Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Synthesis of substituted pyrazolo[4,3-*b*]pyridines via Copper-mediated intramolecular C-N cross-coupling of primary allylamines

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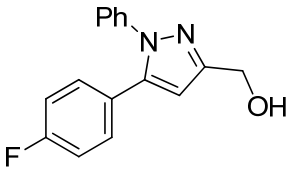
General Procedure for the preparation of compounds 1a-j and 6a-c. To a stirred solution of appropriate acetophenone (5 mmol) in dry toluene (25 mL) was added NaH (12.5 mmol, 60% in oil) and the mixture was warmed to 40 ^{o}C. At this temperature a solution of diethyl oxalate (7.46 mmol) in dry toluene (20 mL) was added dropwise under stirring. The reaction mixture was refluxed for another 1.5 h. After completion of reaction, the mixture was cool to room temperature and neutralized with 5% HCl solution and the resultant solution was pass through a Celite bed. Thereafter layers were seperated and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Column chromatography of the crude product over silica gel furnished the pure 2,4-diketoester derivatives in 90-95% yield. To a stirred solution of 2,4-diketoester derivatives (5 mmol) in EtOH (25 mL) was added appropriately substituted hydrazine (5 mmol) and TFA (0.5 mmol) and the reaction mixture was heated at reflux for 2 h. Thereafter EtOH was evaporated and water (50 mL) was added and extracted with EtOAc (3x25 mL). The combined organic layer was dried and evaporated under vacuum to obtain a mixture of regioisomeric 3- and 5- pyrazole carboxylate which were used as such for further reaction.

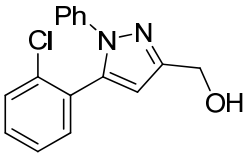
To a stirred solution of 3- and 5- pyrazole carboxylates (5 mmol) in dry THF (30 mL) was added $LiAlH_4$ (5 mmol) at 0 ^{o}C and stirred at room temperature for 1 h. Thereafter reaction mixture was again cool to 0 ^{o}C and quenched with 10 % aq NaOH solution. Thereafter reaction mixture was passed through a Celite bed and washed with EtOAc. The filtrate was dried and evaporated under vacuum to obtain the corresponding alcohols which were seperated via column chromatography to obtain the substituted (1- substituted phenyl or methyl-1*H*-pyrazol-3-yl)methanol as the major product (61-74%) and (1-substituted phenyl or methyl-1*H*-pyrazol-5-yl)methanol as the minor product (12-20%). To a stirred solution of appropriate alcohol (5 mmol) in dry CH_2Cl_2 (30 mL) was added PCC (10 mmol) and the reaction mixture was stirred at room temperature for 8 h. After completion, the reaction, mixture was passed through a small band of silica gel using hexanes-EtOAc (85:15, v/v) as eluent to obtain pure substituted 3-pyrazolecarbaldehydes (55-57 %) or substituted 5-pyrazolecarbaldehydes (75-80 %) as solids.

To a stirred solution of pyrazole-3-carboxaldehyde or pyrazole-5-carboxaldehyde (1 mmol) in dry $CHCl_3$ (50 mL) K_2CO_3 (3 mmol) was added and cool to 0 ^{o}C in icebath. Thereafter ICl (3 mmol) was added dropwise and stirred at room temperature for 10 h. On completion of the reaction Na_2SO_3 solution (30 mL) was added and layers were seperated. The aqueous layer was again extracted with $CHCl_3$ (2 x 25 ml). The organic layers were combined, washed with H_2O

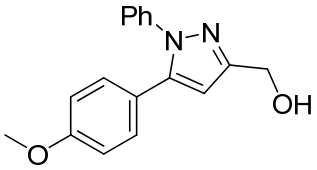
(50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated under vacuum to obtain the crude product which was crystallized with EtOAc-Hexanes to afford pure substituted 4-iodopyrazole-3-carboxaldehydes or 4-iodopyrazole-5-carboxaldehydes as white solid (92-96%).



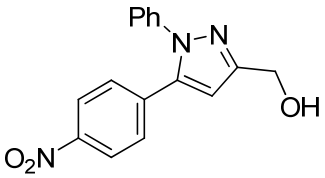
[5-(4-Fluorophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol. 93 % as a white solid (402 mg from 500 mg); mp 84-85 ^{o}C; R_f = 0.17 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3420 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (brs), 4.79 (s, 2H), 6.49 (s, 1H), 6.99 (t, 2H, J = 8.5 Hz), 7.17-7.21 (m, 2H), 7.26-7.27 (m, 2H), 7.32-7.35 (m, 3H) ppm; ESIMS (*m/z*) 269.3 $[M+H]^+$.



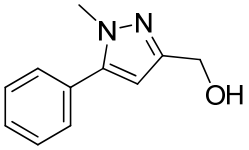
[5-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol. 93 % as a white solid (405 mg from 500 mg); mp 114-115 ^{o}C; R_f = 0.15 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3422 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (brs, 1H), 4.82 (s, 2H), 6.52 (s, 1H), 7.24-7.33 (m, 7H), 7.39 (d, 1H, J = 7.7 Hz) ppm; ESIMS (*m/z*) 285.3 $[M+H]^+$.



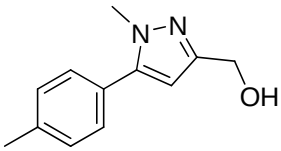
[5-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol. 95 % as a white solid (413 mg from 500 mg); mp 85-87 ^{o}C; R_f = 0.18 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3416 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (brs, 1H), 3.80 (s, 3H), 4.78 (s, 2H), 6.46 (s, 1H), 6.82 (d, 2H, J = 8.8 Hz), 7.14 (d, 2H, J = 8.8 Hz), 7.27-7.32 (m, 5H) ppm; ESIMS (*m/z*) 281.3 $[M+H]^+$.



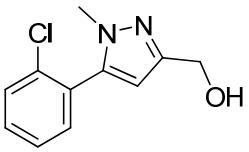
[5-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol. 90 % as a white solid (394 mg from 500 mg); mp 145-146 ^{o}C; R_f = 0.18 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3416 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (brs, 1H, CH_2OH), 4.81 (s, 2H, CH_2OH), 6.66 (s, 1H, ArH), 7.26-7.28 (m, 2H, ArH), 7.37-7.39 (m, 5H, ArH), 8.16 (d, 2H, J = 8.8 Hz, ArH) ppm; ESIMS (*m/z*) 296.3 $[M+H]^+$.



(1-Methyl-5-phenyl-1*H*-pyrazol-3-yl)methanol. 92 % as a white solid (376 mg from 500 mg); mp 96-97 ^{o}C; R_f = 0.11 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3435 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (brs, 1H), 3.85 (s, 3H), 4.71 (s, 2H), 6.31 (s, 1H), 7.41-7.45 (m, 5H) ppm; ESIMS (*m/z*) 189.3 $[M+H]^+$.

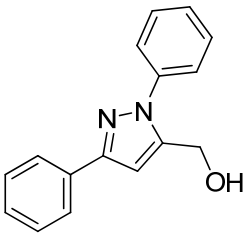


[1-Methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methanol. 95 % as a white solid (393 mg from 500 mg); mp 68-70 ^{o}C; R_f = 0.11 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3440 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.83 (s, 3H), 4.70 (s, 2H), 6.26 (s, 1H), 7.24-7.28 (m, 4H), ppm; ESIMS (*m/z*) 203.3 $[M+H]^+$.

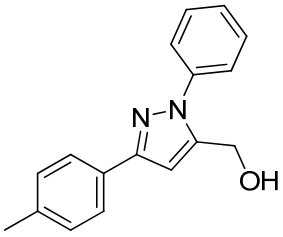


[5-(2-Chlorophenyl)-1-methyl-1*H*-pyrazol-3-yl]methanol. 94 % as a white solid (395 mg from 500 mg); mp 133-134 ^{o}C; R_f = 0.10 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3432 (OH) cm^{-}

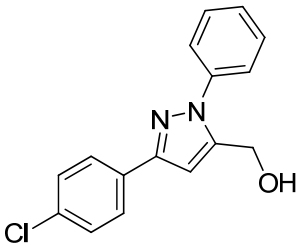
[1]; ^{1}H NMR (300 MHz, $CDCl_3$): 1.98 (brs, 1H), 3.96 (s, 3H), 4.71 (s, 2H), 6.71 (s, 1H), 7.22-7.32 (m, 2H), 7.41-7.44 (m, 1H), 7.76 (dd, 1H, *J* = 1.7 & 7.5 Hz) ppm; ESIMS (*m/z*) 223.3 $[M+H]^+$.



(1,3-Diphenyl-1*H*-pyrazol-5-yl)methanol. 93 % as a white solid (398 mg from 500 mg); mp 99-100 ^{o}C; R_f = 0.25 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3435 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (brs, 1H), 4.67 (s, 2H), 6.75 (s, 1H), 7.31-7.51 (m, 6H), 7.65 (d, 2H, *J*= 7.6 Hz), 7.86-7.88 (m, 2H) ppm; ESIMS (*m/z*) 251.3 $[M+H]^+$.

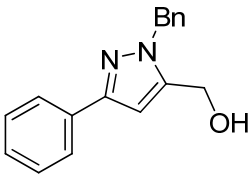


[3-(4-Methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methanol. 91 % as a white solid (393 mg from 500 mg); mp 92-93 ^{o}C; R_f = 0.24 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3432 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (brs, 1H, CH_2OH), 2.38 (s, 3H, CH_3), 4.69 (s, 2H, CH_2OH), 6.73 (s, 1H, ArH), 7.22 (d, 2H, *J*= 7.9 Hz, ArH), 7.39 (t, 1H, *J*= 7.2 Hz, ArH), 7.49 (t, 2H, *J*= 7.5 Hz, ArH), 7.66 (d, 2H, *J*= 7.5 Hz, ArH), 7.76 (d, 2H, *J*= 7.9 Hz, ArH) ppm; ESIMS (*m/z*) 265.3 $[M+H]^+$.

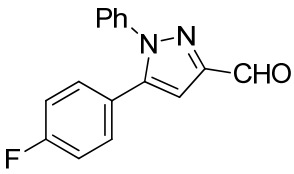


[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl]methanol. 94 % as a white solid (409 mg from 500 mg); mp 91-92 ^{o}C; R_f = 0.23 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 3429 (OH) cm^{-1};

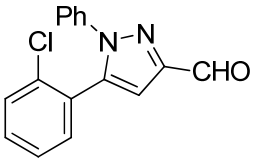
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96 (brs, 1H, CH_2OH), 4.70 (s, 2H, CH_2OH), 6.74 (s, 1H, ArH), 7.37-7.41 (m, 4H, ArH), 7.48-7.53 (m, 3H, ArH), 7.65 (d, 2H, *J*= 7.5 Hz, ArH), 7.80 (d, 2H, *J*= 8.4 Hz, ArH) ppm; ESIMS (*m/z*) 285.3 $[M+H]^+$.



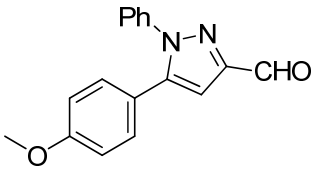
(1-Benzyl-3-phenyl-1*H*-pyrazol-5-yl)methanol. 92 % as colourless oil (397 mg from 500 mg); R_f = 0.24 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 3432 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65 (brs, 1H), 4.58 (s, 2H), 5.47 (s, 2H), 6.56 (s, 1H), 7.29-7.32 (m, 4H), 7.37-7.42 (m, 4H), 7.81 (d, 2H, *J* = 7.6 Hz) ppm; ESIMS (*m/z*) 265.1 $[M+H]^+$.



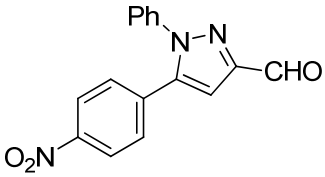
5-(4-Fluorophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde. 74 % as a white solid (367 mg from 500 mg); mp 76-77 ^{o}C; R_f = 0.44 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1700 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (s, 1H), 7.04 (d, 2H, *J* = 8.5 Hz), 7.18-7.22 (m, 2H), 7.30-7.34 (m, 2H), 7.40-7.42 (m, 3H), 10.07 (s, 1H, CHO) ppm; ESIMS (*m/z*) 267.3 $[M+H]^+$.



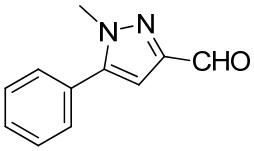
5-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde. 74 % as a white solid (367 mg from 500 mg); mp 103-104 ^{o}C; R_f = 0.45 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1695 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 1H), 7.26-7.44 (m, 9H), 7.11 (d, 1H, *J* = 3.0 Hz) ppm; ESIMS (*m/z*) 283.3 $[M+H]^+$.



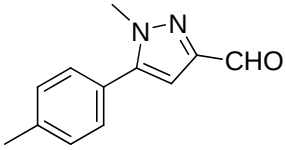
5-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde. 76 % as a white solid (377 mg from 500 mg); mp 159-160 ^{o}C; R_f = 0.43 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1698 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ δ 3.81 (s, 3H, OMe), 6.84 (d, 2H, J = 8.3 Hz, ArH), 6.96 (s, 1H, ArH), 7.14 (d, 2H, J = 8.3 Hz, ArH), 7.36-7.39 (m, 5H, ArH), 10.07 (s, 1H, CHO) ppm; ESIMS (*m/z*) 279.3 $[M+H]^+$.



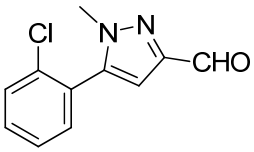
5-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde. 74 % as a yellow solid (367 mg from 500 mg); mp 173-175 ^{o}C; R_f = 0.40 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1700 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (s, 1H), 7.33-7.34 (m, 2H), 7.40 (d, 2H, J = 8.8 Hz), 7.44-7.46 (m, 3H), 8.19 (d, 2H, J = 8.8 Hz), 10.09 (s, 1H) ppm; ESIMS (*m/z*) 294.3 $[M+H]^+$.



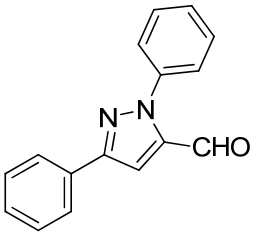
1-Methyl-5-phenyl-1*H*-pyrazole-3-carbaldehyde. 75 % as a white solid (371 mg from 500 mg); mp 102-103 ^{o}C; R_f = 0.38 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1703 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.97 (s, 3H), 6.83 (s, 1H), 7.41-7.49 (m, 5H), 9.98 (s, 1H) ppm; ESIMS (*m/z*) 187.3 $[M+H]^+$.



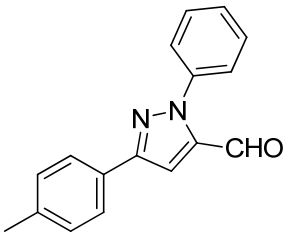
1-Methyl-5-(4-methylphenyl)-1*H*-pyrazole-3-carbaldehyde. 76 % as a white solid (376 mg from 500 mg); mp 150-152 ^{o}C; R_f = 0.37 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1697 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.96 (s, 3H), 6.80 (s, 1H), 7.21-7.30 (m, 4H), 9.97 (s, 1H) ppm; ESIMS (*m/z*) 201.3 $[M+H]^+$.



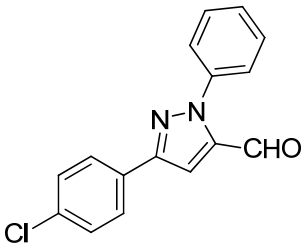
5-(2-Chlorophenyl)-1-methyl-1*H*-pyrazole-3-carbaldehyde. 72 % as a white solid (357 mg from 500 mg); mp 75-76 ^{o}C; R_f = 0.39 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1701 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.25 (s, 3H), 7.29-7.36 (m, 2H), 7.44 (s, 1H), 7.47 (dd, *J* = 1.5, 7.2 Hz), 7.83 (dd, *J* = 2.1, 7.4 Hz), 9.91 (s, 1H) ppm; ESIMS (*m/z*) 221.3 $[M+H]^+$.



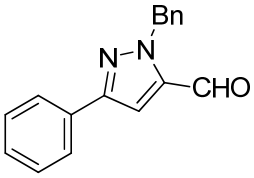
1,3-Diphenyl-1*H*-pyrazole-5-carbaldehyde. *ARKIVOC* **2007**, *xiv*, 185-203.



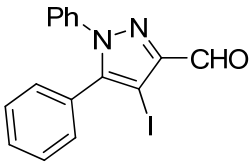
1-Phenyl-3-(4-methylphenyl)-1*H*-pyrazole-5-carbaldehyde. *ARKIVOC* **2007**, *xiv*, 185-203.



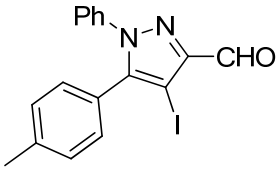
3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole-5-carbaldehyde. *ARKIVOC* **2007**, *xiv*, 185-203.



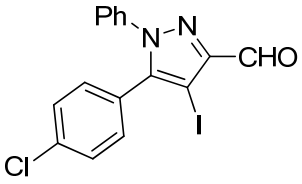
1-Benzyl-3-phenyl-1*H*-pyrazole-5-carbaldehyde. 81 % as a white solid (402 mg from 500 mg); mp 110-112 ^{o}C; R_f = 0.47 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1688 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (s, 2H), 7.19 (s, 1H), 7.27-7.46 (m, 8H), 7.85 (d, 2H, J = 8.0 Hz), 9.87 (s, 1H) ppm; ESIMS (m/z) 263.1 $[M+H]^+$.



4-Iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde (1a). ref- *ARKIVOC* **2007**, *xiv*, 185-203.

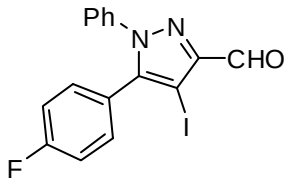


4-Iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1b). ref- *ARKIVOC* **2007**, *xiv*, 185-203.



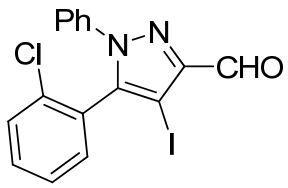
5-(4-Chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1c). ref- *ARKIVOC* **2007**, *xiv*, 185-203.

5-(4-Fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1d). 95 % as a white solid (700 mg from 500 mg); mp 124-125 ^{o}C; R_f= 0.35 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1703 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (t, 2H, J = 8.6 Hz), 7.22-7.29 (m, 4H), 7.35-7.40 (m, 3H), 10.08 (s, 1H) ppm; ^{13}C



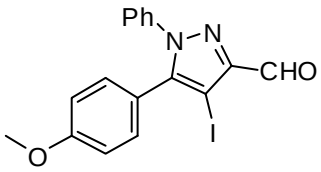
NMR (75 MHz, $CDCl_3$): δ 62.4, 116.0, 116.3, 125.1, 129.0, 129.1, 129.4, 129.5, 132.6, 132.7, 139.3, 146.0, 149.2, 165.1, 186.0 ppm; ESIMS (*m/z*) 393.0 $[M+H]^+$; Anal. Calcd. for $C_{16}H_{10}FIN_2O$ (Exact Mass: 391.9822); C, 49.00; H, 2.57; N, 7.14. Found C, 49.19; H, 2.71; N, 6.98.

5-(2-Chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1e). 96 % as a white solid



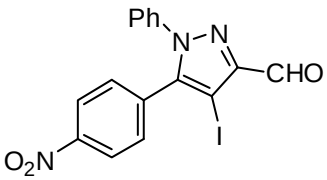
(694 mg from 500 mg); mp 86-87 ^oC; R_f= 0.34 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1693 (CHO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.26-7.47 (m, 9H, ArH), 10.11 (s, 1H, CHO) ppm; ESIMS (*m/z*) 409.0 $[M+H]^+$; Anal. Calcd. for $C_{16}H_{10}ClIN_2O$ (Exact Mass: 407.9526); C, 47.03; H, 2.47; N, 6.86. Found C, 47.23; H, 2.29; N, 7.01.

4-Iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1f). 96 % as a white solid (698 mg from 500 mg); mp 159-161 ^oC; R_f= 0.37 (hexanes: EtOAc, 90:10, v/v); IR (KBr):



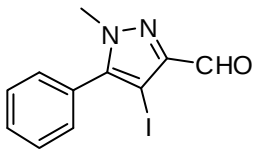
ν_{max} 1700 (CHO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.90 (d, 2H, *J* = 8.7 Hz), 7.18 (d, 2H, *J* = 8.7 Hz), 7.26 (s, 2H), 7.33-7.35 (m, 3H), 10.08 (s, 1H) ppm; ESIMS (*m/z*) 405.1 $[M+H]^+$; Anal. Calcd. for $C_{17}H_{13}IN_2O_2$ (Exact Mass: 404.0022); C, 50.51; H, 3.24; N, 6.93. Found C, 50.71; H, 3.40; N, 6.75.

4-Iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (1g). 95 % as a white solid

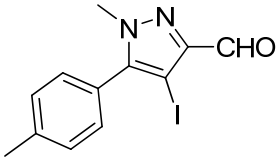


(679 mg from 500 mg); mp 164-166 ^oC; R_f= 0.34 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1696 (CHO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.21-7.25 (m, 2H), 7.38-7.40 (m, 3H), 7.48 (d, 2H, *J* = 8.7 Hz), 8.25 (d, 2H, *J* = 8.7 Hz), 10.10 (s, 1H) ppm; ESIMS (*m/z*) 420.1 $[M+H]^+$; Anal. Calcd. for $C_{16}H_{10}IN_3O_3$ (Exact Mass: 418.9767); C, 45.85; H, 2.40; N, 10.02. Found C, 46.09; H, 2.61; N, 9.80.

4-Iodo-1-methyl-5-phenyl-1*H*-pyrazole-3-carbaldehyde (1h). 94 % as a white solid (788 mg

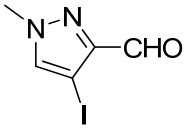


from 500 mg); mp 95-96 ^oC; R_f= 0.28 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1700 (CHO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.36-7.39 (m, 2H), 7.53-7.56 (m, 3H), 9.97 (s, 1H) ppm; ESIMS (*m/z*) 313.0 $[M+H]^+$; Anal. Calcd. for $C_{11}H_9IN_2O$ (Exact Mass: 311.9760); C, 42.33; H, 2.91; N, 8.98. Found C, 42.16; H, 2.77; N, 9.10.

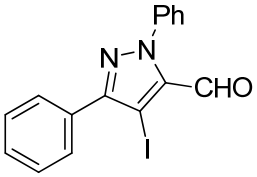


4-Iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazole-3-carbaldehyde (1i). ref-7

5-(2-Chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazole-3-carbaldehyde (1j). 93 % as a white solid (731 mg from 500 mg); mp 97-98 ^{o}C; R_f= 0.29 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1692 (CHO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 7.31 (dd, 1H, J = 1.5, 7.4 Hz), 7.42-7.54 (m, 2H), 7.57-7.60 (m, 1H), 9.98 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.1, 62.2, 127.5, 130.4, 132.0, 132.7, 134.9, 148.1, 185.7 ppm; ESIMS (*m/z*) 347.0 $[M+H]^+$; Anal. Calcd. for $C_{11}H_8ClIN_2O$ (Exact Mass: 345.9370); C, 38.12; H, 2.33; N, 8.08. Found C, 38.33; H, 2.46; N, 7.89.

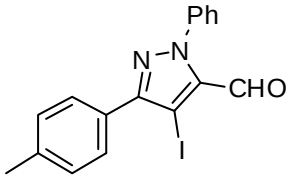


4-Iodo-1-methyl-1*H*-pyrazole-3-carbaldehyde (1k). ref-6

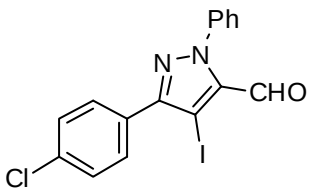


4-Iodo-1,3-diphenyl-1*H*-pyrazole-5-carbaldehyde (6a). ref- *ARKIVOC* **2007**, *xiv*, 185-203.

4-Iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazole-5-carbaldehyde (6b) 91 % as a white solid (674 mg from 500 mg); mp 146-147 ^{o}C; IR (KBr): ν_{max} 1689 (CHO) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.24-7.26 (m, 2H), 7.52-7.57 (m, 5H), 7.79 (d, 2H, J = 8.0 Hz), 9.90 (s, 1H) ppm; ESIMS (*m/z*) 389.2 $[M+H]^+$; Anal. Calcd. for $C_{17}H_{13}IN_2O$ (Exact mass: 388.0073); C, 52.60; H, 3.38; N, 7.22. Found: C, 52.83; H, 3.57; N, 7.00.

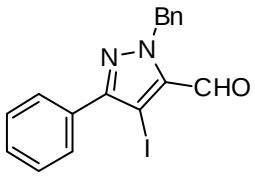


3-(4-Chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-5-carbaldehyde (6c). 93 % as a white solid (673 mg from 500 mg); mp 151-152 ^{o}C; IR (KBr): ν_{max} 1684 (CHO) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (d, 2H, J = 8.4 Hz), 7.52 (s, 5H), 7.85 (d, 2H, J = 8.4 Hz), 9.88 (s, 1H) ppm; ESIMS (*m/z*) 409.2

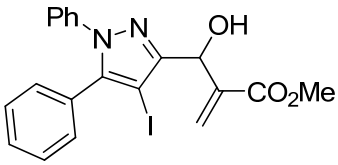


$[M+H]^+$; Anal. Calcd. for $C_{16}H_{10}ClIN_2O$ (Exact mass: 407.9526); C, 47.03; H, 2.47; N, 6.86. Found: C, 47.23; H, 2.11; N, 7.05.

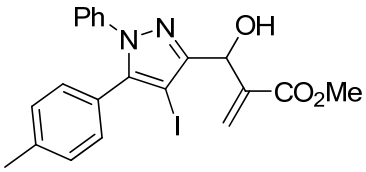
1-Benzyl-4-iodo-3-phenyl-1*H*-pyrazole-5-carbaldehyde (6l). 96 % as a white solid (711 mg from 500 mg); mp 164-166 ^oC; R_f= 0.41 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1685 (CHO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.77 (s, 2H), 7.30-7.35 (m, 5H), 7.43-7.51 (m, 3H), 7.84 (d, 2H, J = 6.5 Hz), 9.84 (s, 1H) ppm; ESIMS (*m/z*) 389.1 $[M+H]^+$; ESI-HRMS Calcd. for $C_{17}H_{14}IN_2O$ $[MH]^+$: 389.0151. Found: 389.0142.



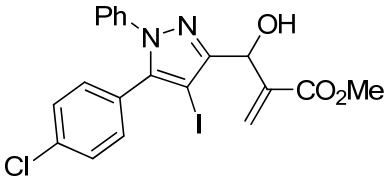
For procedure of Morita-Baylis-Hillman reactions refer to S. Nag, V. Singh, S. Batra. *ARKIVOC* **2007**, *xiv*, 185-203.



Methyl 2-[hydroxy(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)methyl]acrylate (2a). ref-6

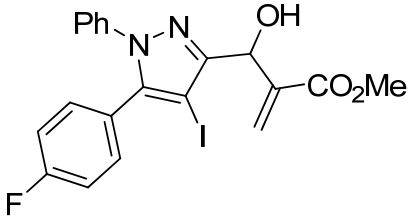


Methyl 2-{hydroxy[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (2b). ref-6



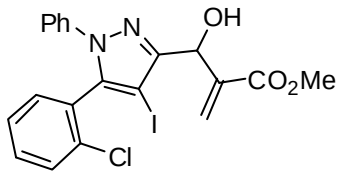
Methyl 2-[[5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (2c). ref-6

Methyl 2-[[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (2d). 88 % as a white solid (537 mg from 500 mg); mp 185-

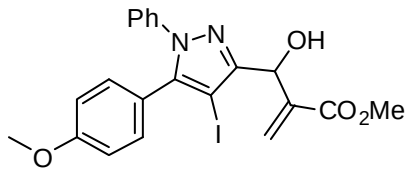


186 °C; R_f= 0.16 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1721 (CO_2Me), 3405 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.29 (d, 1H, J = 6.9 Hz), 3.82 (s, 3H), 5.76 (d, 1H, J = 6.0 Hz), 6.00 (s, 1H), 6.45 (s, 1H), 7.06 (t, 2H, J = 8.7 Hz), 7.14-7.17 (m, 2H), 7.22-7.28 (m, 5H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.2, 64.3, 68.4, 115.7, 116.1, 124.9, 125.0, 127.1, 127.9, 129.0, 129.1, 132.3, 132.5, 139.7, 140.0, 153.6, 166.8 ppm; ESIMS (*m/z*) 478.7 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{16}FIN_2O_3$ (Exact Mass: 478.0190); C, 50.23; H, 3.37; N, 5.86. Found C, 50.41; H, 3.52; N, 5.70.

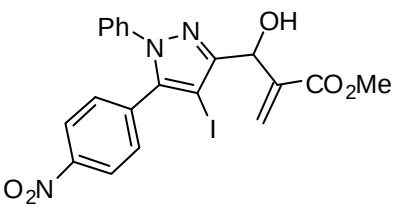
Methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (2e). 89 % as a white solid (539 mg from 500 mg); mp 93-94 °C; R_f= 0.17 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1720 (CO_2Me), 3413 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.34 (d, 1H, J = 7.1 Hz), 3.82 (s, 3H), 5.78 (d, 1H, J = 6.9 Hz), 5.97 (s, 1H), 6.44 (s, 1H), 7.21-7.35 (m, 6H), 7.38-7.45 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.2, 67.1, 68.3, 123.8, 127.1, 127.7, 128.9, 129.5, 130.0, 131.2, 132.6, 134.8, 139.8, 139.9, 140.1, 143.2, 153.3, 166.8 ppm; ESIMS (*m/z*) 494.7 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{16}ClIN_2O_3$ (Exact Mass: 493.9894); C, 48.56; H, 3.26; N, 5.66. Found C, 48.42; H, 3.09; N, 5.84.



Methyl 2-{hydroxy[4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (2f). 88 % as a white solid (534 mg from 500 mg); mp 93-94 °C; R_f= 0.16 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1716 (CO_2Me), 3430 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.27 (d, 1H, J = 7.1 Hz), 3.81 (s, 3H), 3.82 (s, 3H), 5.76 (d, 1H, J = 6.5 Hz), 5.99 (s, 1H), 6.44 (s, 1H), 6.88 (d, 2H, J = 8.6 Hz), 7.16-7.19 (m, 4H), 7.25-7.26 (m, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.2, 55.4, 64.0, 68.4, 114.1, 121.9, 124.9, 127.1, 127.6, 128.9, 131.8, 140.1, 144.7, 153.4, 160.1, 166.9 ppm; ESIMS (*m/z*) 490.8 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{19}IN_2O_4$ (Exact Mass: 490.0390); C, 51.44; H, 3.91; N, 5.71. Found C, 51.63; H, 3.74; N, 5.86.

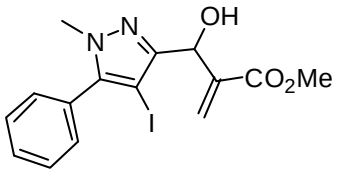


Methyl 2-{hydroxy[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (2g). 89 % as colorless oil (536 mg from 500 mg); R_f= 0.14 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1711 (CO_2Me), 3404 (OH) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.30 (d, 1H, J = 7.4 Hz), 3.82 (s, 3H), 5.77 (d, 1H, J = 7.2 Hz), 6.04 (s, 1H), 6.47 (s, 1H), 7.12-7.20 (m, 2H),

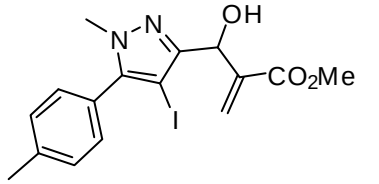


7.29-7.32 (m, 3H), 7.46 (d, 2H, *J* = 8.8 Hz), 8.22 (d, 2H, *J* = 8.8 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.3, 64.9, 68.5, 123.9, 125.1, 127.2, 128.5, 129.3, 130.8, 131.5, 136.2, 139.3, 139.8, 142.5, 148.0, 154.2, 166.8 ppm; ESIMS (*m/z*) 505.7 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{16}IN_3O_5$ (Exact Mass: 505.0135); C, 47.54; H, 3.19; N, 8.32. Found C, 47.32; H, 3.39; N, 8.55.

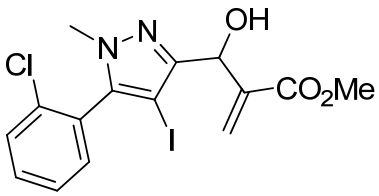
Methyl 2-[hydroxy(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (2h). 88 % as a colourless oil (561 mg from 500 mg); R_f= 0.21 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1716 (CO_2Me), 3425 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.17 (d, 1H, *J* = 5.6 Hz), 3.79 (s, 3H), 3.80 (m, 3H), 5.68 (d, 1H, *J* = 4.4 Hz), 5.97 (s, 1H), 6.43 (s, 1H), 7.35-7.38 (m, 2H), 7.44-7.53 (m, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.4, 52.0, 61.0, 68.0, 126.6, 128.7, 129.4, 130.0, 140.1, 145.6, 151.9, 166.7 ppm; ESIMS (*m/z*) 398.7 $[M+H]^+$; Anal. Calcd. for $C_{15}H_{15}IN_2O_3$ (Exact Mass: 398.0127); C, 45.24; H, 3.80; N, 7.04. Found C, 45.40; H, 3.62; N, 7.18.



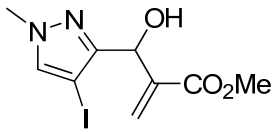
Methyl 2-{hydroxy[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (2i). 87 % as a colourless oil (550 mg from 500 mg); R_f= 0.20 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1719 (CO_2Me), 3400 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.31 (d, 1H, *J* = 6.3 Hz), 3.78 (s, 3H), 3.79 (s, 3H), 5.68 (d, 1H, *J* = 5.5 Hz), 5.98 (s, 1H,), 6.43 (s, 1H), 7.24-7.31 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.5, 38.5, 52.1, 61.1, 68.1, 126.7, 129.5, 129.6, 130.0, 139.5, 140.2, 145.8, 147.5, 151.9, 166.8 ppm; ESIMS (*m/z*) 412.6 $[M+H]^+$; Anal. Calcd. for $C_{16}H_{17}IN_2O_3$ (Exact Mass: 412.0284); C, 46.62; H, 4.16; N, 6.80. Found C, 46.51; H, 4.28; N, 6.65.



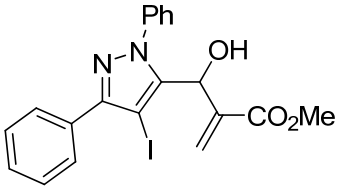
Methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (2j). 86 % as a white solid (537 mg from 500 mg); mp 88-89 ^{o}C; R_f= 0.20 (hexanes: EtOAc, 80:20, v/v); IR (KBr): ν_{max} 1717 (CO_2Me), 3411 (OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.20 (d, 1H, *J* = 6.6 Hz), 3.71 (s, 3H), 3.81 (s, 3H), 5.69 (d, 1H, *J*= 6.5 Hz), 5.95 (s, 1H), 6.43 (s, 1H), 7.29-7.32 (m, 1H), 7.37-7.48 (m, 2H), 7.53-7.56 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.3, 52.2, 62.0, 68.1, 126.9, 127.2, 129.0, 130.1, 131.4, 132.6, 134.9, 140.1, 143.9, 151.9, 166.8 ppm; ESIMS (*m/z*) 432.7 $[M+H]^+$; Anal. Calcd. for



$C_{15}H_{14}ClIN_2O_3$ (Exact Mass: 431.9738); C, 41.64; H, 3.26; N, 6.47. Found C, 41.83; H, 3.46; N, 6.31.

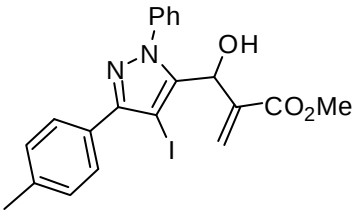


Methyl 2-[hydroxy(4-iodo-1-methyl-1*H*-pyrazol-3-yl)methyl]acrylate (1k). ref-6

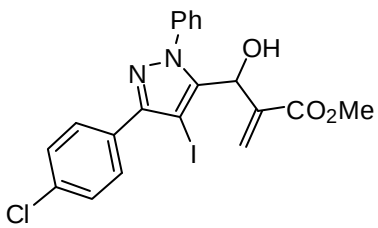


Methyl 2-[hydroxy(4-iodo-1,3-diphenyl-1*H*-pyrazol-5-yl)methyl]acrylate (7a). ref-6

Methyl 2-{hydroxy[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (7b). 89 % as a colourless oil (544 mg from 500 mg); R_f= 0.23 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1717 (CO_2Me), 3423 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.70 (s, 3H), 5.82 (s, 1H), 5.87 (d, 1H, J = 1.4 Hz), 6.38 (d, 1H, J = 1.2 Hz), 7.24 (s, 1H), 7.44-7.50 (m, 6H), 7.74 (d, 2H, J = 8.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 52.2, 61.3, 65.8, 126.6, 127.8, 128.7, 128.99, 129.03, 129.1, 129.6, 137.7, 138.4, 139.6, 142.2, 153.1, 165.9 ppm; ESIMS (*m/z*) 475.2 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{19}IN_2O_3$ (Exact Mass: 474.0440); C, 53.18; H, 4.04; N, 5.91. Found C, 53.30; H, 4.19; N, 5.75.

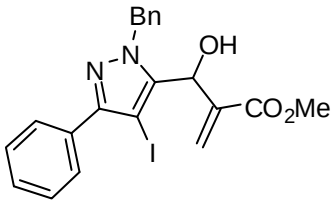


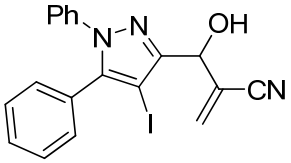
Methyl 2-[[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl](hydroxy)methyl]acrylate (7c). 87 % as a colourless oil (527 mg from 500 mg); R_f= 0.22 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1717 (CO_2Me), 3414 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 3H), 5.81 (s, 1H), 5.86 (d, 1H, J = 1.6 Hz), 6.38 (d, 1H, J = 1.2 Hz), 7.41 (d, 2H, J = 8.5 Hz), 7.44-7.48 (m, 5H), 7.81 (d, 2H, J = 8.5 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.3, 61.0, 66.0, 126.6, 127.9, 128.6, 129.1, 129. 3,



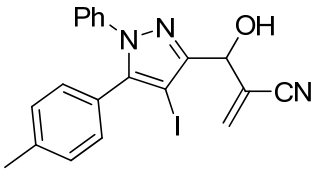
130.1, 131.1, 134.6, 137.6, 139.6, 142.5, 152.0, 166.0 ppm; ESIMS (*m/z*) 495.1 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{16}ClIN_2O_3$ (Exact Mass: 493.9894); C, 48.56; H, 3.26; N, 5.66. Found C, 48.40; H, 3.11; N, 5.85.

Methyl 2-[(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)(hydroxy)methyl]acrylate (7l). 90 % as colorless oil (550 mg from 500 mg); R_f= 0.19 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1716 (CO_2Me), 3406 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.22 (s, 1H), 3.78 (s, 3H), 5.55 (s, 2H), 5.57 (s, 1H), 5.93 (s, 1H), 6.28 (s, 1H), 7.24-7.26 (m, 4H), 7.37-7.44 (m, 4H) 7.84 (d, 2H, *J* = 7.4 Hz) ppm; ESIMS (*m/z*) 475.0 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{19}IN_2O_3$ (Exact Mass: 474.0440); C, 53.18; H, 4.04; N, 5.91. Found C, 53.39; H, 3.82; N, 6.07.

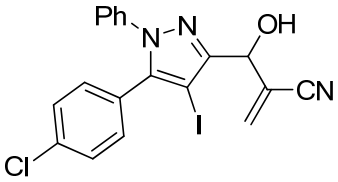




2-[Hydroxy(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)methyl]acrylonitrile (11a). ref-6

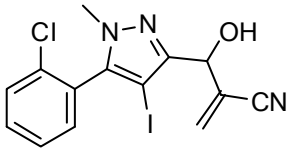


2-{Hydroxy[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylonitrile (11b). ref-6



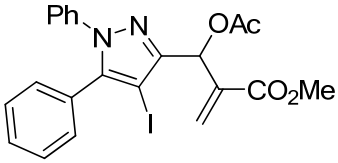
2-[[5-(4-Chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylonitrile (11c). ref-6

2-[[5-(2-Chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylonitrile (11j). 88 % as colorless oil (507 mg from 500 mg); R_f= 0.15 (hexanes: EtOAc, 80:20, v/v); IR

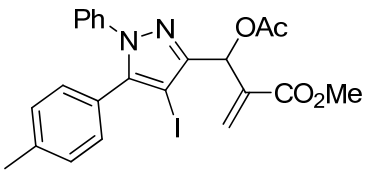


(Neat): ν_{max} 2229 (CN), 3405 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.24 (d, 1H, J = 5.9 Hz), 3.75 (s, 3H), 5.38 (d, 1H, J = 3.6 Hz), 6.14 (d, 1H, J = 1.0 Hz), 6.25 (d, 1H, J = 1.3 Hz), 7.32 (dd, 1H, J = 1.5, 7.2 Hz), 7.40-7.50 (m, 2H), 7.56 (dd, 1H, J = 1.4, 7.9 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.5, 61.4, 69.2, 117.0, 124.5, 127.3, 128.4, 130.2, 131.4, 131.7, 132.5, 134.8, 144.5, 149.7 ppm; ESIMS (*m/z*) 399.9 $[M+H]^+$; Anal. Calcd. for $C_{14}H_{11}ClIN_3O$ (Exact Mass: 398.9635); C, 42.08; H, 2.77; N, 10.52. Found C, 42.22; H, 2.93; N, 10.32.

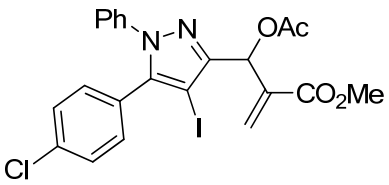
General Procedure for the preparation of compounds 3a-k, 8a-c,l and 12a-c,j as Exemplified 3a. To a stirred solution of compound **2a** (500 mg, 1.09 mmol) in CH_2Cl_2 (30 mL) was added pyridine (0.114 mL ,1.41 mmol) and cool to 0 ^oC. There after acetyl chloride (0.116 ml, 1.63 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise and stirred for 1 h. After completion of the reaction, H_2O (50 mL) was added to it and layers were seperated. The aqueous layer was again extracted with CH_2Cl_2 (2x25 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. Column chromatography of the crude product over silica gel furnished the pure **3a** as a colorless oil (ethyl acetate/hexanes, 1:19; yield: 513 mg, 94 %).



Methyl 2-[(acetyloxy)(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)methyl]acrylate (3a). ref-6

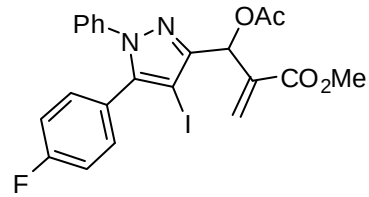


Methyl 2-{(acetyloxy)[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (3b). ref-6

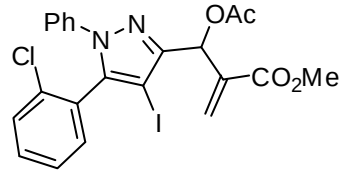


Methyl 2-{(acetyloxy)[5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (3c). ref-6

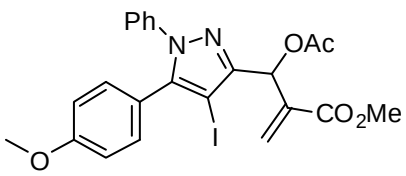
Methyl 2-{(acetyloxy)[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (3d). 92 % as a white solid (501 mg from 500 mg); mp 130-131 ^{o}C; R_f= 0.33 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1736 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.79 (s, 3H), 6.00 (s, 1H), 6.53 (s, 1H), 6.87 (s, 1H), 7.02-7.08 (m, 2H), 7.11-7.15 (m, 2H), 7.22-7.26 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 52.3, 66.0, 68.0, 115.7, 116.0, 125.0, 125.1, 127.1, 128.0, 129.0, 129.1, 132.4, 132.5, 137.2, 139.6, 144.0, 150.8, 161.4, 165.6, 169.6 ppm; ESIMS (*m/z*) 542.9 $[M+Na]^+$; Anal. Calcd. for $C_{22}H_{18}FIN_2O_4$ (Exact Mass: 520.0295); C, 50.79; H, 3.49; N, 5.38. Found C, 50.92; H, 3.64; N, 5.24.



Methyl 2-{(acetyloxy)[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (3e). 94 % as colorless oil (510 mg from 500 mg); R_f= 0.32 (hexanes: EtOAc, 90:10, v/v); IR (Neat): ν_{max} 1735 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 3.78 (s, 3H), 6.02 (s, 1H), 6.51 (s, 1H), 6.90 (s, 1H), 7.19-7.25 (m, 7H), 7.28-7.37 (m, 1H), 7.40-7.43 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 52.1, 68.1, 124.1, 126.7, 127.0, 127.3, 128.7, 130.0, 130.3, 132.1, 133.9, 138.4, 139.8, 140.4, 149.8, 165.6, 169.6 ppm; ESIMS (*m/z*) 558.9 $[M+Na]^+$; Anal. Calcd. for $C_{22}H_{18}ClIN_2O_4$ (Exact Mass: 536.0000); C, 49.23; H, 3.38; N, 5.22. Found C, 49.40; H, 3.51; N, 5.07.

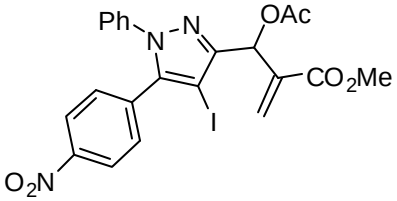


Methyl 2-(acetoxy(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-3-yl)methyl)acrylate (3f). 94 % as colorless oil (510 mg from 500 mg); R_f= 0.32 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1733 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 6.00 (s, 1H), 6.52 (s, 1H), 6.86-6.89 (m, 3H), 7.14-7.19 (m, 4H),

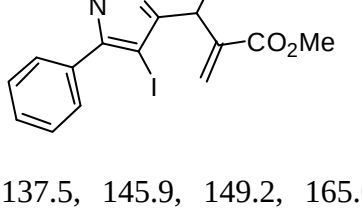


7.24-7.26 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 52.2, 55.4, 68.2, 77.4, 114.1, 121.9, 125.0, 127.2, 127.7, 128.9, 131.8, 137.4, 140.0, 144.9, 150.6, 160.2, 165.7, 169.7 ppm; ESIMS (*m/z*) 533.1 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{21}IN_2O_5$ (Exact Mass: 532.0495); C, 51.89; H, 3.98; N, 5.26. Found C, 52.12; H, 4.17; N, 5.06.

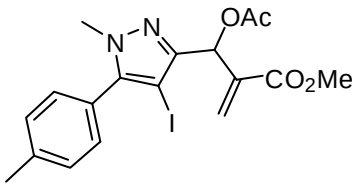
Methyl 2-{(acetyloxy)[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (3g). 93 % as colorless oil (504 mg from 500 mg); R_f= 0.29 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1732 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.80 (s, 3H), 6.03 (d, 1H, *J* = 0.6 Hz), 6.54 (s, 1H), 6.87 (s, 1H), 7.10-7.17 (m, 2H), 7.28-7.31 (m, 3H), 7.46 (d, 2H, *J* = 8.6 Hz), 8.21 (d, 2H, *J* = 8.6 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 52.3, 67.9, 77.4, 123.8, 125.2, 127.3, 128.5, 129.3, 131.5, 136.1, 137.0, 139.3, 142.5, 148.0, 151.5, 165.6, 169.6 ppm; ESIMS (*m/z*) 488.0 $[M-OAc]^+$; Anal. Calcd. for $C_{22}H_{18}IN_3O_6$ (Exact Mass: 547.0240); C, 48.28; H, 3.31; N, 7.68. Found C, 48.47; H, 3.53; N, 7.45.



Methyl 2-[(acetyloxy)(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (3h). 93 % as colourless oil (514 mg from 500 mg); R_f= 0.33 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1721 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 3.78 (s, 6H), 5.96 (s, 1H), 6.51 (s, 1H), 6.80 (s, 1H), 7.36-7.39 (m, 2H), 7.43-7.50 (m, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 38.7, 52.2, 62.3, 68.1, 126.6, 128.8, 129.6, 130.2, 137.5, 145.9, 149.2, 165.6, 169.6 ppm; ESIMS (*m/z*) 440.7 $[M+H]^+$; Anal. Calcd. for $C_{17}H_{17}IN_2O_4$ (Exact Mass: 440.0233); C, 46.38; H, 3.89; N, 6.36. Found C, 46.22; H, 4.08; N, 6.18.

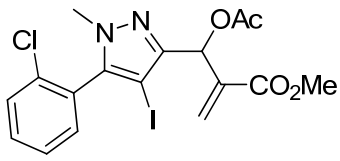


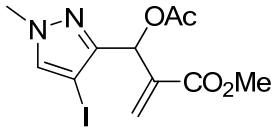
Methyl 2-{(acetyloxy)[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (3i). 94 % as a colourless oil (518 mg from 500 mg); R_f= 0.32 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1730 (COMe & CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 2.43 (s, 3H), 3.78 (s, 6H), 5.96 (s, 1H), 6.51 (s, 2H), 6.79 (s, 1H), 7.25-7.32 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 21.5, 38.6, 52.2, 62.2,



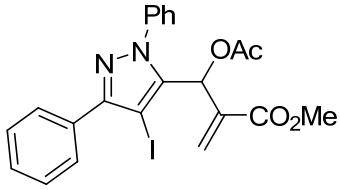
68.0, 126.6, 129.5, 129.61, 129.64, 130.0, 137.5, 139.6, 144.4, 149.1, 165.6, 169.6 ppm; ESIMS (*m/z*) 476.9 $[M+Na]^+$; Anal. Calcd. for $C_{18}H_{19}IN_2O_4$ (Exact Mass: 454.0390); C, 47.59; H, 4.22; N, 6.17. Found C, 47.77; H, 4.36; N, 6.00.

Methyl 2-{(acetyloxy)[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]methyl}acrylate (3j). 93 % as colourless oil (510 mg from 500 mg); R_f= 0.33 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1729 (COMe & CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H), 3.70 (s, 3H), 3.76 (s, 3H), 5.91 (s, 1H), 6.46 (s, 1H), 6.78 (s, 1H), 7.29-7.33 (m, 1H), 7.36-7.48 (m, 2H), 7.53-7.56 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.1, 38.4, 52.2, 63.5, 67.9, 126.7, 126.9, 127.2, 130.1, 131.5, 132.5, 132.7, 134.8, 137.5, 149.1, 165.5, 169.6 ppm; ESIMS (*m/z*) 497.1 $[M+Na]^+$; Anal. Calcd. for $C_{17}H_{16}ClIN_2O_4$ (Exact Mass: 473.9843); C, 43.01; H, 3.40; N, 5.90. Found C, 43.18; H, 3.59; N, 5.75.



