SUPPORTING INFORMATION

Silica supported NiO nanocomposite prepared *via* sol-gel technique and its excellent catalytic performance for one-pot multicomponent synthesis of benzodiazepine derivatives under microwave irradiation

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HRMS spectra of compounds 4a to 4u

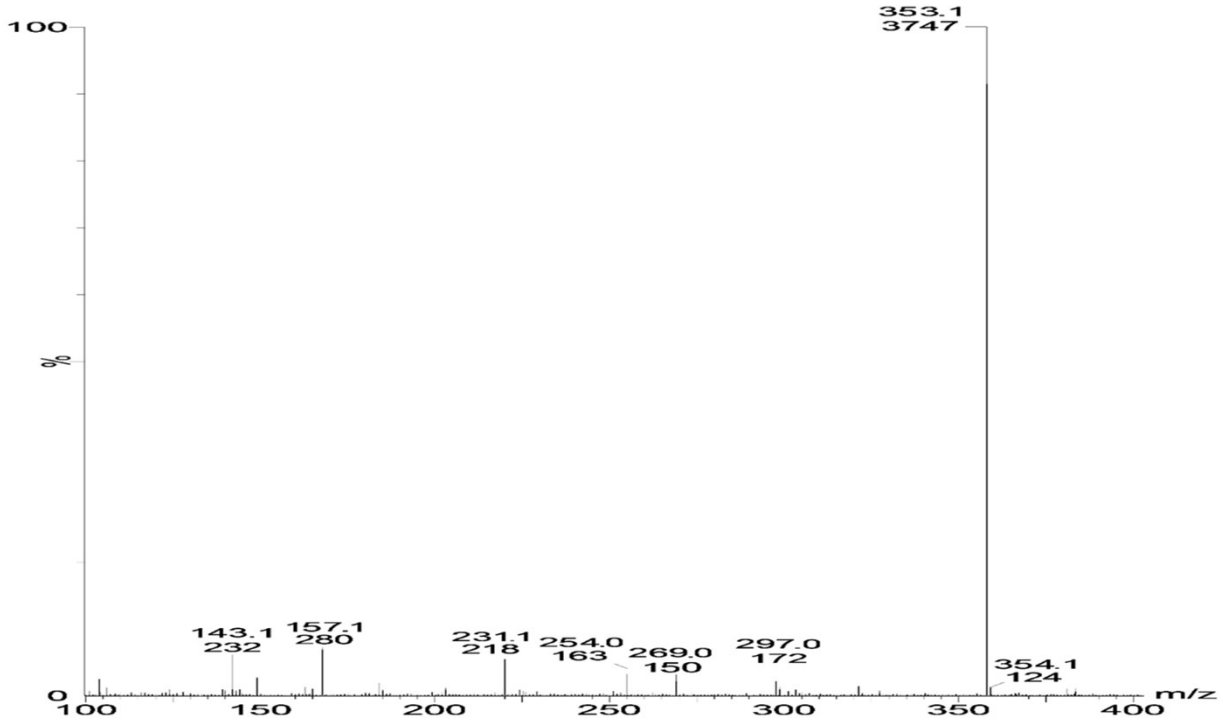


Fig. L_1. 11-(3,5-difluorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4a)**.

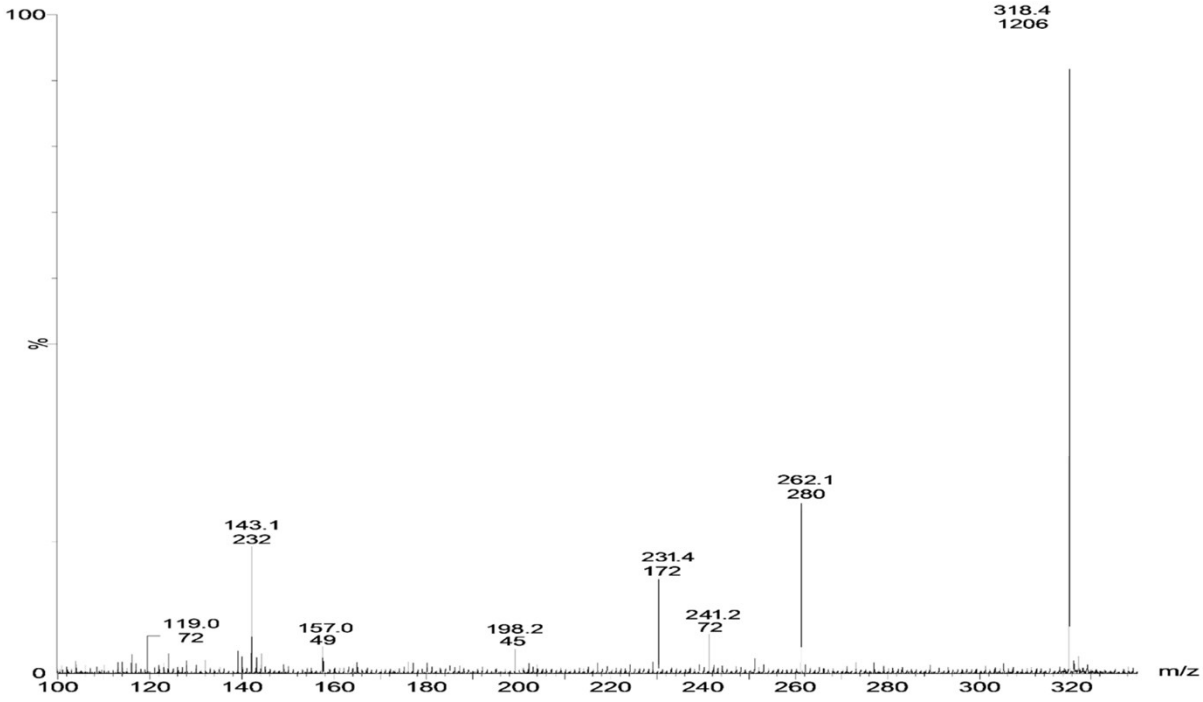


Fig. L_2. 3,3-dimethyl-11-(pyridin-2-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4b)**.

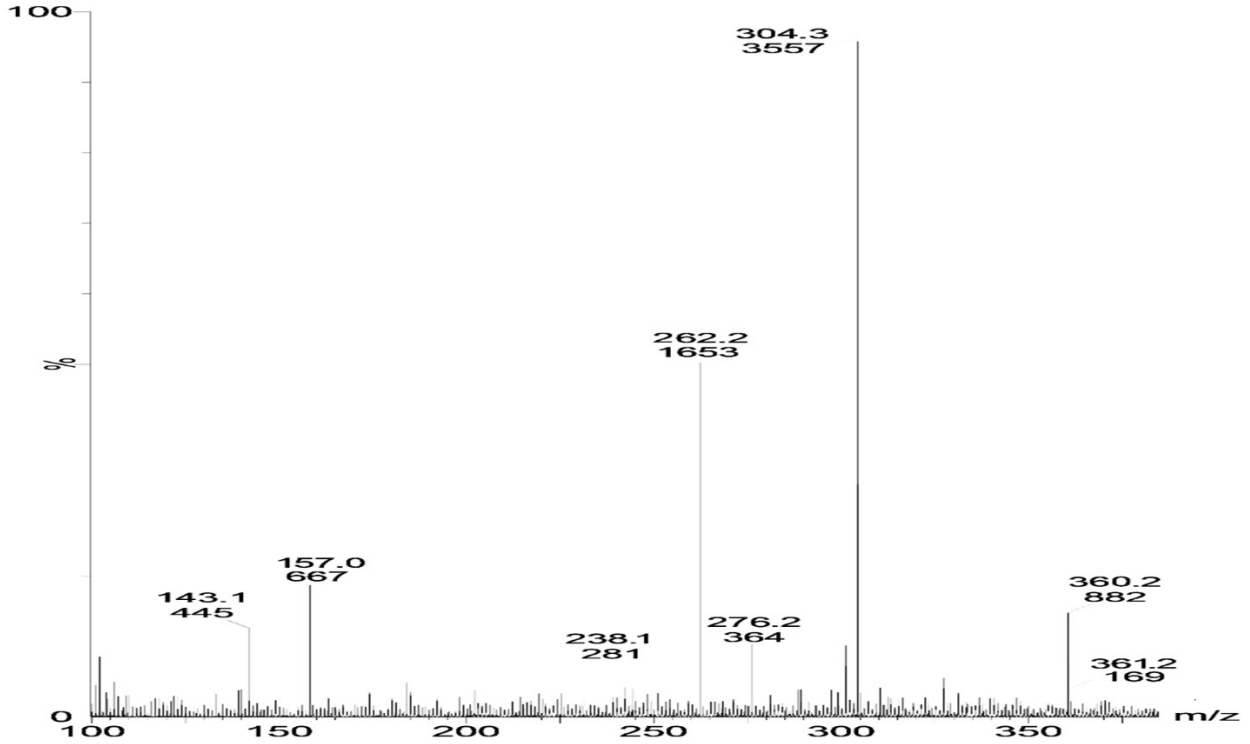


Fig. L_3. 11-(4-(dimethylamino)phenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4e)**.

