

Supporting Information

Triazine-based porous organic polymer: a novel heterogeneous basic organocatalyst for facile one-pot synthesis of 2-amino-4*H*-chromenes

Sudipta K. Kundu and Asim Bhaumik*

¹H and ¹³C NMR chemical shifts for different 2-amino-chromene products:

2-amino-3-cyano-7-hydroxy-4-phenyl-4*H*-chromene (Table 1, Entry 1), ¹H NMR (500 MHz, DMSO-d₆) δ 9.691 (s, 1H), 7.288-7.318 (t, 2H), 7.156-7.216 (m, 3H), 6.848 (s, 2H), 6.793-6.809 (d, 1H, *J*= 8 Hz), 6.470-6.491 (m, 1H), 6.405-6.409 (d, 1H, *J*= 2 Hz), 4.614 (s, 1H); **¹³C NMR (500 MHz, DMSO-d₆)** δ 56.31, 102.15, 112.33, 113.72, 120.56, 126.57, 127.31, 128.52, 129.84, 146.29, 148.83, 157.02, 160.21.

2-amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4*H*-chromene (Table 1, Entry 2), ¹H NMR (500 MHz, DMSO-d₆) δ 9.636 (s, 1H), 7.014-7.090 (m, 3H), 6.744-6.789 (m, 2H), 6.370-6.459 (m, 2H), 5.735 (s, 2H), 4.543 (s, 1H), 2.067 (s, 3H); **¹³C NMR (500 MHz, DMSO-d₆)** δ 20.52, 56.43, 102.09, 112.27, 113.86, 120.63, 127.24, 129.06, 129.83, 130.16, 135.68, 143.36, 148.80, 156.95, 160.10.

2-amino-3-cyano-7-hydroxy-4-(4-fluorophenyl)-4*H*-chromene (Table 1, Entry 3), ¹H NMR (500 MHz, DMSO-d₆) δ 9.700 (s, 1H), 7.181-7.209 (m, 2H), 7.107-7.142 (m, 2H), 6.867 (s, 2H), 6.776-6.793 (d, 1H, *J*= 8.5 Hz), 6.476-6.497 (m, 1H), 6.402-6.406 (d, 1H, *J*= 2 Hz), 4.657 (s, 1H); **¹³C NMR (500 MHz, DMSO-d₆)** δ 56.21, 102.16, 112.40, 113.50, 115.15, 115.32, 120.46, 129.16, 129.22, 129.82, 142.50, 148.77, 157.10, 160.15.

2-amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4*H*-chromene (Table 1, Entry 4), ¹H NMR (500 MHz, DMSO-d₆) δ 9.712 (s, 1H), 7.357-7.373 (d, 2H, *J* = 8 Hz), 7.179-7.196 (d, 2H, *J* = 8.5 Hz), 6.895 (s, 2H), 6.775-6.792 (d, 1H, *J* = 8.5 Hz), 6.478-6.499 (m, 1H), 6.404-6.408 (d, 1H, *J* = 2 Hz), 4.663 (s, 1H); **¹³C NMR (400 MHz, DMSO-d₆)** δ 55.90, 102.21, 112.46, 113.19, 120.43, 128.53, 129.25, 129.85, 131.21, 145.29, 148.82, 157.20, 160.23.

2-amino-3-cyano-7-hydroxy-4-(4-bromophenyl)-4*H*-chromene (Table 1, Entry 5), ¹H NMR (500 MHz, DMSO-d₆) δ 9.717 (s, 1H), 7.491-7.507 (d, 2H, *J* = 8 Hz), 7.120-7.137 (d, 2H, *J* = 8.5 Hz), 6.902 (s, 2H), 6.773-6.789 (d, 1H, *J* = 8 Hz), 6.480-6.497 (d, 1H, *J* = 8.5 Hz), 6.406 (s, 1H), 4.648 (s, 1H); **¹³C NMR (400 MHz, DMSO-d₆)** δ 55.80, 102.19, 112.43, 113.08, 119.68, 120.45, 129.61, 129.83, 131.42, 145.67, 148.77, 157.17, 160.20.

2-amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4*H*-chromene (Table 1, Entry 6), ¹H NMR (500 MHz, DMSO-d₆) δ 9.80 (b, 1H), 8.29-8.31 (m, 2H), 7.44-7.46 (d, 2H), 7.02 (s, 2H), 6.79-6.81 (d, 1H), 6.44-6.53 (m, 2H), 4.86 (s, 1H); **¹³C NMR (500 MHz, DMSO-d₆)** δ 55.34, 79.62, 102.89, 112.82, 113.11, 118.66, 120.74, 124.44, 129.17, 130.39, 146.80, 154.20, 157.99, 160.90.

2-amino-7-hydroxy-4-(thiophen-2-yl)-4*H*-chromene-3-carbonitrile (Table 1, Entry 7), NMR (400 MHz, DMSO-d₆) δ 9.724 (s, 1H), 7.328-7.343 (m, 1H), 6.899-6.971 (m, 5H), 6.508-6.535 (m, 1H), 6.377-6.383 (d, 1H), 4.969 (s, 1H); **¹³C NMR (400 MHz, DMSO-d₆)** δ 35.82, 57.05, 102.74, 112.94, 114.09, 120.99, 124.55, 125.56, 127.26, 130.39, 149.11, 152.01, 157.88, 160.87.

3-Amino-2-cyano-1-phenyl-4*H*-benzo[f]-chromene (Table 1, Entry 8), ¹H NMR (400 MHz, DMSO-d₆) δ 7.890-7.939 (m, 2H), 7.816-7.838 (m, 1H), 7.398-7.433 (m, 2H), 7.320-7.342 (d, 1H, *J* = 8.8 Hz), 7.228-7.265 (t, 2H), 7.119-7.183 (m, 3H), 6.949 (s, 2H), 5.283 (s, 1H); **¹³C NMR (400 MHz, DMSO-d₆)** δ 38.06, 57.91, 115.63, 116.74, 120.40, 123.57, 124.87, 126.54, 126.93, 127.02, 128.41, 128.64, 129.44, 130.13, 130.79, 145.65, 146.79, 159.65.

3-Amino-2-cyano-1-(4-methylphenyl)-4H-benzo[f]-chromene(Table 1, Entry 9), ¹H NMR (400 MHz, DMSO-d₆) δ 7.889-7.941 (m, 2H), 7.768-7.790 (m, 1H), 7.391-7.456 (m, 2H), 7.299-7.334 (m, 3H), 7.183-7.210 (m, 2H), 6.998 (s, 2H), 5.340 (s, 1H), 2.300 (s, 3H); ¹³C NMR (400 MHz, DMSO-d₆) δ 22.10, 37.29, 57.40, 115.10, 116.76, 120.28, 123.48, 124.93, 127.10, 128.82, 129.64, 130.0, 130.80, 131.10, 132.08, 144.60, 146.76, 159.66.

3-Amino-2-cyano-1-(4-chlorophenyl)-4H-benzo[f]-chromene(Table 1, Entry 10), ¹H NMR (400 MHz, DMSO-d₆) δ 7.898-7.950 (m, 2H), 7.788-7.810 (m, 1H), 7.398-7.463 (m, 2H), 7.303-7.338 (m, 3H), 7.186-7.213 (m, 2H), 7.010 (s, 2H), 5.344 (s, 1H); ¹³C NMR (400 MHz, DMSO-d₆) δ 37.34, 57.44, 115.11, 116.77, 120.26, 123.49, 124.96, 127.13, 128.80, 129.67, 130.01, 130.80, 131.14, 132.09, 144.63, 146.77, 159.68.

3-Amino-2-cyano-1-(4-bromophenyl)-4H-benzo[f]-chromene(Table 1, Entry 11), ¹H NMR (400 MHz, DMSO-d₆) δ 7.900-7.951 (m, 2H), 7.785-7.804 (m, 1H), 7.416-7.459 (m, 4H), 7.314-7.336 (d, 1H, *J* = 8.8 Hz), 7.127-7.148 (d, 2H, *J* = 8.4 Hz), 7.014 (s, 2H), 5.331 (s, 1H); ¹³C NMR (400 MHz, DMSO-d₆) δ 37.40, 57.34, 115.04, 116.75, 119.63, 120.23, 123.50, 124.96, 127.14, 128.48, 129.18, 129.67, 130.01, 130.80, 131.57, 132.08, 132.64, 145.04, 146.77, 159.66.

3-Amino-2-cyano-1-(3-bromophenyl)-4H-benzo[f]-chromene(Table 1, Entry 12) ¹H NMR (400 MHz, DMSO-d₆) δ 7.915-7.965 (m, 2H), 7.824-7.844 (d, 1H, *J* = 8 Hz), 7.427-7.471 (m, 2H), 7.351-7.379 (m, 3H), 7.203-7.222 (t, 1H), 7.165-7.185 (d, 1H, *J* = 8 Hz), 7.051 (s, 2H), 5.367 (s, 1H); ¹³C NMR (400 MHz, DMSO-d₆) δ 37.46, 57.33, 114.99, 116.78, 120.23, 121.92, 123.48, 125.05, 127.24, 128.52, 129.50, 129.56, 129.78, 130.04, 130.81, 130.99, 146.88, 148.39, 159.81.

3-Amino-2-cyano-1-(2-bromophenyl)-4H-benzo[f]-chromene(Table 1, Entry 13)¹H NMR (500 MHz, DMSO-d₆) δ 7.925-7.960 (m, 2H), 7.627-7.657 (t, 2H), 7.415-7.496 (m, 2H), 7.341-7.359 (d, 1H, *J* = 9 Hz), 7.192-7.221 (t, 1H), 7.087-7.118 (m, 1H), 7.031 (s, 2H), 6.918-6.933 (d, 1H), 5.691 (s, 1H); ¹³C NMR (400 MHz, DMSO-d₆) δ 37.38, 56.37, 115.00, 116.78, 119.58, 121.71, 122.79, 125.00, 127.38, 128.66, 128.70, 128.76, 129.88, 130.01, 130.09, 130.75, 132.69, 144.29, 147.05, 159.73.

3-Amino-2-cyano-1-(4-methoxyphenyl)-4H-benzo[f]-chromene(Table 1, Entry 14)¹H NMR (400 MHz, DMSO-d₆) δ 7.880-7.918 (m, 2H), 7.824-7.844 (d, 1H, *J* = 8 Hz), 7.395-7.432 (m, 2H), 7.303-7.325 (d, 1H, *J* = 8.8 Hz), 7.077-7.099 (d, 2H, *J* = 8.8 Hz), 6.909 (s, 2H), 6.789-6.810 (d, 2H, *J* = 8.4 Hz), 5.229 (s, 1H), 3.654 (s, 3H); ¹³C NMR (400 MHz, DMSO-d₆) δ 37.29, 54.95, 58.25, 114.02, 115.92, 116.74, 120.49, 123.64, 124.83, 126.96, 128.00, 128.40, 129.31, 130.15, 130.80, 137.86, 146.67, 157.82, 159.53.

