SUPPLEMENTARY MATERIAL TO

Synthesis and characterization of novel benzimidazole embedded 1,3,5-trisubstituted pyrazolines as antimicrobial agents

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ANALYTICAL AND SPECTRAL DATA FOR SYNTHESISED COMPOUNDS

*1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-phenylprop-2-en-1-one (**8**)*[1]. Yield: 80 %; off-white solid; m.p.: 112-114 ^{O}C; Anal. Calcd. for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28 %. Found: C, 81.70; H, 5.28; N, 8.16 %; IR (KBr, cm^{-1}): 1661 (C=O), 1597 (C=N); ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ / ppm): 8.25 (1H, *d*, *J* = 20 Hz, H$_\alpha$), 7.94 (1H, *d*, *J* = 10 Hz, Ar–H), 7.89-7.84 (3H, *m*, H$_\beta$, Ar-H), 7.75 (1H, *d*, *J* = 10 Hz, Ar–H), 7.50-7.39 (5H, *m*, Ar-H), 7.32-7.29 (2H, *m*, Ar-H), 7.26-7.23 (1H, *m*, Ar-H), 7.19 (2H, *d*, *J* = 5 Hz, Ar-H), 6.01 (2H, *s*, –CH$_2$); ^{13}C NMR (125 MHz, DMSO-d$_6$, δ / ppm): 182.52 (C=O), 146.88, 144.59, 141.80, 137.75, 136.98, 134.74, 131.57, 129.62, 129.39, 129.11, 127.92, 127.22, 126.66, 124.38, 123.40, 121.96, 112.46, 48.47 (–CH$_2$); ESI-MS m/z: 339.2 [M+H].

*1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(p-tolyl)prop-2-en-1-one (**9**).* Yield: 78 %; pale yellow solid m.p.: 179-182 ^{O}C; Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95 %. Found: C, 81.67; H, 5.80; N, 7.85 %; IR (KBr, cm^{-1}): 1651(C=O), 1588 (C=N); ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ / ppm): 8.19 (1H, *d*, *J* = 17.5 Hz, H$_\alpha$), 7.92 (1H, *d*, *J* = 10 Hz, Ar–H), 7.83 (1H, *d*, *J* = 17.5 Hz, H$_\beta$), 7.74 (3H, *d*, *J* = 10 Hz, Ar-H), 7.47-7.44 (1H, *m*, Ar–H), 7.41-7.38 (1H, *m*, Ar–H), 7.31-7.28 (4H, *m*, Ar-H), 7.25-7.22 (1H, *m*, Ar-H), 7.18 (2H, *d*, *J* = 10 Hz, Ar-H), 5.99 (2H, *s*, –CH$_2$), 2.36 (3H, *s*, –CH$_3$); ^{13}C NMR (125 MHz, DMSO-d$_6$, δ / ppm): 182.53 (C=O), 146.95, 144.70, 141.83, 141.78, 137.76, 136.95, 132.04, 130.28, 129.45, 129.11, 127.92, 127.20, 126.60, 124.35, 122.37, 121.91, 112.44, 48.44 (–CH$_2$), 21.61 (–CH$_3$); ESI-MS m/z: 353.2 [M+H].

*1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (**10**)*[1]. Yield: 74 %; off-white solid; m.p.: 156-158 ^{O}C; Anal. Calcd. for $C_{23}H_{17}ClN_2O$: C, 74.09; H, 4.60; N, 7.51 %. Found: C, 73.87; H, 4.51; N, 7.70 %; IR (KBr, cm^{-1}): 1652 (C=O) 1587(C=N); ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ / ppm): 8.24 (1H, *d*, *J* = 20 Hz, H$_\alpha$), 7.93-7.83 (4H, *m*, H$_\beta$, Ar-H), 7.75 (1H, *d*, *J* = 10.0 Hz, Ar–H), 7.54 (2H, *d*, *J* = 7.5, Ar-H), 7.48-7.39 (2H, *m*, Ar-H), 7.31-7.18 (5H, *m*, Ar-H), 5.99 (2H, *s*, –CH$_2$); ^{13}C NMR (125 MHz, DMSO-d$_6$, δ / ppm):

182.40 (C=O), 146.79, 143.10, 141.78, 137.71, 136.99, 136.03, 133.70, 131.10, 129.66, 129.11, 127.94, 127.21, 126.74, 124.43, 124.09, 121.96, 112.48, 48.46 (–$\underline{C}H_2$); ESI-MS m/z: 373.1 [M+H].

1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-bromophenyl)prop-2-en-1-one ***(11)***. Yield: 78 %; pale yellow solid; m.p.: 198-200 ^{O}C; Anal. Calcd. for $C_{23}H_{17}BrN_2O$: C, 66.20; H, 4.11; N, 6.71 %. Found: C, 66.16; H, 4.04; N, 6.58 %; IR (KBr, cm^{-1}): 1652 (C=O), 1594 (C=N), 1581; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.26 (1H, *d*, *J* = 15 Hz, H_α), 7.93 (1H, *d*, *J* = 7.5 Hz, Ar–H) 7.86-7.82 (3H, *m*, H_β, Ar-H,), 7.76 (1H, *d*, *J* = 10 Hz, Ar–H), 7.69 (2H, *d*, *J* = 5 Hz, Ar-H), 7.49-7.46 (1H, *m*, Ar–H), 7.43-7.40 (1H, *m*, Ar–H), 7.32-7.29 (2H, *m*, Ar-H), 7.26-7.23 (1H, *m*, Ar-H), 7.19 (2H, *d*, *J* = 5 Hz, Ar-H), 6.0 (2H, s, –CH_2); ^{13}C NMR (125 MHz, DMSO-d_6, δ / ppm): 182.41 (C=O), 146.80, 143.19, 141.79, 137.72, 137.00, 134.03, 132.60, 131.28, 129.11, 127.93, 127.21, 126.74, 124.94, 124.42, 124.14, 121.97, 112.49, 48.47 (–$\underline{C}H_2$); ESI-MS m/z: 417.1 [M+H].

1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-fluorophenyl)prop-2-en-1-one ***(12)***. Yield: 83 %; white solid; m.p.: 160-162 ^{O}C; Anal. Calcd. for $C_{23}H_{17}FN_2O$: C, 77.51; H, 4.81; N, 7.86 %. Found: 77.04; H, 4.96; N, 8.02 %; IR (KBr, cm^{-1}): 1662 (C=O), 1590 (C=N); ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.19 (1H, *d*, *J* = 16 Hz, Hα), 7.95-7.92 (3H, *m*, Ar–H) 7.87 (1H, *d*, *J* = 16 Hz, H_β), 7.75 (1H, *d*, *J* = 8.0 Hz, Ar–H), 7.48-7.45 (1H, *m*, Ar–H), 7.42-7.39 (1H, *m*, Ar–H), 7.34-7.29 (4H, *m*, Ar-H), 7.26-7.24 (1H, *m*, Ar-H), 7.20-7.18 (2H, *m*, Ar-H), 6.0 (2H, *s*,–CH_2); ^{13}C NMR (125 MHz, DMSO-d_6, δ / ppm): 182.47 (C=O), 165.12, 163.13, 146.84, 143.38, 141.79, 137.74, 136.97, 131.87, 131.80, 131.45, 131.43, 129.10, 127.92, 127.21, 126.65, 124.37, 123.30, 121.93, 116.74, 116.57, 112.46, 48.46 (–$\underline{C}H_2$); ESI-MS m/z: 357.1 [M+H].

1-benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole ***(13)***. Yield: 70 %; white solid; m.p.: 208-210 ^{O}C; Anal. Calcd. for $C_{29}H_{24}N_4$: C, 81.28; H, 5.65; N, 13.07 %. Found: C, 81.45; H, 5.46; N, 12.78 %; IR (KBr, cm^{-1}): 1595 (C=N), 1543, 1503, 1495, 1463, 1456, 1408, 1392, 1325 (C-N), 1306, 1164; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.85 (1H, *d*, *J* = 10 Hz, Ar-H), 7.52-7.49 (2H, *m*, Ar–H) 7.36-7.31 (4H, *m*, Ar–H) 7.28-7.23 (2H, *m*, Ar–H), 7.20-7.15 (4H, *m*, Ar–H), 7.07-7.04 (1H, *m*, Ar-H), 6.99-6.96 (2H, *m*, Ar-H), 6.83-6.80 (3H, *m*, Ar–H), 5.75 (1H, *dd*, J_{AX} = 10 Hz, J_{BX} = 15 Hz, H_X), 5.39 (1H, *d*, J_{DC} = 20 Hz , H_D), 5.34 (1H, *d*, J_{CD} = 20 Hz, H_C), 3.71 (1H, *dd*, J_{BX} = 15 Hz, J_{AB} = 20 Hz, H_B), 3.06 (1H, *dd*, J_{AX} = 10.0 Hz, J_{AB} = 20.0 Hz, H_A); ^{13}C NMR (125 MHz, $CDCl_3$, δ / ppm): 153.04 (C3 pyrazoline), 147.80, 145.14, 142.12 136.81, 135.67, 131.83, 129.14, 129.01, 128.85. 128.60, 128.47, 127.49, 126.10, 125.86, 123.44, 122.65, 120.14, 120.00,

113.55, 110.14, 60.36 (C5 pyrazoline), 47.35 (-$\underline{C}H_2$ benzyl), 40.03 (C4 pyrazoline); ESI-MS m/z: 429.0 [M+H].

1-benzyl-2-(1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole ***(14)***. Yield: 71 %; white solid; m.p.: 206-208 ^{O}C; Anal. Calcd. for $C_{30}H_{26}N_4$: C, 81.42; H, 5.92; N, 12.66 %. Found: C, 81.32; H, 5.70; N, 12.46 %; IR (KBr, cm^{-1}): 1596 (C=N), 1576, 1498, 1462, 1455,1409,1379,1318 (C-N), 1307, 1159, 1118; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.85 (1H, *d*, *J* = 10 Hz, Ar-H), 7.41 (2H, *d*, Ar–H), 7.33-7.30 (1H, *m*, Ar–H), 7.27-7.21 (3H, *m*, Ar–H), 7.18-7.14, (5H, *m*, Ar-H), 7.06 (1H, *t*, *J* = 7.5, Ar-H), 7.0-6.96 (2H, *m*, Ar-H), 6.82-6.78 (3H, *m*, Ar–H), 5.72 (1H, *dd*, J_{AX} = 10 Hz, J_{BX} = 15 Hz , H_X), 5.38 (1H, *d*, J_{DC} = 17.5 Hz , H_D), 5.33 (1H, *d*, J_{CD} = 17.5 Hz , H_C), 3.70 (1H, *dd*, J_{BX} = 15 Hz, J_{AB} = 20 Hz, H_B), 3.05 (1H, *dd*, J_{AX} = 10 Hz, J_{AB} = 20 Hz, H_A), 2.37 (3H, *s*, –CH_3); ^{13}C NMR (125 MHz, CDCl3): 153.19 (C3 pyrazoline), 147.97, 145.34, 142.11, 139.18, 136.76, 135.68, 129.60, 129.45, 129.20. 129.11, 129.08, 128.84, 128.61, 127.48, 126.14, 125.87, 123.55, 123.41, 122.63, 120.00, 119.97, 113.53, 110.20, 60.34 (C5 pyrazoline), 47.39 (-$\underline{C}H_2$ benzyl), 40.16 (C4 pyrazoline), 21.45 (–$\underline{C}H_3$); ESI-MS m/z: 443.1[M+H].

1-benzyl-2-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole ***(15)***. Yield: 60 %; off-white solid; m.p.: 207-209 ^{O}C; Anal. Calcd. for $C_{29}H_{23}ClN_4$: C, 75.23; H, 5.01; N, 12.10 %. Found: C, 75.12; H, 4.90; N, 11.92 %; IR (KBr, cm^{-1}): 1596 (C=N), 1571, 1505, 1492, 1453, 1410, 1392, 1328 (C-N), 1088; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.84 (1H, *d*, *J* = 8 Hz, Ar-H), 7.42-7.39 (2H, *m*, Ar–H), 7.34-7.25 (5H, *m*, Ar–H), 7.19-7.14 (4H, *m*, Ar–H), 7.06 (1H, *t*, *J* = 7.5, Ar-H), 7.01-6.98 (2H, *m*, Ar-H), 6.84-6.80 (3H, *m*, Ar–H), 5.75 (1H, *dd*, J_{AX} = 9.2 Hz, J_{BX} = 13.7 Hz, H_X), 5.37 (1H, *d*, J_{DC} = 17.0 Hz , H_D), 5.33 (1H, *d*, J_{CD} = 17.0 Hz, H_C), 3.65 (1H, *dd*, J_{BX} = 13.5 Hz, J_{AB} = 17.5 Hz, H_B), 2.99 (1H, *dd*, J_{AX} = 9.2 Hz, J_{AB} = 17.7 Hz, H_A); ^{13}C NMR (125 MHz, DMSO-d_6): 153.74 (C3 pyrazoline), 146.68, 144.49, 142.52 136.98, 136.24, 133.69, 131.30, 130.32, 129.35, 129.19, 129.16, 128.08, 127.76, 127.12, 123.15, 122.47, 119.72, 119.55, 113.26, 111.29, 57.54 (C5 pyrazoline), 47.01(-$\underline{C}H_2$ benzyl); ESI-MS m/z: 463.1 [M+H].

1-benzyl-2-(5-(4-bromophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole ***(16)***. Yield: 72 %; white solid; m.p.: 198-200 ^{O}C; Anal. Calcd. for $C_{29}H_{23}BrN_4$: C, 68.64; H, 4.57; N, 11.04 %. Found: C, 68.50; H, 4.49; N, 10.86 %; IR (KBr, cm^{-1}): 1597 (C=N), 1571, 1503, 1488, 1351, 1304 (C-N), 1044; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 7.64-7.55 (5H, *m*, Ar-H), 7.52-7.50 (1H, *m*, Ar–H), 7.29-7.26 (4H, *m*, Ar–H), 7.24-7.18 (2H, *m*, Ar–H), 7.11-7.07 (3H, *m*, Ar-H), 6.86 (2H, *d*, *J* = 10, Ar-H), 6.71 (1H, *t*, *J* = 7.5 Hz, Ar–H), 5.88 (1H, *dd*, J_{AX} = 5 Hz, J_{BX} = 15 Hz, H_X), 5.69 (1H, *d*, J_{DC} = 17.5 Hz, H_D), 5.56 (1H, *d*,

J_{CD} = 17.5 Hz, H_C), 3.85 (1H, *dd*, J_{BX} = 15 Hz, J_{AB} = 20 Hz, H_B), 3.25 (1H, *dd*, J_{AX} = 5 Hz, J_{AB} = 20 Hz, H_A); ^{13}C NMR (125 MHz, $CDCl_3$): 152.74 (C3 pyrazoline), 146.68, 144.78, 141.97 136.78, 135.67, 131.63, 130.82, 129.21, 128.66. 127.59, 127.23, 126.04, 123.57, 122.98, 122.76, 120.37, 120.01, 113.56, 110.08, 60.34 (C5 pyrazoline), 47.27 (-$\underline{C}H_2$ benzyl), 39.77 (C4 pyrazoline); ESI-MS m/z: 506.9 [M+H].

*1-benzyl-2-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (**17**).* Yield: 62 %; white solid; m.p.: 188-190 ^{O}C; Anal. Calcd. for $C_{29}H_{23}FN_4$: C, 78.01; H, 5.19; N, 12.55 %. Found: C, 78.21; H, 5.12; N, 12.31 %; IR (KBr, cm^{-1}): 1597 (C=N), 1531, 1497, 1330 (C-N), 1223; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 7.72-7.69 (2H, *m*, Ar-H), 7.59 (1H, *dd*, *J* = 5, 10 Hz Ar–H), 7.50 (1H, *d*, *J* = 10 Ar–H), 7.29-7.25 (5H, *m*, Ar–H), 7.24-7.18 (2H, *m*, Ar-H), 7.10-7.07 (4H, *m*, Ar-H), 6.87 (2H, *d*, *J* = 10, Ar-H) , 6.71 (1H, *t*, *J* = 7.5, Ar–H), 5.85 (1H, *dd*, J_{AX} = 7.5 Hz, J_{BX} = 12.5 Hz, H_X), 5.68 (1H, *d*, J_{DC} = 17.5 Hz, H_D), 5.56 (1H, *d*, J_{CD} = 17.5 Hz, H_C), 3.86 (1H, *dd*, J_{BX} = 12.5 Hz, J_{AB} = 17.5 Hz, H_B), 3.26 (1H, *dd*, J_{AX} = 7.5 Hz, J_{AB} = 17.5 Hz, H_A); ^{13}C NMR (125 MHz, DMSO-d_6): 163.85, 161.89, 153.83 (C3 pyrazoline), 146.95, 144.74, 142.52, 136.99, 136.26, 129.34, 129.14, 129.02, 129.00, 128.31. 128.25, 128.06, 127.11, 123.14, 122.46, 119.72, 119.39, 116.25, 116.08, 113.19, 111.29, 57.60 (C5 pyrazoline), 47.01 (-$\underline{C}H_2$ benzyl); ESI-MS m/z: 446.8 [M+H].

*3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (**18**).* Yield: 76 %; pale yellow solid; m.p.: 232-234 ^{O}C; Anal. Calcd. for $C_{24}H_{21}N_5S$: C, 70.05; H, 5.14; N, 17.02 %. Found: C, 70.25; H, 5.04; N, 16.80 %; IR (KBr, cm^{-1}): 3406 & 3238 (NH_2), 1595 (C=N), 1506, 1446, 1369, 1292 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.30 (1H, *brs*, -NH), 7.85 (1H, *brs*, -NH), 7.76-7.72 (2H, *m*, Ar–H), 7.36 (1H, *t*, *J* = 8.5 Hz, Ar–H), 7.30-7.27 (4H, *m*, Ar–H), 7.23-7.17 (3H, *m*, Ar–H), 7.12 (2H, *d*, *J* = 6.5 Hz, Ar-H), 6.94 (2H, *d*, *J* = 6.5 Hz, Ar-H), 6.17 (1H, *d*, J_{DC} = 16.5 Hz, H_D), 6.07 (1H, *d*, J_{CD} = 16.5 Hz, H_C), 5.92 (1H, *dd*, J_{AX} = 2.7 Hz, J_{BX} = 10.2 Hz, H_X), 4.10 (1H, *dd*, J_{BX} = 12.2 Hz, J_{AB} = 17.5 Hz, H_B), 3.12 (1H, *dd*, J_{AX} = 3 Hz, J_{AB} = 18.5 Hz, H_A); ^{13}C NMR (125 MHz, DMSO-d_6): 176.88 (C=S), 148.67 (C3 pyrazoline), 144.33, 142.89, 142.79, 138.26, 137.21, 129.07, 128.96, 127.76, 127.49, 127.11, 125.53, 125.09, 123.39, 120.40, 111.66, 62.62 (C5 pyrazoline), 48.18 (-$\underline{C}H_2$ benzyl), 44.45 (C4 pyrazoline); ESI-MS m/z: 412.1 [M+H].

*3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**19**).* Yield: 60 %; pale yellow solid; m.p.: 240-242 ^{O}C; Anal. Calcd. for $C_{25}H_{23}N_5S$: C, 70.56; H, 5.45; N, 16.46 %. Found: C, 70.32; H, 5.38; N, 16.18 %; IR (KBr, cm^{-1}): 3410 & 3244 (NH_2), 1595 (C=N), 1509, 1443, 1366, 1296 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6, δ /

ppm): 8.26 (1H, *brs*, -NH), 7.81 (1H, *brs*, -NH), 7.77-7.72 (2H, *m*, Ar–H), 7.38-7.35 (1H, *m*, Ar–H), 7.33-7.30 (4H, *m*, Ar–H), 7.13-7.12 (2H, *m*, Ar–H), 7.03 (2H, *d*, J = 5 Hz, Ar-H), 6.83 (2H, *d*, J = 5 Hz, Ar-H), 6.17 (1H, *d*, J_{DC} = 20 Hz, H_D), 6.07 (1H, *d*, J_{CD} = 20 Hz, H_C), 5.87 (1H, *dd*, J_{AX} = 5 Hz, J_{BX} = 15 Hz, H_X), 4.08 (1H, *dd*, J_{BX} = 15 Hz, J_{AB} = 20 Hz, H_B), 3.10 (1H, *dd*, J_{AX} = 5 Hz, J_{AB} = 20 Hz, H_A), 2.24 (3H, *s*, $–CH_3$); ^{13}C NMR (125 MHz, DMSO-d_6): 176.81 (C=S), 148.68 (C3 pyrazoline), 144.35, 142.88, 139.87, 138.26, 137.20, 136.61, 129.48, 129.07, 127.76, 127.11, 125.53, 125.07, 123.38, 120.39, 111.67, 62.40 (C5 pyrazoline), 48.15 (-$\underline{C}H_2$ benzyl), 44.43 (C4 pyrazoline), 21.10 (–$\underline{C}H_3$); ESI-MS m/z: 426.0 [M+H].