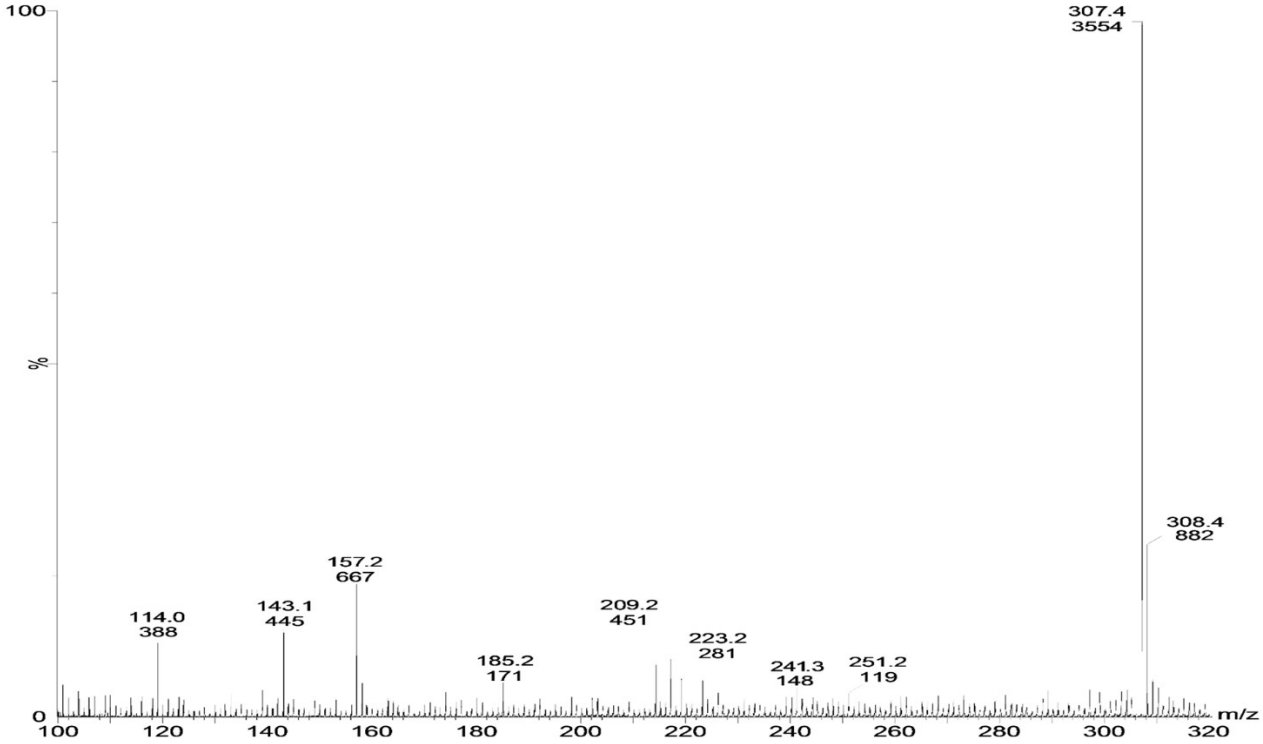


Fig. L_4. 11-(furan-2-yl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4f)**.

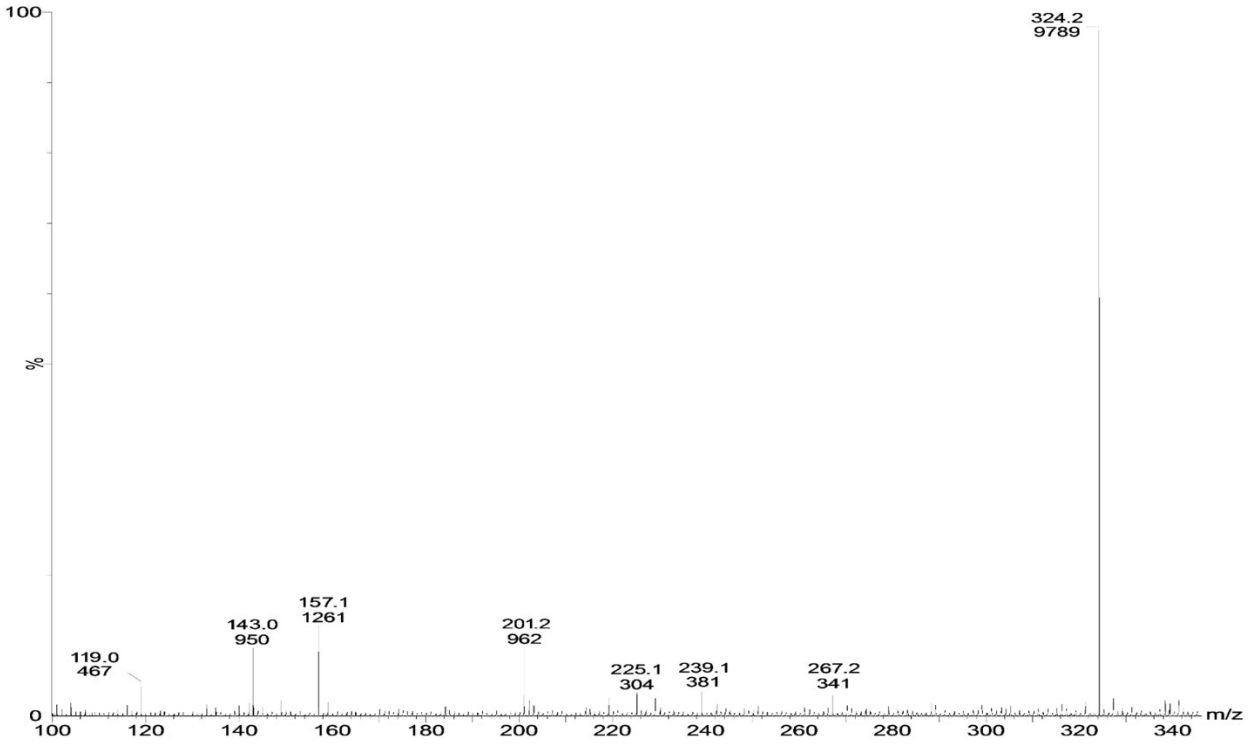


Fig. L_5. 3,3-dimethyl-11-(thiophen-2-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4g)**.

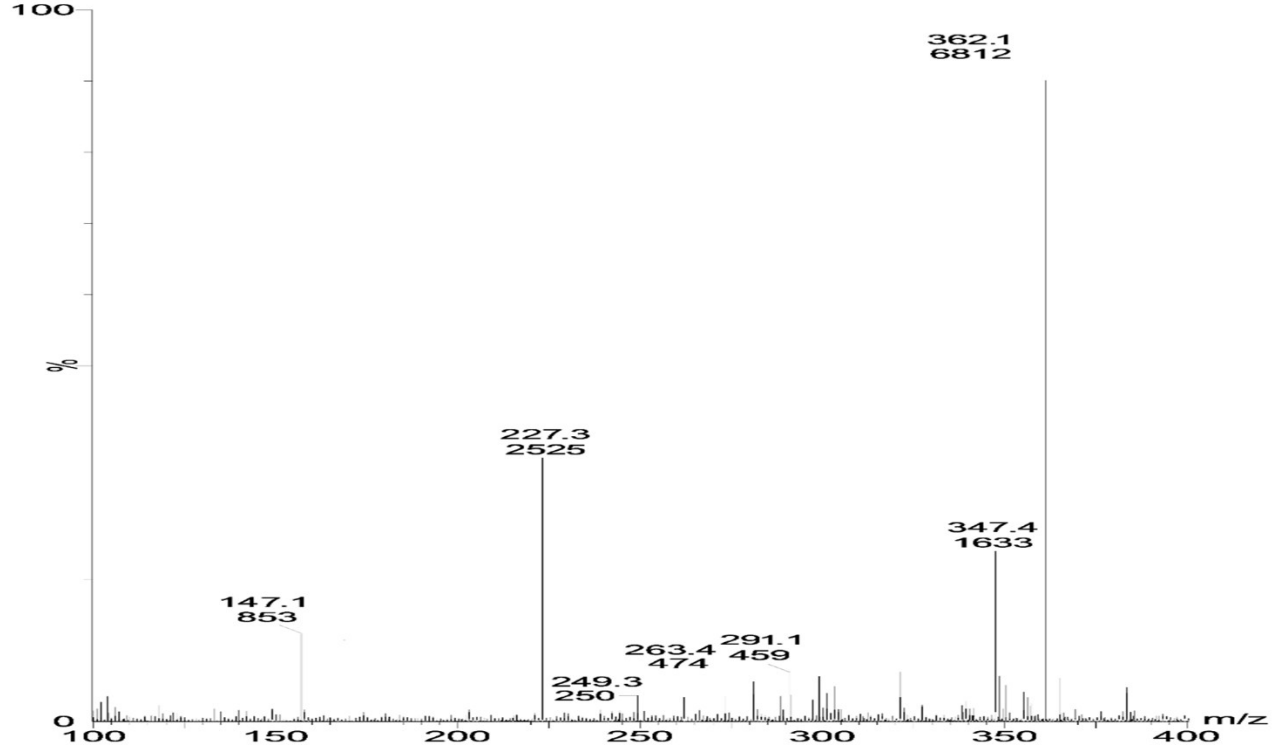


Fig. L_6. 11-(2-hydroxy-3-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4h)**.

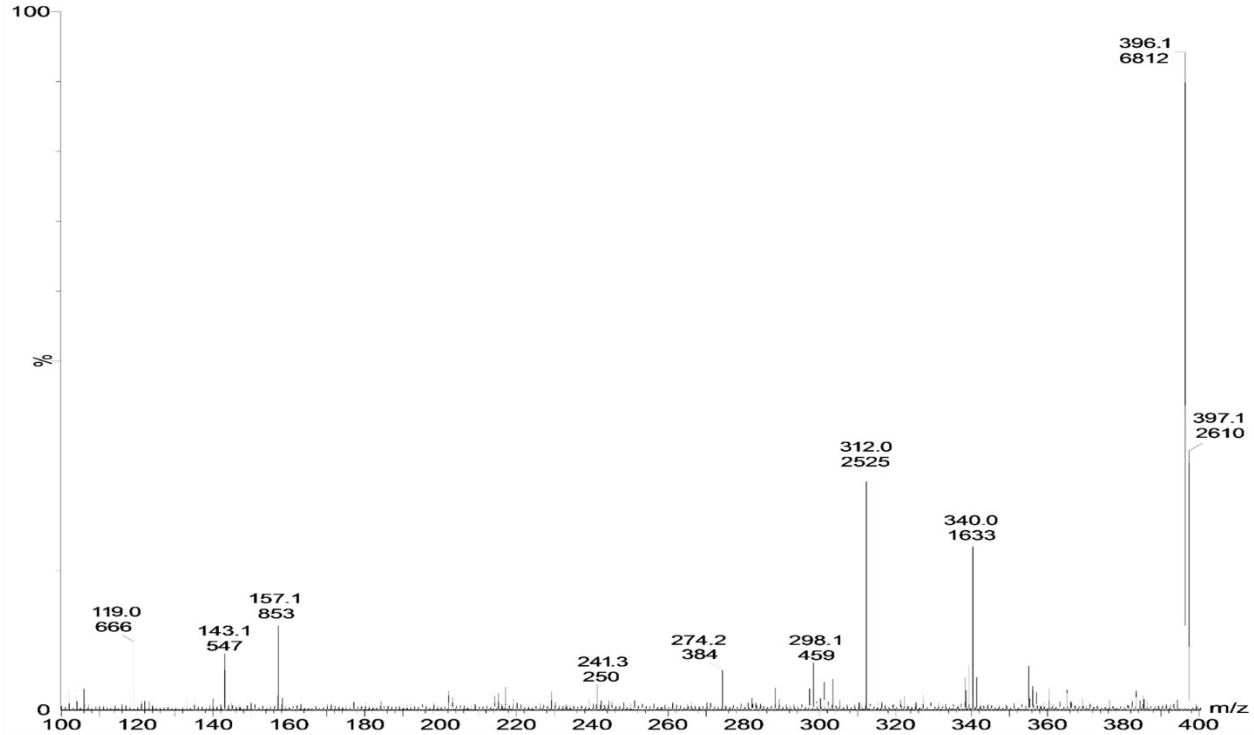


Fig. L_7. 11-(4-chloro-3-nitrophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4j)**.

