Supporting Information

Pd-Catalyzed Desulfitative Arylation for Synthesis of 2,5-Diarylated Oxazole-4-Carboxylates with Dioxygen as the Terminal Oxidant

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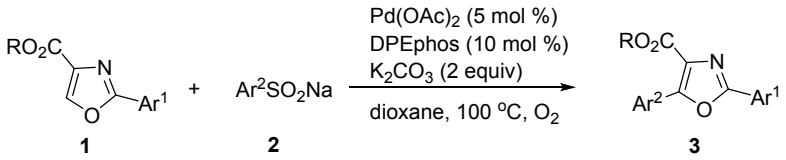
General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100-400 mesh silica gel plates, and visualization was effected at 254 nm.

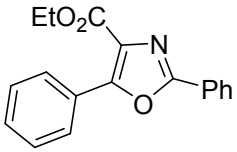
Experimental Procedure for Compounds 3



1 **2** **3**

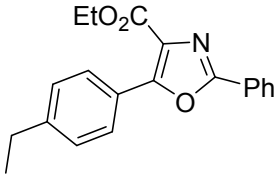
The mixture of 2-aryloxazole-4-carboxylate **1** (0.3 mmol), sodium arylsulfinates **2** (0.6 mmol), $Pd(OAc)_2$ (5 mol%), DPEphos (10 mol %), K_2CO_3 (0.6 mmol) in dioxane (3 mL) was stirred at 100 °C under O_2 for 20 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The organic extracts were dried over $MgSO_4$. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford desired product.

Characterization Data for All Products 3



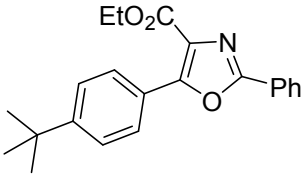
Ethyl 2,5-diphenyloxazole-4-carboxylate (3a)[1]

Yellow solid (71.2 mg, 81%); m.p. = 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 1H), 8.06 – 8.03 (m, 2H), 7.46 – 7.39 (m, 6H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 159.8, 155.0, 131.0, 130.2, 128.8, 128.5, 128.3, 128.3, 127.1, 126.8, 126.4, 61.4, 14.2. MS (EI, 70 eV) *m/z*: 77, 105, 221, 293. IR (KBr): 3062, 2982, 1720, 1488, 1215, 1098, 710, 688 cm^{-1}.



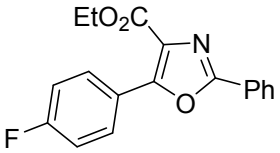
Ethyl 5-(4-ethylphenyl)-2-phenyloxazole-4-carboxylate (3b)

Yellow oil (73.2 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.47 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 3H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 159.5, 155.4, 146.9, 130.9, 128.7, 128.6, 127.9, 127.8, 126.8, 126.5, 124.5, 61.4, 28.8, 15.3, 14.3. IR (KBr): 2969, 1721, 1505, 1453, 1216, 1097, 711 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$, 344.1257; found, 344.1259.



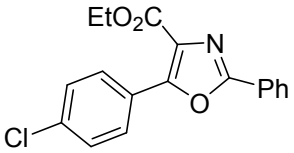
Ethyl 5-(4-(tert-butyl)phenyl)-2-phenyloxazole-4-carboxylate (3c)

Yellow oil (76.4 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.48 (m, 5H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.4, 153.7, 130.9, 128.7, 128.3, 127.8, 126.8, 126.5, 125.3, 124.3, 61.4, 34.9, 31.1, 14.3. IR (KBr): 2961, 1721, 1613, 1503, 1454, 1216, 1092, 710 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{23}NNaO_3$ $[M+Na]^+$, 372.1570; found, 372.1576.



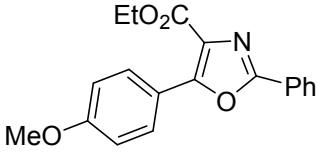
Ethyl 5-(4-fluorophenyl)-2-phenyloxazole-4-carboxylate (3d)[2]

White solid (61.6 mg, 66%). m.p. = 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 4H), 7.50 – 7.45 (m, 3H), 7.17 (t, *J* = 8.7 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 250 Hz), 162.2, 159.6, 154.2, 131.0, 130.7 (d, *J* = 9 Hz), 128.8, 128.0, 126.8, 126.2, 123.3 (d, *J* = 3 Hz), 115.5 (d, *J* = 22 Hz), 61.5, 14.2. IR (KBr): 2984, 1712, 1603, 1503, 1455, 1090, 842, 705 cm^{-1}. MS (EI, 70 eV) m/z: 77, 95, 105, 239, 311.



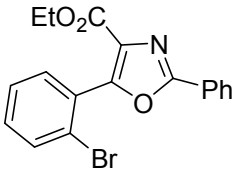
Ethyl 5-(4-chlorophenyl)-2-phenyloxazole-4-carboxylate (3e)[2]

Whtie solid (62.8 mg, 64%). m.p. = 117-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 2H), 8.10 – 8.07 (m, 2H), 7.49 – 7.44 (m, 5H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.8, 153.9, 136.3, 131.1, 129.7, 128.8, 128.7, 128.6, 126.8, 126.2, 125.5, 61.5, 14.2. IR (KBr): 2985, 1718, 1487, 1214, 1094, 755, 712 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 139, 255, 327 (Cl^{35}).



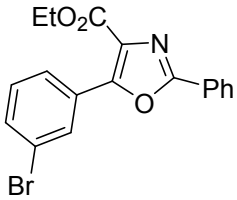
Ethyl 5-(4-methoxyphenyl)-2-phenyloxazole-4-carboxylate (3f)[3]

White solid (55.2 mg, 57%); m.p. = 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 4H), 7.51 – 7.47 (m, 3H), 7.02 (d, *J* = 8.9 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 161.1, 159.1, 155.4, 130.8, 130.2, 128.7, 127.0, 126.7, 126.5, 119.6, 113.8, 61.3, 55.4, 14.3. IR (KBr): 2926, 1715, 1505, 1212, 1091, 709 cm^{-1}. MS (EI, 70 eV) *m/z*: 77, 105, 135, 207, 251, 323.



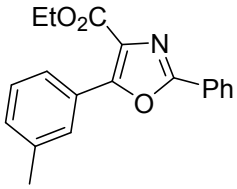
Ethyl 5-(2-bromophenyl)-2-phenyloxazole-4-carboxylate (3g)

Yellow solid (82.4 mg, 74%); m.p. = 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 2H), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.41 – 7.36 (m, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 161.0, 153.7, 133.0, 132.5, 131.6, 131.1, 130.7, 129.2, 128.8, 126.9, 126.9, 126.4, 123.8, 61.2, 14.0. IR (KBr): 2983, 1721, 1491, 1463, 1218, 1026, 767, 731, 692 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ (Br^{79}) $[M+Na]^+$, 394.0049; found, 394.0053.



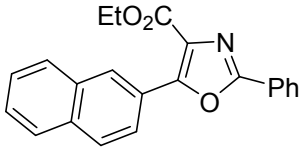
Ethyl 5-(3-bromophenyl)-2-phenyloxazole-4-carboxylate (3h)

Yellow solid (83.5 mg, 75%); m.p. = 124-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.17 – 8.12 (m, 2H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 3H), 7.35 (t, *J* = 8.0 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 160.1, 153.0, 133.0, 131.2, 131.1, 129.8, 129.0, 128.9, 128.8, 127.0, 126.9, 126.0, 122.3, 61.6, 14.2. IR (KBr): 2986, 1720, 1563, 1478, 1221, 1109, 746 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ (Br^{79}) $[M+Na]^+$, 394.0049; found, 394.0054.



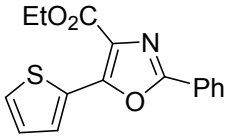
Ethyl 2-phenyl-5-(m-tolyl)oxazole-4-carboxylate (3i)

Yellow oil (71.8 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.7, 155.2, 138.0, 131.0, 130.9, 129.0, 128.7, 128.2, 128.2, 127.0, 126.8, 126.4, 125.8, 61.3, 21.4, 14.2. IR (KBr): 2982, 1721, 1564, 1485, 1213, 1100, 712 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_3$ $[M+Na]^+$, 330.1011; found, 330.1012.



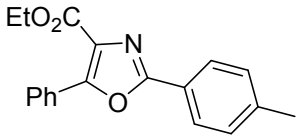
Ethyl 5-(naphthalen-2-yl)-2-phenyloxazole-4-carboxylate (3j)

White solid (68.9 mg, 67%); m.p. = 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.22 – 8.19 (m, 2H), 8.17 – 8.13 (m, 1H), 7.98 – 7.92 (m, 2H), 7.89 – 7.85 (m, 1H), 7.58 – 7.49 (m, 5H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 159.8, 155.0, 133.8, 132.7, 131.0, 128.8, 128.8, 128.7, 128.5, 127.9, 127.6, 127.4, 126.8, 126.6, 126.3, 125.0, 124.3, 61.4, 14.3. IR (KBr): 2984, 1718, 1553, 1490, 1265, 1222, 1097, 754 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{17}NNaO_3$ $[M+Na]^+$, 366.1101; found, 366.1094.



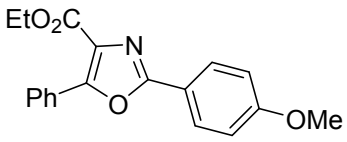
Ethyl 2-phenyl-5-(thiophen-2-yl)oxazole-4-carboxylate (3k)[4]

Brown oli (56.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 –8.13 (m, 3H), 7.54 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.17 (dd, *J* = 4.9, 4.0 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 158.8, 150.9, 131.0, 130.1, 129.5, 128.7, 128.5, 127.6, 126.8, 126.2, 126.1, 61.4, 14.3. IR (KBr): 2927, 1663, 1605, 1576, 1511 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 111, 227, 299.



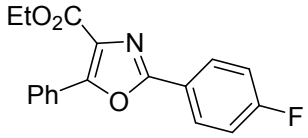
Ethyl 5-phenyl-2-(p-tolyl)oxazole-4-carboxylate (3l)

White solid (69.1 mg, 75%); m.p. = 82-83 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.0, 154.7, 141.4, 130.1, 129.4, 128.4, 128.3, 128.1, 127.2, 126.8, 123.6, 61.3, 21.5, 14.2. IR (KBr): 2982, 1719, 1588, 1497, 1213, 1098, 1025, 761, 693 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_3$ $[M+Na]^+$, 330.1101; found, 330.1102.



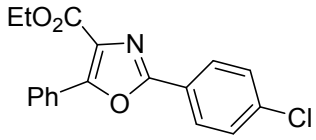
Ethyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3m)[5]

Yellow oil (67.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 4H), 7.51 – 7.42 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 161.8, 133.4, 130.0, 128.5, 128.4, 128.3, 128.3, 128.0, 127.2, 119.0, 114.1, 61.3, 55.3, 14.2. IR (KBr): 2984, 1718, 1614, 1503, 1218, 838, 741 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 135, 207, 323.



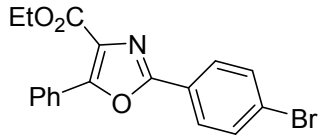
Ethyl 2-(4-fluorophenyl)-5-phenyloxazole-4-carboxylate (3n)

White solid (78.4 mg, 84%); m.p. = 96-97 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.14 (m, 2H), 8.12 – 8.06 (m, 2H), 7.54 – 7.43 (m, 3H), 7.23 – 7.12 (m, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, *J* = 251 Hz), 162.2, 159.0, 155.1, 130.3, 129.1 (d, *J* = 9 Hz), 128.5, 128.4, 128.3, 127.0, 122.8 (d, *J* = 3 Hz), 116.1 (d, *J* = 22Hz), 61.5, 14.2. IR (KBr): 2985, 1713, 1501, 1451, 1227, 1092, 840, 706 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}FNNaO_3$ $[M+Na]^+$, 334.0850; found, 334.0855.



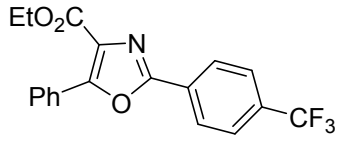
Ethyl 2-(4-chlorophenyl)-5-phenyloxazole-4-carboxylate (3o)[6]

White solid (83.4 mg, 85%); m.p. = 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 4H), 7.50 – 7.40 (m, 5H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 158.7, 155.1, 137.1, 130.3, 129.0, 128.4, 128.3, 128.3, 128.0, 126.8, 124.7, 61.4, 14.1. IR (KBr): 2983, 1718, 1564, 1487, 1266, 1014, 1099, 755 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 139, 206, 327 (Cl^{35}).



Ethyl 2-(4-bromophenyl)-5-phenyloxazole-4-carboxylate (3p)

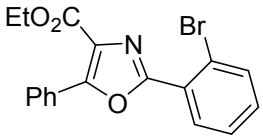
White solid (87.9 mg, 79%); m.p. = 109-110 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.46 (m, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 158.9, 155.2, 132.1, 130.4, 128.5, 128.3, 128.2, 126.9, 125.6, 125.2, 61.5, 14.2. IR (KBr): 2982, 2926, 1731, 1560, 1474, 1100, 758 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ (Br^{79}) $[M+Na]^+$, 394.0049; found, 394.0056.



Ethyl 5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (3q)

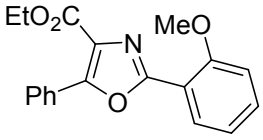
White solid (94.2 mg, 87%); m.p. = 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 2H), 8.12 – 8.08 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.47 (m, 3H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.3, 155.7, 132.5 (q, *J* = 33 Hz), 129.5, 128.6, 128.4, 127.0, 126.7, 125.8 (q, *J* = 4 Hz), 123.7 (q, *J* = 271 Hz), 61.5, 14.2. IR (KBr): 2963, 1721, 1619, 1495, 1128, 847, 756, 708 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{14}F_3NNaO_3$ $[M+Na]^+$, 384.0818; found,

384.0823.



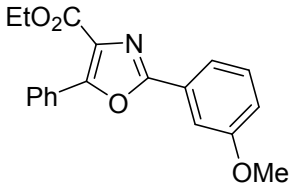
Ethyl 2-(2-bromophenyl)-5-phenyloxazole-4-carboxylate (3r)

White solid (73.5 mg, 66%); m.p. = 96-97 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 8.07 – 8.05 (m, 1H), 7.72 – 7.70 (m, 1H), 7.53 – 7.39 (m, 4H), 7.34 – 7.30 (m, 1H), 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, 158.4, 155.6, 134.3, 131.9, 131.8, 130.3, 128.5, 128.4, 127.9, 127.6, 127.3, 126.9, 121.2, 61.4, 14.2. IR (KBr): 2923, 1721, 1485, 1214, 1097, 822, 756, 694 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrNNaO_3$ (Br^{79}) $[M+Na]^+$, 394.0049; found, 394.0053.



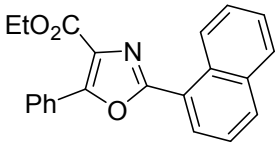
Ethyl 2-(2-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3s)[2]

Yellow oil(54.3 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.13 (m, 2H), 8.05 – 8.03 (m, 1H), 7.52 – 7.36 (m, 4H), 7.06 – 7.01 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.5, 157.9, 154.7, 132.3, 130.7, 130.0, 128.4, 128.3, 127.9, 127.3, 120.5, 115.5, 111.8, 61.2, 55.9, 14.2. IR (KBr): 2961, 1718, 1488, 1215, 1103, 1023, 913, 745, 696 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 135, 249, 323.



Ethyl 2-(3-methoxyphenyl)-5-phenyloxazole-4-carboxylate (3t)

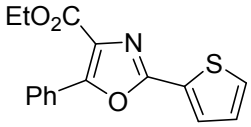
Yellow oil (60.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.75 – 7.71 (m, 1H), 7.68 – 7.67 (m, 1H), 7.53 – 7.46 (m, 3H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.05 – 7.02 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 159.9, 159.7, 155.0, 130.3, 129.9, 128.5, 128.3, 128.2, 127.5, 127.1, 119.3, 117.6, 111.4, 61.4, 55.5, 14.2. IR (KBr): 2925, 1719, 1565, 1097, 1037, 758 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{17}NNaO_4$ $[M+Na]^+$, 346.1050; found, 346.1046.



Ethyl 2-(naphthalen-1-yl)-5-phenyloxazole-4-carboxylate (3u)[2]

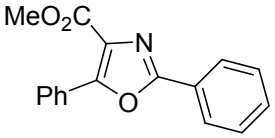
White solid (80.3 mg, 78%); m.p. = 121-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.6 Hz, 1H), 8.29 (d, *J* = 7.1 Hz, 1H), 8.22 – 8.16 (m, 2H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.61 – 7.48 (m, 5H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 162.4, 159.7, 154.7, 133.8, 131.8, 130.2, 130.2, 128.5, 128.4, 128.4, 128.2, 127.8, 127.1, 126.4, 125.9, 124.8, 122.9, 61.3, 14.2. IR (KBr): 2984, 1718, 1491, 1223, 1097, 757 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 127, 155, 343.



Ethyl 5-phenyl-2-(thiophen-2-yl)oxazole-4-carboxylate (3v)

Yellow solid (66.4 mg, 74%); m.p. = 72-73 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 2H), 7.81 (s, 1H), 7.51 – 7.41 (m, 4H), 7.14 – 7.12 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 156.0, 154.5, 130.2, 129.3, 129.0, 128.6, 128.5, 128.3, 128.1, 127.9, 126.8, 61.4, 14.3. IR (KBr): 2983, 1721, 1594, 1494, 1207, 1094, 758 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{13}NNaO_3$ $[M+Na]^+$, 322.0508; found, 322.0522.



Methyl 2,5-diphenyloxazole-4-carboxylate (3w)[1]

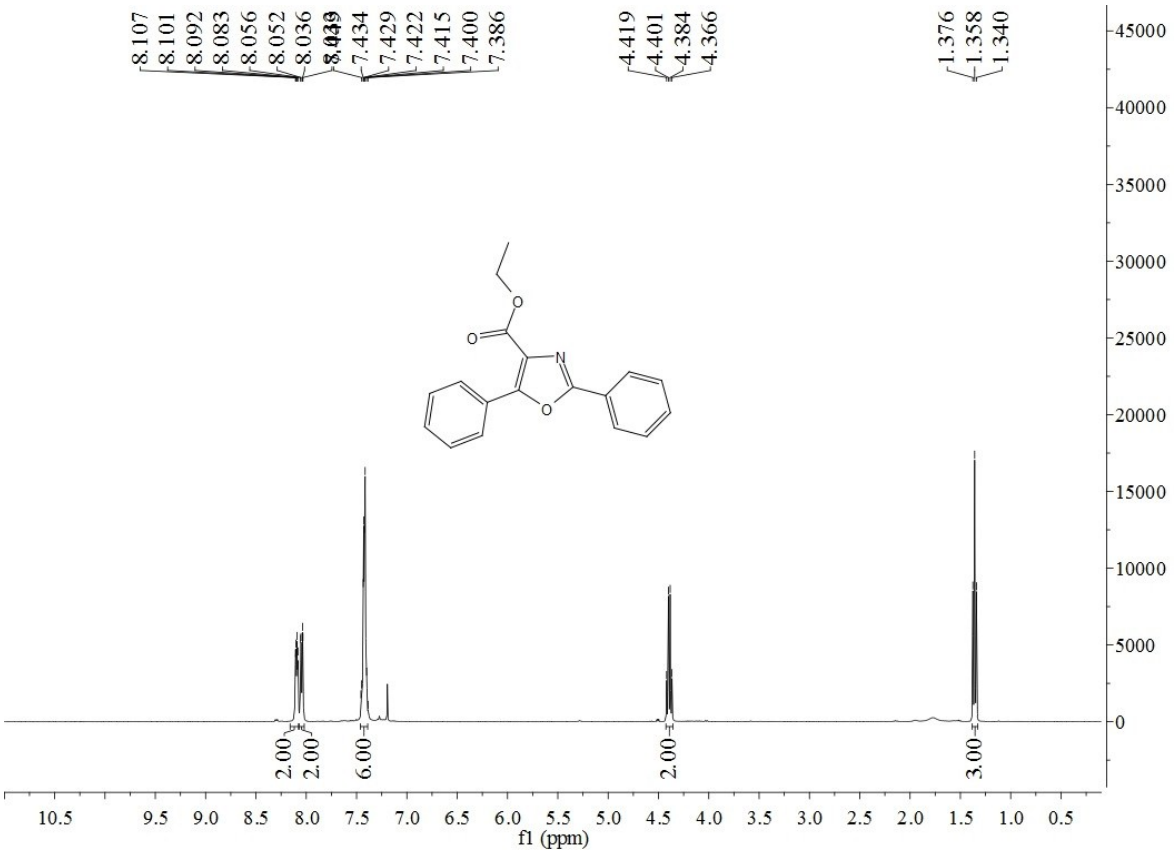
White solid (66.1 mg, 79%); m.p. = 85-86 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 4H), 7.55 – 7.46 (m, 6H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 162.60, 133.5, 131.0, 130.3, 130.0, 128.7, 128.4, 127.8, 126.9, 126.7, 126.2, 52.3. IR (KBr): 3061, 2952, 1721, 1489, 1102, 710, 688 cm^{-1}. MS (EI, 70 eV) m/z: 77, 105, 165, 279.

