

Supplementary Information

Fe₃O₄@ Nano-Almond shell/OSi(CH₂)₃/DABCO: A novel magnetic nanocatalyst for synthesis of chromenes

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2-Amino-4-phenyl-4H-benzo[f]chromen-3-carbonitrile (5a)

Brown solid, M.p. 272-274 °C; FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3433, 3338, 2182, 1642, 1590,

1512, 1453, 1404, 1212, 812. ¹H NMR (400 MHz, CDCl₃) / δ ppm: 7.83 (m, 2H), 7.70 (d, *J* = 3.2

Hz, 1H), 7.42 (m, 2H), 7.29 (m, 1H), 7.25 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 3H), 5.26 (s, 1H), 4.57

(s, 2H, NH₂).

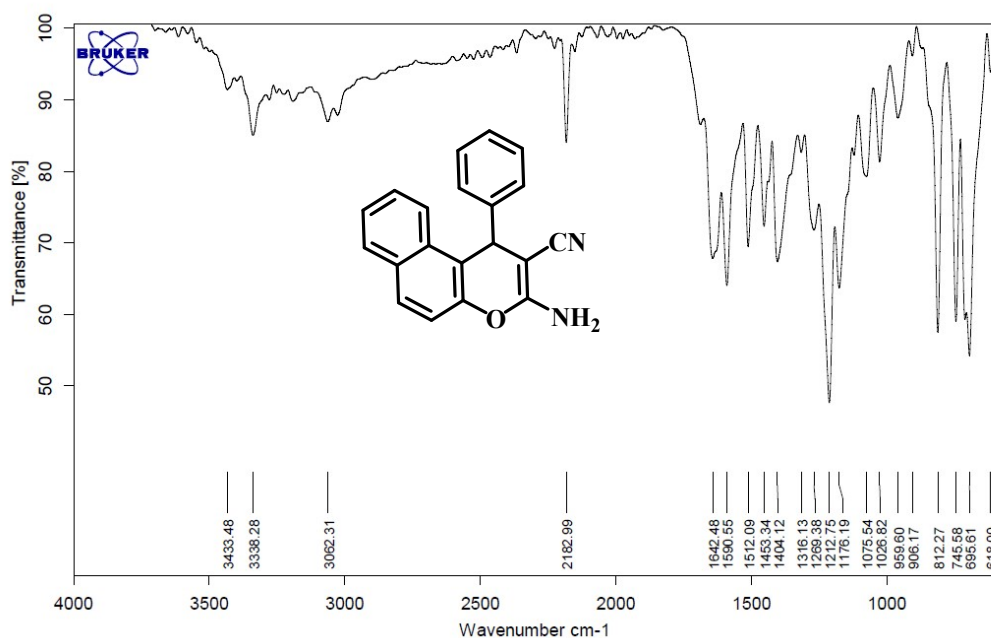


Figure S1: IR (ATR) spectrum of 2-Amino-4-phenyl-4H-benzo[f]chromen-3-carbonitrile

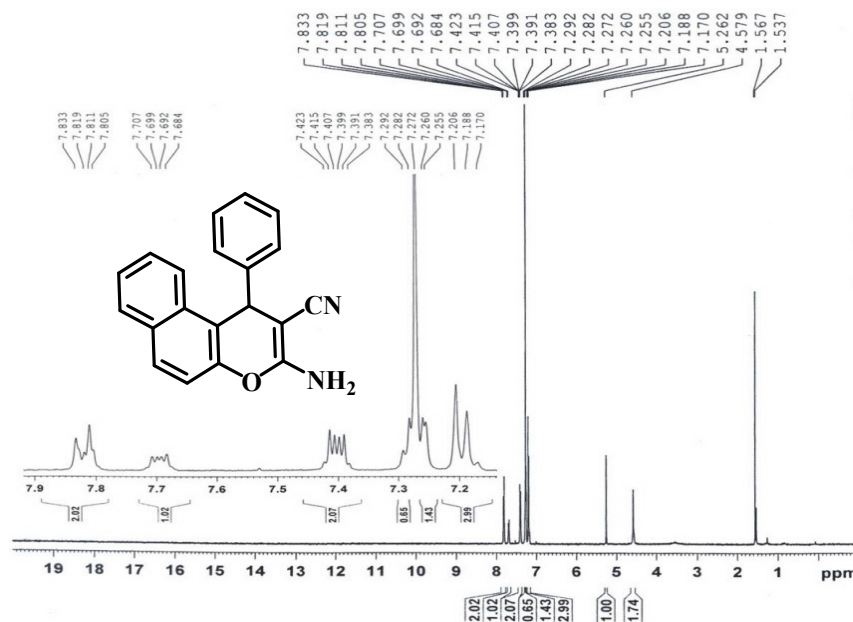


Figure S2: ¹H NMR spectrum of 2-Amino-4-phenyl-4H-benzo[f]chromen-3-carbonitrile

2-Amino-4-(4-nitrophenyl)-4H-benzo[f]chromen-3-carbonitrile (5b)

Yellow Solid, M.p. 185-187 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3445, 3327, 2184, 1657, 1586, 1513, 1411, 1341, 815. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 8.38 (m, 2H), 8.10 (m, 2H), 7.93 (br, 1H), 7.71-7.89 (m, 2H), 7.42-7.75 (m, 2H), 7.33 (br, 1H), 7.06 (s, 2H), 5.52 (s, 1H).

¹³C NMR (125 MHz, DMSO-d₆) / δ ppm: 159.92, 152.99, 146.21, 130.86, 130.07, 129.30, 128.61, 127.36, 126.10, 125.98, 124.16, 123.44, 122.64, 120.11, 118.59, 116.88, 114.47, 56.58.

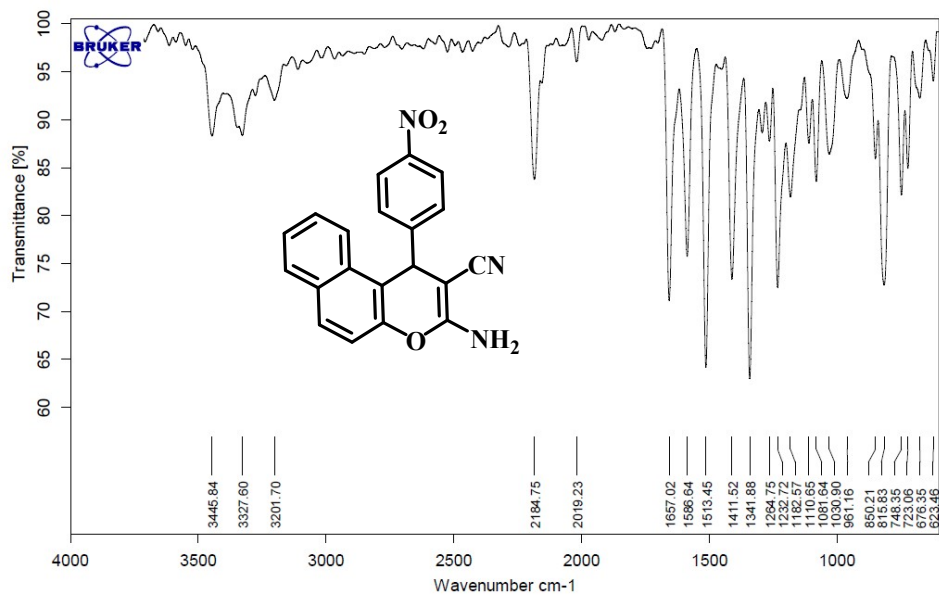


Figure S3: IR (ATR) spectrum of 2-Amino-4-(4-nitrophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

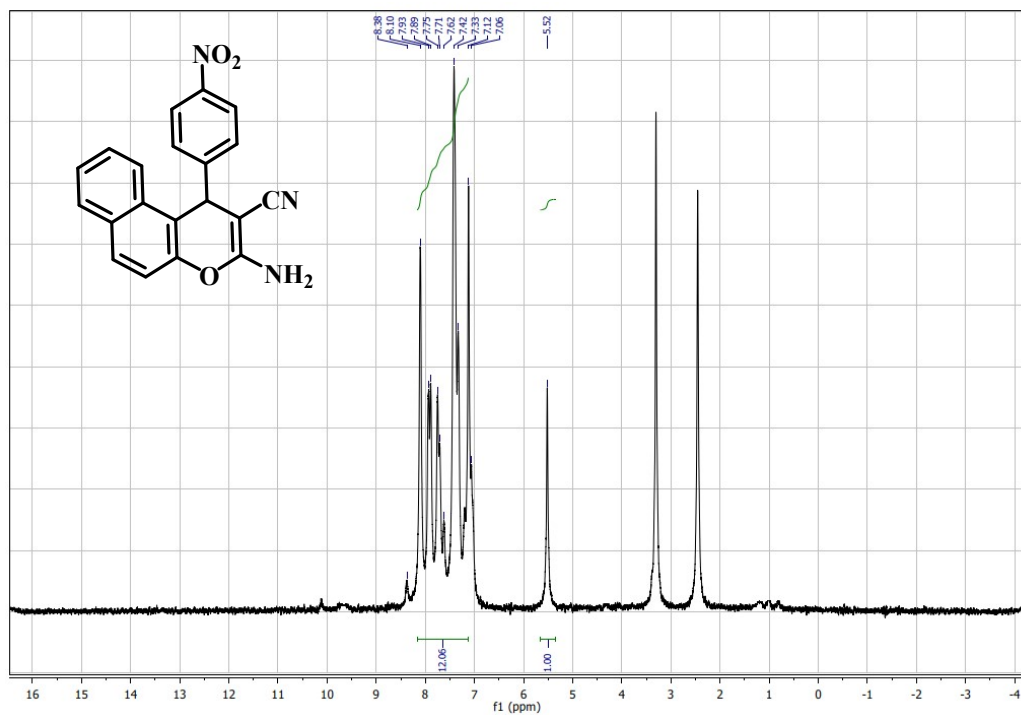


Figure S4: ^1H NMR spectrum of 2-Amino-4-(4-nitrophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

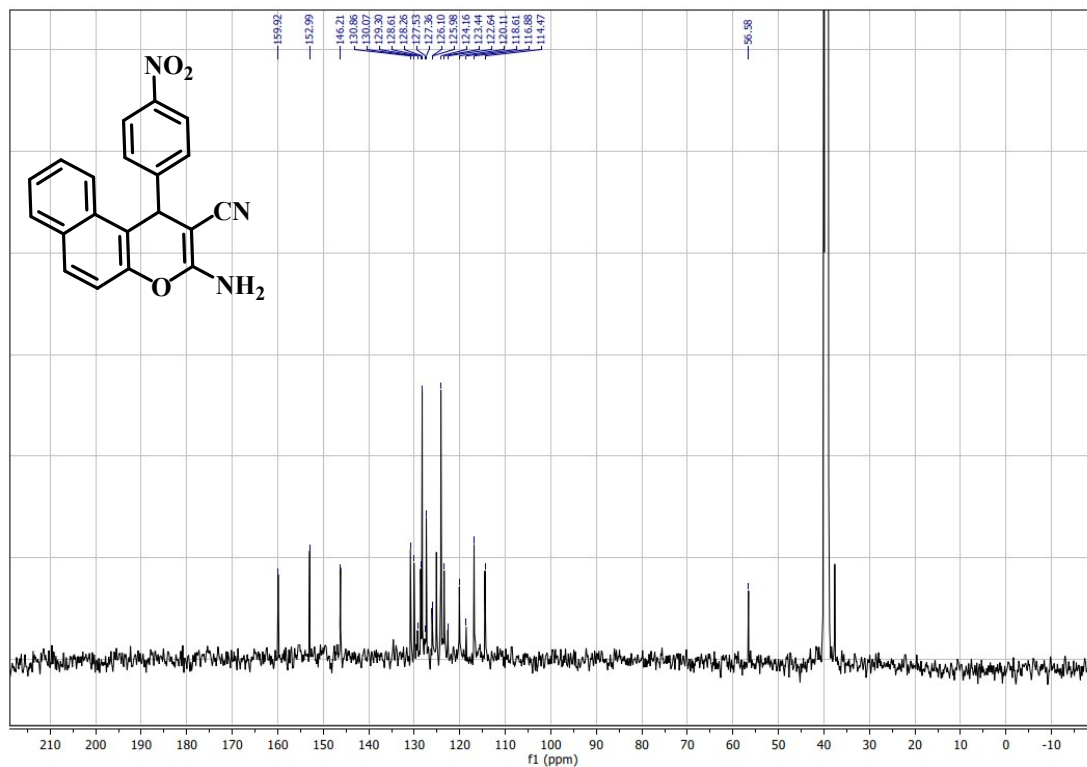


Figure S5: ¹³C NMR spectrum of 2-Amino-4-(4-nitrophenyl)-4H-benzo[f]chromen-3-carbonitrile

2-Amino-4-(4-hydroxyphenyl)-4H-benzo[f]chromen-3-carbonitrile (5c)

Cream Solid, M.p. 282-284 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3449, 3305, 3173, 2193, 1649, 1587,

1511, 1447, 1232, 766. ¹H NMR (400 MHz, DMSO-d₆) / δ ppm: 9.88 (s, 1H, OH), 7.905–7.92

(br, s, 2H, ArH), 7.73 (br, s, 1H, ArH), 7.40 (m, 2H, ArH), 7.36 (d, 1H, ArH), 6.91 (d, 2H), 6.89

(s, 2H, NH₂), 6.63 (d, 2H), 5.16 (s, 1H, CH).

