Novel Synthesis of Substituted furo[3,2-c]chromen-4-ones via Four-component Reaction from Substituted Nitrostyrenes, Aromatic Aldehydes, Coumarins, and Ammonium Acetate

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General. All melting points were determined in a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded in a Bruker AV-600 spectrometer with TMS as internal reference in $CDCl_3$ solutions. The *J* values are given in hertz. Only discrete or characteristic signals for the ^{1}H NMR are reported. The MS spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. The elemental analyses were performed in a Perkin-Elmer 240C instrument. Flash chromatography was performed on silica gel (230-400 mesh) eluting with ethyl acetate-hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

General procedure for preparation of 2-arylideneamino-3-aryl-4H-furo [3,2-c]chromen-4-ones.

The 4-hydroxycoumarin (324 mg, 2 mmol), appropriate 2-aryl-1-nitroethene (2 mmol) and piperidine (85 mg, 1 mmol) were dissolved in 10 mL of methanol at room temperature, and the resultant mixture was stirred at room temperature for 12. Then,

to the resultant solution appropriate aromatic aldehyde (2 mmol) and ammonium acetate (230 mg, 3 mmol) were added at room temperature. The reaction mixture was stirred at room temperature for 12 h and under reflux for 3 h, and the completion of reaction was confirmed by TLC (EtOAc/methanol 10:1). Subsequently, the precipitated product was filtered off and the solid washed with methanol and diethyl ether two times to give a product **4a**{*1,1,1*}-**4s**{*5,9,1*}. The filtrate was purified by flash chromatography (silica gel, EtOAc/CH_2Cl_2, 10/1) to give other product **4a**{*1,1,1*}-**4s**{*5,9,1*}. The merged crude product was purified ulteriorly by crystallization from hot ethanol-ethyl acetate or ethyl acetate-dichloromethane to yield pure **4a**{*1,1,1*}-**4s**{*5,9,1*}. The air-dried product showed a single spot on TLC and was pure enough for all analytical purposes.

2-(4-methoxybenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (**4a**)

Mp 218-219 ^{o}C (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.78 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 162.20 (*J* = 242 Hz), 158.76, 156.40 153.49, 152.97, 150.54, 136.73, 133.65, 131.20 (*J* = 7.8 Hz), 130.14, 129.10, 128.22, 123.48 (*J* = 3.2 Hz), 120.46, 117.74, 116.26, 113.80 (*J* = 21 Hz), 112.45, 111.23, 109.46, 54.31; IR (KBr, cm^{-1}): 2963, 2855, 1727, 1609, 1556, 1422, 1384, 1161, 1074, 804; MS(EI): (M+1): 414.55 (78%); Anal. calcd. for $C_{25}H_{16}FNO_4$ (%):C, 72.63; H, 3.90; N, 3.39; Found: C, 72.82; H, 4.06; N, 3.40.

2-(4-methoxybenzylideneamino)-3-phenyl-4H-furo[3,2-c]chromen-4-one (**4b**)

Mp 223-225 ^{o}C (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.80 (s, 1H), 7.89 (d, *J* = 6.6 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H) , 7.33 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.84, 156.43, 154.88, 153.02, 151.96, 151.80, 130.06, 129.90, 129.80, 128.41, 128.11, 126.92, 126.77, 123.40, 119.92, 116.22, 115.82, 113.41,

111.37, 109.52, 54.48; IR (KBr, cm^{-1}): 2984, 2851, 1731, 1594, 1515, 1489, 1383, 1095, 1027, 901, 845, 739; MS(EI): (M+1): 396.44 (100%); Anal. calcd. for $C_{25}H_{17}NO_4$ (%):C, 75.94; H, 4.33; N, 3.54; Found: C, 76.18; H, 4.49; N, 3.47.

2-(4-chlorobenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (**4c**)

Mp 222-223 ^oC (MeOH/ CH_2Cl_2); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.78 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 158.76, 156.40 153.49, 152.97, 152.11, 150.54, 136.73, 133.65, 131.25, 130.14, 129.10, 128.22, 123.48, 120.46, 120.03, 117.74, 116.26, 112.45, 111.23, 109.46, 54.31; IR (KBr, cm^{-1}): 2923, 1749, 1611, 1590, 1265, 1165, 1091, 1044, 1029, 902, 837, 749; MS(EI): (M+1): 430.34 (100%); Anal. calcd. for $C_{25}H_{16}ClNO_4$ (%): C, 69.85; H, 3.75; N, 3.26; Found: C, 69.65; H, 3.90; N, 3.38.

2-(4-methoxybenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (**4d**)

Mp 216-217 ^oC (MeOH/ CH_2Cl_2); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.77 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 6.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.82 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.71, 158.50, 156.61, 154.18, 151.94, 131.19, 129.94, 129.74, 128.23, 123.36, 120.82, 119.92, 116.20, 115.69, 113.68, 113.40, 112.36, 111.42, 111.30, 109.48, 54.48, 54.30; IR (KBr, cm^{-1}): 2935, 2838, 1738, 1609, 1514, 1256, 1165, 1030, 960, 830; MS(EI): (M+1): 426.41 (70%); Anal. calcd. for $C_{26}H_{19}NO_5$(%):C, 73.40; H, 4.50; N, 3.29; Found: C, 73.27; H, 4.68; N, 3.42.

2-(2-methoxybenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (**4e**)

Mp 237-238 ^oC (MeOH/ CH_2Cl_2); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.24 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.46 (t, *J* = 6.6 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H),

6.94 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 158.81, 158.53, 156.60, 153.16, 151.99, 151.74, 150.54, 132.18, 131.26, 129.79, 126.68, 123.78, 123.35, 120.85, 120.15, 119.98, 116.42, 116.16, 112.37, 111.41, 110.13, 109.46, 54.62, 54.29; IR (KBr, cm^{-1}): 2940, 2839, 1736, 1607, 1513, 1292, 1103, 1068, 1028, 903, 833, 751; MS(EI): (M+1): 426.42 (62%); Anal. calcd. for $C_{26}H_{19}NO_5$(%):C, 73.40; H, 4.50; N, 3.29; Found: C, 73.44; H, 4.72; N, 3.37.

2-(4-(dimethylamino)benzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (**4f**)

Mp 236-237 ^{o}C ($MeOH/CH_2Cl_2$); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.70 (s, 1H), 7.87 (d, *J* = 6.0 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 6H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.80 (*J* = 245 Hz), 156.72, 155.48, 152.54, 152.47, 151.91, 151.71, 131.61 (*J* = 8.7 Hz), 130.15, 129.42, 124.89 (*J* = 3.7 Hz), 123.35, 122.99, 119.82, 116.11, 113.70 (*J* = 22 Hz), 112.55, 111.46, 110.56, 109.40, 39.08; IR (KBr, cm^{-1}): 2921, 1739, 1615, 1543, 1313, 1232, 1172, 1098, 1030, 964, 755; MS(EI): (M+1): 427.46 (98%); Anal. calcd. for $C_{26}H_{19}FN_2O_3$ (%):C, 73.23; H, 4.49; N, 6.57; Found: C, 73.22; H, 4.65; N, 6.70.

2-(4-fluorobenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (**4g**)

Mp 214-215 ^{o}C ($MeOH/CH_2Cl_2$); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.83 (s, 1H), 7.90 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.84-7.85 (m, 2H), 7.82-7.84 (m, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 171.69, 164.12 (*J* = 252 Hz), 162.20 (*J* = 248 Hz), 156.40, 154.00, 153.43, 152.07, 151.07, 131.73 (*J* = 7.5 Hz), 131.34, 130.23, 130.2 (*J* = 7.5 Hz), 124.18 (*J* = 3.7 Hz), 123.57, 120.03, 116.37 (*J* = 3.7 Hz), 116.34, 115.34 (*J* = 22 Hz), 113.90 (*J* = 22 Hz), 111.18, 109.36; IR (KBr, cm^{-1}): 2921, 1753, 1628, 1595, 1511, 1497, 1405, 1095, 1065, 961, 823, 748; MS (EI): (M+1): 402.53 (100%); Anal. calcd. for $C_{24}H_{13}F_2NO_3$ (%):C, 71.82; H, 3.26; N, 3.49; Found: C, 72.92; H, 3.46; N, 3.65.

2-(4-methylbenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (**4h**)

Mp 245-246 ^{o}C (MeOH/ CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.82 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 3.0 Hz, 1H), 7.84 (t, *J* = 3.0 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 9.0 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H) , 7.32 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.80 (*J* = 245 Hz), 156.46, 155.56, 153.26, 152.01, 151.45, 141.86, 132.43, 131.74 (*J* = 8.7 Hz), 130.04, 129.79, 128.71, 128.20, 127.58, 123.51 (*J* = 3.7 Hz), 120.01, 116.27, 115.63, 113.80 (*J* = 22 Hz), 111.25, 20.77; IR (KBr, cm^{-1}): 2921, 1751, 1628, 1511, 1307, 1228, 1067, 961, 823, 748; MS(EI): (M+1): 398.52 (100%); Anal. calcd. for $C_{25}H_{16}FNO_3$ (%):C, 75.56; H, 4.06; N, 3.52; Found: C, 75.79; H, 4.28; N, 3.82.

2-((thiophen-2-yl)methyleneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (**4i**)

Mp 238-239 ^{o}C (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.87 (s, 1H), 7.89 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.84-7.85 (m, 1H), 7.82-7.83 (m, 2H), 7.57 (d, *J* = 5.4 Hz, 1H), 7.47-7.50 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.32-7.33 (m, 1H), 7.30-7.32 (m, 1H), 7.09-7.13 (m, 2H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.55 (*J* = 242 Hz), 160.91, 156.44, 153.29, 152.03, 151.29, 149.56, 139.80, 131.70 (*J* = 7.8 Hz), 130.44, 130.09, 126.02, 124.98 (*J* = 3.2 Hz), 123.53, 119.98, 116.31, 115.75, 113.80 (*J* = 21 Hz), 111.24, 109.39; IR (KBr, cm^{-1}): 2924, 1745, 1627, 1383, 1227, 1160, 1068, 962, 874, 748; MS(EI): (M+1): 390.36 (100%); Anal. calcd. for $C_{22}H_{12}FNO_3S$(%):C, 67.86; H, 3.11; N, 3.60; Found: C, 67.63; H, 3.26; N, 3.78.

2-(4-(dimethylamino)benzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chrome n-4-one (**4j**)

Mp 237-238 ^{o}C (MeOH/ CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.72 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.96 (s, 6H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 165.40, 158.21, 156.80, 154.78, 152.42, 152.17, 151.77, 151.73, 131.12, 130.03, 129.28, 123.27, 121.28, 119.80, 116.09, 112.34, 112.31, 111.58, 110.58, 104.08, 54.28, 39.10; IR (KBr, cm^{-1}): 2904, 1731, 1612, 1534, 1367, 1250, 1170,

1067, 954, 815, 762; MS(EI): (M+1): 439.48 (58%); Anal. calcd. for $C_{27}H_{22}N_2O_4$ (%):C, 73.96; H, 5.06; N, 6.39; Found: C, 73.85; H, 5.28; N, 6.44.

2-(4-methylbenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (**4k**)

Mp 225-227 ^oC (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.82 (s, 1H), 7.88 (d, *J* = 6.6 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 6.6 Hz, 2H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 8.4 Hz, 3H), 2.36 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 156.40, 155.79, 153.33, 152.01, 151.59, 141.98, 133.10, 132.37, 131.20, 130.10, 128.73, 128.25, 127.04, 126.80, 123.53, 120.01, 116.27, 115.49, 111.19, 109.25, 20.78; IR (KBr, cm^{-1}): 2921, 1750, 1625, 1497, 1384, 1150, 1095, 902, 814, 750; MS(EI): (M+1): 414.35 (100%); Anal. calcd. for $C_{25}H_{16}ClNO_3$ (%): C, 72.55; H, 3.90; N, 3.38; Found: C, 72.74; H, 4.14; N, 3.29.

2-(4-methoxybenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (**4l**)

Mp 217-218 ^oC (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.88 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 9.0 Hz, 4H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 3H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 162.01, 156.47, 156.02, 155.62, 155.23, 153.12, 151.95, 151.83, 133.96, 131.17, 129.97, 127.95, 127.02, 126.95, 123.51, 119.95, 116.26, 114.62, 113.48, 111.25, 54.51; IR (KBr, cm^{-1}): 2925, 1748, 1611, 1263, 1165, 1094, 1070, 1029, 902, 828, 754; MS(EI): (M+1): 430.44 (100%); Anal. calcd. for $C_{25}H_{16}ClNO_4$ (%):C, 69.85; H, 3.75; N, 3.26; Found: C, 69.68; H, 3.98; N, 3.47.

2-(4-chlorobenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (**4m**)

Mp 239-240 ^oC (MeOH/CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.81 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 8.4 Hz, 5H), 7.33 (d, *J* = 7.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 156.27, 154.13, 153.65, 152.14, 151.07, 150.17, 137.19, 133.39, 131.19, 130.38, 129.25, 128.34, 127.13, 126.58, 123.62, 120.07, 116.71, 116.37,

111.09, 109.30; IR (KBr, cm^{-1}): 2924, 1742, 1595, 1551, 1497, 1405, 1095, 1065, 901, 829, 749; MS(EI): (M+1): 434.01 (24%); Anal. calcd. for $C_{24}H_{13}Cl_2NO_3$ (%):C, 66.38; H, 3.02; N, 3.23; Found: C, 66.24; H, 3.28; N, 3.37.

2-(4-(dimethylamino)benzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (**4n**)

Mp 236-237 ^oC ($MeOH/CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.74 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 3H), 7.30 (t, *J* = 7.8 Hz, 1H) , 6.66 (d, *J* = 8.4 Hz, 2H), 3.02 (s, 6H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.35, 156.70, 155.72, 154.41, 152.59, 150.86, 138.47, 132.50, 131.13, 129.52, 127.61, 127.45, 127.40, 126.92, 123.40, 123.00, 122.59, 119.83, 116.17, 110.14, 39.12; IR (KBr, cm^{-1}): 2921, 1739, 1615, 1543, 1313, 1232, 1172, 1098, 1030, 964, 755; MS (EI): (M+1): 443.38 (82%); Anal. calcd. for $C_{26}H_{19}ClN_2O_3$ (%): C, 70.51; H, 4.32; N, 6.33; Found: C, 70.24; H, 4.48; N, 6.21.

2-(4-methyl)benzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (**4o**)

Mp 238-240^oC ($MeOH/ CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.84 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H) , 7.32 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 158.44, 156.40, 155.86, 153.36, 152.02, 151.57, 142.01, 132.38, 131.49, 130.12, 130.00, 129.45, 128.75, 128.28, 127.30, 123.54, 120.02, 116.29, 111.20, 109.22, 20.79; IR (KBr, cm^{-1}): 2931, 1751, 1628, 1511, 1385, 1307, 1228, 1067, 961, 823, 748; MS (EI): (M+1): 458.34 (72%); Anal. calcd. for $C_{25}H_{16}BrNO_3$ (%): C, 65.52; H, 3.52; N, 3.06; Found: C, 65.72; H, 3.66; N, 3.33.

2-(4-bromobenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (**4p**)

Mp 251-252^oC ($MeOH/ CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.80 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 5.4 Hz, 2H), 7.55 (d, *J* = 5.4 Hz, 2H), 7.50 (t, *J* = 8.4 Hz, 1H) , 7.39 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 161.62, 154.28,

153.70, 152.15, 148.26, 133.78, 131.46, 131.31, 130.40, 130.08, 129.40, 127.06, 125.80, 123.62, 121.76, 120.07, 116.83, 116.37, 111.07, 109.26; IR (KBr, cm^{-1}): 2929, 1742, 1595, 1546, 1497, 1385, 1095, 1065, 901, 827, 749; MS(EI): (M+1): 518.93 (34%); Anal. calcd. for $C_{24}H_{13}Br_2NO_3$ (%): C, 55.10; H, 2.50; N, 2.68; Found: C, 55.24; H, 2.58; N, 2.76.

2-(4-methoxybenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (**4q**)

Mp 243-244 ^oC ($MeOH/CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.78 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H) , 7.31 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 162.02, 156.44, 155.25, 153.12, 151.33, 151.78, 131.45, 130.13, 129.96, 127.93, 127.42, 123.50, 121.30, 119.93, 116.38, 116.24, 114.62, 113.49, 111.22, 109.20, 54.50; IR (KBr, cm^{-1}): 2929, 1746, 1609, 1546, 1509, 1385, 1311, 1263, 1164, 1065, 963, 827; MS (EI): (M+1): 474.47 (24%); Anal. calcd. for $C_{25}H_{16}BrNO_4$ (%):C, 63.31; H, 3.40; N, 2.95; Found: C, 63.28; H, 3.29; N, 3.04.