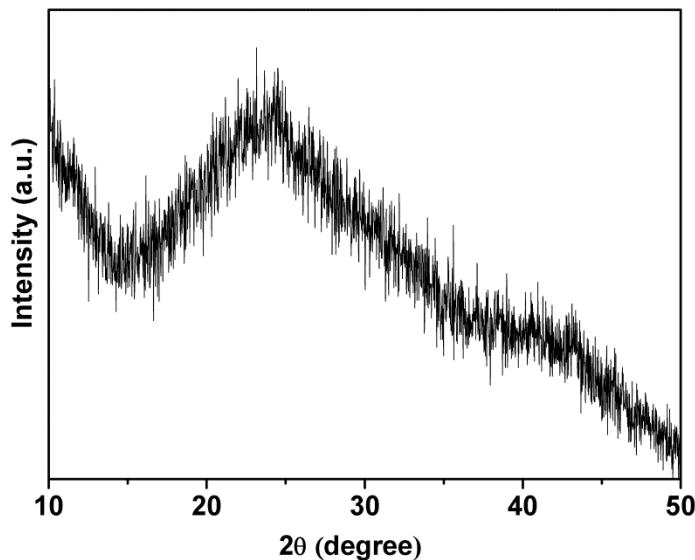
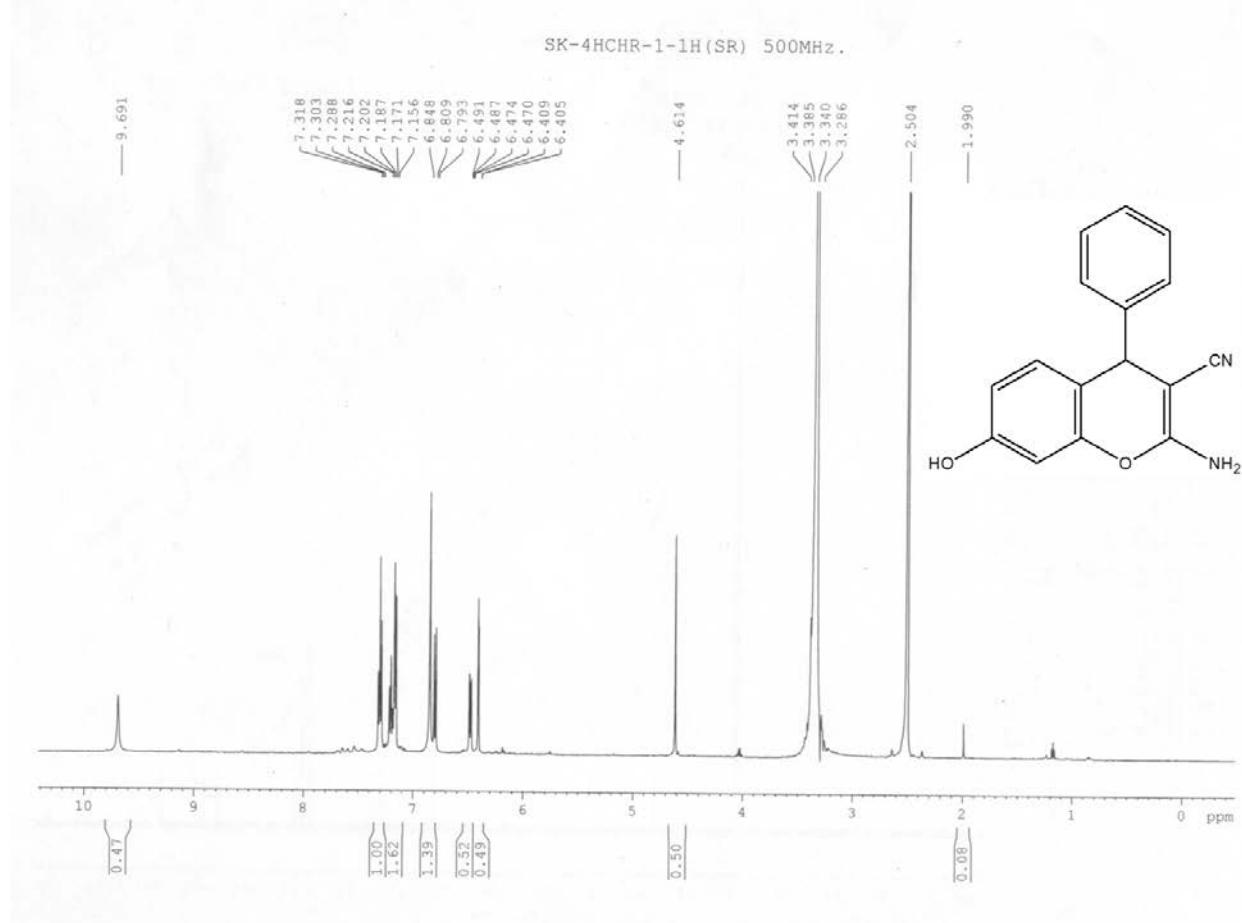


Fig. S1. Wide angle PXRD pattern of reused catalyst (after four consecutive cycles)

¹H NMR of 2-amino-3-cyano-7-hydroxy-4-phenyl-4H-chromene

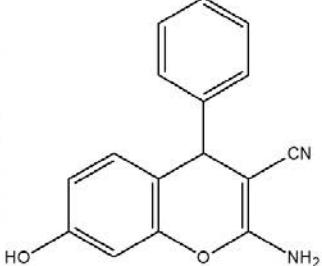


¹³C NMR of 2-amino-3-cyano-7-hydroxy-4-phenyl-4H-chromene

SK-4HCHR-1-13C (SI)

— 160.21
 — 157.42
 — 148.83
 — 146.29

129.84
 128.52
 127.31
 126.57
 120.56
 113.72
 112.33



56.31
 40.00
 39.92
 39.63
 39.50
 39.33
 39.17
 39.00

— 102.15

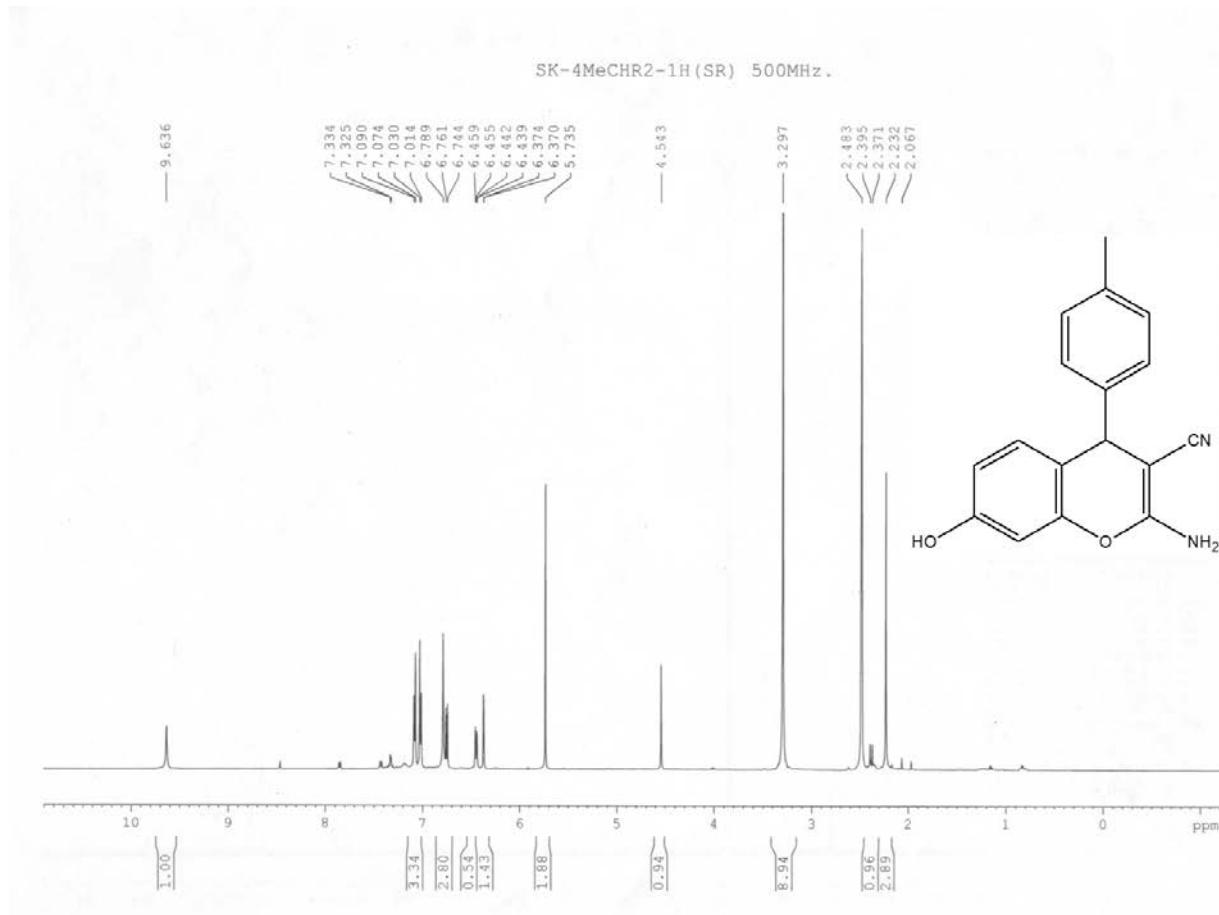
NAME SK-4HCHR-1-13C
 EXPNO 1
 PROCN0 1
 Date_ 20140603
 Time_ 17.59
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpp30
 TD 32768
 SOLVENT DMSO
 MS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.908261 Hz
 AQ 0.5505524 sec
 RG 32
 DW 16.800 usec
 DE 6.50 usec
 TE 299.6 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 PI 9.88 usec
 PL1 0.50 dB
 PLLW 82.16106415 W
 SF01 125.7703643 MHz

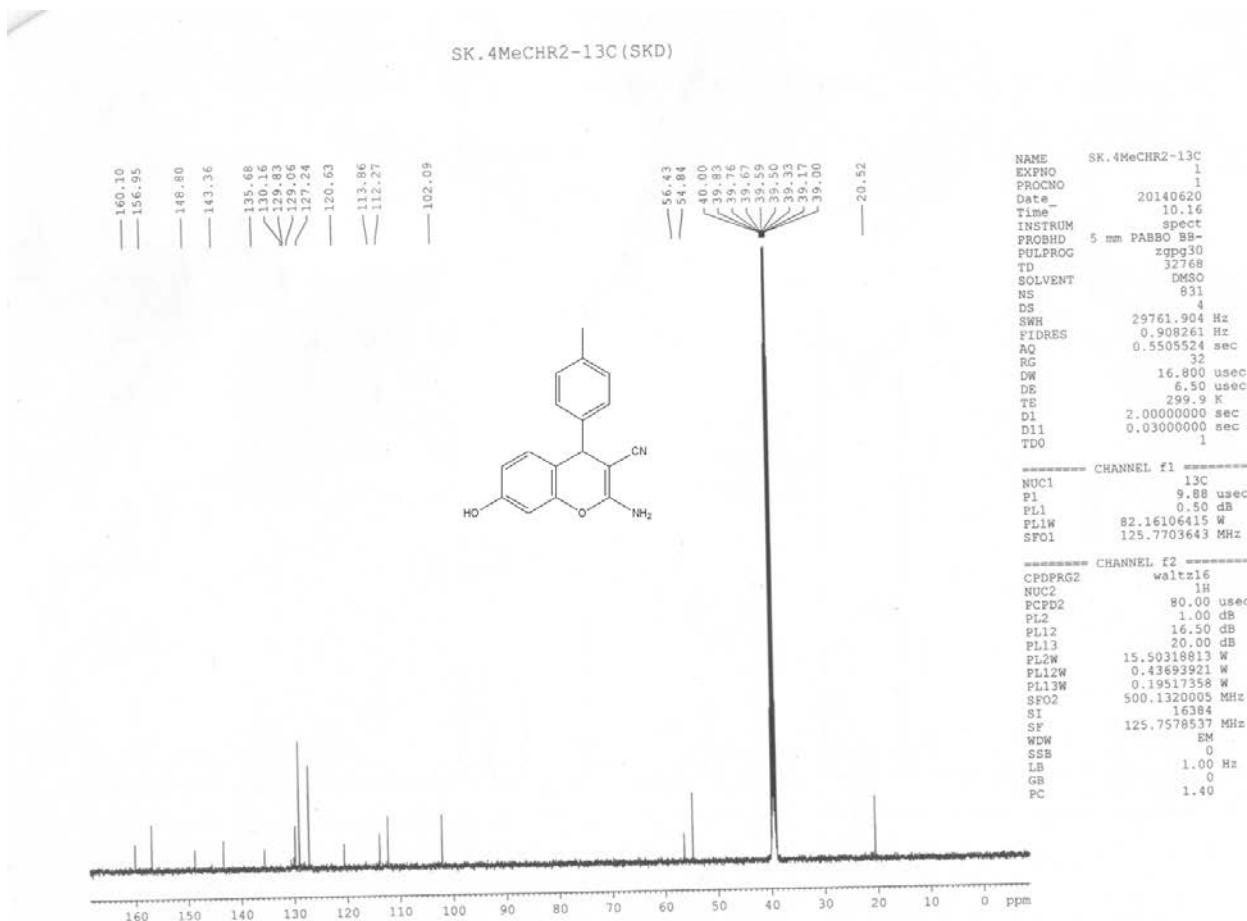
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLO 1.00 dB
 PLL2 15.34 dB
 PLL3 2.00 dB
 PLLW 15.50318813 W
 PLL2W 0.57071728 W
 PLL3W 0.19517258 W
 SF02 500.1320005 MHz
 SI 16384
 SF 125.7578536 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