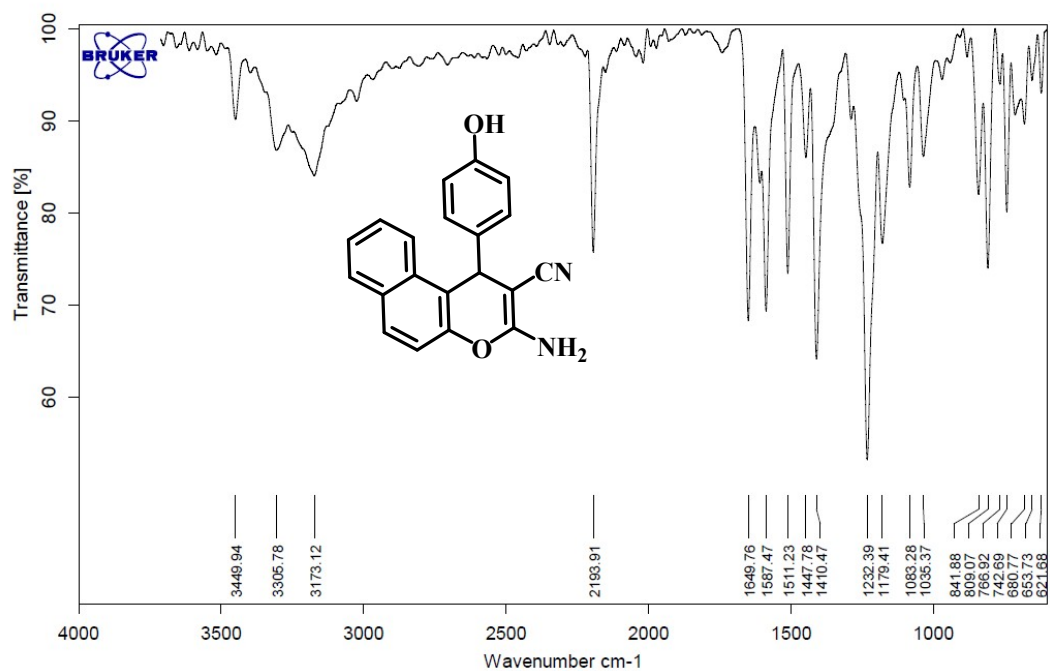


Figure S6: IR (ATR) spectrum of 2-Amino-4-(4-hydroxyphenyl)-4H-benzo[f]chromen-3-carbonitrile

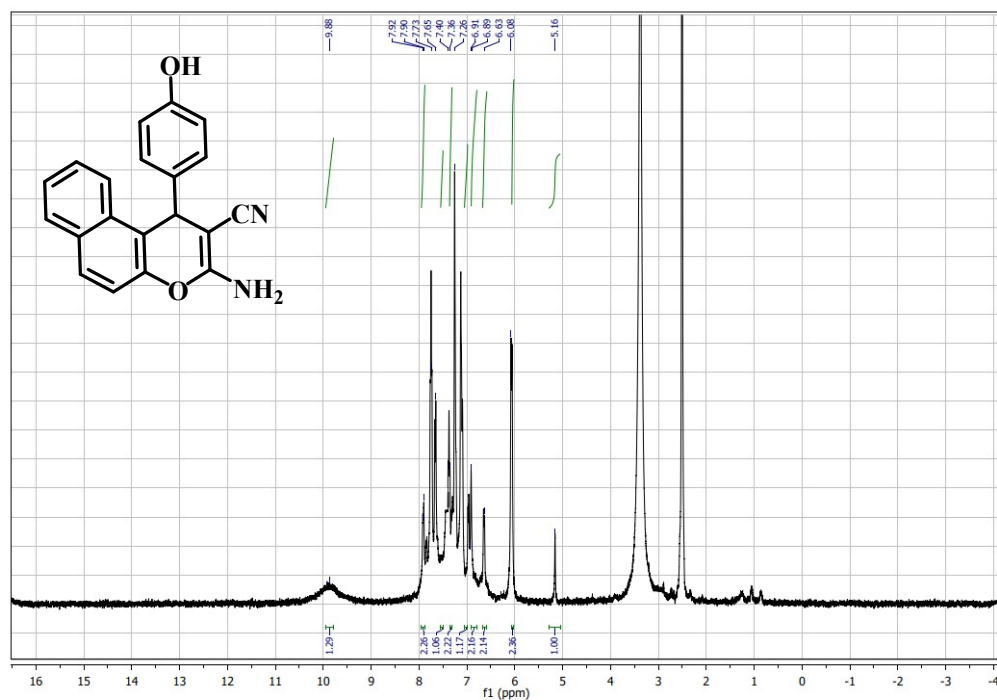


Figure S7: ¹H NMR spectrum of 2-Amino-4-(4-hydroxyphenyl)-4H-benzo[f]chromen-3-carbonitrile

2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5d)

Orange Solid, M.p. 232-233 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3463, 3355, 2189, 1655, 1588, 1523, 1408, 1346, 808. ¹H NMR (400 MHz, acetone) / δ (ppm) = 8.13 (brs, 1H), 8.08 (d, *J* = 8 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.93 (m, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 8, 1H), 7.46 (m, 2H), 7.38 (d, *J* = 9.2, 1H), 6.42 (s, 2H, NH₂), 5.6 (s, 1H).

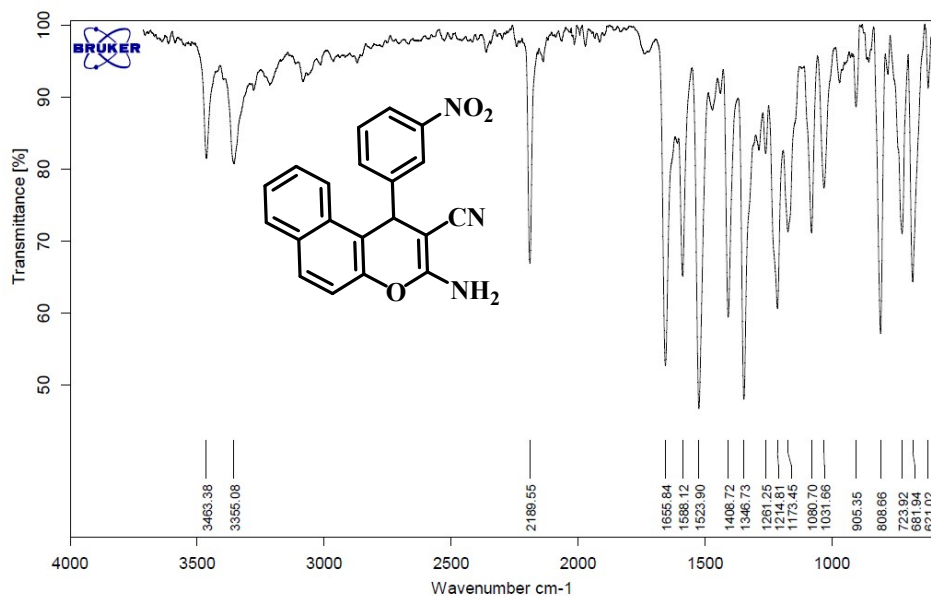


Figure S8: IR (ATR) spectrum of 2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

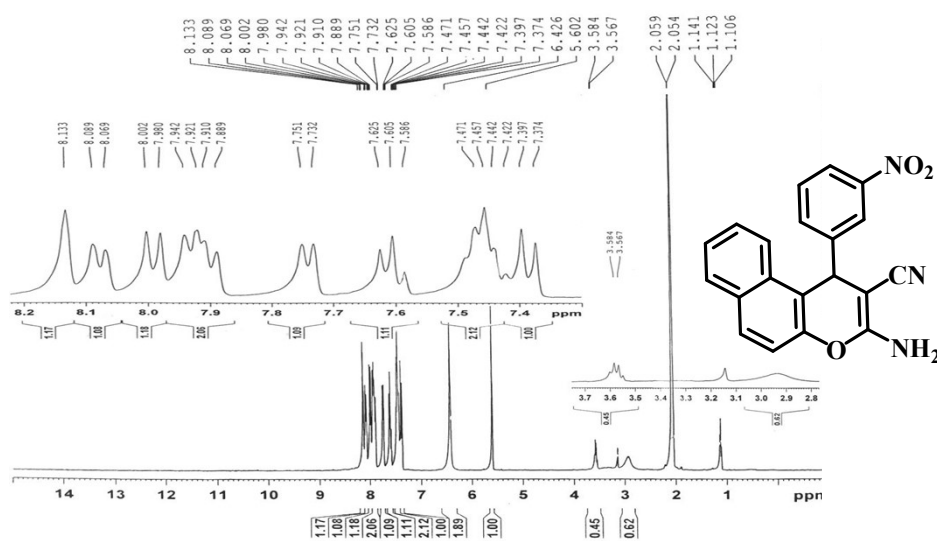


Figure S9: ¹H NMR spectrum of 2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5f)

Brown Solid, M.p. 220-222 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3458, 3322, 3189, 2199, 1658, 1583,

1404, 1261, 844, 739, 622 . ¹H NMR (400 MHz, CDCl₃) / δ (ppm) = 7.83 (m, 2H), 7.60 (d, *J* =

7.2, 1H), 7.44 (m, 3H), 7.25 (m, 1H), 7.04 (d, *J* = 8.4, 1H), 6.83 (d, *J* = 8.4, 1H), 5.84 (s, 1H),

4.65 (s, 2H, NH₂).

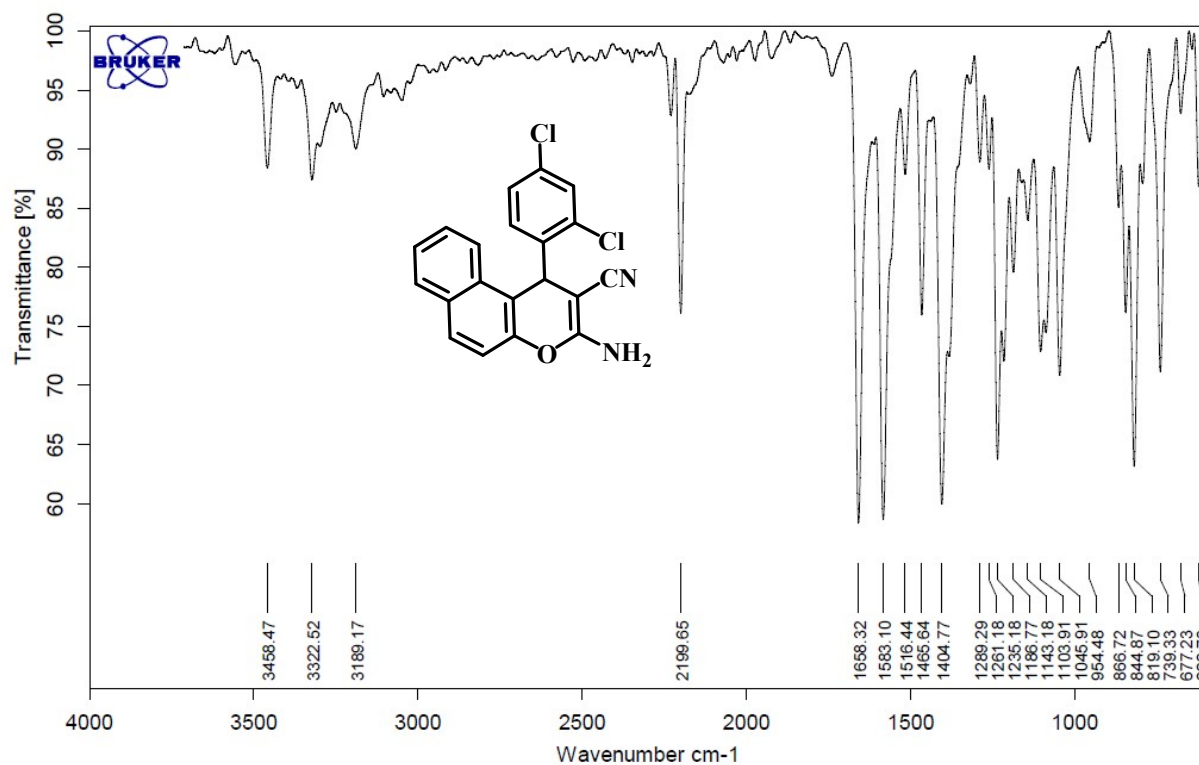


Figure S12: IR (ATR) spectrum of 2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

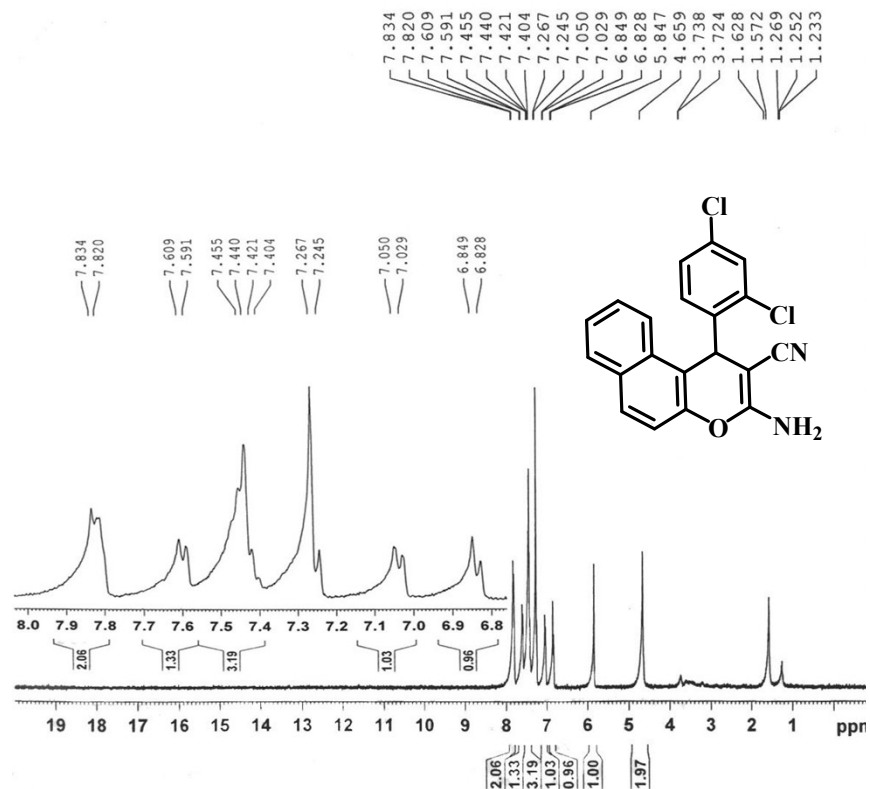


Figure S13: ^1H NMR spectrum of 2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(2,6-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5g)

Cream Solid, M.p. 220-222 °C, FT-IR (ATR) $\bar{\nu}$ (cm^{-1}): 3495, 3426, 3343, 2158, 1682, 1627, 1576, 1448, 1254. ^1H NMR (400 MHz, DMSO-d_6)/ δ (ppm) = 8.23 (m, 1H), 7.78 (br s, 1 H), 7.65-7.57 (m, 4 H), 7.38-7.30 (m, 2 H), 7.25 (br s, 2 H, NH_2), 6.84 (br s, 1 H), 5.95 (s, 1 H).

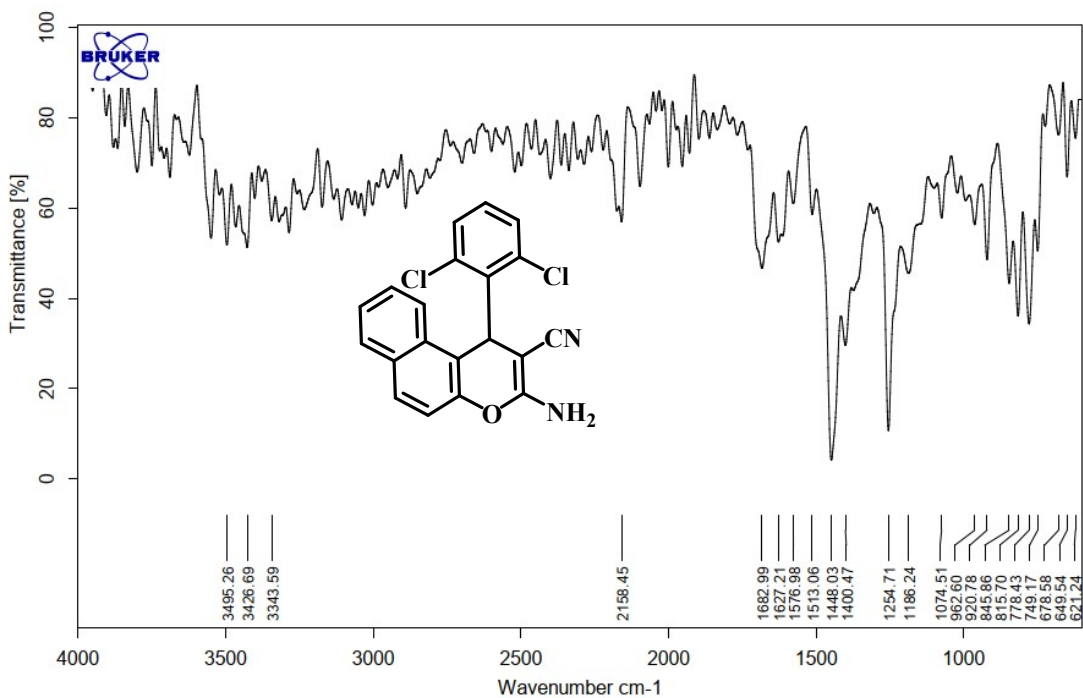


Figure S14: IR (ATR) spectrum of 2-Amino-4-(2,6-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

