A novel and simple route to construct methylthio-substituted pyridazine from aryl methyl ketones under room temperature

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Supporting informations

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Section A: General information

All aryl methyl ketones, hydrazine hydrate (2) and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm\(^{-1}\). \(^1\)H NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of 3a and 4a were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

Section B: Experimental procedures

1. Synthesis of 2-(Methylthio)-1,4-diaryl-2-butene-1,4-diones (1a-1p)

2. Synthesis of methylthio-substituted pyridazine (3a):
A mixture of 2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione 1a (283 mg, 1 mmol), potassium hydroxide (56 mg, 1 mmol), and hydrazine hydrate 2 (89 mg, 1.5 mmol) in anhyd isopropanol (5 ml) was stirred at room temperature for about 1h and monitored to completion by TLC analysis. After that, H\(_2\)O (50 ml) was added and the aqueous mixture was extracted with EtOAc 3 times (3 × 50 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as the eluent to give the expected product 3a in 93% yield.

3. Synthesis of 4-(methylsulfinyl)-3,6-diphenylpyridazine (4a):
A mixture of 4-(methylthio)-3,6-diphenylpyridazine 3a (278 mg, 1 mmol) and m-CPBA (173 mg, 1.1 mmol) in CH\(_2\)Cl\(_2\) (5 ml) was stirred at 0 °C for about 1h and monitored to completion by TLC analysis. After that, the reaction mixture was allowed to warm to room temperature over 0.5 - 1 h. Then, H\(_2\)O (50ml) was added and the aqueous mixture was extracted with CH\(_2\)Cl\(_2\) 3 times (3 × 50 mL). The combined organic extracts were washed with saturated aqueous NaHCO\(_3\) (20 ml) and brine (20 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as the eluent to give the expected product 4a in 75% yield.

Section C: Characterization data
(Z)-1,4-bis(3-methoxyphenyl)-2-(methylthio)but-2-ene-1,4-dione (1f)
yellow solid; mp 116.6-118.8 °C; 1H NMR (CDCl₃, 600MHz): δ (ppm) 7.62 (d, J=7.8 Hz, 1H), 7.58 (s, 1H), 7.51 (s, 1H), 7.48 (d, J=7.8 Hz, 1H), 7.42 (t, J=8.1 Hz, 1H), 7.34 (t, J=8.1 Hz, 1H), 7.22-7.20 (m, 1H), 7.09-7.06 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.17 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 191.5, 187.6, 160.6, 159.9, 159.7, 139.0, 135.9, 130.0, 129.4, 123.0, 119.1, 115.8, 113.0, 112.1, 55.4, 55.2, 15.3; IR (KBr, cm⁻¹) : 3450, 1659, 1591, 1536, 1465, 1427, 1333, 1270, 1218, 1088, 1035, 877, 796, 746, 676, 517; HRMS (APCI): m/z [M+H]⁺ calcd for C₁₉H₁₉O₄S: 343.0999; found: 343.0999.

(OH₂)O

(E)-1,4-bis(3-methoxyphenyl)-2-(methylthio)but-2-ene-1,4-dione (1f)
yellow solid; mp 120.5-122.3 °C; 1H NMR (CDCl₃, 600MHz): δ (ppm) 7.59 (s, 1H), 7.52 (q, J=7.8 Hz, 2H), 7.41 (s, 1H), 7.35 (t, J=7.8 Hz, 2H), 7.12-7.08 (m, 2H), 7.01 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.45 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 193.5, 184.7, 161.0, 159.8, 159.7, 138.4, 135.9, 129.7, 129.4, 121.6, 120.9, 120.3, 119.7, 115.6, 112.4, 112.1, 55.3, 14.9; IR (KBr, cm⁻¹) : 3447, 2838, 1664, 1633, 1576, 1534, 1483, 1451, 1355, 1286, 1255, 1202, 1166, 1041, 958, 909, 873, 822, 790, 733, 683, 651, 569, 531; HRMS (APCI): m/z [M+H]⁺ calcd for C₁₉H₁₉O₄S: 343.0999; found: 343.0999.

(F)-1,4-bis(4-fluorophenyl)-2-(methylthio)but-2-ene-1,4-dione (1g)
yellow solid; mp 107.2-108.7 °C; 1H NMR (CDCl₃, 400MHz): δ (ppm) 8.12-8.08 (m, 2H), 7.98-7.95 (m, 2H), 7.21 (t, J=8.6 Hz, 2H), 7.13 (t, J=8.6 Hz, 2H), 7.03 (s, 1H), 2.16 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 189.9, 186.3, 167.8, 166.5, 165.2, 164.0, 160.3, 133.9, 132.6, 132.5, 131.1, 130.5, 130.4, 116.4, 116.1, 115.6, 115.4, 15.2; IR (KBr, cm⁻¹) : 3451, 1667, 1630, 1596, 1539, 1502, 1427, 1341, 1300, 1261, 1236, 1153, 1084, 1046, 904, 855, 829, 755, 612, 548, 503; HRMS (APCI): m/z [M+H]⁺ calcd for C₁₇H₁₃F₂O₂S: 319.0599; found: 319.0599.
(E)-1,4-bis(4-fluorophenyl)-2-(methylthio)but-2-ene-1,4-dione (1g)
yellow solid; mp 89.3-92.2 °C; 1H NMR (CDCl₃, 400MHz): δ (ppm) 8.03-8.00 (m, 2H), 7.95-7.92 (m, 2H), 7.13 (q, J=8.8 Hz, 4H), 6.98 (s, 1H), 2.46 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 192.1, 183.5, 167.2, 166.9, 164.7, 164.3, 160.9, 133.3, 131.3, 131.2, 131.1, 131.0, 116.1, 115.9, 115.8, 115.6, 115.2, 14.9; IR (KBr, cm⁻¹): 3442, 1678, 1639, 1597, 1542, 1505, 1413, 1354, 1225, 1156, 1050, 927, 845, 746, 650, 599, 553, 502; HRMS (APCI): m/z [M+H]+ calcd for C₁₇H₁₃F₂O₂S: 319.0599; found: 319.0599.

