Supporting Information

Ionic liquids confined zeolite system: A novel approaches towards water mediated room temperature synthesis of spiro[pyrazolo[3,4-*e*]benzothiazepines]

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Characterization data of synthesized compounds (4b-r):_

7-ethoxy-5'-methyl-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*/b/*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4b) : R_f= 0.60 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) v = 3410 (NH), 1680 (C=O), 1615 (C=N), 1180 (C-N), 1160 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.80 (s, 1H, NH), 8.40 (s, 1 H, NH), 7.80-6.72 (m, 11 H, Ar-H), 4.02 (q, 2H, J=7 Hz, CH2), 3.57 (s, 3H, OCH_3), 1.98 (s, 3H, CH_3), 1.28 (t, 3H, J=7 Hz, CH3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =174.6 (C=O), 155.8 (C-OCH_3), 153.7 (C=N), 150.3 (C-OCH_2CH_3), 147.9, 146.8, 144.2 (C-N), 138.5, 136.2, 132.8, 130.3, 129.7, 124.6, 124.2, 122.9, 121.1, 120.2, 118.9, 115.8, 112.9, 111.4, 105.7, 67.5 (O-CH_2CH_3), 59.5 (OCH_3), 56.7 (C), 14.3 (OCH_2CH_3), 8.5 (CH_3). DIPMS: m/z (%) 484 [M^+]. Analysis: Found (calcd) for $C_{27}H_{24}N_4O_3S$: C, 66.98 (66.92); H, 5.02 (4.99); N, 11.51 (11.56); S, 6.58(6.62).

3,7-dimethyl-1-phenyl-1,2',3'-tetrahydrospiro[benzo*/b/*pyrazolo [3,4-e][1,5]thiazepine-4,1'-indene] (4c) : R_f= 0.65 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) v = 3410 (NH), 1615 (C=N), 1170 (C-N). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.52 (s, 1 H, NH), 7.70-6.91 (m, 12 H, Ar-H), 3.10 (d, 2H, J=12.4 Hz, CH_2), 2.94 (d, 2H, J=12.4 Hz, CH_2), 2.75 (s, 3H, CH_3), 2.05 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ = 152.1 (C=N), 147.2, 145.9, 143.2 (C-N), 141.3, 139.3, 137.5, 135.8, 133.4, 131.7, 129.4, 125.8, 124.9, 123.1, 121.4, 120.7, 118.3, 115.4, 112.6, 110.9, 107.2, 55.2 (C), 41.3 (CH_2), 30.4 (CH_2), 21.8 (CH_3), 7.4 (CH_3). DIPMS: m/z (%) 409 [M^+]. Analysis: Found (calcd) for $C_{26}H_{23}N_3S$: C, 76.32 (76.25); H, 5.62 (5.66); N, 10.21 (10.26); S, 7.87 (7.83).

7-chloro -5'fluoro-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*/b/*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4d) : R_f= 0.58 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) v = 3410 (NH), 1690 (C=O), 1610 (C=N), 1180 (C-N), 780 (C-Cl). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.72 (s, 1H, NH), 8.38 (s, 1 H, NH), 7.92-6.80 (m, 11 H, Ar-H),

2.08 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =161.3 (C-F), 154.3 (C=N), 149.3, 146.2, 145.3 (C-N), 140.7, 138.5, 137.1, 136.1, 134.7, 131.4 (C-Cl), 129.2, 127.3, 125.8, 123.7, 121.1, 120.2, 118.9, 115.8, 112.9, 111.4, 109.2, 57.2 (C), 7.6 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) *δ*(ppm): -119.6 (s, F). DIPMS: m/z (%) 464 $[M+2]^+$, 462 $[M^+]$. Analysis: Found (calcd) for $C_{24}H_{16}ClFN_4OS$: C, 62.22 (62.27); H, 3.52 (3.48); N, 12.05 (12.10); S, 6.88(6.93).

7- fluoro-3-methyl-1-phenyl-5'(trifluoromethyl)-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4e) : R_f= 0.65 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *ν* = 3420 (NH), 1680 (C=O), 1620 (C=N), 1175 (C-N), 740 (C-F). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm**=** 8.83 (s, 1H, NH), 8.42 (s, 1 H, NH), 7.72-6.54 (m, 11 H, Ar-H), 2.04 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =162.8 (C-F), 155.6 (C=N), 148.8, 146.8, 144.1 (C-N), 141.5, 139.3, 137.5, 135.7, 133.9, 130.2, 129.7 (C-CF_3), 126.7, 125.2, 123.5, 122.2, 121.1, 119.2 (C-CF_3), 118.4, 116.7, 113.8, 112.5, 110.2, 58.5 (C), 8.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) *δ* (ppm): -63.08 (s, 3F, -CF_3), -119.3 (s, F). DIPMS: m/z (%) 496 $[M^+]$. Analysis: Found (calcd) for $C_{25}H_{16}F_4N_4OS$: C, 60.53 (60.48); H, 3.28 (3.25); N, 11.25 (11.28); S, 6.49 (6.46).

