Supporting Information

Copper-Catalyzed Arylation of Biguanide Derivatives *via* C–N Cross–Coupling Reactions

Chen Zhang [a,], Bo Huang [a], Ai-Qing Bao [b], Xiao Li [a], Shunna Guo [a], Jinquan Zhang [a], Junzhi Xu [a] and Dong-Mei Cui [b]**

[a] *College of Pharmaceutical Sciences, Zhejiang University, Hangzhou 310058, China*

[b] *College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 10014, China*

E-mail Address: chenzhang@zju.edu.cn

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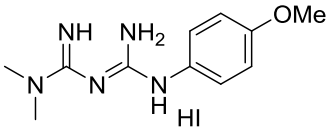
General Methods:

Under otherwise noted, materials such as compound **2** were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) was performed using silica gel 60 F254 and visualized using UV light. Column chromatography was performed with silica gel (mesh 300~400). ^{1}H NMR and ^{13}C NMR spectra recorded on a Bruker Avance 500 MHz spectrometer in DMSO-d_6 with Me_4Si as an internal standard. All products are new compounds, data were reported as follows: chemical shift in parts per million (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), coupling constant in Hertz (Hz) and integration.

General Procedure for Synthesis of Biguanide hydroiodide:

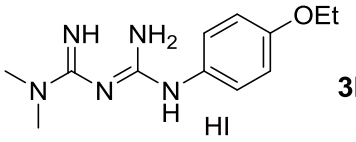
To a mixture of biguanide hydroiodide (1.0 mmol), aryl iodide (1.0 mmol), 2-(pyridin-2-yl) pyridine (0.2 mmol), and K_3PO_4 (6.0 mmol) in THF (5 mmol), was added CuI (10 mol %). The resulting mixture was than sealed and stirred for 12 h at 80 ℃. After completion, the reaction mixture was filtered and the precipitates were washed with methanol. The mixture was evaporated under vacuum, and the residue was purified by flash chromatography with CH_2Cl_2 and CH_3OH (3:1) as the eluent to give the pure product.



3a

***N*-(4-methoxyphenyl)-dimethylbiguanide hydroiodide (3a)**

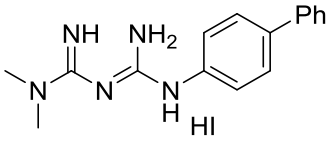
Yellow solid; Mp: 203-204 ℃; IR (KBr, cm^{-1}): 3850.68, 3448.42, 2357.29, 1634.31, 1583.19, 1558.78, 1435.81, 1258.91, 1087.14, 771.21; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.83 (s, 1H), 7.46 (s, 2H), 7.24 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.62 (s, 2H), 3.73 (s, 3H), 2.94 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.9, 155.8, 154.3, 131.1, 123.5, 113.9, 55.2, 37.6; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{11}H_{18}N_5O$ 236.1511, found 236.1510. Anal. Calcd for $C_{11}H_{18}IN_5O$: C, 36.38; H, 5.00; N, 19.28. Found: C, 36.33; H, 5.04; N, 19.26.



3b

***N*-(4-ethoxyphenyl)-dimethylbiguanide hydroiodide (3b)**

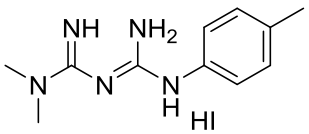
Yellow solid; mp 161-162℃; IR (KBr, cm^{-1}): 3295.08, 3196.88, 2973.78, 2920.38, 1628.41, 1585.84, 1537.92, 1511.00, 1413.88, 1238.72, 1043.71, 823.61; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (s, 1H), 7.43 (s, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.59 (s, 2H), 3.98 (d, J = 6.5 Hz, 2H), 2.94 (s, 6H), 1.30 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.9, 155.2, 154.3, 131.1, 123.6, 114.5, 63.2, 37.6, 14.7; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{12}H_{20}N_5O$ 250.1668, found 250.1664.



3c

***N*-(1, 1'-biphenyl)-dimethylbiguanide hydroiodide (3c)**

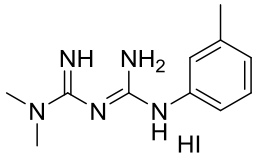
Yellow solid; mp: 223-224℃; IR(KBr,cm^{-1}):3365.02, 3296.09, 2923.39, 1629.50, 1583.88, 1527.46, 1409.62, 1381.35, 1050.64, 826.32; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.60-7.66 (m, 6H), 7.30-7.48 (m, 5H), 6.69 (s, 2H), 2.98 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 153.2, 139.5, 138.2, 134.8, 128.8, 127.0, 125.8, 125.2, 121.0, 37.6; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{16}H_{20}N_5$ 282.1719, found 282.1722.



3d

***N*-(4-methylphenyl)-dimethylbiguanide hydroiodide (3d)**

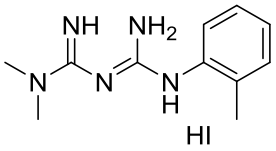
Yellow solid; mp: 195-196℃; IR (KBr, cm^{-1}): 3343.42, 3190.06, 2923.06, 2855.17, 1630.82, 1588.19, 1545.25, 1541.90, 1415.37, 1204.94, 1052.22, 810.68; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 (s, 1H), 7.51 (s, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.61 (s, 2H), 2.95 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.1, 153.8， 135.9， 132.6， 129.2，121.3, 37.7， 20.4; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{11}H_{18}N_5$ 220.1562, found 220.1570.



3e

***N*-(3-methylphenyl)-dimethylbiguanidehydroiodide (3e)**

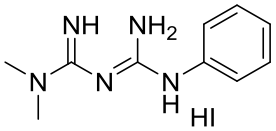
Yellow solid; mp: 203-204℃; IR (KBr, cm^{-1}): 3421.56, 3366.23, 2923.92, 1635.22, 1595.50, 1548.05, 1421.21, 1302.22, 1133.87, 777.93. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.90 (s, 1H), 7.54 (s, 2H), 7.14-7.19 (m, 3H), 6.83-6.90 (m, 1H), 6.63 (s, 2H), 2.96 (s, 6H), 2.26 (s, 3H); 13C NMR (125 MHz, DMSO-d_6) δ 160.0, 153.4, 138.5, 137.9, 128.5, 124.0, 121.4, 118.1, 37.6, 21.1;HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{11}H_{18}N_5$ 220.1562, found 220.1568.



