Supporting Information

KI- catalyzed reaction of aryl hydrazines with *α*-oxocarboxylic acids in the presence of CO_2: access to 1,3,4-oxadiazol-2(3*H*)-ones

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List of contents

1. General methods

^{1}H and ^{13}C NMR spectra were recorded by using a Bruker DRX-400 spectrometer and $CDCl_3$ as the solvent. The chemical shifts were referenced to signals at 7.26 and 77.23 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS were obtained on a high resolution mass spectrometer (LCMS-IT-TOF). Melting points were determined with a Büchi Melting Point B-545 instrument.

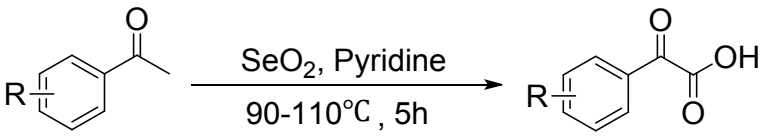
2. General procedure for the synthesis of 1,3,4-oxadiazol-2(3*H*)-one

In a typical procedure, phenylhydrazine **1a** (0.5 mmol), 2-oxo-2-phenylacetic acid **2a** (0.5 mmol), KI (0.2 equiv.), TBHP (4.0 equiv. 70% in water) and K_2CO_3 (2 equiv.) were dissolved in 5 mL MeOH in a dried 15 mL polyterafluoroethylene (PTFE) reaction vessel. The vessel was fixed into a stainless-steel autoclave with a pressure regulating system. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 4.5 h and the pressure was kept constant during the reaction. After the reaction was completed, the vessel was cooled and the pressure was released slowly to atmospheric pressure. Then reaction mixture was diluted with H_2O (20 mL) and extracted with EtOAc (15 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$ and then filtered. The solvent was removed under vacuo and the crude product was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to give the desired product **3** or **4**.

3. General procedure for *α*-oxocarboxylic acids[1]

The substituted α-oxocarboxylic acids (**2a–2j**) were prepared by oxidation of corresponding methyl ketones with SeO_2 (Scheme S1). Methyl ketones (5 mmol), SeO_2 (6 mmol), 20 mL of pyridine were added in a 50 mL round-bottom flask. The reaction mixture was stirred at 110 ℃ for 1 h, then reduce the temperature to 90 ℃ for 4 h. The desired products (**2a–2j**) were isolated by silica-gel column chromatography

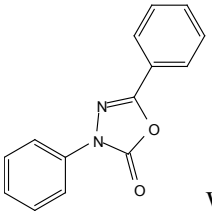
in excellent yields (65–90%).



Scheme S1 Preparation of *α*-oxocarboxylic acids.

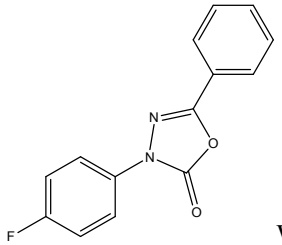
4. Characterization data

3,5-diphenyl-1,3,4-oxadiazol-2(3*H*)-one (3a)[2]



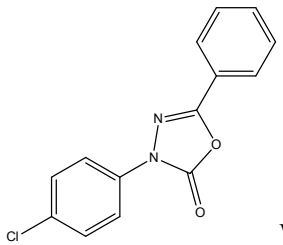
White solid, mp 109–110˚C; **^{1}H NMR** (400 MHz, $CDCl_3$)：δ (ppm) 7.83 (t, *J* = 7.4 Hz, 4H), 7.42 – 7.33 (m, 5H), 7.16 (t, *J* = 7.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.7, 150.8, 136.2, 132.1, 129.3, 129.2, 126.3, 126.1, 123.6, 118.4.

3-(4-fluorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3b)[2]



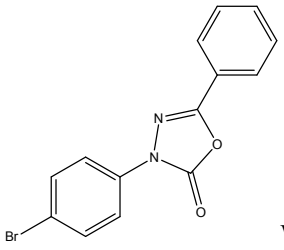
White solid, mp 148–150 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (td, *J* = 6.8, 3.1 Hz,4H), 7.55 – 7.49 (m, 3H), 7.18 – 7.13 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 160.8 (d, *J* = 244.7 Hz), 153.8, 150.9, 132.4 (d, *J* = 2.8 Hz), 132.3, 129.3, 126.2, 123.5, 120.4 (d, *J* = 8.2 Hz), 116.2 (d, *J* = 22.8 Hz).

3-(4-chlorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3c)[2]



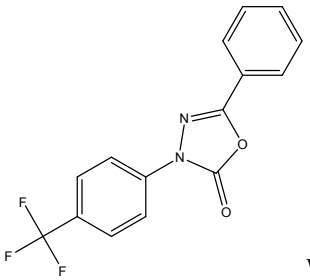
White solid, mp 143–145 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (t, *J* = 8.3 Hz, 4H), 7.55 – 7.48 (m, 3H), 7.42 (d, *J* = 8.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.9, 150.6, 134.8, 132.3, 131.7, 129.5, 129.3, 126.2, 123.4, 119.6.

3-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3d)[3]



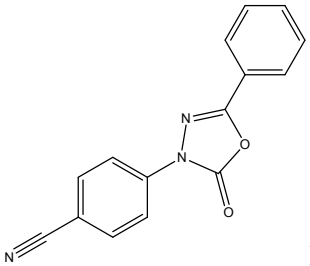
White solid, mp 135–137 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.1 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.56 – 7.47 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.9, 150.5, 135.3, 132.4, 132.3, 129.3, 126.2, 123.4, 119.8, 119.4.

5-phenyl-3-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2(3*H*)-one (3e)



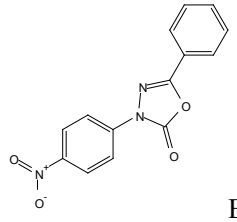
White solid, mp 111–113 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.05 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.45 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.1, 150.4, 138.9, 132.4, 129.3 (q, *J* = 87.8 Hz), 129.2, 126.6 (q, *J* = 3.7 Hz), 126.2, 124.0 (q, *J* = 273.6 Hz), 123.1, 117.9; **HRMS** (ESI) *m/z*: calcd for $C_{15}H_9F_3N_2NaO_2$ $[M+Na]^+$ 329.0508, found 329.0509.

4-(2-oxo-5-phenyl-1,3,4-oxadiazol-3(2*H*)-yl)benzonitrile (3f)[2]



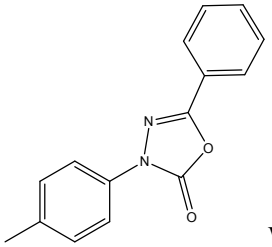
Brown solid, mp 165–167 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J* = 8.8 Hz, 2H), 7.93 – 7.91 (m, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J* = 18.0, 7.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 174.8, 154.4, 150.2, 139.5, 133.5, 132.7, 129.3, 126.3, 122.9, 118.2, 109.3.

3-(4-nitrophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3g)[2]



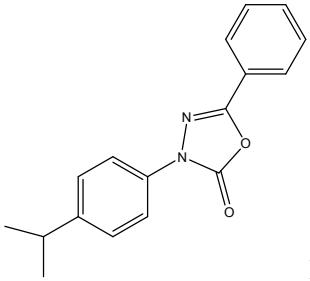
Brown solid, mp 167–169 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.32 (d, *J* = 7.9 Hz, 2H), 8.16 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 6.3 Hz, 2H), 7.56 (dd, *J* = 18.0, 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.6, 150.2, 145.1, 141.0, 132.8, 129.4, 126.4, 125.2, 122.8, 118.0.

5-phenyl-3-(p-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (3h)[3]



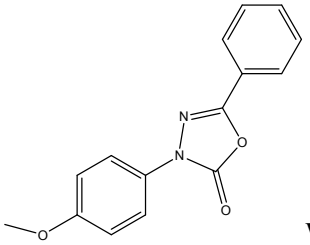
White solid, mp 154-156°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.46 (m, 3H), 7.24 (d, *J* = 8.6 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.5, 150.9, 136.1, 133.8, 132.0, 129.9, 129.2, 126.1, 123.7, 118.5, 21.1.

3-(4-isopropylphenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3i)



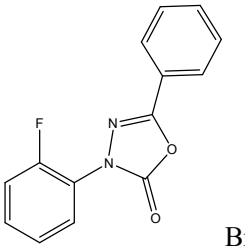
Brown oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.85 – 7.81 (m, 2H), 7.53 – 7.47 (m, 3H), 7.32 (d, *J* = 8.6 Hz, 2H), 2.94 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.6, 151.0, 147.3, 134.0, 132.0, 129.2, 127.3, 126.1, 123.8, 118.8, 33.9, 24.1; **HRMS** (ESI) *m/z*: calcd for $C_{17}H_{16}N_2NaO_2$ $[M+Na]^+$ 303.1104, found 303.1102.

3-(4-methoxyphenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3j)[3]



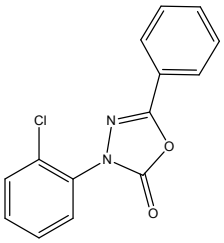
White solid, mp 138–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.83 – 7.80 (m, 2H), 7.53 – 7.47 (m, 3H), 6.98 – 6.96 (m, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 158.1, 153.5, 151.1, 132.0, 129.5, 129.2, 126.1, 123.8, 120.4, 114.5, 55.7.

3-(2-fluorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3k)



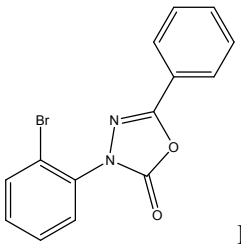
Brown solid, mp 101–103 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.51 (dt, *J* = 14.7, 7.4 Hz, 3H), 7.42 (dd, *J* = 12.9, 7.6 Hz, 1H), 7.26 (dd, *J* = 12.3, 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 156.6 (d, *J* = 253.5 Hz), 154.7, 151.7, 132.2, 130.7 (d, *J* = 7.7 Hz), 129.2, 127.1, 126.1, 124.9 (d, *J* = 3.9 Hz), 123.6, 123.1 (d, *J* = 11.6 Hz), 117.3 (d, *J* = 19.2 Hz); **HRMS** (ESI) *m/z*: calcd for $C_{14}H_{10}FN_2O_2$ $[M+H]^+$ 257.0721, found 257.0717.

3-(2-chlorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3l)



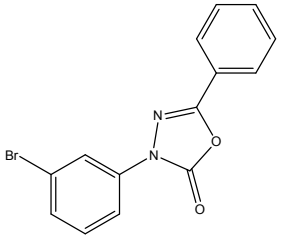
White solid, mp 121–123 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.6 Hz, 2H), 7.55 (s, 2H), 7.50 (dd, *J* = 13.9, 6.6 Hz, 3H), 7.43 – 7.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.5, 151.9, 132.6, 132.2, 132.1, 131.1, 131.0, 129.2, 129.1, 128.0, 126.1, 123.7. **HRMS** (ESI) *m/z*: calcd for $C_{14}H_{10}ClN_2O_2$ $[M+H]^+$ 273.0425, found 273.0419.

3-(2-bromophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3m)



Brown solid, mp 123–125 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.51 (ddd, *J* = 20.6, 13.4, 7.7 Hz, 5H), 7.37 (t, *J* = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.4, 151.8, 134.2, 134.2, 132.2, 131.5, 129.5, 129.3, 128.7, 126.1, 123.7, 121.8; **HRMS** (ESI) *m/z*: calcd for $C_{14}H_{10}BrN_2O_2$ $[M+H]^+$ 316.9920, found 316.9912.

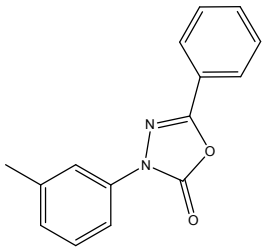
3-(3-bromophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3n)



White solid, mp 125–127 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$):δ (ppm) 8.12 (t, *J* = 1.9 Hz, 1H), 7.93 (dt, *J* = 8.4, 1.7 Hz, 3H), 7.55 – 7.48 (m, 3H), 7.39 (dd, *J* = 8.0, 1.6 Hz,

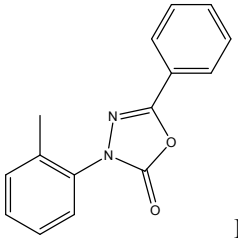
1H), 7.31 (t, *J* = 8.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.0, 150.5, 137.3, 132.4, 130.7, 129.3, 129.2, 126.2, 123.3, 123.1, 121.3, 116.7; **HRMS** (ESI) *m/z*: calcd for $C_{14}H_{10}BrN_2O_2$ $[M+H]^+$ 316.9920, found 316.9916.

5-phenyl-3-(m-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (3o)



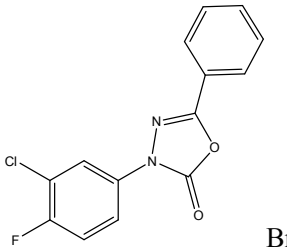
Brown solid, mp 99–101 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.94 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.75 (d, *J* = 12.0 Hz, 2H), 7.54 – 7.47 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.7, 150.9, 139.5, 136.2, 132.1, 129.2, 127.2, 126.2, 123.7, 119.1, 115.7 , 21.8. **HRMS** (ESI) *m/z*: calcd for $C_{15}H_{13}N_2O_2$ $[M+H]^+$ 253.0972, found 253.0968.

5-phenyl-3-(o-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (3p)



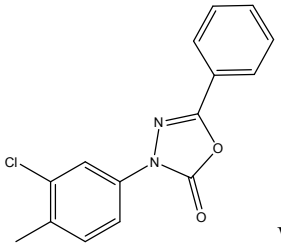
Brown solid, mp 107–109 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 6.8 Hz, 2H), 7.52 (dd, *J* = 10.9, 7.2 Hz, 3H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.32 (m, 3H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.2, 152.3, 135.3, 134.0, 132.0, 131.7, 129.7, 129.2, 127.1, 126.7, 126.0, 123.9, 18.3. **HRMS** (ESI) *m/z*: calcd for $C_{15}H_{13}N_2O_2$ $[M+H]^+$ 253.0972, found 253.0966.

3-(3-chloro-4-fluorophenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3q)



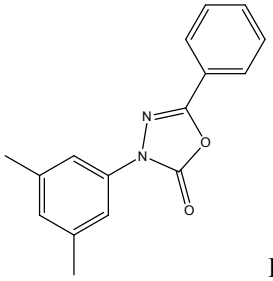
Brown solid, mp 126–128 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 4.1 Hz, 1H), 7.90 (dd, *J* = 24.2, 8.1 Hz, 3H), 7.53 (dt, *J* = 14.2, 6.9 Hz, 3H), 7.22 (d, *J* = 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 156.2 (d, *J* = 247.4 Hz), 154.1, 150.5, 132.8 (d, *J* = 3.2 Hz), 132.5, 129.3, 126.3, 123.3, 122.0 (d, *J* = 18.9 Hz), 120.7, 118.0 (d, *J* = 7.1 Hz), 117.2 (d, *J* = 22.2 Hz); **HRMS** (ESI) *m/z*: calcd for $C_{14}H_8ClFN_2NaO_2$ $[M+Na]^+$ 313.0151, found 313.0150.

3-(3-chloro-4-methylphenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3r)



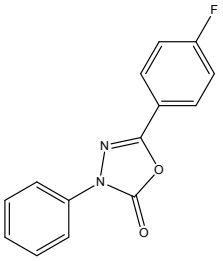
White solid, mp 152–154 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, *J* = 177.9, 75.8 Hz, 8H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.8, 150.5, 135.1, 134.9, 134.0, 132.2, 131.4, 129.2, 126.1, 123.4, 118.8, 116.3, 19.7; **HRMS** (ESI) *m/z*: calcd for $C_{15}H_{11}ClN_2NaO_2$ $[M+Na]^+$ 309.0401, found 309.0403.

3-(3,5-dimethylphenyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3s)



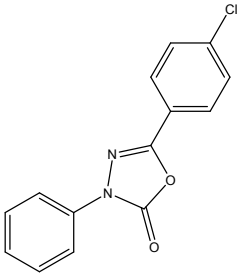
Brown oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 6.9 Hz, 2H), 7.56 – 7.48 (m, 5H), 6.91 (s, 1H), 2.38 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$):δ (ppm) 153.6, 151.0, 139.3, 136.1, 132.1, 129.2, 128.1, 126.1, 123.7, 116.3, 21.7; **HRMS** (ESI) *m/z*: calcd for $C_{16}H_{14}N_2NaO_2$ $[M+Na]^+$ 289.0947, found 289.0949.

5-(4-fluorophenyl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4a)[2]



White solid, mp 141–143 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 – 7.91 (m, 4H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.19 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 165.1 (d, *J* = 252.2 Hz), 153.0, 150.7, 136.2, 129.4, 128.5 (d, *J* = 8.9 Hz), 126.4, 120.0 (d, *J* = 3.2 Hz), 118.5, 116.7 (d, *J* = 8.6 Hz).

