

Supplementary data

Tandem cyclocondensation-Knoevenagel-Michael reaction of phenylhydrazine, acetoacetate derivatives and arylaldehydes

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6541835583, Iran.

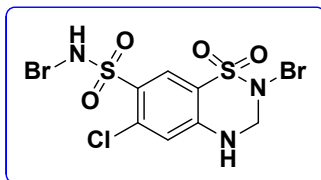
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Zare)

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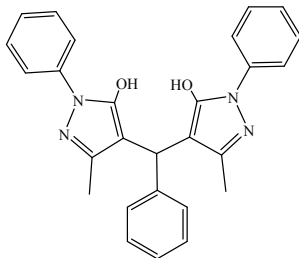
N,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide.



White solid; m.p. 255 °C, IR (KBr): 3377, 3232, 1579, 1495, 1362, 1308, 1244, 1147, 1058, 1025, 794, 716, 675, 579, 545 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 4.70 (s, 2H), 6.85 (s, 1H), 7.20 (s, 1H), 7.88 (s, 1H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 55.08, 107.26, 110.65, 122.57, 127.55, 136.34, 142.14; MS: m/z = 455 (M^+).

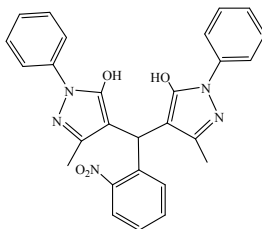
Data of Compounds:

4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (1).



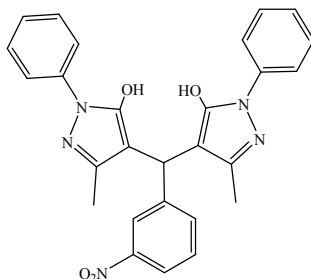
White solid; m.p. 160-162 °C (lit. [14] mp 168-170 °C); IR (KBr, cm^{-1}): 3515, 3129, 3081, 2919, 1603, 1584, 1501, 1414, 1316, 1286, 1189, 1126, 1027, 792, 760. ^1H NMR (DMSO-d_6): δ 2.31 (s, 6H), 4.87 (s, 1H), 7.05 (m, 1H), 7.19 (m, 6H), 7.44 (t, $J = 7.2$ Hz, 4H), 7.58 (d, $J = 7.9$ Hz, 4H); ^{13}C NMR (DMSO-d_6): δ 12.1, 33.5, 121.3, 126.3, 126.7, 127.6, 128.2, 129.2, 137.3, 142.9, 146.6.

4,4'-((2-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (2).



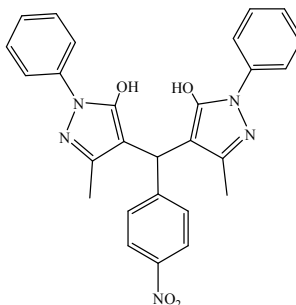
Yellow solid; m.p. 217-218 °C (lit. [14] mp 221-223°C); IR (KBr, cm^{-1}): 3436, 3070, 2916, 1612, 1558, 1519, 1499, 1458, 1406, 1374, 1351, 1089, 837, 753, 723. ^1H NMR (DMSO-d_6): δ 2.28 (s, 6H), 5.45 (s, 1H), 7.20-7.28 (m, 2H), 7.41-7.47 (m, 5H), 7.62-7.76 (m, 7H).

4,4'-((3-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3).



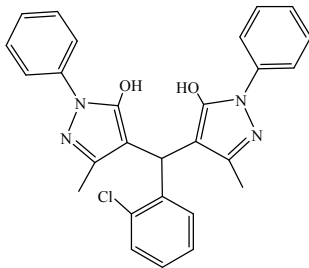
Yellow solid; m.p. 232-234 °C; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 2.33 (s, 6H), 5.13 (s, 1H), 7.24 (2H), 7.43 (4H), 7.60 (1H), 7.67-7.68 (m, 5H), 8.06 (2H), 12.64 (s, 1H, OH), 13.88 (s, 1H, OH); ^{13}C NMR (DMSO- d_6): δ (ppm) 12.1, 33.3, 121.1, 121.7, 122.2, 126.1, 126.3, 129.4, 130.2, 134.9, 137.5, 145.1, 146.8, 148.2; IR (KBr, cm^{-1}): 3427, 3150, 3106, 3079, 2921, 1599, 1583, 1523, 1502, 1408, 1346, 1276, 1026, 902, 781, 758, 734.

4,4'-((4-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (4).



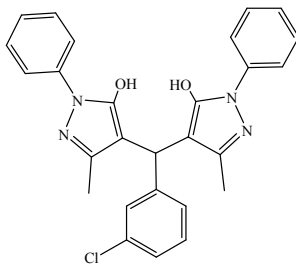
Yellow solid; m.p. 228-230 °C (lit. [14] mp 229-231°C); IR (KBr, cm^{-1}): 3435, 3067, 2922, 1601, 1582, 1515, 1501, 1479, 144, 1415, 1346, 1296, 1106, 1070, 983, 822, 749, 690; ^1H NMR (DMSO- d_6): δ 2.34 (s, 6H), 5.12 (s, 1H), 7.24-7.27 (m, 2H), 7.42 (t, J = 7.2 Hz, 4H), 7.53 (d, J = 8.1 Hz), 7.71 (d, J = 8.1 Hz, 4H), 8.18 (d, J = 8.2 Hz, 2H), 12.65 (s, 1H, OH), 13.87 (s, 1H, OH); ^{13}C NMR (DMSO- d_6): δ 12.3, 19.4, 34.2, 56.8, 121.5, 124.3, 126.6, 129.6, 129.8, 146.9, 147.2, 151.3.

4,4'-((2-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (5).



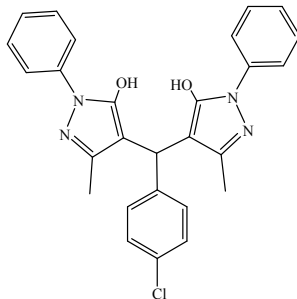
White solid; m.p. 235-236 °C (lit. [16] mp 235-236°C); ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 2.27 (s, 6H), 5.12 (s, 1H), 7.23-7.28 (m, 3H), 7.37-7.43 (m, 5H), 7.66-7.68 (m, 4H), 7.74 (s, 2H), 12.69 (s, 1H, OH), 13.95 (s, 1H, OH); ¹³C NMR (DMSO-d₆): δ (ppm) 12.3, 32.1, 121.1, 126.1, 127.4, 128.5, 129.4, 129.9, 130.7, 132.3, 137.7, 139.9, 146.5; IR (KBr, cm⁻¹): 3435, 3062, 2912, 1614, 1582, 1560, 1499, 1401, 1368, 1213, 1086, 1033, 837, 746, 690.