7-methoxy-3-methyl-1-phenyl- 1,10- dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,1'-cyclohexane] (4f): R_f= 0.62 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *ν* = 3415 (NH), 1690 (C=O), 1625 (C=N), 1180 (C-N), 1140 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm**=** 8.78 (s, 1H, NH), 8.45 (s, 1 H, NH), 7.79-6.94 (m, 8 H, Ar-H), 3.72 (s, 3H, OCH_3), 3.59 (d, *J* = 12.9 Hz, 1H), 3.45 (d, *J* = 12.3 Hz, 1H), 1.98 (s, 3H, CH_3), 2.38 (t, *J* = 6.9 Hz, 2H), 1.89-1.80 (m, 4H), 1.69-1.63 (m, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ =158.3 (C-OCH_3), 154.3 (C=N), 149.2, 145.7, 145.2 (C-N), 140.6, 138.1, 135.9, 134.1, 131.7, 126.3, 123.2, 120.4, 115.8, 114.1, 55.9 (OCH_3), 50.1 (C), 43.4 (CH_2), 37.3(CH_2), 31.6(CH_2), 28.4 (CH_2), 25.3 (CH_2), 8.8 (CH_3). DIPMS: m/z (%) 391 $[M^+]$. Analysis: Found (calcd) for $C_{23}H_{25}N_3OS$: C, 70.51 (70.56); H, 6.48 (6.44); N, 10.69 (10.73); S, 8.22 (8.19).

7-ethoxy-3-methyl-1-phenyl- 1,10- dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,1'-cyclohexane] (4g) : R_f= 0.68 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *ν* = 3425 (NH), 1685 (C=O), 1620 (C=N), 1180 (C-N), 1160 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm**=** 8.66 (s, 1H, NH), 8.38 (s, 1 H, NH), 7.94-6.92 (m, 8 H, Ar-H), 4.08 (q, 2H, J=7 Hz, OCH_2CH_3), 3.62 (d, 1H, *J* = 12.9 Hz), 3.43 (d, 1H, *J* = 12.3 Hz), 2.07 (s, 3H, CH_3), 2.32 (t, 2H, *J* = 6.9 Hz, CH_2), 1.82-1.74 (m, 4H, CH_2), 1.65-1.61 (m, 2H, CH_2), 1.32 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =154.3 (C=N),151.3 (C-OCH_2CH_3), 148.7, 144.3 (C-N), 142.8, 140.1, 137.5, 136.2, 133.5, 131.2, 125.4, 122.8, 119.7, 117.3, 113.8, 67.5 (O-CH_2CH_3), 49.5 (C), 44.7 (CH_2), 39.3 (CH_2), 33.8 (CH_2), 29.2 (CH_2), 24.8 (CH_2), 15.8

($OCH_2\underline{C}H_3$), 8.3 ($\underline{C}H_3$). DIPMS: m/z (%) 405 [M^+]. Analysis: Found (calcd) for $C_{24}H_{27}N_3OS$: C, 70.99 (71.08); H, 6.75 (6.71); N, 10.40 (10.36); S, 7.94 (7.91).

7-ethoxy-3,5'-dimethyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4h) : R_f= 0.72 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3430 (NH), 1690 (C=O), 1625 (C=N), 1165 (C-N), 1150 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.85 (s, 1H, NH), 8.40 (s, 1 H, NH), 7.70-6.68 (m, 11 H, Ar-H), 4.08 (q, 2H, J=7 Hz, CH_2), 2.68 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.29 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =174.5 ($\underline{C}$=O), 156.8 ($\underline{C}$=N), 150.4($\underline{C}$-OCH_2CH_3),147.3,145.2($\underline{C}$-N), 142.4, 140.2, 136.7, 135.5, 134.2, 132.3,129.4, 127.3, 125.8, 122.7, 121.5, 120.2, 118.9, 115.9, 113.5, 112.8, 109.7, 107.4, 68.4 (O-$\underline{C}H_2CH_3$), 56.3 ($\underline{C}$), 22.5 (CH_3), 17.2 ($OCH_2\underline{C}H_3$),7.5 ($\underline{C}H_3$). DIPMS: m/z (%) 468 [M^+]. Analysis: Found (calcd) for $C_{27}H_{24}N_4O_2S$: C, 69.16 (69.21); H, 5.19 (5.16); N, 11.93 (11.96); S, 6.88 (6.84).