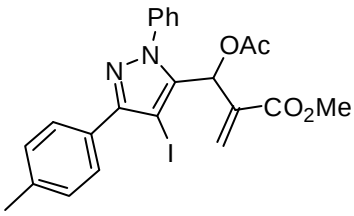


Methyl 2-[(acetyloxy)(4-iodo-1-methyl-1*H*-pyrazol-3-yl)methyl]acrylate (3k). ref-6

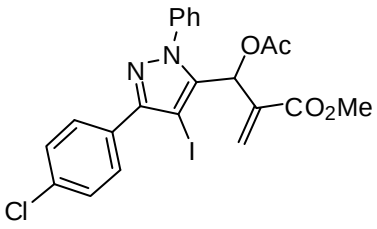


Methyl 2-[(acetyloxy)(4-iodo-1,3-diphenyl-1*H*-pyrazol-5-yl)methyl]acrylate (8a). ref-6

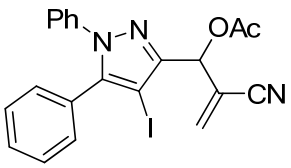
Methyl 2-{(acetyloxy)[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (8b). 94 % as a colourless oil (512 mg from 500 mg); R_f= 0.32 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1732 (COMe & CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 3H), 2.40 (s, 3H), 3.69 (s, 3H), 5.70 (d, 1H, J = 1.5 Hz), 6.41 (d, 1H, J = 1.1 Hz), 6.82 (s, 1H), 7.25 (d, 2H, J = 8.2 Hz), 7.47 (s, 5H), 7.75 (d, 2H, J = 8.1 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.7, 21.5, 52.3, 62.1, 66.4, 126.7, 128.7, 129.0, 129.07, 129.14, 129.3, 129.6, 134.9, 138.4, 139.5, 139.6, 153.4, 164.9, 169.1 ppm; ESIMS (*m/z*) 517.1 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{21}IN_2O_4$ (Exact Mass: 516.0546); C, 53.50; H, 4.10; N, 5.43. Found C, 53.65; H, 3.94; N, 5.61.



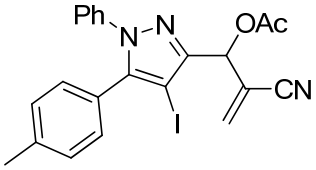
Methyl 2-{(acetyloxy)[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (8c). 95 % as a colourless oil (516 mg from 500 mg); R_f= 0.33 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1730 (COMe & CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 3.69 (s, 3H), 5.70 (d, 1H, J = 1.4 Hz), 6.41 (d, 1H, J = 1.1 Hz), 6.81 (s, 1H), 7.41 (d, 2H, J = 8.6 Hz), 7.47 (s, 5H), 7.82 (d, 2H, J = 8.5 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.7, 52.4, 61.9, 66.3, 126.7, 128.5, 129.1, 129.2, 129.5, 130.1, 131.0, 134.6, 134.8, 139.5, 139.9, 152.2, 164.8, 169.1 ppm; ESIMS (*m/z*) 537.2 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{18}ClIN_2O_4$ (Exact Mass: 536.0000); C, 49.23; H, 3.38; N, 5.22. Found C, 49.40; H, 3.51; N, 5.06.



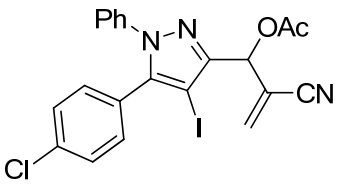
Methyl 2-(acetoxy(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)methyl)acrylate (8l). 92 % as colorless oil (501 mg from 500 mg); R_f= 0.29 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1731 (COMe & CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 3H), 3.73 (s, 3H), 5.47-5.61 (m, 2H), 5.72 (s, 1H), 6.43 (s, 1H), 6.93 (s, 1H), 7.05 (d, 2H, J = 6.8 Hz), 7.23-7.30 (m, 3H), 7.37-7.46 (m, 3H), 7.85 (d, 2H, J = 6.8 Hz) ppm; ESIMS (*m/z*) 516.9 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{21}IN_2O_4$ (Exact Mass: 516.0546); C, 53.50; H, 4.10; N, 5.43. Found C, 53.70; H, 4.33; N, 5.24.



2-Cyano-1-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)allyl acetate (14a). ref-6

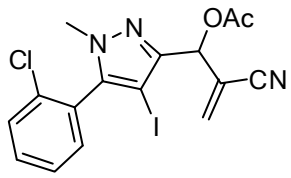


2-Cyano-1-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]allyl acetate (14b). ref-6



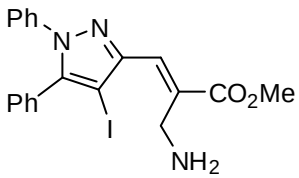
1-[5-(4-Chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]-2-cyanoallyl acetate (14c). ref-6

1-[5-(2-Chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]-2-cyanoallyl acetate (14j). 94 % as colorless oil (519 mg from 500 mg); R_f= 0.23 (hexanes: EtOAc, 80:20, v/v); IR (Neat): ν_{max} 1751 (COMe), 2231 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H), 3.76 (s, 3H), 6.11 (d, 1H, J = 1.4 Hz), 6.21 (d, 1H, J = 1.0 Hz), 6.48 (s, 1H), 7.31-7.32 (m, 1H), 7.44-7.48 (m, 2H), 7.54-7.55 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.9, 38.5, 62.3, 68.9, 116.4, 120.7, 127.3, 128.4, 130.1, 131.6, 132.7, 133.2, 134.7, 144.3, 146.7, 169.4 ppm; ESIMS (*m/z*) 441.8 $[M+H]^+$; Anal. Calcd. for $C_{16}H_{13}ClIN_3O_2$ (Exact Mass: 440.9741); C, 43.51; H, 2.97; N, 9.51. Found C, 43.30; H, 2.82; N, 9.68.

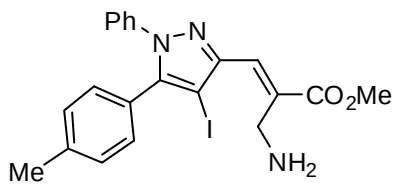


General Procedure for the preparation of compounds 4a-k, 9a-c,l and 13a-c,j as Exemplified 4a. To a stirred solution of MeOH-NH_3 (100 mL), compound **3a** (500 mg, 0.996 mmol) in MeOH (200 mL) was added slowly with stirring. After completion (*ca* 30 min) of the reaction MeOH was removed under vacuum. Column chromatography of the crude product over silica gel furnished the pure 4a as a white solid (ethyl acetate/hexanes, 9:1; yield: 375 mg, 82 %).

Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (4a). 81 % as a white solid (370 mg from 500 mg); mp 215-216 ^oC; R_f= 0.24 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1718 (CO_2Me), 3423 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 4.10 (s, 2H), 7.22-7.29 (m, 7H), 7.39-7.40 (m, 3H), 7.68 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 37.3, 52.1, 70.0, 124.2, 127.8, 128.3, 128.6, 129.1, 129.8, 130.9, 131.4, 138.9, 144.7, 147.9, 167.1 ppm; ESIMS (*m/z*) 459.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{19}IN_3O_2$ $[MH]^+$: 460.0522. Found: 460.0528.

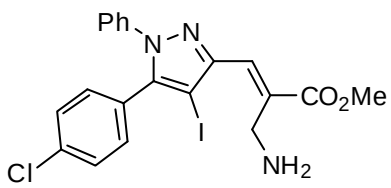


Methyl (*E*)-2-(aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (4b). 81 % as a white solid (371 mg from 500 mg); mp 87-88 ^oC; R_f= 0.23 (EtOAc: MeOH, 95: 5, v/v); IR (KBr):

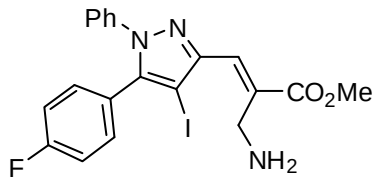


ν_{max} 1715 (CO_2Me), 3450 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.87 (s, 3H), 4.15 (s, 2H), 7.13-7.23 (m, 4H), 7.26-7.32 (m, 5H), 7.73 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 37.7, 52.7, 66.9, 124.7, 126.3, 128.3, 129.0, 129.2, 129.6, 130.2, 131.4, 132.0, 139.6, 139.7, 145.4, 148.5, 167.6 ppm; ESIMS (*m/z*) 473.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{21}H_{21}IN_3O_2$ $[MH]^+$: 474.0678. Found: 474.0680.

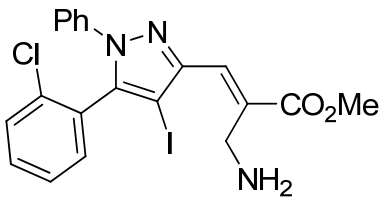
Methyl (*E*)-2-(aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate (4c). 80 % as a white solid (368 mg from 500 mg); mp 115-116 ^oC; R_f= 0.23 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1714 (CO_2Me), 3425 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 4.26 (s, 2H), 7.19-7.22 (m, 4H), 7.34-7.39 (m, 5H), 7.80 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 37.3, 51.9, 71.0, 124.3, 127.4, 127.9, 128.5, 128.7, 129.6, 131.3, 132.6, 134.6, 138.8, 143.3, 147.9, 166.9 ppm; ESIMS (*m/z*) 493.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{18}ClIN_3O_2$ $[MH]^+$: 494.0132. Found: 494.0136.



Methyl (*E*)-2-(aminomethyl)-3-[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (4d). 78 % as a white solid (358 mg from 500 mg); mp 202-203 ^oC; R_f= 0.25 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1713 (CO_2Me), 3413 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 4.12 (s, 2H), 7.09 (t, 2H, J = 8.6 Hz), 7.22-7.33 (m, 7H), 7.69 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 36.6, 51.5, 70.1, 114.8, 115.1, 123.8, 127.4, 127.9, 128.2, 128.3, 128.4, 130.1, 131.3, 131.4, 138.3, 143.2, 147.3, 160.3, 166.3 ppm; ESIMS (*m/z*) 477.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{18}FIN_3O_2$ $[MH]^+$: 478.0428. Found: 478.0423.



Methyl (*E*)-2-(aminomethyl)-3-(5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate (4e). 79 % as colorless oil (363 mg from 500 mg); R_f= 0.22 (EtOAc: MeOH, 95: 5, v/v); IR (Neat): ν_{max} 1708 (CO_2Me), 3408 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 4.31-4.42 (s, 2H), 7.26-7.38 (m, 7H), 7.40-7.46 (m, 2H), 7.87 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.8, 53.0, 72.3, 124.0, 126.3, 127.4, 128.9, 129.4, 130.3, 131.7, 132.6, 134.2, 134.8, 139.2, 148.2, 166.6 ppm; ESIMS (*m/z*) 493.8 $[M+1]^+$; DART-HRMS Calcd. for $C_{20}H_{18}ClIN_3O_2$ $[MH]^+$: 494.0132. Found: 494.0129.



Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate (4f). 82 % as a white solid (377 mg from 500 mg); mp 204-206 ^{o}C; R_f= 0.22 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1710 (CO_2Me), 3452 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.87 (s, 3H), 4.19 (s, 2H), 6.90 (d, 2H, J = 8.5 Hz), 7.18 (d, 2H, J = 8.2 Hz), 7.26-7.32 (m, 5H), 7.72 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 37.2, 52.1, 54.9, 70.0, 113.8, 120.7, 124.2, 127.8, 128.7, 131.2, 131.5, 139.0, 144.8, 147.8, 159.9, 166.9 ppm; ESIMS (*m/z*) 489.8 $[M+H]^+$; ESI-HRMS Calcd. for $C_{21}H_{21}IN_3O_3$ $[MH]^+$: 490.0628. Found: 474.0608.

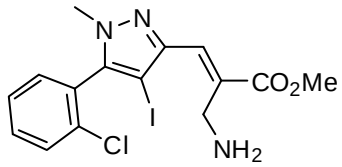
Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate (4g) 79 % as a white solid (364 mg from 500 mg); mp 200-202 ^{o}C; R_f= 0.18 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1714 (CO_2Me), 3426 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H), 4.17 (s, 2H), 7.26-7.27 (m, 2H), 7.35-7.38 (m, 3H), 7.50 (d, 2H, J = 8.4 Hz), 7.70 (s, 1H), 8.25 (d, 2H, J = 8.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 37.6, 52.5, 70.6, 123.7, 124.7, 128.8, 129.3, 130.9, 131.2, 132.0, 135.5, 138.7, 142.7, 148.0, 148.9, 167.1 ppm; ESIMS (*m/z*) 504.8 $[M+H]^+$; ESI-HRMS Calcd. for $C_{20}H_{18}IN_4O_4$ $[MH]^+$: 505.0373. Found: 505.0365.

Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)prop-2-enoate (4h). 82 % as a white solid (370 mg from 500 mg); mp 198-199 ^{o}C; R_f= 0.19 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1711 (CO_2Me), 3423 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H), 3.90 (s, 3H), 4.09 (s, 2H), 7.37-7.40 (m, 2H), 7.51-7.52 (m, 3H), 7.64 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 37.2, 39.3, 52.0, 67.2, 128.5, 129.3, 129.5, 130.6, 130.9, 145.6, 146.4, 167.3 ppm; ESIMS (*m/z*) 397.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{15}H_{17}IN_3O_2$ $[MH]^+$: 398.0365. Found: 398.0361.

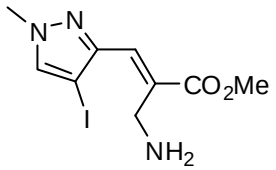
Methyl (*E*)-2-(aminomethyl)-3-[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]prop-2-enoate (4i). 82 % as a white solid (371 mg from 500 mg); mp 129-130 ^{o}C; R_f= 0.18 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1718 (CO_2Me), 3419 (NH_2) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 4.12 (s, 2H), 7.24-7.36 (m,

4H), 7.68 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6, 37.2, 39.2, 52.6, 67.6, 126.0, 129.6, 129.64, 129.7, 129.8, 129.9, 132.4, 140.0, 146.4, 146.9, 167.6 ppm; ESIMS (*m/z*) 411.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{16}H_{19}IN_3O_2$ $[MH]^+$: 412.0522. Found: 412.0532.

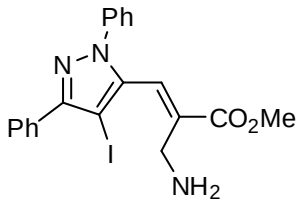
Methyl (*E*)-2-(aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enoate (4j). 80 % as a white solid (364 mg from 500 mg); mp 120-121 ^{o}C; R_f= 0.18 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1715 (CO_2Me), 3422 (NH_2) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.84 (s, 3H), 3.87 (s, 3H), 4.15 (s, 2H), 7.28-7.33 (m, 1H), 7.40-7.59 (m, 3H), 7.67 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.4, 39.0, 52.6, 68.8, 127.5, 128.5, 130.2, 130.3, 131.8, 131.9, 132.5, 134.8, 144.5, 147.1, 167.7 ppm; ESIMS (*m/z*) 431.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{15}H_{16}ClIN_3O_2$ $[MH]^+$: 431.9976. Found: 432.0001.



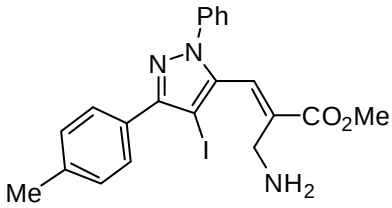
Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-1*H*-pyrazol-3-yl)prop-2-enate (4k). 83 % as a white solid (366 mg from 500 mg); mp 121-122 ^{o}C; R_f= 0.15 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1710 (CO_2Me), 3400 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.98 (s, 5H), 7.46 (m, 1H), 7.51 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.5, 40.2, 52.5, 64.1, 128.9, 130.8, 136.1, 148.1, 167.9 ppm; ESIMS (*m/z*) 321.8 $[M+H]^+$; DART-HRMS Calcd. for $C_9H_{13}IN_3O_2$ $[MH]^+$: 322.0052. Found: 322.0057.



Methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,3-diphenyl-1*H*-pyrazol-5-yl)prop-2-enoate (9a). 72 % as a white solid (329 mg from 500 mg); mp 199-200 ^{o}C; R_f= 0.21 (EtOAc); IR (KBr): ν_{max} 1720 (CO_2Me), 3427 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 3.87 (s, 2H), 7.35-7.47 (m, 6H), 7.51 (s, 1H), 7.59 (d, 2H, *J* = 7.5 Hz), 7.83 (d, 2H, *J* = 6.4 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 37.9, 52.8, 66.2, 123.6, 128.0, 128.4, 129.1, 132.3, 138.5, 138.78, 138.84, 153.4, 164.7 ppm; ESIMS (*m/z*) 459.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{19}IN_3O_2$ $[MH]^+$: 460.0522. Found: 460.0529.

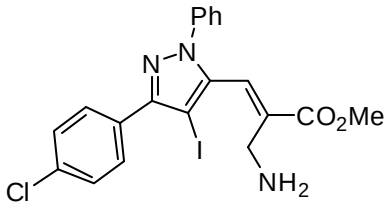


Methyl (*E*)-2-(aminomethyl)-3-[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (9b). 70 % as a white solid (321 mg from 500 mg); mp 110-111 ^{o}C; R_f= 0.22 (EtOAc); IR (KBr): ν_{max} 1714 (CO_2Me), 3403 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.38 (s, 2H), 3.85 (s, 3H), 7.27 (d, 2H, *J* = 7.9 Hz), 7.35 (s, 1H), 7.39 (d, 1H, *J* = 6.6 Hz), 7.44-

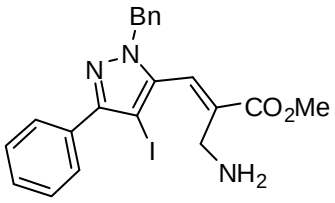


7.52 (m, 4H), 7.80 (d, 2H, J = 7.8 Hz) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ 20.9, 38.7, 52.3, 66.2, 124.1, 126.0, 127.9, 128.2, 129.0, 129.3, 138.0, 139.3, 139.4, 140.6, 152.4, 166.4 ppm; ESIMS (m/z) 473.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{21}H_{21}IN_3O_2$ $[MH]^+$: 474.0678. Found: 474.0682.

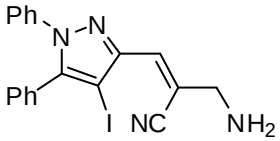
Methyl (*E*)-2-(aminomethyl)-3-[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (9c). 68 % as a white solid (313 mg from 500 mg); mp 85-86 ^{o}C; R_f= 0.20 (EtOAc); IR (KBr): ν_{max} 1711 (CO_2Me), 3413 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 2H), 3.85 (s, 3H), 7.32 (s, 1H), 7.42-7.50 (m, 7H), 7.87 (d, 2H, J = 8.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.7, 52.6, 64.6, 124.1, 124.2, 127.1, 128.6, 128.7, 128.9, 129.0, 129.6, 129.8, 130.8, 134.8, 139.5, 139.7, 140.6, 152.5, 166.6 ppm; ESIMS (m/z) 493.8 $[M+1]^+$; DART-HRMS Calcd. for $C_{20}H_{18}ClIN_3O_2$ $[MH]^+$: 494.0132. Found: 494.0146.



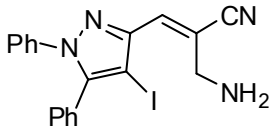
Methyl (*E*)-2-(aminomethyl)-3-(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)prop-2-enoate (9l). 75 % as a white solid (344 mg from 500 mg); mp 200-202 ^{o}C; R_f= 0.25 (EtOAc: MeOH, 95: 5, v/v); IR (KBr): ν_{max} 1723 (CO_2Me), 3428 (NH_2) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.42 (s, 2H), 3.86 (s, 3H), 5.36 (s, 2H), 7.16-7.19 (m, 2H), 7.30-7.33 (m, 3H), 7.39-7.49 (m, 4H), 7.84-7.88 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 39.8, 52.5, 55.4, 62.2, 127.1, 127.4, 128.3, 128.9, 132.4, 135.9, 140.6, 152.1, 166.1 ppm; ESIMS (m/z) 474.2 $[M+H]^+$; ESI-HRMS Calcd. for $C_{21}H_{21}IN_3O_2$ $[MH]^+$: 474.0678. Found: 474.0666.



(*Z*)-2-(Aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enenitrile (15a). 77 % as a white solid (350 mg from 500 mg); mp 169-170 ^{o}C; R_f= 0.26 (EtOAc); IR (KBr): ν_{max} 2212 (CN), 3407 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 2H), 7.07 (s, 1H), 7.18-7.28 (m, 6H), 7.40-7.42 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 45.4, 67.8, 114.9, 116.9, 123.4, 123.6, 127.0, 127.8, 128.0, 128.5, 129.3, 130.6, 138.6, 143.7, 146.3 ppm; ESIMS (m/z) 426.9 $[M+H]^+$; DART-HRMS Calcd. for $C_{19}H_{16}IN_4$ $[MH]^+$: 427.0420. Found: 427.0402.

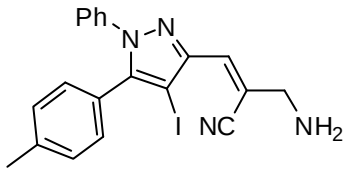


(*E*)-2-(Aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enenitrile (15a). 80 % as a white solid (200 mg from 250 mg); mp 152-154 ^{o}C; R_f= 0.30 (EtOAc); IR (KBr): ν_{max} 2212 (CN), 3407 (NH_2) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.00 (s, 2H), 7.14 (s, 1H), 7.19-7.31 (m,

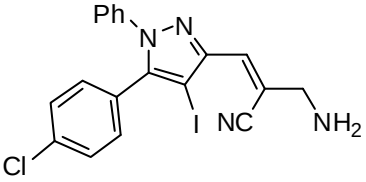


7H), 7.39-7.40 (m, 3H) ppm; ESIMS (*m/z*) 426.9 $[M+H]^+$; DART-HRMS Calcd. for $C_{19}H_{16}IN_4$ $[MH]^+$: 427.0420. Found: 427.0409.

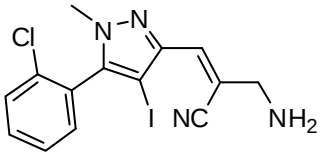
(*Z*)-2-(Aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (15b). 76 % as a white solid (346 mg from 500 mg); mp 109-110 ^oC; R_f= 0.25 (EtOAc); IR (KBr): ν_{max} 2204 (CN), 3387 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 4.00 (s, 2H), 7.11-7.22 (m, 7H), 7.29-7.31 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 41.6, 69.6, 118.9, 120.1, 124.4, 124.6, 126.2, 128.3, 129.0, 129.1, 129.6, 130.1, 133.9, 139.6, 139.7, 145.3, 148.1 ppm; ESIMS (*m/z*) 440.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{18}IN_4$ $[MH]^+$: 441.0576. Found: 441.0579.



(*Z*)-2-(Aminomethyl)-3-[5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (15c). 74 % as yellow oil (338 mg from 500 mg); R_f= 0.27 (EtOAc); IR (KBr): ν_{max} 2212 (CN), 3423 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.98 (s, 2H), 7.14 (s, 1H), 7.18-7.25 (m, 4H), 7.28-7.38 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 69.7, 119.3, 120.0, 124.6, 124.7, 127.6, 128.5, 129.2, 129.3, 129.4, 131.1, 131.6, 133.5, 135.8, 139.2, 143.9, 148.2 ppm; ESIMS (*m/z*) 460.8 $[M+H]^+$; DART-HRMS Calcd. for $C_{19}H_{15}ClIN_4$ $[MH]^+$: 461.0030. Found: 461.0020.

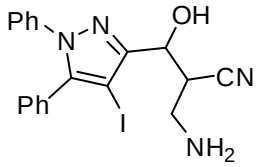


(*Z*)-2-(Aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (5j). 76 % as yellow oil (343 mg from 500 mg); R_f= 0.23 (EtOAc); IR (Neat): ν_{max} 2213 (CN), 3395 (NH_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 2H), 3.82 (s, 3H), 6.96 (s, 1H), 7.27-7.31 (m, 1H), 7.40-7.50 (m, 2H), 7.56 (d, 1H, J = 7.7 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.0, 46.8, 67.0, 114.5, 118.0, 127.4, 128.6, 130.2, 131.7, 131.8, 132.5, 134.8, 144.0, 145.8 ppm; ESIMS (*m/z*) 398.7 $[M+H]^+$; DART-HRMS Calcd. for $C_{14}H_{13}ClIN_4$ $[MH]^+$: 398.9873. Found: 398.9870.



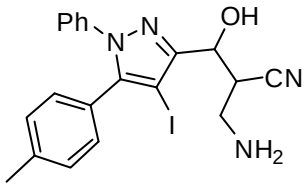
General Procedure for the preparation of compounds 12a-c. These compounds were prepared following the above mentioned general procedure for the preparation of the primary allylamines. However the reaction time for these compounds varied between 6-8 h.

2-(Aminomethyl)-3-hydroxy-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)propanenitrile (diastereomeric mixture) (12a). 92 % as a yellow solid (239 mg from 250 mg); mp 129-130 ^{o}C;

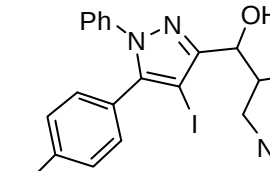


R_f= 0.30 (EtOAc); IR (KBr): ν_{max} 2244 (CN), 3438 (NH_2 & OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.27-3.48 (m, 3H), 5.13-5.26 (m, 1H), 7.18-7.22 (m, 7H), 7.36-7.38 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.2, 41.4, 42.0, 42.3, 62.7, 64.0, 67.9, 68.4, 119.1, 119.4, 124.9, 125.0, 128.0, 128.7, 129.0, 129.3, 130.4, 139.7, 145.1, 152.2, 152.8 ppm; ESIMS (*m/z*) 445.0 $[M+H]^+$; DART-HRMS Calcd. for $C_{19}H_{18}IN_4O$ $[MH]^+$: 445.0525. Found: 445.0557.

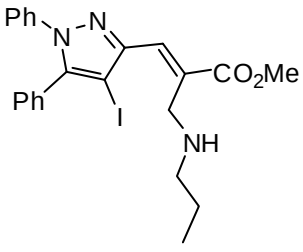
2-(Aminomethyl)-3-hydroxy-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]propanenitrile (diastereomeric mixture) (12b). 91 % as a yellow solid (236 mg from 250 mg); mp 175-176 ^{o}C; R_f= 0.31 (EtOAc); IR (KBr): ν_{max} 2239 (CN), 3430 (NH_2 & OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.26-3.42 (m, 3H), 5.11-5.24 (m, 1H), 7.14-7.26 (m, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6, 39.0, 39.1, 41.3, 42.2, 63.9, 64.5, 67.9, 68.4, 119.1, 119.4, 125.0, 126.4, 126.5, 127.9, 129.0, 129.4, 130.3, 139.4, 139.5, 139.7, 139.8, 145.2, 145.4, 147.6, 152.0, 152.6 ppm; ESIMS (*m/z*) 459.0 $[M+H]^+$; DART-HRMS Calcd. for $C_{20}H_{20}IN_4O$ $[MH]^+$: 459.0682. Found: 459.0725.



2-(Aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl)-3-hydroxypropanenitrile (diastereomeric mixture) (12c). 90 % as a yellow solid (233 mg from 250 mg); mp 110-111 ^{o}C; R_f= 0.30 (EtOAc); IR (KBr): ν_{max} 2247 (CN), 3435 (NH_2 & OH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.29-3.47 (m, 3H), 5.11-5.24 (m, 1H), 7.15-7.27 (m, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.7, 41.6, 44.1, 44.2, 60.6, 61.7, 64.2, 67.4, 119.3, 122.3, 124.8, 124.9, 127.7, 127.8, 128.1, 128.9, 129.0, 129.1, 131.6, 135.4, 135.5, 139.3, 139.4, 143.8, 143.9, 151.5, 154.3 ppm; ESIMS (*m/z*) 478.9 $[M+H]^+$; DART-HRMS Calcd. for $C_{19}H_{17}ClIN_4O$ $[MH]^+$: 479.0136. Found: 479.0151.

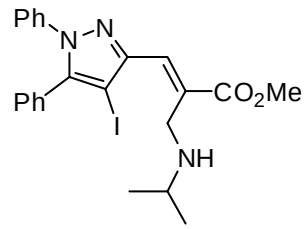


Methyl (*E*)-2-[(propylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (16). 91 % as a white solid (227 mg from 250 mg); mp 84-85 ^{o}C; R_f= 0.14 (hexanes: EtOAc, 50:50, v/v); IR (KBr): ν_{max} 1702 (CO_2Me), 3437 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 3H, J = 7.4 Hz), 1.49-1.59 (m, 2H), 2.71 (t, 2H, J = 7.4 Hz), 3.89 (s, 3H), 4.14 (s, 2H), 7.22-7.32 (m, 7H), 7.39-

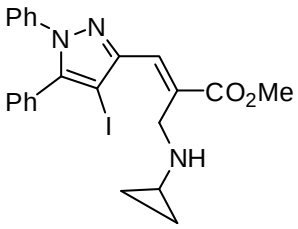


7.40 (m, 3H), 7.80 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.4, 22.9, 44.1, 49.0, 52.9, 70.6, 124.9, 127.4, 128.1, 128.8, 129.2, 129.4, 131.2, 131.6, 133.4, 135.9, 139.2, 144.4, 148.6, 167.3 ppm; ESIMS (*m/z*) 502.1 $[M+H]^+$; DART-HRMS Calcd. for $C_{23}H_{25}IN_3O_2$ $[MH]^+$: 502.0991. Found: 502.0995.

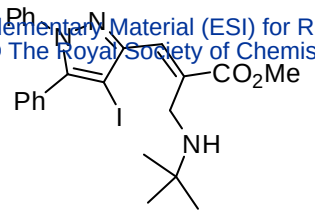
Methyl (*E*)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)-2-((isopropylamino)methyl) prop-2-enoate (17). 85 % as a white solid (424 mg from 500 mg); mp 91-92 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 50:50, v/v); IR (KBr): ν_{max} 1704 (CO_2Me), 3412 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.07 (s, 3H), 2.81-2.89 (m, 1H), 3.87 (s, 3H), 4.03 (s, 2H), 7.21-7.23 (m, 2H), 7.26-7.28 (m, 5H), 7.38-7.40 (m, 3H), 7.69 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.0, 43.7, 48.1, 52.4, 70.5, 124.6, 128.0, 128.8, 129.0, 129.4, 129.7, 130.4, 130.7, 133.8, 139.8, 144.8, 148.9, 168.5 ppm; ESIMS (*m/z*) 501.9 $[M+H]^+$; DART-HRMS Calcd. for $C_{23}H_{25}IN_3O_2$ $[MH]^+$: 502.0991. Found: 502.0996.



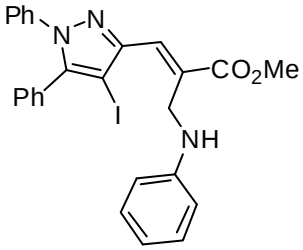
Methyl (*E*)-2-((cyclopropylamino)methyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl) prop-2-enoate (18). 87 % as a white solid (432 mg from 500 mg); mp 93-94 ^{o}C; R_f= 0.25 (hexanes: EtOAc, 50:50, v/v); IR (KBr): ν_{max} 1718 (CO_2Me), 3400 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.41-0.47 (m, 2H), 0.54-0.56 (m, 2H), 2.20-2.27 (m, 1H), 3.88 (s, 3H), 4.19 (s, 2H), 7.23-7.29 (m, 7H), 7.39-7.40 (m, 3H), 7.76 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.9, 29.7, 45.0, 52.5, 70.5, 124.6, 128.1, 128.7, 129.0, 129.46, 129.49, 130.3, 131.5, 132.0, 139.6, 144.9, 148.7, 168.2 ppm; ESIMS (*m/z*) 499.9 $[M+H]^+$; DART-HRMS Calcd. for $C_{23}H_{23}IN_3O_2$ $[MH]^+$: 500.0835. Found: 500.0832.



Methyl (*E*)-2-[(tert-butylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (19). 86 % as a white solid (441 mg from 500 mg); mp 111-112 ^{o}C; R_f= 0.28 (hexanes: EtOAc, 50:50, v/v); IR (KBr): ν_{max} 1702 (CO_2Me), 3446 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 3.89 (s, 3H), 4.06 (s, 2H), 7.21-7.31 (m, 6H), 7.38-7.40 (m, 4H), 7.74 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 29.0, 39.6, 52.4, 70.4, 74.5, 124.8, 128.1, 128.7, 128.9, 129.4, 129.6, 130.4, 133.6, 139.8, 144.9, 148.9, 168.4 ppm; ESIMS (*m/z*) 516.0 $[M+H]^+$; DART-HRMS Calcd. for $C_{24}H_{27}IN_3O_2$ $[MH]^+$: 516.1148. Found: 516.1139.



Methyl (*E*)-2-(anilinomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (20). 84 % as a yellow solid (224 mg from 250 mg); mp 204-205 ^{o}C; R_f= 0.41 (hexanes: EtOAc, 90:10, v/v); IR (KBr): ν_{max} 1702 (CO_2Me), 3371 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 1H), 3.82 (s, 3H), 4.67 (s, 2H), 6.90-7.00 (m, 3H), 7.17-7.23 (m, 3H), 7.26-7.31 (m, 6H), 7.40-7.42 (m, 3H), 7.81 (s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.0, 52.5, 70.7, 114.1, 117.6, 124.5, 128.1, 128.8, 129.1, 129.2, 129.5, 130.4, 130.9, 132.9, 139.6, 144.9, 148.5, 148.7, 168.3 ppm; ESIMS (*m/z*) 535.9 [M+H]$^{+}$; DART-HRMS Calcd. for $C_{26}H_{23}IN_3O_2$ [MH]$^{+}$: 536.0835. Found: 536.0833.



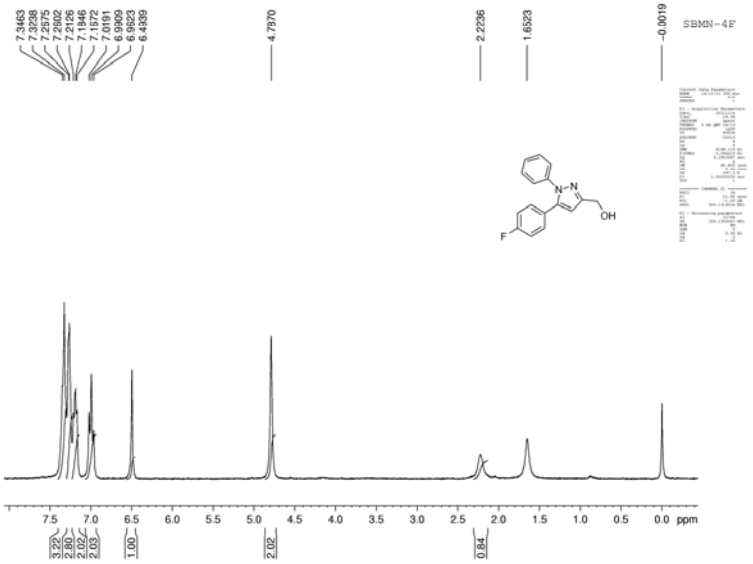


Fig-1: [1]H-spectrum of [5-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol.

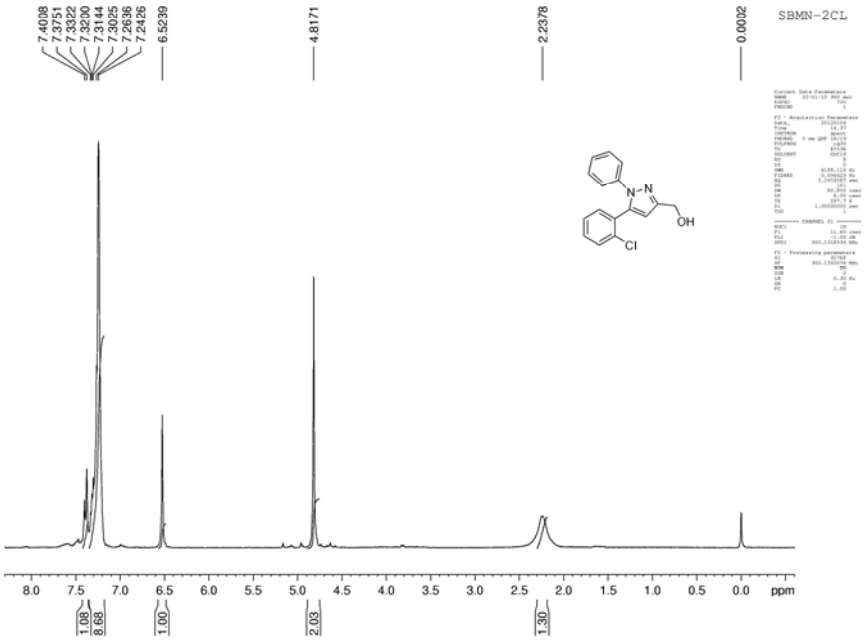


Fig-2: [1]H-spectrum of [5-(2-chlorophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol.

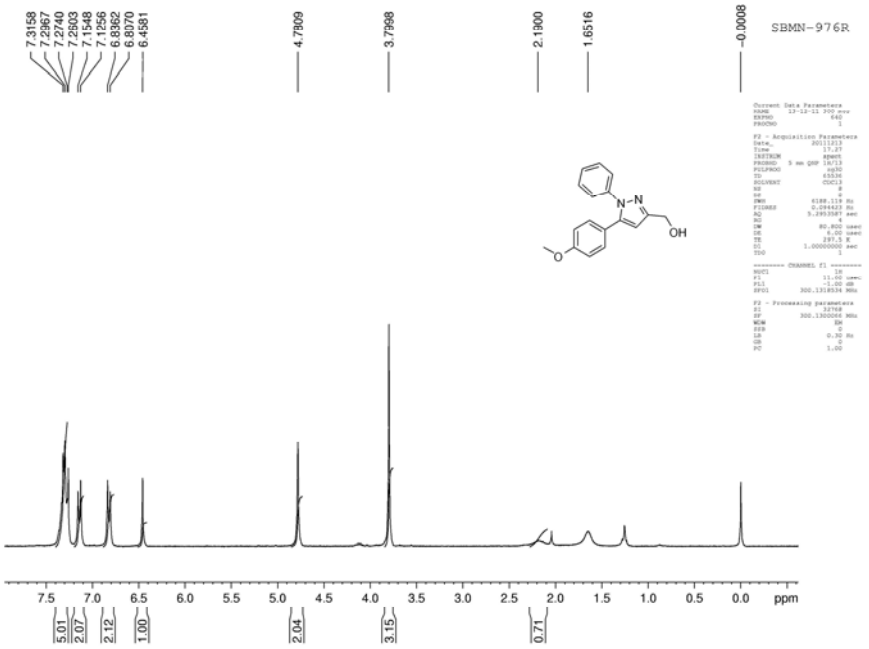


Fig-3: ^{1}H-spectrum of [5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol.

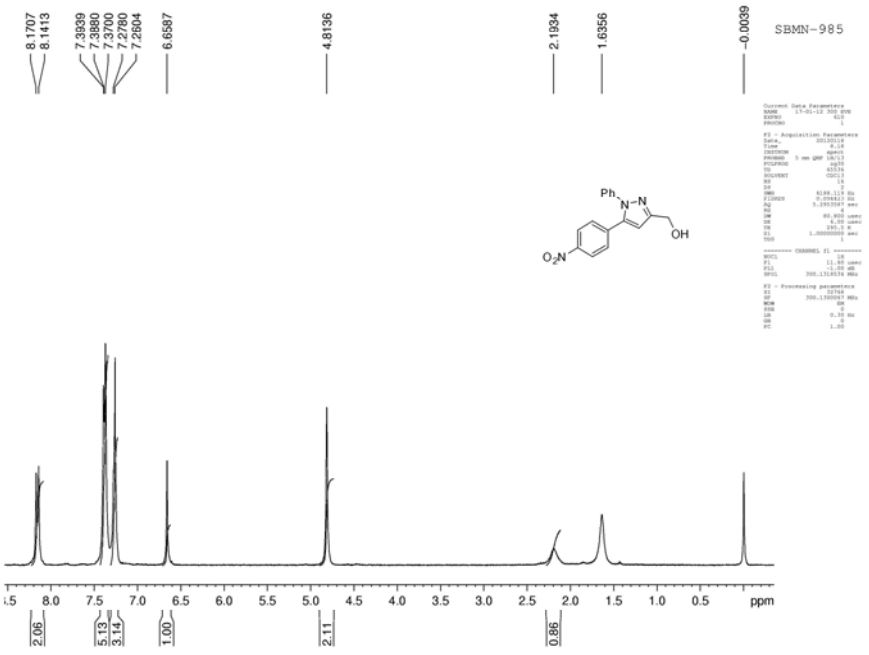


Fig-4: ^{1}H-spectrum of [5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methanol.

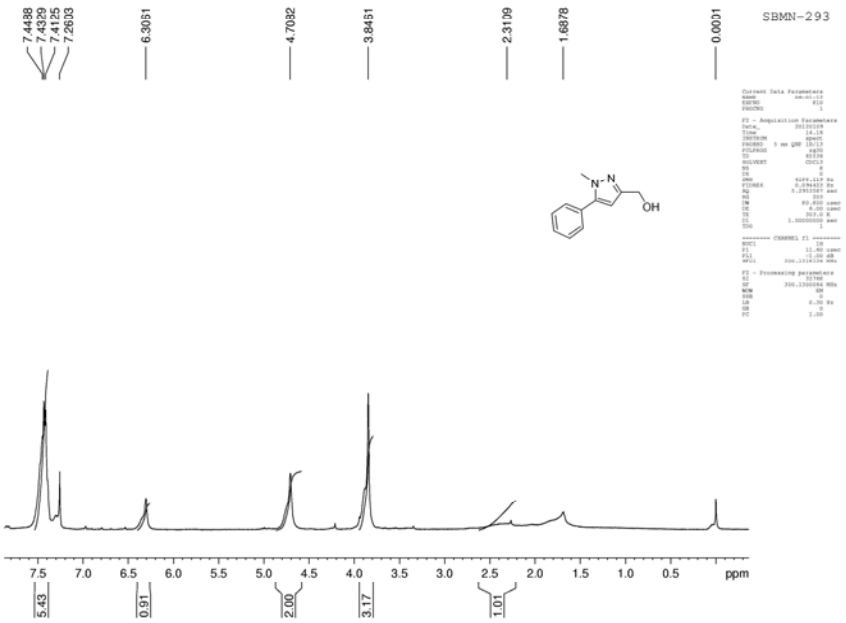


Fig-5: ^{1}H-spectrum of (1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methanol.

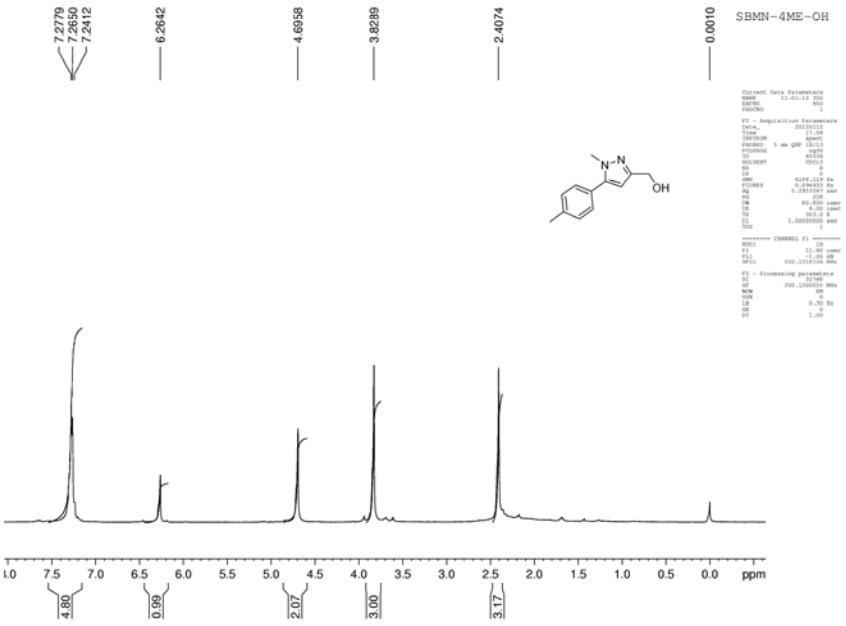


Fig-6: ^{1}H-spectrum of [1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methanol.

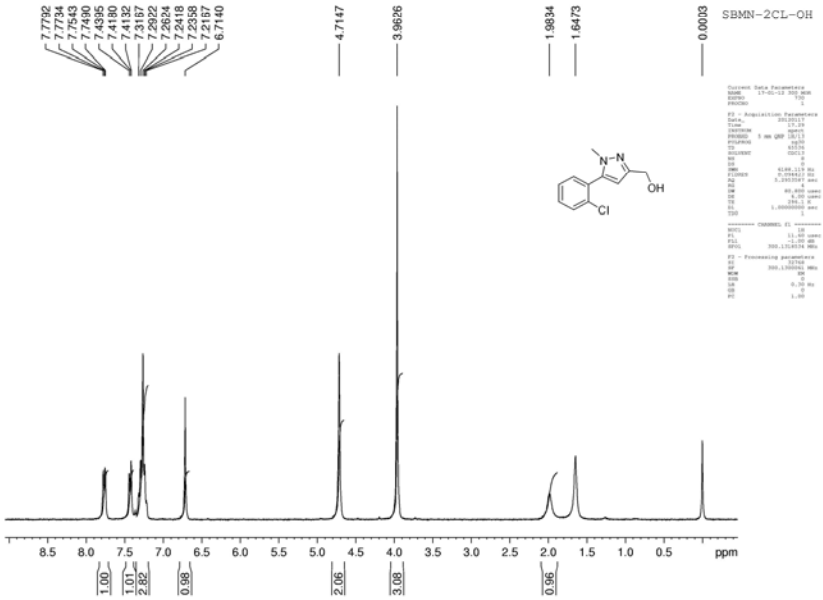


Fig-7: ^{1}H-spectrum of [5-(2-chlorophenyl)-1-methyl-1*H*-pyrazol-3-yl]methanol.

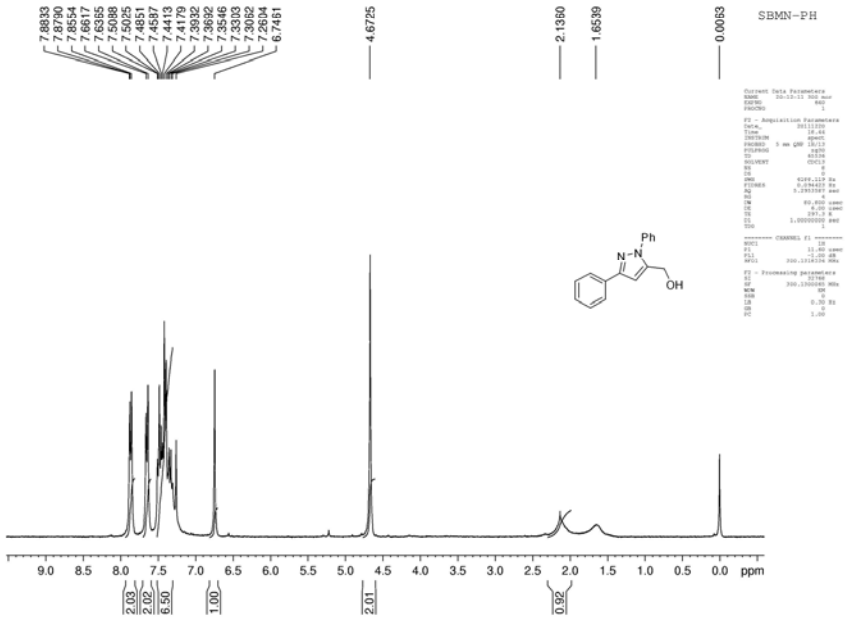


Fig-8: ^{1}H-spectrum of (1,3-diphenyl-1*H*-pyrazol-5-yl)methanol.

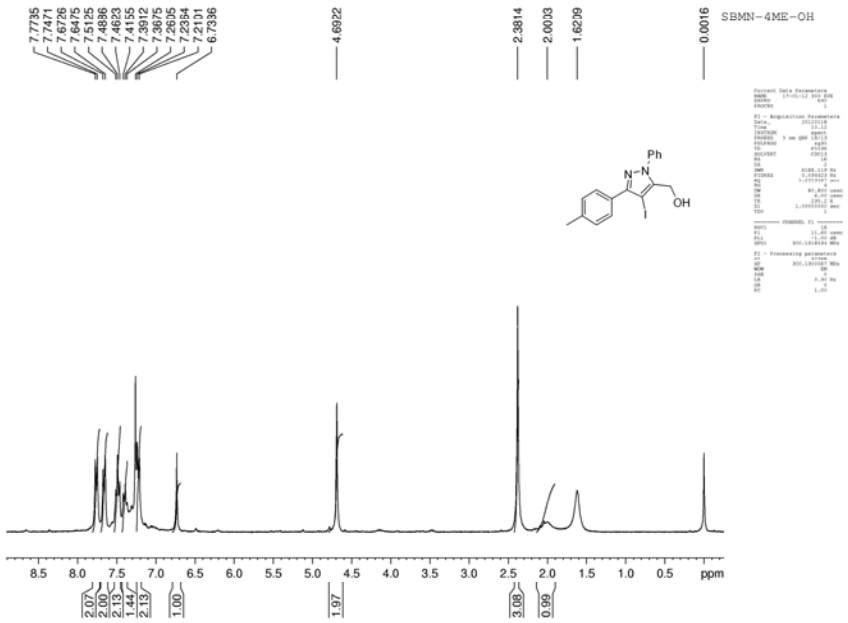


Fig-9: ^{1}H-spectrum of [3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methanol.

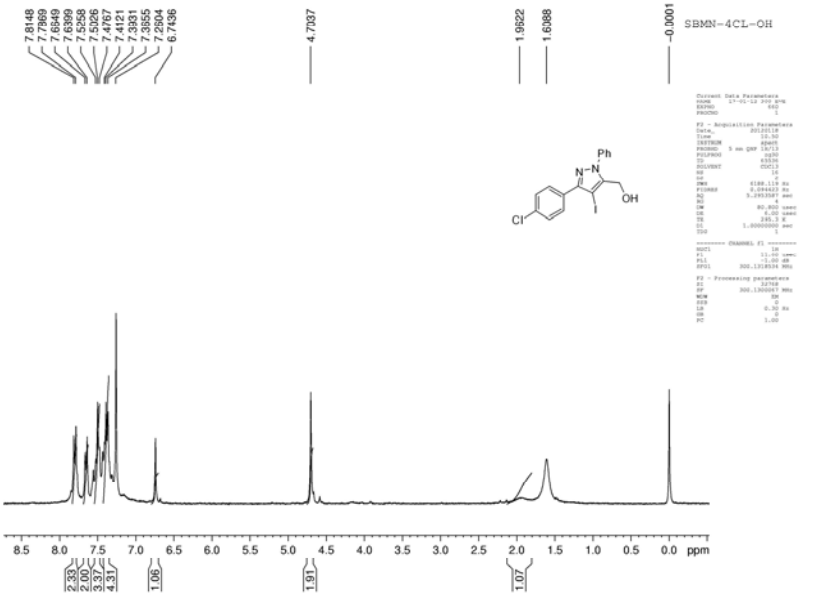


Fig-10: ^{1}H-spectrum of [3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl]methanol.