4,4'-((3-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (6).



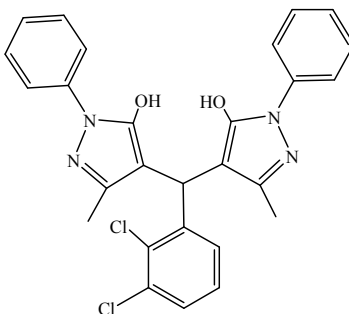
White solid; m.p. 153-154 °C (lit. [14] mp 150-152 °C); IR (KBr, cm⁻¹): 3436, 3141, 3073, 2923, 1605, 1594, 1580, 1473, 1501, 1473, 1411, 1372, 1298, 1175, 1126, 1073, 1035, 912, 859, 780, 755.

4,4'-((4-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (7).



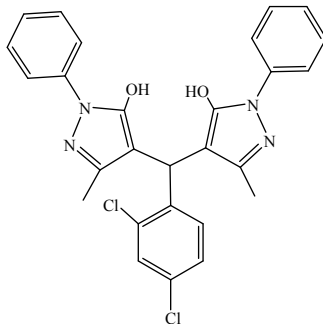
White solid; m.p. 209-210 °C (lit. [14] mp 213-215 °C); IR (KBr, cm^{-1}): 3443, 3066, 2977, 1600, 1580, 1501, 1487, 1407, 1373, 1296, 1198, 1087, 1024, 1015, 906, 810, 748, 690; ^1H NMR (DMSO-d_6): δ 2.31 (s, 6H), 4.95 (s, 1H), 7.25 (d, $J = 8.4$ Hz, 4H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.41 (t, $J = 7.3$ Hz, 4H), 7.73 (d, $J = 7.7$ Hz, 4H).

4,4'-((2,3-dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (8).



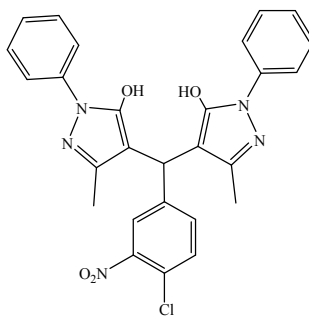
White solid; m.p. 243-244 °C ; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.26 (s, 6H), 5.15 (s, 1H), 7.24 (2H), 7.32 (1H), 7.42- 7.48 (6H), 7.58- 7.67 (4 H), 12.75 (s, 1H, OH), 13.84 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.3, 33.2, 121.1, 127.2, 128.1, 129.1, 129.3, 129.4, 130.5, 132.3, 137.6, 142.4, 146.6; IR (KBr, cm^{-1}): 3439, 3079, 2923, 1598, 1575, 1500, 1452, 149, 1366, 1191, 1111, 1069, 1014, 856, 779, 751, 590; MS (EI, 70 eV): m/z (%) =504 (M^+).

4,4'-((2,4-dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (9).



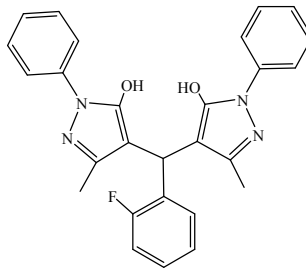
White solid; m.p. 219-221 °C (lit. [20] mp 227-229 °C); ¹H NMR (90 MHz, DMSO-d₆): δ (ppm) 2.30 (s, 6H), 5.11 (s, 1H), 7.25-7.73 (13H), 12.25 (s, 1H, OH), 13.57 (s, 1H, OH); ¹³C NMR (DMSO-d₆): δ (ppm) 11.7, 31.6, 120.7, 125.7, 126.9, 128.9, 131.6, 132.5, 137.1, 138.3, 146.4; IR (KBr, cm⁻¹): 3435, 3057, 2918, 1597, 1572, 1500, 1471, 1382, 1365, 1297, 1190, 1102, 904, 885, 750, 705, 589.

4,4'-((4-chloro-3-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (10).



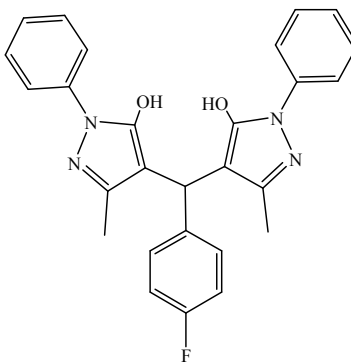
White solid; m.p. 232-235 °C (lit. [15] mp 232-238 °C); IR (KBr, cm⁻¹): 3439, 3126, 3055, 1923, 1597, 1570, 1530, 1501, 1479, 1383, 1368, 1111, 1050, 932, 827, 785, 751, 691, 670, 604; ¹H NMR (DMSO-d₆): δ 2.04 (s, 6H), 5.07 (s, 1H), 7.23 (t, *J* = 7.31 Hz, 2H), 7.42 (t, *J* = 7.77 Hz, 4H), 7.58 (d, *J* = 8.37 Hz, 1H), 7.69 (m, 5H), 7.84 (s, 1H), 12.47 (s, 1H, OH), 13.85 (s, 1H, OH); ¹³C NMR (DMSO-d₆): δ 12.4, 32.6, 119.0, 120.6, 125.5, 128.7, 129.5, 130.9, 132.7, 141.7, 146.2.

4,4'-((2-fluorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (11).



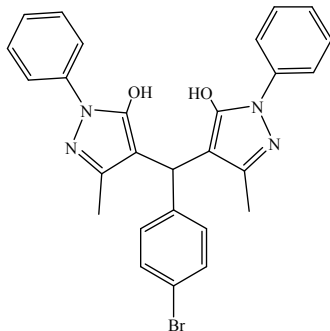
White solid; m.p. 157-159 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 2.27 (s, 6H), 5.10 (s, 1H), 7.12 (2, 2H), 7.23 (s, 3H), 7.42 (s, 4H), 7.68 (s, 5H), 12.62 (s, 1H, OH), 14.31 (s, 1H, OH); ¹³C NMR (DMSO-d₆): δ (ppm) 12.0, 31.1, 115.6, 121.2, 124.4, 124.5, 126.2, 128.6, 129.4, 129.7, 129.9, 137.7, 146.4, 158.9, 161.3; IR (KBr, cm⁻¹): 3455, 3137, 3081, 2975, 1602, 1582, 1500, 1486, 1455, 1412, 1369, 1282, 1184, 1052, 1040, 885, 805, 758, 691, 595; MS (EI, 70 eV): m/z (%) =454 (M⁺).

4,4'-((4-fluorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (12).