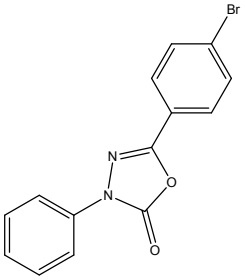
5-(4-chlorophenyl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4b)[2]



White solid, mp 136–138 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 9.4 Hz, 4H), 7.28 (t, *J* = 7.7 Hz, 1H); **^{13}C**

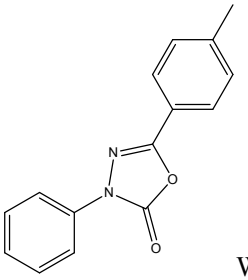
NMR (100 MHz, $CDCl_3$): δ (ppm) 152.9, 150.6, 138.5, 136.1, 129.7, 129.4, 127.4, 126.5, 122.1, 118.5.

5-(4-bromophenyl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4c)[2]



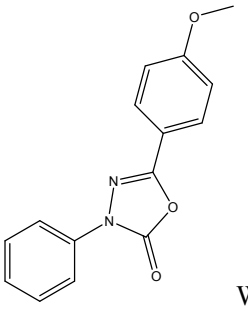
White solid, mp 124–126 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.28 (dd, *J* = 13.5, 6.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.1, 150.7, 136.2, 132.7, 129.5, 127.6, 126.9, 126.5, 122.6, 118.6.

3-phenyl-5-(p-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (4d)[2]



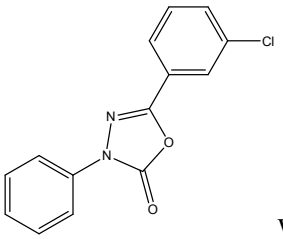
White solid, mp 149–151 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 2H), 7.30 – 7.24 (m, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.9, 150.9, 142.8, 136.3, 129.9, 129.4, 126.2, 126.1, 120.9, 118.4, 21.9.

5-(4-methoxyphenyl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4e)[2]



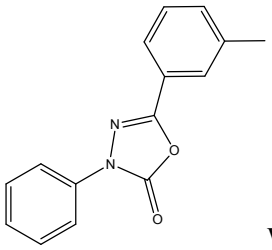
White solid, mp 143–145 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 162.7, 153.7, 150.9, 136.3, 129.3, 127.9, 126.1, 118.3, 116.0, 114.7, 55.6.

5-(3-chlorophenyl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4f)



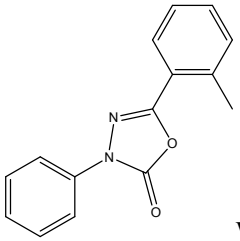
White solid, mp 107–109 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 7.9 Hz, 3H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.47 (dt, *J* = 17.5, 8.8 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 152.6, 150.6, 136.1, 135.5, 132.2, 130.6, 129.5, 126.6, 126.2, 125.3, 124.2, 118.5; **HRMS** (ESI) *m/z*: calcd for $C_{14}H_9ClN_2NaO_2$ $[M+Na]^+$, 295.0245, found 295.0239.

3-phenyl-5-(m-tolyl)-1,3,4-oxadiazol-2(3*H*)-one(4g)[2]



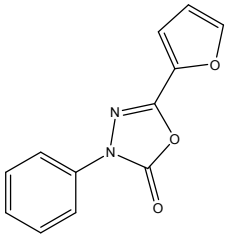
White solid, mp 126–128 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 8.1 Hz, 2H), 7.74 – 7.70 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.26 (t, *J* = 6.8 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.9, 150.9, 139.1, 136.3, 132.9, 129.4, 129.1, 126.6, 126.2, 123.5, 123.3, 118.4, 21.5.

3-phenyl-5-(o-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (4h)[2]



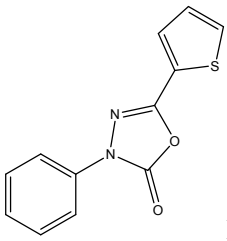
White solid, mp 95–97 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.44 (dt, *J* = 19.9, 7.5 Hz, 3H), 7.34 – 7.25 (m, 3H), 2.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 154.1, 150.6, 138.3, 136.4, 132.1, 131.6, 129.4, 128.4, 126.5, 126.2, 122.3, 118.4, 22.4.

5-(furan-2-yl)-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (4i)[3]



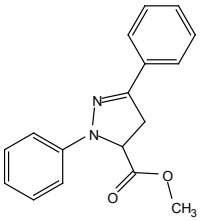
Brown solid, mp 106–108 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 8.1 Hz, 2H), 7.65 (s, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.09 (d, *J* = 3.4 Hz, 1H), 6.61 – 6.60 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 150.0, 147.1, 146.2, 138.8, 136.1, 129.4, 126.5, 118.5, 114.7, 112.3.

3-phenyl-5-(thiophen-2-yl)-1,3,4-oxadiazol-2(3*H*)-one (4j)[2]



Brown solid, mp 134–136 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.9 Hz, 2H), 7.68 (s, 1H), 7.55 (d, *J* = 4.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 6.5 Hz, 1H), 7.15 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 150.6, 150.3, 136.1, 130.4, 130.1, 129.4, 128.3, 126.4, 125.2, 118.5.

methyl 1,3-diphenyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate (5a)



White solid, mp 97–99 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.23 (m, 5H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.85 (t, *J* = 6.9 Hz, 1H), 4.75 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.69 (s, 3H), 3.62 – 3.52 (m, 1H), 3.35 (dd, *J* = 17.0, 6.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.1, 147.1, 144.7, 132.1, 129.3, 129.0, 128.7, 126.0, 119.9, 113.0, 61.7, 52.8, 38.3; **HRMS** (ESI) *m/z*: calcd for $C_{17}H_{17}N_2O_2$ $[M+Na]^+$, 281.1285, found 281.1286.

5. Reference

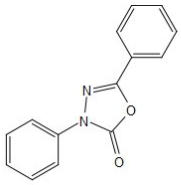
(1) W. Kuldeep, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434.

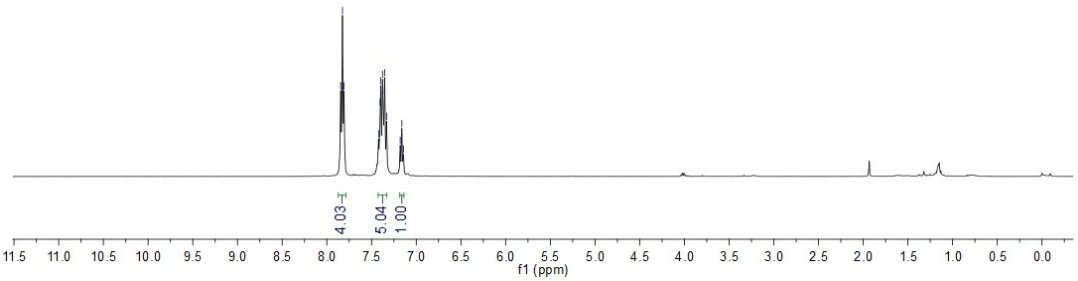
(2) Y. Wang, X. Meng, Y.-T. Yang, L.-T. Zhang, S.-B. Guo, D. Tang, Y.-X. Li and B.-H. Chen, *Chem. Commun.,* 2015, **51**, 1905.

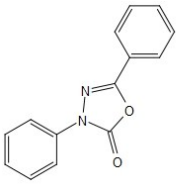
(3) C.-X. Guo, W.-Z. Zhang, N. Zhang and X.-B. Lu, *J. Org. Chem.,* 2017, **82**, 7637.

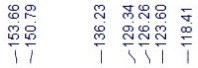
6. NMR spectra

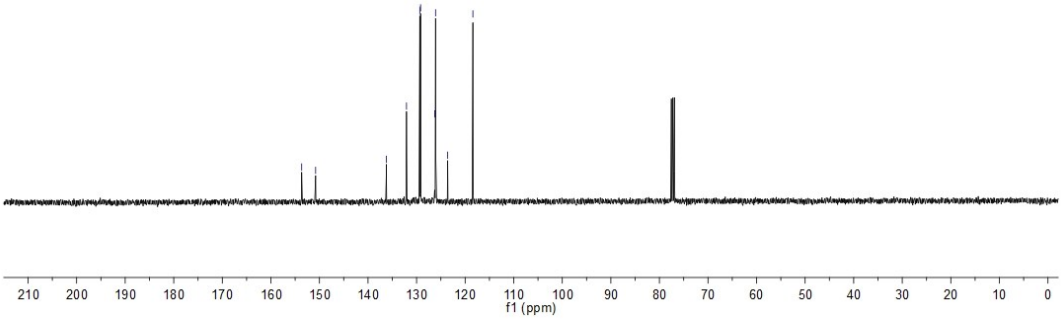
3a



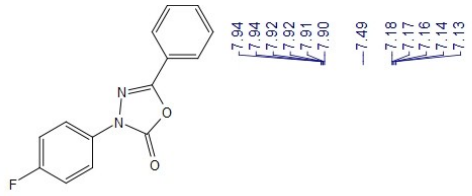


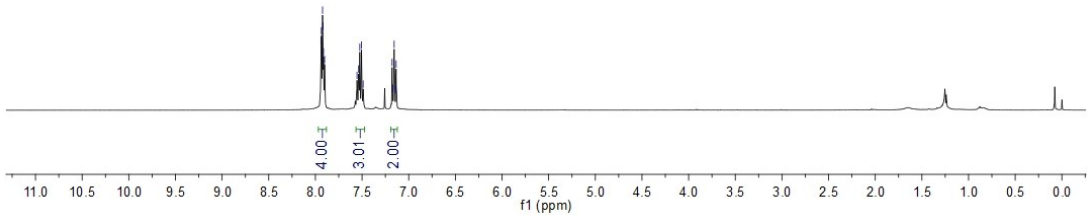


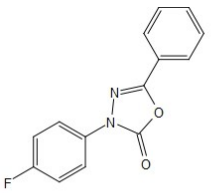


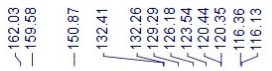


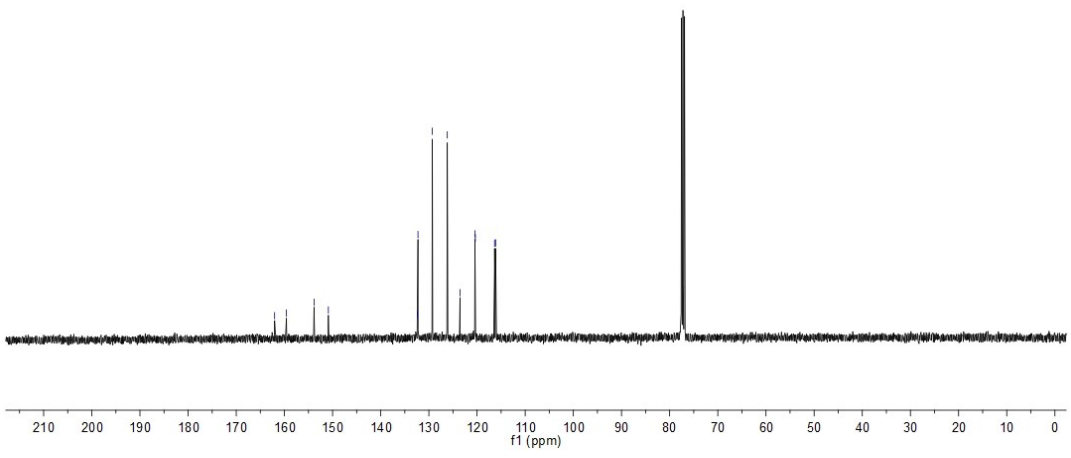
3b


7.94
7.94
7.92
7.92
7.91
7.90
7.49
7.18
7.17
7.16
7.14
7.13
N
N
O
O
F

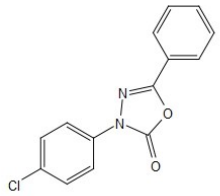

4.00
3.01
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
N
O
O
F

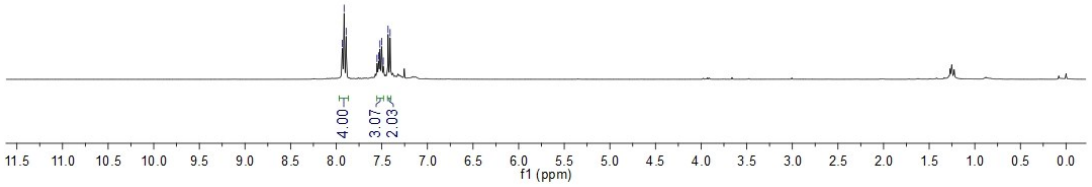

162.03
159.58
150.87
132.41
132.26
129.29
126.18
123.54
120.44
120.35
116.36
116.13

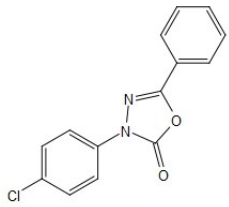

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

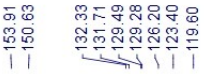
3c

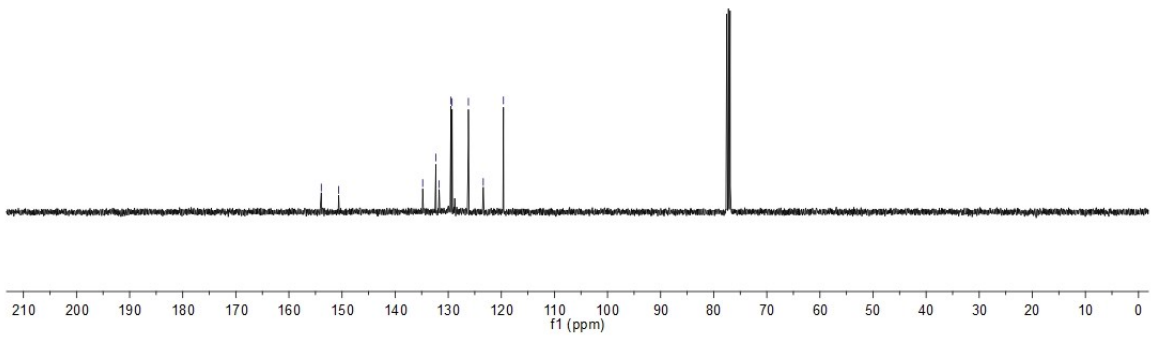

N
N
O
O
Cl


7.93
7.91
7.89
7.55
7.54
7.52
7.50
7.48
7.43
7.41


4.00
3.07
2.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
N
O
O
Cl


153.91
150.63
132.33
131.71
129.49
129.28
126.20
123.40
119.60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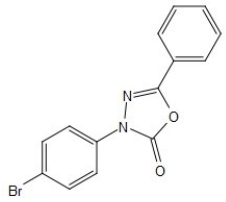
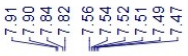
f1 (ppm)

3d


Br
N
N
O
O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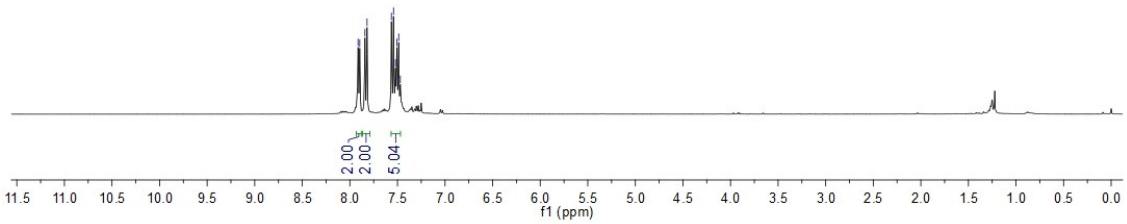
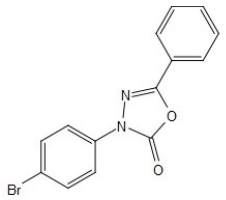
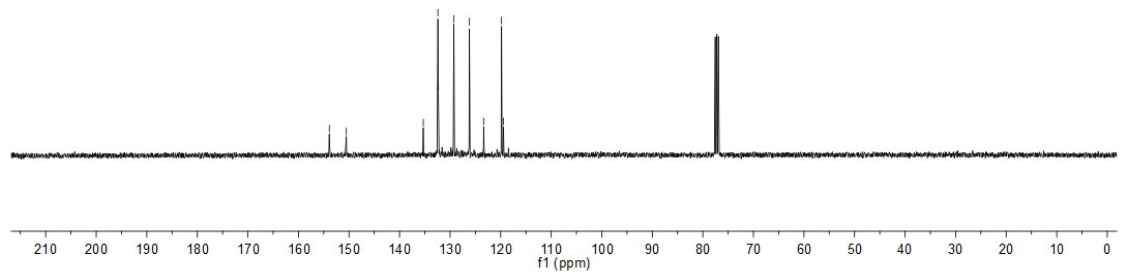
7.54
7.52
7.51
7.49
7.47