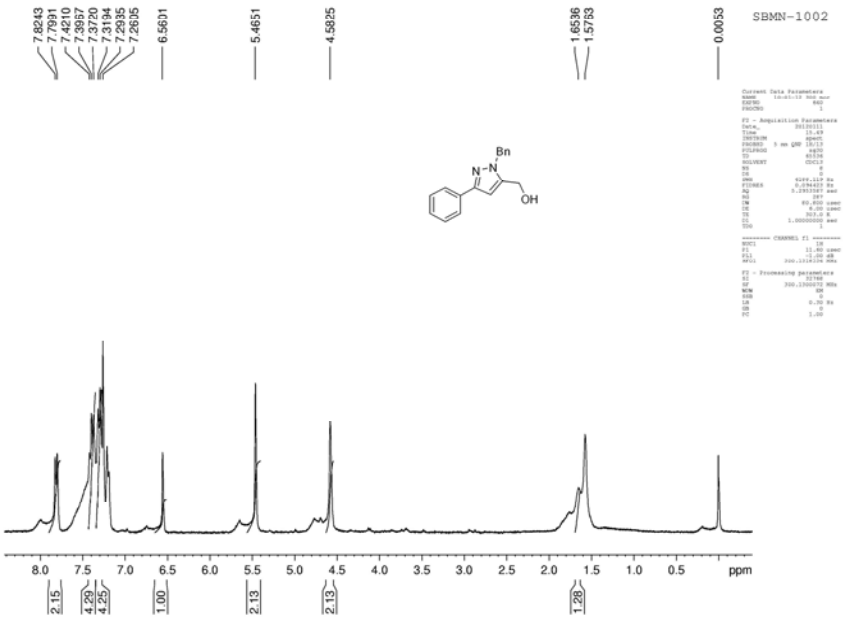


Fig-11: ^{1}H-spectrum of (1-benzyl-3-phenyl-1*H*-pyrazol-5-yl)methanol.

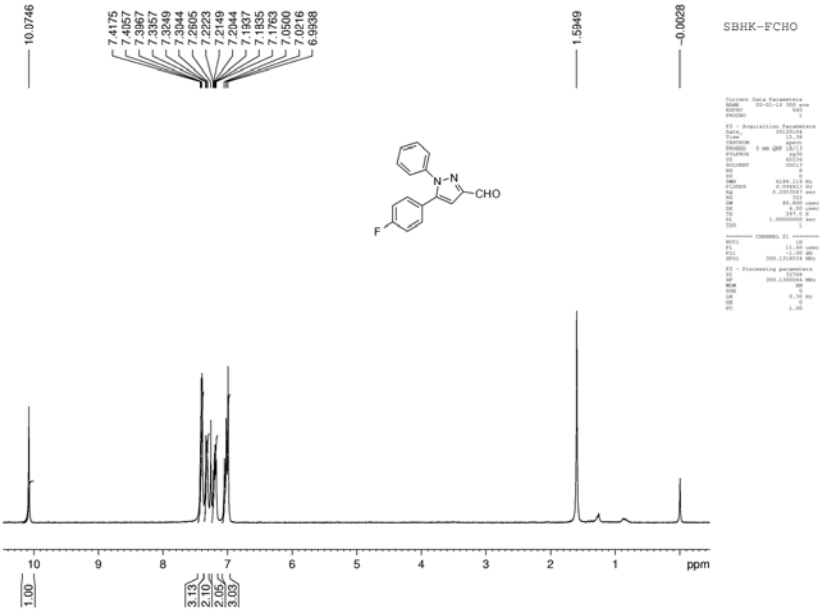


Fig-12: ^{1}H-spectrum of 5-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde.

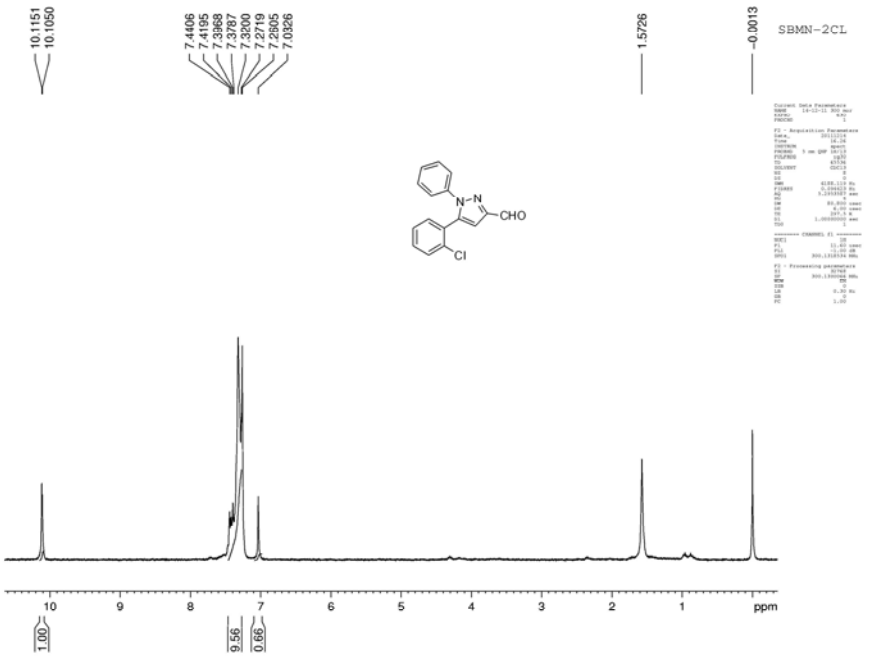


Fig-13: ^{1}H-spectrum of 5-(2-chlorophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde.

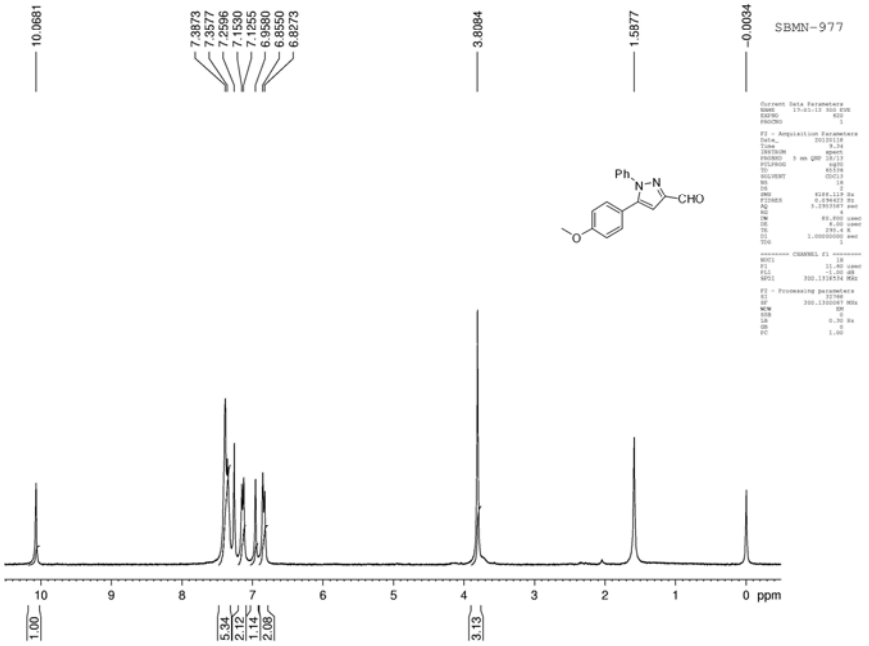


Fig-14: ^{1}H-spectrum of 5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde.

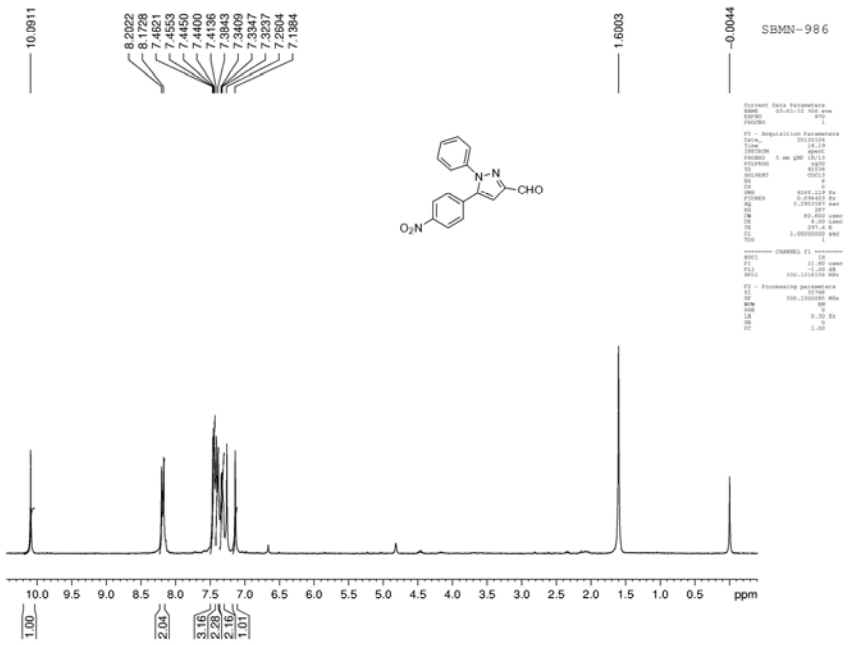


Fig-15: ^{1}H-spectrum of 5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde.

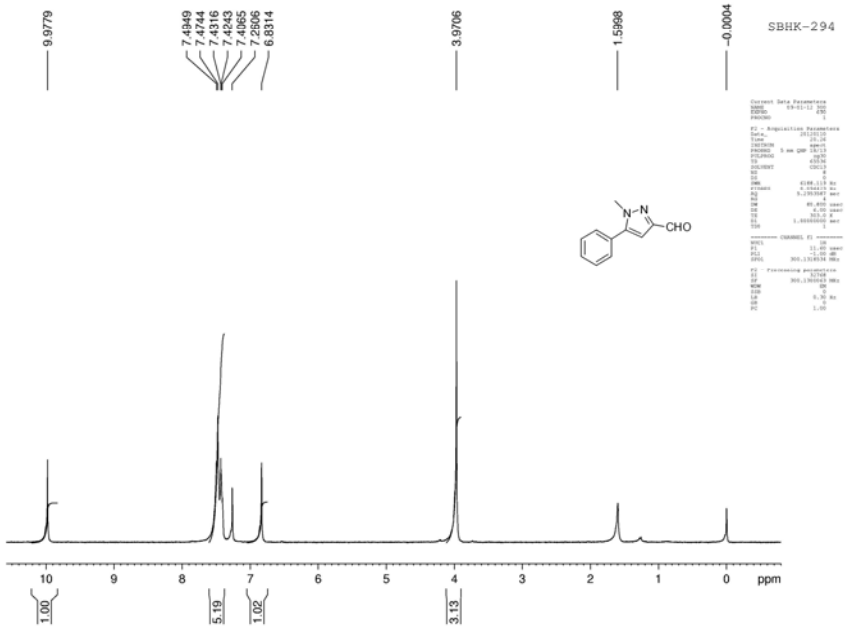


Fig-16: ^{1}H-spectrum of 1-methyl-5-phenyl-1*H*-pyrazole-3-carbaldehyde.

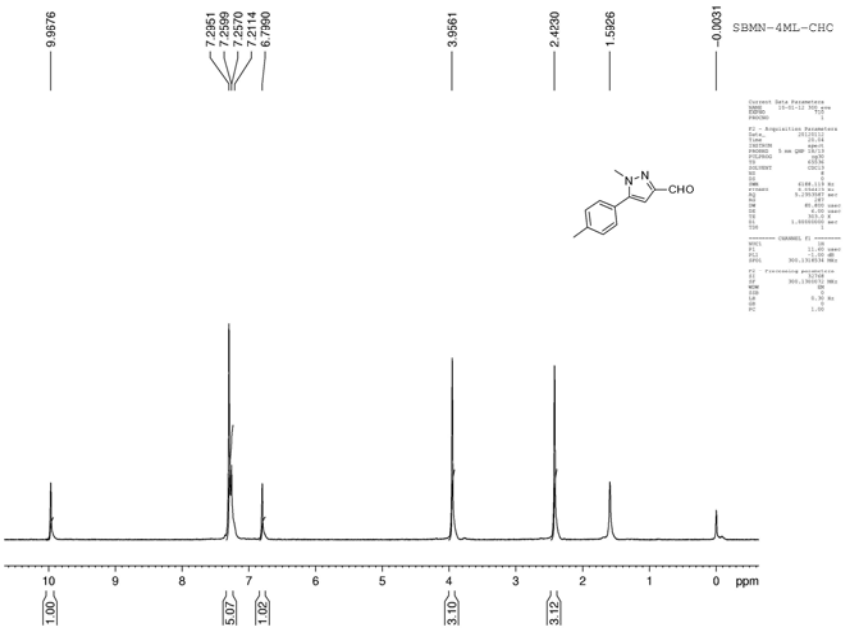


Fig-17: ^{1}H-spectrum of 1-methyl-5-(4-methylphenyl)-1*H*-pyrazole-3-carbaldehyde.

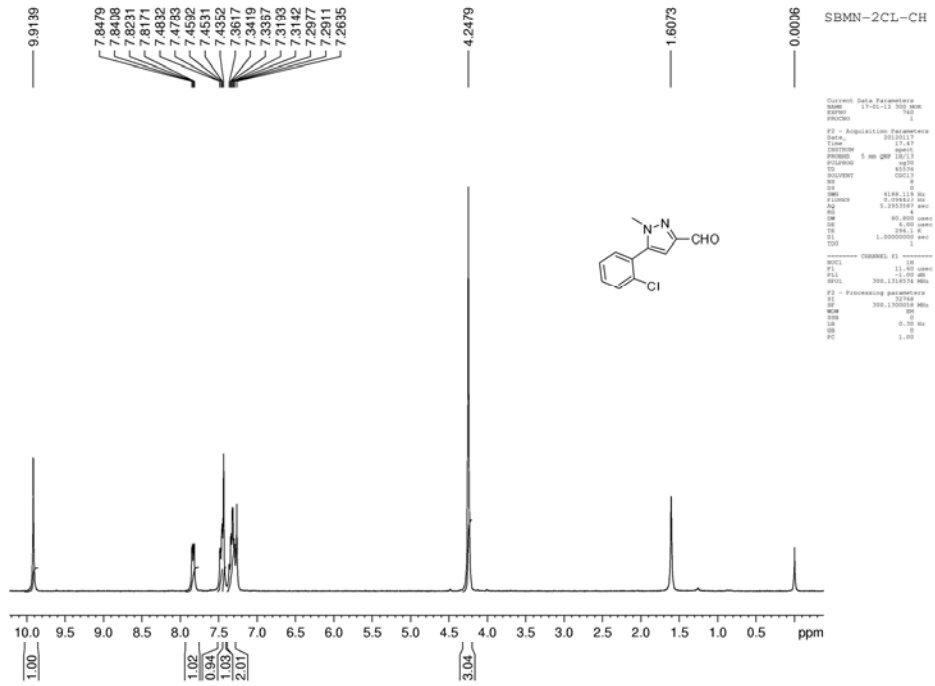


Fig-18: ^{1}H-spectrum of 5-(2-chlorophenyl)-1-methyl-1*H*-pyrazole-3-carbaldehyde.

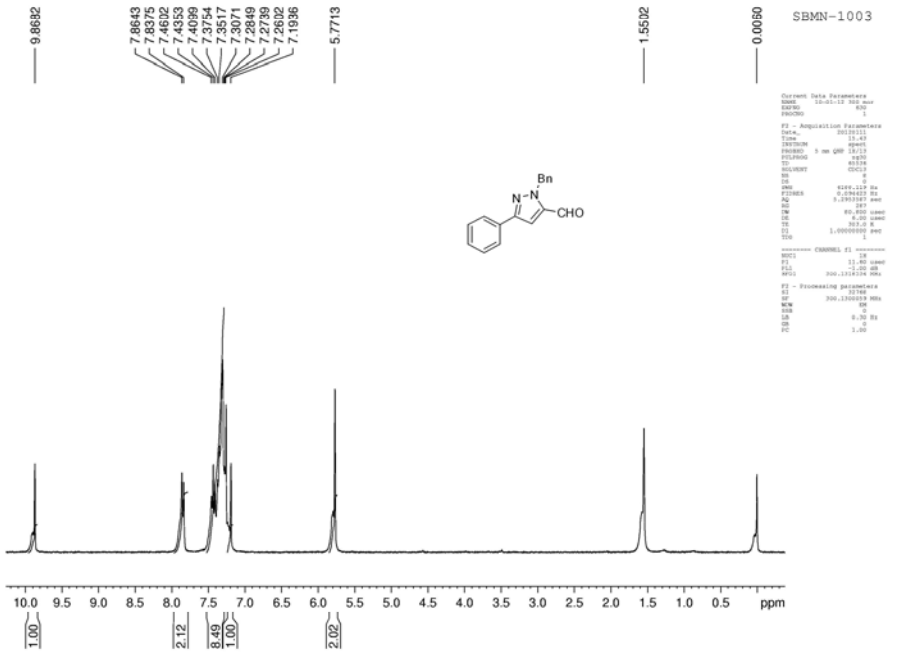


Fig-19: ^{1}H-spectrum of 1-benzyl-3-phenyl-1*H*-pyrazole-5-carbaldehyde.

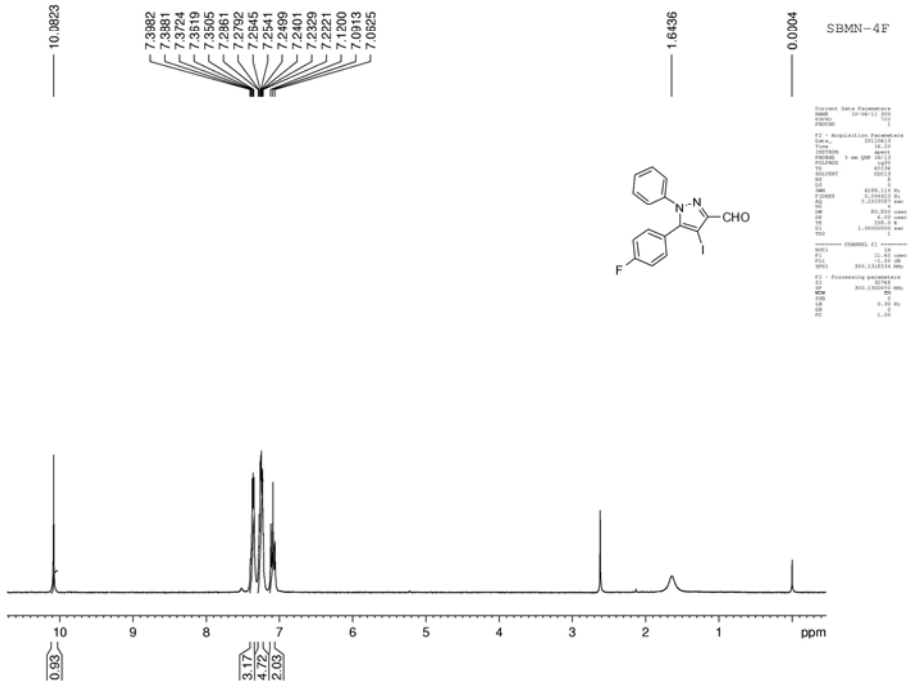


Fig-20: ^{1}H-spectrum of 5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (**1d**).

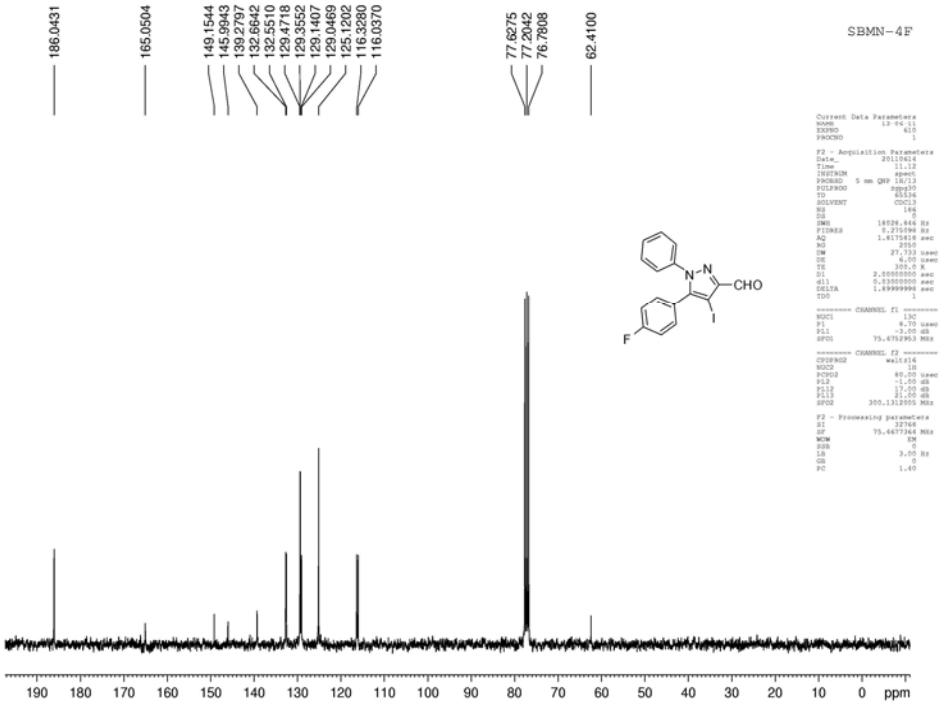


Fig-21: ^{13}C spectrum of 5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (**1d**).

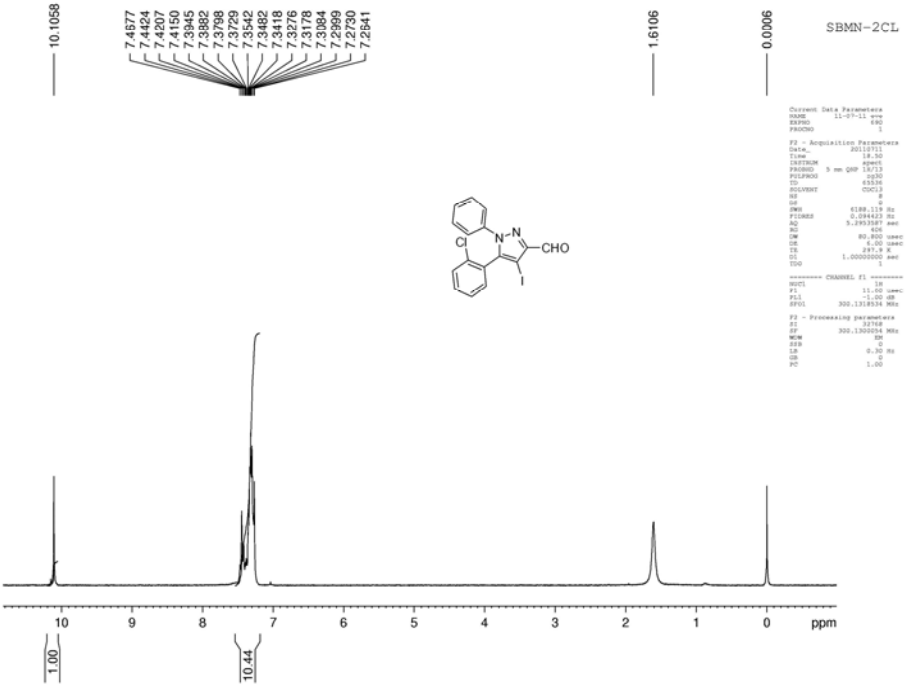


Fig-22: ^{1}H-spectrum of 5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (**1e**).

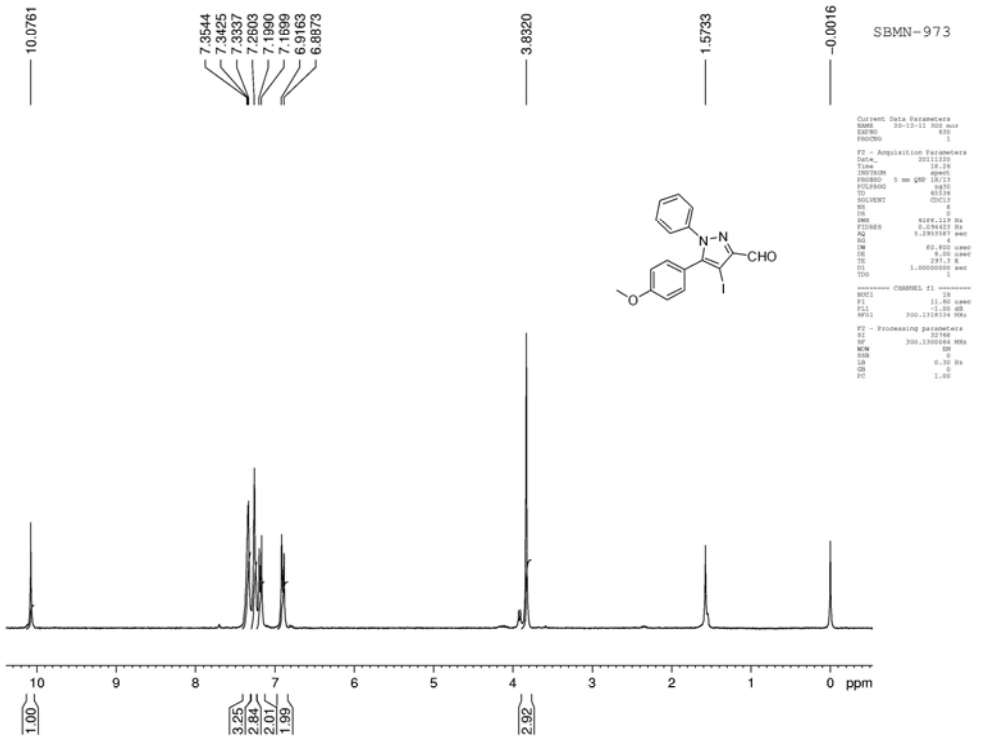


Fig-23: ^{1}H-spectrum of 4-Iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (**1f**).

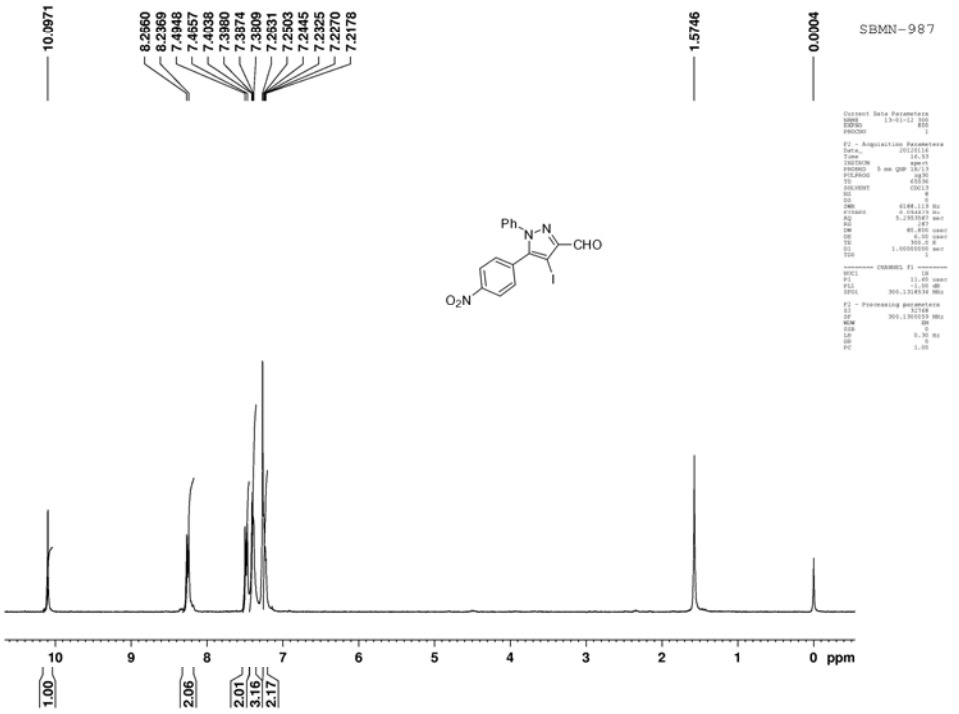


Fig-24: ^{1}H-spectrum of 4-Iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (**1g**).

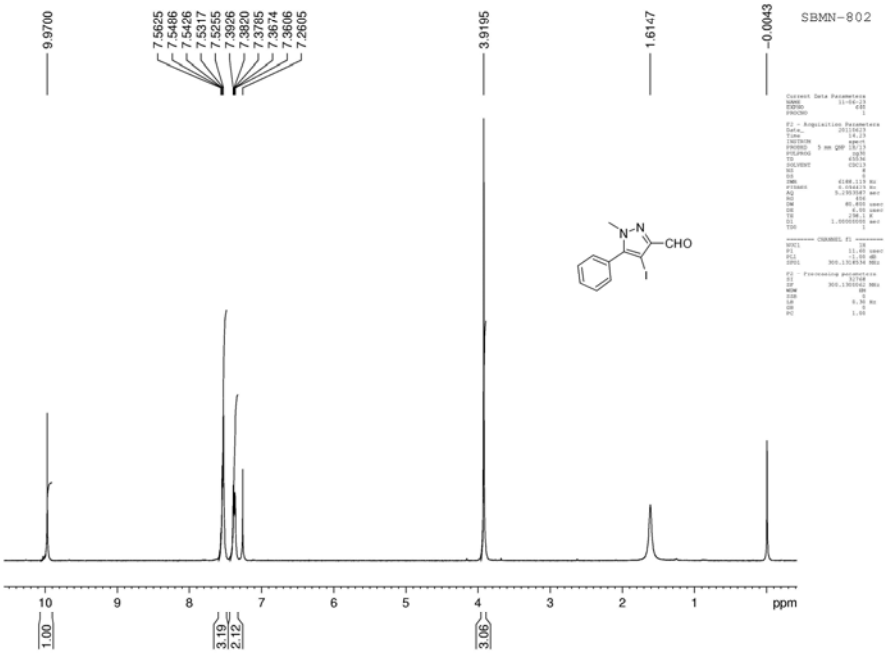


Fig-25: ^{1}H-spectrum of 4-Iodo-1-methyl-5-phenyl-1*H*-pyrazole-3-carbaldehyde (**1h**).

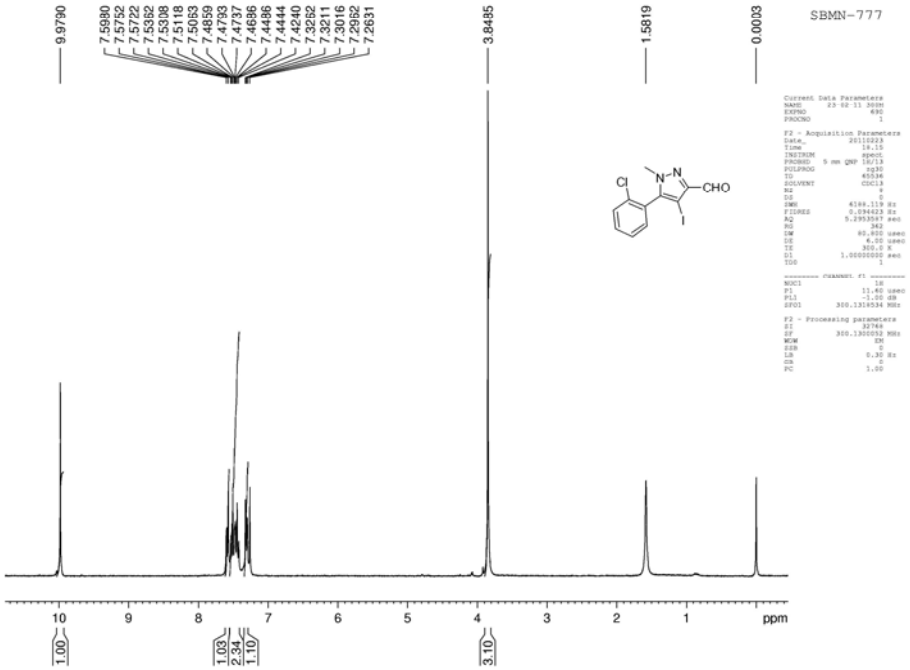


Fig-26: ^{1}H-spectrum of 5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazole-3-carbaldehyde (**1j**).

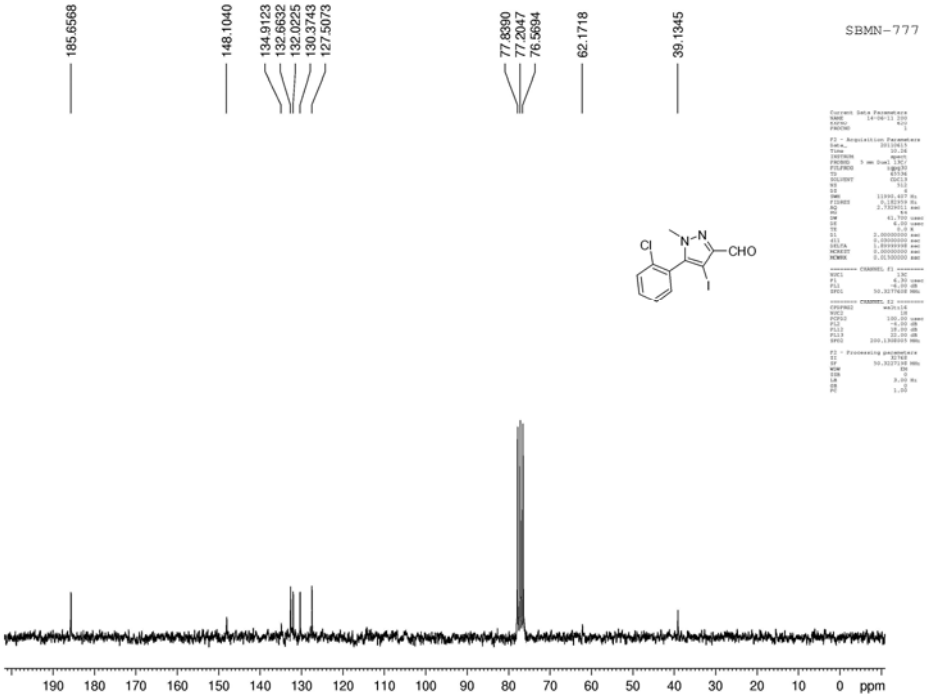


Fig-27: ^{13}C spectrum of 5-(2-Chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazole-3-carbaldehyde (**1j**).

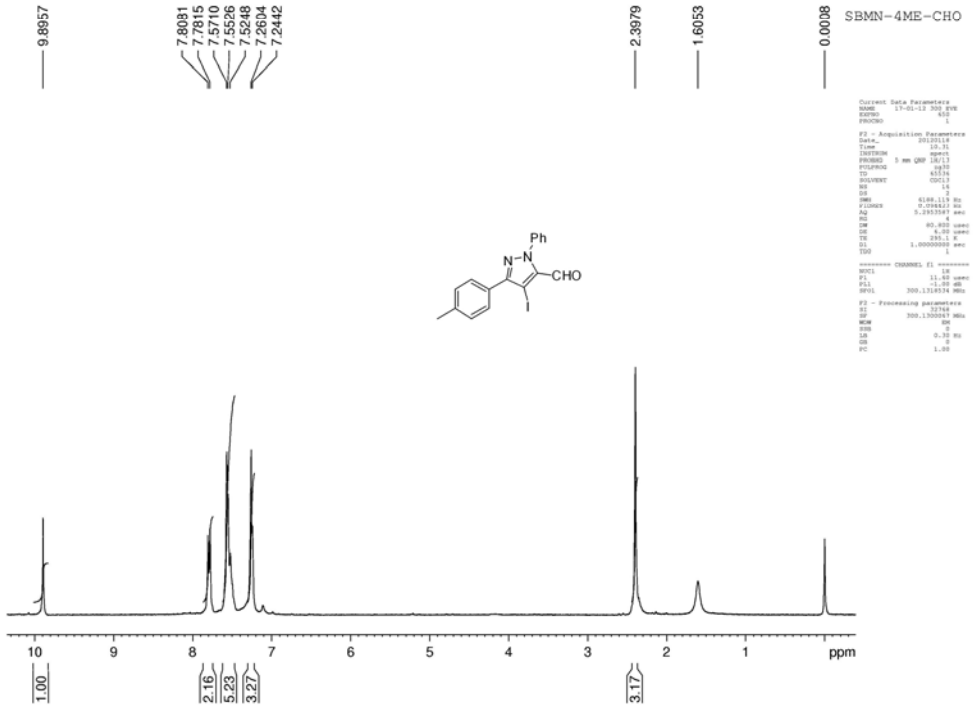


Fig-28: ^{1}H-spectrum of 4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazole-5-carbaldehyde **(6b).**

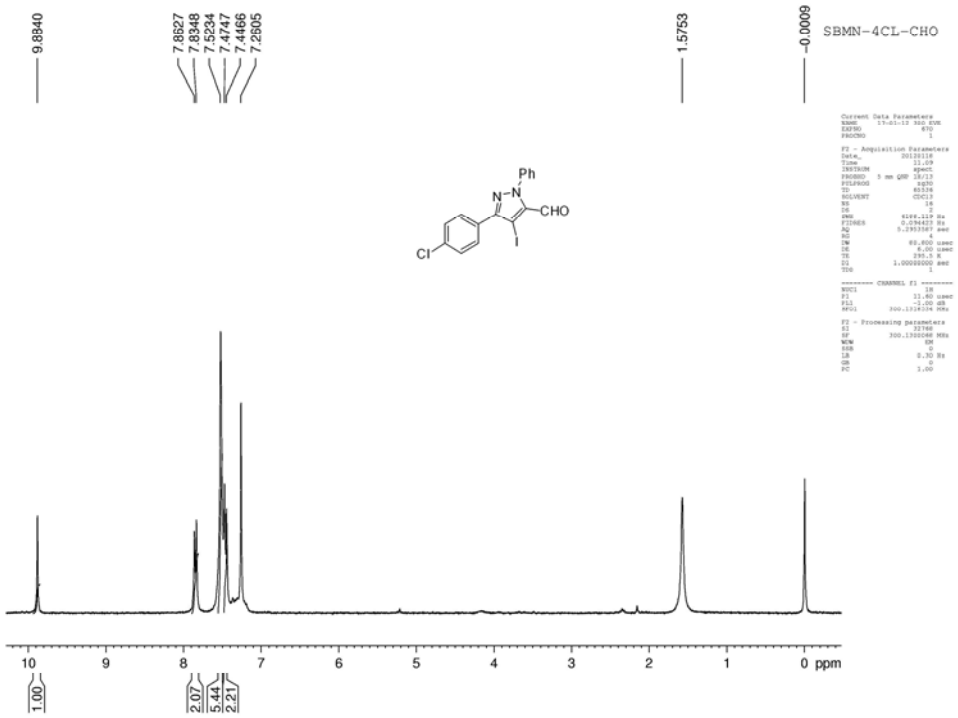


Fig-29: ^{1}H-spectrum of 3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-5-carbaldehyde **(6c).**

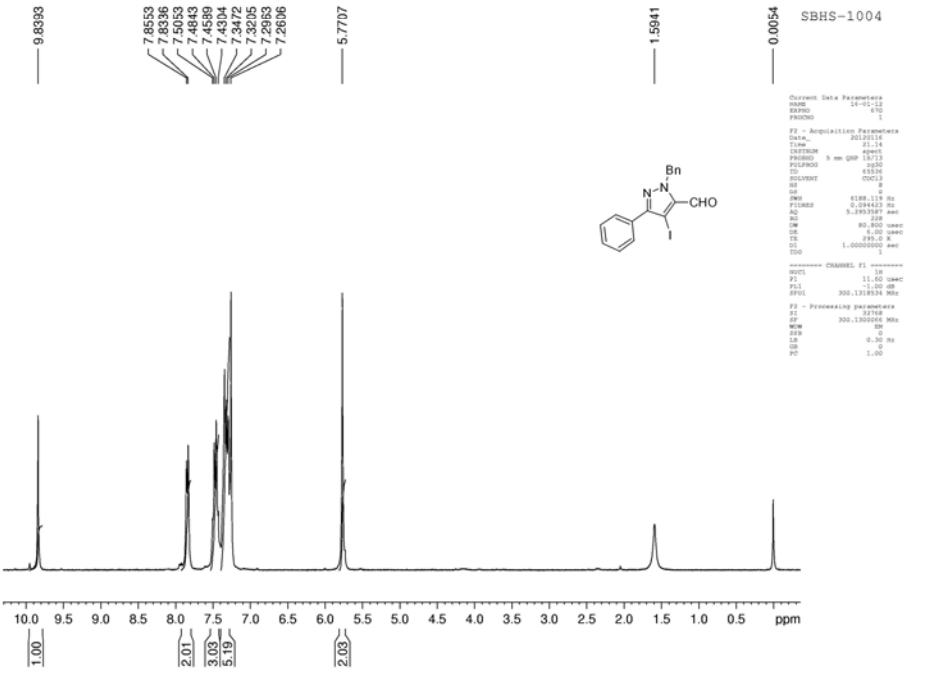


Fig-30: ^{1}H-spectrum of methyl 1-benzyl-4-iodo-3-phenyl-1*H*-pyrazole-5-carbaldehyde **(6l).**

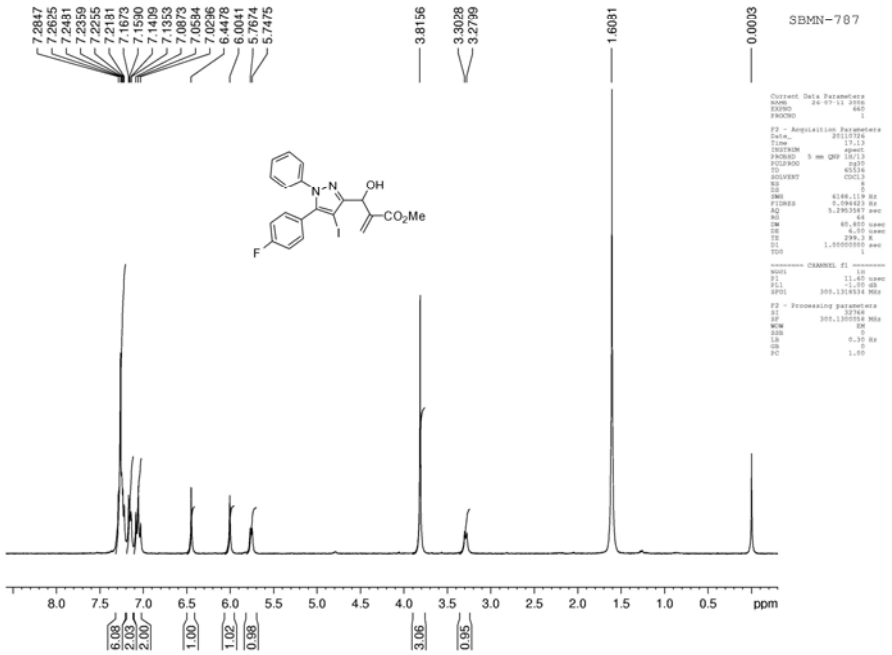


Fig-31: ^{1}H-spectrum of methyl 2-[[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2d**).

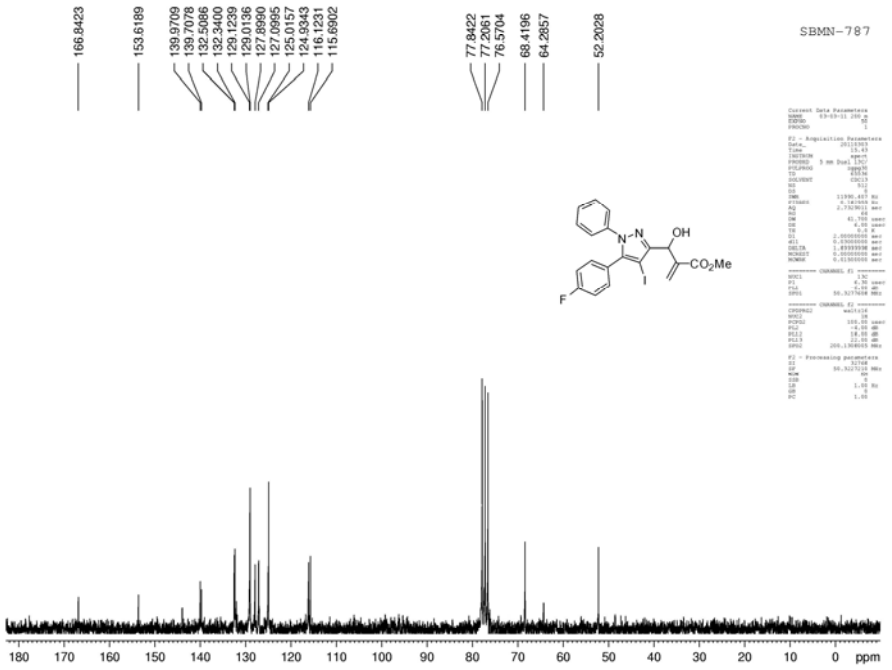


Fig-32: ^{13}C spectrum of methyl 2-[[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2d**).

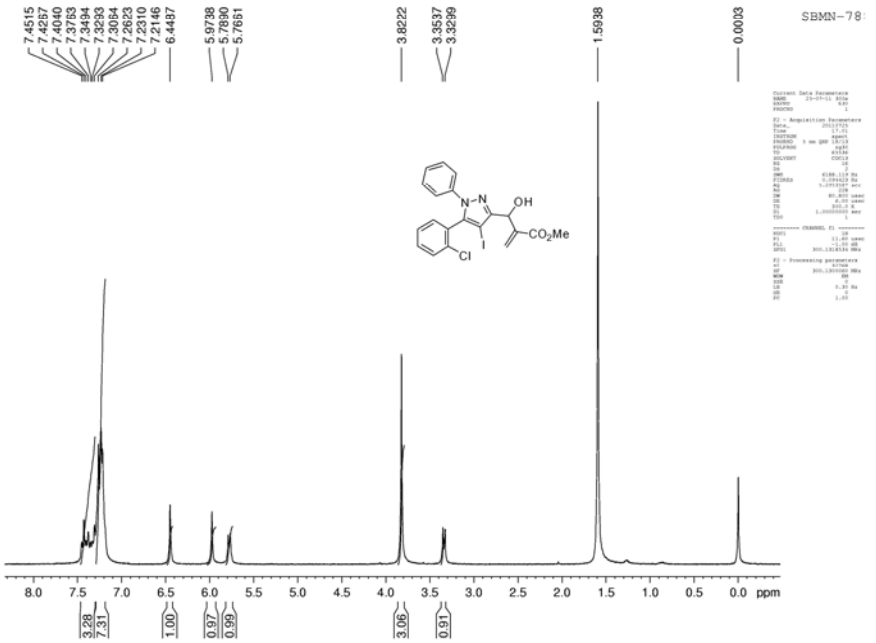


Fig-33: ^{1}H-spectrum of methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2e**).

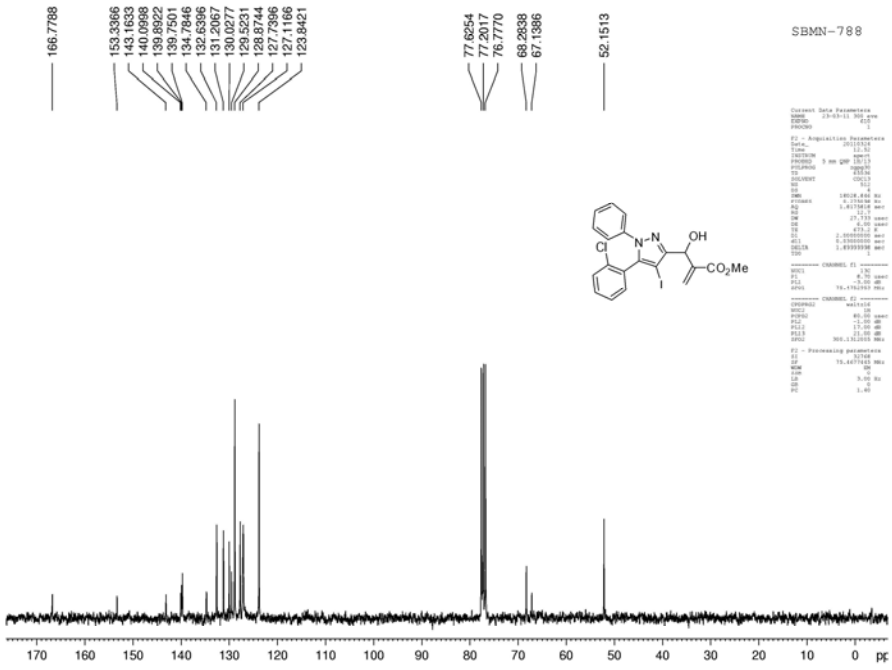


Fig-34: ^{13}C spectrum of methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2e**).

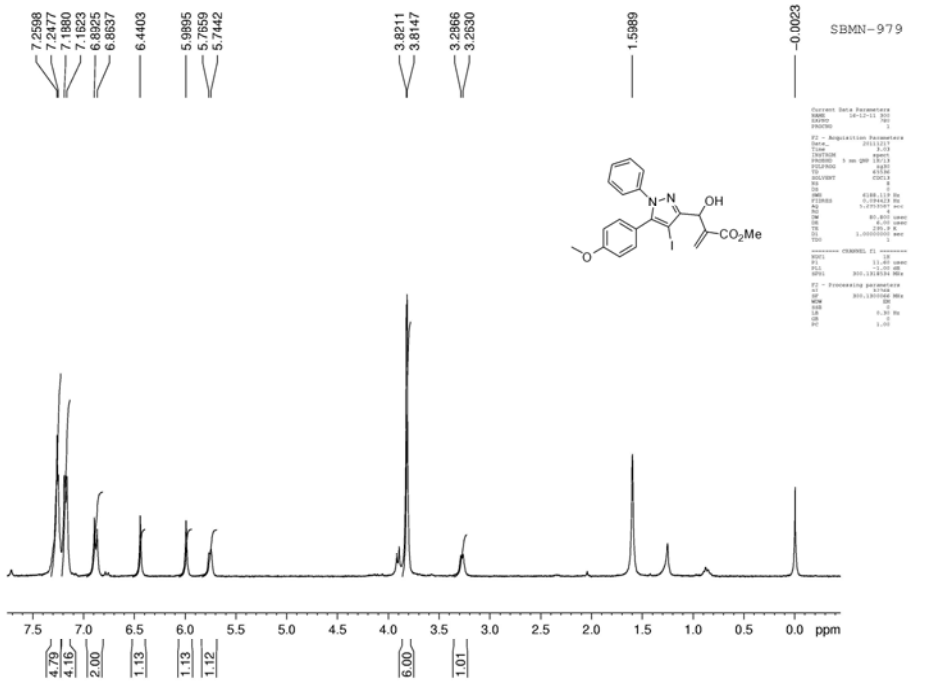


Fig-35: ^{1}H-spectrum of methyl 2-{hydroxy[4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**2f**).