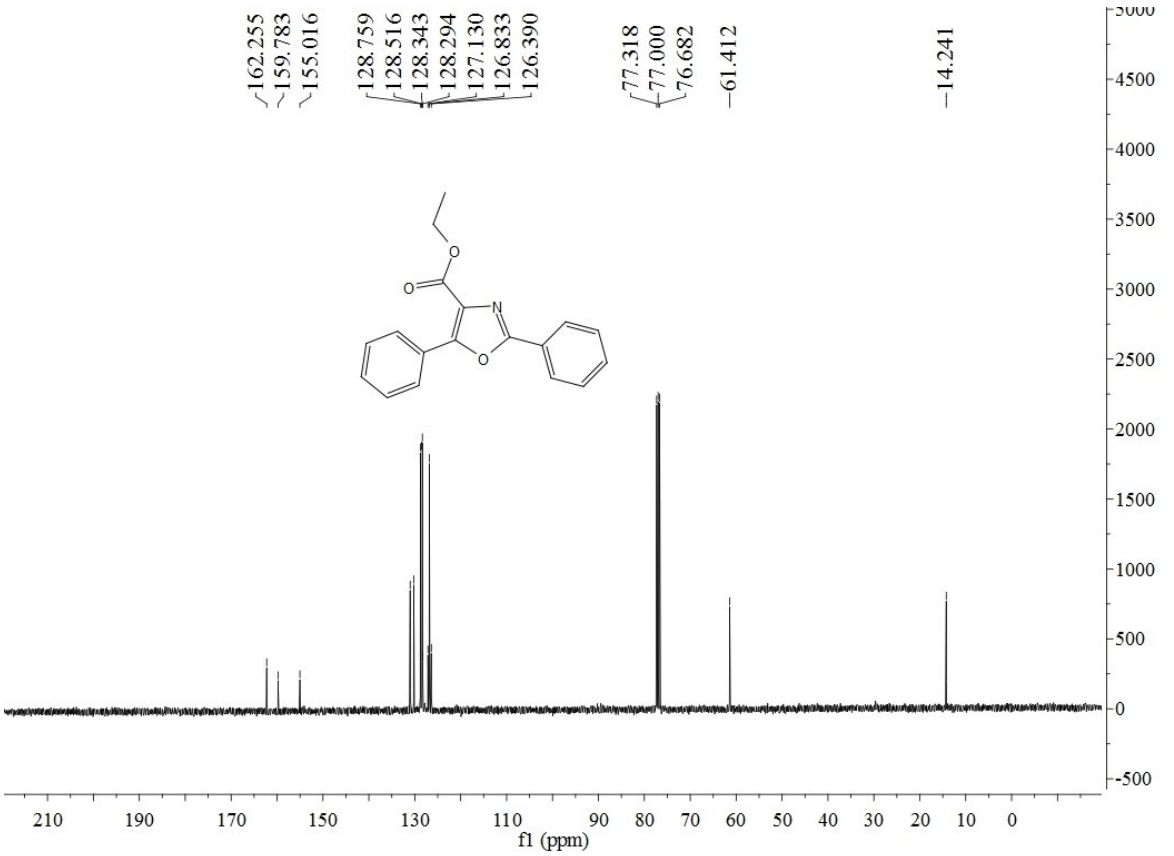
References

1. B. Liu, Y. Zhang, G. Huang, X. Zhang, P. Niu, J. Wu, W. Yu and J. Chang, *Org. Biomol. Chem*., 2014, **12**, 3912.
2. J. Zheng, M. Zhang, L. Huang, X. Hu, W. Wu, H. Huang and H. Jiang, *Chem. Commun*., 2014, **50**, 3609.
3. S. V. Kumar, B. Saraiah, N. C. Misra and H. Ila, *J. Org. Chem*., 2012, **77**, 10752.
4. C. Verrier, T. Martin, C. Hoarau and F. Marsais, *J. Org. Chem*., 2008, **73**, 7383.
5. L. Théveau, C. Verrier, P. Lassalas, T. Martin, G. Dupas, O. Querolle, L. V. Hijfte, F. Marsais and C. Hoarau, *Chem. Eur. J*., 2011, **17**, 14450.
6. C. Verrier, C. Fiol-Petit, C. Hoarau and F. Marsais, *Org. Biomol. Chem*., 2011, **9**, 6215.

NMR Spectra for All Compounds 3

3a





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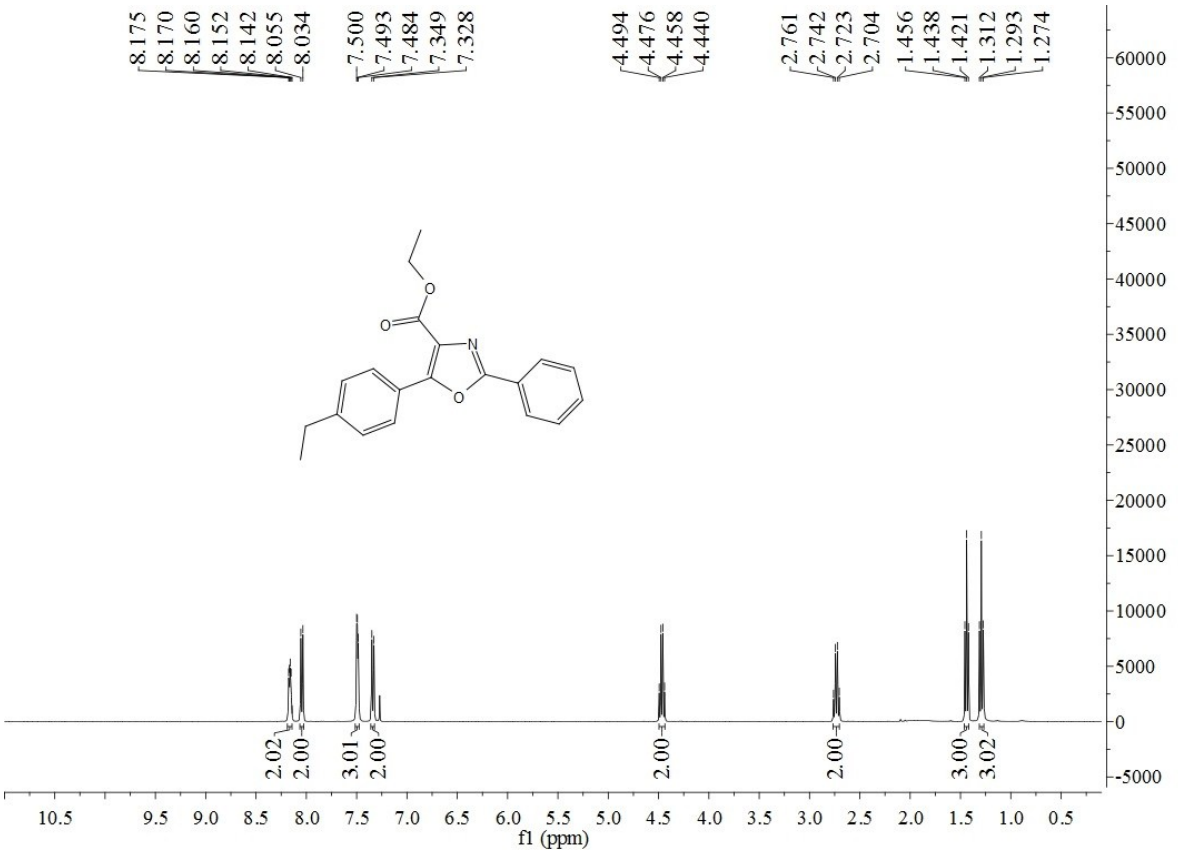
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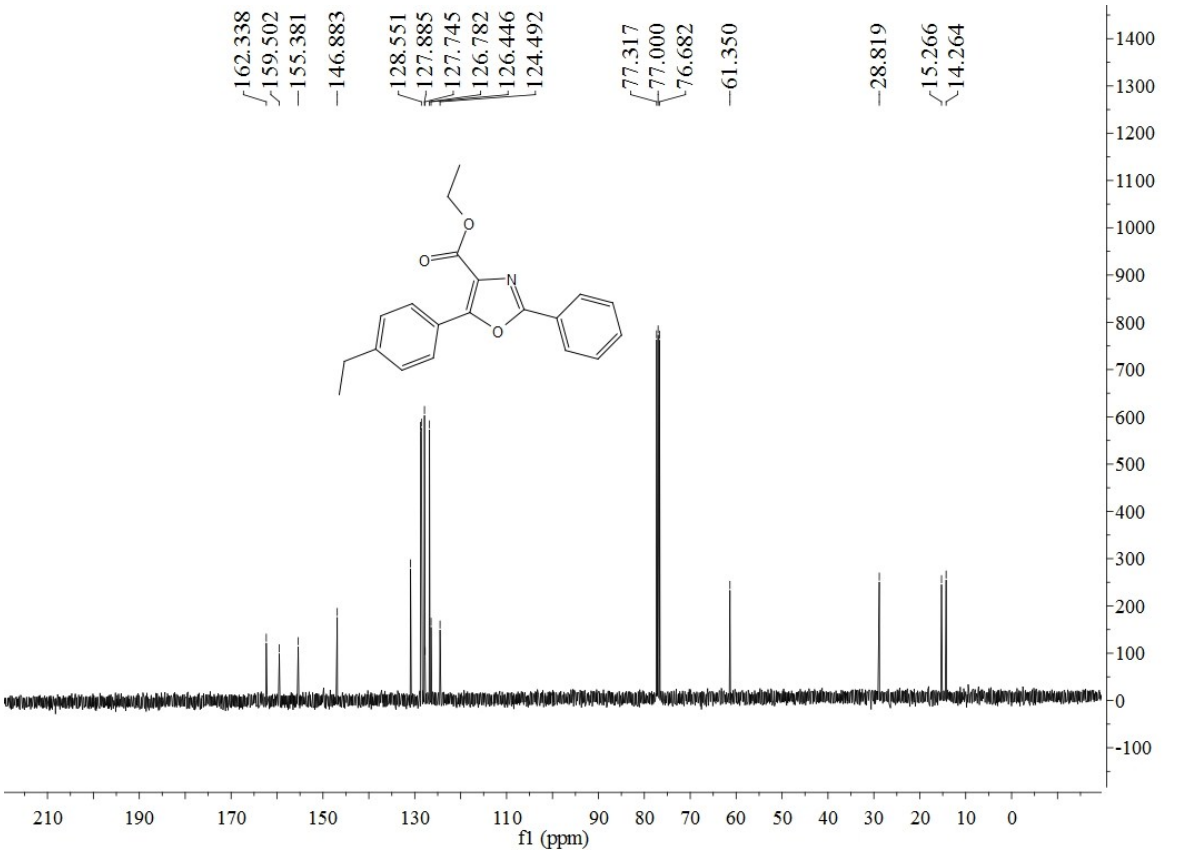
2.00
2.00
3.00
3.02
f1 (ppm)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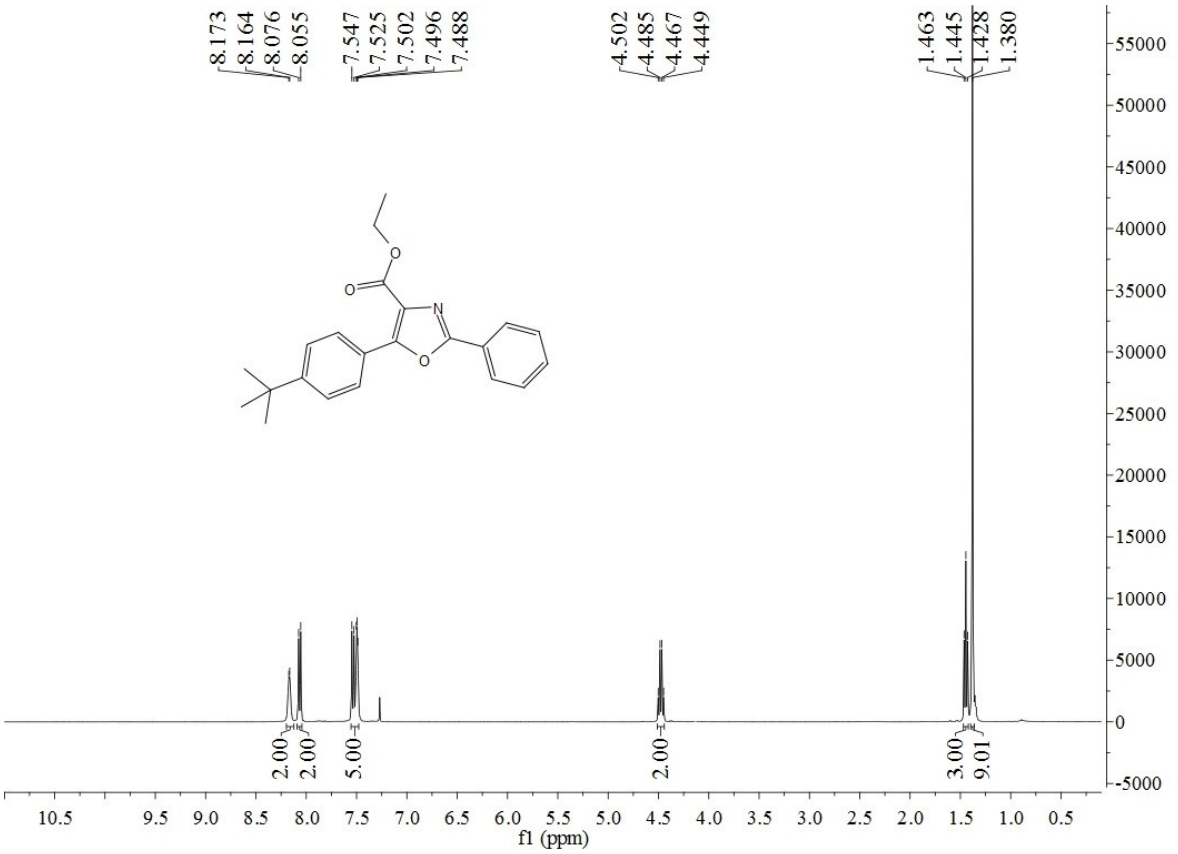
f1 (ppm)

3c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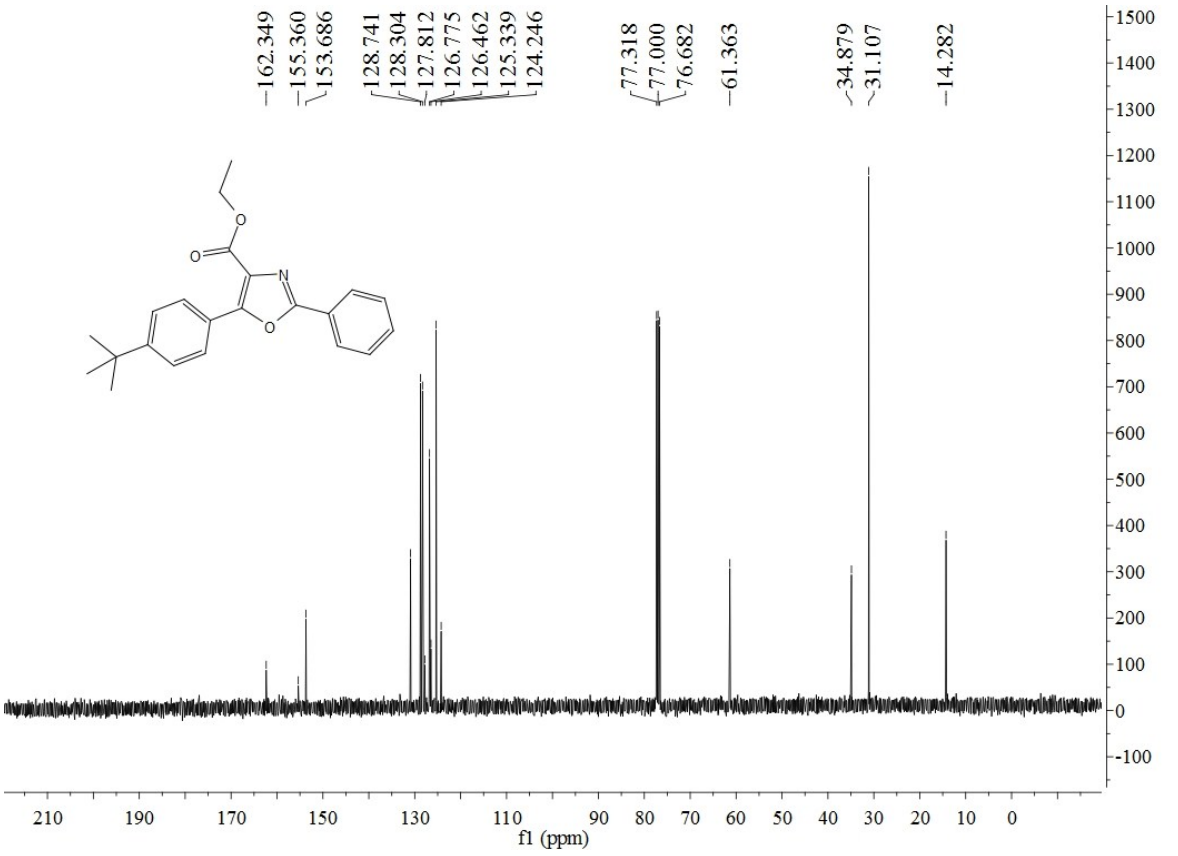
9.01
f1 (ppm)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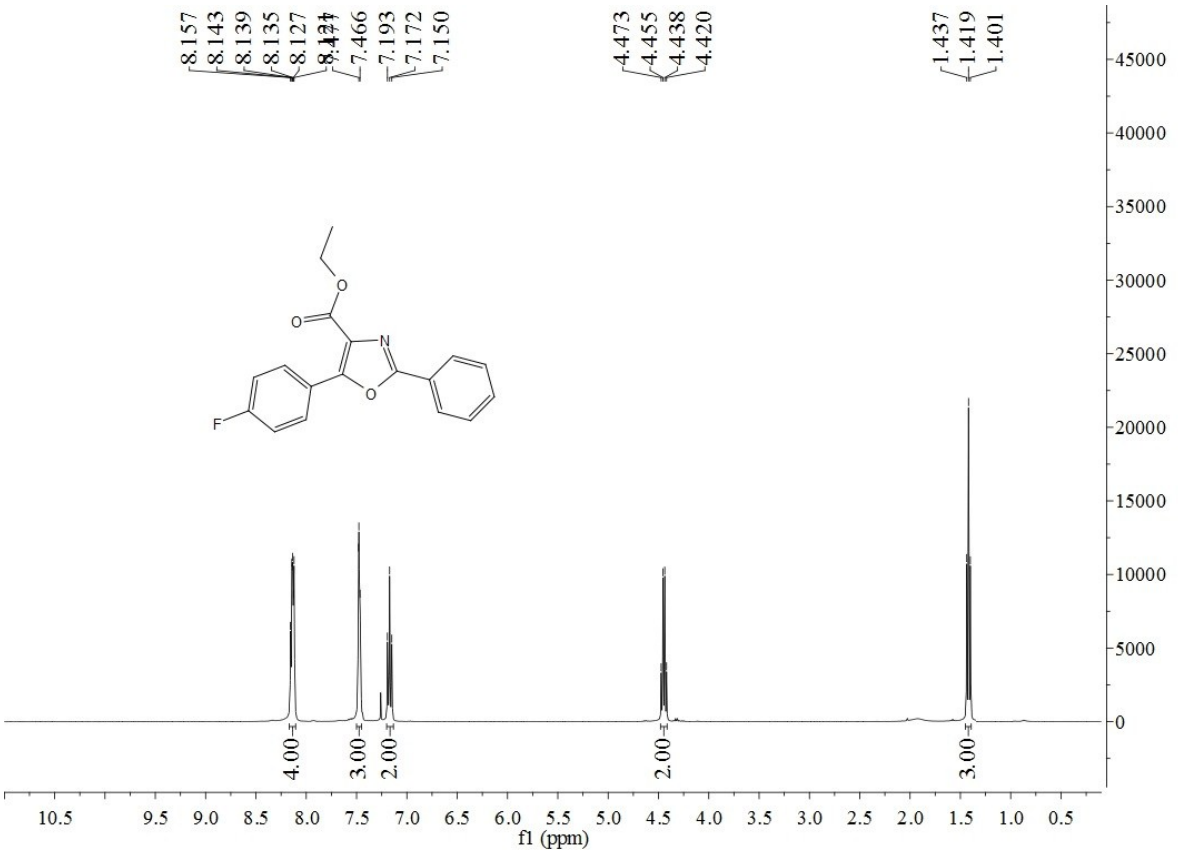
f1 (ppm)