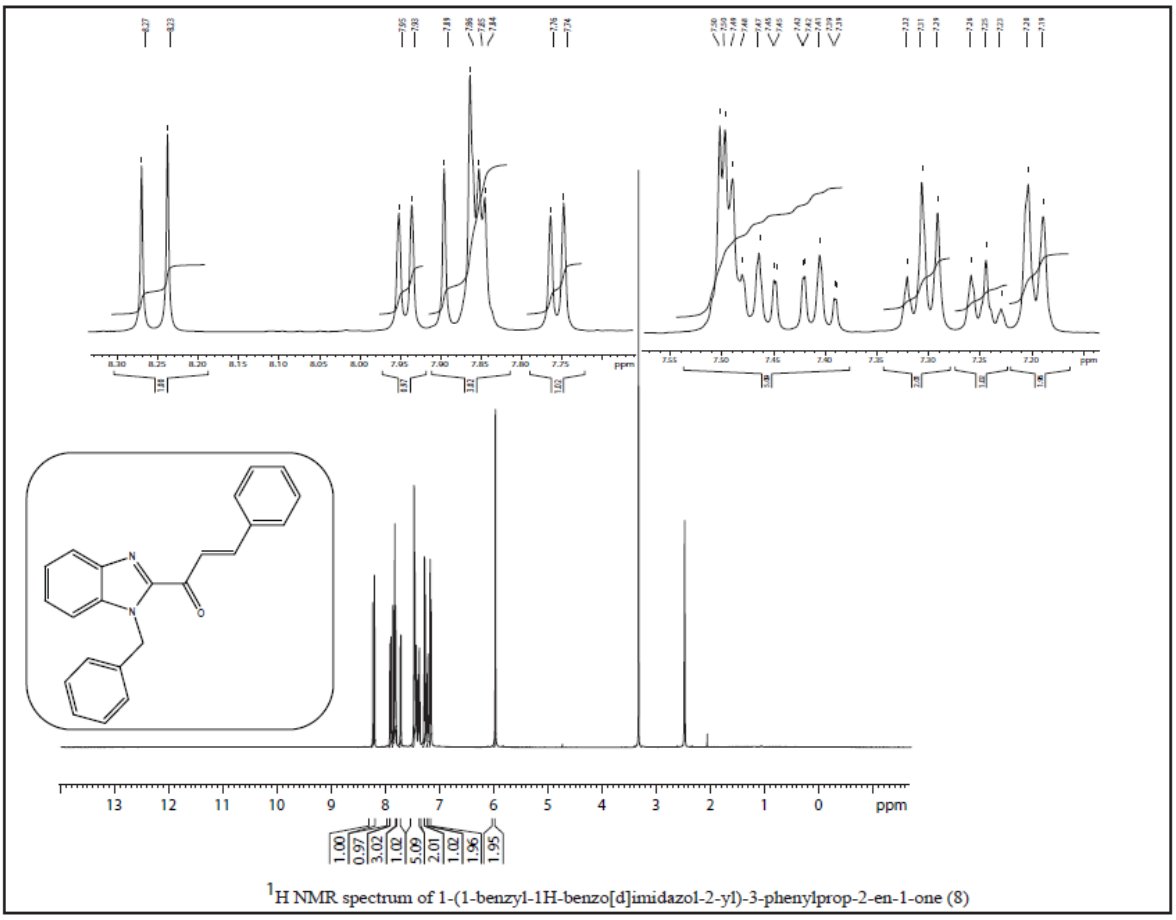
*3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**20**).* Yield: 72 %; pale yellow solid; m.p.: 242-244 ^{O}C; Anal. Calcd. for $C_{24}H_{20}ClN_5S$: C, 64.64; H, 4.52; N, 15.70 %. Found: C, 64.28; H, 4.71; N, 15.48 %; IR (KBr, cm^{-1}): 3406 & 3241 (NH_2), 1595 (C=N), 1501, 1446, 1369, 1294 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.34 (1H, *brs*, -NH), 7.86 (1H, *brs*, -NH), 7.77-7.73 (2H, *m*, Ar–H), 7.38-7.35 (1H, *m*, Ar–H), 7.33-7.27 (6H, *m*, Ar–H), 7.13-7.11 (2H, *m*, Ar–H), 6.96 (2H, *d*, J = 10 Hz, Ar-H), 6.15 (1H, *d*, J_{DC} = 17.5 Hz, H_D), 6.08 (1H, *d*, J_{CD} = 17.5 Hz, H_C), 5.90 (1H, *dd*, J_{AX} = 5 Hz, J_{BX} = 10 Hz, H_X), 4.11 (1H, *dd*, J_{BX} = 10 Hz, J_{AB} = 20 Hz, H_B), 3.13 (1H, *dd*, J_{AX} = 5, J_{AB} = 20 Hz, H_A); ^{13}C NMR (125 MHz, DMSO-d_6): 176.85 (C=S), 148.63 (C3 pyrazoline), 144.25, 142.90, 141.82, 138.29, 137.23, 132.01, 129.09, 128.90, 127.75, 127.63, 127.12, 125.09, 123.39, 120.42, 111.67, 62.06 (C5 pyrazoline), 48.18 (-$\underline{C}H_2$ benzyl), 44.22 (C4 pyrazoline); ESI-MS m/z: 446.1 [M+H].

*3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**21**).* Yield: 75 %; pale yellow solid; m.p. 245-247 ^{O}C; Anal. Calcd. for $C_{24}H_{20}BrN_5S$: C, 58.78; H, 4.11; N, 14.28 %. Found: C, 59.05; H, 4.11; N, 13.91 %; IR (KBr, cm^{-1}): 3408 & 3244 (NH_2), 1594 (C=N), 1507, 1490, 1451, 1436, 1370, 1298 (C-N), 1073, 1031; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.38 (1H, br, s, -NH), 7.89 (1H,br, s, -NH), 7.75 (2H, t, J = 7.5 Hz, Ar–H), 7.42 (2H, *d*, J = 10 Hz, Ar–H), 7.38-7.34 (1H, *m*, Ar–H), 7.33-7.26 (4H, *m*, Ar–H), 7.12 (2H, *d*, J = 5 Hz, Ar–H), 6.90 (2H, *d*, J = 10 Hz, Ar-H), 6.16 (1H, *d*, J_{DC} = 17.5 Hz, H_D), 6.08 (1H, *d*, J_{CD} = 17.5 Hz, H_C), 5.90 (1H, *dd*, J_{AX} = 5 Hz, J_{BX} = 10 Hz, H_X), 4.11 (1H, *dd*, J_{BX} = 10 Hz, J_{AB} = 20 Hz, H_B), 3.13 (1H, *dd*, J_{AX} = 5 Hz, J_{AB} = 20 Hz, H_A); ^{13}C NMR (125 MHz, DMSO-d_6): 176.79 (C=S), 148.63 (C3 pyrazoline), 144.22, 142.89, 142.25, 138.30, 137.23, 131.82, 129.09, 127.98, 127.76, 127.14, 127.11, 125.11, 123.41, 120.52, 120.42, 111.68, 62.12 (C5 pyrazoline), 48.17 (-$\underline{C}H_2$ benzyl), 44.17 (C4 pyrazoline); ESI-MS m/z: 491.8 [M+H].

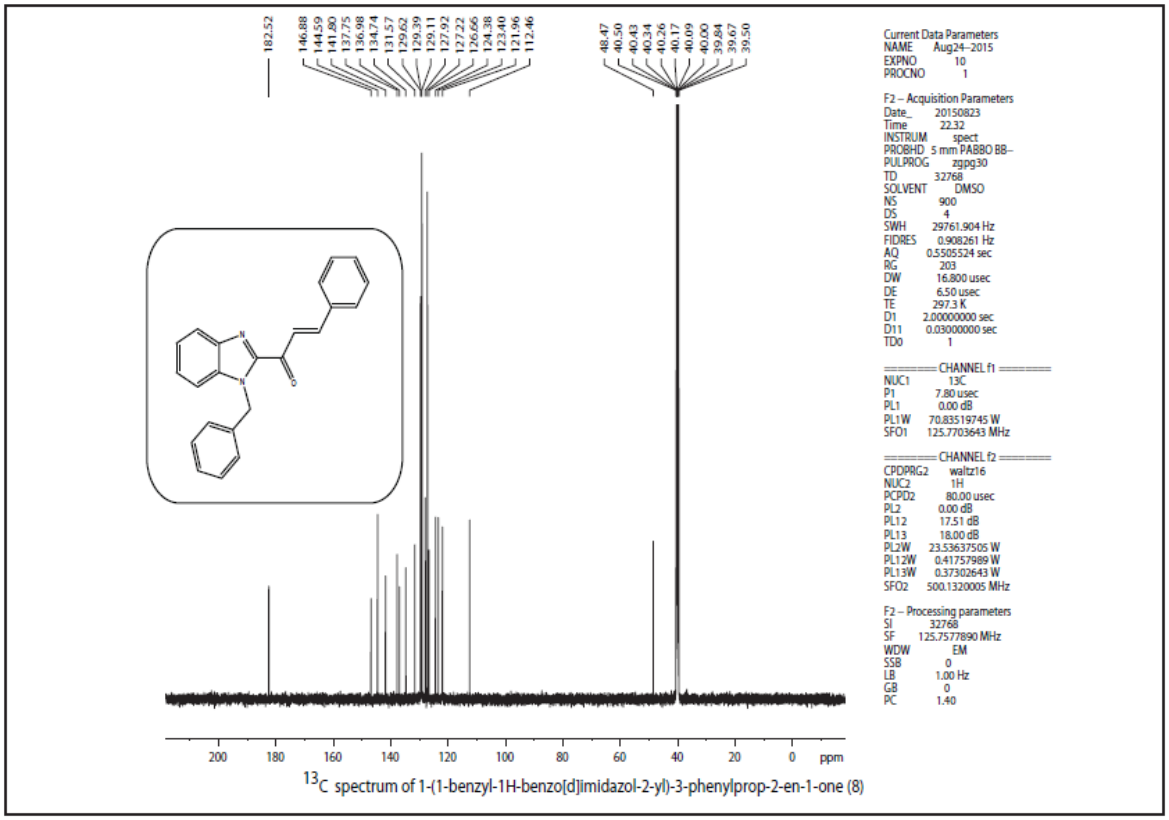
*3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (**22**).* Yield: 70 %; pale yellow solid; m.p.: 241-243 ^{O}C; Anal. Calcd. for $C_{24}H_{20}FN_5S$: C, 67.11; H, 4.69; N, 16.31 %. Found: C, 66.90; H, 4.59; N, 16.20 %; IR (KBr, cm^{-1}): 3413 & 3237 (NH_2), 1595 (C=N), 1509, 1453, 1436, 1371, 1283 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 8.33 (1H, *brs*, -NH), 7.86 (1H, *brs*, -NH), 7.75 (2H, t, *J* = 10 Hz, Ar–H), 7.37 (1H, t, *J* = 7.5 Hz, Ar–H), 7.33-7.28 (4H, *m*, Ar–H), 7.13-7.11 (2H, *m*, Ar–H), 7.07-7.04 (2H, *m*, Ar-H), 6.99-6.96 (2H, *m*, Ar-H), 6.16 (1H, *d*, J_{DC} = 17.5 Hz, H_D), 6.08 (1H, *d*, J_{CD} = 17.5 Hz , H_C), 5.92 (1H, dd, J_{AX} = 5, J_{BX} = 15 Hz, H_X), 4.10 (1H, dd, J_{BX} =15, J_{AB} =20 Hz, H_B), 3.13 (1H, dd, J_{AX} = 5, J_{AB} = 20 Hz, H_A); ^{13}C NMR (DMSO-d_6): 176.82 (C=S), 162.54, 160.61, 148.64 (C3 pyrazoline), 144.29, 142.89, 139.02, 139.00, 138.31, 137.24, 129.09, 127.77, 127.69, 127.11, 125.09, 123.39, 120.41, 115.75, 115.58, 111.68, 61.98 (C5 pyrazoline), 48.16 (-$\underline{C}H_2$ benzyl), 44.33 (C4 pyrazoline); ESI-MS m/z: 430.0 [M+H].

COPIES OF 1D-2D NMR AND MASS SPECTRA

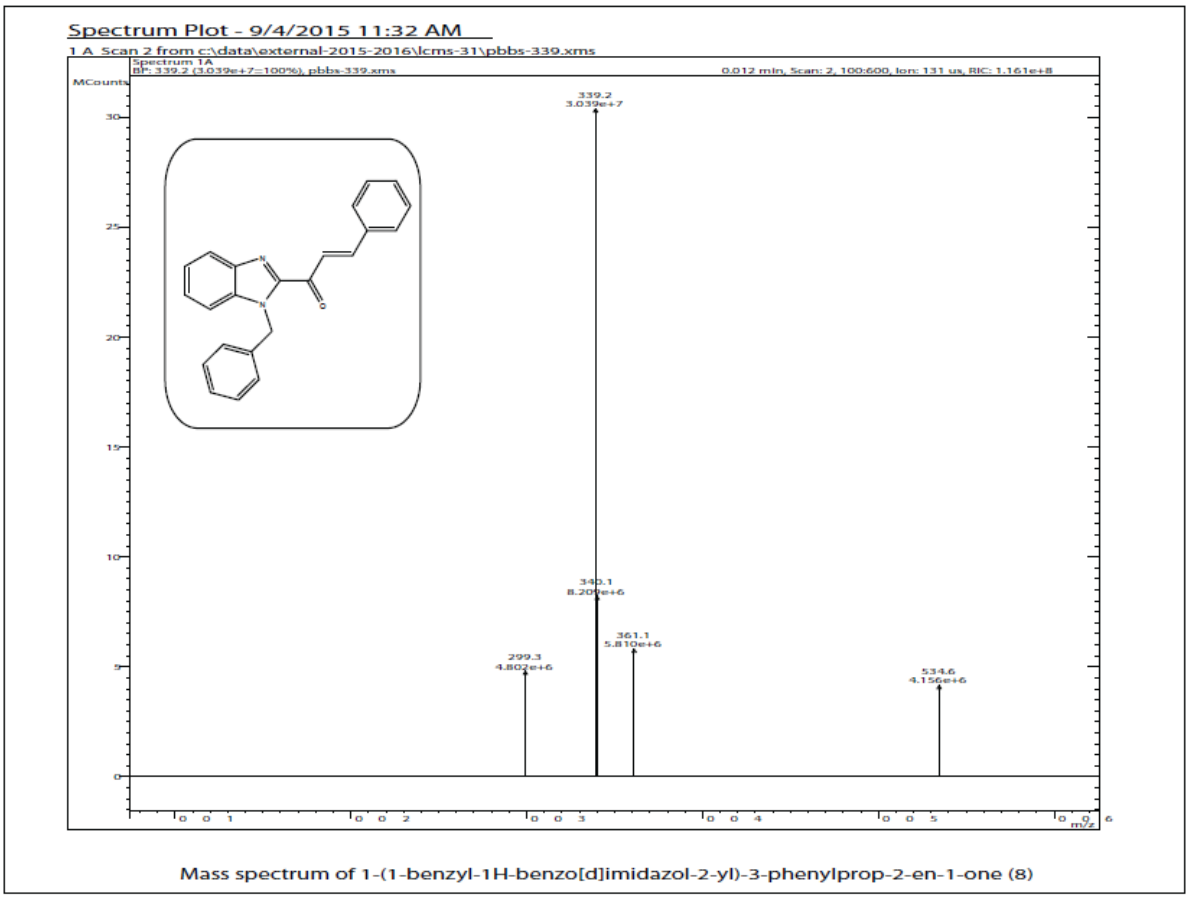
Compound **8**



^{1}H NMR spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-phenylprop-2-en-1-one (8)

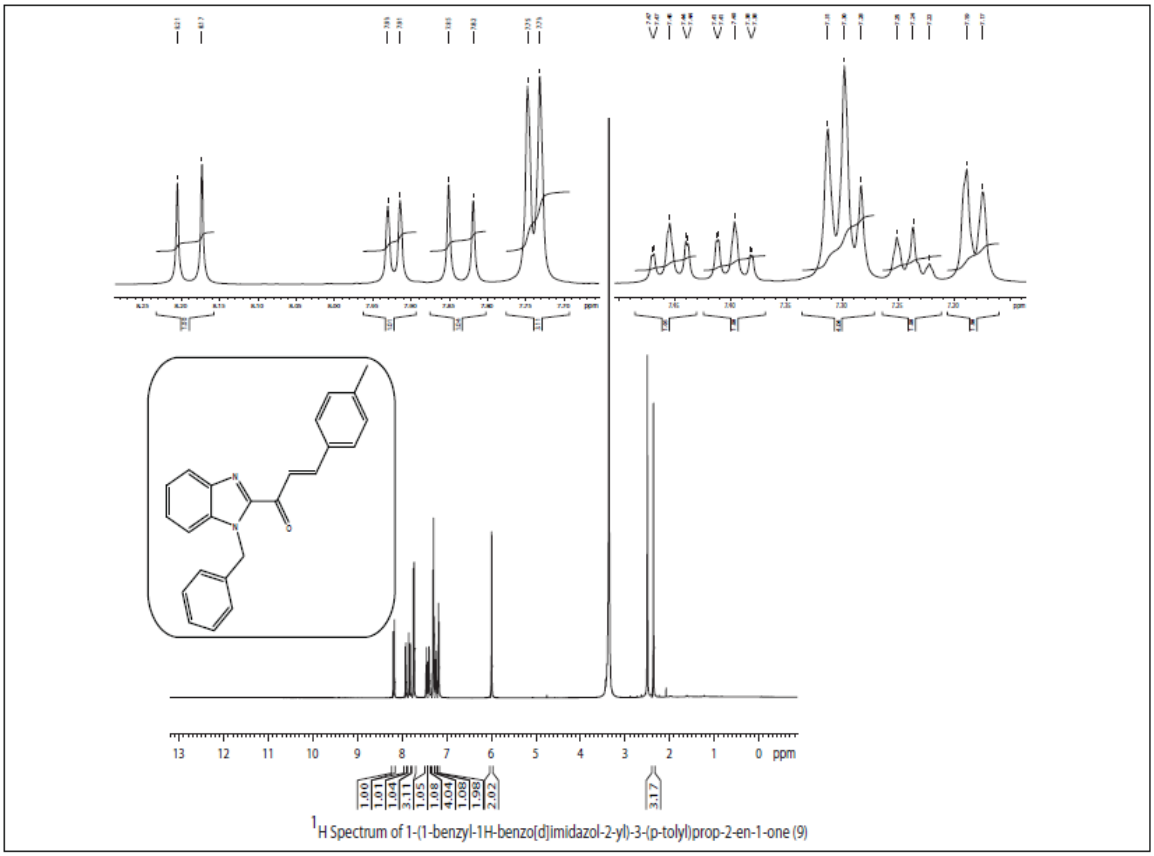


^{13}C spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-phenylprop-2-en-1-one (8)

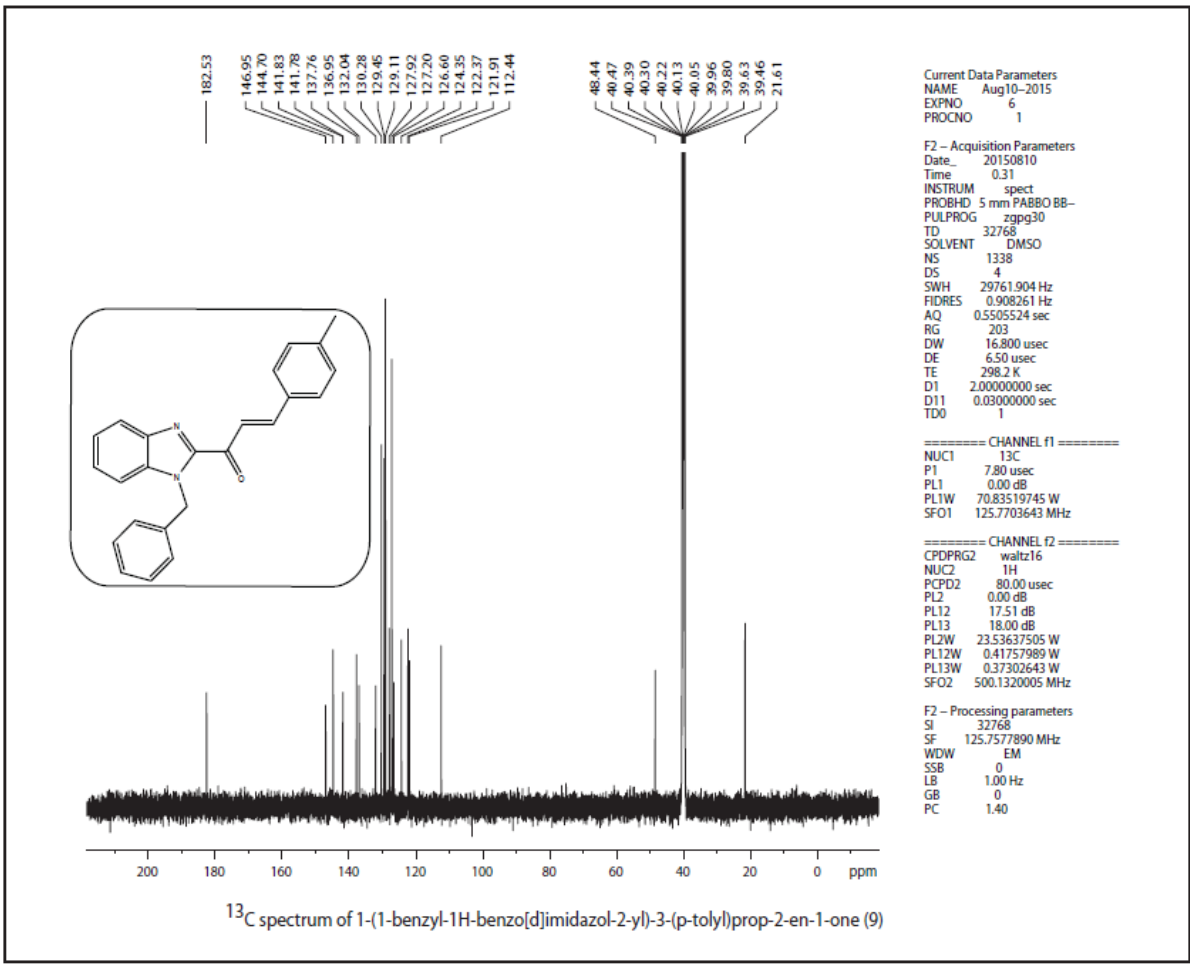


Mass spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-phenylprop-2-en-1-one (8)

Compound **9**



^{1}H Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(p-tolyl)prop-2-en-1-one (9)



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PROCNO 1

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SOLVENT DMSO
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FIDRES 0.908261 Hz
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DW 16.800 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

