Supporting information for:

Synthesis, Insecticidal Activities and SAR Studies of Novel Pyridylpyrazole Acid Derivatives Based on Amide Bridge Modification of Anthranilic Diamide Insecticides

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***N*'-(2-Methyl-4-(perfluoropropan-2-yl)phenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-chloro-1*H*-praz ole-5-carbonyl)thiourea 19a**: light yellow solid, yield 57 %, mp 175-177 ^{o}C; IR (KBr, cm^{-1}): 3410, 3229, 3176, 3052, 1686, 1582, 1541, 1499, 1467, 1281, 1162; ^{1}H NMR (400MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), 7.01 (s, 1H, Pyrazol-H), 7.47-7.52 (m, 3H, Ph-H), 7.99 (d, J = 8.4 Hz, 1H, Py-H), 8.05 (d, J = 9.2 Hz, 1H, Py-H), 8.60 (d, J = 4.8 Hz, 1H, Py-H), 10.09 (s, 1H, NH), 11.78 (s, 1H, NH); HRMS calcd for $C_{20}H_{12}Cl_2F_7N_5OS$ ([M-H]$^-$), 571.9950; found, 571.9955.

***N*'-(2-Methyl-4-(perfluoropropan-2-yl)phenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-pra zole-5-carbonyl)thiourea 19b**: yellow solid, yield 54 %, mp 187-190 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), 7.10 (s, 1H, Pyrazol-H), 7.47-7.51 (m, 3H, Ph-H), 7.99 (d, J = 8.0 Hz, 1H, Py-H), 8.06 (d, J = 8.4 Hz, 1H, Py-H), 8.58 (d, J = 3.6 Hz, 1H, Py-H), 10.00 (s, 1H, NH), 11.77 (s, 1H, NH) ; HRMS calcd for $C_{20}H_{12}BrClF_7N_5OS$ ([M+Na]$^+$), 639.9415; found, 639.9412.

***N*'-(2-Bromo-4,6-difluorophenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbon yl)thiourea 19c**: white solid, yield 62 %, mp 187-189 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 6.90-6.94 (m, 1H, Ph-H), 7.11 (s, 1H, Pyrazol-H), 7.22-7.26 (m, 1H, Ph-H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.99 (d, J = 8.0 Hz, 1H, Py-H), 8.57 (d, J = 3.2 Hz, 1H, Py-H), 10.11 (s, 1H, NH), 11.13 (s, 1H, NH); HRMS calcd for $C_{16}H_8Br_2ClF_2N_5OS$ ([M+H]$^+$), 549.8546; found, 549.8599.

***N*'-(2,4,6-Trichlorophenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thio urea 19d**: white solid, yield 36 %, mp 188-190 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.17 (s, 1H, Pyrazol-H), 7.42 (s, 2H, Ph-H), 7.49 (dd, J = 8.0 Hz, J = 4.8 Hz, 1H, Py-H), 7.99 (d, J = 8.0 Hz, 1H, Py-H), 8.56 (d, J = 4.8 Hz, 1H, Py-H), 10.27 (s, 1H, NH), 11.28 (s, 1H, NH); HRMS calcd for $C_{16}H_8BrCl_4N_5OS$ ([M-H]$^-$), 535.8309; found, 535.8318.

***N*'-(2,6-Dibromo-4-(trifluoromethoxy)phenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-chloro-1*H*-praz**

ole-5-carbonyl)thiourea 19e: light yellow solid, yield 44 %, mp 170-172 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (s, 1H, Pyrazol-H), 7.49 (dd, J = 8.0 Hz, J = 4.4 Hz, 1H, Py-H), 7.51 (s, 2H, Ph-H), 7.99 (d, J = 8.0 Hz, 1H, Py-H), 8.56 (d, J = 4.4 Hz, 1H, Py-H), 10.16 (s, 1H, NH), 11.34 (s, 1H, NH); Elemental analysis for $C_{17}H_8Br_2Cl_2F_3N_5O_2S$, calcd: C 32.20, H 1.27, N 11.05; found: C 31.78, H 1.32, N 10.95.

***N*'-(2,6-Dibromo-4-(trifluoromethoxy)phenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-praz ole-5-carbonyl)thiourea 19f**: light yellow solid, yield 43 %, mp 189-191 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14 (s, 1H, Pyrazol-H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H, Py-H), 7.51 (s, 2H, Ph-H), 7.99 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.56 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 1H, Py-H), 10.13 (s, 1H, NH), 11.34 (s, 1H, NH); HRMS calcd for $C_{17}H_8Br_3ClF_3N_5O_2S$ ([M-H]$^-$), 673.7511; found, 673.7519.