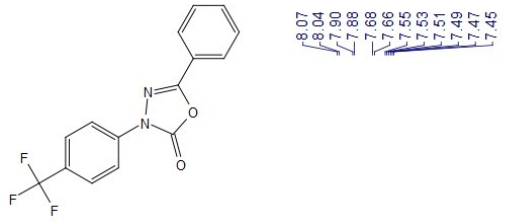

2.00
2.00
5.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

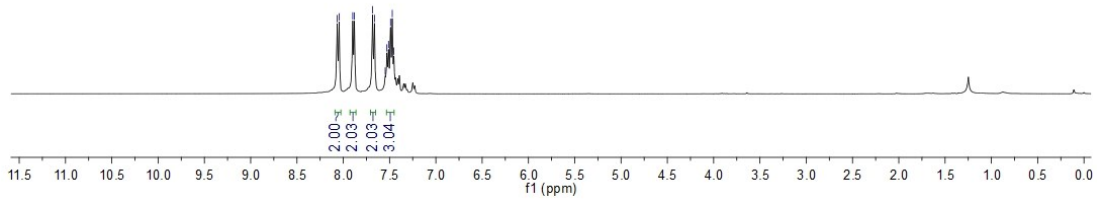

Br
N
N
O
O

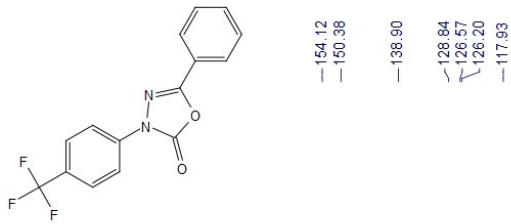

153.89
150.53
135.30
132.41
132.32
129.26
126.18
123.37
119.82
119.44

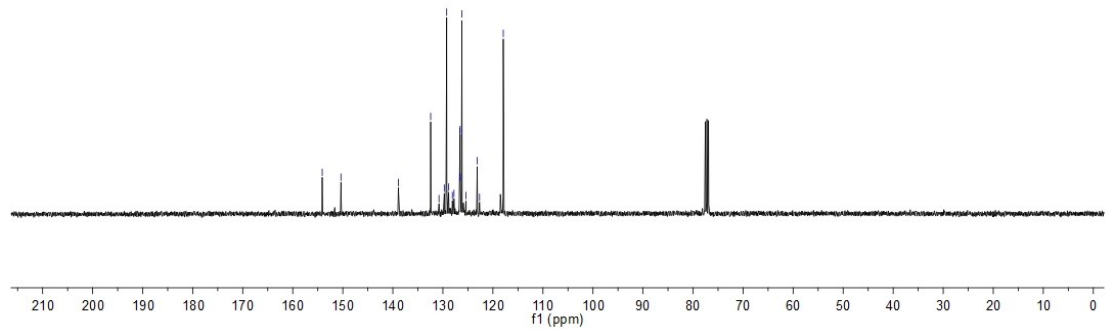

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3e

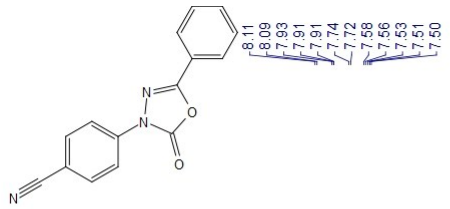

8.07
8.04
7.90
7.88
7.68
7.66
7.55
7.53
7.51
7.49
7.47
7.45
N
N
O
O
F
F
F

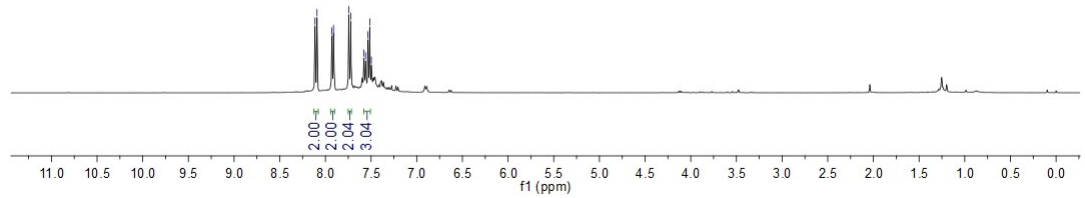

2.00
2.03
2.03
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

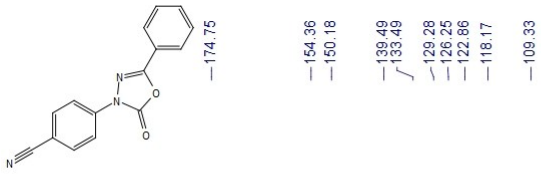

154.12
150.38
138.90
128.84
126.57
126.20
117.93
N
N
O
O
F
F
F

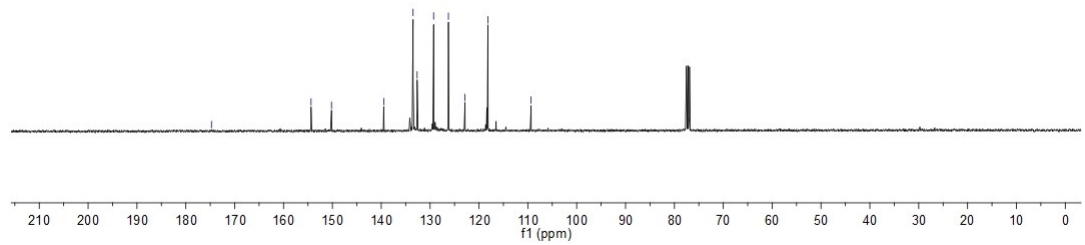

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3f

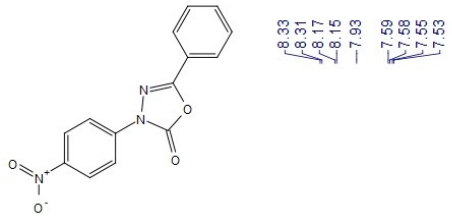

8.11
8.09
7.93
7.91
7.91
7.74
7.72
7.58
7.56
7.53
7.51
7.50
N
N
O
O
N

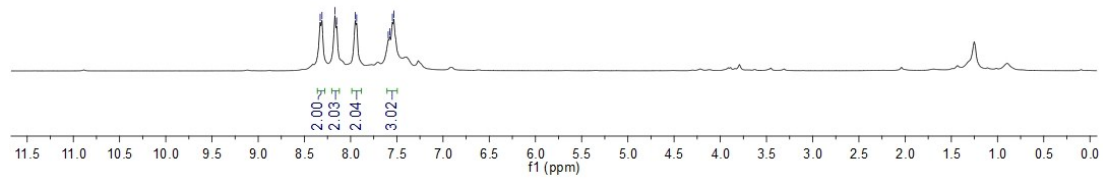

2.00
2.00
2.04
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

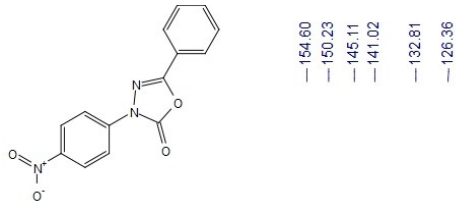

174.75
154.36
150.18
139.49
133.49
129.28
126.25
122.86
118.17
109.33
N
N
O
O
N

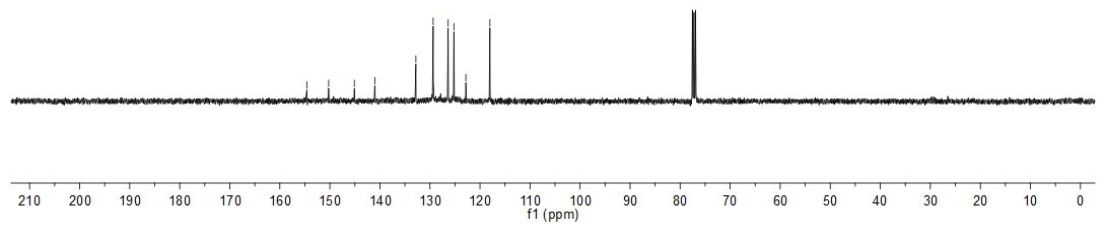

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3g

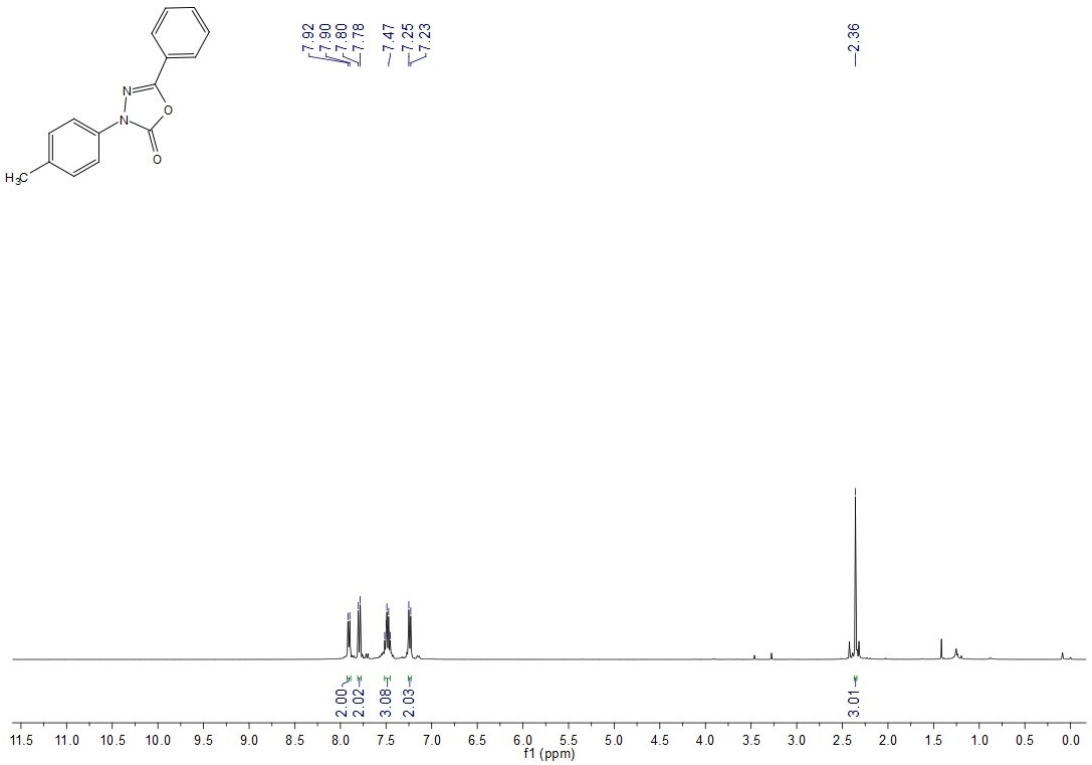

8.33
8.31
8.17
8.15
7.93
7.59
7.58
7.55
7.53

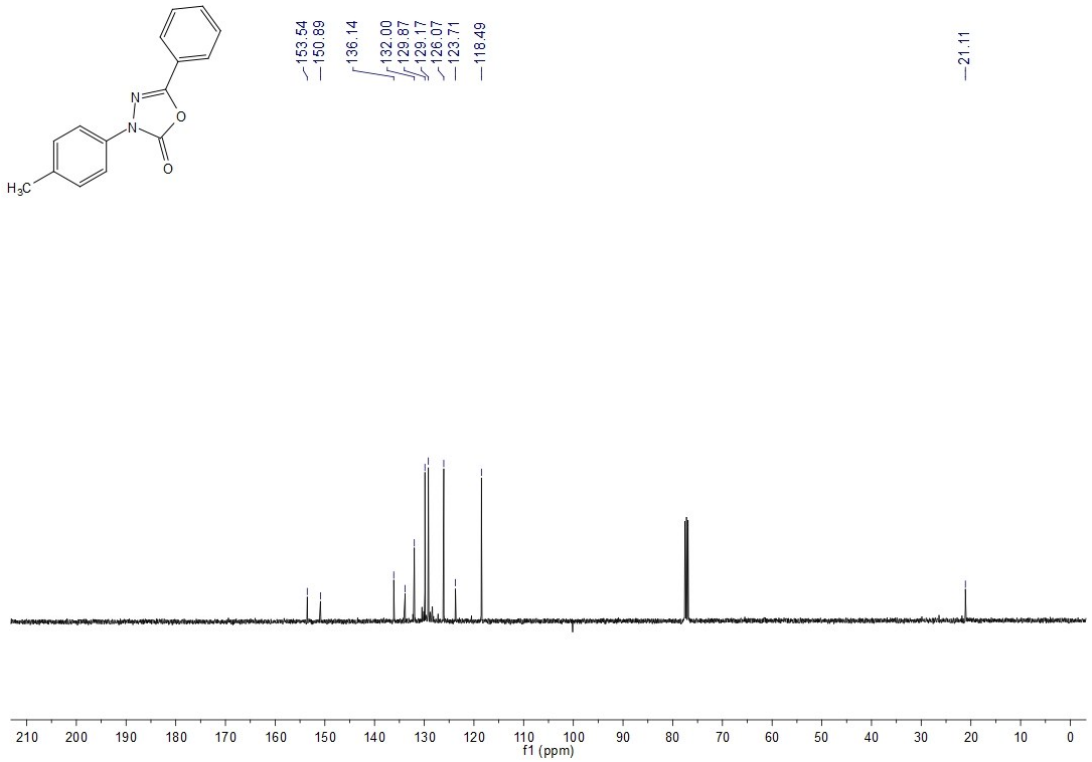

2.00
2.03
2.04
3.02
f1 (ppm)


154.60
150.23
145.11
141.02
132.81
126.36
122.82
118.01

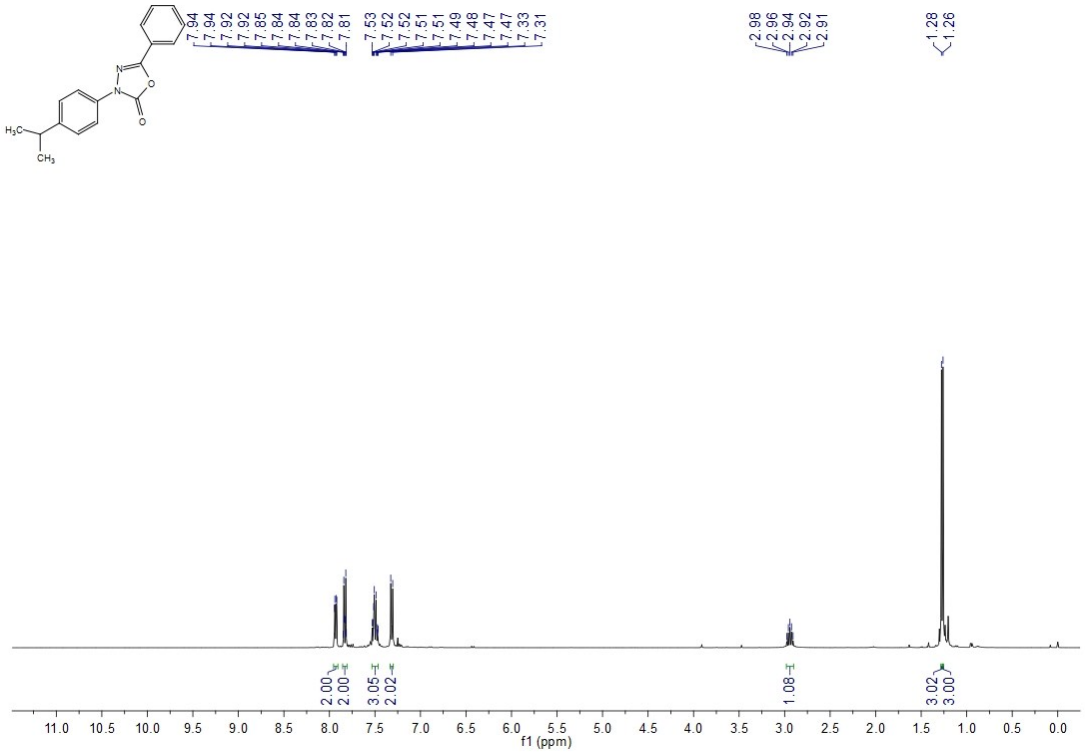

f1 (ppm)

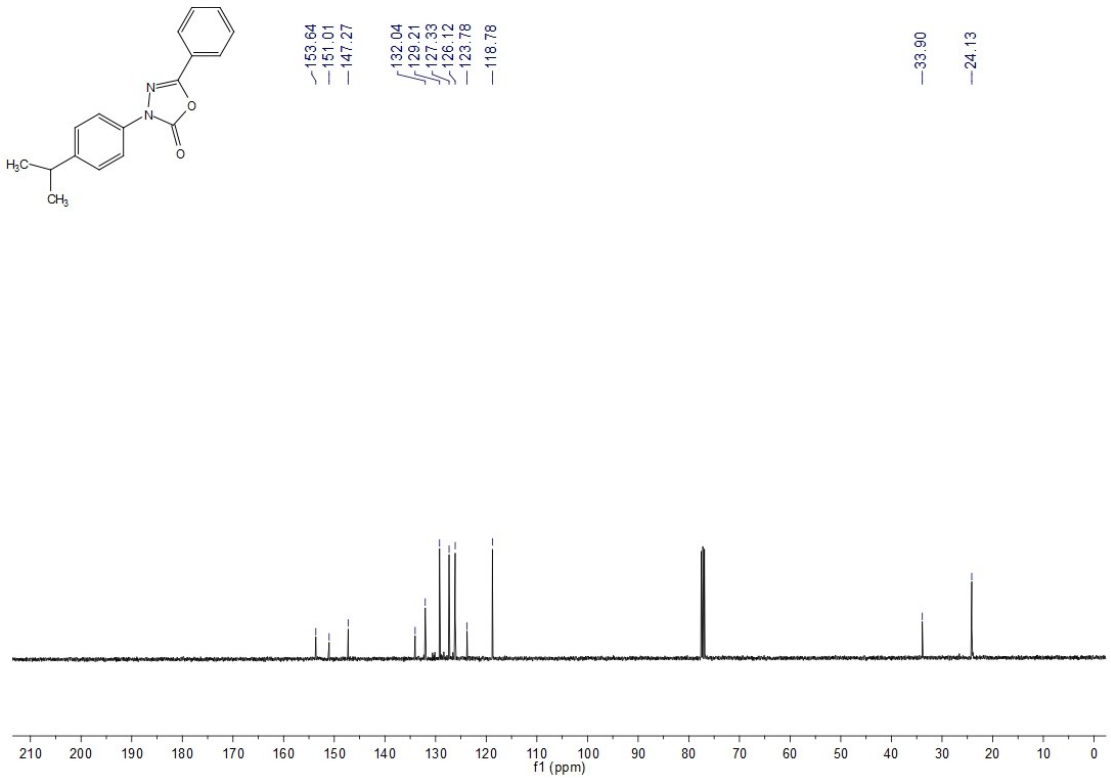
3h


7.92
7.90
7.80
7.78
7.47
7.25
7.23
2.36
2.00
2.02
3.08
2.03
3.01
f1 (ppm)