4-(methylthio)-3,6-diphenylpyridazine (3a).
Yield 93%; white solid; mp 117.6-119.2 °C; 1H NMR (CDCl₃, 400MHz): δ (ppm) 8.12 (d, J=7.2 Hz, 2H), 7.78-7.76 (m, 2H), 7.56-7.51 (m, 7H), 2.51 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 157.5, 156.8, 142.9, 136.3, 136.0, 130.0, 129.5, 129.1, 129.0, 128.3, 127.2, 117.9, 14.2; IR (KBr, cm⁻¹): 3447, 3052, 2994, 2919, 1550, 1484, 1441, 1394, 1107, 1022, 882, 847, 764, 694, 642, 562, 501; HRMS (APCI): m/z [M+H]+ calcd for C₁₇H₁₅N₂S: 279.0950; found: 279.0951.

4-(methylthio)-3,6-di-p-tolylpyridazine (3b).
Yield 93%; white solid; mp 140.5-142.3 °C; 1H NMR (CDCl₃, 600MHz): δ (ppm) 8.00 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.8 Hz, 2H), 7.50 (s, 1H), 7.32 (t, J=9.0 Hz, 4H), 2.47 (s, 3H), 2.43 (s, 6H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 157.0, 156.4, 142.5, 139.9, 139.3, 133.3, 131.1, 129.5, 128.9, 126.8, 117.3, 21.3, 21.2, 14.0; IR (KBr, cm⁻¹): 3442, 3031, 2918, 2858, 1611, 1553, 1514, 1483, 1438, 1399, 1182, 1105, 1049, 1015, 883, 852, 820, 780, 718, 631, 559, 499, 439; HRMS (APCI): m/z [M+H]+ calcd for C₁₉H₁₉N₂S: 307.1263; found: 307.1265.

3,6-bis(4-methoxyphenyl)-4-(methylthio)pyridazine (3c).
Yield 95%; white solid; mp 171.1-173.2 °C; 1H NMR (CDCl₃, 600MHz): δ (ppm) 8.07 (d, J=7.8 Hz, 2H), 7.73 (d, J=7.8 Hz, 2H), 7.47 (s, 1H), 7.04 (m, 4H), 3.88 (s, 6H), 2.49 (s, 3H); 13C NMR (CDCl₃, 100MHz): δ (ppm) 161.1, 160.4, 156.5, 155.9, 142.3, 130.5, 128.7, 128.5, 128.3, 117.0, 114.2, 113.6, 55.3, 55.2, 14.1; IR (KBr,
\( \text{cm}^{-1} \): 3452, 2928, 1637, 1603, 1553, 1512, 1414, 1385, 1292, 1249, 1174, 1104, 1024, 832, 772, 629, 561, 500; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O\(_2\)S: 339.1162; found: 339.1163.

3,6-bis(4-ethoxyphenyl)-4-(methylthio)pyridazine (3d).

Yield 94\%; light yellow solid; mp 176.2-177.4 °C; \(^1\)H NMR (CDCl\(_3\), 600MHz): \( \delta \) (ppm) 8.05 (d, \( J=9.0 \text{ Hz}, 2\)H), 7.71 (d, \( J=8.4 \text{ Hz}, 2\)H), 7.46 (s, 1H), 7.04-7.00 (m, 4H), 4.12-4.10 (m, 4H), 2.48 (s, 3H), 1.47-1.44 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \( \delta \) (ppm) 160.4, 159.8, 156.5, 155.9, 142.3, 130.4, 128.3, 116.9, 114.7, 114.1, 63.5, 63.4, 14.7, 14.1; IR (KBr, cm\(^{-1}\) ) : 3448, 2978, 2931, 2876, 1603, 1553, 1514, 1478, 1417, 1387, 1290, 1249, 1175, 1108, 1040, 918, 844, 671, 564, 515; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_2\)S: 367.1475; found: 367.1475.

3,6-bis(benzo[d][1,3]dioxol-5-yl)-4-(methylthio)pyridazine (3e).

Yield 97\%; light yellow solid; mp 184.1-185.5 °C; \(^1\)H NMR (CDCl\(_3\), 600MHz): \( \delta \) (ppm) 7.67 (s, 1H), 7.56 (d, \( J=7.8 \text{ Hz}, 1\)H), 7.43 (s, 1H), 7.25 (s, 2H), 6.94 (t, \( J=7.5 \text{ Hz}, 2\)H), 6.05 (d, \( J=6.0 \text{ Hz}, 4\)H), 2.49 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \( \delta \) (ppm) 156.5, 155.9, 149.2, 148.5, 148.3, 147.6, 142.5, 130.3, 129.8, 123.3, 121.2, 117.2, 109.5, 108.5, 107.3, 101.5, 101.3, 14.2; IR (KBr, cm\(^{-1}\) ) : 3448, 2978, 2931, 2876, 1603, 1553, 1514, 1478, 1417, 1387, 1290, 1249, 1175, 1108, 1040, 918, 844, 671, 564, 515; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{19}\)H\(_{15}\)N\(_2\)O\(_4\)S: 367.0747; found: 367.0748.

3,6-bis(3-methoxyphenyl)-4-(methylthio)pyridazine (3f).

Yield 91\%; white solid; mp 115.3-116.2 °C; \(^1\)H NMR (CDCl\(_3\), 600MHz): \( \delta \) (ppm) 7.78 (s, 1H), 7.60 (d, \( J=7.8 \text{Hz}, 1\)H), 7.54 (s, 1H), 7.46-7.41 (m, 2H), 7.35 (d, \( J=7.8 \text{Hz}, 1\)H), 7.32 (s, 1H), 7.07-7.04 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 2.50 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \( \delta \) (ppm) 160.0, 159.5, 157.3, 156.5, 142.9, 137.6, 137.2, 129.9, 129.3, 121.4, 119.3, 117.9, 116.0, 115.7, 114.1, 112.2, 55.4, 55.3, 14.1; IR (KBr, cm\(^{-1}\) ) : 3445, 3071, 3006, 2936, 2836, 1582, 1554, 1457, 1429, 1391, 1285, 1251, 1216, 1178, 1150, 1088, 1045, 1026, 895, 852, 794, 699, 562; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O\(_2\)S: 339.1162; found: 339.1162.
3,6-bis(4-fluorophenyl)-4-(methylthio)pyridazine (3g).
Yield 88%; white solid; mp 166.2-167.5 °C; $^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 8.12-8.09 (m, 2H), 7.78-7.74 (m, 2H), 7.50 (s, 1H), 7.22 (t, $J$=8.8 Hz, 4H), 2.52 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 165.3, 164.7, 162.8, 162.2, 156.4, 155.9, 142.9, 132.3, 132.0, 131.1, 131.0, 129.1, 129.0, 117.5, 116.1, 115.9, 115.5, 115.3, 14.1; IR (KBr, cm$^{-1}$): 3449, 3066, 2922, 1601, 1554, 1515, 1489, 1405, 1230, 1159, 1098, 1051, 1008, 845, 645, 564, 499; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{13}$F$_2$N$_2$S: 315.0762; found: 315.0763.