***N*'-(2-Chloro-6-nitrophenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)th iourea 19g**: light yellow solid, yield 71 %, mp 202-204 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.16 (s, 1H, Pyrazol-H), 7.49-7.53 (m, 1H, Ph-H), 7.61 (d, J = 11.8 Hz, 1H, Py-H), 8.00-8.08 (m, 2H, Ph-H + Py-H), 8.59 (d, J = 4.4 Hz, 1H, Py-H), 9.44 (s, 1H, Ph-H), 10.42 (s, 1H, NH), 12.34 (s, 1H, NH); Elemental analysis for $C_{16}H_9BrCl_2N_6O_3S$, calcd: C 37.23, H 1.76, N 16.28; found: C 37.48, H 2.36, N 16.11.

***N*'-(4-Methoxyl-2-nitrophenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl) thiourea 19h**: yellow solid, yield 42 %, mp 113-116 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 3.89 (s, 3H, OCH_3), 7.11 (s, 1H, Pyrazol-H), 7.19 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, Ph-H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Ph-H), 7.57 (d, J = 2.8 Hz, 1H, Ph-H), 8.00 (d, J = 8.0 Hz, 1H, Py-H), 8.09 (d, J = 8.8, 1H, Py-H), 8.57 (d, J = 4.8 Hz, 1H, Py-H), 10.02 (s, 1H, NH), 12.48 (s, 1H, NH);

Elemental analysis for $C_{17}H_{12}BrClN_6O_4S$, calcd: C 39.90, H 2.36, N 16.42; found: C 39.87, H 2.87, N 16.40.

***N*'-(2,6-Difluorophenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thiourea 19i**: light yellow solid, yield 51 %, mp 191-192 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.99 (t, J = 8.4 Hz, 2H, Ph-H), 7.11 (s, 1H, Pyrazol-H), 7.29-7.36 (m, 1H, Ph-H), 7.49 (dd, J_1 = 8.4 Hz, J_2 = 4.4 Hz, 1H, Py-H), 7.99 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.57 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 1H, Py-H), 10.09 (s, 1H, NH), 11.10 (s, 1H, NH); HRMS for $C_{16}H_9BrClF_2N_5OS$, calcd: 469.9290; found: 469.9296 ($[M-H]^-$).

***N*'-(4-Bromo-2-methylphenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl) thiourea 19j**: white solid, yield 63 %, mp 187-189 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 (s, 3H, CH_3), 7.09 (s, 1H, Pyrazol-H), 7.35 (d, J = 8.4 Hz, 1H, Ph-H), 7.40 (s, 1H, Ph-H), 7.48-7.54 (m, 2H, Ph-H + Py-H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.57 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, Py-H), 9.90 (s, 1H, NH), 11.48 (s, 1H, NH); Elemental analysis for $C_{17}H_{12}Br_2ClN_5OS$, calcd: C 38.55, H 2.28, N 13.22; found: C 38.46, H 3.00, N 13.31.

***N*'-(4-Iodo-2-methylphenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thiourea 19k**: light yellow solid, yield 71 %, mp 181-183 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 (s, 3H, CH_3), 7.11 (s, 1H, Pyrazol-H), 7.39 (d, J = 8.4 Hz, 1H, Ph-H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.55 (d, J = 8.4 Hz, 1H, Ph-H), 7.60 (s, 1H, Ph-H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 0.4 Hz, 1H, Py-H), 8.57 (dd, J_1 = 4.4 Hz, J_2 = 0.4 Hz, 1H, Py-H), 9.93 (s, 1H, NH), 11.50 (s, 1H, NH); HRMS calcd for $C_{17}H_{12}BrClIN_5OS$ ($[M-H]^-$), 573.8601; found, 573.8610.

***N*'-(2,4,6-Trimethylphenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thiourea 19l**: light yellow solid, yield 80 %, mp 194-196 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 (s,

6H, CH_3), 2.28 (s, 3H, CH_3), 6.91 (s, 2H, Ph-H), 7.09 (s, 1H, Pyrazol-H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.56 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, Py-H), 9.73 (s, 1H, NH), 11.08 (s, 1H, NH); HRMS calcd for $C_{19}H_{17}BrClN_5OS$ ($[M-H]^-$), 475.9947; found, 475.9955.