3f

***N*-(2-methylphenyl)-dimethylbiguanide hydroiodide (3f)**

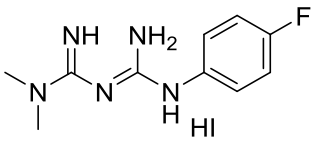
Yellow solid; mp: 177-178℃; IR (KBr, cm^{-1}): 3422.89, 3360.99, 1631.56, 1537.20, 1487.97, 1402.70, 1384.20, 1045.63, 891.45; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.38 (s, 1H), 7.40 (s, 2H), 7.07-7.39 (m, 4H), 6.73 (s, 2H), 2.91 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.7, 154.9, 136.1, 132.2, 130.3, 126.1, 125.7, 125.3, 37.5, 17.7; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{11}H_{18}N_5$ 220.1562, found 220.1565.



3g

***N*-phenyl-dimethylbiguanide hydroiodide (3g)**

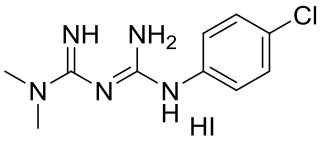
Yellow solid; mp: 168-169℃; IR (KBr, cm^{-1}): 3345.46, 3198.33, 2921.70, 1634.49, 1587.18, 1549.85, 1415.50, 1381.24, 1048.22, 934.46, 756.77; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.97 (s, 1H), 7.57 (s, 2H), 7.39 -7.21 (m, 4H), 7.05 (t, J = 7.3 Hz, 1H), 6.64 (s, 2H), 2.96 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.1, 153.4, 138.6, 128.7, 123.2, 120.8, 37.7; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{10}H_{16}N_5$ 206.1406, found 206.1399.



3h

***N*-(4-fluoropHenyl)-dimethylbiguanide hydroiodide (3h)**

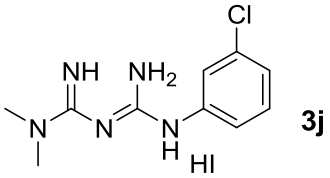
Yellow solid; mp: 168-169℃; IR (KBr, cm^{-1}): 3376.72, 3301.46, 2925.41, 1640.13, 1595.19, 1536.78, 1496.55, 1406.29, 1379.67, 1051.30, 842.41; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.98 (s, 1H), 7.54 (s, 2H), 7.34-7.37 (m, 2H), 7.11-7.15 (m, 2H), 6.64 (s, 2H), 2.95 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 158.3 (d, J = 226.9 Hz), 153.6, 134.9 (d, J = 1.8 Hz), 123.2 (d, J = 7.9 Hz), 115.3 (d, J = 22.5 Hz), 37.72; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{10}H_{15}FN_5$ 224.1311, found 224.1306.



3i

***N*-(4-chlorophenyl)-dimethylbiguanide hydroiodide (3i)**

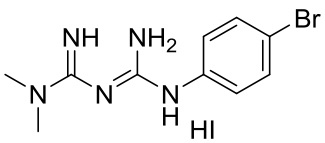
Yellow solid; mp: 168-169℃; IR (KBr, cm^{-1}): 3377.11, 3206.11, 2922.65, 1637.41, 1597.10, 1484.61, 1376.84, 1086.14, 834.77; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.63 (s, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 6.67 (s, 2H), 2.96 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 153.0, 137.7, 128.5, 126.8, 122.2, 37.6; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{10}H_{15}ClN_5$ 240.1016, found 240.1011.



3j

***N*-(3-chlooropHenyl)-dimethylbiguanidehydroiodide (3j)**

Yellow solid; mp: 225-226℃; IR (KBr, cm^{-1}): 3345.10, 3197.02, 3125.67, 1634.71, 1599.66, 1582.43, 1539.95, 1416.99, 1376.01, 1049.72, 949.85; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.12 (s, 1H), 7.68 (s, 2H), 7.57 (s, 1H), 7.29-7.34 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.08(d, J = 8.0 Hz, 1H), 6.70 (s, 2H), 2.92 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.3, 152.7, 140.4, 132.9, 130.2, 122.6, 119.9, 118.8, 37.7; H RMS (ESI) m/z $[M-I]^+$ calcd for $C_{10}H_{15}ClN_5$ 240.1016, found 240.1011.

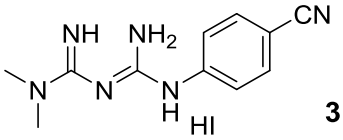


3k

***N*-(4-bromophenyl)-dimethylbiguanide hydroiodide (3k)**

Yellow solid; mp: 236-237℃; IR(KBr, cm^{-1}): 3411.59, 3295.95, 3188.29, 1615.58,

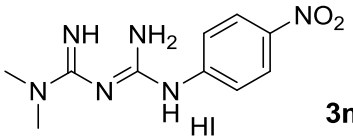
530.72, 1479.56, 1401.73, 1286.09, 1048.19, 831.22; ^{1}HNMR (500 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.64 (s, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.69 (s, 2H), 2.96 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 153.0, 138.2, 131.4, 122.5, 114.8, 37.7; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{10}H_{15}BrN_5$ 284.0511, found 284.0507.



3l

***N*-(4-cyanpHenyl)-dimethylbiguanide hydroiodide (3l)**

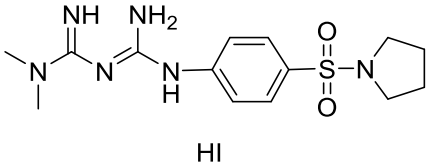
Yellow solid; mp: 236-237℃; IR (KBr, cm^{-1}): 3379.63, 3297.74, 2926.87, 2218.26, 1637.21, 1572.67, 1523.88, 1408.49, 1377.86, 1112.62, 941.96; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.41 (s, 1H), 7.79 (s, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 6.78 (s, 2H), 2.98 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.4, 152.0, 143.5, 133.0, 119.7, 119.1, 104.1, 37.8; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{11}H_{15}N_6$ 231.1358, found 231.1358.