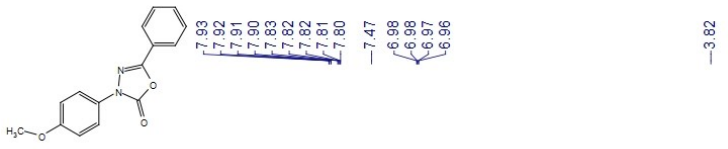

153.54
150.89
136.14
132.00
129.87
129.17
126.07
123.71
118.49
21.11
f1 (ppm)

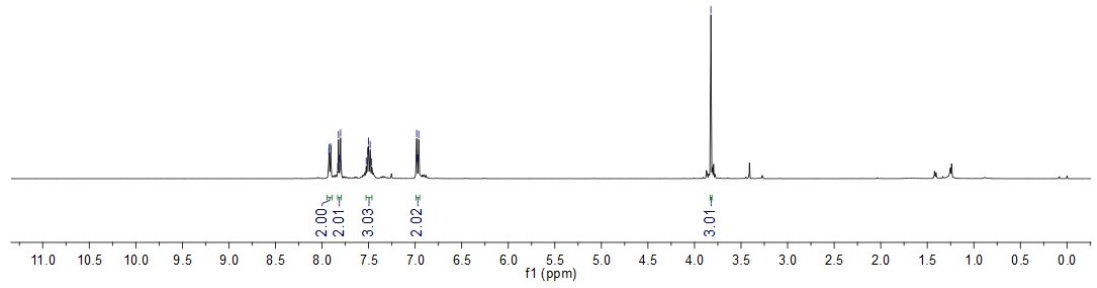
3i

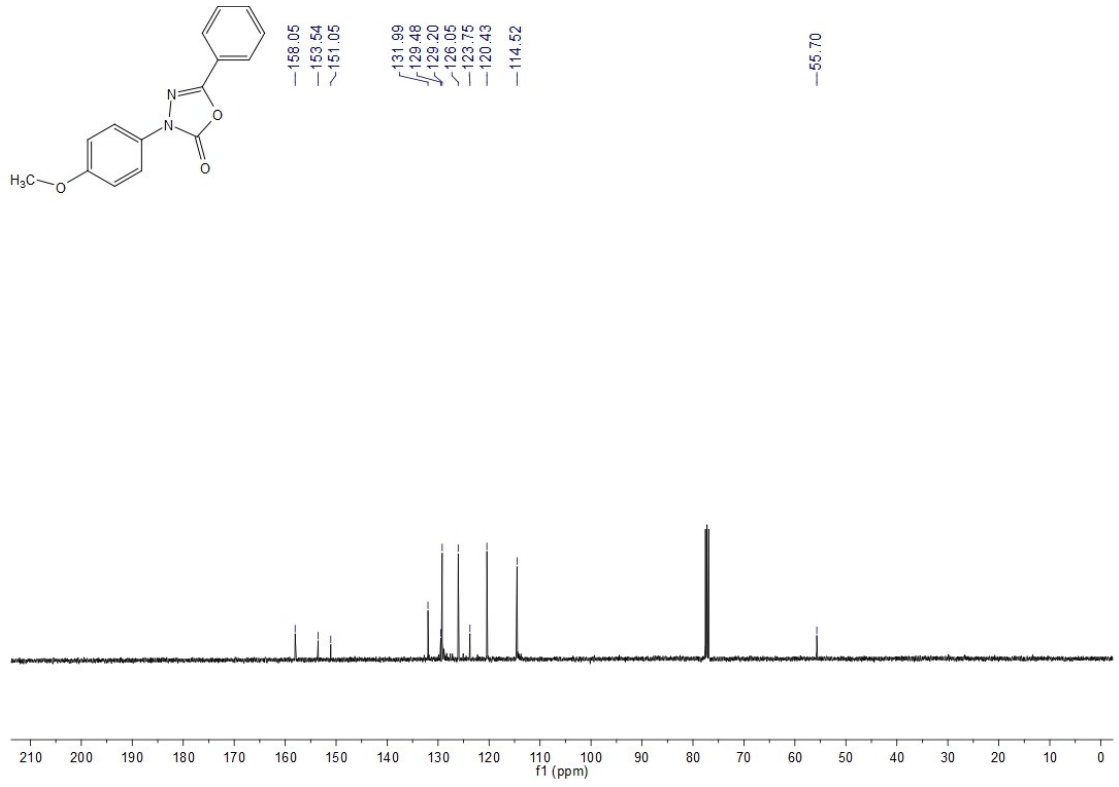

7.94
7.94
7.92
7.92
7.85
7.84
7.84
7.83
7.82
7.81
7.53
7.52
7.52
7.51
7.51
7.49
7.48
7.47
7.47
7.33
7.31
2.98
2.96
2.94
2.92
2.91
1.28
1.26
2.00
2.00
3.05
2.02
1.08
3.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.64
151.01
147.27
132.04
129.21
127.33
126.12
123.78
118.78
33.90
24.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

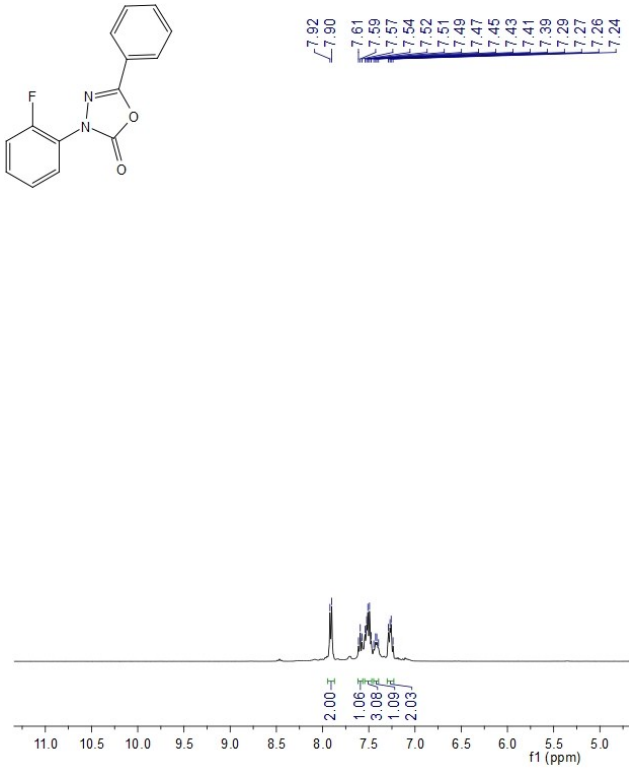
3j

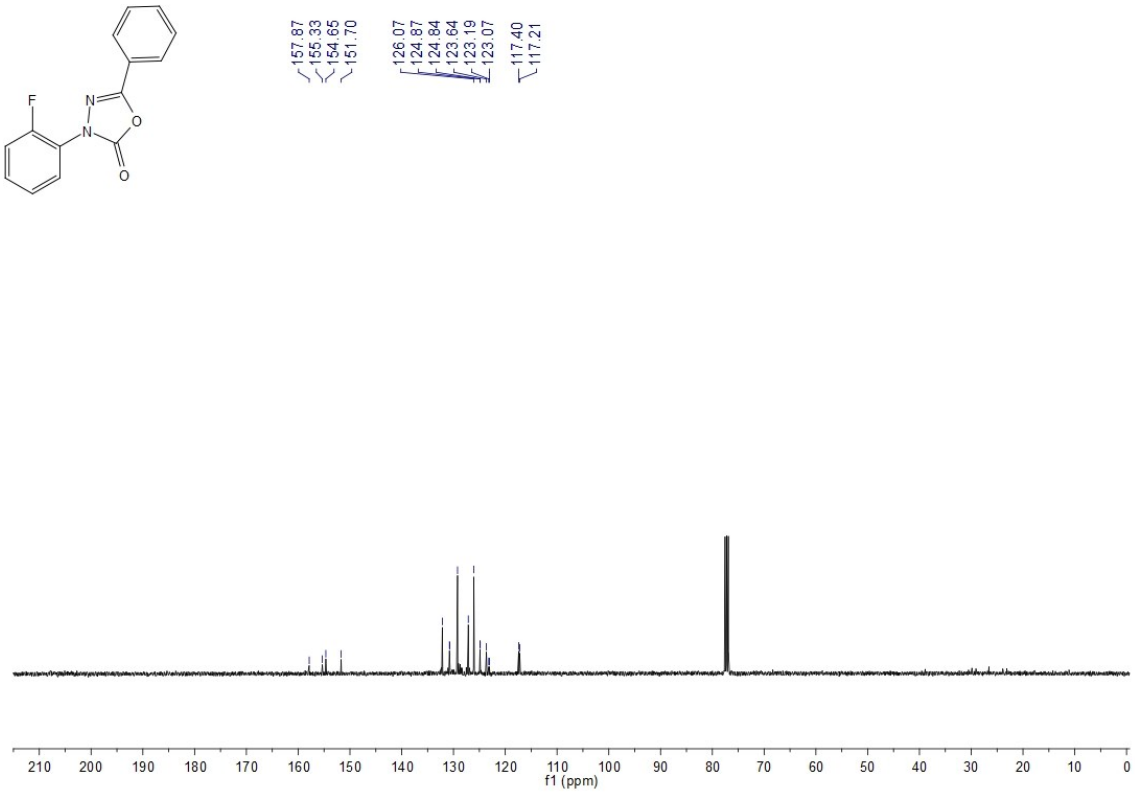

7.93
7.92
7.91
7.90
7.83
7.82
7.82
7.81
7.80
7.47
6.98
6.98
6.97
6.96
3.82


2.00
2.01
3.03
2.02
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

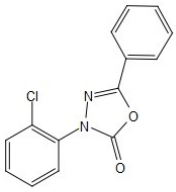

158.05
153.54
151.05
131.99
129.48
129.20
126.05
123.75
120.43
114.52
55.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

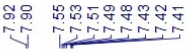
3k

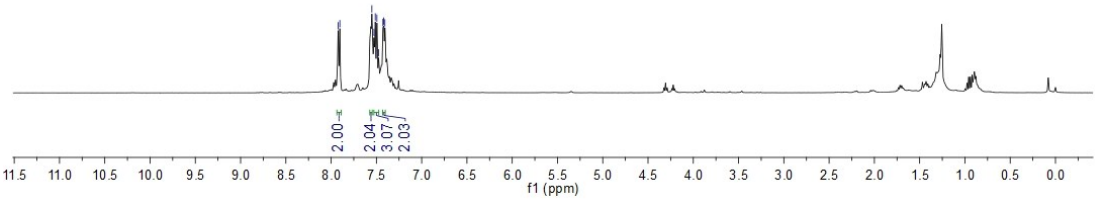

F
N
N
O
O
7.92
7.90
7.61
7.59
7.57
7.54
7.52
7.51
7.49
7.47
7.45
7.43
7.41
7.39
7.29
7.27
7.26
7.24
2.00
1.06
3.08
1.09
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

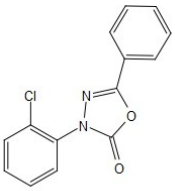

F
N
N
O
O
157.87
155.33
154.65
151.70
126.07
124.87
124.84
123.64
123.19
123.07
117.40
117.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3l

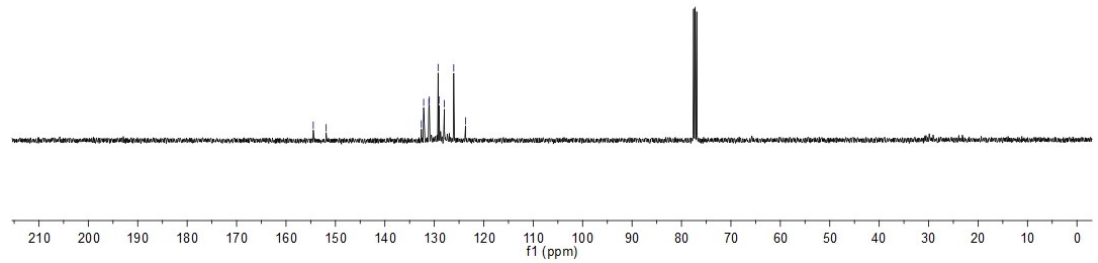

Cl
N
N
O
O


7.92
7.90
7.55
7.53
7.51
7.49
7.48
7.43
7.42
7.41

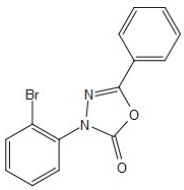

2.00
2.04
3.07
2.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
N
O
O

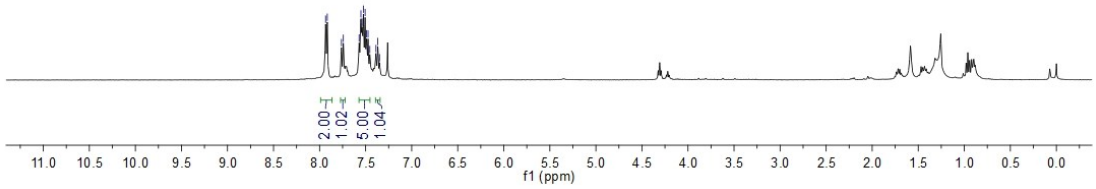

154.49
151.88
132.62
132.16
132.12
131.11
131.01
129.24
129.05
127.97
126.07
123.68