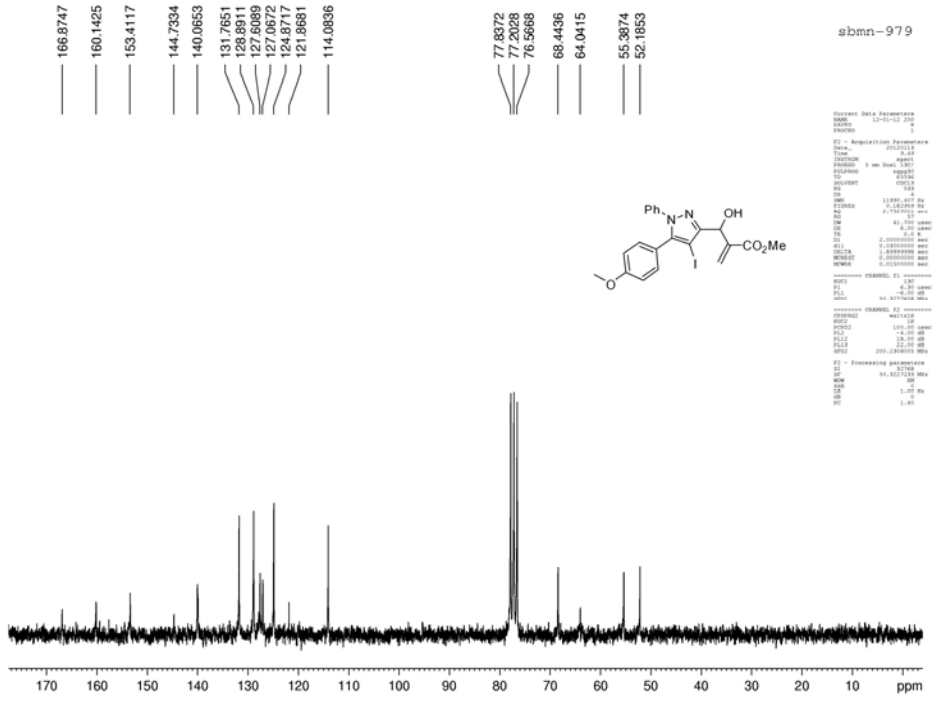


Fig-36: ^{13}C spectrum of methyl 2-{hydroxy[4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**2f**).

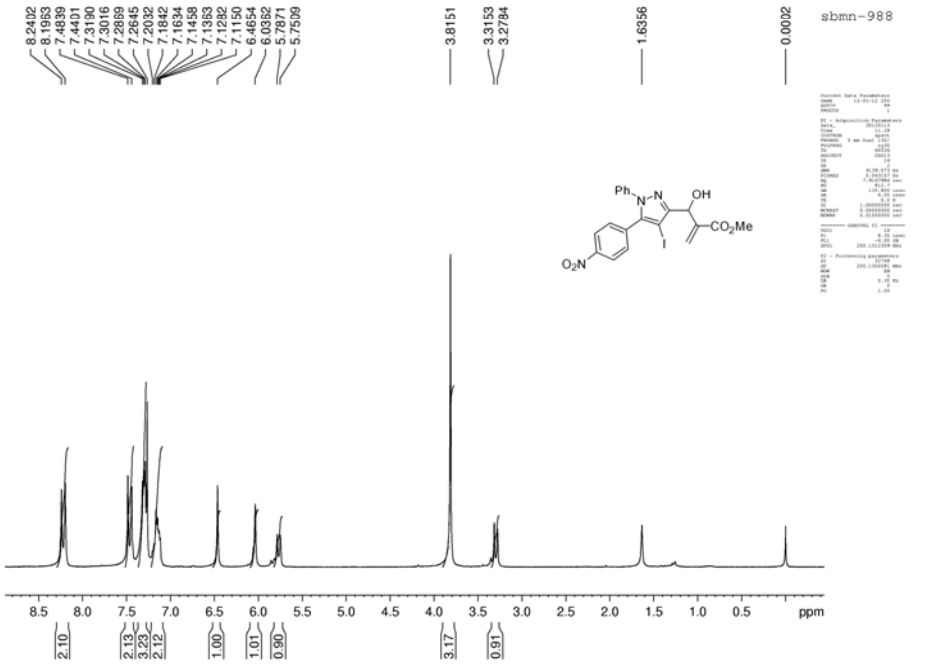


Fig-37: ^{1}H-spectrum of methyl 2-{hydroxy[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**2g**).

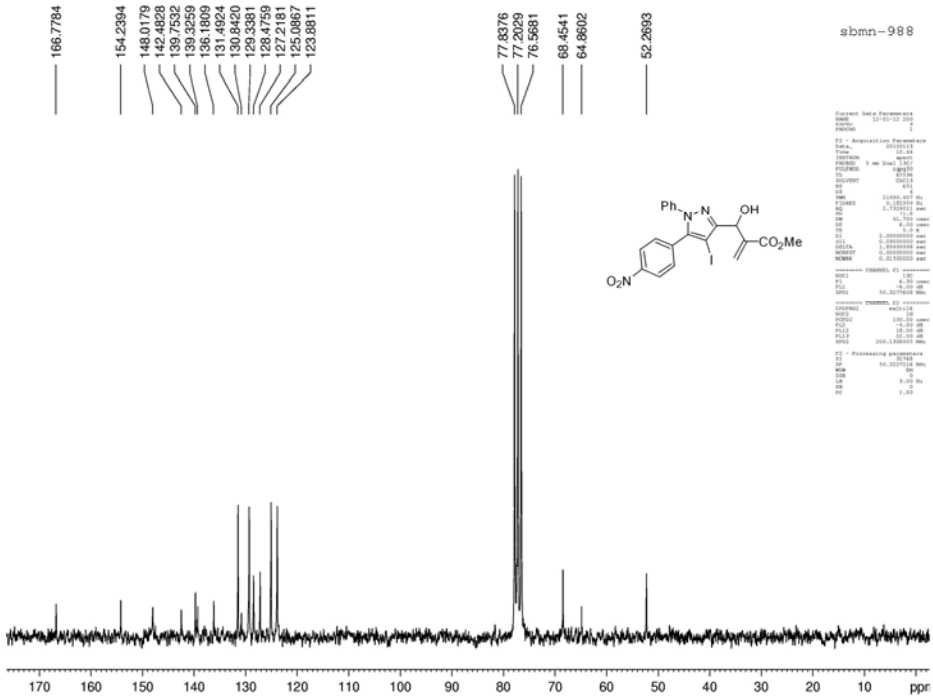


Fig-38: ^{13}C spectrum of methyl 2-{hydroxy[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**2g**).

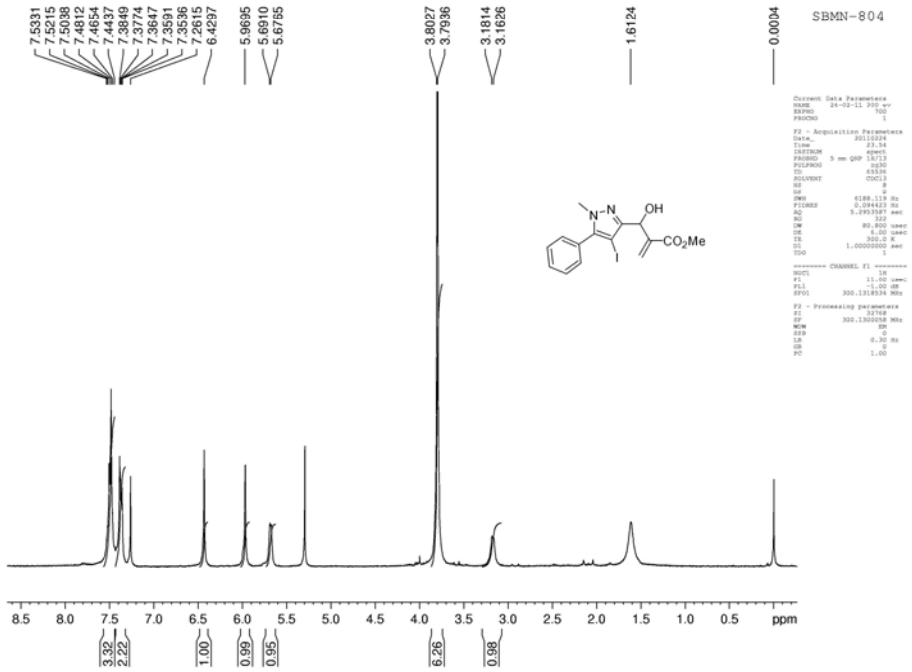


Fig-39: ^{1}H-spectrum of methyl 2-[hydroxy(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (**2h**).

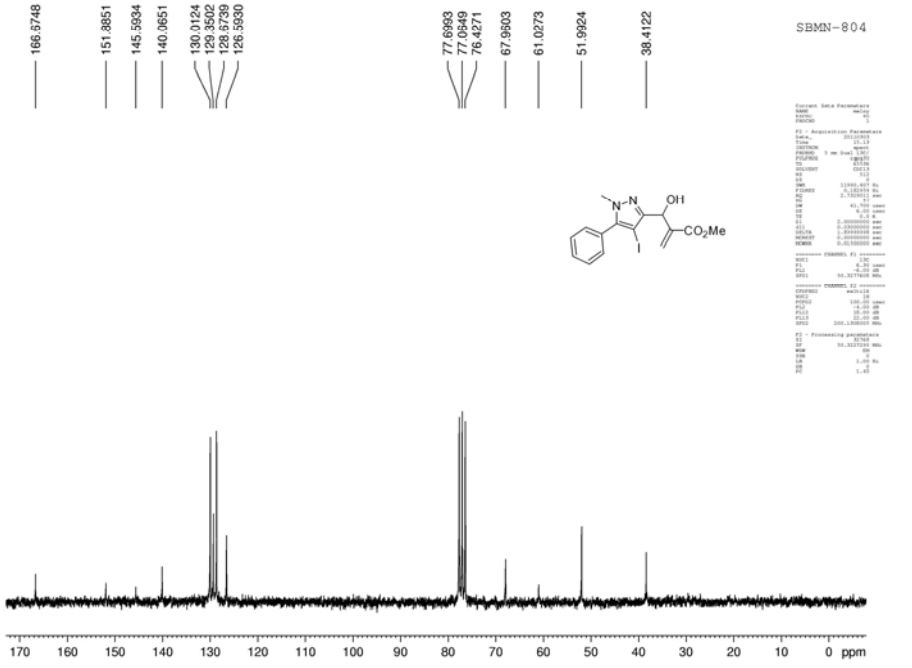


Fig-40: ^{13}C spectrum of methyl 2-[hydroxy(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (**2h**).

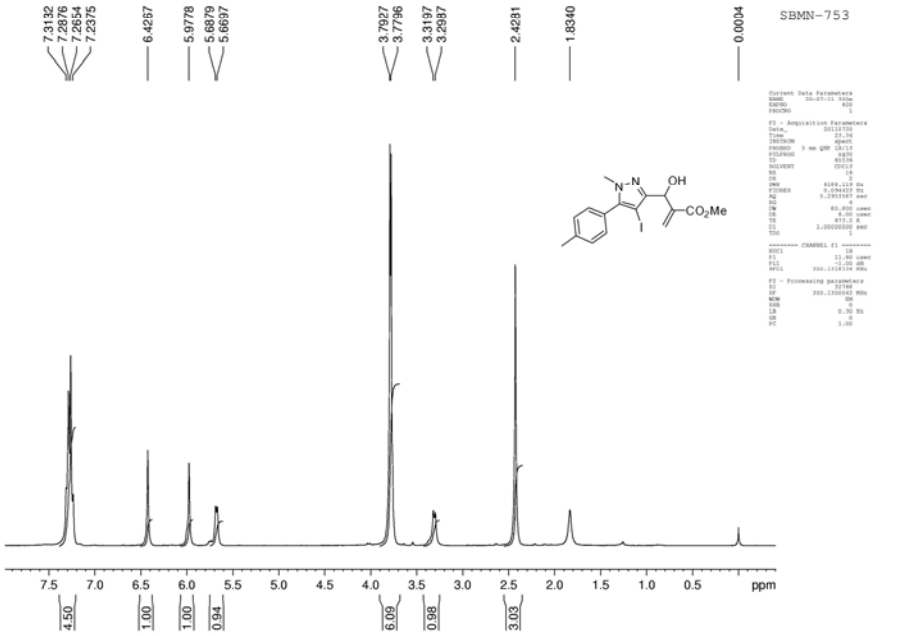


Fig-41: ^{1}H-spectrum of methyl 2-{hydroxy[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (**2i**).

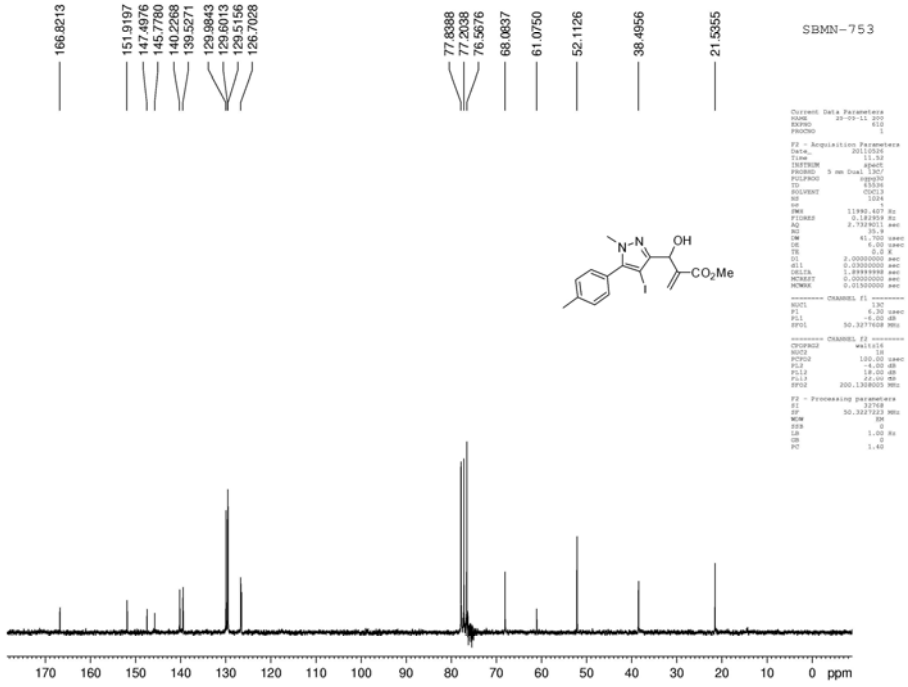


Fig-42: ^{13}C spectrum of methyl 2-{hydroxy[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (**2i**).

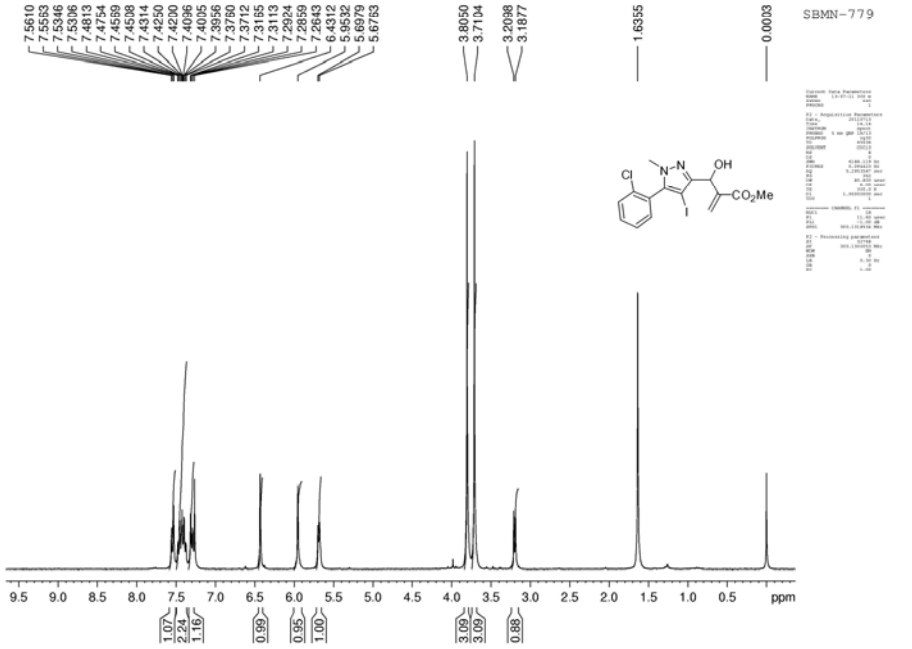


Fig-43: ^{1}H-spectrum of methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2j**).

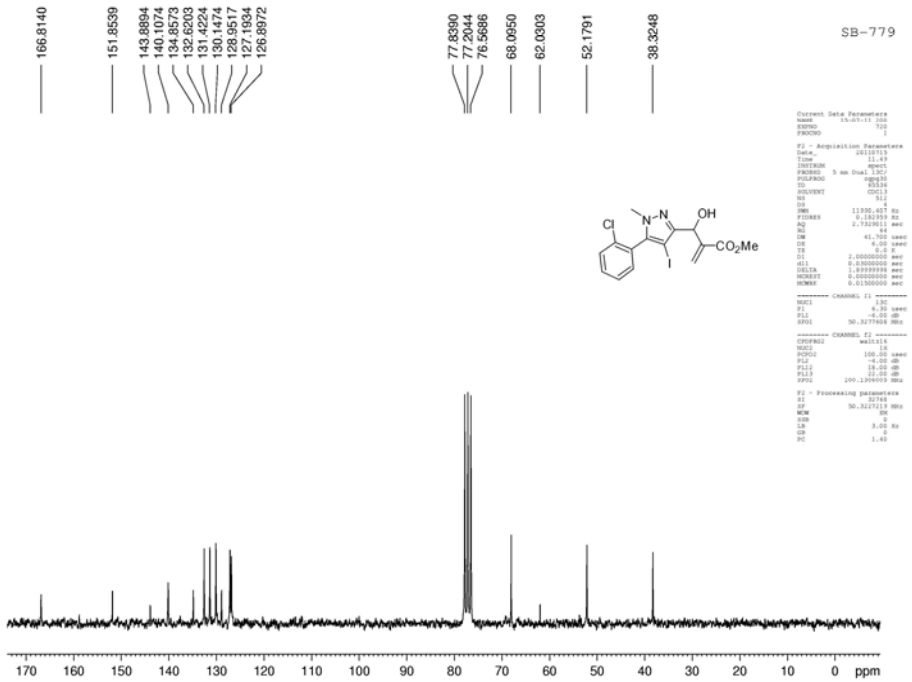


Fig-44: ^{13}C spectrum of methyl 2-[[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylate (**2j**).

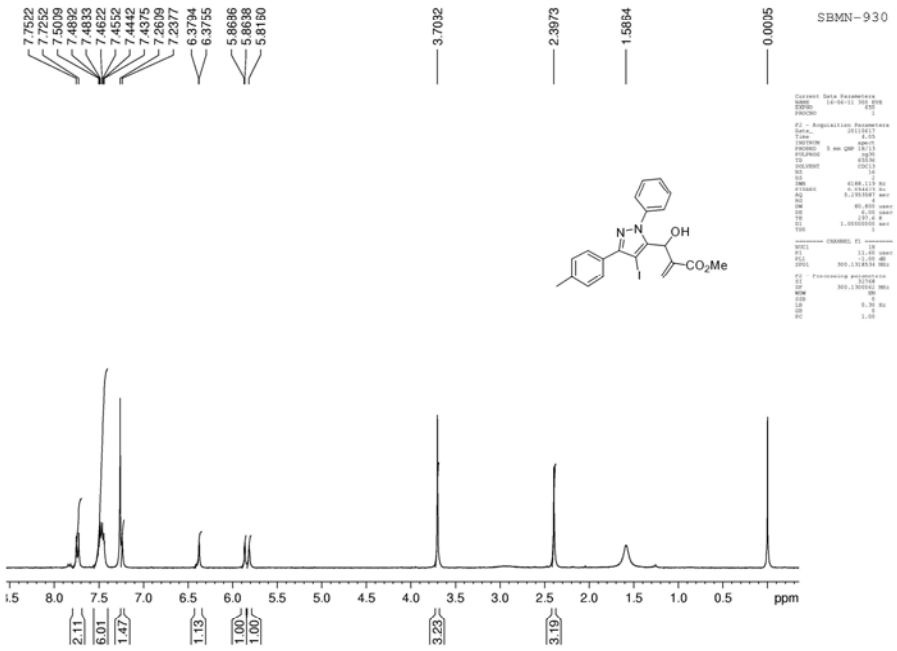


Fig-45: ^{1}H-spectrum of methyl 2-{hydroxy[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**7b**).

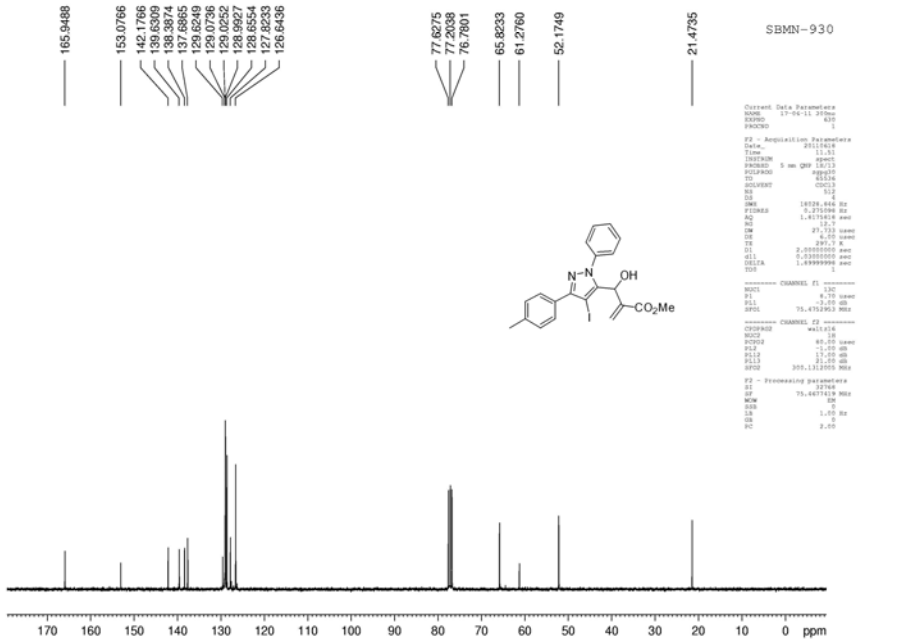


Fig-46: ^{13}C spectrum of methyl 2-{hydroxy[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**7b**).

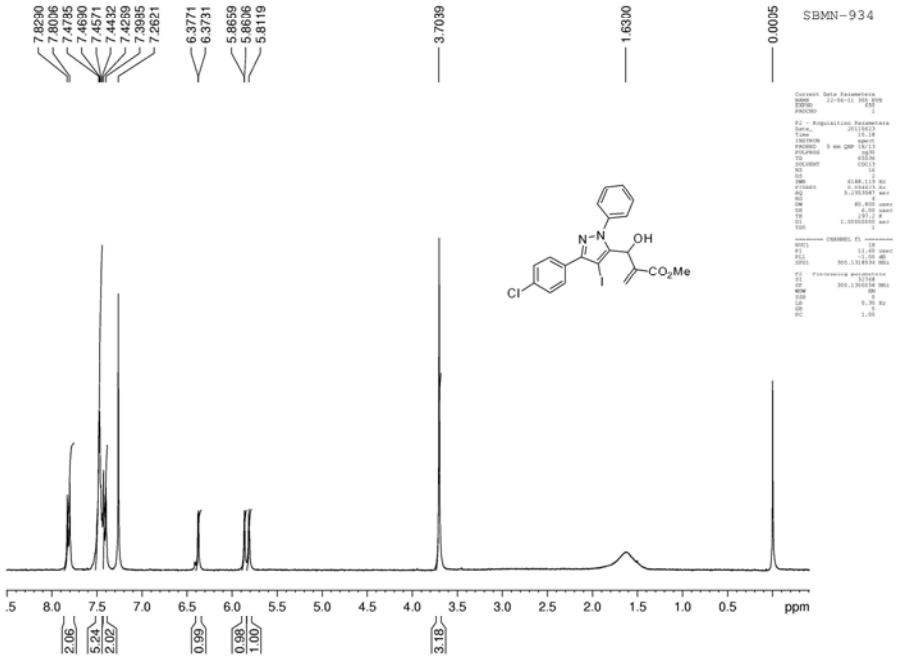


Fig-47: ^{1}H-spectrum of methyl 2-[[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl](hydroxy)methyl]acrylate (**7c**).

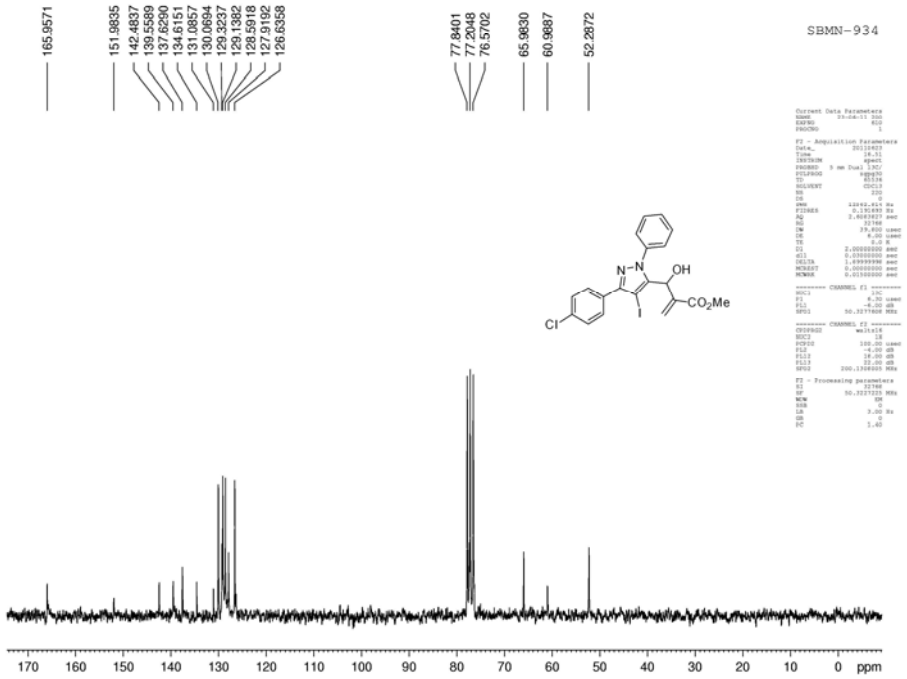


Fig-48: ^{13}C spectrum of methyl 2-[[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl](hydroxy)methyl]acrylate (**7c**).

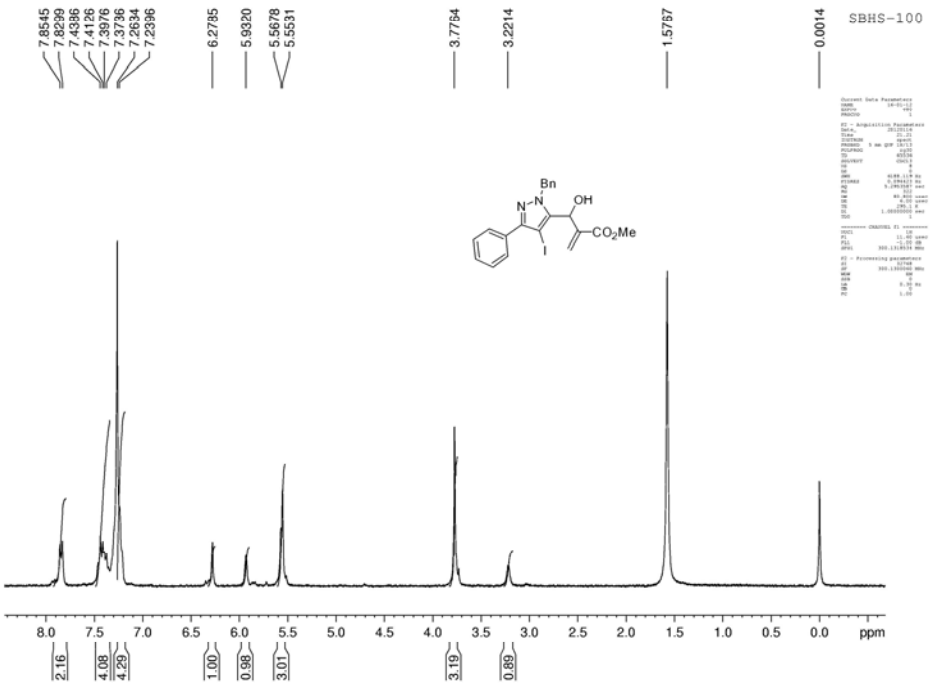


Fig-49: ^{1}H-spectrum of methyl 2-[(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)(hydroxy)methyl]acrylate **(7l).**

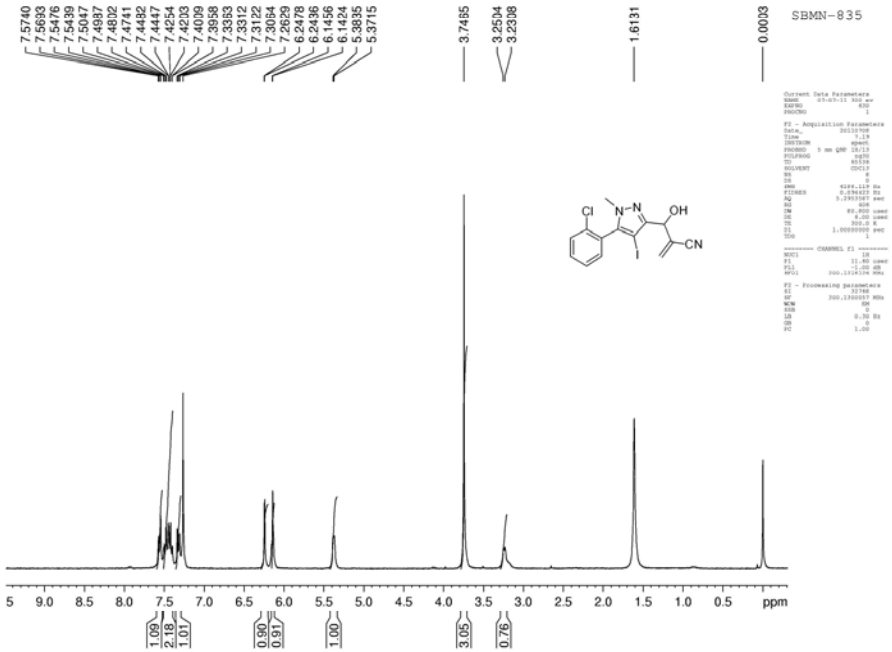


Fig-50: ^{1}H-spectrum of 2-[[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylonitrile (**11j**).

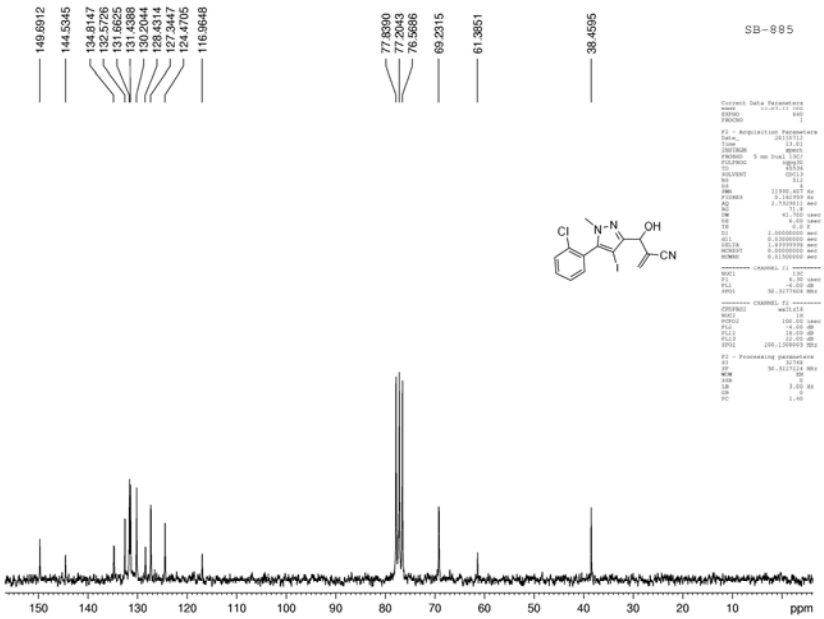


Fig-51: ^{13}C spectrum of 2-[[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl](hydroxy)methyl]acrylonitrile (**11j**).

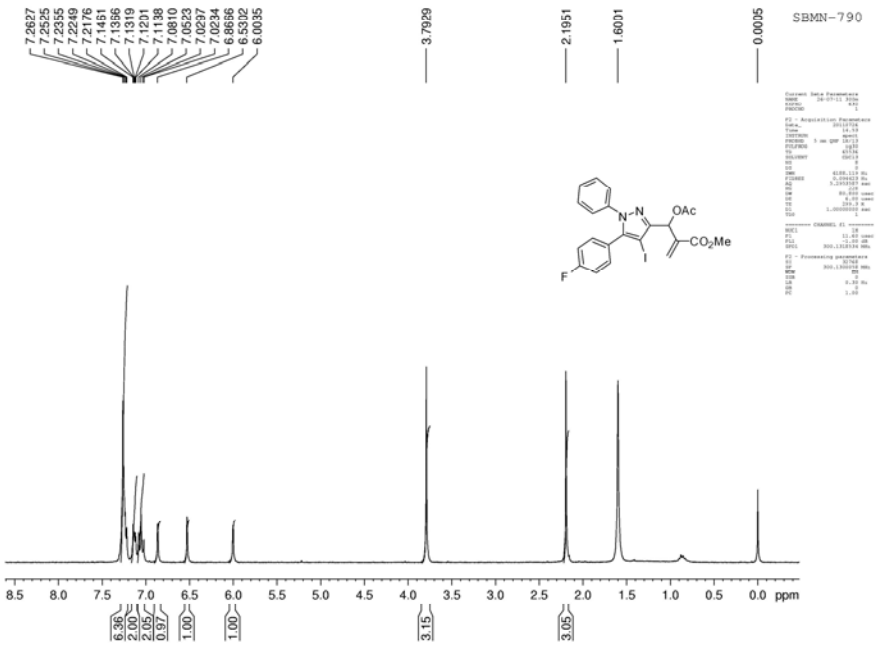


Fig-52: ^{1}H-spectrum of methyl 2-{(acetyloxy)[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**3d**).

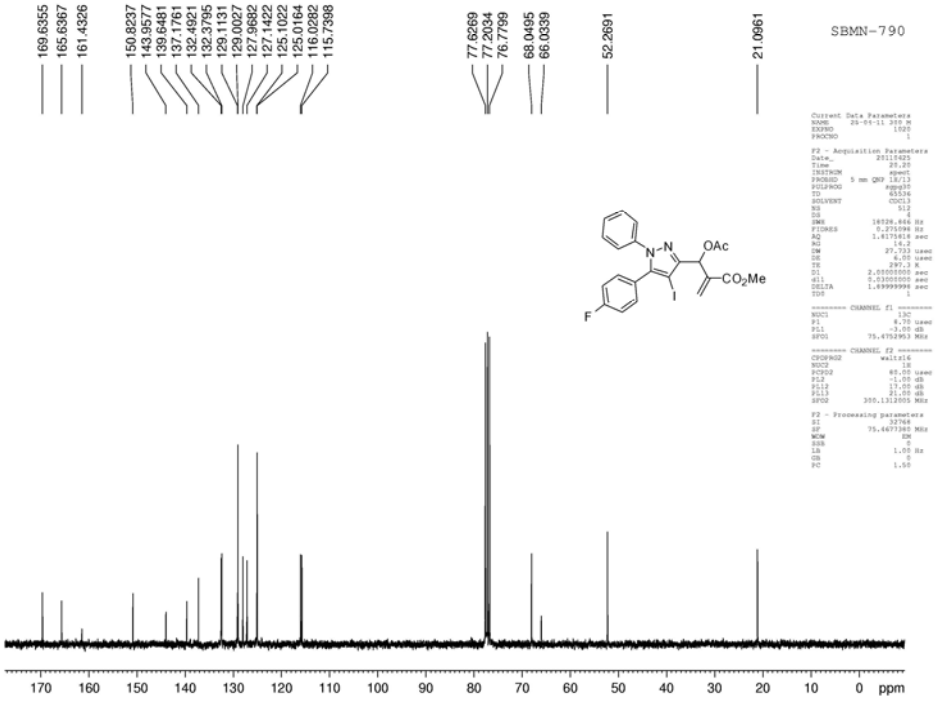


Fig-53: ^{13}C spectrum of methyl 2-{(acetyloxy)[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**3d**).

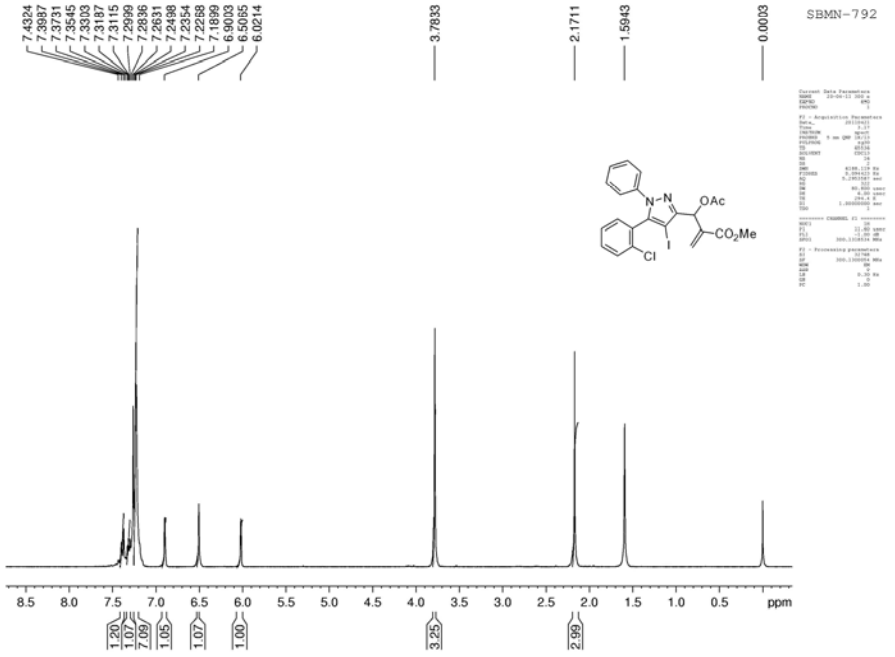


Fig-54: ^{1}H-spectrum of methyl 2-{(acetyloxy)[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**3e**).

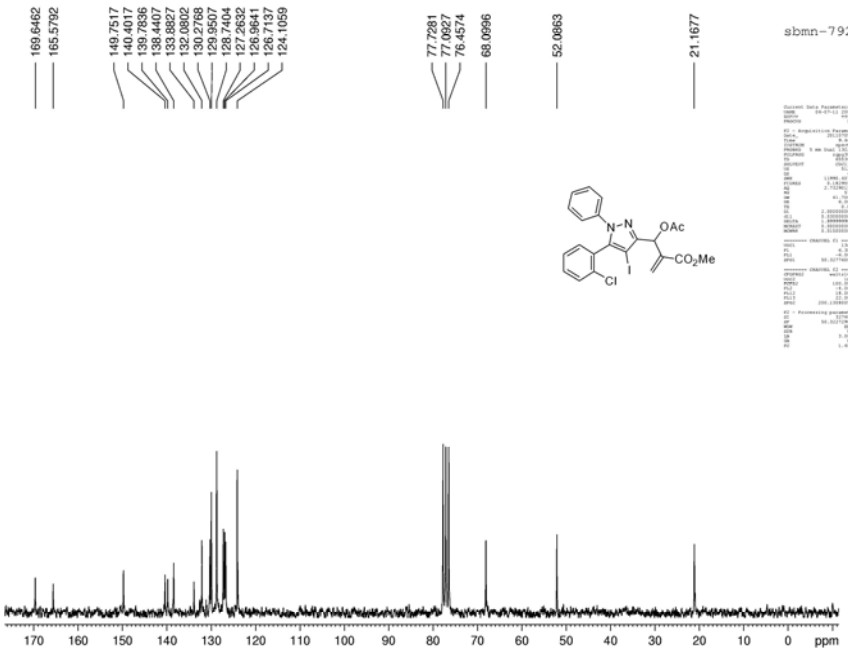


Fig-55: ^{13}C spectrum of methyl 2-{(acetyloxy)[5-(2-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate (**3e**).

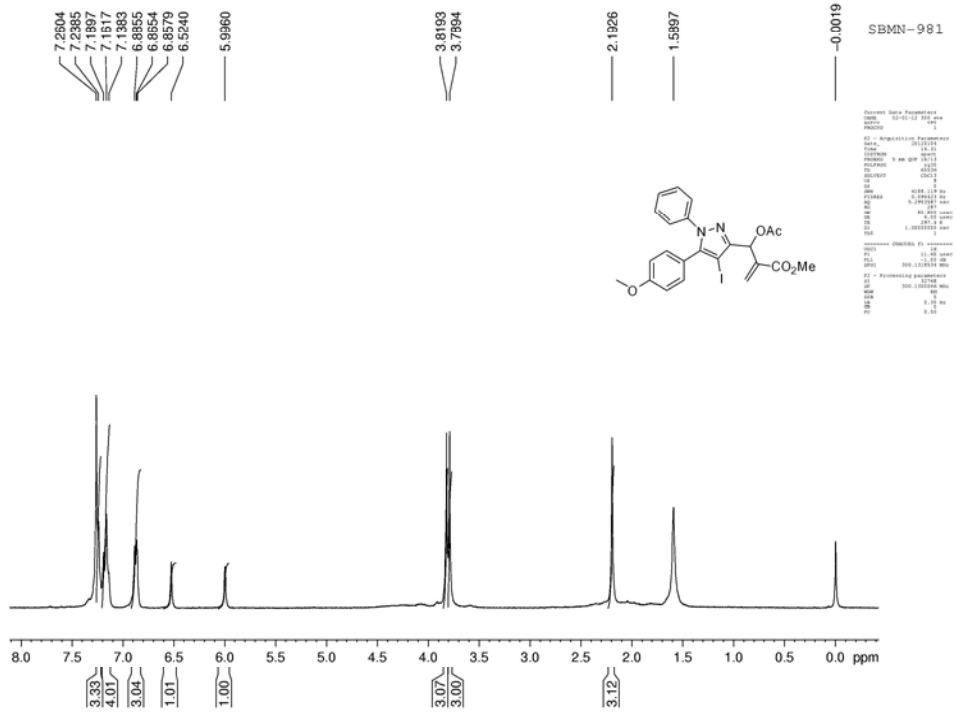


Fig-56: ^{1}H-spectrum of methyl 2-(acetoxy(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-3-yl)methyl)acrylate **(3f).**

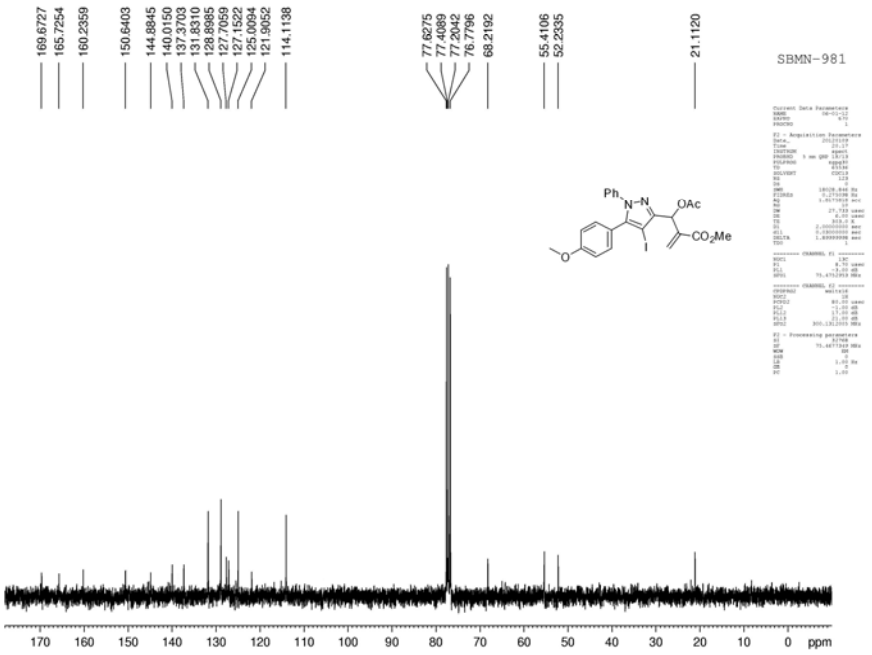


Fig-57: ^{13}C spectrum of methyl 2-(acetoxy(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-3-yl)methyl)acrylate **(3f).**

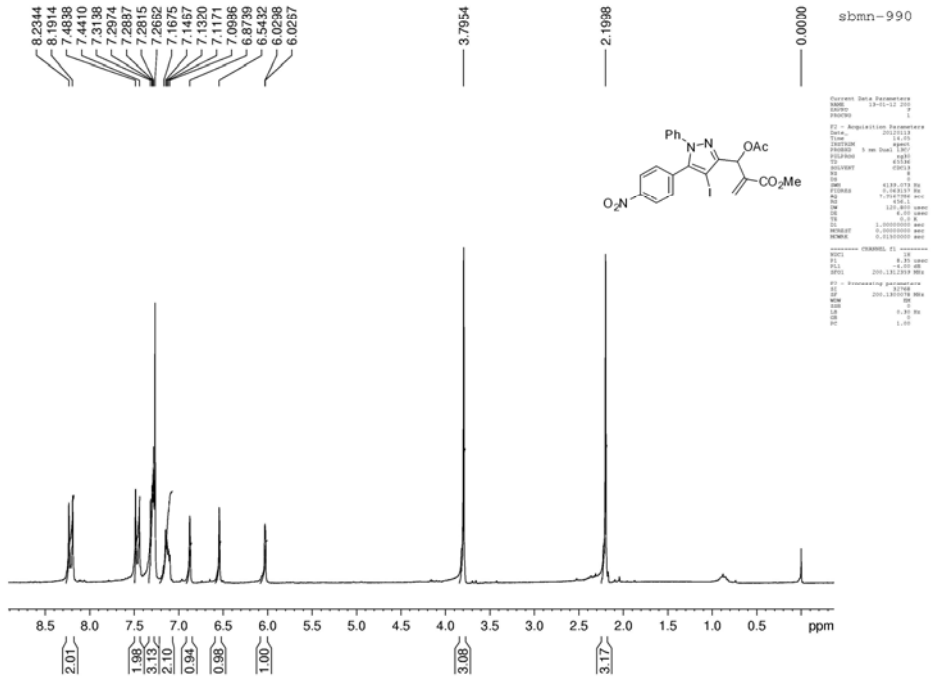


Fig-58: ^{1}H-spectrum of methyl 2-{(acetyloxy)[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate **(3g).**

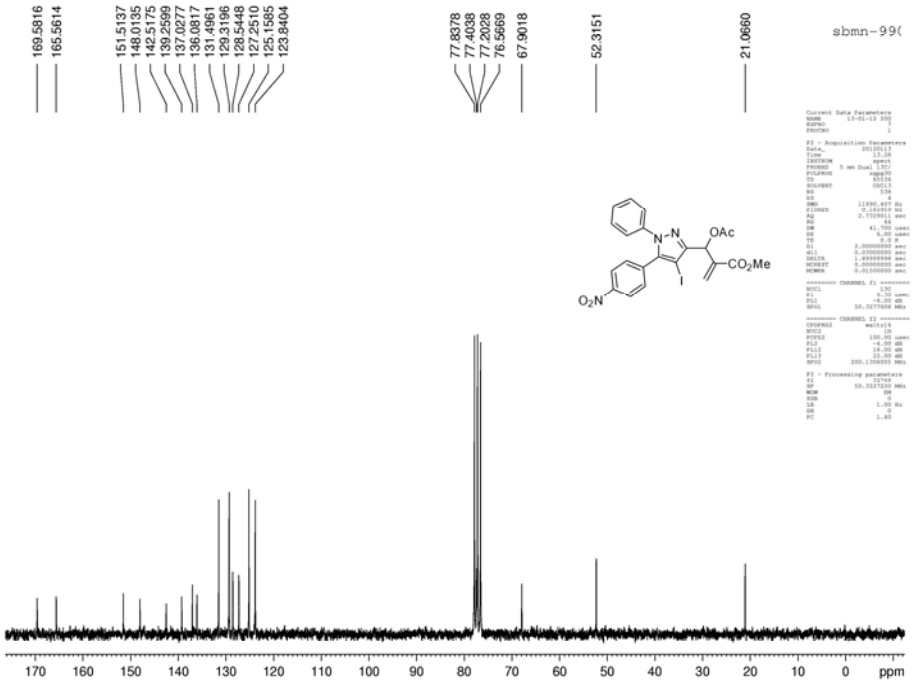


Fig-59: ^{13}C spectrum of methyl 2-{(acetyloxy)[4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl]methyl}acrylate **(3g).**

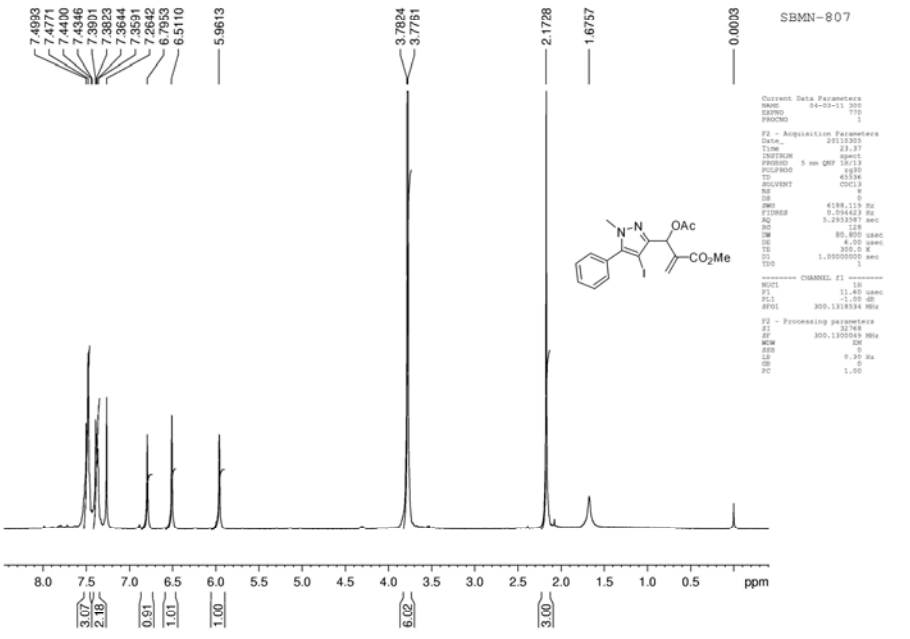


Fig-60: ^{1}H-spectrum of methyl 2-[(acetyloxy)(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (**3h**).