3d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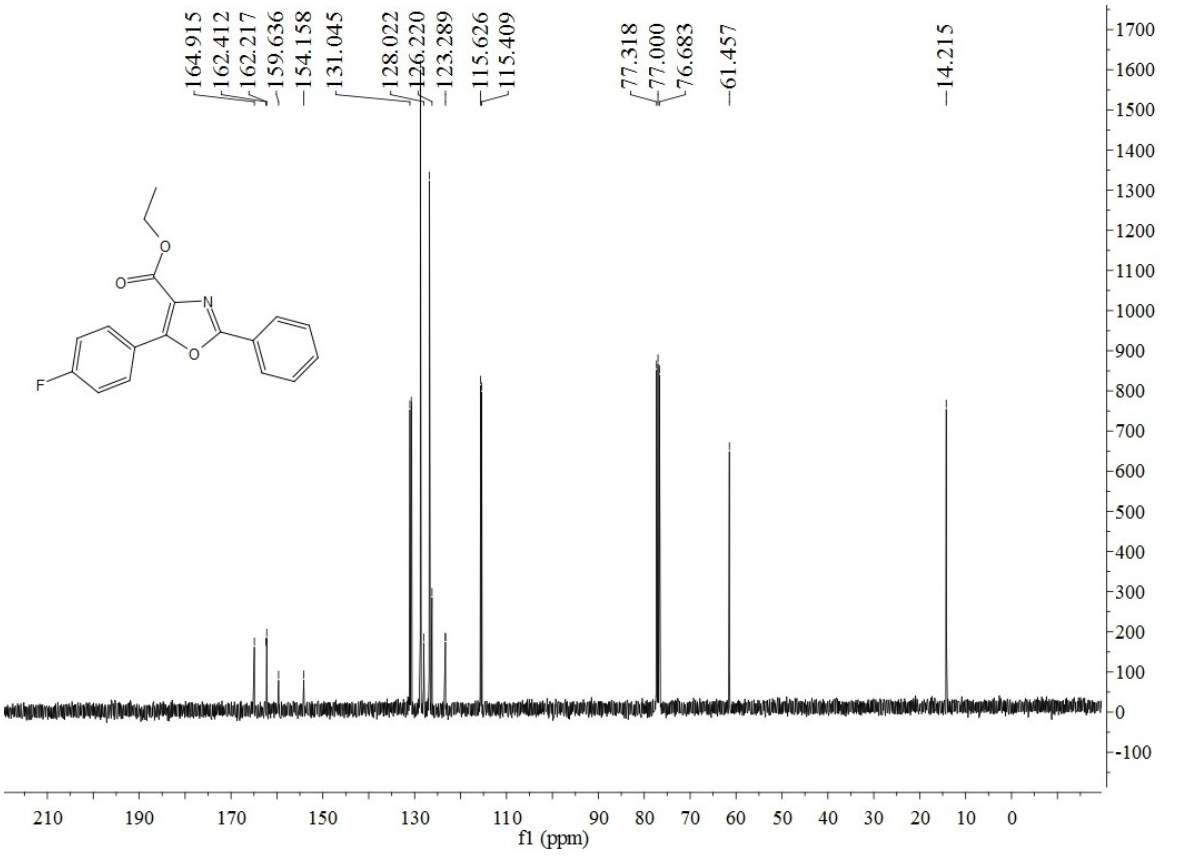
f1 (ppm)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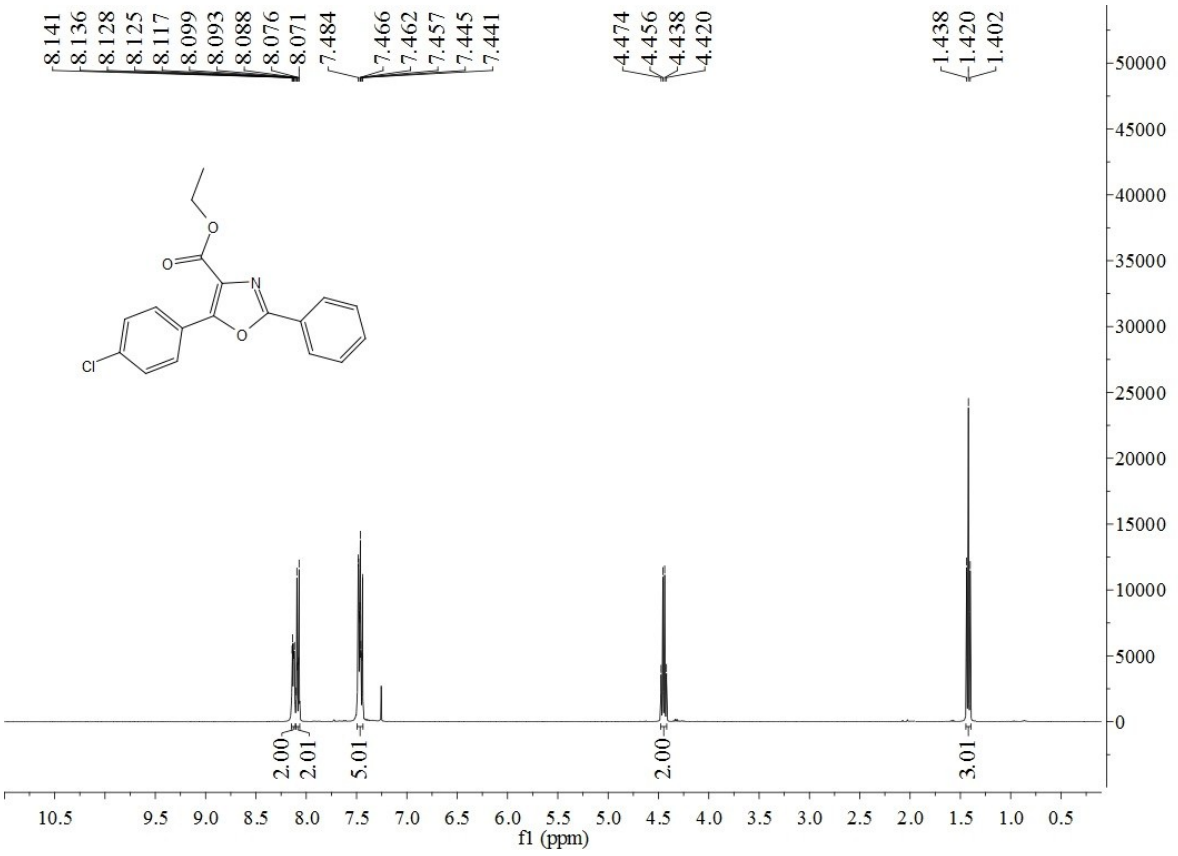
3e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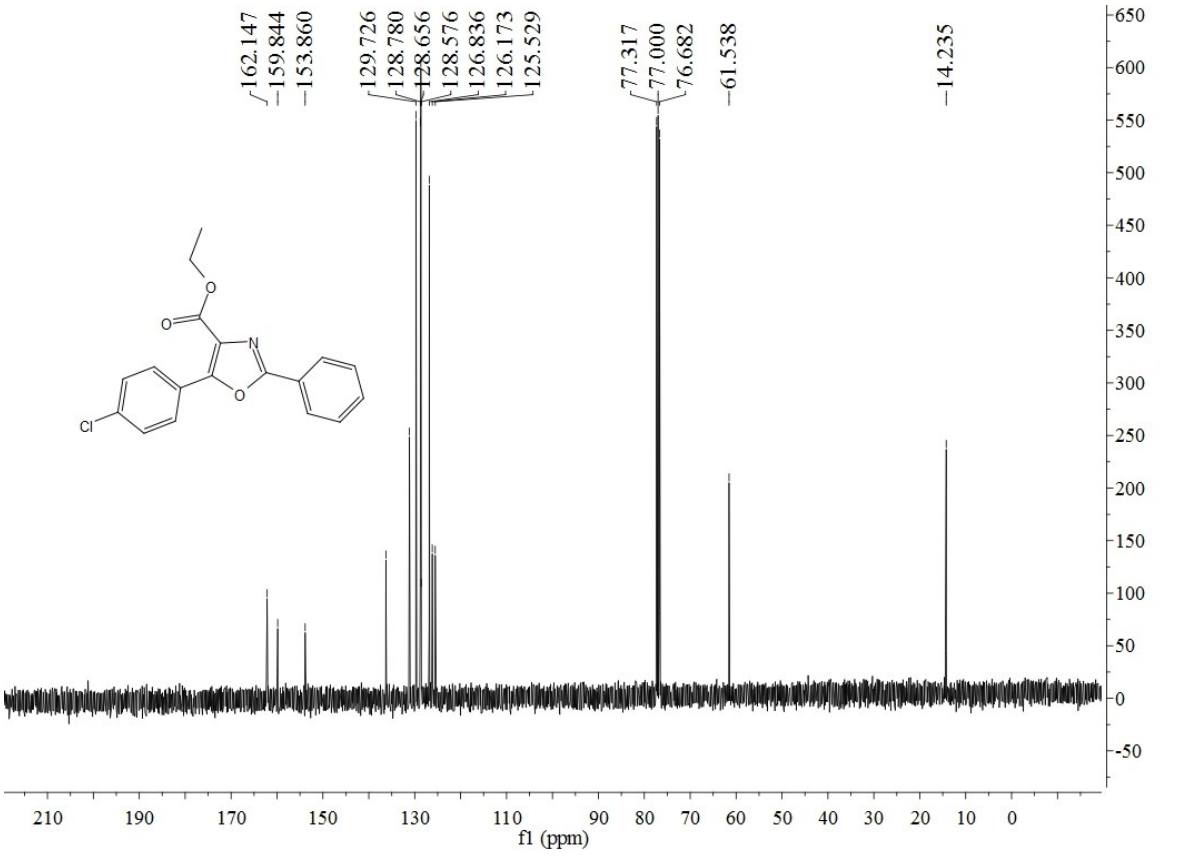
f1 (ppm)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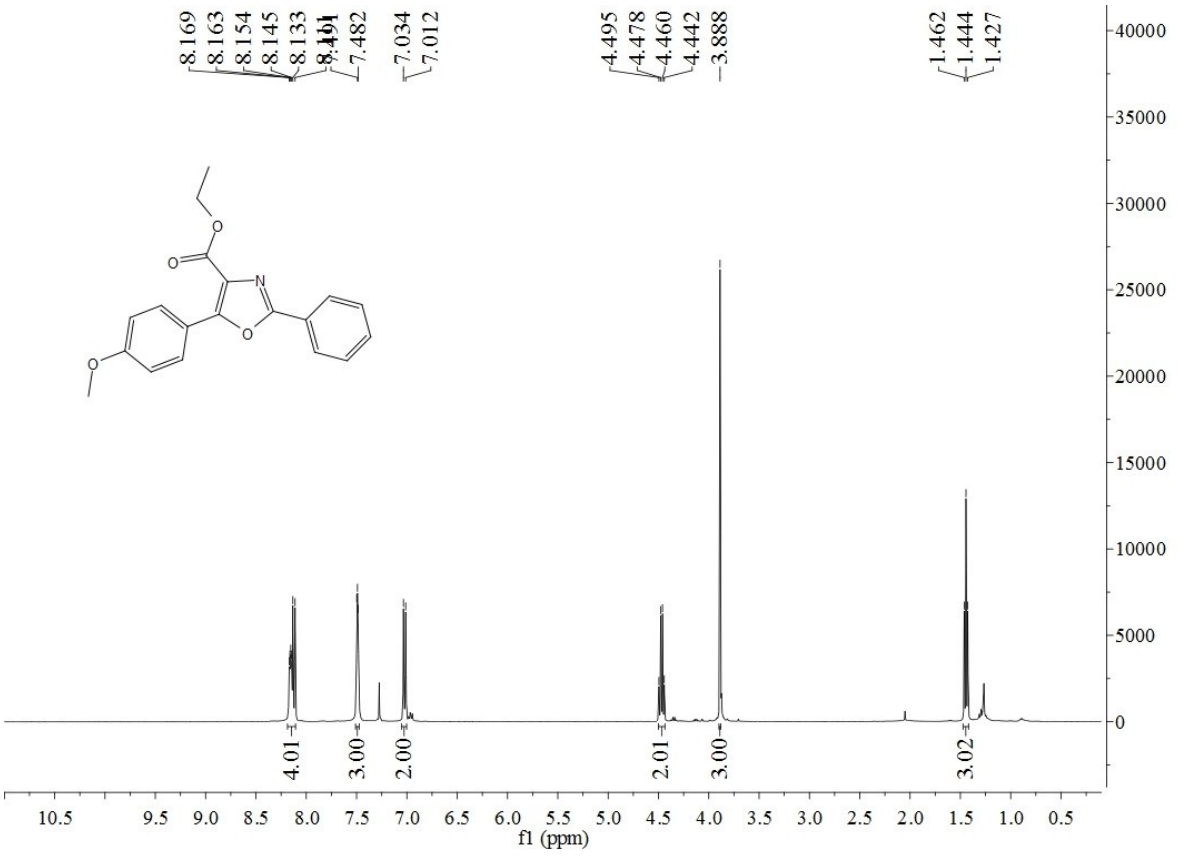
3f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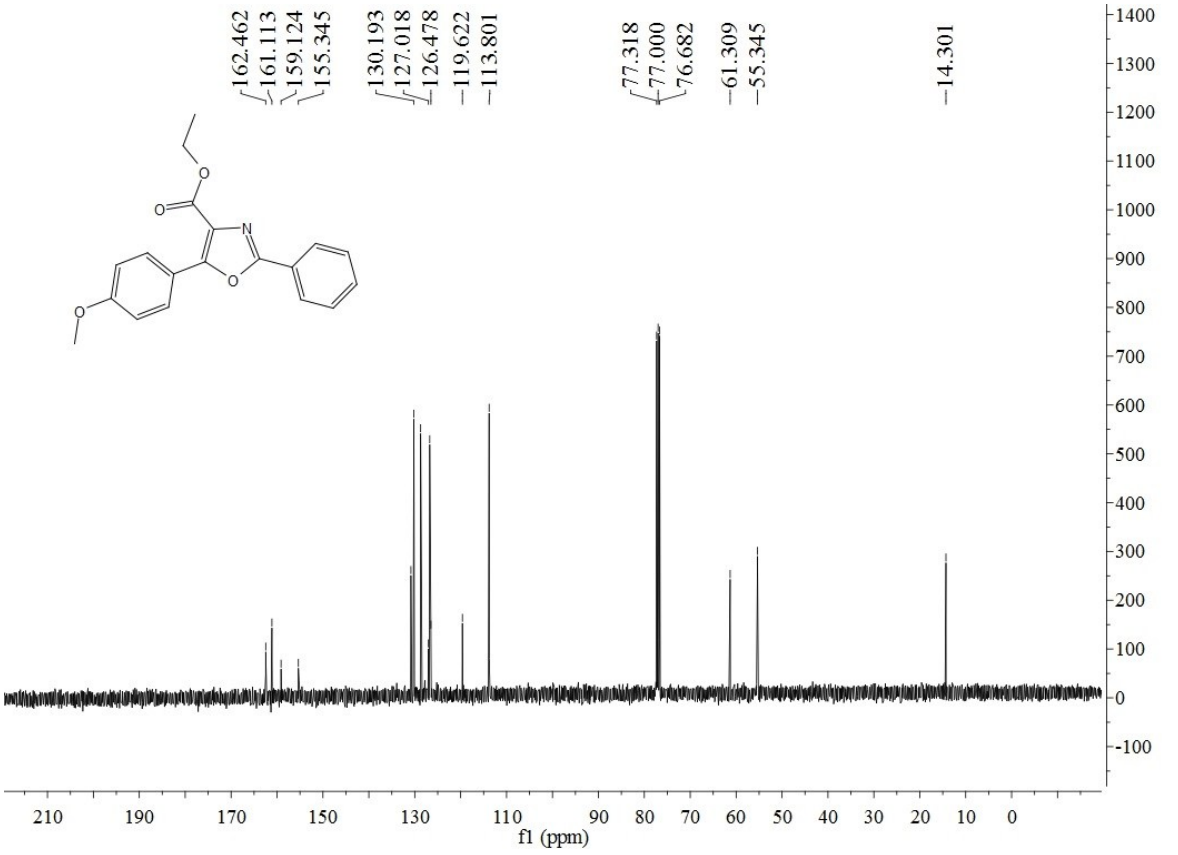
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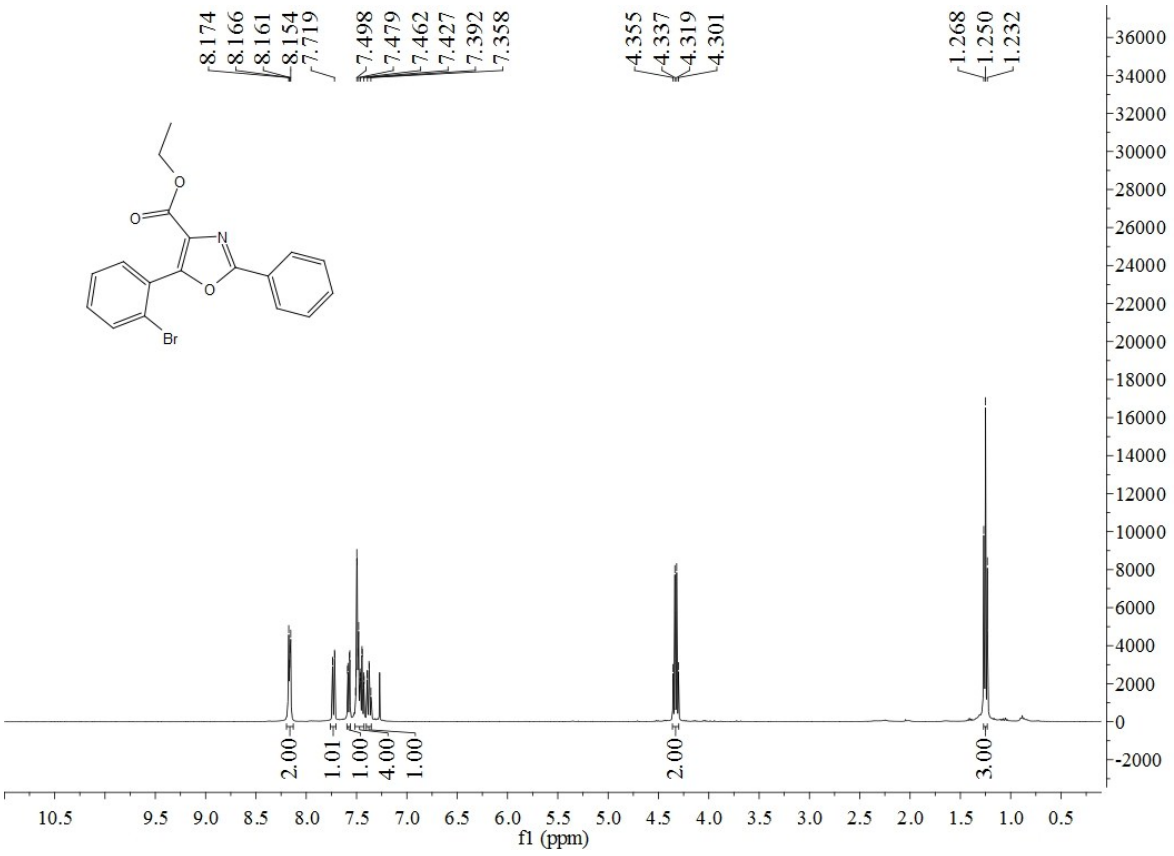
3g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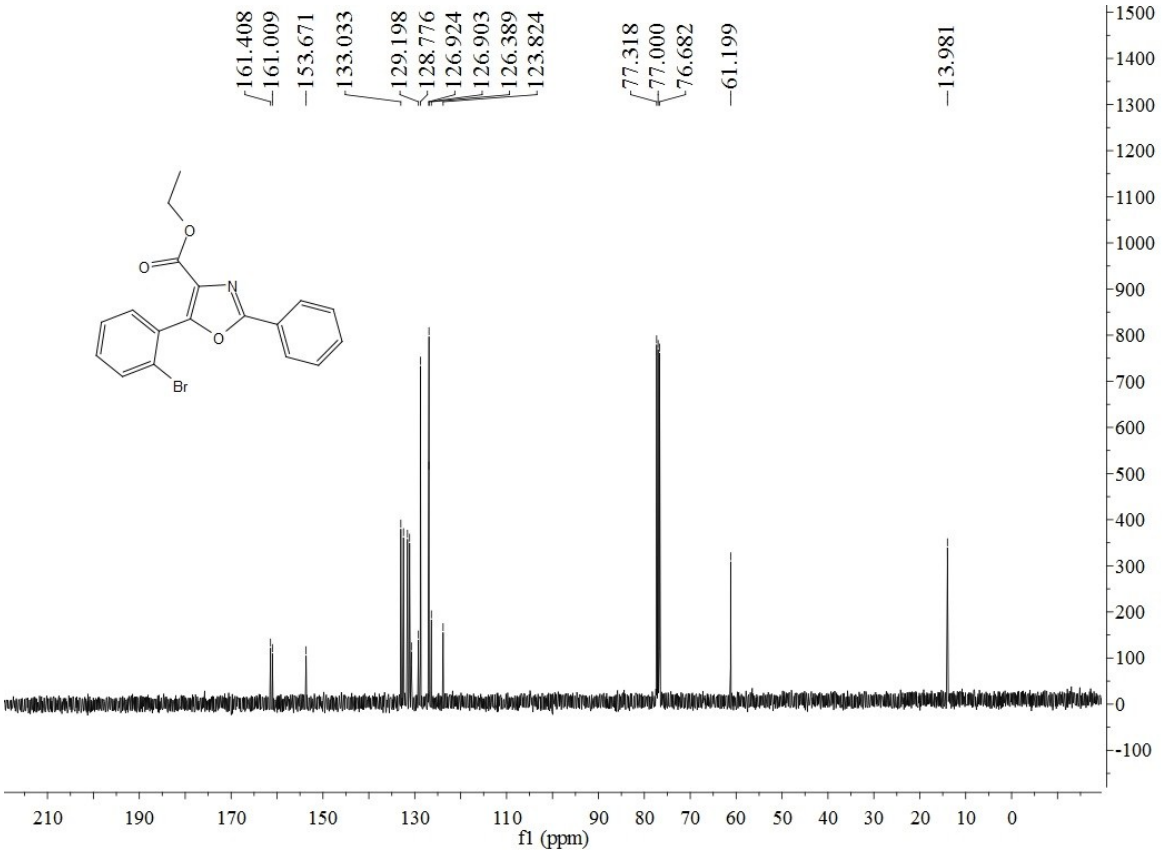
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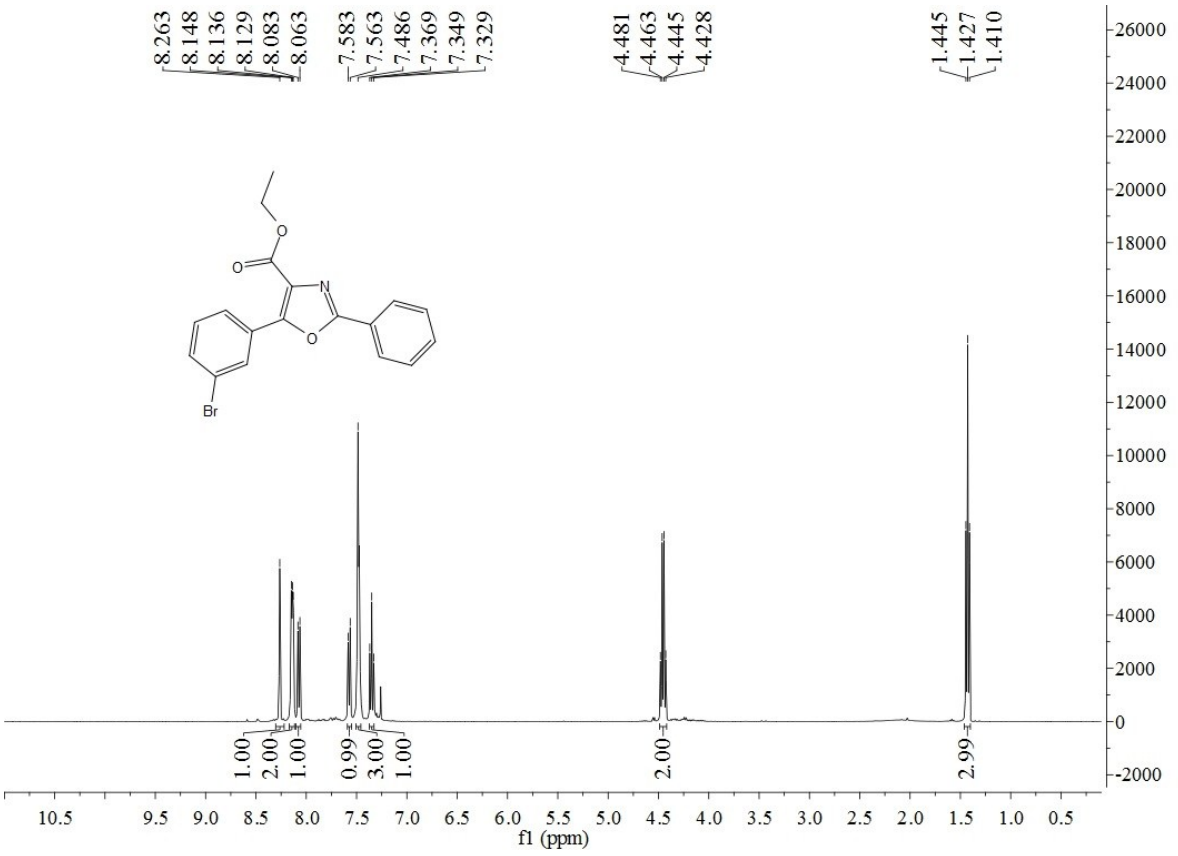