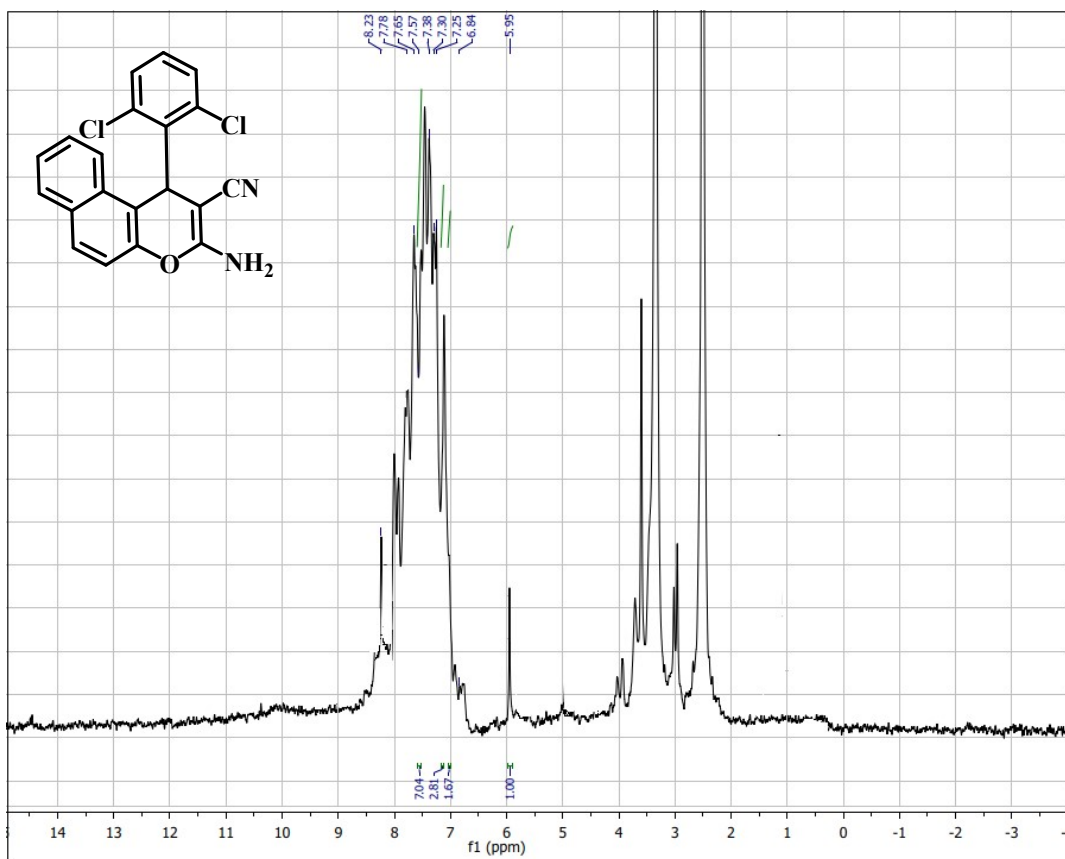


Figure S15: ^1H NMR spectrum of 2-Amino-4-(2,6-dichlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(2-chlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5h)

Brown Solid, M.p. 270-271 °C, FT-IR (ATR) $\bar{\nu}$ (cm^{-1}): 3457, 3347, 2176, 1654, 1589, 1409, 1219, 799. ^1H NMR (400 MHz, CDCl_3) δ ppm: 7.82 (m, 2H), 7.67 (d, $J = 8$ Hz, 1H), 7.45 (m, 3H), 7.25 (m, 1H), 7.11 (m, 2H), 6.91 (d, $J = 7.2$ Hz, 1H), 5.90 (s, 1H), 4.62 (s, 2H, NH_2).

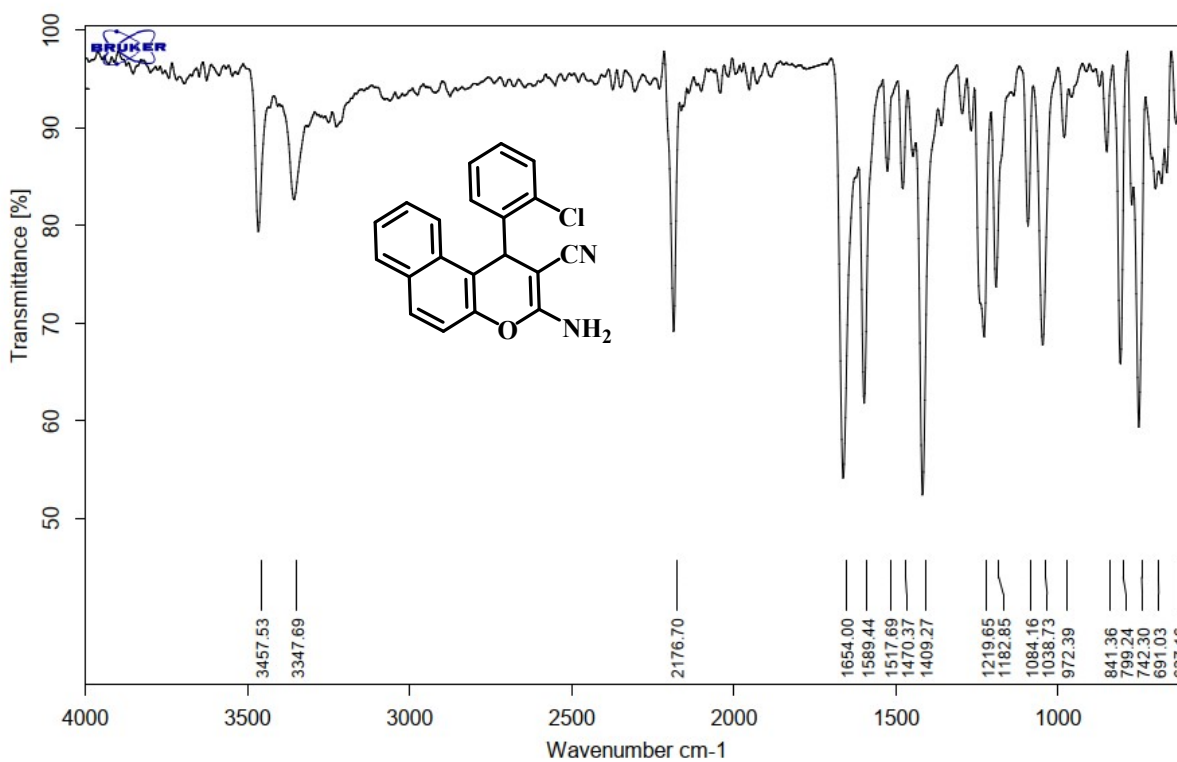


Figure S16: IR (ATR) spectrum of 2-Amino-4-(2-chlorophenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

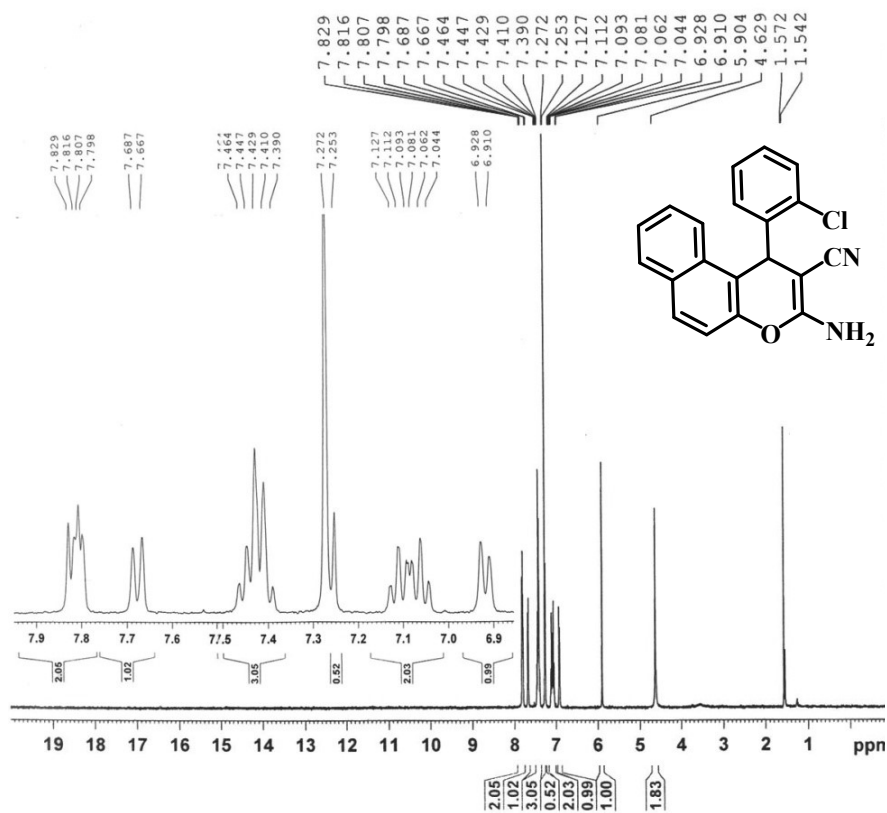


Figure S17: ¹H NMR spectrum of 2-Amino-4-(2-chlorophenyl)-4H-benzo[f]chromen-3-carbonitrile

2-Amino-4-(4-methyl Benzoate)-4H-benzo[f]chromen-3-carbonitrile (5i)

Light brown Solid, M.p. = 230-232 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3384, 3317, 3195, 2194, 1708, 1649, 1589, 1286, 816. ¹H NMR (400 MHz, CDCl₃) / δ (ppm) = 7.95 (d, *J* = 8.4 Hz, 2H), 7.84 (m, 2H), 7.61 (m, 1H), 7.41 (m, 2H), 7.27 (t, *J* = 2.8 Hz, 3H), 5.31 (s, 1H), 4.65 (s, 2H, NH₂), 3.87 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆) / δ ppm: 166.51, 165.84, 151.48, 147.48, 135.68, 131.43, 131.14, 130.69, 130.51, 130.38, 129.13, 128.64, 128, 127.80, 125.62, 124.09, 120.84, 117.43, 115.47, 57.71, 52.62, 38.58.

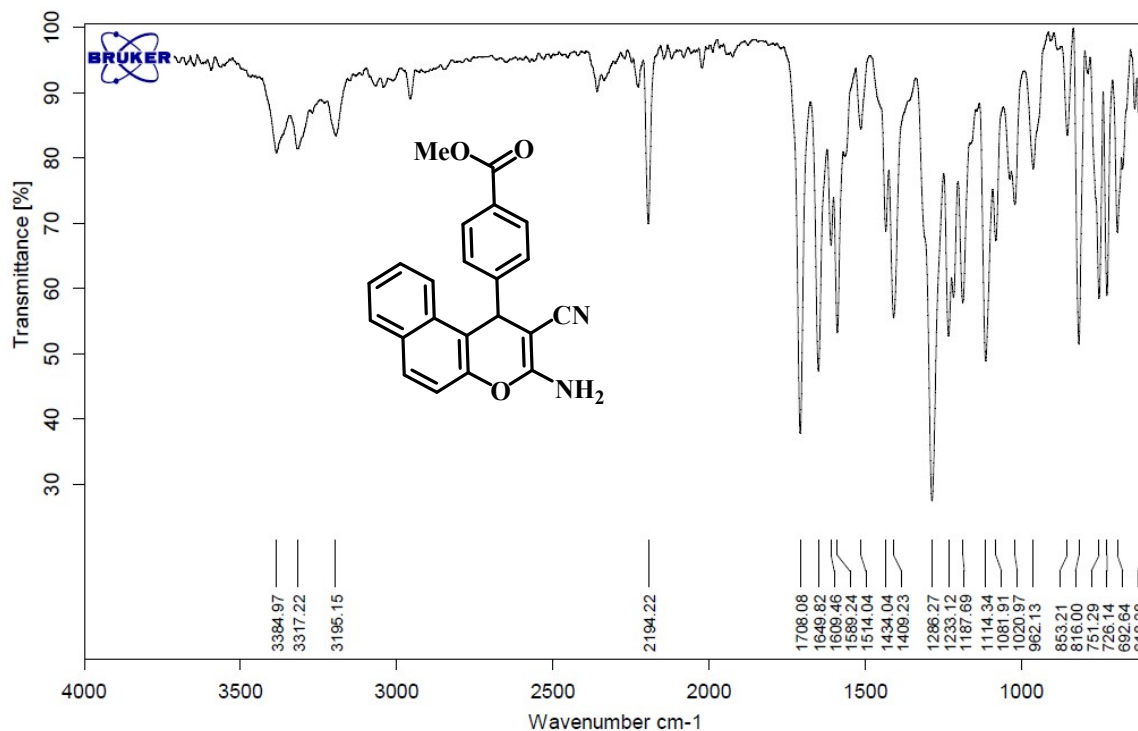


Figure S18: IR (ATR) spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*f*]chromen-3-carbonitrile

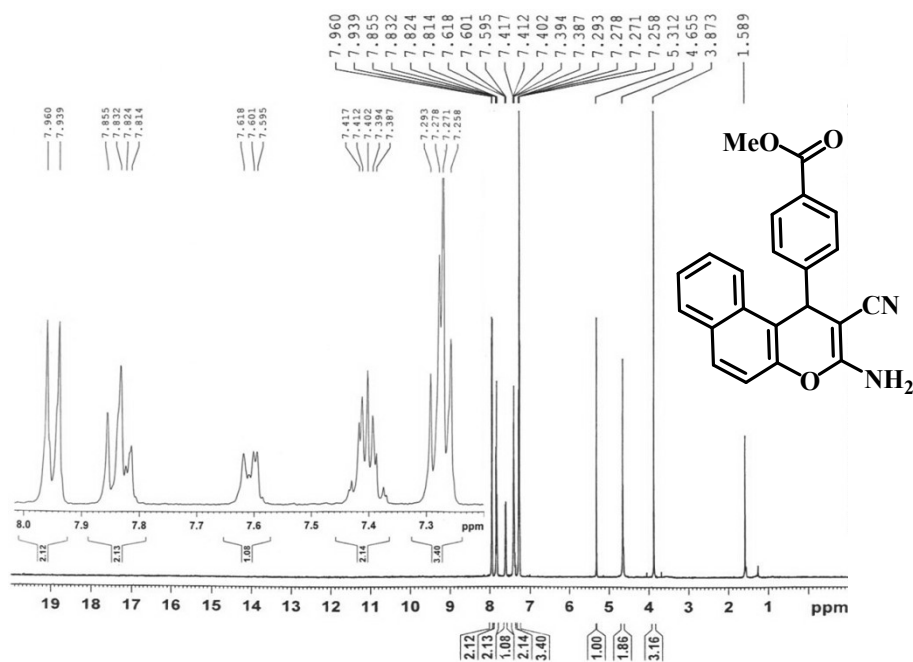


Figure S19: ¹H NMR spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*f*]chromen-3-carbonitrile