3m

***N*-(4-nitrylphenyl)-dimethylbiguanide hydroiodide (3m)**

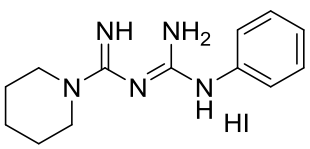
Yellow solid; mp: 219-220℃; IR (KBr, cm^{-1}): 3421.64, 3075.92, 1634.00, 1549.05, 1505.03, 1406.95, 1384.27, 1108.01; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.63 (s, 1H), 8.19 (d, J = 9.2 Hz, 2H), 7.85 (s, 2H), 7.65 (d, J = 9.2 Hz, 2H), 6.84 (s, 2H), 3.00 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.5, 151.8, 145.7, 141.6, 124.8, 119.1, 37.8; HRMS (ESI) m/z $[M-I]^+$ $C_{10}H_{15}N_6O_2$ 251.1256, found 251.1253.



3n

***N*-(4-(pyrrolidin-1-ylsulfonyl))-dimethylbiguanide hydroiodide (3n)**

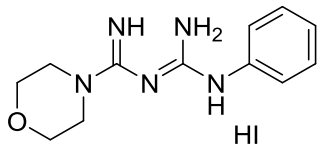
Yellow solid; mp: 225-226℃; IR (KBr, cm^{-1}): 3373.98, 3294.60, 3194.54, 1631.60,1571.95, 1522.20, 1427.74, 1377.26, 1338.24, 1241.62, 1067.31, 711.90; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.40 (s, 1H), 7.77 (s, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 6.77 (s, 2H), 3.11 (t, J = 6.5 Hz, 4H), 2.99 (s, 6H), 1.64 (t, J = 6.5 Hz, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.4, 152.3, 143.3, 129.4, 128.4, 119.4, 47.7, 37.7, 24.7; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{14}H_{23}N_6O_2S$ 339.1603, found 339.1603.



3s

***N*-(amino(phenylamino)methylene)piperidine-1-carboximidamide hydroiodide (3s)**

Yellow solid; mp: 207-208℃; IR (KBr, cm^{-1}): 3203.69, 3128.73, 1631.34, 1578.22, 1542.40, 1446.38, 1382.24, 1295.83, 1101.09, 753.52; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.99 (s, 1H), 7.62 (s, 2H), 7.29-7.36 (m, 4H), 7.03-7.07 (m, 1H), 6.69 (s, 2H), 3.43 (t, J = 5.2 Hz , 4H), 1.54-1.60 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.3, 153.9, 138.6, 128.7, 123.3, 120.9, 45.9, 25.0, 23.4; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{13}H_{21}N_5$ 246.1719, found 246.1723.



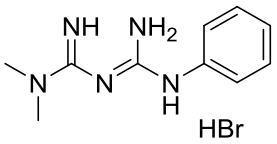
3t

2-[imino(morpholino)methyl]-1-phenylguanidine hydroiodide (3t)

Yellow solid; mp: 186-187℃; IR (KBr, cm^{-1}): 3406.89, 3303.83, 3196.52, 1632.72, 1537.59, 1487.44, 1444.11, 1383.91, 1121.80, 1006.53, 759.57; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.13 (s, 1H), 7.71 (s, 2H), 7.33-7.29 (m, 4H), 7.07 (s, 1H), 6.84 (s, 2H), 3.63 (t, J = 4.7 Hz s, 4H), 3.44 (t, J = 4.7 Hz s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.8, 154.6, 138.2, 128.7, 123.6, 121.2, 65.3, 45.0; HRMS (ESI) m/z $[M-I]^+$ calcd for $C_{12}H_{18}N_5O$ 248.1511, found 248.1509.

General Procedure for Synthesis of biguanide hydrobromides:

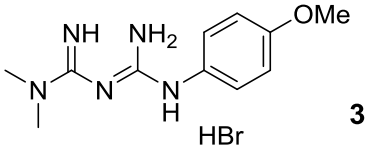
To a mixture of biguanide hydrochloride (1.0 mmol), aryl bromide (1.0 mmol), 2-(pyridin-2-yl)pyridine (0.2 mmol), and K_2CO_3 (6.0 mmol) in dioxane (5 mmol), was added CuI (10 mol %). The resulting mixture was than sealed and stirred for 12 h at 110 ℃. After completion, the reaction mixture was filtered and the precipitates were washed with methanol. The mixture was evaporated under vacuum, and the residue was purified by flash chromatography with CH_2Cl_2 and CH_3OH (3:1) as the eluent to give the pure product.



3o

***N*-phenyl-dimethylbiguanide hydrobromide (3o)**

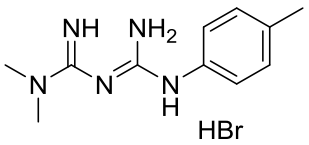
White solid; mp: 239-240℃;IR (KBr, cm^{-1}): 3422.24, 1637.21, 1587.56, 1551.56, 1488.87, 1383.99, 1261.09, 1047.83, 757.24. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.46 (s, 1H), 7.62 (s, 2H), 6.98 - 7.44 (m, 5H), 6.81 (s, 2H), 2.97 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 153.4, 138.9, 128.6, 122.9, 120.4, 37.7; HRMS (ESI) m/z [M-Br]$^+$ calcd for $C_{10}H_{16}N_5$ 206.1406, found 206.1403.



3p

***N*-(4-methoxyphenyl)-dimethylbiguanide hydrobromide (3p)**

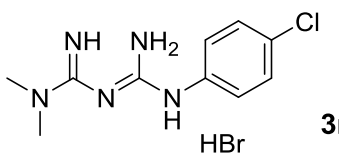
White solid; mp: 205-206℃;IR (KBr, cm^{-1}): 3410.23, 3340.57, 3176.18, 1633.76, 1592.42, 1556.73, 1513.30, 1240.26, 1033.23, 831.01; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.53 (s, 1H), 7.52 (s, 2H), 7.27 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.83 (s, 1H), 6.74 (s, 1H), 3.71 (s, 3H), 2.95 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.0, 155.5, 154.3, 131.7, 122.7, 113.8, 55.2, 37.6; HRMS (ESI) m/z [M-Br]$^+$ calcd for $C_{11}H_{18}N_5O$ 236.1511, found 236.1515. Anal. Calcd for $C_{11}H_{18}BrN_5O$: C, 41.78; H, 5.74; N, 22.15 Found: C, 41.77; H, 5.78; N, 22.11.