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P1 7.80 usec
PL1 0.00 dB
PL1W 70.83519745 W
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
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PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.51 dB
PL13 18.00 dB
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PL12W 0.41757989 W
PL13W 0.37302643 W
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F2 -- Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
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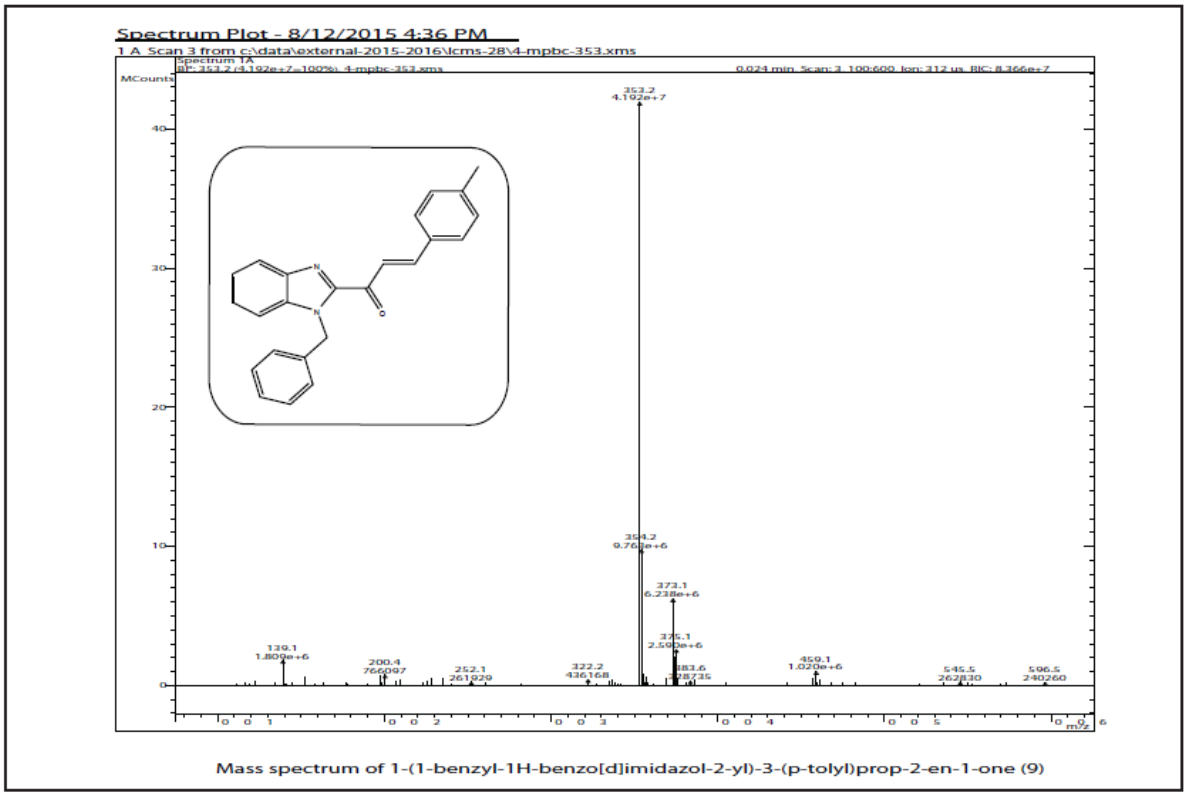
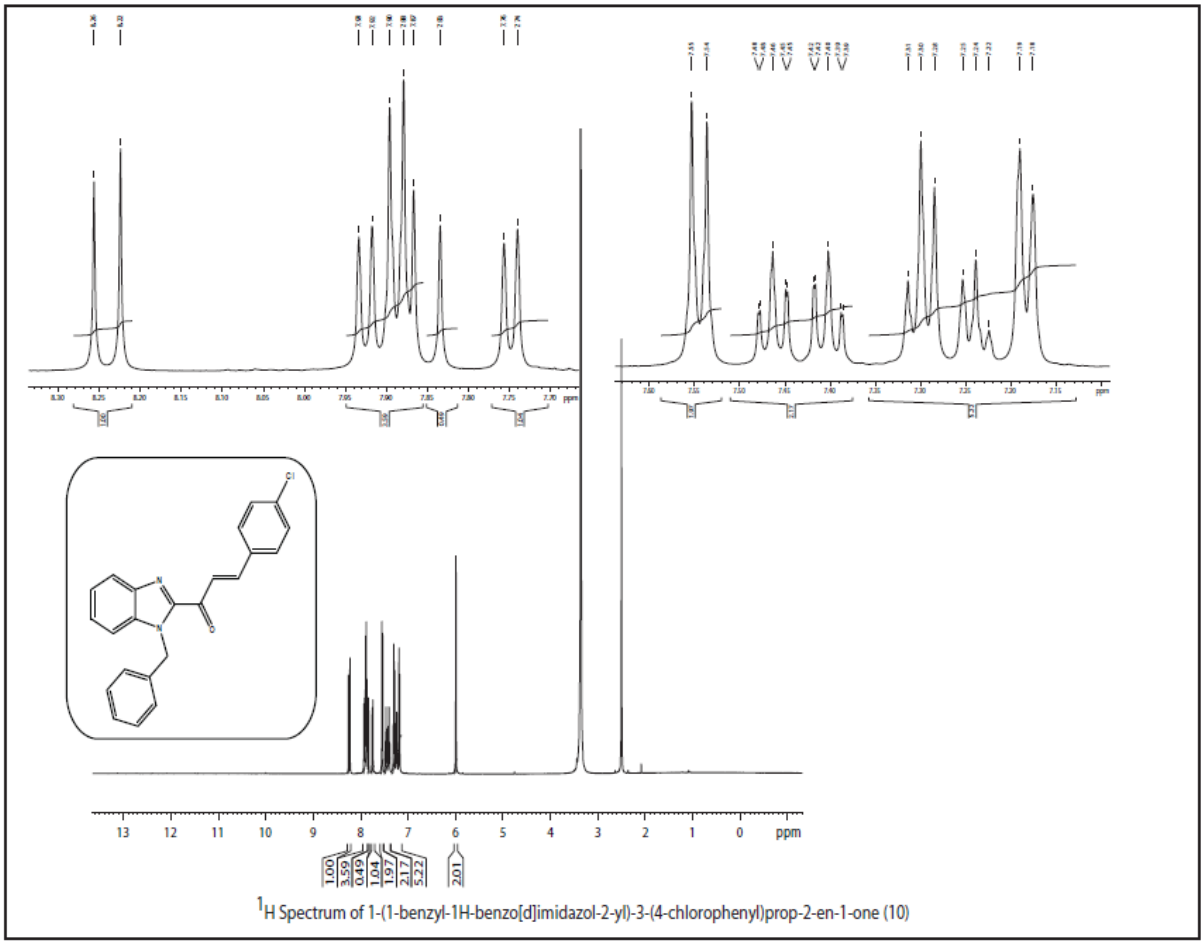
^{13}C spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(p-tolyl)prop-2-en-1-one (9)

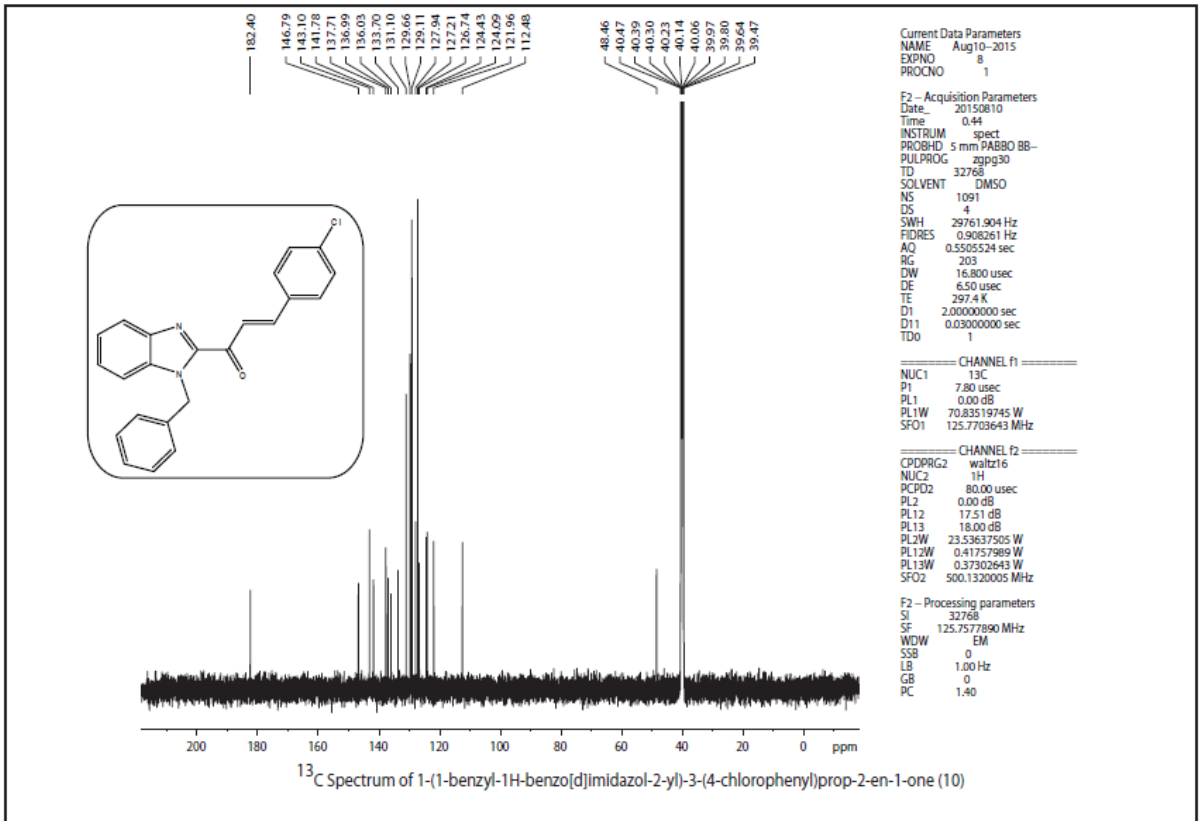


Mass spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(p-tolyl)prop-2-en-1-one (9)

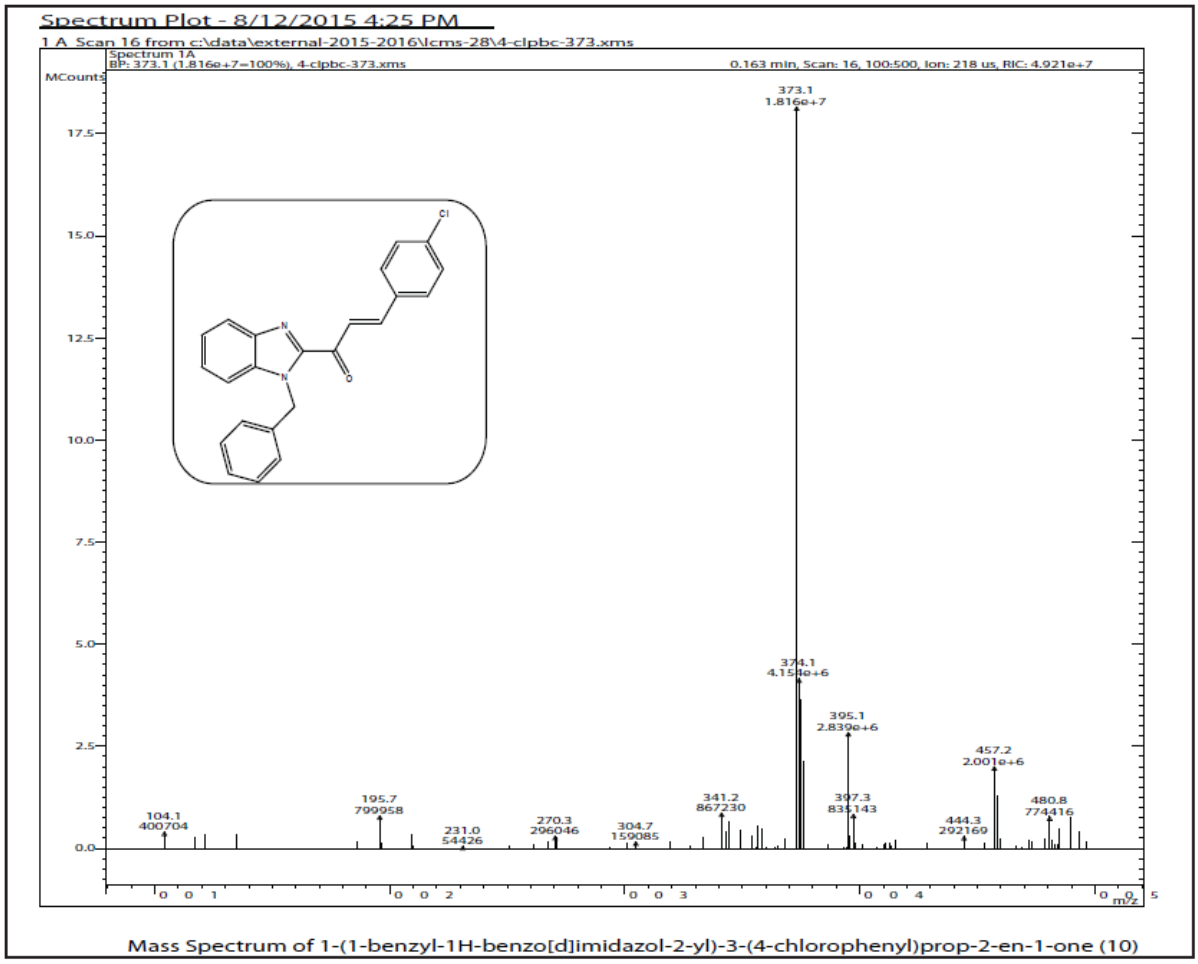
Compound **10**



^{1}H Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (10)

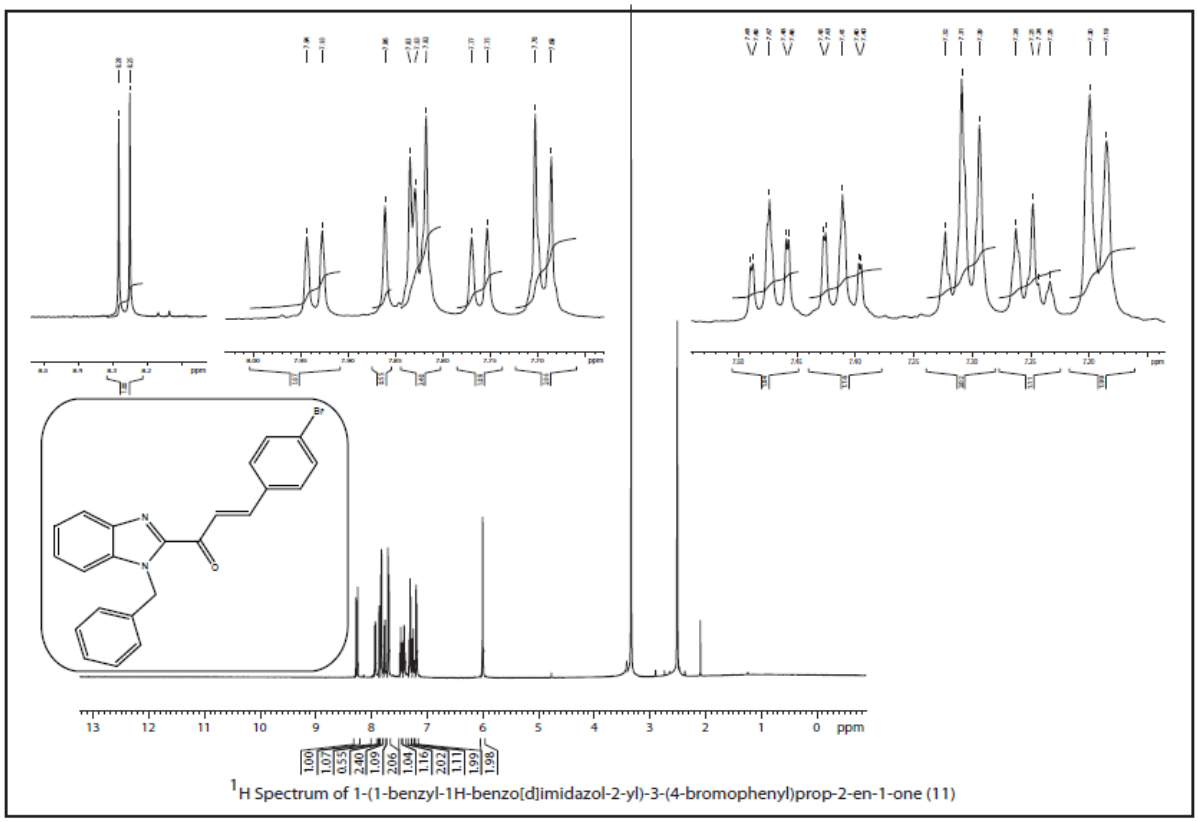


^{13}C Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (10)



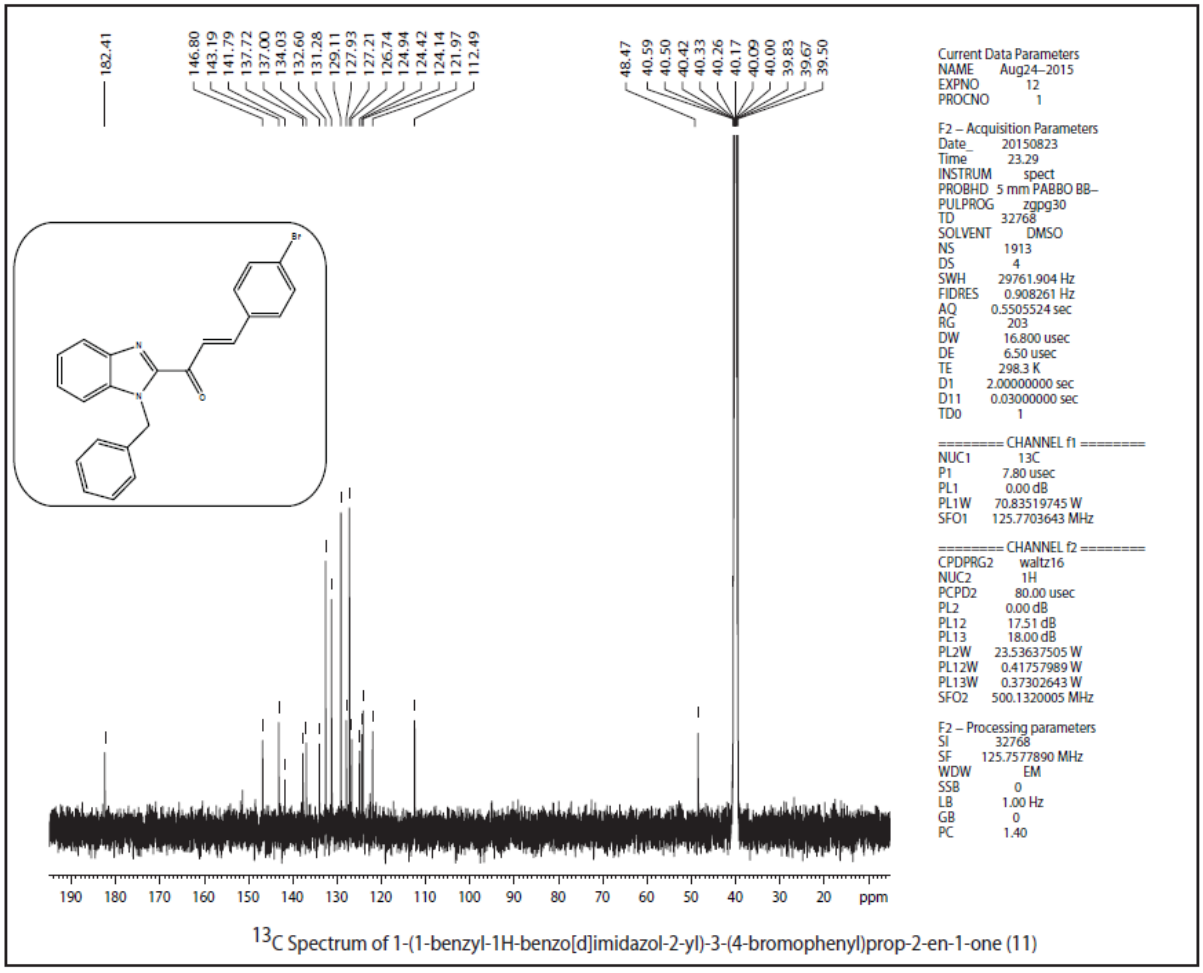
Mass Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (10)

Compound **11**

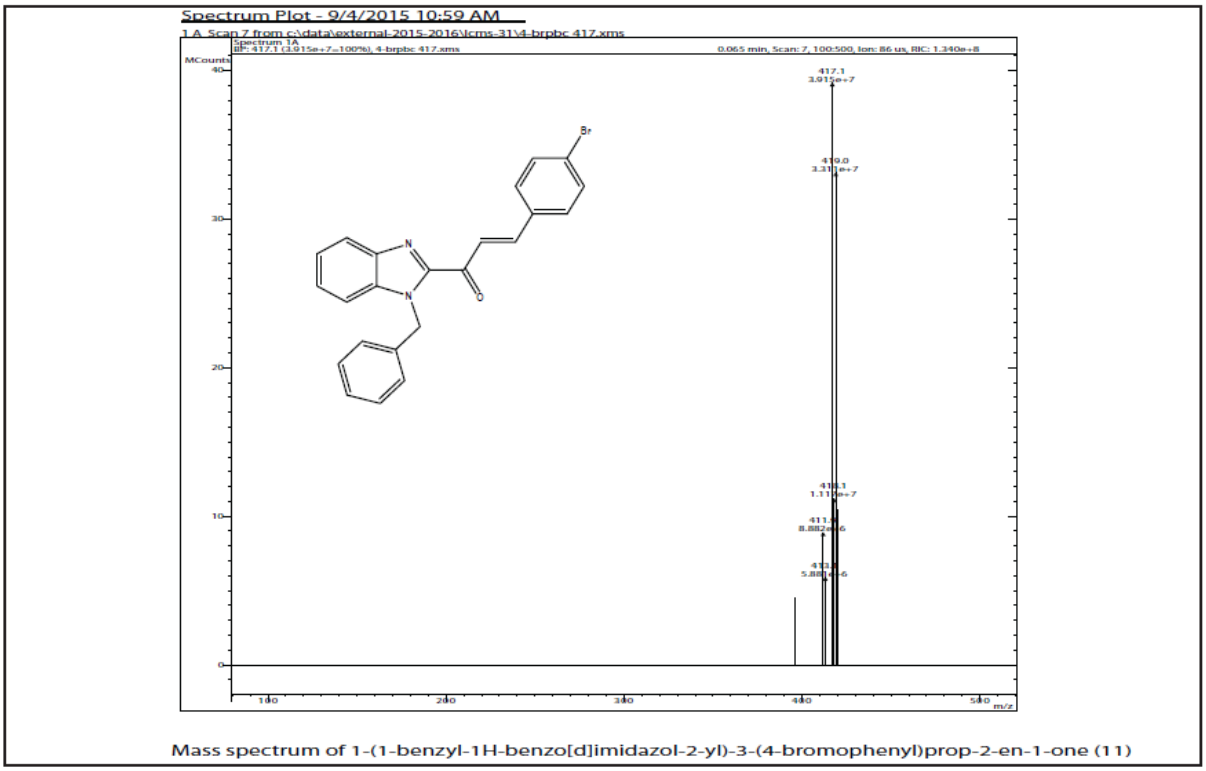


^{1}H Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-bromophenyl)prop-2-en-1-one (11)

218



^{13}C Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-bromophenyl)prop-2-en-1-one (11)

