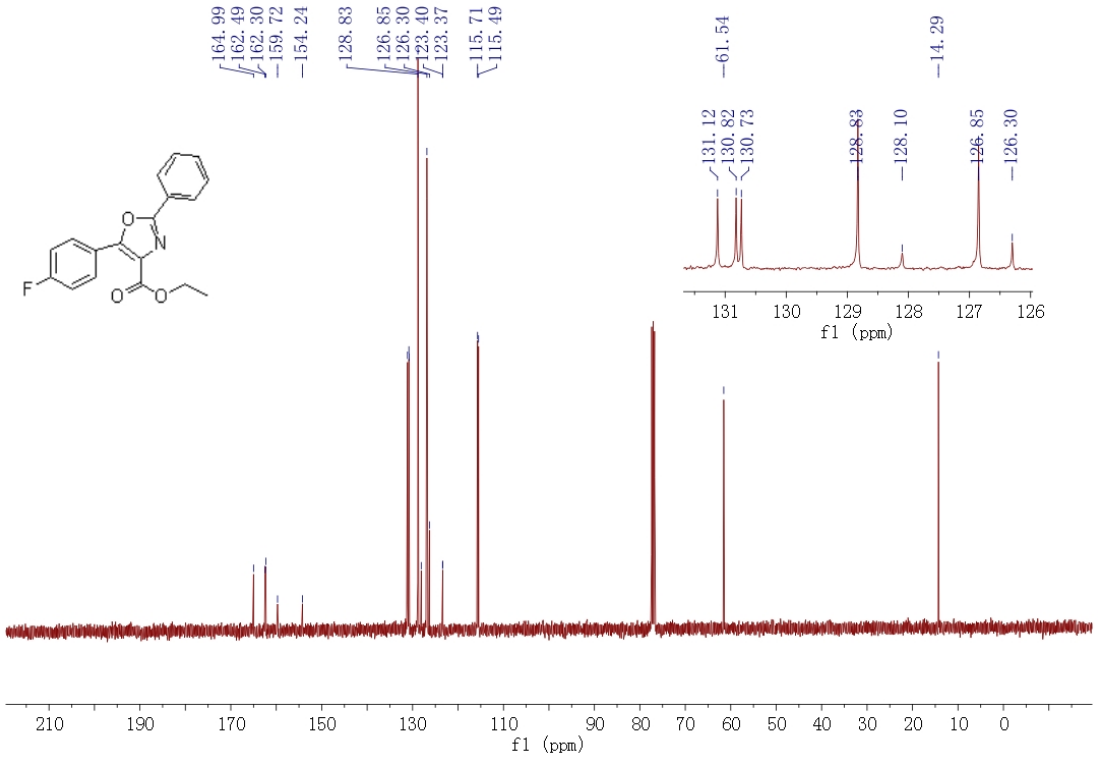
3ba-H


162.21
159.91
153.92
136.34
131.20
129.79
128.84
128.72
128.64
126.90
126.24
125.59
61.60
14.30
131.20
129.79
128.84
128.72
128.64
126.90
126.24
125.59
Cl
O
N
O
O
131
130
129
128
127
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

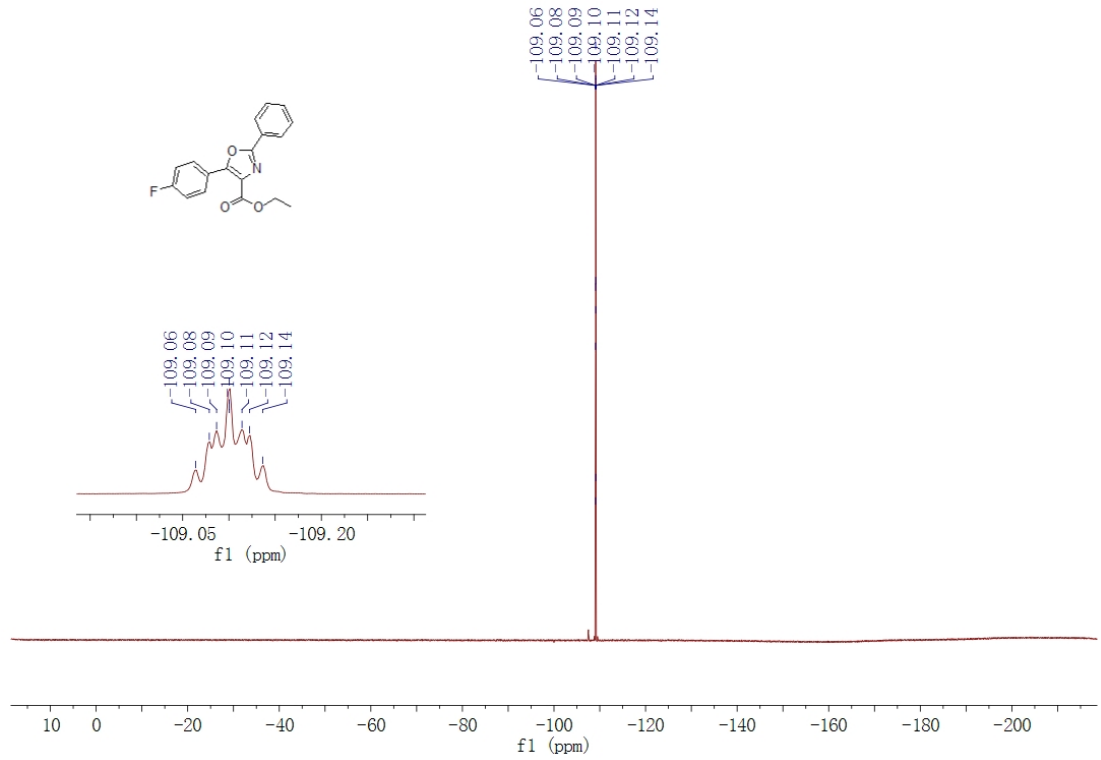
3ba-C


8.17
8.15
8.15
8.14
8.14
8.13
7.49
7.47
7.20
7.18
7.16
4.48
4.46
4.45
4.43
1.45
1.43
1.41
3.97
3.00
1.92
1.98
3.00
F
O
N
O
O
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
f1 (ppm)

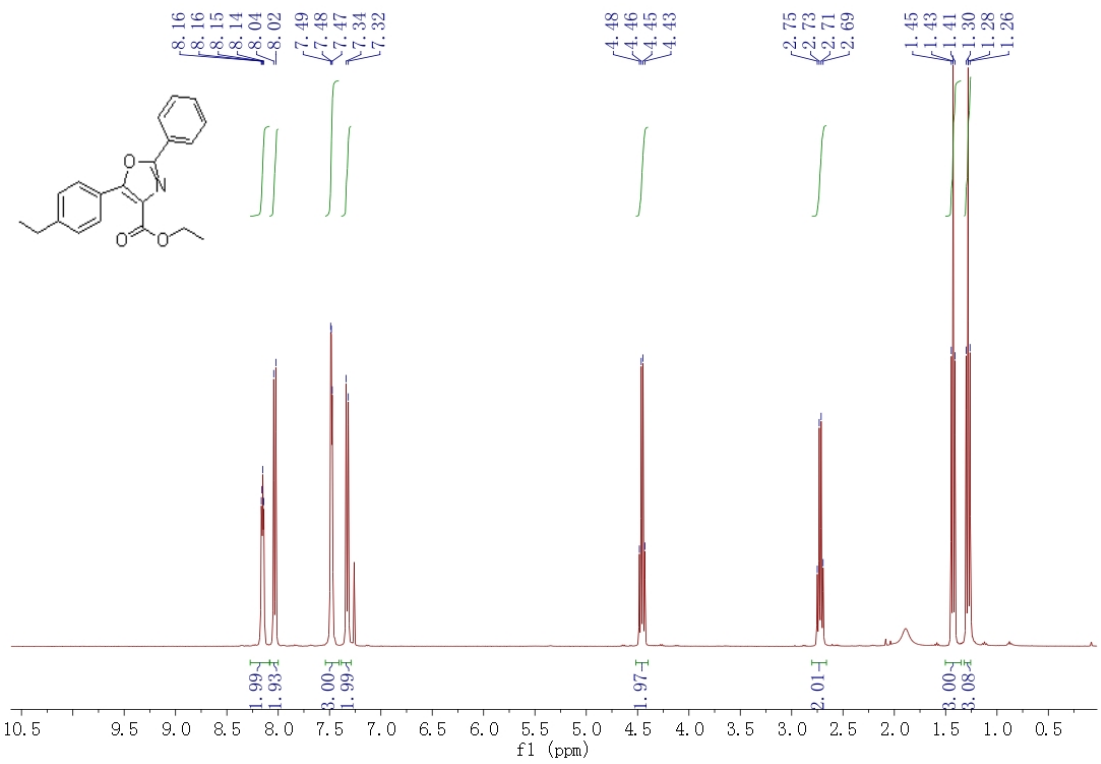
3ca-H


164.99
162.49
162.30
159.72
154.24
128.83
126.85
126.30
123.40
123.37
115.71
115.49
61.54
14.29
131.12
130.82
130.73
128.83
128.10
126.85
126.30
F
O
N
O
O
131 130 129 128 127 126
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

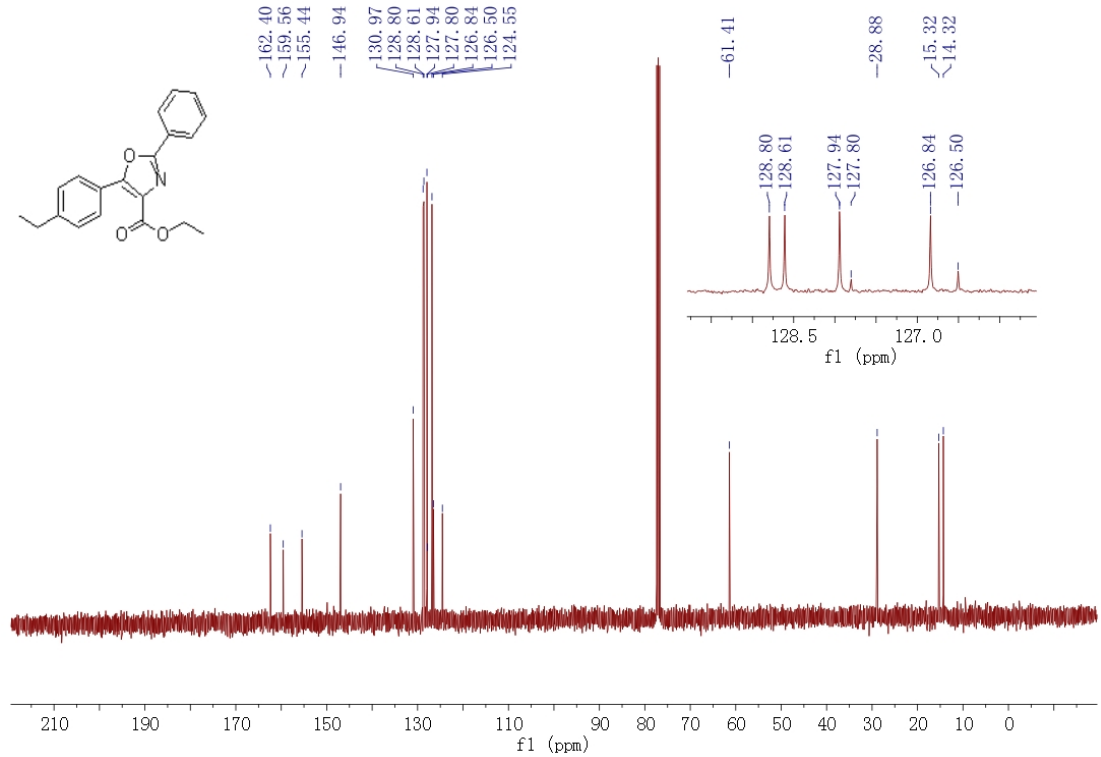
3ca-C


-109.06
-109.08
-109.09
-109.10
-109.11
-109.12
-109.14
O
N
F
O
O
-109.05
-109.20
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