3q

***N*-(4-methylphenyl)-dimethylbiguanide hydrobromide (3q)**

White solid; mp: 240-241℃;IR(KBr, cm^{-1}): 3422.23, 1633.96, 1540.93, 1486.07, 1414.87, 1383.81, 1121.80, 1049.57, 813.90; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.56 (s, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.76 (s, 2H), 2.96 (s,6H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.1, 153.7, 136.2, 132.1, 129.0, 120.8, 37.6, 20.4; HRMS (ESI) m/z [M-Br] + calcd for $C_{11}H_{18}N_5$ 220.1562, found 220.1559.

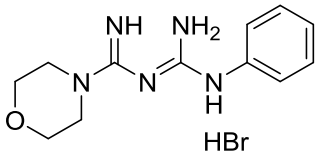


3r

***N*-(4-chlorophenyl)-dimethylbiguanide hydrobromide (3r)**

Yellow solid; mp: 244-245℃; IR (KBr, cm^{-1}): 3406.78, 1633.08, 1544.34, 1484.95, 1383.80, 1091.24, 809.72; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.79 (s, 1H), 7.68 (s, 2H), 7.42

(d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.9 Hz, 2H), 6.87 (s, 2H), 2.97 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.3, 153.1, 138.1, 128.5, 126.4, 121.6, 37.7; HRMS (ESI) m/z $[M-Br]^+$ calcd for $C_{10}H_{15}ClN_5$ 240.1016, found 240.1020.

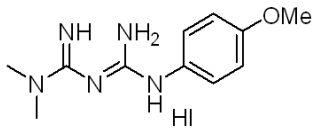


3u

2-(imino(morpholino)methyl)-1-phenylguanidine hydrobromide (3u)

Yellow solid; mp: 227-228℃; IR (KBr, cm^{-1}): 3423.71, 1631.82, 1536.34, 1489.41,1445.79, 1115.21, 1006.08, 758.31; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.41 (s, 1H), 7.75 (s, 2H), 7.29-7.36 (m, 4H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.93 (s, 2H), 3.60-3.68 (m, 4H), 3.42-3.50 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.9, 154.6, 138.5, 128.7, 123.4, 120.9, 65.3, 45.1; IR (KBr, cm^{-1}): 3423.71, 1631.82, 1536.34, 1489.41, 1445.79, 1115.21, 1006.08, 758.31. HRMS (ESI) m/z $[M-Br]^+$ calcd for $C_{12}H_{18}N_5O$ 248.1511, found 248.1516.

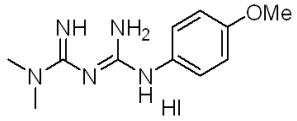
130105
BAQ121212 DMSO



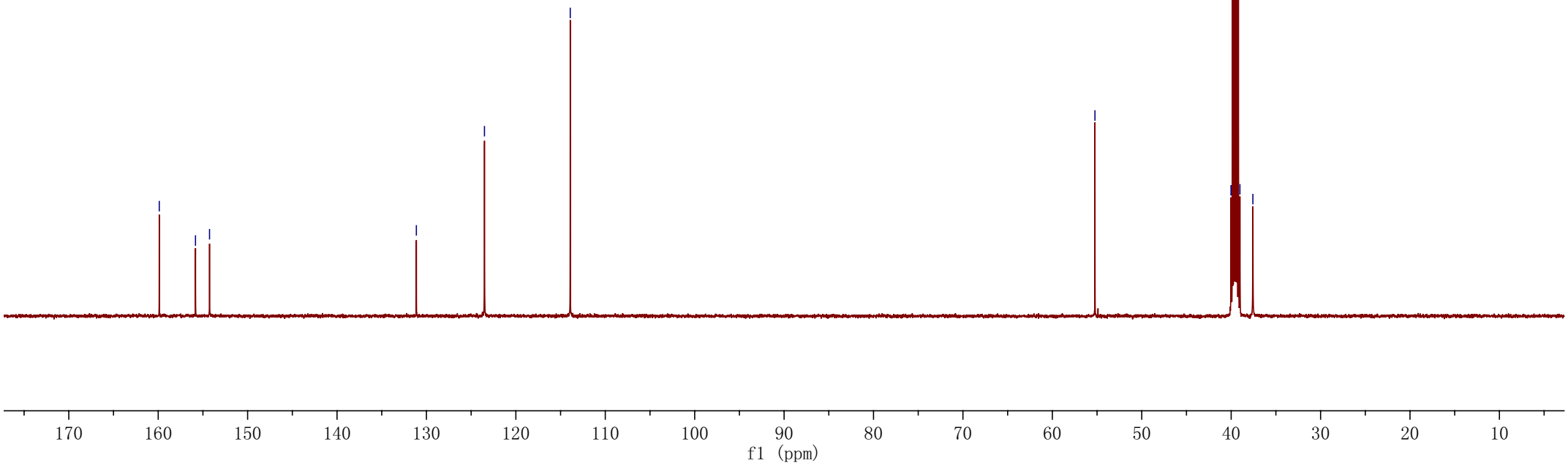
3a

130514
BAQ140423 DMSO

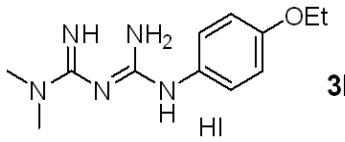
159.8823
155.8306
154.2599
131.1284
123.5116
113.9177
55.2351
40.0225
39.8557
39.6886
39.5216
39.3547
39.1876
39.0208
37.5713