(E)-2-(4-chlorobenzylideneamino)-3-(2-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (4r)

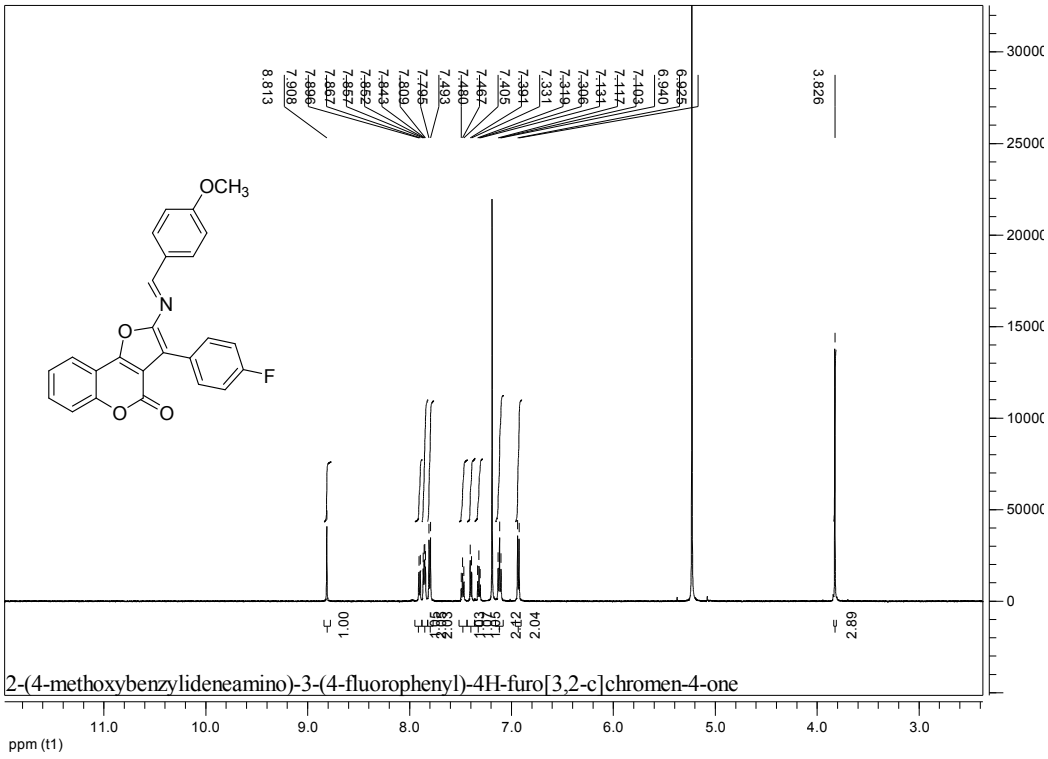
Yellow solid, yield 54%, m.p. 226-227 ^oC ($MeOH/ CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.75 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 156.90, 155.77, 153.41, 152.10, 151.43, 136.70, 133.54, 131.33, 129.81, 129.11, 128.12, 123.33, 119.94, 119.17, 117.59, 116.28, 114.87, 111.49, 109.91, 54.56; IR (KBr, cm^{-1}): 2972, 1761, 1594, 1498, 1278, 1165, 1091, 1044, 1031, 902, 837, 750; MS(EI): (M+1): 430.62(58%).

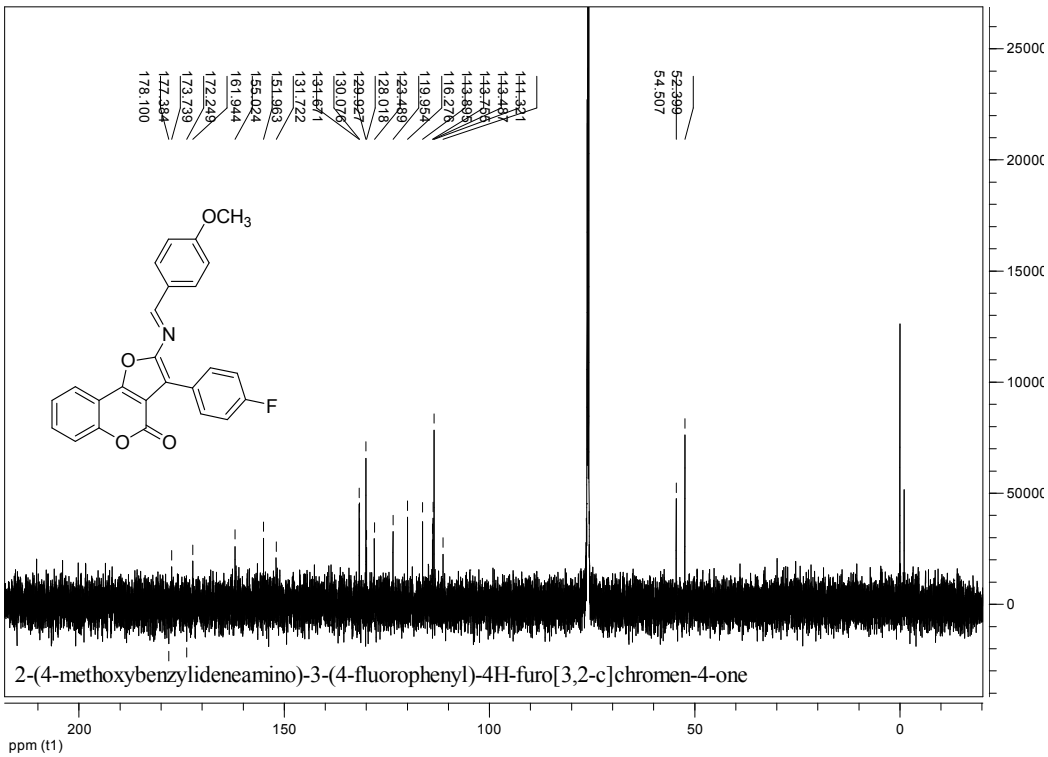
(E)-2-(3-methoxybenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4s)

Yellow solid, yield 60%, m.p. 213-214 ^oC ($MeOH/ CH_2Cl_2$); ^1H-NMR ($CDCl_3$, 600

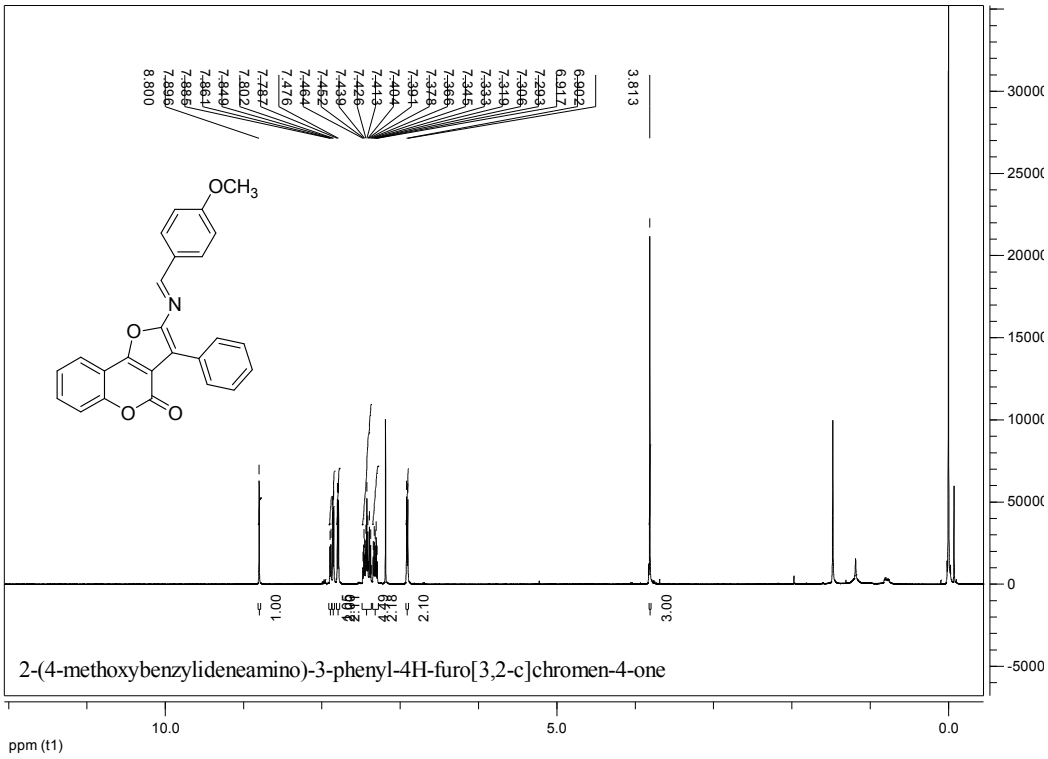
MHz) δ (ppm): 8.77 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 3H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 3.79 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 158.96, 156.30, 155.56, 153.53, 152.02, 151.14, 136.22, 131.48, 130.25, 129.95, 128.91, 127.13, 123.56, 121.59, 121.50, 120.05, 117.50, 116.26, 116.17, 111.73, 111.04, 109.12, 54.33; IR (KBr, cm^{-1}): 3067, 2961, 1750, 1596, 1569, 1265, 1165, 1091, 1044, 1029, 902, 847, 746; MS(EI): (M+1): 474.56 (22%).

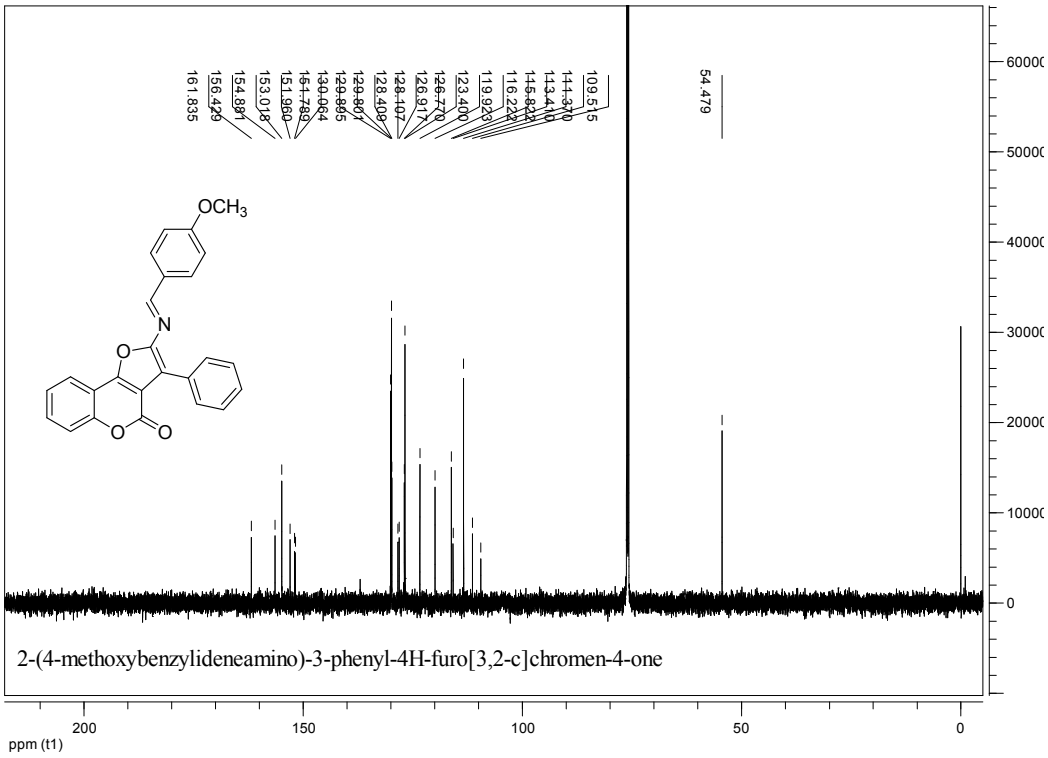
2-(4-methoxybenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (4a)



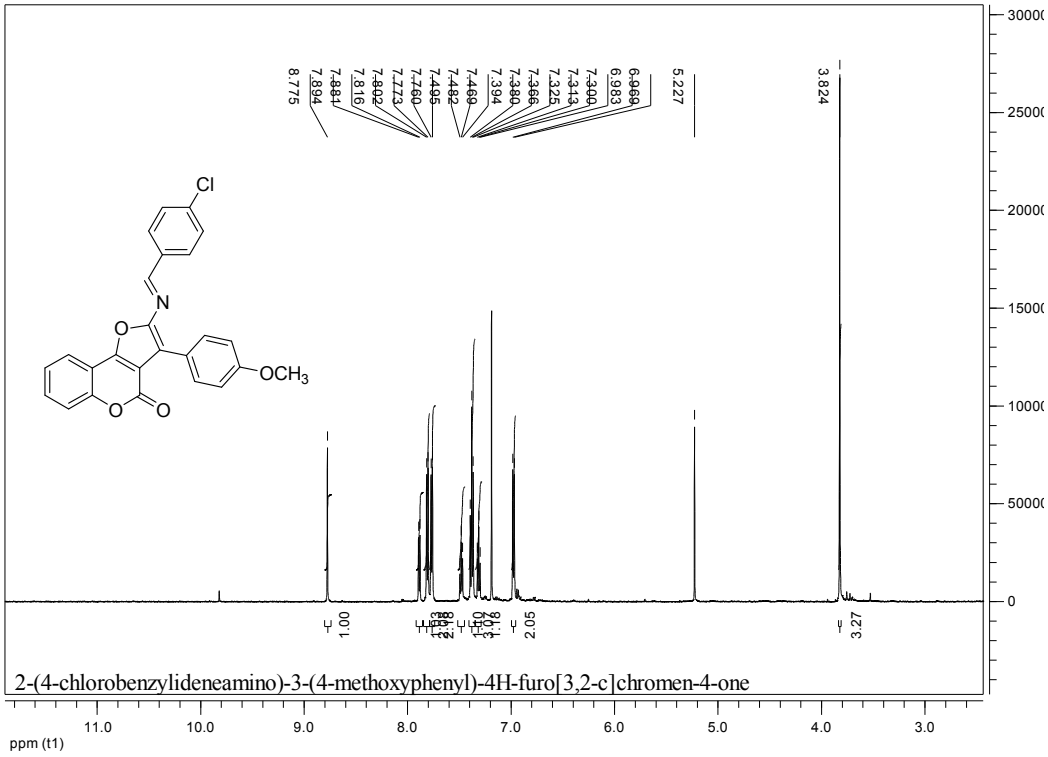


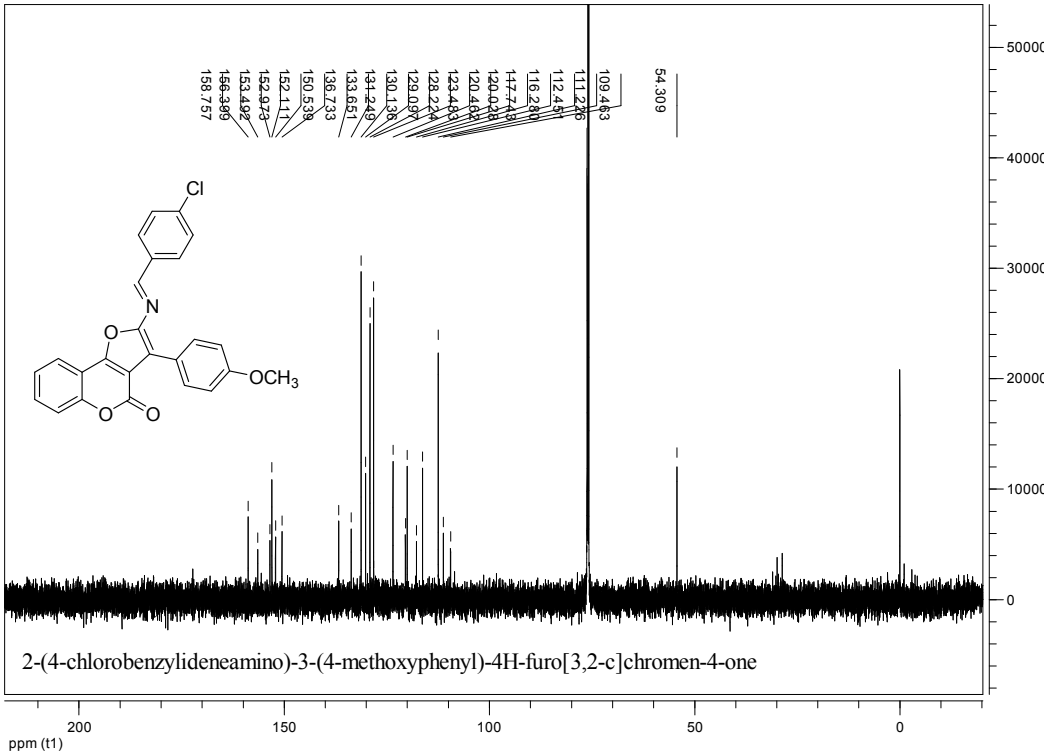
2-(4-methoxybenzylideneamino)-3-phenyl-4H-furo[3,2-c]chromen-4-one (4b)