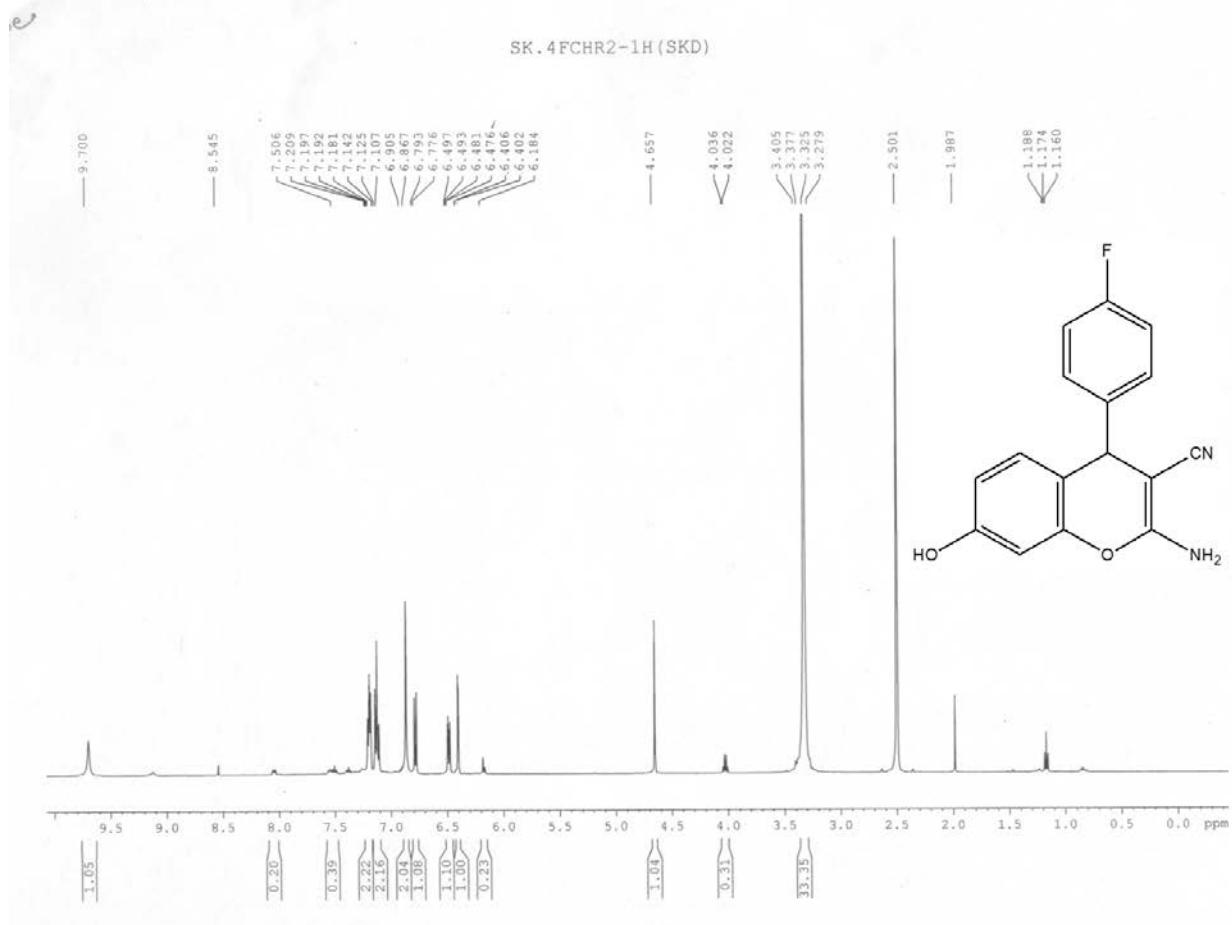
¹H NMR of 2-amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene



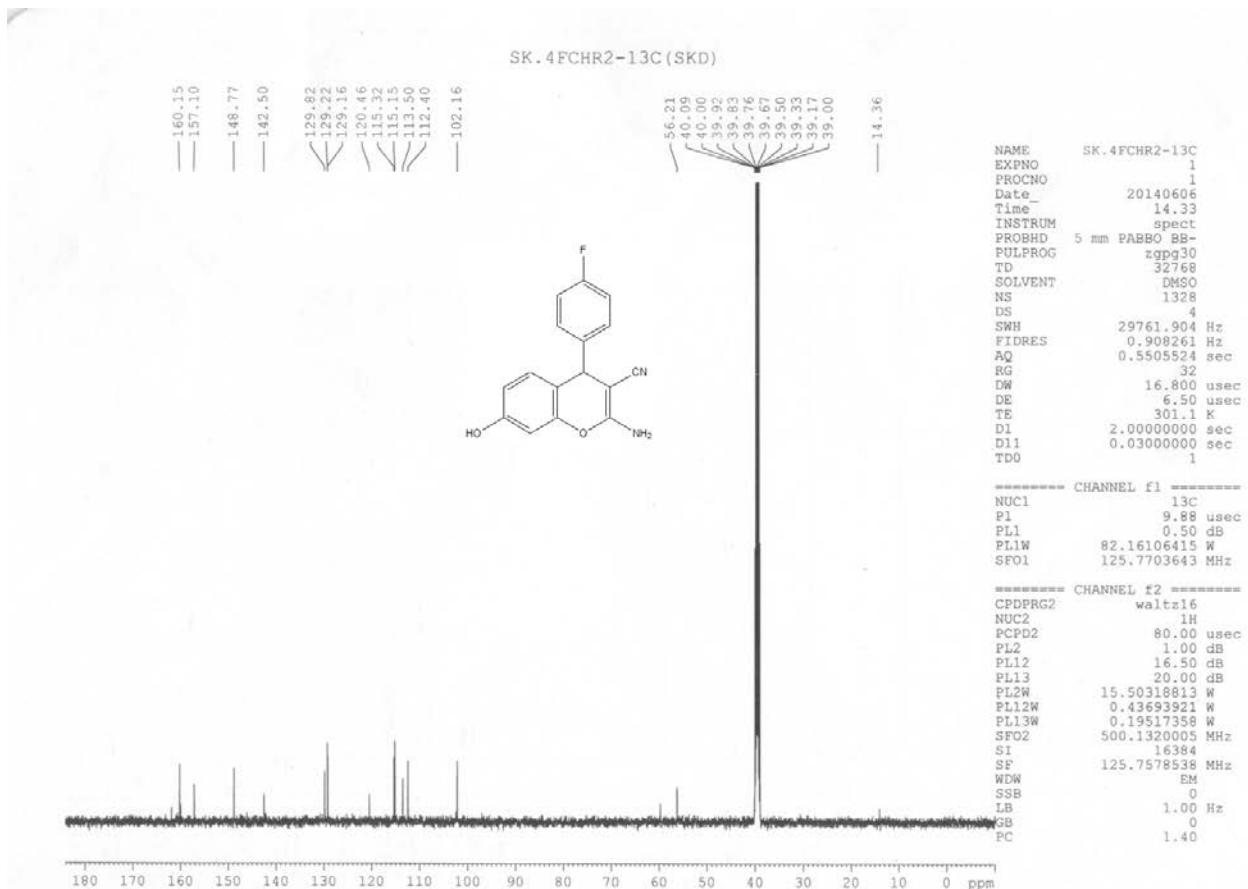
¹³C NMR of 2-amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene



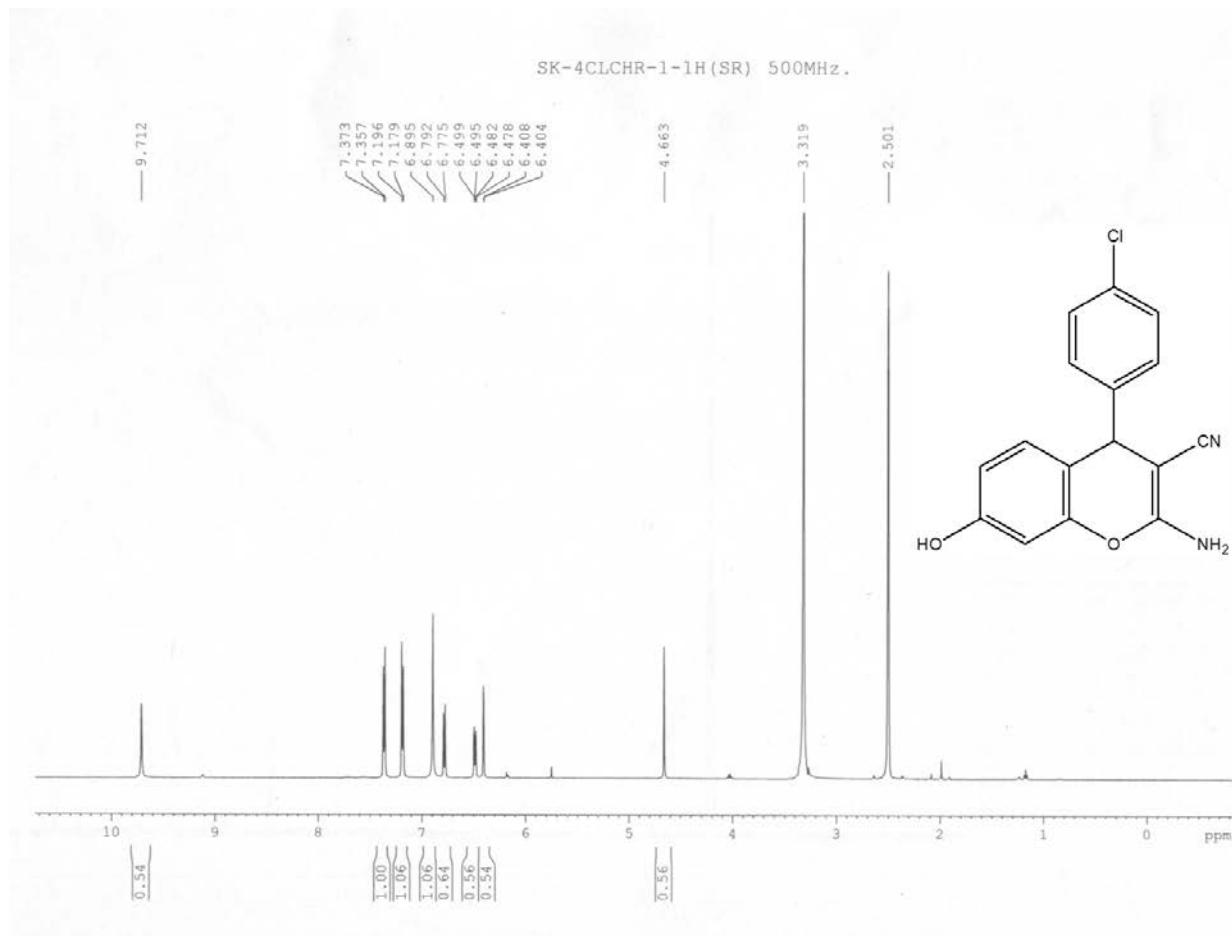
¹H NMR of 2-amino-3-cyano-7-hydroxy-4-(4-fluorophenyl)-4H-chromene