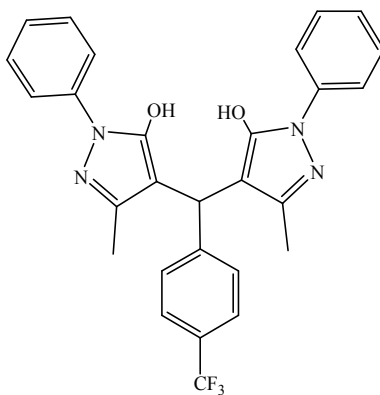
White solid; m.p. 180-181 °C (lit. [31] mp 181-183 °C); IR (KBr, cm⁻¹): 3439, 3065, 2955, 2925, 1599, 1580, 1503, 1415, 1222, 1157, 805, 753, 691, 593; ¹H NMR (DMSO-d₆): δ 2.33 (s, 6H), 5.34 (s, 1H), 7.18-7.39 (m, 4H), 7.40-7.47 (m, 5H), 7.68-7.71 (m, 5H), 11.43 (s, 1H, OH), 13.91 (s, 1H, OH); ¹³C NMR (DMSO-d₆): δ 12.3, 32.5, 114.6, 114.8, 117.9, 120.5, 124.7, 125.5, 128.8, 128.8, 129.0, 138.2, 146.2, 159.4, 161.9.

4,4'-((4-bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (13).



White solid; m. p. 185-186 °C; ^1H NMR (lit. [19] mp 183-184 °C); IR (KBr, cm^{-1}): 3440, 3062, 2921, 1597, 1579, 1501, 1485, 1404, 1377, 1338, 1260, 1185, 1071, 1009, 834, 804, 750, 687, 602, 507; ^1H NMR ($\text{DMSO}-d_6$): δ 2.31 (s, 6H), 4.92 (s, 1H), 7.17 (d, $J = 8.81$ Hz, 3H), 7.22 (t, $J = 8.73$ Hz, 1H), 7.43-7.47 (m, 6H), 7.69 (d, $J = 7.9$ Hz, 4H), 12.58 (s, 1H, OH), 13.89 (s, 1H, OH); ^{13}C NMR ($\text{DMSO}-d_6$): 12.3, 32.7, 118.8, 120.4, 125.5, 128.9, 129.5, 130.9, 141.6, 146.2.

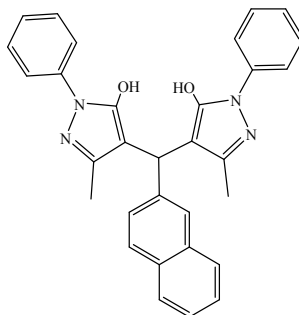
4,4'-((4-(trifluoromethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (14).



White solid; m. p. 223-224 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ (ppm) 2.31, (s, 6H), 5.05 (s, 1H), 7.24 (s, 2H), 4.44 (7H), 7.68 (5H), 12.63 (s, 1H, OH), 13.87 (s, 1H, OH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ (ppm) 12.1, 33.4, 121.0, 121.1, 125.6, 126.2,

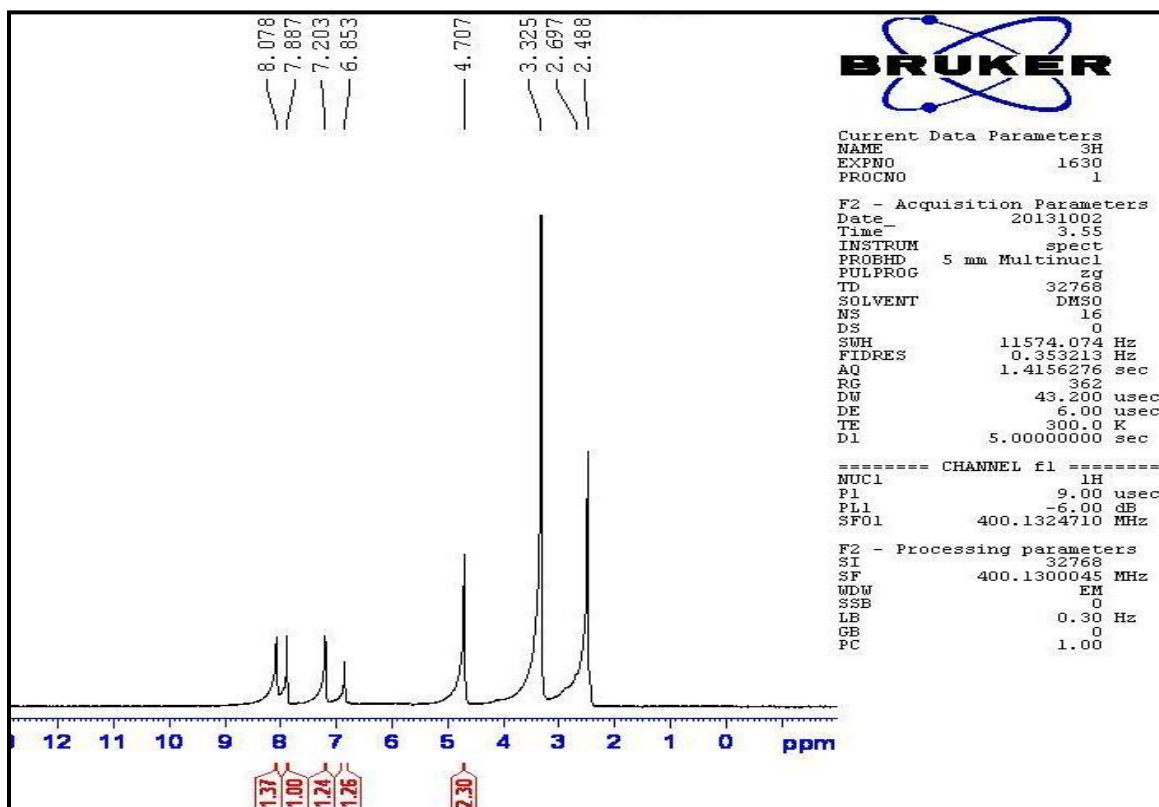
126.3, 127.0, 127.3, 128.6, 129.4, 137.7, 137.8, 146.8, 147.5; IR (KBr, cm^{-1}): 3442, 3071, 2979, 1602 1583, 1501, 1416, 1374, 1322, 1297, 1199, 1165, 1116, 1108, 1066, 1019, 841, 750, 690, 602, 499; MS (EI, 70 eV): m/z (%) = 504 (M^+).

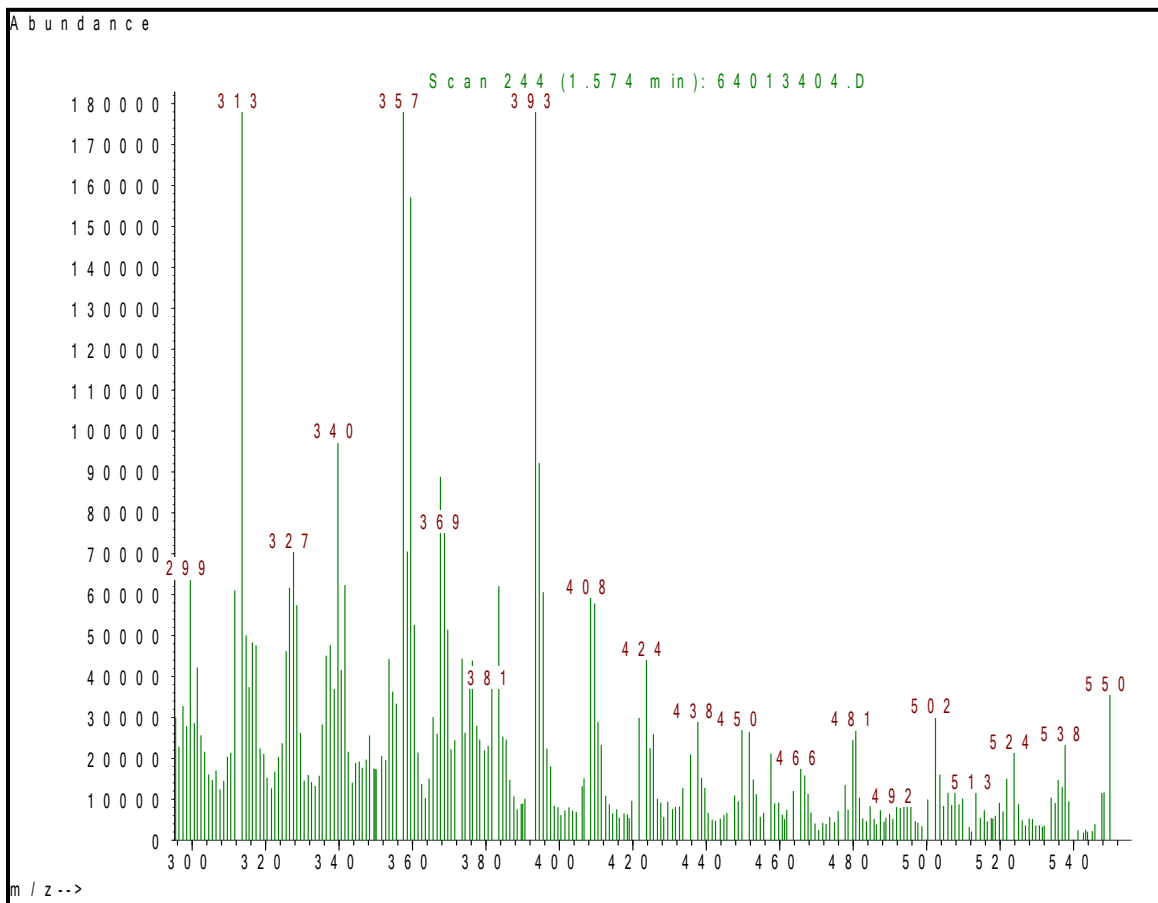
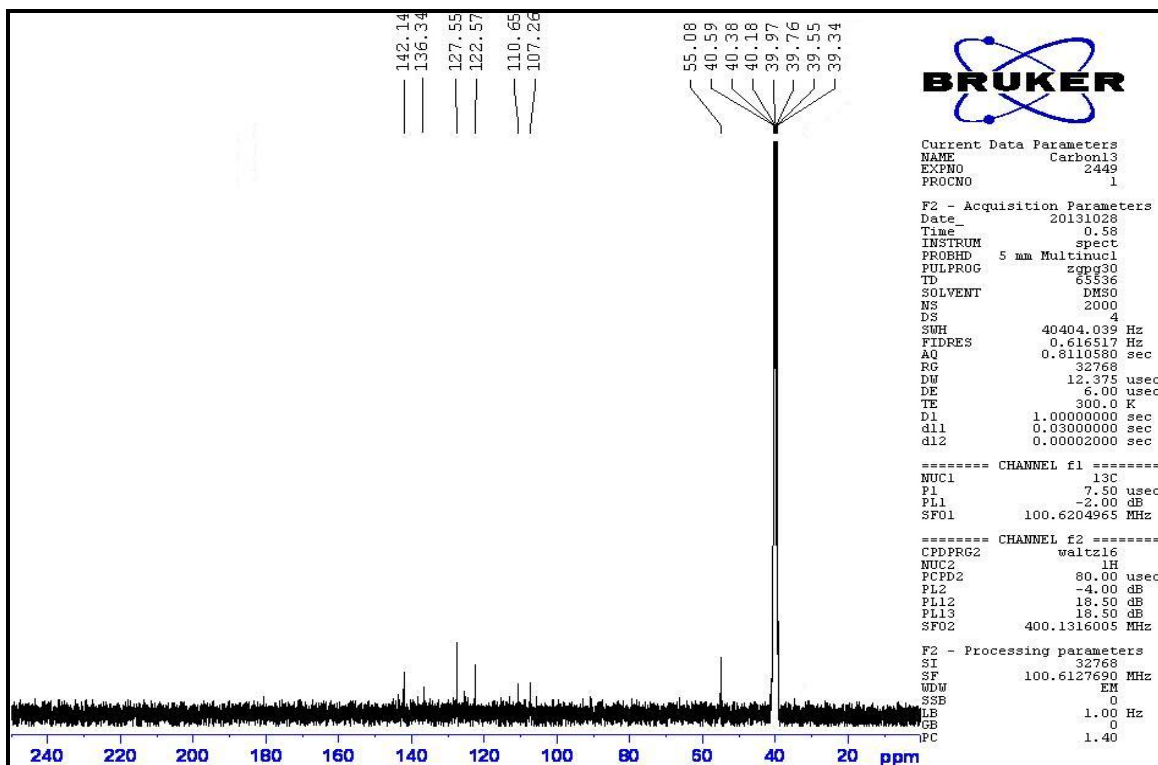
4,4'-(naphthalen-2-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (15).

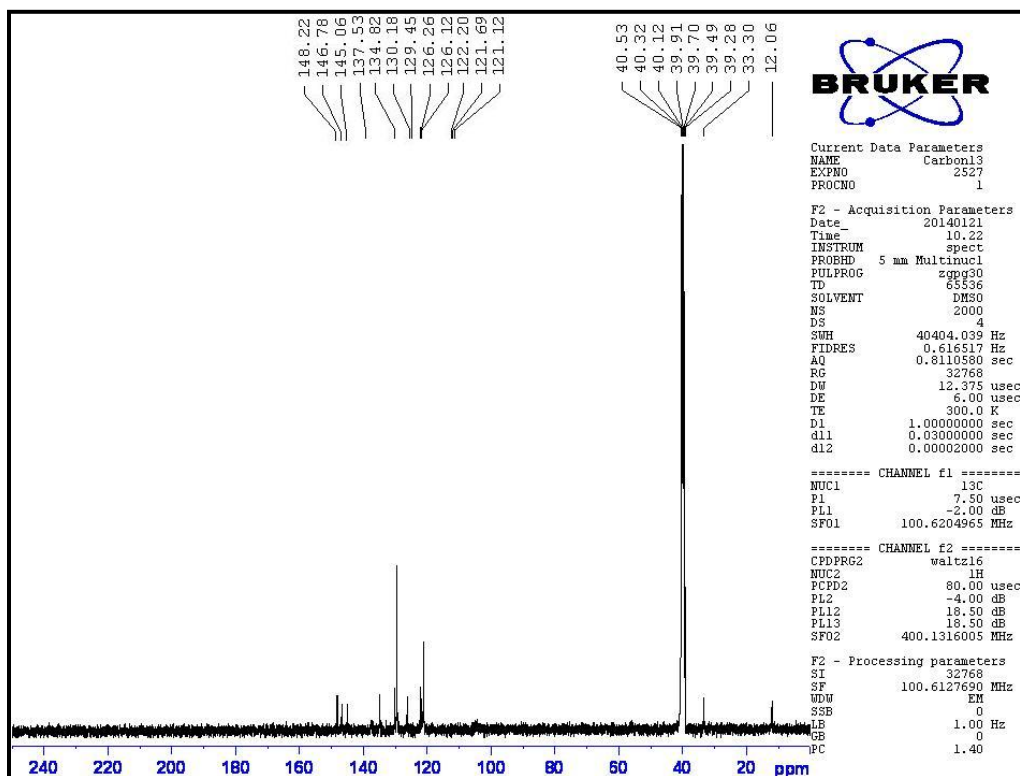
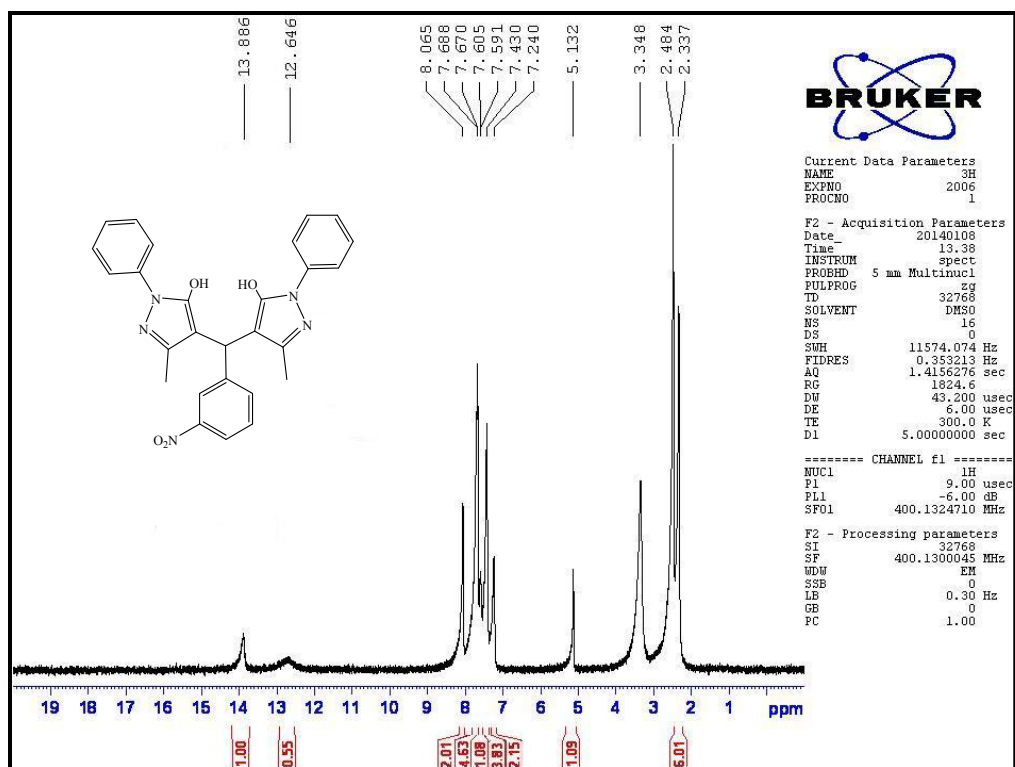


White solid; m. p. 204-206 °C (lit. [15] mp 203-207 °C); IR (KBr, cm^{-1}): 3436, 3054, 2979, 1596, 1582, 1493, 1392, 1368, 1293, 1254, 1199, 1135, 1023, 914, 865, 813, 788, 743, 690, 495, 480; ^1H NMR (DMSO-d_6): δ 2.37 (s, 6H), 5.14 (s, 1H), 7.25 (d, J = 7.3 Hz, 2H), 7.43-7.45 (m, 7H), 7.70-7.72 (m, 5H), 7.80-7.88 (m, 3H), 12.44 (s, 1H, OH), 13.88 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.9, 33.4, 120.5, 124.9, 125.5, 125.9, 126.4, 127.3, 127.7, 127.7, 128.8, 131.6, 132.9, 139.8, 147.6.

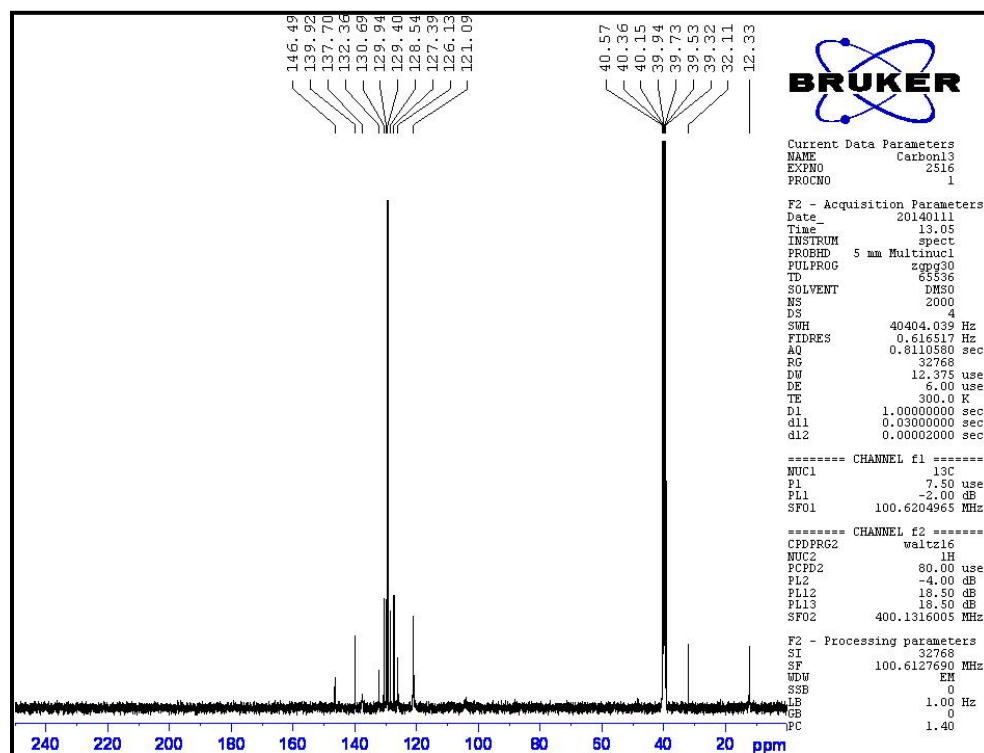
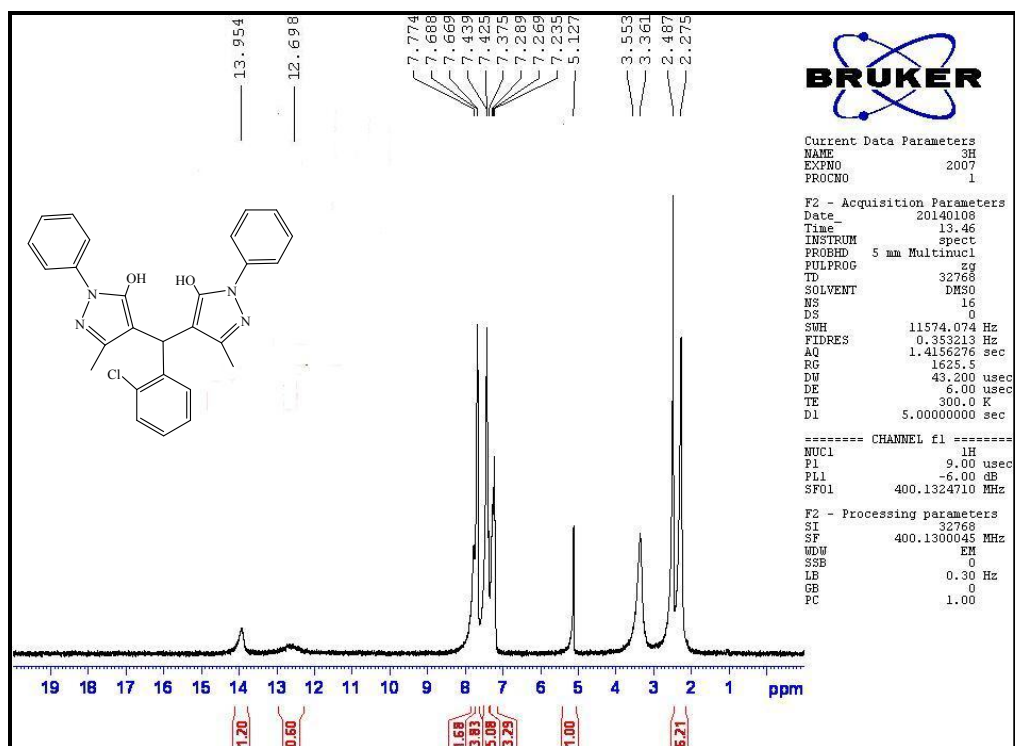
N,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide



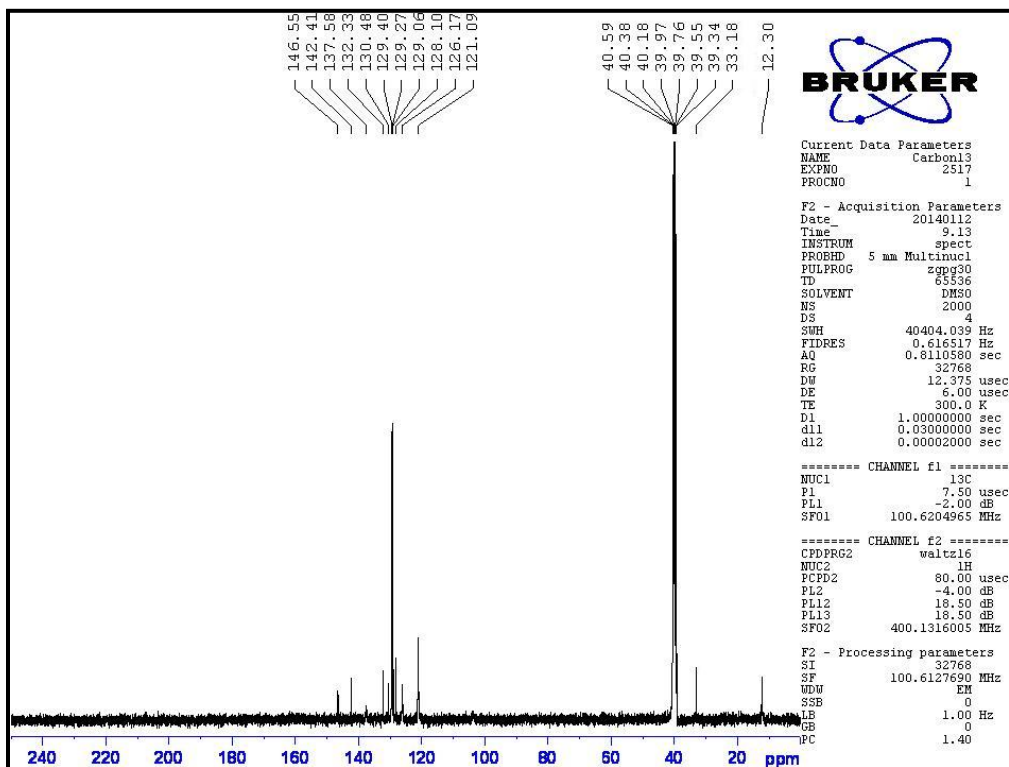
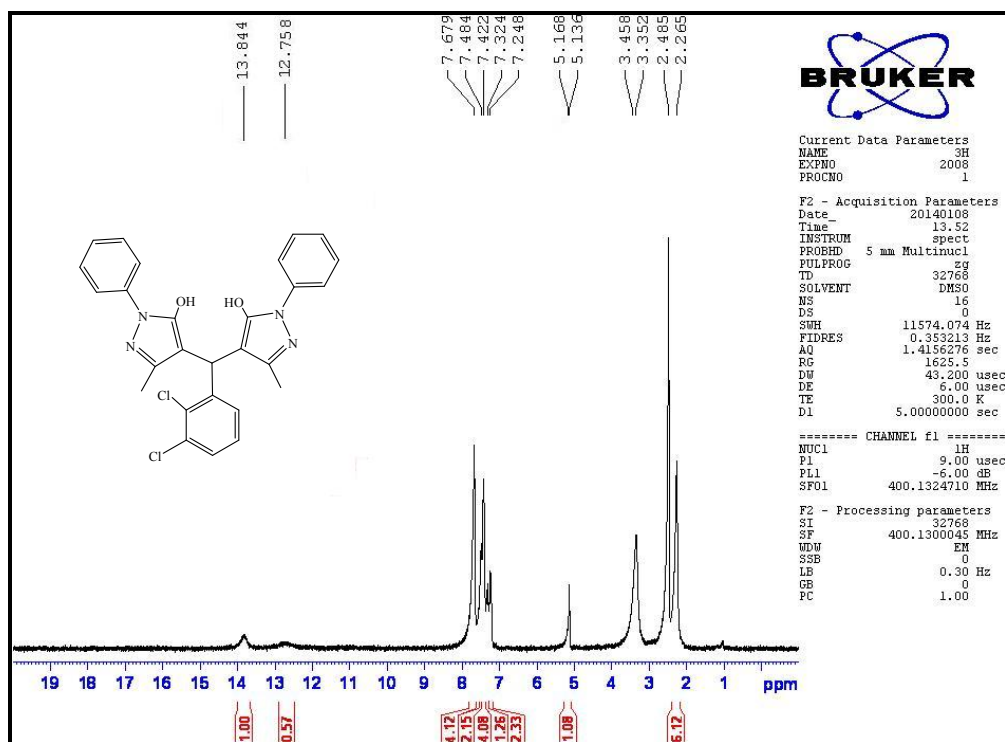


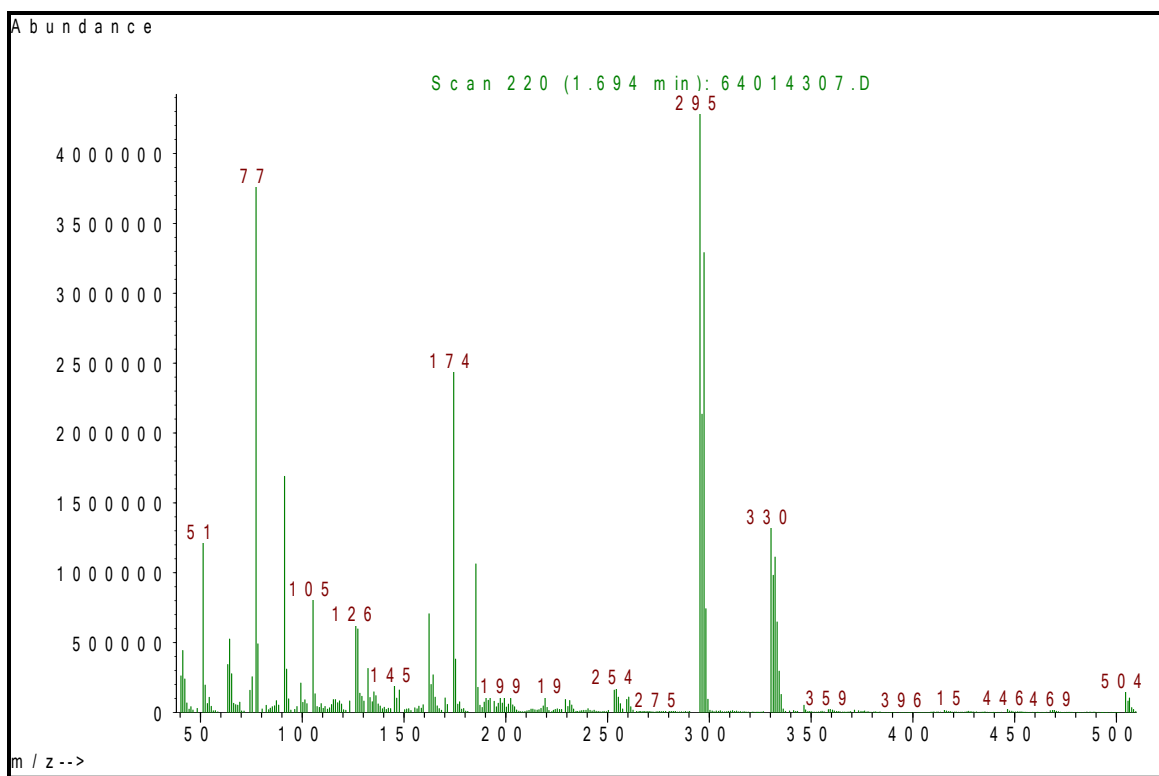


4,4'-((2-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) 5.

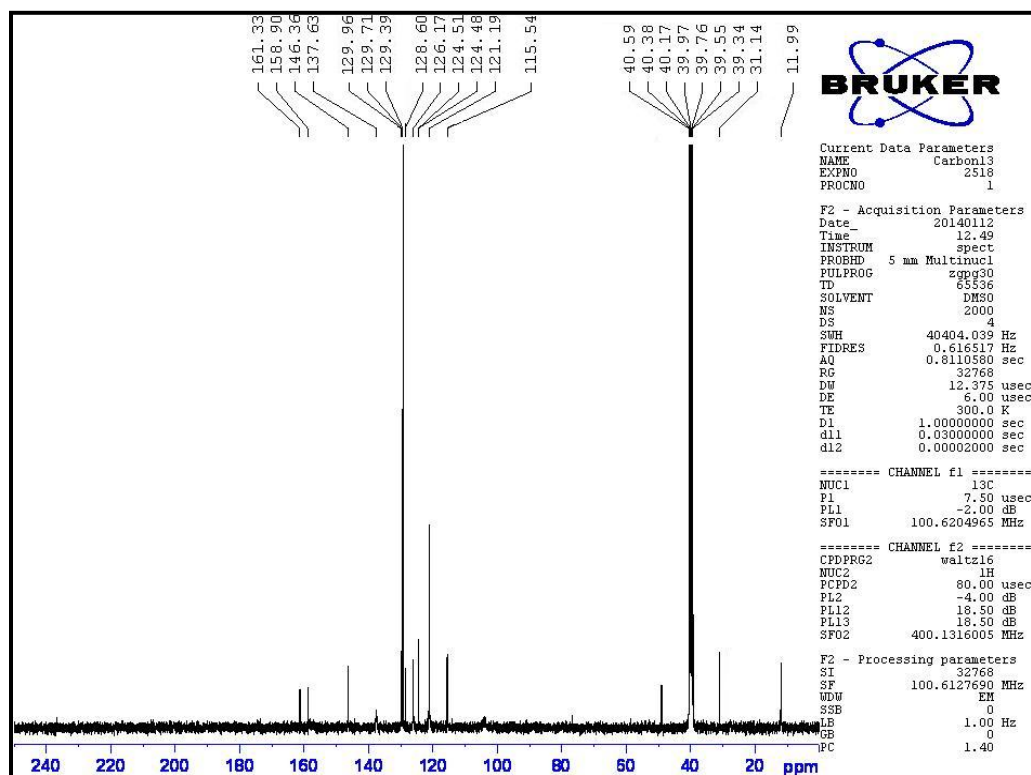
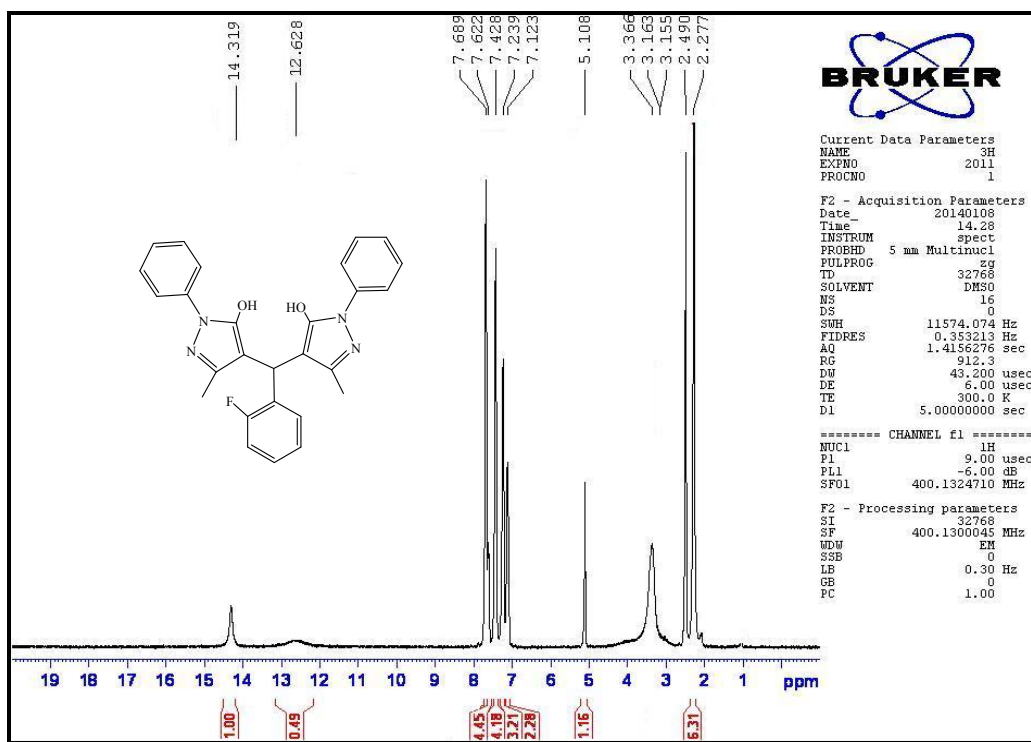


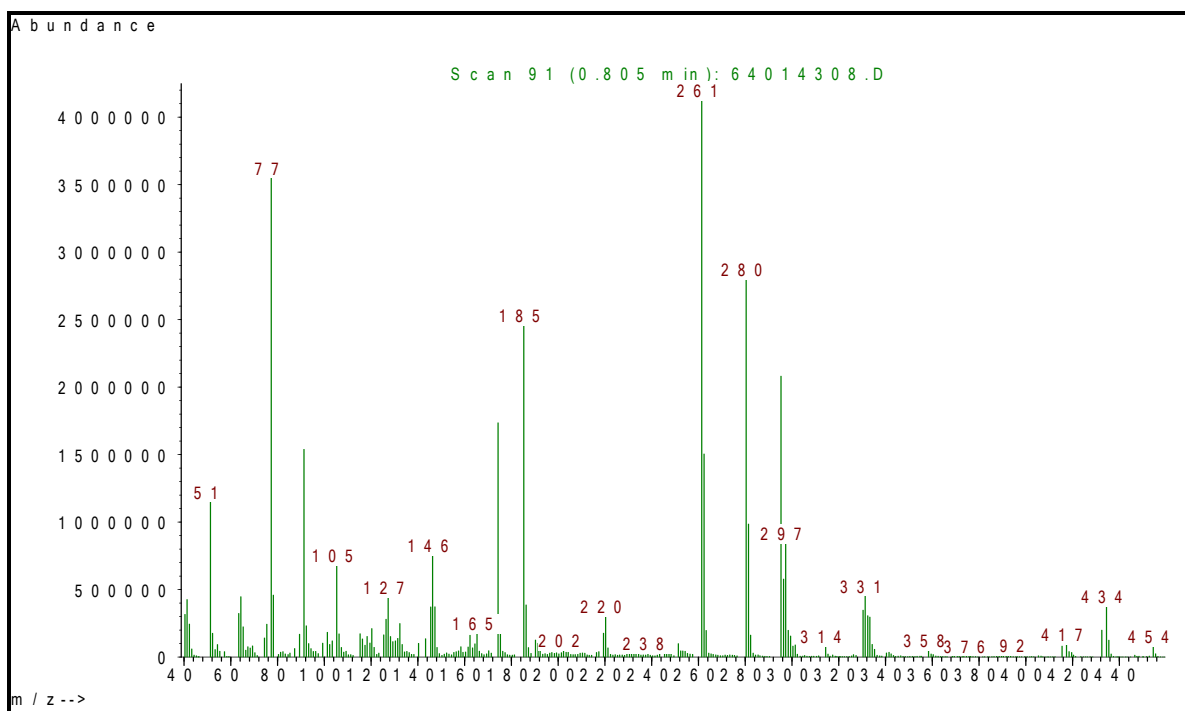
4,4'-((2,3-dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) 8.





4,4'-((2-fluorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) 11.





4,4'-((4-(trifluoromethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

14.

