Electronic Supplementary Information (ESI) for

Synthesis, Insecticidal Activity, and Structure–Activity Relationship (SAR) and Density Functional Theory (DFT) of Novel Anthranilic Diamides Analogs Containing 1,3,4-Oxadiazole Rings

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1) The characterization of compounds 5a-x

1. **3-bromo-*N*-(4-bromo-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5a).** Yield 80.4 %; mp: 213-214 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.55 (s, 1H), 8.44 (dd, 1H, J = 5.2 Hz, 1.4 Hz)), 8.13 (dd, 1H, J = 8.2 Hz, 1.4 Hz), 8.08 (d, =1H, 2.0 Hz), 7.98 (dd, =1H, J = 5.0 Hz, 1.0 Hz), 7.83 (t, =1H, J = 1.0 Hz), 7.79 (dd, 1H, J = 4.0 Hz, 1.2 Hz), 7.58 (dd, =1H, J = 8.0 Hz, 4.8 Hz), 7.44 (s, 1H), 7.29 (dd, =1H, J = 5.0 Hz, 3.8 Hz), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 161.1, 160.5, 155.8, 148.3, 147.1, 140.4, 139.3, 139.0, 136.2, 132.5, 132.1, 130.7, 129.3, 128.7, 127.8, 126.8, 126.6, 123.9, 123.2, 120.2, 111.0, 17.6; MS (ESI) *m/z* 619.0 (M^- + 2 - H, 100 %), 621.0 (M^- + 4 - H, 76 %), 617.0 (M^- - H, 41 %).
2. **3-bromo-*N*-(4-bromo-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5b).** Yield 40.7 %; mp: 220-221 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.58 (s, 1H), 8.44 (dd, 1H, J = 4.6 Hz, 1.4 Hz)), 8.13 (dd, 2H, J = 7.0 Hz, 1.4 Hz)), 8.00 (t, 2H, J = 4.2 Hz), 7.84 (d, 1H, J = 2.0 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.60-7.55 (m, 3H), 7.45 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 164.3, 161.9, 156.0, 148.4, 147.2, 140.6, 139.4, 139.0, 136.3, 132.6, 132.4, 129.4, 127.9, 127.0, 126.9, 126.8, 123.5, 123.0, 120.5, 111.1, 17.7; MS (ESI) *m/z* 613.0 (M^- + 2 - H, 100 %), 615.0 (M^- + 4 - H, 72 %), 611.0 (M^- - H, 44 %).
3. **3-bromo-*N*-(4-bromo-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5c).** Yield 73.0 %; mp: 208-209 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.60 (s, 1H), 9.22 (d, 1H, J = 1.6 Hz), 8.82 (dd, 1H, J = 4.8 Hz, 1.6 Hz), 8.42 (dd, 1H, J = 4.8 Hz, 1.6 Hz), 8.40 (m, 1H), 8.17 (d, 1H, J = 1.8 Hz), 8.14 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.86 (d, 1H, J = 2.0 Hz), 7.64-7.62 (m, 1H), 7.60-7.57 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 162.5, 162.2, 156.0, 152.8, 148.4, 147.5, 147.2, 140.6, 139.4, 139.1, 136.5, 134.4, 132.7, 129.6, 127.9, 127.0, 126.8, 124.4, 123.3, 120.5, 119.7, 111.0, 17.7; MS (ESI) *m/z* 614.0 (M^- + 2 - H, 100 %), 616.0 (M^- + 4 - H, 72 %), 612.0 (M^- - H, 43 %).
4. **3-bromo-*N*-(4-bromo-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5d).** Yield 51.3 %; mp: 230-231 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.94 (s, 1H), 9.56 (d, 1H, J = 0.8 Hz), 8.82 (s, 2H), 8.44 (dd, 1H, J = 4.8 Hz, 1.2 Hz), 8.12 (d, 1H, J = 2.0 Hz), 7.84 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.59 (d, 1H, J = 2.0 Hz), 7.37 (dd, 1H, J = 8.0 Hz, 4.8 Hz), 7.26 (d, 1H, J = 3.2 Hz), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 164.0, 161.9, 155.6, 149.0, 147.2, 147.0, 145.0, 144.6, 139.3, 139.2, 139.1, 139.0, 138.0, 133.3, 129.1, 129.0, 128.5, 125.9, 120.4, 118.8, 111.1, 19.6; MS (ESI) *m/z* 615.0 (M^- + 2 - H, 100 %), 617.0 (M^- + 4 - H, 72 %), 613.0 (M^- - H, 39 %).
5. **3-bromo-*N*-(4-chloro-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5e).** Yield 77.2 %; mp: 201-202 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.56 (s, 1H), 8.44 (dd, 1H, J = 2.6 Hz, 1.4 Hz), 8.14 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.98 (dd, 1H, J = 5.0 Hz, 1.0 Hz), 7.95 (d, 1H, J = 2.4 Hz), 7.79 (dd, 1H, J = 3.6 Hz, 1.2 Hz), 7.71 (d, 1H, J = 2.0 Hz), 7.59 (dd, 1H, J = 8.0 Hz, 4.8 Hz), 7.44 (s, 1H), 7.29 (dd, 1H, J = 4.8 Hz, 3.6 Hz), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 161.3, 160.5, 156.0, 148.3, 147.1, 140.3, 139.3, 139.0, 133.4, 132.1, 132.0, 130.8, 128.7, 127.8, 126.9, 126.7, 126.5, 124.0, 123.0, 111.0, 17.8; MS (ESI) *m/z* 575.0 (M^- + 2 - H, 100 %), 573.0 (M^- - H, 58 %), 577.0 (M^- + 4 - H, 51 %).
6. **3-bromo-*N*-(4-chloro-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5f).** Yield 85.2 %; mp: 193-194 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.59 (s, 1H), 8.44 (dd, 1H, J = 4.8 Hz, J = 1.6 Hz), 8.14 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 8.02 (d, 2H, J = 2.8 Hz), 8.00 (d, 1H, J = 1.6 Hz), 7.71 (d, 1H, J = 2.4 Hz), 7.67-7.63 (m, 1H), 7.60-7.55 (m, 3H), 7.45 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 164.2, 161.9, 156.0, 148.4, 147.1, 140.4, 139.3, 139.0, 133.3, 132.3, 132.1, 129.3, 127.9, 126.9, 126.8, 126.7, 126.5, 123.2, 123.0, 111.0, 17.8; MS (ESI) *m/z* 569.1 (M^- + 2 - H, 100 %), 567.1 (M^- - H, 61 %), 571.1 (M^- + 4 - H, 48 %).

7. **3-bromo-*N*-(4-chloro-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5g).** Yield 67.1 %; mp: 195-196 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.60 (s, 1H), 9.22 (d, 1H, J = 1.6 Hz), 8.82 (dd, 1H, J = 4.8 Hz, 2.0 Hz), 8.43-8.42 (dd, 1H, J = 4.6 Hz, 1.4 Hz), 8.40-8.38 (m, 1H), 8.14 (dd, 1H, J = 8.2 Hz, 1.4 Hz), 8.06 (d, 1H, J = 2.4 Hz), 7.73 (d, 1H, J = 2.4 Hz), 7.64-7.60 (m, 1H), 7.58 (dd, 1H, J = 8.2 Hz, 4.6 Hz), 7.44 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 162.4, 162.2, 156.0, 152.8, 148.4, 147.5, 147.1, 140.3, 139.3, 139.0, 134.3, 133.5, 132.2, 132.1, 127.8, 126.9, 126.7, 126.6, 124.3, 123.0, 119.6, 111.0, 17.7; MS (ESI) *m/z* 570.1 (M^- + 2 - H, 100 %), 568.1 (M^- - H, 61 %), 572.1 (M^- + 4 - H, 50 %).
8. **3-bromo-*N*-(4-chloro-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide (5h).** Yield 44.8 %; mp: 235-236 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.66 (s, 1H), 9.41 (d, 1H, J = 1.2 Hz), 8.91 (d, 1H, J = 2.4 Hz), 8.85 (t, 1H, J = 2.0 Hz), 8.41 (dd, 1H, J = 4.6 Hz, 1.4 Hz), 8.13 (dd, 1H, J = 8.2 Hz, 1.4 Hz), 8.10 (d, 1H, J = 2.0 Hz), 7.87 (d, 1H, J = 2.0 Hz), 7.57 (dd, 1H, J = 8.0 Hz, 4.8 Hz), 7.47 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 162.9, 162.0, 156.1, 148.2, 147.3, 147.1, 145.1, 143.8, 140.4, 139.4, 139.2, 138.8, 133.7, 132.4, 132.1, 127.7, 126.8, 126.6, 124.5, 122.8, 111.3, 17.8; MS (ESI) *m/z* 595.0 (M^+ + 2 + Na, 100 %), 593.0 (M^+ + Na, 65 %), 597.0 (M^+ + 4 + Na, 46 %).
9. ***N*-(4-bromo-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)benzamide (5i).** Yield 62.2 %; mp: 187-189 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.22 (s, 1H), 8.10 (d, 1H, J = 2.4 Hz), 8.01 (t, 2H, J = 4.4 Hz), 7.90 (dd, 1H, J = 5.0 Hz, 1.0 Hz), 7.86 (d, 1H, J = 1.6 Hz), 7.63 (dd, 1H, J = 8.4 Hz, 6.4 Hz), 7.56-7.52 (m, 3H), 7.19 (dd, 1H, J = 5.0 Hz, 3.8 Hz), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 165.8, 161.7, 160.4, 140.5, 136.2, 134.6, 133.9, 132.1, 132.0, 130.5, 129.2, 128.7, 128.6, 127.8, 124.0, 123.3, 119.6, 17.9; MS (ESI) *m/z* 440.1 (M^- + 2 - H, 60 %).
10. ***N*-(4-bromo-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5j).** Yield 43.5 %; mp: 173-175 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.19 (s, 1H), 8.10 (d, 1H, J = 2.0 Hz), 7.96 (t, 2H, J = 4.4 Hz), 7.80 (d, 1H, J = 1.6 Hz), 7.74 (t, 2H, J = 4.0 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.52-7.47 (m, 3H), 7.37 (t, 2H, J = 7.7 Hz), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 165.8, 164.7, 162.3, 140.7, 136.2, 134.6, 133.8, 132.3, 132.1, 129.4, 129.3, 128.7, 127.9, 126.6, 123.5, 123.0, 119.7, 17.9; MS (ESI) *m/z* 456.1 (M^+ + Na, 100 %).
11. ***N*-(4-bromo-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5k).** Yield 47.9 %; mp: 184-186 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.26 (s, 1H), 9.06 (s, 1H), 8.76 (d, 1H, J = 3.6 Hz), 8.22-8.20 (m, 2H), 8.01 (d, 2H, J = 7.2 Hz), 7.88 (d, 1H, J = 2.0 Hz), 7.63 (t, 1H, J = 7.4 Hz), 7.54 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 165.8, 162.7, 162.3, 152.7, 147.3, 140.6, 136.4, 134.7, 134.2, 133.9, 132.1, 129.4, 128.7, 127.8, 124.4, 123.3, 119.8, 17.9; MS (ESI) *m/z* 459.1 (M^+ + 2 + Na, 100 %), 457.1 (M^+ + Na, 93 %).
12. ***N*-(4-bromo-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5l).** Yield 61.6 %; mp: 209-210 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 9.50 (s, 1H), 8.79 (s, 2H), 8.14 (d, 1H, J = 2.4 Hz), 8.11 (dd, 2H, J = 5.4 Hz, 3.4 Hz), 7.68 (d, 1H, J = 2.4 Hz), 7.62-7.52 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 163.4, 161.8, 147.1, 145.0, 144.5, 139.4, 139.3, 138.0, 135.2, 133.9, 132.5, 129.0, 128.8, 128.0, 119.6, 118.6, 19.8; MS (ESI) *m/z* 460.0 (M^+ + 2 + Na, 100 %), 458.0 (M^+ + Na, 65 %), 461.0 (M^+ + 3 + Na, 27 %).
13. ***N*-(4-chloro-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)benzamide (5m).** Yield 63.8 %; mp: 202-203 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.12 (s, 1H), 8.09 (t, 2H, J = 4.0 Hz), 7.85-7.82 (m, 2H), 7.61-7.56 (m, 3H), 7.54-7.50 (m, 2H),

7.48 (d, 1H, J = 2.4 Hz), 7.20 (dd, 1H, J = 5.0 Hz, 3.8 Hz), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 162.4, 160.7, 138.9, 134.5, 134.4, 133.9, 132.4, 131.6, 131.2, 130.7, 129.0, 128.6, 128.0, 125.4, 124.5, 118.5, 19.9; MS (ESI) *m/z* 418.1 (M^+ + Na, 100 %), 420.1 (M^+ + 2 + Na, 39 %).

14. ***N*-(4-chloro-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5n).** Yield 51.2 %; mp: 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.16 (s, 1H), 8.11-8.09 (m, 4H), 7.88 (d, 1H, J = 2.0 Hz), 7.61-7.51 (m, 6H), 7.49 (d, 1H, J = 2.4 Hz), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 164.4, 163.0, 138.9, 134.5, 134.4, 134.0, 132.5, 132.4, 131.6, 129.4, 129.0, 128.0, 127.3, 125.5, 123.2, 118.7, 19.9; MS (ESI) *m/z* 412.1 (M^+ + Na, 100 %), 414.1 (M^+ + 2 + Na, 34 %).

15. ***N*-(4-chloro-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5o).** Yield 42.1 %; mp: 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.05 (s, 1H), 9.34 (s, 1H), 8.81 (s, 1H), 8.38-8.36 (m, 1H), 8.09 (t, 2H, J = 4.2 Hz), 7.88 (d, 1H, J = 2.0 Hz), 7.61-7.59 (m, 1H), 7.58-7.50 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 163.4, 162.3, 153.0, 148.2, 139.1, 134.6, 134.4, 134.3, 133.8, 132.4, 131.8, 129.0, 127.9, 125.6, 124.0, 118.6, 19.8; MS (ESI) *m/z* 413.1 (M^+ + Na, 100 %), 415.1 (M^+ + 2 + Na, 36 %).

16. ***N*-(4-chloro-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)-phenyl)benzamide (5p).** Yield 31.7 %; mp: 193-195 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.28 (s, 1H), 9.27 (d, 1H, J = 1.2 Hz), 8.85 (d, 1H, J = 2.4 Hz), 8.79 (dd, 1H, J = 2.6 Hz, 1.4 Hz), 7.99 (t, 2H, J = 2.2 Hz), 7.97 (d, 1H, J = 1.2 Hz), 7.76 (d, 1H, J = 2.0 Hz), 7.62-7.58 (m, 1H), 7.52 (t, 2H, J = 7.4 Hz), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 166.0, 163.3, 161.8, 147.2, 145.1, 143.6, 140.3, 138.7, 134.4, 134.1, 133.6, 131.8, 131.4, 128.4, 127.8, 126.5, 122.8, 18.0; MS (ESI) *m/z* 414.1 (M^+ + Na, 100 %), 416.1 (M^+ + 2 + Na, 36 %).

17. ***N*-(4-bromo-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)methacrylamide (5q).** Yield 47.2 %; mp: 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.68 (s, 1H, Ph-NH-C=O), 7.95 (d, 1H, J = 2.0 Hz), 7.86 (dd, 1H, J = 3.6 Hz, 0.6 Hz,), 7.62 (dd, 1H, J = 4.8 Hz, 1.2 Hz), 7.59 (d, 1H, J = 2.0 Hz), 7.22 (dd, 1H, J = 4.8 Hz, 3.6 Hz), 6.11 (s, 1H), 5.58 (d, 1H, J = 0.8 Hz), 2.33 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.5, 162.2, 160.6, 139.7, 139.0, 137.2, 134.8, 131.2, 130.7, 128.5, 128.2, 124.5, 122.2, 119.1, 118.6, 19.9, 18.9; MS (ESI) *m/z* 428.0 (M^+ + 2 + Na, 100 %).

18. ***N*-(4-bromo-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5r).** Yield 46.9 %; mp: 214-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.76 (s, 1H), 8.13 (dd, 2H, J = 8.0 Hz, 1.6 Hz), 7.97 (d, 1H, J = 2.4 Hz), 7.59-7.53 (m, 4H), 6.12 (s, 1H), 5.59 (s, 1H), 2.33 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.5, 164.3, 162.8, 139.7, 139.0, 137.2, 134.8, 132.4, 129.4, 128.2, 127.2, 123.2, 122.2, 119.1, 118.8, 19.7, 18.9; MS (ESI) *m/z* 422.1 (M^+ + 2 + Na, 100 %).

19. ***N*-(4-bromo-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5s).** Yield 20.7 %; mp: 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.59 (s, 1H), 9.02 (d, 1H, J = 1.6 Hz), 8.71 (dd, 1H, J = 4.8 Hz, 1.2 Hz), 8.15 (d, 1H, J = 2.0 Hz), 8.12-8.09 (m, 1H), 7.74 (d, 1H, J = 1.6 Hz), 7.32-7.26 (m, 1H), 5.54 (s, 1H), 5.46 (s, 1H), 2.60 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.7, 161.0, 155.6, 153.4, 148.8, 144.8, 139.4, 138.8, 138.2, 135.5, 127.0, 126.9, 123.8, 122.0, 120.7, 120.6, 21.6, 17.4; MS (ESI) *m/z* 423.0 (M^+ + 2 + Na, 100 %), 423.0 (M^+ + Na, 94 %).