3,6-bis(4-chlorophenyl)-4-(methylthio)pyridazine (3h).
Yield 89%; white solid; mp 187.2-189.6 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 8.06 (d, $J$=7.8 Hz, 2H), 7.72 (d, $J$=7.8 Hz, 2H), 7.52-7.48 (m, 5H), 2.52 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 156.5, 155.8, 143.0, 136.3, 135.7, 134.5, 134.2, 130.4, 129.2, 128.6, 128.3, 117.5, 14.1; IR (KBr, cm$^{-1}$): 3447, 2919, 1902, 1632, 1595, 1551, 1480, 1401, 1331, 1176, 1093, 1008, 956, 826, 717, 623, 556, 507; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{13}$Cl$_2$N$_2$S: 347.0171; found: 347.0172.

3,6-bis(4-bromophenyl)-4-(methylthio)pyridazine (3i).
Yield 91%; white solid; mp 193.2-195.8 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 7.98 (d, $J$=7.2 Hz, 2H), 7.68-7.65 (m, 6H), 7.51 (s, 1H), 2.52 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 156.5, 155.8, 143.0, 134.9, 134.7, 132.1, 131.6, 130.7, 128.6, 124.7, 124.1, 117.5, 14.1; IR (KBr, cm$^{-1}$): 3451, 2975, 2913, 1634, 1589, 1550, 1479, 1401, 1327, 1179, 1102, 1071, 1006, 822, 714, 642, 559, 505; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{13}$Br$_2$N$_2$S: 434.9161; found: 434.9162.

3,6-bis(3,4-dichlorophenyl)-4-(methylthio)pyridazine (3j).
Yield 83%; light yellow solid; mp 187.6-189.2 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 8.21 (s, 1H), 7.96 (d, $J$=8.4 Hz, 1H), 7.89 (s, 1H), 7.63-7.58 (m, 3H), 7.50 (s,
1H), 2.56 (s, 3H); $^{13}$C NMR (CDCl3, 100MHz): $\delta$ (ppm) 155.6, 154.9, 143.4, 135.8, 135.5, 134.6, 134.0, 133.4, 132.7, 131.1, 131.0, 130.4, 128.9, 128.4, 126.2, 117.5, 14.2; IR (KBr, cm$^{-1}$): 3445, 3074, 2924, 1630, 1556, 1467, 1400, 1137, 1104, 1029, 879, 821, 757, 579, 438; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{11}$Cl$_4$N$_2$S: 414.9392; found: 414.9392.

4-(methylthio)-3,6-di(naphthalen-1-yl)pyridazine (3k)
Yield 85%; white solid; mp 194.5-196.8 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 8.20 (s, 1H), 8.03-8.01 (m, 2H), 7.97-7.95 (m, 2H), 7.80 (d, $J$=7.2 Hz, 1H), 7.68-7.61 (m, 4H), 7.58-7.53 (m, 4H), 7.49 (t, $J$=7.5 Hz, 1H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 159.2, 157.3, 144.5, 135.2, 133.8, 133.6, 133.3, 131.1, 131.0, 129.8, 128.5, 128.4, 128.0, 127.6, 126.9, 126.5, 126.2, 125.2, 125.1, 121.6, 13.7; IR (KBr, cm$^{-1}$): 3449, 3046, 1634, 1593, 1548, 1506, 1416, 1372, 1244, 1207, 1088, 1016, 958, 868, 774, 628, 557; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{25}$H$_{19}$N$_2$S: 379.1263; found: 379.1264.

4-(methylthio)-3,6-di(naphthalen-2-yl)pyridazine (3l)
Yield 87%; yellow solid; mp 159.8-161.2 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 8.59 (s, 1H), 8.29-8.28 (m, 2H), 8.00-7.97 (m, 3H), 7.93-7.89 (m, 4H), 7.68 (s, 1H), 7.56-7.52 (m, 4H), 2.52 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 157.1, 156.4, 143.0, 133.9, 133.5, 133.4, 133.3, 133.1, 132.7, 128.9, 128.7, 128.5, 128.0, 127.6, 127.0, 126.9, 126.8, 126.5, 126.3, 124.2, 117.8, 14.1; IR (KBr, cm$^{-1}$): 3449, 3053, 1633, 1546, 1482, 1430, 1398, 1195, 1129, 1096, 949, 892, 860, 823, 751, 478; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{25}$H$_{19}$N$_2$S: 379.1263; found: 379.1264.

3,6-di(furan-2-yl)-4-(methylthio)pyridazine (3m)
Yield 90%; white solid; mp 143.4-145.6 °C; $^1$H NMR (CDCl$_3$, 600MHz): $\delta$ (ppm) 7.68 (s, 1H), 7.60 (s, 1H), 7.56 (s, 1H), 7.39 (s, 1H), 7.33 (s, 1H), 6.61 (s, 2H), 2.58 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) 150.5, 150.3, 148.4, 146.9, 144.1, 143.9, 140.5, 115.1, 112.8, 112.5, 111.8, 110.5, 14.0; IR (KBr, cm$^{-1}$): 3448, 1633, 1597, 1543, 1398, 1357, 1217, 1154, 1105, 1006, 877, 811, 751, 593; HRMS (APCI): m/z
\[ [\text{M+H}]^+ \text{ calcd for } C_{13}H_{11}N_2O_2S: 259.0536; \text{ found: } 259.0536. \]

![Image of compound structure]

3,6-di(benzofuran-2-yl)-4-(methylthio)pyridazine (3n)
Yield 73%; yellow solid; mp 196.2-198.8 °C; \(^1\)H NMR (CDCl\(_3\), 400MHz): \(\delta\) (ppm) 7.81 (s, 1H), 7.76 (s, 1H), 7.71 (s, 1H), 7.70 (s, 2H), 7.64 (d, \(J=8.4\) Hz, 1H), 7.57 (d, \(J=8.4\) Hz, 1H), 7.41-7.36 (m, 2H), 7.30 (t, \(J=7.4\) Hz, 2H), 2.67 (s,3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \(\delta\) (ppm) 155.5, 155.2, 152.0, 151.7, 149.1, 147.6, 142.1, 128.6, 128.0, 125.9, 125.8, 123.6, 123.4, 122.2, 121.9, 116.2, 111.8, 111.5, 109.5, 107.2, 14.3; IR (KBr, cm\(^{-1}\)) : 3445, 3099, 1592, 1533, 1448, 1394, 1333, 1260, 1148, 1101, 1050, 922, 874, 841, 810, 748, 684, 614; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{21}\)H\(_{15}\)N\(_2\)O\(_2\)S: 359.0849; found: 359.0849.