***N*'-(2-Methyl-6-ethylphenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thiourea 19m**: light yellow solid, yield 73 %, mp 187-189 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (t, J = 7.6 Hz, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.56 (q, J = 7.6 Hz, 2H, CH_2), 7.10 (s, 1H, Pyrazol-H), 7.09-7.14 (m, 2H, Ph-H), 7.23 (t, J = 7.6 Hz, 1H, Ph-H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.98 (d, J = 8.0 Hz, 1H, Py-H), 8.56 (d, J = 4.8 Hz, 1H, Py-H), 9.77 (s, 1H, NH), 11.20 (s, 1H, NH); HRMS calcd for $C_{19}H_{17}BrClN_5OS$ ($[M-H]^-$), 475.9947; found, 475.9957.

***N*'-(2,6-Diethylphenyl)-*N*-(1-(3-chloro-2-pyridyl)-3-bromo-1*H*-prazole-5-carbonyl)thiourea 19n**: light yellow solid, yield 66 %, mp 183-185 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.18 (t, J = 7.6 Hz, 6H, CH_3), 2.57 (q, J = 7.6 Hz, 4H, CH_2), 7.10 (s, 1H, Pyrazol-H), 7.14 (d, J = 7.2 Hz, 2H, Ph-H), 7.28 (t, J = 8.0 Hz, 1H, Ph-H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.56 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, Py-H), 9.76 (s, 1H, NH), 11.21 (s, 1H, NH); HRMS calcd for $C_{20}H_{19}BrClN_5OS$ ($[M-H]^-$), 490.0104; found, 490.0112.

***N*-(4-Chloro-2-methyl-6-(methylcarbamoyl)phenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20a**: white solid, yield 69%, mp 178-180 ^oC; IR (KBr, cm^{-1}): 3255, 3147, 1670, 1273, 1160; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H, CH_3), 2.89 (d, J = 4.8 Hz, 3H, CH_3), 4.69 (q, J = 8.0 Hz, 2H, CH_2), 6.46 (br, 1H, NH), 6.61 (s, 1H, Pyrazol-H), 7.32 (s, 1H, Ph-H), 7.35 (s, 1H, Ph-H), 7.45 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.96 (d, J = 8.0 Hz, 1H, Py-H), 8.54 (d, J = 4.4 Hz, 1H, Py-H), 10.05 (s, 1H, NH), 11.38 (s,

1H, NH); HRMS calcd for $C_{21}H_{17}Cl_2F_3N_6O_3S$ ($[M+Na]^+$), 583.0304; found, 583.0300.

***N*-(4-Chloro-2-methyl-6-(propylcarbamoyl)phenylcarbamothioyl)-1-(3-chloropyridin-2-yl) -3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20b**: white solid, yield 72%, mp 183-185 ^oC; IR (KBr, cm^{-1}): 3231, 3149, 1674, 1656, 1279, 1161; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J = 7.2 Hz, 3H, CH_3), 1.49 (m, 2H, CH_2), 2.23 (s, 3H, CH_3), 3.27 (m, 2H, CH_2), 4.68 (q, J = 8.4 Hz, 2H, CH_2), 6.57 (t, J = 6.0 Hz, 1H, NH), 6.63 (s, 1H, Pyrazol-H), 7.31 (d, J = 2.0 Hz, 1H, Ph-H), 7.36 (d, J = 2.0 Hz, 1H, Ph-H), 7.45 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.96 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, Py-H), 8.53 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H, Py-H), 10.16 (s, 1H, NH), 11.35 (s, 1H, NH); Elemental analysis for $C_{23}H_{21}Cl_2F_3N_6O_3S$, calcd: C 46.87, H 3.59, N 14.26; found: C 46.60, H 3.59, N 13.87.

***N*-(4-Chloro-2-(isopropylcarbamoyl)-6-methylphenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20c**: white solid, yield 84%, mp 193-195 ^oC; IR (KBr, cm^{-1}): 3244, 3165, 1705, 1624, 1278, 1163 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.09 (br, 3H, CH_3), 1.15 (br, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.13 (m, 1H, CH), 4.68 (q, J = 8.1 Hz, 2H, CH_2), 6.44 (br, 1H, NH), 6.61 (s, 1H, Pyrazol-H), 7.25-7.35 (m, 2H, Ph-H), 7.45 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 1H, Py-H), 7.95 (dd, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 1H, Py-H), 8.52 (d, J = 3.0 Hz, 1H, Py-H), 10.07 (s, 1H, NH), 11.31 (s, 1H, NH); Elemental analysis for $C_{23}H_{21}Cl_2F_3N_6O_3S$, calcd: C 46.87, H 3.59, N 14.26; found: C 46.40, H 3.92, N 14.02.