20. ***N*-(4-bromo-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5t).** Yield 46.1 %; mp: 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.04 (s, 1H), 9.38 (d, 1H, J = 1.6 Hz), 8.83 (d, 1H, J = 2.4 Hz), 8.54 (dd, 1H, J = 2.2 Hz, 1.4 Hz), 8.17 (s, 1H), 7.72 (s, 1H), 5.52 (d, 1H, J = 0.8 Hz), 5.41 (d, 1H, J = 0.8 Hz), 2.60 (s, 3H), 2.18 (d, 3H, J = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.6, 159.6, 155.7, 148.7, 145.0, 143.1, 142.8, 139.2, 138.6, 138.2, 127.2, 122.3, 120.6, 120.5, 21.6, 17.4; MS (ESI) *m/z* 424.1 (M^+ + 2 + Na, 100 %).

21. ***N*-(4-chloro-2-methyl-6-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)phenyl)methacrylamide (5u).** Yield 45.1 %; mp: 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.67 (s, 1H), 7.86 (dd, 1H, J = 3.6 Hz, 1.2 Hz), 7.81 (d, 1H, J = 2.4 Hz), 7.62 (dd, 1H, J = 5.0 Hz, 1.0 Hz), 7.44 (d, 1H, J = 2.4 Hz), 7.22 (dd, 1H, J = 5.0

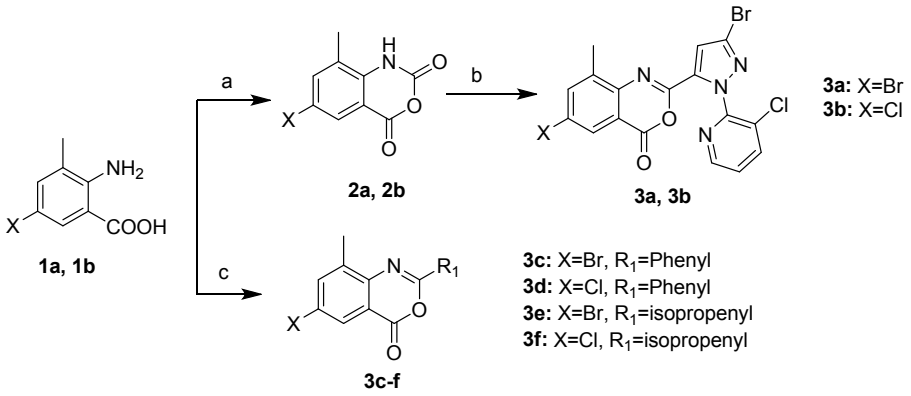
Hz, 3.8 Hz), 6.11 (s, 1H), 5.58 (s, 1H,), 2.34 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.5, 162.3, 160.6, 139.7, 138.8, 134.3, 131.5, 131.2, 130.7, 128.6, 125.3, 124.5, 122.2, 118.4, 19.7, 18.9; MS (ESI) *m/z* 382.1 (M^+ + Na, 100 %), 384.1 (M^+ + 2 + Na, 47 %).

22. ***N*-(4-chloro-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5v).** Yield 33.7 %; mp: 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.74 (s, 1H), 8.14 (dd, 2H, *J* = 8.2 Hz, 1.4 Hz), 7.84 (d, 1H, *J* = 2.4 Hz), 7.62-7.53 (m, 3H), 7.45 (d, 1H, *J* = 2.4 Hz), 6.12 (s, 1H), 5.59 (d, 1H, *J* = 0.4 Hz), 2.34 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 164.3, 162.9, 139.7, 138.8, 134.3, 134.2, 132.4, 131.5, 129.4, 127.2, 125.4, 123.3, 122.2, 118.6, 19.7, 18.9; MS (ESI) *m/z* 376.1 (M^+ + Na, 100 %), 378.1 (M^+ + 2 + Na, 35 %).

23. ***N*-(4-chloro-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5w).** Yield 28.3 %; mp: 215-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.63 (s, 1H), 9.38 (s, 1H), 8.84 (d, 1H, *J* = 4.0 Hz), 8.42 (d, 1H, *J* = 8.0 Hz), 7.85 (s, 1H), 7.53 (dd, 1H, *J* = 7.6 Hz, 5.2 Hz), 7.45 (s, 1H), 6.12 (s, 1H), 5.60 (s, 1H), 2.35 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 163.4, 162.3, 153.1, 148.2, 139.7, 139.0, 134.6, 134.4, 131.7, 125.5, 124.1, 122.2, 119.9, 118.4, 19.7, 18.9; MS (ESI) *m/z* 377.1 (M^+ + Na, 100 %), 379.1 (M^+ + 2 + Na, 34 %).

24. ***N*-(4-chloro-2-methyl-6-(5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)-phenyl)methacrylamide (5x).** Yield 37.2 %; mp: 172-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.58 (s, 1H), 9.53 (s, 1H), 8.80 (s, 2H), 7.96 (d, 1H, *J* = 2.4 Hz), 7.48 (d, 1H, *J* = 2.4 Hz), 6.12 (s, 1H), 5.60 (d, 1H, *J* = 0.8 Hz), 2.35 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 164.3, 161.7, 147.0, 144.9, 144.5, 139.7, 139.3, 139.0, 134.9, 134.5, 131.9, 125.9, 122.2, 118.2, 19.7, 18.8; MS (ESI) *m/z* 378.1 (M^+ + Na, 100 %), 380.1 (M^+ + 2 + Na, 40 %).

2) Scheme S1. General synthetic route for intermediates 3a-f



Scheme S1 Reagents and conditions: (a) ClCOOEt, Dioxane, reflux, $ClCOCH_3$, 55 °C; (b) 3-bromo-1-(3-chloropyridin-2-yl)-1H-pyrazole-5-carbonyl chloride, anhydrous pyridine, anhydrous pyridine 60 °C; (c) Methacrylic anhydride/Benzoic anhydride, Pyridine, reflux.

3) General synthetic method for intermediates 3a-b：

A slurry of 1a or 1b (43.5 mmol) in 1,4-dioxane (60 g) was added with ethyl chloroformate (205.5 mmol). And the the mixture was stirred at 88 °C for 6 h. Subsequently, acetyl chloride (284.1 mmol) was added at 50-55 °C. The solution was stirred for 10 h. Furthermore, a white solid (2a-b) was precipitated from the solution. After filtration and drying, 2a or 2b (0.10 mol) was added slowly to a mixture of 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carbonyl chloride (0.12 mol), pyridine (40 mL) and acetonitrile (40 mL) at 70 °C about 0.5 h, then allowed to react 4

h. The mixture was cooled to room temperature and flitered to afford off-white solid, washed with a small quantity of acetonitrile and dried at room temperature to get product (3a or 3b) without further purification.

*2-(3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl)-6-bromo-8-methyl-4H-1,3-benzoxazin-4-one (**3a**)*

Yield 43.3 %; mp: 215-219 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.62 (dd, 1H, J = 4.7 HZ, J = 1.4 HZ), 8.35 (dd, 1H, J = 8.1 HZ, J = 1.4 HZ), 8.01 (d, 1H, J = 1.0 HZ), 7.89 (d, 1H, J = 0.8 HZ), 7.76 (dd, 1H, J = 8.1 HZ, J = 4.7 HZ), 7.53 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 157.2, 149.6, 147.4, 147.2, 143.0, 140.4, 139.2, 138.3, 136.1, 129.8, 129.0, 128.8, 126.2, 122.3, 118.4, 173.6, 16.5; MS (ESI) m/z 495.0 (M^+ + H, 100 %).

*2-(3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl)-6-chloro-8-methyl-4H-1,3-benzoxazin-4-one (**3b**)*

Yield 50.1 %; mp: 238-240 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.62 (dd, 1H, J = 4.7 HZ, J = 1.5 HZ), 8.35 (dd, 1H, J = 8.1 HZ, J = 1.4 HZ), 7.89 (d, 1H, J = 2.3 HZ), 7.77 (dd, 2H), 7.53 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 157.4, 149.5, 147.3, 147.0, 142.6, 139.2, 138.2, 137.5, 136.0, 134.4, 129.8, 128.8, 126.2, 125.8, 118.2, 113.6, 16.6; MS (ESI) *m/z* 453.1 (M^+ + H, 100 %).

General synthetic method for intermediates 3c-f:

Benzoic anhydride or Methacrylic anhydride (55.3 mmol) was added dropwise to a solution of pyridine (80 mL) and heated to 80 ^{o}C. The 2-Amino-5-bromo-3-methylbenzoic acid 1a or 1b (21.7 mmol) was added into it. After all, the mixture was refluxed for 10 h and poured into a flask containing 500 mL 10% Na_2CO_3 solution. The solid was filtered, washed with water, and dried to afford 3c-f.

*6-bromo-8-methyl-2-phenyl-4H-1,3-benzoxazin-4-one (**3c**)*

Yield 45.1 %; mp: 167-168 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.31 (d, 2H, J = 7.5 HZ), 8.19 (s, 1H), 7.76 (s, 1H), 7.58-7.48 (m, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 158.8, 156.3, 144.3, 140.1, 138.6, 132.8, 130.2, 128.8, 128.6, 128.4, 121.0, 118.2, 17.0; MS (ESI) *m/z* 316.0 (M^+ + H, 100 %)

*6-chloro-8-methyl-2-phenyl-4H-1,3-benzoxazin-4-one (**3d**)*

Yield 48.2 %;153-155 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.27 (d, 2H, J = 7.3 HZ), 8.19 (s, 1H), 7.58-7.46 (m, 4H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 159.0, 156.1, 143.9, 138.4, 137.3, 133.2, 132.8, 130.1, 128.8, 128.3, 125.4, 117.9, 17.0; MS (ESI) *m/z* 294.0 (M^+ + Na, 100 %)

*6-bromo-8-methyl-2-(prop-1-en-2-yl)-4H-1,3-benzoxazin-4-one (**3e**)*

Yield 57.1 %;126-128 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.16 (s, 1H), 7.74 (s, 1H), 6.34 (s, 1H), 5.72 (s, 1H), 2.52 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 158.8, 156.6, 144.1, 140.0, 138.9, 135.9, 128.5, 124.4, 121.3, 118.4, 18.7, 16.8; MS (ESI) *m/z* 381.0 (M^+ + Ka, 100 %)

*6-chloro-8-methyl-2-(prop-1-en-2-yl)-4H-1,3-benzoxazin-4-one (**3f**)*

Yield 62.3 %;111-112 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.00 (s, 1H), 7.59 (s, 1H), 6.33 (s, 1H), 5.71 (s, 1H), 2.55 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 159.0, 156.5, 143.7, 138.7, 137.2, 135.9, 133.4, 125.4, 124.3, 118.1, 18.7, 16.9; MS (ESI) *m/z* 258.0 (M^+ + Na, 100 %)

4) Table S1. Crystal and Structure refinement data of compound 5u

compound	5u	compound	5u
Chemical formula	$C_{17}H_{14}ClN_3O_2S$	μ (mm^{-1})	0.36
Formula weight	359.82	F (0 0 0)	372
Crystal system	triclinic	θ range (°)	9-12
Space group	*P-1*	Index range	$0 \le h \le 11$
a (Å)	9.774(2)		$-11 \le k \le 11$
b (Å)	9.830(2)		$-11 \le h \le 11$
c (Å)	9.908(2)	Reflns collected	3311
α (°)	91.70(3)	Unique reflns (R_{int})	3113 (0.087)
β (°)	110.52(3)	Refinement mothod on F^2	Least-squares matrix: full
γ (°)	106.41(3)	GOF on F^2	1.01
V (Å^3), Z	846.4(3)/2	R [$F^2 > 2\sigma$ (F^2)]	0.070
D_{calc} (g cm^{-3})	1.412	wR [F^2]	0.171

5) The geometrical parameters of the compounds calculated 5a, 5d and 5t

5.1) The geometrical parameters of the compounds calculated 5a

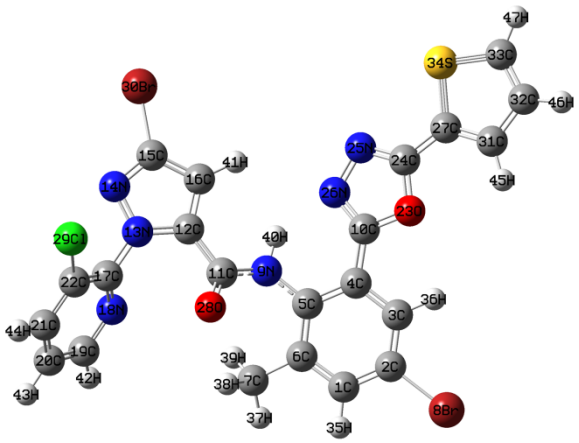


Figure S1 Optimized molecular structure of **5a**

Table S2. The geometrical parameters of **5a** calculated at B3LYP/6-31G*

Bond length (Å)				Angle (°)				Dihedral angle (°)			
C2-C1	1.39	N25-C24	1.30	C3-C2-C1	120.83	N26-C10-C4	129.67	C4-C3-C2-C1	2.26	C27-C24-O23-C10	179.74
C3-C2	1.38	N26-C10	1.31	C4-C3-C2	119.28	C27-C24-O23	119.15	C5-C4-C3-C2	0.30	O28-C11-N9-C5	-9.55
C4-C3	1.40	C27-C24	1.44	C5-C4-C3	120.27	O28-C11-N9	124.68	C6-C1-C2-C3	-1.513	Cl29-C22-C21-C20	-177.18
C5-C4	1.42	O28-C11	1.22	C6-C1-C2	121.24	Cl29-C22-C21	119.50	C7-C6-C1-C2	175.52	Br30-C15-N14-N13	-178.82
C6-C1	1.40	Cl29-C22	1.74	C7-C6-C1	118.99	Br30-C15-N14	120.61	Br8-C2-C1-C6	-179.90	C31-C27-C24-C23	-0.13
C7-C6	1.51	Br30-C15	1.89	Br8-C2-C1	119.64	C31-C27-C24	128.02	N9-C5-C4-C3	179.20	C32-C31-C27-C24	-179.95
Br8-C2	1.91	C31-C27	1.38	N9-C5-C4	119.06	C32-C31-C27	112.66	C10-C4-C3-C2	-178.42	C33-C32-C31-C27	0.01
N9-C5	1.41	C32-C31	1.42	C10-C4-C3	118.17	C33-C32-C31	112.55	C11-N9-C5-C4	-125.81	S34-C33-C32-C31	0.00
C10-C4	1.46	C33-C32	1.37	C11-N9-C5	124.51	S34-C33-C32	112.39	C12-C11-N9-C5	169.91	H35-C1-C2-C3	176.94
C11-N9	1.38	S34-C33	1.73	C12-C11-N9	113.39	H35-C1-C2	119.56	N13-C12-C11-N9	155.61	H36-C3-C2-C1	-177.61
C12-C11	1.49	H35-C1	1.08	N13-C12-C11	121.66	H36-C3-C2	120.61	N14-N13-C12-C11	175.24	H37-C7-C6-C1	-20.80
N13-C12	1.37	H36-C3	1.08	N14-N13-C12	112.30	H37-C7-C6	110.19	C15-N14-N13-C12	-1.58	H38-C7-C6-C1	100.36
N14-N13	1.36	H37-C7	1.09	C15-N14-N13	104.13	H38-C7-C6	111.11	C16-C12-C11-N9	-32.40	H39-C7-C6-C1	-141.07
C15-N14	1.32	H38-C7	1.09	C16-C12-C11	131.52	H39-C7-C6	110.96	C17-N13-C12-C11	-15.68	H40-N9-C5-C4	27.80
C16-C12	1.38	H39-C7	1.09	C17-N13-C12	127.90	H40-N9-C5	114.85	N18-C17-N13-C12	-53.00	H41-C16-C12-C11	3.40
C17-N13	1.42	H40-N9	1.02	N18-C17-N13	115.94	H41-C16-C12	128.15	C19-N18-C17-N13	-178.94	H42-C19-N18-C17	-179.41
N18-C17	1.33	H41-C16	1.08	C19-N18-C17	118.50	H42-C19-N18	116.04	C20-C19-N18-C17	1.27	H43-C20-C19-N18	179.00
C19-N18	1.34	H42-C19	1.09	C20-C19-N18	122.99	H43-C20-C19	120.77	C21-C20-C19-N18	-1.39	H44-C21-C20-C19	-178.91
C20-C19	1.39	H43-C20	1.08	C21-C20-C19	118.42	H44-C21-C20	121.45	C22-C21-C20-C19	0.17	H45-C31-C27-C24	-0.01
C21-C20	1.39	H44-C21	1.08	C22-C21-C20	118.93	H45-C31-C27	122.94	O23-C10-C4-C3	-10.14	H46-C32-C31-C27	180.00
C22-C21	1.39	H45-C31	1.08	O23-C10-C4	119.22	H46-C32-C31	123.85	C24-O23-C10-C4	178.29	H47-C33-C32-C31	180.00
O23-C10	1.37	H46-C32	1.08	C24-O23-C10	103.07	H47-C33-C32	128.01	N25-C24-O23-C10	-0.08		
C24-O23	1.37	H47-C33	1.08	N25-C24-O23	112.11			N26-C10-C4-C3	167.59		