![Image of compound structure]

4-(methylthio)-3,6-di(thiophen-2-yl)pyridazine (3o)
Yield 63%; light yellow solid; mp 183.8-185.1 °C; \(^1\)H NMR (CDCl\(_3\), 600MHz): \(\delta\) (ppm) 7.91 (s, 1H), 7.67 (s, 1H), 7.49 (q, \(J=5.4\) Hz, 2H), 7.42 (s, 1H), 7.17-7.14 (m, 2H), 2.59 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \(\delta\) (ppm) 151.3, 150.9, 140.8, 140.4, 139.9, 129.1, 129.0, 128.0, 127.5, 125.9, 115.9, 14.3; IR (KBr, cm\(^{-1}\)) : 3450, 3064, 1634, 1551, 1481, 1430, 1383, 1333, 1252, 1150, 1094, 1052, 951, 849, 793, 720, 644; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{11}\)N\(_2\)S\(_3\): 291.0079; found: 291.0080.

![Image of compound structure]

4-(methylthio)-3,6-di(thiophen-3-yl)pyridazine (3p)
Yield 92%; white solid; mp 142.1-143.6 °C; \(^1\)H NMR (CDCl\(_3\), 400MHz): \(\delta\) (ppm) 8.06-8.05 (m, 1H), 7.99-7.98 (m, 1H), 7.79 (d, \(J=4.8\) Hz, 1H), 7.75-7.73 (m, 1H), 7.45-7.40 (m, 3H), 2.51 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): \(\delta\) (ppm) 152.3, 142.2, 138.5, 137.1, 128.5, 126.84, 126.81, 126.0, 125.3, 124.8, 117.3, 14.1; IR (KBr, cm\(^{-1}\)) : 3449, 3086, 2985, 2913, 1551, 1490, 1427, 1351, 1306, 1233, 1201, 1098, 1021, 965, 864, 826, 797, 760, 703, 673; HRMS (APCI): m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{11}\)N\(_2\)S\(_3\): 291.0079; found: 291.0079.
4-(methylsulfinyl)-3,6-diphenylpyridazine (4a)
Yield 80%; white solid; mp 151.8-153.6 °C; $^1$H NMR (CDCl$_3$, 400MHz): δ (ppm) 8.60 (s, 1H), 8.29-8.28 (m, 2H), 7.78-7.77 (m, 2H), 7.58-7.57 (m, 6H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): δ (ppm) 159.0, 155.1, 147.9, 135.1, 134.8, 130.8, 130.5, 129.4, 129.2, 128.8, 127.3, 119.0, 40.2; IR (KBr, cm$^{-1}$): 3449, 2990, 1632, 1565, 1486, 1445, 1390, 1337, 1178, 1091, 1074, 1057, 1043, 1024, 972, 945, 906, 793, 771, 707, 690, 639, 569, 476; HRMS (APCI): m/z [M+H]$^+$ calcd for C$_{17}$H$_{15}$N$_2$OS: 295.0900; found: 295.0901.

_Section D: H$^1$, C$^{13}$ spectrum and HRMS_
cdcl3 600M

(z)-1f
cdcl3 100M

(Z)-1f
$\text{cdcl3  100M}$

(E)-1f
400M cdcl3

(Z)-1g
100M cdcl3

(Z)-1g
400M cdcl3

(E)-1g
100M CDCl3

(F)-1g
cdcl3  400M

3a
cdcl3  100M

3a
cdcl3 600M

3b

[Chemical structure and spectrum diagram]
cdcl3 100M

3b
3c

CDCl₃ 100M
$\text{cdcl}_3$ 600M

$\text{H}_3\text{CS}$

3d
cdcl3  600M

3e
$^1$H NMR in CDCl$_3$, 100 MHz

3e
cdcl3  600M

3f
$\text{cdcl3 400M}$

3g
cdcl3 100M

3g
cdCl3 600M

H3CS

3h

f1 (ppm)
cdcl3 100M

3h
CDCl₃ 600M

3j

Chemical shifts:
- 8.206 ppm
- 7.951 ppm
- 7.894 ppm
- 7.633 ppm
- 7.621 ppm
- 7.608 ppm
- 7.584 ppm
- 7.564 ppm
- 7.532 ppm
- 7.523 ppm
- 7.502 ppm

Resonance peaks at:
- 2.557 ppm
- 1.606 ppm
- 0.000 ppm
cdcl3  600M

3k
cdcl3 100M

3k
cdCl₃ 600M

3I
cdcl3  100M

3I
\text{cdcl3} 600M

3m

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\end{figure}
cdcl3  400M

3n
$^{1}H_3CS$ 3n

cdcl3 100M
cdcl3 600M

3o

![Chemical Structure](image)

![NMR Spectrum](image)
cdcl3  100M

3o
cdcl3  400M

3p
400M cdcl3

4a
100M cdcl3

4a

N-N

S=O

H3C
## Analysis Info

**Analysis Name:** E:\zhouchq\20120421\20120421\WLM175A_APCI_POS_000002.d  
**Method:** Metal_Trypsin digestion  
**Sample Name:** WLM175A_APCI_POS  
**Comment**

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<tr>
<td>Ion Accumulation Time</td>
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### Mass Spectrum SmartFormula Report

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<th>rdb</th>
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(Z)-1f
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:zhouchq\20120421\20120421\WLM175B_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM175B_APCI_POS
Comment

Acquisition Parameter
Polarity: Positive
Averaged Scans: 2
Broadband Low Mass: 100.3 m/z
Broadband High Mass: 2000.0 m/z
Acquisition Mode: Single MS
Pulse Program: basic
Source Accumulation: 0.0 sec
Ion Accumulation Time: 0.0 sec
Flight Time to Acq. Cell: 0.0 sec