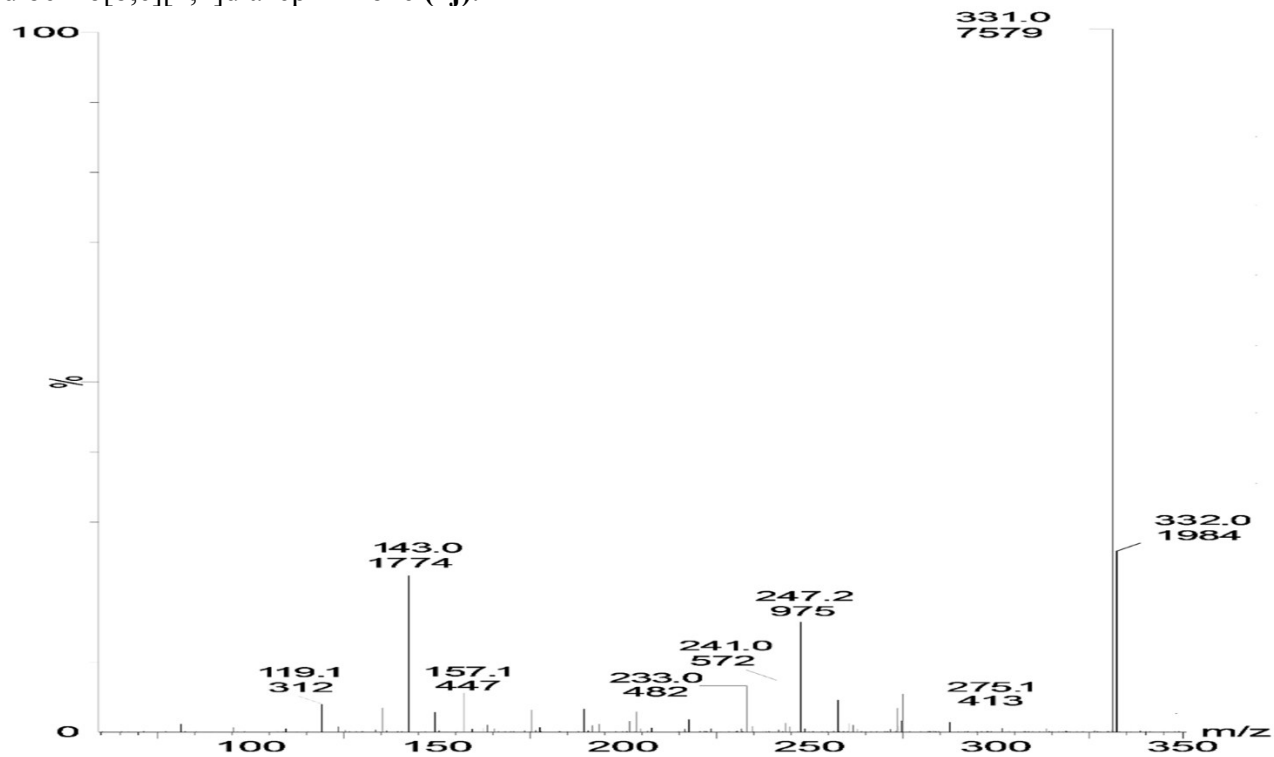


Fig. L_8. 3,3-dimethyl-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4k)**.

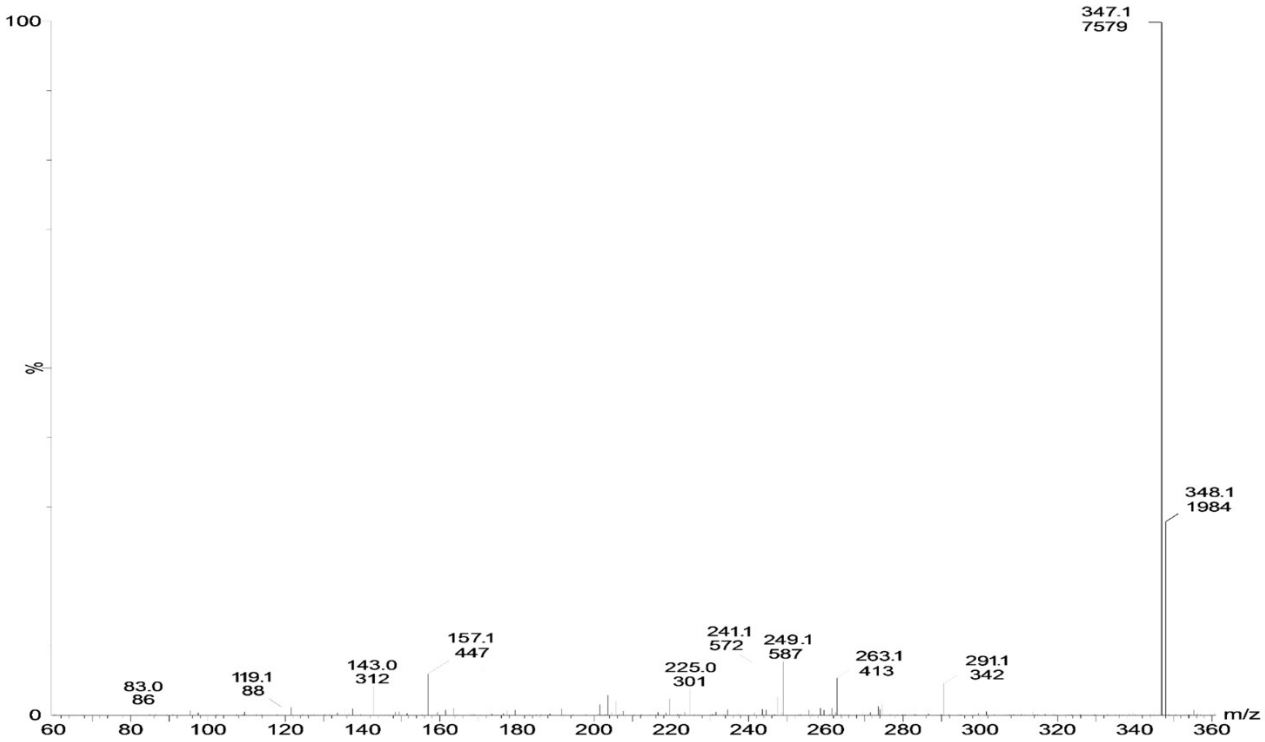


Fig. L_9. 11-(4-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4l)**.

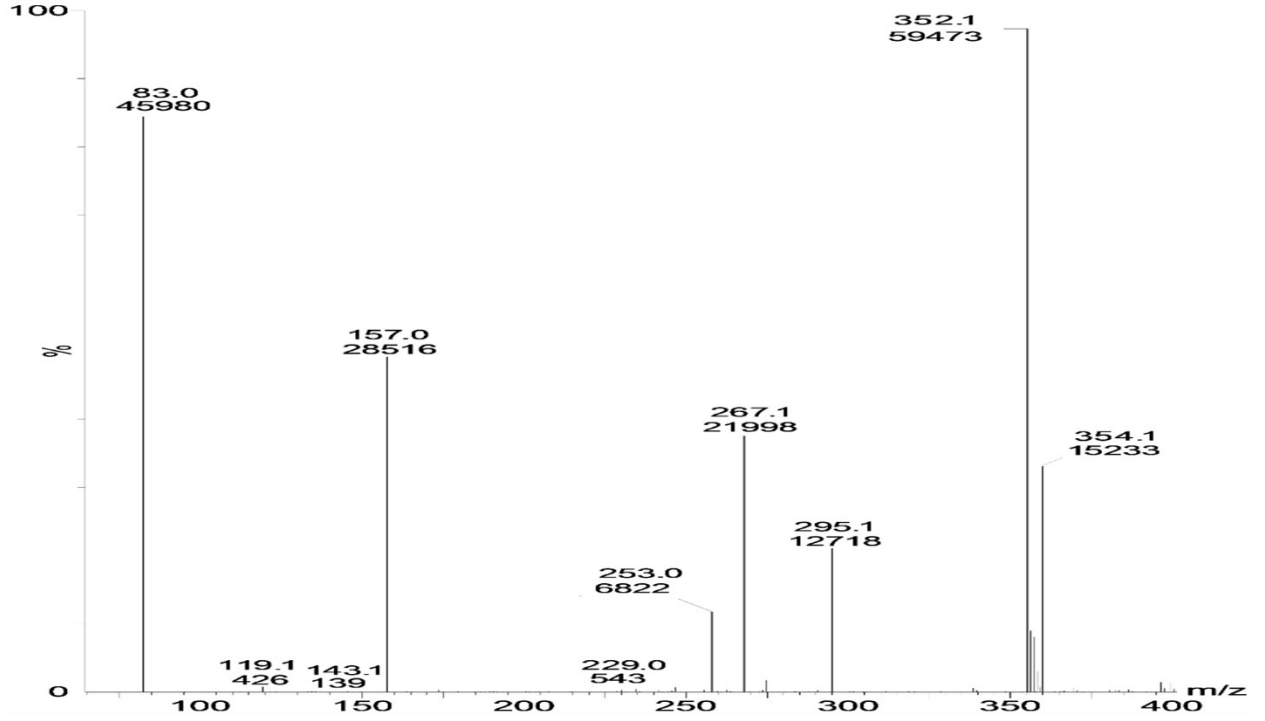


Fig. L_{10}. 11-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4o)**.