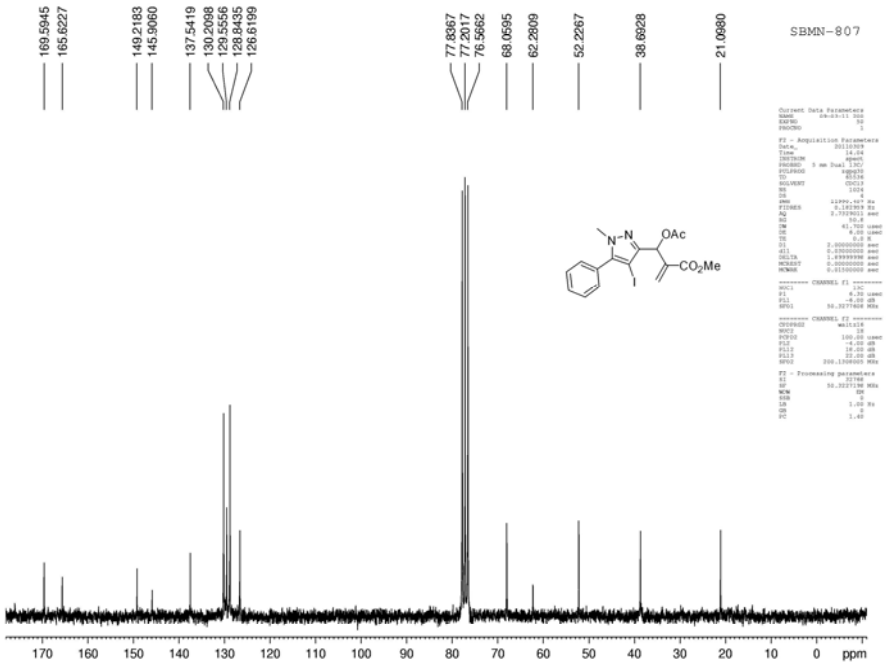


Fig-61: ^{13}C spectrum of methyl 2-[(acetyloxy)(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl]acrylate (**3h**).

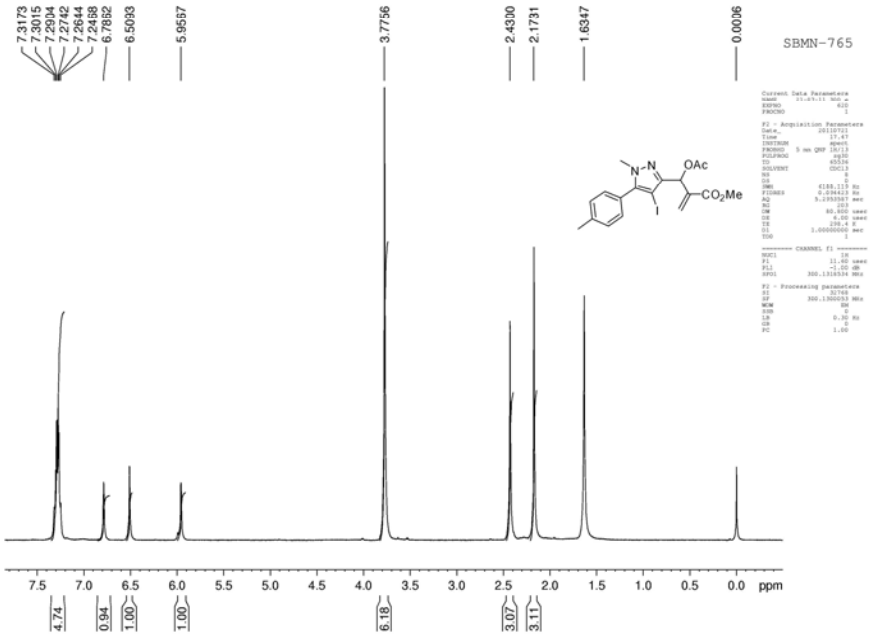


Fig-62: ^{1}H-spectrum of methyl 2-{(acetyloxy)[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (**3i**).

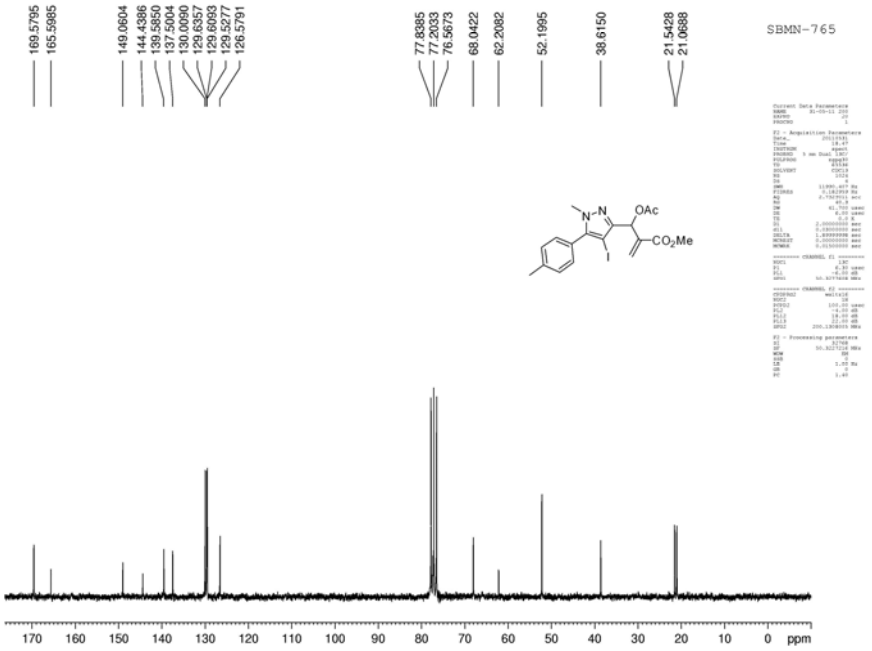


Fig-63: ^{13}C spectrum of methyl 2-{(acetyloxy)[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]methyl}acrylate (**3i**).

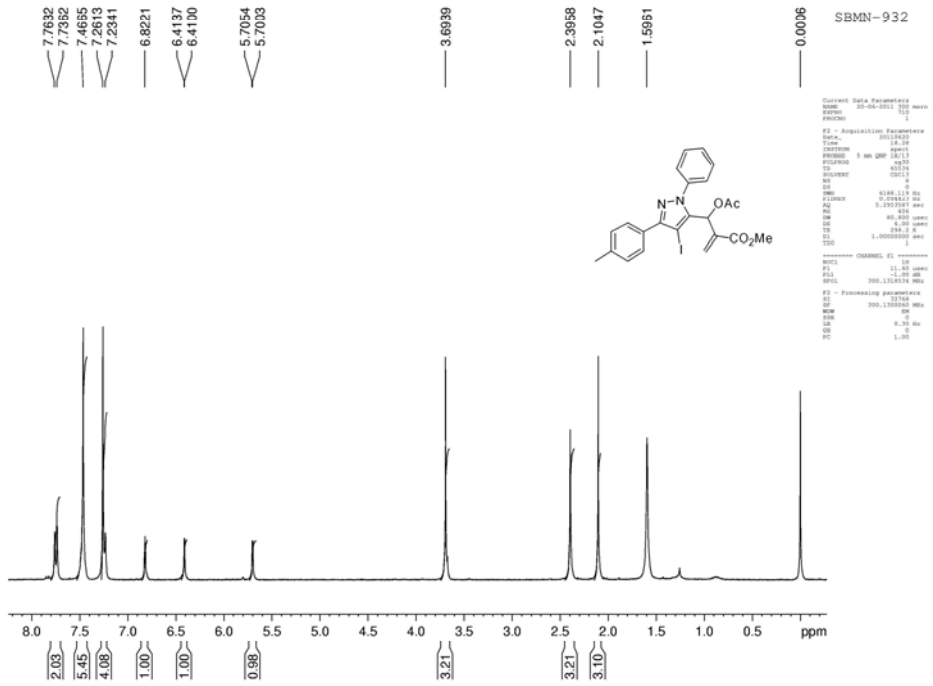


Fig-64: ^{1}H-spectrum of methyl 2-{(acetyloxy)[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**8b**).

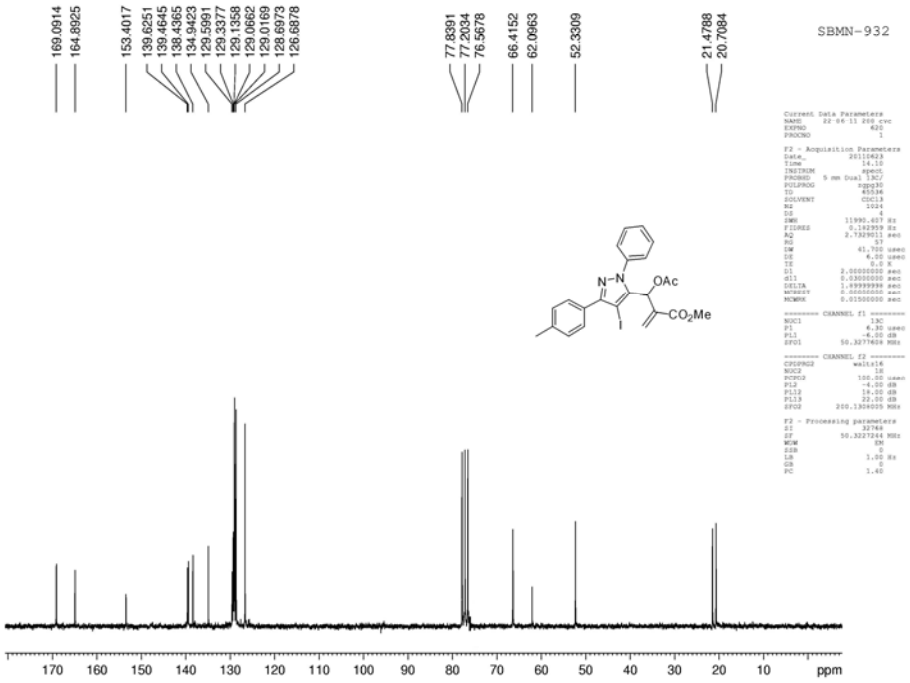


Fig-65: ^{13}C spectrum of methyl 2-{(acetyloxy)[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**8b**).

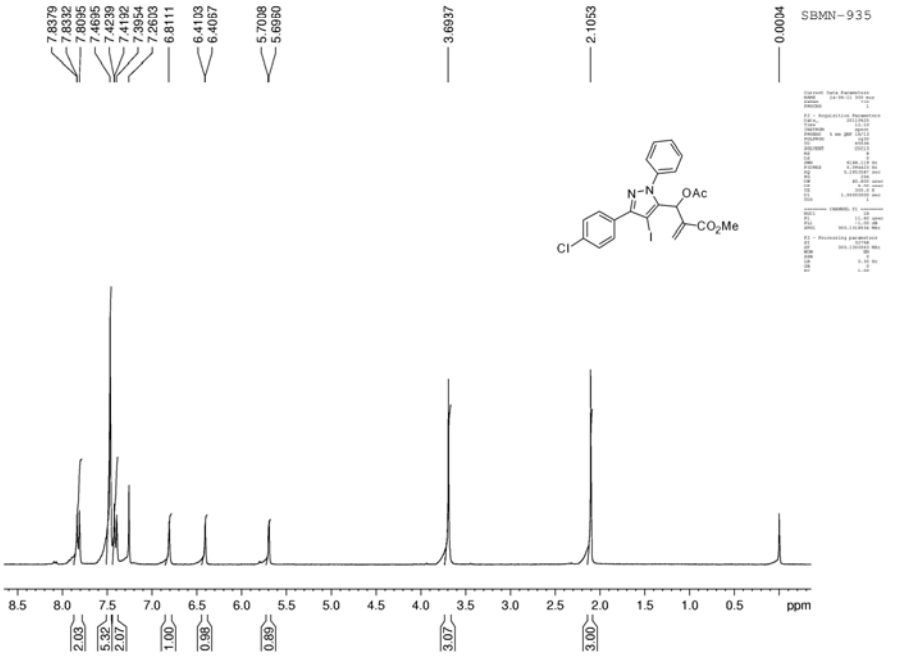


Fig-66: ^{1}H-spectrum of methyl 2-{(acetyloxy)[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**8c**).

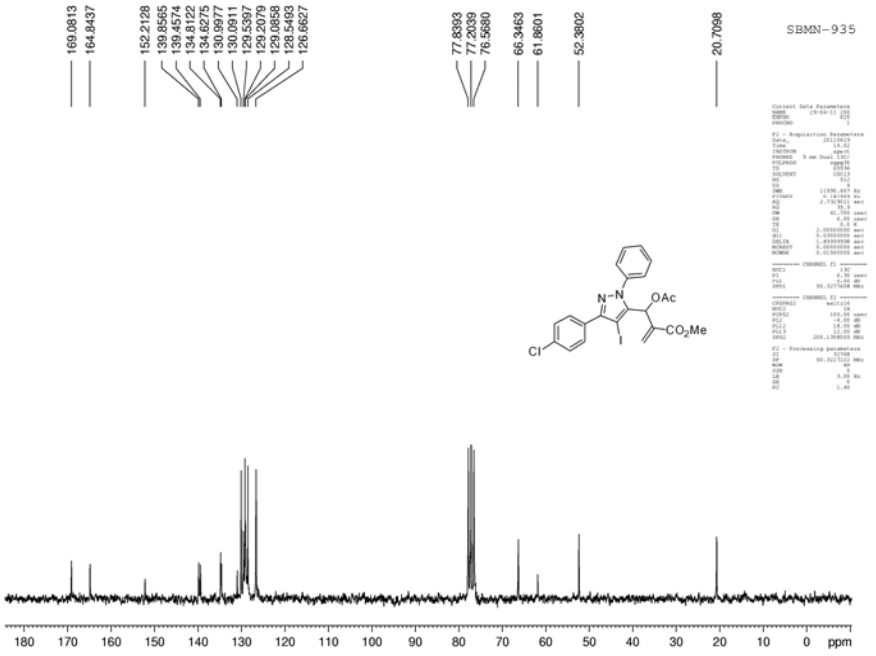


Fig-67: ^{13}C spectrum of methyl 2-{(acetyloxy)[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]methyl}acrylate (**8c**).

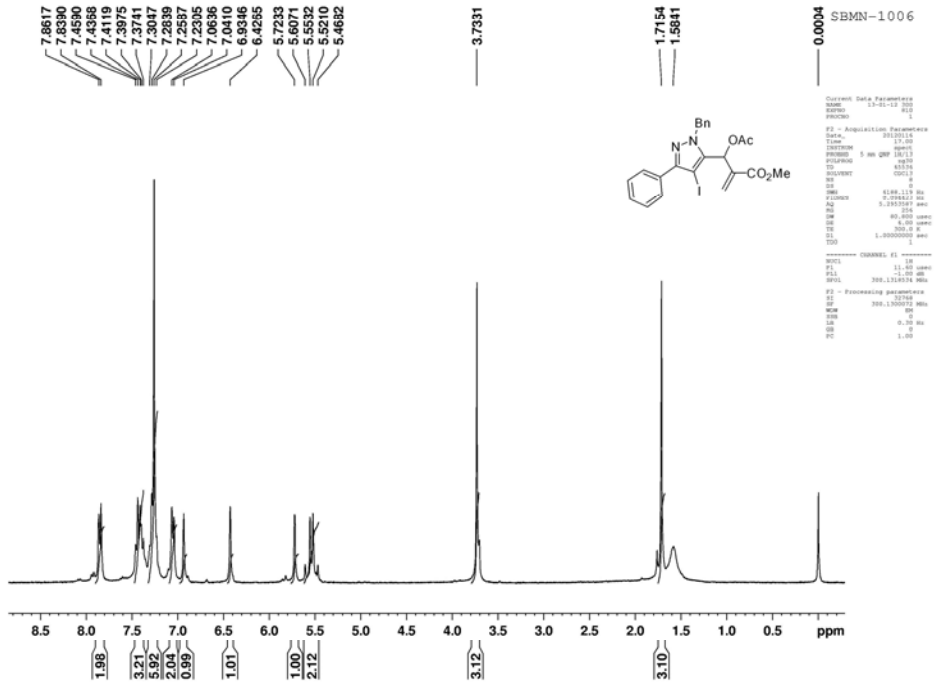


Fig-68: ^{1}H-spectrum of methyl 2-(acetoxy(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)methyl)acrylate **(8l).**

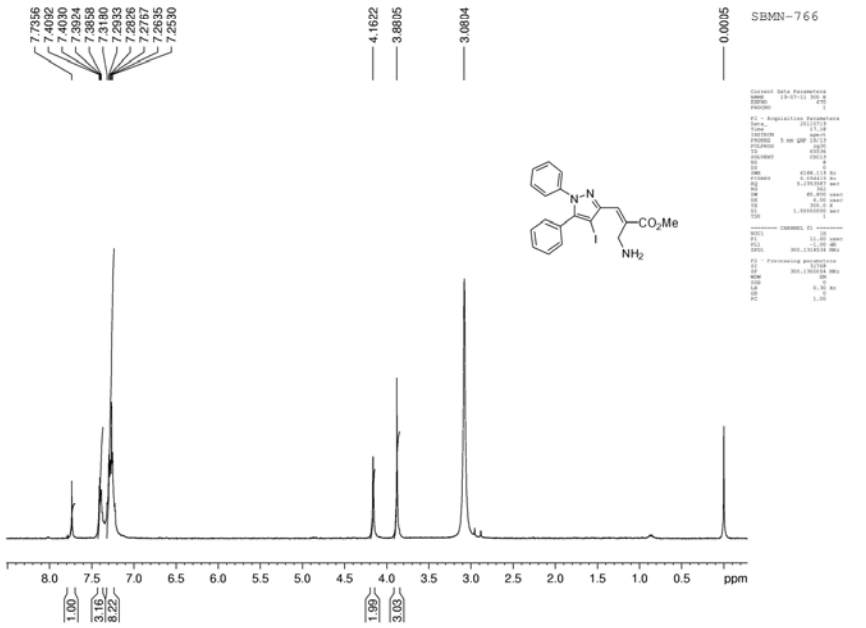


Fig-69: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**4a**).

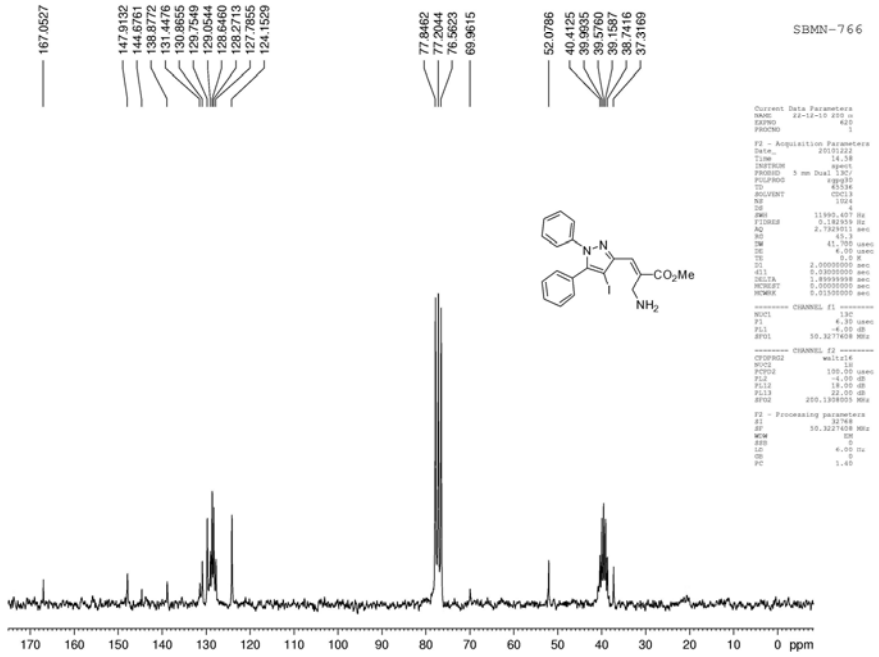


Fig-70: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**4a**).

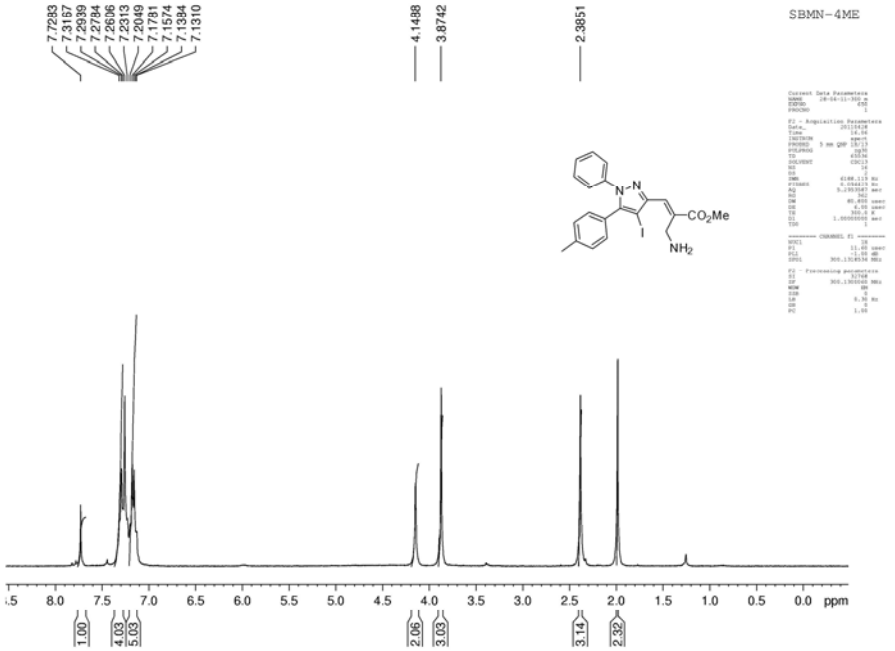


Fig-71: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4b**).

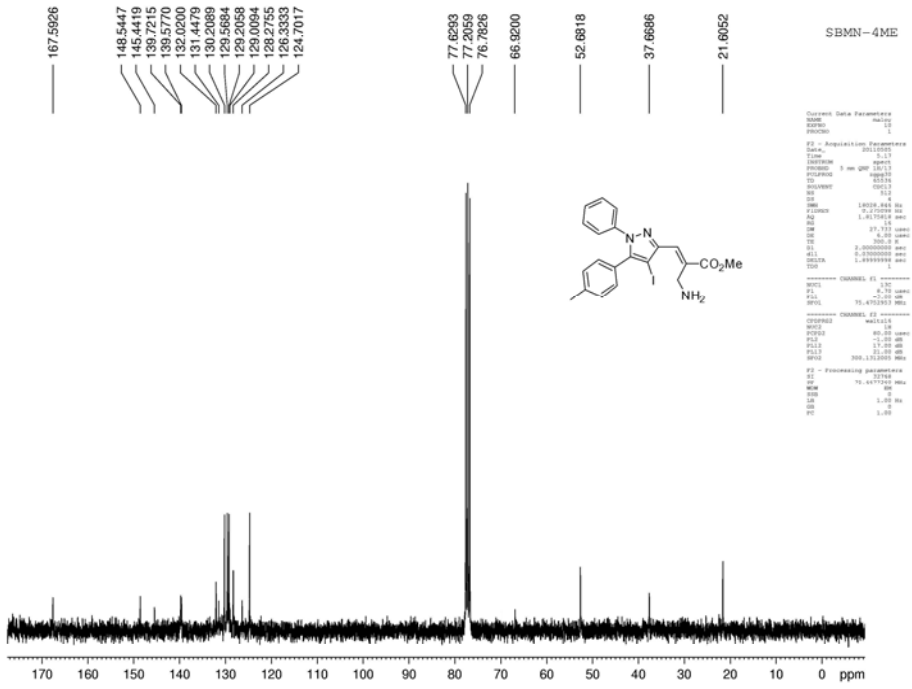


Fig-72: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4b**).

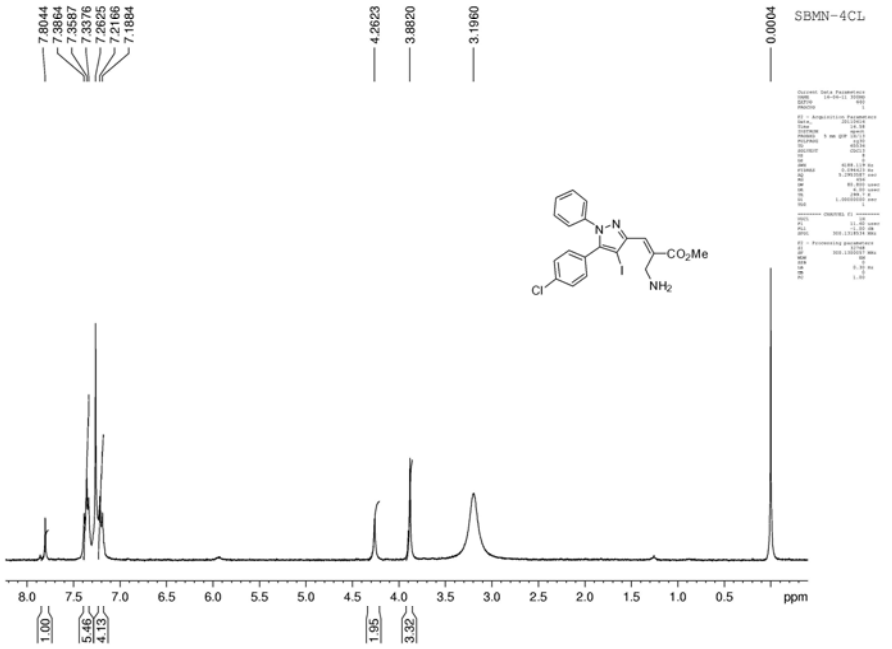


Fig-73: ^{1}H-spectrum of methyl (E)- 2-(aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1H-pyrazol-3-yl) prop-2-enoate (**4c**).

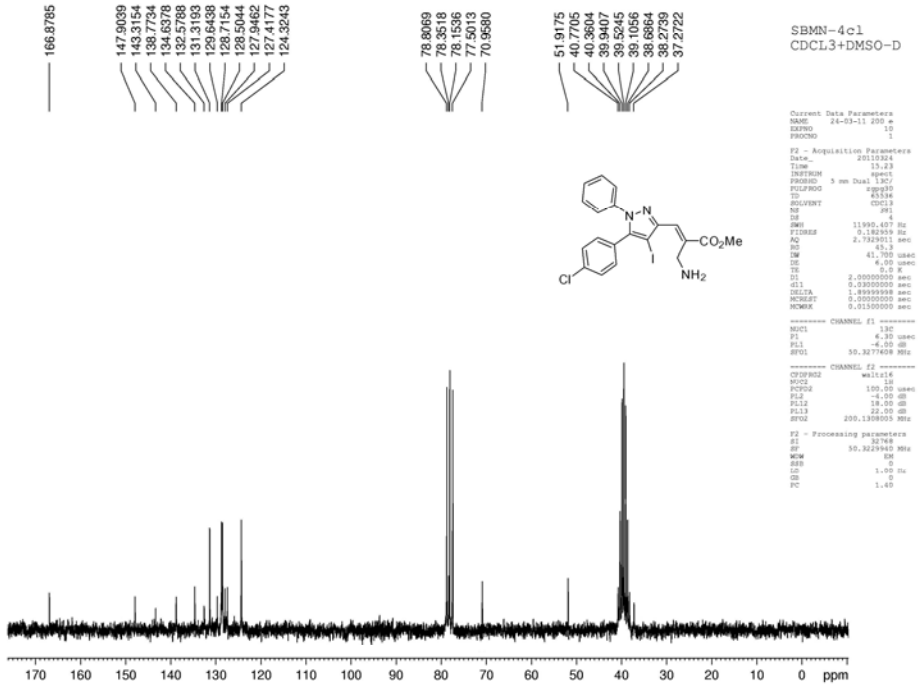


Fig-74: ^{13}C spectrum of methyl (E)- 2-(aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1H-pyrazol-3-yl) prop-2-enoate (**4c**).

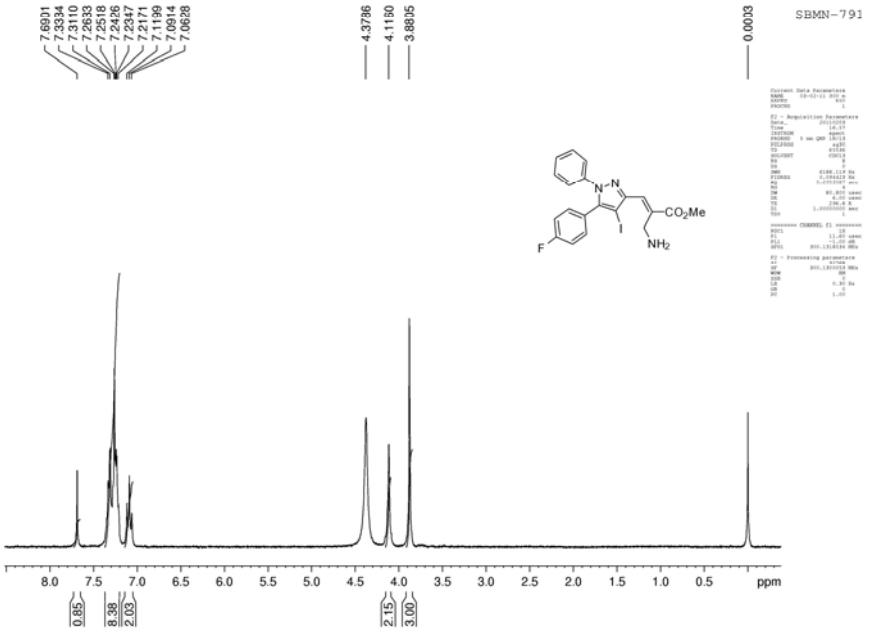


Fig-75: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4d**).

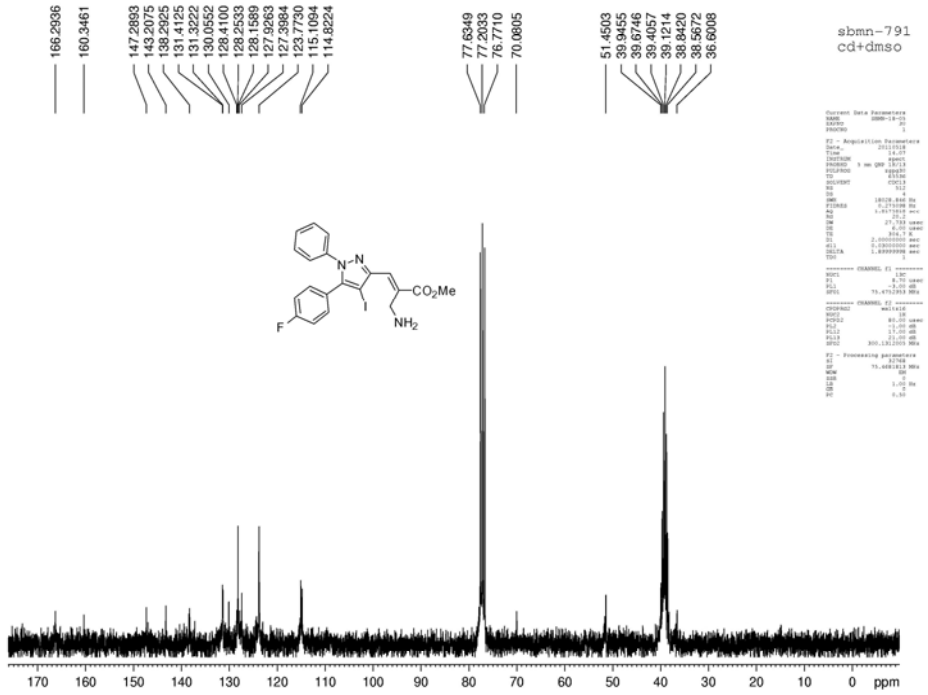


Fig-76: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[5-(4-fluorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4d**).

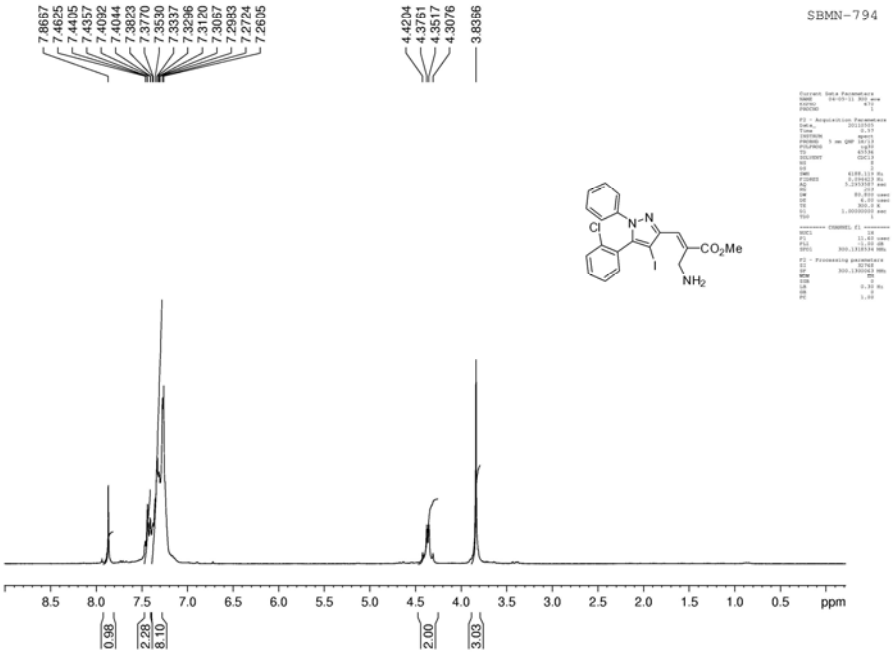


Fig-77: ^{1}H-spectrum of methyl (E)- 2-(aminomethyl)-3-(5-(2-chlorophenyl)-4-iodo-1-phenyl-1H-pyrazol-3-yl) prop-2-enoate (**4e**).

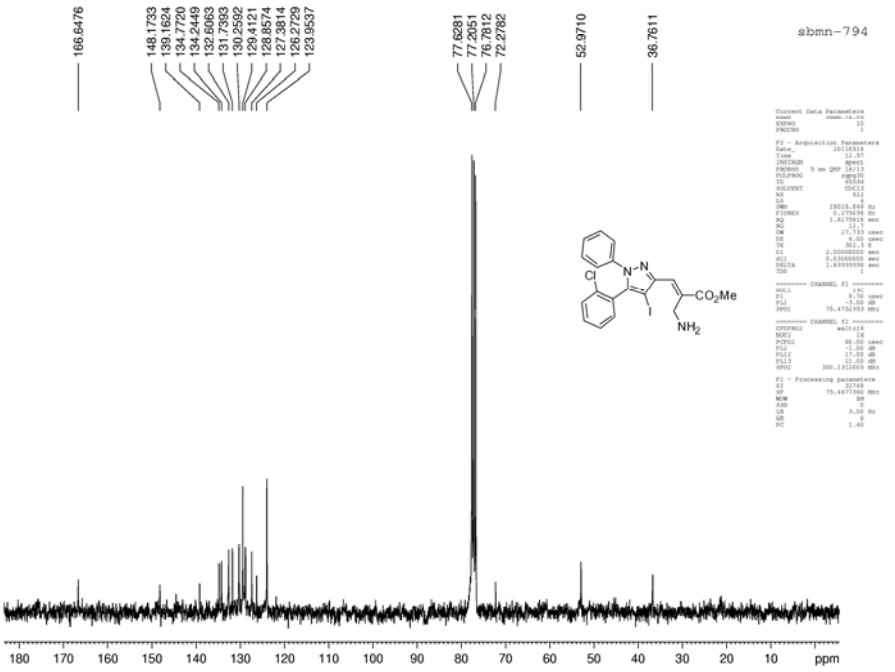


Fig-78: ^{13}C spectrum of methyl (E)- 2-(aminomethyl)-3-(5-(2-chlorophenyl)-4-iodo-1-phenyl-1H-pyrazol-3-yl) prop-2-enoate (**4e**).

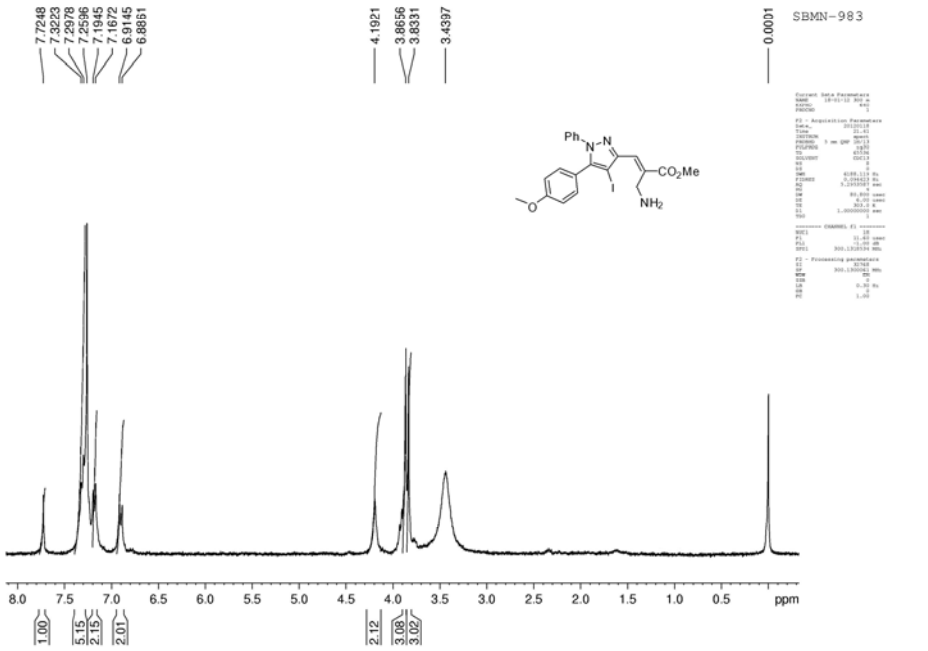


Fig-79: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate **(4f).**

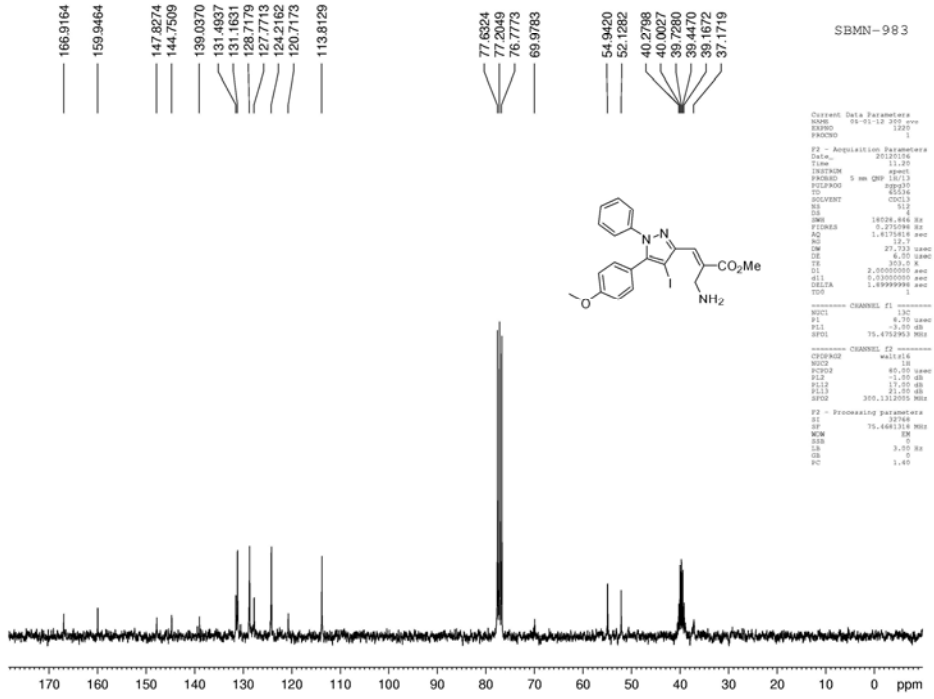


Fig-80: ^{13}C spectrum of methyl methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate **(4f).**

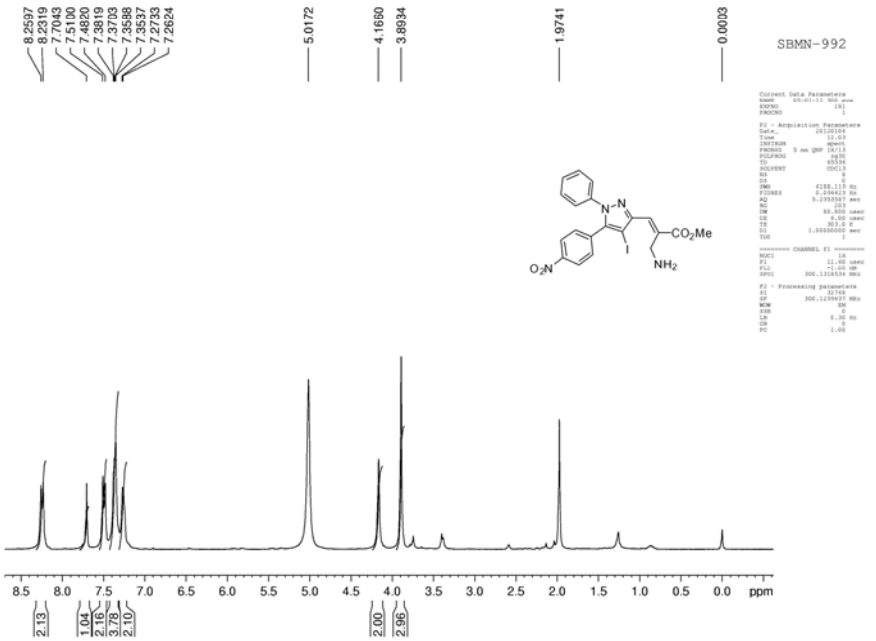


Fig-81: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate **(4g).**

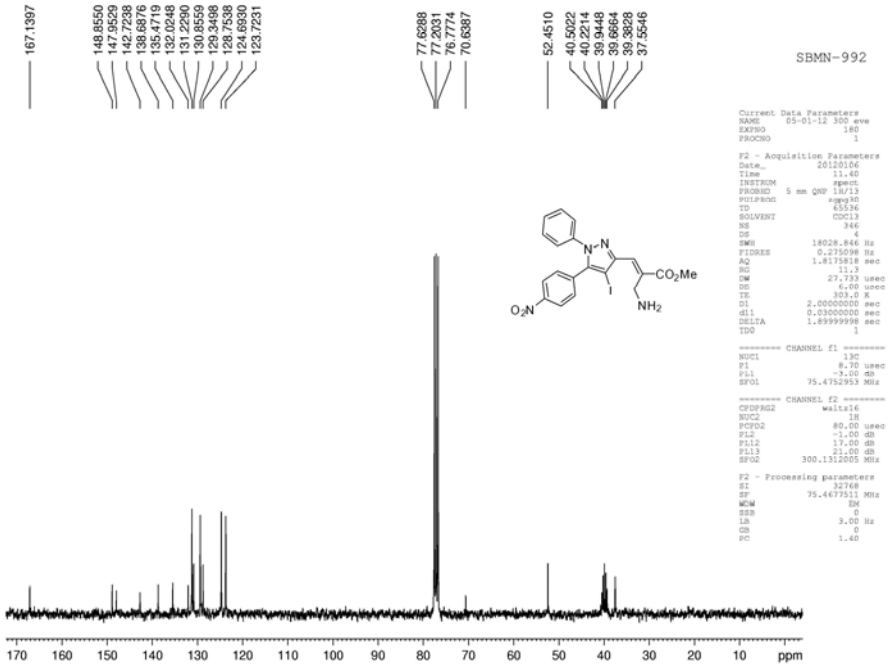


Fig-82: ^{13}C spectrum of methyl methyl (*E*)-2-(aminomethyl)-3-(4-iodo-5-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-3-yl) prop-2-enoate **(4g).**

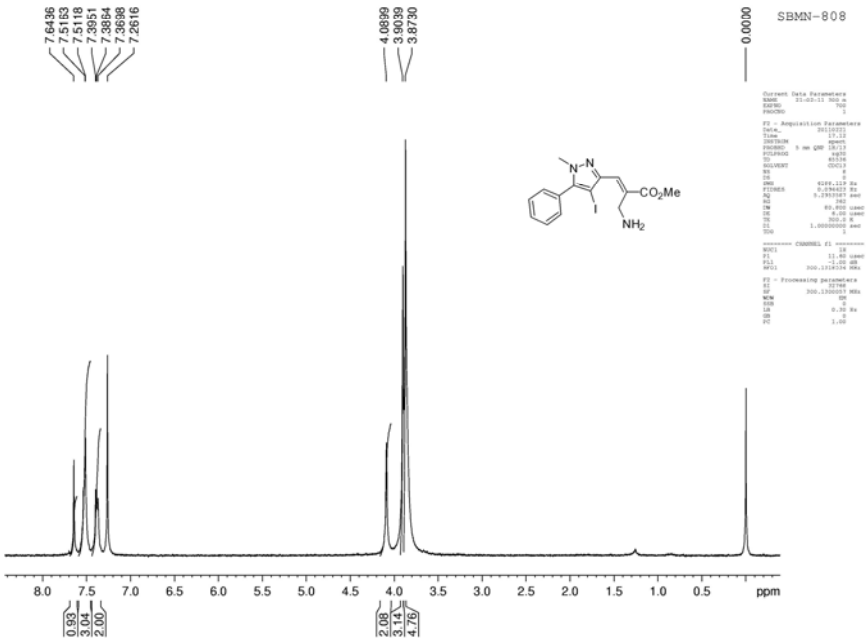


Fig-83: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**4h**).

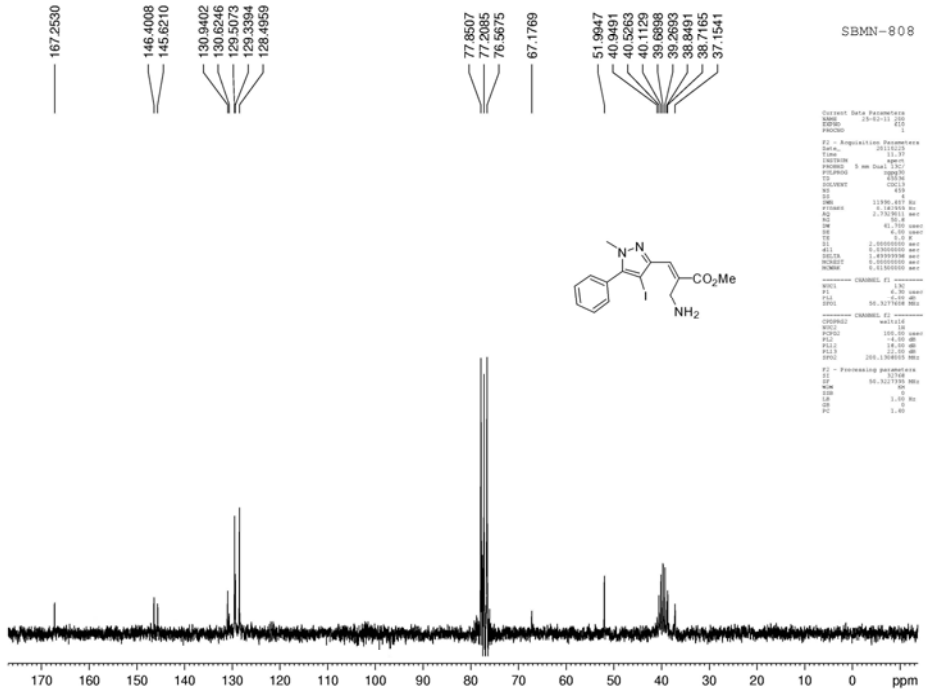


Fig-84: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-5-phenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**4h**).

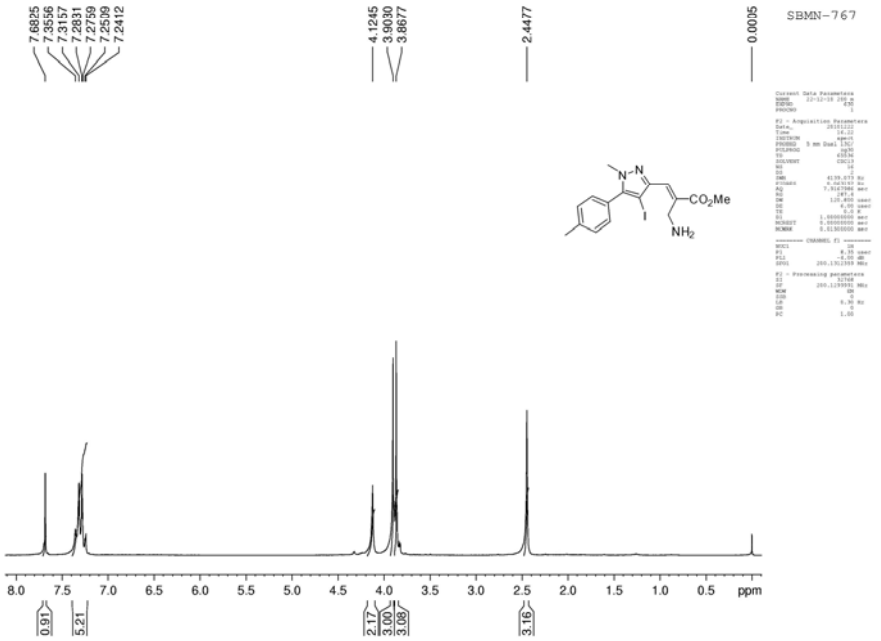


Fig-85: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]prop-2-enoate (**4i**).