5.2) The geometrical parameters of the compounds calculated 5d

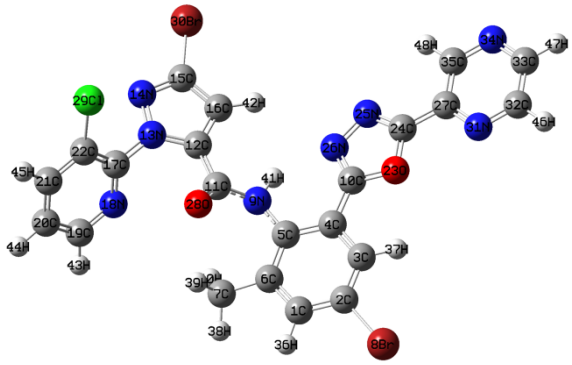


Figure S2 Optimized molecular structure of **5d**

Table S3. The geometrical parameters of **5d** calculated at B3LYP/6-31G*

Bond length (Å)				Angle (°)				Dihedral angle (°)			
C2-C1	1.39	N26-C10	1.31	C3-C2-C1	120.79	C27-C24-O23	120.03	C4-C3-C2-C1	2.26	O28-C11-N9-C5	-9.36
C3-C2	1.38	C27-C24	1.44	C4-C3-C2	119.18	O28-C11-N9	124.65	C5-C4-C3-C2	0.33	Cl29-C22-C21-C20	-177.19
C4-C3	1.40	O28-C11	1.22	C5-C4-C3	120.42	Cl29-C22-C21	119.51	C6-C1-C2-C3	-1.55	Br30-C15-N14-N13	-178.82
C5-C4	1.42	Cl29-C22	1.74	C6-C1-C2	121.35	Br30-C15-N14	120.64	C7-C6-C1-C2	175.51	N31-C27-C24-C23	1.08
C6-C1	1.40	Br30-C15	1.89	C7-C6-C1	119.00	N31-C27-C24	117.93	Br8-C2-C1-C6	-179.94	C32-N31-C27-C24	179.86
C7-C6	1.51	N31-C27	1.34	Br8-C2-C1	119.61	C32-C31-C27	115.98	N9-C5-C4-C3	179.13	C33-C32-N31-C27	-0.04
Br8-C2	1.91	C32-C31	1.33	N9-C5-C4	119.16	C33-C32-C31	122.04	C10-C4-C3-C2	-178.37	N34-C33-C32-N31	0.06
N9-C5	1.41	C33-C32	1.40	C10-C4-C3	117.94	N34-C33-C32	122.01	C11-N9-C5-C4	-125.94	C35-N34-C33-C32	0.00
C10-C4	1.46	N34-C33	1.34	C11-N9-C5	124.53	C35-N34-C33	116.36	C12-C11-N9-C5	170.07	H36-C1-C2-C3	176.91
C11-N9	1.38	C35-N34	1.33	C12-C11-N9	113.37	H36-C1-C2	119.50	N13-C12-C11-N9	155.61	H37-C3-C2-C1	-177.68
C12-C11	1.49	H36-C1	1.08	N13-C12-C11	121.68	H37-C3-C2	120.73	N14-N13-C12-C11	175.30	H38-C7-C6-C1	-20.83
N13-C12	1.37	H37-C3	1.08	N14-N13-C12	112.30	H38-C7-C6	110.18	C15-N14-N13-C12	-1.57	H39-C7-C6-C1	100.32
N14-N13	1.36	H38-C7	1.09	C15-N14-N13	104.14	H39-C7-C6	111.12	C16-C12-C11-N9	-32.30	H40-C7-C6-C1	-141.08
C15-N14	1.32	H39-C7	1.09	C16-C12-C11	131.51	H40-C7-C6	110.97	C17-N13-C12-C11	-15.60	H41-N9-C5-C4	28.00
C16-C12	1.38	H40-C7	1.09	C17-N13-C12	127.90	H41-N9-C5	114.99	N18-C17-N13-C12	-53.09	H42-C16-C12-C11	3.30
C17-N13	1.42	H41-N9	1.02	N18-C17-N13	115.92	H42-C16-C12	128.13	C19-N18-C17-N13	-178.93	H43-C19-N18-C17	-179.43
N18-C17	1.33	H42-C16	1.08	C19-N18-C17	118.49	H43-C19-N18	116.04	C20-C19-N18-C17	1.25	H44-C20-C19-N18	179.00
C19-N18	1.34	H43-C19	1.09	C20-C19-N18	122.98	H44-C20-C19	120.76	C21-C20-C19-N18	-1.38	H45-C21-C20-C19	-178.91
C20-C19	1.39	H44-C20	1.08	C21-C20-C19	118.43	H45-C21-C20	121.45	C22-C21-C20-C19	0.18	H46-C32-N31-C27	179.98
C21-C20	1.39	H45-C21	1.08	C22-C21-C20	118.93	H46-C32-N31	116.88	O23-C10-C4-C3	-9.49	H47-C33-C32-N31	-179.95
C22-C21	1.39	H46-C32	1.09	O23-C10-C4	119.13	H47-C33-C32	120.98	C24-O23-C10-C4	178.22	H48-C35-N34-C33	179.95
O23-C10	1.37	H47-C33	1.09	C24-O23-C10	103.14	H48-C35-N34	117.82	N25-C24-O23-C10	-0.04		
C24-O23	1.37	H48-C35	1.09	N25-C24-O23	112.25			N26-C10-C4-C3	168.20		
N25-C24	1.30			N26-C10-C4	129.66			C27-C24-O23-C10	179.94		

5.3) The geometrical parameters of the compounds calculated 5t

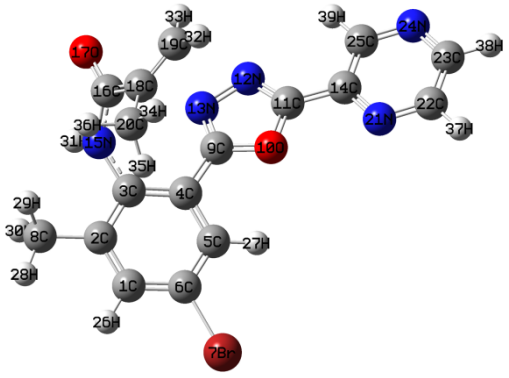


Figure S3 Optimized molecular structure of **5t**

Table S3. The geometrical parameters of **5t** calculated at B3LYP/6-31G*

Bond length (Å)				Angle (°)				Dihedral angle (°)			
C2-C1	1.40	N21-C14	1.34	C3-C2-C1	119.44	C22-N21-C14	115.98	C4-C3-C2-C1	2.55	C23-C22-N21-C14	-0.02
C3-C2	1.41	C22-N21	1.33	C4-C3-C2	119.60	C23-C22-N21	122.10	C5-C4-C3-C2	-4.49	N24-C23-C22-N21	0.04
C4-C3	1.41	C23-C22	1.40	C5-C4-C3	119.89	N24-C23-C22	121.98	C6-C5-C4-C3	3.12	C25-C24-C23-C22	-0.03
C5-C4	1.40	N24-C23	1.34	C6-C5-C4	119.54	C25-C24-C23	116.34	Br7-C6-C5-C4	179.54	H26-C1-C6-C5	179.12
C6-C5	1.39	C25-C24	1.33	Br7-C6—C5	119.49	H26-C1-C6	119.79	C8-C2-C1-C6	-178.36	H27-C5-C4-C3	-178.65
Br7-C6	1.91	H26-C1	1.08	C8-C2-C1	120.16	H27-C5-C4	119.94	C9-C4-C3-C2	172.50	H28-C8-C2-C1	7.24
C8-C2	1.51	H27-C5	1.08	C9-C4-C3	122.66	H28-C8-C2	110.92	O10-C9-C4-C3	160.21	Hl29-C8-C2-C1	128.34
C9-C4	1.47	H28-C8	1.09	O10-C9-C4	117.88	Hl29-C8-C2	111.13	C11-O10-C9-C4	176.62	Hr30-C8-C2-C1	-112.68
O10-C9	1.37	Hl29-C8	1.09	C11-O10-C9	102.69	Hr30-C8-C2	111.57	N12-C11-O10-C9	-0.09	H31-N15-C3-C2	-70.39
C11-O10	1.36	Hr30-C8	1.10	N12-C11-O10	112.22	H31-N15-C3	117.06	N13-C9-C4-C3	-24.32	H32-C19-C18-C16	177.01
N12-C11	1.30	H31-N15	1.02	N13-C9-C4	130.09	H32-C19-C18	121.41	C14-C11-O10-C9	-179.94	H33-C19-C18-C16	-2.69
N13-C9	1.30	H32-C19	1.09	C14-C11-O10	120.18	H33-C19-C18	121.02	N15-C3-C2-C1	-177.95	H34-C20-C18-C16	-171.30
C14-C11	1.46	H33-C19	1.08	N15-C3-C2	117.80	H34-C20-C18	110.22	C16-N15-C3-C2	129.19	H35-C20-C18-C16	67.93
N15-C3	1.42	H34-C20	1.09	C16-N15-C3	129.49	H35-C20-C18	112.98	O17-C16-N15-C3	162.14	H36-C20-C18-C16	-52.07
C16-N15	1.39	H35-C20	1.09	O17-C16-N15	119.37	H36-C20-C18	110.74	C18-C16-N15-C3	-21.70	H37-C22-N21-C14	-180.00
O17-C16	1.22	H36-C20	1.10	C18-C16-N15	118.45	H37-C22-N21	116.85	C19-C18-C16-N15	140.81	H38-C23-C22-N21	-179.96
C18-C16	1.51	H37-C22	1.09	C19-C18-C16	116.99	H38-C23-C22	121.00	C20-C18-C16-N15	-44.51	H39-C25-N24-C23	-179.97
C19-C18	1.34	H38-C23	1.09	C20-C18-C16	119.88	H39-C25-N24	117.88	N21-C14-C11-O10	1.28		
C20-C18	1.51	H39-C25	1.09	N21-C14-C11	118.14			C22-N21-C14-C11	179.79		

