Supporting Information

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Piperidine-functionalized Fe_3O_4 supported graphene quantum dots as an efficient catalyst for the synthesis of 2-aminochromenes under solvent-free conditions

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S1. Selected spectroscopic data of compounds 4a-4k

*3-Amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile (**4a**)*: White solid, yield, 98%, m p = 277-279 °C. FTIR (KBr, cm^{-1}): 3434 (N-H), 3343 (N-H), 3075 (-CH aromatic), 2184 (CN), 1641 (NH), 1591, 1000–1300, 814, 717. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.29 (s, 1 H, CH), 7.00 (s, 2 H, NH_2), 7.14–7.27(m, 5 H), 7.33–7.35 (d, 1 H, *J* = 8.92 Hz), 7.39-7.44 (m, 2 H), 7.82–7.84 (d, 1 H, *J* = 7.42 Hz), 7.89-7.94 (m, 2 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 38.09 (aliphatic carbon), 57.89 (-C-CN), 115.71 (CN), 116.84, 120.55, 123.66, 124.98, 126.65, 127.02, 127.12, 128.51, 128.75, 129.54, 130.18, 130.85, 145.75, 146.85, 159.73 (-C-NH_2).

*3-Amino-1-(2-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (**4b**)*: White solid, yield, 98%, m p = 266-267 °C. FTIR (KBr, cm^{-1}): 3455 (-NH), 3340 (-NH), 3196 (aromatic hydrogens), 2187(CN), 1654 (NH), 1592, 1521(NO_2), 1343 (NO_2), 1300–1000, 812, 727. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.08(s, 1 H, CH), 6.98 (s, 2 H, NH_2), 7.02 (d, 1 H, Ar, J = 7.64 Hz), 7.20–7.23 (m, 2 H, Ar), 7.28 (d, 1H, Ar, *J* = 7.86 Hz), 7.38 (d, 1 H, Ar, *J* = 7.47 Hz), 7.45-7.48 (m, 2 H, Ar), 7.57 (d, 1 H, Ar, *J* = 7.28 Hz), 7.80(d, 1 H, Ar, *J* = 7.58 Hz), 8.00 (d, 1 H, Ar, *J* = 8.46 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 35.24 (aliphatic carbon), 59.2 (-C-CN), 113.78 (CN), 117.08, 120.43, 121.02 121.58, 123.20, 124.67, 127.68, 128.12, 129.04, 129.78, 130.04, 130.32, 133.20, 146.58, 147.30, 147.98, 160.00 (-C-NH_2).

*3-Amino-1-(3-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (**4c**)*: White solid, yield, 90%, m p = 230-232 °C. FTIR (KBr, cm^{-1}): 3464 (NH), 3358 (NH), 3220 (aromatic hydrogens), 2190 (CN), 1656 (NH), 1590, 1529 (NO_2), 1410 1349, 1300–1000, 812; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.61(s, 1 H, CH), 7.16 (s, 2 H, NH_2), 7.37-7.39 (d, 1 H, Ar, *J*= 8.96 Hz), 7.41–7.47 (m, 2 H, Ar), 7.56 (t, 1 H, Ar, J = 7.76), 7.65 (d,1 H, Ar, *J* = 7.75 Hz), 7.84- 7.86 (d, 1 H, Ar, *J* = 7.9 Hz), 7.92 (d, 1 H, Ar), 7.97- 8 (d, 1 H, Ar, *J* = 9), 8.03-8.06 (m, 2 H, Ar); ^{13}C NMR (DMSO-d^6, 100 MHz,): δ = 37.32 (aliphatic carbon), 58.6 (-C-CN), 114.60 (CN), 116.90, 120.17, 121.31, 121.88, 123.50, 125.20, 127.44, 128.64, 129.93, 130.125, 130.50, 130.89, 133.74, 146.99, 147.89, 148.02, 159.99.