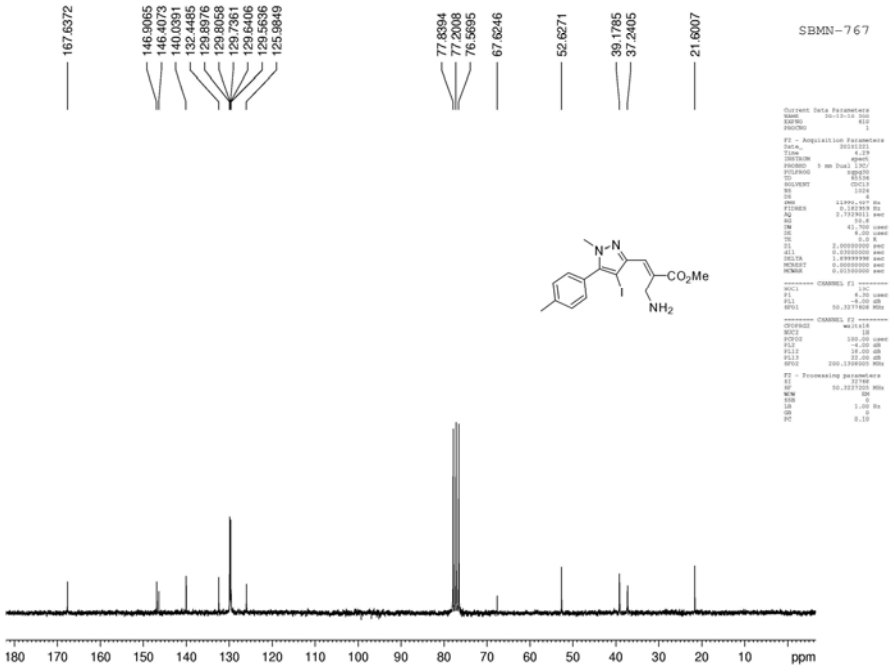


Fig-86: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-1-methyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl]prop-2-enoate (**4i**).

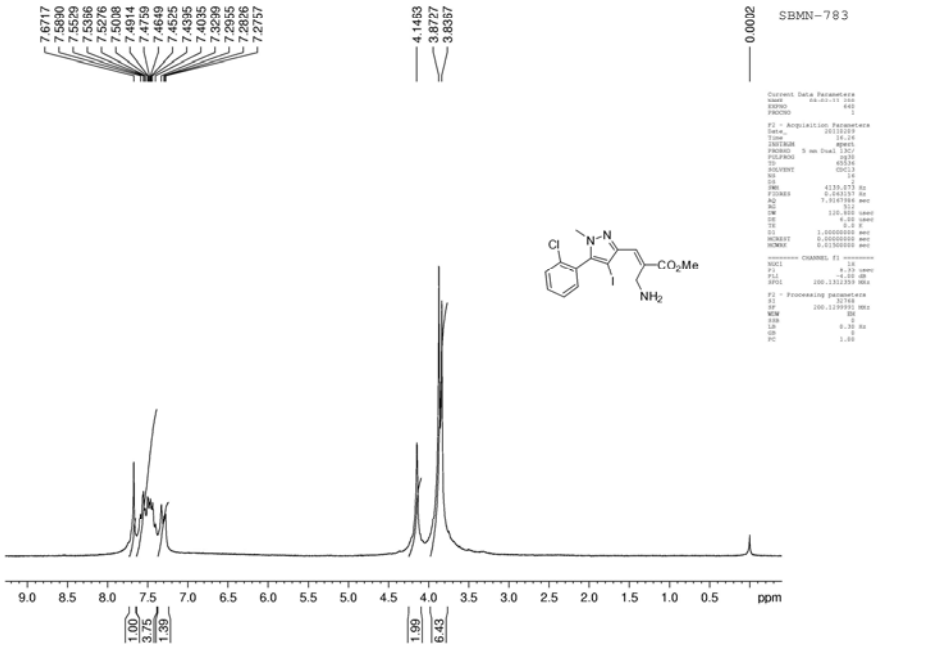


Fig-87: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4j**).

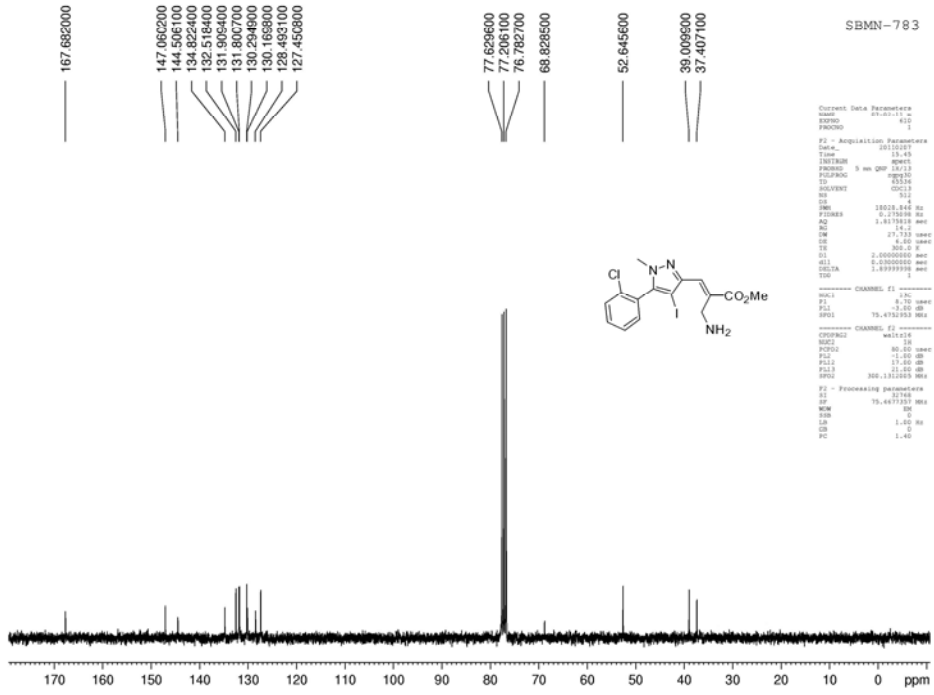


Fig-88: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enoate (**4j**).

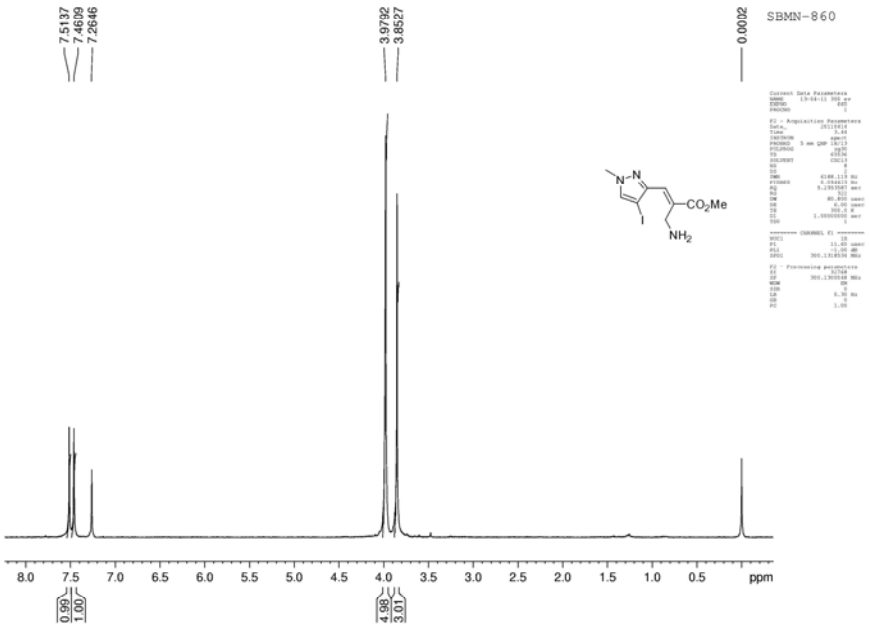


Fig-89: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-1*H*-pyrazol-3-yl)prop-2-enate (**4k**).

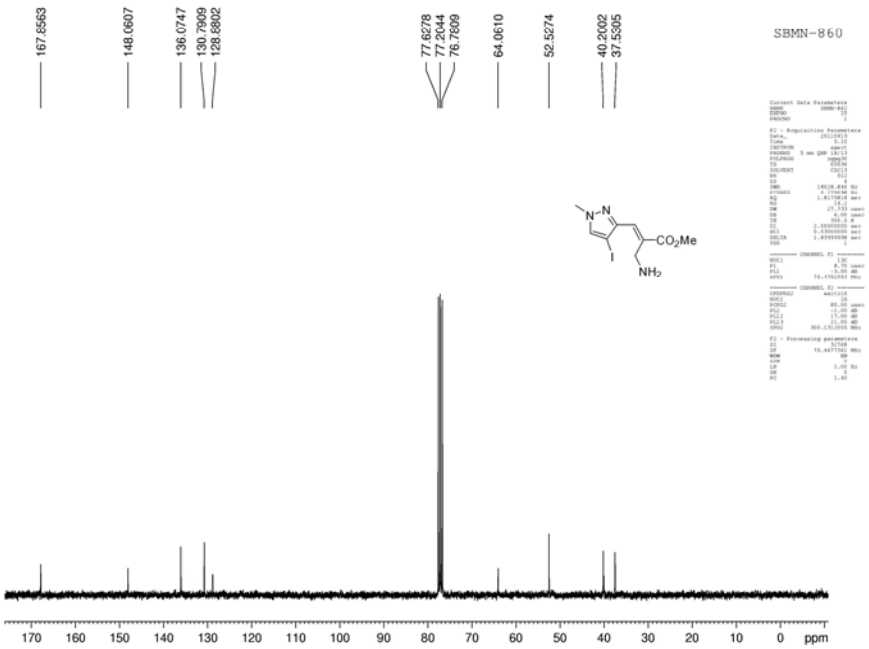


Fig-90: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1-methyl-1*H*-pyrazol-3-yl)prop-2-enate (**4k**).

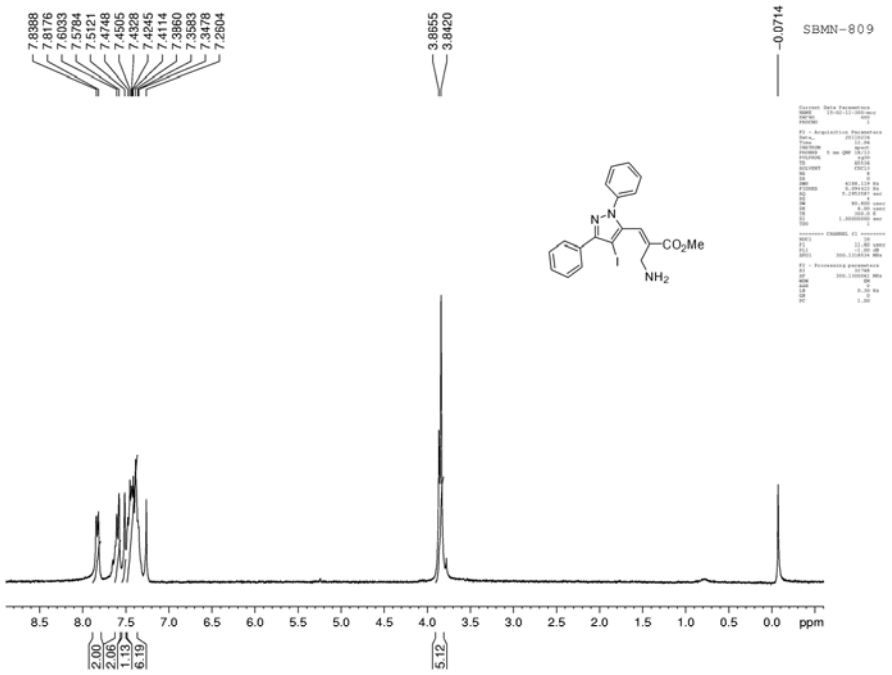


Fig-91: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,3-diphenyl-1*H*-pyrazol-5-yl)prop-2-enoate (**9a**).

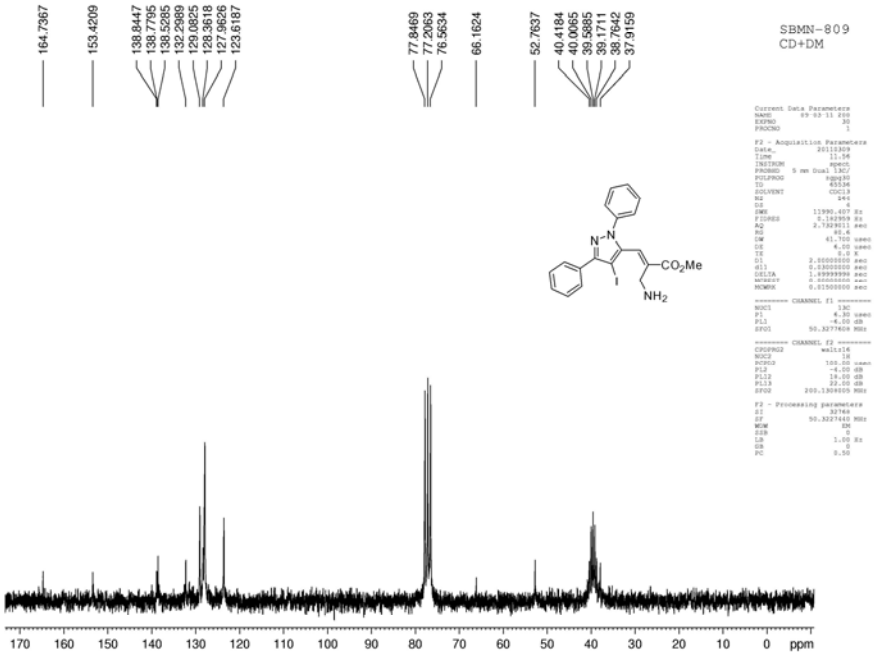


Fig-92: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-(4-iodo-1,3-diphenyl-1*H*-pyrazol-5-yl)prop-2-enoate (**9a**).

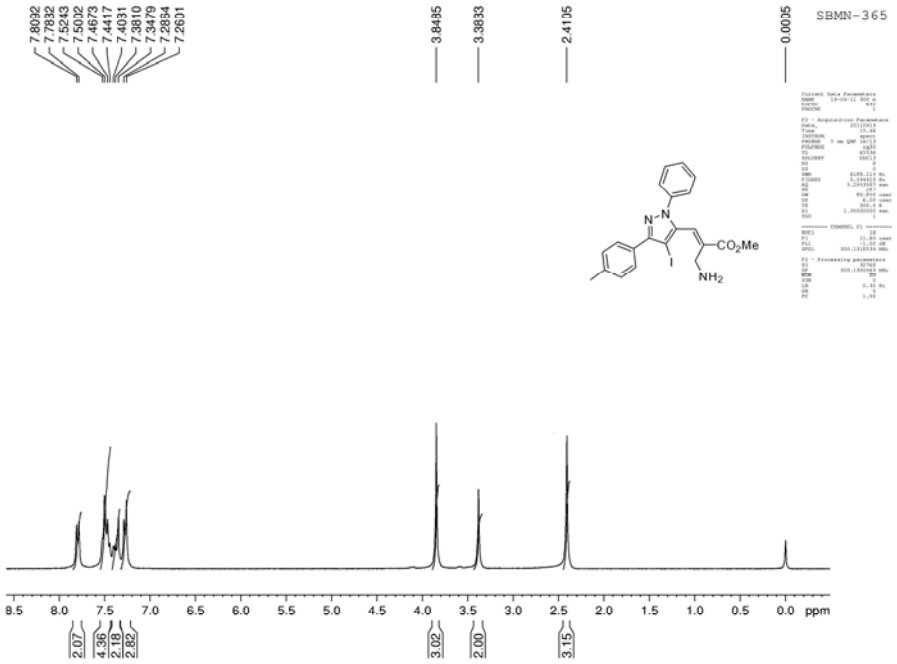


Fig-93: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (**9b**).

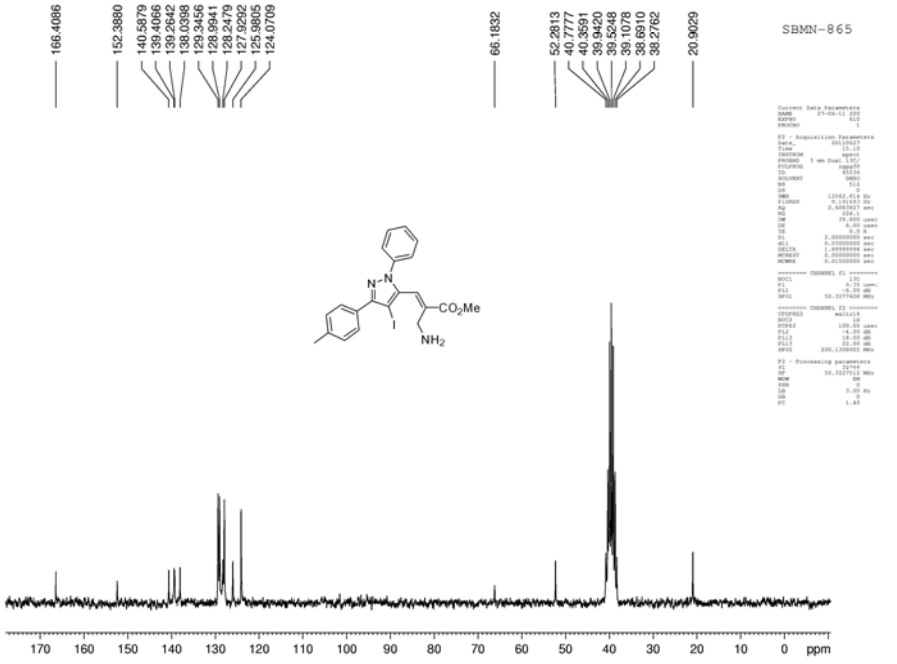


Fig-94: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[4-iodo-3-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (**9b**).

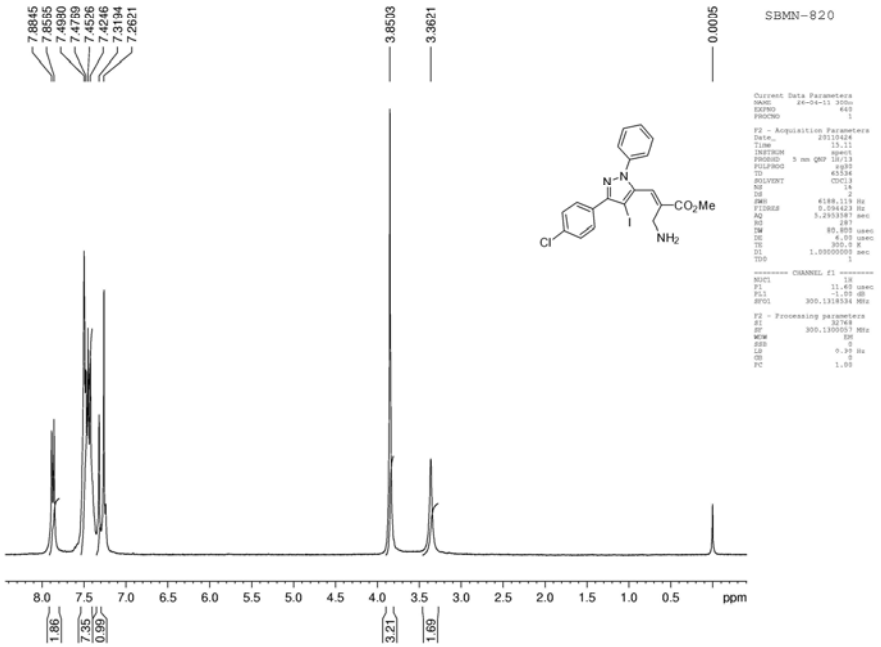


Fig-95: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (**9c**).

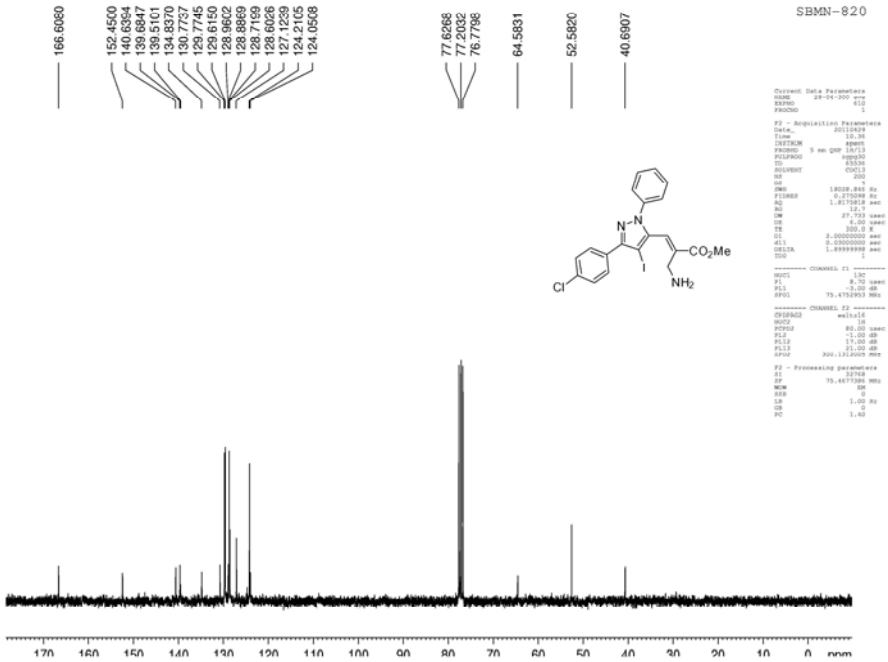


Fig-96: ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-[3-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-5-yl]prop-2-enoate (**9c**).

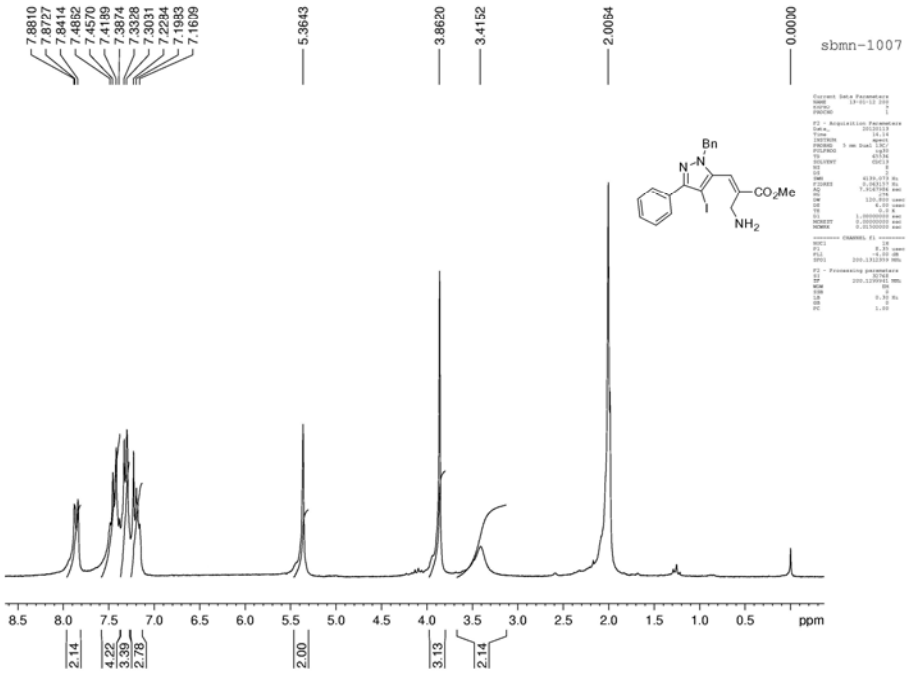


Fig-97: ^{1}H-spectrum of methyl (*E*)-2-(aminomethyl)-3-(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)prop-2-enoate **(9l).**

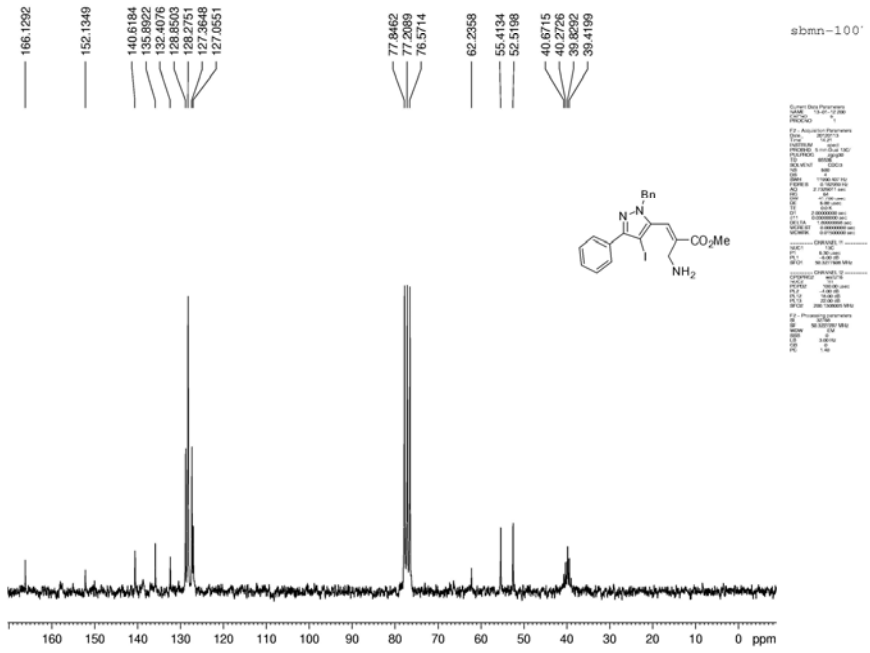


Fig-98 ^{13}C spectrum of methyl (*E*)-2-(aminomethyl)-3-(1-benzyl-4-iodo-3-phenyl-1*H*-pyrazol-5-yl)prop-2-enoate **(9l).**

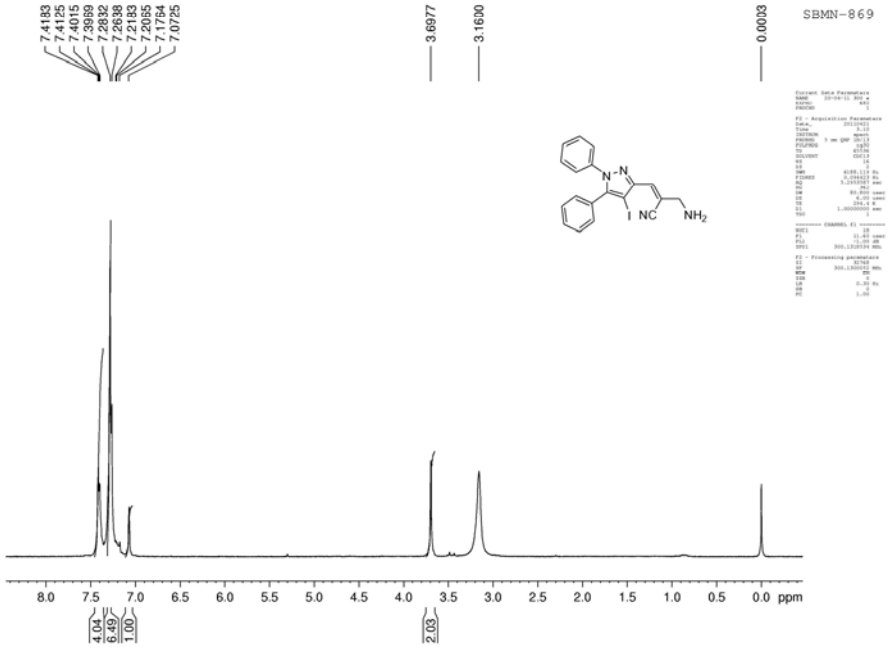


Fig-99: ^{1}H-spectrum of (*Z*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enenitrile (**15a**).

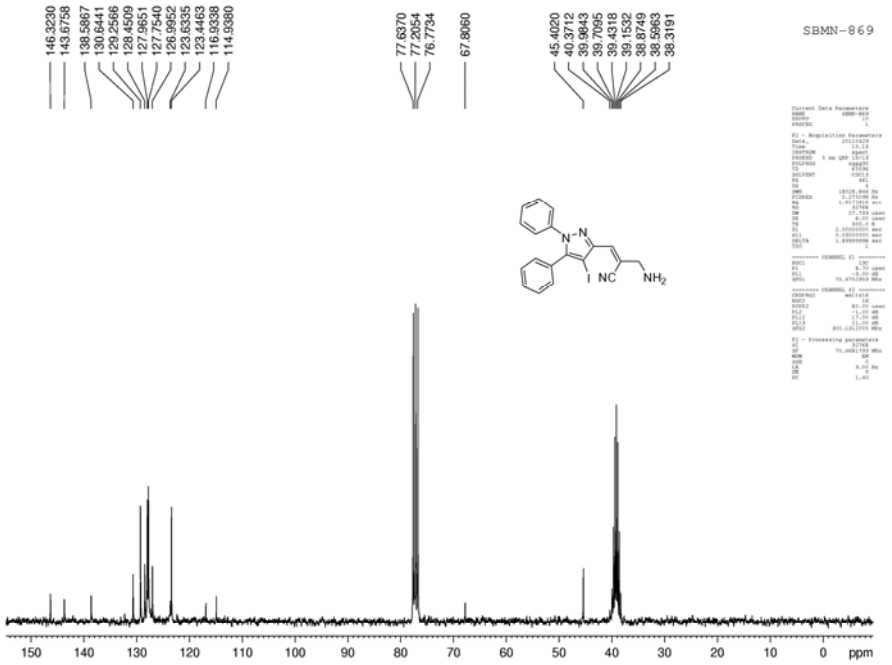


Fig-100: ^{13}C spectrum of (*Z*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enenitrile (**15a**).

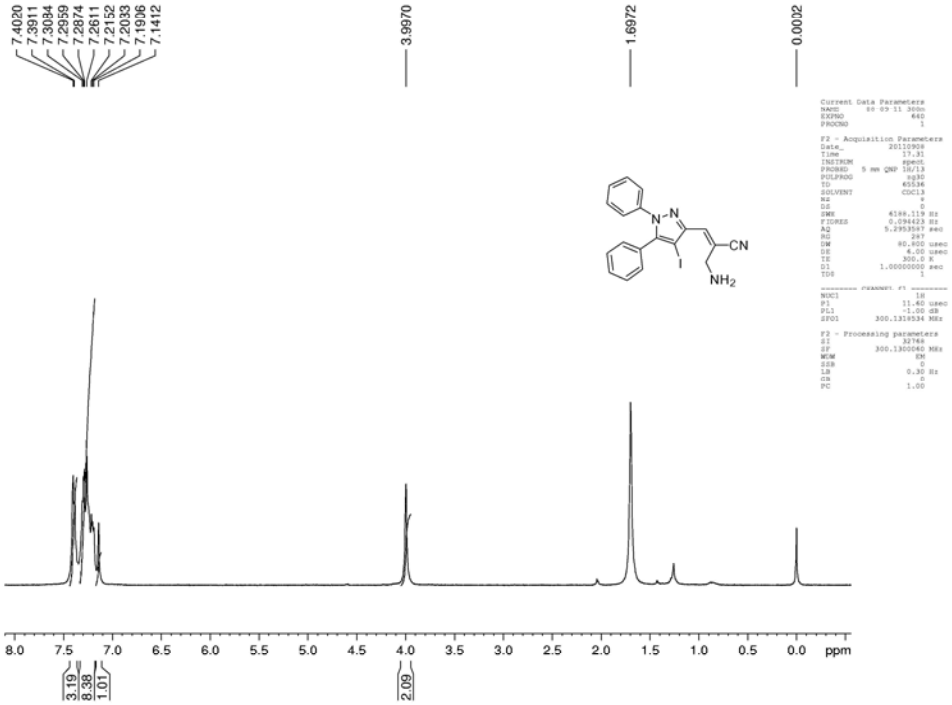


Fig-101: ^{13}C spectrum of (*E*)-2-(aminomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enenitrile (**15a**)

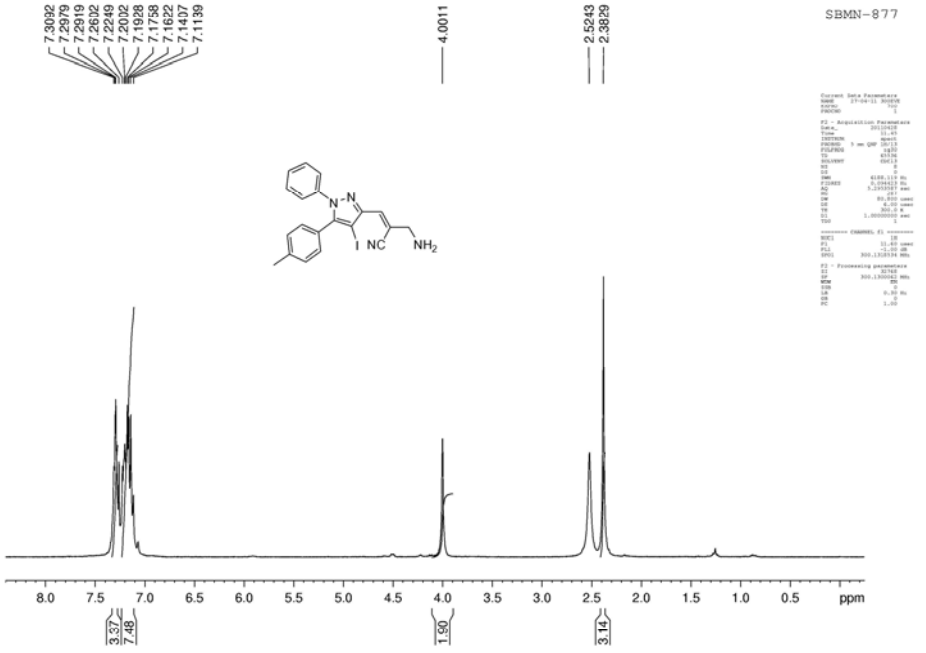


Fig-102: ^{1}H-spectrum of (*Z*)-2-(aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (**15b**).

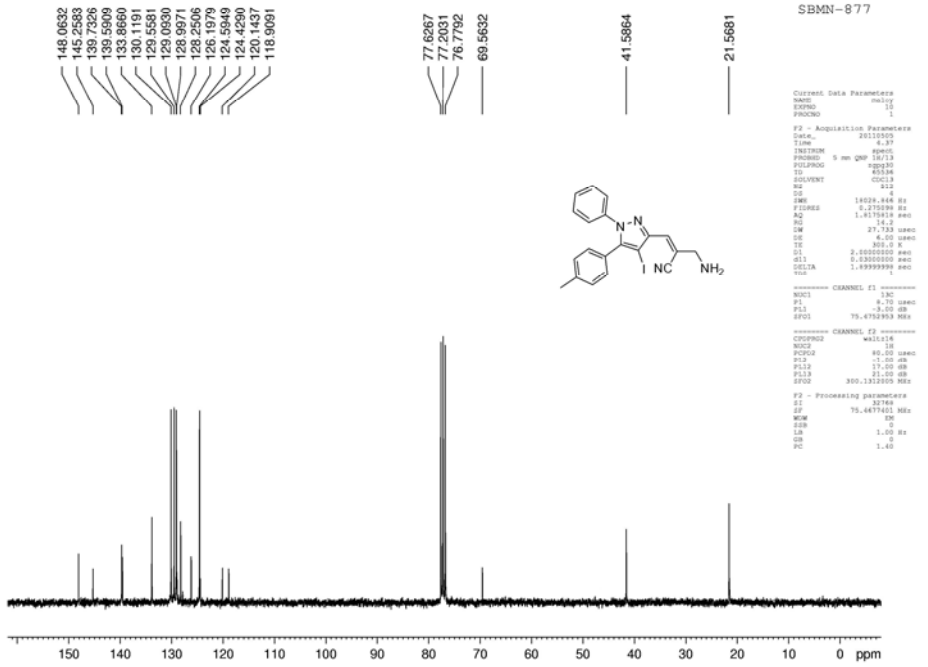


Fig-103: ^{13}C spectrum of (*Z*)-2-(aminomethyl)-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (**15b**).

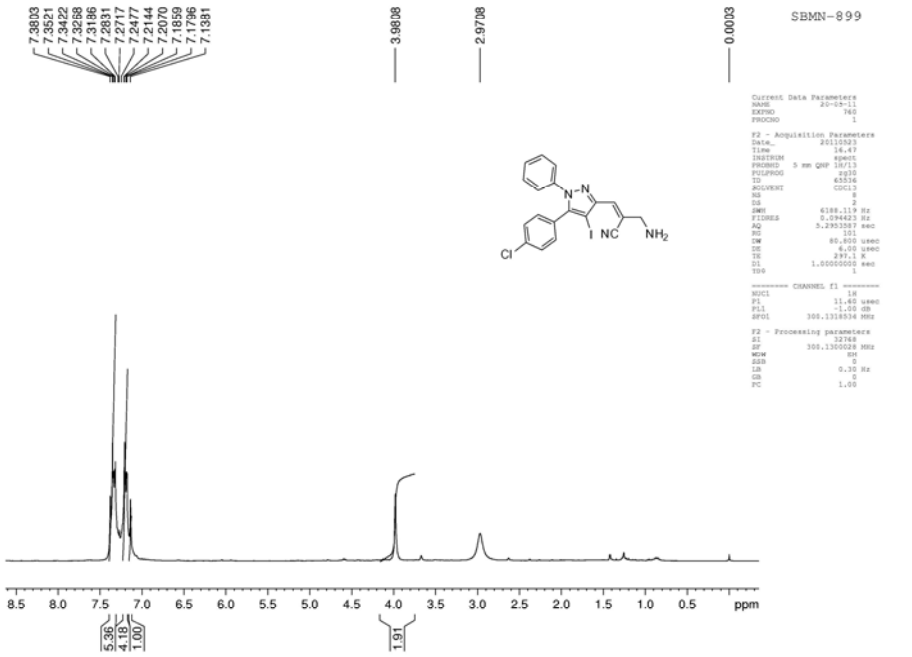


Fig-104: ^{1}H-spectrum of (*Z*)-2-(aminomethyl)-3-[5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (**15c**).

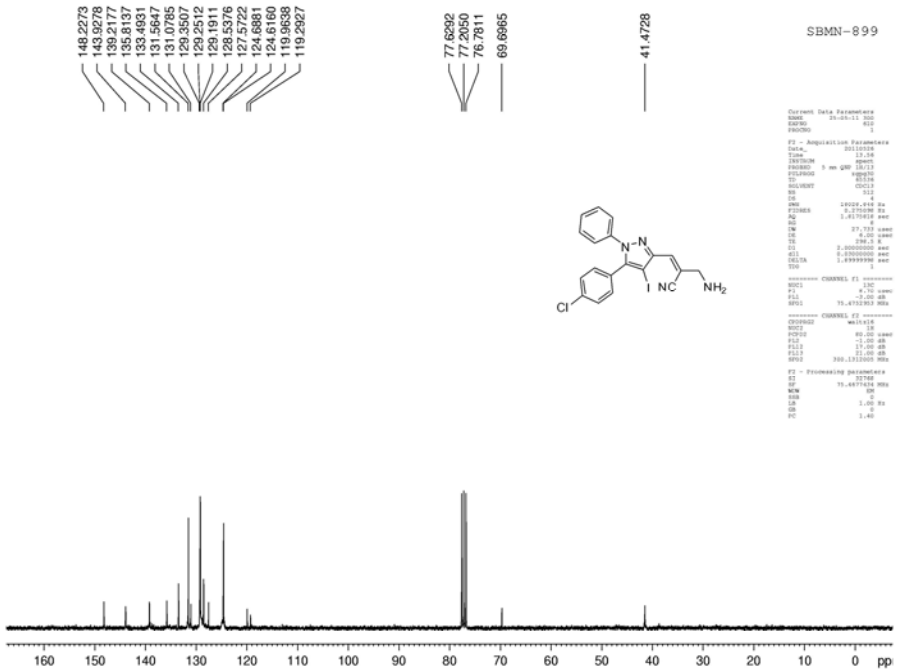


Fig-105: ^{13}C spectrum of (*Z*)-2-(aminomethyl)-3-[5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (**15c**).

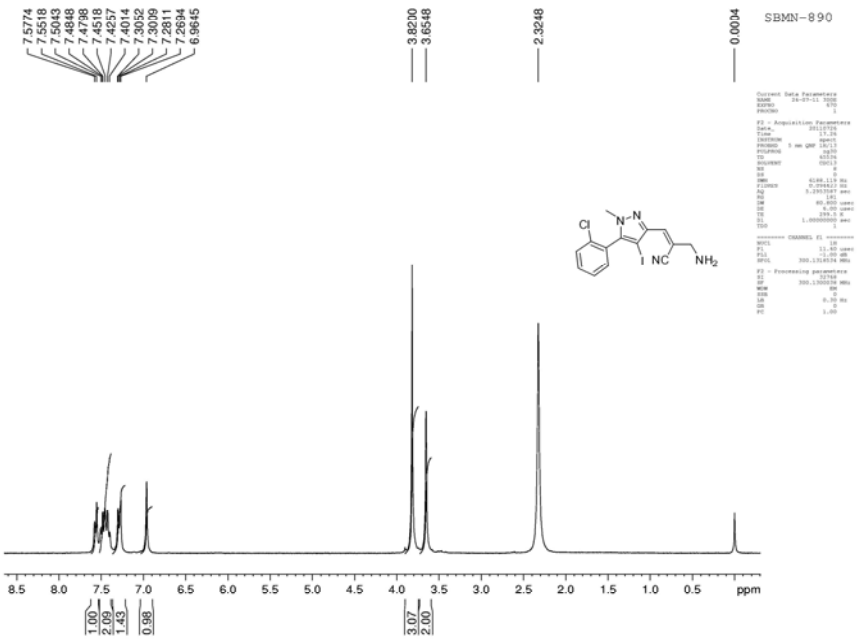


Fig-106: ^{1}H-spectrum of (*Z*)-2-(aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (1**5j**).

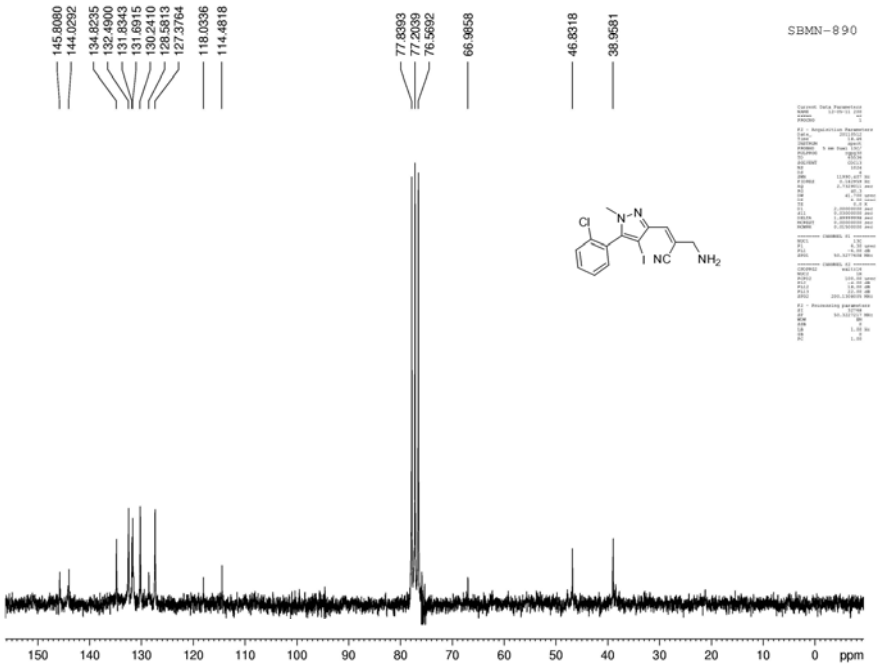


Fig-107: ^{13}C spectrum of (*Z*)-2-(aminomethyl)-3-[5-(2-chlorophenyl)-4-iodo-1-methyl-1*H*-pyrazol-3-yl]prop-2-enenitrile (**15j**).

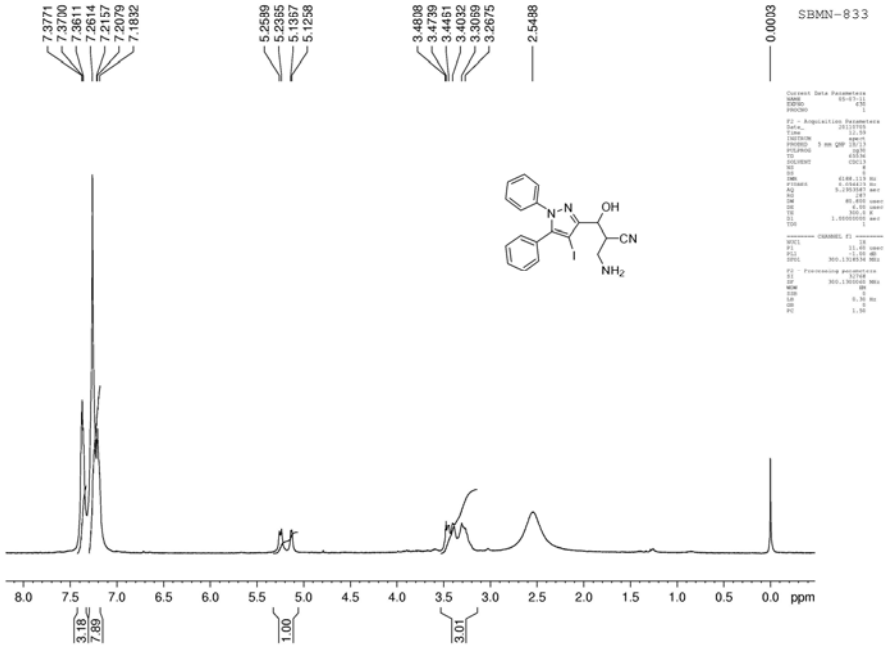


Fig-108: ^{1}H-spectrum of 2-(aminomethyl)-3-hydroxy-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)propanenitrile (**12a**).

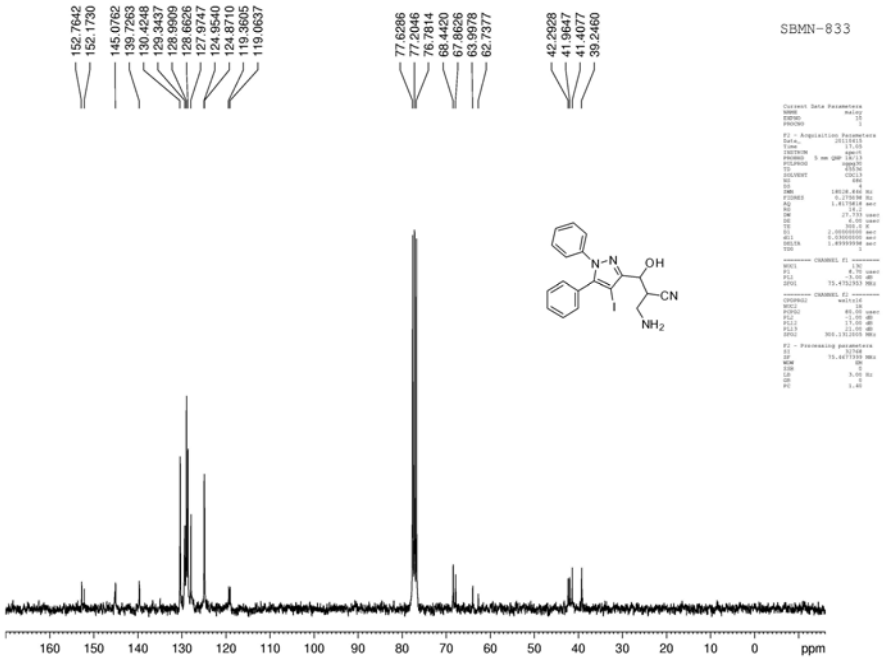


Fig-109: ^{13}C spectrum of 2-(aminomethyl)-3-hydroxy-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)propanenitrile (**12a**).

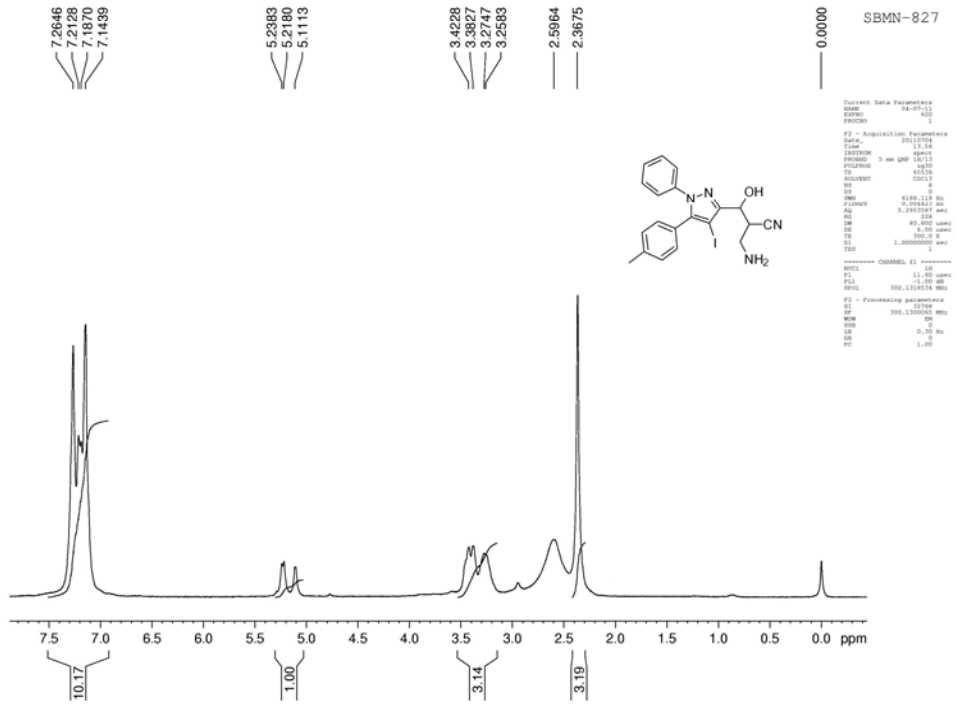


Fig-110: ^{1}H-spectrum of 2-(aminomethyl)-3-hydroxy-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]propanenitrile (**12b**).