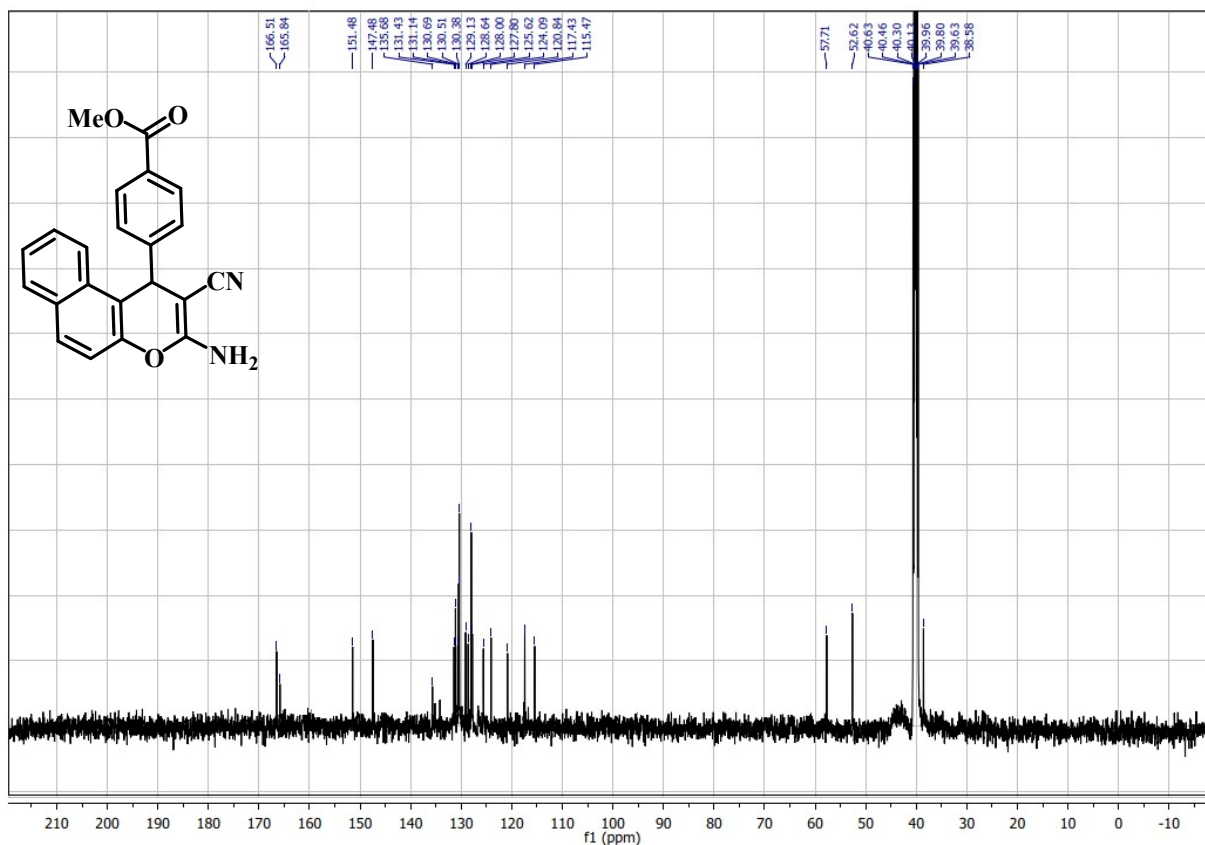


Figure S20: ¹³C NMR spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(2,4-dimethoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5j)

Yellow Solid, M.p. = 151-152 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3340, 2939, 2190, 1652, 1628, 1587, 1504, 1456, 1326, 1231, 1120, 813, 746. ¹H NMR (400 MHz, DMSO-*d*₆) / δ ppm: 7.88-7.78 (m, 3H), 7.34-7.43 (m, 2H), 7.09 (m, 1H), 6.94 (s, 2H), 6.85-6.73(m, 3H), 5.44 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H).

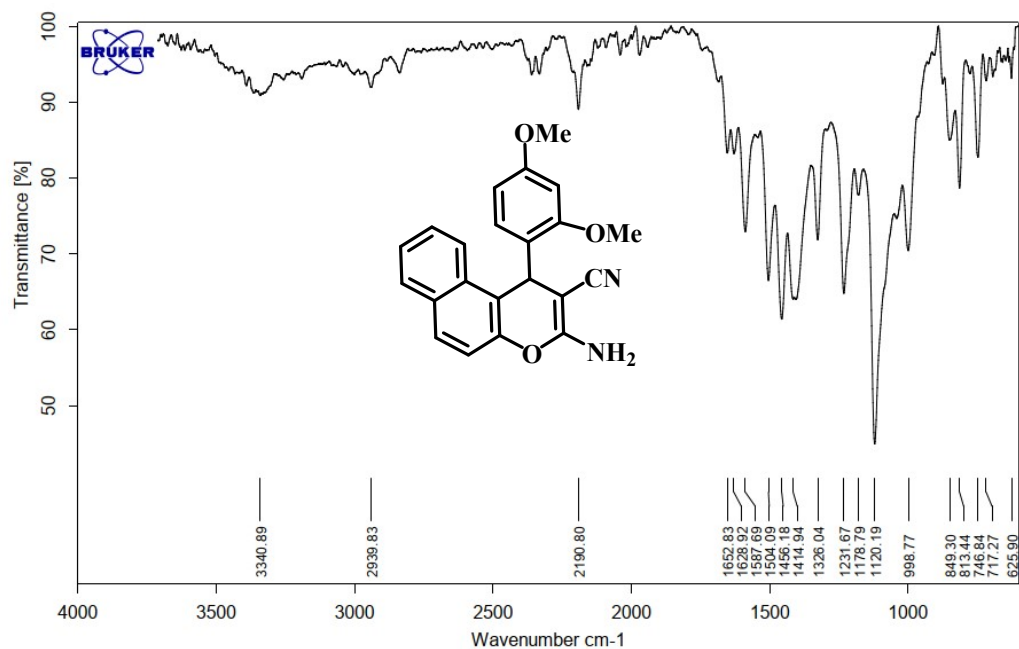


Figure S21: IR (ATR) spectrum of 2-Amino-4-(2,4-dimethoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

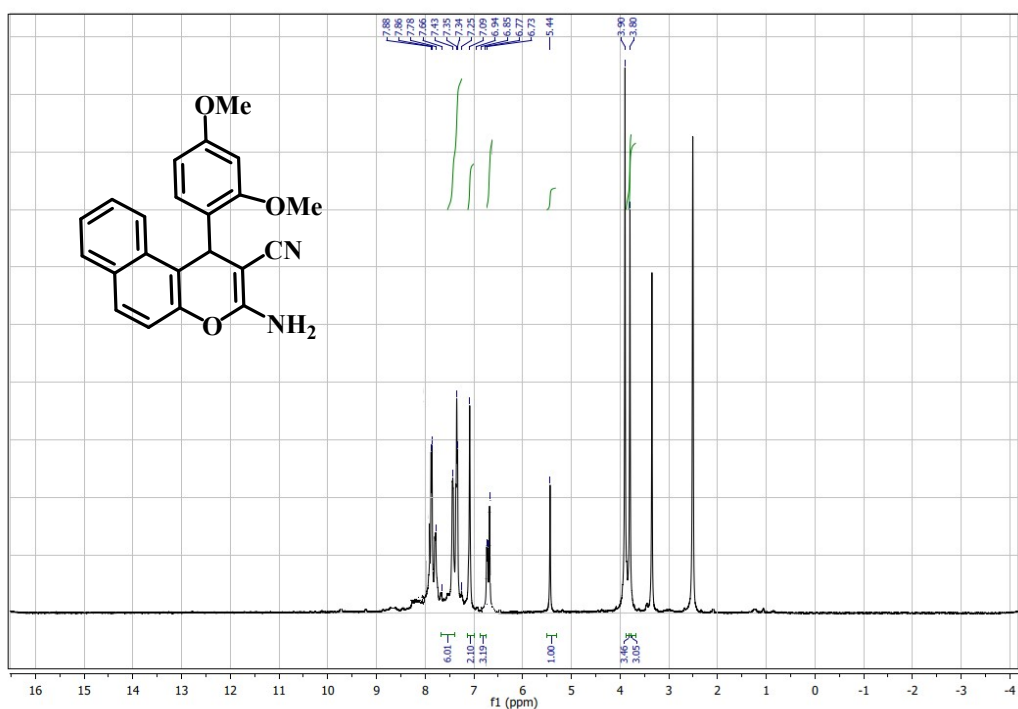


Figure S22: ^1H NMR spectrum of 2-Amino-4-(2,4-dimethoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(3,4-dimethoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5k)

Yellow Solid, M.p. = 190-192 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3425, 3332, 2183, 1646, 1590, 1508, 1453, 1403, 1338, 1257, 1180, 806, 753. ¹H NMR (400 MHz, CDCl₃), δ (ppm) = 7.81 (d, *J* = 8.4, 2H), 7.70 (m, 1H), 7.42 (m, 2H), 7.25 (d, *J* = 9.6 Hz, 1H), 6.74 (d, *J* = 6.8, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 1H), 4.60 (s, 2H, NH₂), 3.80 (d, *J* = 1.6, 6H).

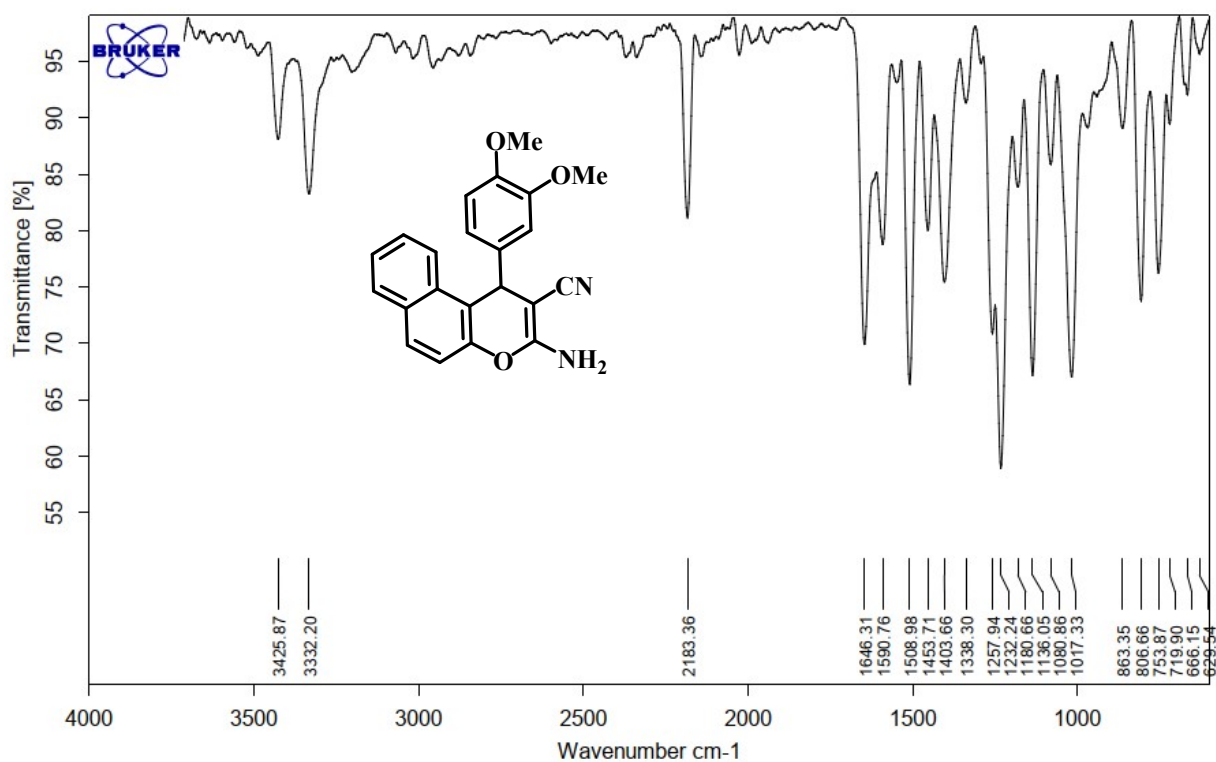


Figure S23: IR (ATR) spectrum of 2-Amino-4-(3,4-dimethoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

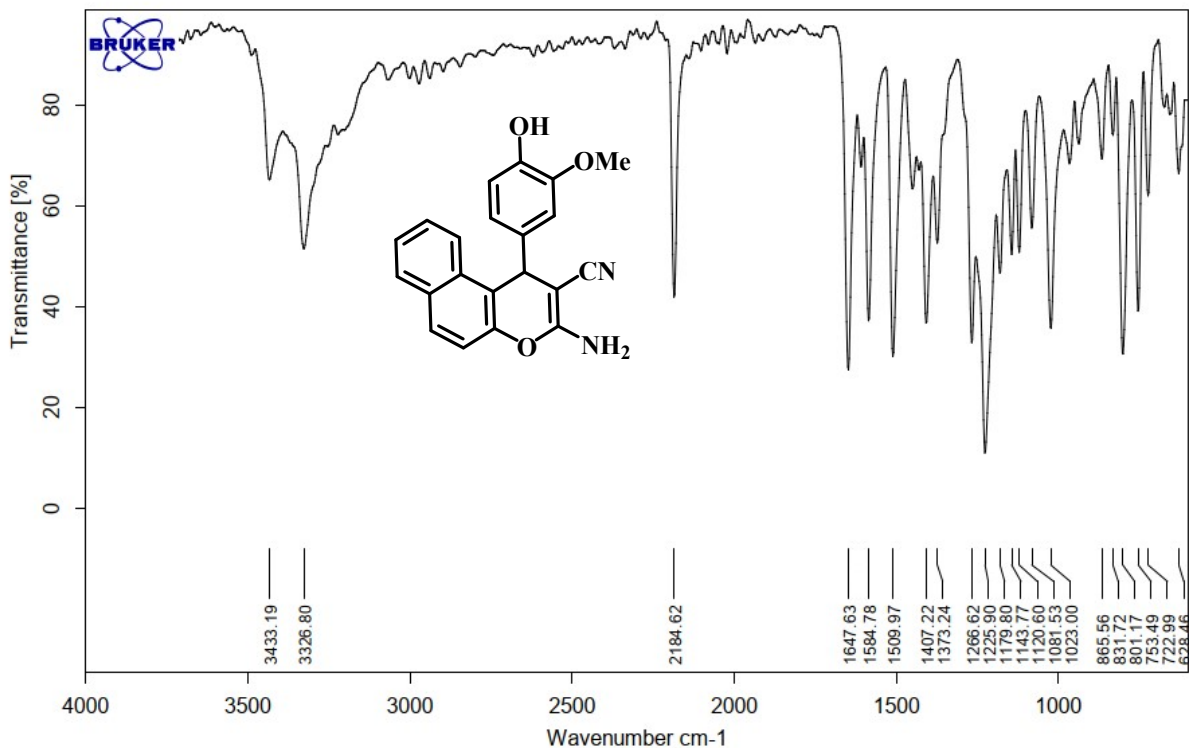


Figure S25: IR (ATR) spectrum of 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

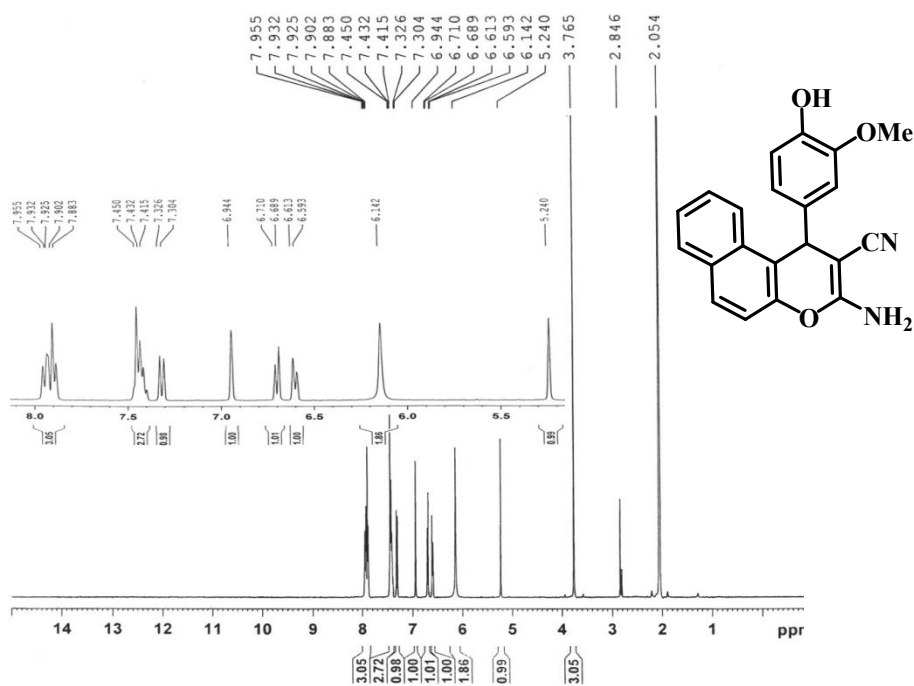


Figure S26: ^1H NMR spectrum of 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile

2-Amino-4-(4-isopropylphenyl) 4*H*-benzo[*f*]chromene-3-carbonitrile (5m)

Brown Solid, M.p. = 217-219 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3424, 3335, 3199, 2959, 2191, 1646, 1589, 1411, 1233, 811. ¹H NMR (400 MHz, CDCl₃) / δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (m, 1H), 7.41 (m, 2H), 7.26 (m, 1H), 7.10 (s br, 4H), 5.23 (s, 1H), 4.55 (s, 2H, NH₂), 2.83 (sept. *J* = 7.2 Hz, 1H), 1.18 (d, *J* = 7 Hz, 6H).