***N*-(4-Chloro-2-(cyclopropylcarbamoyl)-6-methylphenylcarbamothioyl)-1-(3-chloropyridin -2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20d**: white solid, yield 98%, mp 194-196 ^oC; IR (KBr, cm^{-1}): 3246, 3151, 1673, 1654, 1276, 1161; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.48 (m, 2H, cyclopropyl-H), 0.78 (m, 2H, cyclopropyl-H), 2.24 (s, 3H, CH_3), 2.81 (m, 1H, CH),

4.71 (q, J = 8.1 Hz, 2H, CH_2), 6.64 (br, 1H, NH), 6.65 (s, 1H, Pyrazol-H), 7.28-7.36 (m, 2H, Ph-H), 7.46 (m, 1H, Py-H), 7.98 (t, J = 4.8 Hz, 1H, Py-H), 8.55 (d, J = 3.3 Hz, 1H, Py-H), 10.13 (s, 1H, NH), 11.33 (s, 1H, NH); Elemental analysis for $C_{23}H_{19}Cl_2F_3N_6O_3S$, calcd: C 47.03, H 3.26, N 14.31; found: C 46.72, H 3.48, N 13.92.

***N*-(2-(Tert-butylcarbamoyl)-4-chloro-6-methylphenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20e**: yellow solid, yield 95%, mp 186-189 ^oC; IR (KBr, cm^{-1}): 3315, 3164, 1678, 1644, 1277, 1162; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 9H, CH_3), 2.23 (s, 3H, CH_3), 4.68 (q, J = 8.1 Hz, 2H, CH_2), 6.32 (s, 1H, NH), 6.61 (s, 1H, Pyrazol-H), 7.28-7.33 (m, 2H, Ph-H), 7.45 (dd, J_1 = 8.1 Hz, J_2 = 4.5 Hz, 1H, Py-H), 7.95 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.52 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 1H, Py-H), 9.99 (s, 1H, NH), 11.29 (s, 1H, NH); HRMS calcd for $C_{24}H_{23}Cl_2F_3N_6O_3S$ ($[M+Na]^+$), 625.0774; found, 625.0778.

***N*-(4-Bromo-2-(isopropylcarbamoyl)-6-methylphenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20f**: white solid, yield 76%, mp 198-200 ^oC; IR (KBr, cm^{-1}): 3316, 3152, 1685, 1629, 1275, 1163; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.08 (d, J = 4.8 Hz, 3H, CH_3), 1.15 (d, J = 4.8 Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.13 (m, 1H, CH), 4.68 (q, J = 8.0 Hz, 2H, CH_2), 6.44 (d, J = 6.0 Hz, 1H, NH), 6.62 (s, 1H, Pyrazol-H), 7.44-7.51 (m, 3H, Ph-H + Py-H), 7.95 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, Py-H), 8.53 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, Py-H), 10.10 (s, 1H, NH), 11.31 (s, 1H, NH); Elemental analysis for $C_{23}H_{21}BrClF_3N_6O_3S$, calcd: C 43.58, H 3.34, N 13.26; found: C 43.53, H 3.68, N 12.89.

***N*-(4-Bromo-2-(cyclopropylcarbamoyl)-6-methylphenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 20g**: white solid, yield 95%, mp 176-178 ^oC; IR (KBr, cm^{-1}): 3308, 3169, 1687, 1629, 1278, 1152; ^1H NMR ($CDCl_3$, 300 MHz) δ

0.47 (m, 2H, cyclopropyl-H), 0.77 (m, 2H, cyclopropyl-H), 2.22 (s, 3H, CH_3), 2.80 (m, 1H, CH), 4.68 (q, J = 8.1 Hz, 2H, CH_2), 6.64 (br, 2H, Pyrazol-H + NH), 7.43-7.50 (m, 3H, Ph-H + Py-H), 7.97 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.54 (dd, J_1 = 4.7 Hz, J_2 = 1.5 Hz, 1H, Py-H), 10.12 (s, 1H, NH), 11.31 (s, 1H, NH); HRMS calcd for $C_{23}H_{19}BrClF_3N_6O_3S$ ($[M+Na]^+$), 652.9956; found, 652.9959.