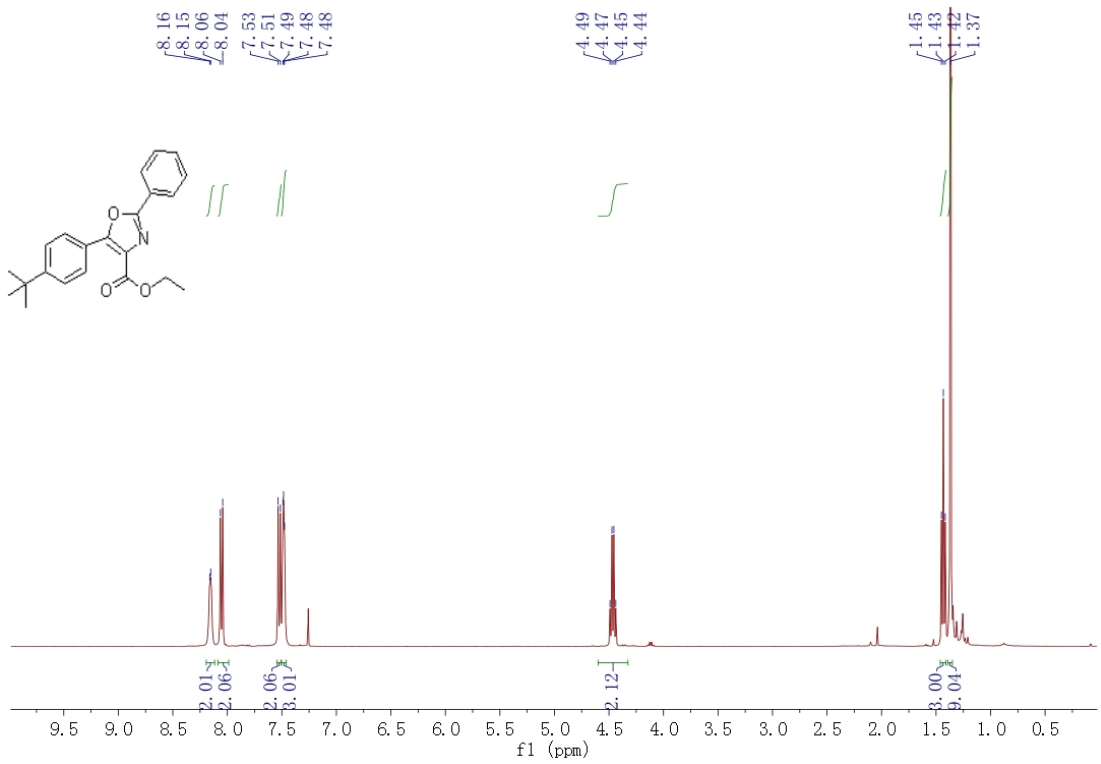
3ca-F


8.16
8.16
8.15
8.14
8.04
8.02
7.49
7.48
7.47
7.34
7.32
4.48
4.46
4.45
4.43
2.75
2.73
2.71
2.69
1.45
1.43
1.41
1.30
1.28
1.26
1.99
1.93
3.00
1.99
1.97
2.01
3.00
3.08
f1 (ppm)

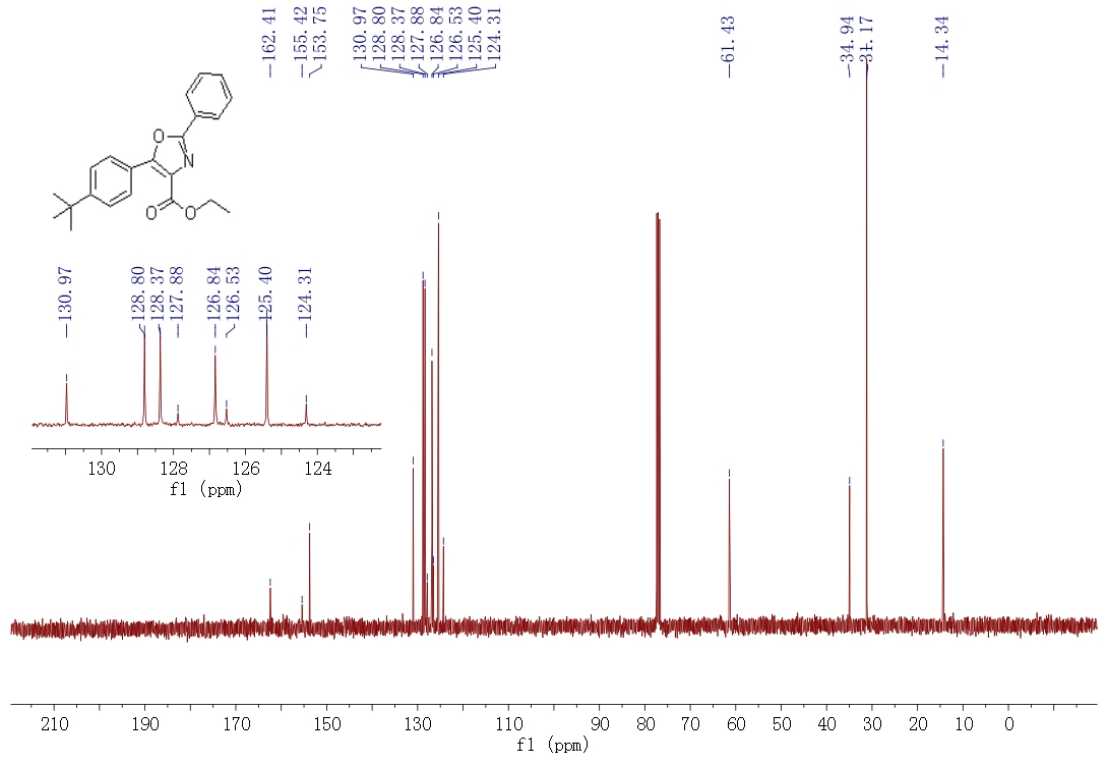
3da-H


162.40
159.56
155.44
146.94
130.97
128.80
128.61
127.94
127.80
126.84
126.50
124.55
61.41
28.88
15.32
14.32
128.80
128.61
127.94
127.80
126.84
126.50
128.5
127.0
f1 (ppm)
f1 (ppm)

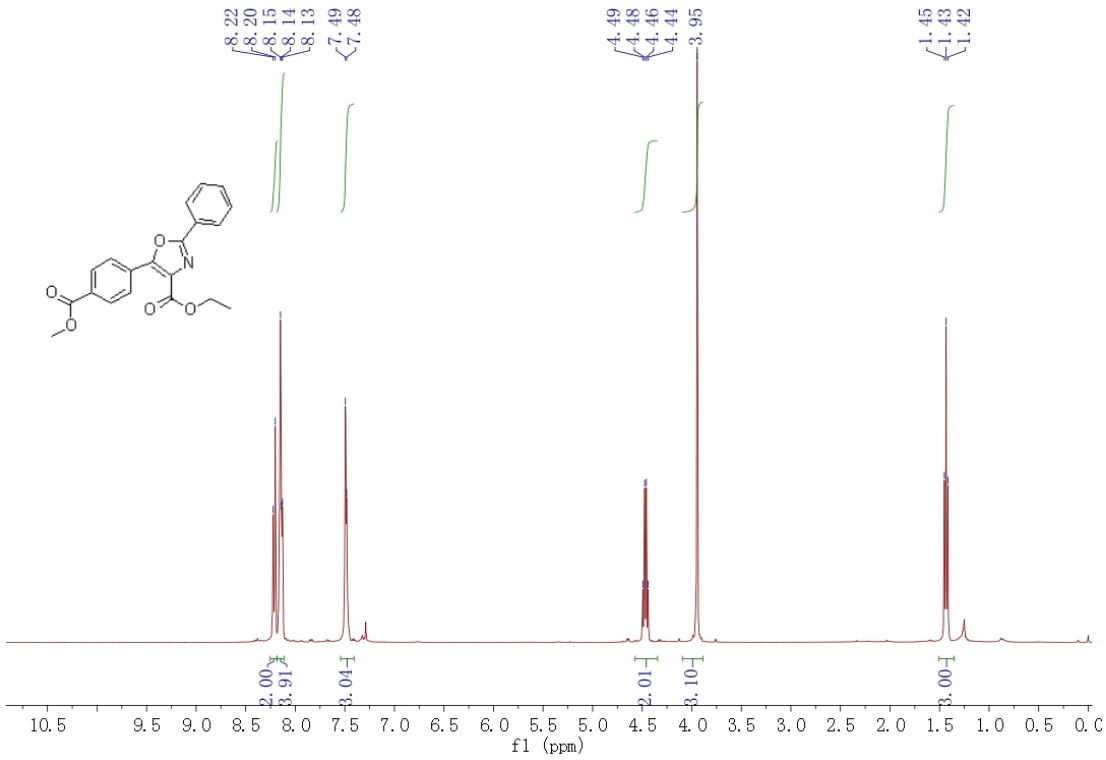
3da-C


8.16
8.15
8.06
8.04
7.53
7.51
7.49
7.48
7.48
4.49
4.47
4.45
4.44
1.45
1.43
1.42
1.37
2.01
2.06
2.06
3.01
2.12
3.00
9.04
f1 (ppm)