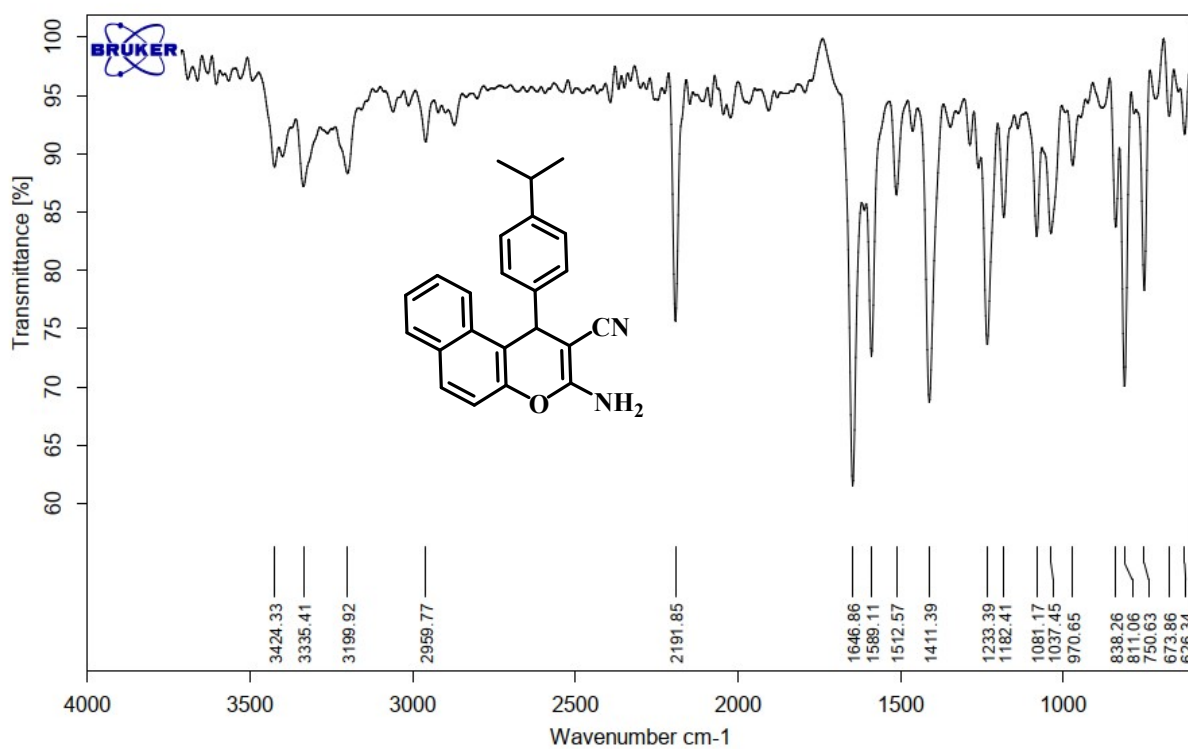


Figure S27: IR (ATR) spectrum of 2-Amino-4-(4-isopropylphenyl) 4*H*-benzo[*f*]chromene-3-carbonitrile

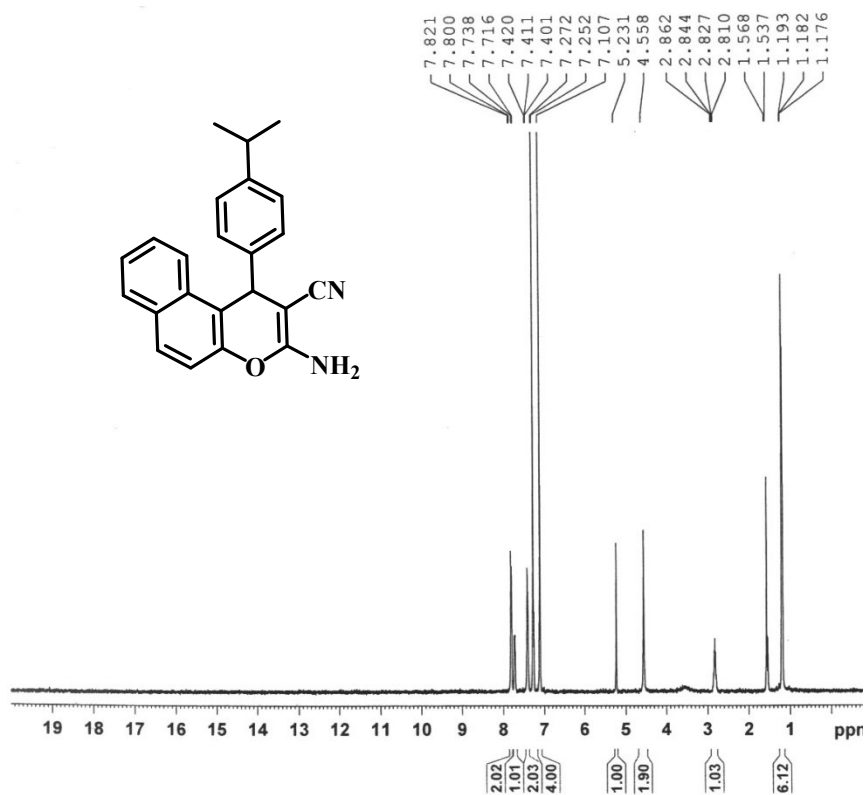


Figure S28: ^1H NMR spectrum of 2-Amino-4-(4-isopropylphenyl) 4*H*-benzo[*f*]chromene-3-carbonitrile

2-Amino-4-(4-phenylphenyl)-4*H*-benzo[*f*]chromen-3-carbonitrile (5n)

Brown Solid, M.p. = 210-212 °C, FT-IR (ATR) $\bar{\nu}$ (cm^{-1}): 3392, 3346, 3026, 2962, 2222, 1657, 1598, 1561, 1481, 1304, 694. ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.31 (m, 9H), 7.12 (d, J = 6.8 Hz, 1H), 7.04 (d, J = 8 Hz 1H), 5.06 (s, 1H), 3.8 (s, 2H, NH_2), 3.05 (t, J = 7.6 Hz, 2H), 2.7 (t, J = 8 Hz, 2H).

4, 4'-(1,4-phenylene) bis (2-Amino-4*H*-benzo[*f*]chromene-3-carbonitrile) (5o)

Brown Solid, M.p. = 172-174 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3336, 3181, 3043, 2190, 1650, 1586,

1402, 1217, 1079, 814, 746. ¹H NMR (400 MHz, DMSO-d₆) / δ ppm: 7.93-6.91(m, 16H), 5.21 (s, 2H).

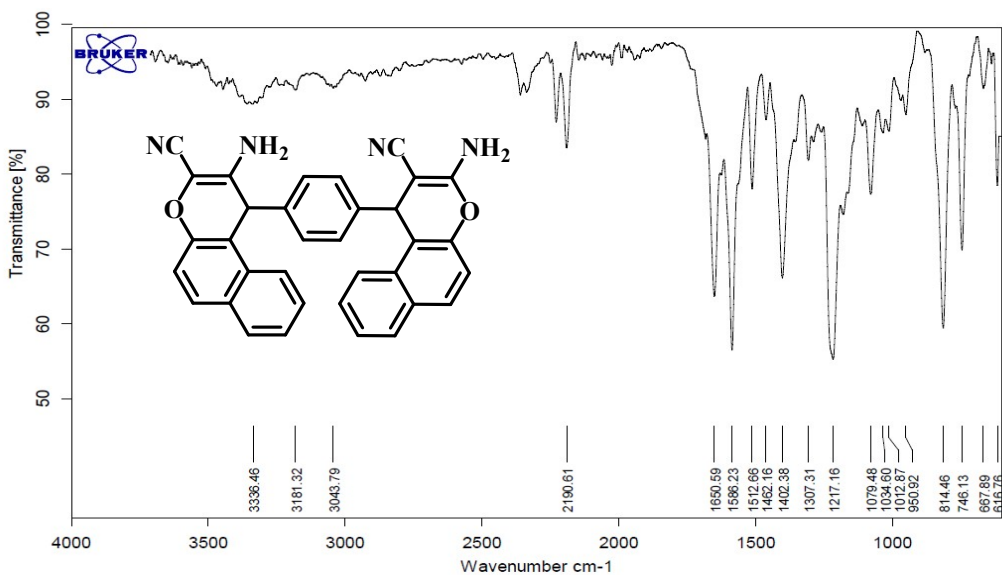
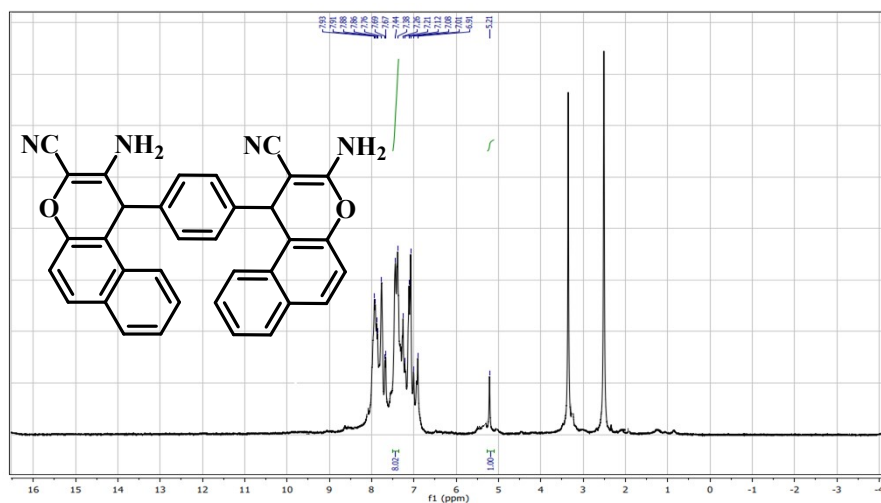


Figure S31: IR (ATR) spectrum of 4, 4'-(1,4-phenylene) bis (2-Amino-4*H*-benzo[*f*]chromene-3-carbonitrile)



2-Amino-1*H*-benzo[*f*]chromene-3-carbonitrile (**5p**)

Brown Solid, M.p. = 110-112 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3263, 2193, 1628, 1598, 1508, 1462, 1405, 1242, 1212, 1170, 1015, 956, 845, 741. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 9.72, 7.34 (s, 2H, NH₂), 7.73-7.63 (m, 3H), 7.22 (d, *J* = 5, 1H), 7.14-7.05 (m, 2H), 3.57 (s, 2H, CH₂), ¹³C NMR (125 MHz, DMSO-d₆) / δ ppm: 155.29, 134.60, 129.30, 127.72, 127.54, 126.12, 125.99, 122.64, 118.62, 116.44, 108.64, 58.41.