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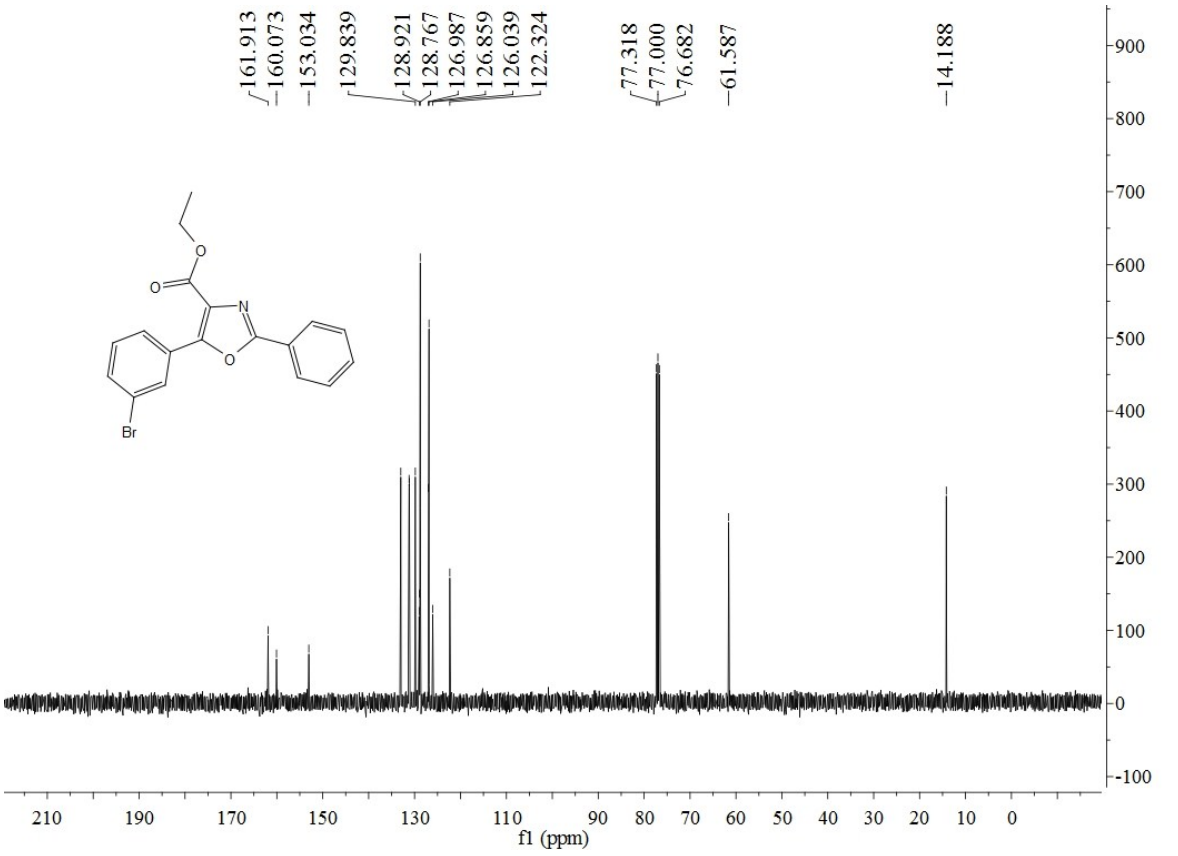
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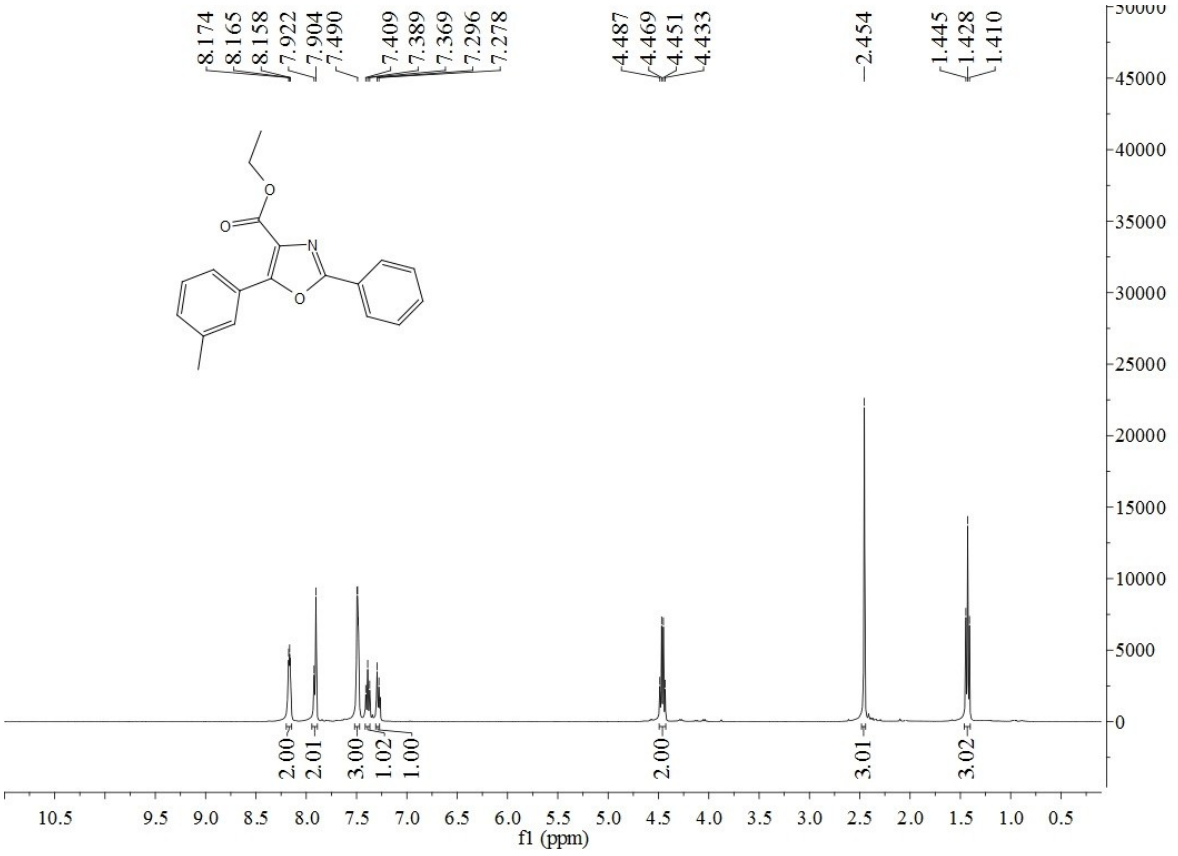
3i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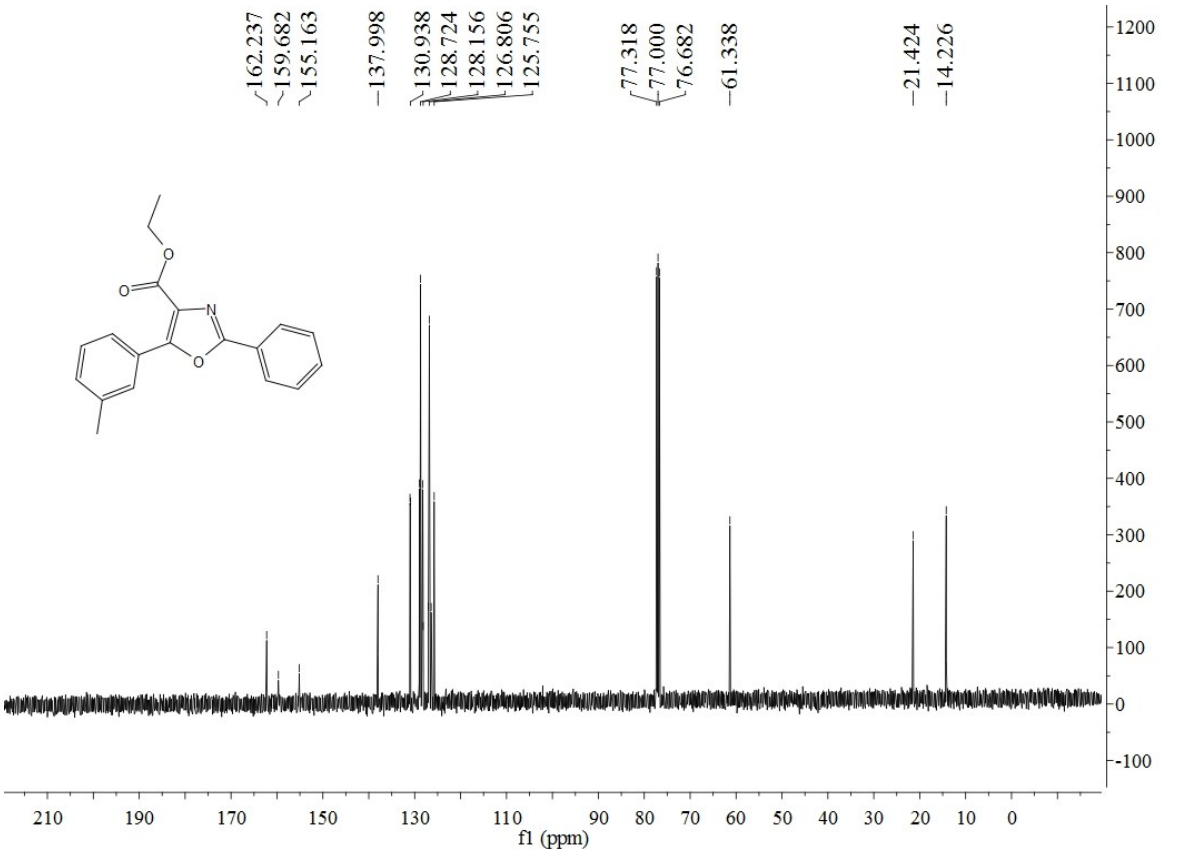
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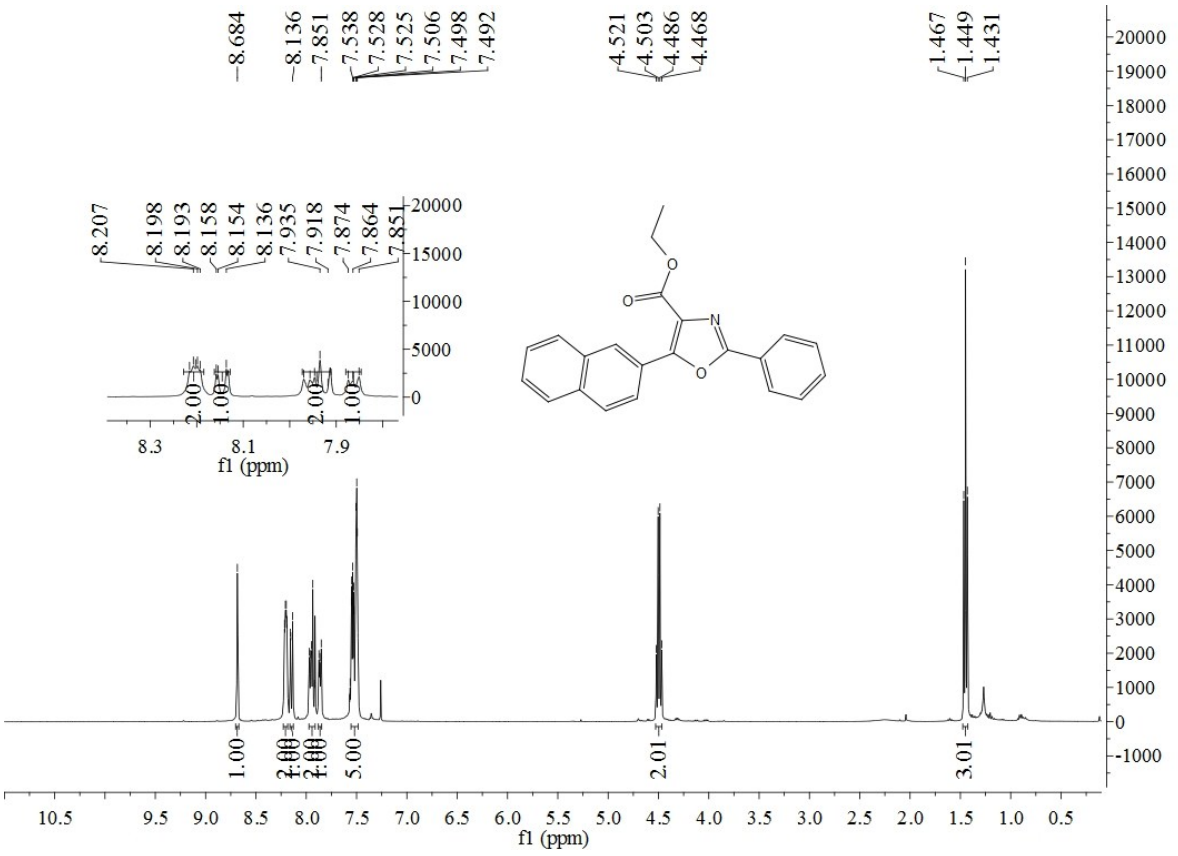
3j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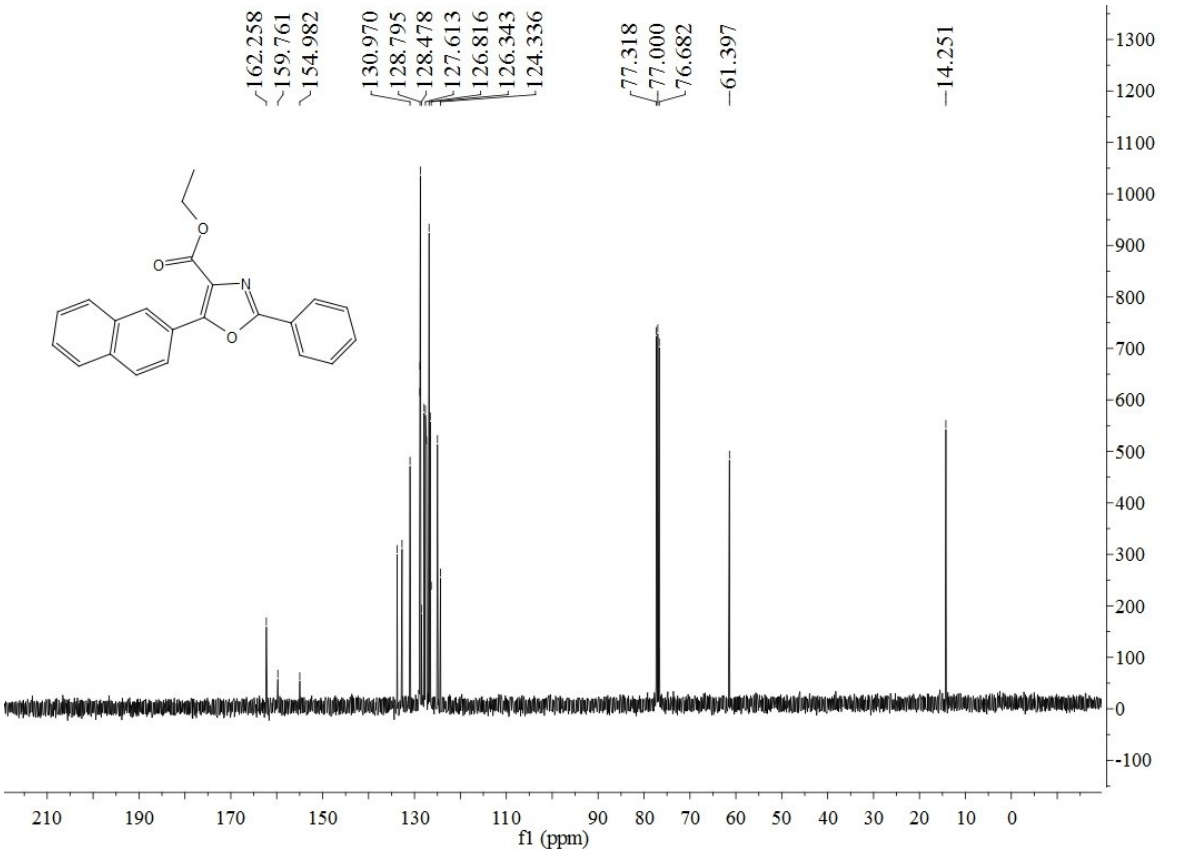
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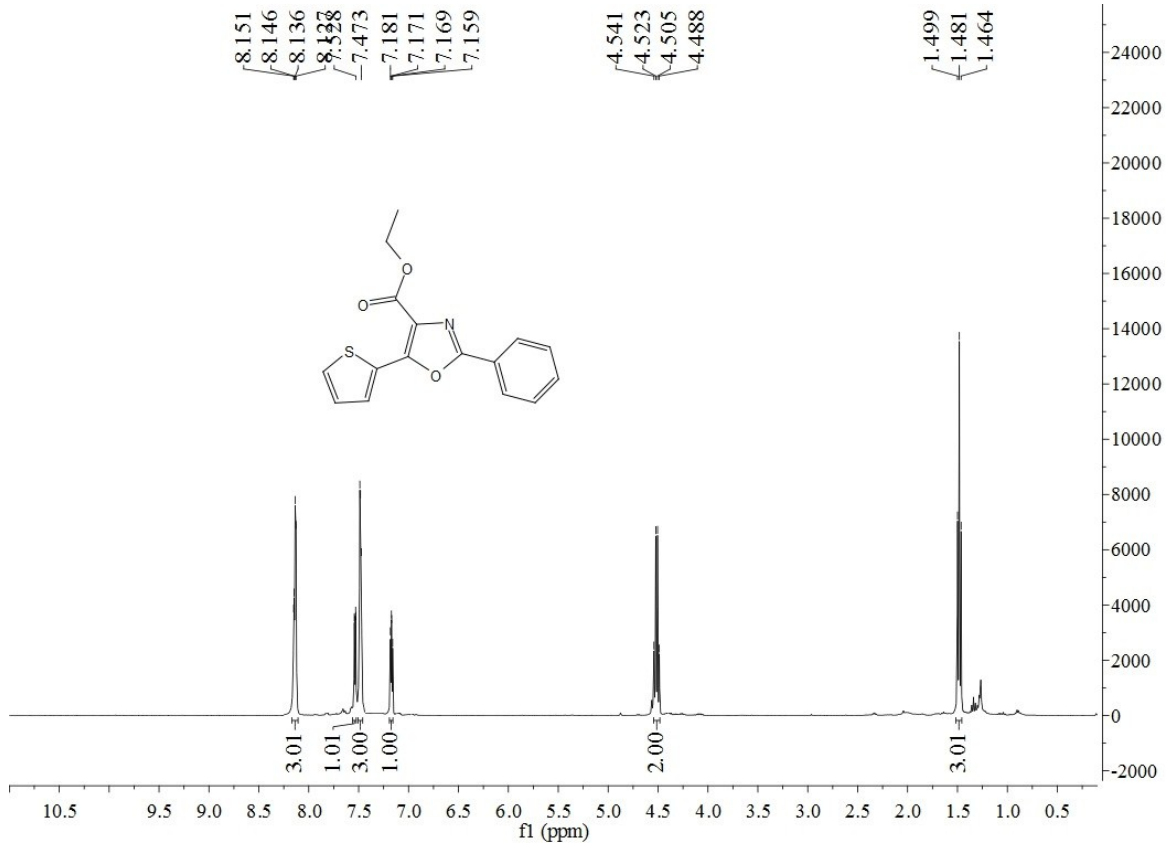
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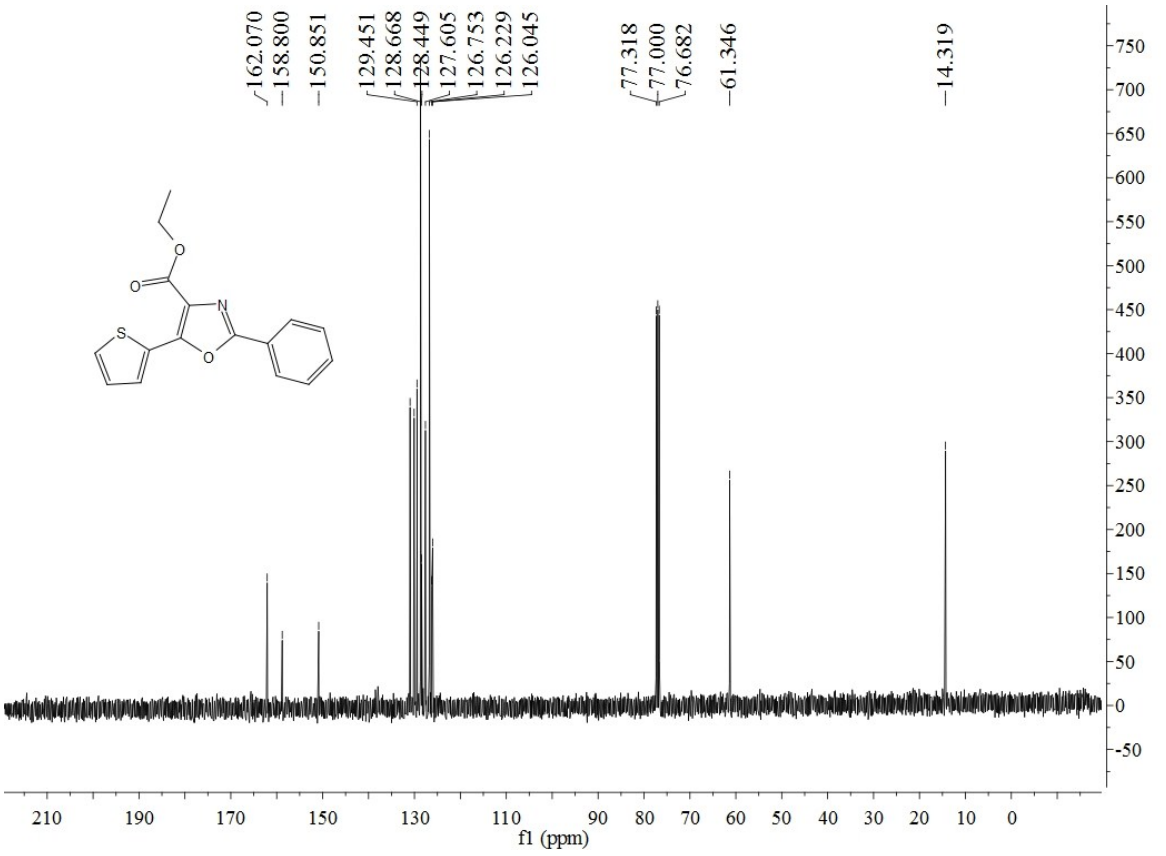
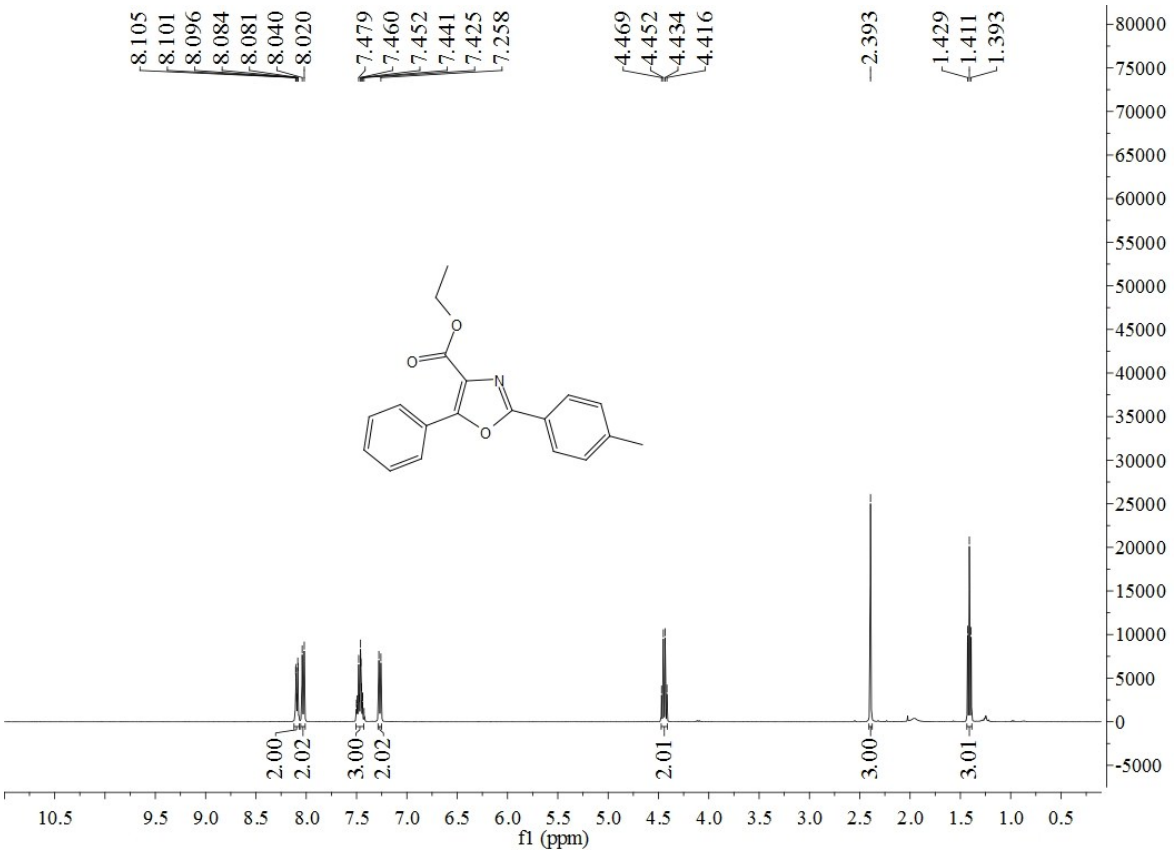
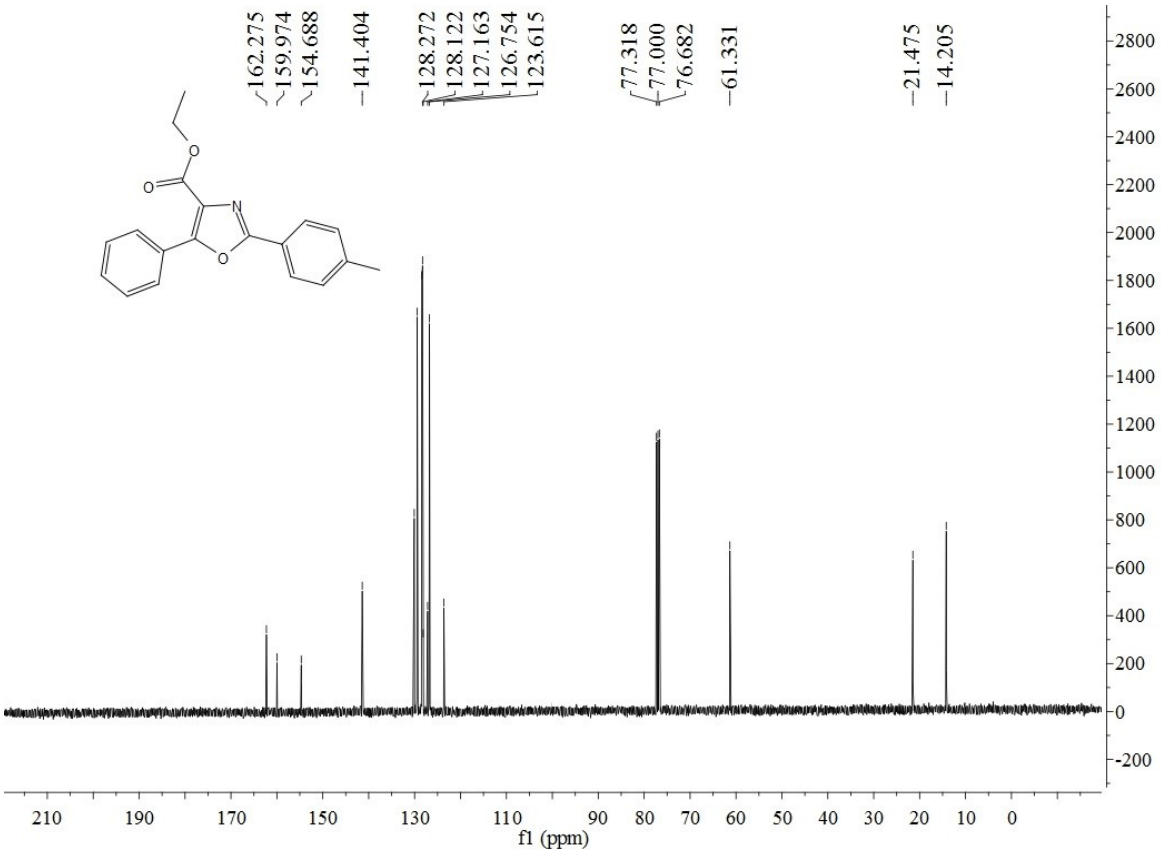
1.499
1.481
1.464
3.01
1.01
3.00
1.00
2.00
3.01
f1 (ppm)