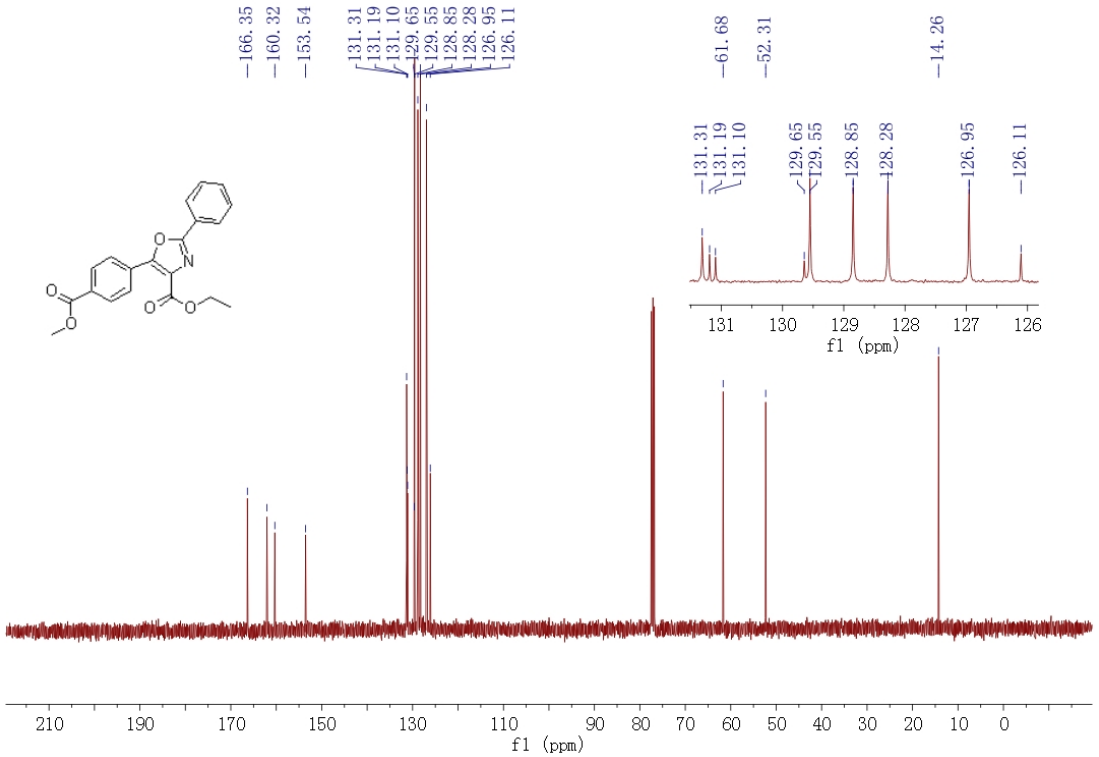
3ea-H


162.41
155.42
153.75
130.97
128.80
128.37
127.88
126.84
126.53
125.40
124.31
61.43
34.94
31.17
14.34
f1 (ppm)

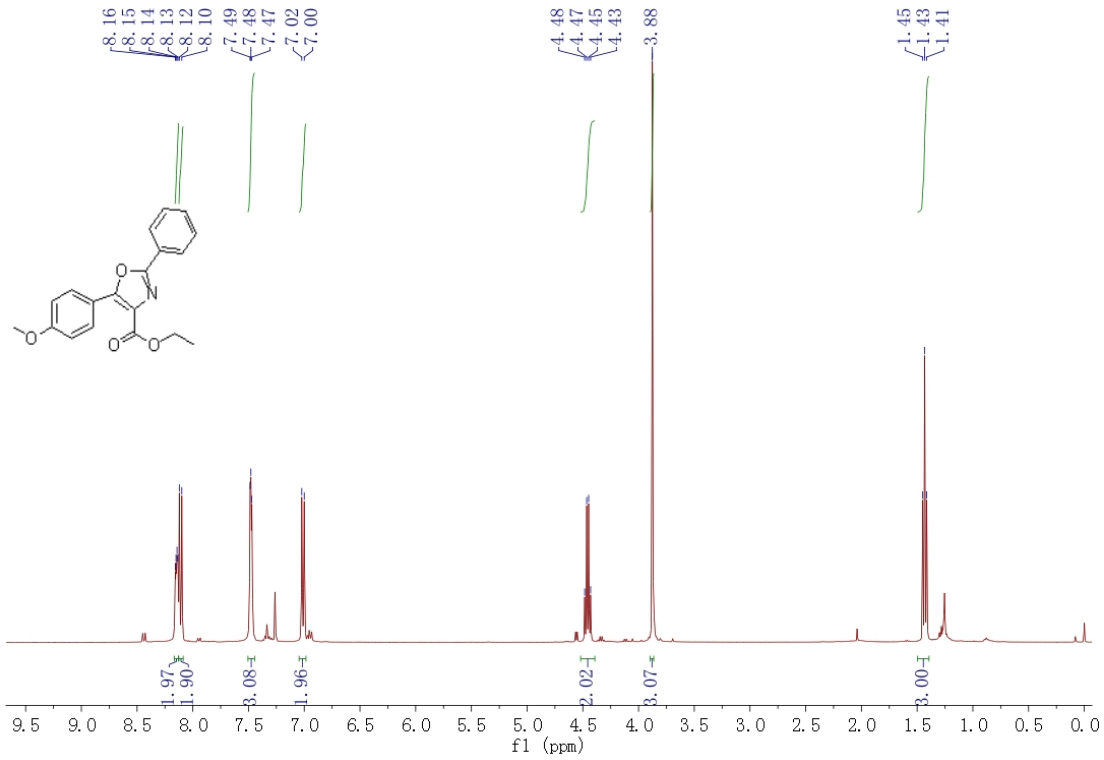
3ea-C


8.22
8.20
8.15
8.14
8.13
7.49
7.48
4.49
4.48
4.46
4.44
3.95
1.45
1.43
1.42
2.00
3.91
3.04
2.01
3.10
3.00
f1 (ppm)

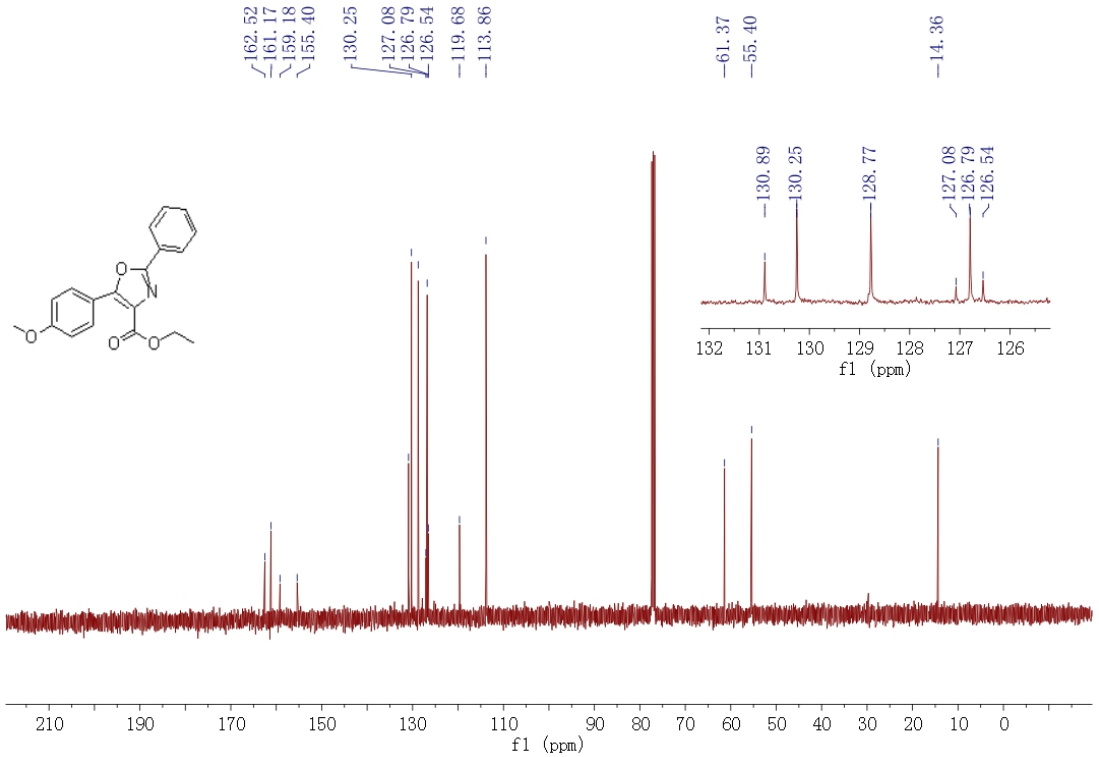
3fa-H


166.35
160.32
153.54
131.31
131.19
131.10
129.65
129.55
128.85
128.28
126.95
126.11
61.68
52.31
14.26
f1 (ppm)

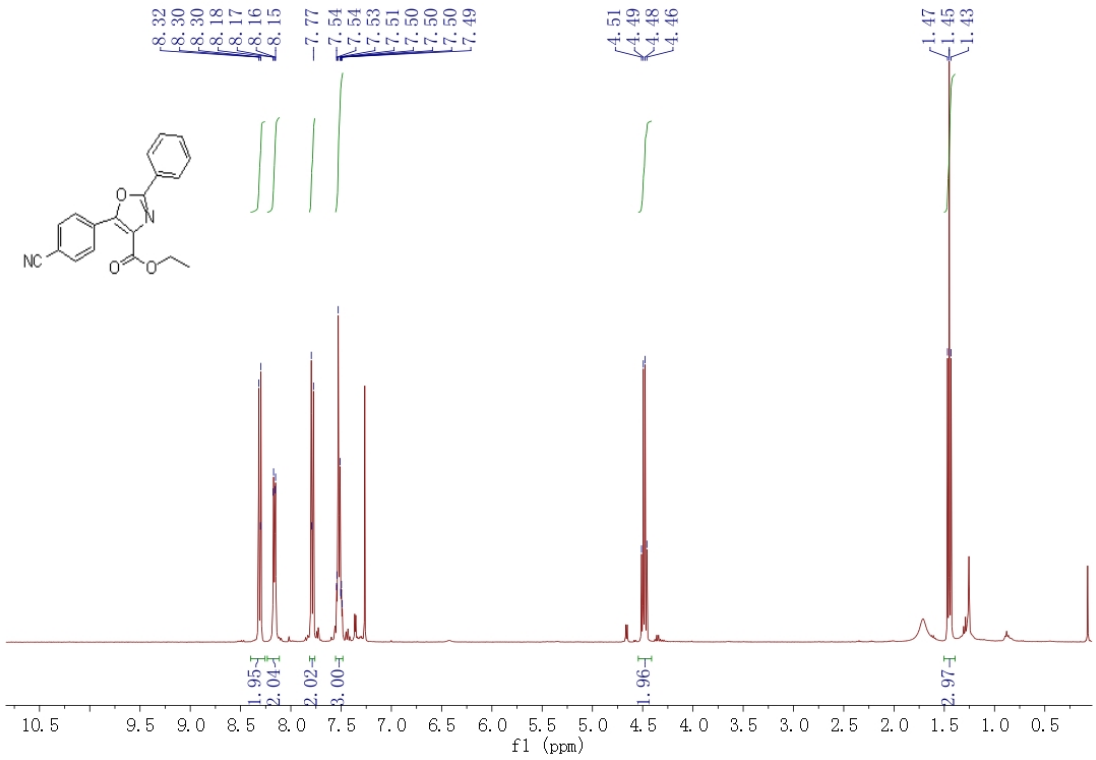
3fa-C


8.16
8.15
8.14
8.13
8.12
8.10
7.49
7.48
7.47
7.02
7.00
4.48
4.47
4.45
4.43
3.88
1.45
1.43
1.41
1.97
1.90
3.08
1.96
2.02
3.07
3.00
f1 (ppm)