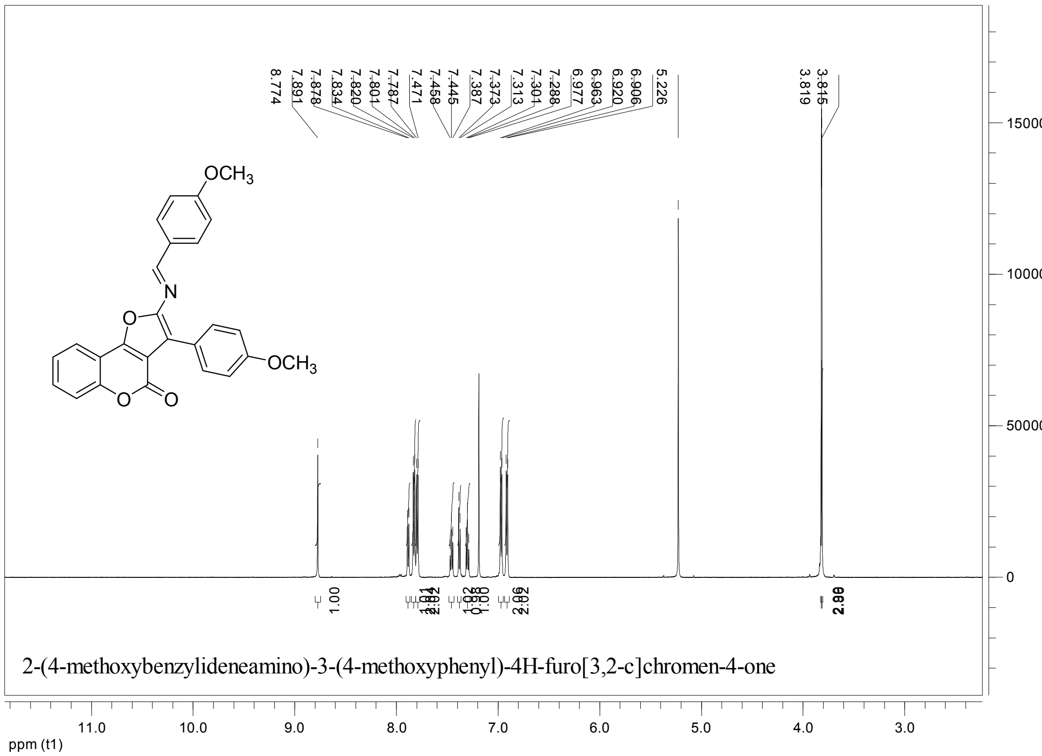


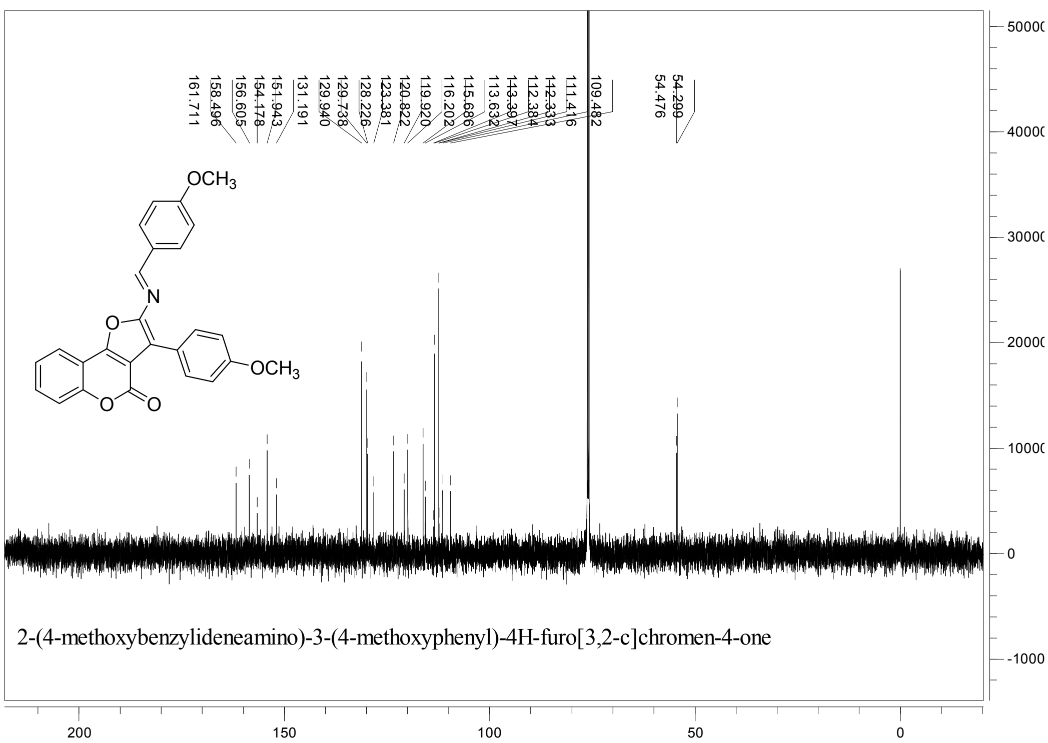
2-(4-chlorobenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (4c)



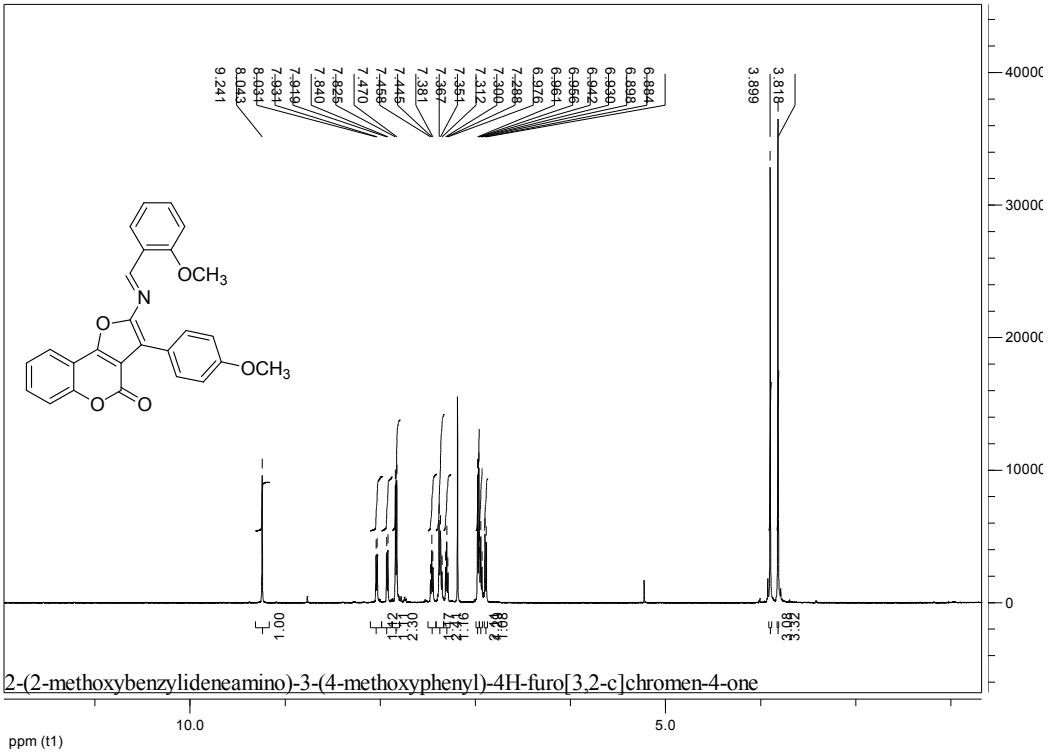


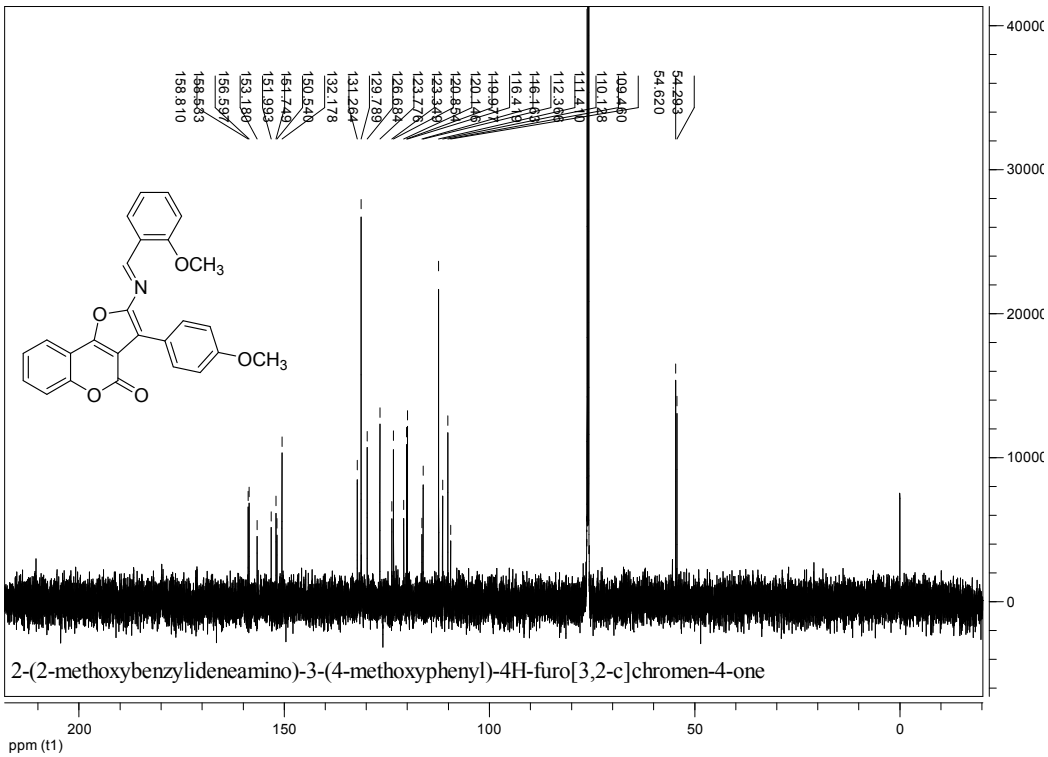
2-(4-methoxybenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (4d)



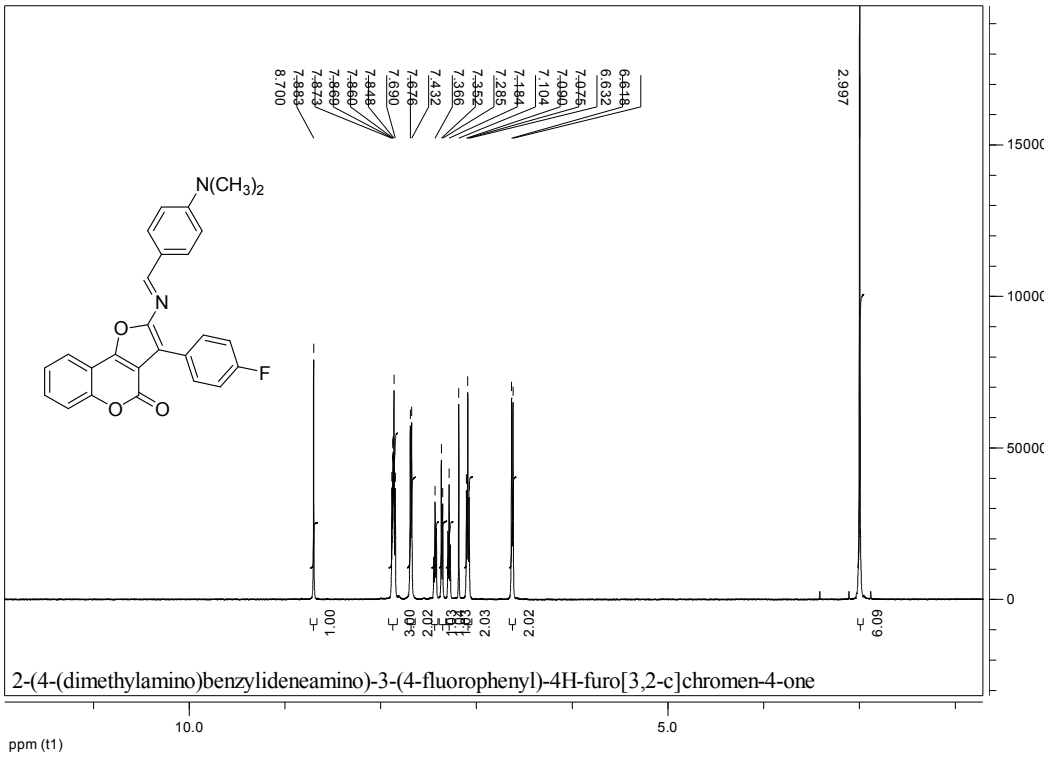


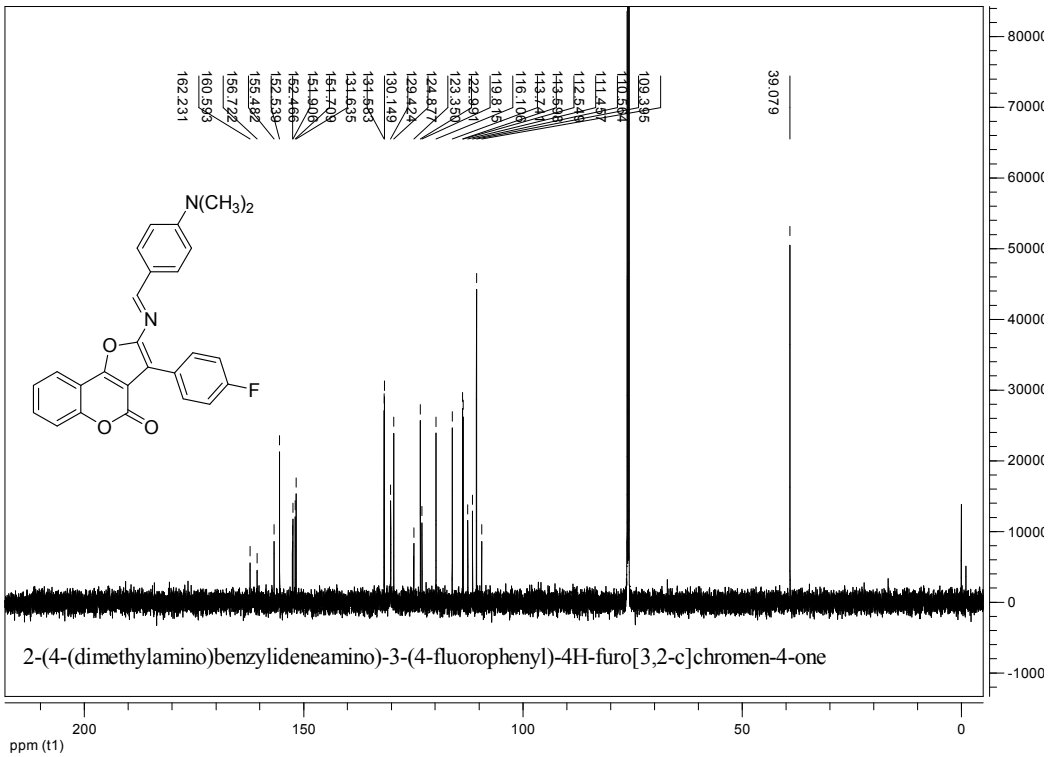
2-(2-methoxybenzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (4e)



