Supporting Information

DMSO as a Dual Carbon Synthon and Water as Oxygen Donor for the Construction of 1,3,5-Oxadiazines from Amidines

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General methods. *N*-Phenyl amidines (**1**) were prepared according to the previously reported literature.[1] Their analysis data were identical with the reported data. Other starting materials, reagents and solvents were purchased commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively. High-resolution mass spectra (HRMS) were performed with a Q-TOF-Premier mass spectrometer. HPLC analyses were carried out on an Agilent 1260 Infinity II instrument. Melting points were determined using a X-4 digital micro melting point apparatus. Diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å). All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F_{254}).

General Produce for the synthesis of 3,4-diaryl-3,6-dihydro-2H-1,3,5-oxadiazine (2). The reaction was carried out with **1** (1 mmol), $Cu(OTf)_2$ (10 mmol%), DMSO (2 mL), H_2O (one drop), Selectfluor (2 equiv.) at 110 ºC in an oil bath for 26 h. After being cooled to room temperature, the reaction was extracted with CH_2Cl_2. The combine organic layer was washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to afford the desired product (**2**).

3,4-Diphenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2a*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (152.3 mg, 64%), mp 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.32 – 7.14 (m, 5H), 7.03 (t, *J*=7.4 Hz, 1H), 6.88 (d, *J*=7.2 Hz, 2H), 5.39 (s, 2H), 5.13 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 145.6, 135.6, 129.9, 129.1, 128.7, 128.1, 125.0, 124.9, 80.9, 80.4.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}N_2O$ 239.1179; Found 239.1180.

3-(4-Fluorophenyl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2b*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (125.4 mg, 49%), mp 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.18 (m, 3H), 6.89-6.85 (m, 4H), 5.38 (s, 2H), 5.07 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 243 Hz), 155.3, 141.9 (d, *J* = 2.9 Hz), 135.4, 130.0, 128.7, 128.18, 126.6 (d, *J* = 8.4 Hz), 116.0 (d, *J* = 22.5 Hz).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}FN_2O$ 257.1090; Found 257.1083.

3-(4-Methoxyphenyl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2c*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (168.8 mg, 63%), mp 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.17 (m, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 5.37 (s, 2H), 5.05 (s, 2H), 3.71 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 155.6, 138.9, 135.7, 129.8, 128.7, 128.0, 126.5, 114.4, 81.2, 80.4, 55.4.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_2$ 269.1285; Found 269.1292.

4-Phenyl-3-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2d*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (156.2 mg, 62%), mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.32-7.19 (m, 3H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.38 (s, 2H), 5.11 (s, 2H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 145.6, 139.0, 135.6, 129.8, 128.8, 128.6, 128.1, 125.7, 125.5, 122.2, 80.9, 80.4, 21.3.
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O$ 253.1335; Found 253.1337.

3-(3-Chlorophenyl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2e*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oli (127.8 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 1H), 5.38 (s, 2H), 5.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 146.9, 135.1, 134.6, 130.2, 129.9, 128.5, 128.3, 124.9, 124.7, 123.7, 80.7, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}ClN_2O$ 273.0795; Found 273.0791.

3-(2-Bromophenyl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2f*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (139.0 mg, 44%), mp 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (d, *J* = 6.6 Hz, 2H), 7.28-7.20 (m, 3H), 7.03 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 (td, *J* = 7.7, 1.8 Hz, 1H), 6.85 (dd, *J* = 7.6, 1.8 Hz, 1H), 5.49 – 5.27 (m, 2H), 5.17 (d, *J* = 9.6 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 144.0, 135.3, 133.5, 130.1, 129.3, 128.3, 128.2, 128.0, 127.5, 120.8, 80.6, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}BrN_2O$ 317.0290; Found 317.0281.

3-([1,1'-Biphenyl]-2-yl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2g*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (204.1 mg, 65%), mp 117-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 7H), 7.27 – 7.21 (m, 2H), 7.19 – 7.11 (m, 4H), 6.93 – 6.87 (m, 1H), 5.35-5.20 (m, 2H), 4.87-4.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 142.7, 139.2, 136.5, 135.5, 131.6, 129.6, 129.2, 128.6, 128.5, 128.1, 127.8, 127.4, 127.3, 125.9, 80.6, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O$ 315.1492; Found 315.1489.

3-(4'-Methyl-[1,1'-biphenyl]-2-yl)-4-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2h*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (203.4 mg, 62%), mp 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 4H), 7.29-7.07 (m, 9H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.35-5.20 (m, 2H), 4.84-4.72 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 142.7, 137.1, 136.5, 136.3, 135.6, 131.5, 129.6, 129.2, 129.1, 129.0, 128.6, 127.8, 127.3, 125.9, 80.6, 80.4, 21.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O$ 329.1648; Found 329.1656.

4-(4-Methoxyphenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2i*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (171.5 mg, 64%), mp 85-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 5.37 (s, 2H), 5.10 (s, 2H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 146.0, 130.2, 129.1, 127.9, 124.9, 113.4, 80.9, 80.4, 55.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_2$ 269.1285; Found 269.1280.

4-(4-Ethylphenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2j*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (154.3 mg, 58%), mp 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 5.38 (s, 2H), 5.11 (s, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 146.2, 145.9, 132.9, 129.0, 128.6, 127.6, 124.3, 124.6, 80.9, 80.4, 28.6, 15.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O$ 267.1492; Found 267.1488.

4-(4-Fluorophenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2k*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (133.1 mg, 52%), mp 71-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.81 (m, 4H), 5.37 (s, 2H), 5.11 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (d, *J* = 248 Hz), 154.4, 145.6, 131.7 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 8.5 Hz), 129.2, 125.0, 125.0, 115.2 (d, *J* = 21.7 Hz), 80.9, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}FN_2O$ 257.1085; Found 257.1080.

3-Phenyl-4-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2l*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (137.7 mg, 45%), mp 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 2H), 5.39 (s, 2H), 5.12 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 145.2, 139.0, 131.6 (q, *J* = 32.6 Hz), 129.6, 128.9, 125.2, 125.09 (q, *J* = 3.8 Hz), 124.9, 123.8 (q, *J* = 271 Hz), 80.9, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}F_3N_2O$ 307.1053; Found 307.1058.

3-Phenyl-4-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2m*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (153.7 mg, 61%), mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.23 (d, *J* = 6.7 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.11 – 7.00 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 2H), 5.38 (s, 2H), 5.12 (s, 2H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 145.8, 137.9, 135.5, 130.7, 129.2, 129.1, 127.9, 125.8, 124.9, 124.7, 80.9, 80.4, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O$ 253.1335; Found 253.1333.

4-(3-Fluorophenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2n*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (140.8 mg, 55%), mp 71-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.20 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.37 (s, 2H), 5.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 244 Hz), 154.3, 145.4, 137.9, 129.6 (d, *J* = 8.1 Hz), 129.3, 125.1, 124.9, 124.3 (d, *J* = 2.9 Hz), 117.0 (d, *J* = 21.1 Hz), 115.6 (d, *J* = 22.9 Hz), 80.9, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}FN_2O$ 257.1085; Found 257.1089.

3-Phenyl-4-(o-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2o*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (161.3 mg, 64%), mp 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.05 (m, 4H), 7.05 – 6.93 (m, 2H), 6.82 (d, *J* = 7.9 Hz, 2H), 5.34 (s, 2H), 5.17 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 143.9, 136.3, 135.5, 130.6, 129.7, 129.1, 128.8, 125.6, 125.0, 124.6, 80.2, 79.8, 19.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O$ 253.1335; Found 253.1337.

4-(2-Chlorophenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2p*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (157.8 mg, 58%), mp 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.24 – 7.08 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 5.35 (s, 2H), 5.17 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 143.1, 134.9, 132.5, 131.2, 130.3, 129.9, 128.8, 126.6, 125.4, 125.0, 80.1, 79.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}ClN_2O$ 273.0789; Found 273.0784.

4-(4-Fluoro-3-methylphenyl)-3-phenyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2q*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (135.0 mg, 50%), mp 96-97 °C. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.23 - 7.18 (m, 4H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 2H), 5.36 (s, 2H), 5.09 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 243 Hz), 154.4, 145.6, 135.3 (d, *J* = 7.5 Hz), 131.1 (d, *J* = 5.2 Hz), 129.2, 126.9 (d, *J* = 7.3 Hz), 125.0, 124.9, 124.0 (d, *J* = 3.6 Hz,), 115.1 (d, *J* = 23.9 Hz), 80.9, 80.4, 14.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FN_2O$ 271.1241; Found 271.1245.

3-(4-Fluorophenyl)-4-(4-methoxyphenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2s*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (148.7 mg, 52%), mp 107-108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 6.89 – 6.86 (m, 4H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.36 (s, 2H), 5.04 (s, 2H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.93 (d, *J* = 243 Hz), 155.0, 142.3 (d, *J* = 2.9 Hz), 130.2, 127.7, 126.6 (d, *J* = 8.3 Hz), 115.9 (d, *J* = 22.5 Hz), 113.5, 81.1, 80.4, 55.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FN_2O_2$ 287.1190; Found 287.1194.

3-(4-Fluorophenyl)-4-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2t*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oli (135.0 mg, 50%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.12 - 7.06 (m, 2H), 6.87 (d, *J* = 6.5 Hz, 4H), 5.37 (s, 2H), 5.06 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0 (d, *J* = 243 Hz), 155.5, 142.0, 138.0, 135.3, 130.8, 129.2, 127.9, 126.6 (d, *J* = 8.3 Hz), 125.8, 115.9 (d, *J* = 22.6 Hz), 81.1, 80.4, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FN_2O$ 271.1241; Found 271.1244.

4-(3-Fluorophenyl)-3-(4-fluorophenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2u*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (126.0 mg, 46%), mp 61-62 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.24-7.15 (m, 2H), 7.02 - 6.97 (m, 1H), 6.94 – 6.86 (m, 4H), 5.37 (s, 2H), 5.06 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 245 Hz), 160.2 (d, *J* = 244 Hz), 154.2, 141.6, 137.6, 129.7 (d, *J* = 8.1 Hz), 126.6 (d, *J* = 8.4 Hz), 124.3 (d, *J* = 2.8 Hz), 117.1 (d, *J* = 21.4 Hz), 116.1 (d, *J* = 22.8 Hz), 115.6 (d, *J* = 23.1 Hz), 81.1, 80.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}F_2N_2O$ 275.0990; Found 275.0987.

3-(3-Chlorophenyl)-4-(4-ethylphenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2v*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (141.0 mg, 47%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.06 (m, 3H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.93 (t, *J* = 2.1 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.38 (s, 2H), 5.09 (s, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 147.2, 146.7, 134.6, 132.5, 129.9, 128.5, 127.8, 124.8, 124.7, 123.2, 80.8, 80.4, 28.7, 15.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}ClN_2O$ 301.1102; Found 301.1198.

3-(3-Chlorophenyl)-4-(4-fluorophenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2w*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (121.8 mg, 42%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.8, 5.6 Hz 2H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 8.4 Hz), 6.99 – 6.83 (m, 3H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.37 (s, 2H), 5.09 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (d, *J* = 249 Hz), 153.9, 146.8, 134.8, 131.2 (d, *J* = 3.1 Hz), 130. 6 (d, *J* = 8.6 Hz), 130.1, 125.2, 124.8, 123.2, 115.4 (d, *J* = 21.7 Hz), 80.8, 80.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}ClFN_2O$ 291.0695; Found 291.0698.

3-(3-Chlorophenyl)-4-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2x*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (139.4 mg, 41%), mp 85-86 °C. ^1H

NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.07 (td, *J* = 8.8, 1.6 Hz 1H), 6.93 (t, *J* = 2.0 Hz, 1H), 6.72 (td, *J* = 7.7, 1.6 Hz, 1H), 5.39 (s, 2H), 5.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 146.4, 138.5, 134.9, 131.9 (q, *J* = 32.3 Hz), 130.2, 128.9, 125.5, 125.3 (q, *J* = 3.7 Hz) 124.7, 123.8 (q, *J* = 271 Hz), 123.2, 80.8, 80.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}ClF_3N_2O$ 341.0663; Found 341.0659.

3-(3-Chlorophenyl)-4-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2y*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (145.9 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.15 – 7.04 (m, 3H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.93 (t, *J* = 2.1 Hz, 1H), 6.73 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 5.37 (s, 2H), 5.09 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 147.0, 138.1, 135.1, 134.6, 131.0, 129.9, 129.1, 128.0, 125.7, 124.9, 124.7, 123.2, 80.8, 80.4, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}ClN_2O$ 287.0946; Found 287.0942.

4-(4-Methoxyphenyl)-3-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2z*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (177.7 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.76 – 6.72 (m, 3H), 6.67 (d, *J* = 7.9 Hz, 1H), 5.36 (s, 2H), 5.08 (s, 2H), 3.75 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 155.2, 146.0, 139.0, 130.1, 128.8, 128.0, 125.6, 125.5, 122.2, 113.4, 81.0, 80.4, 55.2, 21.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2$ 283.1441; Found 283.1444.

3-(m-Tolyl)-4-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2a'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (156.8 mg, 49%), mp 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.39 (s, 2H), 5.10 (s, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 145.1, 139.4, 139.2, 131.5 (q, *J* = 32.2 Hz), 129.0, 128.9, 126.2, 125.5, 125.1 (d, *J* = 4.2 Hz), 123.9 (d, *J* = 271 Hz), 122.2, 81.0, 80.4, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}F_3N_2O$ 321.1209; Found 321.1205.

3,4-di-m-Ttolyl-3,6-dihydro-2H-1,3,5-oxadiazine (*2b'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (154.3 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.09 – 7.02 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.37 (s, 2H), 5.09 (s, 2H), 2.28 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 145.7, 139.0, 137.8, 135.6, 130.7, 129.1, 128.8, 127.8, 125.8, 125.7, 125.4, 122.2, 80.9, 80.4, 21.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O$ 267.1492; Found 267.1497.

4-(3-Fluorophenyl)-3-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2c'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (132.3 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.15 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.97 (td, *J* = 8.3, 1.1 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.37 (s, 2H), 5.08 (s, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 244 Hz), 154.4, 145.4, 139.2, 138.1 (d, *J* = 7.4 Hz), 129.6 (d, *J* = 8.1 Hz), 129.0, 126.0, 125.5, 124.3, 122.1, 116.9 (d, *J* = 21.4 Hz), 115.6 (d, *J* = 23.1 Hz), 80.9, 80.4, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FN_2O$ 271.1241; Found 271.1246.

3-([1,1'-Biphenyl]-2-yl)-4-(4-methoxyphenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2d'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; Yellow oil (220.2 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.49 – 7.31 (m, 5H), 7.32 – 7.20 (m, 3H), 7.16 (dd, *J* = 6.0, 4.0 Hz 2H), 6.90 (dd, *J* = 6.0, 4.0 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.33 - 5.18 (m, 2H), 4.84 – 4.72 (m, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 154.7, 142.9, 139.3, 136.5, 131.6, 130.1, 129.1, 128.5, 128.1, 127.9, 127.3, 127.3, 125.8, 113.1, 80.6, 80.4, 55.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O_2$ 345.1598; Found 345.1594.

3-([1,1'-Biphenyl]-2-yl)-4-(m-tolyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2e'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (196.8 mg, 60%), mp 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 2H), 7.10 (s, 1H), 7.07 – 6.98 (m, 3H), 6.95 – 6.89 (m, 1H), 5.35 – 5.20 (m, 2H), 4.90 – 4.76 (m, 2H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 142.7, 139.2, 137.5, 136.7, 135.4, 131.5, 130.4, 129.4, 129.2, 128.4, 128.1, 127.4, 127.3, 127.2, 125.9, 125.6, 80.6, 80.3, 21.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O$ 329.1648; Found 329.1645.

3-([1,1'-Biphenyl]-2-yl)-4-(3-fluorophenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (2f'). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (182.6 mg, 55%), mp 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 7.25 – 7.15 (m, 3H), 7.12 – 7.05 (m, 1H), 7.02 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.97 – 6.91 (m, 3H), 5.38 – 5.16 (m, 2H), 4.96 – 4.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 244 Hz), 153.8, 142.3, 139.0, 137.9 (d, *J* = 7.6 Hz), 136.8, 131.7, 129.2, 129.1 (d, *J* = 8.0 Hz), 128.5, 128.3, 127.4, 127.0, 126.2, 124.1 (d, *J* = 1.8 Hz), 116.4 (d, *J* = 21.3 Hz), 115.6 (d, *J* = 23.2 Hz), 80.6, 80.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}FN_2O$ 333.1398; Found 333.1395.

3-(4-Chlorophenyl)-4-(4-methoxyphenyl)-3,6-dihydro-2H-1,3,5-oxadiazine (*2g'*). Petroleum ether/ethyl acetate/Et_3N (5:1:0.04) as eluent; White solid (151.0 mg, 50%), mp 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 5.36 (s, 2H), 5.07 (s, 2H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 154.6, 144.7, 130.2, 130.1, 129.2, 127.5, 126.1, 113.6, 80.9, 80.4, 55.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}ClN_2O_2$ 303.0895; Found 303.0899.

2-Phenylbenzo[*h*]quinazoline (3).[2] Petroleum ether/ethyl acetate (5:1) as eluent; White solid (82 mg, 32%), mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 – 9.32 (m, 1H), 9.31 (s, 1H), 8.68 (d, *J* = 7.6 Hz, 2H), 7.85 – 7.82 (m, 1H), 7.76 – 7.69 (m, 3H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.52 – 7.43 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 157.6, 149.7, 137.3, 137.5, 129.6, 129.3, 129.1, 127.6, 127.5, 127.4, 127.4, 127.0, 126.4, 124.0, 121.9, 120.5.

ESI-MS m/z $[M + H]^+$ 257.

References

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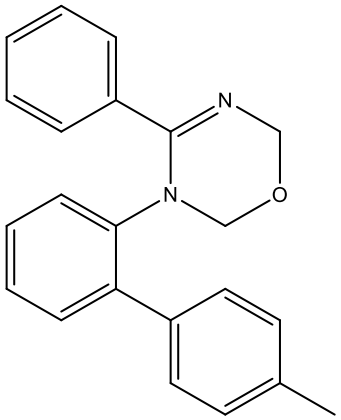
2. Cheng, X., Wang, H., Xiao, F. & Deng, G.-J. Lewis acid-catalyzed 2-arylquinazoline formation from N '-arylbenzimidamides and paraformaldehyde. *Green Chem.* **2016**, *18*, 5773-5776.

Crystal Data

The crystal of **2h** was obtained from CH_2Cl_2/petroleum ether at room temperature The structure of compound **2h** was assigned by single crystal X-ray analysis. Diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å). The crystal date of compound **2h** have been deposited in CCDC with number 2074241.



2h

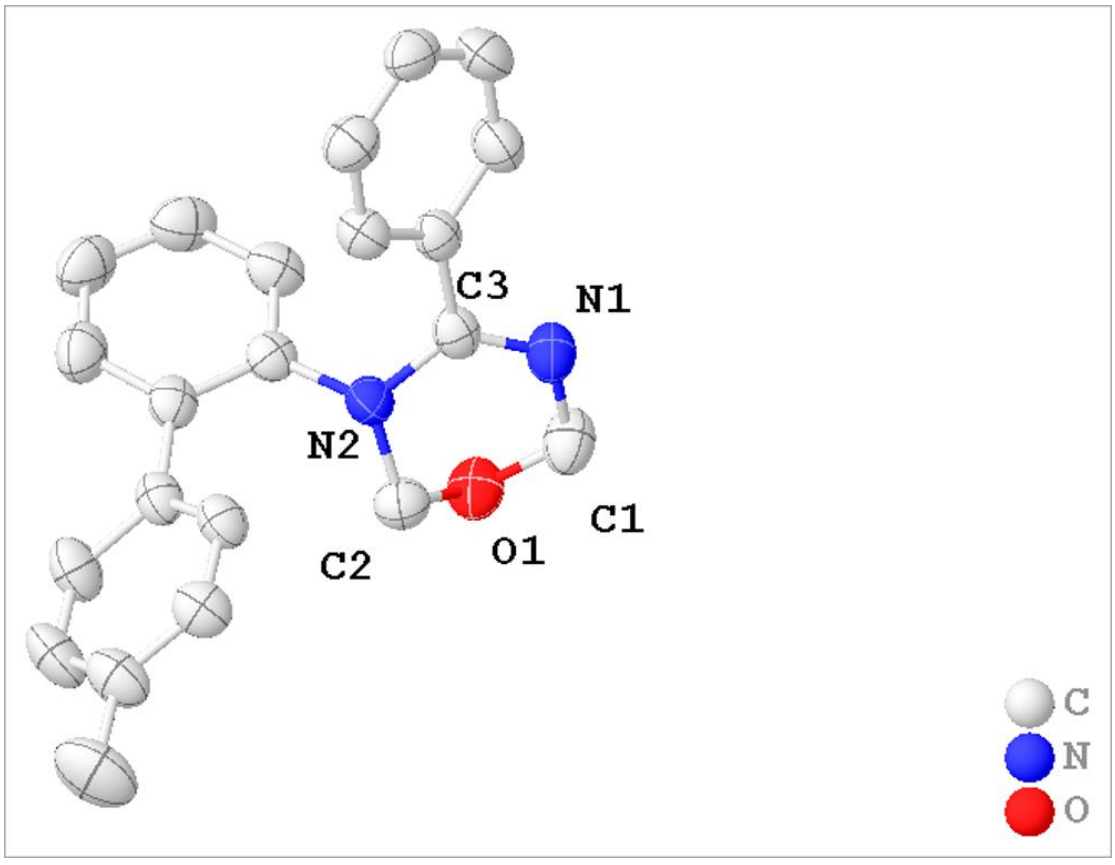


Figure S1 X-ray structure of compound **2h** (CCDC 2074241**)** (Thermal ellipsoids are drawn at the 50% probability level).

Table S1 Crystal data and structure refinement for 2h.

Identification code	**2h**
Empirical formula	$C_{30}H_{23}N$
Formula weight	397.49
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	10.272(7)
b/Å	10.906(7)
c/Å	11.716(8)
α/°	78.548(14)
β/°	69.715(14)
γ/°	63.003(12)
Volume/Å^3	1095.7(13)
Z	2
ρ_{calc}g/cm^3	1.205
μ/mm^{-1}	0.069
F(000)	420.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.71 to 60.694
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	10945
Independent reflections	5623 [R_{int} = 0.0645, R_{sigma} = 0.0961]
Data/restraints/parameters	5623/0/282
Goodness-of-fit on F^2	0.959
Final R indexes [I>=2σ (I)]	R_1 = 0.0643, wR_2 = 0.1526
Final R indexes [all data]	R_1 = 0.1224, wR_2 = 0.1859
Largest diff. peak/hole / e Å^{-3}	0.34/-0.21

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2h**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	7720.6(8)	9381.9(8)	5143.4(5)	56.3(3)
N1	7120.3(10)	8409.5(10)	6055.3(6)	52.9(3)
N2	6719.3(9)	7904.9(9)	4996.5(5)	42.1(3)
C1	7823.7(14)	9159.7(13)	5808.2(8)	61.2(5)
C2	7649.3(11)	8444.3(12)	4808.1(8)	49.7(4)
C3	6573.6(11)	7893.4(11)	5663.0(7)	42.6(3)
C4	5785.3(11)	7183.1(11)	5925.0(6)	42.2(3)
C5	5567.7(12)	6255.6(12)	5635.5(7)	48.7(4)
C6	4871.1(12)	5592.7(13)	5905.4(8)	55.3(4)
C7	4370.0(12)	5845.2(15)	6462.8(8)	56.8(4)
C8	4563.5(14)	6770.3(16)	6749.9(8)	64.4(5)
C9	5272.5(13)	7433.5(14)	6485.7(7)	56.1(4)
C10	5839.6(11)	8013.9(10)	4587.1(7)	41.6(3)
C11	5018.2(13)	8599.6(12)	4797.1(8)	52.0(4)
C12	4157.0(13)	8735.6(14)	4421.6(9)	62.8(5)
C13	4110.6(13)	8276.5(15)	3828.3(9)	66.1(5)
C14	4924.1(13)	7701.1(14)	3614.0(8)	58.4(4)
C15	5819.2(11)	7558.0(11)	3974.5(6)	44.7(4)
C16	6676.0(11)	6954.3(11)	3688.0(7)	44.8(3)
C17	6851.5(14)	7009.1(13)	3026.2(7)	58.3(4)
C18	7586.0(16)	6420.1(14)	2732.8(8)	68.0(5)
C19	8198.9(15)	5753.5(13)	3074.7(8)	61.2(5)
C20	8042.7(13)	5704.4(12)	3732.3(8)	53.4(4)
C21	7299.8(12)	6288.1(11)	4033.2(7)	47.2(4)
C22	9003.0(19)	5113.9(17)	2747.6(10)	93.9(7

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2h**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	64.5(7)	45.9(6)	58.4(7)	5.5(5)	-5.6(5)	-9.7(5)
N1	60.5(8)	52.0(8)	46.1(7)	0.8(6)	-8.7(6)	-7.3(6)
N2	43.7(7)	44.8(7)	37.8(6)	0.8(5)	1.1(5)	-2.6(5)
C1	69.3(11)	55.5(11)	58.8(10)	1.9(8)	-14.5(8)	-12.6(9)
C2	47.7(9)	48.1(9)	53.2(9)	1.8(7)	2.9(7)	-2.7(7)
C3	47.9(8)	40.9(8)	39.1(8)	0.2(6)	-2.5(6)	5.1(6)
C4	45.1(8)	43.6(8)	37.9(7)	3.2(6)	-3.0(6)	3.6(6)
C5	51.5(9)	49.0(9)	45.8(9)	-0.1(7)	4.1(7)	0.2(7)
C6	52.5(9)	51.4(10)	62.1(11)	3.1(8)	-3.0(7)	-3.8(7)
C7	44.9(9)	71.2(12)	54.4(10)	15.7(8)	-3.0(7)	-7.6(8)
C8	61.5(11)	88.3(14)	43.3(9)	1.0(9)	9.6(8)	-1.1(10)
C9	63.0(10)	61.5(11)	43.7(9)	-6.1(8)	3.1(7)	-1.3(8)
C10	45.3(8)	38.7(8)	40.8(8)	7.9(6)	0.0(6)	-0.6(6)
C11	57.1(10)	49.5(10)	49.5(9)	6.5(7)	5.1(7)	7.5(7)
C12	53.0(10)	67.9(12)	67.4(12)	17.3(9)	4.0(8)	12.8(8)
C13	50.4(10)	79.4(13)	68.3(12)	19.5(10)	-11.9(8)	2.0(9)
C14	59.5(10)	66.0(11)	49.8(9)	7.5(8)	-10.0(7)	-4.1(9)
C15	50.7(8)	43.4(8)	40.0(8)	8.0(6)	-3.1(6)	-4.3(7)
C16	53.7(9)	42.8(8)	37.7(7)	1.1(6)	-1.0(6)	-4.3(7)
C17	78.9(12)	57.6(10)	38.3(8)	4.6(7)	-1.8(8)	3.7(9)
C18	97.5(14)	68.6(12)	38.0(8)	-3.3(8)	12.8(9)	-0.8(11)
C19	79.4(12)	51.2(10)	53.1(10)	-5.3(8)	15.1(8)	-0.1(9)
C20	62.0(10)	44.1(9)	54.0(9)	3.0(7)	4.4(7)	1.7(8)
C21	58.3(10)	46.3(9)	37.2(7)	2.8(6)	2.2(6)	-2.2(7)
C22	117.0(18)	80.9(15)	83.8(15)	-13.2(12)	34.1(13)	20.2(13)