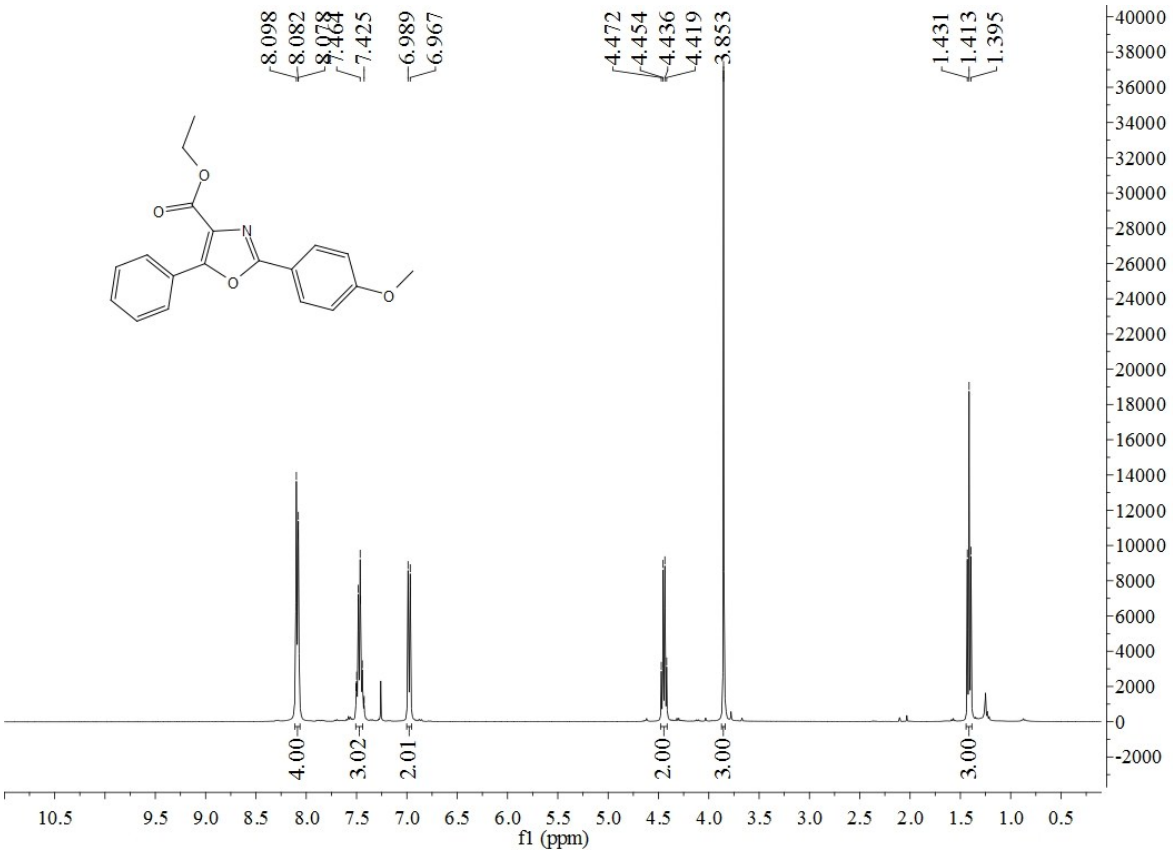

162.070
158.800
150.851
129.451
128.668
128.449
127.605
126.753
126.229
126.045
77.318
77.000
76.682
61.346
14.319
f1 (ppm)

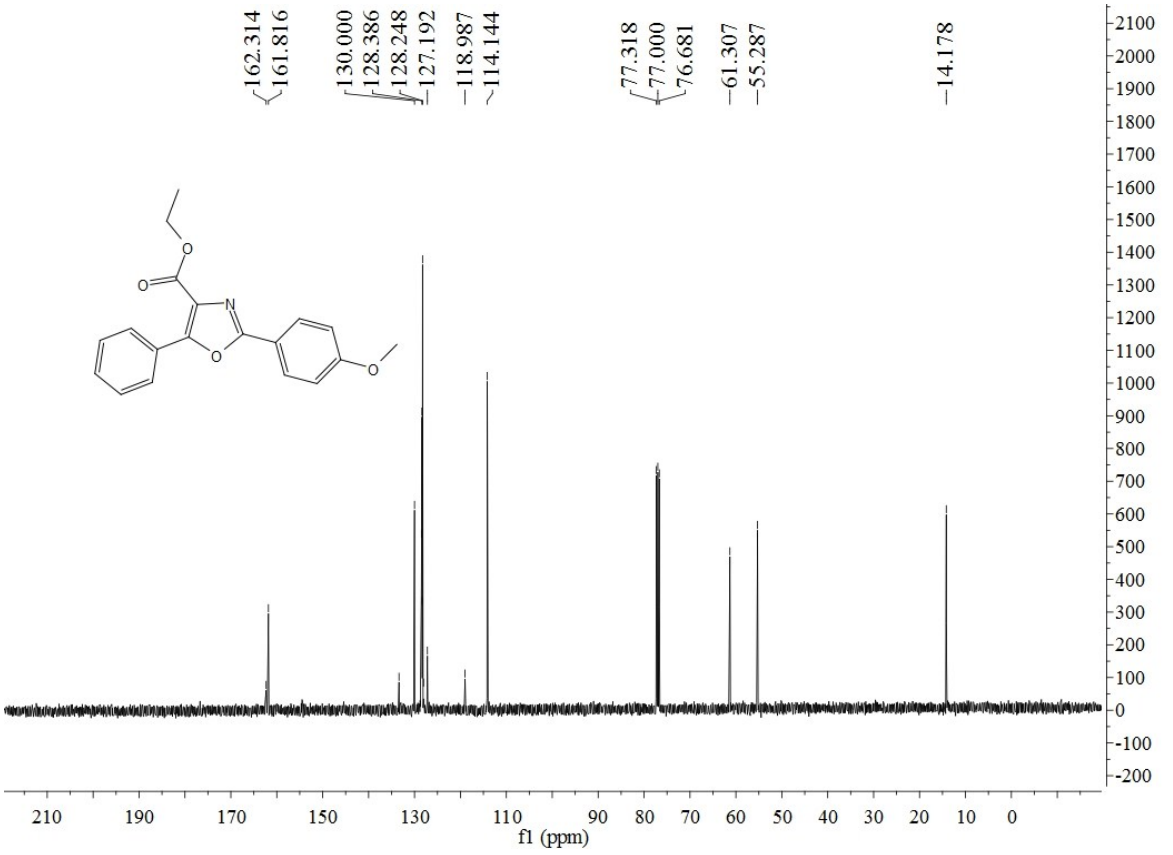
3l


8.105
8.101
8.096
8.084
8.081
8.040
8.020
7.479
7.460
7.452
7.441
7.425
7.258
4.469
4.452
4.434
4.416
2.393
1.429
1.411
1.393
2.00
2.02
3.00
2.02
2.01
3.00
3.01
f1 (ppm)

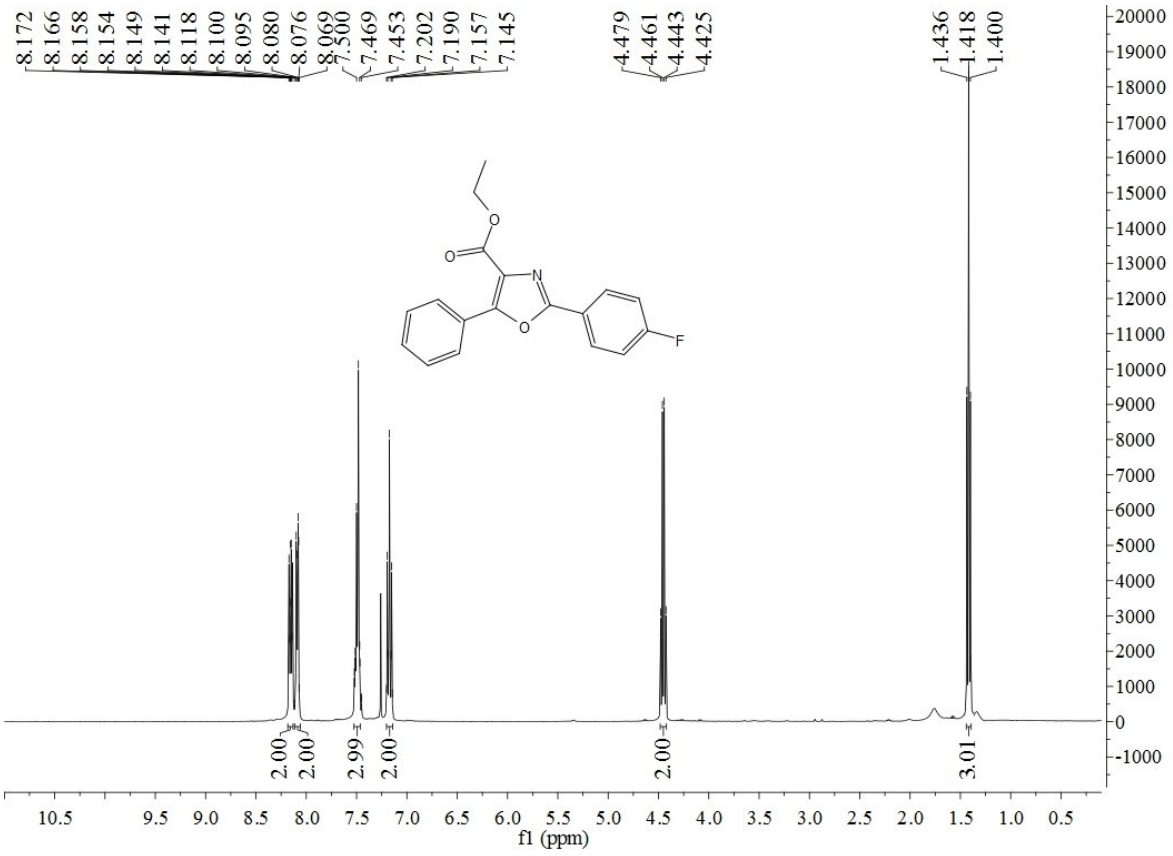

162.275
159.974
154.688
141.404
128.272
128.122
127.163
126.754
123.615
77.318
77.000
76.682
61.331
21.475
14.205
f1 (ppm)