3, 5',7- trimethyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4i) : R_f= 0.69 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3425 (NH), 1680 (C=O), 1620 (C=N), 1170 (C-N). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.76 (s, 1H, NH), 8.34 (s, 1 H, NH), 7.92-6.86 (m, 11 H, Ar-H), 2.74 (s, 3H, CH_3), 2.12 (s, 3H, CH3), 2.01 (s, 3H, CH_3).^{13}C NMR (200 MHz, $CDCl_3$): δ =172.9 (C=O), 154.3 ($\underline{C}$=N),146.5,144.8($\underline{C}$-N), 141.7, 138.7, 137.2, 135.4, 133.9, 131.9, 130.7, 128.4,126.7, 124.9, 122.3, 121.8, 120.6, 119.3, 116.4, 113.1, 110.4, 108.3, 59.2 ($\underline{C}$), 25.2 (C-$\underline{C}H_3$), 21.8 (C-$\underline{C}H_3$), 8.3 ($\underline{C}H_3$). DIPMS: m/z (%) 438 [M^+]. Analysis: Found (calcd) for $C_{26}H_{22}N_4OS$: C, 71.15 (71.21); H, 5.09 (5.06); N, 12.83 (12.78); S, 7.35 (7.31).

7-chloro-3,5'-dimethyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo[3,4-e][1,5]thiazepine-4,3'-indolin]-2'one(4j): R_f= 0.59 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3420 (NH), 1690 (C=O), 1615 (C=N), 1165 (C-N), 770 (C-Cl). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.77 (s, 1H, NH), 8.42 (s, 1 H, NH), 7.88-6.91 (m, 11 H, Ar-H), 2.67 (s, 3H, CH_3), 2.06 (s, 3H, CH_3).^{13}C NMR (200 MHz, $CDCl_3$): δ =174.8 (C=O), 155.9 ($\underline{C}$=N),148.3,146.1($\underline{C}$-N), 142.8, 140.9, 138.3, 136.2, 134.9, 132.6, 130.7 ($\underline{C}$-Cl), 129.2,127.3, 125.7, 123.4, 121.3, 120.4, 118.9, 115.4, 112.8, 108.9, 107.6, 60.4 ($\underline{C}$), 24.8 (C-$\underline{C}H_3$), 7.6 ($\underline{C}H_3$). DIPMS: m/z (%) 460 [M+2]$^+$, 458 [M^+]. Analysis: Found (calcd) for $C_{25}H_{19}ClN_4OS$: C, 65.48 (65.42); H, 4.21 (4.17); N, 12.25 (12.21); S, 6.95 (6.99).

5',7-dimethoxy-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4k) : R_f= 0.58 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3420 (NH), 1680 (C=O), 1620 (C=N), 1190 (C-N), 1140 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.87 (s, 1H, NH), 8.45 (s, 1 H, NH), 7.93-6.87 (m, 11 H, Ar-H), 3.68 (s, 6H, OCH_3), 2.12 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =178.3 ($\underline{C}$=O), 162.4 ($\underline{C}$-OCH_3), 158.3 ($\underline{C}$-OCH3),

153.7 (C=N), 151.2, 148.4, 146.8 (C-N), 143.2, 141.5, 139.4, 138.2, 136.5, 133.8, 130.7, 127.9, 126.1, 124.6, 122.8, 121.6, 119.7, 116.4, 113.7, 111.2, 58.9 (OCH_3), 54.7 (C), 7.1 (CH_3). DIPMS: m/z (%) 470 [M^+]. Analysis: Found (calcd) for $C_{26}H_{22}N_4O_3S$: C, 66.43 (66.37); H, 4.75 (4.71); N, 11.95 (11.91); S, 6.78 (6.81).