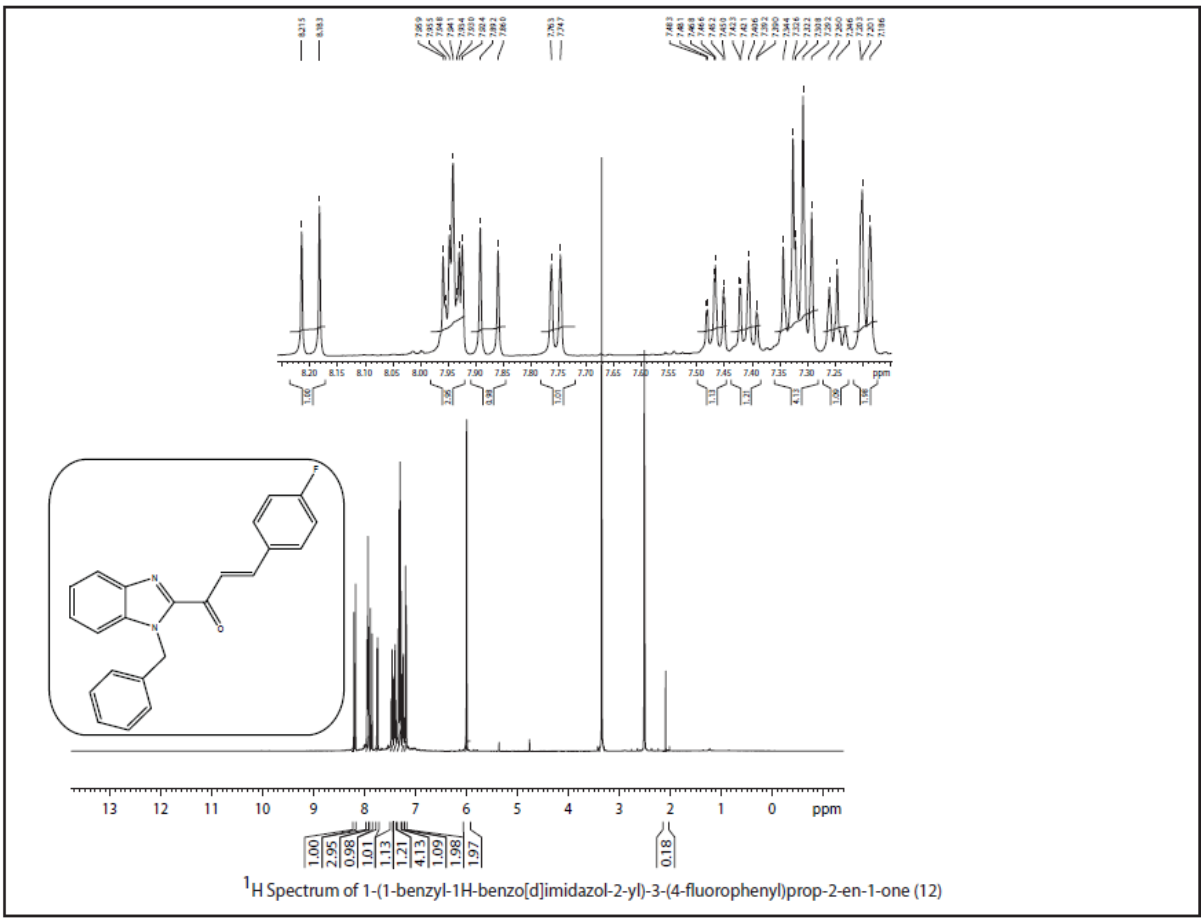


Mass spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-bromophenyl)prop-2-en-1-one (11)

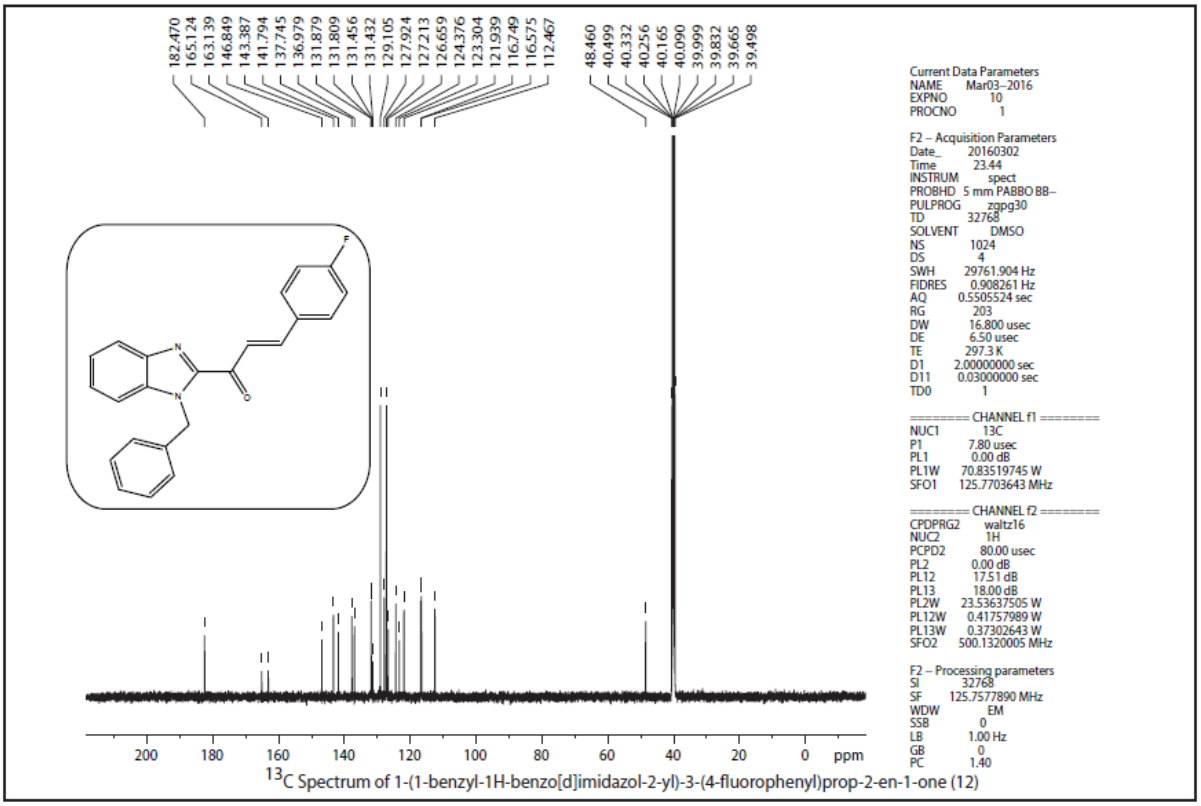
219

220

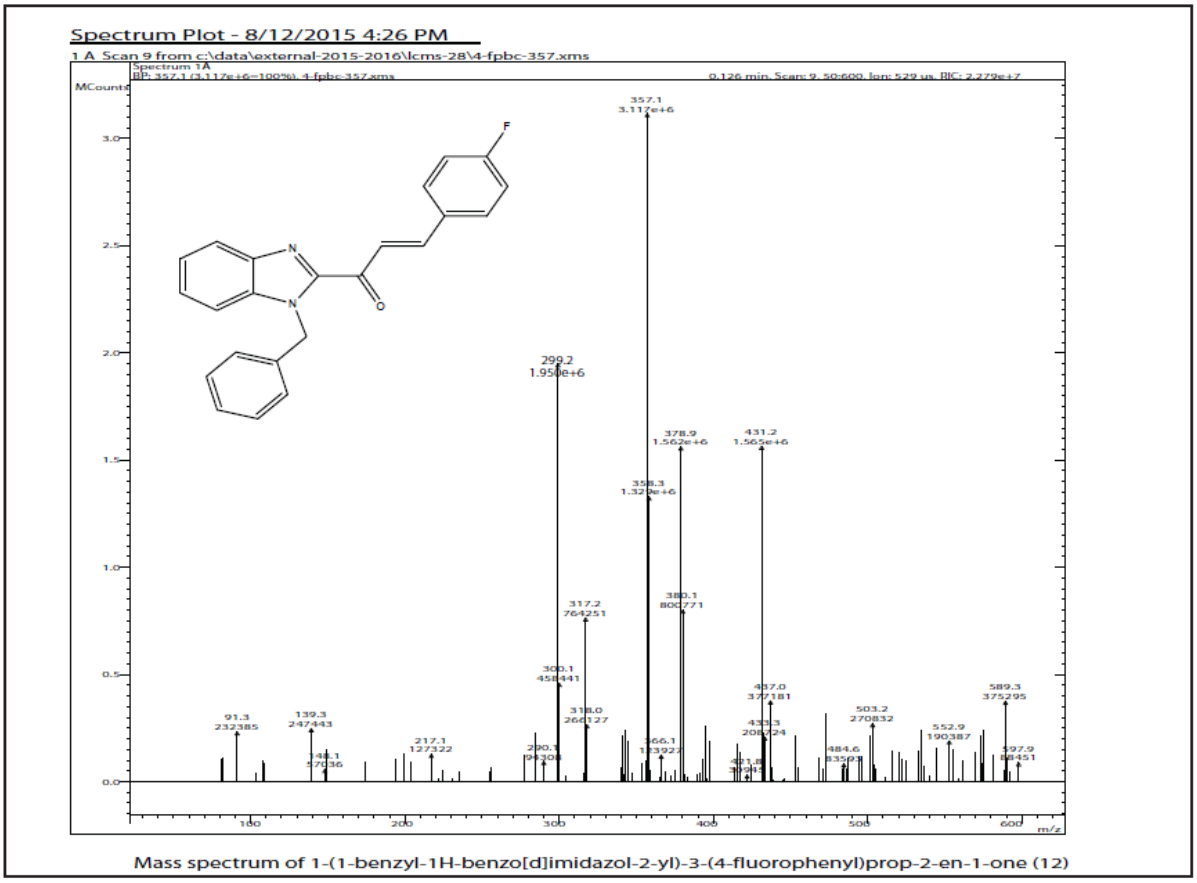
Compound **12**



^{1}H Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-fluorophenyl)prop-2-en-1-one (12)

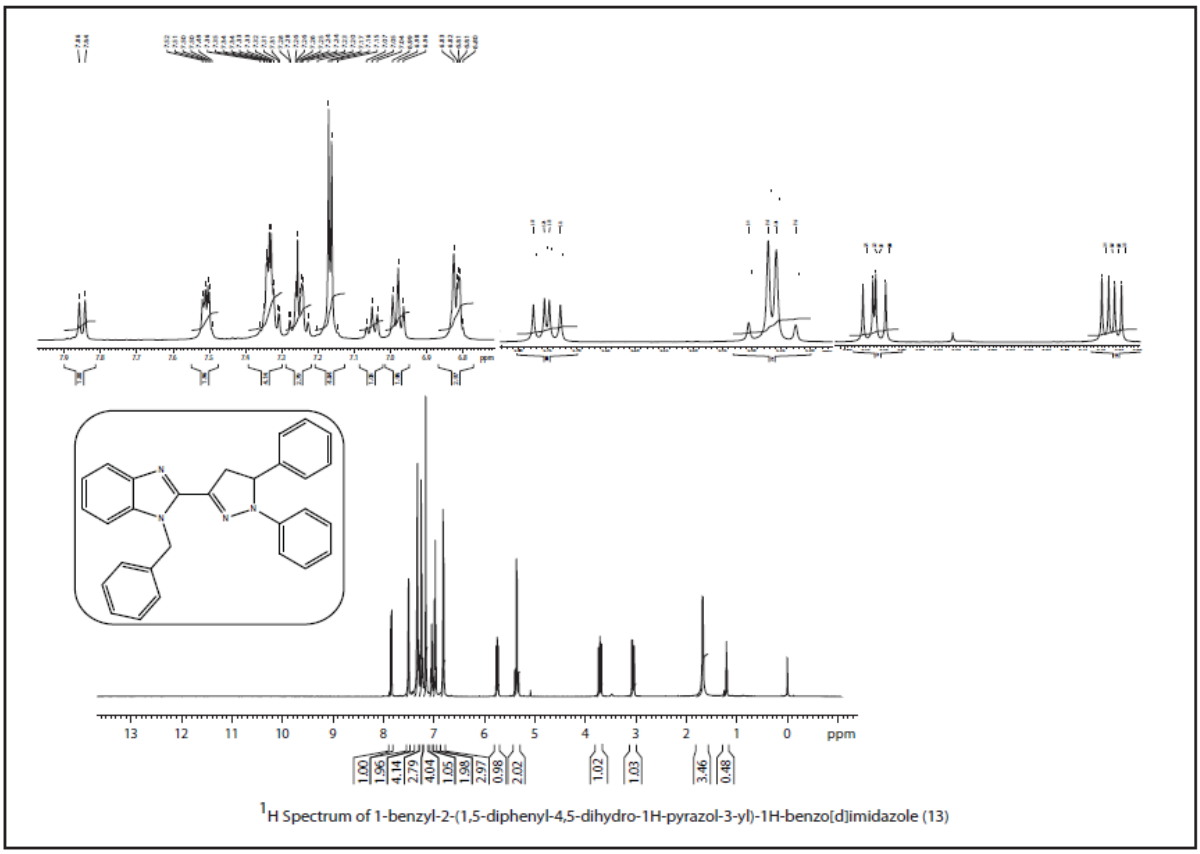


^{13}C Spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-fluorophenyl)prop-2-en-1-one (12)



Mass spectrum of 1-(1-benzyl-1H-benzo[d]imidazol-2-yl)-3-(4-fluorophenyl)prop-2-en-1-one (12)

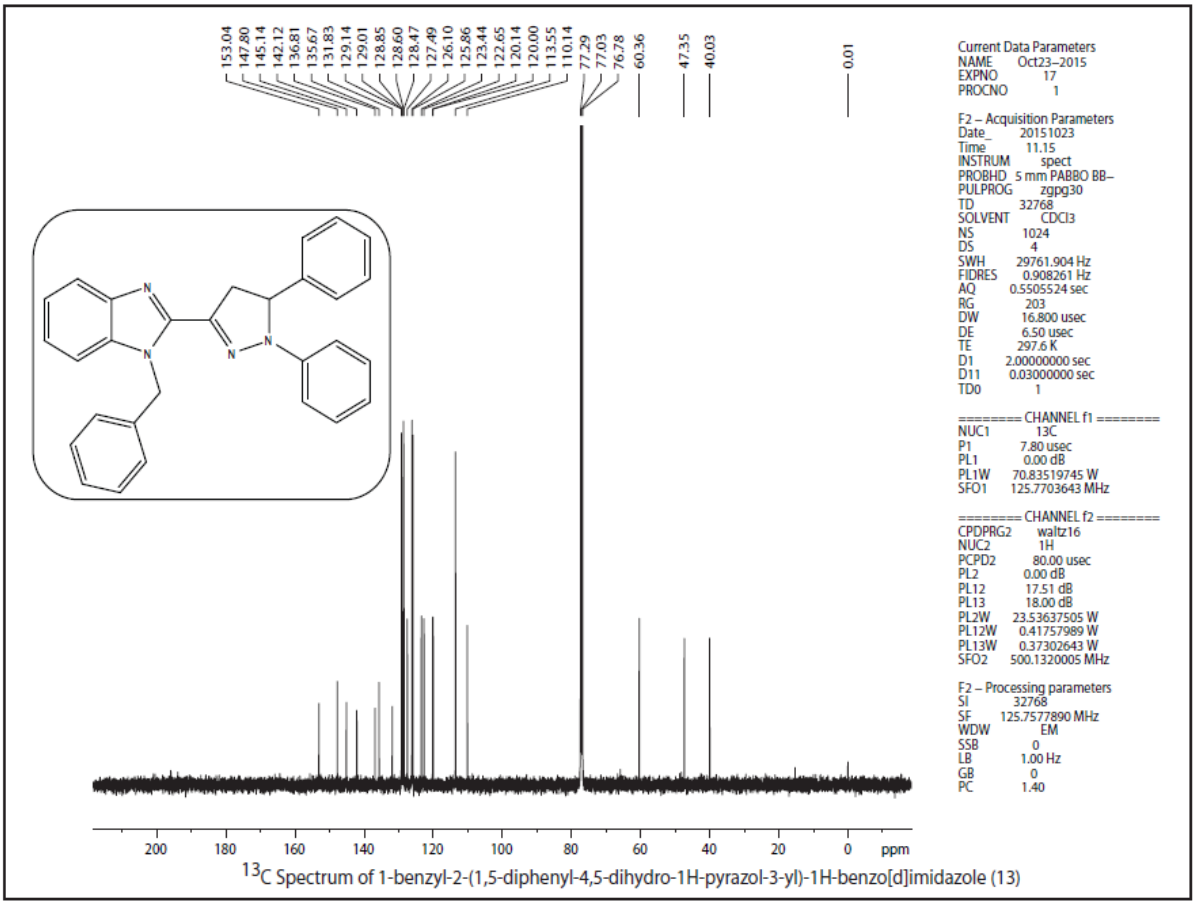
Compound **13**



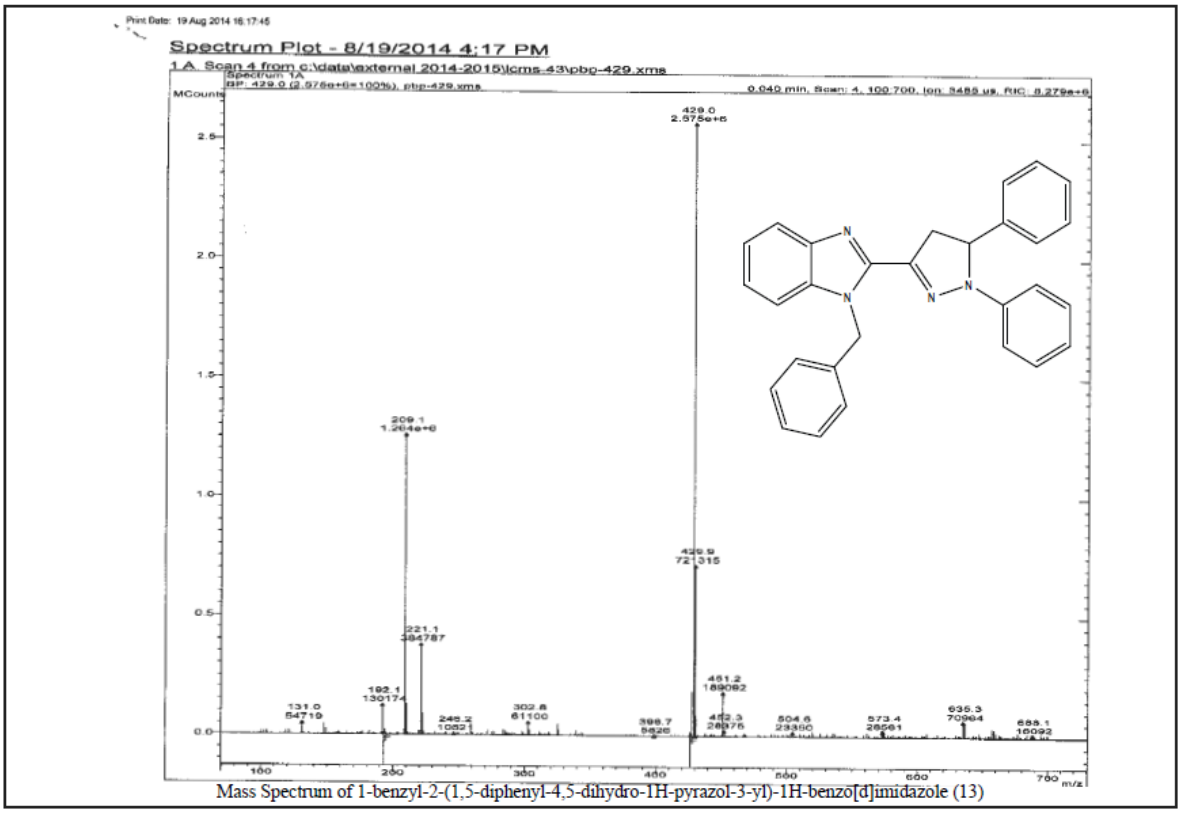
^{1}H Spectrum of 1-benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (13)

228

229

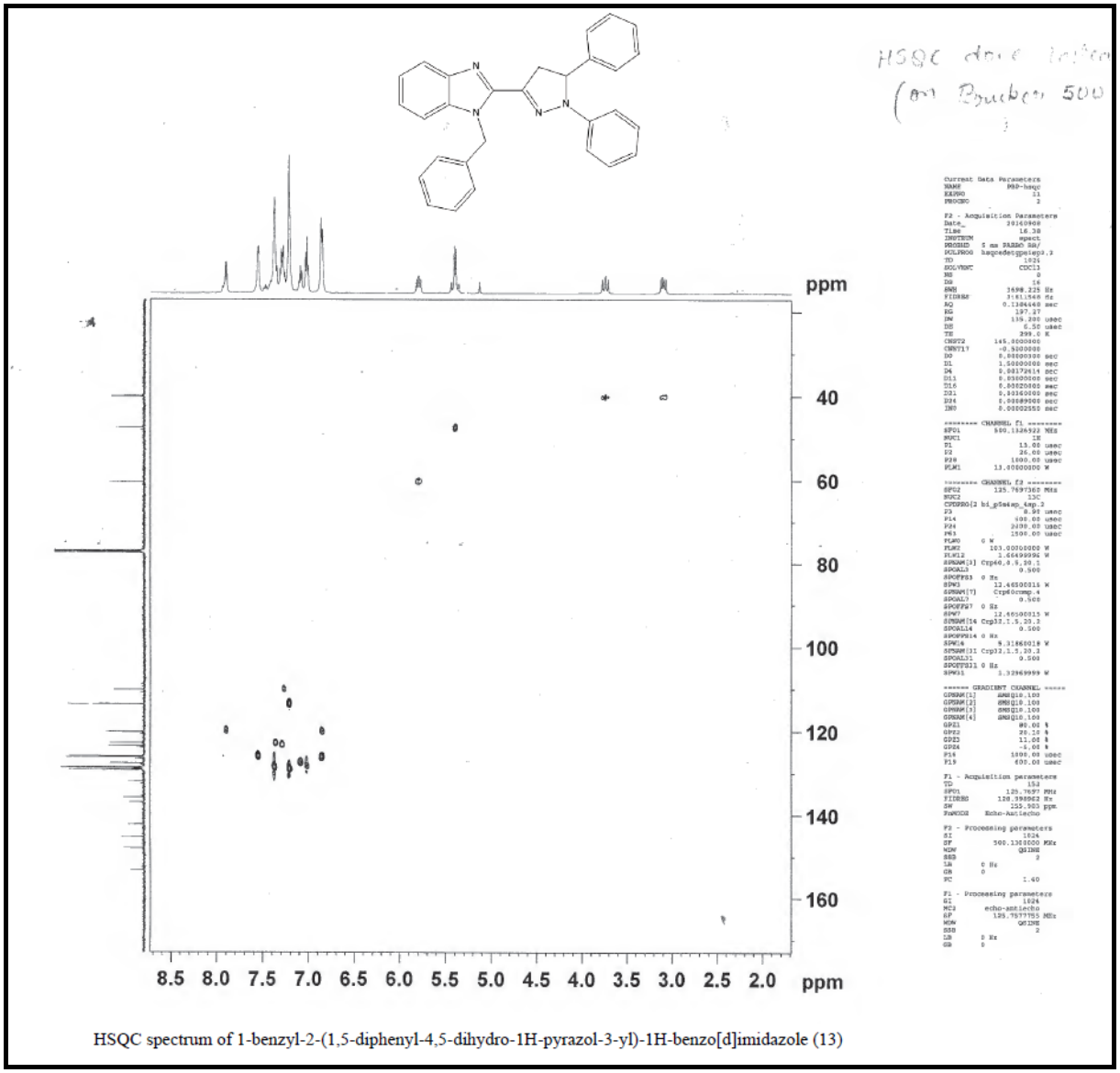


^{13}C Spectrum of 1-benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (13)



