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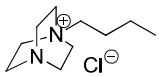
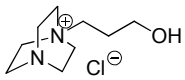
Characterization Data of Ionic Liquid Catalysts



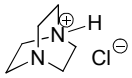
1-Butyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride ([Dabco-C_4]Cl)

^{1}H NMR (400MHz, D_2O): δ = 0.87-0.91 (m, 3H, CH_3), 1.27-1.34 (m, 2H, CH_2), 1.64-1.70 (m, 2H, CH_2), 3.14-3.21 (m, 8H, CH_2), 3.32-3.35 (m, 6H, CH_2); ^{13}C NMR (100MHz, D_2O): δ = 12.8, 19.2, 23.2, 44.2, 52.1, 64.5.



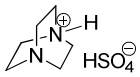
1-(3-Hydroxypropyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride ([Dabco-C_3OH]Cl)

^{1}H NMR (400MHz, D_2O): δ = 1.92-1.99 (m, 2H, CH_2), 3.14 (t, 6H, *J* = 7.6 Hz, CH_2), 3.29-3.33 (m, 2H, CH_2), 3.37 (t, 6H, *J* = 8.0 Hz, CH_2), 3.62 (t, 2H, *J* = 6.0 Hz, CH_2); ^{13}C NMR (100MHz, D_2O): δ = 24.2, 44.2, 52.2, 58.2, 62.0.



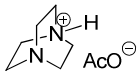
1,4-Diazabicyclo[2.2.2]octan-1-ium chloride ([Dabco-H]Cl)

^{1}H NMR (400MHz, D_2O): δ = 3.06 (s, 12H, CH_2); ^{13}C NMR (100MHz, D_2O): δ = 43.9.



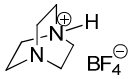
1,4-Diazabicyclo[2.2.2]octan-1-ium hydrogensulfate ([Dabco-H][HSO_4])

^{1}H NMR (400MHz, D_2O): δ = 3.32 (s, 12H, CH_2); ^{13}C NMR (100MHz, D_2O): δ = 43.6.



1,4-Diazabicyclo[2.2.2]octan-1-ium acetate ([Dabco-H][AcO])

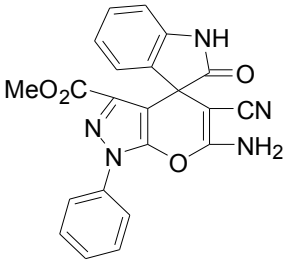
^{1}H NMR (400MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.91-2.93 (m, 12H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 22.4, 45.6, 176.1.



1,4-Diazabicyclo[2.2.2]octan-1-ium hydrotetrafluoroborate ([Dabco-H][BF_4])

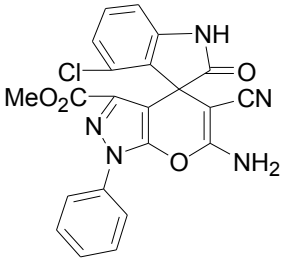
^{1}H NMR (400MHz, D_2O): δ = 3.10 (s, 12H); ^{13}C NMR (100MHz, D_2O): δ = 43.9; ^{19}F NMR (100MHz, D_2O): δ = -150.4.

Characterization Data of Compounds 5a-l



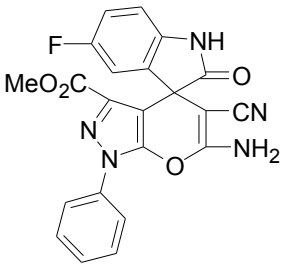
Methyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5a)[1]

White solid, mp 253-255 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.46 (s, 3H, Me), 6.89-6.96 (m, 2H, ArH), 7.11 (d, 1H, *J*= 7.2 Hz, ArH), 7.21 (t, 1H, *J*= 7.6 Hz, ArH), 7.48-7.55 (m, 3H, ArH and NH_2), 7.61 (t, 2H, *J* = 7.6 Hz, ArH), 7.87 (d, 2H, *J* = 7.6 Hz, ArH), 10.63 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 48.4, 51.8, 58.4, 99.4, 109.8, 112.1, 117.9, 122.4, 122.5, 123.4, 124.5, 126.3, 128.8, 129.2, 130.1, 134.1, 136.9, 138.1, 142.7, 160.3, 160.8, 177.9.



Methyl 6'-amino-4-chloro-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5b)

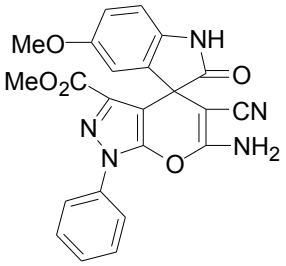
Purple solid, mp 257-260 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.44 (s, 3H, Me), 6.91 (d, 1H, *J* = 8.0 Hz, ArH), 7.26 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz, ArH),7.34 (d, 1H, *J* = 2.0 Hz, ArH) 7.51 (t, 1H, *J* = 7.6 Hz, ArH), 7.59-7.63 (m, 4H, ArH and NH_2), 7.87 (d, 2H, *J* = 8.0 Hz, ArH), 10.58 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 48.6, 51.9, 57.7, 98.7, 111.2, 117.9, 122.5, 124.9, 126.4, 128.9, 129.1, 130.1, 136.2, 136.9, 137.9, 141.6, 146.8, 160.4, 160.9, 177.0. Anal. Calcd. for $C_{22}H_{14}ClN_5O_4$: C, 59.00; H, 3.15; N, 15.64; Found: C, 59.08; H, 3.11; N, 15.71.



Methyl 6'-amino-5'-cyano-5-fluoro-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5c)[1]

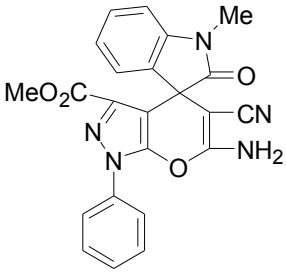
Purple solid, mp 194-196 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.50 (s, 3H, Me), 6.87-6.90 (m, 1H, ArH), 7.02-7.07 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz, ArH), 7.14-7.17 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.4 Hz, ArH) 7.51 (t, 1H, *J* = 7.4 Hz, ArH), 7.59-7.63 (m, 4H, ArH and NH_2), 7.87 (d, 2H, *J* = 7.6 Hz, ArH), 10.67 (s, 1H, NH); ^{13}C NMR

(100MHz, DMSO-d_6): δ = 48.8, 51.8, 57.8, 98.8, 110.5, 110.6, 112.3, 112.6, 115.4, 115.6, 117.9, 122.4, 128.9, 130.1, 135.8, 135.9, 136.9, 137.9, 138.8, 146.7, 157.6, 160.4, 160.8, 177.9.



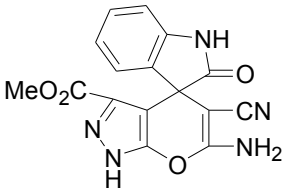
Methyl 6'-amino-5'-cyano-5-methoxy-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5d)[1]

Grey solid, mp 237-239 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.48 (s, 3H, Me), 3.65 (s, 3H, Me), 6.76-6.82 (m, 3H, ArH), 7.48-7.54 (m, 3H, ArH and NH_2), 7.61 (t, 2H, J = 8.0 Hz, ArH), 7.88 (d, 2H, J = 8.0 Hz, ArH), 10.45 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 48.9, 51.7, 55.9, 56.1, 58.5, 99.4, 110.2, 110.7, 111.4, 112.9, 113.9, 122.3, 128.8, 130.1, 135.4, 135.9, 137.0, 138.1, 155.7, 160.2, 160.8, 177.8.



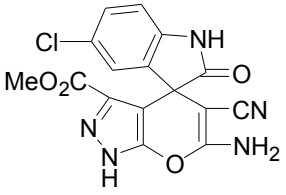
Methyl 6'-amino-5'-cyano-1-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5e)

Yellow solid, mp 222-225 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.24 (s, 3H, Me), 3.44 (s, 3H, Me), 7.01 (t, 1H, J = 7.4 Hz, ArH), 7.11 (d, 1H, J = 7.6 Hz, ArH), 7.18 (d, 1H, J= 6.8 Hz, ArH), 7.32 (td, 1H, J_1 = 0.8 Hz, J_1 = 8.0 Hz, ArH), 7.50 (t, 1H, J = 7.4 Hz, ArH), 7.59-7.63 (m, 4H, ArH and NH_2), 7.88 (d, 2H, J = 7.6 Hz, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 26.9, 47.9, 52.1, 57.9, 99.2, 108.8, 117.8, 122.4, 123.2, 124.2, 128.8, 128.9, 129.4, 130.1, 133.2, 136.9, 137.9, 144.1, 146.6, 160.4, 160.8, 176.3. Anal. Calcd. for $C_{23}H_{17}N_5O_4$: C, 64.63; H, 4.01; N, 16.39; Found: C, 64.59; H, 4.04; N, 16.45.



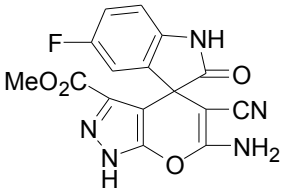
Methyl 6'-amino-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5f)[1]

Red solid, mp 258-260 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.51 (s, 3H, Me), 6.87-6.96 (m, 4H, ArH and NH_2), 7.19 (t, 1H, J = 7.4 Hz, ArH), 7.30 (s, 2H, NH_2), 10.78 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 47.9, 52.1, 57.1, 101.2, 109.7, 112.1, 118.5, 122.6, 124.2, 129.0, 134.4, 142.7, 158.2, 161.6, 177.9.



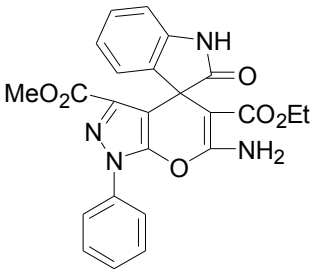
Methyl 6'-amino-5-chloro-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5g)[1]

Brown solid, mp 228-230 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.49 (s, 3H, Me), 6.89 (d, 1H, J = 8.4 Hz, ArH), 7.12 (d, 1H, J = 1.6 Hz, ArH), 7.23-7.26 (dd, 1H, J = 8.0 Hz, J = 1.6 Hz, ArH), 7.38 (s, 2H, NH_2), 10.73 (s, 1H, NH), 13.95 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 47.9, 52.1, 57.1, 101.2, 109.7, 112.1, 118.5, 122.6, 124.2, 129.0, 134.3, 142.6, 158.2, 161.5, 177.9.



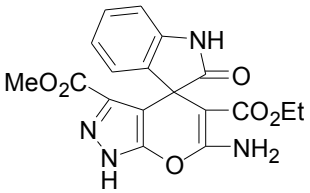
Methyl 6'-amino-5'-cyano-5-fluoro-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5h)[1]

Brown solid, mp >300 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.47 (s, 3H, Me), 6.85-6.88 (m, 1H, ArH), 6.95-6.98 (dd, 1H, J = 8.0 Hz, J = 2.0 Hz, ArH), 7.00-7.05 (td, 1H, J = 8.8 Hz, J = 2.0 Hz ArH), 7.38 (s, 2H, NH_2), 10.61 (s, 1H, NH), 13.95 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 48.4, 52.1, 100.6, 110.4, 110.5, 112.0, 112.3, 115.3, 118.4, 135.9, 135.9, 138.9, 157.6, 161.6, 178.0.



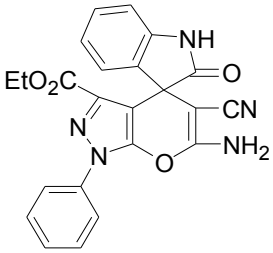
5'-Ethyl 3'-methyl 6'-amino-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3',5'-dicarboxylate (5i)

White solid, mp 222-224 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.80 (t, 3H, CH_2CH_3), 3.50 (s, 3H, CH_3), 3.71-3.79 (m, 2H, CH_2CH_3), 6.78-6.81 (m, 2H, ArH), 6.95 (d, 1H, ArH), 7.12 (t, 1H, J = 7.0 Hz, ArH), 7.49 (t, 1H, J = 7.4 Hz, ArH), 7.60 (t, 2H, J = 7.8 Hz, ArH), 7.88 (d, 2H, J = 7.6 Hz, ArH), 8.24 (s, 2H, NH_2), 10.42 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.5, 48.2, 51.7, 59.6, 76.3, 101.1, 108.8, 121.5, 122.2, 123.6, 128.1, 128.6, 130.1, 136.4, 137.0, 138.7, 144.2, 145.4, 160.9, 161.1, 168.3, 179.5. Anal. Calcd. for $C_{24}H_{20}N_4O_6$: C, 62.60; H, 4.38; N, 12.17; Found: C, 62.54; H, 4.33; N, 12.23.



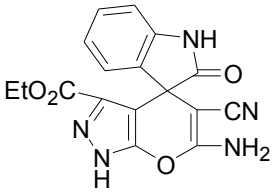
5'-Ethyl 3'-methyl 6'-amino-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3',5'-dicarboxylate (5j)[2]

Brown solid, mp 238-240 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.78 (t, 3H, J = 7.0 Hz, CH_2CH_3), 3.51 (s, 3H, CH_3), 3.69-3.76 (m, 2H, CH_2CH_3), 6.75-6.79 (m, 3H, ArH), 7.09 (t, 1H, J = 7.0 Hz, ArH), 8.11 (s, 2H, NH_2), 10.37 (s, 1H, NH), 13.80 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.5, 47.9, 51.9, 59.3, 75.7, 102.9, 108.7, 121.5, 123.1, 127.9, 136.8, 144.2, 158.5, 162.2, 168.5, 170.6.



Ethyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5k)[1]

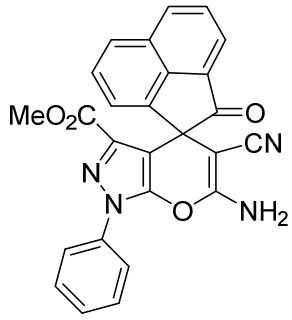
Pink solid, mp 248-250 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.96 (t, 3H, *J*= 6.8 Hz ,CH_2CH_3), 3.88-4.00 (m, 2H, CH_2CH_3), 6.88-6.95 (m, 2H, ArH), 7.12 (d, 1H, *J*= 6.8 Hz, ArH), 7.22 (t, 1H, *J*= 7.2 Hz, ArH), 7.49-7.54 (m, 3H, ArH and NH_2), 7.61 (t, 2H, *J* = 7.2 Hz, ArH), 7.87 (d, 2H, *J* = 7.6 Hz, ArH), 10.64 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 14.2, 48.4, 58.5, 60.8, 99.0, 109.9, 117.9, 122.5, 124.50, 128.8, 129.2, 130.1, 134.2, 136.9, 138.4, 142.7, 146.6, 160.2, 160.4, 177.9.



Ethyl 6'-amino-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5l)[2]

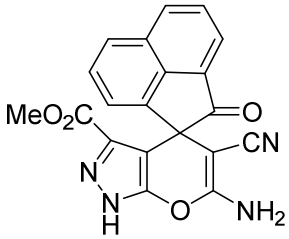
Red solid, mp 277-280 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.93 (t, 3H, *J* = 7.0 Hz, CH_2CH_3), 3.87-3.99 (m, 2H, CH_2CH_3), 6.87-6.96 (m, 4H, ArH and NH_2), 7.20 (t, 1H, *J* = 7.2 Hz, ArH), 7.28 (s, 2H, NH_2), 10.58 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.9, 47.9, 57.3, 61.3, 100.6, 109.8, 118.5, 122.5, 124.2, 128.9, 129.4, 134.6, 142.6, 156.5, 158.0, 161.4, 177.9.

Characterization Data of Compounds 7a-b



Methyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H,2H-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (7a)

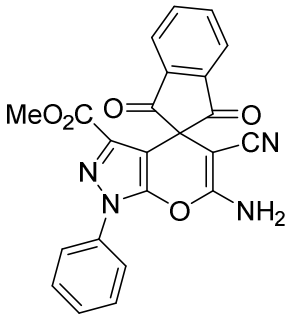
Dark purple solid, mp 235-237 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.74 (s, 3H, Me), 7.54 (d, 2H, *J*= 6.0 Hz, ArH), 7.66-7.71 (m, 5H, ArH and NH_2), 7.93 (d, 3H, *J* = 6.4 Hz, ArH), 8.03 (d, 1H, *J* = 7.6 Hz, ArH), 8.09 (d, 1H, *J* = 6.0 Hz, ArH), 8.38 (d, 1H, *J* = 7.2 Hz, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.7, 58.4, 99.4, 117.6, 120.8, 121.9, 122.1, 124.9, 128.4, 128.6, 129.1, 129.6, 129.8, 131.6, 132.0, 136.5, 137.5, 141.2, 142.2, 146.3, 159.7, 159.9, 202.8. Anal. Calcd. for $C_{26}H_{16}N_4O_4$: C, 69.64; H, 3.60; N, 12.49; Found: C, 69.69; H, 3.54; N, 12.53.



Methyl 6'-amino-5'-cyano-2-oxo-1'H,2H-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (7b)[3]

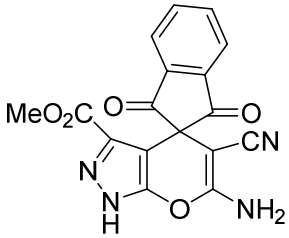
Yellow solid, mp >300 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.71 (s, 3H, CH_3), 7.42-8.38 (m, 8H, ArH and NH_2), 13.89 (br s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.9, 51.3, 57.2, 101.1, 118.2, 120.5, 122.0, 124.7, 128.6, 129.2, 129.8, 131.6, 132.0, 141.2, 142.5, 156.1, 157.4, 160.9, 203.1.

Characterization Data of Compounds 9a-b



Methyl 6'-amino-5'-cyano-1,3-dioxo-1'-phenyl-1,3-dihydro-1'H-spiro[indene-2,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (9a)

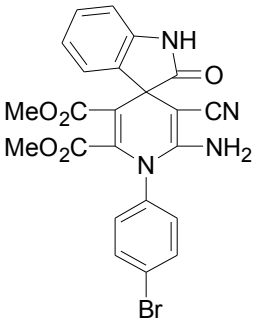
Yellow solid, mp 278-280 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.30 (s, 3H, Me), 7.53 (t, 1H, J = 7.6 Hz, ArH), 7.62 (t, 2H, J = 8.0 Hz, ArH), 7.87 (d, 2H, J = 8.0 Hz, ArH), 7.98 (s, 2H, NH_2), 8.11-8.16 (m, 4H, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 51.6, 53.4, 96.1, 116.9, 122.1, 123.7, 128.8, 129.7, 136.2, 136.9, 137.1, 140.8, 146.8, 160.5, 160.9, 198.1. Anal. Calcd. for $C_{23}H_{14}N_4O_5$: C, 64.79; H, 3.31; N, 13.14; Found: C, 64.81; H, 3.27; N, 13.19.



Methyl 6'-amino-5'-cyano-1,3-dioxo-1,3-dihydro-1'H-spiro[indene-2,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (9b)[4]

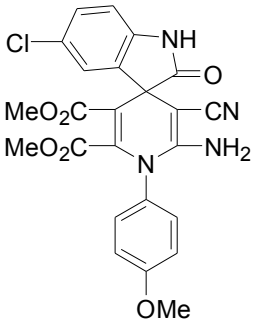
Brown solid, mp >300 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.03 (s, 1H, NH), 3.21 (s, 3H, Me), 7.70 (s, 2H, NH_2), 8.12 (s, 4H, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 51.7, 51.9, 52.4, 97.5, 97.5, 117.5, 123.6, 137.1, 140.8, 156.3, 157.5, 162.1, 196.6.

Characterization Data of Compounds 11a-k



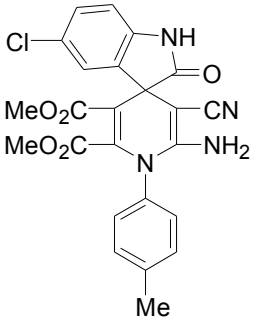
Dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11b)[5]

Pink solid, mp 290-292 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.32 (s, 3H, Me), 3.37 (s, 3H, Me), 5.97 (s, 2H, NH_2), 6.81 (d, 1H, J = 7.6 Hz, ArH), 6.99 (t, 1H, J = 7.2 Hz, ArH), 7.20 (t, 1H, J = 7.6 Hz, ArH), 7.27 (d, 1H, J = 7.2 Hz, ArH), 7.37 (d, 2H, J = 8.0 Hz, ArH), 7.72 (d, 2H, J = 8.4 Hz, ArH), 10.46 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 49.6, 51.7, 52.6, 60.0, 104.1, 109.3, 118.3, 121.9, 123.5, 123.8, 128.6, 132.39, 132.6, 134.9, 135.4, 141.3, 143.0, 151.3, 162.5, 163.9, 178.6.



Dimethyl 2'-amino-5-chloro-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11c)

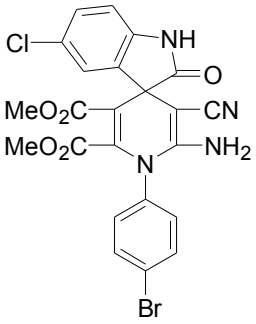
Yellow solid, mp 270-272 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.35 (s, 3H, Me), 3.36 (s, 3H, Me), 3.81 (s, 3H, OMe), 5.82 (s, 2H, NH_2), 6.83 (d, 1H, J = 8.4 Hz, ArH), 7.03 (s, 1H, ArH), 7.06 (s, 1H, ArH), 7.26 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz, ArH), 7.36-7.39 (m, 3H, ArH), 10.56 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.1, 51.8, 52.4, 55.5, 55.9, 110.7, 114.6, 118.4, 123.9, 125.9, 127.1, 128.5, 131.7, 137.9, 140.3, 144.5, 151.5, 160.1, 162.4, 163.9, 178.7. Anal. Calcd. for $C_{24}H_{19}ClN_4O_6$: C, 58.25; H, 3.87; N, 11.32; Found: C, 58.21; H, 3.90; N, 11.35.



Dimethyl 2'-amino-5-chloro-3'-cyano-2-oxo-1'-(p-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11d)[6]

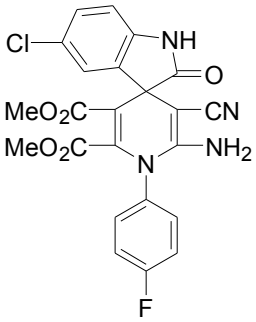
Yellow solid, mp 232-234 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.38 (s, 3H, Me), 3.34 (d, 6H, J = 4.0 Hz, Me), 5.78 (s, 2H, NH_2), 6.83 (d, 1H, J = 8.4 Hz, ArH), 7.25 (d, 1H, J = 8.4 Hz, ArH), 7.32 (s, 4H, ArH), 7.36 (s, 1H, ArH), 10.58 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 21.3, 50.6, 52.3, 52.9, 59.6, 102.3, 111.2, 114.5,

118.8, 124.4, 126.4, 129.0, 130.5, 132.9, 138.3, 140.4, 140.8, 144.7, 151.8, 162.8, 164.5, 179.1.



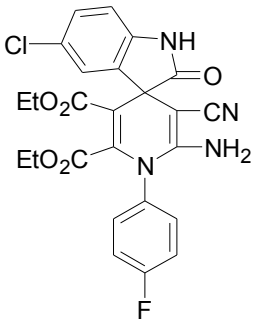
Dimethyl 2'-amino-1'-(4-bromophenyl)-5-chloro-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11e)

Yellow brown solid, mp 278-280 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.35 (s, 3H, Me), 3.37 (s, 3H, Me), 6.01 (s, 2H, NH_2), 6.83 (d, 1H, J = 8.4 Hz, ArH),7.25 (d, 1H, J = 8.4 Hz, ArH),7.42-7.43 (m, 3H, ArH), 7.71 (d, 2H, J = 8.4 Hz, ArH), 10.57 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.6, 52.3, 53.0, 59.6, 102.7, 111.2, 118.8, 124.2, 124.5, 126.4, 129.1, 133.1, 133.2, 134.9, 138.2, 140.8, 144.3, 151.6, 162.8, 164.4, 179.1. Anal. Calcd. for $C_{23}H_{16}BrClN_4O_5$: C, 50.80; H, 2.97; N, 10.30; Found: C, 50.86; H, 2.92; N, 10.37.



Dimethyl 2'-amino-5-chloro-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11f)

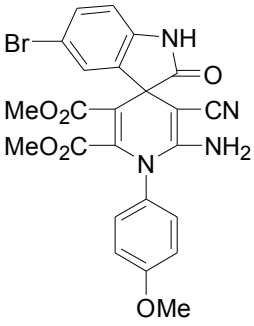
Grey solid, mp 290-292 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.35 (s, 6H, Me), 5.97 (s, 2H, NH_2), 6.83 (d, 1H, J = 8.4 Hz, ArH), 7.25 (d, 1H, J = 8.0 Hz, ArH), 7.35 (t, 2H, J = 8.4 Hz, ArH), 7.42 (s, 1H, ArH), 7.51-7.54 (m, 2H, ArH), 10.56 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.6, 52.3, 52.9, 59.5, 102.4, 111.2, 117.1, 118.8, 124.6, 126.4, 129.0, 131.69, 133.4, 133.5, 138.3, 140.8, 144.6, 151.8, 162.8, 164.4, 179.2. Anal. Calcd. for $C_{23}H_{16}ClFN_4O_5$: C, 57.21; H, 3.34; N, 11.60; Found: C, 57.16; H, 3.37; N, 11.65.