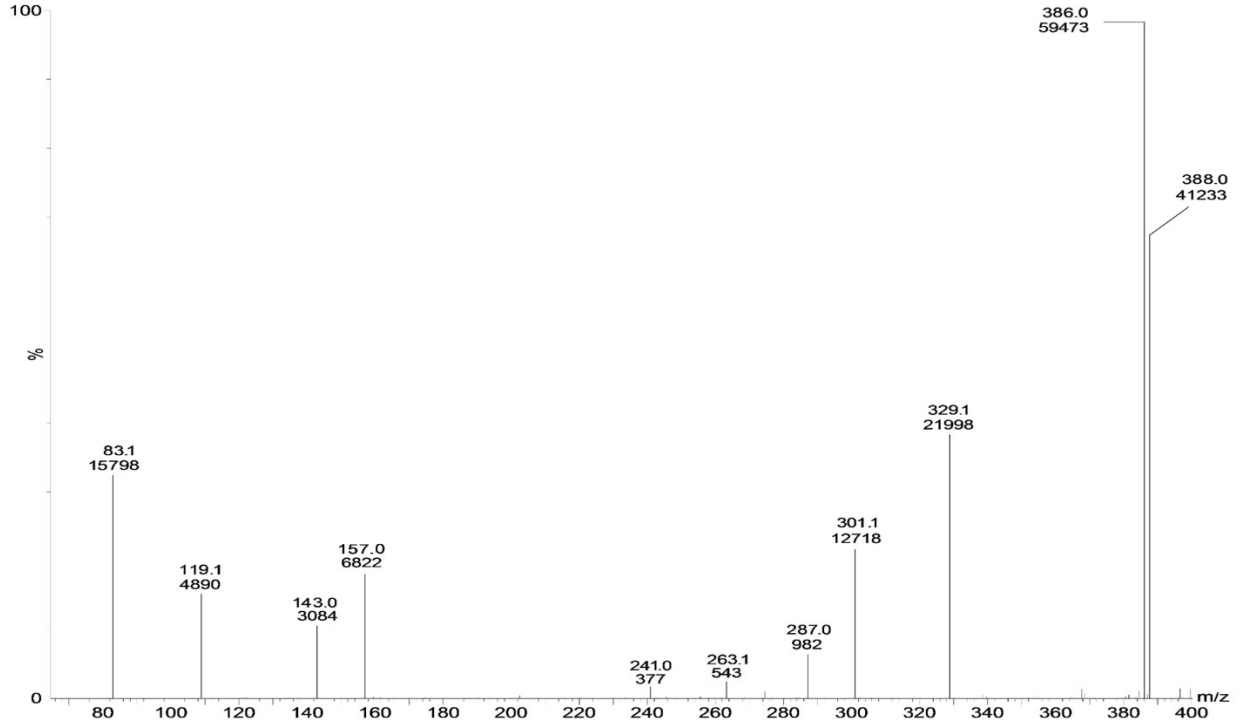


Fig. L_{11}. 11-(2,4-dichlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4q)**.

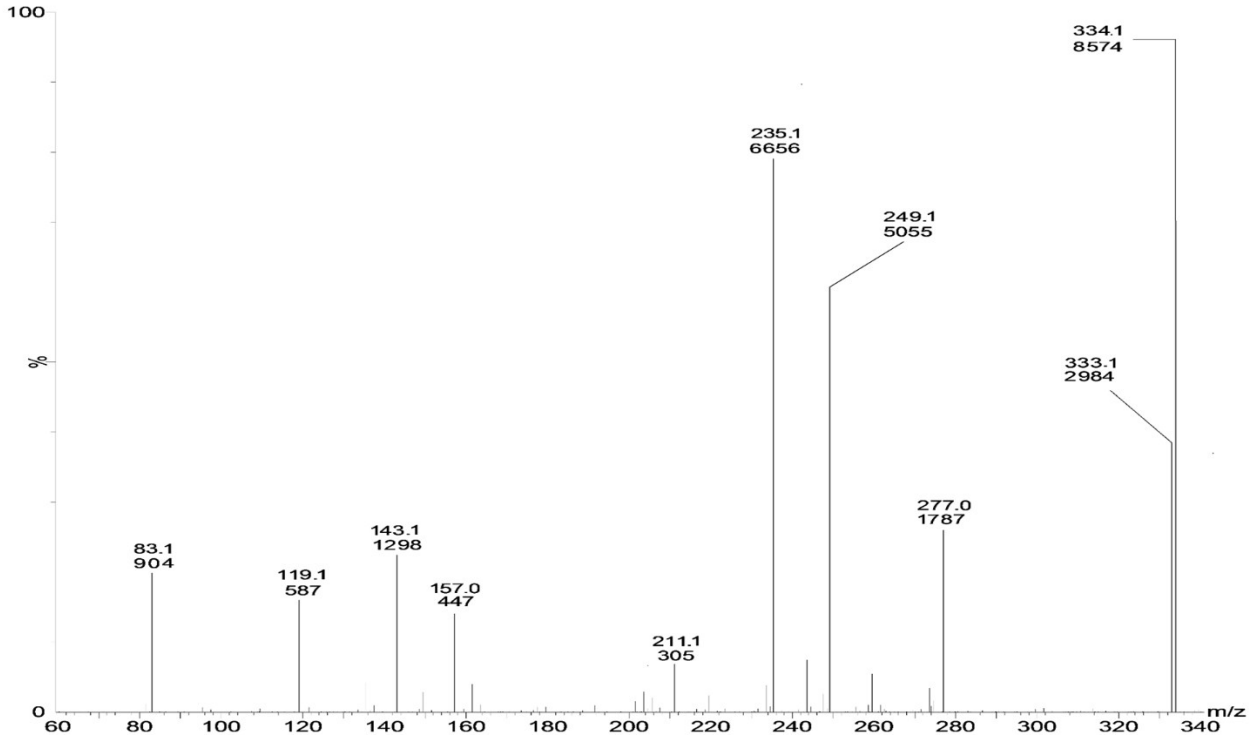


Fig. L_{12}. 11-(3-hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one **(4u)**.

Characterization data of compounds 4a to 4u

(4a): ***11-(3,5-difluorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3082, 1559, 1386 (C-H, aromatic), 3302, 3218 (NH), 1615 (C=C), 1633 (C=O), 1168, 1159 (2×C-F); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 0.97 (3H, s, CH_3), 1.04 (3H, s, CH_3), 2.09 (2H, s, CH_2), 2.32 (2H, s, CH_2-C=O), 5.74 (1H, s, CH), 6.12 (s, 1H, NH, exchangeable with D_2O), 8.63 (s, 1H, NH, exchangeable with D_2O), 6.57-7.01 (m, 7H, C_6H_4, C_6H_3); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.3, 29.1, 35.5, 41.3, 52.6, 54.1, 106.7, 110.8, 116.2, 119.9, 125.1, 127.9, 132.7, 137.1, 138.5, 140.1, 142.5, 146.2, 157.3, 161.5, 195.0; Anal. Calcd for $C_{21}H_{20}F_2N_2O$; C, 71.17; H, 5.69; N, 7.90 found; C, 71.19; H, 5.70; N, 7.88; MS (EI): *m/z* 354 ($M^{+\cdot}$).

(4b): ***3,3-dimethyl-11-(pyridin-2-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3084, 1556, 1384 (C-H, aromatic), 1634 (C=N), 3304, 3219 (NH), 1612 (C=C), 1630 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 0.94 (3H, s, CH_3), 1.01 (3H, s, CH_3), 2.20 (2H, s, CH_2), 2.46 (2H, s, CH_2-C=O), 5.62 (1H, s, CH), 6.06 (s, 1H, NH, exchangeable with D_2O), 8.31 (s, 1H, NH, exchangeable with D_2O), 6.52-7.67 (m, 8H, C_6H_4, C_5H_4N); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.2, 29.4, 33.6, 42.3, 53.1, 55.3, 109.2, 117.4, 120.7, 122.1, 123.2, 125.9, 126.3, 128.1, 139.3, 141.5, 143.5, 150.2, 157.6, 196.7; Anal. Calcd for $C_{20}H_{21}N_3O$; C, 75.21; H, 6.63; N, 13.16 found; C, 75.19; H, 6.64; N, 13.14; MS (EI): *m/z* 319 ($M^{+\cdot}$).

(4c): ***3,3-dimethyl-11-(pyridin-3-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3081, 1553, 1381 (C-H, aromatic), 1633 (C=N), 3317, 3210 (NH), 1620 (C=C), 1627 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 0.96 (3H, s, CH_3), 1.05 (3H, s, CH_3), 2.12 (2H, s, CH_2), 2.50 (2H, s, CH_2-C=O), 5.67 (1H, s, CH), 6.11 (s, 1H, NH, exchangeable with D_2O), 8.39 (s, 1H, NH, exchangeable with D_2O), 6.54-7.71 (m, 8H, C_6H_4, C_5H_4N); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.7, 29.1, 34.6, 41.2, 54.5, 57.1, 110.3, 116.1, 121.3, 124.2, 125.5, 126.3, 127.2, 130.0, 138.1, 142.8, 145.2, 153.1, 158.4, 194.6; Anal. Calcd for $C_{20}H_{21}N_3O$; C, 75.21; H, 6.63; N, 13.16 found; C, 75.23; H, 6.62; N, 13.17; MS (EI): *m/z* 319 ($M^{+\cdot}$).

(4d): ***3,3-dimethyl-11-(pyridin-4-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3086, 1558, 1380 (C-H, aromatic), 1636 (C=N), 3312, 3220 (NH), 1617 (C=C), 1624 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 0.98 (3H, s, CH_3), 1.02 (3H, s, CH_3), 2.17 (2H, s, CH_2), 2.55 (2H, s, CH_2-C=O), 5.62 (1H, s, CH), 6.19 (s, 1H, NH, exchangeable with D_2O), 8.32 (s, 1H, NH, exchangeable with D_2O), 6.50-7.89 (m, 8H, C_6H_4, C_5H_4N); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.5, 29.2, 33.3, 43.1, 52.6, 56.9, 108.8, 118.5, 120.9, 123.0, 125.1, 127.7, 128.1, 131.1, 137.9, 143.4, 146.1, 155.6, 157.2, 197.4; Anal. Calcd for $C_{20}H_{21}N_3O$; C, 75.21; H, 6.63; N, 13.16 found; C, 75.17; H, 6.61; N, 13.15; MS (EI): *m/z* 319 ($M^{+\cdot}$).