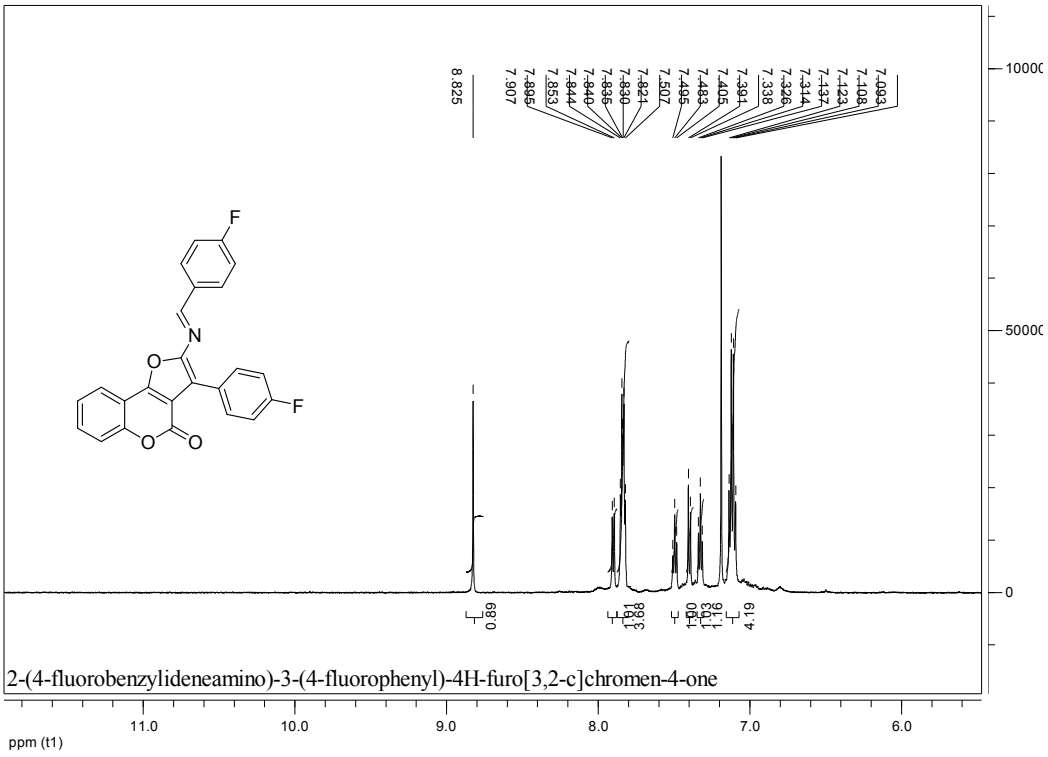


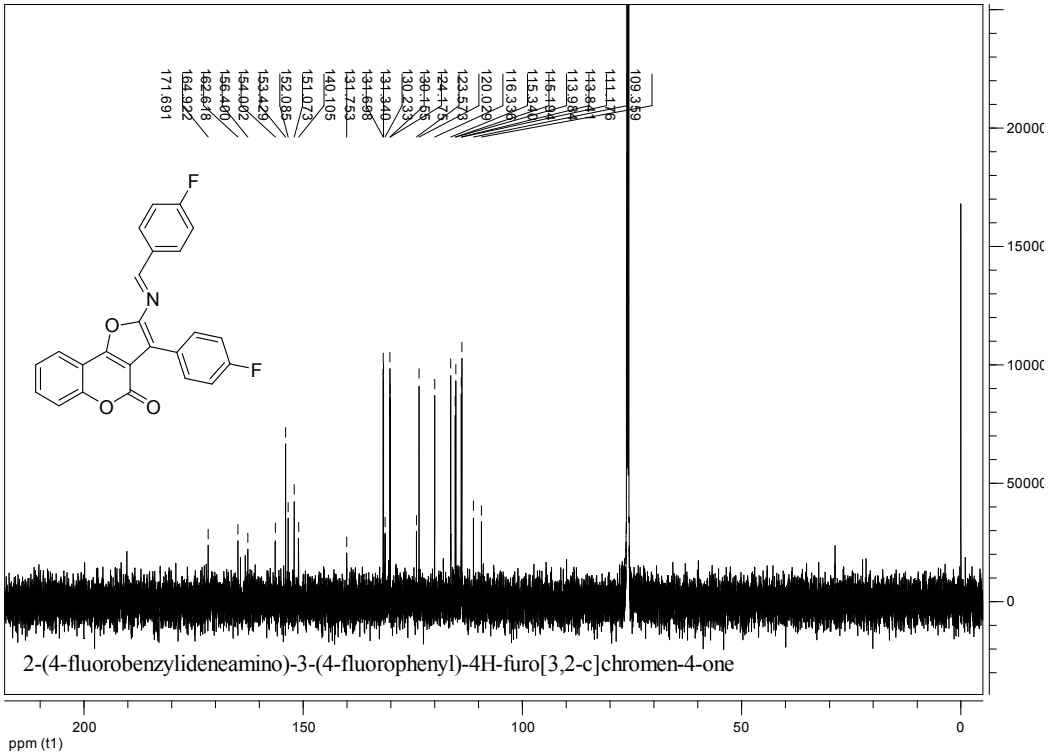
2-(4-(dimethylamino)benzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (4f)



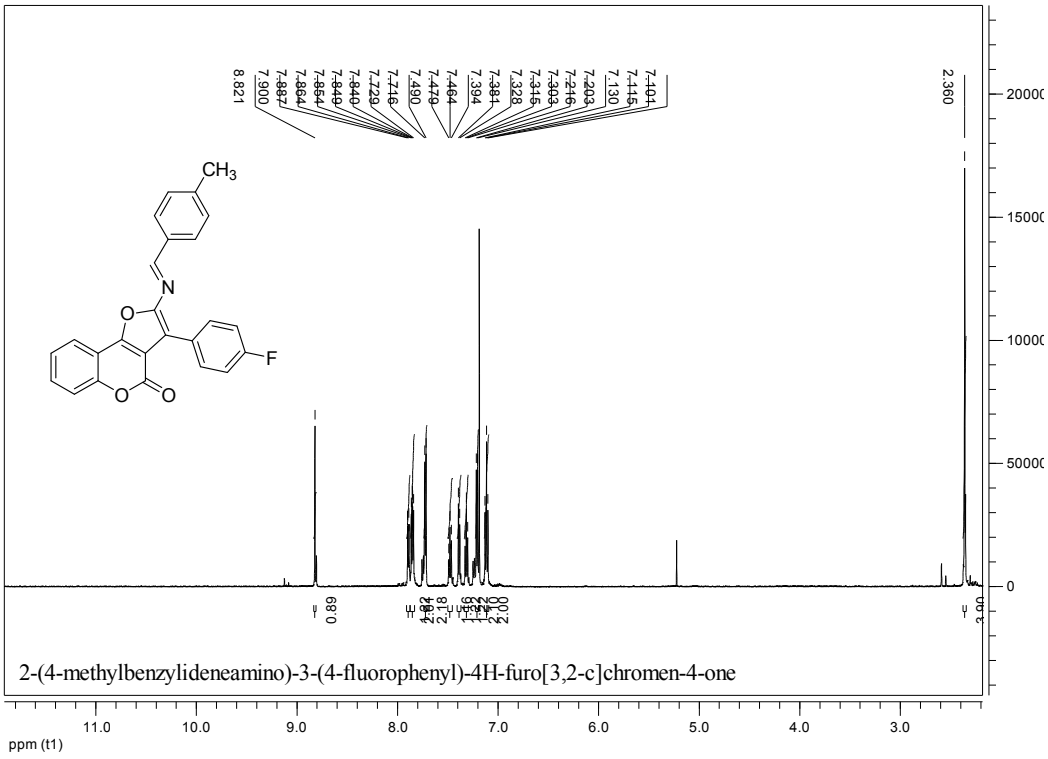


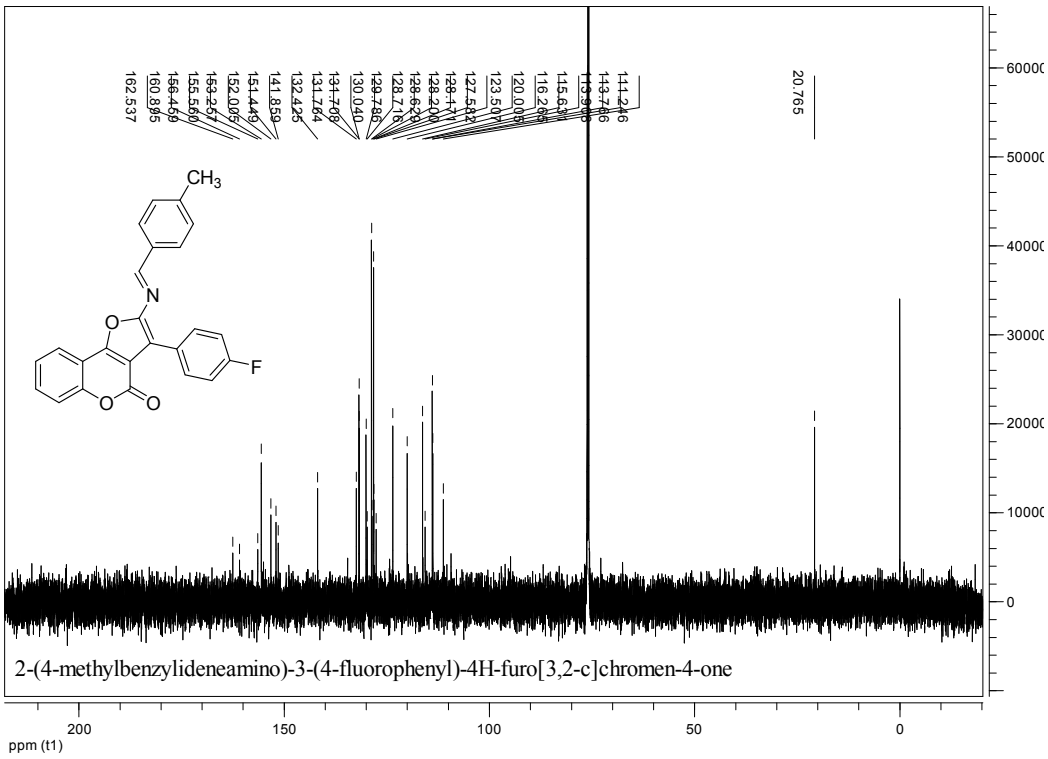
2-(4-fluorobenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (4g)



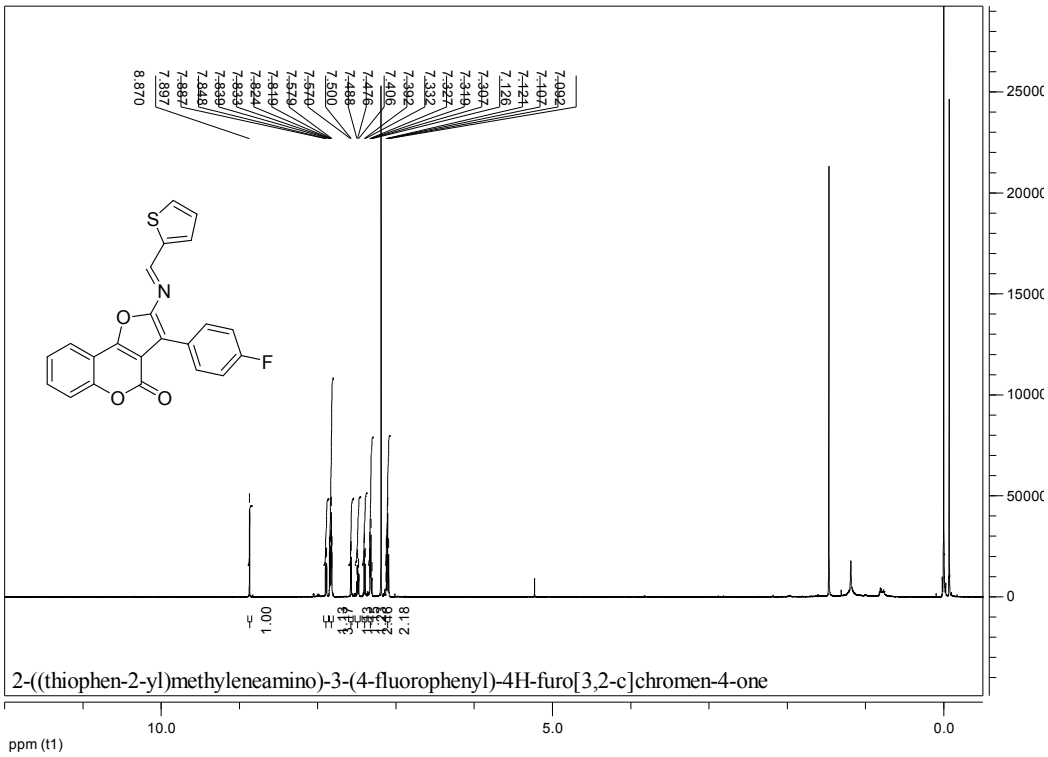


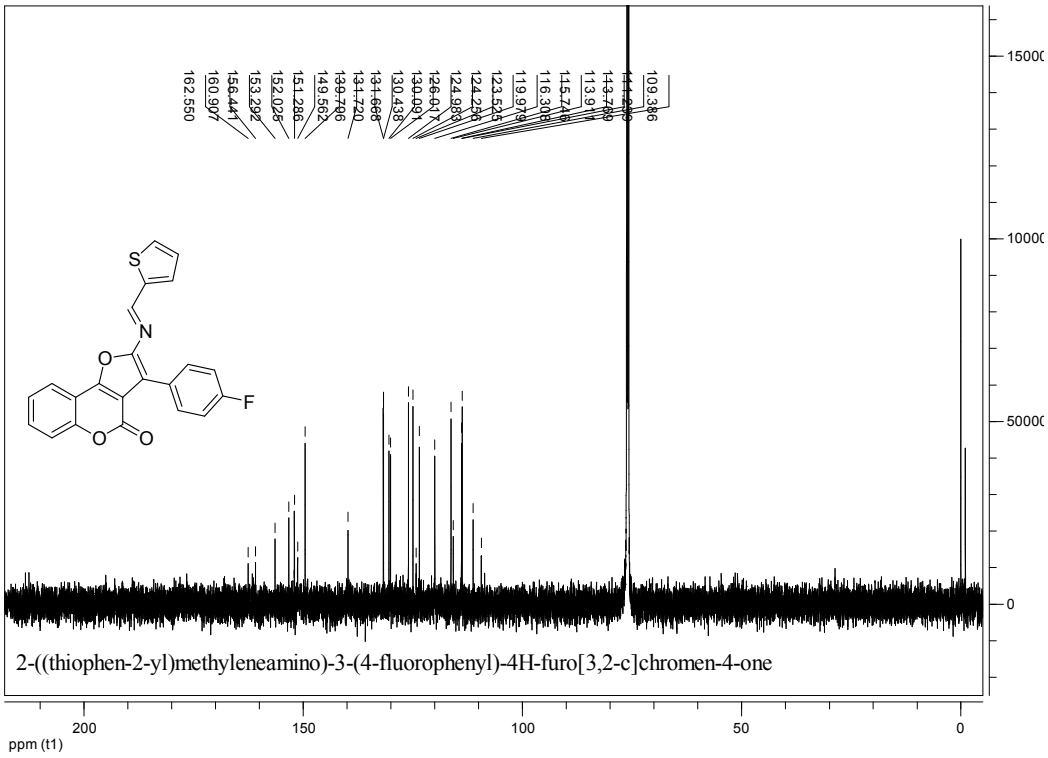
2-(4-methylbenzylideneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (4h)