Table S4 Bond Lengths for **2h.**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C1	1.422(2)	C10	C11	1.386(2)
O1	C2	1.4150(19)	C10	C15	1.409(2)
N1	C1	1.438(2)	C11	C12	1.379(2)
N1	C3	1.2771(18)	C12	C13	1.376(3)
N2	C2	1.4553(18)	C13	C14	1.374(2)
N2	C3	1.4017(17)	C14	C15	1.399(2)
N2	C10	1.4351(18)	C15	C16	1.491(2)
C3	C4	1.488(2)	C16	C17	1.400(2)
C4	C5	1.385(2)	C16	C21	1.392(2)
C4	C9	1.385(2)	C17	C18	1.372(2)
C5	C6	1.375(2)	C18	C19	1.380(3)
C6	C7	1.372(2)	C19	C20	1.387(2)
C7	C8	1.374(3)	C19	C22	1.504(3)
C8	C9	1.381(2)	C20	C21	1.383(2)

Table S5 Bond Angles for **2h.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C2	O1	C1	108.06(12)		C11	C10	C15	120.36(13)
C3	N1	C1	119.11(13)		C15	C10	N2	120.76(13)
C3	N2	C2	112.65(11)		C12	C11	C10	121.30(16)
C3	N2	C10	118.82(11)		C13	C12	C11	119.29(16)
C10	N2	C2	117.07(12)		C14	C13	C12	119.84(16)
O1	C1	N1	115.37(13)		C13	C14	C15	122.74(17)
O1	C2	N2	109.99(12)		C10	C15	C16	124.95(13)
N1	C3	N2	123.59(14)		C14	C15	C10	116.45(14)
N1	C3	C4	118.66(13)		C14	C15	C16	118.60(14)
N2	C3	C4	117.61(12)		C17	C16	C15	119.30(13)
C5	C4	C3	121.91(13)		C21	C16	C15	124.14(13)
C5	C4	C9	118.45(14)		C21	C16	C17	116.49(14)
C9	C4	C3	119.61(14)		C18	C17	C16	121.62(16)
C6	C5	C4	120.64(15)		C17	C18	C19	121.86(16)
C7	C6	C5	120.51(16)		C18	C19	C20	117.03(15)
C6	C7	C8	119.58(16)		C18	C19	C22	121.34(16)
C7	C8	C9	120.17(16)		C20	C19	C22	121.62(17)
C8	C9	C4	120.64(16)		C21	C20	C19	121.68(15)
C11	C10	N2	118.86(13)		C20	C21	C16	121.32(14)

Table S6 Torsion Angles for **2h.**

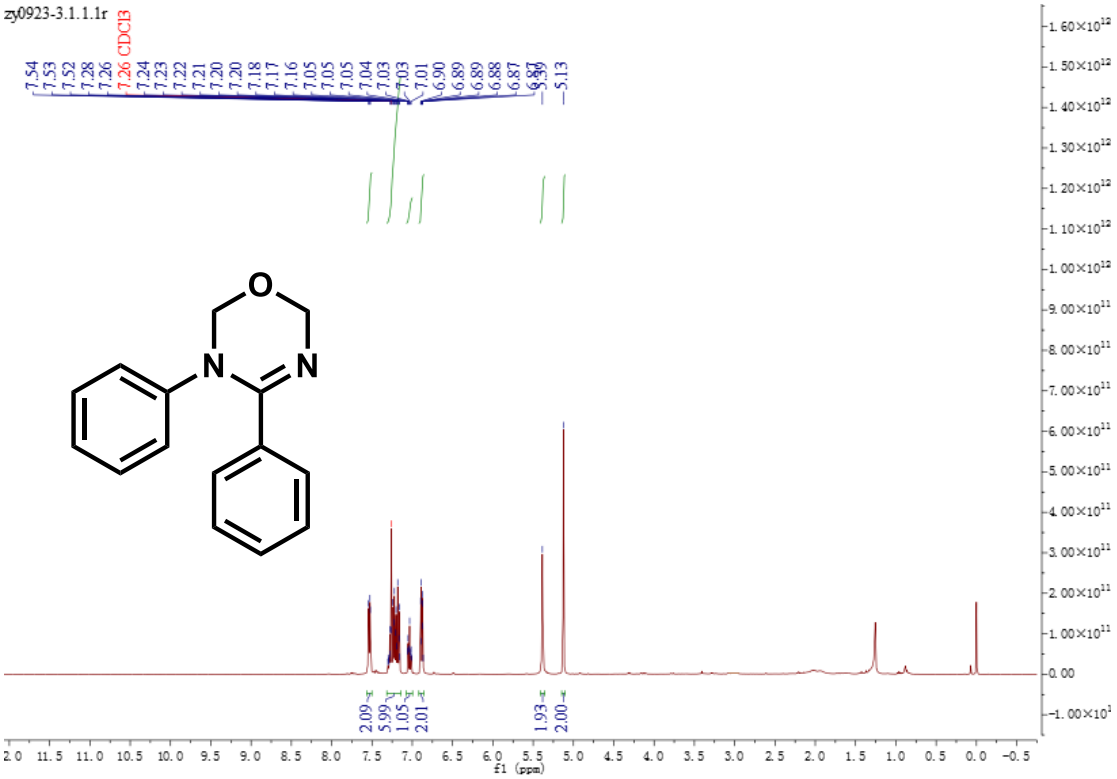
A	**B**	**C**	**D**	**Angle/°**		**A**	**B**	**C**	**D**	**Angle/°**
N1	C3	C4	C5	-144.03(15)		C9	C4	C5	C6	-1.1(2)
N1	C3	C4	C9	33.9(2)		C10	N2	C2	O1	97.14(15)
N2	C3	C4	C5	31.8(2)		C10	N2	C3	N1	-133.89(15)
N2	C3	C4	C9	-150.35(14)		C10	N2	C3	C4	50.55(17)
N2	C10	C11	C12	179.56(14)		C10	C11	C12	C13	0.3(3)
N2	C10	C15	C14	179.48(13)		C10	C15	C16	C17	-145.25(15)
N2	C10	C15	C16	-1.2(2)		C10	C15	C16	C21	37.9(2)
C1	O1	C2	N2	64.15(15)		C11	C10	C15	C14	-2.3(2)
C1	N1	C3	N2	9.6(2)		C11	C10	C15	C16	177.07(14)
C1	N1	C3	C4	-174.86(14)		C11	C12	C13	C14	-0.8(3)
C2	O1	C1	N1	-46.64(19)		C12	C13	C14	C15	-0.3(3)
C2	N2	C3	N1	8.5(2)		C13	C14	C15	C10	1.8(2)
C2	N2	C3	C4	-167.04(12)		C13	C14	C15	C16	-177.56(15)
C2	N2	C10	C11	-107.84(15)		C14	C15	C16	C17	34.1(2)
C2	N2	C10	C15	70.45(17)		C14	C15	C16	C21	-142.79(16)
C3	N1	C1	O1	10.3(2)		C15	C10	C11	C12	1.3(2)
C3	N2	C2	O1	-45.98(16)		C15	C16	C17	C18	-175.77(16)
C3	N2	C10	C11	32.95(19)		C15	C16	C21	C20	176.11(14)
C3	N2	C10	C15	-148.76(13)		C16	C17	C18	C19	-0.9(3)
C3	C4	C5	C6	176.84(14)		C17	C16	C21	C20	-0.8(2)
C3	C4	C9	C8	-177.75(15)		C17	C18	C19	C20	-0.1(3)
C4	C5	C6	C7	0.8(2)		C17	C18	C19	C22	-179.85(19)
C5	C4	C9	C8	0.2(2)		C18	C19	C20	C21	0.6(3)
C5	C6	C7	C8	0.4(2)		C19	C20	C21	C16	-0.1(2)
C6	C7	C8	C9	-1.2(3)		C21	C16	C17	C18	1.3(2)
C7	C8	C9	C4	0.9(3)		C22	C19	C20	C21	-179.65(17)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2h.**

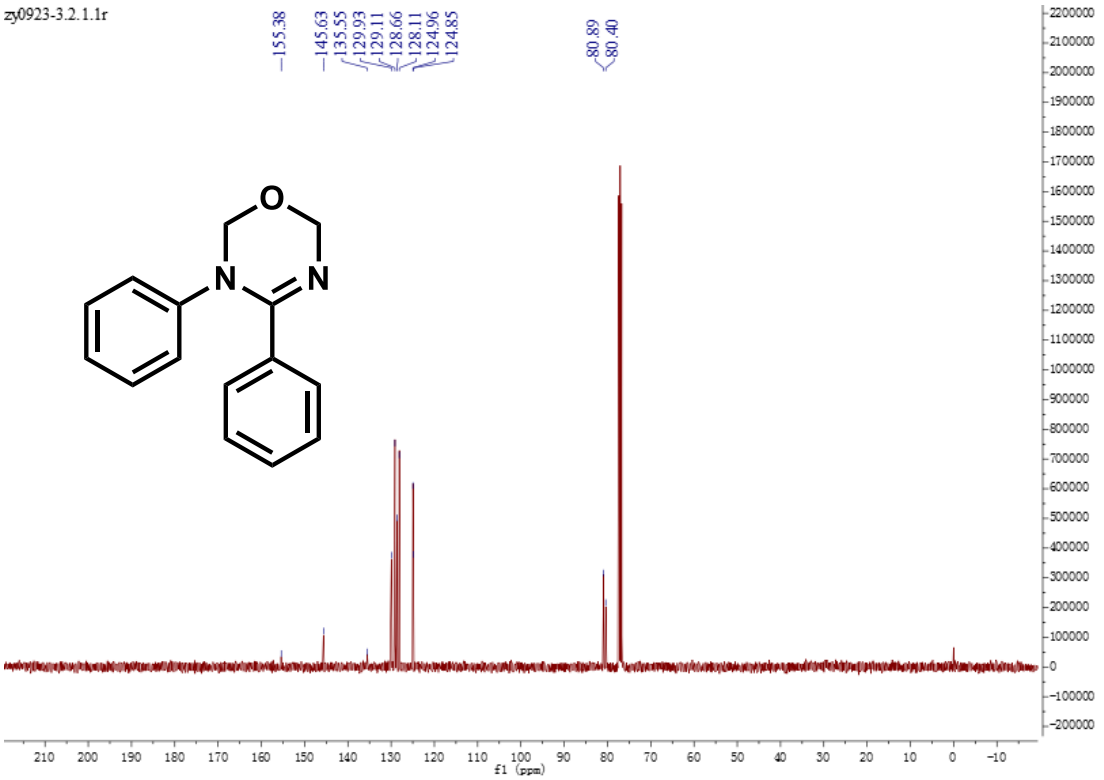
Atom	***x***	***y***	***z***	**U(eq)**
H1A	7731	9789	6048	73
H1B	8519	8923	5886	73
H2A	8245	8026	4903	60
H2B	7637	8573	4350	60
H5	5896	6079	5255	58
H6	4739	4968	5709	66
H7	3902	5393	6645	68
H8	4216	6951	7123	77
H9	5407	8054	6686	67
H11	5049	8907	5199	62
H12	3613	9133	4568	75
H13	3530	8356	3573	79
H14	4878	7394	3213	70
H17	6461	7456	2779	70
H18	7673	6471	2291	82
H20	8448	5268	3977	64
H21	7215	6235	4475	57
H22A	9426	4789	3065	141
H22B	9421	5542	2480	141
H22C	8675	4602	2489	141

NMR Spectra

^{1}H NMR of Compound **2a** (400 MHz, $CDCl_3$)

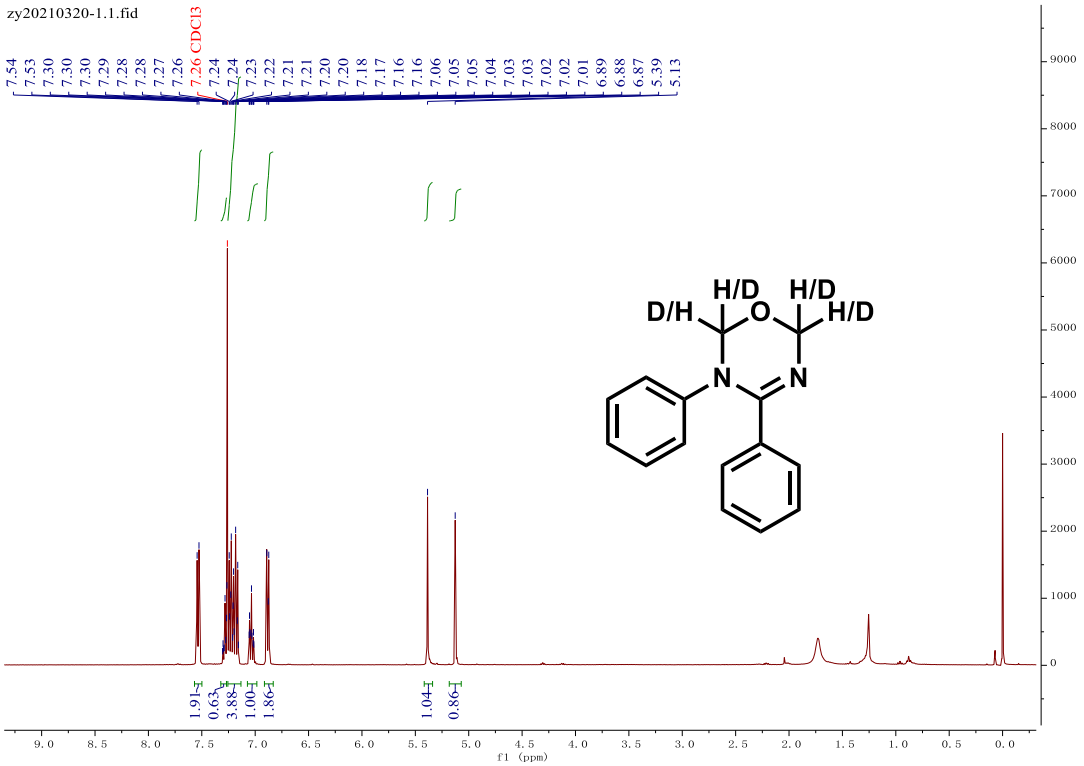


^{13}C{H} NMR of Compound **2a** (101 MHz, $CDCl_3$)



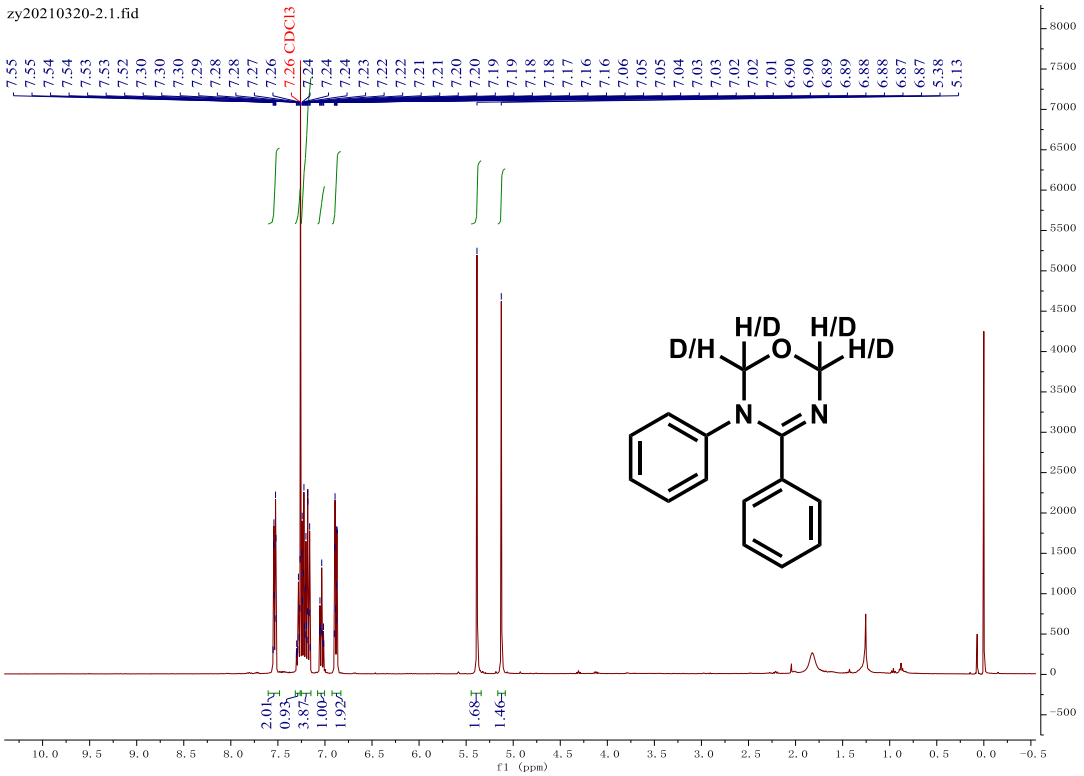
^{1}H NMR of Compound **2"a** (400 MHz, $CDCl_3$)

The reaction was carried out in DMSO-d_6

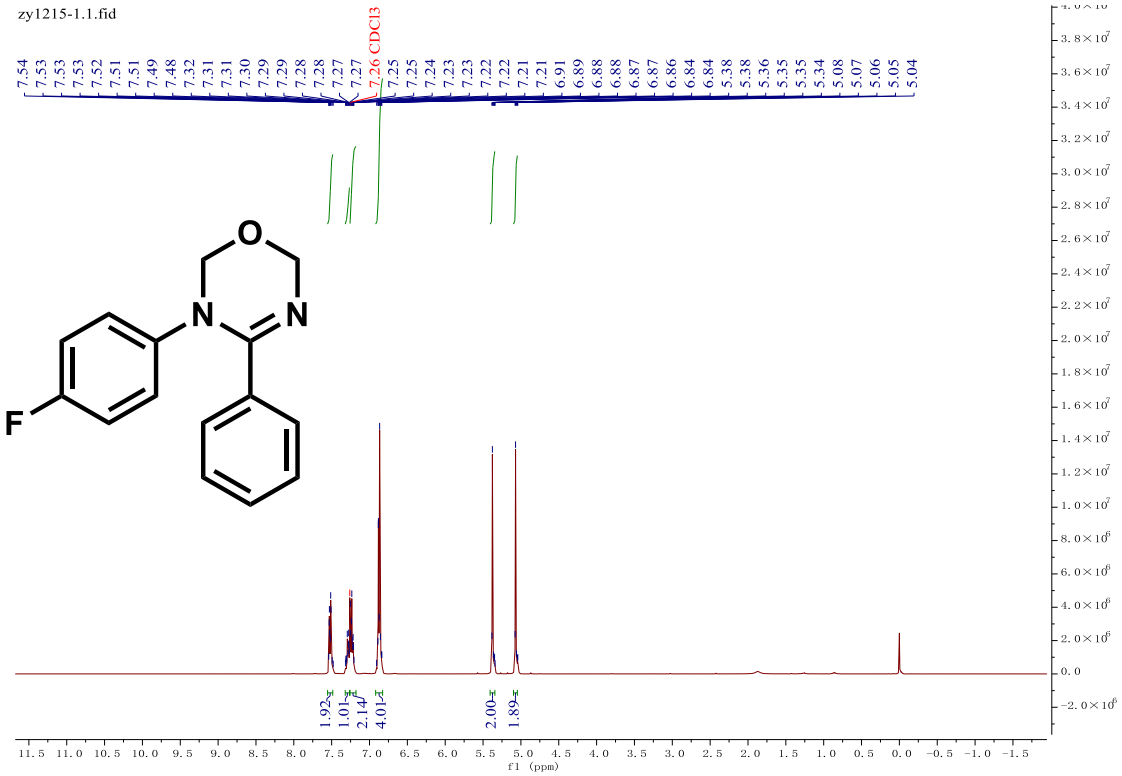


^{1}H NMR of Compound **2"a** (400 MHz, $CDCl_3$)

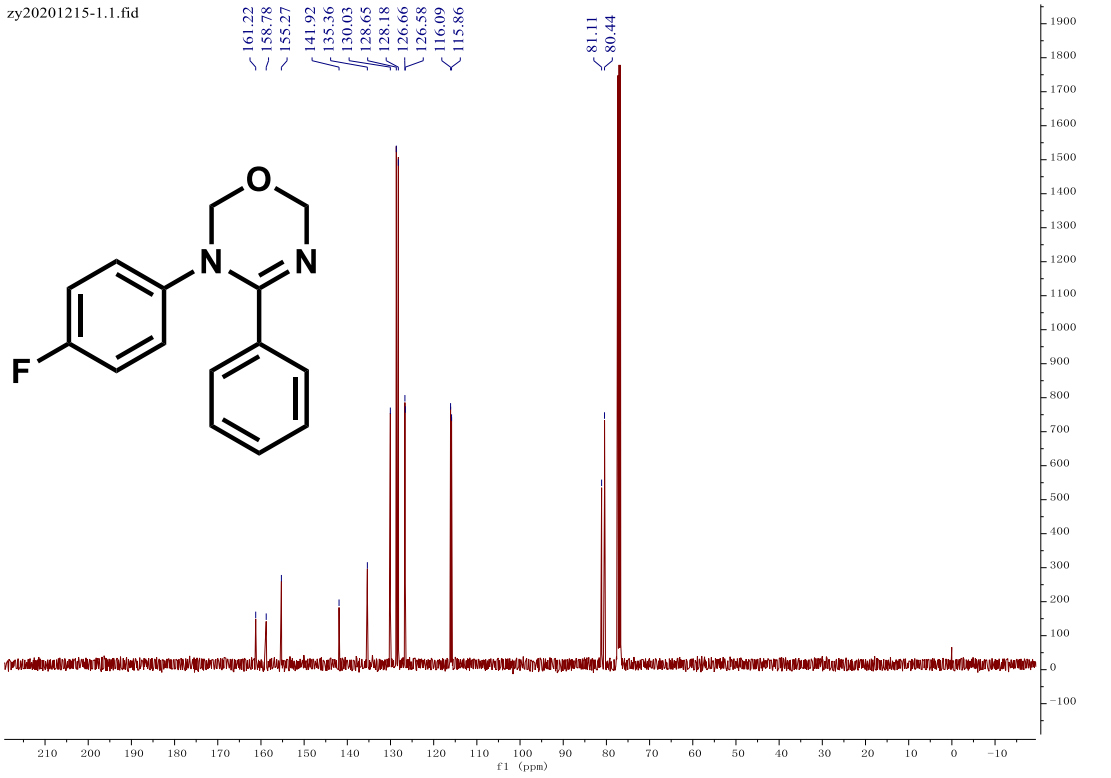
The reaction was carried out in DMSO : DMSO-d_6 = 1:1



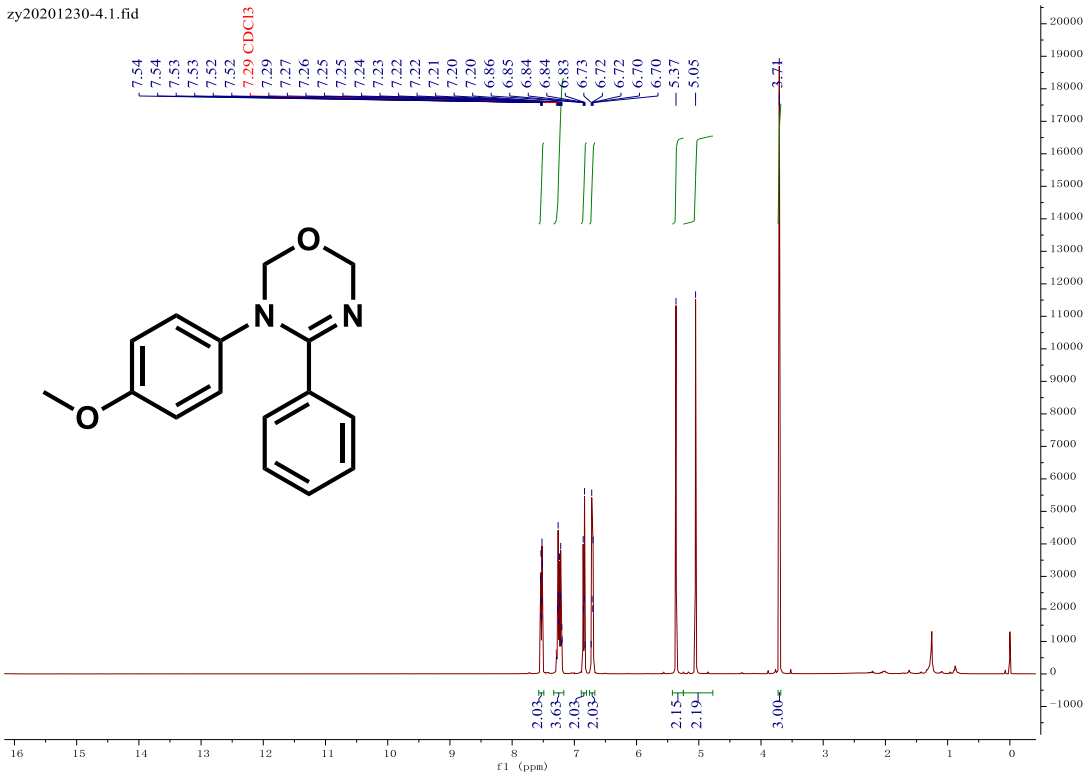
^{1}H NMR of Compound **2b** (400 MHz, $CDCl_3$)