(4e): ***11-(4-(dimethylamino)phenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3078, 1560, 1389 (C-H, aromatic), 3320, 3225 (NH), 1622 (C=C), 1635 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.04 (3H, s, CH_3), 1.07 (3H, s, CH_3), 2.15 (2H, s, CH_2), 2.49 (2H, s, CH_2-C=O), 5.59 (1H, s, CH), 6.01 (s, 1H, NH, exchangeable with D_2O), 8.59

(s, 1H, NH, exchangeable with D_2O), 2.55 {s, 6H, $N(CH_3)_2$}, 6.49-7.07 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.6, 30.1, 34.1, 41.2, 42.4, 43.2, 54.6, 55.1, 108.6, 114.3, 115.1, 119.8, 124.4, 128.4, 129.2, 129.5, 130.7, 132.6, 134.3, 139.7, 144.6, 157.5, 194.3; Anal. Calcd for $C_{23}H_{27}N_3O$; C, 76.42; H, 7.53; N, 11.62 found; C, 76.44; H, 7.51; N, 11.59; MS (EI): *m/z* 361 ($M^{+\cdot}$).

(4f): ***11-(furan-2-yl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, *v* cm^{-1}): 3085, 1550, 1378 (C-H, aromatic), 3326, 3231 (NH), 1621 (C=C), 1629 (C=O), 1058 (C-O); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.12 (3H, s, CH_3), 1.15 (3H, s, CH_3), 2.14 (2H, s, CH_2), 2.55 (2H, s, CH_2-C=O), 5.25 (1H, s, CH), 5.01 (s, 1H, NH, exchangeable with D_2O), 6.98 (s, 1H, NH, exchangeable with D_2O), 6.32-7.72 (m, 7H, C_6H_4, C_4H_3O); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.5, 29.3, 35.6, 45.1, 55.3, 57.8, 110.8, 111.1, 116.3, 117.3, 122.9, 123.1, 126.7, 131.2, 140.2, 143.8, 149.1, 158.4, 195.3; Anal. Calcd for $C_{19}H_{20}N_2O_2$; C, 74.00; H, 6.54; N, 9.08 found; C, 74.02; H, 6.52; N, 9.10; MS (EI): *m/z* 308 ($M^{+\cdot}$).

(4g): ***3,3-dimethyl-11-(thiophen-2-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, *v* cm^{-1}): 3092, 1562, 1381 (C-H, aromatic), 3315, 3255 (NH), 1627 (C=C), 1632 (C=O), 718 (C-S); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.06 (3H, s, CH_3), 1.13 (3H, s, CH_3), 2.19 (2H, s, CH_2), 2.52 (2H, s, CH_2-C=O), 5.69 (1H, s, CH), 6.07 (s, 1H, NH, exchangeable with D_2O), 8.62 (s, 1H, NH, exchangeable with D_2O), 6.53-7.49 (m, 7H, C_6H_4, C_4H_3S); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.9, 29.1, 31.7, 43.0, 53.2, 58.6, 112.0, 120.4, 123.9, 126.4, 127.4, 129.0, 130.7, 131.5, 132.3, 138.1, 142.5, 156.4, 194.8; Anal. Calcd for $C_{19}H_{20}N_2OS$; C, 70.34; H, 6.21; N, 8.63 found; C, 70.31; H, 6.22; N, 8.61; MS (EI): *m/z* 324 ($M^{+\cdot}$).

(4h): ***11-(2-hydroxy-3-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3089, 1561, 1384 (C-H, aromatic), 3311, 3239 (NH), 1625 (C=C), 1631 (C=O), 1059 (C-O), 3221 (O-H), 2825 (OCH_3); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.09 (3H, s, CH_3), 1.17 (3H, s, CH_3), 2.17 (2H, s, CH_2), 2.51 (2H, s, CH_2-C=O), 5.57 (1H, s, CH), 6.02 (s, 1H, NH, exchangeable with D_2O), 8.65 (s, 1H, NH, exchangeable with D_2O), 8.89 (1H, s, OH), 3.79 (3H, s, OCH_3), 6.47-6.99 (m, 7H, C_6H_4, C_6H_3); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.2, 29.9, 35.5, 47.4, 52.3, 56.1, 60.1, 109.9, 113.7, 125.3, 126.6, 127.5, 129.9, 131.2, 132.8, 133.1, 135.7, 139.8, 144.5, 159.2, 161.5, 197.6; Anal. Calcd for $C_{22}H_{24}N_2O_3$; C, 72.50; H, 6.64; N, 7.69 found; C, 72.48; H, 6.63; N, 7.71; MS (EI): *m/z* 364 ($M^{+\cdot}$).

(4i): ***3,3-dimethyl-11-(5-nitrothiophen-2-yl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3098, 1572, 1390 (C-H, aromatic), 3341, 3255 (NH), 1630 (C=C), 1633 (C=O), 1535, 1355 (N-O), 715 (C-S); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 0.99 (3H, s, CH_3), 1.07 (3H, s, CH_3), 2.24 (2H, s, CH_2), 2.55 (2H, s, CH_2-C=O), 5.83 (1H, s, CH), 6.30 (s, 1H, NH, exchangeable with D_2O), 8.87 (s, 1H, NH, exchangeable with D_2O), 6.62-7.92 (m, 6H, C_6H_4, C_4H_2S); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.3, 29.7, 32.4, 45.1, 54.4, 61.1, 110.9, 121.7, 125.1, 128.7, 129.9, 132.2, 133.8, 135.6, 140.4, 142.7, 153.2, 159.5, 194.8 Anal. Calcd for $C_{19}H_{19}N_3O_3S$; C, 61.77; H, 5.18; N, 11.37 found; C, 61.79; H, 5.20; N, 11.36; MS (EI): *m/z* 369 ($M^{+\cdot}$).

(4j): ***11-(4-chloro-3-nitrophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3095, 1569, 1389 (C-H, aromatic), 3317, 3245 (NH), 1628 (C=C), 1632 (C=O), 1533, 1341 (N-O), 742 (C-Cl); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.04 (3H, s, CH_3), 1.11 (3H, s, CH_3), 2.19 (2H, s, CH_2), 2.57 (2H, s, CH_2-C=O), 6.01 (1H, s, CH), 5.98 (s, 1H, NH, exchangeable with D_2O), 8.82 (s, 1H, NH, exchangeable with D_2O), 6.57-7.99 (m, 7H, C_6H_4, C_6H_3); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.7, 29.1, 34.2, 44.7, 56.2, 60.1, 107.2, 120.1, 121.7, 124.4, 127.1, 131.2, 133.3, 136.3, 139.2, 141.1, 143.2, 145.1, 149.2, 155.1, 196.2; Anal. Calcd for $C_{21}H_{20}ClN_3O_3$; C, 63.40; H, 5.07; N, 10.56 found; C, 63.42; H, 5.08; N, 10.54; MS (EI): *m/z* 397/399 ($M^{+\cdot}$).

(4k): ***3,3-dimethyl-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3092, 1571, 1385 (C-H, aromatic), 3321, 3251 (NH), 1629 (C=C), 1632 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.07 (3H, s, CH_3), 1.13 (3H, s, CH_3), 2.07 (2H, s, CH_2), 2.51 (2H, s, CH_2-C=O), 2.29 (3H, s, CH_3), 5.78 (1H, s, CH), 5.89 (s, 1H, NH, exchangeable with D_2O), 8.61 (s, 1H, NH, exchangeable with D_2O), 6.49-7.18 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 25.9, 28.3, 29.4, 35.2, 45.5, 54.4, 63.3, 112.2, 119.1, 122.6, 126.2, 129.9, 136.2, 137.1, 139.2, 139.9, 140.6, 142.5, 145.1, 149.5, 152.1, 197.9; Anal. Calcd for $C_{22}H_{24}N_2O$; C, 79.48; H, 7.28; N, 8.43 found; C, 79.50; H, 7.27; N, 8.45; MS (EI): *m/z* 332 ($M^{+\cdot}$).

(4l): ***11-(4-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3078, 1558, 1378 (C-H, aromatic), 3345, 3255 (NH), 1626 (C=C), 1635 (C=O), 1057 (C-O), 2855 (OCH_3); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.05 (3H, s, CH_3), 1.11 (3H, s, CH_3), 2.15 (2H, s, CH_2), 2.58 (2H, s, CH_2-C=O), 5.62 (1H, s, CH), 5.92 (s, 1H, NH,

exchangeable with D_2O), 8.59 (s, 1H, NH, exchangeable with D_2O), 3.57 (3H, s, OCH_3), 6.43-7.02 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.7, 29.8, 33.1, 43.2, 56.7, 59.5, 61.8, 111.9, 119.6, 120.2, 121.5, 126.7, 129.3, 135.2, 139.5, 141.7, 142.3, 143.2, 144.3, 151.4, 168.7, 195.1; Anal. Calcd for $C_{22}H_{24}N_2O_2$; C, 75.83; H, 6.94; N, 8.04 found; C, 75.81; H, 6.93; N, 8.06; MS (EI): *m/z* 348 ($M^{+\cdot}$).

(4m): ***11-(2-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3071, 1560, 1373 (C-H, aromatic), 3342, 3252 (NH), 1627 (C=C), 1631 (C=O), 1061 (C-O), 2822 (OCH_3); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.02 (3H, s, CH_3), 1.17 (3H, s, CH_3), 2.21 (2H, s, CH_2), 2.61 (2H, s, CH_2-C=O), 5.91 (1H, s, CH), 5.83 (s, 1H, NH, exchangeable with D_2O), 8.65 (s, 1H, NH, exchangeable with D_2O), 3.81 (3H, s, OCH_3), 6.52-7.13 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.3, 29.1, 35.4, 44.7, 55.5, 60.0, 62.2, 113.1, 121.6, 122.2, 126.4, 127.8, 131.2, 137.3, 140.6, 143.5, 144.5, 145.7, 146.2, 155.3, 167.5, 196.6; Anal. Calcd for $C_{22}H_{24}N_2O_2$; C, 75.83; H, 6.94; N, 8.04 found; C, 75.85; H, 6.96; N, 8.01; MS (EI): *m/z* 348 ($M^{+\cdot}$).