*3-Amino-1-(4-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (**4d**)*: Yellow solid, yield, 96%, m p = 187-188 °C. FTIR (KBr, cm^{-1}): 3427 (NH), 3332 (NH), 2190 (CN), 1656, 1589, 1517, 1411, 1343 (NO_2), 1233, 1185, 1038, 827. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.40 (s, 1 H, CH), 7.16 (s, 2 H, NH_2). 7.34–7.50 (m, 3 H, Ar), 7.60–8.00 (m, 2 H, Ar), 7.97 (d, 1 H, Ar, *J* = 9.00 Hz), 7.42 (d, 2 H, Ar), 8.09(d, 2 H, Ar). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 37.83 (aliphatic carbon), 59.88 (-C-CN), 115.95 (CN), 116.94, 120.76, 123.84, 124.69, 126.90, 127.20, 128.93, 129.08, 129.34, 130.02, 130.76, 135.80, 142.91, 146.75, 159.83 (-C-NH_2).

*3-Amino-1-(4-chlorophenyl)-1Hbenzo[f]chromene-2-carbonitrile (**4e**)*: White solid, yield, 99%, m p = 207-208 °C. FTIR (KBr, cm^{-1}): 3417 (NH), 3334 (NH), 2194 (CN), 1648, 1593, 1410, 1260, 1112, 1048, 817. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.58 (2 H, NH_2) , 5.00 (s, 1 H, CH), 7.06 (d, 2 H, ArH, *J* = 8.4 Hz), 7.20 (d, 2 H, ArH, *J* = 8.94 Hz), 7.22 (d, 1 H, ArH, *J* =1.32 Hz), 7.30 (dd, 2 H, ArH, *J* = 5.8 & 6.8 Hz), 7.54 (dd, 1 H, ArH, *J* = 9.56 & 6.72 Hz), 7.76 (t, 2 H, ArH, *J* = 7.86 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 37.42 (aliphatic carbon), 57.40 (-C-CN), 115.46 (CN), 117.00, 120.64, 123.78, 125.20, 126.60, 127.54, 128.68, 128.82, 130.08, 130.14, 130.45, 130.76, 144.48, 146.20, 160.00 (-C-NH_2).

*3-Amino-1-(3-methoxyphenyl)-1Hbenzo[f]chromene-2-carbonitrile (**4f**)*: White solid, yield, 94%, m p = 255-257 °C. FTIR (KBr, cm^{-1}): 3457 (NH), 3348 (NH), 2190 (CN), 1662, 1608, 1548, 15220, 1258, 1194, 1078, 754. ^{1}H NMR (DMSO-*d6*, 400 MHz): δ = 3.76 (s, 3 H, Ar- OC*H3*), 5.18 (s, 1 H, CH), 6.10 (2 H, N*H2*), 6.72 – 6.75 (m, 2 H, ArH), 6.80 (d, 1 H, ArH, *J* = 7.7 Hz), 7.18 – 7.22 (m, 1 H, ArH), 7.31 (d, 1 H, ArH, *J* = 8.9 Hz), 7.38 – 7. 46 (m, 1 H, ArH), 7.72 – 7.76 (m, 2 H, ArH), 7.84 (d, 2 H, ArH, *J* = 9.1 Hz). ^{13}C NMR (DMSO-d^6, 100 MHz): δ 38.48 (aliphatic carbon), 55.42 (-OCH_3), 58.28 (-C-CN), 111.70, 113.94, 116.12, 117.20, 119.74, 121.02, 124.14, 125.42, 127.64, 129.00, 129.98, 130.34, 130.70, 131.28, 147.34, 147.72, 159.84, 160.38 (-C-NH_2).