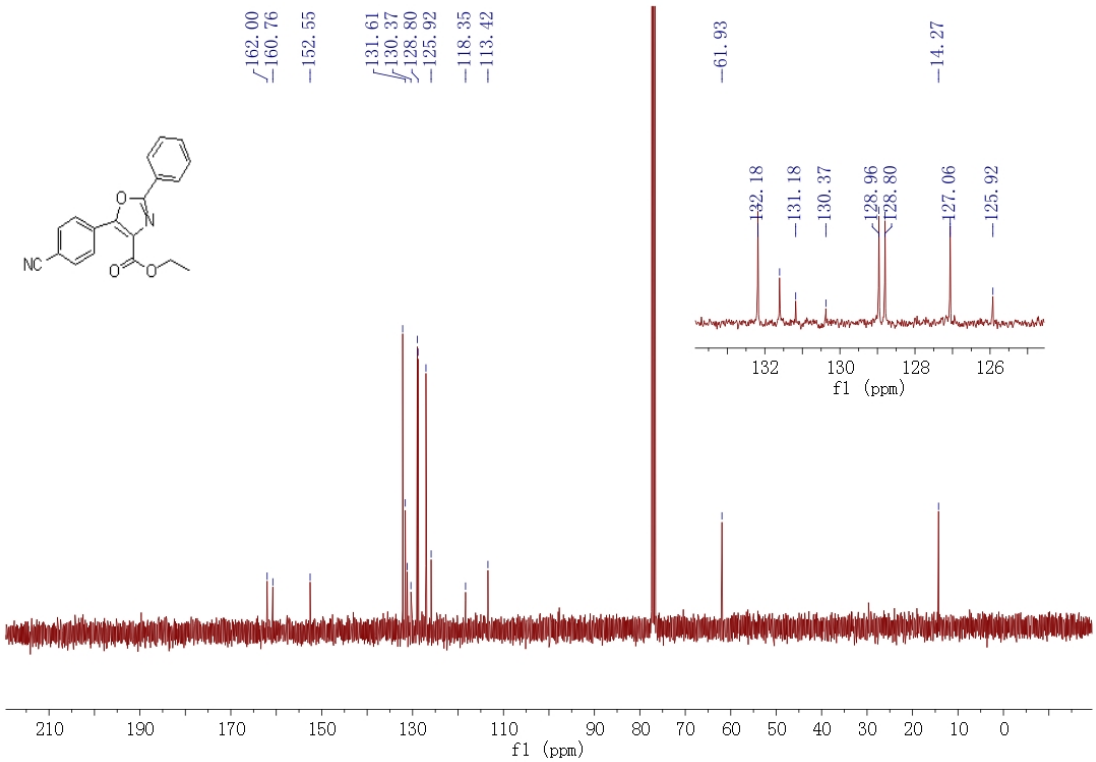
3ga-H


162.52
161.17
159.18
155.40
130.25
127.08
126.79
126.54
119.68
113.86
61.37
55.40
14.36
130.89
130.25
128.77
127.08
126.79
126.54
f1 (ppm)

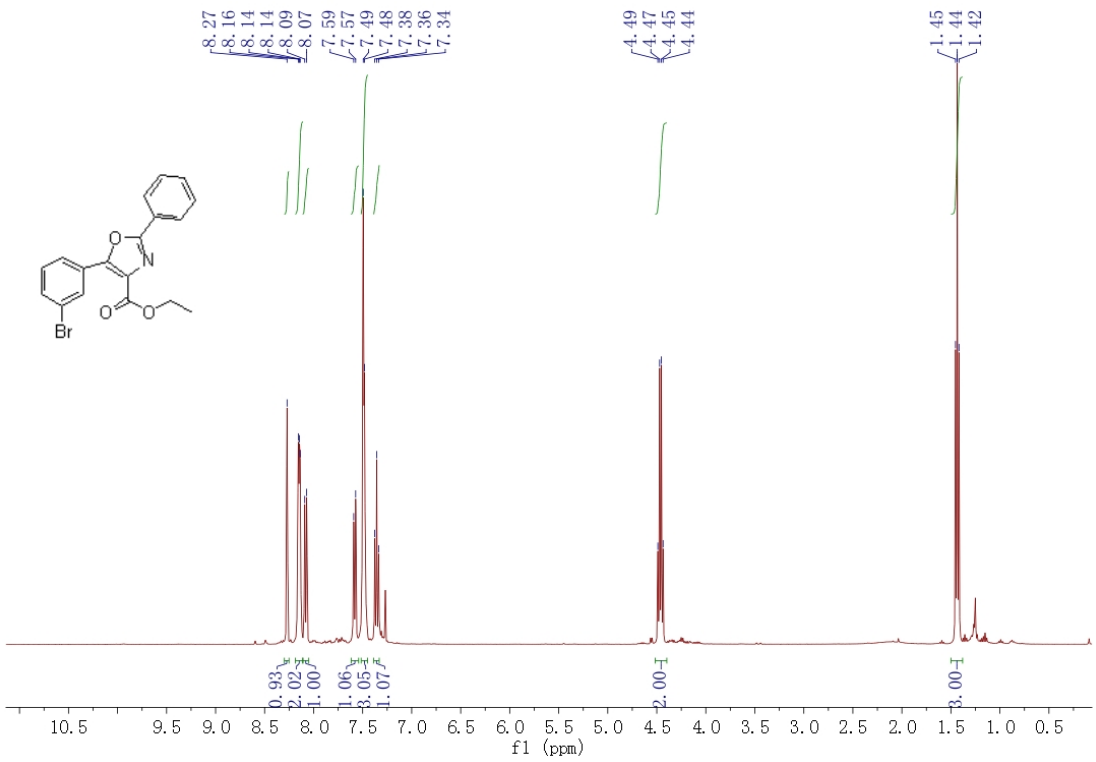
3ga-C


8.32
8.30
8.30
8.18
8.17
8.16
8.15
7.77
7.54
7.54
7.53
7.51
7.50
7.50
7.50
7.49
4.51
4.49
4.48
4.46
1.47
1.45
1.43
NC
O
N
O
O
1.95
2.04
2.02
3.00
1.96
2.97
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
f1 (ppm)

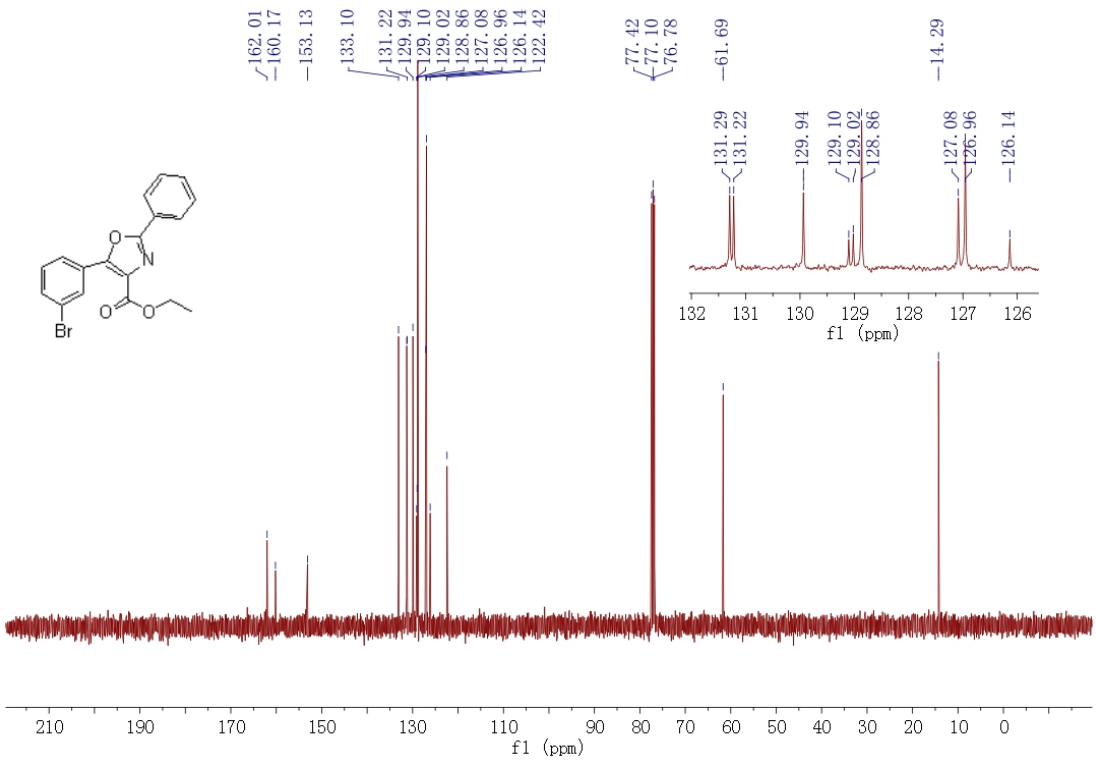
3ha-H


162.00
160.76
152.55
131.61
130.37
128.80
125.92
118.35
113.42
61.93
14.27
132.18
131.18
130.37
128.96
128.80
127.06
125.92
NC
O
N
O
O
132
130
128
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