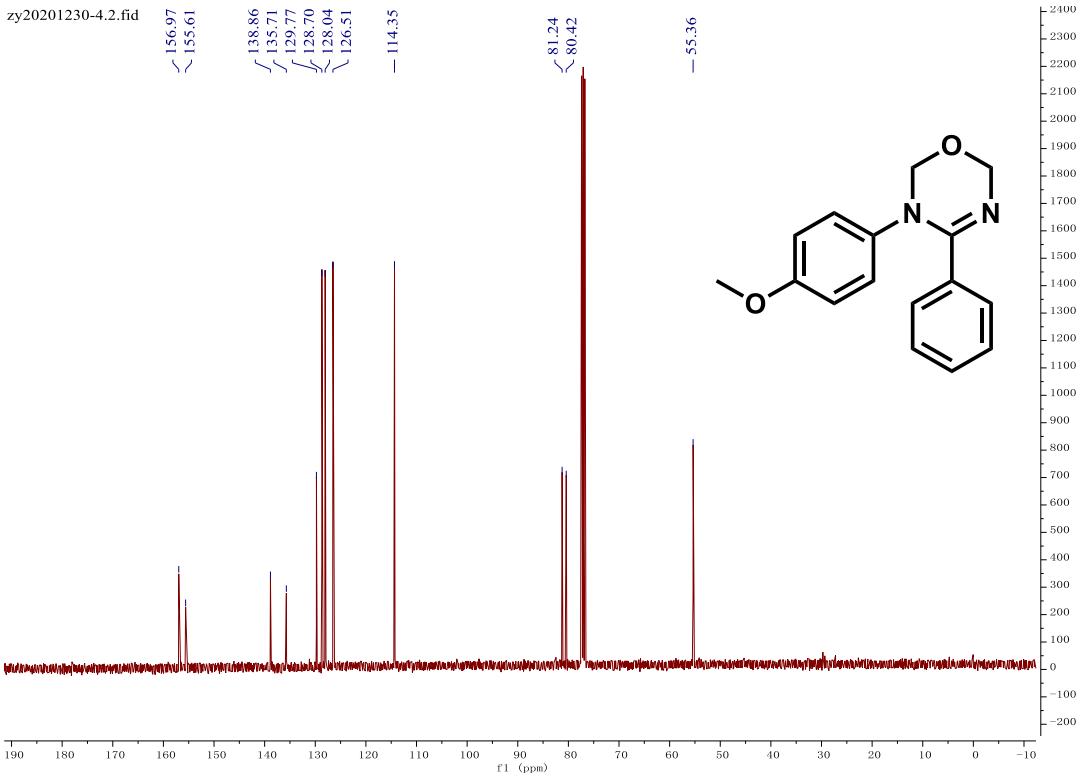
^{13}C{H} NMR of Compound **2b** (101 MHz, $CDCl_3$)



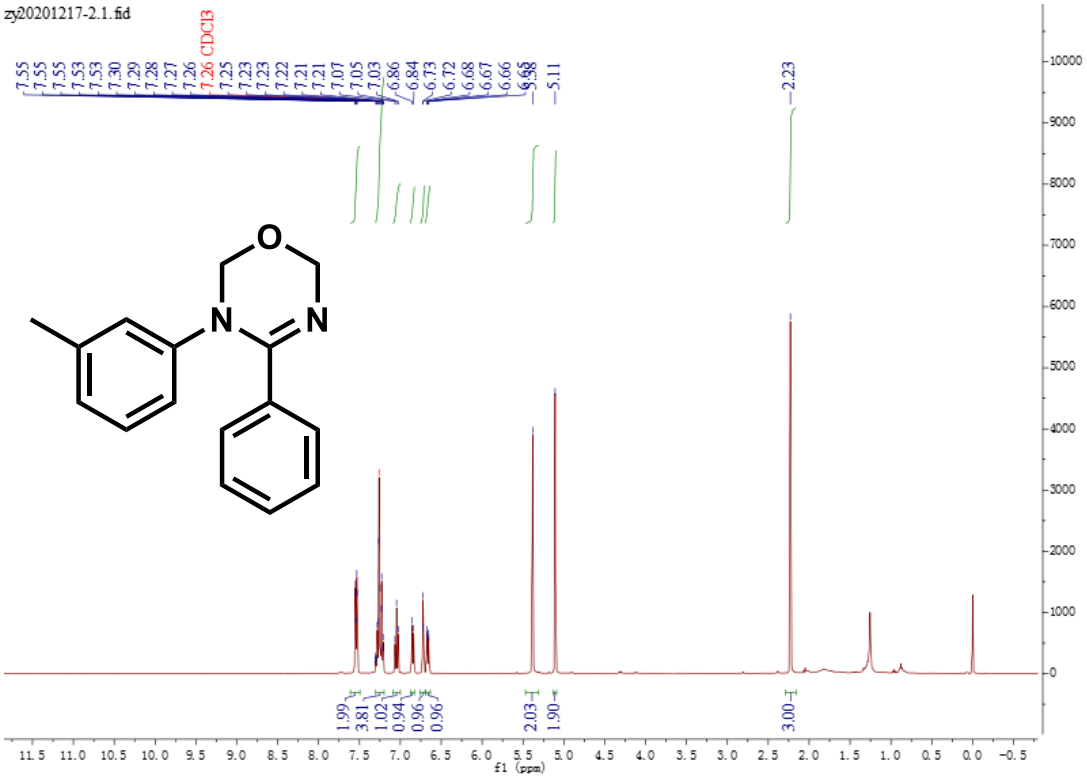
^{1}H NMR of Compound **2c** (400 MHz, $CDCl_3$)



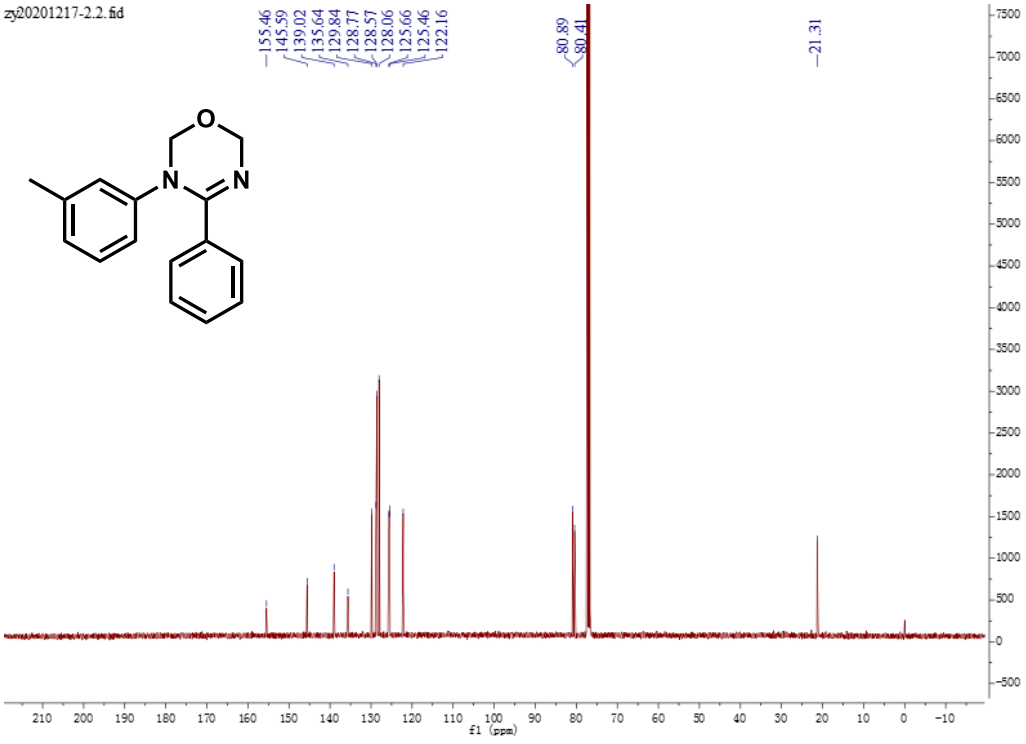
^{13}C{H} NMR of Compound **2c** (101 MHz, $CDCl_3$)



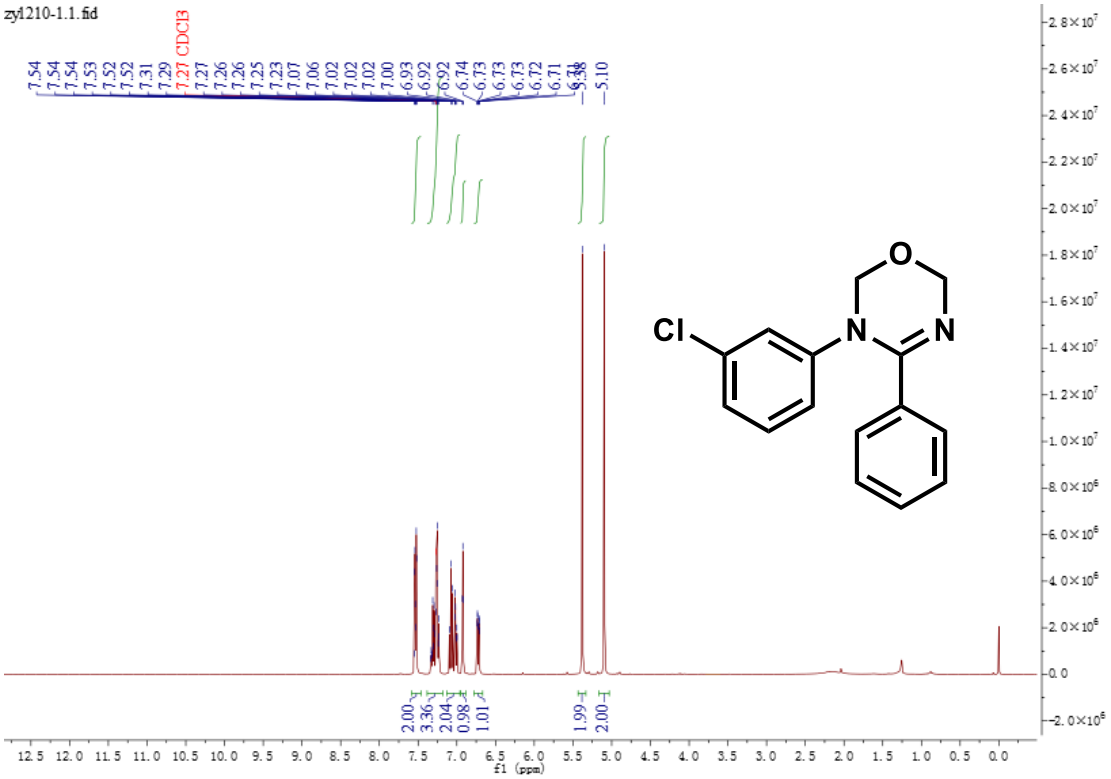
^{1}H NMR of Compound **2d** (400 MHz, $CDCl_3$)



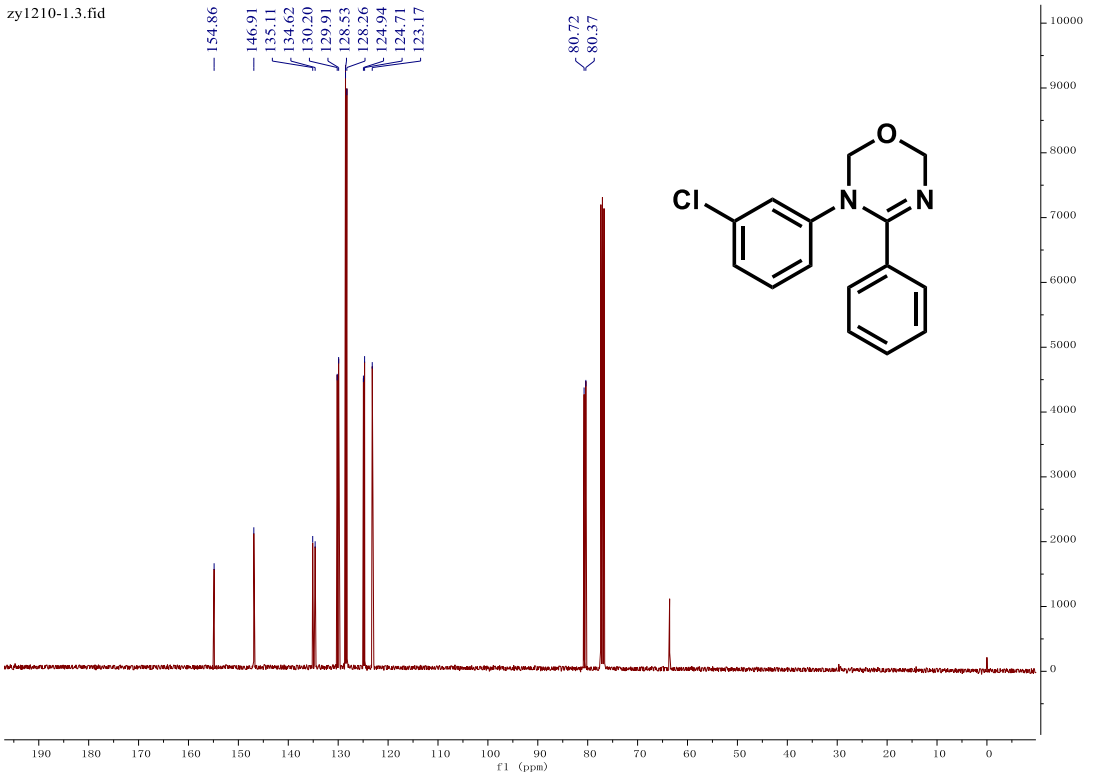
$^{13}C\{H\}$ NMR of Compound **2d** (101 MHz, $CDCl_3$)



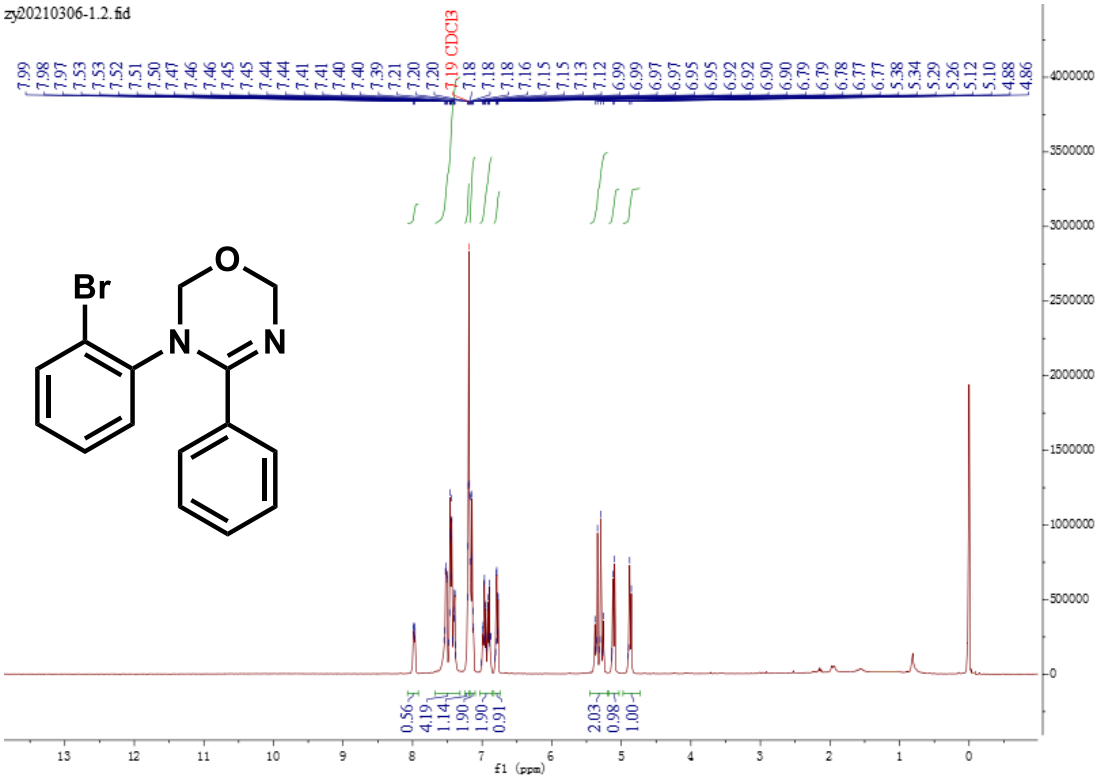
^{1}H NMR of Compound **2e** (400 MHz, $CDCl_3$)



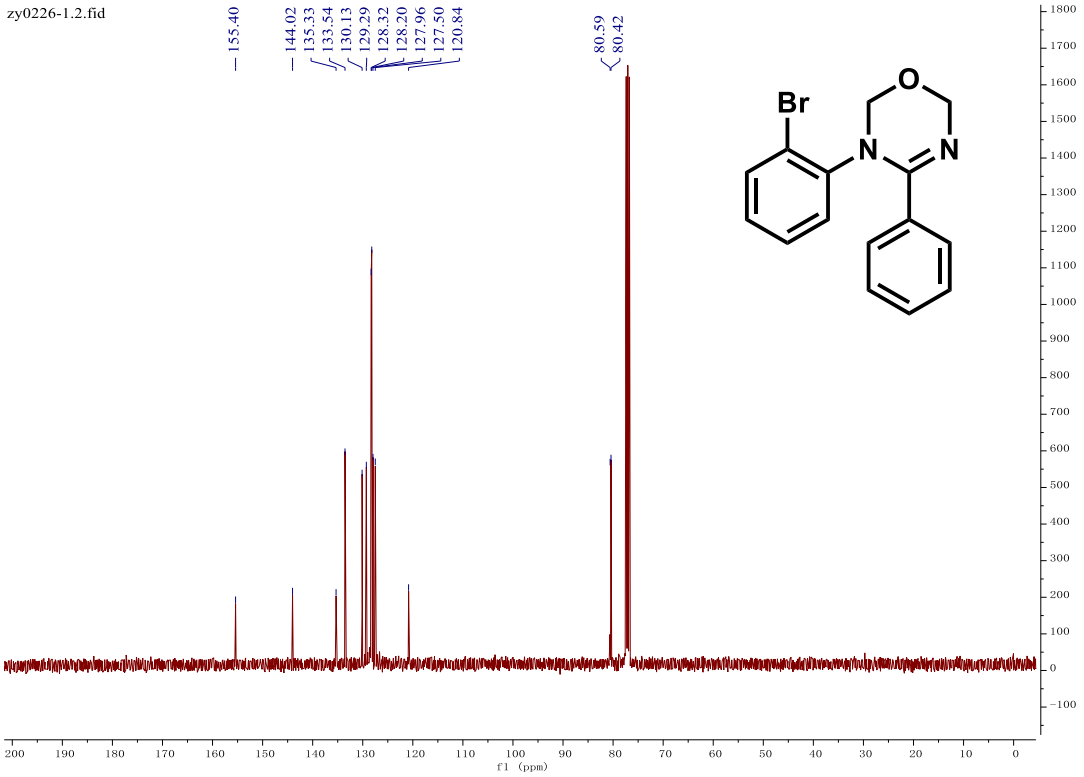
^{13}C{H} NMR of Compound **2e** (101 MHz, $CDCl_3$)



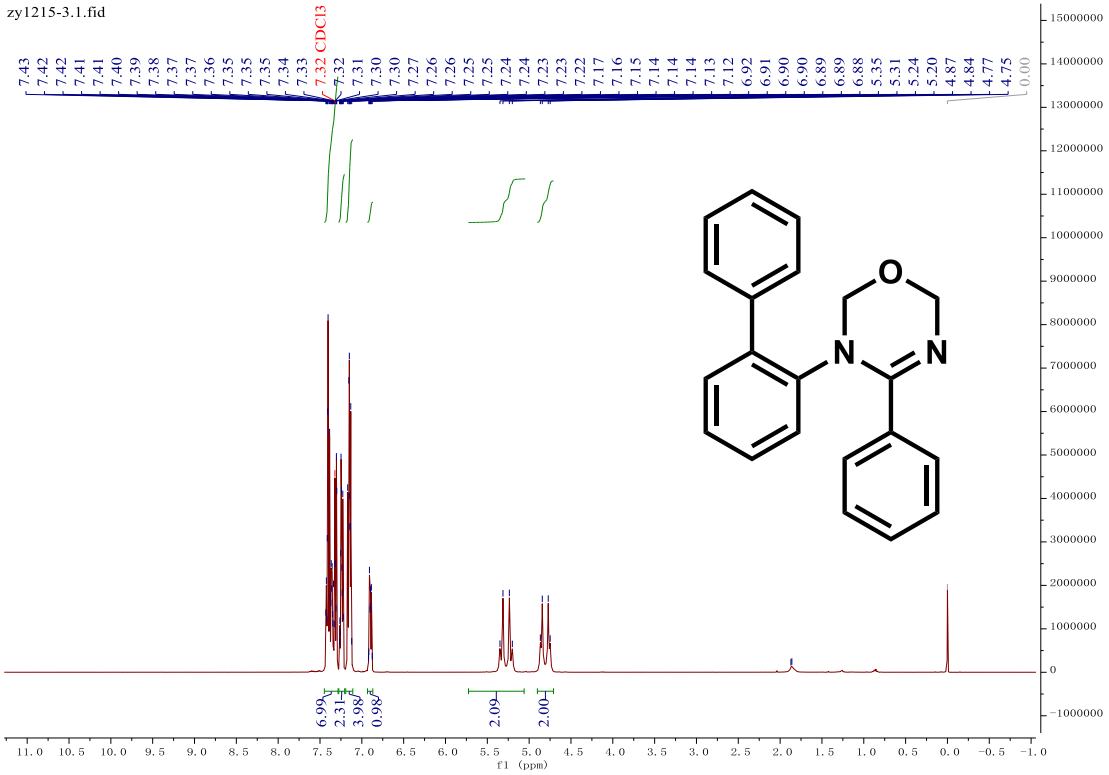
^{1}H NMR of Compound **2f** (400 MHz, $CDCl_3$)



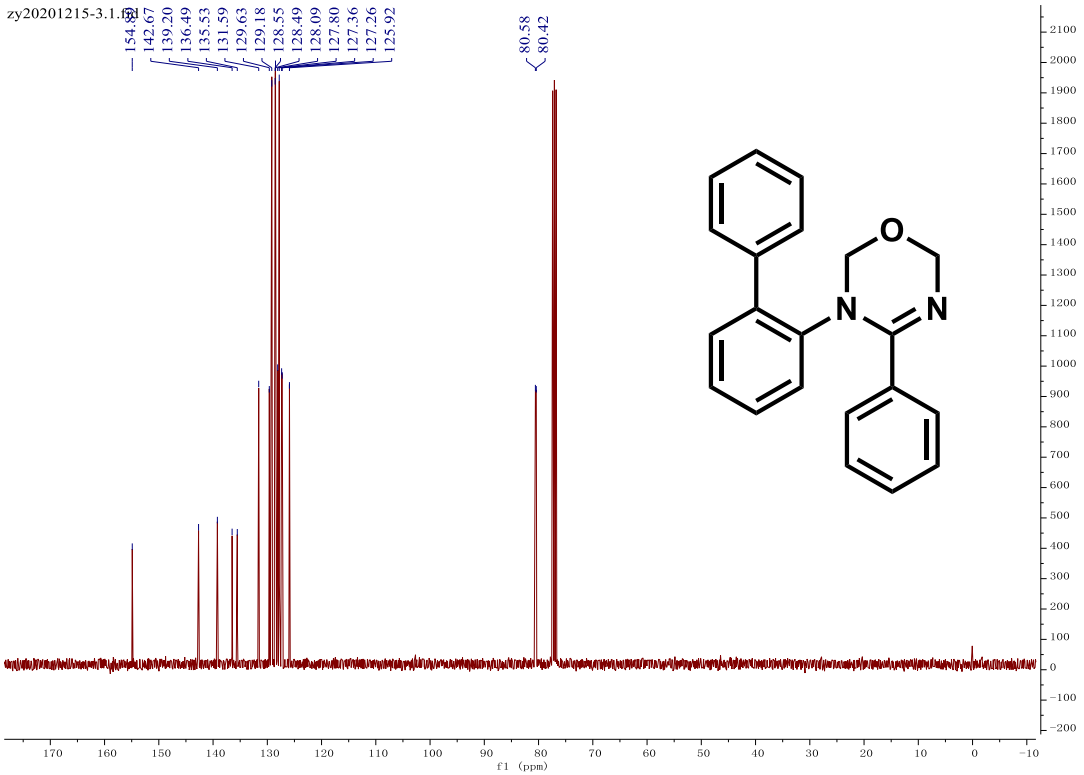
^{13}C{H} NMR of Compound **2f** (101 MHz, $CDCl_3$)



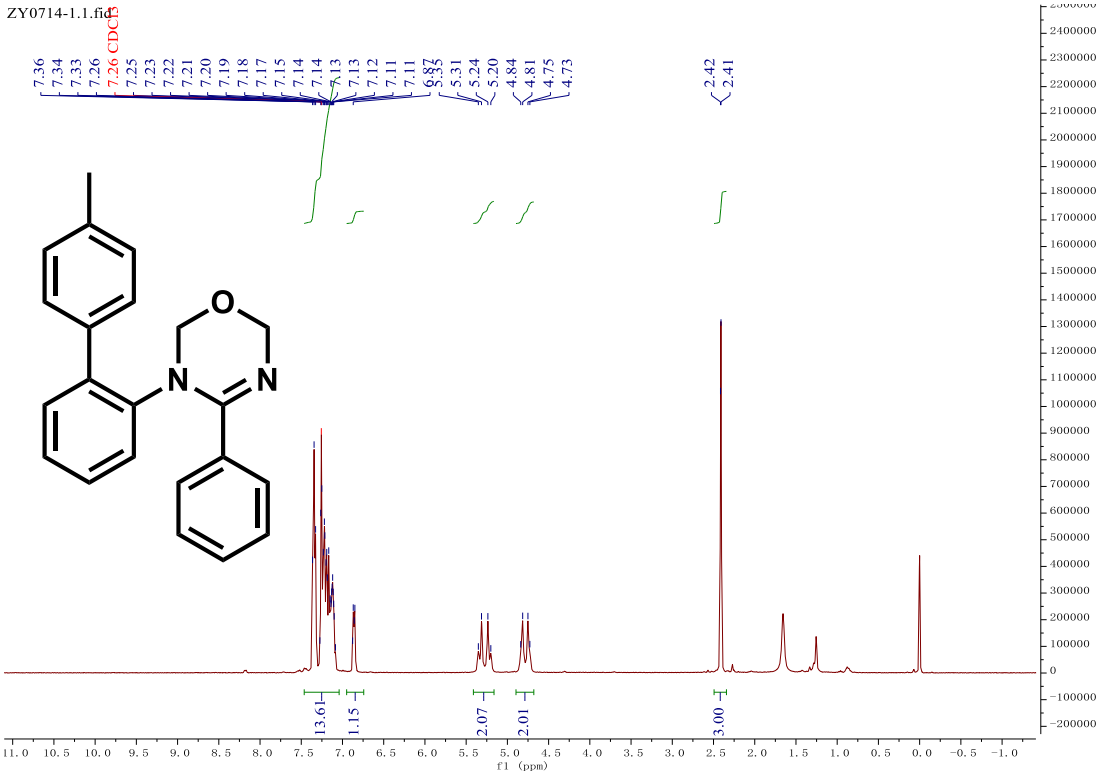
^{1}H NMR of Compound **2g** (400 MHz, $CDCl_3$)