3-Bromo-*N*-(4-chloro-2-methyl-6-(5-methyl-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 21a: white solid, yield 57 %, mp 234-236 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.20 (s, 1H, Pyrazol-H), 7.35-7.39 (m, 2H, Ph-H + Py-H), 7.72 (d, J = 2.0 Hz, 1H, Ph-H), 7.84 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, Py-H), 8.45 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H, Py-H), 10.08 (s, 1H, NH); HRMS calcd for $C_{19}H_{13}BrCl_2N_6O_2$ ($[M+Na]^+$), 528.9558; found, 528.9549.

3-Bromo-*N*-(4-bromo-2-methyl-6-(5-methyl-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 21b: white solid, yield 70 %, mp 186-188 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 2.26 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.21 (s, 1H, Pyrazol-H), 7.37 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.53 (s, 1H, Ph-H), 7.86 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, Py-H), 7.88 (s, 1H, Ph-H), 8.45 (d, J = 3.6 Hz, 1H, Py-H), 10.11 (s, 1H, NH); Elemental analysis for $C_{19}H_{13}Br_2ClN_6O_2$, calcd: C 41.30, H 2.37, N 15.21; found: C 41.17, H 3.19, N 15.24.

***N*-(4-Bromo-2-methyl-6-(5-methyl-1,3,4-oxadiazol-2-yl)phenyl)-1-(3-chloropyridin-2-yl)-3-(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 21c**: white solid, yield 60 %, mp 105-107 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.23 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.92 (q, J = 8.8 Hz, 2H, CF_3CH_2O), 6.83 (s, 1H, Pyrazol-H), 7.54 (dd, J_1 = 7.2 Hz, J_2 = 5.2 Hz, 1H, Py-H), 7.66 (s, 1H, Ph-H), 7.77 (s, 1H, Ph-H), 8.11 (d, J = 8.0 Hz, 1H, Py-H), 8.43 (d, J = 4.4 Hz, 1H, Py-H), 10.40 (s,

1H, NH); HRMS calcd for $C_{21}H_{15}Cl_2F_3N_6O_3$ ([M-H]$^-$), 525.0457; found, 525.0464.

***N*-(2-(5-(2-Azidopyridin-3-yl)-1,3,4-oxadiazol-2-yl)-4-chloro-6-methylphenyl)-3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 22**: yellow solid, yield 44 %, mp 152-155 ^oC; ^1H NMR (DMSO-d_6, 300 MHz) δ 2.31 (s, 3H, CH_3), 7.47 (s, 1H, Pyrazol-H), 7.56 (dd, J_1 = 7.8 Hz, J_2 = 4.5 Hz, 1H, Py-H), 7.63 (t, J = 7.2 Hz, 1H, Py-H), 7.77 (d, J = 1.8 Hz, 1H, Ph-H), 8.05 (d, J = 1.8 Hz, 1H, Ph-H), 8.12 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1H, Py-H), 8.38 (dd, J_1 = 4.5 Hz, J_2 = 0.9 Hz, 1H, Py-H), 8.61 (d, J = 7.2 Hz, 1H, Py-H), 9.60 (d, J = 6.9 Hz, 1H, Py-H), 10.70 (s, 1H, NH); HRMS calcd for $C_{23}H_{13}BrCl_2N_{10}O_2$ ([M-H]$^-$), 608.9705; found, 608.9708.

3-Bromo-*N*-(4-chloro-2-methyl-6-(5-methyl-1,3,4-oxadiazol-2-yl)phenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 23: yellow solid, yield 56 %, mp 115-117 ^oC; IR (KBr, cm^{-1}): 3289, 3143, 2958, 2928, 1685, 1617, 1578, 1530, 1462, 1357, 1159; ^1H NMR (400MHz, $CDCl_3$) δ 2.36 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 7.12 (s, 1H, Pyrazol-H), 7.43 (d, J = 1.6 Hz, 1H, Ph-H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.83 (d, J = 1.6 Hz, 1H, Ph-H), 7.98 (d, J = 8.0 Hz, 1H, Py-H), 8.57 (d, J = 4.4 Hz, 1H, Py-H), 9.86 (s, 1H, NH), 11.55 (s, 1H, NH); HRMS calcd for $C_{20}H_{14}BrCl_2N_7O_2S$ ([M-H]$^-$), 563.9412; found, 563.9419.