3-Amino-1-p-tolyl-1H-benzo[f]chromene-2- carbonitrile ***(4g)***: White solid, yield, 92%, FTIR (KBr, cm^{-1}): 3464 (-NH), 3353 (-NH) , 2978, 2172 (CN), 1668, 1604, 1543, 1502, 1275, 1193, 1084, 765.^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.22 (s, 3 H, Ar-CH3), 5.18 (s, 1 H, CH), 5.64 (2 H, NH2) , 7.04 – 7.09 (m, 4 H, ArH), 7.28 (d, 1H, *J* = 8.92 Hz), 7.39 (dd, , 2 H, *J* = 5.2 & 4.6 Hz), 7.72 (t, 1H, *J* = 6.87 Hz), 7.81 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (DMSO-*d6*, 100 MHz): δ= 20.88 (-OCH_3), 38.10 (aliphatic carbon), 58.41 (-C-CN), 116.16, 117.10, 120.88, 124.00, 125.23, 127.27, 128.76, 129.56, 129.72, 130.54, 131.13, 136.01, 143.17, 147.10, 160.02.

3-Amino-1-(4-bromophenyl)-1Hbenzo[f]chromene-2-carbonitrile ***(4i)***: White solid, yield, 96%, FTIR (KBr, cm^{-1}): 3418 (NH), 3325 (NH), 3197, 3051, 2195 (CN), 1644, 1592, 1488, 1414, 1238, 1082, 1015, 821, 737. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.67 (s, 2H, NH_2), 5.26 (s, 1H, CH), 7.10 (d, 2 H, *J = 8.4 Hz*), 7.30 (d, 2 H, *J = 6.3 Hz*), 7.43–7.48 (m, 3H), 7.66 (d, 1H, *J = 6.4* Hz), 7.87(d, 2H, *J = 8.5* Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 38.8 (aliphatic carbon), 58.4 (-C-CN), 115.9, 117.8, 120.6, 120.9, 124.2, 125.6, 127.9, 129.4, 129.9, 130.4, 130.7, 131.5, 132.4, 145.8, 147.6, 160.4.

3-Amino-1-(3-chlorophenyl)-1Hbenzo[f]chromene-2-carbonitrile ***(4j)***: White solid, yield, 95%, FTIR (KBr, cm^{-1}): 3400 (NH), 3270, 2180 (CN), 1670, 1400, 1102, 1045, 808, 760 cm-1. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.19 (s, 1H, CH), 5.88 (2H, NH_2), 7.09 (s, 1H, ArH), 7.13 (d, 2H, *J* = 8.2 Hz), 7.21 (t, 1H, *J* = 7.4 Hz), 7.28 (d, 1H, *J* = 9.0 Hz,), 7.41(dd, 2H, *J* = 5.3 & 3.3 Hz), 7.65 (d, 1H, *J* = 6.7 Hz), 7.82 (d, 2H, *J* = 7.9 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz,): δ = 37.97 (aliphatic carbon), 57.75 (-C-CN), 115.40, 117.26, 120.71, 123.96, 125.51, 126.16, 127.13, 127.71, 128.98, 130.24, 130.47, 131.21, 133.65, 147.32, 148.59, 160.28.

3-Amino-1-(3-methoxyphenyl)-1Hbenzo[f]chromene-2-carbonitrile ***(4k)***: White solid, yield, 94%, FTIR (KBr, cm^{-1}): 3465 (NH), 3354 (NH), 2989, 2183 (CN), 1668, 1604, 1544, 1503, 1307, 1255, 1194, 1083, 765. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.71 (d, 2H, *J* = 9.1 Hz, ArH), 7.59 – 7.63 (m, 2H, ArH), 3.63 (s, 3H, Ar- OCH3), 5.06 (s, 1H, CH), 6.00 (2H, NH_2), 6.57 – 6.59 (m, 2H, ArH), 6.67 (d, 1H, *J* = 7.7 Hz), 7.04 – 7.08 (m, 1H, ArH), 7.17 (d, 1H, *J* = 8.9 Hz), 7.26 – 7. 32 (m, 1H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 38.21 (aliphatic carbon), 55.16, 58.202 (-C-CN), 111.42, 113.67, 115.93, 117.00, 119.41, 120.73, 123.88, 125.18, 127.33, 128.68, 129.73, 130.09, 130.46, 131.03, 147.06, 147.48, 159.58, 160.02.