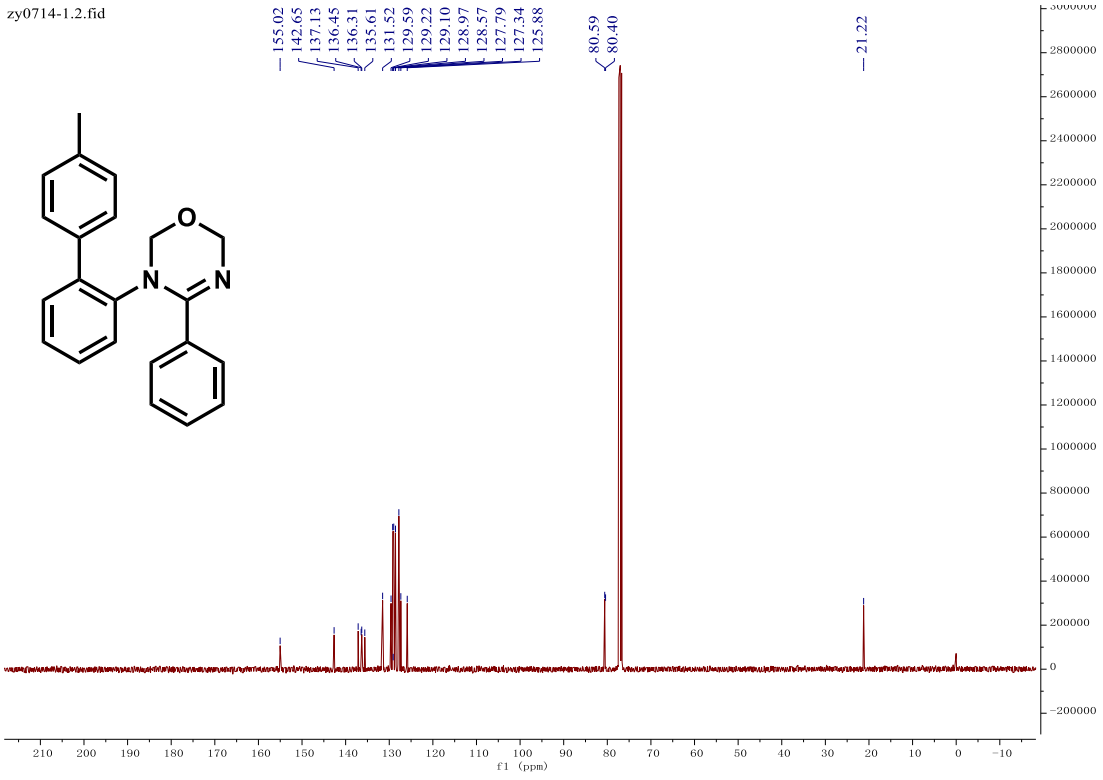
^{13}C{H} NMR of Compound **2g** (101 MHz, $CDCl_3$)



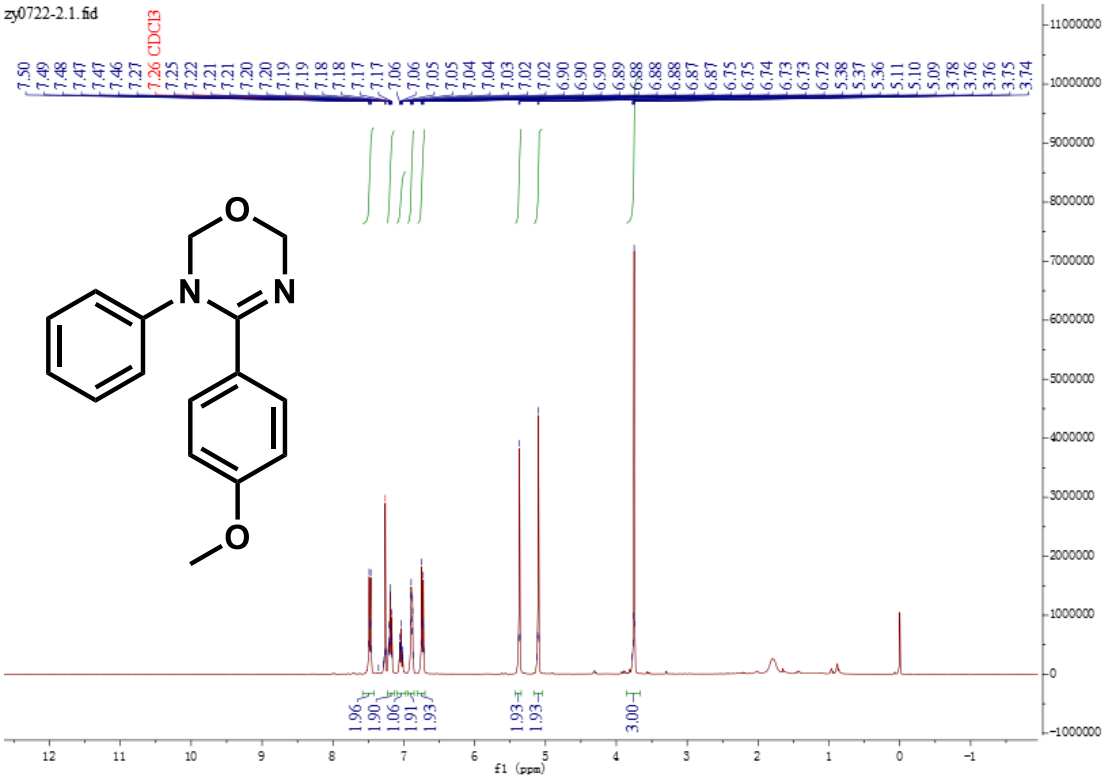
^{1}H NMR of Compound **2h** (400 MHz, $CDCl_3$)



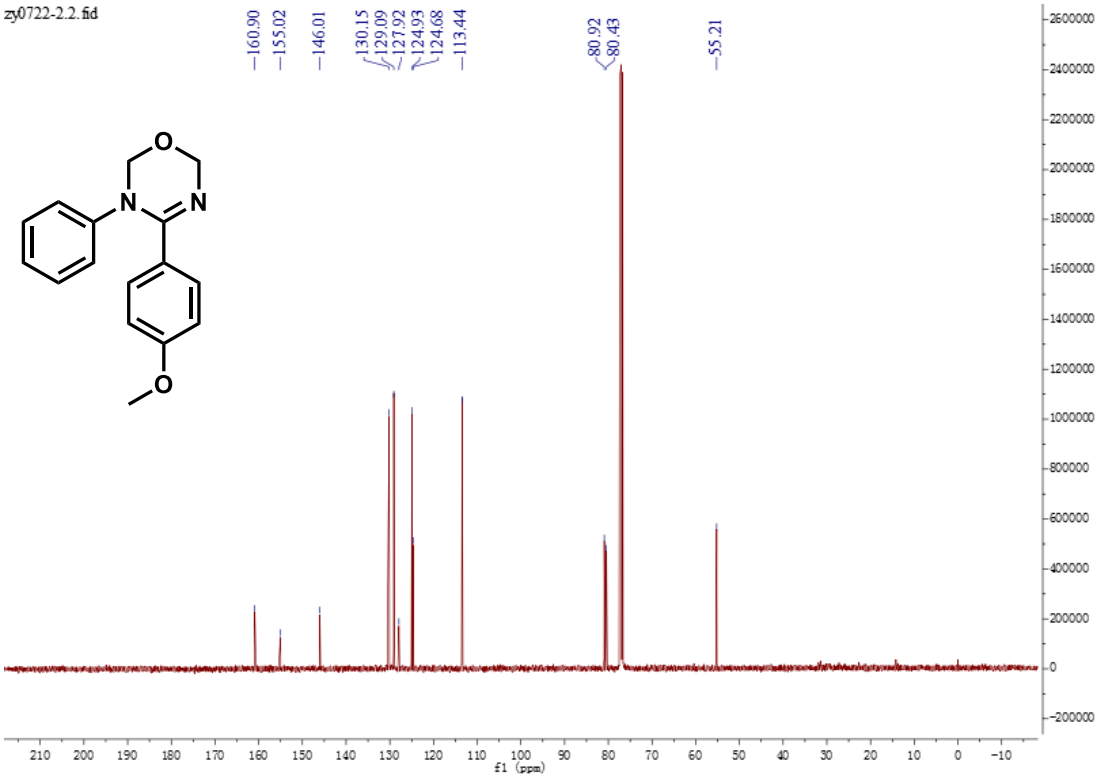
^{13}C{H} NMR of Compound **2h** (101 MHz, $CDCl_3$)



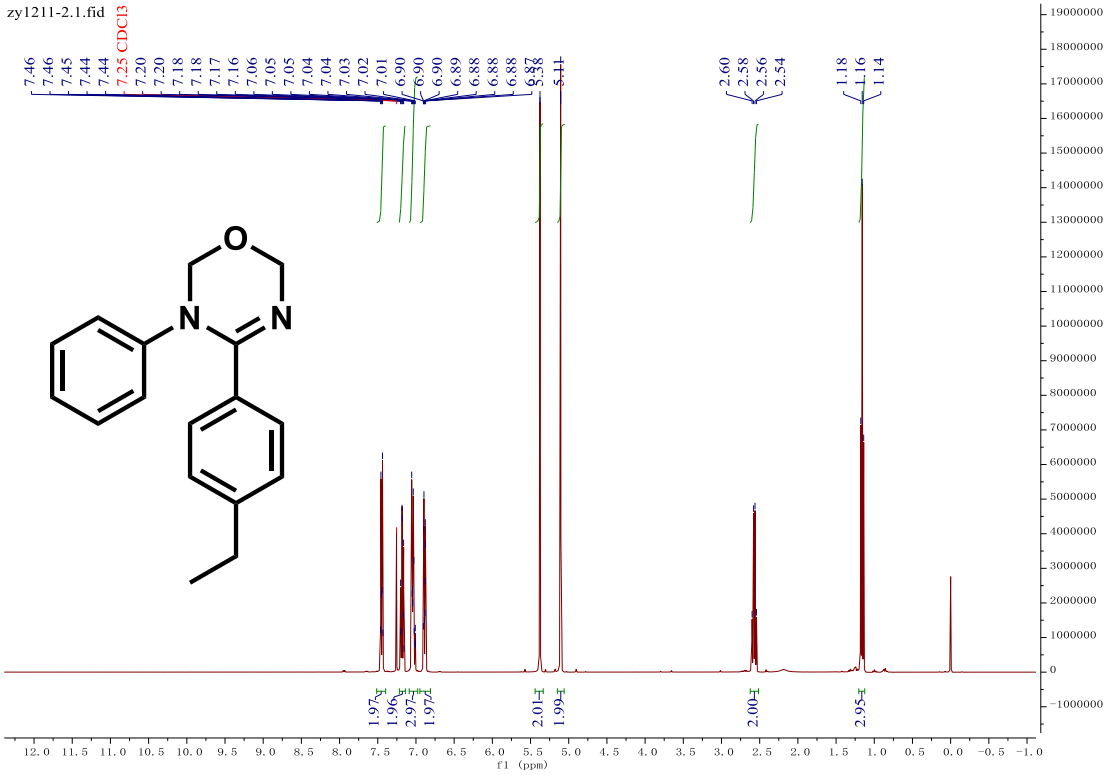
^{1}H NMR of Compound **2i** (400 MHz, $CDCl_3$)



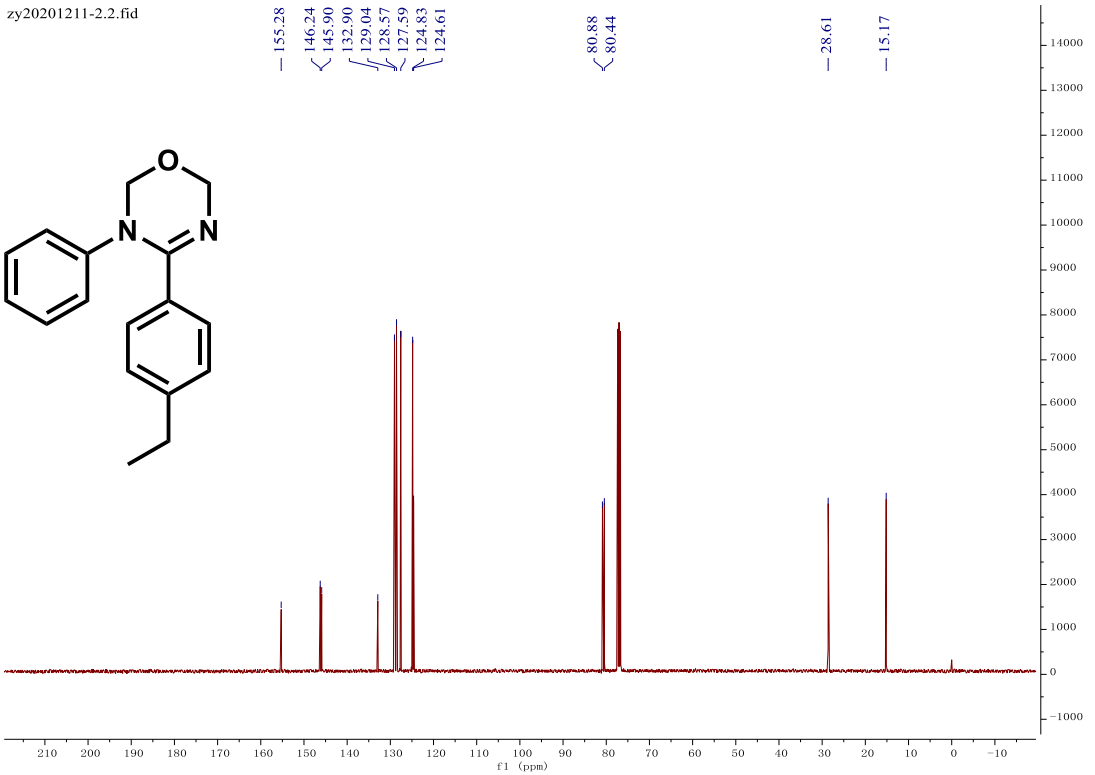
^{13}C{H} NMR of Compound **2i** (101 MHz, $CDCl_3$)



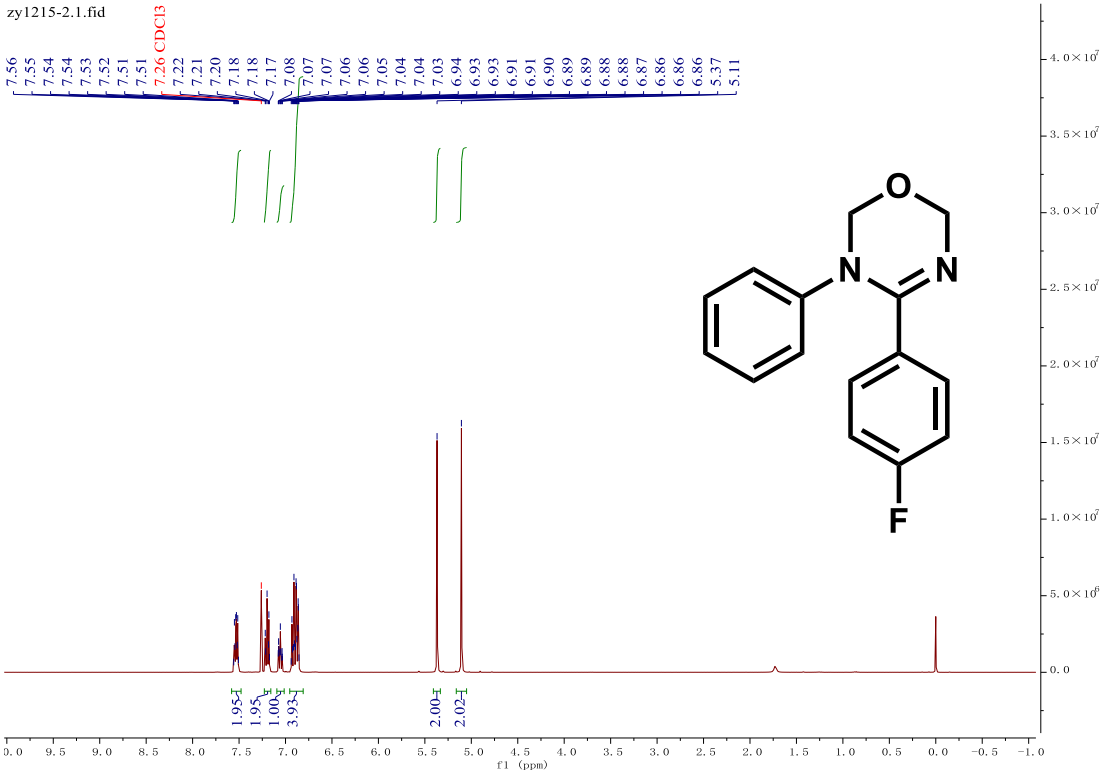
^{1}H NMR of Compound **2j** (400 MHz, $CDCl_3$)



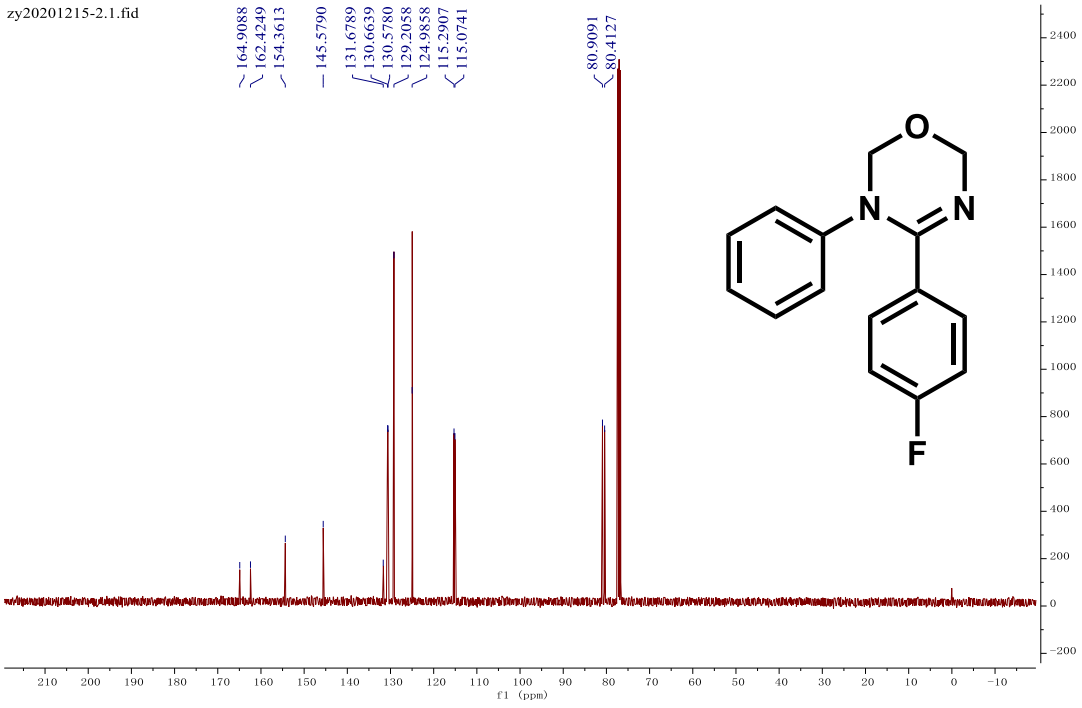
^{13}C{H} NMR of Compound **2j** (101 MHz, $CDCl_3$)



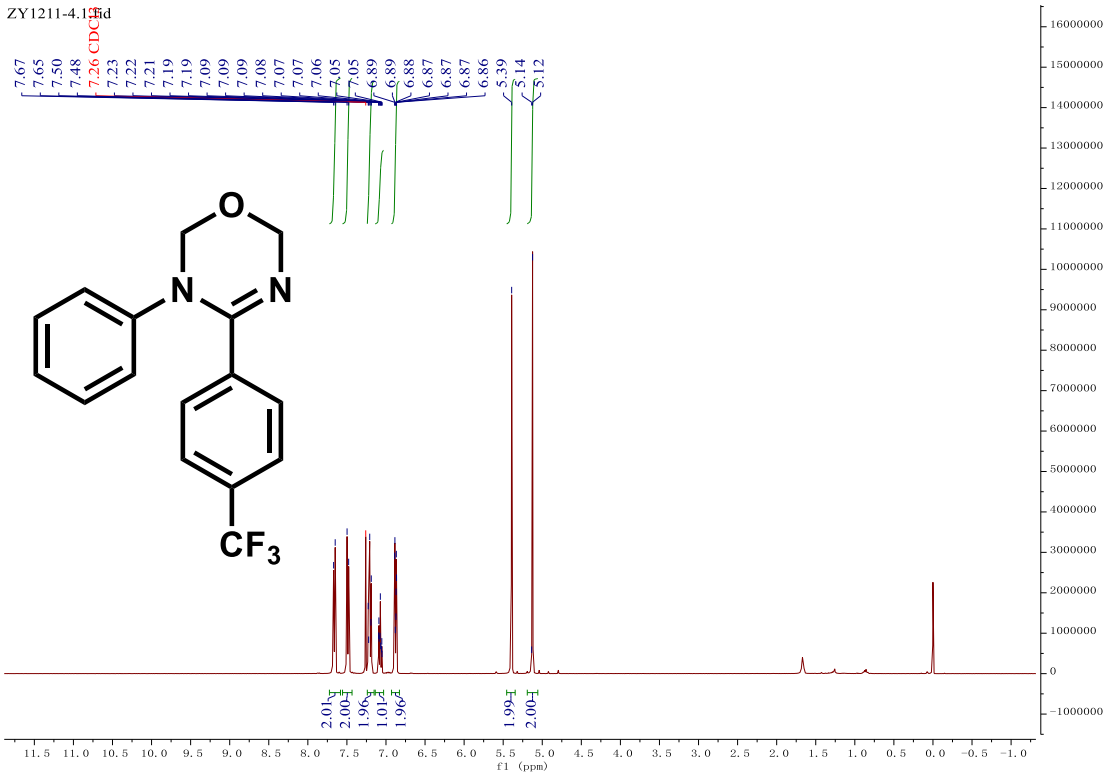
^{1}H NMR of Compound **2k** (400 MHz, $CDCl_3$)



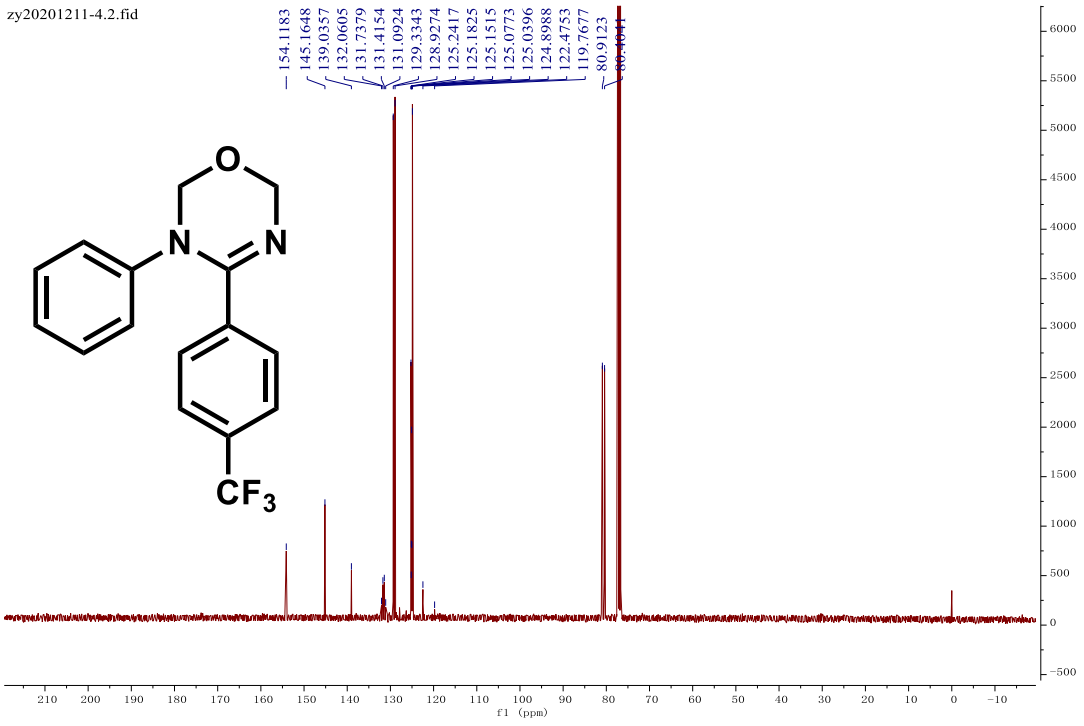
^{13}C{H} NMR of Compound **2k** (101 MHz, $CDCl_3$)



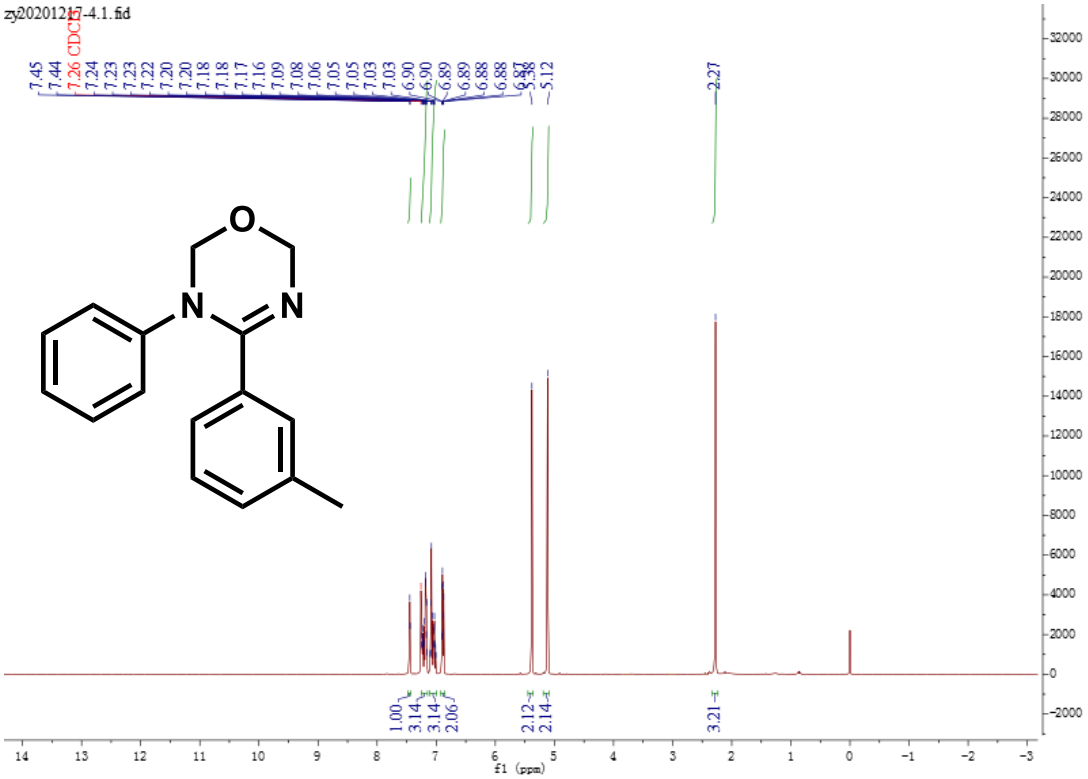
^{1}H NMR of Compound **2l** (400 MHz, $CDCl_3$)