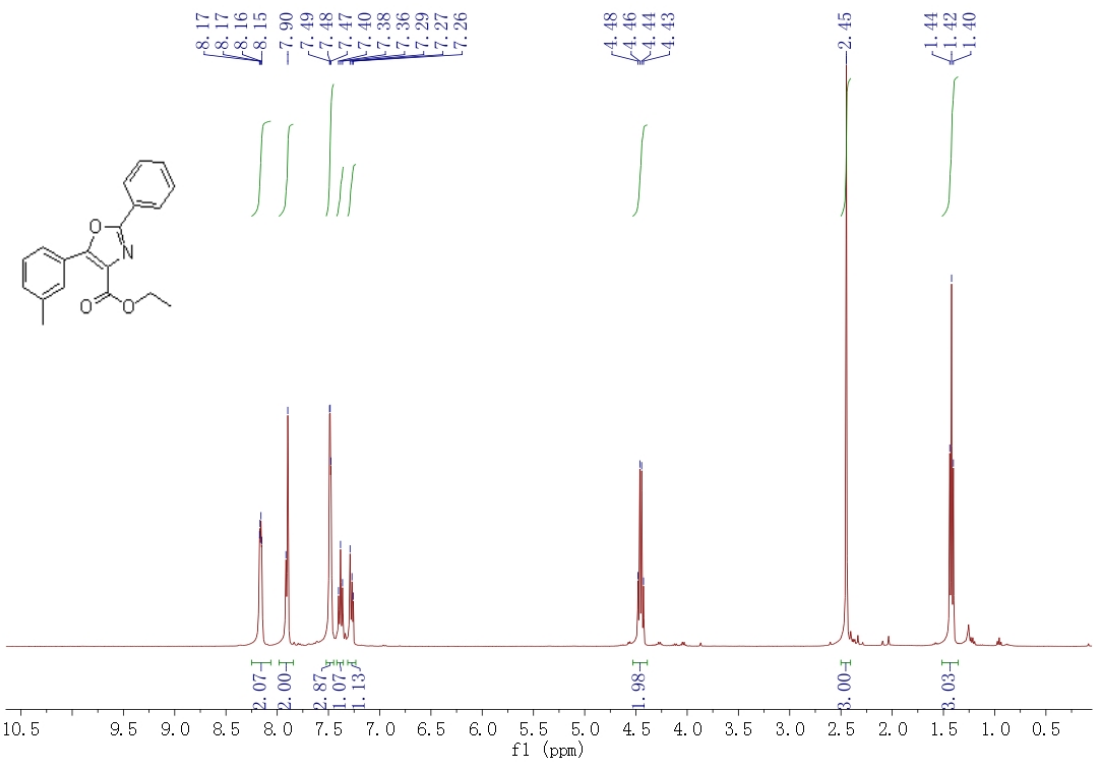
3ha-C


8.27
8.16
8.14
8.14
8.09
8.07
7.59
7.57
7.49
7.48
7.38
7.36
7.34
4.49
4.47
4.45
4.44
1.45
1.44
1.42
0.93
2.02
1.00
1.06
3.05
1.07
2.00
3.00
O
N
O
O
Br
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
f1 (ppm)

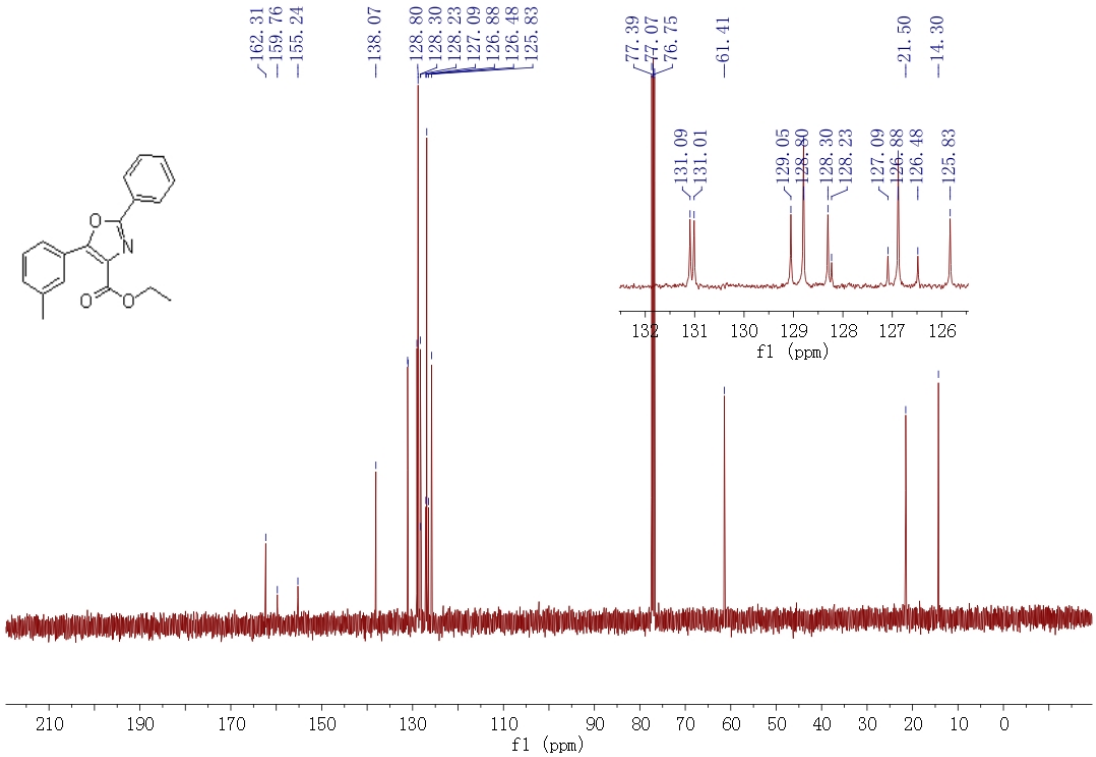
3ia-H


162.01
160.17
153.13
133.10
131.22
129.94
129.10
129.02
128.86
127.08
126.96
126.14
122.42
77.42
77.10
76.78
61.69
14.29
131.29
131.22
129.94
129.10
129.02
128.86
127.08
126.96
126.14
O
N
O
O
Br
132
131
130
129
128
127
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

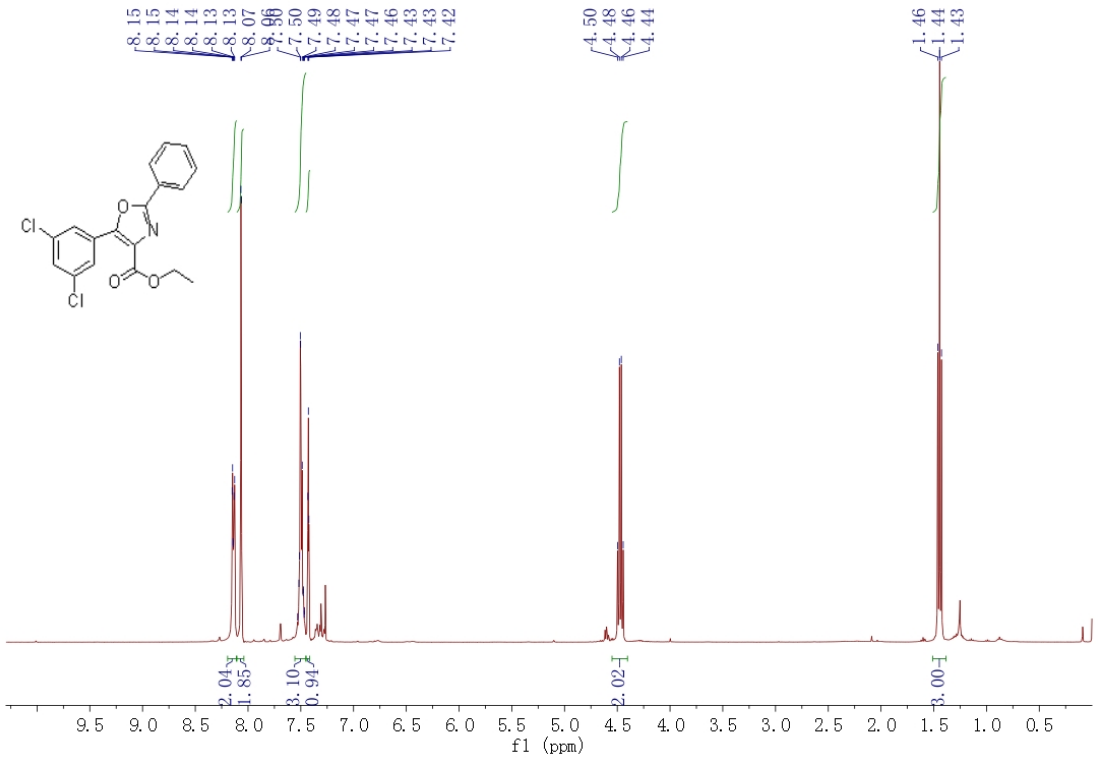
3ia-C


8.17
8.17
8.16
8.15
7.90
7.49
7.48
7.47
7.40
7.38
7.36
7.29
7.27
7.26
4.48
4.46
4.44
4.43
2.45
1.44
1.42
1.40
2.07
2.00
2.87
1.07
1.13
1.98
3.00
3.03
f1 (ppm)

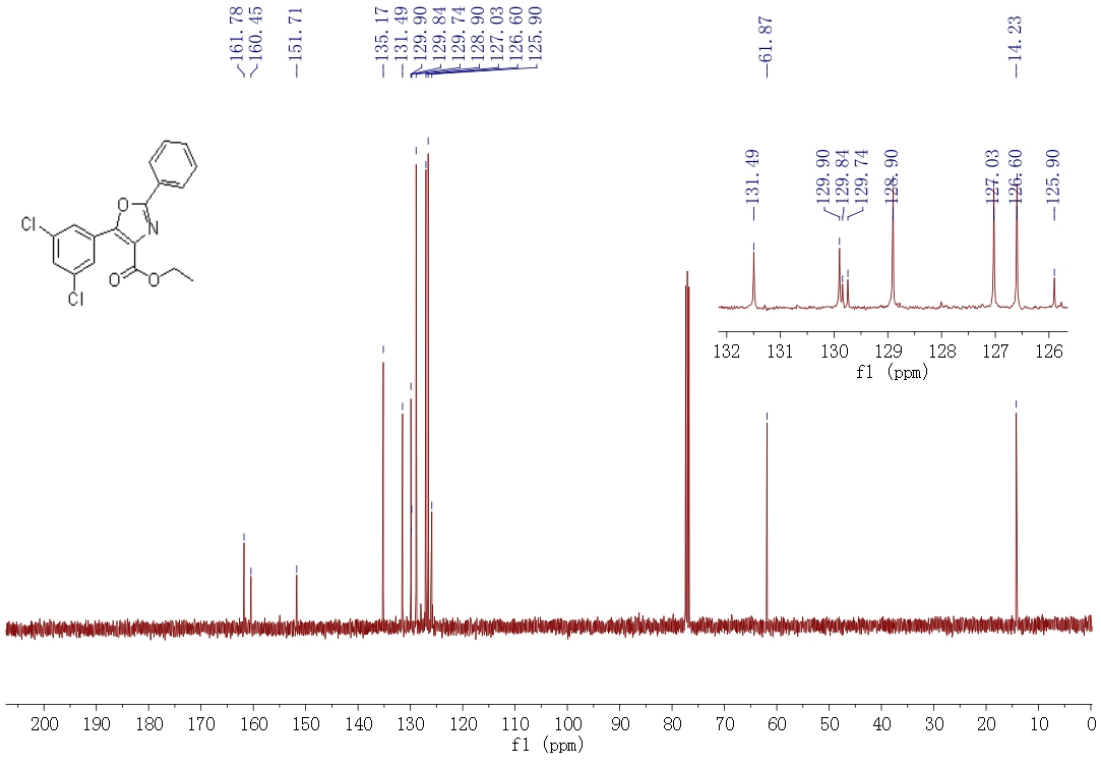
3ja-H


162.31
159.76
155.24
138.07
128.80
128.30
128.23
127.09
126.88
126.48
125.83
77.39
77.07
76.75
61.41
21.50
14.30
131.09
131.01
129.05
128.80
128.30
128.23
127.09
126.88
126.48
125.83
f1 (ppm)
f1 (ppm)