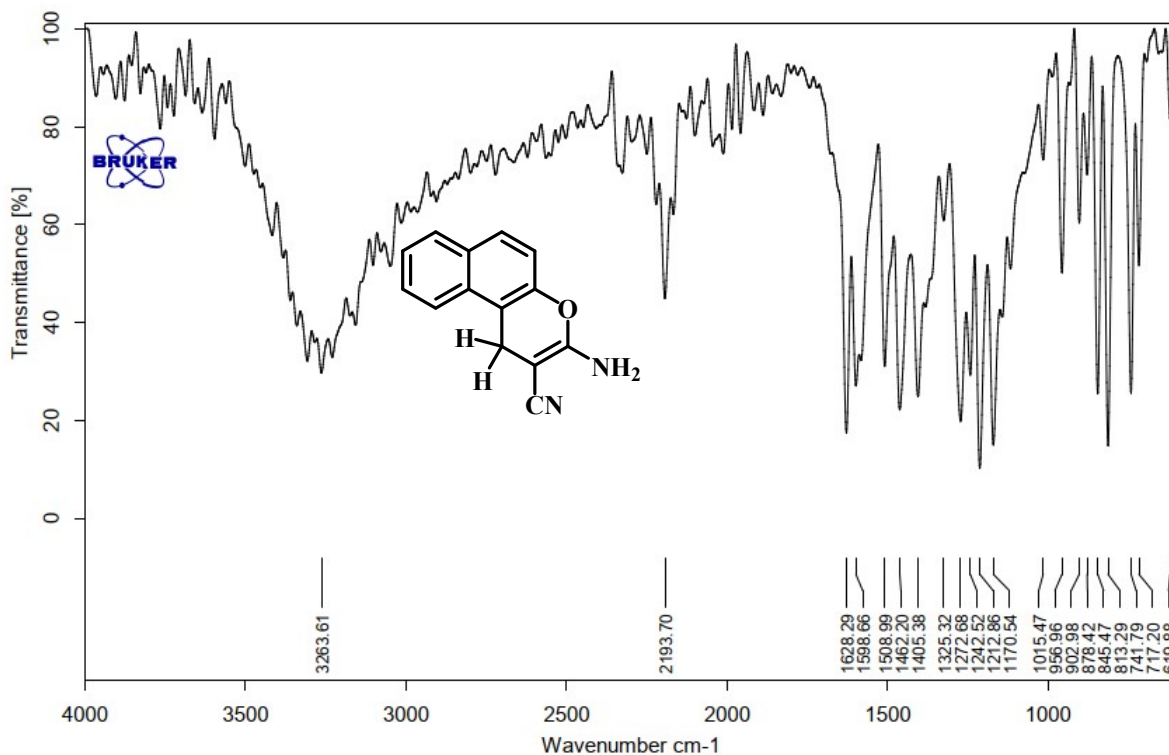


Figure S33: IR (ATR) spectrum of 2-Amino-1*H*-benzo[*f*]chromene-3-carbonitrile

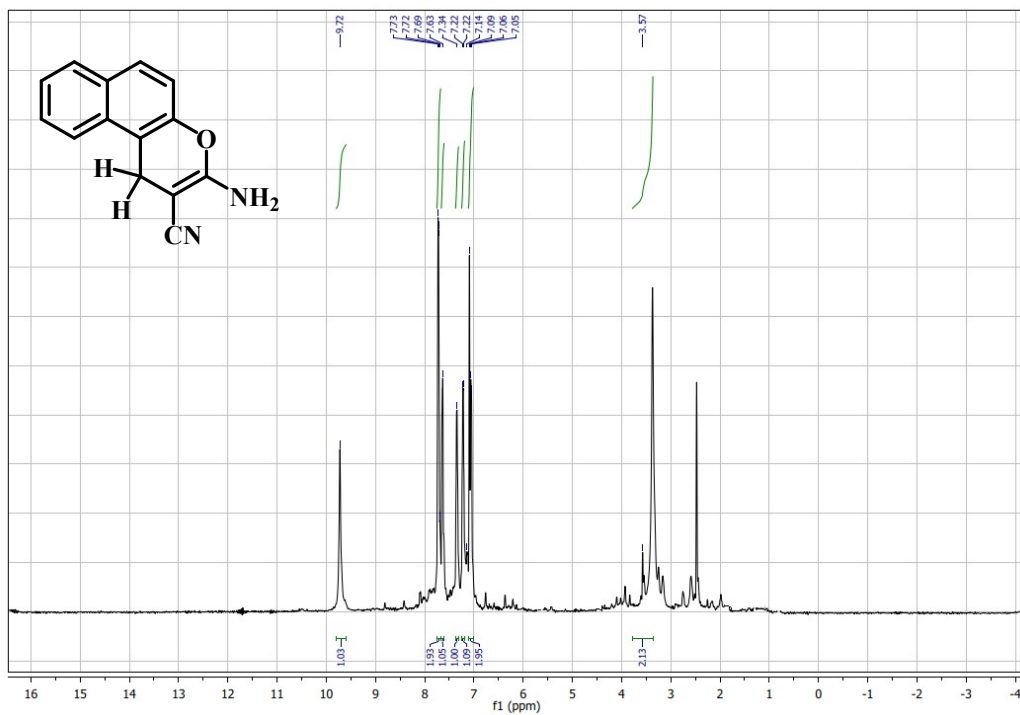


Figure S34: ¹H NMR spectrum of 2-Amino-1*H*-benzo[*f*]chromene-3-carbonitrile

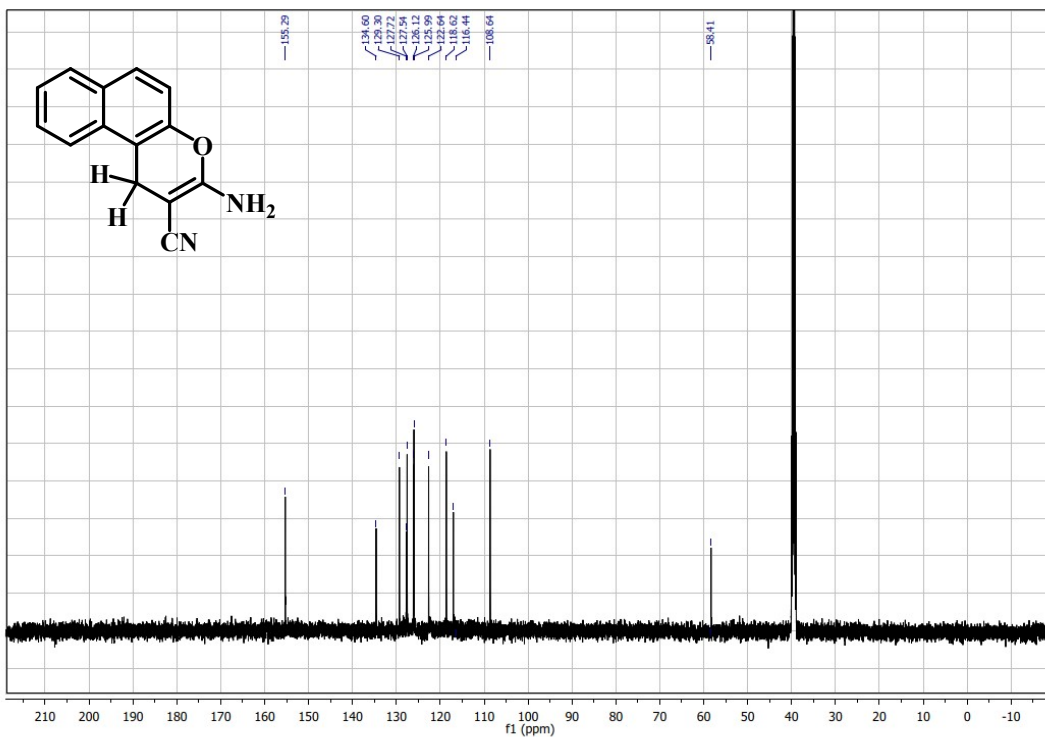


Figure S35: ¹³C NMR spectrum of 2-Amino-1*H*-benzo[*f*]chromene-3-carbonitrile

2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (6a)

Brown Solid, M.p. = 214-215 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3413, 3388, 3318, 3198, 3060, 2190, 1657, 1578, 1467, 1375, 1102, 811, 763. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 8.23 (d, *J* = 5, 1H), 7.98-7.77(m, 1H), 7.60-7.54 (m, 4H), 7.31(m, 2H), 7.27 (s, 2H, NH₂), 6.93 (d, *J* = 5, 1H), 5.36 (s, 1H).

¹³C NMR (125 MHz, DMSO-d₆) / δ ppm: 160.41, 156.51, 143.08, 141.28, 135.47, 132.59, 132.51, 130.02, 129.16, 128.48, 128.29, 126.96, 126.78, 125.30, 124.17, 122.67, 120.05, 116.02, 54.52.

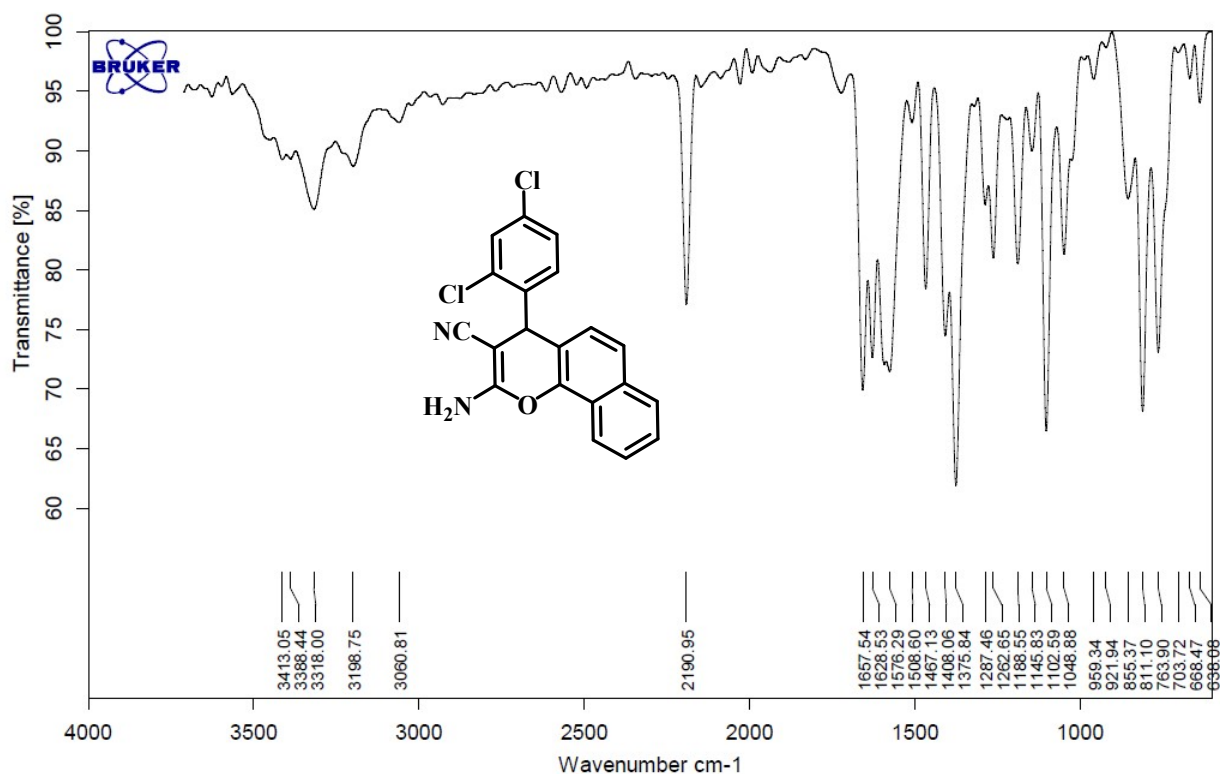


Figure S36: IR (ATR) spectrum of 2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile

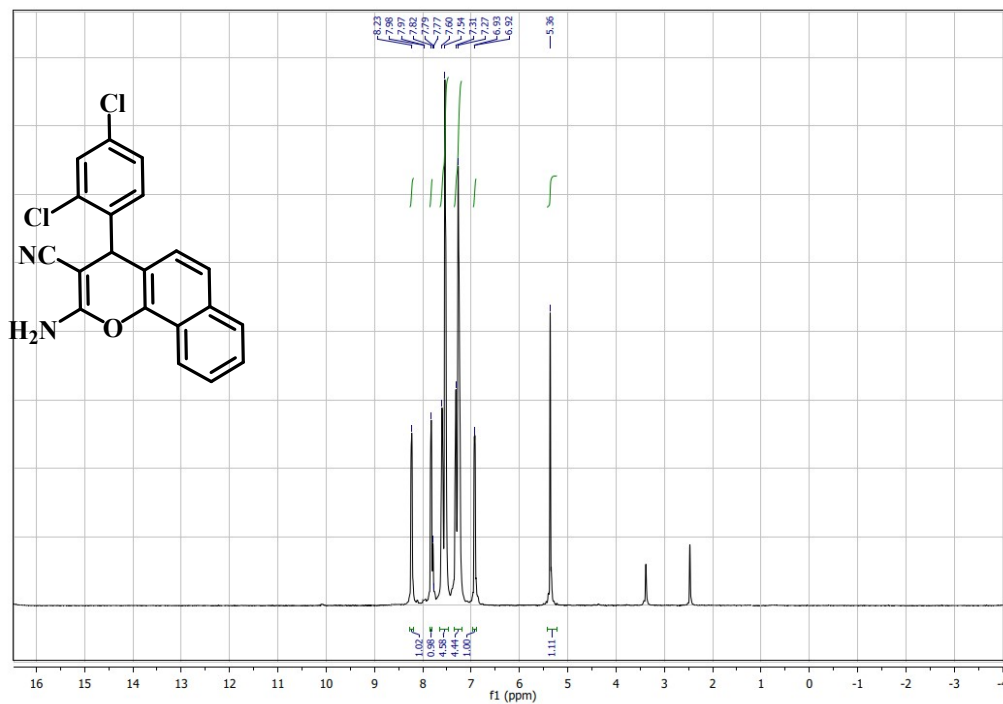


Figure S37: ¹H NMR spectrum of 2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile

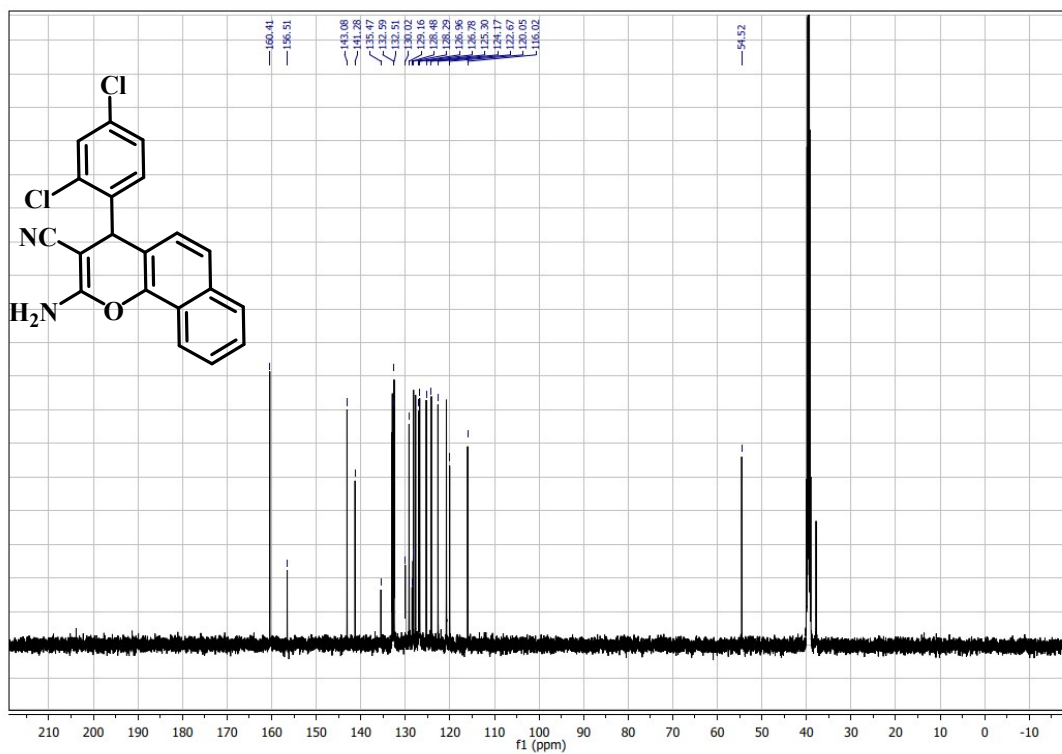


Figure S38: ¹³C NMR spectrum of 2-Amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile

2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*h*]chromen-3-carbonitrile (6b)

Dark brown Solid, M.p. = 259-260 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3393, 3334, 3208, 2195, 1710, 1665, 1573, 1103, 750. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 8.24 (d, *J* = 5, 1H), 7.89-7.83 (m, 3H), 7.61-7.54 (m, 3H), 7.38 (d, *J* = 9, 2H), 7.26 (s, 2H, NH₂), 7.06 (d, *J* = 9, 1H), 4.99 (s, 1H), 3.78 (s, 3H, OCH₃).

¹³C NMR (125 MHz, DMSO-d₆)/ δ ppm: 165.98, 160.27, 150.88, 142.88, 132.82, 129.76, 128.35, 128.13, 127.71, 126.91, 126.76, 126.04, 124.06, 122.78, 120.76, 120.35, 117.11, 55.65, 52.07.