Source
No. of Cell Fills: 1
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Skimmer 1: 20.0 V
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
Skimmer 2: 20.0 V
MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm

APCI
No. of Laser Shots: 20
Laser Power: 51.0 %

Calibration Date: Wed Jan 4 05:51:21 2012
Data Acquisition Size: 131072
Apodization: Sine-Bell Multiplication

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb eConf N-Rule
343.0999 1 C 19 H 19 O 4 S 100.00 343.0999 -0.1 -0.2 18.4 10.5 even ok

(E)-1f
Mass Spectrum SmartFormula Report

Analysis Info
- Analysis Name: E:\zhouchq\20120421\20120421\WLM216A_APCI_POS_000002.d
- Method: Metal_Trypsin digestion
- Sample Name: WLM216A_APCI_POS
- Acquisition Date: 2012/4/21 13:53:00
- Operator: apex-Ultra

Acquisition Parameter
- Polarity: Positive
- Source: APCI
- No. of Laser Shots: 20
- Laser Power: 51.0 %
- MALDI Plate: 300.0 V
- Imaging Spot Diameter: 2000.0 μm
- Averaged Scans: 2
- End Plate: 1500.0 V
- Capillary Entrance: 2000.0 V
- No. of Cell Fills: 1

Instrument: apex-Ultra

Acquisition Mode: Single MS
- Drying Gas Temperature: 180.0 °C
- Drying Gas Flow Rate: 4.0 L/min
- Data Acquisition Size: 131072
- Source Accumulation: 0.0 sec
- Capillary Entrance: 20.0 V
- Calibration Date: Wed Jan 4 05:51:21 2012
- Source Accumulation: 0.0 sec
- Drying Gas Flow Rate: 4.0 L/min
- Apodization: Sine-Bell Multiplication
- Flight Time to Acq. Cell: 0.0 sec
- Nebulizer Gas Flow Rate: 1.0 L/min

Mass Spectrum SmartFormula Report

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![Molecule Image]

(Z)-1g
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:\zhouchq\20120421\20120421\WLM216B_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM216B_APCI_POS
Instrument: apex-Ultra

Acquisition Parameter
Polarity: Positive
Averaged Scans: 2
Broadband Low Mass: 100.3 m/z
Broadband High Mass: 2000.0 m/z
Acquisition Mode: Single MS
Pulse Program: basic
Source Accumulation: 0.0 sec
Ion Accumulation Time: 0.0 sec
Flight Time to Acq. Cell: 0.0 sec

Acquisition Mode: 20.0 V
Skimmer 1: Single MS
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
No. of Laser Shots: 20
Laser Power: 51.0 %
MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Skimmer 1: 20.0 V

Acquisition Date: 2012/4/21 13:53:57

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e¡¥ Conf N-Rule
319.0599 1 C 17 H 13 F 2 O 2 S 100.00 319.0599 -0.0 -0.1 15.6 10.5 even ok

(E)-1g

Bruker Compass DataAnalysis 4.0 printed: 2012/4/21 22:41:09 Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:\zhouchq\20120421\20120421\WLM139_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM139_APCI_POS
Comment:

Acquisition Date: 2012/4/21 13:59:40
Analysis Name: E:\zhouchq\20120421\20120421\WLM139_APCI_POS_000002.d
Operator:
Instrument: apex-Ultra

Acquisition Parameter
Polarity: Positive
Averaged Scans: 2
Broadband Low Mass: 100.3 m/z
Acquisition Mode: Single MS
Pulse Program: basic
Source Accumulation: 0.0 sec
Flight Time to Acq. Cell: 0.0 sec

Source: APCI
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Skimmer 1: 20.0 V
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
Apodization: Sine-Bell Multiplication

No. of Laser Shots: 20
Laser Power: 51.0 %
MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm

Source Accumulation: 0.0 sec
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min

Calibration Date: Wed Jan 4 05:51:21 2012
Data Acquisition Size: 131072

Meas. m/z: 279.0951
Score: 100.00
m/z: 279.0950
err [mDa]: -0.0
err [ppm]: -0.2
mSigma: 14.4
rdb: 11.5
eq: even
Conf: ok
N-Rule: ok

Formula: C 17 H 15 N 2 S
3a

Bruker Compass DataAnalysis 4.0
## Mass Spectrum SmartFormula Report

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### Mass Spectrum

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![Mass Spectrum Graph](image_url)
**Mass Spectrum SmartFormula Report**

**Analysis Info**
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- **Method**: Metal_Trypsin digestion
- **Sample Name**: WLM138_APCI_POS
- **Comment**

**Acquisition Parameter**
- **Polarity**: Positive
- **Averaged Scans**: 4
- **Broadband Low Mass**: 100.3 m/z
- **Broadband High Mass**: 2000.0 m/z
- **Acquisition Mode**: Single MS
- **Pulse Program**: basic
- **Source Accumulation**: 0.0 sec
- **Ion Accumulation Time**: 0.0 sec
- **Flight Time to Acq. Cell**: 0.0 sec

**Acquisition Date**: 2012/3/6 20:32:53
**Analysis Parameter**
- **No. of Cell Fills**: 1
- **Laser Power**: 51.0 %
- **MALDI Plate**: 300.0 V
- **Imaging Spot Diameter**: 2000.0 μm
- **Drying Gas Temperature**: 180.0 °C
- **Data Acquisition Size**: 131072
- **Nebulizer Gas Flow Rate**: 1.0 L/min
- **Apoization**: Sine-Bell Multiplication

**Measurement**
- **m/z**: 339.1163
- **Score**: 100.00
- **err [mDa]**: -0.1
- **err [ppm]**: -0.3
- **mSigma**: 17.4
- **rdb**: 11.5
- **e\+Conf**: even
- **N-Rule**: ok

**Chemical Structure**
- **Formula**: C 19 H 19 N 2 O 2 S
- **Score**: 100.00

**Image of Mass Spectrum**

Bruker Compass DataAnalysis 4.0  
printed: 2012/3/6 20:55:15  
Page 1 of 1
### Analysis Info

- **Acquisition Date**: 2012/4/21 14:04:38
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- **Method**: Metal_Trypsin digestion
- **Sample Name**: WLM174_APCI_POS
- **Operator**: apex-Ultra