3-Chloro-*N*-(4-chloro-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)phenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 24a: yellow solid, yield 68 %, mp 183-185 ^oC; IR (KBr, cm^{-1}): 3446, 3215, 3178, 3147, 3087, 2987, 1742, 1691, 1584, 1541, 1508, 1467, 1369, 1165; ^1H NMR (400MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 7.02 (s, 1H, Pyrazol-H), 7.43-8.08 (m, 9H, Ph-H + Py-H), 8.55 (d, J = 4.0 Hz, 1H, Py-H), 10.01 (s, 1H, NH), 11.62 (s, 1H, NH); HRMS calcd for $C_{25}H_{16}Cl_3N_7O_2S$ ([M+Na]$^+$), 606.0044; found, 606.0046.

3-Chloro-*N*-(4-chloro-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)phenylcarbamothi

oyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 24b: yellow solid, yield 54 %, mp 212-215 ^{o}C; IR (KBr, cm^{-1}): 3431, 3178, 3066, 3038, 2925, 1689, 1582, 1540, 1516, 1465, 1366, 1164; ^{1}H NMR (400MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 7.06 (s, 1H, Pyrazol-H), 7.43-7.98 (m, 5H, Ph-H + Py-H), 8.38 (d, J = 8.0 Hz, 1H, Py-H), 8.54 (d, J = 3.6 Hz, 1H, Py-H), 8.79 (d, J = 3.6 Hz, 1H, Py-H), 9.31 (d, J = 1.2 Hz, 1H, Py-H), 10.11 (s, 1H, NH), 11.63 (s, 1H, NH); HRMS calcd for $C_{24}H_{15}Cl_3N_8O_2S$ ([M-H]$^{-}$), 583.0026; found, 583.0038.

3-Bromo-*N*-(4-chloro-2-methyl-6-(5-phenyl-1,3,4-oxadiazol-2-yl)phenylcarbamothioyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 24c: white solid, yield 43 %, mp 172-174 ^{o}C; IR (KBr, cm^{-1}): 3396, 3205, 3168, 3053, 2970, 2927, 1687, 1579, 1541, 1508, 1464, 1361, 1167; ^{1}H NMR (400MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 7.11 (s, 1H, Pyrazol-H), 7.43-8.07 (m, 9H, Ph-H + Py-H), 8.54 (d, J = 3.6 Hz, 1H, Py-H), 10.02 (s, 1H, NH), 11.62 (s, 1H, NH); HRMS calcd for $C_{25}H_{16}BrCl_2N_7O_2S$ ([M-H]$^{-}$), 625.9568; found, 625.9576.

3-Bromo-*N*-(4-chloro-2-methyl-6-(5-methyl-1,3,4-oxadiazol-2-yl)phenylcarbamoyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 26a: white solid, yield 55 %, mp 194-196 ^{o}C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.23 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.62 (d, J = 2.1 Hz, 1H, Ph-H), 7.67 (s, 1H, Pyrazol-H), 7.68 (dd, J_1 = 8.1 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.75 (d, J = 2.1 Hz, 1H, Ph-H), 8.27 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.56 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 1H, Py-H), 9.81 (s, 1H, NH), 11.43 (s, 1H, NH); HRMS calcd for $C_{20}H_{14}BrCl_2N_7O_3$ ([M+Na]$^{+}$), 571.9616; found, 571.9607.

3-Bromo-*N*-(4-chloro-2-methyl-6-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)phenylcarbamoyl)-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carboxamide 26b: light yellow solid, yield 68 %, mp 147-149 ^{o}C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.26 (s, 3H, CH_3), 7.63-7.67 (m, 3H, Ph-H + Py-H),

7.68 (s, 1H, Pyrazol-H), 8.02 (d, J = 2.1 Hz, 1H, Ph-H), 8.23 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H, Py-H), 8.48 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H, Py-H), 8.53 (dd, J_1 = 4.5 Hz, J_2 = 0.9 Hz, 1H, Py-H), 8.85 (d, J = 4.5 Hz, 1H, Py-H), 9.28 (s, 1H, Py-H), 9.93 (s, 1H, NH), 11.53 (s, 1H, NH); HRMS calcd for $C_{24}H_{15}BrCl_2N_8O_3$ ([M-H]$^-$), 610.9749; found, 610.9758.

***O*,*O*-Dimethyl 3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazole-5-carbonylcarbamoylphosphoramidothioate 27a**: white crystal, yield 32 %, mp 169-171 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86 (d, J_{P-H} = 14.8 Hz, 6H, OCH_3), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.60 (s, 1H, Pyrazol-H), 7.95 (d, J = 8.0 Hz, 1H, Py-H), 8.51 (d, J = 4.8 Hz, 1H, Py-H), 9.67 (d, J_{P-H} = 13.6 Hz, 1H, NH), 10.75 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 400 MHz) δ 64.58 (P=S); HRMS calcd for $C_{12}H_{12}BrClN_5O_4PS$ ([M-H]$^-$), 465.9141; found, 465.9146.