6) Figure S4-S27. ^{1}H NMR spectra for compounds 5a-x

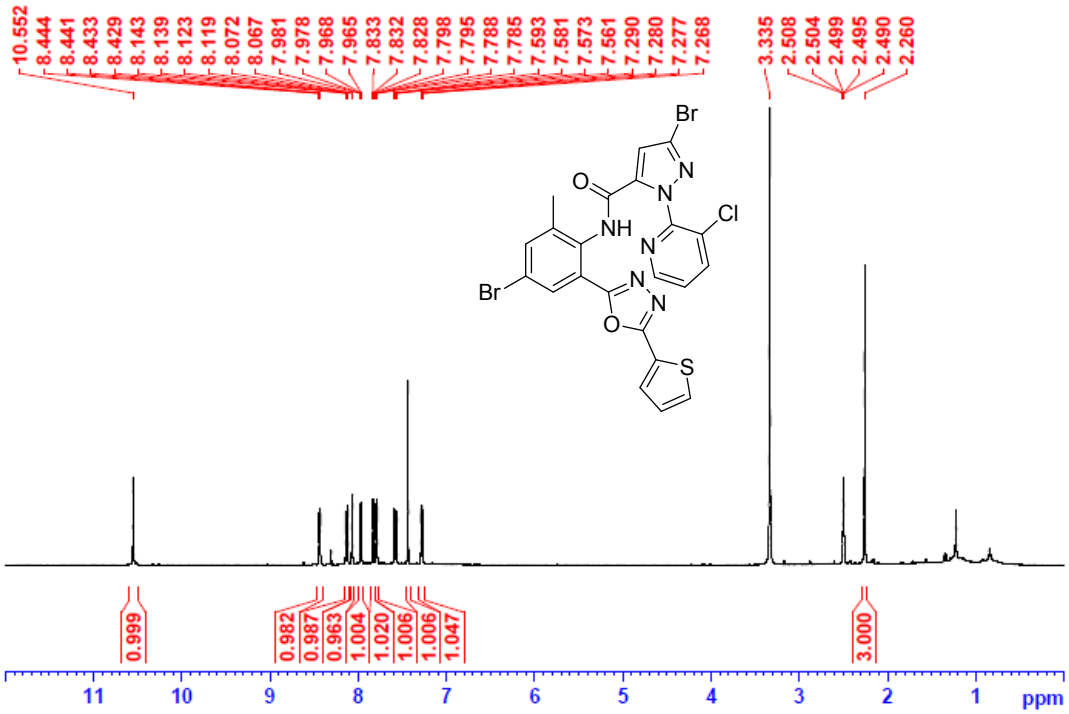


Figure S4 ^{1}H NMR of compound **5a**

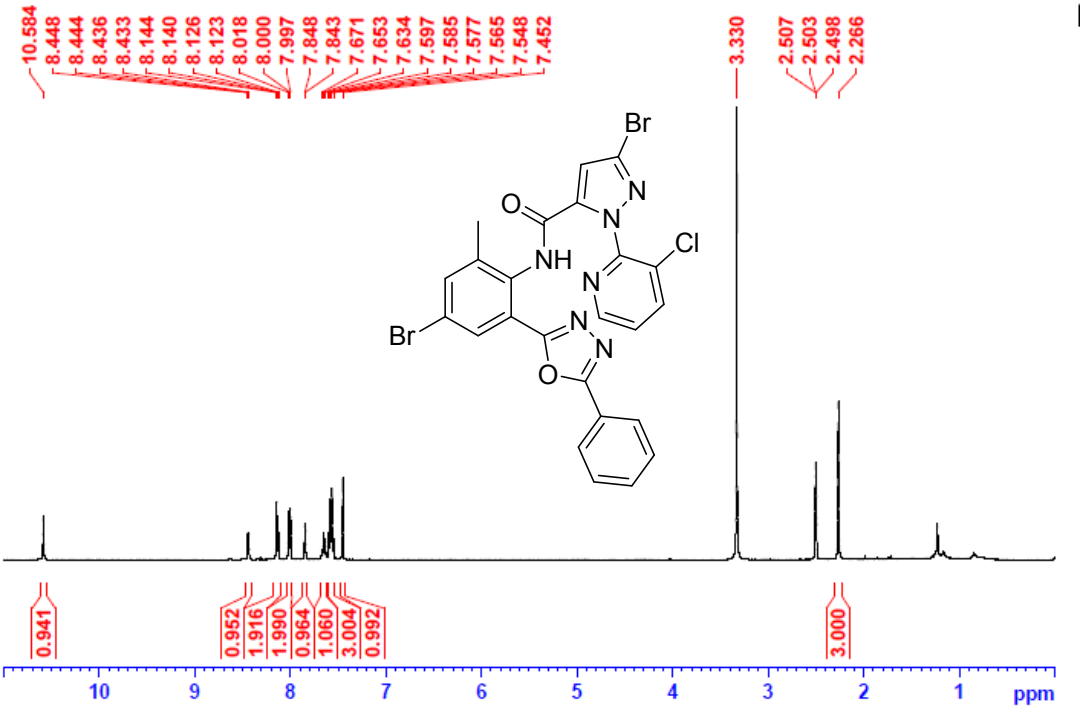


Figure S5 ^{1}H NMR of compound **5b**

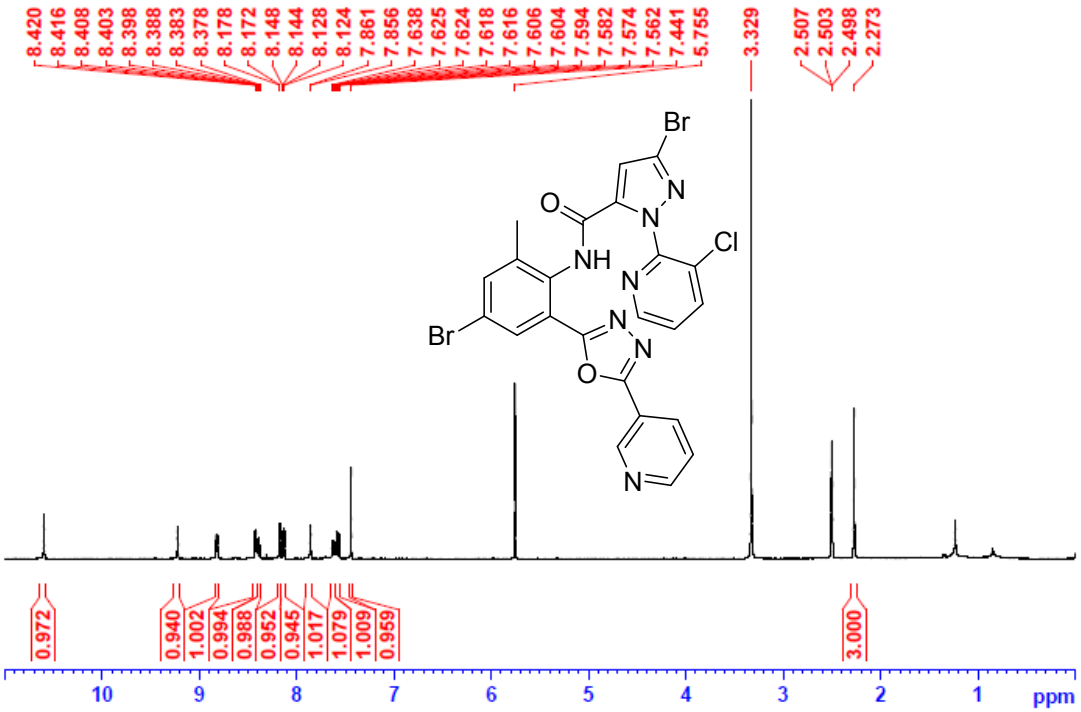


Figure S6 ^{1}H NMR of compound **5c**

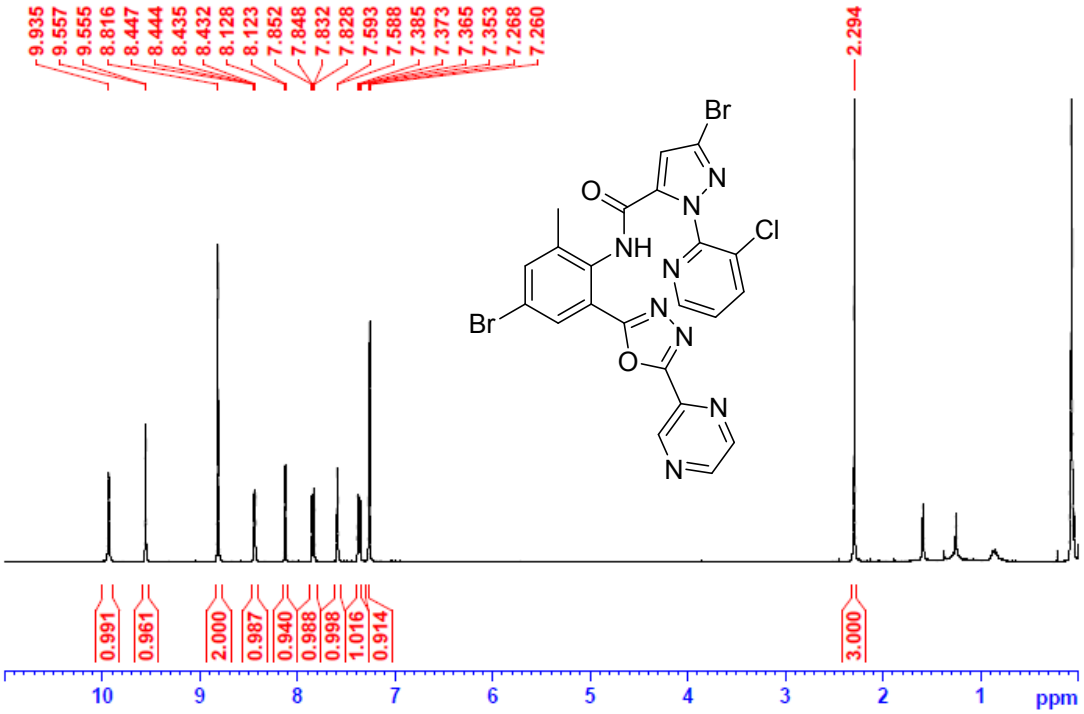


Figure S7 ^{1}H NMR of compound **5d**

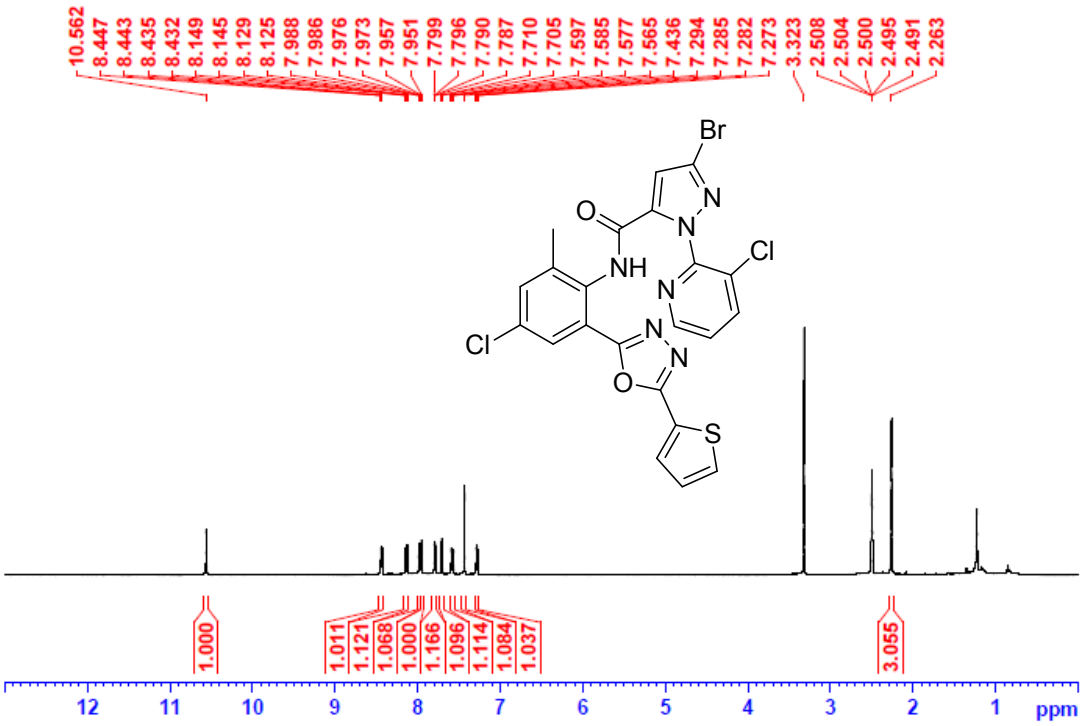


Figure S8 ^{1}H NMR of compound **5e**

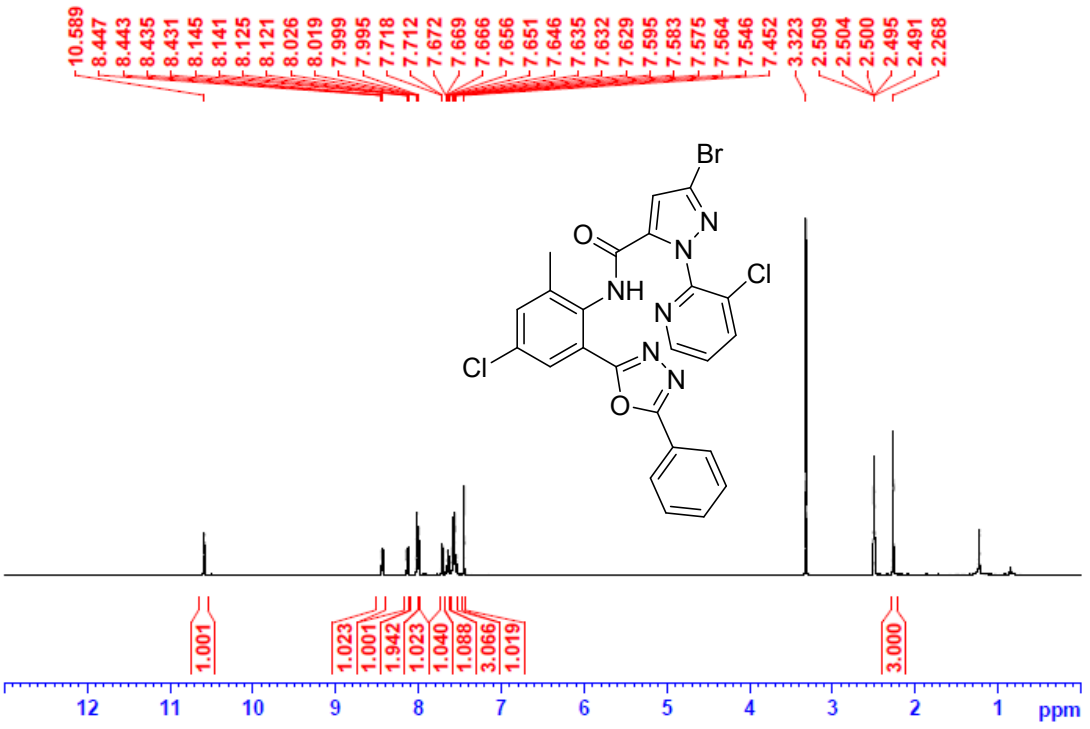


Figure S9 ^{1}H NMR of compound **5f**

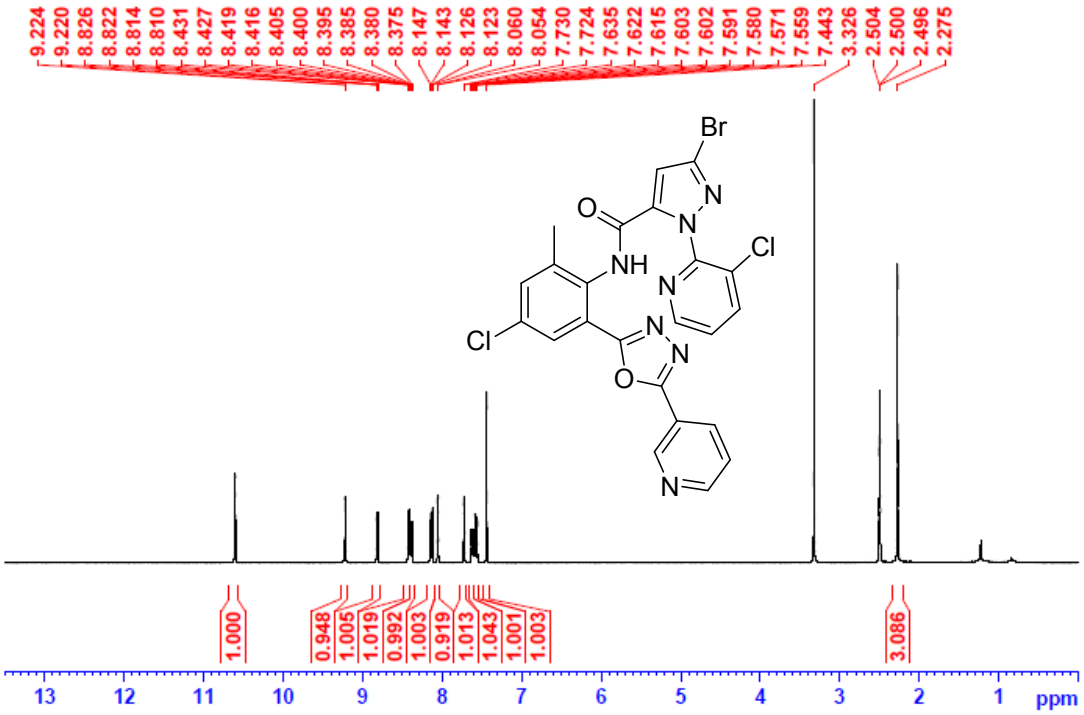


Figure S10 ^{1}H NMR of compound **5g**

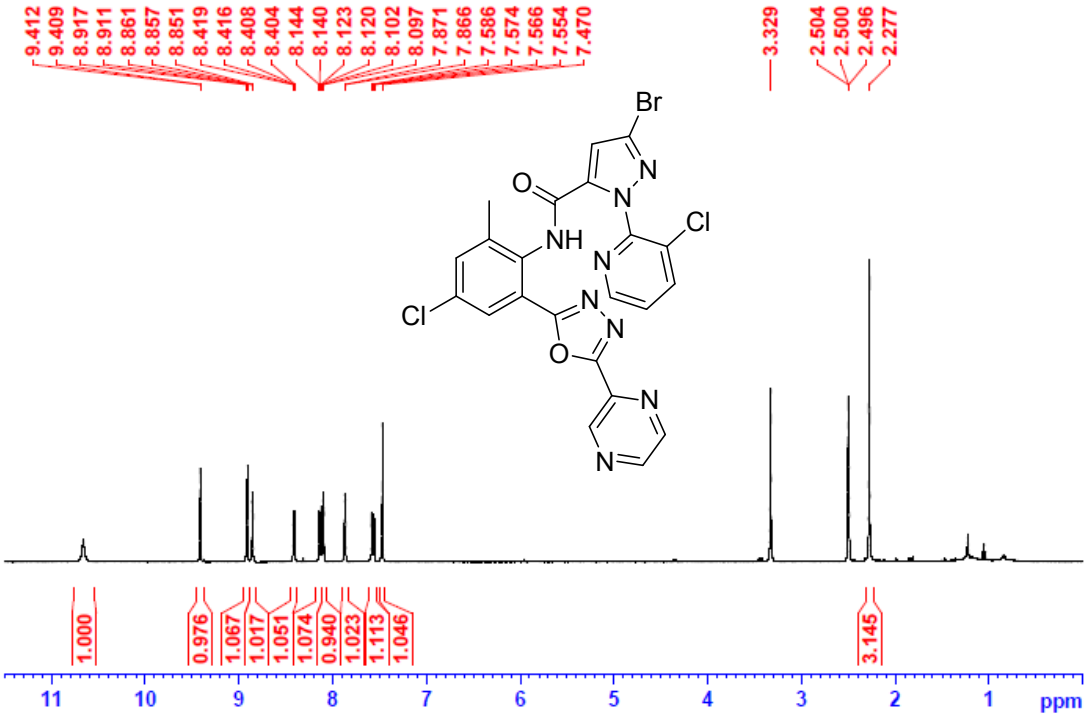


Figure S11 ^{1}H NMR of compound **5h**

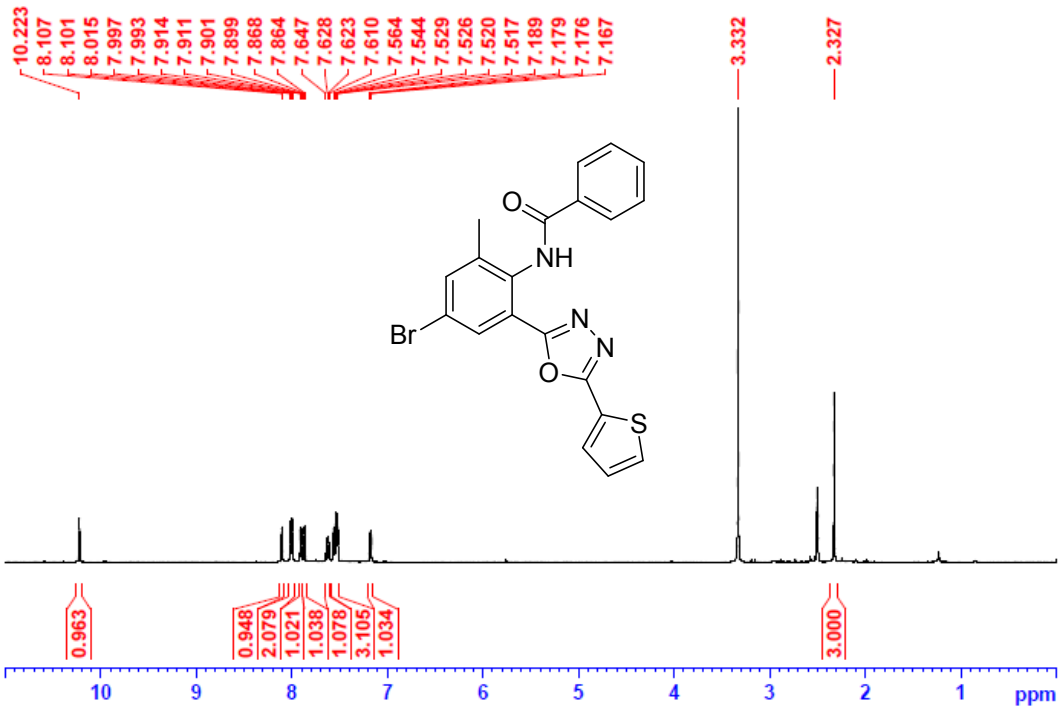


Figure S12 ^{1}H NMR of compound **5i**