3a



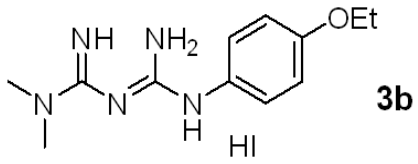
130725
BAQ130715 DMSO



3b

130827
BAQ130715 DMSO

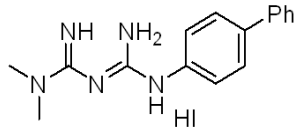
159.9482
155.1577
154.3150
131.0638
123.5734
114.5023
63.2024
40.0714
39.9046
39.7377
39.5708
39.4039
39.2367
39.0703
37.6136
14.6758



3b

BAQ131214

BAQ131214 DMSO



3c

9.0856

7.6458
7.6298
7.6124
7.4687
7.4512
7.4326
7.3467
7.3321
7.3176

6.6910

3.3573

2.9845

2.5082

1.06

6.18

4.12

1.05

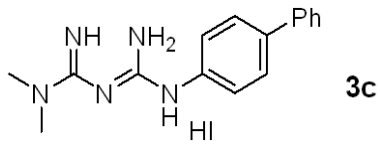
1.93

6.00

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

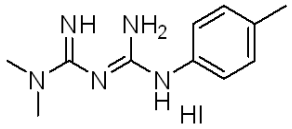
f1 (ppm)

131230
BAQ131214 DMSO



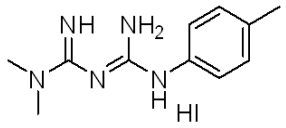
3c

130826
BAQ130823 DMSO



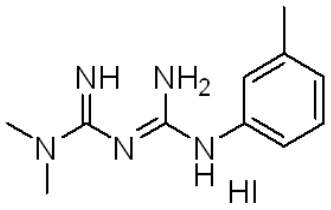
3d

140312
BAQ130823 DMSO



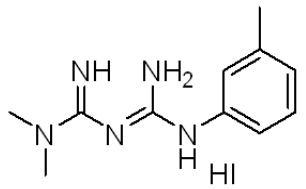
3d

140318
BAQ140317 DMSO



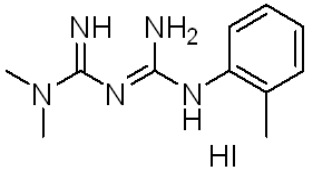
3e

140318
BAQ140317 DMSO



3e

140325
BAQ140318a DMSO



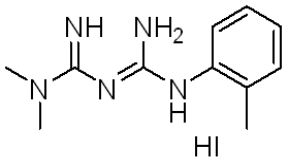
3f

8.3821
7.4031
7.3849
7.3696
7.2355
7.2208
7.1883
7.1751
7.1598
7.1104
7.1084
7.0956
7.0937
7.0898
6.7373
3.3417
2.9129
2.5151
2.5117
2.5081
2.5046
2.5012
2.2479

1.00
2.23
4.10
1.94
6.02
2.92

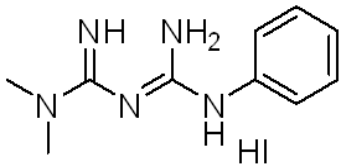
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

140326
BAQ140318a DMSO



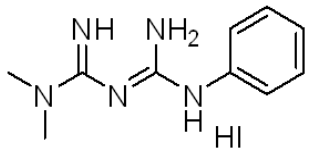
3f

130917
baq130913 DMSO



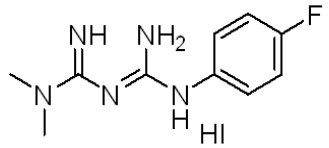
3g

140312
BAQ130913 DMSO



3g

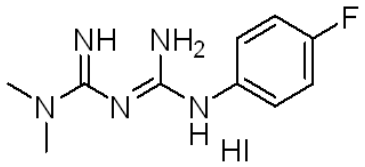
130830
gaq130825 DMSO



3h

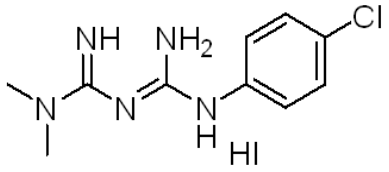
130902
BAQ130825 DMSO

160.2090
159.3029
157.3929
153.6315
134.9495
123.1593
123.0958
115.3765
115.1987
40.0695
39.9022
39.7353
39.5683
39.4013
39.2344
39.0673
37.7166



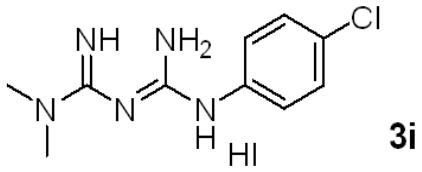
3h

130827
BAQ130824 DMSO



3i

130828
BAQ130824 DMSO



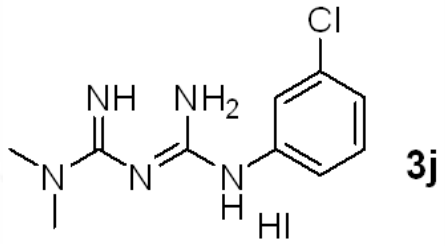
3i

160.2164
153.0061
137.7126
128.4516
126.8196
122.2126
40.0218
39.8550
39.6882
39.5211
39.3542
39.1873
39.0204
37.6344

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

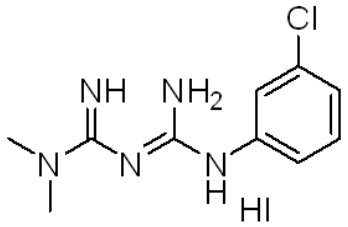
f1 (ppm)