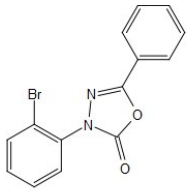

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

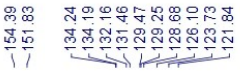
3m

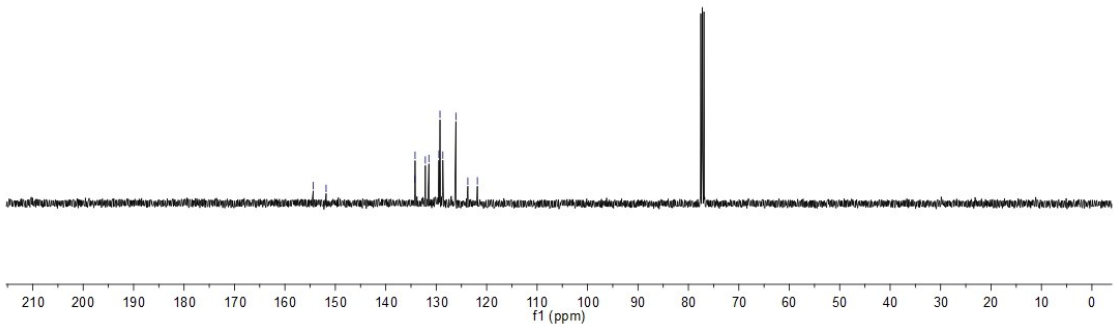

Br
N
N
O
O


7.93
7.92
7.76
7.74
7.57
7.55
7.54
7.52
7.51
7.49
7.47
7.45
7.39
7.37
7.35

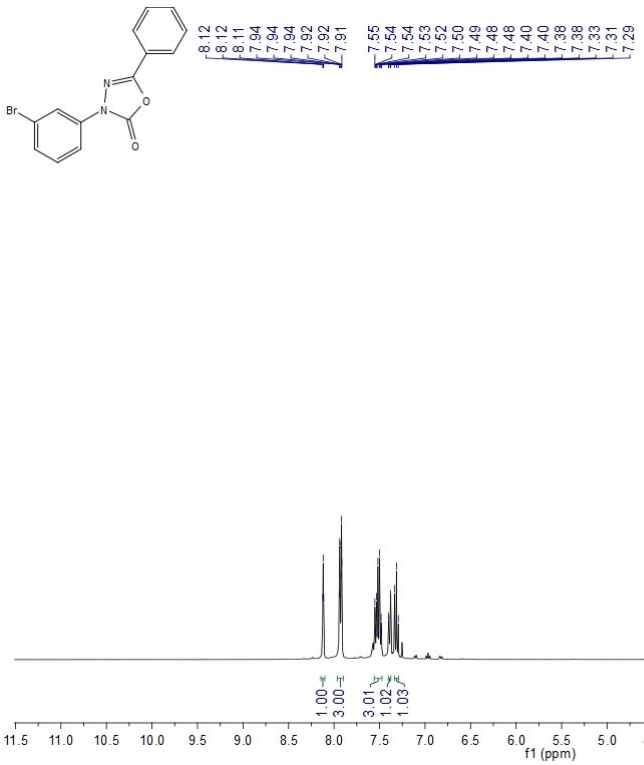

2.00
1.02
5.00
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

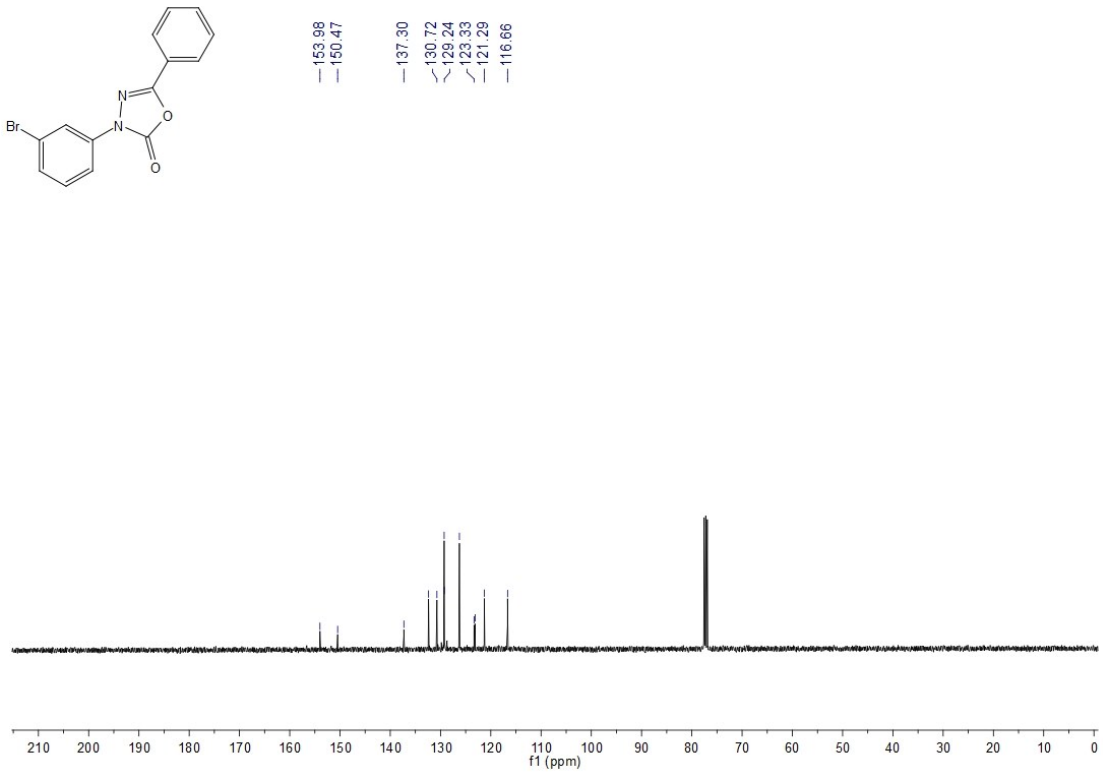

Br
N
N
O
O


154.39
151.83
134.24
134.19
132.16
131.46
129.47
129.25
128.68
126.10
123.73
121.84

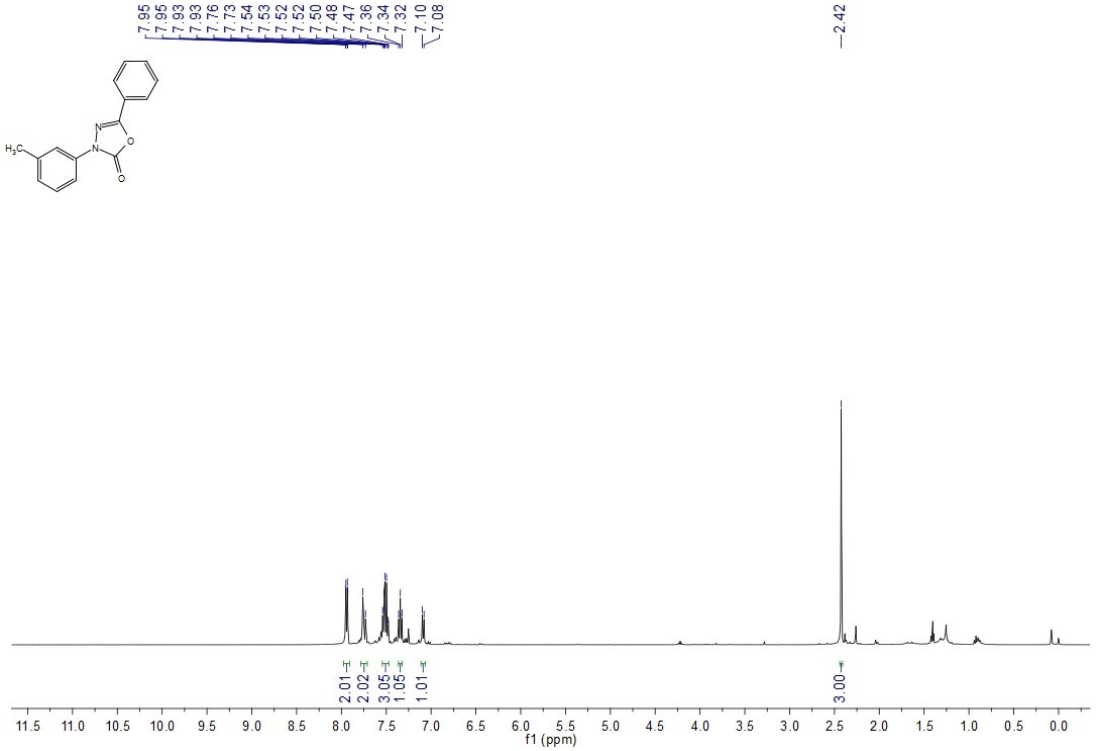

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

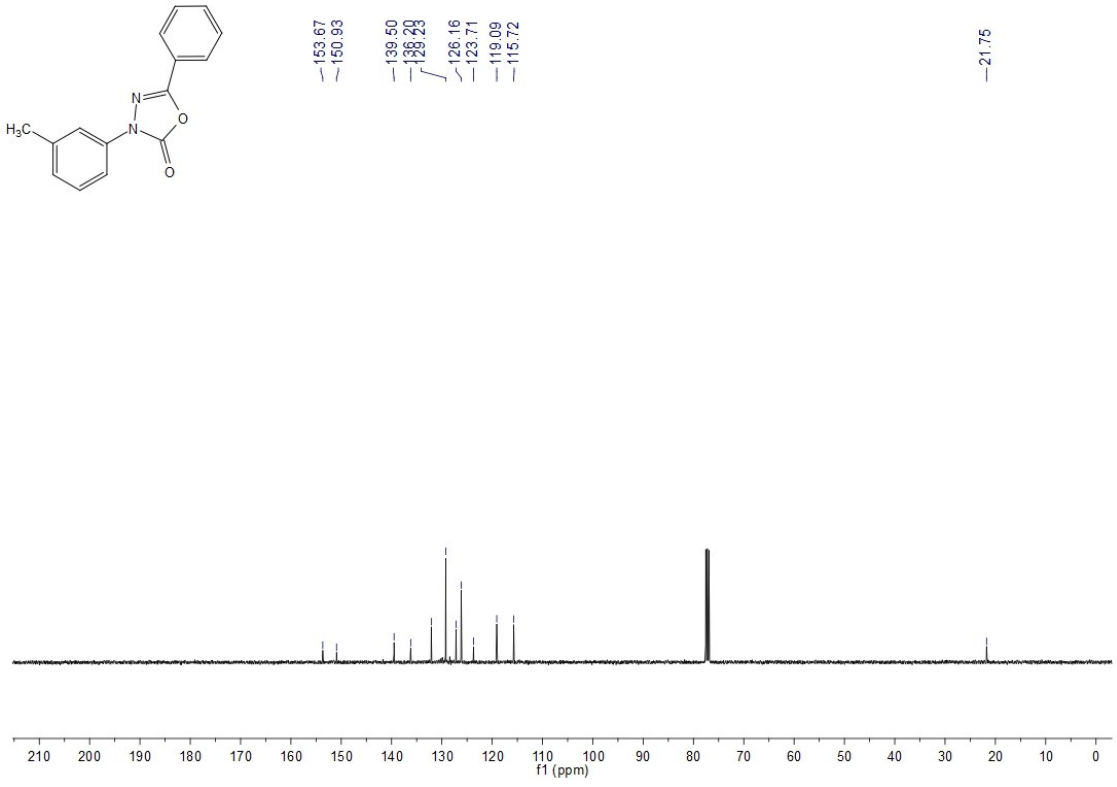
3n


Br
N
O
O
8.12
8.12
8.11
7.94
7.94
7.94
7.92
7.92
7.91
7.55
7.54
7.54
7.53
7.52
7.50
7.49
7.48
7.48
7.40
7.40
7.38
7.38
7.33
7.31
7.29
1.00
3.00
3.01
1.02
1.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

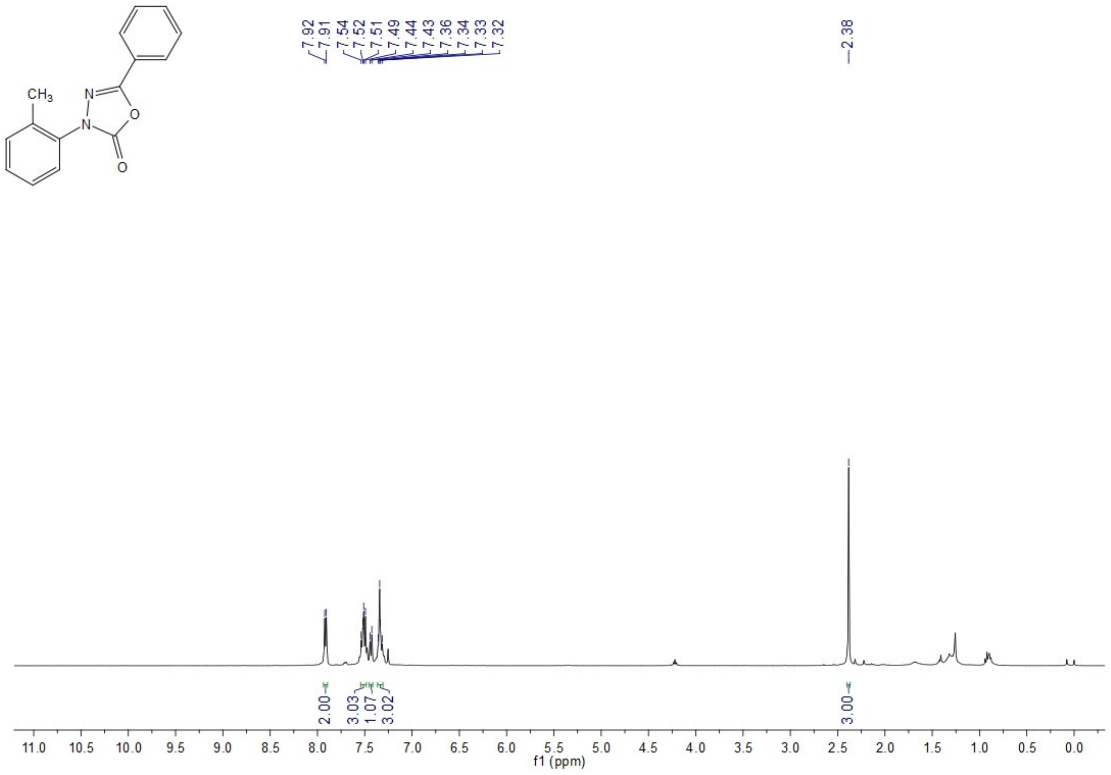

Br
N
O
O
153.98
150.47
137.30
130.72
129.24
123.33
121.29
116.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

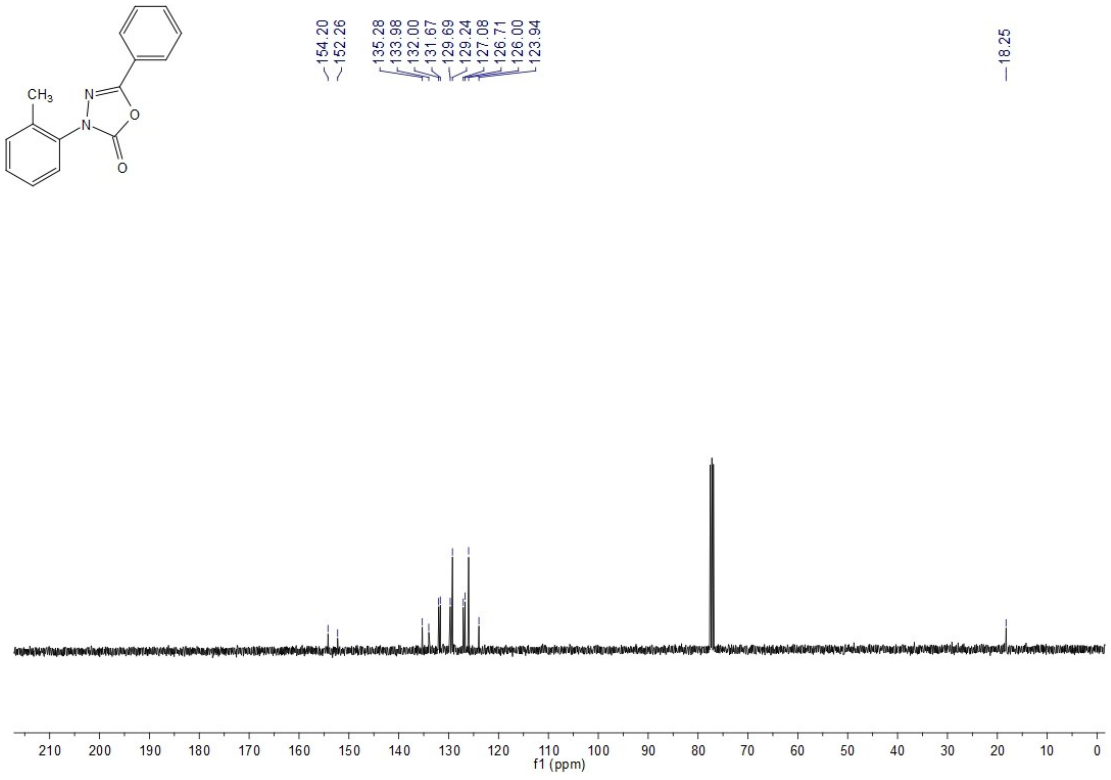
3o


7.95
7.95
7.93
7.93
7.76
7.73
7.54
7.53
7.52
7.52
7.50
7.48
7.47
7.36
7.34
7.32
7.10
7.08
2.42
2.01
2.02
3.05
1.05
1.01
3.00
f1 (ppm)

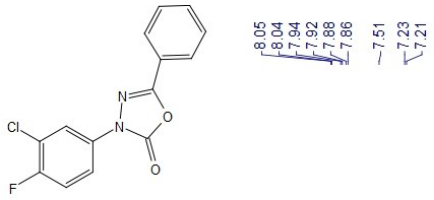

153.67
150.93
139.50
138.20
129.23
126.16
123.71
119.09
115.72
21.75
f1 (ppm)

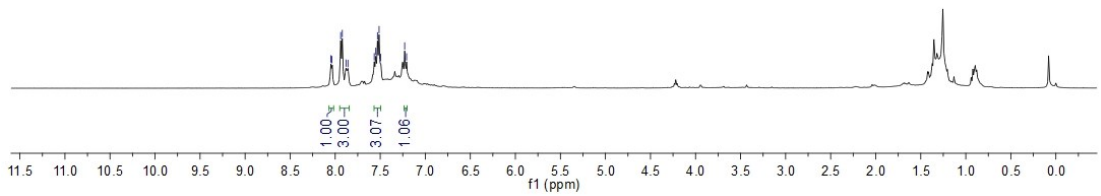
3p

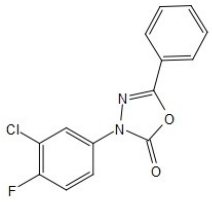

7.92
7.91
7.54
7.52
7.51
7.49
7.44
7.43
7.36
7.34
7.33
7.32
2.38
2.00
3.03
1.07
3.02
3.00
f1 (ppm)