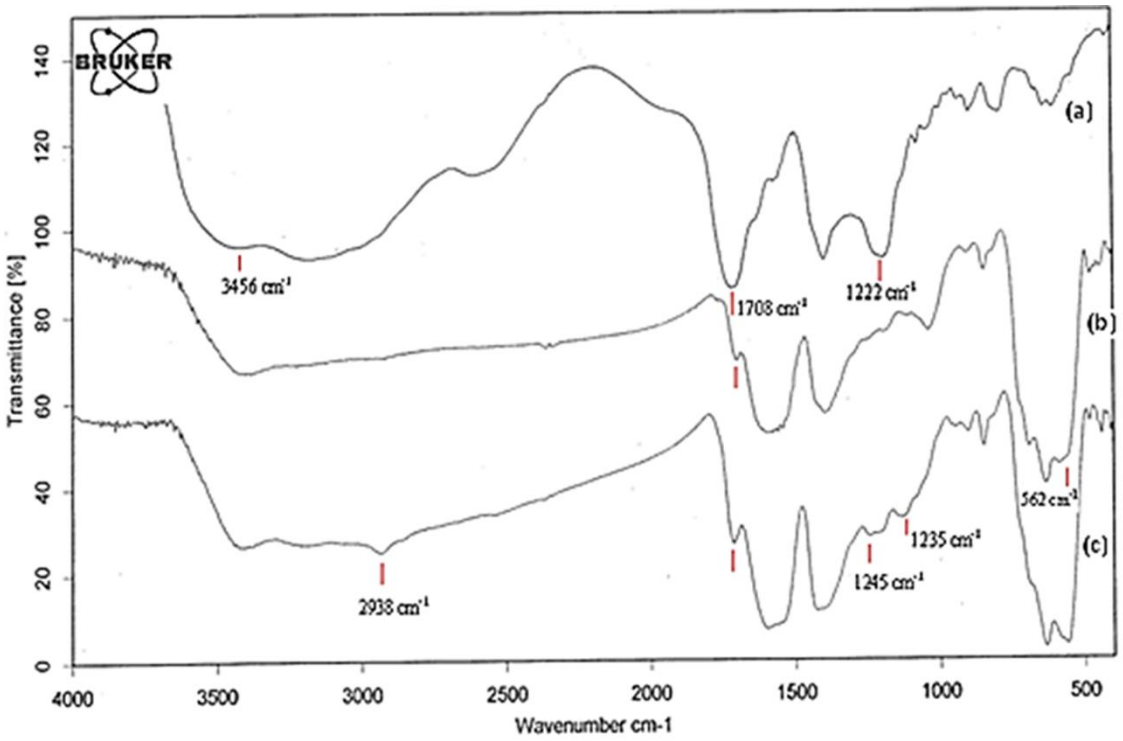

Figure S1. FT-IR spectra: a) GQDs, b) Fe_3O_4@GQDs and c) Fe_3O_4@GQDs-Pip