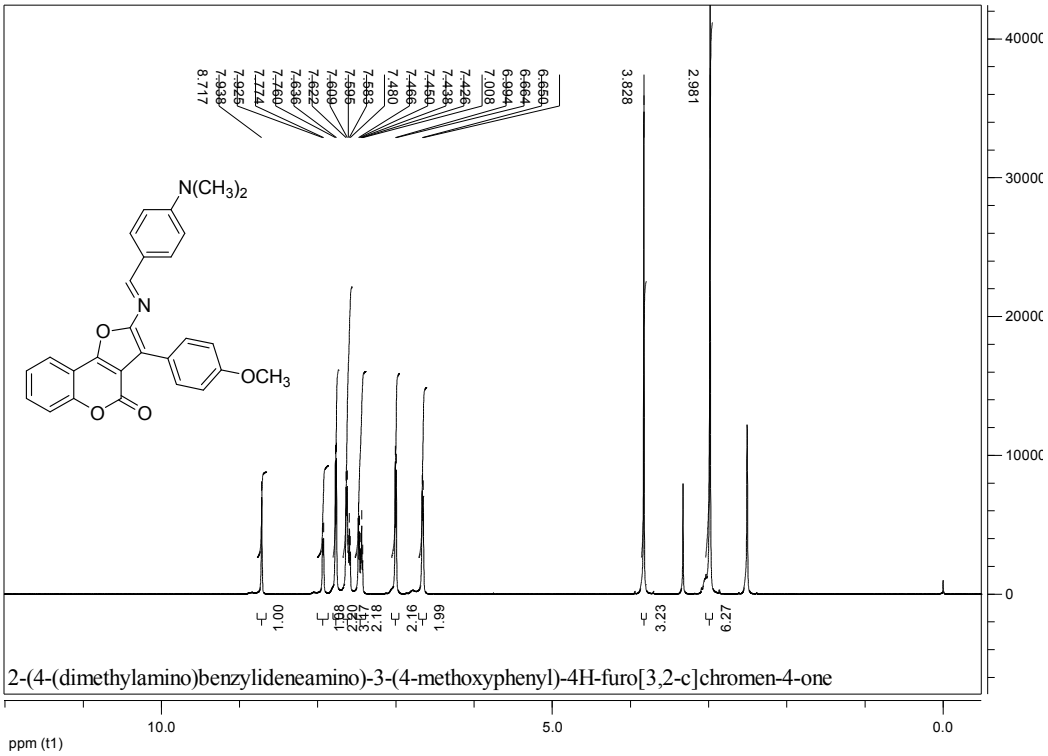


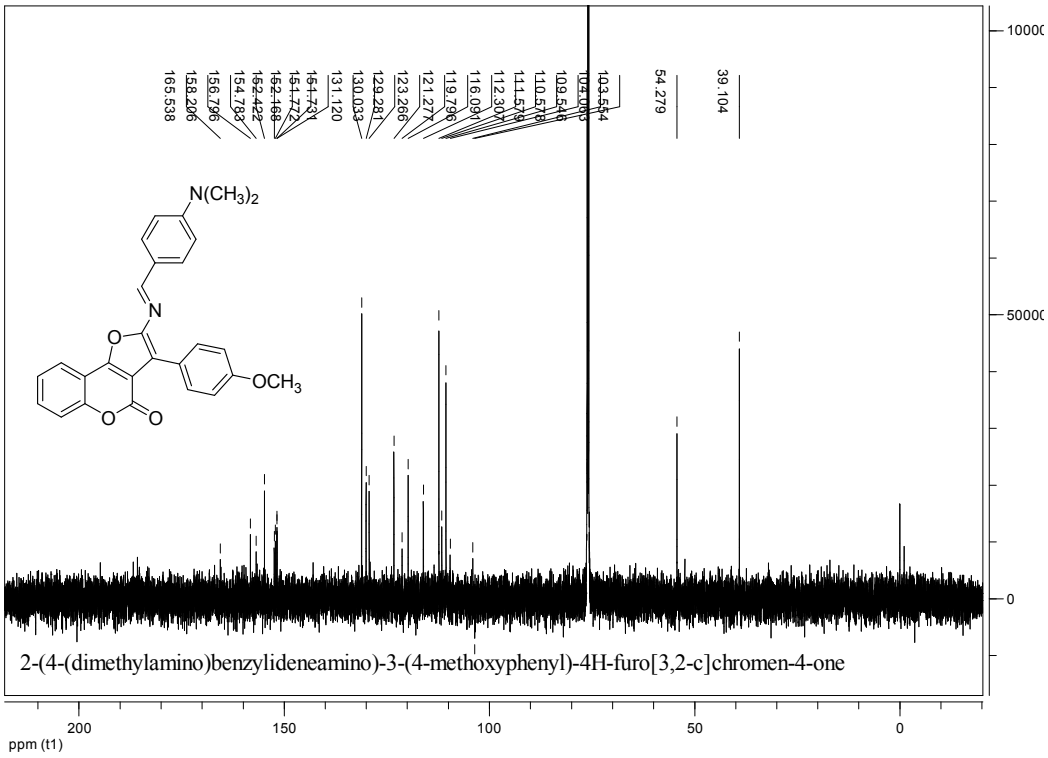
2-((thiophen-2-yl)methyleneamino)-3-(4-fluorophenyl)-4H-furo[3,2-c]chromen-4-one (4i)



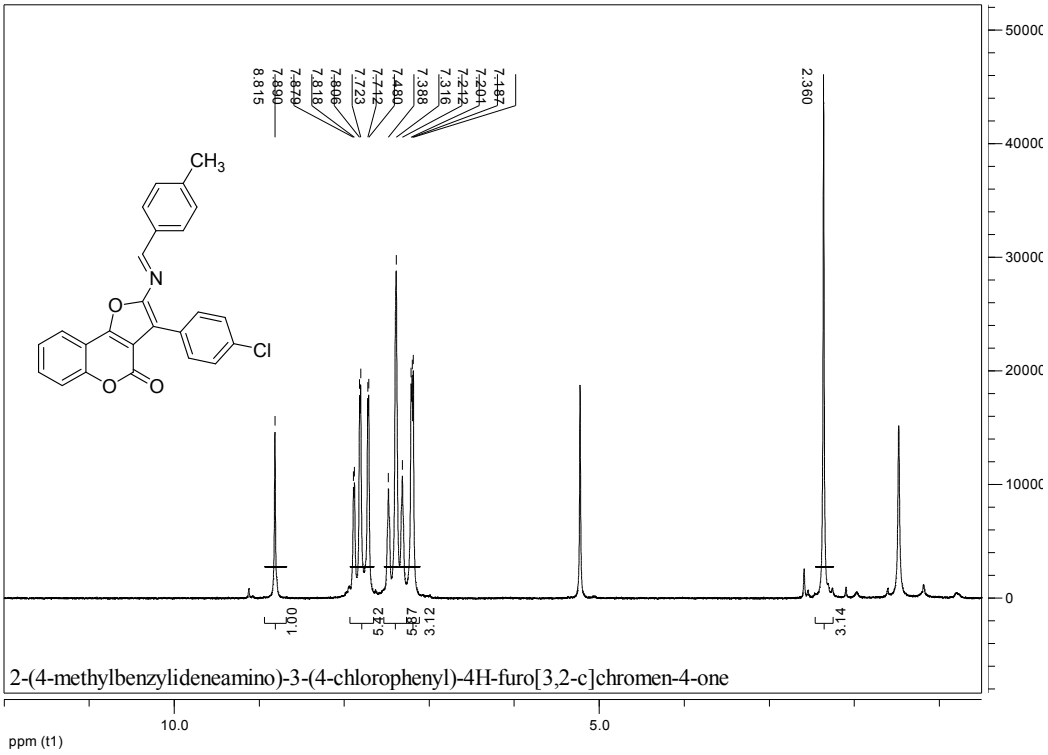


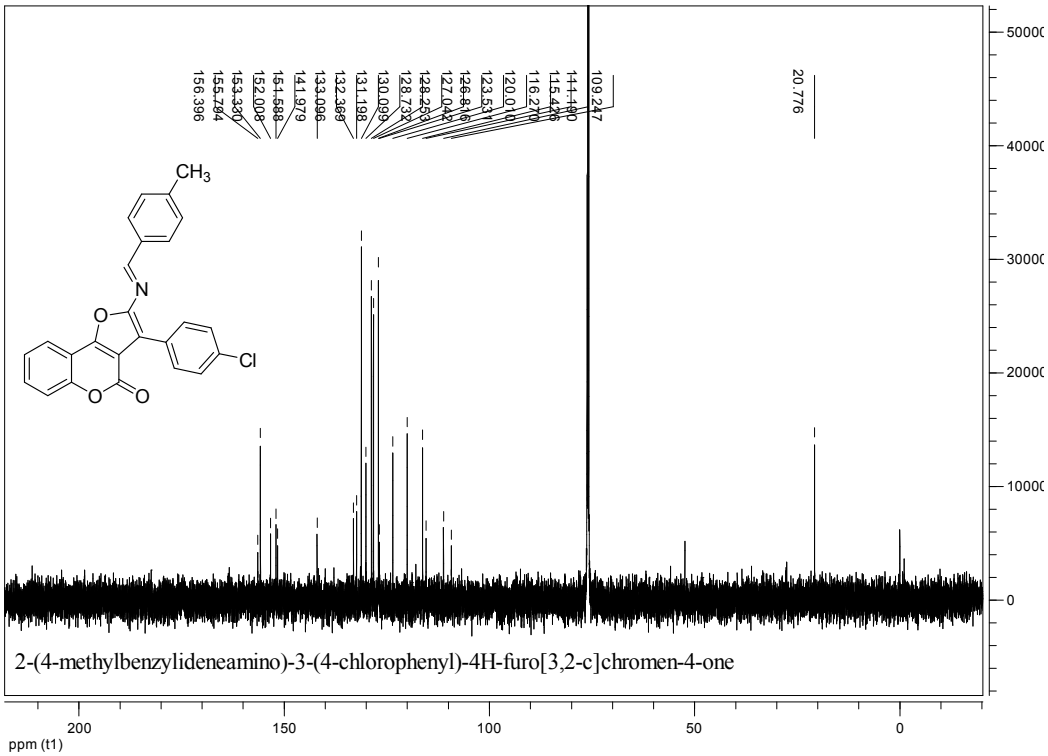
2-(4-(dimethylamino)benzylideneamino)-3-(4-methoxyphenyl)-4H-furo[3,2-c]chrome n-4-one (4j)



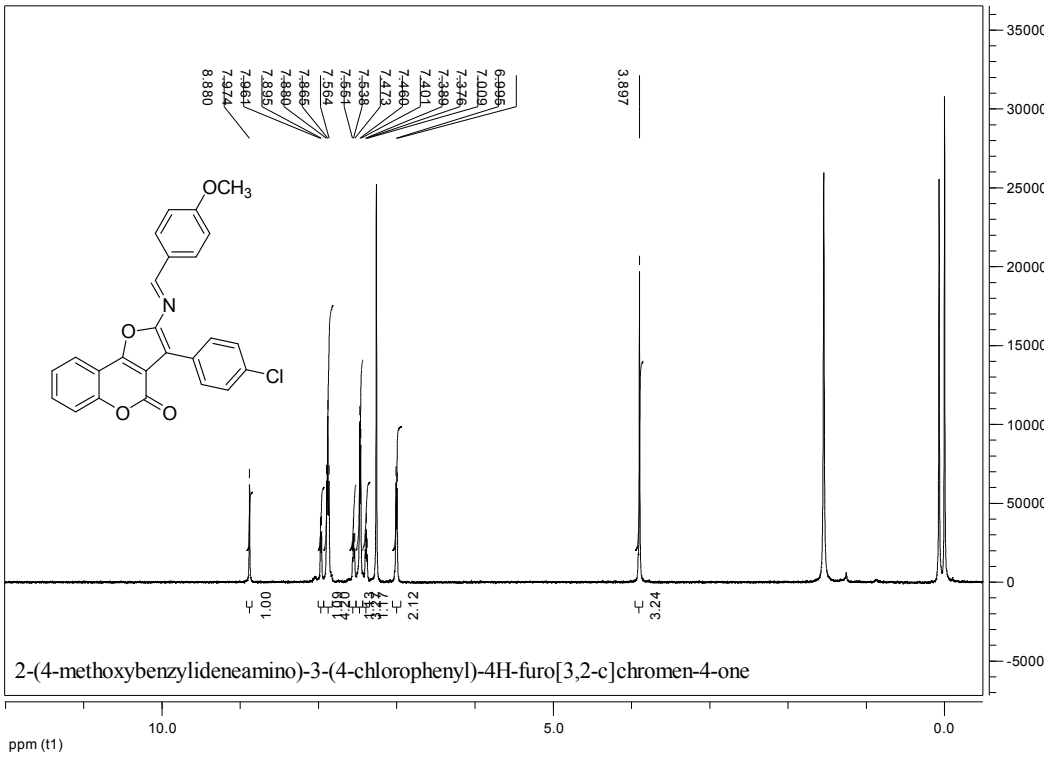


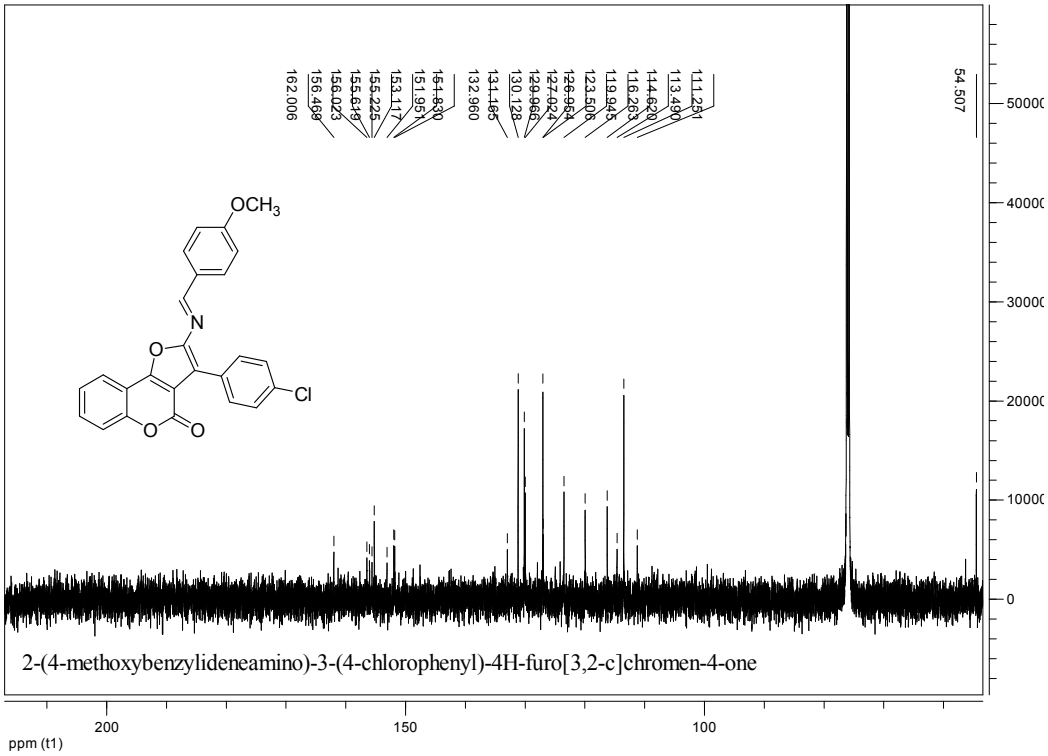
2-(4-methylbenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (4k)



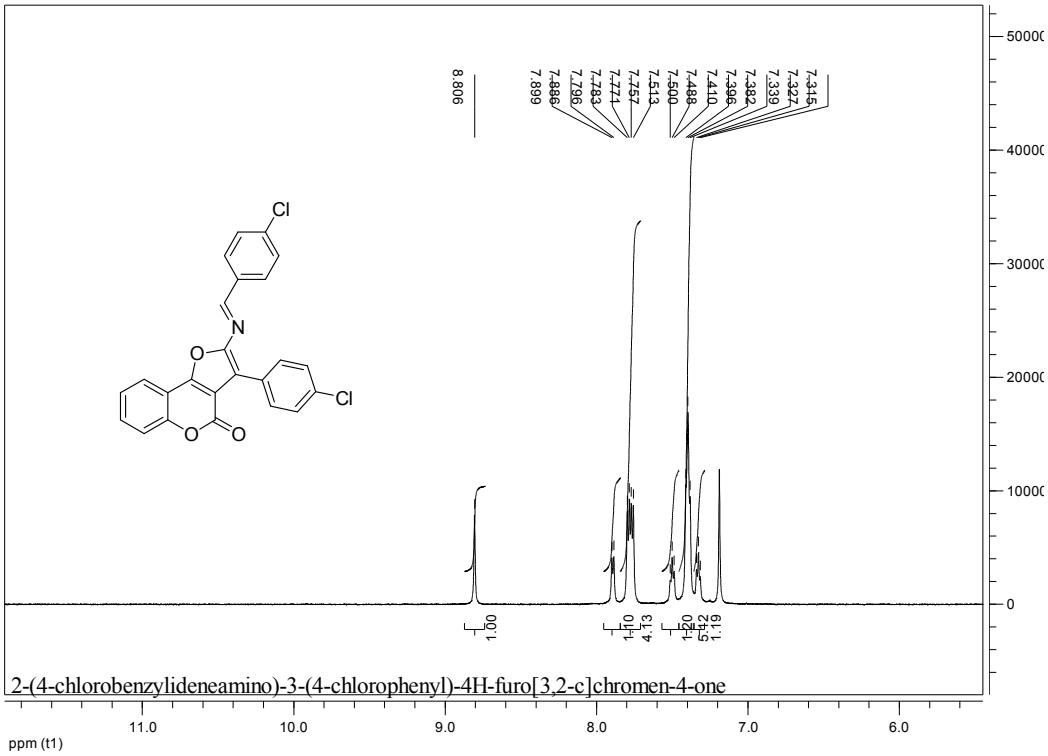


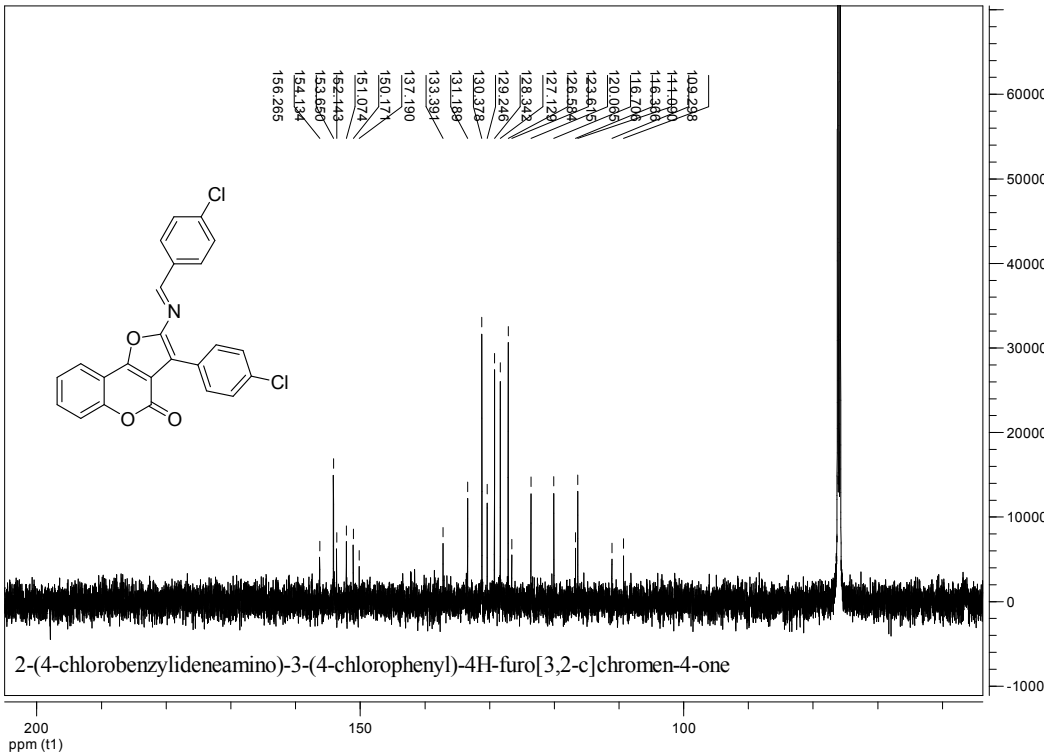
2-(4-methoxybenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (4l)