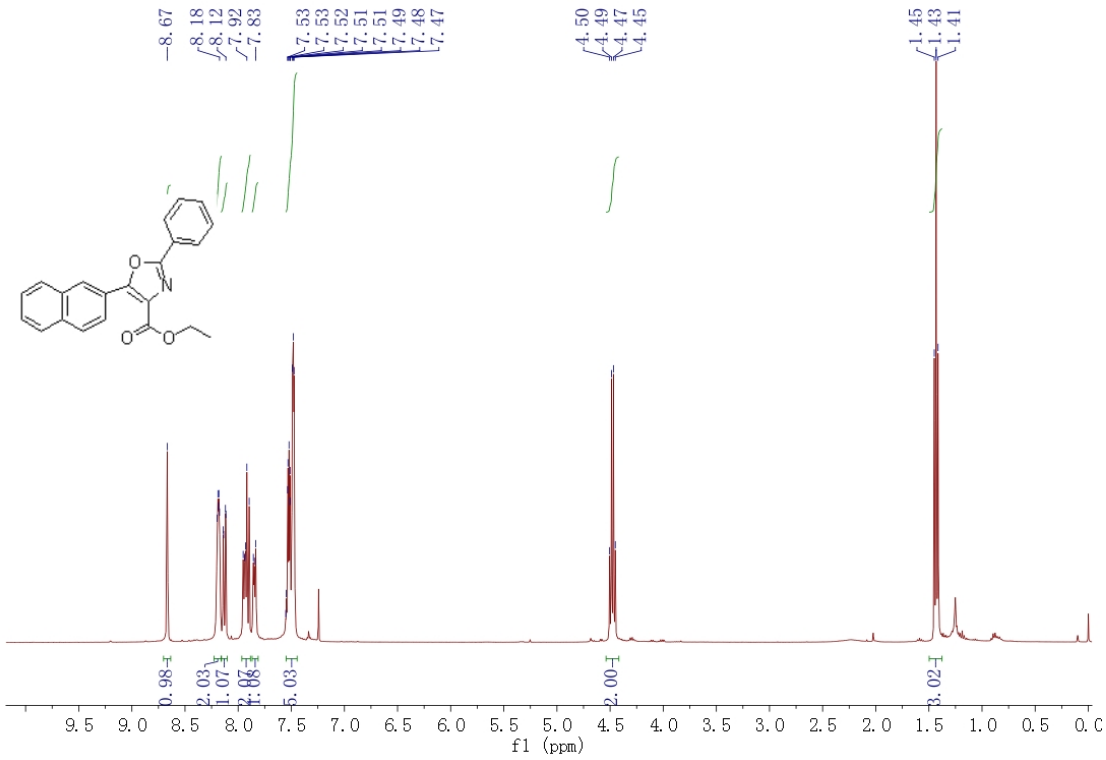
3ja-C


8.15
8.15
8.14
8.14
8.13
8.13
8.07
7.50
7.49
7.48
7.47
7.47
7.46
7.43
7.42
4.50
4.48
4.46
4.44
1.46
1.44
1.43
Cl
Cl
O
N
O
O
2.04
1.85
3.10
0.94
2.02
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
f1 (ppm)

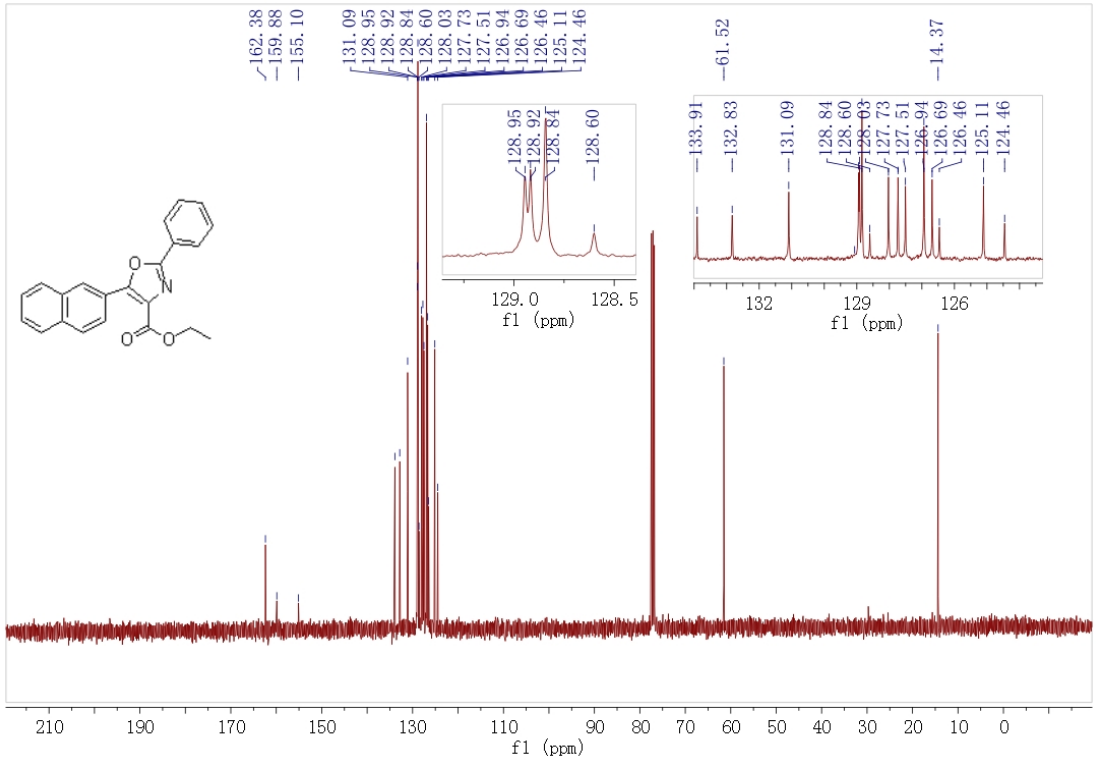
3ka-H


161.78
160.45
151.71
135.17
131.49
129.90
129.84
129.74
128.90
127.03
126.60
125.90
61.87
14.23
Cl
Cl
O
N
O
O
131.49
129.90
129.84
129.74
128.90
127.03
126.60
125.90
132 131 130 129 128 127 126
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

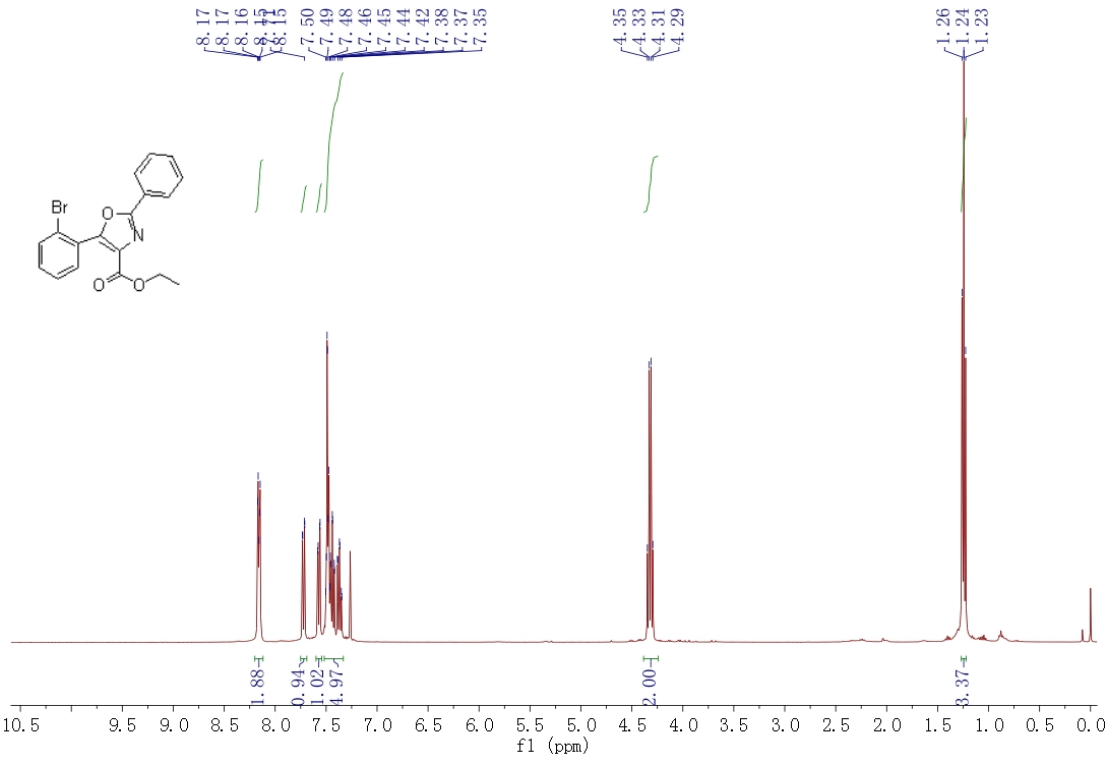
3ka-C


8.67
8.18
8.12
7.92
7.83
7.53
7.52
7.51
7.49
7.48
7.47
4.50
4.49
4.47
4.45
1.45
1.43
1.41
0.98
2.03
1.07
5.03
2.00
3.02
f1 (ppm)