BAQ131221a DMSO 13A11494



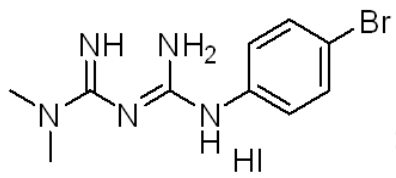
3j

131230
BAQ131221a DMSO



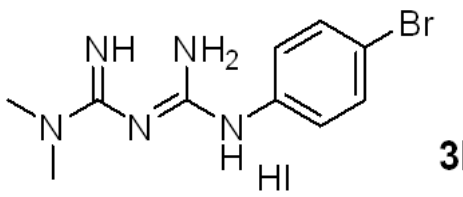
3j

140505
BAQ140409b DMSO



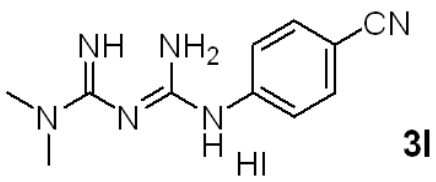
3k

14140506
BAQ140409b DMSO



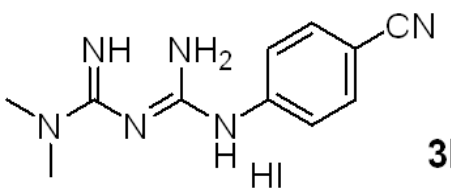
3k

131218
BAQ131215 DMSO



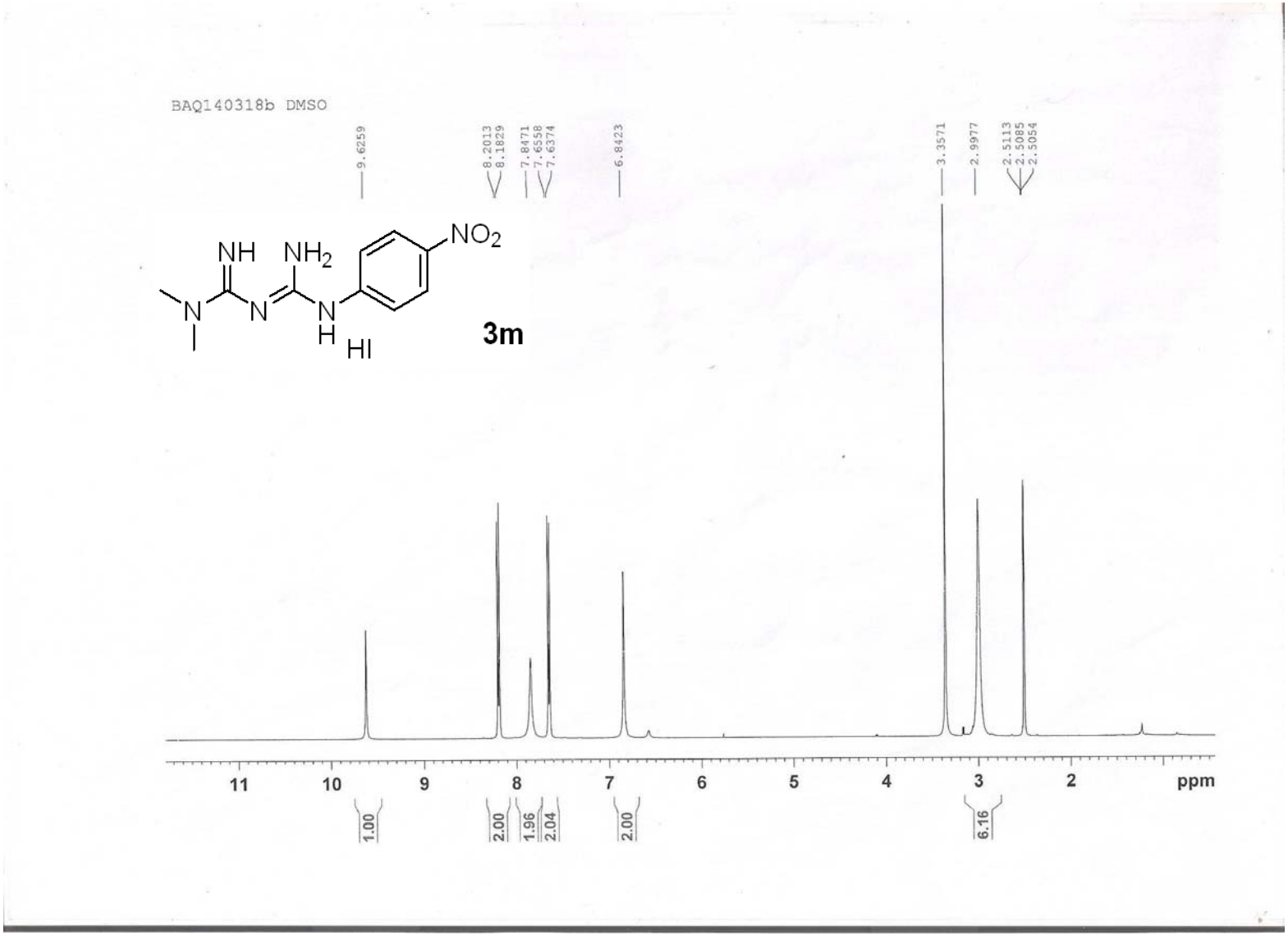
3l

131220
BAQ131215 DMSO

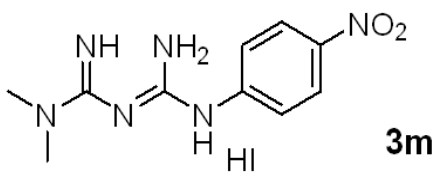


3l

160.4135
152.0530
143.5304
133.0203
119.6936
119.0848
104.0728
40.0096
39.8431
39.6761
39.5090
39.3421
39.1751
39.0078
37.8084

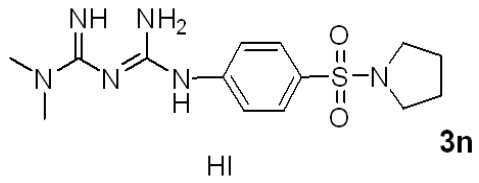

BAQ140318b DMSO
9.6259
8.2013
8.1829
7.8471
7.6558
7.6374
6.8423
3.3571
2.9977
2.5113
2.5085
2.5054
NH
NH2
NO2
N
N
N
H
HI
3m
11
10
9
8
7
6
5
4
3
2
ppm
1.00
2.00
1.96
2.04
2.00
6.16