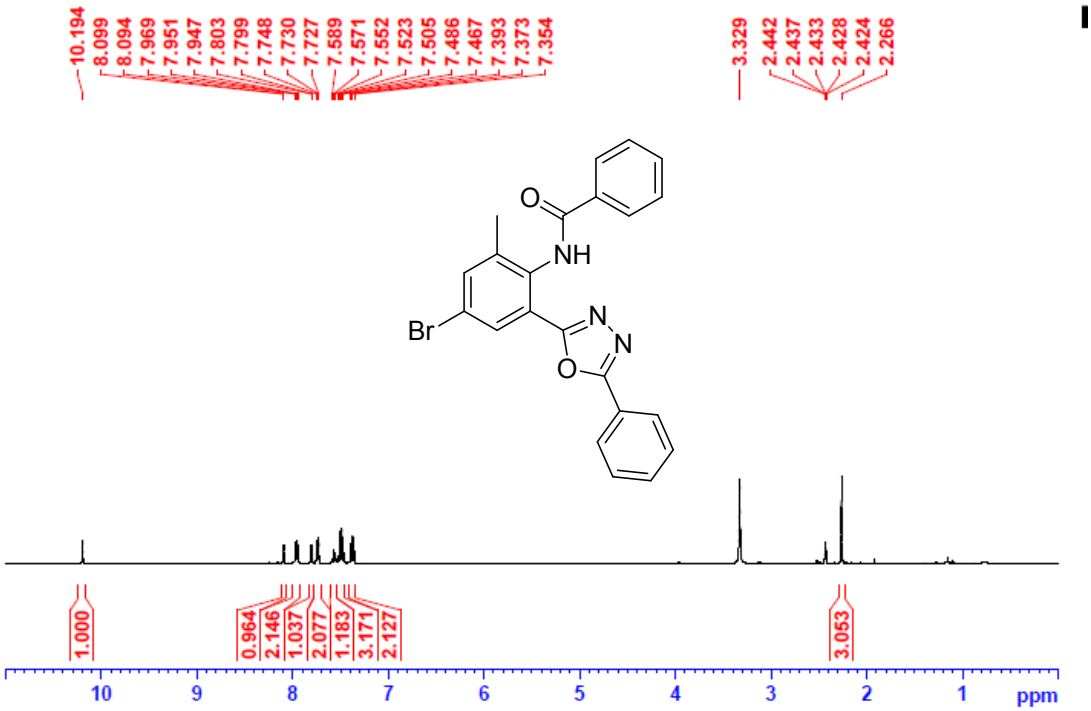


Figure S13 ^{1}H NMR of compound **5j**

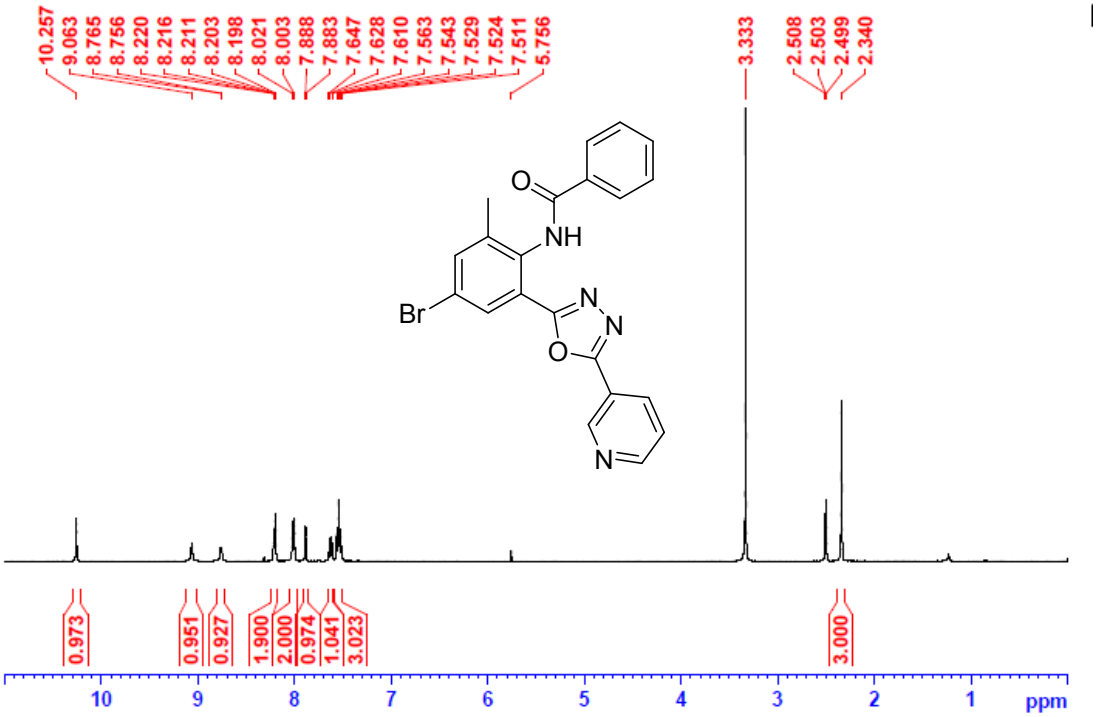


Figure S14 ^{1}H NMR of compound **5k**

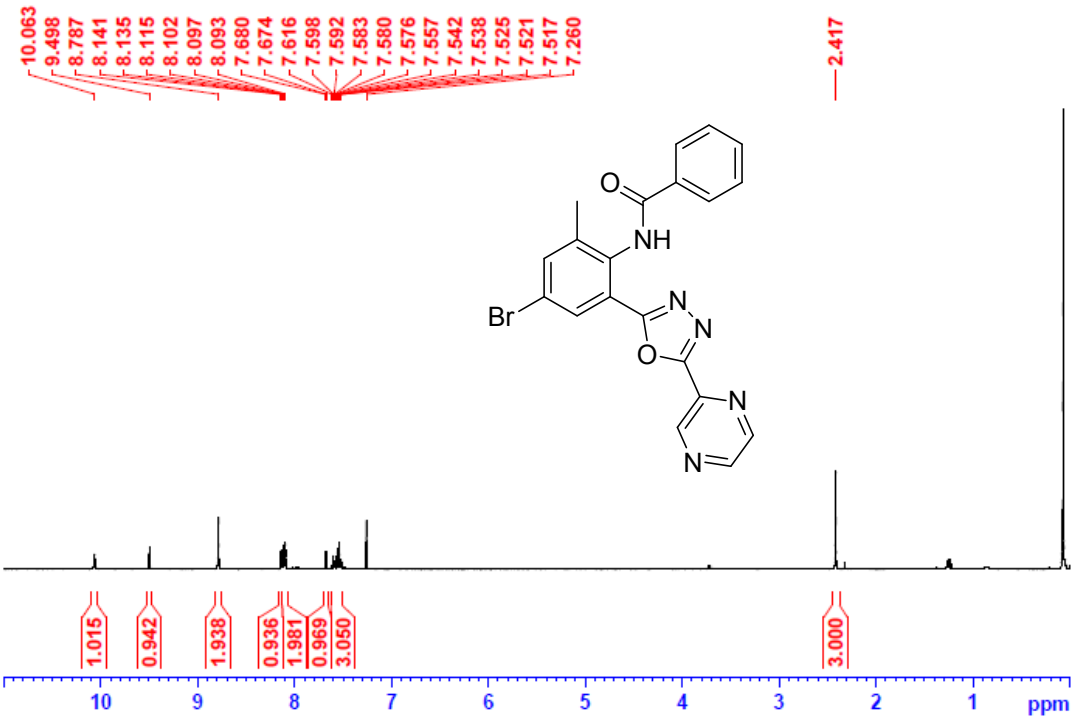


Figure S15 ^{1}H NMR of compound **5l**

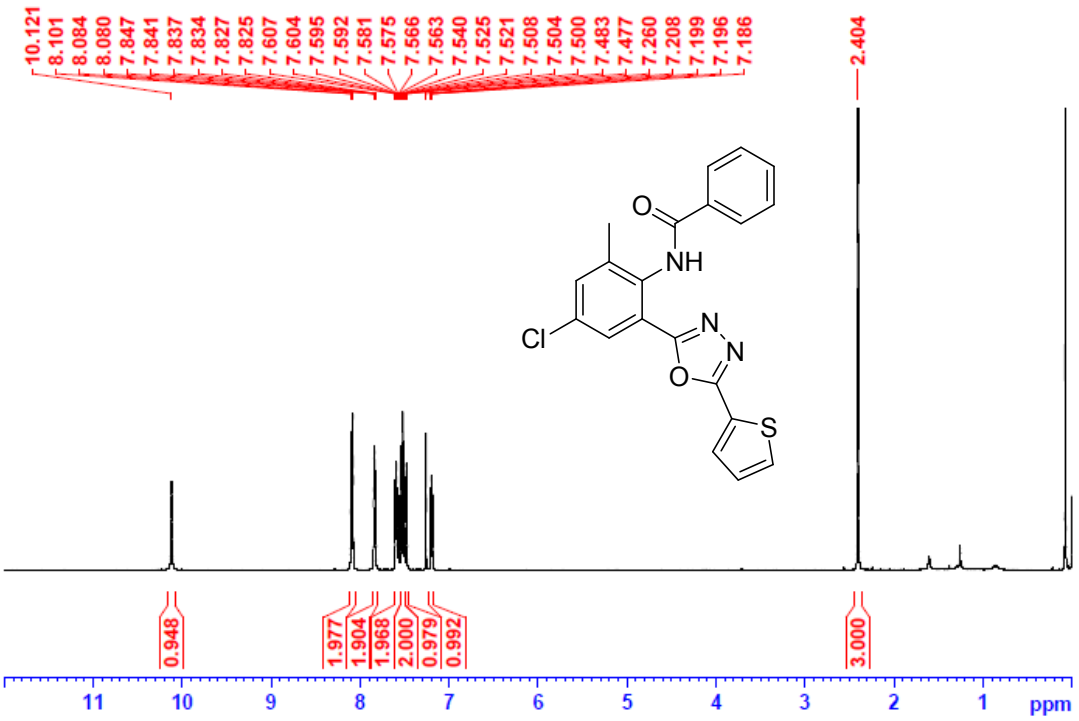


Figure S16 ^{1}H NMR of compound **5m**

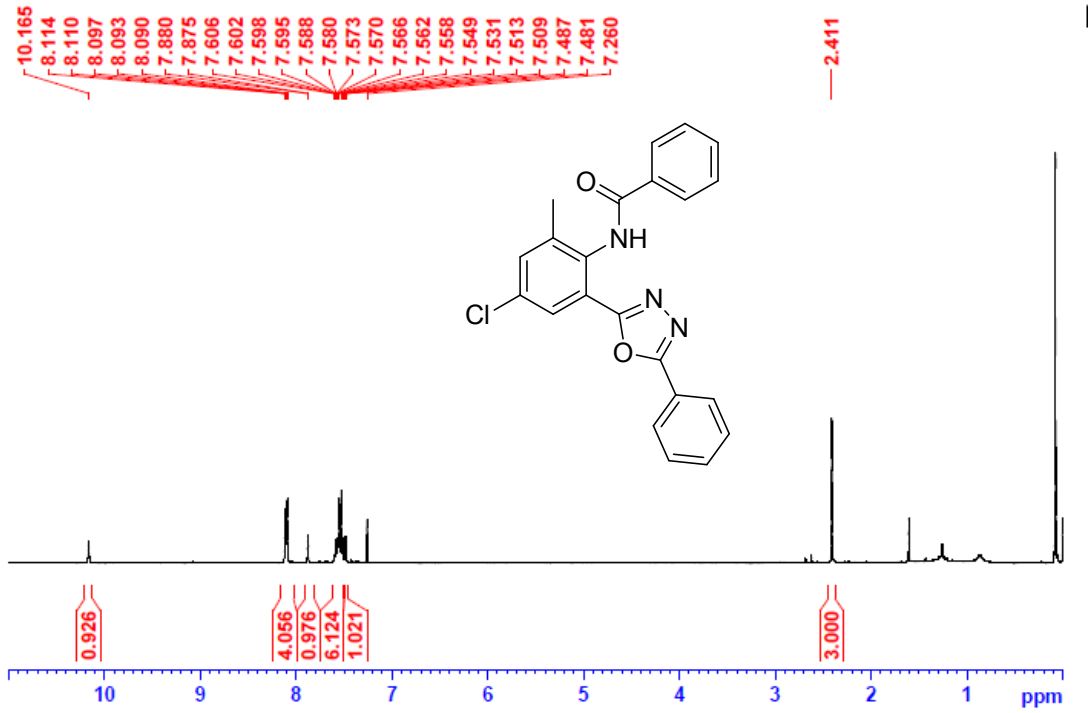


Figure S17 ^{1}H NMR of compound **5n**

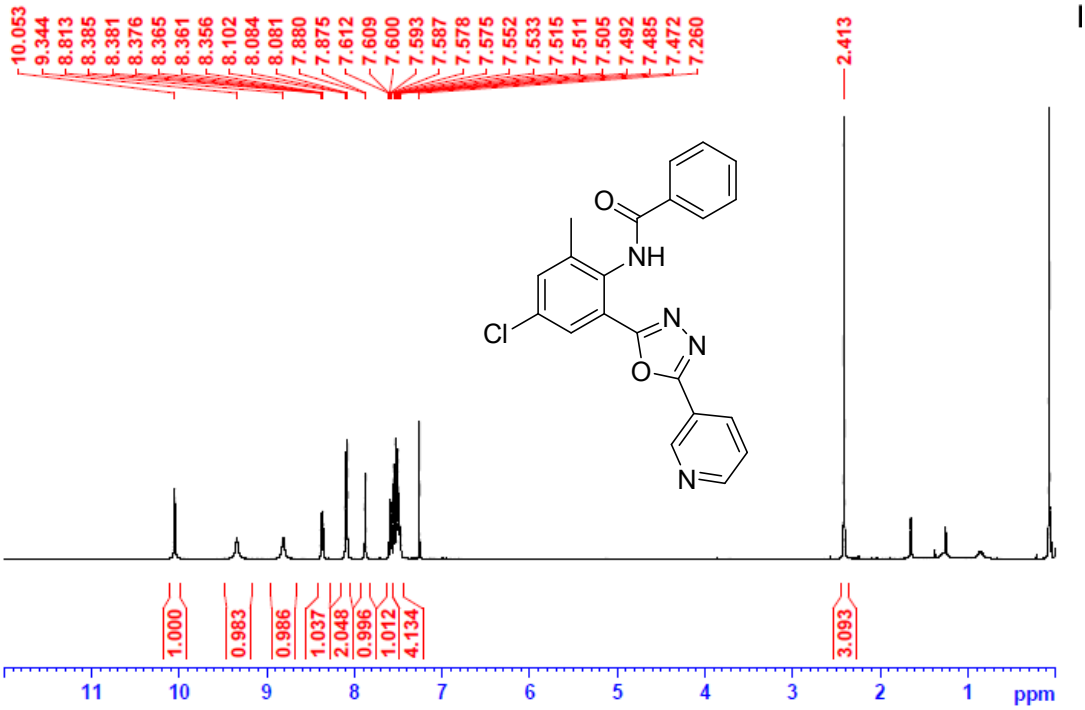


Figure S18 ^{1}H NMR of compound **5o**

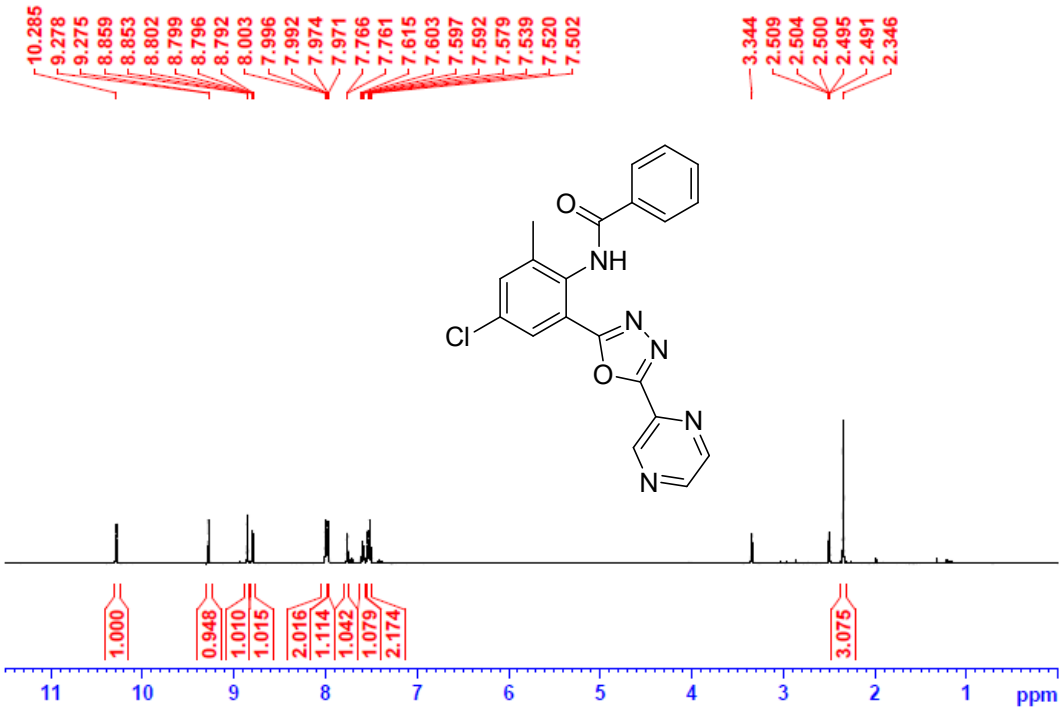


Figure S19 ^{1}H NMR of compound **5p**

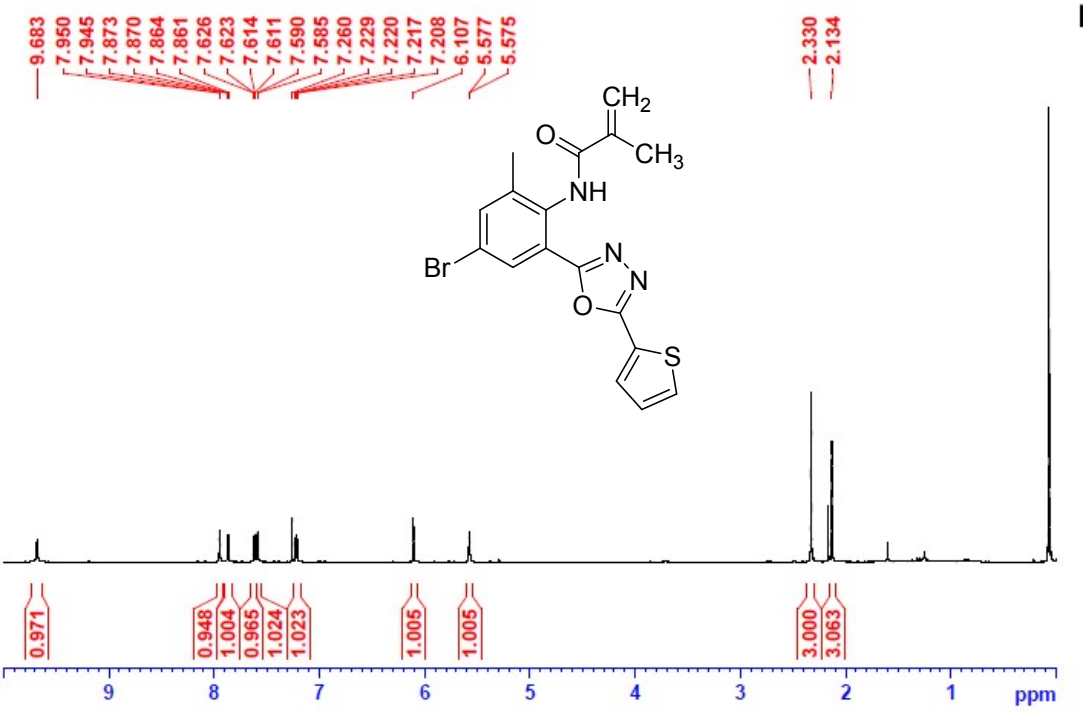


Figure S20 ^{1}H NMR of compound **5q**

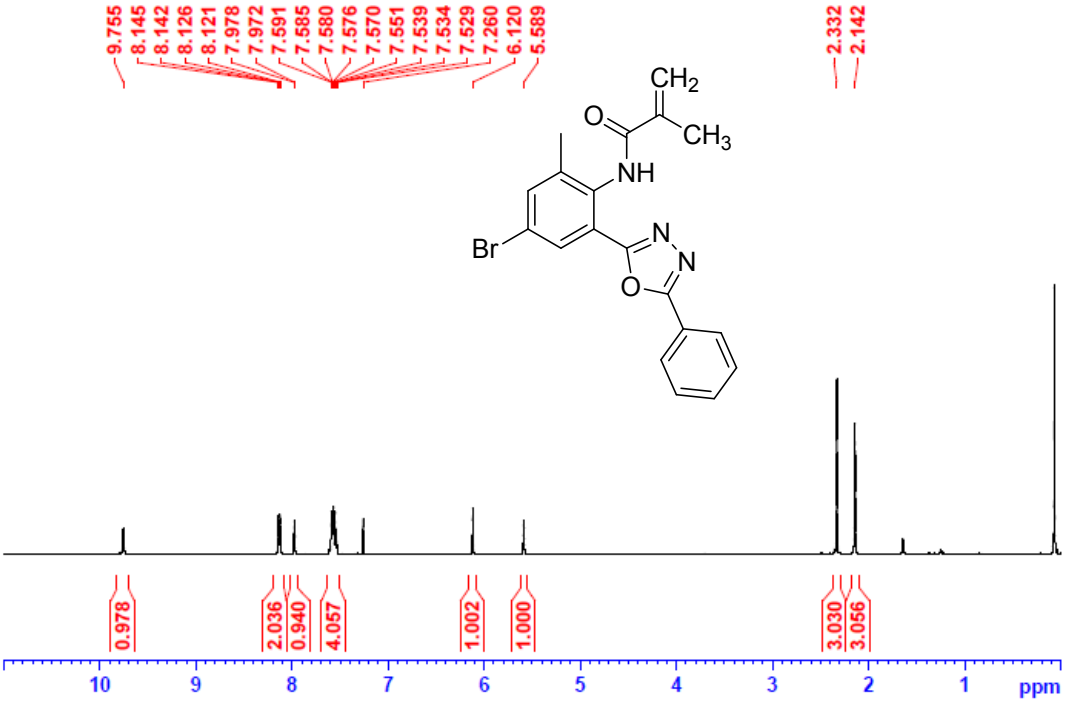


Figure S21 ^{1}H NMR of compound **5r**

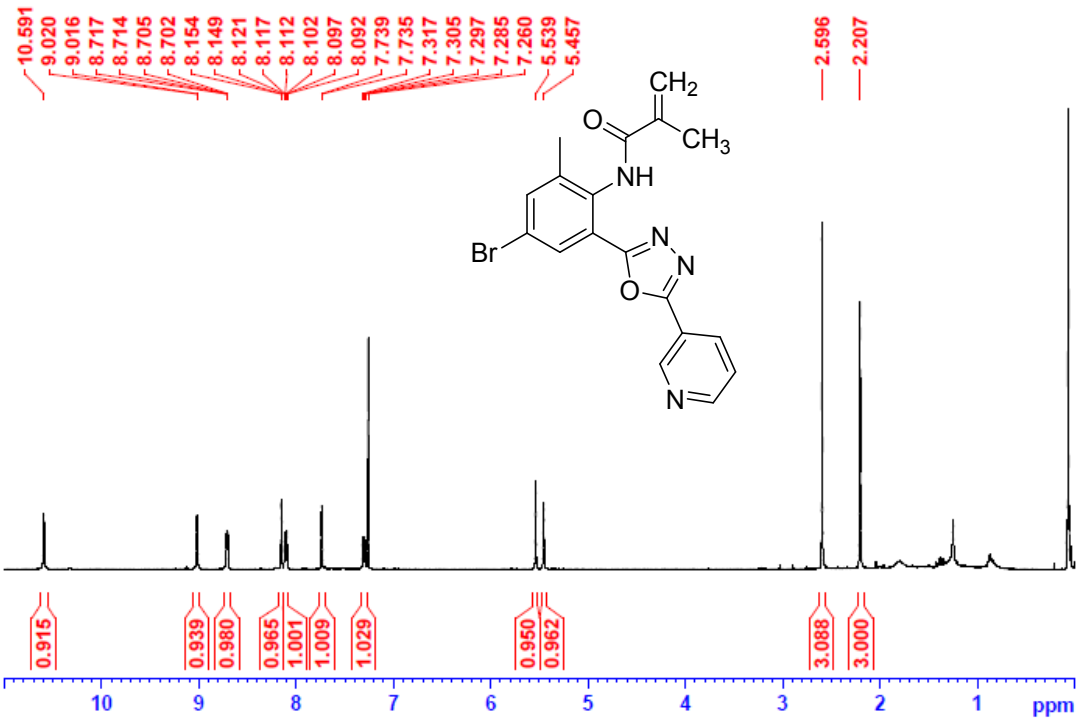