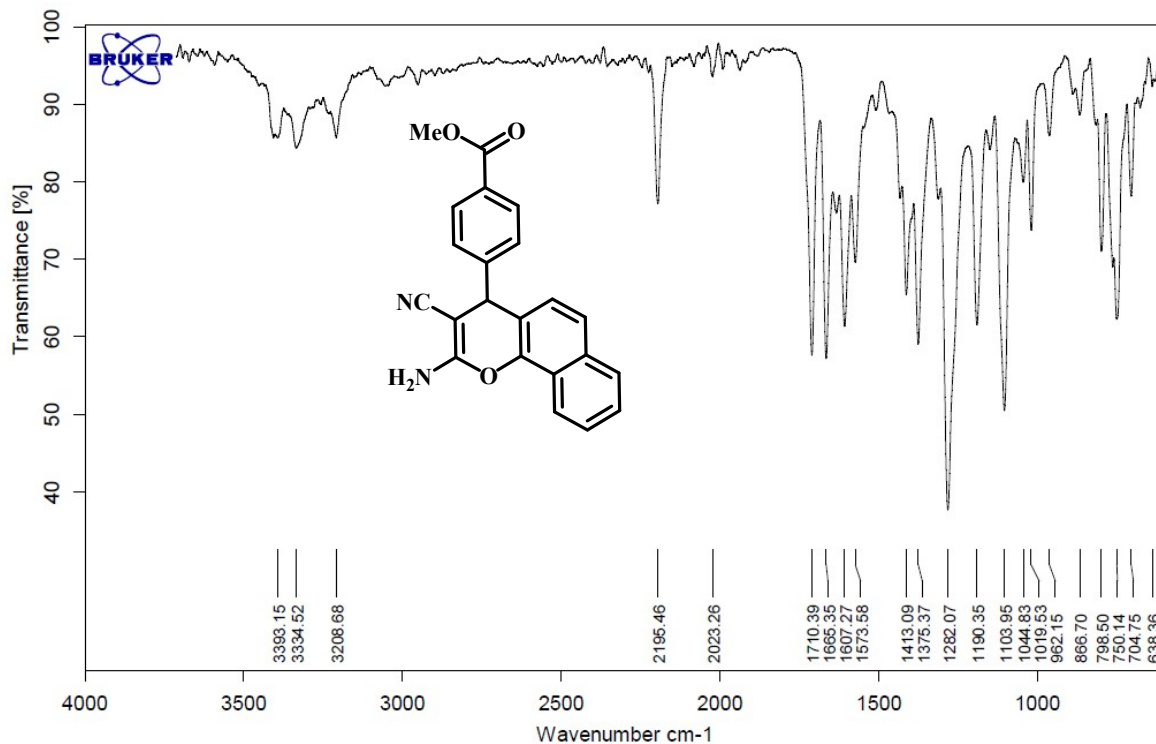


Figure S39: IR (ATR) spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*h*]chromen-3-carbonitrile

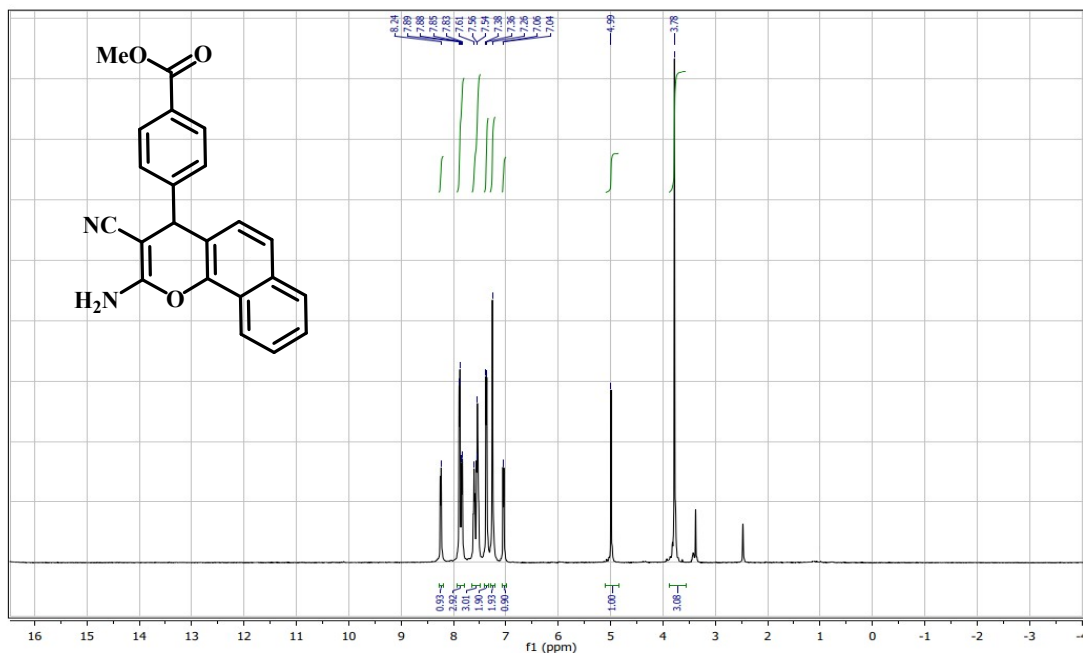


Figure S40: ¹H NMR spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*h*]chromen-3-carbonitrile

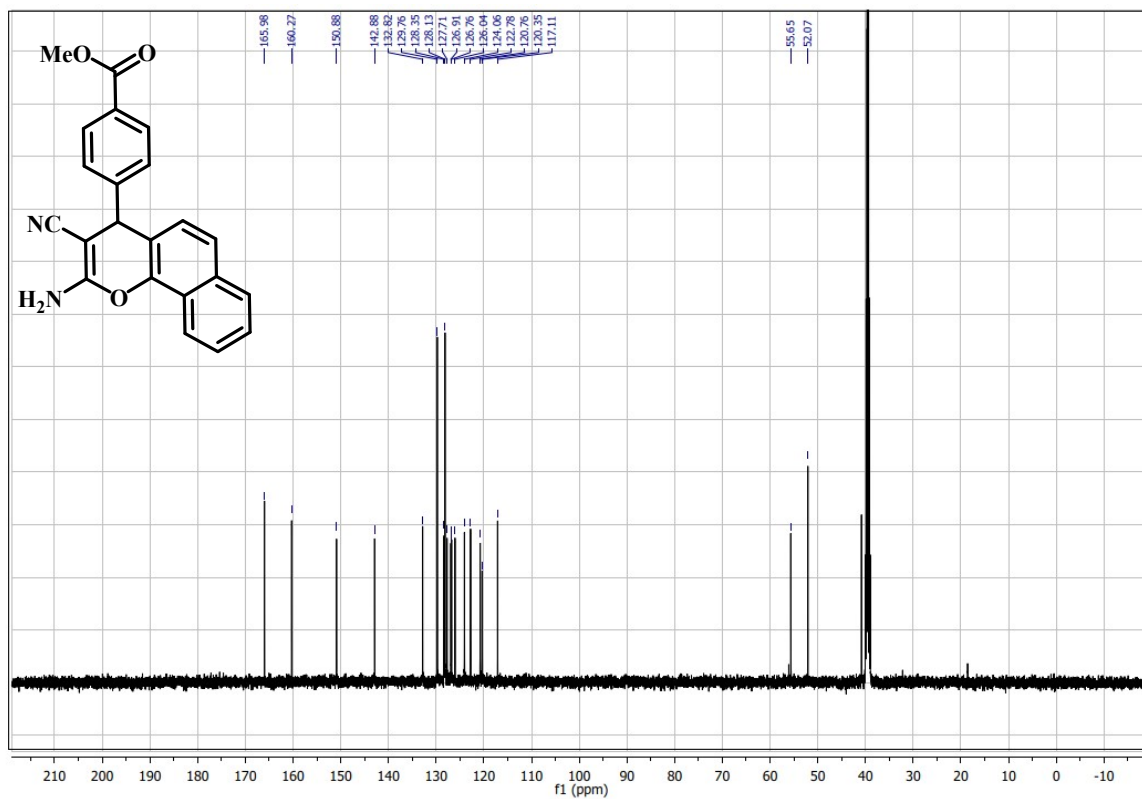


Figure S41: ¹³C NMR spectrum of 2-Amino-4-(4-methyl Benzoate)-4*H*-benzo[*h*]chromen-3-carbonitrile

2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*h*]chromen-3-carbonitrile (6c)

Orange Solid, M.p. 204-206 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3470, 3326, 2191, 1661, 1599, 1521, 1344, 1100, 805, 729. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 8.24 (d, *J* = 9, 1H), 8.11-8.07 (m, 2H), 7.85 (d, *J* = 9, 1H), 7.71-7.55 (m, 5H), 7.32 (s, 2H, NH₂), 7.12 (d, *J* = 5, 1H), 5.18(s, 1H). ¹³C NMR (125 MHz, DMSO-d₆)/ δ ppm: 160.45, 148, 147.87, 142.94, 134.61, 132.89, 130.48, 127.74, 127.04, 126.85, 125.95, 124.25, 122.76, 122.16, 122.07, 120.79, 120.27, 116.81, 55.37.

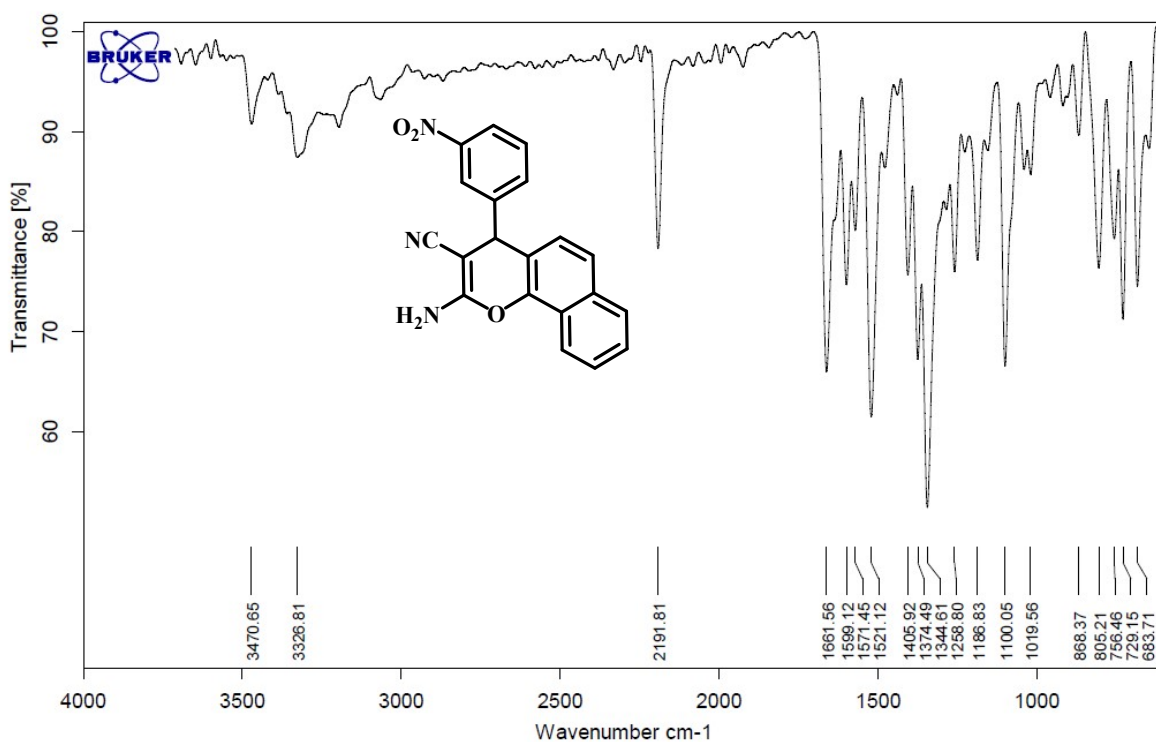


Figure S42: IR (ATR) spectrum of 2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*h*]chromen-3-carbonitrile

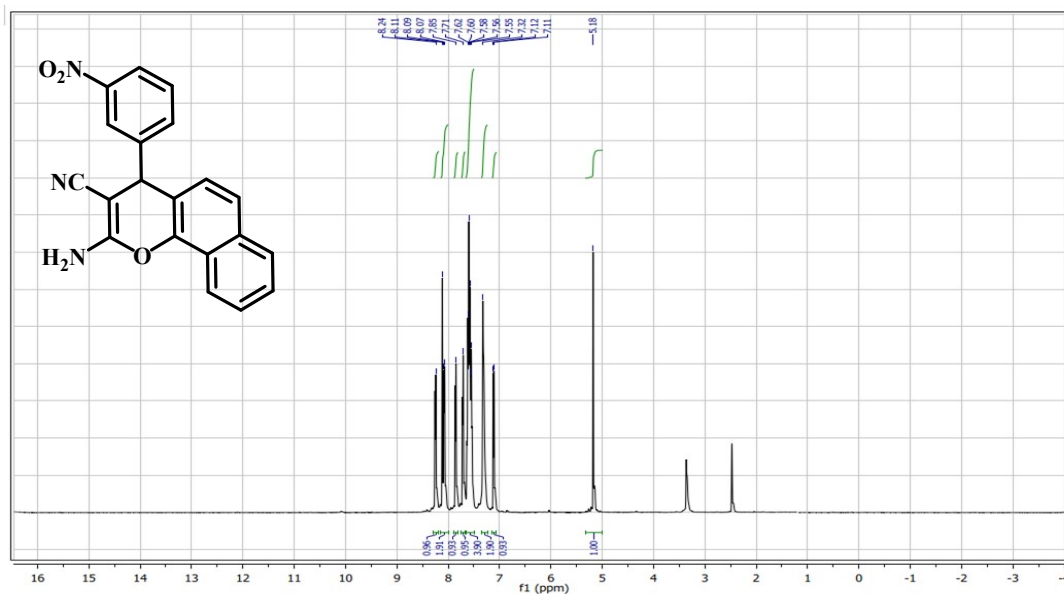


Figure S43: ¹H NMR spectrum of 2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*h*]chromen-3-carbonitrile

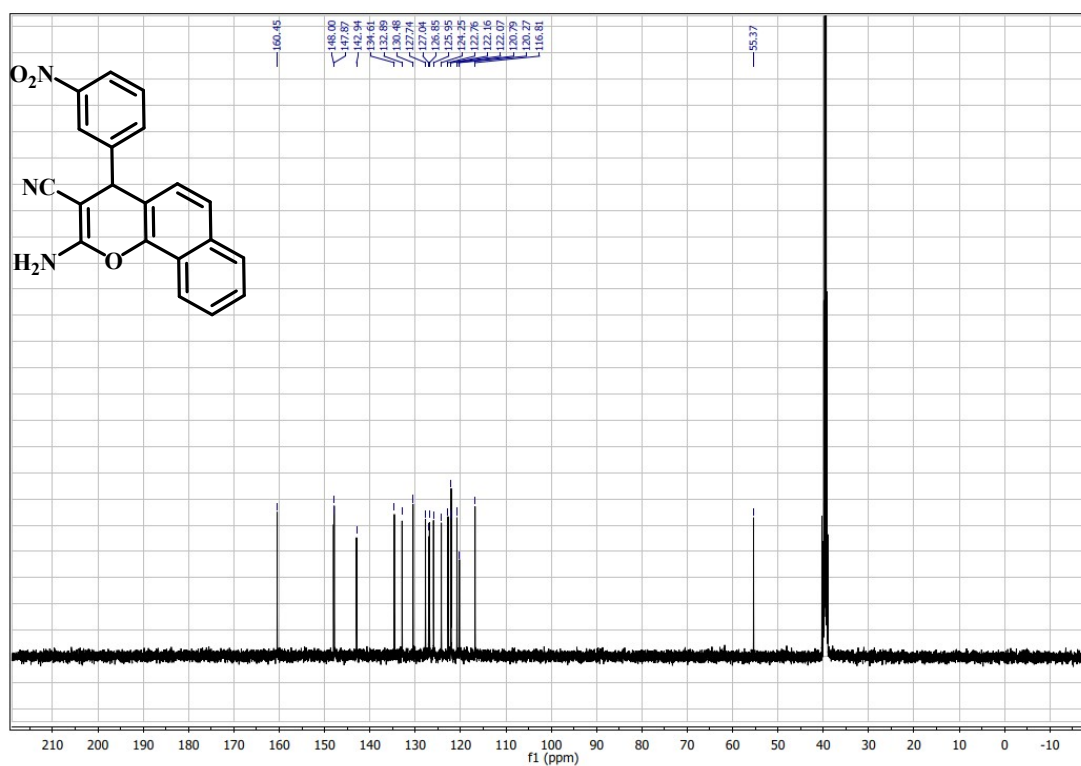


Figure S44: ¹³C NMR spectrum of 2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*h*]chromen-3-carbonitrile

2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4H-benzo[h]chromen-3-carbonitrile (6d)

Brown Solid, M.p. = 222-223 °C, FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3459, 3330, 3202, 2195, 1668, 1584, 1509, 1407, 1225, 1023, 753, 801. ¹H NMR (500 MHz, DMSO-d₆) / δ ppm: 8.89 (s, 1H, OH), 8.23 (d, *J* = 5, 1H), 7.83 (d, *J* = 5, 1H), 7.54 (m, 3H), 7.11(d, *J* = 5, 1H), 7.07(s, 2H, NH₂), 6.85 (s, 1H), 6.71-6.60 (m, 2H), 4.77 (s, 1H), 3.70 (s, 3H, OCH₃).