140324
BAQ0318b DMSO



3m

140110
BAQ131224b DMSO

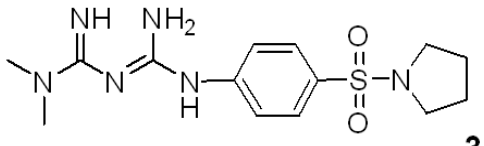


HI

3n

140312
BAQ131224b DMSO

160.4163
152.2887
143.2851
129.4109
128.3856
119.3997
47.7396
40.0253
39.8581
39.7816
39.6909
39.5241
39.3572
39.1901
39.0231
37.7005
24.6592

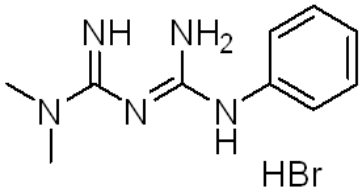


HI

3n

f1 (ppm)

140312
BAQ130301 DMSO

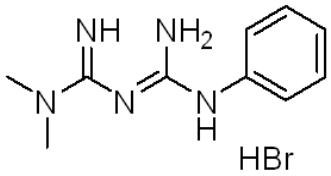


3o

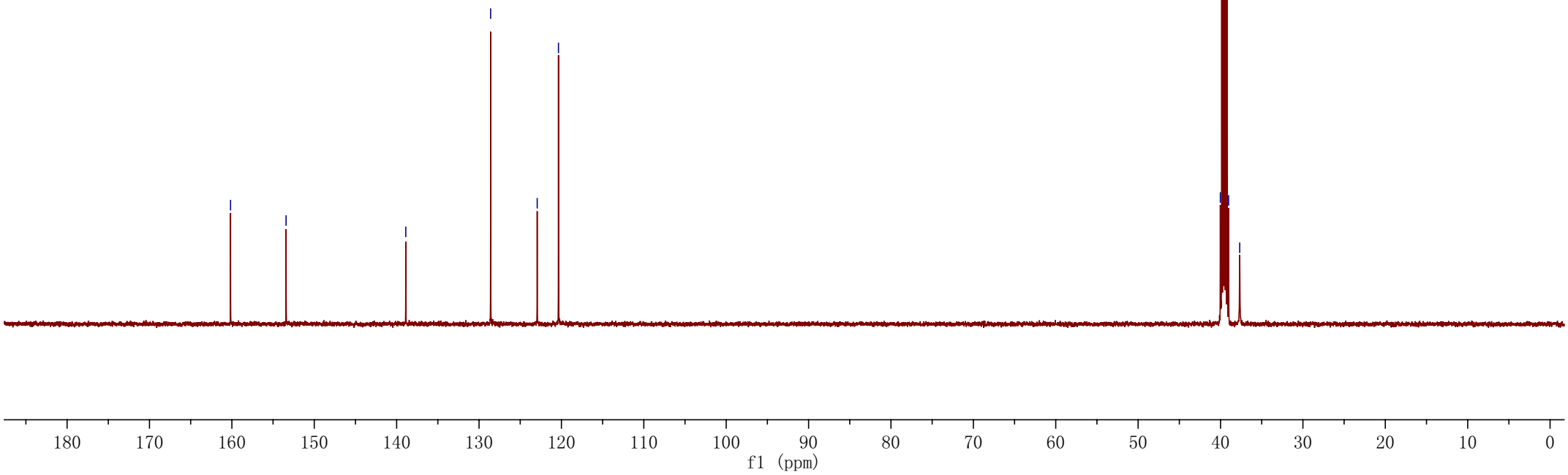
140314
BAQ130301 DMSO

160.1579
153.4196
138.8909
128.5909
122.9386
120.3570

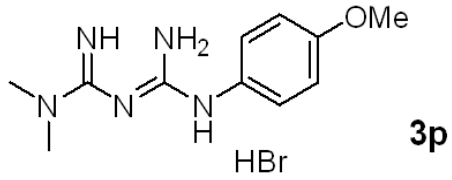
40.0230
39.8562
39.6893
39.5222
39.3553
39.1884
39.0211
37.6714



3o



140312
BAQ140228 DMSO



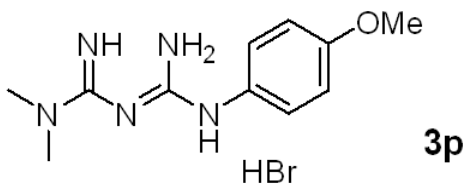
3p

9.5307
7.5187
7.2810
7.2633
6.8764
6.8587
6.8253
6.7396
3.7121
3.3971
2.9468
2.9301
2.5083

0.95
1.93
2.19
2.18
2.04
3.00
6.02

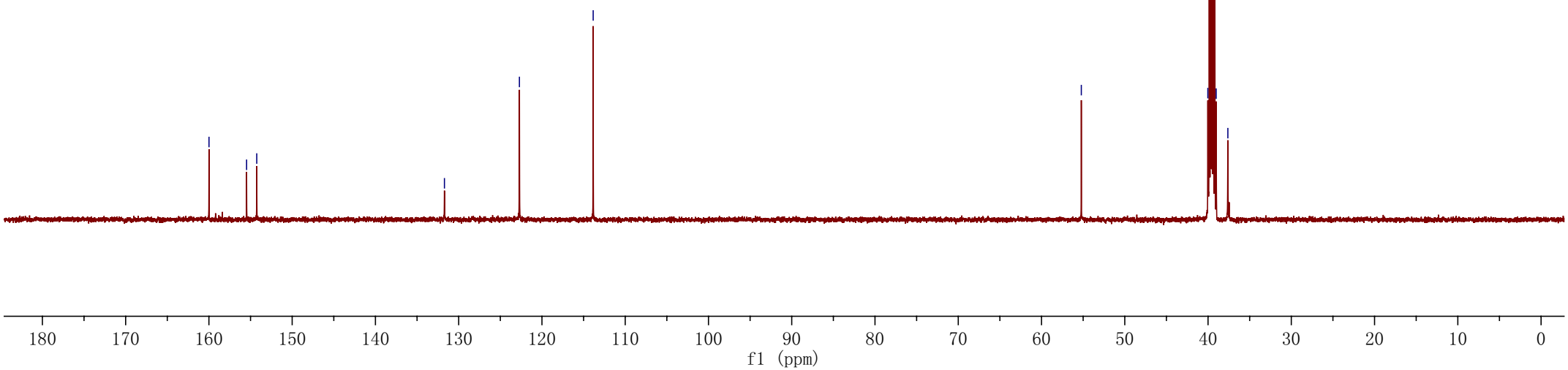
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