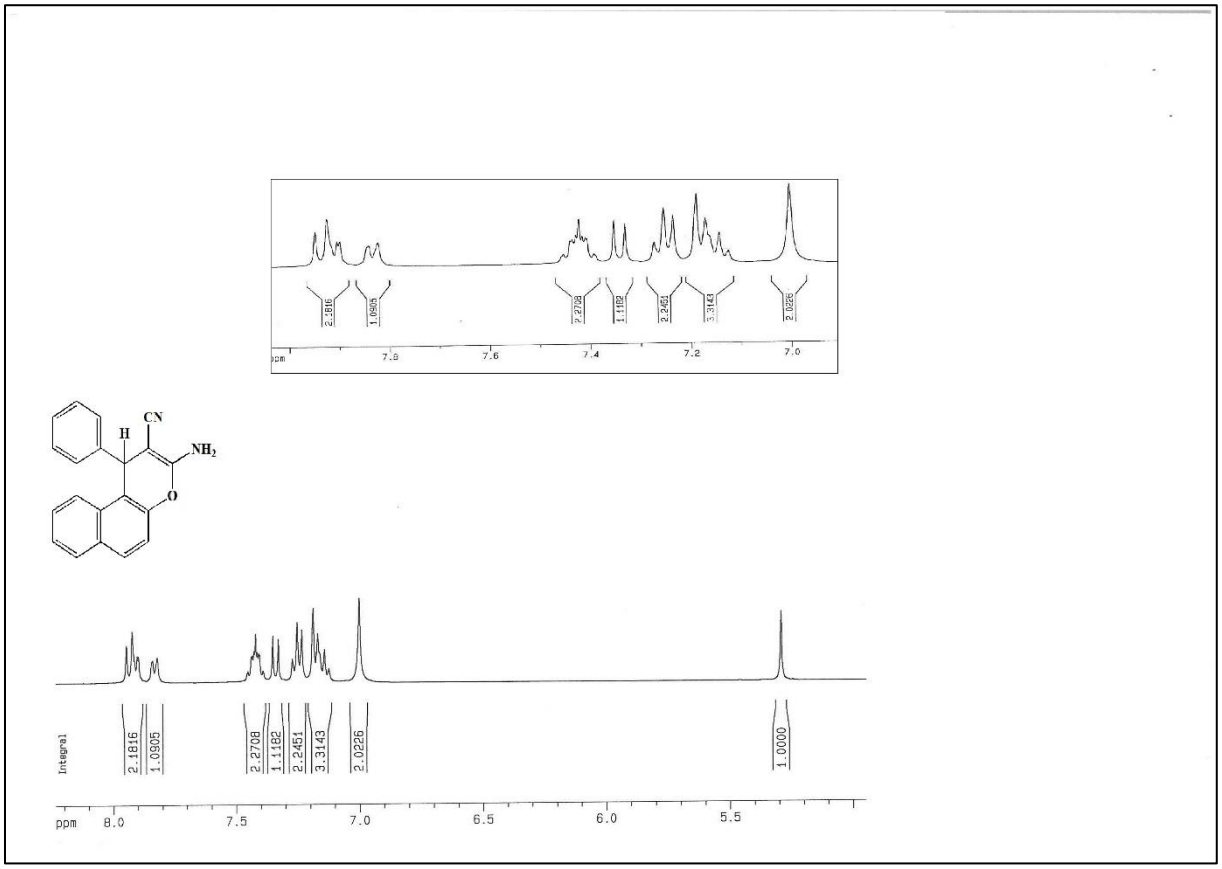

Figure S2. 400 MHz ^{1}H-NMR spectrum of compound **4a**

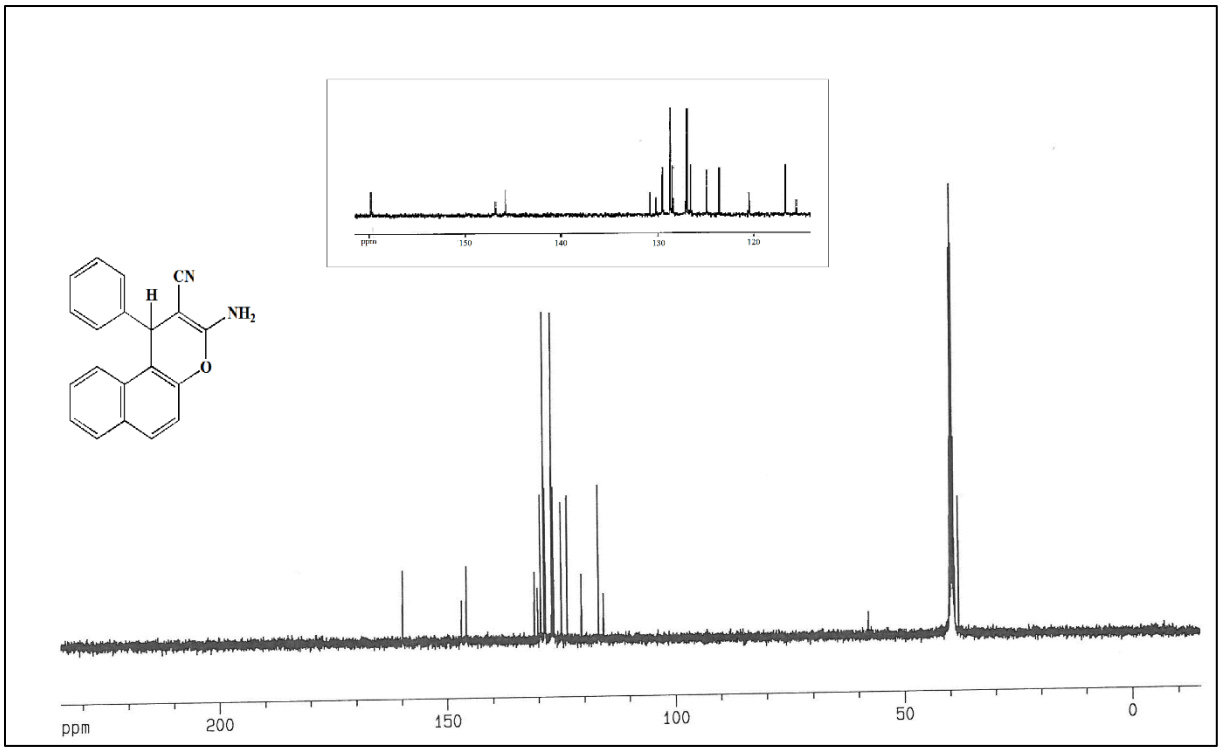

Figure S3. 100 MHz ^{13}C-NMR spectra of compound **4a**

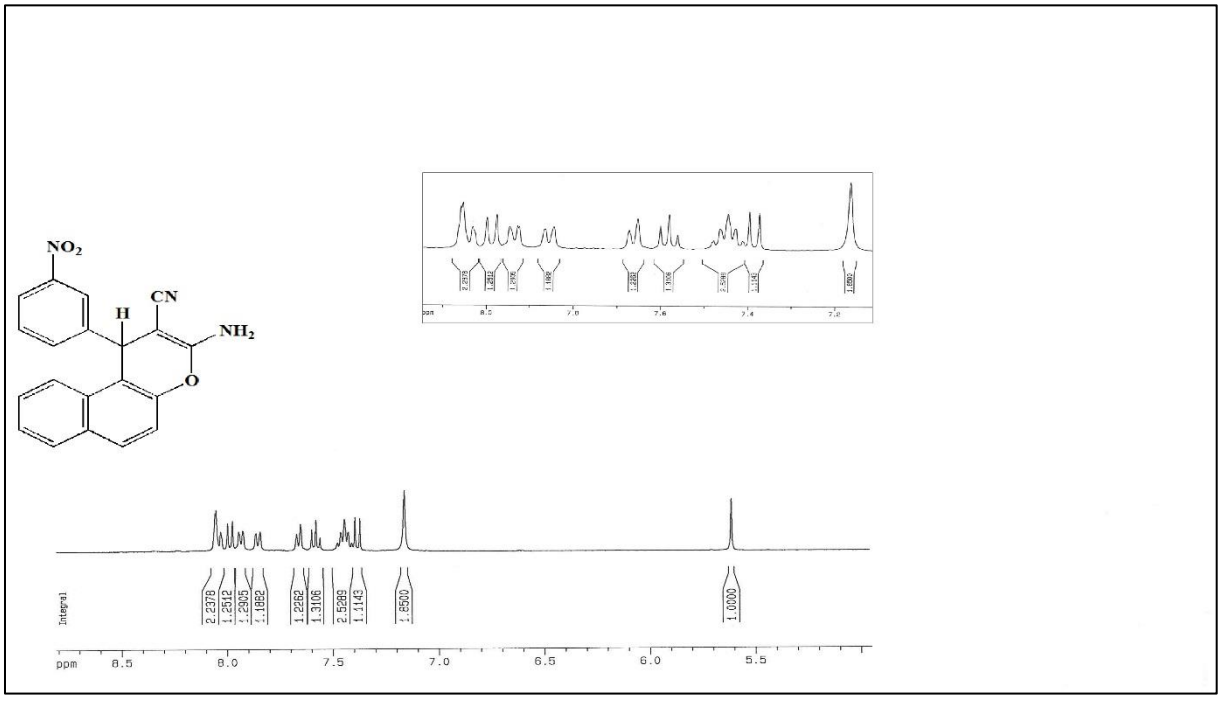

Figure S4. 400 MHz ^{1}H-NMR spectrum of compound **4c**

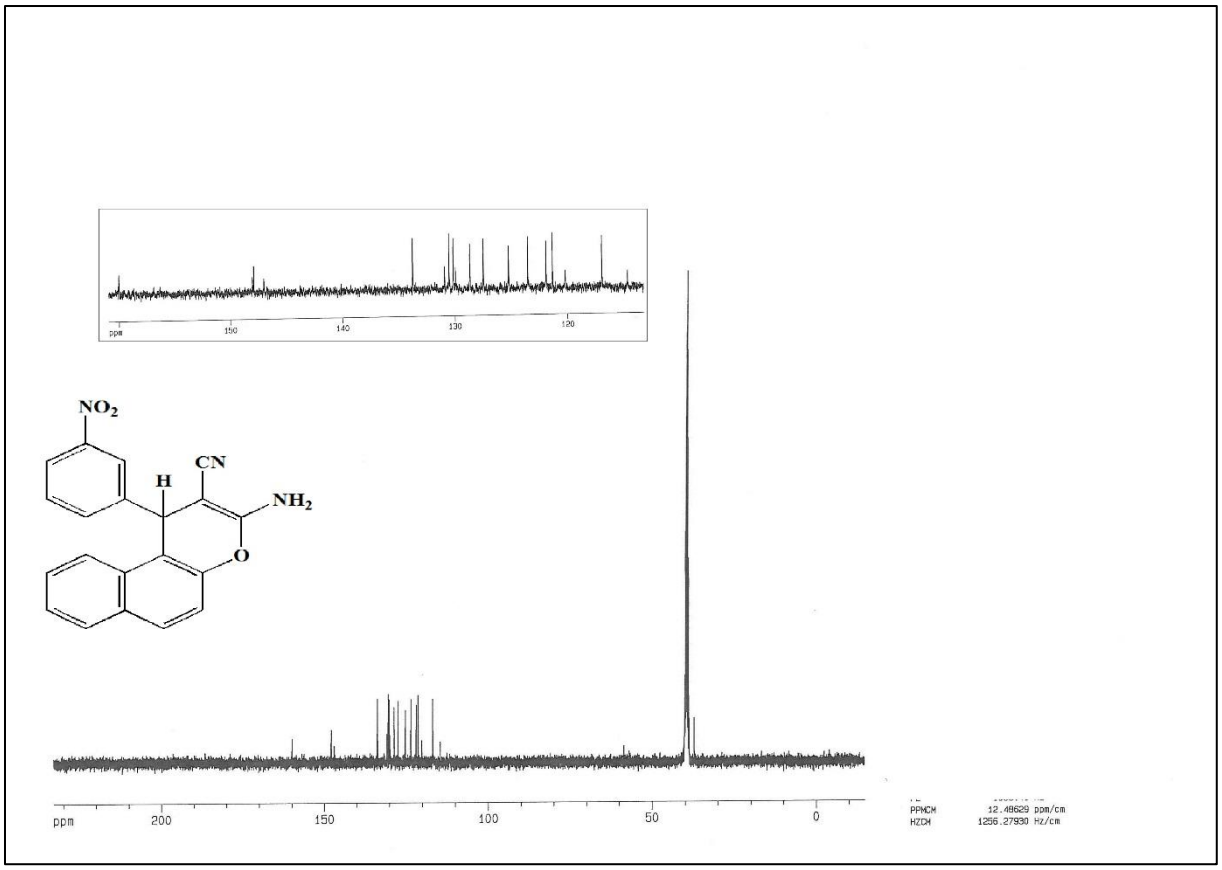

Figure S5. 100 MHz ^{13}C-NMR spectrum of compound **4c**