Figure S22 ^{1}H NMR of compound **5s**

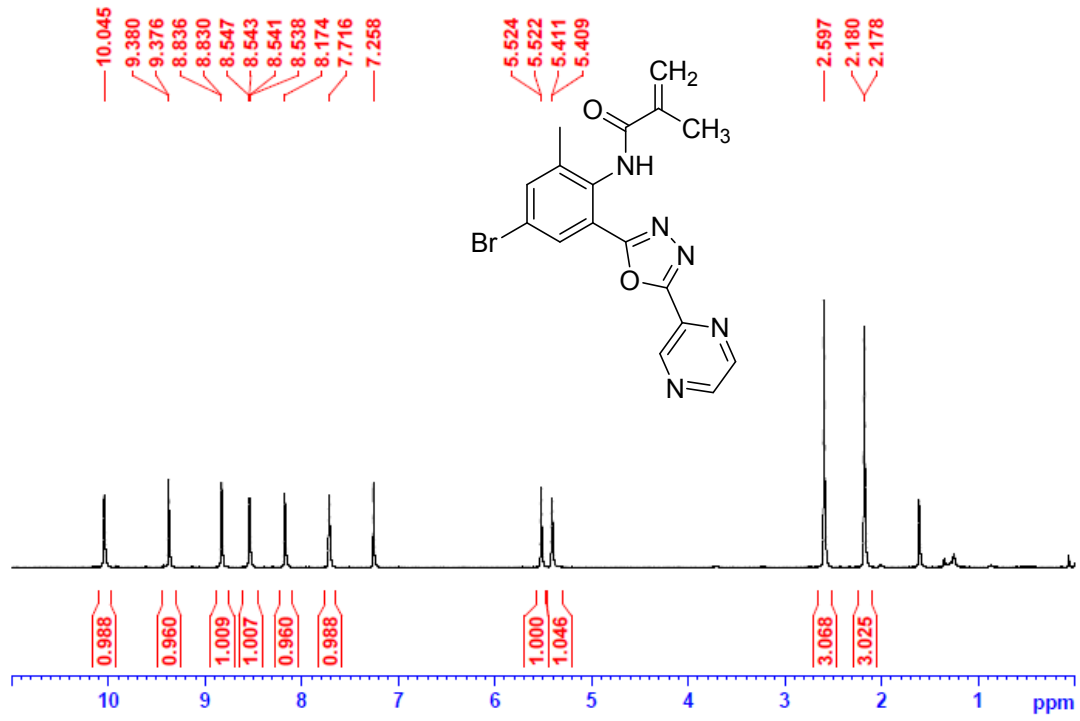


Figure S23 ^{1}H NMR of compound **5t**

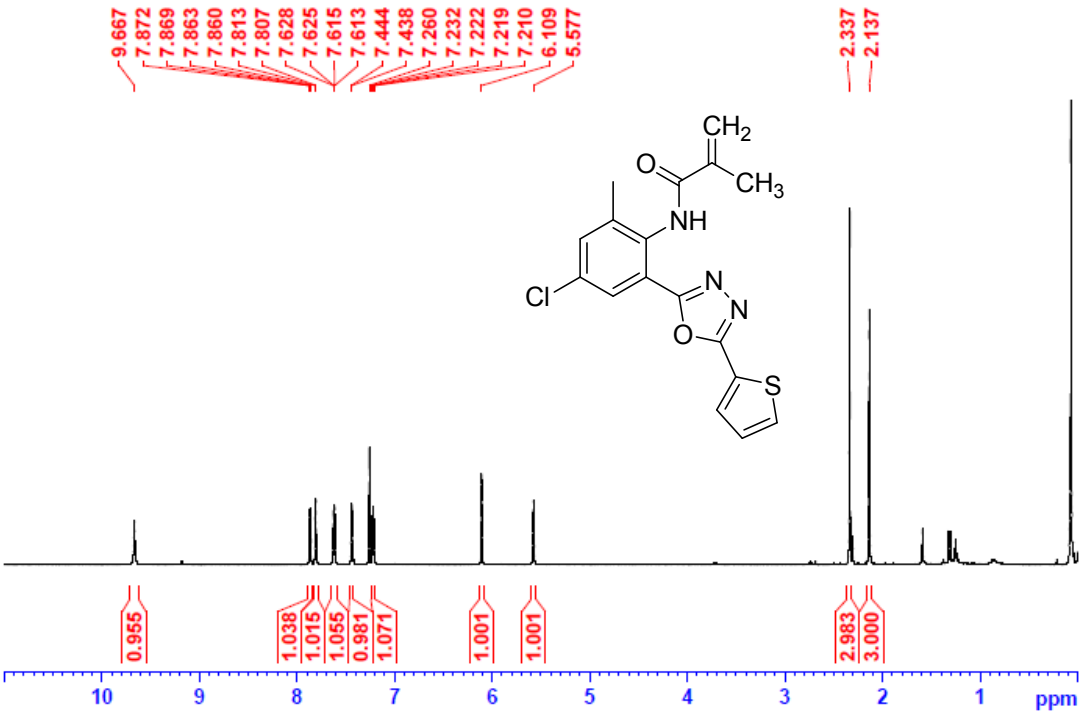


Figure S24 ^{1}H NMR of compound **5u**

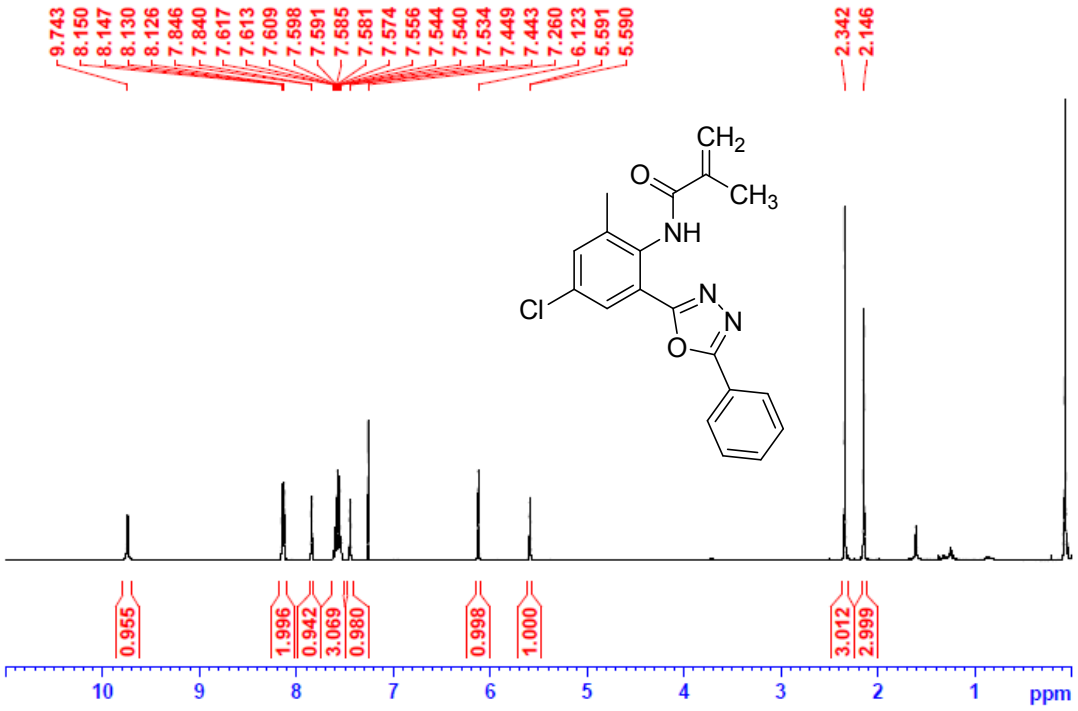


Figure S25 ^{1}H NMR of compound **5v**

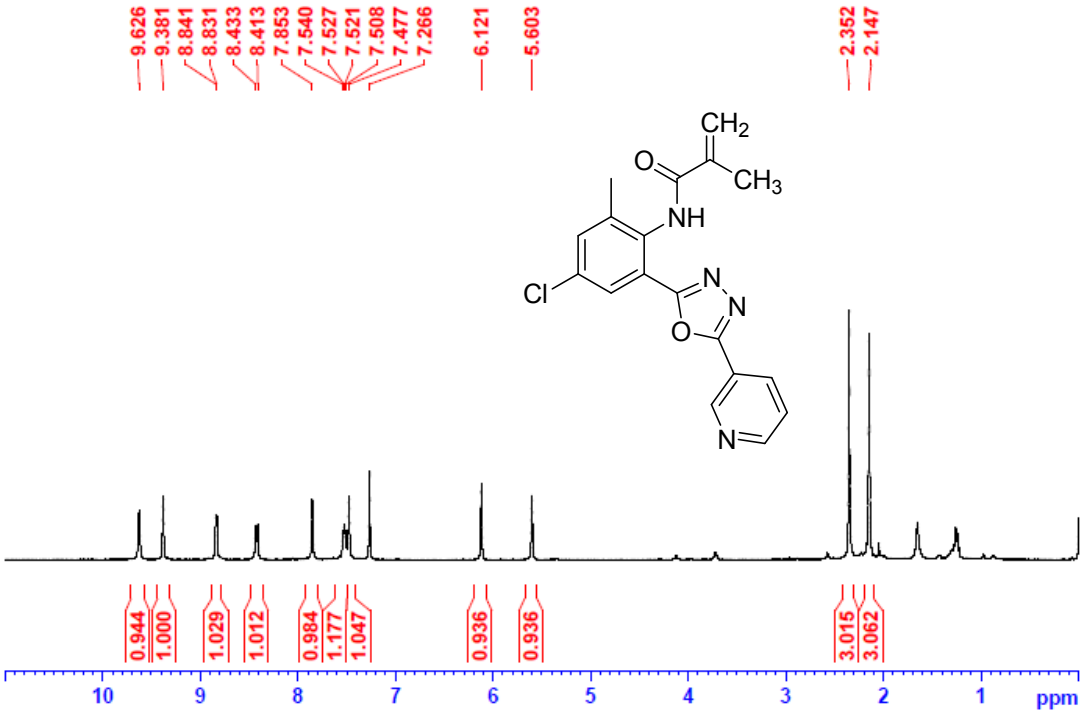


Figure S26 ^{1}H NMR of compound **5w**

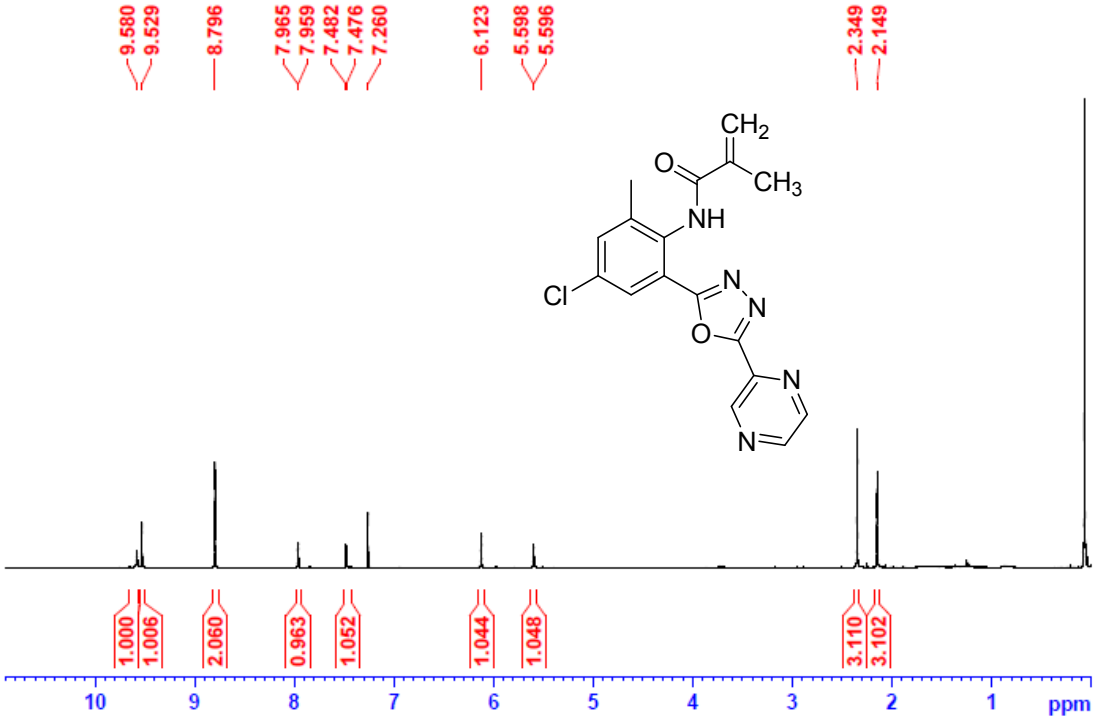


Figure S27 ^{1}H NMR of compound **5x**

7) Figure S28-S51. Mass spectra for compounds 5a-x

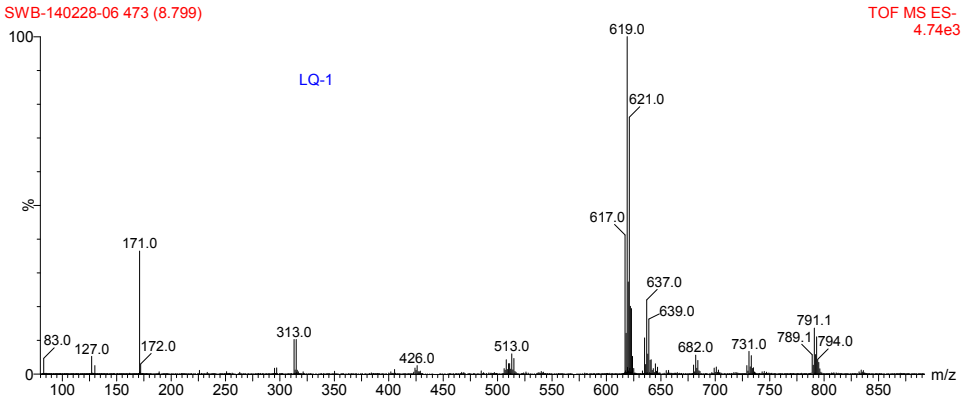


Figure S28 MS of compound **5a**

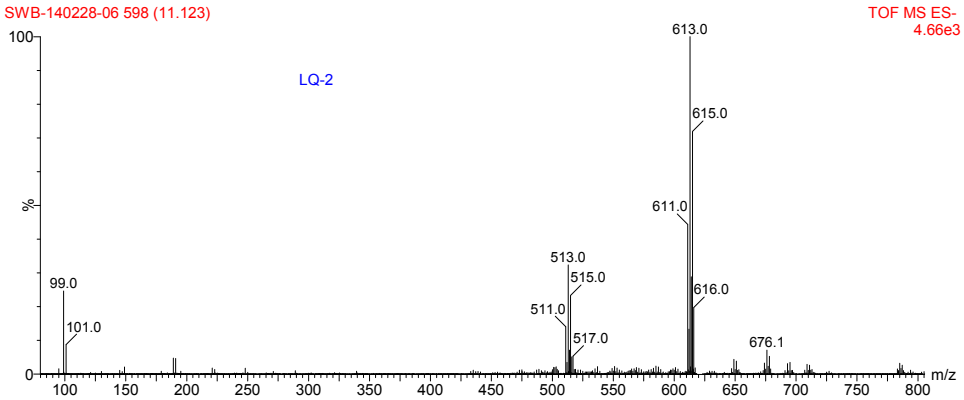


Figure S29 MS of compound **5b**

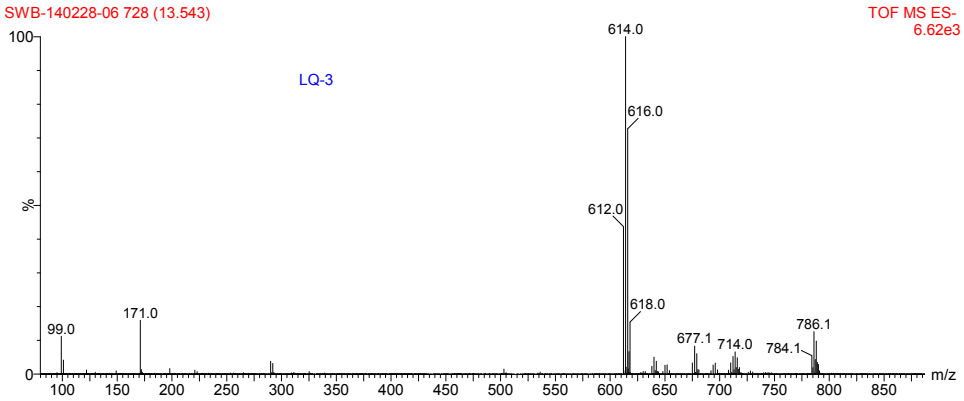


Figure S30 MS of compound **5c**

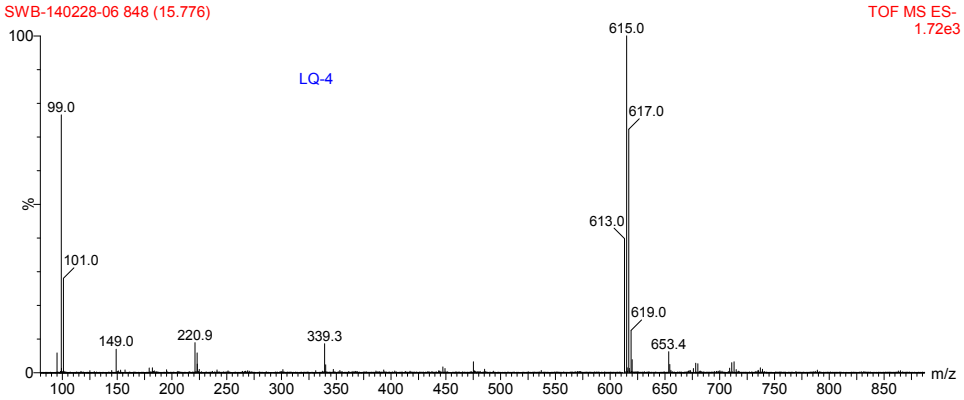


Figure S31 MS of compound **5d**

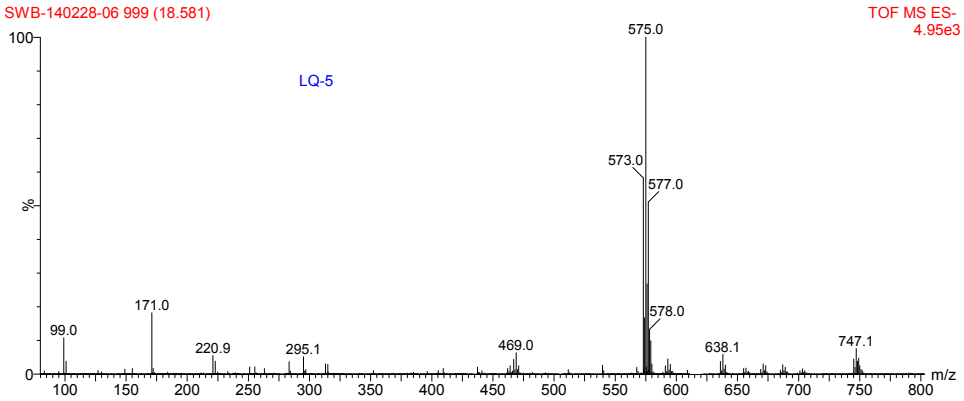


Figure S32 MS of compound **5e**

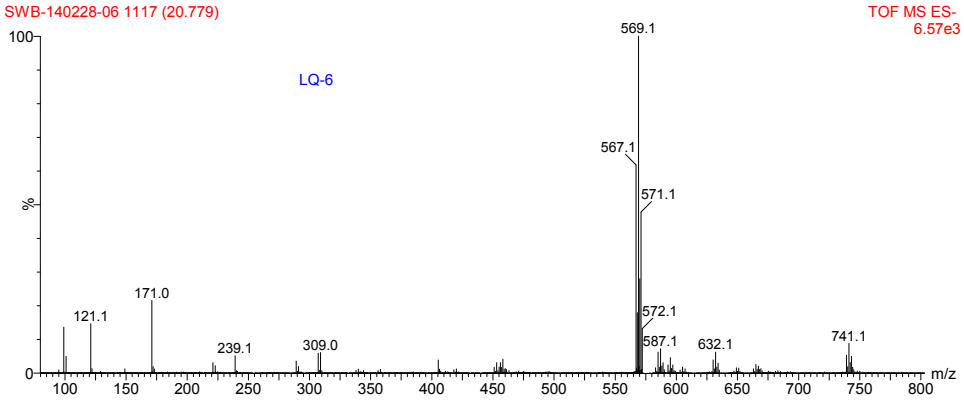


Figure S33 MS of compound **5f**

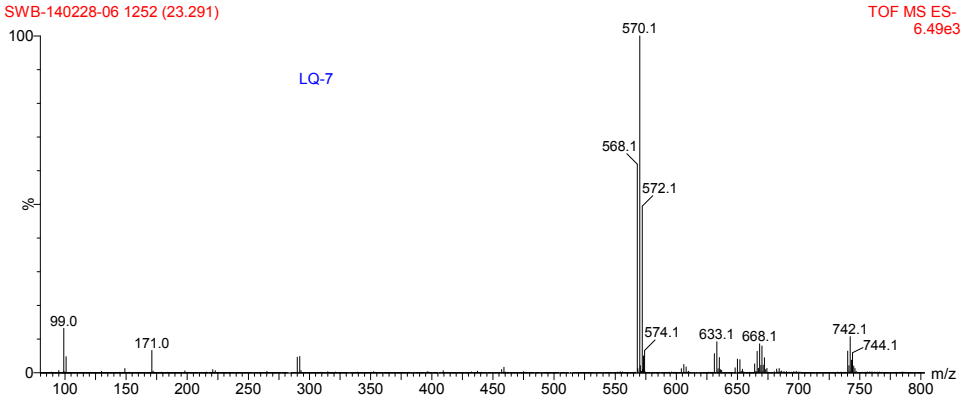


Figure S34 MS of compound **5g**

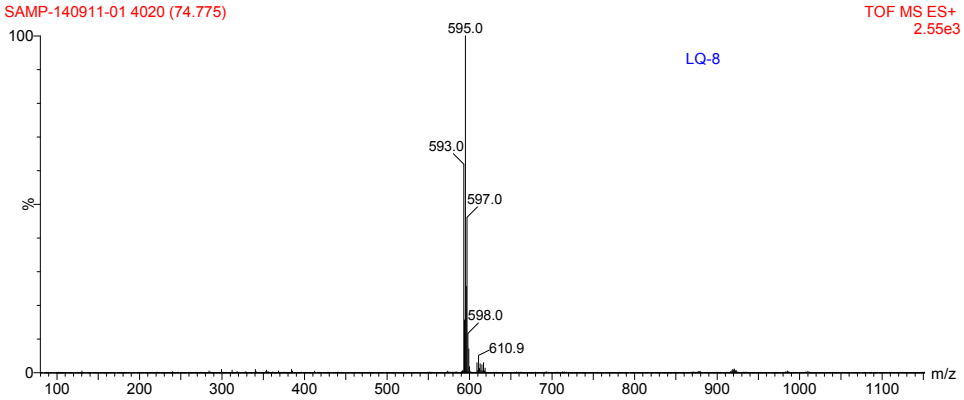


Figure S35 MS of compound **5h**

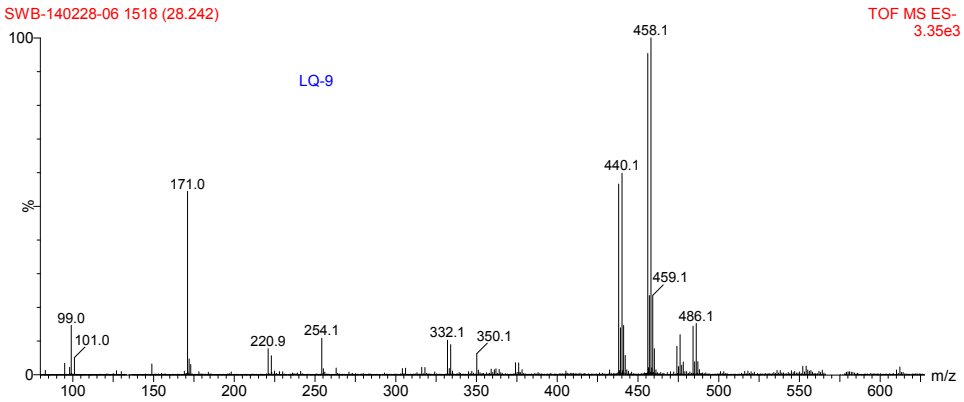


Figure S36 MS of compound **5i**

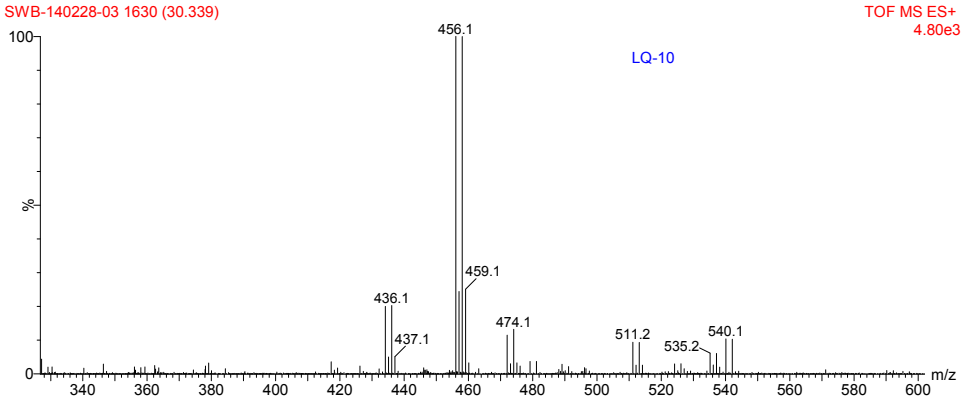


Figure S37 MS of compound **5j**

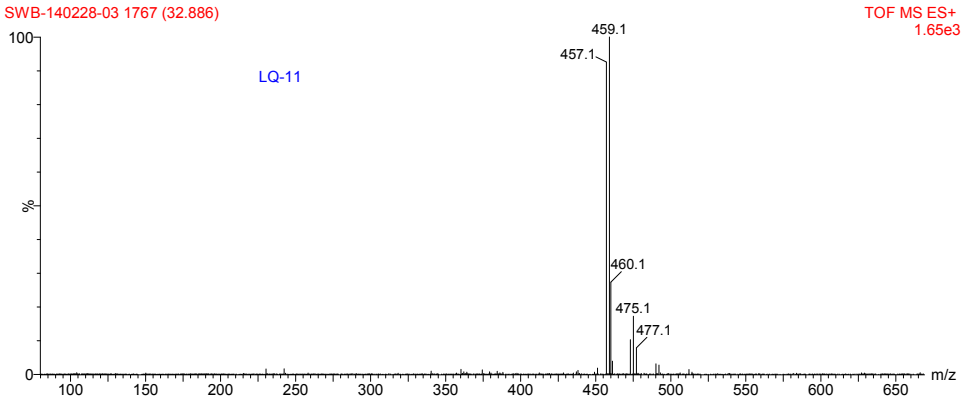


Figure S38 MS of compound **5k**

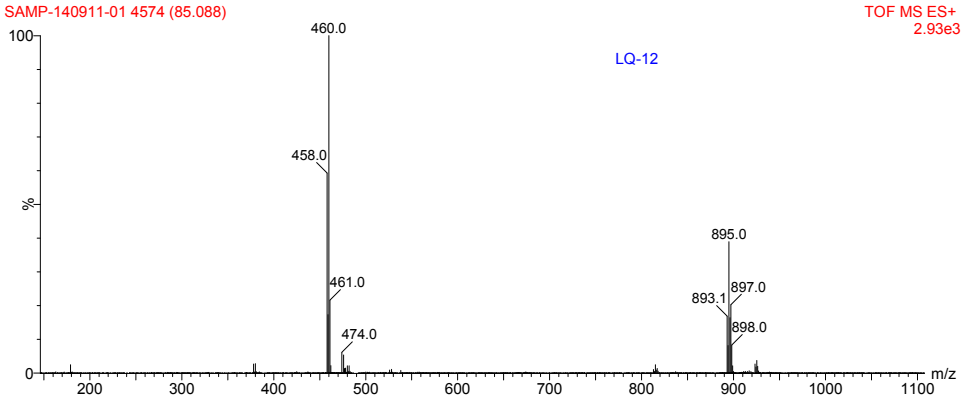


Figure S39 MS of compound **5l**

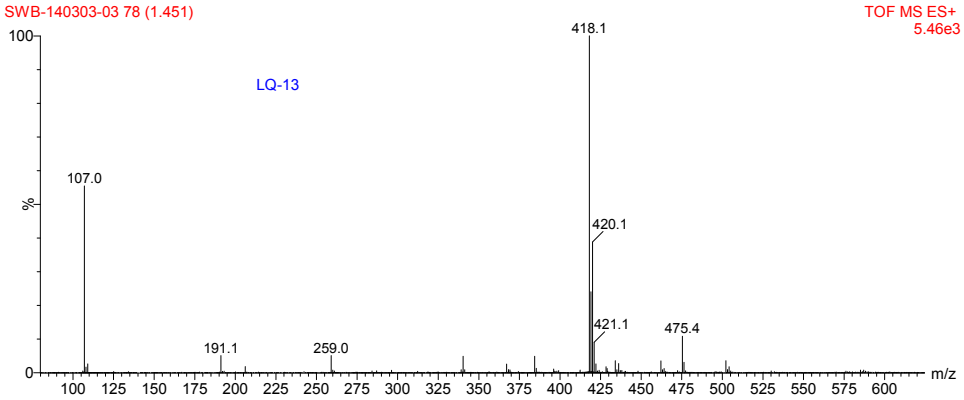


Figure S40 MS of compound **5m**

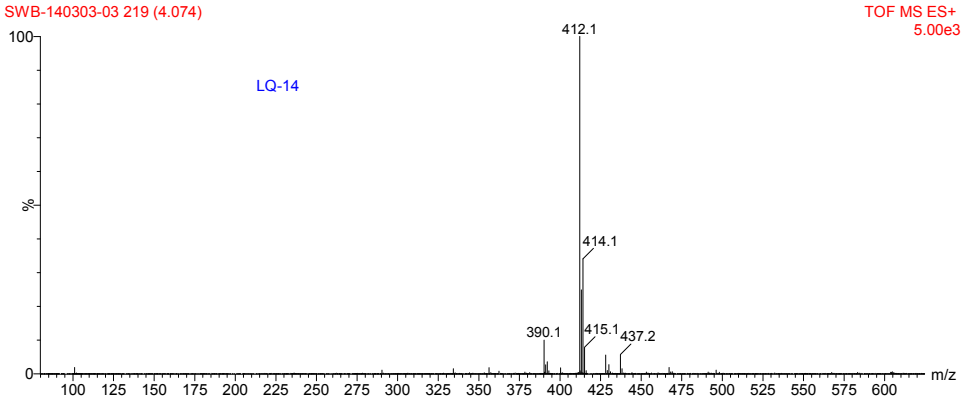


Figure S41 MS of compound **5n**

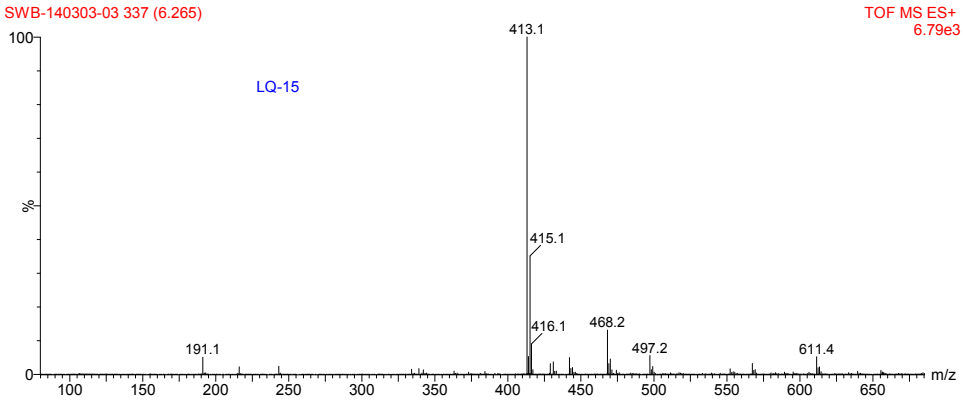


Figure S42 MS of compound **5o**

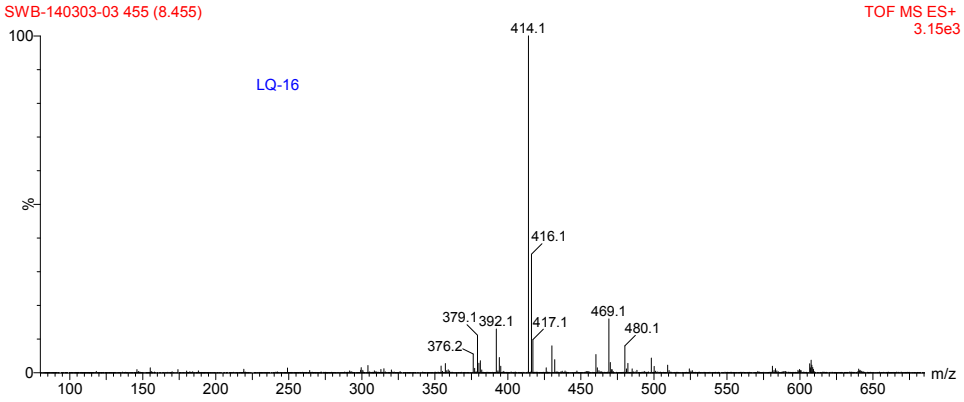


Figure S43 MS of compound **5p**

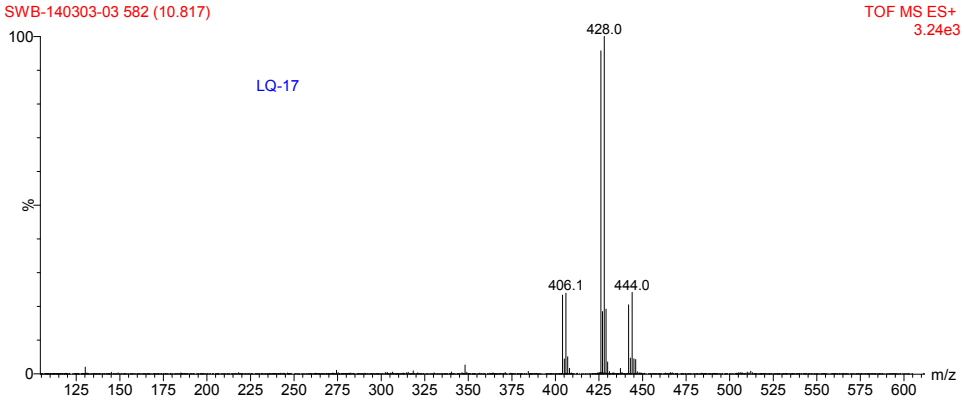


Figure S44 MS of compound **5q**

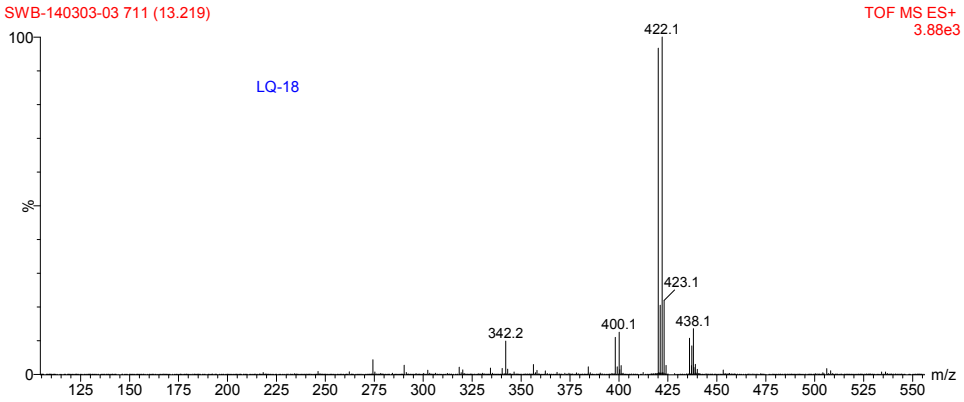


Figure S45 MS of compound **5r**

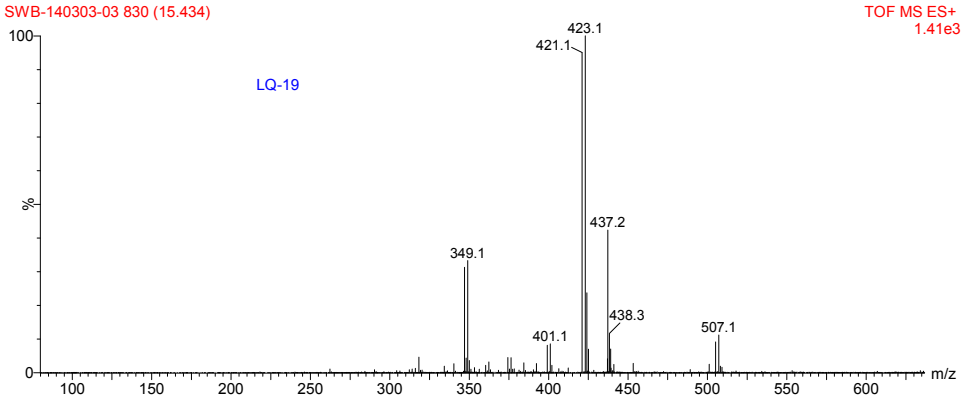


Figure S46 MS of compound **5s**

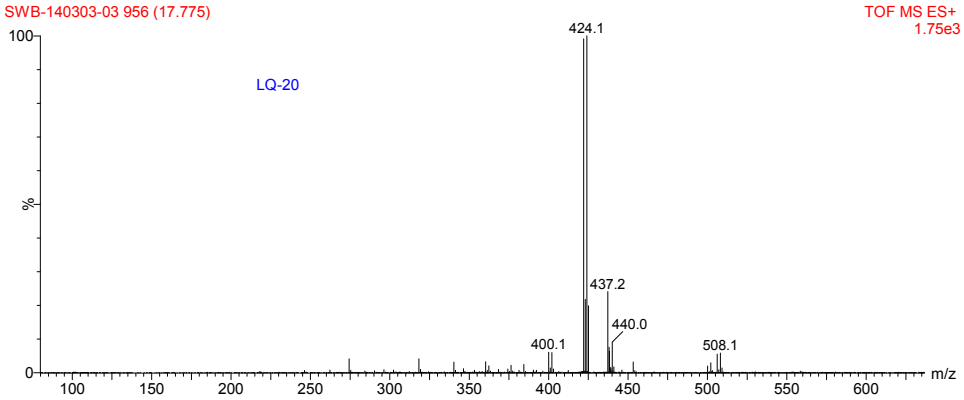


Figure S47 MS of compound **5t**

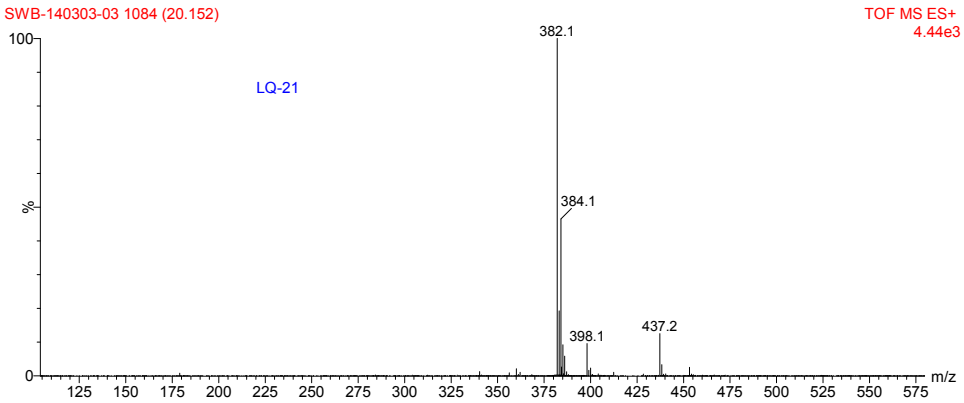


Figure S48 MS of compound **5u**

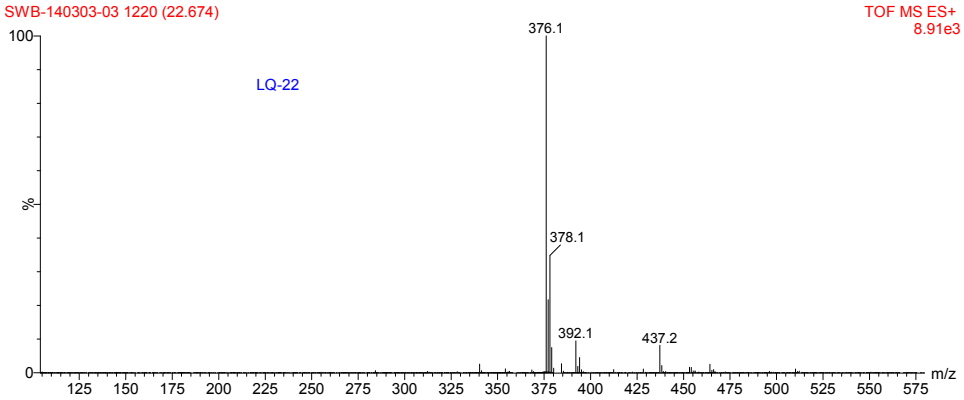


Figure S49 MS of compound **5v**

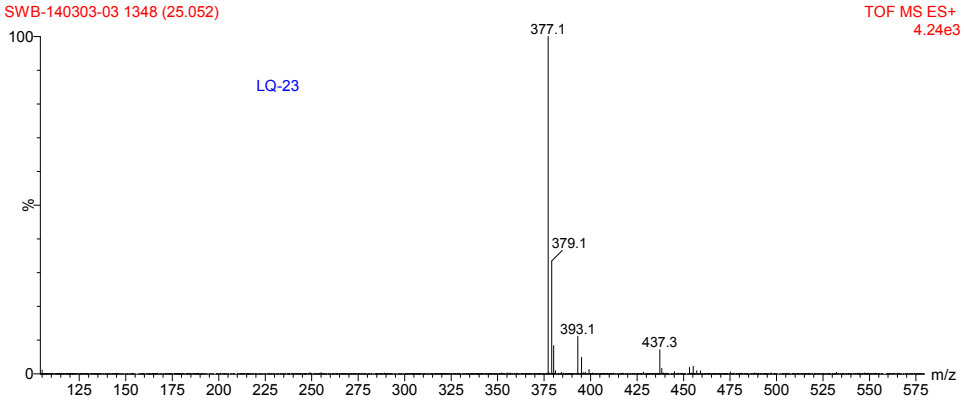


Figure S50 MS of compound **5w**

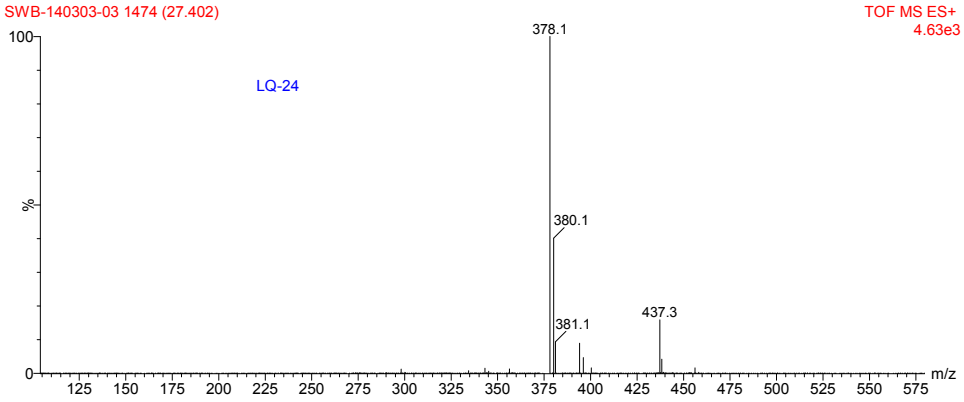


Figure S51 MS of compound **5x**