Diethyl 2'-amino-5-chloro-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11g)

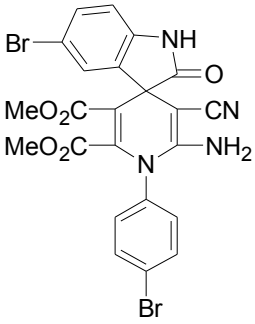
Pink solid, mp 170-172 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.83 (t, 3H, J = 7.2 Hz, Me), 0.89 (t, 3H, J = 7.2 Hz, Me), 3.73-3.85 (m, 4H, CH_2), 5.96 (s, 2H, NH_2), 6.82 (d, 1H, J = 8.4 Hz, ArH), 7.26 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz, ArH), 7.35 (t, 2H, J = 8.8 Hz, ArH), 7.43 (d, 1H, J = 2.0 Hz, ArH), 7.25-7.55 (m, 2H, ArH), 10.56 (s, 1H,

NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 48.6, 51.9, 57.7, 98.7, 111.2, 117.9, 122.5, 124.9, 126.4, 128.9, 129.1, 130.1, 136.2, 136.9, 137.9, 141.6, 146.8, 160.4, 160.9, 177.7. Anal. Calcd. for $C_{25}H_{20}ClFN_4O_5$: C, 58.77; H, 3.95; N, 10.97; Found: C, 58.83; H, 3.92; N, 11.04.



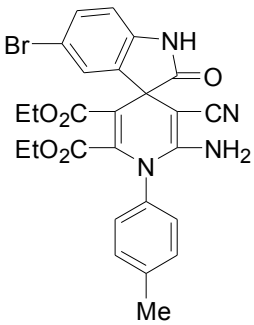
Dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11h)

Pale solid, mp 276-278 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.35 (s, 6H, Me), 3.81 (s, 3H, OMe), 5.84 (s, 2H, NH_2), 6.78 (d, 1H, J = 6.8 Hz, ArH), 7.04 (d, 2H, J = 6.0 Hz, ArH), 7.37 (s, 3H, ArH), 7.49 (s, 1H, ArH), 10.58 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.1, 51.8, 52.4, 55.5, 58.9, 101.4, 111.2, 113.5, 114.6, 118.4, 126.6, 127.1, 131.4, 131.7, 138.3, 140.7, 144.5, 151.5, 160.1, 162.4, 163.9, 178.6. Anal. Calcd. for $C_{24}H_{19}BrN_4O_6$: C, 53.45; H, 3.55; N, 10.39; Found: C, 53.39; H, 3.57; N, 10.44.



Dimethyl 2'-amino-5-bromo-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11i)

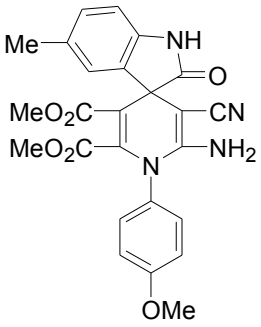
Yellow solid, mp 278-280 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.38 (s, 6H, Me), 6.03 (s, 2H, NH_2), 6.78-6.79 (m, 1H, ArH), 7.42-7.54 (m, 4H, ArH), 7.71-7.78 (m, 2H, ArH), 10.59 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 50.6, 52.4, 53.0, 59.5, 102.5, 111.7, 114.1, 116.2, 118.8, 124.2, 127.2, 131.9, 133.1, 134.9, 138.6, 141.2, 144.3, 151.6, 162.8, 164.4, 179.0. Anal. Calcd. for $C_{23}H_{16}Br_2N_4O_5$: C, 46.96; H, 2.74; N, 9.53; Found: C, 46.95; H, 2.69; N, 9.58.



Diethyl 2'-amino-5-bromo-3'-cyano-2-oxo-1'-(p-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11j)

Yellow solid, mp 280-282 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 0.85 (t, 6H, J = 7.2 Hz, CH_2CH_3), 2.36 (s, 3H,

Me), 3.77 (m, 4H, CH_2CH_3), 5.78 (s, 2H, NH_2), 6.78 (d, 1H, J = 6.4 Hz, ArH), 7.32-7.38 (m, 5H, ArH), 7.47 (s, 1H, ArH), 10.57 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 13.0, 13.1, 20.8, 50.1, 59.1, 60.5, 61.5, 101.6, 111.2, 113.5, 118.4, 126.6, 129.9, 130.3, 131.3, 132.3, 138.4, 139.9, 140.9, 144.2, 151.4, 161.8, 163.5, 178.6. Anal. Calcd. for $C_{26}H_{23}BrN_4O_5$: C, 56.63; H, 4.20; N, 10.16; Found: C, 56.67; H, 4.16; N, 10.21.



Dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-5-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11k)[6]

Brown solid, mp 260-262 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 2.29 (s, 3H, Me), 3.32 (s, 3H, CO_2Me), 3.36 (s, 3H, CO_2Me), 3.81 (s, 3H, OMe), 5.73 (s, 2H, NH_2), 6.70 (d, 1H, J = 8.0 Hz, ArH), 6.99 (d, 1H, J = 8.0 Hz, ArH), 7.03 (s, 1H, ArH), 7.06 (s, 2H, ArH), 7.32 (d, 2H, J = 8.4 Hz, ArH), 10.31 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 21.2, 44.5, 50.2, 52.1, 52.9, 55.9, 109.5, 111.9, 115.2, 119.1, 124.7, 126.2, 127.9, 129.3, 131.3, 132.0, 136.5, 139.3, 144.4, 151.9, 160.5, 163.1, 164.6, 179.4.

References

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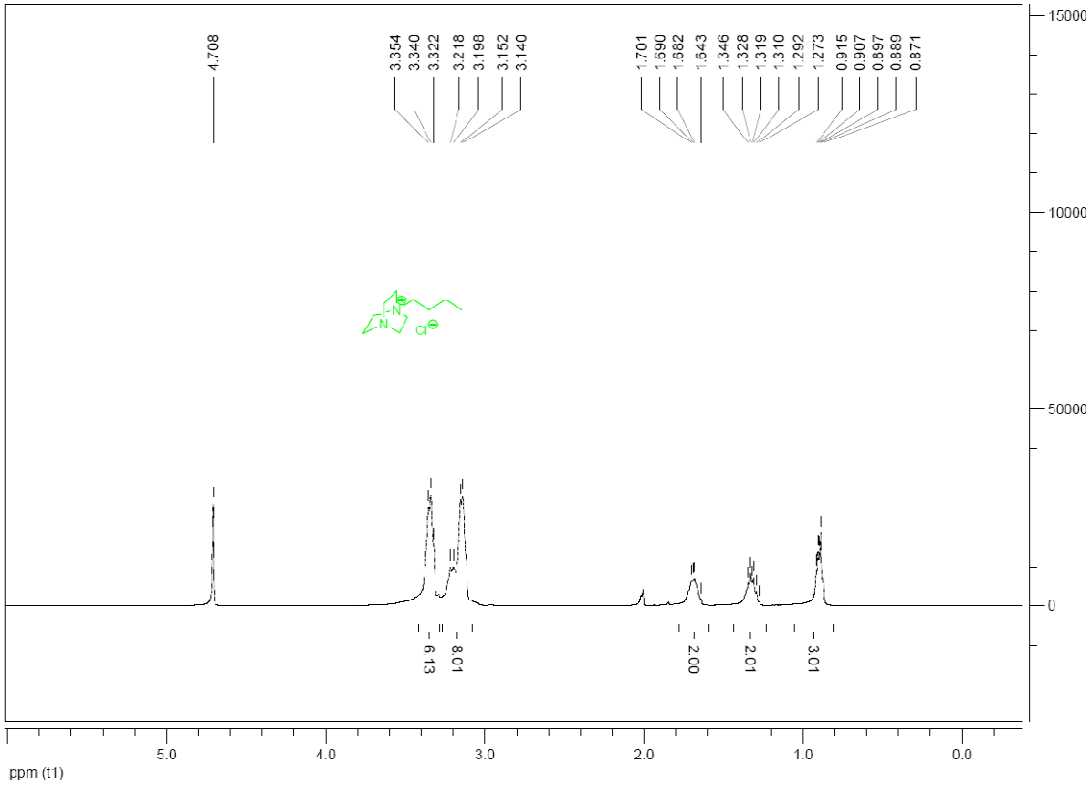
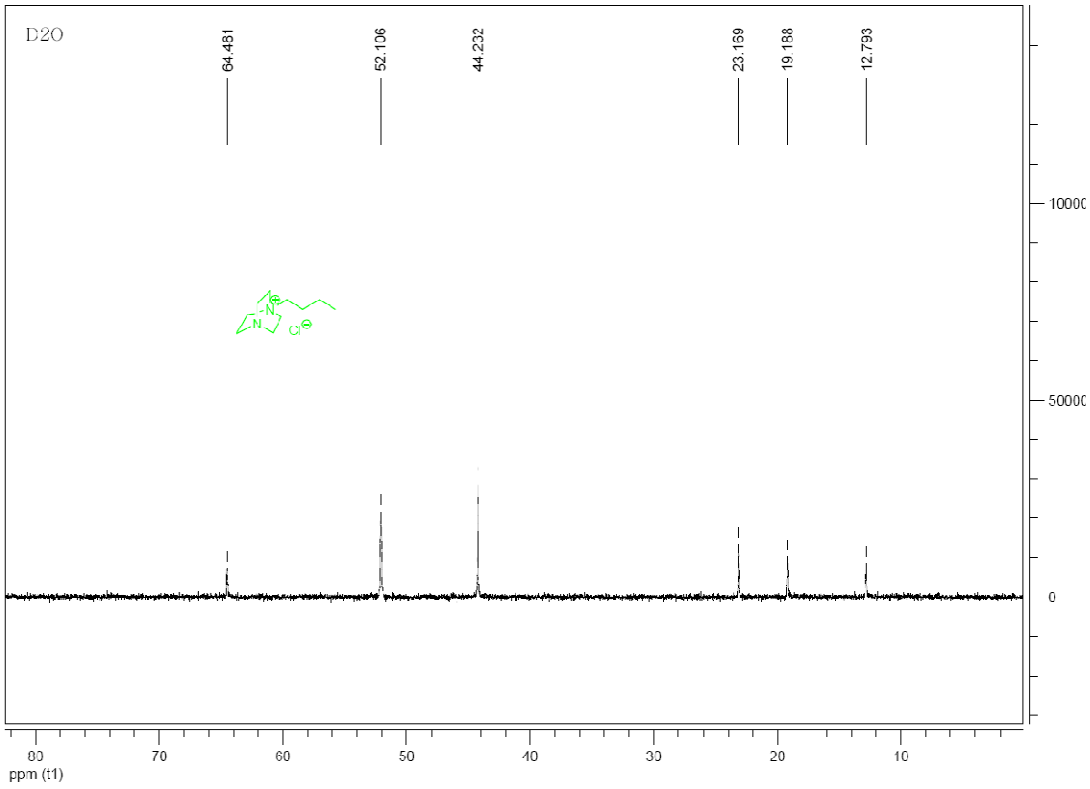
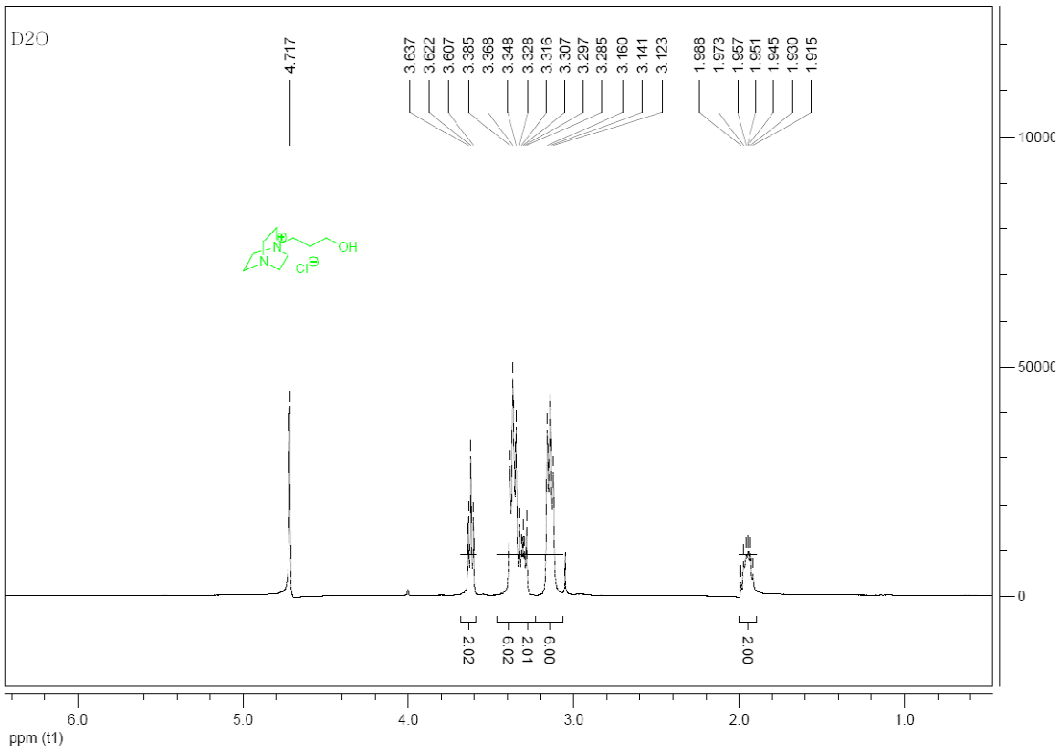
Spectroscopic Data for Ionic Liquid Catalysts



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3.160
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1.957
1.951
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OH
Cl
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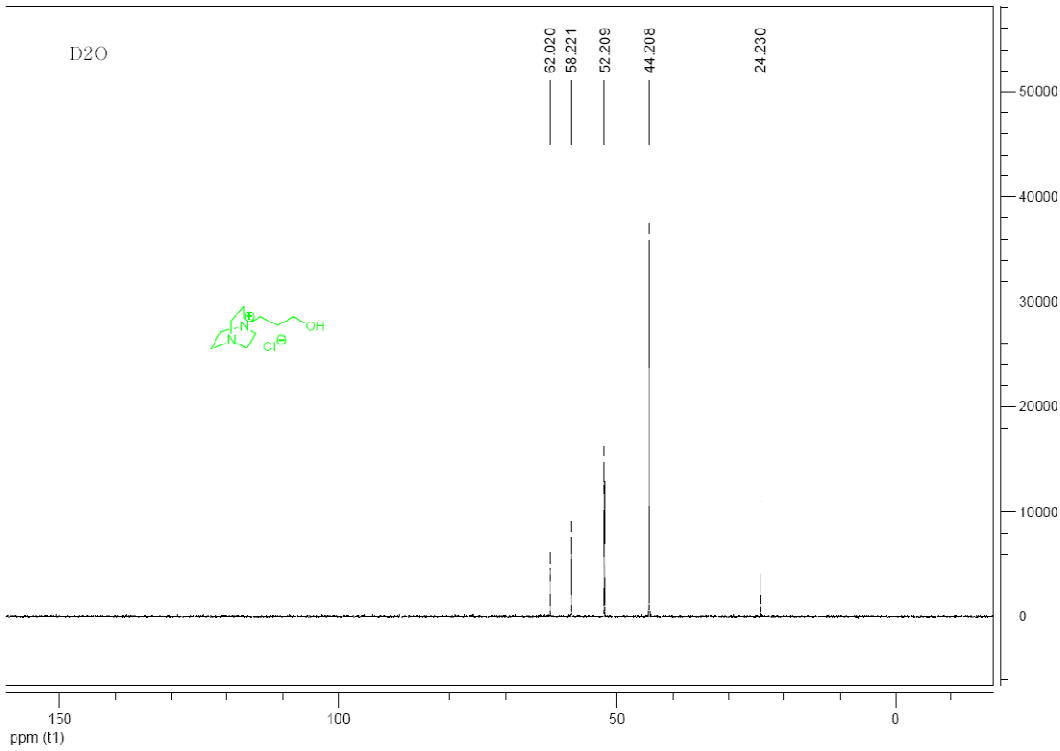
ppm (t1)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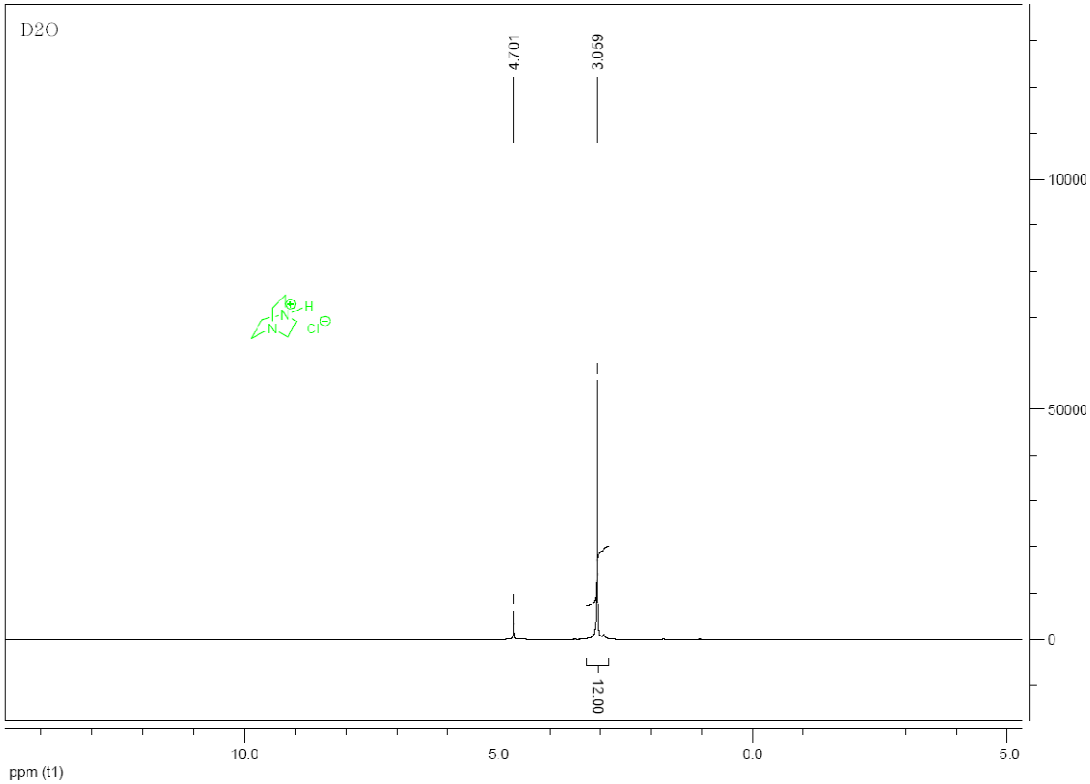
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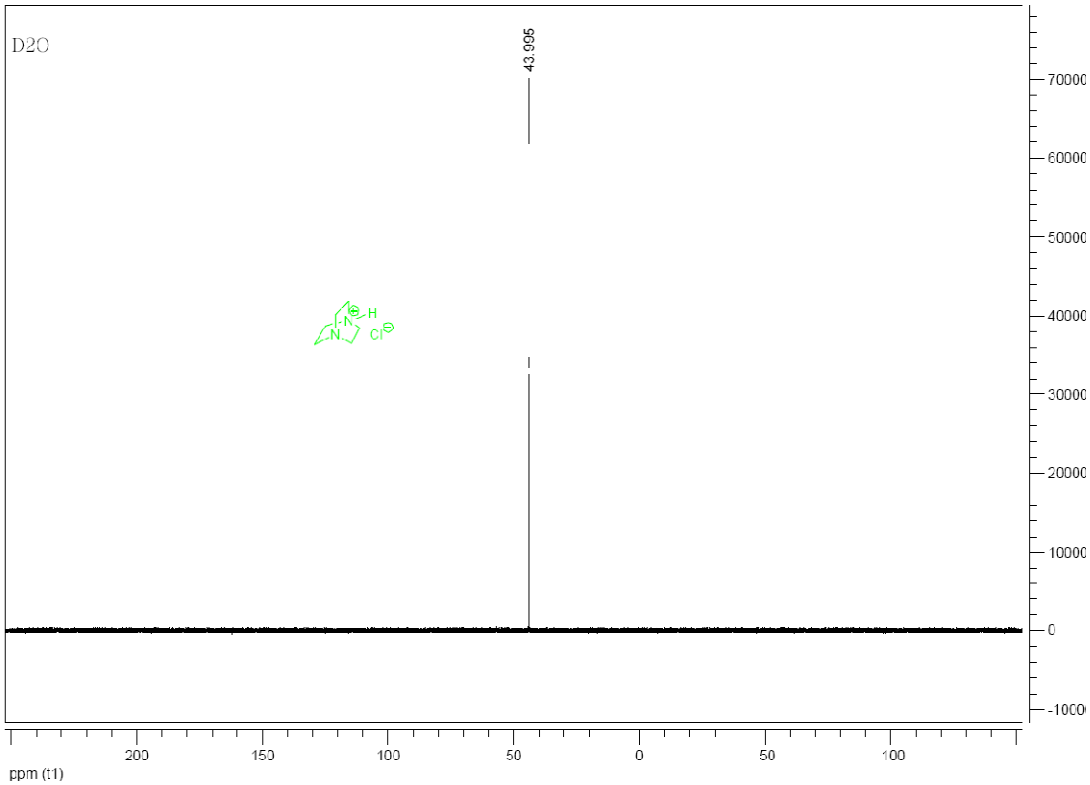
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50
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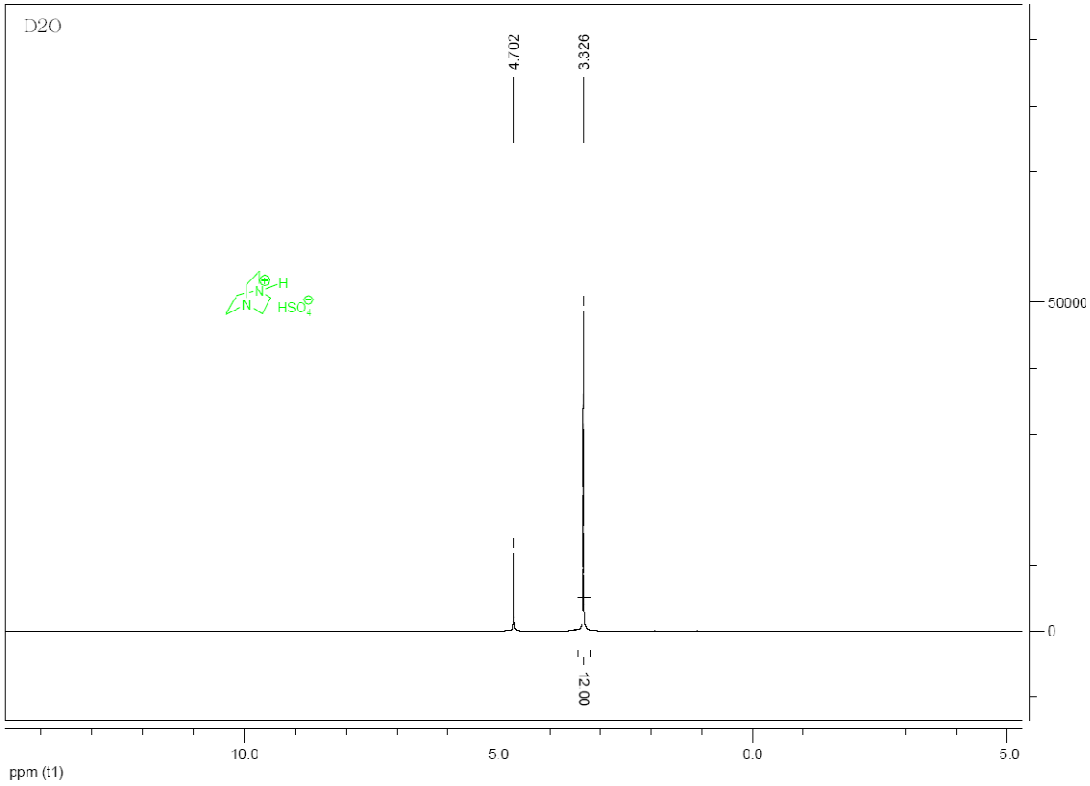
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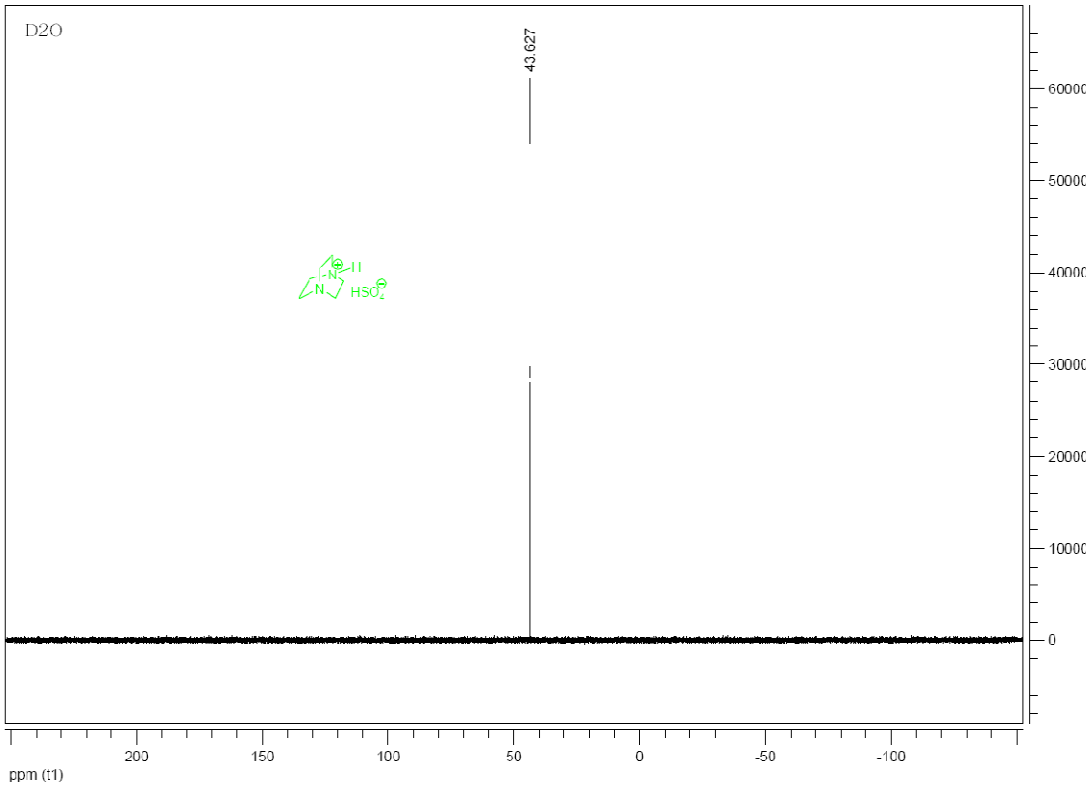
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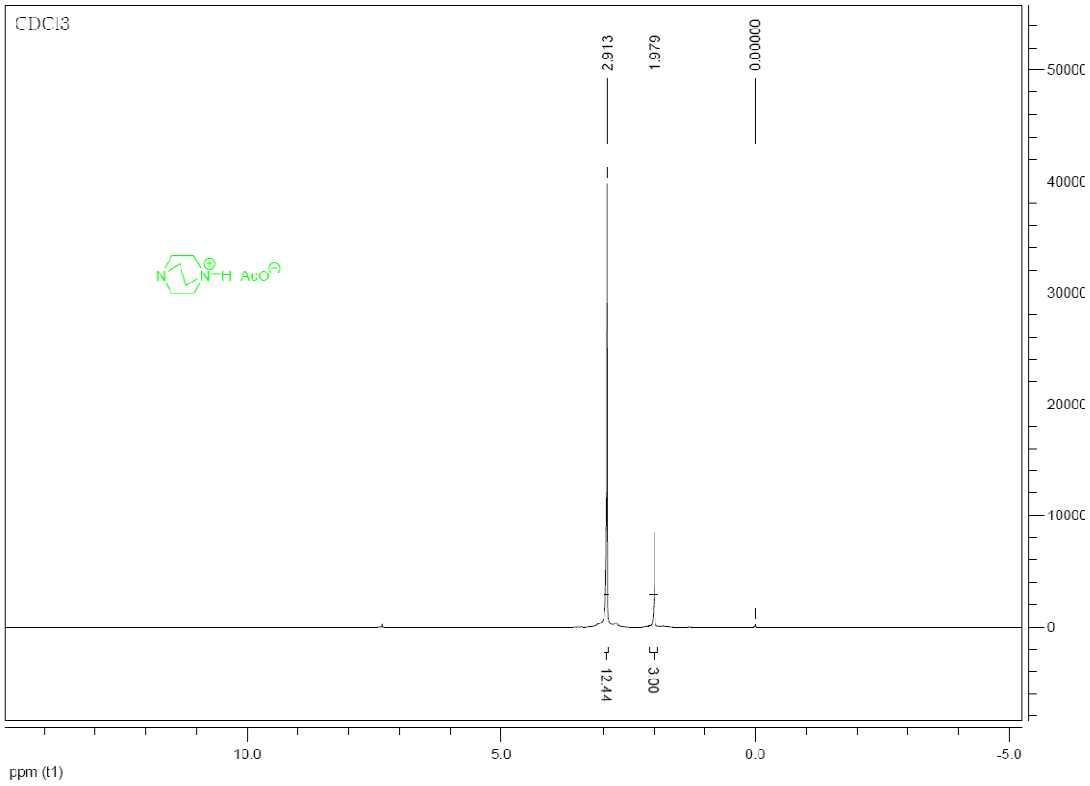
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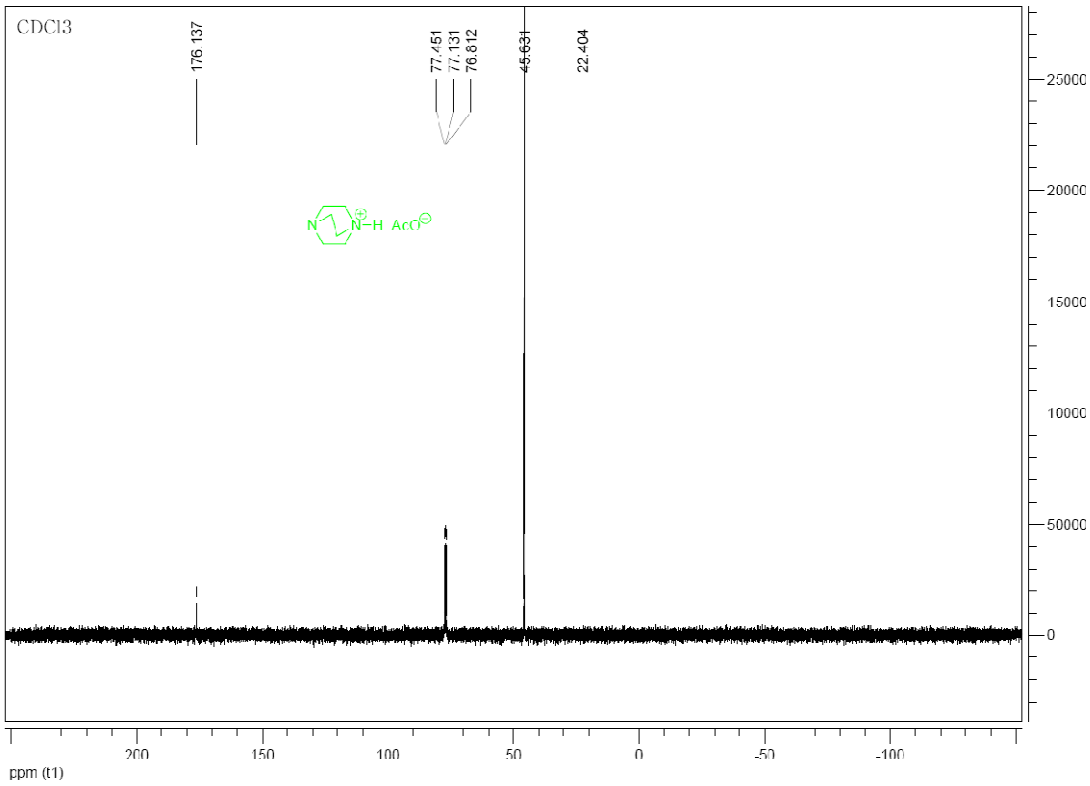
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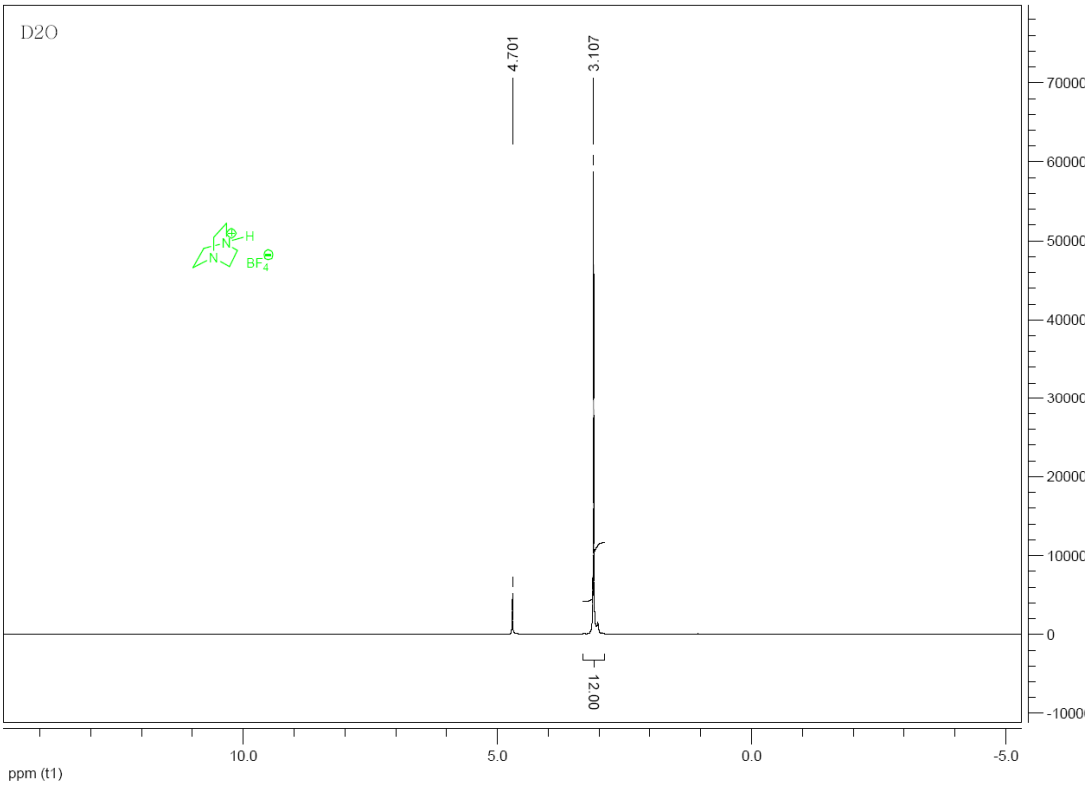
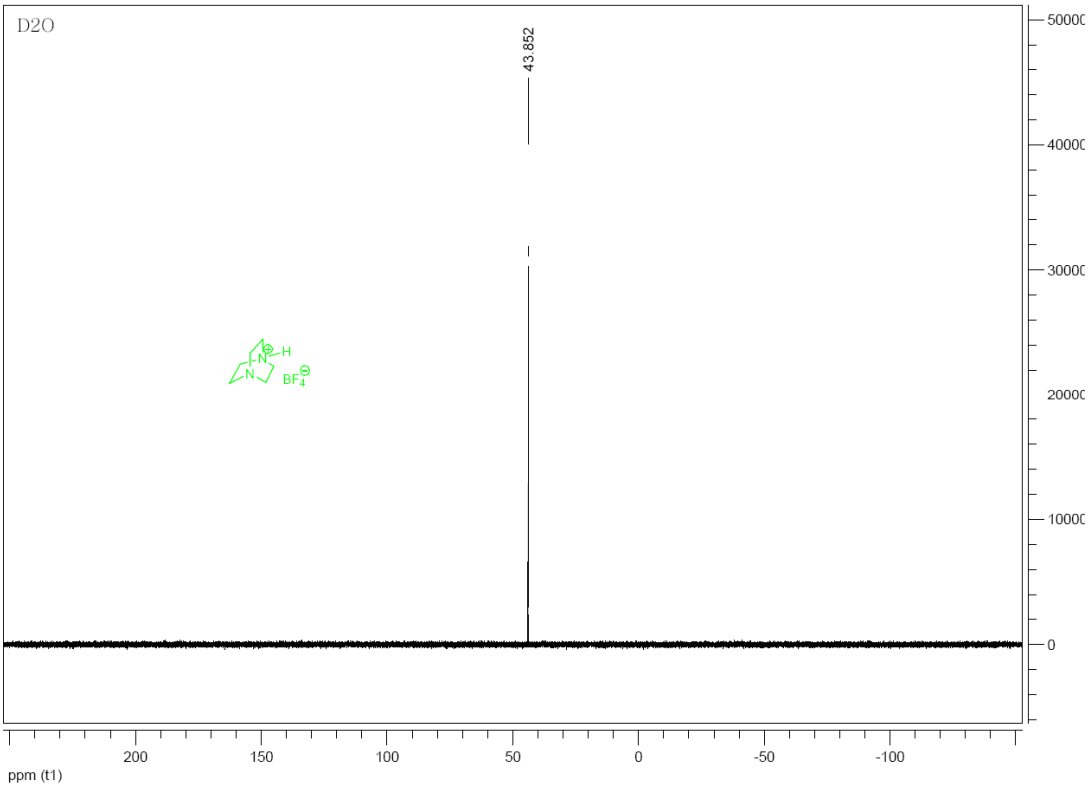
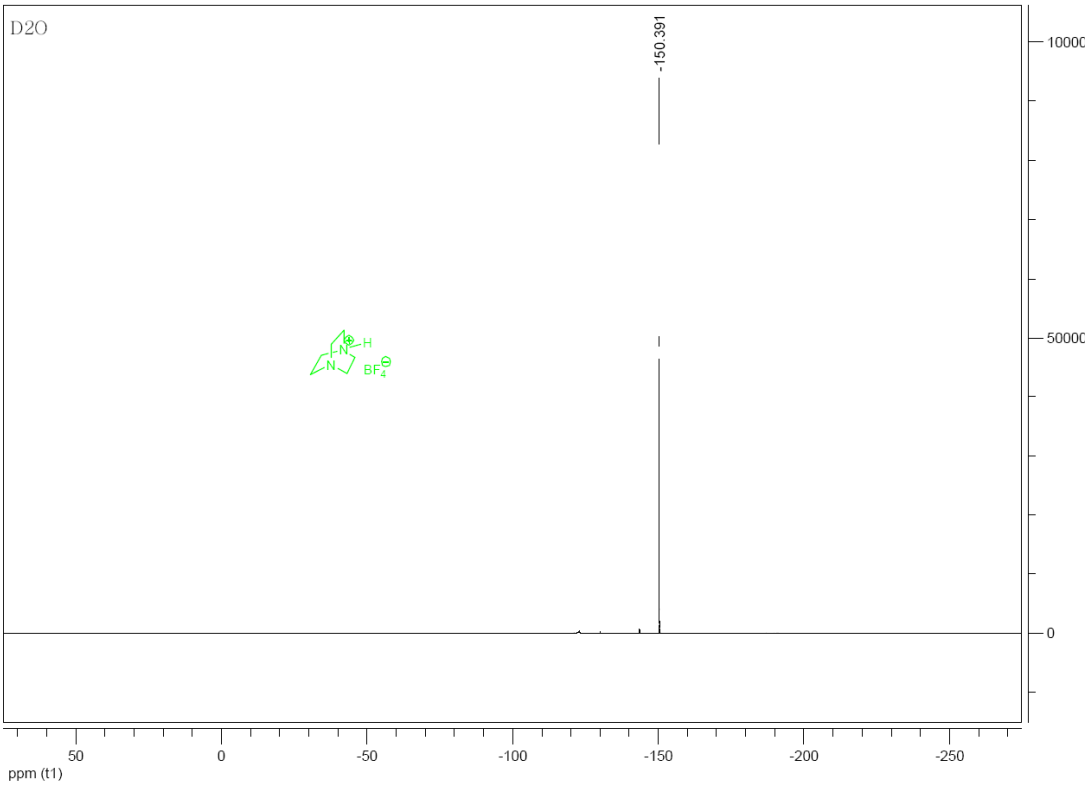
22.404
ppm (t1)

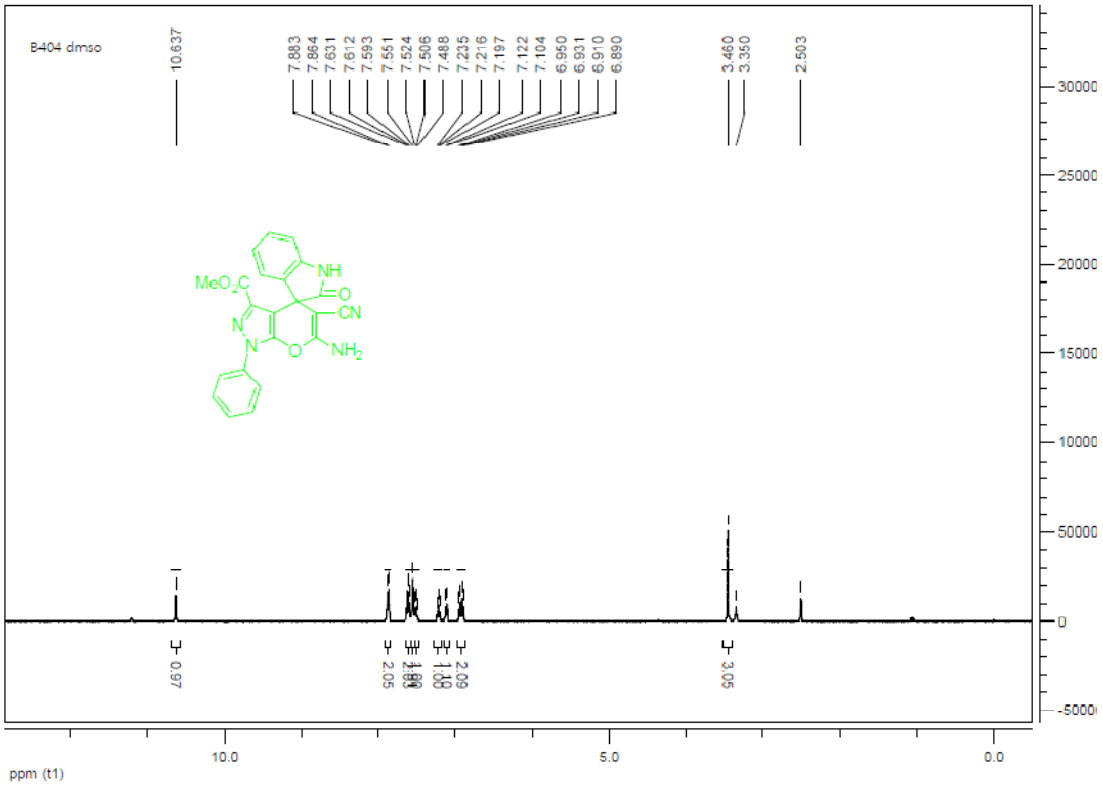

D2O
4.701
3.107
12.00
70000
60000
50000
40000
30000
20000
10000
0
-10000
10.0
5.0
0.0
-5.0
ppm (t1)

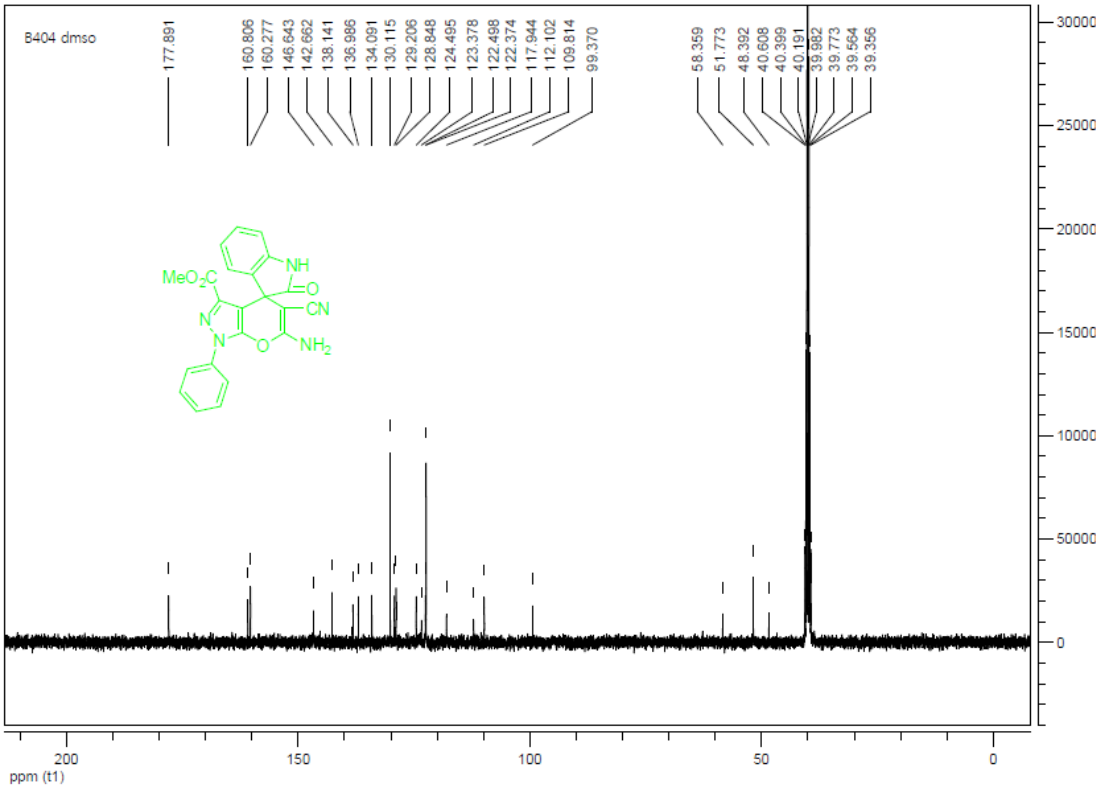

D2O
43.852
50000
40000
30000
20000
10000
0
200
150
100
50
0
-50
-100
ppm (t1)


D2O
-150.391
10000
50000
0
50
0
-50
-100
-150
-200
-250
ppm (t1)

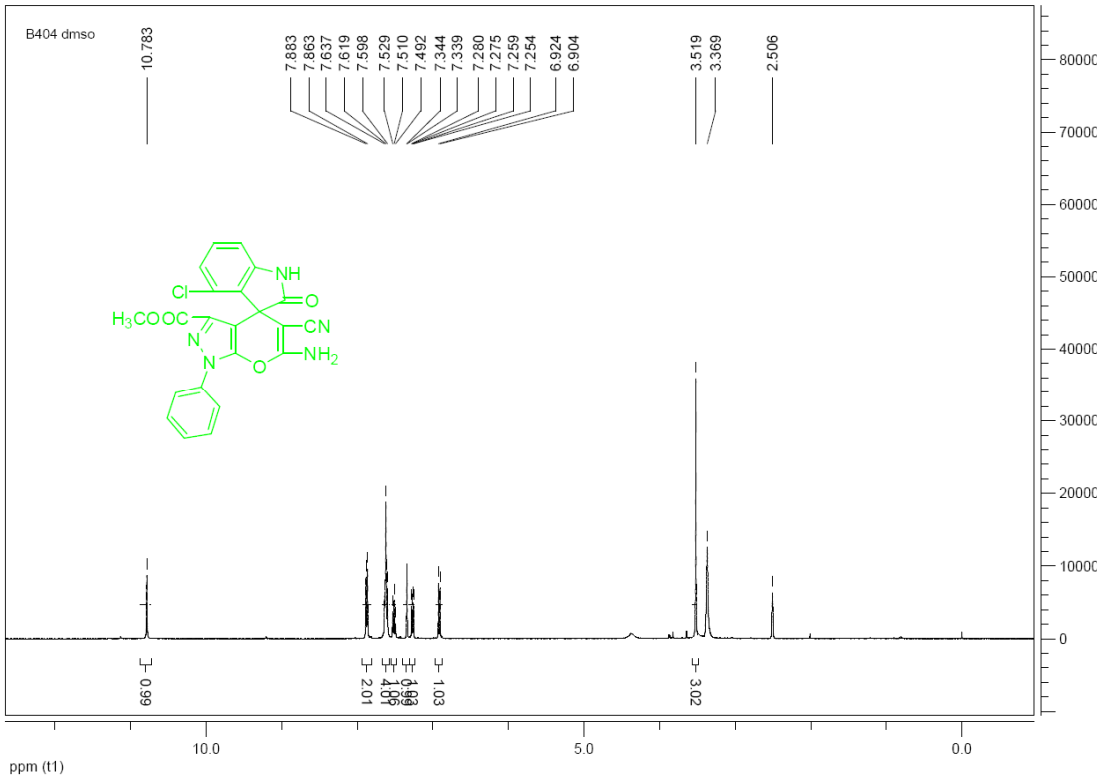
Spectroscopic Data for Compounds 5a-l

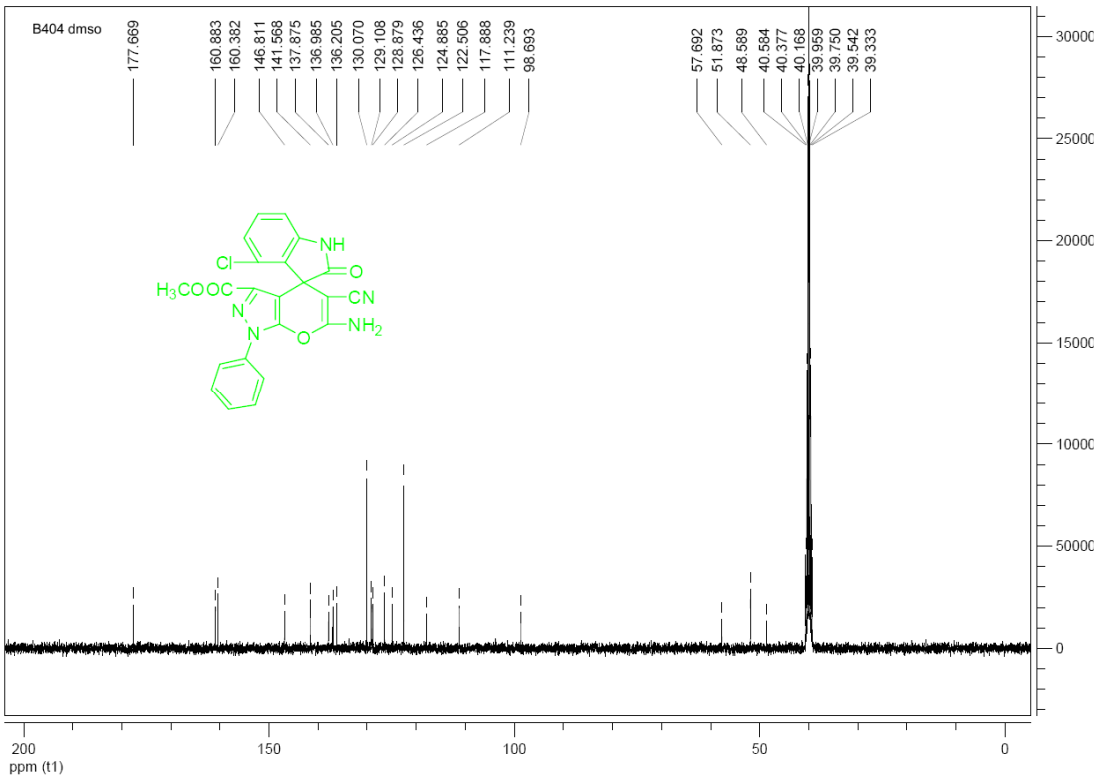
Methyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5a)



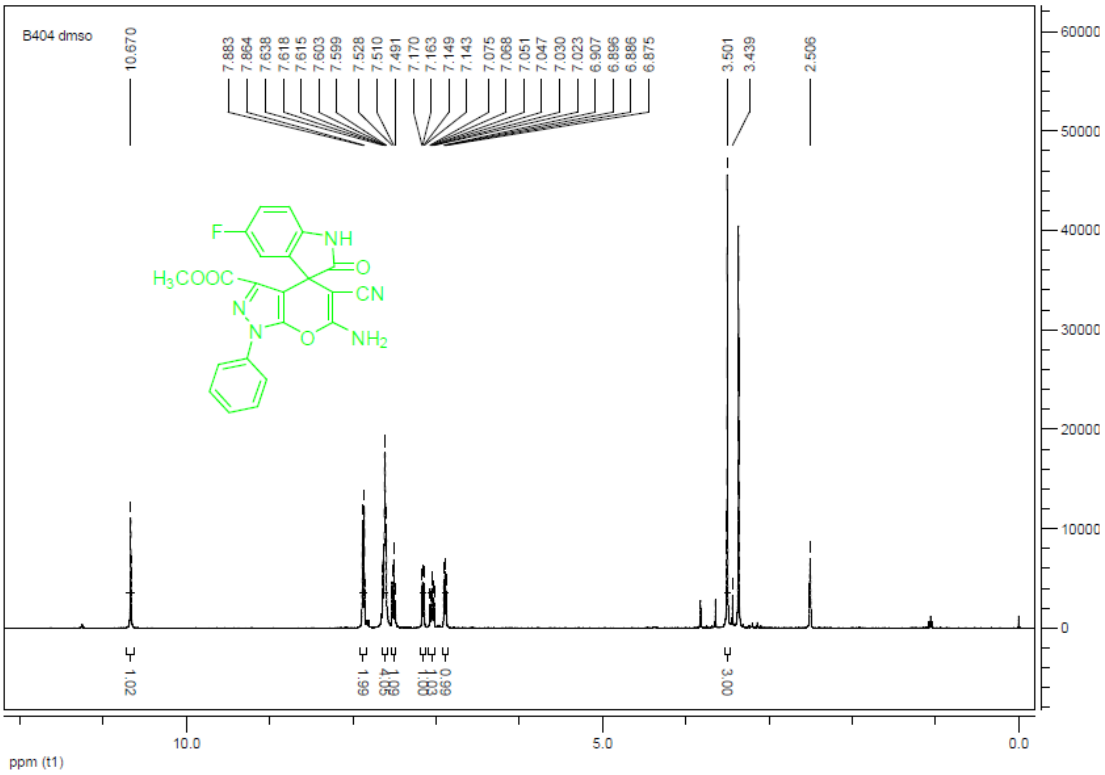


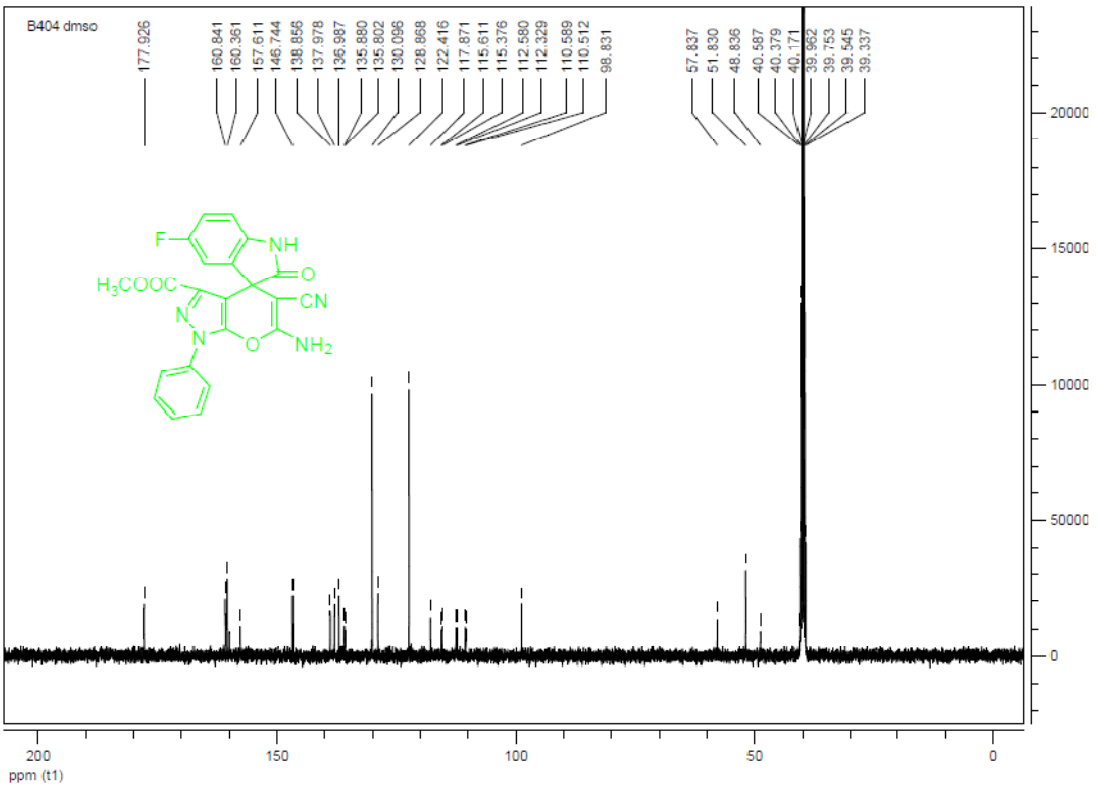
Methyl 6'-amino-4-chloro-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5b)



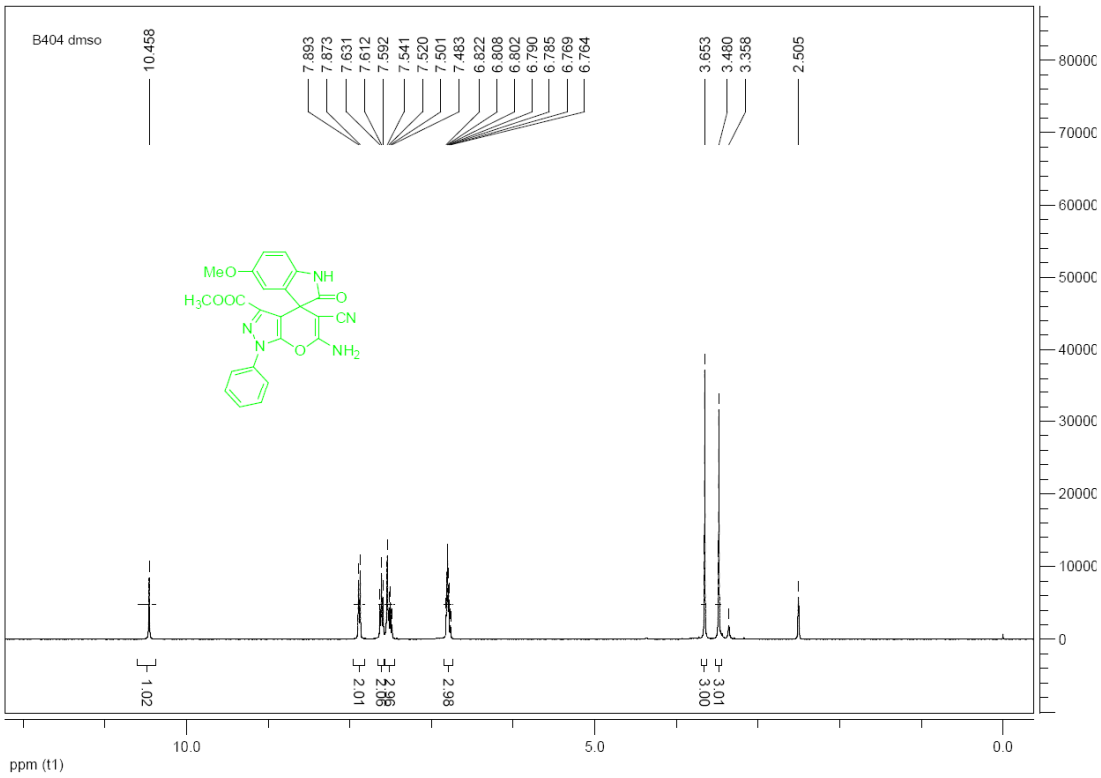


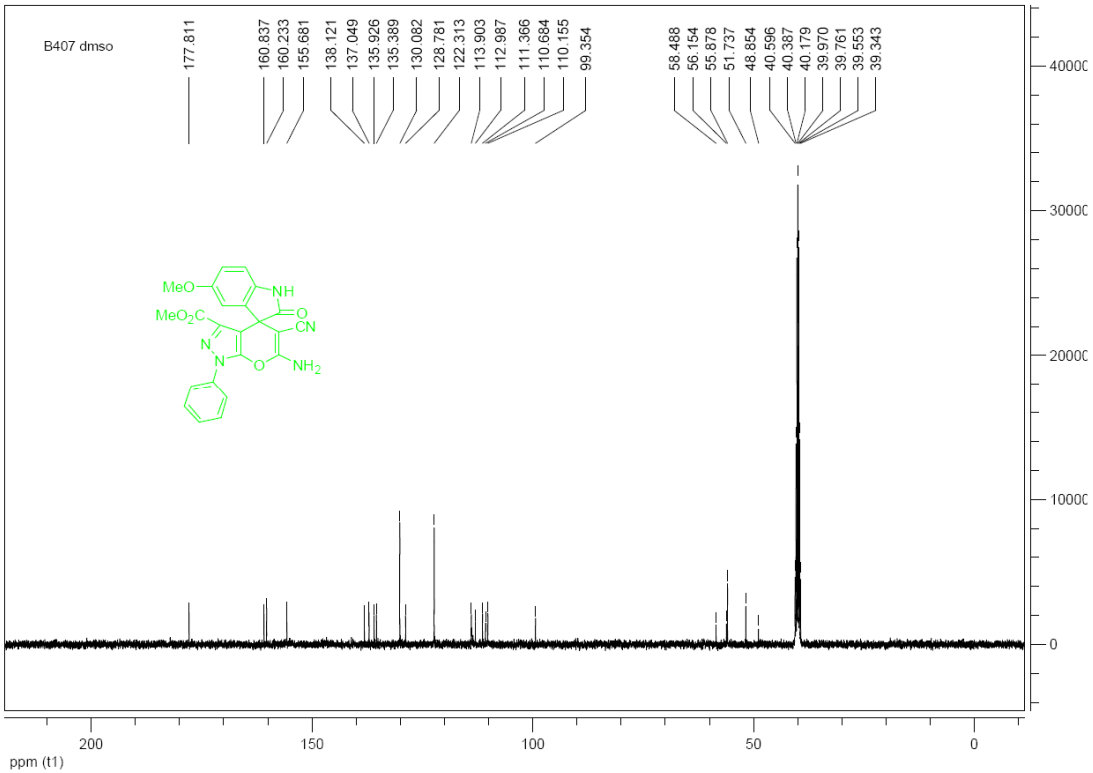
Methyl 6'-amino-5'-cyano-5-fluoro-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5c)



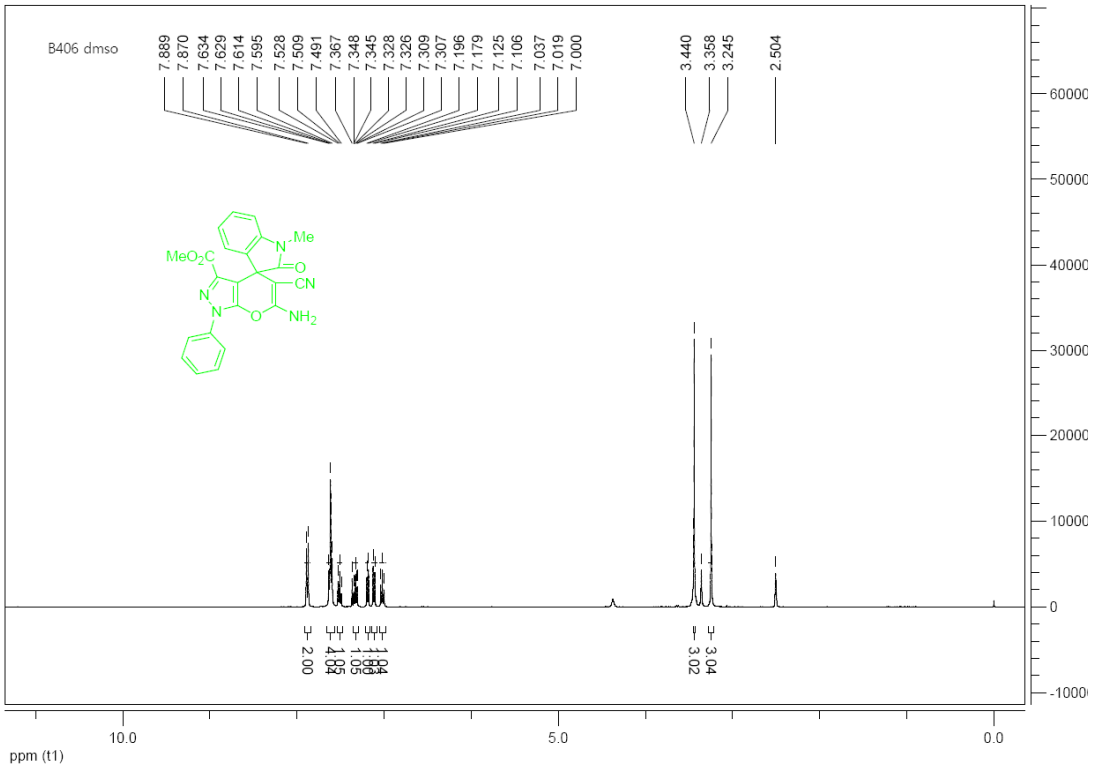


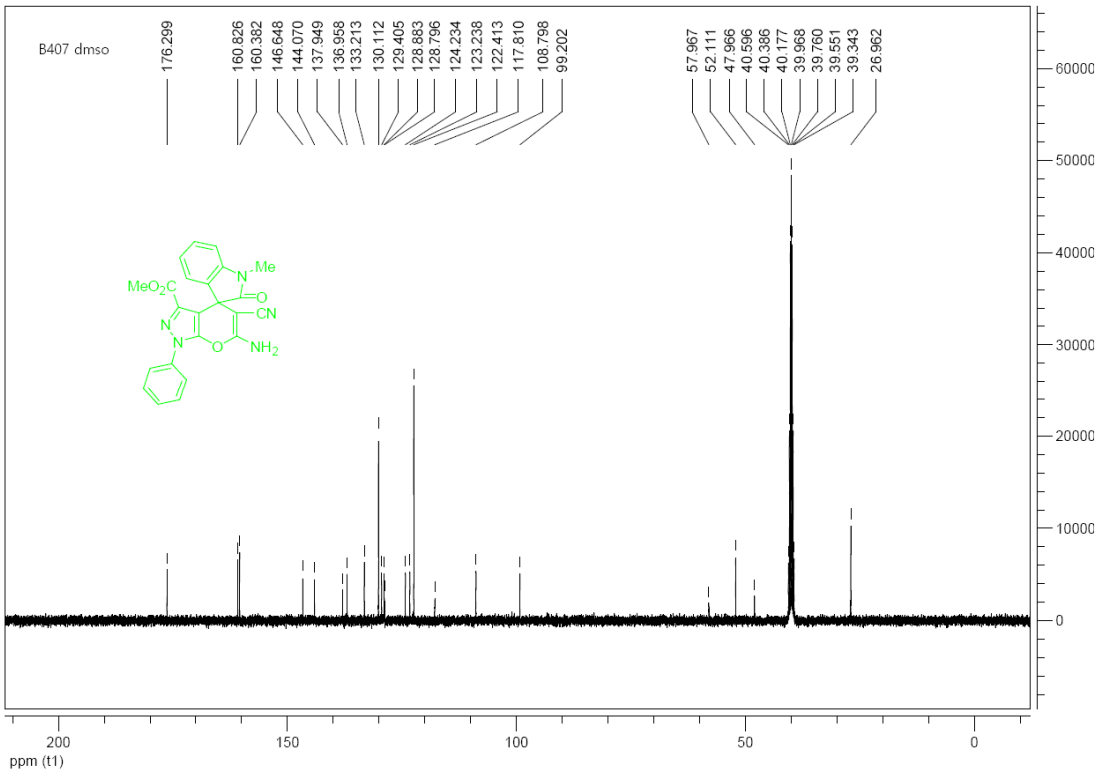
Methyl 6'-amino-5'-cyano-5-methoxy-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5d)



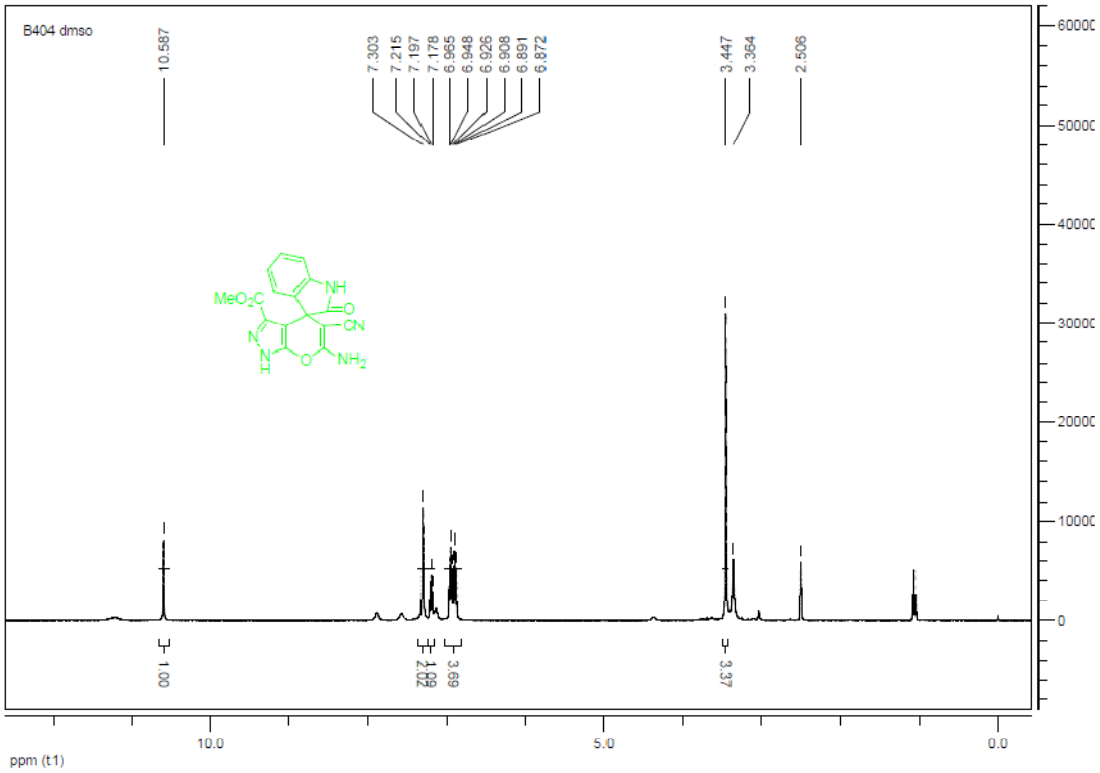


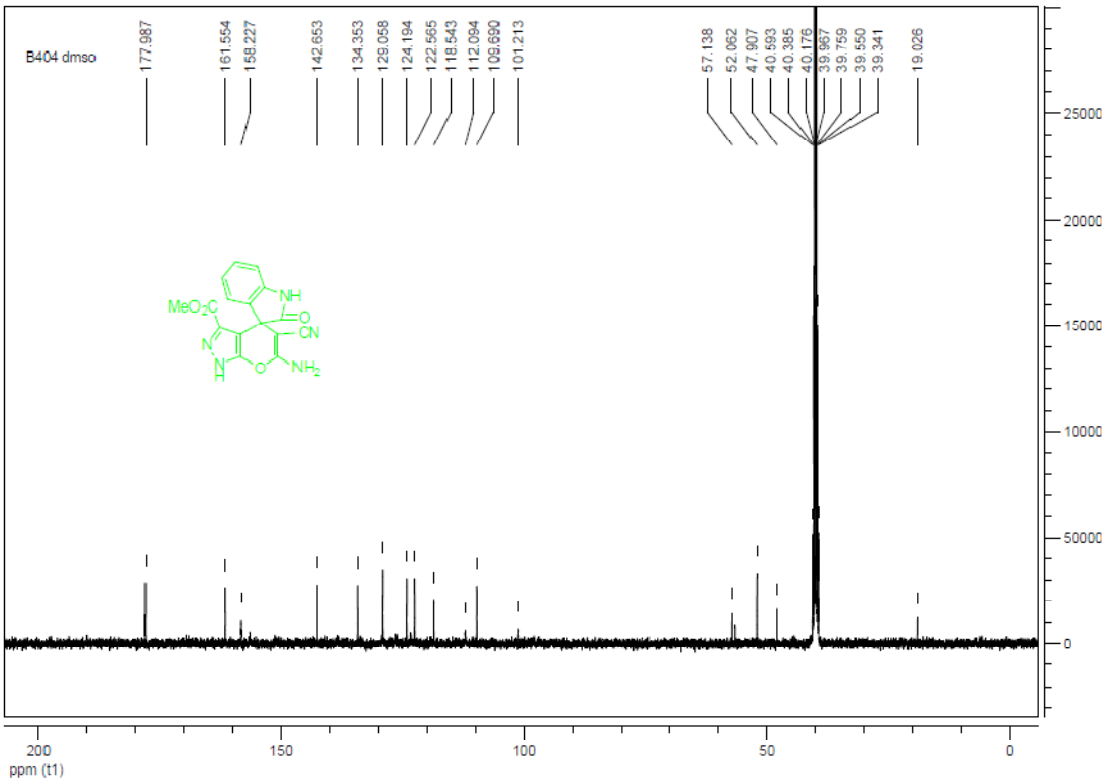
Methyl 6'-amino-5'-cyano-1-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5e)



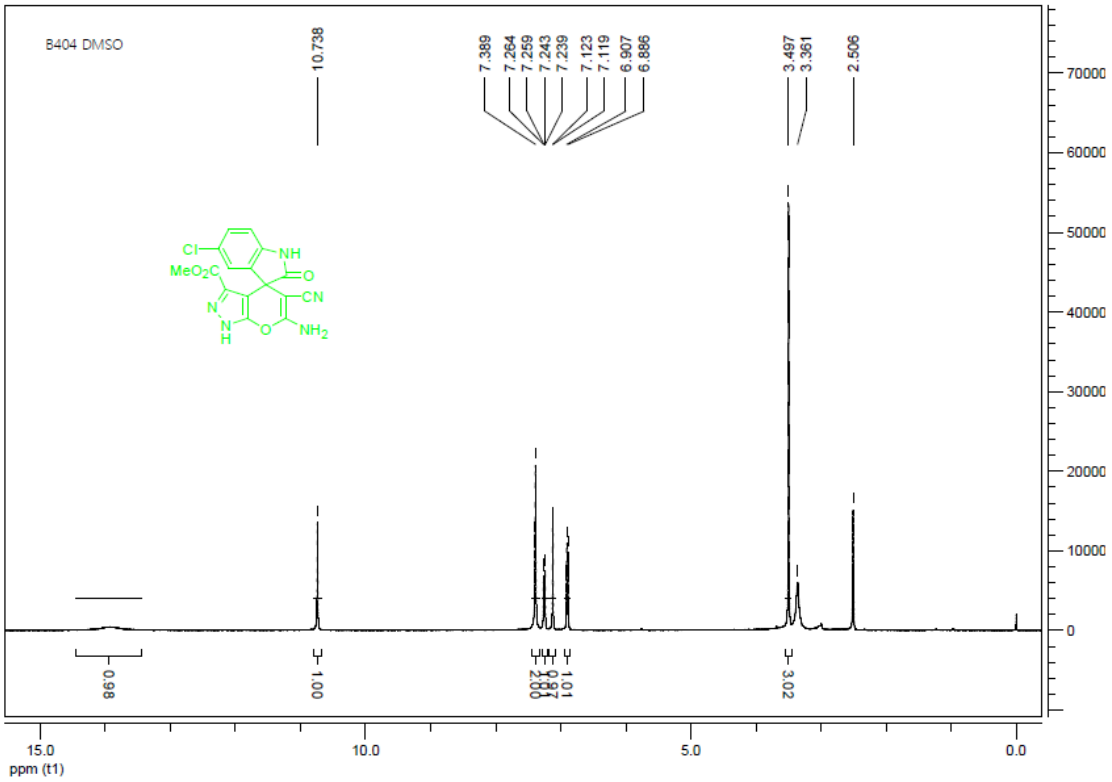


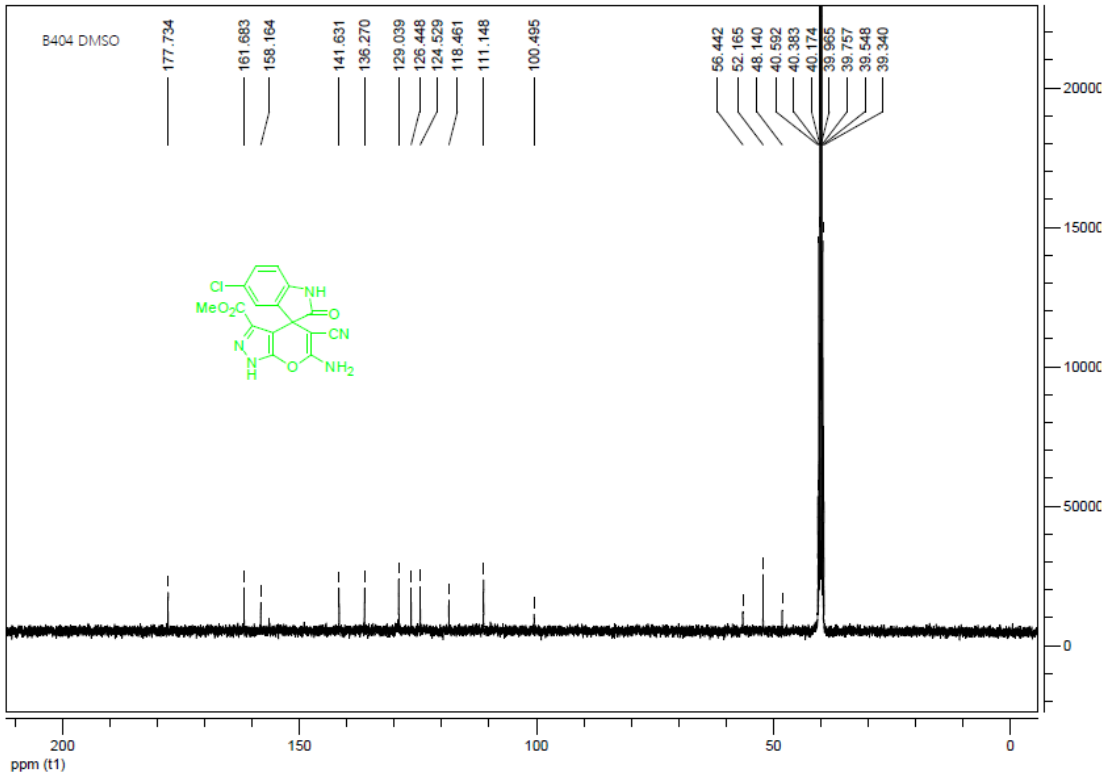
Methyl 6'-amino-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5f)



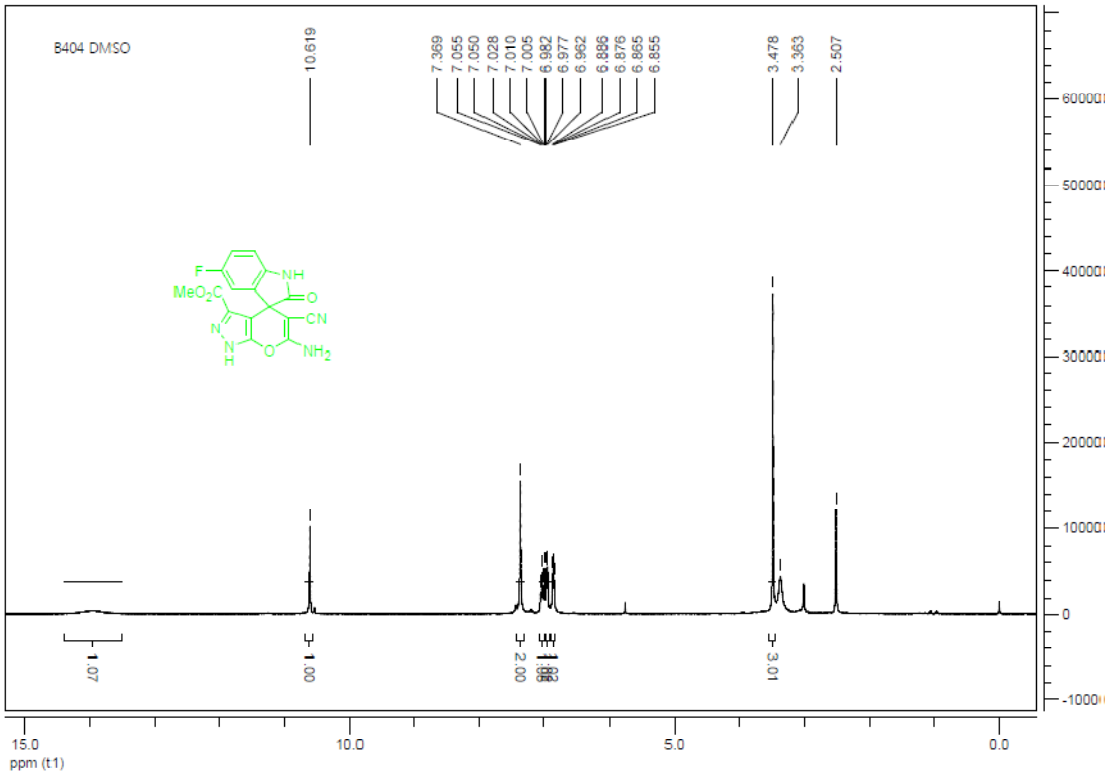


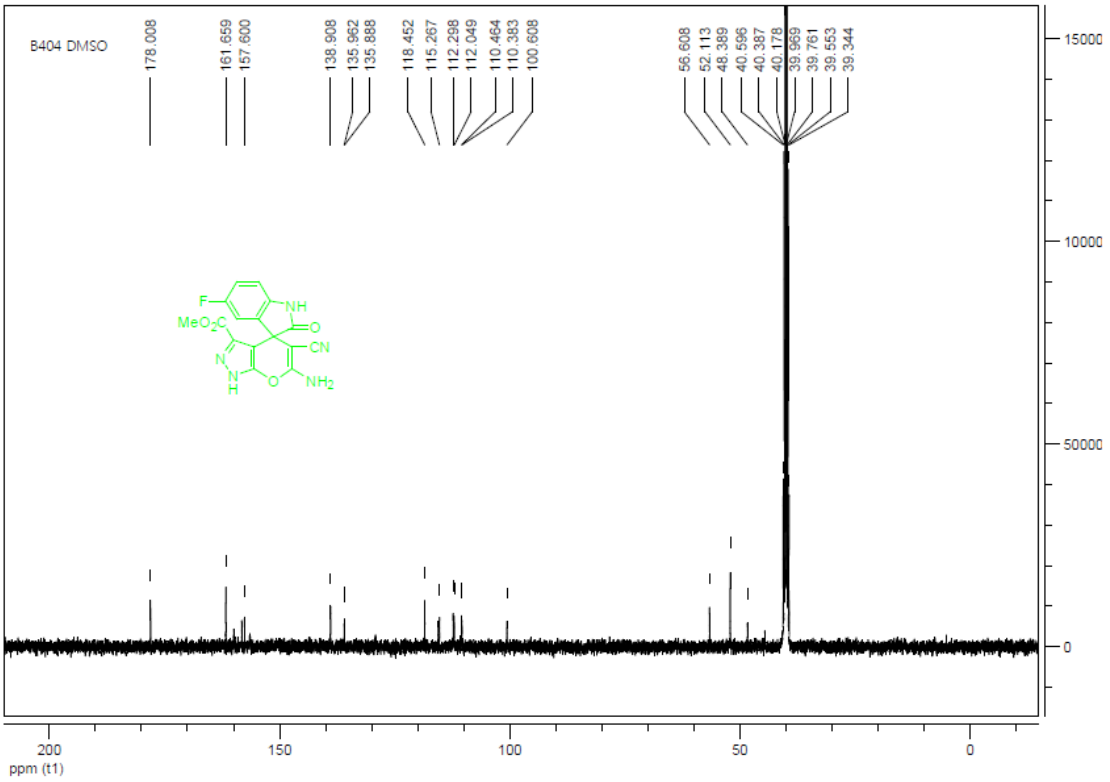
Methyl 6'-amino-5-chloro-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5g)



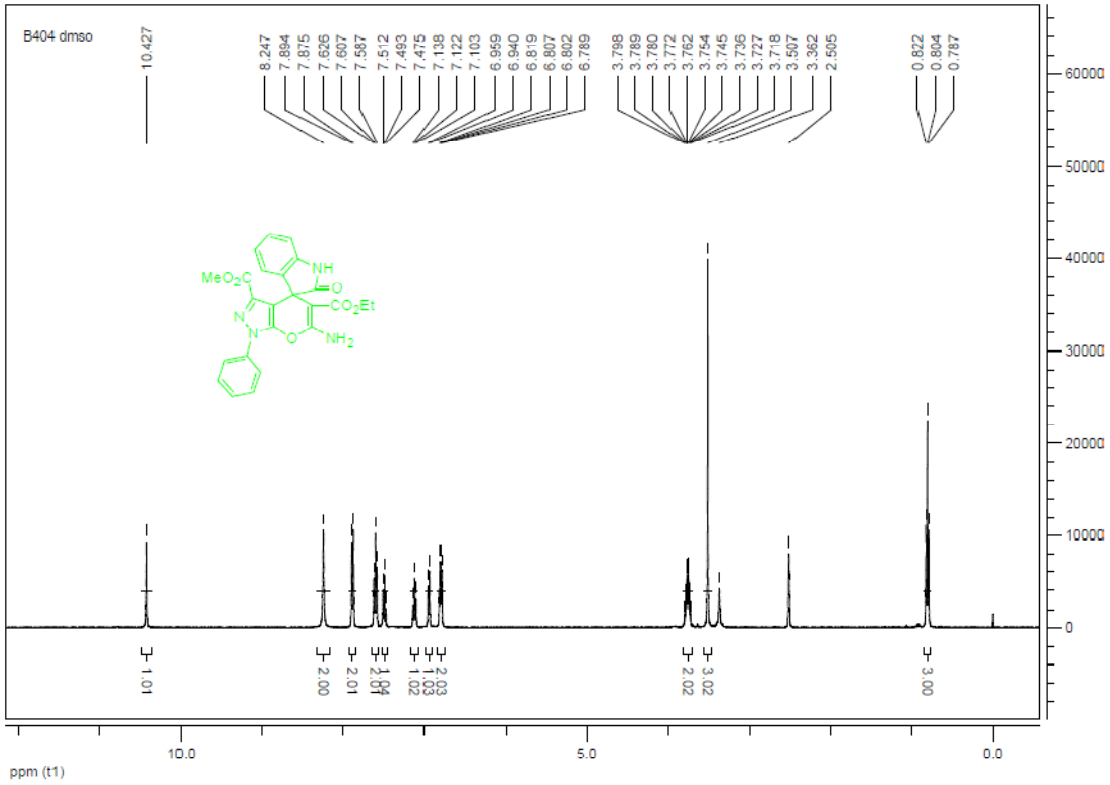


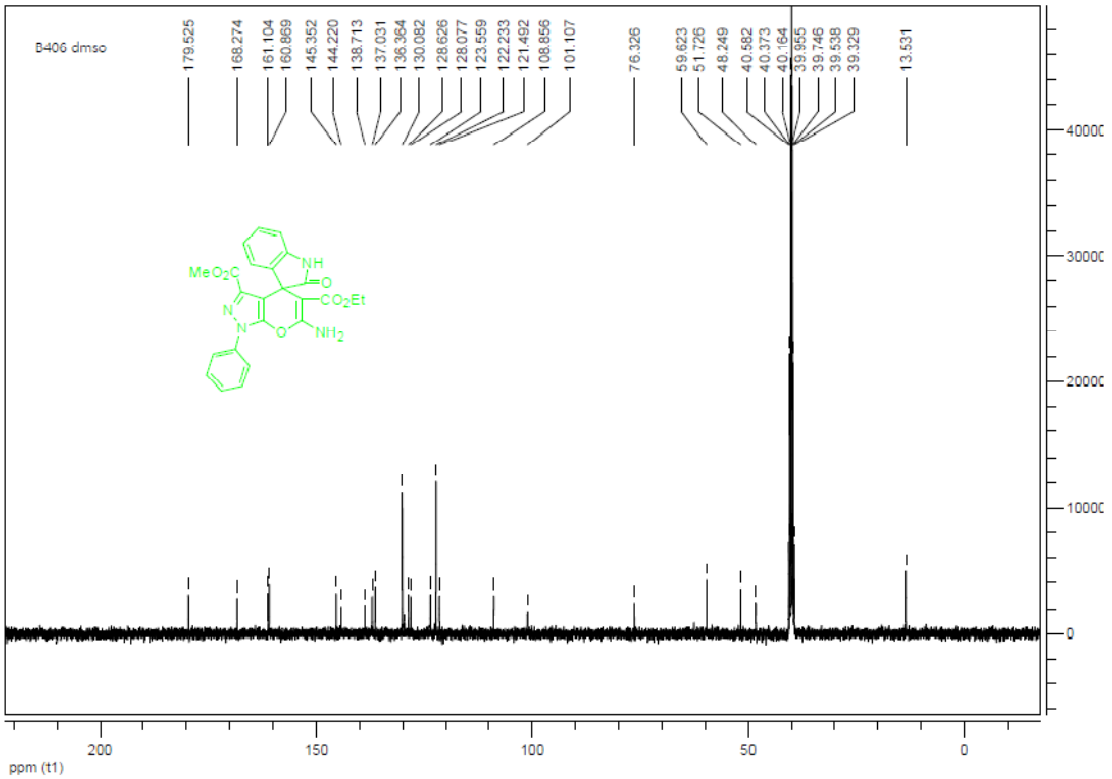
Methyl 6'-amino-5'-cyano-5-fluoro-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5h)



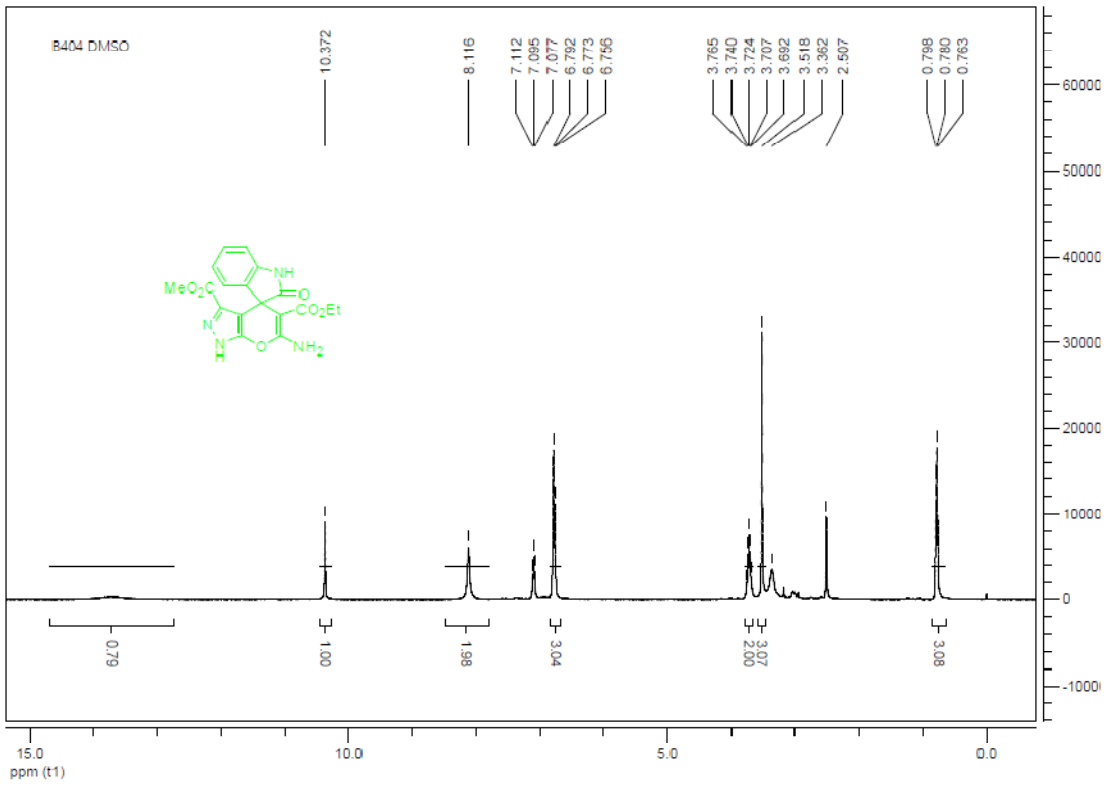


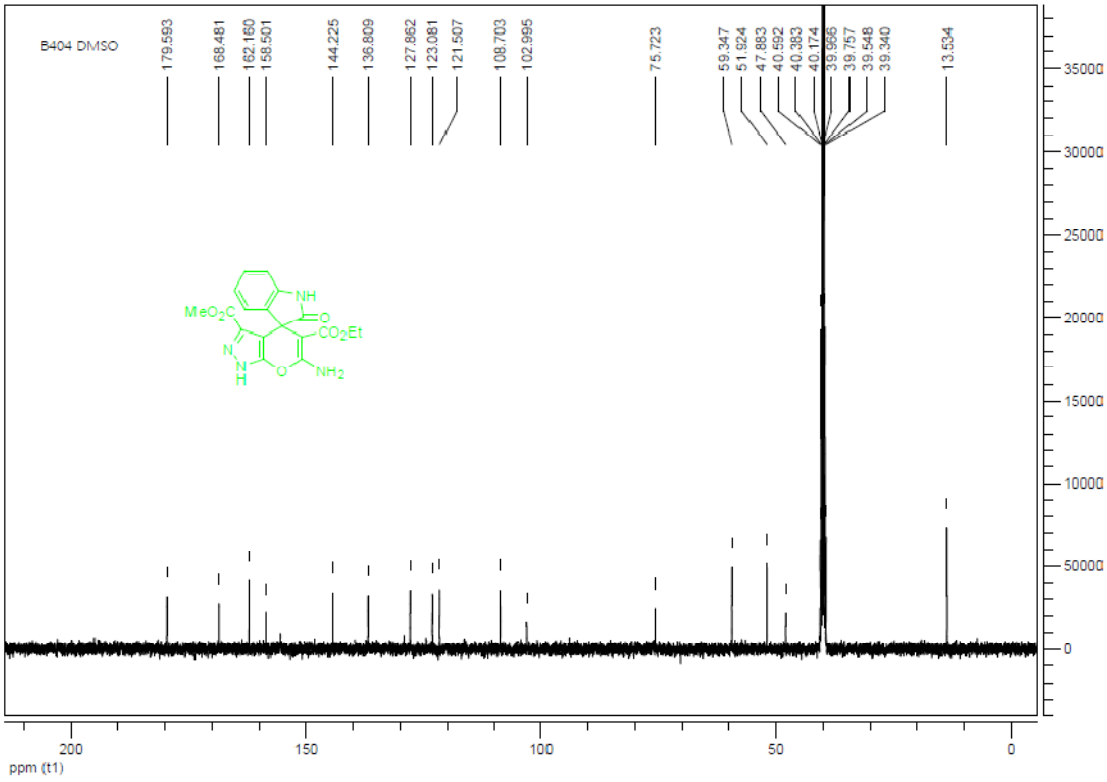
5'-Ethyl 3'-methyl 6'-amino-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3',5'-dicarboxylate (5i)



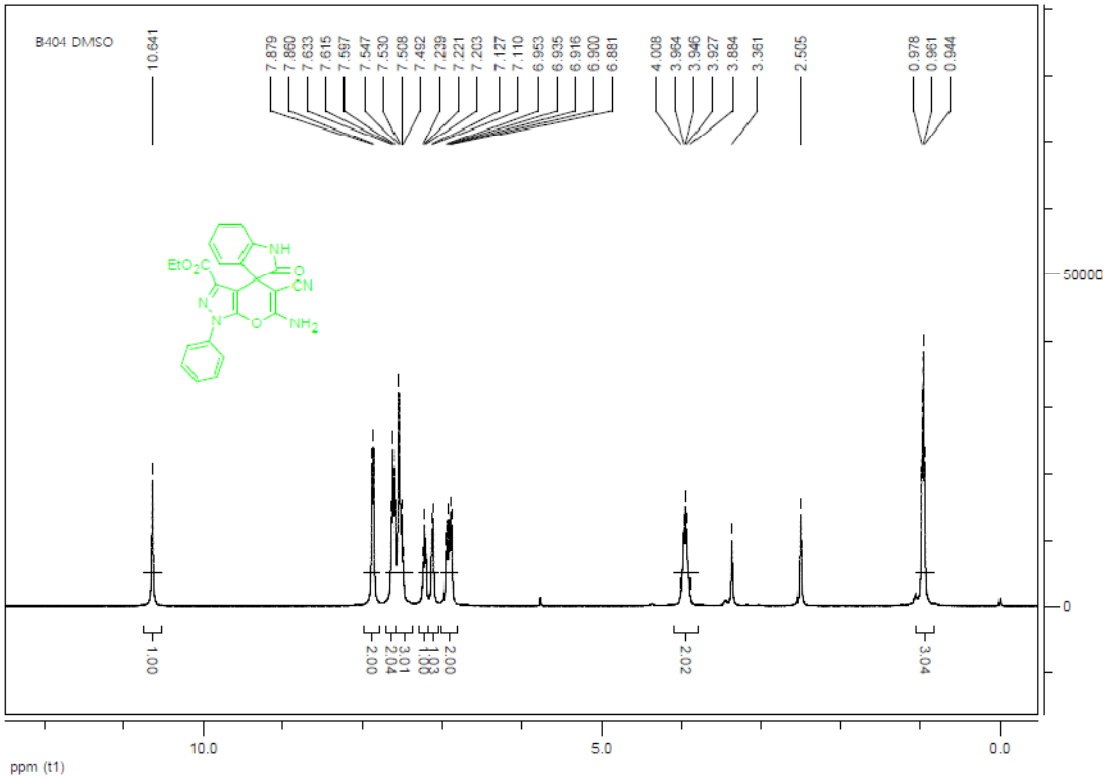


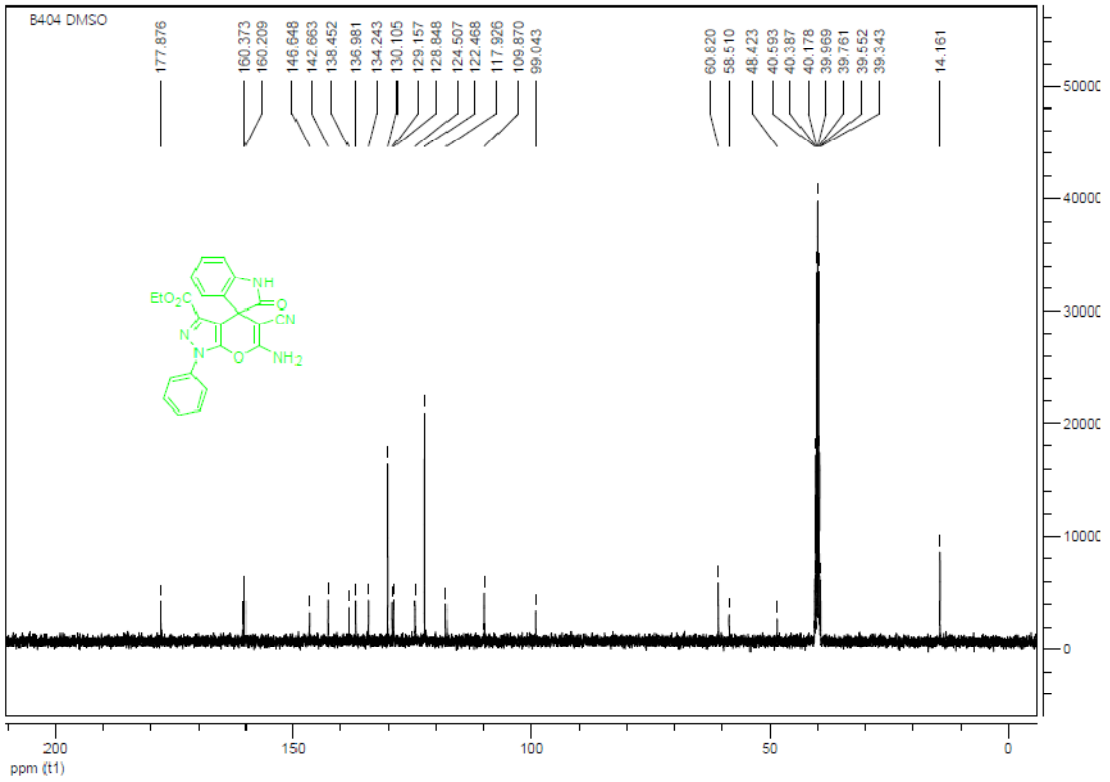
5'-Ethyl 3'-methyl 6'-amino-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3',5'-dicarboxylate (5j)



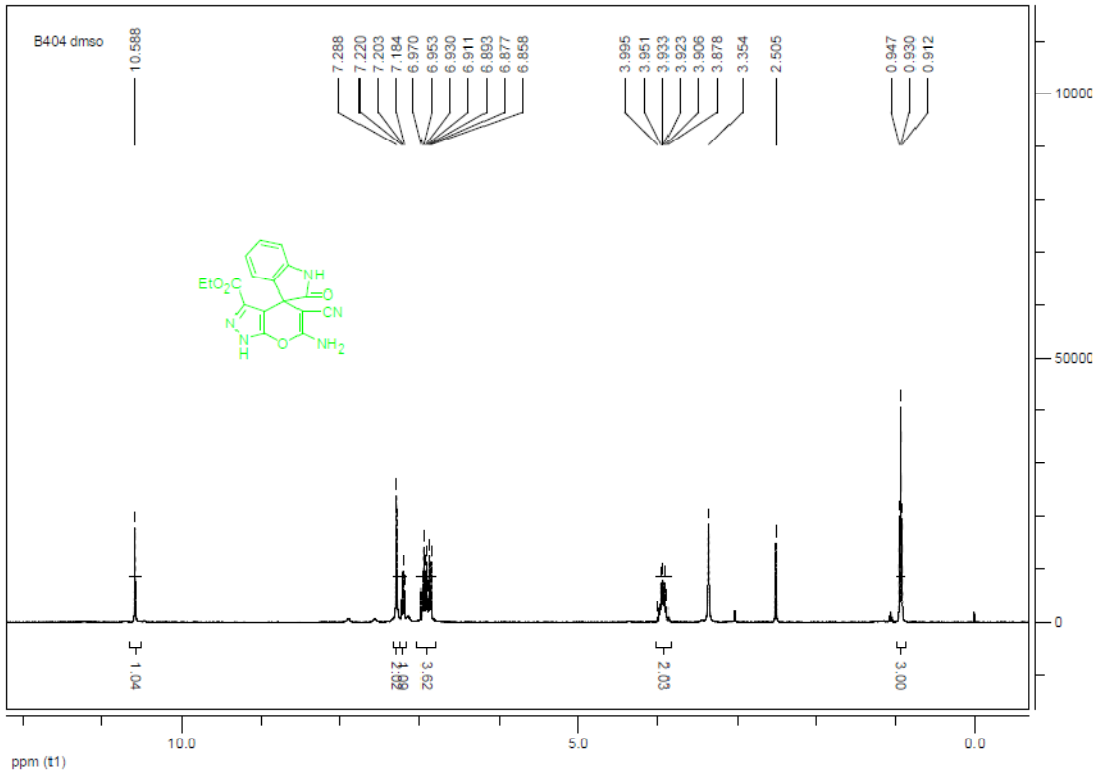


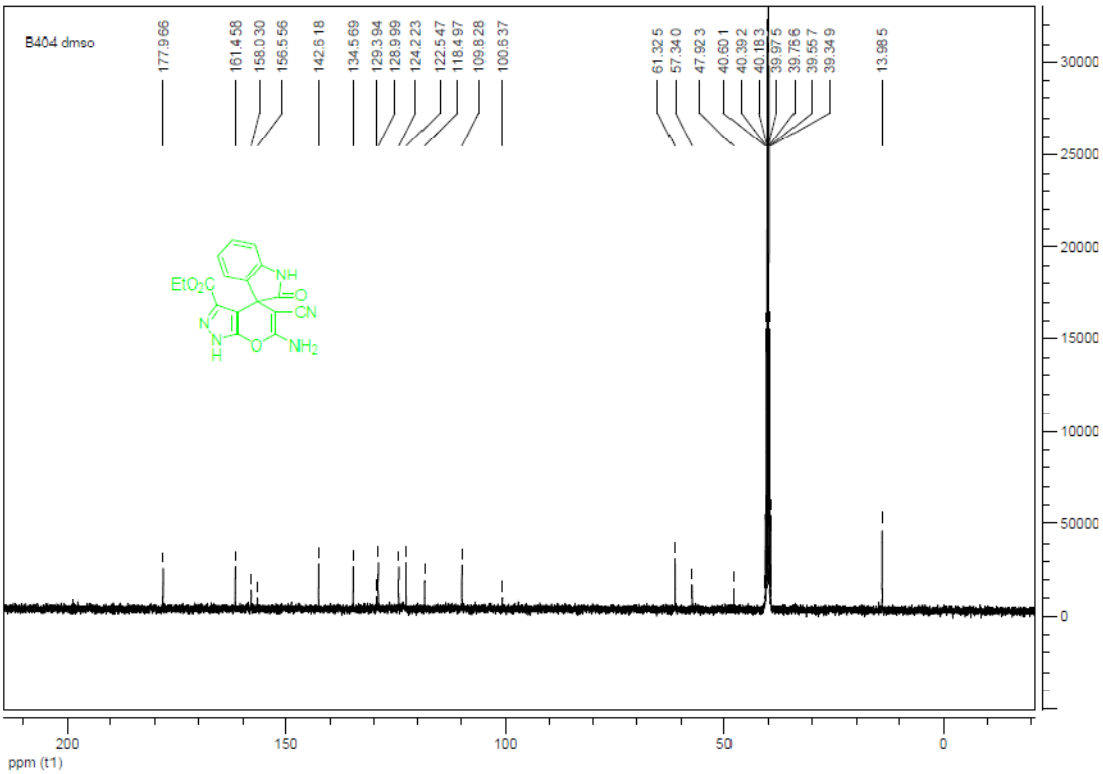
Ethyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5k)





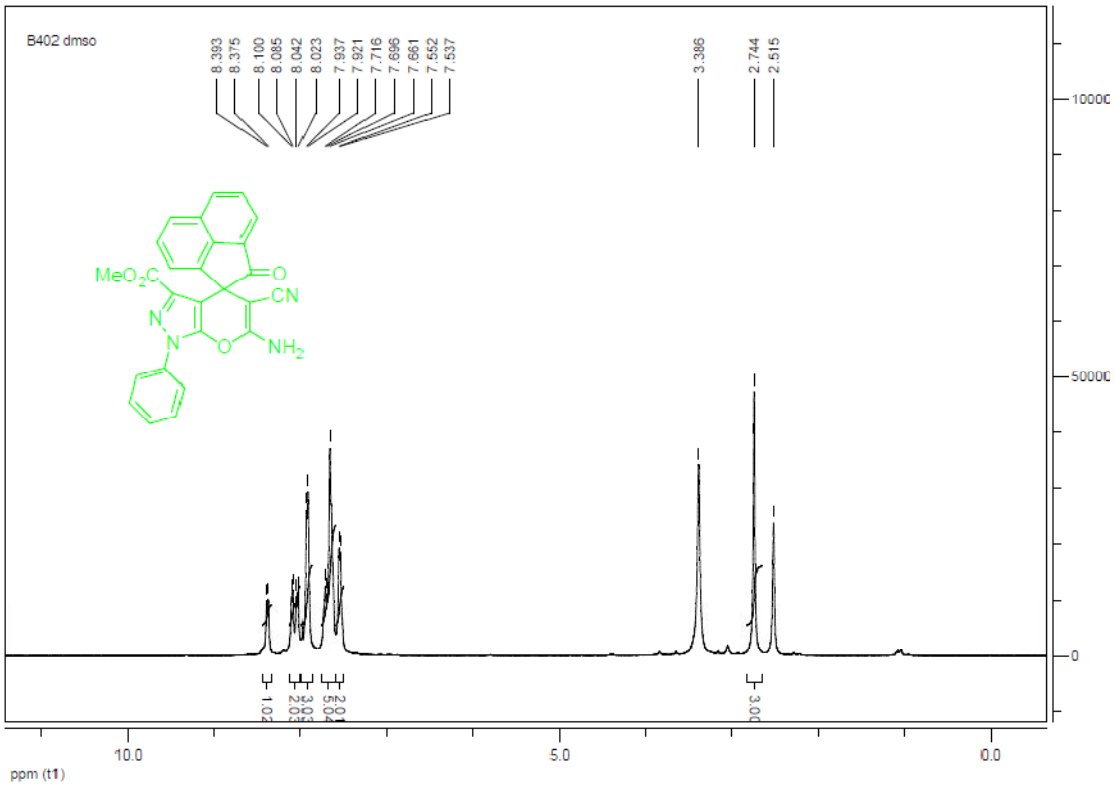
Ethyl 6'-amino-5'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (5l)

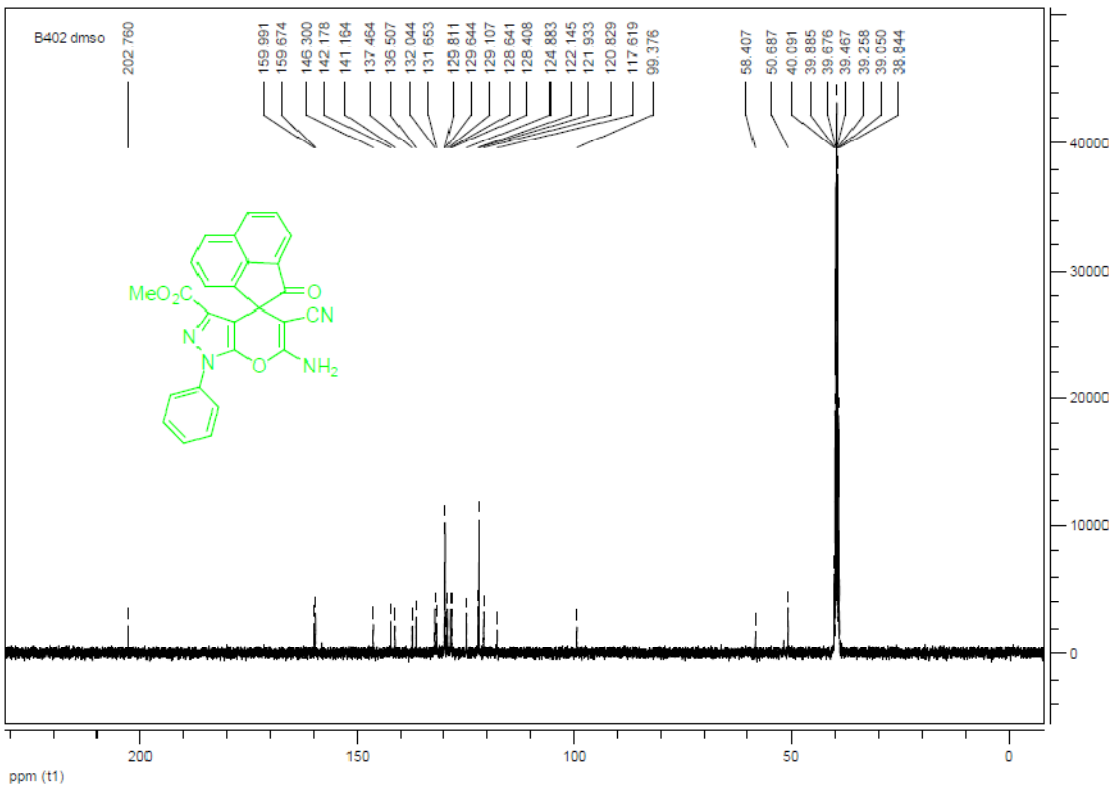




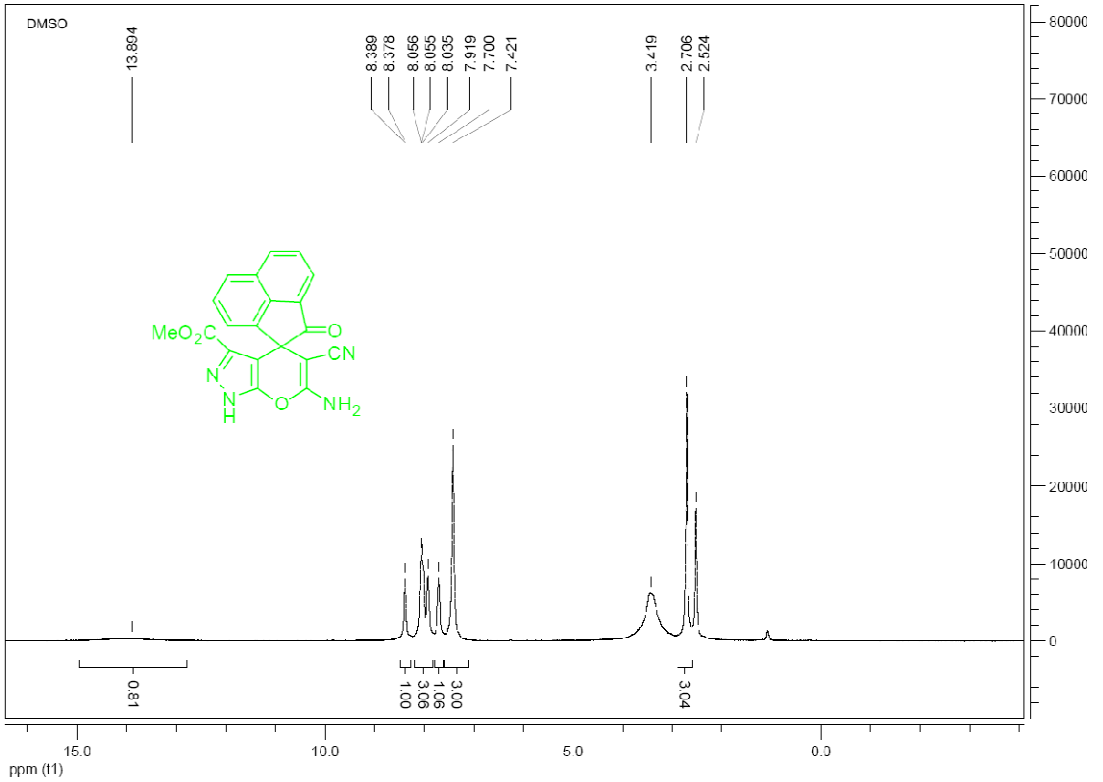
Spectroscopic Data for Compounds 7a-b

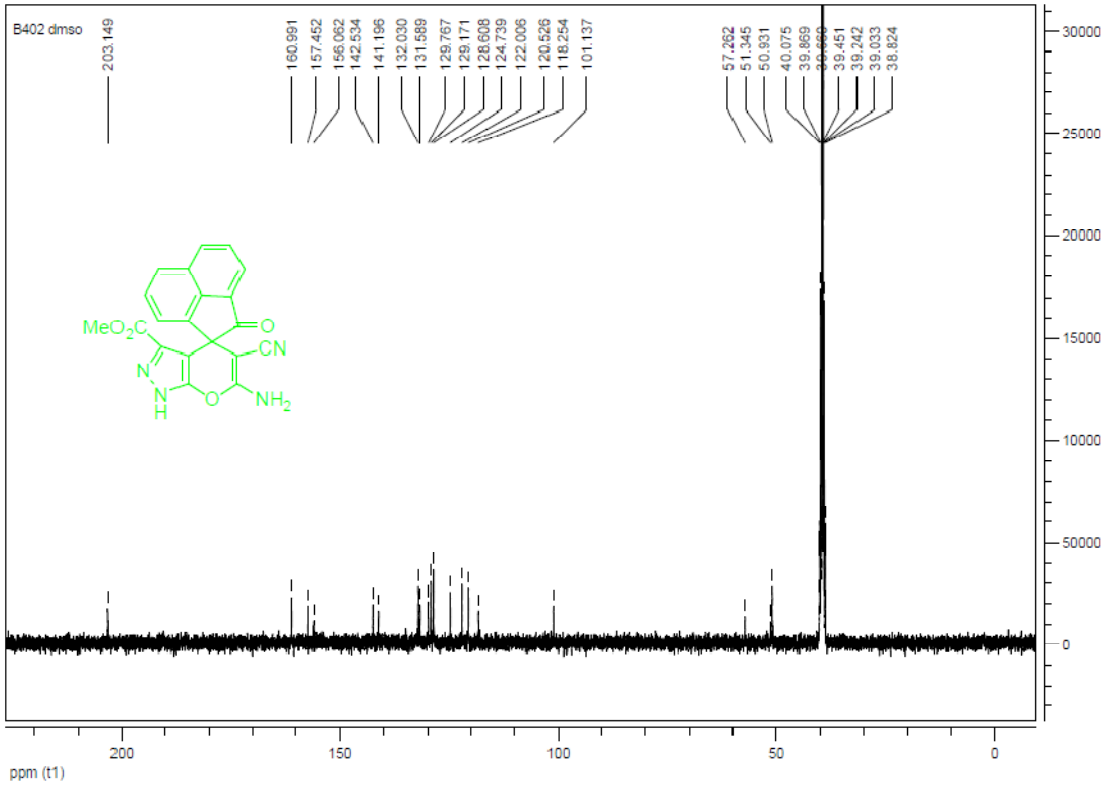
Methyl 6'-amino-5'-cyano-2-oxo-1'-phenyl-1'H,2H-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (7a)





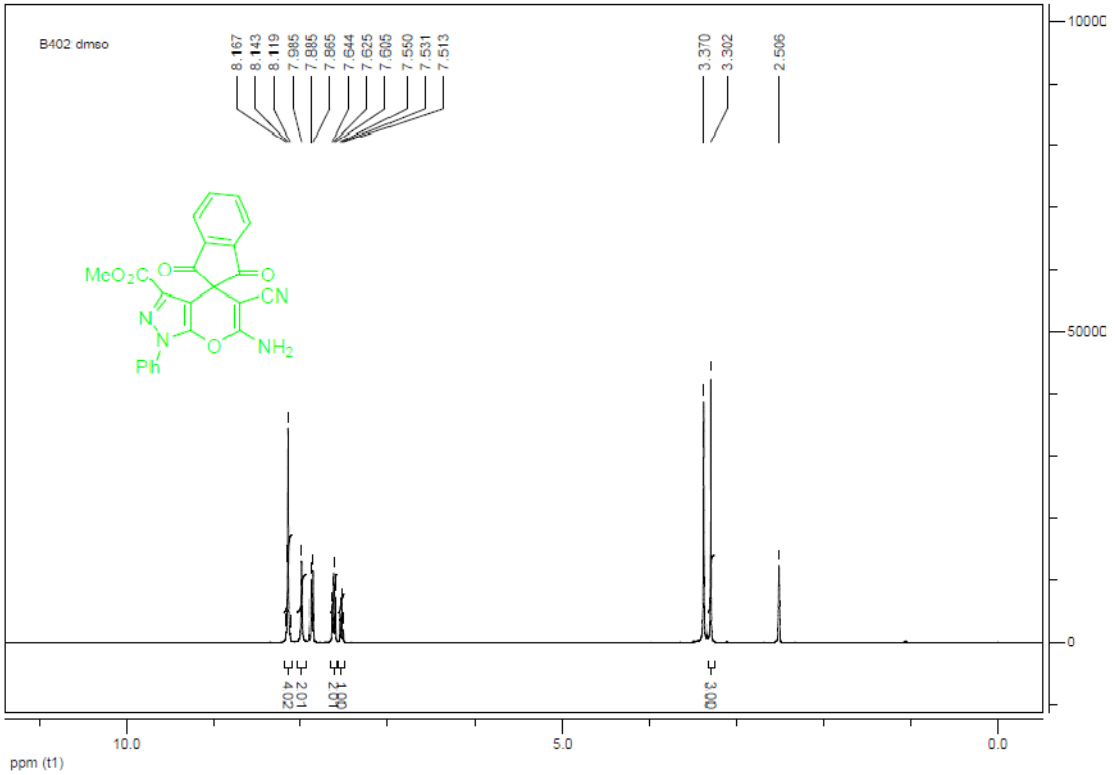
Methyl 6'-amino-5'-cyano-2-oxo-1'H,2H-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (7b)

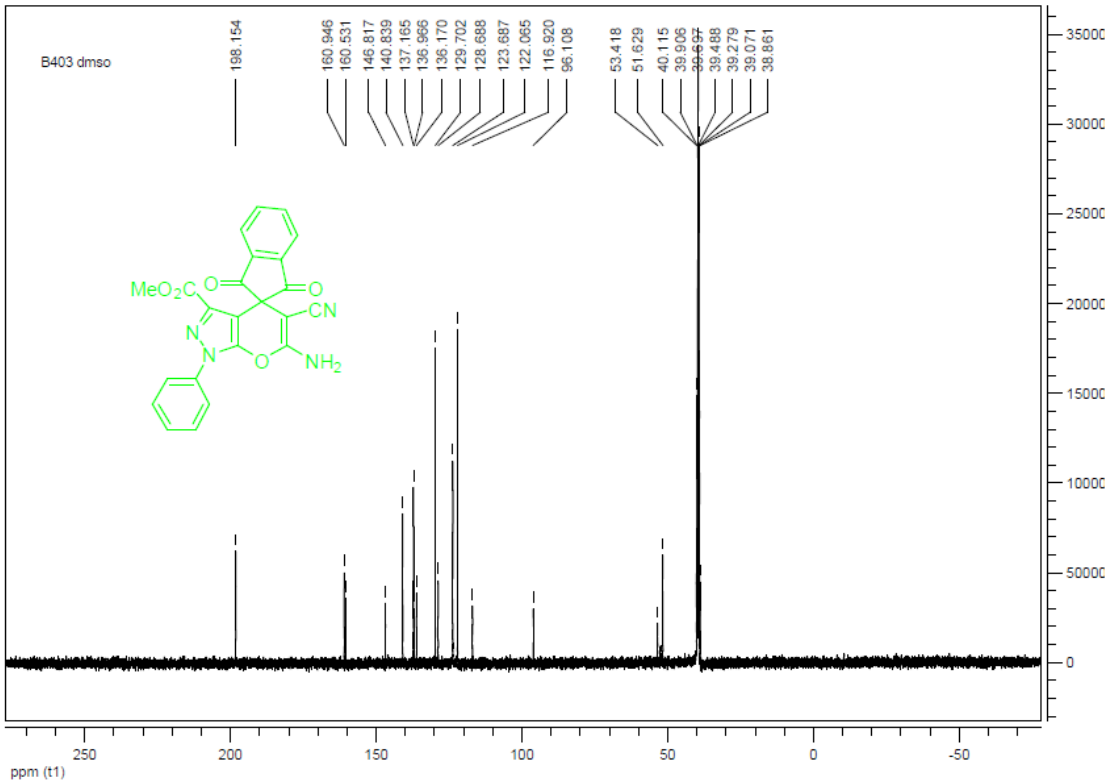




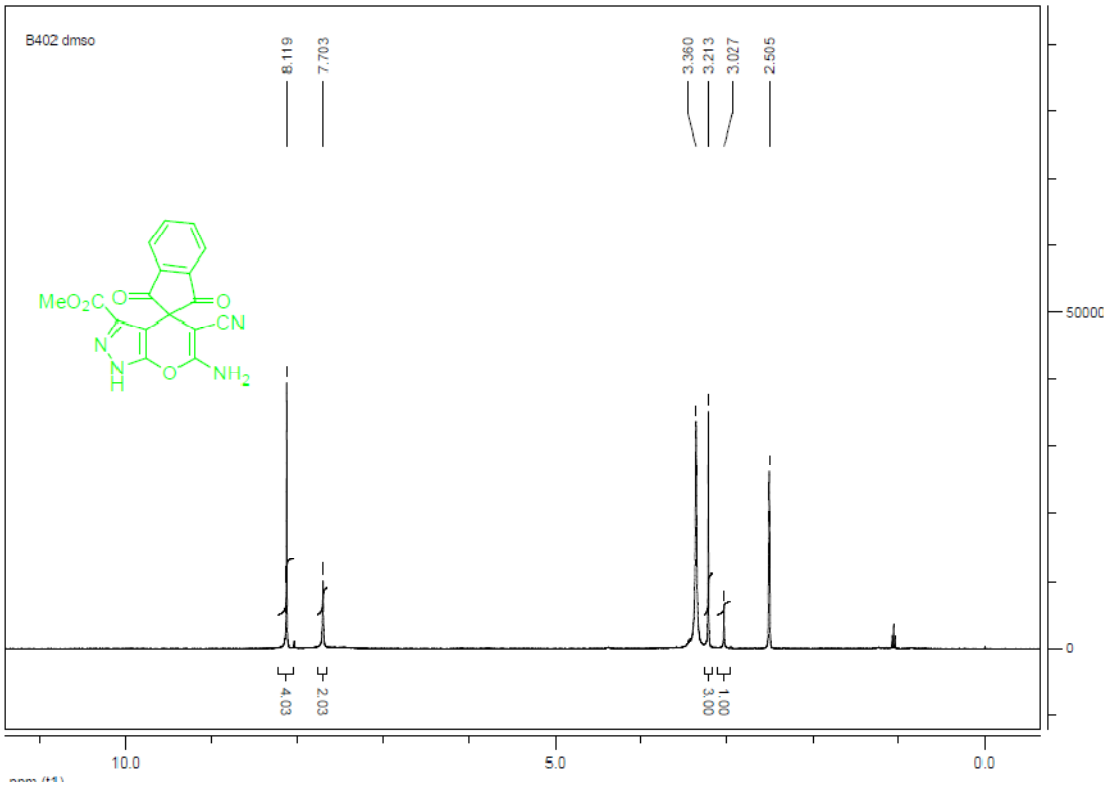
Spectroscopic Data for Compounds 9a-b

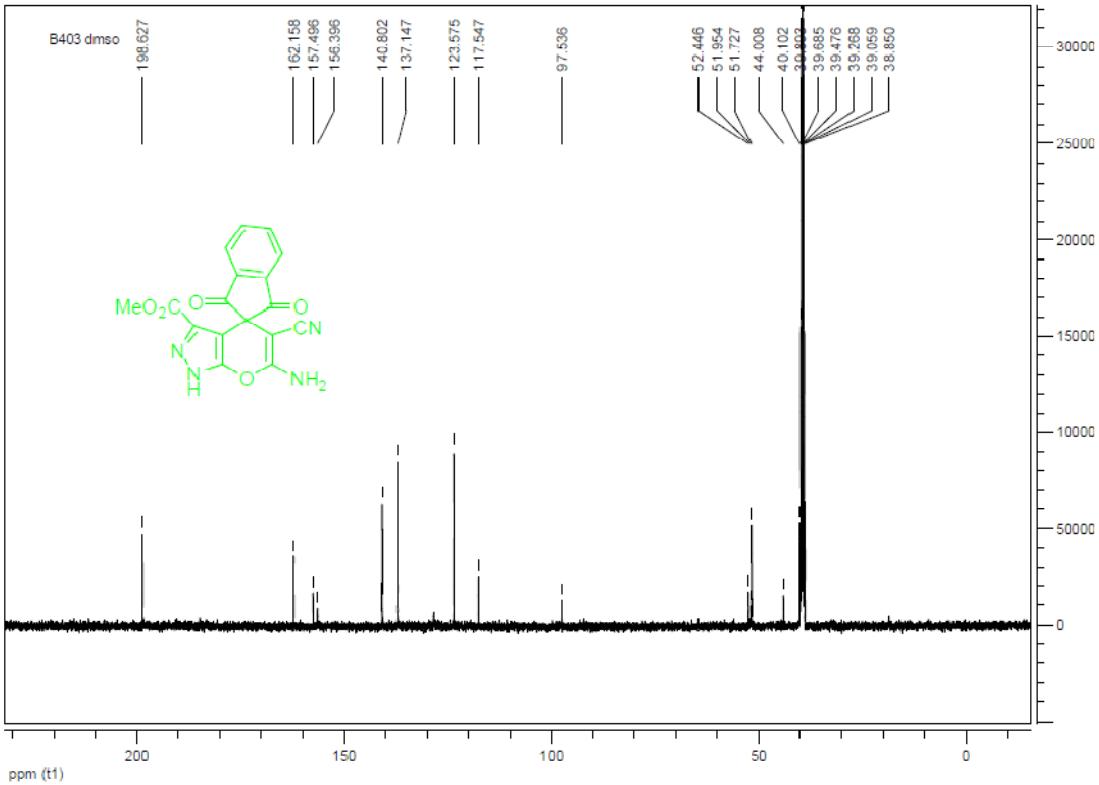
Methyl 6'-amino-5'-cyano-1,3-dioxo-1'-phenyl-1,3-dihydro-1'H-spiro[indene-2,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (9a)





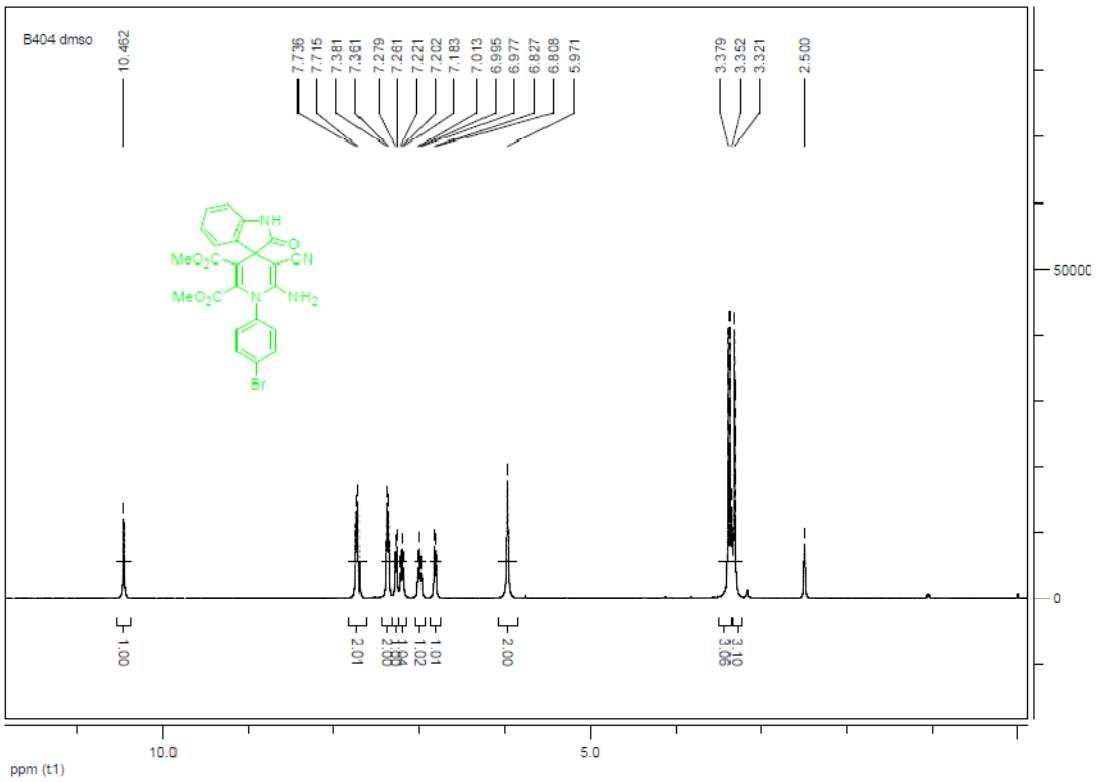
Methyl 6'-amino-5'-cyano-1,3-dioxo-1,3-dihydro-1'H-spiro[indene-2,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (9b)

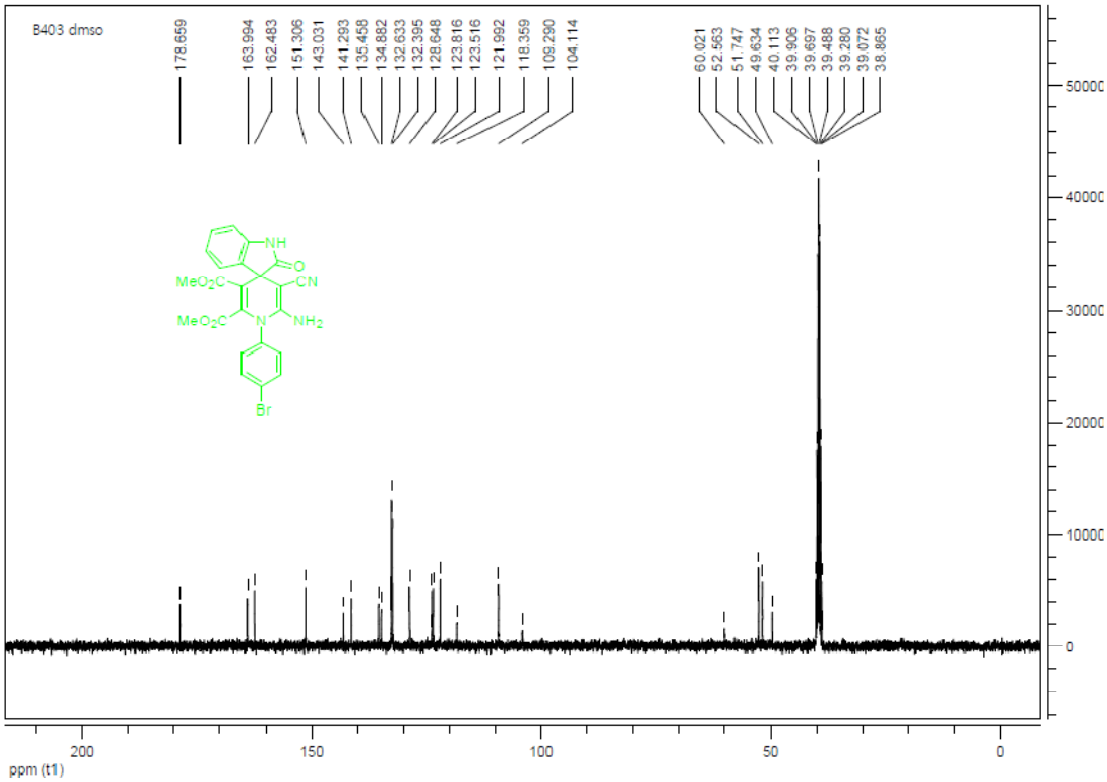




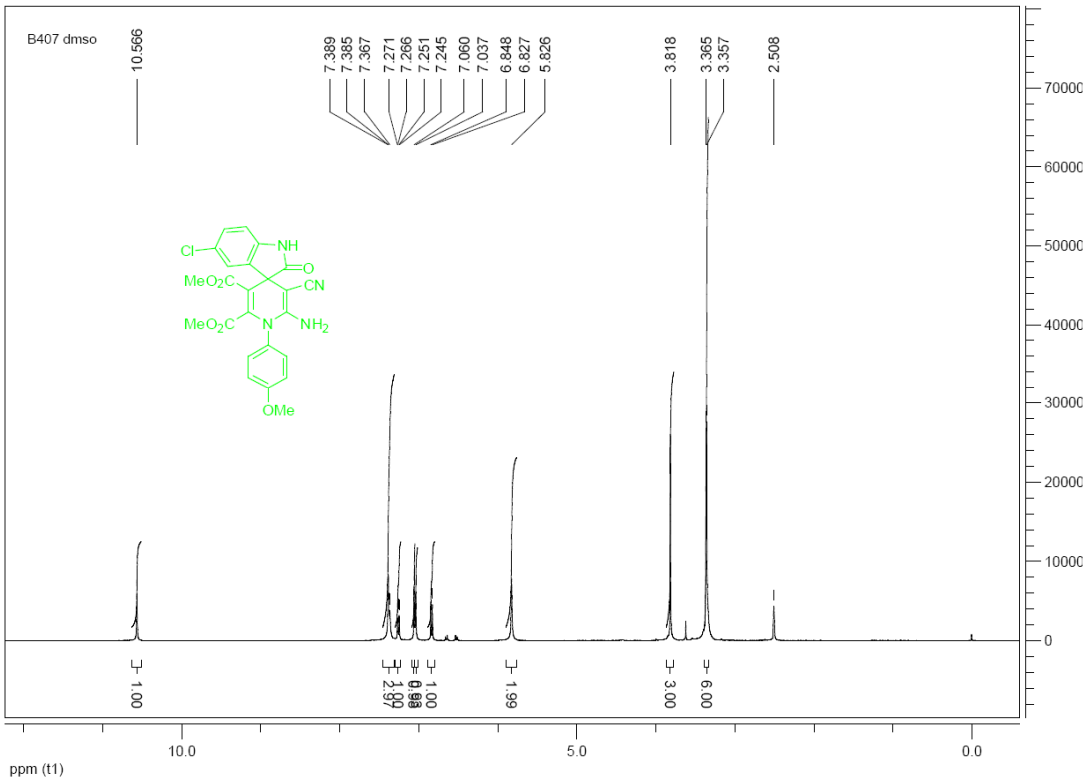
Spectroscopic Data for Compounds 11a-k

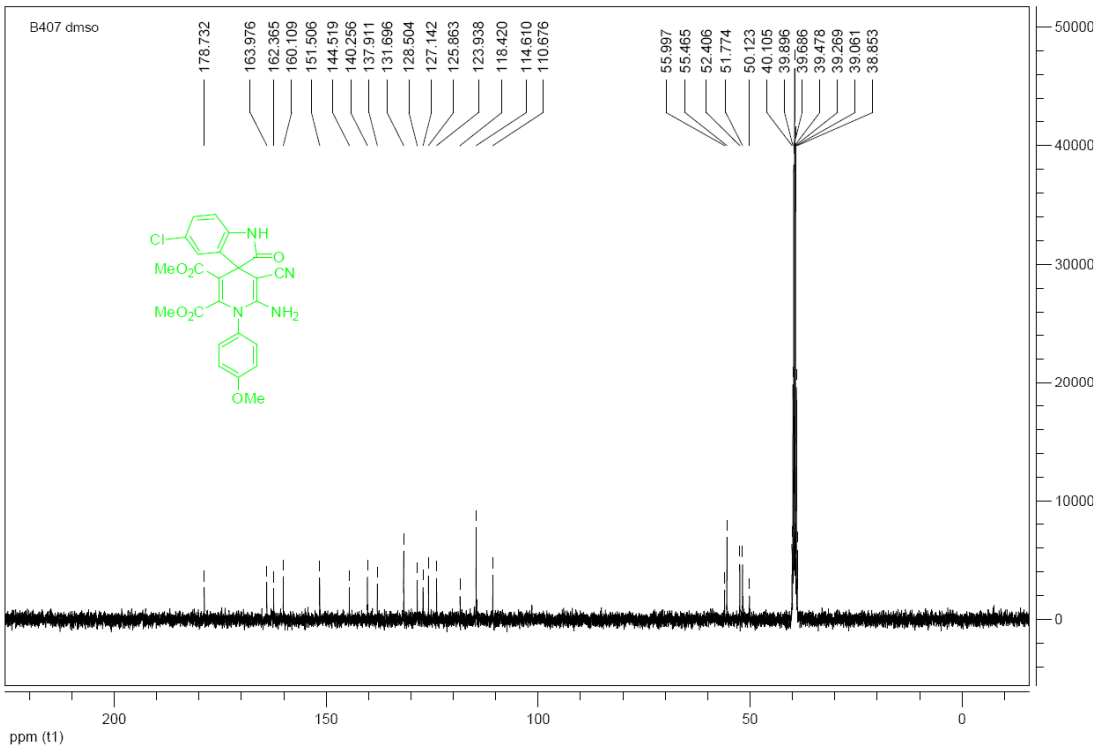
Dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11b)



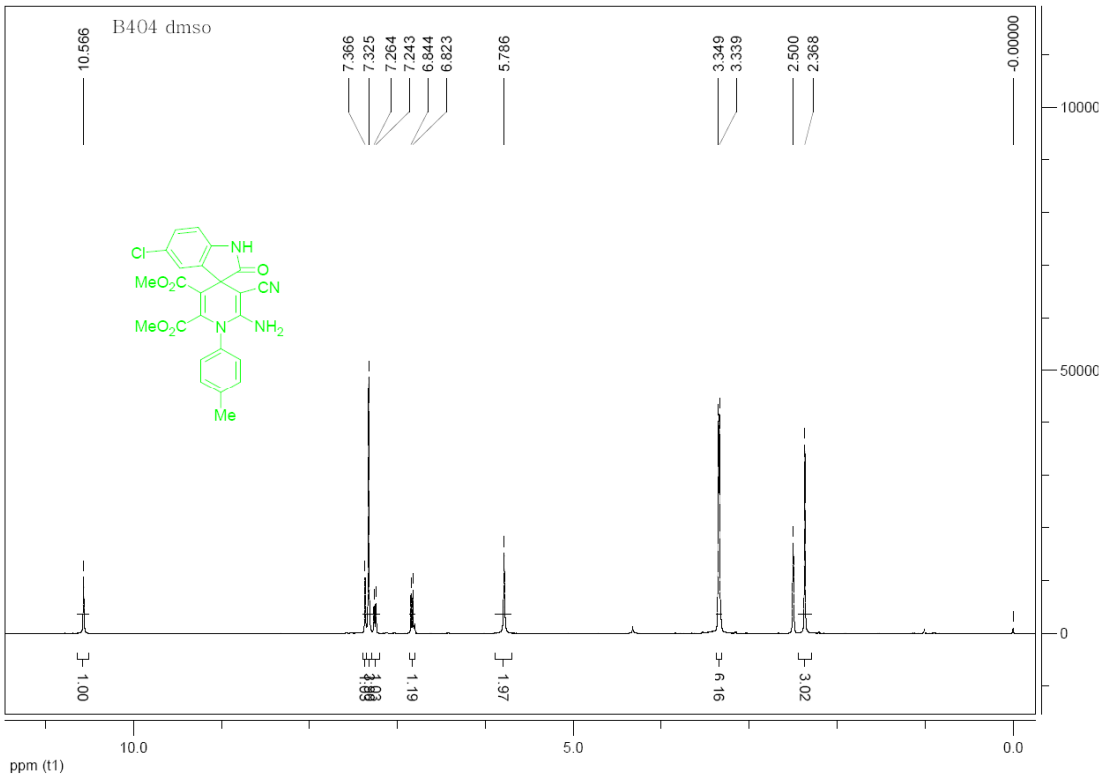


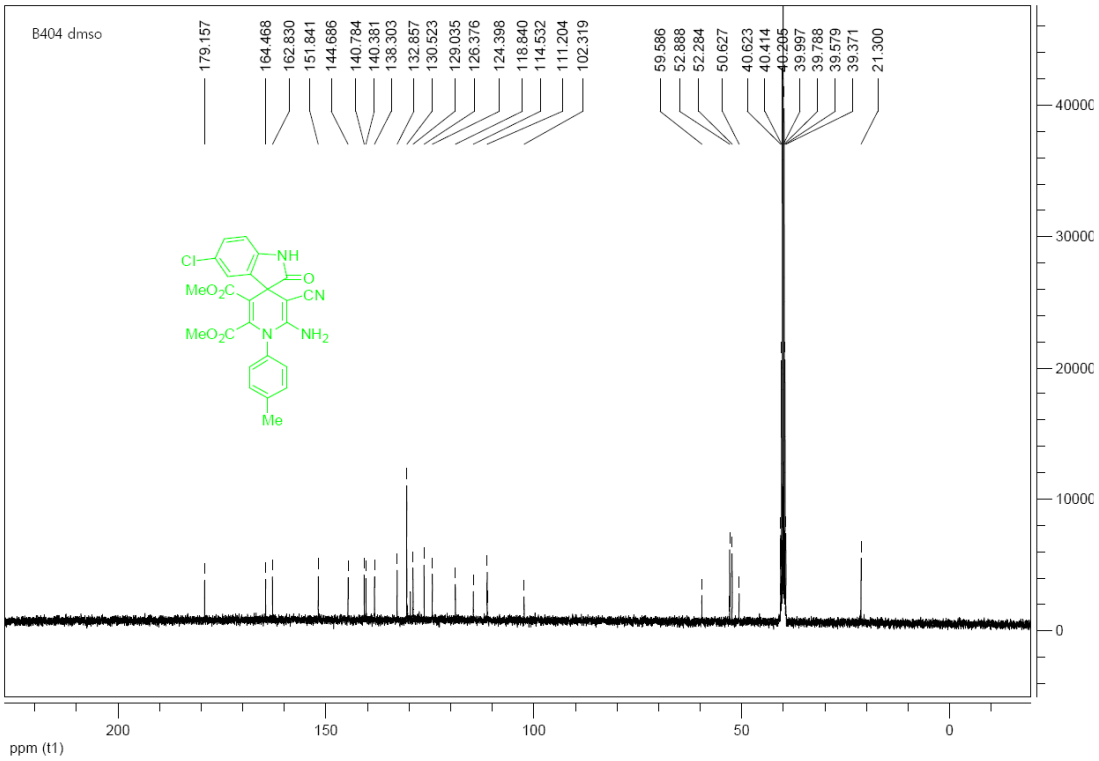
Dimethyl 2'-amino-5-chloro-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11c)



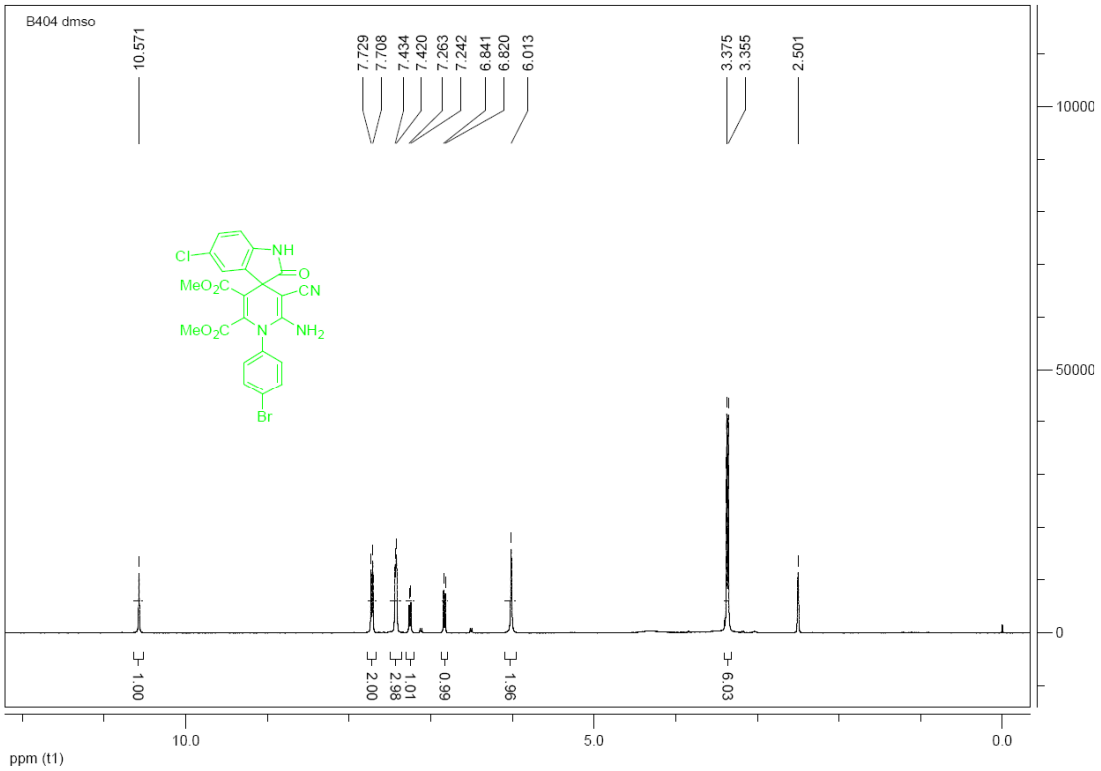


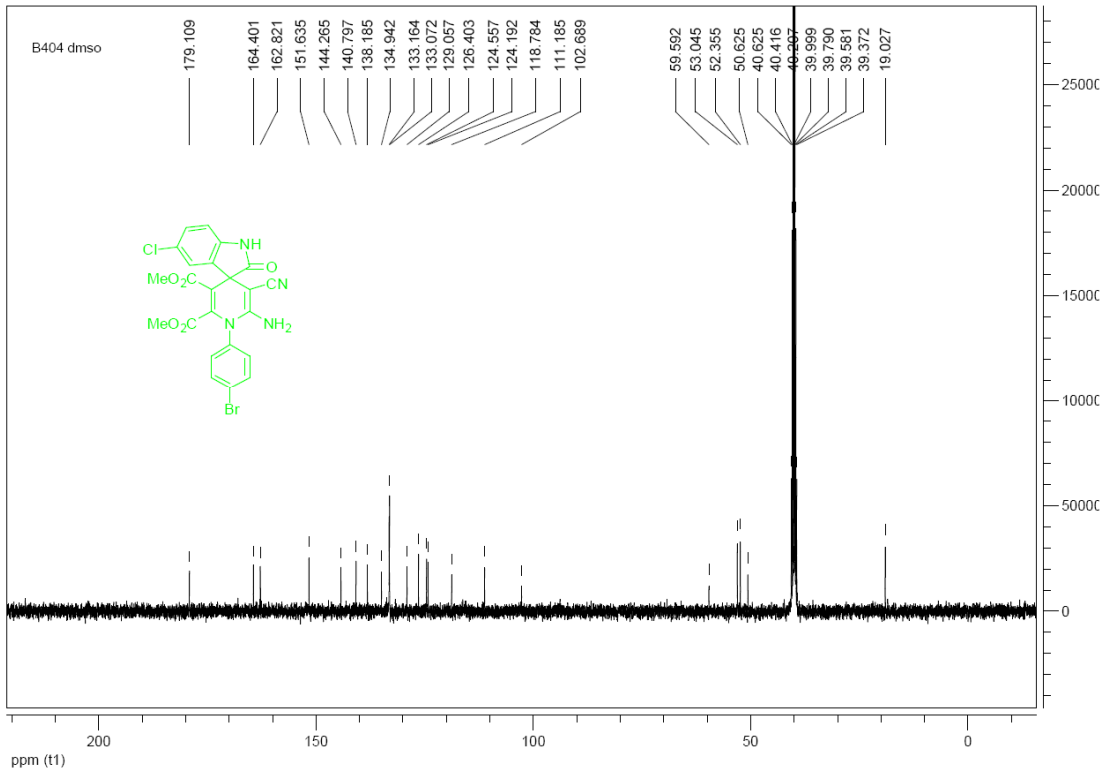
Dimethyl 2'-amino-5-chloro-3'-cyano-2-oxo-1'-(p-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11d)