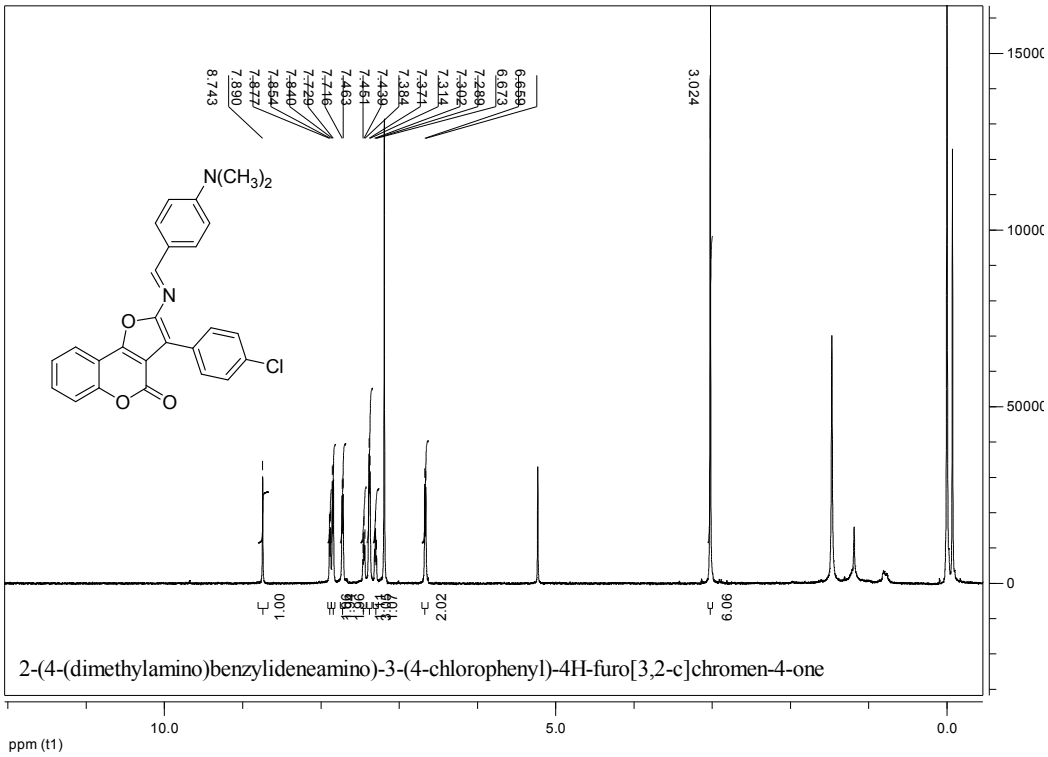


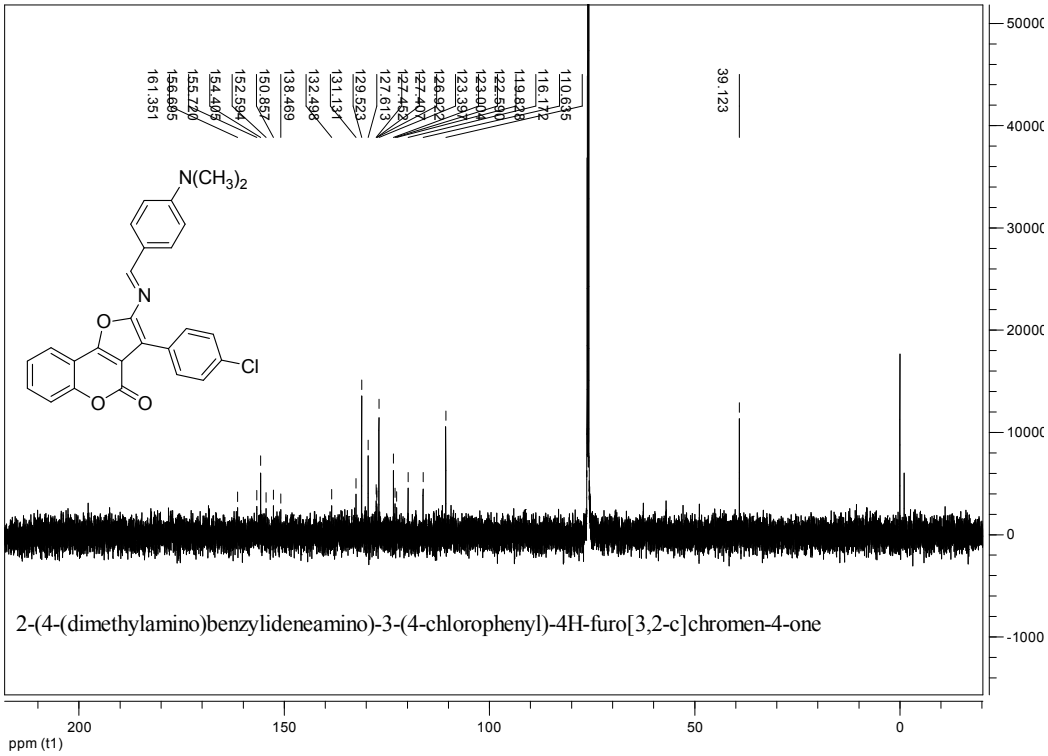
2-(4-chlorobenzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (4m)



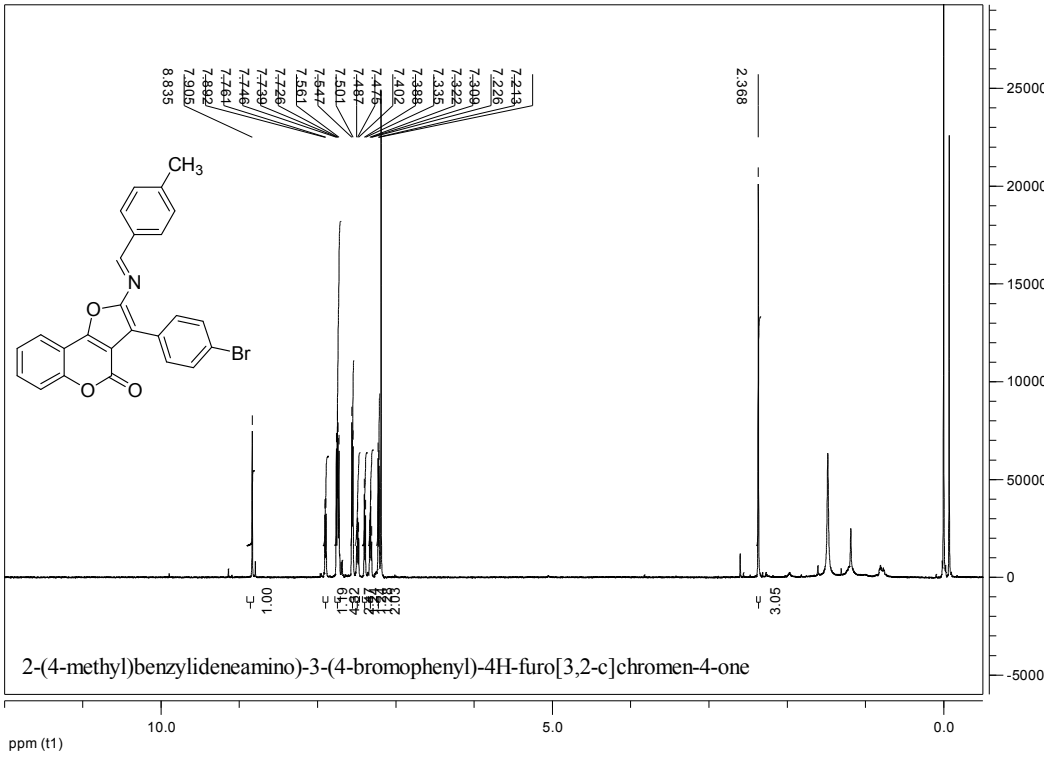


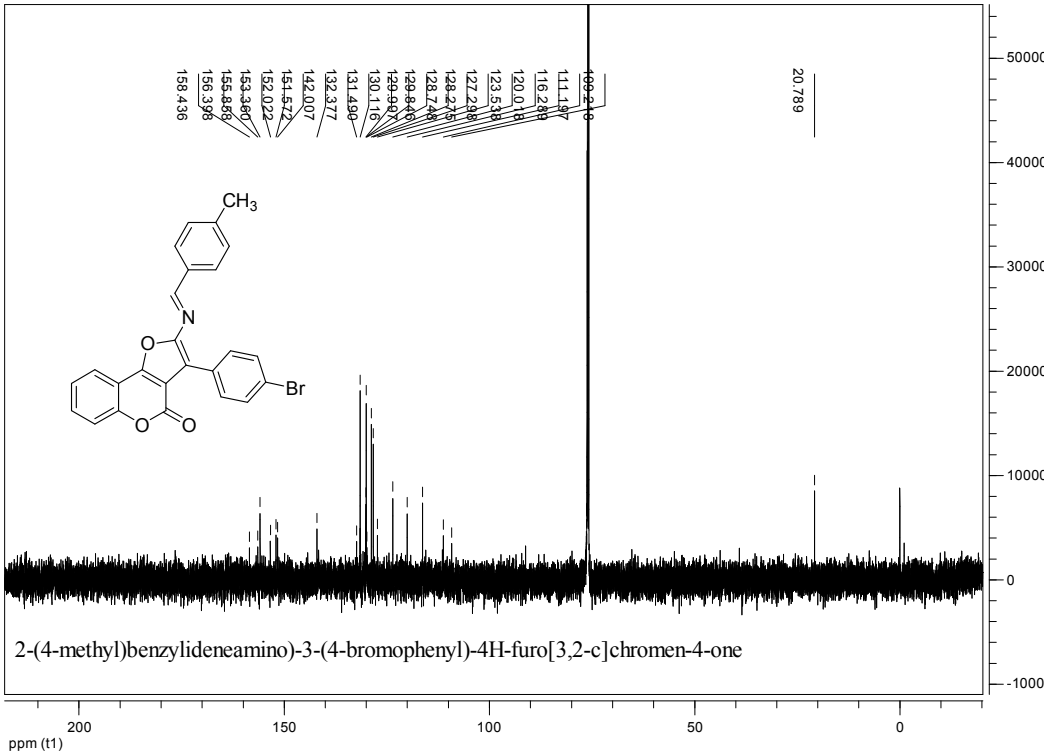
2-(4-(dimethylamino)benzylideneamino)-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one (4n)



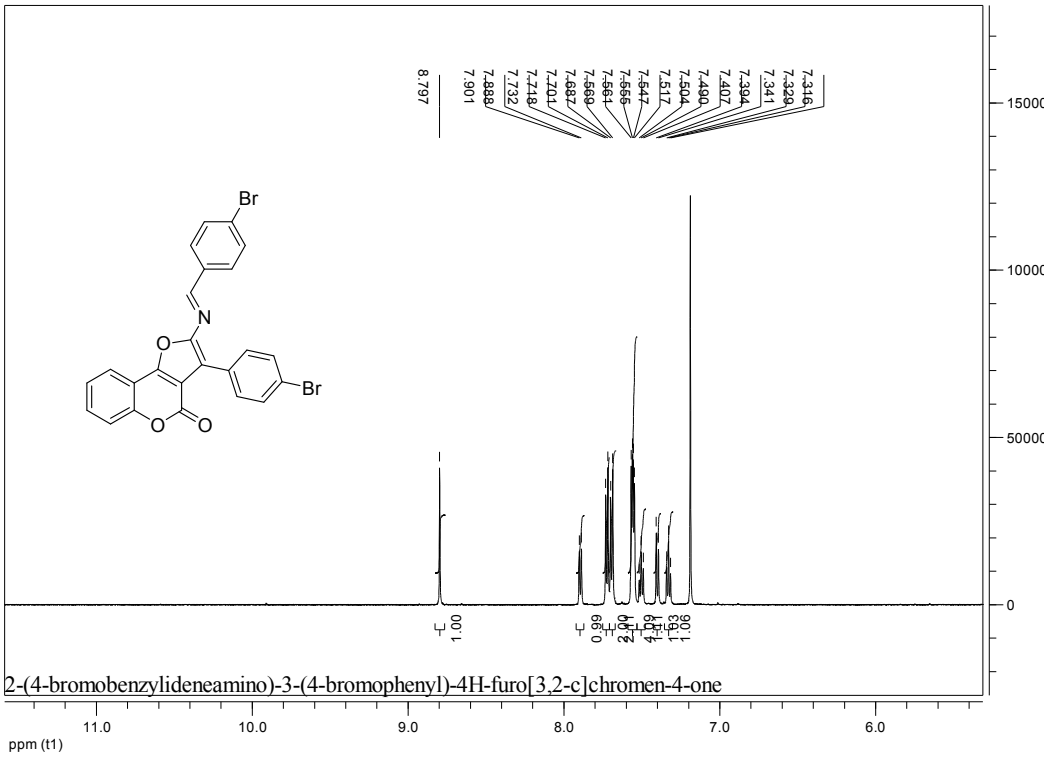


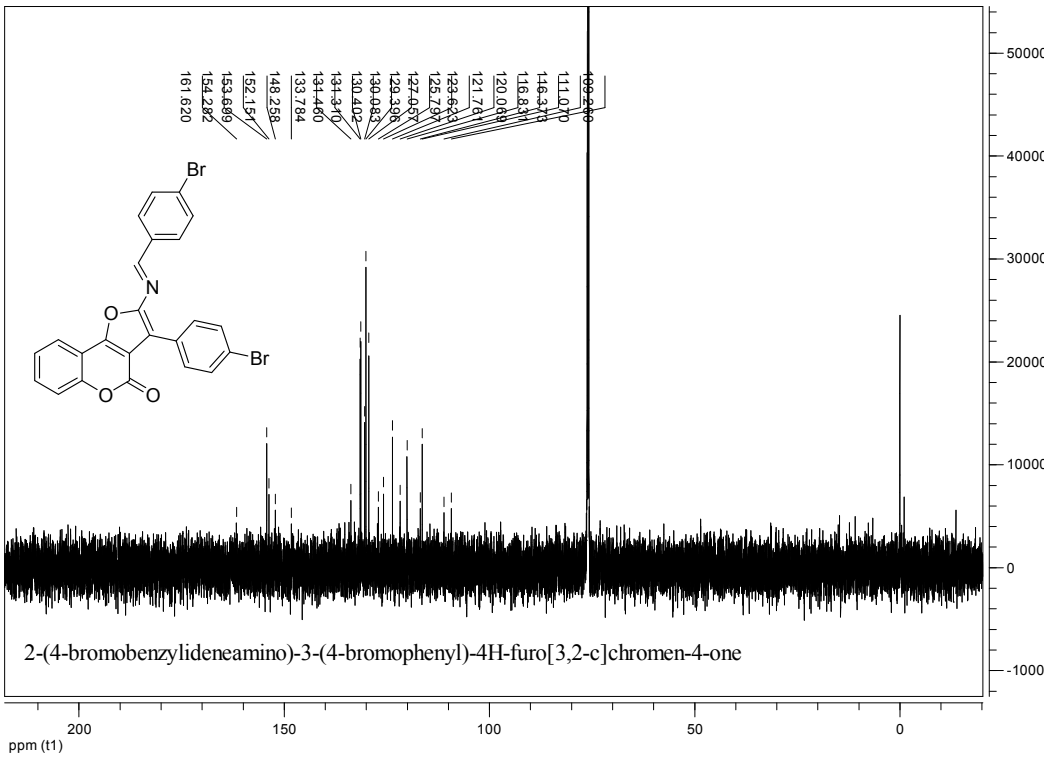
2-(4-methyl)benzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4o)