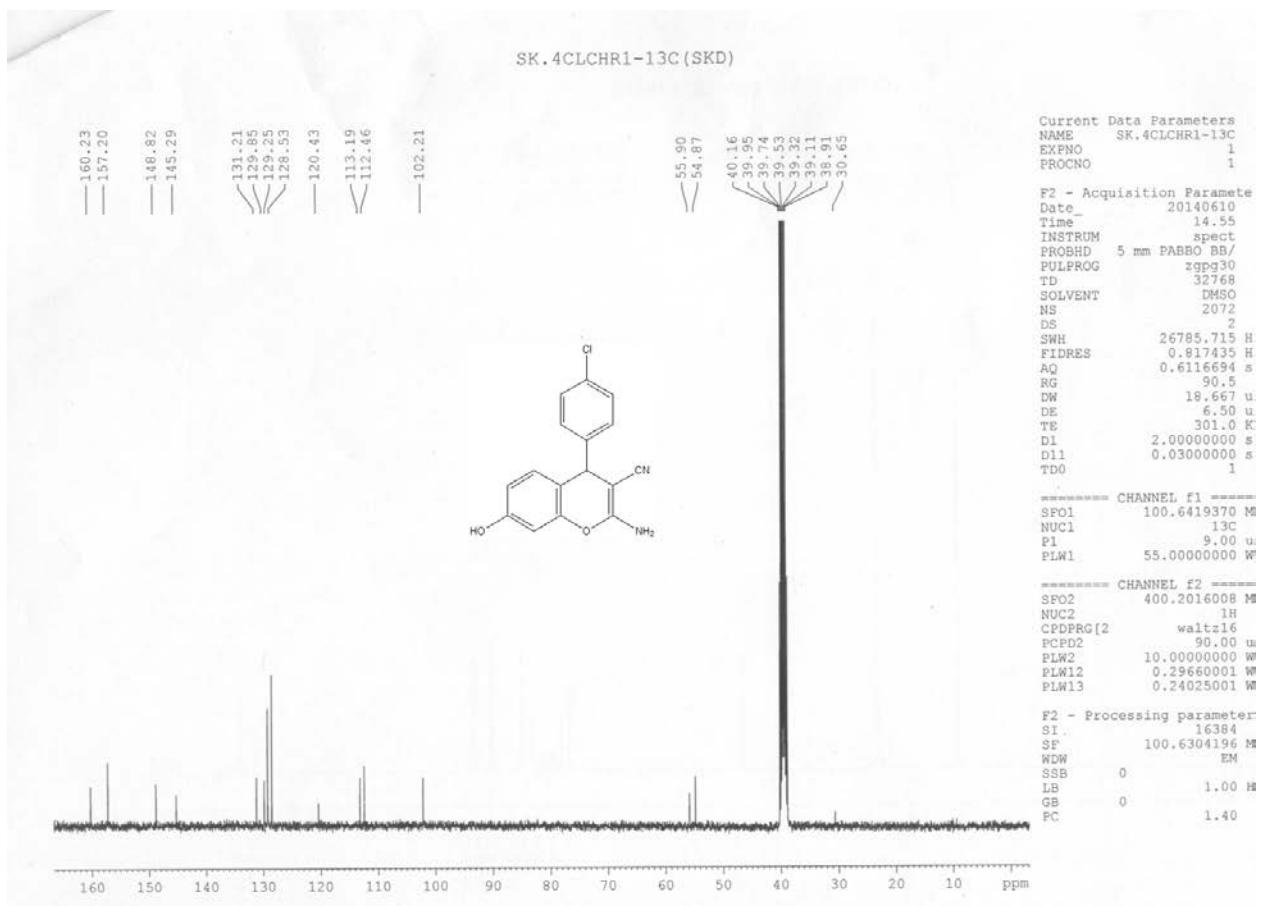
¹³C NMR of 2-amino-3-cyano-7-hydroxy-4-(4-fluorophenyl)-4H-chromene



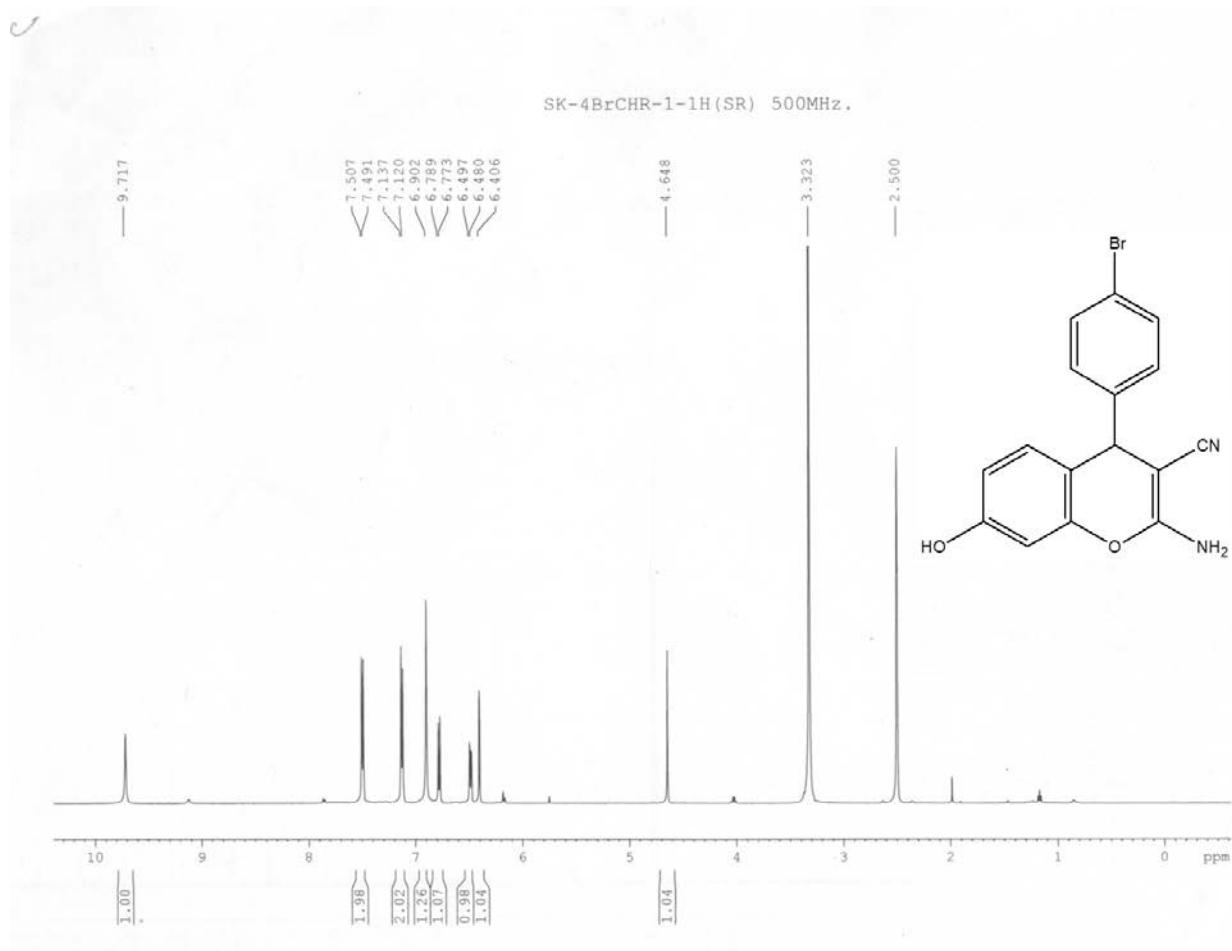
¹H NMR of 2-amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4H-chromene



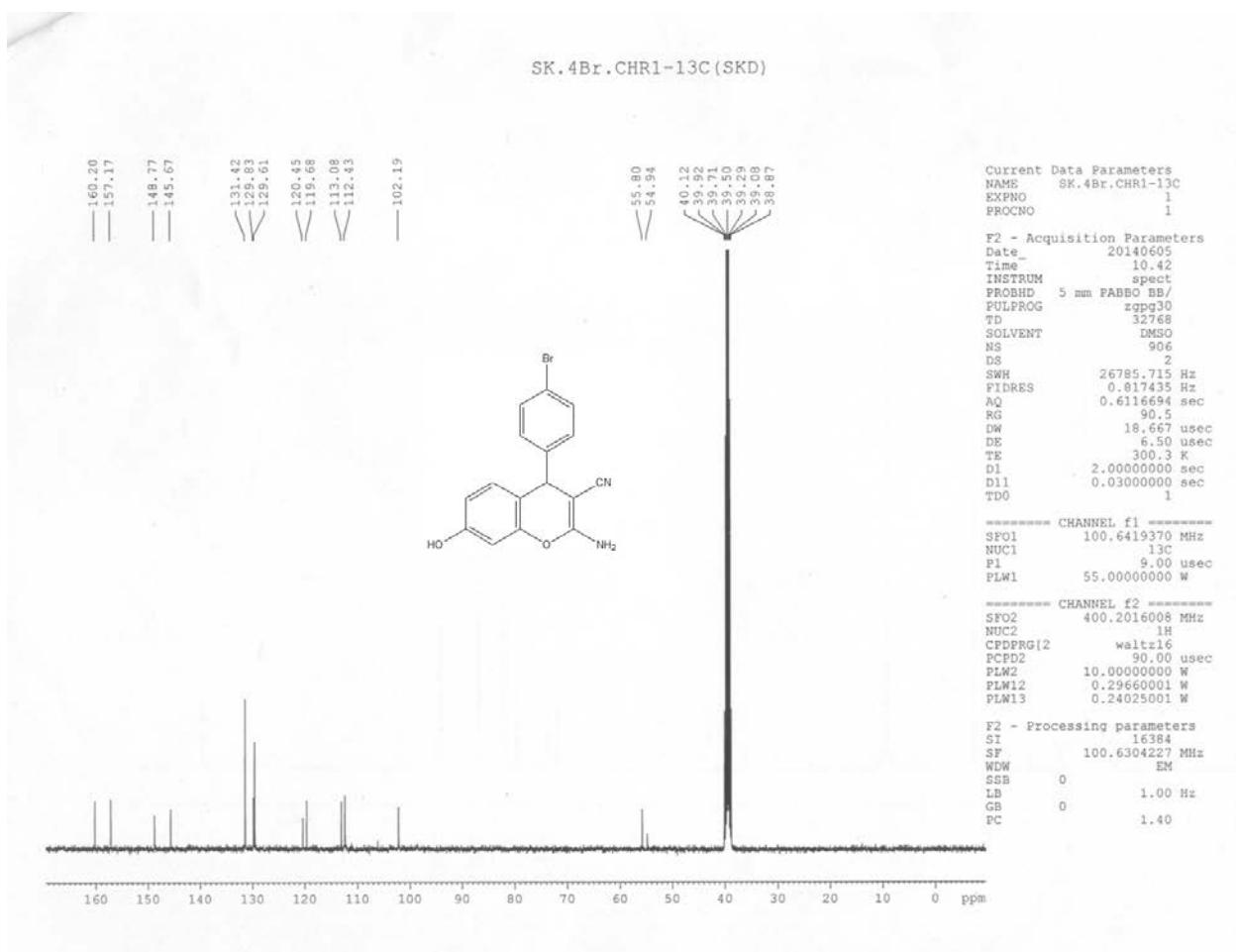
¹³C NMR of 2-amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4H-chromene



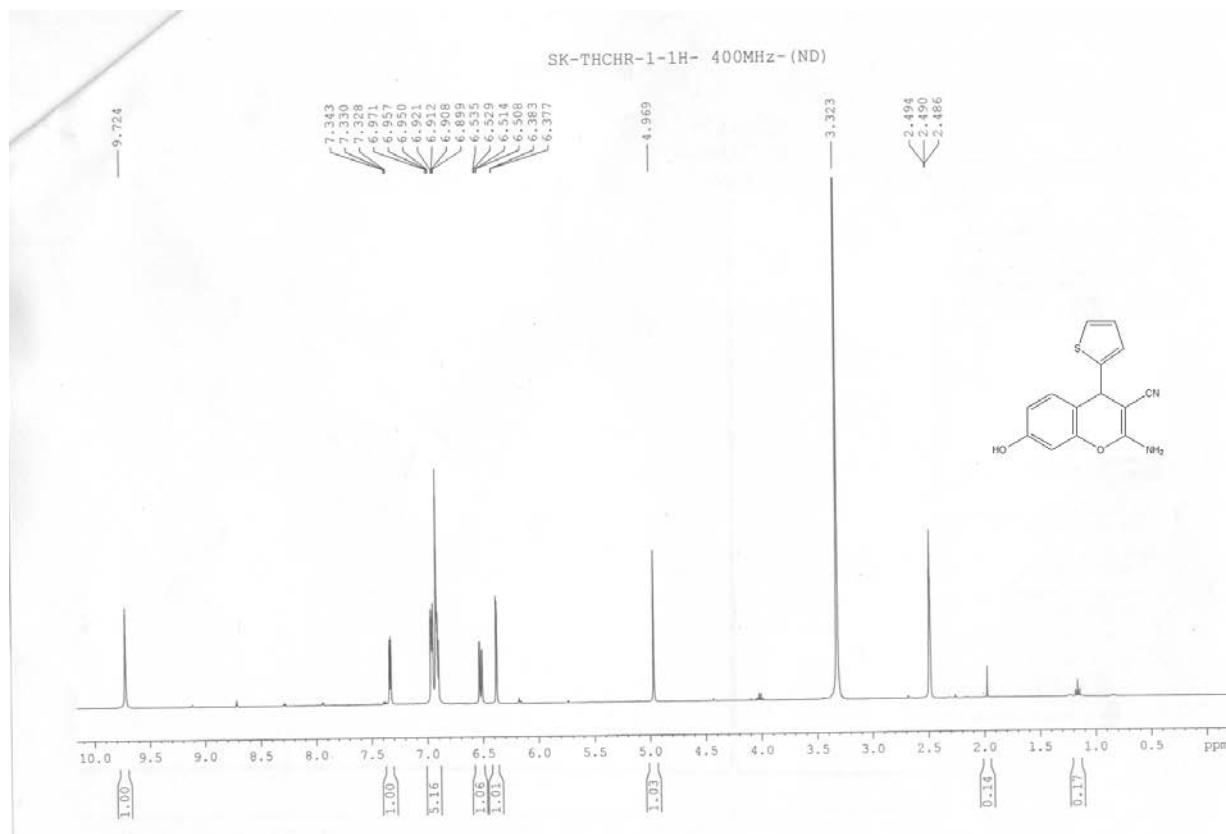
¹H NMR of 2-amino-3-cyano-7-hydroxy-4-(4-bromophenyl)-4H-chromene



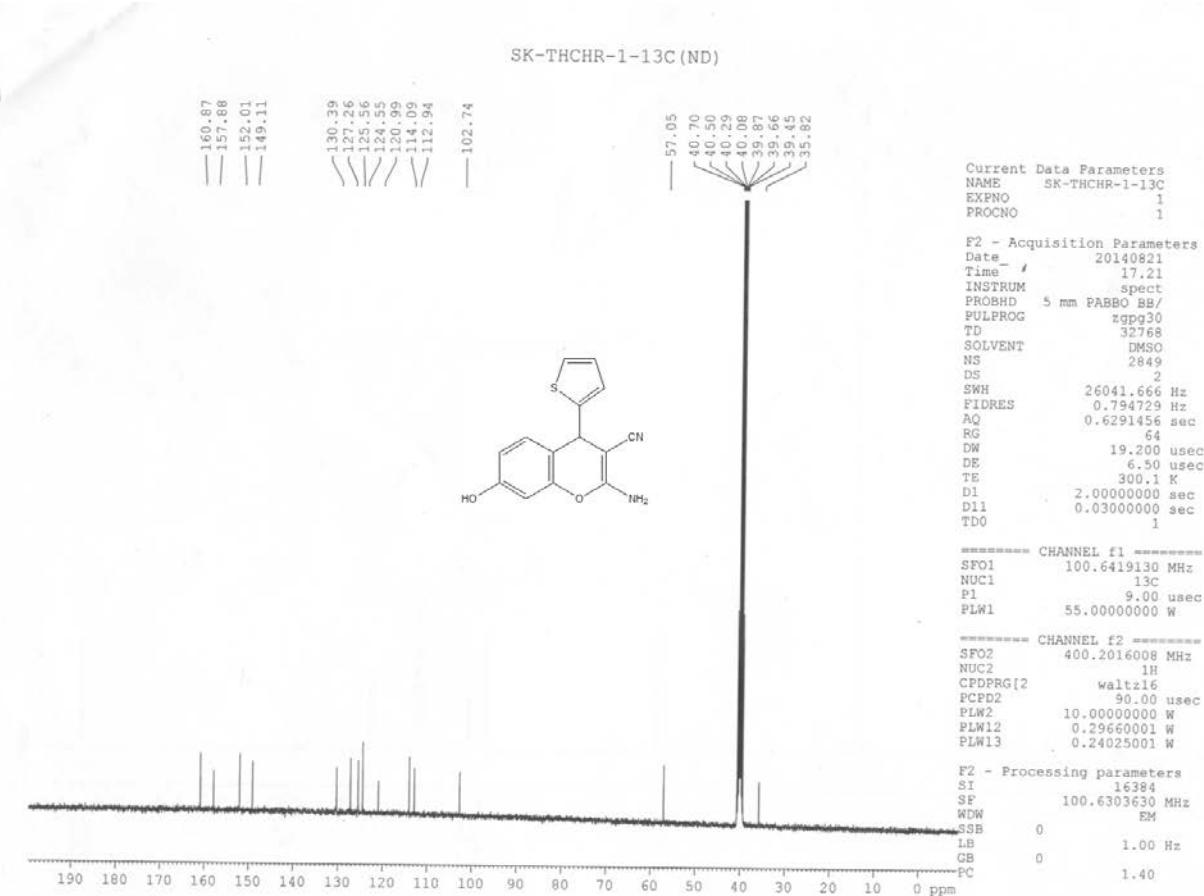
¹³C NMR of 2-amino-3-cyano-7-hydroxy-4-(4-bromophenyl)-4H-chromene



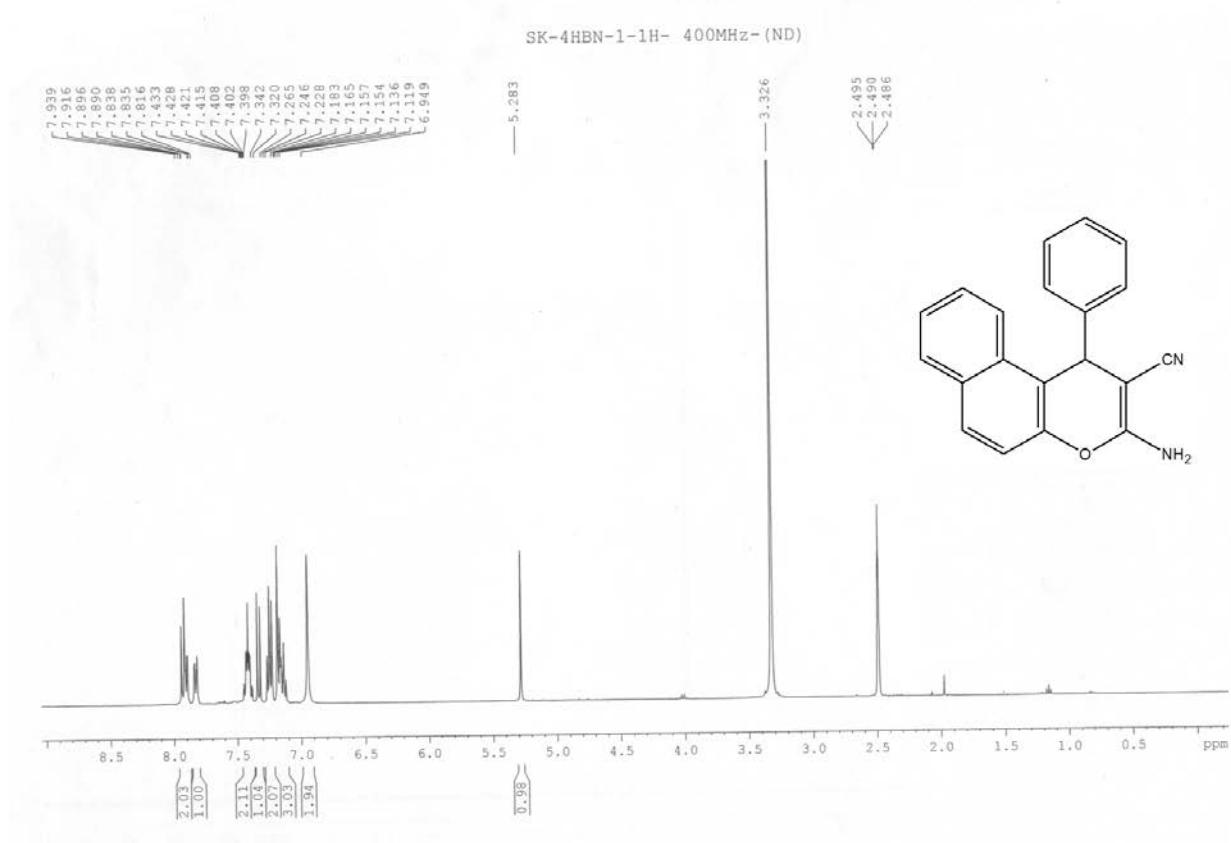
¹H NMR of 2-amino-7-hydroxy-4-(thiophen-2-yl)-4H-chromene-3-carbonitrile



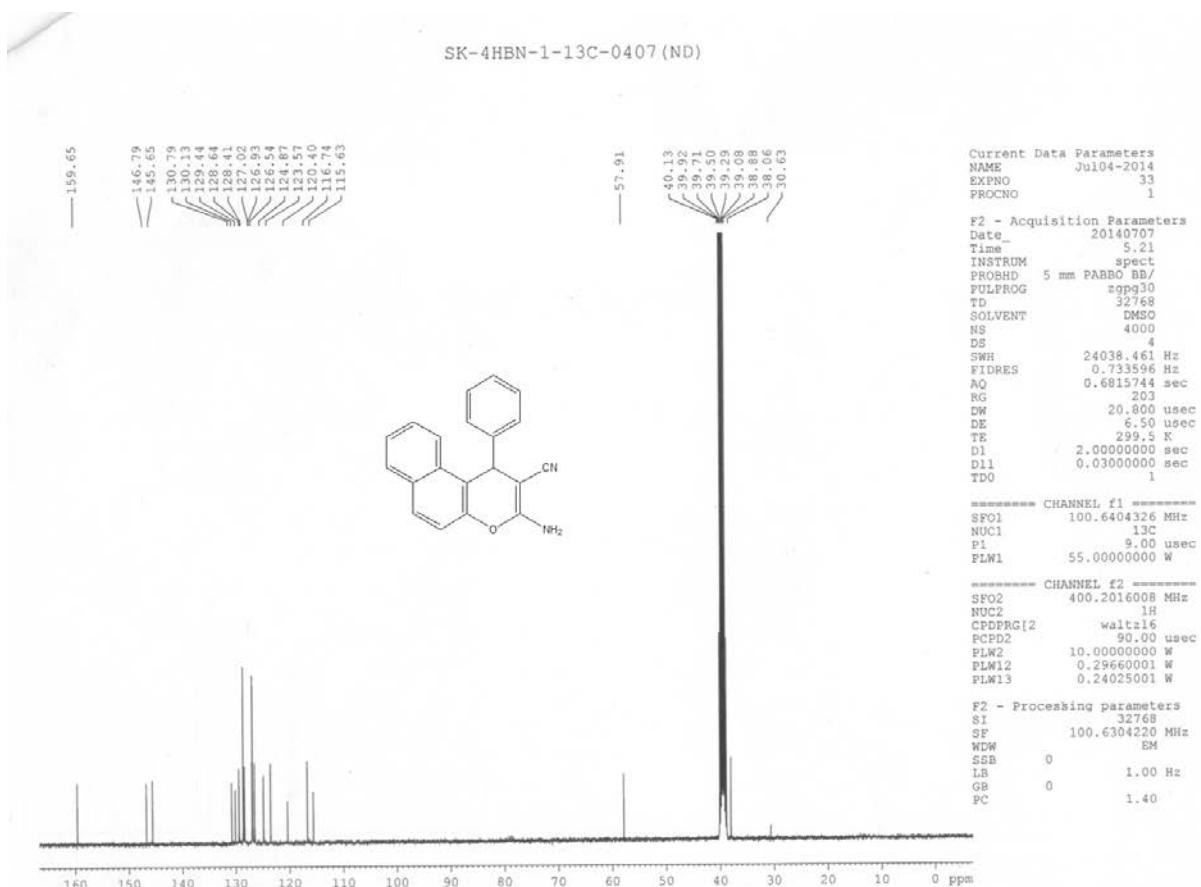
¹³C NMR of 2-amino-7-hydroxy-4-(thiophen-2-yl)-4H-chromene-3-carbonitrile



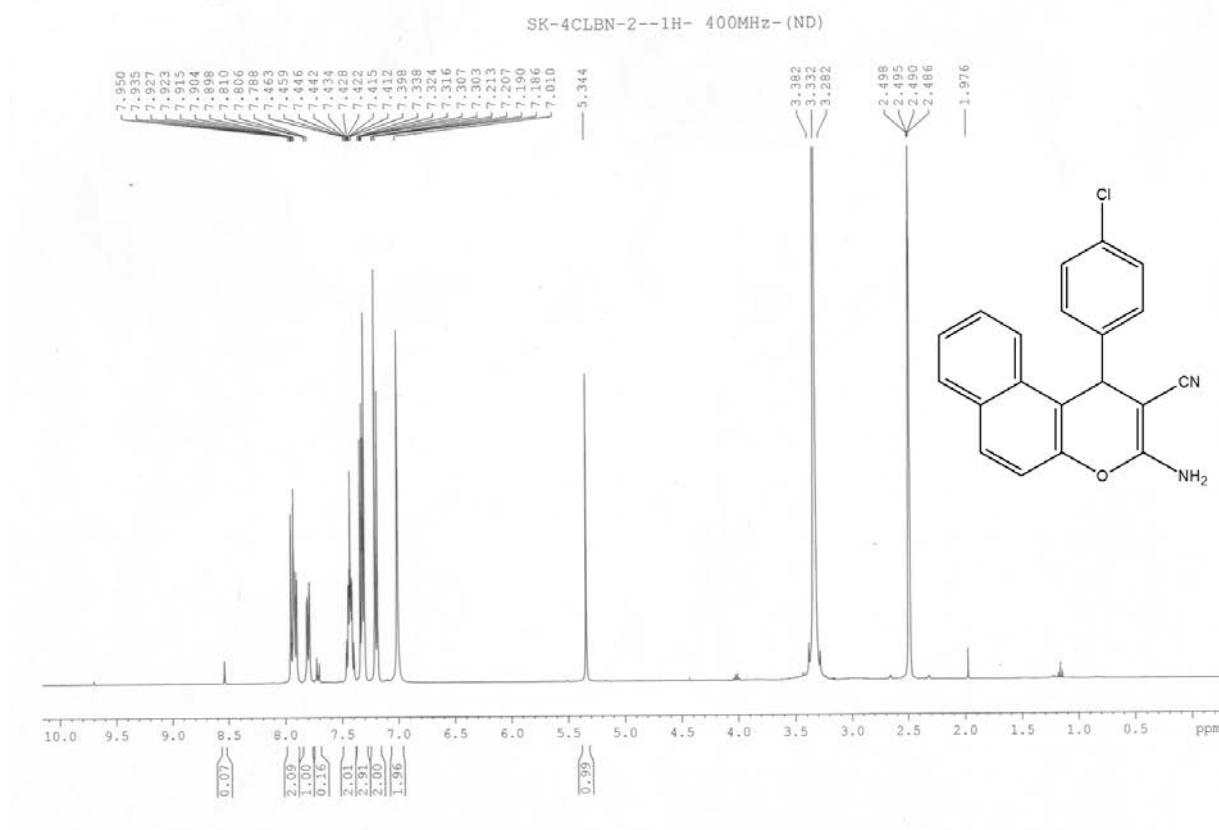
¹H NMR of 3-Amino-2-cyano-1-phenyl-4H-benzo[f]chromene



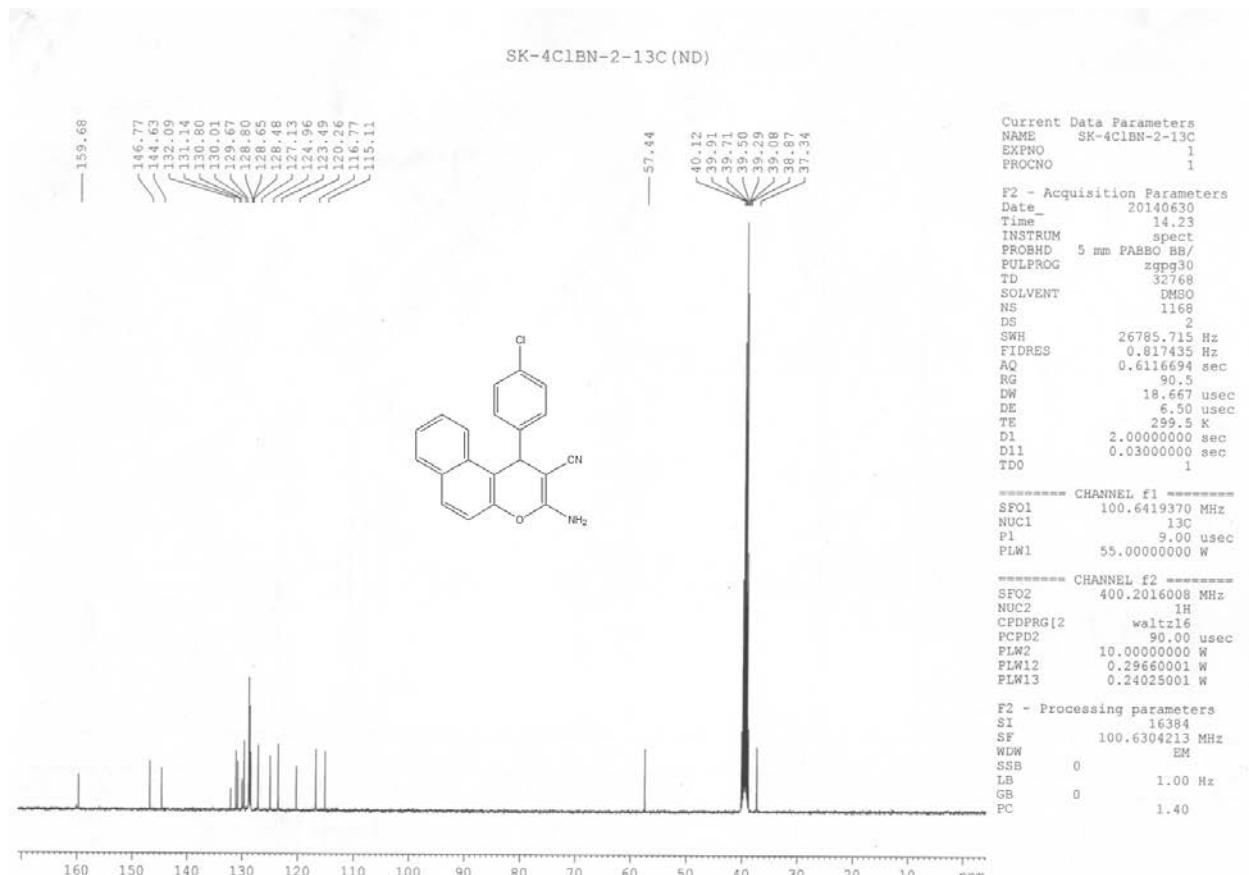
¹³C NMR of 3-Amino-2-cyano-1-phenyl-4H-benzo[f]-chromene



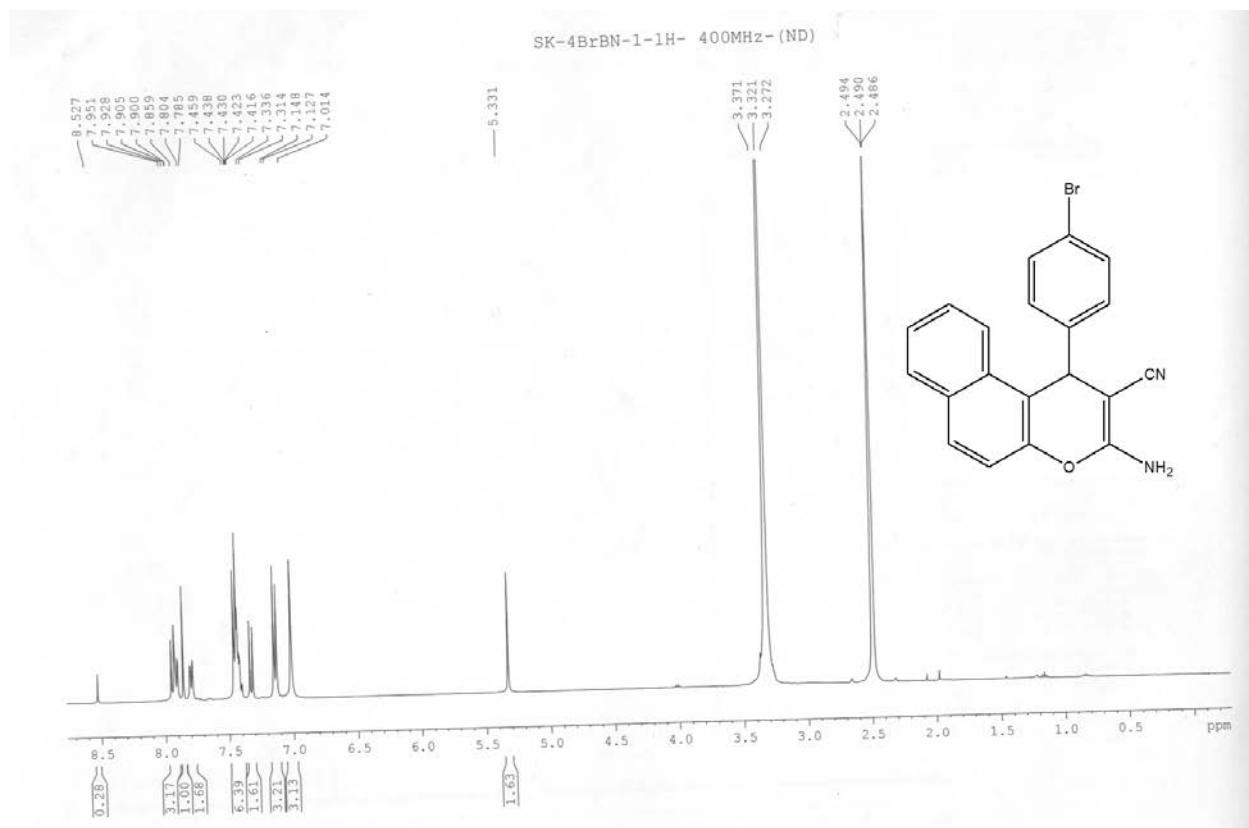
¹H NMR of 3-Amino-2-cyano-1-(4-chlorophenyl)-4H-benzo[f]-chromene



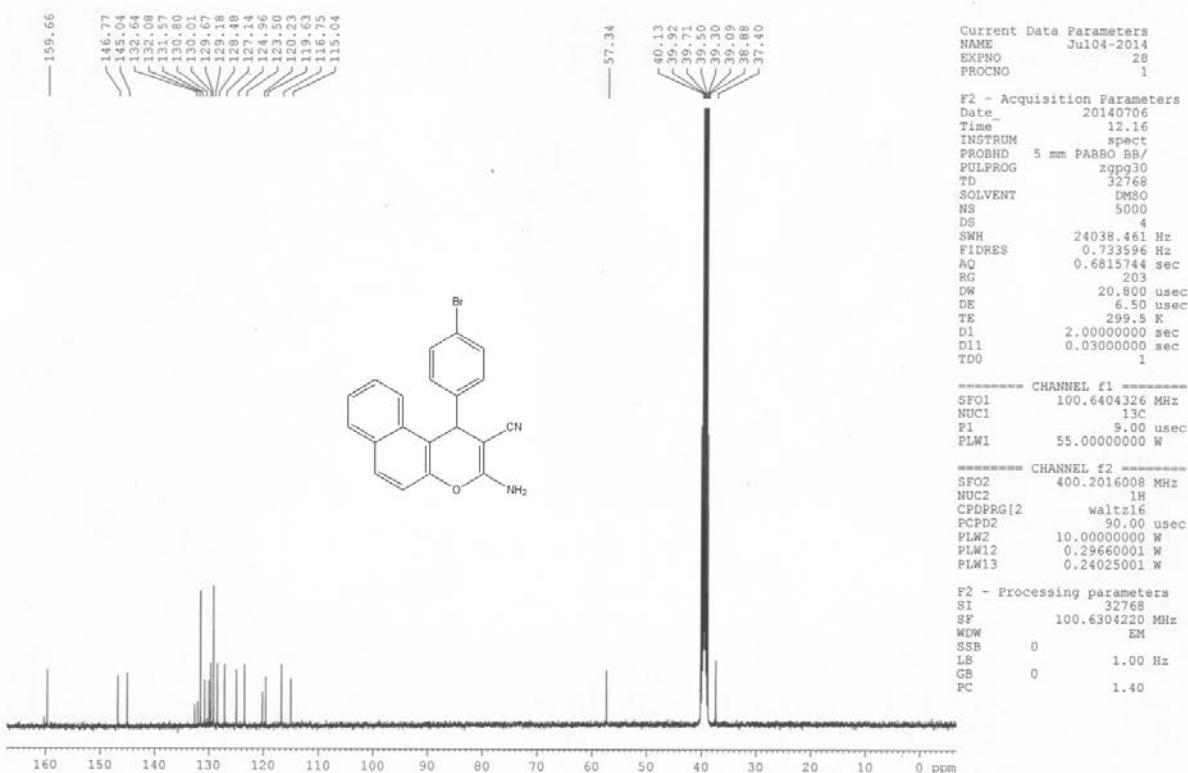
¹³C NMR of 3-Amino-2-cyano-1-(4-chlorophenyl)-4H-benzo[f]-chromene



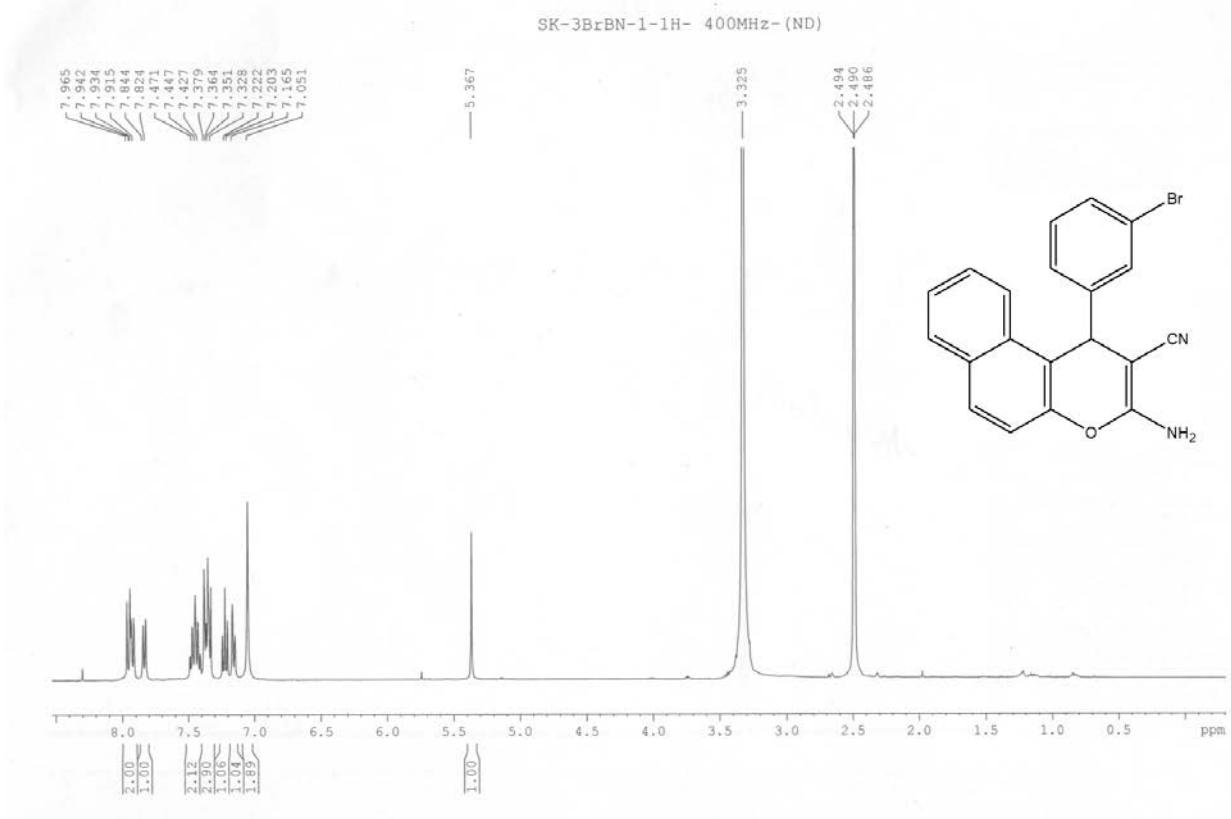
¹H NMR of 3-Amino-2-cyano-1-(4-bromophenyl)-4H-benzo[f]chromene



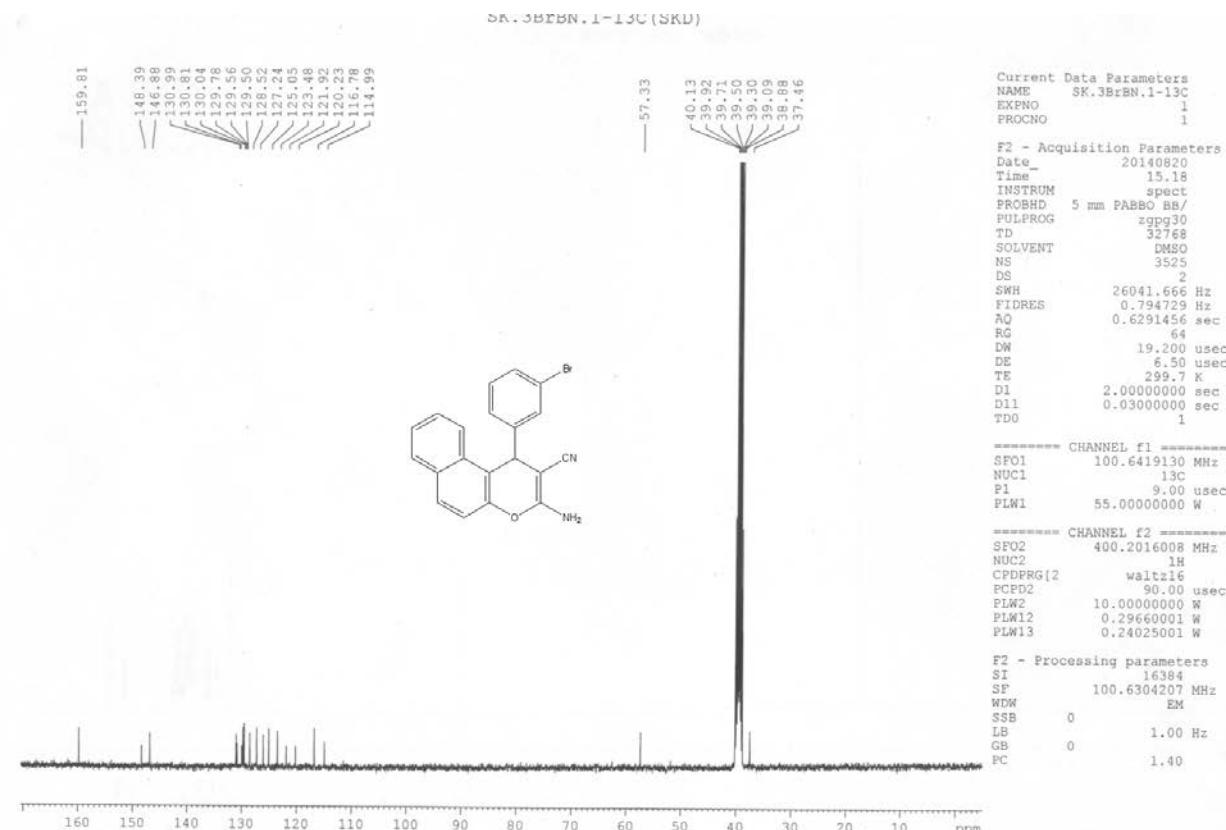
¹³C NMR of 3-Amino-2-cyano-1-(4-bromophenyl)-4H-benzo[f]-chromene