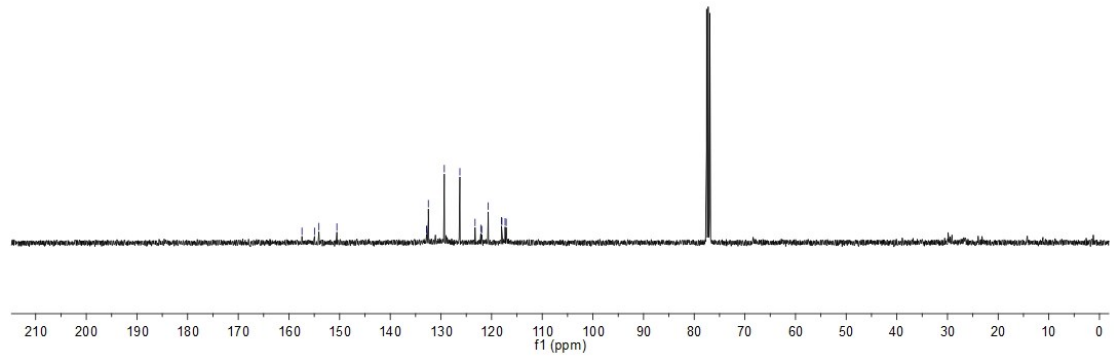

154.20
152.26
135.28
133.98
132.00
131.67
129.69
129.24
127.08
126.71
126.00
123.94
18.25
f1 (ppm)

3q

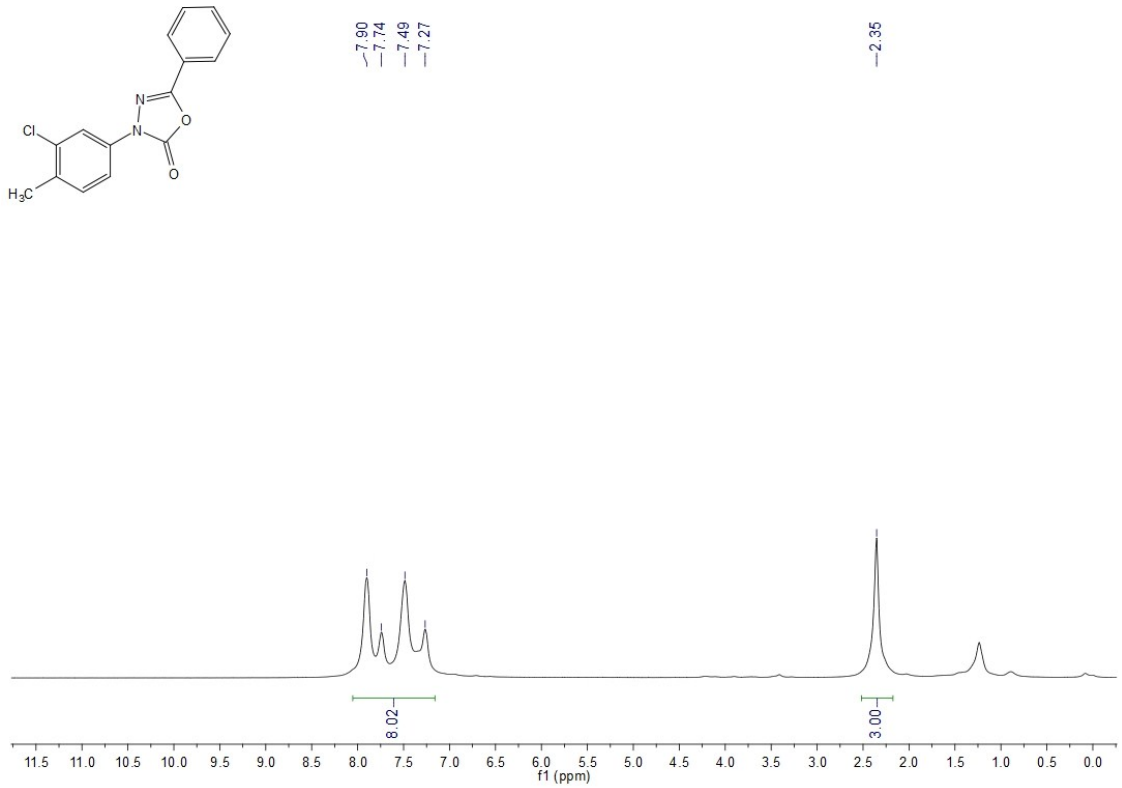

8.05
8.04
7.94
7.92
7.88
7.86
7.51
7.23
7.21
Cl
F
N
O
O

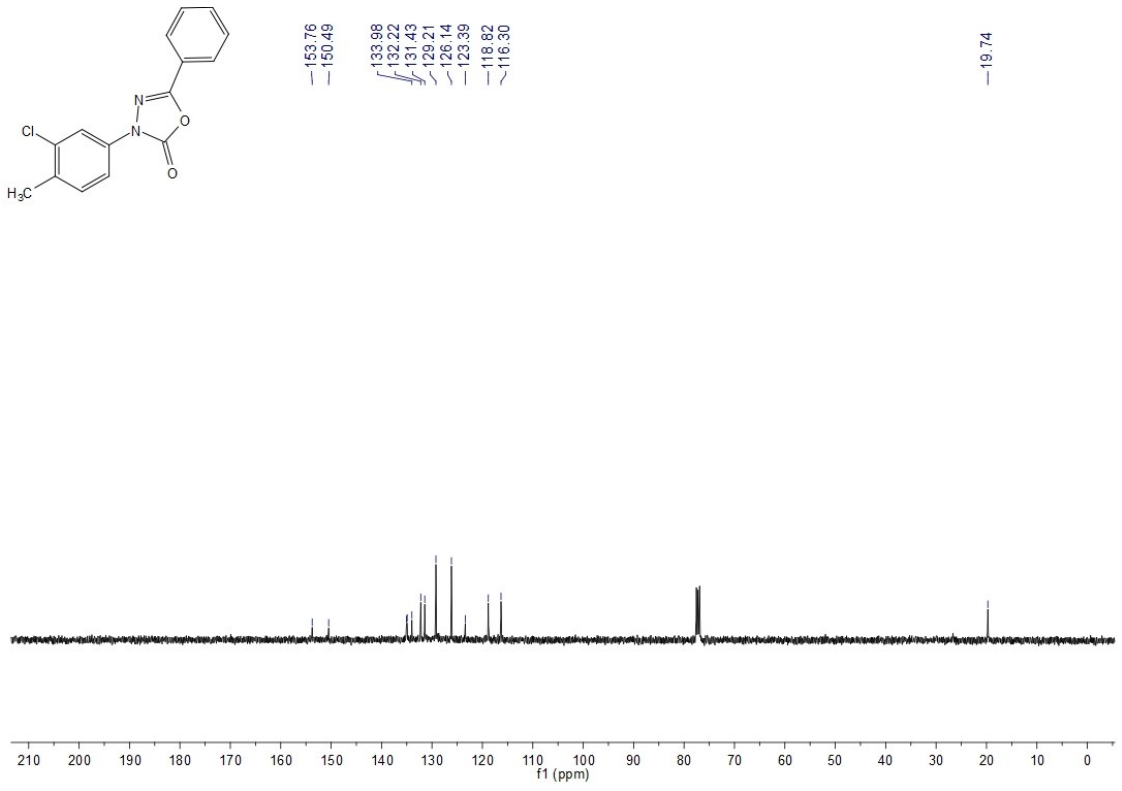

1.00
3.00
3.07
1.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.43
154.95
154.08
150.54
132.82
132.79
132.48
129.33
126.25
123.25
122.13
121.94
120.66
118.03
117.96
117.33
117.11
Cl
F
N
O
O

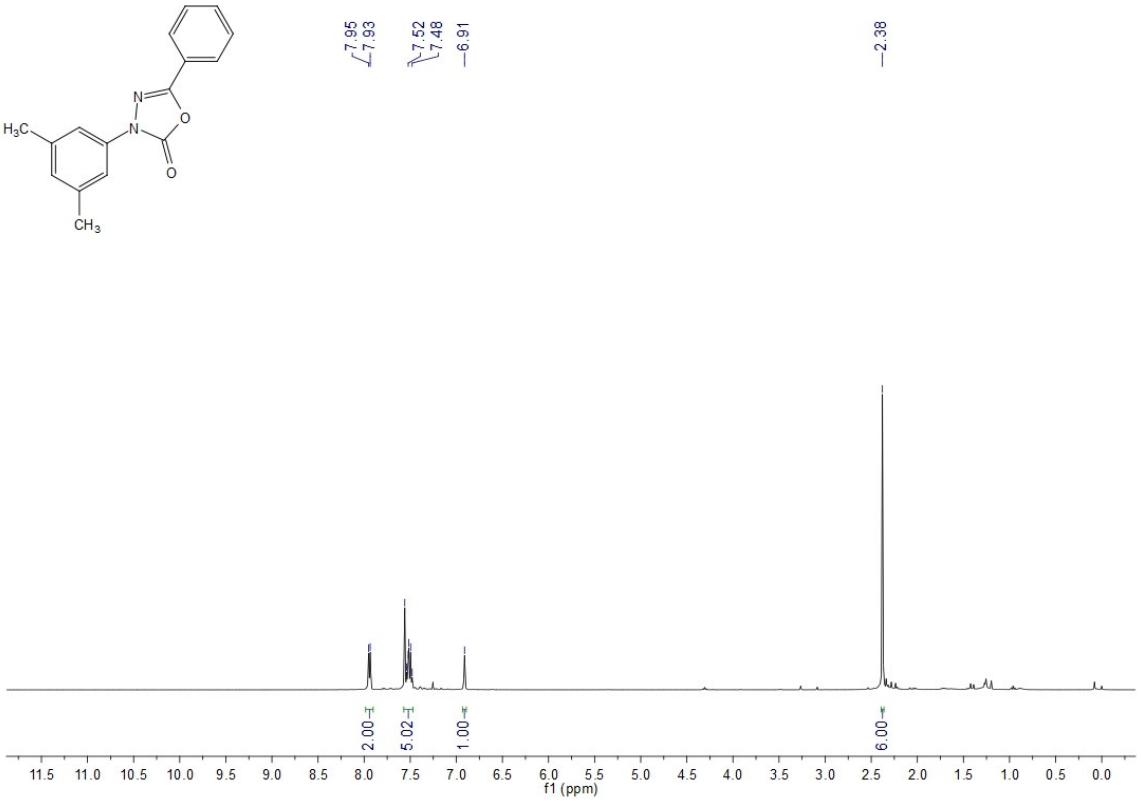

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

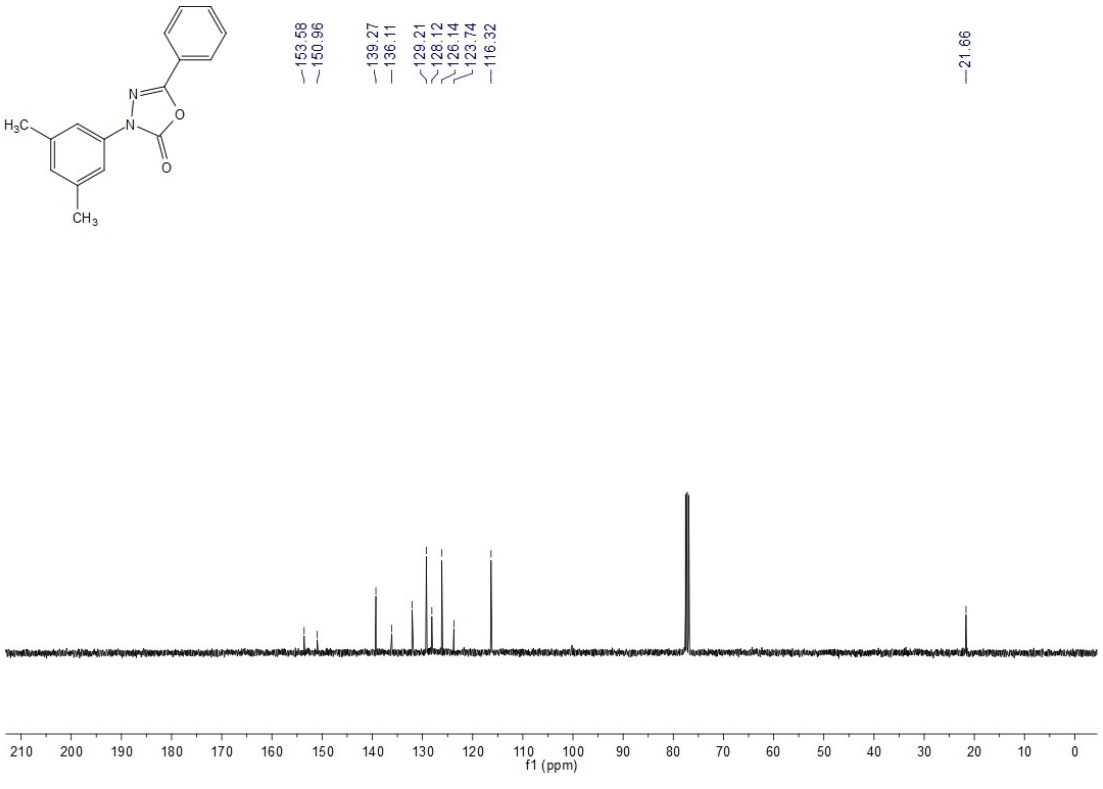
3r


7.90
7.74
7.49
7.27
2.35
Cl
N
N
O
O
H3C
8.02
3.00
f1 (ppm)

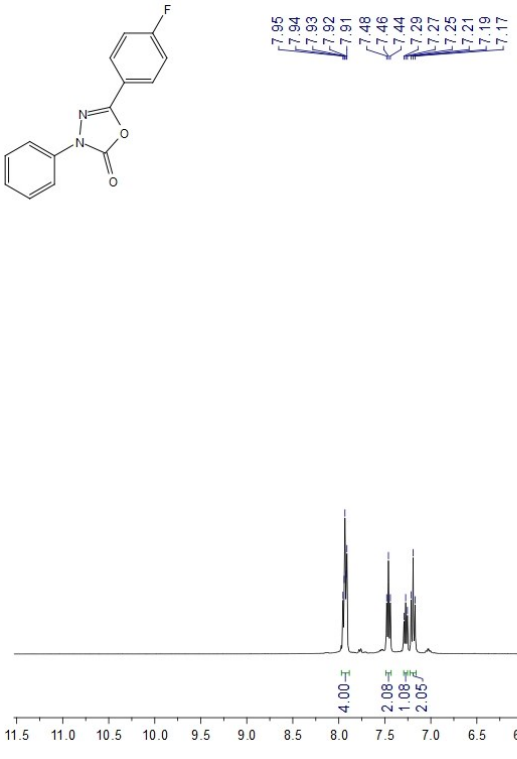

153.76
150.49
133.98
132.22
131.43
129.21
126.14
123.39
118.82
116.30
19.74
Cl
N
N
O
O
H3C
f1 (ppm)

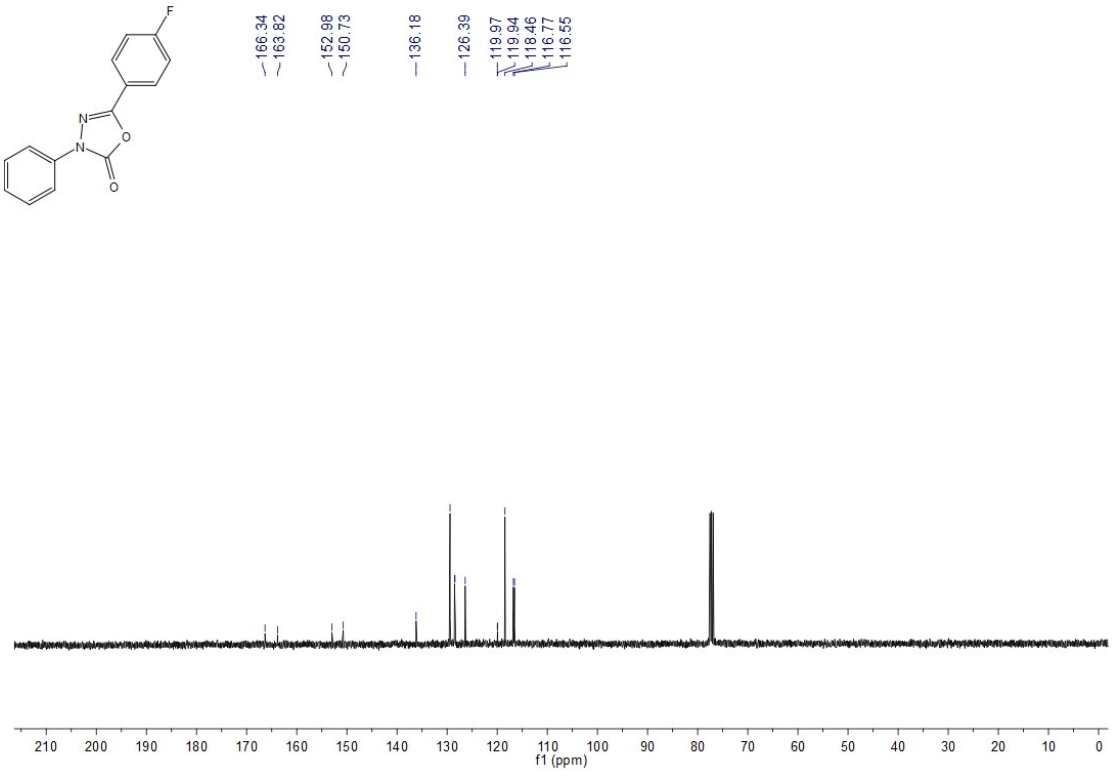
3s


7.95
7.93
7.52
7.48
6.91
2.38
2.00
5.02
1.00
6.00
f1 (ppm)