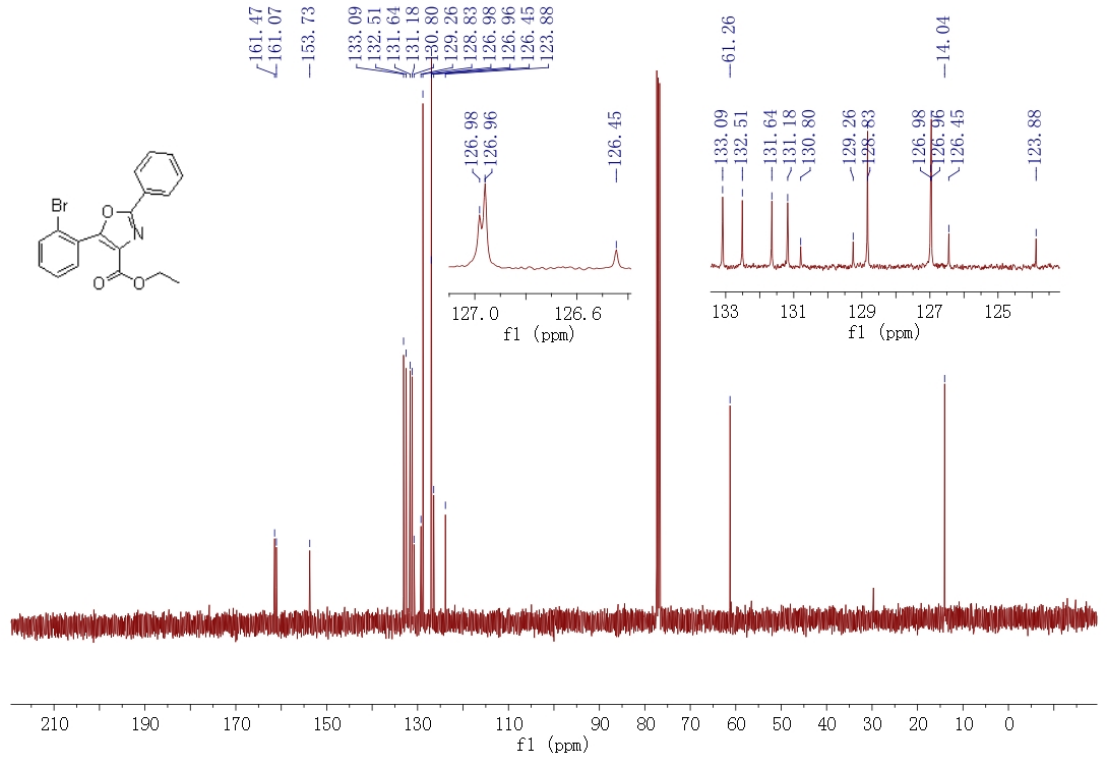
3la-H


162.38
159.88
155.10
131.09
128.95
128.92
128.84
128.60
128.03
127.73
127.51
126.94
126.69
126.46
125.11
124.46
61.52
14.37
f1 (ppm)

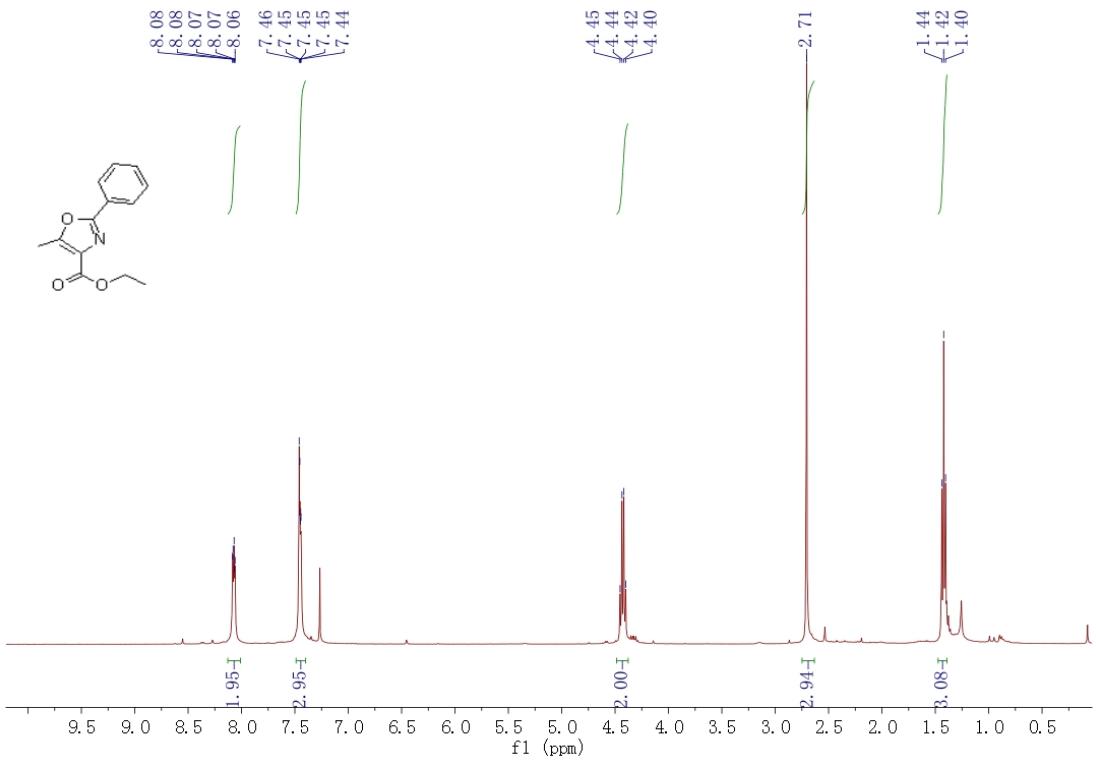
3la-C


8.17
8.16
7.50
7.49
7.48
7.46
7.45
7.44
7.42
7.38
7.37
7.35
4.35
4.33
4.31
4.29
1.26
1.24
1.23
Br
O
N
O
O
1.88
0.94
1.02
4.97
2.00
3.37
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
f1 (ppm)

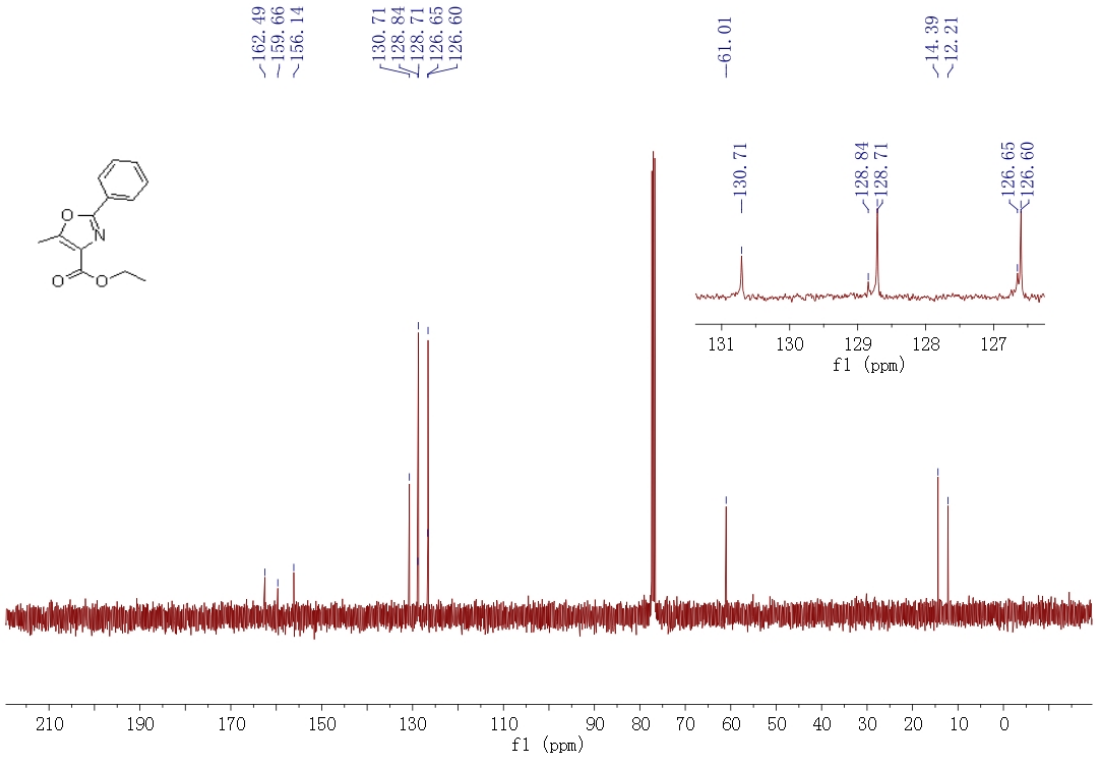
3ma-H


161.47
161.07
153.73
133.09
132.51
131.64
131.18
130.80
129.26
128.83
126.98
126.96
126.45
123.88
61.26
14.04
Br
O
N
O
O
127.0
126.6
f1 (ppm)
133
131
129
127
125
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

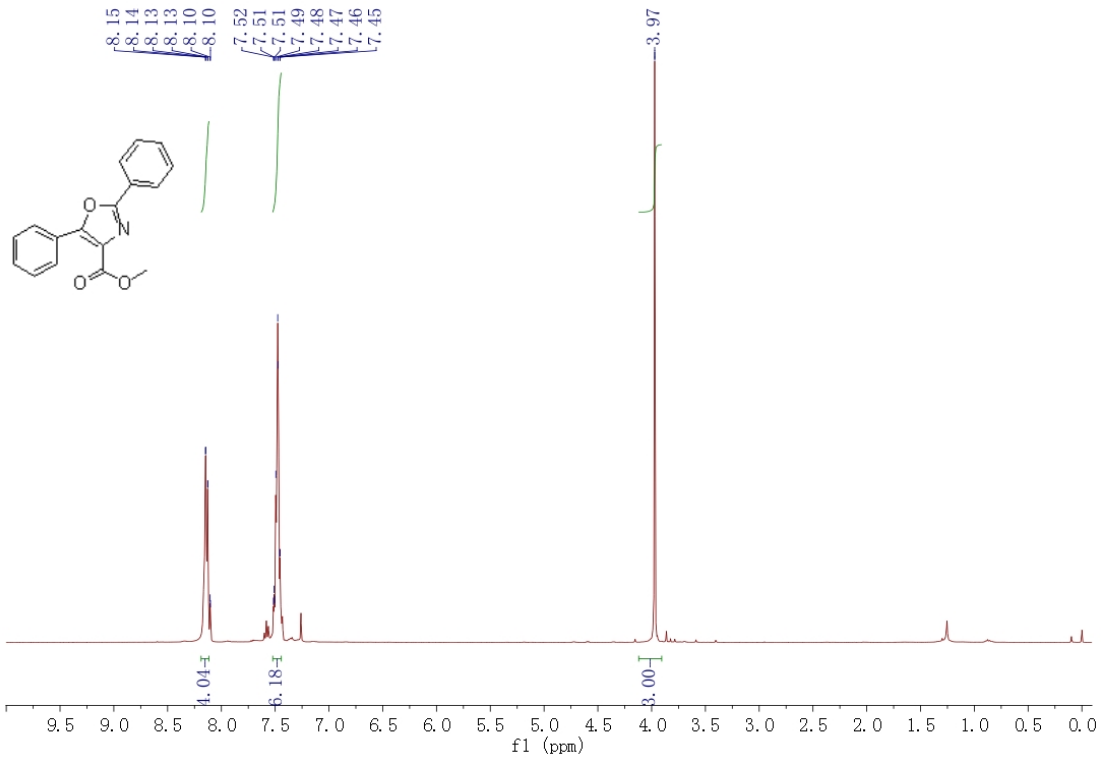
3ma-C


8.08
8.08
8.07
8.07
8.06
7.46
7.45
7.45
7.45
7.44
4.45
4.44
4.42
4.40
2.71
1.44
1.42
1.40
1.95
2.95
2.00
2.94
3.08
f1 (ppm)