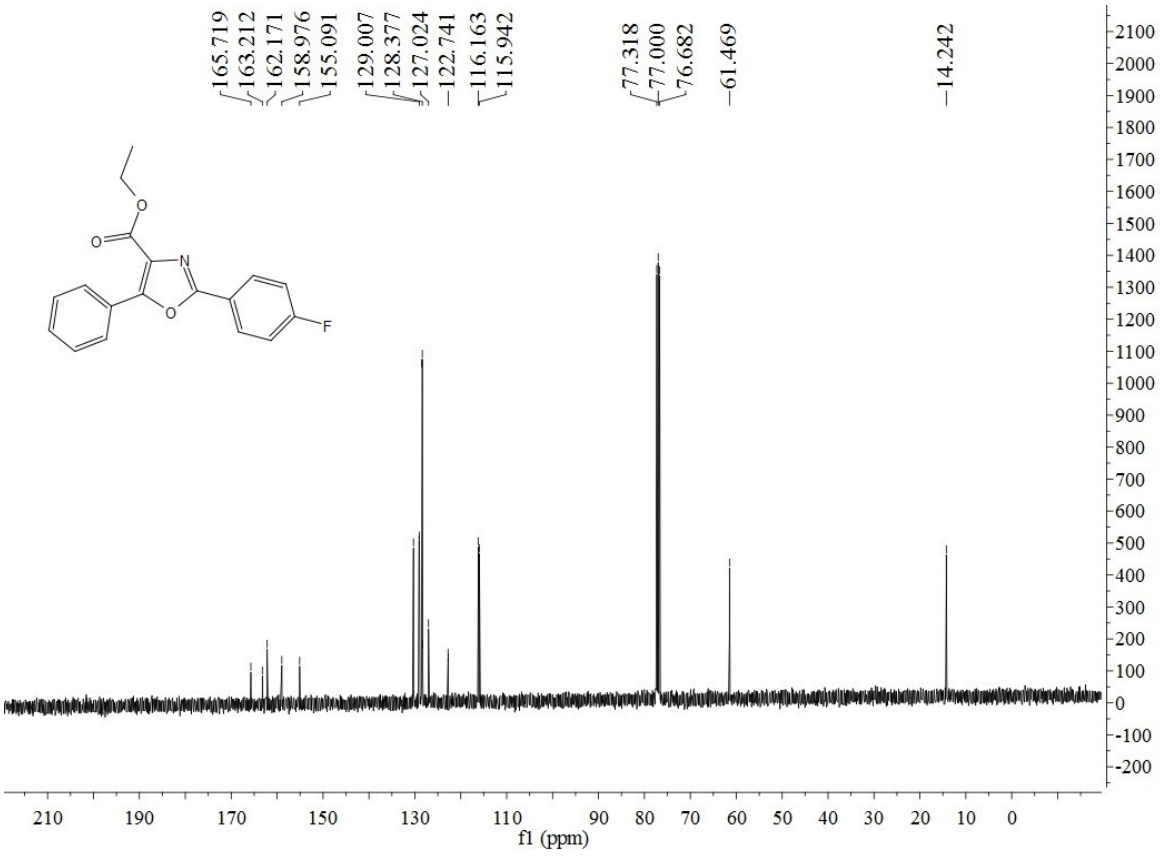
3m


8.098
8.082
8.078
7.464
7.425
6.989
6.967
4.472
4.454
4.436
4.419
3.853
1.431
1.413
1.395
4.00
3.02
2.01
2.00
3.00
3.00
f1 (ppm)

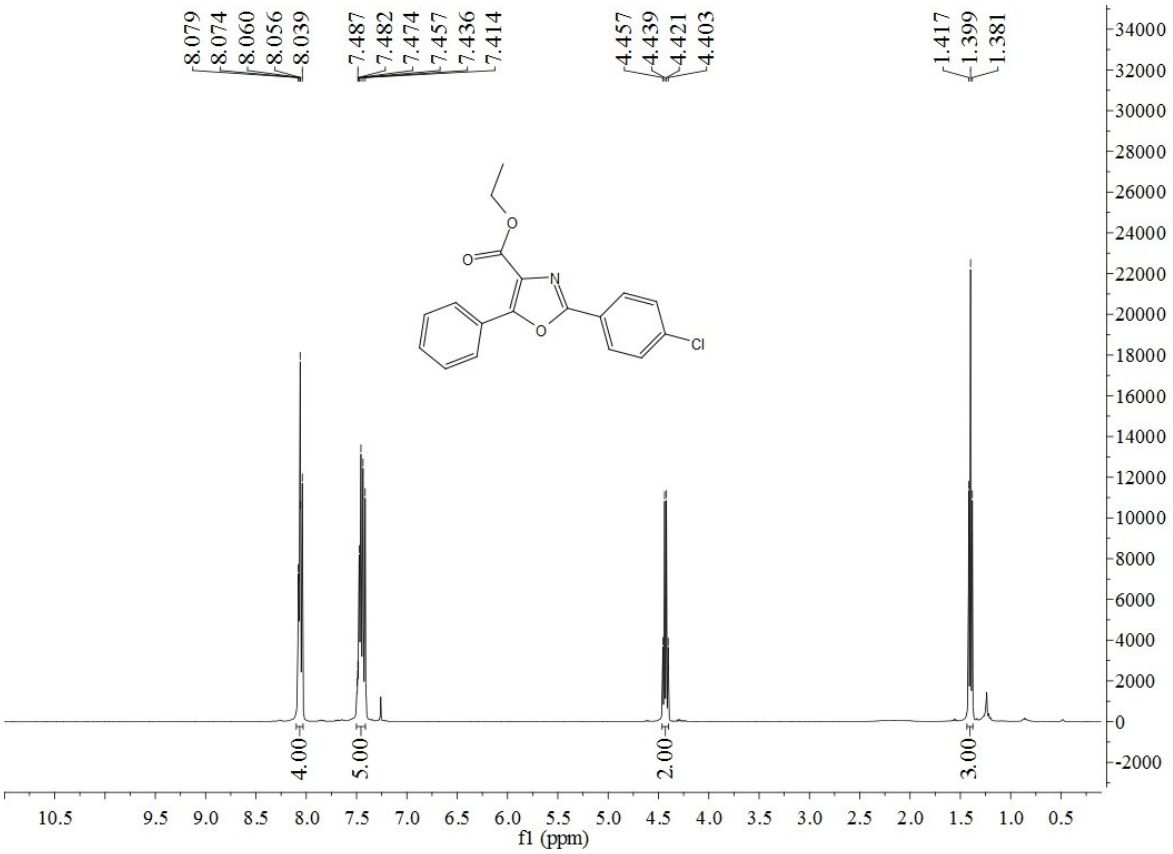

162.314
161.816
130.000
128.386
128.248
127.192
118.987
114.144
77.318
77.000
76.681
61.307
55.287
14.178
f1 (ppm)

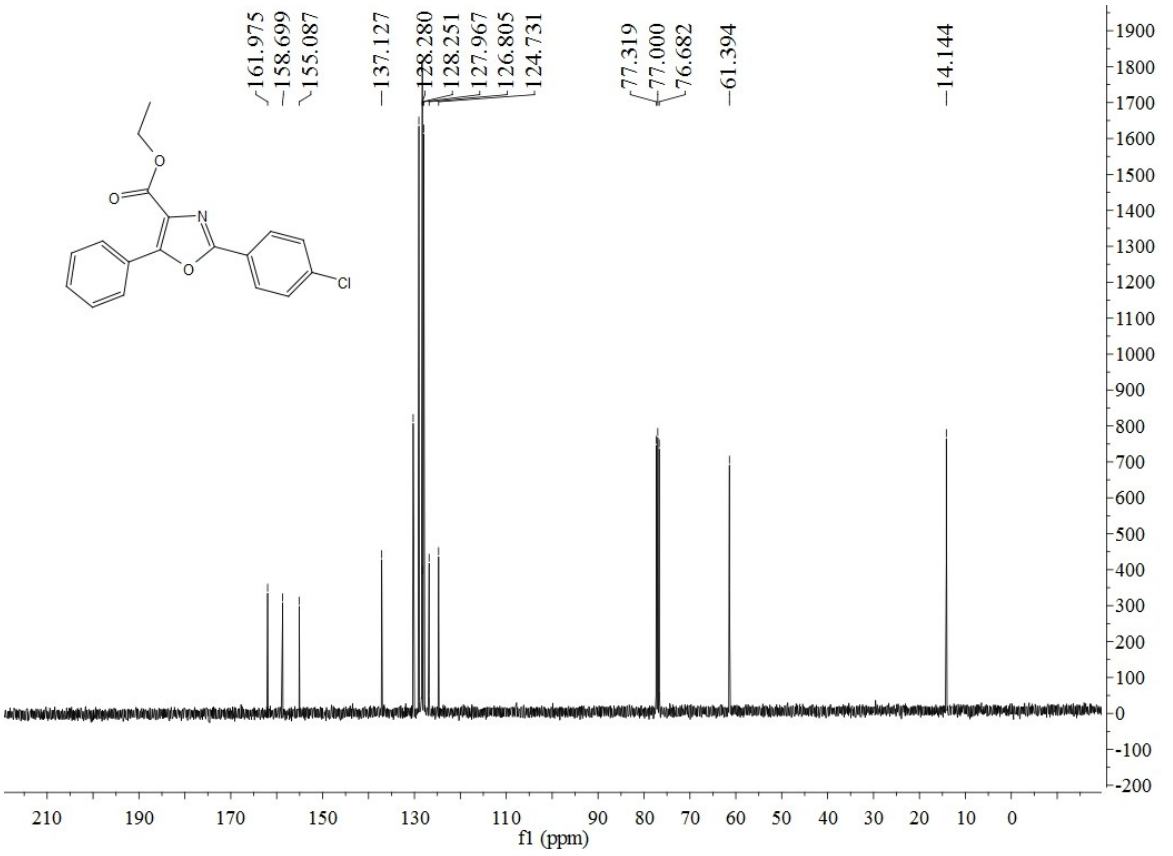
3n


8.172
8.166
8.158
8.154
8.149
8.141
8.118
8.100
8.095
8.080
8.076
8.069
7.500
7.469
7.453
7.202
7.190
7.157
7.145
4.479
4.461
4.443
4.425
1.436
1.418
1.400
2.00
2.00
2.99
2.00
2.00
3.01
f1 (ppm)

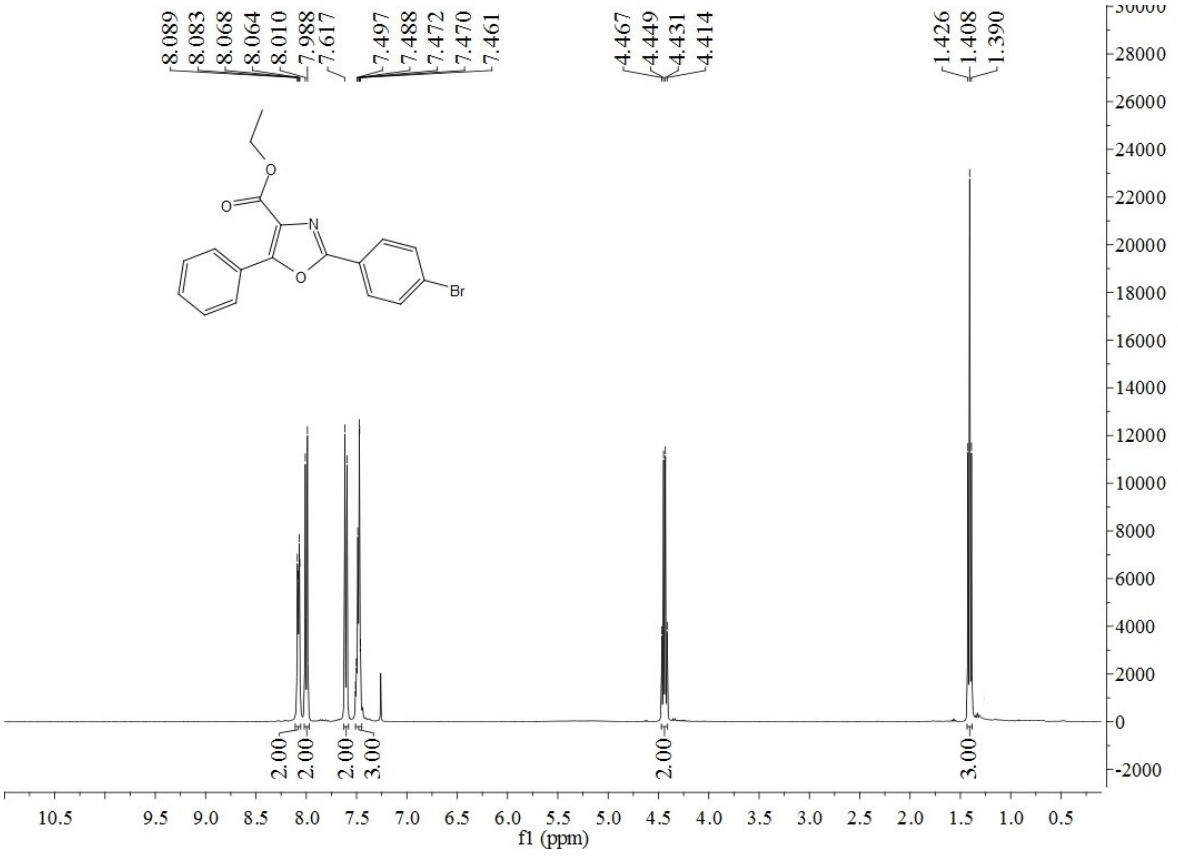

165.719
163.212
162.171
158.976
155.091
129.007
128.377
127.024
122.741
116.163
115.942
77.318
77.000
76.682
61.469
14.242
f1 (ppm)

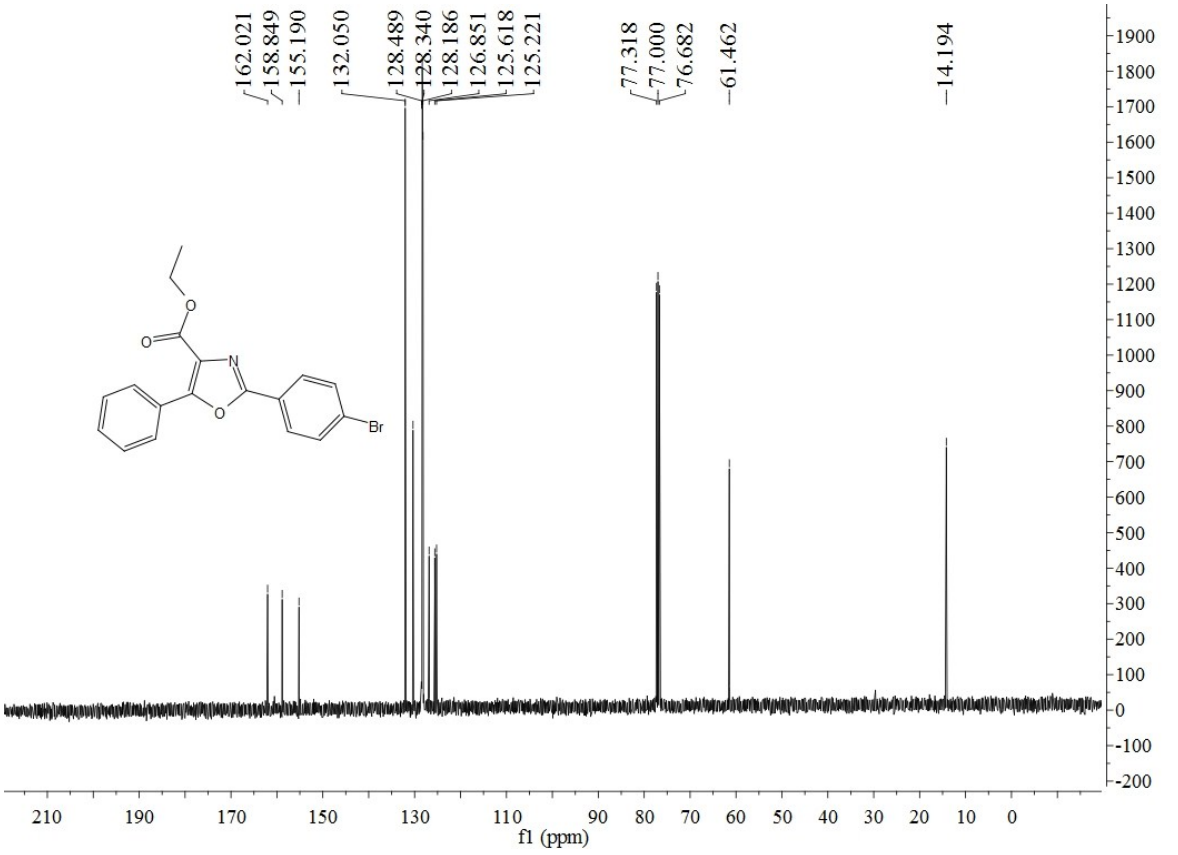
3o


8.079
8.074
8.060
8.056
8.039
7.487
7.482
7.474
7.457
7.436
7.414
4.457
4.439
4.421
4.403
1.417
1.399
1.381
4.00
5.00
2.00
3.00
f1 (ppm)

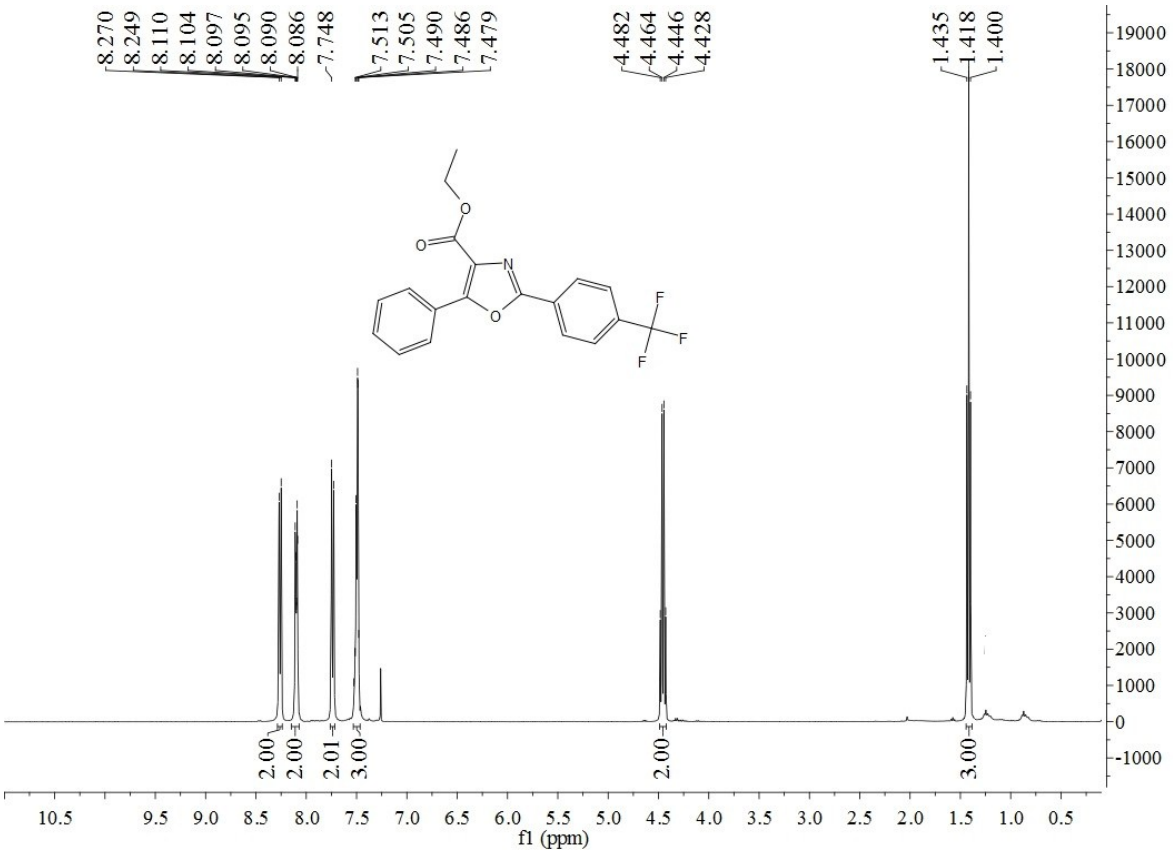

161.975
158.699
155.087
137.127
128.280
128.251
127.967
126.805
124.731
77.319
77.000
76.682
61.394
14.144
f1 (ppm)

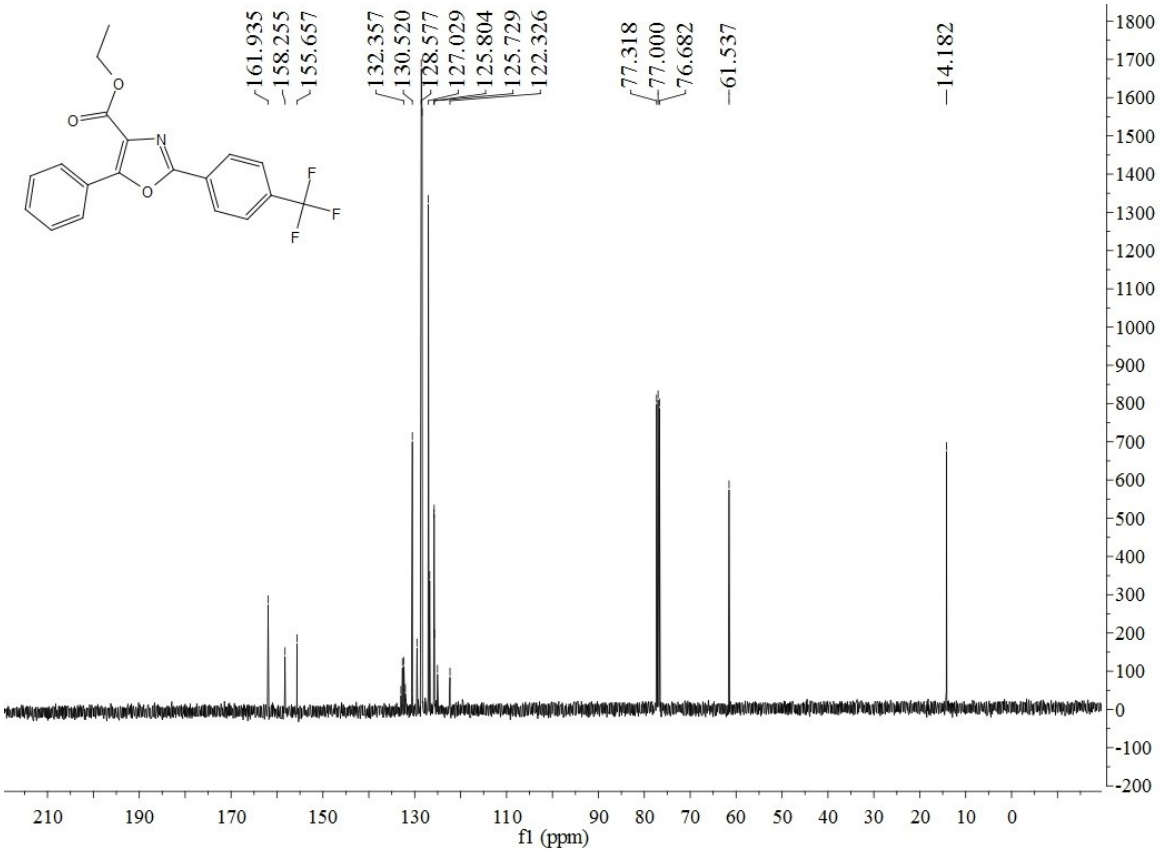
3p


8.089
8.083
8.068
8.064
8.010
7.988
7.617
7.497
7.488
7.472
7.470
7.461
4.467
4.449
4.431
4.414
1.426
1.408
1.390
Br
2.00
2.00
2.00
3.00
2.00
3.00
f1 (ppm)

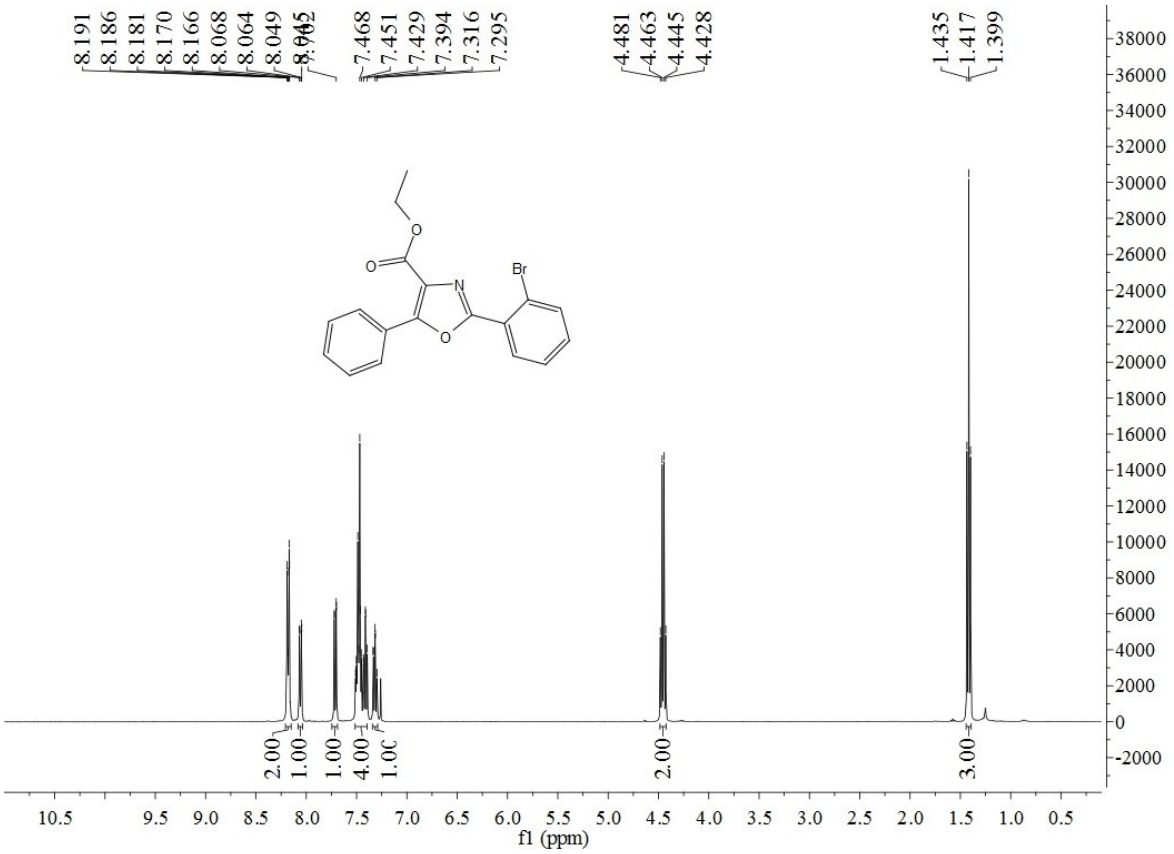

162.021
158.849
155.190
132.050
128.489
128.340
128.186
126.851
125.618
125.221
77.318
77.000
76.682
61.462
14.194
Br
f1 (ppm)

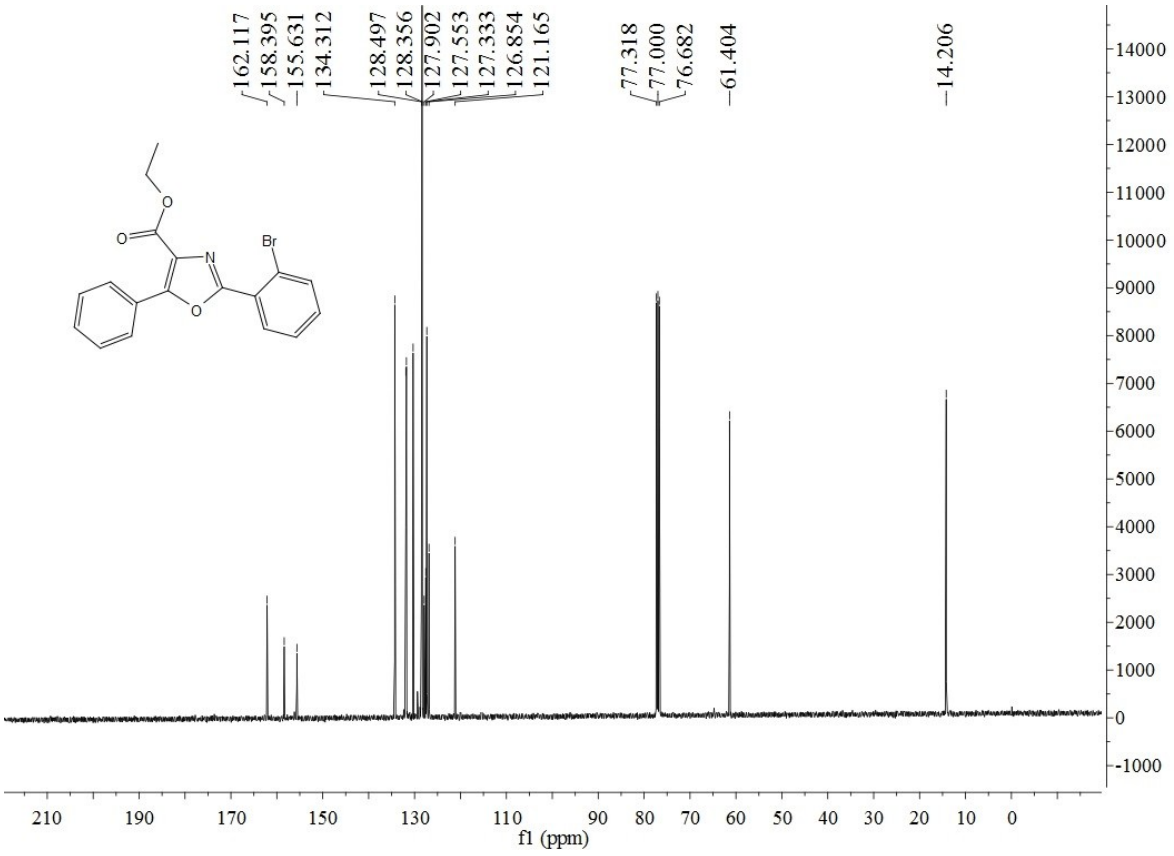
3q


8.270
8.249
8.110
8.104
8.097
8.095
8.090
8.086
7.748
7.513
7.505
7.490
7.486
7.479
4.482
4.464
4.446
4.428
1.435
1.418
1.400
2.00
2.00
2.01
3.00
2.00
3.00
f1 (ppm)

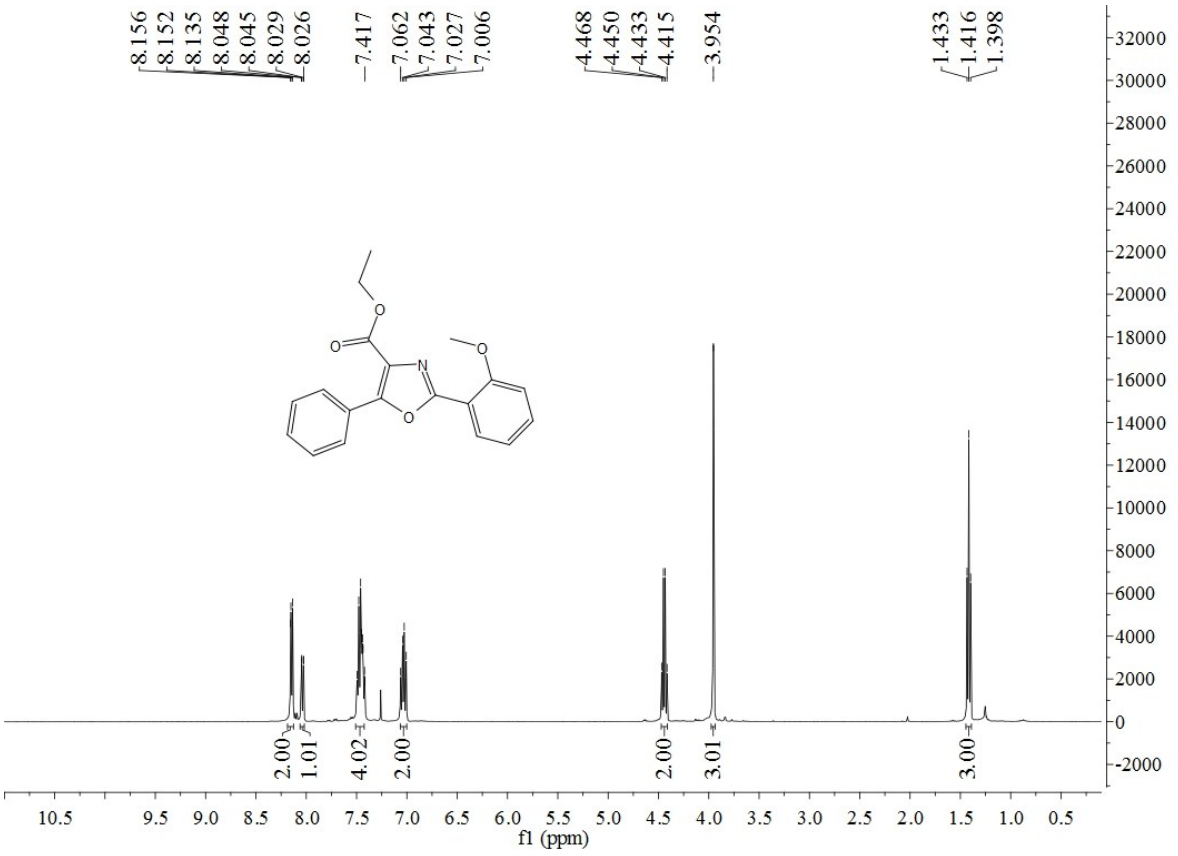

161.935
158.255
155.657
132.357
130.520
128.577
127.029
125.804
125.729
122.326
77.318
77.000
76.682
61.537
14.182
f1 (ppm)

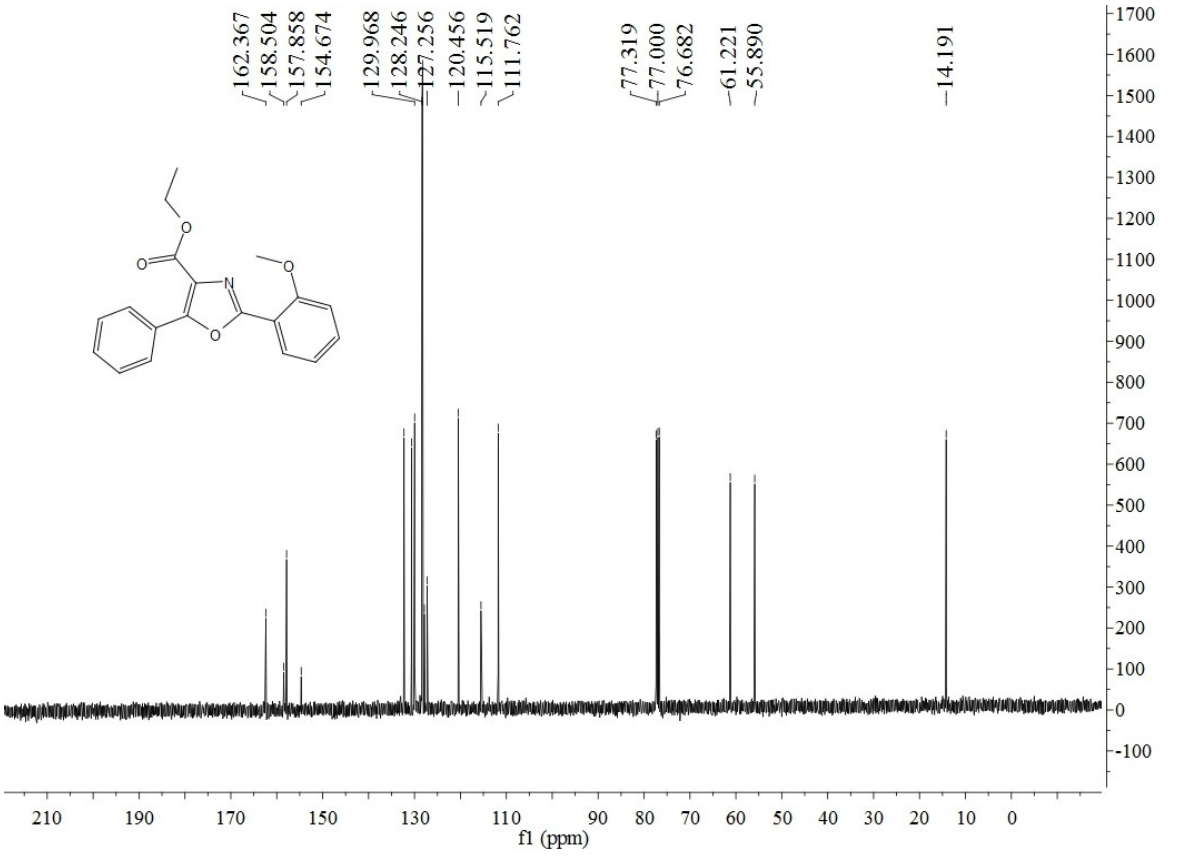
3r


8.191
8.186
8.181
8.170
8.166
8.068
8.064
8.049
7.468
7.451
7.429
7.394
7.316
7.295
4.481
4.463
4.445
4.428
1.435
1.417
1.399
Br
2.00
1.00
1.00
4.00
2.00
3.00
f1 (ppm)

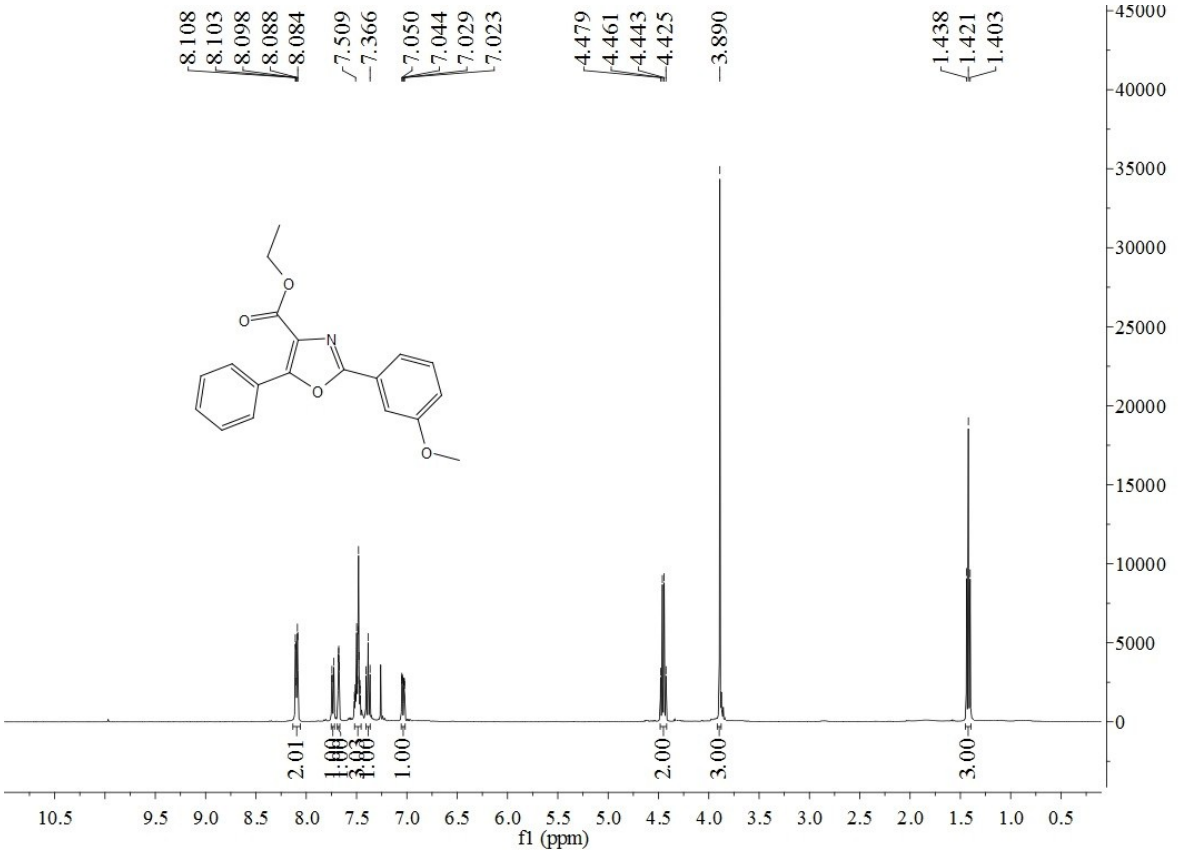

162.117
158.395
155.631
134.312
128.497
128.356
127.902
127.553
127.333
126.854
121.165
77.318
77.000
76.682
61.404
14.206
Br
f1 (ppm)

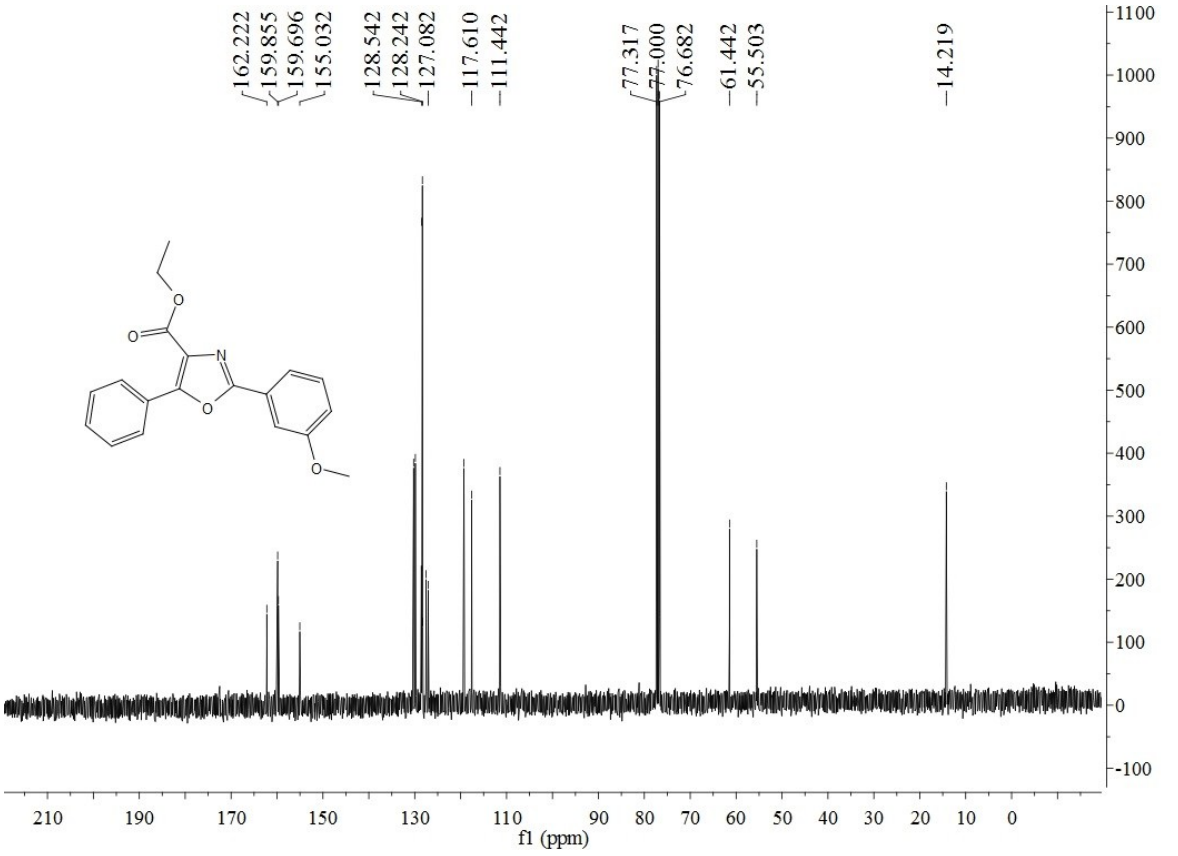
3s


8.156
8.152
8.135
8.048
8.045
8.029
8.026
7.417
7.062
7.043
7.027
7.006
4.468
4.450
4.433
4.415
3.954
1.433
1.416
1.398
2.00
1.01
4.02
2.00
2.00
3.01
3.00
f1 (ppm)