¹³C NMR (125 MHz, DMSO-d₆)/ δ ppm: 160.06, 147.56, 145.56, 142.50, 136.77, 132.63, 127.66, 126.65, 126.59, 126.34, 123.71, 122.79, 120.72, 120.15, 118.36, 115.71, 111.91, 56.63, 55.64, 30.97.

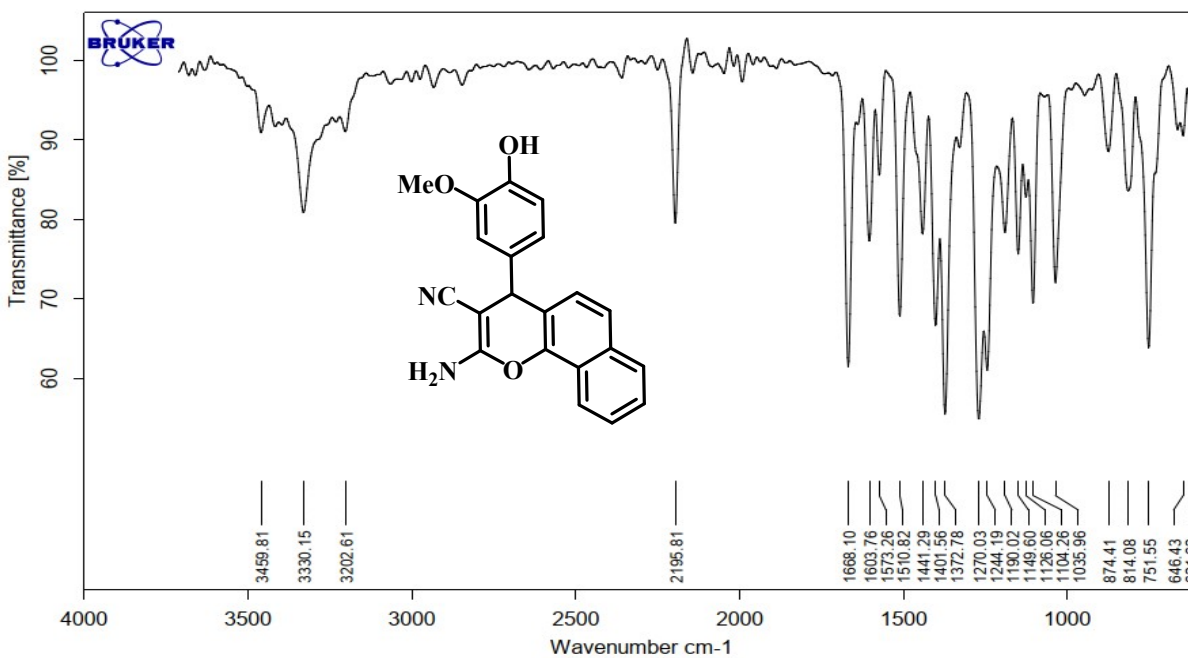


Figure S45: IR (ATR) spectrum of 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4H-benzo[h]chromen-3-carbonitrile

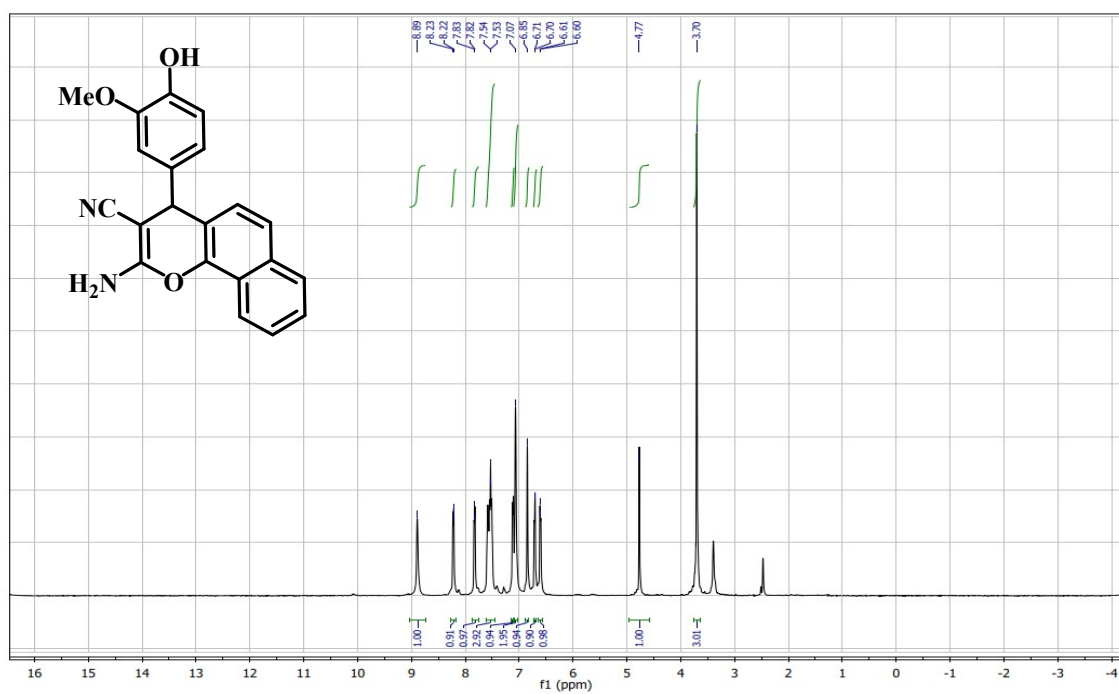


Figure S46: ¹H NMR spectrum of 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4H-

benzo[h]chromen-3-carbonitrile

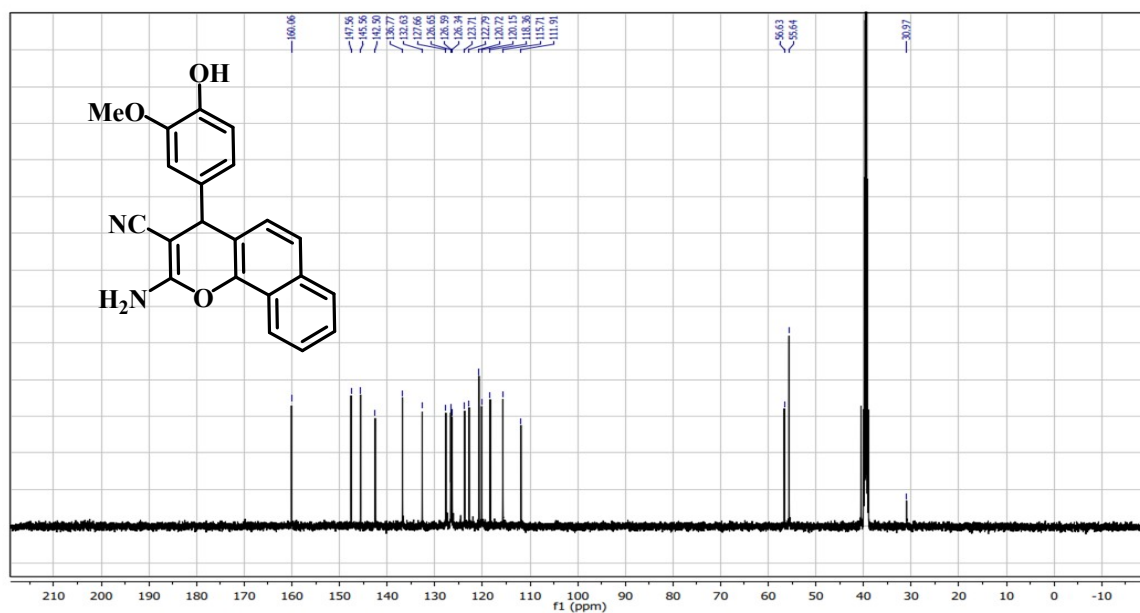


Figure S47: ¹³C NMR spectrum of 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-4H-

benzo[h]chromen-3-carbonitrile

2-(4-(dimethylamino)benzylidene)malononitrile

FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 2909, 2203, 1609, 1561, 1514, 1355, 1176, 938, 814. ¹H NMR (500 MHz, DMSO-d₆) δ ppm: 7.98 (s, 1H), 7.79 (d, *J* = 5, 2H), 6.81 (d, *J* = 9, 2H), 3.07 (s, 6H, NMe₂). ¹³C NMR (125 MHz, DMSO-d₆) δ ppm: 158.82, 154.30, 133.61, 118.76, 116.30, 115.54, 111.78, 68.63.

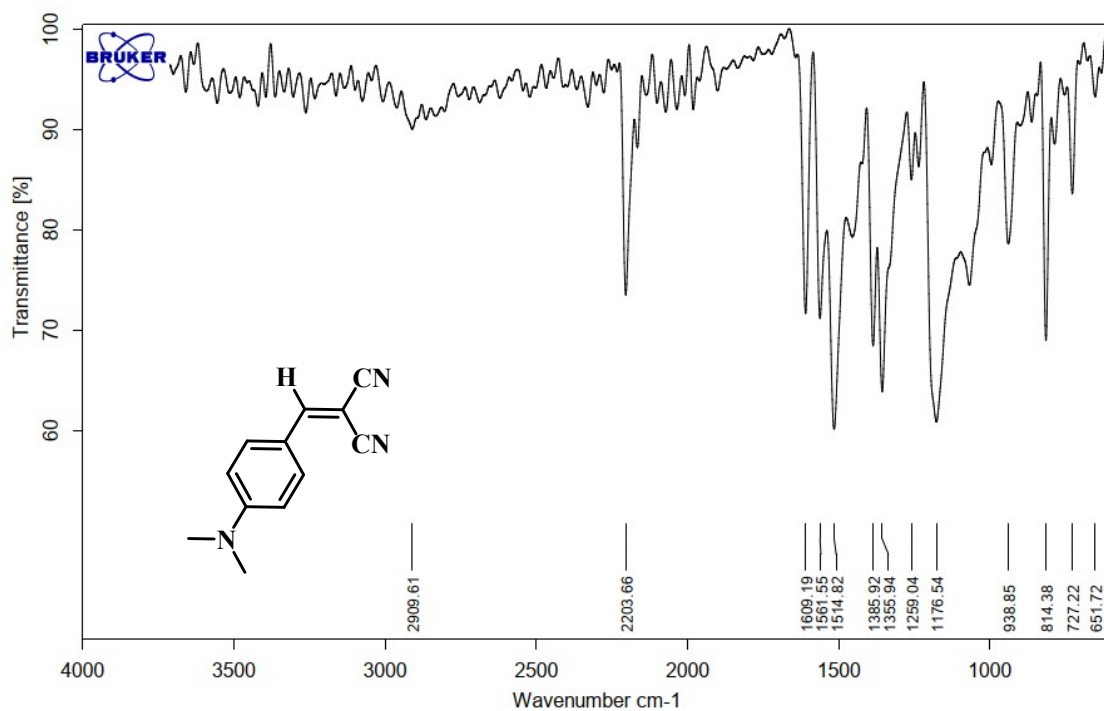


Figure S48: IR (ATR) spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile

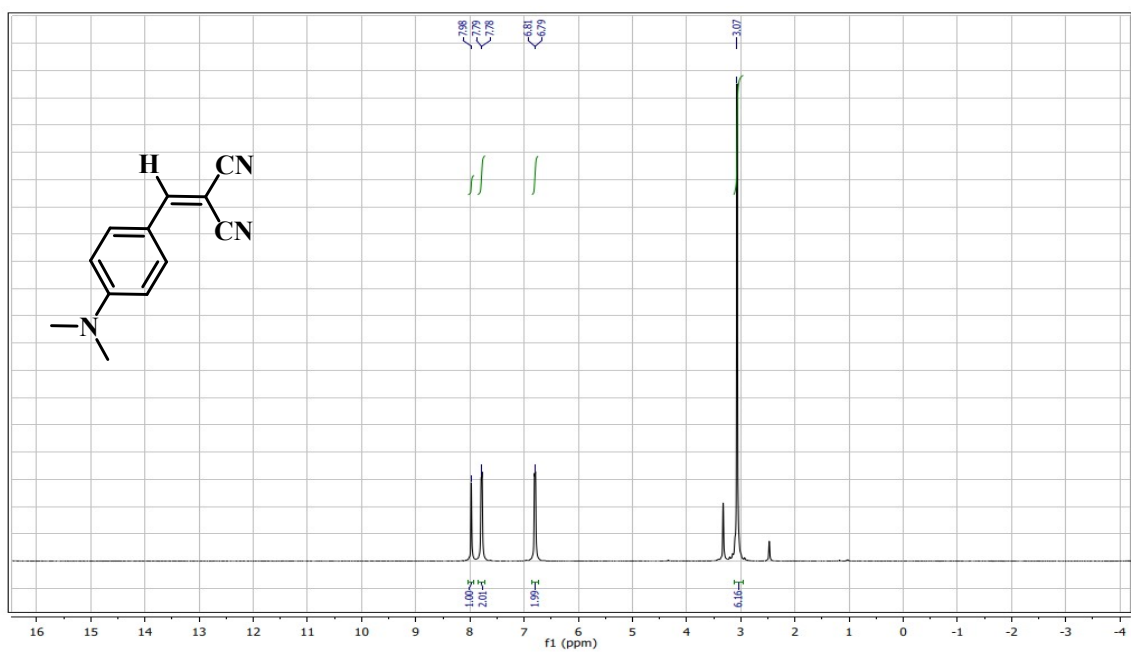


Figure S49: ¹³C NMR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile

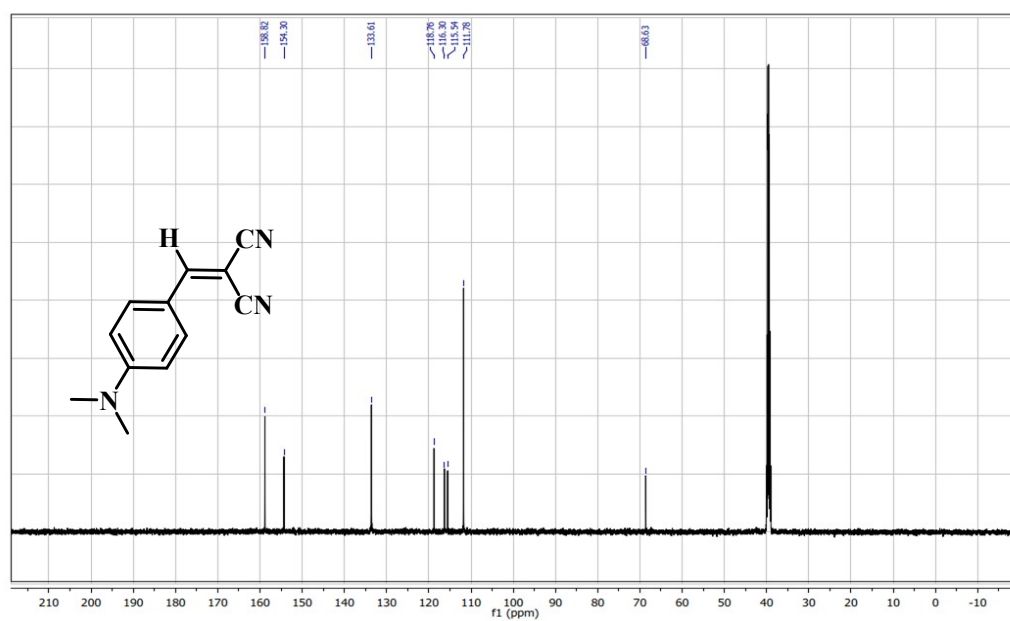


Figure S50: ¹³C NMR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile