Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Multicomponent approaches to 8-carboxylnaphthyl functionalized pyrazolo[3,4-*b*]pyridine derivatives

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Experimental Section

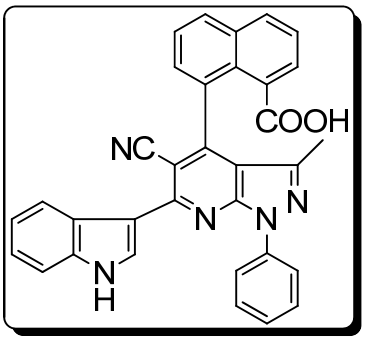
General Experimental method

All reactions were carried out in oven-dried glassware. Progresses of reactions were monitored by Thin Layer Chromatography (TLC). IR spectra were recorded on an FT-IR spectrometer using KBr optics. NMR spectra were recorded at room temperature in DMSO-d_6 at 300/400 Hz and 75/100 Hz. High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source. X-Ray diffraction data were recorded with graphite monochromatic MoKα radiation. Compounds such as 3-cyanoacetyl indoles **1** were previously prepared by Kreher and Wagner[1] and by Bergman[2] via a new facile approach starting from indoles and cyanoacetic acid.

Typical procedure for the synthesis of 8-(5-cyano-3-methyl-6-(1-methyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (4b). A mixture of 3-cyanoacetyl indole **1** (0.5 mmol) with an equimolar amount of acenaphthylene-1,2-dione **2** and 3-methyl-1-phenyl-1*H*-pyrazol-5-amine **3** in 4 mL HOAc at 120 ^{o}C was stirred for 9 h (the reaction progress was monitored by TLC analysis). After the completion of the reaction, the reaction mixture was allowed to cool to room temperature and filtered. The precipitate was washed with ethanol (8 mL) and dried to afford the analytically pure product **4b**.

Reference

1. R. Kreher, P. H. Wagner, *Chem*. *Ber*. 1980, **113**, 3675.
2. J. Slatt, I. Romero, J. Bergman, *Synthesis* 2004, 2760.



8-(5-cyano-6-(1*H*-indol-3-yl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4a**).

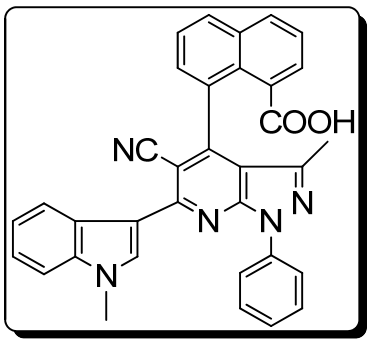
Solid; m.p. >300 °C.

IR (KBr): *v* 3341(s), 2218(m), 1692(s), 1532(s), 1503(s), 1346(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.61 (s, 1H, COOH), 11.86 (s, 1H, NH), 8.52 (d, J = 7.2 Hz, 1H, ArH), 8.35-8.27 (m, 5H, ArH), 7.84-7.76 (m, 3H, ArH), 7.69 (t, J= 7.2 Hz, 1H, ArH), 7.62 (t, J = 7.6 Hz, 2H, ArH), 7.56 (d, J = 7.6, 1H, ArH), 7.41 (d, J = 7.2 Hz, 1H, ArH), 7.28-7.23 (m, 2H, ArH), 1.72 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.26, 155.41, 152.50, 150.40, 144.20, 138.88, 136.60, 133.94, 131.54, 131.03, 130.99, 129.43, 129.27, 128.58, 127.47, 126.21, 126.06, 125.81, 122.70, 121.81, 120.96, 120.89, 119.04, 113.33, 112.72, 112.39, 100.40, 13.92.

HRMS: calculated for $C_{33}H_{21}N_5O_2$ [M^+]: 519.1695, found 519.1692.



8-(5-cyano-3-methyl-6-(1-methyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4b**).

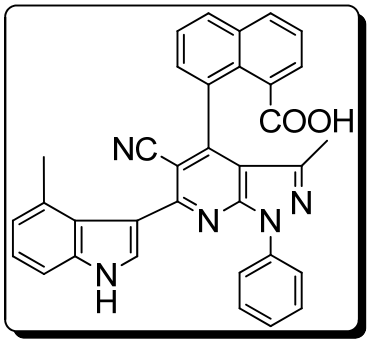
Solid; m.p. >300 °C.

IR (KBr): *v* 3433(s), 2218(m), 1690(s), 1570(s), 1534(s), 1371(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.65 (s, 1H, COOH), 8.51 (d, J = 7.6 Hz, 1H, ArH), 8.33-8.28 (m, 5H, ArH), 7.82-7.76 (m, 3H, ArH), 7.69 (t, J = 7.2 Hz, 1H, ArH), 7.64-7.60 (m, 3H, ArH), 7.41 (t, J = 7.2 Hz, 1H, ArH), 7.35-7.32 (m, 1H, ArH), 7.27 (t, J = 7.2 Hz, 1H, ArH), 3.94 (s, 3H, CH_3), 1.72 (s, 3H, CH_3).

^{13}C NMR (100 Hz, DMSO-d_6) (δ, ppm): 170.07, 154.98, 152.45, 150.38, 144.18, 138.83, 137.10, 133.95, 132.90, 131.98, 131.79, 131.06, 130.99, 130.93, 129.32, 128.72, 127.43, 126.42, 126.30, 125.92, 125.82, 122.81, 121.96, 121.24, 120.94, 118.78, 112.72, 112.40, 110.71, 100.41, 33.33, 13.89.

HRMS: calculated for $C_{34}H_{23}N_5O_2$ [M^+]: 533.1852, found 533.1841.



8-(5-cyano-3-methyl-6-(4-methyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4c**).

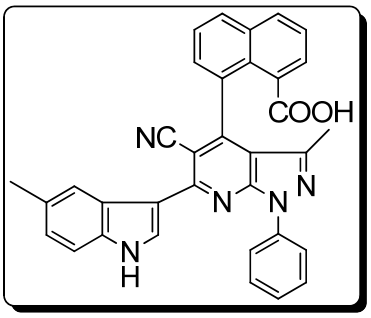
Solid; m.p. >300 °C.

IR (KBr): v 3423(s), 2218(m), 1688(s), 1575(s), 1503(s), 1350(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 11.50 (s, 1H, COOH), 10.42 (s, 1H, NH), 8.42 (d, J = 8.4 Hz, 1H,ArH), 8.15 (d, J = 6.8 Hz, 1H, ArH), 8.10 (d, J = 8.4 Hz, 1H, ArH), 7.95 (t, J = 7.2 Hz, 1H, ArH), 7.86 (t, J = 7.2 Hz, 1H, ArH), 7.61 (s, 2H, ArH), 7.53-7.46 (m, 4H, ArH), 7.37 (t, J = 6.4 Hz, 1H, ArH), 7.27 (d, J = 8 Hz, 1H, ArH), 7.05 (t, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 6.8 Hz, 1H, ArH), 2.64 (s, 3H, CH_3), 1.06 (s, 3H, CH_3).

^{13}C NMR (100 Hz, DMSO-d_6) (δ, ppm): 170.02, 157.42, 151.04, 149.96, 144.26, 138.84, 136.40, 133.87, 131.90, 131.73, 131.04, 130.99, 130.64, 130.28, 129.29, 128.74, 128.52, 127.36, 126.09, 125.75, 124.79, 122.22, 121.77, 120.48, 117.96, 114.34, 113.43, 109.95, 104.68, 21.41, 14.08.

HRMS(ESI): calculated for $C_{34}H_{23}N_5O_2$ [MH^+]: 534.1930, found 534.1925.



8-(5-cyano-3-methyl-6-(5-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4d**).

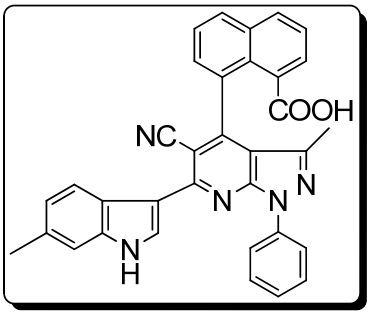
Solid; m.p. >300 °C.

IR (KBr): *v* 3346(s), 2219(m), 1719(s), 1570(s), 1531(s), 1348(m)cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.59 (s, 1H, COOH), 11.75 (s, 1H, NH), 8.46 (s, 1H, ArH), 8.36 (d, J = 9 Hz, 3H, ArH), 8.28 (d, J = 6.3 Hz, 2H, ArH), 7.84-7.77 (m. 3H, ArH), 7.75-7.62 (m, 4H, ArH), 7.44 (d, J = 7.8 Hz, 2H, ArH), 7.10 (d, J = 8.1 Hz, 1H, ArH), 2.47 (s, 3H, CH_3), 1.69 (s, 3H,CH_3).

^{13}C NMR (100 Hz, DMSO-d_6) (δ, ppm): `170.56, 155.99, 152.94, 151.00, 144.67, 139.52, 135.51, 134.51, 132.62, 132.26, 131.61, 131.50, 130.23, 130.05, 129.71, 129.17, 128.67, 126.94, 126.70, 126.35, 126.24, 124.75, 122.51, 121.63, 119.69, 113.42, 113.06, 112.45, 100.43, 80.08, 79.64, 79.20, 22.19, 14.38.

HRMS: calculated for $C_{34}H_{23}N_5O_2$ [M^+]: 533.1852, found 533.1847.



8-(5-cyano-3-methyl-6-(6-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4e**).

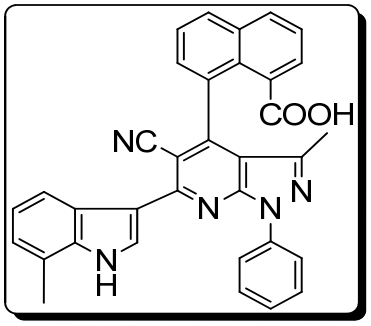
Solid; m.p. >300 °C.

IR (KBr): *v* 3361(s), 2215(m), 1666(s), 1570(s), 1529(s), 1345(m) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.61 (s, 1H, COOH), 11.72 (s, 1H, NH), 8.41 (d, J = 8.4 Hz, 1H, ArH), 8.34-8.30 (m, 5H, ArH), 7.84-7.75 (m, 3H, ArH), 7.70 (d, J = 8.1 Hz, 1H, ArH), 7.63 (t, J = 7.8 Hz, 2H, ArH), 7.43-7.38 (m, 1H, ArH), 7.34 (s, 1H, ArH), 7.06 (d, J = 8.1 Hz, 1H, ArH), 2.46 (s, 3H, CH_3), 1,71 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.10, 155.45, 152.39, 150.43, 144.14, 138.86, 137.02, 133.95, 132.05, 131.97, 131.77, 131.01, 129.27, 128.89, 128.68, 127.45, 126.23, 125.89, 125.79, 123.97, 122.78, 121.65, 120.96, 119.07, 113.28, 112.57, 112.09, 100.14, 21.48, 13.89.

HRMS: calculated for $C_{34}H_{23}N_5O_2$ [M^+]: 533.1852, found 533.1860.



8-(5-cyano-3-methyl-6-(7-methyl-1H-indol-3-yl)-1-phenyl-1H-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4f**).

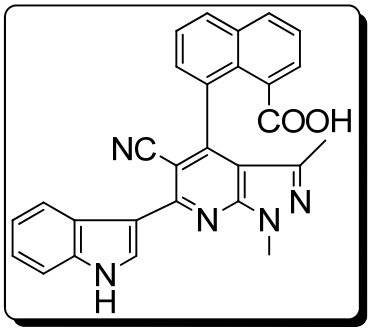
Solid; m.p. >300 °C.

IR (KBr): v 3413(s), 2230(m), 1692(s), 1573(s), 150(s)3, 1347(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 11.74 (s, 1H, COOH), 10.14 (s, 1H, NH), 8.45 (d, J = 8 Hz, 1H, ArH), 8.17 (d, J = 7.2 Hz, 1H, ArH), 8.12 (d, J = 8.4 , 1H, ArH), 7.97 (t, J = 7.6 Hz, 1H, ArH), 7.86 (t, J = 7.6 Hz, 2H, ArH), 7.68-7.65 (m, 3H, ArH), 7.54 (t, J = 7.6 Hz, 3H, ArH), 7.39 (t, J = 7.2 Hz, 1H, ArH), 7.09 (t, J = 7.2 Hz, 1H, ArH), 7.00 (d, J = 6.8 Hz, 1H, ArH), 1.07 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.17, 155.52, 152.38, 150.48, 144.19, 138.93, 136.11, 133.97, 132.08, 131.78, 131.01, 129.25, 129.07, 128.72, 127.49, 126.18, 125.86, 125.79, 123.27, 121.50, 121.24, 120.87, 119.49, 119.11, 113.81, 112.69, 100.46, 16.99, 13.95.

HRMS: calculated for $C_{34}H_{23}N_5O_2$ [M^+]: 533.1852, found 533.1846.



8-(5-cyano-6-(1*H*-indol-3-yl)-1,3-dimethyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4g**).

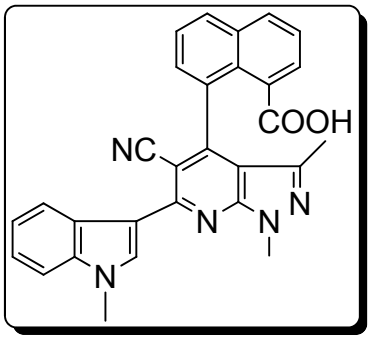
Solid; m.p. >300 °C.

IR (KBr): *v* 3212(s), 2222(m), 1678(s), 1577(s), 1527(s), 1349(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.50 (s, 1H, COOH), 11.79 (s, 1H, NH), 8.61 (d, J = 4.8 Hz, 1H, ArH), 8.34 (s, 1H,ArH), 8.26 (d, J = 7.6 Hz, 2H, ArH), 7.80-7.65 (m, 4H, ArH), 7.55-7.54 (m, 1H, ArH), 7.26 (s, 2H, ArH), 4.09 (s, 3H, CH_3), 1.58 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm):176.61, 161.77, 159.06, 157.55, 148.37, 143.32, 140.76, 138.90, 138.50, 138.20, 137.72, 137.63, 135.67, 135.45, 134.32, 133.12, 132.65, 132.48, 129.37, 129.12, 127.70, 126.19, 120.17, 118.95, 117.60, 105.76, 40.30, 20.27.

HRMS: calculated for $C_{28}H_{19}N_5O_2$ [M^+]: 457.1539, found 457.1541.



8-(5-cyano-1,3-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4h**).

Solid; m.p. >300 °C.

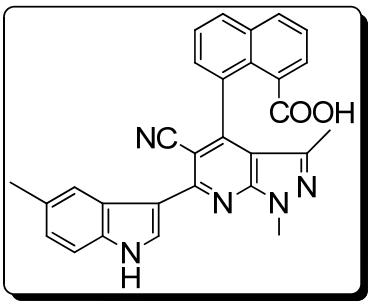
IR (KBr): *v* 3439(s), 2215(m), 1683(s), 1539(s), 1452(s), 1370(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.52 (s, 1H, COOH), 8.61 (d, J = 7.6 Hz, 1H, ArH),

8.30-8.25 (m, 3H, ArH), 7.80-7.74 (m, 2H, ArH), 7.70-7.65 (m, 2H, ArH), 7.59 (d, J = 7.6 Hz, 1H,ArH), 7.35-7.28 (m, 2H, ArH), 4.08 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 1.58 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 176.62, 161.32, 159.11, 157.48, 148.36, 143.82, 140.74, 139.27, 138.81, 138.55, 138.15, 137.74, 137.67, 135.51, 134.31, 133.47, 132,68, 132.51, 129.48, 129.30, 127.99, 126.05, 119.23, 117.58, 117.29, 105.70, 40.32, 40.06, 20.29.

HRMS: calculated for $C_{29}H_{21}N_5O_2$ [M^+]: 471.1695, found 471.1696.



8-(5-cyano-1,3-dimethyl-6-(5-methyl-1*H*-indol-3-yl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4i**).

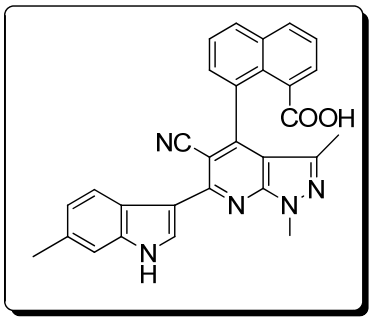
Solid; m.p. >300 °C.

IR (KBr): v 3195(s), 2222(m), 1679(s), 1579(s), 1527(s), 1339(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.47 (s, 1H, COOH), 11.68 (s, 1H, NH), 8.42 (s, 1H, ArH), 8.28-8.25 (m, 3H, ArH), 7.81-7.74 (m, 2H, ArH), 7.71-7.66 (m, 2H, ArH), 7.43 (d, J = 8.4 Hz, 1H, ArH), 7.09 (d, J = 4 Hz, 1H, ArH), 4.10 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 1.58 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.90, 155.12, 152.26, 150.75, 141.60, 134.90, 133.95, 132.10, 131.75, 131.42, 130.98, 130.81, 129.49, 128.97, 128.72, 127.58, 126.64, 125.81, 125.67, 124.15, 122.16, 119.61, 112.91, 111.86, 110.65, 98.75, 33.49, 21.89, 13.55.

HRMS: calculated for $C_{29}H_{21}N_5O_2$ [M^+]: 471.1695, found 471.1694.



8-(5-cyano-1,3-dimethyl-6-(6-methyl-1H-indol-3-yl)-1H-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoi

c acid (**4j**).

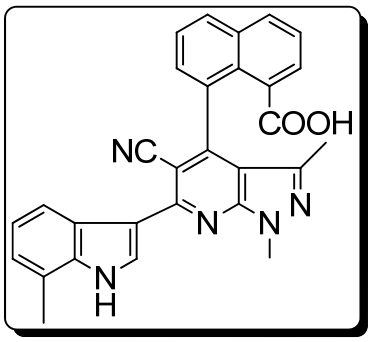
Solid; m.p. >300 °C.

IR (KBr): *v* 3385(s), 2212(m), 1713(s), 1581(s), 1539(s), 1392(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.51 (s, 1H, COOH), 11.65 (s, 1H, NH), 8.49 (d, J = 8 Hz, 1H, ArH), 8.26 (d, J = 9.6 Hz, 3H, ArH), 7.80-7.73 (m, 2H, ArH), 7.70-7.65 (m, 2H, ArH), 7.32 (s, 1H, ArH), 7.08 (d, J = 8 Hz, 1H, ArH), 4.08 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 1.57 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.88, 155.00, 152.29, 150.73, 141.54, 136.94, 133.95, 132.09, 131.77, 131.40, 130.97, 130.85, 128.69, 128.40, 127.52, 125.87, 125.71, 124.22, 122.74, 122.18, 119.54, 113.26, 111.93, 110.64, 98.65, 33.48, 21.51, 13.54.

HRMS: calculated for $C_{29}H_{21}N_5O_2$ [M^+]: 471.1695, found 471.1695.



8-(5-cyano-1,3-dimethyl-6-(7-methyl-1H-indol-3-yl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoi

c acid (**4k**).

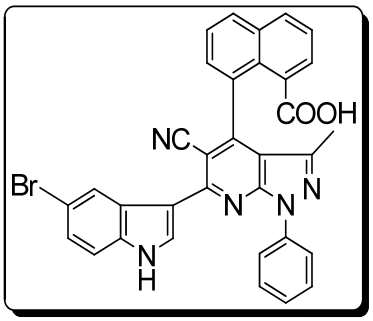
Solid; m.p. >300 °C.

IR (KBr): *v* 3246(s), 2219(m), 1686(m), 1575(s), 1527(s), 1347(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.52 (s, 1H, COOH), 11.79 (s, 1H, NH), 8.43 (d, J = 7.6 Hz, 1H, ArH), 8.30 (s, 1H, ArH), 8.26 (d, J = 8 Hz, 2H, ArH), 7.80-7.74 (m, 2H, ArH), 7.71-7.65 (m, 2H, ArH), 7.16 (t, J = 7.2 Hz, 1H, ArH), 7.06 (d, J = 6.8 Hz, 1H, ArH), 4.08 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 1.59 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 176.62, 161.86, 159.03, 157.60, 148.39, 142.81, 140.78, 138.94, 138.48, 138.24, 137.72, 137.61, 135.44, 135.35, 134.35, 132.91, 132.61, 132.46, 129.90, 127.97, 127.90, 126.74, 126.23, 120.62, 117.61, 105.89, 40.29, 23.64, 20.27.

HRMS: calculated for $C_{29}H_{21}N_5O_2$ [M^+]: 471.1695, found 471.1696.



8-(6-(5-bromo-1*H*-indol-3-yl)-5-cyano-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4l**).

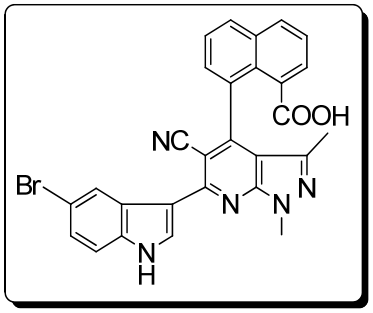
Solid; m.p. >300 °C.

IR (KBr): v 3339(s), 2216(m), 1662(s), 1530(s), 1503(s), 1340(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.59 (s, 1H, COOH), 12.05 (s, 1H, NH), 8.83 (s, 1H, ArH), 8.47 (s, 1H, ArH), 8.30 (s, 4H, ArH), 7.81 (d, J = 8 Hz, 2H, ArH), 7.74 (s, 1H, ArH), 7.68 (d, J = 6.8 Hz, ArH), 7.55 (d, J=8 Hz, 1H, ArH), 7.45-7.40 (m, 2H, ArH), 1.68 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 176.81, 161.47, 159.30, 157.05, 150.97, 145.63, 145.57, 142.11, 140.74, 138.82, 138.51, 137.88, 137.69, 137.45, 136.27, 135.41, 134.58, 134.19, 133.16, 132.68, 132.61, 132.07, 131.26, 127.91, 125.68, 121.16, 120.70, 119.61, 106.87, 20.53.

HRMS: calculated for $C_{33}H_{20}BrN_5O_2$ [M^+]: 597.0800, found 597.0795.



8-(6-(5-bromo-1*H*-indol-3-yl)-5-cyano-1,3-dimethyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4m**).

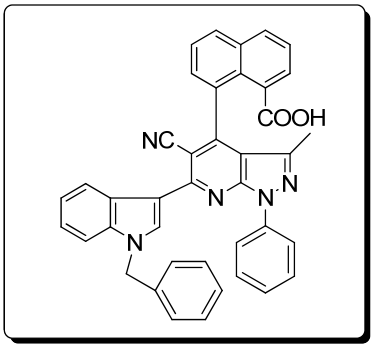
Solid; m.p. >300 °C.

IR (KBr): *v* 3438(s), 2216(m), 1708(s), 1582(s), 1537(s), 1350(m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 12.49 (s, 1H, COOH), 11.98 (s, 1H, NH), 8.77 (s, 1H, ArH), 8.38 (s,1H, ArH), 8.26 (s, 2H, ArH), 7.79 (t, J = 6.8 Hz, 1H, ArH), 7.72-7.67 (m, 4H, ArH), 7.54 (d, J = 8 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 4.09 (s, 3H, CH_3), 1.57 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 176.65, 161.09, 159.09, 157.34, 148.44, 142.01, 140.71, 138.80, 138.52, 137.98, 137.70, 136.89, 135.47, 134.81, 134.25, 132.64, 132.53, 131.91, 131.38, 126.04, 121.07, 119.61, 117,75, 105.67, 40.24, 20.24.

HRMS: calculated for $C_{28}H_{18}BrN_5O_2$ [M^+]: 535.0644, found 535.0635.



8-(6-(1-benzyl-1*H*-indol-3-yl)-5-cyano-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid(**4n**).

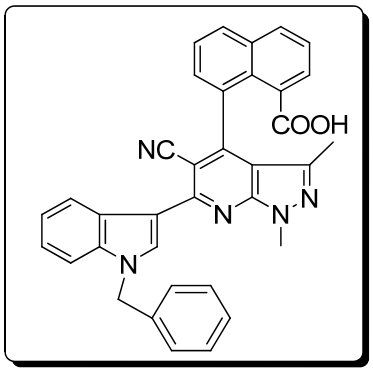
Solid; m.p. = 237.8 – 238.6 °C.

IR (KBr): *v* 3425(s), 3047(m), 2200(m), 1716(s), 1581(s), 1347(m)cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.65(s, 1H, COOH), 8.50(s, 2H, ArH), 8.33(d, J = 7.8Hz, 4H, ArH), 7.78(d, J = 11.1Hz, 3H, ArH), 7.71-7.61(m, 4H, ArH), 7.41-7.30(m, 8H, ArH), 5.60(s, 2H, CH_2), 1.71(s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 175.33, 160.20, 157.67, 155.62, 149.43, 144.08, 142.69, 141.64, 139.19, 137.77, 137.72, 137.24, 137.02, 136.31, 136.18, 134.54, 134.00, 133.01, 132.67, 132.00, 131.49, 131.16, 131.07, 128.20, 127.24, 126.61, 126.14, 124.00, 118.21, 118.14, 116.46, 106.03, 55.02, 19.07.

HRMS(ESI): calculated for $C_{40}H_{27}N_5O_2$ [MH^+]: 610.2243, found 610.2242.



8-(6-(1-benzyl-1*H*-indol-3-yl)-5-cyano-1,3-dimethyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid (**4o**).

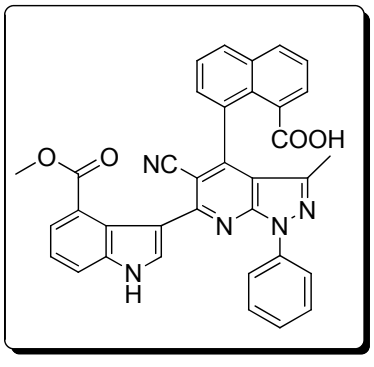
Solid; m.p. = 276.5-277.2°C.

IR (KBr): *v* 3442(s), 2937(m), 2202(m), 1699(s), 1544(s), 1388(m) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.55(s, 1H, COOH), 8.58(s, 1H, ArH), 8.46(s, 1H, ArH), 8.27-8.25(m, 2H, ArH), 7.76-7.59(m, 6H, ArH), 7.29(s, 6H, ArH), 5.59(s, 2H, CH_2), 4.08(s, 3H, CH_3), 1.58(s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 175.15, 166.85, 164.97，159.81, 157.60，155.99,142.86,141.65,139.25，137.35，137.06，136.66，136.28，136.27，136.23，134.06，132.60，131.19，131.02，128.13，128.09，127.77，126.58，124.52，118.31，116.29，108.55，104.62，55.01，38.84，18.78.

HRMS(ESI): calculated for $C_{35}H_{25}N_5O_2$ [MH^+]: 548.2087, found 548.2094.



8-(5-cyano-6-(4-(methoxycarbonyl)-1*H*-indol-3-yl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)-1-naphthoic acid(**4p**).

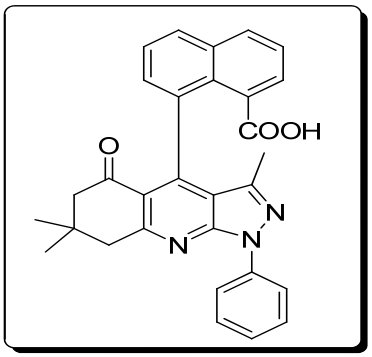
Solid; m.p. = 190.0-190.8°C.

IR (KBr): *v* 3394(s), 2214(m), 1704(s), 1566(m), 1504(s), 1349(m) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.11(s, 1H, COOH), 8.28(d, J = 6.9 Hz, 2H, ArH), 8.21(d, J = 7.5 Hz, 2H, ArH), 7.93(s, 1H, ArH), 7.81(s, 4H, ArH), 7.72-7.62(m, 2H,ArH), 7.49(d, J = 7.5 Hz, 2H, ArH), 7.34(t, J = 7.2 Hz, 2H, ArH), 3.23(s, 3H, CH_3), 1.88(s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.90, 168.42, 158.34, 151.46, 150.72, 144.89, 139.48, 137.91, 134.59, 132.69, 132.39, 131.69, 131.37, 129.83, 129.37, 128.04, 126.63, 126.49, 124.30, 123.53, 122.20, 121.07, 118.50, 117.23, 115.11, 113.83, 104.47, 51.98, 14.81.

HRMS(ESI): calculated for $C_{35}H_{23}N_5O_4$ [MH^+]: 578.1828, found 578.1838.



8-(3,7,7-trimethyl-5-oxo-1-phenyl-5,6,7,8-tetrahydro-1H-pyrazolo[3,4-b]quinolin-4-yl)-1-naphthoic acid(**4q**).

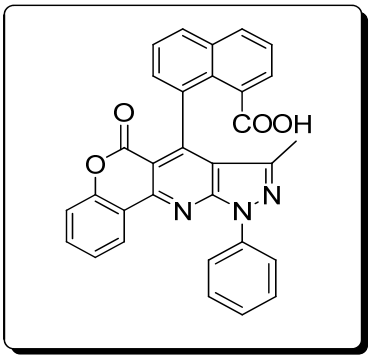
Solid; m.p. = 268.6-269.2°C.

IR (KBr): *v* 3406(s), 3039(m), 1706(s), 1533(s), 1468(s), 1363(m) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 11.93(s, 1H, COOH), 8.60-8.58(m, 2H, ArH), 8.53-8.49(m, 1H, ArH), 8.42-8.39(m, 1H, ArH), 8.30(d, J = 7.2Hz , 2H, ArH), 7.97-7.92(m, 2H, ArH), 7.61-7.57(m, 2H, ArH), 7.41-7.36(m, 1H, ArH), 3.85(s, 2H, CH_2), 2.78(s, 3H, CH_3), 2.39(s, 2H, CH_2), 1.08(s, 6H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 210.05, 198.91, 158.90, 151.23, 150.27, 145.17, 143.20, 142.07, 139.28, 136.12, 134.77, 134.42, 134.39, 133.75, 132.65, 129.09, 128.90, 126.08, 125.25, 114.88, 108.31, 58.98, 55.42, 37.57, 33.52, 32.48, 17.51.

HRMS(ESI): calculated for $C_{30}H_{25}N_3O_3$ [MH^+]: 476.1974, found 476.1969.

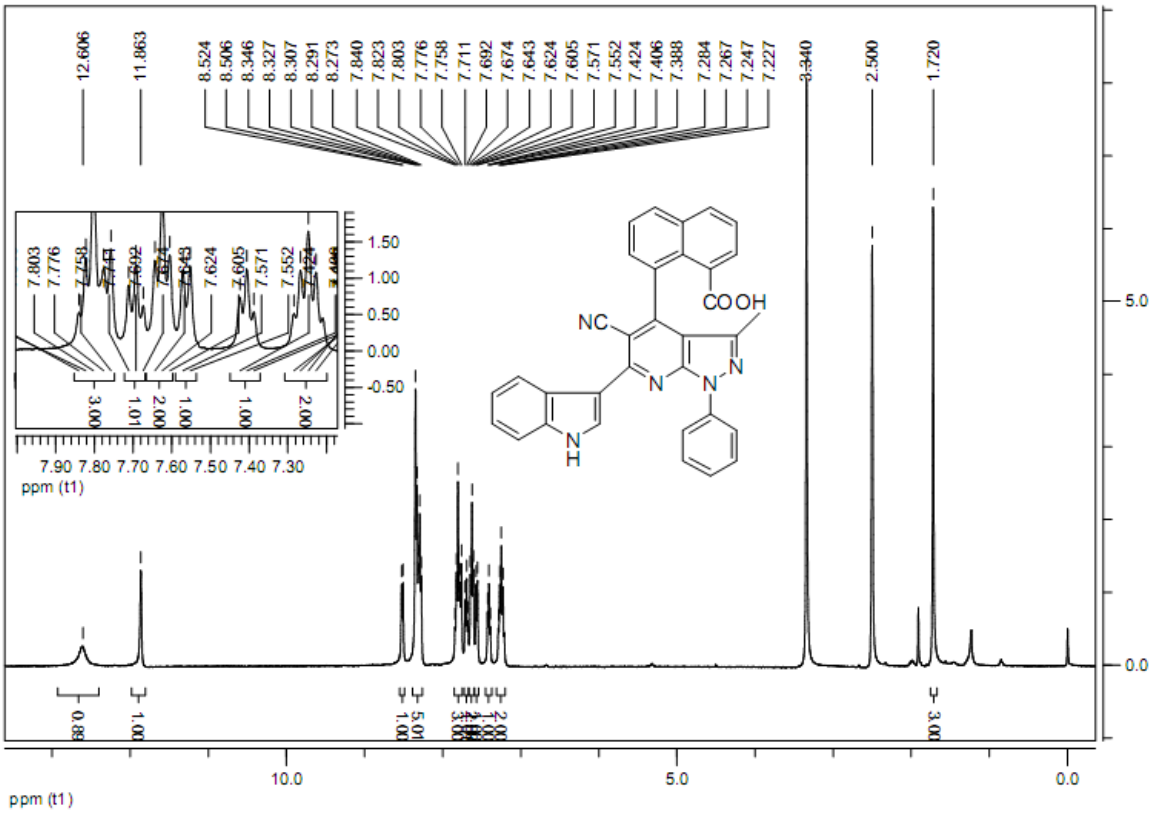


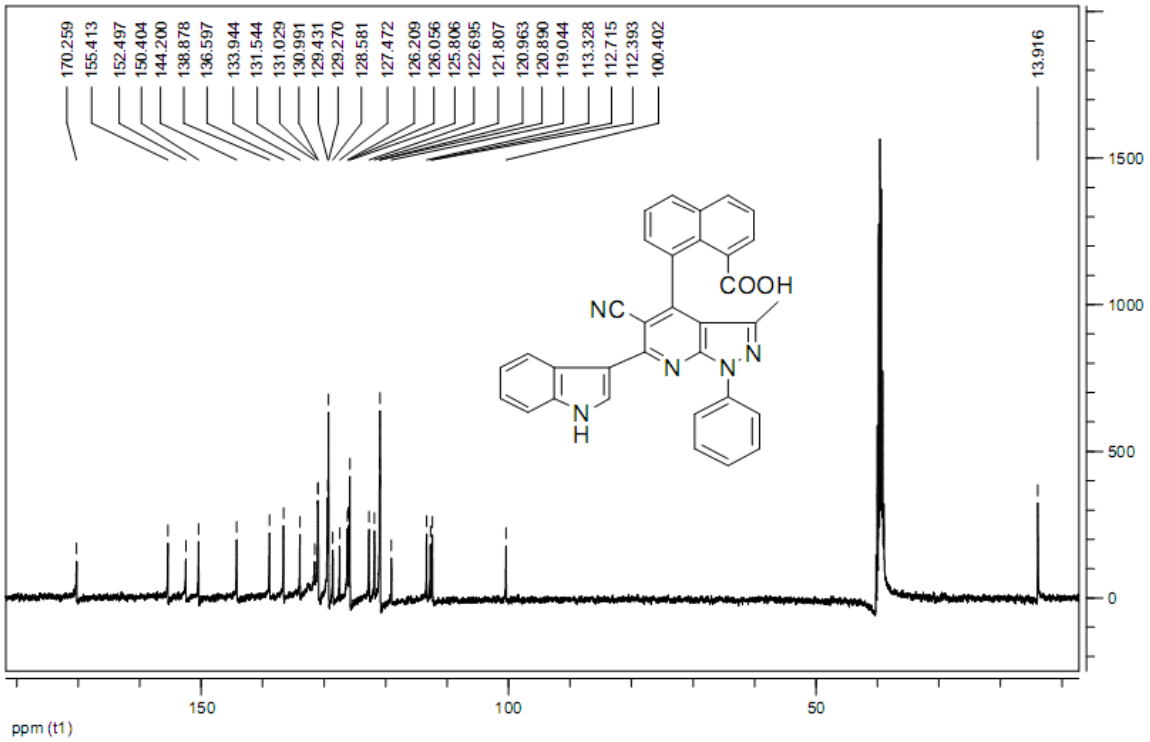
8-(8-methyl-6-oxo-10-phenyl-6,10-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-7-yl)-1-naphth

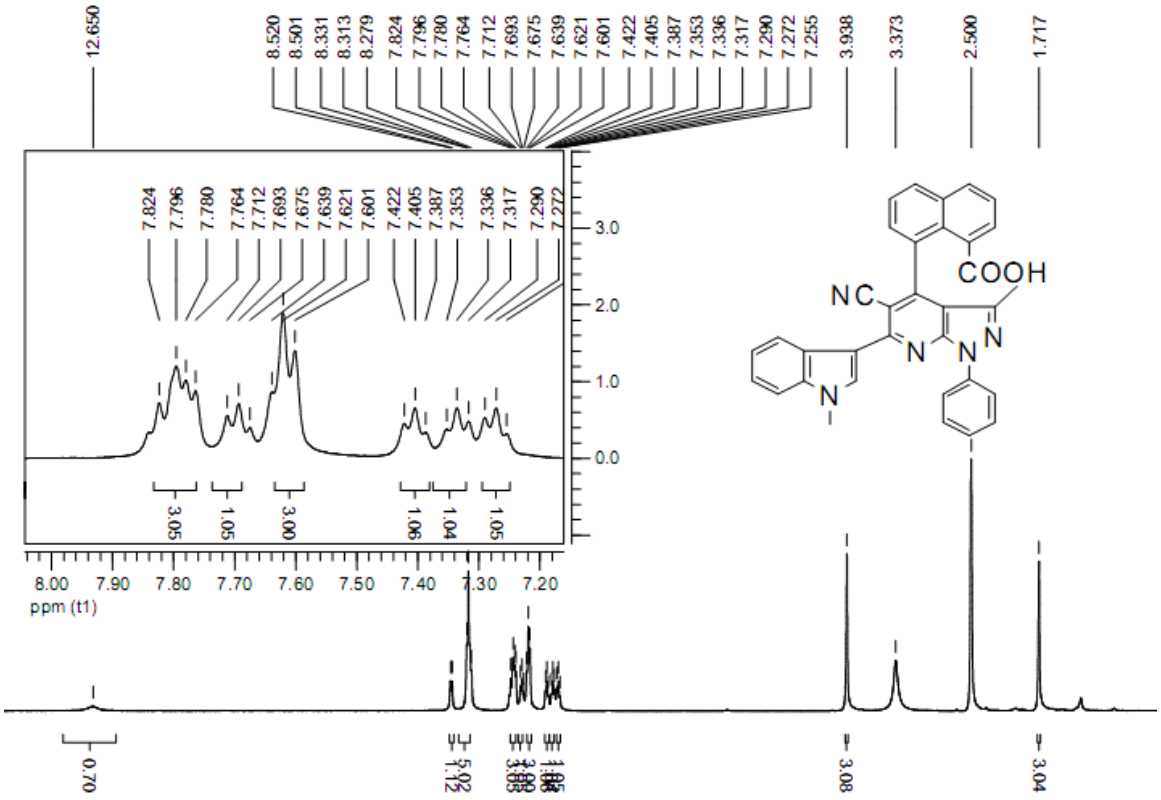
oic acid (**4r**).

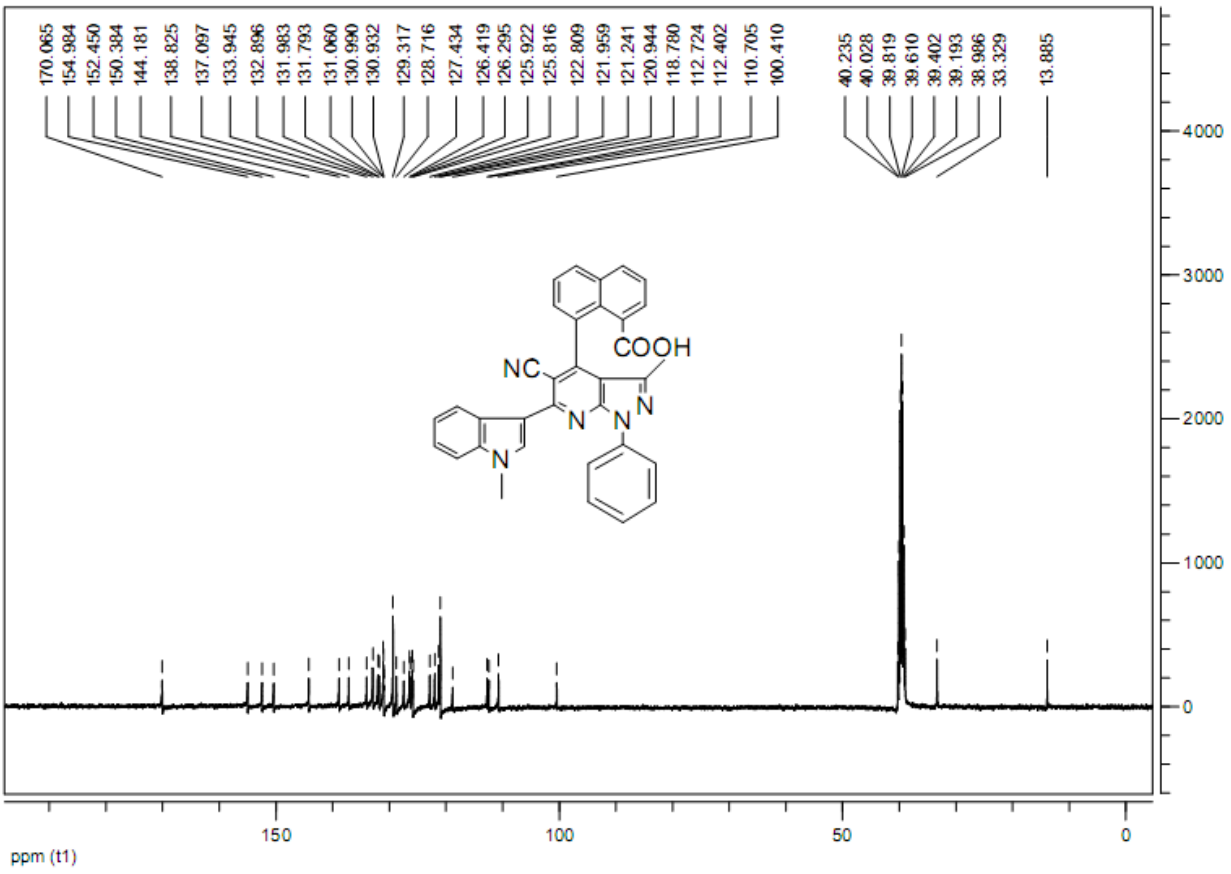
Solid; m.p. = 295.6-296.4°C.

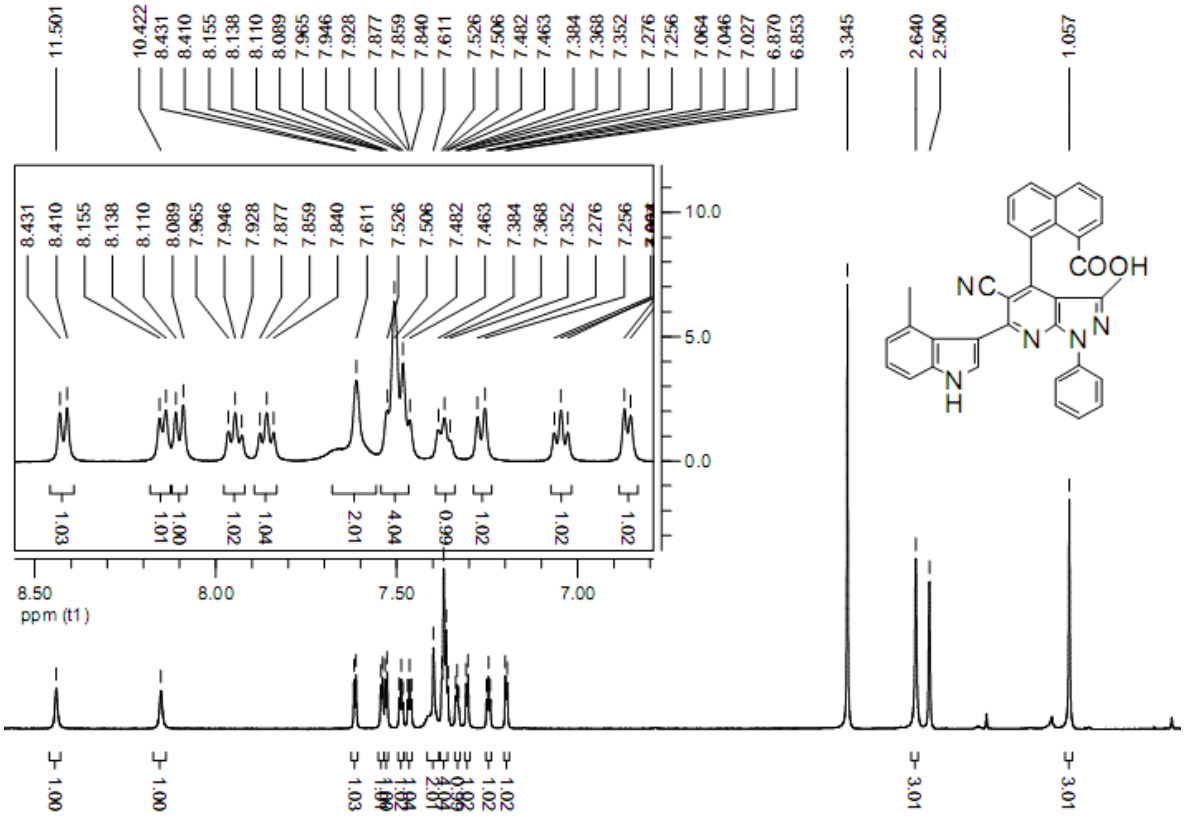
IR (KBr): *v* 3423(s), 1744(s), 1599(s), 1563(s), 1498(s), 1382(m) cm^{-1}.
^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 12.29(s, 1H, COOH), 8.69(d, J = 6.3 Hz , 1H, ArH), 8.41(d, J = 7.2 Hz , 2H, ArH), 8.20(s, 2H, ArH), 7.69-7.60(m, 5H, ArH), 7.52(s, 3H, ArH), 7.40(s, 2H, ArH), 1.53(s, 3H, CH_3).
^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm)**:** 171.21, 158.90, 152.97, 151.74, 151.60, 151.26, 145.99, 139.29, 134.18, 133.42, 132.81, 131.76, 130.23, 130.00, 129.19, 127.80, 127.43, 126.62，126.17, 125.85, 125.76, 125.33, 120.82, 119.95, 118.66, 117.34, 111.84, 14.48.
HRMS(ESI): calculated for $C_{31}H_{19}N_3O_4$ [MH^+]: 498.1454, found 498.1459.

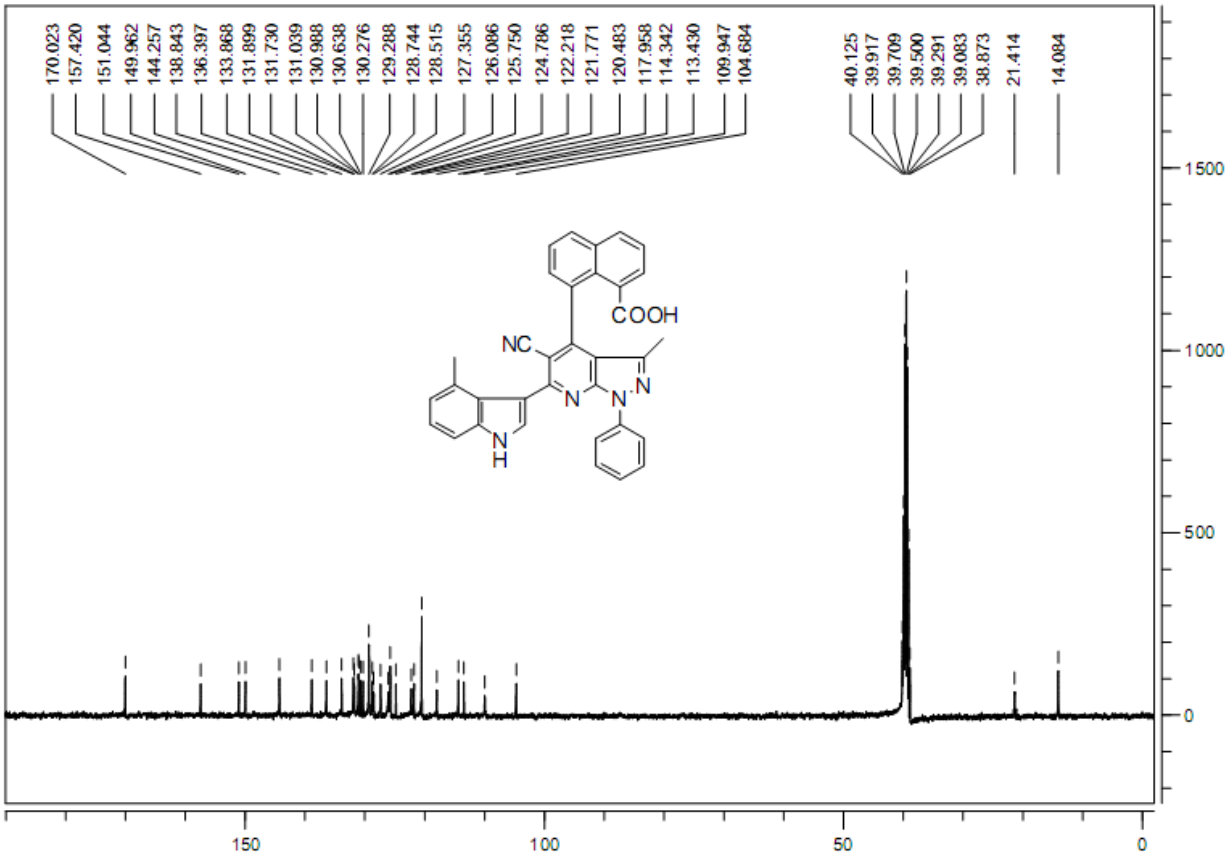


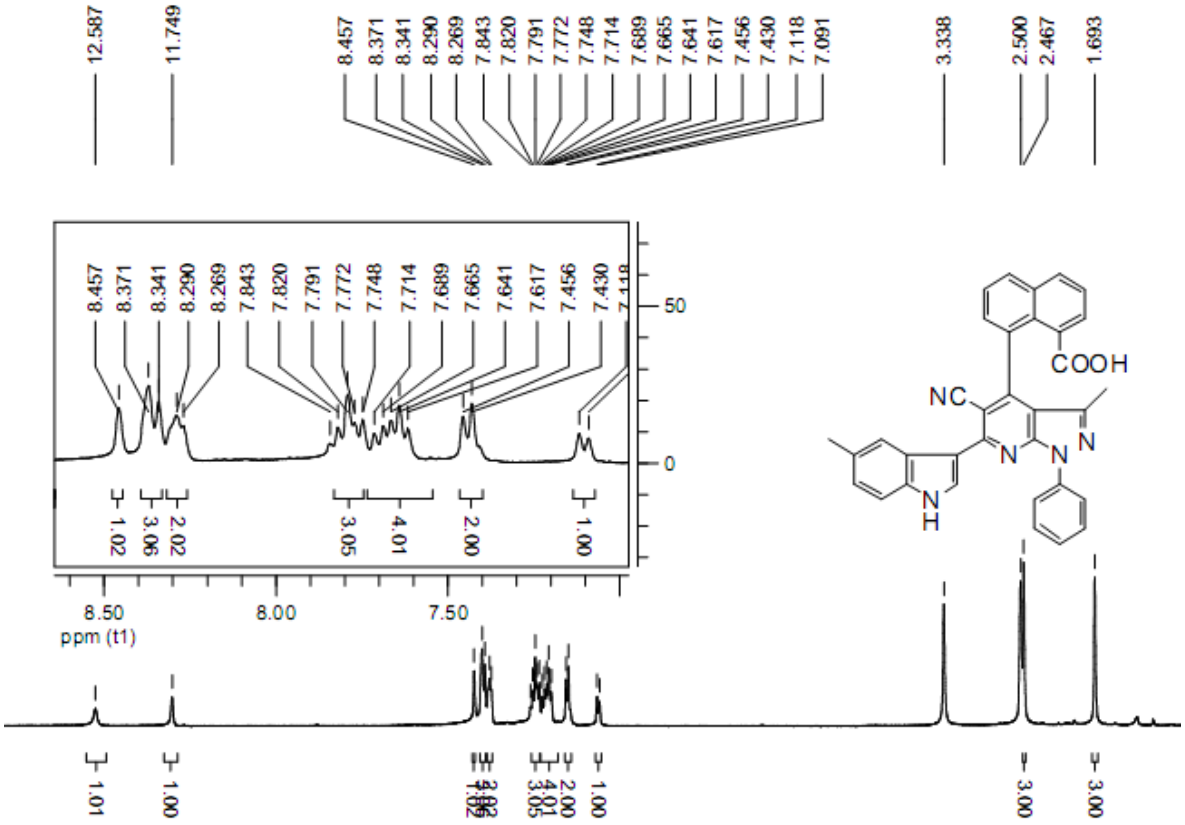


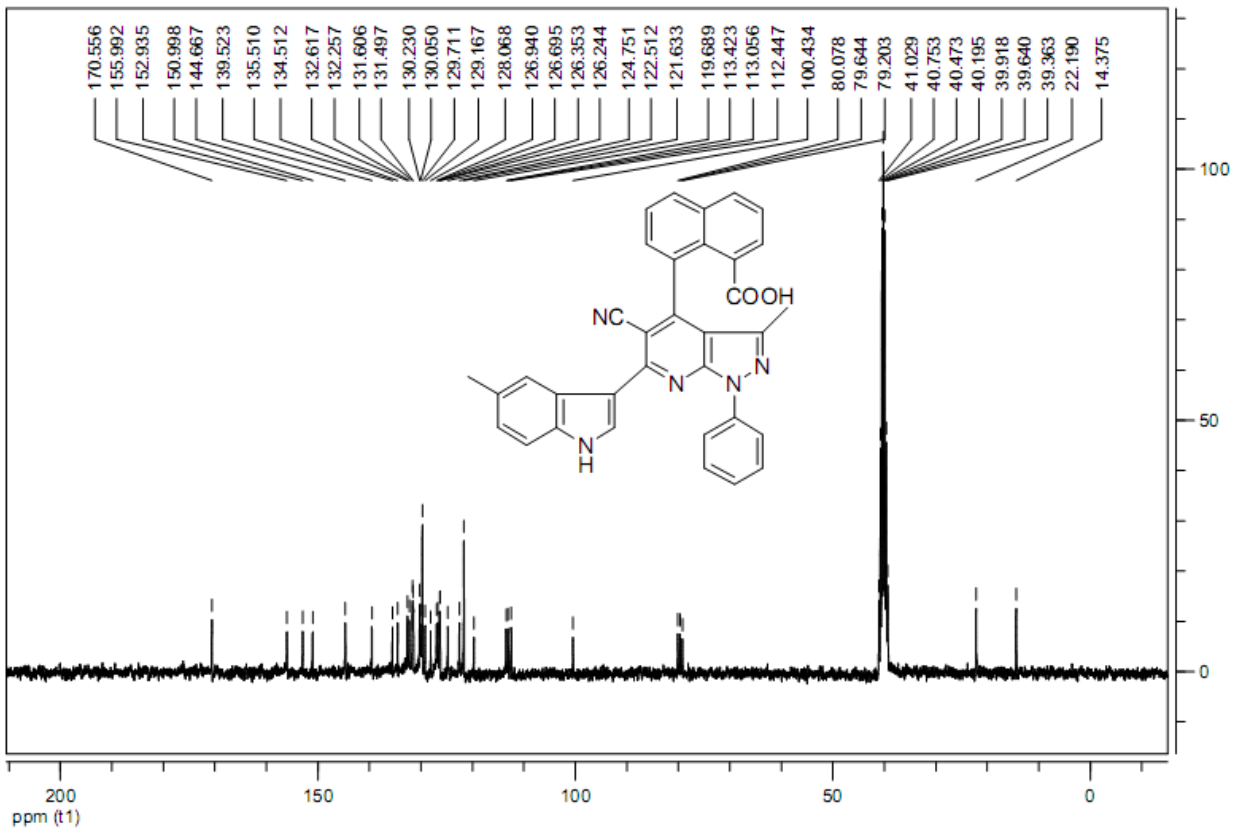


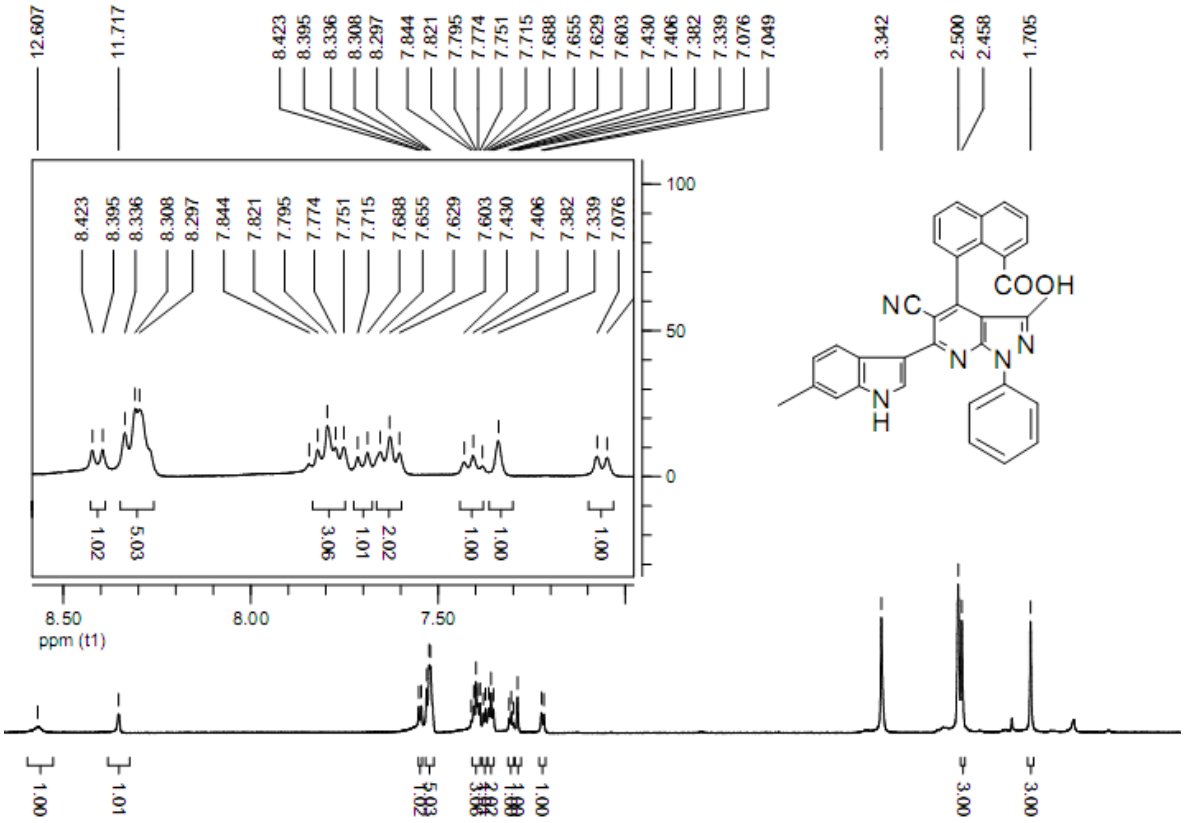


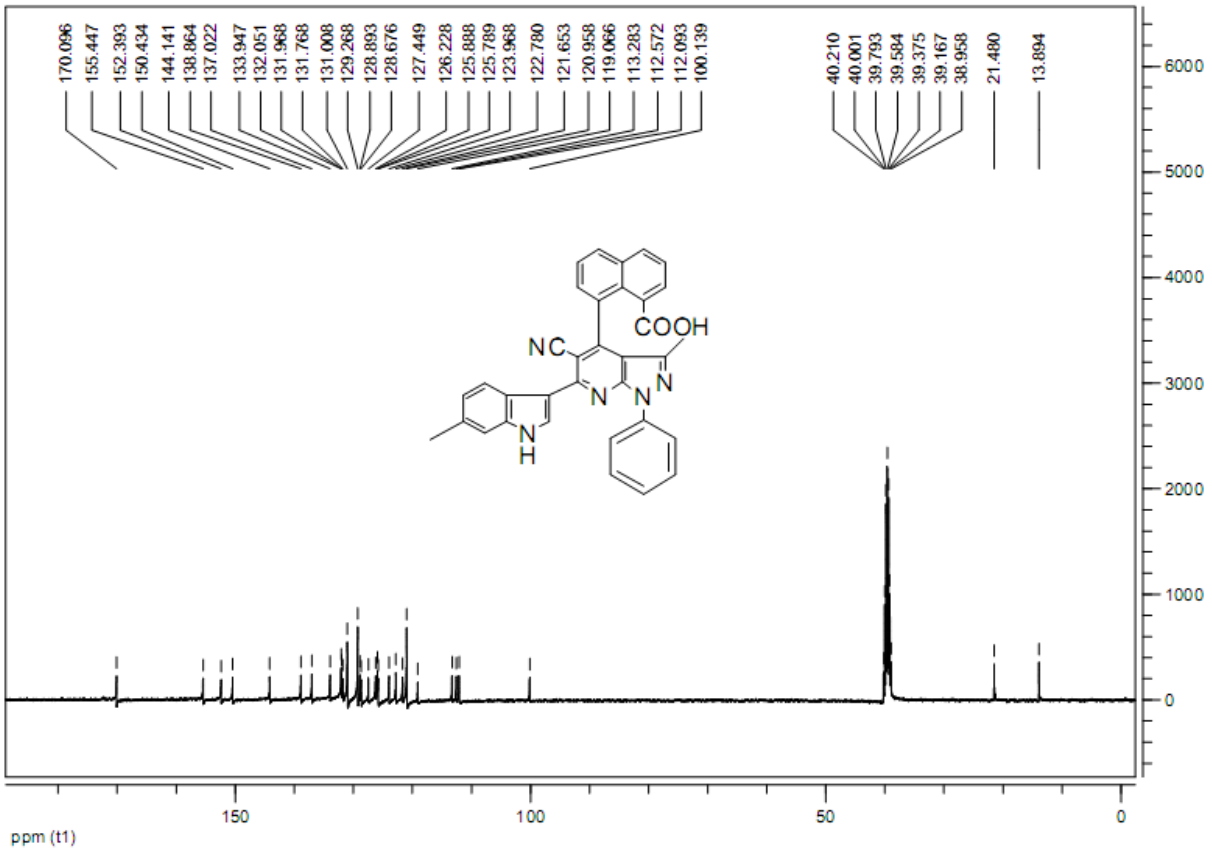


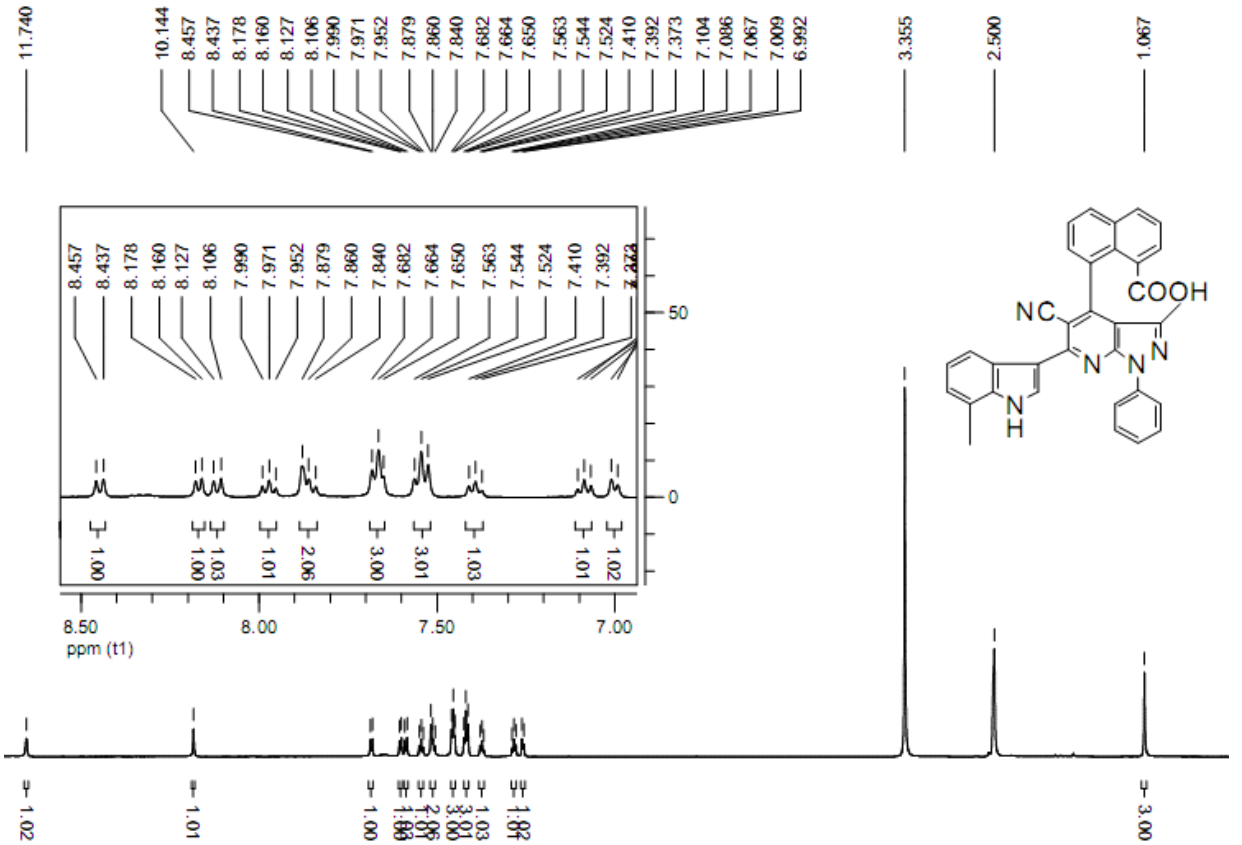


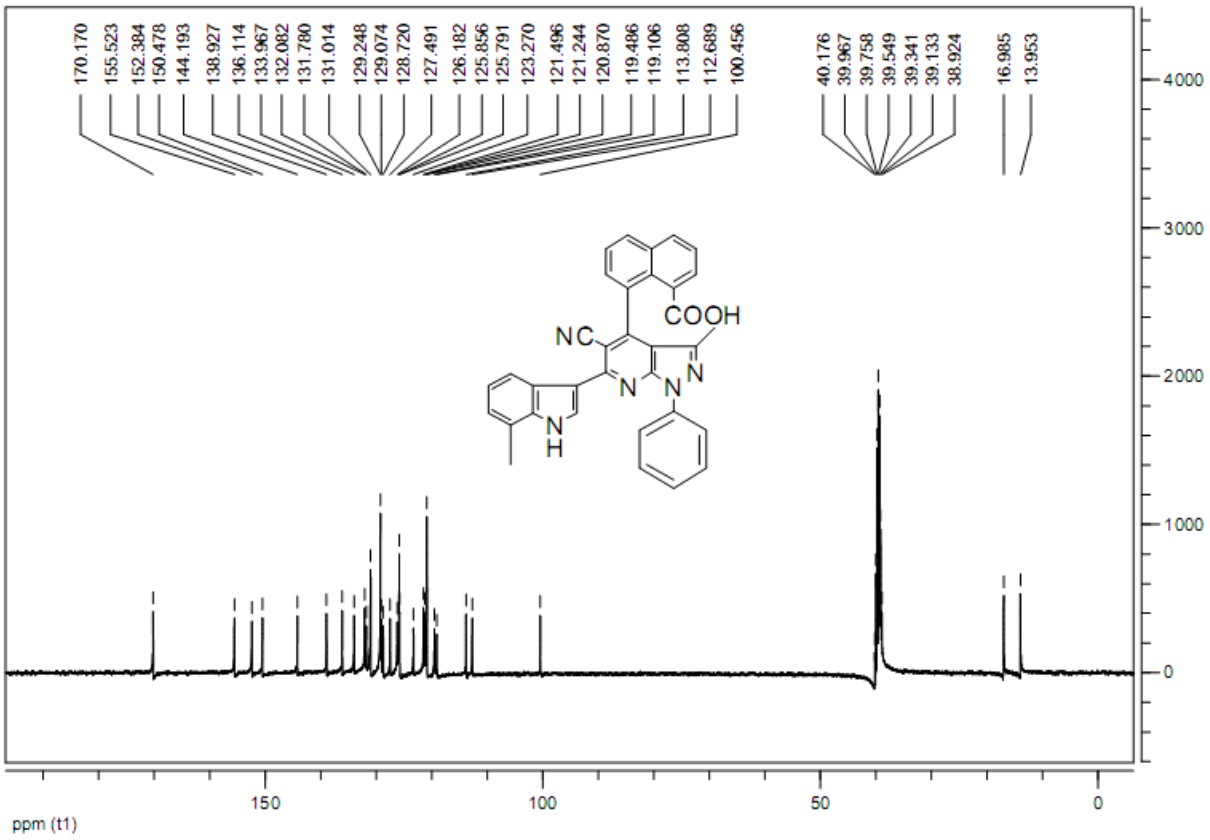


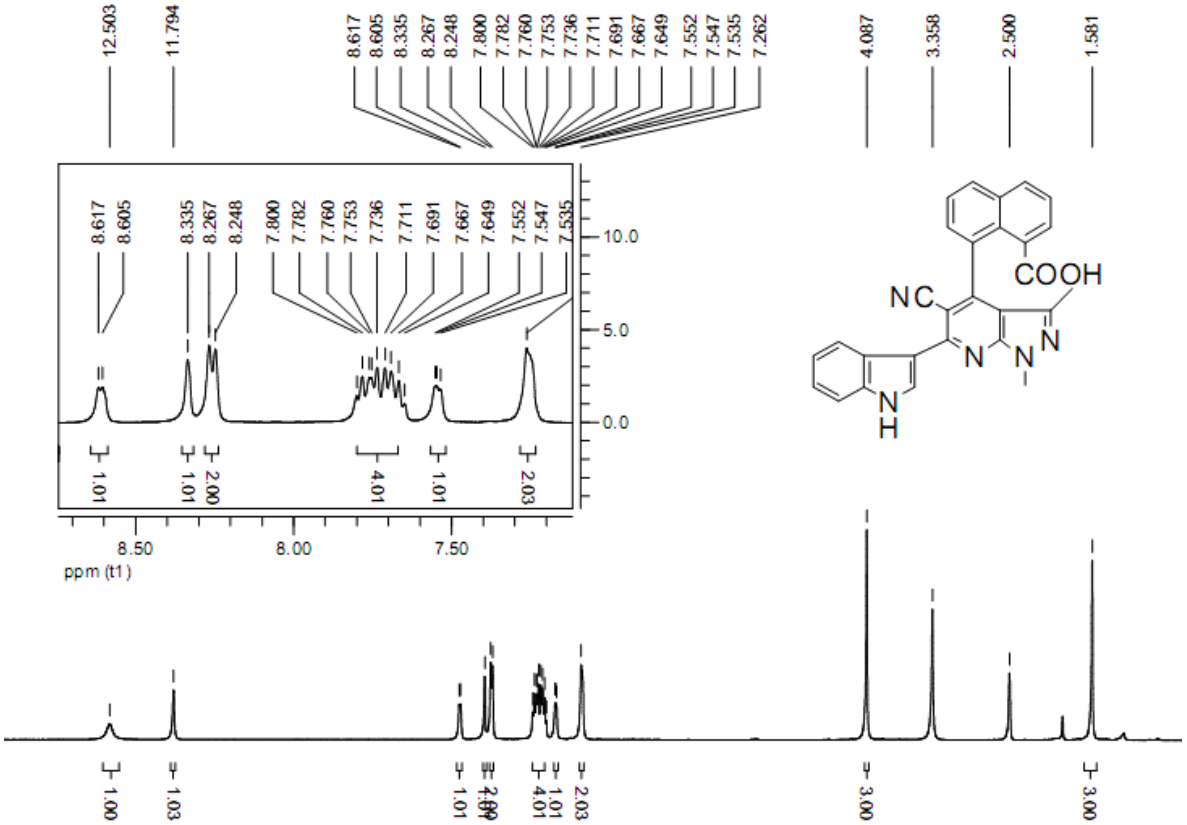








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7.262
4.087
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H
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1.01
2.00
4.01
1.01
2.03
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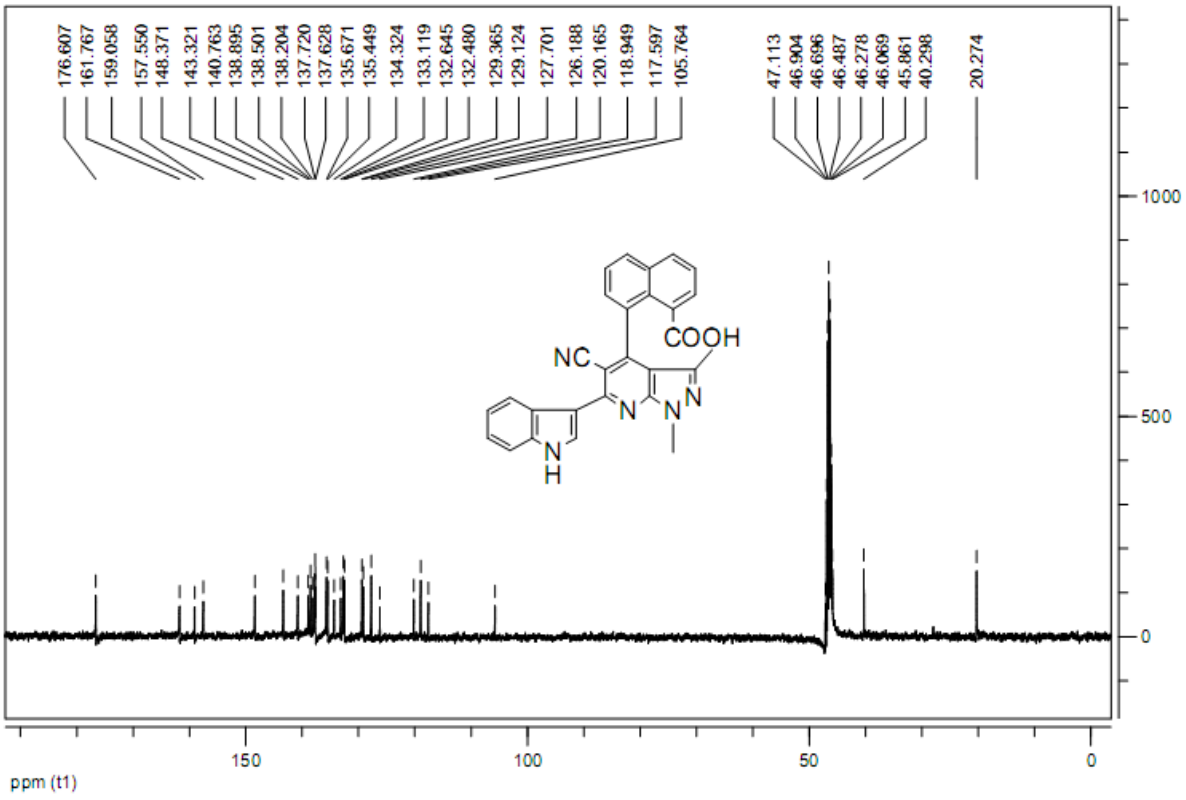
2.03
3.00
3.00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135.449
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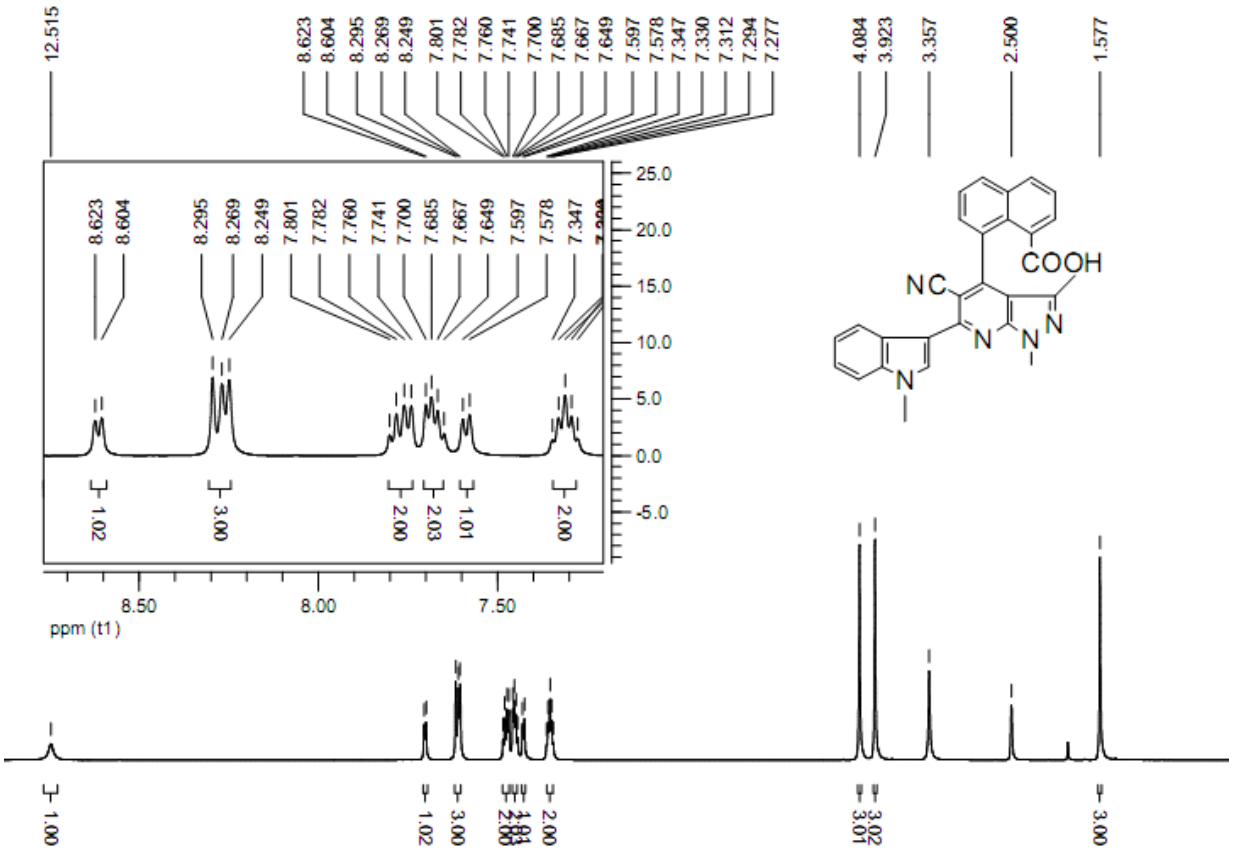
ppm (t1)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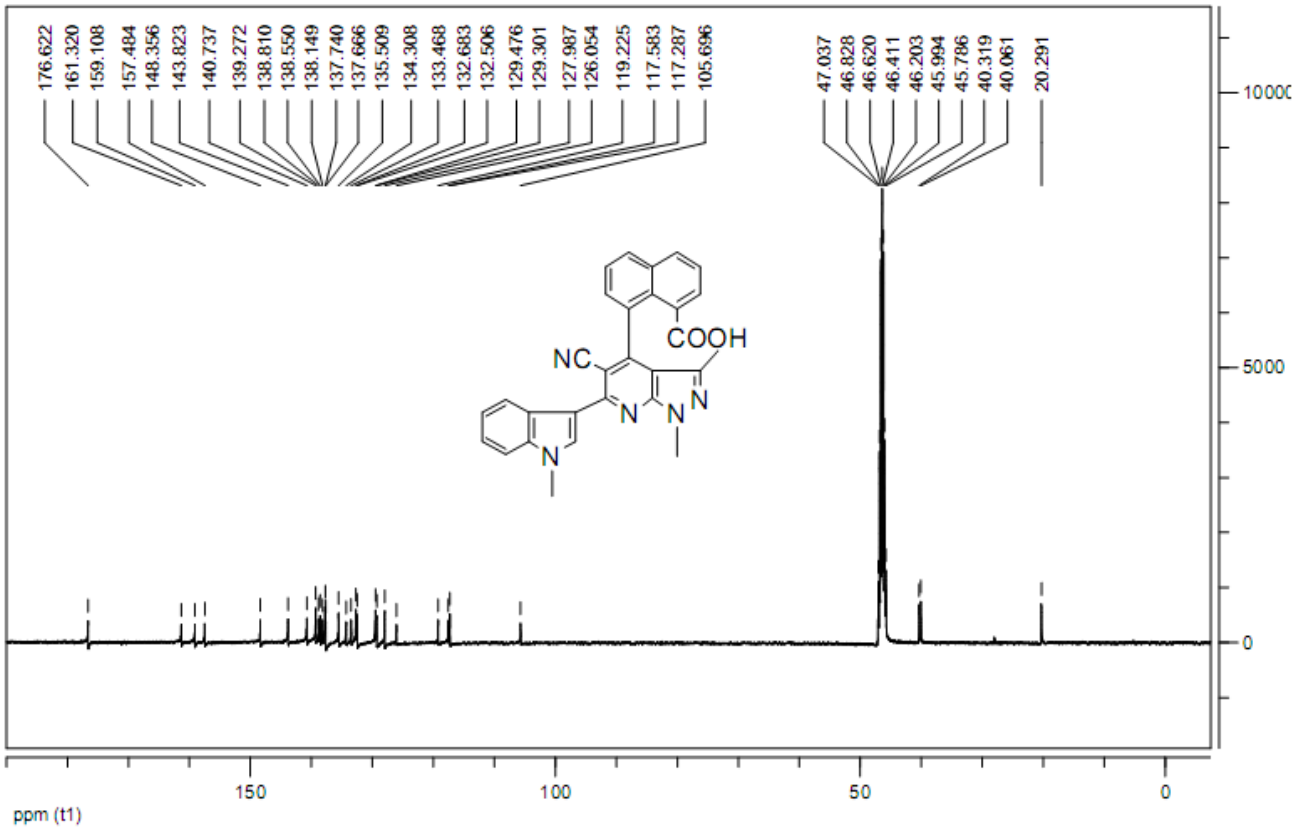
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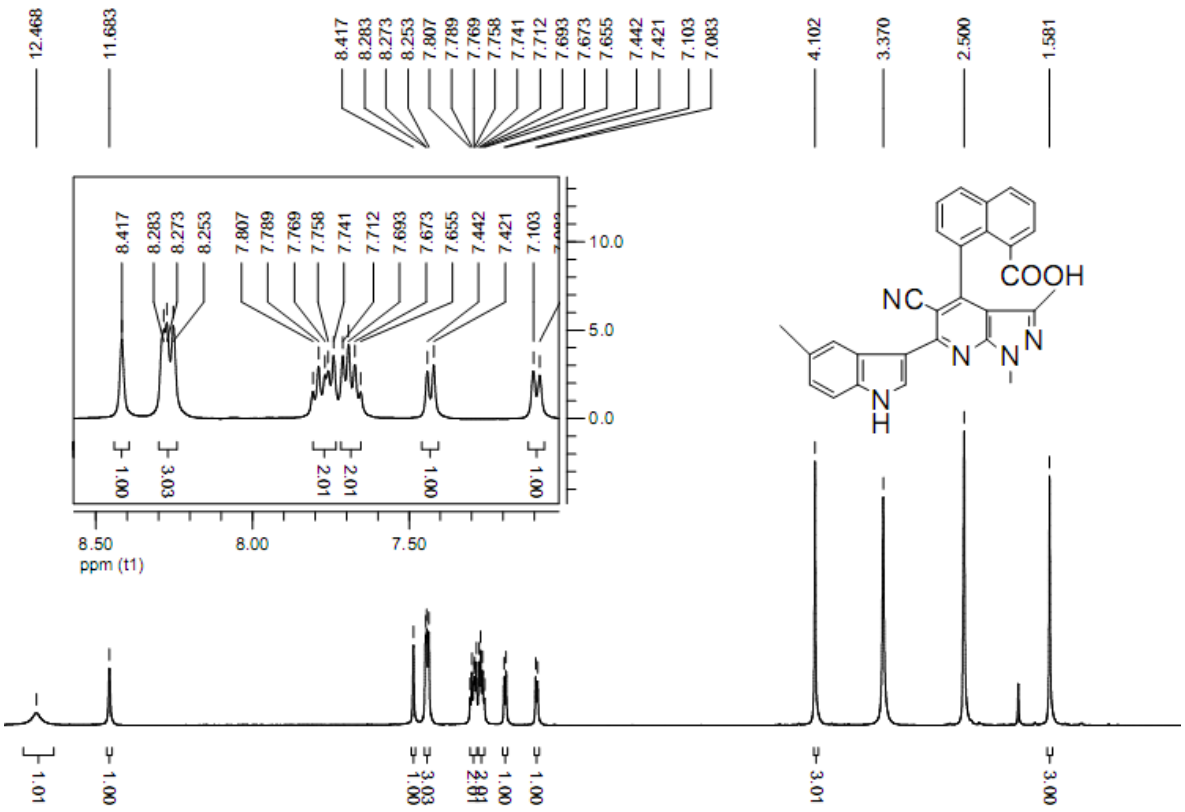
ppm (t1)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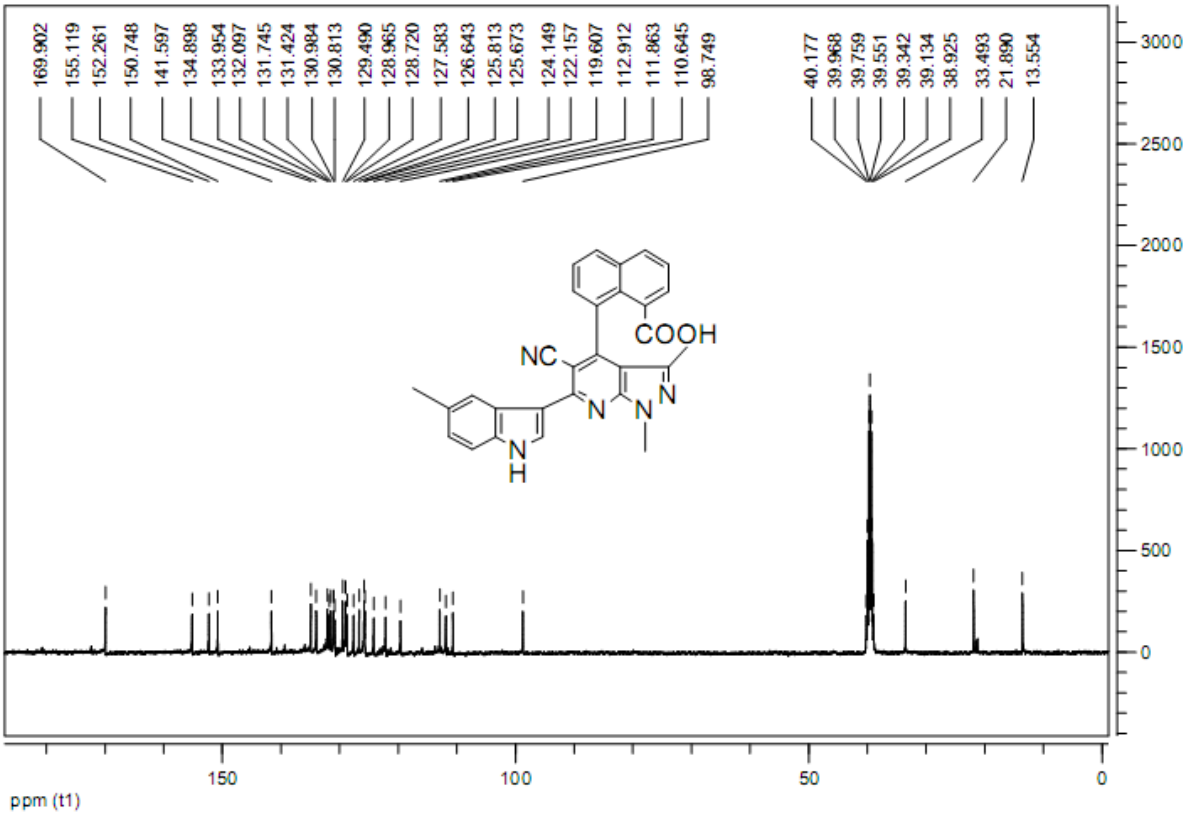
ppm (t1)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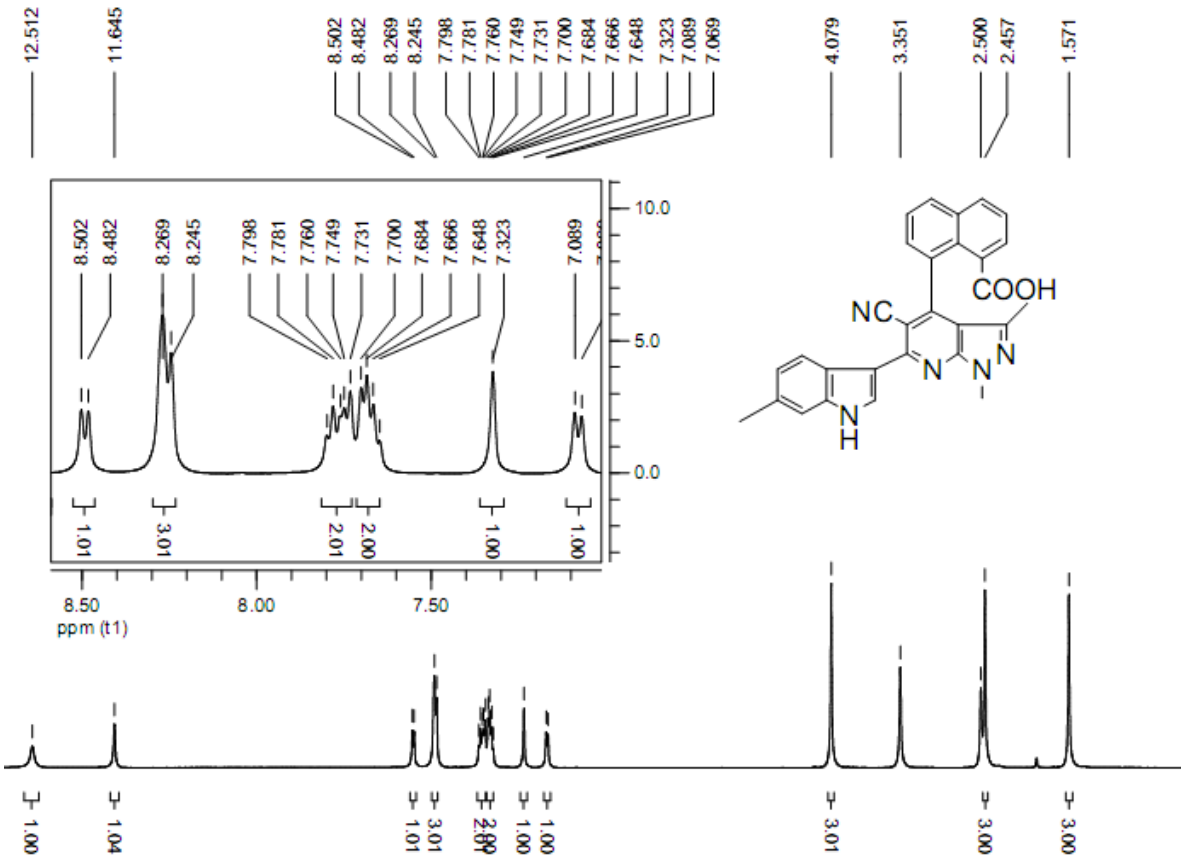
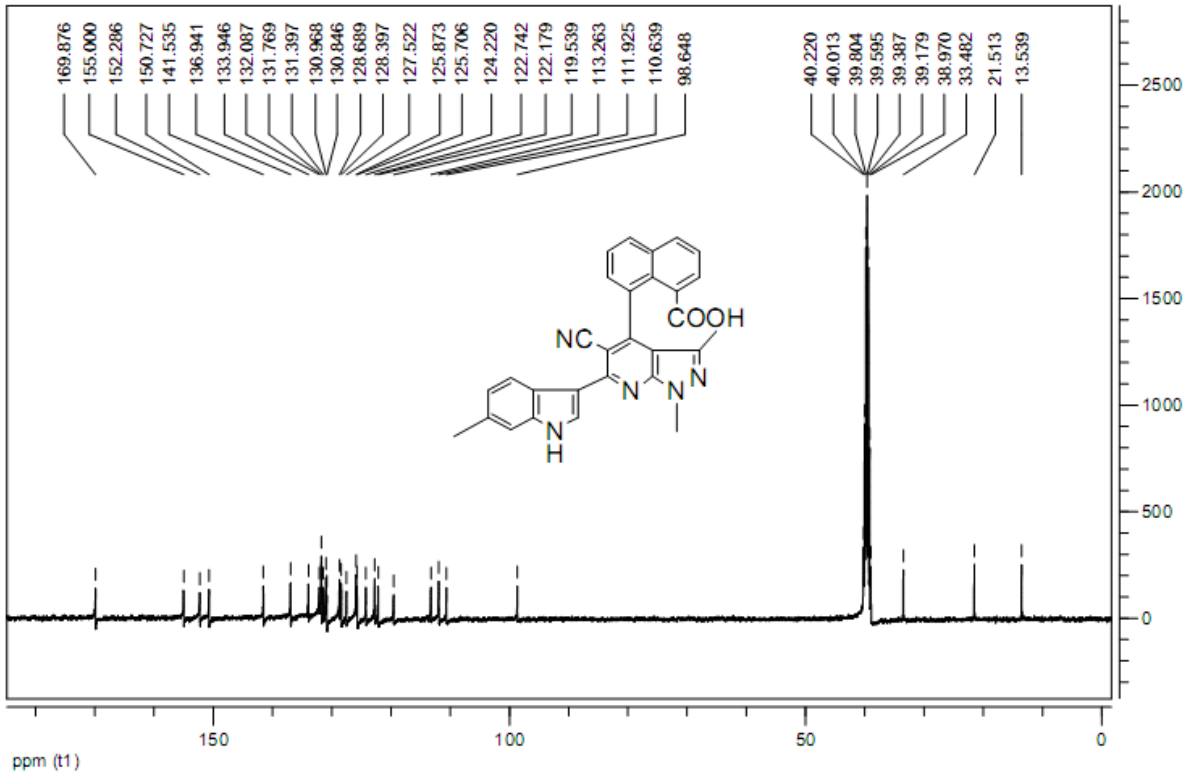
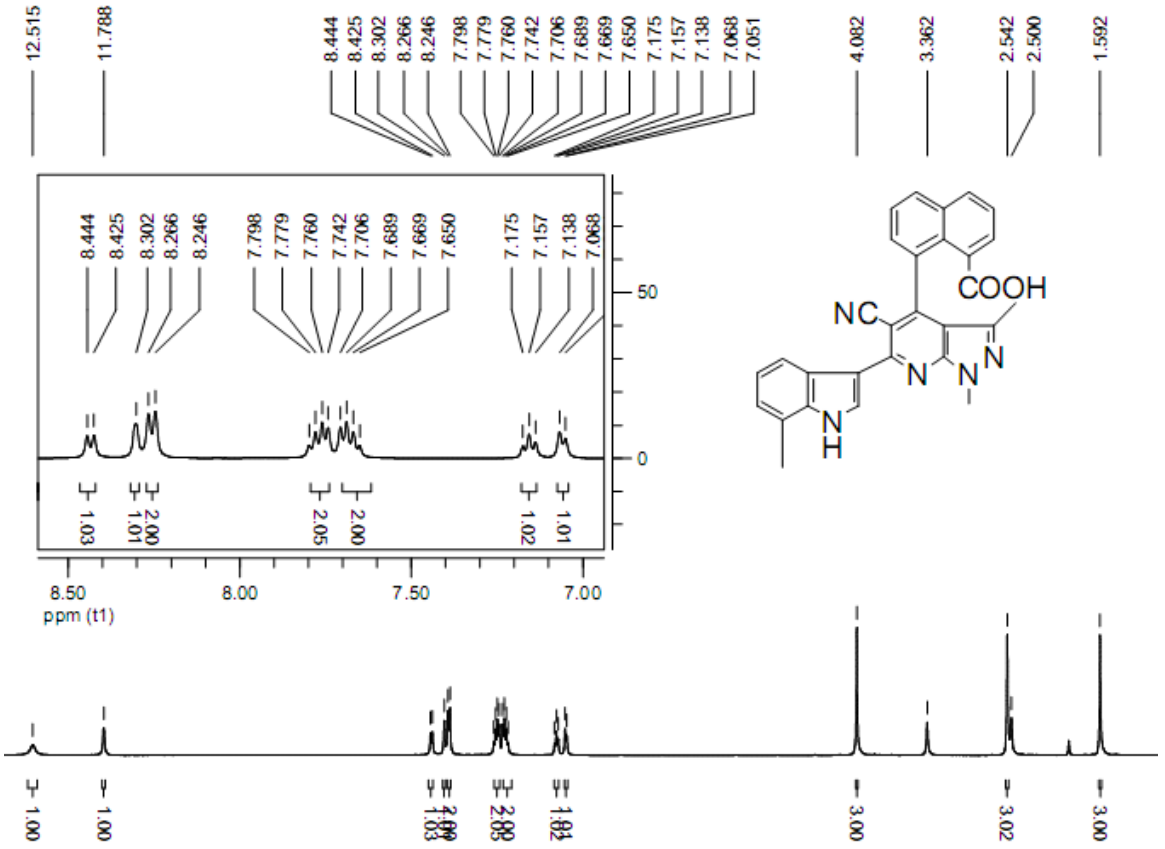
ppm (t1)



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N
N
H
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1.01
2.00
2.05
2.00
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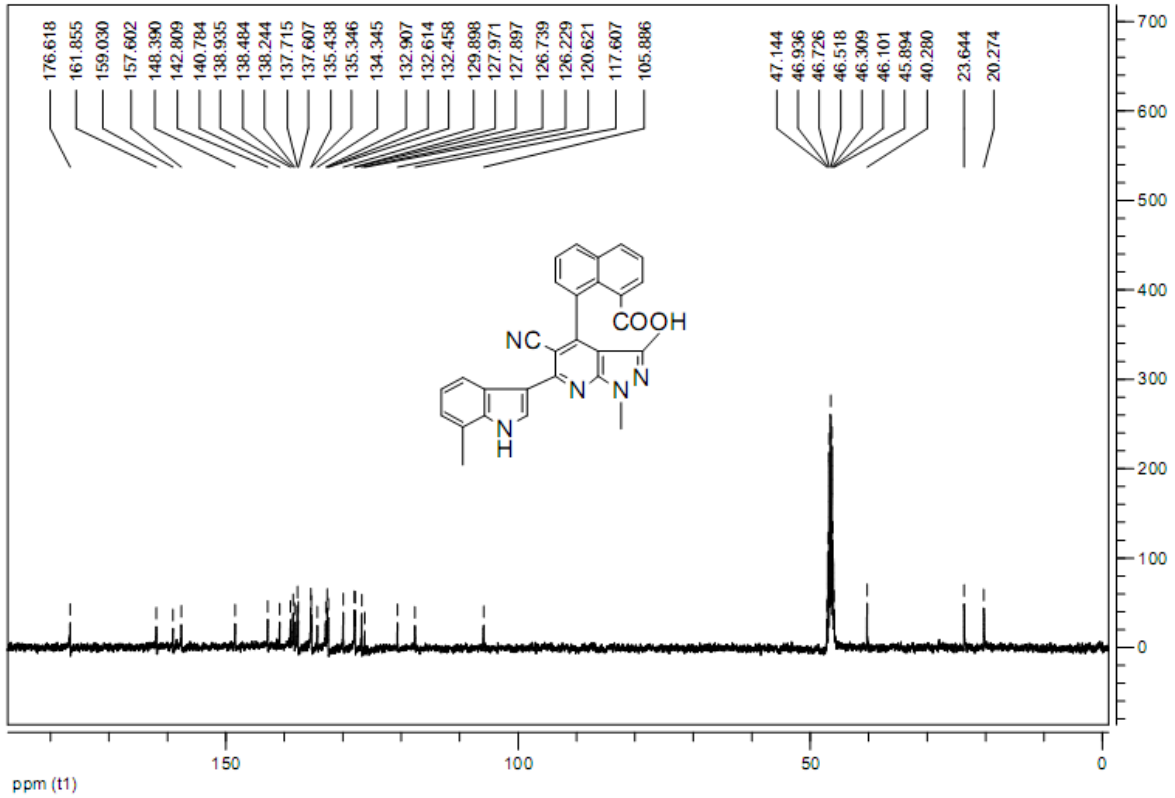
8.50
8.00
7.50
7.00
ppm (t1)
1.00
1.00
3.00
3.02
3.00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20.274
COOH
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N
H
700
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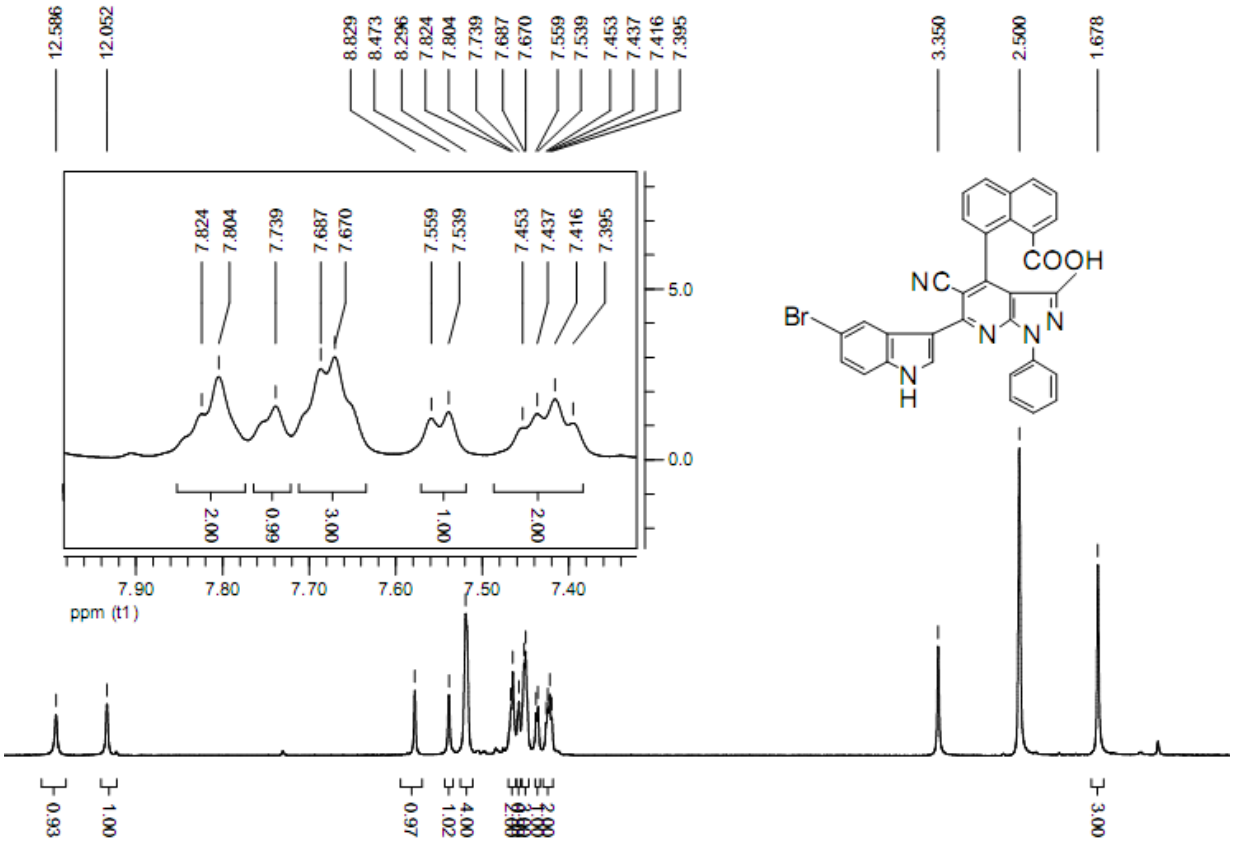

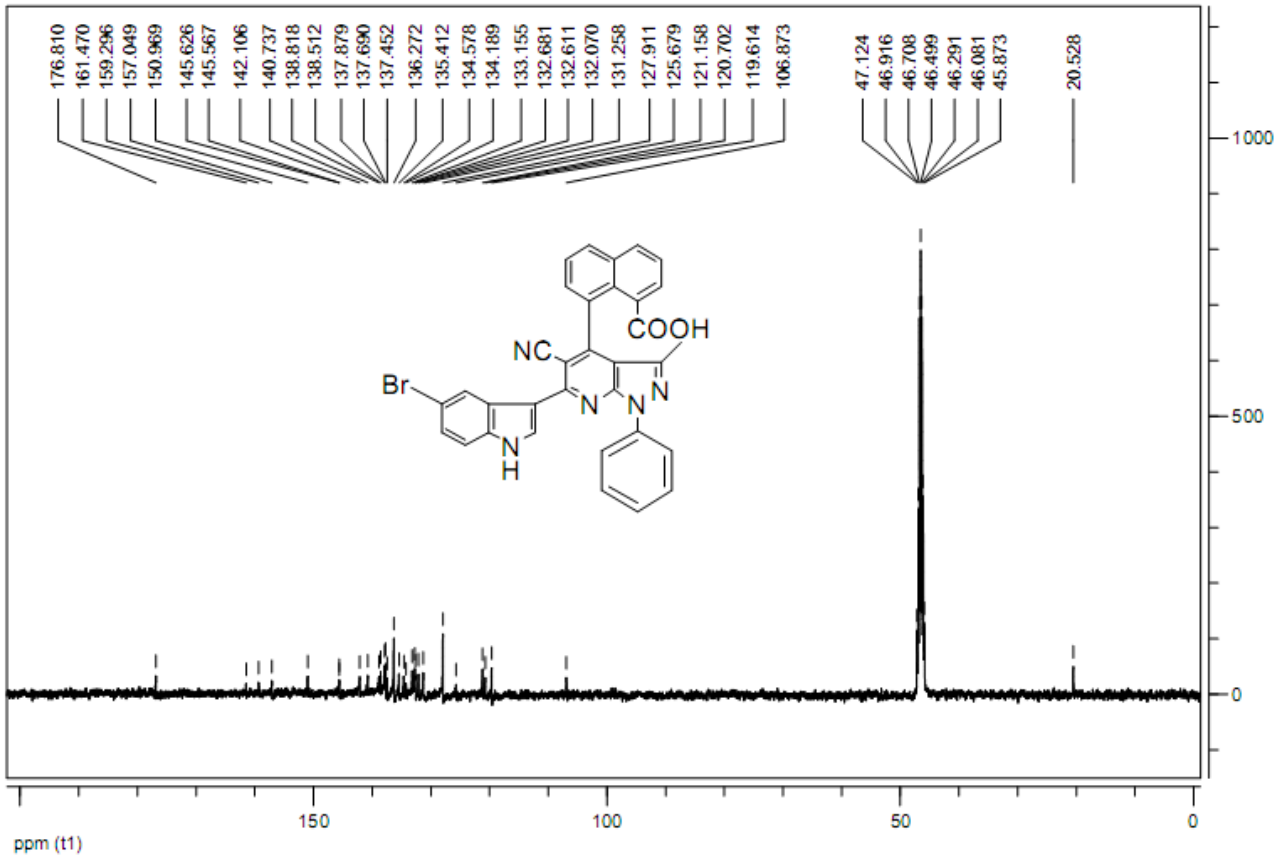

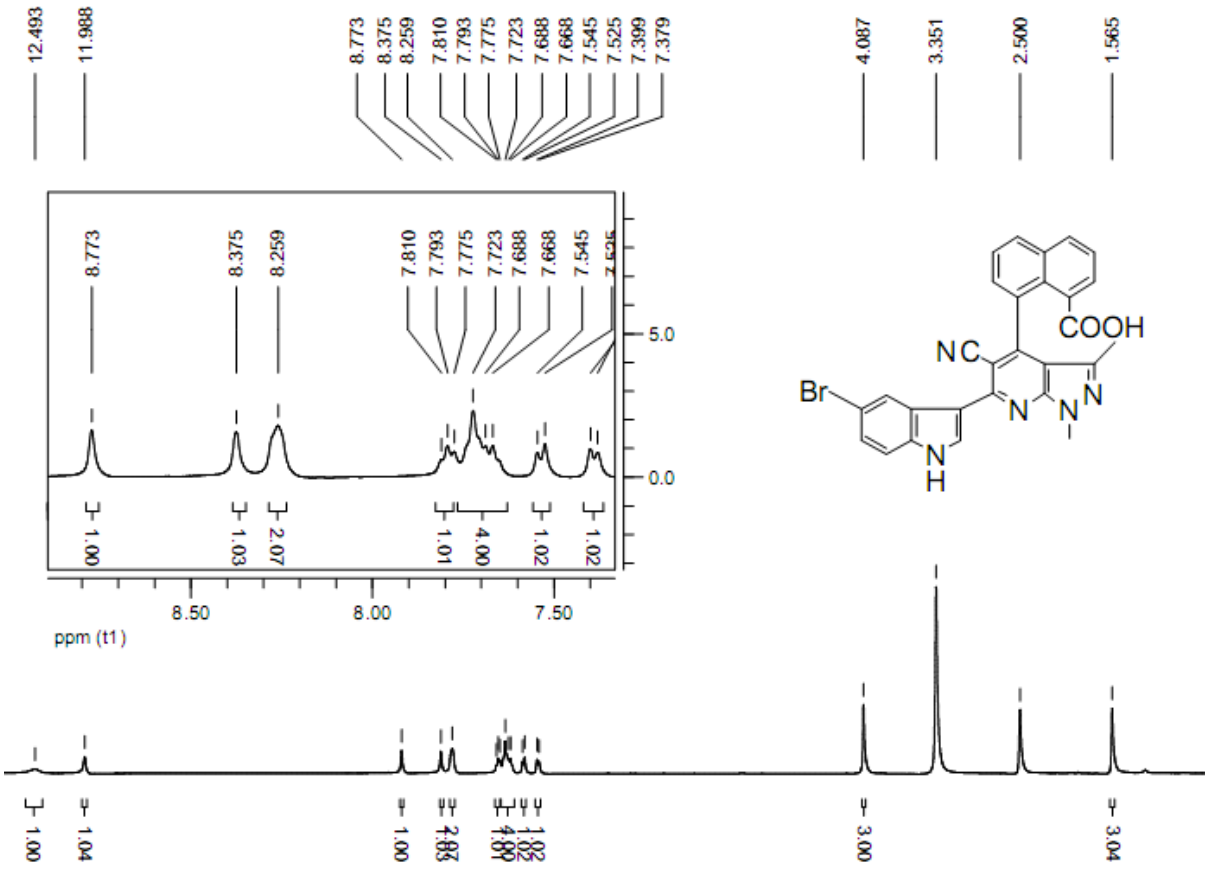
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7.688
7.668
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7.379
4.087
3.351
2.500
1.565
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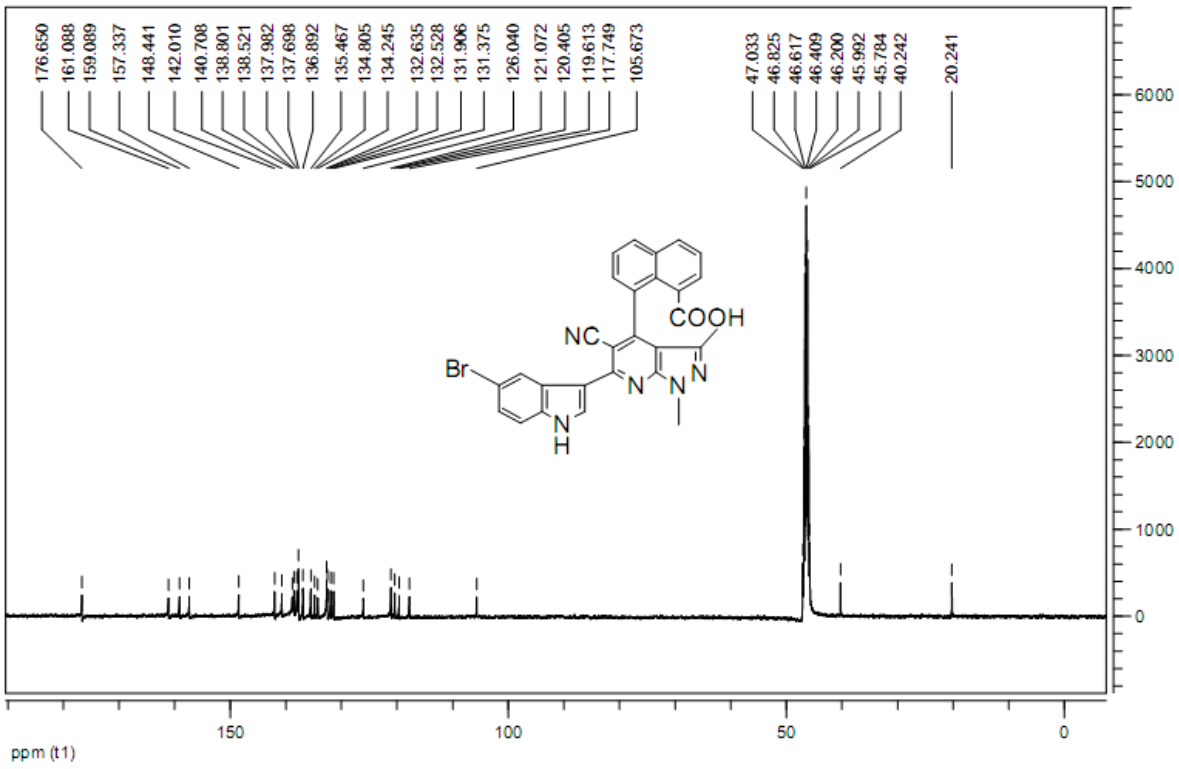
NC
Br
N
H
ppm (t1)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135.467
134.805
134.245
132.635
132.528
131.906
131.375
126.040
121.072
120.405
119.613
117.749
105.673
47.033
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46.409
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20.241
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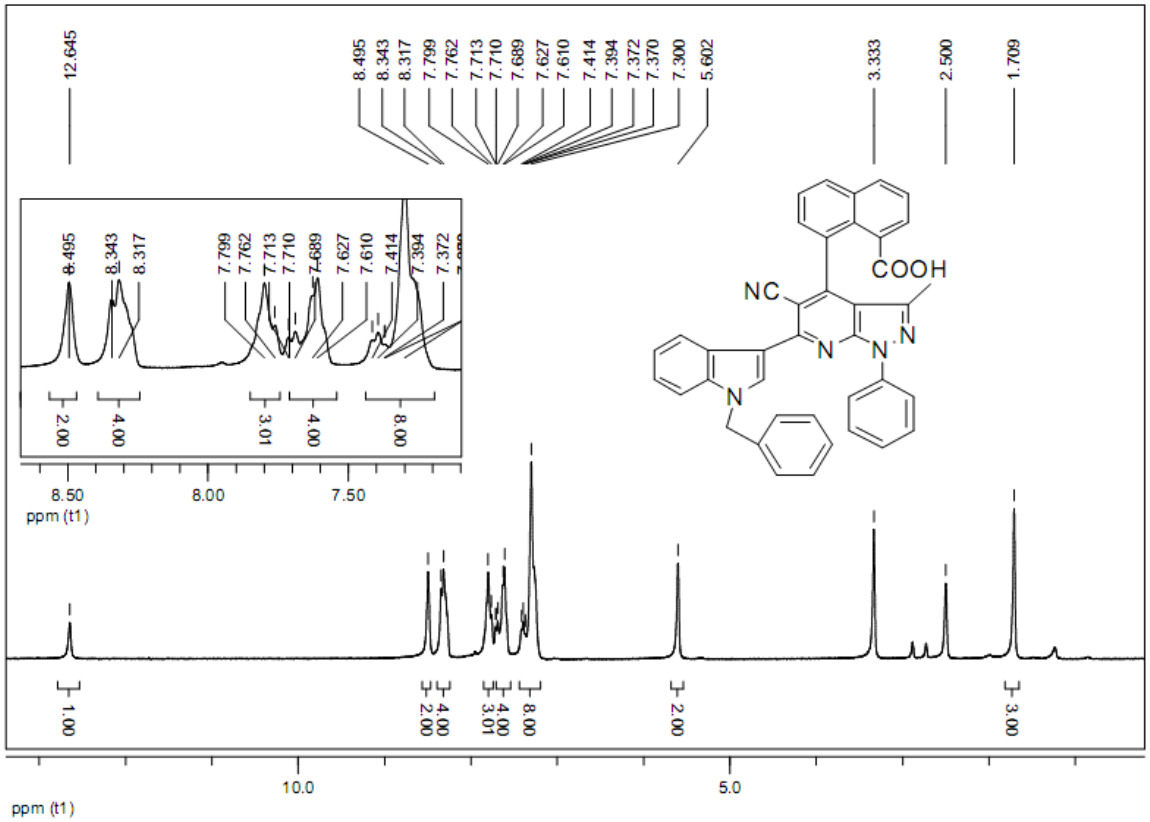
Br
ppm (t1)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7.627
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7.394
7.372
7.370
7.300
5.602
3.333
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1.709
COOH
NC
N
N
N
2.00
4.00
3.01
4.00
8.00
8.50
8.00
7.50
ppm (t1)
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4.00
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4.00
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2.00
3.00
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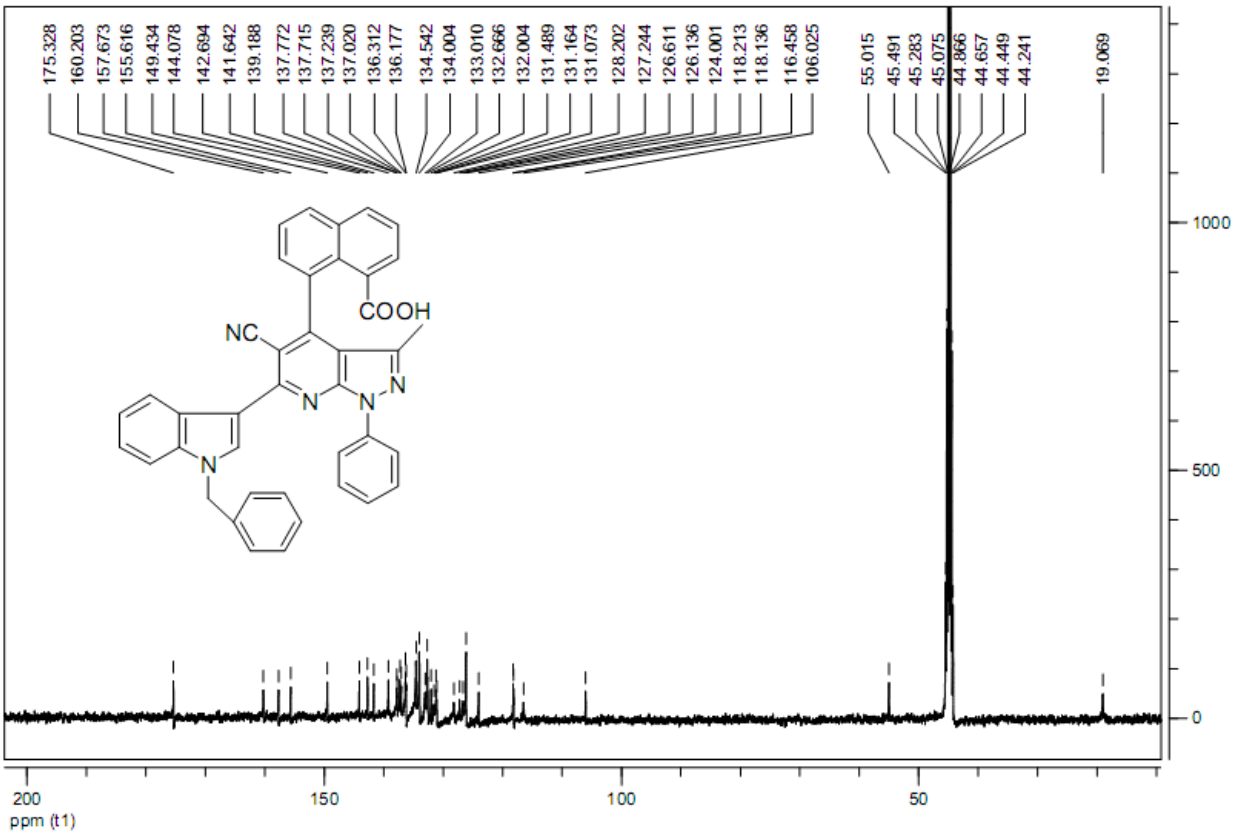
5.0
ppm (t1)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137.020
136.312
136.177
134.542
134.004
133.010
132.666
132.004
131.489
131.164
131.073
128.202
127.244
126.611
126.136
124.001
118.213
118.136
116.458
106.025
55.015
45.491
45.283
45.075
44.866
44.657
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44.241
19.069
COOH
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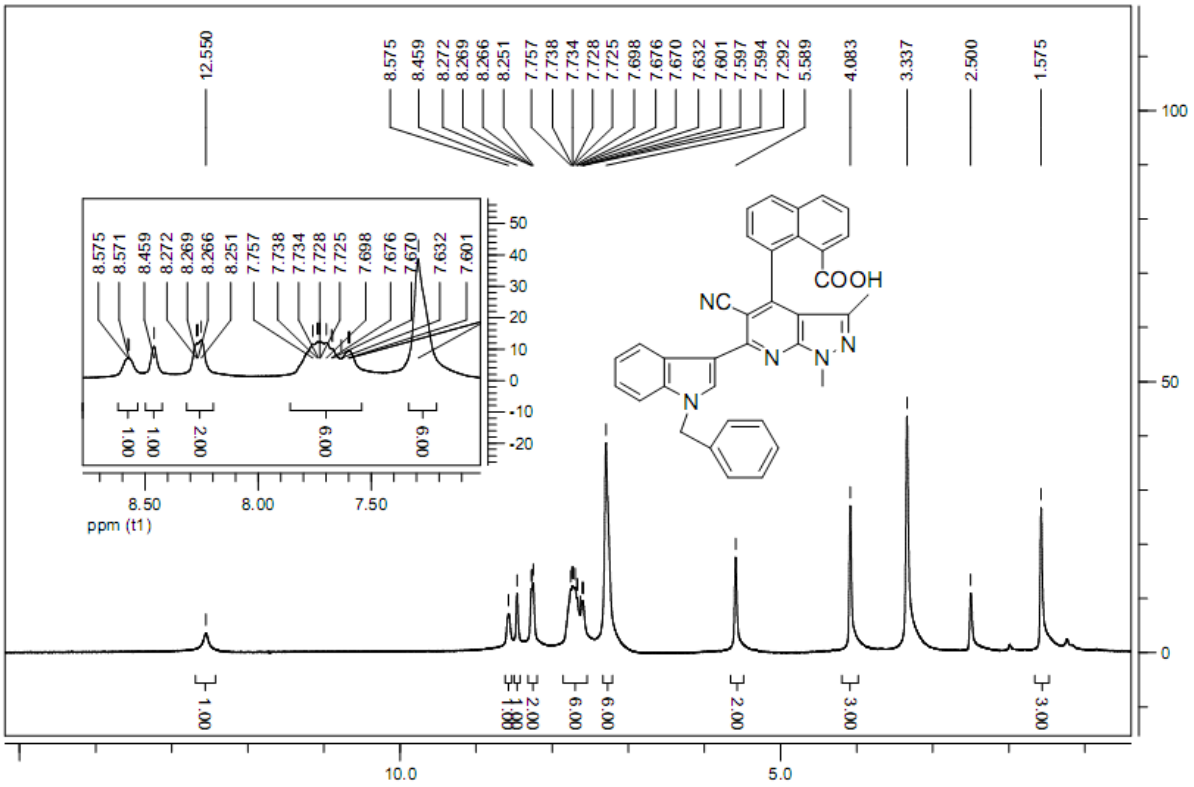
500
0
200
150
100
50
ppm (t1)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7.757
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7.734
7.728
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7.676
7.670
7.632
7.601
7.597
7.594
7.292
5.589
4.083
3.337
2.500
1.575
COOH
NC
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N
N
ppm (t1)
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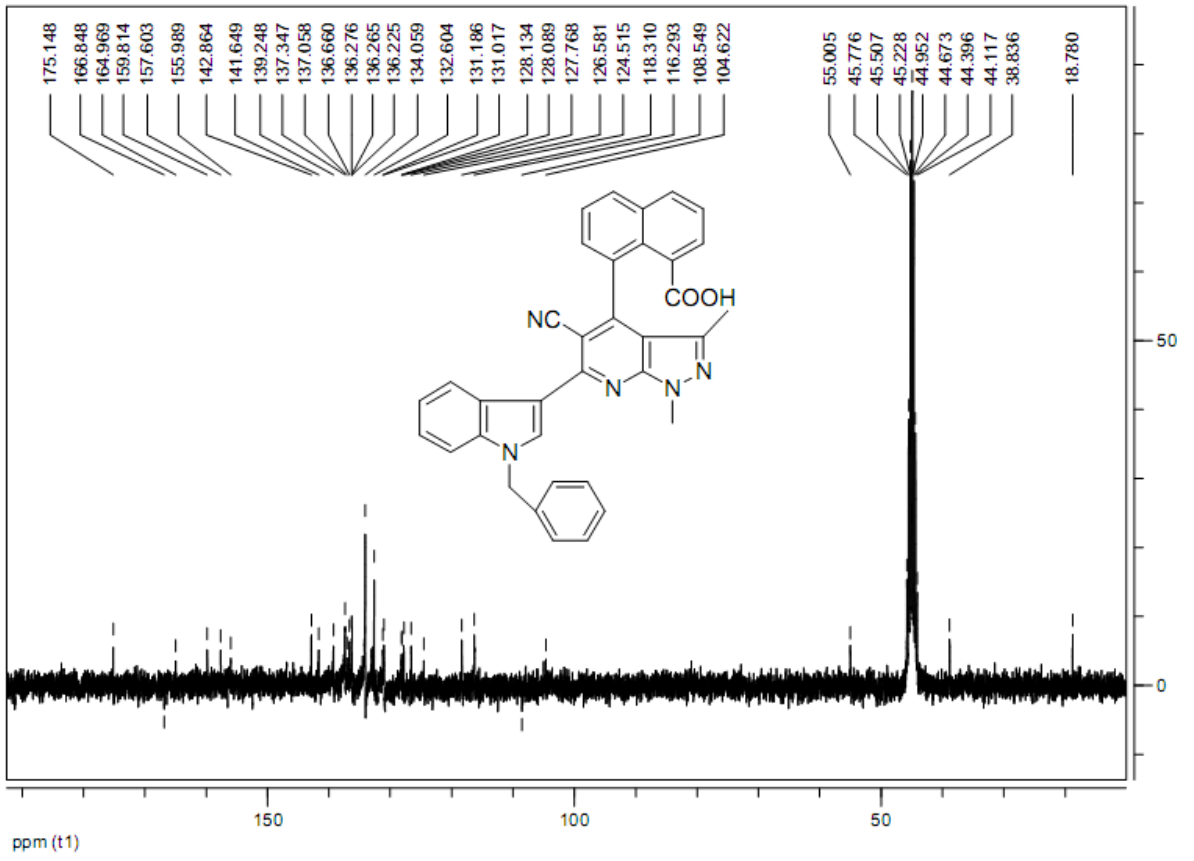
5.0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136.660
136.276
136.265
136.225
134.059
132.604
131.186
131.017
128.134
128.089
127.768
126.581
124.515
118.310
116.293
108.549
104.622
55.005
45.776
45.507
45.228
44.952
44.673
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44.117
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18.780
COOH
NC
N
N
N
ppm (t1)
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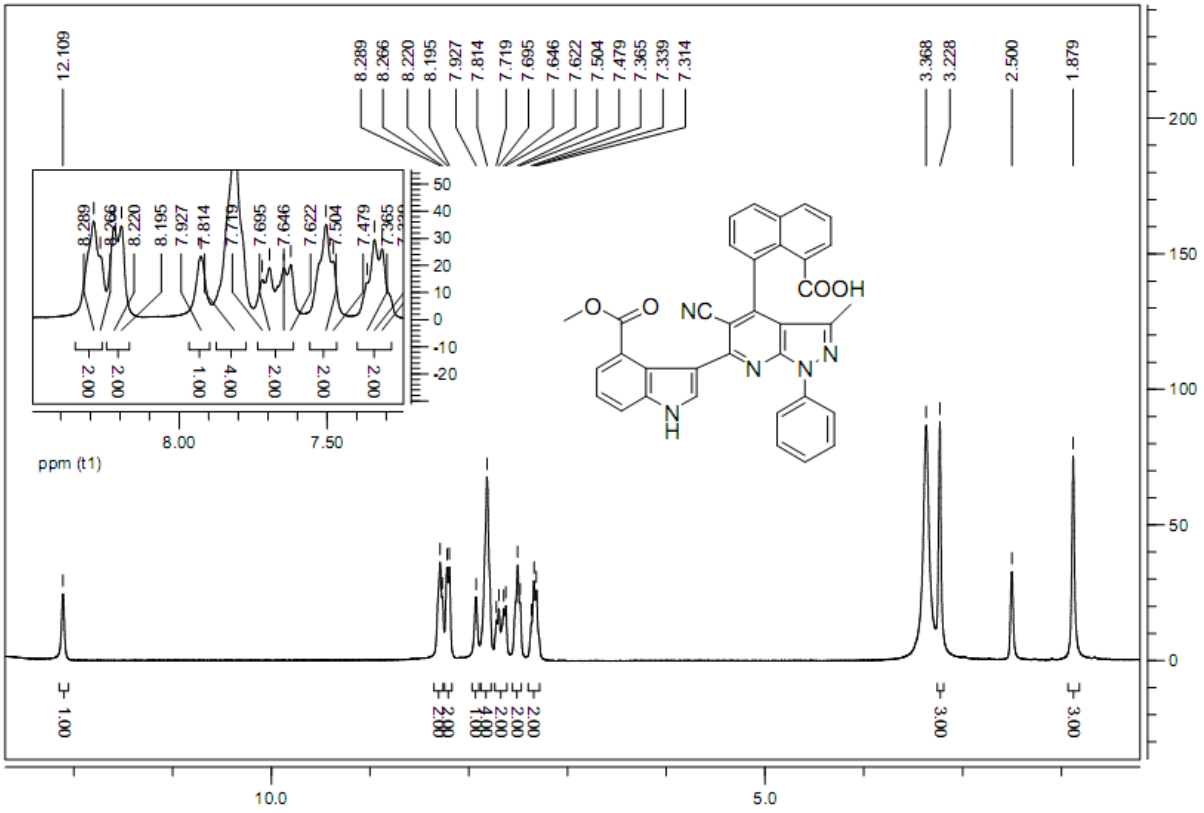
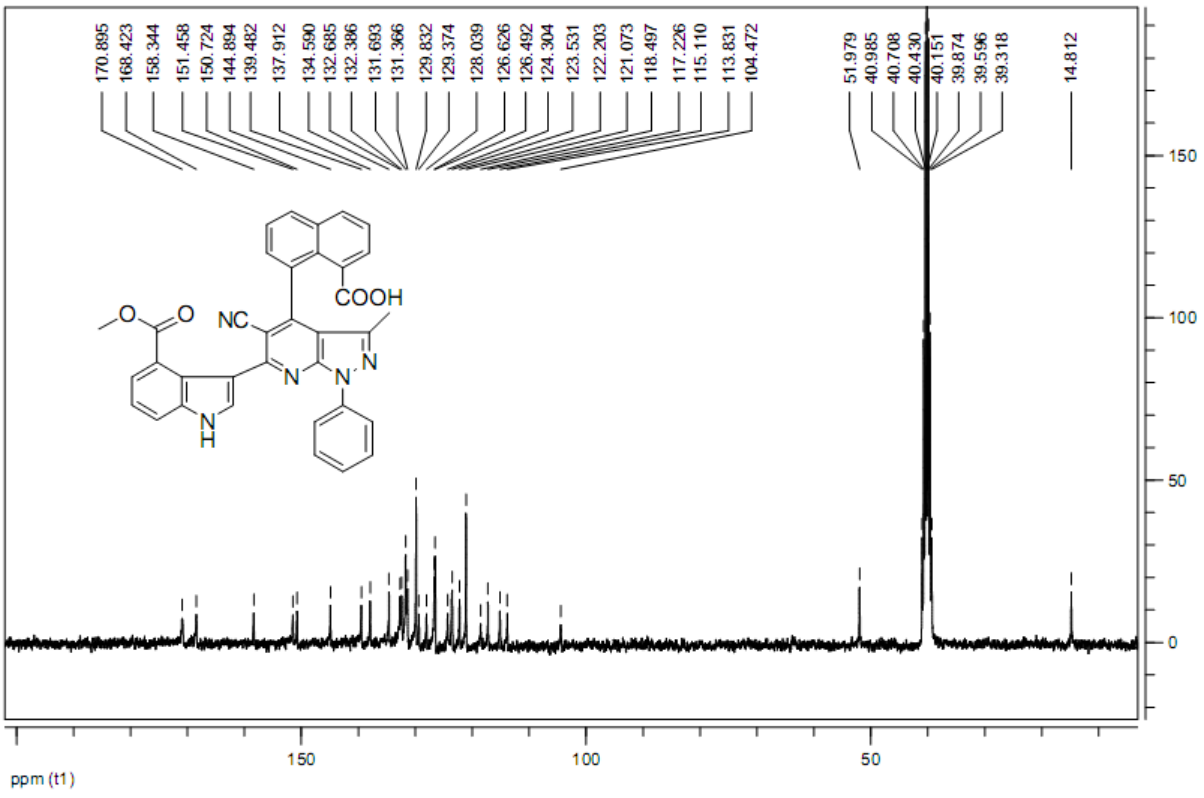
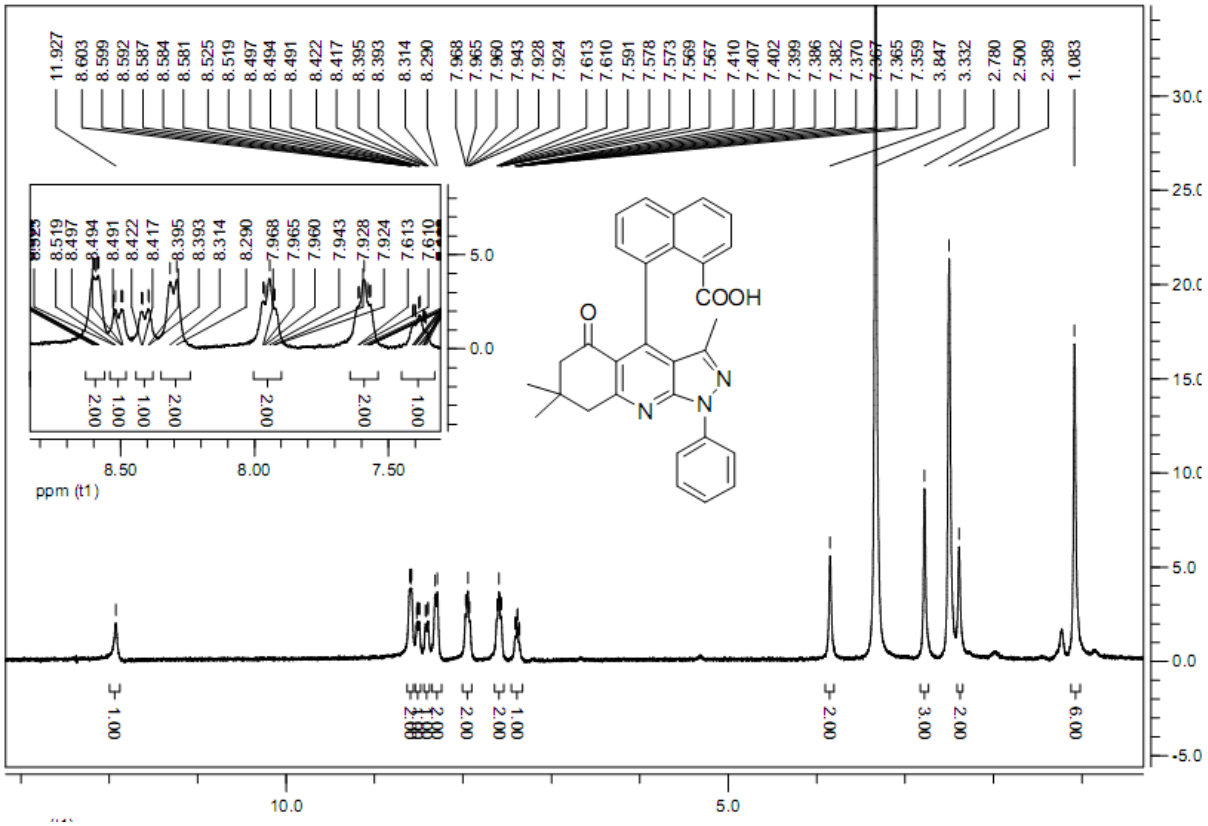
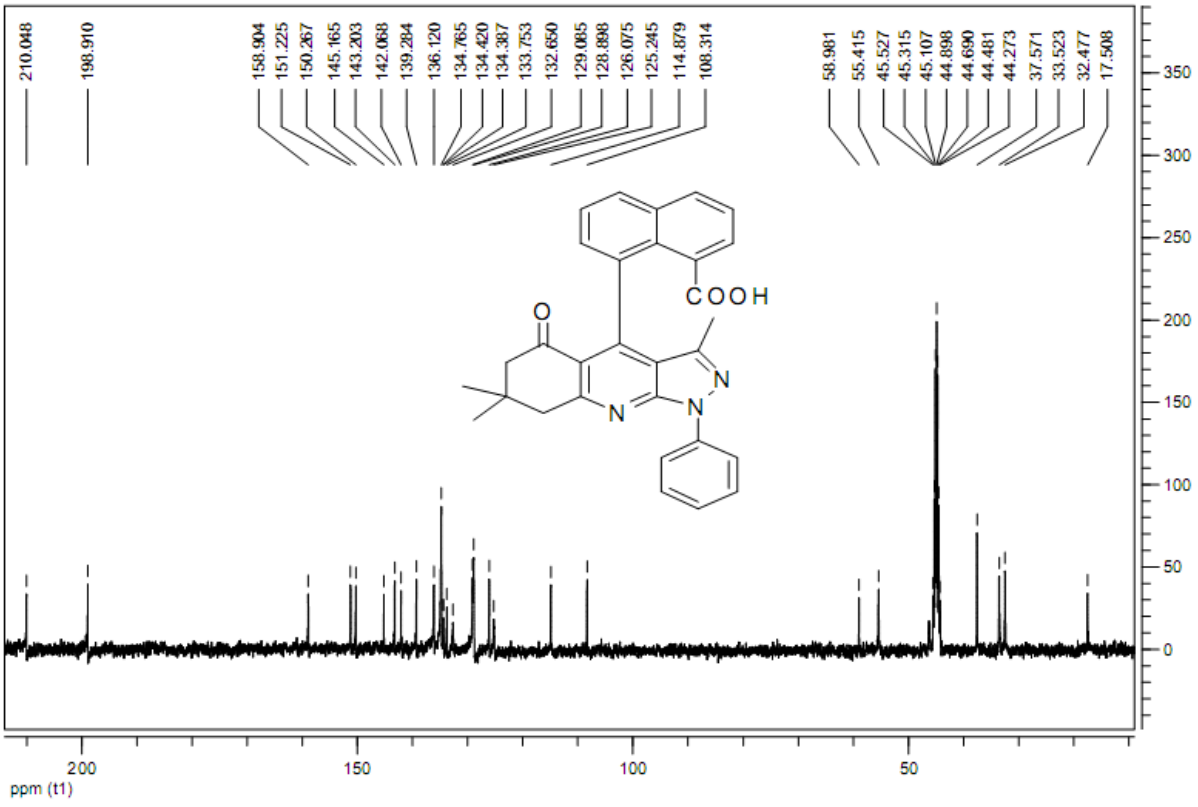
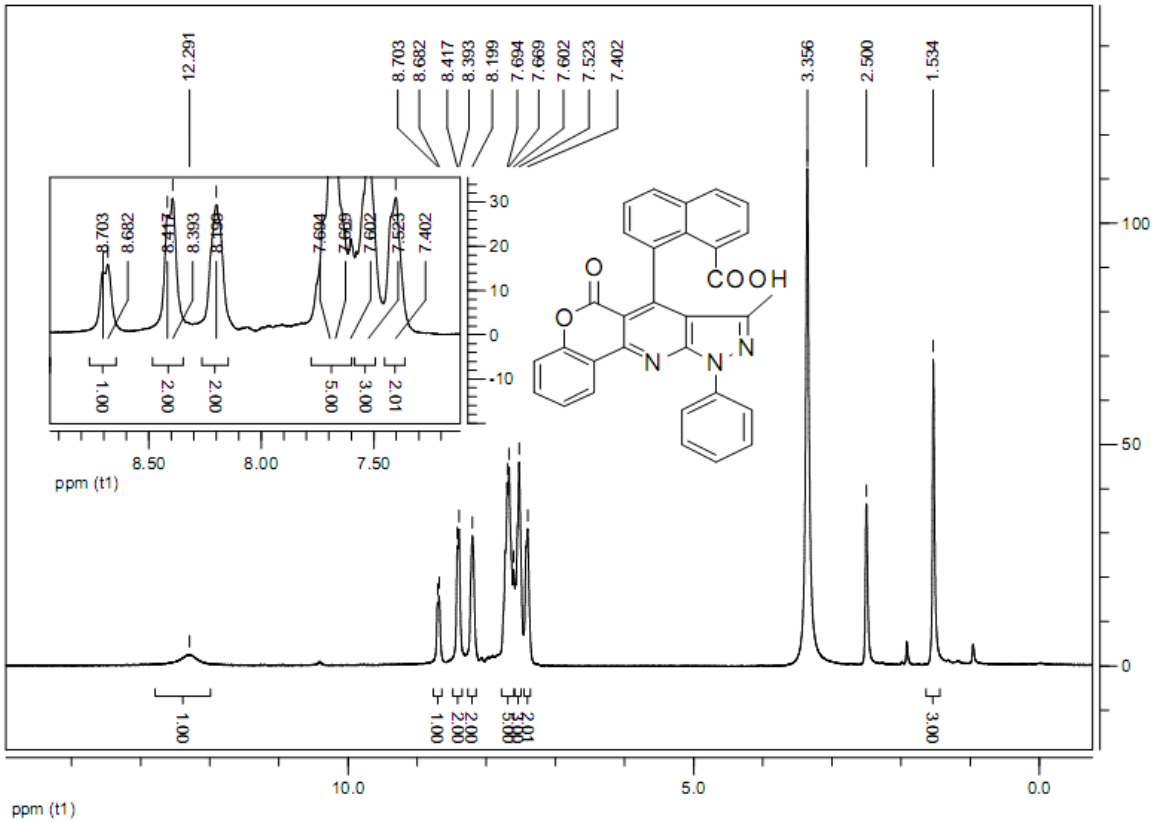
100
50

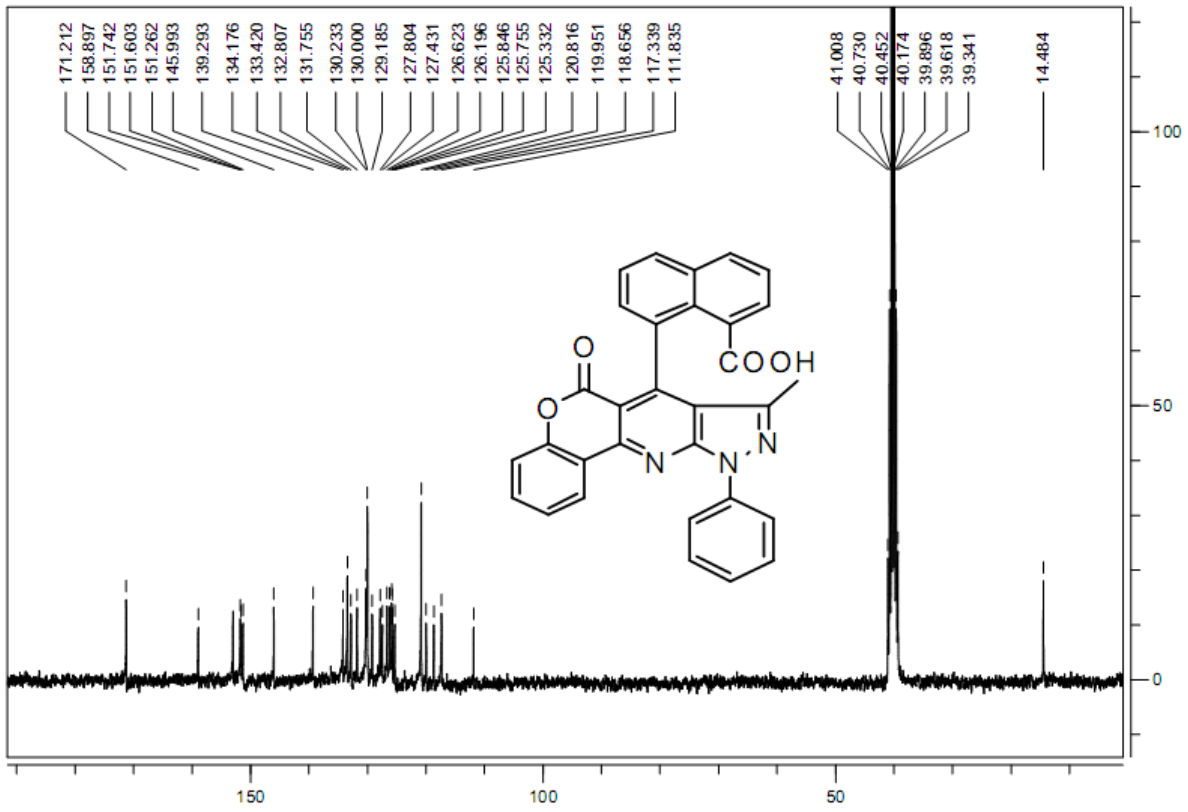












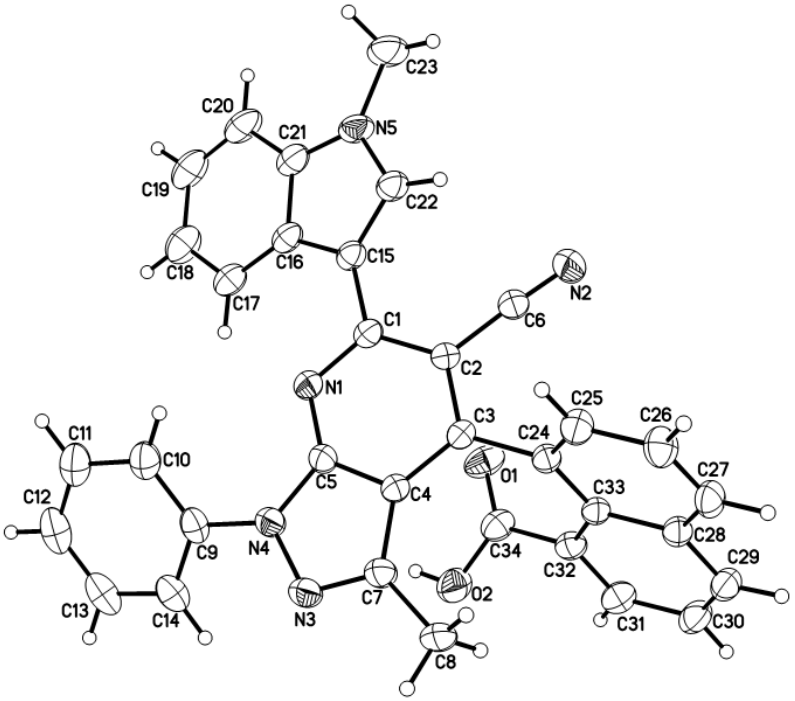


Table 1. Crystal data and structure refinement for shelxl.

Identification code	shelxl
Empirical formula	C37 H30 N6 O3
Formula weight	606.67
Temperature	223(2) K
Wavelength	0.71075 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 11.3442(11) Å alpha = 90°. b = 19.9830(18) Å beta = 99.660(3)°. c = 13.8952(13) Å gamma = 90°.
Volume	3105.3(5) $Å^3$
Z, Calculated density	4, 1.298 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F(000)	1272
Crystal size	0.60×0.50×0.20 mm
Theta range for data collection	3.22 to 27.47.
Limiting indices	-14<=h<=9, -24<=k<=25, -18<=l<=18
Reflections collected / unique	17592 / 7045 [R(int) = 0.0403]
Completeness to theta = 27.47	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.983 and 0.714
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7045 / 0 / 421
Goodness-of-fit on F^2	1.150
Final R indices [I>2sigma(I)]	R1 = 0.0789, wR2 = 0.1621
R indices (all data)	R1 = 0.1144, wR2 = 0.1810

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for shelxl.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	3970(2)	5612(1)	7253(1)	58(1)
O(2)	4312(2)	4812(1)	8392(1)	61(1)
O(3)	4902(2)	6009(1)	2777(2)	81(1)
N(1)	1729(2)	4601(1)	5526(1)	39(1)
N(2)	1309(3)	6969(1)	6044(2)	69(1)
N(3)	1896(2)	3678(1)	7731(2)	48(1)
N(4)	1950(2)	3731(1)	6742(1)	44(1)
N(5)	1183(2)	6125(1)	3026(1)	50(1)
N(6)	4479(2)	6339(2)	4219(2)	68(1)
C(1)	1527(2)	5258(1)	5394(2)	36(1)
C(2)	1378(2)	5685(1)	6193(2)	35(1)
C(3)	1409(2)	5438(1)	7135(2)	34(1)
C(4)	1559(2)	4748(1)	7256(2)	36(1)
C(5)	1742(2)	4378(1)	6436(2)	38(1)
C(6)	1336(2)	6399(1)	6088(2)	45(1)
C(7)	1654(2)	4281(1)	8036(2)	43(1)
C(8)	1485(3)	4398(1)	9070(2)	55(1)
C(9)	2290(2)	3172(1)	6217(2)	45(1)
C(10)	1849(3)	3101(1)	5236(2)	53(1)
C(11)	2222(3)	2562(2)	4726(2)	63(1)
C(12)	3010(3)	2103(2)	5194(3)	66(1)
C(13)	3427(3)	2171(1)	6175(3)	62(1)
C(14)	3071(3)	2703(1)	6702(2)	53(1)
C(15)	1502(2)	5499(1)	4399(2)	38(1)
C(16)	1950(2)	5141(1)	3632(2)	41(1)
C(17)	2550(2)	4537(1)	3578(2)	48(1)
C(18)	2904(3)	4356(2)	2710(2)	61(1)
C(19)	2656(3)	4766(2)	1889(2)	66(1)
C(20)	2075(3)	5362(2)	1913(2)	59(1)
C(21)	1735(2)	5548(1)	2793(2)	48(1)
C(22)	1055(2)	6096(1)	3987(2)	45(1)
C(23)	915(3)	6714(2)	2399(2)	68(1)
C(24)	1280(2)	5903(1)	7953(2)	35(1)
C(25)	167(2)	6166(1)	7952(2)	45(1)
C(26)	-75(3)	6596(1)	8687(2)	51(1)
C(27)	818(3)	6764(1)	9424(2)	47(1)
C(28)	1985(2)	6506(1)	9469(2)	39(1)

C(29)	2889(3)	6666(1)	10267(2)	48(1)
C(30)	3985(3)	6388(1)	10365(2)	53(1)
C(31)	4262(3)	5951(1)	9642(2)	49(1)
C(32)	3440(2)	5807(1)	8822(2)	40(1)
C(33)	2251(2)	6067(1)	8718(2)	35(1)
C(34)	3917(2)	5402(1)	8064(2)	46(1)
C(35)	4554(4)	6215(3)	5258(3)	120(2)
C(36)	3895(3)	6948(2)	3836(3)	86(1)
C(37)	4919(3)	5907(2)	3646(2)	68(1)

Table 3. Selected bond lengths [Å] and angles [deg] for shelxl.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [Å] and angles [°] for shelxl.

O(1)-C(34)	1.214(3)
O(2)-C(34)	1.314(3)
O(2)-H(2)	0.8300
O(3)-C(37)	1.221(4)
N(1)-C(5)	1.338(3)
N(1)-C(1)	1.340(3)
N(2)-C(6)	1.139(3)
N(3)-C(7)	1.323(3)
N(3)-N(4)	1.390(3)
N(4)-C(5)	1.369(3)
N(4)-C(9)	1.422(3)
N(5)-C(22)	1.369(3)
N(5)-C(21)	1.378(4)
N(5)-C(23)	1.465(3)
N(6)-C(37)	1.327(4)
N(6)-C(36)	1.444(4)
N(6)-C(35)	1.453(4)
C(1)-C(2)	1.432(3)
C(1)-C(15)	1.460(3)
C(2)-C(3)	1.395(3)
C(2)-C(6)	1.436(3)
C(3)-C(4)	1.394(3)
C(3)-C(24)	1.494(3)
C(4)-C(5)	1.403(3)
C(4)-C(7)	1.422(3)
C(7)-C(8)	1.499(3)

C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(8)-H(8C)	0.9700
C(9)-C(10)	1.378(4)
C(9)-C(14)	1.385(4)
C(10)-C(11)	1.393(4)
C(10)-H(10)	0.9400
C(11)-C(12)	1.367(4)
C(11)-H(11)	0.9400
C(12)-C(13)	1.373(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.387(4)
C(13)-H(13)	0.9400
C(14)-H(14)	0.9400
C(15)-C(22)	1.382(3)
C(15)-C(16)	1.444(3)
C(16)-C(17)	1.394(4)
C(16)-C(21)	1.408(3)
C(17)-C(18)	1.381(4)
C(17)-H(17)	0.9400
C(18)-C(19)	1.395(4)
C(18)-H(18)	0.9400
C(19)-C(20)	1.364(5)
C(19)-H(19)	0.9400
C(20)-C(21)	1.393(4)
C(20)-H(20)	0.9400
C(22)-H(22)	0.9400
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(23)-H(23C)	0.9700
C(24)-C(25)	1.368(3)
C(24)-C(33)	1.434(3)
C(25)-C(26)	1.398(3)
C(25)-H(25)	0.9400
C(26)-C(27)	1.357(4)
C(26)-H(26)	0.9400
C(27)-C(28)	1.413(4)
C(27)-H(27)	0.9400
C(28)-C(29)	1.415(4)
C(28)-C(33)	1.433(3)
C(29)-C(30)	1.348(4)
C(29)-H(29)	0.9400
C(30)-C(31)	1.406(4)
C(30)-H(30)	0.9400

C(31)-C(32)	1.376(3)
C(31)-H(31)	0.9400
C(32)-C(33)	1.430(3)
C(32)-C(34)	1.500(3)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700
C(35)-H(35C)	0.9700
C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
C(36)-H(36C)	0.9700
C(37)-H(37)	0.9400
C(34)-O(2)-H(2)	109.5
C(5)-N(1)-C(1)	115.51(19)
C(7)-N(3)-N(4)	107.06(18)
C(5)-N(4)-N(3)	110.21(18)
C(5)-N(4)-C(9)	129.0(2)
N(3)-N(4)-C(9)	120.53(19)
C(22)-N(5)-C(21)	108.6(2)
C(22)-N(5)-C(23)	124.7(2)
C(21)-N(5)-C(23)	126.2(2)
C(37)-N(6)-C(36)	121.5(3)
C(37)-N(6)-C(35)	121.4(4)
C(36)-N(6)-C(35)	117.2(3)
N(1)-C(1)-C(2)	121.13(19)
N(1)-C(1)-C(15)	115.41(19)
C(2)-C(1)-C(15)	123.4(2)
C(3)-C(2)-C(1)	121.9(2)
C(3)-C(2)-C(6)	116.3(2)
C(1)-C(2)-C(6)	121.36(19)
C(4)-C(3)-C(2)	116.46(19)
C(4)-C(3)-C(24)	123.29(19)
C(2)-C(3)-C(24)	120.25(19)
C(3)-C(4)-C(5)	117.14(19)
C(3)-C(4)-C(7)	137.1(2)
C(5)-C(4)-C(7)	105.7(2)
N(1)-C(5)-N(4)	125.6(2)
N(1)-C(5)-C(4)	127.7(2)
N(4)-C(5)-C(4)	106.74(19)
N(2)-C(6)-C(2)	177.3(3)
N(3)-C(7)-C(4)	110.3(2)
N(3)-C(7)-C(8)	121.1(2)
C(4)-C(7)-C(8)	128.6(2)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5

H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(14)	120.5(2)
C(10)-C(9)-N(4)	120.3(2)
C(14)-C(9)-N(4)	119.3(2)
C(9)-C(10)-C(11)	119.5(3)
C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	120.5(3)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(13)	119.6(3)
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	121.1(3)
C(12)-C(13)-H(13)	119.4
C(14)-C(13)-H(13)	119.4
C(9)-C(14)-C(13)	118.8(3)
C(9)-C(14)-H(14)	120.6
C(13)-C(14)-H(14)	120.6
C(22)-C(15)-C(16)	105.7(2)
C(22)-C(15)-C(1)	128.7(2)
C(16)-C(15)-C(1)	125.6(2)
C(17)-C(16)-C(21)	118.2(2)
C(17)-C(16)-C(15)	134.8(2)
C(21)-C(16)-C(15)	107.0(2)
C(18)-C(17)-C(16)	119.3(3)
C(18)-C(17)-H(17)	120.3
C(16)-C(17)-H(17)	120.3
C(17)-C(18)-C(19)	120.9(3)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	121.6(3)
C(20)-C(19)-H(19)	119.2
C(18)-C(19)-H(19)	119.2
C(19)-C(20)-C(21)	117.4(3)
C(19)-C(20)-H(20)	121.3
C(21)-C(20)-H(20)	121.3
N(5)-C(21)-C(20)	129.3(3)
N(5)-C(21)-C(16)	108.1(2)
C(20)-C(21)-C(16)	122.6(3)
N(5)-C(22)-C(15)	110.5(2)

N(5)-C(22)-H(22)	124.7
C(15)-C(22)-H(22)	124.7
N(5)-C(23)-H(23A)	109.5
N(5)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
N(5)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(33)	120.5(2)
C(25)-C(24)-C(3)	116.5(2)
C(33)-C(24)-C(3)	123.1(2)
C(24)-C(25)-C(26)	122.0(2)
C(24)-C(25)-H(25)	119.0
C(26)-C(25)-H(25)	119.0
C(27)-C(26)-C(25)	119.4(3)
C(27)-C(26)-H(26)	120.3
C(25)-C(26)-H(26)	120.3
C(26)-C(27)-C(28)	121.3(2)
C(26)-C(27)-H(27)	119.4
C(28)-C(27)-H(27)	119.4
C(27)-C(28)-C(29)	120.2(2)
C(27)-C(28)-C(33)	120.1(2)
C(29)-C(28)-C(33)	119.7(2)
C(30)-C(29)-C(28)	121.4(2)
C(30)-C(29)-H(29)	119.3
C(28)-C(29)-H(29)	119.3
C(29)-C(30)-C(31)	119.8(2)
C(29)-C(30)-H(30)	120.1
C(31)-C(30)-H(30)	120.1
C(32)-C(31)-C(30)	121.3(3)
C(32)-C(31)-H(31)	119.3
C(30)-C(31)-H(31)	119.3
C(31)-C(32)-C(33)	120.3(2)
C(31)-C(32)-C(34)	114.9(2)
C(33)-C(32)-C(34)	124.8(2)
C(32)-C(33)-C(28)	117.3(2)
C(32)-C(33)-C(24)	125.8(2)
C(28)-C(33)-C(24)	116.8(2)
O(1)-C(34)-O(2)	124.5(2)
O(1)-C(34)-C(32)	123.0(2)
O(2)-C(34)-C(32)	112.5(2)
N(6)-C(35)-H(35A)	109.5
N(6)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5

N(6)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
N(6)-C(36)-H(36A)	109.5
N(6)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
N(6)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(3)-C(37)-N(6)	122.7(3)
O(3)-C(37)-H(37)	118.7
N(6)-C(37)-H(37)	118.7

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2$ x 10^3) for shelxl.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
O(1)	51(1)	87(1)	39(1)	4(1)	15(1)	6(1)
O(2)	69(1)	66(1)	49(1)	-5(1)	9(1)	23(1)
O(3)	89(2)	82(2)	74(2)	-18(1)	18(1)	9(1)
N(1)	48(1)	38(1)	32(1)	-1(1)	9(1)	-1(1)
N(2)	119(2)	39(1)	48(1)	5(1)	15(1)	2(1)
N(3)	64(2)	40(1)	40(1)	7(1)	13(1)	5(1)
N(4)	61(1)	35(1)	38(1)	2(1)	13(1)	4(1)
N(5)	63(2)	54(1)	33(1)	12(1)	7(1)	-8(1)
N(6)	52(2)	96(2)	57(1)	-12(2)	14(1)	-10(1)
C(1)	37(1)	40(1)	31(1)	-1(1)	6(1)	-3(1)
C(2)	40(1)	35(1)	31(1)	2(1)	3(1)	0(1)
C(3)	35(1)	37(1)	30(1)	-2(1)	4(1)	0(1)
C(4)	44(1)	35(1)	30(1)	0(1)	8(1)	-1(1)
C(5)	47(1)	33(1)	35(1)	0(1)	9(1)	-2(1)
C(6)	61(2)	40(1)	33(1)	2(1)	10(1)	1(1)
C(7)	54(2)	40(1)	37(1)	5(1)	13(1)	3(1)
C(8)	83(2)	49(2)	35(1)	9(1)	16(1)	4(1)
C(9)	50(2)	33(1)	55(2)	-4(1)	18(1)	-5(1)
C(10)	60(2)	46(1)	55(2)	-9(1)	15(1)	-3(1)
C(11)	70(2)	55(2)	68(2)	-18(2)	21(2)	-10(2)
C(12)	68(2)	44(2)	93(2)	-15(2)	34(2)	-8(2)
C(13)	54(2)	38(1)	99(2)	5(2)	27(2)	2(1)
C(14)	55(2)	39(1)	69(2)	5(1)	19(1)	-2(1)

C(15)	41(1)	42(1)	32(1)	0(1)	7(1)	-8(1)
C(16)	39(1)	52(1)	32(1)	-2(1)	7(1)	-10(1)
C(17)	45(2)	63(2)	37(1)	-5(1)	9(1)	-3(1)
C(18)	56(2)	82(2)	49(2)	-15(2)	16(1)	2(2)
C(19)	68(2)	96(2)	39(2)	-15(2)	21(1)	-12(2)
C(20)	65(2)	84(2)	31(1)	1(1)	13(1)	-19(2)
C(21)	50(2)	58(2)	35(1)	0(1)	6(1)	-15(1)
C(22)	53(2)	47(1)	35(1)	3(1)	8(1)	-7(1)
C(23)	90(2)	66(2)	46(2)	22(1)	6(2)	-11(2)
C(24)	41(1)	34(1)	31(1)	1(1)	10(1)	-1(1)
C(25)	43(2)	47(1)	44(1)	-5(1)	6(1)	1(1)
C(26)	47(2)	51(2)	56(2)	-9(1)	15(1)	8(1)
C(27)	58(2)	43(1)	44(1)	-8(1)	20(1)	3(1)
C(28)	49(2)	36(1)	35(1)	0(1)	14(1)	-5(1)
C(29)	63(2)	45(1)	36(1)	-5(1)	11(1)	-7(1)
C(30)	63(2)	57(2)	36(1)	-5(1)	1(1)	-13(1)
C(31)	45(2)	59(2)	42(1)	0(1)	5(1)	-2(1)
C(32)	41(1)	43(1)	35(1)	4(1)	9(1)	-2(1)
C(33)	44(1)	34(1)	29(1)	2(1)	10(1)	-4(1)
C(34)	37(1)	60(2)	41(1)	-2(1)	3(1)	4(1)
C(35)	81(3)	222(6)	58(2)	-5(3)	17(2)	4(3)
C(36)	76(3)	81(2)	106(3)	-25(2)	31(2)	-7(2)
C(37)	60(2)	82(2)	62(2)	-7(2)	13(2)	-5(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for shelxl.

	x	y	z	U(eq)
H(2)	4527	4595	7942	92
H(8A)	1424	3971	9390	82
H(8B)	760	4654	9075	82
H(8C)	2164	4645	9414	82
H(10)	1302	3414	4914	64
H(11)	1928	2514	4056	76
H(12)	3266	1743	4846	79
H(13)	3964	1852	6496	74
H(14)	3354	2743	7375	64
H(17)	2712	4255	4126	58
H(18)	3317	3952	2673	74
H(19)	2896	4628	1304	79
H(20)	1911	5636	1357	71

H(22)	712	6434	4320	54
H(23A)	488	7041	2724	102
H(23B)	425	6582	1788	102
H(23C)	1656	6909	2269	102
H(25)	-454	6053	7441	54
H(26)	-850	6767	8671	61
H(27)	658	7058	9914	56
H(29)	2722	6973	10739	57
H(30)	4562	6485	10916	64
H(31)	5025	5754	9720	59
H(35A)	4875	5771	5413	180
H(35B)	3763	6248	5432	180
H(35C)	5076	6545	5623	180
H(36A)	3873	6966	3136	128
H(36B)	4335	7331	4140	128
H(36C)	3086	6958	3975	128
H(37)	5257	5507	3920	82

Table 7. Torsion angles [°] for shelxl.

C(7)-N(3)-N(4)-C(5)	0.3(3)
C(7)-N(3)-N(4)-C(9)	175.1(2)
C(5)-N(1)-C(1)-C(2)	2.1(3)
C(5)-N(1)-C(1)-C(15)	-179.4(2)
N(1)-C(1)-C(2)-C(3)	-1.5(4)
C(15)-C(1)-C(2)-C(3)	-179.9(2)
N(1)-C(1)-C(2)-C(6)	170.7(2)
C(15)-C(1)-C(2)-C(6)	-7.7(4)
C(1)-C(2)-C(3)-C(4)	-1.8(3)
C(6)-C(2)-C(3)-C(4)	-174.4(2)
C(1)-C(2)-C(3)-C(24)	178.4(2)
C(6)-C(2)-C(3)-C(24)	5.8(3)
C(2)-C(3)-C(4)-C(5)	4.1(3)
C(24)-C(3)-C(4)-C(5)	-176.1(2)
C(2)-C(3)-C(4)-C(7)	179.3(3)
C(24)-C(3)-C(4)-C(7)	-0.9(5)
C(1)-N(1)-C(5)-N(4)	-178.9(2)
C(1)-N(1)-C(5)-C(4)	0.6(4)
N(3)-N(4)-C(5)-N(1)	180.0(2)
C(9)-N(4)-C(5)-N(1)	5.8(4)
N(3)-N(4)-C(5)-C(4)	0.4(3)
C(9)-N(4)-C(5)-C(4)	-173.8(2)
C(3)-C(4)-C(5)-N(1)	-3.8(4)

C(7)-C(4)-C(5)-N(1)	179.6(2)
C(3)-C(4)-C(5)-N(4)	175.7(2)
C(7)-C(4)-C(5)-N(4)	-0.9(3)
C(3)-C(2)-C(6)-N(2)	6(7)
C(1)-C(2)-C(6)-N(2)	-166(7)
N(4)-N(3)-C(7)-C(4)	-0.8(3)
N(4)-N(3)-C(7)-C(8)	177.6(2)
C(3)-C(4)-C(7)-N(3)	-174.5(3)
C(5)-C(4)-C(7)-N(3)	1.1(3)
C(3)-C(4)-C(7)-C(8)	7.2(5)
C(5)-C(4)-C(7)-C(8)	-177.2(3)
C(5)-N(4)-C(9)-C(10)	-36.1(4)
N(3)-N(4)-C(9)-C(10)	150.2(2)
C(5)-N(4)-C(9)-C(14)	143.6(3)
N(3)-N(4)-C(9)-C(14)	-30.1(4)
C(14)-C(9)-C(10)-C(11)	-1.8(4)
N(4)-C(9)-C(10)-C(11)	178.0(2)
C(9)-C(10)-C(11)-C(12)	0.5(4)
C(10)-C(11)-C(12)-C(13)	0.7(5)
C(11)-C(12)-C(13)-C(14)	-0.6(5)
C(10)-C(9)-C(14)-C(13)	1.9(4)
N(4)-C(9)-C(14)-C(13)	-177.9(2)
C(12)-C(13)-C(14)-C(9)	-0.6(4)
N(1)-C(1)-C(15)-C(22)	163.7(2)
C(2)-C(1)-C(15)-C(22)	-17.8(4)
N(1)-C(1)-C(15)-C(16)	-15.9(3)
C(2)-C(1)-C(15)-C(16)	162.6(2)
C(22)-C(15)-C(16)-C(17)	176.4(3)
C(1)-C(15)-C(16)-C(17)	-4.0(4)
C(22)-C(15)-C(16)-C(21)	-0.5(3)
C(1)-C(15)-C(16)-C(21)	179.2(2)
C(21)-C(16)-C(17)-C(18)	-0.4(4)
C(15)-C(16)-C(17)-C(18)	-177.0(3)
C(16)-C(17)-C(18)-C(19)	-0.8(4)
C(17)-C(18)-C(19)-C(20)	1.0(5)
C(18)-C(19)-C(20)-C(21)	0.0(5)
C(22)-N(5)-C(21)-C(20)	-178.2(3)
C(23)-N(5)-C(21)-C(20)	-5.7(5)
C(22)-N(5)-C(21)-C(16)	0.5(3)
C(23)-N(5)-C(21)-C(16)	173.1(3)
C(19)-C(20)-C(21)-N(5)	177.4(3)
C(19)-C(20)-C(21)-C(16)	-1.1(4)
C(17)-C(16)-C(21)-N(5)	-177.5(2)
C(15)-C(16)-C(21)-N(5)	0.0(3)

C(17)-C(16)-C(21)-C(20)	1.4(4)
C(15)-C(16)-C(21)-C(20)	178.8(2)
C(21)-N(5)-C(22)-C(15)	-0.8(3)
C(23)-N(5)-C(22)-C(15)	-173.5(3)
C(16)-C(15)-C(22)-N(5)	0.8(3)
C(1)-C(15)-C(22)-N(5)	-178.8(2)
C(4)-C(3)-C(24)-C(25)	-107.8(3)
C(2)-C(3)-C(24)-C(25)	72.0(3)
C(4)-C(3)-C(24)-C(33)	71.2(3)
C(2)-C(3)-C(24)-C(33)	-109.0(3)
C(33)-C(24)-C(25)-C(26)	-0.4(4)
C(3)-C(24)-C(25)-C(26)	178.7(2)
C(24)-C(25)-C(26)-C(27)	0.4(4)
C(25)-C(26)-C(27)-C(28)	-0.8(4)
C(26)-C(27)-C(28)-C(29)	-177.3(2)
C(26)-C(27)-C(28)-C(33)	1.2(4)
C(27)-C(28)-C(29)-C(30)	175.0(2)
C(33)-C(28)-C(29)-C(30)	-3.4(4)
C(28)-C(29)-C(30)-C(31)	2.9(4)
C(29)-C(30)-C(31)-C(32)	0.9(4)
C(30)-C(31)-C(32)-C(33)	-4.0(4)
C(30)-C(31)-C(32)-C(34)	172.9(2)
C(31)-C(32)-C(33)-C(28)	3.3(3)
C(34)-C(32)-C(33)-C(28)	-173.2(2)
C(31)-C(32)-C(33)-C(24)	-173.5(2)
C(34)-C(32)-C(33)-C(24)	10.0(4)
C(27)-C(28)-C(33)-C(32)	-178.2(2)
C(29)-C(28)-C(33)-C(32)	0.3(3)
C(27)-C(28)-C(33)-C(24)	-1.1(3)
C(29)-C(28)-C(33)-C(24)	177.4(2)
C(25)-C(24)-C(33)-C(32)	177.5(2)
C(3)-C(24)-C(33)-C(32)	-1.5(3)
C(25)-C(24)-C(33)-C(28)	0.7(3)
C(3)-C(24)-C(33)-C(28)	-178.31(19)
C(31)-C(32)-C(34)-O(1)	-116.0(3)
C(33)-C(32)-C(34)-O(1)	60.7(4)
C(31)-C(32)-C(34)-O(2)	61.2(3)
C(33)-C(32)-C(34)-O(2)	-122.1(3)
C(36)-N(6)-C(37)-O(3)	3.0(5)
C(35)-N(6)-C(37)-O(3)	-177.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 8. Hydrogen bonds for shelxl [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(3)#1	0.83	1.76	2.572(3)	165.7

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1