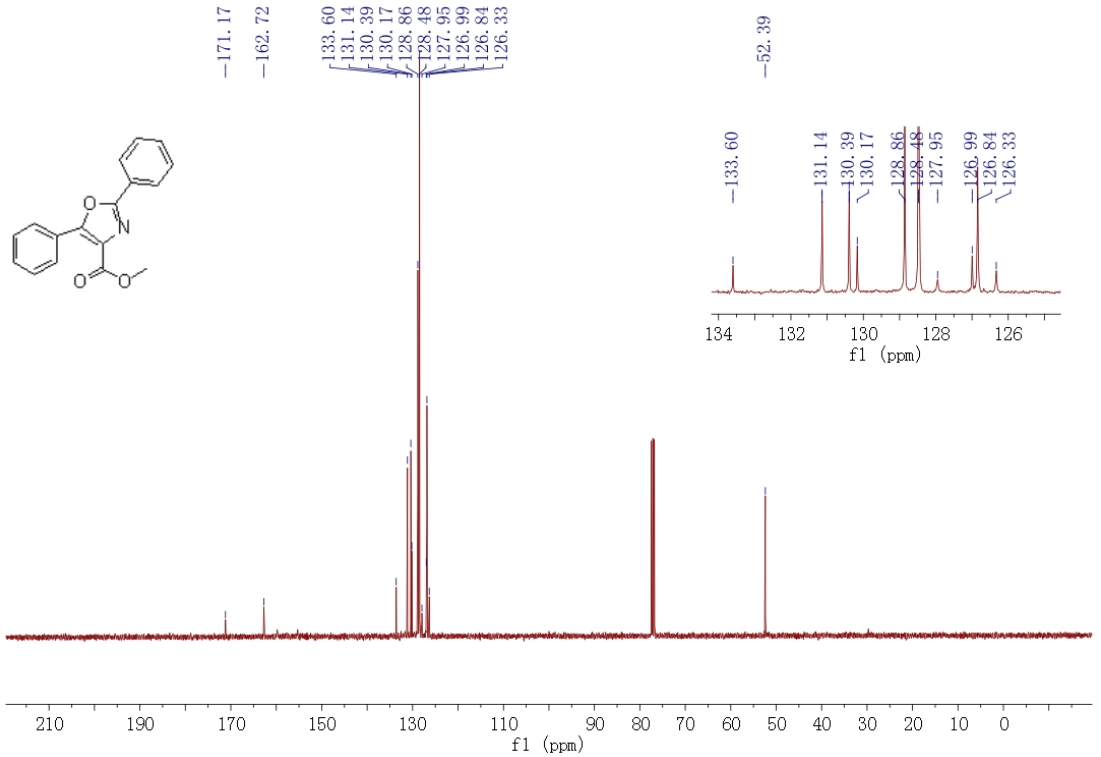
3na-H


162.49
159.66
156.14
130.71
128.84
128.71
126.65
126.60
61.01
14.39
12.21
f1 (ppm)

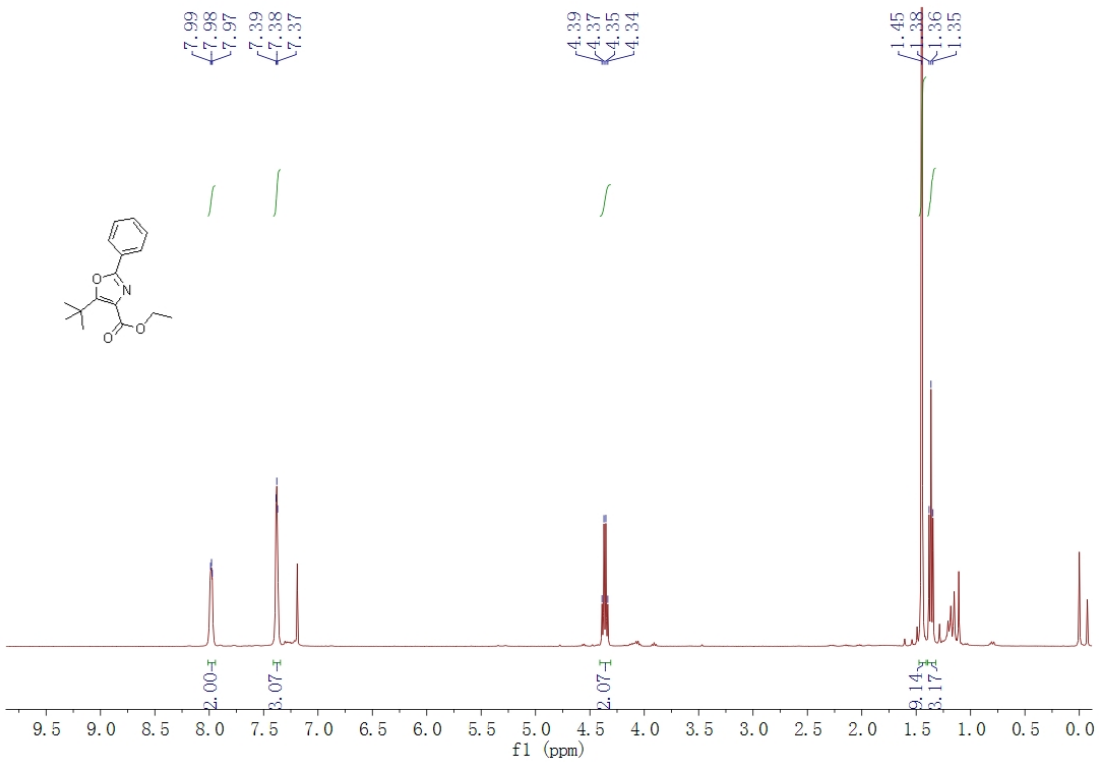
3na-C


8.15
8.14
8.13
8.13
8.10
8.10
7.52
7.51
7.51
7.49
7.48
7.47
7.46
7.45
3.97
4.04
6.18
3.00
f1 (ppm)

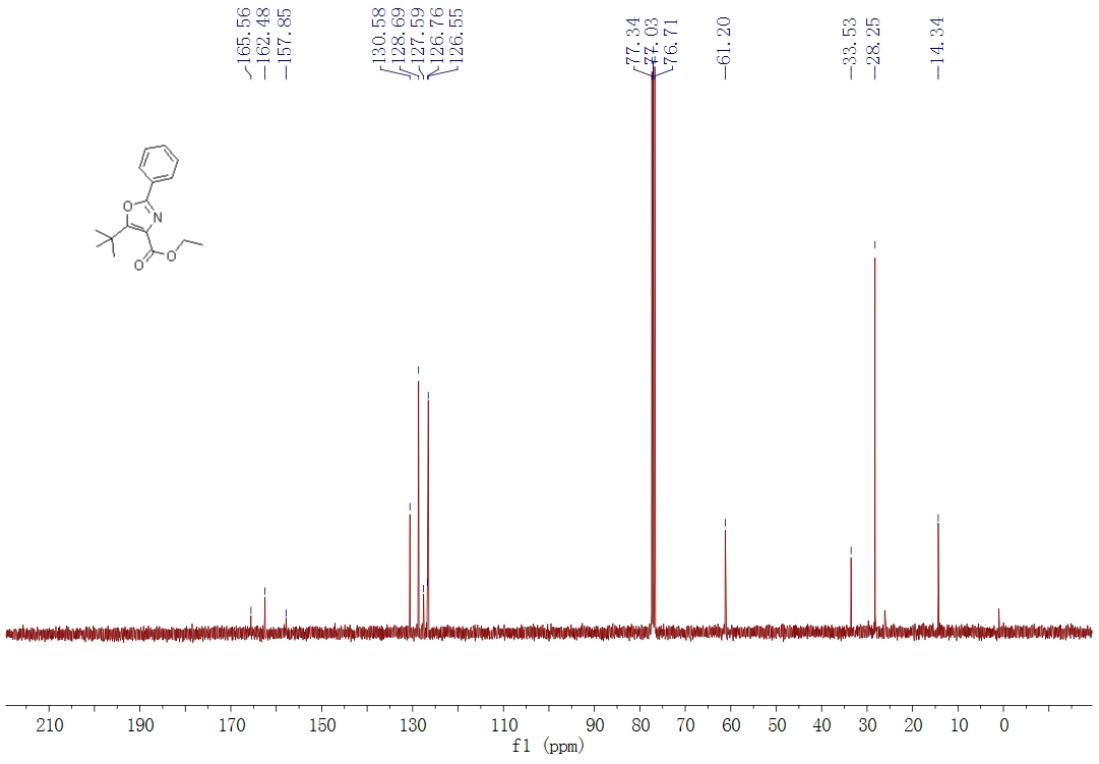
3oa-H


171.17
162.72
133.60
131.14
130.39
130.17
128.86
128.48
127.95
126.99
126.84
126.33
52.39
f1 (ppm)

3oa-C

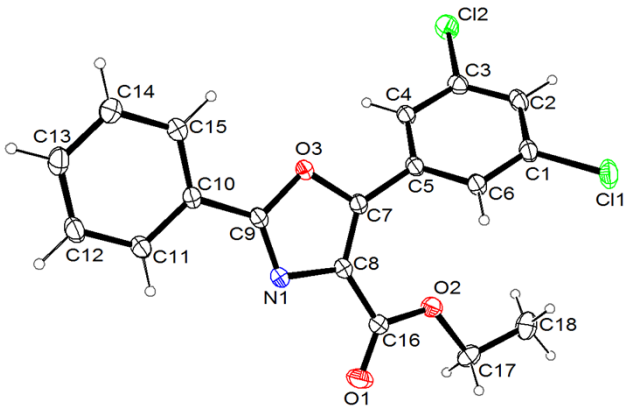

7.99
7.98
7.97
7.39
7.38
7.37
4.39
4.37
4.35
4.34
1.45
1.38
1.36
1.35
2.00
3.07
2.07
9.14
3.17
f1 (ppm)

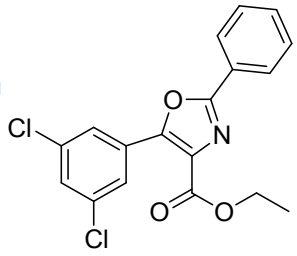
3pa-H


165.56
162.48
157.85
130.58
128.69
127.59
126.76
126.55
77.34
77.03
76.71
61.20
33.53
28.25
14.34
f1 (ppm)

3pa-C

H. X-ray Crystallographic Analysis of 3ka





3ka

Summary of Data CCDC 982238

Compound Name:

Formula: C18 H13 Cl2 N1 O3

Unit Cell Parameters: a 7.4219(15) b 9.3714(19) c 13.520(3) P-1