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<tr>
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<tr>
<td>Drying Gas Flow Rate</td>
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</tr>
<tr>
<td>Laser Power</td>
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</tr>
<tr>
<td>MALDI Plate</td>
<td>300.0 V</td>
</tr>
<tr>
<td>Imaging Spot Diameter</td>
<td>2000.0 µm</td>
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### Mass Spectrum

- **Meas. m/z**: 367.1475
- **Formula**: C21H23N2O2S
- **Score**: 100.00
- **m/z**: 367.1475
- **err [mDa]**: -0.0
- **err [ppm]**: -0.1
- **mSigma**: 16.5
- **rdb**: 11.5
- **eConf**: even
- **N-Rule**: ok

![Mass Spectrum Image](image-url)
Mass Spectrum SmartFormula Report

Analysis Info
Acquisition Date 2012/4/21 13:54:52
Analysis Name E:\zhouchq\20120421\20120421\WLM171_APCI_POS_000002.d
Method Metal_Trypsin digestion
Sample Name WLM171_APCI_POS
Comment

Acquisition Parameter
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<tr>
<td>Broadband High Mass</td>
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<tr>
<td>Acquisition Mode</td>
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<tr>
<td>No. of Cell Fills</td>
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<td>No. of Laser Shots</td>
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<td>MALDI Plate</td>
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<tr>
<td>Capillary Entrance</td>
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<tr>
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<tr>
<td>Drying Gas Temperature</td>
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</tr>
<tr>
<td>Source Accumulation</td>
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<td>Drying Gas Flow Rate</td>
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<tr>
<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
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<tr>
<td>Ion Accumulation Time</td>
<td>0.0 sec</td>
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<tr>
<td>Nebulizer Gas Flow Rate</td>
<td>1.0 L/min</td>
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<tr>
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</tbody>
</table>

Mass Spectrum

Meas. m/z  | Score | m/z  | err [mDa] | err [ppm] | mSigma | rdbr | eConf | N-Rule |
-----------|-------|------|-----------|-----------|--------|------|-------|--------|
367.0748   | 100.00| 367.0747| -0.1 | -0.2 | 15.4 | 13.5 | even | ok     |

Bruker Compass DataAnalysis 4.0  printed: 2012/4/21 22:24:53  Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:\zhouchq\20120421\20120421\WLM182_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM182_APCI_POS

Acquisition Parameter
- Polarity: Positive
- Averaged Scans: 2
- Broadband Low Mass: 100.3 m/z
- Broadband High Mass: 2000.0 m/z
- Acquisition Mode: Single MS
- Pulse Program: basic
- Source Accumulation: 0.0 sec
- Ion Accumulation Time: 0.0 sec
- Flight Time to Acq. Cell: 0.0 sec
- Source: APCI
- End Plate: 150.0 V
- Capillary Entrance: 2000.0 V
- Skimmer 1: 20.0 V
- Drying Gas Temperature: 180.0 °C
- Drying Gas Flow Rate: 4.0 L/min
- Nebulizer Gas Flow Rate: 1.0 L/min
- No. of Cell Fills: 1
- Laser Power: 51.0 %
- MALDI Plate: 300.0 V
- Imaging Spot Diameter: 2000.0 μm
- No. of Laser Shots: 20
- Calibration Date: Wed Jan 4 05:51:21 2012
- Data Acquisition Size: 131072
- Apodization: Sine-Bell Multiplication

![Mass Spectrum](image)

<table>
<thead>
<tr>
<th>Meas. m/z</th>
<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>e</th>
<th>Conf</th>
<th>N-Rule</th>
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</thead>
<tbody>
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Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\SHARE\20120306\WLM163_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM163_APCI_POS
Comment:

Acquisition Date: 2012/3/6 20:34:48
Operator: apex-Ultra

Acquisition Parameter

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<tr>
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<td>100.3 m/z</td>
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<tr>
<td>Broadband High Mass</td>
<td>2000.0 m/z</td>
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<td>Acquisition Mode</td>
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</tr>
<tr>
<td>Source Accumulation</td>
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<tr>
<td>Ion Accumulation Time</td>
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<tr>
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<tr>
<td>Source</td>
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<td>No. of Cell Fills</td>
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<tr>
<td>End Plate</td>
<td>1500.0 V</td>
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<tr>
<td>Capillary Entrance</td>
<td>2000.0 V</td>
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<tr>
<td>Skimmer 1</td>
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<tr>
<td>Drying Gas Temperature</td>
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<tr>
<td>Nebulizer Gas Flow Rate</td>
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<tr>
<td>Skimmer 1</td>
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<td>300.0 V</td>
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<tr>
<td>Imaging Spot Diameter</td>
<td>2000.0 μm</td>
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<tr>
<td>Calibration Date</td>
<td>Wed Jan 4 05:51:21 2012</td>
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<tr>
<td>Source Accumulation</td>
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<tr>
<td>Ion Accumulation Time</td>
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<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
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<td>Source Accumulation</td>
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<tr>
<td>Ion Accumulation Time</td>
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<td>Flight Time to Acq. Cell</td>
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Mass Spectrum

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<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>eConf</th>
<th>N-Rule</th>
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Bruker Compass DataAnalysis 4.0 printed: 2012/3/6 20:59:35 Page 1 of 1
Analysis Info
Analysis Name: D:\SHARE\2012\0306\WLM149_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM149_APCI_POS
Comment

Acquisition Parameter
Polarity: Positive
Averaged Scans: 4
Broadband Low Mass: 100.3 m/z
Pulse Program: basic
Source Accumulation: 0.0 sec
Flight Time to Acq. Cell: 0.0 sec

Broadband High Mass: 2000.0 m/z
Capillary Entrance: 2000.0 V
End Plate: 1500.0 V
No. of Cell Fills: 1500.0 V
MALDI Plate: 300.0 V
No. of Laser Shots: 20
Laser Power: 51.0 %
Imaging Spot Diameter: 2000.0 μm

Acquisition Mode: Single MS
Skimmer 1: 20.0 V
Drying Gas Temperature: 180.0 °C
Calibration Date: Wed Jan 4 05:51:21 2012
Source Accumulation: 0.0 sec
Drying Gas Flow Rate: 4.0 L/min
Data Acquisition Size: 131072
Ion Accumulation Time: 0.0 sec
Nebulizer Gas Flow Rate: 1.0 L/min
Apodization: Sine-Bell Multiplication