(4n): ***11-(3-methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3079, 1565, 1372 (C-H, aromatic), 3339, 3268 (NH), 1623 (C=C), 1638 (C=O), 1058 (C-O), 2870 (OCH_3); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.09 (3H, s, CH_3), 1.15 (3H, s, CH_3), 2.19 (2H, s, CH_2), 2.59 (2H, s, CH_2-C=O), 5.80 (1H, s, CH), 5.78 (s, 1H, NH, exchangeable with D_2O), 8.61 (s, 1H, NH, exchangeable with D_2O), 3.59 (3H, s, OCH_3), 6.49-7.20 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.6, 28.3, 34.2, 43.6, 56.6, 60.3, 61.2, 110.7, 122.6, 123.6, 125.2, 129.9, 133.6, 136.7, 142.8, 144.8, 145.8, 146.8, 147.1,

157.9, 168.4, 194.2; Anal. Calcd for $C_{22}H_{24}N_2O_2$; C, 75.83; H, 6.94; N, 8.04 found; C, 75.79; H, 6.95; N, 8.03; MS (EI): *m/z* 348 ($M^{+\cdot}$).

(4o): ***11-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3081, 1562, 1380 (C-H, aromatic), 3341, 3262 (NH), 1629 (C=C), 1639 (C=O), 745 (C-Cl); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.12 (3H, s, CH_3), 1.22 (3H, s, CH_3), 2.16 (2H, s, CH_2), 2.55 (2H, s, CH_2-C=O), 5.83 (1H, s, CH), 5.75 (s, 1H, NH, exchangeable with D_2O), 8.58 (s, 1H, NH, exchangeable with D_2O), 6.50-7.17 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.4, 30.2, 37.1, 48.2, 56.1, 62.2, 114.5, 121.6, 124.3, 129.5, 131.4, 136.4, 137.8, 138.2, 138.7, 139.9, 142.6, 145.8, 148.6, 152.4, 199.8; Anal. Calcd for $C_{21}H_{21}ClN_2O$; C, 71.48; H, 6.00; N, 7.94 found; C, 71.45; H, 6.01; N, 7.92; MS (EI): *m/z* 352/354 ($M^{+\cdot}$).

(4p): ***11-(2-chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3078, 1564, 1375 (C-H, aromatic), 3337, 3265 (NH), 1612 (C=C), 1640 (C=O), 749 (C-Cl); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.10 (3H, s, CH_3), 1.19 (3H, s, CH_3), 2.14 (2H, s, CH_2), 2.59 (2H, s, CH_2-C=O), 5.98 (1H, s, CH), 5.71 (s, 1H, NH, exchangeable with D_2O), 8.67 (s, 1H, NH, exchangeable with D_2O), 6.47-7.23 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.8, 29.9, 38.2, 47.6, 57.5, 65.8, 116.6, 120.5, 125.6, 128.4, 133.3, 137.8, 138.0, 138.6, 139.6, 140.2, 141.9, 147.7, 149.7, 154.8, 196.2; Anal. Calcd for $C_{21}H_{21}ClN_2O$; C, 71.48; H, 6.00; N, 7.94 found; C, 71.50; H, 5.99; N, 7.96; MS (EI): *m/z* 352/354 ($M^{+\cdot}$).

(4q): ***11-(2,4-dichlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3091, 1571, 1381 (C-H, aromatic), 3326, 3254 (NH), 1621 (C=C), 1642 (C=O), 743 (C-Cl); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.09 (3H, s, CH_3), 1.21 (3H, s, CH_3), 2.12 (2H, s, CH_2), 2.61 (2H, s, CH_2-C=O), 5.95 (1H, s, CH), 5.26 (s, 1H, NH, exchangeable with D_2O), 8.71 (s, 1H, NH, exchangeable with D_2O), 6.48-7.52 (m, 7H, C_6H_4, C_6H_3); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 29.2, 30.6, 36.3, 47.2, 55.3, 66.1, 115.3, 122.4, 126.2, 127.6, 135.3, 137.8, 138.3, 140.3, 141.4, 145.2, 149.2, 149.9, 150.2, 154.6, 193.1; Anal. Calcd for $C_{21}H_{20}Cl_2N_2O$; C, 65.12; H, 5.20; N, 7.23 found; C, 65.10; H, 5.19; N, 7.25; MS (EI): *m/z* 386/388 ($M^{+}\cdot$).

(4r): ***11-(2,3-dichlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3085, 1560, 1389 (C-H, aromatic), 3348, 3261 (NH), 1623 (C=C), 1639 (C=O), 746 (C-Cl); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.05 (3H, s, CH_3), 1.18 (3H, s, CH_3), 2.09 (2H, s, CH_2), 2.63 (2H, s, CH_2-C=O), 5.97 (1H, s, CH), 5.12 (s, 1H, NH, exchangeable with D_2O), 8.69 (s, 1H, NH, exchangeable with D_2O), 6.56-7.45 (m, 7H, C_6H_4, C_6H_3); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.8, 29.7, 35.2, 48.1, 56.2, 64.2, 117.1, 121.3, 124.1, 125.6, 136.2, 137.7, 138.3, 143.5, 144.3, 145.4, 147.4, 150.1, 152.6, 156.2, 194.8; Anal. Calcd for $C_{21}H_{20}Cl_2N_2O$; C, 65.12; H, 5.20; N, 7.23 found; C, 65.15; H, 5.23; N, 7.21; MS (EI): *m/z* 386/388 ($M^{+}\cdot$).

(4s): ***11-(4-hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one***

IR (KBr, ν cm^{-1}): 3083, 1558, 1383 (C-H, aromatic), 3345, 3257 (NH), 1625 (C=C), 1636 (C=O), 3226 (O-H); ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.02 (3H, s, CH_3), 1.20 (3H, s, CH_3), 2.12 (2H, s, CH_2), 2.59 (2H, s, CH_2-C=O), 5.95 (1H, s, CH), 5.25 (s, 1H, NH, exchangeable with

D_2O), 8.71 (s, 1H, NH, exchangeable with D_2O), 9.07 (1H, s, OH), 6.41-7.32 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.9, 28.0, 32.3, 45.7, 53.9, 60.2, 112.2, 120.1, 120.7, 121.2, 125.5, 128.3, 131.3, 135.3, 137.2, 138.0, 141.2, 142.3, 147.7, 162.6, 194.1; Anal. Calcd for $C_{21}H_{22}N_2O_2$; C, 75.42; H, 6.63; N, 8.38 found; C, 75.45; H, 6.61; N, 8.35; MS (EI): *m/z* 334 ($M^{+\cdot}$).

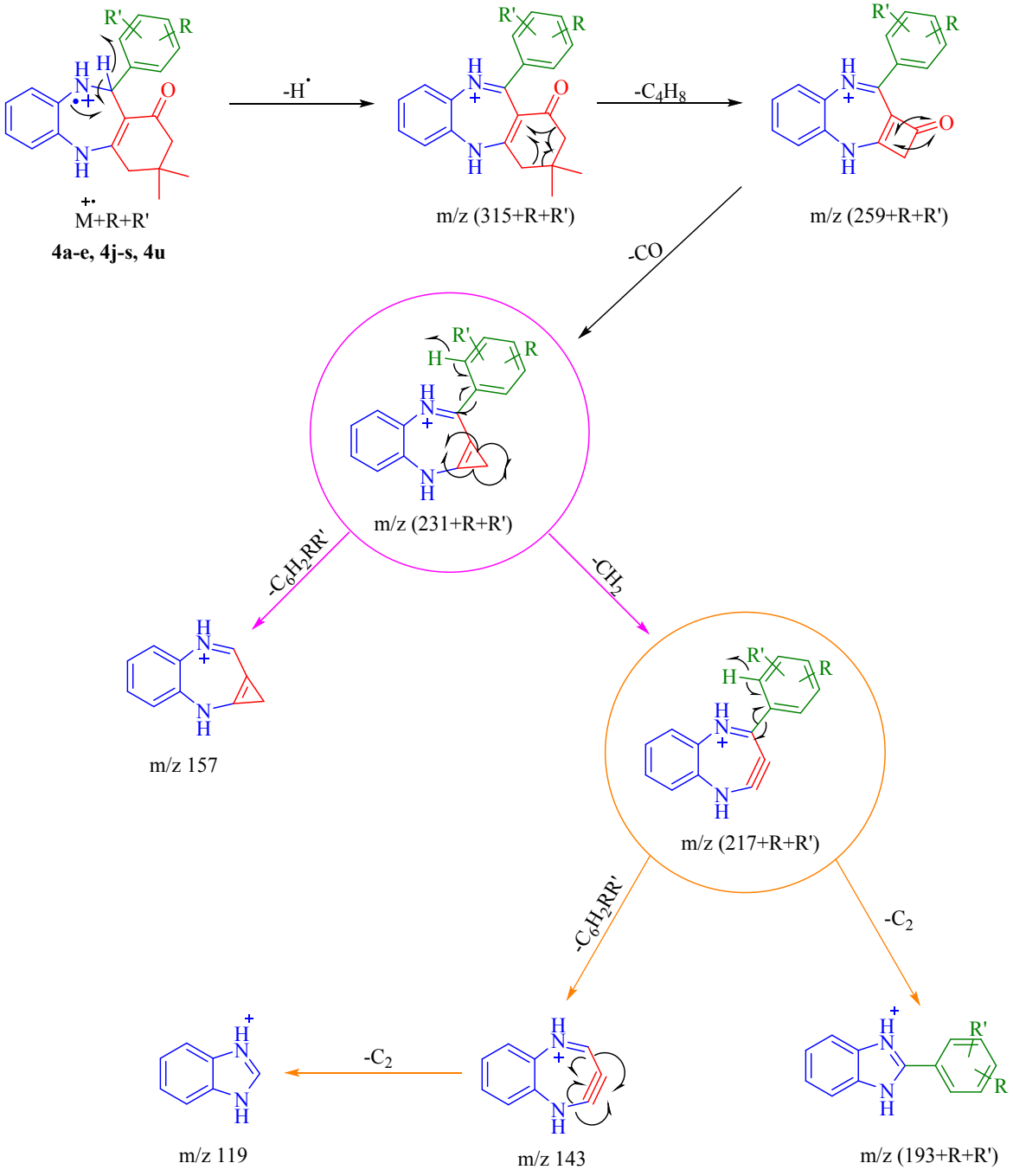
(4t): *11-(2-hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one*