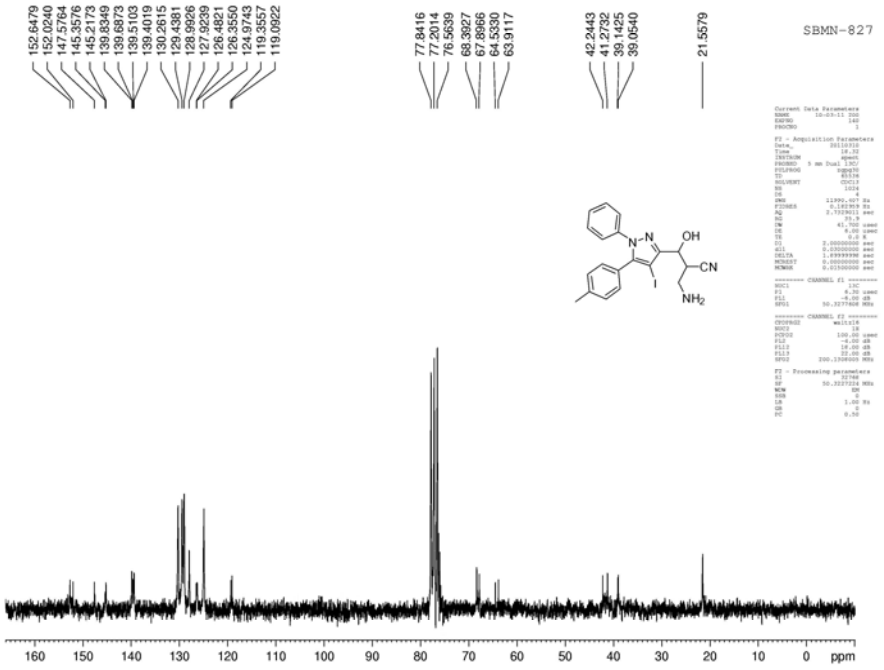


Fig-111: ^{13}C spectrum of 2-(aminomethyl)-3-hydroxy-3-[4-iodo-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]propanenitrile (**12b**).

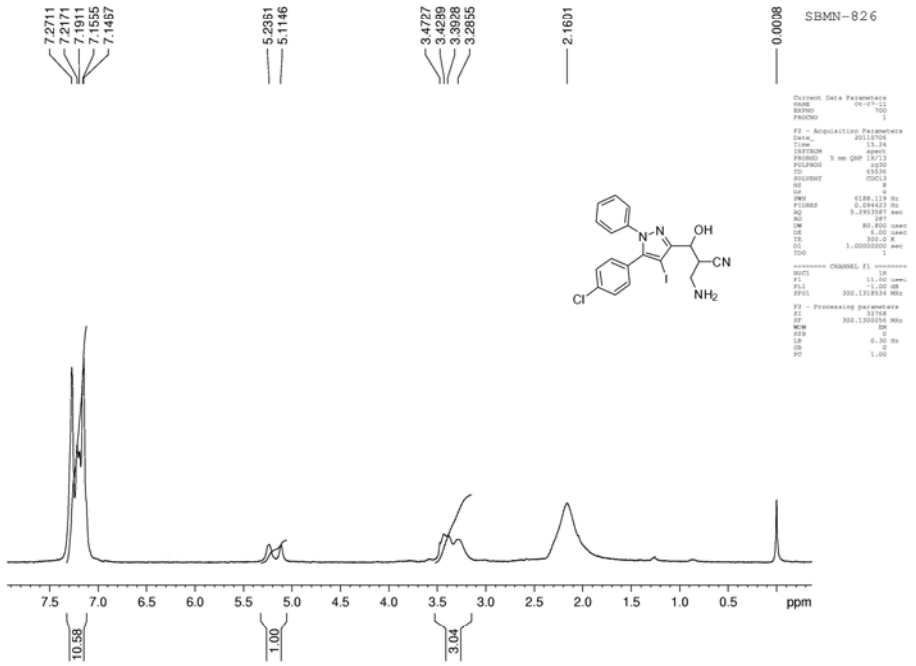


Fig-112: ^{1}H-spectrum of 2-(aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl)-3-hydroxypropanenitrile (**12c**).

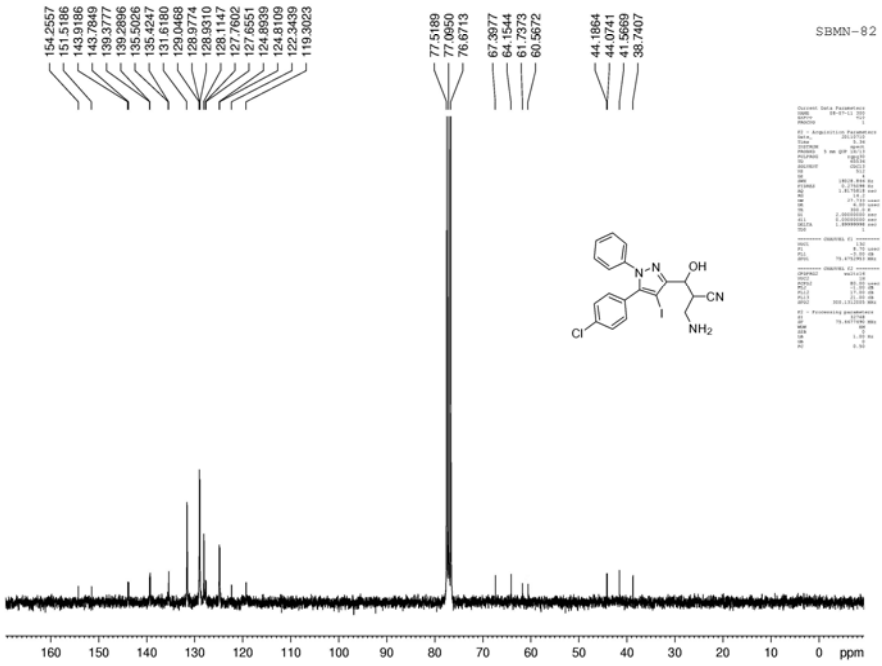


Fig-113: ^{13}C spectrum of 2-(aminomethyl)-3-(5-(4-chlorophenyl)-4-iodo-1-phenyl-1*H*-pyrazol-3-yl)-3-hydroxypropanenitrile (**12c**).

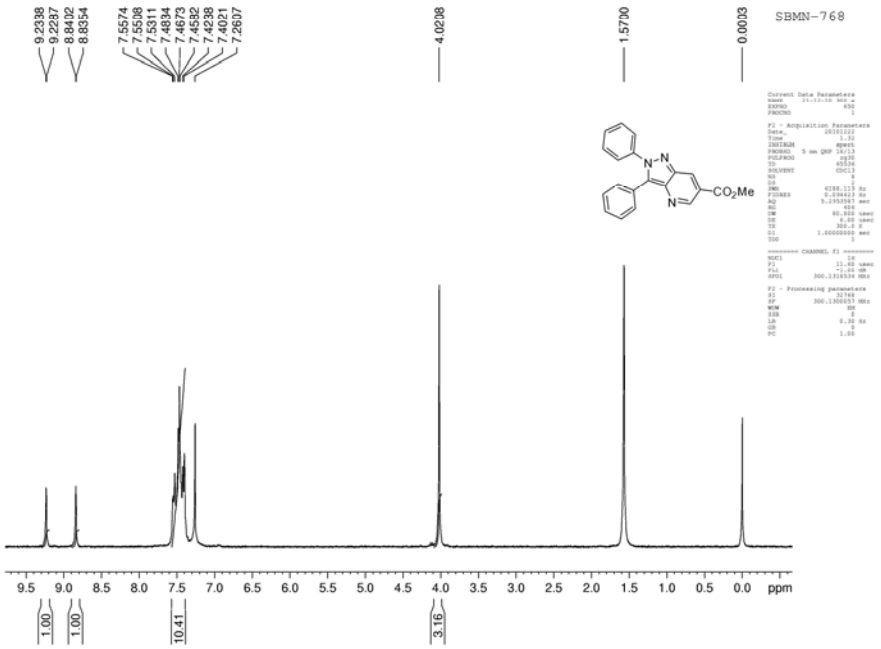


Fig-114: ^{1}H-spectrum of methyl 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5a**).

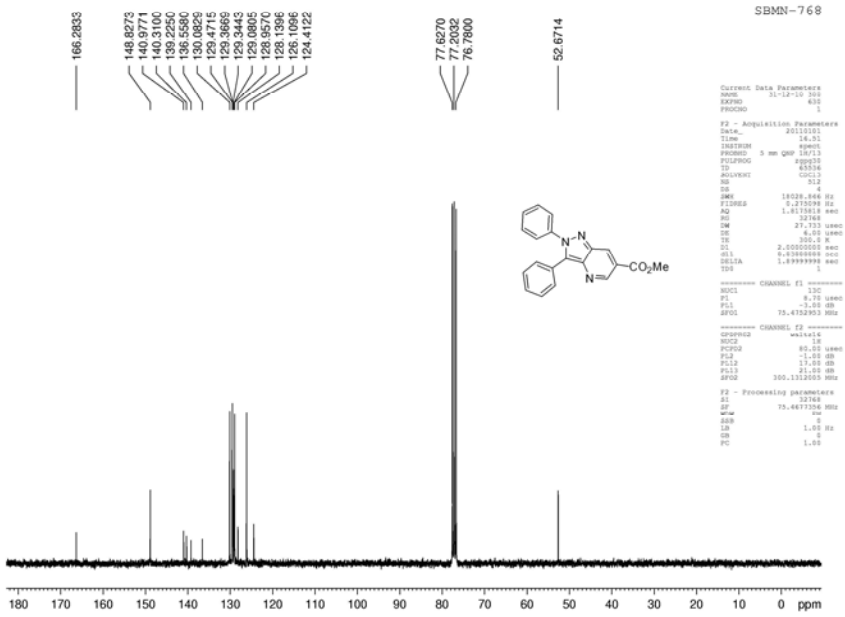


Fig-115: ^{13}C spectrum of methyl 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5a**).

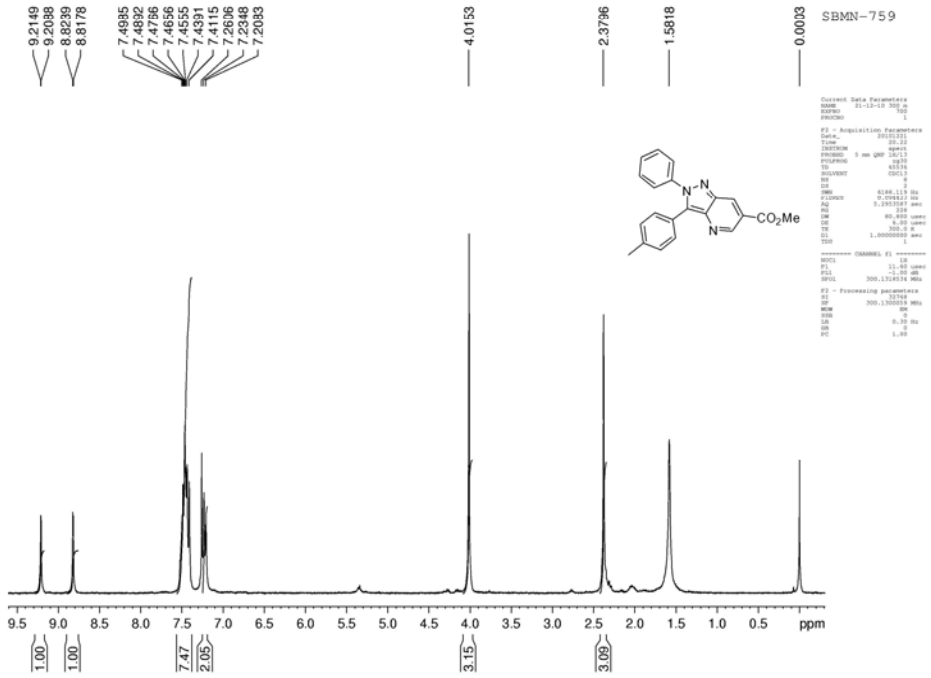


Fig-116: ^{1}H-spectrum of methyl 3-(4-methylphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5b**).

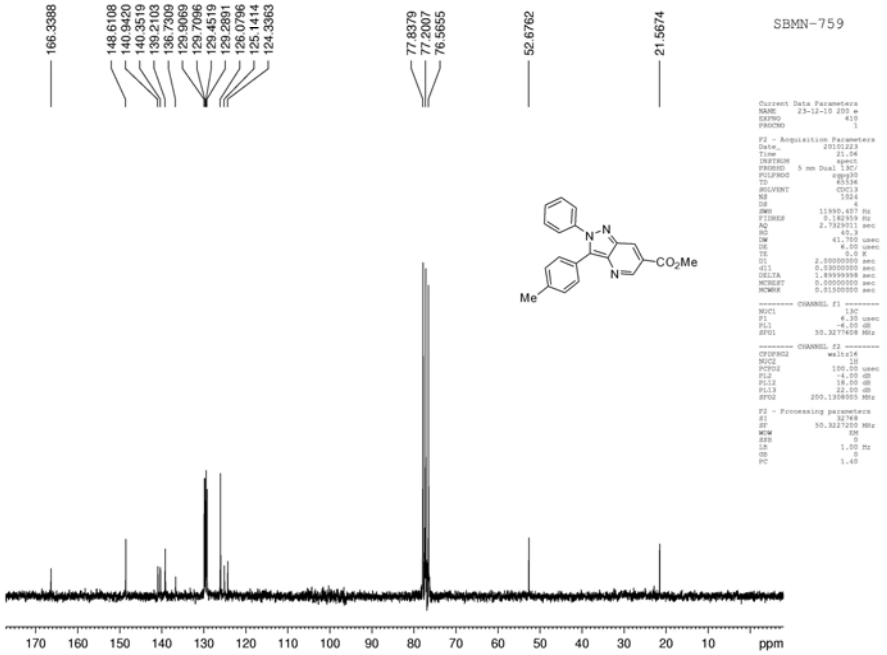


Fig-117: ^{13}C spectrum of methyl 3-(4-methylphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5b**).

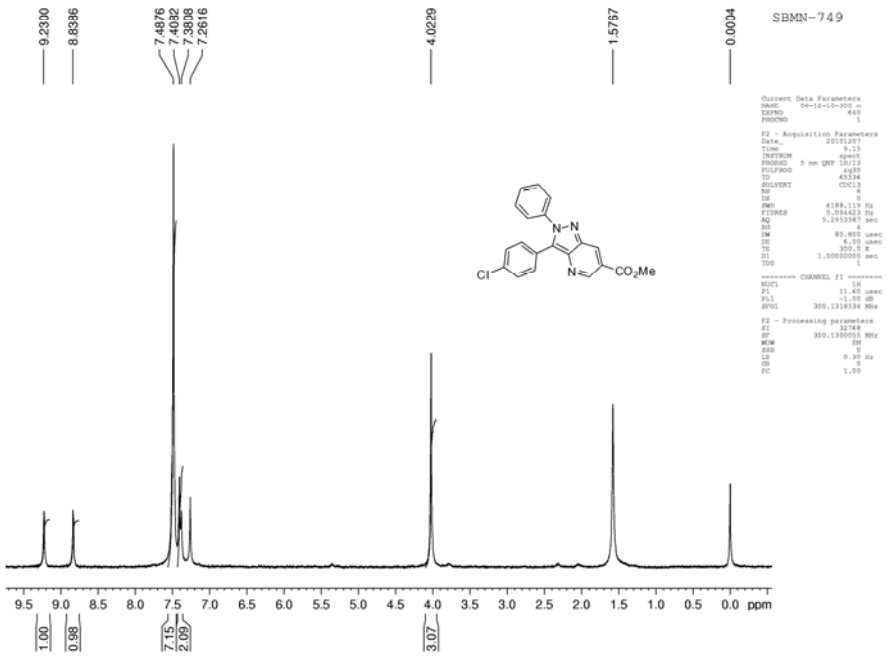


Fig-118: ^{1}H-spectrum of methyl 3-(4-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate(**5c**).

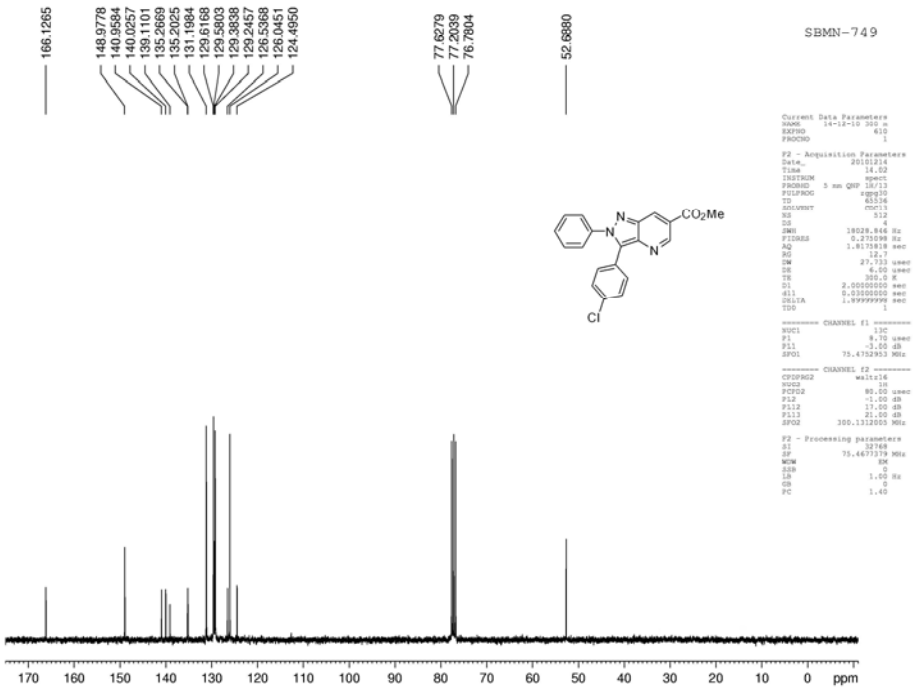


Fig-119: ^{13}C spectrum of methyl 3-(4-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate(**5c**).

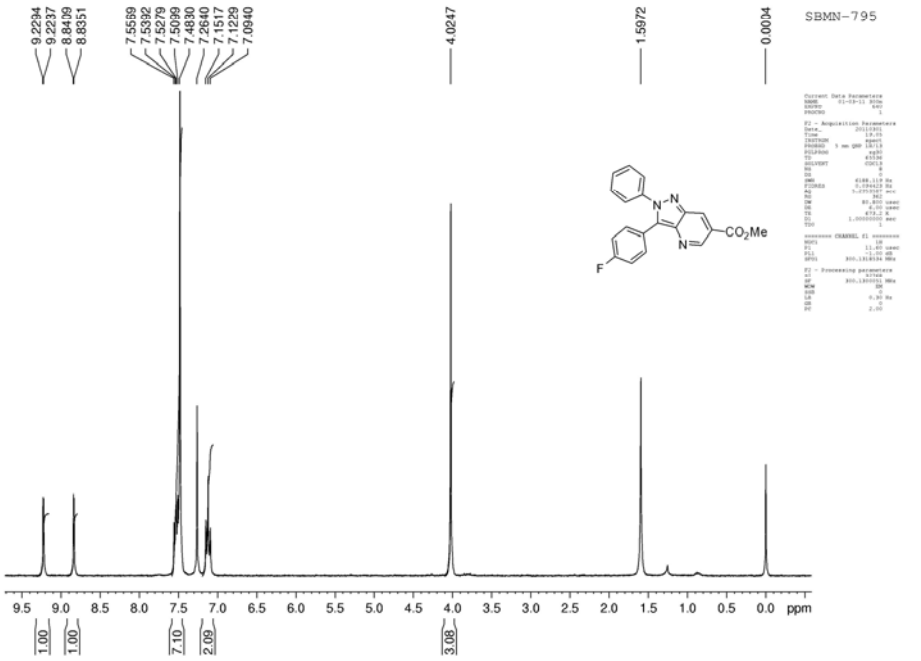


Fig-120: ^{1}H-spectrum of methyl 3-(4-fluorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5d**).

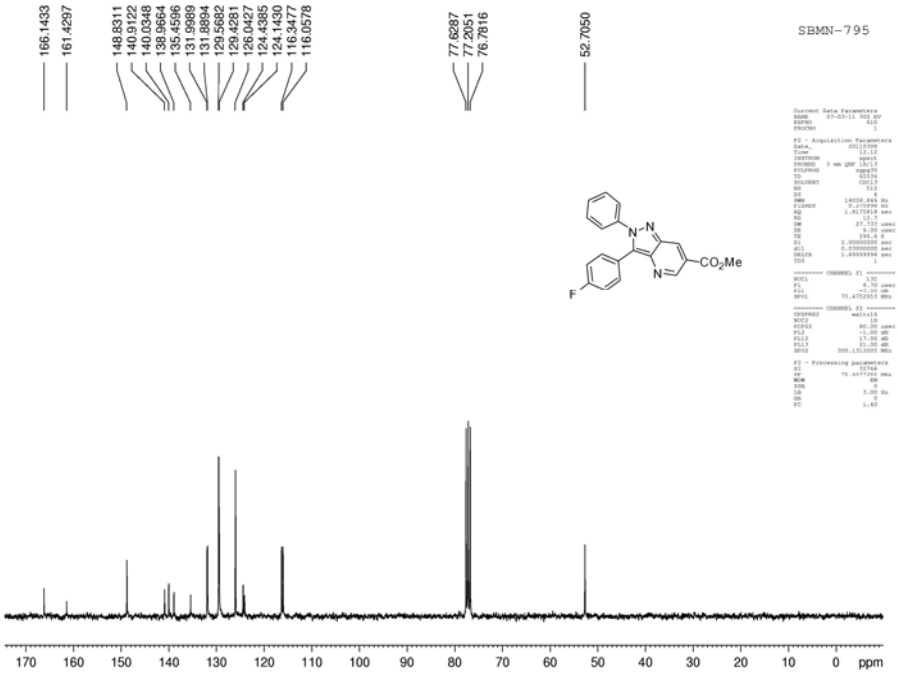


Fig-121: ^{13}C spectrum of methyl 3-(4-fluorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5d**).

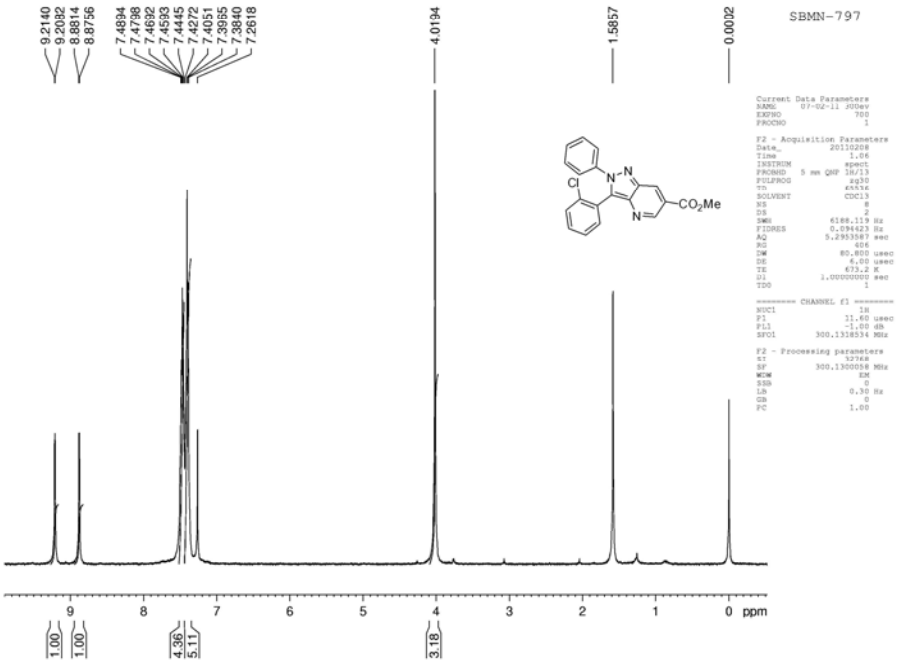


Fig-122: ^{1}H-spectrum of methyl 3-(2-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5e).**

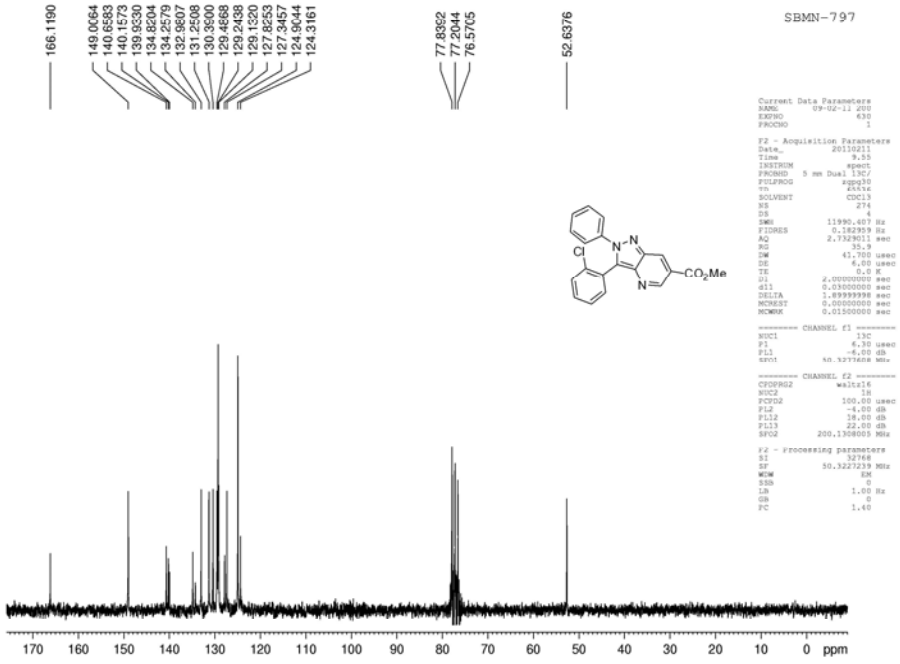


Fig-123: ^{13}C spectrum of methyl 3-(2-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5e).**

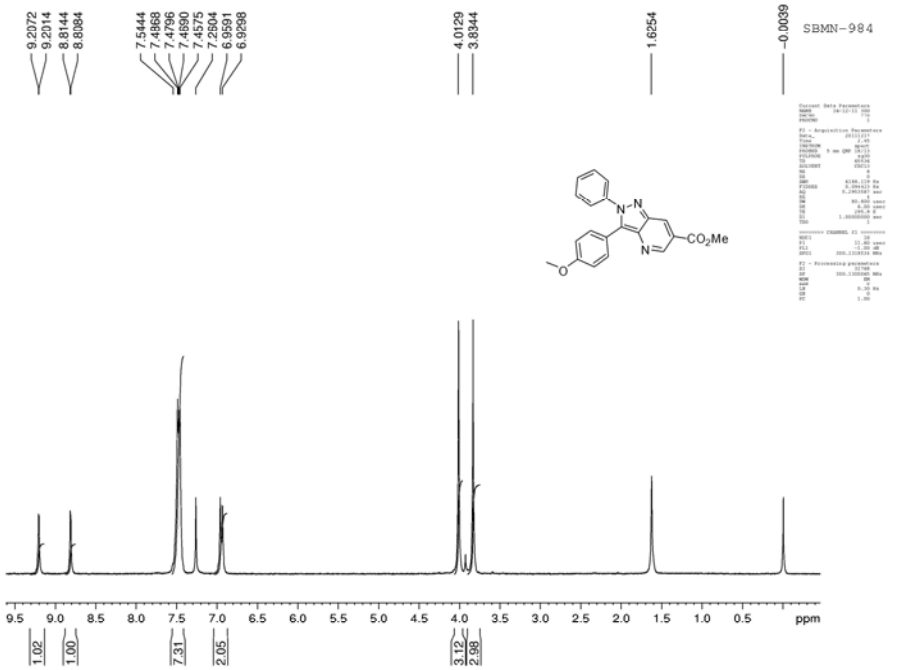


Fig-124: ^{1}H-spectrum of methyl 3-(4-methoxyphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5f).**

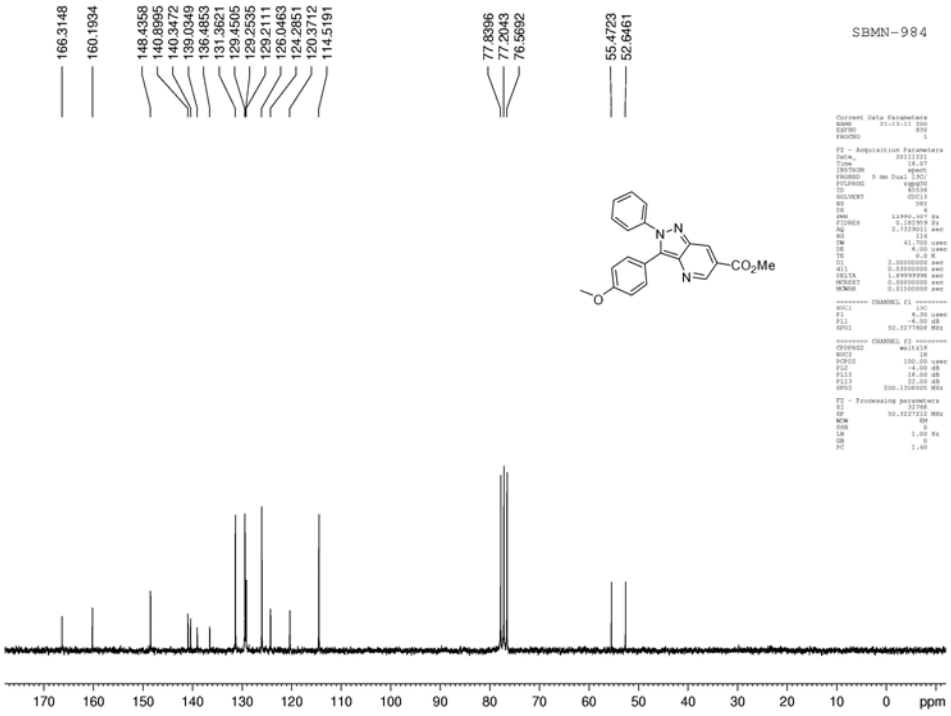


Fig-125: ^{13}C spectrum of methyl 3-(4-methoxyphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5f).**

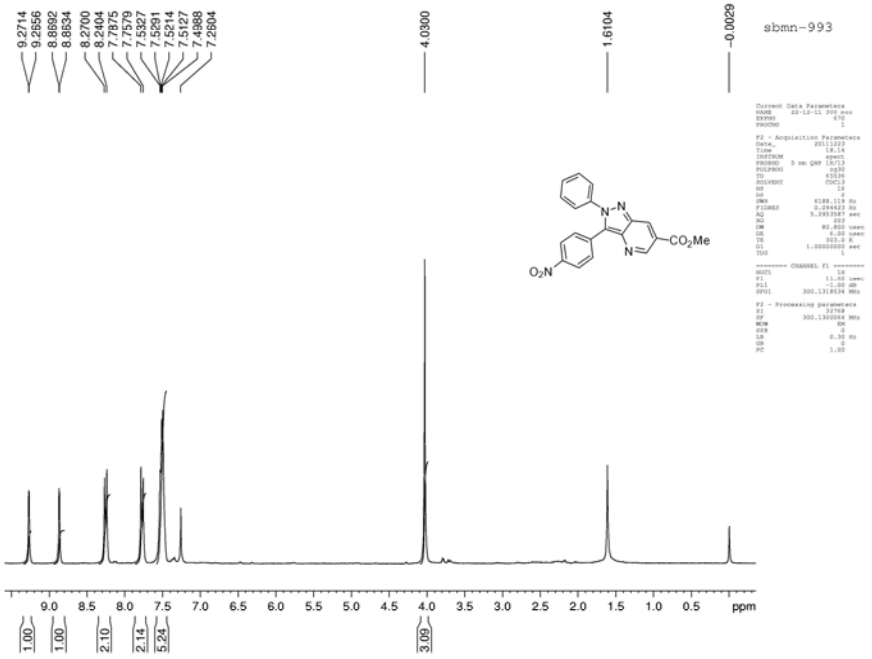


Fig-126: ^{1}H-spectrum of methyl 3-(4-nitrophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5g).**

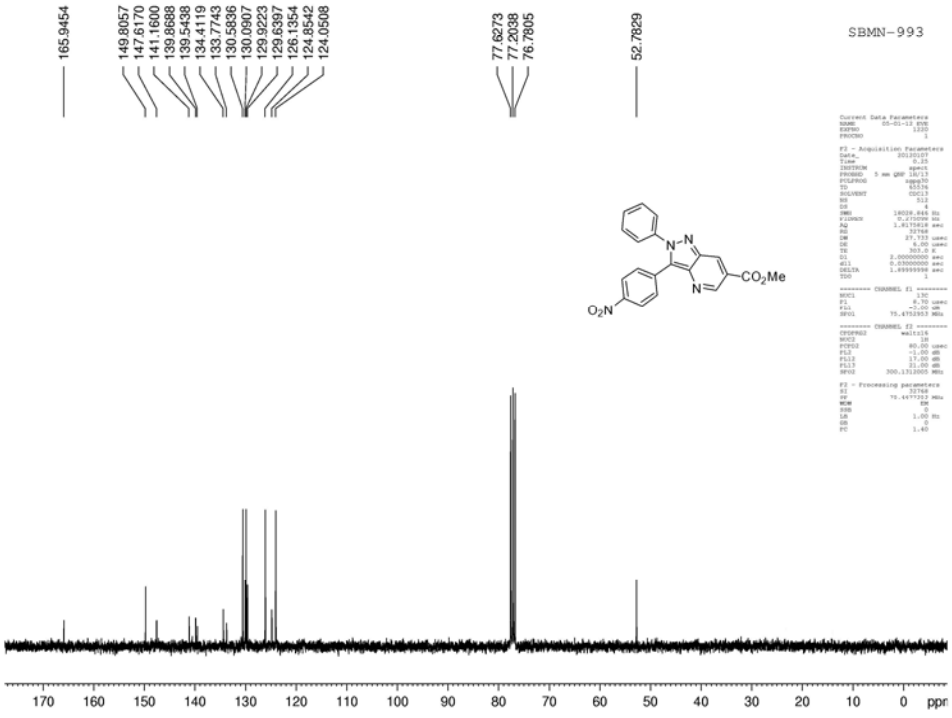


Fig-127: ^{13}C spectrum of methyl 3-(4-nitrophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(5g).**

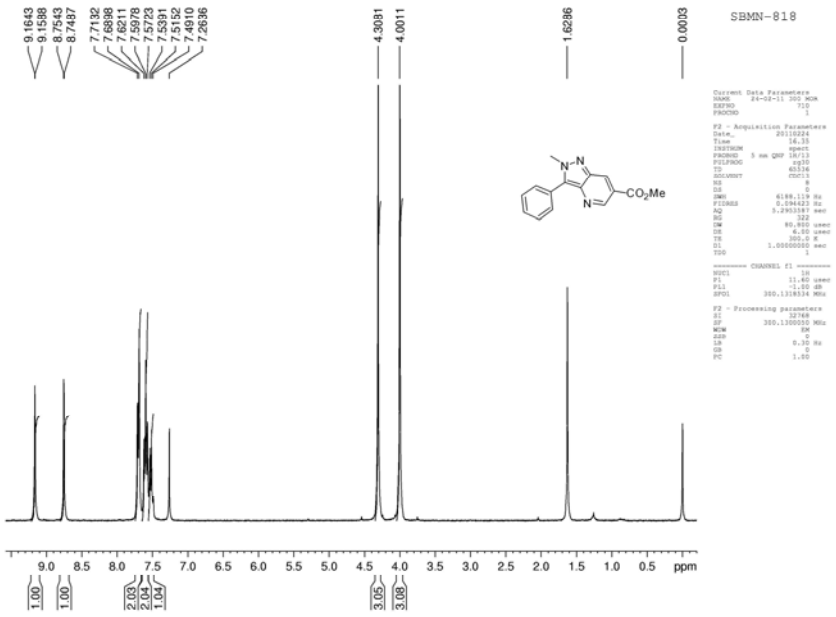


Fig-128: ^{1}H-spectrum of methyl 2-methyl-3-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5h**).

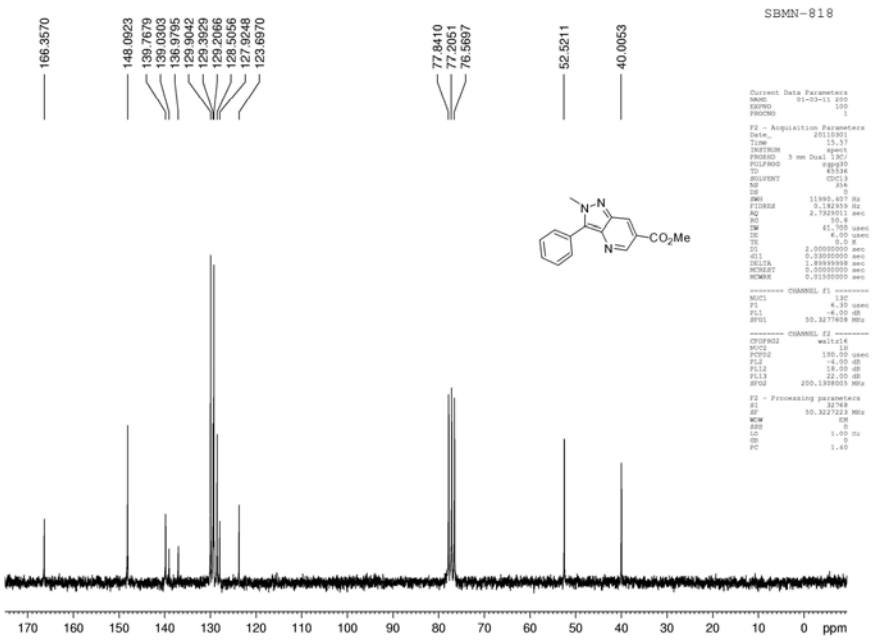


Fig-129: ^{13}C spectrum of methyl 2-methyl-3-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5h**).

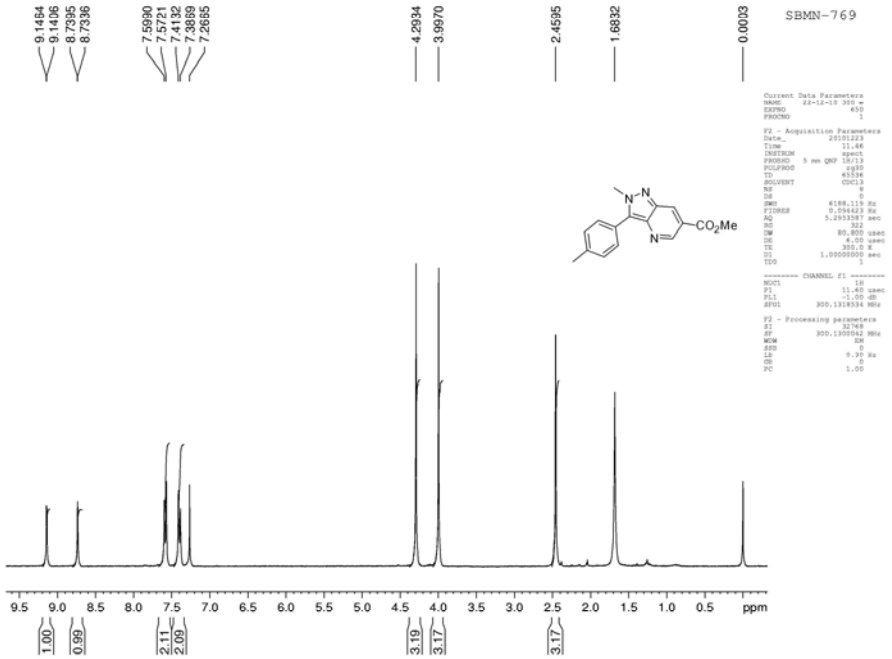


Fig-130: ^{1}H-spectrum of methyl methyl 2-methyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5i**).

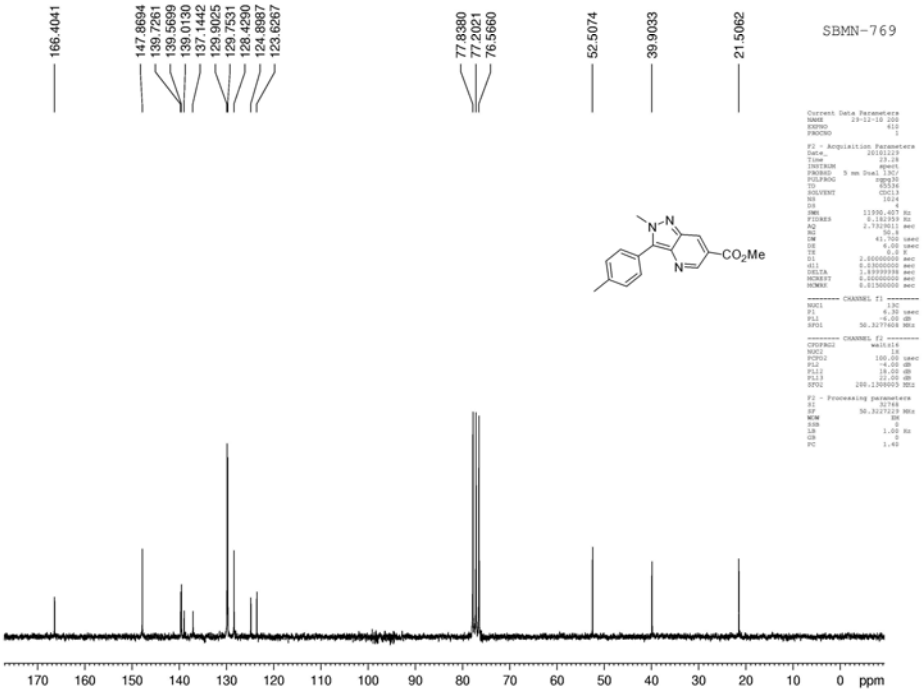


Fig-131: ^{13}C spectrum of methyl 2-methyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5i**).

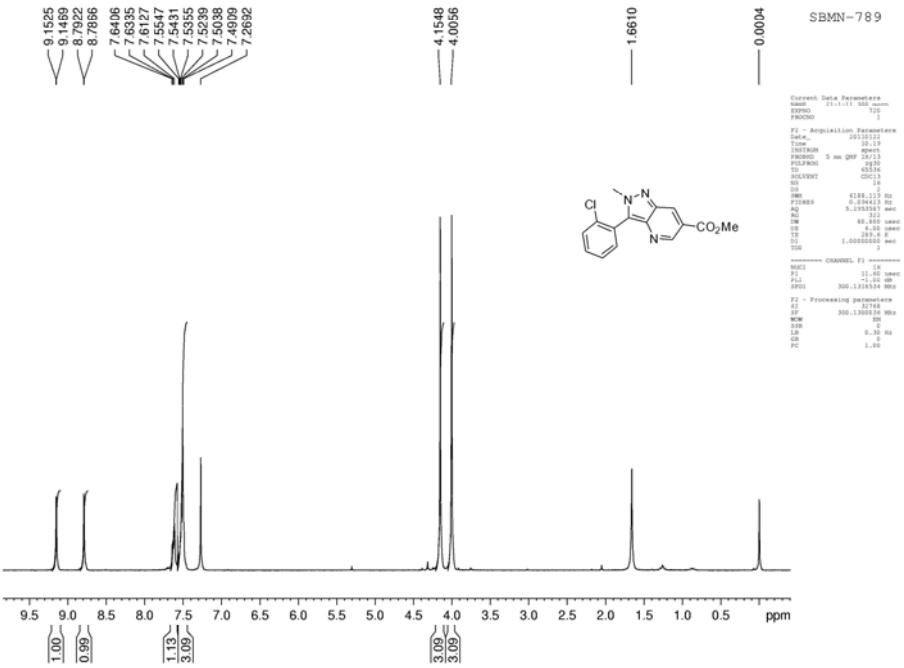


Fig-132: ^{1}H-spectrum of methyl 3-(2-chlorophenyl)-2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5j**).

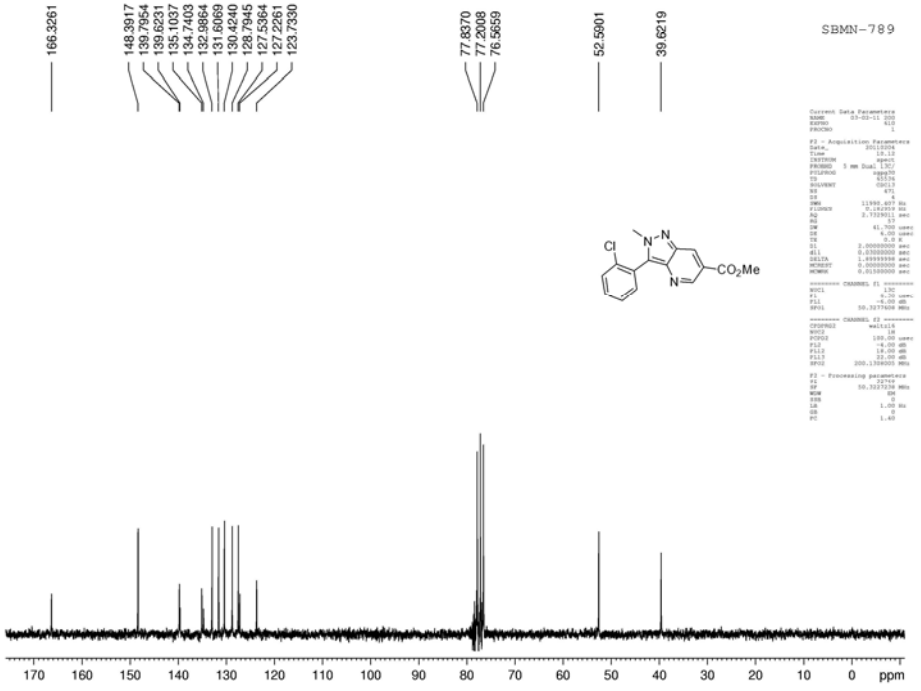


Fig-133: ^{13}C spectrum of methyl 3-(2-chlorophenyl)-2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5j**).

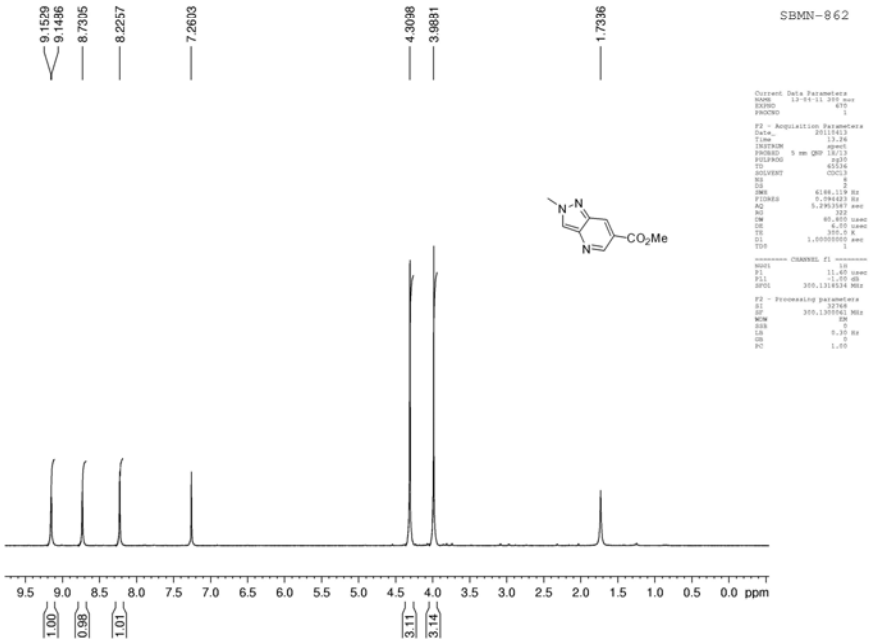


Fig-134: ^{1}H-spectrum of methyl 2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5k**).

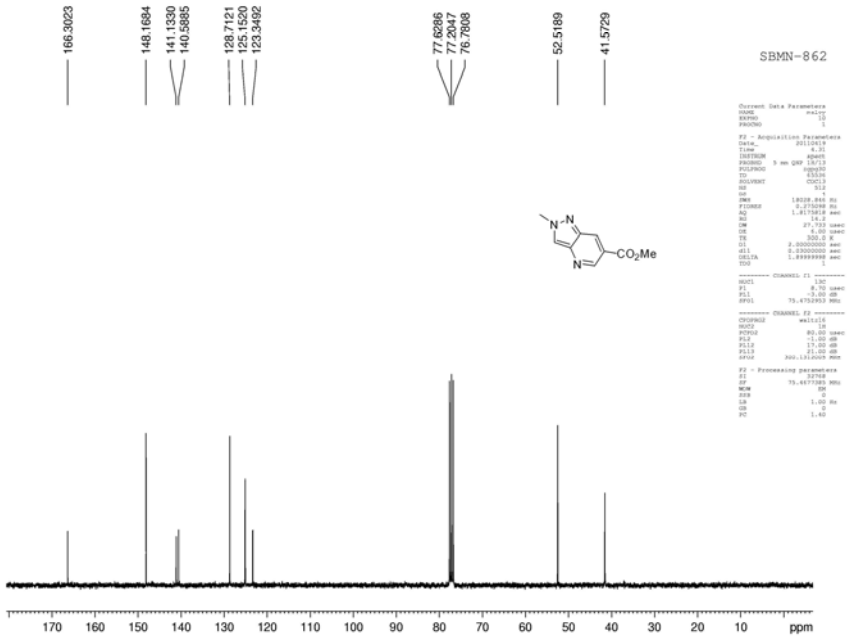


Fig-135: ^{13}C spectrum of methyl 2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**5k**).

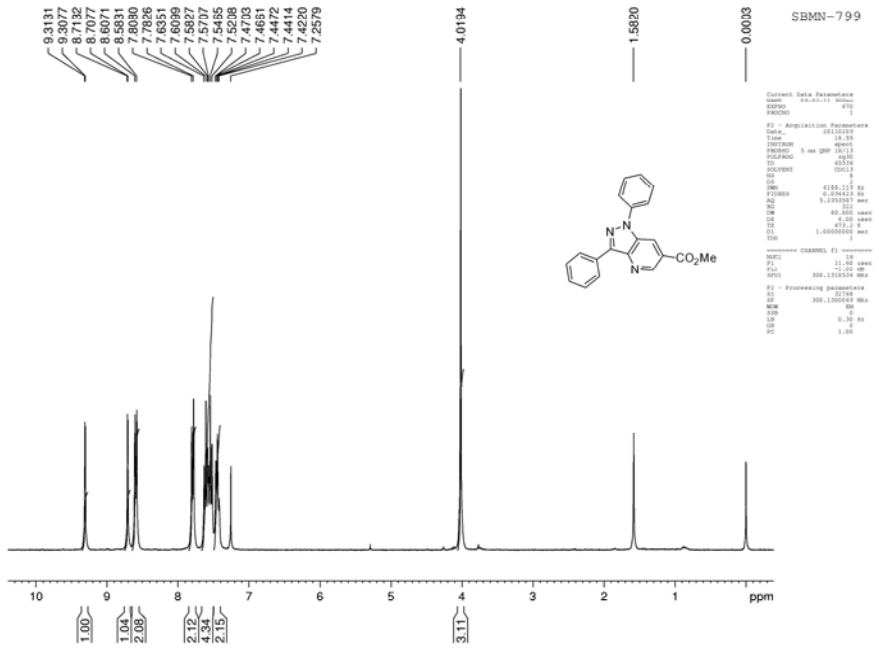


Fig-136: ^{1}H-spectrum of methyl 1,3-diphenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10a**).