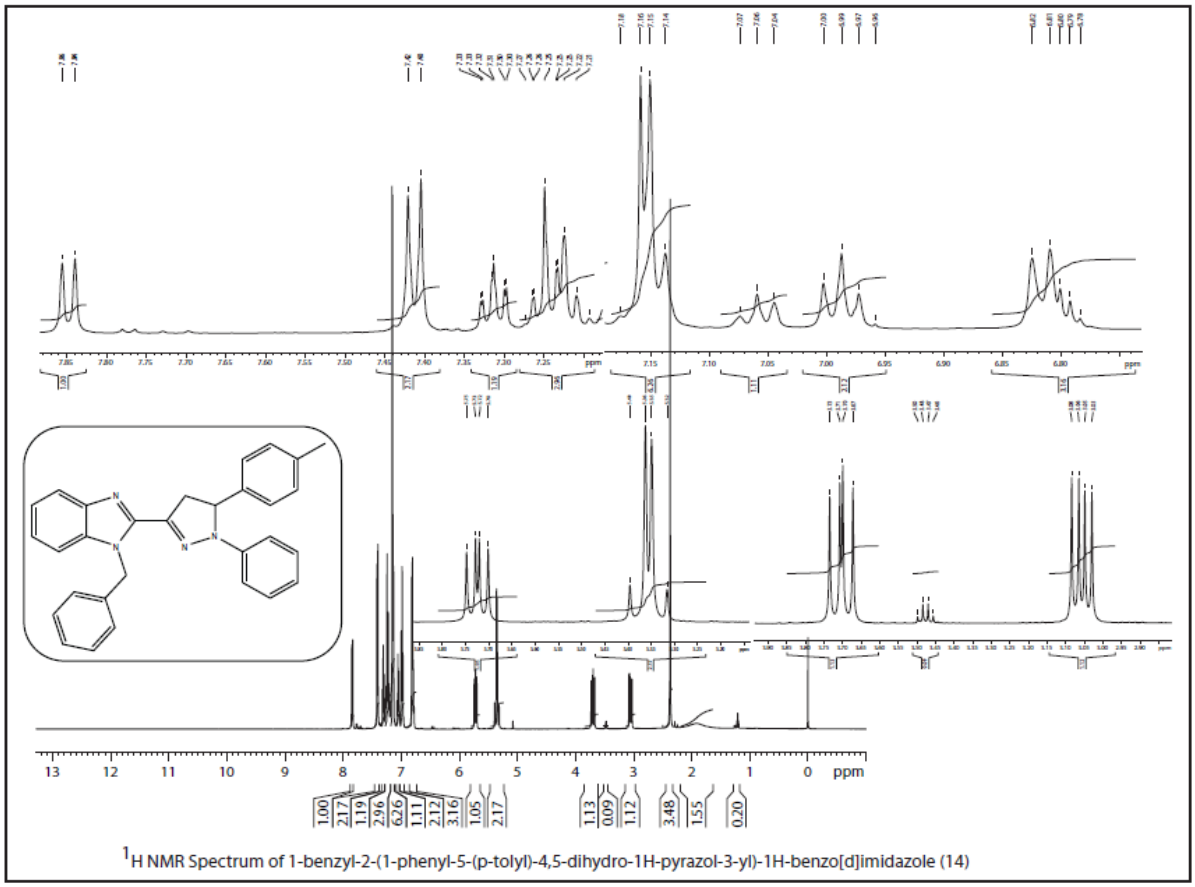
Mass Spectrum of 1-benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (13)

230

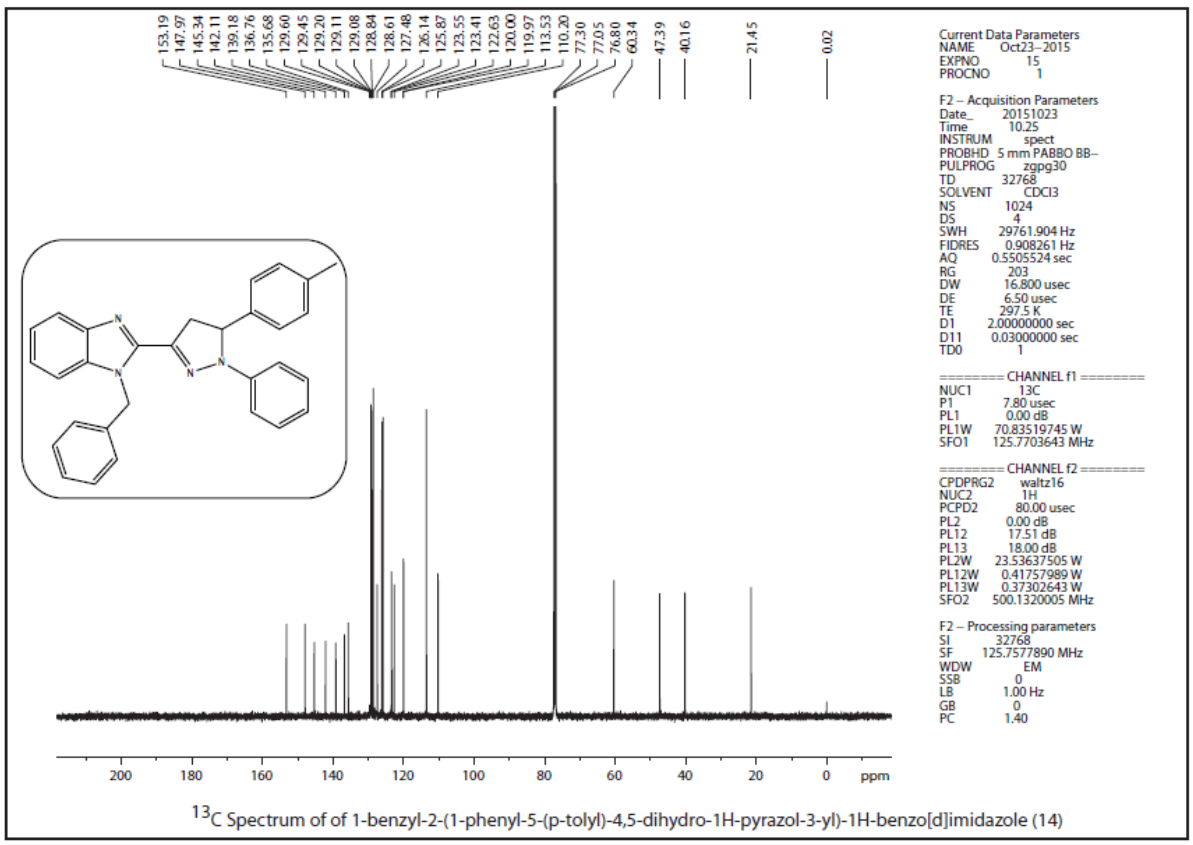


HSQC spectrum of 1-benzyl-2-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (13)

Compound **14**

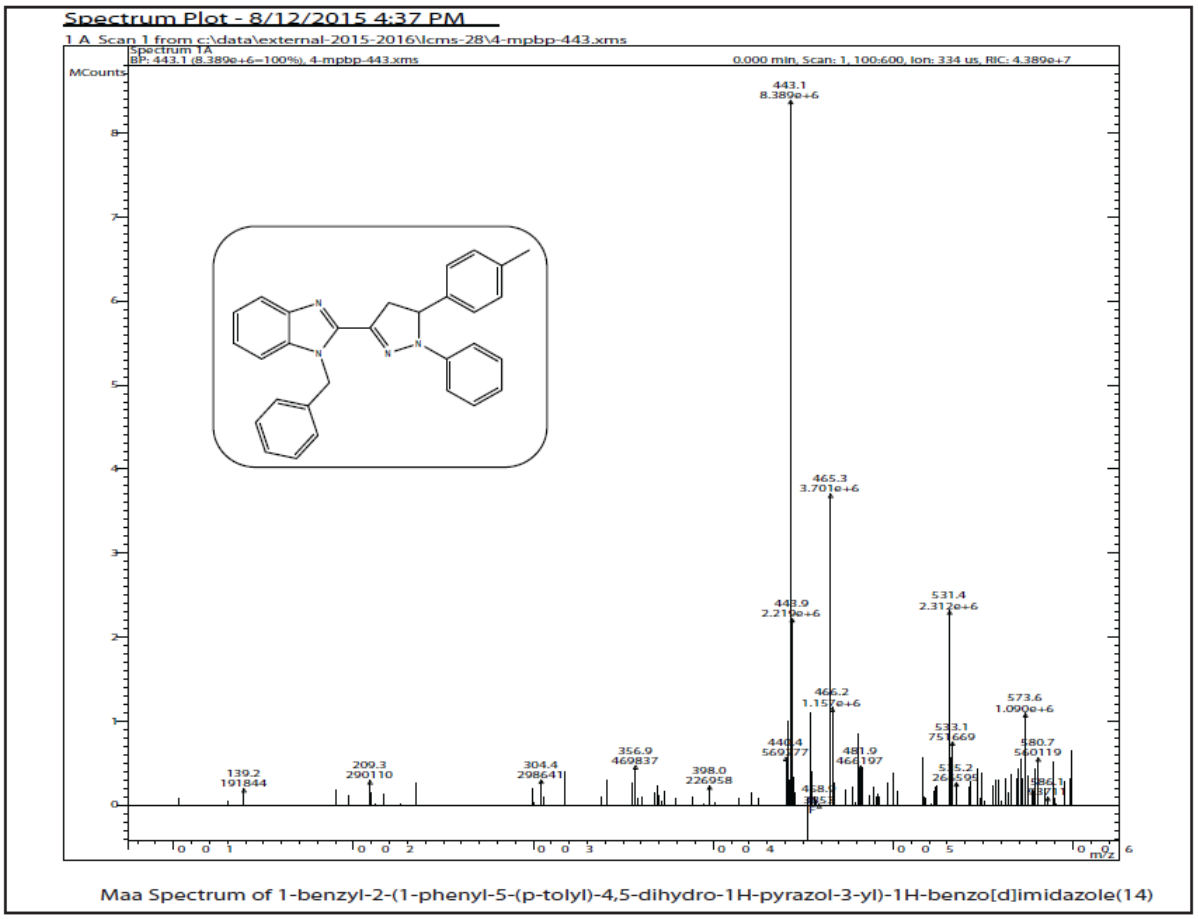


^{1}H NMR Spectrum of 1-benzyl-2-(1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (14)



^{13}C Spectrum of of 1-benzyl-2-(1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (14)

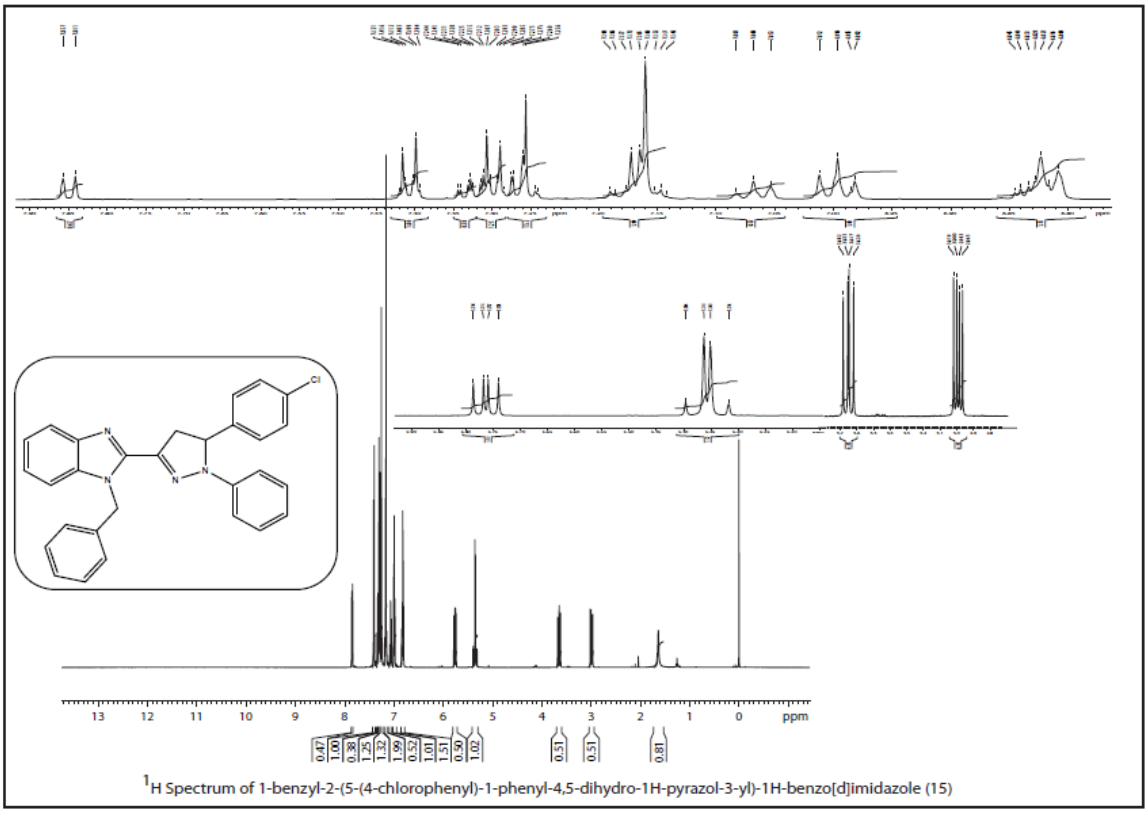
247



Maa Spectrum of 1-benzyl-2-(1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole(14)

248

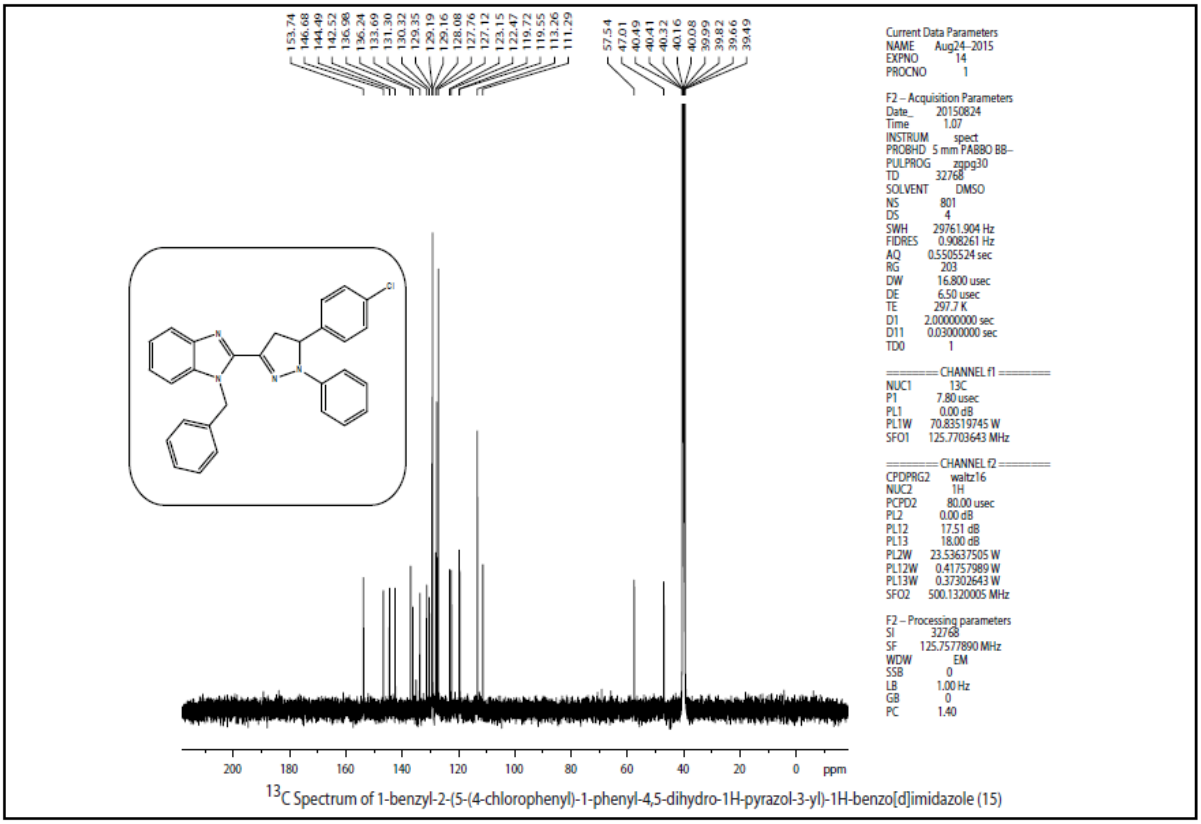
249 *Compound* **15**



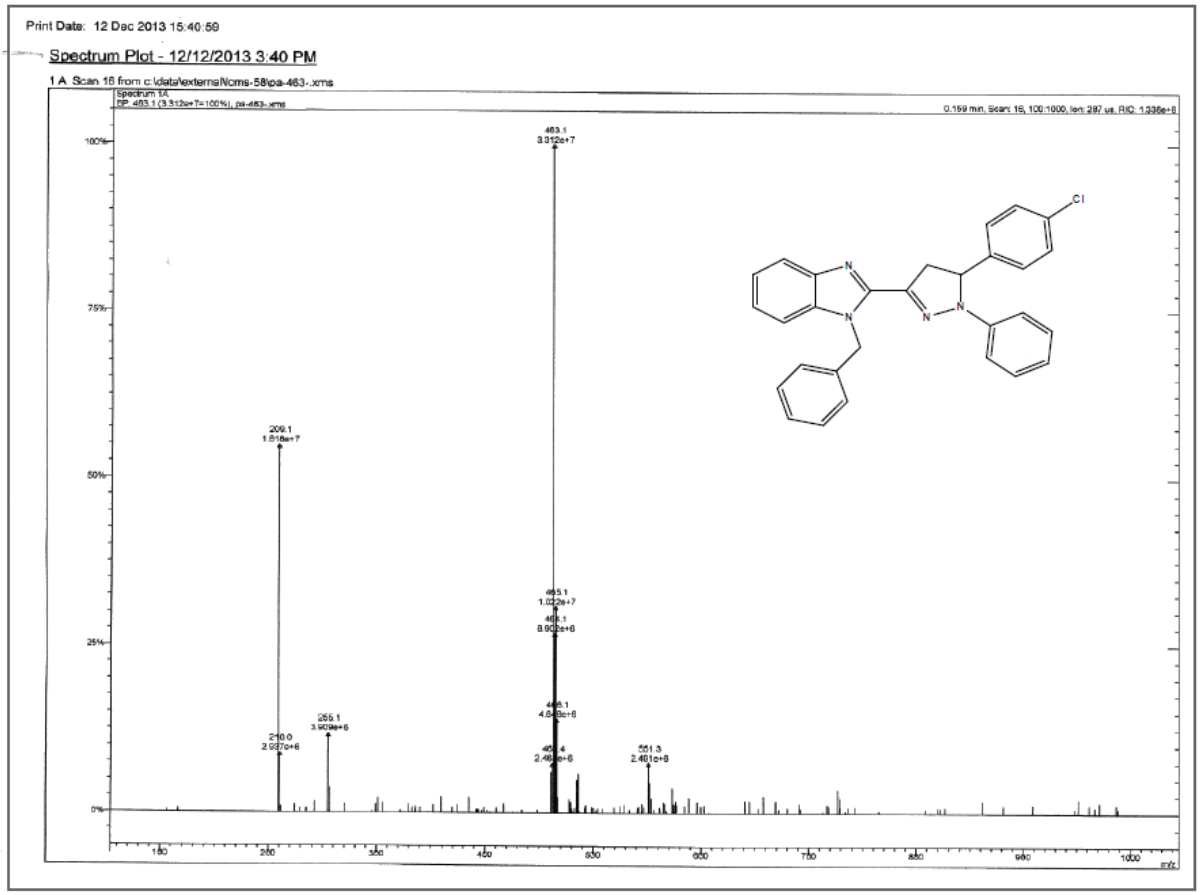
^{1}H Spectrum of 1-benzyl-2-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (15)

250

251

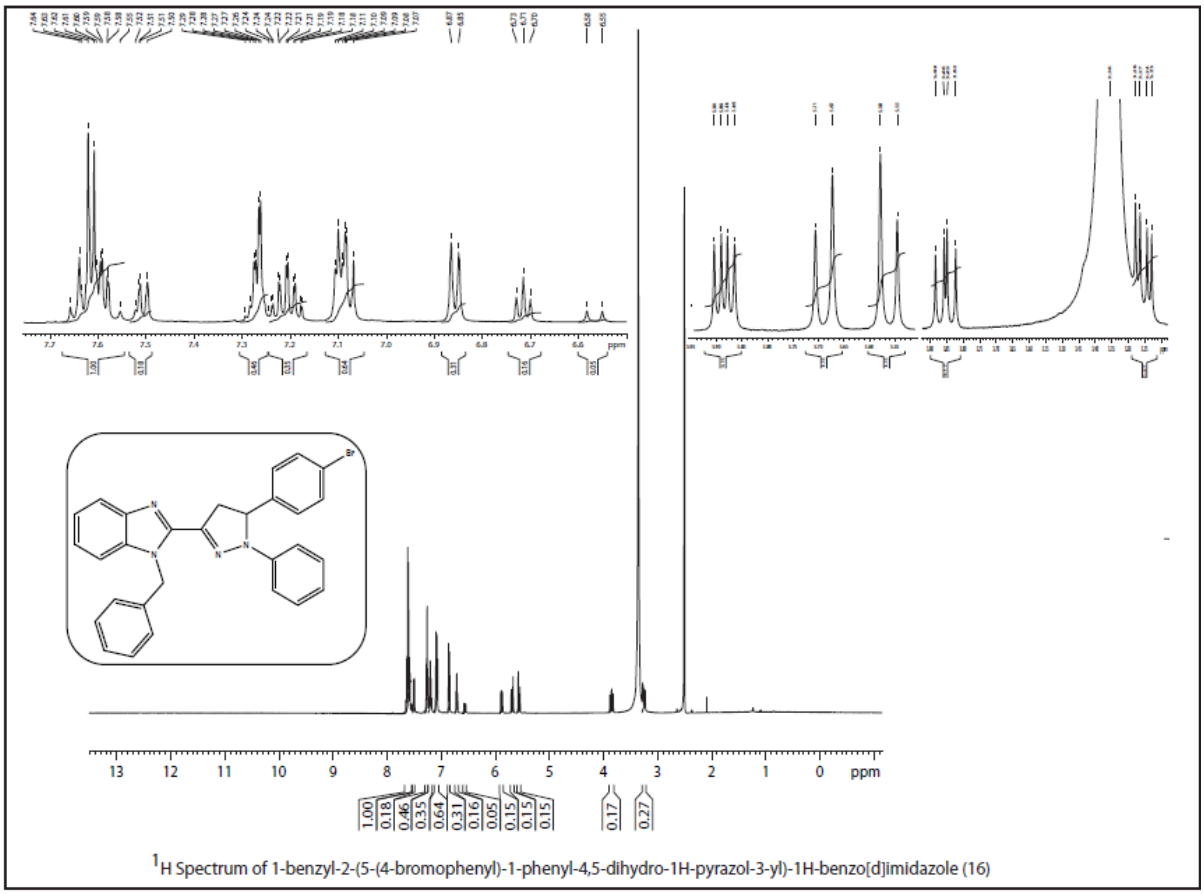


252 ^{13}C Spectrum of 1-benzyl-2-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (15)