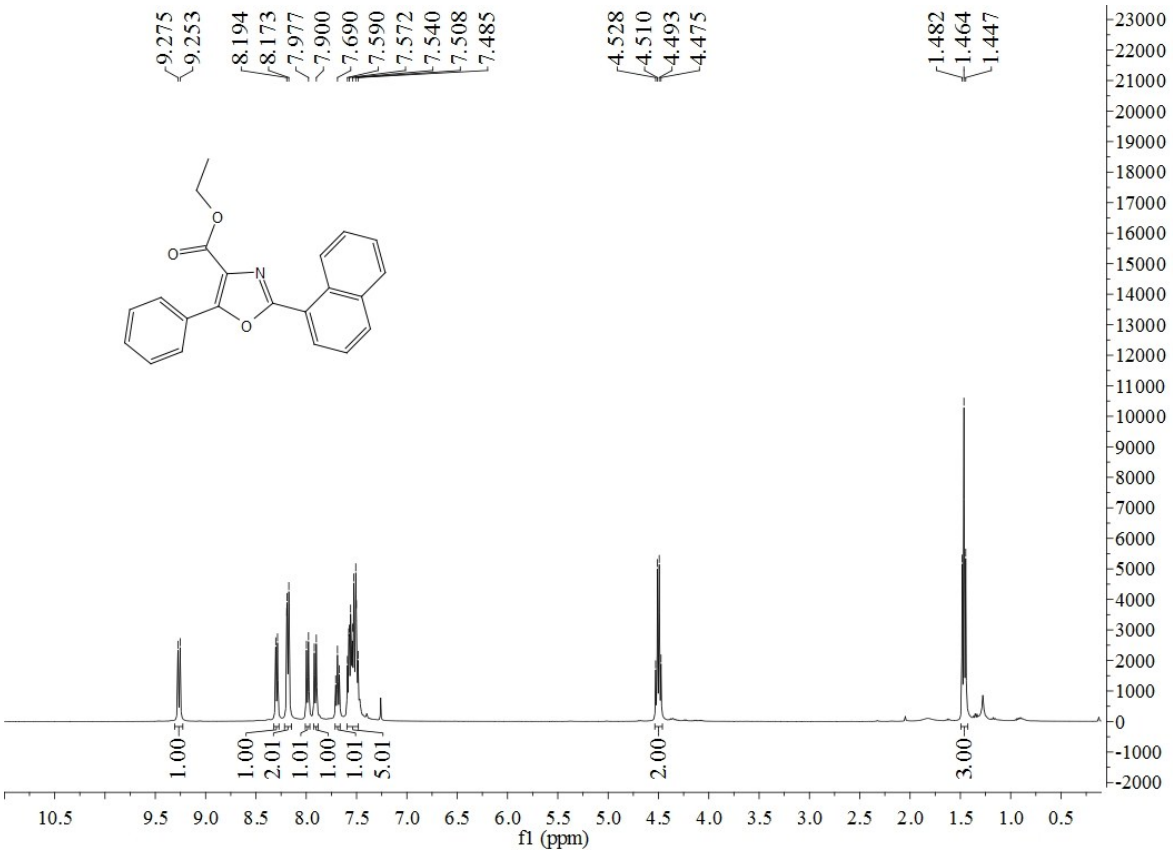

162.367
158.504
157.858
154.674
129.968
128.246
127.256
120.456
115.519
111.762
77.319
77.000
76.682
61.221
55.890
14.191
f1 (ppm)

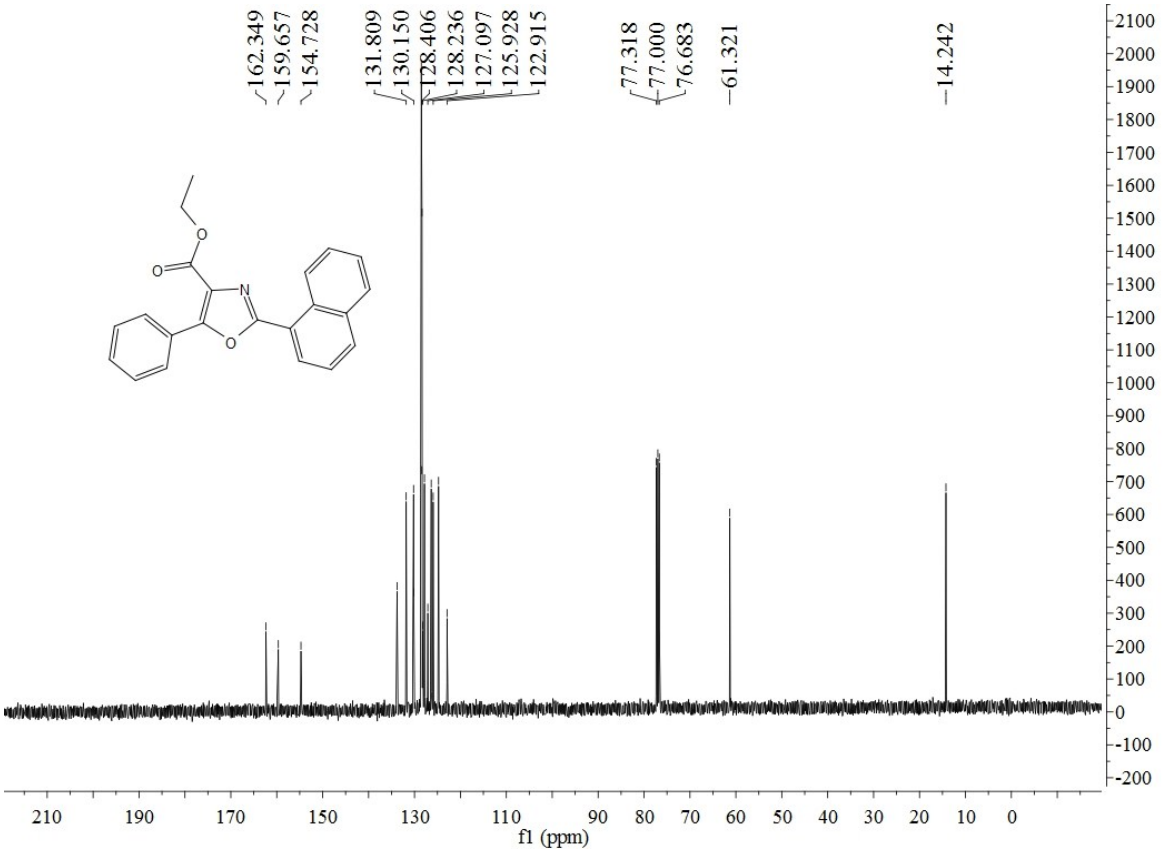
3t


8.108
8.103
8.098
8.088
8.084
7.509
7.366
7.050
7.044
7.029
7.023
4.479
4.461
4.443
4.425
3.890
1.438
1.421
1.403
2.01
1.00
3.03
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

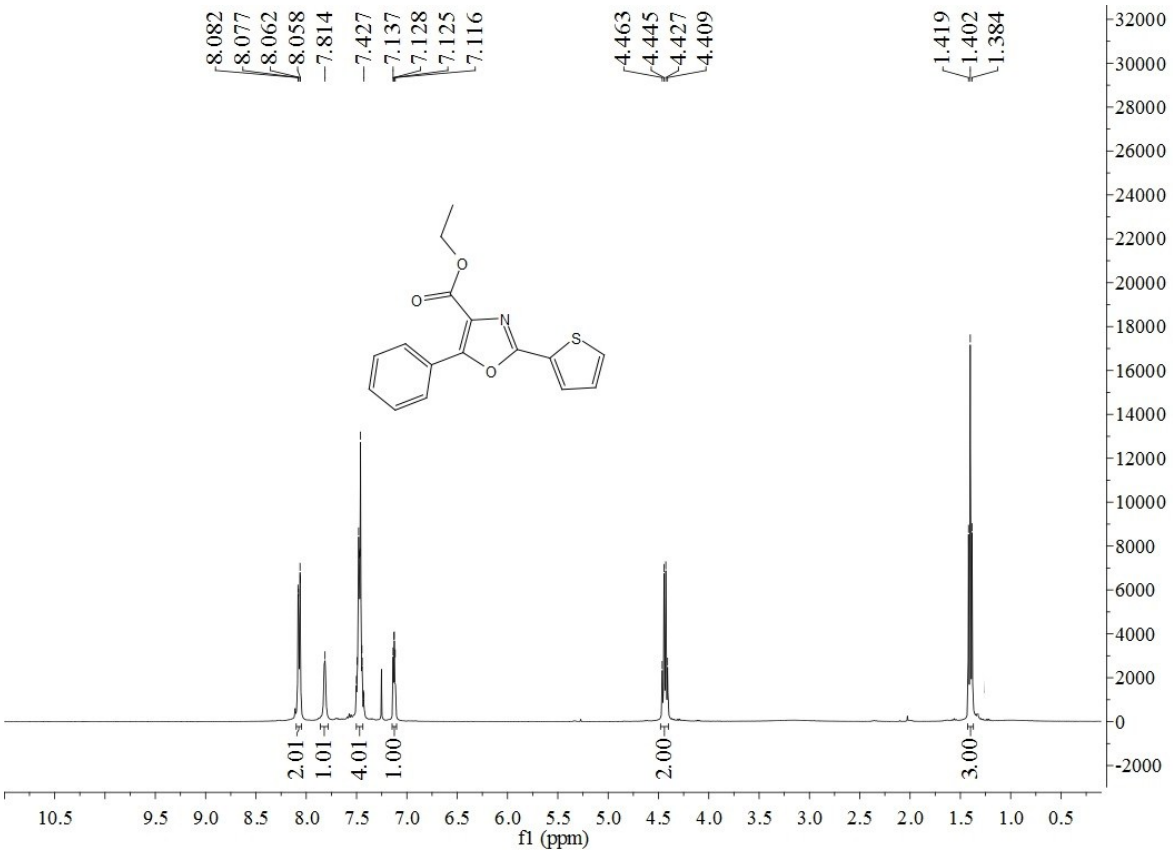

162.222
159.855
159.696
155.032
128.542
128.242
127.082
117.610
111.442
77.317
77.000
76.682
61.442
55.503
14.219
f1 (ppm)

3u


9.275
9.253
8.194
8.173
7.977
7.900
7.690
7.590
7.572
7.540
7.508
7.485
4.528
4.510
4.493
4.475
1.482
1.464
1.447
1.00
1.00
2.01
1.01
1.00
1.01
5.01
2.00
3.00
f1 (ppm)


162.349
159.657
154.728
131.809
130.150
128.406
128.236
127.097
125.928
122.915
77.318
77.000
76.683
61.321
14.242
f1 (ppm)

3v


8.082
8.077
8.062
8.058
7.814
7.427
7.137
7.128
7.125
7.116
4.463
4.445
4.427
4.409
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1.384
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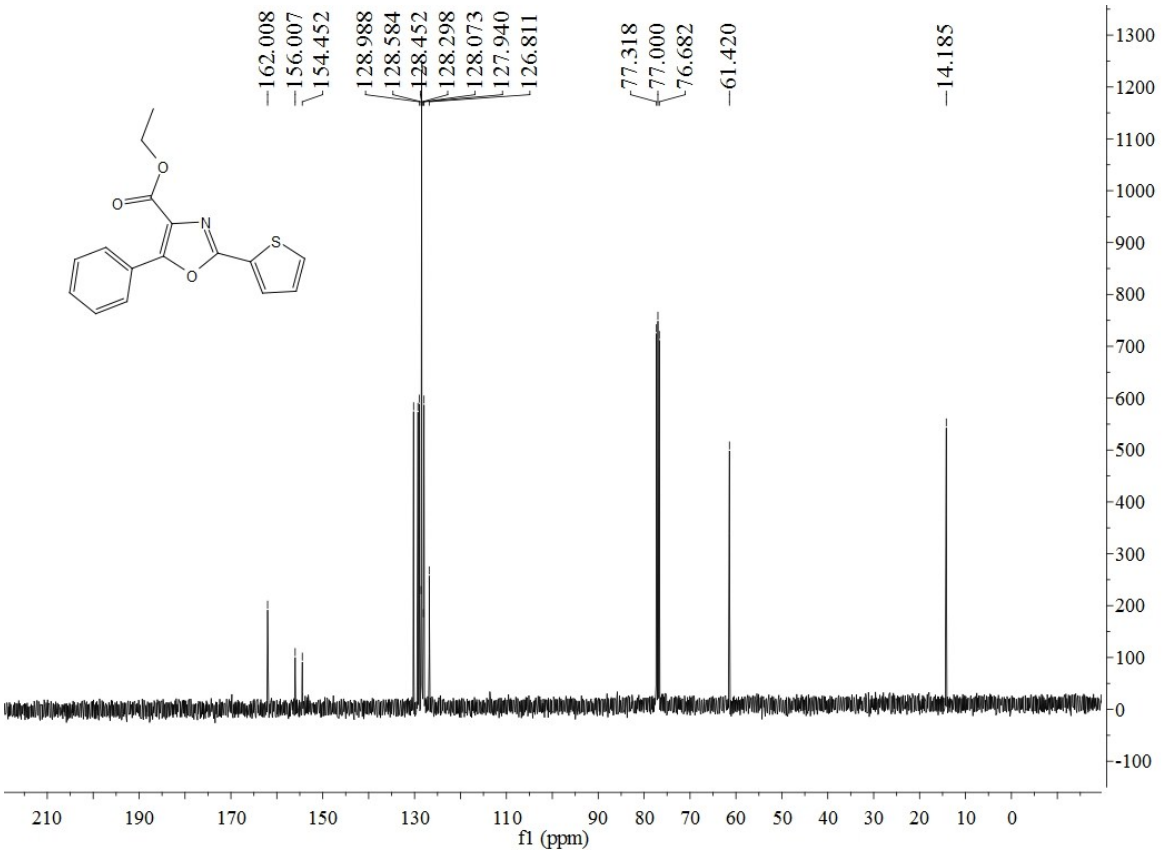
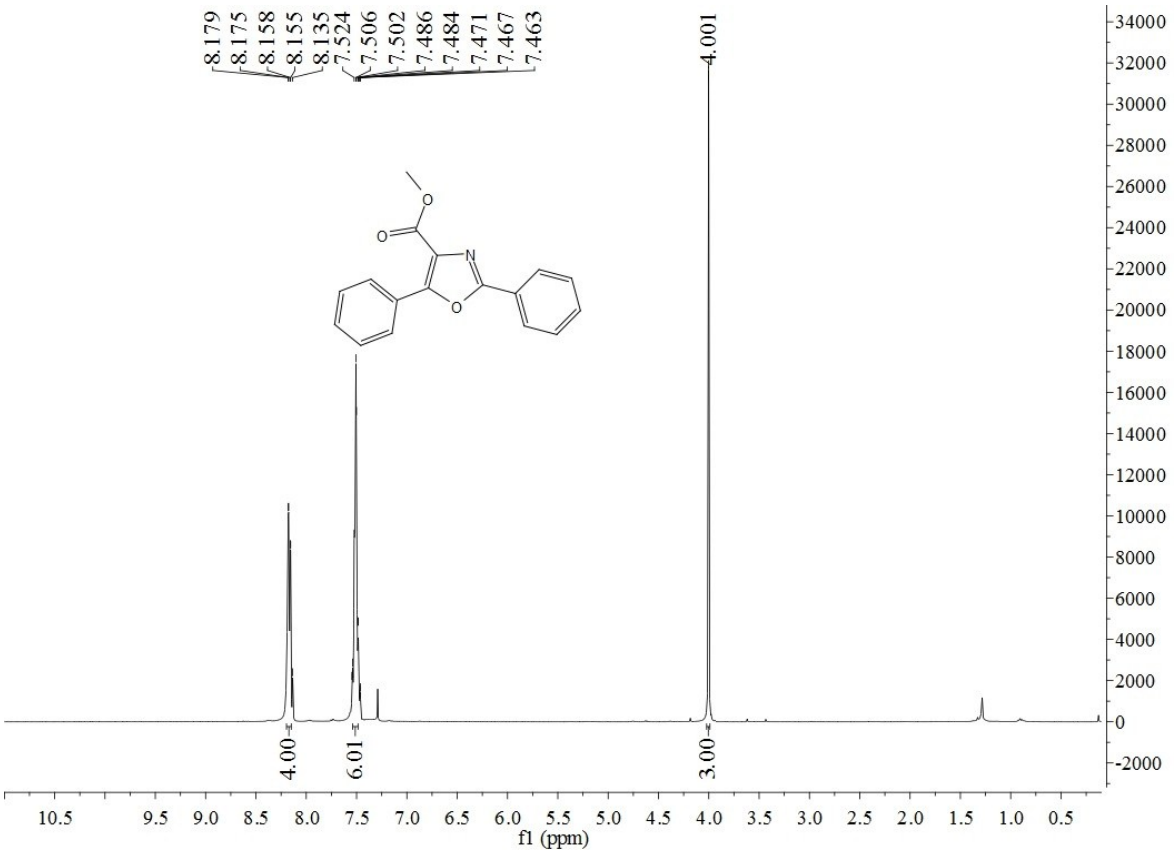
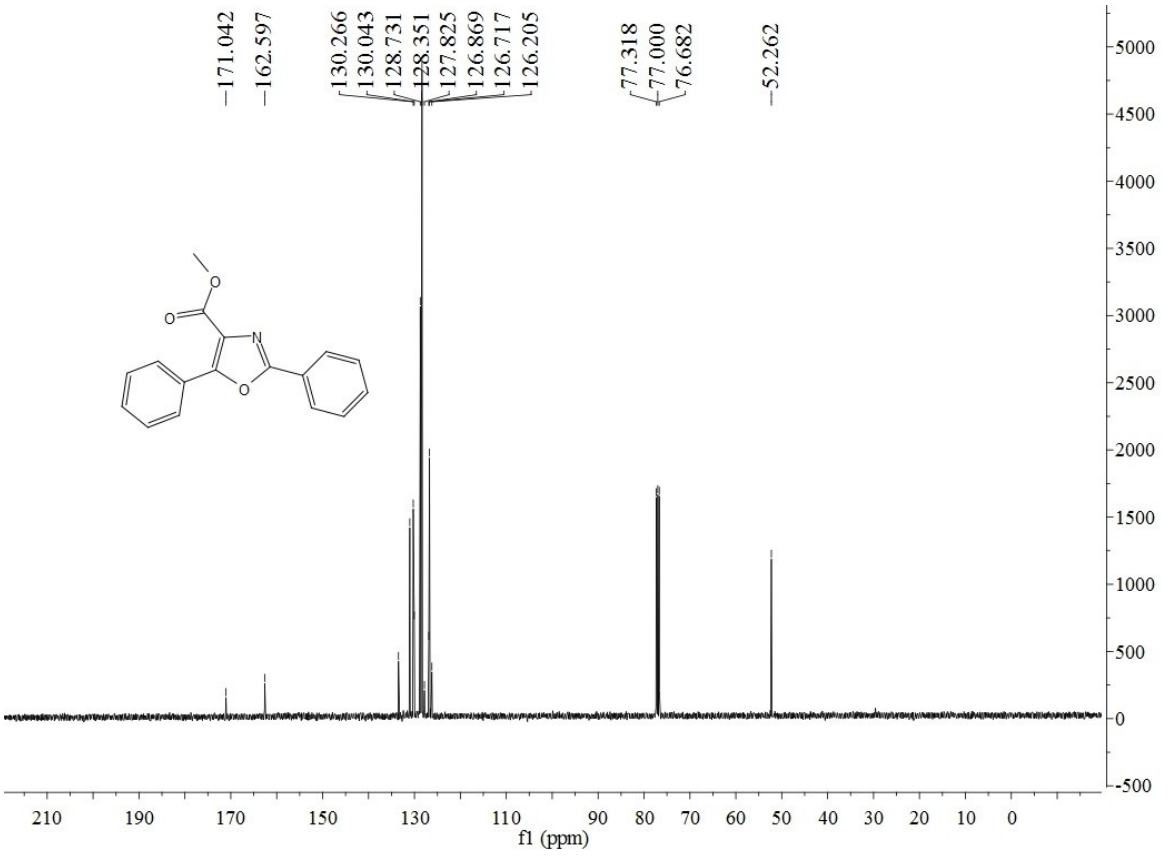
1.01
4.01
1.00
2.00
3.00
f1 (ppm)


162.008
156.007
154.452
128.988
128.584
128.452
128.298
128.073
127.940
126.811
77.318
77.000
76.682
61.420
14.185
f1 (ppm)

3w


8.179
8.175
8.158
8.155
8.135
7.524
7.506
7.502
7.486
7.484
7.471
7.467
7.463
4.001
4.00
6.01
3.00
f1 (ppm)


171.042
162.597
130.266
130.043
128.731
128.351
127.825
126.869
126.717
126.205
77.318
77.000
76.682
52.262
f1 (ppm)