Int. x10^7

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb eConf N-Rule
347.0172 1 C 17 H 13 Cl 2 N 2 S 100.00 347.0171 -0.1 -0.3 7.8 11.5 even ok
2 C 16 H 18 Cl 3 S 0.28 347.0189 1.7 5.0 137.4 6.5 even ok

Mass Spectrum SmartFormula Report
Bruker Compass DataAnalysis 4.0 printed: 2012/3/6 20:57:23
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\SHARE\20120306\WLM164_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM164_APCI_POS
Comment

Acquisition Date: 2012/3/6 20:30:43
Operator
Instrument: apex-Ultra

Acquisition Parameter
Polarity: Positive
Averaged Scans: 4
Broadband Low Mass: 100.3 m/z
Broadband High Mass: 2000.0 m/z
Acquisition Mode: Single MS
Pulse Program: basic
Source Accumulation: 0.0 sec
Ion Accumulation Time: 0.0 sec
Flight Time to Acq. Cell: 0.0 sec

Source: APCI
No. of Cell Fills: 1
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Skimmer 1: 20.0 V
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
Calibration Date: Wed Jan 4 05:51:21 2012

Data Acquisition Size: 131072
Apodization: Sine-Bell Multiplication

Intensity (x10^6)

410 415 420 425 430 435 440 445 m/z
434.9162 1 C 17 H 13 Br 2 N 2 S 100.00 434.9161 -0.1 -0.2 3.1 11.5 even ok
436.9142
434.9162
438.9121

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**Mass Spectrum SmartFormula Report**

**Analysis Info**
- **Analysis Name**: D:\SHARE\20120306\WLM152_APCI_POS_000002.d
- **Method**: Metal_Trypsin digestion
- **Sample Name**: WLM152_APCI_POS
- **Comment**

**Acquisition Date**: 2012/3/6 20:28:36

**Operator**: apex-Ultra

**Acquisition Parameter**

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<tr>
<td>Broadband Low Mass</td>
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<tr>
<td>Broadband High Mass</td>
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<td>Pulse Program</td>
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</tr>
<tr>
<td>Source Accumulation</td>
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<tr>
<td>Ion Accumulation Time</td>
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<tr>
<td>Flight Time to Acq. Cell</td>
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<tr>
<td>Source</td>
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<td>No. of Cell Fills</td>
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<tr>
<td>Capillary Entrance</td>
<td>2000.0 V</td>
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<td>Skimmer 1</td>
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<tr>
<td>End Plate</td>
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<tr>
<td>MALDI Plate</td>
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<tr>
<td>Imaging Spot Diameter</td>
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<td>Drying Gas Temperature</td>
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<td>Apodization</td>
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<td>Nebulizer Gas Flow Rate</td>
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<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
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**Int. x10^8**

![Mass Spectrum](image)

**Meas. m/z** | # | Formula | Score | m/z | err [mDa] | err [ppm] | mSigma | rdb | eConf | N-Rule |
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**printed:** 2012/3/6 20:58:01  Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
- Analysis Name: D:\SHARE\20120306\WLM141_APCI_POS_000001.d
- Method: Metal_Trypsin digestion
- Sample Name: WLM141_APCI_POS
- Comment

Acquisition Parameter
- Polarity: Positive
- Averaged Scans: 2
- Broadband Low Mass: 100.3 m/z
- Broadband High Mass: 2000.0 m/z
- Acquisition Mode: Single MS
- Pulse Program: basic
- Source Accumulation: 0.0 sec
- Ion Accumulation Time: 0.0 sec
- Flight Time to Acq. Cell: 0.0 sec

Polarity: Positive, Source: APCI, No. of Laser Shots: 20
Laser Power: 51.0 %, MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm, End Plate: 1500.0 V
MALDI Plate: 300.0 V
Capillary Entrance: 2000.0 V, Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min, Apodization: Sine-Bell Multiplication
Skimmer 1: 20.0 V, Calibration Date: Wed Jan 4 05:51:21 2012
Source Accumulation: 0.0 sec, Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min, Data Acquisition Size: 131072
Apodization: Sine-Bell Multiplication

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb eConf N-Rule
379.1264 1 C25 H19 N2 S 100.00 379.1263 -0.0 -0.1 19.6 17.5 even ok

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Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:\zhouchq\20120421\20120421\WLM193_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM193_APCI_POS
Comment:

Acquisition Date: 2012/4/21 14:03:43
Instrument: apex-Ultra

Acquisition Parameter
- Polarity: Positive
- Source: APCI
- No. of Laser Shots: 20
- Laser Power: 51.0 %
- MALDI Plate: 300.0 V
- Imaging Spot Diameter: 2000.0 μm
- No. of Cell Fills: 1
- Capillary Entrance: 2000.0 V
- Calibration Date: Wed Jan 4 05:51:21 2012
- MALDI Plate: 300.0 V
- Source Accumulation: 0.0 sec
- Drying Gas Temperature: 180.0 °C
- Data Acquisition Size: 131072
- Pulse Program: basic
- Drying Gas Flow Rate: 4.0 L/min
- Apodization: Sine-Bell Multiplication
- Acquisition Mode: Single MS
- Skimmer 1: 20.0 V
- Mass Spectrum SmartFormula Report

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<tr>
<th>Meas. m/z</th>
<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
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<th>N-Rule</th>
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<tbody>
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Bruker Compass DataAnalysis 4.0  
Page 1 of 1
**Analysis Info**
- **Acquisition Date**: 2012/4/21 14:02:44
- **Analysis Name**: E:\zhouchq\20120421\20120421\WLM206_APCI_POS_000002.d
- **Method**: Metal_Trypsin digestion
- **Sample Name**: WLM206_APCI_POS
- **Comment**: Instrument: apex-Ultra