***O*,*O*-*D*imethyl 1-(3-chloropyridin-2-yl)-3-(trifluoromethyl)-1*H*-pyrazole-5-carbonylcarbamoylphosphoramidothioate 27b**: white crystal, yield 44 %, mp 171-173 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (d, J_{P-H} = 14.8 Hz, 6H, OCH_3), 7.52 (dd, J = 8.0 Hz, J = 4.8 Hz, 1H, Py-H), 7.81 (s, 1H, Pyrazol-H), 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.53 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, Py-H), 9.68 (d, J_{P-H} = 14.4 Hz, 1H, NH), 10.86 (s, 1H, NH); ^{31}P NMR ($CDCl_3$, 400 MHz) δ 64.47 (P=S); HRMS calcd for $C_{13}H_{12}ClF_3N_5O_4PS$ ([M-H]$^-$), 455.9910; found, 455.9910.

2-(3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-5-substituted-1,3,4-oxadiazole (28, 29a-c)

2-(3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-5-methyl-1,3,4-oxadiazole 28: yellow crystal, yield 77 %, mp 191-193 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.53 (s, 3H, CH_3), 7.04 (s, 1H, Pyrazol-H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.6

Hz, 1H, Py-H), 8.51 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 1H, Py-H); Elemental analysis for $C_{11}H_7BrClN_5O$, calcd: C 38.79, H 2.07, N 20.56; found: C 38.77, H 2.64, N 19.98.

2-(3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole 29a: white solid, yield 65 %, mp 146-148 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19 (s, 1H, Pyrazol-H), 7.47-7.56 (m, 4H, Py-H + Ph-H), 7.91-7.94 (m, 2H, Ph-H), 7.98 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.55 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H, Py-H); Elemental analysis for $C_{16}H_9BrClN_5O$, calcd: C 47.73, H 2.25, N 17.39; found: C 47.17, H 2.53, N 16.92.

2-(3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-5-(pyridin-3-yl)-1,3,4-oxadiazole 29b: light yellow solid, yield 62 %, mp 177-179 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.23 (s, 1H, Pyrazol-H), 7.47 (dd, J_1 = 7.5 Hz, J_2 = 4.5 Hz, 1H, Py-H), 7.54 (dd, J_1 = 8.1 Hz, J_2 = 4.8 Hz, 1H, Py-H), 8.00 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.28 (dt, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H, Py-H), 8.55 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.79 (dd, J_1 = 4.8 Hz, J_2 = 1.5 Hz, 1H, Py-H), 9.07 (d, J = 1.8 Hz, 1H, Py-H); HRMS calcd for $C_{15}H_8BrClN_6O$ ($[M+Na]^+$), 424.9529; found, 424.9533.

2-(2-Azidopyridin-3-yl)-5-(3-bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-1,3,4-oxadiazole 29c: yellow solid, yield 42 %, mp 209-210 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.39 (s, 1H, Pyrazol-H), 7.43 (m, 1H, Py-H), 7.58 (dd, J_1 = 8.1 Hz, J_2 = 4.5 Hz, 1H, Py-H), 8.04 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Py-H), 8.52 (d, J = 6.6 Hz, 1H, Py-H), 8.55 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H, Py-H), 9.01 (d, J = 6.3 Hz, 1H, Py-H); HRMS calcd for $C_{15}H_7BrClN_9O$ ($[M+Na]^+$), 465.9543; found, 465.9531.

6-(3-Bromo-1-(3-chloropyridin-2-yl)-1*H*-pyrazol-5-yl)-3-methyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazole 30: pink crystals, yield 83 %, mp 216-217 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.35

(s, 3H, CH_3), 7.73 (s, 1H, Pyrazol-H), 7.81 (br, 1H, Py-H), 8.35 (d, J = 4.8 Hz, 1H, Py-H), 8.64 (br, 1H, Py-H); Elemental analysis for $C_{12}H_7BrClN_7S$, calcd: C 36.34, H 1.78, N 24.72; found: C 35.84, H 2.06, N 24.51.