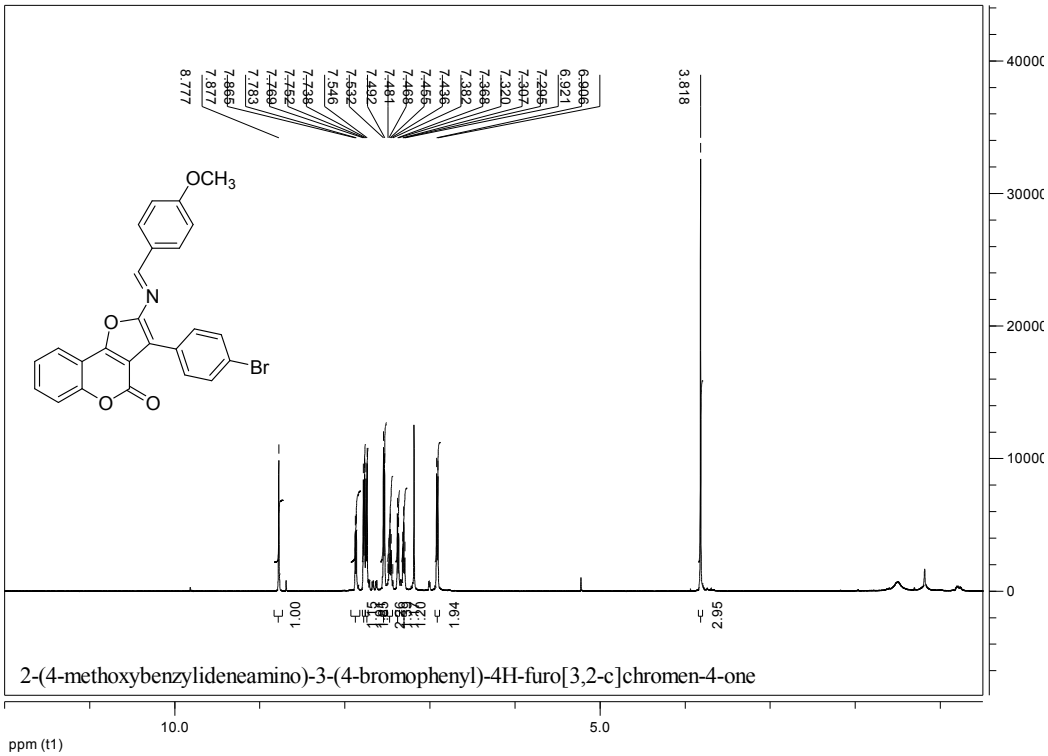


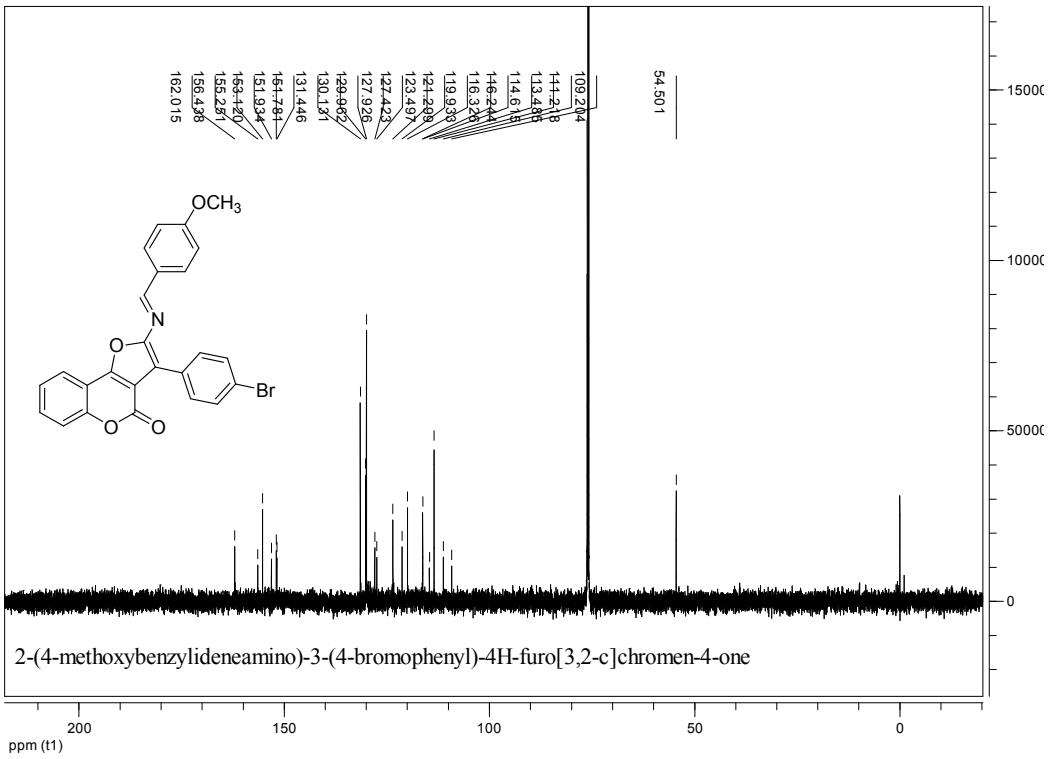
2-(4-bromobenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4p)



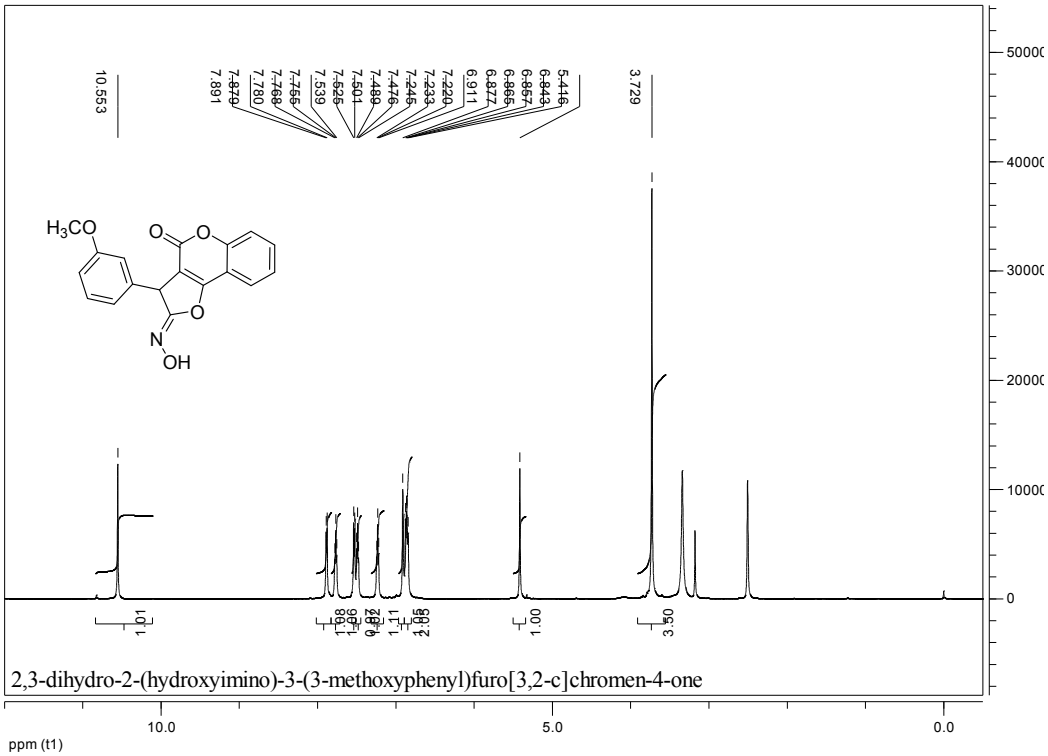


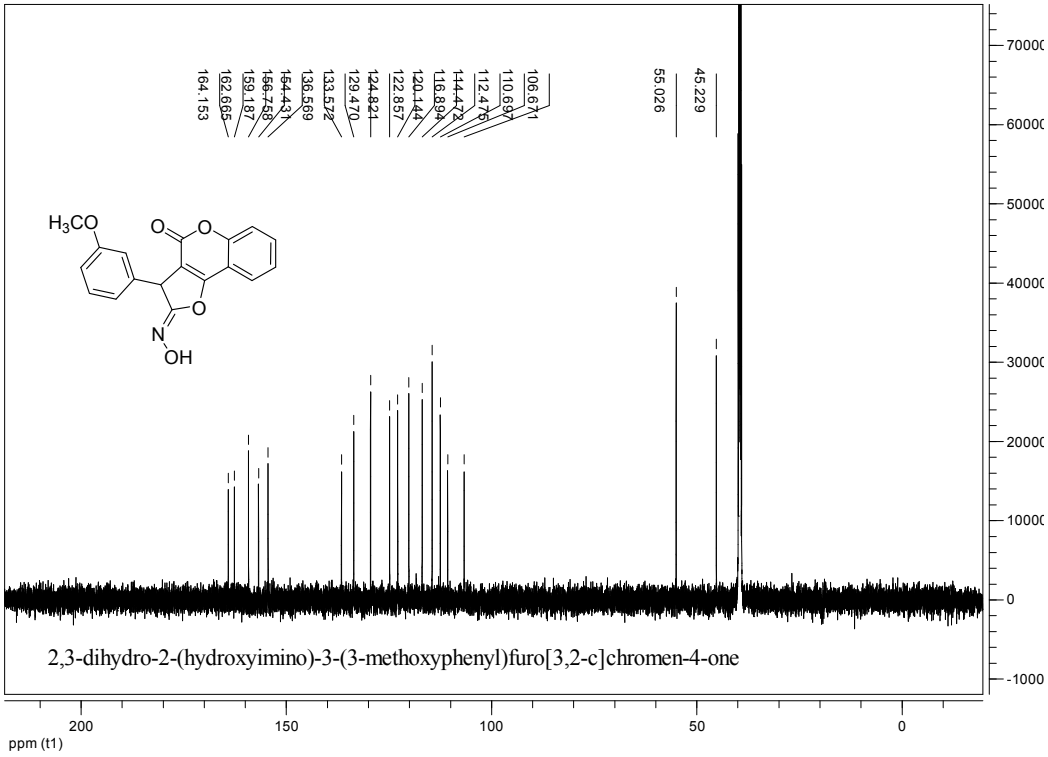
2-(4-methoxybenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4q)



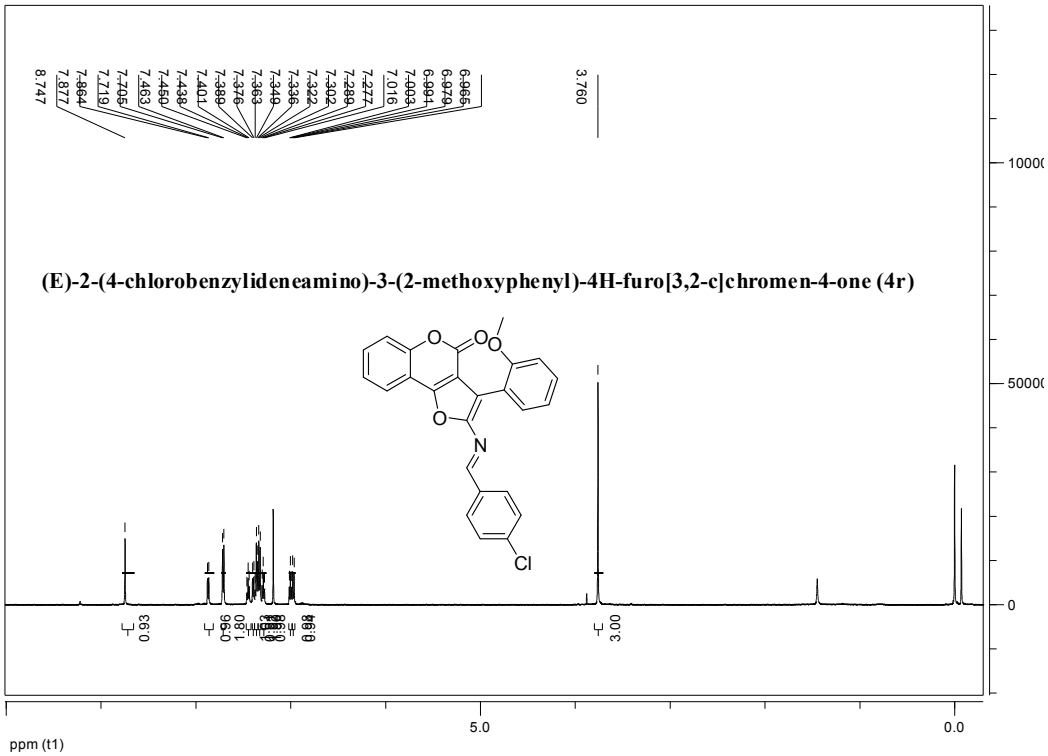


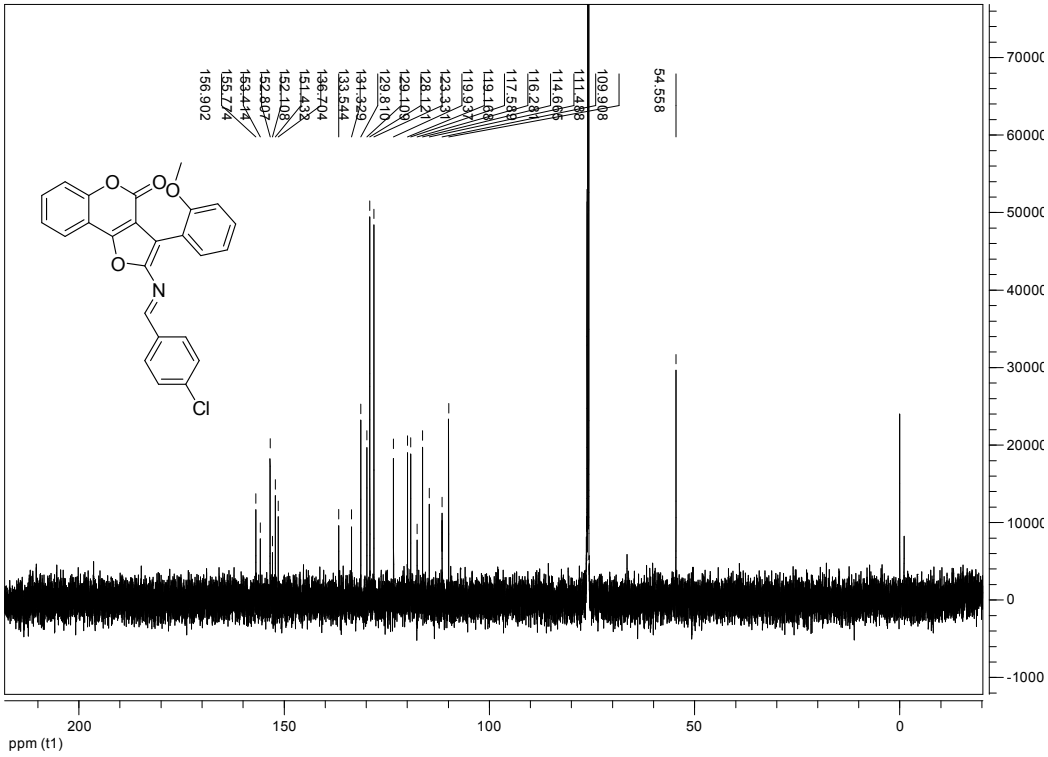
2,3-dihydro-2-(hydroxyimino)-3-(3-methoxyphenyl)furo[3,2-c]chromen-4-one (5)