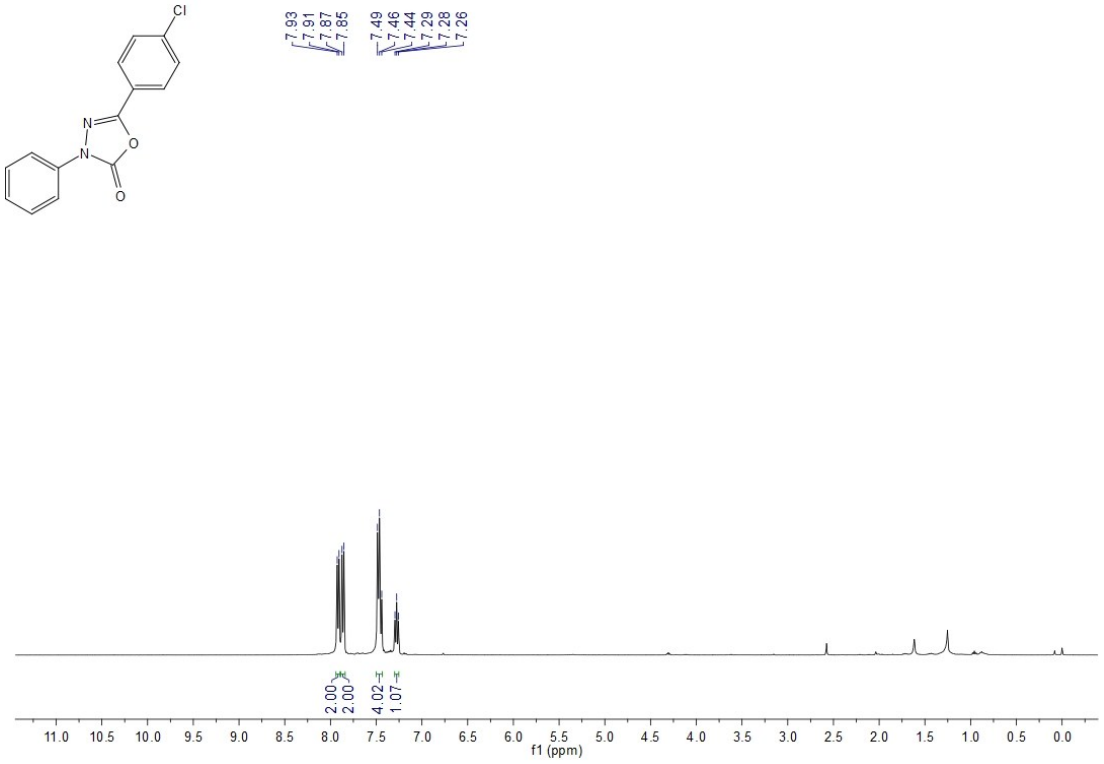

153.58
150.96
139.27
136.11
129.21
128.12
126.14
123.74
116.32
21.66
f1 (ppm)

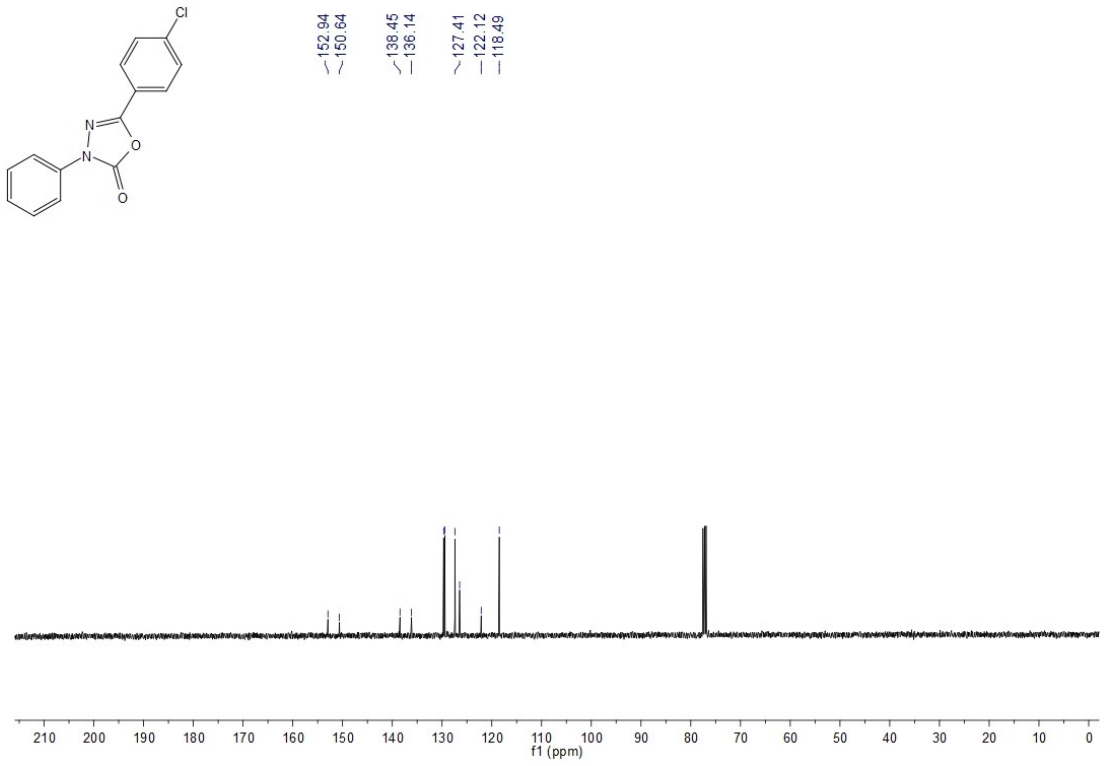
4a


F
N
N
O
O
7.95
7.94
7.93
7.92
7.91
7.48
7.46
7.44
7.29
7.27
7.25
7.21
7.19
7.17
4.00
2.08
1.08
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

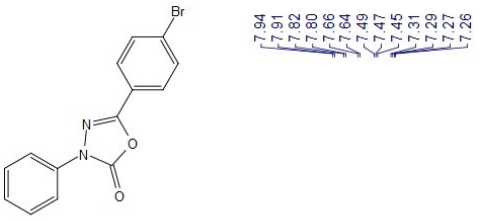

F
N
N
O
O
166.34
163.82
152.98
150.73
136.18
126.39
119.97
119.94
118.46
116.77
116.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

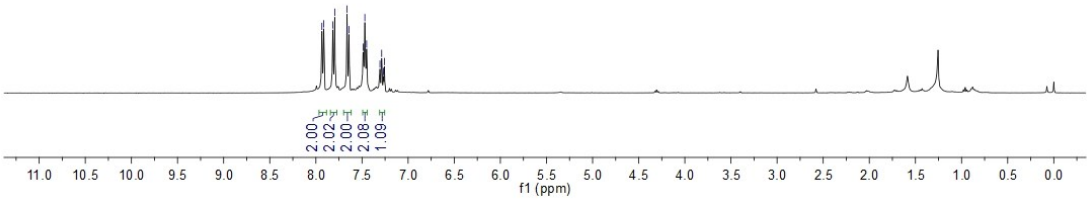
4b

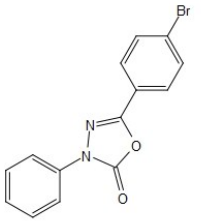

Cl
N
N
O
O
7.93
7.91
7.87
7.85
7.49
7.46
7.44
7.29
7.28
7.26
2.00
2.00
4.02
1.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
N
O
O
152.94
150.64
138.45
136.14
127.41
122.12
118.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