7-chloro-5'-methoxy-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine -4,3'-indolin]-2'one (4l) : R_f= 0.63 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3430 (NH), 1690 (C=O), 1610 (C=N), 1180 (C-N), 1140 (C-O-C), 780 (C-Cl). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.92 (s, 1H, NH), 8.40 (s, 1 H, NH), 7.88-6.95 (m, 11 H, Ar-H), 3.73 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =177.3 (C=O), 159.3 (C-OCH_3), 155.7 (C=N), 153.1, 150.6, 147.3, 145.2 (C-N), 142.8, 140.9, 138.8, 137.1, 135.6, 133.2, 131.2, 128.4 (C-Cl), 126.6, 123.4, 120.6, 118.4, 115.9, 113.1, 110.7, 59.7 (OCH_3), 56.4 (C), 7.8 (CH_3). DIPMS: m/z (%) 476 [M+2]$^+$, 474 [M^+]. Analysis: Found (calcd) for $C_{25}H_{19}ClN_4O_2S$: C, 63.17 (63.22); H, 4.07 (4.03); N, 11.84 (11.80); S, 6.71 (6.75).

7-fluoro-5'-methoxy-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine -4,3'-indolin]-2'one (4m) : R_f= 0.57 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3420 (NH), 1680 (C=O), 1620 (C=N), 1190 (C-N), 1150 (C-O-C), 740 (C-F). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.88 (s, 1H, NH), 8.45 (s, 1 H, NH), 7.95-6.82 (m, 11 H, Ar-H), 3.69 (s, 3H, OCH_3), 2.01 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =175.8 (C=O), 158.4 (C-OCH_3), 154.5 (C=N), 153.8 (C-F), 151.2, 148.9, 147.8 (C-N), 145.6, 143.1, 141.2, 138.3, 136.5, 134.8, 132.4, 130.8, 127.4, 125.2, 122.7, 120.3, 117.9, 115.2, 112.8, 60.2 (OCH_3), 57.8 (C), 8.4 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ(ppm): -118.9 (s, F). DIPMS: m/z (%) 458 [M^+]. Analysis: Found (calcd) for $C_{25}H_{19}FN_4O_2S$: C, 65.55 (65.49); H, 4.22 (4.18); N, 12.18 (12.22); S, 7.04 (6.99).

7-methoxy-3-methyl-1-phenyl-1,2',3'-tetrahydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,1'-indene] (4n) : R_f= 0.68 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3390 (NH), 1620 (C=N), 1190 (C-N), 1170 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.48 (s, 1 H, NH), 7.98-6.81 (m, 12 H, Ar-H), 3.78 (s, 3H, OCH_3), 3.20 (d, 2H, J=12.4 Hz, CH_2), 2.85 (d, 2H, J=12.4 Hz, CH_2), 2.08 (s, 3H, CH_3).^{13}C NMR (200 MHz, $CDCl_3$): δ = 158.9 (C-OCH_3), 153.3 (C=N), 149.8, 146.2, 144.7 (C-N), 142.8, 140.5, 138.2, 136.9, 134.5, 132.8, 130.1, 128.4, 125.7, 124.3, 122.8, 120.2, 117.5, 114.7, 111.6, 109.4, 61.7 (OCH_3), 57.3 (C), 43.8 (CH_2), 33.6 (CH_2), 8.3 (CH_3). DIPMS: m/z (%) 425 [M^+]. Analysis: Found (calcd) for $C_{26}H_{23}N_3OS$: C, 73.32(73.38); H, 5.41 (5.45); N, 9.92 (9.87); S, 7.51 (7.54).

7-ethoxy-3-methyl-1-phenyl-1,2',3'-tetrahydrospiro[benzo*[b]*pyrazolo [3,4-e][1,5]thiazepine-4,1'-indene] (4o): R_f= 0.72 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) ν = 3410 (NH), 1615 (C=N), 1180 (C-N), 1160 (C-O-C). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.52 (s, 1 H, NH), 7.93-6.85 (m, 12 H, Ar-H), 4.12 (q, 2H, J=7 Hz, CH_2), 3.22 (d, 2H,

J=12.4 Hz, CH_2), 2.88 (d, 2H, J=12.4 Hz, CH_2), 2.11 (s, 3H, CH_3), 1.39 (t, 3H, J=7 Hz, CH_3).^{13}C NMR (200 MHz, $CDCl_3$): δ = 156.5 (C=N), 152.4(C-OCH_2CH_3), 148.4, 145.7, 143.5 (C-N), 142.2, 141.1, 137.4, 135.6, 134.9, 131.6, 129.6, 127.4, 125.8, 123.7, 121.7, 118.4, 115.3, 112.5, 110.8, 108.3, 69.3 (O-CH_2CH_3), 59.4 (C), 45.7 (CH_2), 35.9 (CH_2), 18.4 (OCH_2CH_3), 8.1 (CH_3). DIPMS: m/z (%) 439 [M^+]. Analysis: Found (calcd) for $C_{27}H_{25}N_3OS$: C, 73.71(73.77); H, 5.77 (5.73); N, 9.52 (9.56); S, 7.33 (7.29).

7-ethoxy-5'-fluoro-3-methyl-1-phenyl-1,10-dihydrospiro[benzo*/b/*pyrazolo[3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4p) : R_f= 0.64 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *v* = 3420 (NH), 1685 (C=O), 1620 (C=N), 1175 (C-N), 1160 (C-O-C), 740 (C-F). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.78 (s, 1H, NH), 8.35 (s, 1 H, NH), 7.84-6.56 (m, 11 H, Ar-H), 4.15 (q, 2H, J=7 Hz, CH_2), 2.15 (s, 3H, CH_3), 1.34 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =178.3 (C=O), 158.4 (C=N), 155.4 (C-F), 151.7 (C-OCH_2CH_3),148.9, 144.7 (C-N),141.8, 139.3, 137.1, 135.8, 133.2,131.7,128.5,126.9, 124.3, 122.5, 120.9, 117.5, 114.3, 112.8, 110.3, 108.3, 70.3 (O-CH_2CH_3), 58.3 (C), 21.8 (OCH_2CH_3), 8.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) *δ*(ppm): -119.4 (s, F). DIPMS: m/z (%) 472 [M^+]. Analysis: Found (calcd) for $C_{26}H_{21}FN_4O_2S$: C, 66.02 (66.09); H, 4.52 (4.48); N, 11.91 (11.86); S, 6.82 (6.79).

7-chloro-3-methyl-1-phenyl-5'-(trifluoromethyl)-1,10-dihydrospiro[benzo*/b/*pyrazolo [3,4-e][1,5]thiazepine-4,3'-indolin]-2'one (4q) : R_f= 0.65 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *v* = 3430 (NH), 1690 (C=O), 1610 (C=N), 1170(C-N), 790 (C-Cl), 750 (C-F). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.92 (s, 1H, NH), 8.54 (s, 1 H, NH), 7.95-6.50 (m, 11 H, Ar-H), 2.04 (s, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =180.2 (C=O), 160.3 (C=N), 151.8, 148.4, 145.3 (C-N), 143.6, 140.9, 138.4, 136.8, 134.7, 133.8 (C-Cl), 130.9,129.1,127.3 (C-F), 126.2, 124.8, 122.4 (C-CF_3), 119.8, 116.5, 113.2, 112.2, 109.8, 107.5, 61.5 (C), 9.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) *δ*(ppm): -63.08 (s, 3F, -CF_3). DIPMS: m/z (%) 514 [M+2]$^+$,512 [M^+]. Analysis: Found (calcd) for $C_{25}H_{16}ClF_3N_4OS$: C, 58.60 (58.54); H, 3.18 (3.14); N, 10.88 (10.92); S, 6.29 (6.25).

5'-fluoro-3,7-dimethyl-1-phenyl-1,10-dihydrospiro[benzo*/b/*pyrazolo[3,4-e][1,5]thiazepine-4,3'-indolin]-2'one(4r): R_f= 0.56 (ethyl acetate/hexane=1:4); IR (KBr, cm^{-1}) *v* = 3395 (NH), 1685 (C=O), 1615 (C=N), 1180 (C-N), 745 (C-F). ^{1}H NMR (300 MHz, $CDCl_3$):δ ppm= 8.88 (s, 1H, NH), 8.43 (s, 1 H, NH), 7.87-6.67 (m, 11 H, Ar-H), 2.79 (s, 3H, CH_3), 2.05 (s, 1H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$): δ =177.4 (C=O), 158.3 (C=N), 152.3, 147.8, 146.1 (C-N), 144.2, 140.8, 137.9, 135.4, 133.9, 132.4, 131.1, 128.5 (C-CH_3), 126.8 (C-F), 125.2, 123.1, 120.3, 117.3, 115.8, 113.9, 111.6, 110.2, 108.8, 59.3 (C), 9.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) *δ*(ppm): -119.7 (s, F). DIPMS: m/z (%) 442 [M^+]. Analysis: Found (calcd) for $C_{25}H_{19}FN_4OS$: C, 67.80 (67.86); H, 4.36 (4.33); N, 12.62 (12.66); S, 7.29 (7.25).