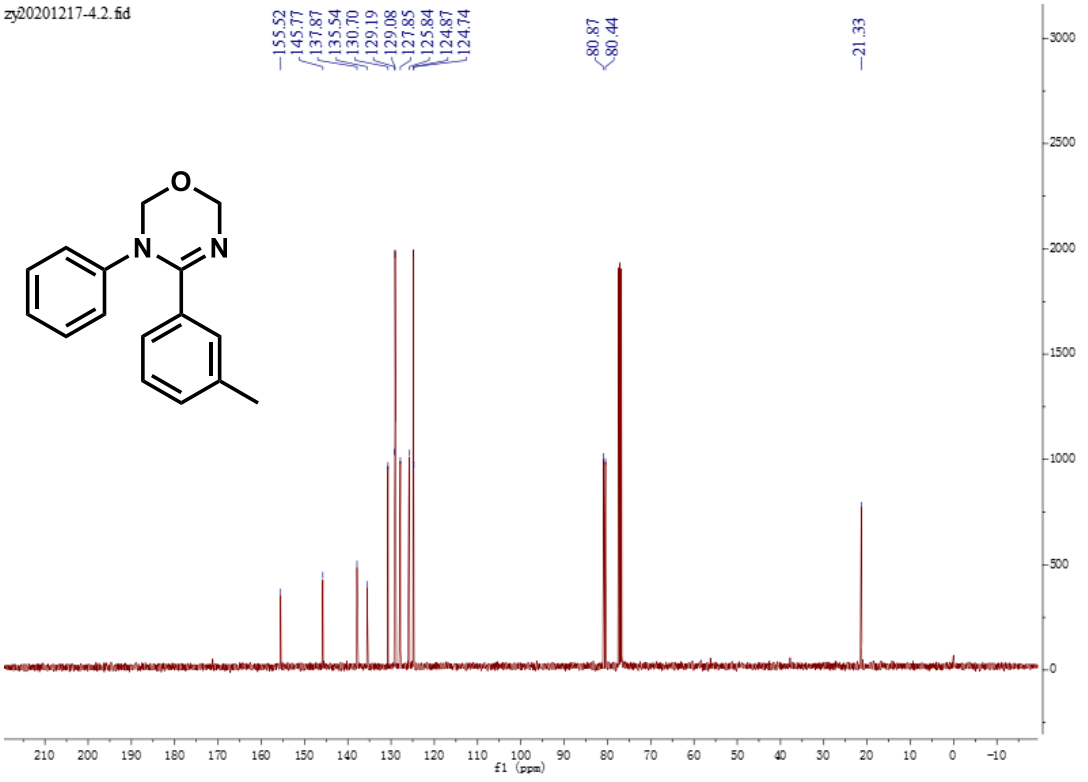
$^{13}C\{H\}$ NMR of Compound **2l** (101 MHz, $CDCl_3$)



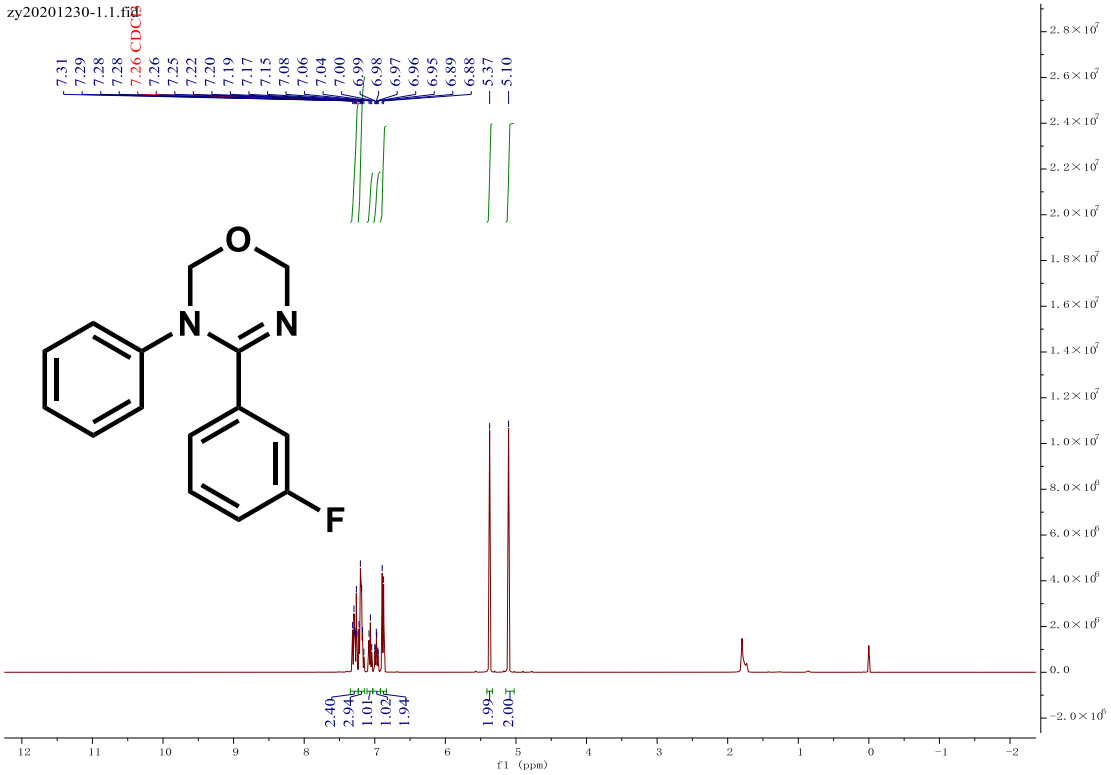
^{1}H NMR of Compound **2m** (400 MHz, $CDCl_3$)



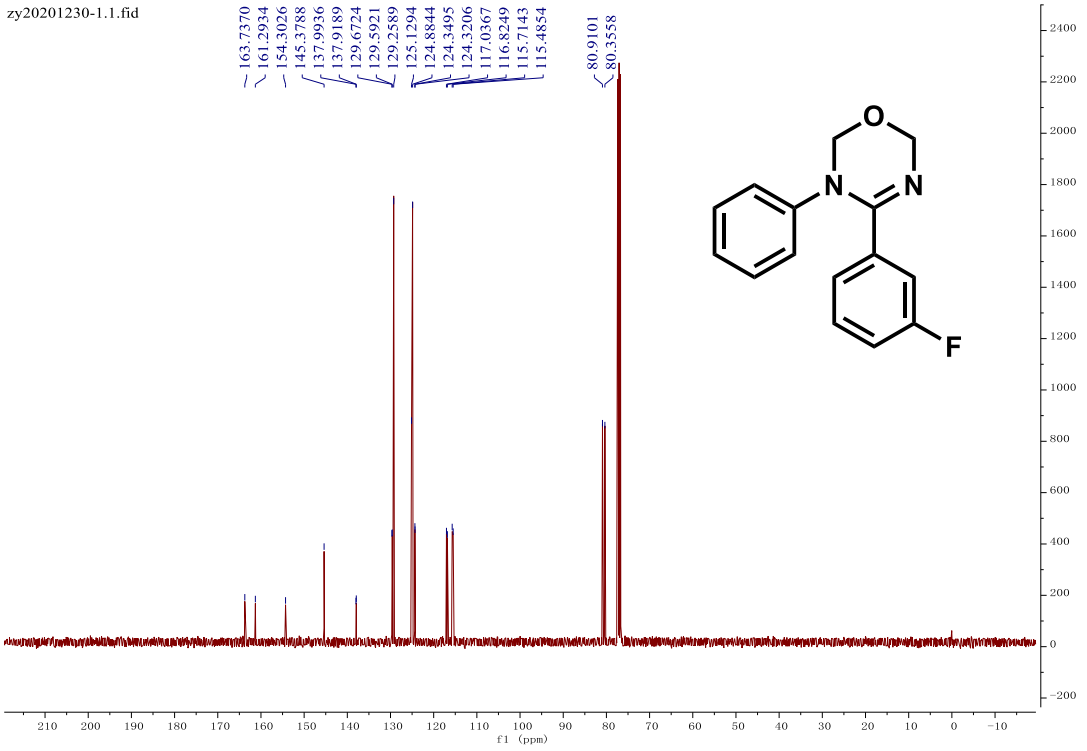
^{13}C{H} NMR of Compound **2m** (101 MHz, $CDCl_3$)



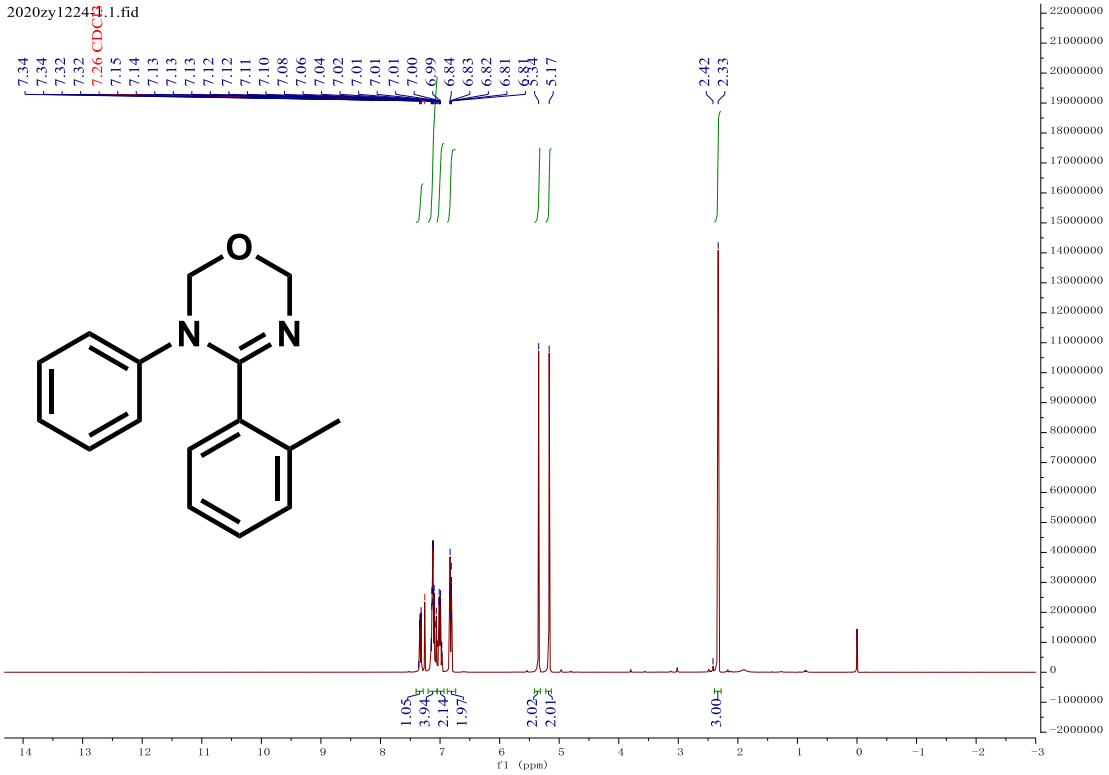
^{1}H NMR of Compound **2n** (400 MHz, $CDCl_3$)



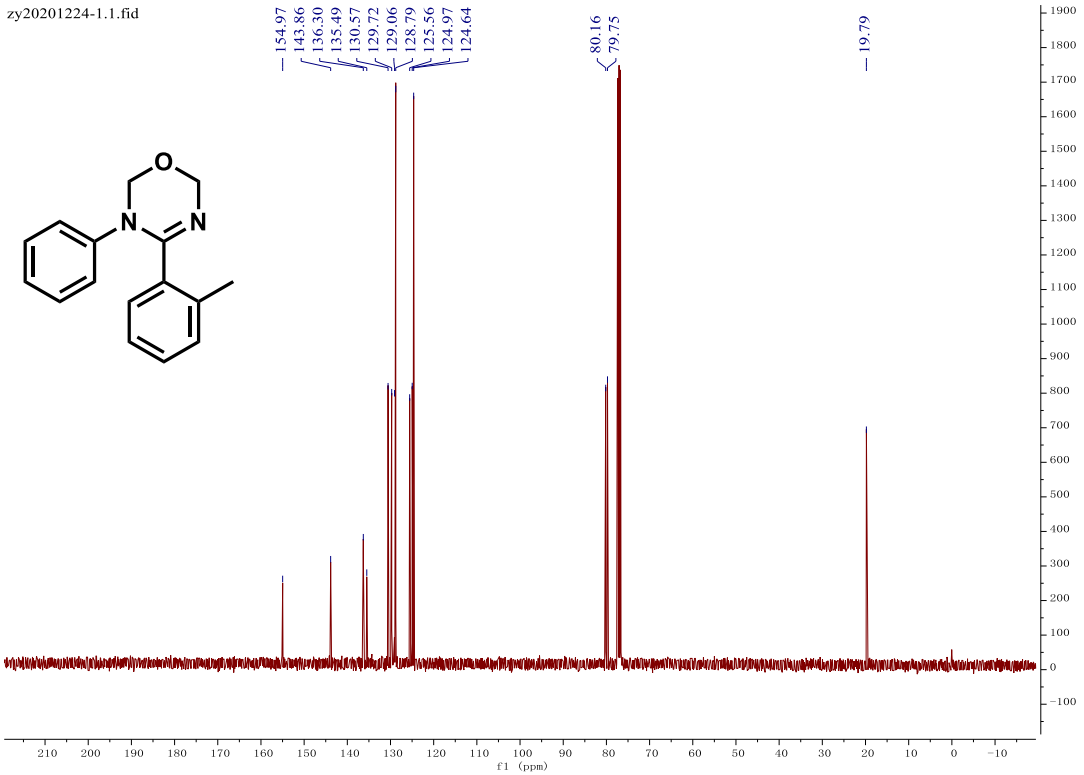
^{13}C{H} NMR of Compound **2n** (101 MHz, $CDCl_3$)



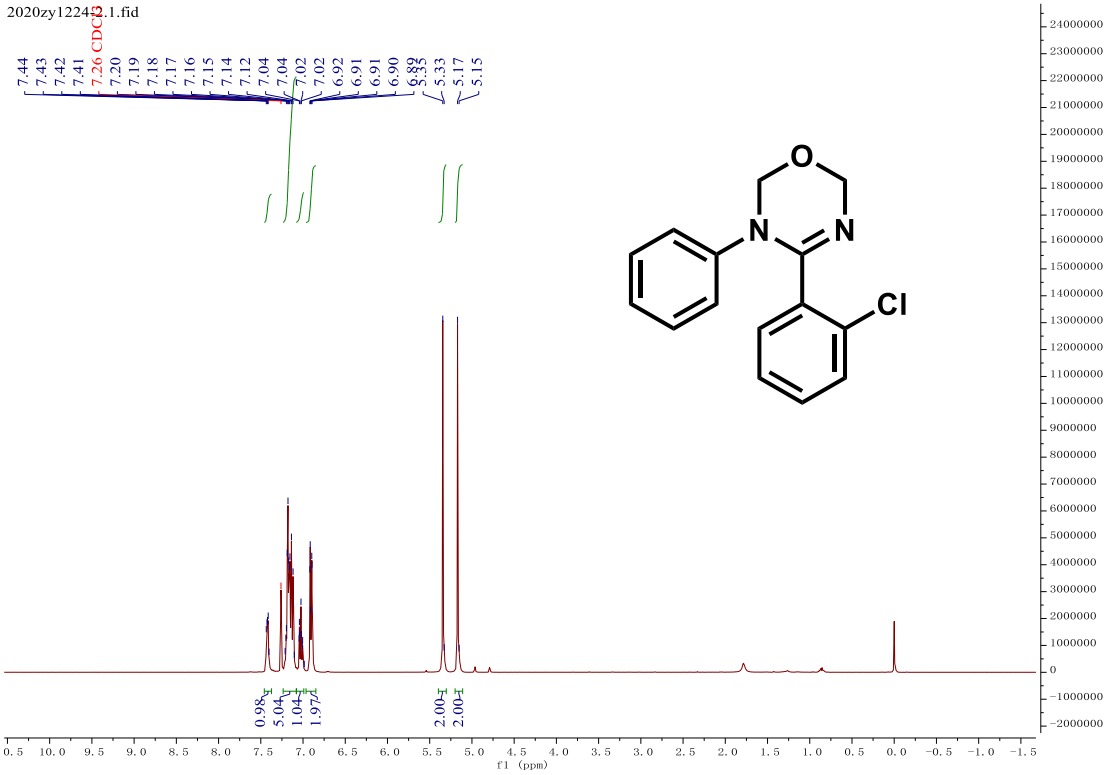
^{1}H NMR of Compound **2o** (400 MHz, $CDCl_3$)



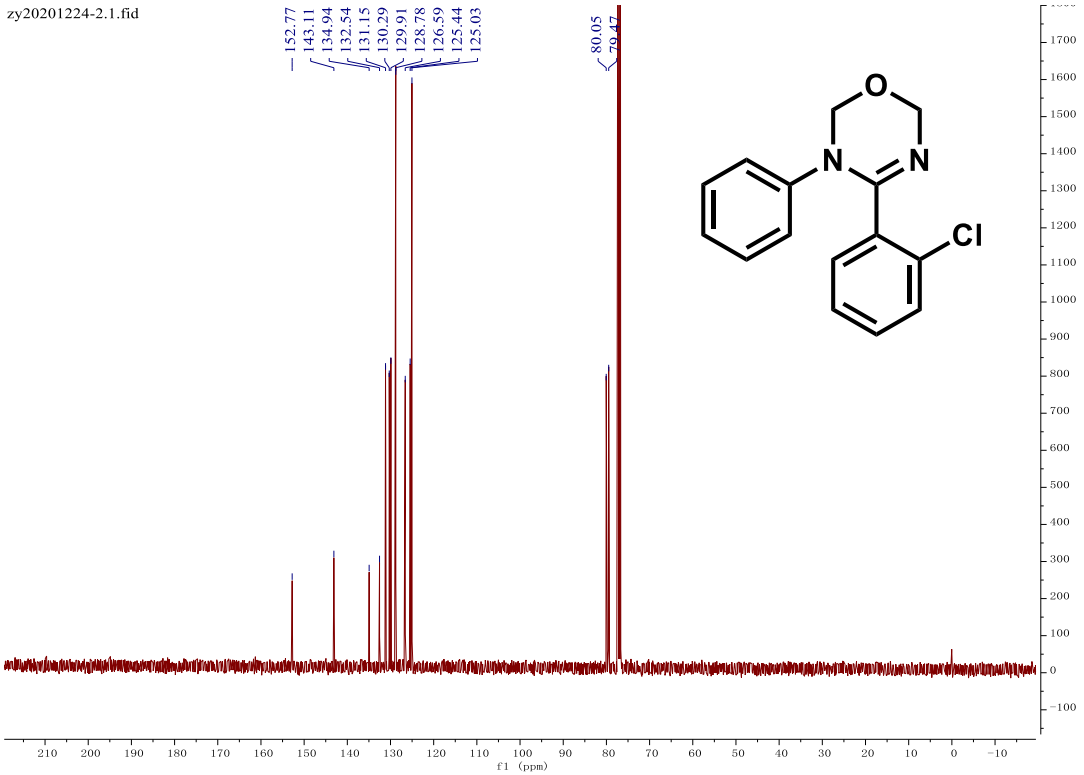
^{13}C{H} NMR of Compound **2o** (101 MHz, $CDCl_3$)



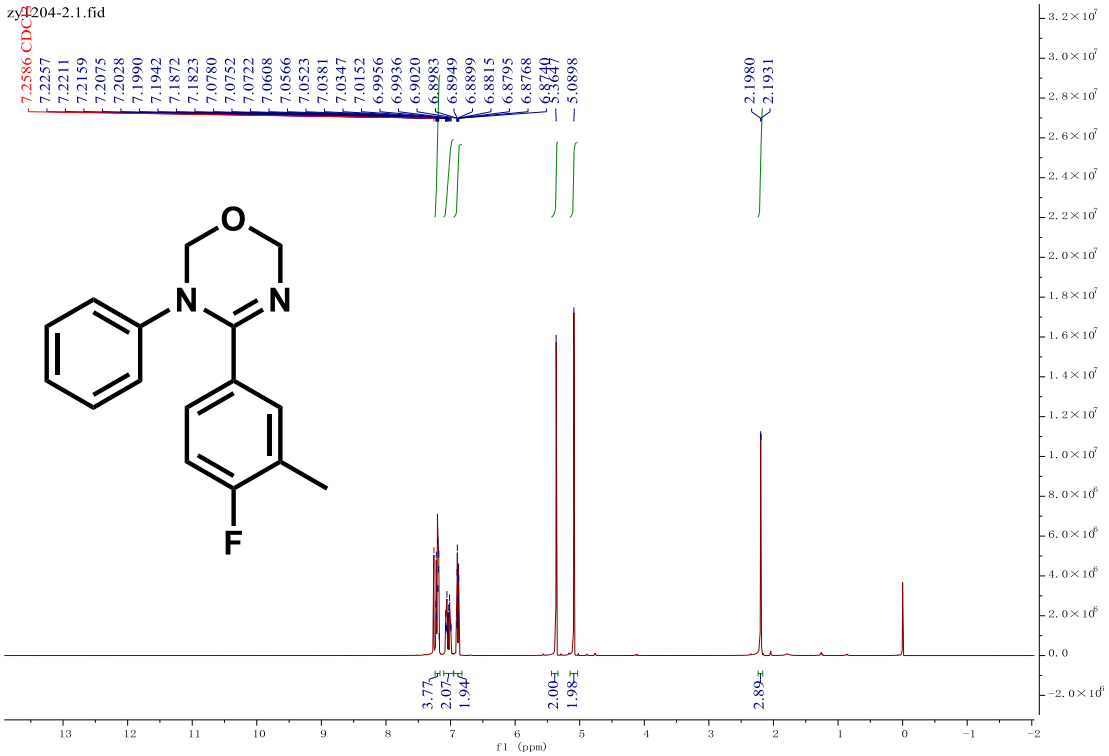
^{1}H NMR of Compound **2p** (400 MHz, $CDCl_3$)



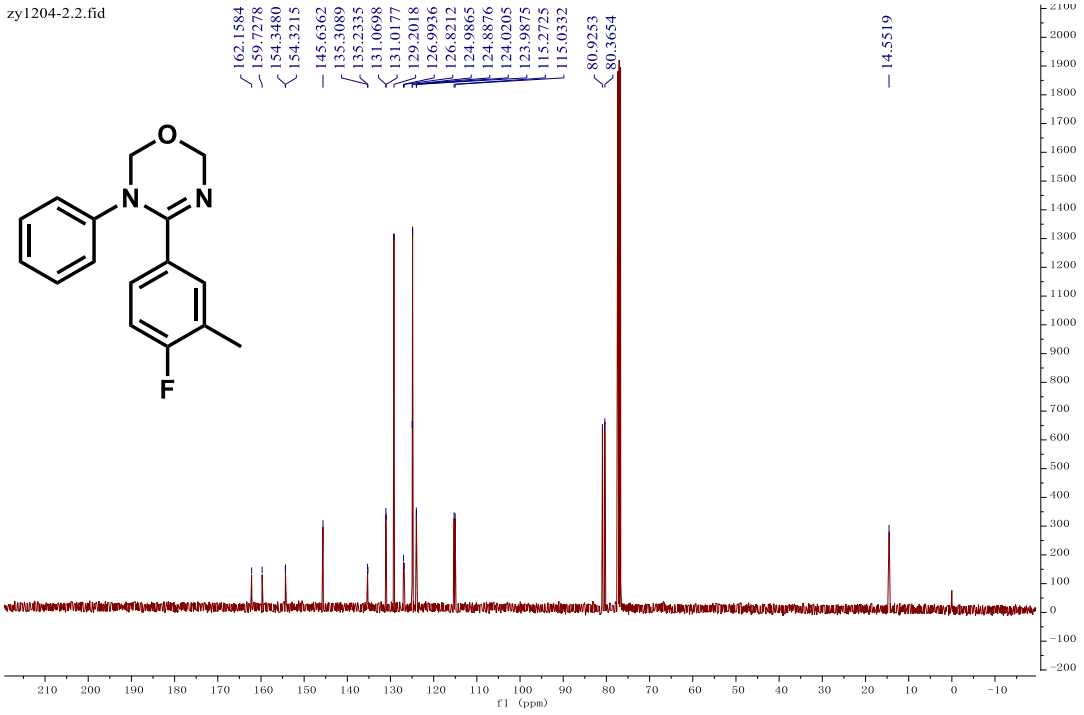
^{13}C{H} NMR of Compound **2p** (101 MHz, $CDCl_3$)



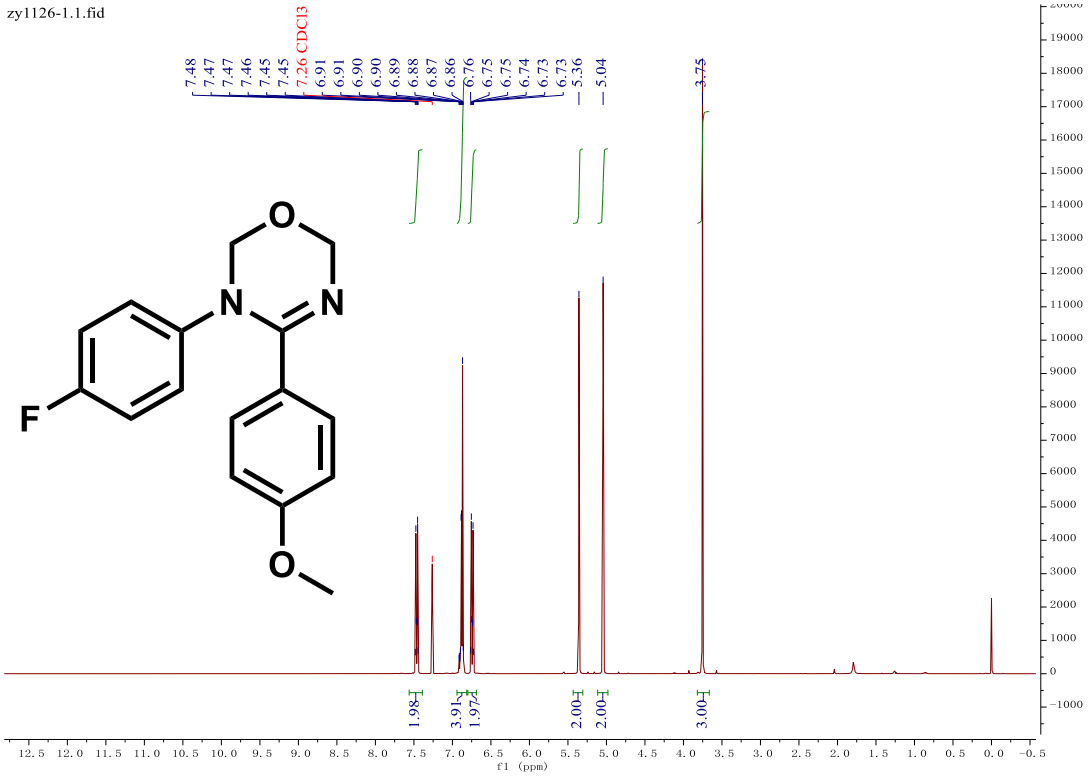
^{1}H NMR of Compound **2q** (400 MHz, $CDCl_3$)