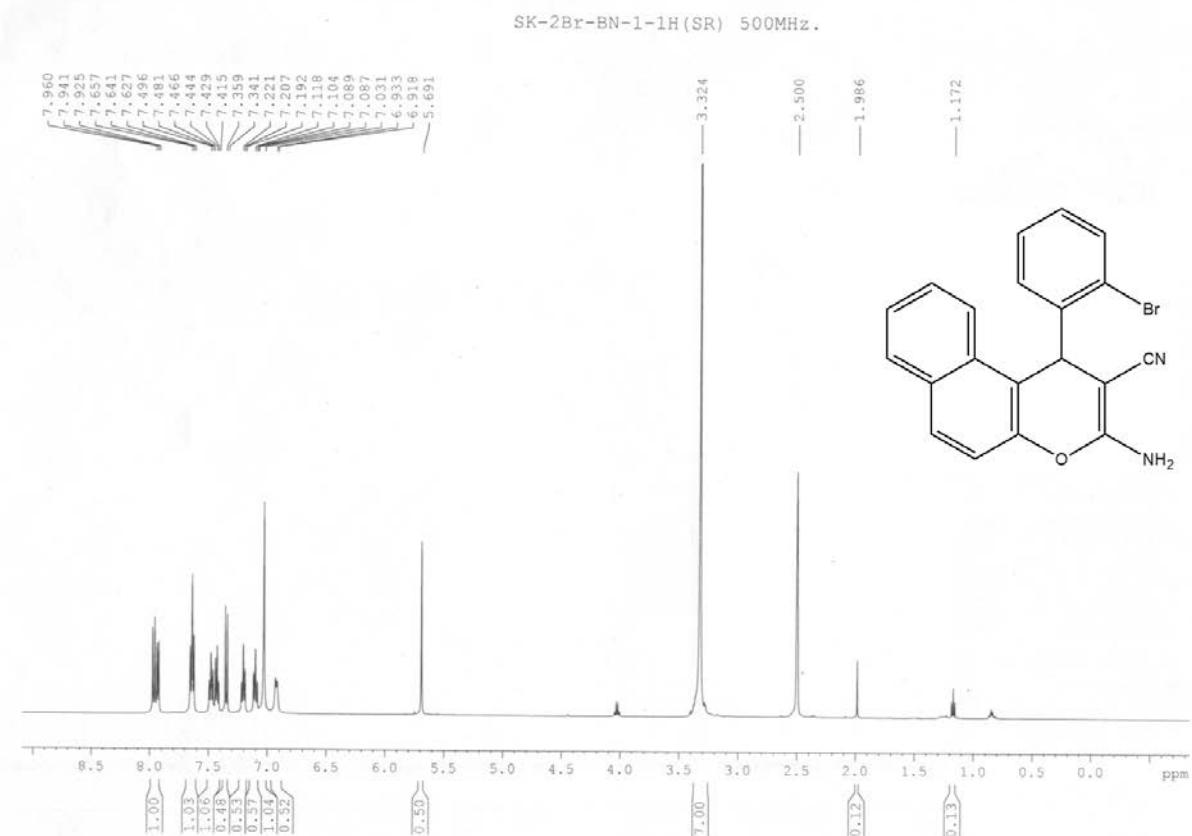
¹H NMR of 3-Amino-2-cyano-1-(3-bromophenyl)-4H-benzo[f]-chromene



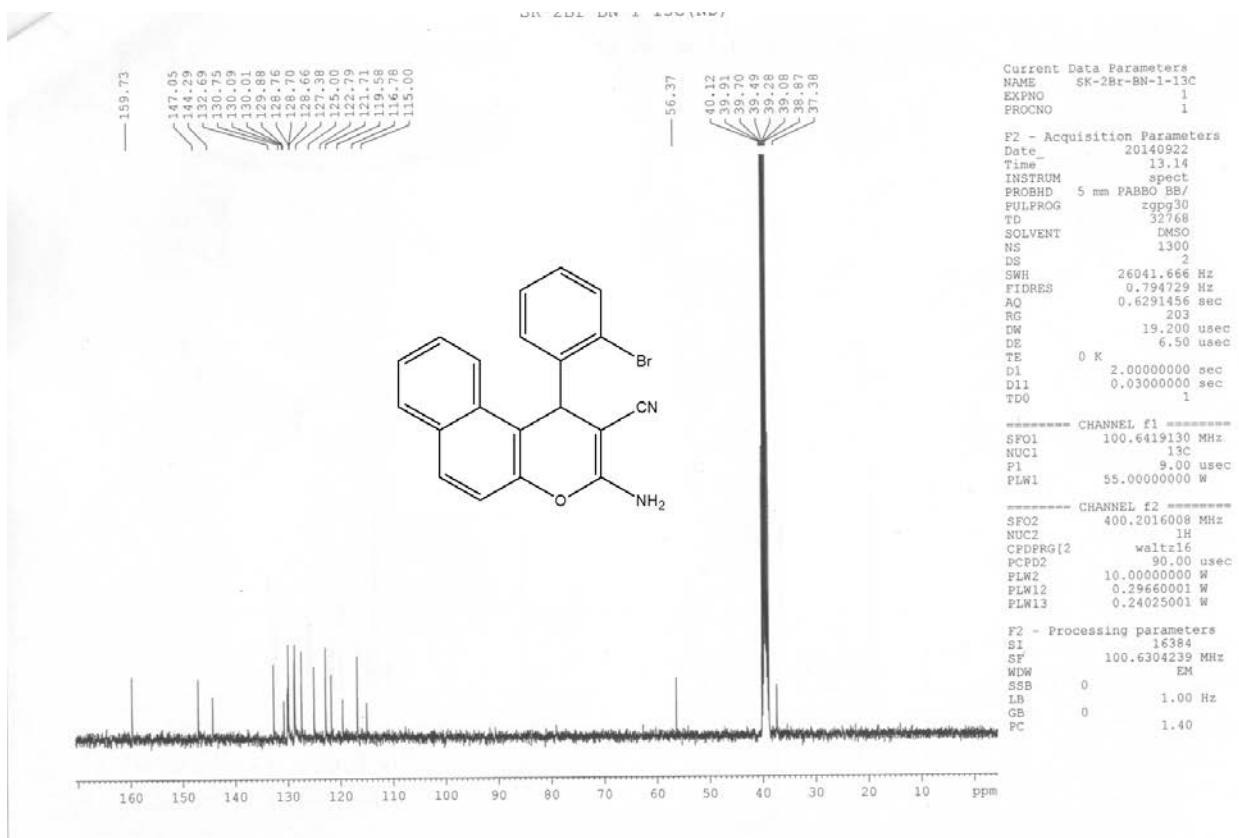
¹³C NMR of 3-Amino-2-cyano-1-(3-bromophenyl)-4H-benzo[f]-chromene



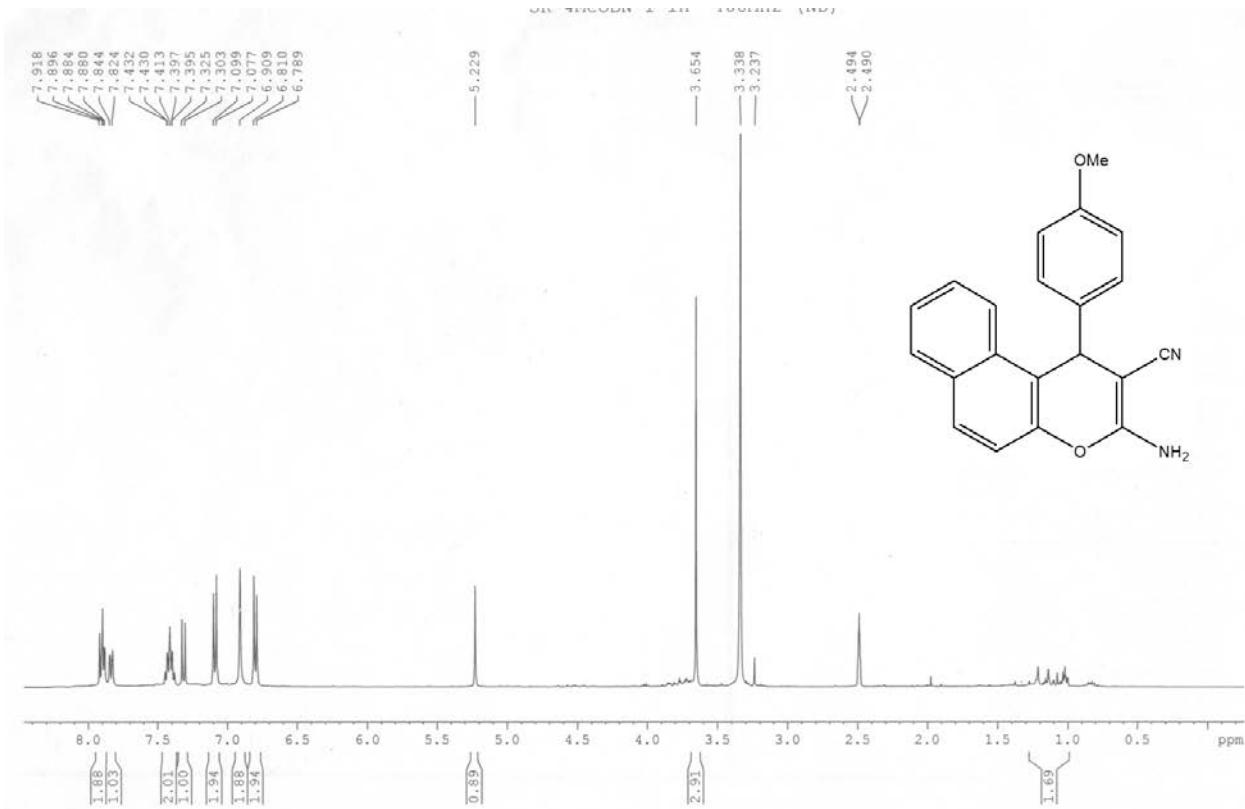
¹H NMR of 3-Amino-2-cyano-1-(2-bromophenyl)-4H-benzo[f]-chromene



¹³C NMR of 3-Amino-2-cyano-1-(2-bromophenyl)-4H-benzo[f]-chromene



¹H NMR of 3-Amino-2-cyano-1-(4-methoxyphenyl)-4H-benzo[f]-chromene



¹³C NMR of 3-Amino-2-cyano-1-(4-methoxyphenyl)-4H-benzo[f]-chromene