140314
BAQ140228 DMSO

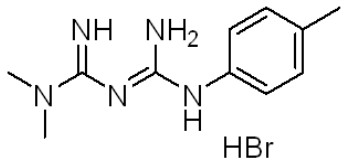


3p

159.9894
155.4749
154.2541
131.7118
122.7068
113.8473
55.2196
40.0230
39.8565
39.6896
39.5225
39.3556
39.1886
39.0216
37.6189

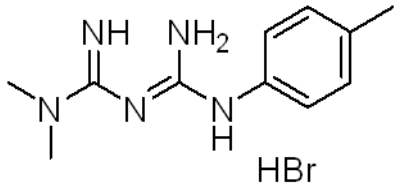


140325
BAQ140323a DMSO



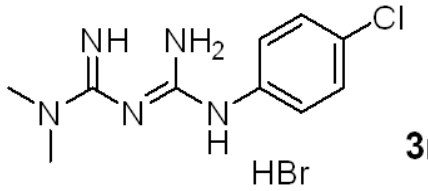
3q

140326
BAQ140323a DMSO



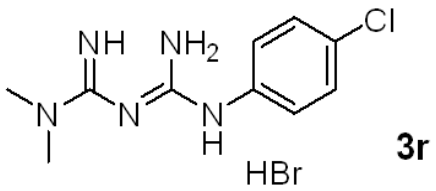
3q

140324
BAQ140319a DMSO



3r

140328
BAQ140319a DMSO



3r

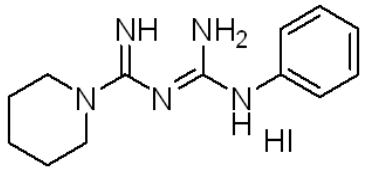
160.2911
153.1508
138.1095
128.4551
126.4335
121.6364

40.0214
39.8542
39.7781
39.6872
39.5203
39.3533
39.1863
39.0193
37.6907

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

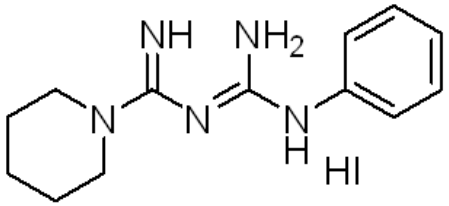
f1 (ppm)

140324
BAQ140320 DMSO



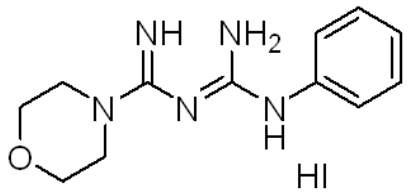
3s

140328
BAQ140320 DMSO



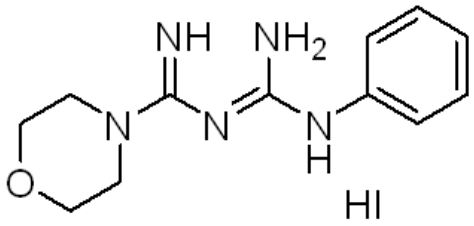
3s

140505
BAQ140421 DMSO



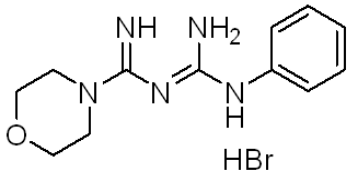
3t

14140506
BAQ140421 DMSO



3t

140409
BAQ140405a DMSO



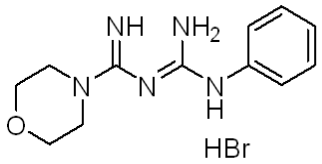
3u

9.4072
7.7471
7.3608
7.3585
7.3437
7.3224
7.3078
7.2910
7.0756
7.0613
7.0469
6.9311
3.6491
3.6402
3.6302
3.4706
3.4609
3.4517
3.3454
2.5117
2.5082
2.5046

1.00
1.93
5.03
1.88
4.01
3.94

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

140409
BAQ140405a DMSO



3u

158.86
154.62
138.47
128.68
123.42
120.94
65.31
45.06
40.02
39.86
39.69
39.52
39.36
39.19
39.02

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

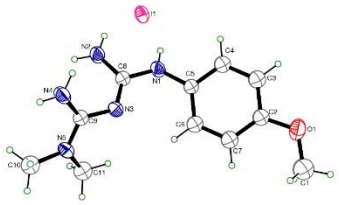


Figure S1. Crystal structure of **3a** (50% ellipsoids). Selected bond lengths (Å): C1-O1 1.414 (5); C2-O1 1.372 (4); C2-C3 1.379 (5); C2-C7 1.384 (5); C3-C4 1.377 (5); C4-C5 1.392 (4); C5-C6 1.382 (4); C5-N1 1.418 (4); C6-C7 1.386 (5); C8-N3 1.299 (4); C8-N1 1.353 (4); C8-N2 1.354 (4); C9-N5 1.320 (4); C9-N4 1.328 (4); C9-N3 1.353 (4); C10-N5 1.456 (4); C11-N5 1.461 (4).

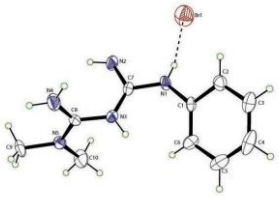


Figure S2. Crystal structure of **3o** (50% ellipsoids). Selected bond lengths (Å): C1–C6 1.355 (13); C1–C 2 1.413 (13); C1–N1 1.412 (11); C2–C3 1.385 (15); C3–C4 1.365 (19); C4–C5 1.354 (19); C5–C 6 1.401 (15); C7–N3 1.271 (12); C7–N2 1.376 (12); C7–N1 1.375 (11); C8–N4 1.318 (13); C8–N5 1.323(11); C8–N3 1.348 (12), C9–N5 1.461 (11); C10–N5 1.480 (12)