**Acquisition Parameter**

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<th>Parameter</th>
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<td>Polarity</td>
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<tr>
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<tr>
<td>Broadband High Mass</td>
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<tr>
<td>Source</td>
<td>APCI</td>
</tr>
<tr>
<td>No. of Cell Fills</td>
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</tr>
<tr>
<td>Capillary Entrance</td>
<td>1500.0 V</td>
</tr>
<tr>
<td>No. of Laser Shots</td>
<td>20</td>
</tr>
<tr>
<td>Laser Power</td>
<td>51.0 %</td>
</tr>
<tr>
<td>Imaging Spot Diameter</td>
<td>2000.0 μm</td>
</tr>
<tr>
<td>End Plate</td>
<td>1500.0 V</td>
</tr>
<tr>
<td>MALDI Plate</td>
<td>300.0 V</td>
</tr>
<tr>
<td>Laser Power</td>
<td>20.0 %</td>
</tr>
<tr>
<td>Calibration Date</td>
<td>Wed Jan 4 05:51:21 2012</td>
</tr>
<tr>
<td>Drying Gas Temperature</td>
<td>180.0 °C</td>
</tr>
<tr>
<td>Drying Gas Flow Rate</td>
<td>4.0 L/min</td>
</tr>
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<td>Data Acquisition Size</td>
<td>131072</td>
</tr>
<tr>
<td>Source Accumulation</td>
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</tr>
<tr>
<td>Drying Gas Flow Rate</td>
<td>4.0 L/min</td>
</tr>
<tr>
<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
</tr>
<tr>
<td>Ion Accumulation Time</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Nebulizer Gas Flow Rate</td>
<td>1.0 L/min</td>
</tr>
<tr>
<td>Flight Time to Acq. Cell</td>
<td>0.0 sec</td>
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<tr>
<td>Nebulizer Gas Flow Rate</td>
<td>1.0 L/min</td>
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<tr>
<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
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</table>

**Mass Spectrum**

![Mass Spectrum Image](image)

**SmartFormula Report**

<table>
<thead>
<tr>
<th>Meas. m/z</th>
<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>eConf</th>
<th>N-Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>359.0849</td>
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<td>C 21 H 15 N 2 O 2 S</td>
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<td>359.0849</td>
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<td>23.0</td>
<td>15.5</td>
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</tr>
</tbody>
</table>

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Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\SHARE\20120306\WLM165_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM165_APCI_POS
Comment: 

Acquisition Date: 2012/3/6 20:27:32
Operator: apex-Ultra

Acquisition Parameter
Polarity: Positive
Averaged Scans: 4
Source: APCI
No. of Laser Shots: 20
Laser Power: 51.0 %
MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Broadband High Mass: 2000.0 m/z
Acquisition Mode: Single MS
Skimmer 1: 20.0 V
Source Accumulation: 0.0 sec
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Data Acquisition Size: 131072
Capillary Entrance: 2000.0 m/z
End Plate: 1500.0 V
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
Apodization: Sine-Bell Multiplication
End Plate: 1500.0 V
Calibration Date: Wed Jan 4 05:51:21 2012
Flight Time to Acq. Cell: 0.0 sec

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e¥Conf N-Rule
291.0080 1 C 13 H 11 N 2 S 3 100.00 291.0079 -0.1 -0.4 7.9 9.5 even ok

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Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: E:\zhouchq\20120421\20120421\WLM214_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM214_APCI_POS
Comment

Acquisition Date: 2012/4/21 14:01:45

Acquisition Parameter

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<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
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<td>Polarity</td>
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<td>Averaged Scans</td>
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<tr>
<td>Broadband Low Mass</td>
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<tr>
<td>Broadband High Mass</td>
<td>2000.0 m/z</td>
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<tr>
<td>Acquisition Mode</td>
<td>Single MS</td>
</tr>
<tr>
<td>Pulse Program</td>
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<tr>
<td>Source</td>
<td>APCI</td>
</tr>
<tr>
<td>Capillary Entrance</td>
<td>2000.0 V</td>
</tr>
<tr>
<td>Skimmer 1</td>
<td>20.0 V</td>
</tr>
<tr>
<td>Drying Gas Temperature</td>
<td>180.0 °C</td>
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<tr>
<td>Drying Gas Flow Rate</td>
<td>4.0 L/min</td>
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<tr>
<td>Nebulizer Gas Flow Rate</td>
<td>1.0 L/min</td>
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<tr>
<td>Apodization</td>
<td>Sine-Bell Multiplication</td>
</tr>
<tr>
<td>Calibration Date</td>
<td>Wed Jan 4 05:51:21 2012</td>
</tr>
<tr>
<td>Source Accumulation</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Ion Accumulation Time</td>
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<tr>
<td>Flight Time to Acq. Cell</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Source Accumulation Time</td>
<td>0.0 sec</td>
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<tr>
<td>Ion Accumulation Time</td>
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<tr>
<td>Flight Time to Acq. Cell</td>
<td>0.0 sec</td>
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<tr>
<td>Source Accumulation</td>
<td>0.0 sec</td>
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<tr>
<td>Ion Accumulation Time</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Flight Time to Acq. Cell</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Source Accumulation Time</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Ion Accumulation Time</td>
<td>0.0 sec</td>
</tr>
<tr>
<td>Flight Time to Acq. Cell</td>
<td>0.0 sec</td>
</tr>
</tbody>
</table>

Mass Spectrum

Meas. m/z: 291.0079
Formula: C13H11N2S3
Score: 100.00
m/z err [mDa]: -0.1
err [ppm]: -0.2
mSigma: 9.5
rdb: 12.7
eConf: 9.5
N-Rule: even
ok

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Analysis Info
Analysis Name: D:\SHARE\20120429\WLM234_APCI_POS_000002.d
Method: Metal_Trypsin digestion
Sample Name: WLM234_APCI_POS
Comment:

Acquisition Parameter
Polarity: Positive
Averaged Scans: 2
Broadband Low Mass: 100.3 m/z
Broadband High Mass: 2000.0 m/z
No. of Laser Shots: APCI
Laser Power: 51.0 %
MALDI Plate: 300.0 V
Imaging Spot Diameter: 2000.0 μm
End Plate: 1500.0 V
Capillary Entrance: 2000.0 V
Skimmer 1: 20.0 V
Drying Gas Temperature: 180.0 °C
Drying Gas Flow Rate: 4.0 L/min
Nebulizer Gas Flow Rate: 1.0 L/min
Source Accumulation: basic
Averaged Scans: No. of Cell Fills
End Plate: Source Accumulation Time: 0.0 sec
Capillary Entrance: Ion Accumulation Time: 0.0 sec
Skimmer 1: Flight Time to Acq. Cell: 0.0 sec

Mass Spectrum SmartFormula Report

<table>
<thead>
<tr>
<th>Meas. m/z</th>
<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>Conf</th>
<th>N-Rule</th>
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<tbody>
<tr>
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