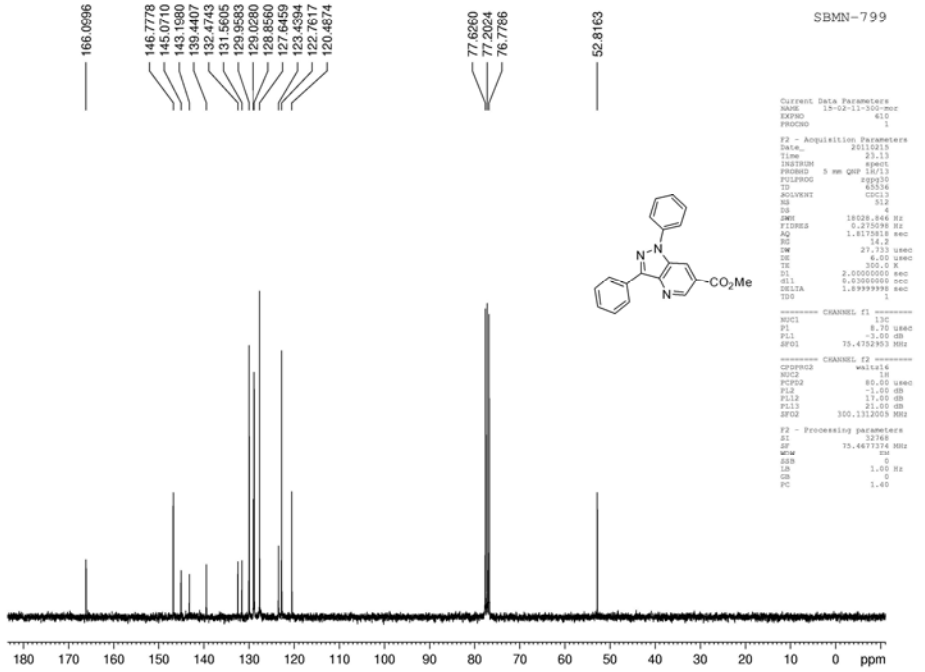


Fig-137: ^{13}C spectrum of methyl 1,3-diphenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10a**).

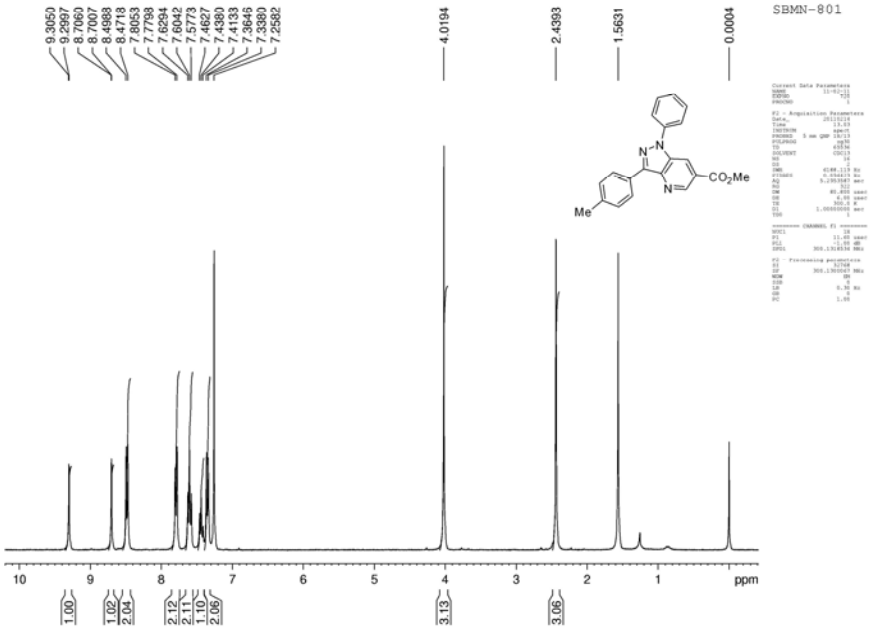


Fig-138: ^{1}H-spectrum of methyl 3-(4-methylphenyl)-1-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10b**).

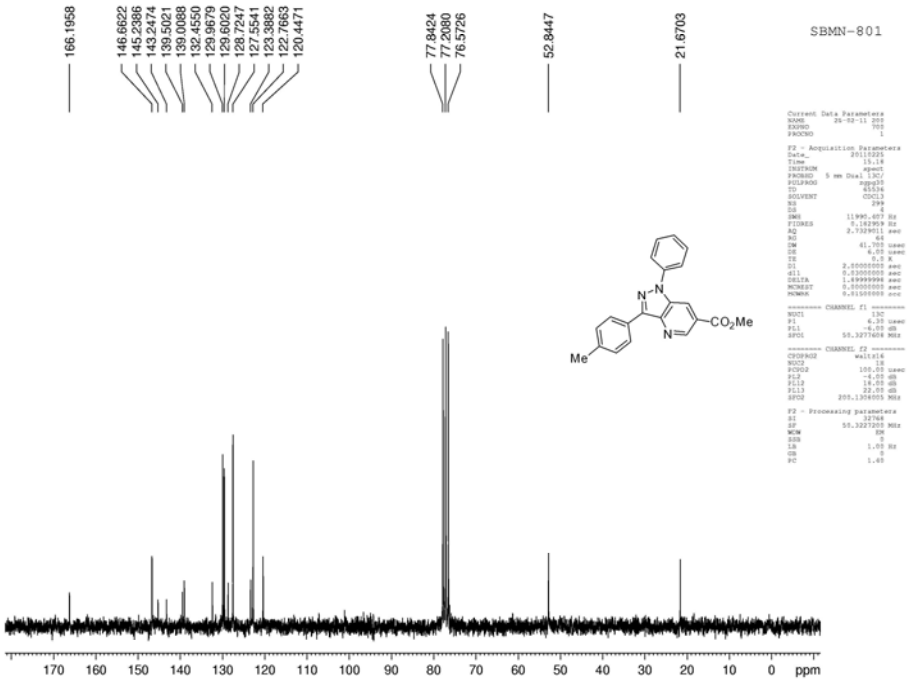


Fig-139: ^{13}C spectrum of methyl 3-(4-methylphenyl)-1-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10b**).

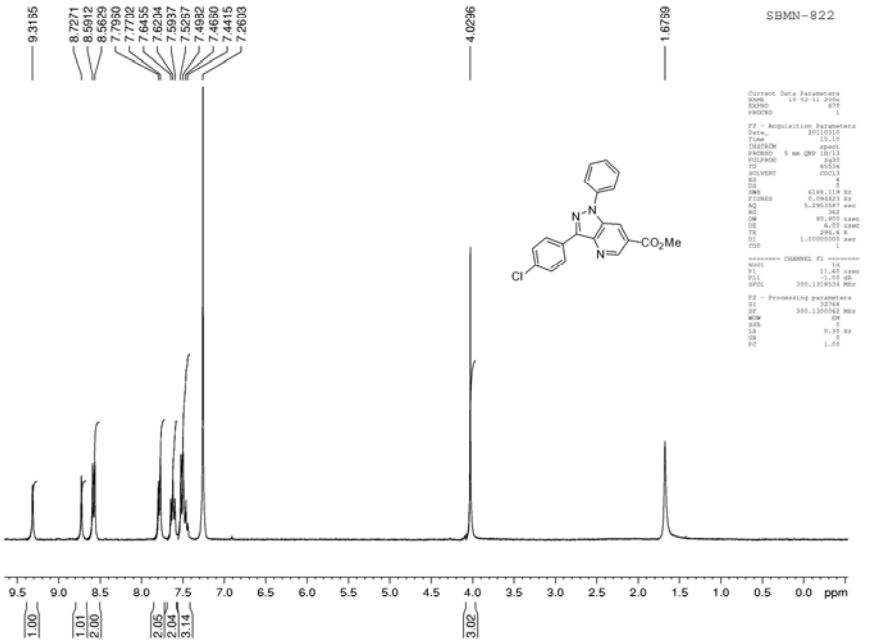


Fig-140: ^{1}H-spectrum of methyl 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10c**).

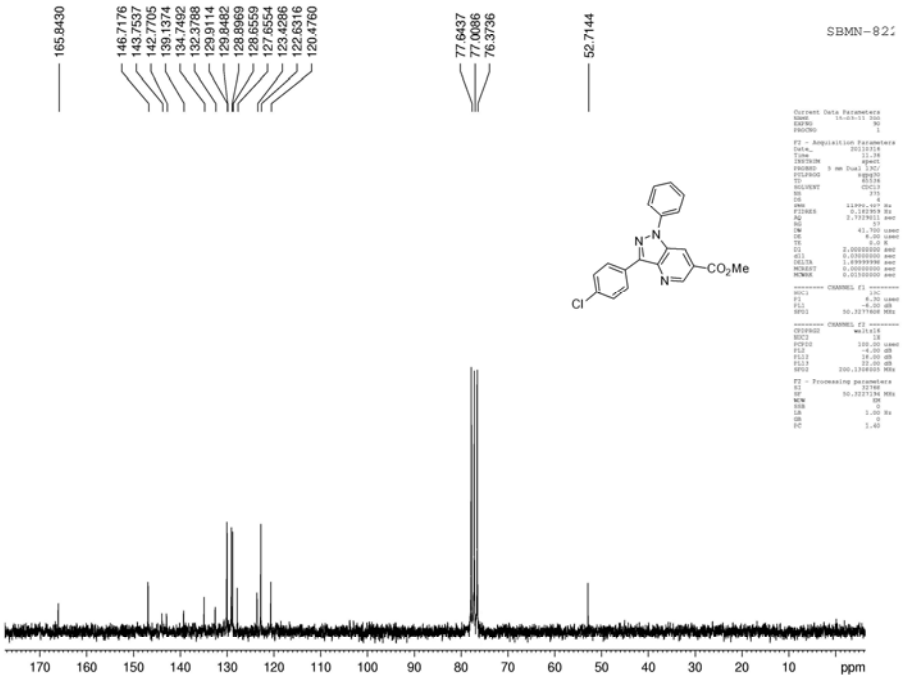


Fig-141: ^{13}C spectrum of methyl 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (**10c**).

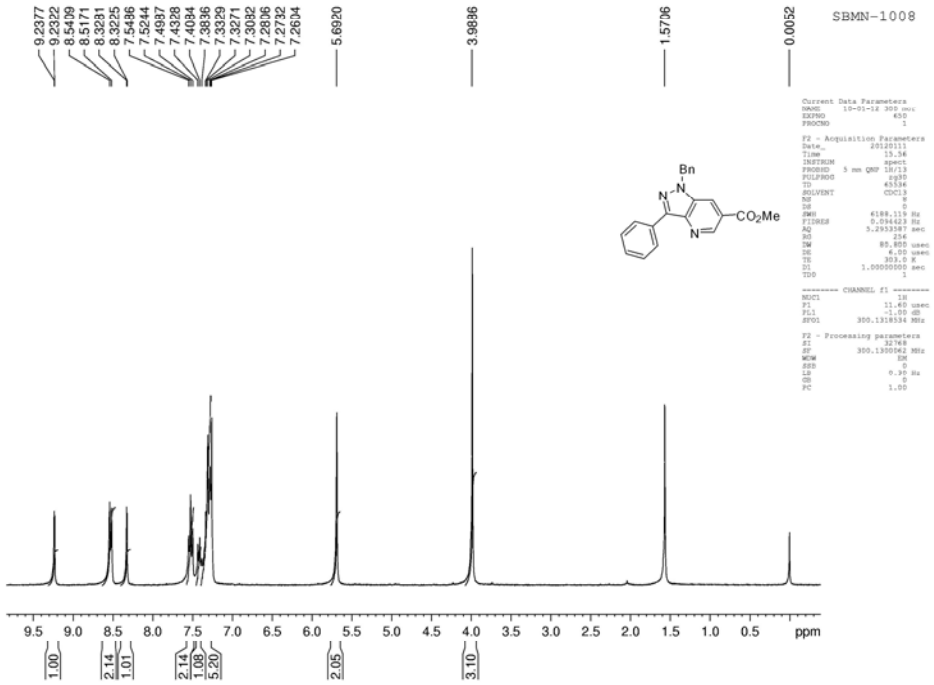


Fig-142: ^{1}H-spectrum of methyl 1-benzyl-3-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(10l).**

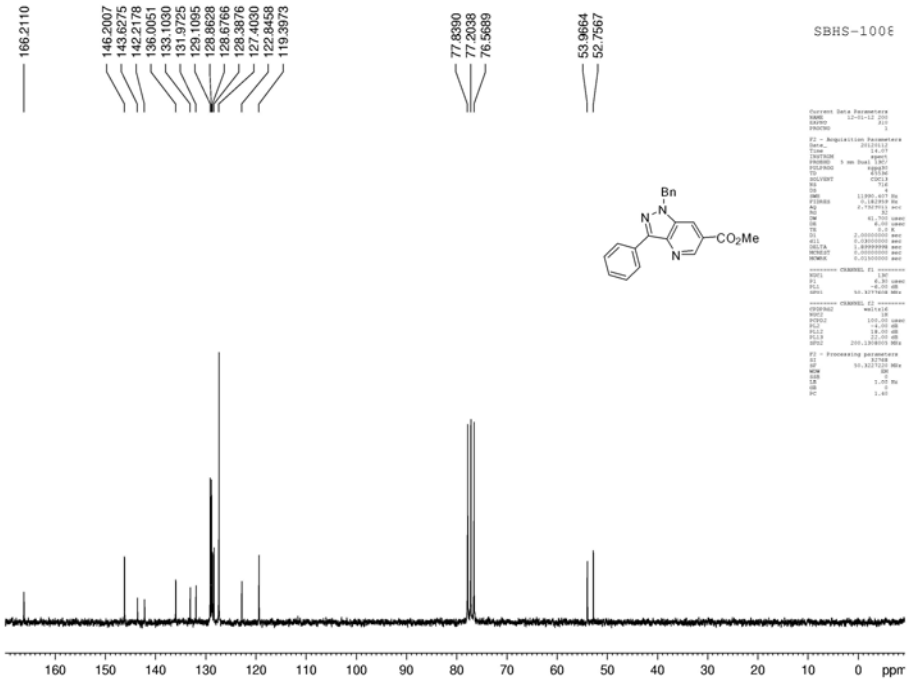


Fig-143: ^{13}C spectrum of methyl 1-benzyl-3-phenyl-1*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate **(10l).**

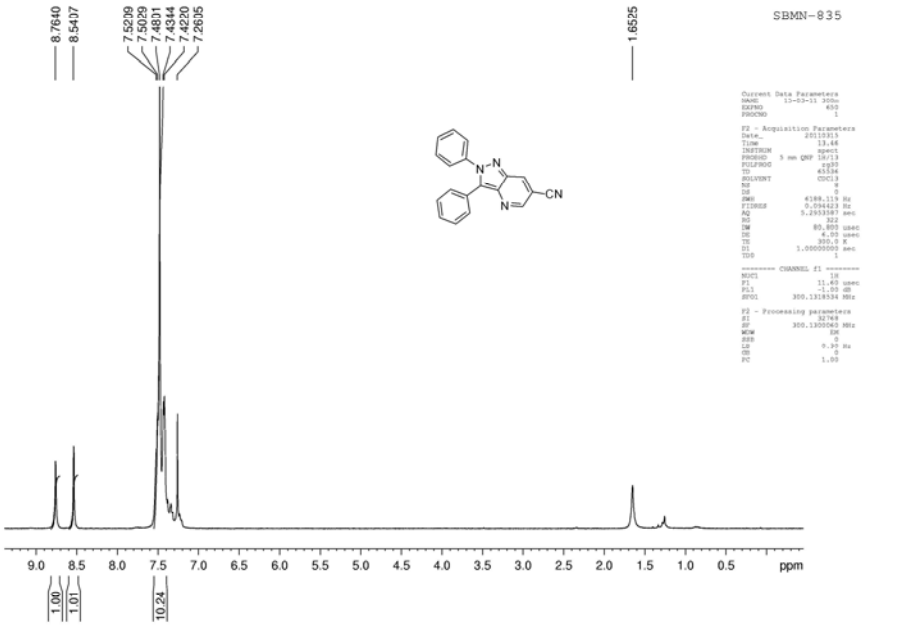


Fig-144: ^{1}H-spectrum of 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13a**).

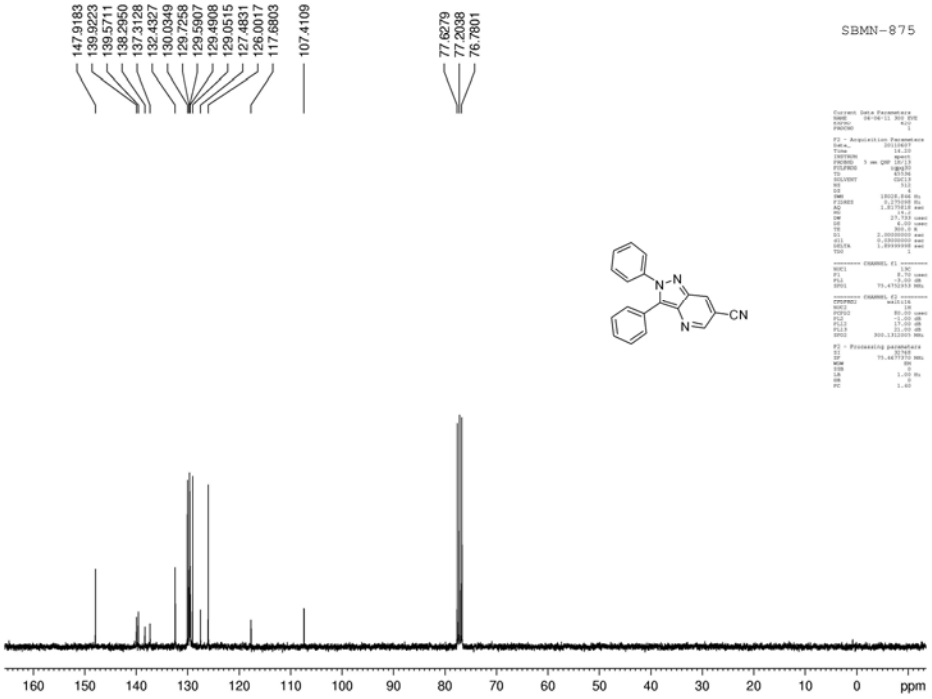


Fig-145: ^{13}C spectrum of 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13a**).

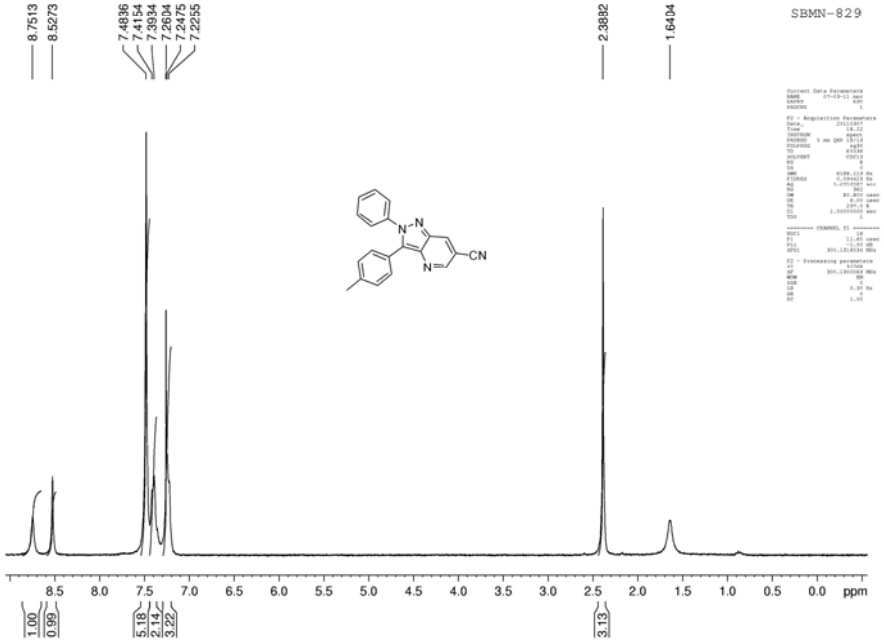


Fig-146: ^{1}H-spectrum of 3-(4-methylphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13b**).

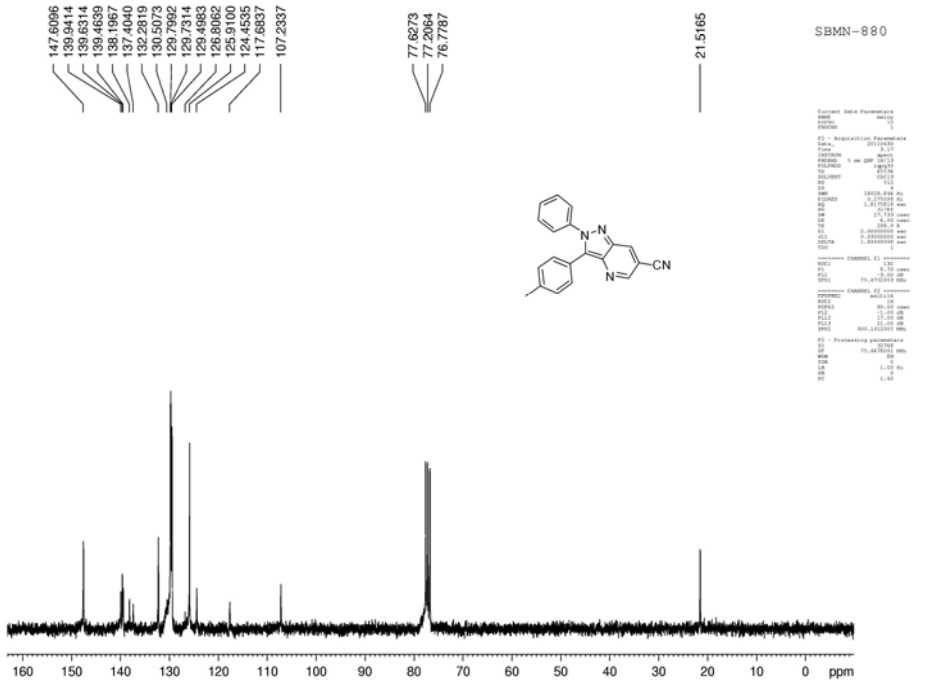


Fig-147: ^{13}C-spectrum of 3-(4-methylphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13b**).

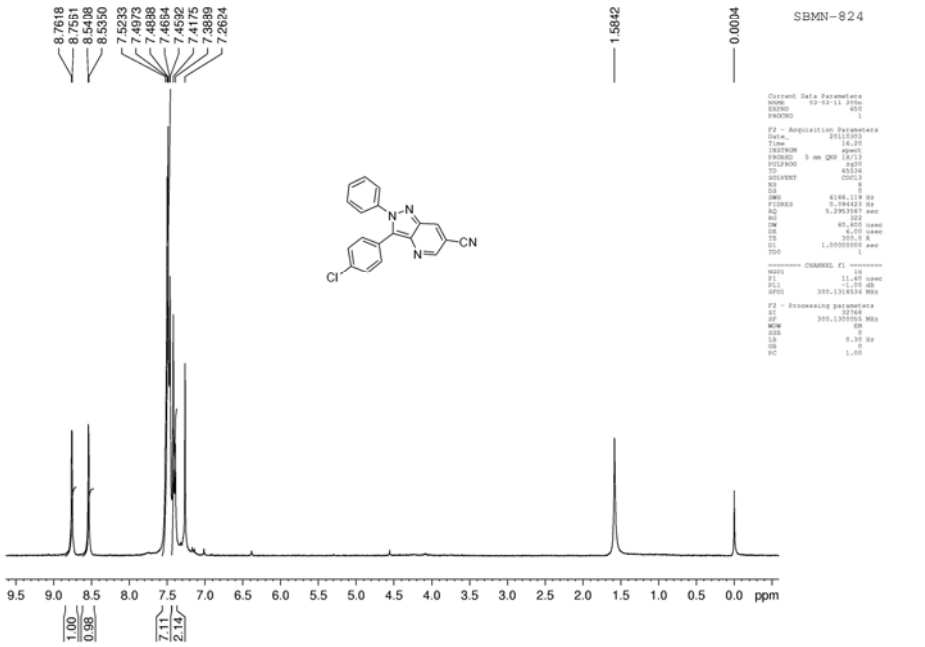


Fig-148: ^{1}H-spectrum of 3-(4-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13c**).

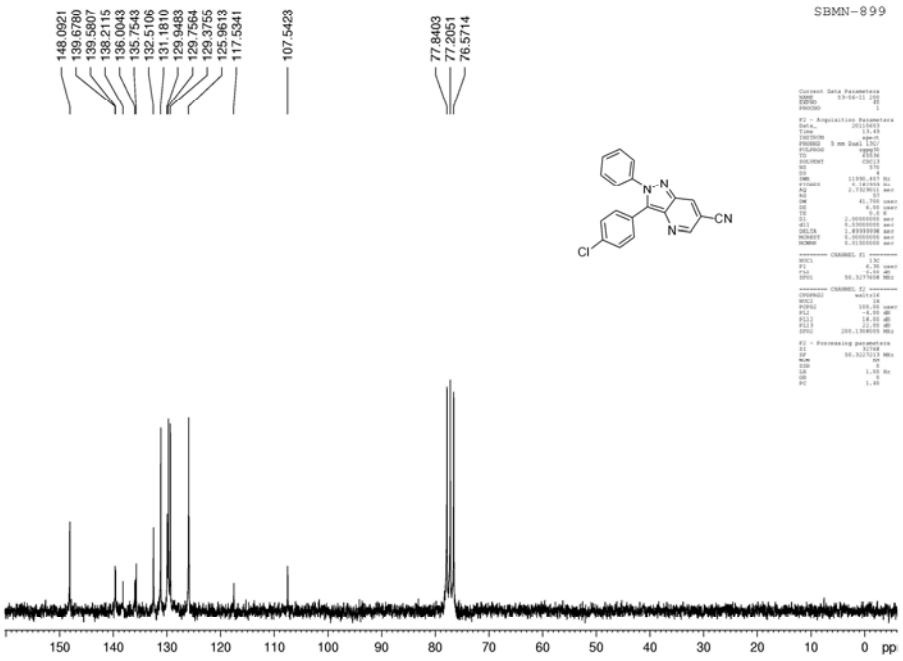


Fig-149: ^{13}C spectrum of 3-(4-chlorophenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13c**).

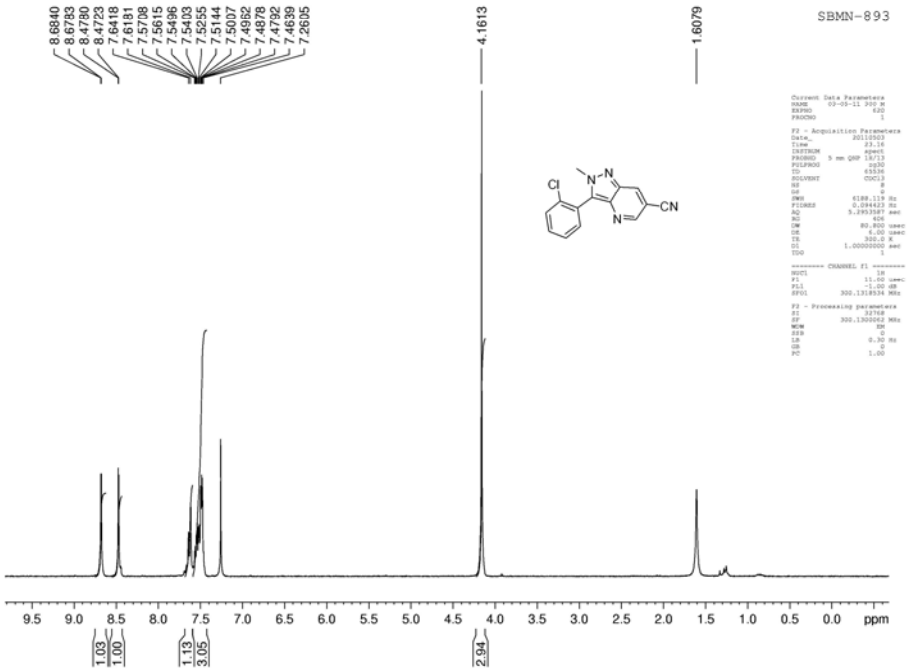


Fig-150: ^{1}H-spectrum of 3-(2-chlorophenyl)-2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13j**).

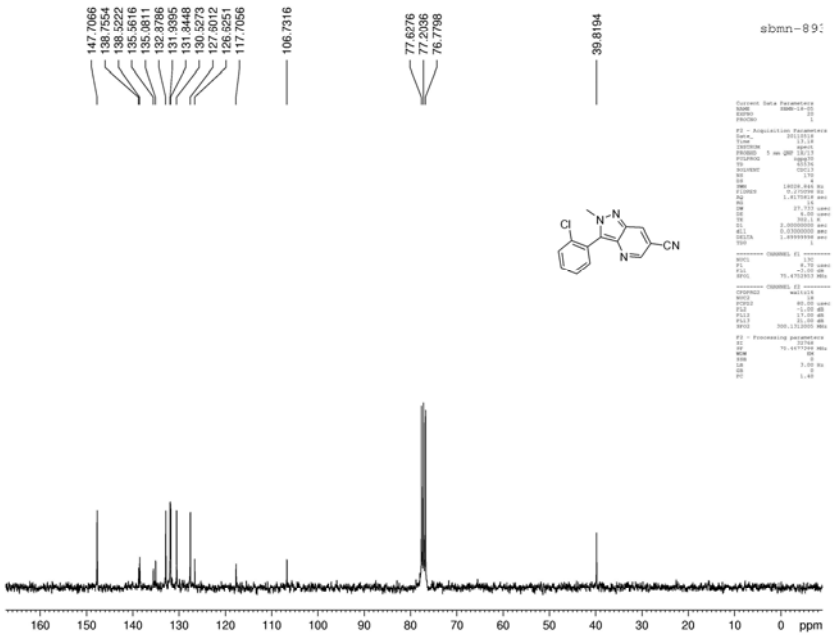


Fig-151: ^{13}C-spectrum of 3-(2-chlorophenyl)-2-methyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carbonitrile (**13j**).

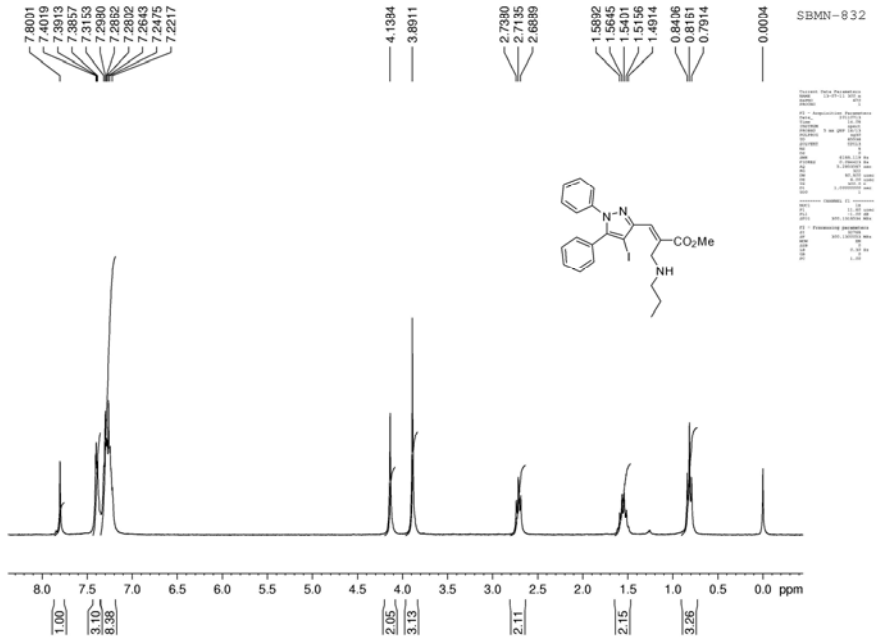


Fig-152: ^{1}H-spectrum of methyl (*E*)-2-[(propylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**16**).

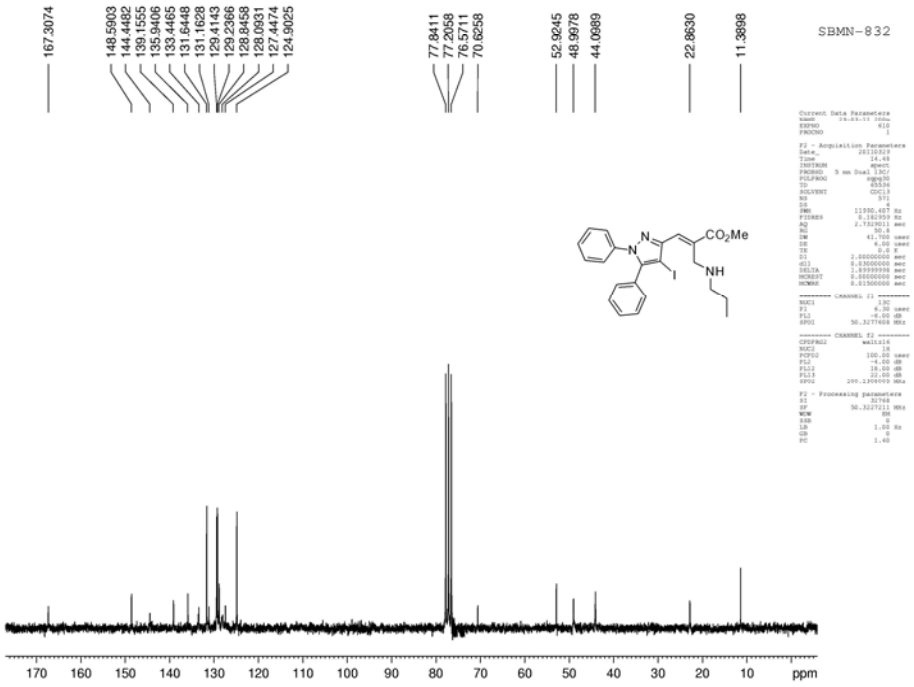


Fig-153: ^{13}C spectrum of methyl (*E*)-2-[(propylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**16**).

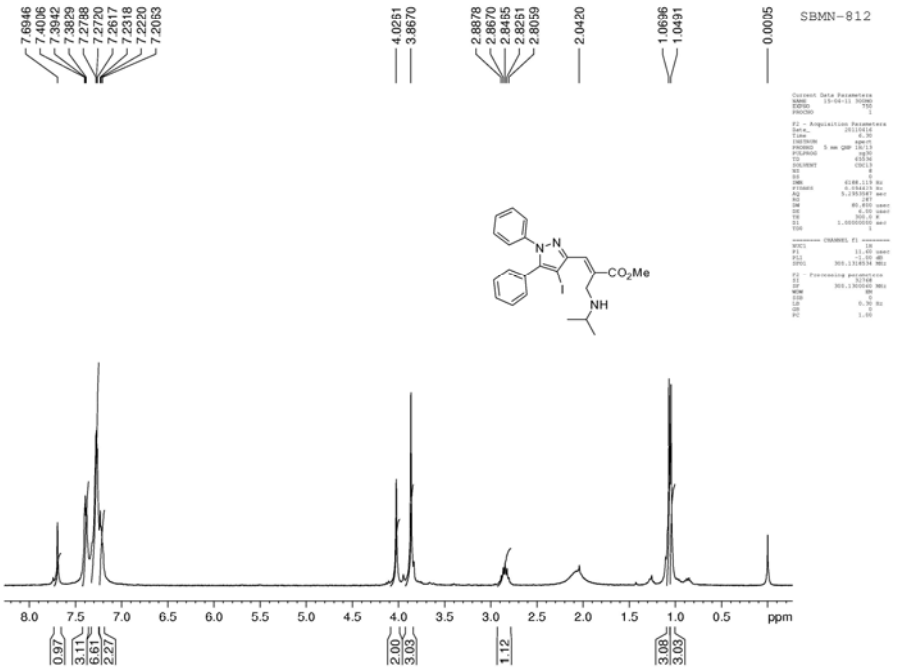


Fig-154: ^{1}H-spectrum of methyl (E)- 3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)-2-((isopropylamino)methyl) prop-2-enoate (**17**).

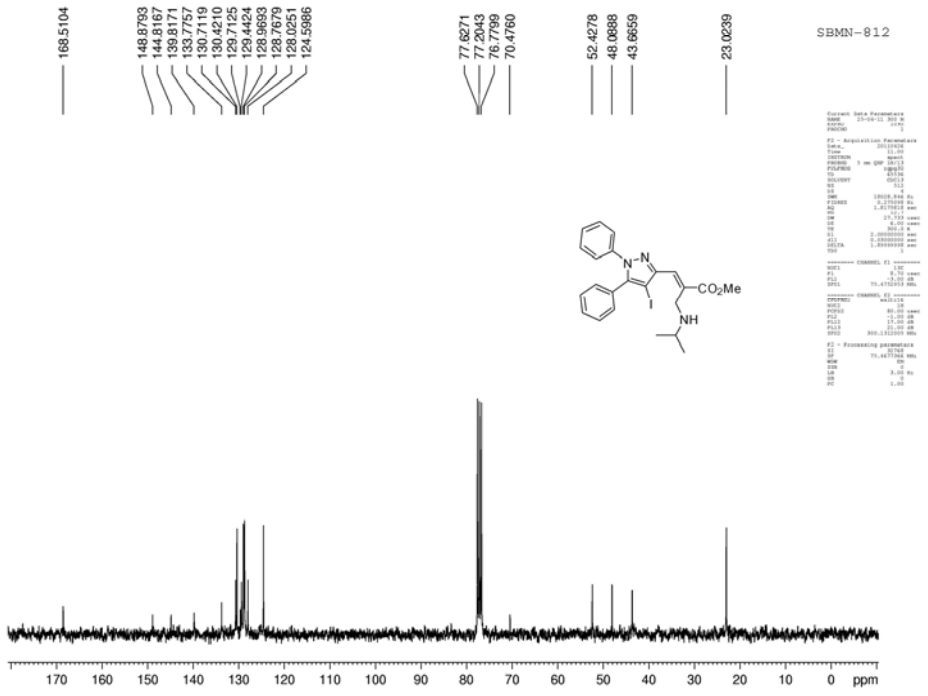


Fig-155: ^{13}C spectrum of methyl (E)- 3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)-2-((isopropylamino)methyl) prop-2-enoate (**17**).

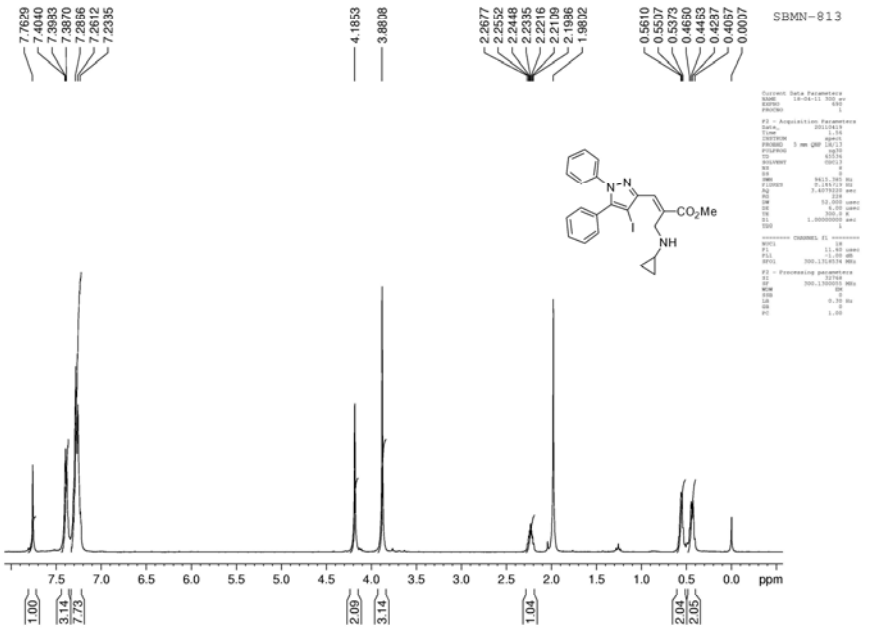


Fig-156: ^{1}H-spectrum of methyl (*E*)-2-((cyclopropylamino)methyl)-3-(4-iodo-1,5-diphenyl-1H-pyrazol-3-yl) prop-2-enoate (**18**).

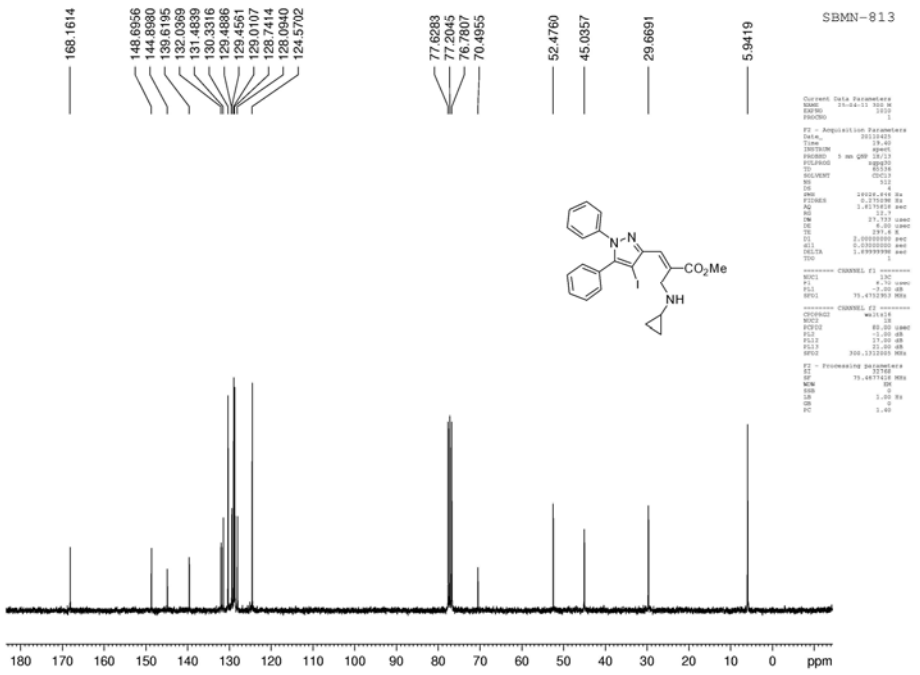


Fig-157: ^{13}C spectrum of methyl (*E*)-2-((cyclopropylamino)methyl)-3-(4-iodo-1,5-diphenyl-1H-pyrazol-3-yl) prop-2-enoate (**18**).

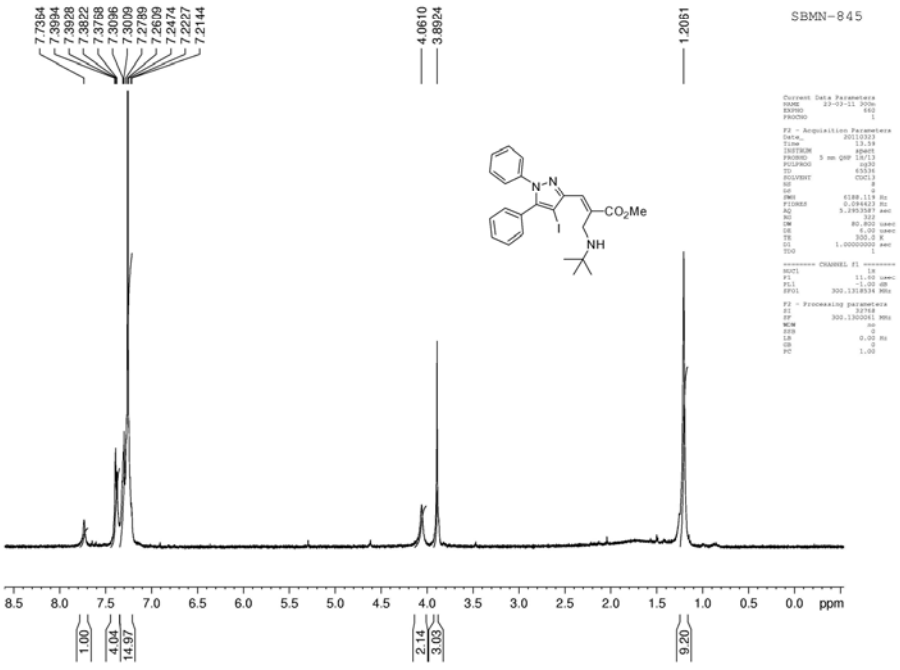


Fig-158: ^{1}H-spectrum of methyl (*E*)-2-[(tert-butylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**19**).

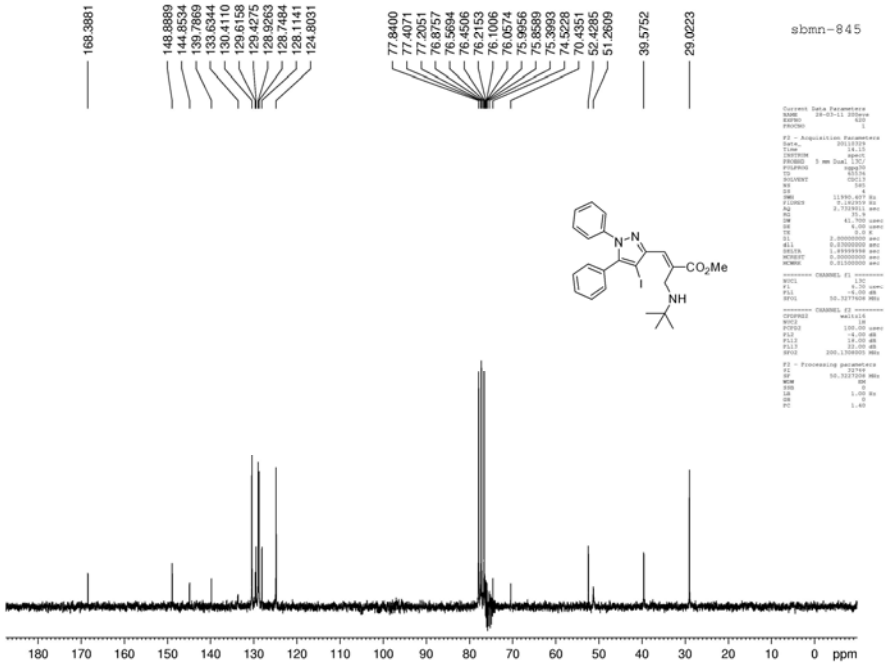


Fig-159: ^{13}C spectrum of methyl (*E*)-2-[(tert-butylamino)methyl]-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**19**).

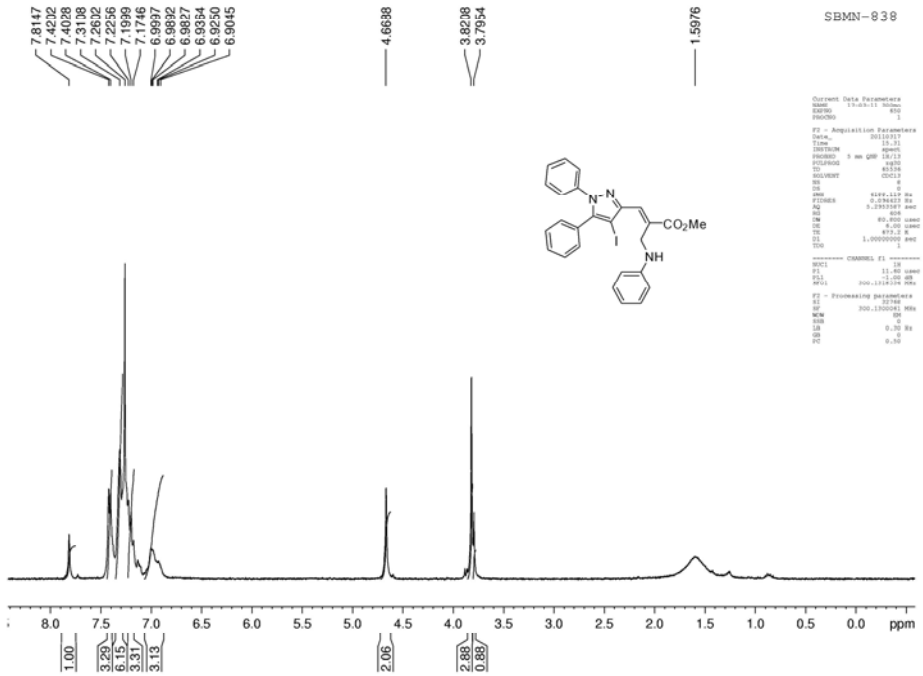


Fig-160: ^{1}H-spectrum of methyl (*E*)-2-(anilinomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**20**).

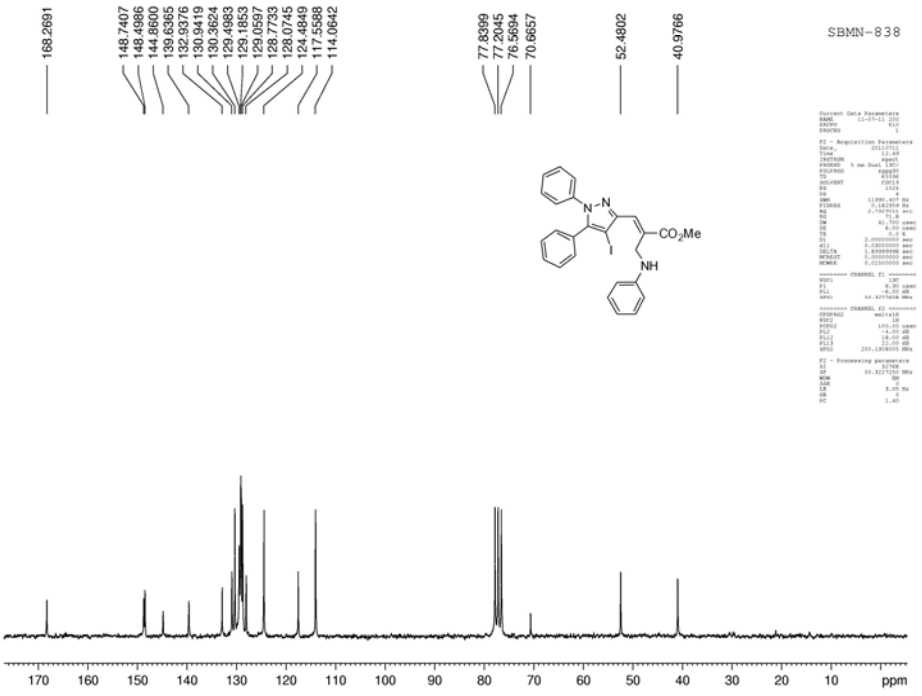


Fig-161: ^{13}C spectrum of methyl (*E*)-2-(anilinomethyl)-3-(4-iodo-1,5-diphenyl-1*H*-pyrazol-3-yl)prop-2-enoate (**20**).