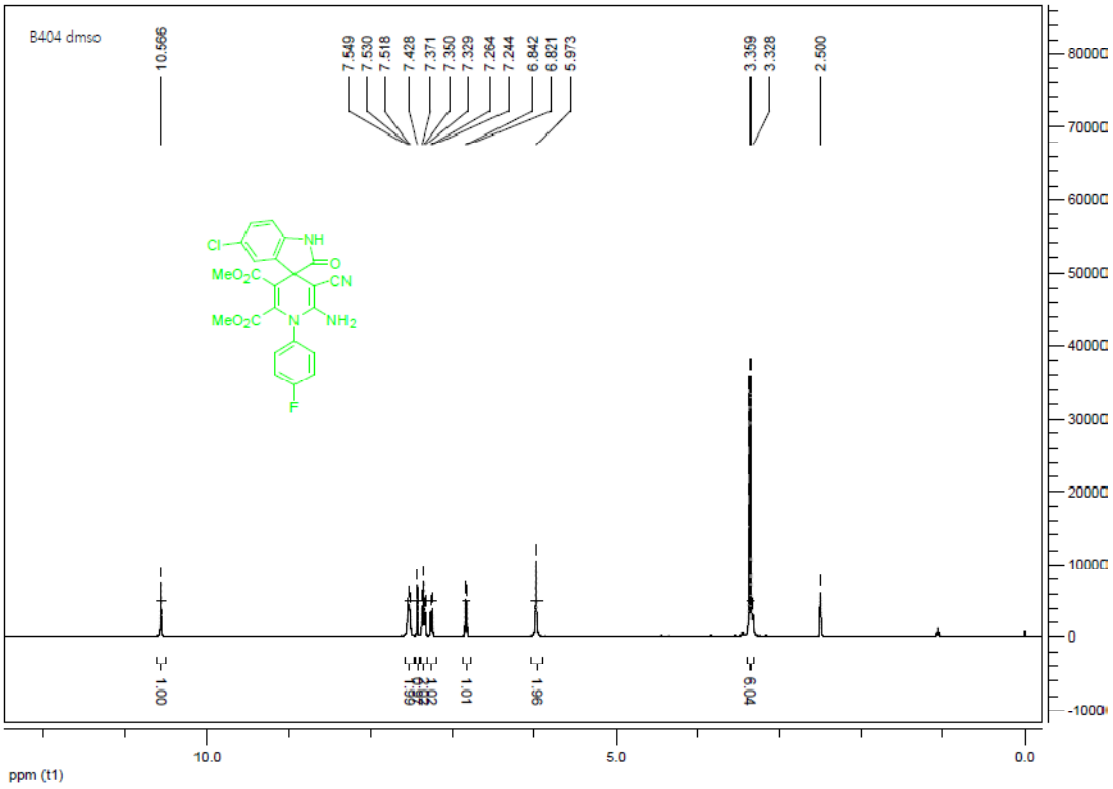


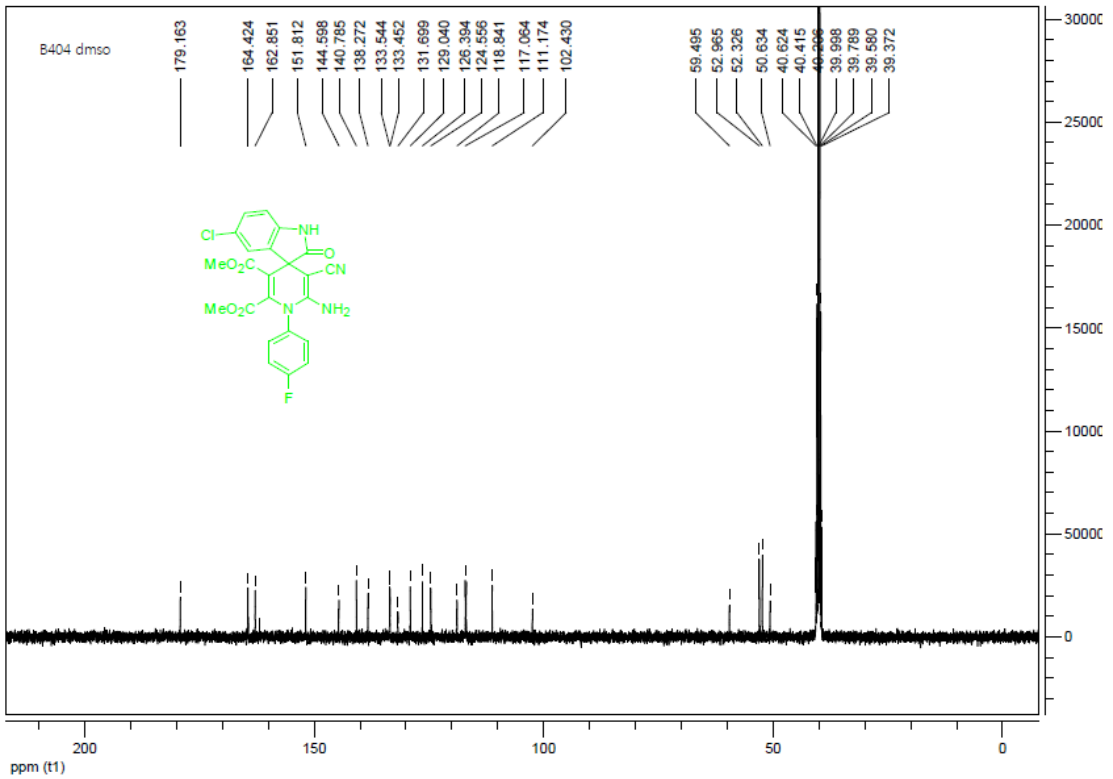
Dimethyl 2'-amino-1'-(4-bromophenyl)-5-chloro-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11e)



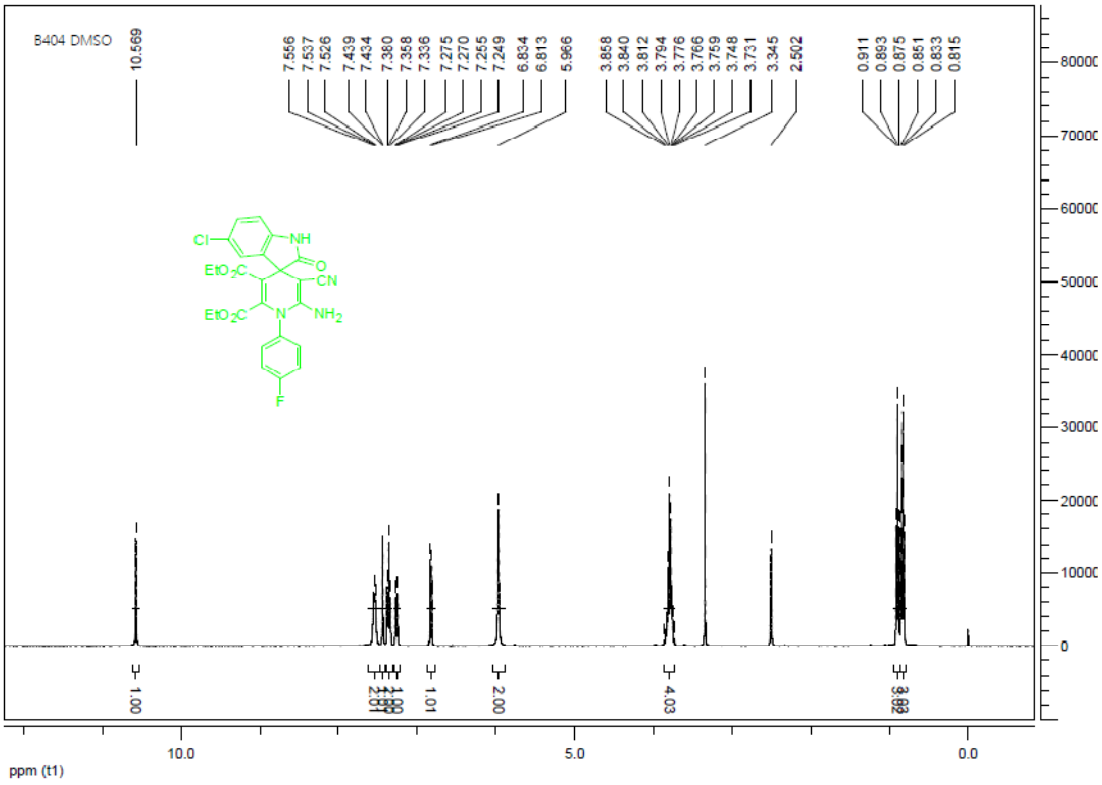


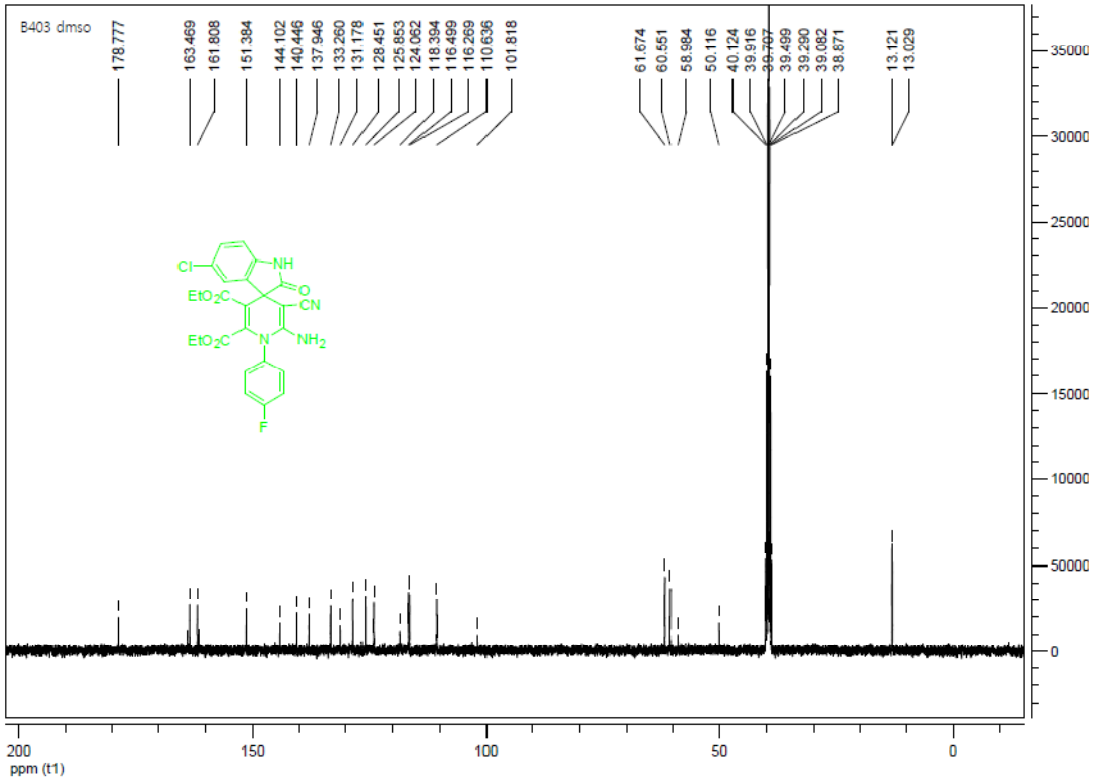
Dimethyl 2'-amino-5-chloro-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11f)



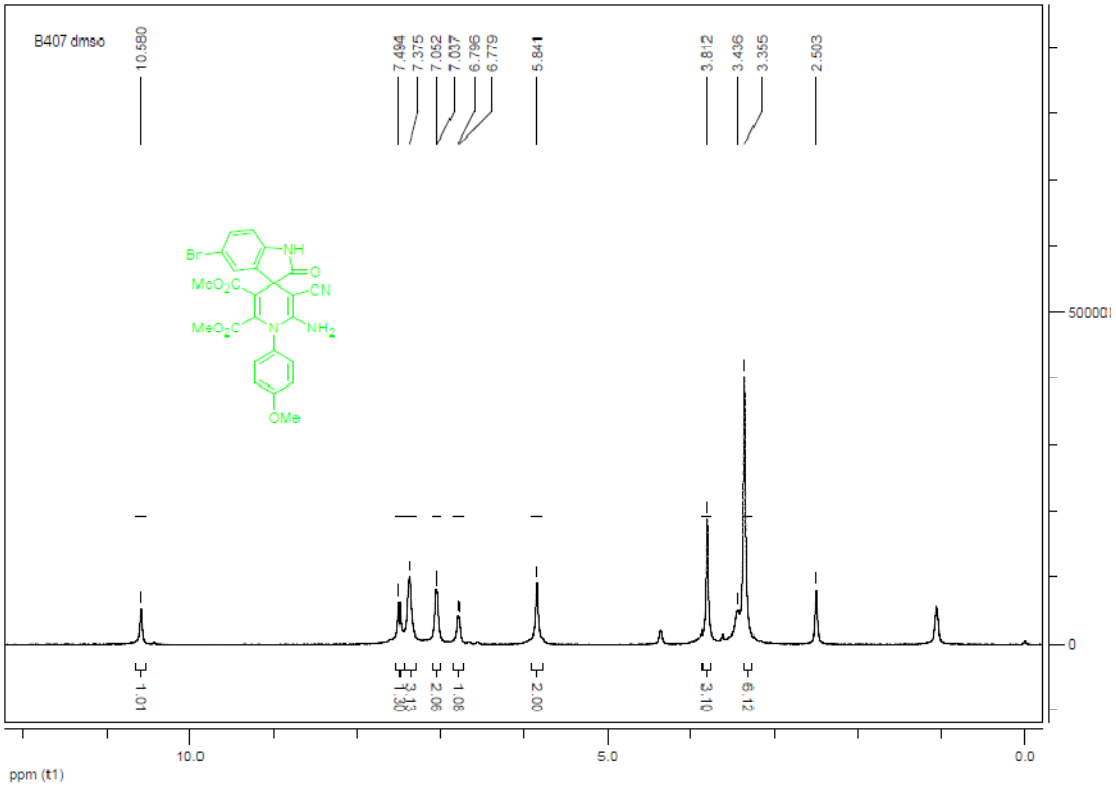


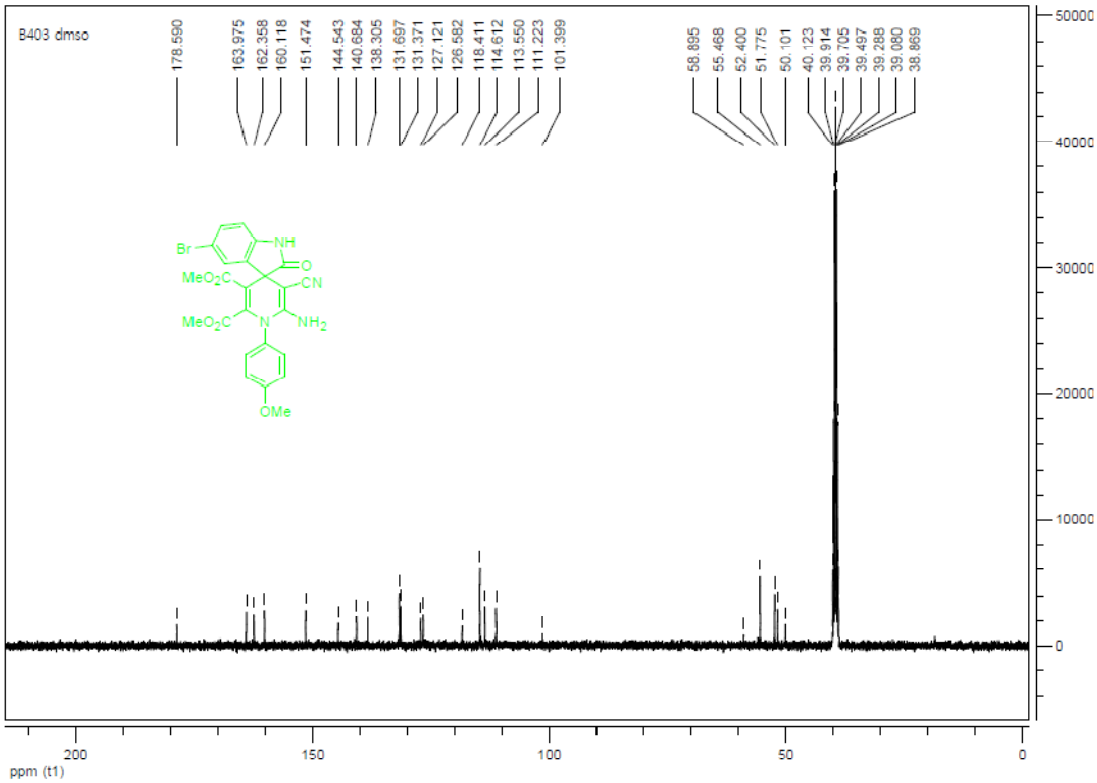
Diethyl 2'-amino-5-chloro-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11g)



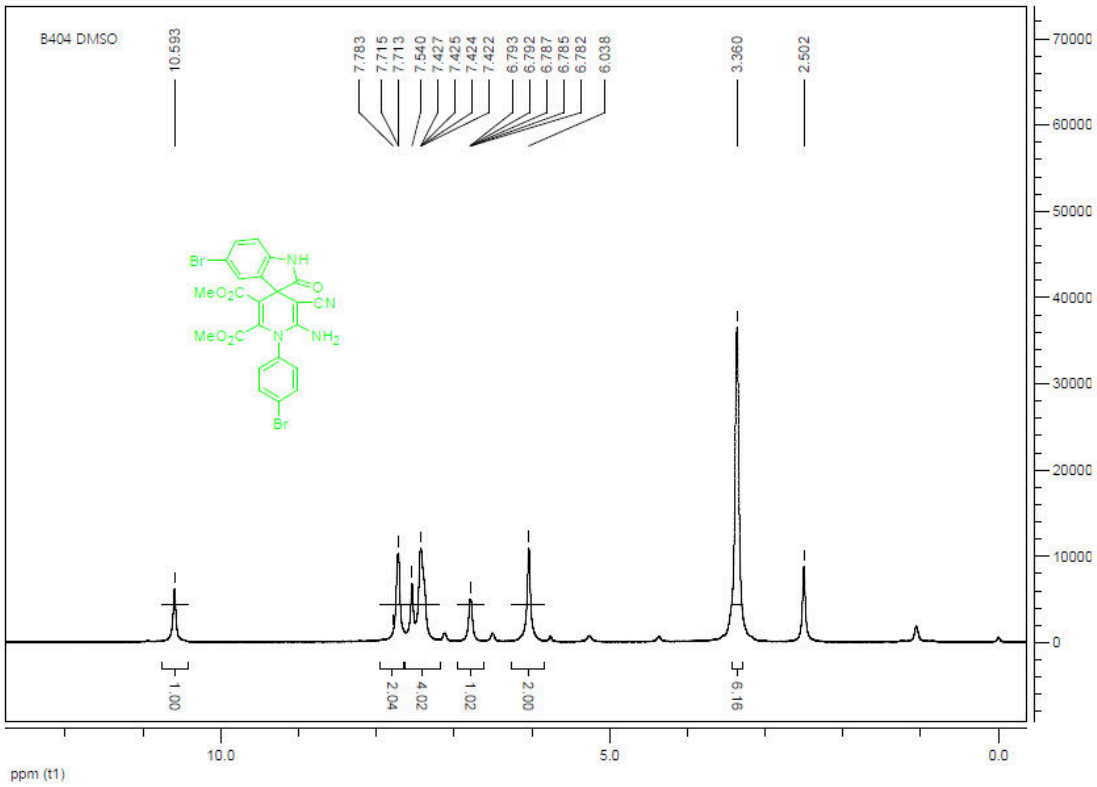


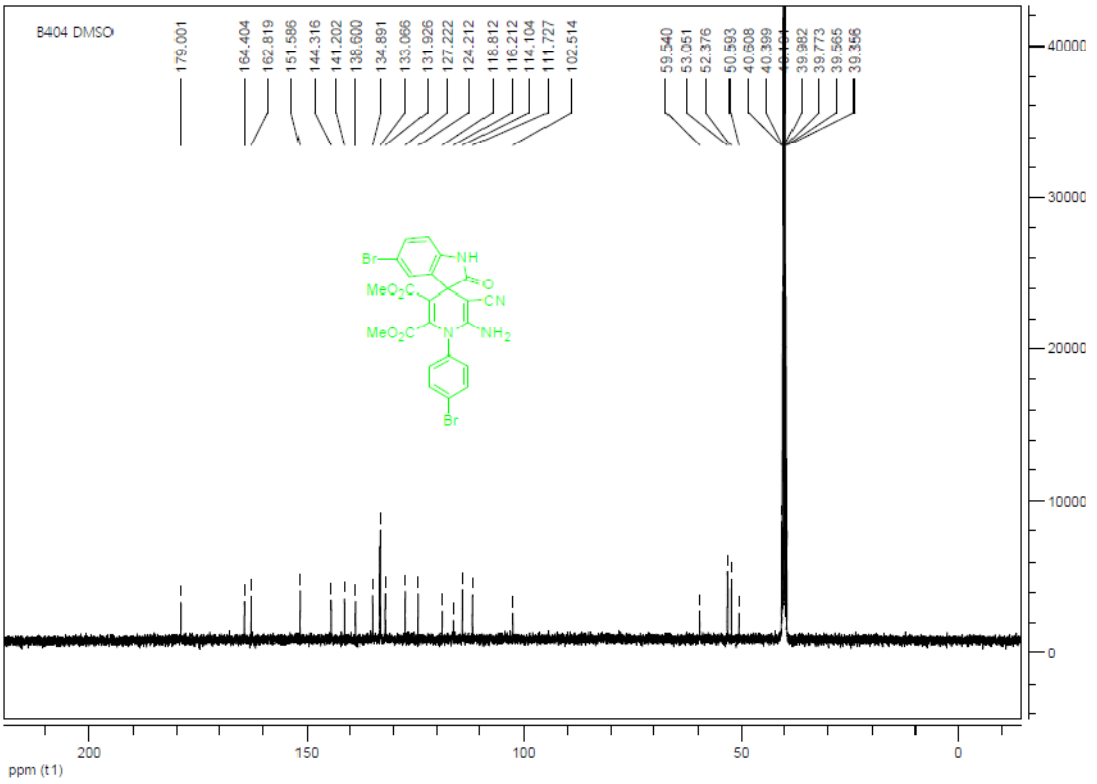
Dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11h)



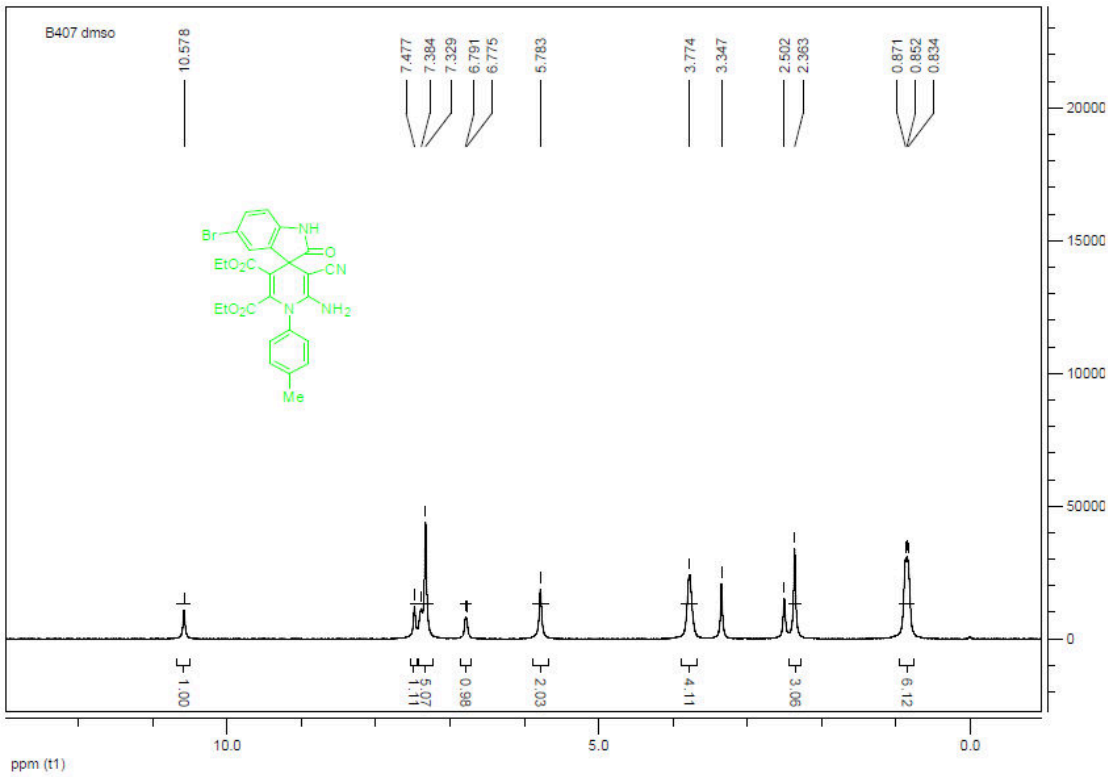


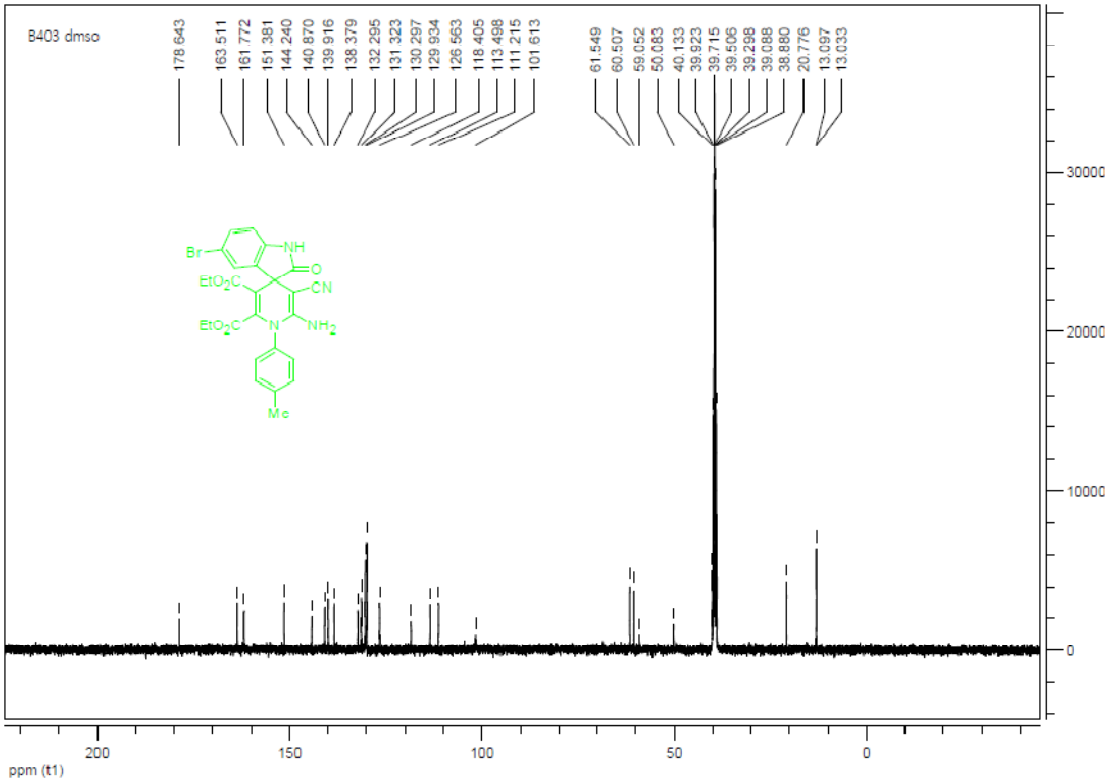
Dimethyl 2'-amino-5-bromo-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11i)





Diethyl 2'-amino-5-bromo-3'-cyano-2-oxo-1'-(p-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11j)





Dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-5-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (11k)