3-Bromo-*N*-(4-chloro-2-methylphenyl)-1-(3-chloropyridin-2-yl)-*N*-(4,5-dihydrothiazol-2-yl)-1*H*-pyrazole-5-carboxamide 34a: white solid, yield 50 %, mp 128-130 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.91 (s, 3H, CH_3), 3.16 (t, J = 6.8 Hz, 2H, CH_2), 4.23 (t, J = 6.8 Hz, 2H, CH_2), 6.49 (d, J = 8.4 Hz, 1H, Ph-H), 6.77 (s, 1H, Pyrazol-H), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, Ph-H), 7.09 (s, 1H, Ph-H), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H, Py-H), 7.86 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, Py-H), 8.39 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 1H, Py-H); HRMS calcd for $C_{19}H_{14}BrCl_2N_5OS$ ($[M+Na]^+$), 531.9377; found, 531.9378.

3-Bromo-1-(3-chloropyridin-2-yl)-*N*-(4,5-dihydrothiazol-2-yl)-*N*-mesityl-1*H*-pyrazole-5-carboxamide 34b: white solid, yield 78 %, mp 150-152 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.88 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 3.19 (t, J = 6.8 Hz, 2H, CH_2), 4.27 (t, J = 6.8 Hz, 2H, CH_2), 6.77 (s, 2H, Ph-H), 6.79 (s, 1H, Pyrazol-H), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H, Py-H), 7.85 (d, J = 8.0 Hz, 1H, Py-H), 8.37 (d, J = 4.4 Hz, 1H, Py-H); Elemental analysis for $C_{21}H_{19}BrClN_5OS$, calcd: C 49.96, H 3.79, N 13.87; found: C 50.18, H 4.20, N 13.65.

3-Bromo-1-(3-chloropyridin-2-yl)-*N*-(4,5-dihydrothiazol-2-yl)-*N*-(2,4,6-trichlorophenyl)-1*H*-pyrazole-5-carboxamide 34c: white solid, yield 41 %, mp 197-200 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.30 (t, J = 6.8 Hz, 2H, CH_2), 4.32 (t, J = 6.8 Hz, 2H, CH_2), 6.99 (s, 1H, Pyrazol-H), 7.28 (s, 2H, Ph-H), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, Py-H), 7.85 (d, J = 8.0 Hz, 1H, Py-H), 8.43 (d, J = 4.8 Hz, 1H, Py-H); HRMS calcd for $C_{18}H_{10}BrCl_4N_5OS$ ($[M+Na]^+$), 585.8441; found, 585.8442.

3-Bromo-1-(3-chloropyridin-2-yl)-*N*-(5-methyl-4,5-dihydrothiazol-2-yl)-*N*-(2,4,6-trichloro phenyl)-1*H*-pyrazole-5-carboxamide 34d: white solid, yield 39 %, mp 123-125 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (d, J = 6.8 Hz, 3H, CH_3), 3.79-3.84 (m, 1H, CH_2), 3.93-3.97 (m, 1H, CH_2), 4.35-4.39 (m, 1H, CH), 6.97 (s, 1H, Pyrazol-H), 7.26 (s, 2H, Ph-H), 7.30 (dd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, 1H, Py-H), 7.85 (d, J = 8.0 Hz, 1H, Py-H), 8.42 (d, J = 5.2 Hz, 1H, Py-H); Elemental analysis for $C_{19}H_{12}BrCl_4N_5OS$, calcd: C 39.34, H 2.08, N 12.07; found: C 39.62, H 2.65, N 11.91.

1-(3-Chloropyridin-2-yl)-*N*-(5-methyl-4,5-dihydrothiazol-2-yl)-*N*-(2,4,6-trichlorophenyl)-3 -(2,2,2-trifluoroethoxy)-1*H*-pyrazole-5-carboxamide 34e: white crystal, yield 44 %, mp 100-102 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (d, J = 6.8 Hz, 3H, CH_3), 3.78-3.83 (m, 1H, CH_2), 3.96-4.00 (m, 1H, CH_2), 4.37-4.42 (m, 1H, CH), 4.65 (q, J = 8.4 Hz, 1H, CF_3CH_2O), 6.42 (s, 1H, Pyrazol-H), 7.22 (dd, J_1 = 7.6 Hz, J_2 = 4.4 Hz, 1H, Py-H), 7.25 (s, 2H, Ph-H), 7.82 (d, J = 7.6 Hz, 1H, Py-H), 8.37 (d, J = 4.4 Hz, 1H, Py-H); HRMS calcd for $C_{21}H_{14}Cl_4F_3N_5O_2S$ ($[M+Na]^+$), 619.9472; found, 619.9473.