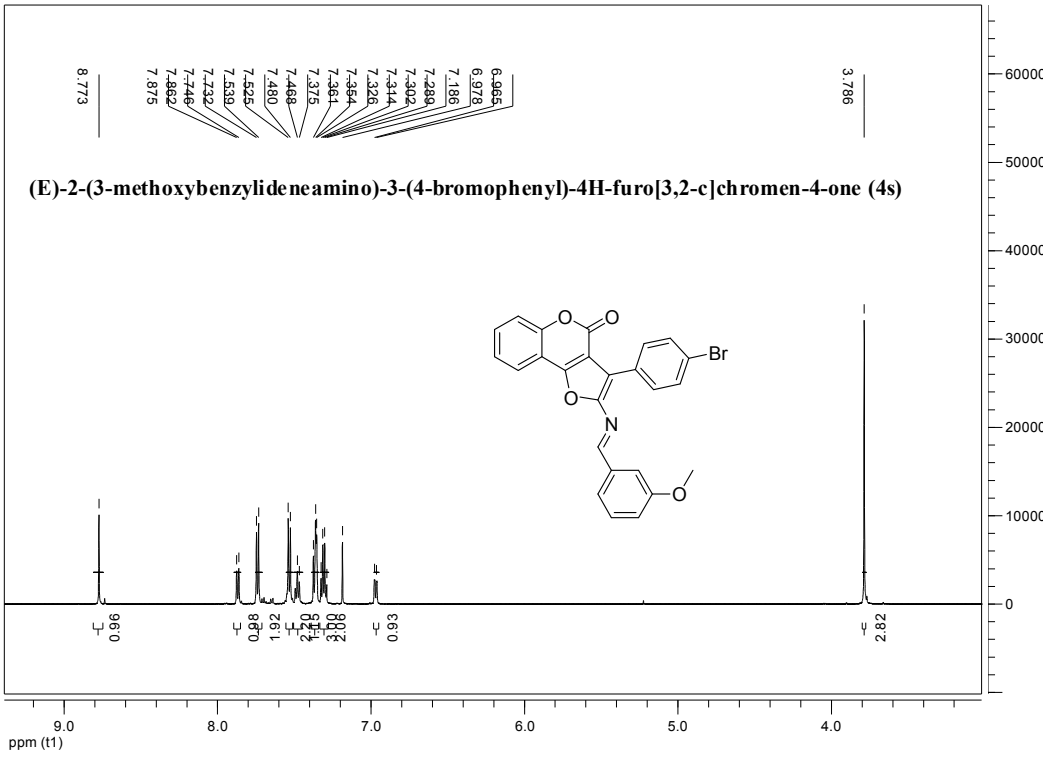


(E)-2-(4-chlorobenzylideneamino)-3-(2-methoxyphenyl)-4H-furo[3,2-c]chromen-4-one (4r)





(E)-2-(3-methoxybenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4s)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7.746
7.732
7.539
7.525
7.480
7.468
7.375
7.361
7.354
7.326
7.314
7.302
7.289
7.186
6.978
6.965
3.786
(E)-2-(3-methoxybenzylideneamino)-3-(4-bromophenyl)-4H-furo[3,2-c]chromen-4-one (4s)
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O
N
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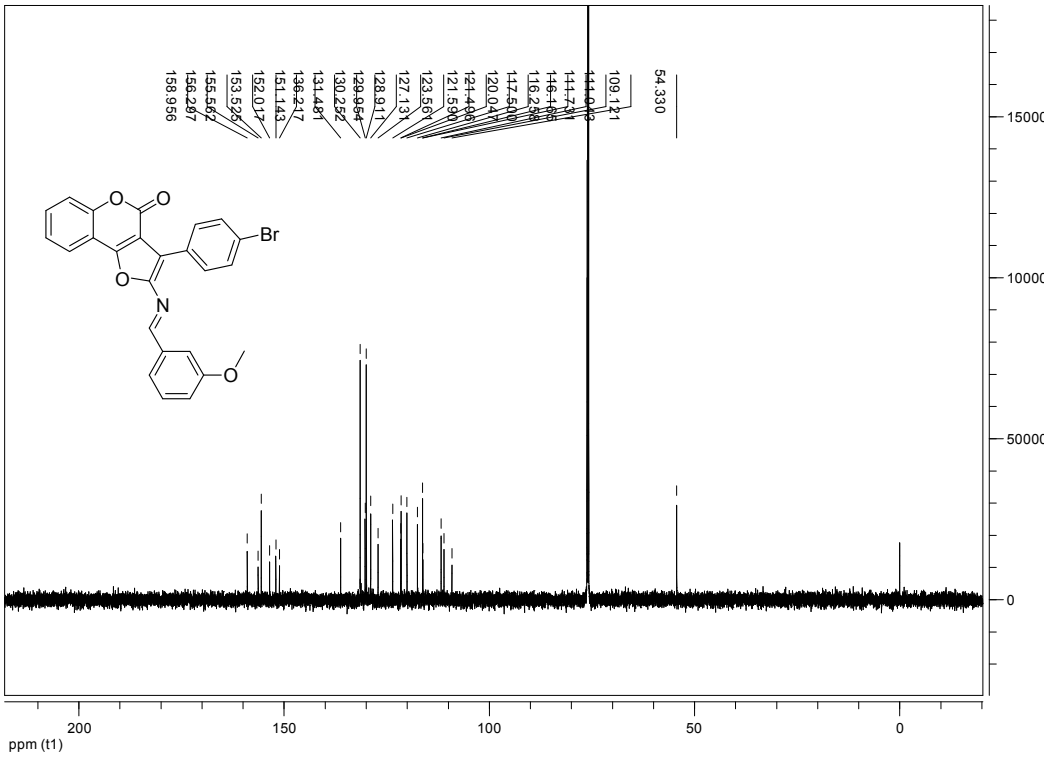
0.88
1.92
2.12
2.08
0.93
2.82
ppm (t1)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155.562
153.526
152.017
151.143
136.217
131.481
130.252
129.954
128.911
127.131
123.561
121.590
121.406
120.041
117.500
116.258
111.731
111.010
109.121
54.330
Br
O
N
ppm (t1)

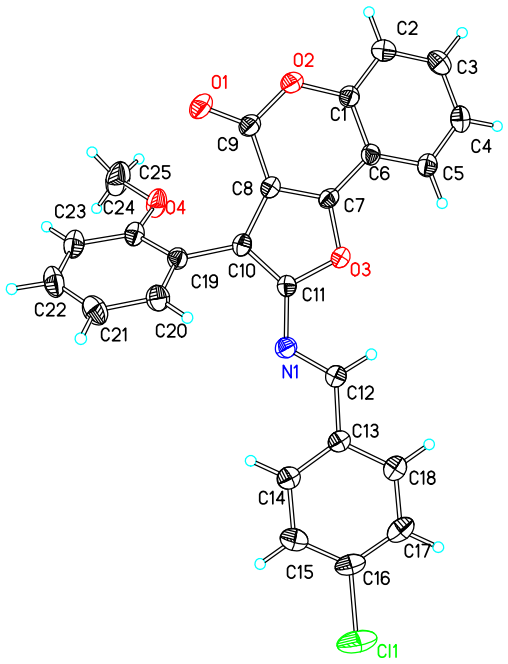

Figure 1 Molecular structure of compound **4r**{*6,2,1*}

Table 7. Crystal data and structure refinement for compound **4r**{*6,2,1*}.

Identification code	lh
Empirical formula	C25 H26 Cl N O4
Formula weight	429.84
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 22.688(3) A alpha = 90 deg.
	b = 12.2447(17) A beta = 94.963(4) deg.
	c = 7.3647(9) A gamma = 90 deg.
Volume	2038.3(5) A^3
Z, Calculated density	4, 1.401 Mg/m^3
Absorption coefficient	0.221 mm^-1
F(000)	888.0
Crystal size	0.14 x 0.08 x 0.04 mm
Theta range for data collection	1.80 to 27.66 deg.
Limiting indices	-27<=h<=29, -15<=k<=15, -9<=l<=9
Reflections collected / unique	27319 / 4735 [R(int) = 0.0527]
Completeness to theta = 27.66	99.5 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.990 and 0.976
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4735 / 0 / 281
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.0925
R indices (all data)	R1 = 0.1150, wR2 = 0.1127
Largest diff. peak and hole	0.205 and -0.229 e.A^-3

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for lh.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	4854(1)	10765(1)	2770(1)	90(1)
O(5)	7999(1)	7528(1)	-95(2)	39(1)
O(2)	9269(1)	5352(1)	-1133(2)	48(1)
N(1)	7053(1)	7305(1)	1023(2)	40(1)
C(1)	9403(1)	6442(1)	-1332(2)	39(1)
C(6)	8995(1)	7258(1)	-1049(2)	35(1)
O(4)	8250(1)	4407(1)	3191(2)	54(1)
O(1)	8672(1)	4002(1)	-529(2)	62(1)
C(10)	7750(1)	5788(1)	571(2)	36(1)
C(8)	8323(1)	5812(1)	-131(2)	36(1)
C(11)	7566(1)	6843(1)	534(2)	36(1)
C(7)	8450(1)	6871(1)	-466(2)	35(1)
C(4)	9710(1)	8586(2)	-1768(2)	50(1)
C(13)	6947(1)	8311(2)	636(2)	43(1)
C(14)	6421(1)	8870(1)	1126(2)	41(1)
C(16)	5506(1)	8937(2)	2540(3)	58(1)
C(25)	7693(1)	4125(1)	2506(2)	42(1)
C(15)	5989(1)	8362(2)	2053(3)	48(1)
C(20)	7420(1)	4843(1)	1213(2)	38(1)
C(5)	9155(1)	8344(2)	-1264(2)	43(1)
C(19)	6349(1)	9965(2)	678(3)	53(1)
C(9)	8736(1)	4970(2)	-563(2)	43(1)
C(24)	7394(1)	3213(2)	3047(3)	52(1)
C(2)	9961(1)	6696(2)	-1829(2)	48(1)
C(23)	6815(1)	3044(2)	2364(3)	60(1)
C(21)	6833(1)	4658(2)	592(2)	48(1)
C(18)	5867(1)	10546(2)	1160(3)	58(1)
C(17)	5453(1)	10029(2)	2104(3)	55(1)
C(22)	6531(1)	3763(2)	1167(3)	57(1)
C(3)	10108(1)	7770(2)	-2054(2)	50(1)
C(26)	8555(1)	3714(2)	4486(3)	83(1)

Table 9. Bond lengths [A] and angles [deg] for lh.

Cl(1)-C(17)	1.737(2)
O(5)-C(7)	1.3489(19)
O(5)-C(11)	1.4000(19)
O(2)-C(1)	1.379(2)
O(2)-C(9)	1.396(2)
N(1)-C(13)	1.282(2)
N(1)-C(11)	1.370(2)
C(1)-C(2)	1.384(2)
C(1)-C(6)	1.391(2)
C(6)-C(5)	1.392(2)
C(6)-C(7)	1.423(2)
O(4)-C(25)	1.364(2)
O(4)-C(26)	1.413(2)
O(1)-C(9)	1.195(2)
C(10)-C(11)	1.357(2)
C(10)-C(8)	1.442(2)
C(10)-C(20)	1.477(2)
C(8)-C(7)	1.356(2)
C(8)-C(9)	1.446(2)
C(4)-C(5)	1.375(3)
C(4)-C(3)	1.375(3)
C(13)-C(14)	1.448(2)
C(14)-C(19)	1.387(3)
C(14)-C(15)	1.389(3)
C(16)-C(15)	1.378(3)
C(16)-C(17)	1.378(3)
C(25)-C(24)	1.384(3)
C(25)-C(20)	1.400(2)
C(20)-C(21)	1.390(3)
C(19)-C(18)	1.377(3)
C(24)-C(23)	1.380(3)
C(2)-C(3)	1.370(3)
C(23)-C(22)	1.368(3)
C(21)-C(22)	1.380(3)
C(18)-C(17)	1.371(3)
C(7)-O(5)-C(11)	106.03(13)
C(1)-O(2)-C(9)	124.03(14)
C(13)-N(1)-C(11)	119.03(15)

O(2)-C(1)-C(2)	117.38(16)
O(2)-C(1)-C(6)	121.63(16)
C(2)-C(1)-C(6)	120.99(17)
C(1)-C(6)-C(5)	119.07(16)
C(1)-C(6)-C(7)	114.36(15)
C(5)-C(6)-C(7)	126.49(16)
C(25)-O(4)-C(26)	118.84(15)
C(11)-C(10)-C(8)	104.96(14)
C(11)-C(10)-C(20)	126.18(16)
C(8)-C(10)-C(20)	128.86(15)
C(7)-C(8)-C(10)	107.28(15)
C(7)-C(8)-C(9)	119.34(16)
C(10)-C(8)-C(9)	133.34(16)
C(10)-C(11)-N(1)	130.79(16)
C(10)-C(11)-O(5)	110.78(15)
N(1)-C(11)-O(5)	118.41(14)
O(5)-C(7)-C(8)	110.90(15)
O(5)-C(7)-C(6)	123.79(15)
C(8)-C(7)-C(6)	125.25(16)
C(5)-C(4)-C(3)	120.94(18)
N(1)-C(13)-C(14)	122.81(17)
C(19)-C(14)-C(15)	118.49(18)
C(19)-C(14)-C(13)	118.72(17)
C(15)-C(14)-C(13)	122.78(17)
C(15)-C(16)-C(17)	119.3(2)
O(4)-C(25)-C(24)	124.04(17)
O(4)-C(25)-C(20)	115.68(15)
C(24)-C(25)-C(20)	120.26(18)
C(16)-C(15)-C(14)	120.69(19)
C(21)-C(20)-C(25)	118.42(16)
C(21)-C(20)-C(10)	121.30(16)
C(25)-C(20)-C(10)	120.27(16)
C(4)-C(5)-C(6)	119.37(18)
C(18)-C(19)-C(14)	121.17(19)
O(1)-C(9)-O(2)	116.63(16)
O(1)-C(9)-C(8)	128.35(18)
O(2)-C(9)-C(8)	115.00(16)
C(23)-C(24)-C(25)	119.41(19)
C(3)-C(2)-C(1)	119.04(18)
C(22)-C(23)-C(24)	121.32(19)
C(22)-C(21)-C(20)	121.12(18)
C(17)-C(18)-C(19)	119.1(2)
C(18)-C(17)-C(16)	121.16(19)
C(18)-C(17)-Cl(1)	119.40(18)

C(16)-C(17)-Cl(1)	119.44(18)
C(23)-C(22)-C(21)	119.3(2)
C(2)-C(3)-C(4)	120.58(18)

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters (A^2 x 10^3) for lh.
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
Cl(1)	75(1)	111(1)	84(1)	-22(1)	7(1)	48(1)
O(5)	41(1)	30(1)	46(1)	5(1)	6(1)	3(1)
O(2)	45(1)	36(1)	65(1)	-3(1)	13(1)	4(1)
N(1)	42(1)	38(1)	40(1)	0(1)	5(1)	4(1)
C(1)	42(1)	35(1)	39(1)	1(1)	4(1)	-1(1)
C(6)	40(1)	35(1)	32(1)	3(1)	3(1)	0(1)
O(4)	56(1)	42(1)	61(1)	16(1)	-14(1)	-4(1)
O(1)	64(1)	30(1)	95(1)	-3(1)	17(1)	2(1)
C(10)	41(1)	32(1)	34(1)	3(1)	-1(1)	-1(1)
C(8)	41(1)	30(1)	36(1)	1(1)	1(1)	1(1)
C(11)	39(1)	34(1)	36(1)	4(1)	4(1)	-1(1)
C(7)	39(1)	32(1)	34(1)	2(1)	1(1)	7(1)
C(4)	55(1)	43(1)	51(1)	9(1)	3(1)	-10(1)
C(13)	44(1)	39(1)	47(1)	5(1)	8(1)	3(1)
C(14)	42(1)	39(1)	42(1)	-1(1)	3(1)	4(1)
C(16)	48(1)	68(2)	59(1)	-4(1)	14(1)	4(1)
C(25)	51(1)	32(1)	41(1)	1(1)	3(1)	-3(1)
C(15)	47(1)	44(1)	55(1)	0(1)	7(1)	4(1)
C(20)	44(1)	33(1)	38(1)	-1(1)	6(1)	-1(1)
C(5)	48(1)	38(1)	43(1)	6(1)	4(1)	0(1)
C(19)	56(1)	44(1)	59(1)	5(1)	7(1)	5(1)
C(9)	45(1)	34(1)	49(1)	-1(1)	5(1)	3(1)
C(24)	73(2)	37(1)	46(1)	5(1)	6(1)	-6(1)
C(2)	43(1)	52(1)	49(1)	-3(1)	6(1)	3(1)
C(23)	76(2)	47(1)	59(1)	-1(1)	16(1)	-25(1)
C(21)	49(1)	47(1)	46(1)	1(1)	2(1)	-5(1)
C(18)	63(2)	43(1)	67(1)	-4(1)	-4(1)	13(1)
C(17)	50(1)	62(1)	51(1)	-14(1)	-2(1)	19(1)
C(22)	53(1)	62(1)	57(1)	-5(1)	6(1)	-20(1)
C(3)	43(1)	62(1)	45(1)	0(1)	6(1)	-10(1)

C(26)	79(2)	66(2)	100(2)	36(1)	-24(2)	3(1)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for lh.

	x	y	z	U(eq)
H(4)	9817	9311	-1918	60
H(13)	7219	8697	13	52
H(16)	5217	8592	3157	69
H(15)	6027	7625	2349	58
H(5)	8889	8902	-1069	52
H(19)	6632	10313	40	64
H(24)	7581	2717	3863	63
H(2)	10233	6146	-2007	57
H(23)	6615	2428	2725	72
H(21)	6640	5147	-225	57
H(18)	5823	11279	849	70
H(22)	6137	3649	746	69
H(3)	10480	7949	-2404	60
H(26A)	8343	3673	5556	125
H(26B)	8944	4000	4807	125
H(26C)	8586	2997	3975	125