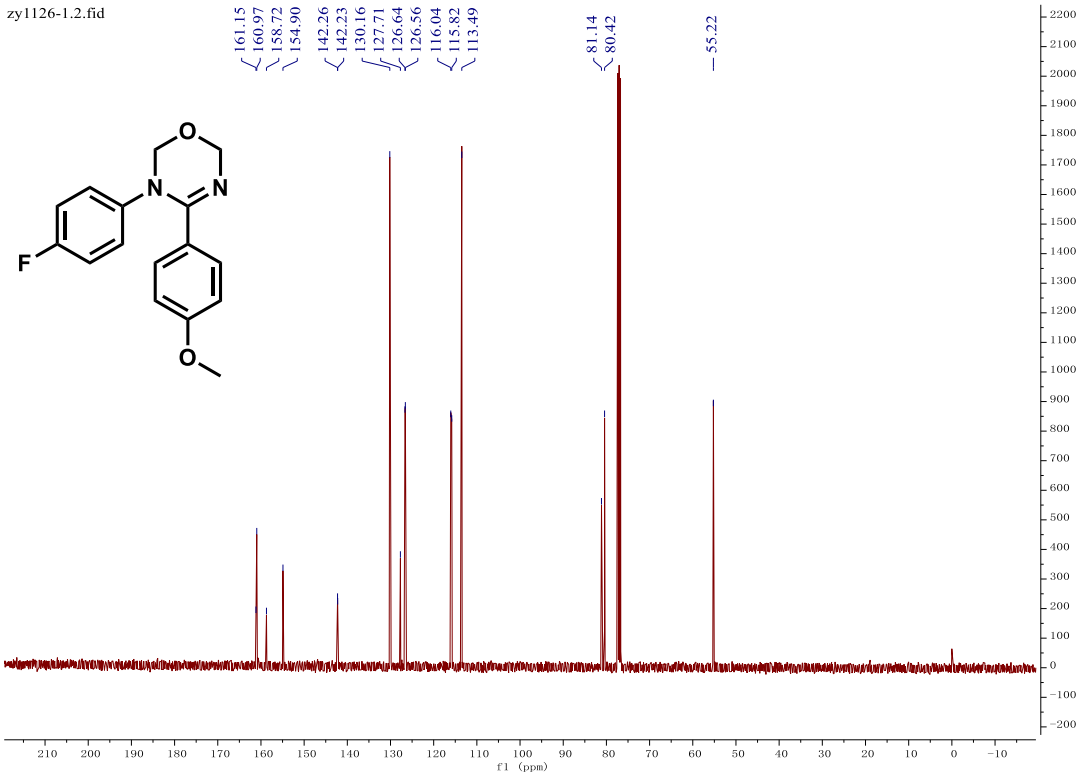
^{13}C{H} NMR of Compound **2q** (101 MHz, $CDCl_3$)



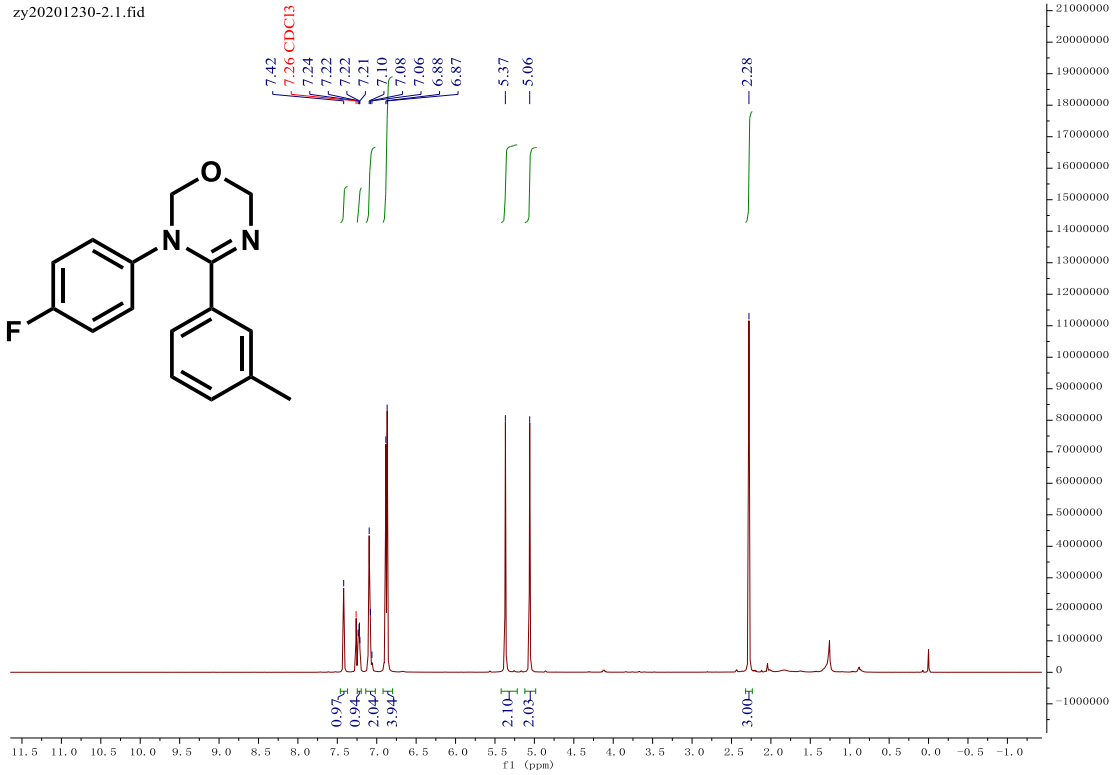
^{1}H NMR of Compound **2s** (400 MHz, $CDCl_3$)



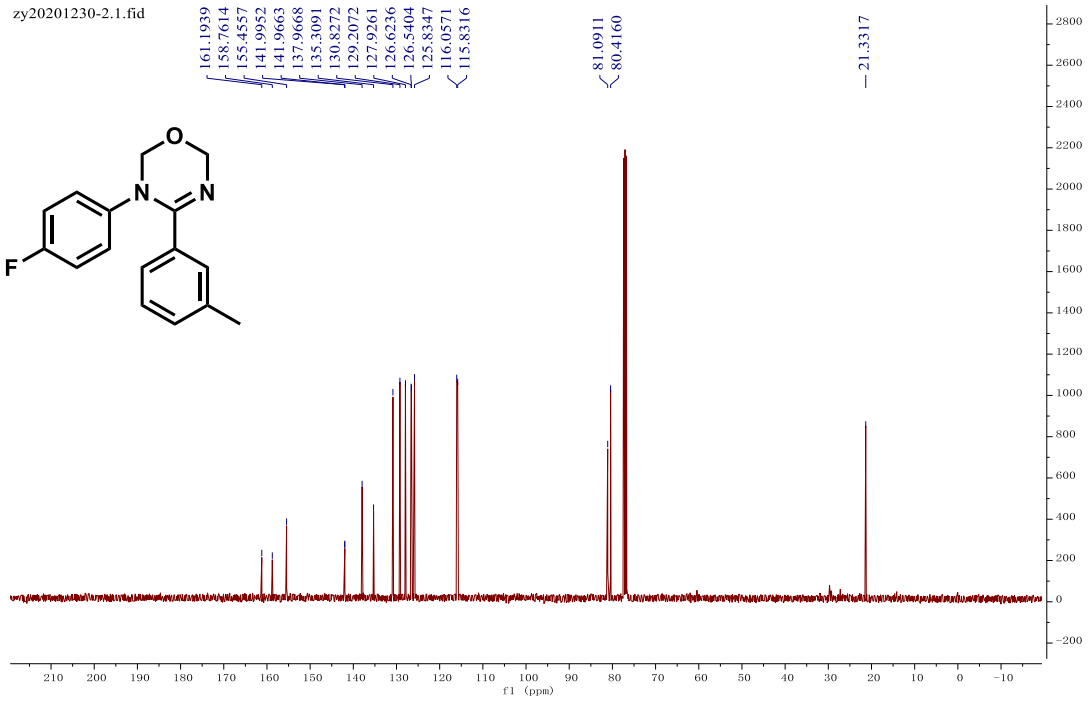
^{13}C{H} NMR of Compound **2s** (101 MHz, $CDCl_3$)



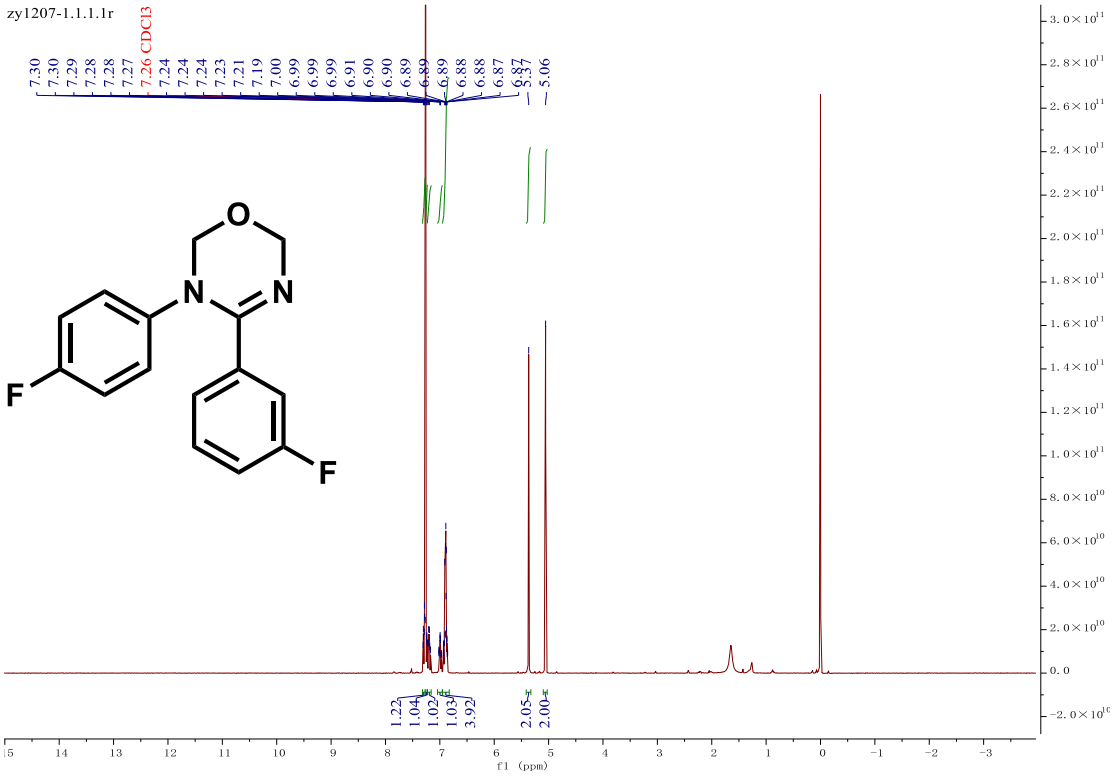
^{1}H NMR of Compound **2t** (400 MHz, $CDCl_3$)



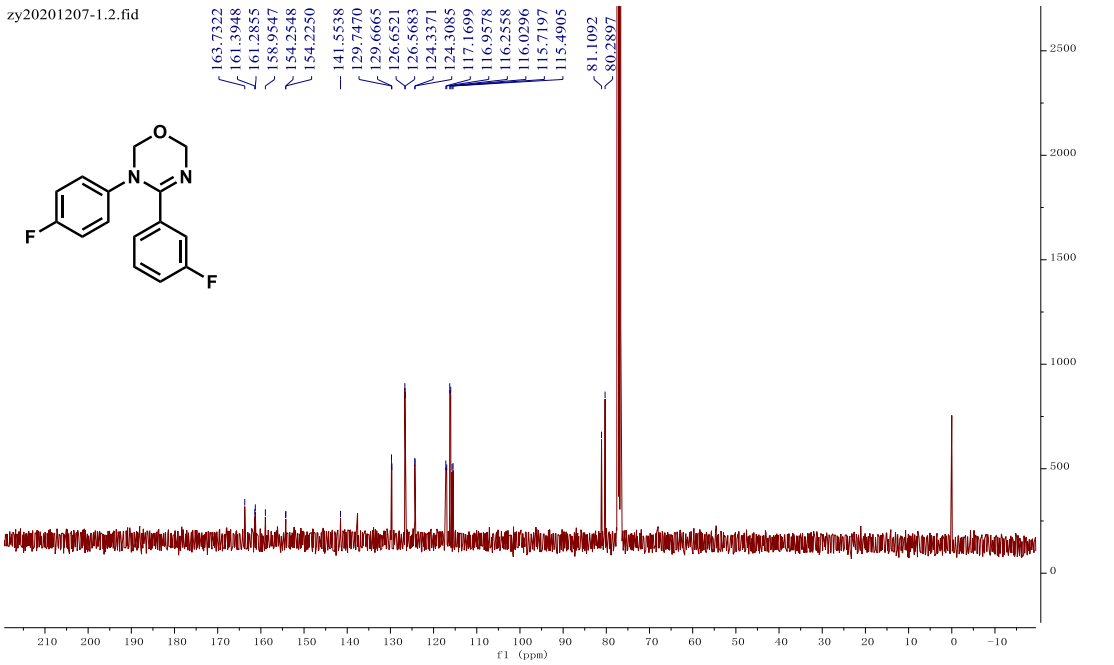
^{13}C{H} NMR of Compound **2t** (101 MHz, $CDCl_3$)



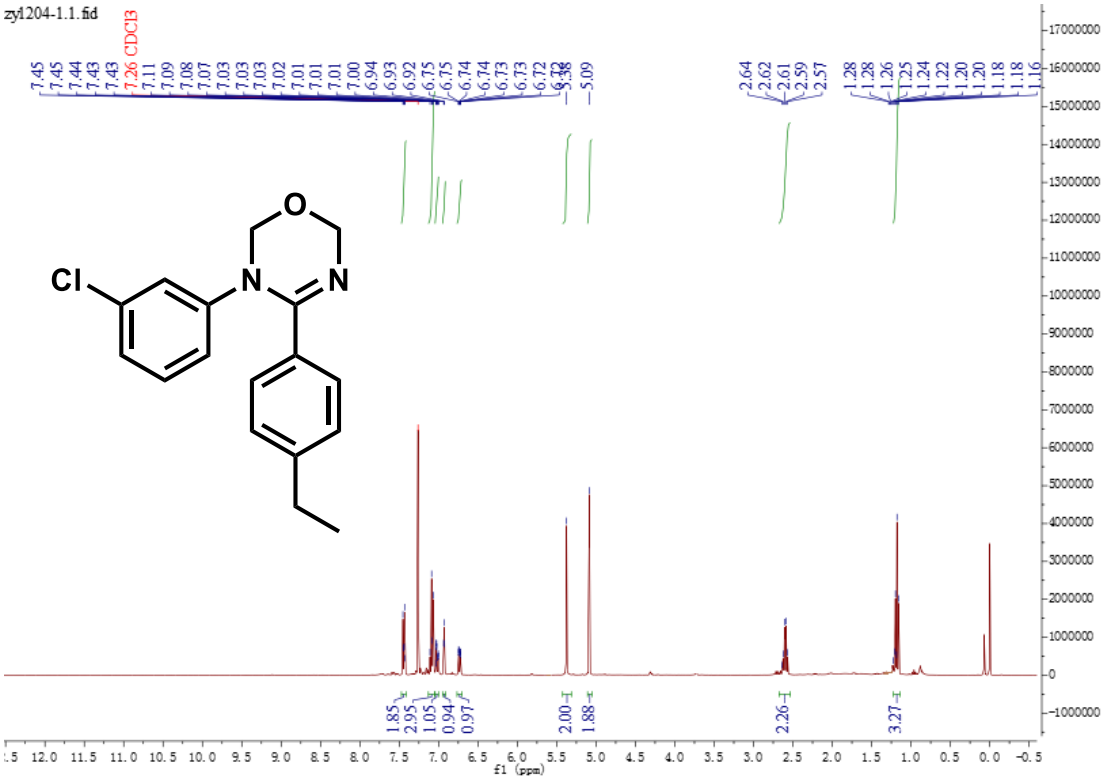
^{1}H NMR of Compound **2u** (400 MHz, $CDCl_3$)



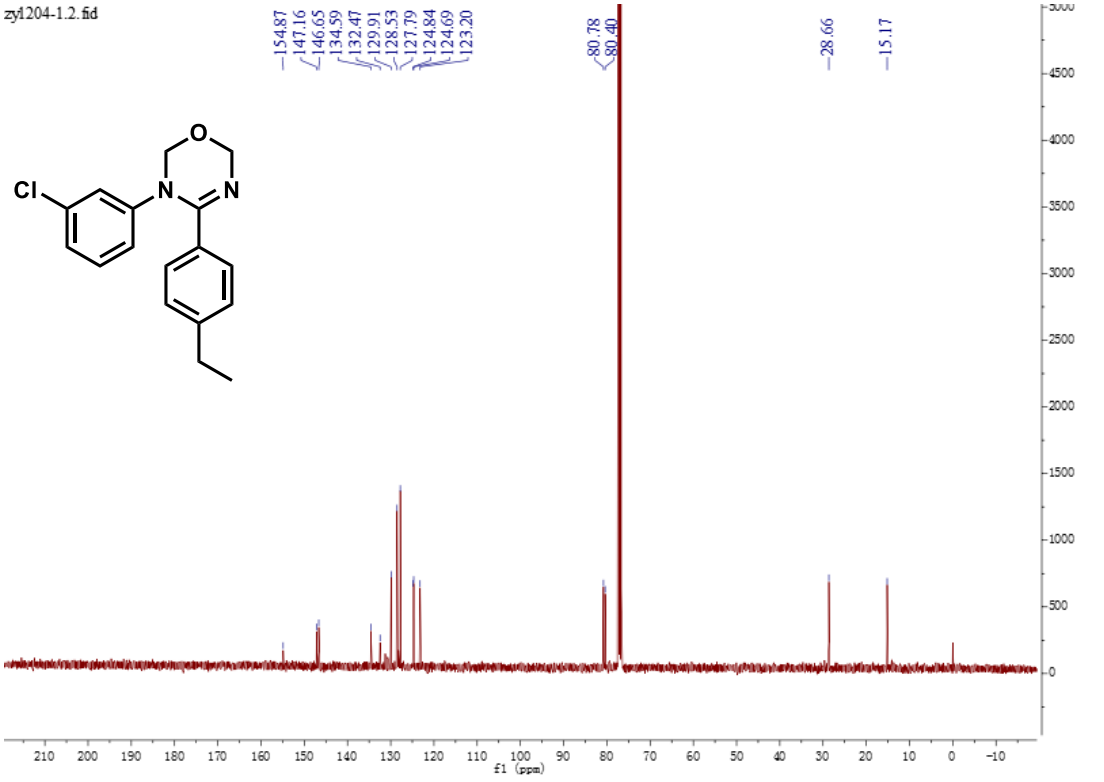
^{13}C{H} NMR of Compound **2u** (101 MHz, $CDCl_3$)



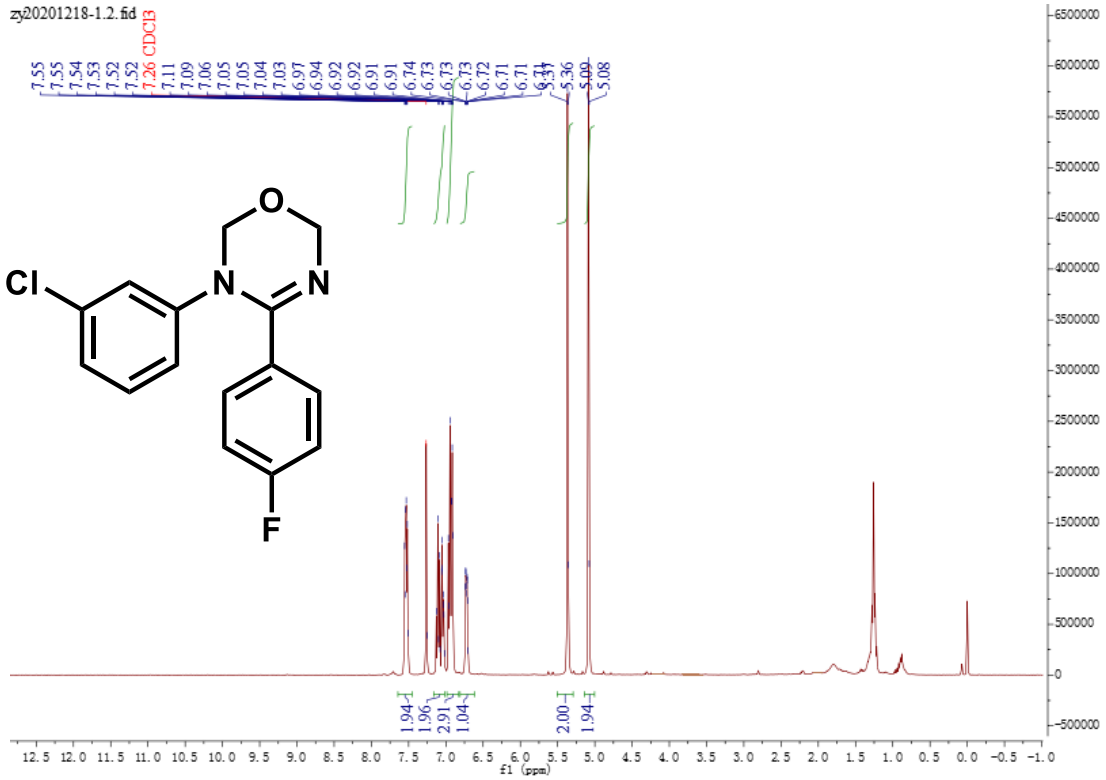
^{1}H NMR of Compound **2v** (400 MHz, $CDCl_3$)



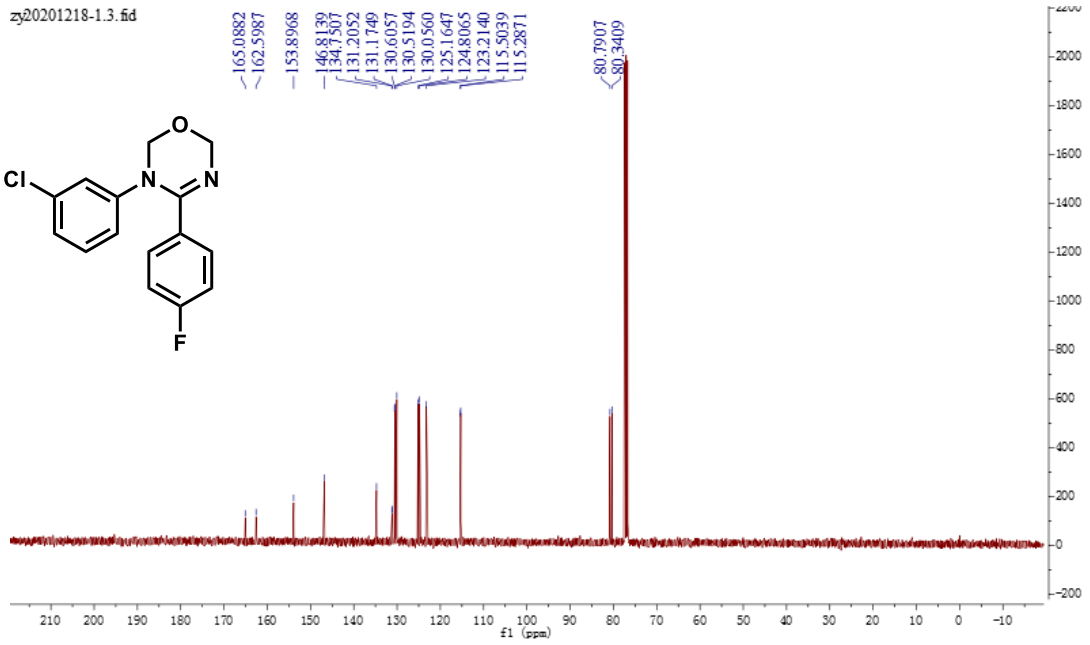
^{13}C{H} NMR of Compound **2v**(101 MHz, $CDCl_3$)



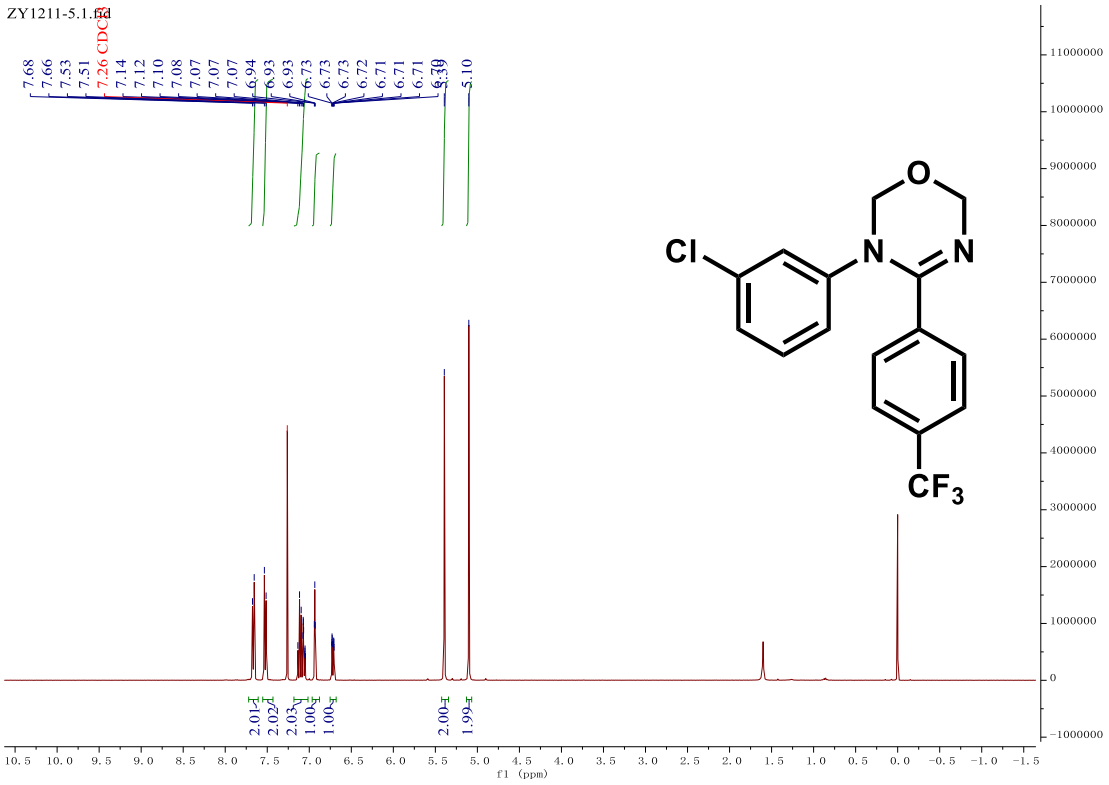
^{1}H NMR of Compound **2w** (400 MHz, $CDCl_3$)



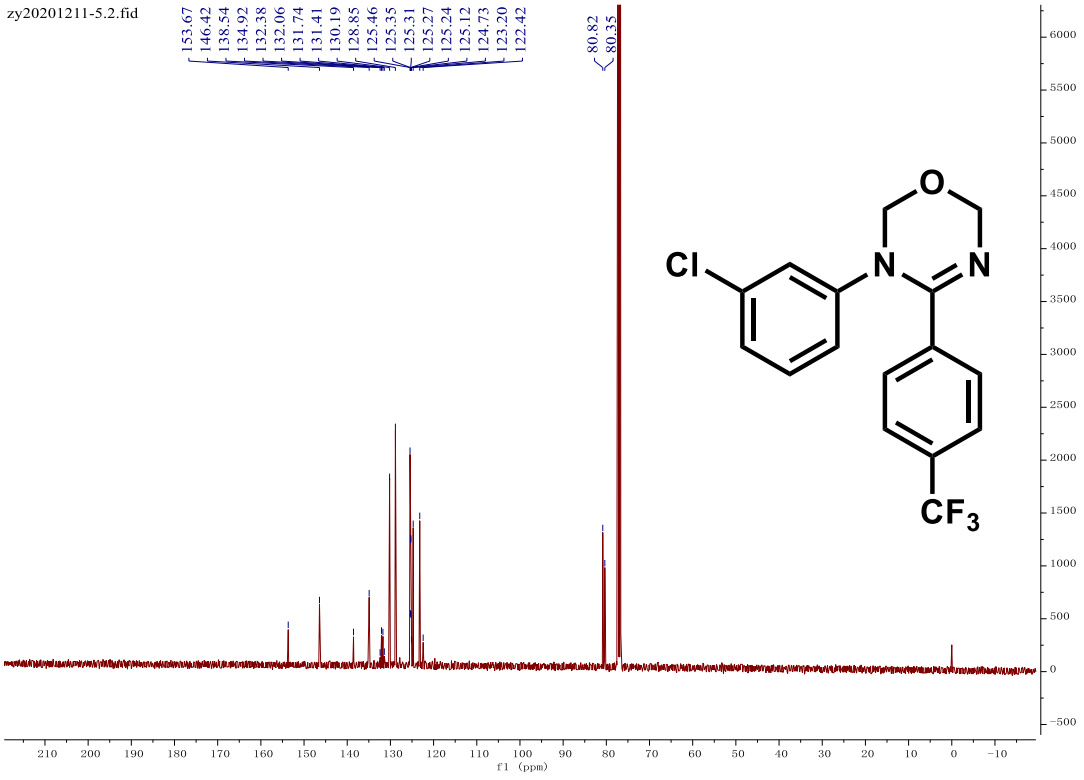
^{13}C{H} NMR of Compound **2w** (101 MHz, $CDCl_3$)



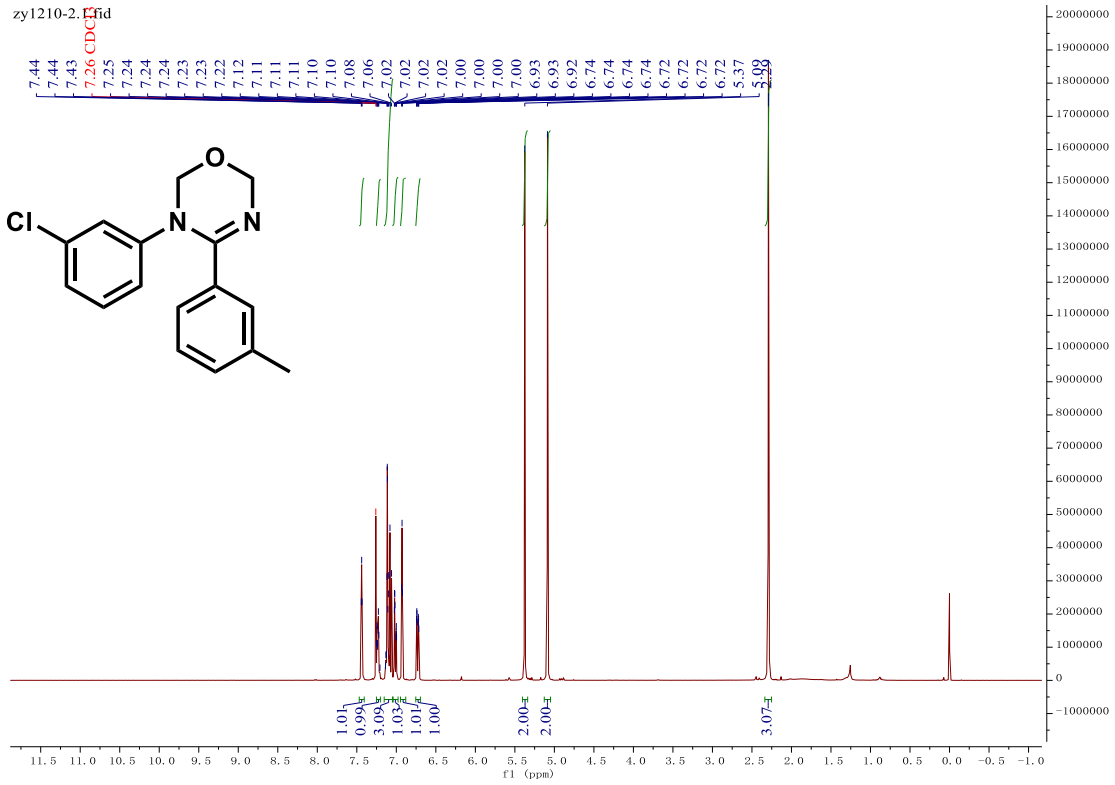
^{1}H NMR of Compound **2x** (400 MHz, $CDCl_3$)



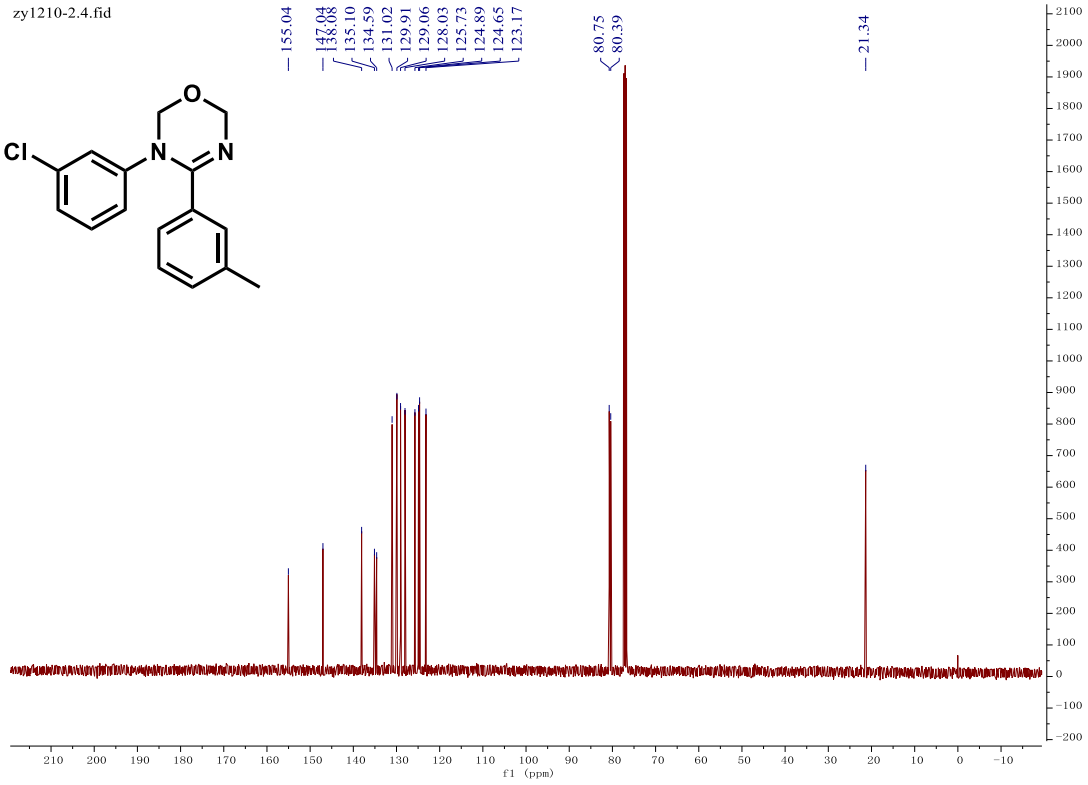
^{13}C{H} NMR of Compound **2x** (101 MHz, $CDCl_3$)



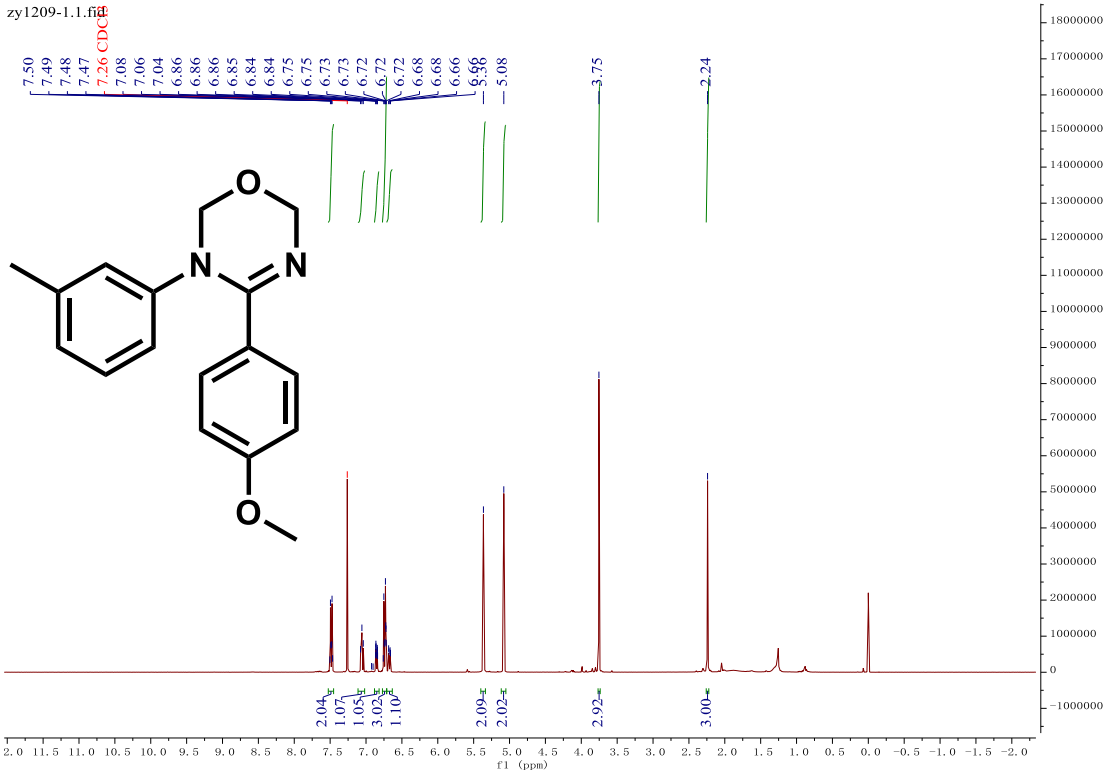
^{1}H NMR of Compound **2y** (400 MHz, $CDCl_3$)



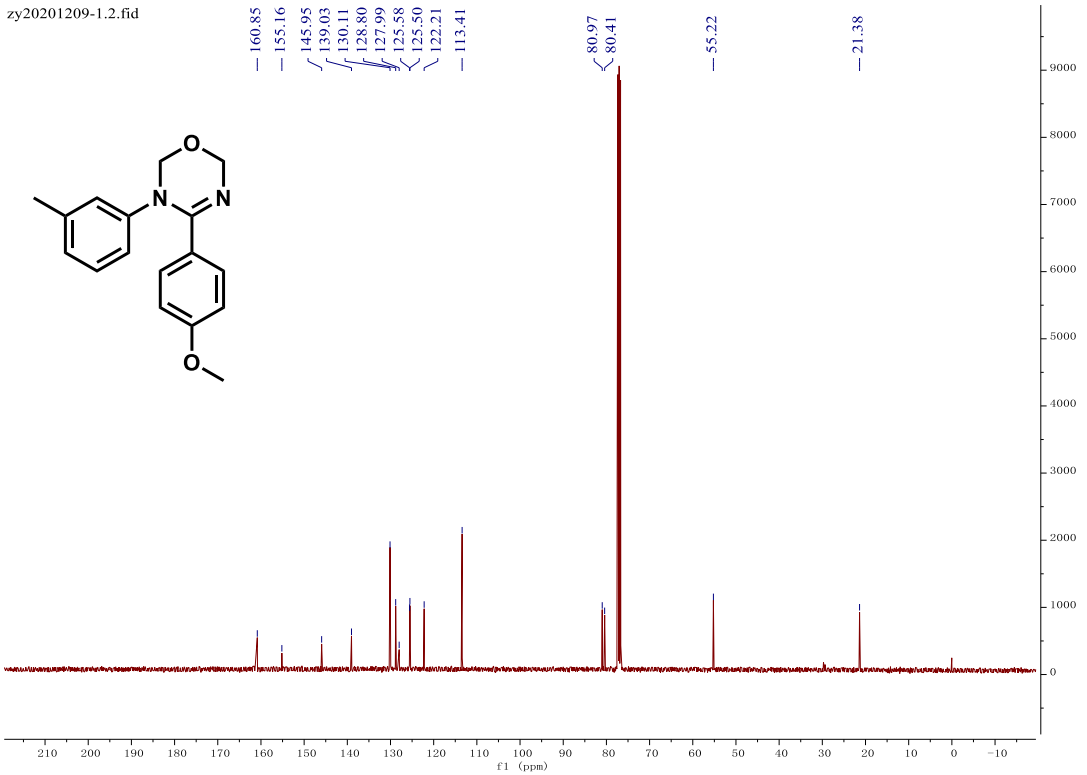
^{13}C{H} NMR of Compound **2y** (101 MHz, $CDCl_3$)



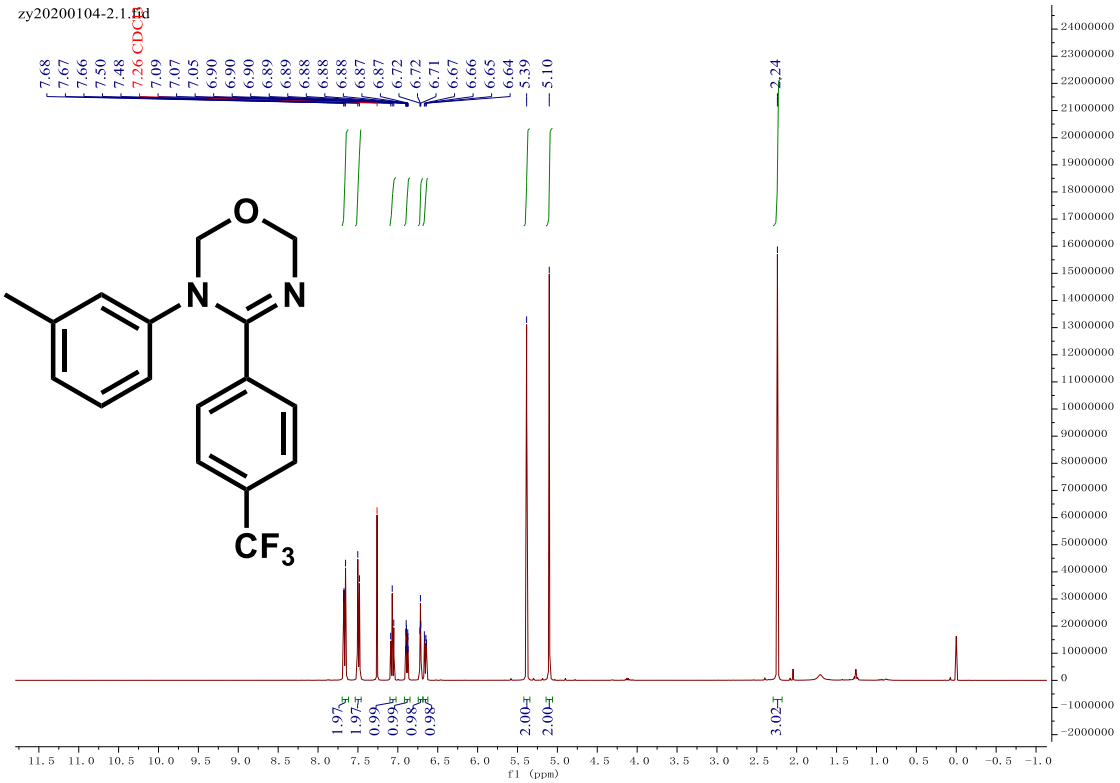
^{1}H NMR of Compound **2z** (400 MHz, $CDCl_3$)



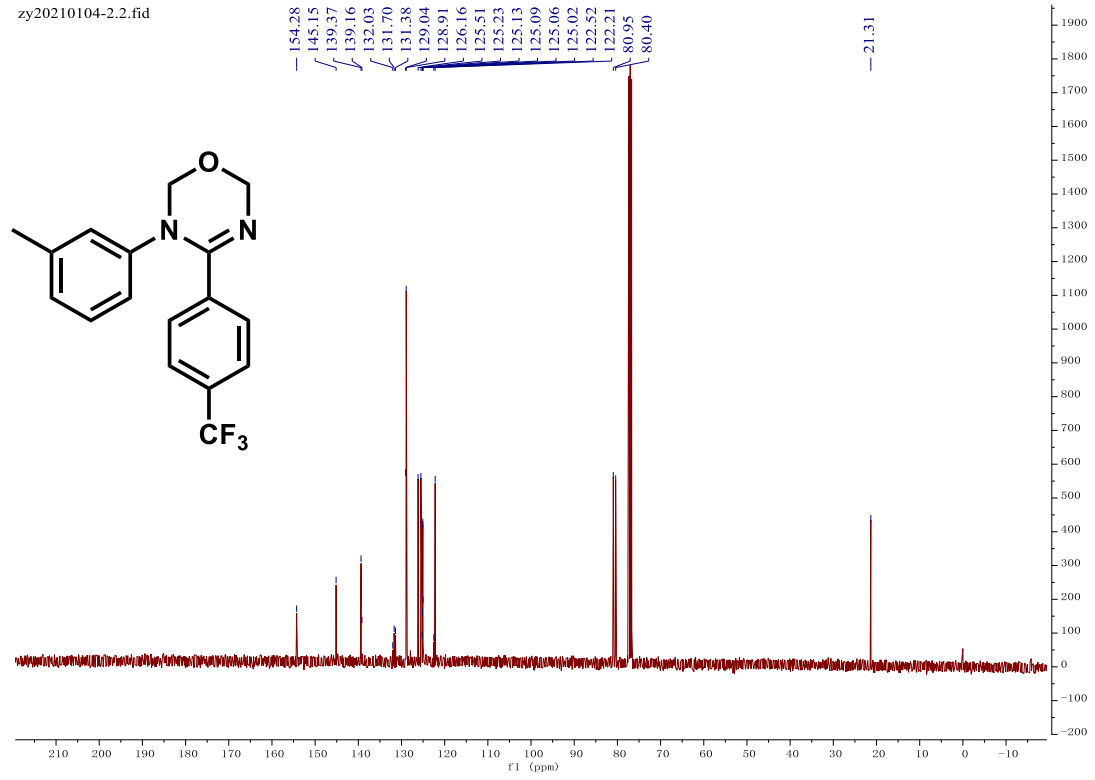
^{13}C{H} NMR of Compound **2z** (101 MHz, $CDCl_3$)



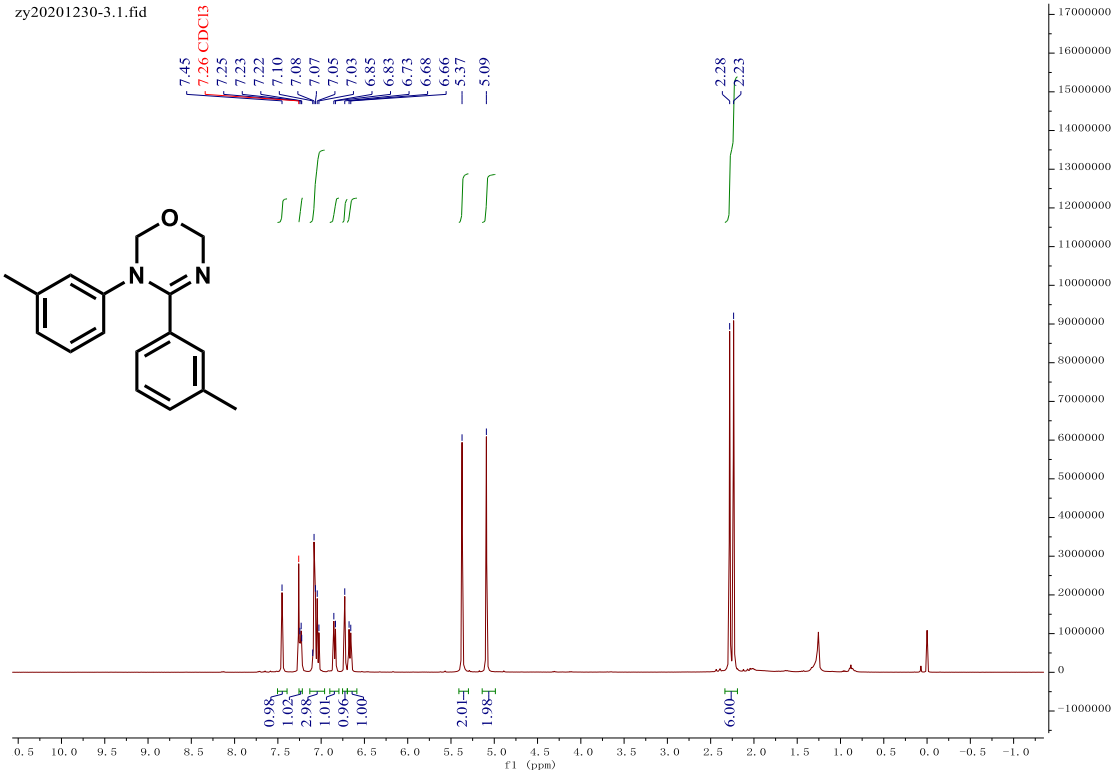
^{1}H NMR of Compound **2a'** (400 MHz, $CDCl_3$)



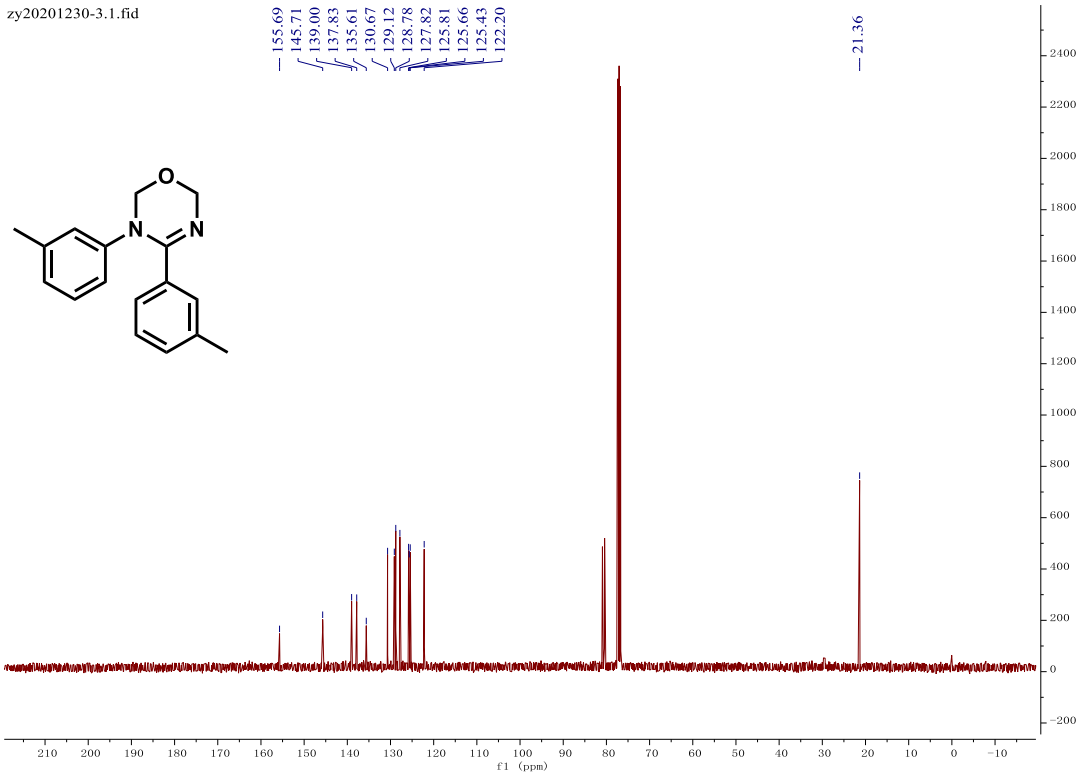
^{13}C{H} NMR of Compound **2a'** (101 MHz, $CDCl_3$)



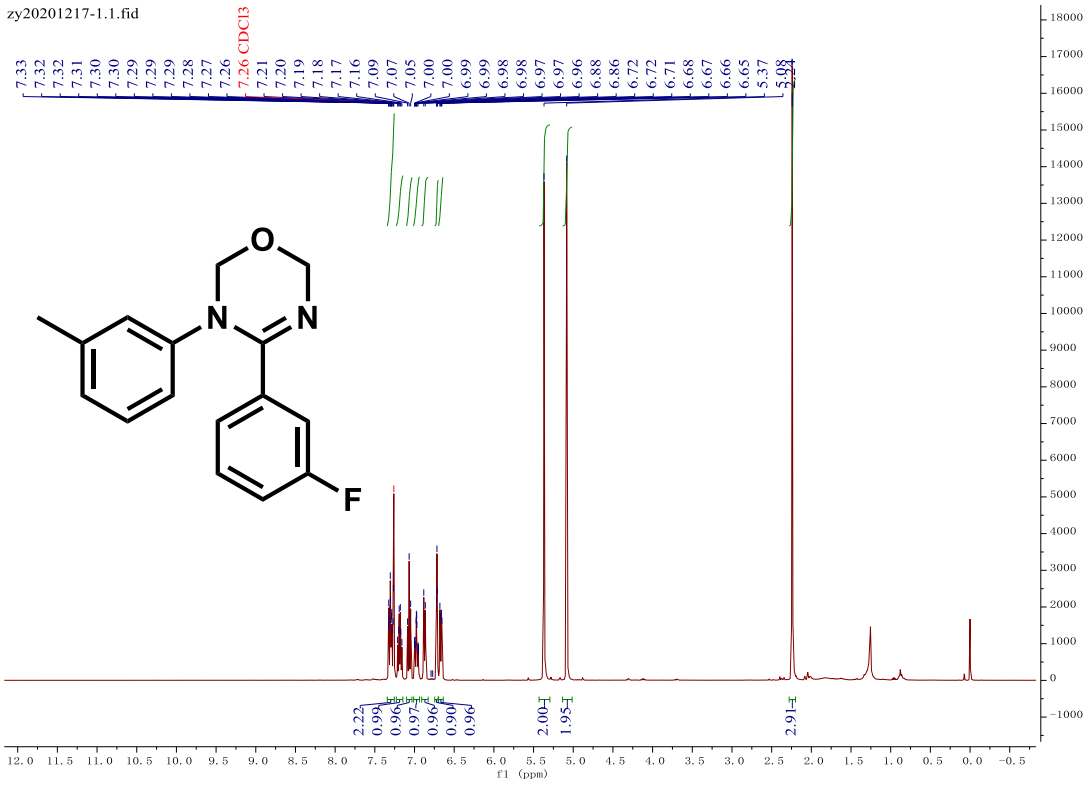
^{1}H NMR of Compound **2b'** (400 MHz, $CDCl_3$)