IR (KBr, ν cm^{-1}): 3088, 1561, 1380 (C-H, aromatic), 3347, 3261 (NH), 1621 (C=C), 1635 (C=O), 3229 (O-H); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.05 (3H, s, CH_3), 1.26 (3H, s, CH_3), 2.07 (2H, s, CH_2), 2.61 (2H, s, CH_2-C=O), 5.91 (1H, s, CH), 5.19 (s, 1H, NH, exchangeable with D_2O), 8.69 (s, 1H, NH, exchangeable with D_2O), 9.04 (1H, s, OH), 6.46-7.29 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 28.1, 29.2, 35.4, 44.2, 56.9, 61.3, 116.7, 121.3, 122.0, 122.6, 124.6, 129.4, 130.1, 134.4, 135.1, 140.5, 143.2, 144.6, 145.2, 163.2, 196.3; Anal. Calcd for $C_{21}H_{22}N_2O_2$; C, 75.42; H, 6.63; N, 8.38 found; C, 75.40; H, 6.65; N, 8.39; MS (EI): *m/z* 334 ($M^{+\cdot}$).

(4u): *11-(3-hydroxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one*

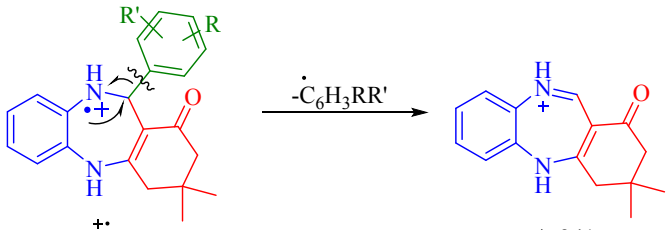
IR (KBr, ν cm^{-1}): 3084, 1556, 1377 (C-H, aromatic), 3351, 3259 (NH), 1628 (C=C), 1638 (C=O), 3225 (O-H); ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 1.08 (3H, s, CH_3), 1.23 (3H, s, CH_3), 2.10 (2H, s, CH_2), 2.58 (2H, s, CH_2-C=O), 5.99 (1H, s, CH), 5.28 (s, 1H, NH, exchangeable with D_2O), 8.73 (s, 1H, NH, exchangeable with D_2O), 8.97 (1H, s, OH), 6.39-7.18 (m, 8H, C_6H_4, C_6H_4); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$): δ 27.5, 28.4, 34.2, 46.3, 55.1, 60.4, 115.8, 120.4, 121.3, 122.4, 125.7, 128.5, 133.0, 136.5, 137.0, 139.0, 143.2, 145.3, 148.3, 162.4, 195.2; Anal. Calcd for $C_{21}H_{22}N_2O_2$; C, 75.42; H, 6.63; N, 8.38 found; C, 75.44; H, 6.59; N, 8.37; MS (EI): *m/z* 334 ($M^{+\cdot}$).

Fragmentation pattern I



Scheme Q_1. Proposed fragmentation mechanisms of molecular ion [$M^{+\cdot}$] of compounds (**4a-e, 4j-s** and **4u**).

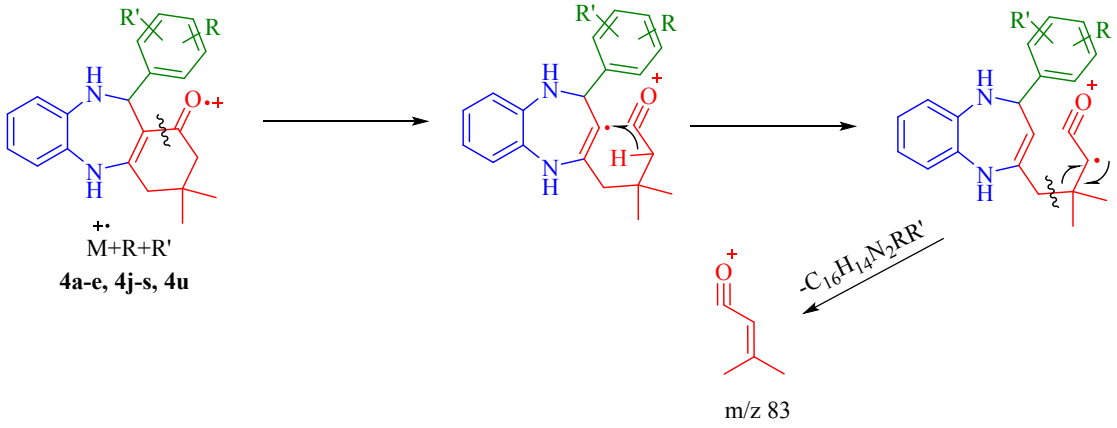
Fragmentation pattern II



M+R+R'

4a-e, 4j-s, 4u

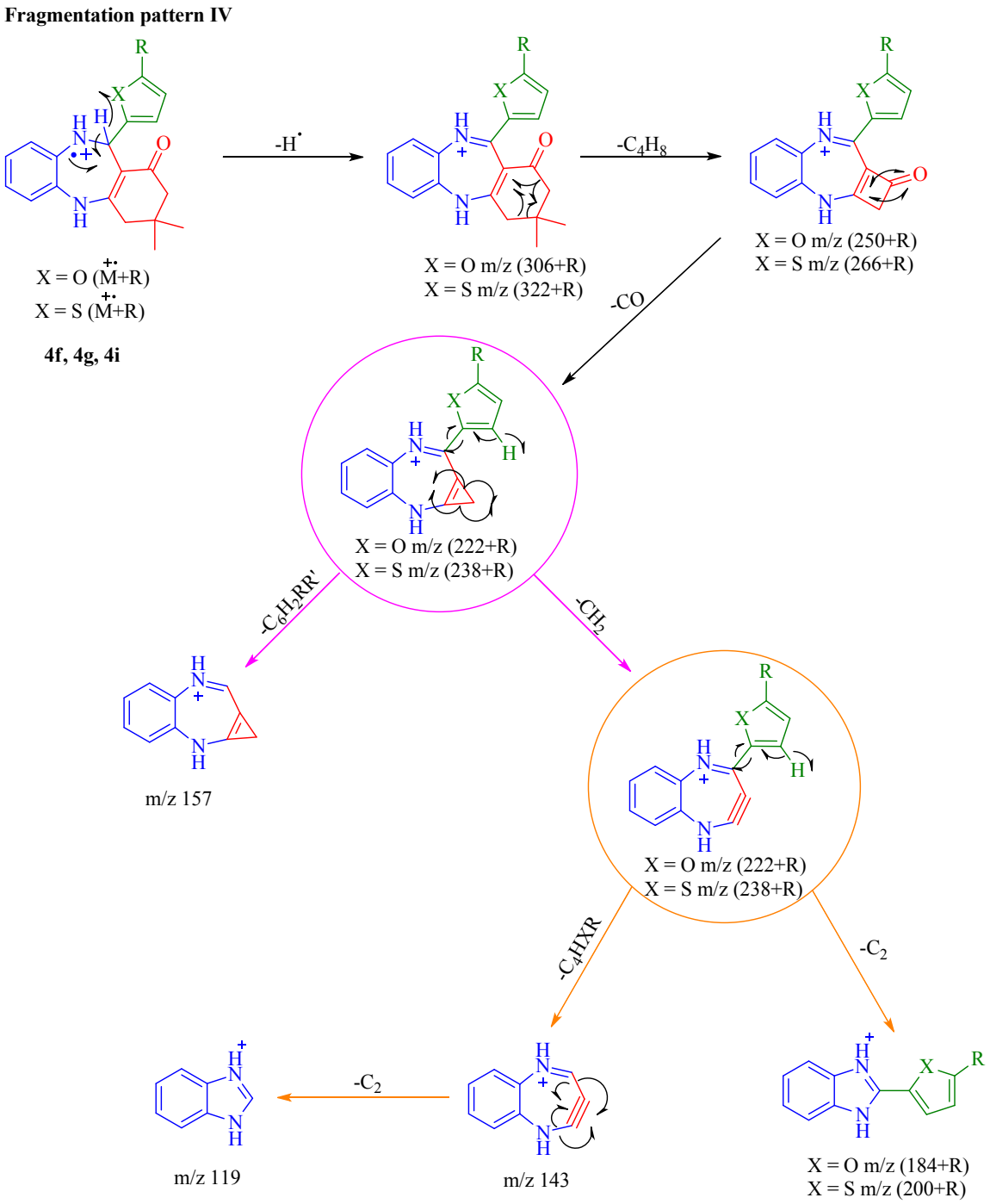
Fragmentation pattern III



M+R+R'

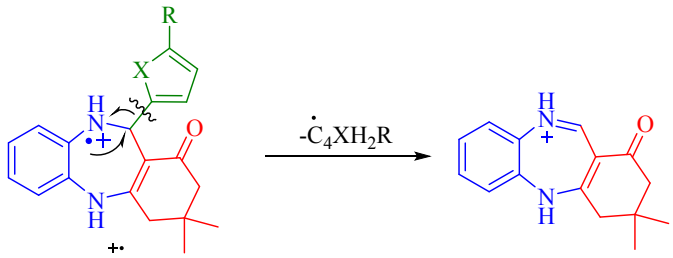
4a-e, 4j-s, 4u

Scheme Q_2. Proposed fragmentation mechanisms of molecular ion [$M^{+\cdot}$] of compounds (**4a-e, 4j-s** and **4u**).



Scheme Q3. Proposed fragmentation mechanisms of molecular ion [$M^{+\cdot}$] of compounds (**4f, 4g** and **4i**).