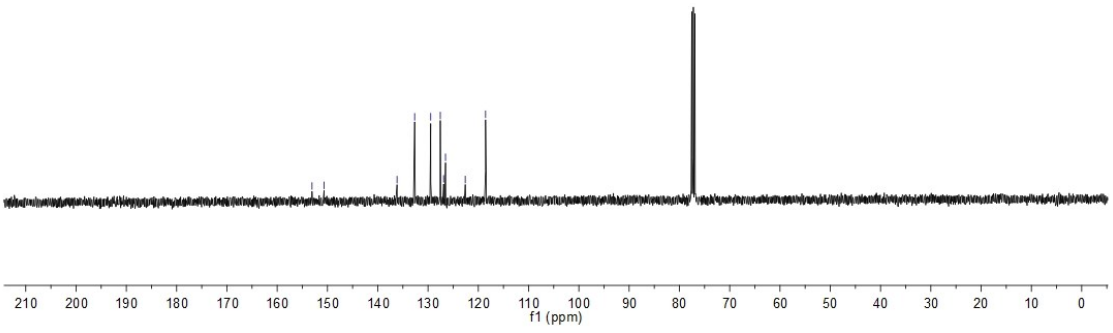
4c


Br
N
N
O
O
7.94
7.91
7.82
7.80
7.66
7.64
7.49
7.47
7.45
7.31
7.29
7.27
7.26

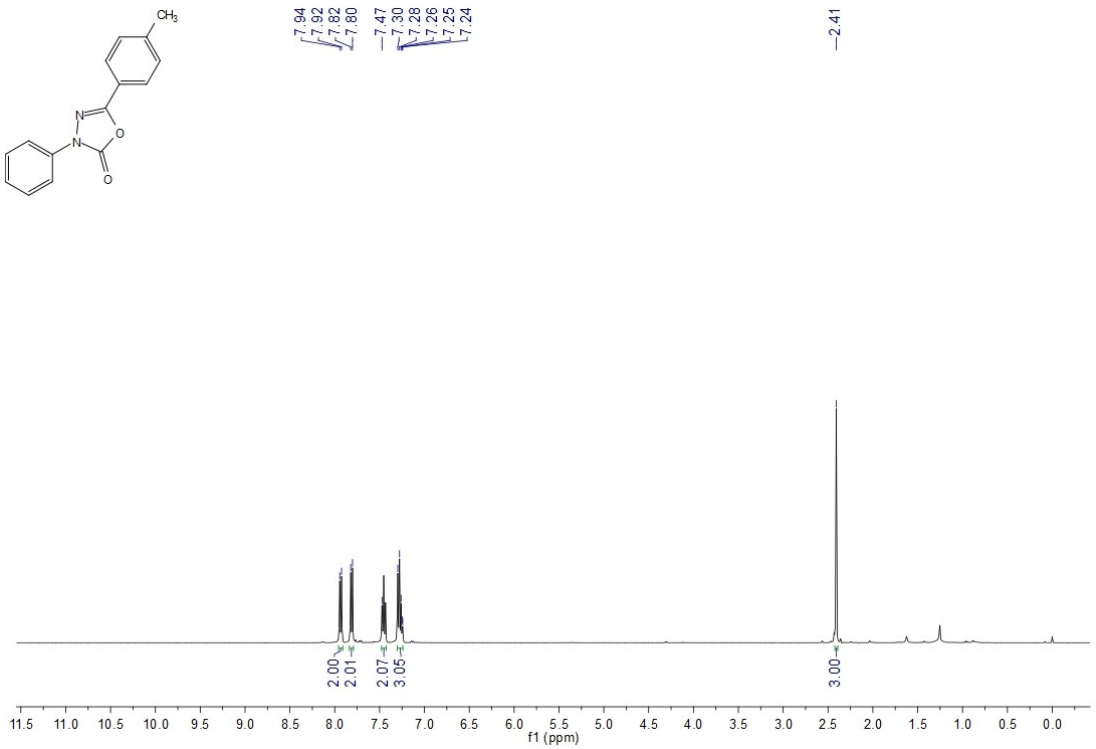

2.00
2.02
2.00
2.08
1.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

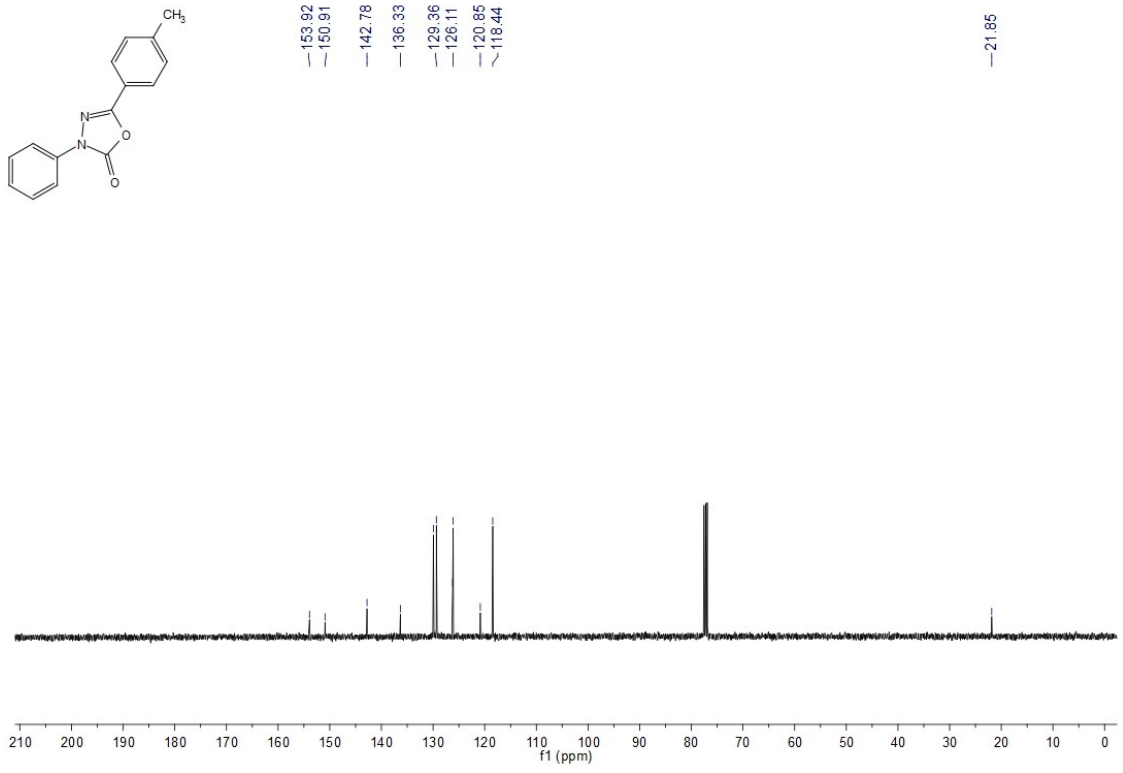

Br
N
N
O
O


153.07
150.67
136.16
127.56
126.52
122.60
118.55

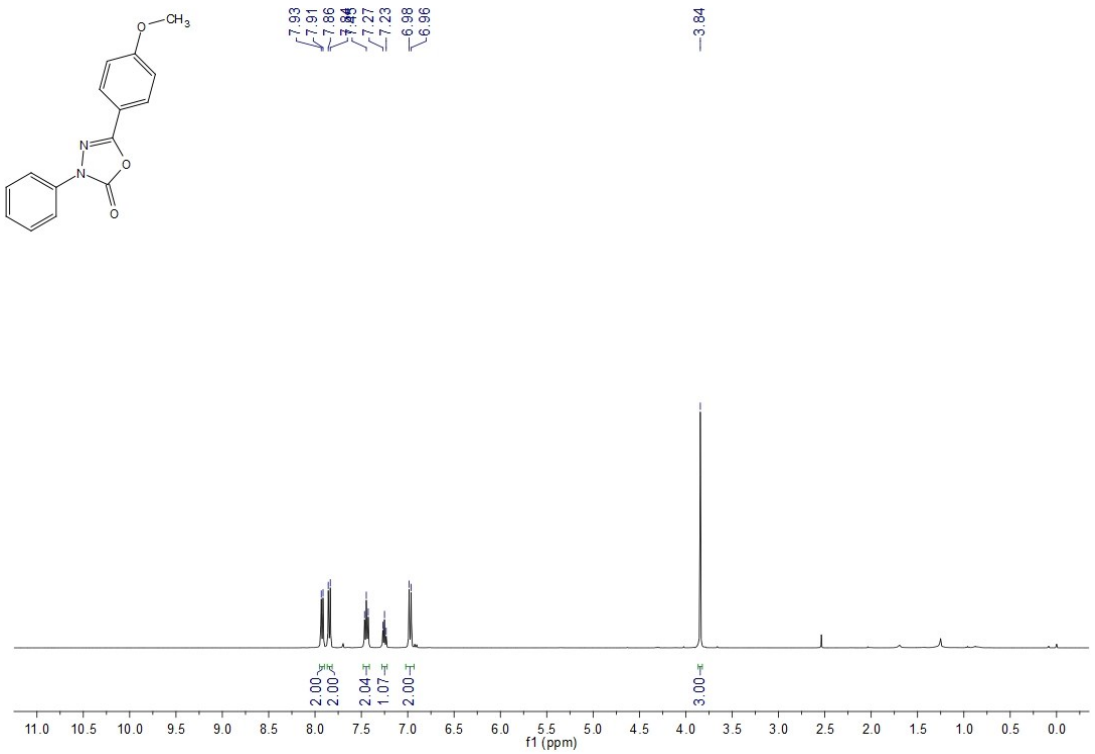

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

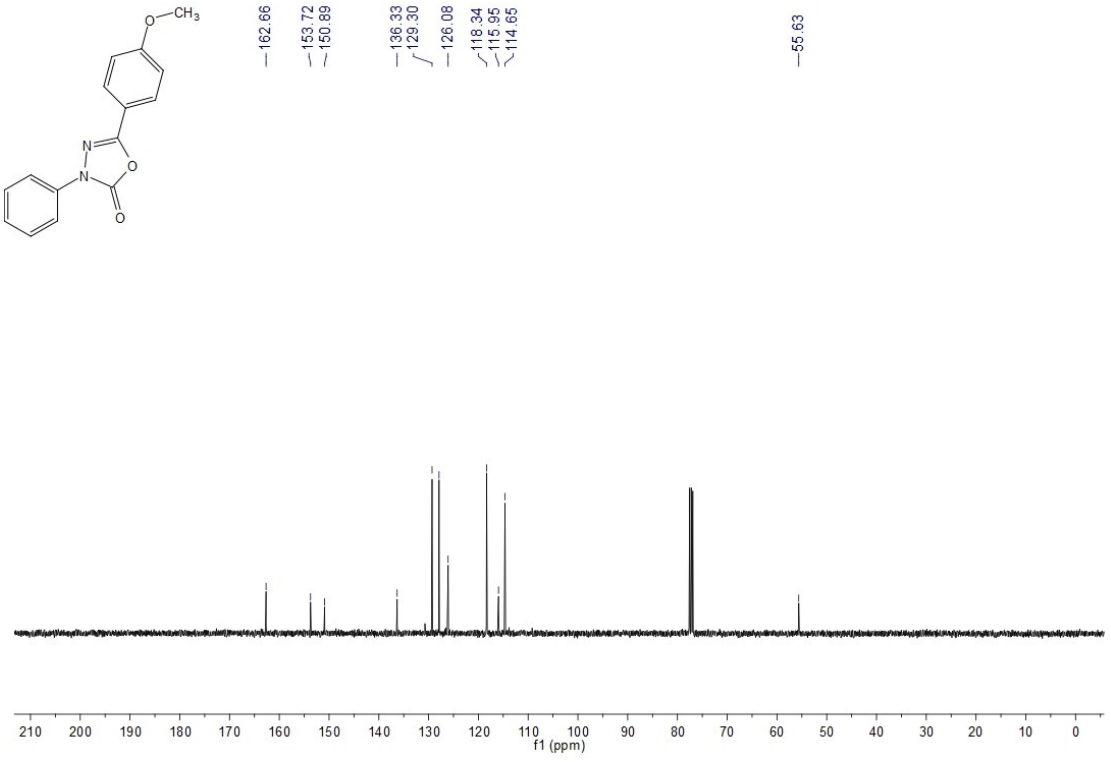
4d


CH3
N
N
O
O
7.94
7.92
7.82
7.80
7.47
7.30
7.28
7.26
7.25
7.24
2.41
2.00
2.01
2.07
3.05
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

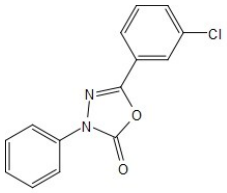

CH3
N
N
O
O
153.92
150.91
142.78
136.33
129.36
126.11
120.85
118.44
21.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4e

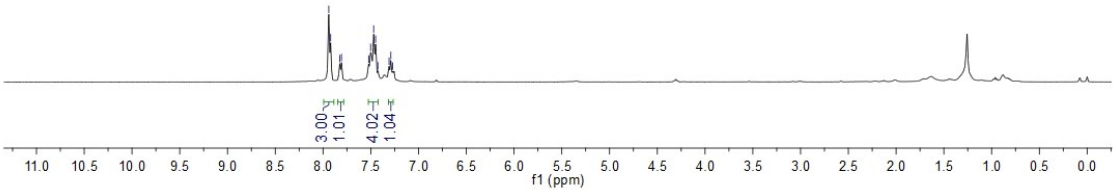

7.93
7.91
7.86
7.27
7.23
6.98
6.96
3.84
2.00
2.00
2.04
1.07
2.00
3.00
f1 (ppm)

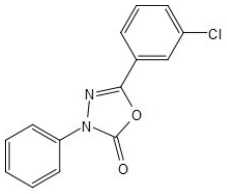

162.66
153.72
150.89
136.33
129.30
126.08
118.34
115.95
114.65
55.63
f1 (ppm)

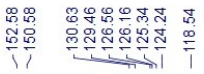
4f

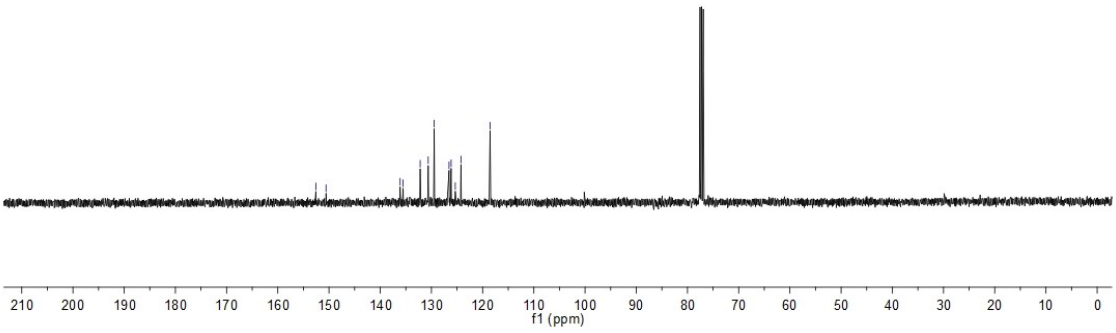

Cl
N
N
O
O

7.94
7.92
7.83
7.81
7.52
7.50
7.47
7.45
7.43
7.31
7.29
7.27

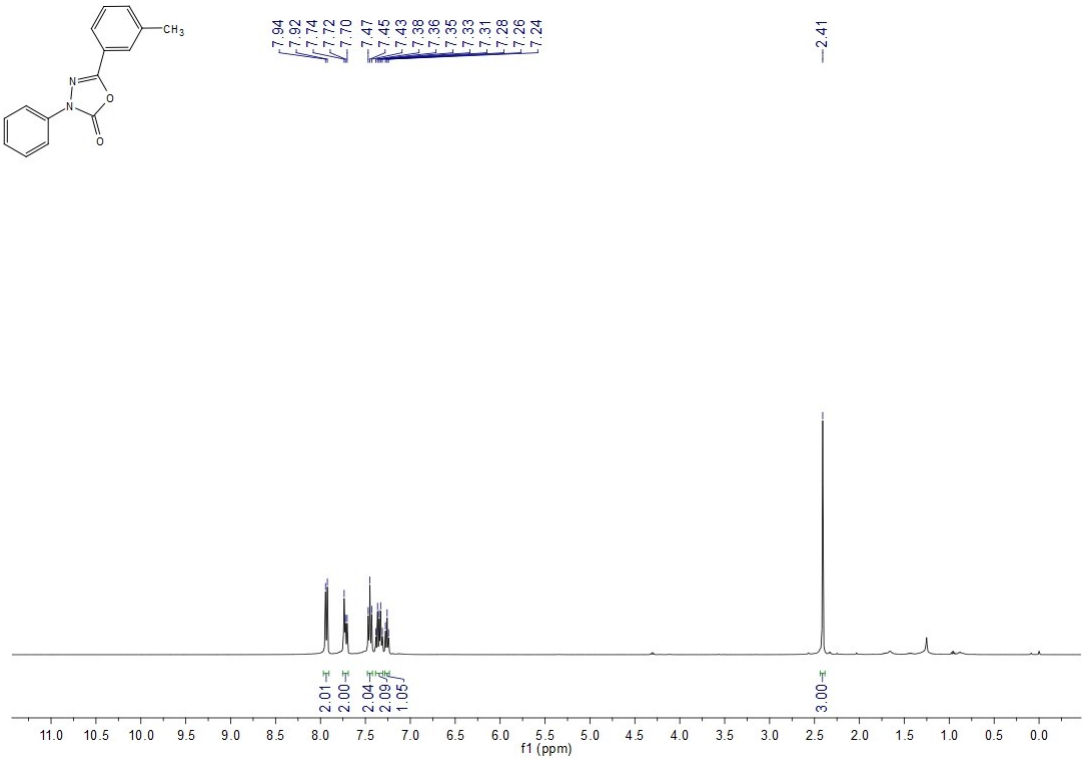

3.00
1.01
4.02
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

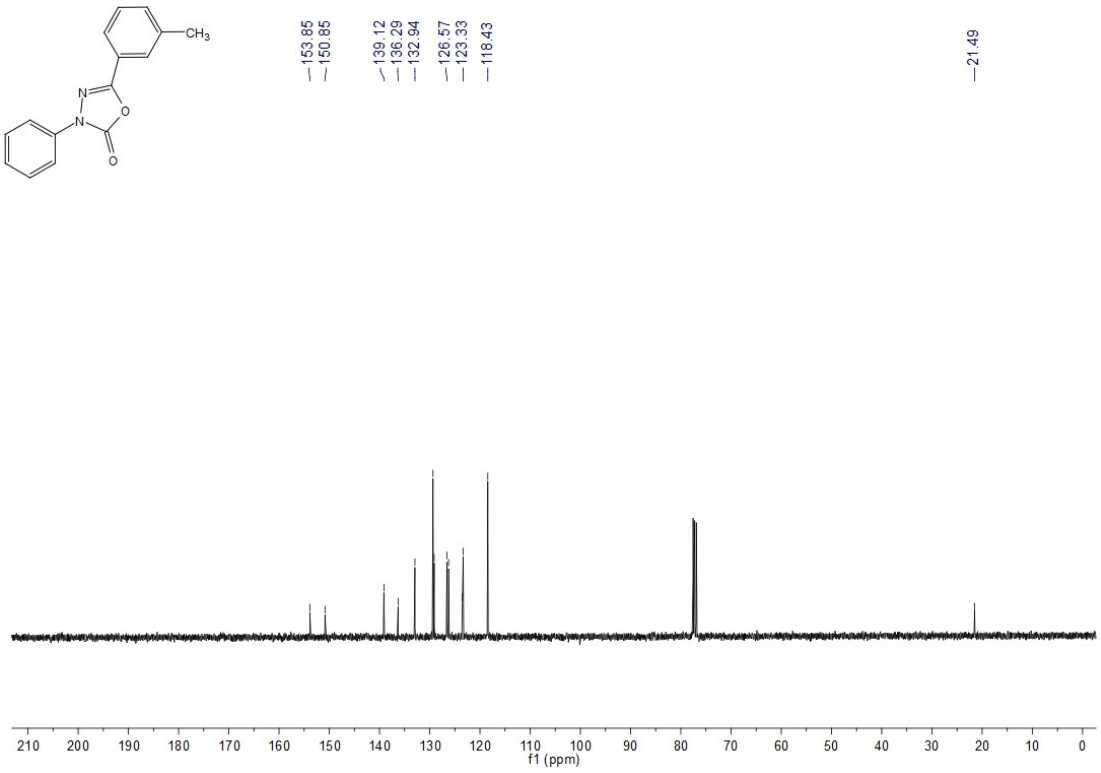

Cl
N
N
O
O


152.58
150.58
130.63
129.46
126.56
126.16
125.34
124.24
118.54

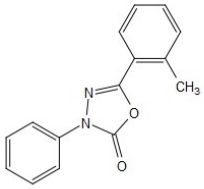

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4g

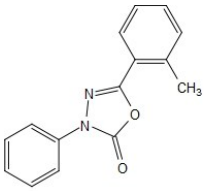

CH3
N
O
O
7.94
7.92
7.74
7.72
7.70
7.47
7.45
7.43
7.38
7.36
7.35
7.33
7.31
7.28
7.26
7.24
2.41
2.01
2.00
2.04
2.09
1.05
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CH3
N
O
O
153.85
150.85
139.12
136.29
132.94
126.57
123.33
118.43
21.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4h

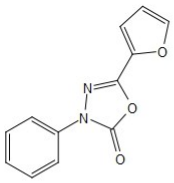

CH3
N
N
O
O

7.96
7.94
7.87
7.85
7.48
7.46
7.44
7.43
7.41
7.39
7.34
7.32
7.29
7.27
7.25
2.69
2.00
1.01
3.06
3.02
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

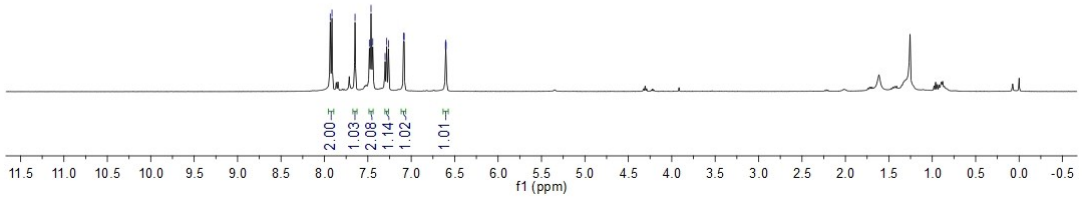

CH3
N
N
O
O

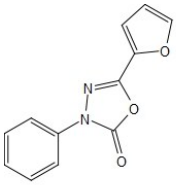
154.08
150.61
138.32
136.36
129.40
126.24
122.34
118.37
22.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4i

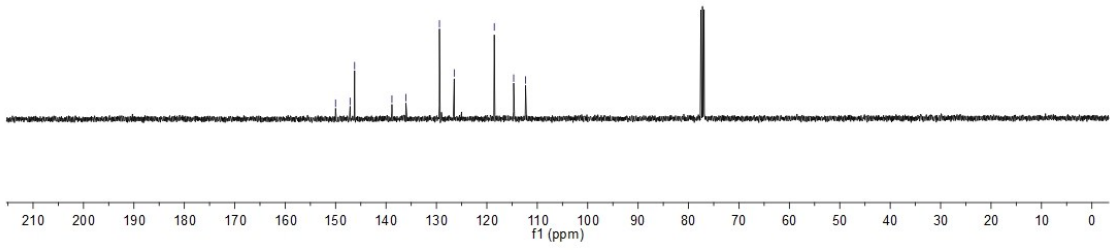



7.93
7.91
7.46
7.28
7.08
6.61
6.60
6.60

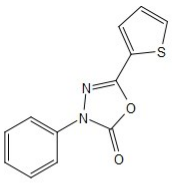

2.00
1.03
2.08
1.14
1.02
1.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

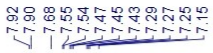


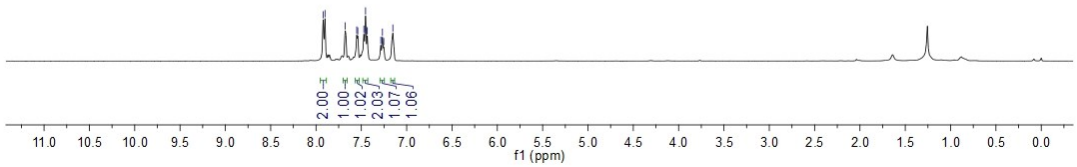

150.01
147.13
146.23
138.83
136.05
129.40
126.48
118.53
114.68
112.31

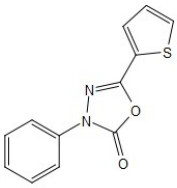

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

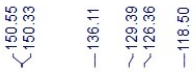
4j

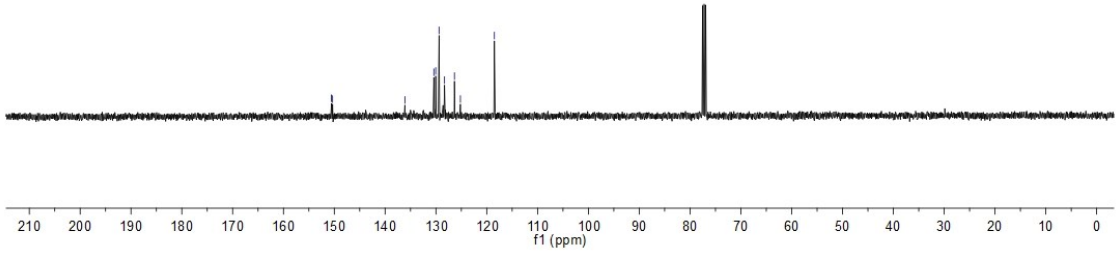

S
N
N
O
O


7.92
7.90
7.68
7.55
7.54
7.47
7.45
7.43
7.29
7.27
7.25
7.15

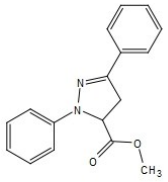

2.00
1.00
1.02
2.03
1.07
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


S
N
N
O
O

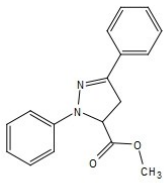

150.55
150.33
136.11
129.39
126.36
118.50


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5a



7.68
7.66
7.34
7.08
6.87
6.85
6.83
4.77
4.75
4.74
4.72
3.69
2.02
5.02
2.07
1.03
1.01
3.00
1.03
1.01
f1 (ppm)



172.06
147.08
144.69
129.30
129.02
128.67
125.95
119.85
113.02
61.72
52.82
38.25
f1 (ppm)