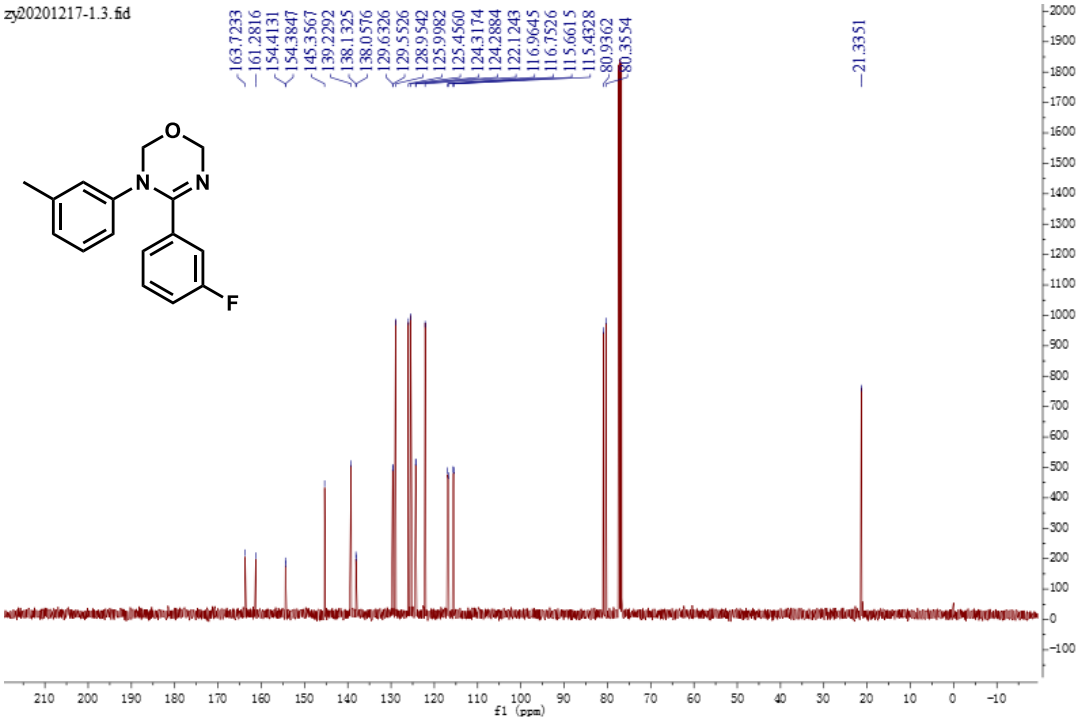
^{13}C{H} NMR of Compound **2b'** (101 MHz, $CDCl_3$)



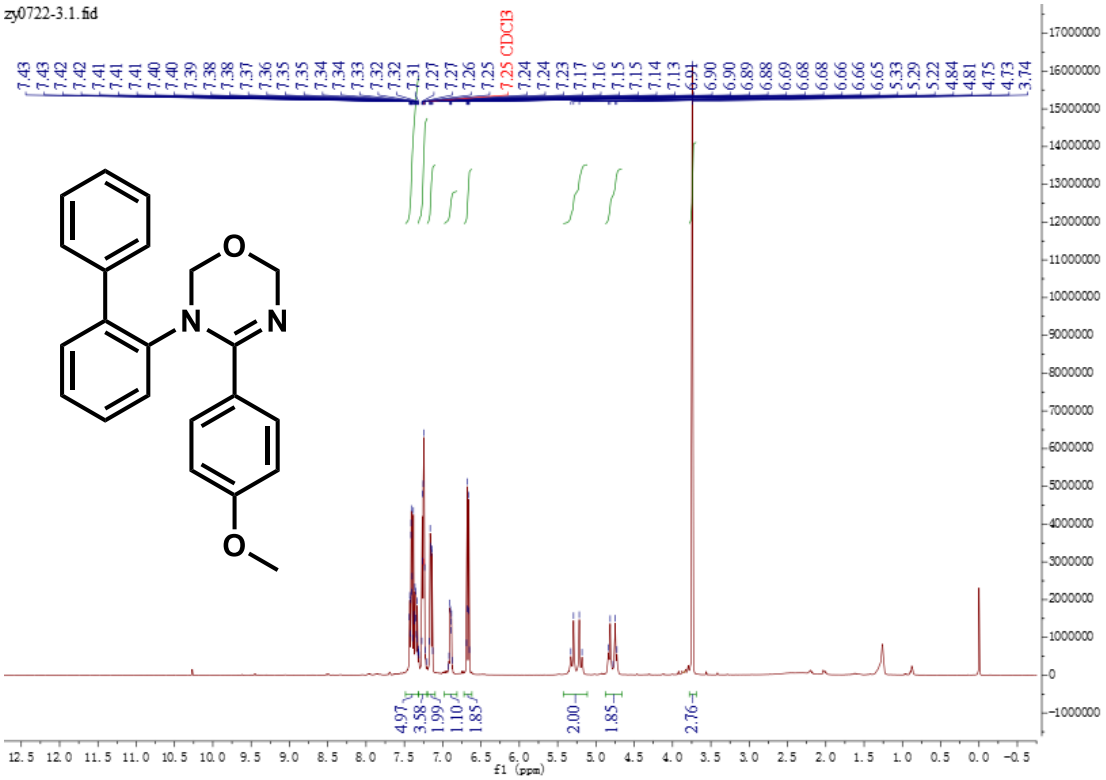
^{1}H NMR of Compound **2c'** (400 MHz, $CDCl_3$)



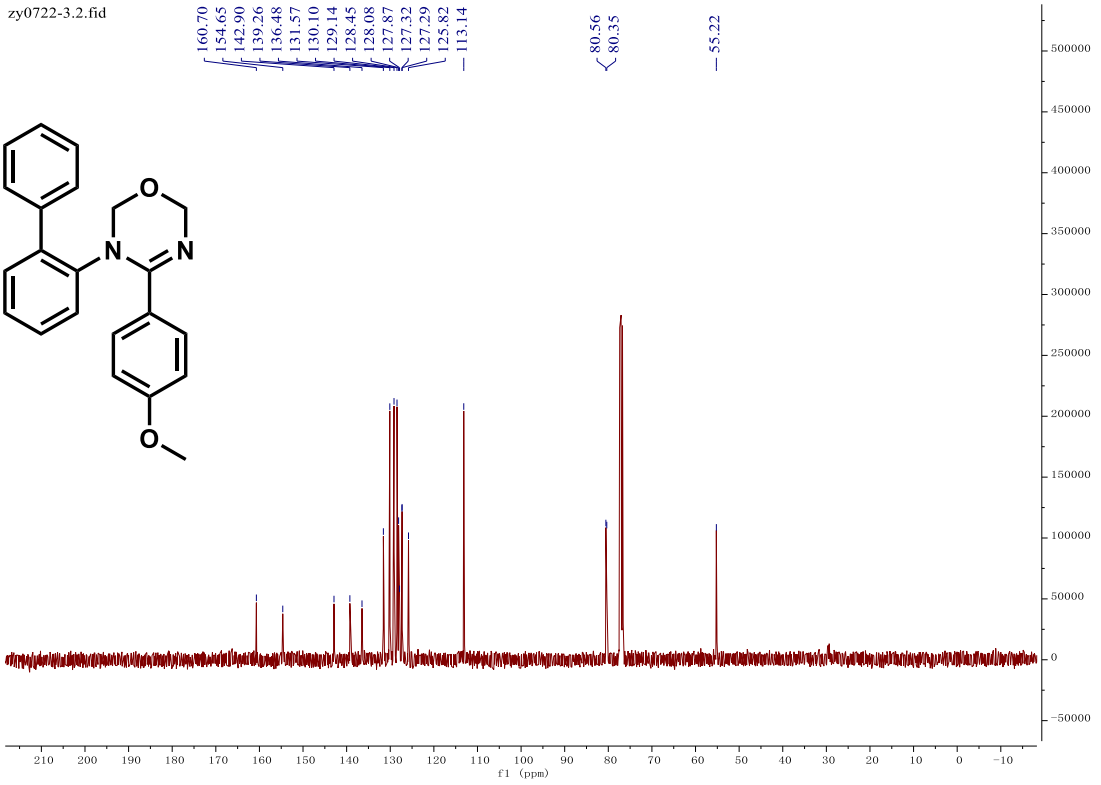
^{13}C{H} NMR of Compound **2c'** (101 MHz, $CDCl_3$)



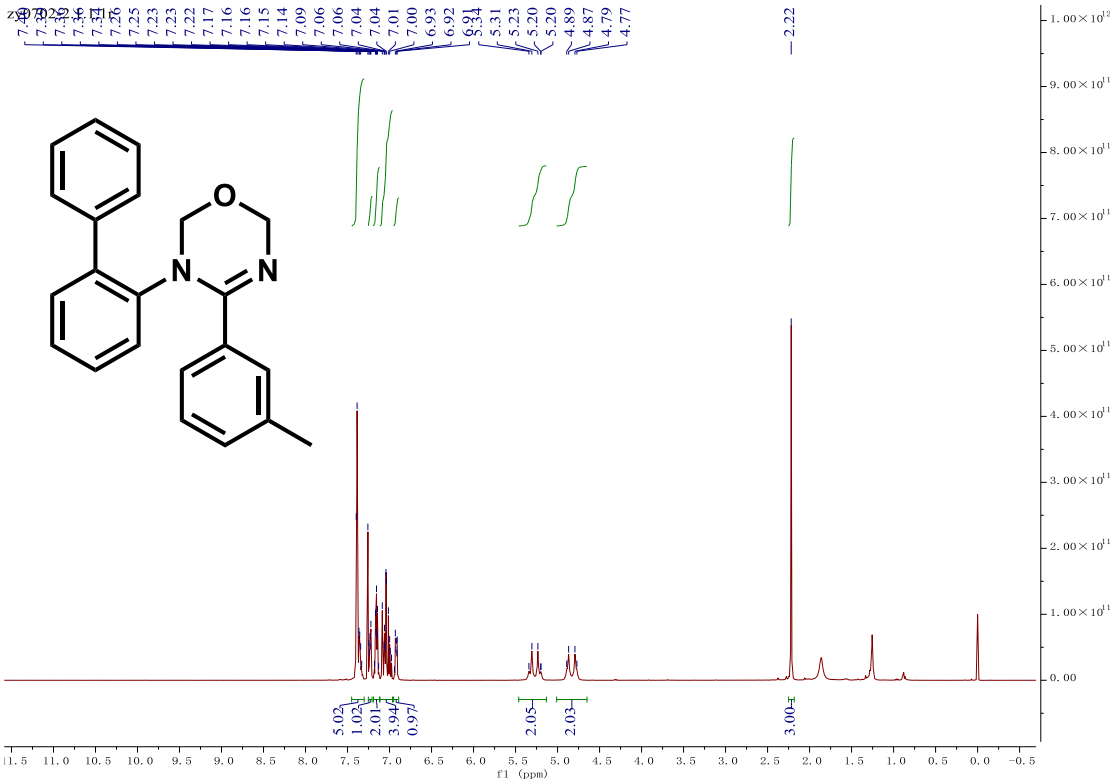
^{1}H NMR of Compound **2d'** (400 MHz, $CDCl_3$)



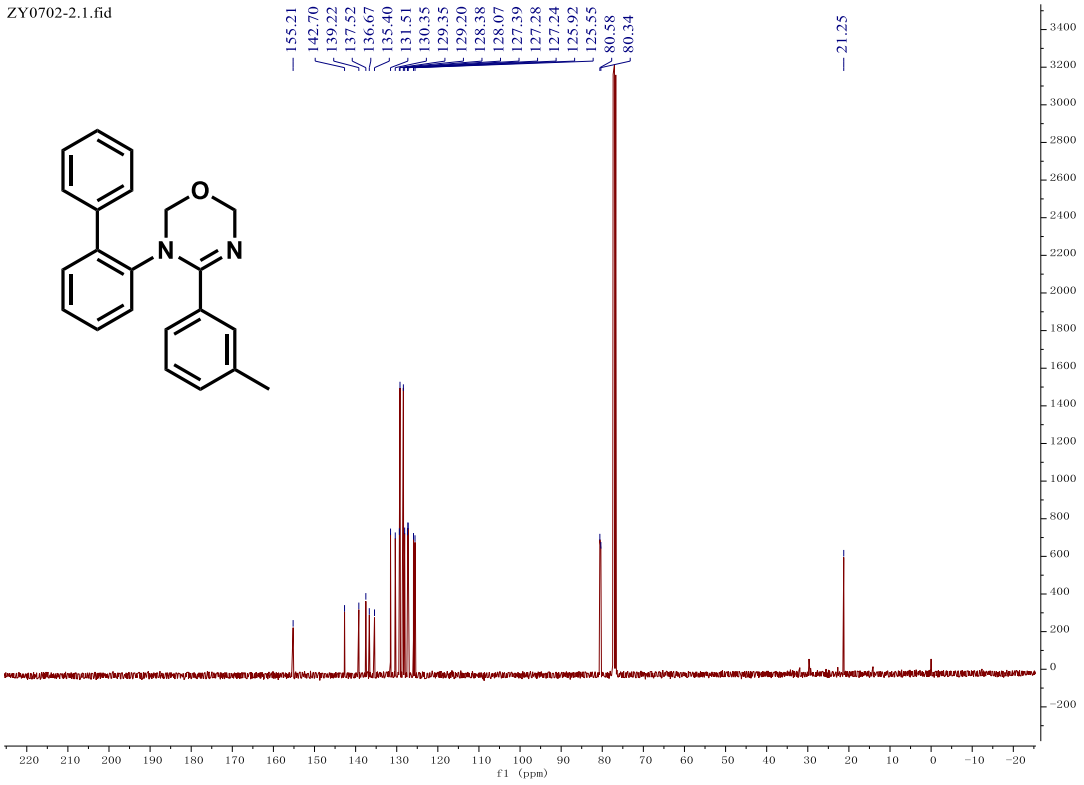
^{13}C{H} NMR of Compound **2d'** (101 MHz, $CDCl_3$)



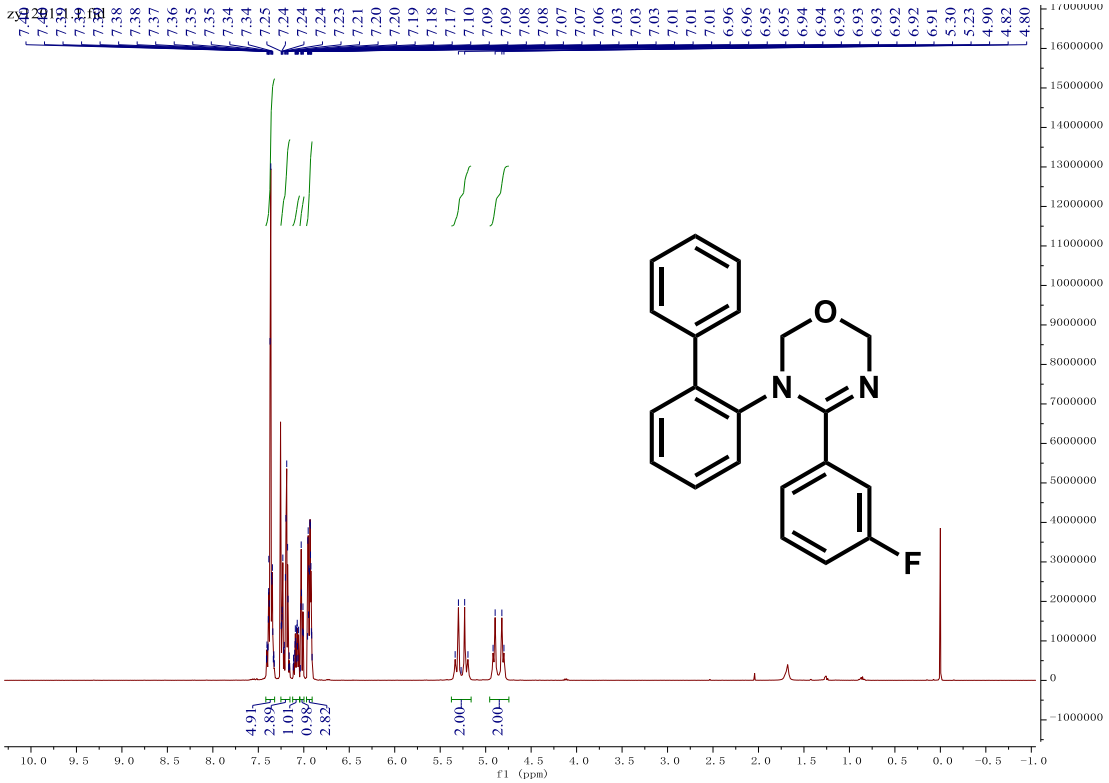
^{1}H NMR of Compound **2e'** (400 MHz, $CDCl_3$)



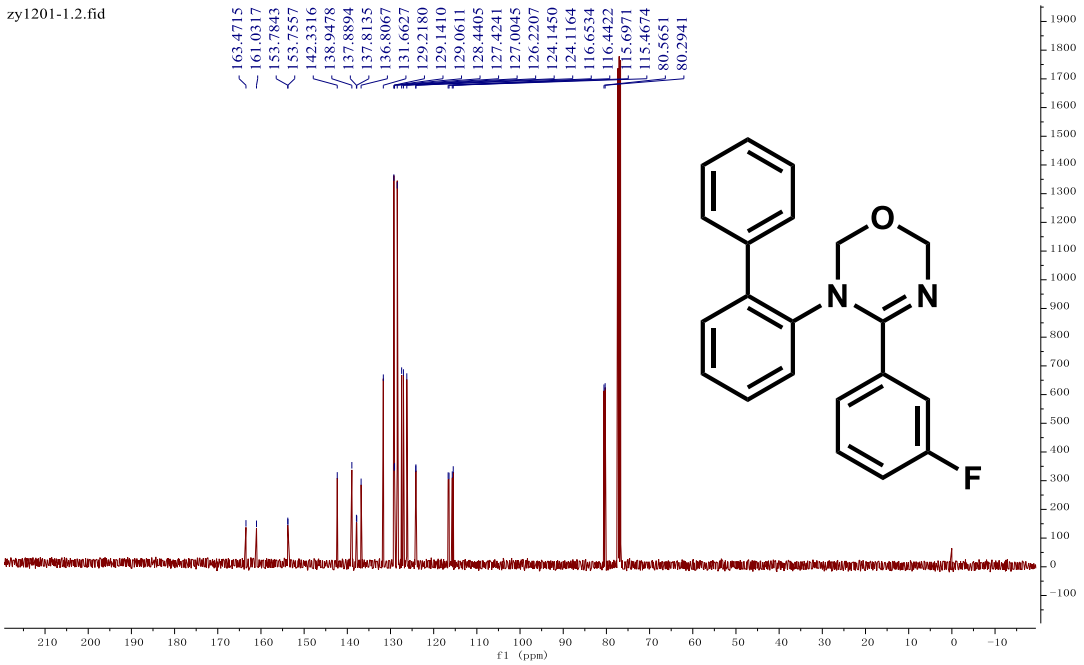
^{13}C{H} NMR of Compound **2e'** (101 MHz, $CDCl_3$)



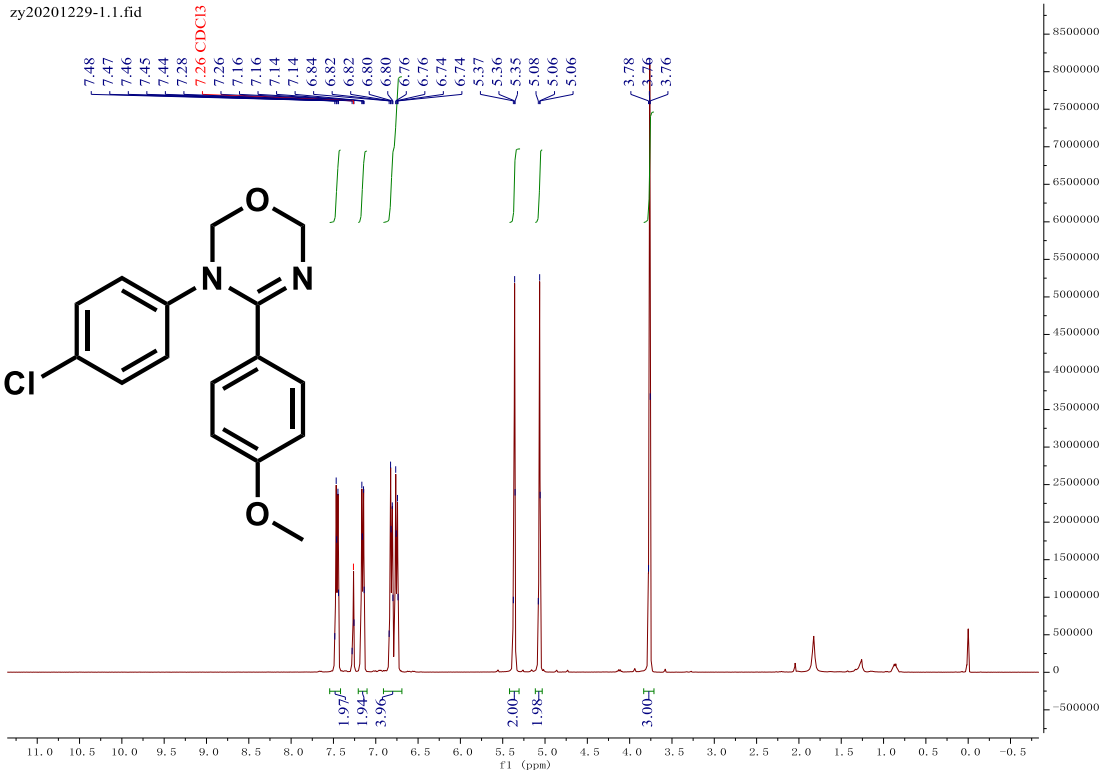
^{1}H NMR of Compound **2f'** (400 MHz, $CDCl_3$)



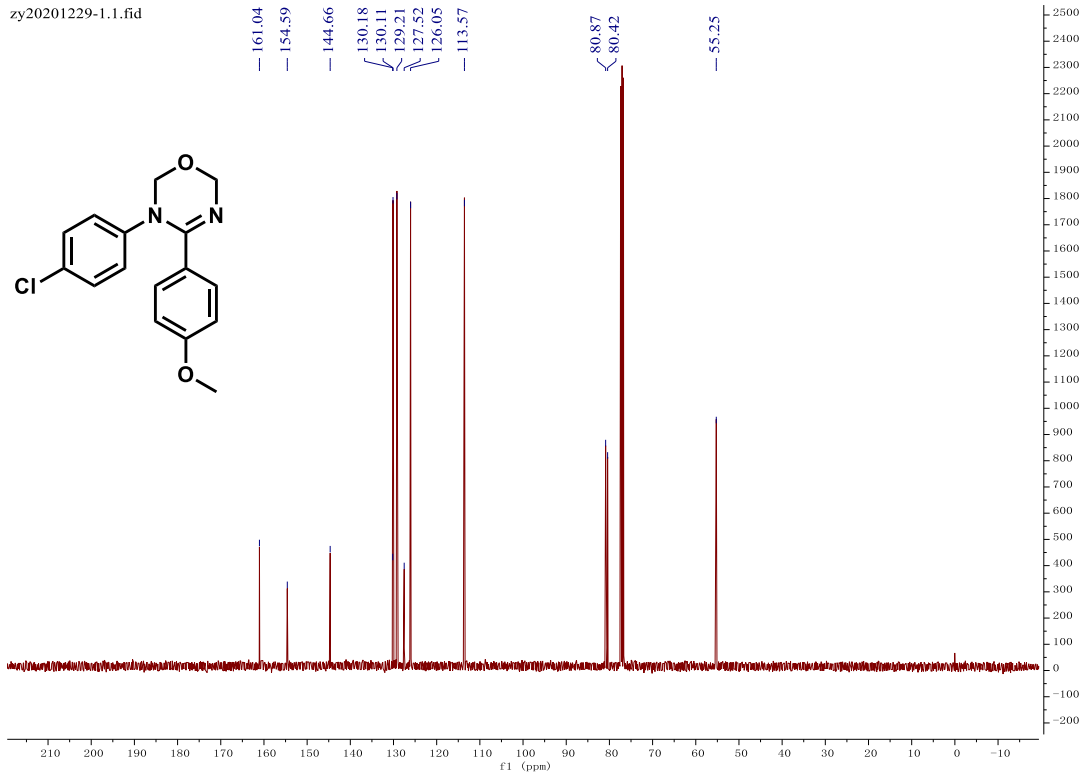
^{13}C{H} NMR of Compound **2f'** (101 MHz, $CDCl_3$)



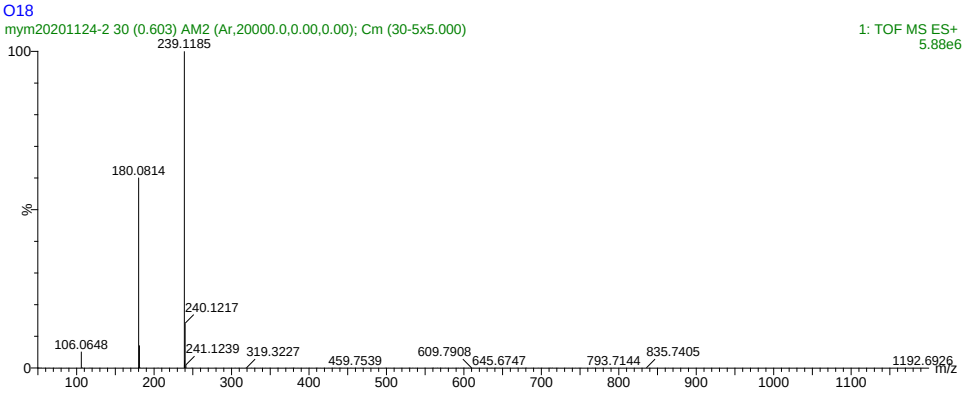
^{1}H NMR of Compound **2g'** (400 MHz, $CDCl_3$)



^{13}C{H} NMR of Compound **2g'** (101 MHz, $CDCl_3$)



Mass spectrum of **2a** (in $^{18}O_2$)



Mass spectrum of **2a** (in $H_2{}^{18}O$)