Fragmentation pattern V

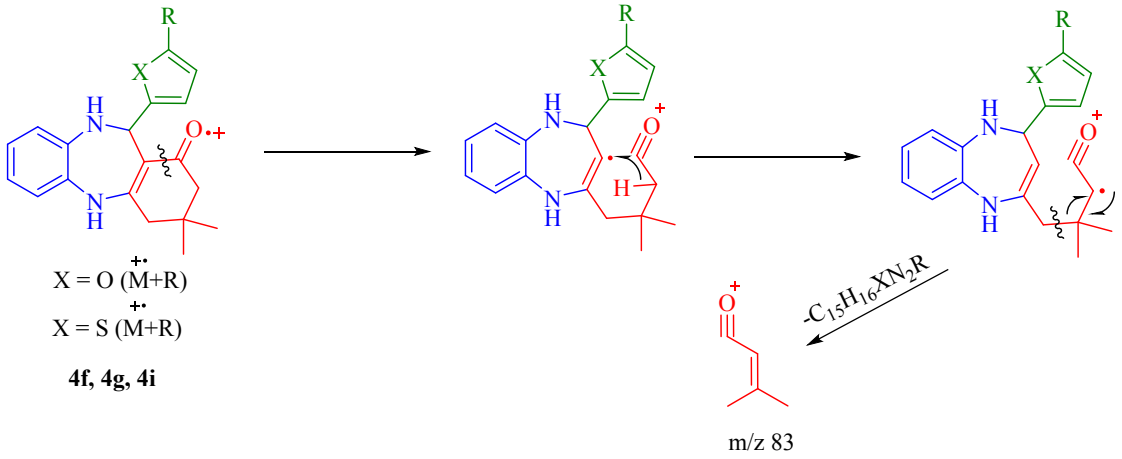


X = O (M+R)

X = S (M+R)

4f, 4g, 4i

Fragmentation pattern VI

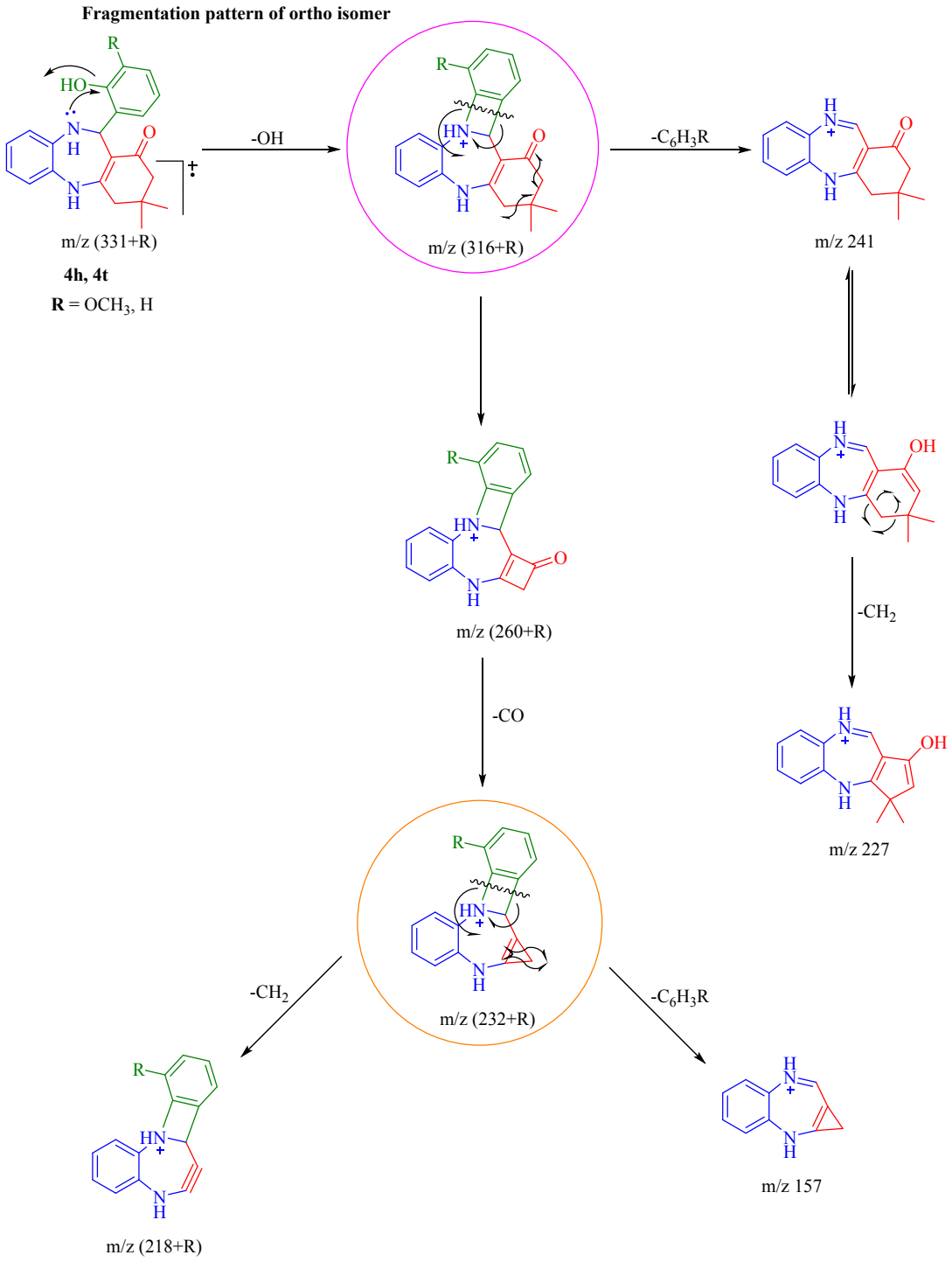


X = O (M+R)

X = S (M+R)

4f, 4g, 4i

Scheme Q4. Proposed fragmentation mechanisms of molecular ion [$M^{+\cdot}$] of compounds (**4f, 4g** and **4i**).



Scheme Q5. Proposed fragmentation mechanisms of molecular ion [$M^{+\cdot}$] of compounds (**4h** and **4t**).

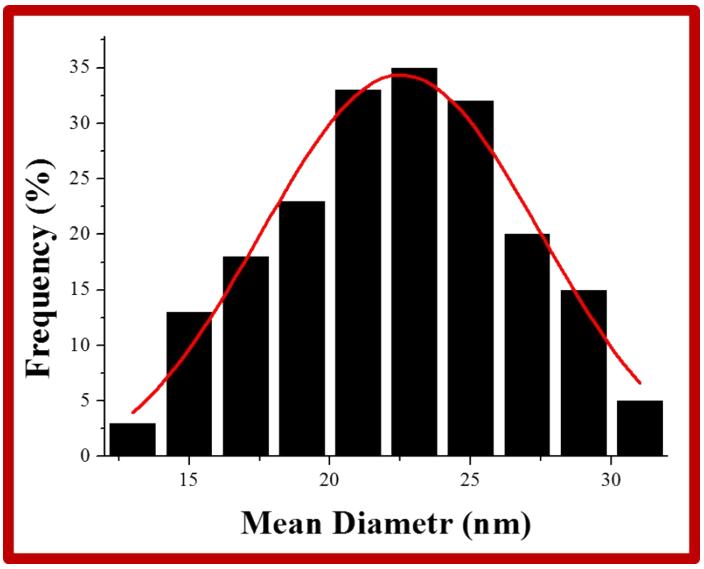


Figure S1. Particle size distribution histogram of **Fig. 5a**.

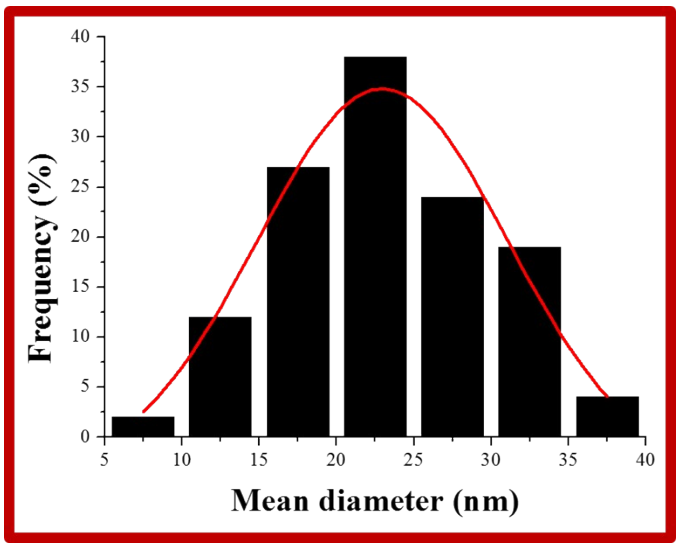


Figure S2. Particle size distribution histogram of **Fig. 5b**.

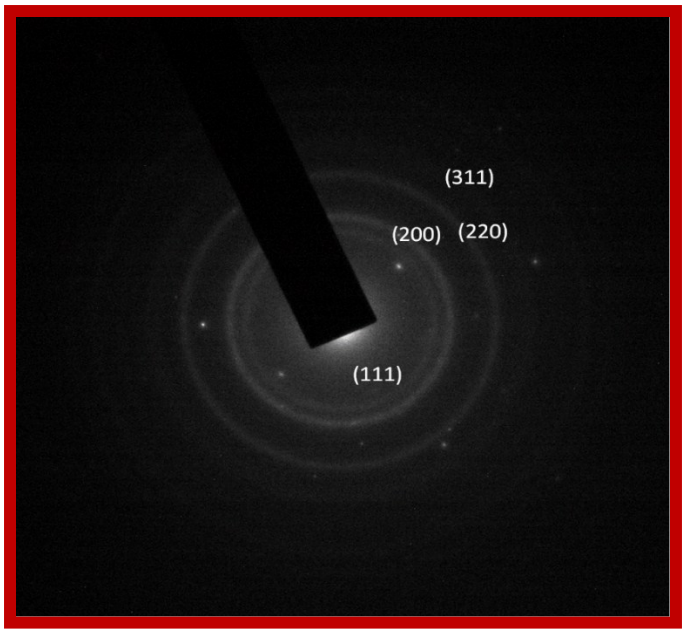


Figure S3. SAED patterns of NiO-SiO_2 NCs.