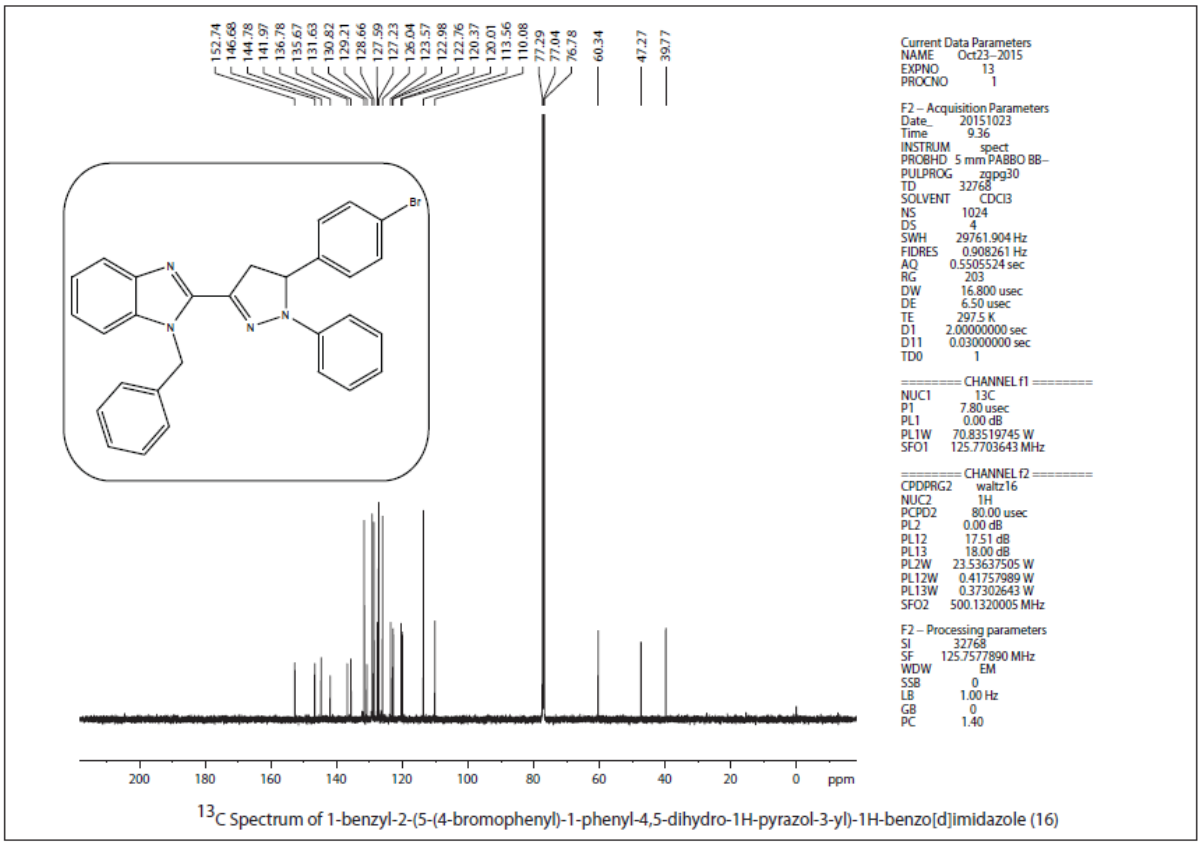


253 Mass spectrum 1-benzyl-2-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (15)

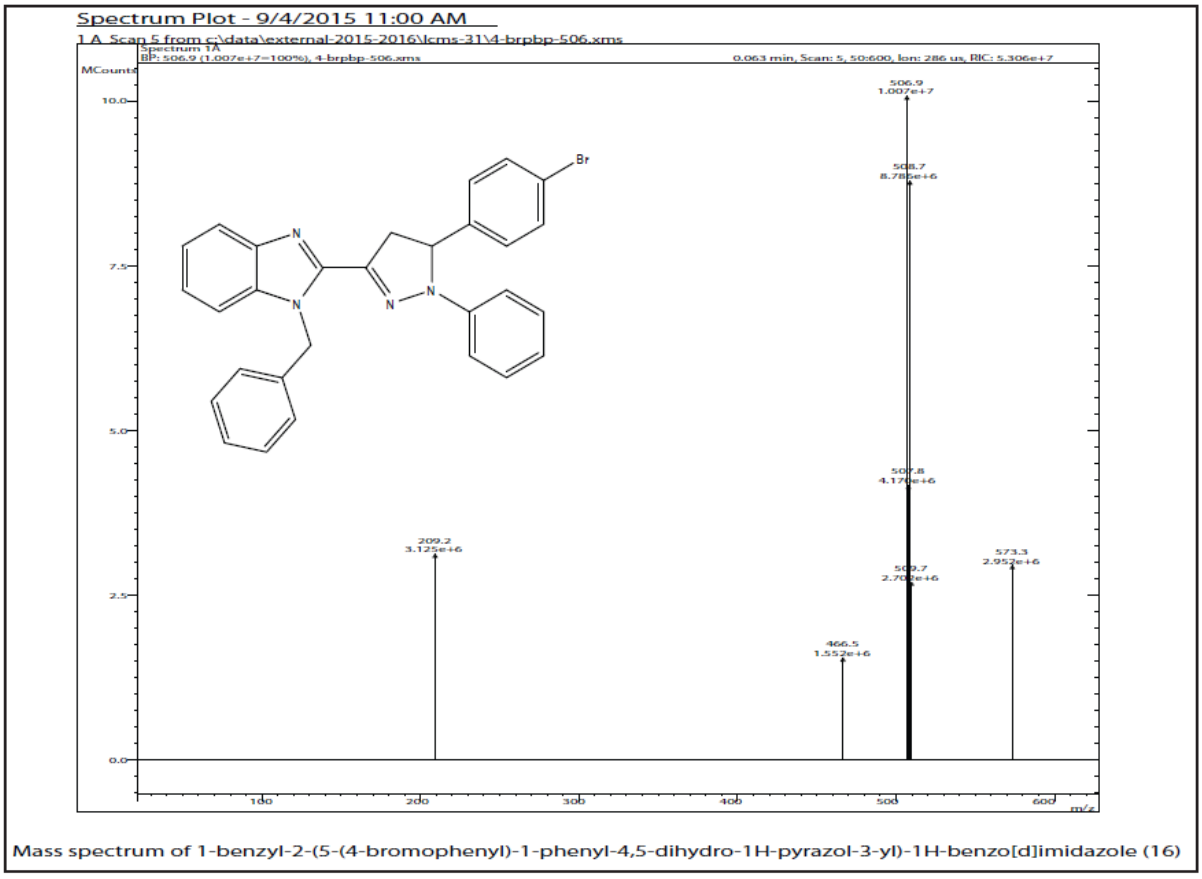
Compound **16**



^{1}H Spectrum of 1-benzyl-2-(5-(4-bromophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (16)

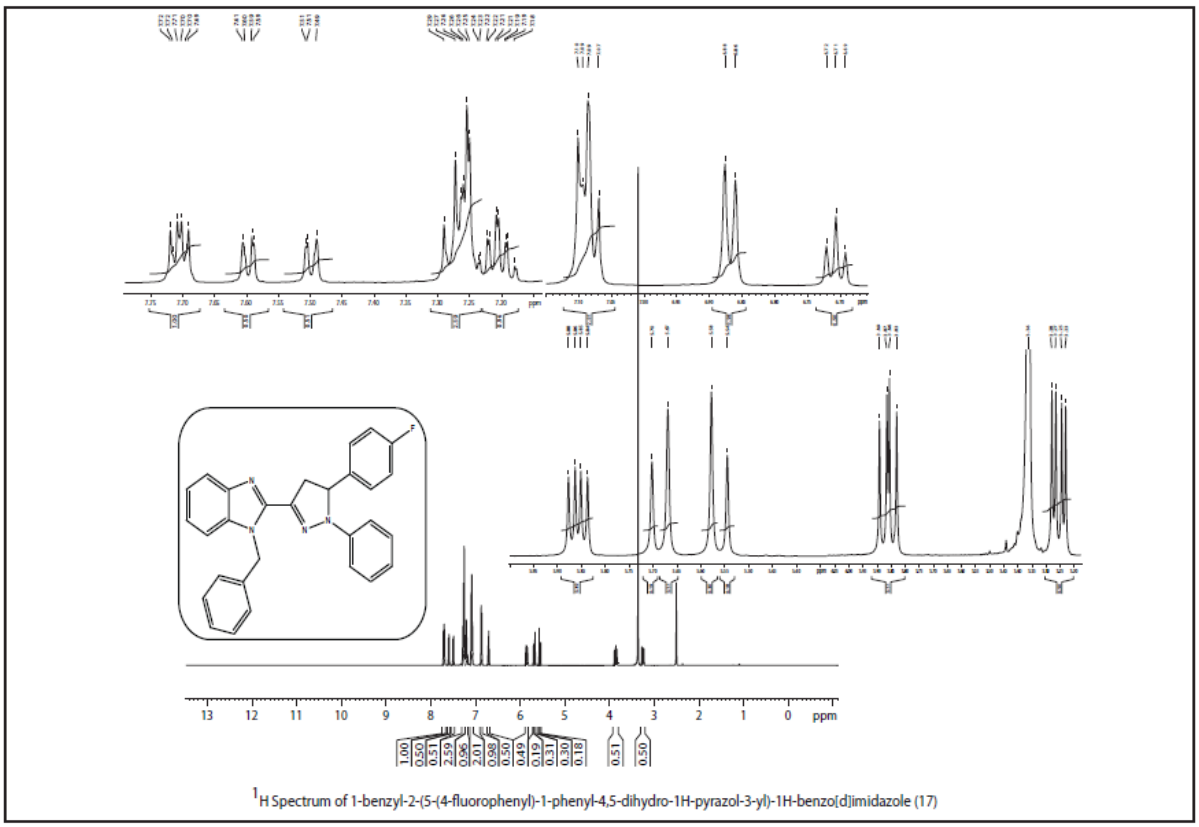


^{13}C Spectrum of 1-benzyl-2-(5-(4-bromophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (16)



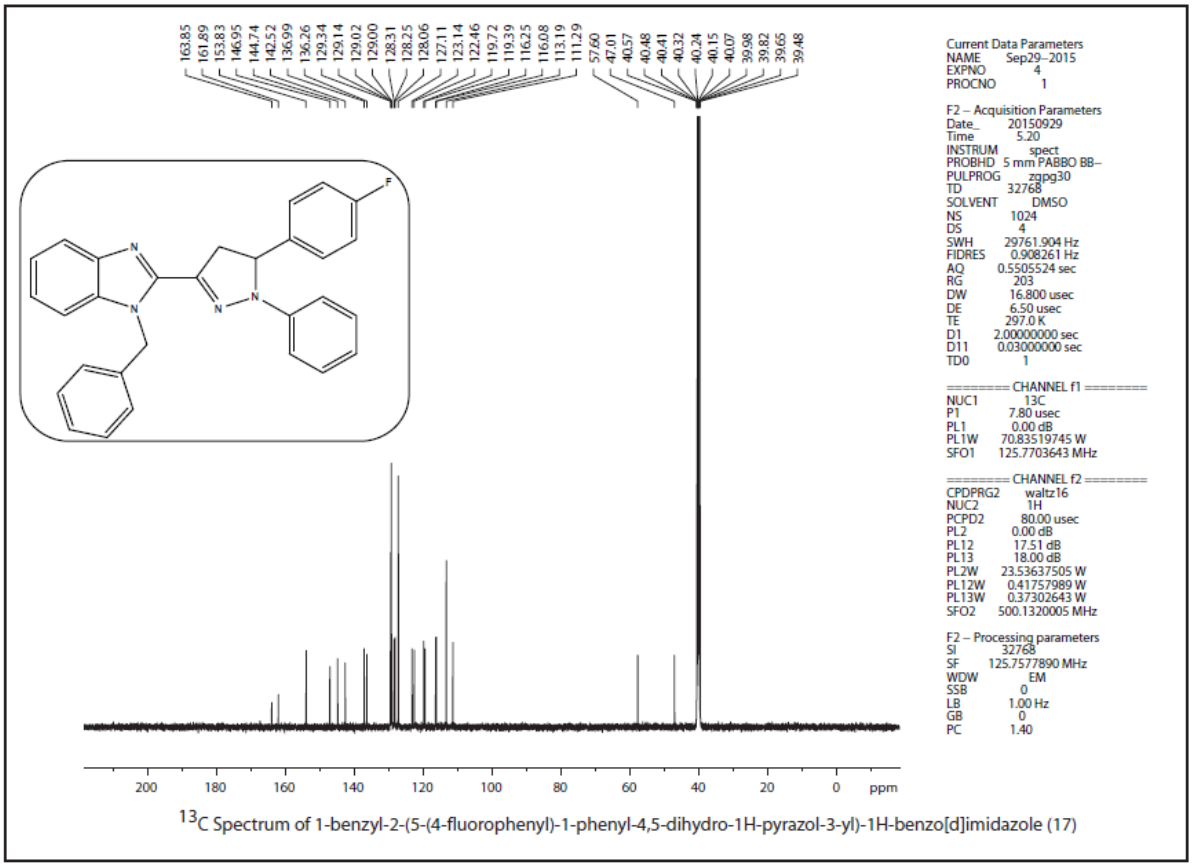
Mass spectrum of 1-benzyl-2-(5-(4-bromophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (16)

Compound **17**

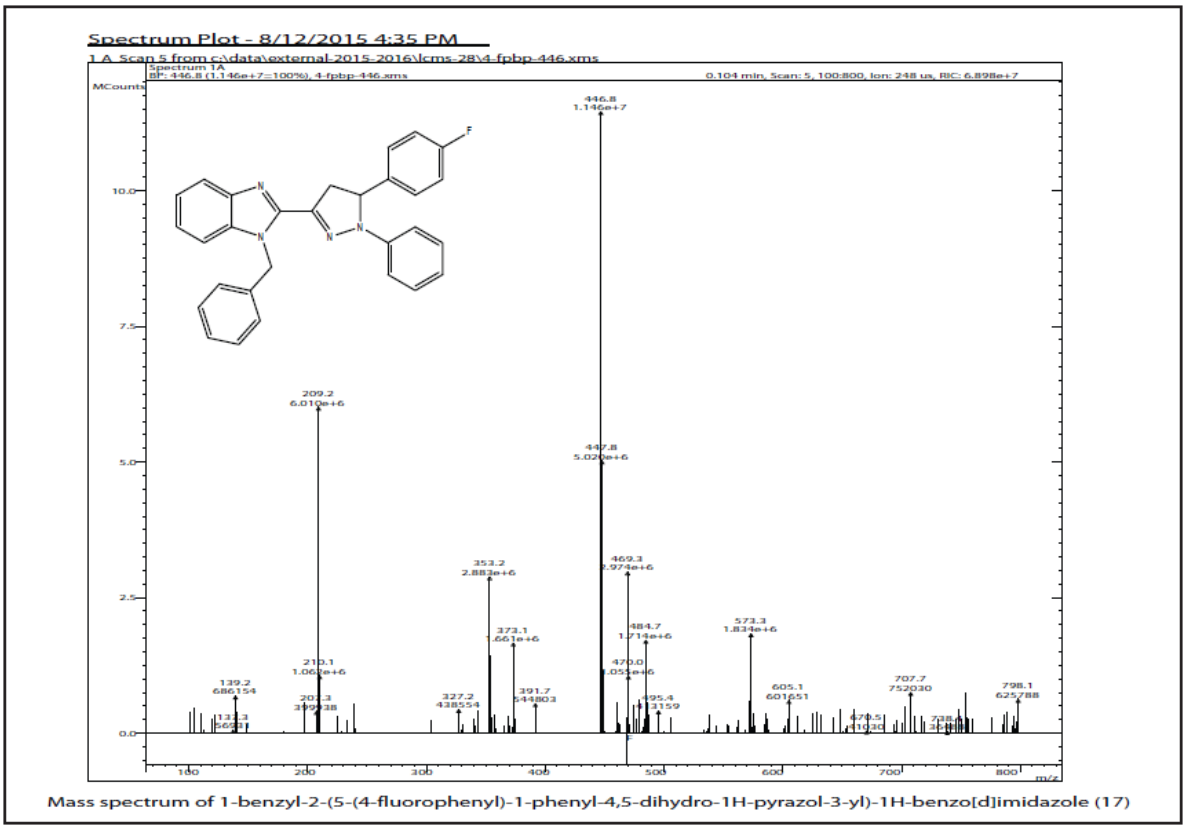


^{1}H Spectrum of 1-benzyl-2-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (17)

260



^{13}C Spectrum of 1-benzyl-2-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (17)

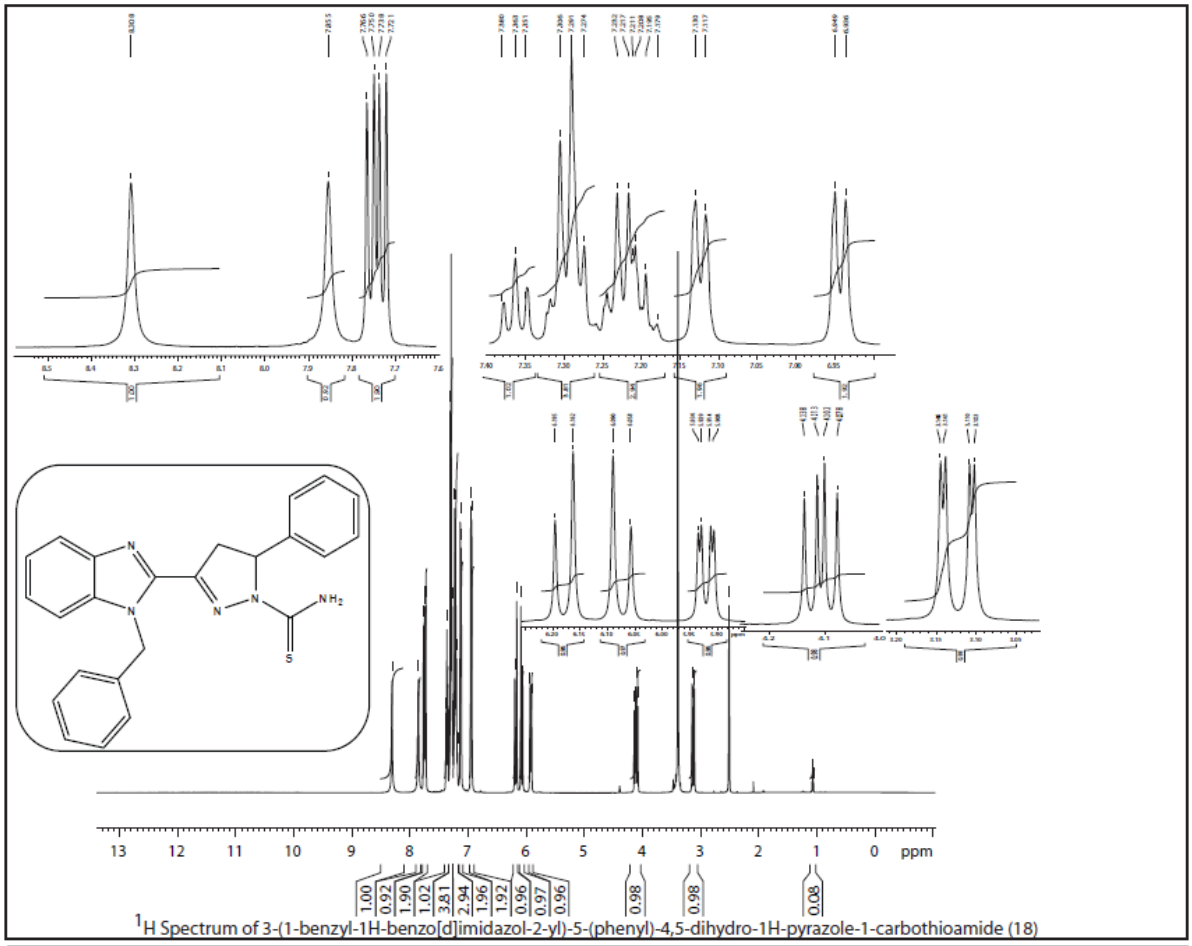


Mass spectrum of 1-benzyl-2-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-1H-benzo[d]imidazole (17)

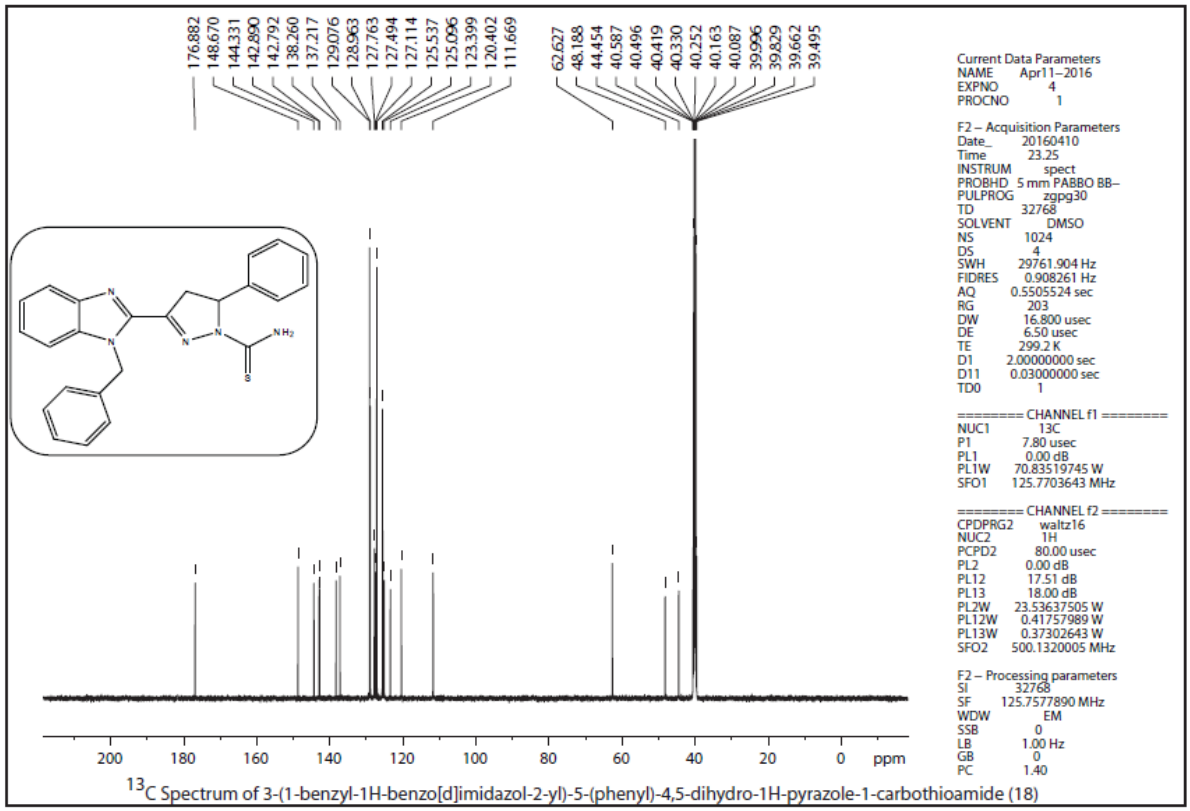
261

262

263 *Compound* **18**

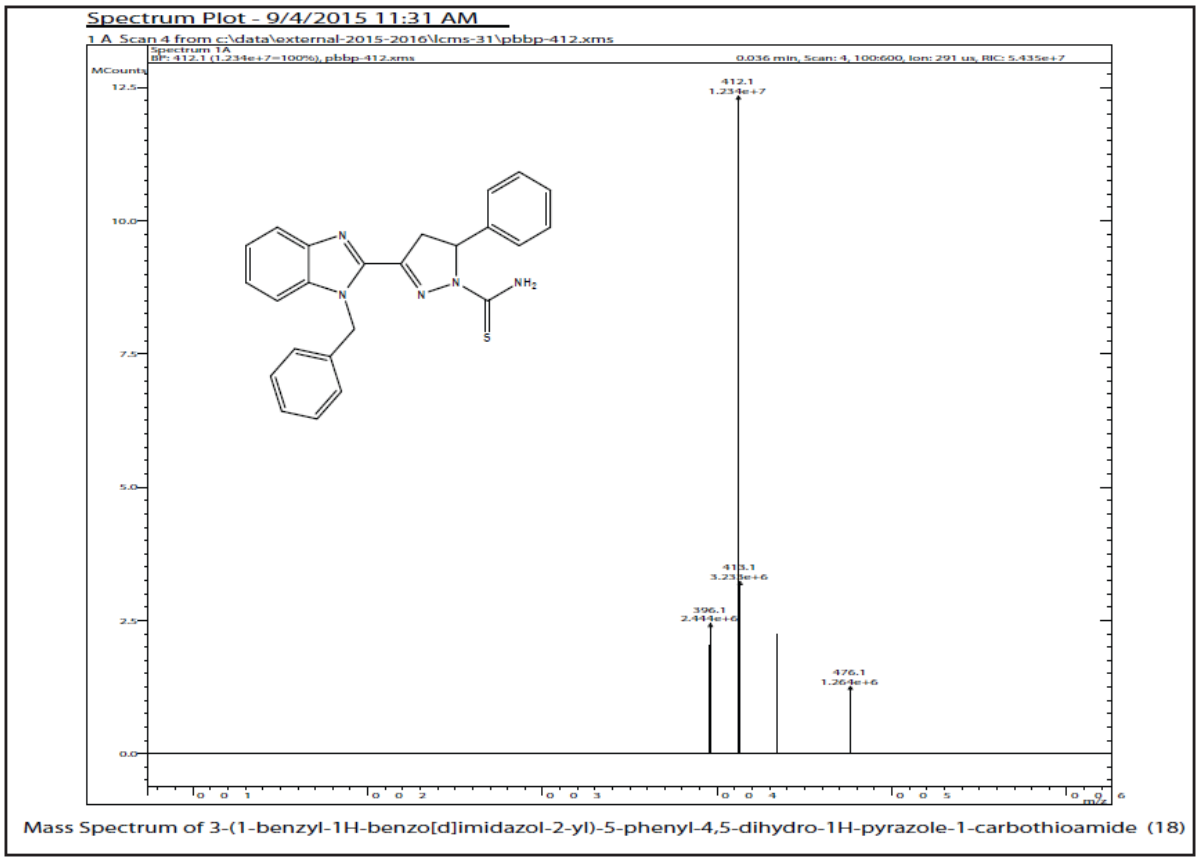


^{1}H Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(phenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (18)



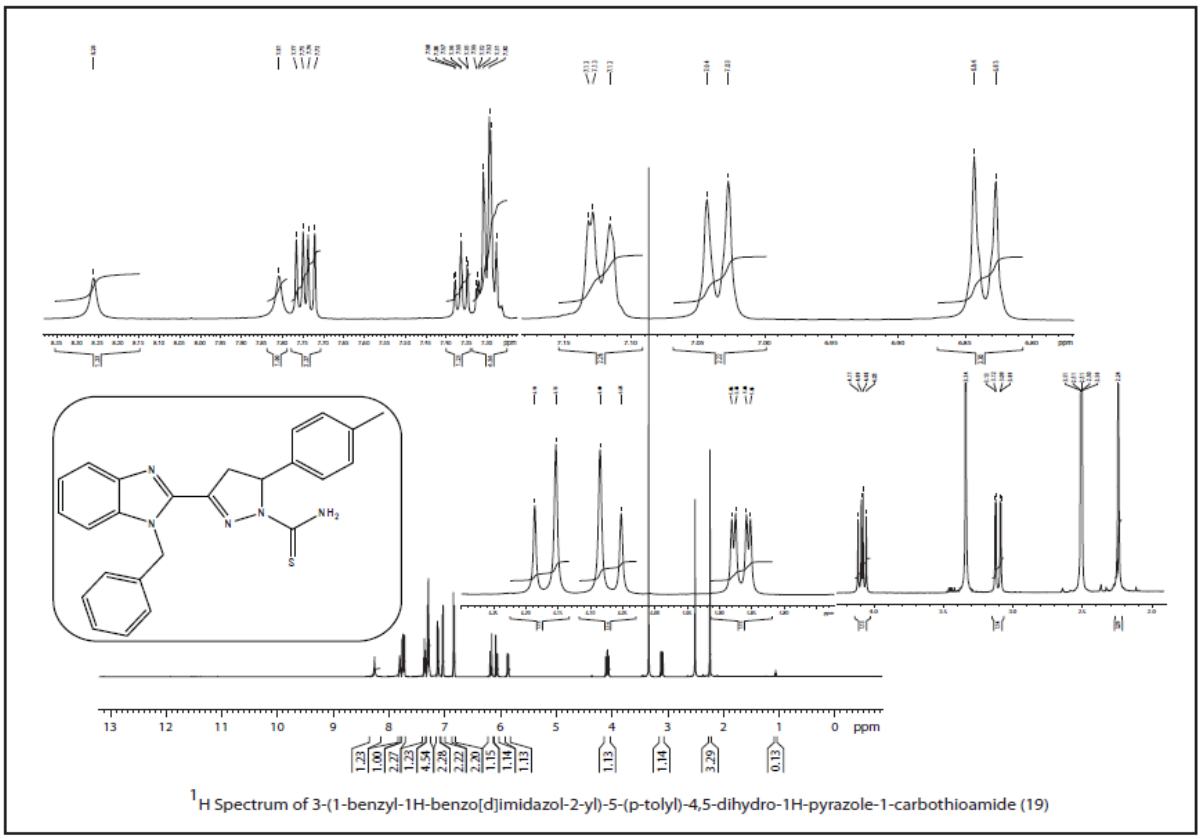
^{13}C Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(phenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (18)

264



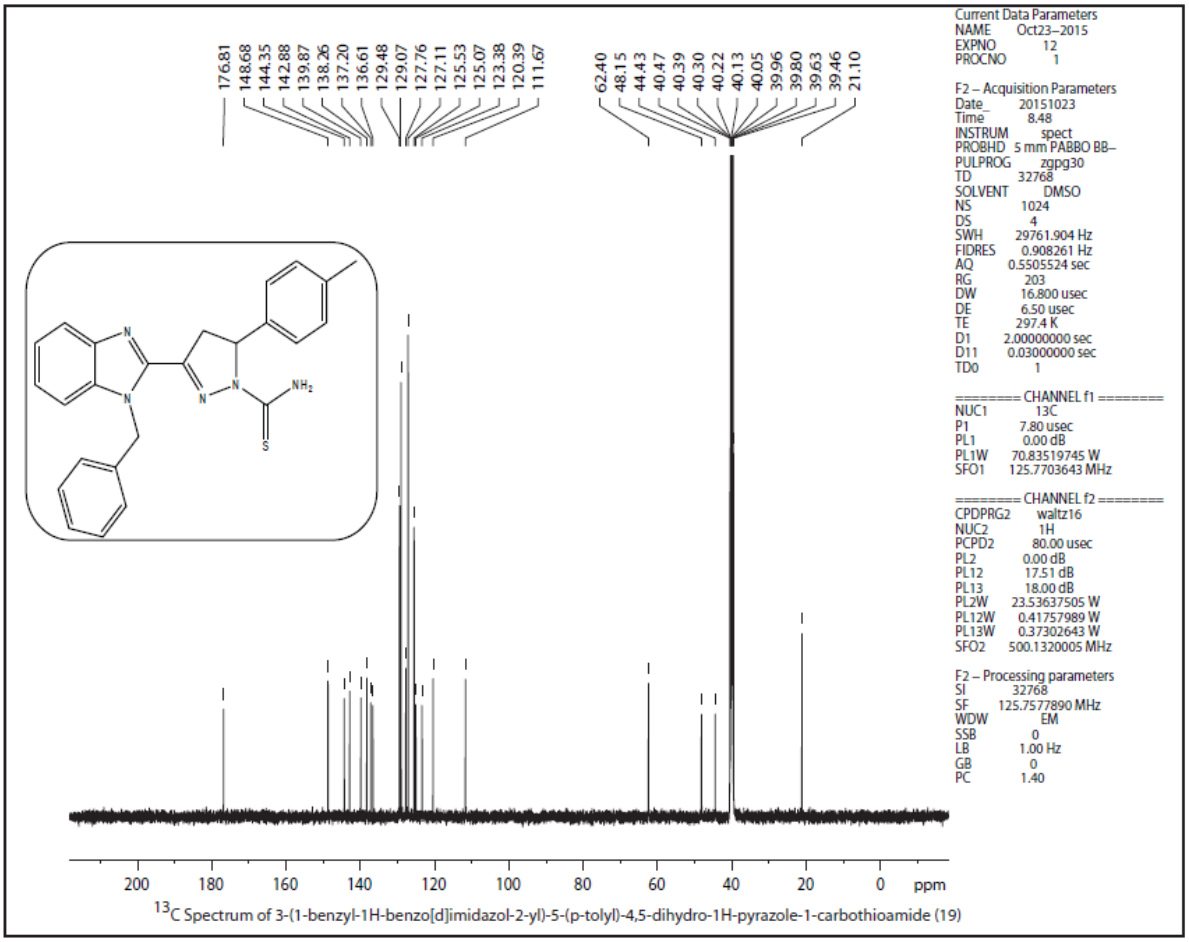
Mass Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (18)

Compound **19**

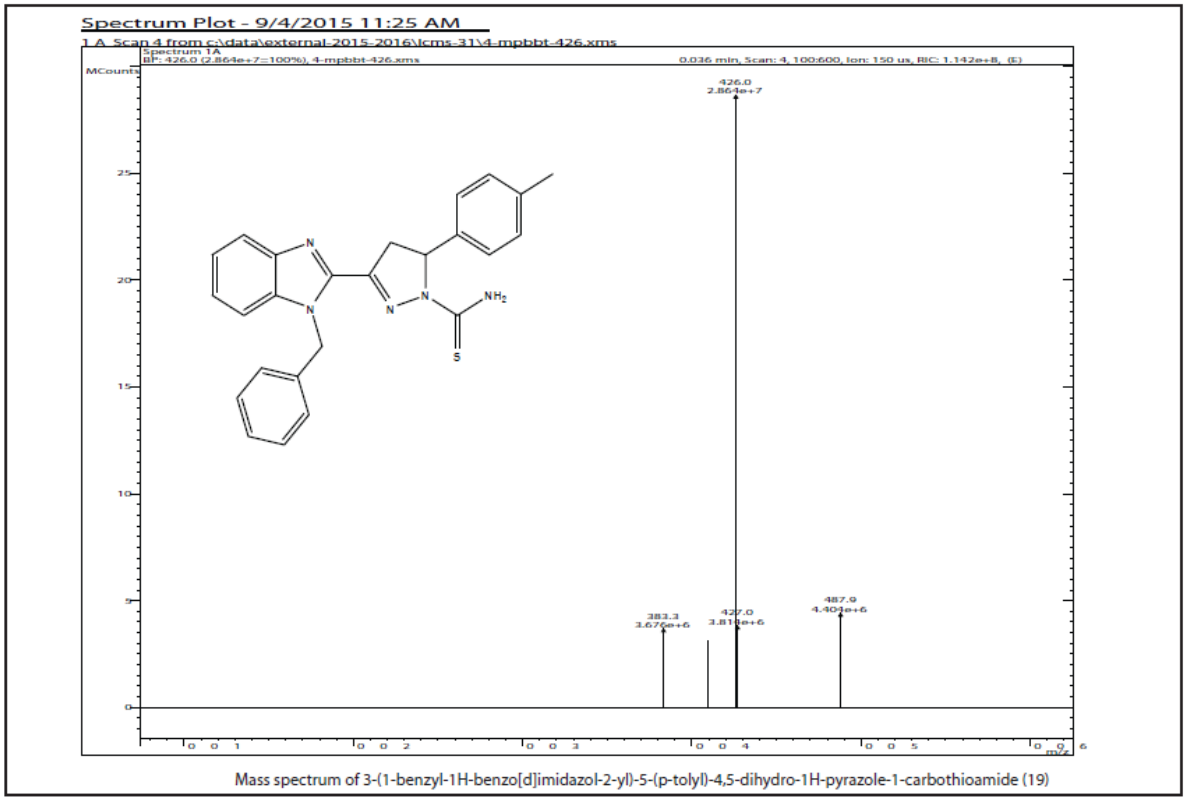


^{1}H Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (19)

269



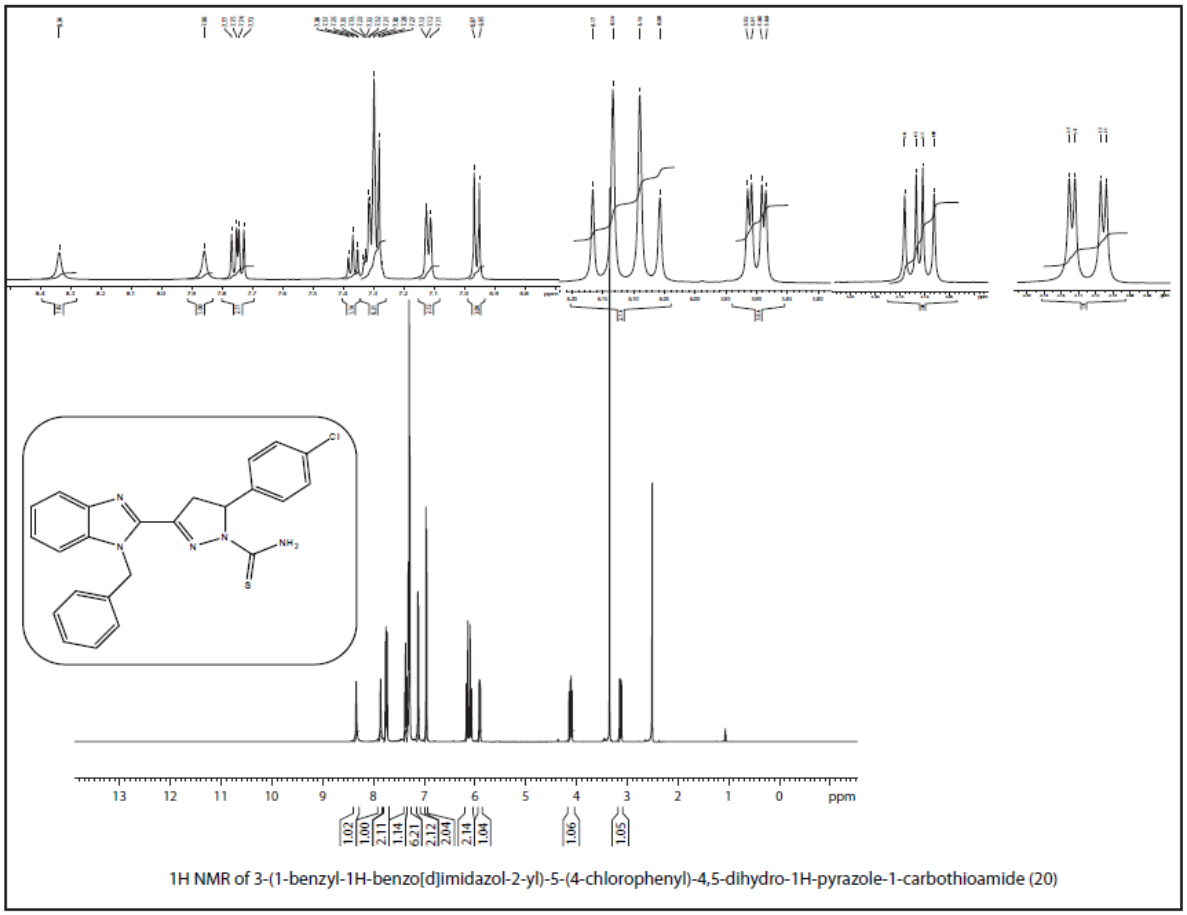
^{13}C Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (19)



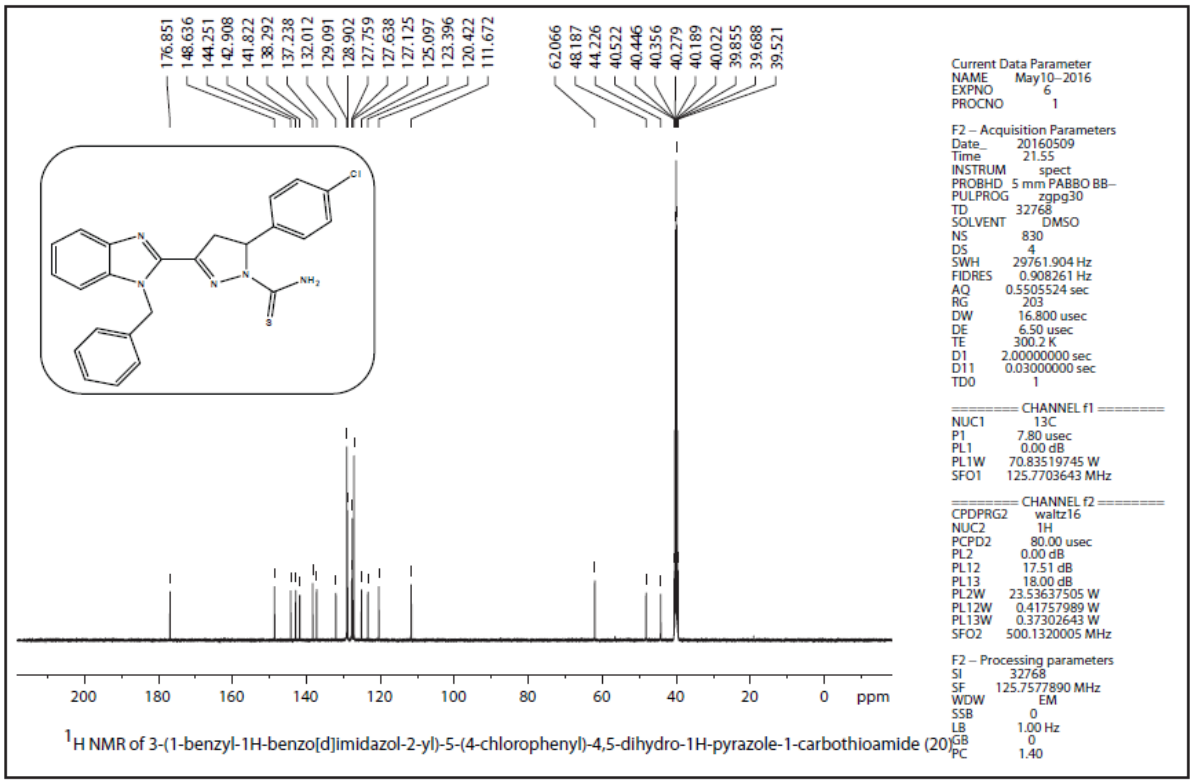
Mass spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(p-tolyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (19)

270

Compound **20**

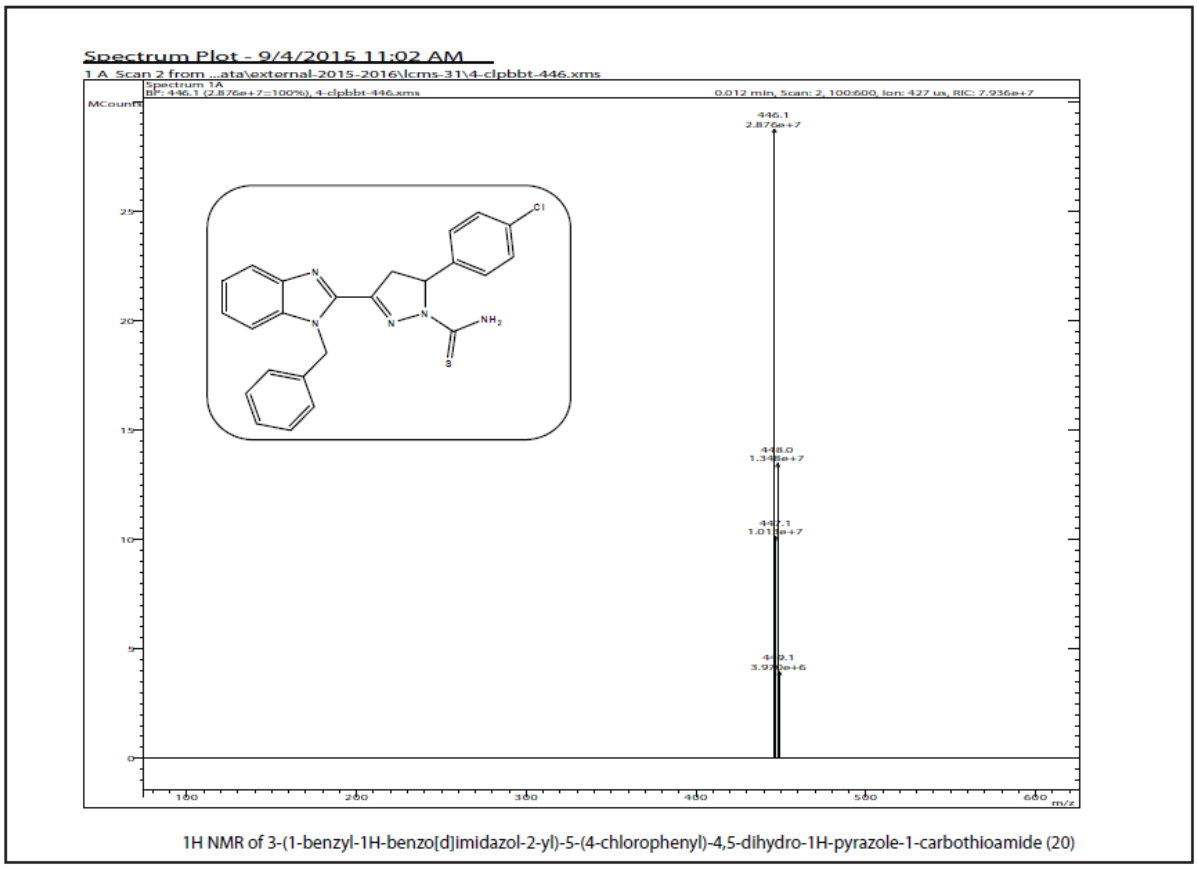


1H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (20)



^{1}H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (20)

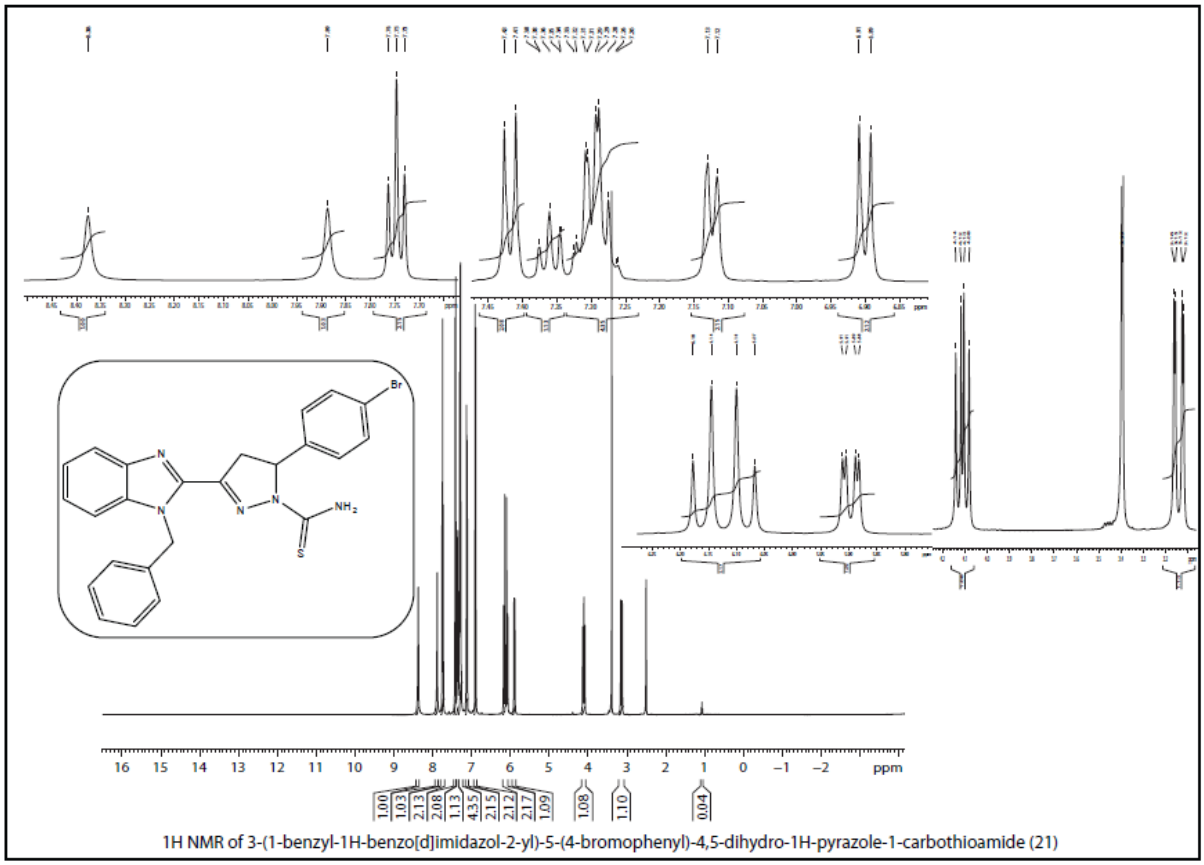
274



1H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (20)

275

276 *Compound* **21**

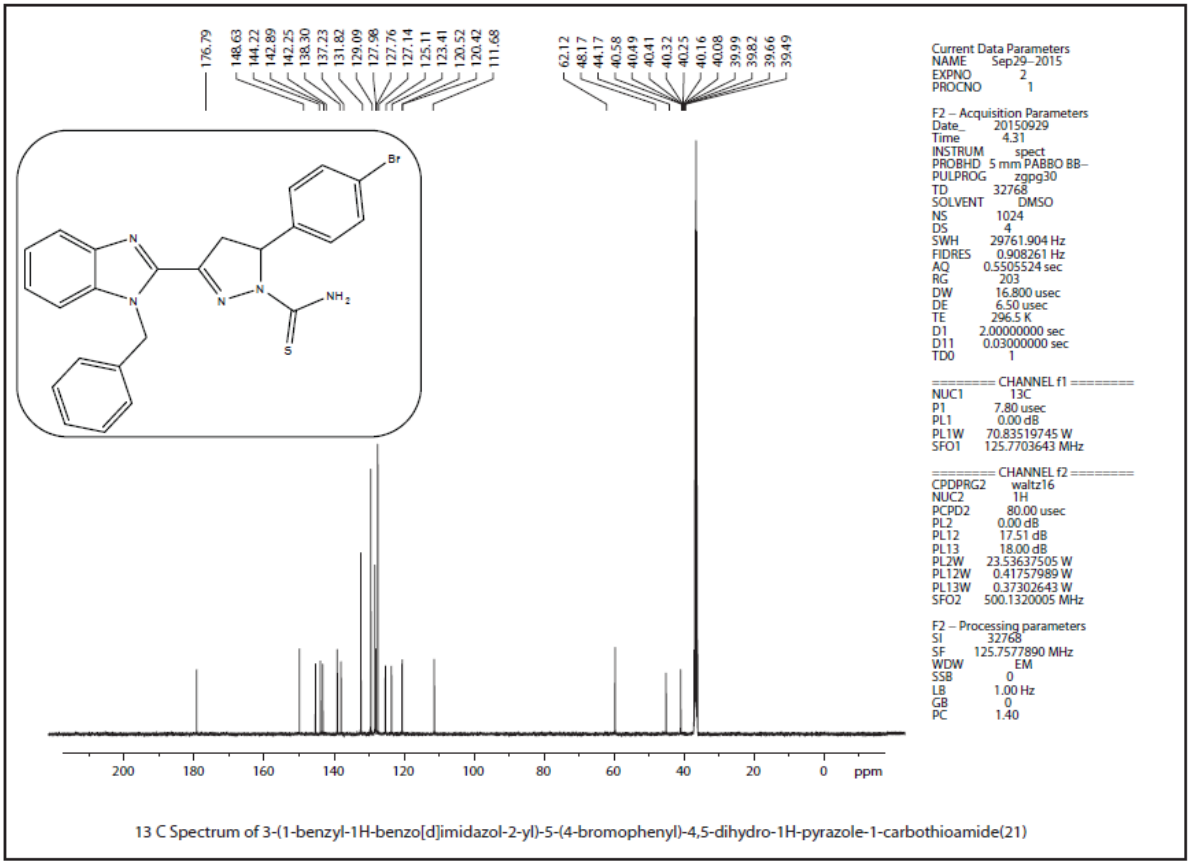


1H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (21)

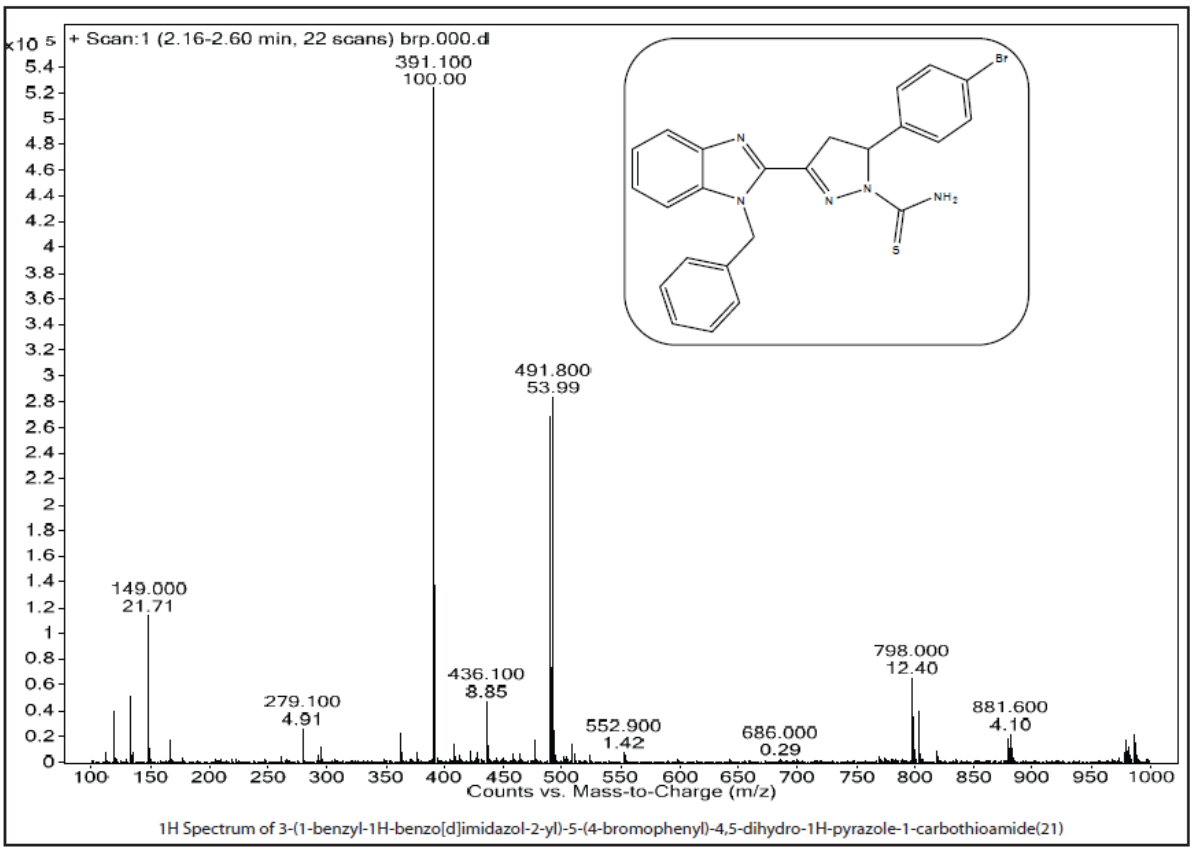
277

278

279



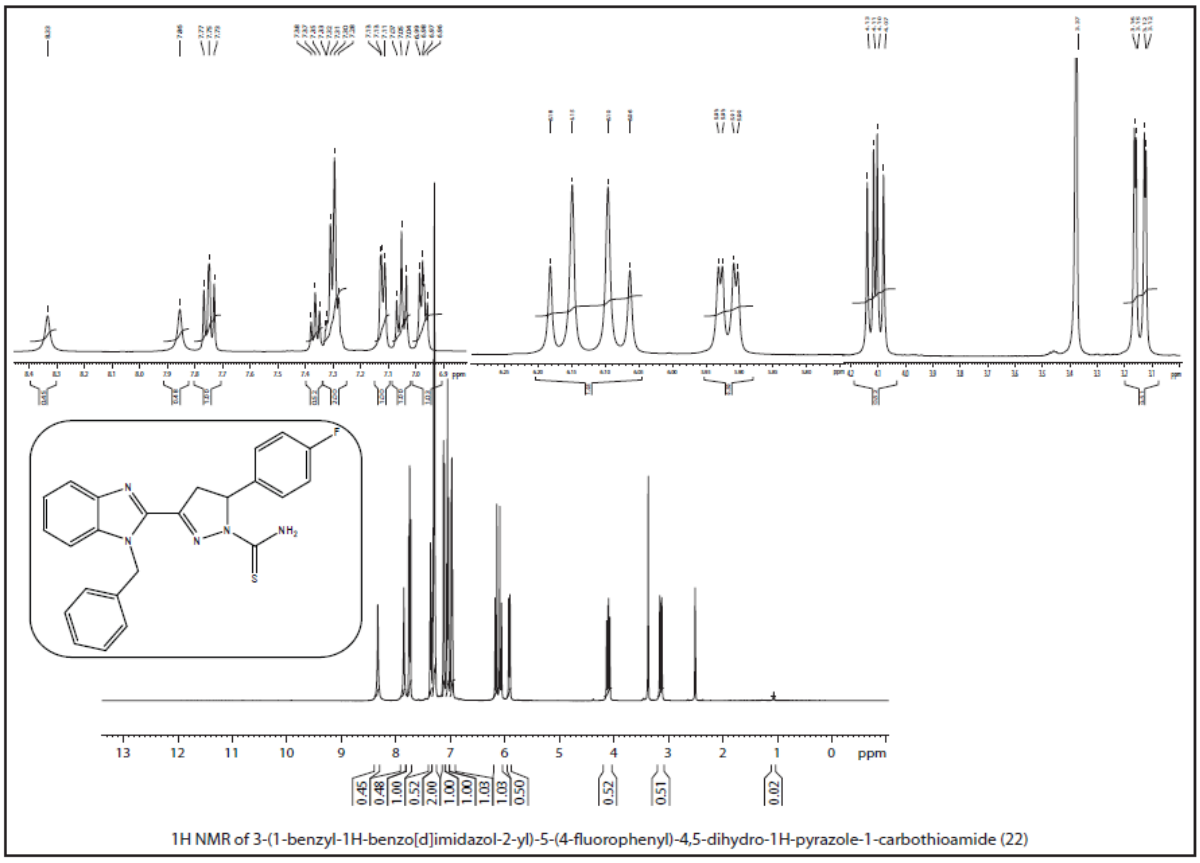
13 C Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide(21)



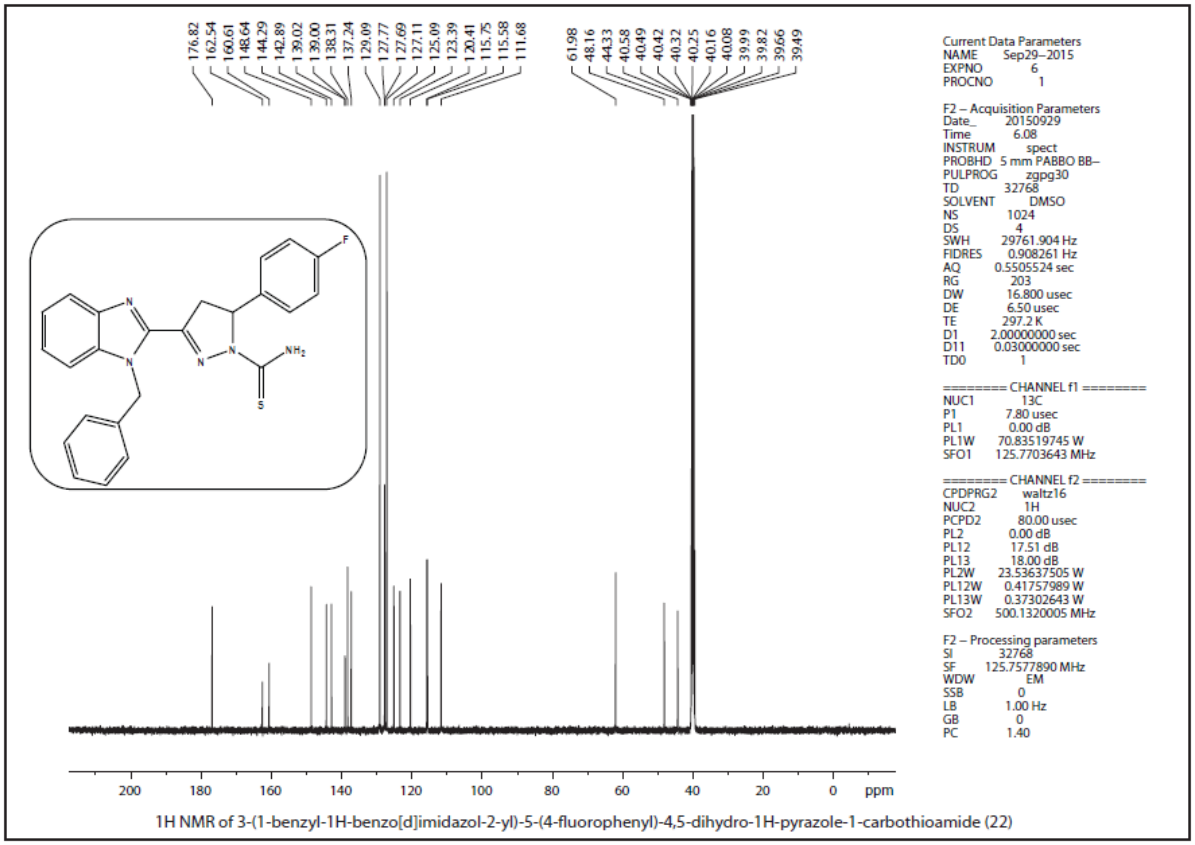
1H Spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide(21)

280

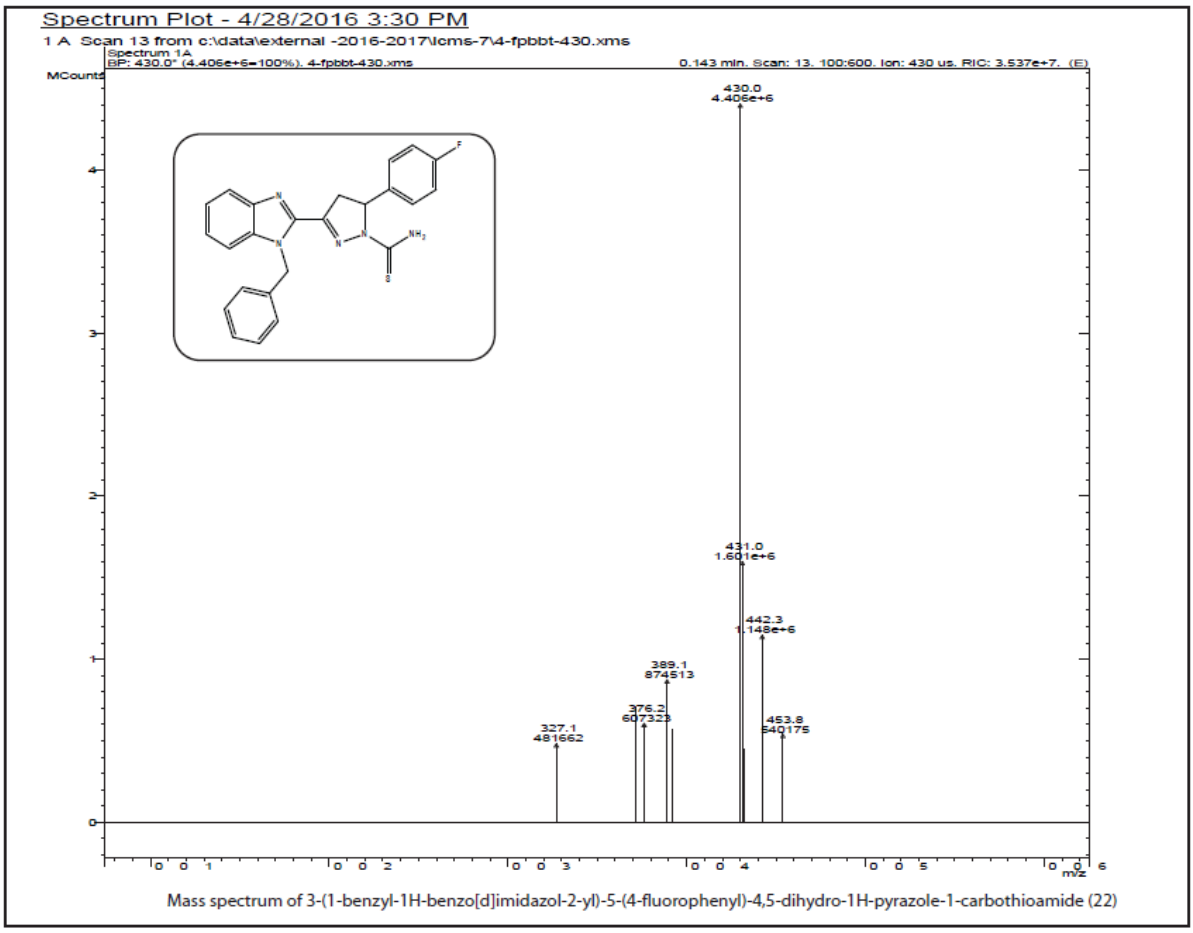
Compound **22**



1H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (22)



1H NMR of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (22)



Mass spectrum of 3-(1-benzyl-1H-benzo[d]imidazol-2-yl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide (22)

REFERENCES

1. P. K. Dubey, C. R. Kumar, B. Babu, *Indian J. Chem., B* **42** (2003) 3128.